Supporting Information

Enantioselective Black Rearrangement Catalyzed by Chiral Bicyclic Imidazole

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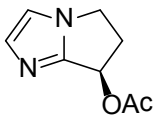
1. General Details

All air- and moisture-sensitive manipulations were carried out under a nitrogen atmosphere. The solvents used in the reactions were distilled under nitrogen after dehydration. All other chemicals and solvents were purchased from commercial company and used as received. The NMR spectra were recorded on a Varian MERCURY plus-400 (400 MHz, ^{1}H; 100 MHz, ^{13}C; 162 MHz, ^{31}P; 376 MHz, ^{19}F) spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvents or the internal standard tetramethylsilane. Infrared spectra were recorded on a PerkinElmer Spectrum 100 FTIR. Mass spectrometry analysis was carried out using an electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Melting points were measured with SGW X-4 micro melting point apparatus. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm. Chiral HPLC analyses were performed using a Shimadzu LC-10Avp system using isopropanol-hexane mobile phase and UV detection.

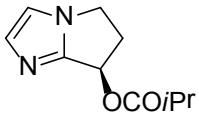
2. Preparation of Catalysts



(*R*)-**2a**

(*R*)-6,7-Dihydro-5*H*-pyrrolo[1,2-*a*]imidazol-7-yl acetate ((*R*)-2a)

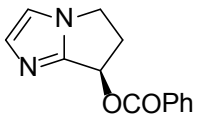
To a dried 25 mL two-necked bottle was added (*R*)-**1** (41.5 mg, 0.33 mmol), Et_3N (0.10 mL, 0.72 mmol, 2.2 eq) and DCM (3 mL). AcCl (0.04 mL, 0.57 mmol, 1.7 eq) was added dropwise at rt and stirred for 2 h. The reaction mixture was extracted by DCM (15 mL × 3) and the combined organic phase was dried over Na_2SO_4. After filtration and removal of DCM, the residue was purified by chromatography (EtOAc/MeOH = 70/1, Rf = 0.38) to give (*R*)-**2a** (48.5 mg, Yield = 88%) as pale yellow oil. **$[\alpha]_D^{20}$** = 39 (*c* 0.129, MeOH). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.19 (s, 1H, Imi-*H*), 6.97 (s, 1H, Imi-*H*), 5.99 (dd, *J* = 7.2 Hz, 2.4 Hz, 1H, OC*H*), 4.22-4.11 (m, 1H, NCH_2), 4.05-3.95 (m, 1H, NCH_2), 3.14-3.01 (m, 1H, CH_2), 2.61-2.49 (m, 1H, CH_2), 2.11 (s, 3H, CH_3). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 169.8, 150.5, 134.0, 115.2, 66.6, 42.4, 34.3, 20.5. **IR (thin film):** ν 3433, 2974, 1736, 1523, 1372, 1238 cm^{-1}. **HRMS (ESI):** calcd. for $C_8H_{11}N_2O_2$ $(M+H)^+$ 167.0821, found 167.0832.



(*R*)-**2b**

(*R*)-6,7-Dihydro-5*H*-pyrrolo[1,2-*a*]imidazol-7-yl isobutyrate ((*R*)-2b)

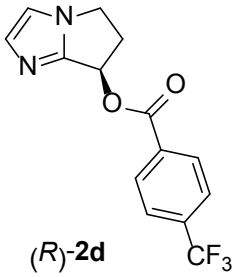
To a dried 25 mL two-necked bottle was added (*R*)-**1** (80.0 mg, 0.64 mmol), Et_3N (0.13 mL, 0.97 mmol, 1.5 eq) and DCM (3 mL). (iPrCO)$_2$O (0.128 mL, 0.77 mmol, 1.2 eq) was added dropwise at rt and stirred for 2 h. The reaction mixture was extracted with DCM (15 mL × 3) and the combined organic phase was dried over Na_2SO_4. After filtration and removal of DCM, the residue was purified by chromatography (EtOAc/ Petroleum ether = 10/1, Rf = 0.38) to give (*R*)-**2b** (123.1 mg, Yield = 99%) as pale yellow oil. **$[\alpha]_D^{20}$** = 40 (*c* 0.381, MeOH). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.19 (s, 1H, Imi-*H*), 6.96 (s, 1H, Imi-*H*), 5.98 (dd, *J* = 8.0 Hz, 2.4 Hz, 1H, OC*H*), 4.19-4.12 (m, 1H, NCH_2), 4.02-3.96 (m, 1H, NCH_2), 3.13-3.04 (m, 1H, C*H*(CH_3)$_2$), 2.61-2.58 (m, 1H, CH_2), 2.54-2.47 (m, 1H, CH_2), 1.18 (d, J = 1.6 Hz, CH(CH_3)$_2$), 1.16 (d, J = 2.4 Hz, CH(CH_3)$_2$). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 176.8, 151.4, 135.0, 115.7, 67.1, 43.1, 35.2, 34.0, 19.2, 18.9. **IR (thin film):** ν 3421, 2976, 1734, 1527, 1388, 1270 cm^{-1}. **HRMS (ESI):** calcd. for $C_8H_{15}N_2O_2$ $[M+H]^+$ 195.1134, found 195.1139.



(*R*)-**2c**

(*R*)-6,7-Dihydro-5*H*-pyrrolo[1,2-*a*]imidazol-7-yl benzoate ((*R*)-2c)

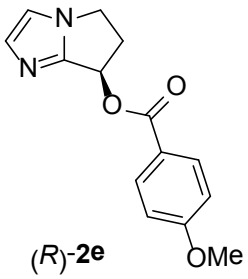
To a dried 25 mL two-necked bottle was added (*R*)-**1** (80.0 mg, 0.64 mmol), Et_3N (0.13 mL, 0.97 mmol, 1.5 eq) and DCM (3 mL). BzCl (0.11 mL, 0.96 mmol, 1.5 eq) was added dropwise at rt and stirred for 2 h. The reaction mixture was extracted with DCM (15 mL × 3) and the combined organic phase was dried over Na_2SO_4. After filtration and removal of DCM, the residue was purified by chromatography (EtOAc/Petroleum ether = 10/1, Rf = 0.34) to give (*R*)-**2c** (144.6 mg, Yield = 99%) as pale yellow oil. **$[\alpha]_D^{20}$** = 11 (*c* 0.243, MeOH). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.05-8.02 (m, 2H, Ar-*H*), 7.57-7.53 (m, 1H, Ar-*H*), 7.43-7.39 (m, 2H, Ar-*H*), 7.23 (s, 1H, Imi-*H*), 7.00 (s, 1H, Imi-*H*), 6.22 (dd, *J* = 5.6 Hz, 2.8 Hz, 1H, OC*H*), 4.26-4.19 (m, 1H, NCH_2), 4.08-4.02 (m, 1H, NCH_2), 3.24-3.16 (m, 1H, CH_2), 2.74-2.67 (m, 1H, CH_2). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 166.3, 151.3, 135.1, 133.4, 130.1, 129.8, 128.5, 115.8, 68.0, 43.2, 35.3. **IR (thin film):** ν 2948, 1717, 1525, 1451, 1343, 1269 cm^{-1}. **HRMS (ESI):** calcd. for $C_{13}H_{13}N_2O_2$ $[M+H]^+$ 229.0977, found 229.0975.



(*R*)-**2d**

(*R*)-6,7-Dihydro-5*H*-pyrrolo[1,2-*a*]imidazol-7-yl 4-(trifluoromethyl)benzoate ((*R*)-2d)

To a dried 25 mL two-necked bottle was added (*R*)-**1** (62.1 mg, 0.50 mmol), Et_3N (84.0 μL, 0.60 mmol, 1.2 eq) and DCM (5 mL). 4-(trifluoromethyl)benzoyl chloride (89.0 μL, 0.60 mmol, 1.2 eq) was added dropwise at rt and stirred for 2 h. The reaction mixture was extracted with DCM (15 mL × 3) and the combined organic phase was dried over Na_2SO_4. After filtration and removal of DCM, the residue was purified by chromatography (EtOAc/Petroleum ether = 10/1, Rf = 0.35) to give (*R*)-**2d** (131.8 mg, Yield = 89%) as pale yellow oil. **$[\alpha]_D^{20}$** = 10 (*c* 0.262, MeOH). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.18-8.13 (m, 2H, Ar-*H*), 7.70-7.66 (m, 2H, Ar-*H*), 7.25 (d, *J* = *0.8* Hz, 1H, Imi-*H*), 7.03 (d, *J* = *0.8* Hz, 1H, Imi-*H*), 6.26 (dd, *J* = 7.2 Hz, 2.4 Hz, 1H, OC*H*), 4.30-4.21 (m, 1H, NCH_2), 4.12-4.05 (m, 1H, NCH_2), 3.28-3.17 (m, 1H, CH_2), 2.77-2.68 (m, 1H, CH_2). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 165.0, 150.9, 135.3, 134.9 (q, *J* = 32.5 Hz), 133.1, 130.5, 125.5 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 270.9 Hz), 115.9, 68.5, 43.2, 35.2. **^{19}F NMR ($CDCl_3$, 376 MHz):** 10.4. **IR (thin film):** ν 2948, 1717, 1525, 1451, 1343, 1269 cm^{-1}. **HRMS (ESI):** calcd. for $C_{14}H_{12}F_3N_2O_2$ $[M+H]^+$ 297.0851, found 297.0830.



(*R*)-**2e**

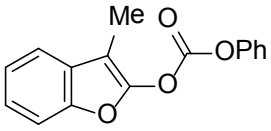
(*R*)-6,7-Dihydro-5*H*-pyrrolo[1,2-*a*]imidazol-7-yl 4-methoxybenzoate ((*R*)-2e)

To a dried 25 mL two-necked bottle was added (*R*)-**1** (62.1 mg, 0.50 mmol), Et_3N (84.0 μL, 0.60 mmol, 1.2 eq) and DCM (5 mL). 4-methoxybenzoyl chloride (89.0 μL, 0.60 mmol, 1.2 eq) was added dropwise at rt and stirred for 2 h. The reaction mixture was extracted with DCM (15 mL × 3) and the combined organic phase was dried over Na_2SO_4. After filtration and removal of DCM, the residue was purified by chromatography (EtOAc/Petroleum ether = 10/1, Rf = 0.35) to give (*R*)-**2e** (118.8 mg, Yield = 92%) as pale yellow oil. $[\alpha]_D^{20}$ = -5 (*c* 0.225, MeOH). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.01-7.96 (m, 2H, Ar-*H*), 7.22 (s, 1H, Imi-*H*), 7.00 (d, *J* = 1.2 Hz, 1H, Imi-*H*), 6.90-6.86 (m, 2H, Ar-*H*), 6.19 (dd, *J* = 7.2 Hz, 2.4 Hz, 1H, OC*H*), 4.26-4.17 (m, 1H, NCH_2), 4.08-4.00 (m, 1H, NCH_2), 3.84 (s, 3H), 3.23-3.11 (m, 1H, CH_2), 2.73-2.64 (m, 1H, CH_2). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 165.9, 163.7, 151.4, 134.8, 132.1, 122.1, 115.8, 113.7, 67.6, 55.6, 43.2, 35.2. **IR (thin film):** ν 2948, 1717, 1525, 1451, 1343, 1269 cm^{-1}. **HRMS (ESI):** calcd. for $C_{14}H_{15}N_2O_3$ $[M+H]^+$ 259.1083, found 259.1088.

3. Preparation of Substrates[1-3]

General procedure:

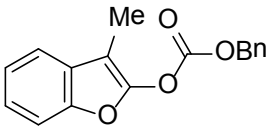
To a solution of Et_3N and benzofuran-2(3*H*)-one in THF was added chloroformate. The reaction mixture was stirred for approximately 3 h until the starting material disappeared according to TLC. After the reaction was completed, THF was evaporated under reduced pressure and the reaction mixture was extracted with EtOAc (15 mL × 3) and the combined organic phase were dried over Na_2SO_4. After filtration and removal of EtOAc, the residue was purified by chromatography (petroleum: ethyl acetate) to give the corresponding product.



3a

3-Methylbenzofuran-2-yl phenyl carbonate (3a)[1]

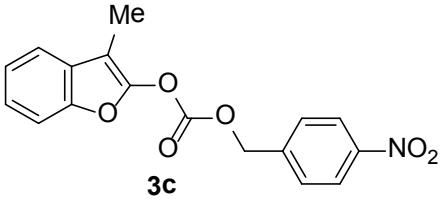
Following the general procedure, Et_3N (0.88 mL, 6.9 mmol), 3-methylbenzofuran-2(3*H*)-one (602 mg, 4.1 mmol), and phenyl chloroformate (0.764 mL, 6.9 mmol) in 20 mL THF gave 3-methylbenzofuran-2-yl phenyl carbonate 773 mg (72% yield) as a colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 2.19 (s, 3H, C*H*$_3$), 7.25-7.32 (m, 5H, Ar-*H*), 7.40-7.49 (m, 4H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 6.9, 99.0, 111.3, 119.7, 120.9, 123.2, 124.4, 127.0, 129.6, 130.0, 149.3, 149.8, 150.4, 151.0.



3b

Benzyl 3-methylbenzofuran-2-yl carbonate (3b)

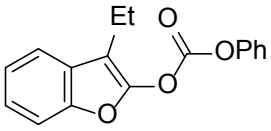
Following the general procedure, Et_3N (0.55 mL, 3.75 mmol), 3-methylbenzofuran-2(3*H*)-one (371 mg, 2.5 mmol), and benzyl chloroformate (0.54 mL, 3.75 mmol) in 20 mL THF gave benzyl 3-methylbenzofuran-2-yl carbonate 565 mg (80% yield) as a white solid. **M.p.:** 43-45 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 2.11 (s, 3H, C*H*$_3$), 5.32 (s, 2H, C*H*$_2$), 7.21-7.29 (m, 2H, Ar-*H*), 7.36-7.47 (m, 7H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 6.8, 71.7, 98.7, 111.2, 119.6, 123.1, 124.3, 128.9, 129.0, 129.3, 129.6, 134.2, 149.6, 149.7, 152.0. **IR (thin film):** ν 2926, 1771, 1669, 1457, 1384, 1240, 1108, 920, 745 cm^{-1}. **HRMS (ESI):** calcd. for $C_{17}H_{14}NaO_4$ $(M+Na)^+$ 305.0790, found 305.0820.



3c

3-Methylbenzofuran-2-yl 3-(4-nitrophenyl)propanoate (3c)

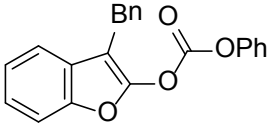
Following the general procedure, Et_3N (0.56 mL, 4.0 mmol), 3-methylbenzofuran-2(3*H*)-one (445 mg, 3 mmol), and 4-nitrobenzyl carbonochloridate (776 mg, 3.6 mmol) in 20 mL THF gave 3-methylbenzofuran-2-yl 3-(4-nitrophenyl)propanoate 752 mg (77% yield) as a yellow solid. **M.p.:** 83-85 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 2.13 (s, 3H, C*H*$_3$), 5.42 (s, 2H, C*H*$_2$), 7.25-7.29 (m, 2H, Ar-*H*), 7.37-7.46 (m, 2H, Ar-*H*), 7.61 (d, J = 9.2 Hz, 2H, Ar-*H*), 8.27-8.30 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 6.7, 69.8, 98.9, 111.2, 119.7, 123.3, 124.1, 124.5, 128.8, 129.5, 141.3, 148.3, 149.3, 149.7, 151.8. **IR (thin film):** ν 2930, 1782, 1659, 1545, 1441, 1354, 1354, 1198, 1089, 880 cm^{-1}. **HRMS (ESI):** calcd. for $C_{17}H_{13}NNaO_6$ $(M+Na)^+$ 350.0641, found 350.0649.



3d

3-Ethylbenzofuran-2-yl phenyl carbonate (3d)[1]

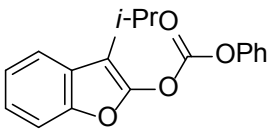
Following the general procedure, Et_3N (0.88 mL, 6.9 mmol), 3-ethylbenzofuran-2(3*H*)-one (601.6 mg, 4.1 mmol), and phenyl chloroformate (0.764 mL, 6.9 mmol) in 20 mL THF gave 3-ethylbenzofuran-2-yl phenyl carbonate 856.5 mg (74% yield) as a colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.32 (t, J = 7.6 Hz, 3H, CH_2CH_3), 2.68 (q, J = 7.2 Hz, 2H, CH_2CH_3), 7.25-7.32 (m, 4H, Ar-*H*), 7.40-7.45 (m, 3H, Ar-*H*), 7.51-7.52(m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 13.4, 16.0, 104.8, 111.4, 119.9, 120.8, 123.1, 124.3, 126.9, 128.8, 129.9, 148.7, 149.9, 150.6, 151.0.



3e

3-Benzylbenzofuran-2-yl phenyl carbonate (3e)[1,2]

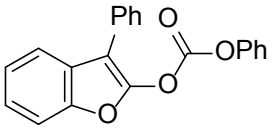
Following the general procedure, Et_3N (0.88 mL, 6.9 mmol), 3-benzylbenzofuran-2(3*H*)-one (897 mg, 4.0 mmol), and phenyl chloroformate (0.764 mL, 6.9 mmol) in 20 mL THF gave 3-benzylbenzofuran-2-yl phenyl carbonate 1005 mg (73% yield) as a colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 4.01 (s, 2H, C*H*$_2$), 7.16-7.19 (m, 1H, , Ar-*H*), 7.22-7.30 (m, 10H, Ar-*H*), 7.39-7.44 (m, 3H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 28.8, 102.4, 111.4, 120.3, 120.8, 121.2, 123.4, 124.5, 126.5, 126.8, 127.0, 128.7, 128.8, 128.9, 129.8, 129.9, 138.4, 149.8, 150.0, 150.4, 151.0.



3f

3-Isopropylbenzofuran-2-yl phenyl carbonate (3f)[2]

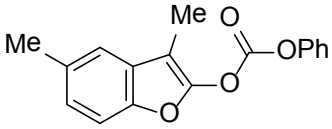
Following the general procedure, Et_3N (0.88 mL, 6.9 mmol), 3-isopropylbenzofuran-2(3*H*)-one (723 mg, 4.1 mmol), and phenyl chloroformate (0.764 mL, 6.9 mmol) in 20 mL THF gave 3-isopropylbenzofuran-2-yl phenyl carbonate 842 mg (71% yield) as a colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.43 (d, J = 7.2 Hz, 6H, CH(CH_3)$_2$), 3.10-3.18 (m, 1H, CH(CH$_3$)$_2$), 7.25-7.33 (m, 5H, Ar-*H*), 7.42-7.44 (m, 3H, Ar-*H*), 7.59-7.62 (m, 1H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 21.9, 24.4, 108.8, 111.5, 120.6, 120.8, 123.0, 124.2, 127.0, 128.1, 130.0, 148.0, 150.0, 150.7, 151.1.



3g

Phenyl 3-phenylbenzofuran-2-yl carbonate (3g)[1]

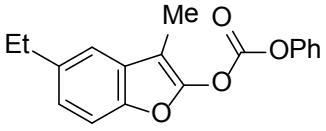
Following the general procedure, Et_3N (0.16 mL, 1.1 mmol), 3-phenylbenzofuran-2(3*H*)-one (150 mg, 0.7 mmol), and phenyl chloroformate (0.13 mL, 1.06 mmol) in 8 mL THF gave phenyl 3-phenylbenzofuran-2-yl carbonate 183 mg (79% yield) as a light orange oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.20-7.22 (m, 2H, Ar-*H*), 7.25-7.36 (m, 4H, Ar-*H*), 7.38-7.42 (m, 3H, Ar-*H*), 7.49-7.53 (m, 3H, Ar-*H*), 7.65-7.75 (m, 1H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 105.2, 111.7, 120.6, 120.8, 121.2, 124.0, 125.0, 126.6, 127.0, 127.8, 128.0, 128.5, 129.3, 129.9, 130.0, 130.3, 149.0, 150.1, 150.3, 151.1, 151.3.



3h

3,5-Dimethyl-2,3-dihydrobenzofuran-2-yl phenyl carbonate (3h)

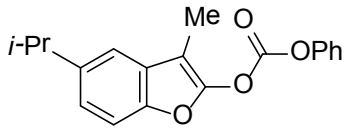
Following the general procedure, Et_3N (0.43 mL, 3.0 mmol), 3,5-dimethylbenzofuran-2(3*H*)-one (408 mg, 2.5 mmol), and phenyl chloroformate (0.38 mL, 3.0 mmol) in 10 mL THF gave 3,5-dimethyl-2,3-dihydrobenzofuran-2-yl phenyl carbonate 600 mg (85% yield) as a white solid. **M.p.:** 57-59 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.17 (s, 3H, CH_3), 2.45 (s, 3H, Ar-CH_3), 7.08-7.10 (m, 1H, Ar-*H*), 7.25-7.32 (m, 5H, Ar-H), 7.41-7.45 (t, J = 8.0 Hz, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 6.9, 21.7, 98.7, 110.8, 119.6, 120.9, 125.5, 127.0, 129.6, 130.0, 132.7, 148.1, 149.4, 150.5, 151.1. **IR (thin film):** ν 3044, 2916, 1782, 1660, 1593, 1495, 1458, 1239, 1069, 870, 823 cm^{-1}. **HRMS (ESI):** calcd. for $C_{17}H_{14}O_4Na$ $(M+Na)^+$ 305.0790, found 305.0804.



3i

5-Ethyl-3-methyl-2,3-dihydrobenzofuran-2-yl phenyl carbonate (3i)

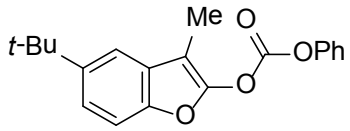
Following the general procedure, Et_3N (1.04 mL, 7.2 mmol), 5-ethyl-3-methylbenzofuran-2(3*H*)-one (1057 mg, 6 mmol), phenyl chloroformate (0.91 mL, 7.2 mmol) in 20 mL THF gave 5-ethyl-3-methyl-2,3-dihydrobenzofuran-2-yl phenyl carbonate 1438 mg (81% yield) as a white solid. **M.p.:** 28-29 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.28 (t, J = 7.6 Hz, 3H, CH_2CH_3), 2.17 (s, 3H, CH_3), 2.73 (q, J = 7.2 Hz, 2H, CH_2CH_3), 7.10-7.14 (m, 1H, Ar-*H*), 7.27-7.33 (m, 5H, Ar-*H*), 7.39-7.45 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 6.9, 16.6, 29.2, 98.9, 110.9, 118.4, 120.9, 124.5, 126.9, 129.6, 129.9, 139.4, 148.3, 149.4, 150.5, 151.0. **IR (thin film):** ν 3024, 2965, 2929, 1785, 1660, 1593, 1493, 1455, 1211, 867, 734 cm^{-1}. **HRMS (ESI):** calcd. for $C_{18}H_{17}O_4$ $(M+H)^+$ 297.1127, found 297.1131.



3j

5-Isopropyl-3-methyl-2,3-dihydrobenzofuran-2-yl phenyl carbonate (3j)

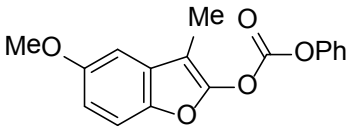
Following the general procedure, Et_3N (1.04 mL, 7.2 mmol), 5-isopropyl-3-methylbenzofuran-2(3*H*)-one (1140 mg, 6 mmol), phenyl chloroformate (0.91 mL, 7.2 mmol) in 20 mL THF gave 5-isopropyl-3-methyl-2,3-dihydrobenzofuran-2-yl phenyl carbonate 1489 mg (80% yield) as a white solid. **M.p.:** 30-31 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.29 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$), 2.18 (s, 3H, CH_3), 2.90-3.05 (m, 1H, $CH(CH_3)_2$), 7.14-7.17 (m, 1H, Ar-*H*), 7.24-7.33 (m, 5H, Ar-*H*), 7.40-7.45 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 6.9, 24.8, 34.5, 98.9, 110.9, 116.9, 120.9, 123.2, 126.9, 129.5, 129.9, 144.1, 148.3, 149.4, 150.5, 151.0. **IR (thin film):** ν 3023, 2962, 2927, 2870, 1797, 1664, 1592, 1493, 1458, 1224, 1122, 876, 734 cm^{-1}. **HRMS (ESI):** calcd. for $C_{19}H_{19}O_4$ $(M+H)^+$ 311.1283, found 311.1280.



3k

5-*tert*-Butyl-3-methylbenzofuran-2-yl phenyl carbonate (3k)

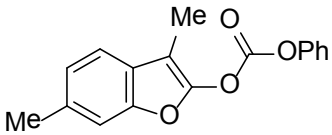
Following the general procedure, Et_3N (0.87 mL, 6 mmol), 5-*tert*-butyl-3-methylbenzofuran-2(3*H*)-one (1021 mg, 5 mmol), phenyl chloroformate (0.76 mL, 6 mmol) in 20 mL THF gave 5-*tert*-butyl-3-methylbenzofuran-2-yl phenyl carbonate 1281 mg (79% yield) as a white solid. **M.p.:** 83-85 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.38 (s, 9H, $C(CH_3)_3$), 2.20 (s, 3H, CH_3), 7.27-7.37 (m, 5H, Ar-*H*), 7.40-7.48 (m, 3H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 6.9, 32.1, 35.0, 99.1, 110.6, 115.9, 120.9, 122.3, 127.0, 129.1, 130.0, 146.3, 148.0, 149.4, 150.5, 151.0. **IR (thin film):** ν 3068, 2959, 1797, 1664, 1591, 1494, 1458, 1393, 1366, 1224, 1125, 885, 730 cm^{-1}. **HRMS (ESI):** calcd. for $C_{20}H_{21}O_4$ $(M+H)^+$ 325.1440, found 305.1431.



3l

5-Methoxy-3-methylbenzofuran-2-yl phenyl carbonate (3l)

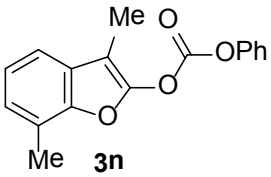
Following the general procedure, Et_3N (0.87 mL, 6 mmol), 5-methoxy-3-methylbenzofuran-2(3*H*)-one (890.9 mg, 5 mmol), phenyl chloroformate (0.76 mL, 6 mmol) in 20 mL THF gave 5-methoxy-3-methylbenzofuran-2-yl phenyl carbonate 1163 mg (78% yield) as a white solid. **M.p.:** 78-80 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 2.17 (s, 3H, C*H*$_3$), 3.86 (s, 3H, OC*H*$_3$), 6.86-6.94 (m, 2H, Ar-*H*), 7.30 (d, *J* = 9.2 Hz, 4H, Ar-*H*), 7.44 (t, *J* = 7.6 Hz, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 6.9, 56.1, 99.2, 102.7, 111.9, 112.6, 120.8, 127.0, 129.9, 135.2, 144.5, 149.7, 150.4, 151.0, 156.3. **IR (thin film):** ν 3070, 2966, 2913, 1779, 1658, 1595, 1497, 1457, 1247, 1174, 879, 728 cm^{-1}. **HRMS (ESI):** calcd. for $C_{17}H_{15}O_5$ $(M+H)^+$ 299.0919, found 299.0902.



3m

3,6-Dimethylbenzofuran-2-yl phenyl carbonate (3m)

Following the general procedure, Et_3N (1.34 mL, 9.6 mmol), 3,6-dimethylbenzofuran-2(3*H*)-one (1300 mg, 8 mmol), phenyl chloroformate (1.21 mL, 8 mmol) in 30 mL THF gave 3,6-dimethylbenzofuran-2-yl phenyl carbonate 1827 mg (81% yield) as a white solid. **M.p.:** 76-78 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 2.17 (s, 3H, C*H*$_3$), 2.46 (s, 3H, Ar-C*H*$_3$), 7.07-7.09 (m, 1H, Ar-*H*), 7.21-7.32 (m, 4H, Ar-*H*), 7.35 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.41-7.46 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 6.9, 21.9, 98.8, 111.6, 119.2, 120.9, 121.2, 124.5, 127.0, 129.9, 134.7, 148.9, 150.1, 150.6, 151.1. **IR (thin film):** ν 3064, 2938, 1815, 1762, 1495, 1452, 1138, 1071, 815, 744 cm^{-1}. **HRMS (ESI):** calcd. for $C_{17}H_{14}NaO_4$ $(M+Na)^+$ 305.0790, found 305.0815.

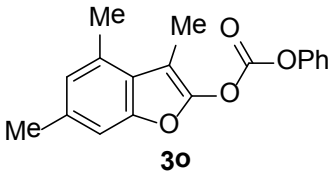


3n

3,7-Dimethylbenzofuran-2-yl phenyl carbonate (3n)

Following the general procedure, Et_3N (1.34 mL, 9.6 mmol), 3,7-dimethylbenzofuran-2(3*H*)-one (1300 mg, 8 mmol), phenyl chloroformate (1.21 mL, 8 mmol) in 30 mL THF gave 3,7-dimethylbenzofuran-2-yl phenyl carbonate 1895 mg (84% yield) as a white solid. **M.p.:** 67-68 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 2.18 (s, 3H, C*H*$_3$), 2.49 (s, 3H, Ar-C*H*$_3$), 7.08-7.10 (m, 1H, Ar-*H*), 7.17 (t, *J* = 7.2 Hz, 1H, Ar-*H*), 7.26-7.46 (m,

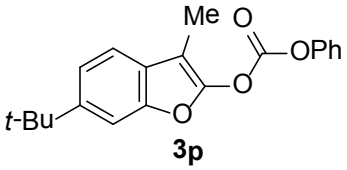
6H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 7.0, 15.1, 99.2, 117.1, 120.9, 121.5, 123.3, 125.6, 126.9, 129.1, 130.0, 148.8, 149.2, 150.5, 151.0. **IR (thin film):** ν 3065, 2937, 1813, 1762, 1492, 1456, 1189, 1095, 874, 746 cm^{-1}. **HRMS (ESI):** calcd. for $C_{17}H_{15}O_4$ $(M+H)^+$ 283.0970, found 283.0977.



3o

Phenyl 3,4,6-trimethylbenzofuran-2-yl carbonate (3o)

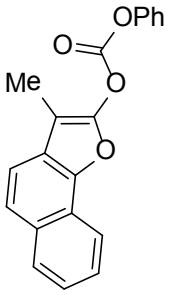
Following the general procedure, Et_3N (1.04 mL, 7.2 mmol), 3,4,6-trimethylbenzofuran-2(3*H*)-one (1057 mg, 6 mmol), phenyl chloroformate (0.91 mL, 7.2 mmol) in 20 mL THF gave phenyl 3,4,6-trimethylbenzofuran-2-yl carbonate 1367 mg (77% yield) as a white solid. **M.p.:** 55-57 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** *δ* 2.31 (s, 3H, C*H*$_3$), 2.40 (s, 3H, Ar-C*H*$_3$), 2.58 (s, 3H, Ar-C*H*$_3$), 6.81 (s, 1H, Ar-*H*), 7.04 (s, 1H, Ar-*H*), 7.29-7.31 (m, 3H, Ar-*H*), 7.41-7.44 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** *δ* 9.3, 19.0, 21.8, 99.5, 109.3, 120.9, 125.0, 126.1, 126.9, 129.9, 131.5, 134.4, 148.7, 150.3, 150.7, 151.0. **IR (thin film):** ν 3076, 2917, 1786, 1665, 1590, 1496, 1458, 1261, 1066, 850, 768 cm^{-1}. **HRMS (ESI):** calcd. for $C_{18}H_{17}O_4$ $(M+H)^+$ 297.1127, found 297.1128.



3p

6-*tert*-Butyl-3-methylbenzofuran-2-yl phenyl carbonate (3p)

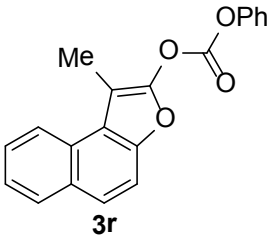
Following the general procedure, Et_3N (0.84 mL, 6.0 mmol), 6-*tert*-butyl-3-methylbenzofuran-2(3*H*)-one (1200 mg, 5 mmol), phenyl chloroformate (0.70 mL, 6.0 mmol) in 20 mL THF gave 6-*tert*-butyl-3-methylbenzofuran-2-yl phenyl carbonate 1257 mg (77% yield) as a white solid. **M.p.:** 75-77 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** *δ* 1.37 (s, 9H, C(C*H*$_3$)$_3$), 2.18 (s, 3H, C*H*$_3$), 7.27-7.35 (m, 4H, Ar-*H*), 7.38-7.46 (m, 4H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** *δ* 6.9, 31.9, 35.3, 98.8, 108.1, 119.1, 120.9, 121.0, 126.6, 127.0, 130.0, 148.5, 149.2, 150.2, 150.6, 151.1. **IR (thin film):** ν 3057, 2962, 1794, 1666, 1591, 1492, 1459, 1228, 1145, 876, 738 cm^{-1}. **HRMS (ESI):** calcd. for $C_{20}H_{20}NaO_4$ $(M+Na)^+$ 347.1259, found 347.1235.



3q

3-Methylnaphtho[1,2-b]furan-2-yl phenyl carbonate (3q)

Following the general procedure, Et_3N (0.59 mL, 4.2 mmol), 3-methylnaphtho[1,2-*b*]furan-2(3*H*)-one (694 mg, 3.5 mmol), phenyl chloroformate (0.53 mL, 4.2 mmol) in 10 mL THF gave 3-methylnaphtho[1,2-b]furan-2-yl phenyl carbonate 858 mg (77% yield) as a white solid. **M.p.:** 94-96 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 2.28 (s, 3H, CH_3), 7.29-7.36 (m, 3H, Ar-*H*), 7.43-7.49 (m, 3H, Ar-*H*), 7.56-7.59 (m, 2H, Ar-*H*), 7.71 (d, J = 8.4 Hz, 1H, Ar-*H*), 7.92 (d, J = 8.4Hz, 1H, Ar-*H*), 8.23 (d, J = 8.0 Hz, 1H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 7.2, 100.4, 118.2, 119.9, 120.9, 121.2, 123.9, 125.3, 126.8, 127.1, 128.8, 129.9, 130.0, 131.6, 144.8, 148.7, 150.8, 151.2. **IR (thin film):** ν 3061, 2954, 1779, 1660, 1591, 1240, 1066, 805, 726 cm^{-1}. **HRMS (ESI):** calcd. for $C_{20}H_{15}O_4$ $(M+H)^+$ 319.0970, found 319.0981.



3r

1-Methylnaphtho[2,1-b]furan-2-yl phenyl carbonate (3r)

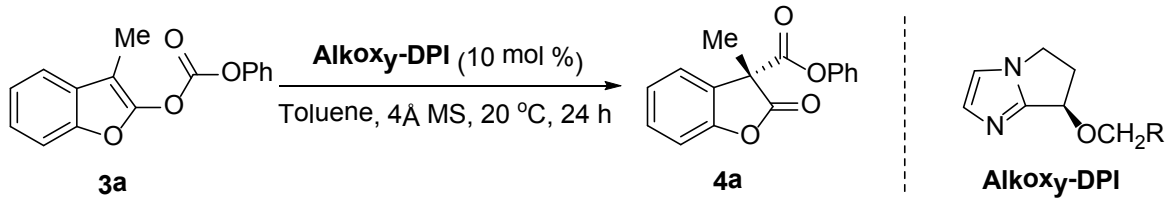
Following the general procedure, Et_3N (0.59 mL, 4.2 mmol), 3-methylnaphtho[1,2-*b*]furan-2(3*H*)-one (694 mg, 3.5 mmol), phenyl chloroformate (0.53 mL, 4.2 mmol) in 10 mL THF gave 3-methylnaphtho[1,2-*b*]furan-2-yl phenyl carbonate 880 mg (79% yield) as a white solid. **M.p.:** 84-85 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 2.58 (s, 3H, CH_3), 7.28-7.34 (m, 3H, Ar-*H*), 7.43-7.57 (m, 5H, Ar-*H*), 7.59 (d, J = 4.8 Hz, 1H, Ar-*H*), 7.95 (d, J = 9.6 Hz, 1H, Ar-*H*), 8.33 (d, J = 8.8 Hz, 1H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 10.0, 101.2, 112.3, 120.9, 122.8, 123.2, 124.7, 125.4, 126.5, 127.0, 129.1, 129.4, 130.0, 131.0, 147.0, 148.9, 150.8, 151.1. **IR (thin film):** ν 3031, 2961, 1781, 1648, 1582, 1239, 1068, 789, 683 cm^{-1}. **HRMS (ESI):** calcd. for $C_{20}H_{15}O_4$ $(M+H)^+$ 319.0970, found 319.0977.

4. Catalytic Enantioselective Rearrangements

General procedure:

The substrate (0.075 mmol) was dissolved in *tert*-amyl alcohol (1 mL) and cooled to 0 °C. The catalyst (*R*)-**2a** (0.10 eq) in *tert*-amyl alcohol (0.5 mL) was added and the vial was sealed with a septum. The reaction mixture was stirred at 0 °C for 36 h. The conversion (product relative to SM) was calculated from ^{1}H NMR spectra. The ee value was determined by chiral HPLC analysis after purification by column chromatography (petroleum ether: ethyl acetate). The absolute configuration of **4a**, **4d**, **4e**, **4f** and **4g** was assigned by comparing the HPLC retention times with the literature data.[1] The absolute configuration of other products were considered to be the same as **4a**.

Table S1. Initial attempts using Alkoxy-DPI (R = H, Ph) as catalysts



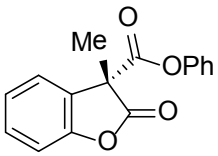
3a **4a** **Alkoxy-DPI**

entry	**Alkoxy-DPI**	solvent	conv. (%)[b]	ee (%)[c]
1	R = H	Toluene	99	43
2	R = Ph	Toluene	97	46

[a] Conditions: **3a** (0.05 mol/L), (*R*)-**2** (10 mol%), Toluene (1.0 mL), 20 °C, 24 h;

[b] Conversions were determined by ^{1}H NMR;

[c] Ees were determined by HPLC with chiral columns.

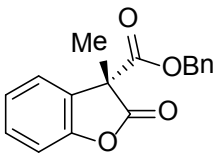


4a

(*R*)-Phenyl 3-methyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4a)[1]

Following the general procedure, enol carbonate (20.12 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 87% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. **HPLC analysis:** 81% ee [Daicel CHIRALPAK OJ column; solvent system: 10% isopropanol/90% hexanes; 1.0 mL/min; retention times: 17.0 min (major), 19.0 min (minor)]. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.89 (s, 3H, CH_3), 6.96-6.98 (m, 2H, Ar-*H*), 7.20-7.26 (m, 3H, Ar-*H*), 7.31-7.35 (m, 2H, Ar-*H*), 7.38-7.42 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 20.8, 54.2, 111.6, 121.1, 123.6, 125.1, 126.6, 128.4, 129.6,

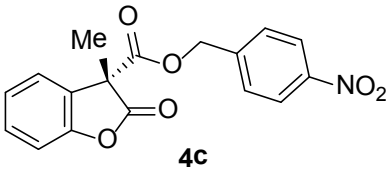
130.5, 150.4, 153.6, 167.0, 173.9.



4b

(*R*)-Benzyl 3-methyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4b)

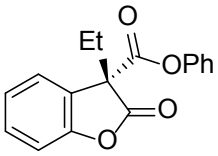
Following the general procedure, enol carbonate (21.20 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 14% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. **M.p.:** 43-44 °C. **HPLC analysis:** 87% ee [Daicel CHIRALPAK OJ column; solvent system: 10% isopropanol/90% hexanes; 1.0 mL/min; retention times: 23.3 min (minor), 27.1 min (major)]. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.79 (s, 3H, CH_3), 5.14 (dd, J = 12.4 Hz, 6 Hz, 2H, CH_2), 7.12-7.17 (m, 4H, Ar-*H*), 7.22-7.30 (m, 4H, Ar-*H*), 7.32-7.38 (m, 1H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz, quantitative):** δ 20.7, 54.1, 68.0, 111.4, 123.7, 124.9, 127.7 (2C), 128.6 (2C), 128.8 (2C), 130.3, 135.1, 153.4, 168.1, 174.3. **IR (thin film):** ν 3058, 2931, 1822, 1760, 1479, 1148, 1066, 771, 715 cm^{-1}. **HRMS (ESI):** calcd. for $C_{17}H_{15}O_4$ $(M+H)^+$ 283.0970, found 383.0989.



4c

(*R*)-4-Nitrobenzyl 3-methyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4c)

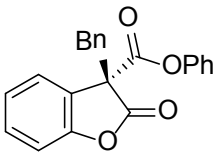
Following the general procedure, enol carbonate (24.50 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 20 °C for 36 h. The conversion (product relative to SM) of 97% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. **M.p.:** 85-87 °C. **HPLC analysis:** 80% ee [Daicel CHIRALPAK OJ column; solvent system: 10% isopropanol/90% hexanes; 1.0 mL/min; retention times: 62.7 min (minor), 68.3 min (major)]. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.80 (s, 3H, CH_3), 5.22 (dd, J = 20.4, 14.0 Hz, 2H, CH_2), 7.16-7.18 (m, 2H, Ar-*H*), 7.19-7.29 (m, 3H, Ar-*H*), 7.37-7.42 (m, 1H, Ar-*H*), 8.41 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 20.6, 53.9, 66.4, 111.5, 123.6, 124.1, 125.0, 127.9, 128.2, 130.5, 142.2, 147.9, 153.4, 167.9, 174.1. **IR (thin film):** ν 3069, 2928, 1813, 1761, 1545, 1493, 1168, 1059, 779, 720. **HRMS (ESI):** calcd. for $C_{17}H_{14}NO_6$ $(M+H)^+$ 328.0821, found 328.0815.



4d

(*R*)-Phenyl 3-ethyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4d)[1]

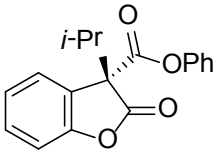
Following the general procedure, enol carbonate (21.17 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 88% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. **HPLC analysis:** 81% ee [Daicel CHIRALPAK OJ column; solvent system: 10% isopropanol/90% hexanes; 0.5 mL/min; retention times: 44.1 min (major), 59.5 min (minor)]. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 0.93 (t, J = 7.2 Hz, 3H, CH_2CH_3), 2.27-2.52 (m, 2H, CH_2CH_3), 6.98-7.00 (m, 2H, Ar-*H*), 7.20-7.27 (m, 3H, Ar-*H*), 7.32-7.36 (m, 2H, Ar-*H*), 7.38-7.44 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 8.6, 28.4, 59.5, 111.4, 121.2, 124.0, 125.0, 126.3, 126.6, 129.7, 130.5, 150.4, 154.0, 166.7, 173.1.



4e

(*R*)-Phenyl 3-benzyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4e)[1,2]

Following the general procedure, enol carbonate (25.83 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 89% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. **HPLC analysis:** 80% ee [Daicel CHIRALPAK OJ column; solvent system: 10% isopropanol/90% hexanes; 1.0 mL/min; retention times: 33.7 min (major), 46.2 min (minor)]. **^{1}H NMR (CDCl3, 400 MHz):** δ 3.70 (s, 2H, CH_2), 6.94-7.02 (m, 5H, Ar-*H*), 7.10-7.14 (m, 3H, Ar-*H*), 7.20-7.24 (m, 2H, Ar-*H*), 7.30-7.38 (m, 3H, Ar-*H*), 7.43-7.47 (m, 1H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 40.5, 60.5, 111.4, 121.3, 124.5, 124.8, 125.9, 126.8, 127.7, 128.5, 129.8, 130.3, 130.6, 133.5, 150.4, 153.8, 166.6, 172.6.

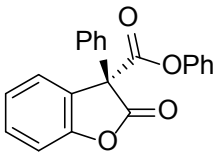


4f

(*R*)-Phenyl 3-isopropyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4f)[1,2]

Following the general procedure, enol carbonate (22.22 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h.

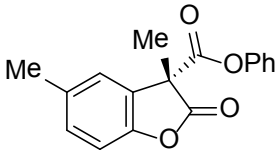
The conversion (product relative to SM) of 21% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. HPLC analysis: 54% ee [Daicel CHIRALPAK OJ column; solvent system: 10% isopropanol/90% hexanes; 0.5 mL/min; retention times: 44.8 min (major), 61.7 min (minor)]. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 0.95 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.22 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 2.87-2.98 (m, 1H, $CH(CH_3)_2$), 7.01-7.04 (m, 2 H, Ar*H*), 7.16-7.26 (m, 3H, Ar-*H*), 7.33-7.42 (m, 3H, Ar-H), 7.45-7.48 (m, 1H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz, read by NUTS software):** δ 16.8, 16.9, 29.3, 35.2, 110.5, 120.7, 124.1, 124.2, 125.4, 126.0, 129.1, 129.7, 149.9, 153.2, 165.9, 171.1.



4g

(*R*)-Phenyl 2-oxo-3-phenyl-2,3-dihydrobenzofuran-3-carboxylate (4g)[1]

Following the general procedure, enol carbonate (24.77 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 29% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. **HPLC analysis:** 70% ee [Daicel CHIRALPAK OJ column; solvent system: 10% isopropanol/90% hexanes; 1.0 mL/min; retention times: 47.5 min (minor), 50.6 min (major)]. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.89 (s, 3H, CH_3), 6.95-7.42 (m, 14H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz, quantitative):** δ 63.1, 111.9, 121.2(2C), 125.3, 125.4, 126.7, 126.9, 128.0(2C), 129.4(3C), 129.9(2C), 131.4, 134.5, 150.6, 154.1, 166.5, 171.5.

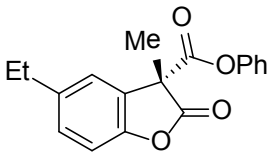


4h

(*R*)-Phenyl 3,5-dimethyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4h)

Following the general procedure, enol carbonate (21.20 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 88% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. **M.p.:** 69-72 °C. **HPLC analysis:** 79% ee [Daicel CHIRALPAK IE column; solvent system: 8% isopropanol / 92% hexane; 0.5 mL/min; retention times: 45.7 min (minor), 50.2 min (major)]. **$[\alpha]^{25}_D$** = –48 (*c* 0.10, CH_2Cl_2). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.86 (s, 3H, CH_3), 2.39 (s, 3H, Ar-CH_3), 6.97-7.00 (m, 2H, Ar-*H*), 7.07-7.10 (m, 1H, Ar-*H*), 7.18-7.24 (m, 3H, Ar-*H*), 7.31-7.36 (m, 2H, Ar-*H*). **^{13}C**

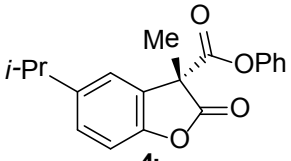
NMR ($CDCl_3$, 100 MHz): δ 20.8, 21.4, 54.3, 111.2, 121.2, 124.0, 126.7, 128.2, 129.7, 130.9, 134.9, 150.4, 151.4, 167.2, 174.3. **IR (KBr, thin film):** ν 3066, 2938, 1821, 1776, 1486, 1451, 1186, 1096, 886, 748 cm^{-1}. **HRMS (ESI):** calcd. for $C_{17}H_{14}NaO_4$ $(M+Na)^+$ 305.0790, found 305.0780.



4i

(*R*)-Phenyl 5-ethyl-3-methyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4i)

Following the general procedure, enol carbonate (22.22 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 99% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a yellow oil. **HPLC analysis:** 81% ee [Daicel CHIRALPAK IE column; solvent system: 8% isopropanol/92% hexanes; 0.5 mL/min; retention times: 13.5 min (major), 16.5 min (minor)]. **$[\alpha]^{20}_D$** = –12 (*c* 0.40, CH_2Cl_2). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.25 (t, *J* = 8.0 Hz, 3H, CH_2CH_3), 1.87 (s, 3H, CH_3), 2.68 (q, *J* = 4.0 Hz, 2H, CH_2CH_3), 6.97 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.11 (d, *J* = 7.6 Hz，1H, Ar-*H*), 7.19-7.25 (m, 3H, Ar-*H*), 7.31-7.35 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 16.1, 20.8, 28.8, 54.4, 111.3, 121.2, 122.9, 126.7, 128.3, 129.7, 129.9, 141.5, 150.4, 151.6, 167.2, 174.4. **IR (thin film):** ν 3066, 2968, 2937, 1812, 1761, 1486, 1467, 1190, 1040, 826, 745 cm^{-1}. **HRMS (ESI):** calcd. for $C_{18}H_{16}NaO_4$ $(M+Na)^+$ 297.1127, found 297.1140.

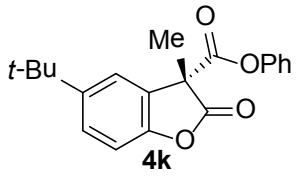


4j

(*R*)-Phenyl 5-isopropyl-3-methyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4j)

Following the general procedure, enol carbonate (23.28 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 99% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. **M.p.:** 70-72 °C. **HPLC analysis:** 86% ee [Daicel CHIRALPAK OJ column; solvent system: 10% isopropanol/90% hexanes; 0.5 mL/min; retention times: 18.2 min (minor), 19.0 min (major)]. **$[\alpha]^{20}_D$** = –19 (*c* 0.40, CH_2Cl_2). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.26 (d, *J* = 7.2 Hz, 6H, $CH(CH_3)_2$), 1.88 (s, 3H, CH_3), 2.90-3.00 (m, 1H, $CH(CH_3)_2$), 6.96-6.98 (m, 2H, Ar-*H*), 7.12 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 7.20-7.27 (m, 3H, Ar-*H*), 7.31-7.36 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 17.6, 19.2, 21.9, 54.4, 109.7, 121.3, 123.6, 126.6, 127.6, 129.7, 134.9, 140.6, 150.4, 153.9, 166.9, 174.6. **IR (thin**

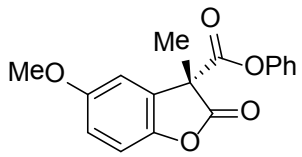
film): ν 3069, 2964, 2938, 2873, 1807, 1758, 1483, 1459, 1191, 1040, 823, 742 cm^{-1}. **HRMS (ESI):** calcd. for $C_{19}H_{19}O_4$ $(M+H)^+$ 311.1283, found 311.1280.



4k

(*R*)-Phenyl 5-tert-butyl-3-methyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4k)

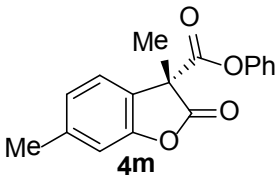
Following the general procedure, enol carbonate (24.33 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 80% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a light yellow solid. **M.p.:** 87-88 °C. **HPLC analysis:** 88% ee [Daicel CHIRALPAK OD column; solvent system: 1% isopropanol/99% hexanes; 0.3 mL/min; retention times: 21.4 min (major), 27.5 min (minor)]. **$[\alpha]^{20}_D$** = –8 (*c* 0.20, CH_2Cl_2). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.34 (s, 9H, $(CH_3)_3$), 1.89 (s, 3H, CH_3), 6.97 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.12 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 7.22-7.36 (m, 3H, Ar-*H*), 7.38-7.44 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 20.9, 31.8, 35.1, 54.5, 110.9, 120.4, 121.2, 126.7, 127.4, 127.9, 129.7, 148.6, 150.4, 151.3, 167.3, 174.4. **IR (thin film):** ν 3065, 2964, 1812, 1760, 1487, 1458, 1193, 1040, 819, 745 cm^{-1}. **HRMS (ESI):** calcd. for $C_{20}H_{21}O_4$ $(M+H)^+$ 325.1440, found 325.1435.



4l

(*R*)-Phenyl 5-methoxy-3-methyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4l)

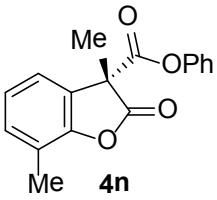
Following the general procedure, enol carbonate (22.37 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 76% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a light yellow solid. **M.p.:** 69-71 °C. **HPLC analysis:** 73% ee [Daicel CHIRALPAK OJ column; solvent system: 7% isopropanol/93% hexanes; 1.0 mL/min; retention times: 30.1 min (minor), 39.0 min (major)]. **$[\alpha]^{20}_D$** = –13 (*c* 0.20, CH_2Cl_2). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.86 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 6.89-6.93 (m, 1H, Ar-*H*), 6.98 (d, *J* = 8.8 Hz, 1H, Ar-*H*), 7.11 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.17-7.26 (m, 1H, Ar-*H*), 7.31(q, *J* = 5.6 Hz, 3H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 20.8, 54.8, 56.2, 109.4, 112.1, 115.5, 121.2, 126.7, 129.1, 129.7, 147.2, 150.4, 157.3, 167.1, 174.4. **IR (thin film):** ν 3072, 2940, 1810, 1760, 1487, 1457, 1190, 809, 745 cm^{-1}. **HRMS (ESI):** calcd. for $C_{17}H_{15}O_5$ $(M+H)^+$ 299.0919, found 299.0928.



4m

(*R*)-Phenyl 3,6-dimethyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4m)

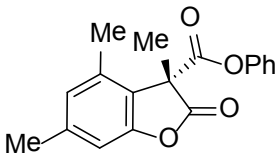
Following the general procedure, enol carbonate (21.20 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 85% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as colorless oil. **HPLC analysis:** 79% ee [Daicel CHIRALPAK OD column; solvent system: 5% isopropanol/95% hexanes; 0.5 mL/min; retention times: 12.5 min (major), 14.1 min (minor)]. **$[\alpha]^{25}_D$** = –70 (*c* 0.30, CH_2Cl_2). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.86 (s, 3H, C*H*$_3$), 2.42 (s, 3H, Ar-C*H*$_3$), 6.95-7.05 (m, 4H, Ar-*H*), 7.21-7.27 (m, 2H, Ar-*H*), 7.33 (t, *J* = 8.0 Hz, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 20.8, 22.1, 54.1, 112.2, 121.2, 123.2, 125.4, 125.8, 126.7, 129.7, 141.3, 150.4, 153.6, 167.3, 174.4. **IR (thin film):** ν 3064, 2938, 1815, 1762, 1495, 1452, 1138, 1071, 815, 744 cm^{-1}. **HRMS (ESI):** calcd. for $C_{17}H_{14}NaO_4$ $(M+Na)^+$ 305.0790, found 305.0775.



4n

(*R*)-Phenyl 3,7-dimethyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4n)

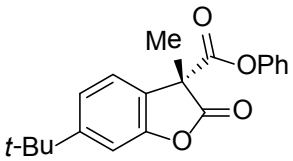
Following the general procedure, enol carbonate (21.20 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 78% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a light yellow oil. **HPLC analysis:** 67% ee [Daicel CHIRALPAK OD column; solvent system: 1% isopropanol/99% hexanes; 1.0 mL/min; retention times: 7.0 min (minor), 9.0 min (major)]. **$[\alpha]^{25}_D$** = –81 (*c* 0.20, CH_2Cl_2). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.87 (s, 3H, C*H*$_3$), 2.38 (s, 3H, Ar-C*H*$_3$), 6.96-6.99 (m, 2H, Ar-*H*), 7.13-7.24 (m, 4H, Ar-*H*), 7.31-7.36 (m, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 15.4, 20.9, 54.6, 120.8, 121.3, 121.9, 124.9, 126.7, 127.9, 129.7, 132.0, 150.4, 152.1, 167.2, 174.2. **IR (thin film):** ν 3065, 2937, 1813, 1762, 1492, 1456, 1189, 1095, 874, 746 cm^{-1}. **HRMS (ESI):** calcd. for $C_{17}H_{14}NaO_4$ $(M+Na)^+$ 305.0790, found 305.0779.



4o

(*R*)-Phenyl 3,4,6-trimethyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4o)

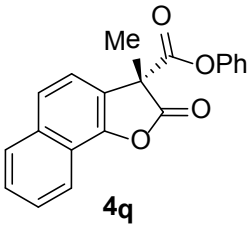
Following the general procedure, enol carbonate (22.22 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 50% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. **M.p.:** 52-54 °C. **HPLC analysis:** 78% ee [Daicel CHIRALPAK OJ column; solvent system: 10% isopropanol/90% hexanes; 0.5 mL/min; retention times: 21.1 min (major), 32.5 min (minor)]. **$[\alpha]^{20}_{D}$** = –45 (*c* 0.30, CH_2Cl_2). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.87 (s, 3H, CH_3), 2.32 (s, 3H, Ar-CH_3), 2.36 (s, 3H, Ar-CH_3), 6.85 (d, *J* = 15.6 Hz, 2H, Ar-*H*), 6.96-6.99 (m, 2H, Ar-*H*), 7.20-7.36 (m, 3H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 20.9, 24.4, 34.2, 54.4, 111.2, 121.2, 121.4, 126.7, 128.2, 128.5, 129.7, 146.2, 150.4, 151.6, 167.3, 174.4. **IR (thin film):** ν 3054, 2939, 1810, 1761, 1484, 1457, 1185, 1098, 850, 747 cm^{-1}. **HRMS (ESI):** calcd. for $C_{18}H_{16}NaO_4$ $(M+Na)^+$ 319.0940, found 319.0943.



4p

(*R*)-Phenyl 6-*tert*-butyl-3-methyl-2-oxo-2,3-dihydrobenzofuran-3-carboxylate (4p)

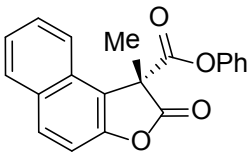
Following the general procedure, enol carbonate (24.30 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 99% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. **M.p.:** 70-73 °C. **HPLC analysis:** 75% ee [Daicel CHIRALPAK OD column; solvent system: 10% isopropanol/90% hexanes; 0.5 mL/min; retention times: 9.4 min (major), 10.2 min (minor)]. **$[\alpha]^{20}_{D}$** = –68 (*c* 0.20, CH_2Cl_2). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 1.35 (s, 9H, C(CH_3)$_3$), 1.87 (s, 3H, CH_3), 6.99 (m, 2H, Ar-*H*), 7.20-7.46 (m, 6H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 20.9, 31.5, 35.5, 54.2, 108.8, 121.3, 122.0, 123.1, 125.3, 126.6, 129.7, 150.5, 153.7, 154.8, 167.2, 174.4. **IR (thin film):** ν 3065, 2965, 1815, 1760, 1494, 1185, 1062, 821, 746 cm^{-1}. **HRMS (ESI):** calcd. for $C_{20}H_{20}NaO_4$ $(M+Na)^+$ 347.1259, found 347.1257.



4q

(*R*)-Phenyl 3-methyl-2-oxo-2,3-dihydronaphtho[1,2-b]furan-3-carboxylate (4q)

Following the general procedure, enol carbonate (23.90 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 82% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a white solid. **M.p.:** 101-104 °C. **HPLC analysis:** 74% ee [Daicel CHIRALPAK OD column; solvent system: 1% isopropanol/99% hexanes; 1.0 mL/min; retention times: 11.1 min (major), 14.1 min (minor)]. **[α]$^{25}_{D}$** = –132 (*c* 0.30, CH_2Cl_2). **^{1}H NMR ($CDCl_3$, 400 MHz):** *δ* 1.97 (s, 3H, C*H*$_3$), 6.96 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.20-7.34 (m, 2H, Ar-*H*), 7.46-7.63 (m, 4H, Ar-*H*), 7.75 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.92 (d, *J* = 7.6 Hz, 2H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** *δ* 20.8, 55.3, 119.6, 120.1, 121.3, 121.6, 122.6, 125.3, 126.7, 127.5, 127.7, 128.6, 129.7, 134.8, 149.5, 150.4, 167.2, 174.6. **IR (thin film):** ν 3060, 2937, 1812, 1760, 1483, 1459, 1184, 1041, 814, 753 cm^{-1}. **HRMS (ESI):** calcd. for $C_{20}H_{15}O_4$ $(M+H)^+$ 319.0970, found 319.0978.



4r

(*R*)-Phenyl 1-methyl-2-oxo-1,2-dihydronaphtho[2,1-b]furan-1-carboxylate (4r)

Following the general procedure, enol carbonate (23.90 mg, 0.075 mmol), catalyst (*R*)-**2a** (1.25 mg, 0.0075 mmol), and *tert*-amyl alcohol (1.5 mL) were reacted at 0 °C for 36 h. The conversion (product relative to SM) of 50% was calculated from ^{1}H NMR spectroscopy of the crude product. The product was isolated by column chromatography (petroleum ether: ethyl acetate = 40 : 1) as a colorless oil. **HPLC analysis:** 58% ee [Daicel CHIRALPAK OD column; solvent system: 10% isopropanol/90% hexanes; 0.5 mL/min; retention times: 13.8 min (minor), 15.5 min (major)]. **[α]$^{25}_{D}$** = 16 (*c* 0.30, CH_2Cl_2). **^{1}H NMR ($CDCl_3$, 400 MHz):** *δ* 2.07 (s, 3H, C*H*$_3$), 6.86-6.88 (m, 2H, Ar-*H*), 7.16-7.29 (m, 3H, Ar-*H*), 7.43-7.53 (m, 2H, Ar-*H*), 7.59-7.64 (m, 1H, Ar-*H*), 7.88-7.97 (m, 3H, Ar-*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** *δ* 20.5, 55.2, 111.9, 120.9, 121.3, 121.9, 125.5, 126.7, 128.7, 128.9, 129.7, 130.0, 131.5, 131.7, 150.4, 151.7, 167.5, 174.9. **IR (thin film):** ν 3065, 2939, 1811, 1759, 1492, 1189, 1068, 813, 745 cm^{-1}. **HRMS (ESI):** calcd. for $C_{20}H_{14}NaO_4$ $(M+Na)^+$ 341.0790, found 341.0799.

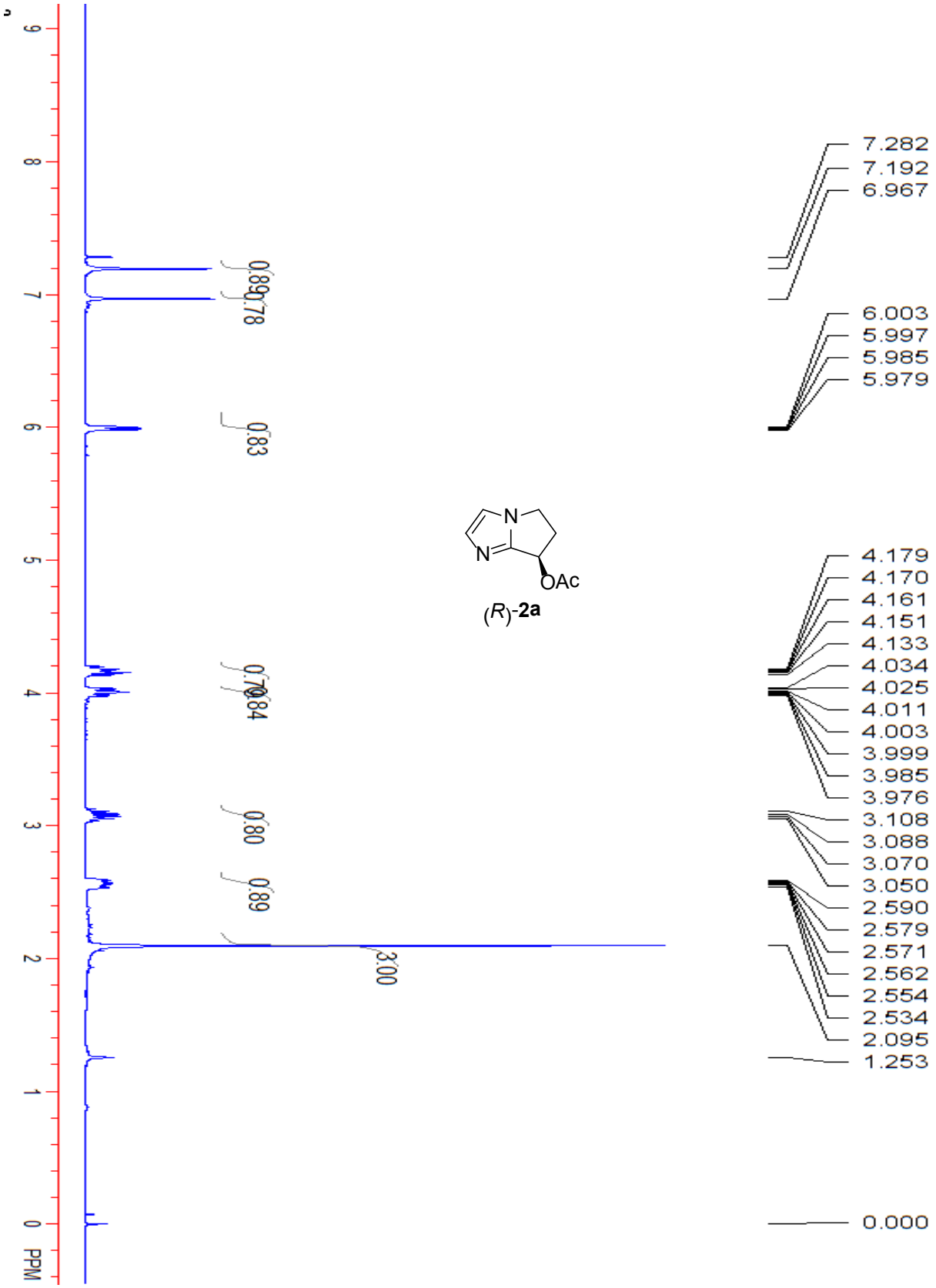
5. Reference

1 a) S. A. Shaw, P. Aleman and E. Vedejs, *J. Am. Chem. Soc.*, 2003, **125**, 13368; c) S. A. Shaw, P. Aleman, J. Christy, J. W. Kampf, P. Va and E. Vedejs, *J. Am. Chem. Soc.*, 2006, **128**, 925.

2 J. E. Thomson, A. F. Kyle, K. A. Gallagher, P. Lenden, C. Concellón, L. C. Morrill, A. J. Miller, C. Joannesse, A. M. Z. Slawin and A. D. Smith, *Synthesis* 2008, 2805.

3 3-substituted benzofuran-2(3*H*)-ones (the starting materials for **3a-3g**) were synthesized according to the method described in references 1 and 2. Others (the starting materials for **3h-3r**) were synthesized according to the method described in following literature: A. Citterio, M. Gandolfi, O. Piccolo, L. Filippini, L. Tinucci, E. Valoti, *Synthesis*, 1984, 760.

6. NMR Spectra



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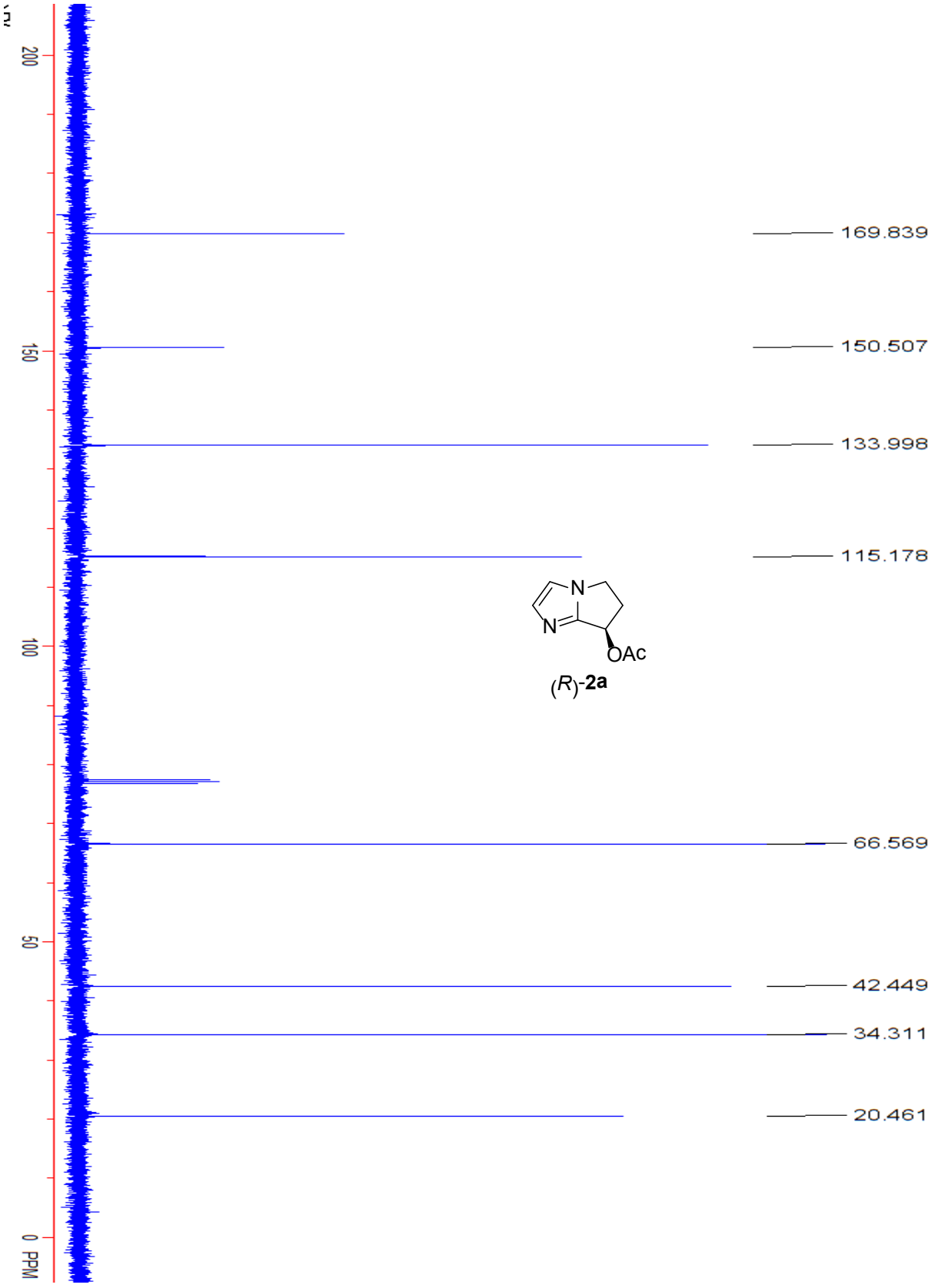
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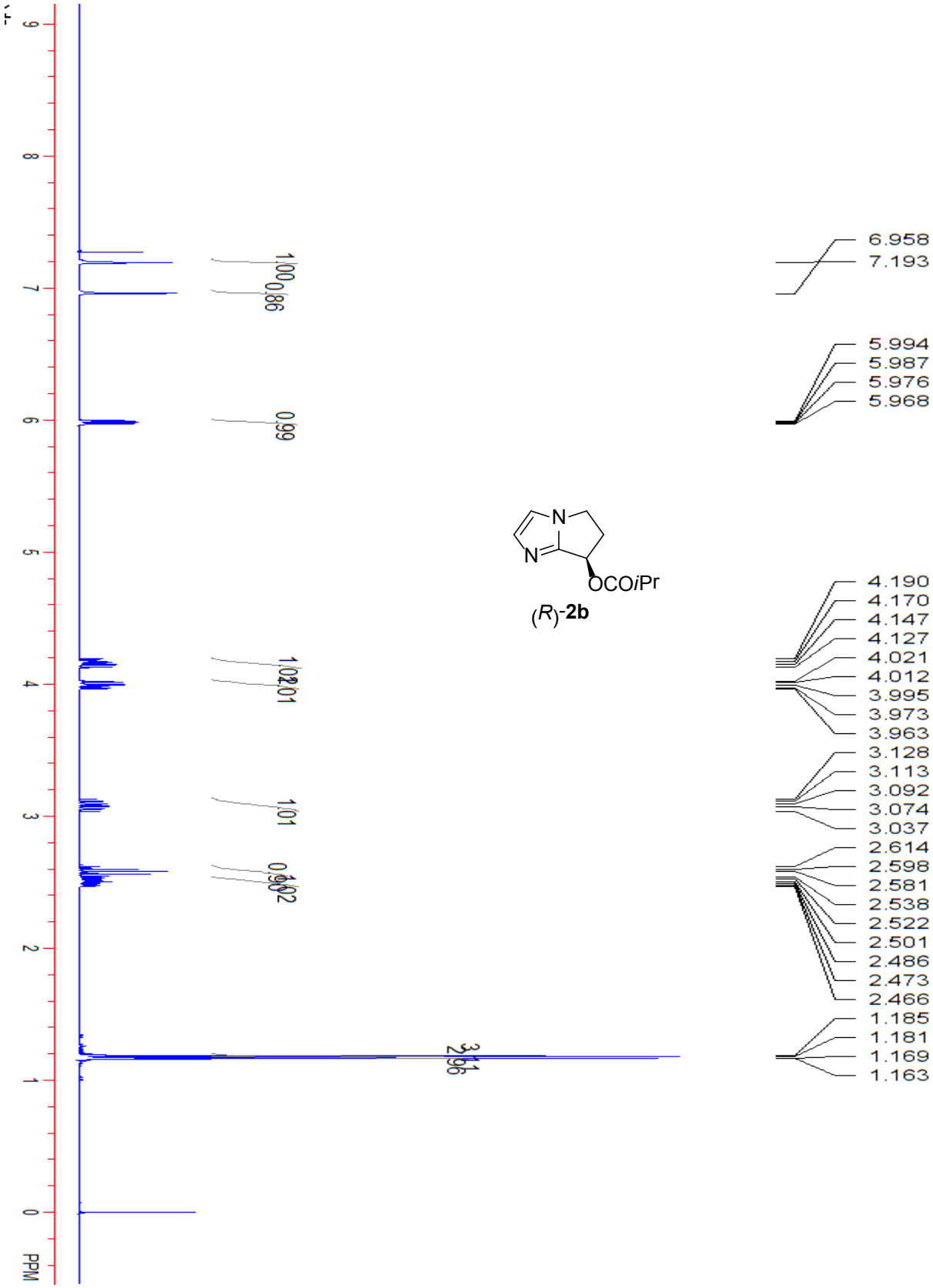

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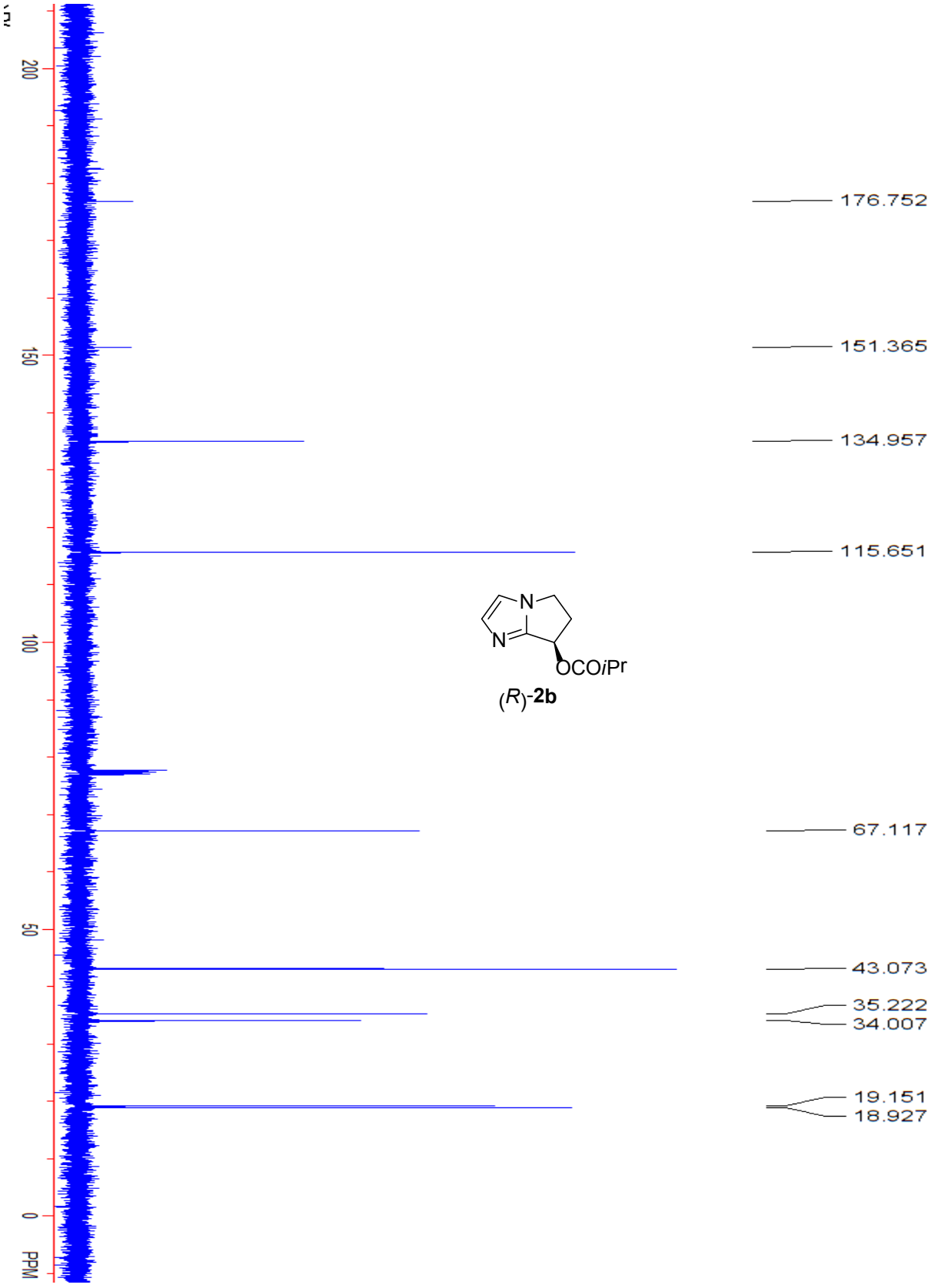
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N
OCO*i*Pr

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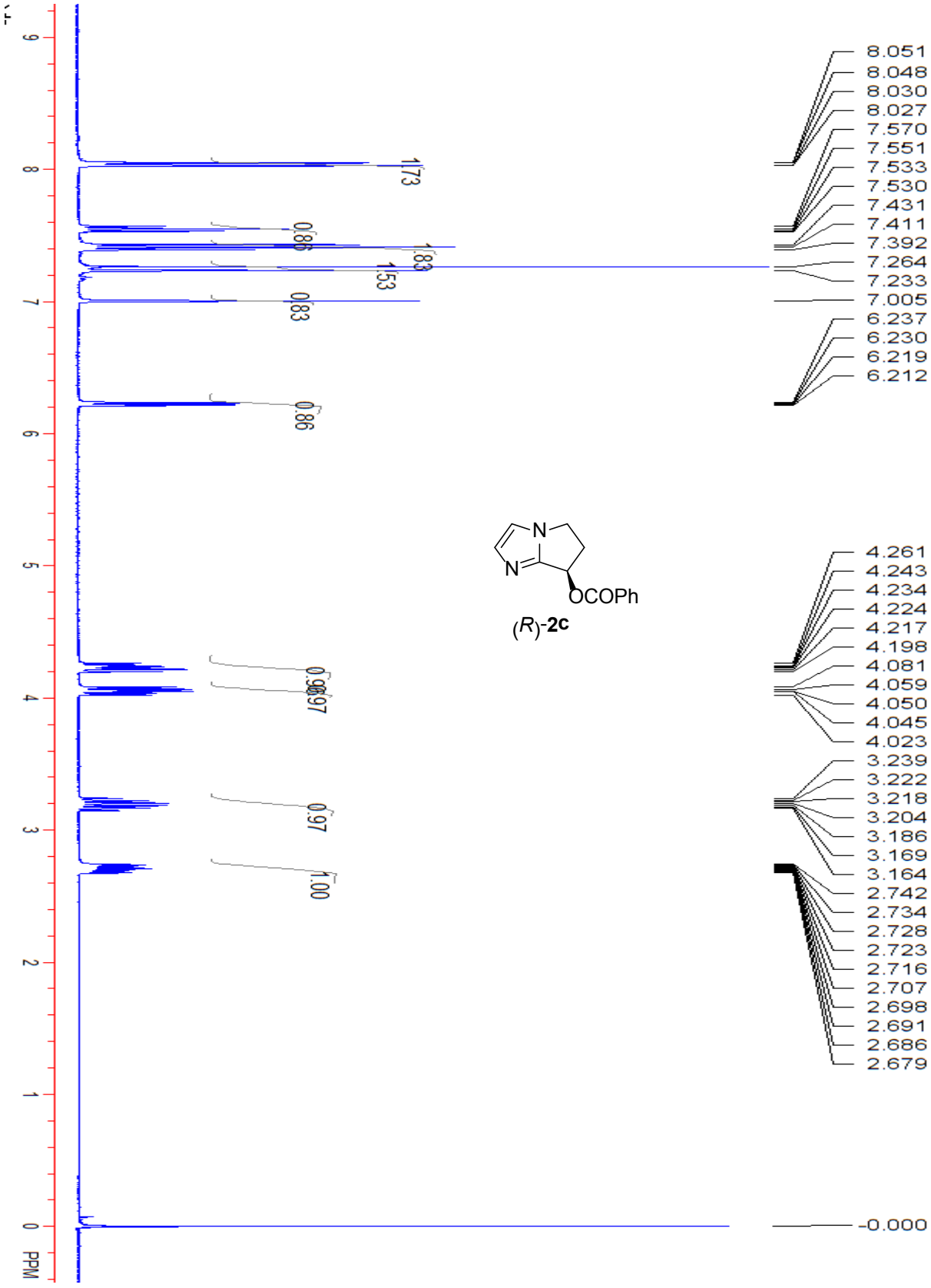
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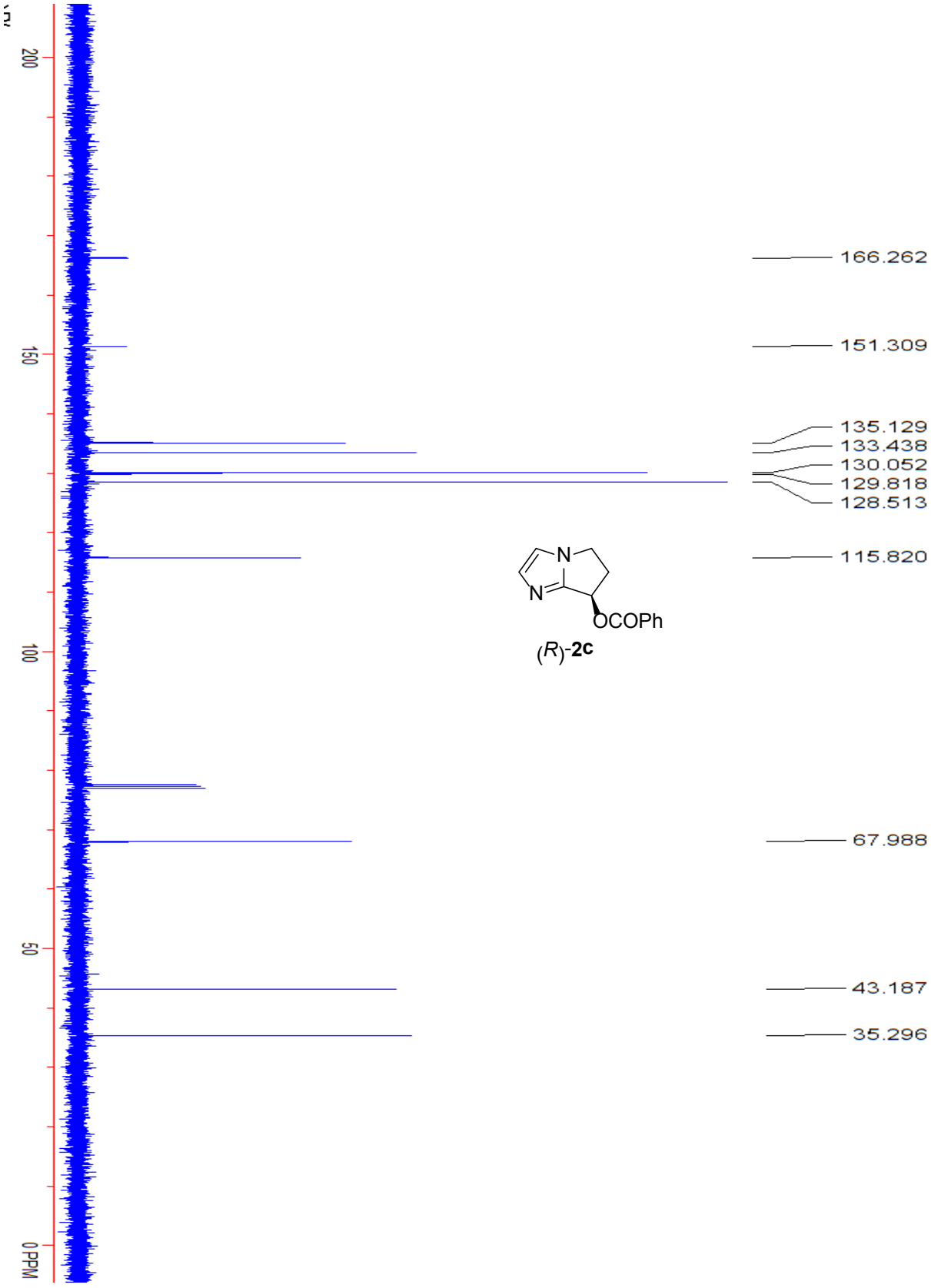
(*R*)-**2c**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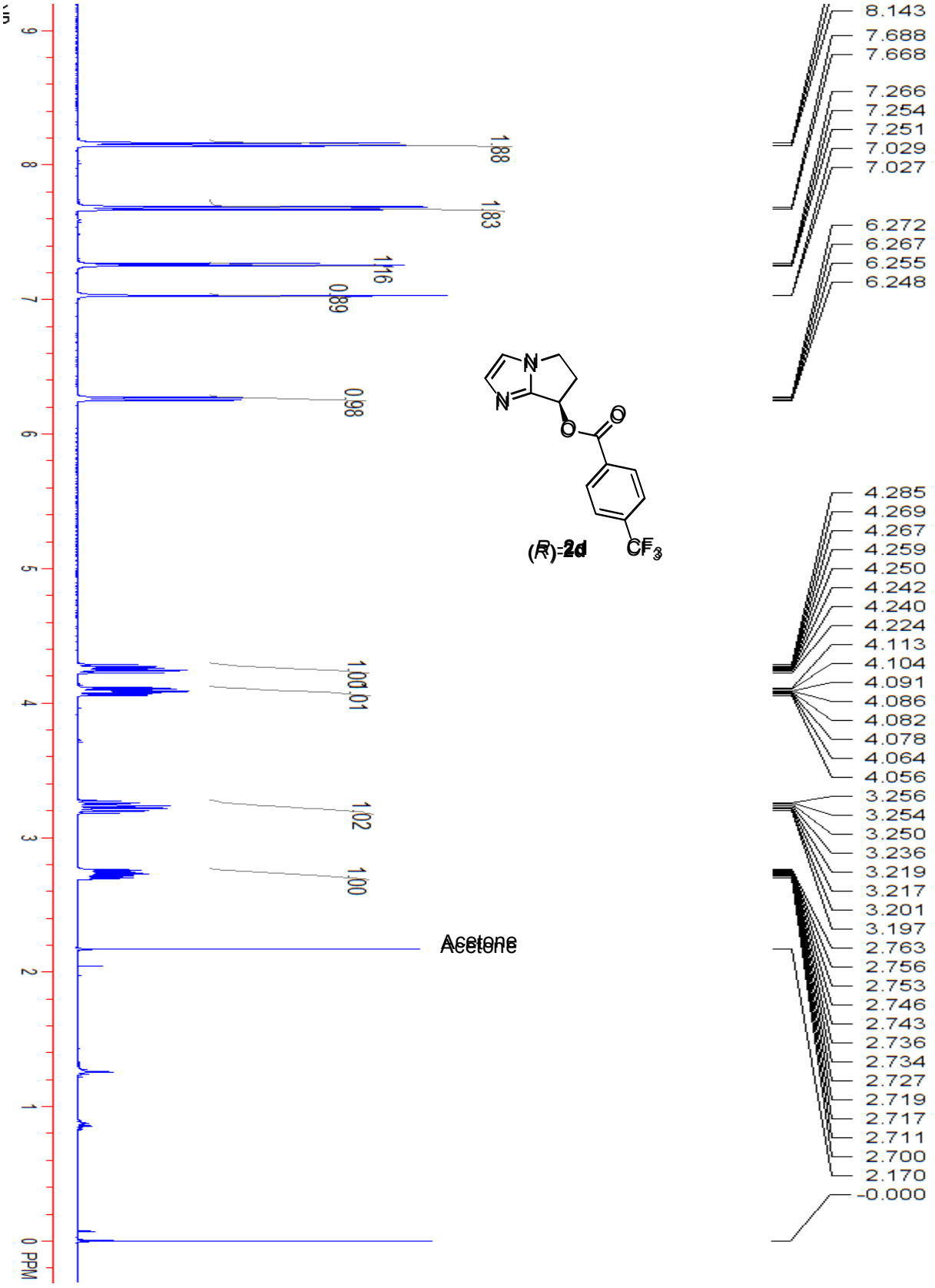
(*R*)-**2c**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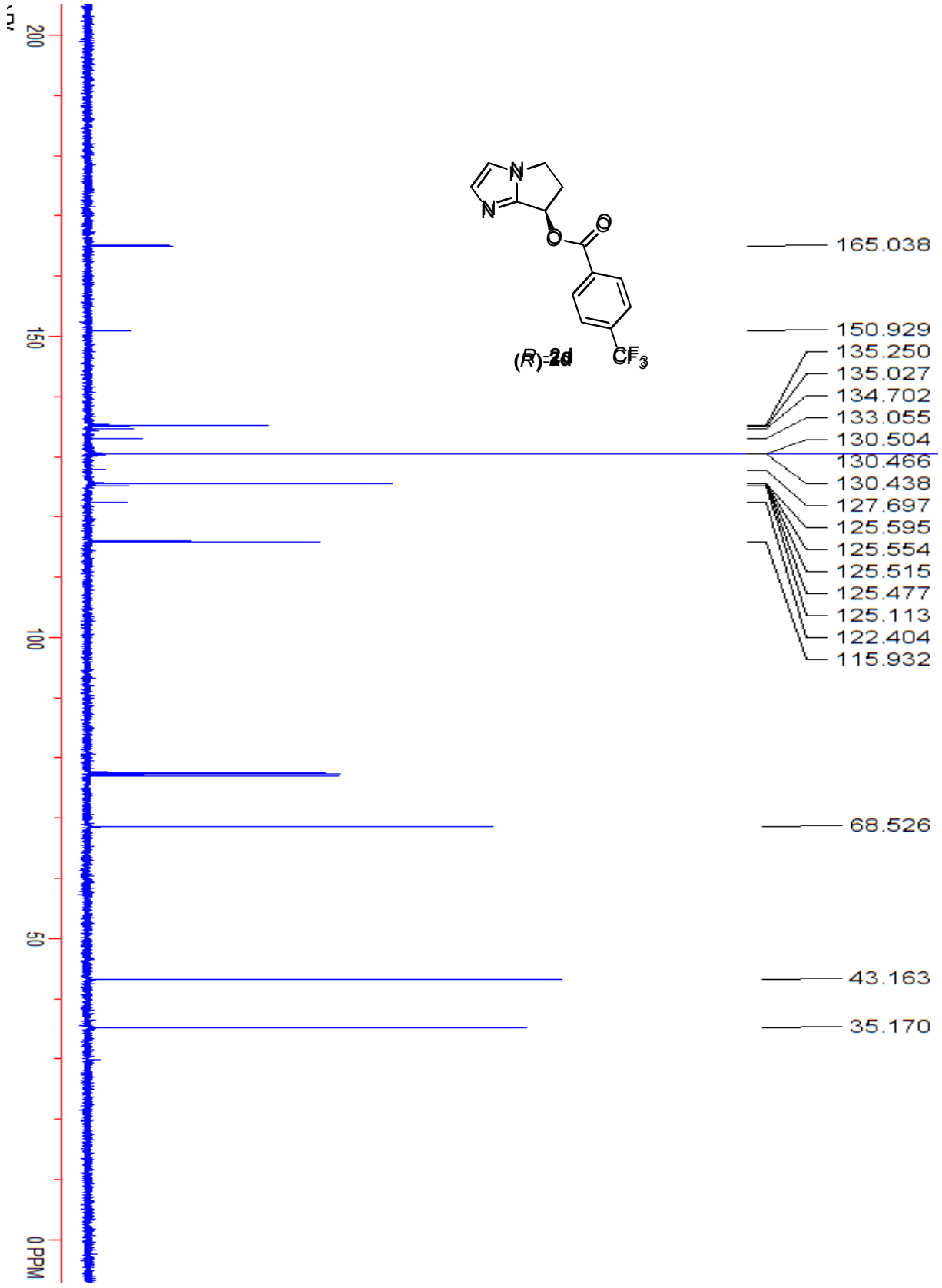
(R)-2d
CF3
PPM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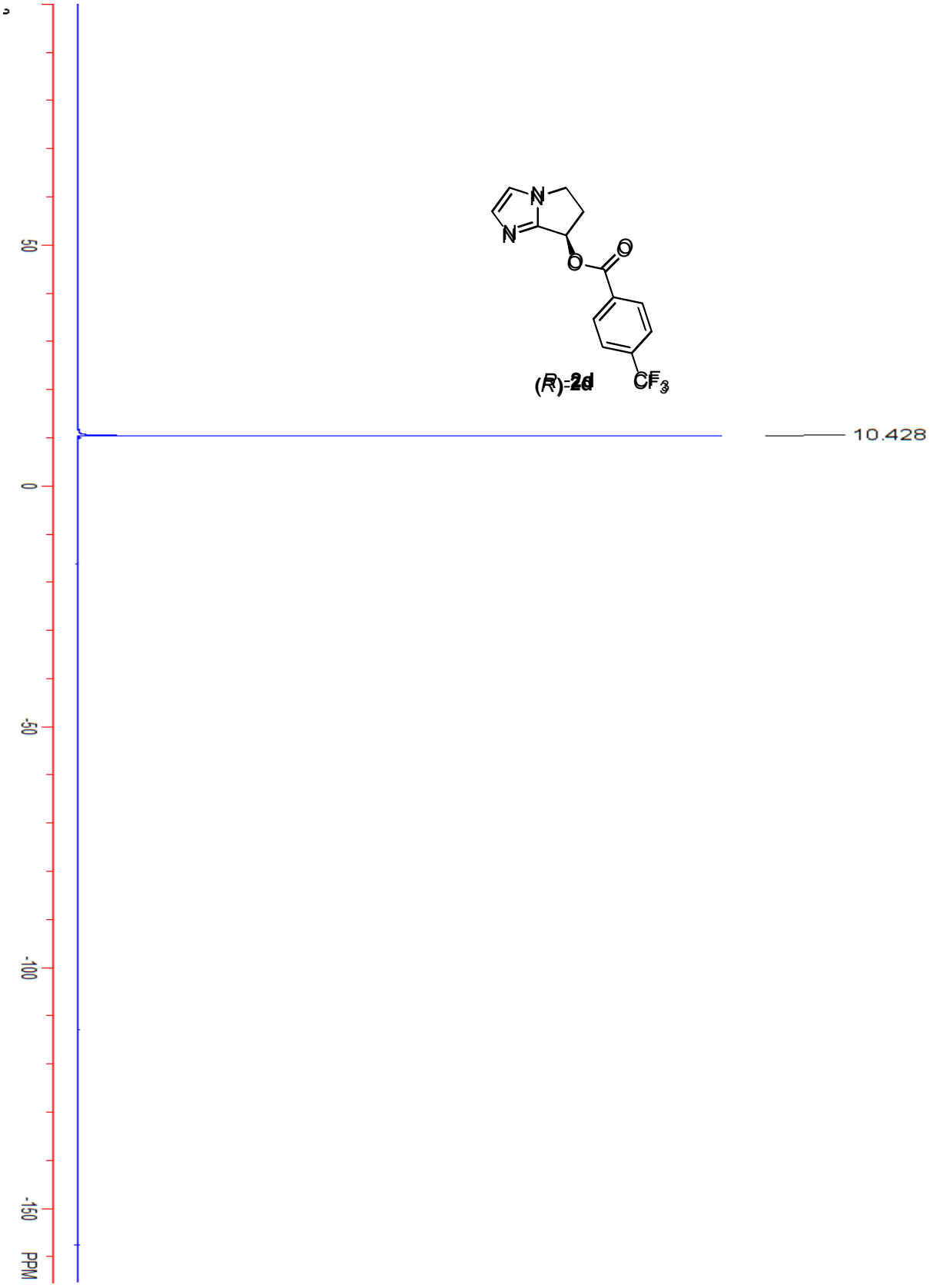
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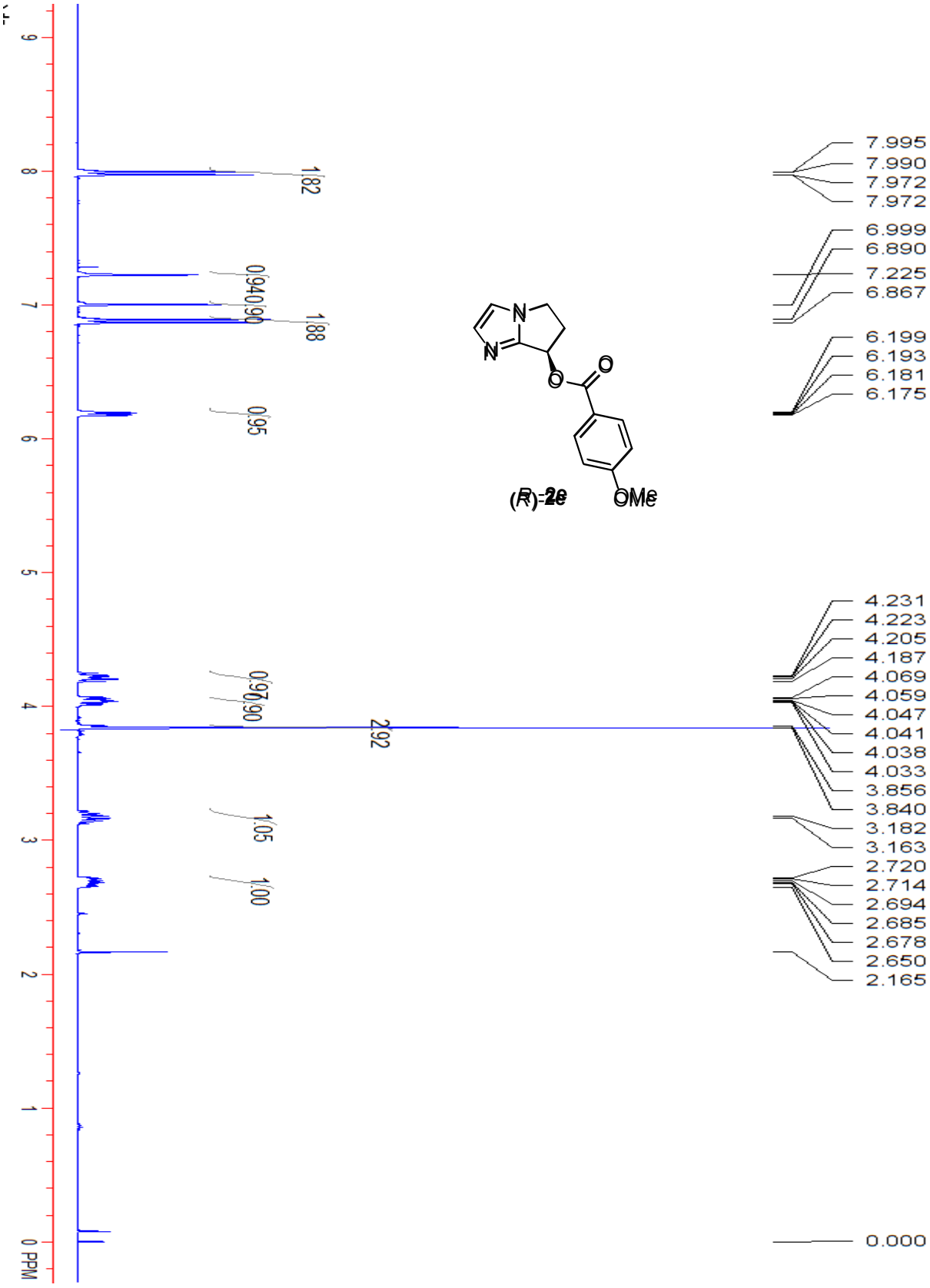
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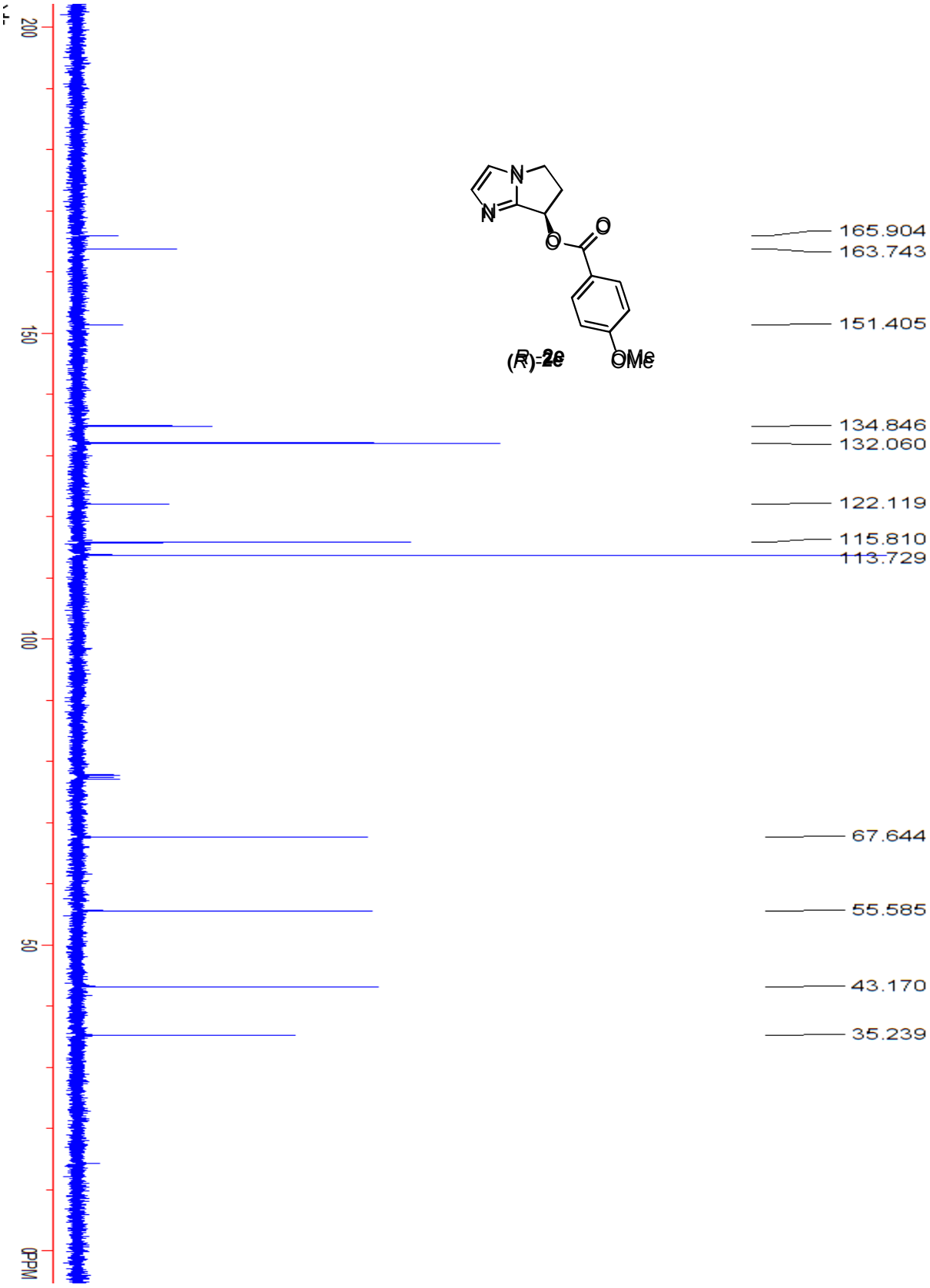
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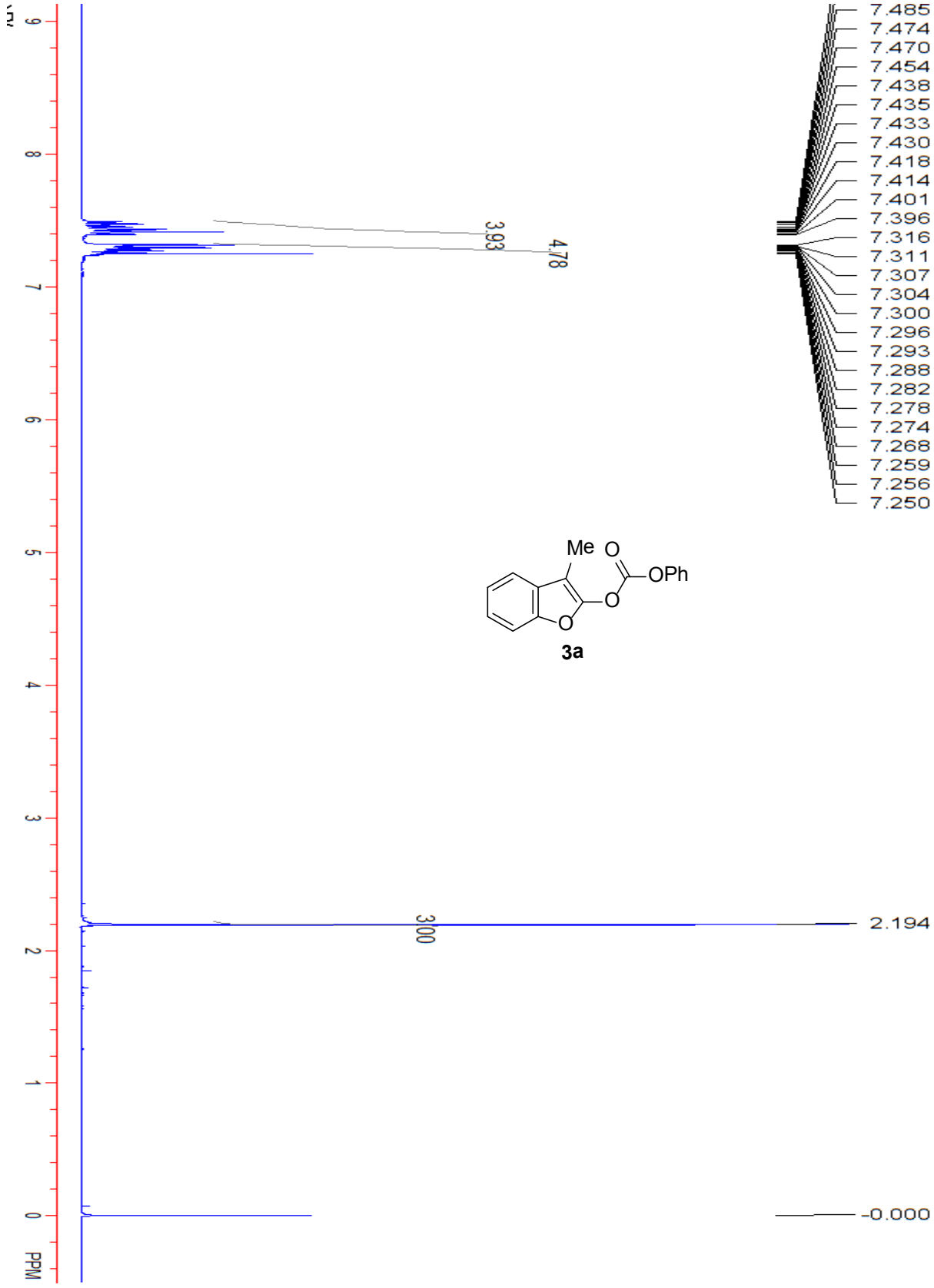
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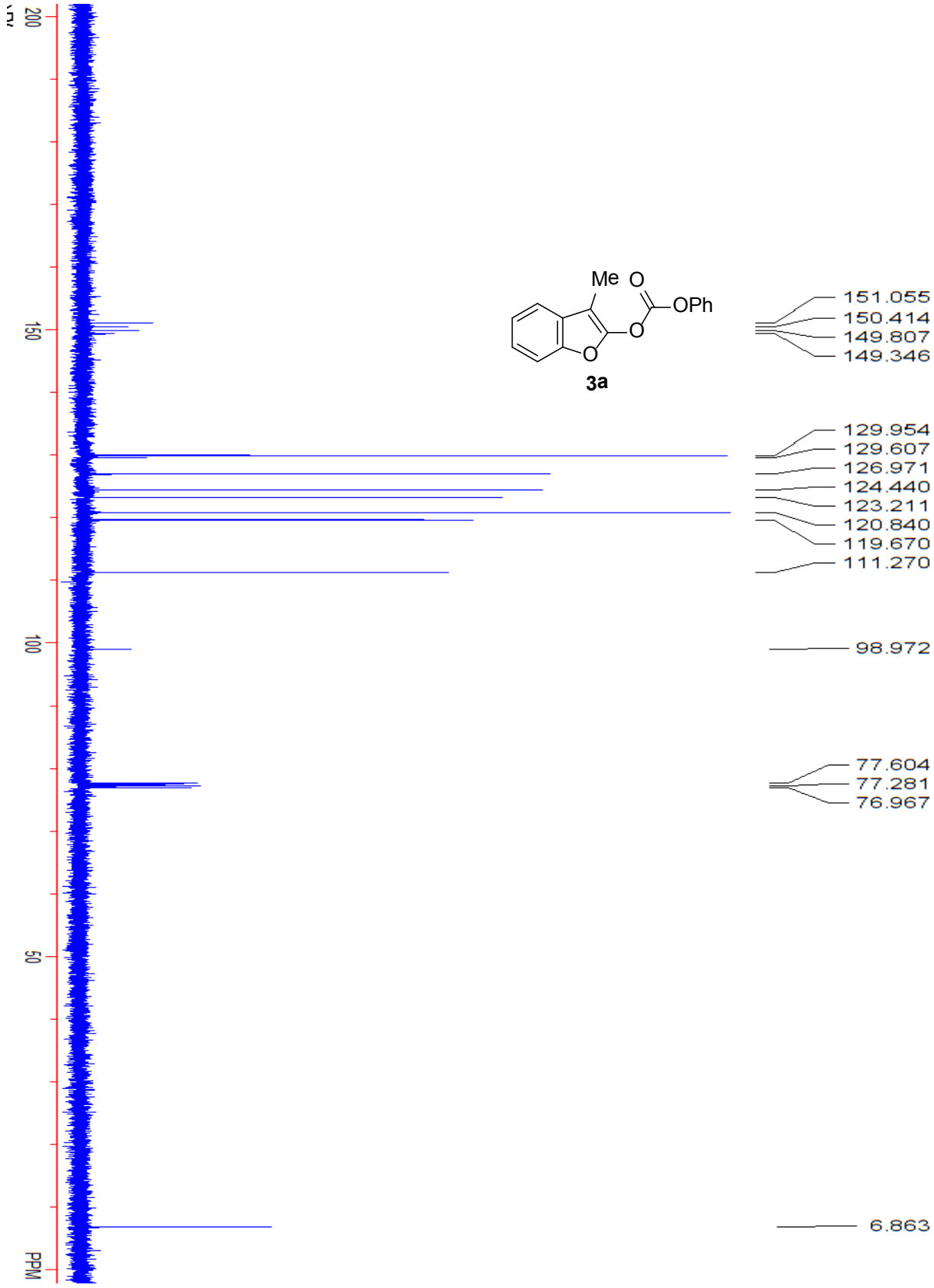
3a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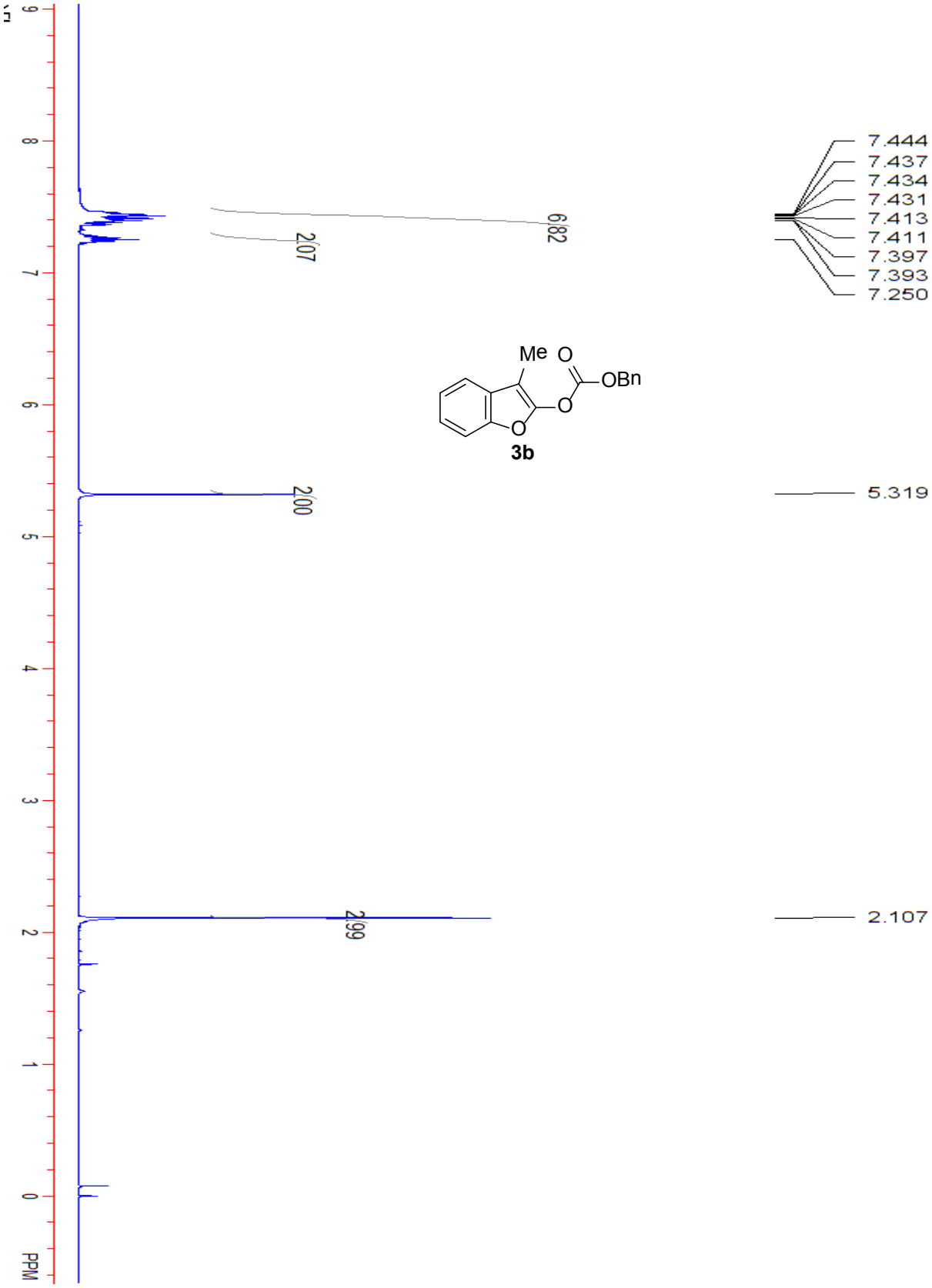
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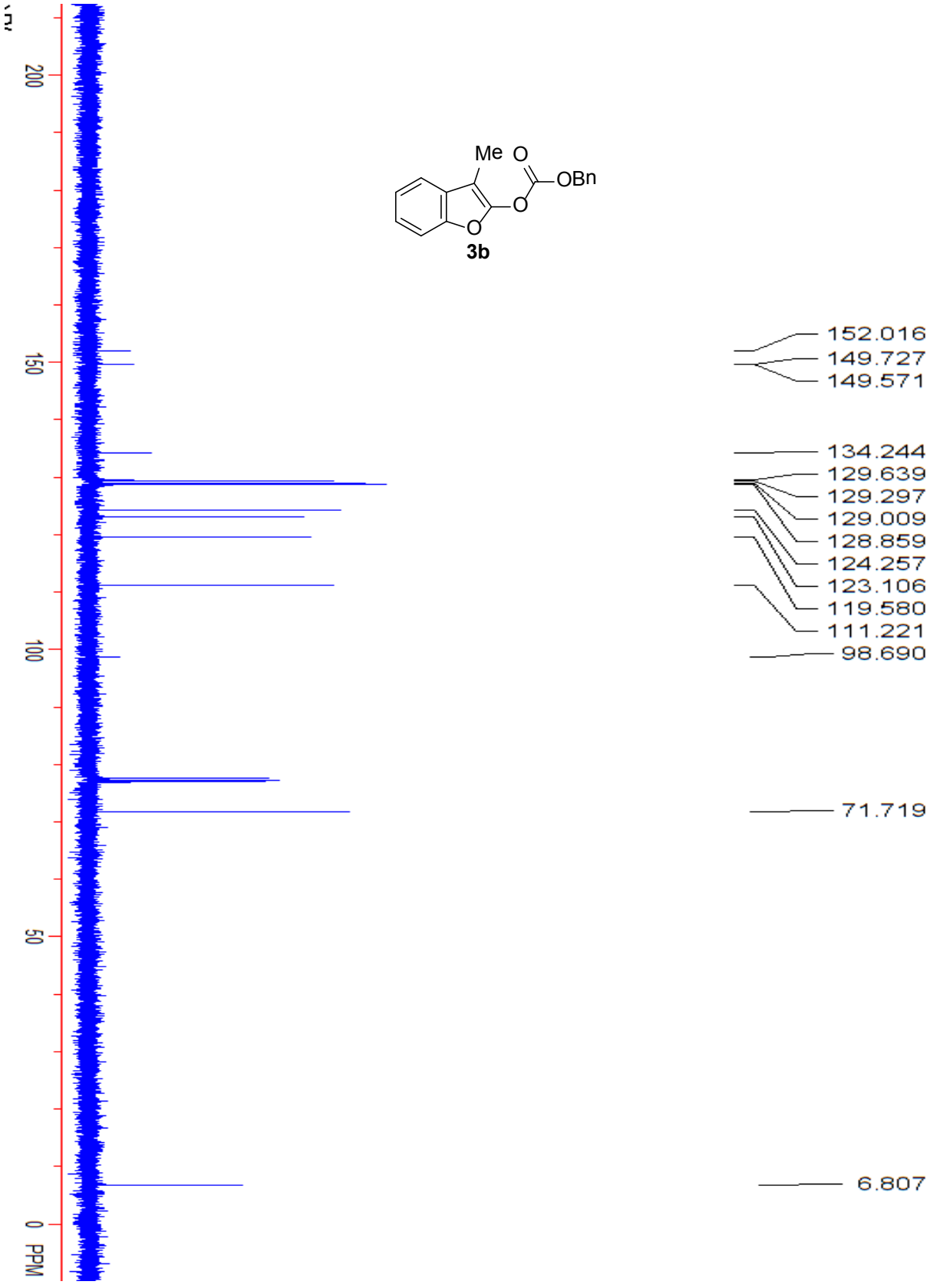
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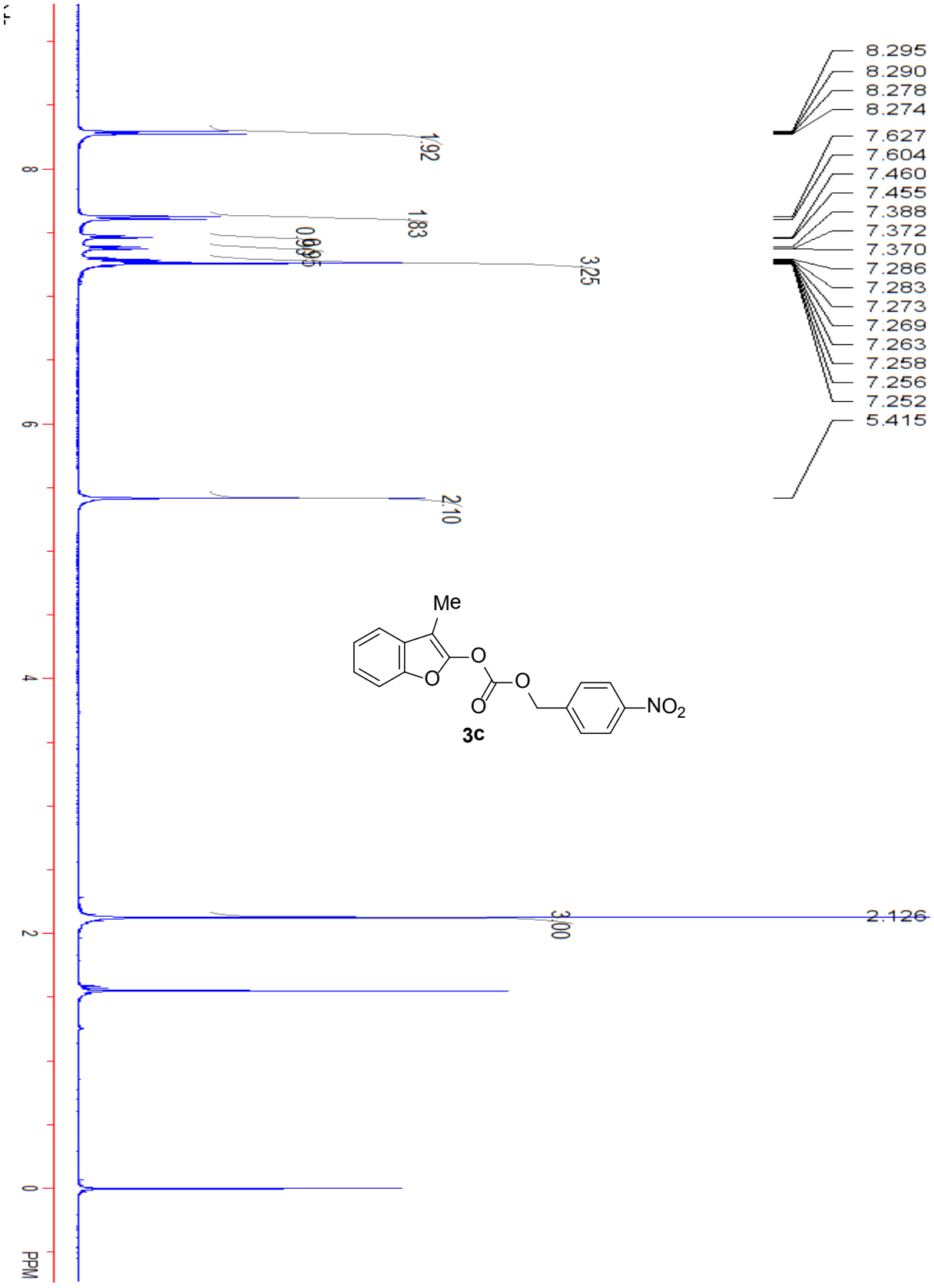
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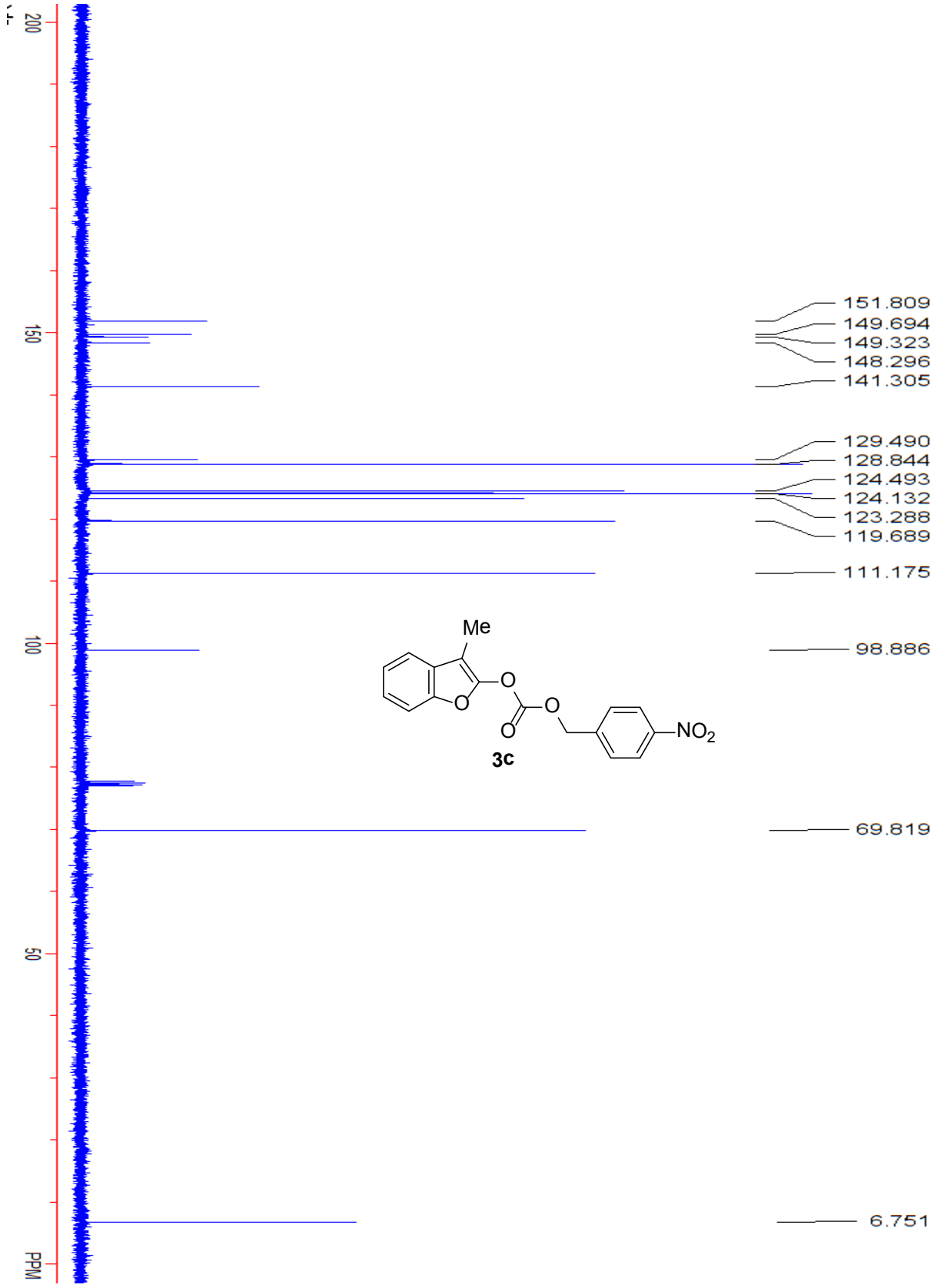
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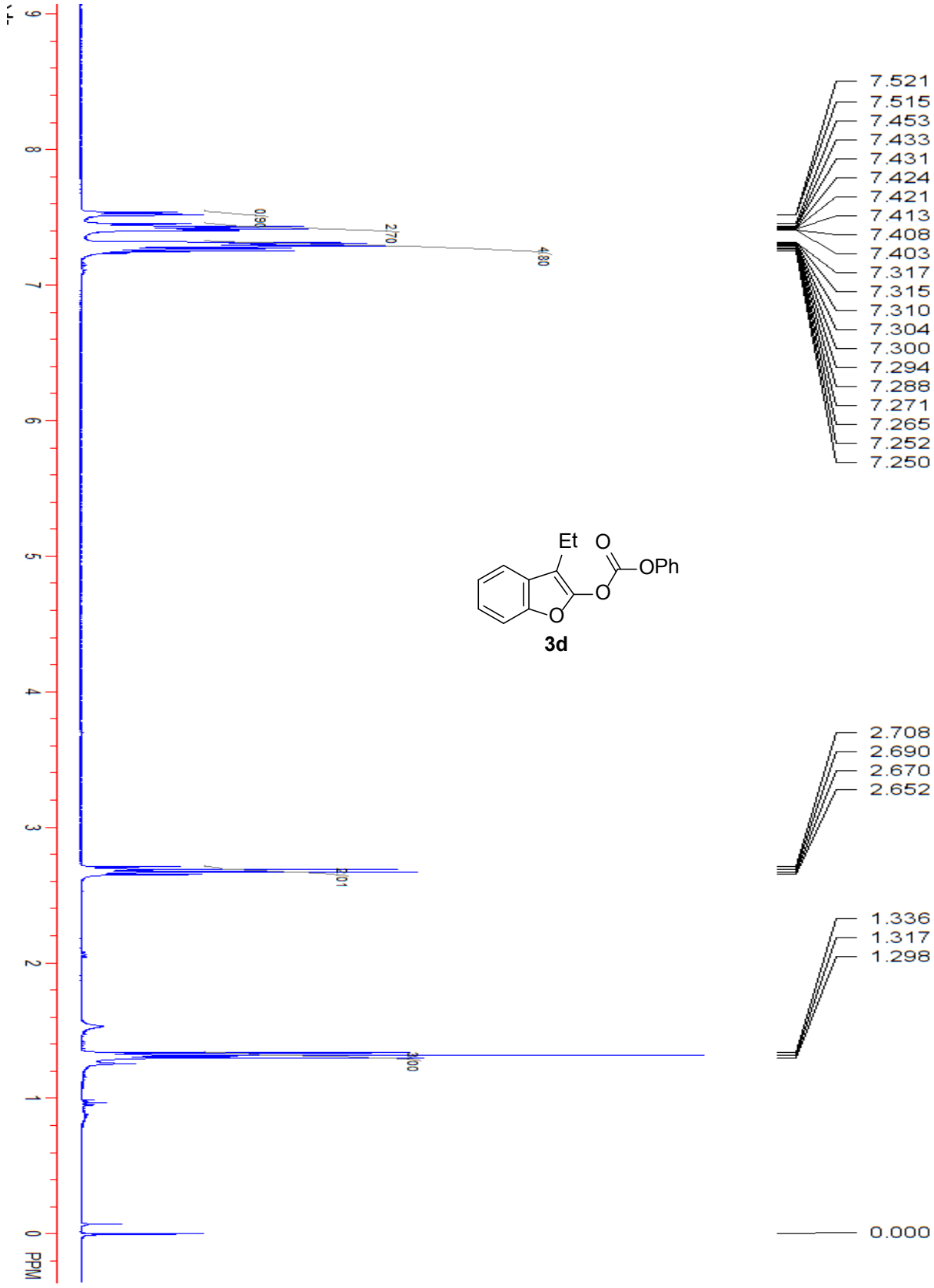
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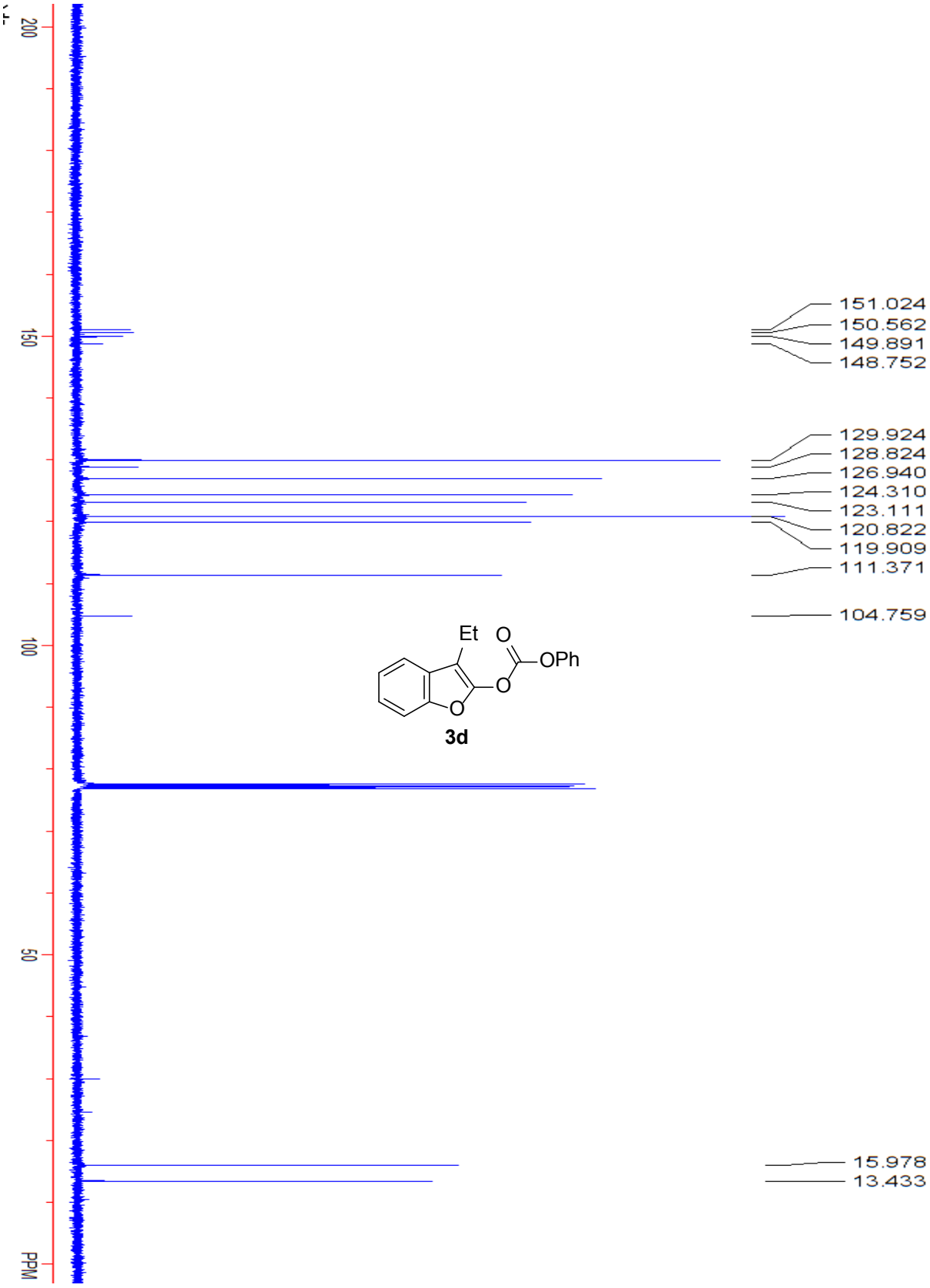
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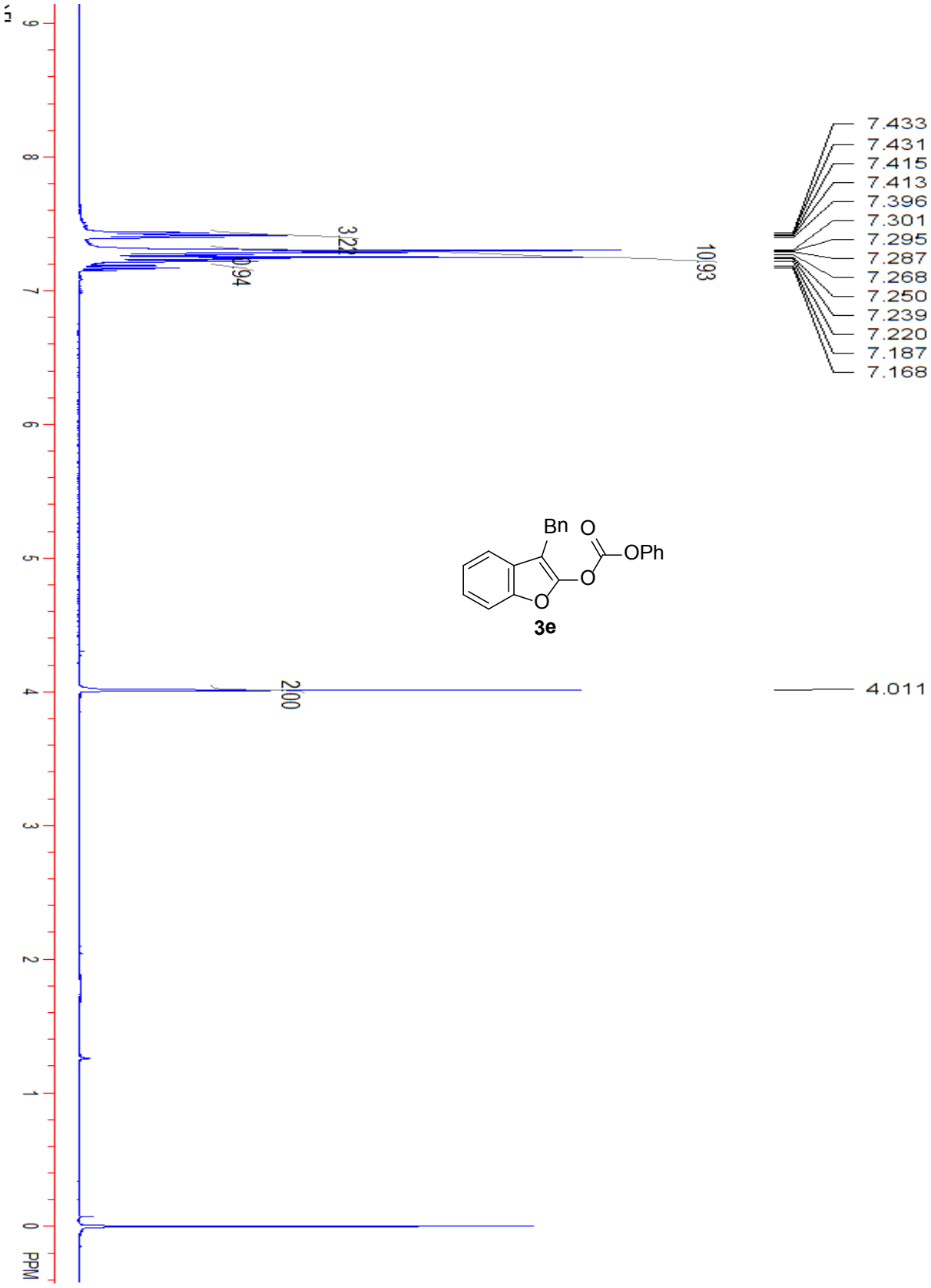
3d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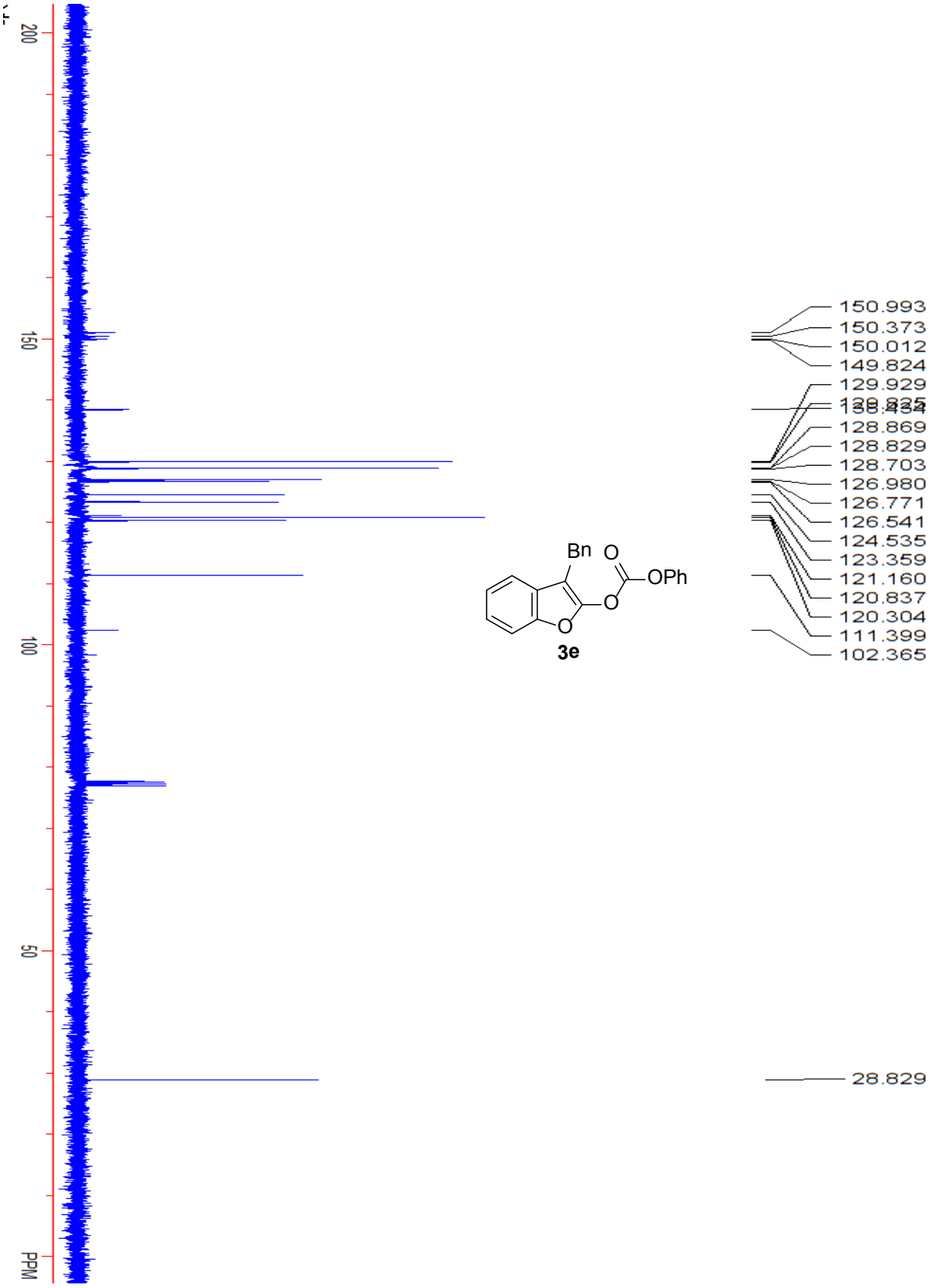
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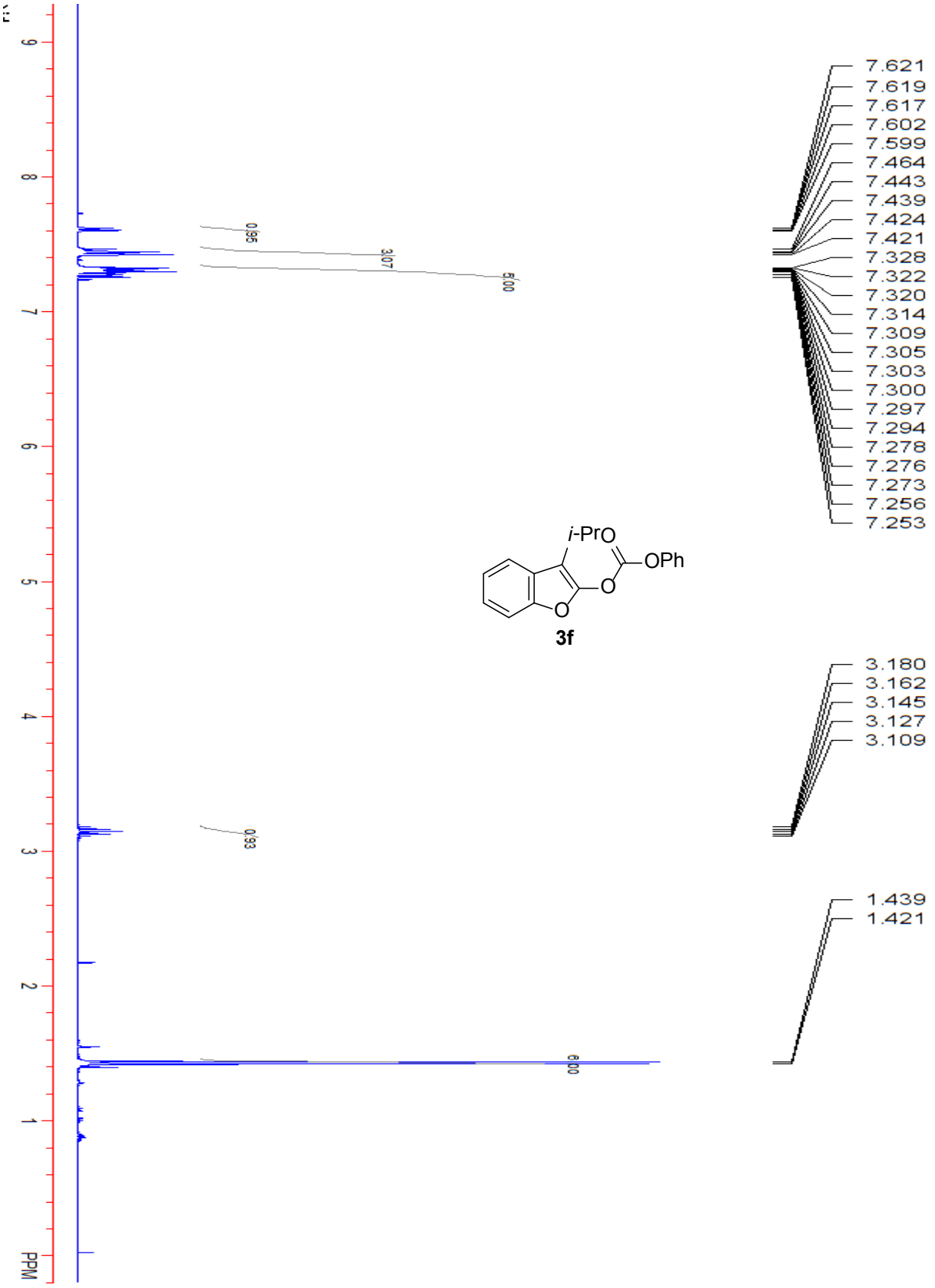
O
O

3e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7.273
7.256
7.253
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3.145
3.127
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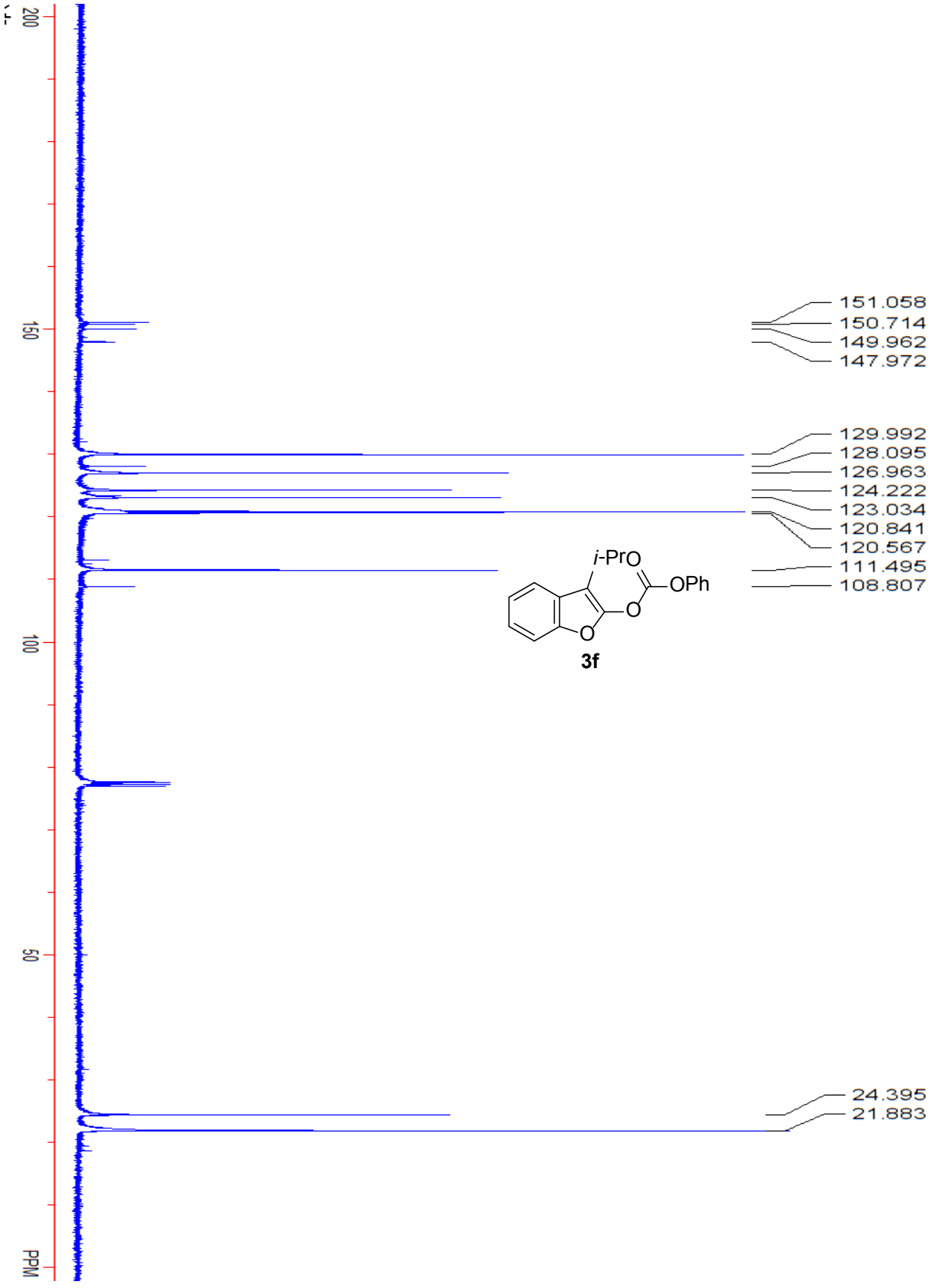
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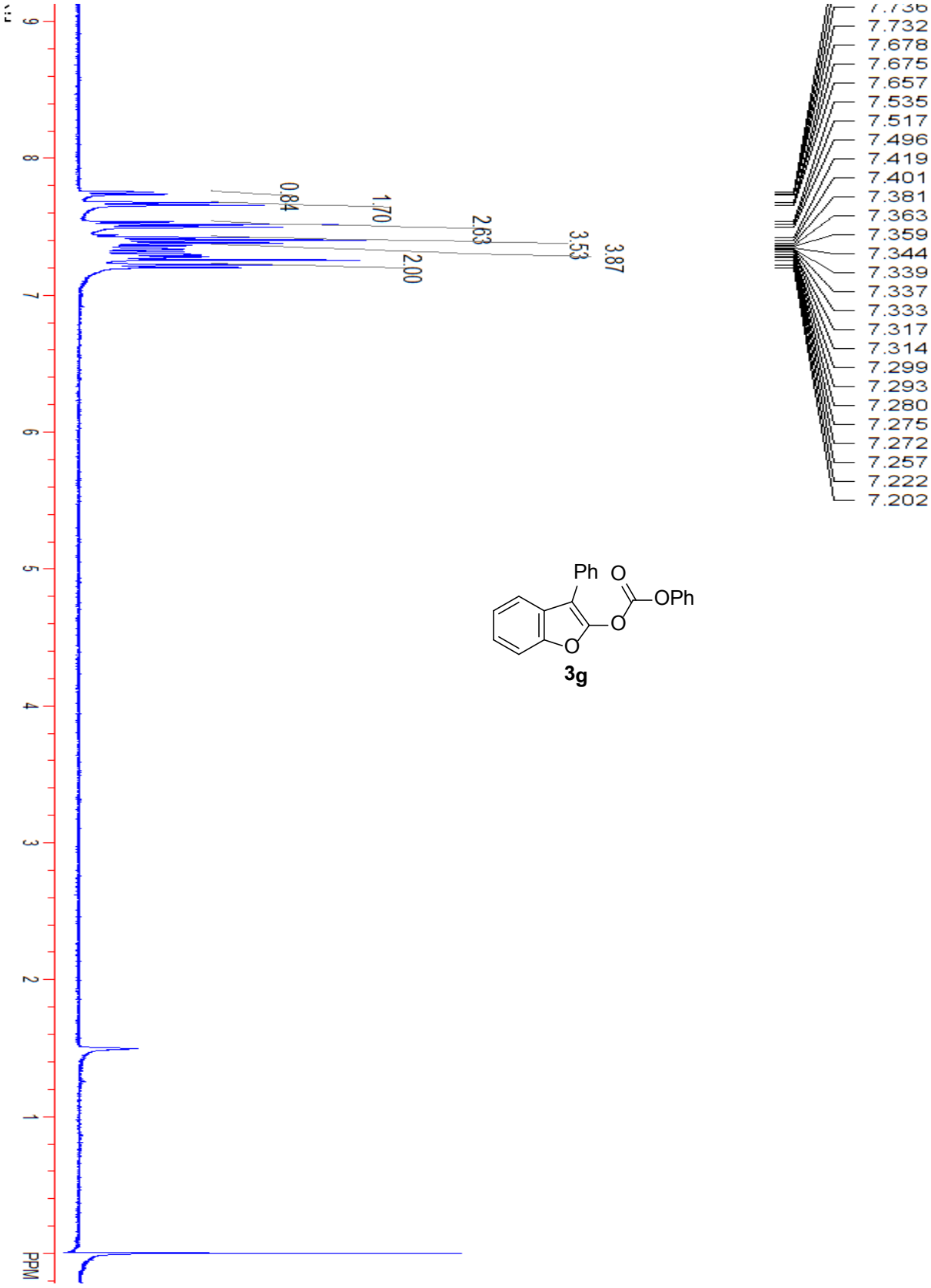
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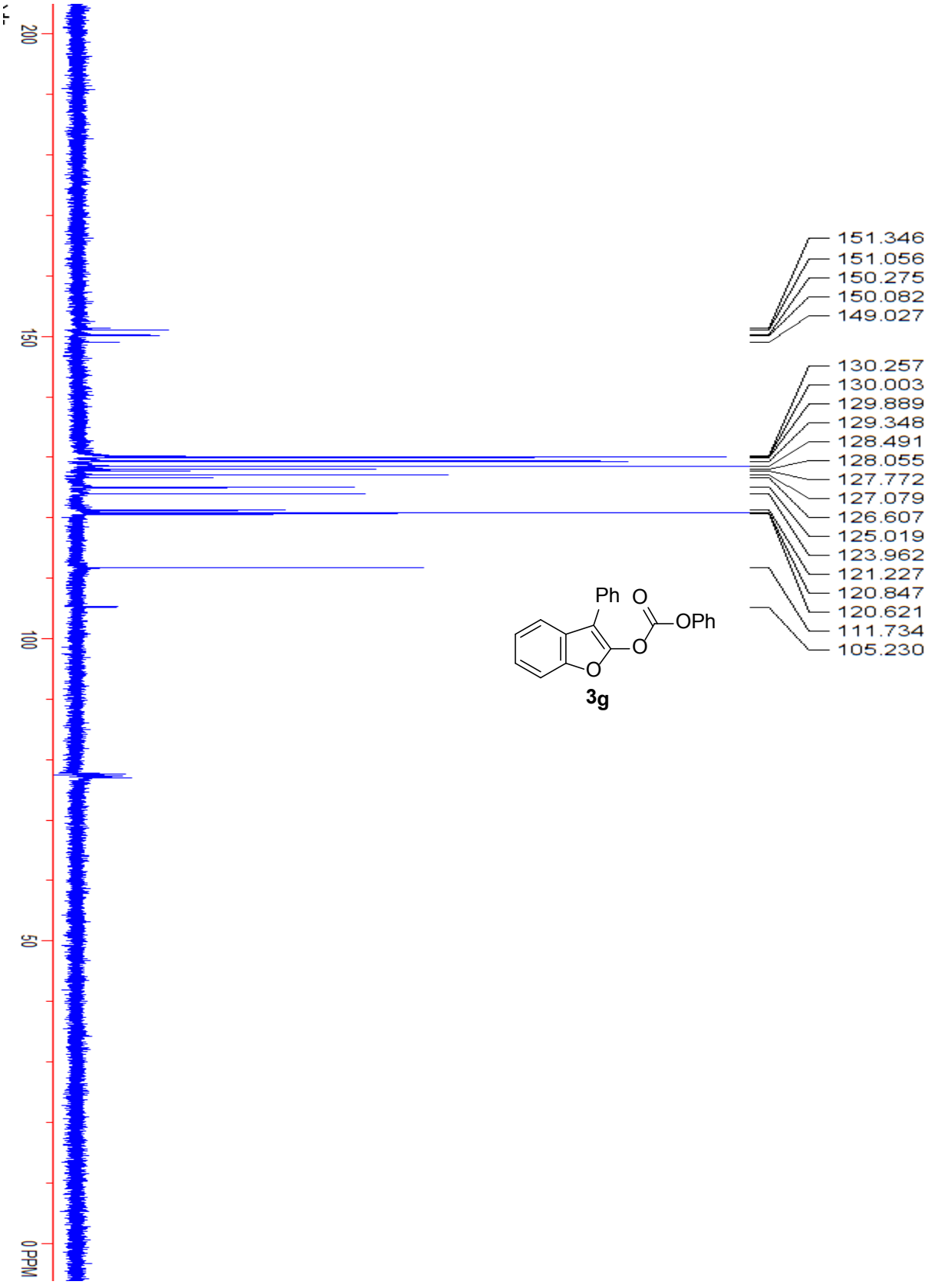
3g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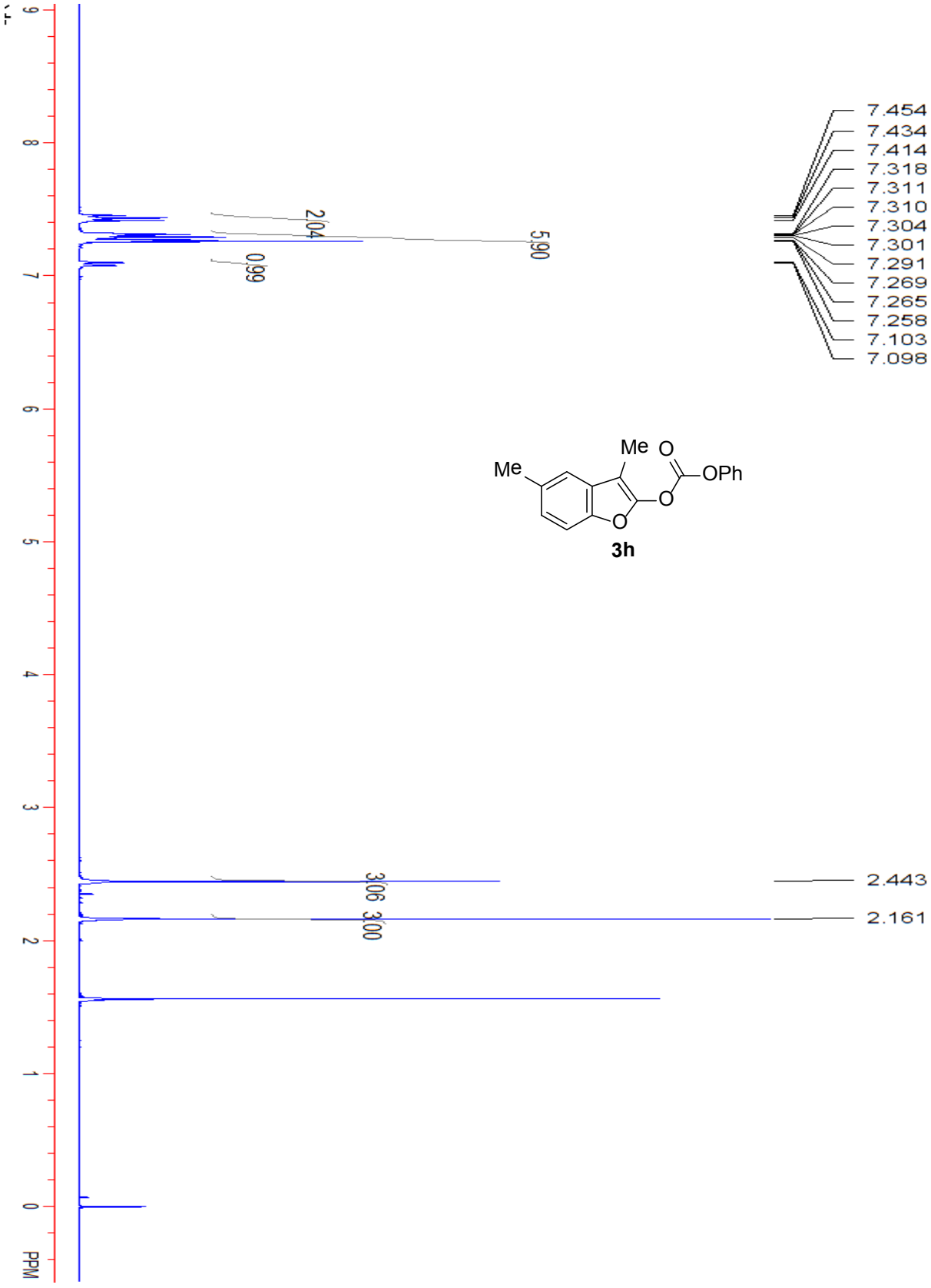
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7.258
7.103
7.098
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O
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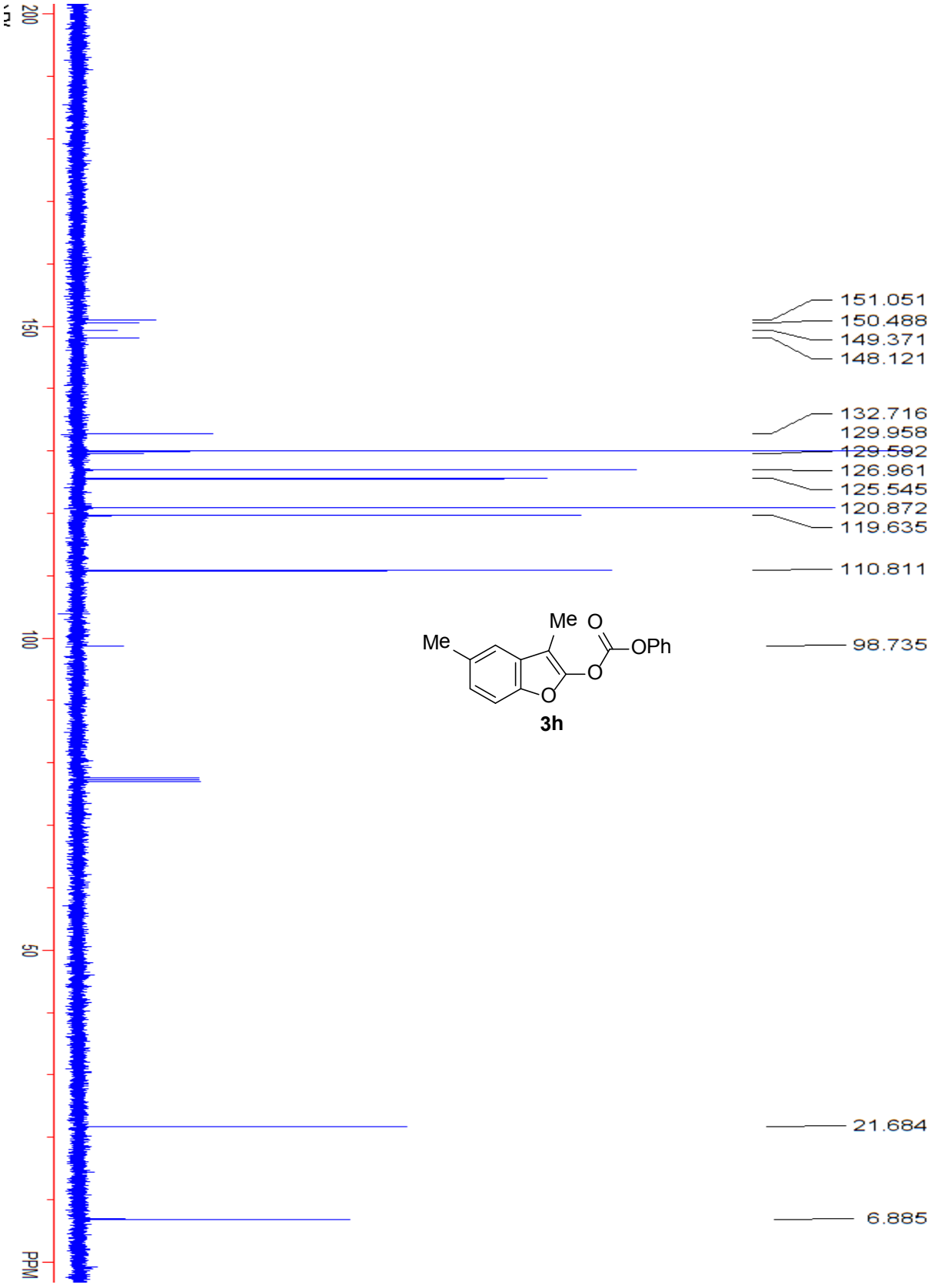
PPM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O

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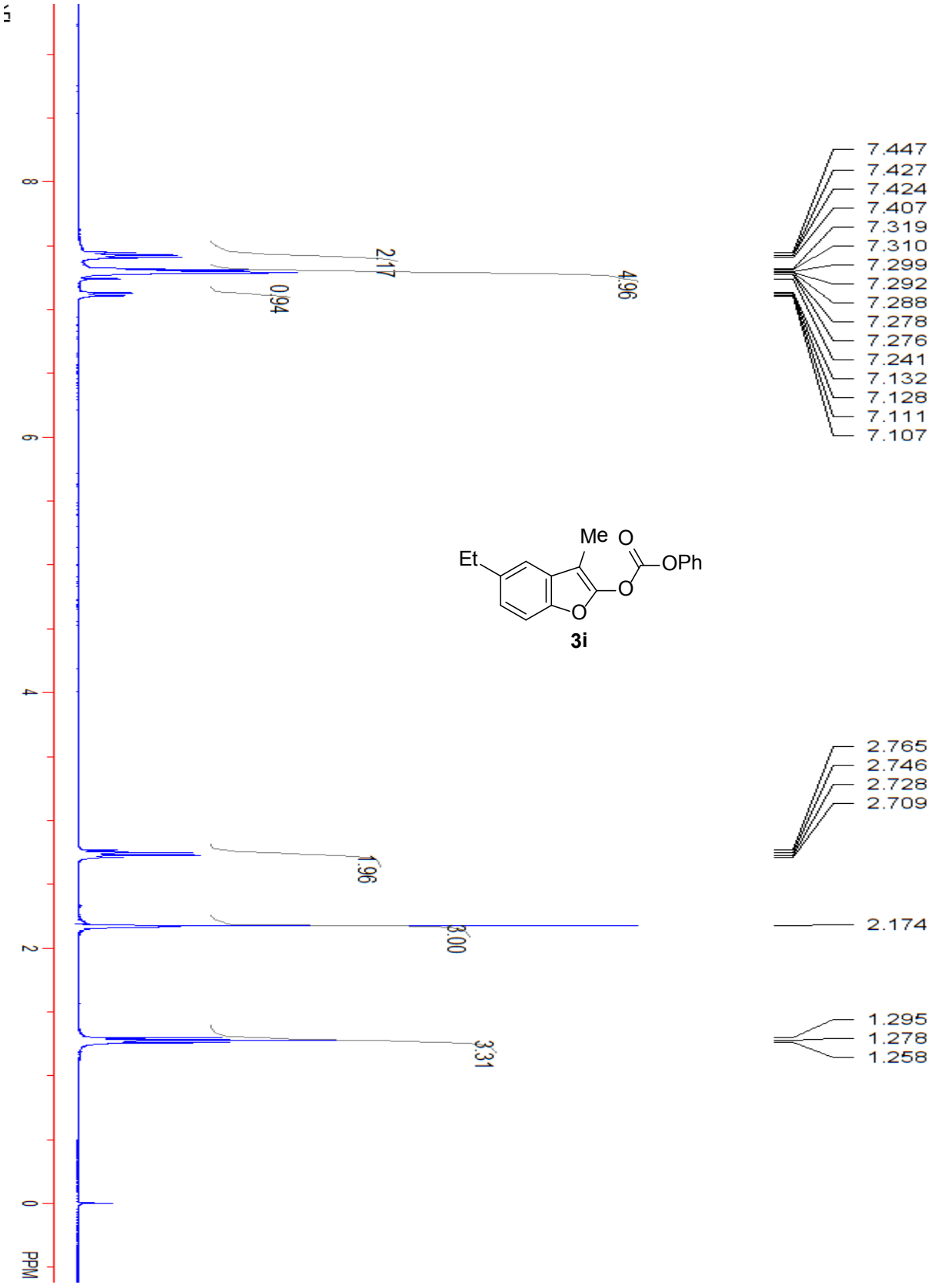
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7.292
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7.276
7.241
7.132
7.128
7.111
7.107
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2.746
2.728
2.709
2.174
1.295
1.278
1.258
4.96
2.17
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3.31
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3i
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4
2
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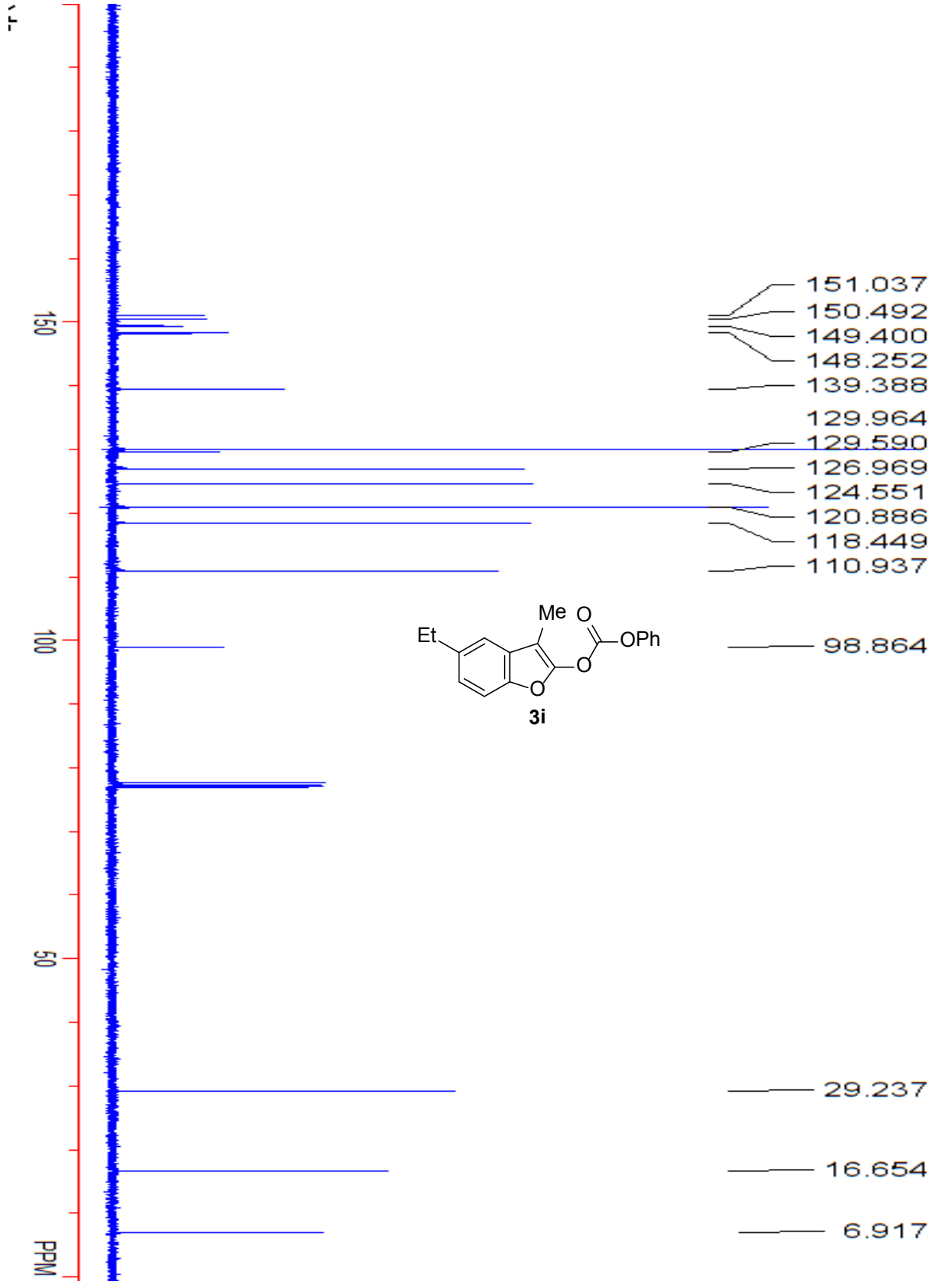
PPM



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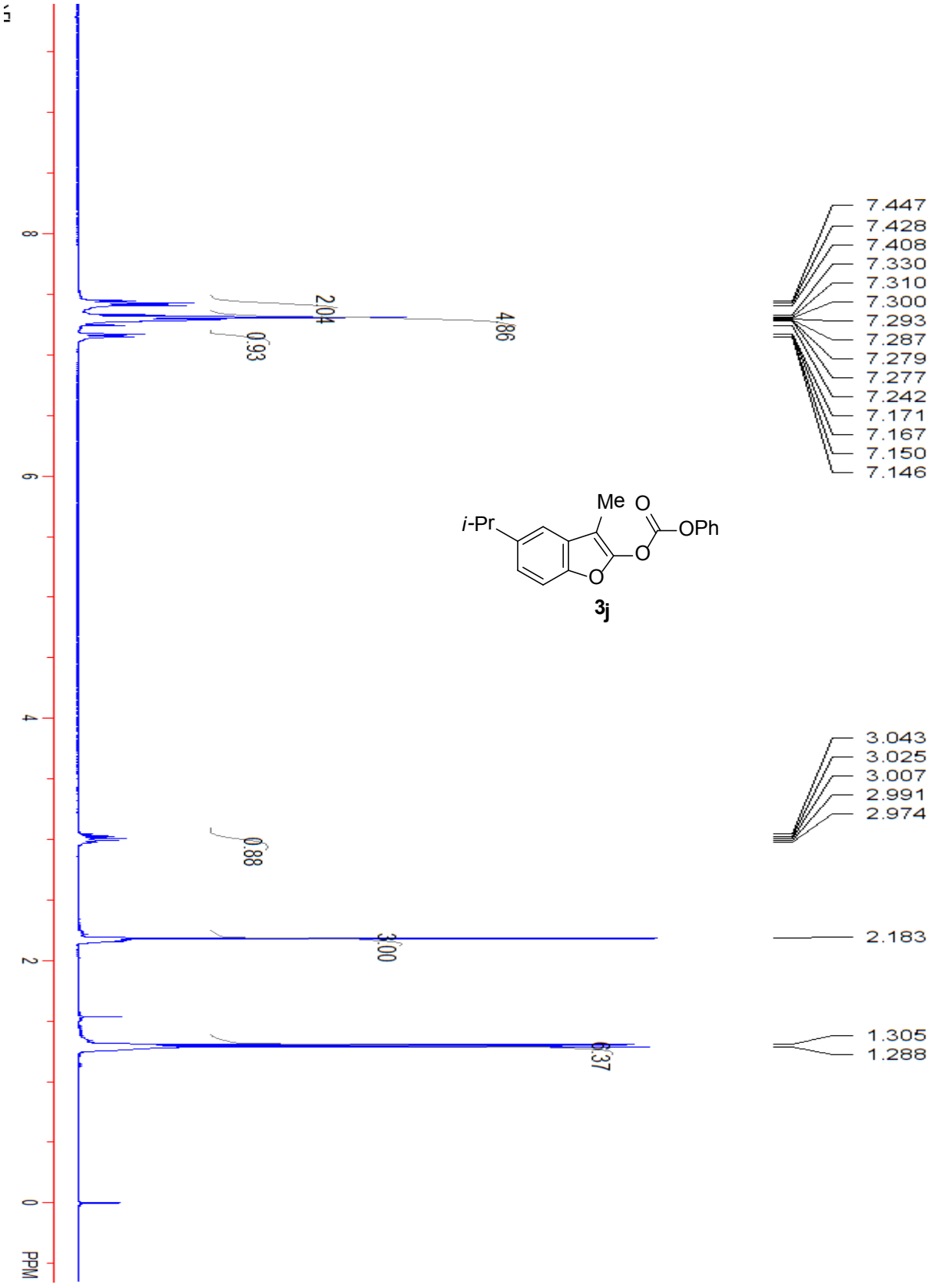
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7.277
7.242
7.171
7.167
7.150
7.146
Me
O
i-Pr
OPh
O
O
3j
3.043
3.025
3.007
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2.974
2.183
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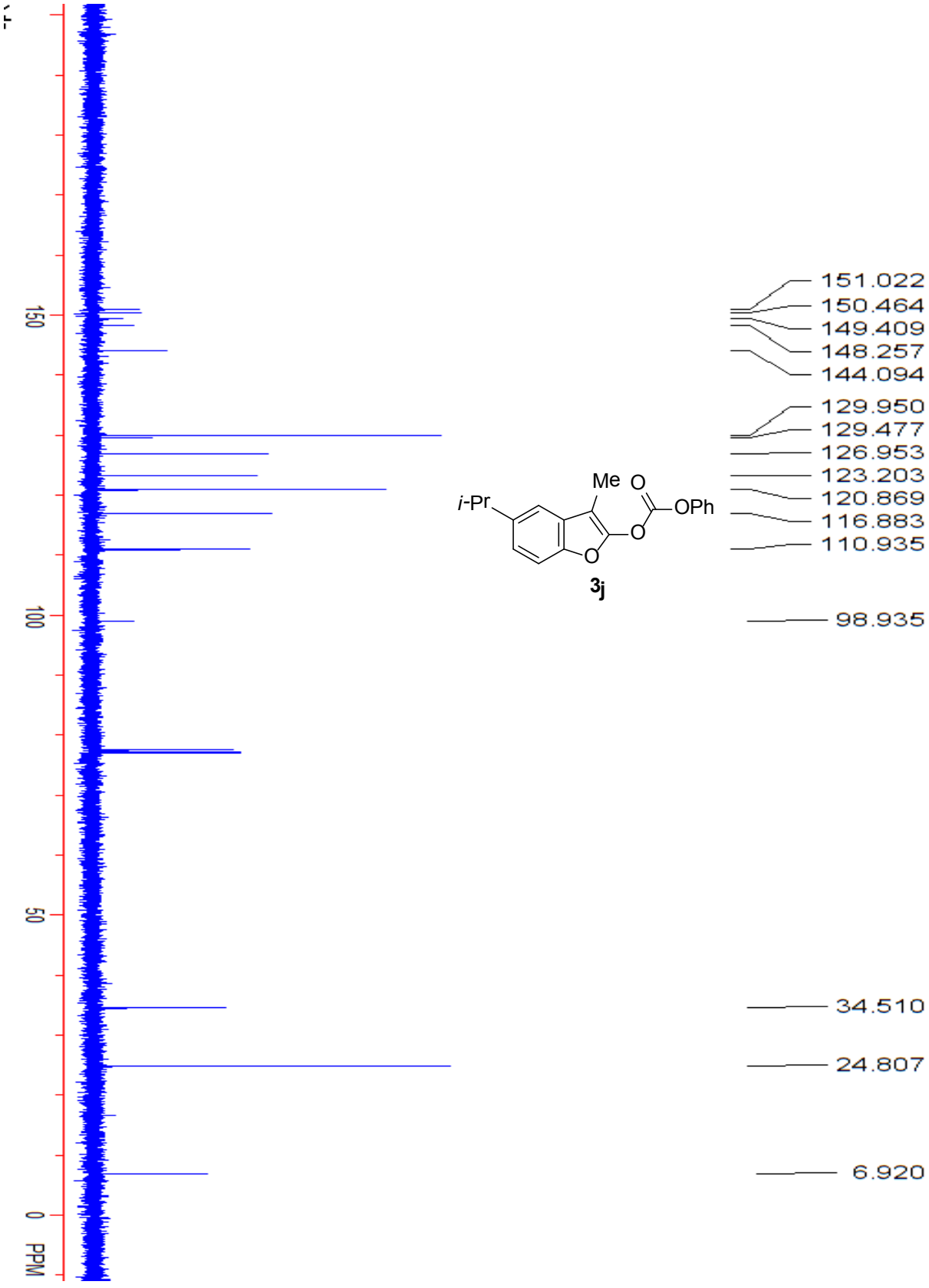
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50
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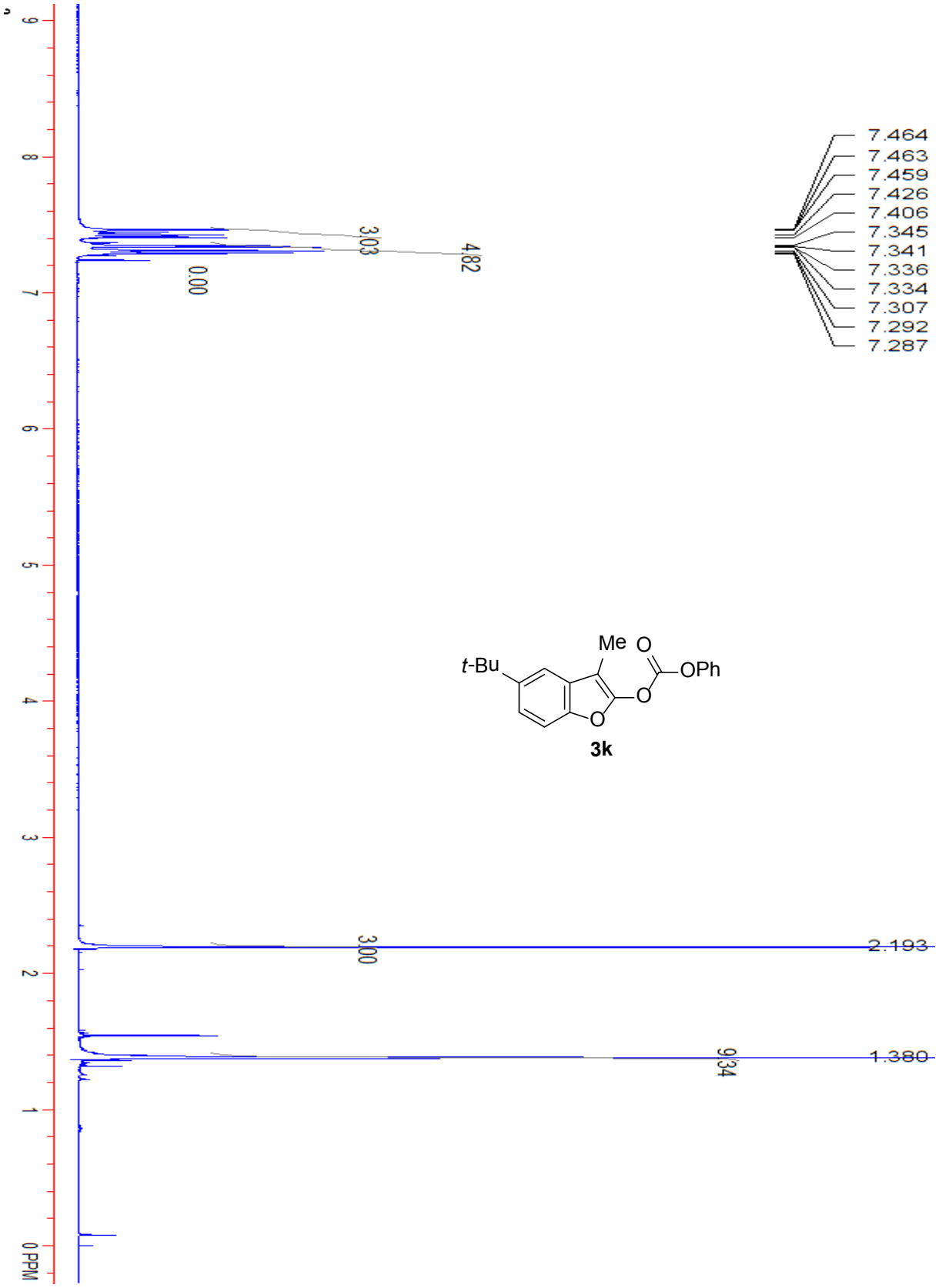
O
i-Pr
OPh
O
O
3j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7.292
7.287
3.03
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O
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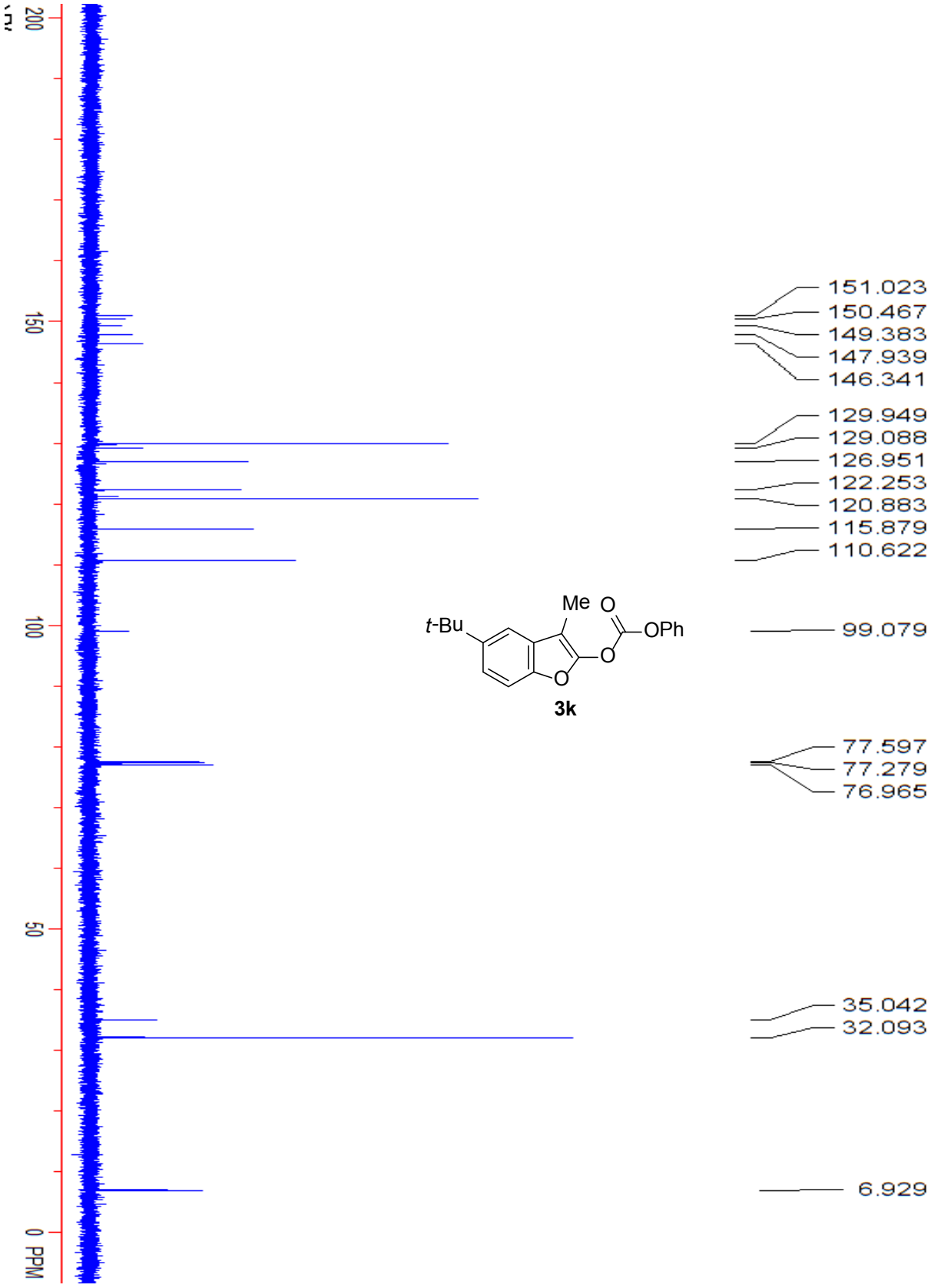
OPh
O
O

3k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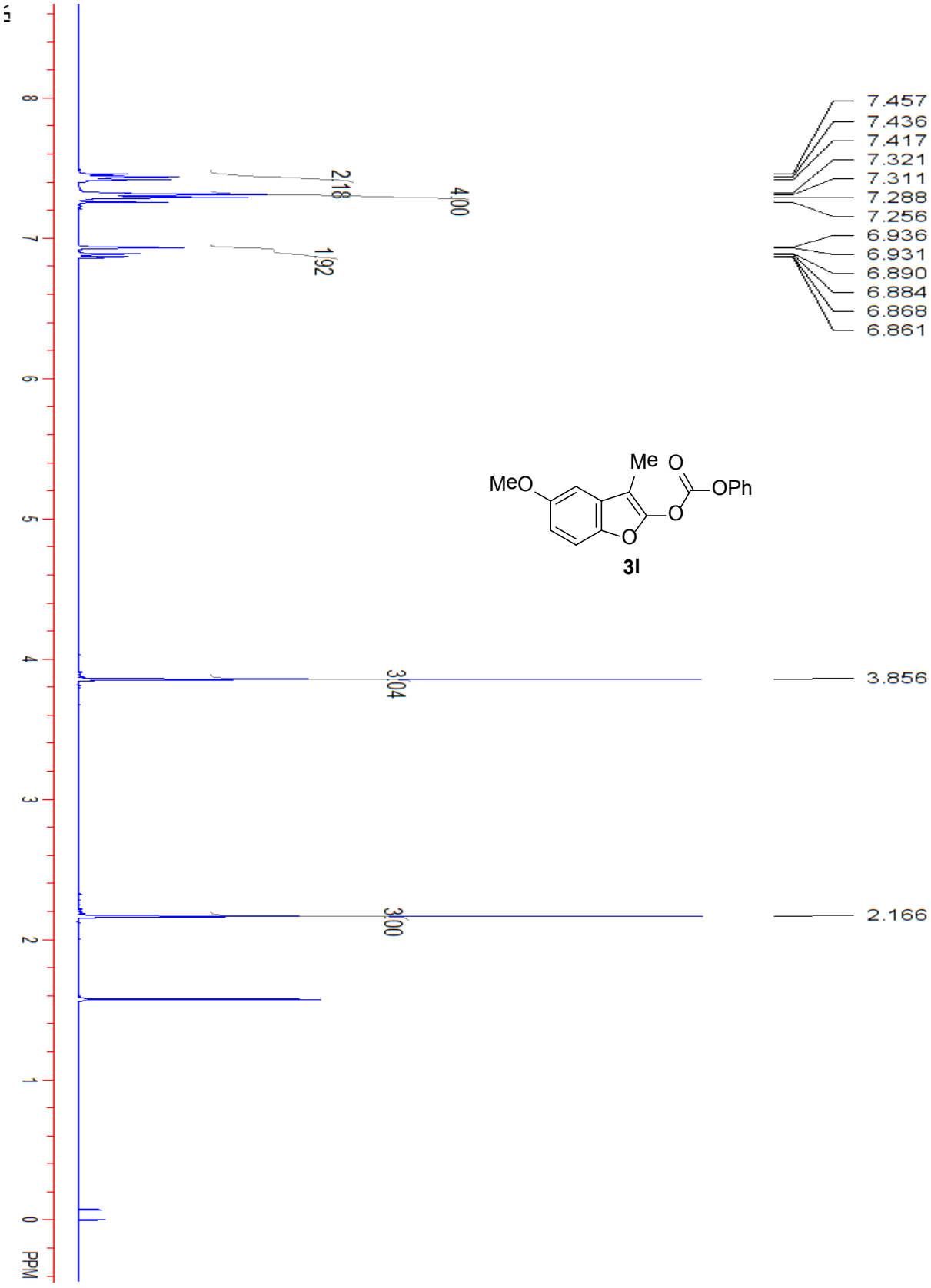
t-Bu
OPh
O
O

3k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O
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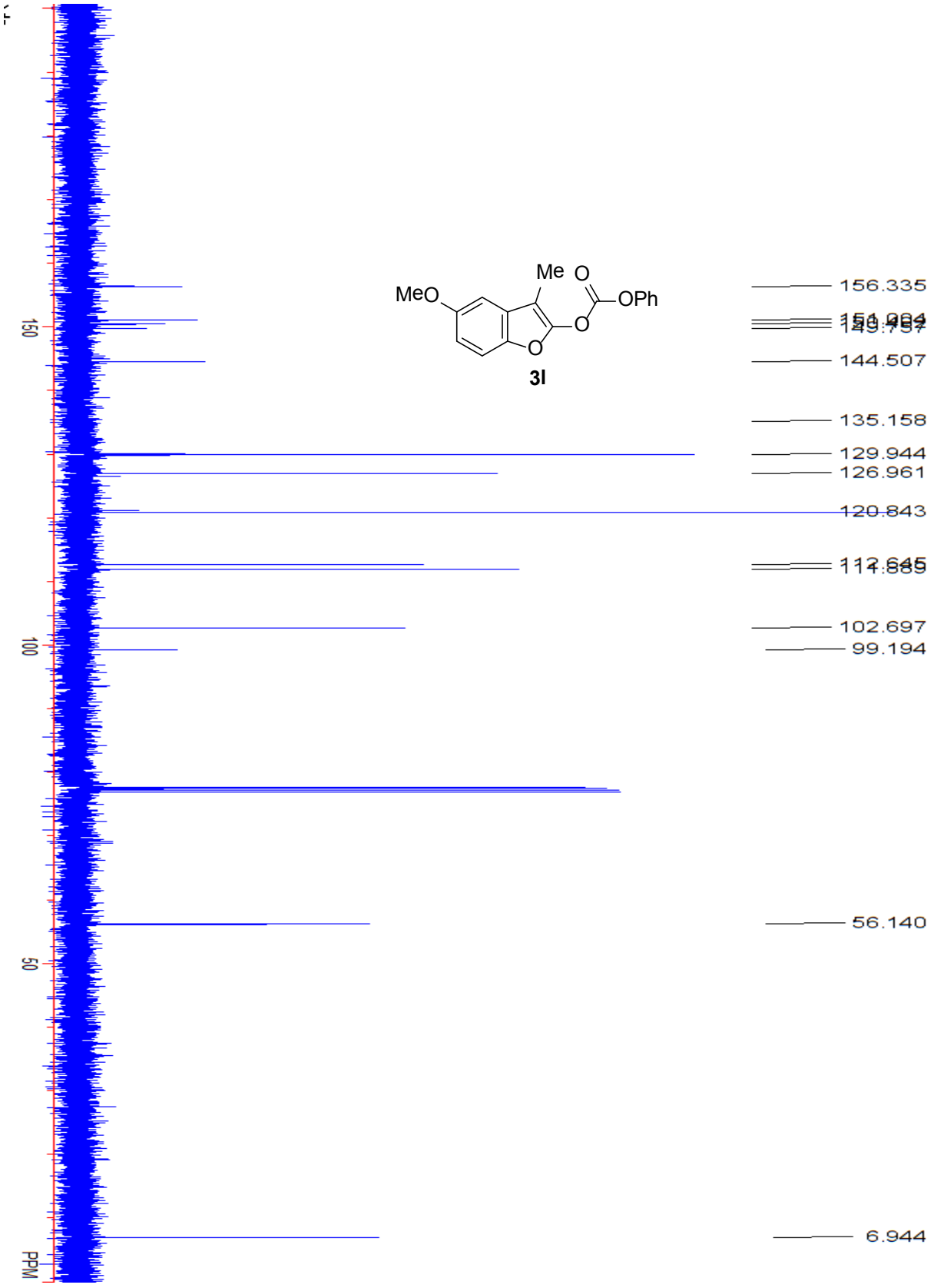

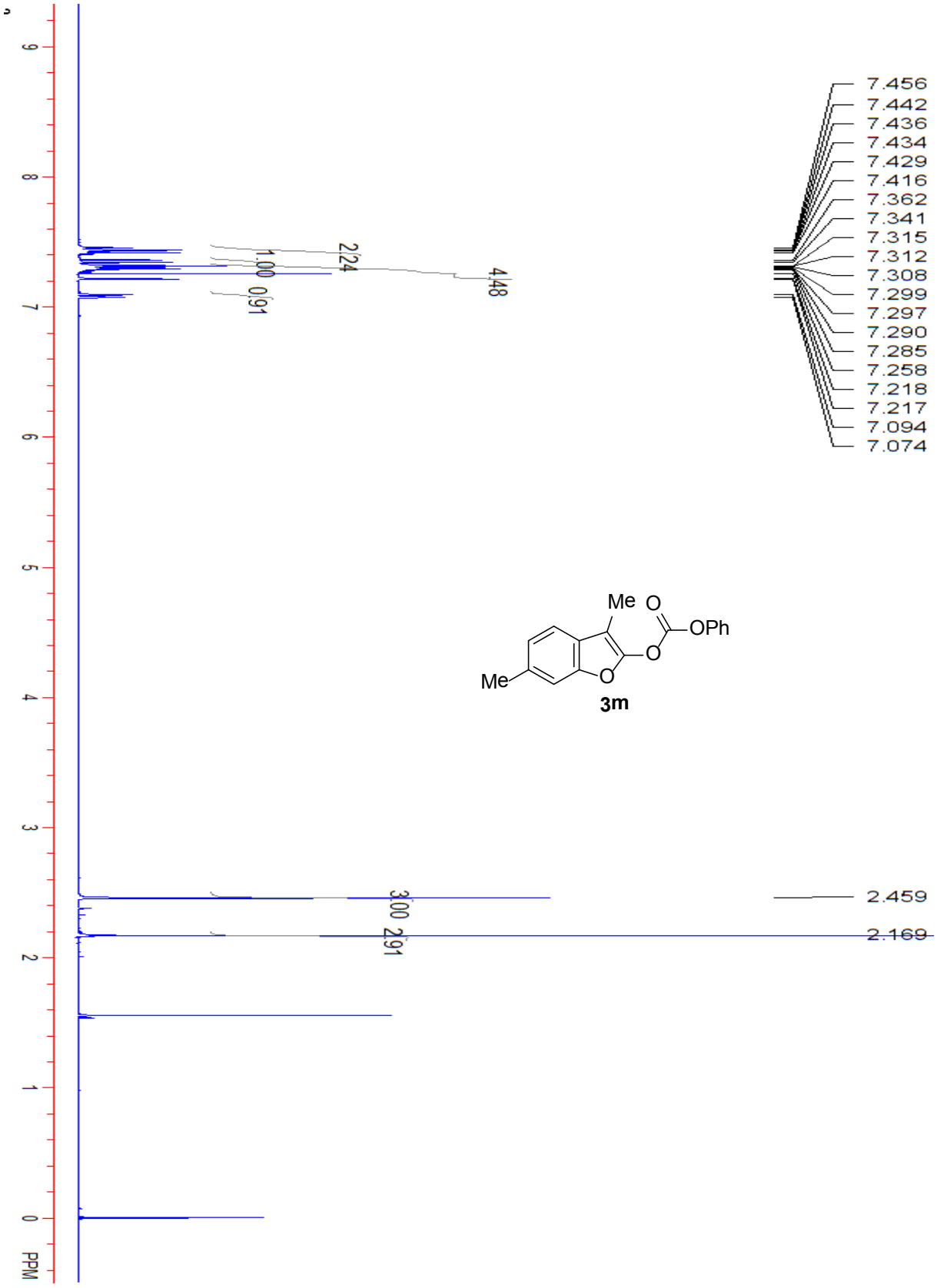
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7.297
7.290
7.285
7.258
7.218
7.217
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7.074
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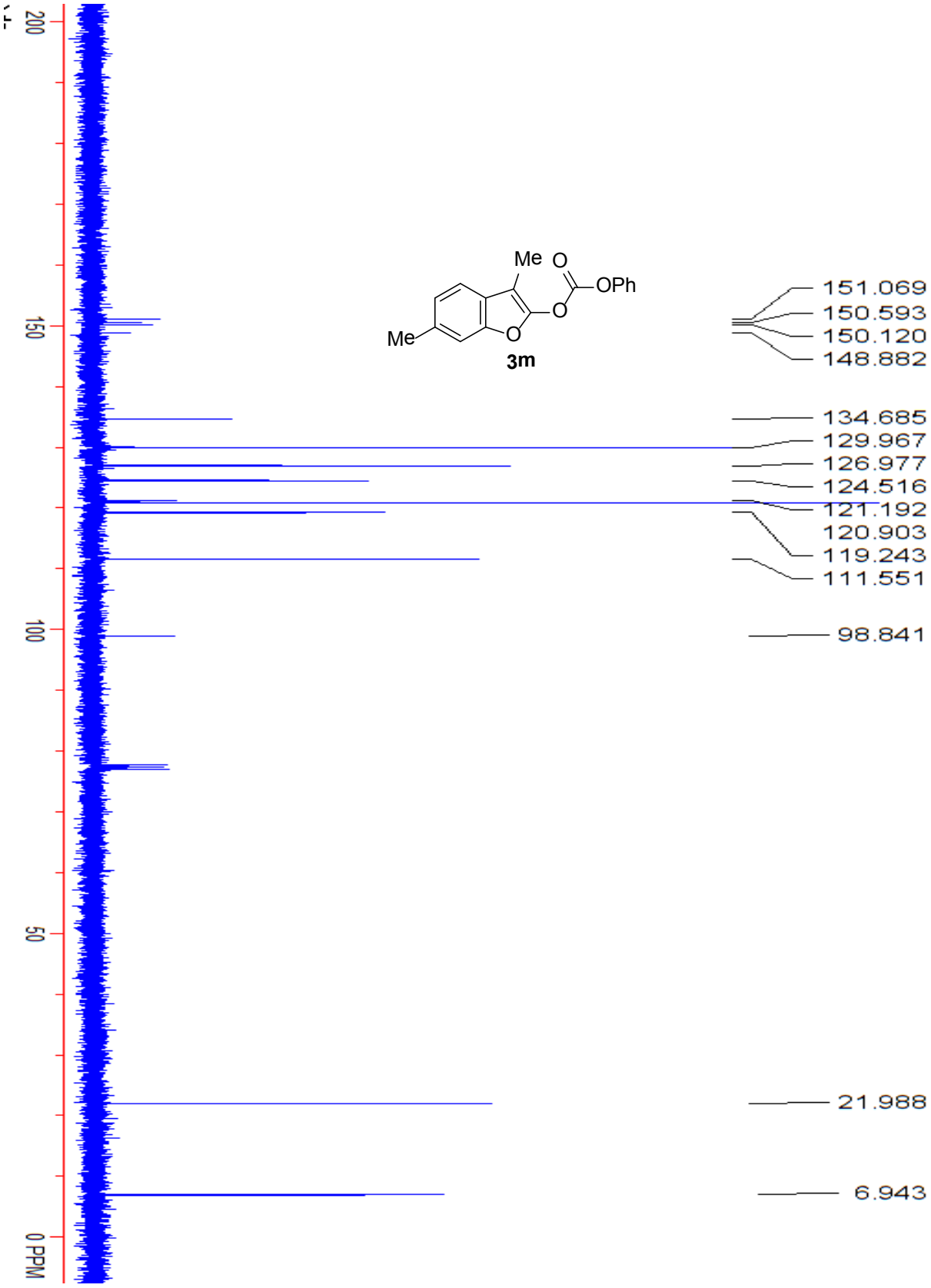
PPM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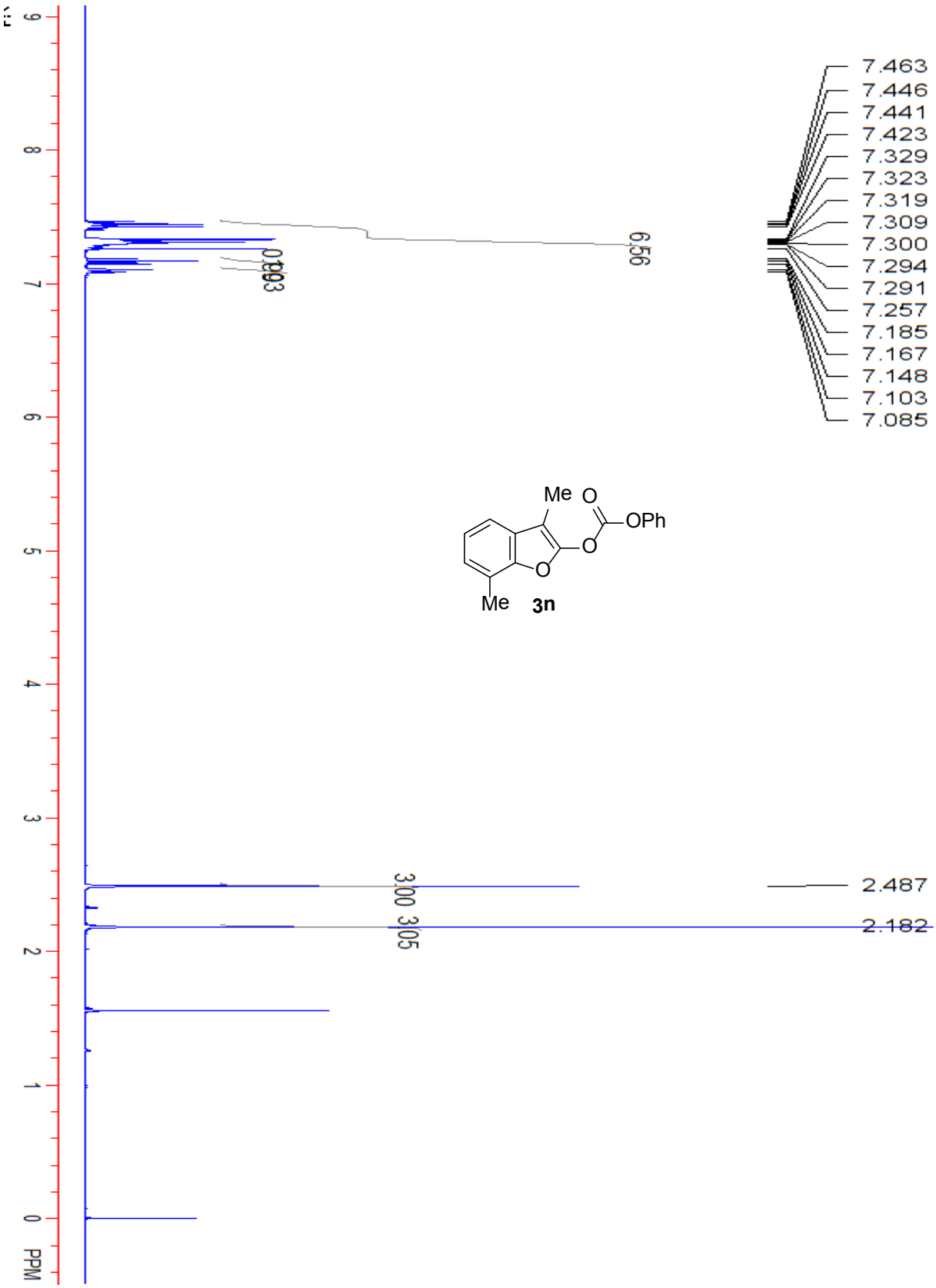

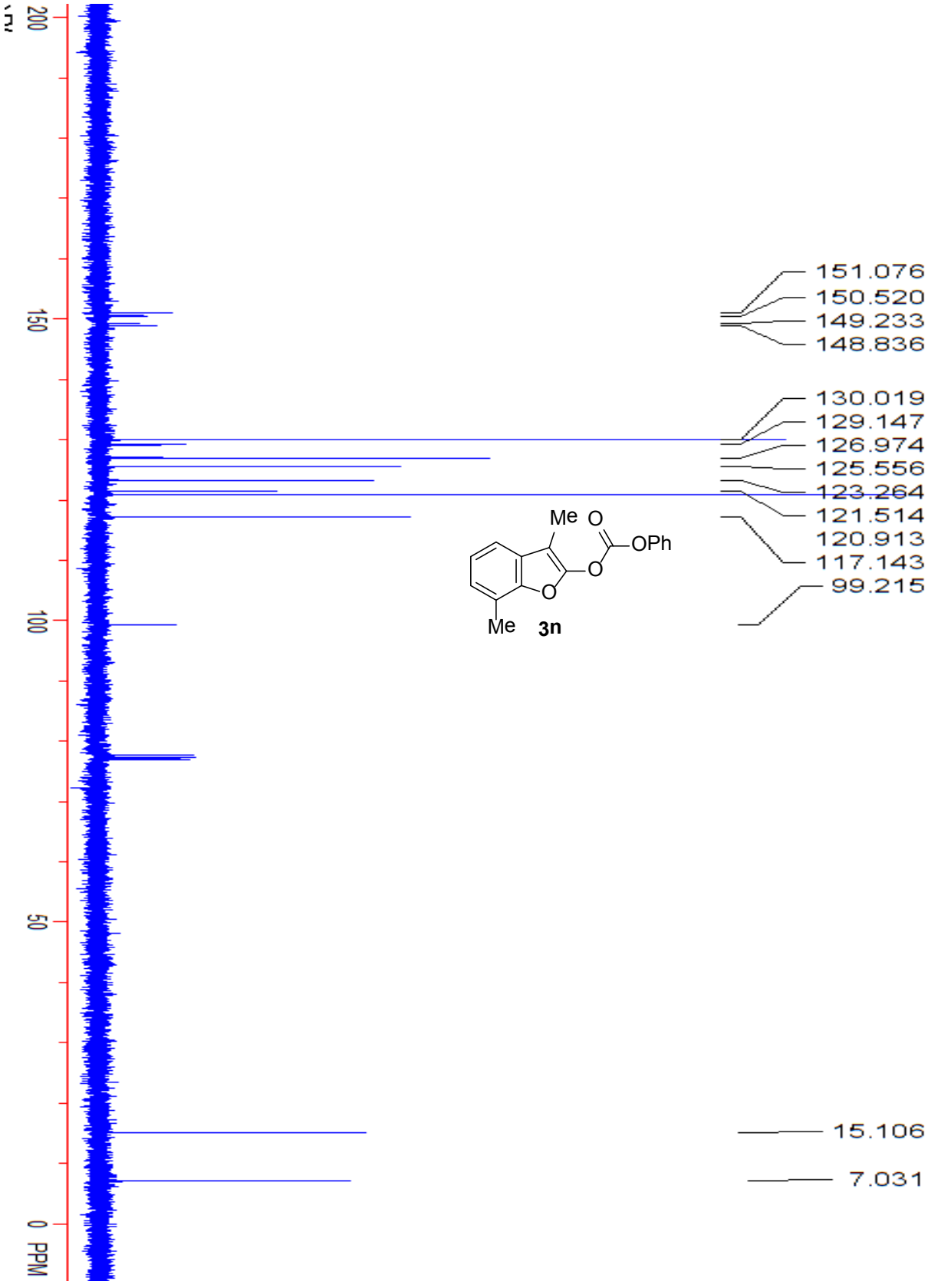
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Me
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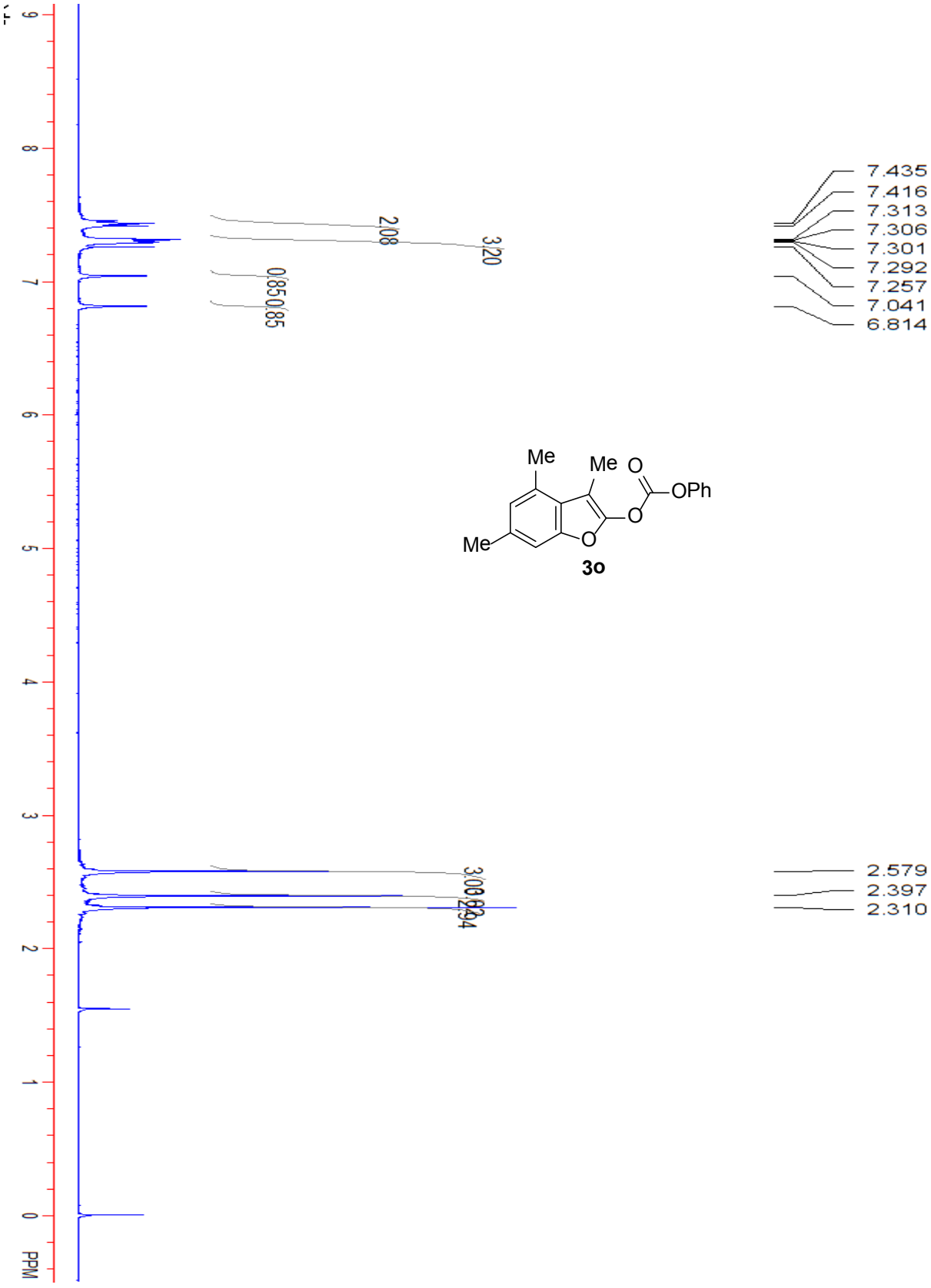
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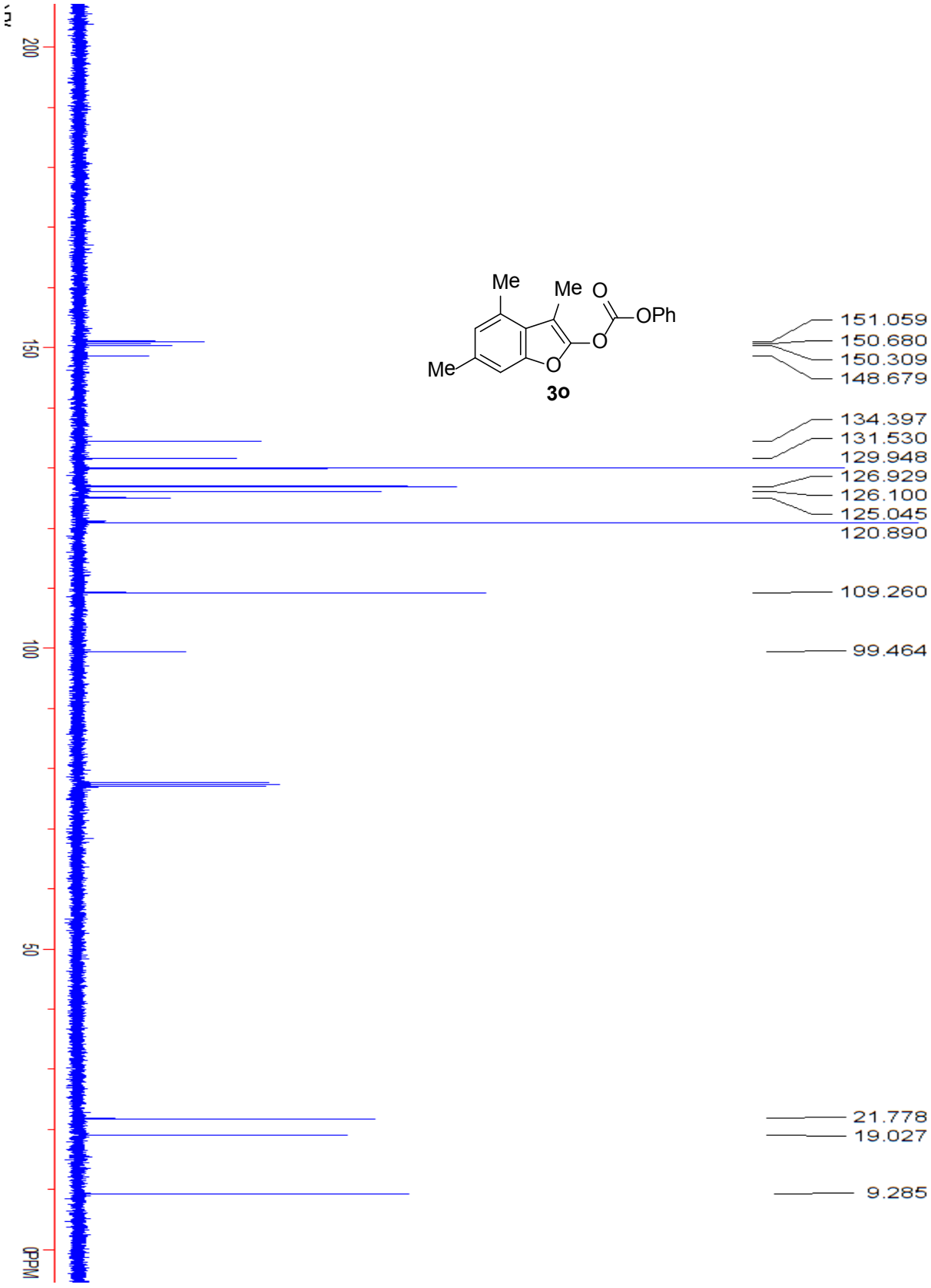
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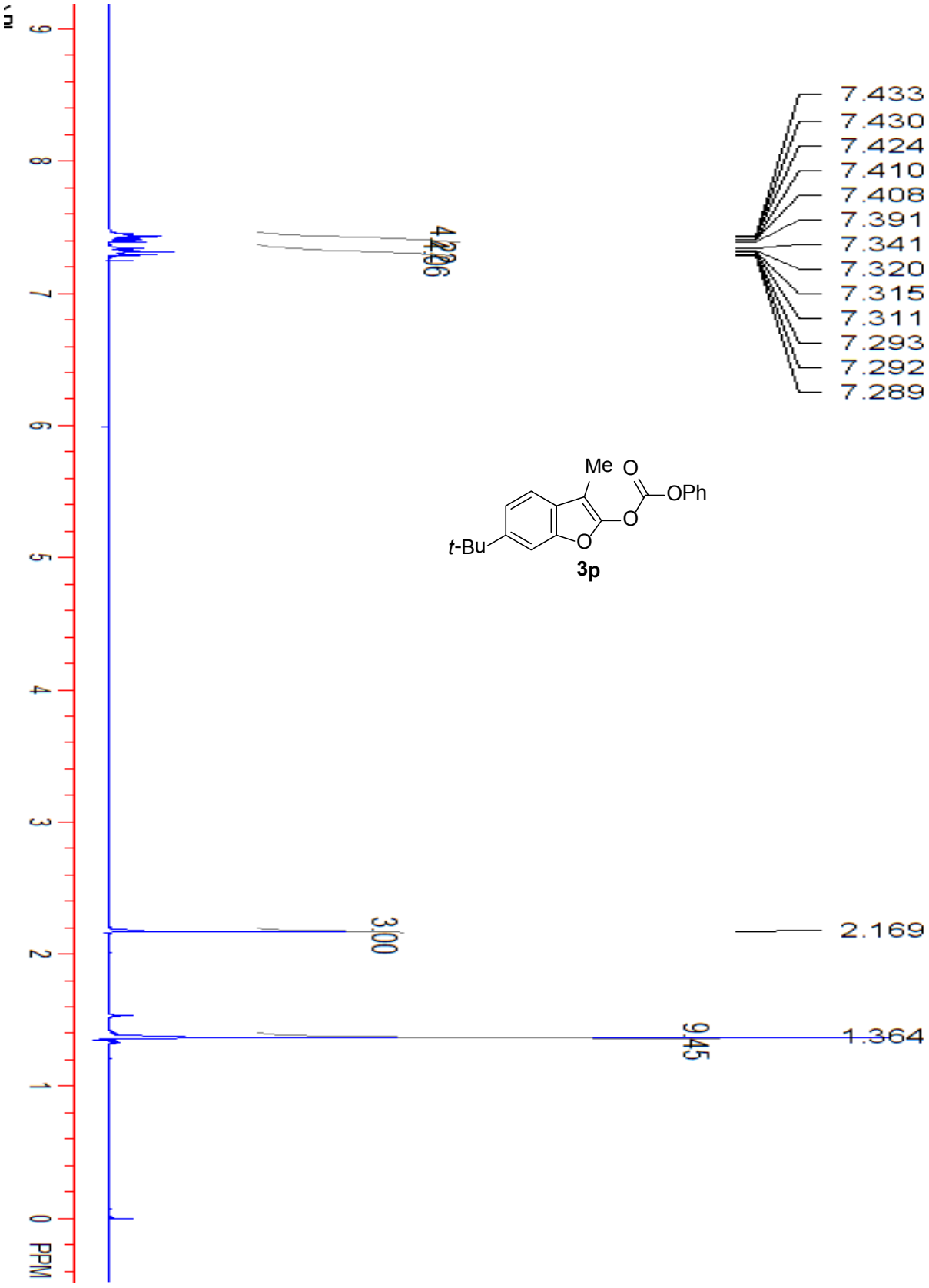

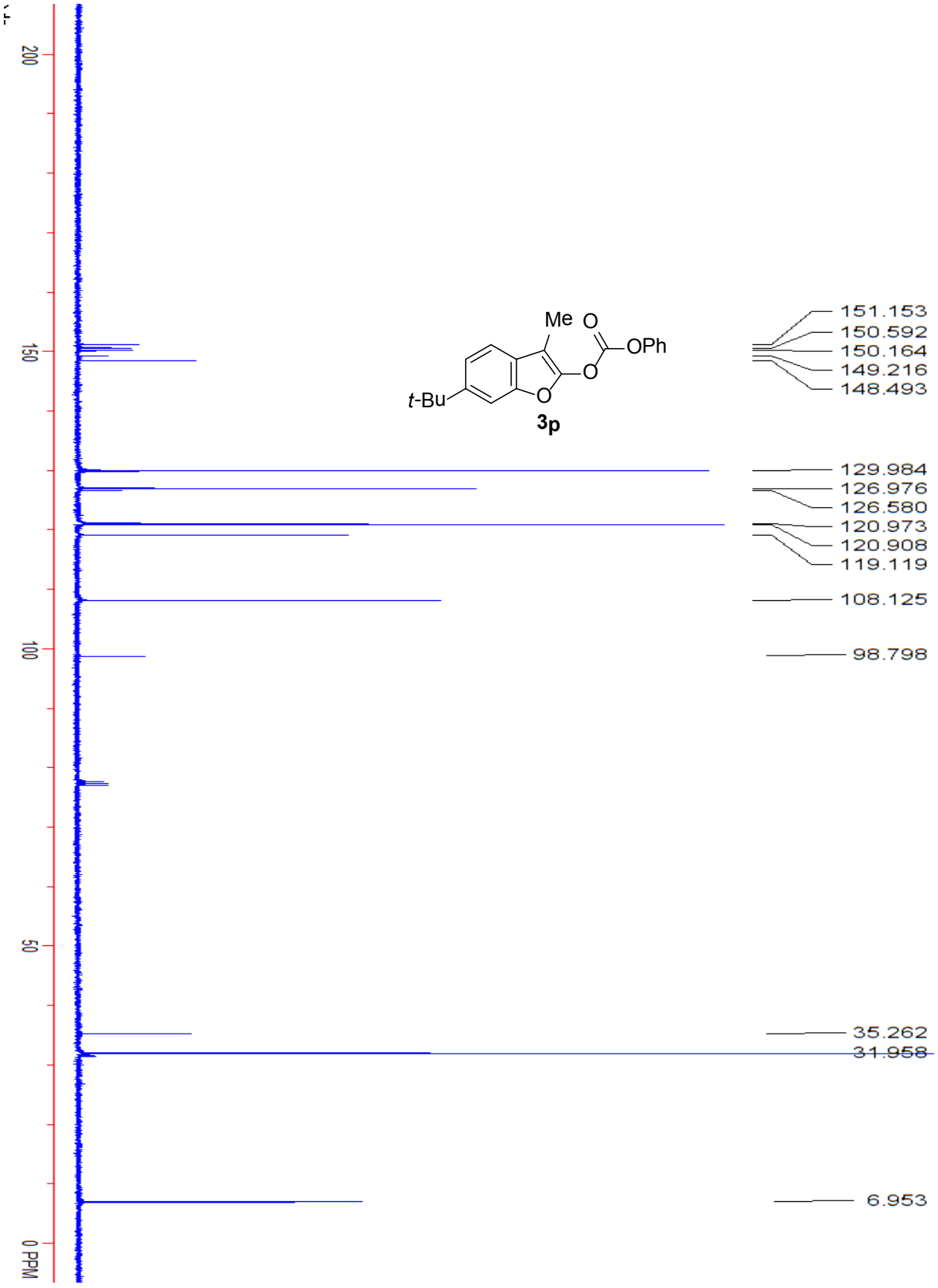
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50
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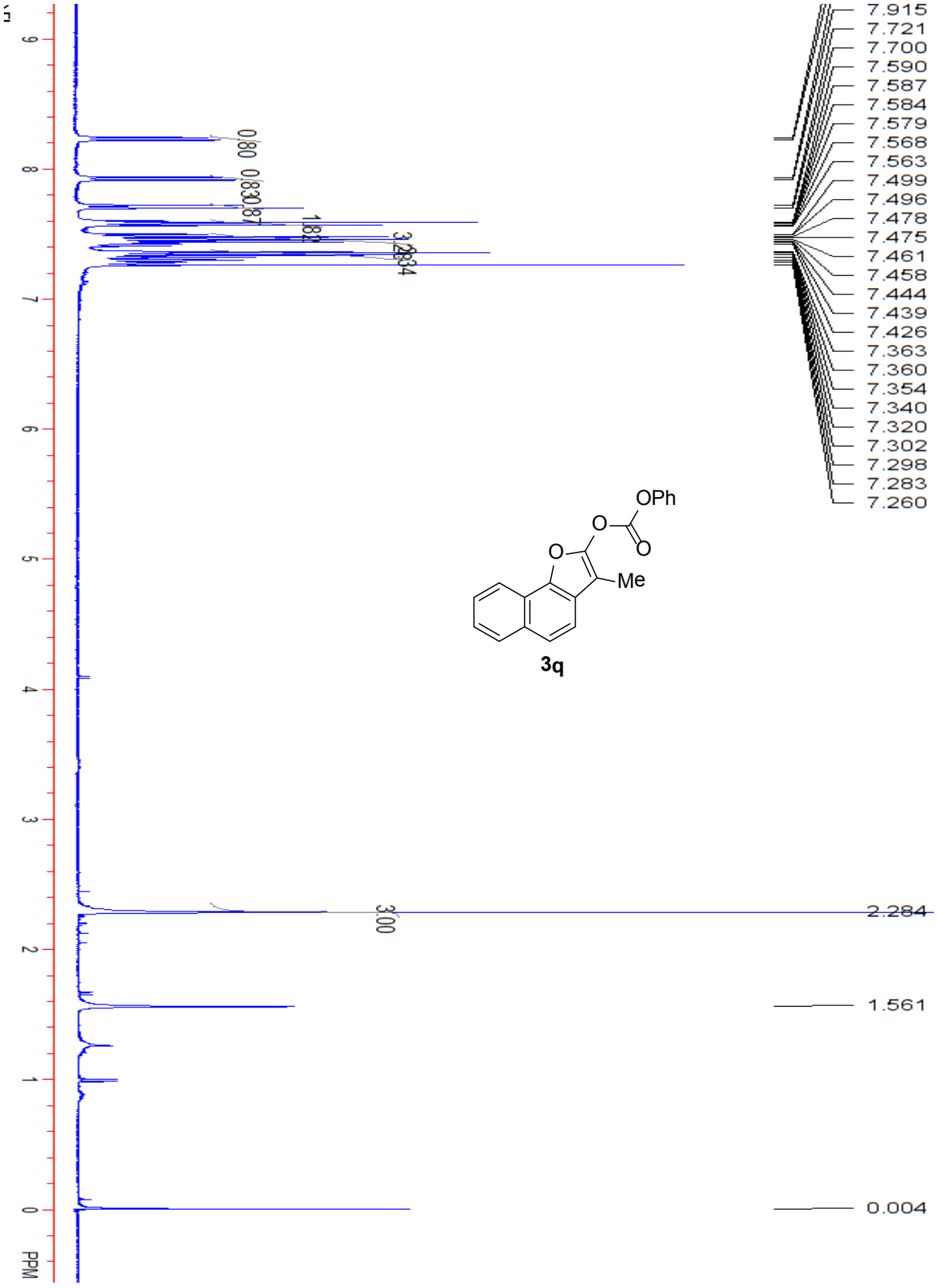
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O
Me

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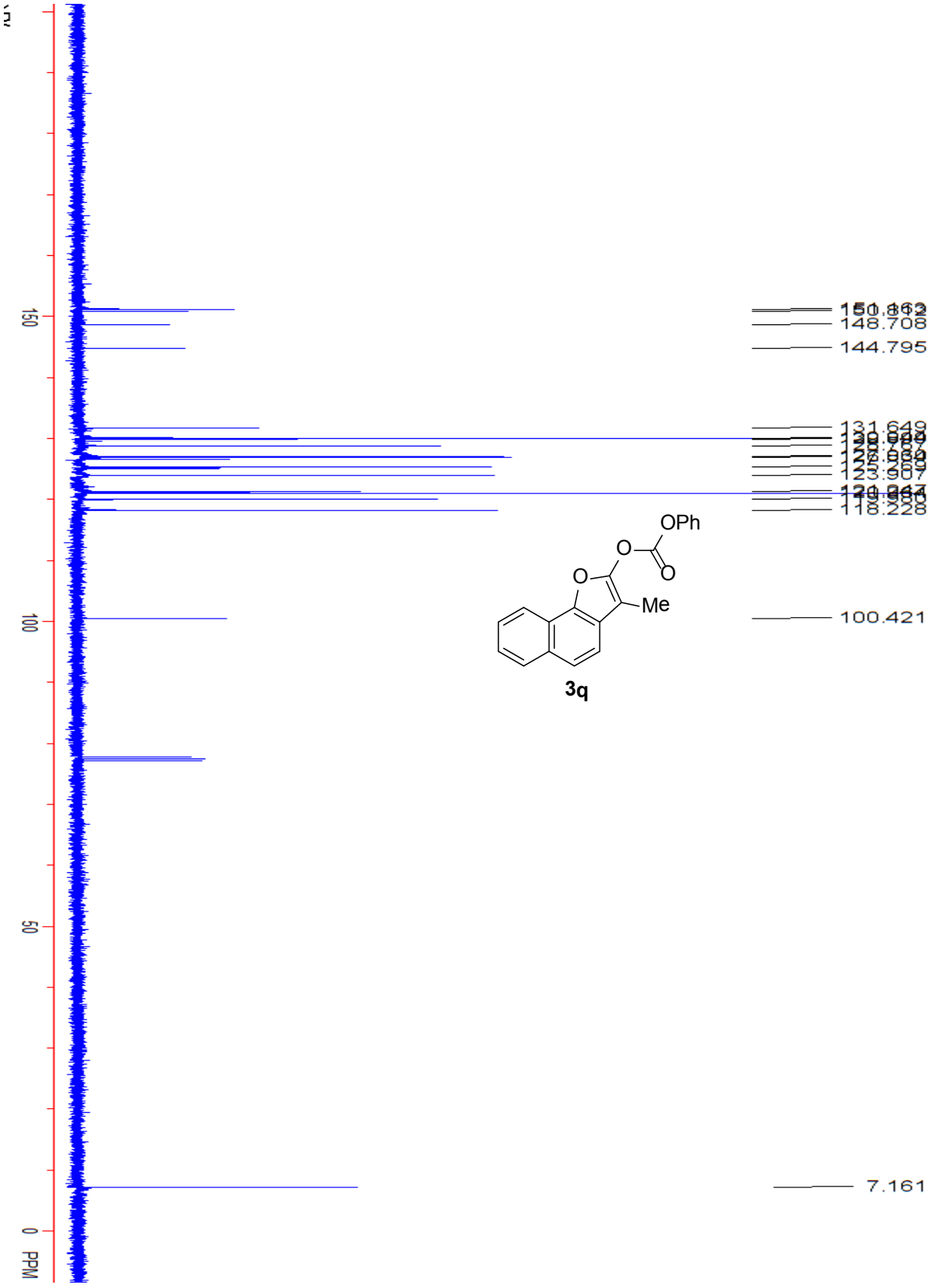
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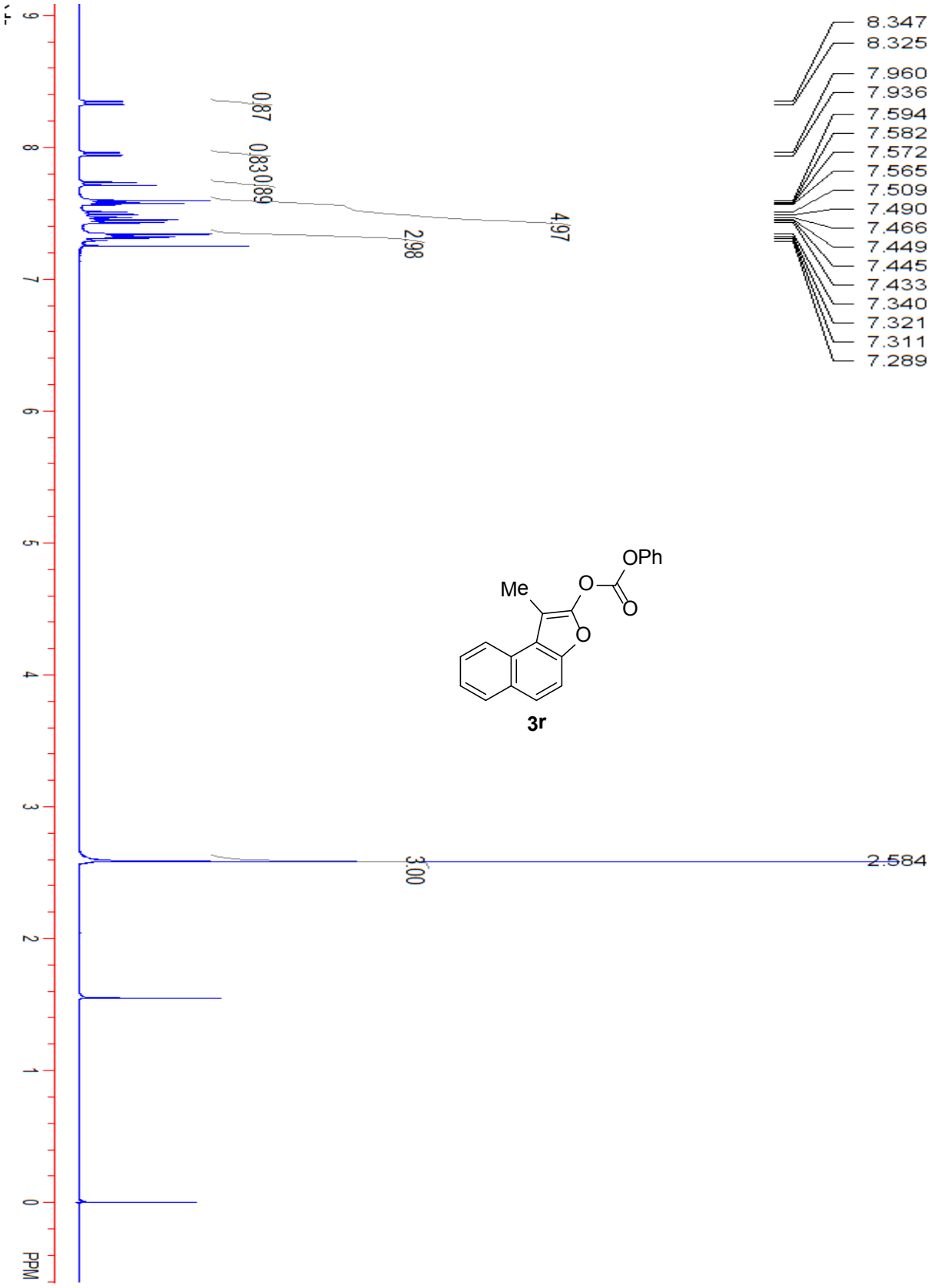
O
Me

3q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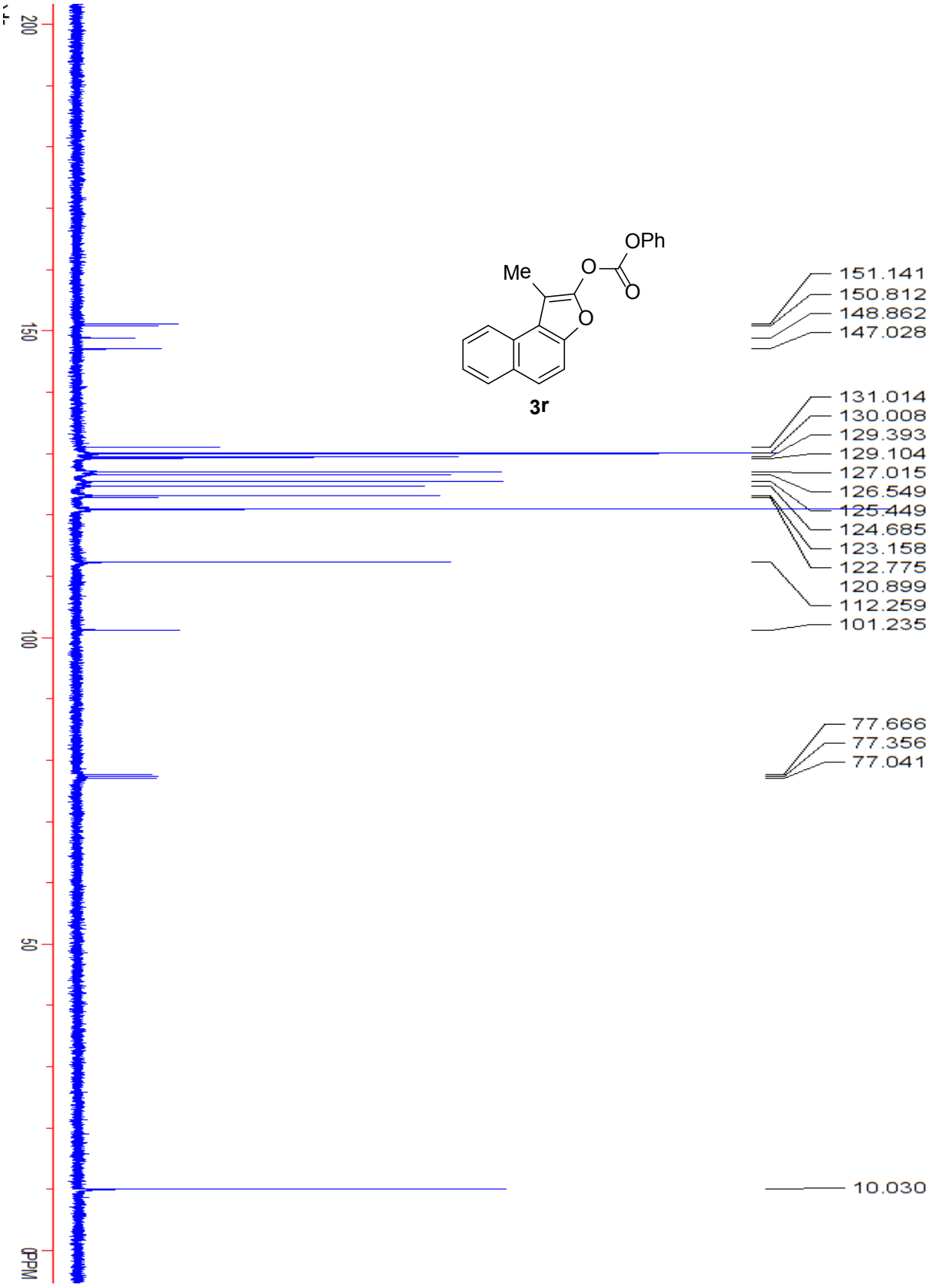
PPM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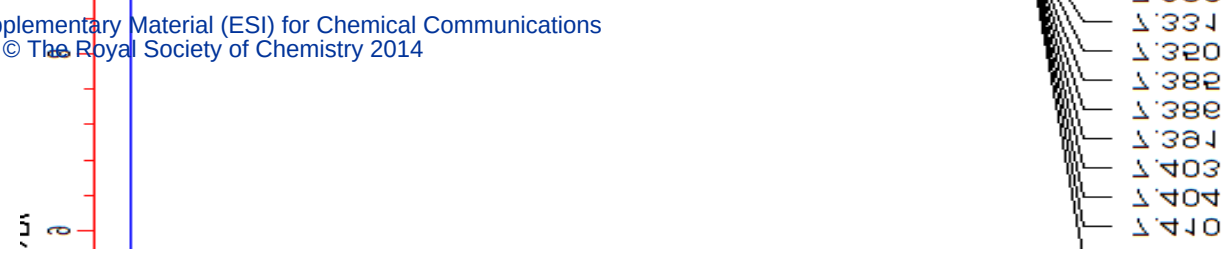

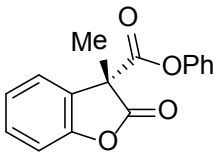

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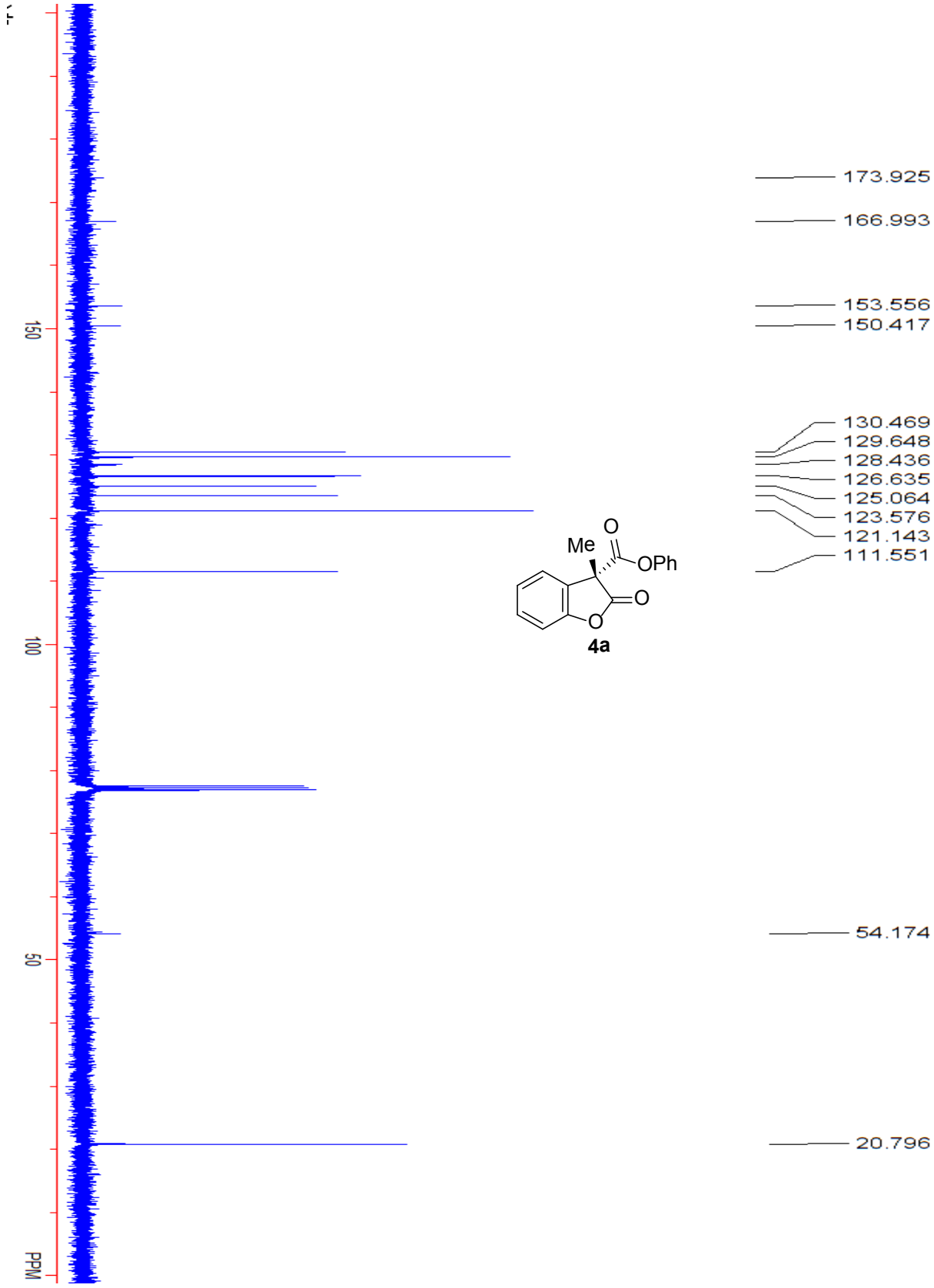
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O
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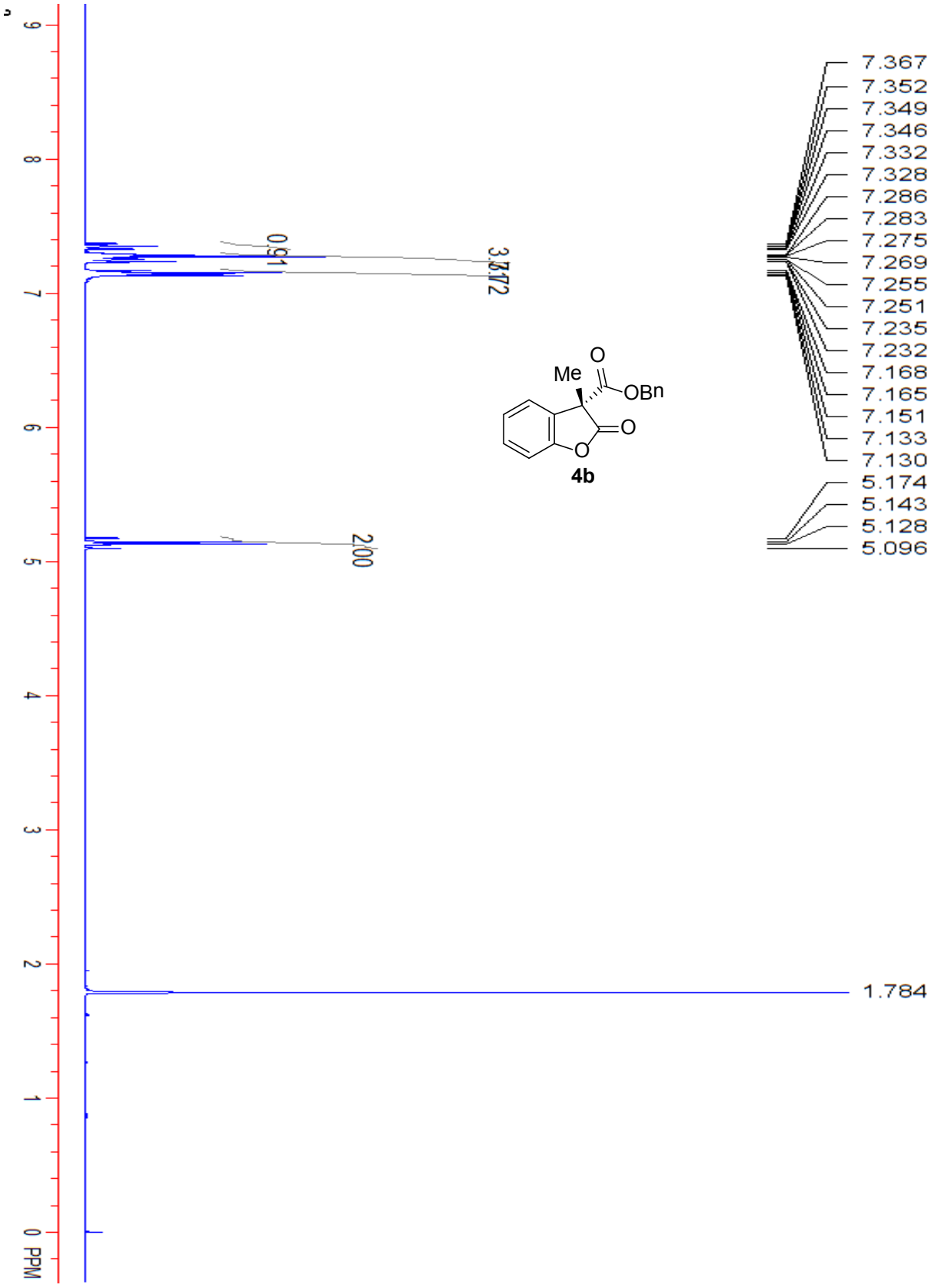
100
50
PPM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O
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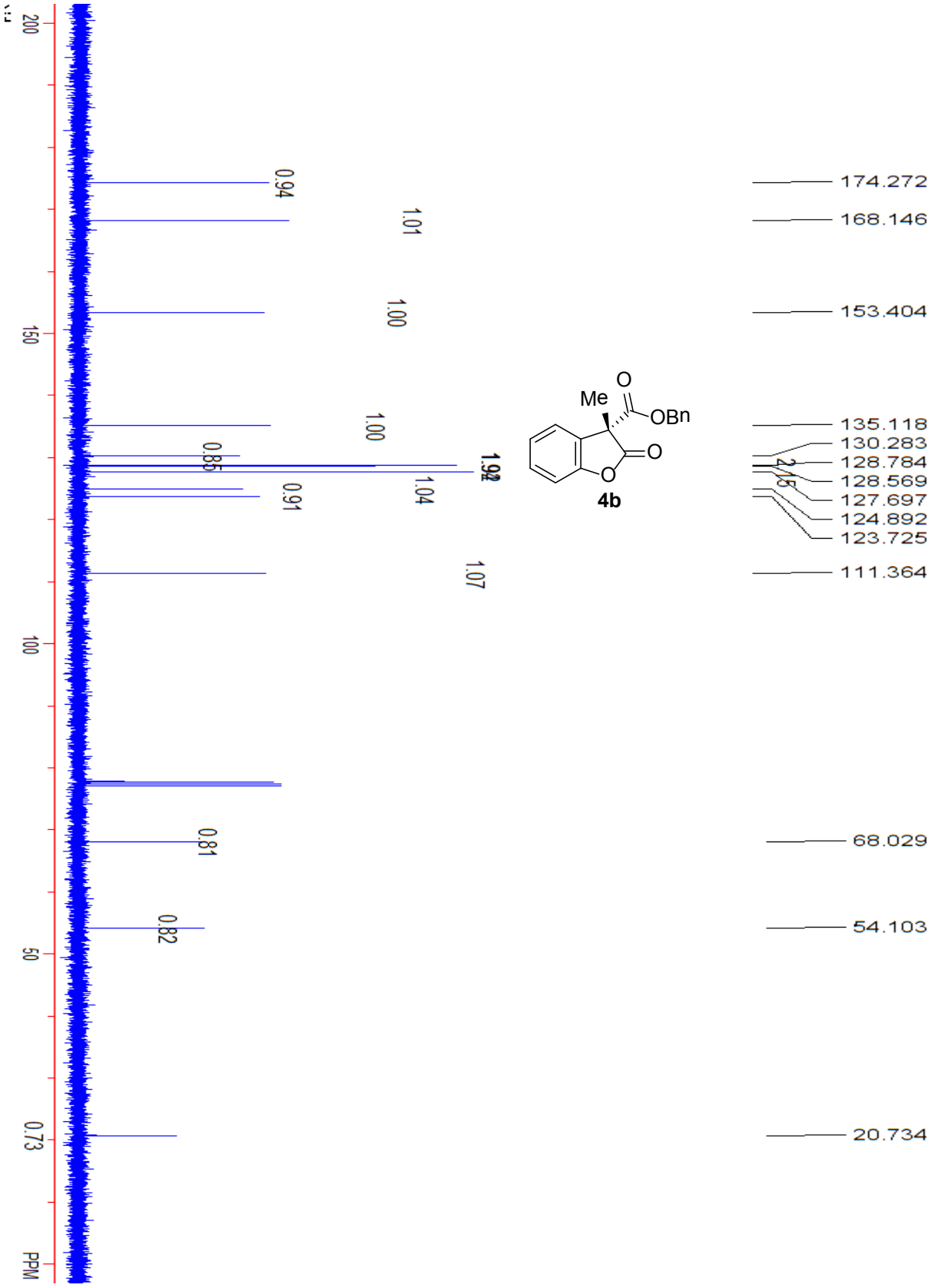
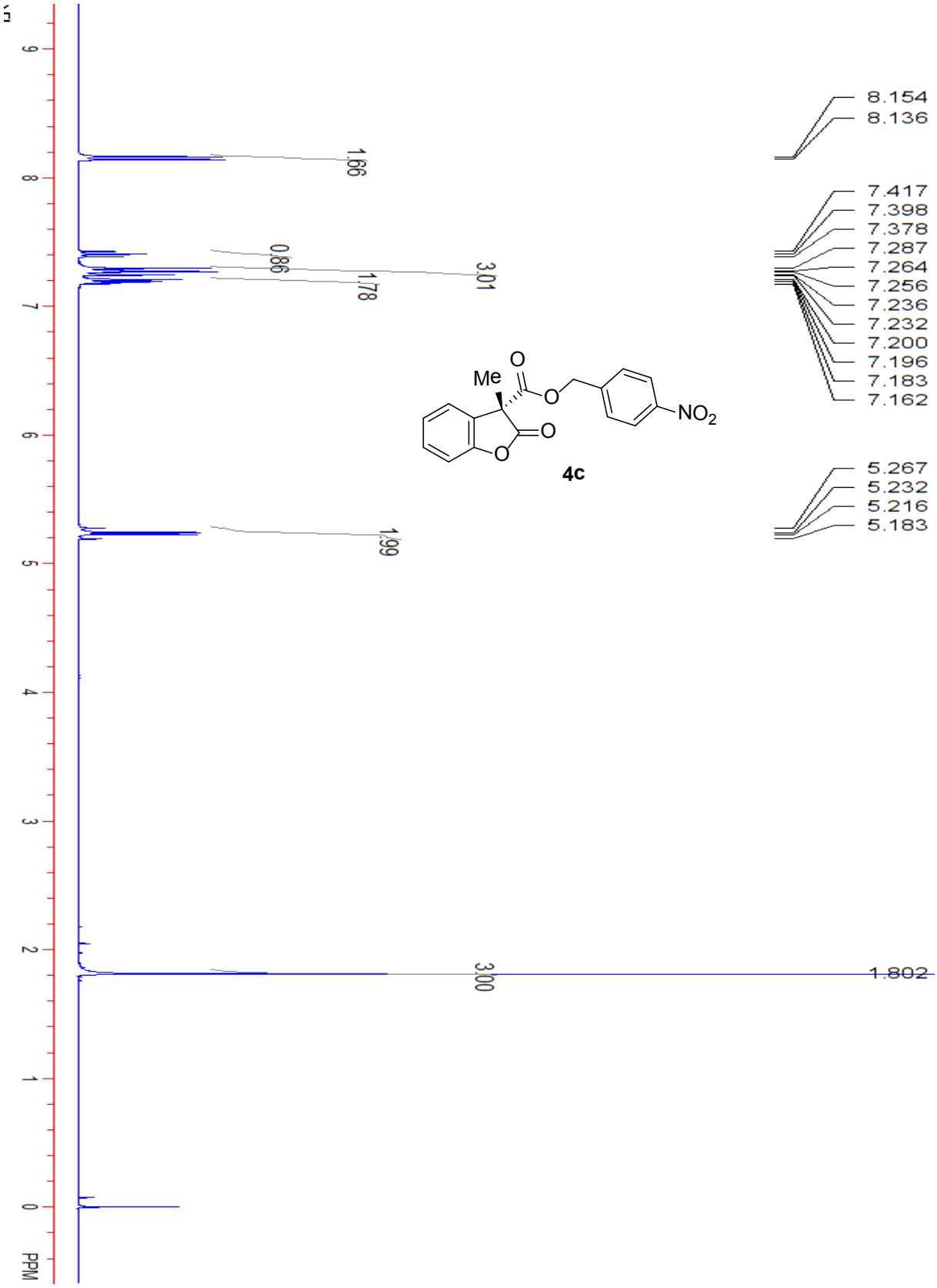
PPM

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3.00
Me
O
O
O
O
NO2
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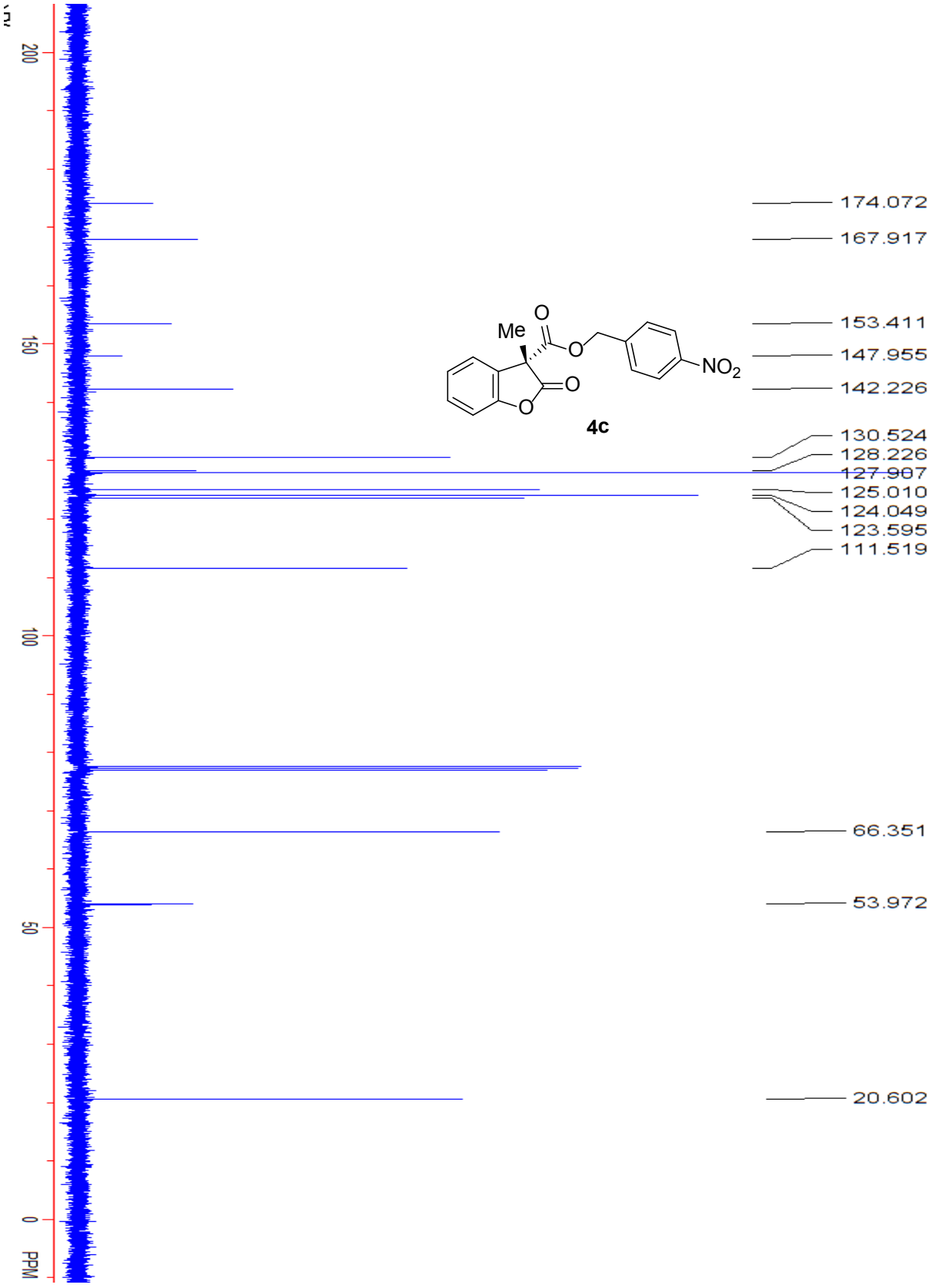
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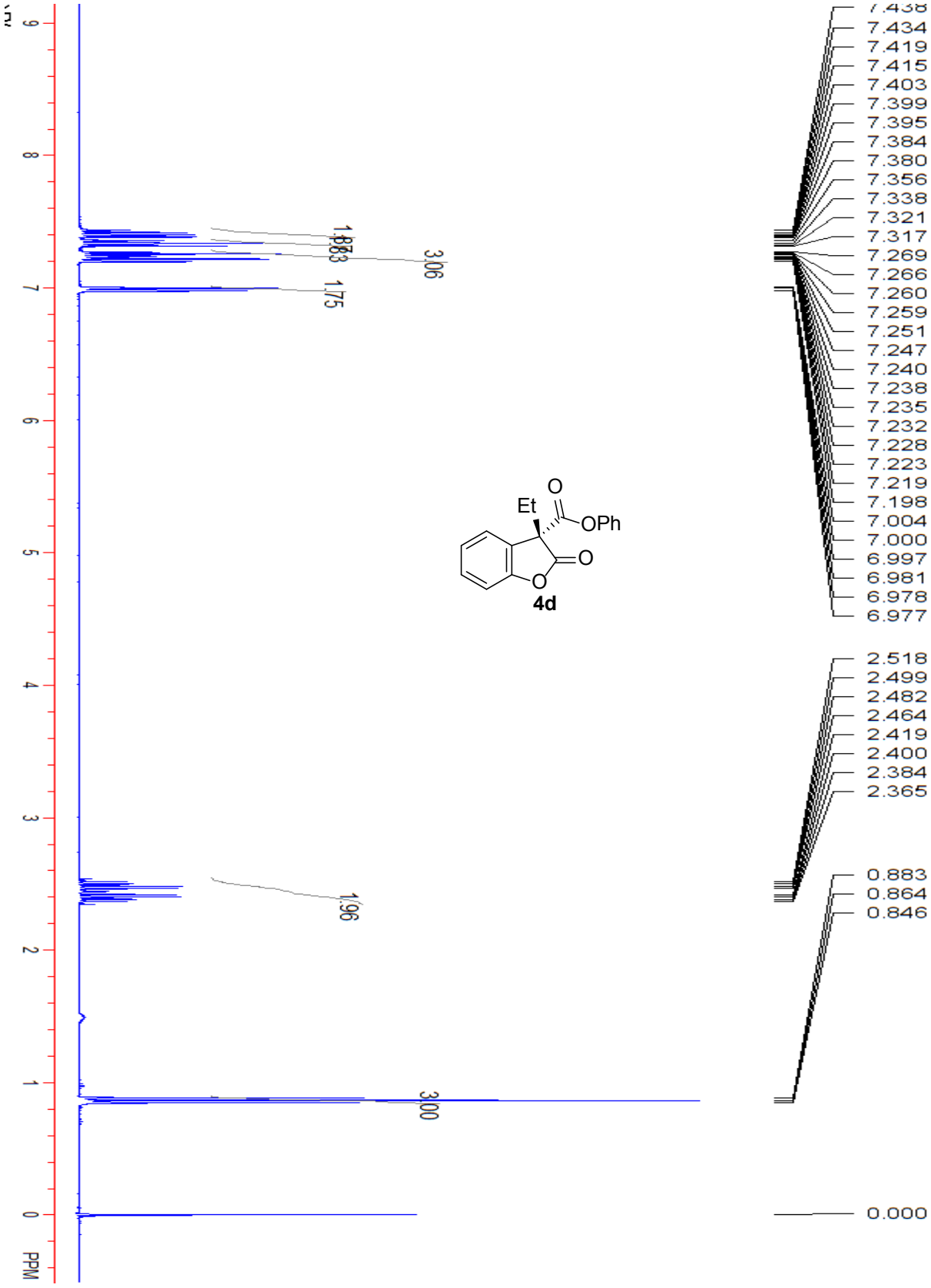
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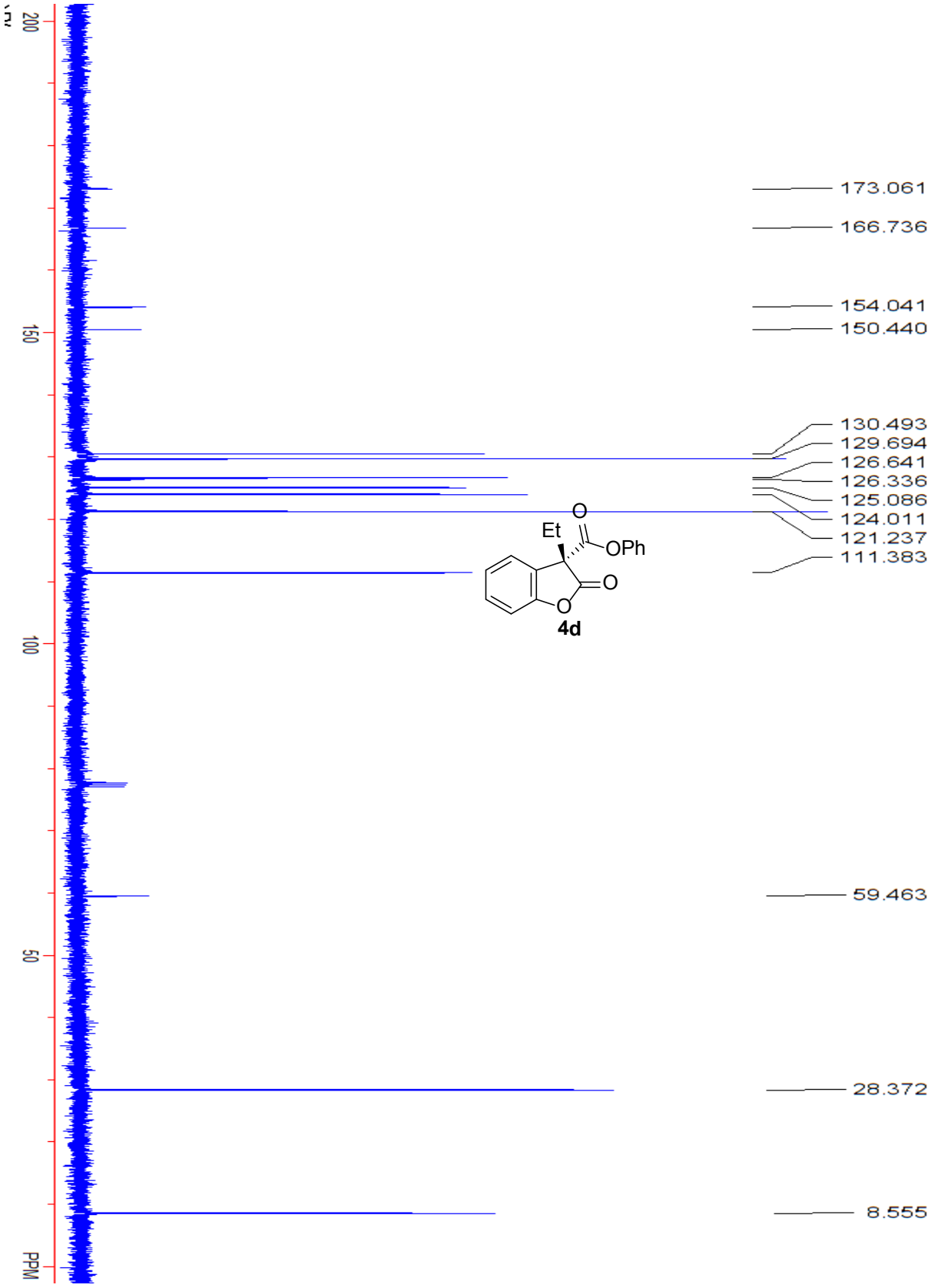

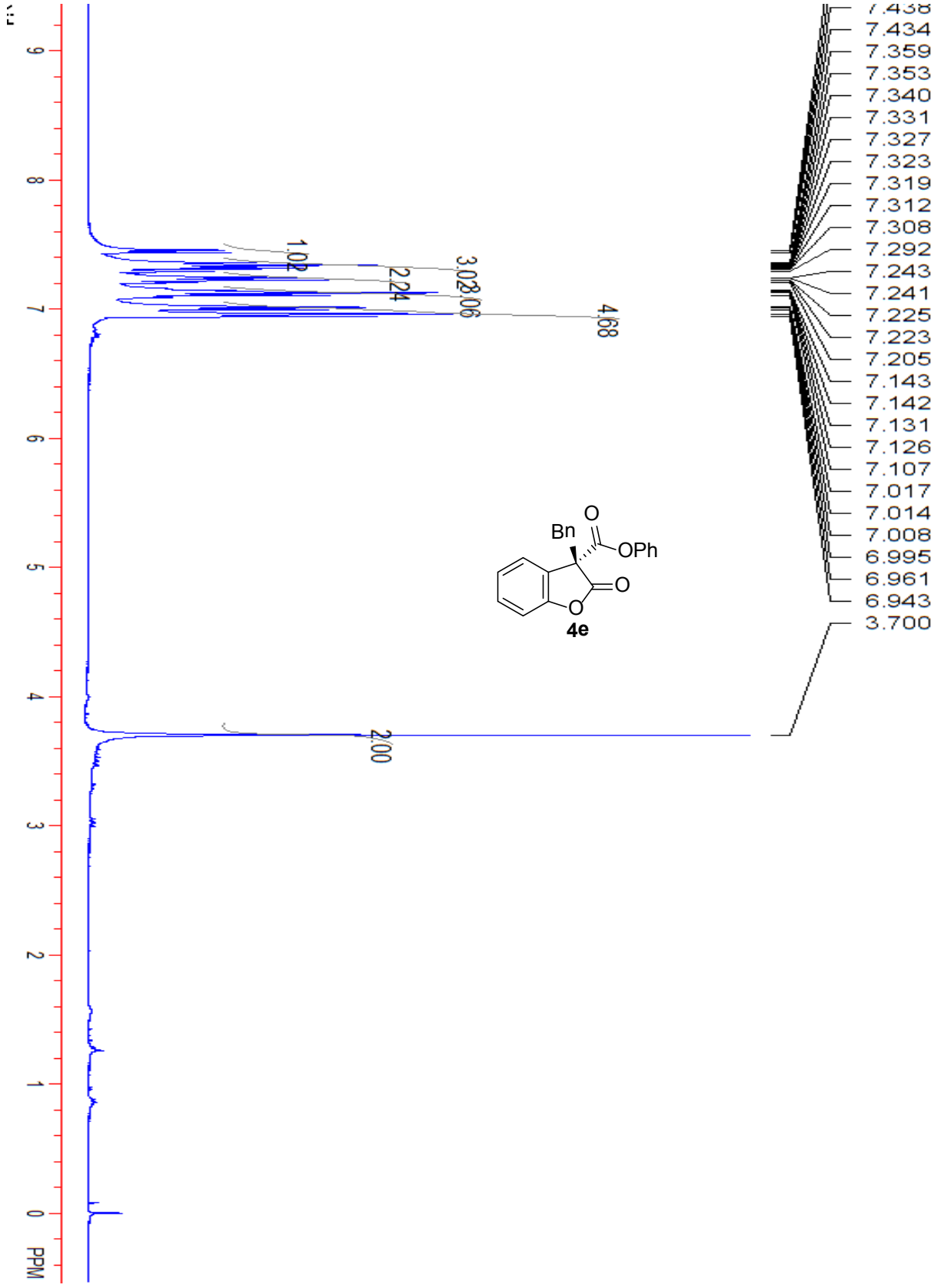
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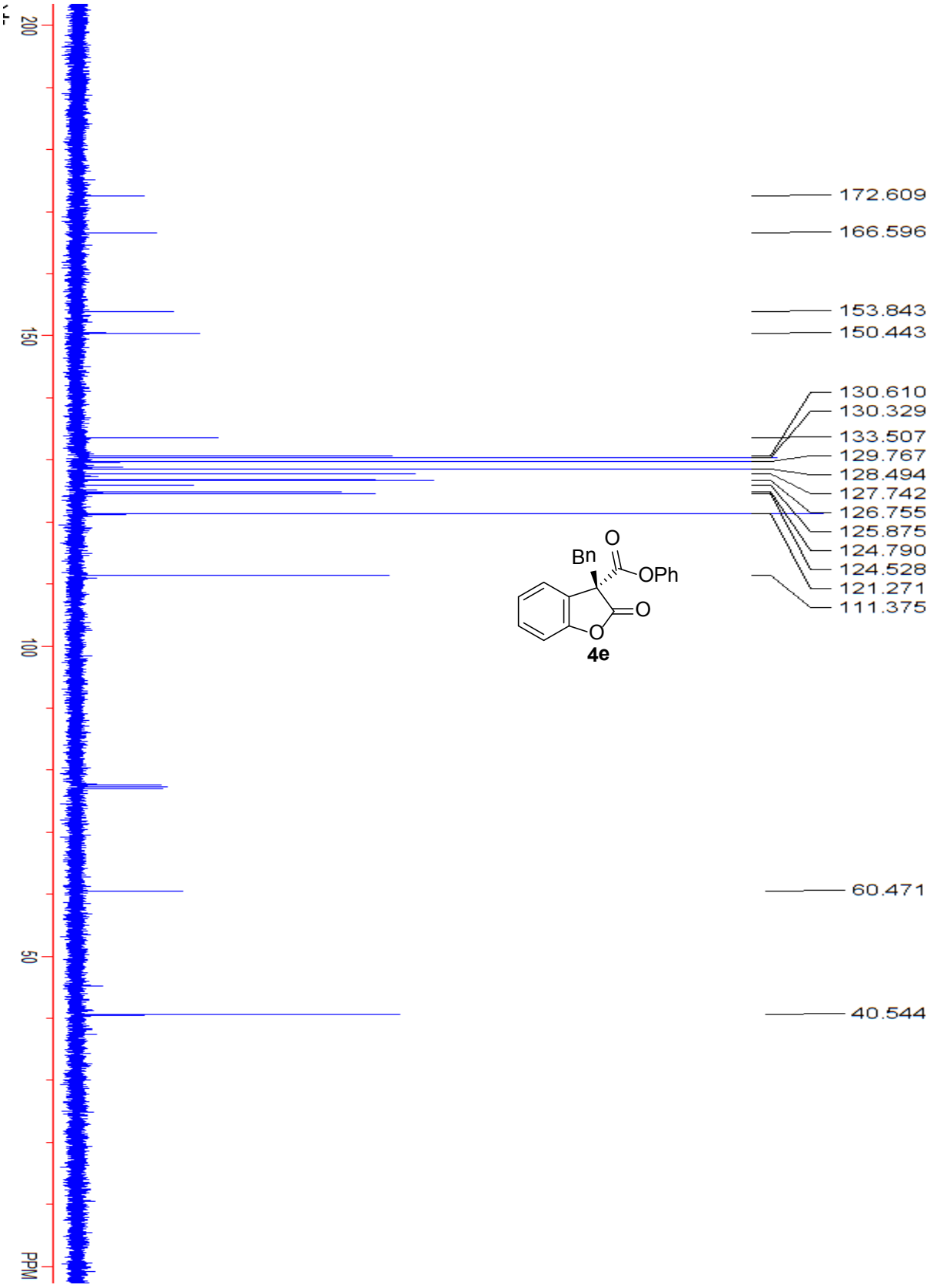
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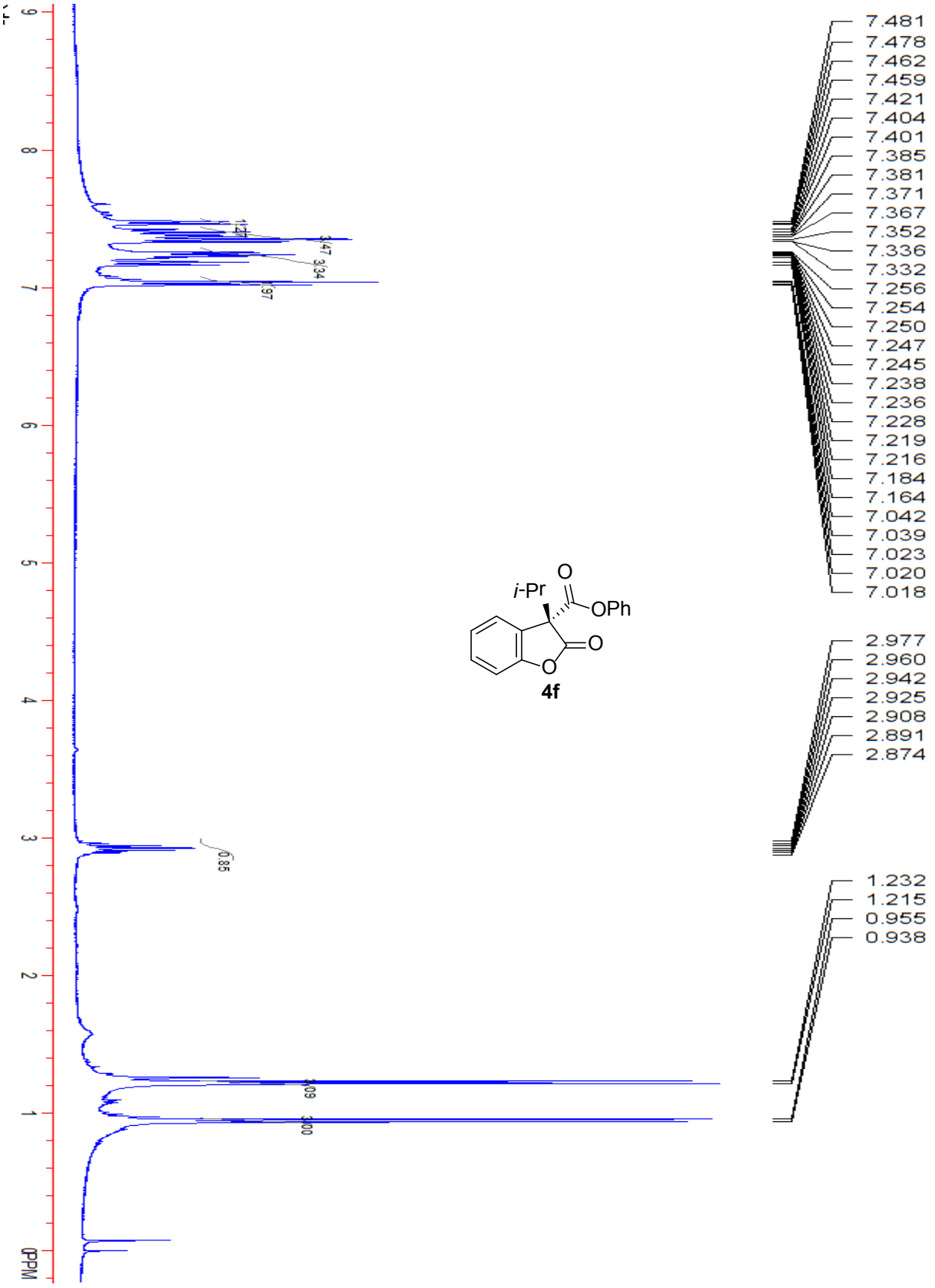
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7.236
7.228
7.219
7.216
7.184
7.164
7.042
7.039
7.023
7.020
7.018
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2.942
2.925
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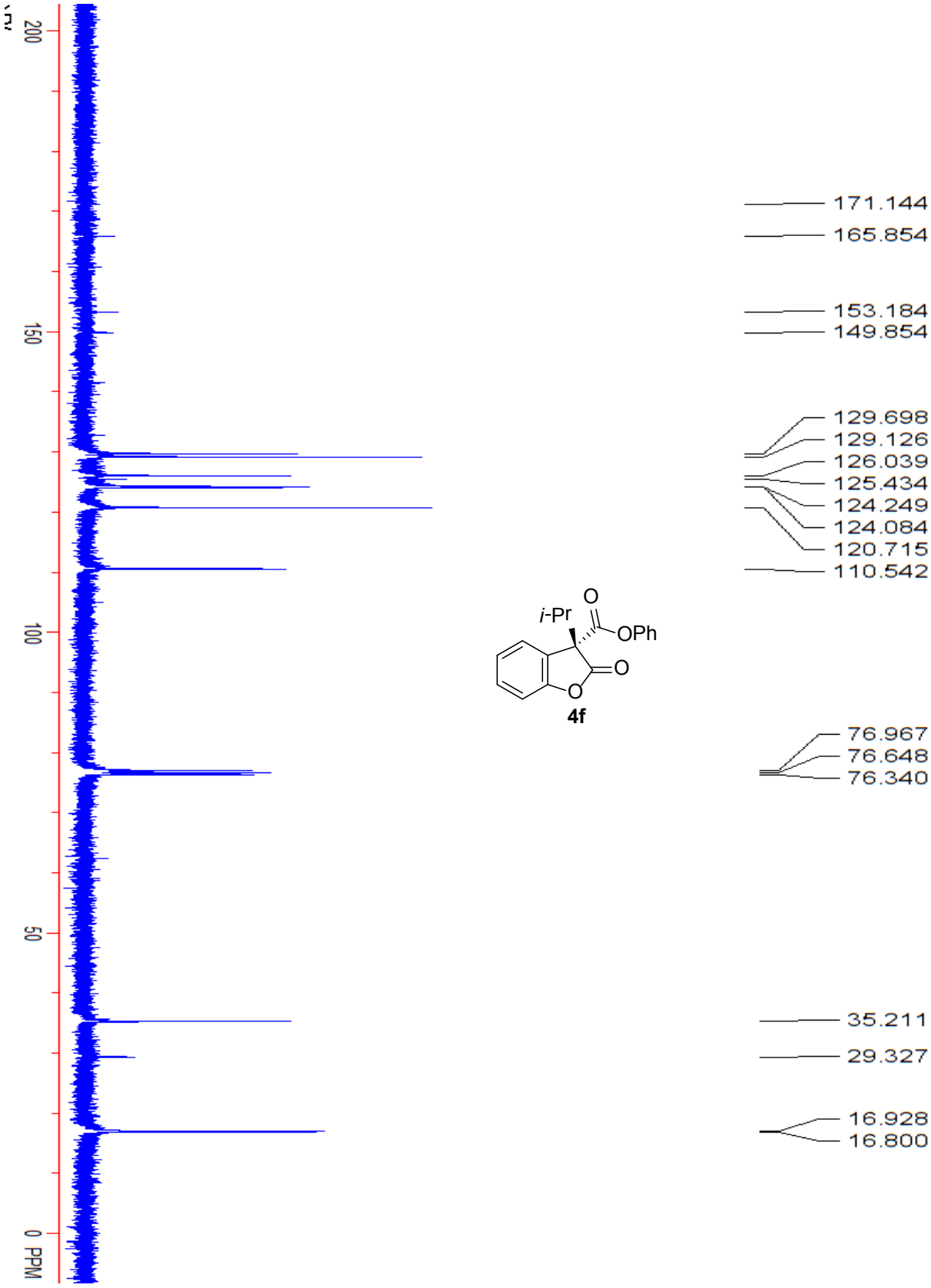
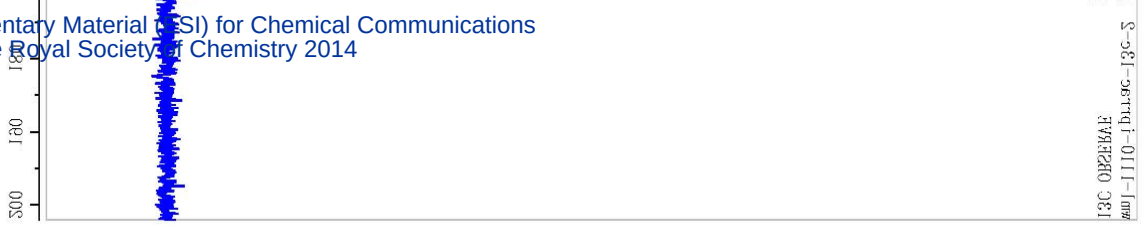
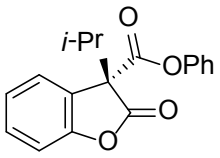
O
4f
PPM



Read by NUTS software.





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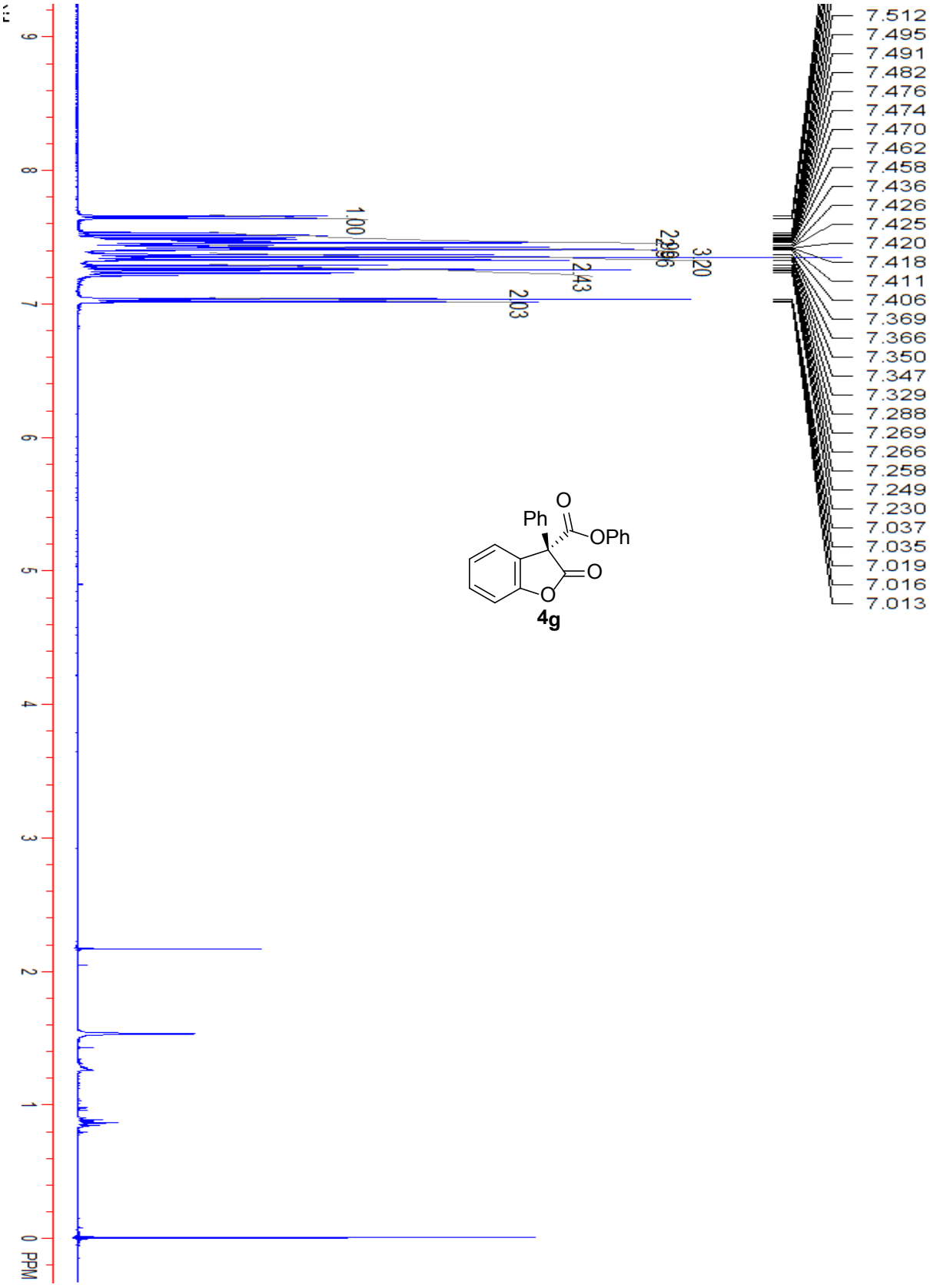
Read by MestReNova software.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7.266
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7.249
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7.035
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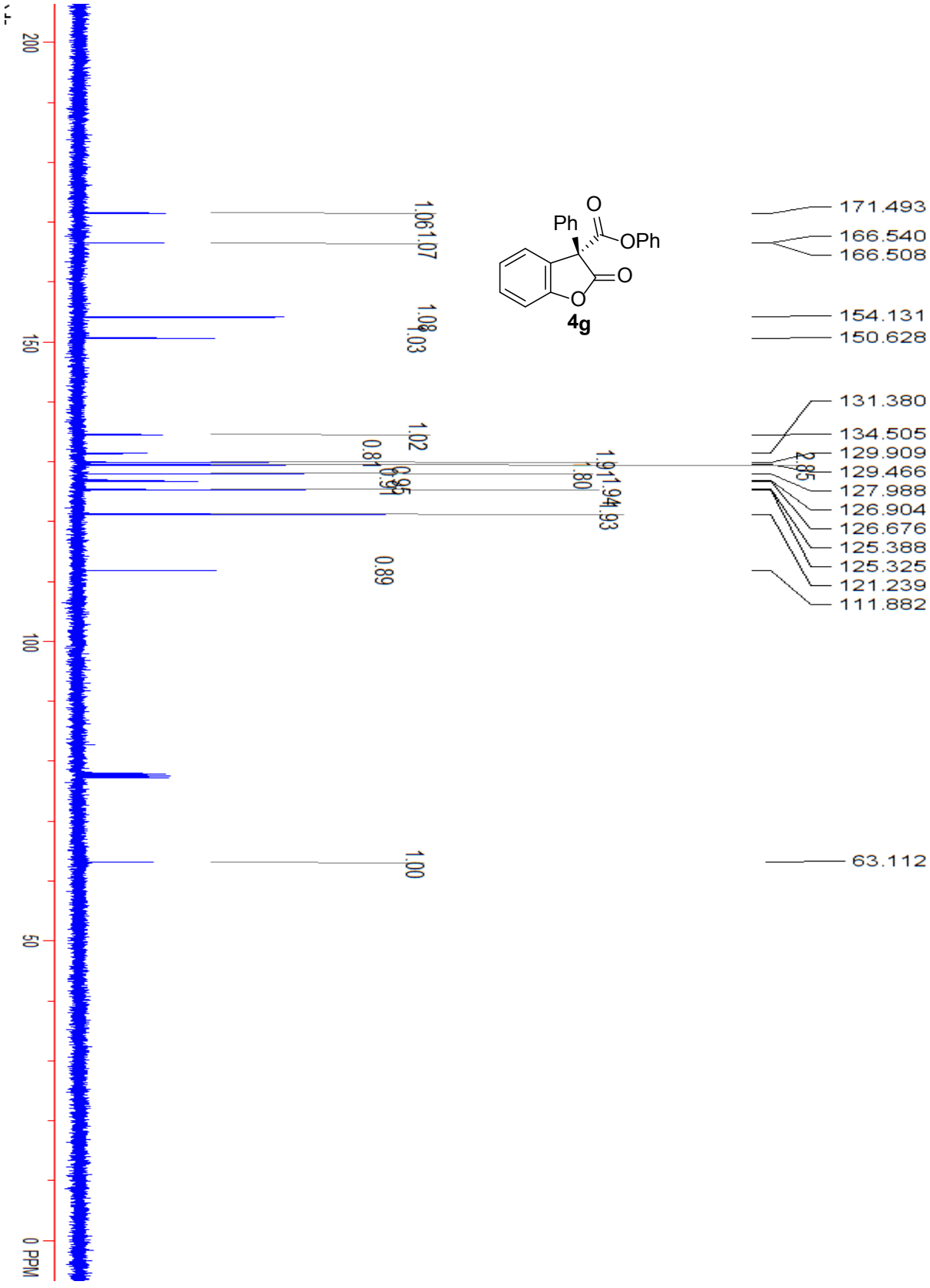
4g
PPM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1.91
1.94
1.93
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OPh
O
O
4g
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166.508
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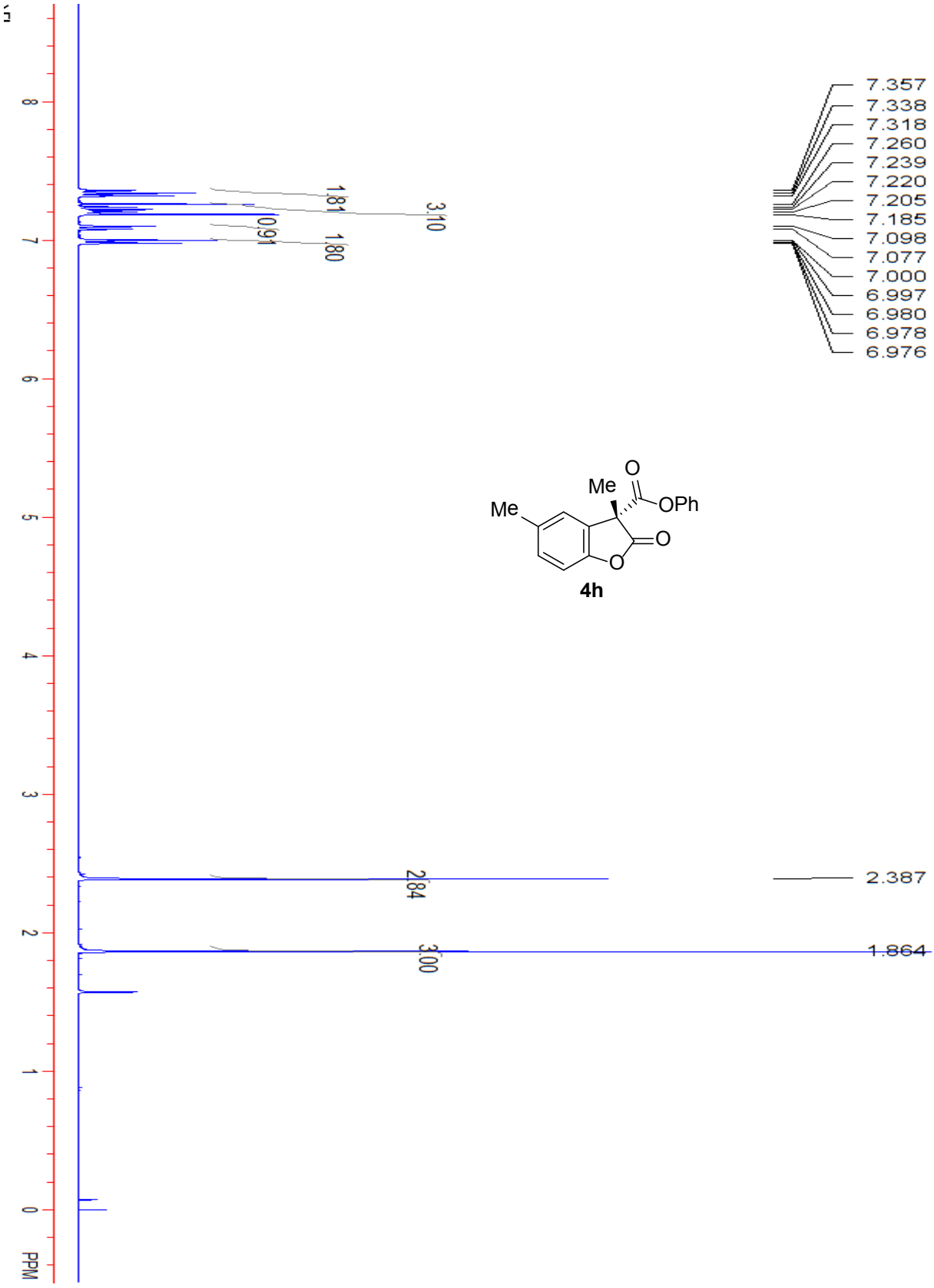
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OPh
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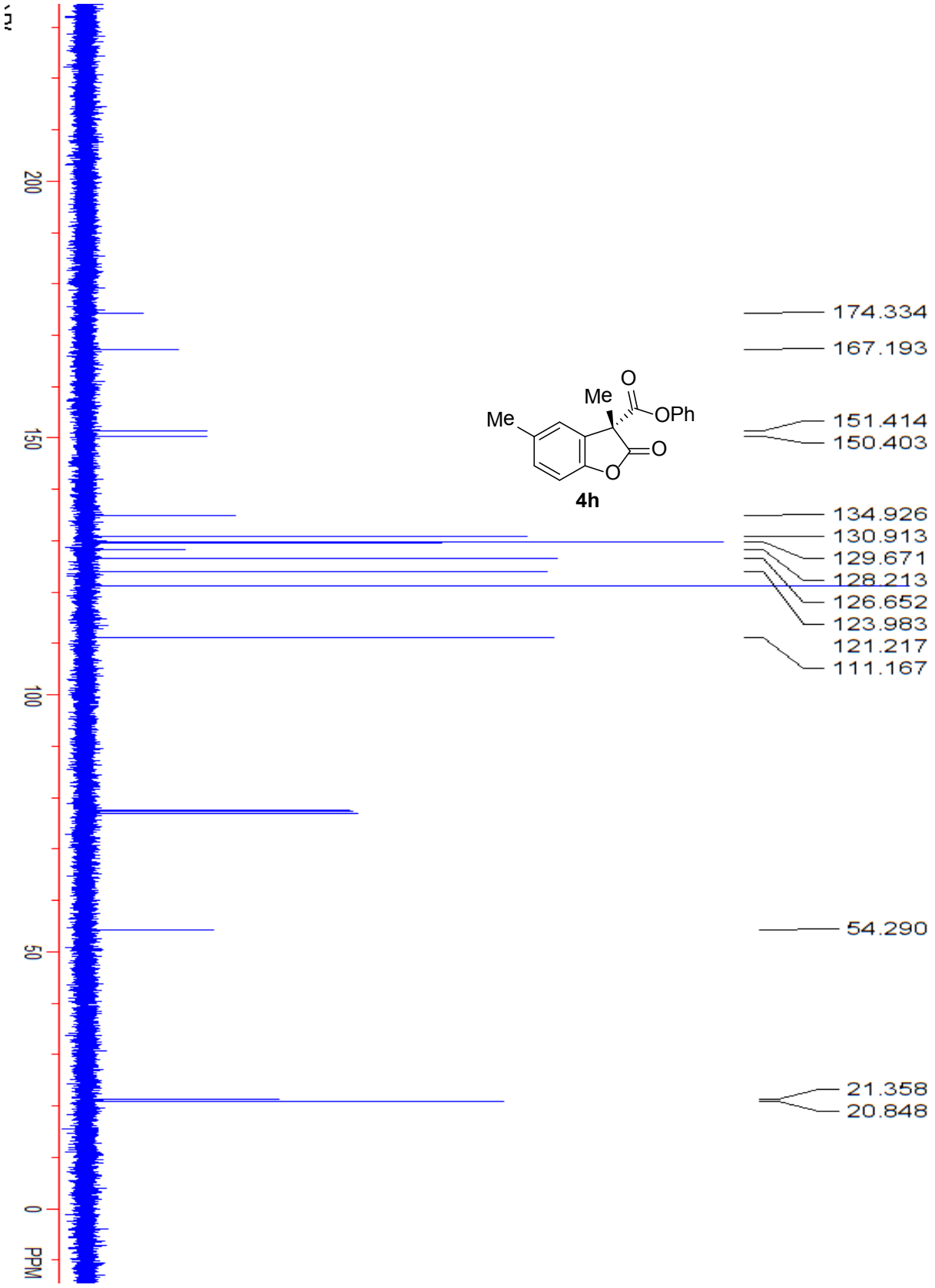
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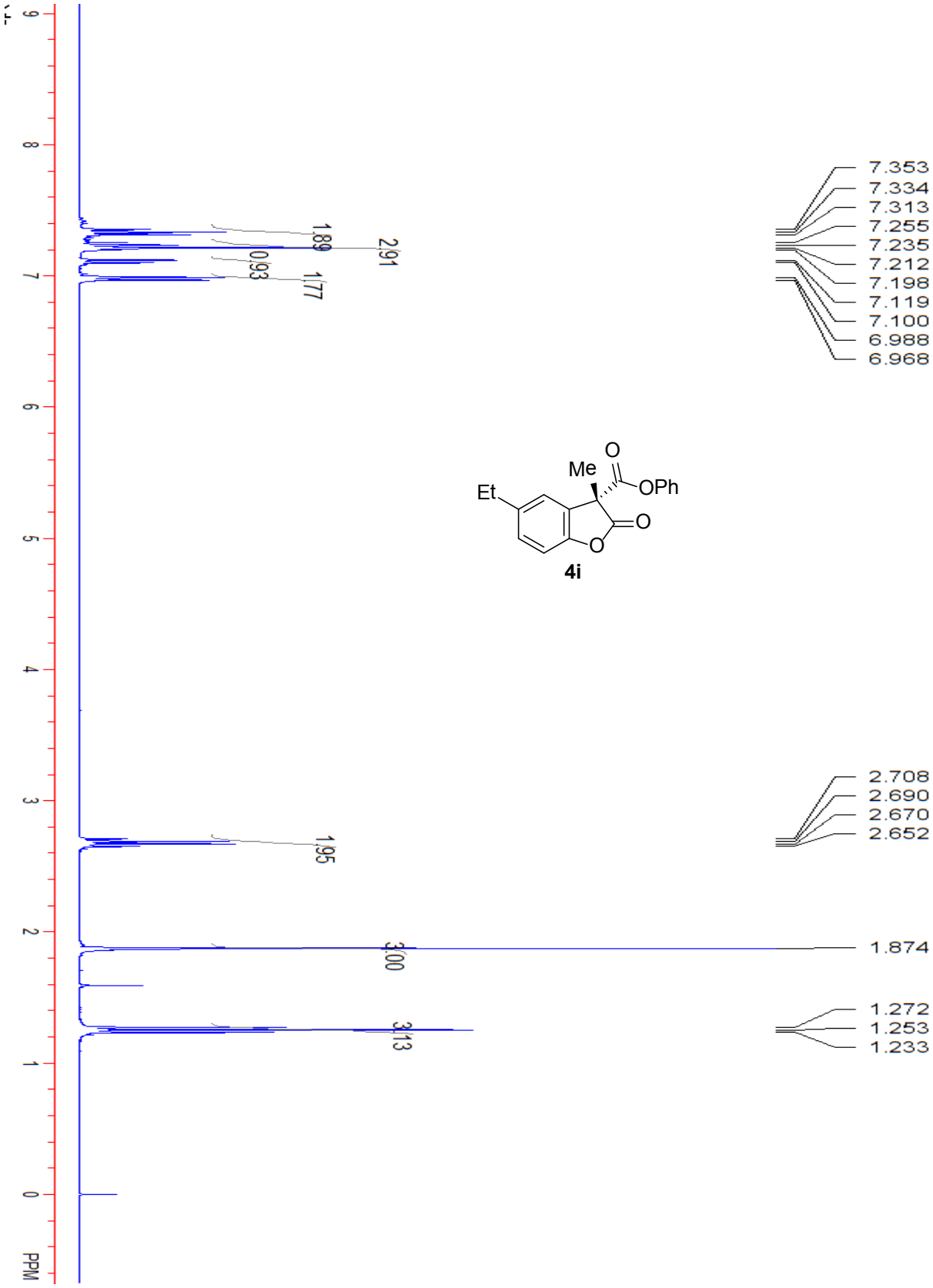
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O
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Et
O
O
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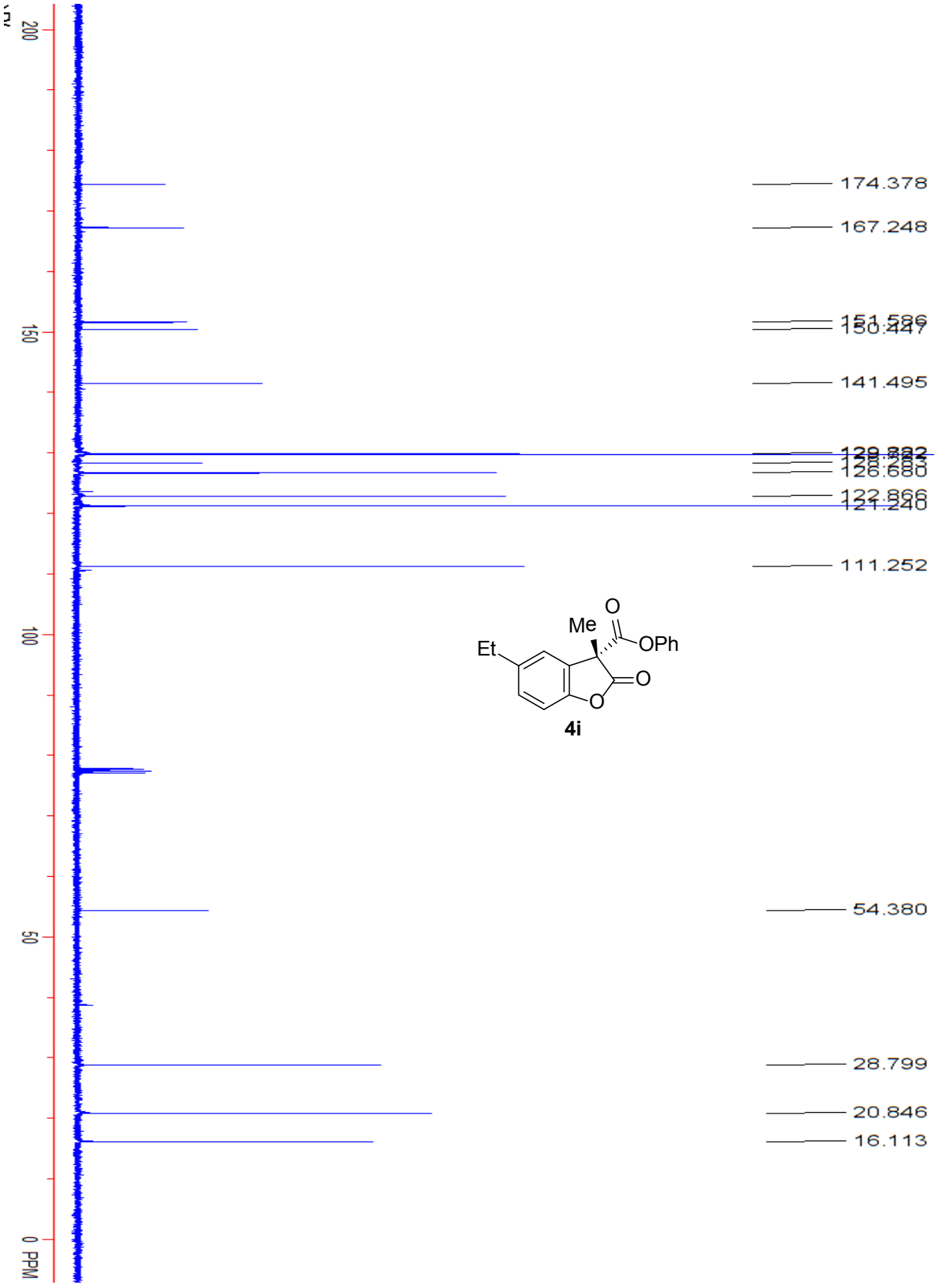
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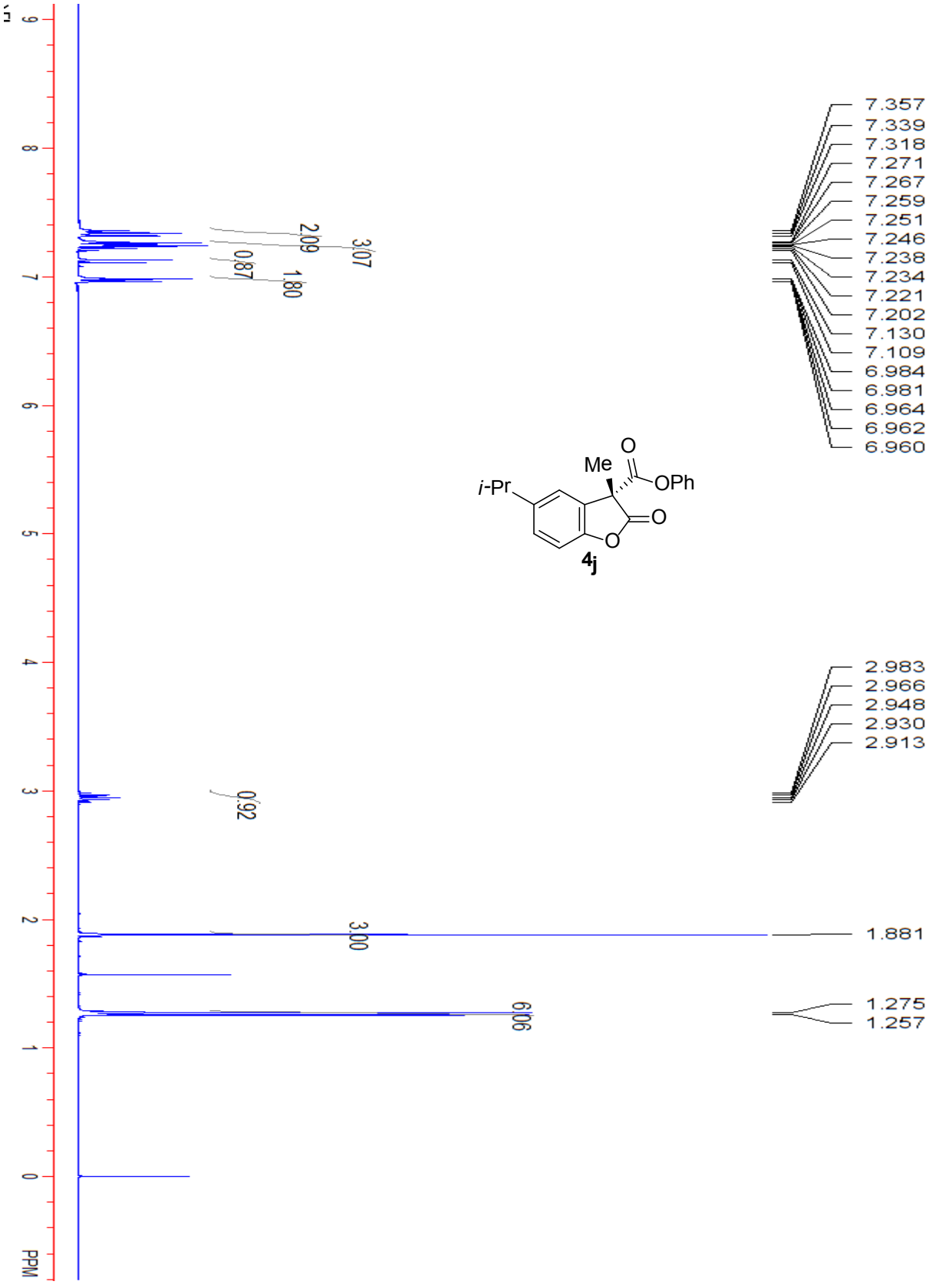
O
O

4i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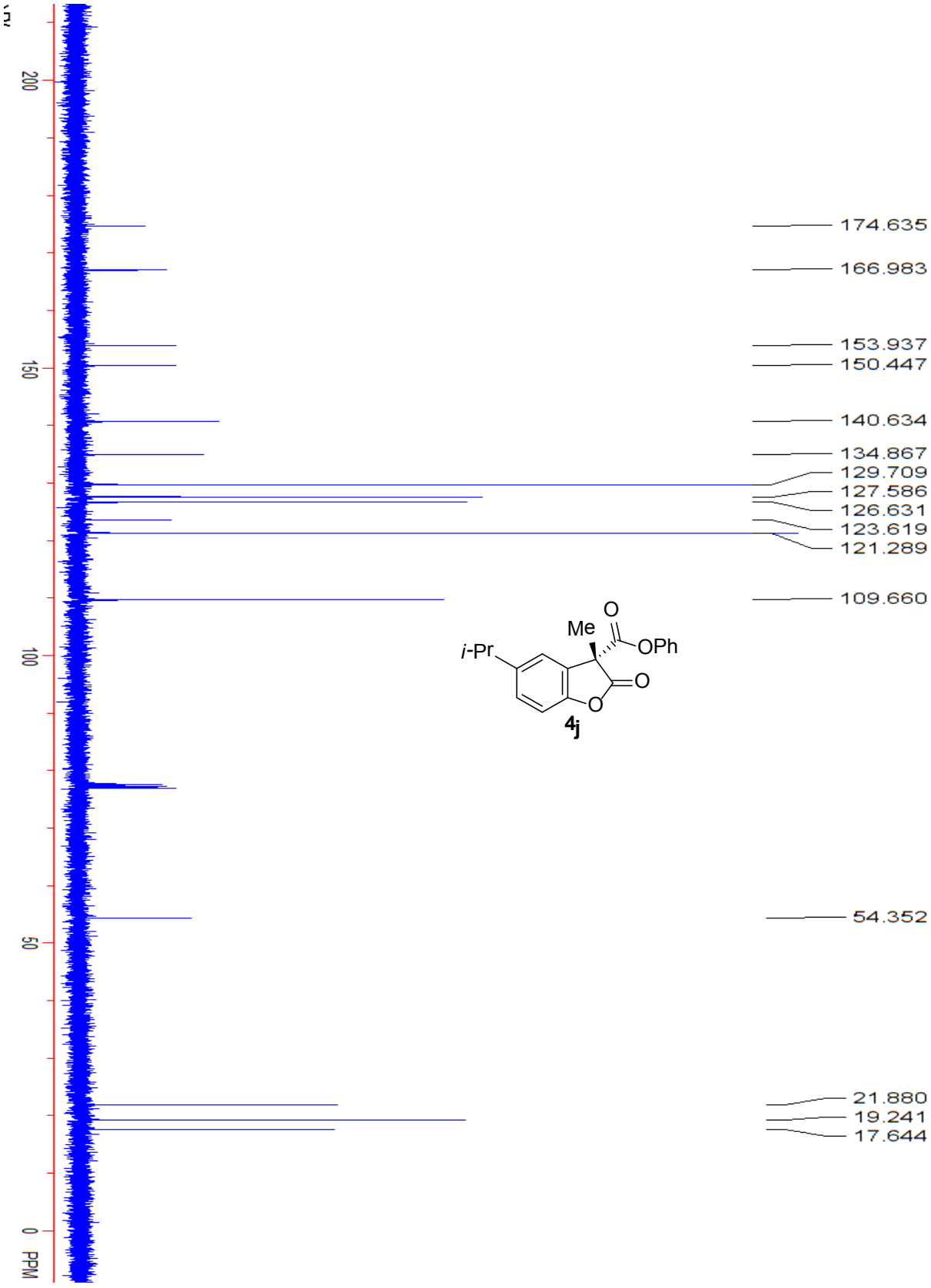
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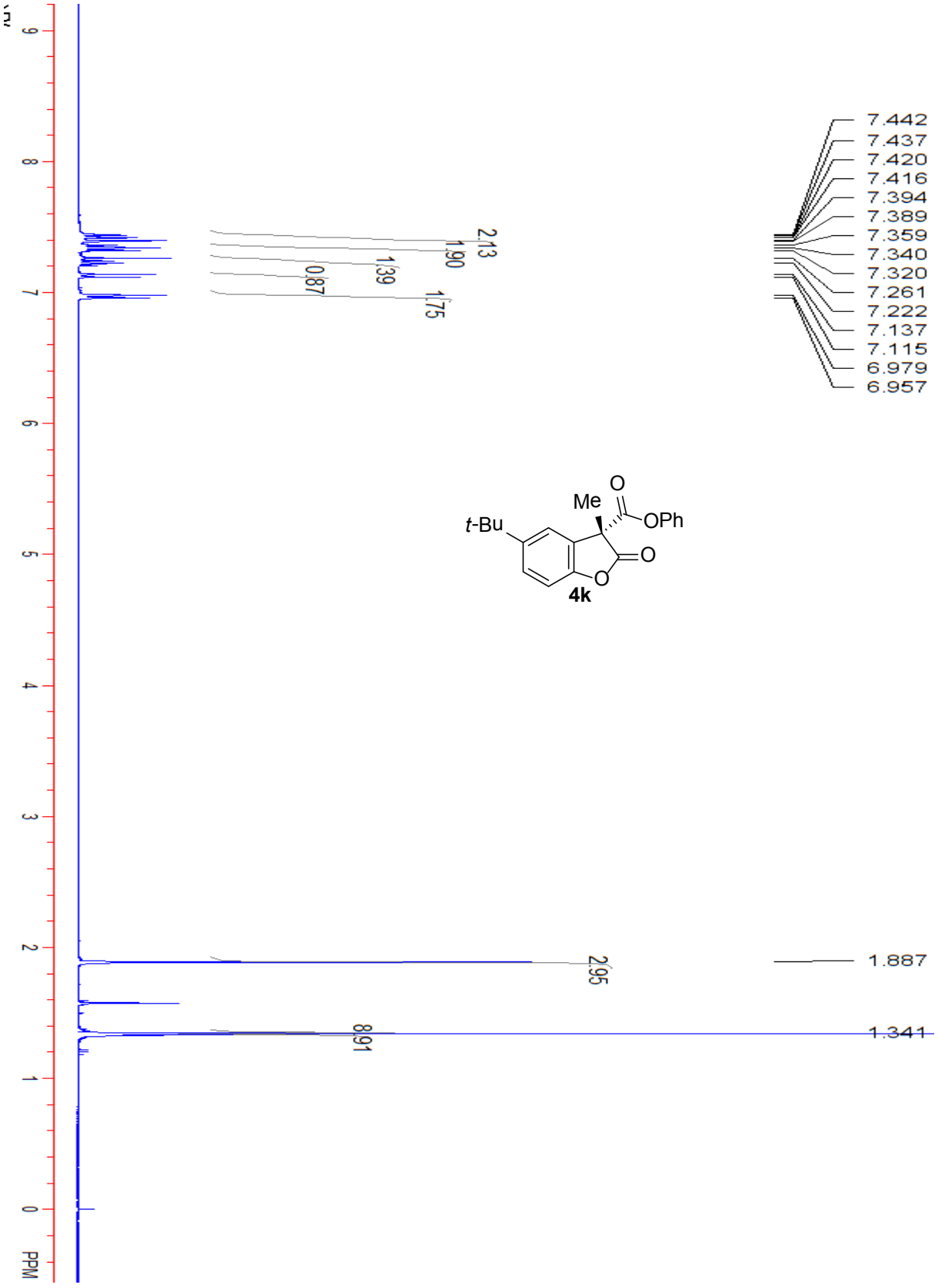
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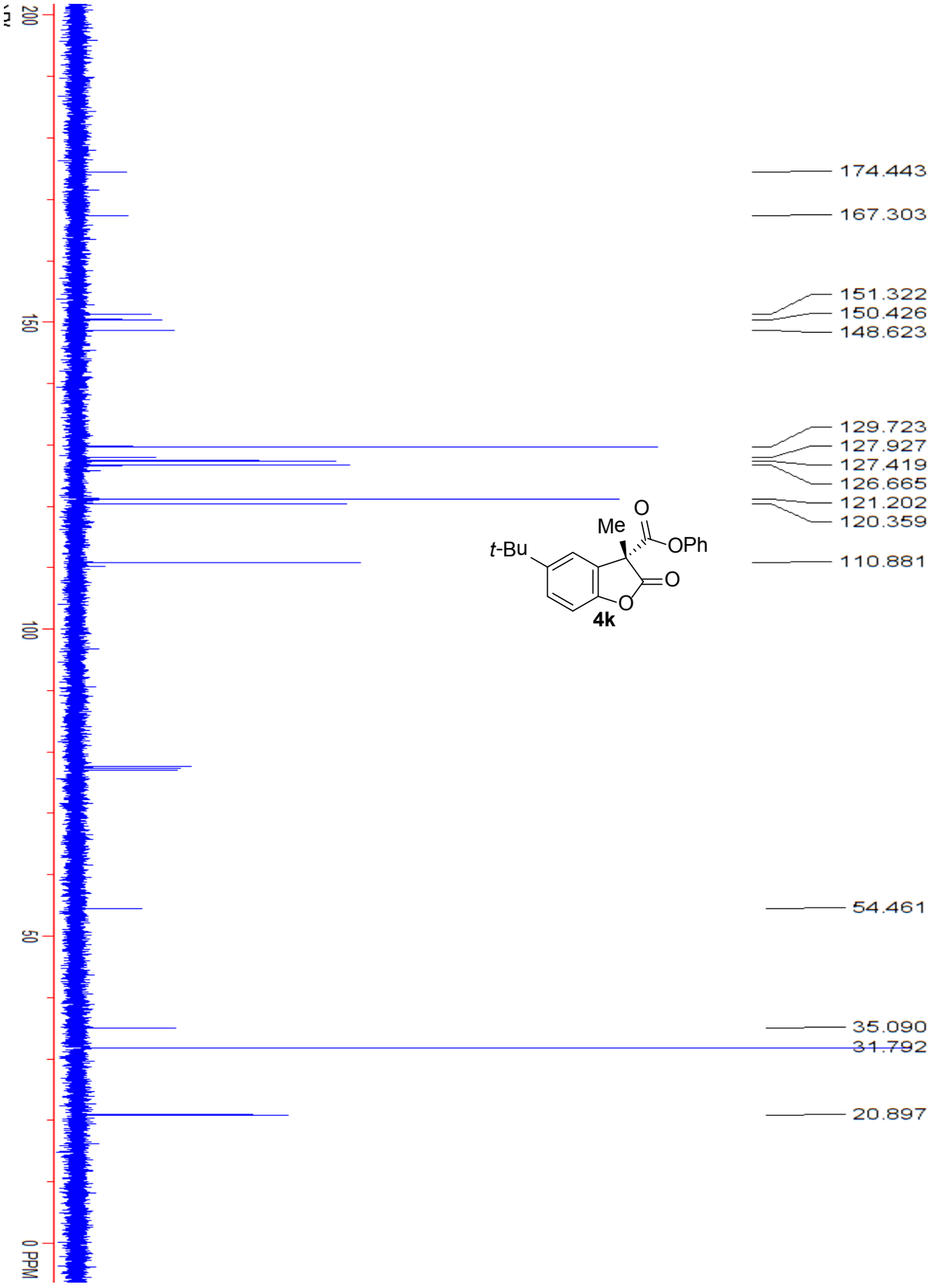
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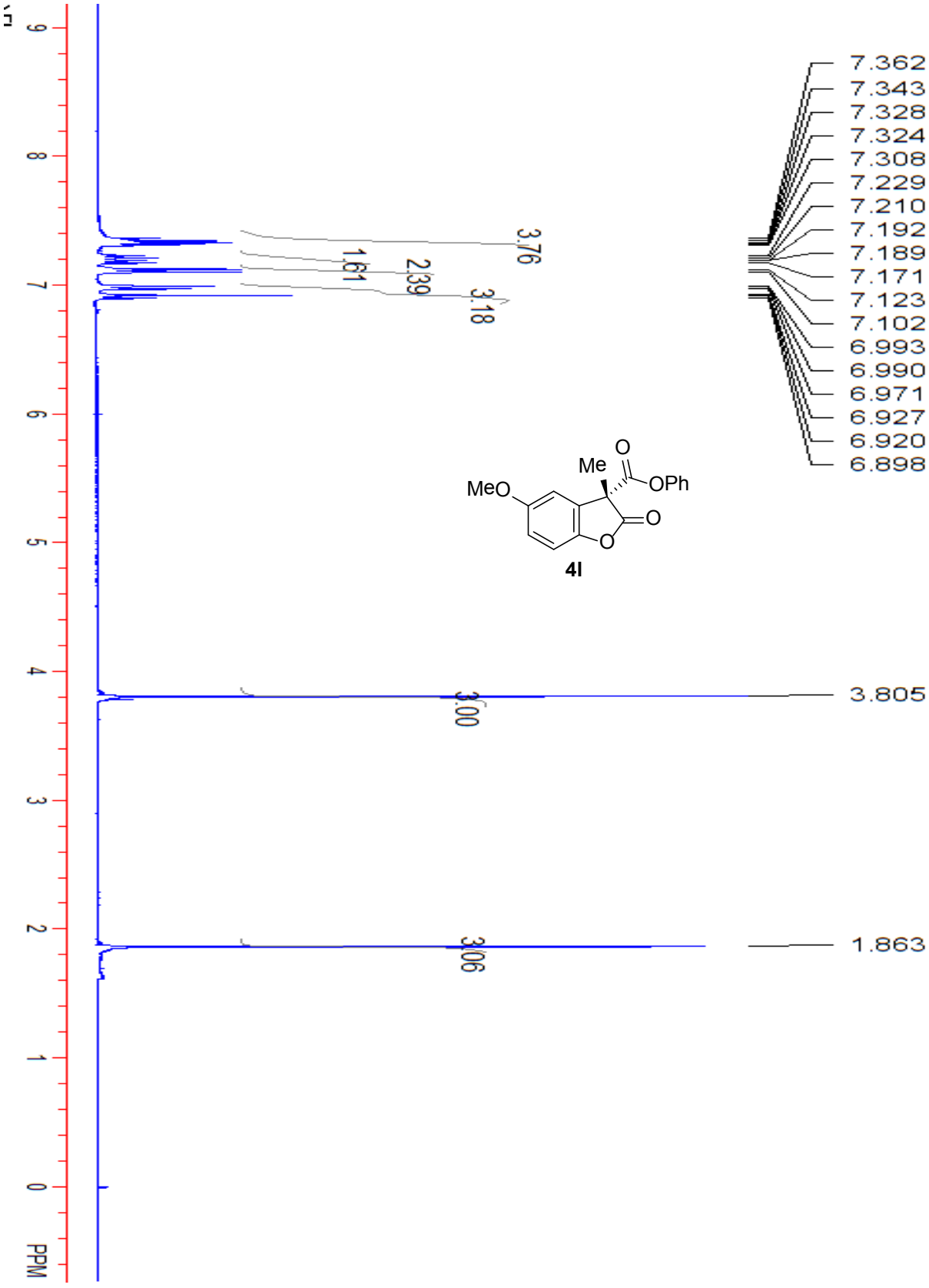
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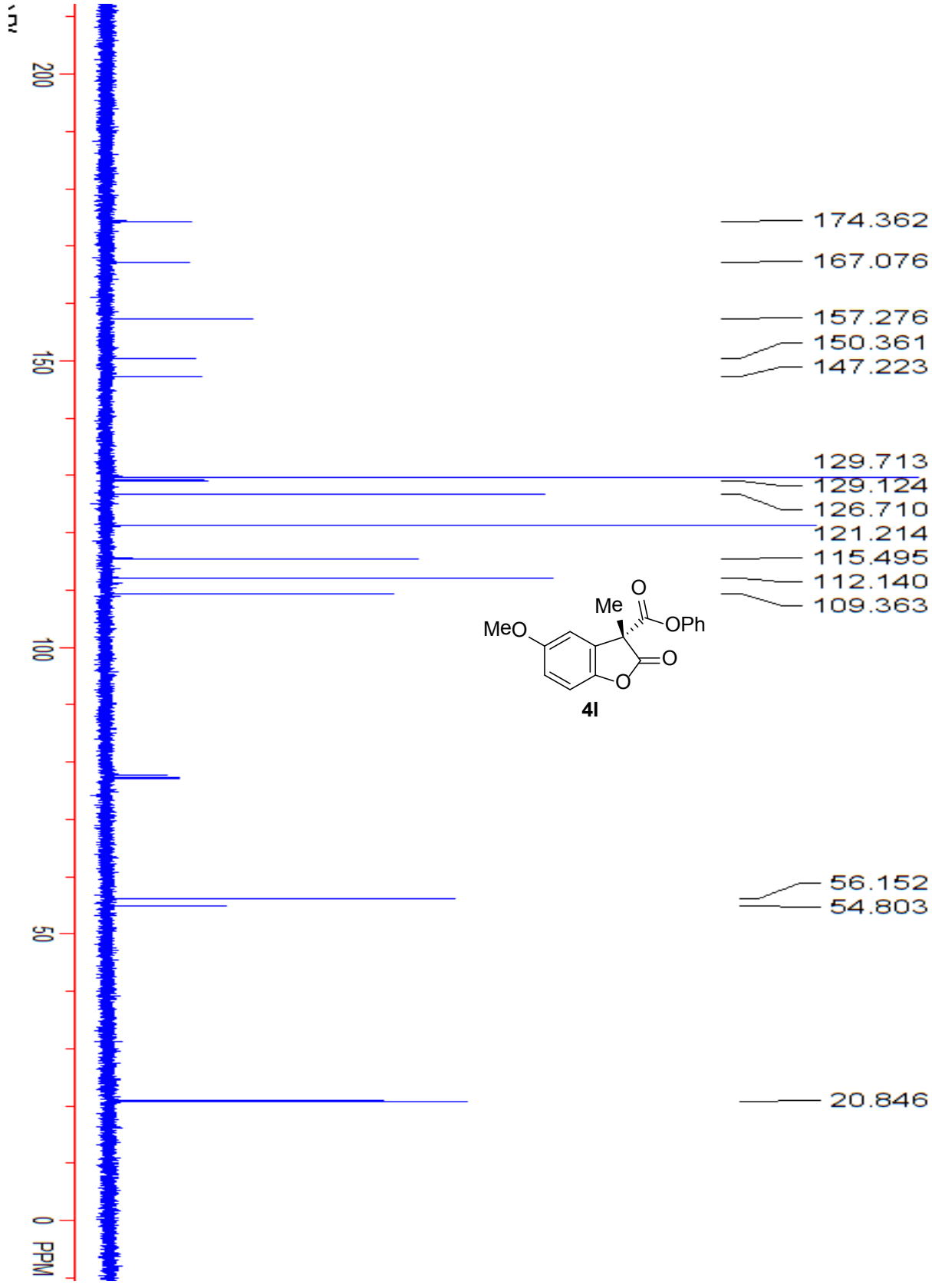

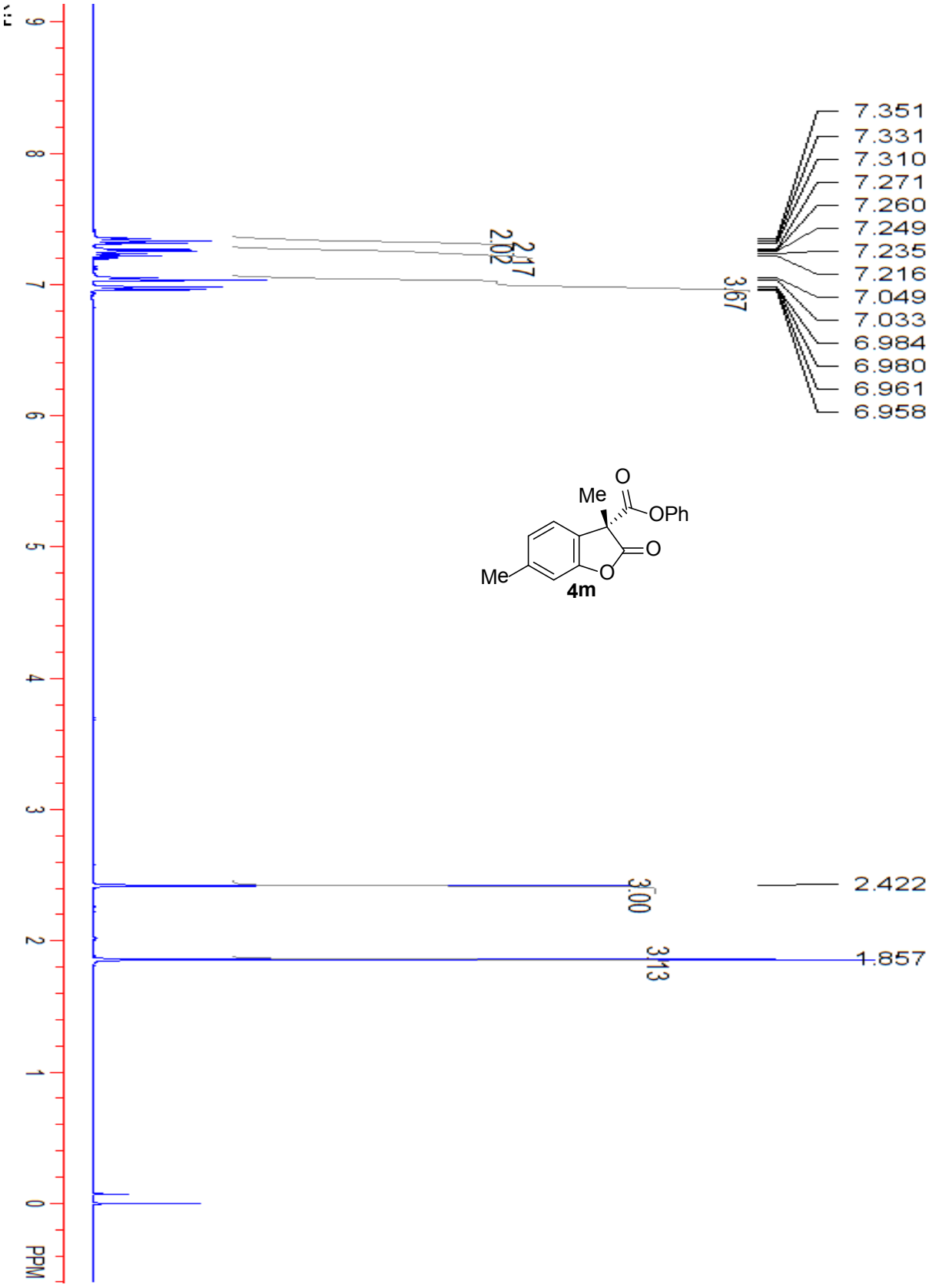
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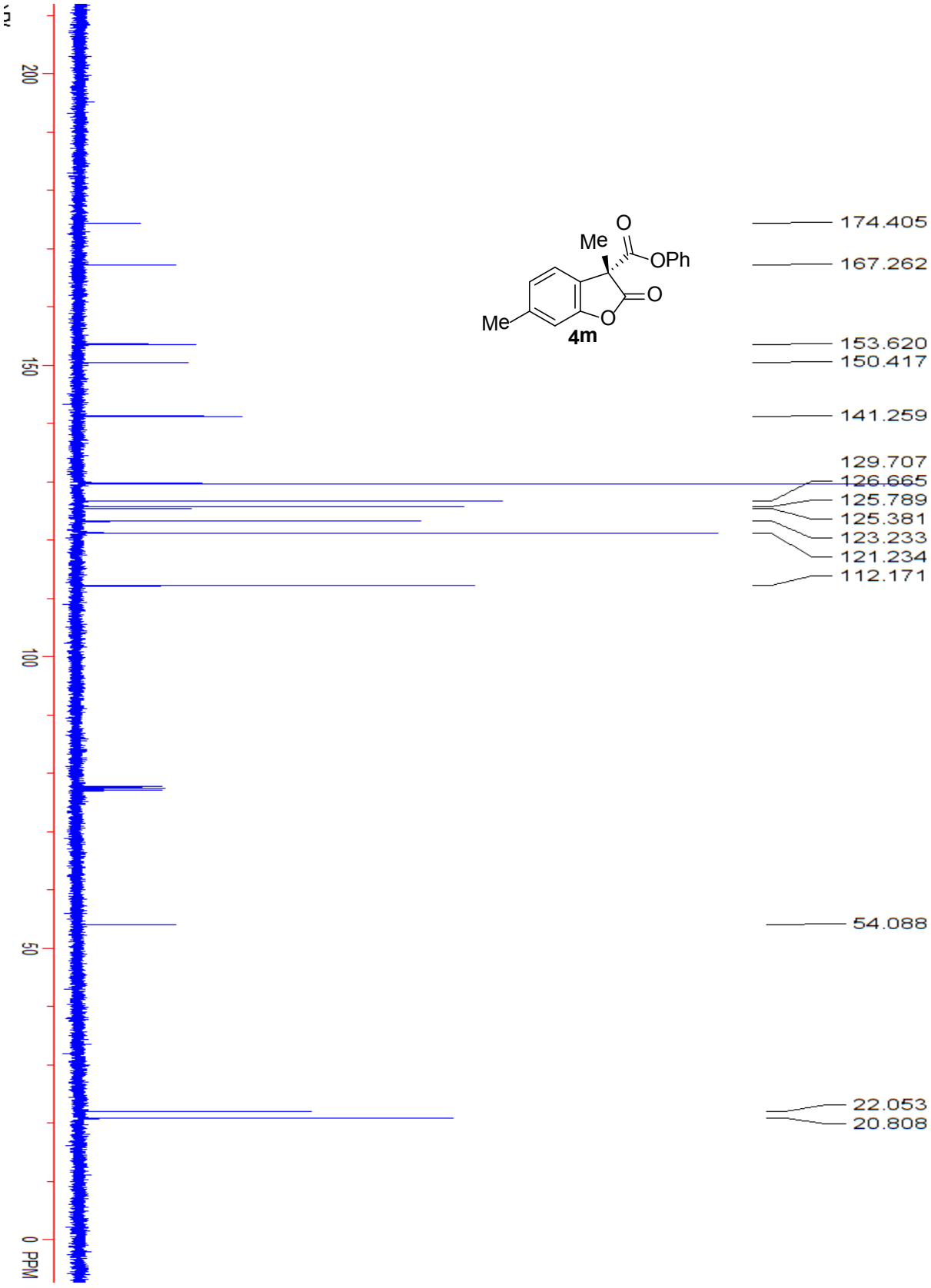

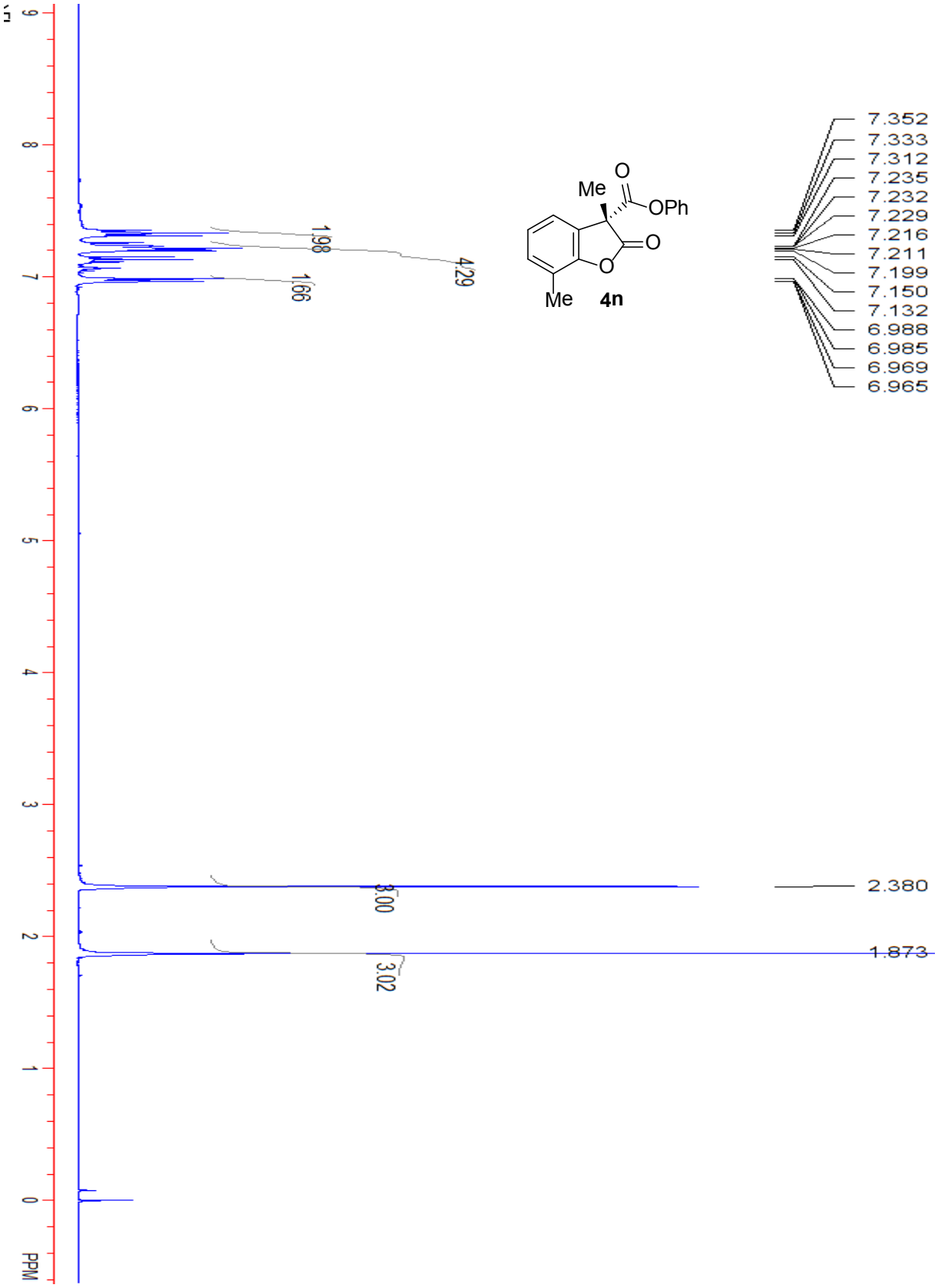
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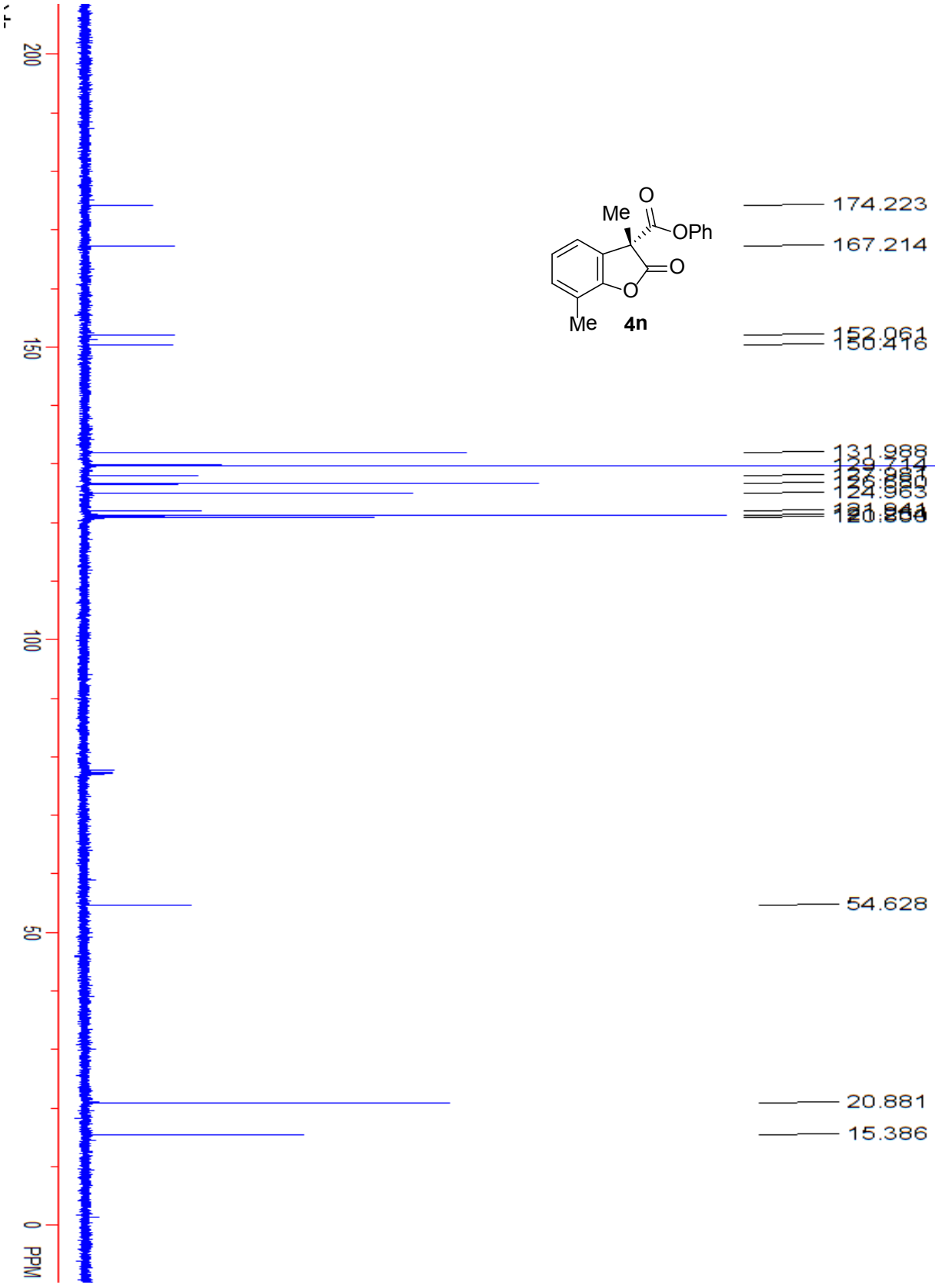
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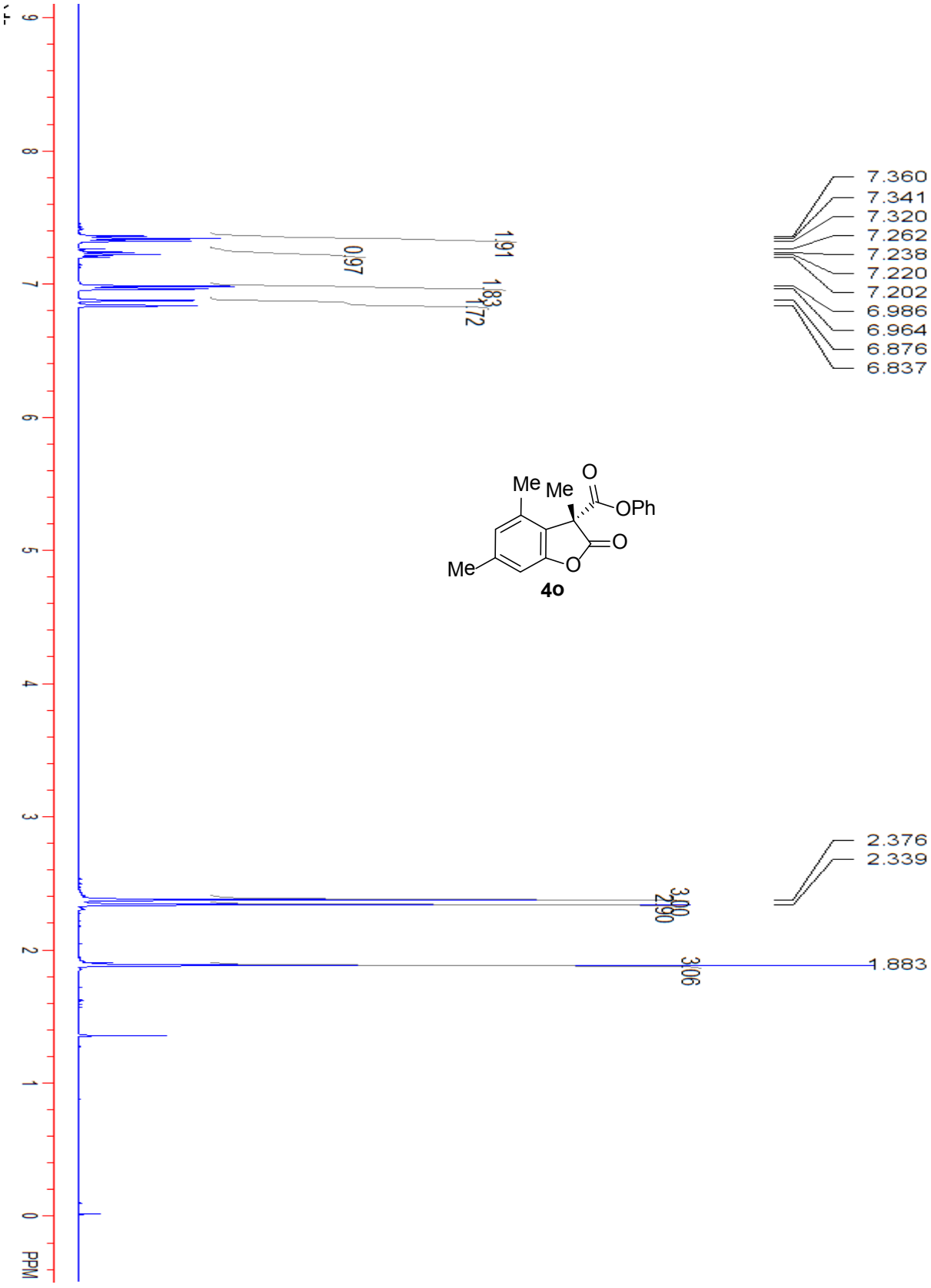
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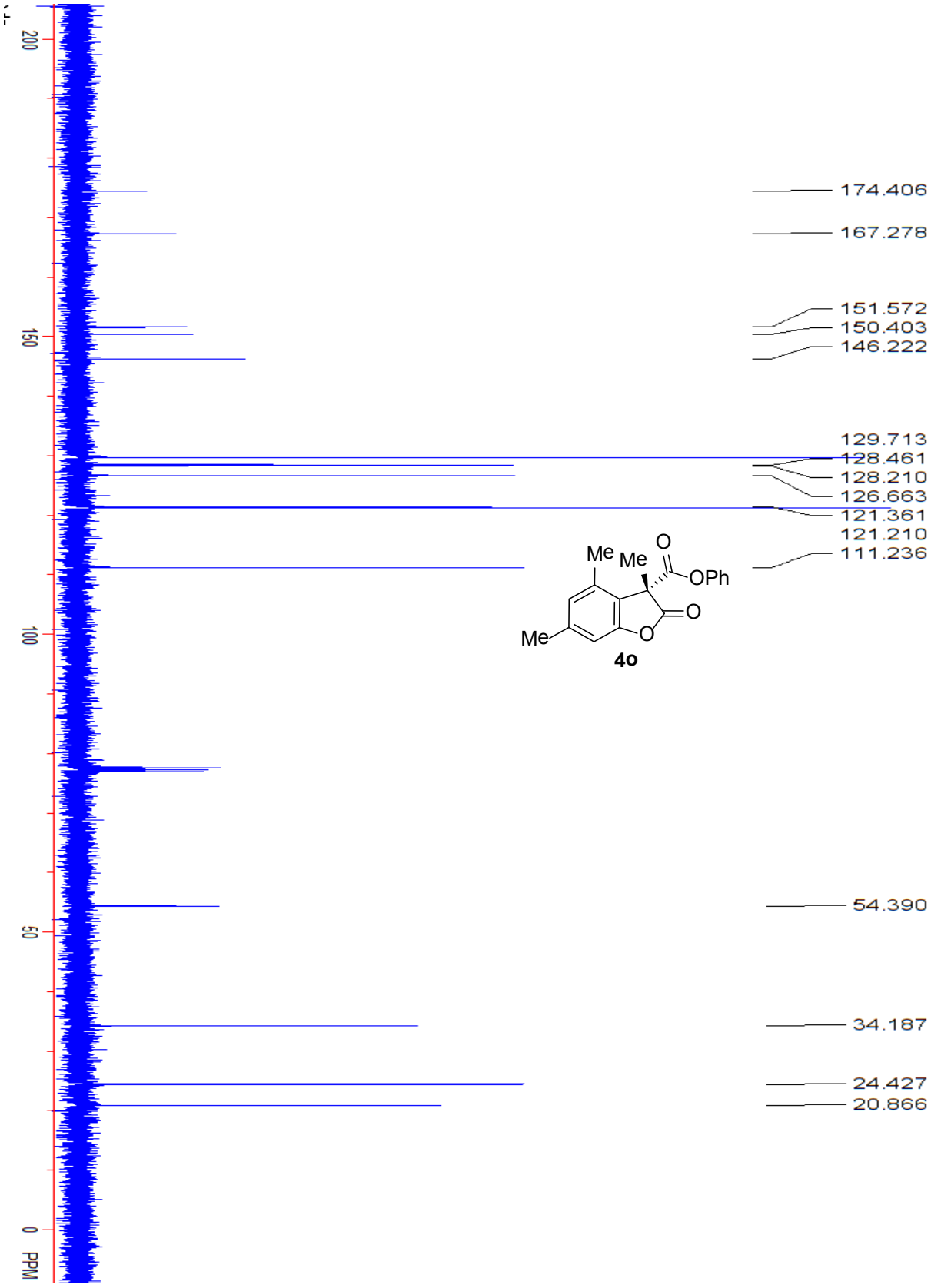

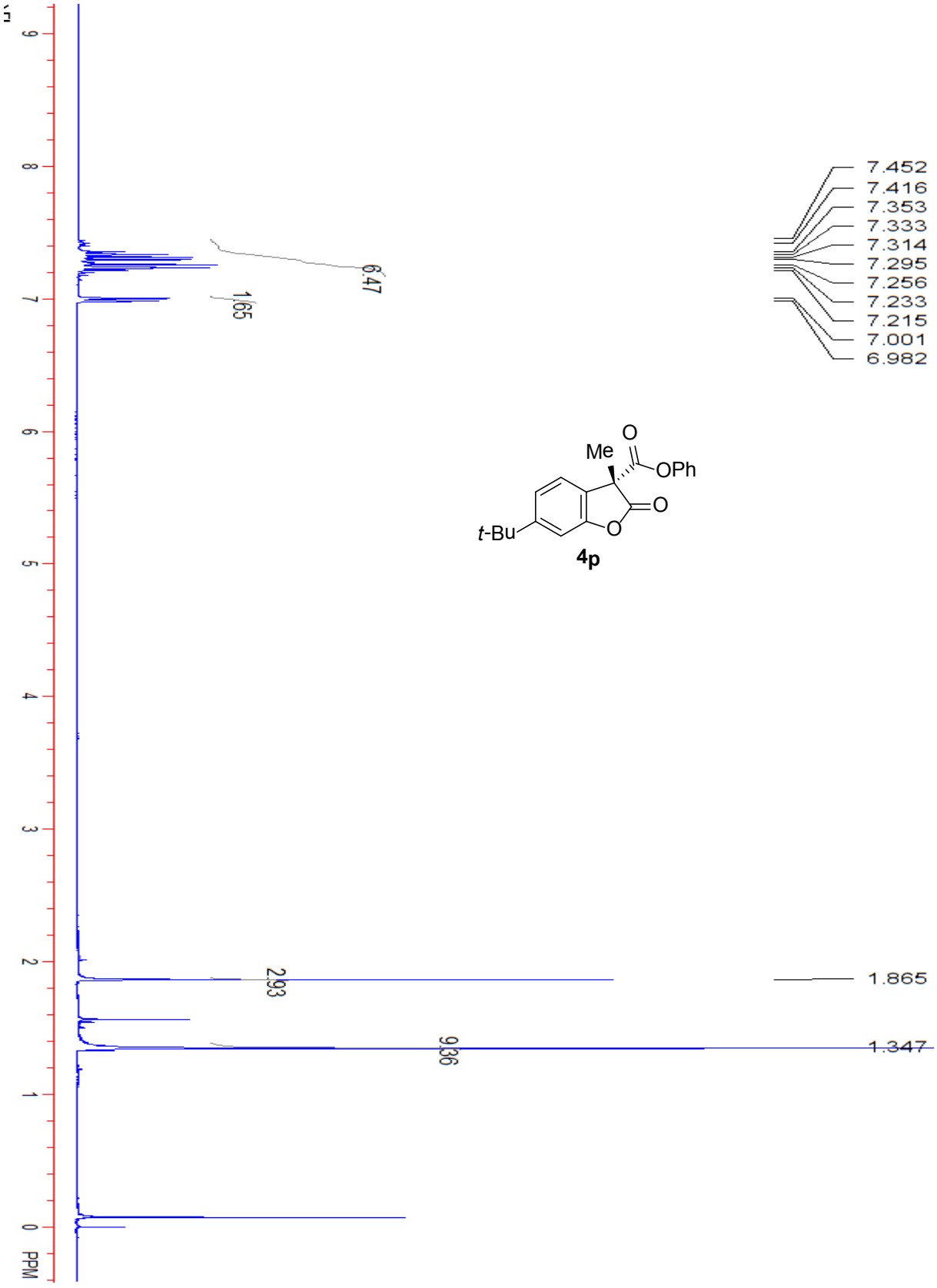
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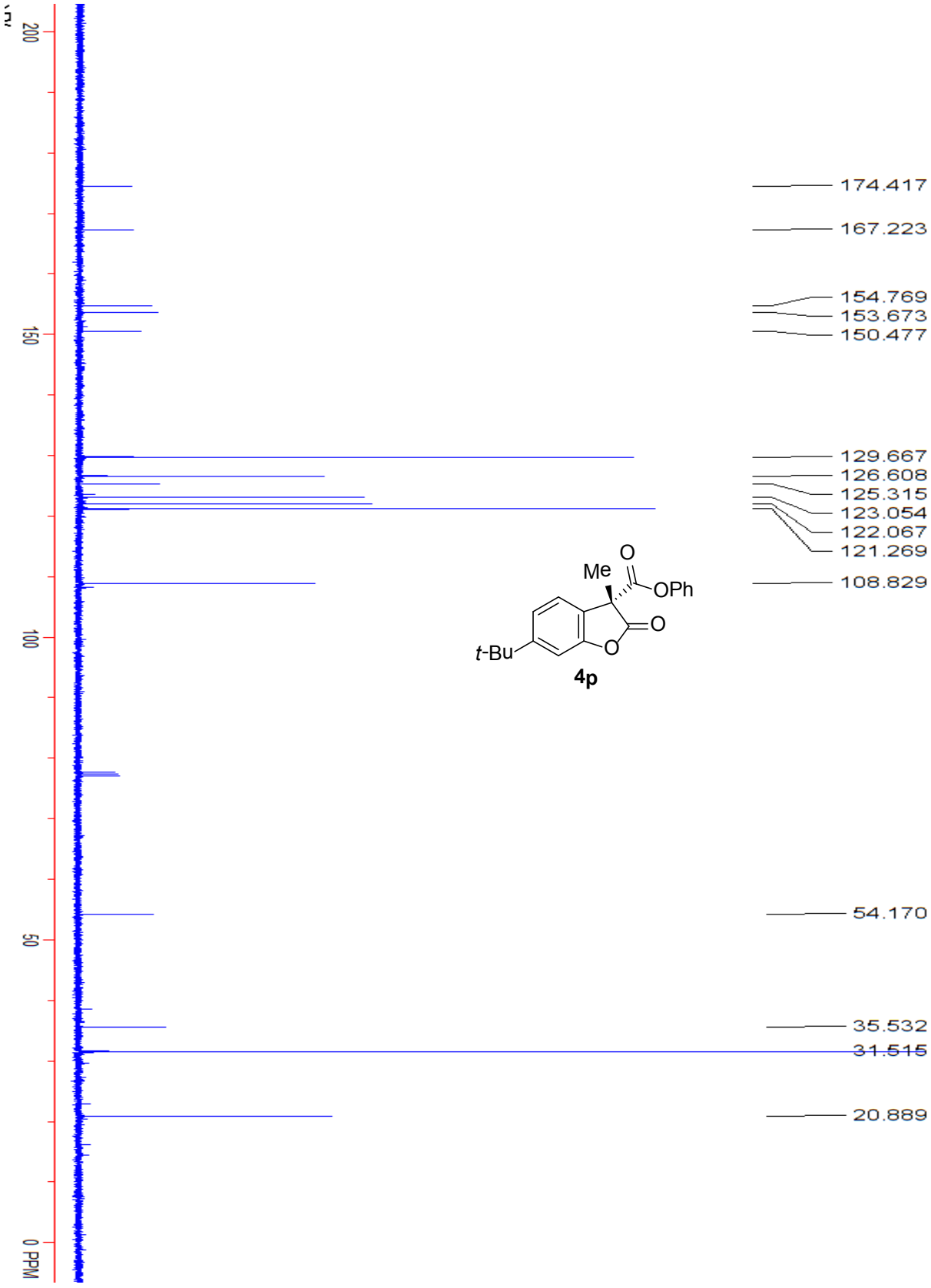

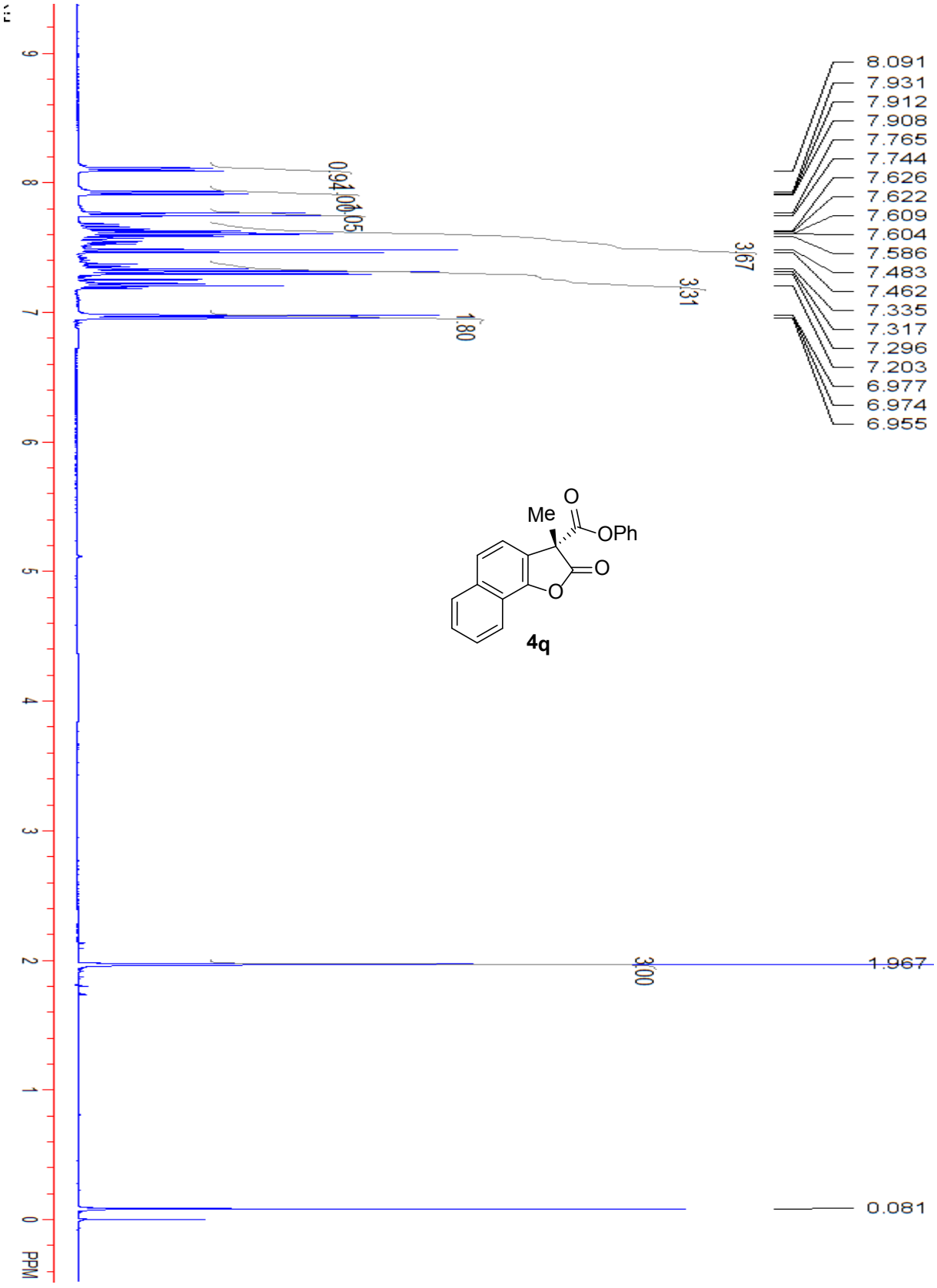
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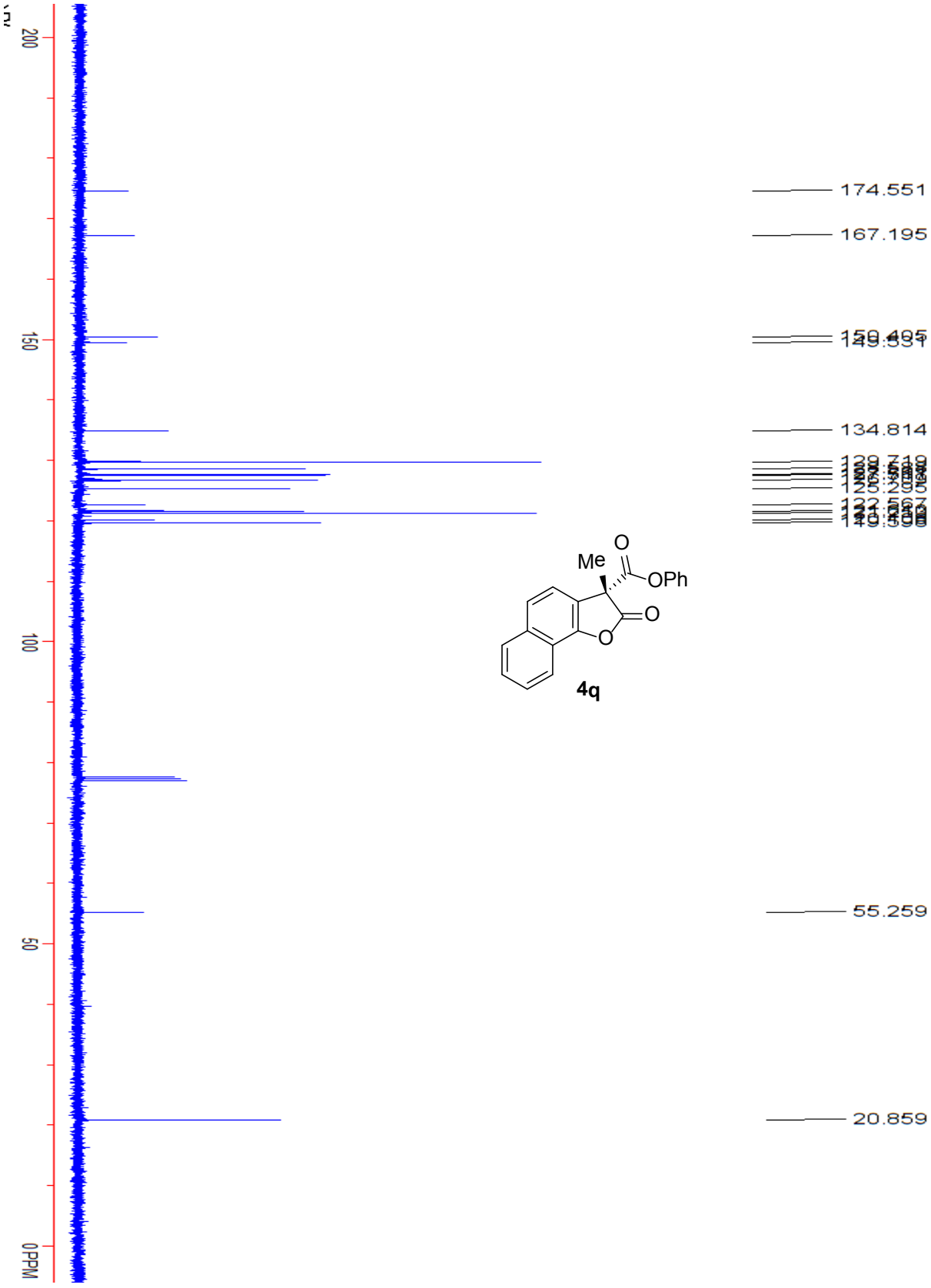
4q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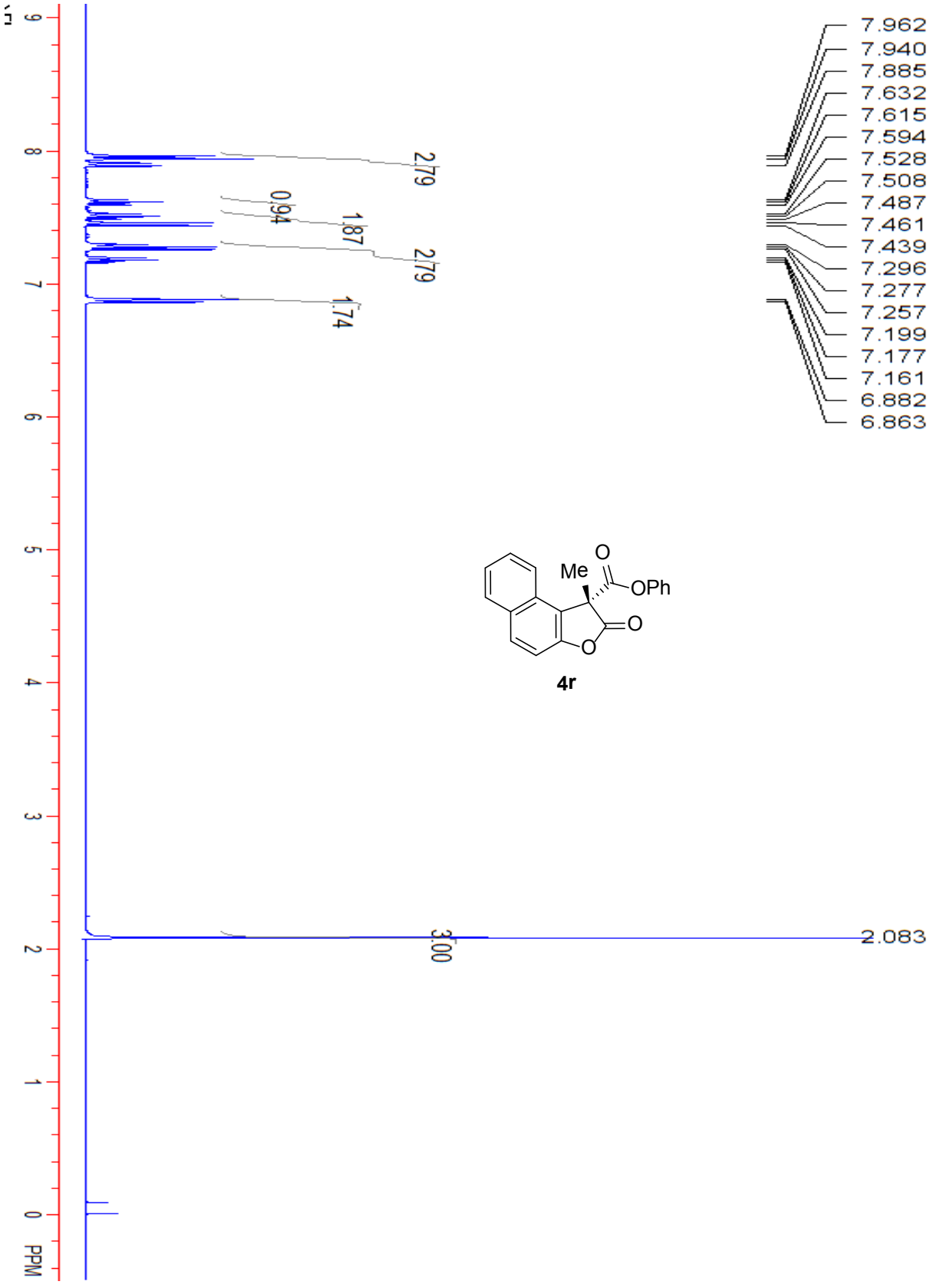
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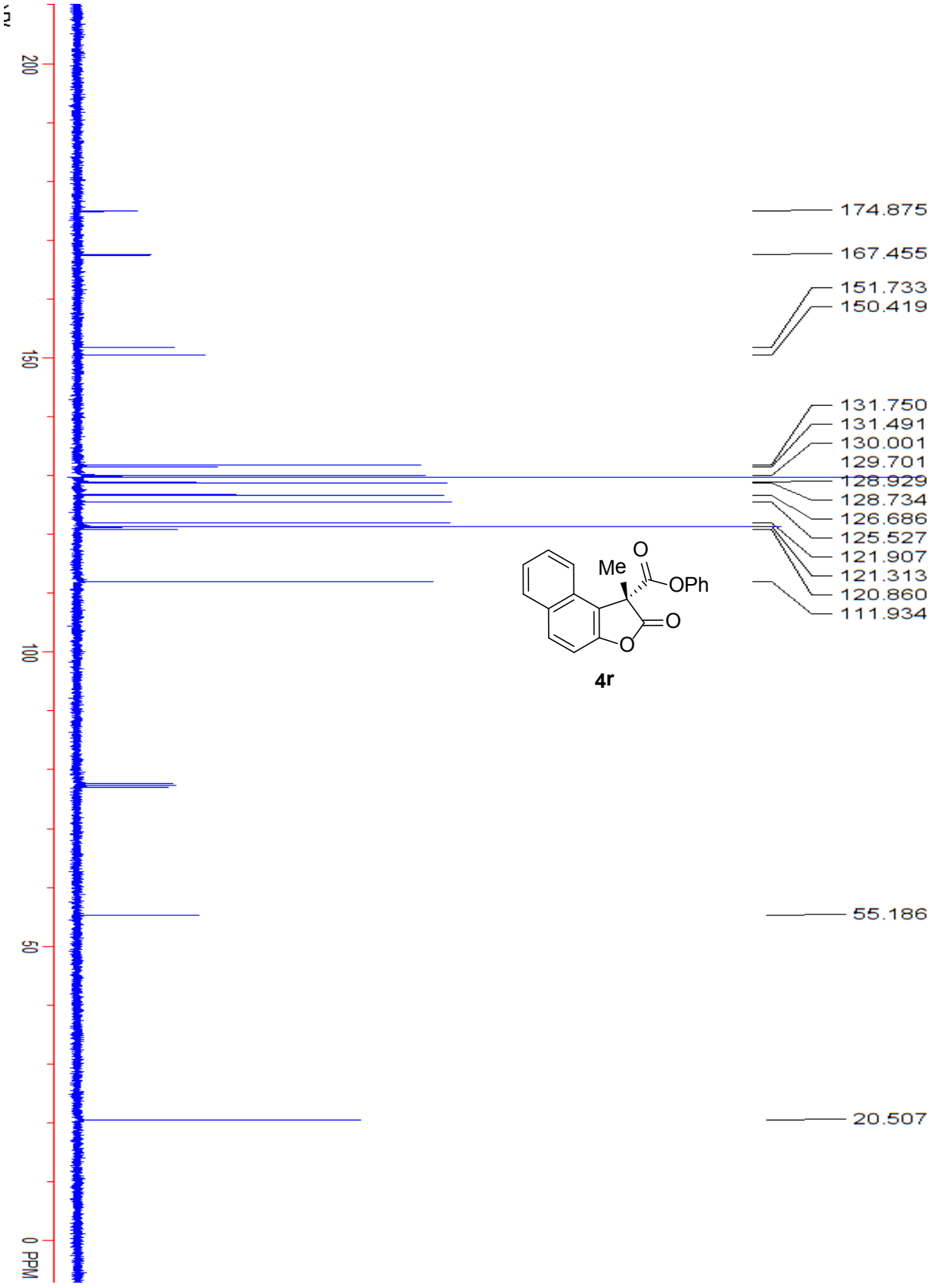
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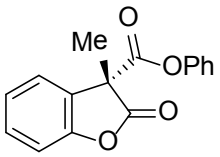
111.934
55.186
20.507
Me
O
OPh
O
O

4r

7. HPLC Charts



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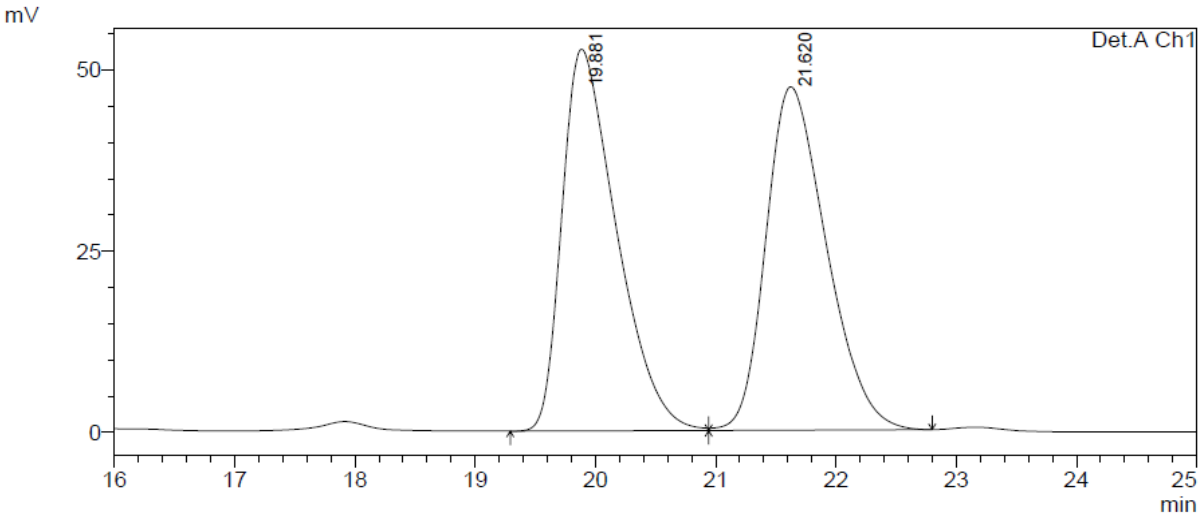
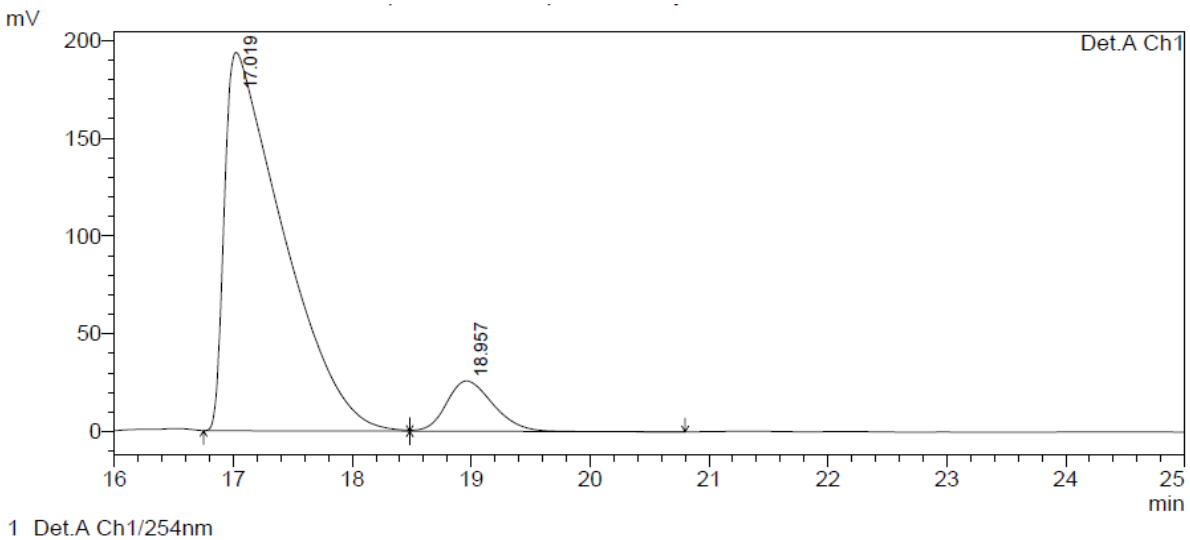


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.881	1661032	52672	50.015	52.641
2	21.620	1660013	47388	49.985	47.359
Total		3321044	100060	100.000	100.000

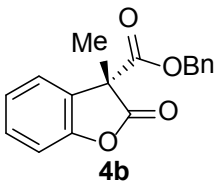


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.019	6642185	193320	90.479	88.267
2	18.957	698968	25697	9.521	11.733
Total		7341154	219017	100.000	100.000



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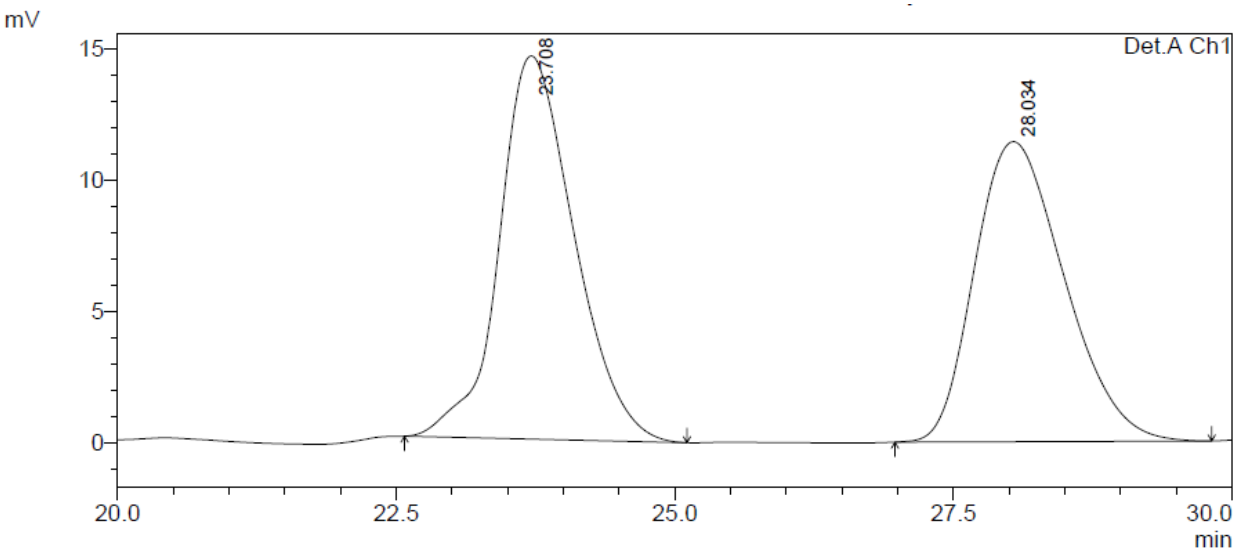
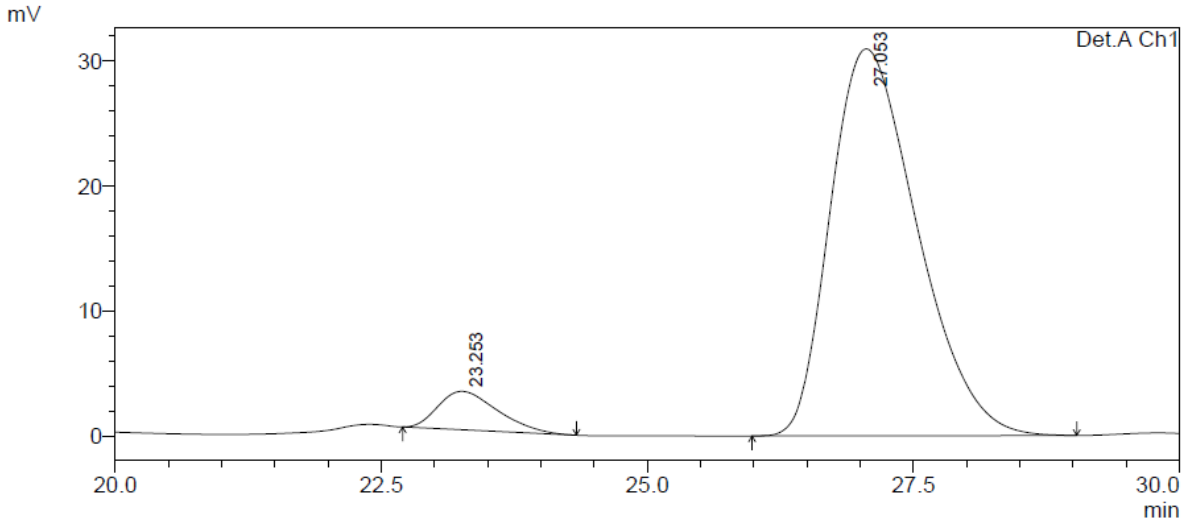


1 Det.A Ch1/254n

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.708	685454	14599	51.724	56.083
2	28.034	639772	11432	48.276	43.917
Total		1325226	26030	100.000	100.000

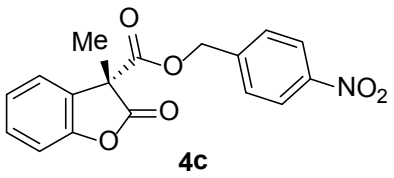


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.253	119876	3069	6.396	9.033
2	27.053	1754359	30908	93.604	90.967
Total		1874235	33977	100.000	100.000



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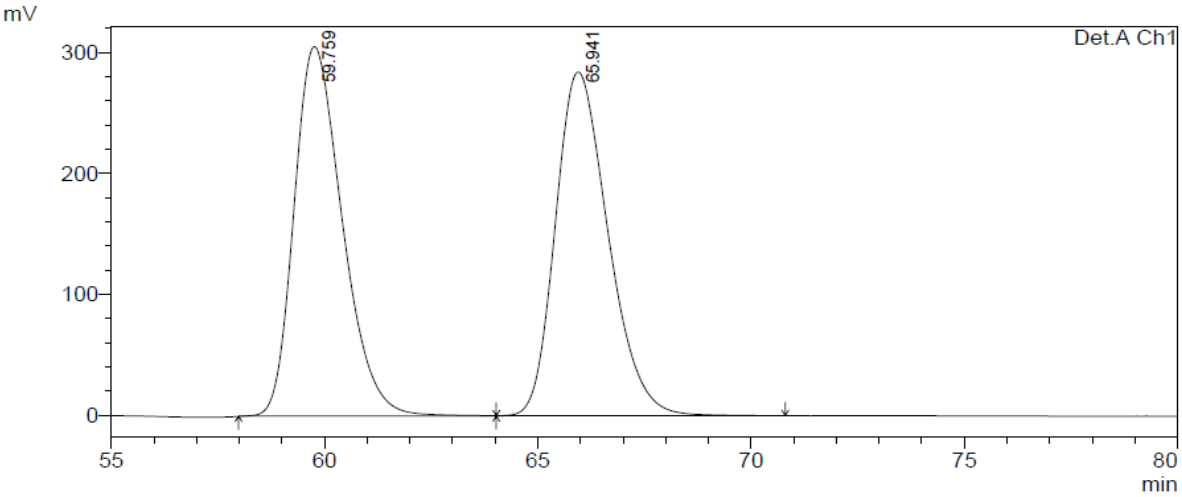
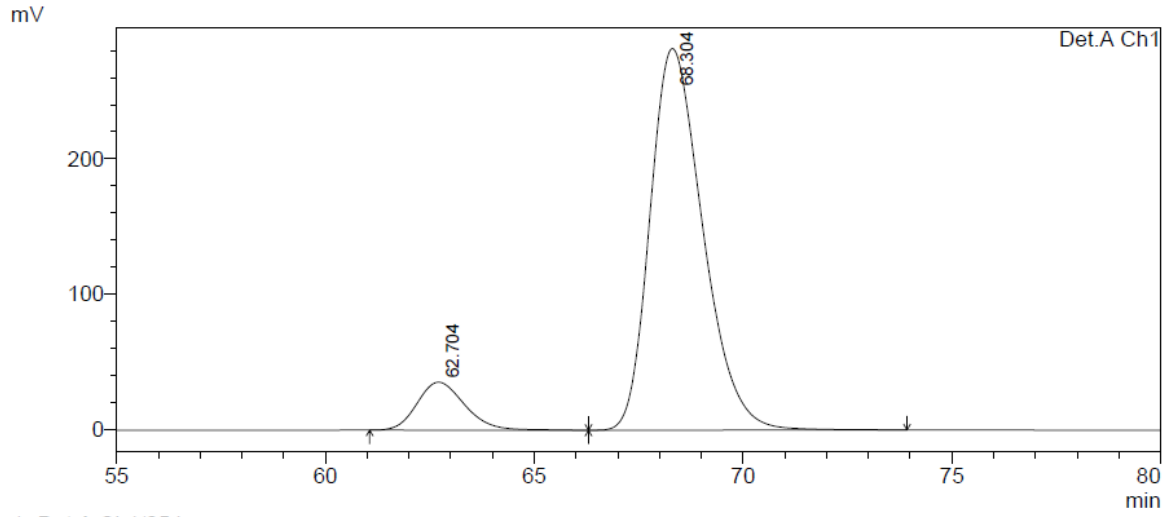


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	59.759	24016165	305467	49.568	51.784
2	65.941	24434575	284421	50.432	48.216
Total		48450740	589889	100.000	100.000

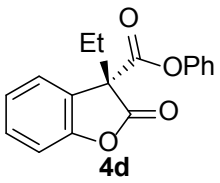


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	62.704	2804604	35408	10.155	11.154
2	68.304	24812501	282030	89.845	88.846
Total		27617105	317438	100.000	100.000



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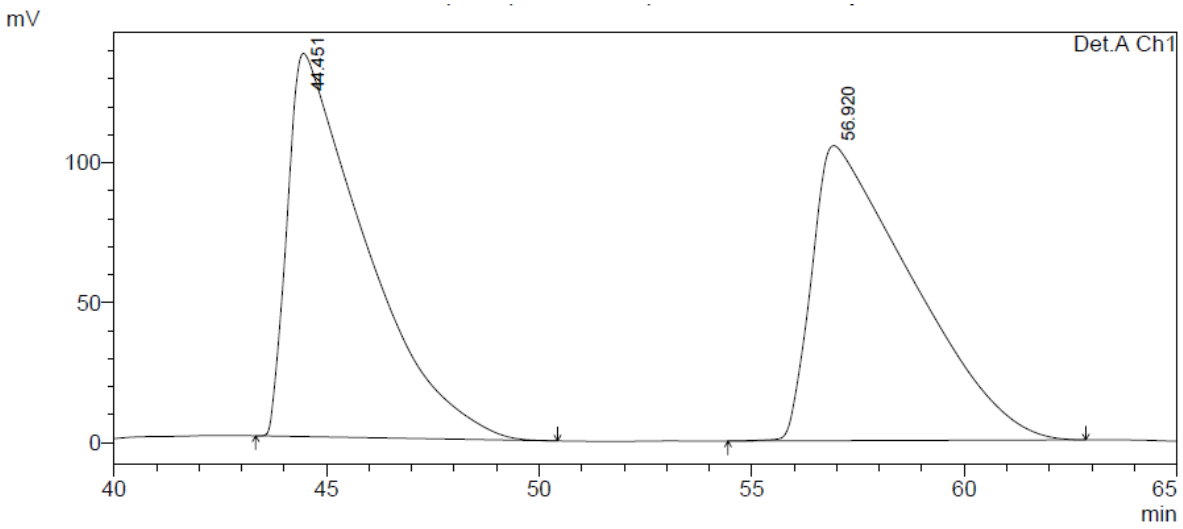
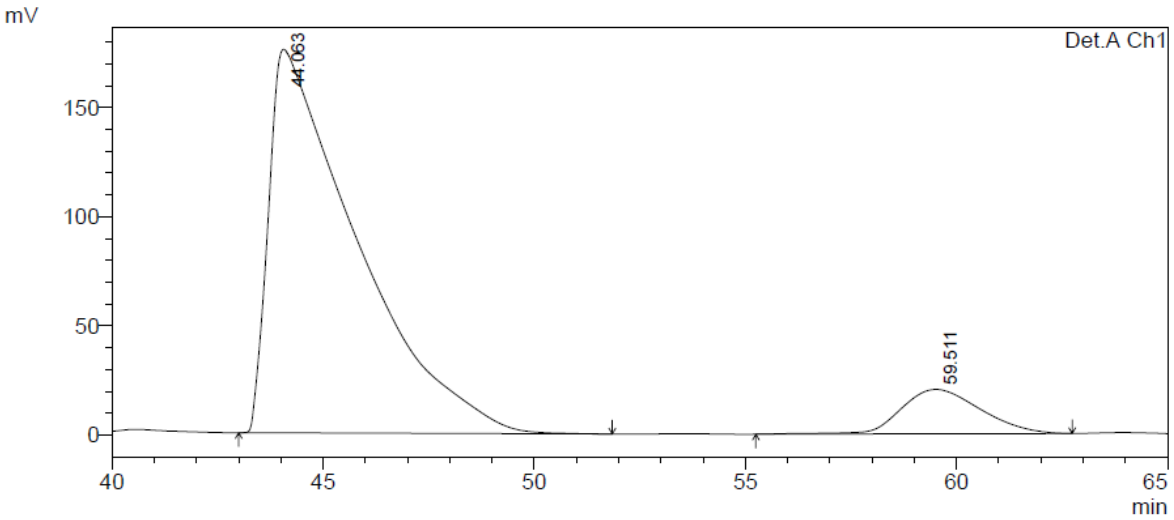


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.451	17527100	137031	50.223	56.497
2	56.920	17371647	105513	49.777	43.503
Total		34898748	242544	100.000	100.000

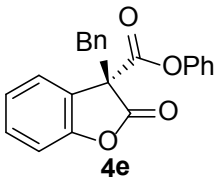


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.063	25475627	175700	90.535	89.623
2	59.511	2663490	20343	9.465	10.377
Total		28139117	196043	100.000	100.000



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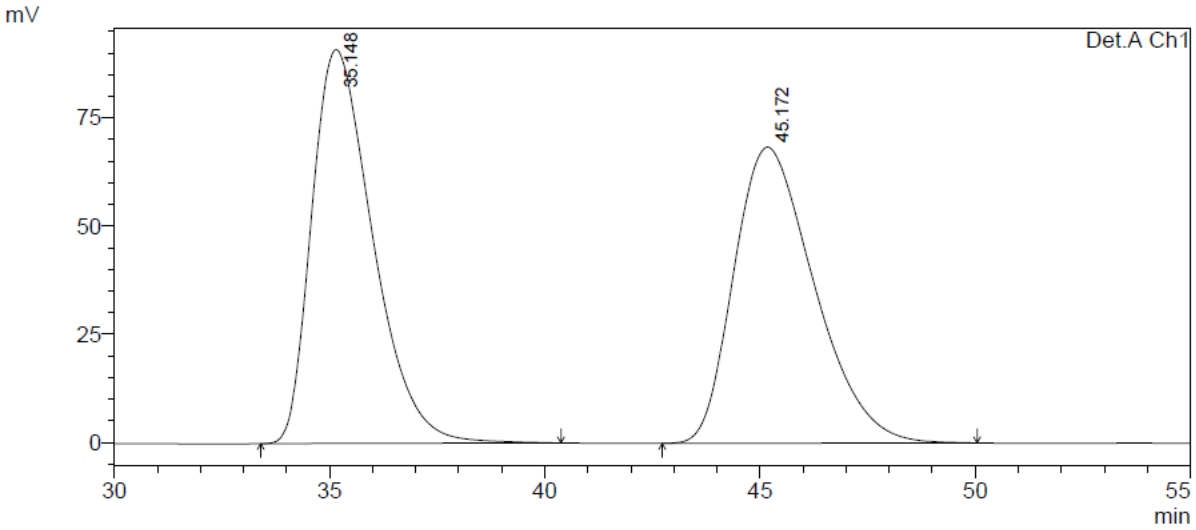
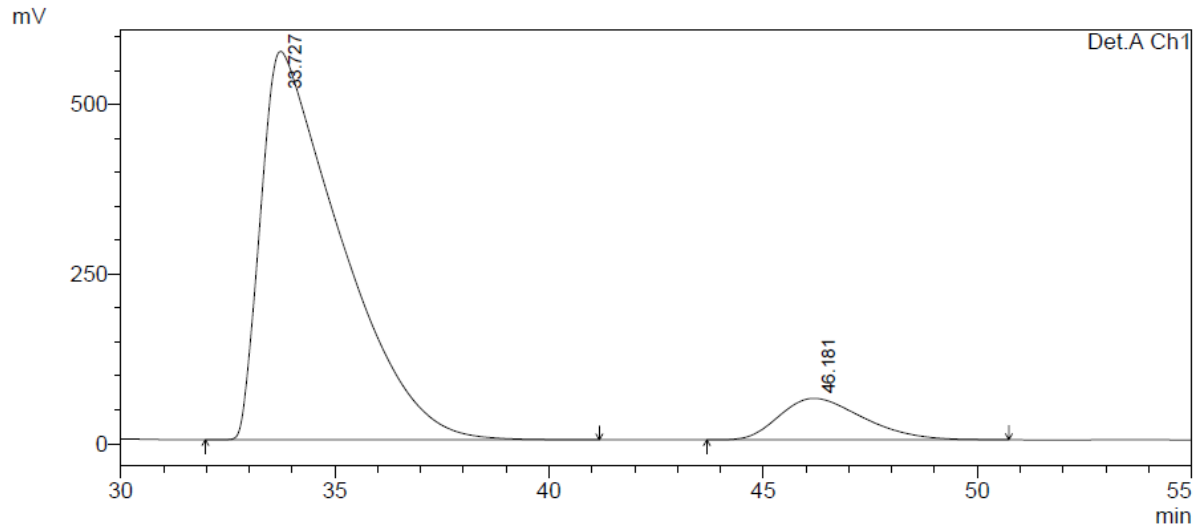


1 Det.A Ch1/230nm

PeakTable

检测器 A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.148	8990992	91010	50.265	57.075
2	45.172	8896327	68446	49.735	42.925
Total		17887319	159456	100.000	100.000

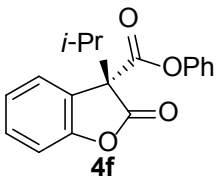


1 Det.A Ch1/230nm

PeakTable

检测器 A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.727	74336650	572327	89.966	90.352
2	46.181	8290947	61112	10.034	9.648
Total		82627597	633440	100.000	100.000



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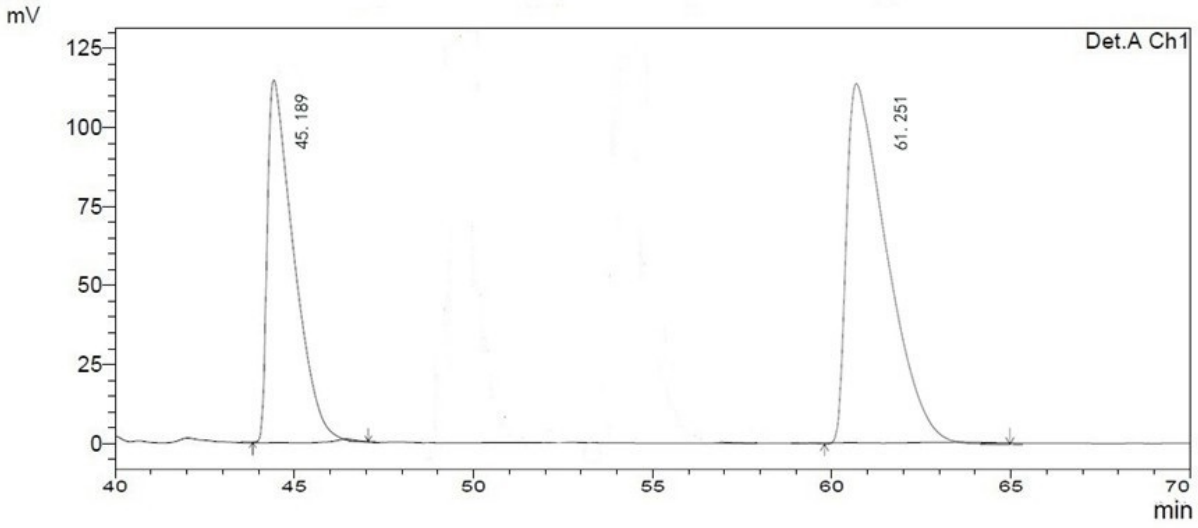
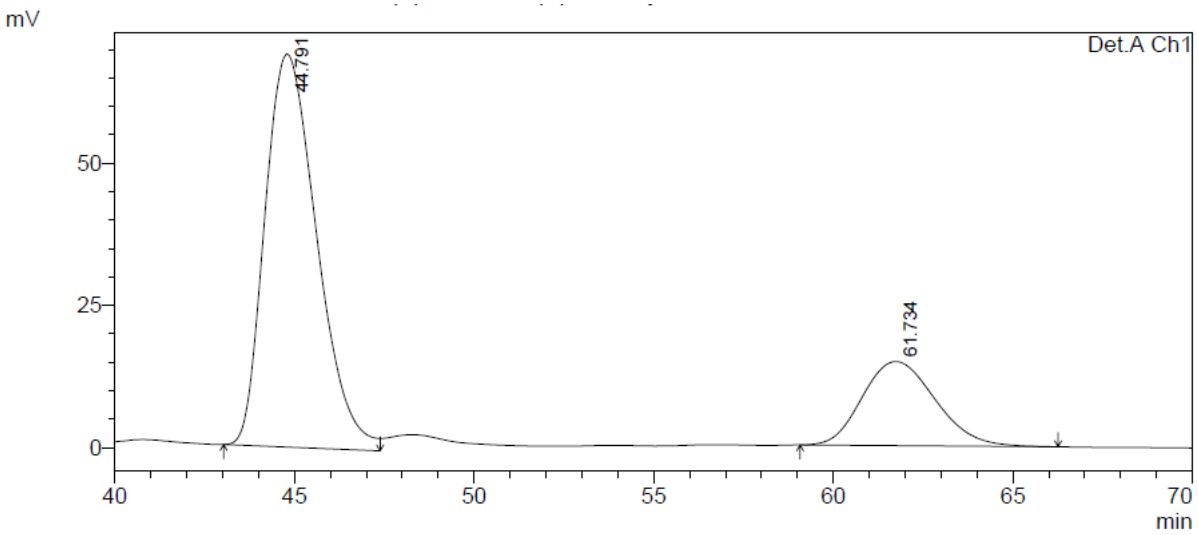


Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.189	6957306	124264	49.742	55.214
2	61.215	7029458	100795	50.258	44.786
Total		13986764	225059	100.000	100.000

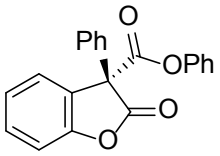


1 Det.A Ch1/230nm

PeakTable

检测器 A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.791	6946289	69104	76.900	82.375
2	61.734	2086553	14786	23.100	17.625
Total		9032841	83890	100.000	100.000



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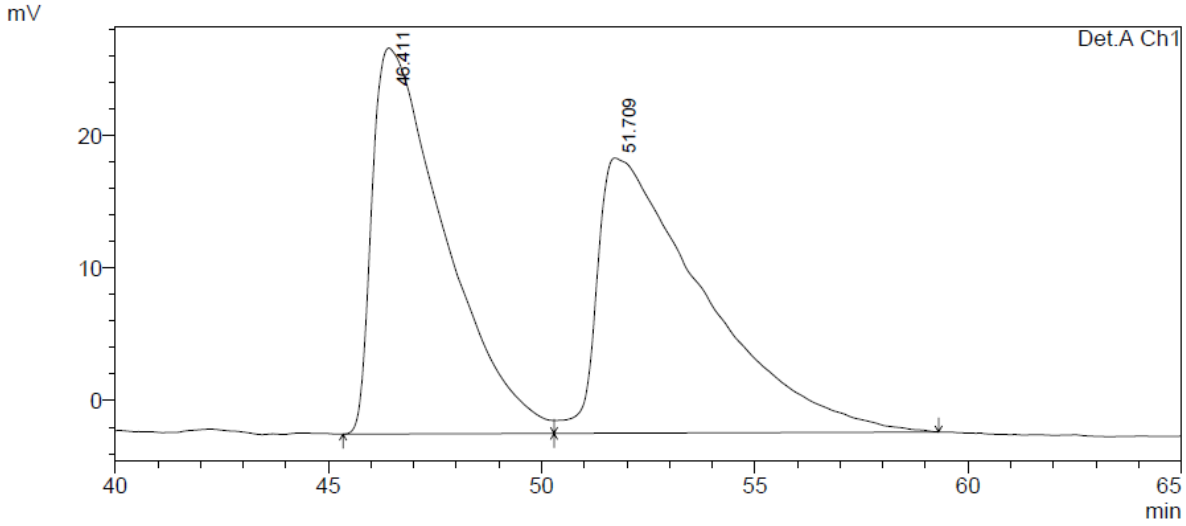
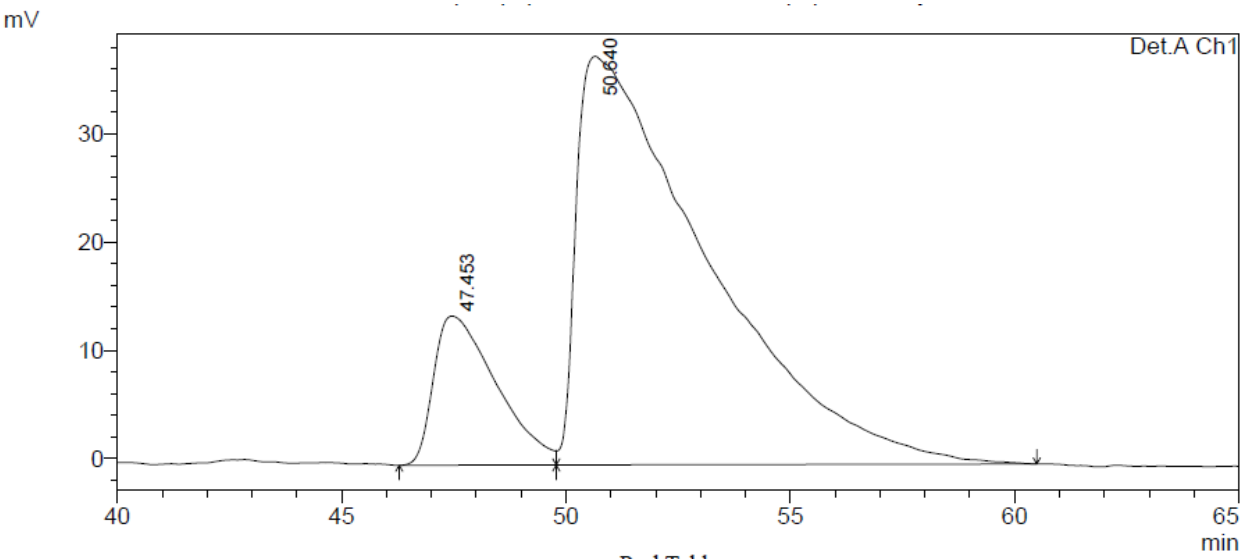


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.411	3466813	29137	48.677	58.375
2	51.709	3655264	20776	51.323	41.625
Total		7122077	49913	100.000	100.000

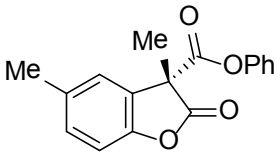


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.453	1344317	13773	14.862	26.724
2	50.640	7700884	37766	85.138	73.276
Total		9045201	51539	100.000	100.000



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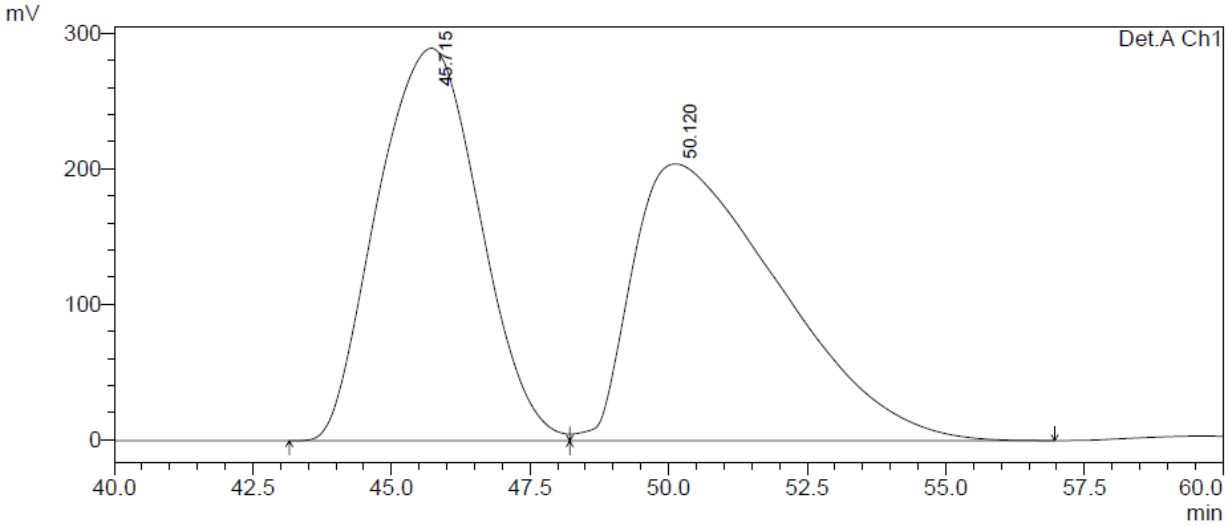
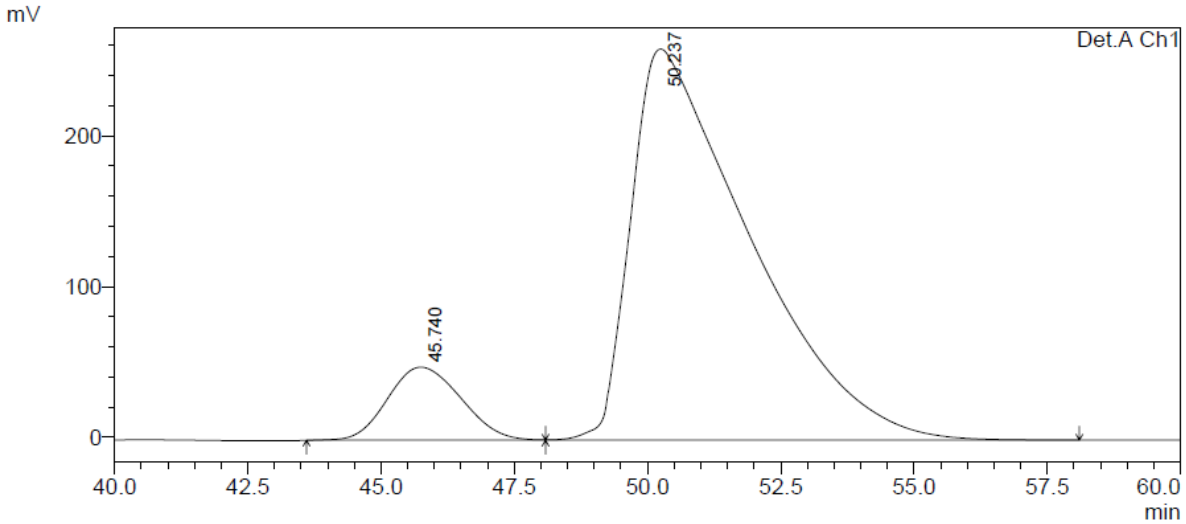


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.715	37203537	289591	49.469	58.649
2	50.120	38001595	204182	50.531	41.351
Total		75205132	493773	100.000	100.000

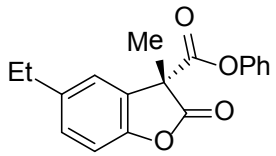


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.740	4628398	48422	10.316	15.724
2	50.237	40239858	259523	89.684	84.276
Total		44868256	307945	100.000	100.000



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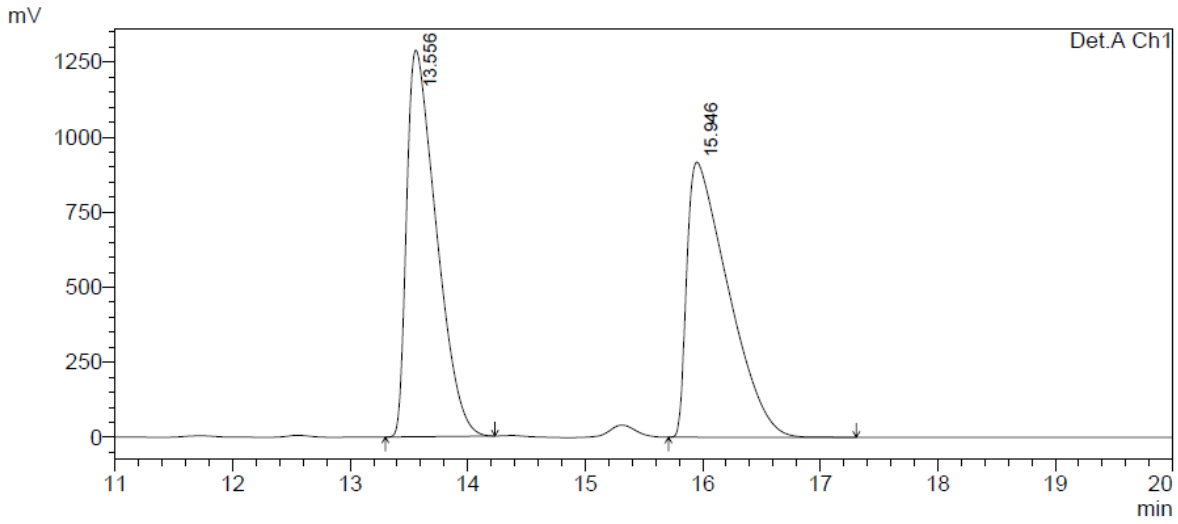
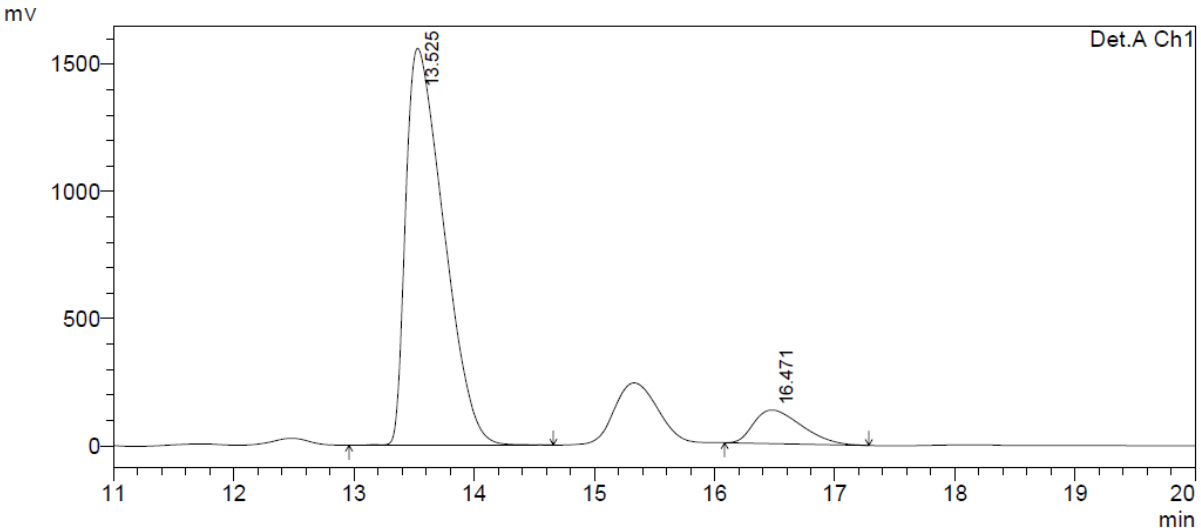


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.556	22591400	1288644	50.227	58.440
2	15.946	22387119	916410	49.773	41.560
Total		44978519	2205054	100.000	100.000

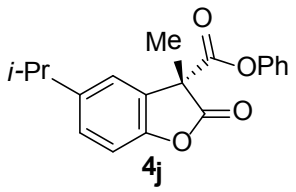


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.525	34240616	1560350	90.373	92.207
2	16.471	3647366	131883	9.627	7.793
Total		37887981	1692233	100.000	100.000



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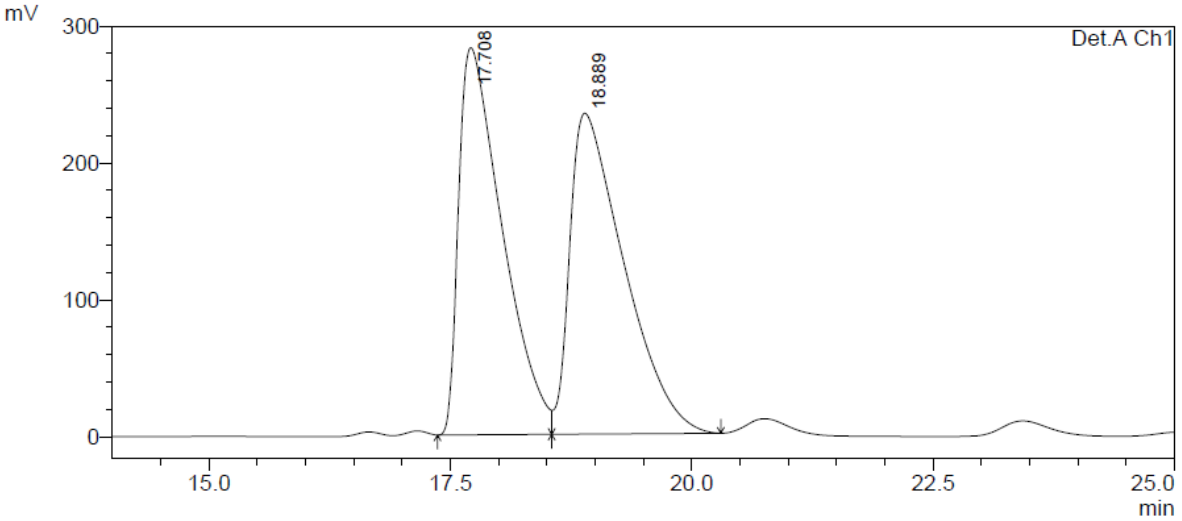
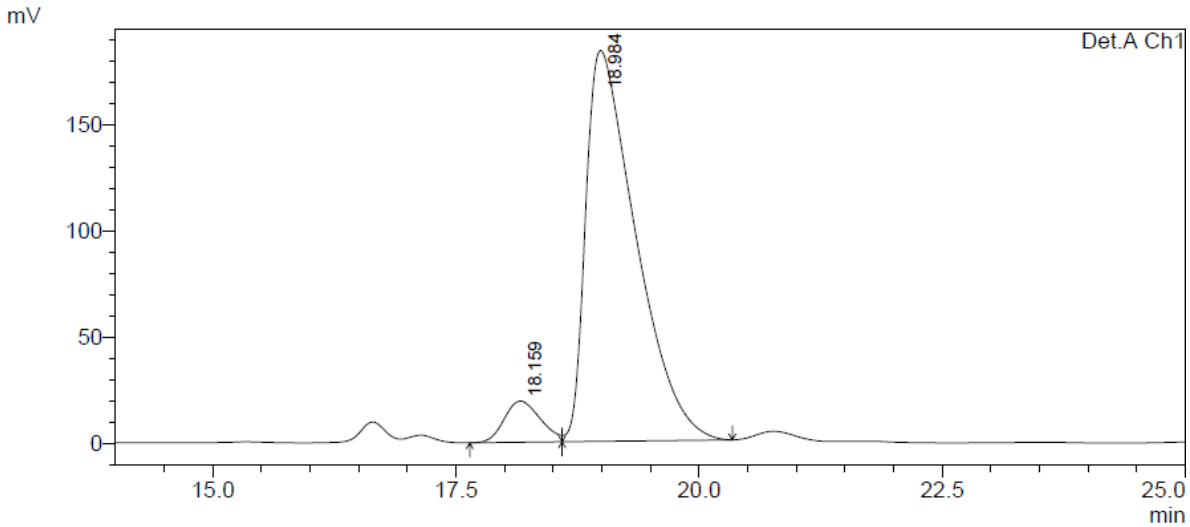


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.708	8874678	282771	49.206	54.681
2	18.889	9161107	234358	50.794	45.319
Total		18035785	517128	100.000	100.000

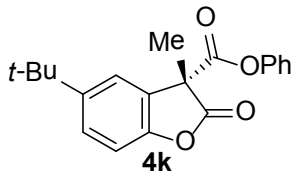


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.159	501055	19358	7.048	9.507
2	18.984	6608045	184255	92.952	90.493
Total		7109100	203612	100.000	100.000



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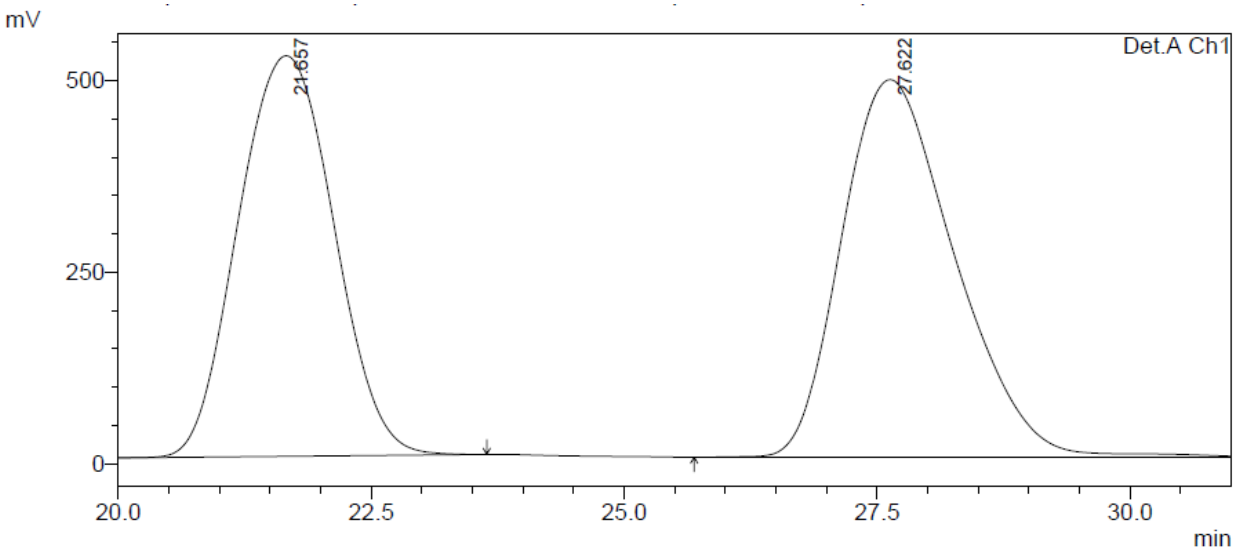
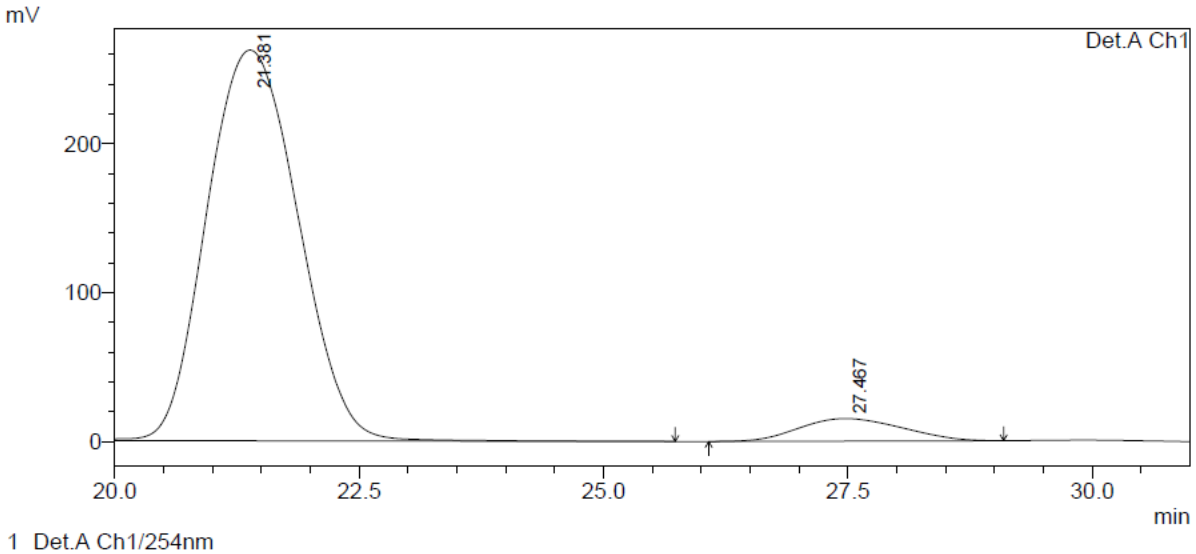


1 Det.A Ch1/25

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.657	34469672	523070	47.384	51.480
2	27.622	38275107	493004	52.616	48.520
Total		72744779	1016074	100.000	100.000

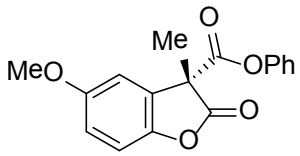


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.381	17078735	262448	93.923	94.561
2	27.467	1105084	15097	6.077	5.439
Total		18183820	277545	100.000	100.000



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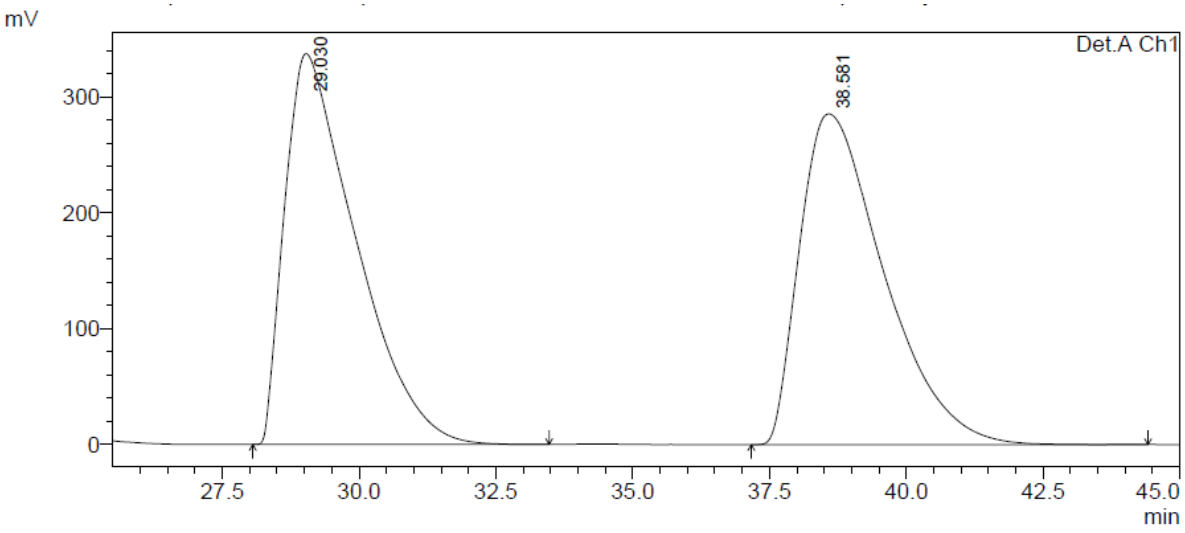
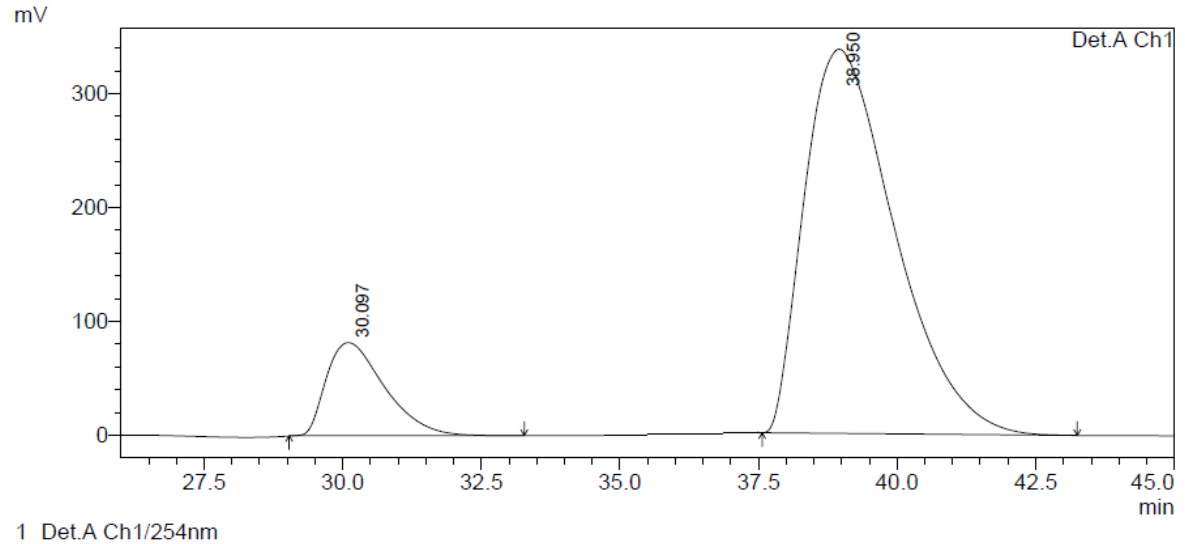


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.030	30469572	337293	49.934	54.160
2	38.581	30549982	285479	50.066	45.840
Total		61019555	622772	100.000	100.000

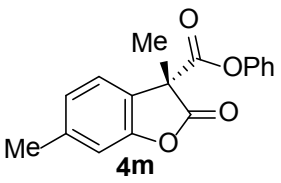


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.097	5951614	81616	13.451	19.474
2	38.950	38296278	337497	86.549	80.526
Total		44247892	419113	100.000	100.000



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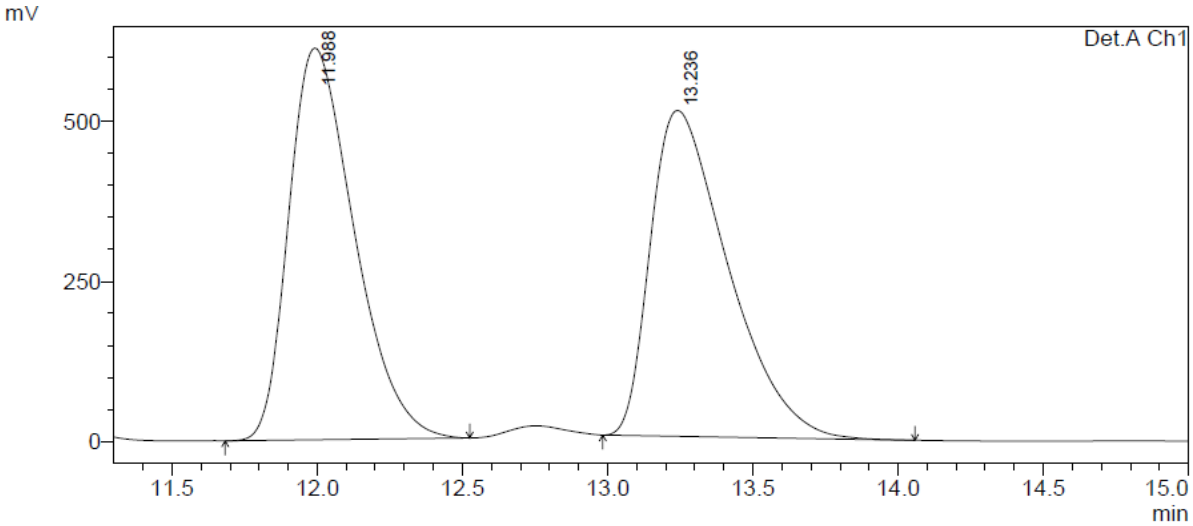
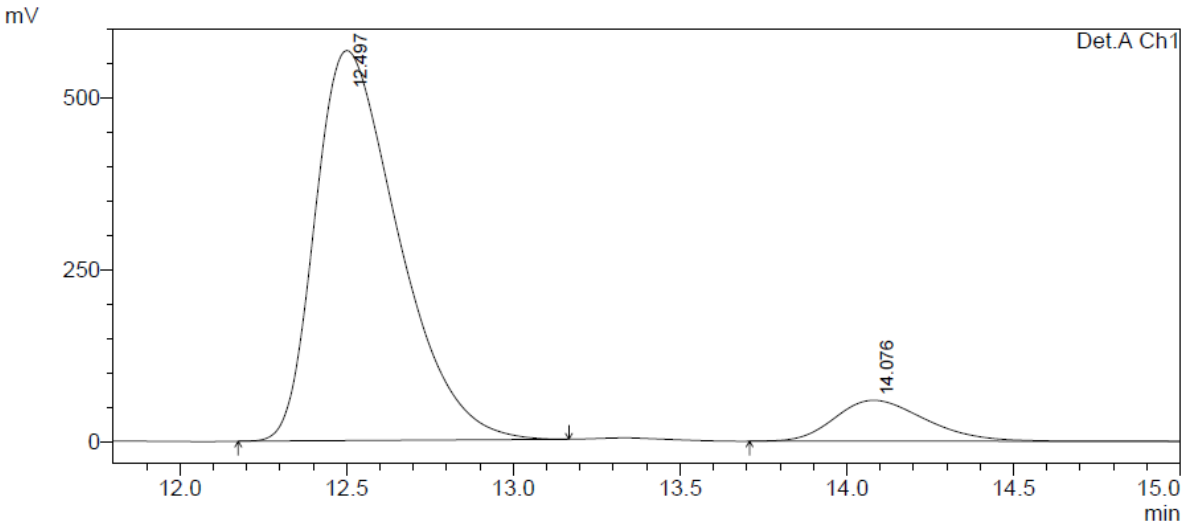


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.988	9620208	612775	50.336	54.586
2	13.236	9491644	509802	49.664	45.414
Total		19111852	1122577	100.000	100.000

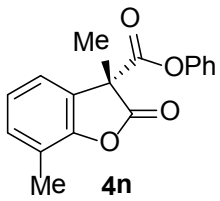


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.497	9851528	567890	89.737	90.526
2	14.076	1126672	59435	10.263	9.474
Total		10978199	627326	100.000	100.000



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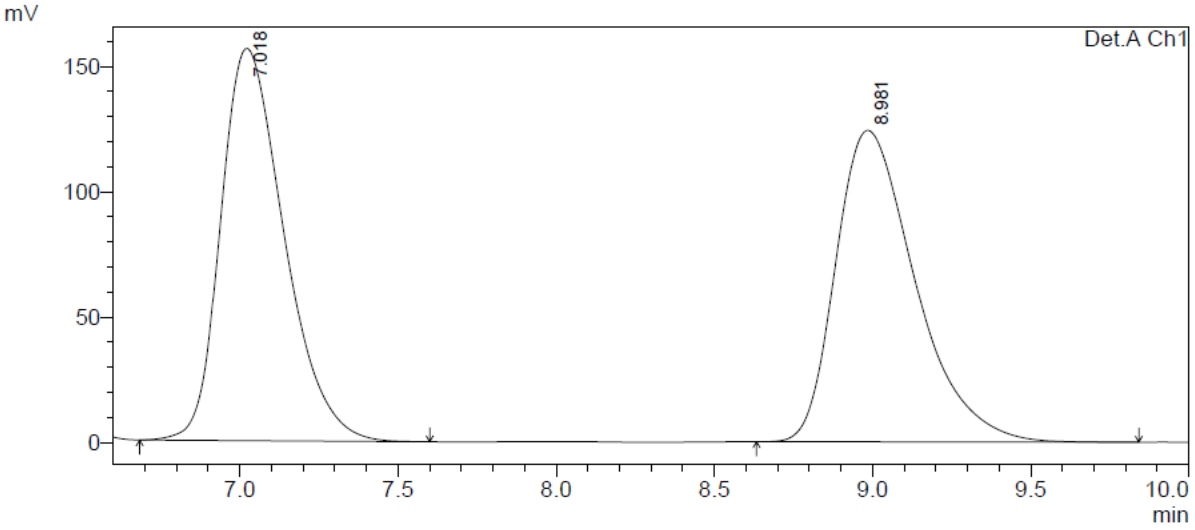
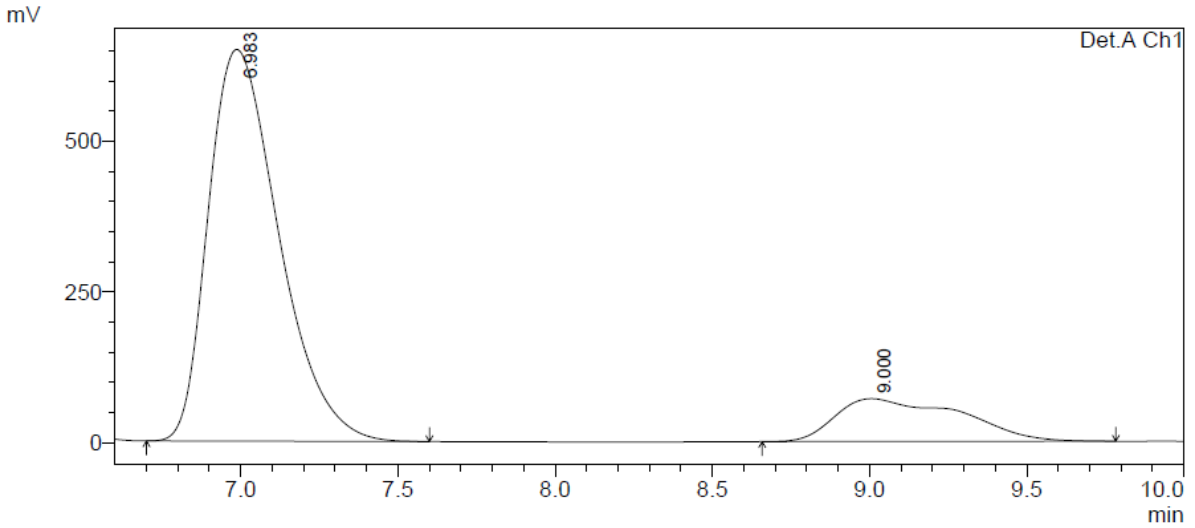


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.018	2180445	156500	50.131	55.747
2	8.981	2169050	124235	49.869	44.253
Total		4349495	280735	100.000	100.000

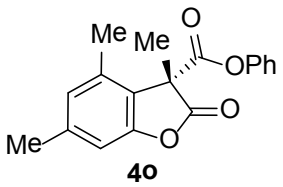


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.983	10147361	650047	83.731	90.140
2	9.000	1971690	71104	16.269	9.860
Total		12119051	721151	100.000	100.000



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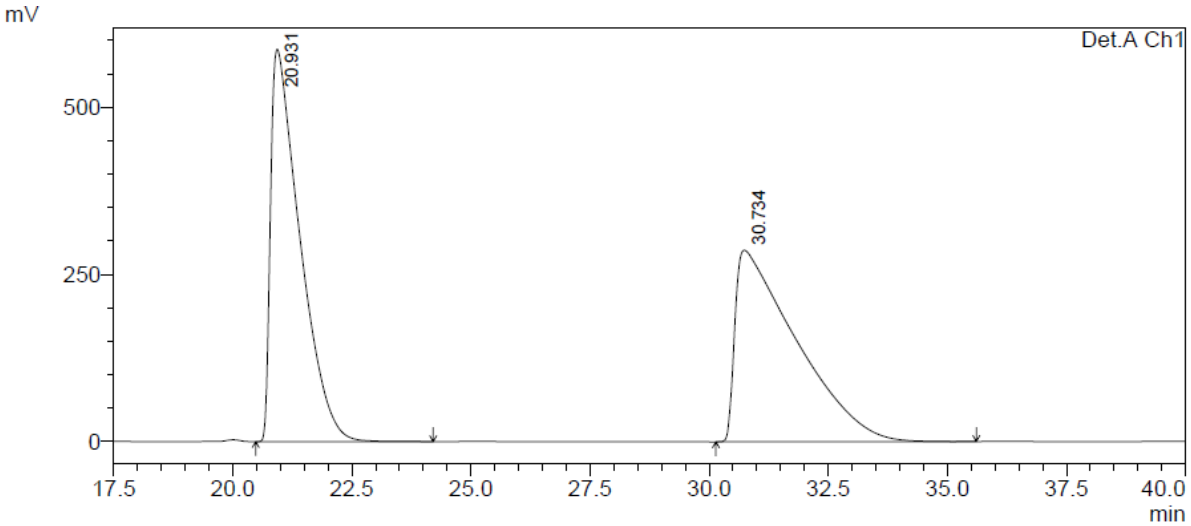
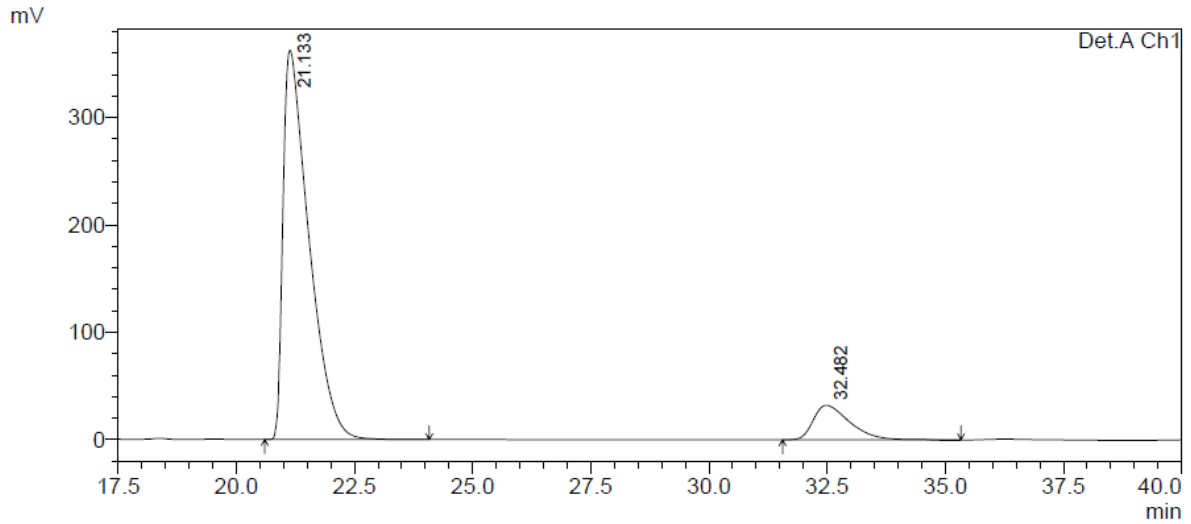


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.931	25128744	586894	49.488	67.196
2	30.734	25648338	286507	50.512	32.804
Total		50777082	873402	100.000	100.000

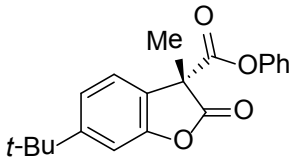


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.133	13826937	362652	88.977	91.868
2	32.482	1712953	32103	11.023	8.132
Total		15539890	394755	100.000	100.000



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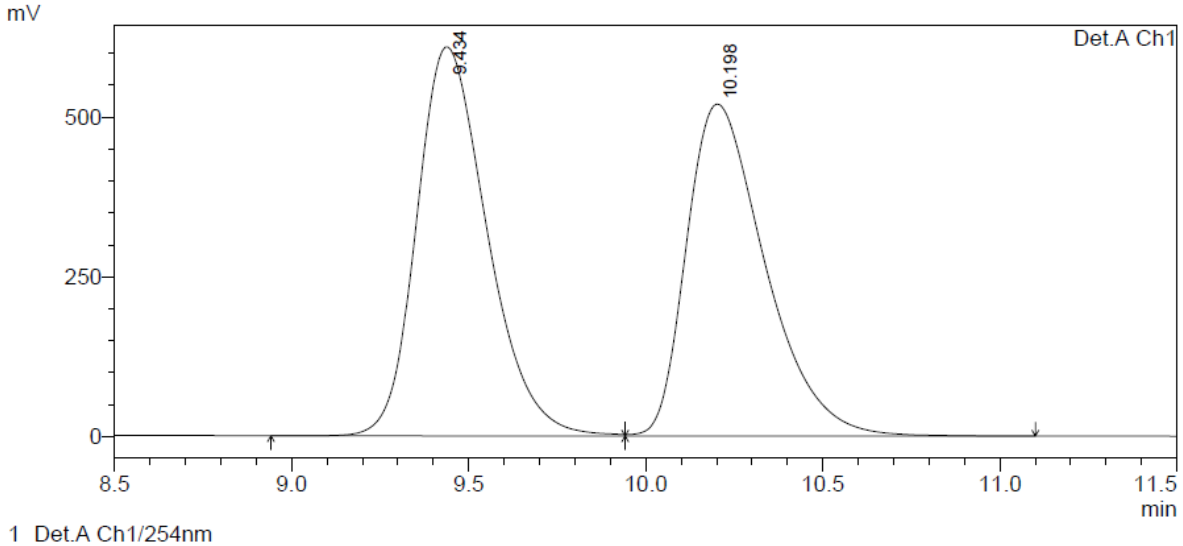
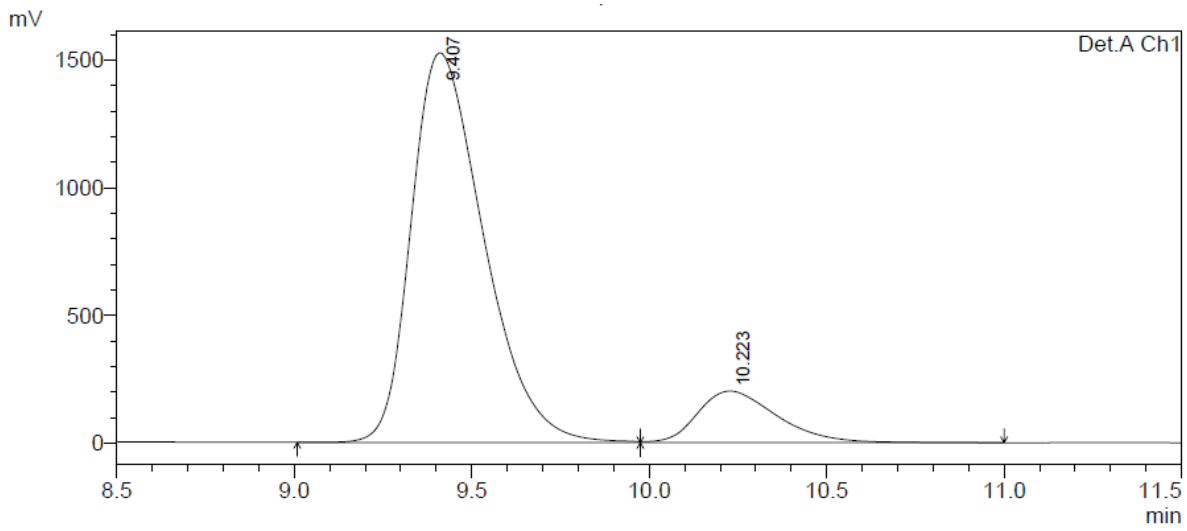


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.434	8445548	608962	51.297	53.956
2	10.198	8018324	519665	48.703	46.044
Total		16463872	1128626	100.000	100.000

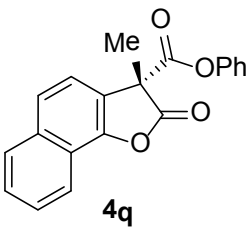


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.407	21722202	1527507	87.397	88.336
2	10.223	3132448	201702	12.603	11.664
Total		24854650	1729209	100.000	100.000



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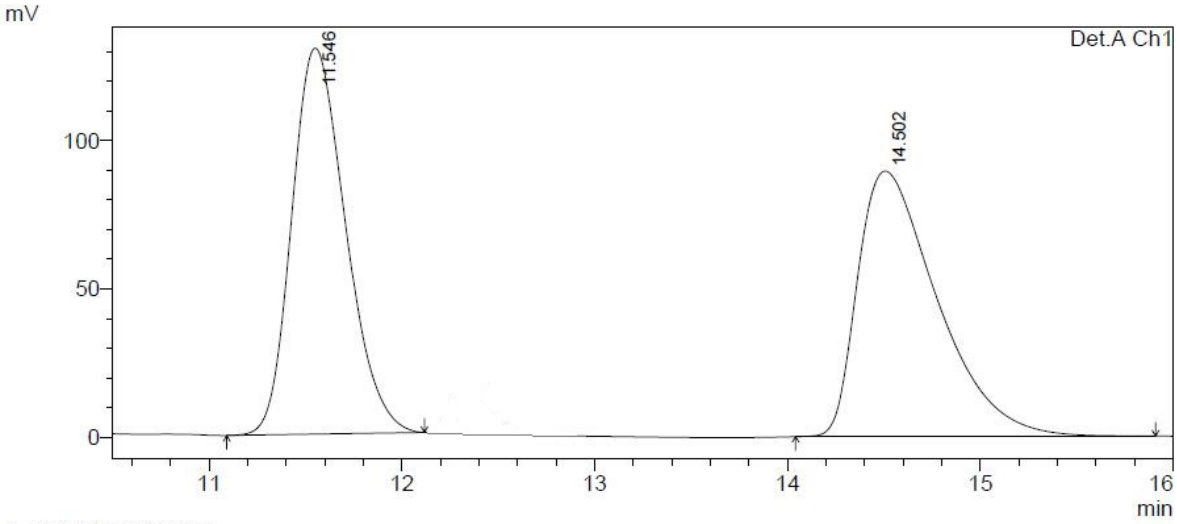
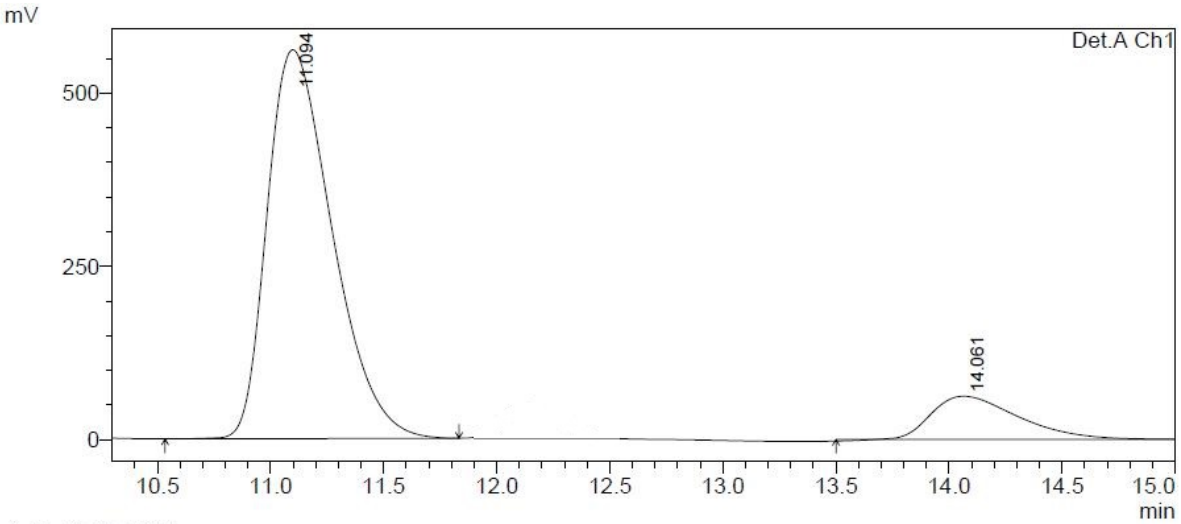


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.546	2529560	130243	49.695	59.270
2	14.502	2560565	89502	50.305	40.730
Total		5090126	219745	100.000	100.000

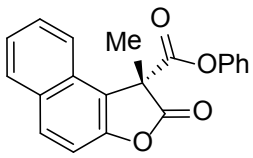


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.094	11231241	561026	87.008	89.995
2	14.061	1677053	62372	12.992	10.005
Total		12908294	623398	100.000	100.000



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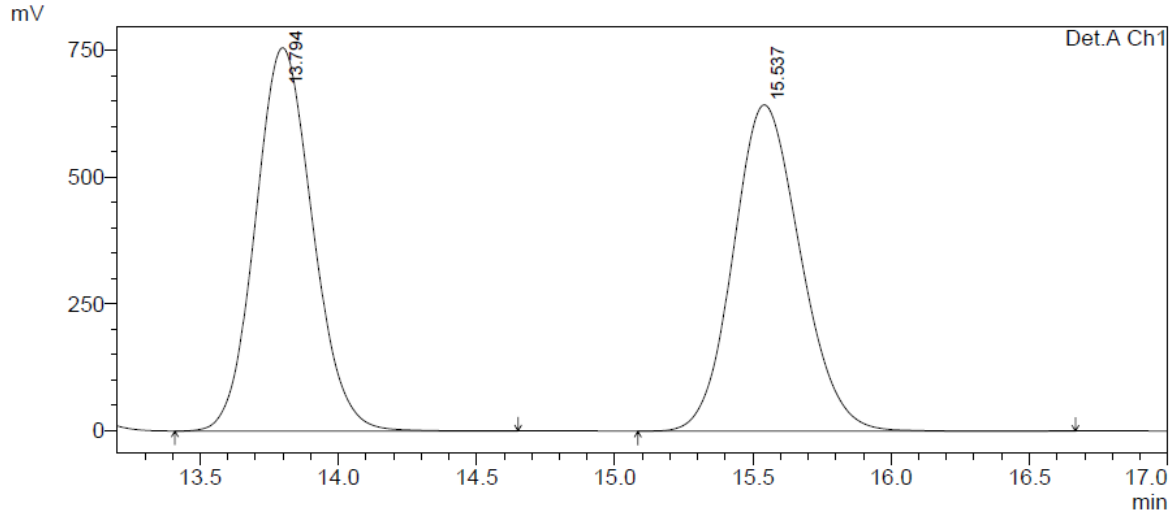
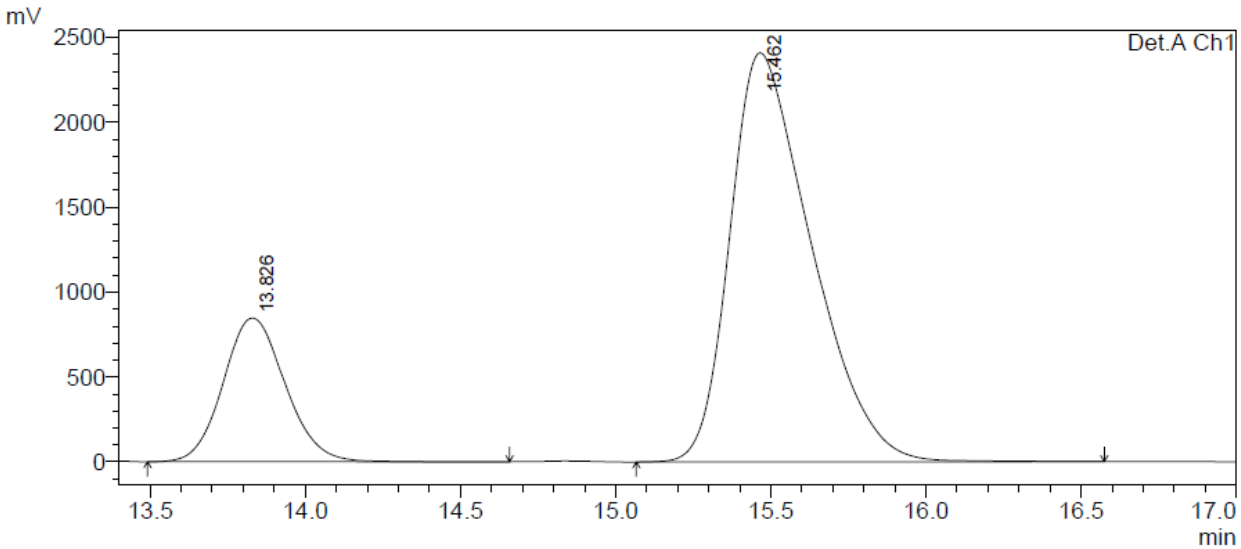


1 Det.A Ch1/254nm

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.794	10875202	755204	49.925	54.003
2	15.537	10908066	643239	50.075	45.997
Total		21783268	1398443	100.000	100.000



1 Det.A Ch1/254

PeakTable

检测器 A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.826	11751495	846381	21.080	25.984
2	15.462	43996045	2410894	78.920	74.016
Total		55747541	3257275	100.000	100.000