Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supplementary Information

Asymmetric Chroman Synthesis via Intramolecular Oxy-Michael Addition by Bifunctional Organocatalysts

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Contents

Instrumentation and Chemicals

^{1}H and ^{13}C Nuclear magnetic resonance spectra were taken on a Varian UNITY INOVA 500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz) spectrometer using tetramethylsilane as an internal standard for ^{1}H NMR (δ = 0 ppm) and $CDCl_3$ as an internal standard for ^{13}C NMR (δ = 77.0 ppm). When a ^{13}C NMR spectrum was measured using C_6D_6 as a solvent, C_6D_6 was used as an internal standard (δ = 128.06 ppm). ^{1}HNMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), integration. ^{19}F NMR spectra were measured on a Varian Mercury 200 (^{19}F, 188 MHz) spectrometer with hexafluorobenzene as an internal standard (δ = 0 ppm). GC-MS analyses and High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. High performance liquid chromatography (HPLC) was performed with a SHIMADZU Prominence. Infrared (IR) spectra were determined on a SHIMADZU IR Affinity-1 spectrometer. Melting points were determined using a YANAKO MP-500D. Optical rotations were measured on a HORIBA SEPA-200. X-ray data were taken on a Bruker Smart APEX X-Ray diffractometer equipped with a large area CCD detector. The structures were solved with the program system SHELXS-97 and refined with SHELXL-97 package from Bruker. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and/or such as an aqueous alkaline $KMnO_4$ solution followed by heating.

Flash column chromatography was carried outusing Kanto Chemical silica gel (spherical, 40–50 μm). Unless otherwise noted, commercially available reagents were used without purification.

Experimental Procedure

General procedure for asymmetric synthesis of 2-substituted chromans 2

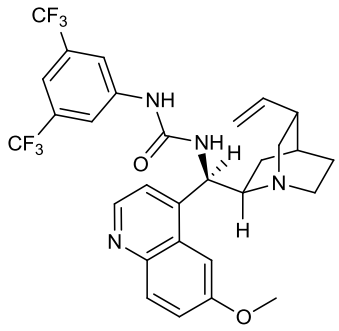
In a 5-mL vial, we sequentially added substrate **1** (0.10 mmol), THF (0.2 mL), and quinidine-derived bifunctional catalyst **3a** (0.010 mmol). The mixture was stirred in an oil bath maintained at 0 °C for 12 h. The reaction mixture was subsequently diluted with hexane/EtOAc (v/v = 1/1), passed through a short silica gel pad to remove **3a**, and concentrated in vacuo. Purification of the reaction mixture by flash silica gel column chromatography using hexane/EtOAc (v/v = 3/1) as an eluent afforded the corresponding 2-substituted chroman **2**.

Racemic compounds were prepared using *p*-toluenesulfonic acid as a catalyst.

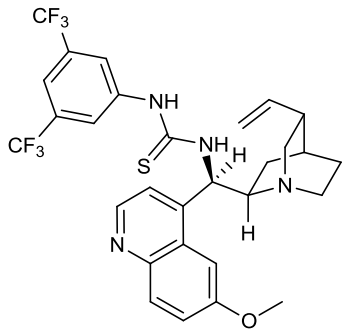
General procedure for preparation of bifunctional catalysts 3

Bifunctional organocatalysts **3** were prepared by the literature procedure.[1] A cinchona alkaloid (5 mmol) and triphenylphosphine (1.6 g, 6 mmol) were dissolved in THF (25 mL), and the solution was cooled to 0 °C. Diethyl azodicarboxylate (1.0 g, 6 mmol) was subsequently added. To the resulting solution was added dropwise the solution of diphenyl phosphoryl azide (1.3 mL, 6 mmol) in THF (10 mL) at 0 °C. The mixture was allowed to warm to ambient temperature. After being stirred for 24 h, it was heated to 50 °C and stirred for 10 h. Triphenylphosphine (1.7 g, 6.5 mmol) was added again, and the mixture was stirred at 50 °C for additional 15 h. After the solution was cooled to ambient temperature, H_2O (0.5 mL) was added, and the solution was stirred for 24 h. The solvents were removed in vacuo, and the residue was dissolved in CH_2Cl_2/10% aqueous hydrochloric acid (25 mL/25 mL). The aqueous phase was separated and washed with CH_2Cl_2 (25 mL × 4). It was subsequently made alkaline with aqueous ammonia, and the aqueous phase was extracted with CH_2Cl_2 (25 mL × 4). The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using EtOAc/CH_3OH (v/v = 9/1) then $CHCl_3$/CH_3OH (v/v = 8/2) as an eluent gave the corresponding 9-amino(9-deoxy)cinchona alkaloids. Next, to the solution of the obtained 9-amino(9-deoxy)cinchona alkaloid in THF (6 mL) was slowly added a solution of 3,5-bis(trifluoromethyl)phenyl isocyanate or isothiocyanate (1 equiv) in THF (4 mL) at ambient temperature. The mixture was stirred overnight, and the solvents were removed in vacuo. Purification by flash silica gel column chromatography using EtOAc/CH_3OH (v/v = 95/5–97.5/2.5) or EtOAc as an eluent gave the corresponding bifunctional organocatalyst **3**.

The characterization results are as below.

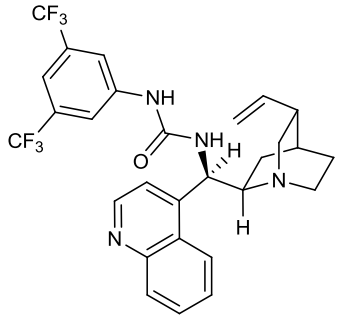


3a. White solid; 30% yield (for 2steps from quinidine). $[\alpha]_D^{18}$ +840.0 (*c* 2.00, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.76 (d, *J* = 4.5 Hz, 1H), 8.05 (d, *J* = 9.5 Hz, 1H), 7.78 (s, 2H), 7.60 (s, 1H), 7.41 (m, 3H), 6.29 (br s, 1H), 5.88 (ddd, *J* = 15.0, 10.0, 4.0 Hz, 1H), 5.33 (br s, 1H), 5.13 (m, 2H), 3.99 (s, 3H), 2.97 (d, *J* = 10.0 Hz, 3H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.23 (m, 1H), 1.82 (br s, 3H), 1.68 (br s, 1H), 1.51 (m, 1H), 1.03 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 158.4, 156.9, 156.2, 155.1, 147.7, 145.1, 140.9, 140.1, 132.3 (q, *J* = 33.2 Hz), 132.1, 128.3, 123.4 (q, *J* = 272.6 Hz), 118.5, 115.9, 115.4, 110.0, 101.7, 60.6, 55.8, 49.3, 47.2, 39.1, 32.2, 27.4, 26.6, 25.5. ^{19}F NMR ($CDCl_3$) δ 98.8. Mp. 133.0–133.5 °C. IR (KBr): 3321, 3080, 2941, 2875, 1705, 1676, 1624, 1570, 1511, 1475, 1434, 1389, 1279, 1245, 1229, 1179, 1132, 1096, 1036, 945, 917, 880, 852, 828, 703, 682 cm^{-1}. HRMS Calcd for $C_{29}H_{29}F_6N_4O_2$: $[M+H]^+$, 580.2223. Found: *m*/*z* 580.2209.

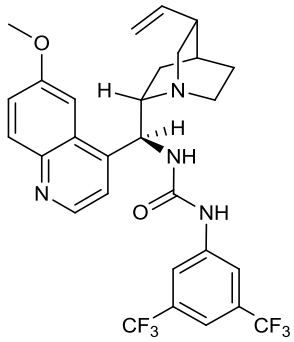


3b. White solid; 41% yield (for 2steps from quinidine). $[\alpha]_D^{23}$ +122.6 (*c* 1.33, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.65 (br s, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.86 (s, 2H), 7.67 (s, 1H), 7.59 (br s, 1H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.23 (br s, 1H), 5.86 (br s, 2H), 5.19 (br s, 1H), 5.15 (d, *J* = 9.5 Hz, 1H), 3.97 (s, 3H), 3.22 (br s, 1H), 3.10 (br s, 1H), 3.03 (m, 2H), 2.94 (m, 1H), 2.38 (m, 1H), 1.70 (s, 1H), 1.61 (m, 2H), 1.27 (br s, 1H), 1.02 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 181.0, 158.1, 147.3, 144.7, 144.5, 140.1, 139.6, 132.5 (q, *J* = 33.6 Hz), 131.6, 128.0, 123.5, 122.9 (q, *J* = 273.0 Hz), 122.3, 118.7, 115.3, 101.7, 61.4, 55.6, 48.5, 47.1, 38.7, 27.1, 26.1, 25.0. Mp. 125.0–125.2 °C. IR (KBr): 3221, 2944, 2361,

1735, 1623, 1511, 1475, 1384, 1278, 1177, 1134, 1034, 959, 916, 884, 850, 826, 682 cm^{-1}. HRMS Calcd for $C_{29}H_{29}F_6N_4OS$: $[M+H]^+$, 595.1966. Found: *m*/*z* 595.1961.

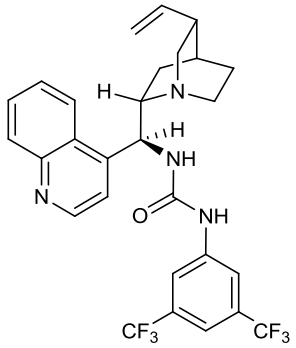


3c. White solid; 40% yield (for 2steps from cinchonine). $[\alpha]_D^{23}$ +194.9 (*c* 0.59, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.91 (d, *J* = 4.5 Hz, 1H), 8.36 (d, *J* = 7.5 Hz, 1H), 8.18 (dd, *J* = 8.3, 0.75 Hz, 1H), 7.79 (s, 2H), 7.76 (dd, *J* = 8.3, 1.3, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 4.5 Hz, 1H), 7.43 (s, 1H), 6.35 (br s, 1H), 5,87 (ddd, *J* = 18.1, 15.0, 6.0 Hz, 1H), 5.30 (br s, 1H), 5.13 (dd, *J* = 24.0, 7.5 Hz, 2H), 2.94 (m, 5H), 2.31 (m, 1H), 1.84 (br s, 1H), 1.65 (br s, 1H), 1.57 (m, 1H), 1.49 (m, 1H), 1.27 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 154.9, 150.1, 148.7, 140.7, 139.6, 132.2 (q, *J* = 33.2 Hz), 130.6, 129.4, 127.0, 123.7 (q, *J* = 273.0 Hz), 123.1, 118.26, 118.23, 115.76, 115.73, 115.70, 115.3, 61.1, 49.0, 47.0, 39.0, 29.7, 27.3, 26.3, 25.0. ^{19}F NMR ($CDCl_3$)δ 98.8. Mp. 193.5–194.0 °C. IR (KBr): 3289, 3238, 3081, 2942, 2875, 2366, 1705, 1676, 1570, 1511, 1475, 1389, 1279, 1243, 1180, 1132, 945, 916, 881, 761, 683, 624 cm^{-1}. HRMS Calcd for $C_{28}H_{27}F_6N_4O$: $[M+H]^+$, 549.2084. Found: *m*/*z* 549.2077.



3d. White solid; 30% yield (for 2steps from quinine). $[\alpha]_D^{23}$ +20.4 (*c* 1.47, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.83 (d, *J* = 4.5 Hz, 1H), 8.06 (d, *J* = 9.5 Hz, 1H), 7.94 (br s, 1H), 7.74 (s, 1H), 7.68 (s, 1H), 7.42 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.34 (d, *J* = 4.5 Hz, 1H), 7.32 (s, 1H), 6.13 (br s, 1H), 5.64 (ddd, *J* = 17.0, 10.3, 6.8 Hz, 2H), 5.01 (d, *J* = 10.0 Hz, 1H), 4.84 (d, *J* = 17.0 Hz, 1H), 4.02 (s, 3H), 3.54 (br s, 1H), 3.18 (br s, 1H), 2.95 (m, 1H),

2.71 (m, 1H), 2.24 (br s, 2H), 2.11 (br s, 1H), 1.66 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 158.4, 154.6, 153.7, 147.3, 145.1, 140.5, 140.4, 131.932 (q, *J* = 33.2 Hz), 131.927, 130.2, 123.0 (q, *J* = 273.0 Hz), 118.4, 115.6, 115.1, 112.5, 109.7, 103.9, 60.1, 55.8, 55.4, 43.6, 41.4, 40.7, 38.6, 27.4, 26.9. ^{19}F NMR ($CDCl_3$) δ 98.6. Mp. 134.0–135.0 °C. IR (KBr): 3327, 3083, 2944, 2869, 2360, 1700, 1623, 1570, 1512, 1476, 1388, 1279, 1245, 1230, 1179, 1132, 1034, 881, 852, 682 cm^{-1}. HRMS Calcd for $C_{29}H_{29}F_6N_4O_2$: $[M+H]^+$, 580.2223. Found: *m*/*z* 580.2181.



3e. White solid; 40% yield (for 2steps from cinchonidine). $[\alpha]_D^{23}$ –16.3 (*c* 3.67, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.93 (d, *J* = 3.0 Hz, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 8.17 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.76 (m, 3H), 7.66 (m, 1H), 7.48 (d, *J* = 5.0 Hz, 1H), 7.38 (s, 1H), 6.49 (br s, 1H), 5.61 (ddd, *J* = 17.3, 10.3, 7,5 Hz, 1H), 5.44 (br s, 1H), 4.90 (m, 2H), 3.17 (br s, 1H), 2.99 (dd, *J* = 13.5, 10.0 Hz, 2H), 2.61 (m, 1H), 2.41 (m, 2H), 2.23 (m, 1H), 1.63 (m, 2H), 1.56 (m, 1H), 1.36 (m, 1H), 0.93 (dd, *J* = 13.5, 6.0 Hz 1H). ^{13}C NMR ($CDCl_3$) δ 154.8, 149.9, 148.6, 148.5, 141.5, 140.8, 140.7, 132.0 (q, *J* = 33.2 Hz), 130.3, 129.6, 127.2, 123.28, 123.11 (q, *J* = 273.0 Hz), 118.2, 115.6, 114.8, 113.0, 61.9, 55.5, 40.9, 39.1, 35.0, 27.6, 27.0, 26.0. ^{19}F NMR ($CDCl_3$) δ 98.7. Mp. 140.0–141.0 °C. IR (KBr): 3309, 3081, 2947, 2869, 2360, 1700, 1623, 1570, 1511, 1473, 1389, 1346, 1279, 1243, 1180, 1132, 882, 760, 704, 683 cm^{-1}. HRMS Calcd for $C_{28}H_{27}F_6N_4O$: $[M+H]^+$, 549.2084. Found: *m*/*z* 549.2076.

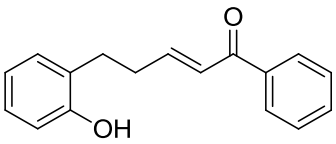
General procedure for preparation of substrate 1

To a solution of an 3,4-dihydrocoumarin derivative (3.1 mL, 25 mmol) in toluene (25 mL) was added DIBAL-H (ca. 1.0 M hexane solution, 25 mL, 25 mmol) dropwise at –78 °C, and the mixture was stirred for 1 h. The reaction mixture was allowed to warm slowly to 0 °C. The reaction was quenched with 1N aquous HCl (20 mL), and the mixture was subsequently extracted with toluene. The combined organic layers

were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flush silica gel column chromatography using hexane/EtOAc (v/v = 3/1) as an eluent gave chroman-2-ol as a colorless oil quantitatively. CAS RN [32560-26-2]. ^{1}H NMR ($CDCl_3$) δ 7.12 (m, 1H), 7.07 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.88 (dt, *J* = 1.0, 7.5 Hz, 1H), 6.82 (dd, *J* = 8.0, 1.0 Hz, 1H), 5.62 (dd, *J* = 4.0, 2.5 Hz, 1H), 2.99 (ddd, *J* = 16.5, 10.5, 6.0 Hz, 1H), 2.71 (dt, *J* = 16.5, 5.0 Hz, 1H), 2.08–1.97 (m, 2H), 1.56 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 152.0, 129.2, 127.4, 122.0, 120.8, 116.9, 92.1, 27.0, 20.2.

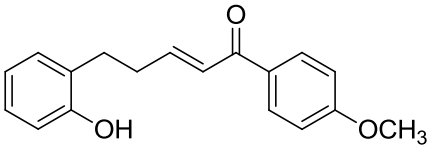
To the solution of chroman-2-ol (0.15 g, 1.0 mmol) in CH_2Cl_2 (10 mL), an ylide (5.0 mmol) was added. The reaction mixture was stirred for 2 days at 30 °C. After the solvent was evaporated, the residue was passed through a short silica gel pad to remove triphenylphosphine oxide, and the filtrate was concentrated in vacuo. Purification by flush silica gel column chromatography using hexane/THF (v/v = 2/1) as an eluent gave (*E*)-5-(2-hydroxyphenyl)-pent-2-en-1-one (**1**) as a white solid in 30–50% yield.
Ylides were prepared by the literature procedure.[2]
The characterization results of **1** are as below.

(*E*)-5-(2-Hydroxyphenyl)-1-phenylpent-2-en-1-one (1a).



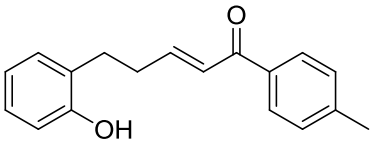
White solid; 35% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.89 (m, 2H), 7.55 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.45 (tt, *J* = 7.5, 1.5 Hz, 2H), 7.12 (m, 3H), 6.88 (m, 2H), 6.77 (dd, *J* = 6.5, 1.0 Hz, 1H), 5.23 (br s, 1H), 2.87 (t, *J* = 6.5 Hz, 2H), 2.66 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 191.8, 153.9, 149.8, 137.8, 132.7, 132.2, 128.6, 128.5, 127.4, 127.2, 126.3, 120.6, 115.4, 33.0, 28.8. Mp. 103.0–103.5 °C. TLC: R_f 0.50 (hexane/THF = 2:1). IR (KBr): 3385, 3058, 2943, 1663, 1610, 1594, 1577, 1458, 1447, 1346, 1306, 1251, 1228, 1180, 1115, 974, 762, 753, 692, 658, 636, 490 cm^{-1}. HRMS Calcd for $C_{17}H_{17}O_2$: $[M+H]^+$, 253.1223. Found: *m*/*z* 253.1227.

(*E*)-5-(2-Hydroxyphenyl)-1-(4-methoxyphenyl)pent-2-en-1-one (1b).



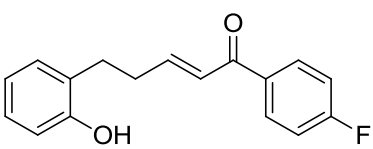
Yellow oil; 40% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.89 (m, 2H), 7.55 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.45 (tt, *J* = 7.5, 1.5 Hz, 2H), 7.10 (dt, *J* = 15.5, 7.0 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.86 (dt, *J* = 15.5, 1.5 Hz, 1H), 6.44 (dd, *J* = 7.5, 2.5 Hz, 1H), 6.36 (d, *J* = 2.5 Hz, 1H), 5.08 (s, 1H), 3.76 (s, 3H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.62 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 191.2, 159.3, 154.3, 149.1, 138.0, 132.6, 130.8, 128.6, 128.5, 126.5, 119.5, 105.9, 102.0, 55.3, 33.3, 28.2. TLC: R_f 0.45 (hexane/THF = 2:1). IR (neat): 3421, 3065, 2931, 2848, 1685, 1620, 1582, 1506, 1449, 1282, 1201, 1157, 1128, 1114, 1036, 834, 756, 691, 474 cm^{-1}. HRMS Calcd for $C_{18}H_{19}O_3$: $[M+H]^+$, 283.1329. Found: *m*/*z* 283.1324.

(*E*)-5-(2-Hydroxyphenyl)-1-(4-methylphenyl)pent-2-en-1-one (1c).



White solid; 30% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.81 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.25 (m, 2H), 7.14 (dd, *J* = 6.0, 1.5 Hz, 1H), 7.09 (m, 2H), 6.89 (dd, *J* = 7.0, 1.5 Hz, 1H), 6.86 (t, *J* =1.5 Hz, 1H), 6.77 (dd, *J* = 7.5, 1.0 Hz, 1H), 5.13 (br s, 1H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.65 (m, 2H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 190.7, 153.6, 148.5, 143.4, 135.4, 130.3, 129.2, 128.7, 127.5, 127.2, 126.4, 120.9, 115.4, 32.9, 28.9, 21.6. Mp. 120.0–121.0 °C. TLC: R_f 0.48 (hexane/THF = 2:1). IR (KBr): 3262, 3024, 2954, 1956, 1654, 1612, 1591, 1564, 1457, 1349, 1254, 1230, 1179, 1110, 814, 760, 652, 461 cm^{-1}. HRMS Calcd for $C_{18}H_{19}O_2$: $[M+H]^+$, 267.1380. Found: *m*/*z* 267.1382.

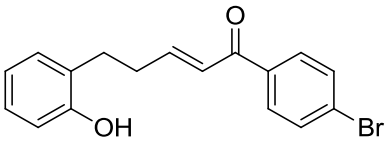
(*E*)-1-(4-Fluorophenyl)-5-(2-hydroxyphenyl)pent-2-en-1-one (1d).



Yellow oil; 30% (for the last step).

^{1}H NMR ($CDCl_3$) δ 7.91 (m, 2H), 7.17–7.08 (m, 5H), 6.88 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.84 (m, 1H), 6.78 (dd, *J* = 7.5, 1.0 Hz, 1H), 5.37 (br s, 1H), 2.87 (t, *J* = 7.5 Hz, 2H), 2.66 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 189.7, 165.6 (d, *J* = 254.3 Hz), 153.7, 149.5, 134.2, 131.2 (d, *J* = 9.6 Hz) 130.3, 127.5, 127.2, 126.0, 120.8, 115.6 (d, *J* = 22.0 Hz), 115.4, 33.0, 28.8. ^{19}F NMR ($CDCl_3$) δ –56.0. TLC: R_f 0.50 (hexane/THF = 2:1). IR (KBr): 3266, 2940, 2371, 1662, 1618, 1597, 1507, 1457, 1335, 1231, 1157, 828, 755, 610 cm^{-1}. HRMS Calcd for $C_{17}H_{16}FO_2$: $[M+H]^+$, 271.1129. Found: *m*/*z* 271.1130.

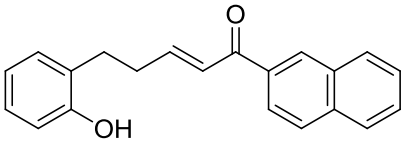
(*E*)-1-(4-Bromophenyl)-5-(2-hydroxyphenyl)pent-2-en-1-one (1e).



White soild; 40% (for the last step).

^{1}H NMR ($CDCl_3$) δ 7.74 (dt, *J* = 7.5, 2.0 Hz, 2H), 7.59 (dt, *J* = 7.5, 2.0 Hz, 2H), 7.10 (m, 3H), 6.88 (dt, *J* = 1.0, 7.5 Hz, 1H), 6.81 (dt, *J* = 15.5, 1.5 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 4.89 (s, 1H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.66 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 190.0, 153.5, 149.6, 136.7, 132.0, 131.8, 130.4, 130.1, 127.6, 127.1, 126.1, 121.0, 115.4, 32.9, 28.8. Mp. 93.0–94.0 °C. TLC: R_f 0.45 (hexane/THF = 2:1). IR (KBr): 3291, 3039, 2926, 2361, 1686, 1488, 1457, 1398, 1233, 1070, 1008, 758, 668, 374 cm^{-1}. HRMS Calcd for $C_{17}H_{16}BrO_2$: $[M+H]^+$, 331.0328. Found: *m*/*z* 331.0331.

(*E*)-5-(2-Hydroxyphenyl)-1-(naphthalen-2-yl)pent-2-en-1-one (1f).

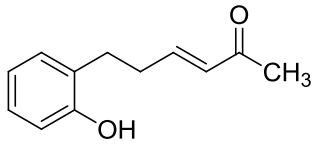


Yellow solid; 25% yield (for the last step).

^{1}H NMR ($CDCl_3$) δ 8.38 (s, 1H), 7.99 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.89 (t, *J* = 7.5 Hz, 2H), 7.60 (m, 1H), 7.55 (m, 1H), 7.18 (m, 2H), 7.12 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.02 (dt, *J* = 15.5, 1.5 Hz, 1H), 6.90 (dt, *J* = 1.0, 7.5 Hz, 1H), 6.77 (dd, *J* =8.0, 1.0 Hz, 1H), 4.92 (s, 1H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.71 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 190.9, 153.5, 148.8, 135.4, 135.3, 132.6, 130.4, 130.0, 129.5, 128.4, 128.3, 127.8, 127.6, 127.2, 126.7, 126.5, 124.6, 121.0, 115.4, 33.0, 28.9. Mp. 139.0–140.0 °C. TLC: R_f 0.35 (hexane/THF = 2:1). IR (KBr): 3416, 3051, 2944, 2364, 1663, 1629, 1613, 1458, 1363, 1246, 1184, 1111, 824, 753, 616 cm^{-1}. HRMS Calcd for $C_{21}H_{19}O_2$:

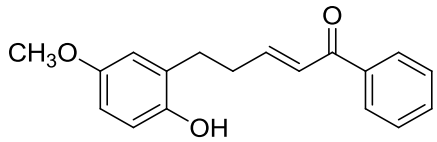
$[M+H]^+$, 303.1380. Found: *m*/*z* 303.1383.

(*E*)-6-(2-Hydroxyphenyl)hex-3-en-2-one (1g).



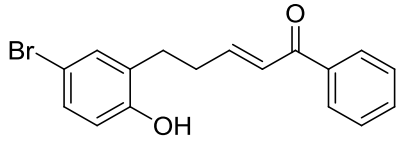
White solid; 20% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.08 (m, 1H), 7.06 (dd, *J* = 7.5, 2.0 Hz, 1H), 6.89 (dt, *J* = 16.0, 7.0 Hz, 1H), 6.84 (dt, *J* = 1.0, 7.5 Hz, 1H), 6.78 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.21 (br s, 1H), 6.11 (dt, *J* = 16.0, 1.5 Hz, 1H), 2.80 (t, *J* = 7.5 Hz, 2H), 2.56 (m, 2H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 199.3, 153.9, 148.4, 131.4, 130.1, 127.5, 127.1, 120.5, 115.3, 32.6, 28.8, 26.7. Mp. 63.5–64.5 °C. TLC: R_f 0.50 (hexane/THF = 2:1). IR (KBr): 3223, 3017, 2924, 2356, 1654, 1636, 1608, 1595, 1460, 1373, 1271, 1235, 1105, 973, 852, 753, 569 cm^{-1}. HRMS Calcd for $C_{12}H_{15}O_2$: $[M+H]^+$, 191.1067. Found: *m*/*z* 191.1070.

(*E*)-5-(2-Hydroxy-5-methoxyphenyl)-1-phenylpent-2-en-1-one (1h).



Pale yellow solid; 40% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.88 (m, 2H), 7.55 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.11 (dt, *J* = 16.5, 7.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.87 (dt, *J* = 15.0, 1.5 Hz, 1H), 6.43 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.37 (d, *J* = 2.0 Hz, 1H), 5.29 (s, 1H), 3.75 (s, 3H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.61 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 191.3, 159.2, 154.3, 149.4, 137.9, 132.7, 130.7, 128.6, 128.5, 126.3, 119.4, 105.7, 101.9, 72.4, 33.3, 28.2. Mp. 70.0–71.0 °C. TLC: R_f 0.36 (hexane/THF = 3:1). IR (KBr): 3084, 2929, 2837, 2349, 1731, 1681, 1659, 1563, 1462, 1189, 1120, 1028 cm^{-1}. HRMS Calcd for $C_{18}H_{19}O_3$: $[M+H]^+$, 283.1329. Found: *m*/*z* 283.1329.

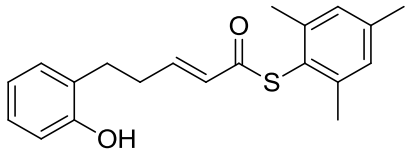
(*E*)-5-(5-Bromo-2-hydroxyphenyl)-1-phenylpent-2-en-1-one (1i).



Colorless oil; 10% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.89 (m, 2H), 7.55 (tt, *J* = 7.0, 1.5 Hz, 1H), 7.49–7.45 (m, 3H), 7.19

(dd, *J* = 8.5, 2.5 Hz, 1H), 7.07 (dt, *J* = 15.5, 7.0 Hz, 1H), 6.87 (dt, *J* = 15.5, 1.5 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 5.30 (s, 1H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.64 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 191.3, 152.71, 148.5, 137.8, 132.9, 132.7, 130.2, 129.6, 128.9, 128.5, 126.6, 117.0, 112.7, 32.8, 28.7. TLC: R_f 0.40 (hexane/THF = 3:1). IR (neat): 3019, 2872, 2788, 2349, 1769, 1737, 1681, 1650, 1567, 1511, 1453, 1426, 1334, 1243, 1173, 1121, 1025, 843 cm^{-1}. HRMS Calcd for $C_{17}H_{16}BrO_2$: $[M+H]^+$, 331.0328. Found: *m*/*z* 331.0327.

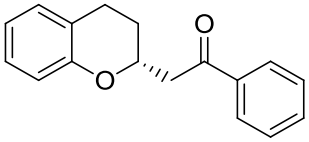
(*E*)-*S*-Mesityl 5-(2-hydroxyphenyl)pent-2-enethioate (1j).



White solid; 32% yield (for the last step).
^{1}H NMR ($CDCl_3$) δ 7.12–7.02 (m, 3H), 6.98 (d, *J* = 0.50 Hz, 2H), 6.87 (dt, *J* = 1.0, 7.5 Hz, 1H), 6.70 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.26 (dt, *J* = 15.5, 1.5 Hz, 1H), 5.03 (s, 1H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.56 (m, 2H), 2.32 (s, 6H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 188.1, 153.5, 145.6, 142.7, 139.8, 130.3, 129.2, 128.3, 127.5, 127.0, 123.5, 120.9, 115.3, 32.4, 28.7, 21.6, 21.1. Mp. 116.0–116.5 °C. TLC: R_f 0.41 (hexane/EtOAc = 3:1). IR (KBr): 3428, 3068, 2948, 1652, 1632, 1591, 1510, 1454, 1341, 1213, 1175, 1139, 1096, 963, 862, 750, 659 cm^{-1}. HRMS Calcd for $C_{20}H_{23}O_2S$: $[M+H]^+$, 327.1413. Found: *m*/*z* 327.1406.

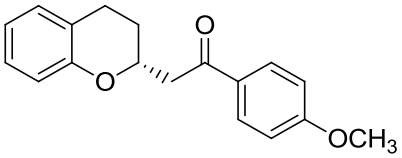
Characterization Data of Products

2-(Chroman-2-yl)-1-phenylethanone (2a).



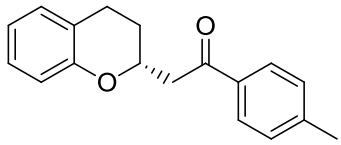
Yield: 95%, 84% *ee*, white solid. $[\alpha]_D^{18}$ –39.5 (*c* 3.61, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.01 (m, 2H), 7.59 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.49 (tt, *J* = 7.5, 1.5 Hz, 2H), 7.09–7.05 (m, 2H), 6.84 (dt, *J* = 1.0, 7.0 Hz, 1H), 6.76 (dd, *J* = 8.5, 1.0 Hz, 1H), 4.69 (m, 1H), 3.57 (dd, *J* =16.0, 6.0 Hz, 1H), 3.18 (dd, *J* = 16.0, 6.5 Hz, 1H), 2.94 (ddd, *J* = 16.5, 11.0, 6.0 Hz, 1H), 2.79 (ddd, *J* = 16.5, 5.5, 4.0 Hz, 1H), 2.20 (m, 1H), 1.82 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 197.6, 154.6, 137.2, 133.2, 129.5, 128.6, 128.2, 127.2, 121.8, 120.3, 116.8, 72.4, 44.2, 27.5, 24.5. Mp. 40.0–40.5 °C. TLC: R_f 0.60 (hexane/THF = 2:1). IR (KBr): 3076, 2916, 1685, 1582, 1487, 1451, 1218, 1116, 1051, 894, 756, 751, 692 cm^{-1}. HRMS Calcd for $C_{17}H_{17}O_2$: $[M+H]^+$, 253.1223. Found: *m*/*z* 253.1217. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm, 40 °C): t_{minor} = 19.8 min, t_{major} = 22.1 min.

2-(Chroman-2-yl)-1-(4-methoxyphenyl)ethanone (2b).



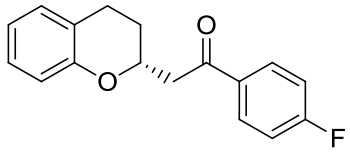
Yield: 81%, 84% *ee*, white solid. $[\alpha]_D^{18}$ –19.0 (*c* 5.20, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.99 (dt, *J* = 9.5, 2.5 Hz, 2H), 7.07 (m, 2H), 6.96 (dt, *J* = 9.5, 2.5 Hz, 2H), 6.84 (dt, *J* = 1.0, 7.5 Hz, 1H), 6.76 (dd, *J* = 7.5, 1.0 Hz, 1H), 4.67 (m, 1H), 3.88, (s, 3H), 3.52 (dd, *J* = 16.5, 5.5 Hz, 1H), 3.13 (dd, *J* = 16.5, 7.5 Hz, 1H), 2.93 (m, 1H), 2.78 (ddd, *J* = 16.0, 5.0, 3.5 Hz, 1H), 2.20 (m, 1H), 1.80 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 196.1, 163.7, 154.6, 130.6, 130.3, 129.5, 127.2, 121.8, 120.2, 116.8, 113.8, 72.3, 55.5, 43.8, 27.5, 24.5. Mp.70.0–71.0 °C. TLC: R_f 0.57 (hexane/EtOAc = 3:1). IR (KBr): 3671, 3037, 2945, 2839, 1674, 1601, 1576, 1487, 1457, 1424, 1266, 1222, 1180, 1116, 895, 840, 769, 610 cm^{-1}. HRMS Calcd for $C_{18}H_{19}O_3$: $[M+H]^+$, 283.1329. Found: *m*/*z* 283.1322. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 90/10, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 10.0 min, t_{minor} = 12.1 min.

2-(Chroman-2-yl)-1-(4-methylphenyl)ethanone (2c).



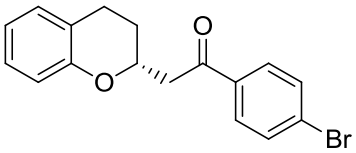
Yield: 95%, 84% *ee*, white solid. $[\alpha]_D^{18}$ –27.0 (*c* 3.95, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ7.89 (dt, *J* = 8.0, 2.0 Hz, 2H), 7.27 (dd, *J* = 8.5, 0.50 Hz, 2H), 7.07–7.03 (m, 2H), 6.83 (dt, *J* = 7.5, 1.5 Hz, 1H), 6.75 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.68 (m, 1H), 3.55 (dd, *J* = 16.5, 6.0 Hz, 1H), 3.16 (dd, *J* = 16.5, 6.5 Hz, 1H), 2.93 (ddd, *J* = 16.5, 11.0, 6.0 Hz, 1H), 2.78 (ddd, *J* = 16.5, 5.0, 3.4 Hz, 1H), 2.43 (s, 3H), 2.20 (m, 1H), 1.81 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 197.3, 154.6, 144.1, 134.6, 129.5, 129.3, 128.4, 127.2, 121.8, 120.2, 116.8, 72.5, 44.0, 27.4, 24.5, 21.6. Mp. 78.0–79.0 °C. TLC: R_f 0.50 (hexane/EtOAc = 3:1). IR (KBr): 3038, 2962, 2358, 1674, 1607, 1570, 1487, 1457, 1361, 1301, 1244, 1180, 1053, 802, 746, 374 cm^{-1}. HRMS Calcd for $C_{18}H_{19}O_2$: $[M+H]^+$, 267.1380. Found: *m*/*z* 267.1373. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 90/10, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 4.8 min, t_{minor} = 5.6 min.

2-(Chroman-2-yl)-1-(4-fluorophenyl)ethanone (2d).



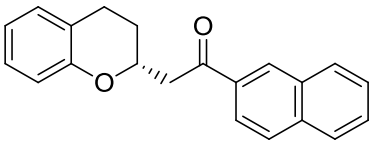
Yield: 95%, 70% *ee*, yellow oil. $[\alpha]_D^{18}$ –27.0 (*c* 3.95, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.04 (m, 2H), 7.15 (m, 2H), 7.07–7.06 (m, 2H), 6.85 (dt, *J* = 1.5, 7.5 Hz, 1H), 6.75 (dd, *J* = 8.0 1.0 Hz, 1H), 4.67 (m, 1H), 3.54 (dd, *J* = 16.5, 6.5 Hz, 1H), 3.14 (dd, *J* = 16.5, 6.5 Hz, 1H), 2.94 (ddd, *J* = 16.5, 10.5, 6.0 Hz, 1H), 2.78 (ddd, *J* = 16.5, 6.0, 7.5 Hz, 1H), 2.20 (m, 1H), 1.83 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 196.0, 165.8 (d, *J* = 255.3 Hz), 154.5, 133.6, 130.9 (d, *J* = 9.2 Hz), 129.5, 127.2, 121.7, 120.3, 116.7, 115.7 (d, *J* = 22.0 Hz), 72.4, 44.1, 27.4, 24.4. ^{19}F NMR ($CDCl_3$) δ –57.0. Mp. 60.0–61.0 °C. TLC: R_f 0.48 (hexane/EtOAc = 3:1). IR (KBr): 3039, 2956, 2356, 1680, 1597, 1506, 1488, 1458, 1411, 1363, 1299, 1232, 1158, 1054, 989, 751, 605, 374, 341 cm^{-1}. HRMS Calcd for $C_{17}H_{16}FO_2$: $[M+H]^+$, 271.1129. Found: *m*/*z* 271.1121. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 90/10, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 5.3 min, t_{minor} = 6.8 min.

(*R*)-1-(4-Bromophenyl)-2-(chroman-2-yl)ethanone (2e).



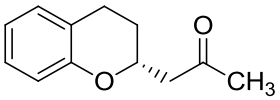
Yield: 99%, 83% *ee*, white solid. $[\alpha]_D^{18}$ –19.6 (*c* 2.80, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.87 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.62 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.08–7.04 (m, 2H), 6.84 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.73 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.66 (m, 1H), 3.52 (dd, *J* = 16.0, 6.0 Hz, 1H), 3.12 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.93 (ddd, *J* = 16.5, 11.0, 6.0 Hz, 1H), 2.78 (ddd, *J* = 16.5, 5.0, 3.0 Hz, 1H), 2.18 (m, 1H), 1.82 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 196.7, 154.5, 136.0, 132.0, 129.8, 129.5, 128.5, 127.3, 121.7, 120.4, 116.8, 72.4, 44.2, 27.5, 24.5. Mp. 77.5–78.0 °C. TLC: R_f 0.50 (hexane/EtOAc = 3:1). IR (KBr): 3067, 2939, 2364, 1680, 1585, 1487, 1457, 1301, 1242, 1201, 1054, 988, 807, 746 cm^{-1}. HRMS Calcd for $C_{17}H_{16}BrO_2$: $[M+H]^+$, 331.0328. Found: *m*/*z* 331.0319. HPLC (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 95/5, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 4.4 min, t_{major} = 5.7 min.

2-(Chroman-2-yl)-1-(naphthalen-2-yl)ethanone (2f).



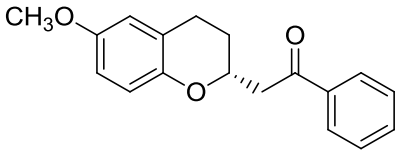
Yield: 66%, 72% *ee*, yellow solid. $[\alpha]_D^{18}$ –2.5 (*c* 2.03, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.52 (d, *J* = 1.5 Hz, 1H), 8.08 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.97 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.89 (dd, *J* = 8.0 , 0.5 Hz, 1H), 7.62 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.57 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.08 (m, 2H), 6.85 (dt, *J* = 1.5, 7.5 Hz, 1H), 6.77 (dt, *J* = 6.5, 1.5 Hz, 1H), 4.75 (m, 1H), 3.72 (dd, *J* = 16.5, 6.5 Hz, 1H), 3.30 (dd, *J* = 16.5, 1.5 Hz, 1H), 2.96 (ddd, *J* = 16.5, 11.0, 6.5 Hz, 1H), 2.81 (m, 1H), 2.25 (m, 1H), 1.87 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 197.6, 154.6, 135.7, 134.5, 132.5, 130.2, 129.6, 129.5, 128.6, 128.5, 127.8, 127.2, 126.8, 123.9, 121.8, 120.3, 116.8, 72.6, 44.2, 27.5, 24.5. Mp. 88.0–89.0 °C. TLC: R_f 0.55 (hexane/EtOAc = 3:1). IR (KBr): 3061, 2891, 2365, 1679, 1582, 1486, 1458, 1436, 1388, 1288, 1238, 1189, 1116, 838, 748 cm^{-1}. HRMS Calcd for $C_{21}H_{19}O_2$: $[M+H]^+$, 303.1380. Found: *m*/*z* 303.1372. HPLC (Daicel Chiralcel OJ-H, hexane/*i*-PrOH = 90/10, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 13.3 min, t_{minor} = 35.2 min.

1-(Chroman-2-yl)propan-2-one (2g).



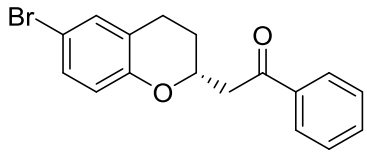
Yield: 64%, 36% *ee*, colorless oil. $[\alpha]_D^{18}$ +32.1 (*c* 0.47, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.07 (m, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.84 (dt, *J* = 1.0, 7.5 Hz, 1H), 6.77 (dd, *J* = 8.5, 1.0 Hz, 1H), 4.48 (m, 1H), 2.92 (dd, *J* =16.0, 7.5 Hz, 1H), 2.88 (dd, *J* = 11.0, 6.0 Hz, 1H), 2.75 (m, 1H), 2.66 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.25 (s, 3H), 2.07 (m, 1H), 1.74 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 206.4, 154.4, 129.5, 127.2, 121.6, 120.4, 116.8, 72.1, 49.1, 30.9, 27.4, 24.4. TLC: R_f 0.45 (hexane/EtOAc = 3:1). IR (neat): 3072, 2926, 2852, 1774, 1716, 1583, 1488, 1457, 1361, 1232, 1117, 977, 885, 756, 665, 462 cm^{-1}. HRMS Calcd for $C_{12}H_{15}O_2$: $[M+H]^+$, 191.1067. Found: *m*/*z* 191.1062. HPLC (Daicel Chiralpak AD-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm, 40 °C): t_{major} = 13.8 min, t_{minor} = 15.0 min.

2-(6-Methoxychroman-2-yl)-1-phenylethanone (2h).



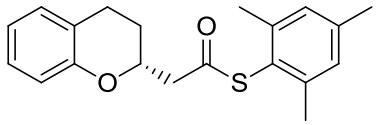
Yield: 86%, 74% *ee*, colorless oil. $[\alpha]_D^{18}$ –292.6 (*c* 0.54, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.01 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.59 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.45 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.32 (d, *J* = 2.5 Hz, 1H), 4.68 (m, 1H), 3.73 (s, 3H), 3.55 (dd, *J* = 16.5, 6.0 Hz, 1H), 3.17 (dd, *J* = 16.5, 6.5 Hz, 1H), 2.86 (ddd, *J* = 16.5, 11.0, 6.0 Hz, 1H), 2.72 (ddd, *J* = 16.5, 6.0, 3.5 Hz, 1H), 2.18 (m, 1H), 1.78 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 197.6, 159.0, 155.2, 137.0, 133.3, 130.0, 128.6, 128.2, 113.9, 107.3, 101.5, 72.4, 55.3, 44.1, 27.6, 23.7. TLC: R_f 0.55 (hexane/EtOAc = 3:1). IR (neat): 3079, 2947, 2868, 2390, 1694, 1619, 1579, 1514, 1453, 1274, 1242, 1139, 1093, 1044, 995, 879, 773, 746 cm^{-1}. HRMS Calcd for $C_{18}H_{19}O_3$: $[M+H]^+$, 283.1329. Found: *m*/*z* 283.1328. HPLC (Daicel Chiralpak IA-H, hexane/*i*-PrOH = 80/20, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 3.7 min, t_{major} = 3.4 min.

2-(6-Bromochroman-2-yl)-1-phenylethanone (2i).



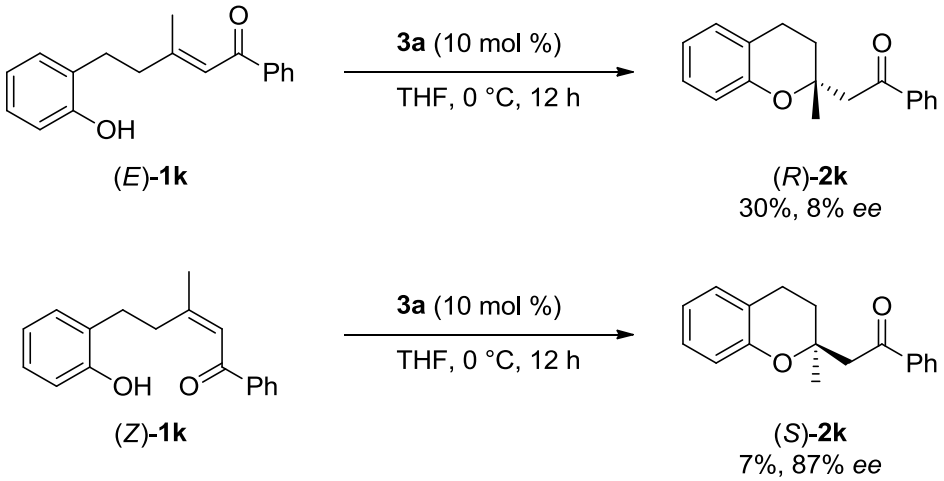
Yield: 68%, 65% *ee*, white solid. $[\alpha]_D^{18}$ –277.8 (*c* 0.18, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.99 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.59 (tt, *J* = 9.0, 1.5 Hz, 1H), 7.49 (tt, *J* = 7.5, 1.5 Hz, 2H), 7.18 (m, 1H), 7.15 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 4.67 (m, 1H), 3.55 (dd, *J* = 16.5, 6.5 Hz, 1H), 3.18 (dd, *J* = 8.5, 6.5 Hz, 1H), 2.91 (ddd, *J* = 16.5, 11.0, 6.0, 1H), 2.75 (ddd, *J* = 16.5, 11.0, 8.5 Hz, 1H), 2.18 (m, 1H), 1.78 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 197.4, 153.7, 136.9, 133.4, 132.0, 130.1, 128.7, 128.2, 123.9, 118.6, 112.3, 72.6, 43.9, 27.0, 24.4. Mp. 85.0–85.5 °C. TLC: R_f 0.60 (hexane/EtOAc = 3:1). IR (KBr): 3085, 2941, 2914, 2283, 1742, 1694, 1660, 1620, 1563, 1480, 1377, 1251, 1191, 1137, 1061, 998, 892, 804 cm^{-1}. HRMS Calcd for $C_{17}H_{16}BrO_2$: $[M+H]^+$, 331.0328. Found: *m*/*z* 331.0327. HPLC (Daicel Chiralpak IA-H, hexane/*i*-PrOH = 80/20, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 3.1 min, t_{major} = 3.4 min.

***S*-Mesityl 2-(Chroman-2-yl)ethanethioate (2j)**.



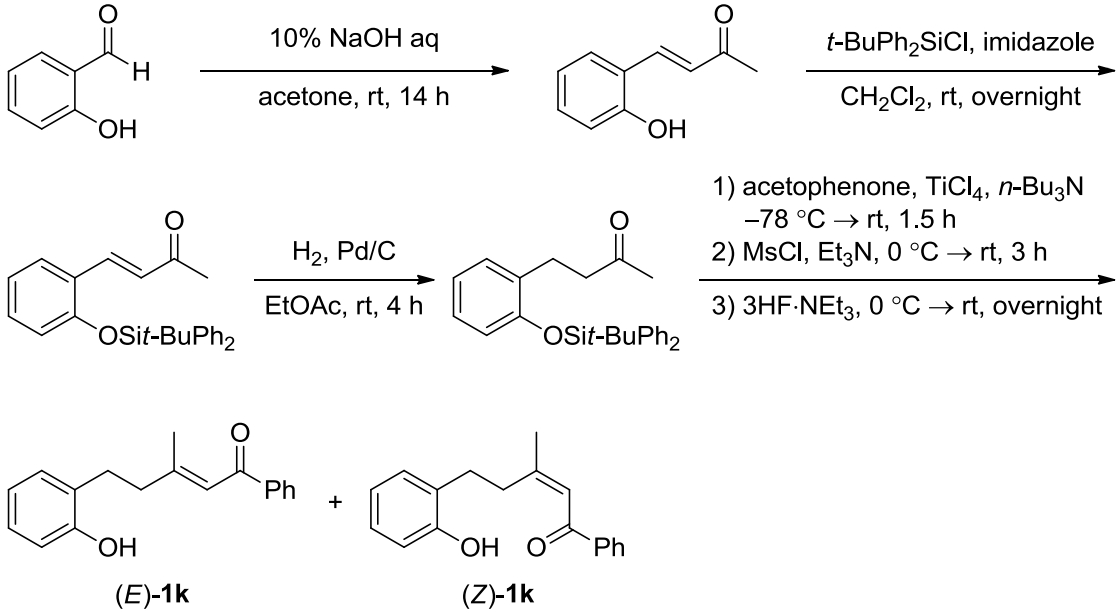
Yield: 38%, 75% *ee*, Colorless oil. $[\alpha]_D^{18}$ –128.8 (*c* 0.40, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.09 (m, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.99 (s, 2H), 6.85 (dt, *J* = 1.5, 7.5 Hz, 1H), 6.79 (dd, *J* = 8.5, 1.5 Hz, 1H), 4.55 (m, 1H), 3.13 (dd, *J* = 15.0, 7.5 Hz, 1H), 2.93–2.86 (m, 2H), 2.79 (ddd, *J* = 16.5, 5.0, 3.5 Hz, 1H), 2.36 (s, 6H), 2.30 (s, 3H), 2.10 (m, 1H), 1.84 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 194.5, 154.6, 142.7, 140.2, 129.7, 129.4, 127.5, 123.9, 121.7, 120.6, 117.1, 73.0, 49.1, 27.4, 24.5, 21.8, 21.3. TLC: R_f 0.50 (hexane/EtOAc = 3:1). IR (neat): 3023, 2924, 2852, 2364, 1696, 1583, 1488, 1457, 1235, 1116, 1059, 979, 894, 851, 753, 482 cm^{-1}. HRMS Calcd for $C_{20}H_{23}O_2S$: $[M+H]^+$, 327.1413. Found: *m*/*z*327.1404. HPLC (Daicel Chiralpak IB-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm, 40 °C): t_{minor} = 12.7 min, t_{major} = 16.2 min.

Scheme S1. Reactions from β-Disubstituted α,β-Unsaturated Ketones



β-Disubstituted α,β-unsaturated ketones **1k** were less reactive through this catalytic process, and the enantiomeric excess of (*R*)-**2k** obtained from (*E*)-**1k** were only slight presumably because of the larger impact of noncatalytic racemic reaction under the current condition. On the other hand, the reaction starting from (*Z*)-**1k** afforded the opposite enantiomer (*S*)-**2k** with high enantioselectivity albeit in modest yield.

Procedure for preparation of 1k



β-Disubstituted α,β-unsaturated ketones **1k** were prepared through the synthetic route indicated above by modified procedures of the literature methods.[3,4]

To a solution of salicylaldehyde (10 g, 82 mmol) in acetone (20 mL) was added 10 wt% aquous NaOH (70 mL, 185 mmol) slowly at ambient temperature. The reaction mixture was stirred for14 h. 1 N Aquous HCl (1 mL) was added, and the aqueous phase was washed with $CHCl_3$ (10 mL × 3). The aqueous phase was subsequently neutralized with 1N aquous HCl until the pH value reachedca. 6, and a orange solid was precipitated. After the precipitate collected by filtration was dried, recrystalization with EtOAc/benzene (v/v = 1/1) as a solvent gave (*E*)-4-(2-hydroxyphenyl)but-3-en-2-one as a yellow solid in 73% yield (9.8 g, 60 mmol). CAS RN [6051-53-2]. ^{1}H NMR ($CDCl_3$) δ 7.87 (d, *J* = 16.5 Hz, 1H), 7.56 (s, 1H), 7.47 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.26 (dt, *J* = 2.5, 1.5 Hz, 1H), 7.04 (d, *J* = 16.5 Hz, 1H), 6.94–6.91 (m, 2H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 201.0, 156.0, 140.6, 131.9, 129.6, 127.7, 121.6, 120.7, 116.6, 26.9.

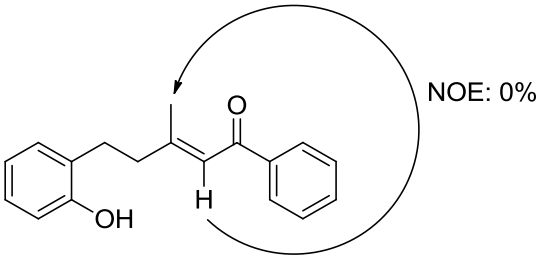
The solution of (*E*)-4-(2-Hydroxyphenyl)but-3-en-2-one (3.0 g, 19 mmol) and imidazole (1.7 g, 26 mmol) in CH_2Cl_2 (30 mL) was cooled to 0°C. To the mixuture wasadded TBDPSCl (5.7 mL, 22 mmol) dropwise slowly. The solution was warmed to ambient temperature and stirred overnight. The reaction mixture was quenched with H_2O (20 mL), and the aqueous phase was extracted with EtOAc (20 mL × 3). The combined organic layers were washed with H_2O (30 mL×2) and brine,dried over Na_2SO_4, and concentrated in vacuo. Purification by flush silica gel column chromatography using hexane/EtOAc (v/v = 10/1) as an eluent gave (*E*)-4-(2-((tert-butyldiphenylsilyl)oxy)phenyl)but-3-en-2-one as a pale yellow oil quantitatively (7.0 g, 19 mmol). ^{1}H NMR ($CDCl_3$) δ 8.22 (d, *J* = 16.5 Hz, 1H), 7.72 (dt, *J* = 6.0, 1.5 Hz, 4H), 7.58 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.45 (tt, *J* = 7.5, 1.5 Hz, 2H), 7.40–7.37 (m, 4H), 6.96 (ddd, *J* = 8.0, 7.5, 1.5 Hz, 1H), 6.89 (ddt, *J* = 1.5, 0.5, 7.0 Hz, 1H), 6.70 (d, *J* = 16.5 Hz, 1H), 6.50 (dd, *J* = 8.5, 1.0 Hz, 1H), 2.40 (s, 3H), 1.16 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 198.8, 154.4, 138.9, 135.4, 132.1, 131.3, 130.2, 128.0, 127.6, 127.1, 125.3, 121.5, 119.9, 31.6, 26.6, 19.6. TLC: R_f 0.46 (hexane/EtOAc = 3:1). IR (neat): 3090, 2959, 2860, 1669, 1599, 1483, 1250, 1114, 925, 822, 755, 701, 615, 572, 507. HRMS Calcd for $C_{26}H_{29}O_2Si$: $[M+H]^+$, 401.1931. Found: *m*/*z* 401.1926.

After Pd/C (10 wt%, 945 mg, 10 mol %) in a 100 mL flask was degassed under reduced pressure, H_2 gas (balloon) was introduced into the flask, and EtOAc (30 mL) was added. The solution of (*E*)-4-(2-((*tert*-butyldiphenylsilyl)oxy)phenyl)but-3-en-2-one (3.4 g, 8.5 mmol) in EtOAc (20 mL) was added, and the mixture was stirred at ambient temperature for 4 h. The reaction mixuture was diluted with EtOAc, passed through a

short celite pad to remove Pd/C, and concentrated in vacuo. Purification by flush silica gel column chromatography using hexane/EtOAc (v/v = 10/1) as an eluent gave 4-(2-((*tert*-butyldiphenylsilyl)oxy)phenyl)butan-2-one as a colorless oil quantitatively (3.4 g, 8.5 mmol). ^{1}H NMR ($CDCl_3$) δ 7.73–7.70 (m, 4H), 7.45–7.41 (m, 2H), 7.39–7.35 (m, 4H), 7.14 (m, 1H), 6.79 (m, 2H), 6.44 (m, 1H), 3.06 (t, *J* = 2.5 Hz, 2H), 2.84 (t, *J* = 2.5 Hz, 2H), 2.14 (s, 3H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 208.1, 153.4, 135.4, 132.8, 130.9, 130.1, 129.9, 127.8, 127.0, 121.1, 119.0, 43.9, 30.0, 26.6, 25.4, 19.5. TLC: R_f 0.35 (hexane/EtOAc = 3:1). IR (neat): 3072, 2959, 2859, 1719, 1583, 1492, 1428, 1252, 1112, 931, 823, 756, 701, 488. HRMS Calcd for $C_{26}H_{31}O_2Si$: $[M+H]^+$, 403.2088. Found: *m*/*z* 403.2083.

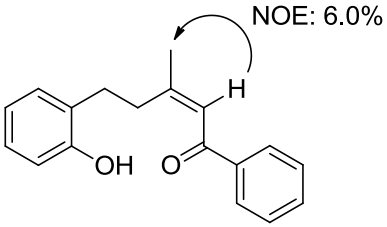
The solution of acetophenone (1.2 mL,10 mmol) in CH_2Cl_2 (15 mL) was cooled to −78 °C. The solution of $TiCl_4$ (2.9 g, 15 mmol) in CH_2Cl_2 (15 mL) and Bu_3N (4.2 mL, 18 mmol) was added, and the mixture was stirred for 1.5 h. 4-(2-((*tert*-Butyldiphenylsilyl)oxy)phenyl)butan-2-one (4.0 g, 10 mmol) was then added slowly, and the solution was warmed to ambient temperature. The mixture was stirred for additional 1.5 h. After the reaction mixture was cooled to 0 °C, mesyl chloride(1.6 mL, 20 mmol) and Et_3N (1.7 mL, 12 mmol) was added. After being stirred for 3h, the reaction was quenched with saturated aquous $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were washed with saturated aquous $NaHCO_3$ (30 mL × 3) and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flush silica gel column chromatography using hexane/EtOAc (v/v = 3/1) as an eluent gave each stereoisomer of 5-(2-((*tert*-butyldiphenylsilyl)oxy)phenyl)-3-methyl-1-phenylpent-2-en-1-one as a pale yellow oil in 10% yield for (*E*)-isomer (500mg, 0.99 mmol) and in 3% yield for (*Z*)-isomer (145mg, 0.29 mmol). The solution of each stereoisomer of 5-(2-((*tert*-butyldiphenylsilyl)oxy)phenyl)-3-methyl-1-phenylpent-2-en-1-one in CH_3CN (0.15 M) was cooled to 0 °C, and 3HF•NEt_3 (3 equiv) was added dropwise. The reaction mixture was subsequently warmed to ambient temperature and stirred overnight. The mixture was quenched by saturated aquous K_2CO_3. The aqueous phase was extracted with EtOAc (15 mL × 3). The combined organic layers were washed with H_2O (30 mL × 2) and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flush silica gel column chromatography using hexane/EtOAc (v/v = 3/1) as an eluent gave the corresponding stereoisomer of 5-(2-hydroxyphenyl)-3-methyl-1-phenylpent-2-en-1-one (**1k**).

(*E*)-5-(2-Hydroxyphenyl)-3-methyl-1-phenylpent-2-en-1-one ((*E*)-1k).



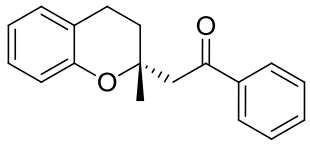
Yield: 20%, Colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.80–7.78 (m, 2H), 7.50 (t, *J* = 7.5, 1.0 Hz, 1H), 7.41 (tt, *J* = 7.5, 1.0 Hz, 2H), 7.14–7.09 (m, 2H), 6.89 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.63 (m, 1H), 5.06 (br s, 1H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.57 (dt, *J* = 7.5, 0.50 Hz, 2H), 2.25 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 192.1, 158.8, 153.6, 139.2, 132.3, 130.4, 128.4, 128.3, 127.4, 121.4, 121.0, 115.3, 41.3, 28.4, 19.8. TLC: R_f 0.36 (hexane/EtOAc = 3:1). IR (neat): 2924, 2853, 1685, 1654, 1506, 1449, 1359, 1242, 1156, 1103, 1042, 856, 753, 689, 477 cm^{-1}. HRMS Calcd for $C_{18}H_{19}O_2$: $[M+H]^+$, 267.1380. Found: *m*/*z* 267.1375.

(*Z*)-5-(2-Hydroxyphenyl)-3-methyl-1-phenylpent-2-en-1-one ((*Z*)-1k).



Yield: 10%, pale yallow oil. ^{1}H NMR ($CDCl_3$) δ 8.30 (s, 1H), 8.02 (t, *J* = 1.5 Hz, 2H), 7.57 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.17 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.13 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.00 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.93 (d, *J* = 1.0 Hz, 1H), 6.85 (dt, *J* = 7.5, 1.5 Hz, 1H), 2.87–2.84 (m, 2H), 2.76–2,72 (m, 2H), 2.16 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 191.4, 162.7, 155.4, 138.7, 132.8, 129.8, 128.54, 128.50, 128.1, 126.1, 120.4, 119.9, 116.6, 36.4, 30.7, 26.8. TLC: R_f 0.36 (hexane/EtOAc = 3:1). IR (neat): 3026, 2978, 2933, 2366, 1676, 1654, 1603, 1503, 1465, 1244, 1221, 1102, 852, 754, 668, 466 cm^{-1}. HRMS Calcd for $C_{18}H_{19}O_2$: $[M+H]^+$, 267.1380. Found: *m*/*z* 267.1374.

2-(2-Methylchroman-2-yl)-1-phenyl-ethanone (2k)



From (*E*)-**1i**: 30% yield, 8% *ee*.

From (*Z*)-**1i**: 7% yield, –87% *ee*; $[\alpha]_D^{18}$ –166.0 (*c* 0.053, CH_2Cl_2).

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.96–7.94 (m, 2H), 7.55 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.46–7.42 (m, 2H), 7.10–7.05 (m, 2H), 6.84 (dt, *J* = 8.0, 1.5 Hz, 1H), 6.71 (dd, *J* = 8.0, 1.0 Hz, 1H), 3.39 (d, *J* = 15.5 Hz, 1H), 3.23 (d, *J* = 15.5 Hz, 1H), 2.78 (m, 2H), 2.19–2.14 (m, 1H), 2.05–2.00 (m, 1H), 1.48 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 198.3, 153.3, 137.9, 133.1, 129.5, 128.5, 128.4, 127.4, 121.1, 120.1, 117.4, 75.8, 46.9, 31.0, 25.0, 22.1. TLC: R_f 0.51 (hexane/EtOAc = 3:1). IR (neat): 2966, 2928, 2856, 2366, 1654, 1636, 1592, 1507, 1457, 1420, 1261, 1105, 752, 665, 465 cm^{-1}. HRMS Calcd for $C_{18}H_{19}O_2$: $[M+H]^+$, 267.1380. Found: *m*/*z* 267.1373. HPLC (Daicel Chiralpak IC-H, hexane/*i*-PrOH = 98/2, flow rate = 0.5 mL/min, λ = 254 nm, 40 °C): t_{major} = 12.4 min, t_{minor} = 13.0 min.

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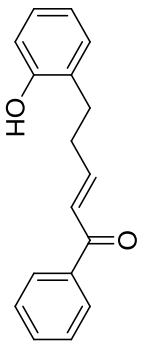
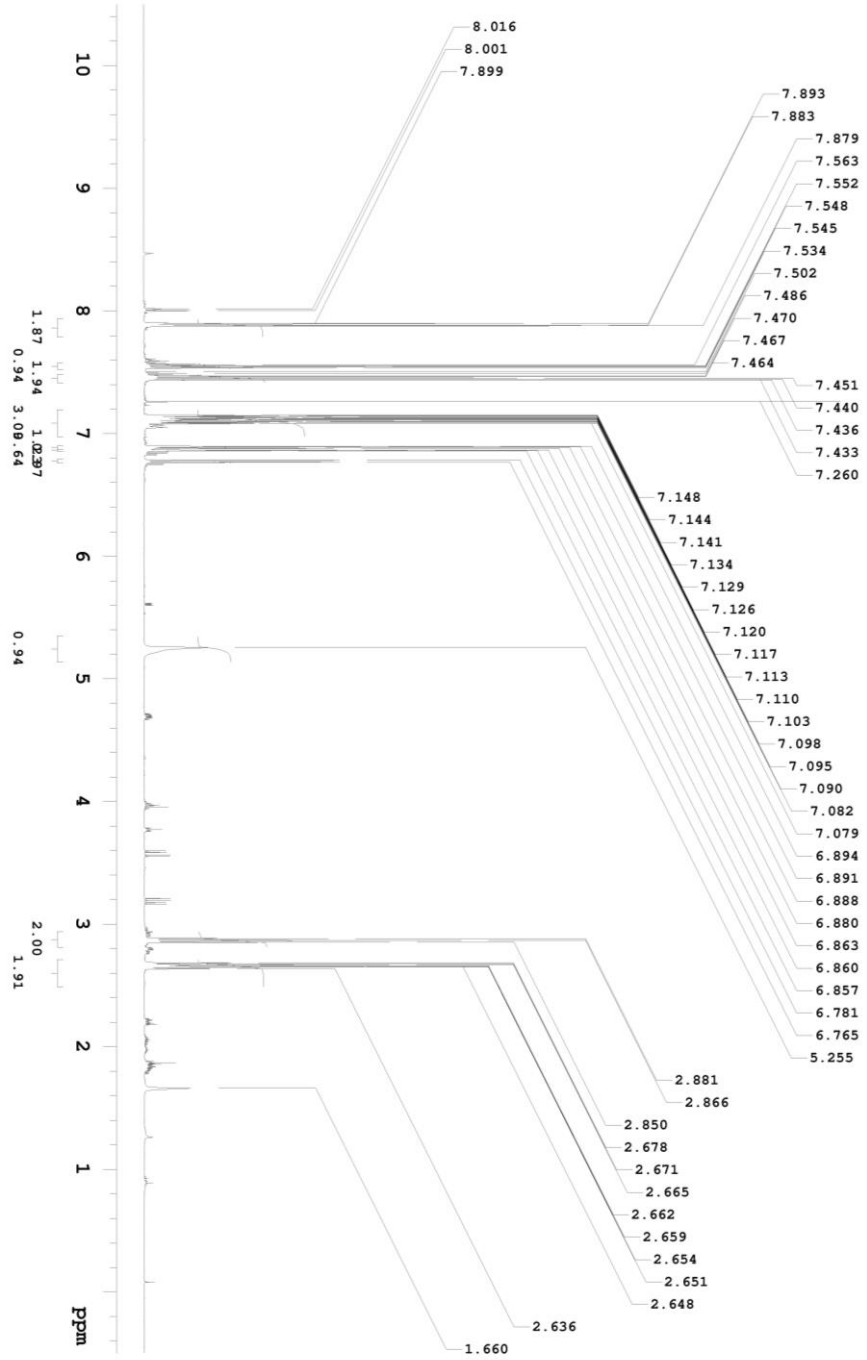
NMR Spectra (^{1}H, ^{13}C) of Substrates

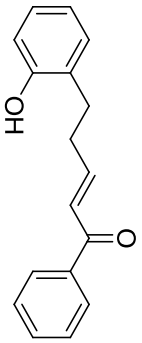


(*E*)-5-(2-Hydroxyphenyl)-1-phenylpent-2-en-1-one (1a)

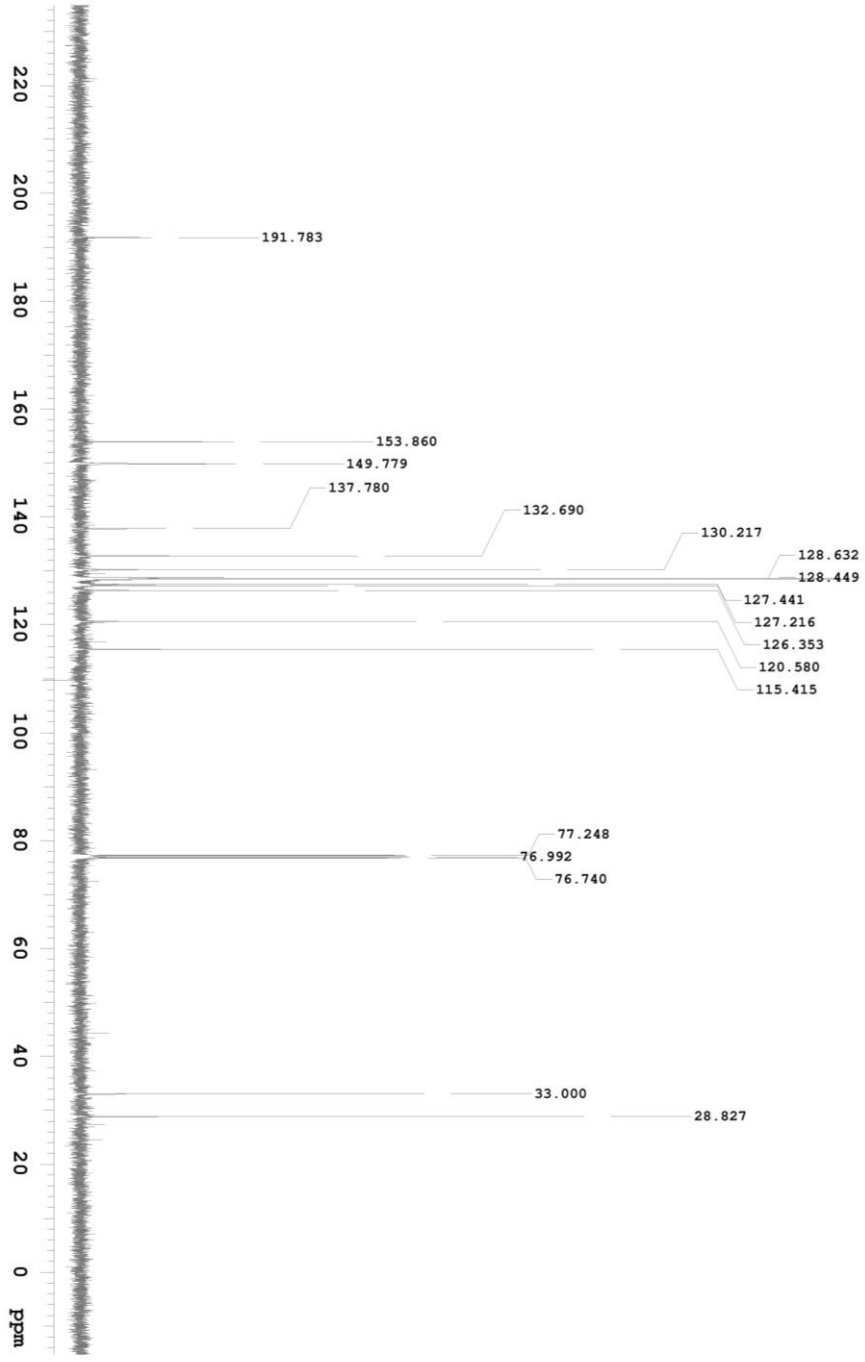
^{1}H NMR



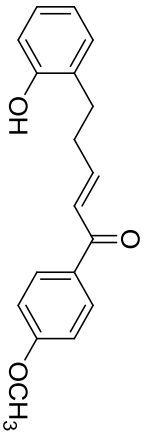
(*E*)-5-(2-Hydroxyphenyl)-1-phenylpent-2-en-1-one (1a)



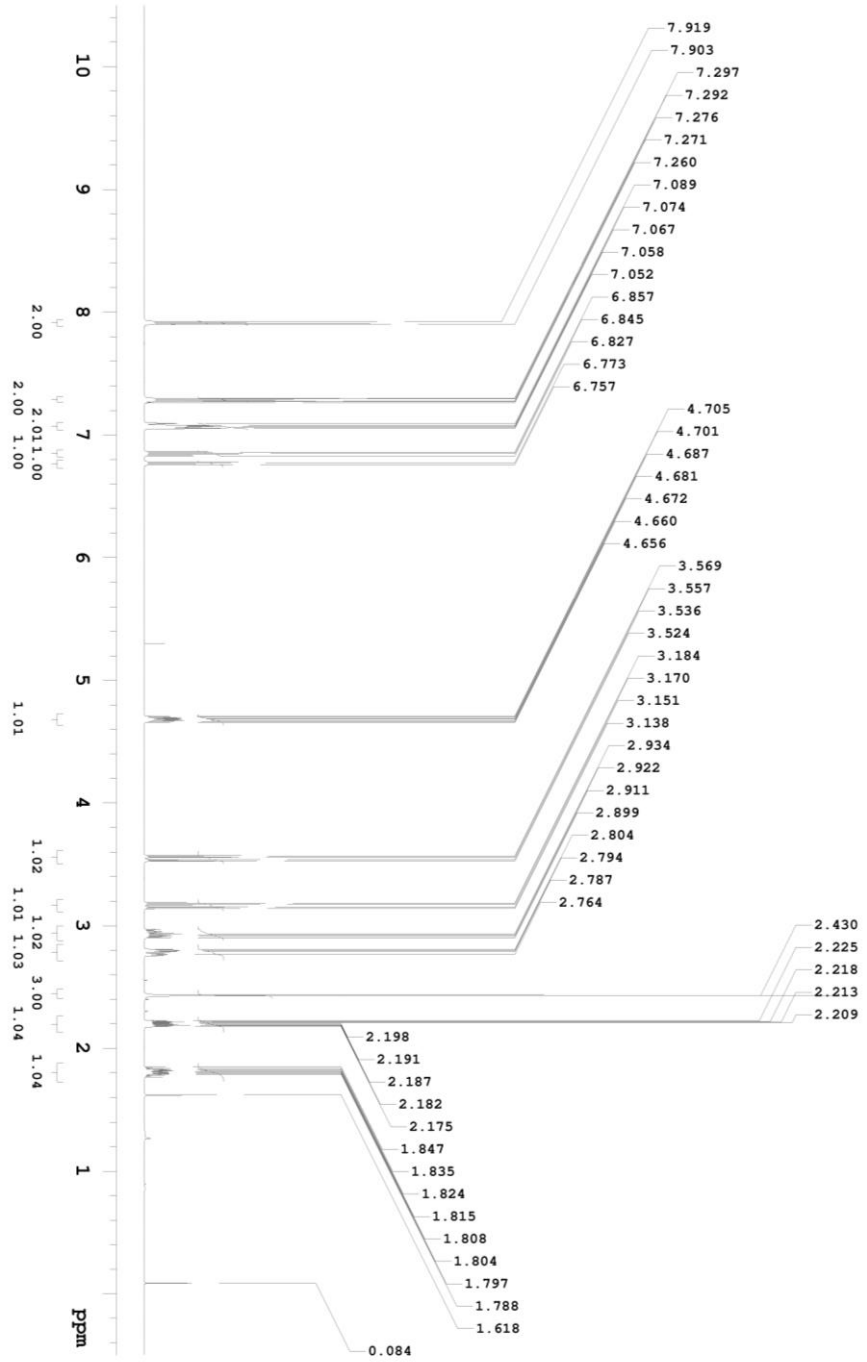
^{13}C NMR



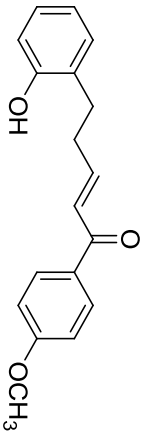
(*E*)-5-(2-Hydroxyphenyl)-1-(4-methoxyphenyl)pent-2-en-1-one (1b)



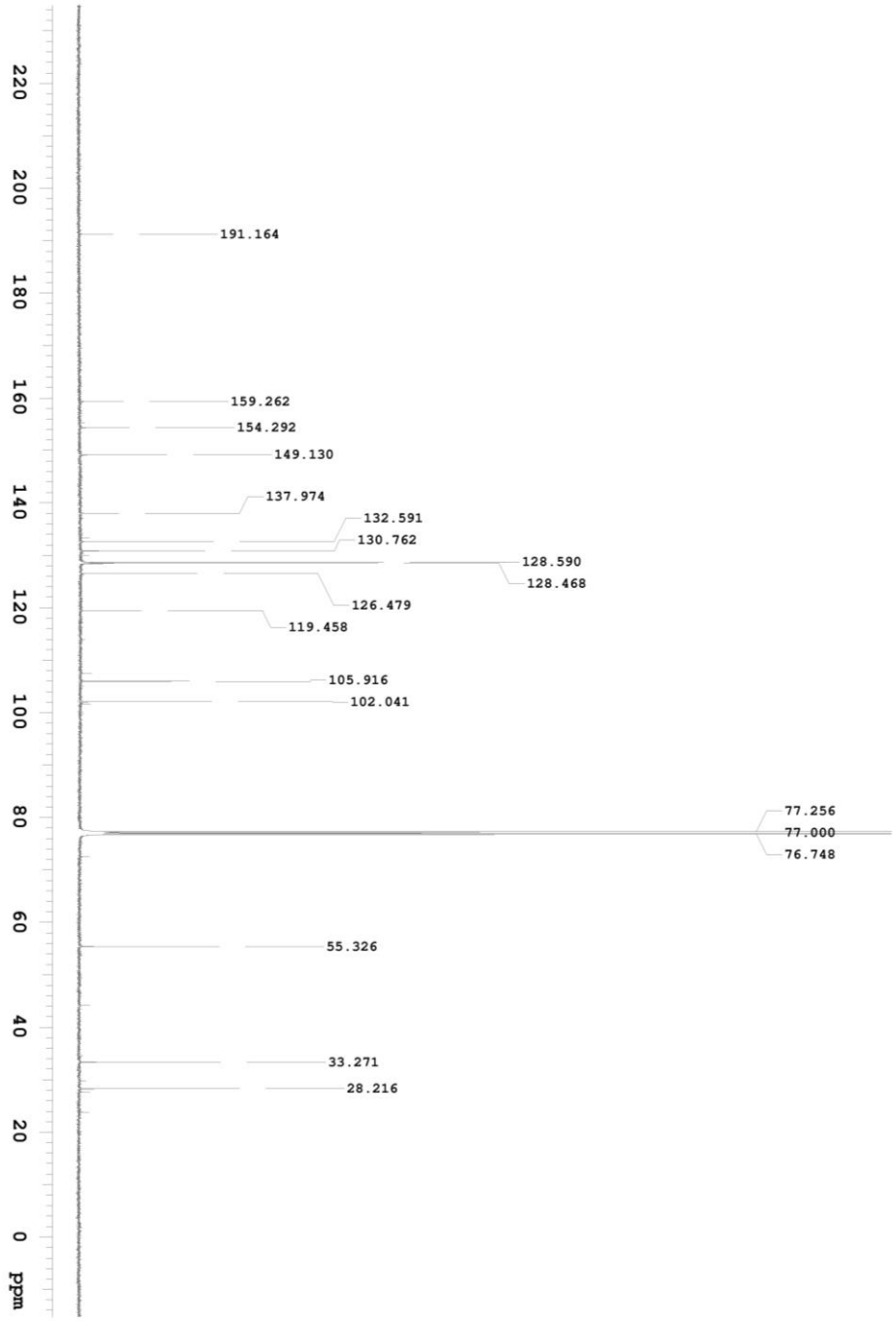
^{1}H NMR



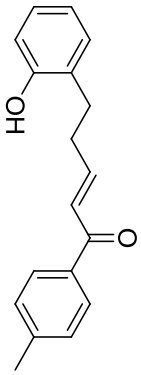
(*E*)-5-(2-Hydroxyphenyl)-1-(4-methoxyphenyl)pent-2-en-1-one (1b)



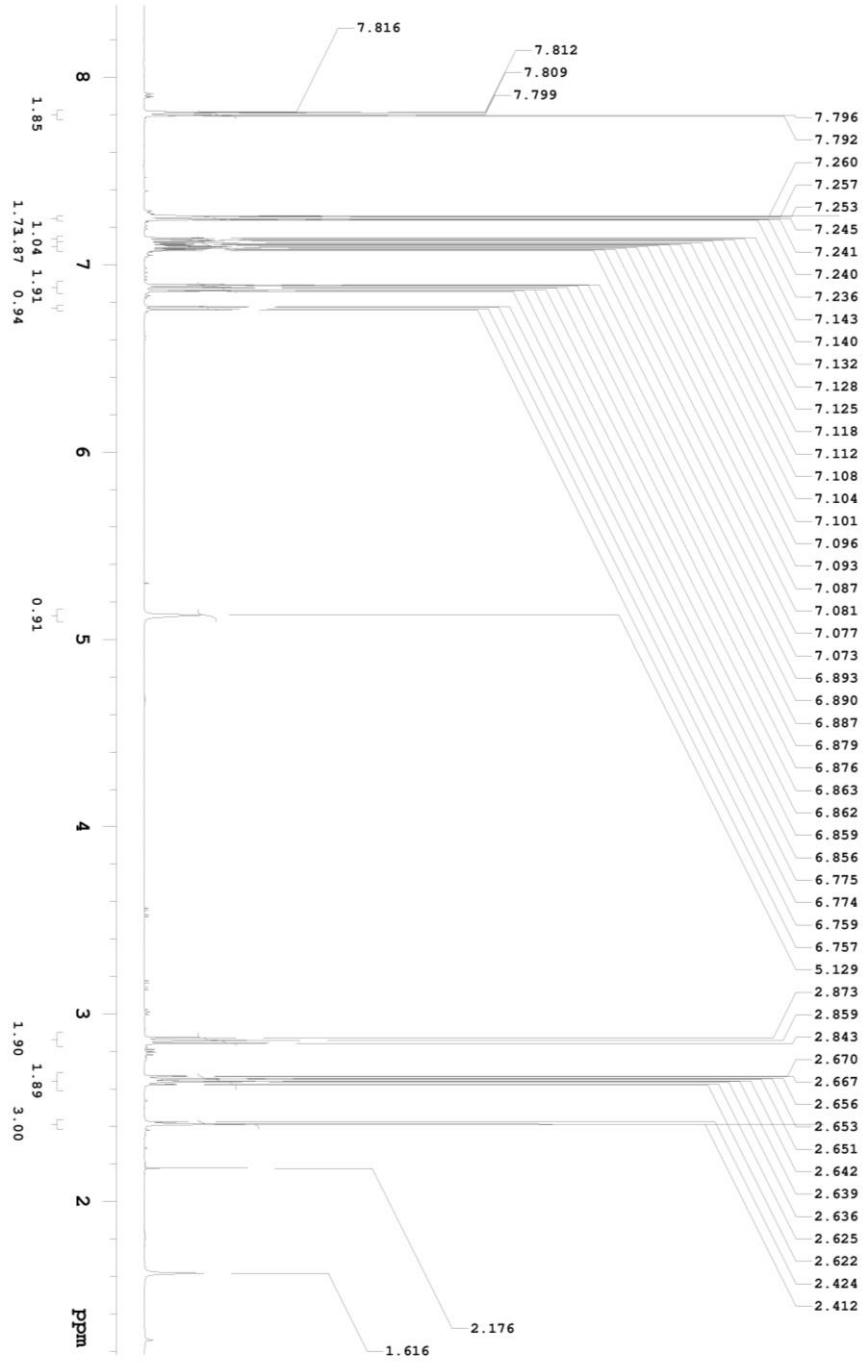
^{13}C NMR



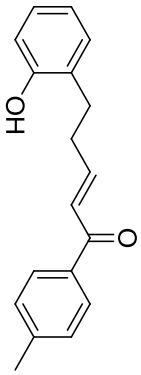
(*E*)-5-(2-Hydroxyphenyl)-1-(4-methylphenyl)pent-2-en-1-one (1c)



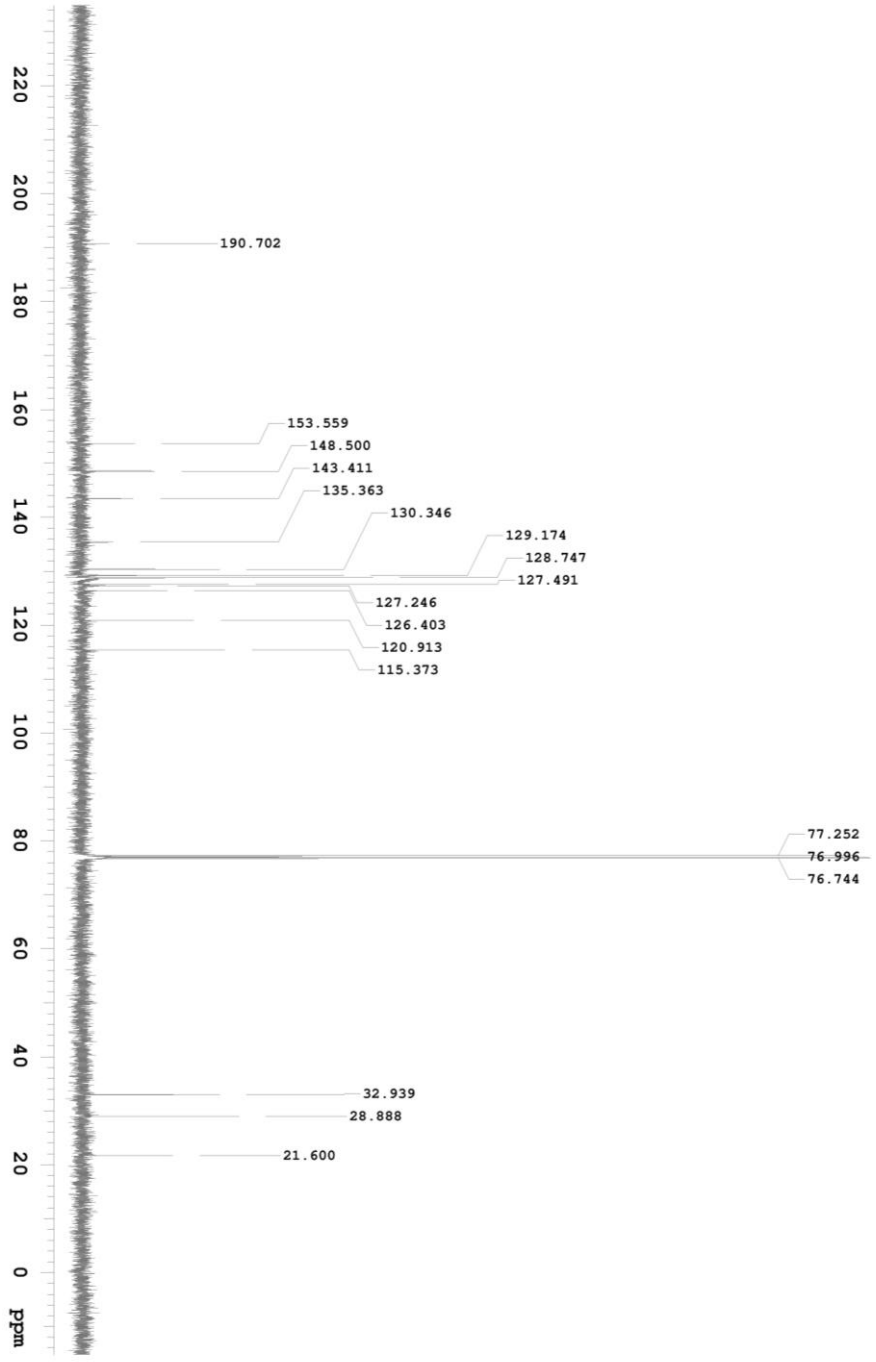
^{1}H NMR



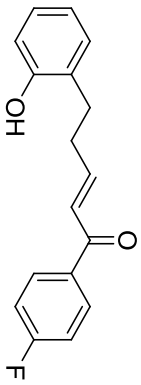
(*E*)-5-(2-Hydroxyphenyl)-1-(4-methylphenyl)pent-2-en-1-one (1c)



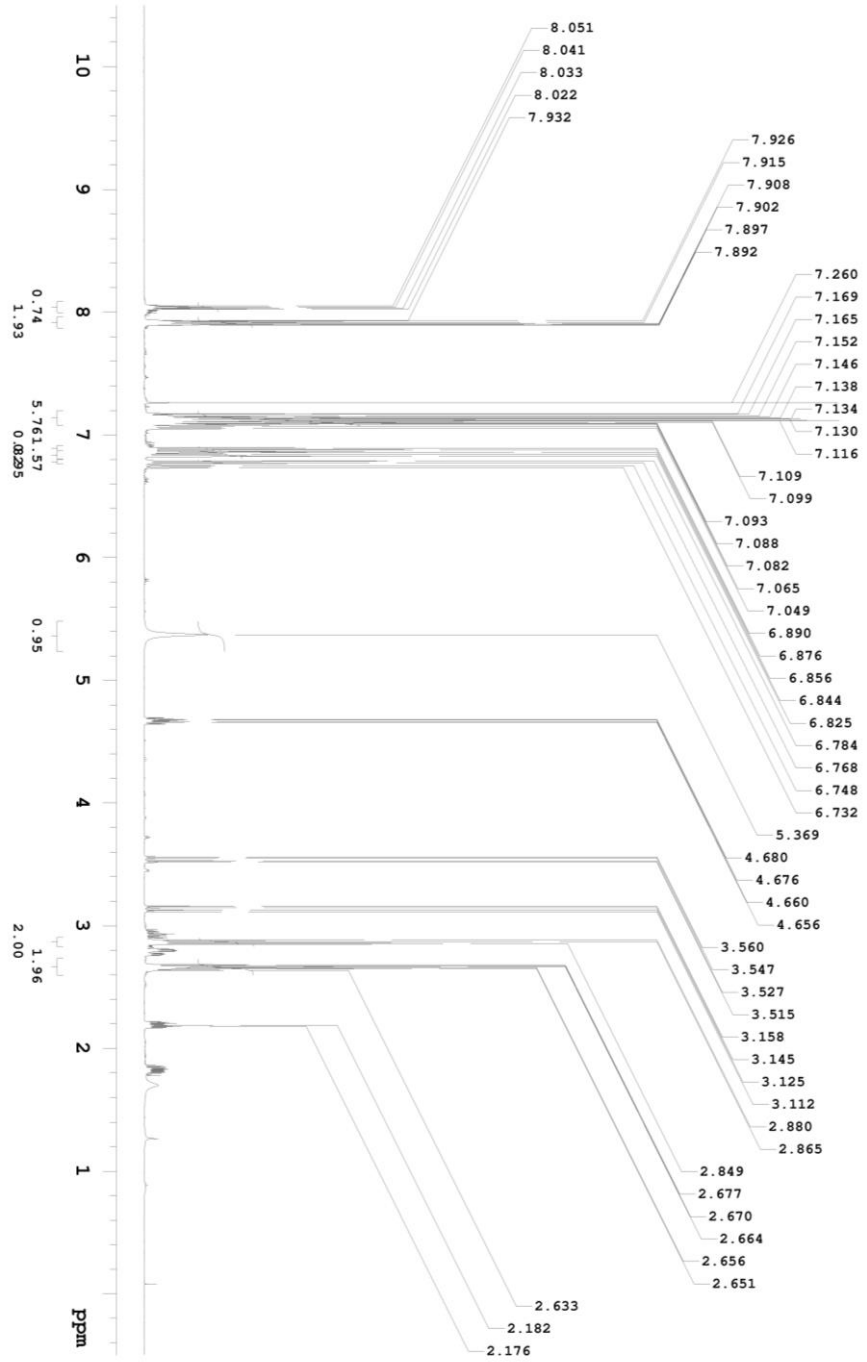
^{13}C NMR



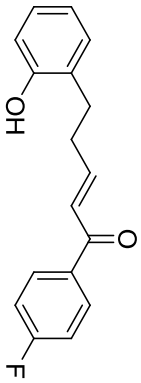
(*E*)-1-(4-Fluorophenyl)-5-(2-hydroxyphenyl)pent-2-en-1-one (1d)



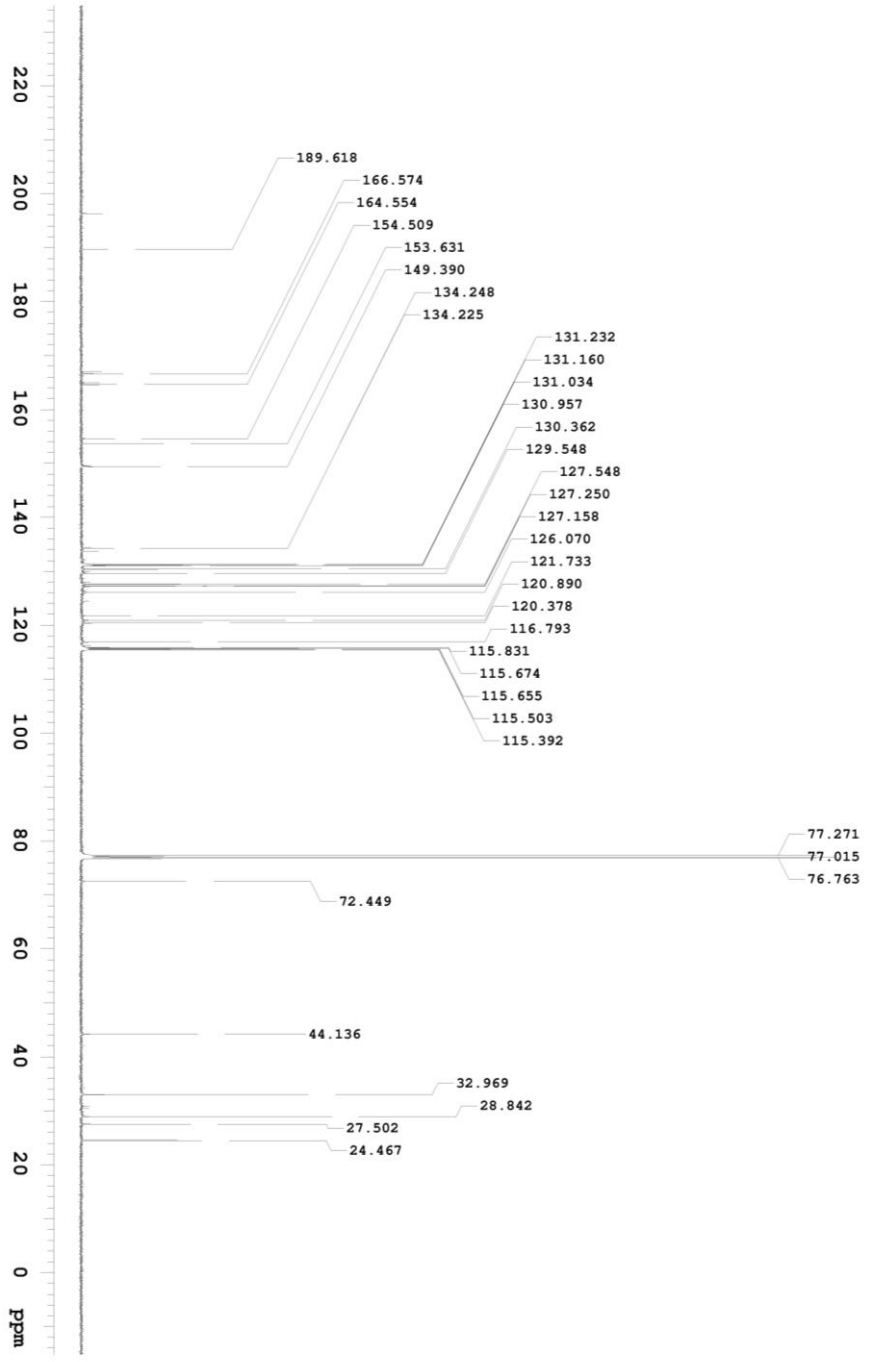
^{1}H NMR



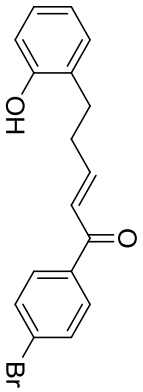
(*E*)-1-(4-Fluorophenyl)-5-(2-hydroxyphenyl)pent-2-en-1-one (1d)



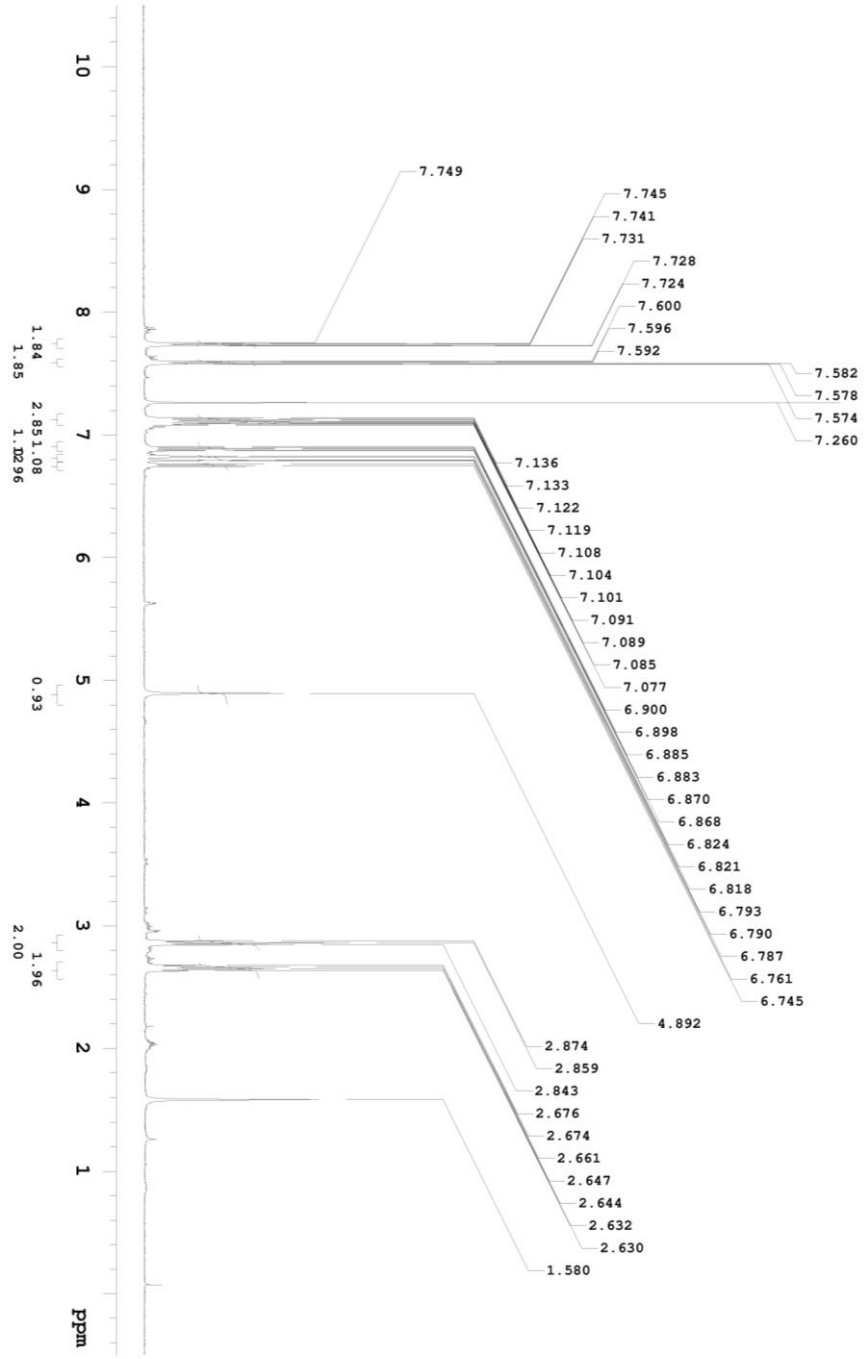
^{13}C NMR



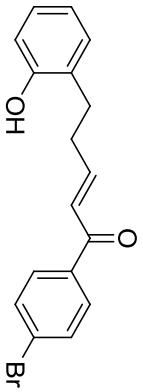
(*E*)-1-(4-Bromophenyl)-5-(2-hydroxyphenyl)pent-2-en-1-one (1e)



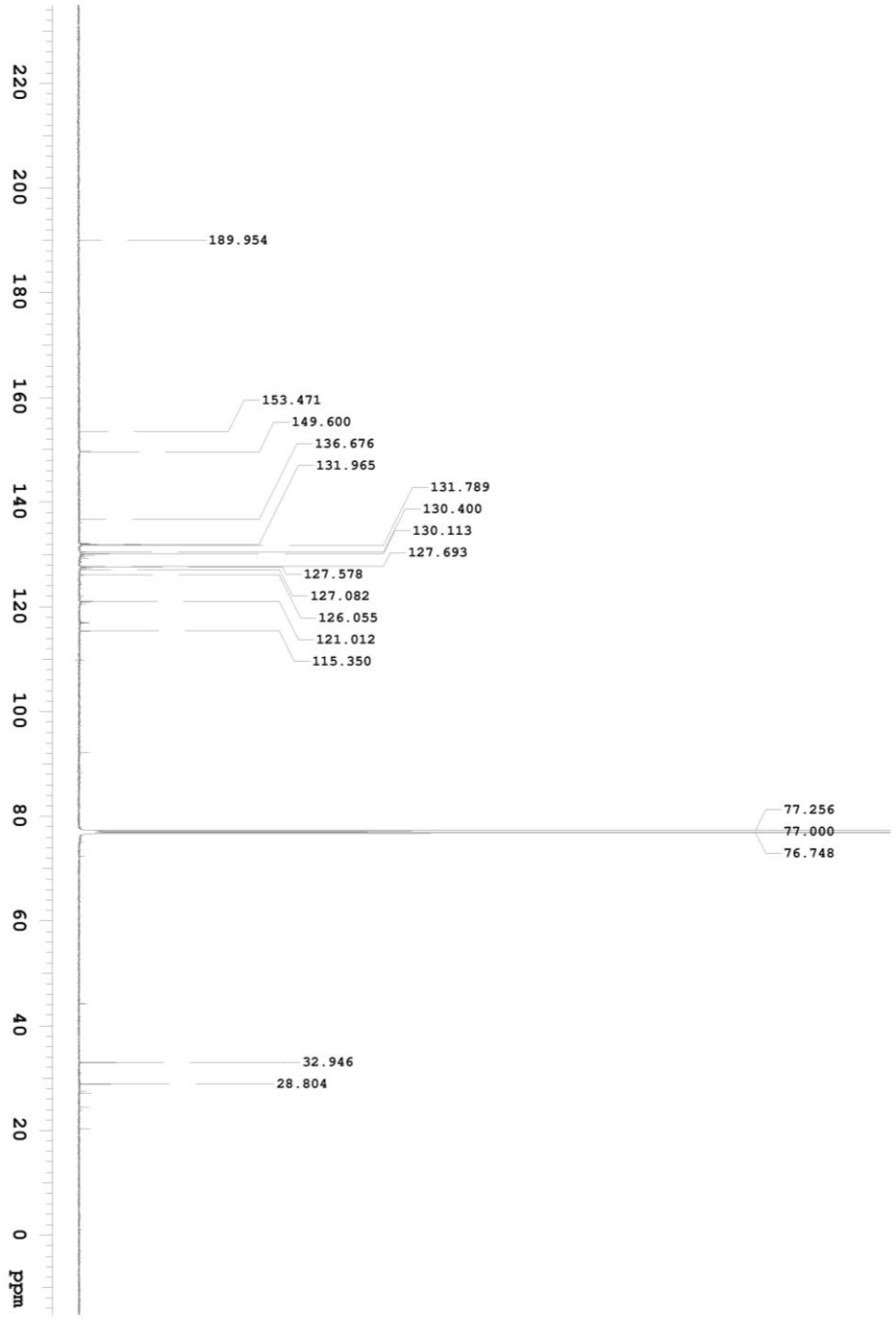
^{1}H NMR



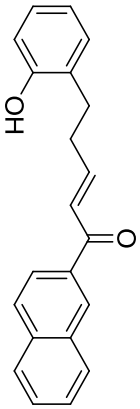
(*E*)-1-(4-Bromophenyl)-5-(2-hydroxyphenyl)pent-2-en-1-one (1e)



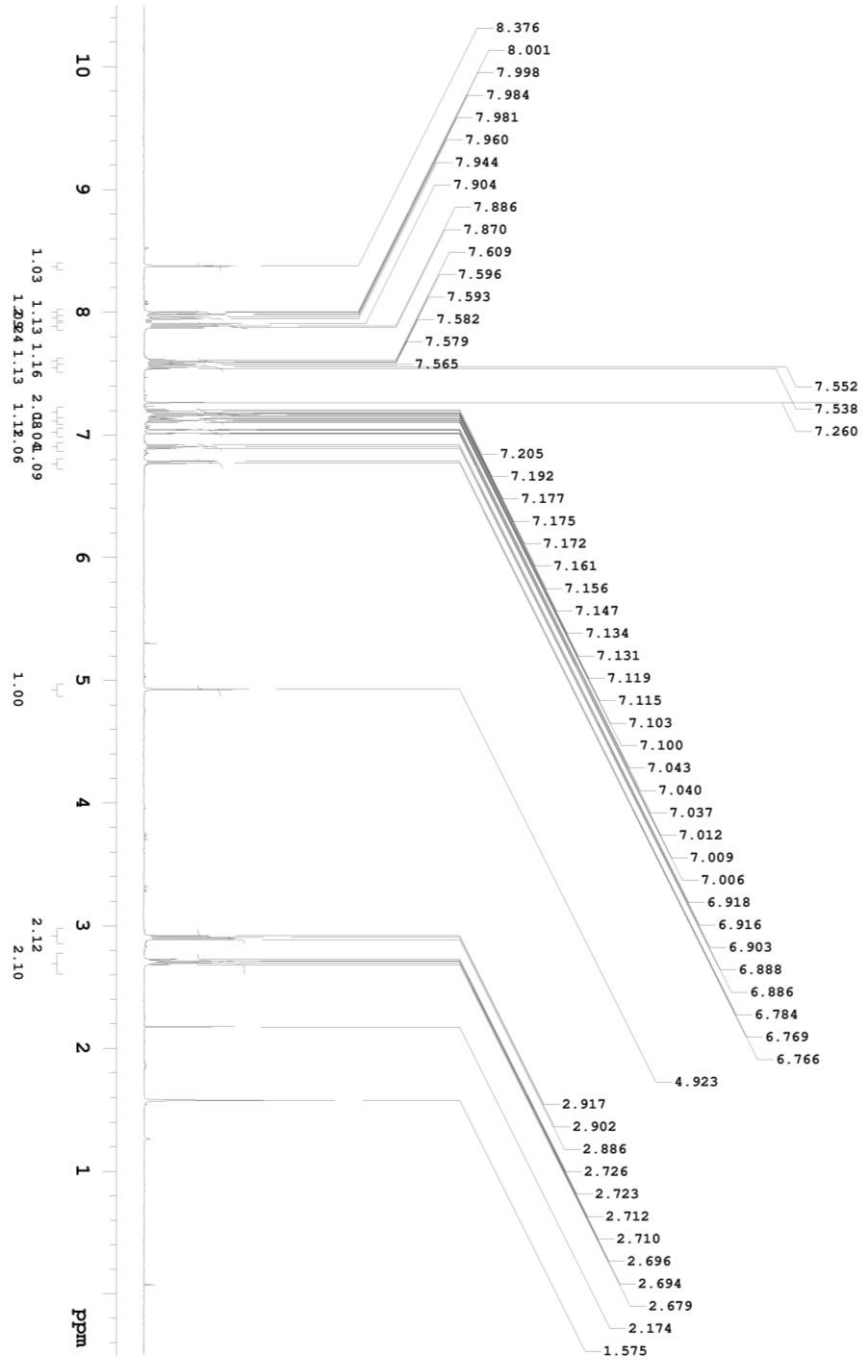
^{13}C NMR



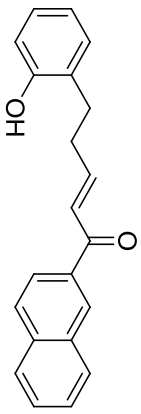
(*E*)-5-(2-Hydroxyphenyl)-1-(naphthalene-2-yl)pent-2-en-1-one (1f)



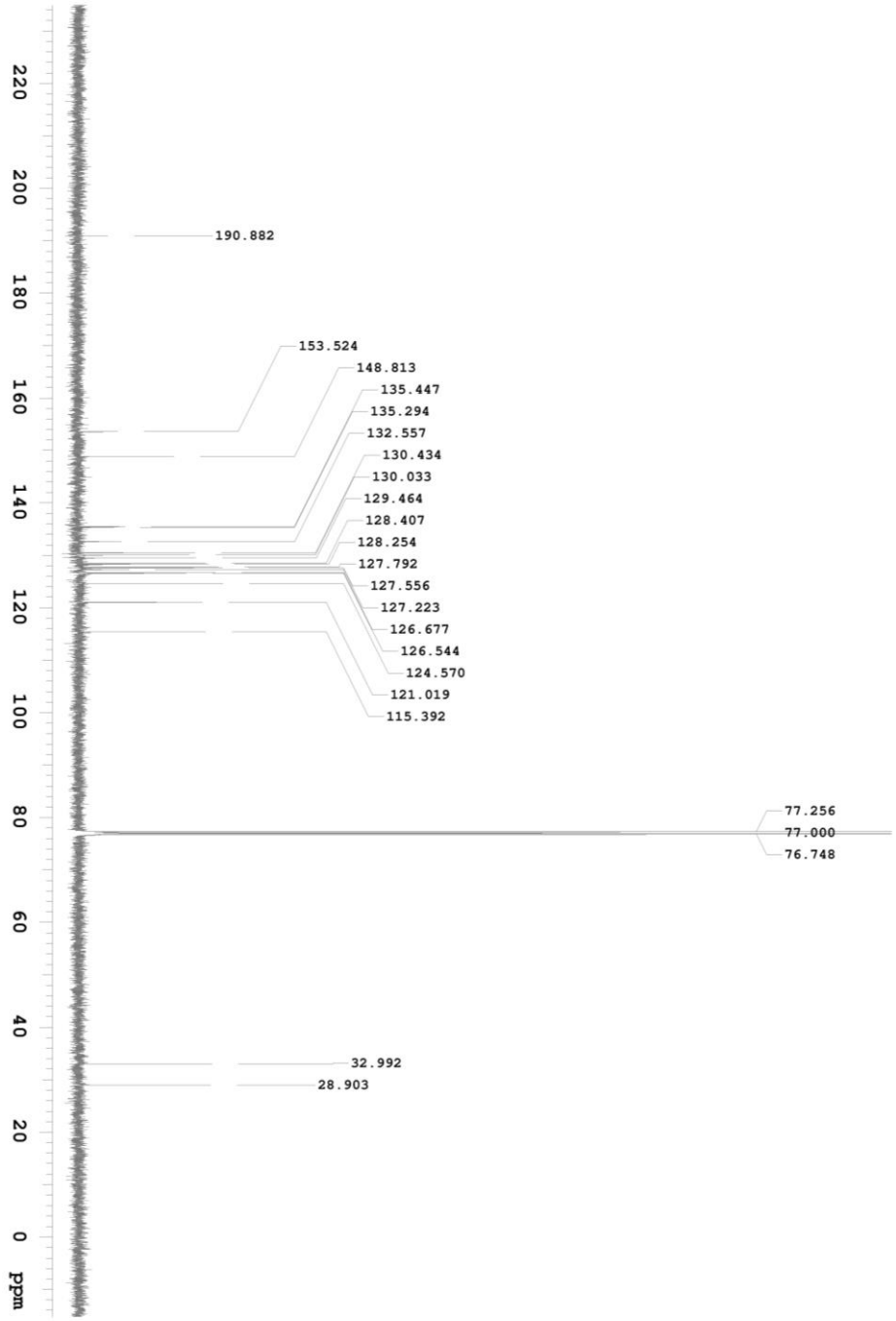
^{1}H NMR



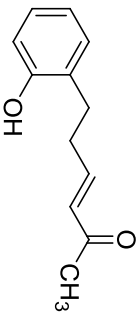
(*E*)-5-(2-Hydroxyphenyl)-1-(naphthalene-2-yl)pent-2-en-1-one (1f)



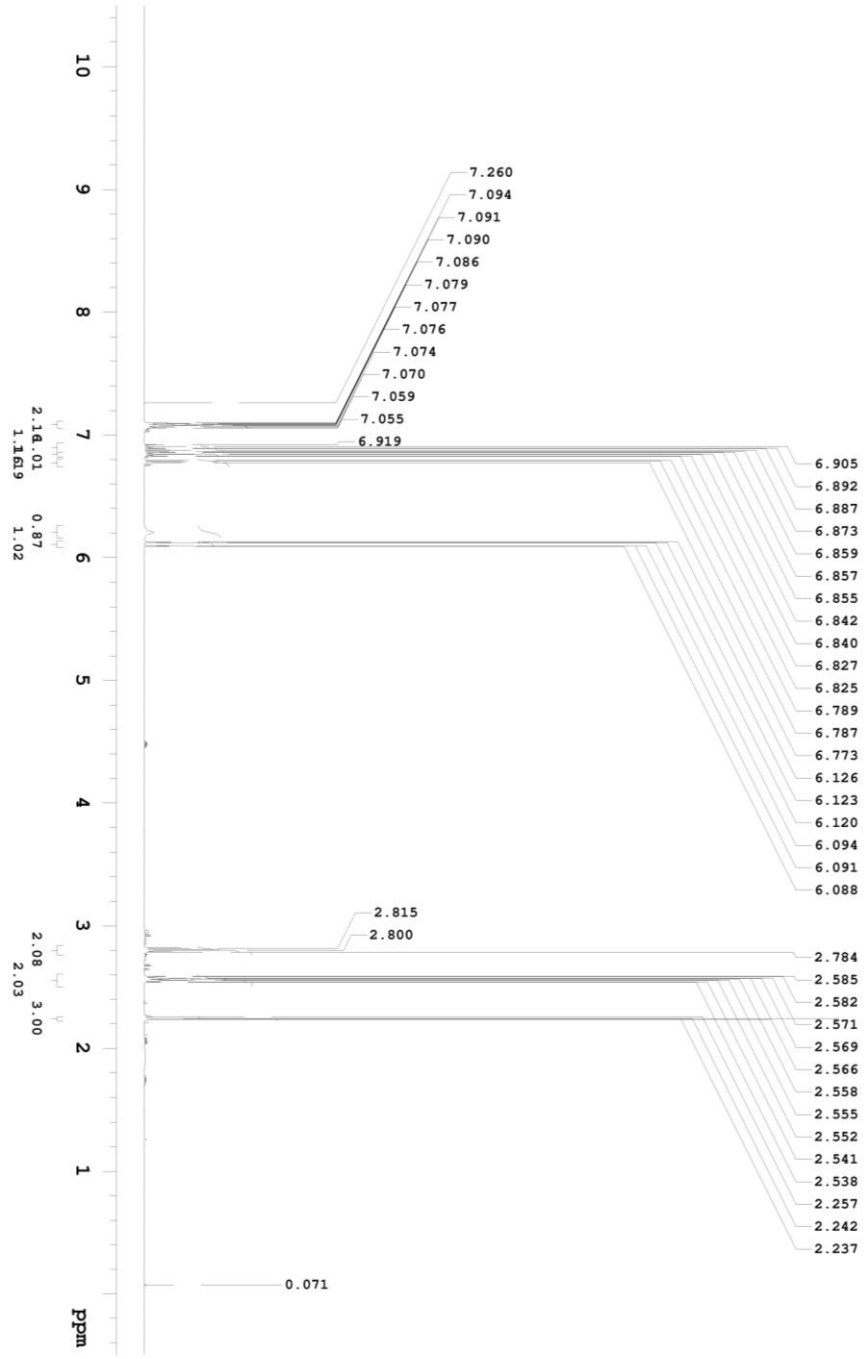
^{13}C NMR



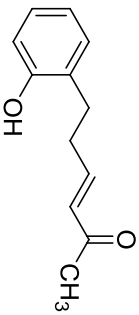
(*E*)-6-(2-Hydroxyphenyl)hex-3-en-2-one (1g)



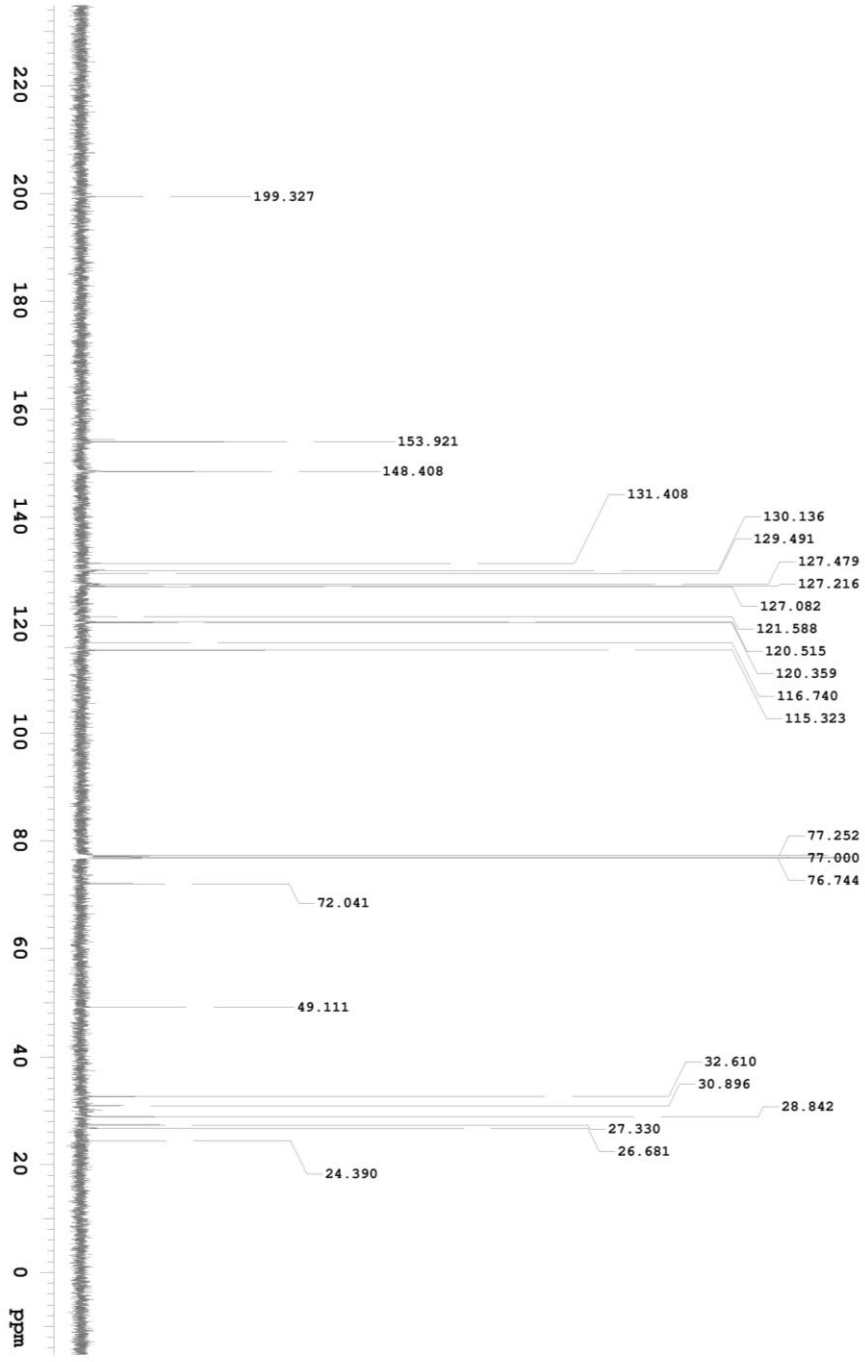
^{1}H NMR



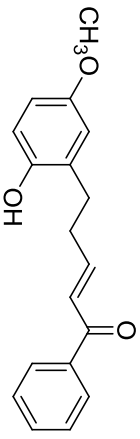
(*E*)-6-(2-Hydroxyphenyl)hex-3-en-2-one (1g)



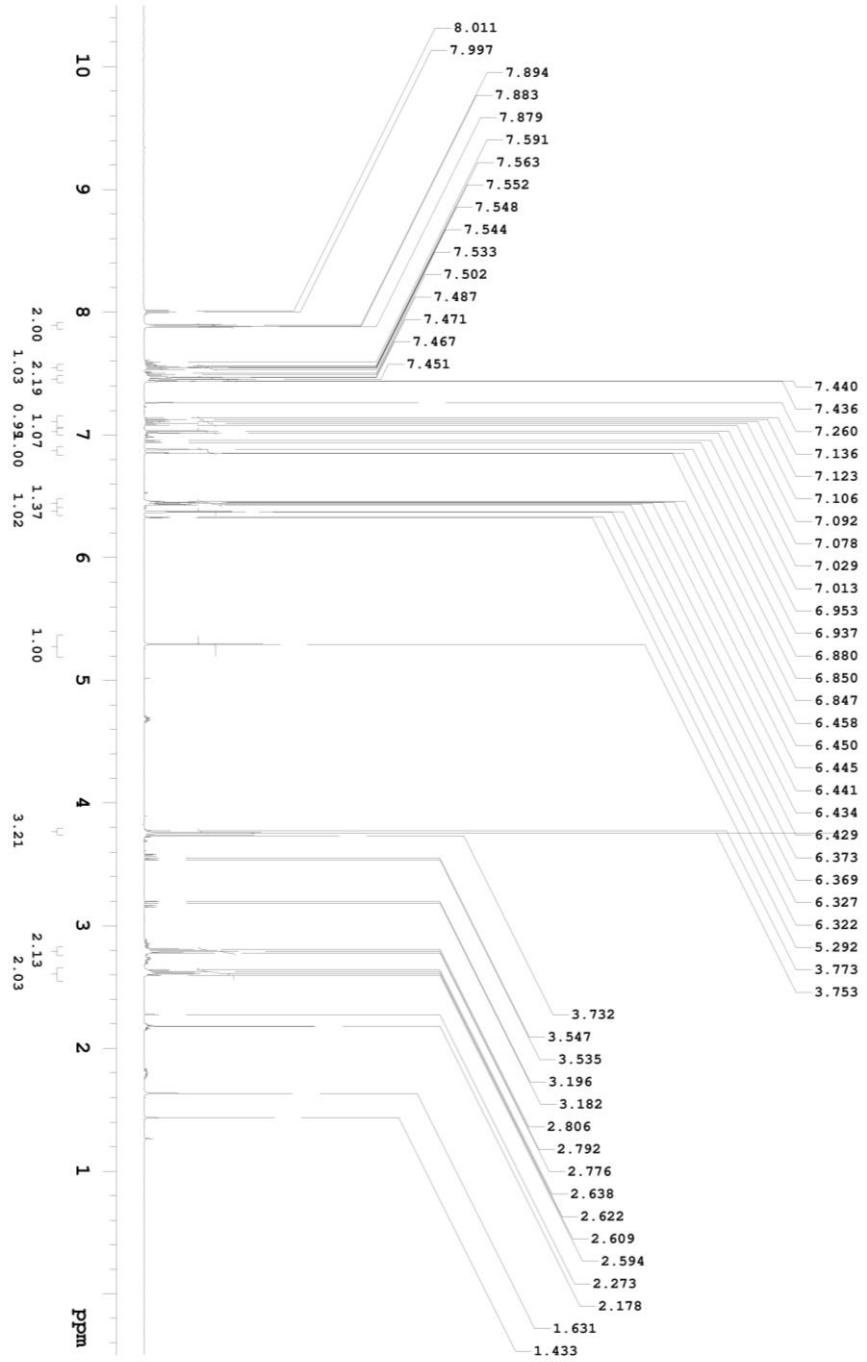
^{13}C NMR



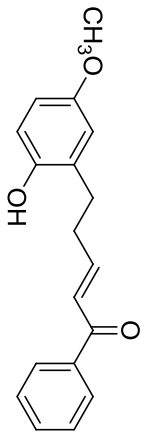
(*E*)-5-(2-Hydroxy-5-methoxyphenyl)-1-phenylpent-2-en-1-one (1h)



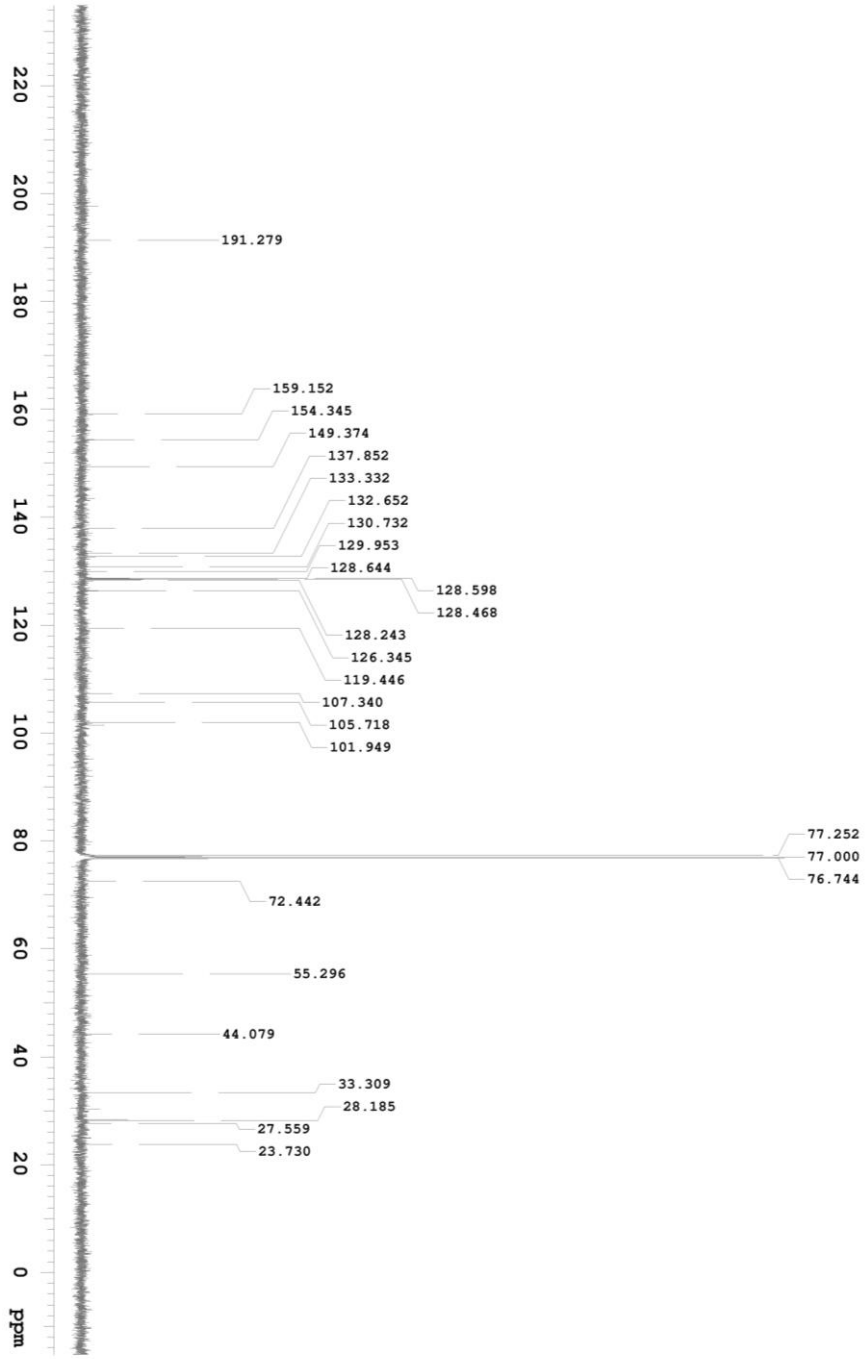
^{1}H NMR



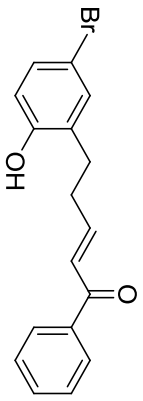
(*E*)-5-(2-Hydroxy-5-methoxyphenyl)-1-phenylpent-2-en-1-one (1h)



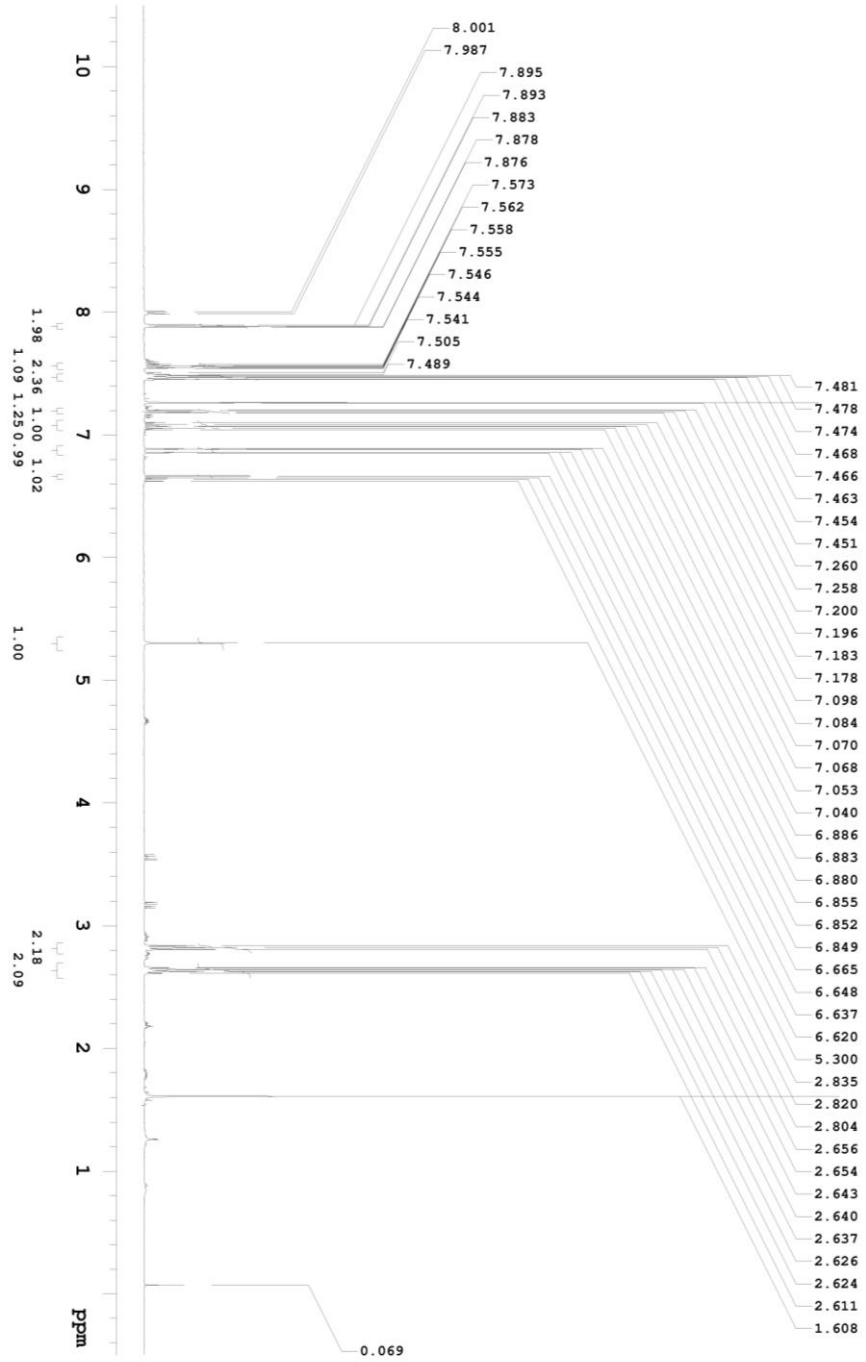
^{13}C NMR



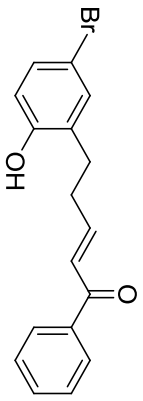
(*E*)-5-(5-Bromo-2-hydroxyphenyl)-1-phenylpent-2-en-1-one (1i)



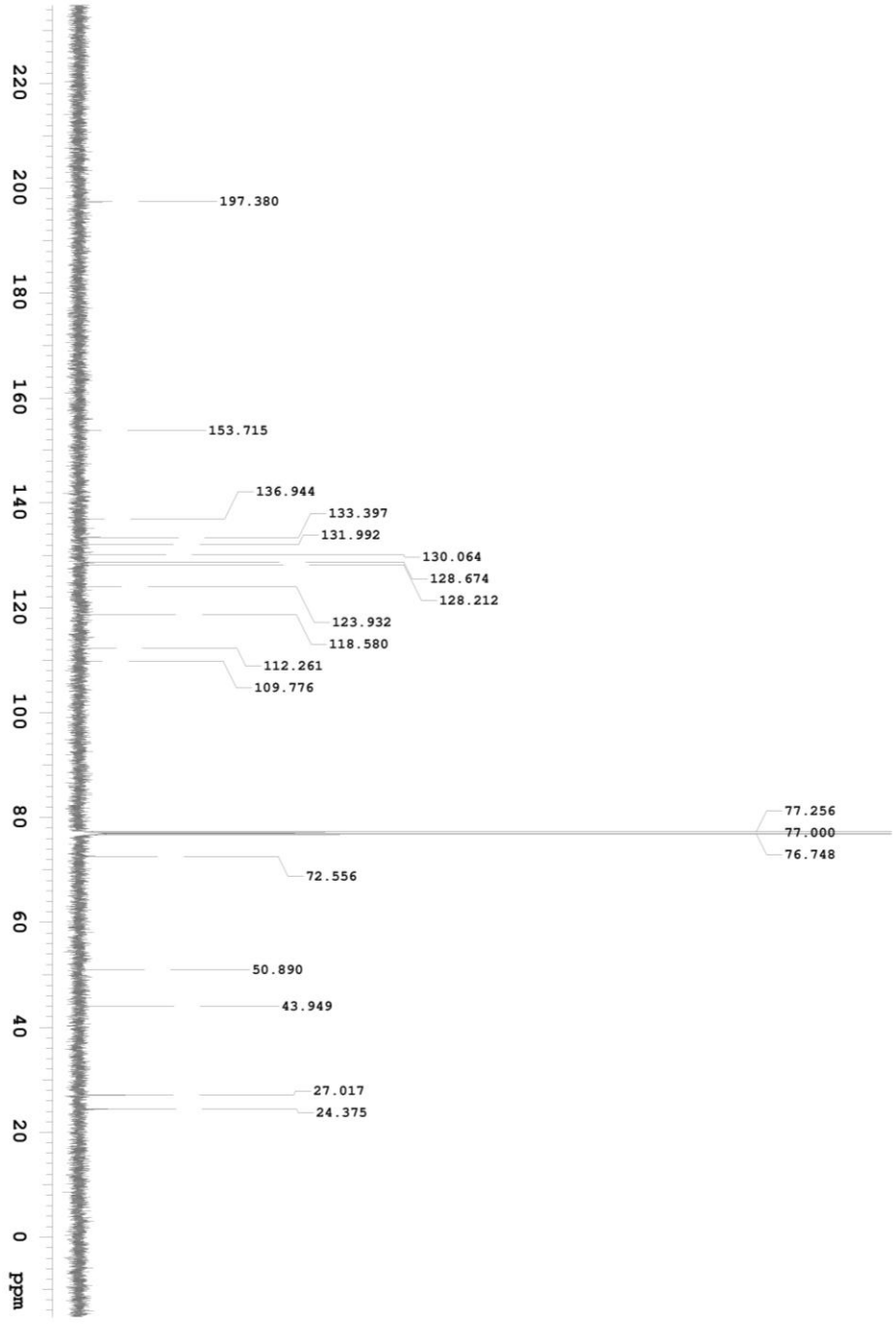
^{1}H NMR



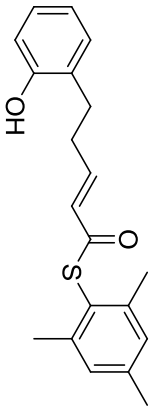
(*E*)-5-(5-Bromo-2-hydroxyphenyl)-1-phenylpent-2-en-1-one (1i)



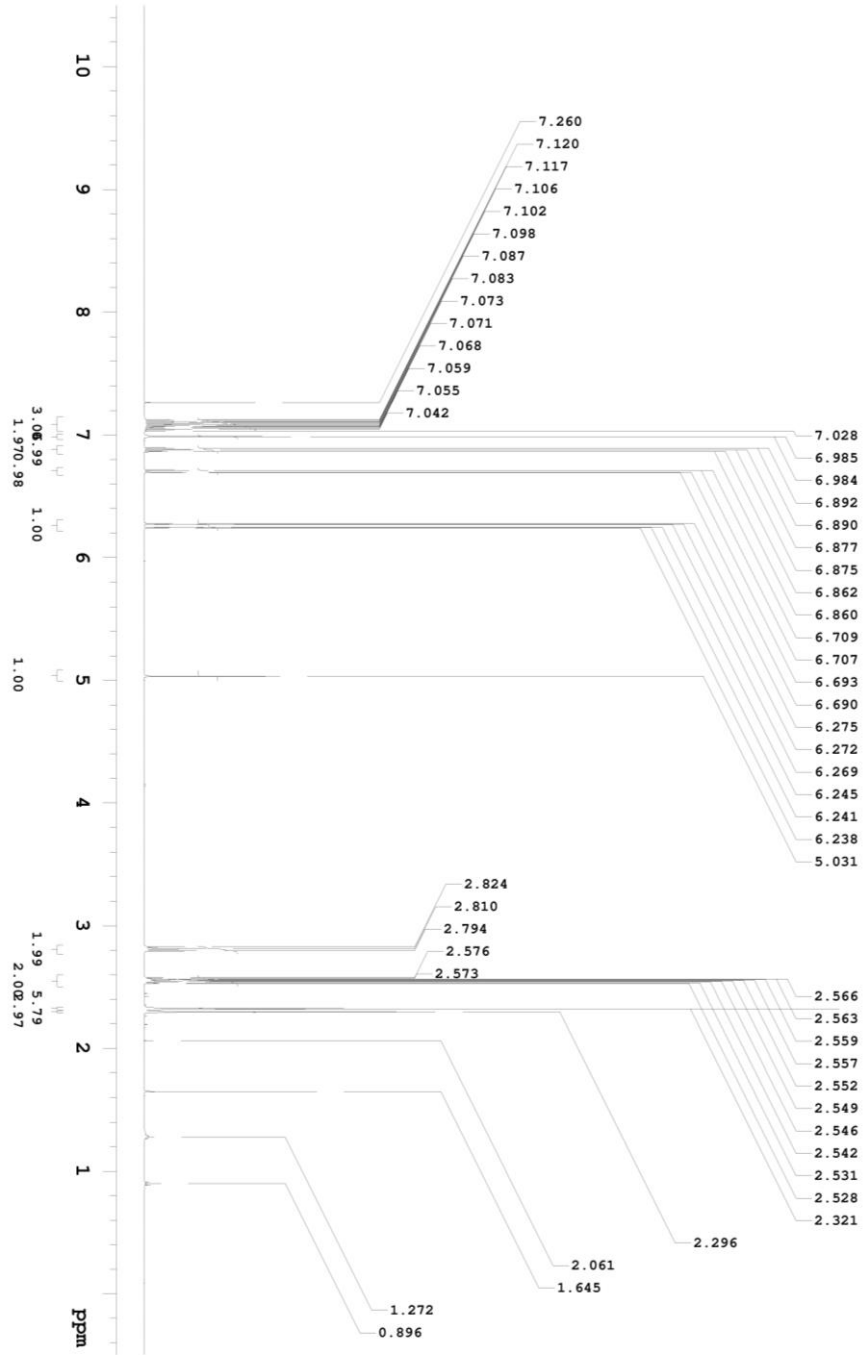
^{13}C NMR



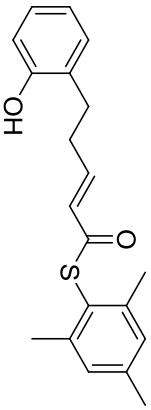
(*E*)-*S*-Mesityl 5-(2-hydroxyphenyl)pent-2-enethioate (1j)



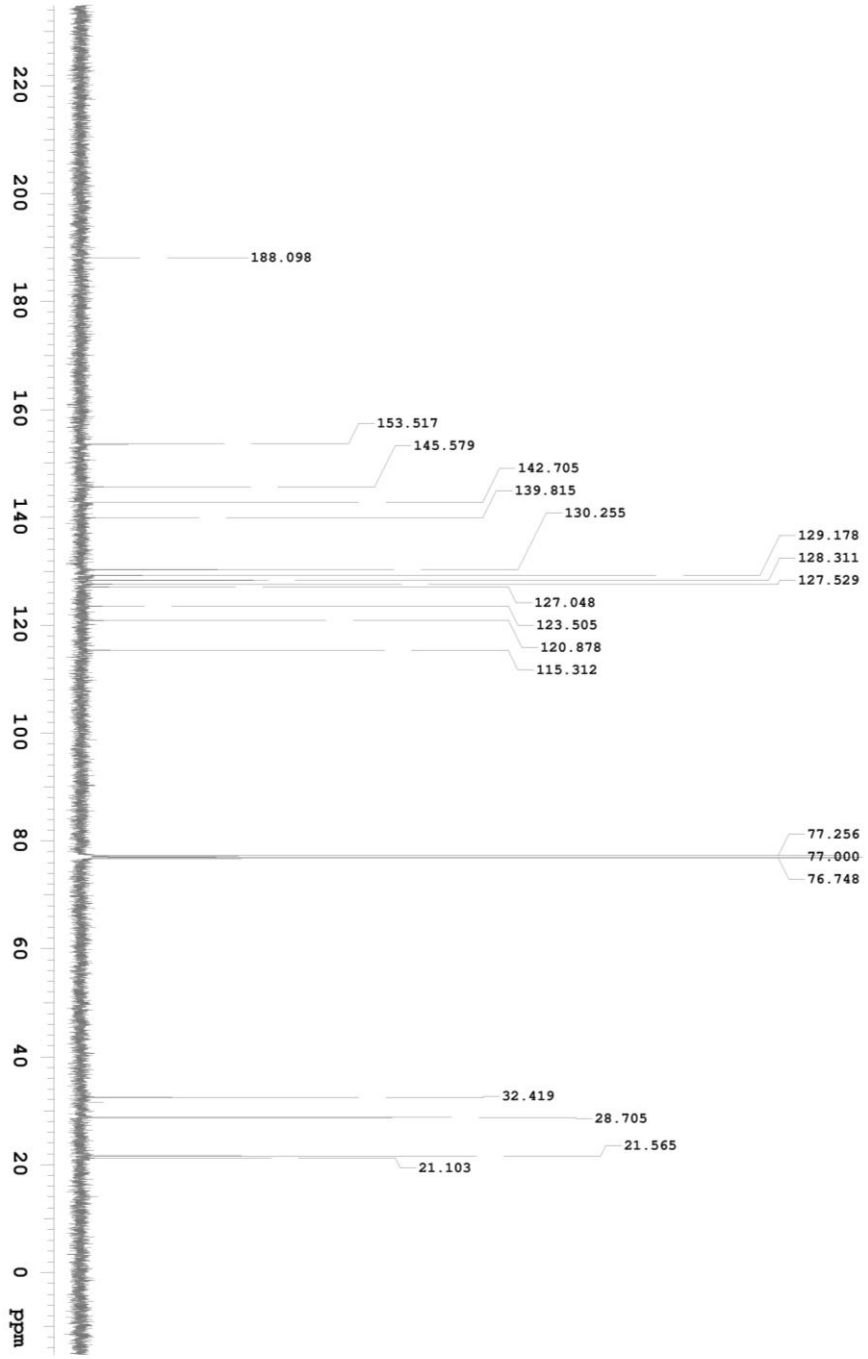
^{1}H NMR



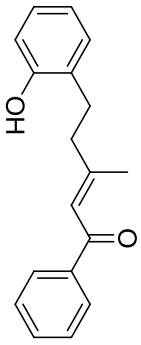
(*E*)-*S*-Mesityl 5-(2-hydroxyphenyl)pent-2-enethioate (1j)



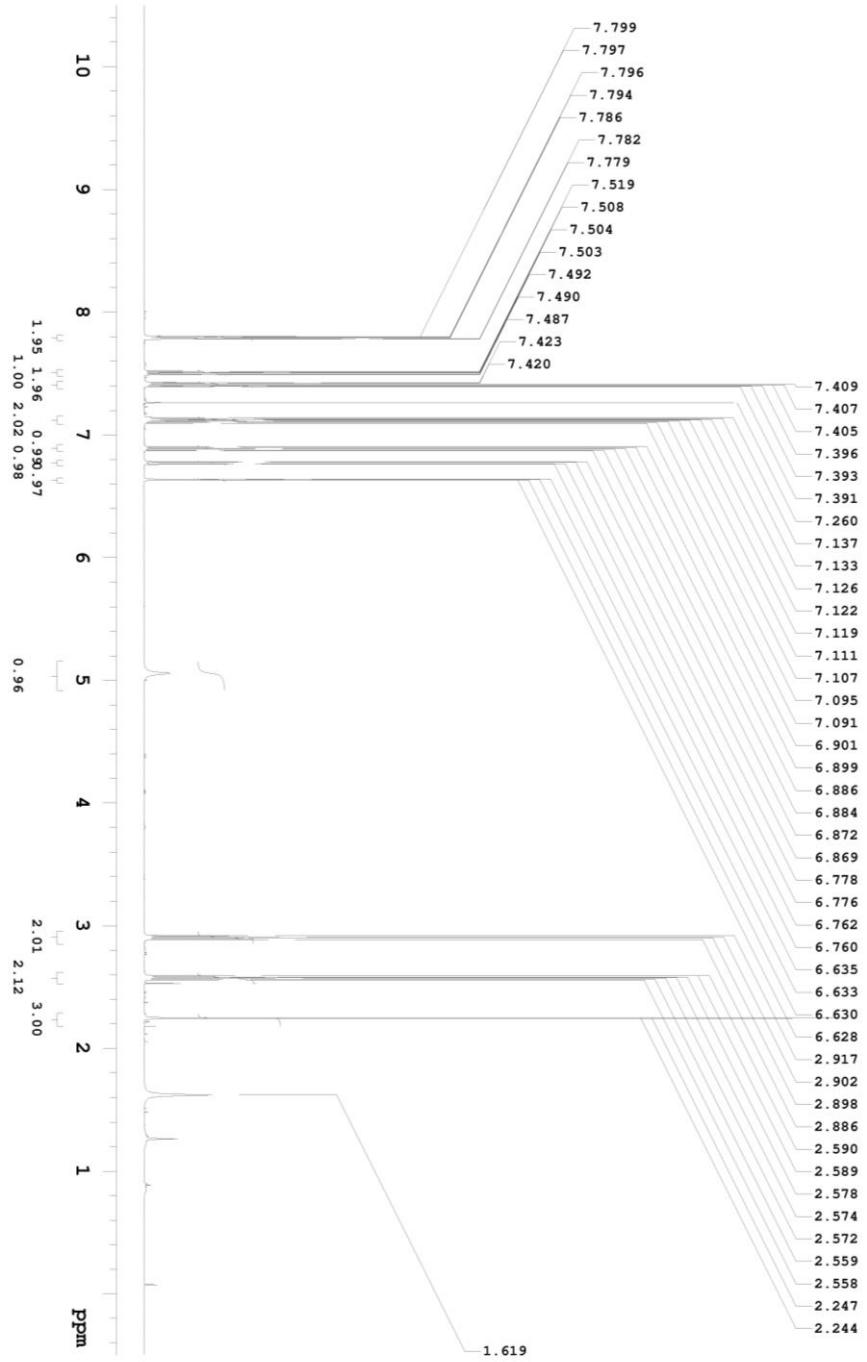
^{13}C NMR



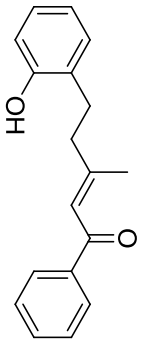
(*E*)-5-(2-Hydroxyphenyl)-3-methyl-1-phenylpent-2-en-1-one ((*E*)-1k)



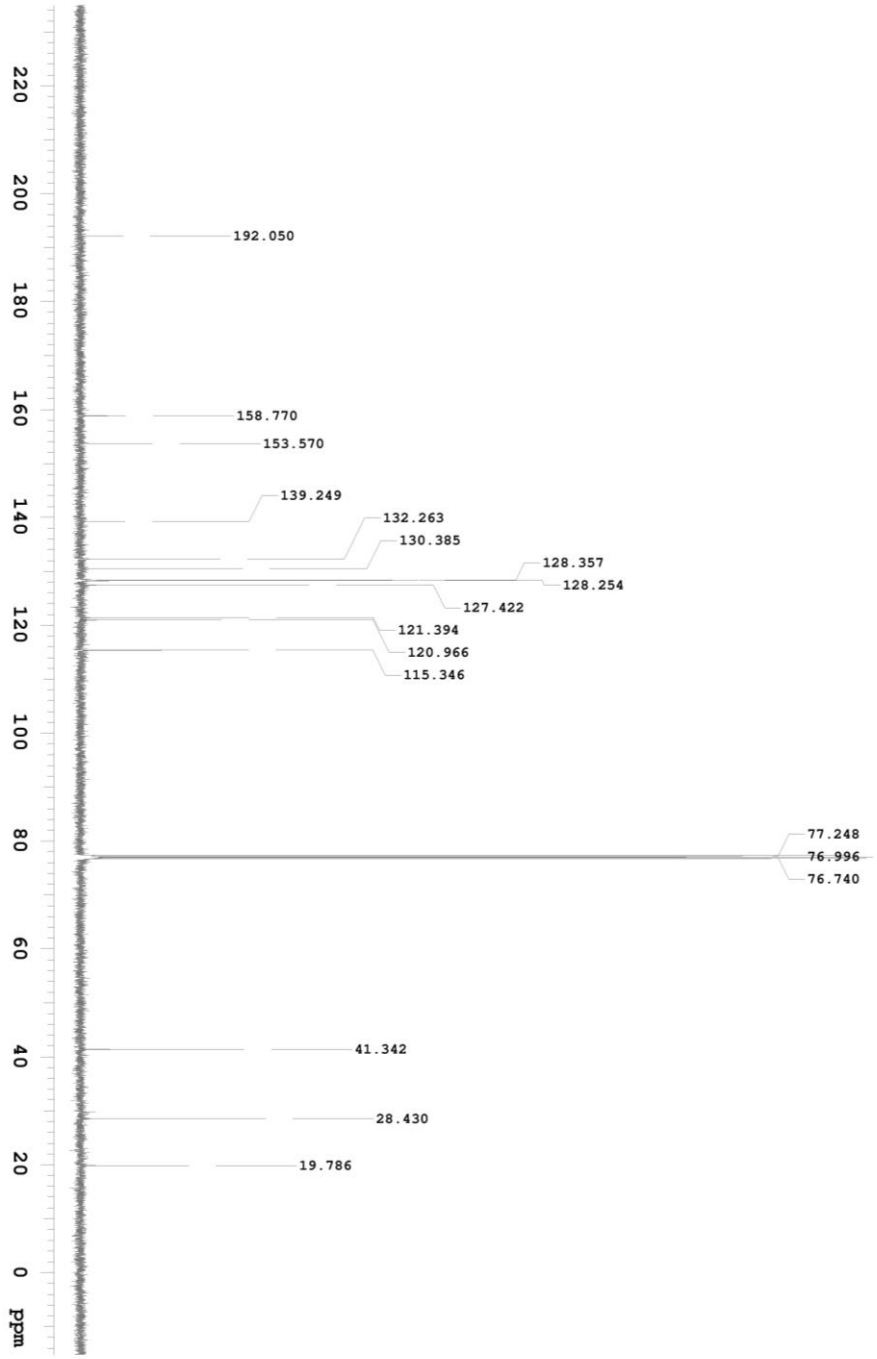
^{1}H NMR



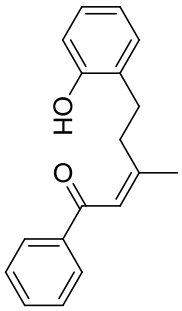
(*E*)-5-(2-Hydroxyphenyl)-3-methyl-1-phenylpent-2-en-1-one ((*E*)-1k)



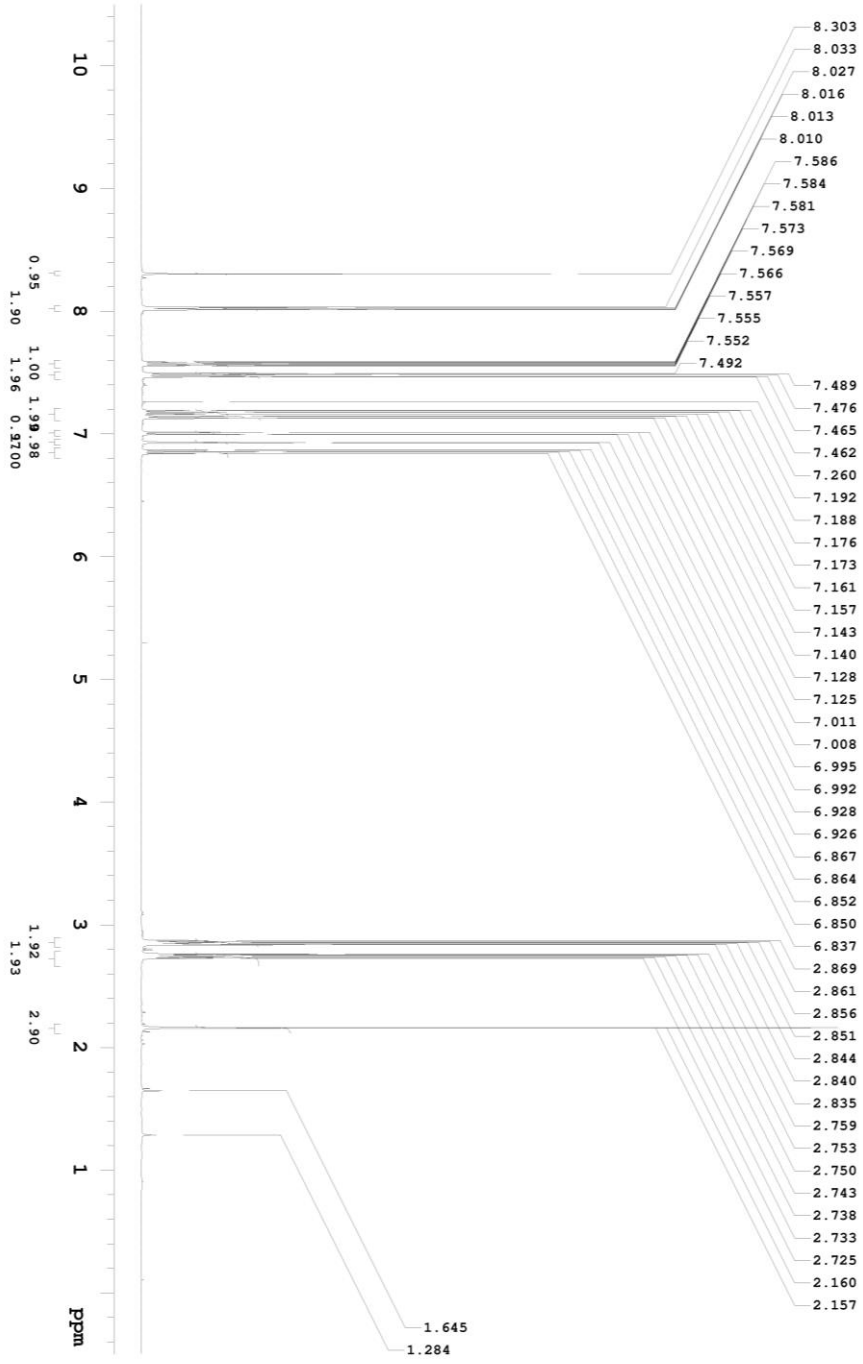
^{13}C NMR



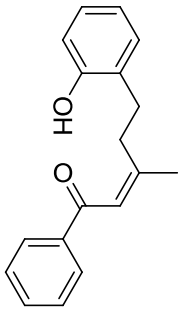
(Z)-5-(2-Hydroxyphenyl)-3-methyl-1-phenylpent-2-en-1-one ((Z)-1k)



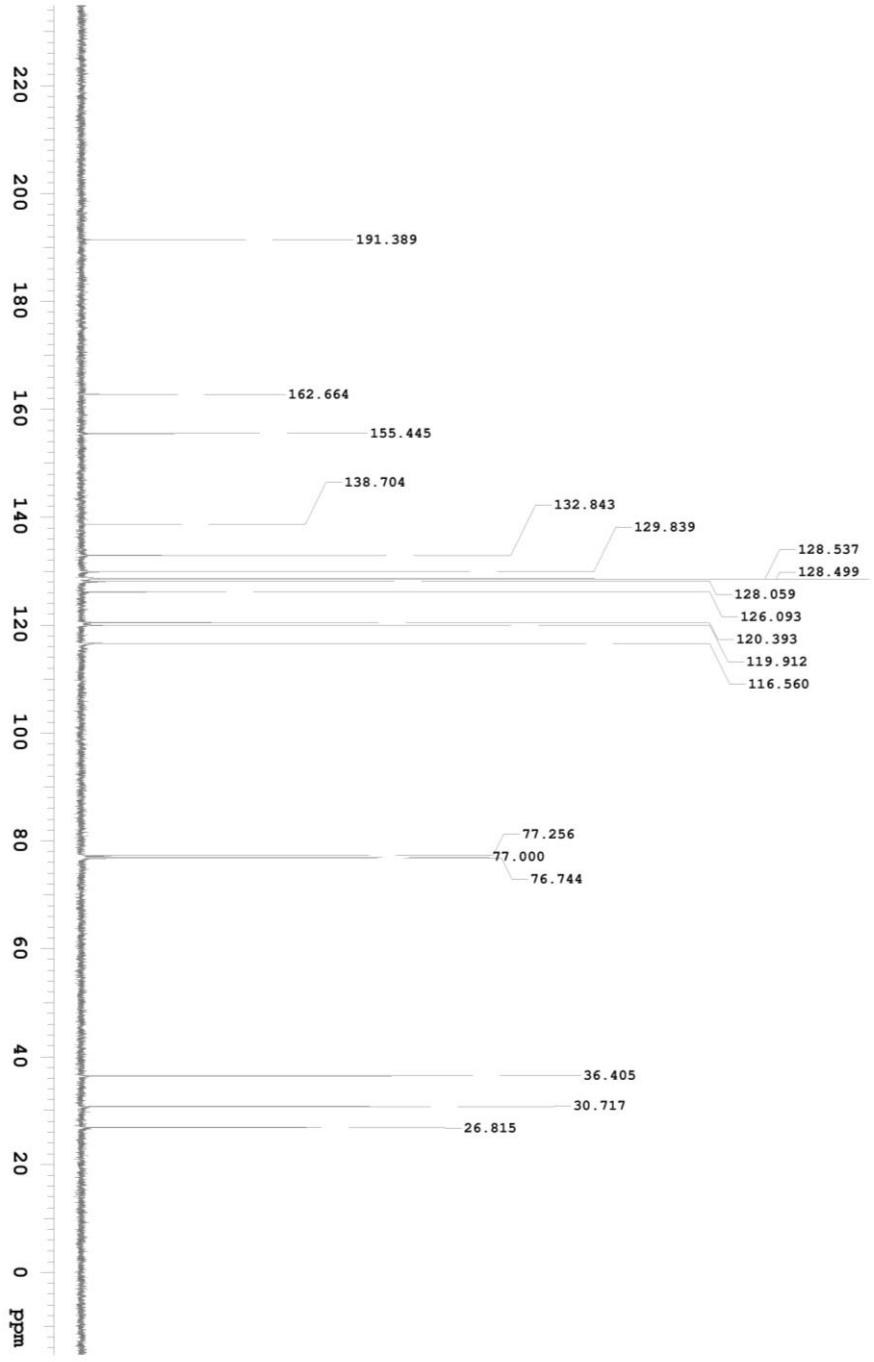
^{1}H NMR



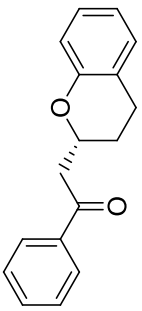
(Z)-5-(2-Hydroxyphenyl)-3-methyl-1-phenylpent-2-en-1-one ((Z)-1k)



^{13}C NMR

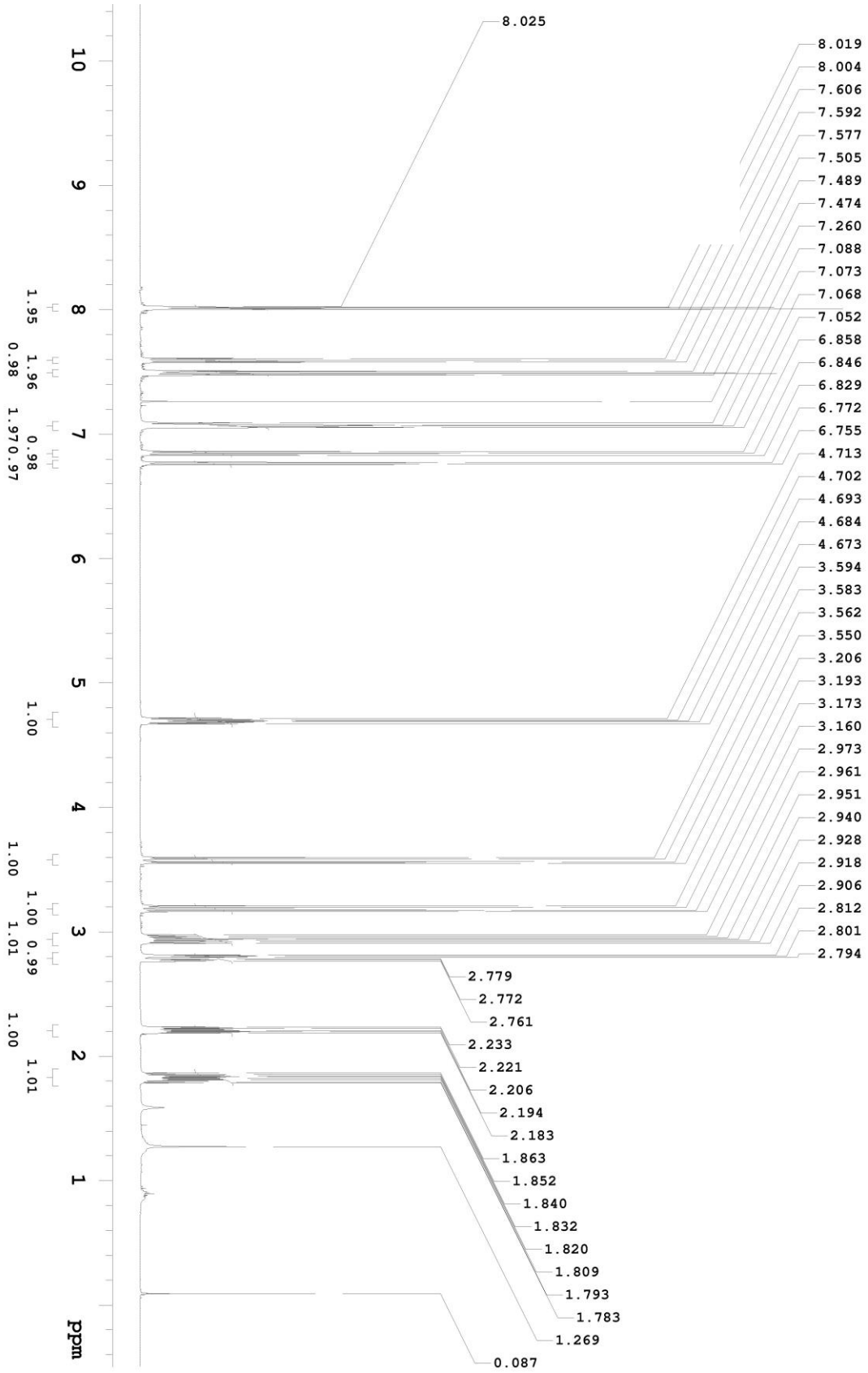


NMR Spectra (^{1}H, ^{13}C) of Products

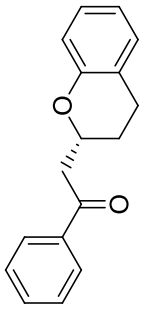


2-(Chroman-2-yl)- 1-phenylethanone (2a)

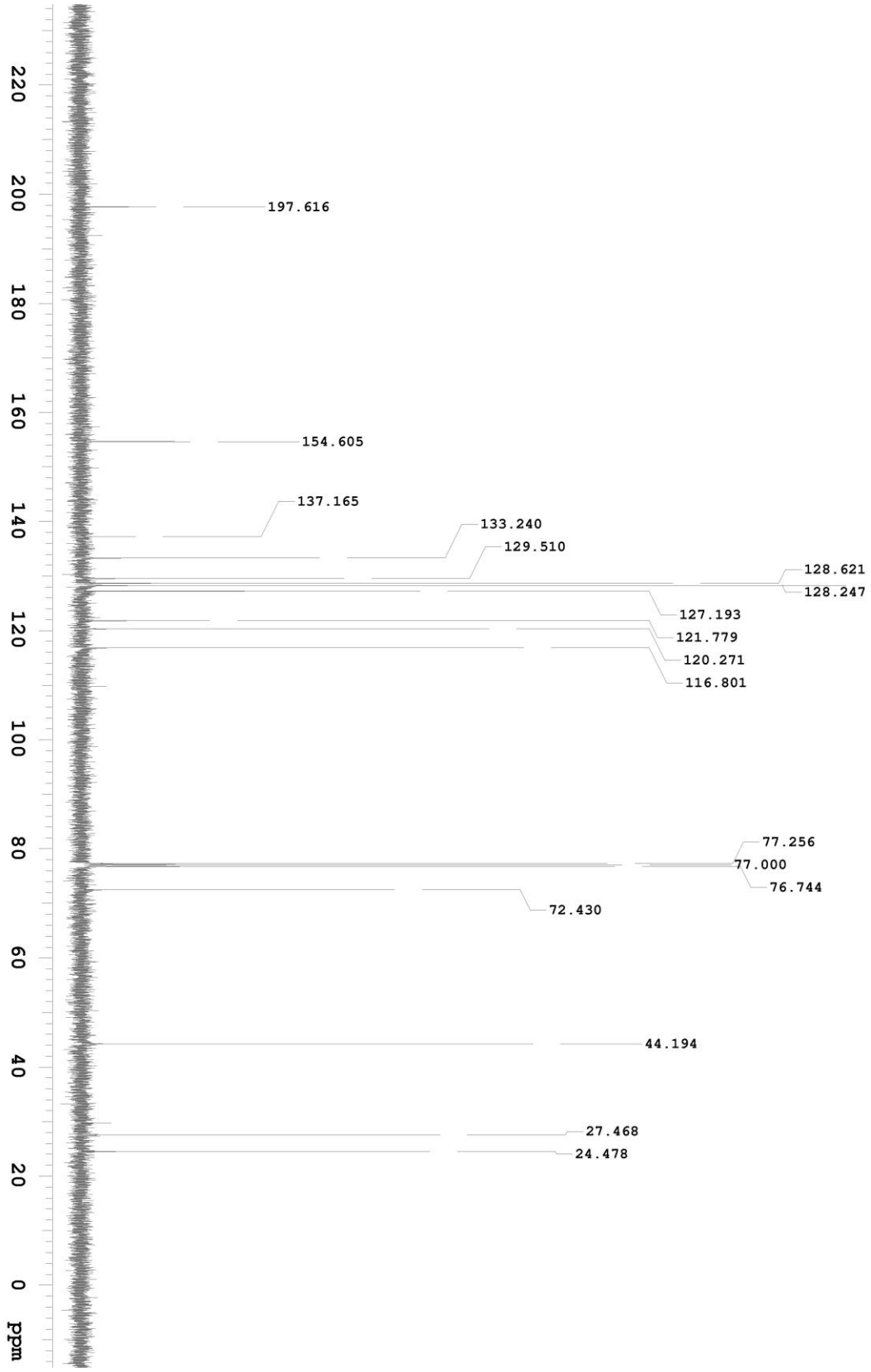
^{1}H NMR



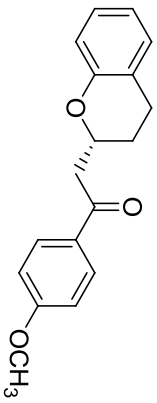
2-(Chroman-2-yl)- 1-phenylethanone (2a)



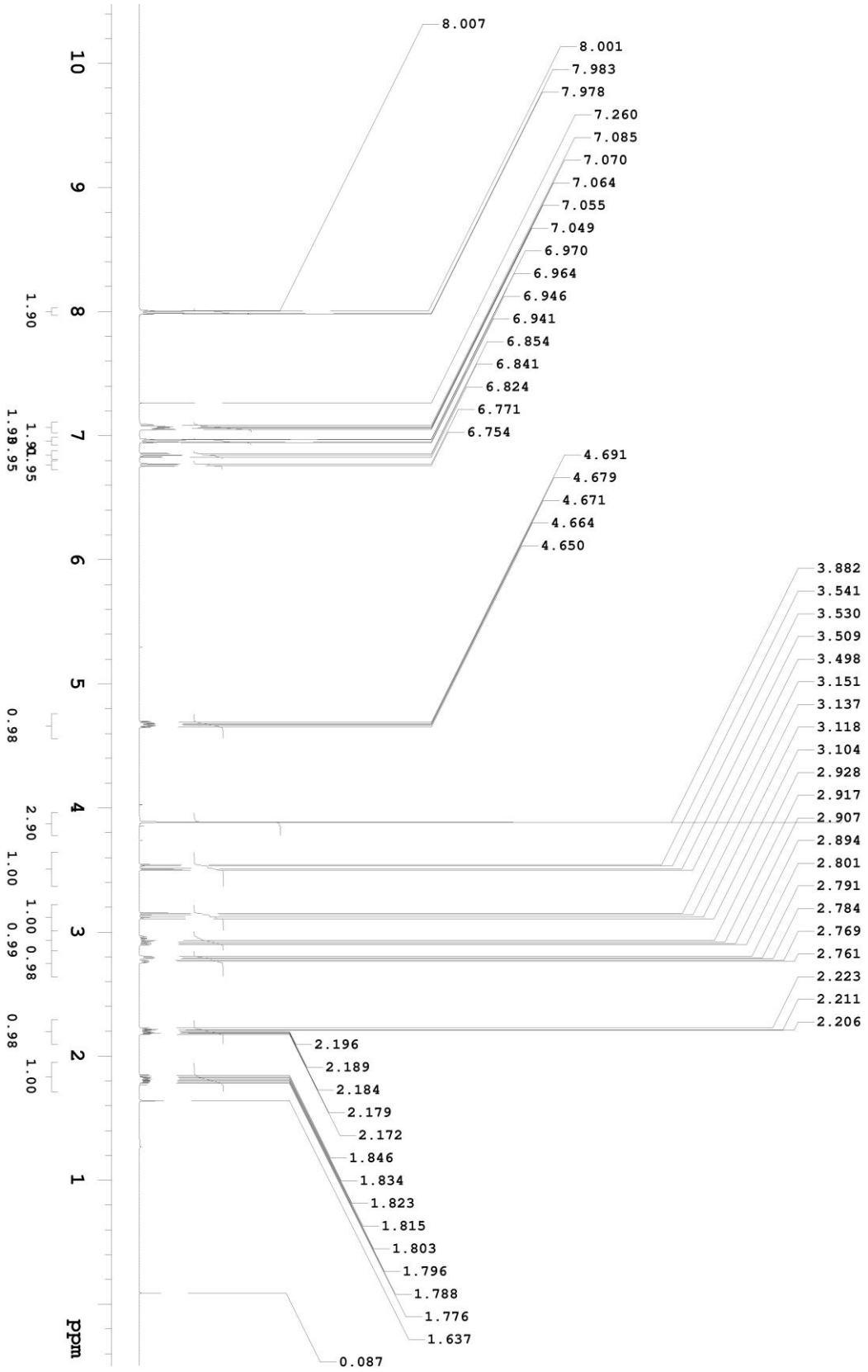
^{13}C NMR



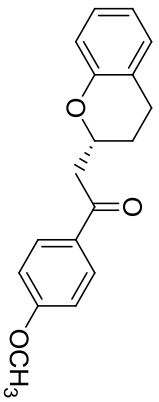
2-(Chroman-2-yl)- 1-(4-methoxyphenyl)ethanone (2b)



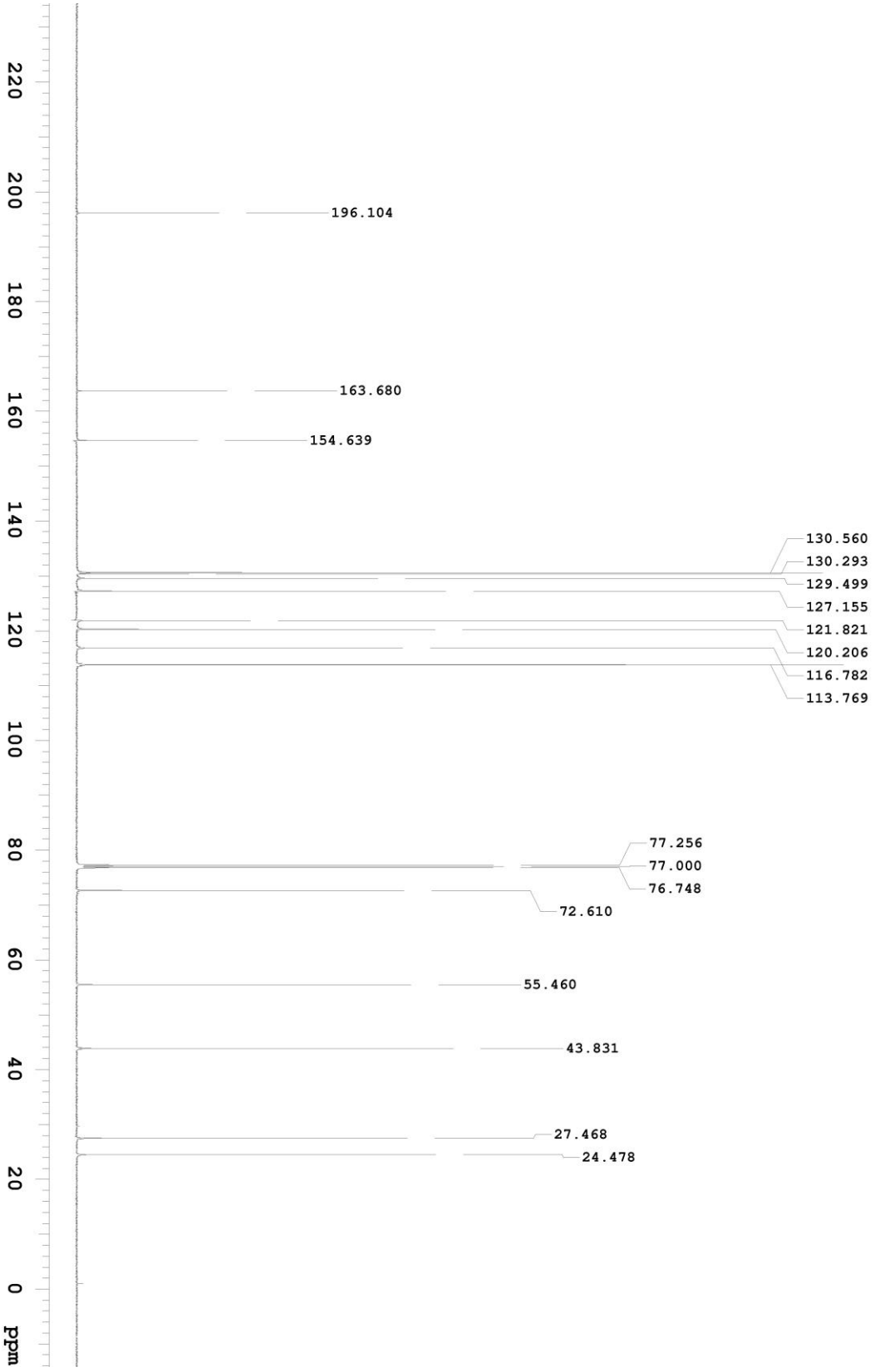
^{1}H NMR



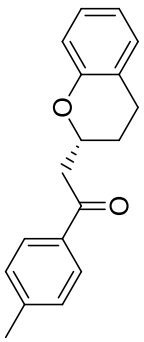
2-(Chroman-2-yl)- 1-(4-methoxyphenyl)ethanone (2b)



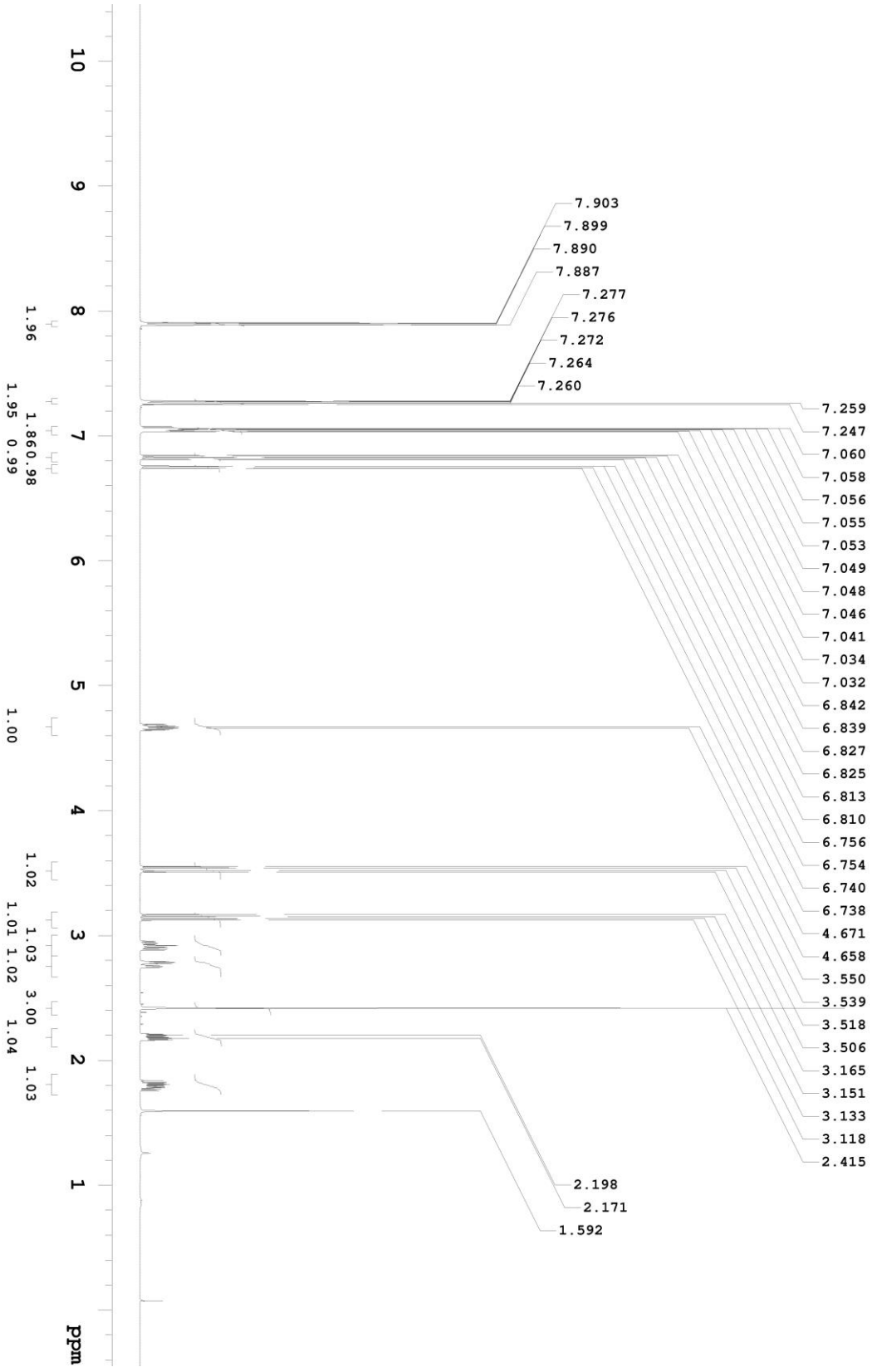
^{13}C NMR



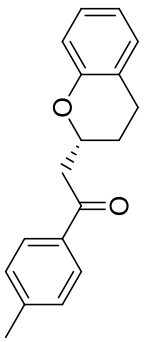
2-(Chroman-2-yl)- 1-(4-methylphenyl)ethanone (2c)



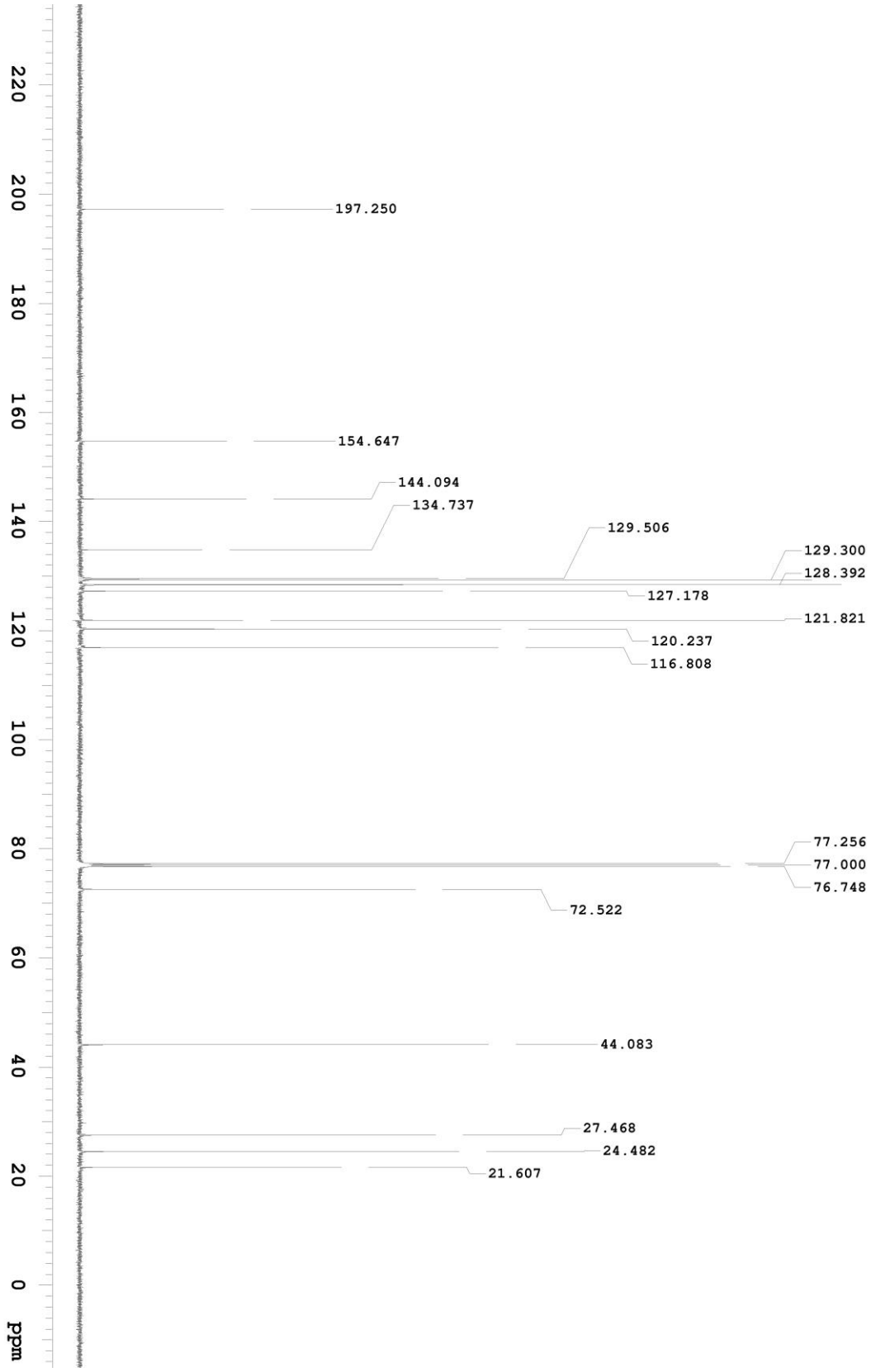
^{1}H NMR



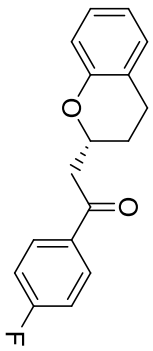
2-(Chroman-2-yl)- 1-phenylethanone (2c)



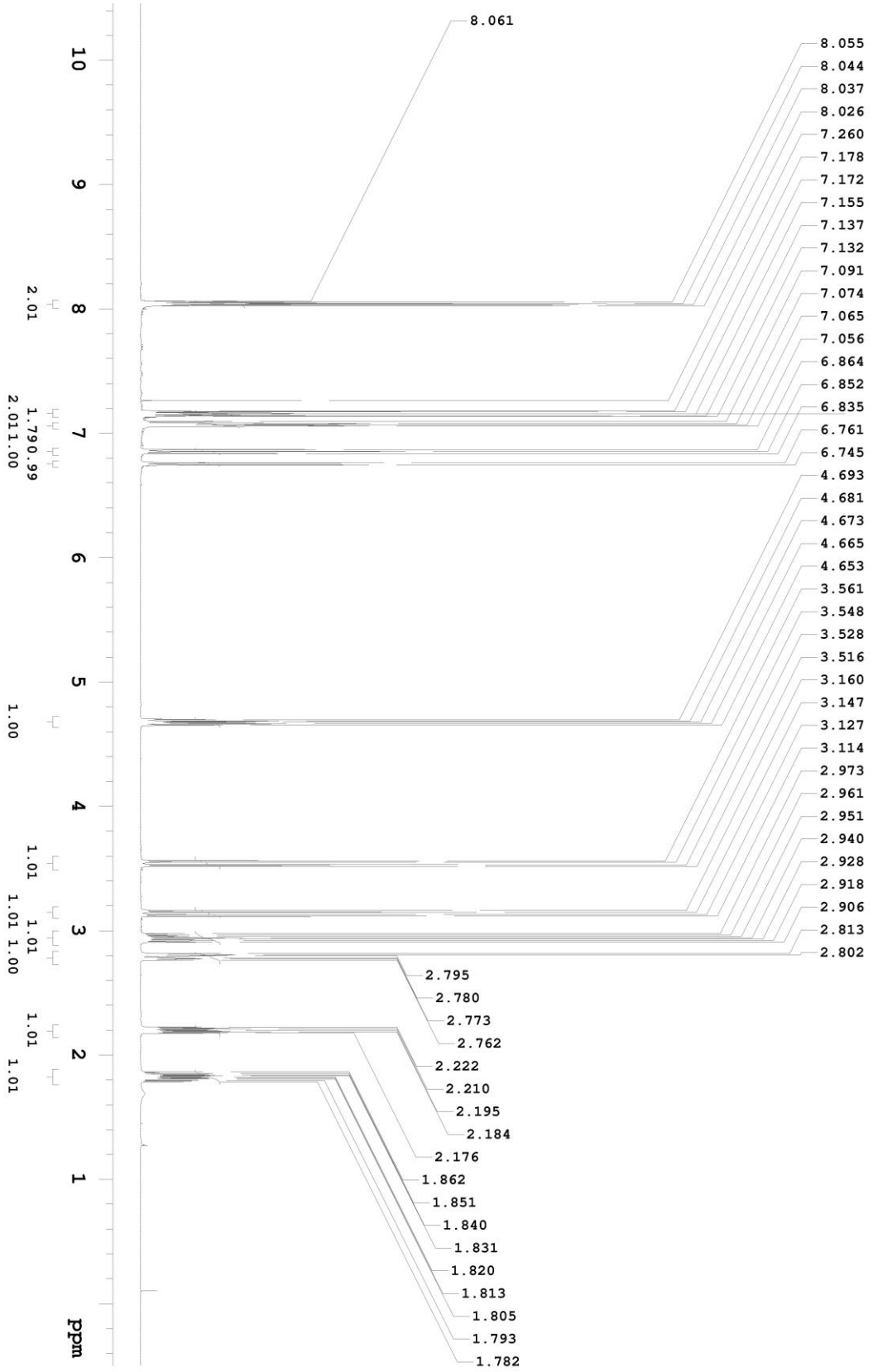
^{13}C NMR



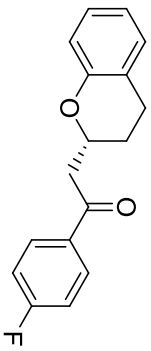
2-(Chroman-2-yl)- 1-(4-fluorophenyl)ethanone (2d)



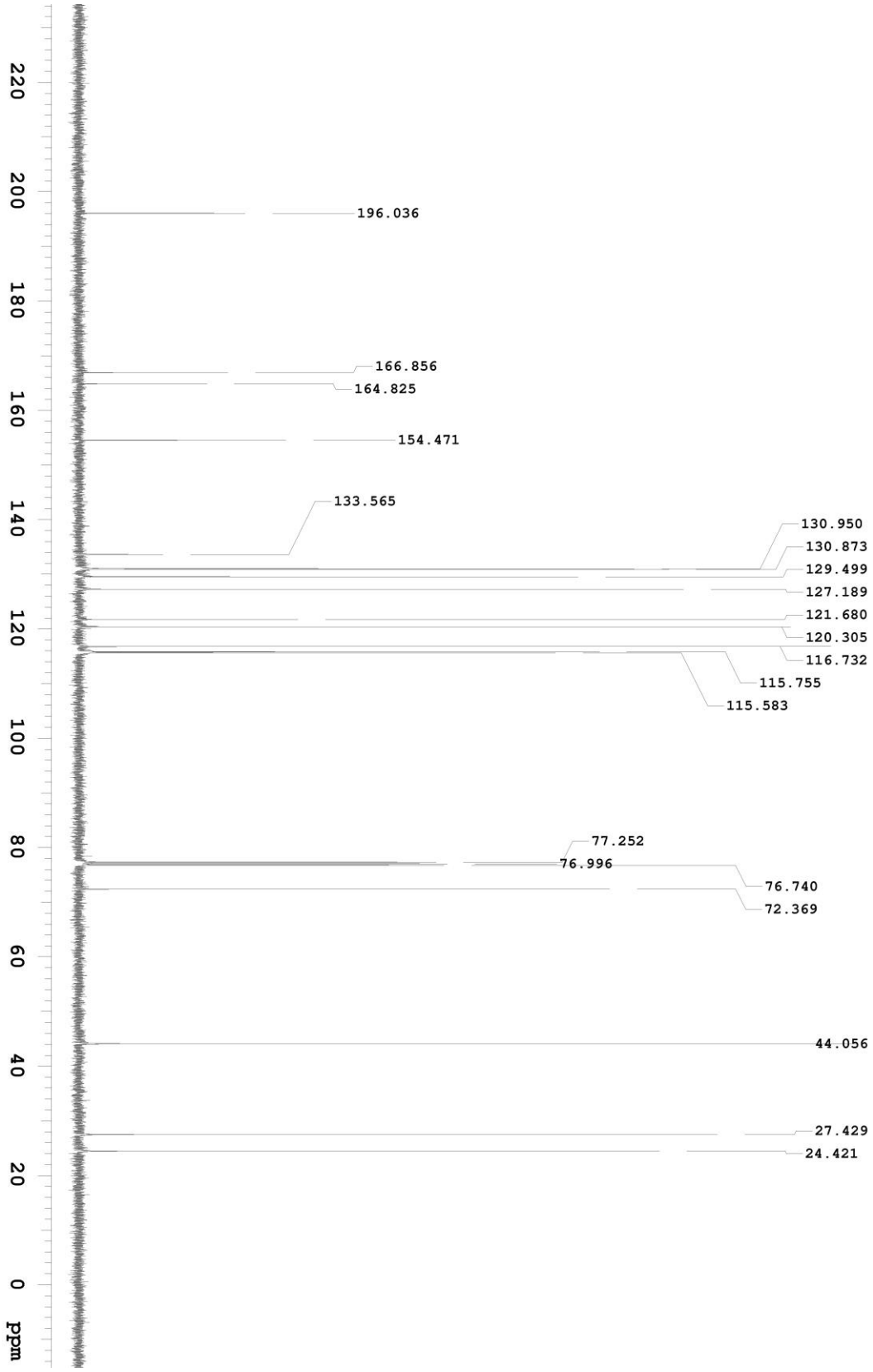
^{1}H NMR



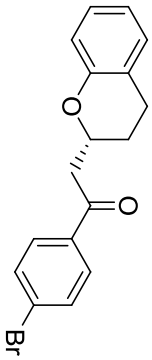
2-(Chroman-2-yl)- 1-(4-fluorophenyl)ethanone (2d)



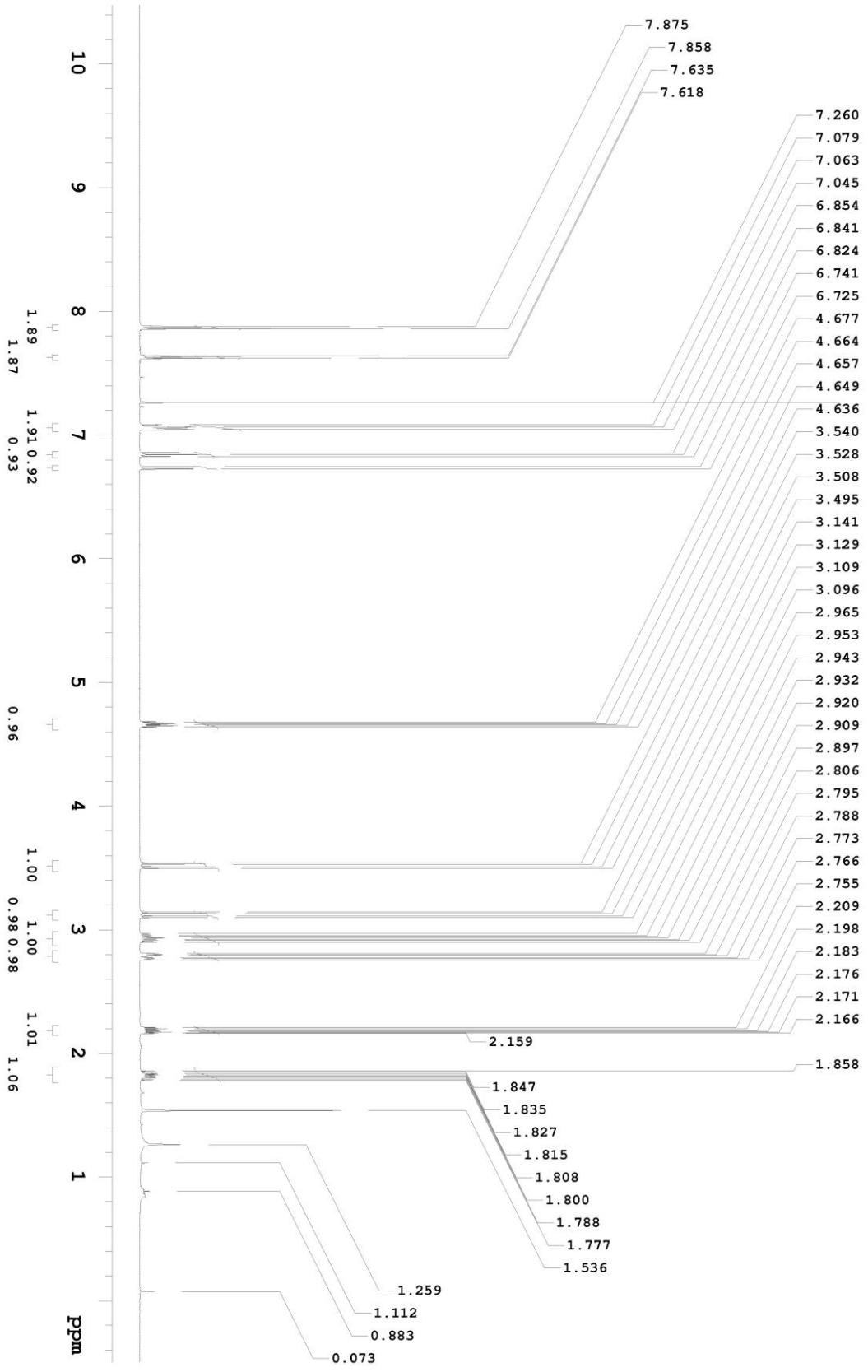
^{13}C NMR



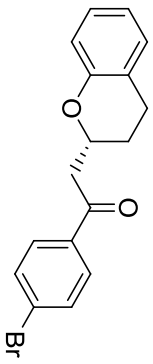
(*R*)-1-(4-Bromophenyl)-2-(chroman-2-yl)ethanone (2e)



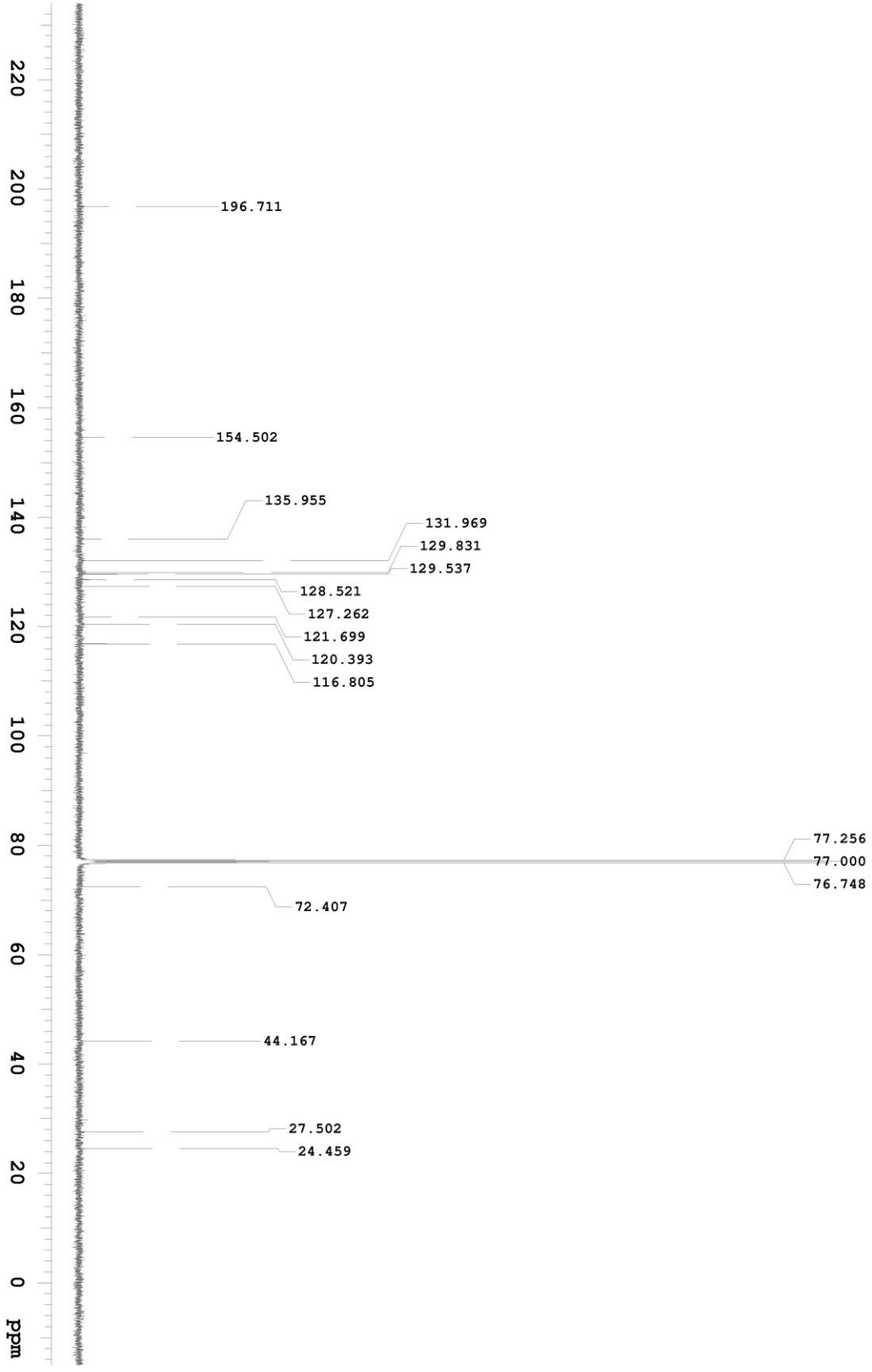
^{1}H NMR



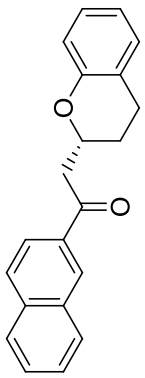
(*R*)-1-(4-Bromophenyl)-2-(chroman-2-yl)ethanone (2e)



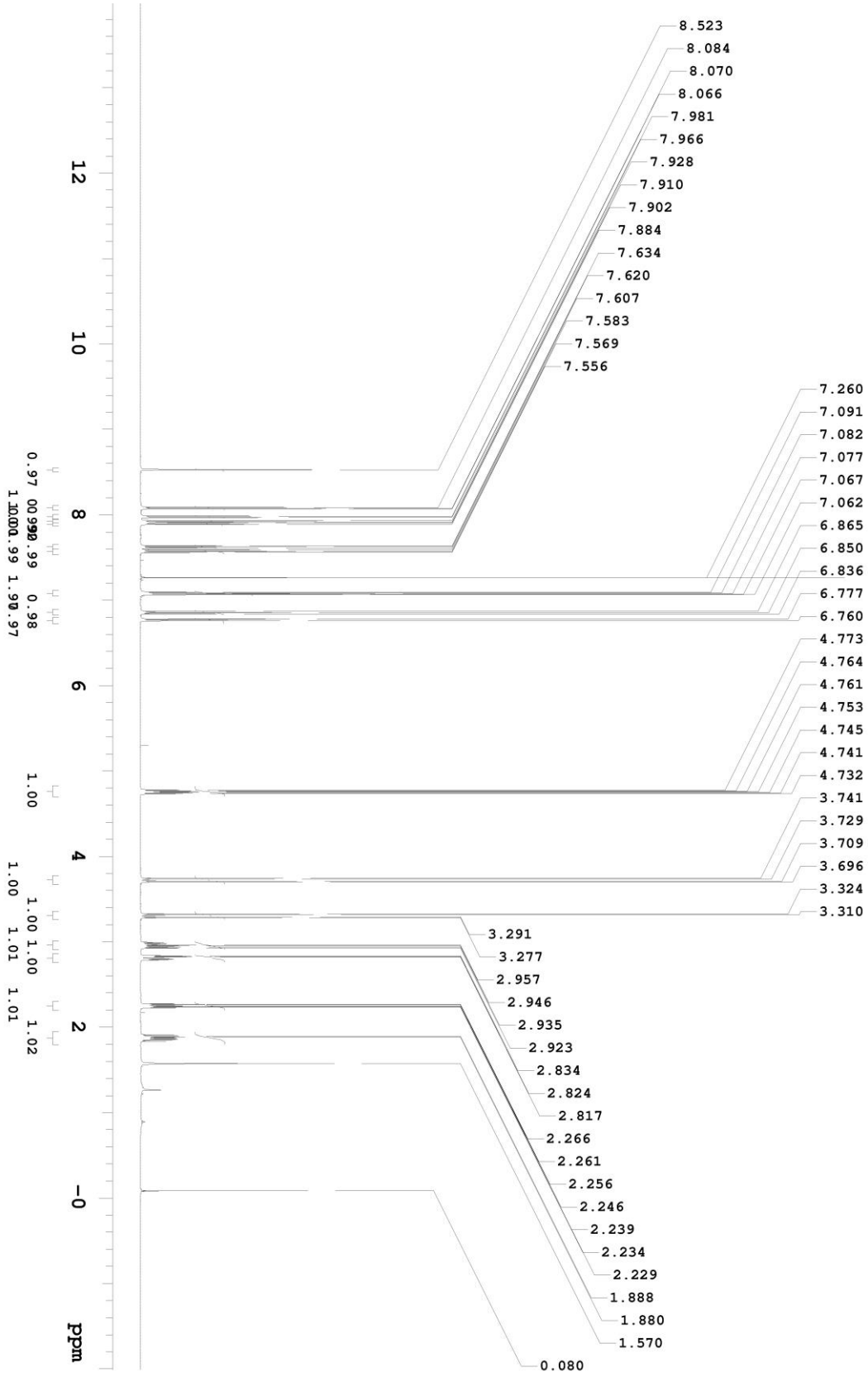
^{13}C NMR



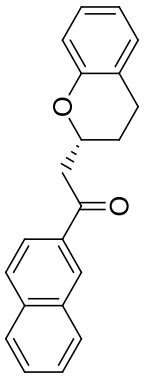
2-(Chroman-2-yl)- 1-(naphthalen-2-yl)ethanone (2f)



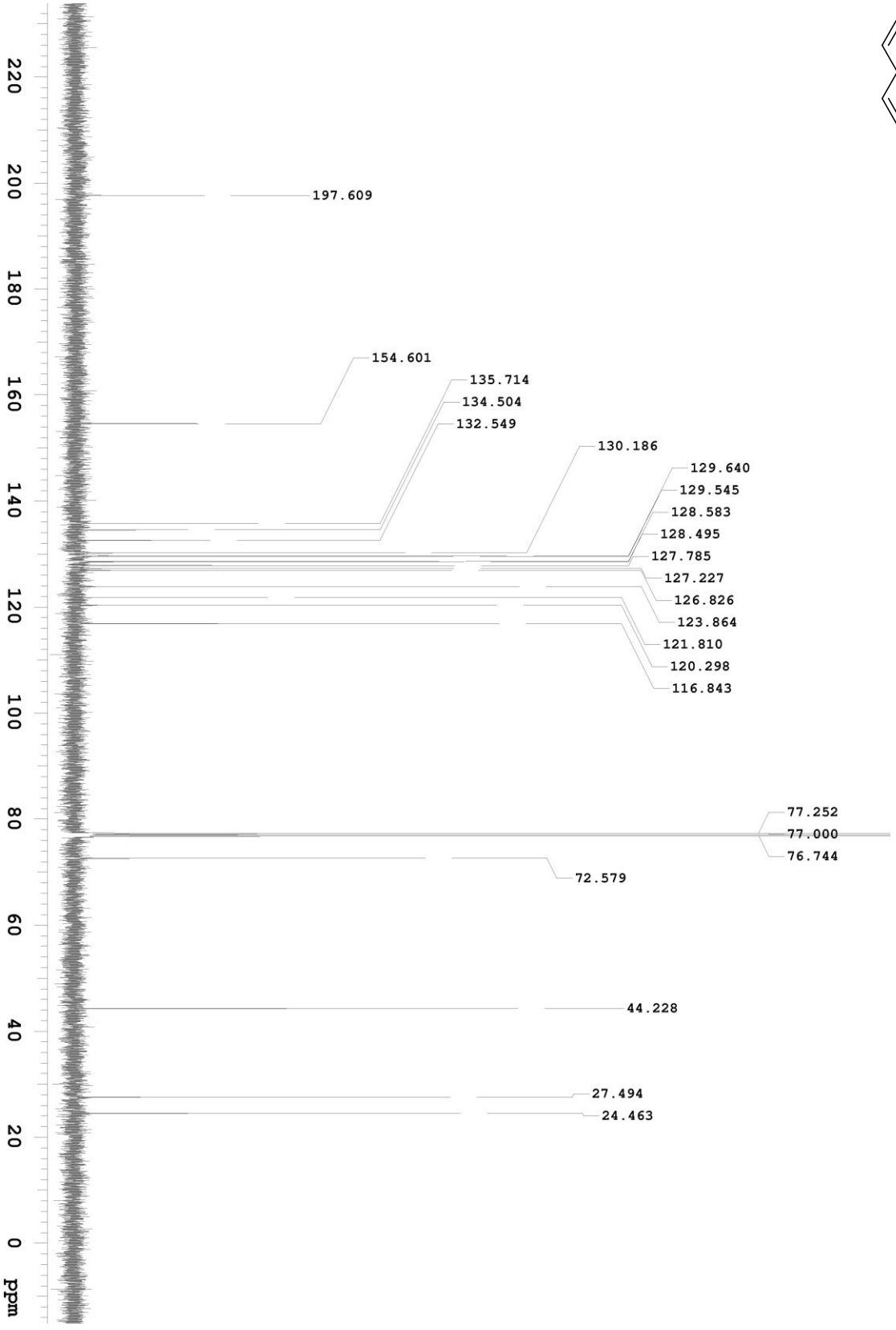
^{1}H NMR



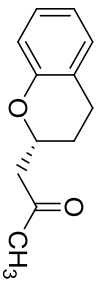
2-(Chroman-2-yl)- 1-(naphthalen-2-yl)ethanone (2f)



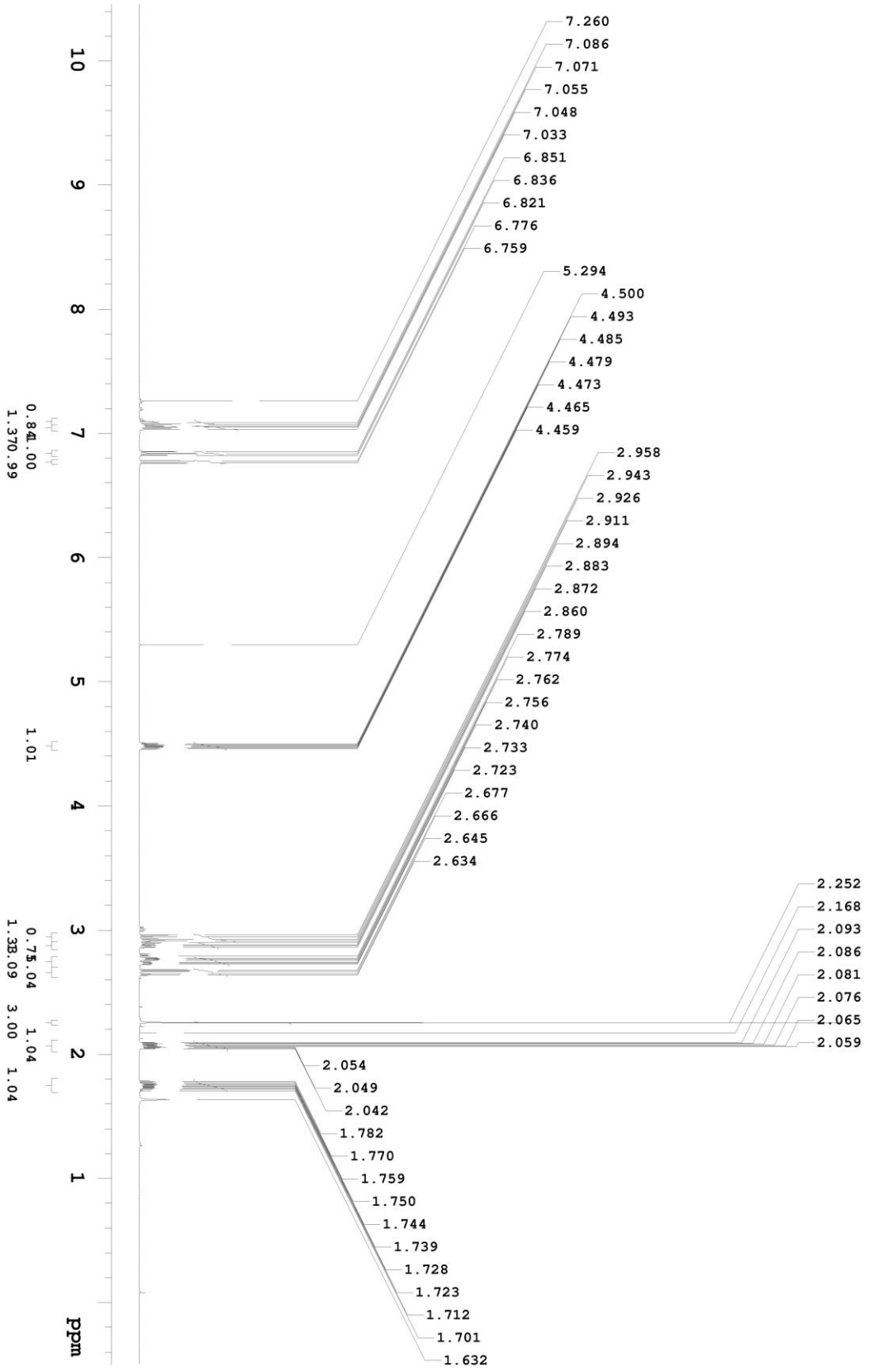
^{13}C NMR



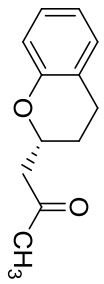
1-(Chroman-2-yl)propan-2-one (2g)



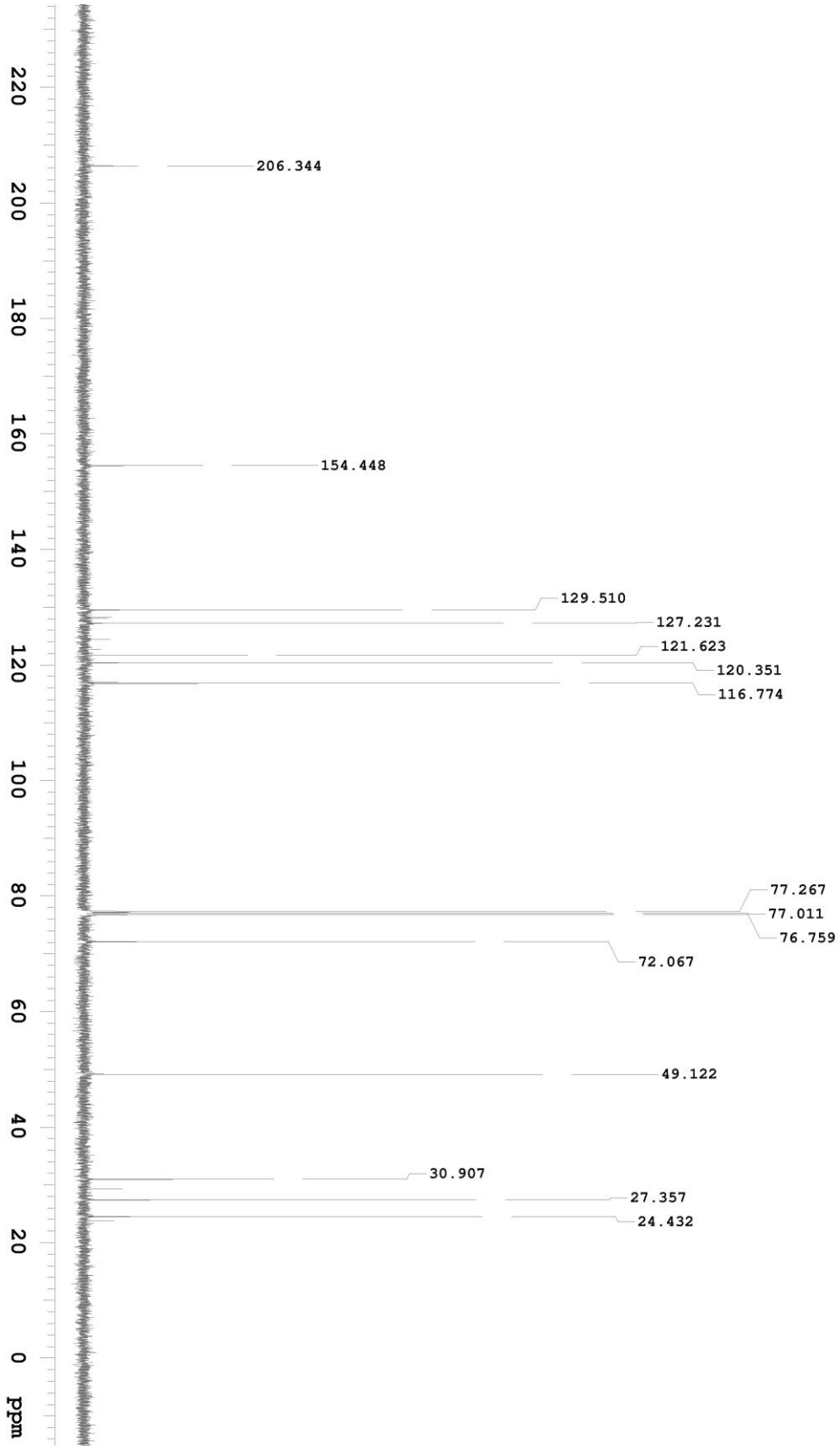
^{1}H NMR



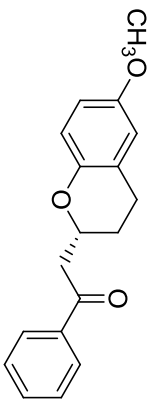
1-(Chroman-2-yl)propan-2-one (2g)



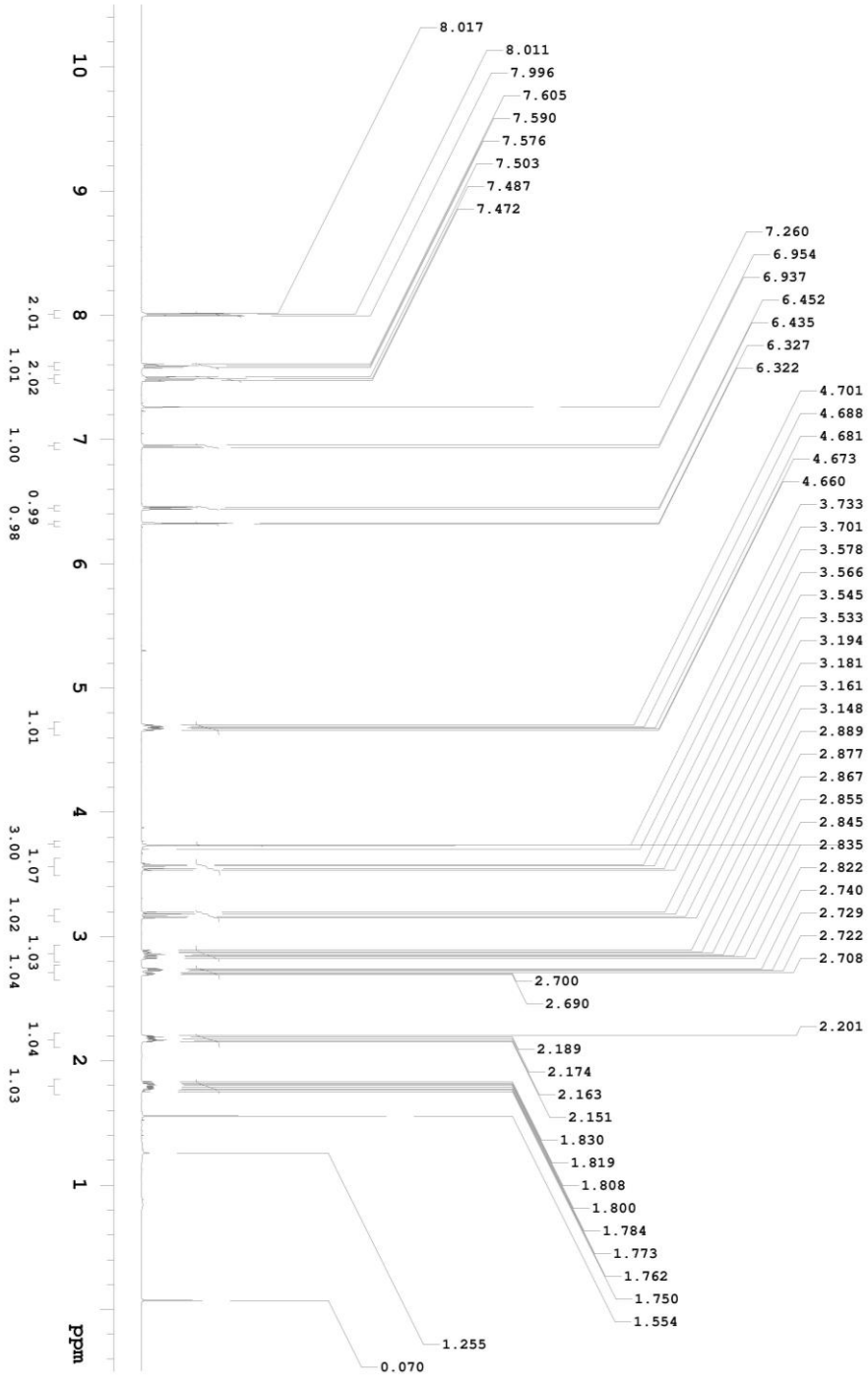
^{13}C NMR



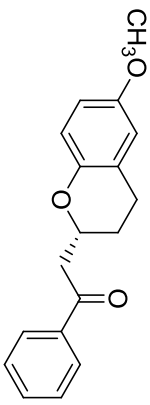
2-(6-Methoxychroman-2-yl)-1-phenylethanone (2h)



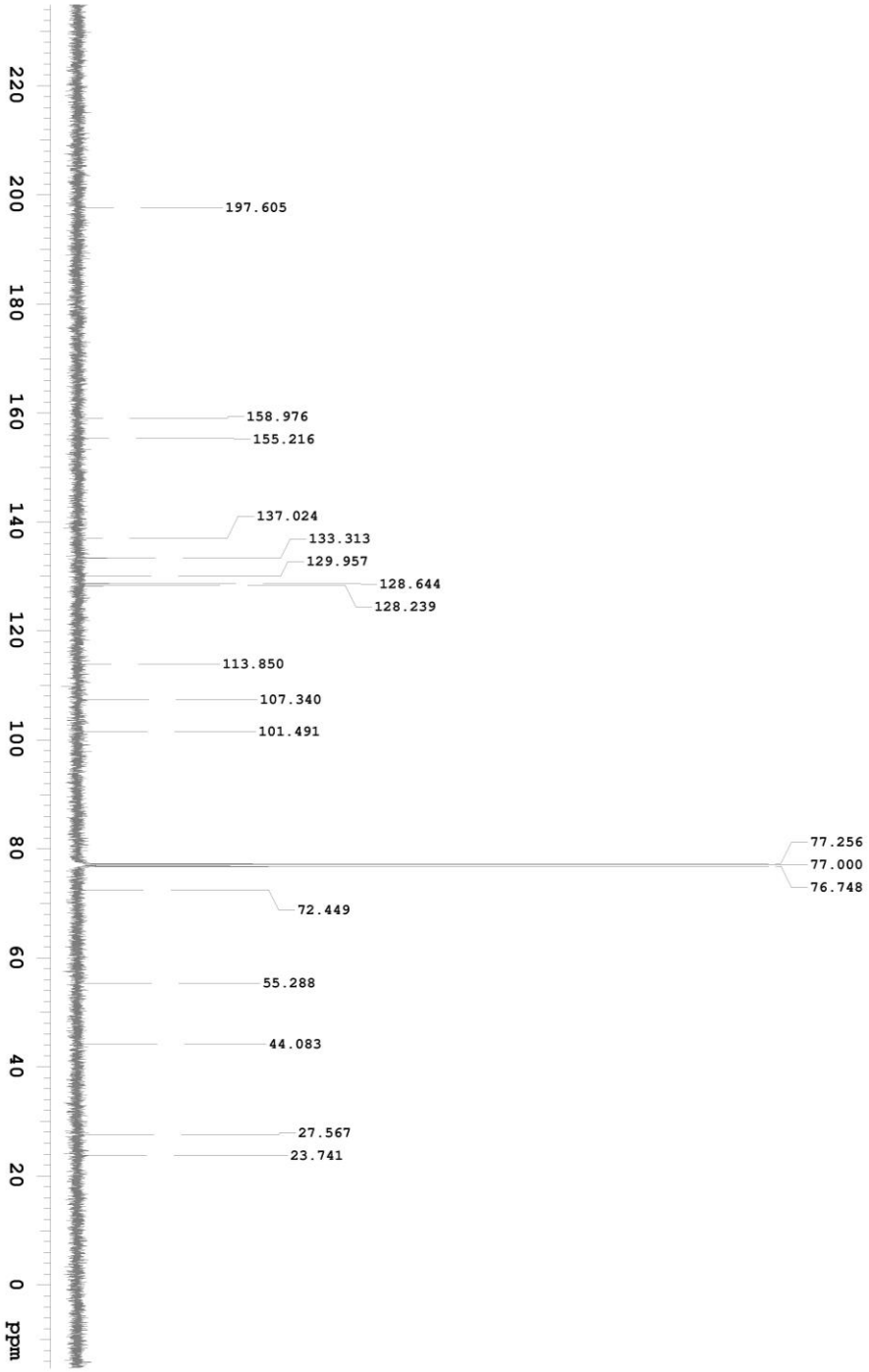
^{1}H NMR



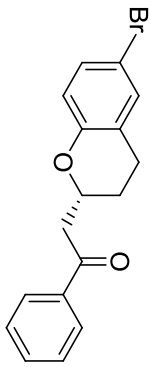
2-(6-Methoxychroman-2-yl)-1-phenylethanone (2h)



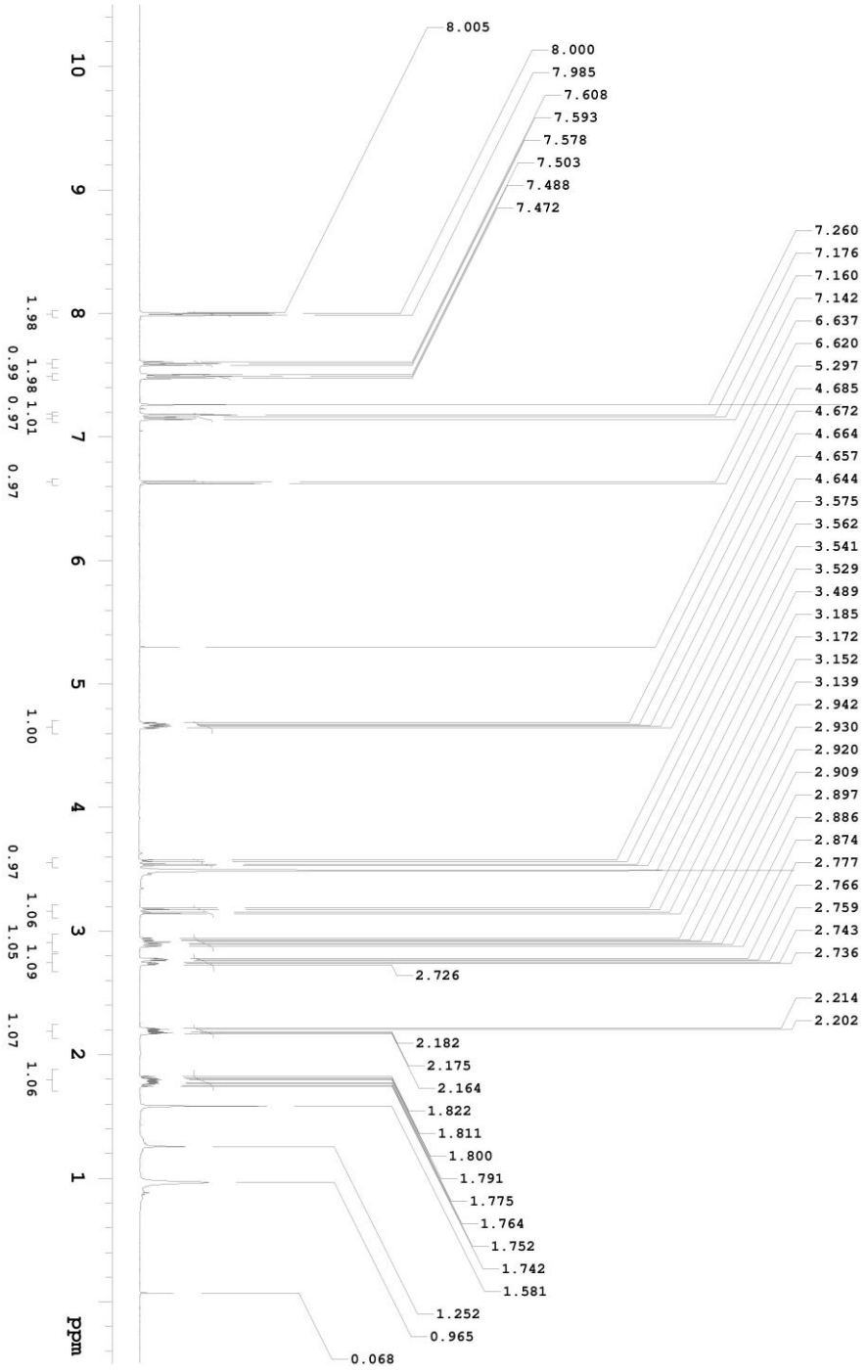
^{13}C NMR



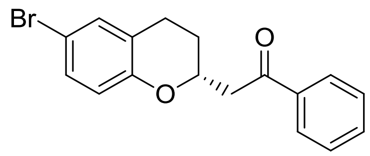
2-(6-Bromochroman-2-yl)-1-phenylethanone (2i)



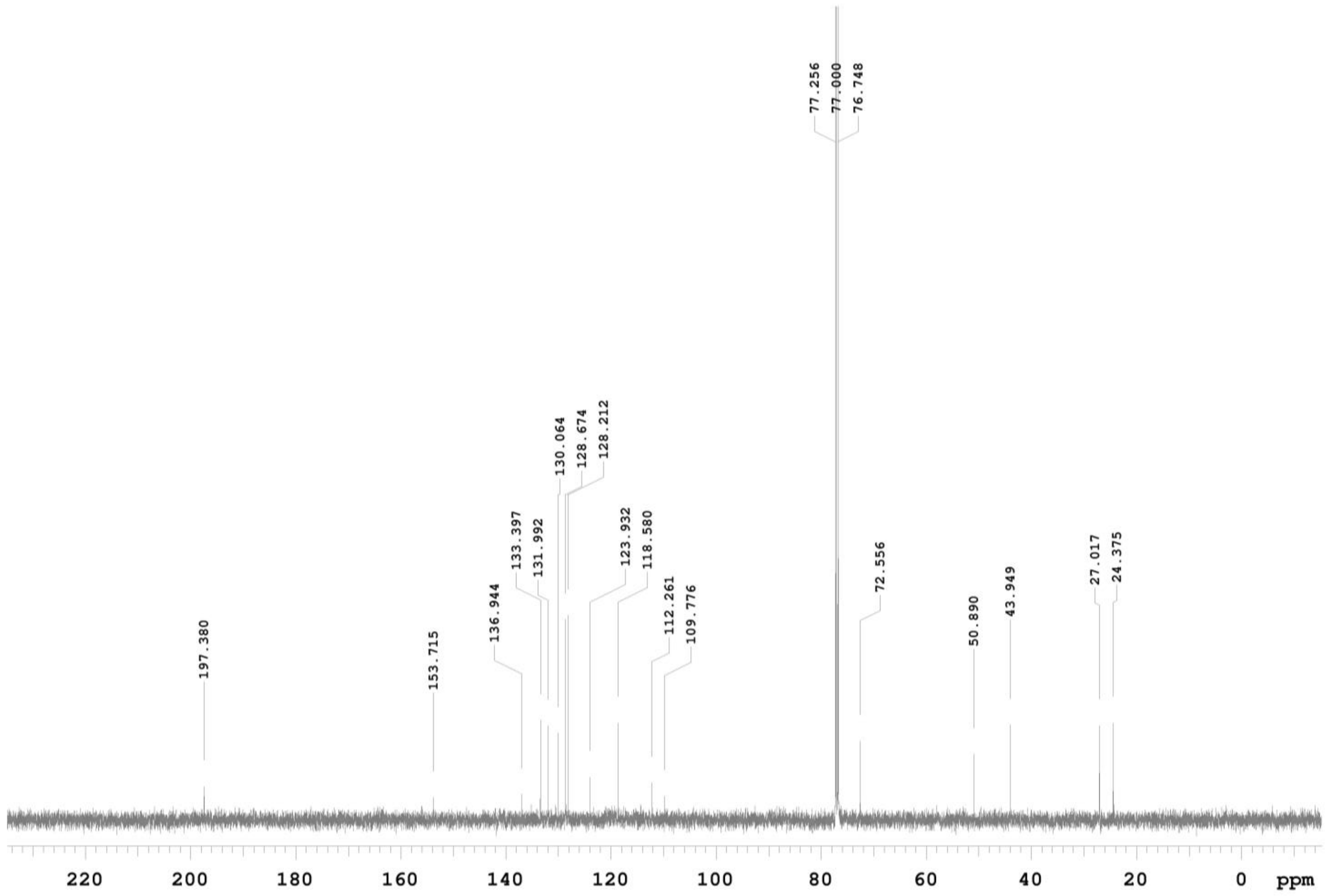
^{1}H NMR



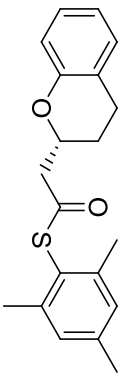
2-(6-Bromochroman-2-yl)-1-phenylethanone (2i)



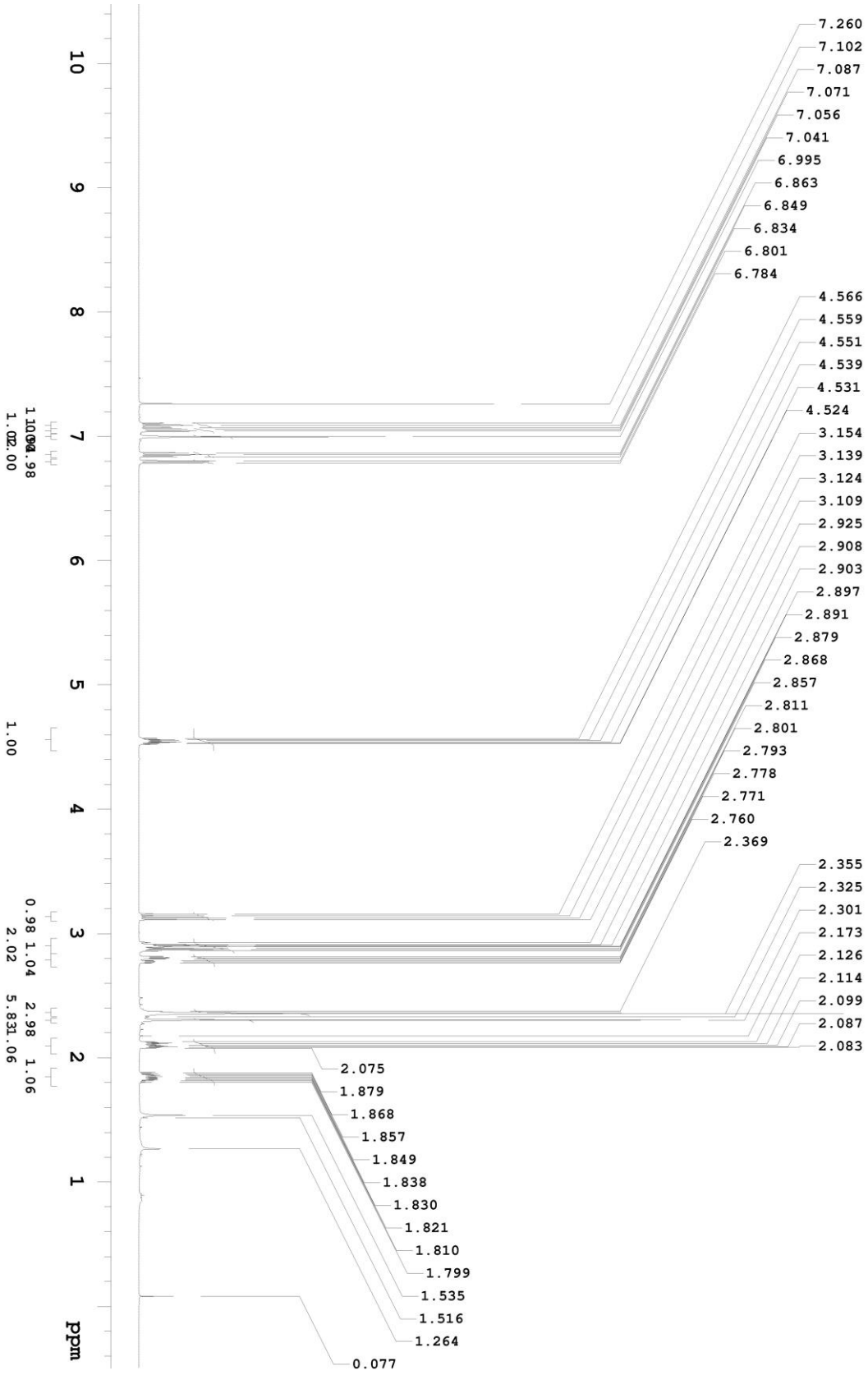
^{13}C NMR



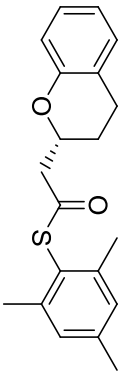
S-Mesithyl-2-(chroman-2-yl)ethanethioate (2j)



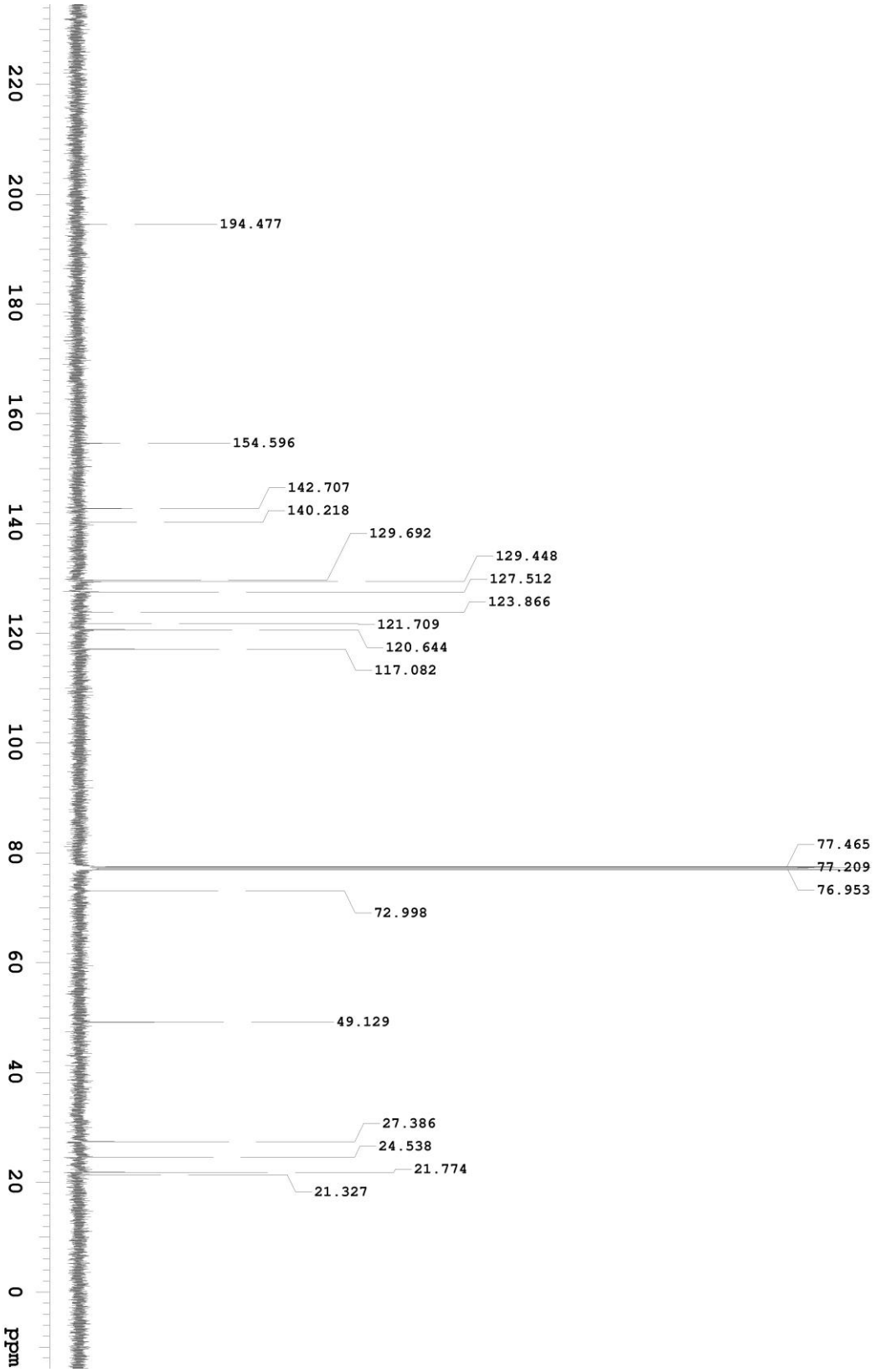
^{1}H NMR



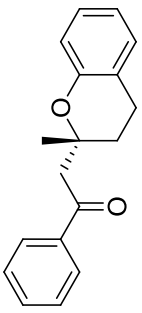
S-Mesithyl-2-(chroman-2-yl)ethanethioatene (2j)



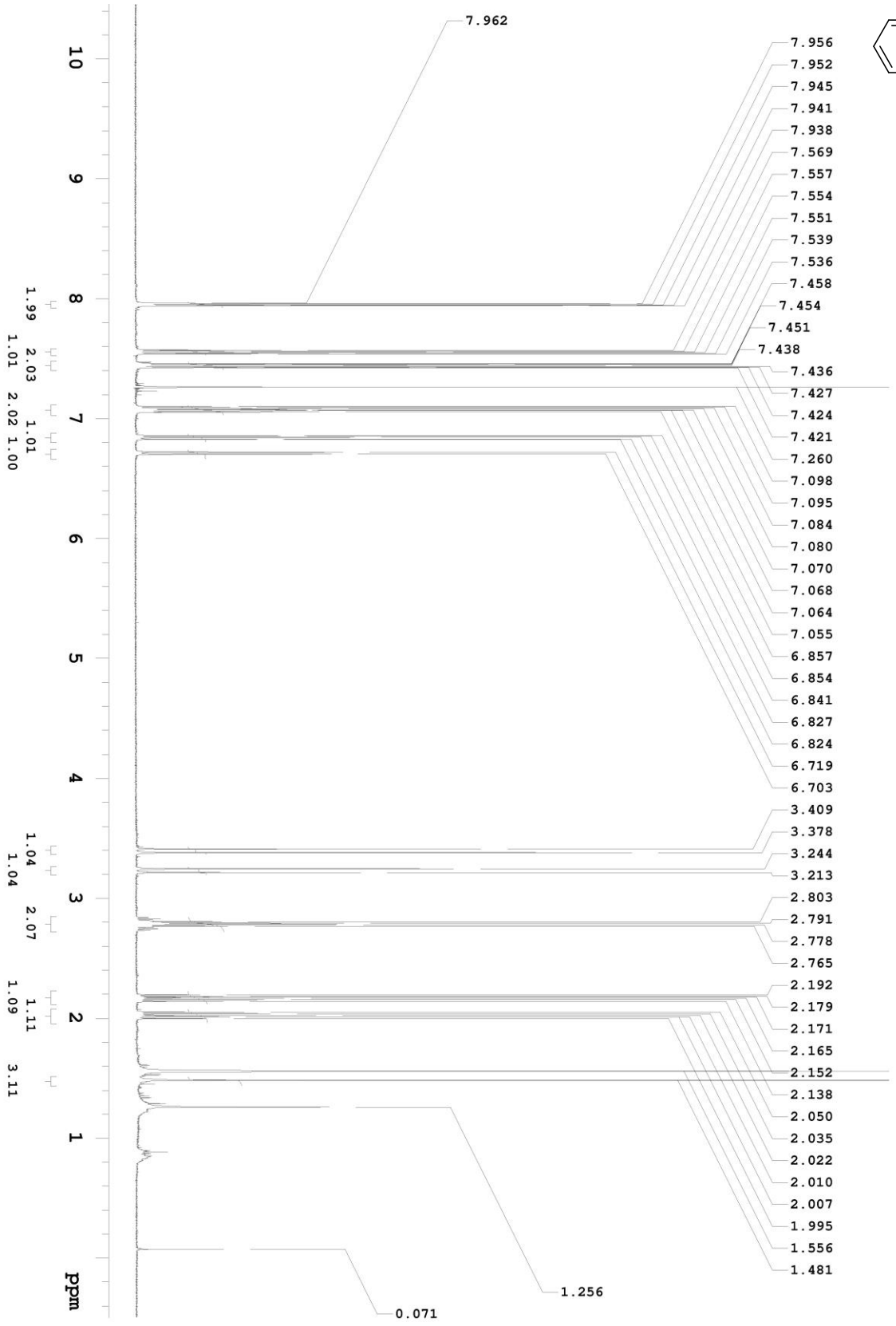
^{13}C NMR



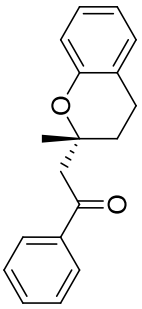
2-(2-Methylchroman-2-yl)-1-phenyl-ethanone (2k)



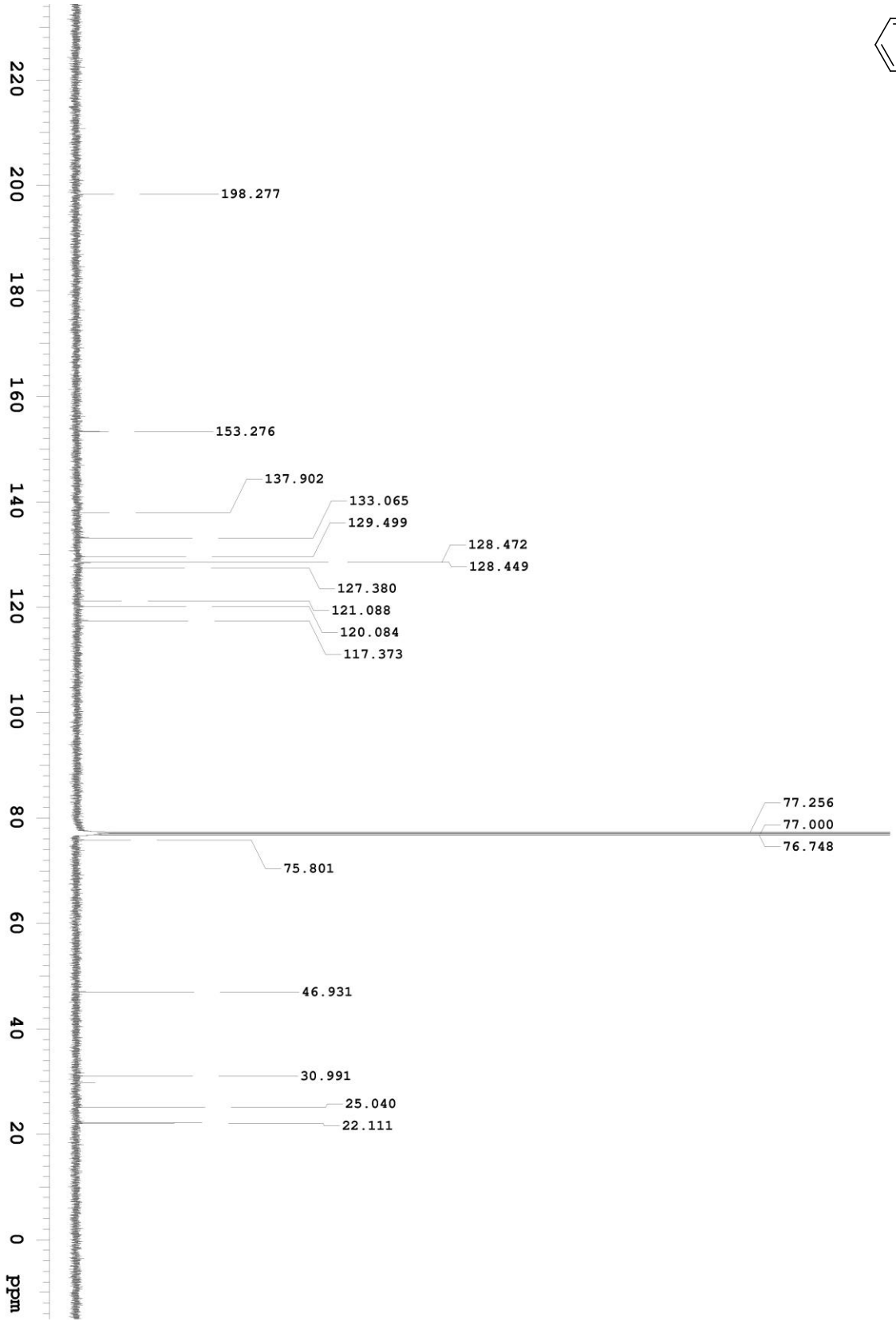
^{1}H NMR



2-(2-Methylchroman-2-yl)-1-phenyl-ethanone (2k)

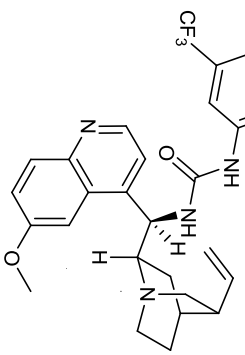


^{13}C NMR

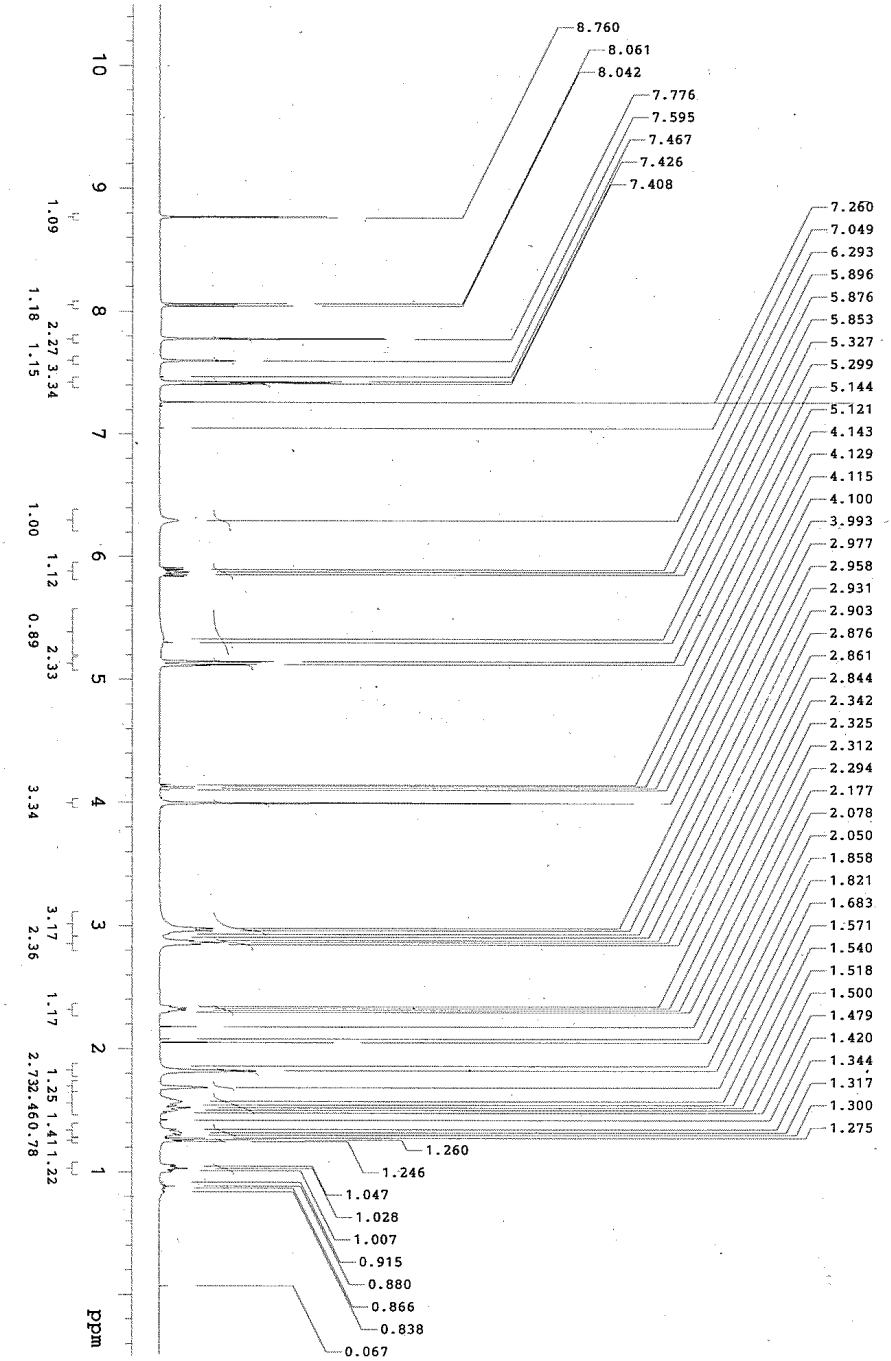


NMR Spectra (^{1}H, ^{13}C) of Catalysts

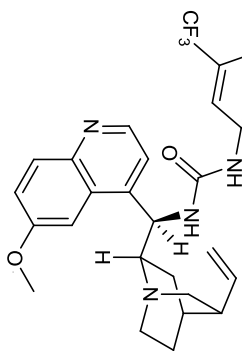
catalyst 3a



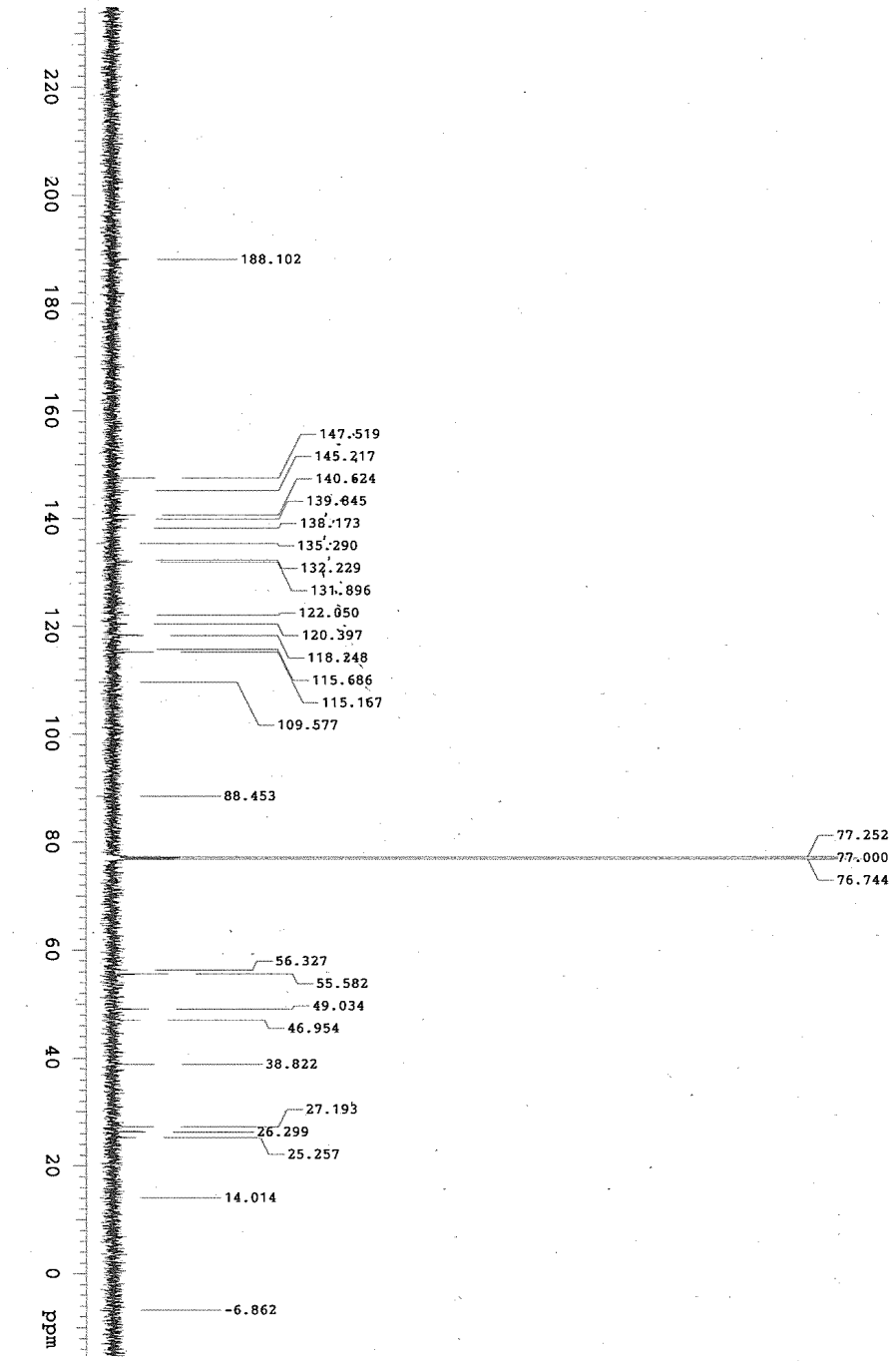
^{1}H NMR



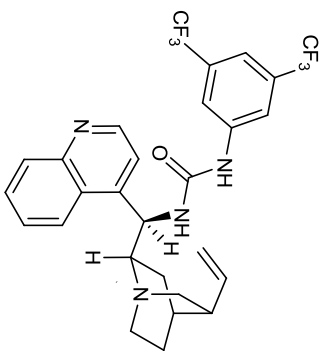
catalyst 3a



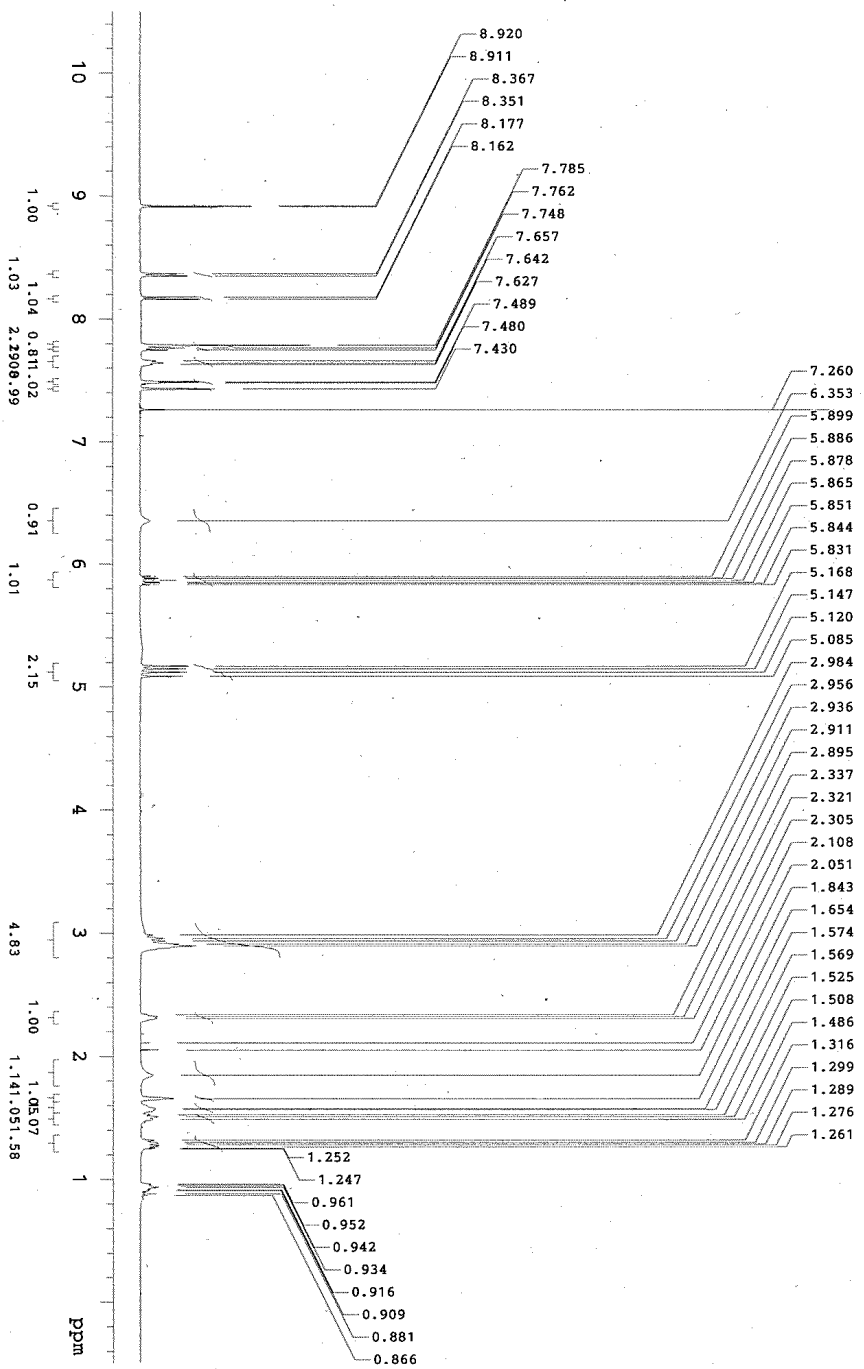
^{13}C NMR



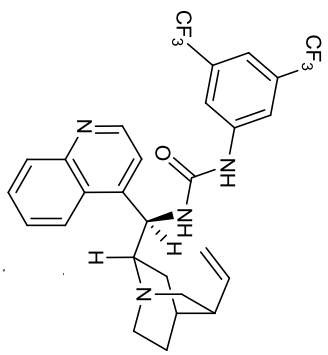
catalyst 3c



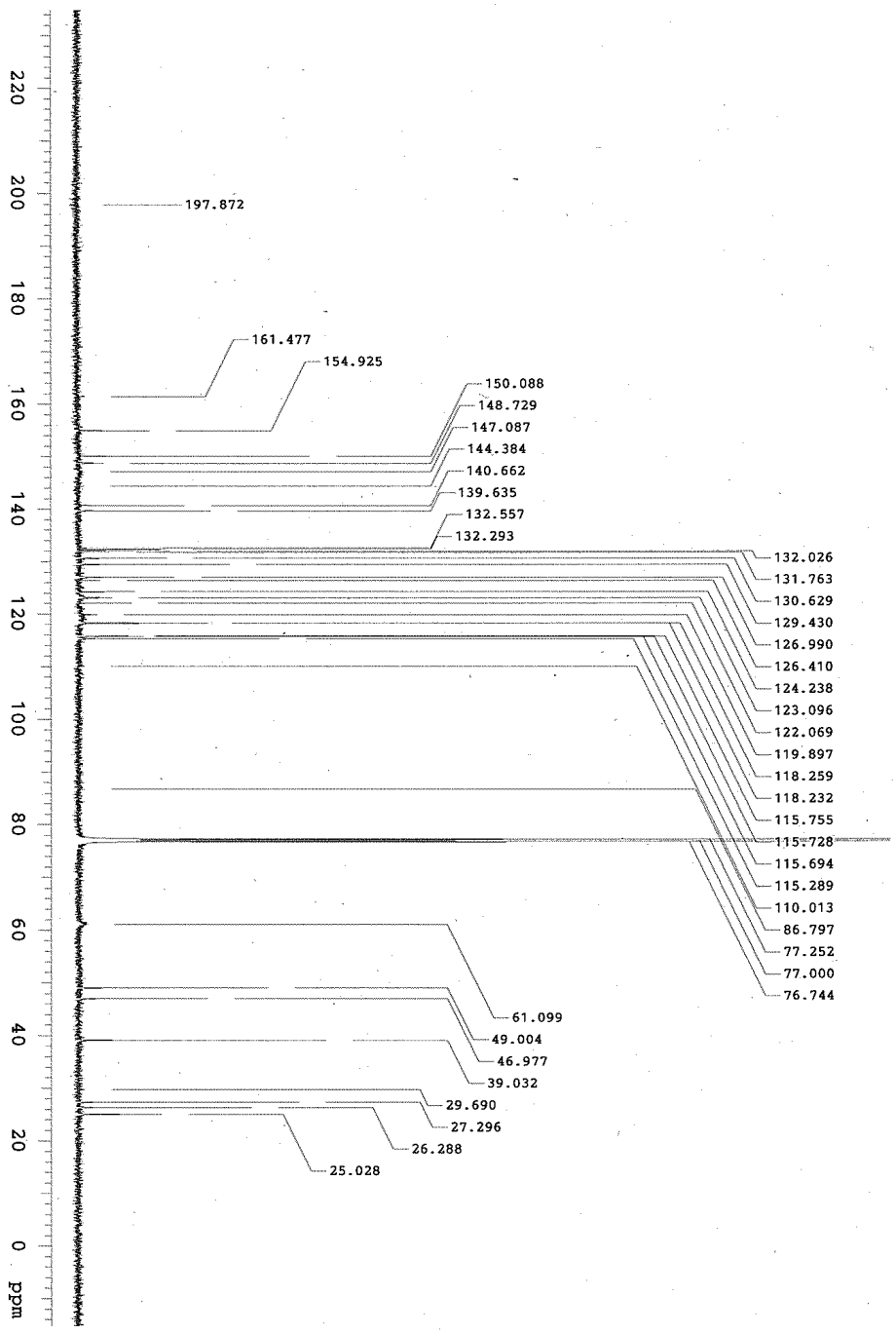
^{1}H NMR



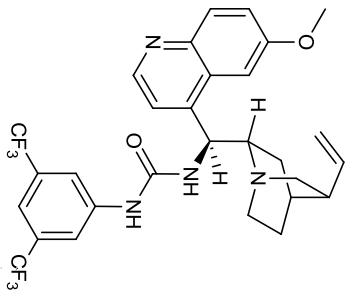
catalyst 3c



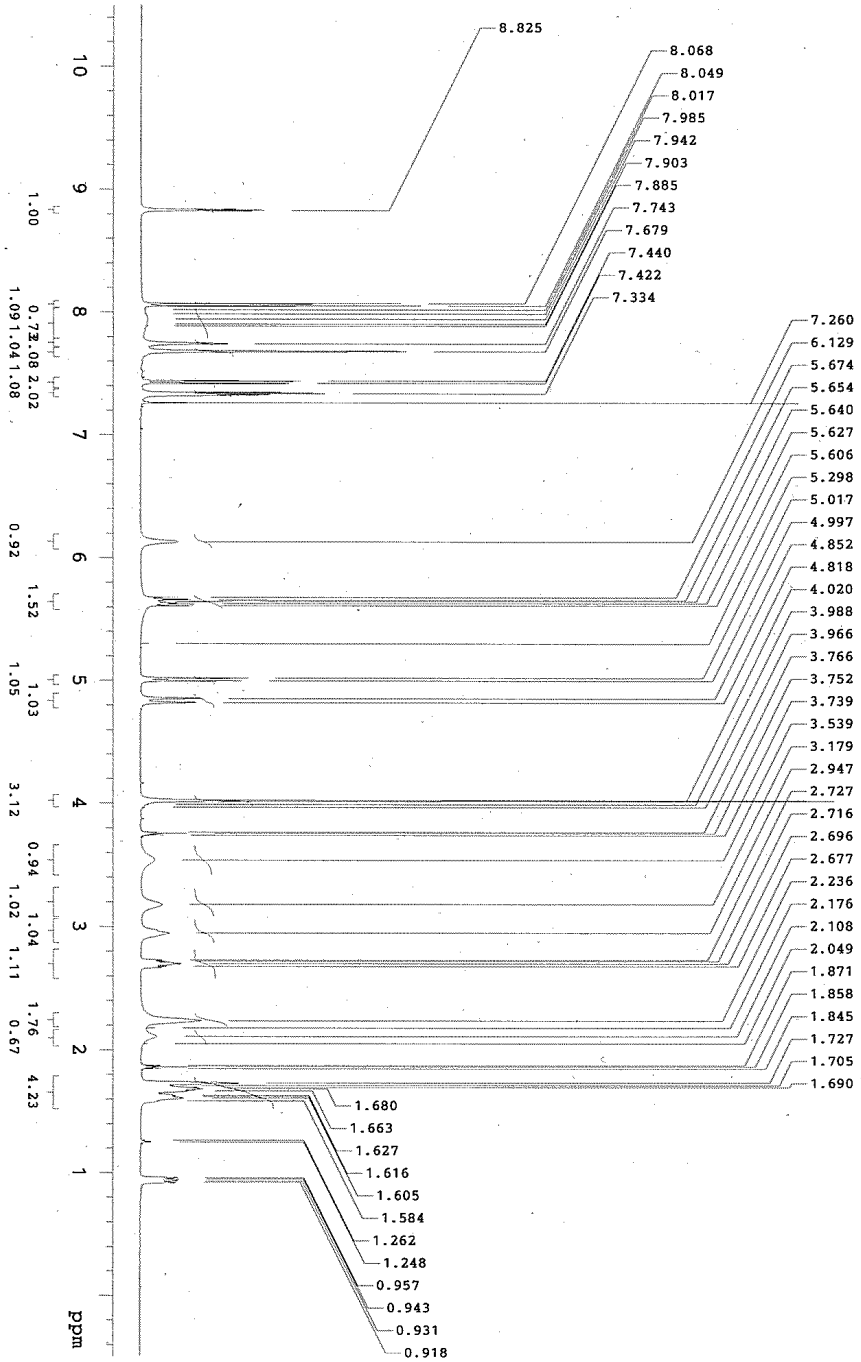
^{13}C NMR



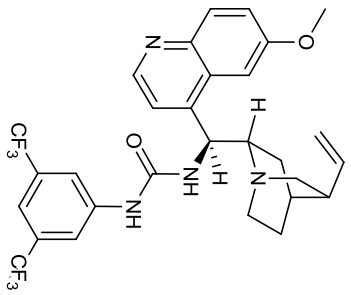
catalyst 3d



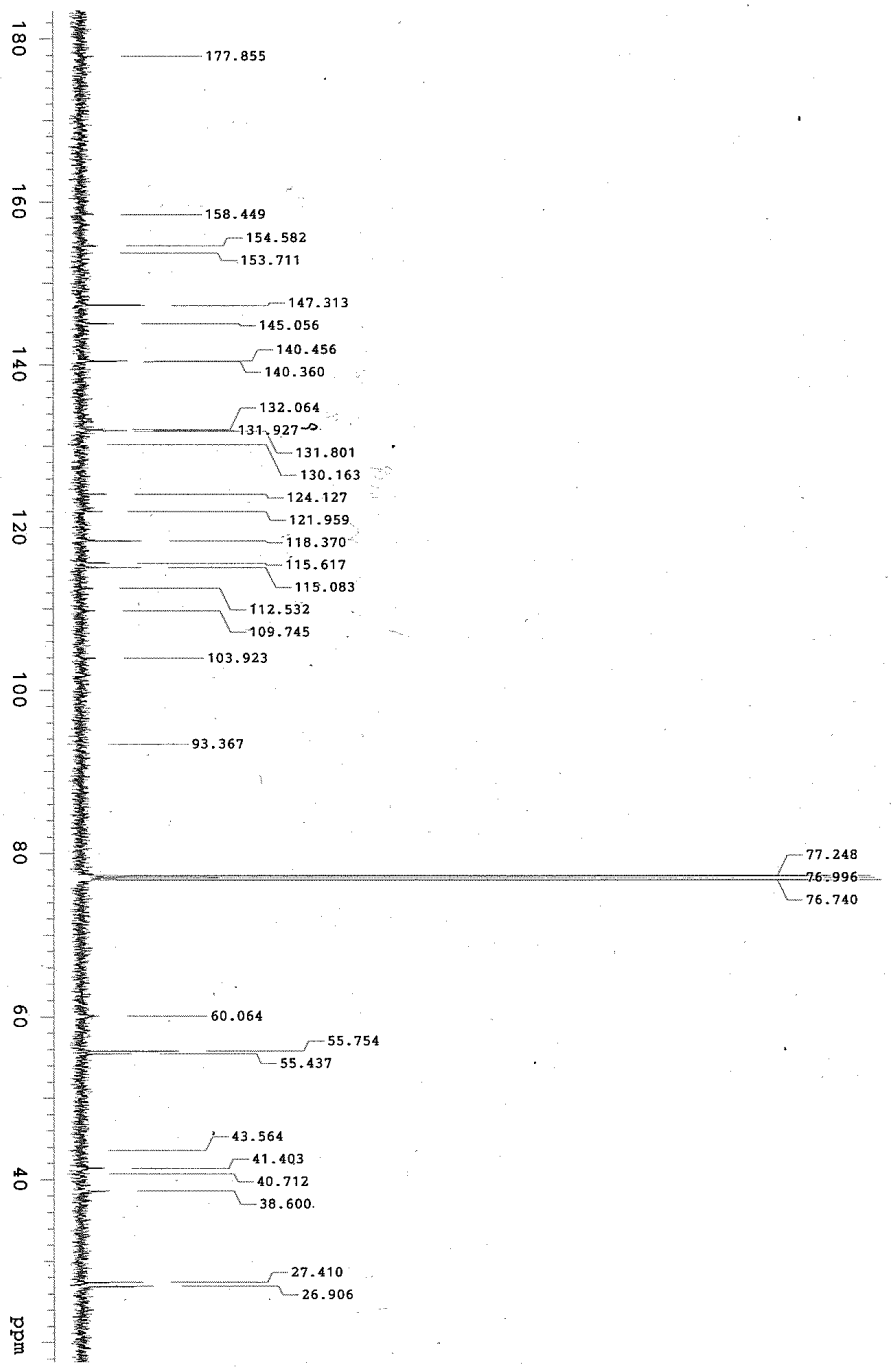
^{1}H NMR



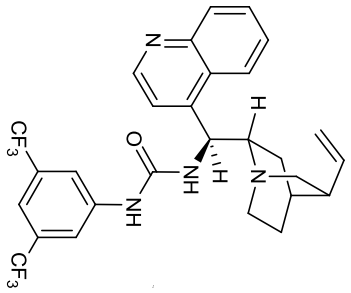
catalyst 3d



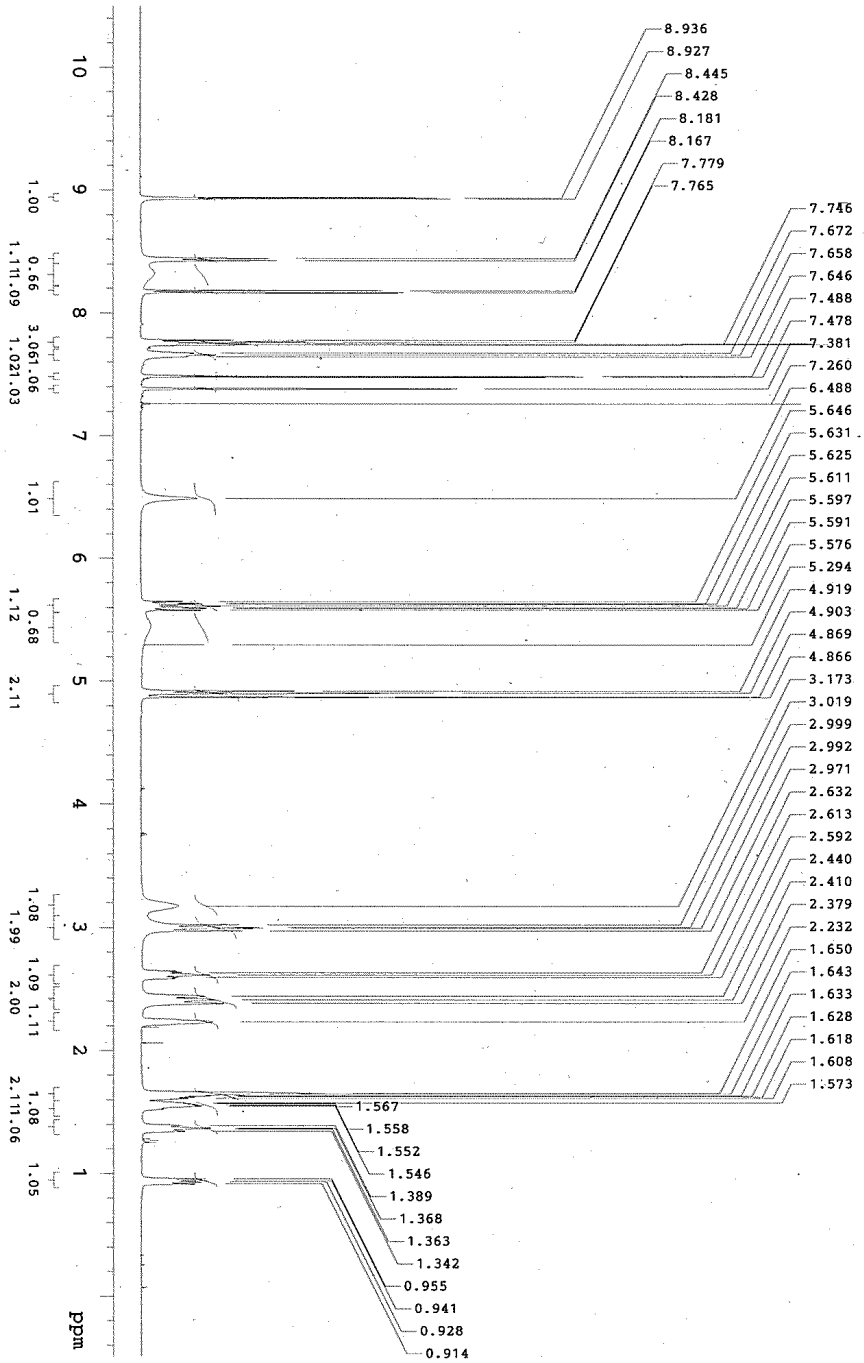
^{13}C NMR



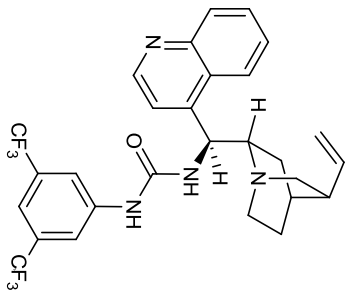
catalyst 3e



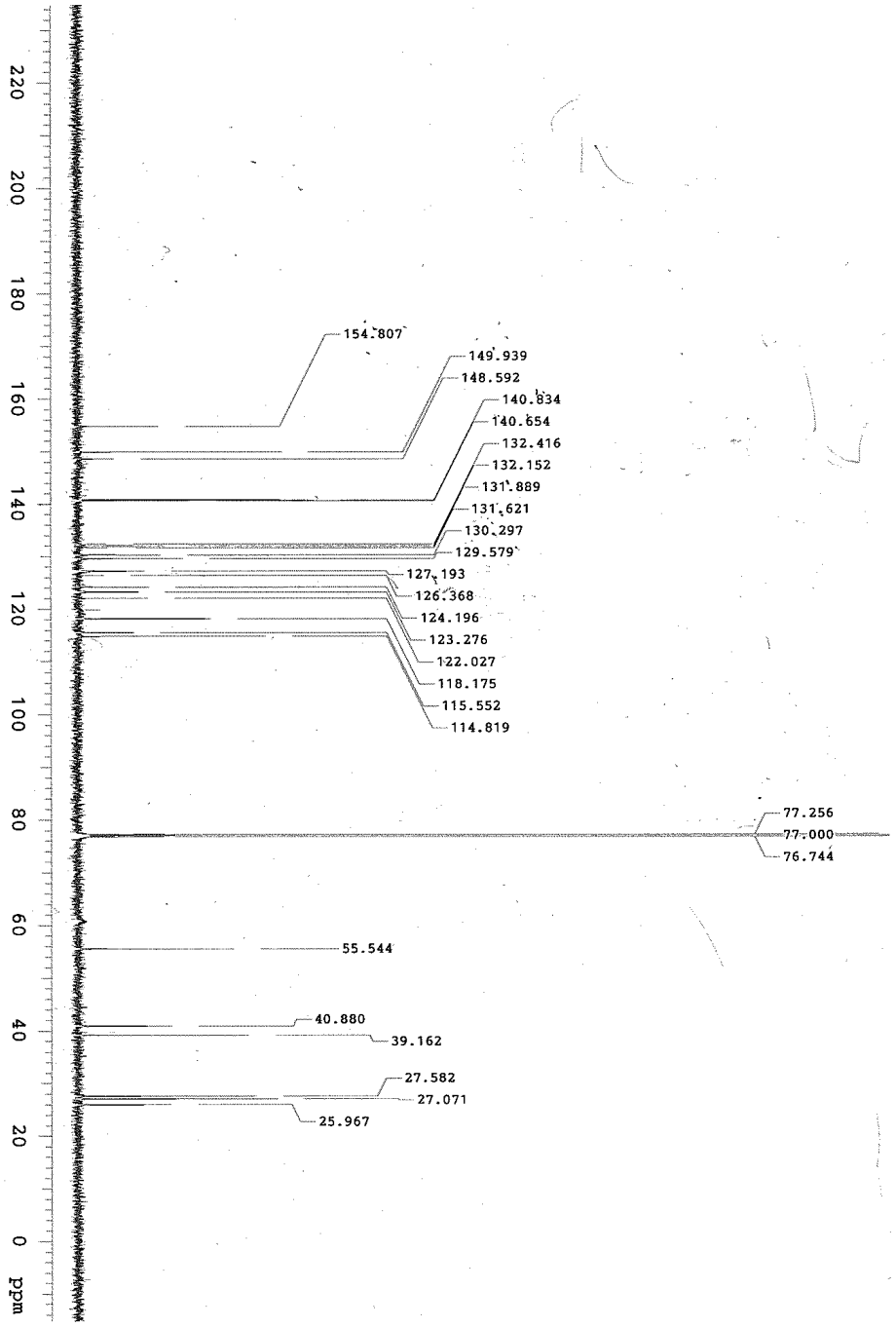
^{1}H NMR



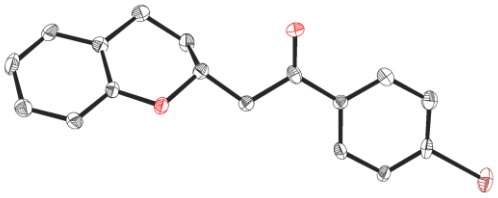
catalyst 3e



^{13}C NMR



ORTEP Drawing of 2e



A. Crystal Data	
Identification code	**2e**
Empirical Formula	$C_{17}H_{15}BrO_2$
Formula Weight	331.21
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.200 X 0.200 X 0.200 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.365(2) Å
	b = 6.054(1) Å
	c = 12.676(2) Å
	β = 90.287(6)°
	V = 718.7(2) $Å^3$
Space Group	$P2_1$ (#4)
Z value	2
D_{calc}	1.530 g/cm^3
F_{000}	336.00
μ(MoKα)	28.663 cm^{-1}
B. Intensity Measurements	
Diffractometer	XtaLAB mini
Radiation	MoKα (λ = 0.71075 Å)
	graphite monochromated
Voltage, Current	50kV, 12mA
Temperature	20.0°C
Detector Aperture	75 mm (diameter)
Data Images	540 exposures
ω oscillation Range	-60.0–120.0°
Exposure Rate	16.0 sec./°
Detector Swing Angle	30.00°
Detector Position	50.00 mm

Pixel Size	0.146 mm
$2\Theta_{max}$	55.0°
No. of Reflections Measured	Total: 7342
	Unique: 3259 (R_{int} = 0.0854)
	Friedel pairs: 1461
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.298–0.564)