Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Enantioselective Synthesis of Benzofurans and Benzoxazines *via* Olefin Cross-Metathesis/Intramolecular Oxo-Michael Reaction

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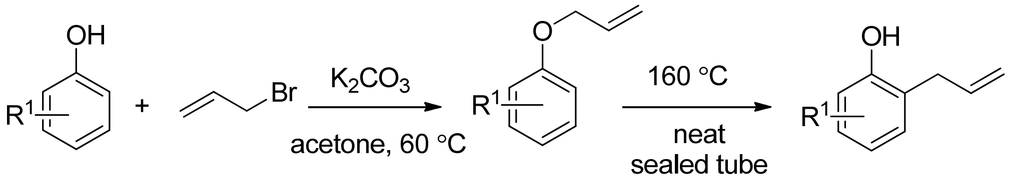
General Methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, 400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

Experimental Sections:

The *ortho*-allylphenols **1**[1]and enones **2**[2] were prepared according to the known procedure. Compound **1a** was commercially available.

General procedure for preparation of *ortho*-allylphenol 1.



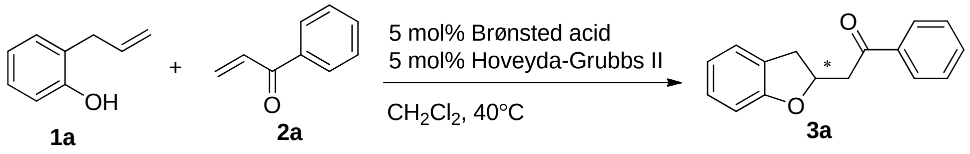
1

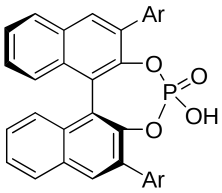
A dry three-necked flask was charged with the corresponding phenol (20 mmol), allyl bromide (3.60 g, 30 mmol) and freshly distilled acetone (20 mL). Then K_2CO_3 (4.14 g, 30 mmol) was added. The mixture was heated at 60 °C overnight. After the reaction was complete (monitored by TLC), the solvent was evaporated under reduced pressure. The residue was diluted with CH_2Cl_2, washed with H_2O and 5 M HCl (aq.) successively. The organic layers were seperated, dried over anhydrous Na_2SO_4, filtrated and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 10: 1) to afford the allyloxy substituted arene.

The allyloxy substituted arene (15 mmol) was placed in a sealed tube. After the reaction was stirred at 160 °C for 6 h, the crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 10: 1) to afford the *ortho*-allylphenol **1**.

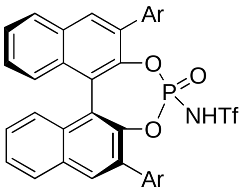
Full screening data

Table 1. optimization of asymmetric oxo-Michael reaction [a]

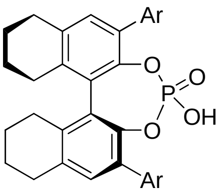




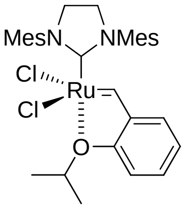
(*S*)-**4**



(*S*)-**8**



(*S*)-**9**



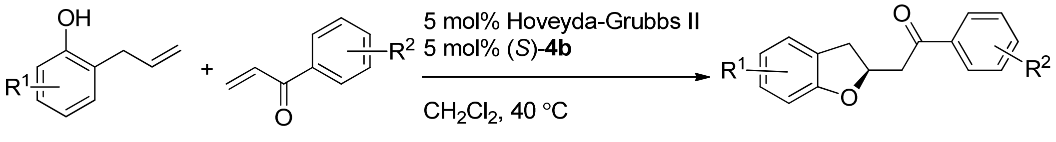
Hoveyda-Grubbs II

entry	catalyst, Ar	time (h)	yield (%)[b]	*ee* (%) [c]
1	**4a**, 2,4,6-(^{i}Pr)$_3$-C$_6$H$_2$	47	82	6
2	**4b, SiPh$_3$**	**48**	**56**	**78**
3	**4c**, 1-naphthyl	66	67	-3
4	**4d**, 9-anthryl	24	33	-30
5	**4e**, 9-phenanthryl	24	62	-31
6	**4f**, 2,6-(^{i}Pr)$_2$-4-anthryl-C$_6$H$_2$	47	43	23
7	**4g**, 3,5-(CF$_3$)$_2$-C$_6$H$_3$	45	39	-19
8	**4h,** 4-biphenyl	45	70	-2
9	**4i**, 4-(3’,5’-(CF$_3$)$_2$-C$_6$H$_3$)-C$_6$H$_4$	45	88	15
10	**4j**, 4-NO$_2$-C$_6$H$_4$	45	90	-13
11	**4k**, 2-^{i}PrO-1-naphthyl	47	45	-26
12	**4l**, 2-methoxy-1-naphthyl	48	43	-22
13	**4m**, 2-butoxy-1- naphthyl	48	62	-21
14	**4n**, P(O)Ph$_2$	66	91	-5
15	**8a**, SiPh$_3$	48	63	1

16	**8b**, 9-anthryl	48	85	-13
17	**8c**, 2,4,6-$(^{i}Pr)_3$-C_6H_2	24	55	13
18	**8d**, 9-phenanthryl	14	88	-16
19	**8e**, 4-pyrene	14	84	-13
20	**9a**, $SiPh_3$	48	52	74
21	**9b**, $P(O)Ph_2$	47	71	40
22[d]	**4b**, $SiPh_3$	21	46	79
22[d,e]	**4b**, $SiPh_3$	24	48	77
22[e,f]	**4b**, $SiPh_3$	24	0	0

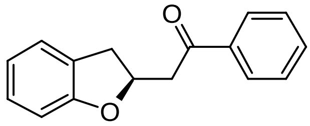
[a] Reactions condition: **1a** (0.20 mmol), **2a** (0.30 mmol), Hoveyda-Grubbs II (5 mol%) and catalyst (5 mol%) in CH_2Cl_2 (2 mL) at 40℃. [b] Isolated yield. [c] Determined by HPLC analysis. [d] **Zhan-1B** was used instead of Hoveyda-Grubbs II. [e] Reaction was carried out in toluene in 60 °C. [f] Grubbs II catalyst was used instead of Hoveyda-Grubbs II.

General procedure for the enantioselective synthesis of 2,3-dihydrobenzofuran (3a-3o).



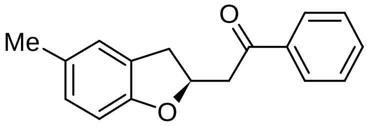
1 **2** **3**

To a solution of *ortho*-allylphenol **1** (0.2 mmol) in dichloromethane (2 mL) was added the enone **2** (0.3 mmol, 1.5 equiv.), then the chiral phosphoric acid (*S*)-**4b** (8.7 mg, 0.01 mmol, 5 mol%) and Hoveyda-Grubbs II (6.3 mg, 0.01 mmol, 5 mol%) were added in one portion. The reaction was stirred 12 h at 40 °C. After the reaction was complete (monitored by TLC), the mixture was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/25) to afford 2,3-dihydrobenzofuran **3**.



(*S*)-2-(2,3-Dihydrobenzofuran-2-yl)-1-phenylethanone (3a)

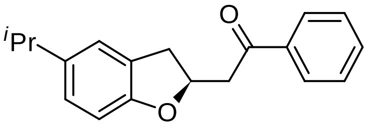
White solid (56% yield, 78% *ee*). Analytical data for **3a**: Mp = 106-107 °C; $[\alpha]_D^{20}$ = +13.3° (c = 0.5 Acetone, 78% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.94 (dd, $J_1 = 7.5$ Hz, $J_2 = 15.9$ Hz, 1H), 3.27 (dd, $J_1 = 7.5$ Hz, $J_2 = 16.8$ Hz, 1H), 3.54 (dd, $J_1 = 9.3$ Hz, $J_2 = 15.9$ Hz, 1H), 3.66 (dd, $J_1 = 6.0$ Hz, $J_2 = 16.8$ Hz, 1H), 5.33-5.43 (m, 1H), 6.78 (d, $J = 7.8$ Hz, 1H), 6.85 (t, $J = 7.2$ Hz, 1H), 7.11 (t, $J = 7.5$ Hz, 1H), 7.17 (d, $J = 7.5$ Hz, 1H), 7.44-7.49 (m, 2H), 7.56-7.60 (m, 1H), 7.97 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.8, 44.6, 78.9, 109.5, 120.4, 125.0, 126.3, 128.0, 128.1, 128.6, 133.4, 136.6, 159.0, 197.4; IR (film) 2923, 2854, 1679, 1595, 1480, 1448, 1379, 1337, 1223, 1159, 1068, 979, 928, 870, 790, 746, 709, 686, 652 cm^{-1}; HRMS (EI) exact mass calcd for $C_{16}H_{14}O_2$ (M) requires *m/z* 238.0994, found *m/z* 238.0993. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 11.50 min, t (minor) = 13.80 min.



(*S*)-2-(5-Methyl-2,3-dihydrobenzofuran-2-yl)-1-phenylethanone (3b)

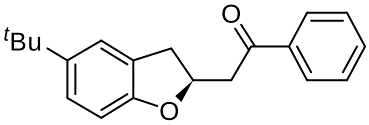
White solid (49% yield, 79% *ee*). Analytical data for **3b**: Mp = 99-100 °C; $[\alpha]_D^{20}$ = +30.5° (c = 0.5 Acetone, 79% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.90 (dd, $J_1 = 6.3$ Hz, $J_2 = 15.3$ Hz, 1H), 3.26 (dd, $J_1 = 7.5$ Hz, $J_2 = 15.6$ Hz, 1H), 3.50 (dd, $J_1 = 10.2$ Hz, $J_2 = 16.8$ Hz, 1H), 3.65 (dd, $J_1 = 6.0$ Hz, $J_2 = 15.6$ Hz, 1H), 5.33-5.38 (m, 1H), 6.67 (d, $J = 7.2$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 6.99 (s, 1H), 7.44-7.50 (m, 2H), 7.56-7.61 (m, 1H), 7.97 (d, $J = 6.9$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7, 35.9, 44.7, 79.0, 109.0, 125.6, 126.4, 128.1, 128.3, 128.6, 129.8, 133.4, 136.7, 156.9, 197.6; IR (film) 2959, 2926, 2856, 1728, 1682, 1596, 1490, 1448, 1409, 1367, 1304, 1239, 1203, 1111, 1075, 957, 809, 792, 758, 740, 688, 651 cm^{-1}; HRMS (EI) exact mass calcd for $C_{17}H_{16}O_2$ (M) requires *m/z* 252.1150, found *m/z* 252.1146. The enantiomeric excess was determined by Daicel Chiralpak

AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 10.46 min, t (minor) = 12.66 min.



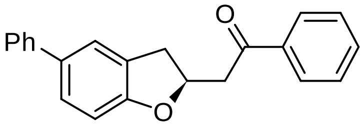
(*S*)-2-(5-Isopropyl-2,3-dihydrobenzofuran-2-yl)-1-phenylethanone (3c)

White solid (72% yield, 78% *ee*). Analytical data for **3c**: Mp = 67-68 °C; $[\alpha]_D^{20}$ = +30.7° (c = 0.5 Acetone, 78% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (d, *J* = 7.2 Hz, 6H), 2.80-2.95 (m, 2H), 3.27 (dd, J_1 = 7.2 Hz, J_2 = 17.1 Hz, 1H), 3.52 (dd, J_1 = 9.0 Hz, J_2 = 15.9 Hz, 1H), 3.65 (dd, J_1 = 6.0 Hz, J_2 = 17.1 Hz, 1H), 5.33-5.38 (m, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 7.05 (s, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.55-7.60 (m, 1H), 7.97 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.3, 24.4, 33.6, 36.0, 44.8, 79.0, 109.0, 122.9, 125.9, 126.3, 128.1, 128.6, 133.4, 136.7, 141.3, 157.1, 197.6; IR (film) 2956, 2917, 2885, 1676, 1594, 1488, 1447, 1411, 1373, 1345, 1316, 1248, 1204, 1158, 1112, 964, 900, 874, 812, 755, 718, 688, 649 cm^{-1}; HRMS (EI) exact mass calcd for $C_{19}H_{20}O_2$ (M) requires *m/z* 280.1463, found *m/z* 280.1461. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 12.20 min, t (minor) = 12.97 min.



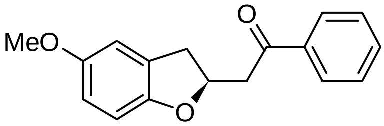
(*S*)-2-(5-(tert-Butyl)-2,3-dihydrobenzofuran-2-yl)-1-phenylethanone (3d)

White solid (64% yield, 76% *ee*). Analytical data for **3d**: Mp = 93-94 °C; $[\alpha]_D^{20}$ = +34.4° (c = 0.5 Acetone, 76% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9H), 2.93 (dd, J_1 = 7.5 Hz, J_2 = 16.2 Hz, 1H), 3.27 (dd, J_1 = 7.5 Hz, J_2 = 17.1 Hz, 1H), 3.53 (dd, J_1 = 9.0 Hz, J_2 = 15.6 Hz, 1H), 3.65 (dd, J_1 = 6.0 Hz, J_2 = 17.1 Hz, 1H), 5.34-5.39 (m, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.21 (s, 1H), 7.44-7.49 (m, 2H), 7.55-7.60 (m, 1H), 7.97 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.7, 34.2, 36.1, 44.8, 79.1, 108.7, 122.0, 124.8, 126.0, 128.1, 128.6, 133.4, 136.7, 143.5, 156.8, 197.6; IR (film) 2960, 2912, 2862, 1674, 1593, 1490, 1447, 1373, 1319, 1297, 1263, 1242, 1210, 1172, 1117, 1081, 1021, 965, 900, 874, 827, 809, 793, 755, 728, 688, 648 cm^{-1}; HRMS (EI) exact mass calcd for $C_{20}H_{22}O_2$ (M) requires *m/z* 294.1620, found *m/z* 294.1622. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 9.20 min, t (minor) = 10.07 min.



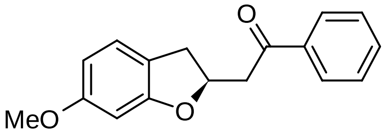
(*S*)-1-Phenyl-2-(5-phenyl-2,3-dihydrobenzofuran-2-yl)ethanone (3e)

White solid (53% yield, 76% *ee*). Analytical data for **3e**: Mp = 152-153 °C; $[\alpha]_D^{20}$ = +95.5° (c = 0.25 Acetone, 76% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.99 (dd, J_1 = 6.6 Hz, J_2 = 15.9 Hz, 1H), 3.31 (dd, J_1 = 7.2 Hz, J_2 = 17.1 Hz, 1H), 3.60 (dd, J_1 = 9.0 Hz, J_2 = 15.9 Hz, 1H), 3.69 (dd, J_1 = 6.0 Hz, J_2 = 17.1 Hz, 1H), 5.41-5.46 (m, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 7.24-7.61 (m, 10H), 7.98 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.8, 44.7, 79.4, 109.6, 123.9, 126.5, 126.8, 127.1, 127.2, 128.1, 128.6, 128.7, 133.5, 134.1, 136.6, 141.2, 158.7, 197.4; IR (film) 2972, 1679, 1593, 1480, 1449, 1381, 1243, 1115, 983, 933, 891, 821, 762, 692, 650 cm^{-1}; HRMS (EI) exact mass calcd for $C_{22}H_{18}O_2$ (M) requires *m/z* 314.1307, found *m/z* 314.1311. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 23.80 min, t (minor) = 20.66 min.



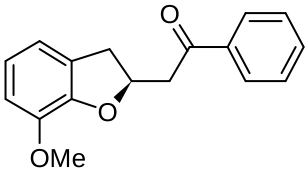
(*S*)-2-(5-Methoxy-2,3-dihydrobenzofuran-2-yl)-1-phenylethanone (3f)

White solid (52% yield, 74% *ee*). Analytical data for **3f**: Mp = 93-94°C; $[\alpha]_D^{20}$ = +30.7° (c = 0.5 Acetone, 74% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.93 (dd, J_1 = 7.2 Hz, J_2 = 15.9 Hz, 1H), 3.28 (dd, J_1 = 6.9 Hz, J_2 = 16.5 Hz, 1H), 3.53 (dd, J_1 = 9.0 Hz, J_2 = 16.2 Hz, 1H), 3.65 (dd, J_1 = 6.0 Hz, J_2 = 14.1 Hz, 1H), 3.76 (s, 3H), 5.34-5.38 (m, 1H), 6.68 (s, 2H), 6.78 (s, 1H), 7.45-7.50 (m, 2H), 7.57-7.59 (m, 1H), 7.98 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.3, 44.6, 56.0, 79.2, 109.4, 111.3, 112.9, 127.4, 128.1, 128.7, 133.4, 136.7, 153.1, 154.1, 197.6; IR (film) 2953, 2923, 2853, 1680, 1596, 1489, 1450, 1432, 1376, 1303, 1251, 1198, 1184, 1108, 1080, 1036, 969, 900, 883, 853, 810, 799, 758, 731, 691, 644, 619 cm^{-1}; HRMS (EI) exact mass calcd for $C_{17}H_{16}O_3$ (M) requires *m/z* 268.1099, found *m/z* 268.1103. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 23.08 min, t (minor) = 26.11 min.



(*S*)-2-(6-Methoxy-2,3-dihydrobenzofuran-2-yl)-1-phenylethanone (3g)

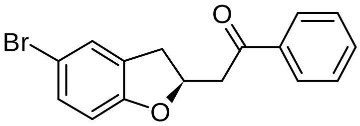
White solid (46% yield, 80% *ee*). Analytical data for **3g**: Mp = 80-81 ^{o}C; $[\alpha]_D^{20}$ = -0.9^{o} (c = 0.5 Acetone, 80% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.87 (dd, J_1 = 7.2 Hz, J_2 = 15.6 Hz, 1H), 3.24 (dd, J_1 = 6.9 Hz, J_2 = 17.1 Hz, 1H), 3.47 (dd, J_1 = 9.0 Hz, J_2 = 15.3 Hz, 1H), 3.65 (dd, J_1 = 6.0 Hz, J_2 = 17.1 Hz, 1H), 3.75 (s, 3H), 5.37-5.43 (m, 1H), 6.38-6.43 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.50-7.59 (m, 1H), 7.97 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.2, 44.7, 55.5, 80.0, 96.3, 106.0, 118.3, 125.0, 128.1, 128.7, 133.4, 136.7, 160.3, 160.3, 197.5; IR (film) 2959, 2925, 2854, 1733, 1685, 1618, 1593, 1495, 1445, 1397, 1377, 1338, 1274, 1196, 1143, 1091, 1028, 982, 947, 853, 820, 806, 753, 704, 687, 655, 627 cm^{-1}; HRMS (EI) exact mass calcd for $C_{17}H_{16}O_3$ (M) requires *m/z* 268.1099, found *m/z* 268.1104. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 19.40 min, t (minor) = 22.00 min.



(*S*)-2-(7-Methoxy-2,3-dihydrobenzofuran-2-yl)-1-phenylethanone (3h)

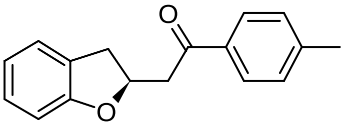
White solid (59% yield, 66% *ee*). Analytical data for **3h**: Mp = 75-76 ^{o}C; $[\alpha]_D^{20}$ = +22.0^{o} (c = 1.0 Acetone, 66% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.87 (dd, J_1 = 6.6 Hz, J_2 = 12.9 Hz, 1H), 3.27 (dd, J_1 = 7.2 Hz, J_2 = 17.1 Hz, 1H), 3.48 (dd, J_1 = 9.3 Hz, J_2 = 15.6 Hz, 1H), 3.64 (dd, J_1 = 6.3 Hz, J_2 = 16.8 Hz, 1H), 3.82 (s, 3H), 5.39-5.45 (m, 1H), 6.40-6.46 (m, 2H), 7.09 (t, *J* = 8.1 Hz, 1H), 7.44-7.49 (m, 2H), 7.55-7.58 (m, 1H), 7.97 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 33.3, 44.8, 55.3, 79.5, 102.9, 103.0, 113.3, 128.1, 128.6, 129.1, 133.4, 136.7, 156.7, 160.4, 197.4; IR (film) 2963, 2925, 2837, 1671, 1600, 1491, 1464, 1372, 1338, 1319, 1269, 1238, 1209, 1185, 1083, 956, 830, 796, 762, 704, 682, 640, 613 cm^{-1}; HRMS (EI) exact mass calcd for $C_{17}H_{16}O_3$ (M) requires *m/z* 268.1099, found *m/z* 268.1101. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 14.33 min, t (minor) = 16.11 min.



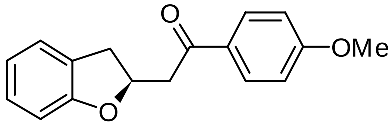
(*S*)-2-(5-Bromo-2,3-dihydrobenzofuran-2-yl)-1-phenylethanone (3i)

White solid (40% yield, 79% *ee*). Analytical data for **3i**: Mp = 122-123 °C; $[\alpha]_D^{20}$ = +49.4° (c = 0.5 Acetone, 79% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.93 (dd, J_1 = 7.5 Hz, J_2 = 16.5 Hz, 1H), 3.28 (dd, J_1 = 6.9 Hz, J_2 = 17.1 Hz, 1H), 3.53 (dd, J_1 = 9.0 Hz, J_2 = 15.6 Hz, 1H), 3.65 (dd, J_1 = 5.7 Hz, J_2 = 17.1 Hz, 1H), 5.36-5.42 (m, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 2.7 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.57-7.62 (m, 1H), 7.96 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.7, 44.5, 79.6, 111.0, 112.2, 128.0, 128.1, 128.7, 129.0, 130.8, 133.5, 136.5, 158.3, 197.2; IR (film) 2971, 2927, 2855, 1681, 1594, 1476, 1448, 1397, 1379, 1340, 1297, 1229, 1210, 1156, 1111, 1072, 983, 929, 876, 853, 806, 756, 689, 656 cm^{-1}; HRMS (EI) exact mass calcd for $C_{16}H_{13}O_2Br$ (M) requires *m/z* 316.0099, found *m/z* 316.0098. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 17.57 min, t (minor) = 20.37 min.



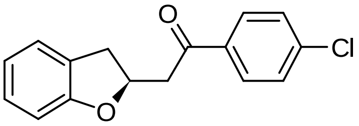
(*S*)-2-(2,3-Dihydrobenzofuran-2-yl)-1-(p-tolyl)ethanone (3j)

White solid (49% yield, 81% *ee*). Analytical data for **3j**: Mp = 100-101 °C; $[\alpha]_D^{20}$ = +18.9° (c = 0.5 Acetone, 81% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.93 (dd, J_1 = 6.9 Hz, J_2 = 15.6 Hz, 1H), 3.25 (dd, J_1 = 7.2 Hz, *J*$_2$ = 16.8 Hz, 1H), 3.53 (dd, *J*$_1$ = 9.0 Hz, *J*$_2$ = 15.9 Hz, 1H), 3.59-3.67 (m, 1H), 5.32-5.42 (m, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 8.1 Hz, 1H); 7.17 (d, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.87 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 21.6, 35.8, 44.6, 79.0, 109.5, 120.4, 125.0, 126.4, 128.0, 128.2, 129.3, 134.2, 144.3, 159.0, 197.1; IR (film) 3051, 2920, 2851, 1672, 1601, 1480, 1406, 1372, 1326, 1309, 1233, 1220, 1174, 1108, 1093, 1018, 967, 920, 896, 862, 812, 767, 740, 709 cm-1; HRMS (EI) exact mass calcd for $C_{17}H_{16}O_2$ (M) requires *m/z* 252.1150, found *m/z* 252.1147. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 9.42 min, t (minor) = 11.00 min.



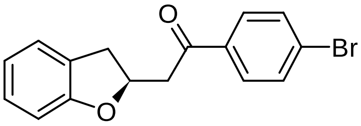
(*S*)-2-(2,3-Dihydrobenzofuran-2-yl)-1-(4-methoxyphenyl)ethanone (3k)

White solid (38% yield, 76% *ee*). Analytical data for **3k**: Mp = 105-106 °C; $[\alpha]_D^{20}$ = +26.3° (c = 0.5 Acetone, 76% *ee*). ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.94 (dd, *J*$_1$ = 7.2 Hz, *J*$_2$ = 15.9 Hz, 1H), 3.22 (dd, *J*$_1$ = 7.2 Hz, *J*$_2$ = 16.8 Hz, 1H), 3.53 (dd, *J*$_1$ = 9.0 Hz, *J*$_2$ = 15.9 Hz, 1H), 3.61 (dd, *J*$_1$ = 6.0 Hz, *J*$_2$ = 17.1 Hz, 1H), 3.87 (s, 3H), 5.34-5.39 (m, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 35.8, 44.3, 55.5, 79.2, 109.5, 113.8, 120.4, 125.0, 126.5, 128.0, 129.9, 130.4, 159.0, 163.7, 196.0; IR (film) 3044, 2999, 2956, 2932, 2902, 2853, 1673, 1595, 1510, 1483, 1452, 1414, 1377, 1303, 1259, 1211, 1166, 1031, 966, 928, 898, 865, 822, 764, 745 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{17}H_{17}O_3$ $(M+H)^+$ requires *m/z* 269.1178, found *m/z* 269.1177. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 15.01 min, t (minor) = 17.72 min.



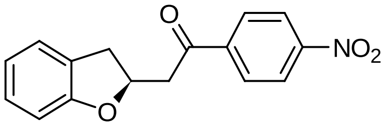
(*S*)-1-(4-Chlorophenyl)-2-(2,3-dihydrobenzofuran-2-yl)ethanone (3l)

White solid (51% yield, 79% *ee*). Analytical data for **3l**: Mp = 96-97 °C; $[\alpha]_D^{20}$ = +29.5° (c = 0.5 Acetone, 79% *ee*). ^1H NMR (300 MHz, $CDCl_3$) δ 2.93 (dd, J_1 = 6.6 Hz, J_2 = 15.6 Hz, 1H), 3.22 (dd, J_1 = 6.9 Hz, J_2 = 17.1 Hz, 1H), 3.49-3.57 (m, 1H), 3.61 (dd, J_1 = 6.3 Hz, J_2 = 17.1 Hz, 1H), 5.31-5.40 (m, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.7, 44.6, 78.8, 109.5, 120.6, 125.0, 126.2, 128.1, 129.0, 129.5, 135.0, 139.9, 158.9, 196.3; IR (film) 3046, 2955, 2924, 1680, 1588, 1480, 1397, 1380, 1328, 1311, 1233, 1205, 1176, 1090, 1015, 973, 926, 898, 864, 827, 812, 788, 749, 713 cm^{-1}; HRMS (EI) exact mass calcd for $C_{16}H_{13}O_2Cl$ (M) requires *m/z* 272.0604, found *m/z* 272.0603. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 11.53 min, t (minor) = 14.58 min.



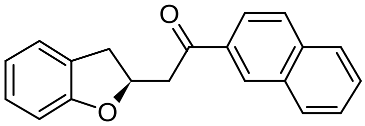
(*S*)-1-(4-Bromophenyl)-2-(2,3-dihydrobenzofuran-2-yl)ethanone (3m)

White solid (61% yield, 77% *ee*). Analytical data for **3m**: Mp = 102-103 °C; $[\alpha]_D^{20}$ = +23.0° (c = 0.5 Acetone, 77% *ee*). ^1H NMR (300 MHz, $CDCl_3$) δ 2.93 (dd, J_1 = 6.6 Hz, J_2 = 15.3 Hz, 1H), 3.22 (dd, J_1 = 6.9 Hz, J_2 = 17.1 Hz, 1H), 3.49-3.57 (m, 1H), 3.61 (dd, J_1 = 6.3 Hz, J_2 = 17.1 Hz, 1H), 5.33-5.38 (m, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.83-6.88 (m, 1H), 7.09-7.19 (m, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.7, 44.6, 78.7, 109.5, 120.6, 125.0, 126.2, 128.1, 128.7, 129.6, 132.0, 135.4, 158.9, 196.5; IR (film) 3064, 3044, 2954, 2925, 2903, 1680, 1584, 1480, 1394, 1312, 1232, 1205, 1177, 1071, 1002, 974, 926, 898, 864, 810, 747, 714 cm^{-1}; HRMS (EI) exact mass calcd for $C_{16}H_{13}O_2Br$ (M) requires *m/z* 316.0099, found *m/z* 316.0096. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 12.96 min, t (minor) = 17.63 min.



(*S*)-2-(2,3-Dihydrobenzofuran-2-yl)-1-(4-nitrophenyl)ethanone (3n)

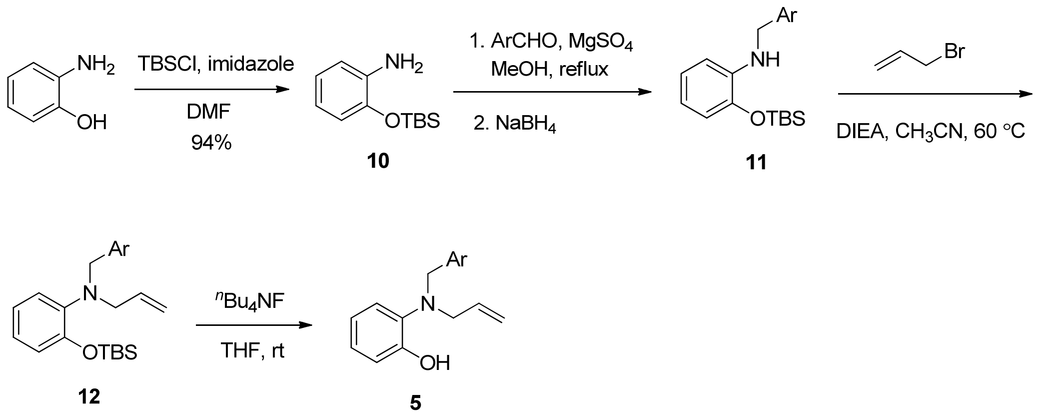
White solid (75% yield, 50% *ee*). Analytical data for **3n**: Mp = 150-151 °C; $[\alpha]_D^{20}$ = +18.6° (c = 0.5 Acetone, 50% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.97 (dd, J_1 = 6.9 Hz, J_2 = 16.2 Hz, 1H), 3.30 (dd, J_1 = 6.3 Hz, J_2 = 17.1 Hz, 1H), 3.57 (dd, J_1 = 9.0 Hz, J_2 = 15.6 Hz, 1H), 3.68 (dd, J_1 = 6.0 Hz, J_2 = 17.1 Hz, 1H), 5.33-5.42 (m, 1H), 6.75 (d, J = 8.4 Hz, 1H), 6.87 (t, J = 7.2 Hz, 1H), 7.09-7.36 (m, 2H), 8.12 (d, J = 8.7 Hz, 2H), 8.31 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.6, 45.1, 78.5, 109.6, 120.7, 123.9, 125.1, 126.0, 128.2, 129.2, 141.0, 150.4, 158.8, 196.1; IR (film) 2954, 2925, 2905, 2853, 1687, 1597, 1516, 1481, 1403, 1349, 1311, 1233, 1202, 1153, 1107, 974, 932, 903, 866, 844, 797, 785, 759, 745, 715, 685 cm^{-1}; HRMS (EI) exact mass calcd for $C_{16}H_{13}NO_4$ (M) requires *m/z* 283.0845, found *m/z* 283.0844. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) 59.54 min, t (minor) = 69.94 min.



(*S*)-2-(2,3-Dihydrobenzofuran-2-yl)-1-(naphthalen-2-yl)ethanone (3o)

White solid (70% yield, 79% *ee*). Analytical data for **3o**: Mp = 104-105 °C; $[\alpha]_D^{20}$ = +28.7° (c = 0.5 Acetone, 79% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.98 (dd, J_1 = 6.6 Hz, J_2 = 15.6 Hz, 1H), 3.38 (dd, J_1 = 6.3 Hz, J_2 = 17.1 Hz, 1H), 3.56 (dd, J_1 = 9.0 Hz, J_2 = 15.6 Hz, 1H), 3.78 (dd, J_1 = 6.0 Hz, J_2 = 16.8 Hz, 1H), 5.40-5.45 (m, 1H), 6.79 (d, J = 7.5 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 7.12 (t, J = 7.8 Hz, 1H), 7.18-7.23 (d, J = 7.2 Hz, 1H), 7.51-7.62 (m, 2H), 7.85-7.94 (m, 3H), 8.03 (d, J = 8.4 Hz, 1H), 8.45 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.8, 44.7, 79.0, 109.5, 120.5, 123.6， 125.1, 126.4, 126.8, 127.7, 128.0, 128.5, 128.6, 129.6, 130.1, 132.4, 134.0, 135.6, 159.0, 197.4; IR (film) 3048, 2959, 2927, 2854, 1682, 1594, 1480, 1381, 1239, 1177, 1126, 1016, 982, 928, 871, 846, 817, 742, 707 cm^{-1}; HRMS (EI) exact mass calcd for $C_{20}H_{16}O_2$ (M) requires *m/z* 288.1150, found *m/z* 288.1151. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 15.22 min, t (minor) = 17.29 min.

General procedure for preparation of compound 5.



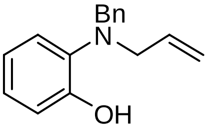
To a solution of 2-aminophenol (10.9 g, 100 mmol) in DMF 150 mL was added TBSCl (16.5 g, 110 mmol) and imidazole (10.2 g, 150 mmol) sequentially. The mixture was stirred at room temperature overnight. After the reaction was complete (monitored by TLC), it was quenched with saturated aqueous ammonium chloride solution and extracted with EtOAc three times. The combined organic layers were washed with H_2O and brine successively, then dried over anhydrous Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 100: 1) to afford **10** (20.9 g, 94% yield).

In a dry flask, aromatic aldehyde (1.0 equiv.) and $MgSO_4$ (0.2 equiv.) were added to a solution of 2-((tert-butyldimethylsilyl)oxy)aniline (1.0 equiv.) in CH_3OH. The reaction was refluxed for 3 h. After $NaBH_4$ (2.0 equiv.) was cautiously added to the above solution at 0 °C, the reaction was stirred at room temperature for another one hour. The mixture was quenched with water cautiously and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4

and filtrated. After the solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (hexane/ethylacetate 100/1) to give **11**.

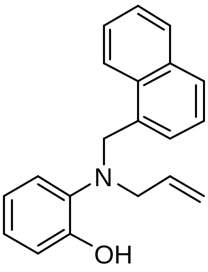
To a solution of **11** (1.0 equiv) in CH_3CN was added DIEA (1.5 equiv.) and allyl bromide (1.5 equiv.). After the reaction was stirred at 60 ^{o}C overnight until completion (monitored by TLC), the solvent was evaporated under reduced pressure. Then to the mixture was added 1 M HCl (aq.) and extracted with ethyl acetate three times. The combined organic layers were washed with brine, dired over anhydrous Na_2SO_4, filtrated and concencetrated under reduced pressure, the residue was purified by silica gel column chromatography (hexane/ethylacetate 100/1) to give **12**.

To a solution of **12** (1.0 equiv.) in THF (5 mL), $^{n}Bu_4NF$ (1.5 equiv.) was added. The reaction was stirred at room temperature until completion (monitored by TLC). The solvent was evaporated under reduced pressure, the residue was purified by silica gel column chromatography (hexane/ethylacetate 500/1) to give **5**.



2-(Allyl(benzyl)amino)phenol (5a)

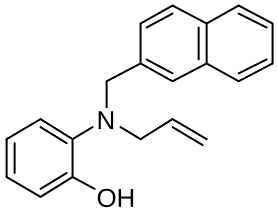
Colourless liquid (54% yield over three steps). Analytical data for **5a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.37 (d, *J* = 6.0 Hz, 2H), 3.90 (s, 2H), 4.98-5.03 (m, 2H), 5.60-5.74 (m, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.90-6.96 (m, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 7.11-7.14 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.2, 58.8, 113.9, 118.6, 119.6, 123.6, 126.5, 127.3, 128.2, 129.1, 133.9, 136.8, 137.4, 152.4; IR (film) 1589, 1491, 1454, 1363, 1252, 1206, 1076, 1029, 922, 833, 746, 733, 698 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{16}H_{18}NO$ $(M+H)^+$ requires *m/z* 240.1388, found *m/z* 240.1372.



2-(Allyl(naphthalen-1-ylmethyl)amino)phenol (5b)

Colourless liquid (34% yield over three steps). Analytical data for **5b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.53 (d, *J* = 6.6 Hz, 2H), 4.47 (s, 2H), 5.10-5.16 (m, 2H), 5.80-5.89 (m, 1H), 6.80-6.90 (m, 2H), 7.01-7.07 (m, 1H), 7.21-7.33 (m, 3H), 7.45-7.56 (m, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 8.12 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (75 MHz,

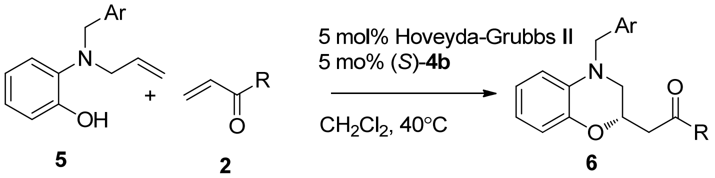
$CDCl_3$) δ 56.8, 58.1, 114.0, 119.2, 119.8, 123.4, 123.8, 125.0, 125.7, 126.4, 126.7, 128.0, 128.4, 128.9, 132.1, 133.1, 133.6, 133.9, 137.0, 152.8; IR (film) 1689, 1589, 1509, 1490, 1464, 1395, 1374, 1254, 1232, 1216, 1091, 1055, 992, 925, 832, 801, 778, 747 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{20}H_{20}NO$ $(M+H)^+$ requires *m/z* 290.1545, found *m/z* 290.1529.



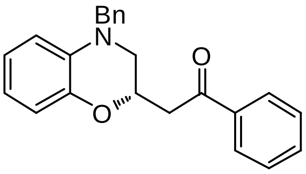
2-(Allyl(naphthalen-2-ylmethyl)amino)phenol (5c)

Colourless liquid (24% yield over three steps). Analytical data for **5c**: ^1H NMR (300 MHz, $CDCl_3$) δ 3.40 (d, *J* = 6.3 Hz, 2H), 4.05 (s, 2H), 4.99-5.09 (m, 2H), 5.62-5.74 (m, 1H), 6.72 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.86-7.01 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.31-7.36 (m, 2H), 7.52 (s, 1H), 7.64-7.69 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.4, 59.0, 114.1, 118.8, 119.8, 123.8, 125.9, 126.1, 126.7, 127.1, 127.7, 127.8, 128.0, 128.2, 132.8, 133.3, 134.0, 135.1, 137.0, 152.5; IR (film) 1693, 1589, 1491, 1346, 1253, 1212, 1091, 1035, 1020, 991, 923, 855, 817, 743 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{20}H_{20}NO$ $(M+H)^+$ requires *m/z* 290.1545, found *m/z* 290.1528.

General procedure for the enantioselective synthesis of 3,4-dihydro-2*H*-benzo[b][1,4]oxazine (6a-6m).

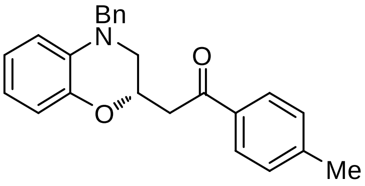


To a solution of phenol **5** (0.2 mmol) in dichloromethane (2 mL) was added the enone **2** (0.3 mmol, 1.5 equiv.), then chiral phosphoric acid (*S*)-**4b** (8.7 mg, 0.01 mmol, 5 mol%) and Hoveyda-Grubbs II catalyst (6.3 mg, 0.01 mmol, 5 mol%) were added in one portion. The reaction was stirred at 40°C. After the reaction was complete (monitored by TLC), the mixture was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/50~1/30) to afford 3,4-dihydro-2*H*-benzo[b][1,4]oxazine **6**.



(*S*)-2-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)-1-phenylethanone (6a)

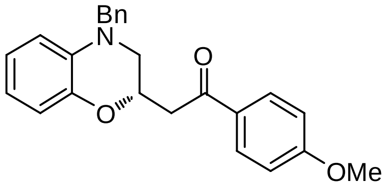
White solid (65% yield, 77% *ee*). Analytical data for **6a**: Mp = 98-99 °C; $[\alpha]_D^{20}$ = -5.4° (c = 0.5 Acetone, 77% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.17-3.26 (m, 2H), 3.48-3.55 (m, 2H), 4.38 (AB, *J* = 16.2 Hz, 1H), 4.50 (BA, *J* = 15.9 Hz, 1H), 4.86-4.88 (m, 1H), 6.62-6.70 (m, 2H), 6.77-6.82 (m, 2H), 7.22-7.28 (m, 5H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.5, 51.1, 54.8, 69.8, 112.4, 116.5, 117.9, 121.6, 127.0, 127.1, 128.1, 128.5, 128.6, 133.4, 134.9, 136.7, 137.9, 143.1, 197.2; IR (film) 2922, 2853, 1685, 1603, 1578, 1503, 1451, 1381, 1356, 1305, 1268, 1238, 1220, 1183, 1171, 1099, 1045, 994, 959, 916, 800, 752, 733, 696, 685, 649 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{23}H_{22}NO_2$ $(M+H)^+$ requires *m/z* 344.1651, found *m/z* 344.1636. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 70 / 30, 0.8 mL/min, λ = 254 nm, t (major) = 9.83 min, t (minor) = 8.49 min.



(*S*)-2-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)-1-(p-tolyl)ethanone (6b)

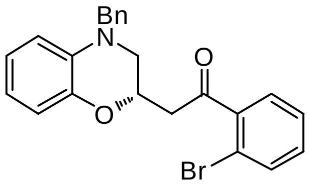
White solid (54% yield, 74% *ee*). Analytical data for **6b**: Mp = 118-119 °C; $[\alpha]_D^{20}$ = -4.4° (c = 0.5 Acetone, 74% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.15-3.26 (m, 2H), 3.46-3.53 (m, 2H), 4.39 (AB, *J* = 15.9 Hz, 1H), 4.50 (BA, *J* = 16.2 Hz, 1H), 4.85-4.89 (m, 1H), 6.61-6.70 (m, 2H), 6.77-6.82 (m, 2H), 7.22-7.27 (m, 7H), 7.85 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 41.4, 51.2, 54.9, 69.9, 112.4, 116.5, 117.9, 121.5, 127.0, 127.1, 128.3, 128.6, 129.3, 134.3, 134.9, 138.0, 143.2, 144.3, 196.8; IR (film)

2922, 2901, 2851, 1681, 1606, 1579, 1503, 1452, 1407, 1352, 1305, 1244, 1222, 1173, 1108, 1050, 1000, 920, 903, 806, 769, 738, 694, 664 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{24}H_{24}NO_2$ $(M+H)^+$ requires *m/z* 358.1807, found *m/z* 358.1791. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 12.64 min, t (minor) = 10.15 min.



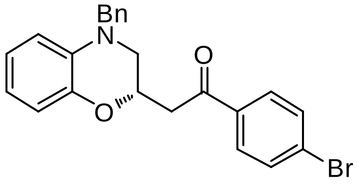
(*S*)-2-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)-1-(4-methoxyphenyl)ethanone (6c)

White solid (64% yield, 67% *ee*). Analytical data for **6c**: Mp = 103-104 °C; $[\alpha]_D^{20}$ = -5.0° (c = 0.5 Acetone, 67% *ee*). ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.11-3.26 (m, 2H), 3.43-3.53 (m, 2H), 3.02 (s, 3H), 4.38 (AB, *J* = 16.2 Hz, 1H), 4.50 (BA, *J* = 16.2 Hz, 1H), 4.82-4.88 (m, 1H), 6.61-6.70 (m, 2H), 6.76-6.81 (m, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 7.22-7.31 (m, 5H), 7.93 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 41.2, 51.3, 54.9, 55.5, 70.0, 112.4, 113.7, 116.5, 117.9, 121.5, 127.0, 127.1, 128.6, 129.9, 130.5, 134.9, 138.0, 143.2, 163.7, 195.7; IR (film) 2960, 2922, 2852, 1673, 1601, 1575, 1502, 1452, 1421, 1381, 1356, 1305, 1239, 1220, 1172, 1099, 1073, 1048, 1026, 990, 904, 842, 813, 738, 717, 694 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{24}H_{24}NO_3$ $(M+H)^+$ requires *m/z* 374.1756, found *m/z* 374.1746. The enantiomeric excess was determined by Daicel Chiralpak OD-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 36.87 min, t (minor) = 45.20 min.



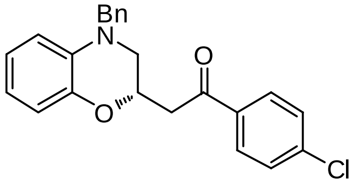
(*S*)-2-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)-1-(2-bromophenyl)ethanone (6d)

White solid (44% yield, 69% *ee*). Analytical data for **6d**: Mp = 56-57 °C; $[\alpha]_D^{20}$ = -20.0° (c = 0.5 Acetone, 69% *ee*). ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.16-3.27 (m, 2H), 3.38-3.50 (m, 2H), 4.41 (AB, *J* = 16.2 Hz, 1H), 4.49 (BA, *J* = 16.2 Hz, 1H), 4.78-4.81 (m, 1H), 6.61-6.69 (m, 2H), 6.76-6.81 (m, 2H), 7.25-7.45 (m, 8H), 7.60 (dd, J_1 = 0.6 Hz, J_2 = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 45.6, 51.1, 54.9, 69.7, 112.5, 116.6, 118.0, 118.7, 121.7, 127.1, 127.2, 127.5, 128.6, 128.7, 131.9, 133.7, 134.8, 137.9, 141.1, 143.0, 201.1; IR (film) 3063, 2924, 2854, 1699, 1605, 1585, 1502, 1466, 1452, 1428, 1356, 1299, 1215, 1166, 1048, 1027, 992, 953, 917, 798, 735, 696, 638 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{23}H_{21}BrNO_2$ $(M+H)^+$ requires *m/z* 422.0756, found *m/z* 422.0753. The enantiomeric excess was determined by Daicel Chiralpak IC (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 13.86 min, t (minor) = 11.35 min.



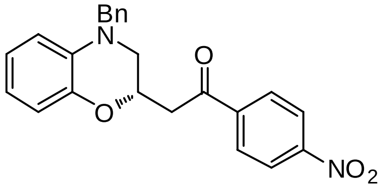
(*S*)-2-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)-1-(4-bromophenyl)ethanone (6e)

White solid (52% yield, 76% *ee*). Analytical data for **6e**: Mp = 107-108 °C; $[\alpha]_D^{20}$ = -12.5° (c = 0.5 Acetone, 76% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.11-3.25 (m, 2H), 3.42-3.50 (m, 2H), 4.38 (AB, *J* = 16.2 Hz, 1H), 4.50 (BA, *J* = 16.5 Hz, 1H), 4.83-4.85 (m, 1H), 6.62-6.72 (m, 2H), 6.78-6.82 (m, 2H), 7.22-7.26 (m, 5H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.4, 50.9, 54.8, 69.7, 112.5, 116.6, 118.0, 121.6, 127.1, 127.2, 128.6, 128.7, 129.7, 131.9, 134.8, 135.4, 137.9, 143.0, 196.3; IR (film) 2925, 2854, 1670, 1605, 1581, 1502, 1468, 1349, 1270, 1238, 1221, 1169, 1095, 1071, 1047, 998, 961, 908, 840, 784, 740, 697 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{23}H_{21}BrNO_2$ $(M+H)^+$ requires *m/z* 422.0756, found *m/z* 422.0735. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 13.42 min, t (minor) = 11.18 min.



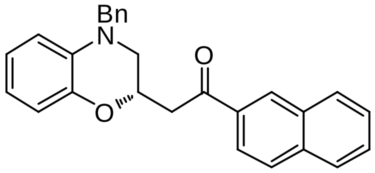
(*S*)-2-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)-1-(4-chlorophenyl)ethanone (6f)

White solid (48% yield, 73% *ee*). Analytical data for **6f**: Mp = 96-97 °C; $[\alpha]_D^{20}$ = -7.6° (c = 0.5 Acetone, 73% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.12-3.25 (m, 2H), 3.43-3.50 (m, 2H), 4.38 (AB, *J* = 16.2 Hz, 1H), 4.50 (BA, *J* = 15.9 Hz, 1H), 4.84-4.85 (m, 1H), 6.62-6.71 (m, 2H), 6.78-6.82 (m, 2H), 7.26 (m, 5H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.4, 51.0, 54.8, 69.7, 112.5, 116.6, 118.0, 121.6, 127.1, 127.2, 128.6, 128.9, 129.6, 134.8, 135.0, 137.9, 139.9, 143.0, 196.1; IR (film) 3025, 2920, 2856, 1671, 1606, 1584, 1568, 1502, 1468, 1453, 1397, 1349, 1306, 1269, 1238, 1221, 1169, 1091, 999, 961, 907, 842, 826, 788, 739, 697 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{23}H_{21}ClNO_2$ $(M+H)^+$ requires *m/z* 378.1261, found *m/z* 378.1260. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 15.07 min, t (minor) = 12.20 min.



(*S*)-2-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)-1-(4-nitrophenyl)ethanone (6g)

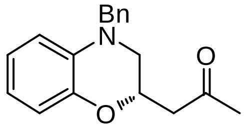
White solid (52% yield, 75% *ee*). Analytical data for **6g**: Mp = 69-70 °C; $[\alpha]_D^{20}$ = -7.1° (c = 0.5 Acetone, 75% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.17-3.26 (m, 2H), 3.46-3.58 (m, 2H), 4.39 (AB, *J* = 16.5 Hz, 1H), 4.51 (BA, *J* = 16.2 Hz, 1H), 4.85-4.88 (m, 1H), 6.63-6.68 (m, 1H), 6.72-6.84 (m, 3H), 7.25-7.32 (m, 5H), 8.09 (d, *J* = 8.7 Hz, 2H), 8.31 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.0, 50.7, 54.7, 69.6, 112.5, 116.6, 118.2, 121.8, 123.8, 127.1, 127.2, 128.7, 129.2, 134.8, 137.8, 141.1, 142.8, 150.4, 195.9; IR (film) 2919, 2850, 1693, 1675, 1603, 1580, 1526, 1502, 1467, 1452, 1344, 1261, 1238, 1222, 1169, 1096, 1071, 1047, 1003, 962, 909, 854, 792, 740, 697 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{23}H_{21}N_2O_4$ $(M+H)^+$ requires *m/z* 389.1501, found *m/z* 389.1503. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 45.53 min, t (minor) = 39.13 min.



(*S*)-1-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)propan-2-one (6h)

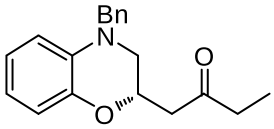
White solid (51% yield, 76% *ee*). Analytical data for **6h**: Mp = 95-96 °C; $[\alpha]_D^{20}$ = -5.4° (c = 0.5 Acetone, 76% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.25-3.38 (m, 2H), 3.53-3.70 (m, 2H), 4.41

(AB, *J* = 15.9 Hz, 1H), 4.52 (BA, *J* = 15.9 Hz, 1H), 4.92-4.95 (m, 1H), 6.63-6.73 (m, 2H), 6.79-6.84 (m, 2H), 7.21-7.28 (m, 5H), 7.54-7.64 (m, 2H), 7.87-7.96 (m, 3H), 8.02 (d, *J* = 8.4 Hz, 1H), 8.46 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.5, 51.1, 54.8, 70.0, 112.5, 116.6, 118.0, 121.6, 123.6, 126.9, 127.1, 127.1, 127.8, 128.5, 128.6, 128.7, 129.6, 130.2, 132.4, 134.0, 135.0, 135.7, 137.9, 143.1, 197.2; IR (film) 2924, 2853, 1712, 1675, 1626, 1603, 1502, 1451, 1390, 1359, 1302, 1245, 1220, 1189, 1171, 1047, 908, 865, 838, 818, 739, 694 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{27}H_{24}NO_2$ $(M+H)^+$ requires *m/z* 394.1807, found *m/z* 394.1791. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 18.67 min, t (minor) = 15.40 min.



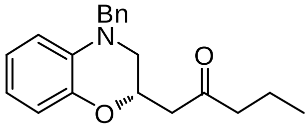
(*S*)-1-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)propan-2-one (6i)

White solid (76% yield, 76% *ee*). Analytical data for **6i**: Mp = 86-87 °C; $[\alpha]_D^{20}$ = -9.1° (c = 0.5 Acetone, 76% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.20 (s, 3H), 2.63 (dd, J_1 = 6.0 Hz, J_2 = 16.5 Hz, 1H), 2.90 (dd, J_1 = 6.6 Hz, J_2 = 16.8 Hz, 1H), 3.11 (dd, J_1 = 6.9 Hz, J_2 = 11.7 Hz, 1H), 3.35 (dd, J_1 = 2.4 Hz, J_2 = 12.0 Hz, 1H), 4.37 (AB, *J* = 16.2 Hz, 1H), 4.47 (BA, *J* = 16.2 Hz, 1H), 4.61-4.67 (m, 1H), 6.61-6.69 (m, 2H), 6.76-6.81 (m, 2H), 7.26-7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.8, 46.3, 51.0, 54.7, 69.3, 112.4, 116.5, 117.9, 121.6, 127.0, 127.1, 128.6, 134.8, 137.9, 143.0, 205.9; IR (film) 2921, 2852, 1714, 1606, 1579, 1505, 1468, 1451, 1362, 1307, 1258, 1225, 1164, 1102, 1089, 1075, 1050, 1021, 911, 799, 741, 722, 698 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{18}H_{20}NO_2$ $(M+H)^+$ requires *m/z* 282.1494, found *m/z* 282.1481. The enantiomeric excess was determined by Daicel Chiralpak IC (25 cm), Hexanes / IPA = 90 / 10, 0.5 mL/min, λ = 254 nm, t (major) = 20.42 min, t (minor) = 19.64 min.



(*S*)-1-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)butan-2-one (6j)

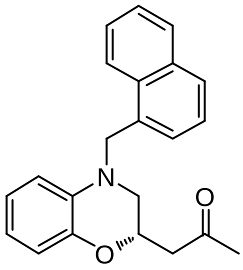
White solid (81% yield, 78% *ee*). Analytical data for **6j**: Mp = 79-80 °C; $[\alpha]_D^{20}$ = -12.0° (c = 0.5 Acetone, 78% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (t, *J* = 6.9 Hz, 3H), 2.44-2.53 (m, 2H), 2.61 (dd, J_1 = 6.0 Hz, J_2 = 16.5 Hz, 1H), 2.90 (dd, J_1 = 6.9 Hz, J_2 = 16.5 Hz, 1H), 3.14 (dd, J_1 = 6.9 Hz, J_2 = 11.7 Hz, 1H), 3.37 (dd, J_1 = 2.7 Hz, J_2 = 12.0 Hz, 1H), 4.37 (AB, *J* = 15.9 Hz, 1H), 4.48 (BA, *J* = 15.9 Hz, 1H), 4.62-4.69 (m, 1H), 6.61-6.69 (m, 2H), 6.76-6.81 (m, 2H), 7.23-7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.5, 36.9, 45.2, 51.1, 54.8, 69.5, 112.4, 116.5, 117.9, 121.6, 127.1, 127.2, 128.6, 134.9, 137.9, 143.0, 208.6; IR (film) 2921, 2851, 1712, 1605, 1579, 1505, 1468, 1451, 1410, 1390, 1361, 1308, 1251, 1221, 1173, 1104, 1050, 1011, 958, 910, 800, 744, 697, 656 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{19}H_{22}NO_2$ $(M+H)^+$ requires *m/z* 296.1651, found *m/z* 296.1636. The enantiomeric excess was determined by Daicel Chiralpak AS-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 11.89 min, t (minor) = 13.06 min.



(*S*)-1-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)pentan-2-one (6k)

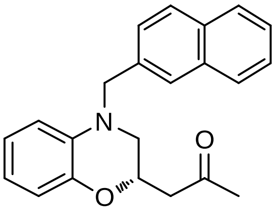
White solid (67% yield, 82% *ee*). Analytical data for **6k**: Mp = 61-62 °C; $[\alpha]_D^{20}$ = -16.1° (c = 0.5 Acetone, 82% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.5 Hz, 3H), 1.61 (dt, J_1 = 7.8 Hz, J_2 = 15.0 Hz, 2H), 2.40-2.47 (m, 2H), 2.60 (dd, J_1 = 6.0 Hz, J_2 = 16.5 Hz, 1H), 2.89 (dd, J_1 = 6.3 Hz, J_2 = 16.5 Hz, 1H), 3.12 (dd, J_1 = 6.9 Hz, J_2 = 11.7 Hz, 1H), 3.37 (dd, J_1 = 3.0 Hz, J_2 = 11.7 Hz, 1H), 4.37 (AB, *J* = 15.6 Hz, 1H), 4.47 (BA, *J* = 16.2 Hz, 1H), 4.62-4.69 (m, 1H), 6.60-6.69 (m, 2H), 6.76-6.81 (m, 2H), 7.22-7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 16.9, 45.4, 45.6, 51.1, 54.8, 69.4, 112.4, 116.5, 117.9, 121.6, 127.0, 127.1, 128.6, 134.8, 137.9, 143.0, 208.2; IR (film) 2955, 2920, 2850, 1711, 1606, 1577, 1505, 1467, 1451, 1390, 1450, 1291, 1246, 1220, 1171, 1119, 1048, 1025, 906, 841, 802, 740, 694 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{20}H_{24}NO_2$ $(M+H)^+$ requires *m/z* 310.1807, found *m/z* 310.1791. The enantiomeric excess was determined by Daicel Chiralpak

OJ-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 19.84 min, t (minor) = 22.08 min.



(*S*)-1-(4-(Naphthalen-1-ylmethyl)-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)propan-2-one (6l)

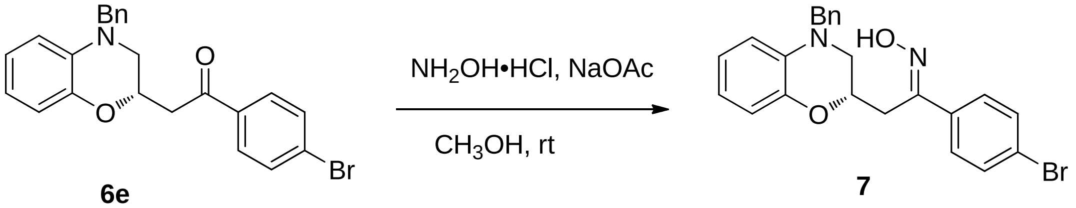
White solid (58% yield, 79% *ee*). Analytical data for **6l**: Mp = 109-110 °C; $[\alpha]_D^{20}$ = -13.5° (c = 0.5 Acetone, 79% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (s, 3H), 2.53 (dd, J_1 = 6.0 Hz, J_2 = 16.5 Hz, 1H), 2.81 (dd, J_1 = 6.6 Hz, J_2 = 16.8 Hz, 1H), 3.04 (dd, J_1 = 6.3 Hz, J_2 = 11.7 Hz, 1H), 3.24 (dd, J_1 = 2.7 Hz, J_2 = 12.0 Hz, 1H), 4.60-4.67 (m, 1H), 4.72 (AB, J = 15.6 Hz, 1H), 4.89 (BA, J = 15.6 Hz, 1H), 6.66-6.71 (m, 1H), 6.75-6.85 (m, 3H), 7.40 (d, J_1 = 5.4 Hz, 2H), 7.49-7.52 (m, 2H), 7.77-7.80 (m, 1H), 7.87-7.90 (m, 1H), 7.98-8.01 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.5, 46.2, 49.7, 52.5, 69.6, 112.2, 116.5, 118.2, 121.6, 123.1, 125.4, 125.7, 125.8, 126.2, 128.1, 128.8, 131.3, 132.2, 133.8, 134.9, 143.2, 205.8; IR (film) 2923, 2852, 1712, 1606, 1596, 1578, 1503, 1468, 1355, 1295, 1245, 1224, 1170, 1154, 1073, 1051, 981, 913, 799, 771, 750, 735; HRMS (ESI) exact mass calcd for $C_{22}H_{22}NO_2$ $(M+H)^+$ requires *m/z* 332.1651, found *m/z* 332.1635. The enantiomeric excess was determined by Daicel Chiralpak IC (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 11.02 min, t (minor) = 9.84 min.



(*S*)-1-(4-(Naphthalen-2-ylmethyl)-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)propan-2-one (6m)

White solid (63% yield, 64% *ee*). Analytical data for **6m**: Mp = 124-125 °C; $[\alpha]_D^{20}$ = -4.3° (c = 0.5 Acetone, 64% *ee*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.61 (dd, J_1 = 5.7 Hz, J_2 = 16.8 Hz, 1H), 2.90 (dd, J_1 = 6.6 Hz, J_2 = 16.8 Hz, 1H), 3.13 (dd, J_1 = 7.2 Hz, J_2 = 11.7 Hz, 1H), 3.27 (d, J = 11.7 Hz, 1H), 4.50 (AB, J = 16.5 Hz, 1H), 4.58 (BA, J = 16.2 Hz, 1H), 4.66-4.68 (m, 1H), 6.65-6.67 (m, 1H), 6.72-6.83 (m, 3H), 7.37-7.46 (m, 3H), 7.70 (s, 1H), 7.78-7.81 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.8, 46.4, 51.1, 55.1, 69.4, 112.5, 116.5, 118.1, 121.7, 125.2, 125.6, 125.7, 126.2, 127.6, 127.7, 128.5, 132.7, 133.4, 134.9, 143.1, 135.4, 205.9; IR (film) 2921, 2851, 1710, 1605, 1578, 1502, 1468, 1360, 1297, 1258, 1220, 1169, 1107, 1051, 958, 906, 860, 814, 737 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{22}H_{22}NO_2$ $(M+H)^+$ requires *m/z* 332.1651, found *m/z* 332.1637. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 0.8 mL/min, λ = 254 nm, t (major) = 11.47 min, t (minor) = 10.76 min.

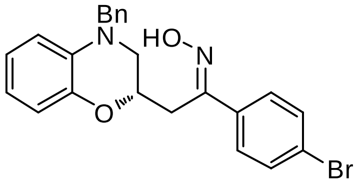
Synthesis of 2-(4-benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)-1-(4-bromophenyl)ethanone oxime 7



6e
99% *ee*

7
71% yield, 99% *ee*

To a solution of **6e** (42 mg, 0.1 mmol, 99% *ee*) in CH_3OH (1 mL) in a dry flask was added hydroxylamine hydrocholoride (69 mg, 0.3 mmol) and NaOAc (8.2mg, 0.1 mmol). After the mixture was stirred for 30 h at room temperature until completion (monitored by TLC), the solvent was removed under reduced pressure. The residue was purified by silia gel column chromatography (ethyl acetate/petroleum ether = 1/10) to afford the product **7** (31 mg, 71% yield, 99% *ee*) as a white solid.



(*S*)-2-(4-Benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)-1-(4-bromophenyl)ethanone oxime (7)

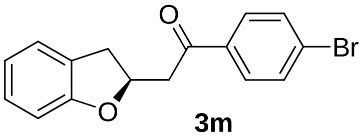
White solid (71% yield, 99% *ee*). Analytical data for **7**: Mp = 159-160 °C; $[\alpha]_D^{20}$ = -21.6° (c = 0.5 Acetone, 99% *ee*).^{1}H NMR (300 MHz, $CDCl_3$) δ 3.07 (dd, J_1 = 7.2 Hz, J_2 = 13.2 Hz, 1H), 3.18-3.27 (m, 2H), 3.36 (dd, J_1 = 2.4 Hz, J_2 = 12.0 Hz, 1H), 4.42 (s, 2H), 4.61-4.63 (m, 1H), 6.60-6.81 (m, 4H), 7.24-7.34 (m, 5H), 7.48-7.56 (m, 4H), 8.67 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.2, 51.6, 54.9, 70.7, 112.4, 116.5, 118.0, 121.7, 123.8, 127.0, 127.1, 128.2, 128.6, 131.6, 134.6, 134.8, 137.9, 143.1, 155.8; IR (film) 3233, 2909, 1739, 1606, 1504, 1467, 1452, 1371, 1291, 1242, 1221, 1168, 1099, 1073, 1047, 1008, 937, 912, 827, 793, 736, 696 cm^{-1}; HRMS (ESI) exact mass calcd for $C_{23}H_{22}BrN_2O_2$ $(M+H)^+$ requires *m/z* 437.0865, found *m/z* 437.0859. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min, λ = 254 nm, t (major) = 12.64 min, t (minor) = 18.22 min.

X-ray structure of enantiopure (S)-1-(4-bromophenyl)-2-(2,3-dihydrobenzofuran-2-yl)ethanone ***3m*** [CCDC 937446 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

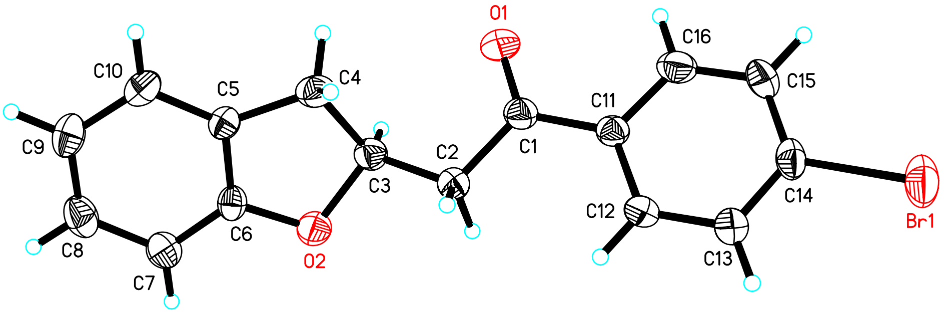
Table 1.   Crystal data and structure refinement for cd21218.

Identification code	cd21218	
Empirical formula	C16 H13 Br O2	
Formula weight	317.17	
Temperature	293(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)	
Unit cell dimensions	a = 7.2969(11) A	alpha = 90 deg.
	b = 11.1694(16) A	beta = 90 deg.
	c = 16.483(2) A	gamma = 90 deg.
Volume	1343.4(3) A^3	
Z, Calculated density	4, 1.568 Mg/m^3	
Absorption coefficient	3.054 mm^-1	
F(000)	640	
Crystal size	0.231 x 0.156 x 0.037 mm	
Theta range for data collection	2.20 to 26.00 deg.	
Limiting indices	-9<=h<=5, -13<=k<=13, -19<=l<=20	

Reflections collected / unique	7736 / 2627 [R(int) = 0.0400]
Completeness to theta = 26.00	99.7 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.51956
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2627 / 1 / 172
Goodness-of-fit on F^2	0.920
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.1001
R indices (all data)	R1 = 0.0632, wR2 = 0.1122
Absolute structure parameter	0.026(14)
Largest diff. peak and hole	0.339 and -0.209 e.A^-3



3m



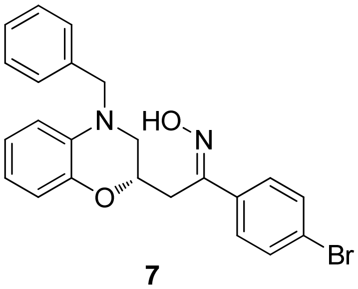
X-ray structure of enantiopure

(S,E)-2-(4-benzyl-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-yl)-1-(4-bromophenyl)ethanone oxime **7** [CCDC 937447 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Table 1. Crystal data and structure refinement for cd212491.

Identification code	cd212491

Empirical formula	C23 H21 Br N2 O2
Formula weight	437.33
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 5.1604(7) A alpha = 104.433(3) deg.
	b = 13.8657(19) A beta = 90.414(3) deg.
	c = 14.351(2) A gamma = 95.735(3) deg.
Volume	988.9(2) A^3
Z, Calculated density	2, 1.469 Mg/m^3
Absorption coefficient	2.100 mm^-1
F(000)	448
Crystal size	0.342 x 0.121 x 0.078 mm
Theta range for data collection	1.52 to 25.49 deg.
Limiting indices	-6<=h<=6, -16<=k<=16, -16<=l<=17
Reflections collected / unique	5735 / 3686 [R(int) = 0.0276]
Completeness to theta = 25.49	99.6 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.55005
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3686 / 112 / 338
Goodness-of-fit on F^2	1.131
Final R indices [I>2sigma(I)]	R1 = 0.0954, wR2 = 0.2263
R indices (all data)	R1 = 0.1173, wR2 = 0.2364
Largest diff. peak and hole	0.496 and -0.458 e.A^-3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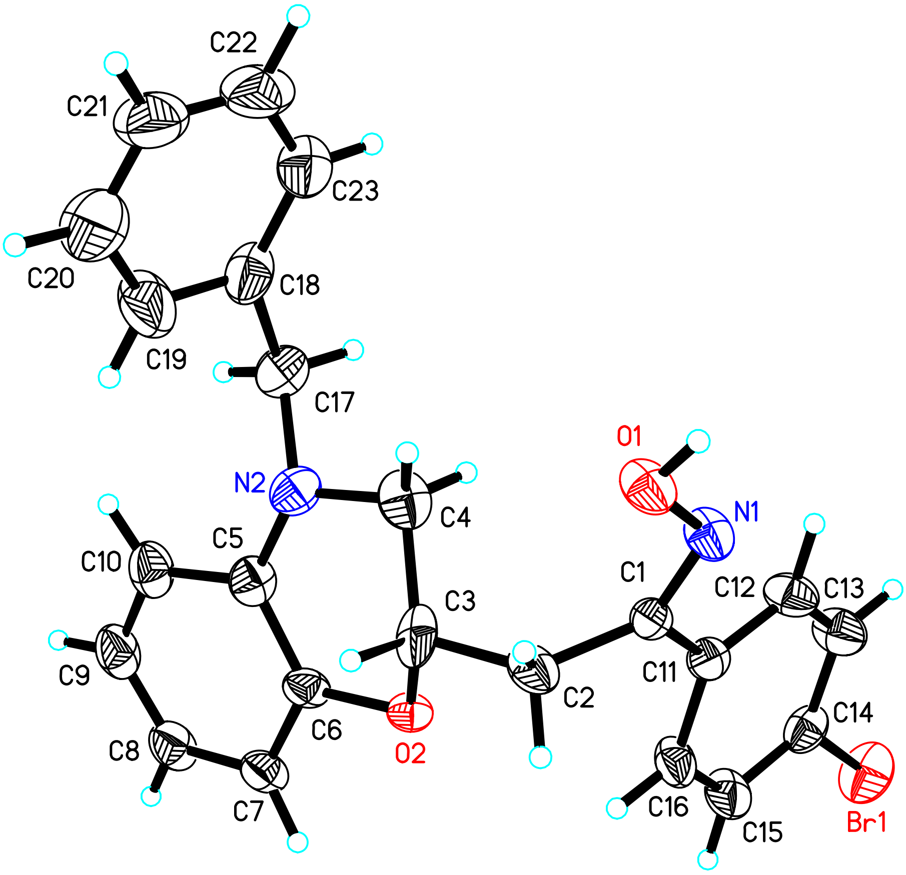
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C6
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C8
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C16
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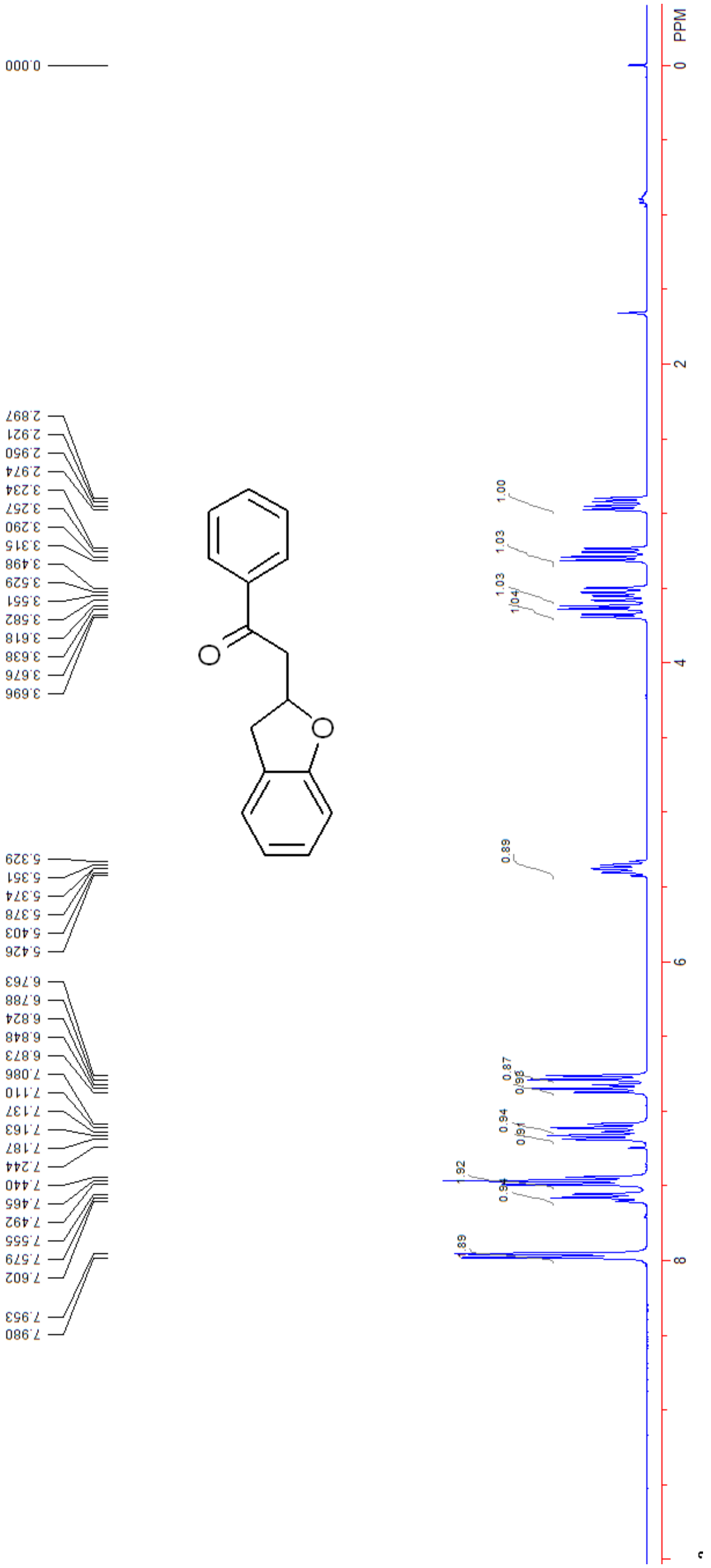
(1) (a) W. Kurosawa, T. Kan and T. Fukuyama, *J. Am. Chem. Soc.* 2003, **125**, 8112. (b) V. Singh, P. K. Sahu, B. C. Sahu and S. M. Mobin, *J. Org. Chem.* 2009, **74**, 6092. (c) L. Kong, Q. Lin, X. Lv, Y. Yang, Y. Jia and Y. Zhou, *Green Chem.* 2009, **11**, 1108. (d) D. J. Berg, T. Barclay and X. Fei, *Journal of Organometallic Chemistry* 2010, **695**, 2703. (e) W. Chen, X.-D. Yang, Y. Li, L.-J. Yang, X.-Q. Wang, G.-L. Zhang and H.-B. Zhang, *Org. Biomol. Chem.* 2011, **9**, 4250.

(2) Q. Cai, Z.-A. Zhao and S.-L. You, *Angew. Chem., Int. Ed.* 2009, **48**, 7428.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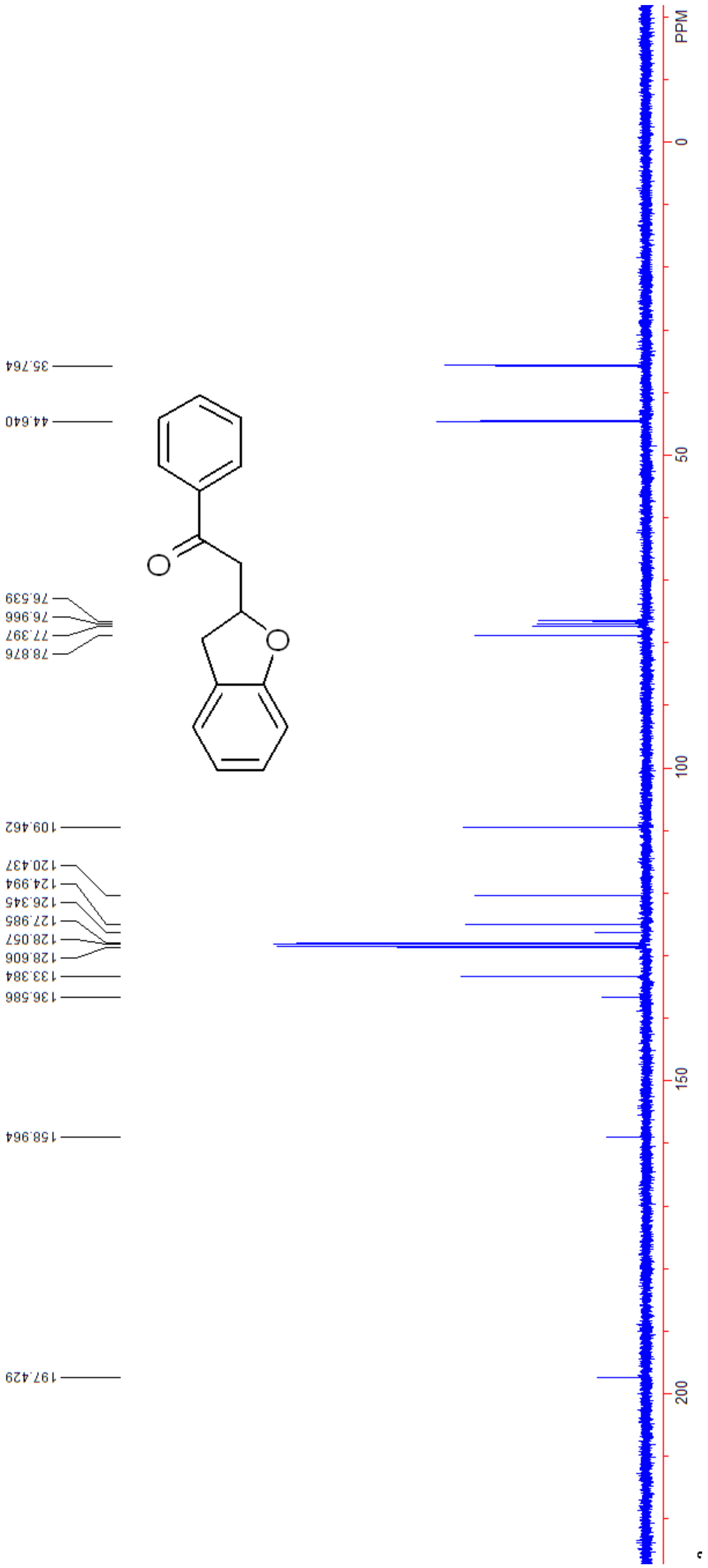
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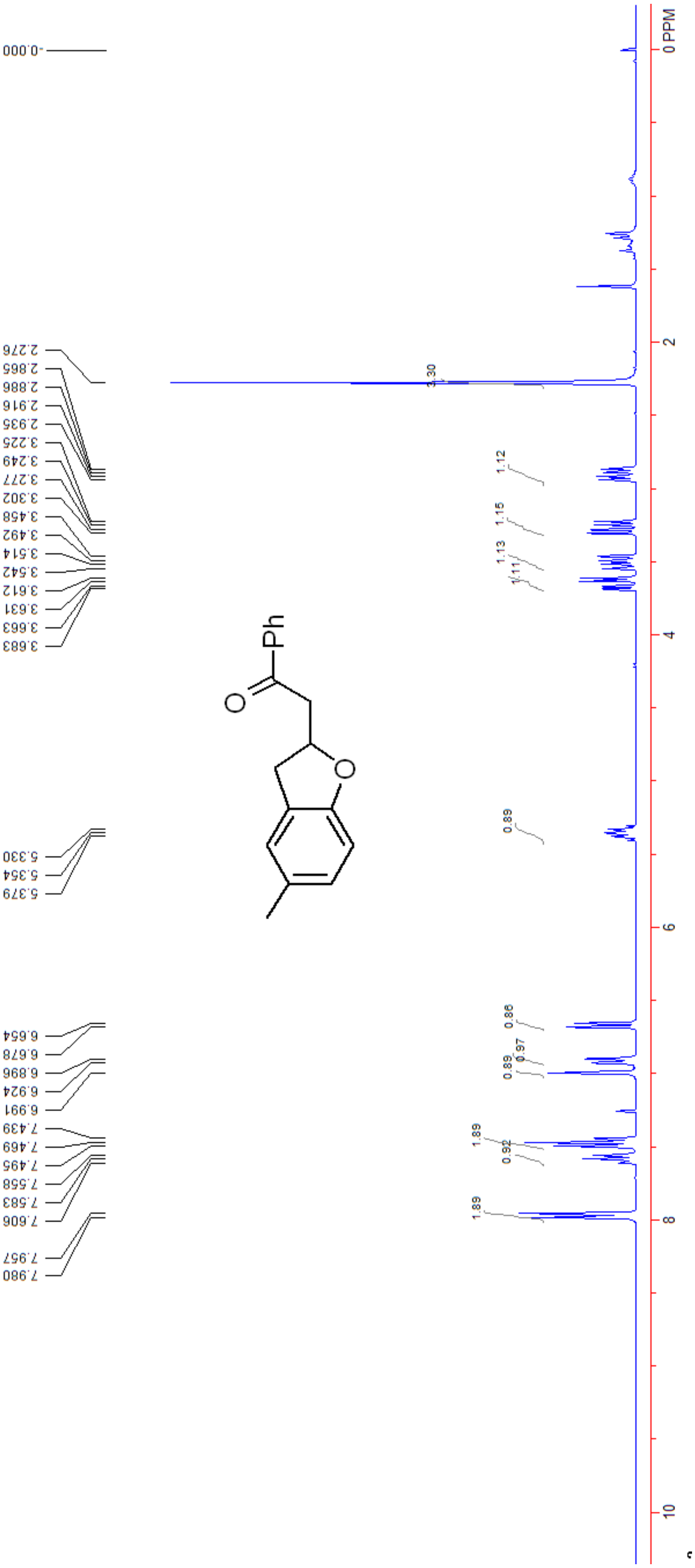
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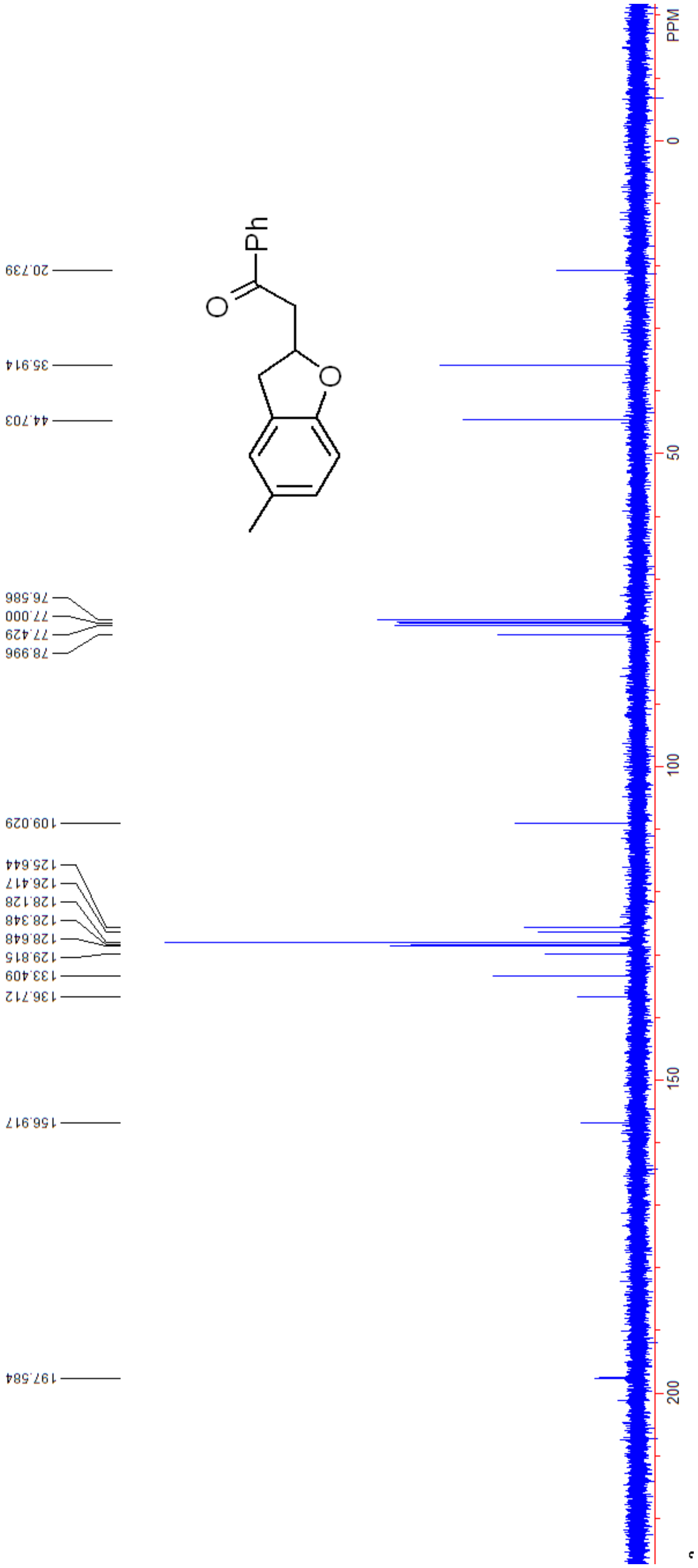
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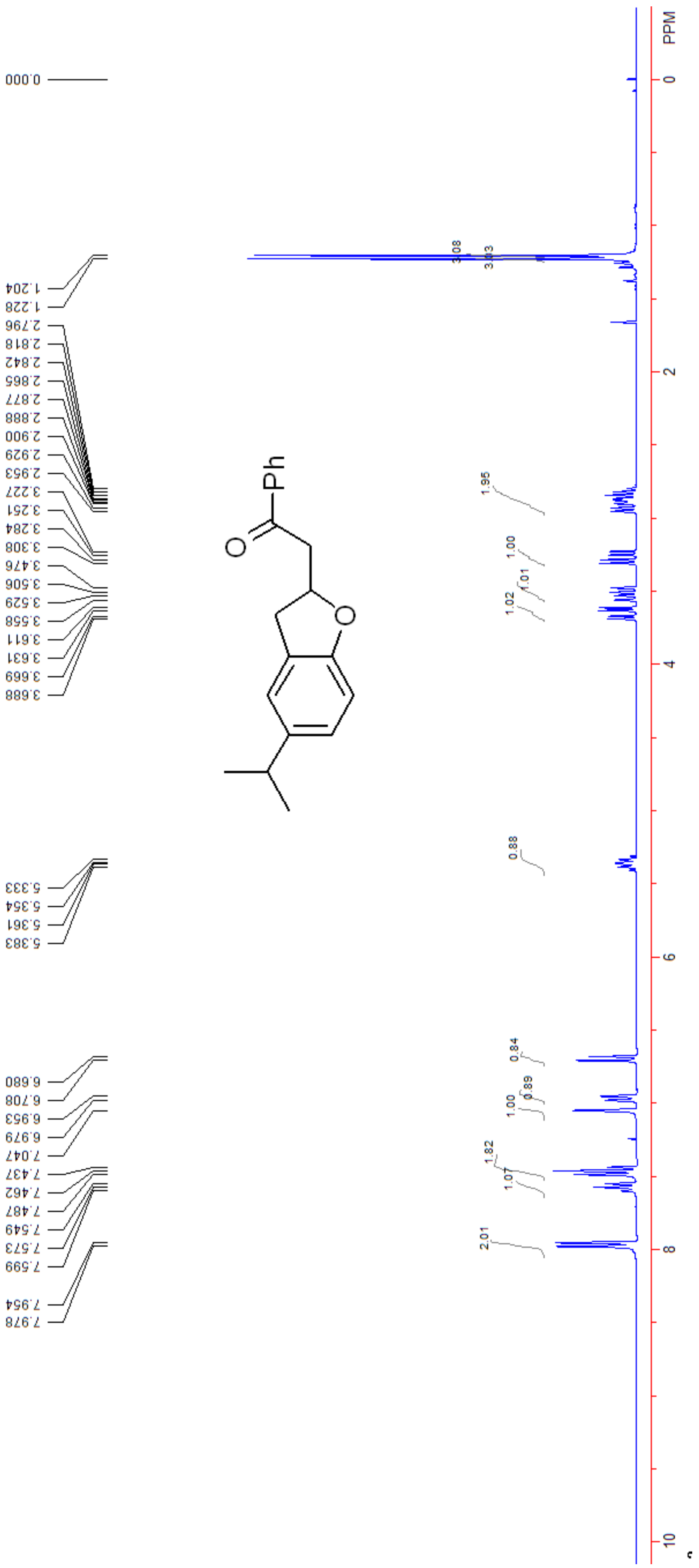
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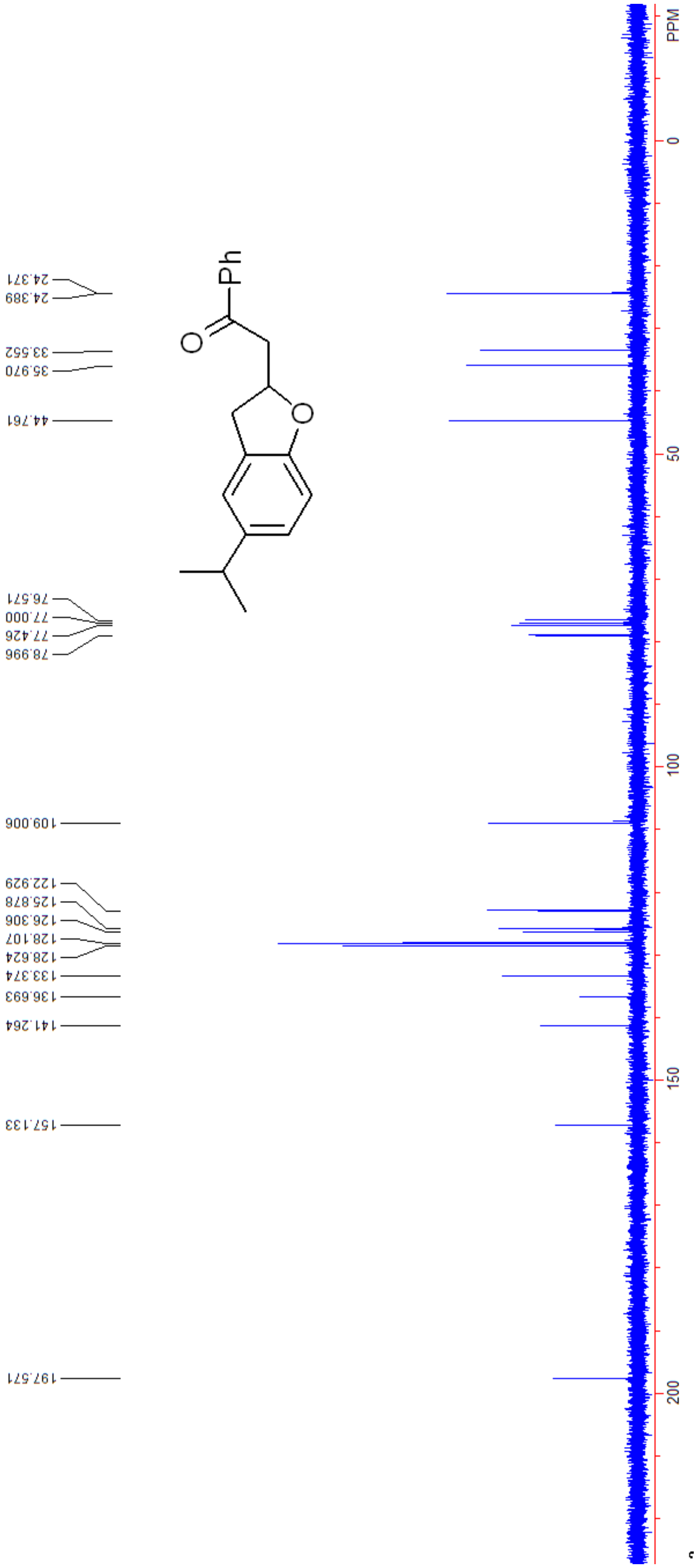
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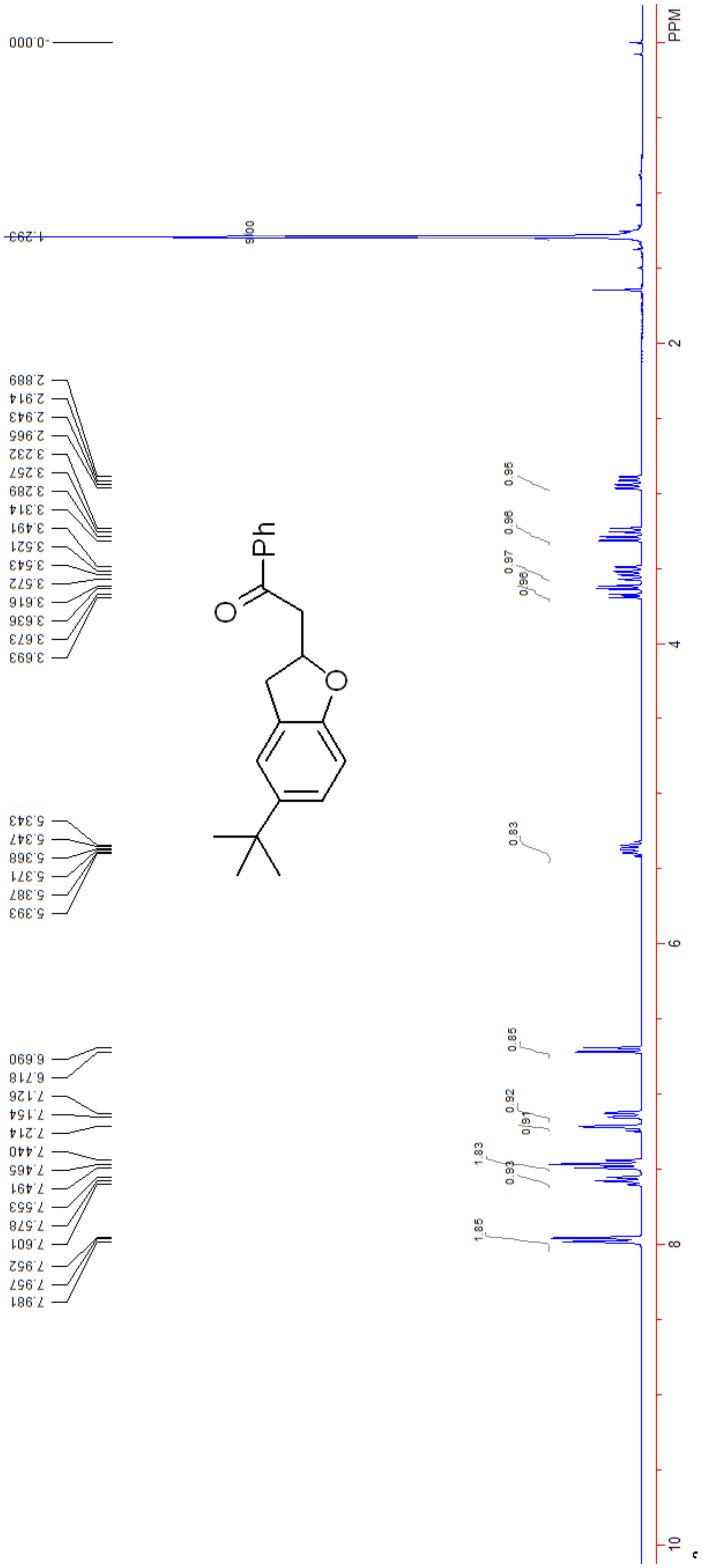
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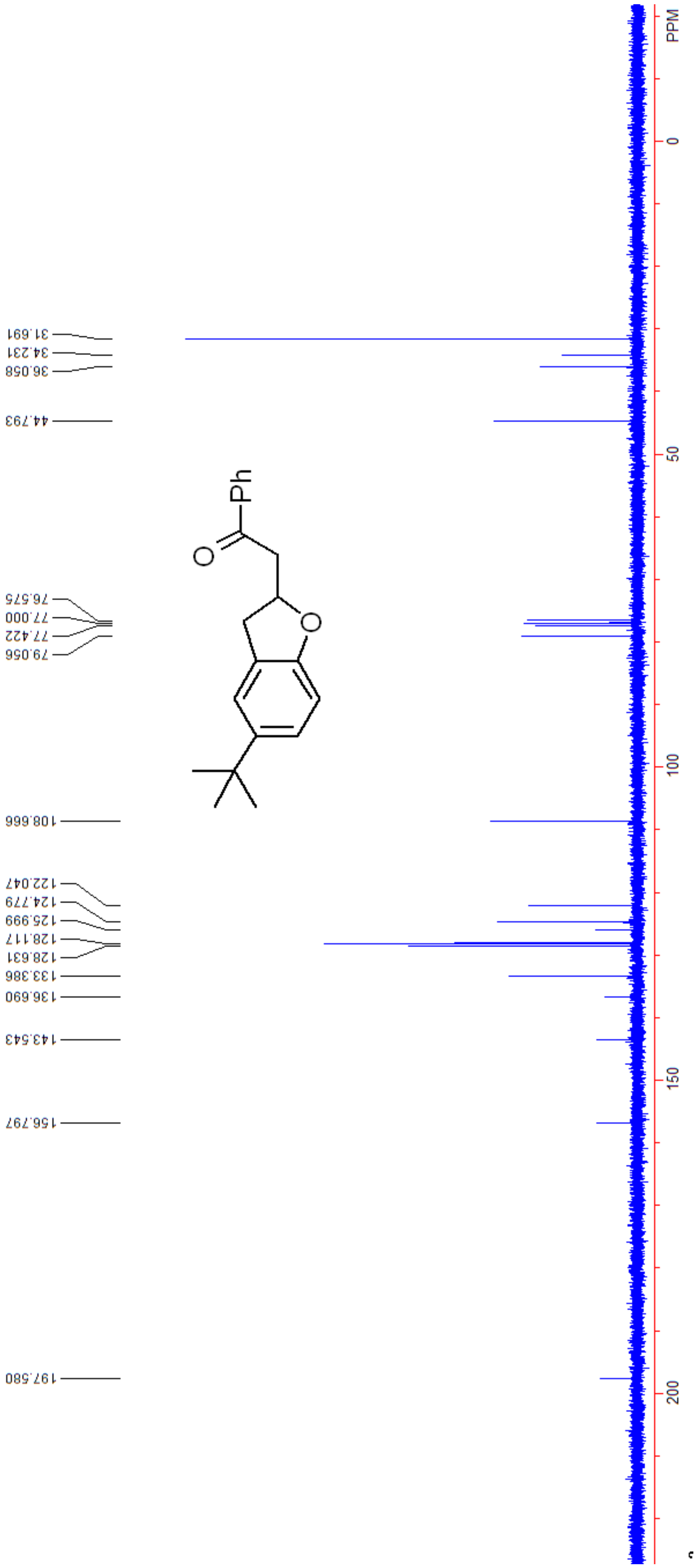
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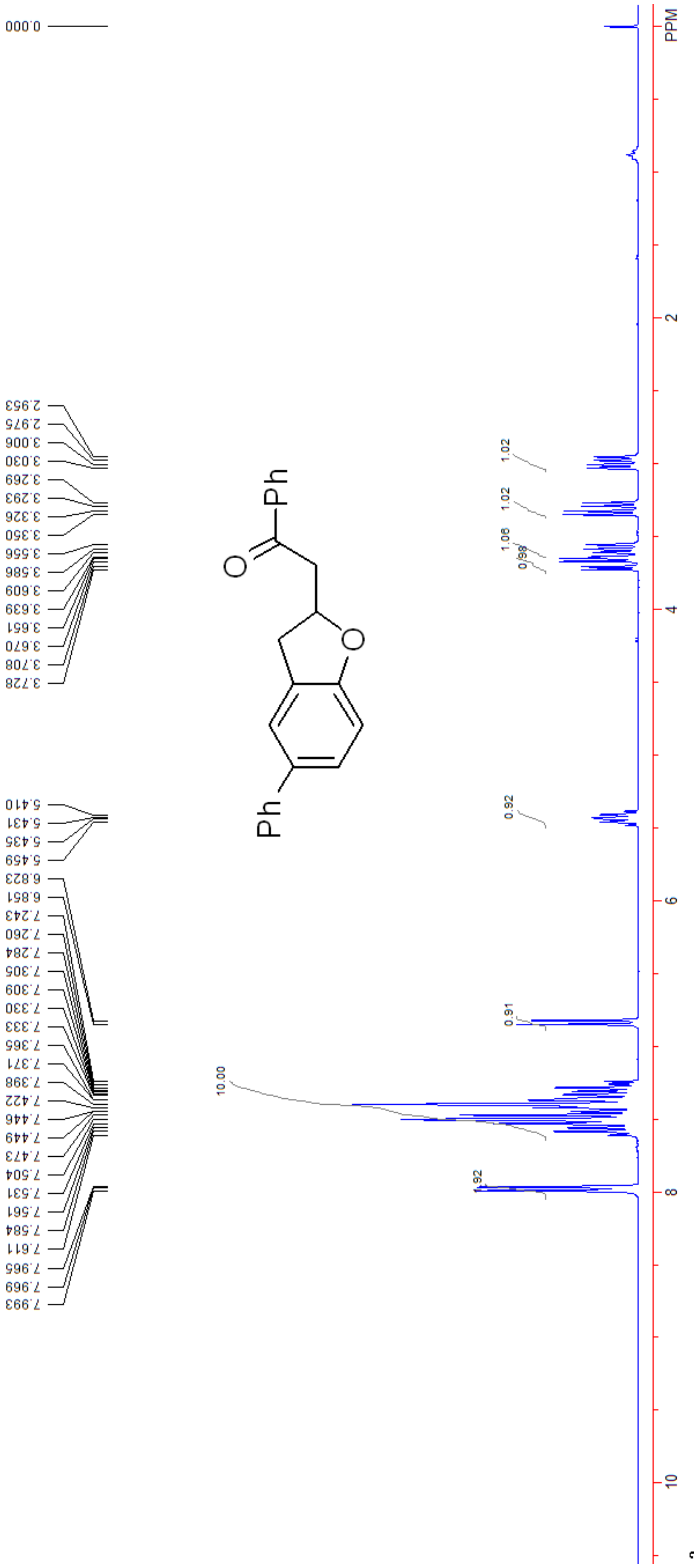
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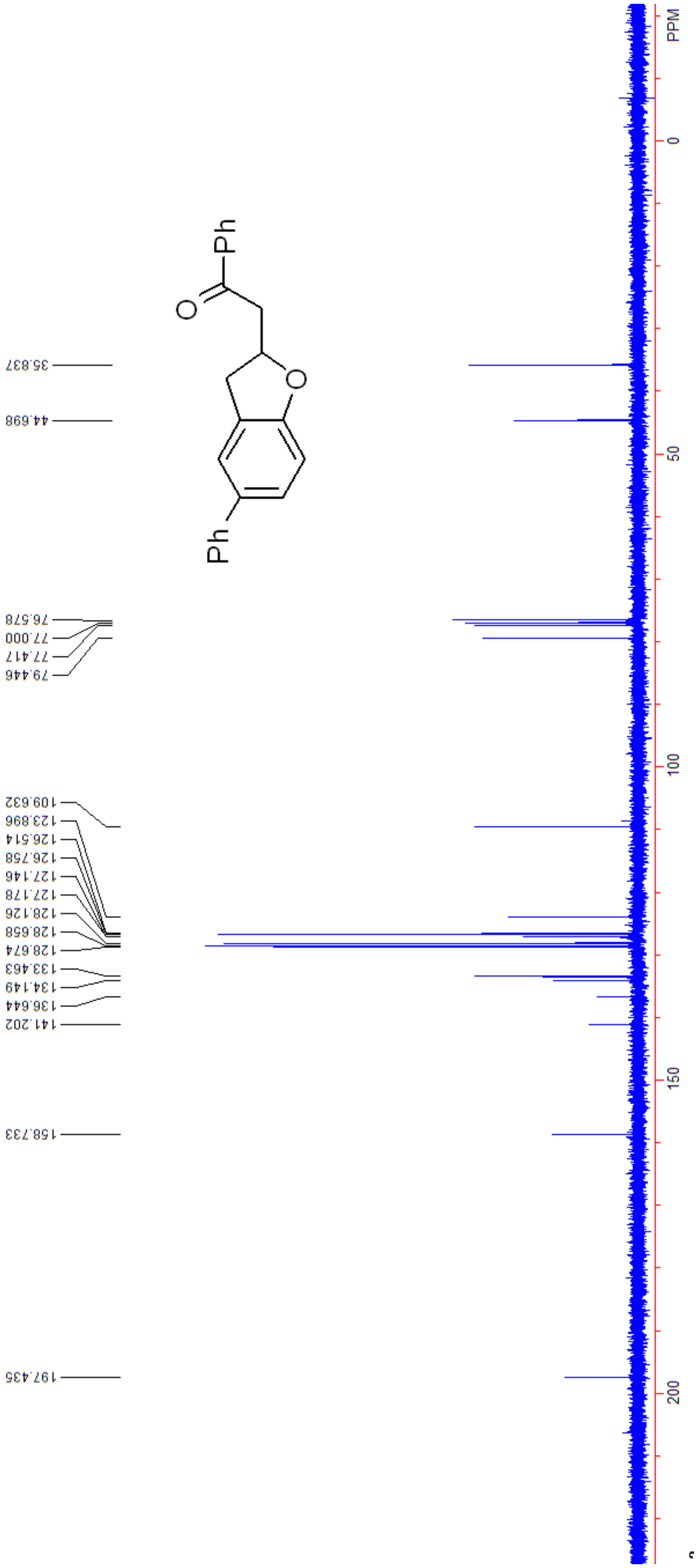
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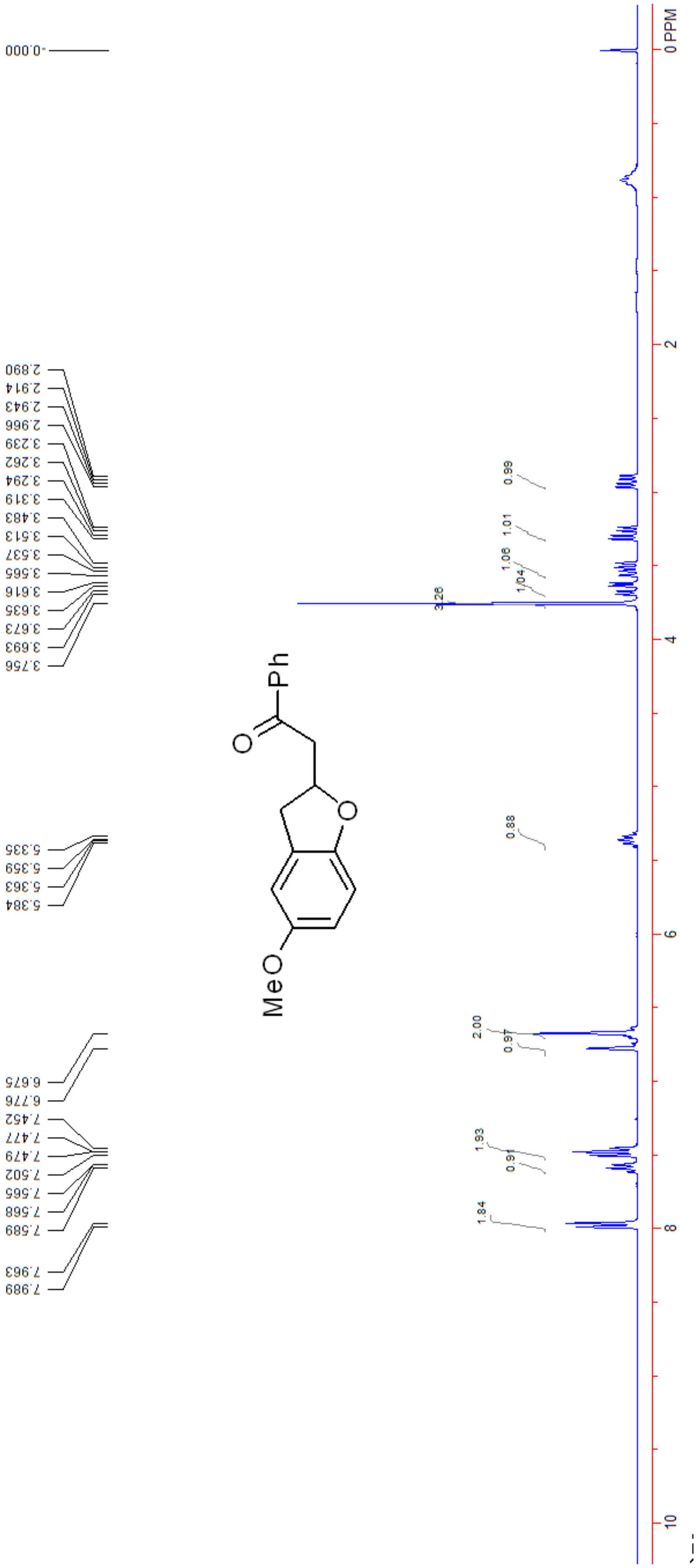
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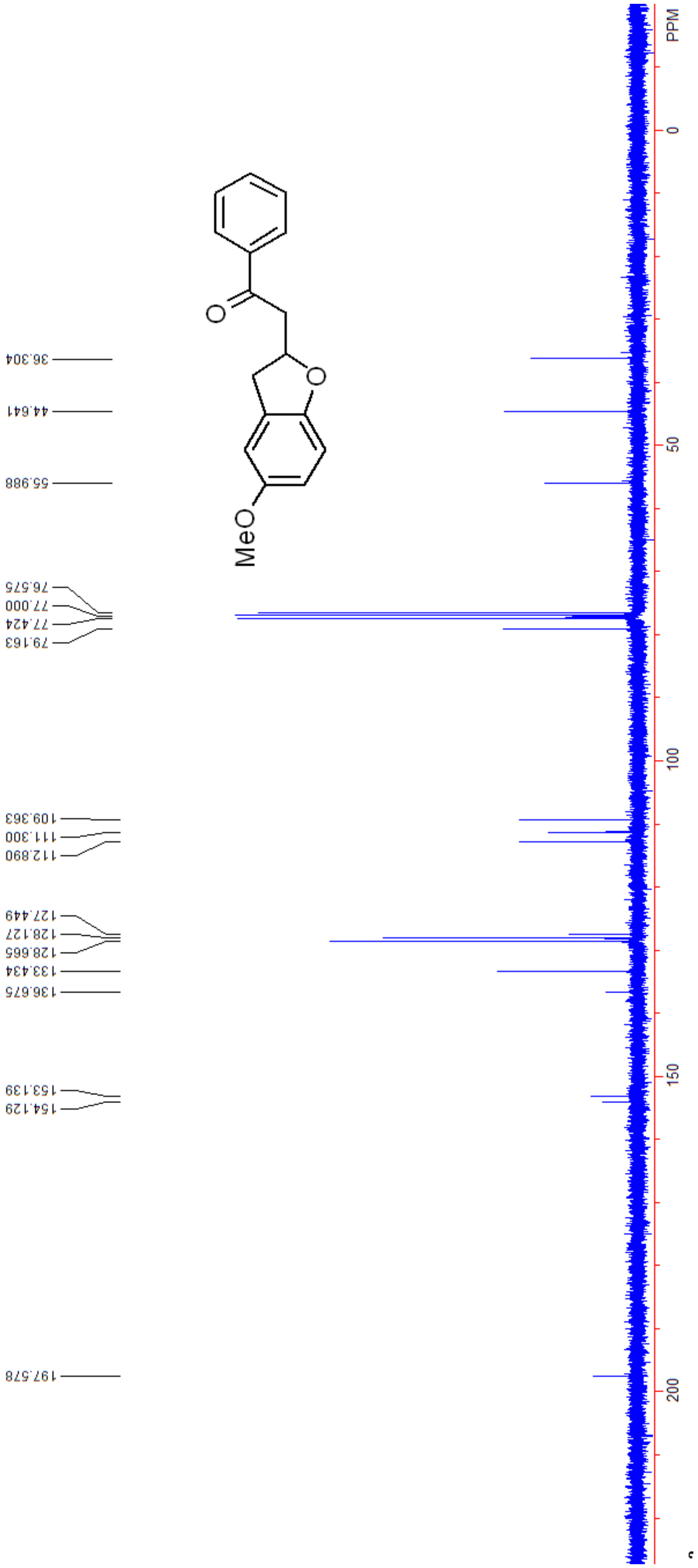
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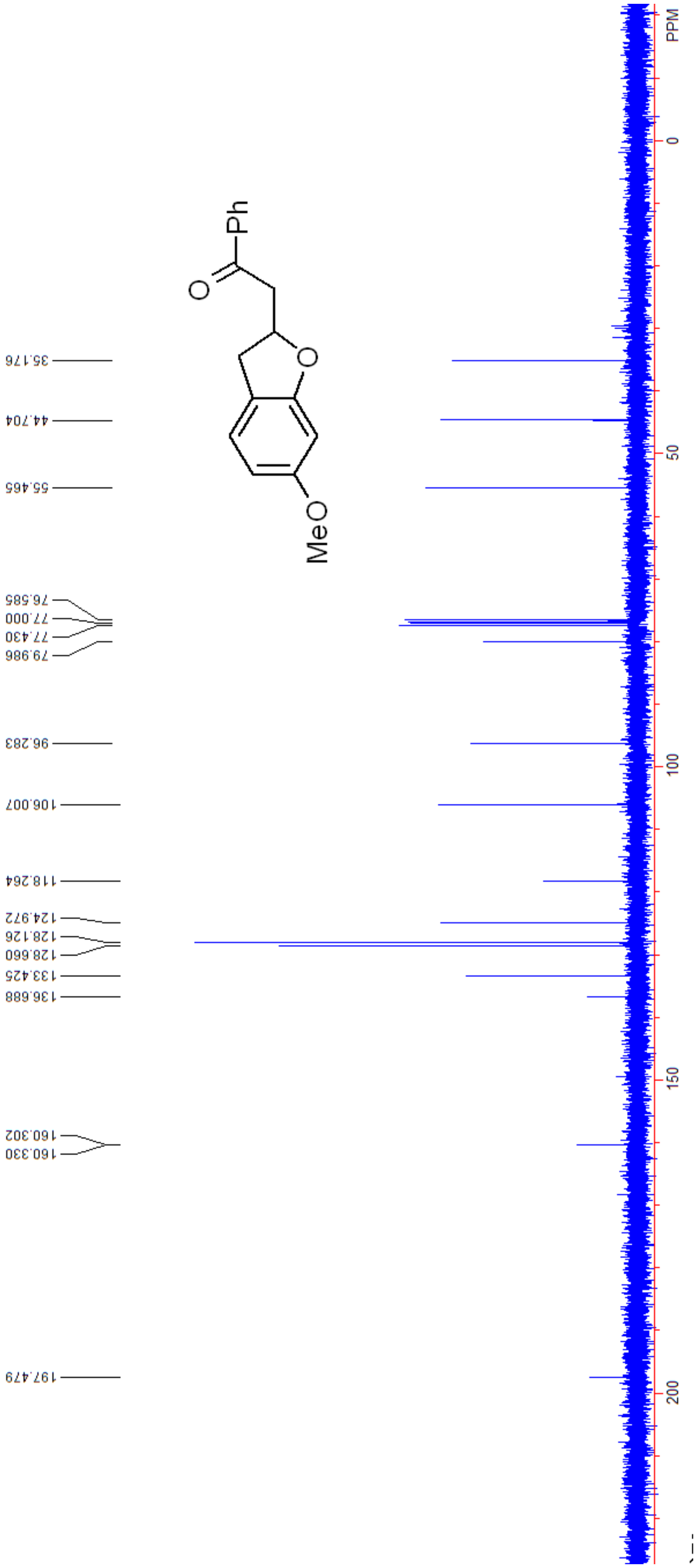
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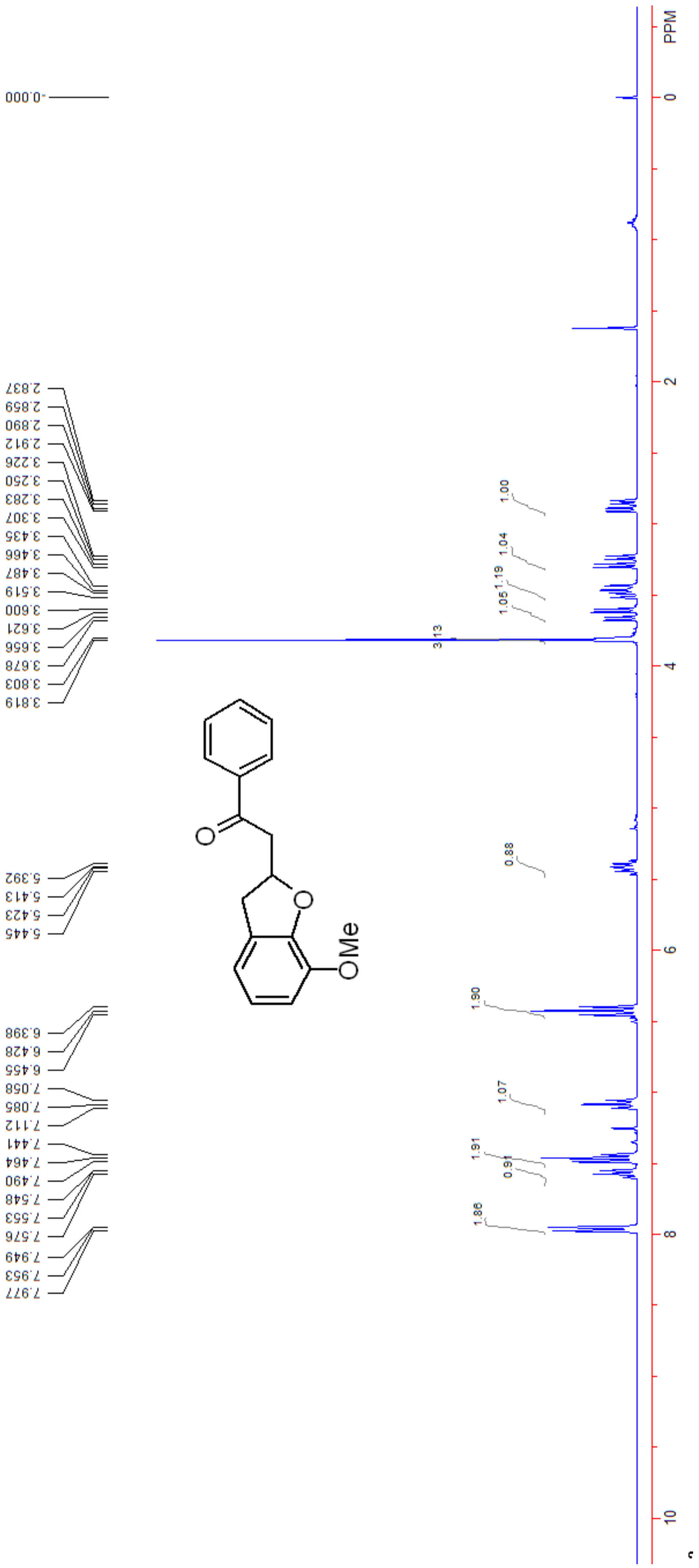
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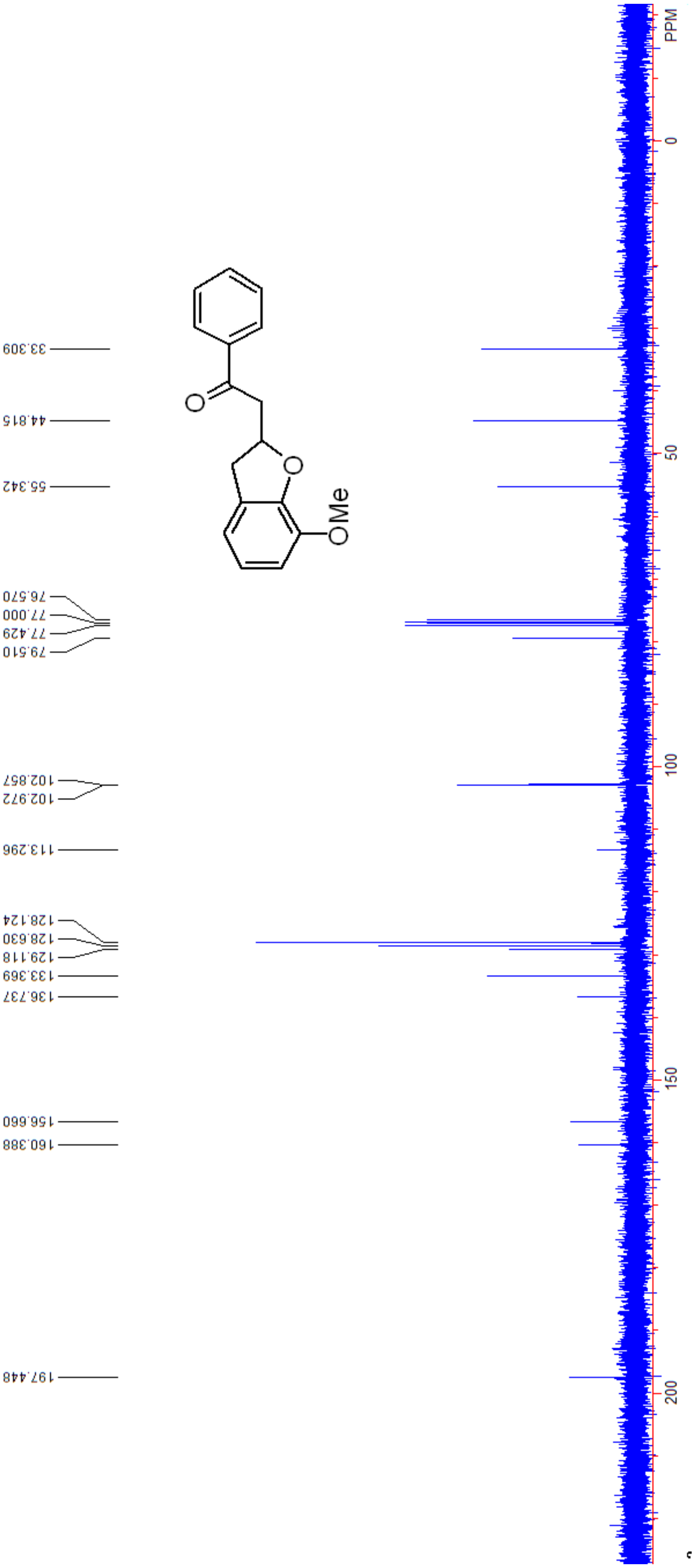
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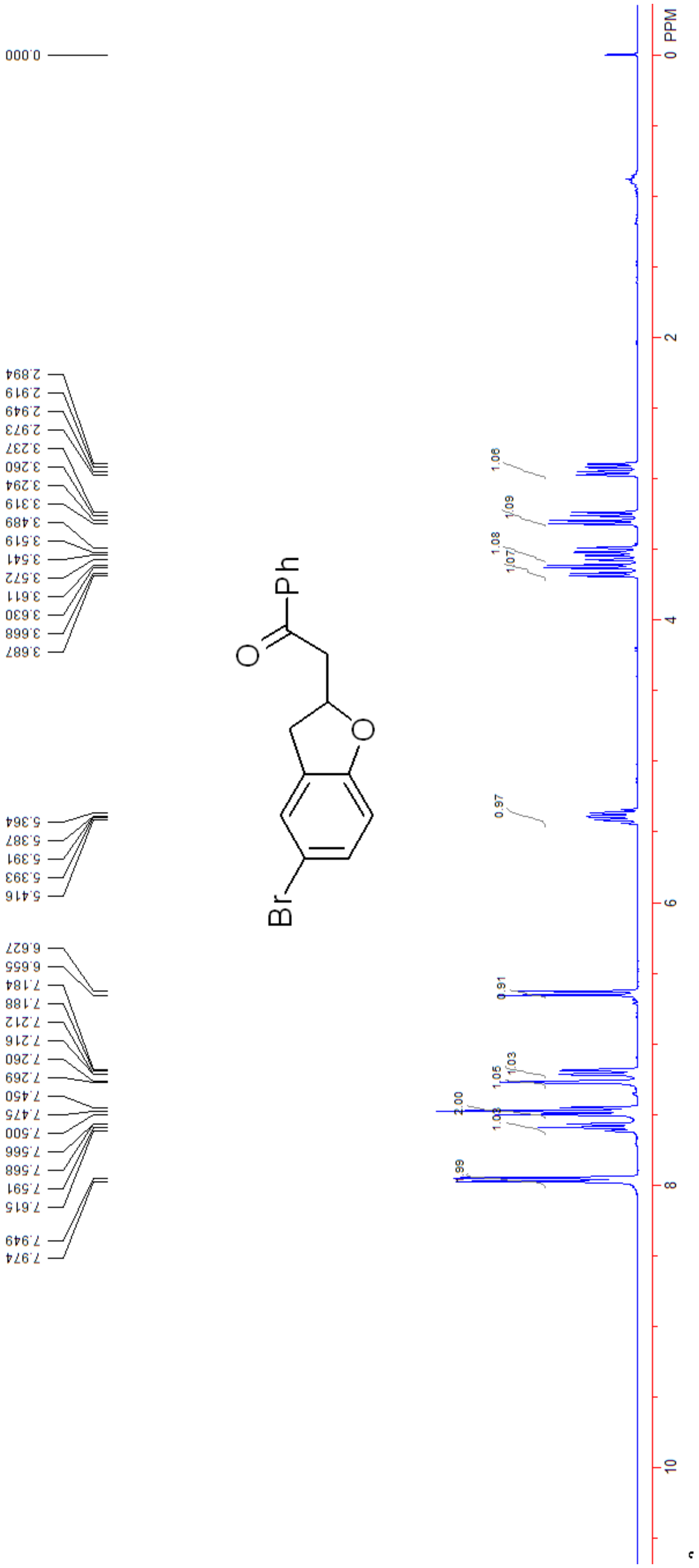
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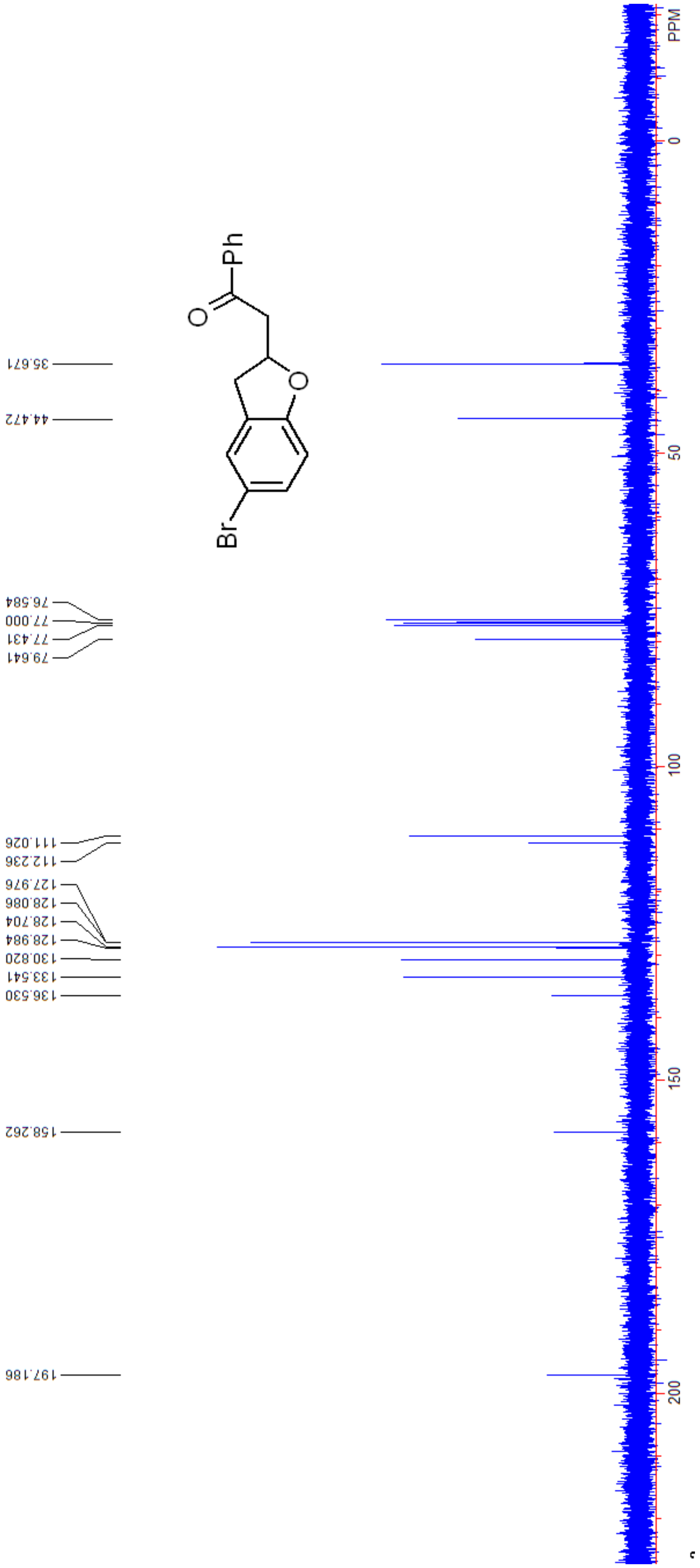
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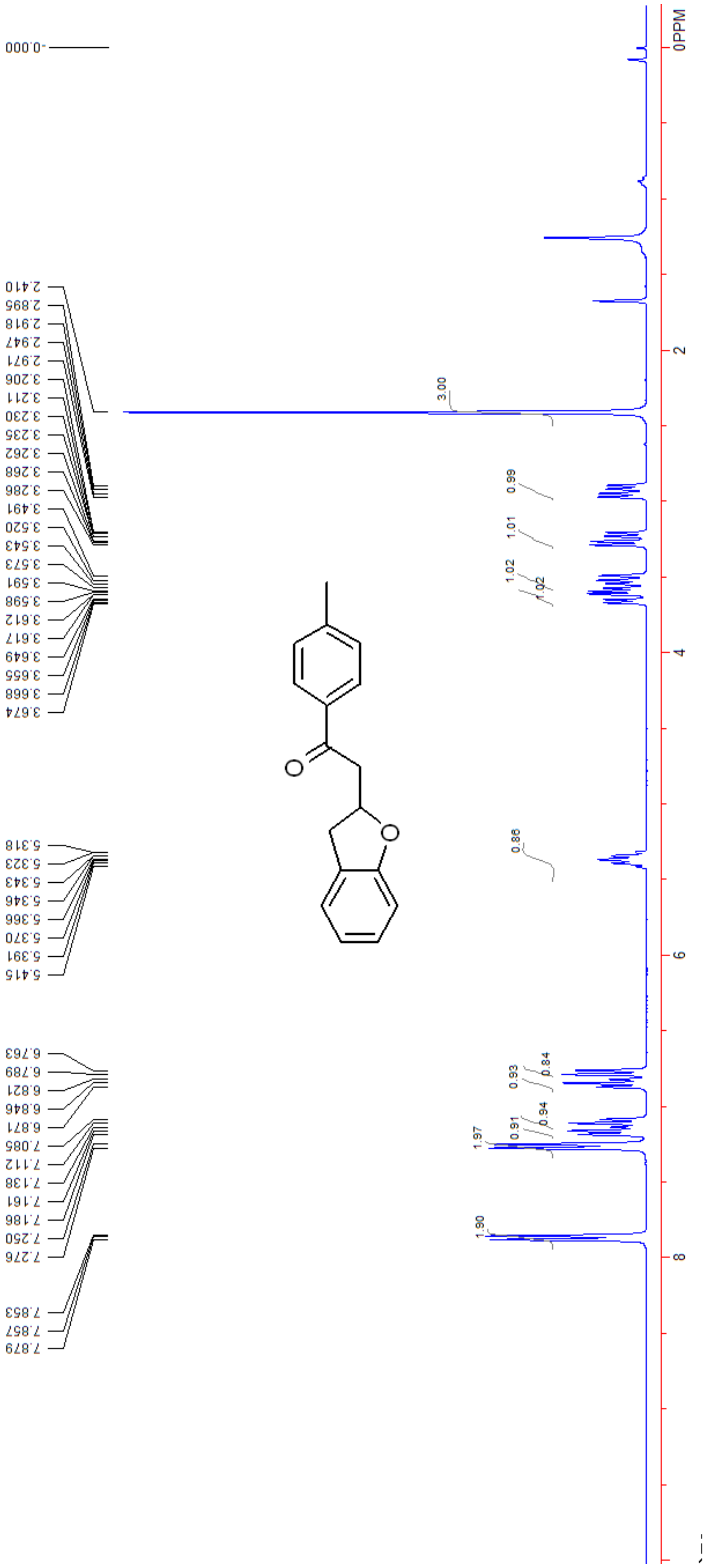
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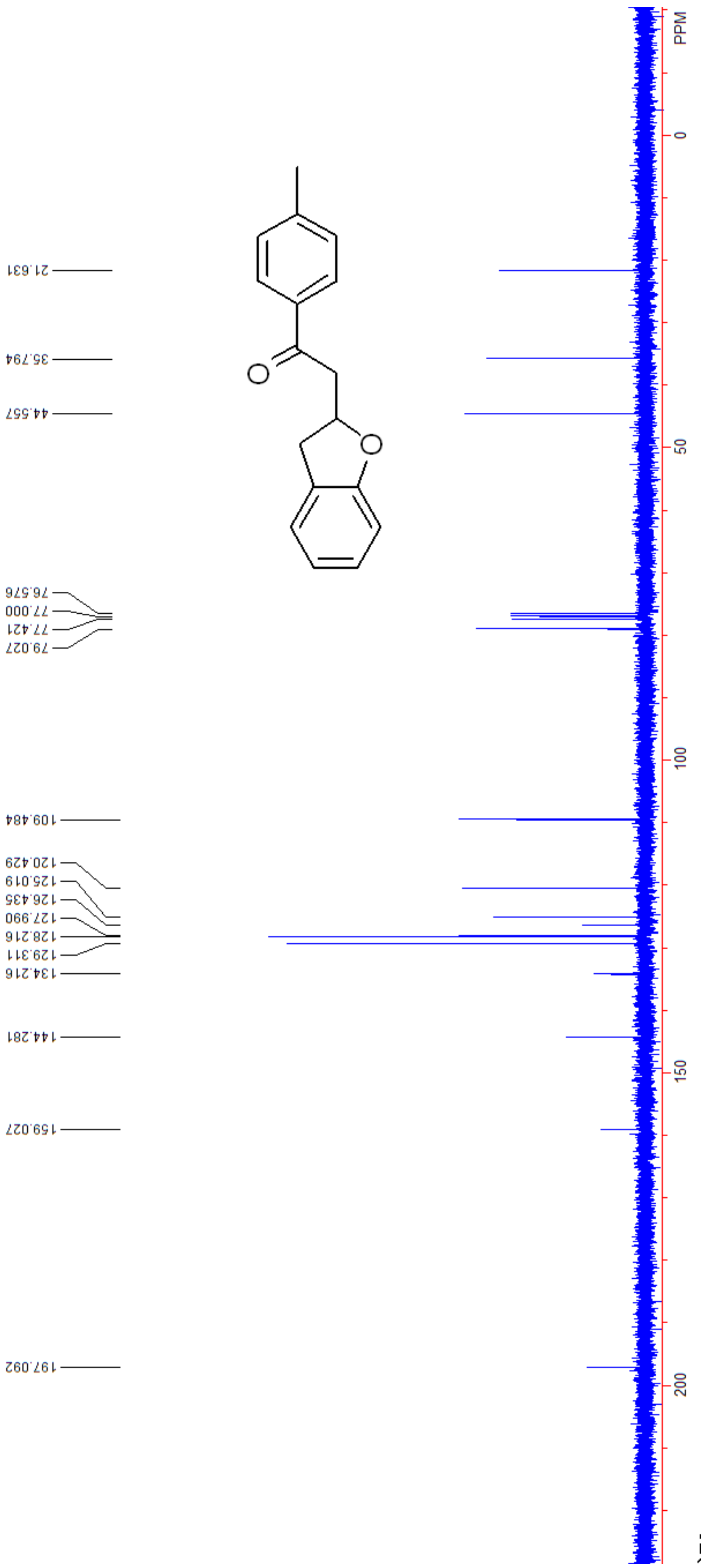
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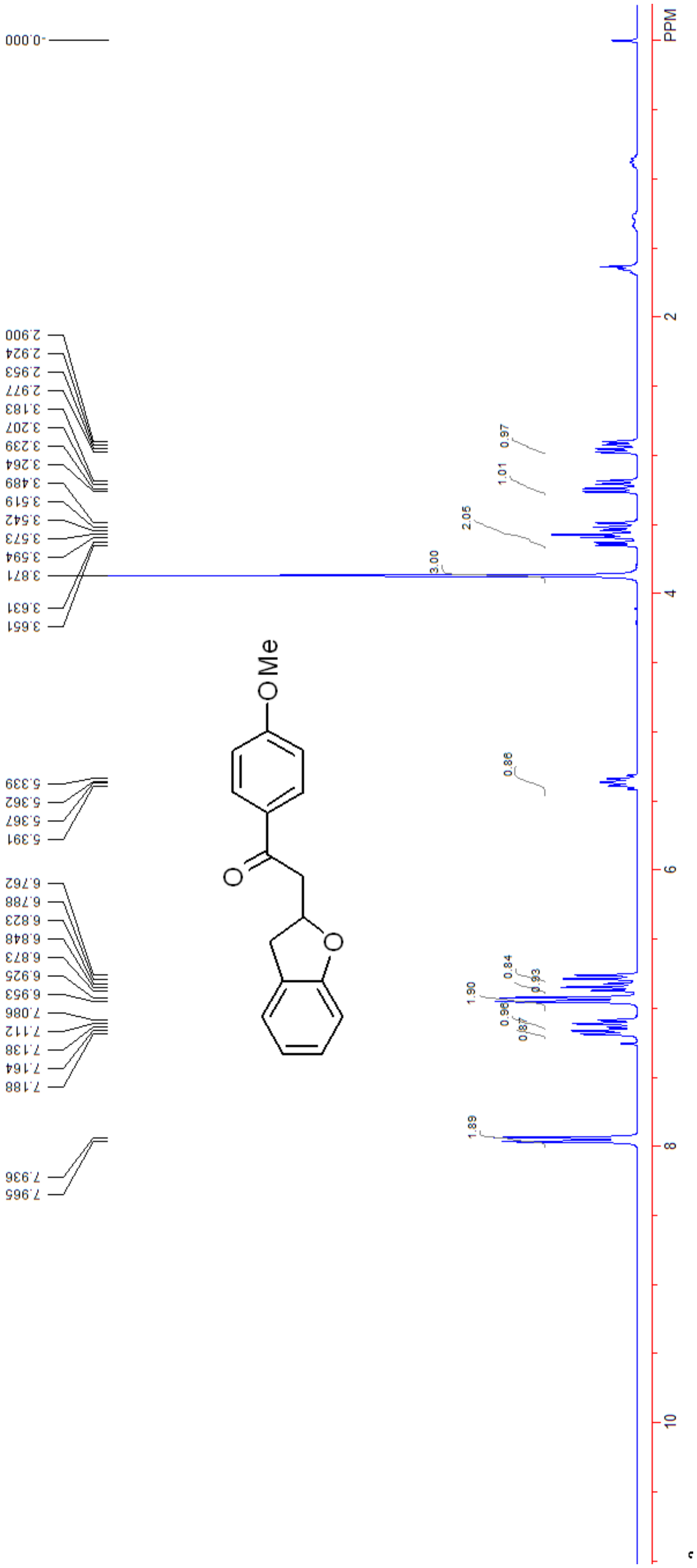
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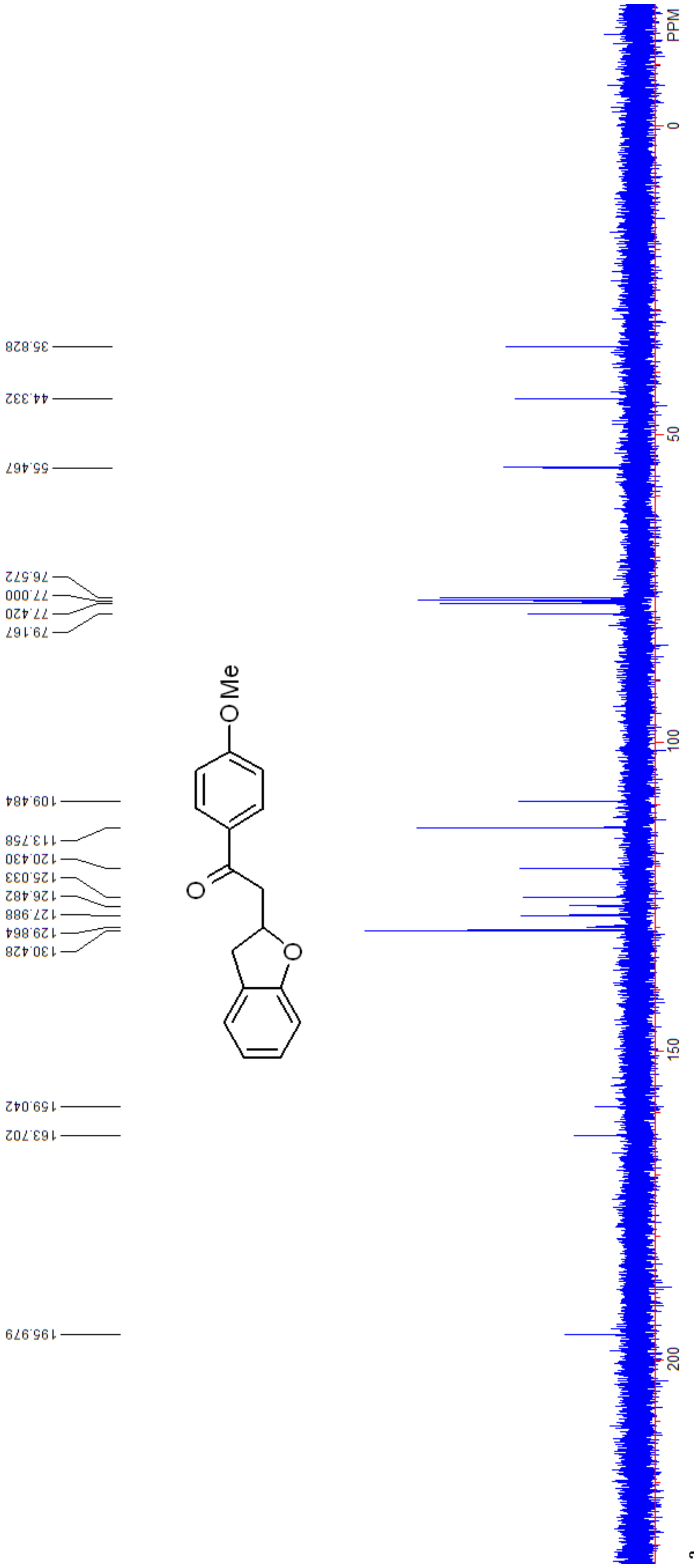
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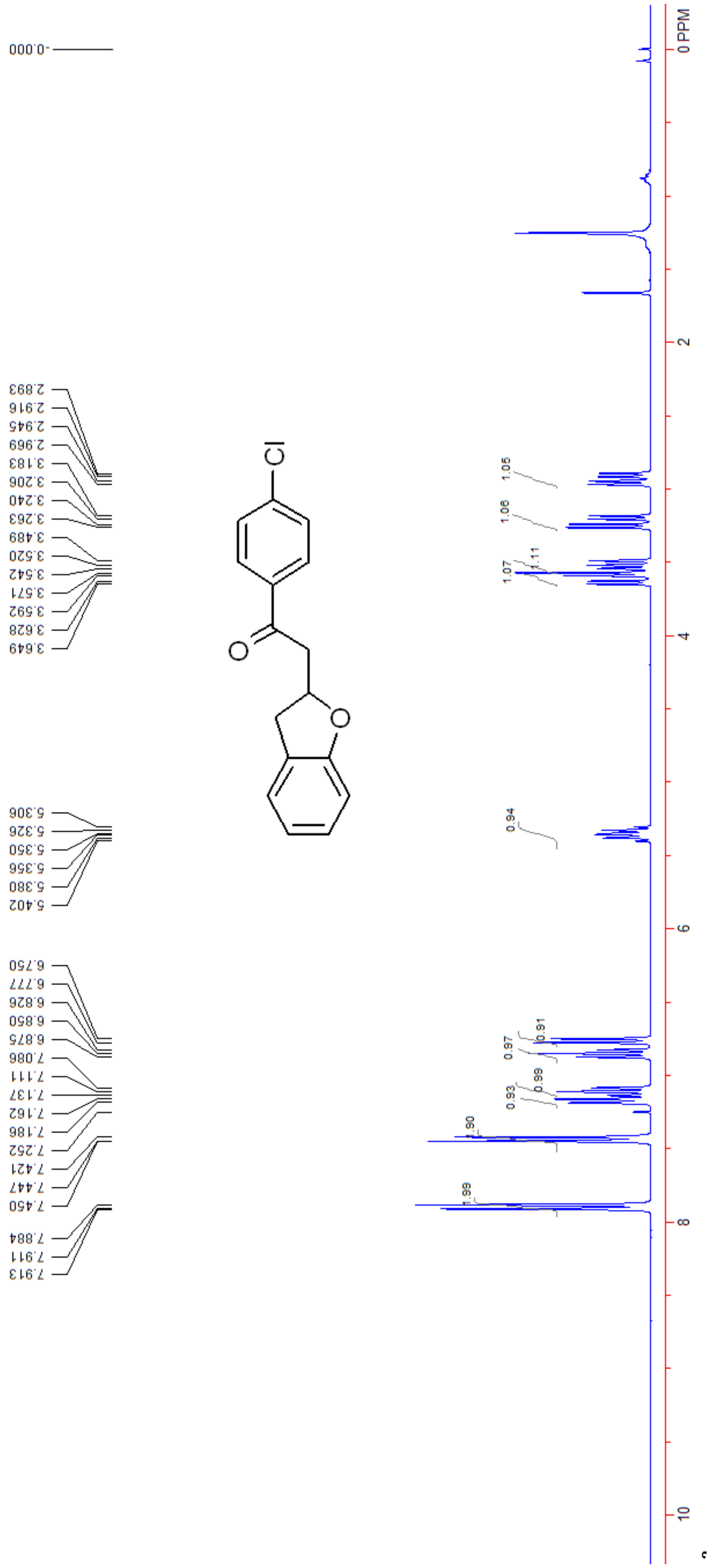
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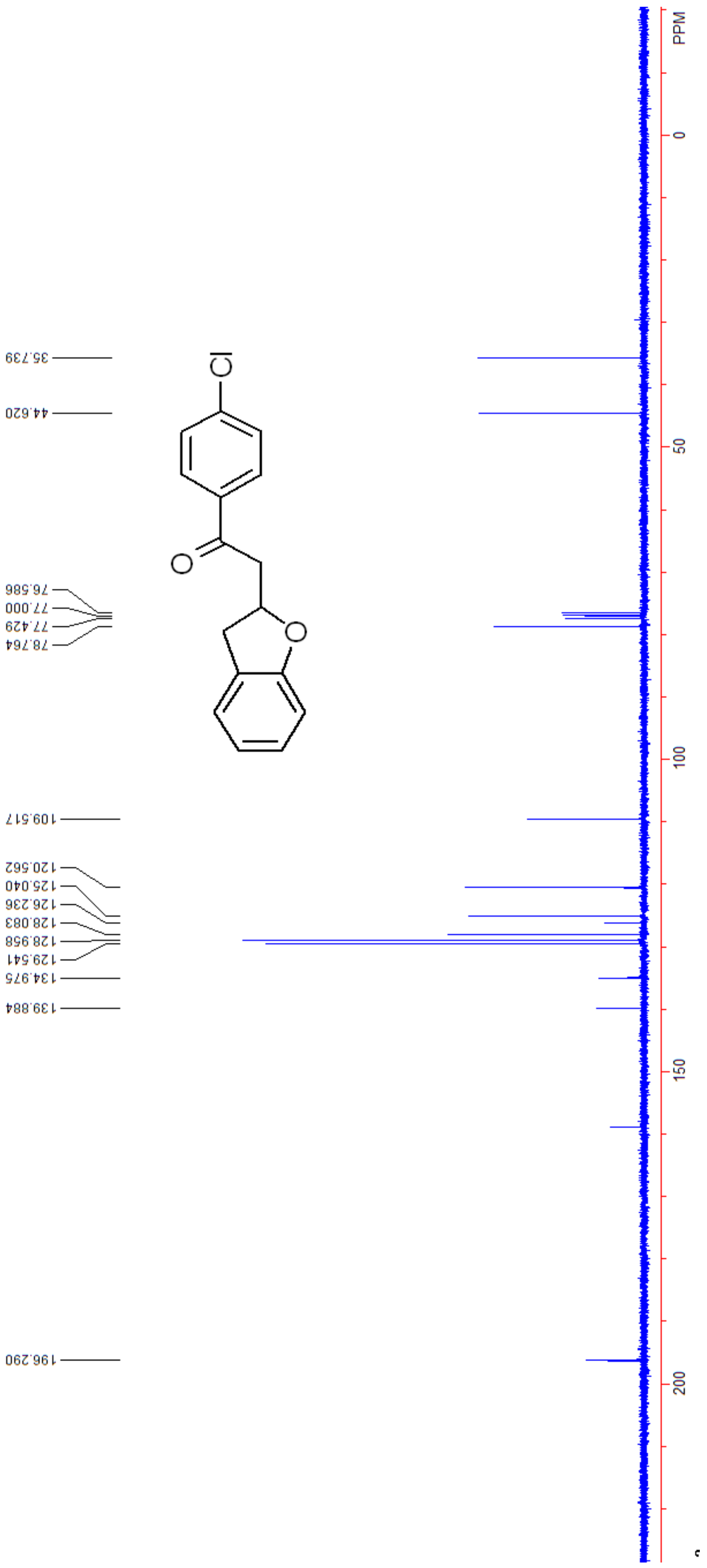
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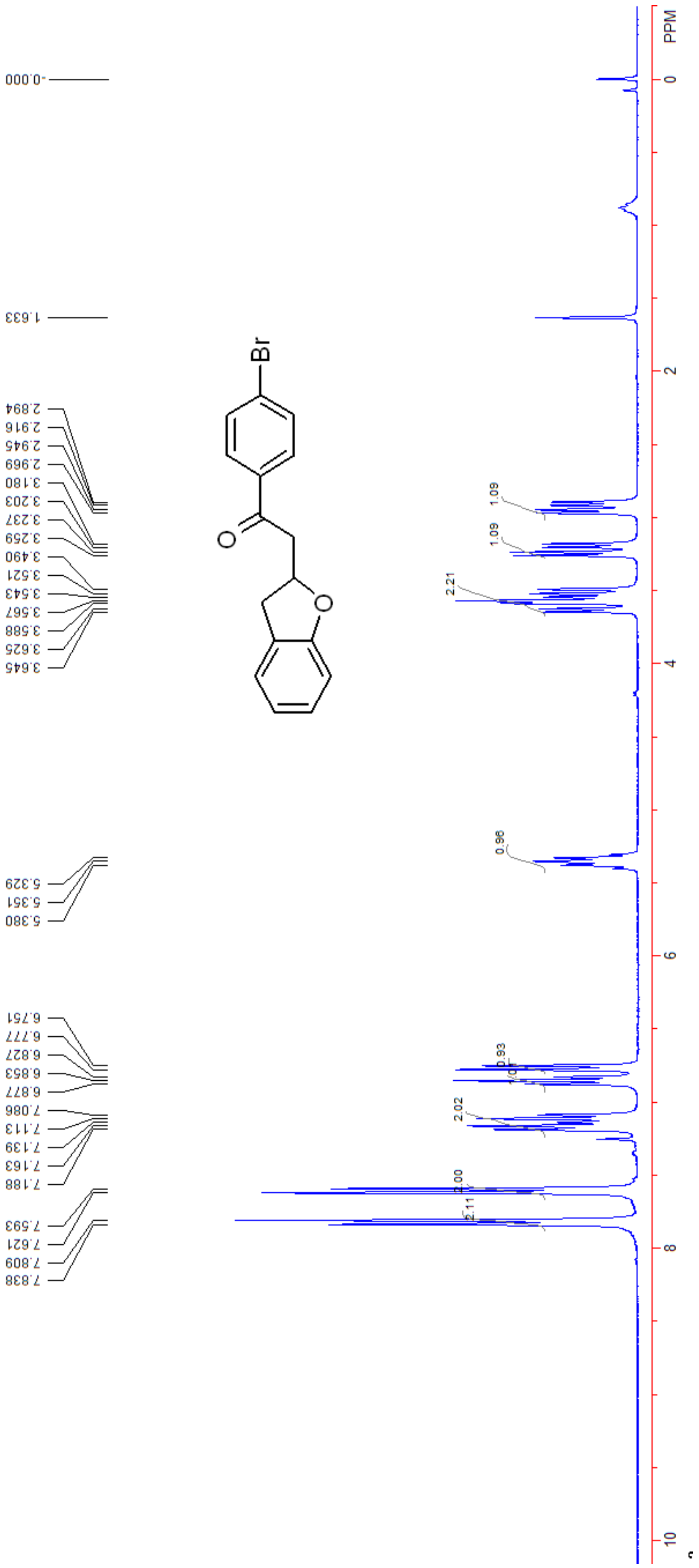
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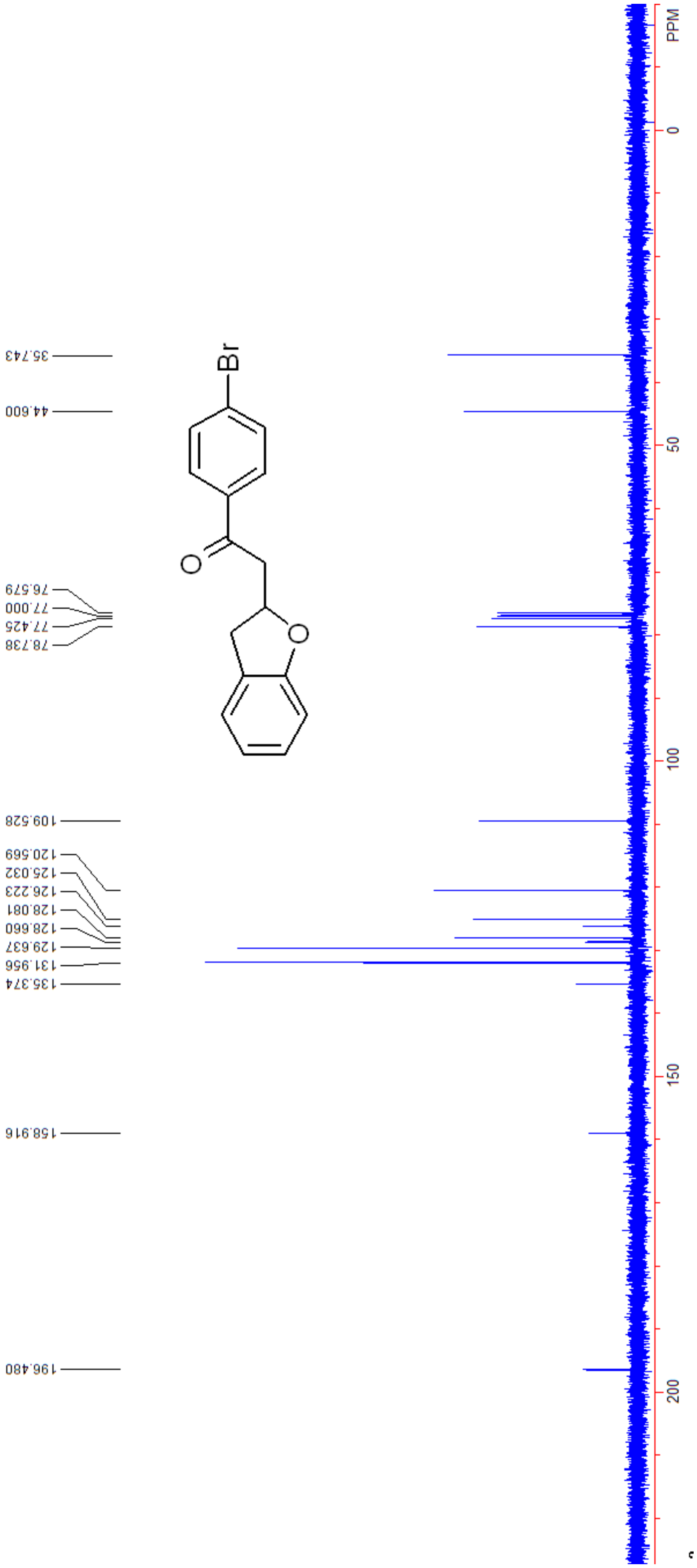
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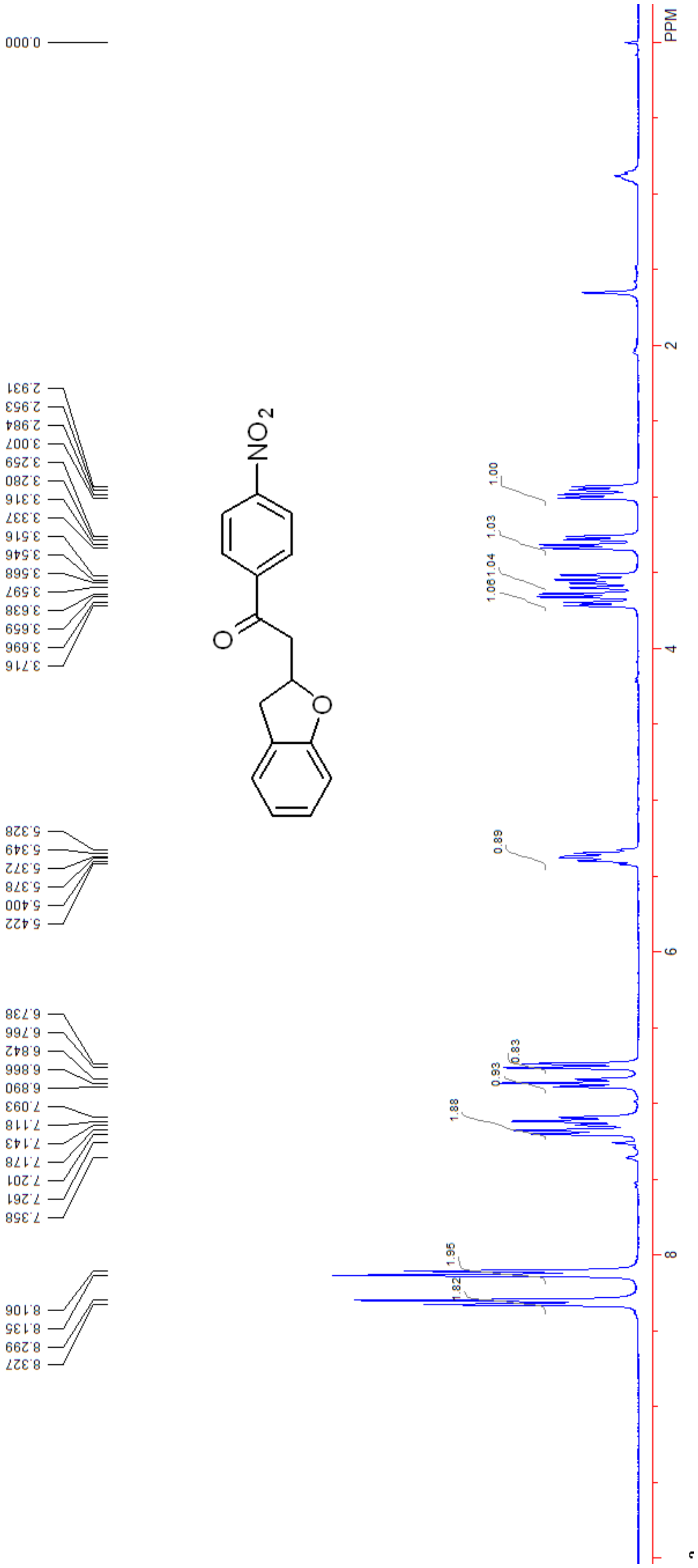
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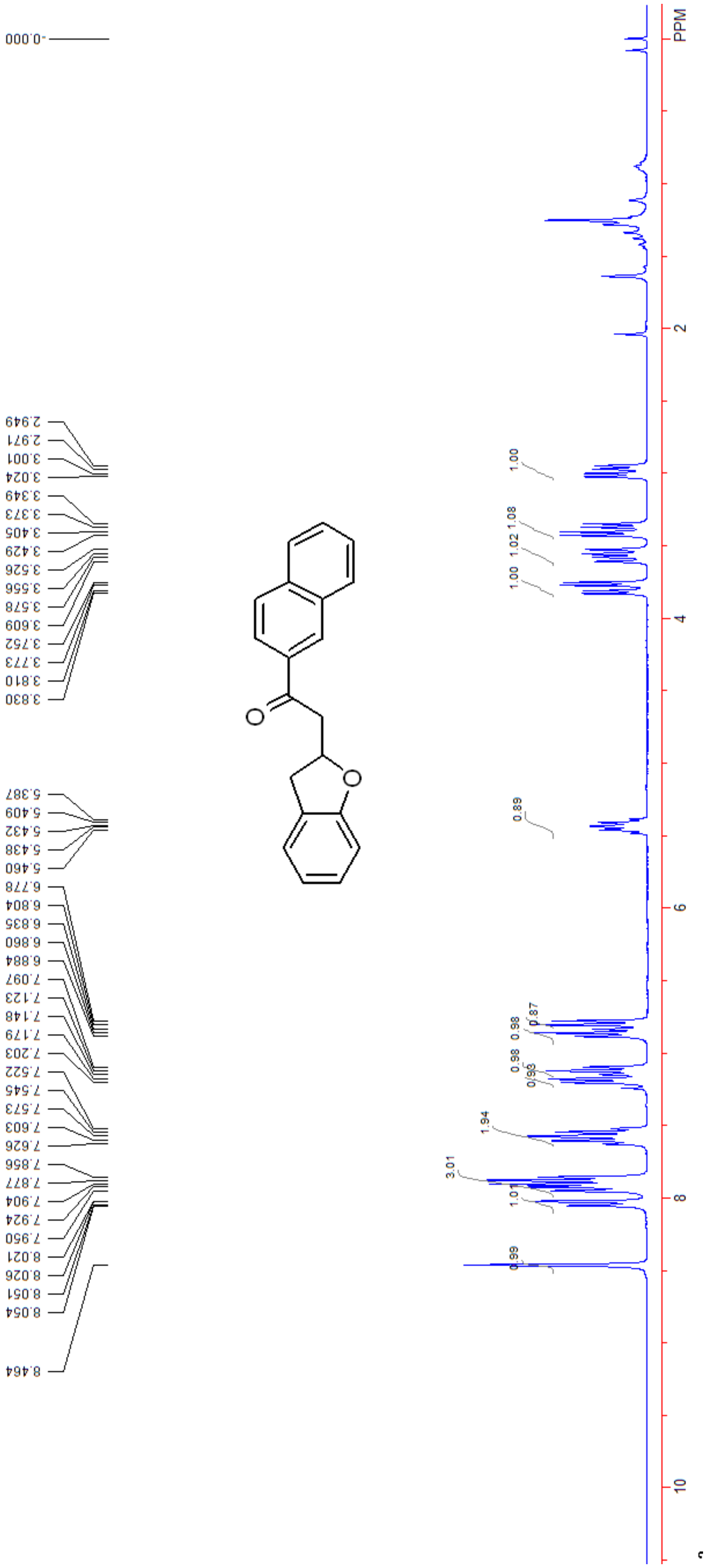
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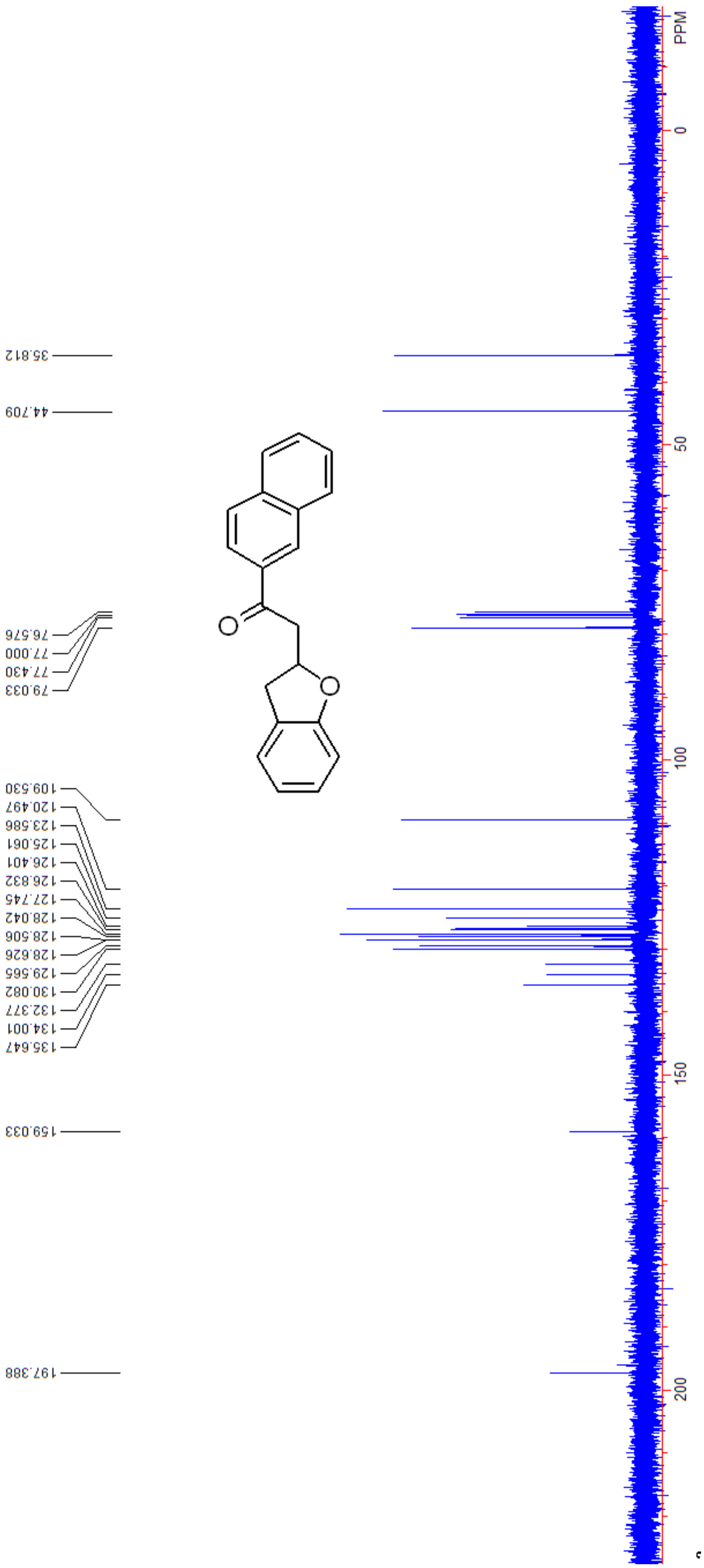
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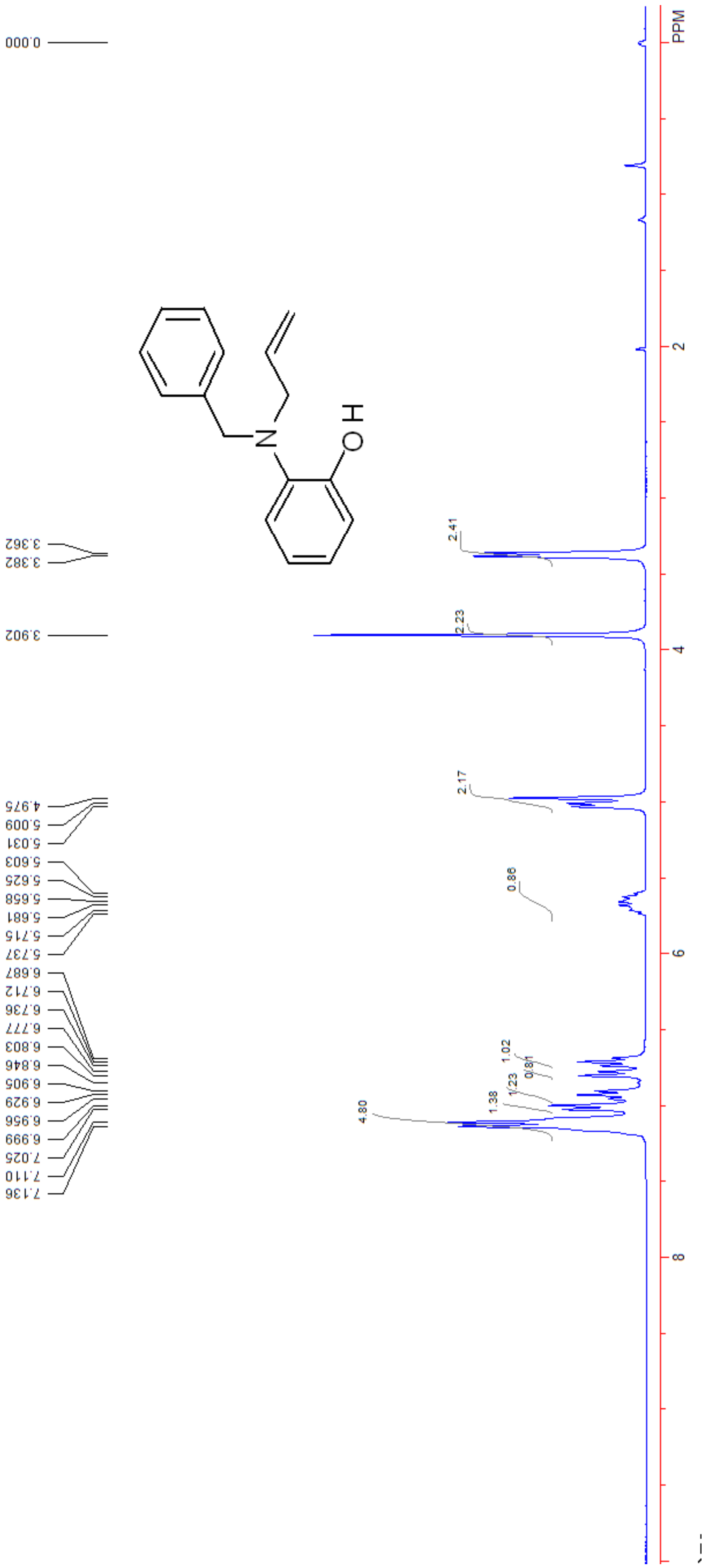
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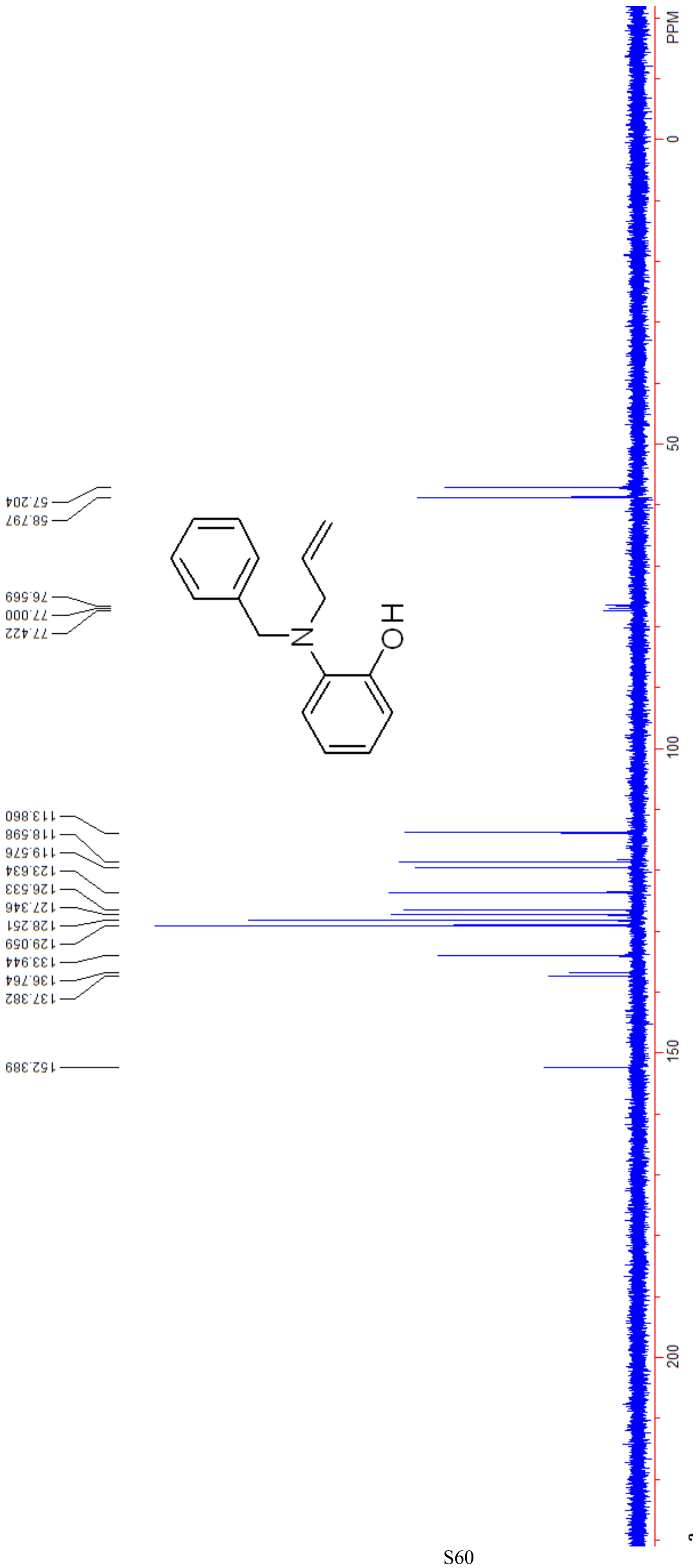
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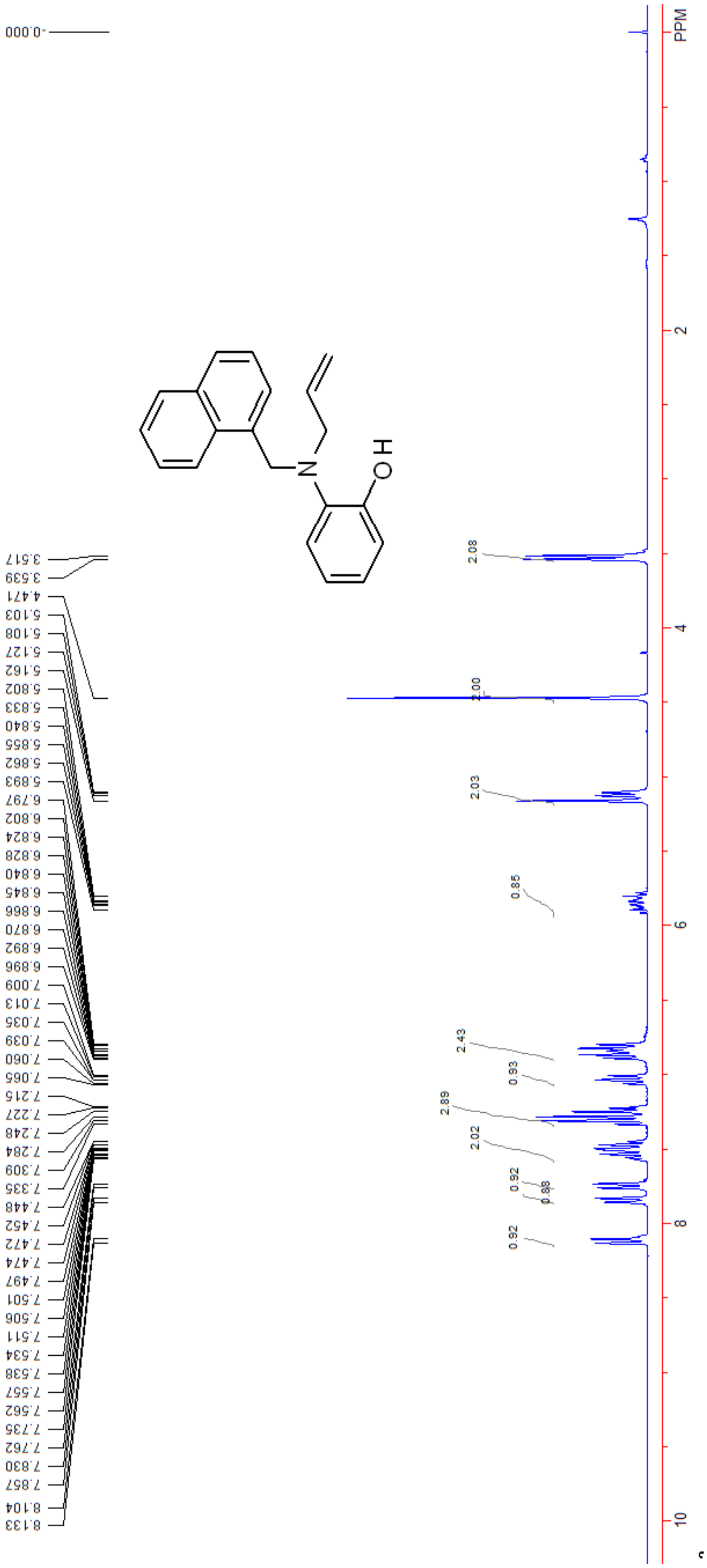
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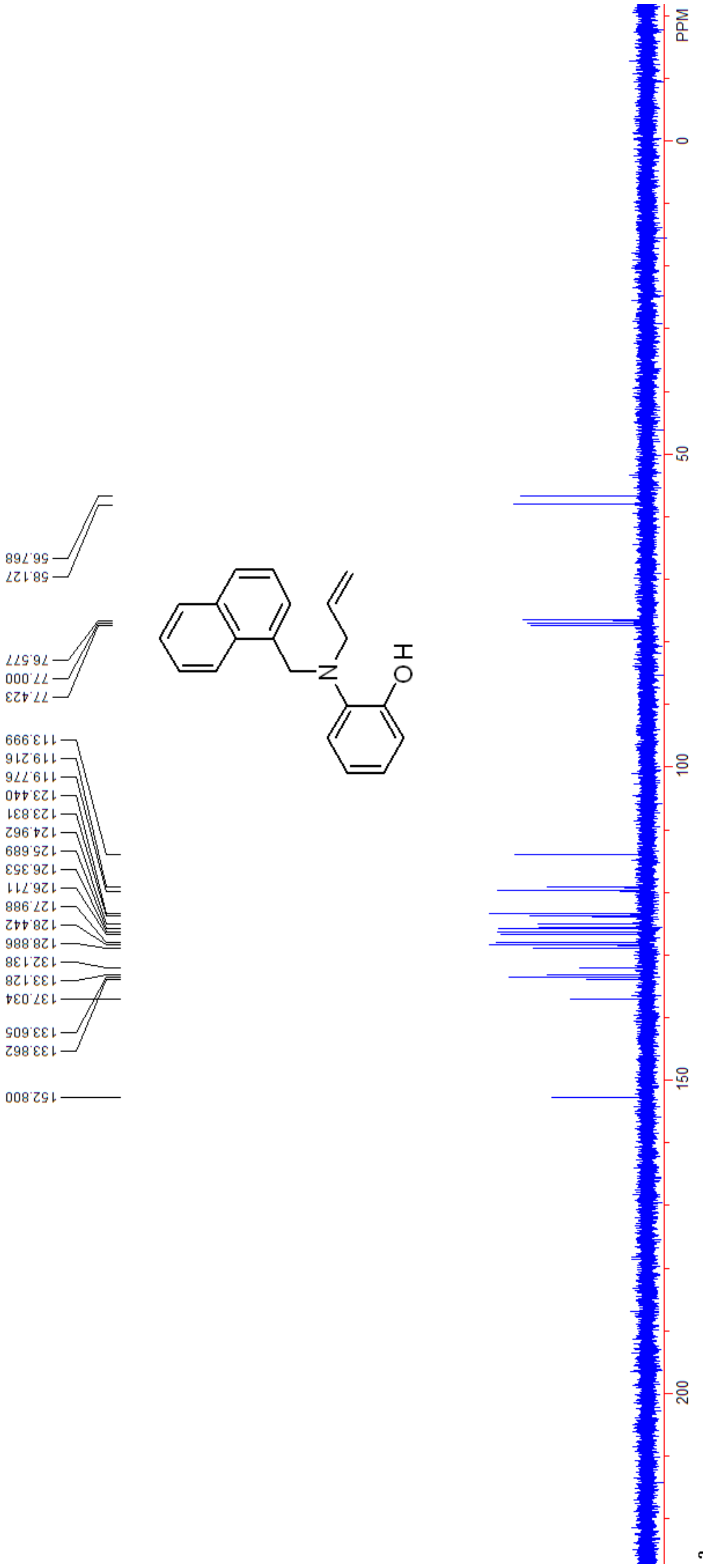
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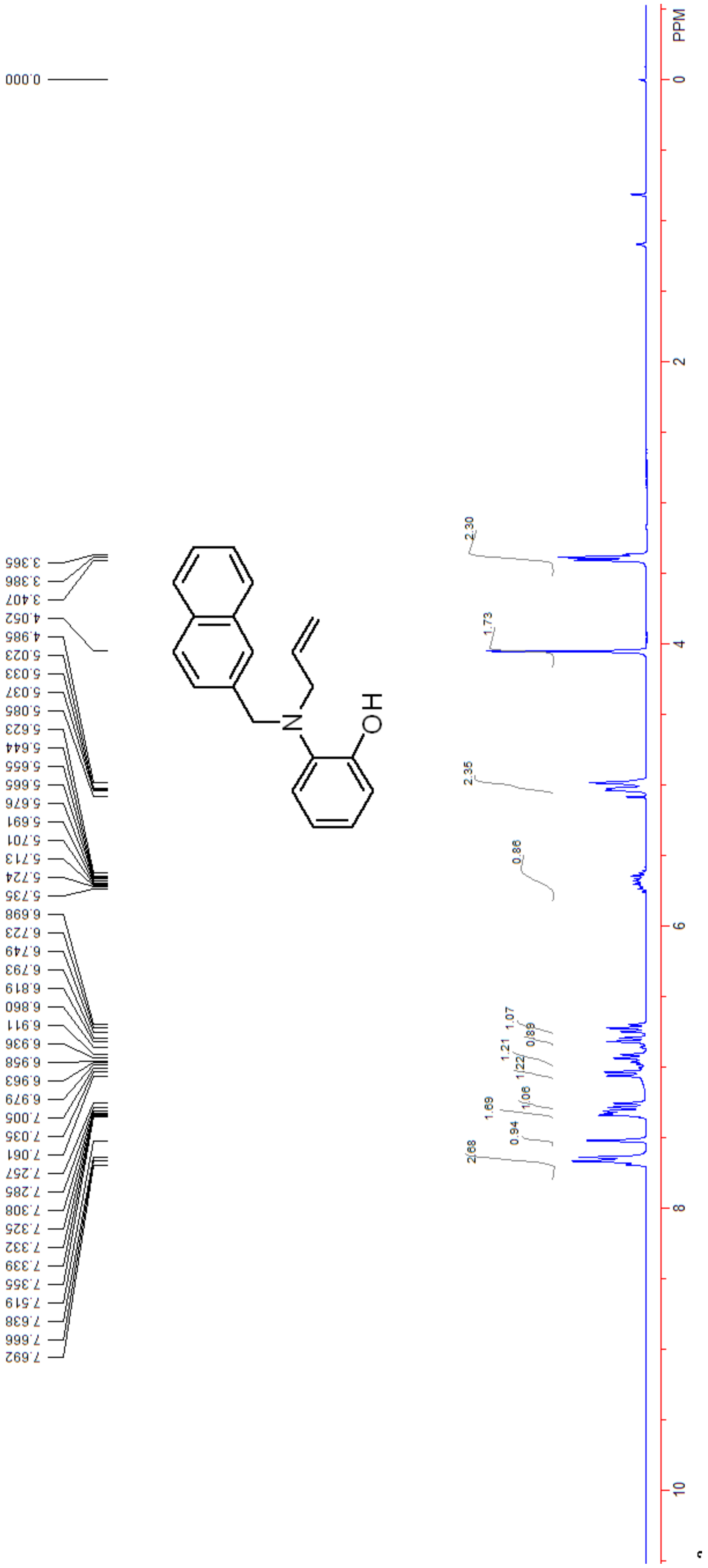
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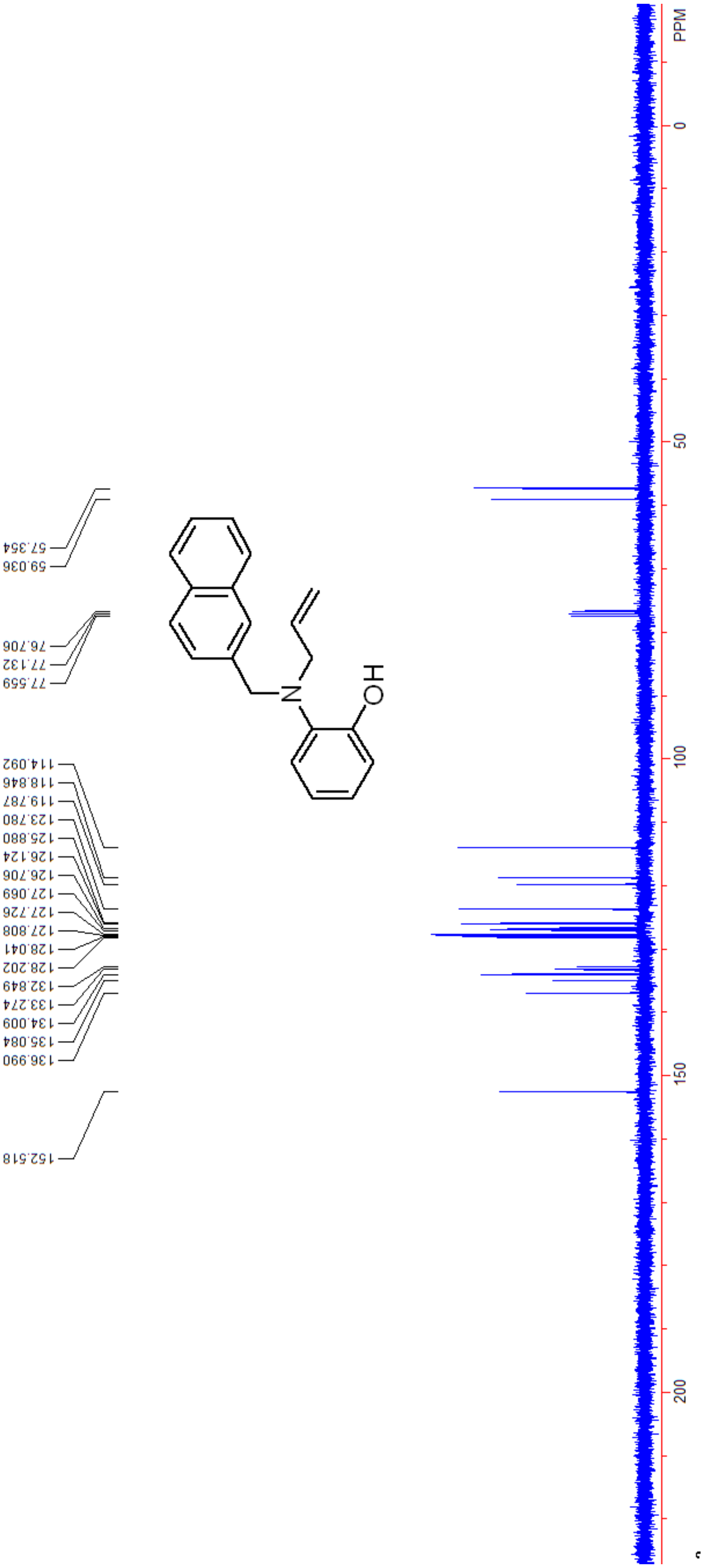
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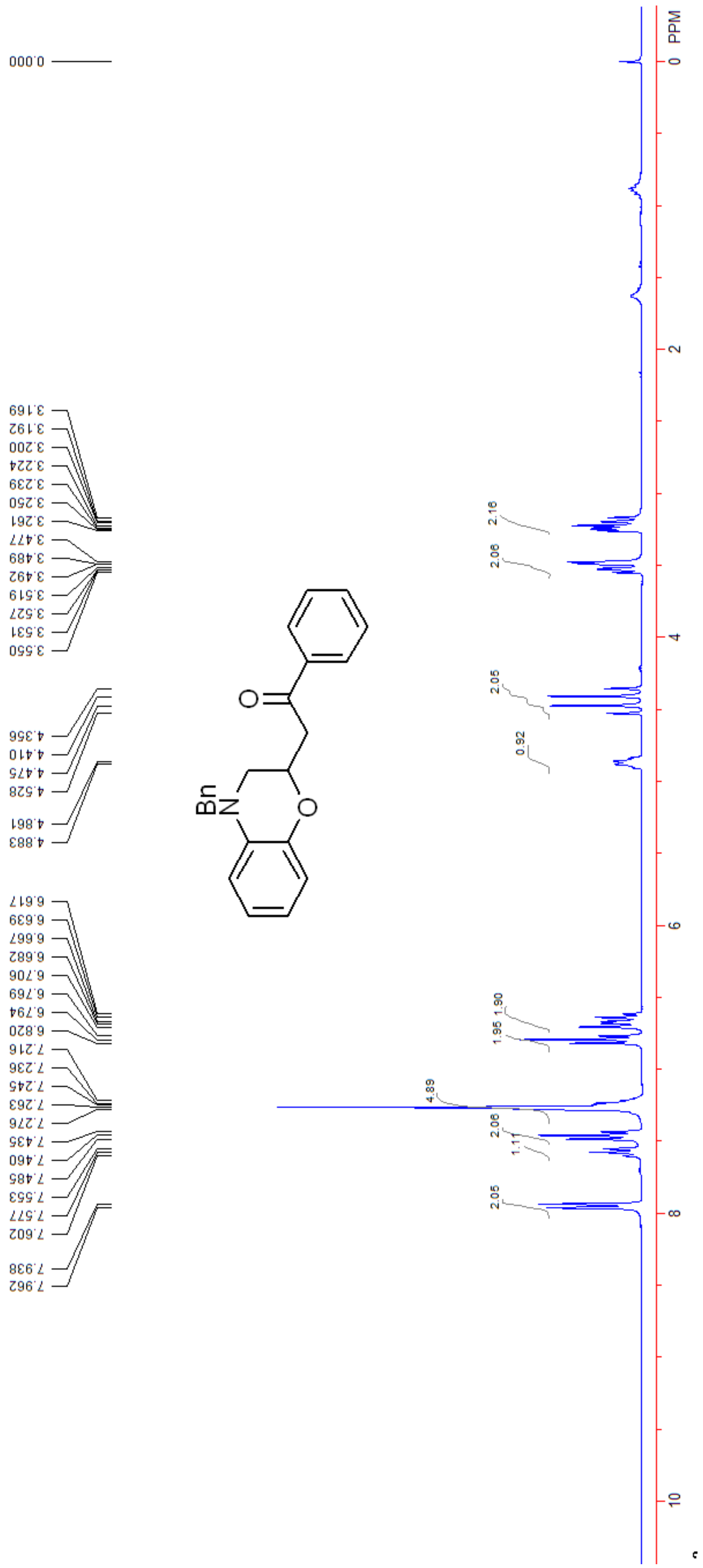
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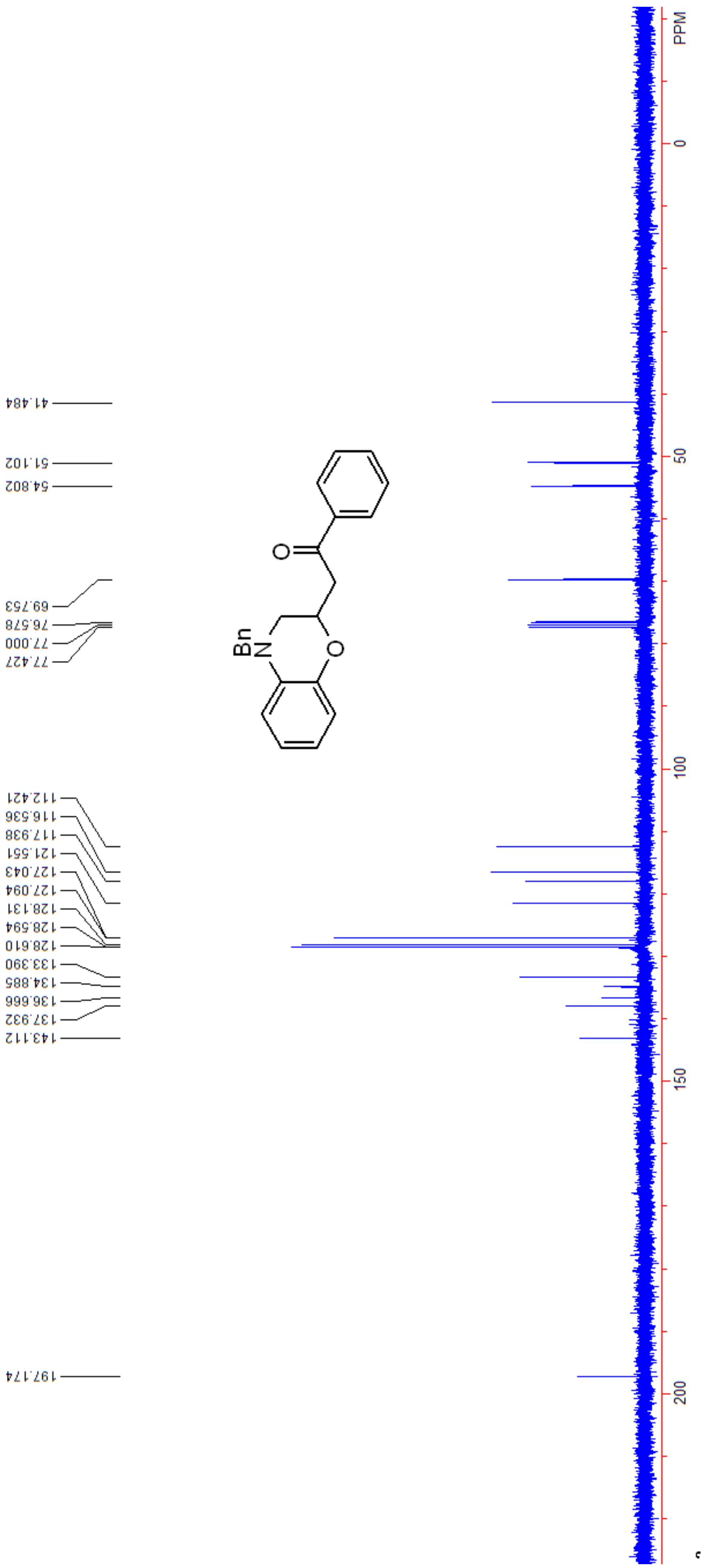
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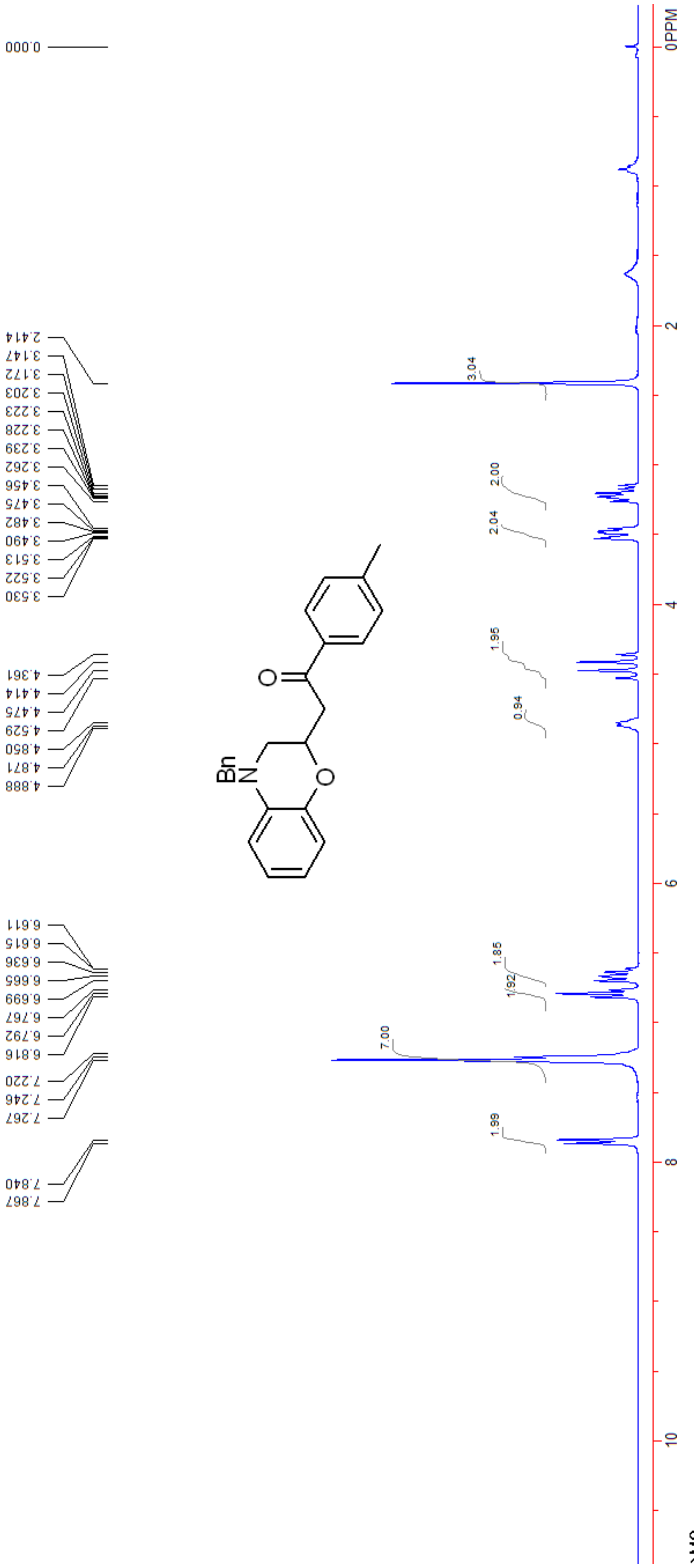
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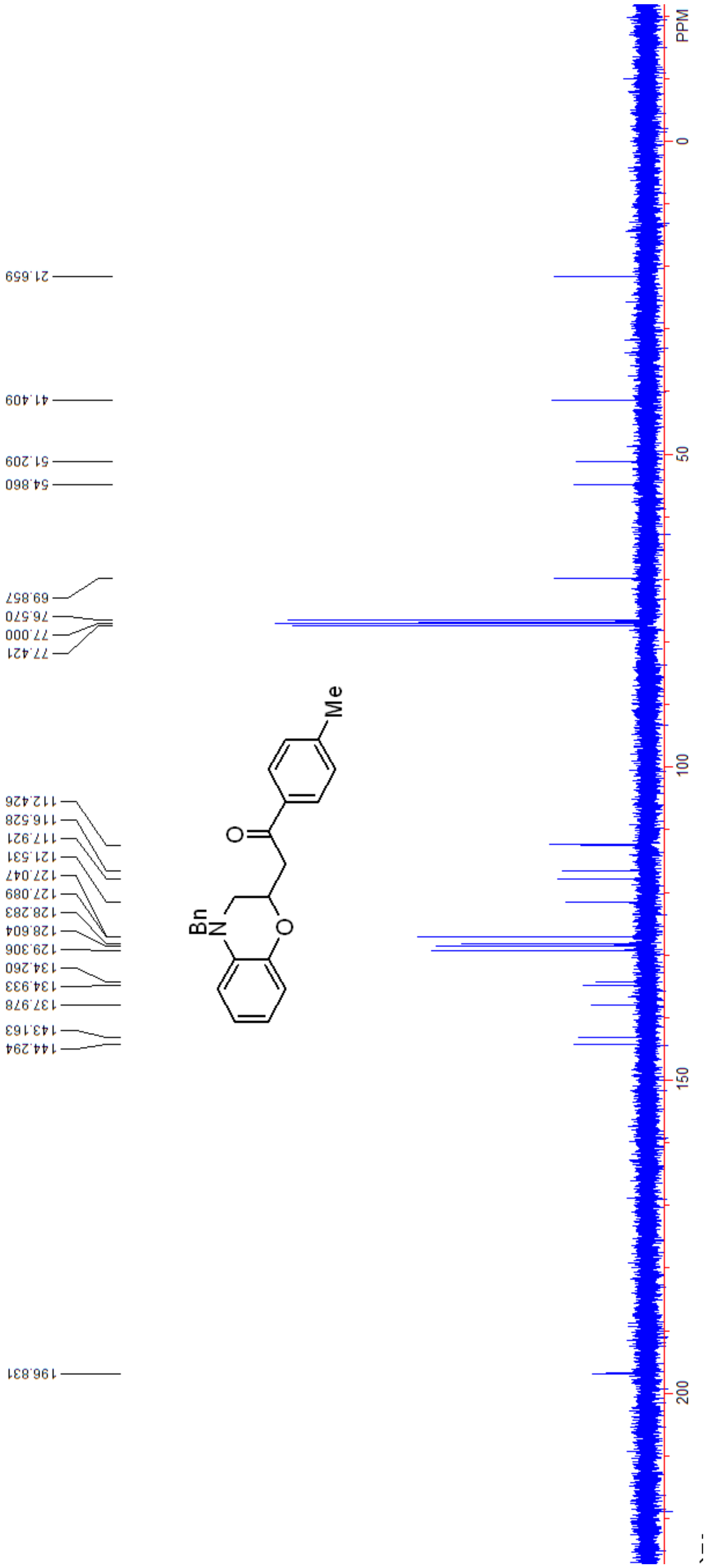
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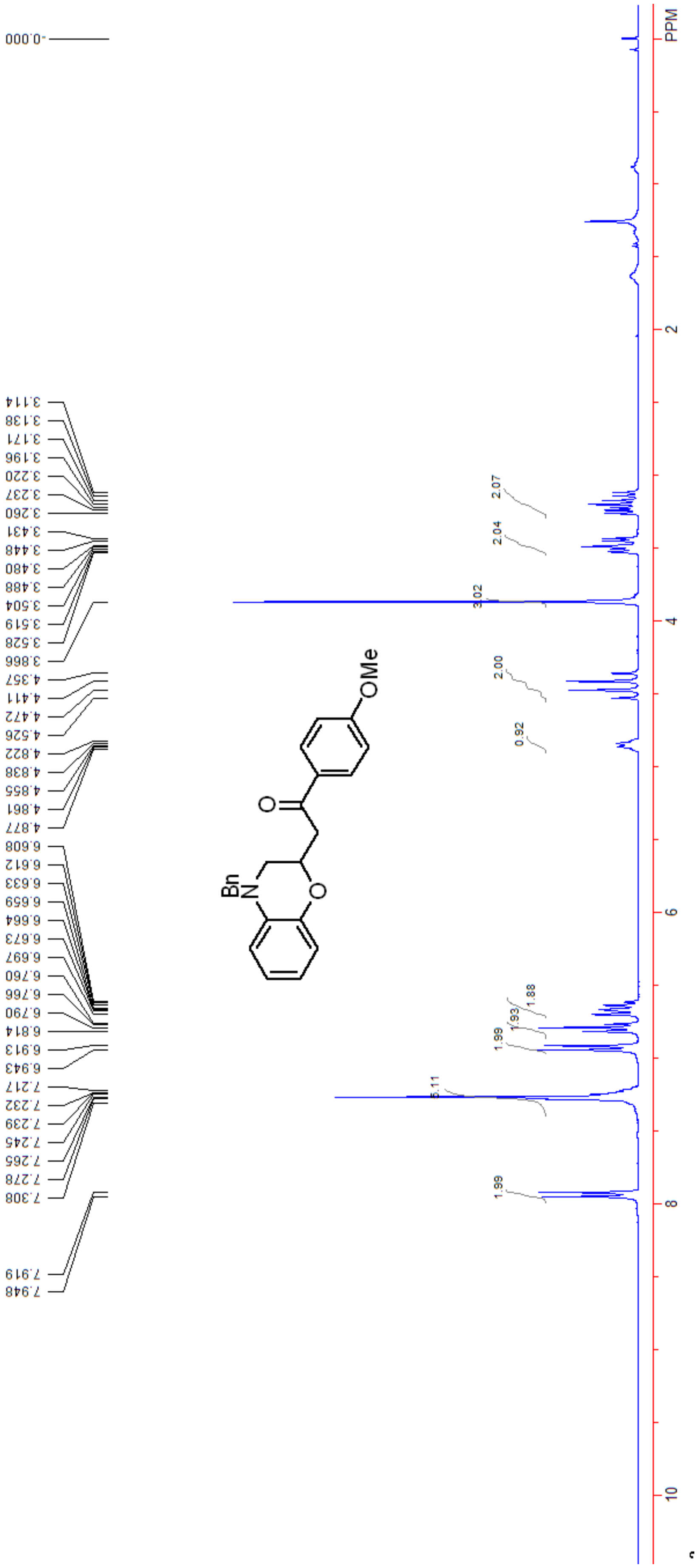
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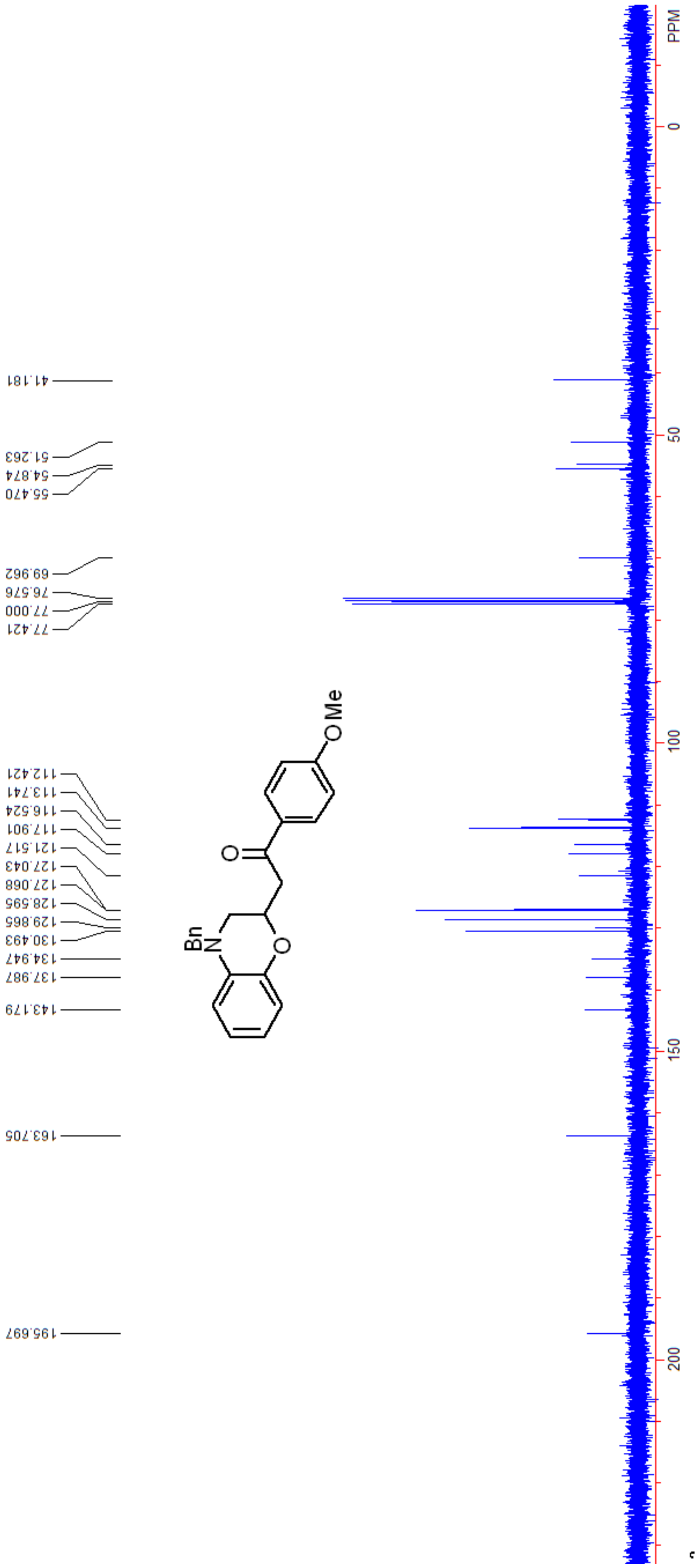
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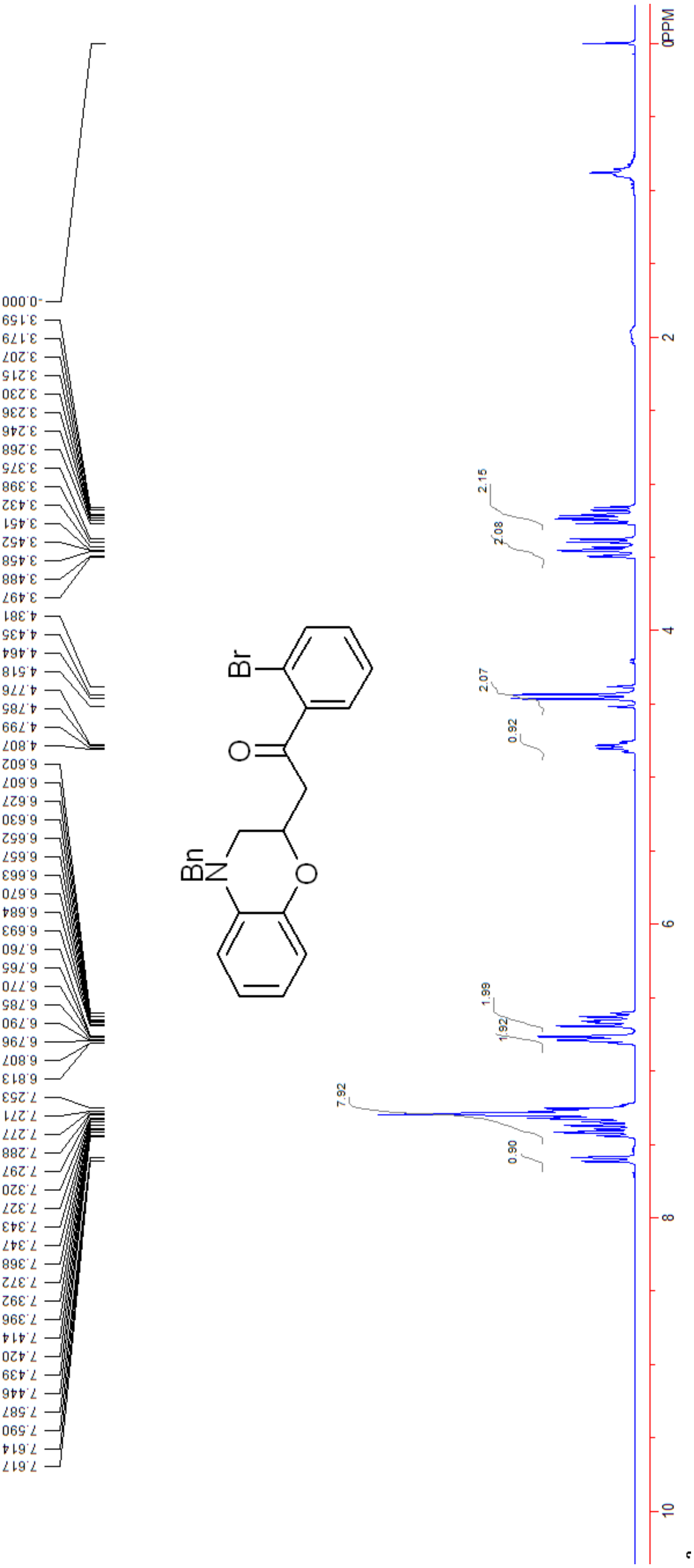
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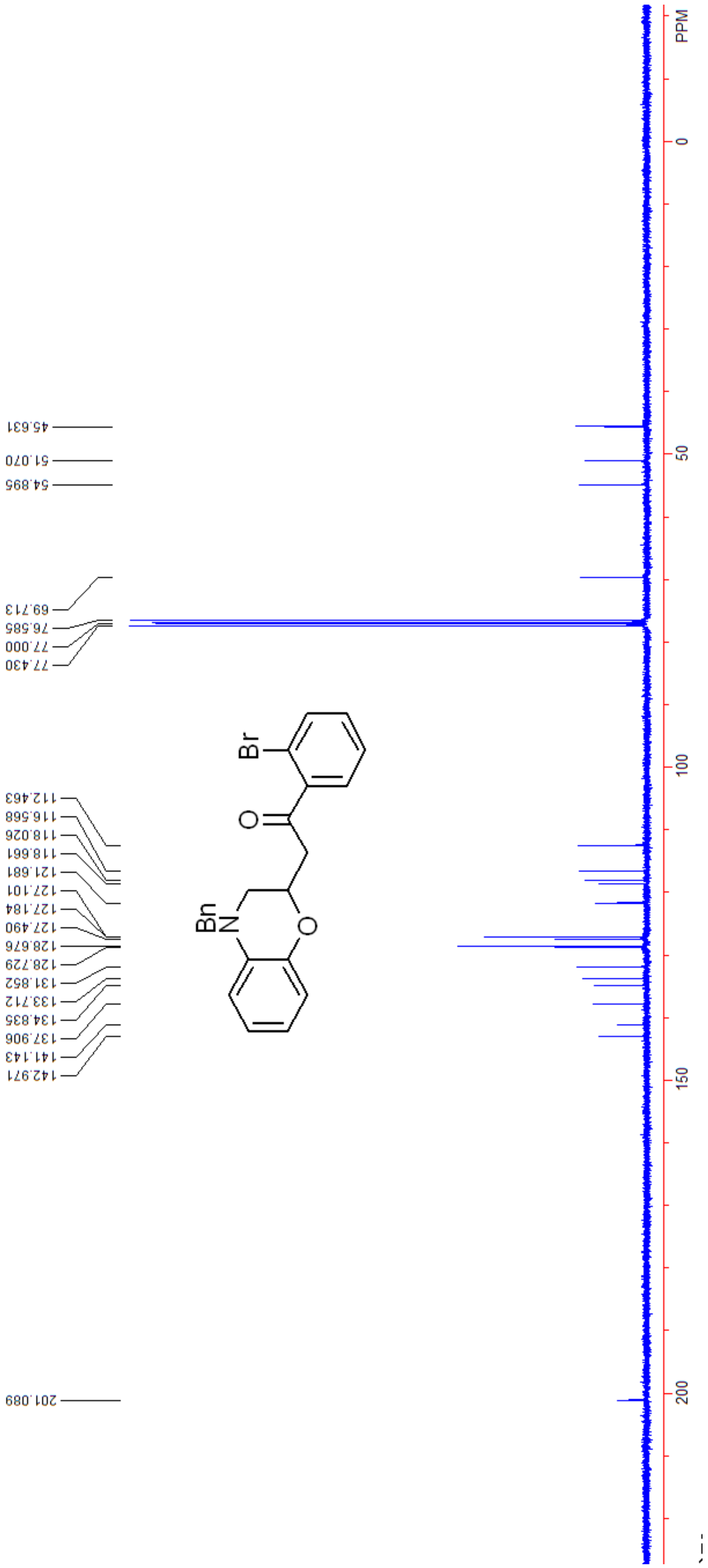
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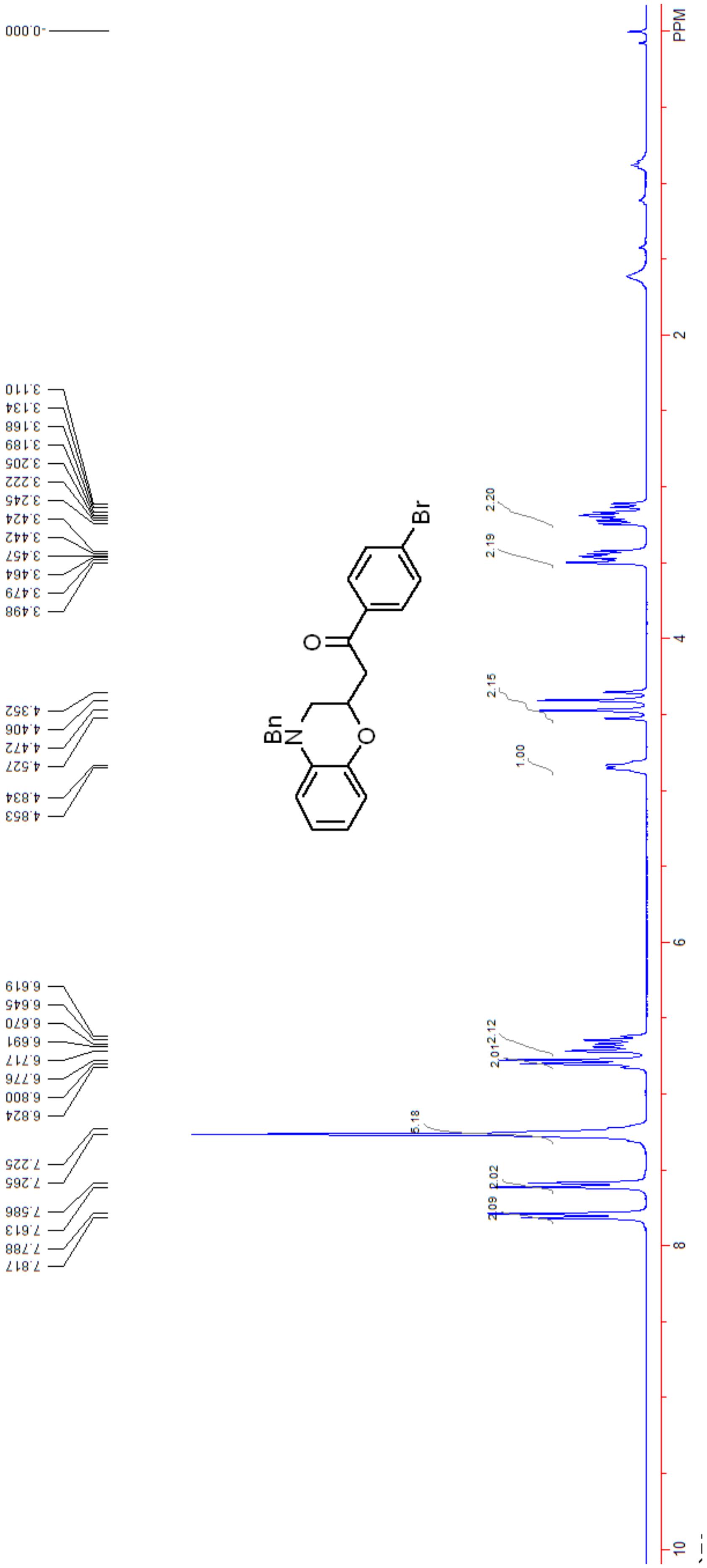
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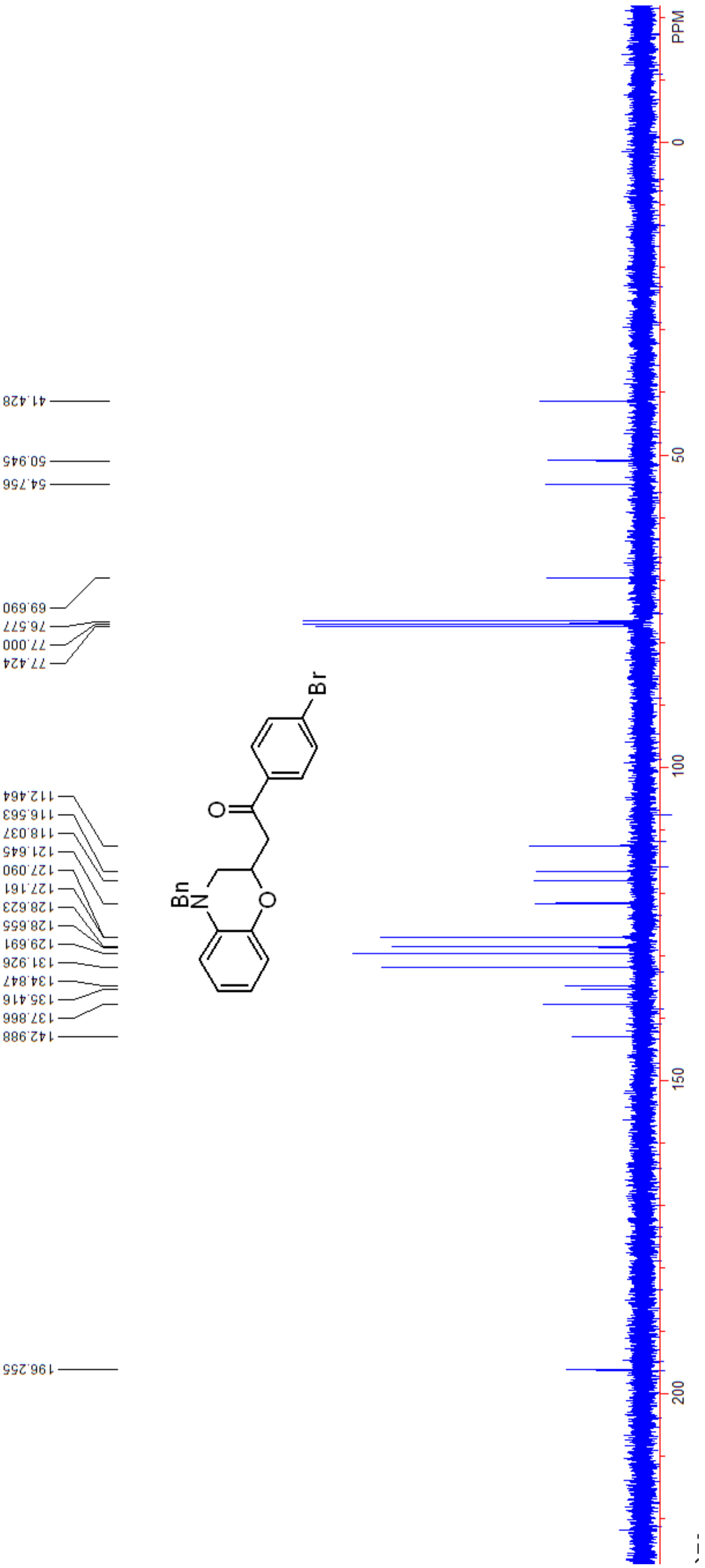
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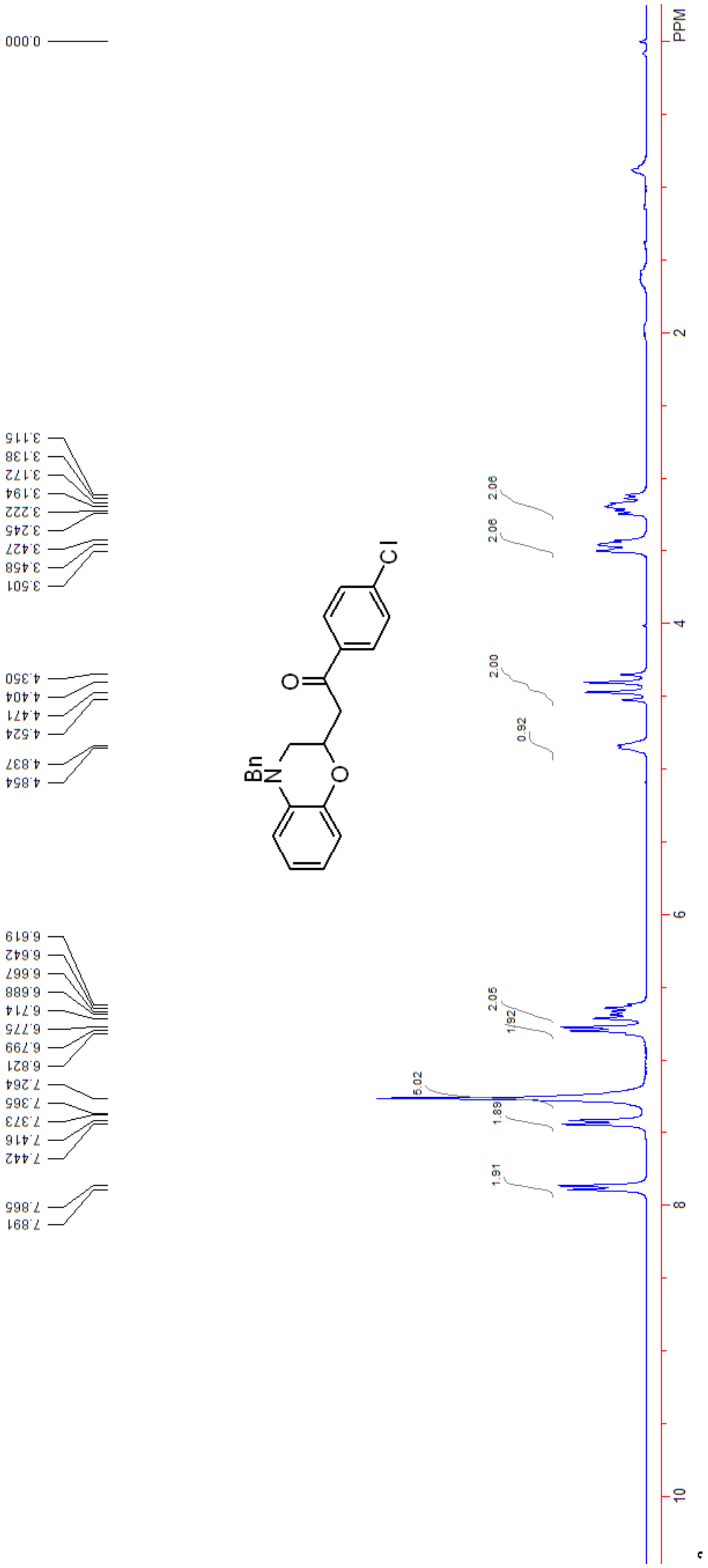
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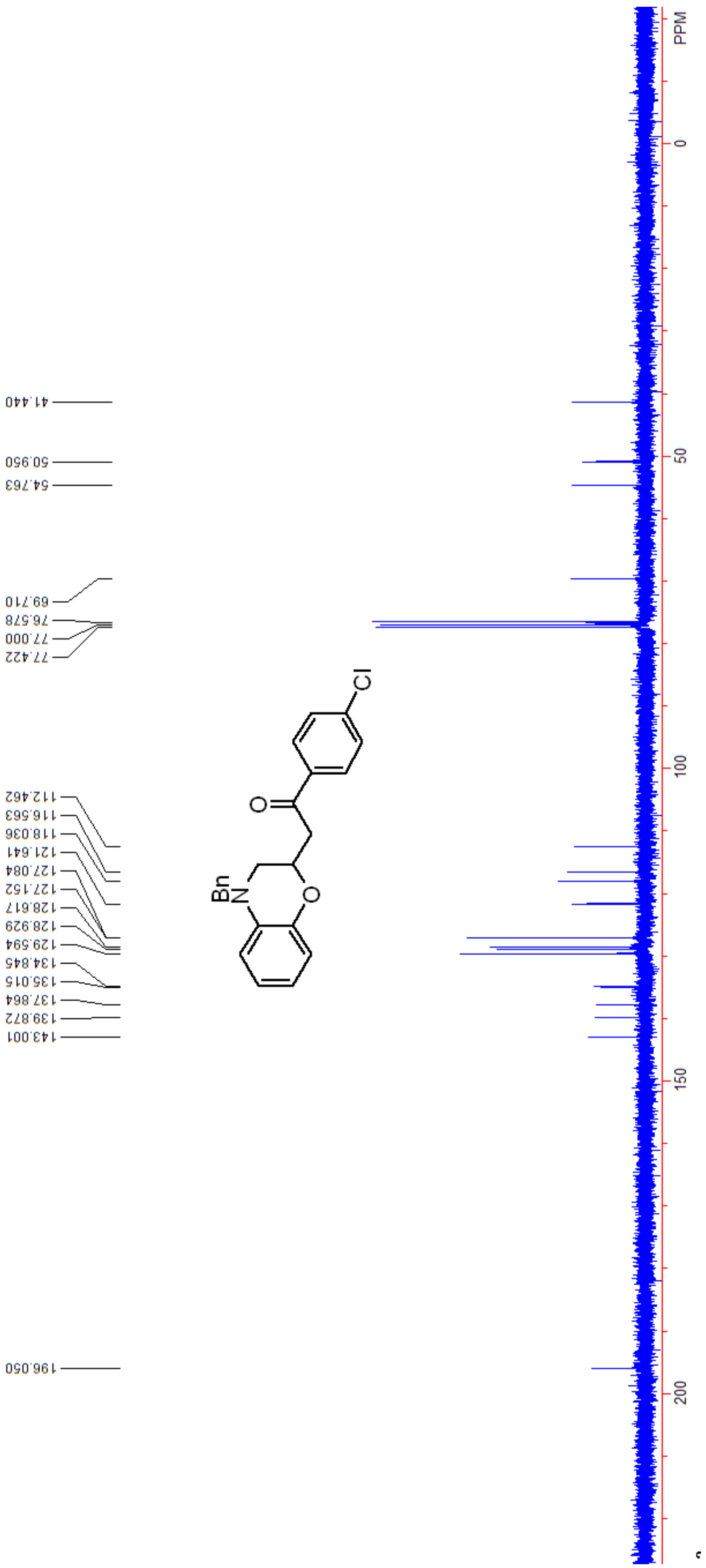
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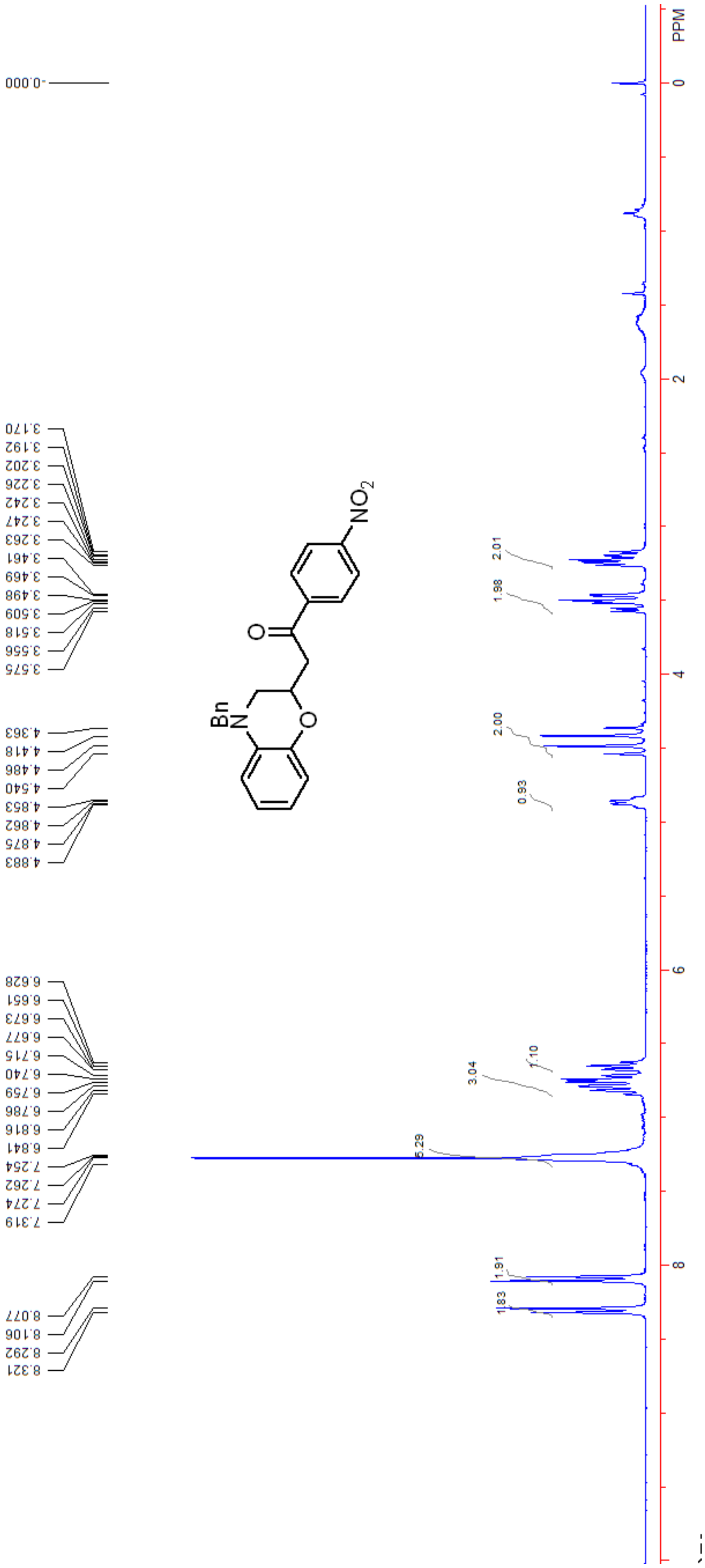
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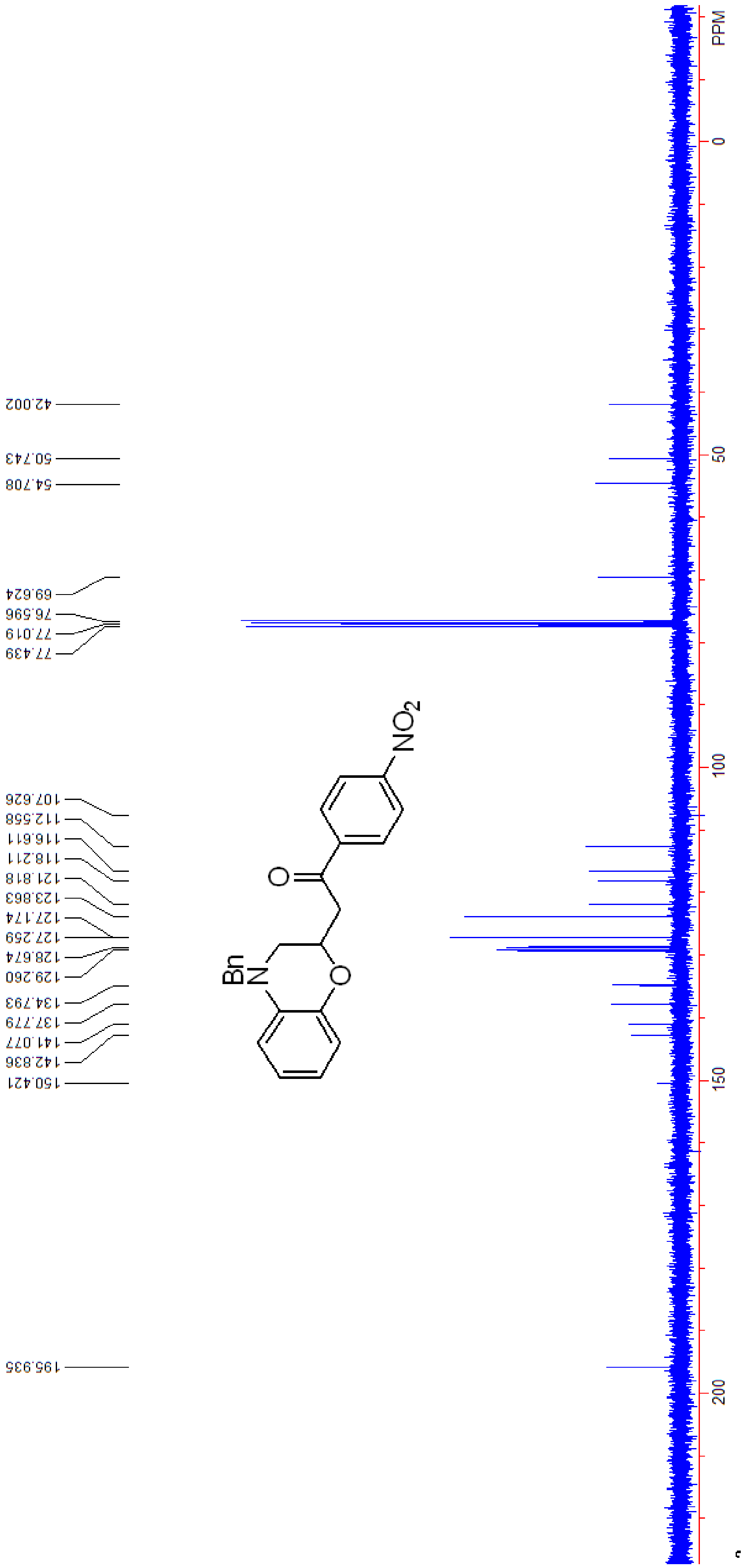
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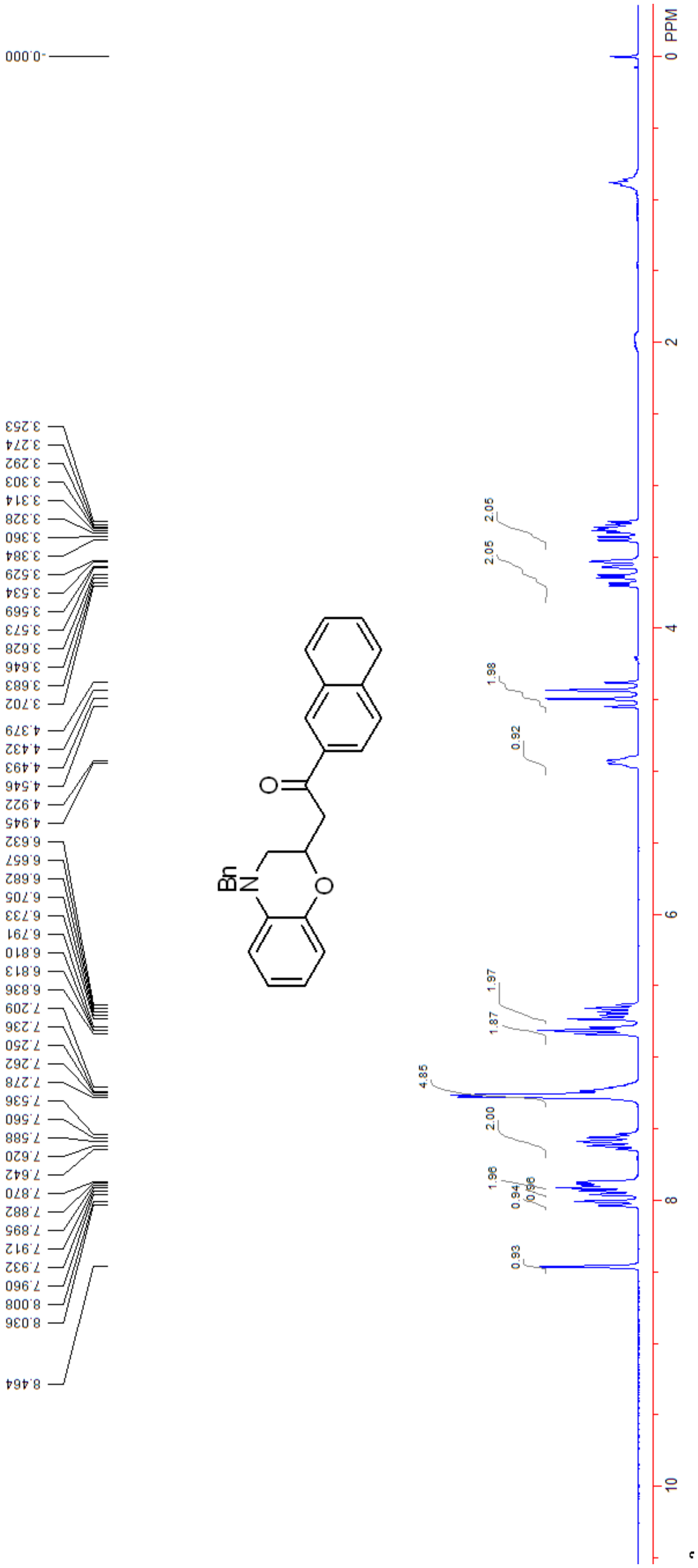
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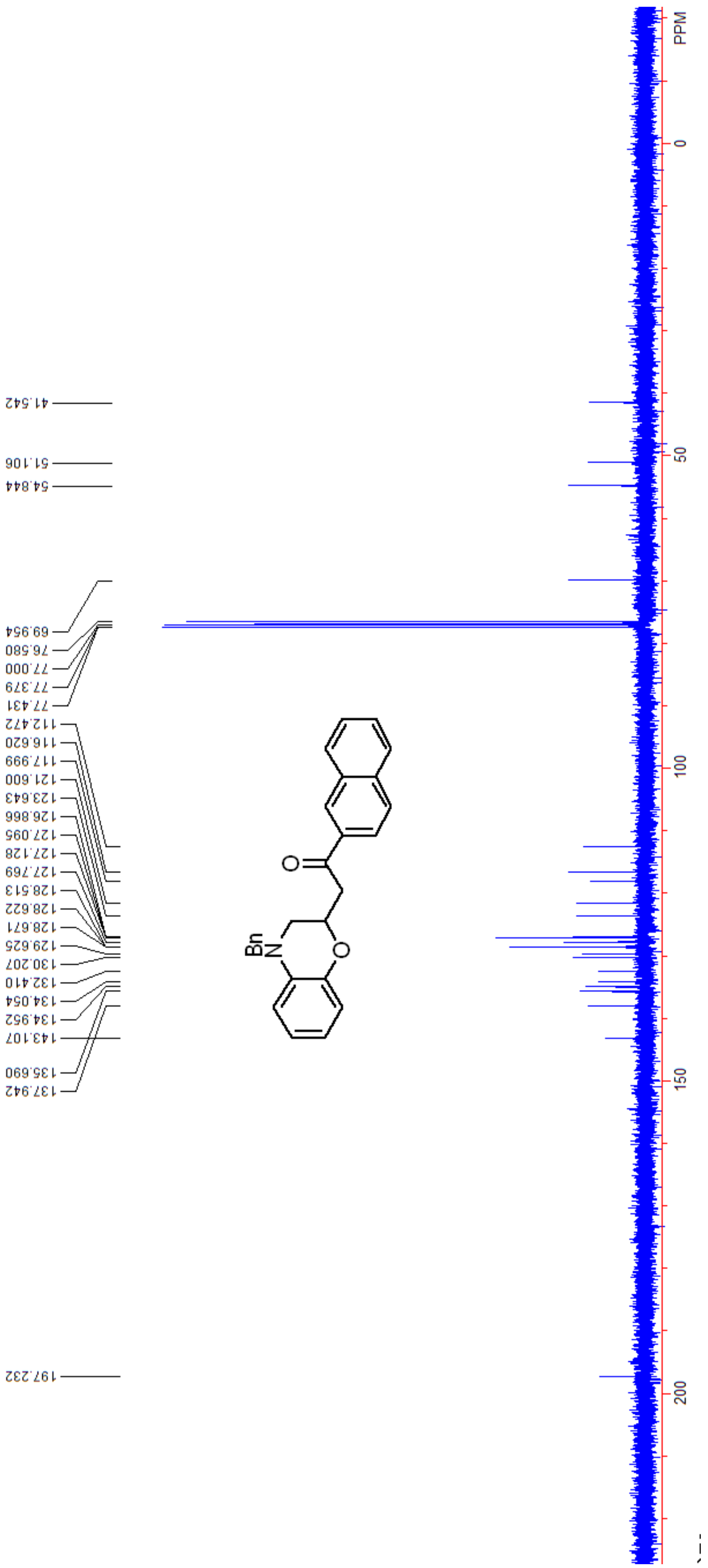
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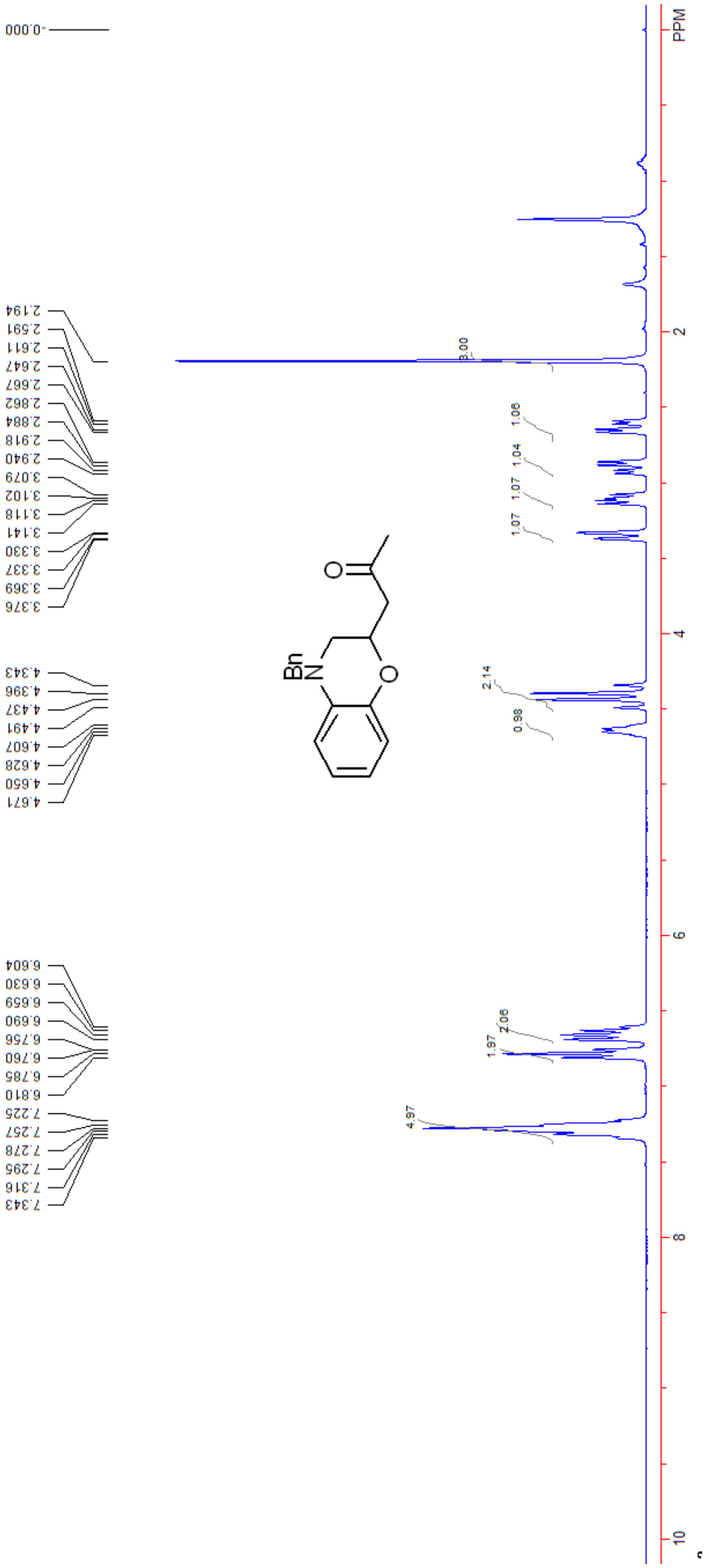
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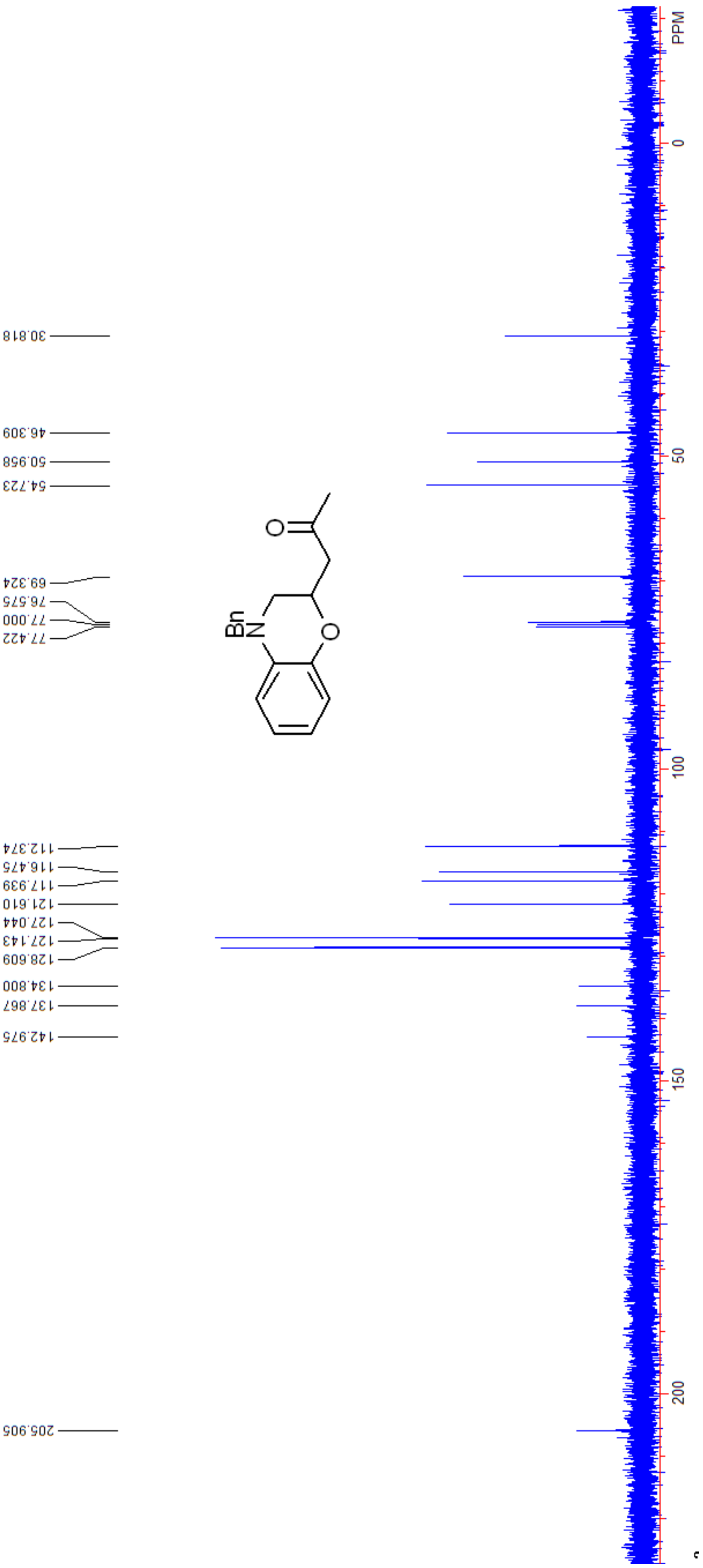
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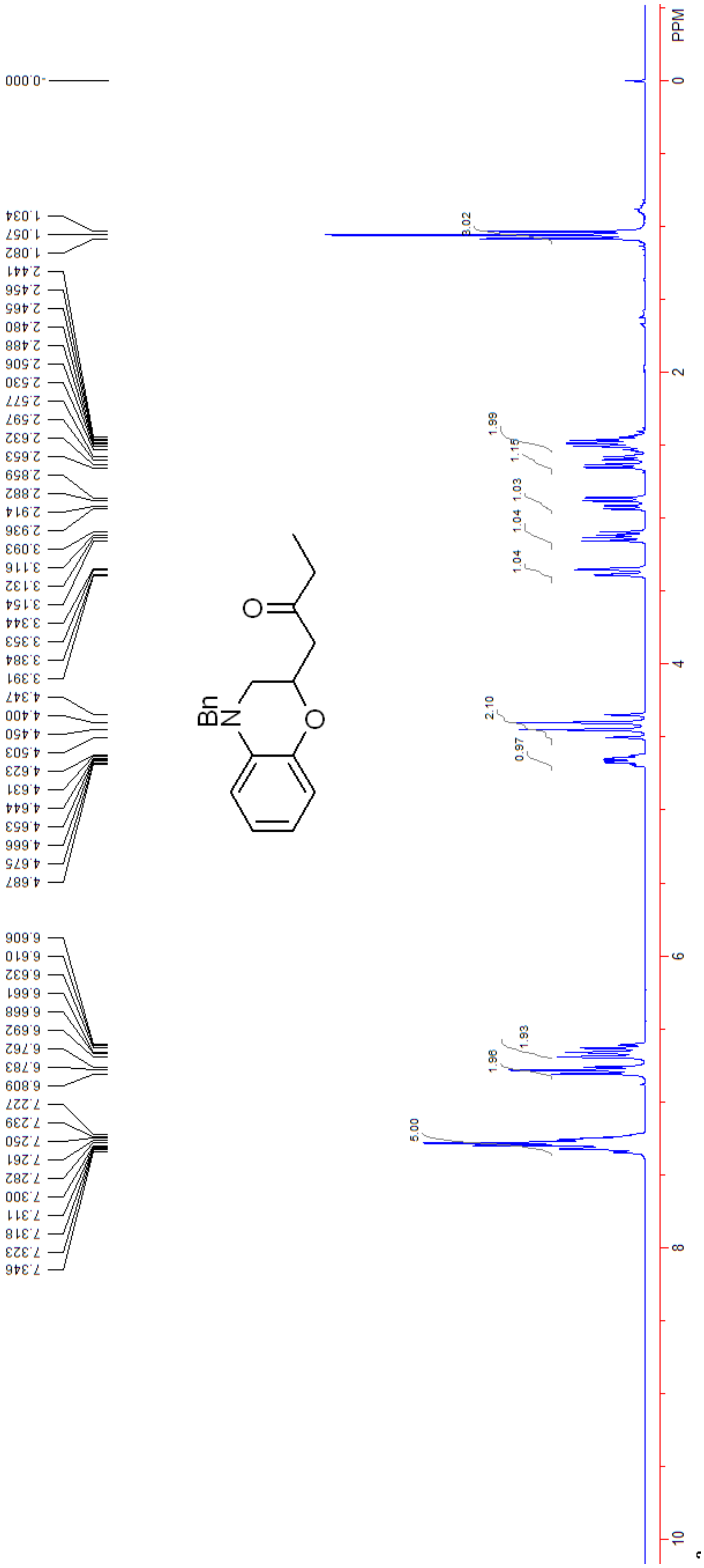
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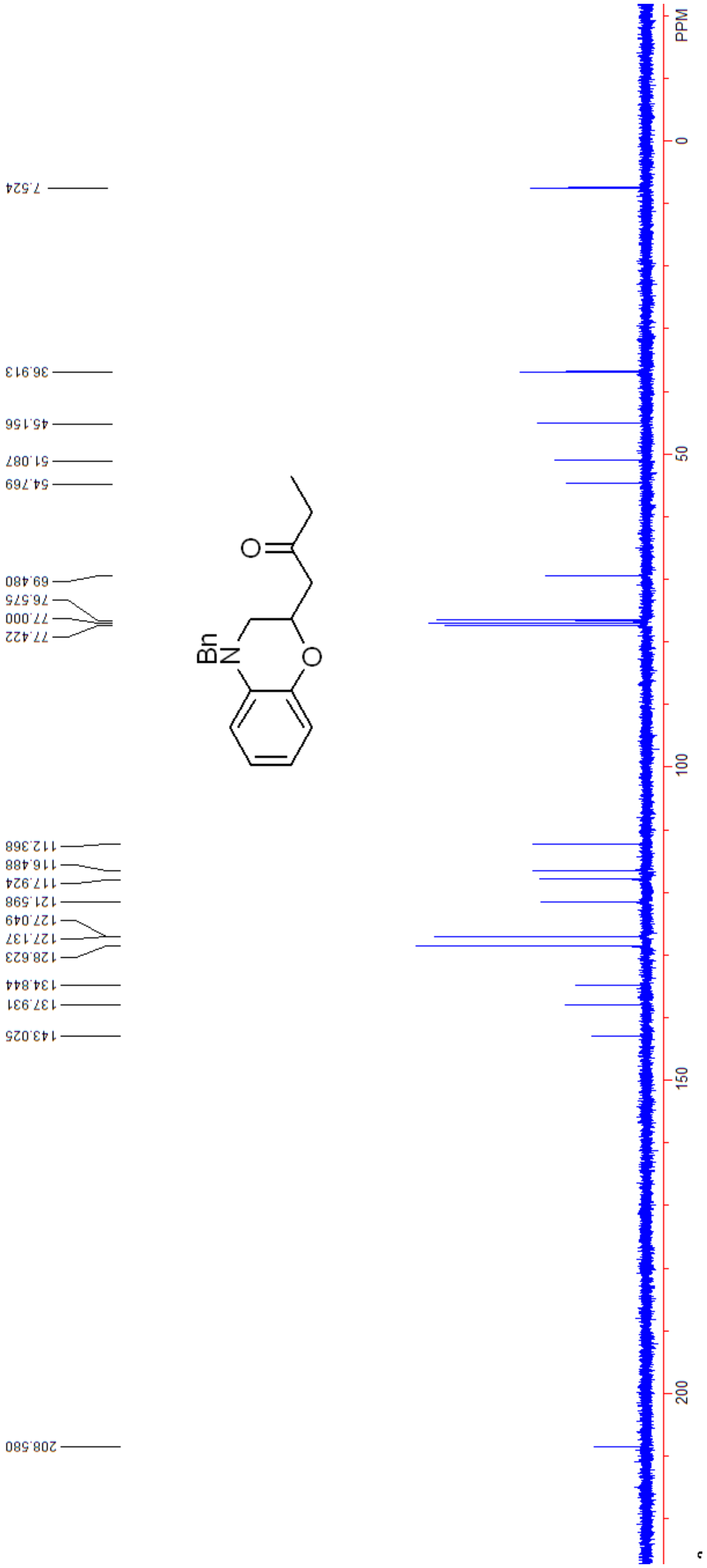
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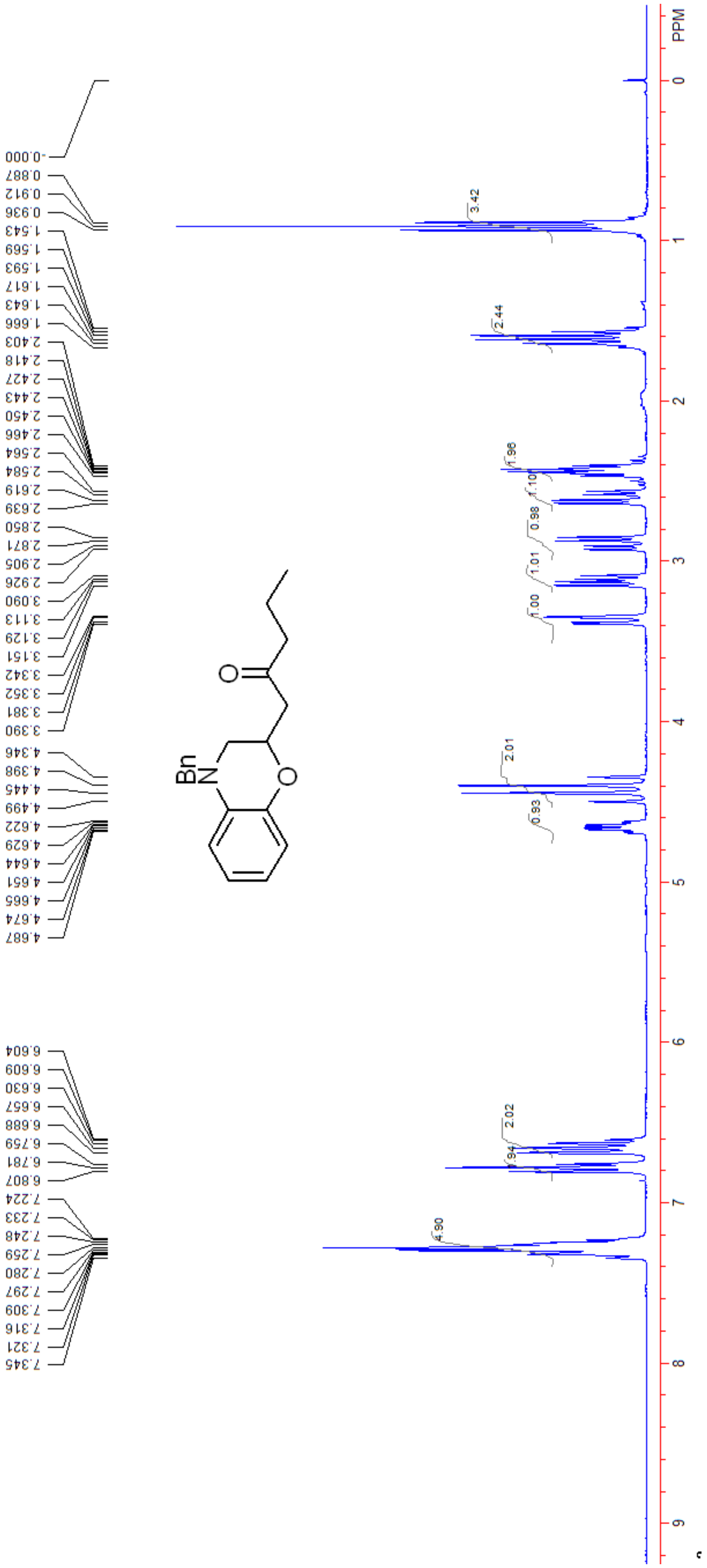
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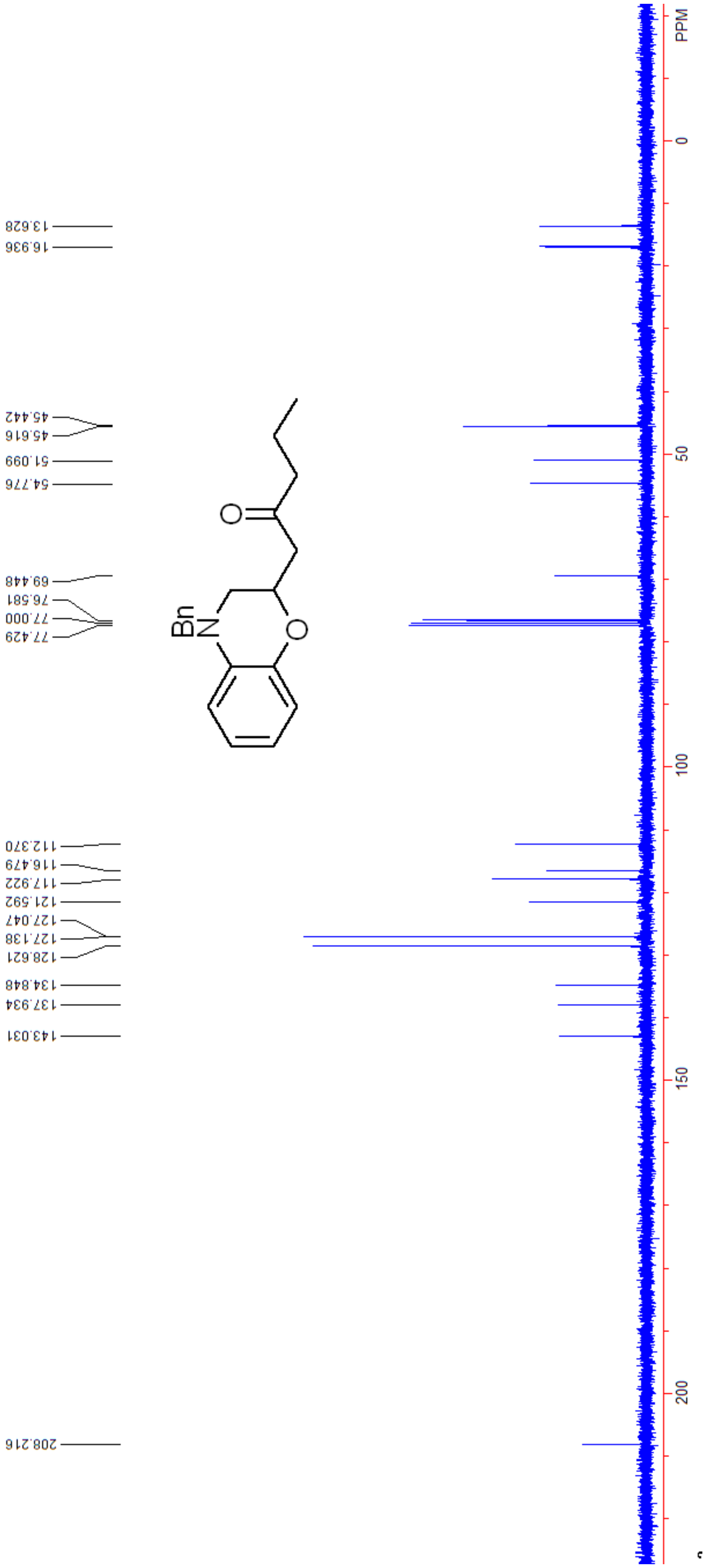
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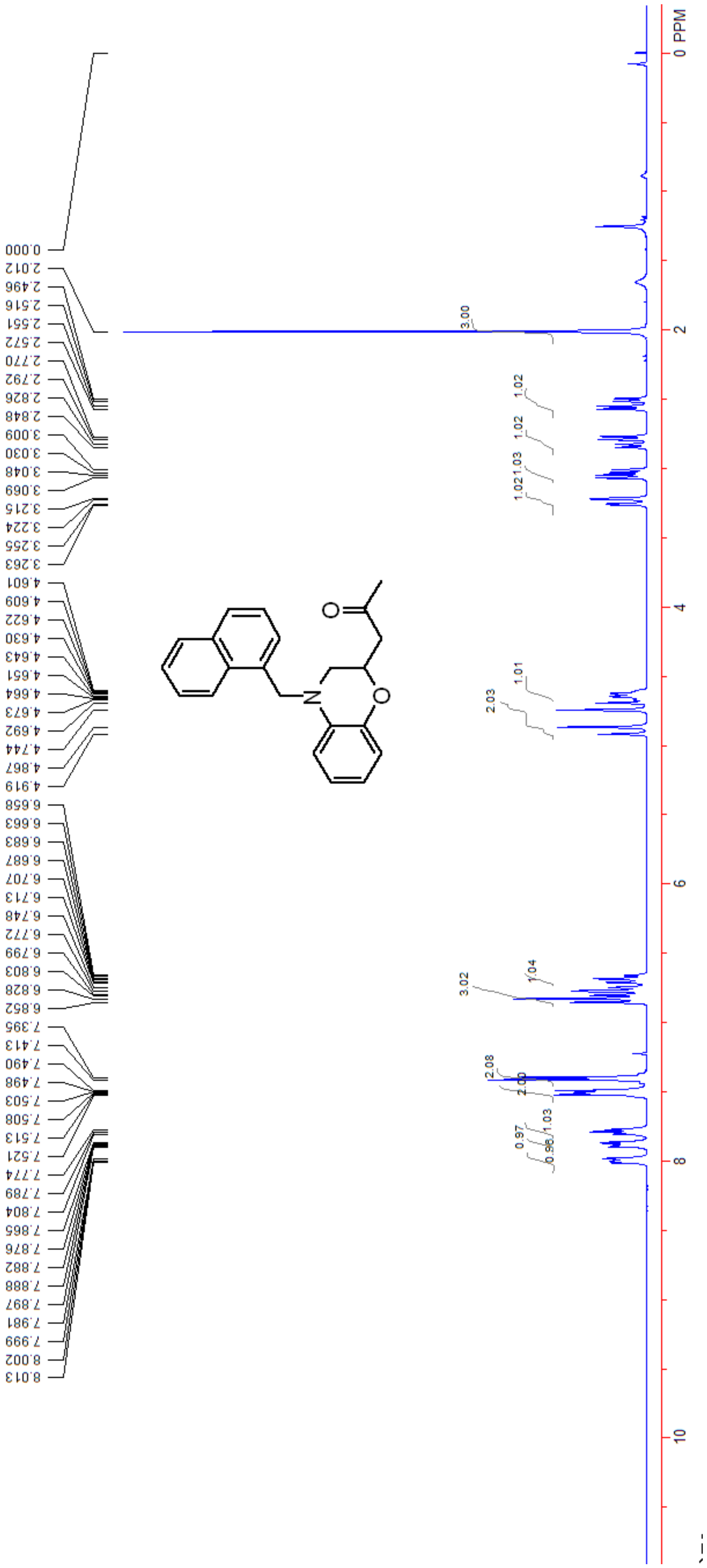
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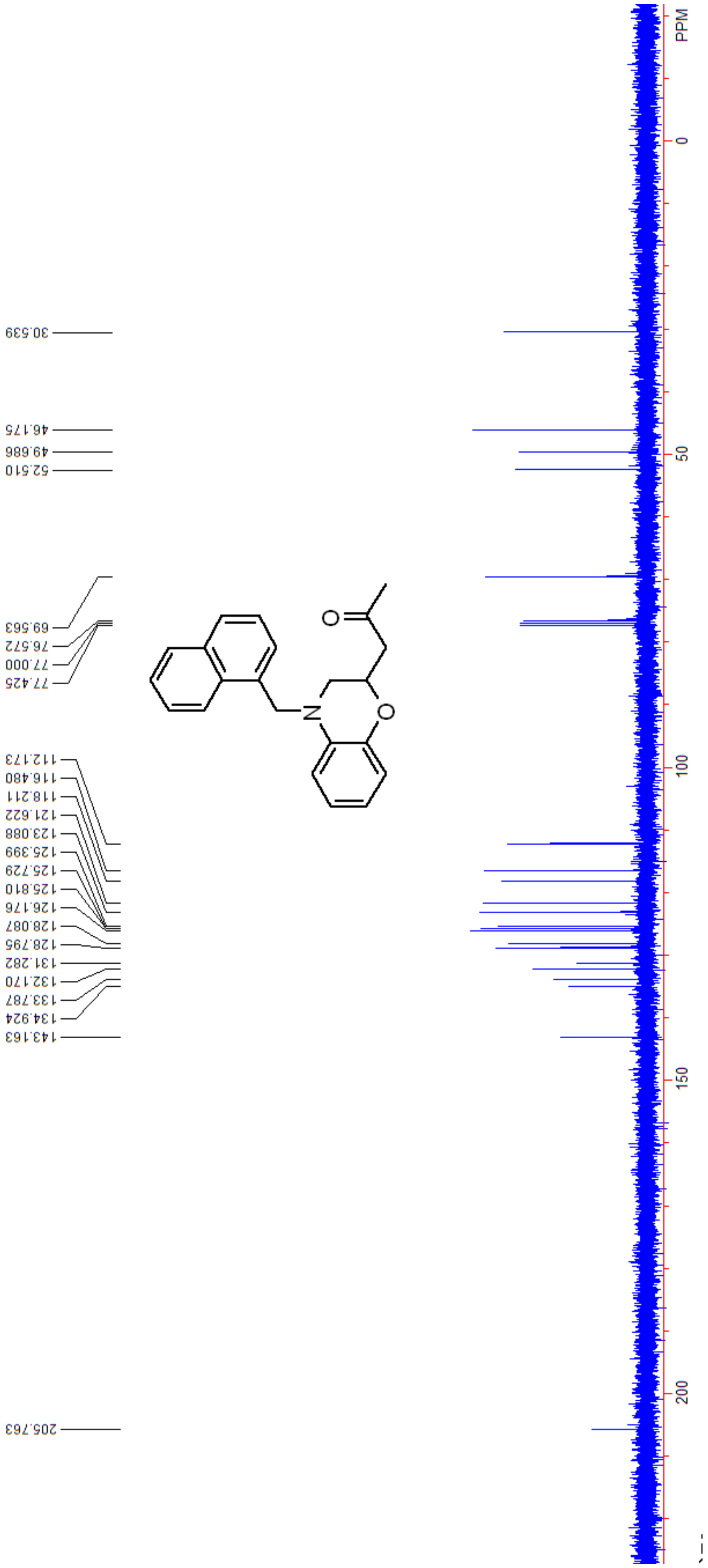
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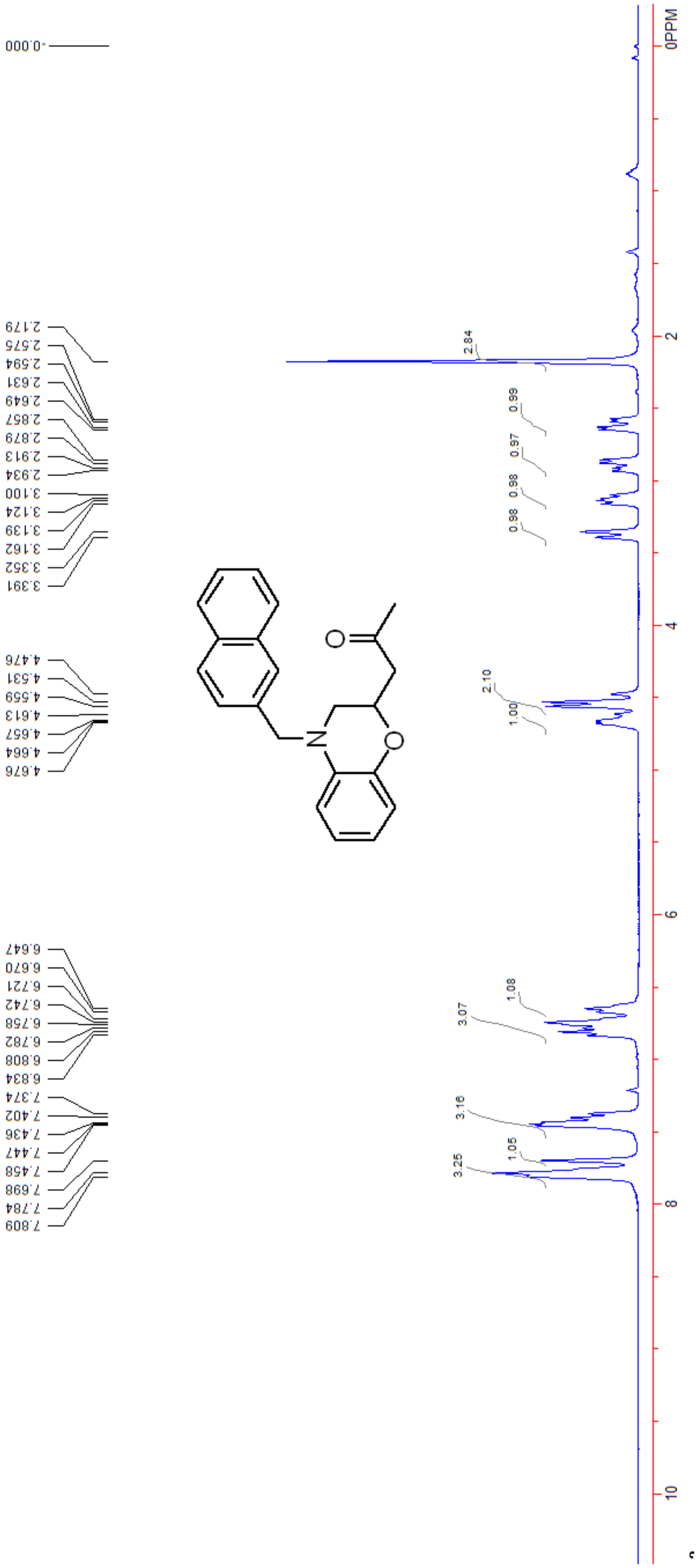
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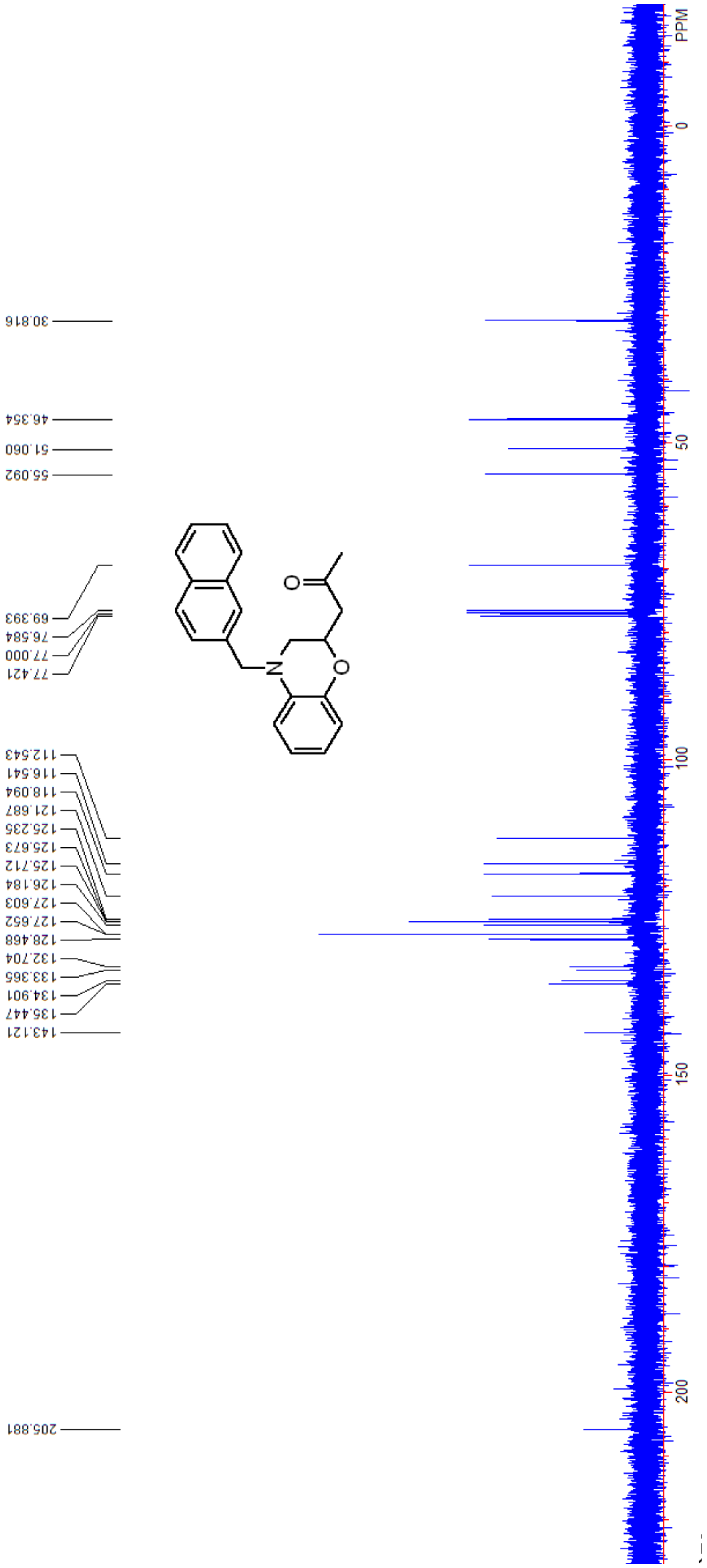
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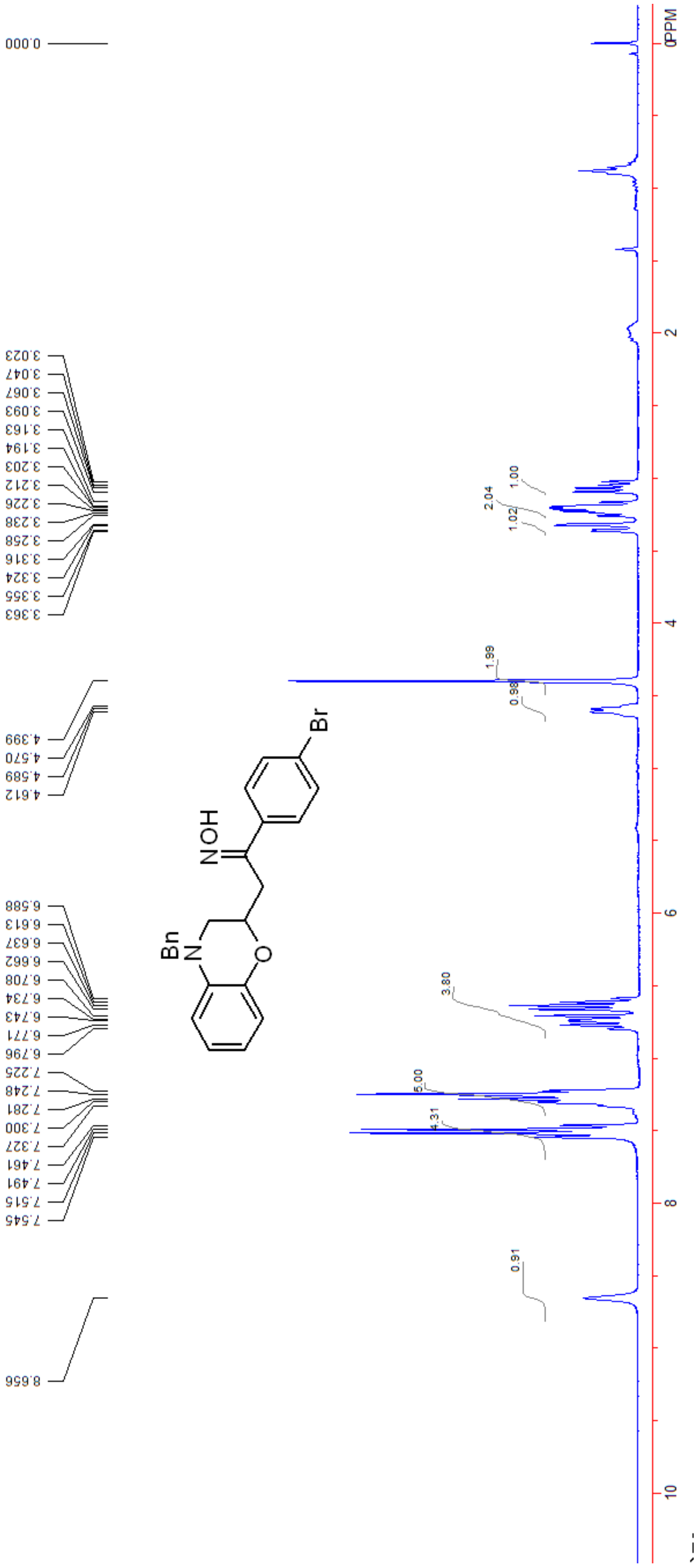
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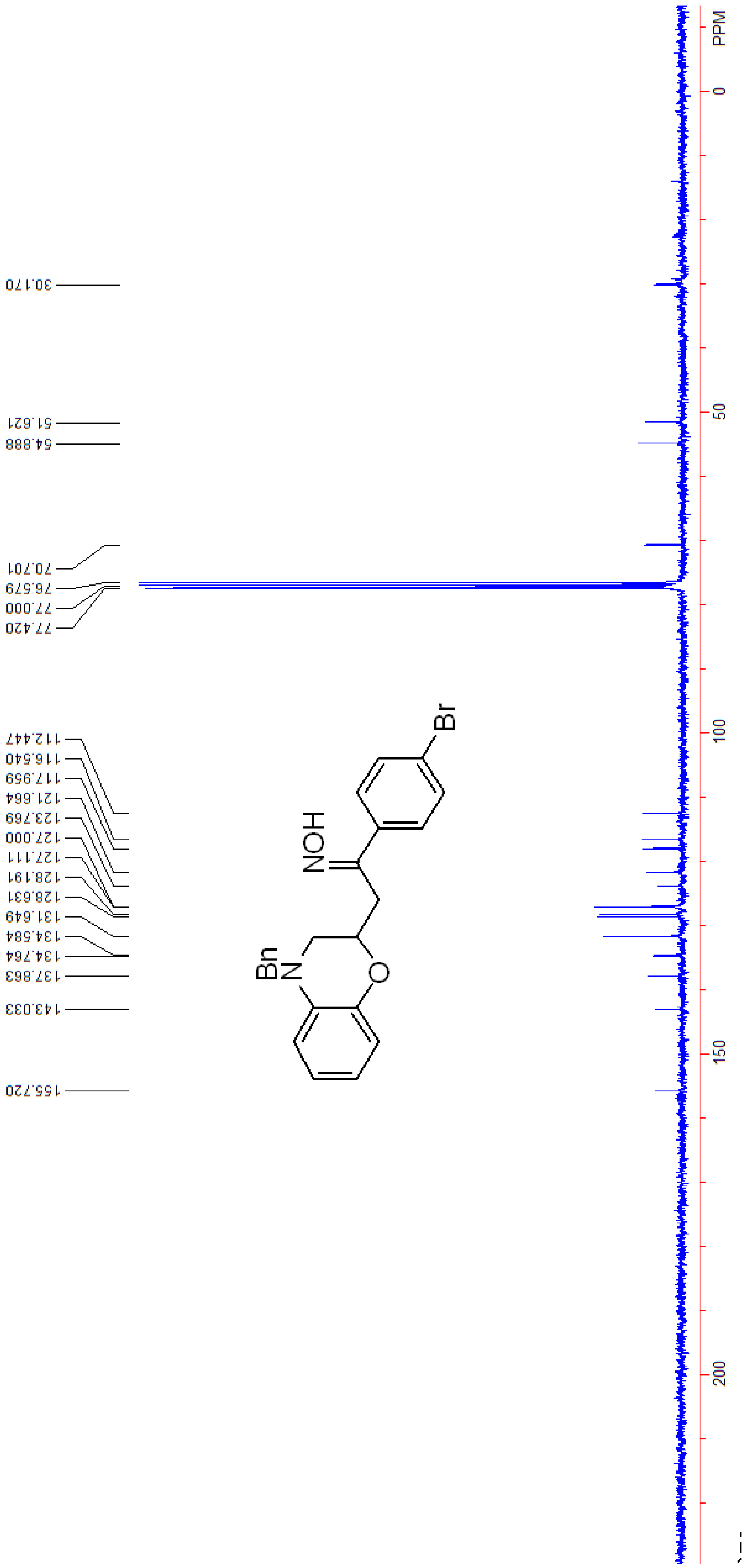
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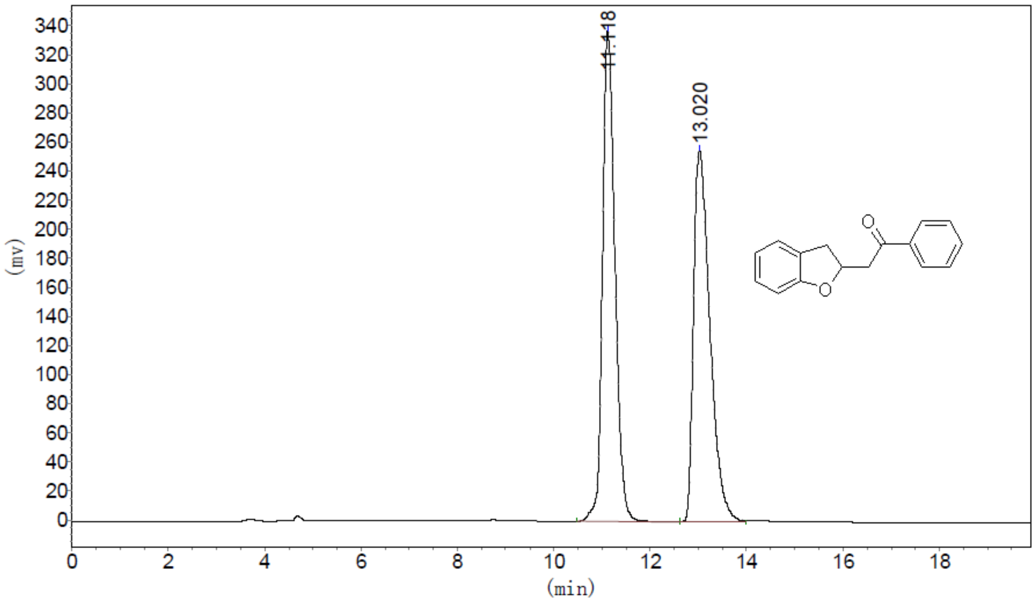
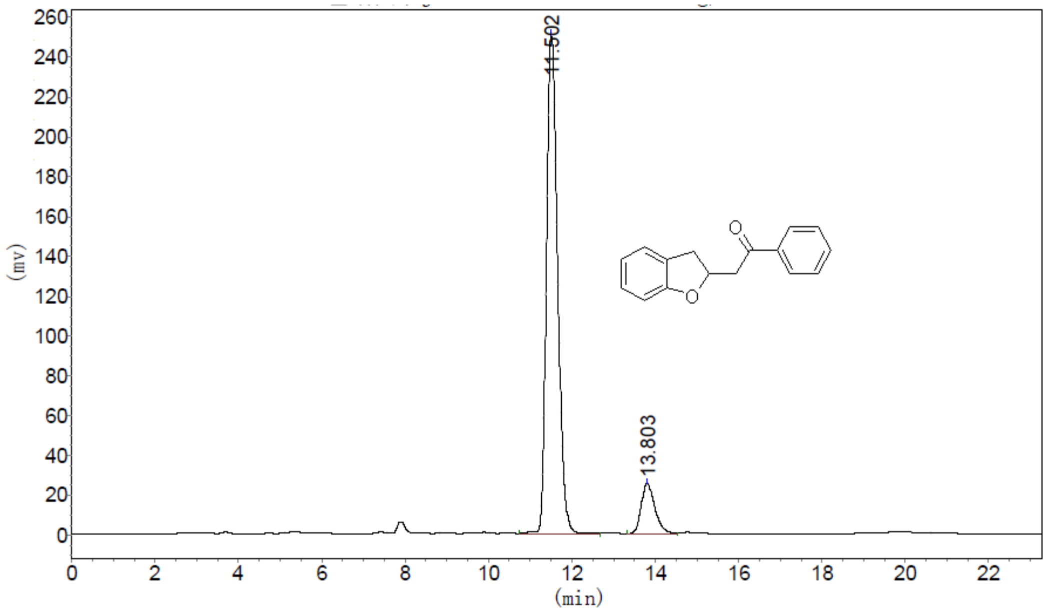
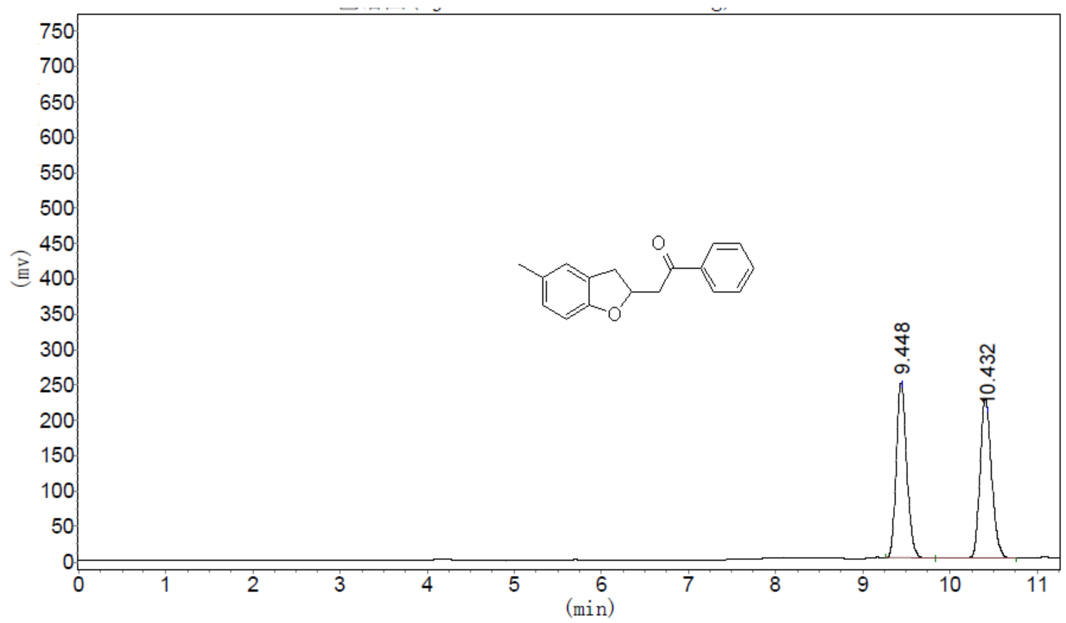


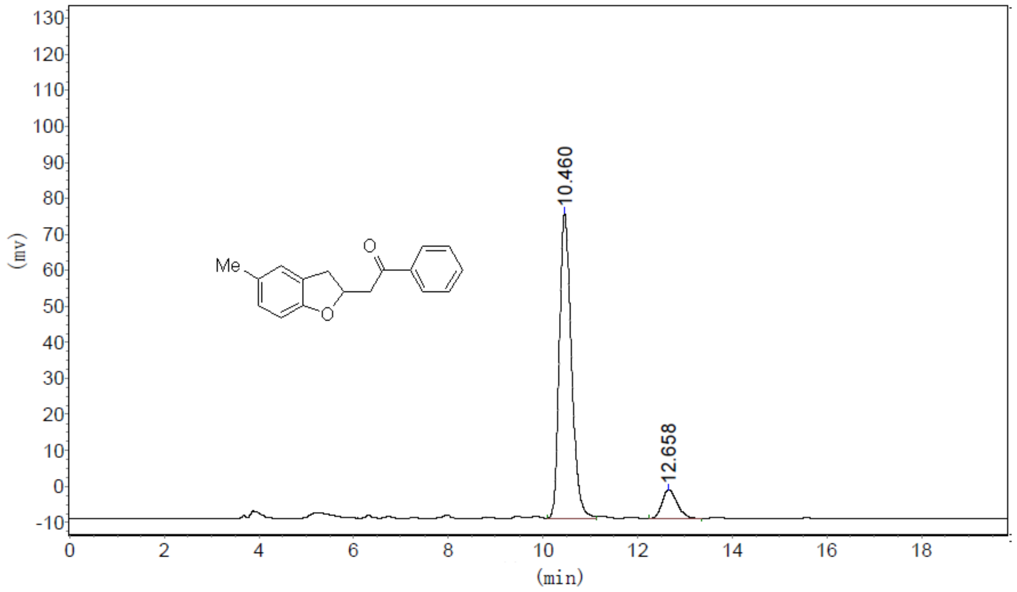
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 118	337553. 750	6044924. 000	50. 0711
2	13. 020	255622. 109	6027764. 000	49. 9289
Total		593175. 859	12072688. 000	100. 0000



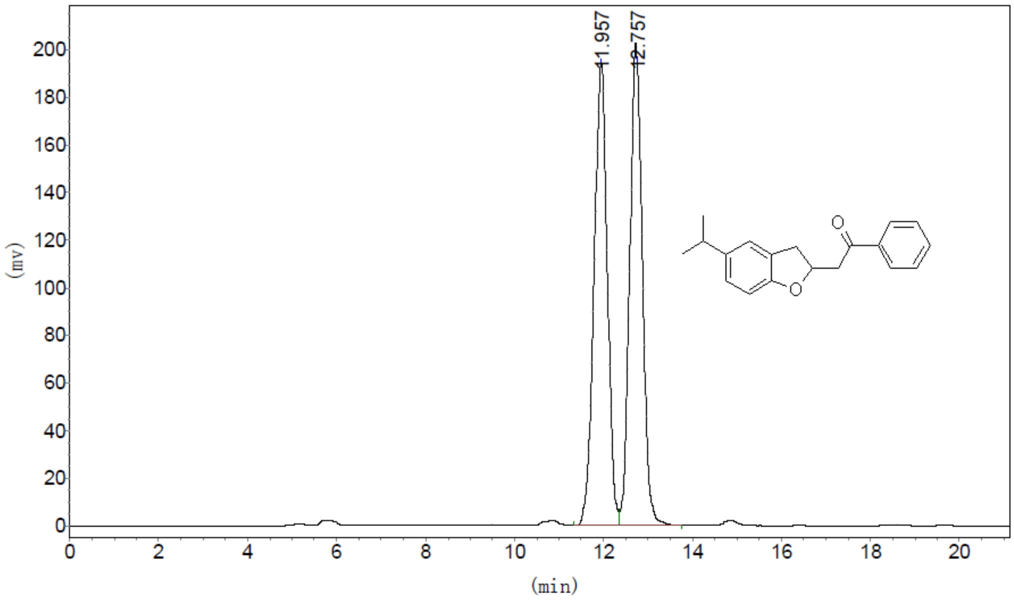
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 502	250178. 422	4671990. 500	89. 0156
2	13. 803	25149. 906	576518. 625	10. 9844
Total		275328. 328	5248509. 125	100. 0000



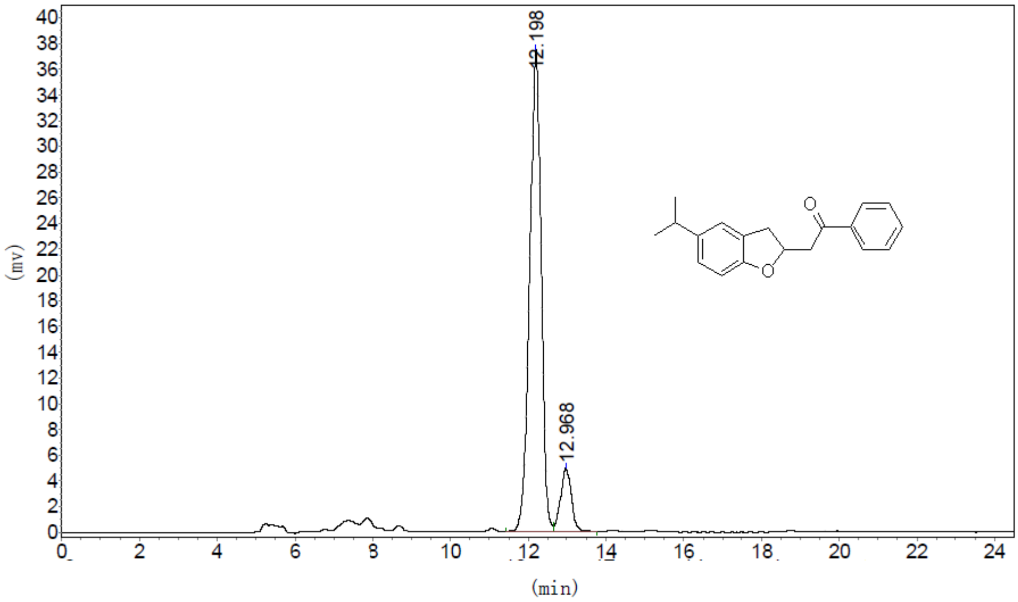
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9. 448	248361. 938	2151104. 750	49. 3778
2	10. 432	221846. 969	2205315. 250	50. 6222
Total		470208. 906	4356420. 000	100. 0000



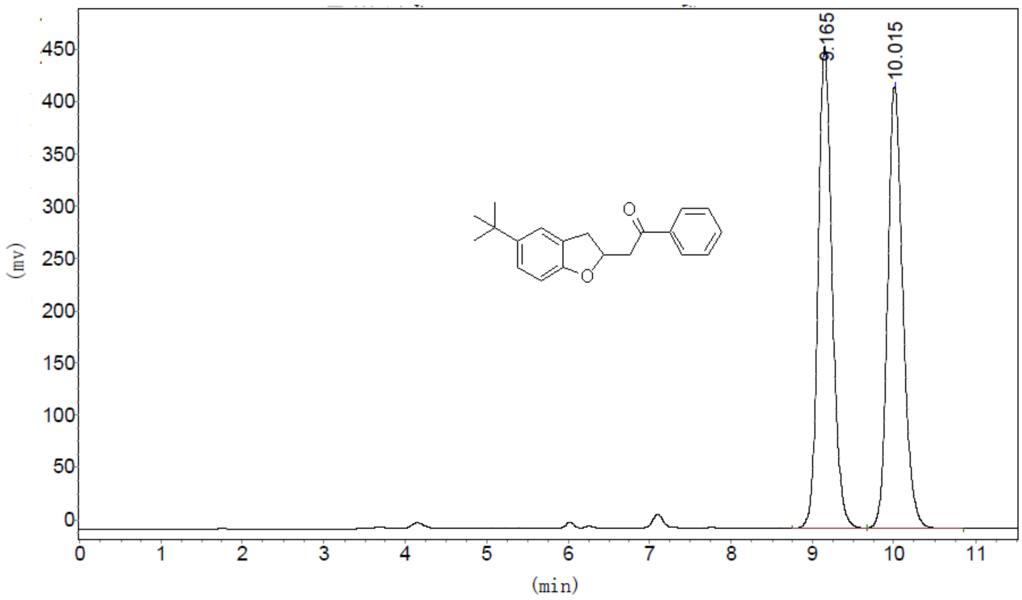
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	10. 460	85058. 367	1511738. 250	89. 3827
2	12. 658	8059. 916	179572. 047	10. 6173
Total		93118. 283	1691310. 297	100. 0000



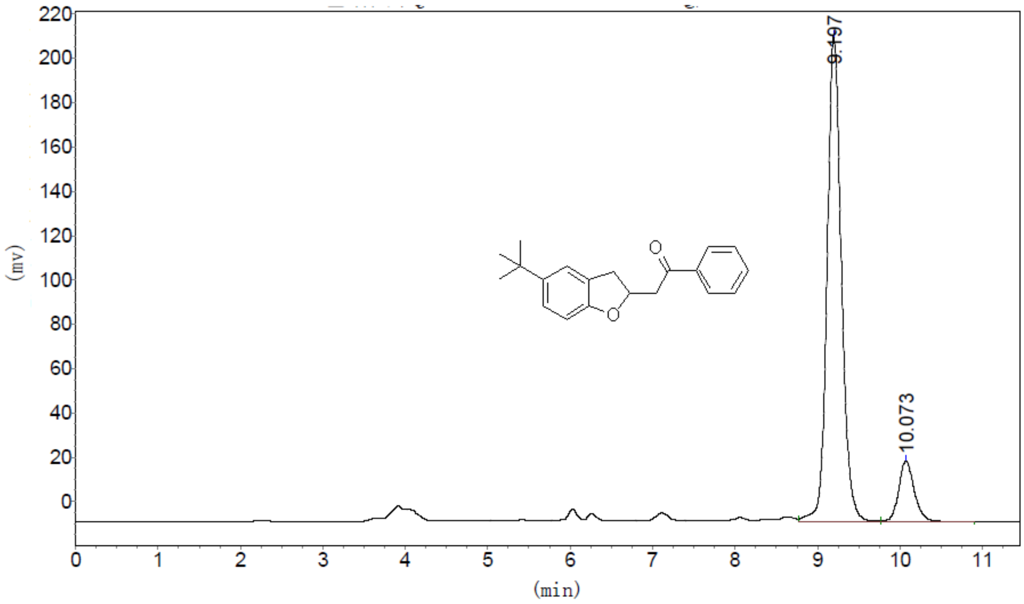
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 957	193580. 969	4010442. 250	49. 8899
2	12. 757	200139. 109	4028139. 500	50. 1101
Total		393720. 078	8038581. 750	100. 0000



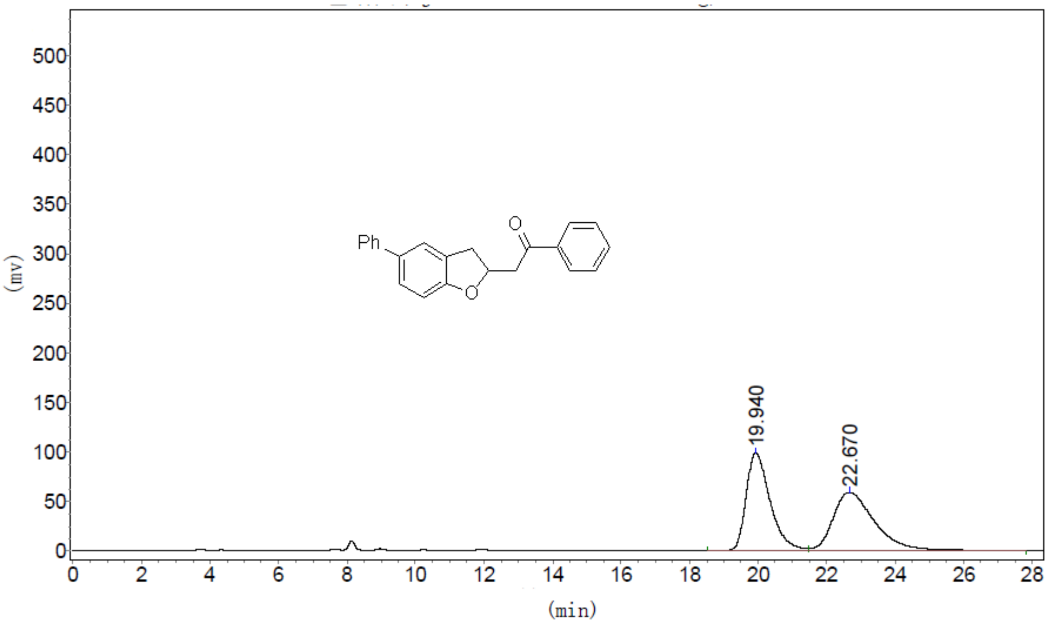
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12. 198	37448. 320	776115. 188	88. 9387
2	12. 968	4927. 634	96525. 133	11. 0613
Total		42375. 954	872640. 320	100. 0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9. 165	458019. 031	5527373. 000	49. 8895
2	10. 015	422654. 813	5551849. 500	50. 1105
Total		880673. 844	11079222. 500	100. 0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9. 197	218941. 500	2621254. 000	87. 9915
2	10. 073	27469. 727	357731. 781	12. 0085
Total		246411. 227	2978985. 781	100. 0000



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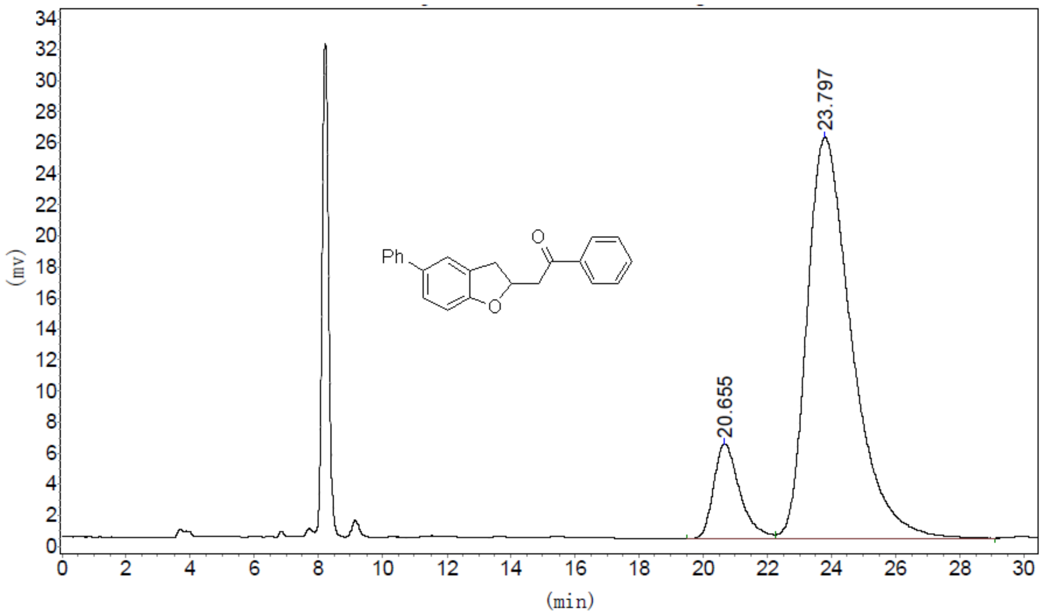
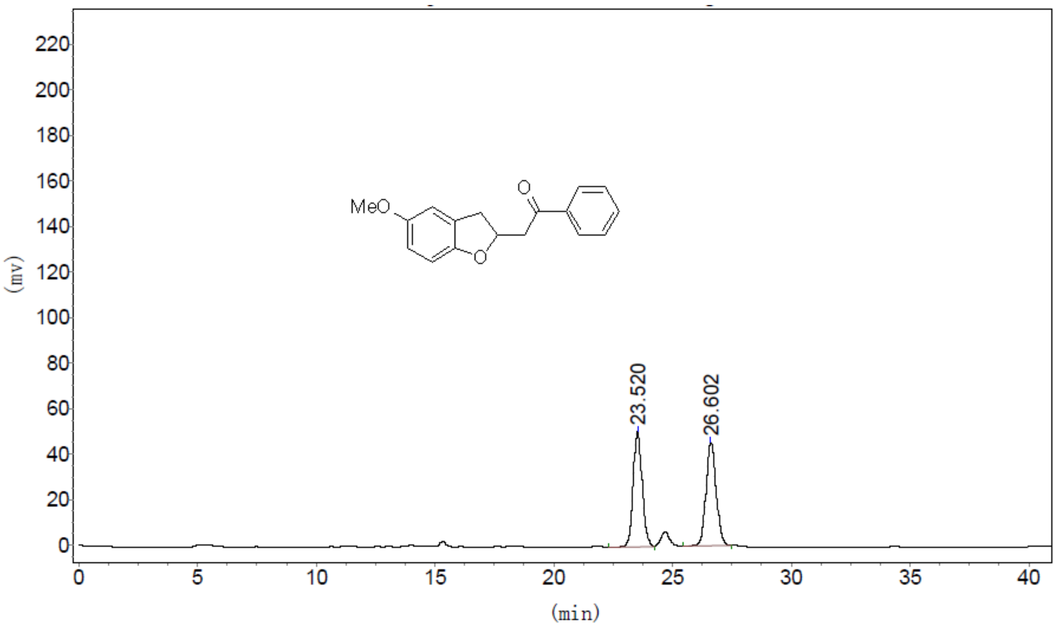
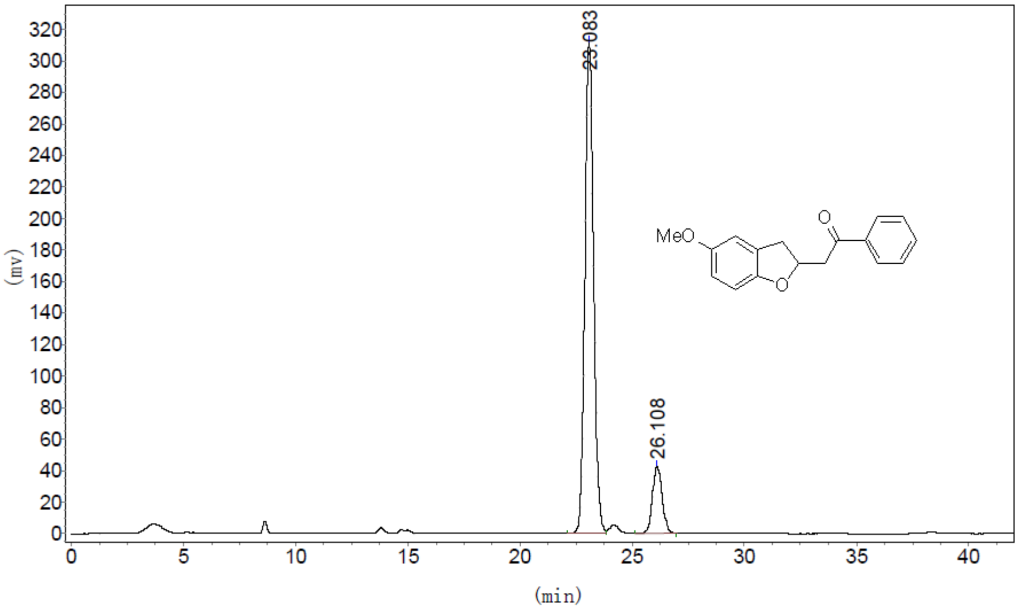
1	19. 940	98287. 813	4772196. 000	49. 3348
2	22. 670	58776. 602	4900889. 000	50. 6652
Total		157064. 414	9673085. 000	100. 0000



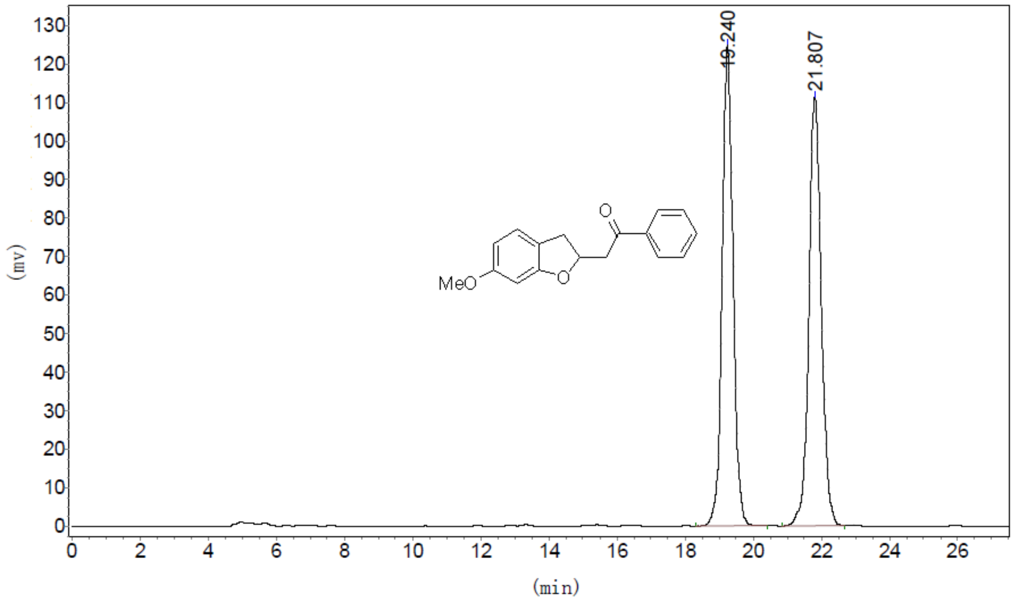
Peak No.	**R. Time**	**Peak Height**	**Peak Area**	**Percent**
1	20. 655	6135. 802	348887. 594	12. 2313
2	23. 797	25853. 293	2503530. 500	87. 7687
Total		31989. 095	2852418. 094	100. 0000



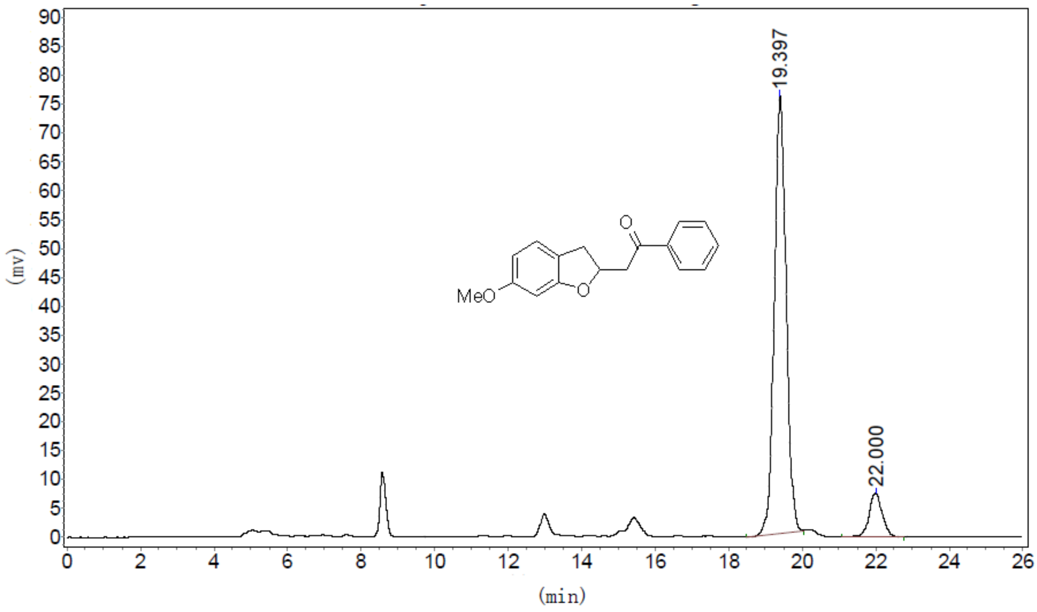
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	23. 520	50654. 191	1336873. 500	49. 9302
2	26. 602	45202. 508	1340610. 000	50. 0698
Total		95856. 699	2677483. 500	100. 0000



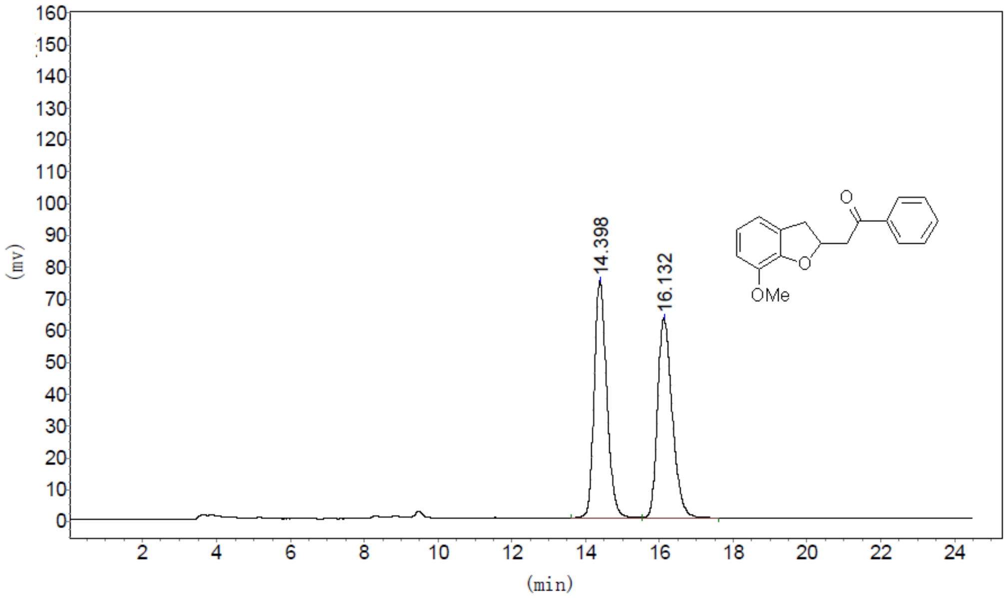
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	23. 083	312469. 969	8369732. 000	86. 8223
2	26. 108	43052. 613	1270344. 000	13. 1777
Total		355522. 582	9640076. 000	100. 0000



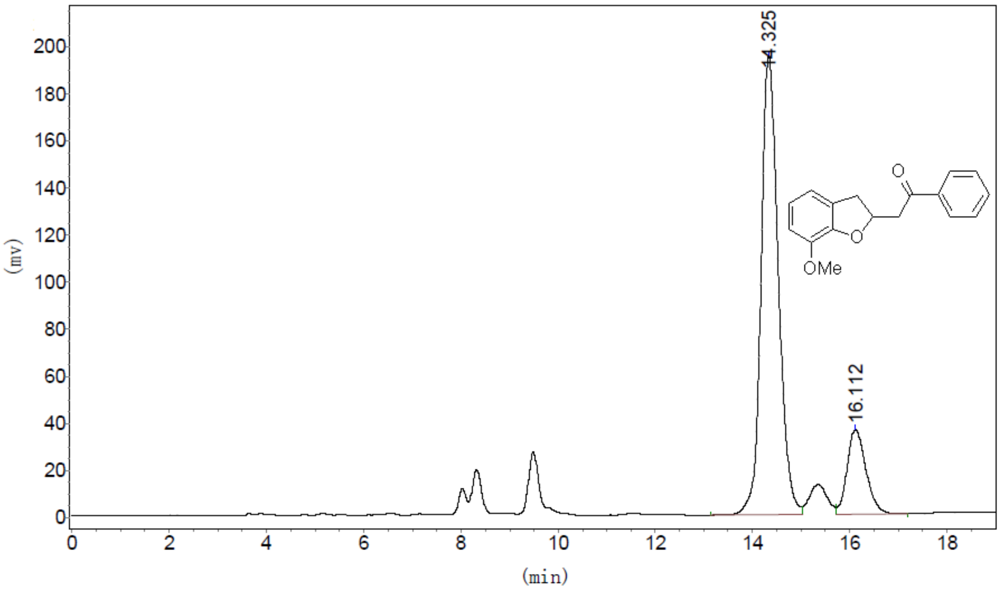
Peak No.	**R. Time**	**Peak Height**	**Peak Area**	**Percent**
1	19. 240	124081. 898	2781610. 750	49. 6474
2	21. 807	111025. 688	2821115. 750	50. 3526
Total		235107. 586	5602726. 500	100. 0000



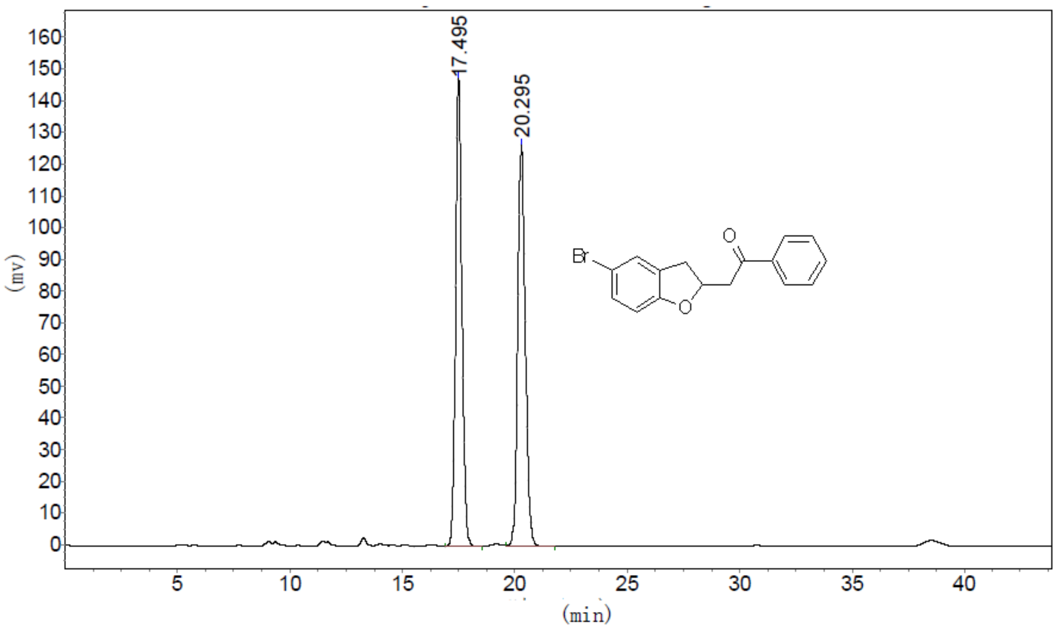
Peak No.	**R. Time**	**Peak Height**	**Peak Area**	**Percent**
1	19. 397	75730. 156	1675795. 375	89. 8323
2	22. 000	7557. 636	189674. 750	10. 1677
Total		83287. 792	1865470. 125	100. 0000



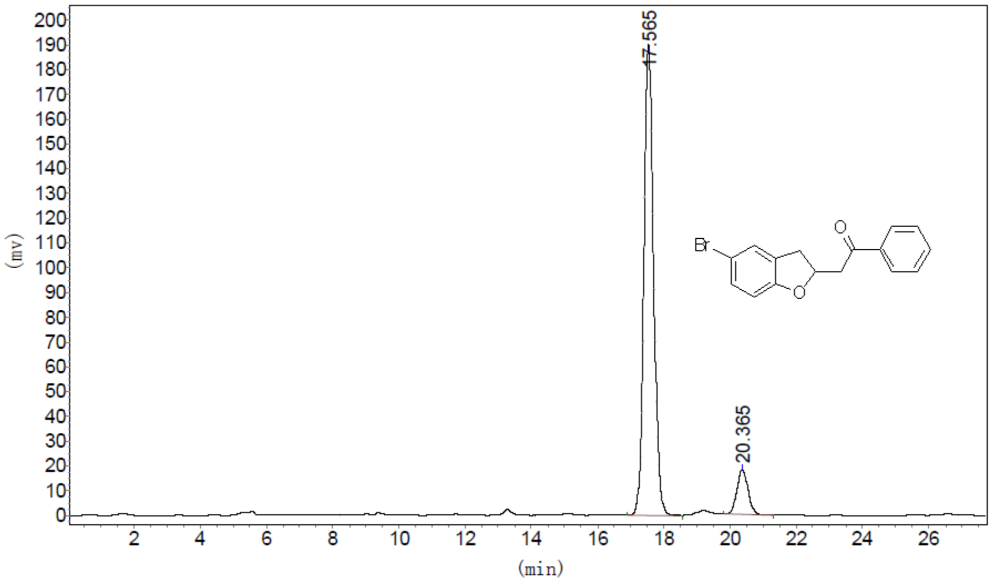
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	14. 398	74694. 500	1771671. 250	50. 4656
2	16. 132	62844. 773	1738981. 125	49. 5344
Total		137539. 273	3510652. 375	100. 0000



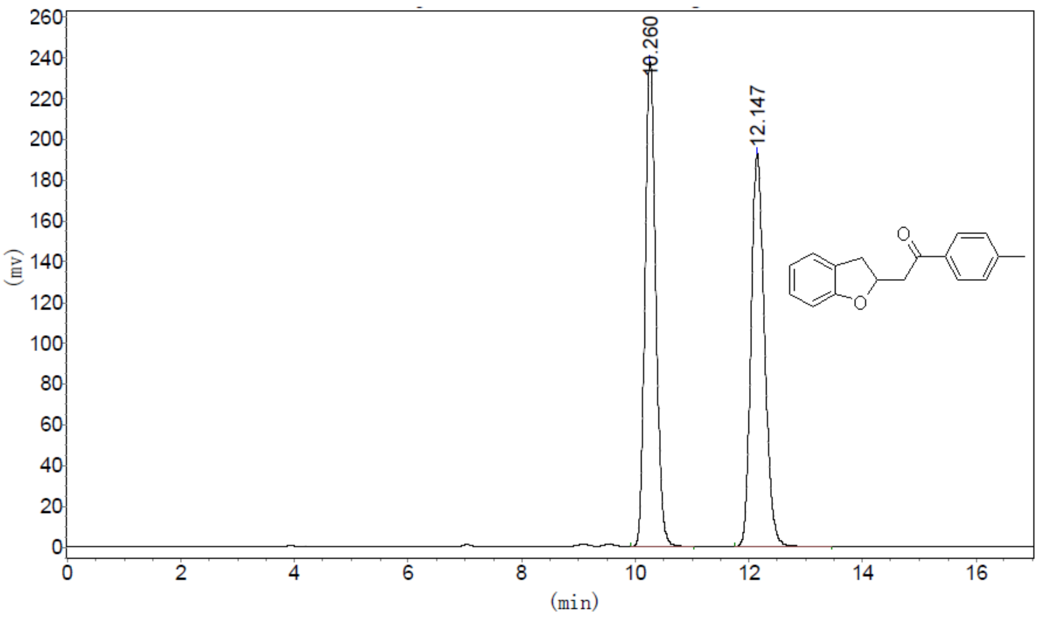
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	14. 325	194953. 797	4818740. 000	83. 1994
2	16. 112	36087. 133	973056. 625	16. 8006
Total		231040. 930	5791796. 625	100. 0000



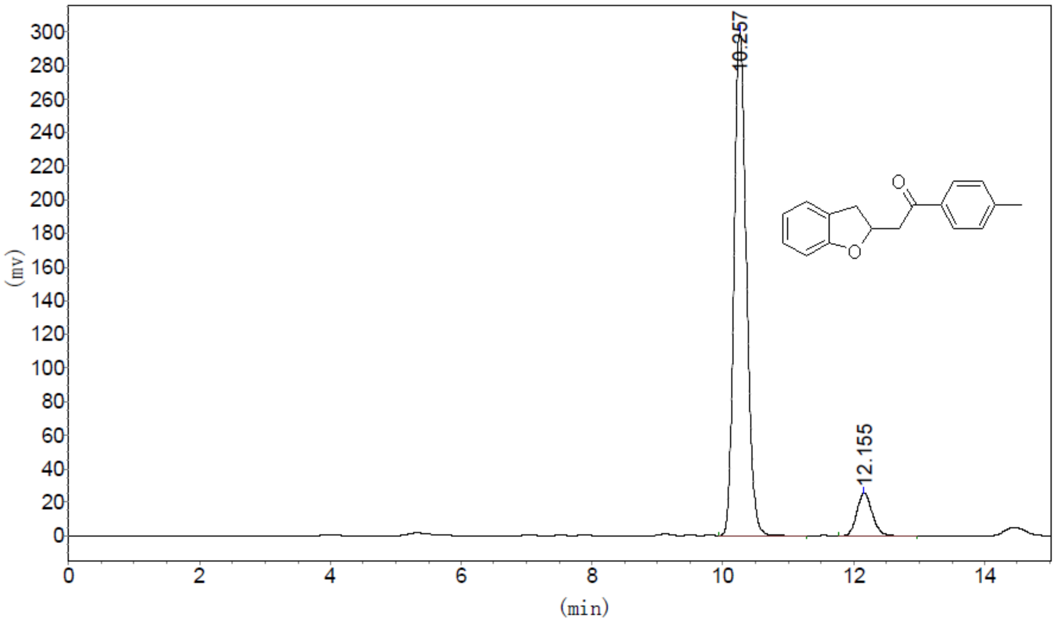
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	17. 495	147839. 734	2923728. 000	49. 8870
2	20. 295	126851. 289	2936968. 500	50. 1130
Total		274691. 023	5860696. 500	100. 0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	17. 565	189322. 781	3832929. 750	89. 3429
2	20. 365	18412. 418	457202. 375	10. 6571
Total		207735. 199	4290132. 125	100. 0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	10. 260	238391. 266	3153730. 500	49. 9604
2	12. 147	192857. 906	3158729. 000	50. 0396
Total		431249. 172	6312459. 500	100. 0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	10. 257	300390. 781	3971160. 500	90. 5983
2	12. 155	25448. 574	412101. 063	9. 4017
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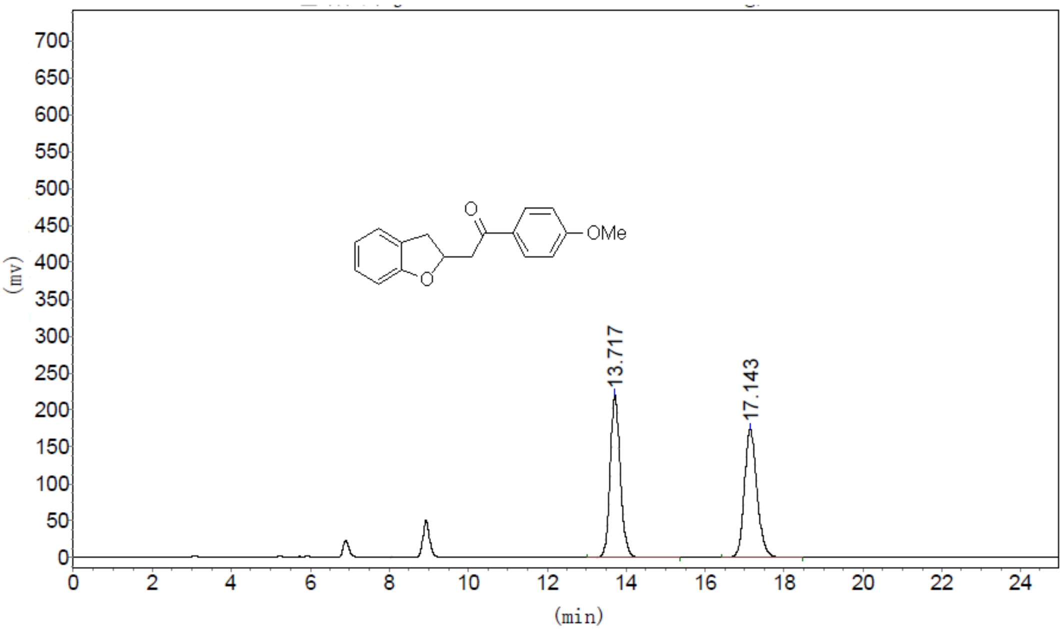
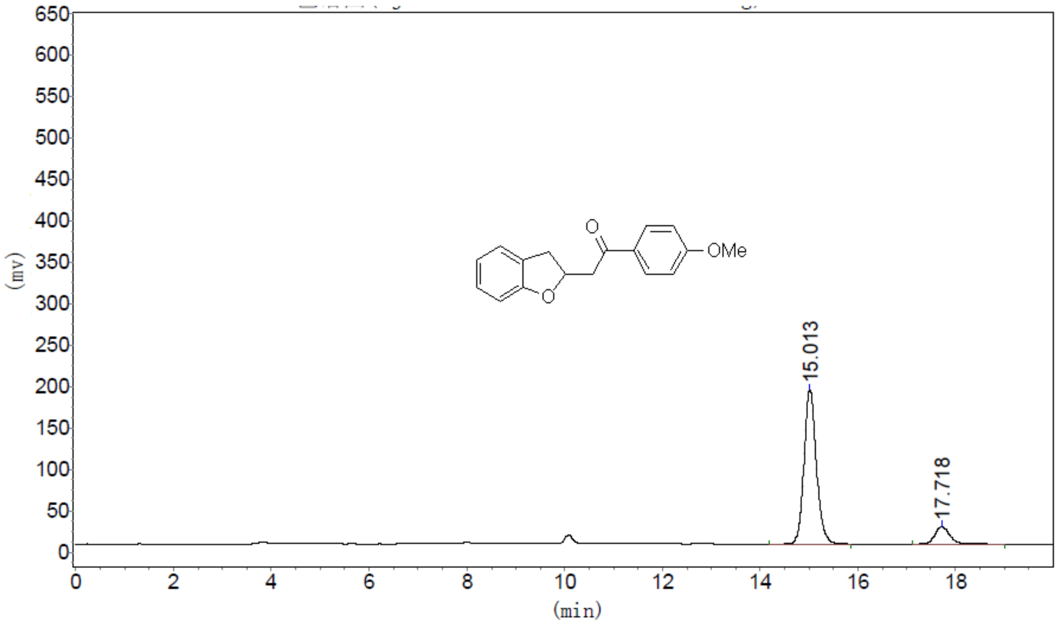


Peak No.	**R. Time**	**Peak Height**	**Peak Area**	**Percent**
1	13. 717	220629. 656	3891852. 750	49. 9952
2	17. 143	174627. 891	3892606. 000	50. 0048
Total		395257. 547	7784458. 750	100. 0000



Peak No.	**R. Time**	**Peak Height**	**Peak Area**	**Percent**
1	15. 013	186643. 391	3287285. 750	87. 9548
2	17. 718	21298. 008	450188. 094	12. 0453
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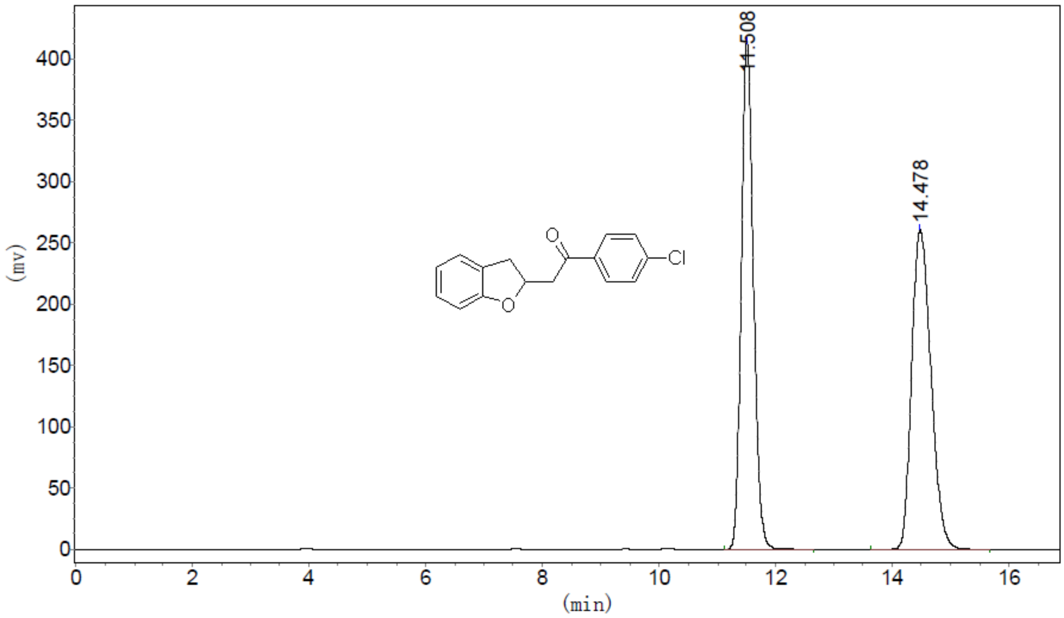
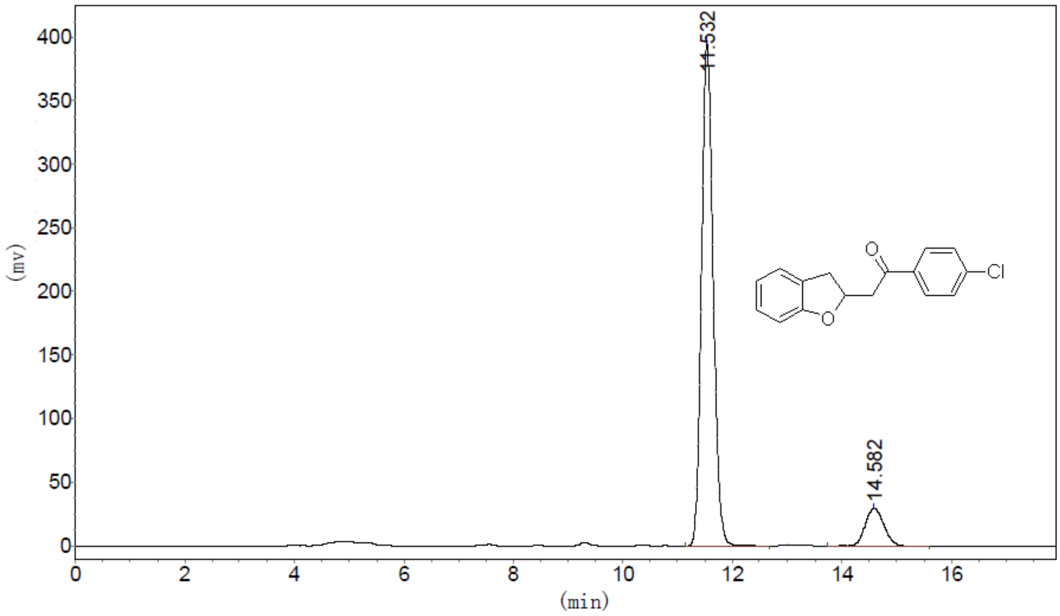
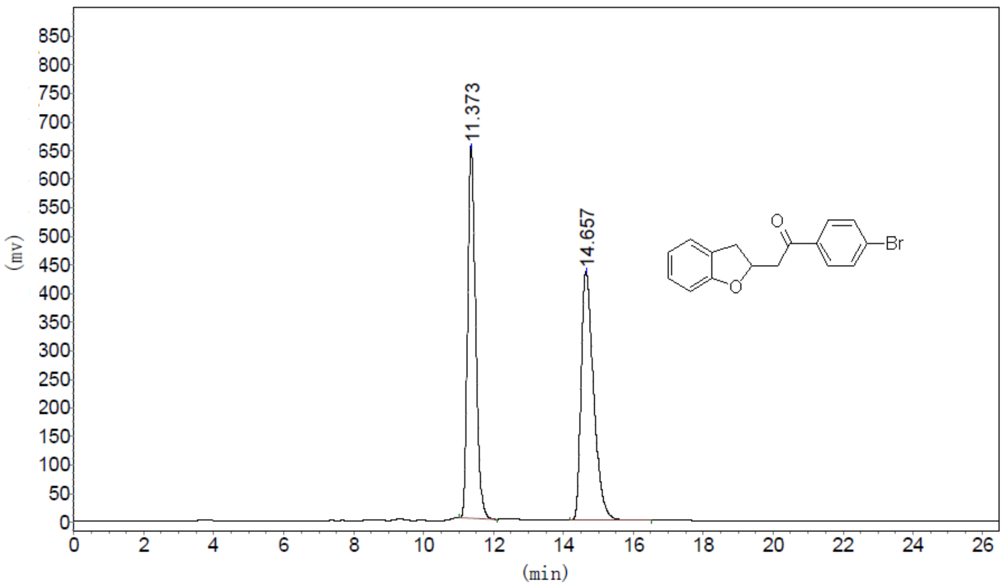


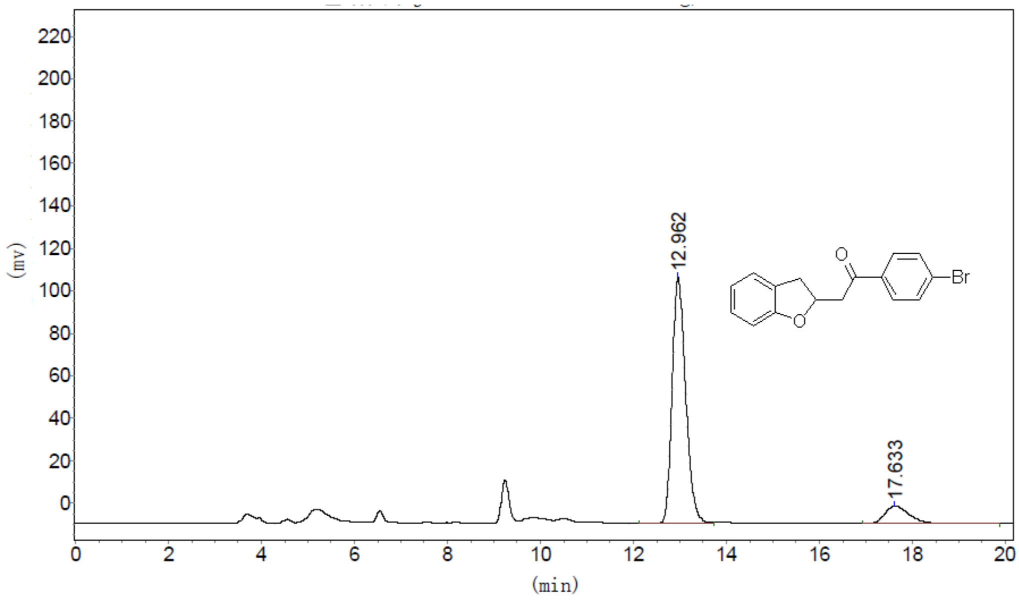
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 508	412527. 781	6021218. 500	49. 9799
2	14. 478	260700. 906	6026069. 500	50. 0201
Total		673228. 688	12047288. 000	100. 0000



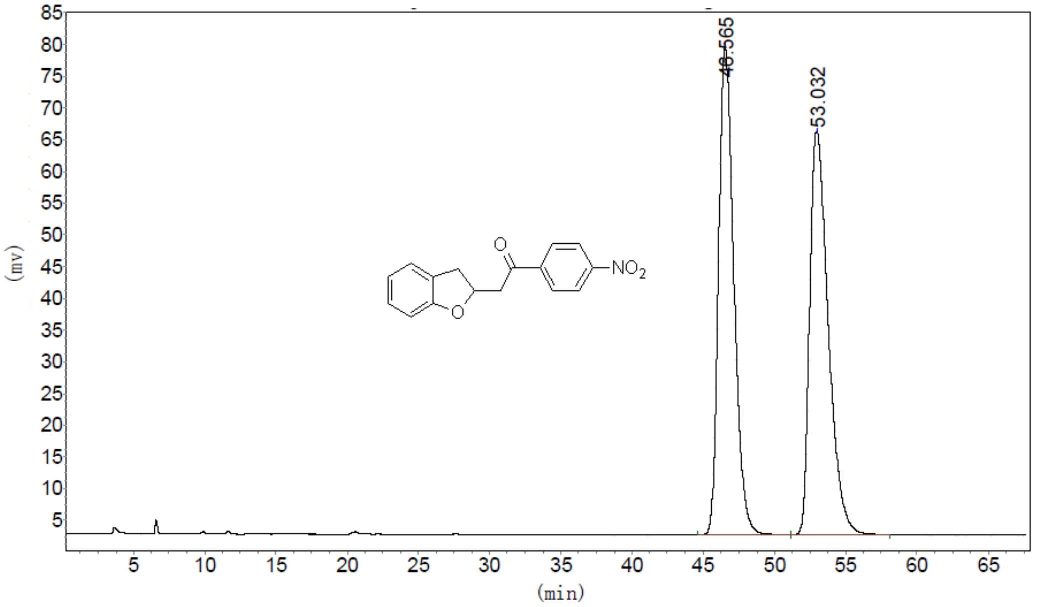
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 532	395309. 438	5799157. 500	89. 2420
2	14. 582	29522. 238	699082. 188	10. 7580
Total		424831. 676	6498239. 688	100. 0000



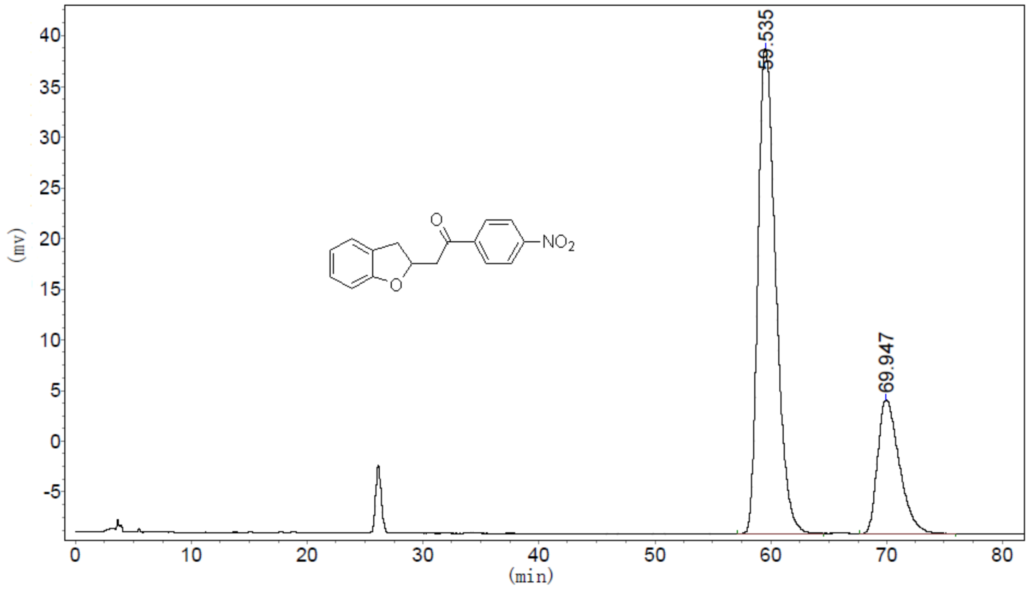
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 373	654762. 688	10671433. 000	49. 6851
2	14. 657	434098. 031	10806697. 000	50. 3149
Total		1088860. 719	21478130. 000	100. 0000



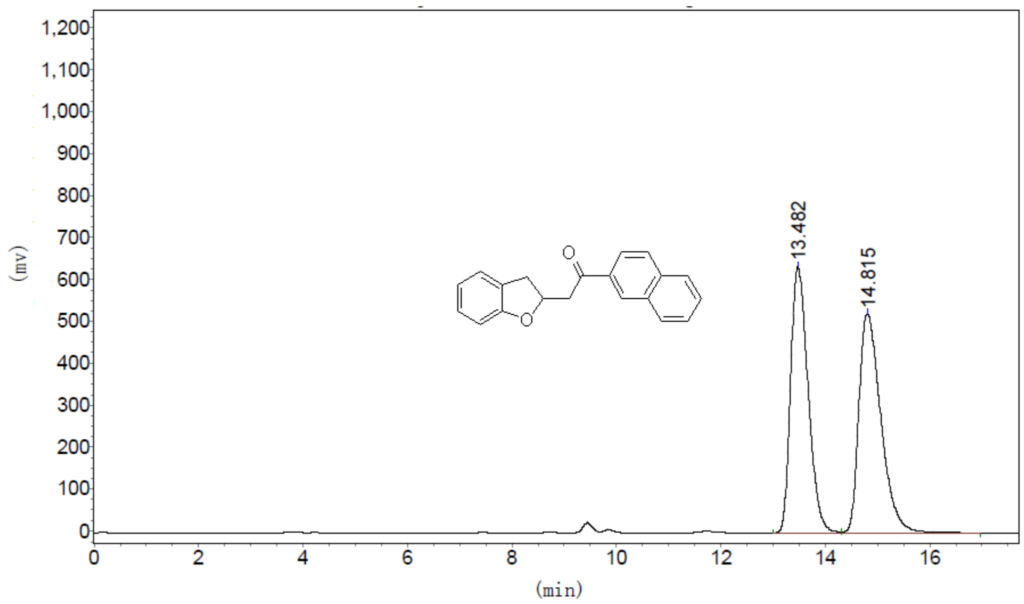
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12. 962	115699. 297	2338820. 000	88. 6038
2	17. 633	8199. 400	300818. 469	11. 3962
Total		123898. 697	2639638. 469	100. 0000



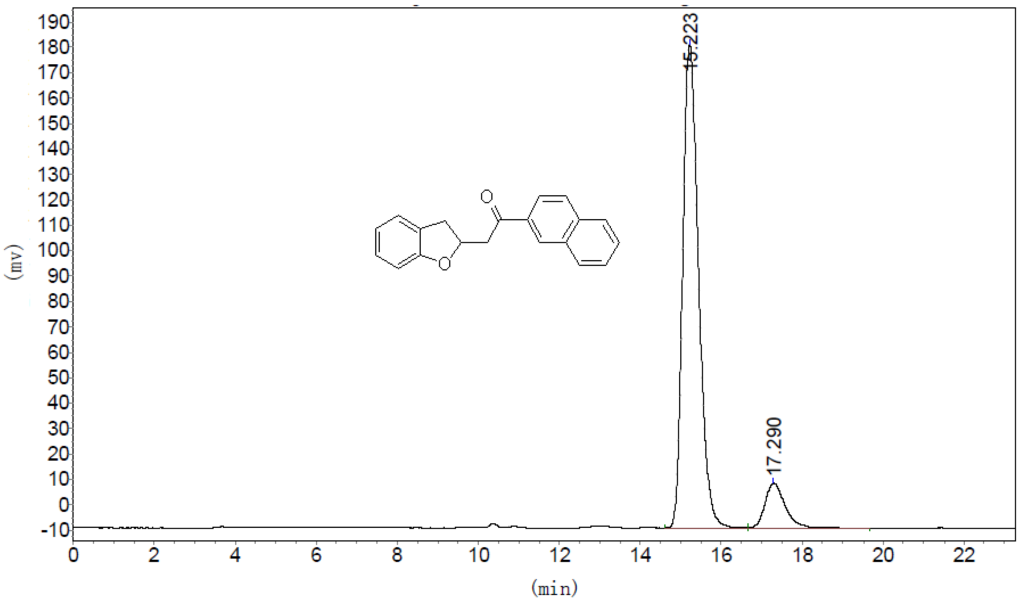
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	46.565	77046.367	5791181.500	50.0488
2	53.032	63539.098	5779885.000	49.9512
Total		140585.465	11571066.500	100.0000



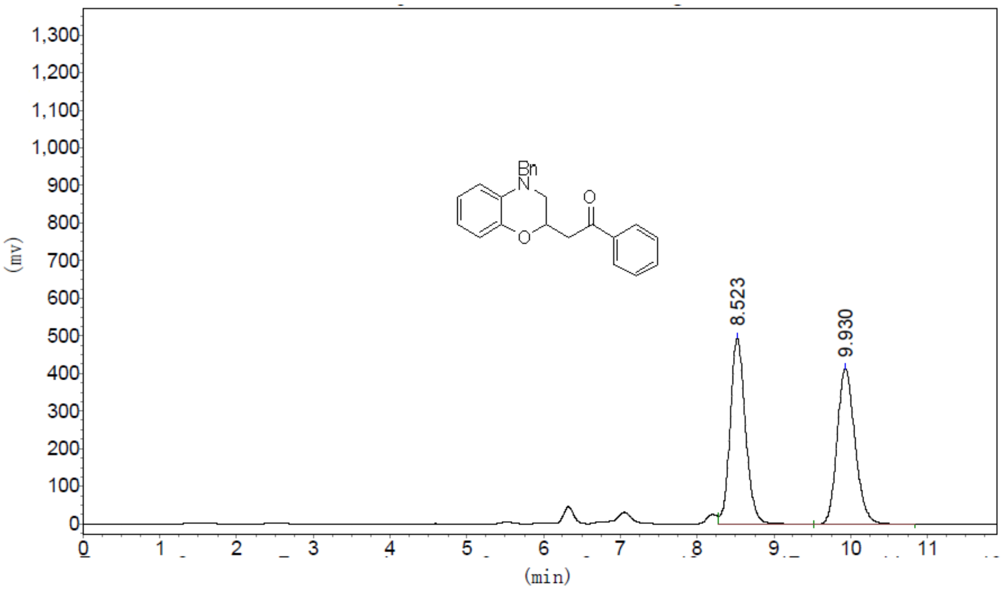
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	59.535	47927.195	5095960.000	74.7568
2	69.947	13255.105	1720755.625	25.2432
Total		61182.301	6816715.625	100.0000)



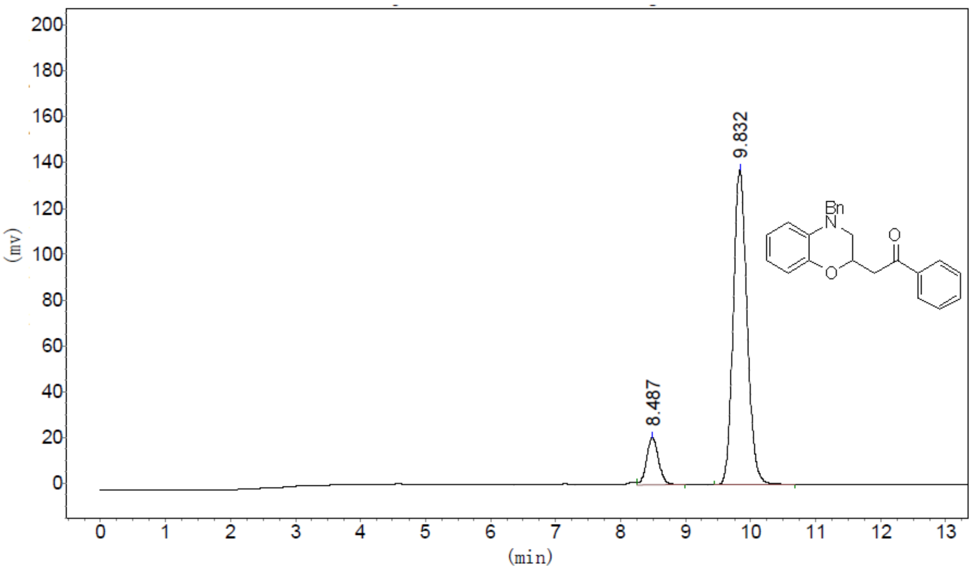
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13. 482	633697. 813	14845958. 000	49. 1307
2	14. 815	523344. 531	15371336. 000	50. 8693
Total		1157042. 344	30217294. 000	100. 0000



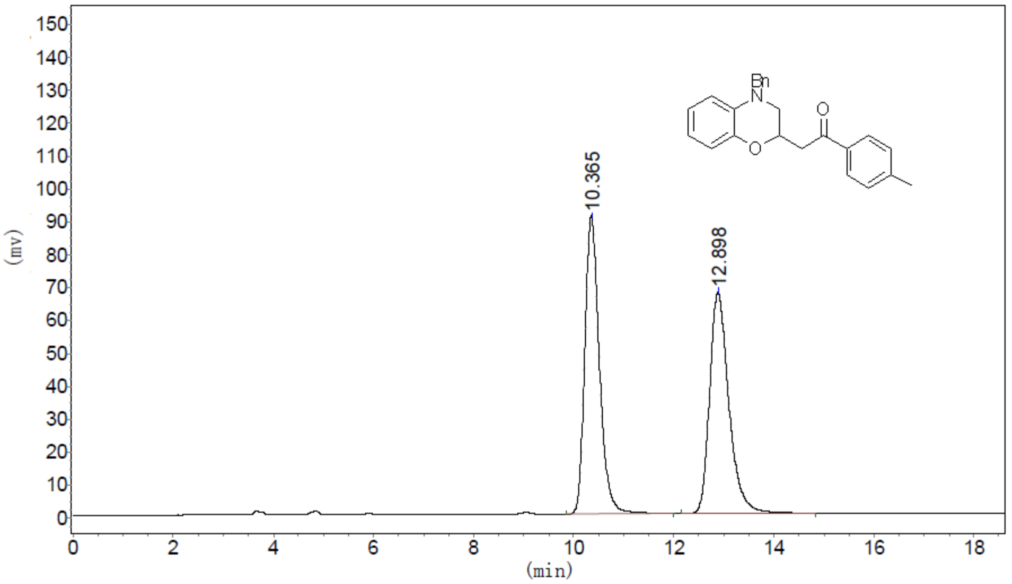
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15. 223	189949. 797	5136087. 500	89. 5876
2	17. 290	17516. 756	596948. 750	10. 4124
Total		207466. 553	5733036. 250	100. 0000



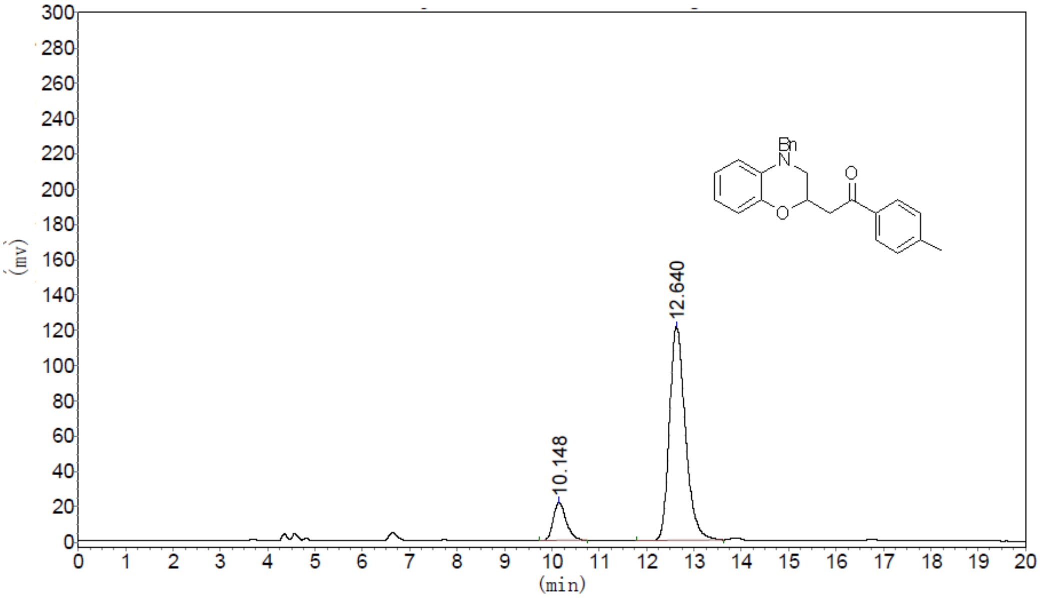
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	8. 523	494404. 375	6803529. 000	50. 3103
2	9. 930	412804. 063	6719598. 500	49. 6897
Total		907208. 438	13523127. 500	100. 0000



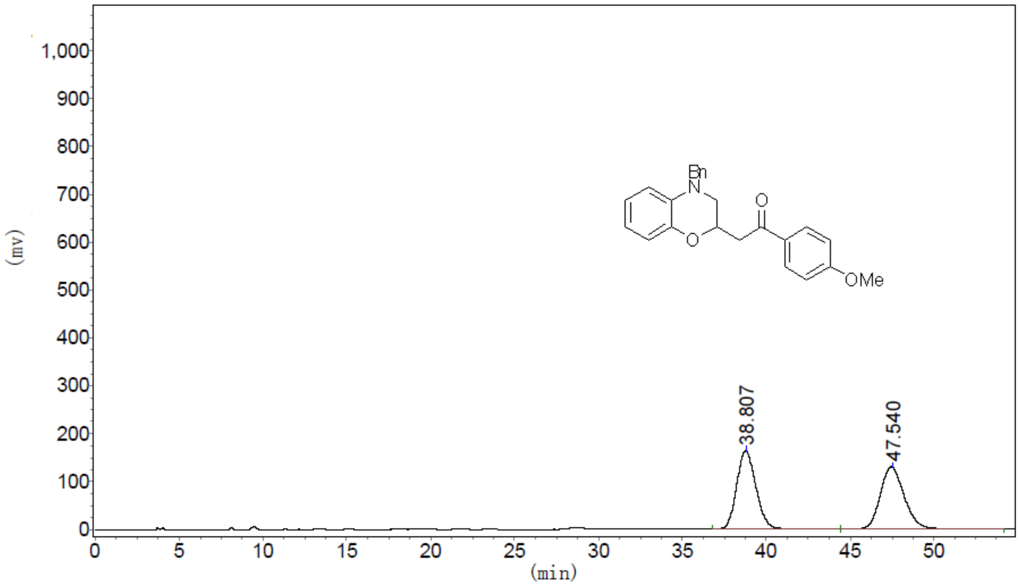
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	8. 487	20759. 209	261902. 422	11. 4396
2	9. 832	137295. 438	2027530. 375	88. 5604
Total		158054. 646	2289432. 797	100. 0000



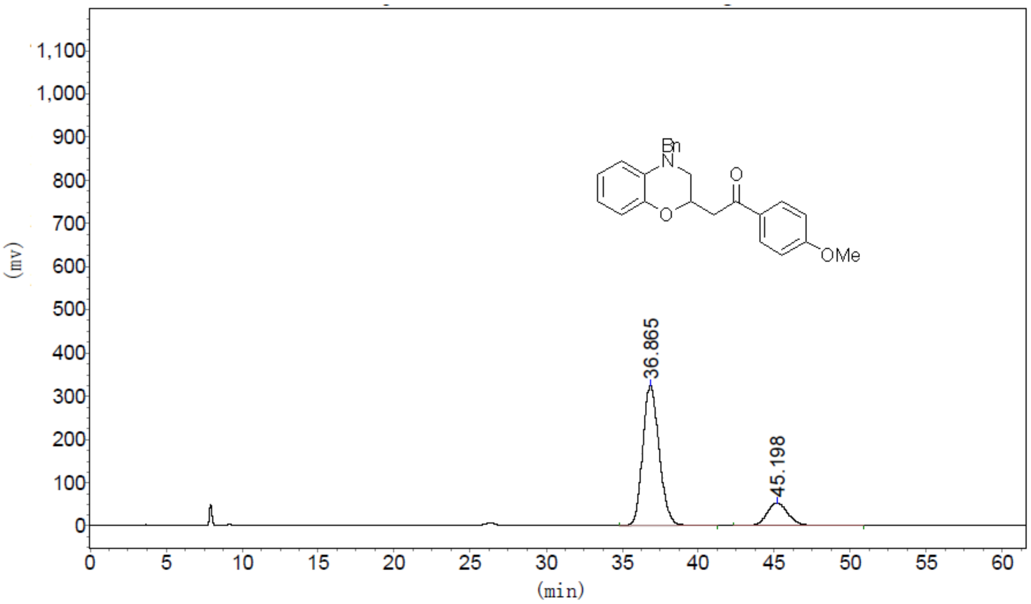
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	10. 365	90545. 047	1819145. 000	50. 2108
2	12. 898	67268. 594	1803868. 125	49. 7892
Total		157813. 641	3623013. 125	100. 0000



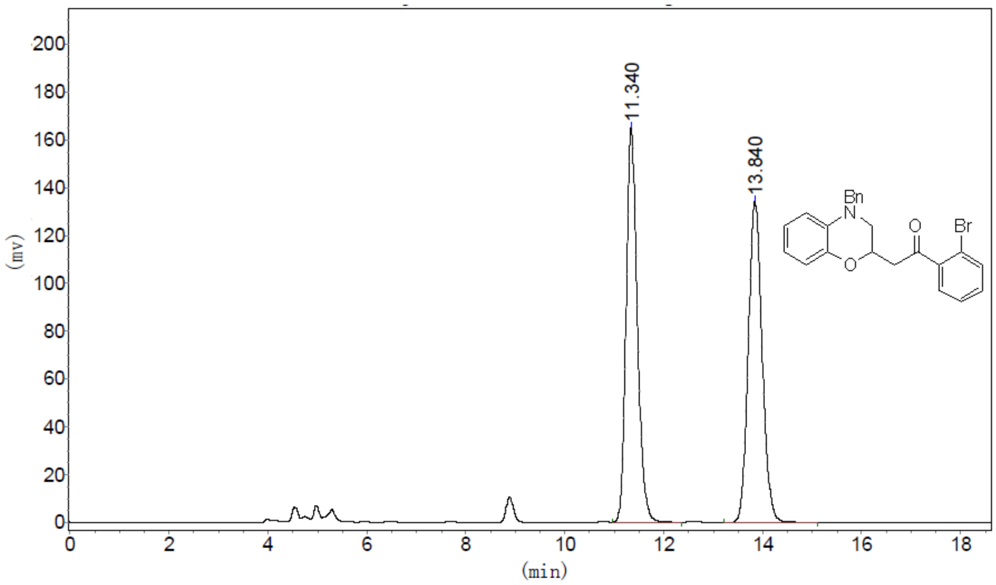
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	10. 148	21751. 881	415875. 719	12. 7592
2	12. 640	121385. 406	2843547. 750	87. 2408
Total		143137. 287	3259423. 469	100. 0000



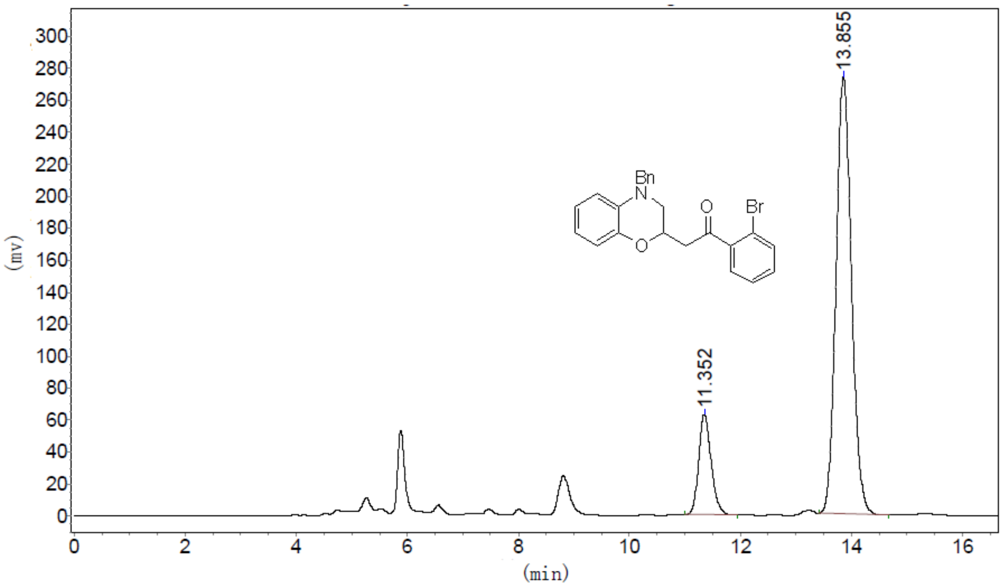
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	38. 807	163270. 859	12943384. 000	50. 2259
2	47. 540	129150. 398	12826928. 000	49. 7741
Total		292421. 258	25770312. 000	100. 0000)



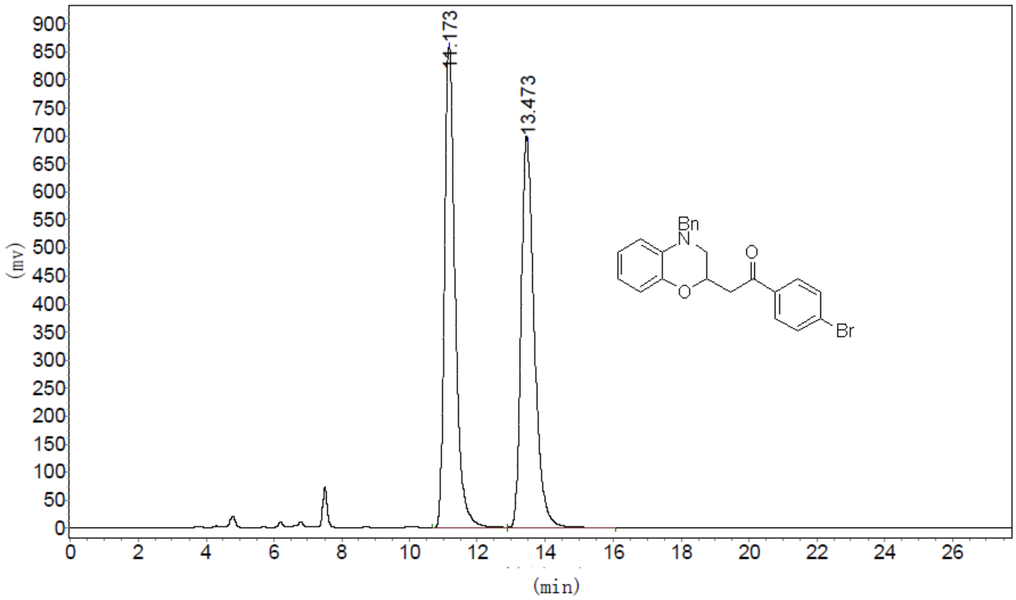
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	36. 865	323625. 781	24460054. 000	83. 2280
2	45. 198	52325. 555	4929156. 000	16. 7720
Total		375951. 336	29389210. 000	100. 0000



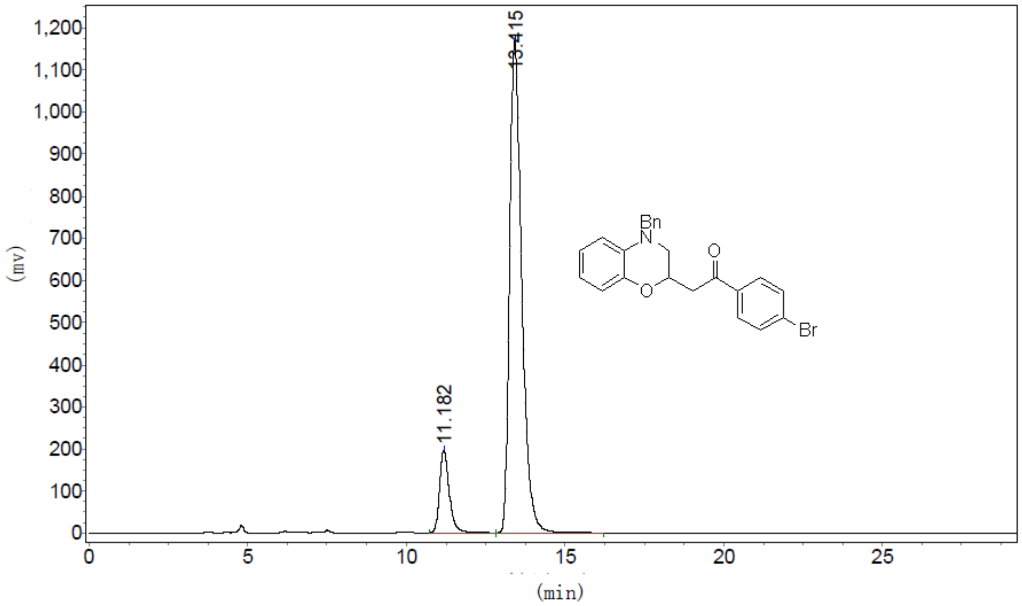
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 340	164555. 750	2617310. 000	49. 9966
2	13. 840	134148. 172	2617662. 000	50. 0034
Total		298703. 922	5234972. 000	100. 0000



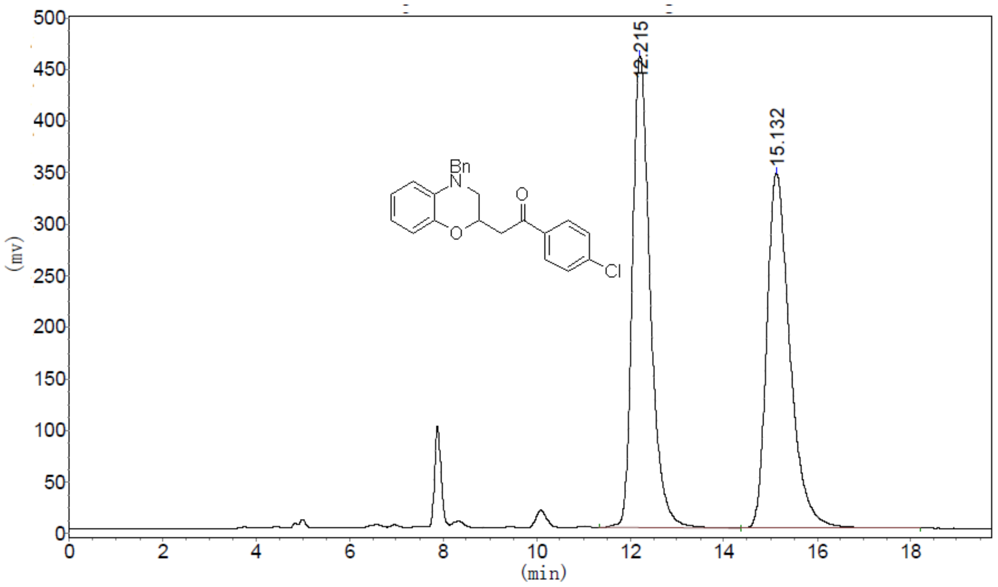
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 352	62808. 656	981999. 188	15. 6772
2	13. 855	273347. 625	5281852. 500	84. 3228
Total		336156. 281	6263851. 688	100. 0000



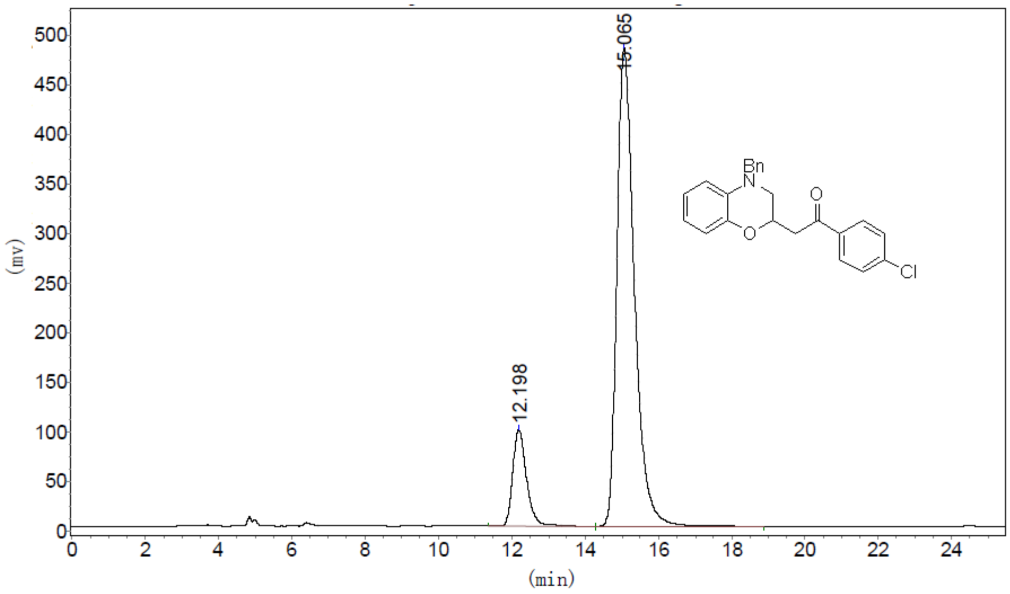
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 173	860976. 250	18771260. 000	50. 0954
2	13. 473	695708. 875	18699782. 000	49. 9046
Total		1556685. 125	37471042. 000	100. 0000



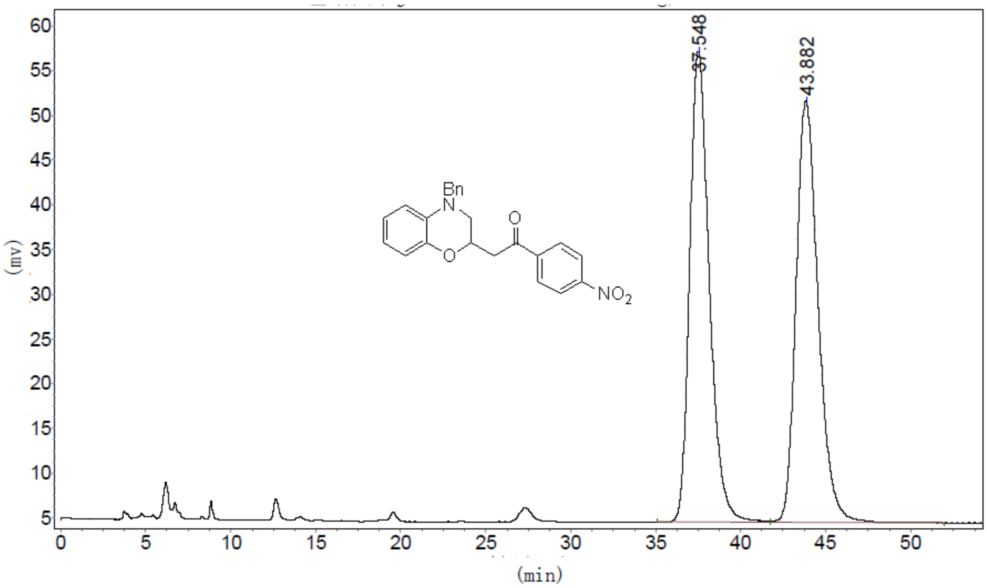
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 182	194933. 563	4190289. 250	11. 9658
2	13. 415	1166127. 875	30828578. 000	88. 0342
Total		1361061. 438	35018867. 250	100. 0000



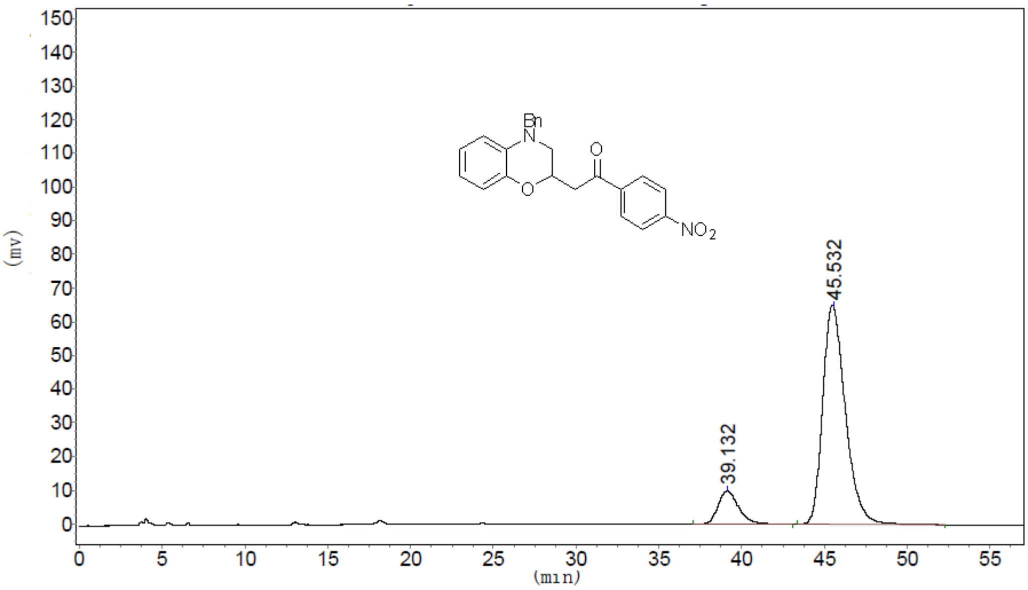
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12. 215	458416. 906	12172224. 000	50. 5420
2	15. 132	344220. 250	11911165. 000	49. 4580
Total		802637. 156	24083389. 000	100. 0000



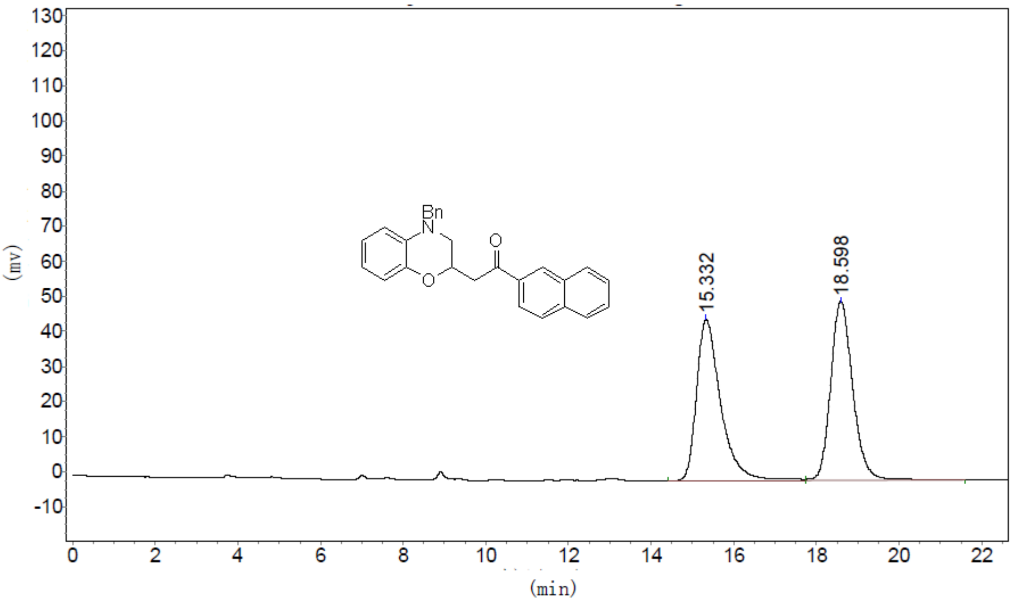
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12. 198	97094. 750	2565870. 250	13. 7687
2	15. 065	480496. 906	16069709. 000	86. 2313
Total		577591. 656	18635579. 250	100. 0000



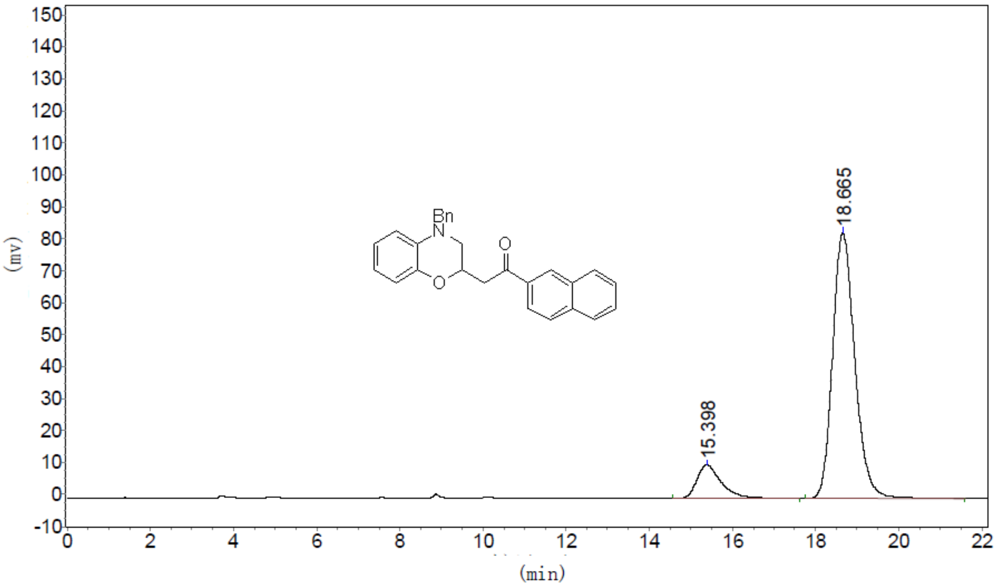
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	37. 548	52631. 215	4246201. 500	50. 0364
2	43. 882	47165. 016	4240031. 500	49. 9636
Total		99796. 230	8486233. 000	100. 0000



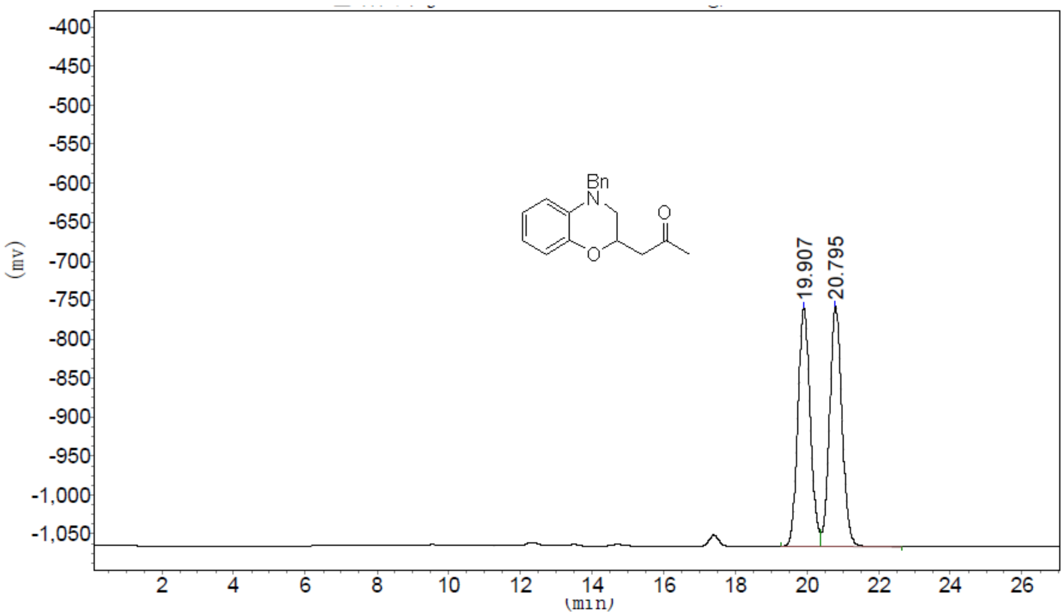
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	39. 132	9937. 044	860687. 000	12. 2624
2	45. 532	64978. 008	6158197. 000	87. 7375
Total		74915. 052	7018884. 000	100. 0000



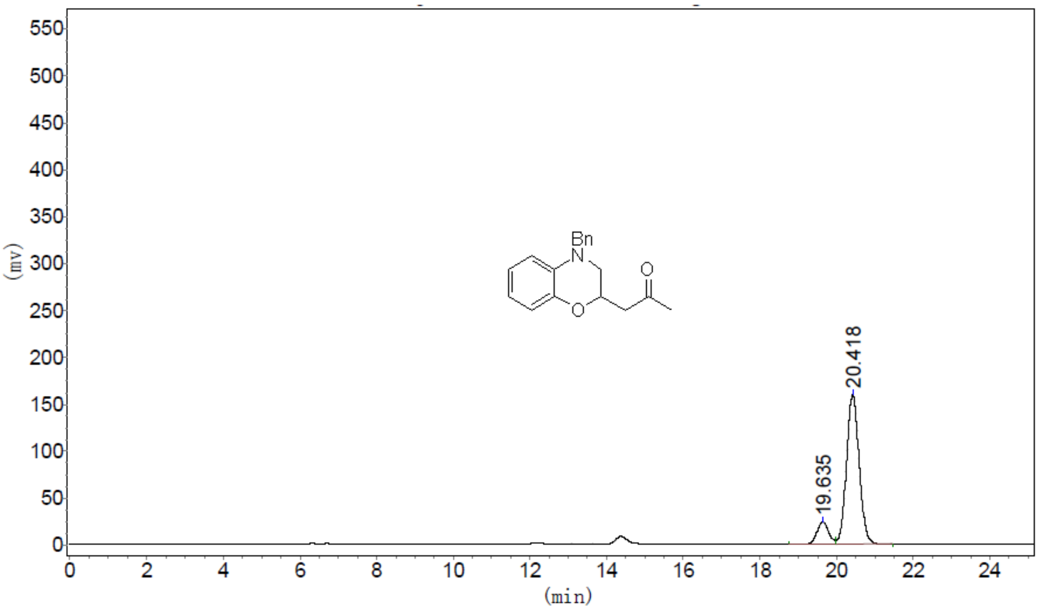
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15. 332	45861. 582	1849922. 500	49. 7533
2	18. 598	50816. 820	1868267. 375	50. 2467
Total		96678. 402	3718189. 875	100. 0000



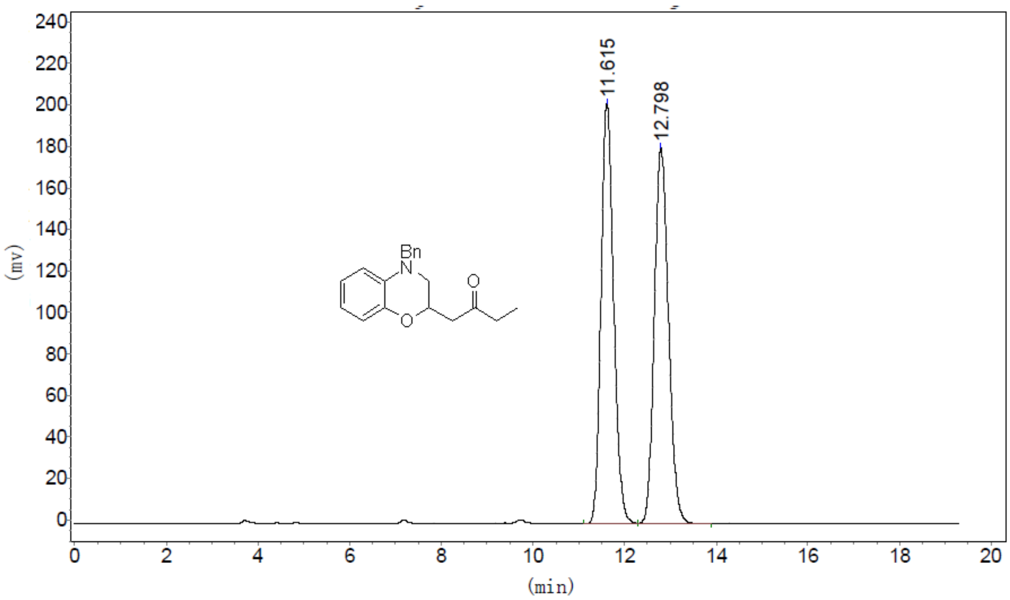
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15. 398	10427. 892	424930. 688	12. 1159
2	18. 665	83161. 820	3082280. 500	87. 8841
Total		93589. 712	3507211. 188	100. 0000



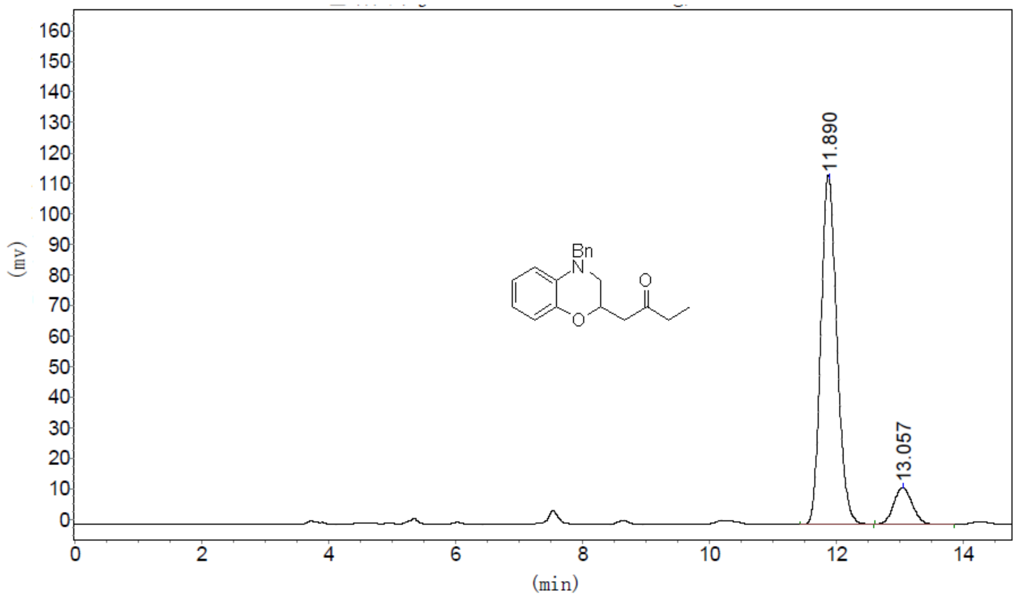
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	19. 907	306831. 719	7324298. 500	49. 7200
2	20. 795	308193. 844	7406781. 000	50. 2800
Total		615025. 563	14731079. 500	100. 0000



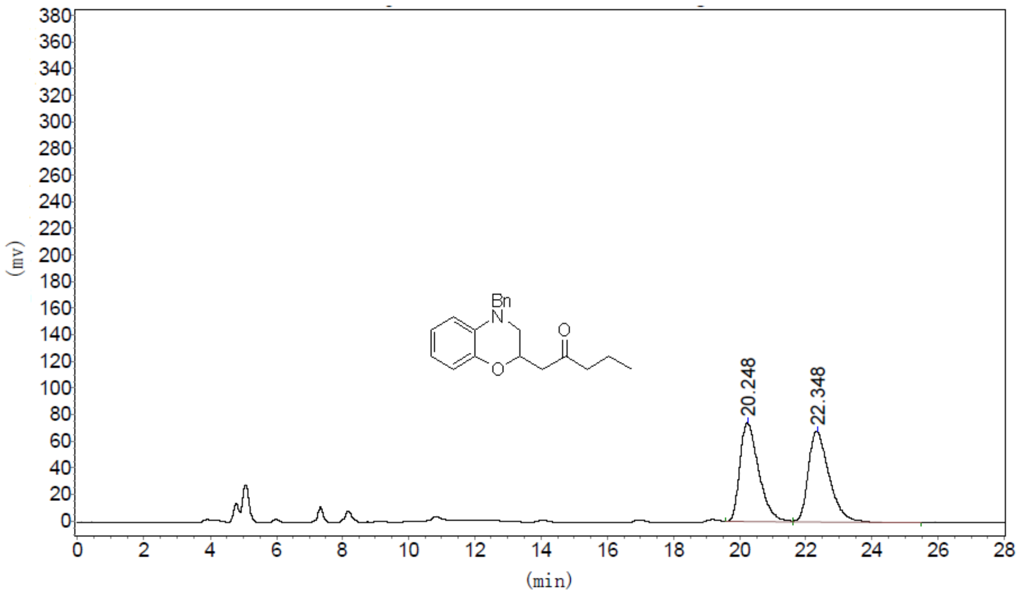
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	19. 635	23617. 455	507054. 469	12. 2480
2	20. 418	159684. 594	3632828. 500	87. 7520
Total		183302. 049	4139882. 969	100. 0000



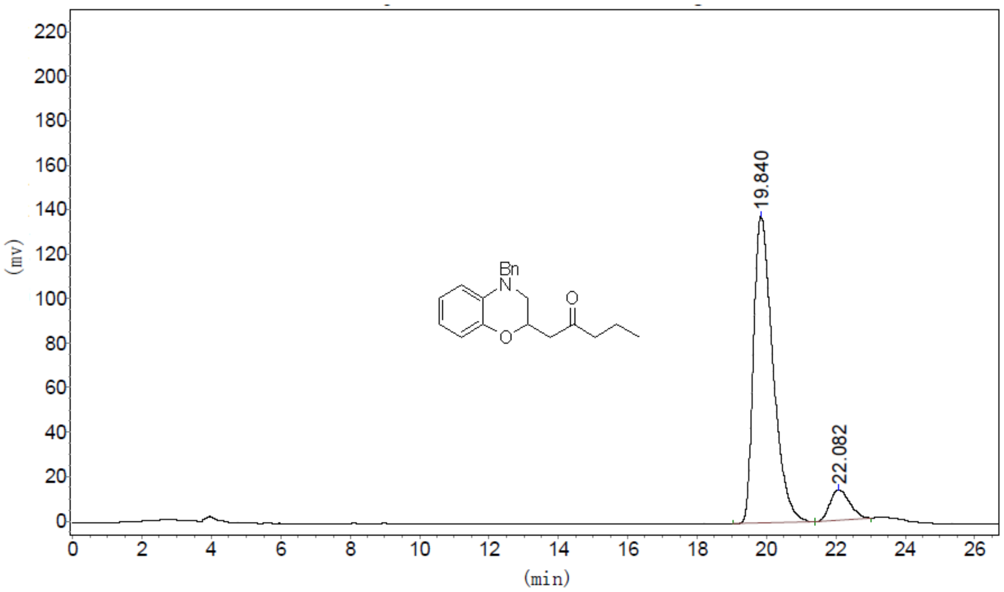
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 615	202470. 188	3877598. 750	50. 0223
2	12. 798	181206. 078	3874144. 750	49. 9777
Total		383676. 266	7751743. 500	100. 0000



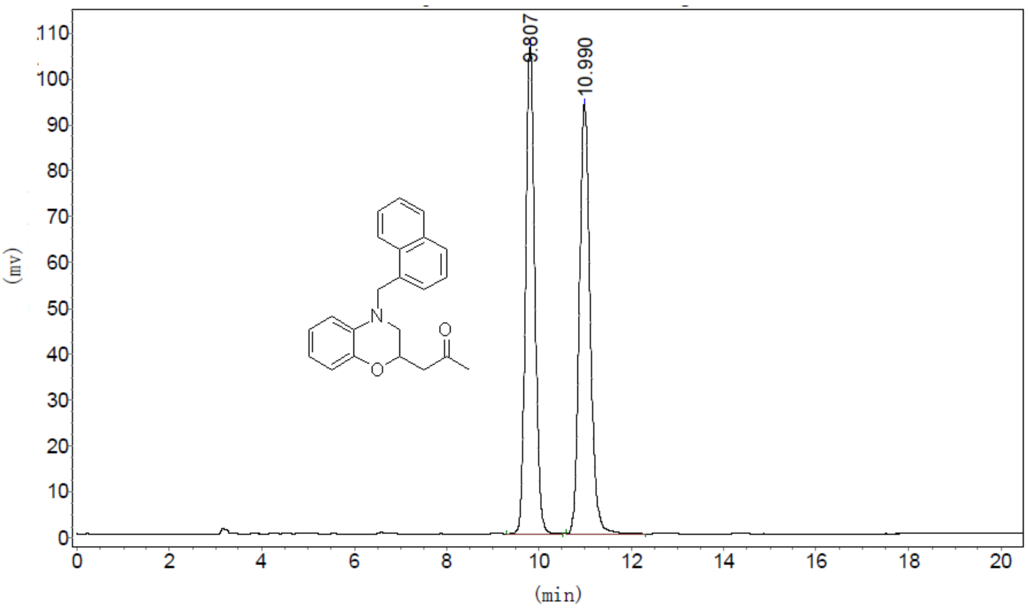
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11. 890	114043. 750	2002308. 125	88. 8353
2	13. 057	12108. 459	251646. 813	11. 1647
Total		126152. 209	2253954. 938	100. 0000



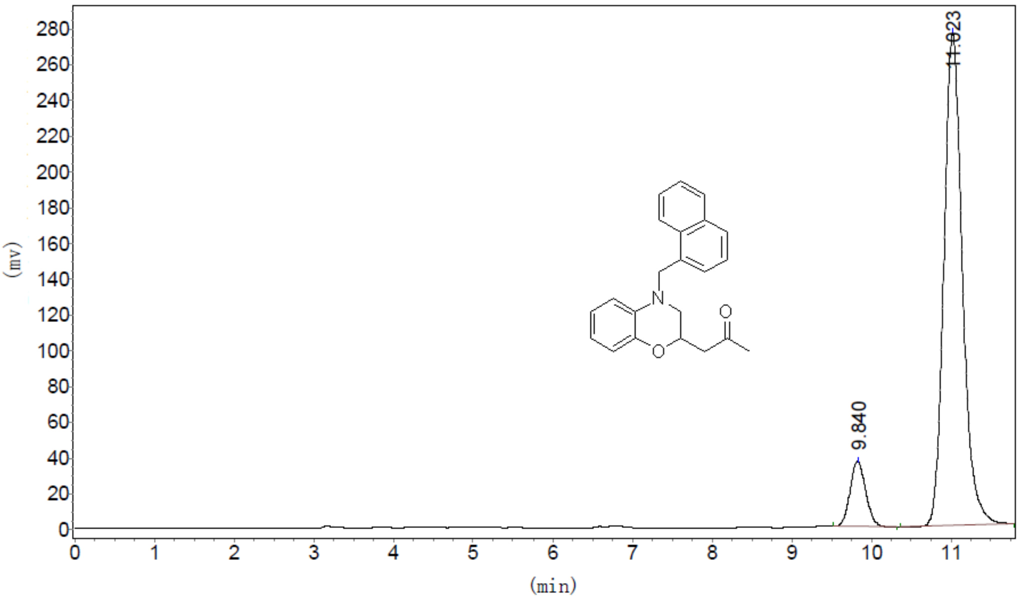
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	20. 248	74569. 039	2977884. 750	49. 8090
2	22. 348	68220. 992	3000724. 000	50. 1910
Total		142790. 031	5978608. 750	100. 0000



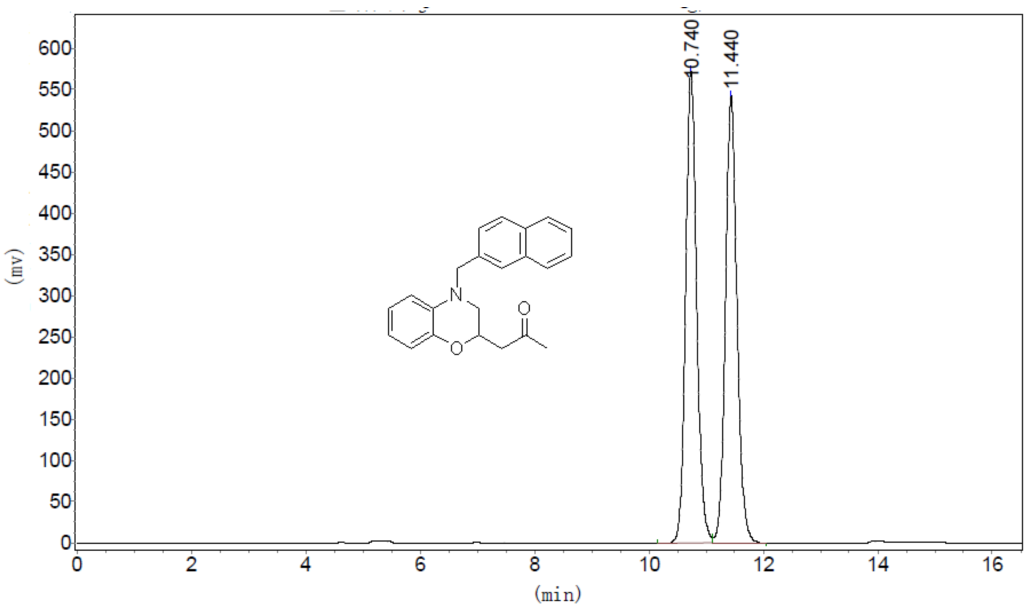
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	19. 840	138053. 438	5361588. 000	90. 9254
2	22. 082	13667. 600	535102. 688	9. 0746
Total		151721. 037	5896690. 688	100. 0000



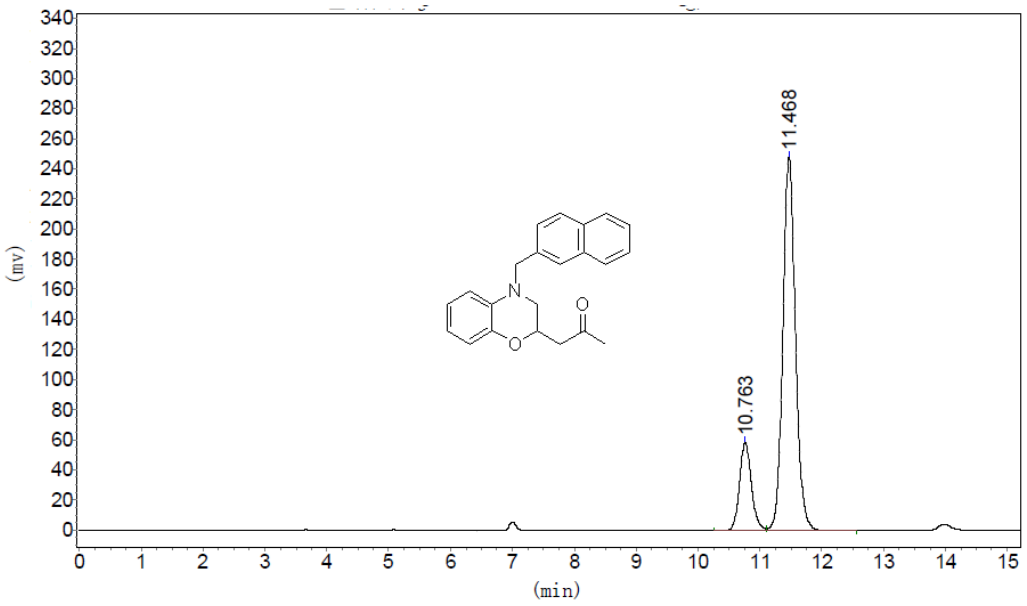
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9. 807	106244. 617	1463394. 875	49. 2787
2	10. 990	93498. 750	1506233. 875	50. 7213
Total		199743. 367	2969628. 750	100. 0000



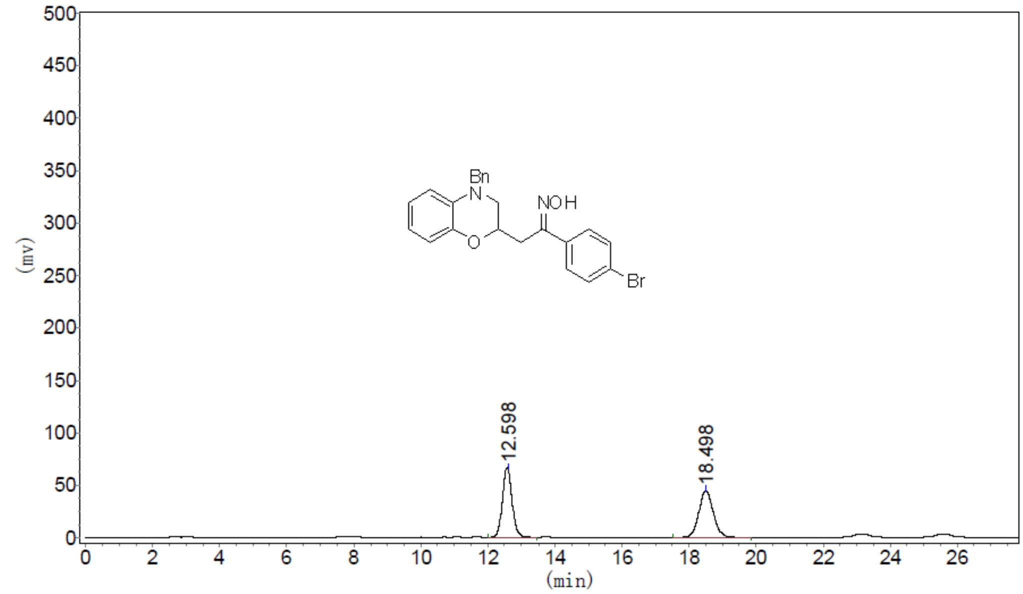
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9. 840	36703. 922	511351. 719	10. 3201
2	11. 023	272078. 781	4443576. 000	89. 6799
Total		308782. 703	4954927. 719	100. 0000



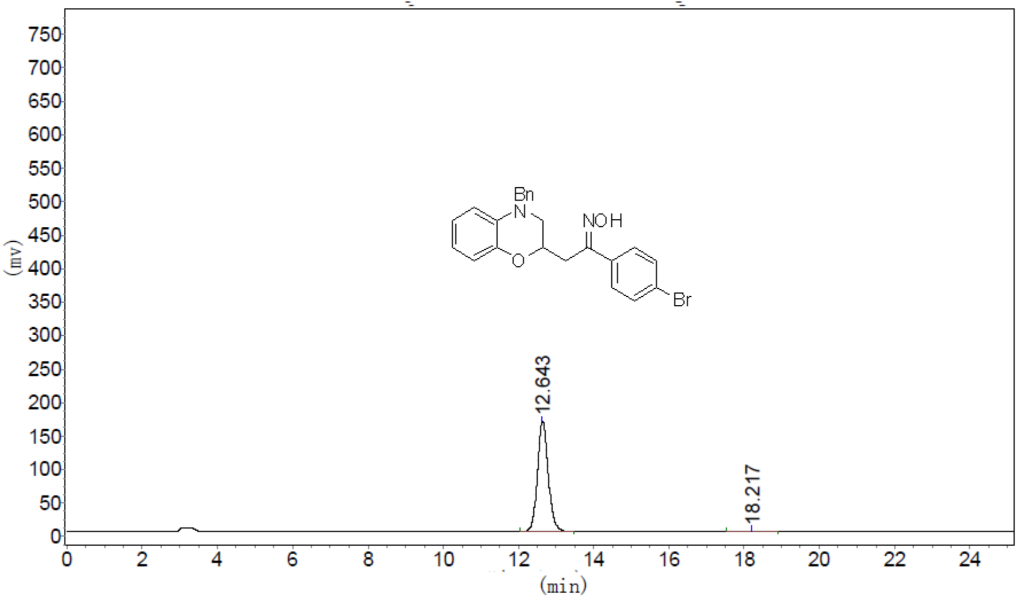
Peak No.	**R. Time**	**Peak Height**	**Peak Area**	**Percent**
1	10. 740	573673. 125	7613372. 500	49. 9320
2	11. 440	540195. 438	7634105. 500	50. 0680
Total		1113868. 563	15247478. 000	100. 0000



Peak No.	**R. Time**	**Peak Height**	**Peak Area**	**Percent**
1	10. 763	59076. 441	786131. 188	18. 2229
2	11. 468	248855. 578	3527841. 500	81. 7771
Total		307932. 020	4313972. 688	100. 0000



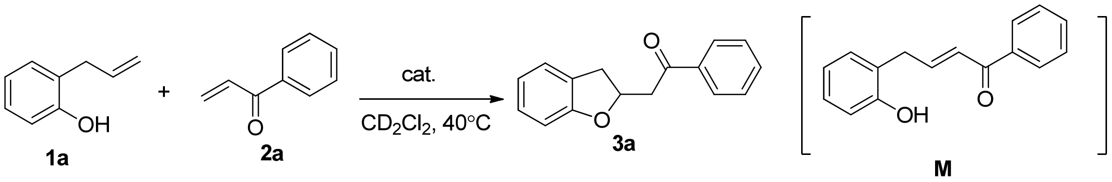
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12. 598	66307. 953	1310175. 125	49. 9852
2	18. 498	43923. 059	1310950. 500	50. 0148
Total		110231. 012	2621125. 625	100. 0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12. 643	162803. 406	3240494. 250	99. 4314
2	18. 217	643. 108	18531. 529	0. 5686
Total		163446. 514	3259025. 779	100. 0000

The Promoting Effect of Chiral Phosphoric Acid

We performed two parallel reactions (with or without (*S*)-**4b**) in CD_2Cl_2 with CH_2Br_2 as the internal standard, and monitored their reaction progess by ^{1}H NMR.[a]



Time	Hoveyda-Grubbs II			Hoveyda-Grubbs II + (*S*)-**4b**		
	M yield[b]	**3a** yield[b]	combined yield.[b]	**M** yield[b]	**3a** yield[b]	combined yield.[b]
0	0	0	0	0	0	0
10 min	24	0	24	20	2	22
30 min	20	0	20	18	9	27
1 h	21	0	21	17	12	29
2 h	18	1	19	17	20	37
4 h	20	2	22	17	22	39
6 h	21	3	24	19	25	44
8 h	19	4	23	18	26	44
17 h	19	5	24	18	27	45
24 h	19	9	28	18	31	49
42 h	19	13	32	18	32	50
48 h	19	17	36	17	31	48
100 h	19	25	44	17	35	52
120 h	20	28	48	16	32	48

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), CH_2Br_2 (0.2 mmol), Hoveyda-Grubbs II (5 mol%) and (S)-**4b** (5 mol%) in CD_2Cl_2 (0.8 mL) at 40℃, the reaction was proceeded in a sealed nmr-tubes. [b] Yield by the ^{1}H NMR.