SUPPORTING INFORMATION

Copper-catalysed chemo- and ortho-selective C-H bond functionalization of phenol derivatives with α-aryl-α-diazoesters

Ben Ma,[ab] Zhiqiong Tang,[a] Junliang Zhang[abc] and Lu Liu*[ab]*

[a] School of Chemistry and Molecular Engineering, East China Normal University, 500 Dongchuan Road Shanghai, 200241, P. R. China; E-mail: lliu@chem.ecnu.edu.cn.

[b] Shanghai Engineering Research Center of Molecular Therapeutics and New Drug Development, East China Normal University, Shanghai 200062, P. R. China

[c] Department of Chemistry, Fudan University, 2005 Songhu Road, Shanghai 200438, P. R. China; E-mail: junliangzhang@fudan.edu.cn.

Fax:(+86)-021-6223-3213; E-mail: lliu@chem.ecnu.edu.cn, jlzhang@chem.ecnu.edu.cn

Content:

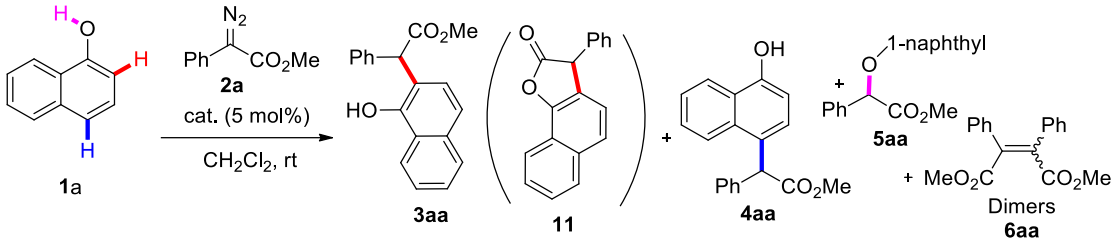
1. General Information:

Unless otherwise noted, all reactions were carried out in standard Schlenk techniques with magnetic stirring bar under air. Materials obtained from commercial suppliers were used directly without further purification. ^{1}H NMR spectra were recorded on a BRUKER 500 (500 MHz), BRUKER 400 (400 MHz) spectrometer or a Bruker 300 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with tetramethylsilane (TMS: 0 ppm) with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a BRUKER 500 (125 MHz), BRUKER 400 (100 MHz) spectrometer and a Bruker 300 (75.0 MHz) spectrometer in $CDCl_3$ with complete proton decoupling. Chemical shifts are reported in ppm with the deuterium solvent as the internal standard (e.g. $CDCl_3$: 77.0 ppm).

Anhydrous tetrahydrofuran (THF), toluene, dichloromethane (DCM) and diethyl ether (Et_2O) were distilled from sodium and benzophenone to use; AgOTf, $AgSbF_6$, $AgNTf_2$, $AgBF_4$, and $AgPF_6$ were purchased from Alfa-Aesar Company and used directly.

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with hexane/ethyl acetate or hexane/ CH_2Cl_2.

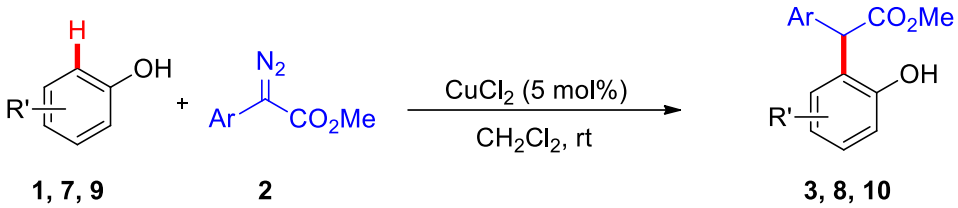
2. Table S1. Optimization of Reaction Conditions.[a]



entry	Cat. (5 mol%)	Solvent	3/4/5/6
1	$Cu(CH_3CN)_4BF_4$	DCM	44(30)/0/5/76
2	CuOAc	DCM	68(10)/0/4/35
3	CuOTf	DCM	54(24)/0/2/66
4	$Cu(ClO_4)_2·6H_2O$	DCM	60(12)/0/2/33
5	CuF_2	DCM	70(12)/0/2/24
6	CuCl	DCM	72(4)/0/0/22
7	**$CuCl_2$**	**DCM**	**85(2)/0/2/3**
8	$CuCl_2$	DCE	76(2)/0/5/5
9	$CuCl_2$	toluene	53/0/3/35
10	$CuCl_2$	THF	25/0/5/31

[a] Unless specific note, the solution of **2a** (0.4 mmol) in 1 mL of solvent was introduced into **1a** (0.6 mmol) and catalyst (5 mol%) in solvent (1 mL) at room temperature by a syringe in 15 min. [b] NMR yield. The number in parenthesis is the corresponding lactone **11**. [c] NR means no reaction. [d] - means not detected.

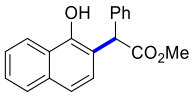
3. General procedure for copper-catalyzed *ortho*-selective C-H bond functionalization of naphthols



1, 7, 9 **2** **3, 8, 10**

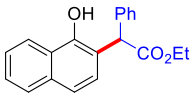
In a dried glass tube, $CuCl_2$ (2.36 mg, 0.02 mmol, 5 mol%), naphthalen-1-ol **1a** (86.5 mg, 0.6 mmol, 1.5 equiv) and DCM (1 mL) was added at room temperature. Then a solution of **2a** (76.2 mg, 0.4 mmol) dissolved in 1 mL DCM was introduced into the reaction mixture by a syringe. The resulting mixture was continually stirred at room temperature until **2a** was consumed completely determined by TLC analysis. After being filtrated through celite and concentrated, the residue was purified by column chromatography on silica gel to afford the desired product.

1) Methyl 2-(1-hydroxynaphthalen-2-yl)-2-phenylacetate (3aa)



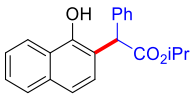
96 mg; 82% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.31-8.29 (m, 1H), 7.78-7.75 (m, 1H), 7.48-7.45 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.31-7.20 (m, 6H), 5.21 (s, 1H), 3.84 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.6, 151.4, 136.6, 134.4, 129.0, 128.7, 127.5, 127.2, 126.6, 126.3, 125.4, 122.6, 120.3, 116.0, 55.9, 53.3; **MS** (EI): m/z (%): 292 (M^+, 15.46), 231 (100); **HRMS** (EI) calcd. for $C_{19}H_{16}O_3$: 292.1099, found: 292.1108.

2) Ethyl 2-(1-hydroxynaphthalen-2-yl)-2-phenylacetate (3ab)[a]



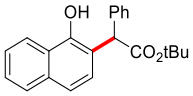
98.0 mg, 80% yield; colorless oil.

3) Isopropyl 2-(1-hydroxynaphthalen-2-yl)-2-phenylacetate (3ac)[a]



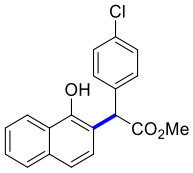
90.9 mg, 71% yield; colorless oil.

4) *tert*-Butyl 2-(1-hydroxynaphthalen-2-yl)-2-phenylacetate (3ad)[a]



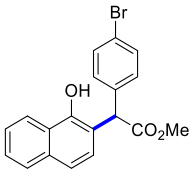
108.3 mg, 81% yield was obtained as a colorless oil.

5) Methyl 2-(4-chlorophenyl)-2-(1-hydroxynaphthalen-2-yl)acetate (3ae)



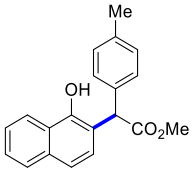
105 mg, 80% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.29-8.26 (m, 1H), 7.79-7.76 (m, 1H), 7.48 (t, *J* = 4.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 9.2 Hz, 3H), 5.17 (s, 1H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 151.2, 135.2, 134.5, 133.5, 129.0, 128.8, 128.7, 127.3, 126.7, 126.2, 125.5, 122.4, 120.5, 115.9, 55.0, 53.3; **HRMS** (ESI) calculated for $[C_{19}H_{16}ClO_3][M+H]^+$: 327.0782, found: 327.0779.

6) Methyl 2-(4-bromophenyl)-2-(1-hydroxynaphthalen-2-yl)acetate (3af)



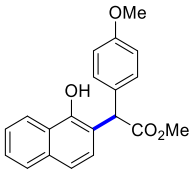
120 mg, 81% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.27-8.25 (m, 1H), 7.77-7.74 (m, 1H), 7.47-7.44 (m, 2H), 7.39 (dd, *J* = 8.4, 2.0 Hz, 3H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.14 (s, 1H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.0, 151.1, 135.7, 134.4, 131.8, 129.4, 128.6, 127.3, 126.7, 126.2, 125.5, 122.3, 121.6, 120.5, 115.9, 54.9, 53.3; **HRMS** (ESI) calculated for $[C_{19}H_{15}BrO_3][M+Na]^+$: 393.0097, found: 393.0101.

7) Methyl 2-(1-hydroxynaphthalen-2-yl)-2-(p-tolyl)acetate (3ag)



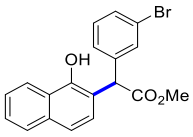
102 mg, 83% yield; colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.43 (d, *J* = 4.5 Hz, 1H), 7.88 (d, *J* = 4.0 Hz, 1H), 7.58-7.50 (m, 3H), 7.34-7.20 (m, 5H), 5.31 (s, 1H), 3.93 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.6, 151.2, 137.2, 134.3, 133.6, 129.4, 128.9, 127.4, 127.2, 126.5, 126.2, 125.3, 122.5, 120.2, 116.3, 55.4, 53.1, 20.9; **HRMS** (ESI) calculated for $[C_{20}H_{18}NaO_3][M+Na]^+$: 329.1149, found: 329.1150.

8) Methyl 2-(1-hydroxynaphthalen-2-yl)-2-(4-methoxyphenyl)acetate (3ah)



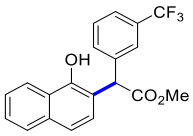
119 mg, 92% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.31-8.28 (m, 1H), 7.77-7.74 (m, 1H), 7.47-7.44 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.17 (dd, *J* = 13.6, 8.4 Hz, 3H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.15 (s, 1H), 3.82 (s, 3H), 3.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.7, 158.9, 151.2, 134.4, 128.9, 128.7, 128.6, 127.2, 126.5, 126.3, 125.3, 122.5, 120.2, 116.4, 114.1, 55.2, 55.1, 53.2; **HRMS** (ESI) calculated for $[C_{20}H_{19}O_4][M+H]^+$: 323.1278, found: 323.1283.

9) Methyl 2-(3-bromophenyl)-2-(1-hydroxynaphthalen-2-yl)acetate (3ai)



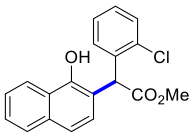
115.4 mg, 78% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.28-8.25 (m, 1H), 7.78-7.76 (m, 1H), 7.47 (t, *J* = 4.4 Hz, 2H), 7.41-7.36 (m, 3H), 7.22-7.11 (m, 3H), 5.18 (s, 1H), 3.84 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.8, 151.2, 139.0, 134.5, 130.7, 130.2, 128.6, 127.3, 126.8, 126.3, 126.2, 125.6, 122.8, 122.4, 120.6, 115.8, 55.1, 53.4; **HRMS** (ESI) calculated for $[C_{19}H_{15}BrNaO_3][M+Na]^+$: 393.0097, found: 393.0101.

10) Methyl 2-(1-hydroxynaphthalen-2-yl)-2-(3-(trifluoromethyl)phenyl)acetate (3aj)



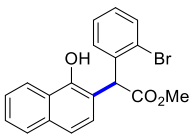
116.6 mg, 81% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.26-8.24 (m, 1H), 7.79-7.76 (m, 1H), 7.54-7.38 (m, 7H), 7.21 (d, *J* = 8.4 Hz, 1H), 5.27 (s, 1H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.7, 151.1, 137.9, 134.5, 131.5, 131.0 (q, *J* = 33.0 Hz), 129.2, 128.5, 128.0, 127.4, 126.8, 126.2, 125.6, 124.4 (q, *J* = 4.0 Hz), 123.9 (q, *J* = 271 Hz), 122.3, 120.7, 115.8, 55.1, 53.4; **HRMS** (ESI) calculated for $[C_{20}H_{16}F_3O_3][M+H]^+$: 361.1059, found: 361.1046.

11) Methyl 2-(2-chlorophenyl)-2-(1-hydroxynaphthalen-2-yl)acetate (3ak)



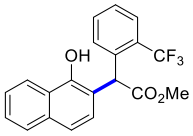
108.2 mg, 83% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27-8.24 (m, 1H), 7.79-7.76 (m, 2H), 7.49-7.47 (m, 2H), 7.43-7.39 (m, 2H), 7.24-7.15 (m, 4H), 5.51 (s, 1H), 3.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.0, 151.1, 134.4, 134.2, 134.0, 130.0, 129.9, 129.1, 128.6, 127.4, 127.1, 126.7, 125.8, 125.6, 122.1, 120.8, 114.7, 53.3, 52.9; **HRMS** (ESI) calculated for $[C_{19}H_{16}ClO_3][M+H]^+$: 327.0782, found: 327.0782.

12) Methyl 2-(2-bromophenyl)-2-(1-hydroxynaphthalen-2-yl)acetate (3al)



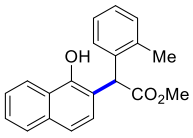
131.7 mg, 89% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23-8.21 (m, 1H), 7.78-7.75 (m, 1H), 7.59-7.55 (m, 2H), 7.48-7.46 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.28-7.26 (m, 1H), 7.22-7.20 (m, 2H), 7.13-7.09 (m, 1H), 5.55 (s, 1H), 3.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6, 150.8, 135.9, 134.3, 133.2, 130.3, 129.3, 128.3, 127.7, 127.5, 126.7, 125.7, 125.6, 124.8, 121.9, 120.8, 115.4, 54.8, 53.2; **HRMS** (ESI) calculated for $[C_{19}H_{15}BrNaO_3][M+Na]^+$: 393.0097, found: 393.0106.

13) Methyl 2-(1-hydroxynaphthalen-2-yl)-2-(2-(trifluoromethyl)phenyl)acetate (3am)



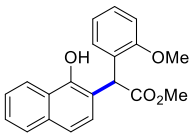
76.3 mg, 53% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14-8.11 (m, 1H), 7.80-7.78 (m, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.55-7.38 (m, 6H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.96 (s, 1H), 5.77 (s, 1H), 3.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2, 149.8, 135.6, 134.2, 132.3, 131.3, 128.5 (q, *J* = 39.6 Hz), 127.8, 127.7, 127.4, 126.6, 126.3 (q, *J* = 5.8 Hz), 125.8, 125.4, 124.4 (q, *J* = 272 Hz), 121.3, 120.9, 117.2, 53.1, 49.7; **HRMS** (ESI) calculated for $[C_{20}H_{15}F_3NaO_3][M+Na]^+$: 383.0864, found: 383.0865.

14) Methyl 2-(1-hydroxynaphthalen-2-yl)-2-(o-tolyl)acetate (3an)



88 mg, 72% yield; colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.29 (t, *J* = 5.0 Hz, 1H), 7.85-7.83 (m, 1H), 7.76 (s, 1H), 7.55-7.53 (m, 2H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.28-7.23 (m, 4H), 5.54 (s, 1H), 3.87 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.4, 150.5, 136.5, 134.9, 134.1, 130.9, 128.2, 128.0, 127.7, 127.5, 126.4, 126.3, 125.6, 125.4, 121.7, 120.5, 116.6, 52.9, 51.7, 19.8; **HRMS** (ESI) calculated for $[C_{20}H_{18}NaO_3][M+Na]^+$: 329.1150, found: 329.1148.

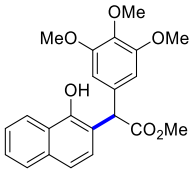
15) Methyl 2-(1-hydroxynaphthalen-2-yl)-2-(2-methoxyphenyl)acetate (3ao)



126.4 mg, 98% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 3.6 Hz, 1H), 8.20 (s, 1H), 7.76-7.74 (m, 1H), 7.45 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.28-7.21 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.88-6.83 (m, 2H), 5.30 (s, 1H), 3.84 (s, 3H), 3.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.0, 156.5, 151.4, 134.3, 128.9, 128.9, 128.8, 127.2, 126.5, 125.9, 125.3, 124.6, 122.6, 120.9, 120.3, 114.7, 110.6, 55.6, 52.8, 49.9; **HRMS** (ESI) calculated for

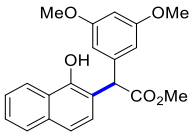
$[C_{20}H_{18}NaO_4][M+Na]^+$: 345.1097, found: 345.1099.

16) Methyl 2-(1-hydroxynaphthalen-2-yl)-2-(3,4,5-trimethoxyphenyl)acetate (3ap)



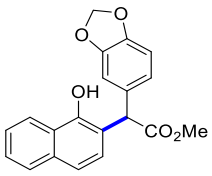
131.4 mg, 86% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.29-8.27 (m, 1H), 7.78-7.75 (m, 1H), 7.48-7.45 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.24-7.20 (m, 1H), 6.54 (s, 2H), 5.18 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.75 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.9, 153.3, 151.0, 137.5, 134.3, 132.3, 128.6, 127.3, 126.5, 126.1, 125.4, 122.3, 120.4, 116.4, 105.2, 60.7, 56.1, 55.4, 53.2; **HRMS** (EI) calculated for $[C_{22}H_{22}O_6]$: 382.1416, found: 382.1412.

17) Methyl 2-(3,5-dimethoxyphenyl)-2-(1-hydroxynaphthalen-2-yl)acetate (3aq)



101.2 mg, 82% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.29-8.27 (m, 1H), 7.76-7.74 (m, 1H), 7.47-7.44 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.42 (d, *J* = 1.6 Hz, 2H), 6.35 (t, *J* = 2.0 Hz, 1H), 5.15 (s, 1H), 3.83 (s, 3H), 3.69 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.0, 161.0, 151.2, 139.0, 134.4, 128.8, 127.2, 126.5, 126.2, 125.3, 122.5, 120.3, 116.1, 106.1, 99.0, 55.7, 55.3, 55.2, 53.2; **HRMS** (ESI) calculated for $[C_{21}H_{21}O_5][M+H]^+$: 353.1383, found: 353.1388.

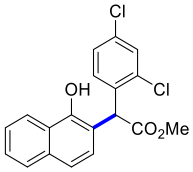
18) Methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(1-hydroxynaphthalen-2-yl)acetate (3ar)



110.2 mg, 82% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.29-8.27 (m, 1H), 7.76-7.74 (m, 1H), 7.47-7.44 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.20-7.17 (m, 1H), 6.73 (s, 1H),

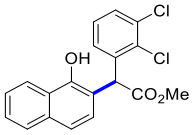
6.70 (d, *J* = 0.8 Hz, 2H), 5.87 (s, 2H), 5.12 (s, 1H), 3.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.4, 151.1, 148.0, 147.0, 134.4, 130.4, 128.7, 127.2, 126.6, 126.2, 125.4, 122.4, 120.8, 120.3, 116.3, 108.3, 101.1, 55.3, 53.2; **HRMS** (ESI) calculated for $[C_{20}H_{16}NaO_5][M+Na]^+$: 359.0890, found: 359.0893.

19) Methyl 2-(2,4-dichlorophenyl)-2-(1-hydroxynaphthalen-2-yl)acetate (3as)



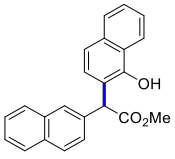
114.1 mg, 79% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21-8.18 (m, 1H), 7.78-7.75 (m, 1H), 7.63 (s, 1H), 7.48-7.40 (m, 4H), 7.20-7.11 (m, 3H), 5.48 (s, 1H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 150.9, 134.8, 134.4, 134.2, 132.9, 131.0, 129.6, 128.2, 127.5, 127.3, 126.8, 125.7, 125.6, 121.9, 121.0, 114.8, 53.3, 52.0; **HRMS** (EI) calculated for $[C_{19}H_{14}Cl_2O_3]$: 360.0320, found: 360.0317.

20) Methyl 2-(2,3-dichlorophenyl)-2-(1-hydroxynaphthalen-2-yl)acetate (3at)



125.3 mg, 87% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14-8.13 (m, 1H), 7.72-7.69 (m, 1H), 7.52 (br, 1H), 7.43-7.40 (m, 2H), 7.36-7.30 (m, 2H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.05-6.99 (m, 2H), 5.46 (s, 1H), 3.73 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.5, 151.0, 136.4, 134.5, 133.5, 132.5, 129.8, 128.4, 128.3, 127.5, 127.4, 126.8, 125.7, 121.9, 121.0, 114.7, 53.5, 53.4; **HRMS** (EI) calculated for $[C_{19}H_{14}Cl_2O_3]$: 360.0320, found: 360.0319.

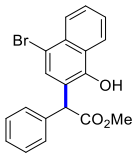
21) Methyl 2-(1-hydroxynaphthalen-2-yl)-2-(naphthalen-2-yl)acetate (3au)



101.2 mg, 74% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.30-8.28 (m, 1H),

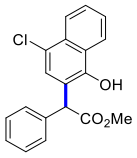
7.78-7.70 (m, 5H), 7.48-7.32 (m, 5H), 7.33 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 5.36 (s, 1H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.3, 151.4, 134.5, 134.0, 133.3, 132.6, 129.0, 128.6, 128.1, 127.5, 127.3, 126.6, 126.3, 126.1, 125.7, 125.4, 122.5, 120.4, 116.1, 55.8, 53.3; **HRMS** (ESI) calculated for $[C_{23}H_{19}O_3][M+H]^+$: 343.1329, found: 343.1335.

22) Methyl 2-(4-bromo-1-hydroxynaphthalen-2-yl)-2-phenylacetate (3ba)



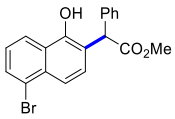
141.1 mg, 95% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.59-7.48 (m, 3H), 7.29-7.22 (m, 5H), 5.12 (s, 1H), 3.84 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.4, 151.4, 136.1, 132.5, 132.2, 128.9, 128.0, 127.8, 127.6, 127.4, 126.6, 126.1, 123.1, 116.9, 113.0, 55.6, 53.4; **HRMS** (ESI) calculated for $[C_{19}H_{15}BrNaO_3][M+Na]^+$: 393.0107, found: 393.0097.

23) Methyl 2-(4-chloro-1-hydroxynaphthalen-2-yl)-2-phenylacetate (3ca)



113.7 mg, 87% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.58-7.54 (m, 1H), 7.50-7.46 (m, 1H), 7.32-7.18 (m, 6H), 5.13 (s, 1H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.3, 150.5, 136.1, 131.2, 129.6, 128.8, 128.5, 127.7, 127.6, 127.5, 127.3, 126.1, 124.0, 123.0, 116.5, 55.4, 53.3; **HRMS** (ESI) calculated for $[C_{19}H_{16}ClO_3][M+H]^+$: 327.0782, found: 327.0784.

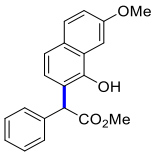
24) Methyl 2-(5-bromo-1-hydroxynaphthalen-2-yl)-2-phenylacetate (3da)



143.6 mg, 97% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.69-7.65 (m, 2H), 7.23-7.12 (m, 7H), 5.11 (s, 1H), 3.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$)

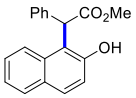
δ 176.6, 151.5, 136.3, 132.9, 130.7, 130.3, 128.8, 127.7, 127.6, 127.4, 125.6, 122.7, 122.2, 119.4, 117.0, 55.9, 53.4; **HRMS** (ESI) calculated for $[C_{19}H_{15}BrNaO_3][M+Na]^+$: 393.0097, found: 393.0095.

25) Methyl 2-(1-hydroxy-7-methoxynaphthalen-2-yl)-2-phenylacetate (3ea)



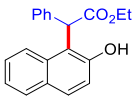
87.7 mg, 68% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.35-7.22 (m, 6H), 7.14 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 1H), 3.91 (s, 3H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.8, 157.6, 150.4, 136.6, 130.0, 128.8, 128.7, 127.5, 127.4, 126.7, 120.1, 119.6, 116.6, 100.7, 56.1, 55.3, 53.3; **HRMS** (ESI) calculated for $[C_{20}H_{18}NaO_4][M+Na]^+$: 345.1099, found: 345.1097.

26) Methyl 2-(2-hydroxynaphthalen-1-yl)-2-phenylacetate (8aa)



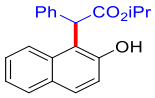
91.2 mg, 78% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.49-7.45 (m, 1H), 7.35-7.31 (m, 1H), 7.24-7.21 (m, 5H), 7.13 (d, *J* = 8.8 Hz, 1H), 5.97 (s, 1H), 3.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.4, 153.6, 136.6, 133.2, 130.3, 129.4, 128.9, 128.6, 127.8, 127.3, 127.1, 123.2, 121.8, 120.1, 115.0, 53.1, 48.3; **MS** (EI): m/z (%): 292 (M^+, 15.46), 231 (100); **HRMS** (EI) calcd. for $C_{19}H_{16}O_3$: 292.1099, found: 292.1105.

27) Ethyl 2-(2-hydroxynaphthalen-1-yl)-2-phenylacetate (8ab)[a]



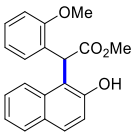
93.1 mg, 76% yield; colorless oil.

28) Isopropyl 2-(2-hydroxynaphthalen-1-yl)-2-phenylacetate (8ac)[a]



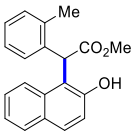
91.0 mg, 71% yield; colorless oil.

29) Methyl 2-(2-hydroxynaphthalen-1-yl)-2-(2-methoxyphenyl)acetate (8ad)



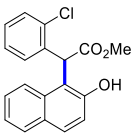
97.9 mg, 76% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.2 Hz, 2H), 7.79 (t, *J* = 9.2 Hz, 1H), 7.48-7.44 (m, 1H), 7.36-7.20 (m, 4H), 6.92 (dd, *J* = 13.2, 8.0 Hz, 2H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.01 (s, 1H), 3.90 (s, 3H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.7, 157.3, 154.5, 133.4, 130.4, 129.6, 128.9, 128.8, 127.0, 123.9, 123.2, 122.0, 120.8, 120.2, 112.4, 110.6, 55.7, 52.9, 44.1; **HRMS** (ESI) calculated for $[C_{20}H_{18}NaO_4][M+Na]^+$: 345.1099, found: 345.1097.

30) Methyl 2-(2-hydroxynaphthalen-1-yl)-2-(o-tolyl)acetate (8ae)



65.0 mg, 58% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.77 (m, 2H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.45-7.41 (m, 1H), 7.34-7.29 (m, 2H), 7.23-7.16 (m, 2H), 7.10-7.04 (m, 3H), 5.92 (s, 1H), 3.75 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.7, 153.4, 136.8, 134.4, 133.2, 130.8, 130.1, 129.5, 128.9, 128.0, 127.6, 127.1, 126.3, 123.2, 122.0, 119.5, 114.6, 52.9, 46.9, 19.9; **HRMS** (ESI) calculated for $[C_{20}H_{18}NaO_3][M+Na]^+$: 329.1149, found: 329.1148.

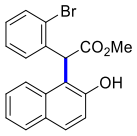
31) Methyl 2-(2-chlorophenyl)-2-(2-hydroxynaphthalen-1-yl)acetate (8af)



128.1 mg, 98% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.46-7.44 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.26 (s, 1H), 7.21-7.17 (m, 1H),

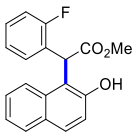
7.11-7.07 (m, 3H), 6.12 (s, 1H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2, 152.8, 134.6, 134.4, 133.1, 130.3, 130.2, 129.4, 129.3, 128.8, 128.7, 127.2, 127.0, 123.3, 122.1, 118.9, 114.8, 53.0, 46.8; **HRMS** (ESI) calculated for $[C_{19}H_{16}ClO_3][M+H]^+$: 327.0795, found: 327.0782.

32) Methyl (S)-2-(2-bromophenyl)-2-(2-hydroxynaphthalen-1-yl)acetate (8ag)



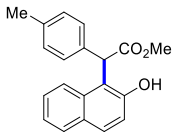
124 mg, 84% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (t, *J* = 6.8 Hz, 2H), 7.63 (q, *J* = 2.8 Hz, 2H), 7.44-7.40 (m, 1H), 7.34 (s, 1H), 7.32-7.28 (m, 1H), 7.07-7.00 (m, 4H), 6.07 (s, 1H), 3.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.1, 152.6, 136.2, 133.1, 132.7, 130.5, 130.2, 129.3, 129.0, 128.7, 127.7, 127.3, 125.5, 123.3, 122.2, 118.8, 115.3, 53.0, 49.5; **HRMS** (ESI) calculated for $[C_{19}H_{15}BrNaO_3][M+Na]^+$: 393.0097, found: 393.0099.

33) Methyl (S)-2-(2-fluorophenyl)-2-(2-hydroxynaphthalen-1-yl)acetate (8ah)



96.8 mg, 78% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.64 (s, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.22-7.19 (m, 1H), 7.12-7.10 (m, 1H), 7.09-7.04 (m, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.05 (s, 1H), 3.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.4, 161.1 (d, *J* = 244.0 Hz), 153.3, 133.1, 130.4, 129.9 (d, *J* = 3.0 Hz), 129.4, 129.3 (d, *J* = 8.0 Hz), 128.9, 127.2, 124.1 (d, *J* = 4.0 Hz), 123.6 (d, *J* = 14.0 Hz), 123.4, 121.9, 119.4, 115.2 (d, *J* = 22.0 Hz), 113.5, 53.2, 42.5; **HRMS** (ESI) calculated for $[C_{19}H_{15}FNaO_3][M+Na]^+$: 333.0897, found: 333.0894.

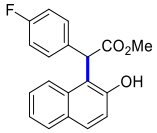
34) Methyl 2-(2-hydroxynaphthalen-1-yl)-2-(p-tolyl)acetate (8ai)



104.1 mg, 85% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.99 (d, *J* = 8.4 Hz,

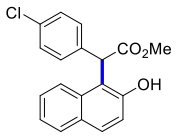
1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.50-7.46 (m, 1H), 7.36-7.32 (m, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.08 (s, 4H), 5.96 (s, 1H), 3.81 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.6, 153.8, 137.0, 133.5, 133.3, 130.3, 129.4, 129.3, 128.9, 127.5, 127.1, 123.2, 121.8, 120.4, 114.9, 53.1, 48.0, 21.0; **HRMS** (ESI) calculated for $[C_{20}H_{18}NaO_3][M+Na]^+$: 329.1151, found: 329.1148.

35) Methyl 2-(4-fluorophenyl)-2-(2-hydroxynaphthalen-1-yl)acetate (8aj)



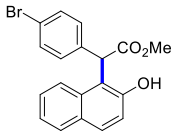
105.5 mg, 85% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92-7.69 (m, 4H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.20 (d, *J* = 5.3 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 2H), 5.88 (s, 1H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.2, 161.9 (d, *J* = 244 Hz), 153.1, 133.0, 132.4 (d, *J* = 4 Hz), 130.3, 129.7 (d, *J* = 8 Hz), 129.4, 128.9, 127.2, 123.3, 121.8, 119.7, 115.3 (d, *J* = 22 Hz), 115.2, 53.1, 47.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.26; **HRMS** (ESI) calculated for $[C_{19}H_{15}FNaO_3][M+Na]^+$: 333.0897, found: 333.0893.

36) Methyl 2-(4-chlorophenyl)-2-(2-hydroxynaphthalen-1-yl)acetate (8ak)



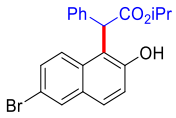
124.2 mg, 95% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.49-7.44 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.19 (dd, *J* = 24.8, 8.8 Hz, 4H), 7.09 (d, *J* = 8.8 Hz, 1H), 5.87 (s, 1H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.9, 153.1, 135.3, 133.1, 133.0, 130.4, 129.5, 129.4, 129.0, 128.6, 127.3, 123.4, 121.8, 119.7, 115.1, 53.1, 47.7; **HRMS** (ESI) calculated for $[C_{19}H_{16}ClO_3][M+H]^+$: 327.0798, found: 327.0788.

37) Methyl 2-(4-bromophenyl)-2-(2-hydroxynaphthalen-1-yl)acetate (8al)



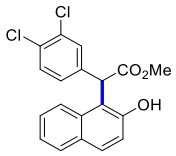
126.2 mg, 85% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.37-7.30 (m, 3H), 7.11-7.05 (m, 3H), 5.83 (s, 1H), 3.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.8, 152.9, 135.9, 132.9, 131.5, 130.3, 129.9, 129.4, 128.9, 127.2, 123.3, 121.8, 121.2, 119.5, 115.1, 53.1, 47.8; **HRMS** (ESI) calculated for $[C_{19}H_{15}BrNaO_3][M+Na]^+$: 393.0097, found: 393.0101.

38) Isopropyl 2-(6-bromo-2-hydroxynaphthalen-1-yl)-2-phenylacetate (8bc)



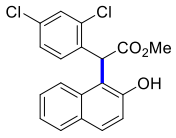
84.6 mg, 68% yield; white solid. The chemical shifts of **8bc** is consistent with previously reported structure.[1]

39) Methyl 2-(3,4-dichlorophenyl)-2-(2-hydroxynaphthalen-1-yl)acetate (8am)



124.3 mg, 86% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.34 (s, 1H), 7.31-7.27 (m, 2H), 6.97-6.87 (m, 3H), 6.12 (s, 1H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.9, 152.5, 137.0, 133.0, 132.9, 132.8, 130.3, 129.6, 129.3, 128.8, 128.5, 127.4, 127.3, 123.4, 121.9, 118.5, 114.9, 53.0, 47.6; **MS** (EI): m/z (%): 360 (M^+, 0.96), 328 (100); **HRMS** (EI) calcd. for $C_{19}H_{14}O_3Cl_2$: 360.0320, found:360.0323.

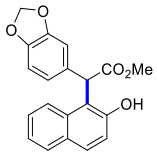
40) Methyl 2-(2,4-dichlorophenyl)-2-(2-hydroxynaphthalen-1-yl)acetate (8an)



122.8 mg, 85% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (ddd, *J* = 6.8 Hz, 3H), 7.51-

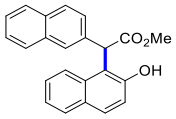
7.48 (m, 2H), 7.40-7.36 (m, 1H), 7.12-7.07 (m, 3H), 7.03 (d, *J* = 6.8 Hz, 1H), 6.08 (s, 1H), 3.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6, 152.8, 135.2, 134.0, 133.0, 131.2, 130.6, 129.5, 129.3, 128.9, 127.5, 127.3, 123.6, 121.9, 119.0, 114.1, 53.2, 46.4; **MS** (EI): m/z (%): 360 (M^+, 11.16), 328 (100); **HRMS** (EI) calcd. for $C_{19}H_{14}O_3Cl_2$: 360.0320, found:360.0321.

41) Methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(2-hydroxynaphthalen-1-yl)acetate (8ao)



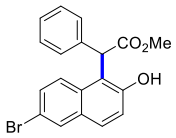
102.2 mg, 71% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.93 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.49-7.45 (m, 1H), 7.35-7.33 (m, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.71 (d, *J* = 3.6 Hz, 3H), 5.85 (s, 2H), 5.84 (s, 1H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.3, 153.3, 147.9, 146.8, 133.1, 130.4, 130.2, 129.4, 128.9, 127.2, 123.3, 121.7, 121.1, 120.0, 115.2, 108.6, 108.1, 101.0, 53.1, 48.1; **MS** (EI): m/z (%): 336 (M^+, 7.28), 304 (100); **HRMS** (EI) calcd. for $C_{20}H_{16}O_5$: 336.0998, found: 336.0995.

42) Methyl 2-(2-hydroxynaphthalen-1-yl)-2-(naphthalen-2-yl)acetate (8ap)



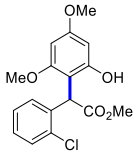
112.2 mg, 82% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.76 (d, *J* = 5.6 Hz, 1H), 7.74-7.66 (m, 5H), 7.51-7.47 (m, 1H), 7.42-7.39 (m, 2H), 7.37-7.33 (m, 1H), 7.29 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.15 (d, *J* = 9.2 Hz, 1H), 6.13 (s, 1H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.3, 153.9, 133.9, 133.3, 133.2, 132.6, 130.4, 129.5, 129.0, 128.4, 128.0, 127.5, 127.2, 126.3, 126.2, 126.0, 125.9, 123.3, 121.8, 120.3, 114.8, 53.2, 48.5; **MS** (EI): m/z (%): 342 (M^+, 22.13), 310 (100); **HRMS** (EI) calcd. for $C_{23}H_{18}O_3$: 342.1256, found: 342.1255.

43) Methyl 2-(6-bromo-2-hydroxynaphthalen-1-yl)-2-phenylacetate (8ba)



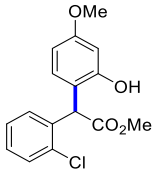
119.9 mg, 81% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.79 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.38 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.15-7.08 (m, 5H), 6.97 (d, *J* = 9.2 Hz, 1H), 5.78 (s, 1H), 3.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 153.5, 136.4, 131.7, 130.7, 130.5, 130.2, 129.2, 128.6, 127.9, 127.4, 123.9, 120.9, 116.9, 115.6, 53.1, 48.4; **HRMS** (ESI) calculated for $[C_{19}H_{15}BrNaO_3][M+Na]^+$: 393.0097, found: 393.0103.

44) Methyl 2-(2-chlorophenyl)-2-(2-hydroxy-4,6-dimethoxyphenyl)acetate (10a)



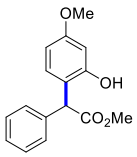
131.7 mg, 98% yield; colorless oil. **^{1}H NMR** (400 MHz, DMSO-*d*6) δ 9.62 (s, 1H), 7.19-7.17 (m, 1H), 6.99-6.95 (m, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.93 (s, 2H), 5.34 (s, 1H), 3.50 (s, 3H), 3.46 (s, 3H), 3.34 (d, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO-*d*6) δ 172.0, 160.1, 158.6, 156.3, 136.6, 134.1, 130.2, 128.7, 128.2, 126.7, 106.3, 93.9, 90.1, 55.7, 54.9, 51.6, 42.9; **MS** (EI): m/z (%): 336 (M^+, 11.52), 304 (100).

45) Methyl 2-(2-chlorophenyl)-2-(2-hydroxy-4-methoxyphenyl)acetate (10b)



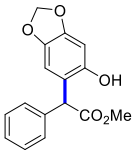
111.6 mg, 91% yield; colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43-7.42 (m, 1H), 7.28-7.23 (m, 3H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.75-6.73 (m, 1H), 6.50-6.46 (m, 2H), 5.49 (s, 1H), 3.80 (s, 3H), 3.78 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.5, 160.5, 155.4, 135.1, 134.2, 131.2, 129.9, 129.7, 128.8, 126.9, 115.0, 106.5, 102.8, 55.3, 52.9, 50.2 ; **MS** (EI): m/z (%): 306 (M^+, 26.89), 211 (100). **HRMS** (EI) calcd. for $C_{16}H_{15}ClO_4$: 306.0659, found: 306.0664.

46) Methyl 2-(2-hydroxy-4-methoxyphenyl)-2-phenylacetate (10c)



103.4 mg, 95% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (br, 1H), 7.22-7.14 (m, 5H), 6.85 (dd, *J* = 6.4, 2.8 Hz, 1H), 5.02 (s, 1H), 3.66 (s, 3H), 3.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.6, 160.3, 155.4, 137.3, 131.1, 128.6, 128.0, 127.3, 116.8, 106.2, 102.9, 55.2, 53.0, 52.7; **MS** (EI): m/z (%): 272 (M^+, 24.55), 240 (100). The chemical shifts of **10c** is consistent with previously reported structure.[2]

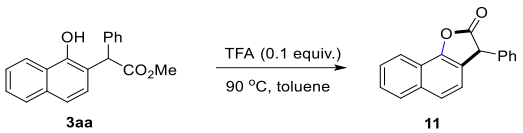
47) Methyl 2-(6-hydroxybenzo[d][1,3]dioxol-5-yl)-2-phenylacetate (10d)



86.9 mg, 76% yield; colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.15 (m, 5H), 6.84 (br, 1H), 6.45 (s, 1H), 6.30 (s, 1H), 5.75 (s, 2H), 5.03 (s, 2H), 3.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2, 149.2, 147.6, 141.4, 137.1, 128.7, 128.1, 127.4, 116.3, 109.5, 101.1, 99.3, 52.8, 52.7; **MS** (EI): m/z (%): 286 (M^+, 23.65), 254 (100); **HRMS** (EI) calcd. for $C_{16}H_{14}O_5$: 286.0841, found: 286.0839.

4. Synthetic Application

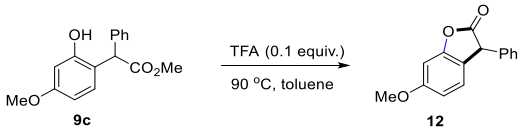
1) 3-Phenylnaphtho[1,2-b]furan-2(3H)-one (11)



3aa **11**

The general procedure was followed using **3aa** (1 mmol, 292 mg) and TFA (11.4 mg, 0.1 mmol) was heated to 90 °C for 6 h. Then the reaction was cooled to room temperature and purified by column chromatography (PE/EA 10:1), **11** (257.4 mg, 99%) was obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.80(d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.53-7.45 (m, 2H), 7.30-7.24 (m, 3H), 7.20-7.15 (m, 3H), 4.96 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.6, 149.6, 135.1, 134.1, 129.1, 128.3, 128.2, 128.1, 126.9, 124.4, 121.5, 121.2, 119.8, 50.7; **HRMS** (EI) calculated for [$C_{18}H_{12}O_2$]: 260.0837, found: 260.0835. The chemical shifts of **11** is consistent with previously reported structure.[1]

2) 3-Phenylnaphtho[1,2-b]furan-2(3H)-one (12)

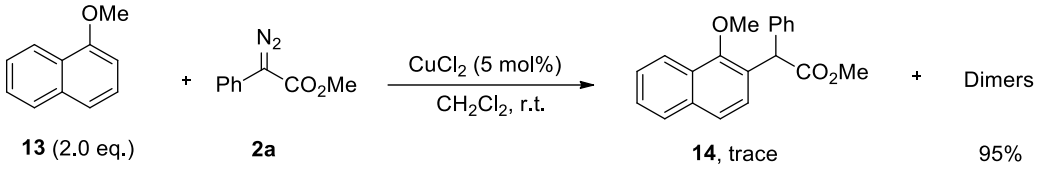


9c **12**

The general procedure was followed using **9c** (1 mmol, 272.3 mg) and TFA (11.4 mg, 0.1 mmol) was heated to 90 °C for 8 h. Then the reaction was cooled to room temperature and. After purification by column chromatography (PE/EA 10:1), **12** (237.9 mg, 95%) was obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 3H), 7.16-7.14 (m, 2H), 7.01 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 6.63 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.76 (s, 1H), 3.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.5, 160.8, 154.9, 135.5, 129.0, 128.1, 128.0, 125.7, 118.6, 110.2, 97.4, 55.7, 49.3; **HRMS** (EI) calculated for [$C_{15}H_{12}O_3$]: 240.0786, found: 240.0788.

5. Mechanistic studies

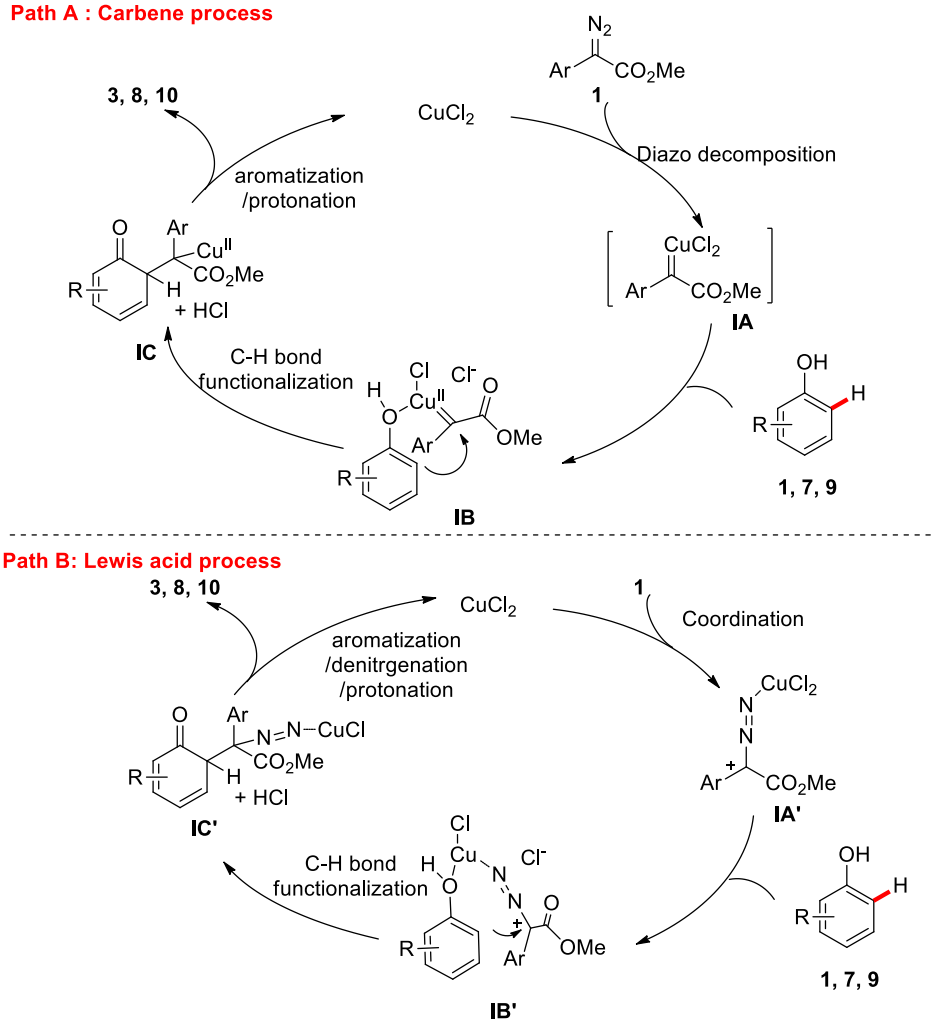
1) The role of hydroxyl



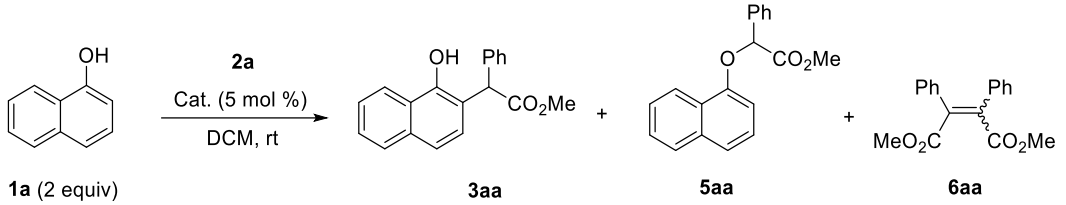
The reaction of 1-methoxynaphthalene **13** with the diazoester **2a** in standard condition only delivered a trace amount of *ortho*-selective C–H bond functionalization products **14**. This result indicated that the hydroxyl was vital not only for site-selectivity but also for reactivity.

2) Passible catalytic pathway

In this reaction, two possible catalytic cycles were proposed as below. Path A is Cu-carbene pathway, while path B is Lewis acid pathway, in which $CuCl_2$ served as Lewis acid via coordinating nitrogen of diazo compounds to activate the substrate.



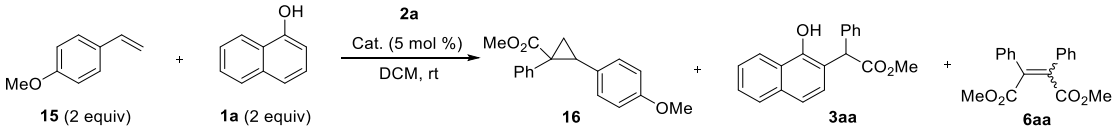
We did the reaction using the well-known Lewis acids (BF_3 and scandium triflate) and the results were shown as below. Although the yield were low (entry 1, 2), these result indicated that the Lewis acid process (Path B) should be involving in this reaction.



1a (2 equiv) **3aa** **5aa** **6aa**

Entry	Cat.	Time (h)	**3aa/5aa/6aa (%)**
1	$Sc(OTf)_3$	12	25/5/62
2	$BF_3{\cdot}OEt_2$	12	30/3/63

In order to further understand this reaction, we did several control experiments. From the results, the Lewis acid cannot catalyze the cyclopropanation (entry 1, 2) while both Cu(I) and Cu(II) can catalyze the cyclopropanation (entry 3-2). This results indicated that $CuCl_2$ can decompose diazo **2a** to form copper-carbene. In addition, the formation of Cu(II)-carbene of $CuCl_2$ and α-aryl-α-diazoacetate was also supported by DFT calculation[3]. The Cu(II)-carbene should be reasonable in this case.

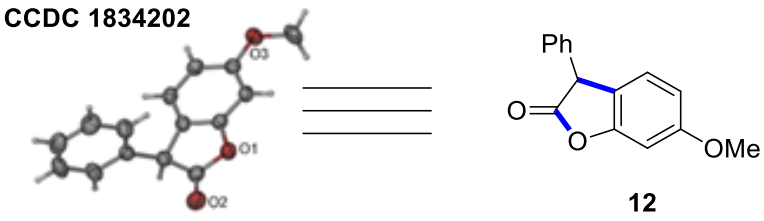


15 (2 equiv) **1a** (2 equiv) **16** **3aa** **6aa**

Entry	Cat.	Time (h)	**16/3aa/6aa (%)**
1	$Sc(OTf)_3$	12	Trace/20/73
2	$BF_3{\cdot}OEt_2$	12	Trace/27/68
3	CuCl	12	45/10/40
4	CuOTf	10	27/20/35
5	$CuCl_2$	12	46/37/-

In conclusion, we suggested that $CuCl_2$ served as dual catalyst in this reaction. Both Path A and Path B were existed together in this reaction.

6. Crystal structure of 12



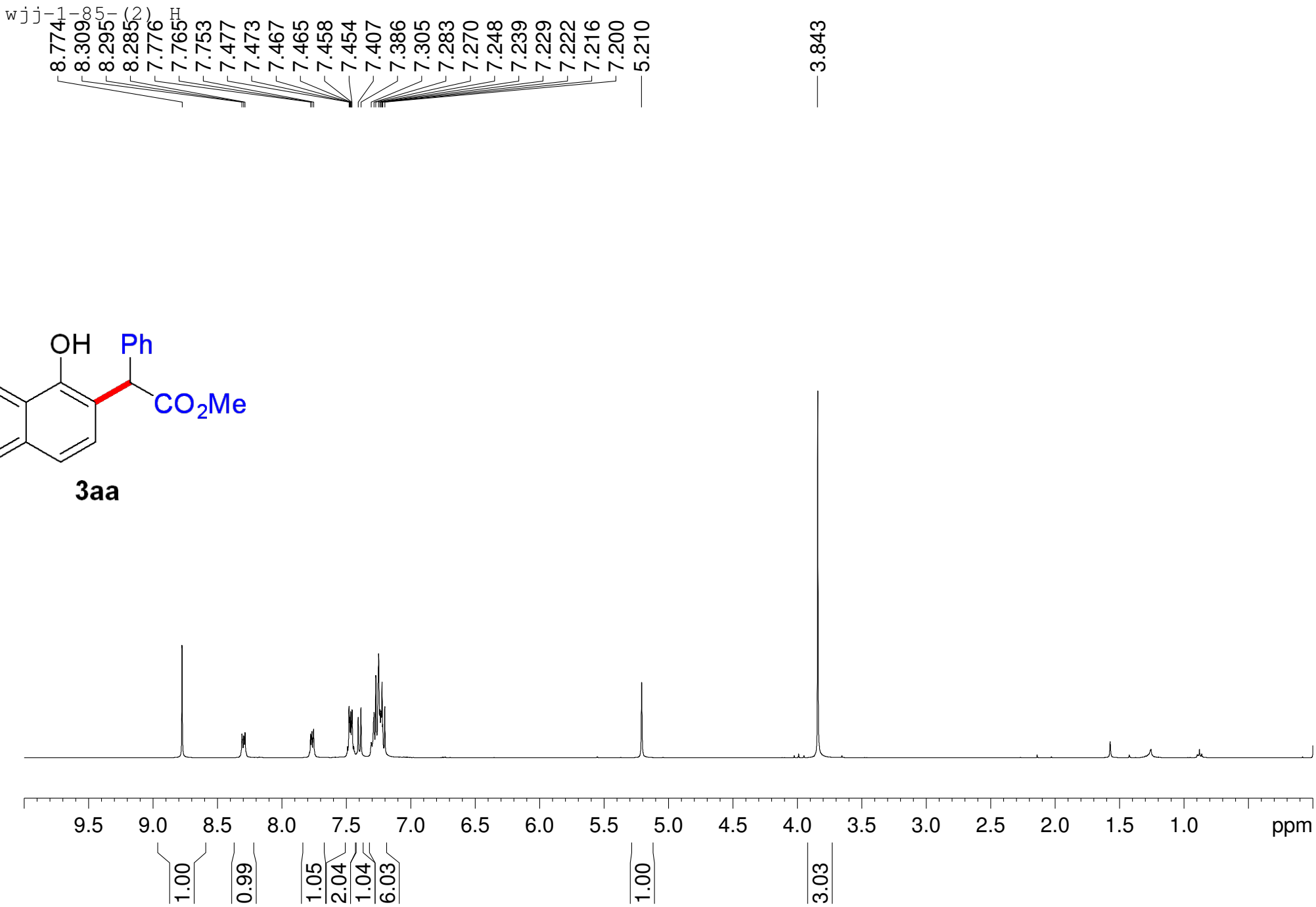
7. Reference

1 Z. Yu, Y. Li, P. Zhang, L. Liu and J. Zhang, *Chem. Sci.*, 2019, **10**, 6553.

2 Z. Yu, B. Ma, M. Chen, H.-H. Wu, L. Liu and J. Zhang, *J. Am. Chem. Soc*. 2014, **136**, 6904;

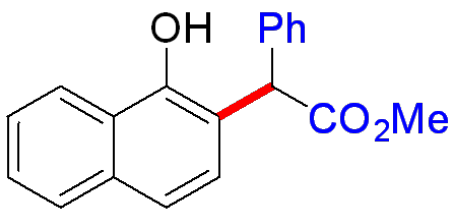
3 F. Li, J. Z. Zhang and F. Xia, *J. Phys. Chem. A* 2020, **124**, 2029.

8. NMR spectra of new compounds


wjj-1-85-(2) H
8.774
8.309
8.295
8.285
7.776
7.765
7.753
7.477
7.473
7.467
7.465
7.458
7.454
7.407
7.386
7.305
7.283
7.270
7.248
7.239
7.229
7.222
7.216
7.200
5.210
3.843
OH
Ph
CO2Me
3aa
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.99
1.05
2.04
1.04
6.03
1.00
3.03

wjj-1-85-(2)

176.56
151.34
136.61
134.41
129.03
128.73
127.54
127.51
127.23
126.61
126.30
125.39
122.54
120.27
116.02
77.32
77.00
76.68
55.85
53.27



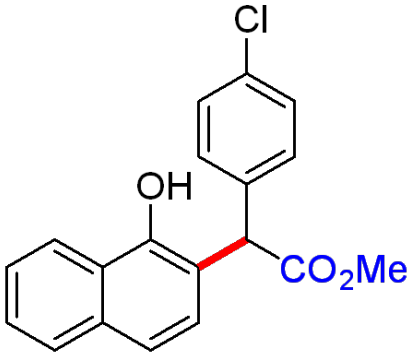
3aa

mb-9-120

8.620
8.287
8.274
8.264
7.785
7.775
7.762
7.492
7.481
7.470
7.418
7.397
7.265
7.244
7.204
7.181
7.158

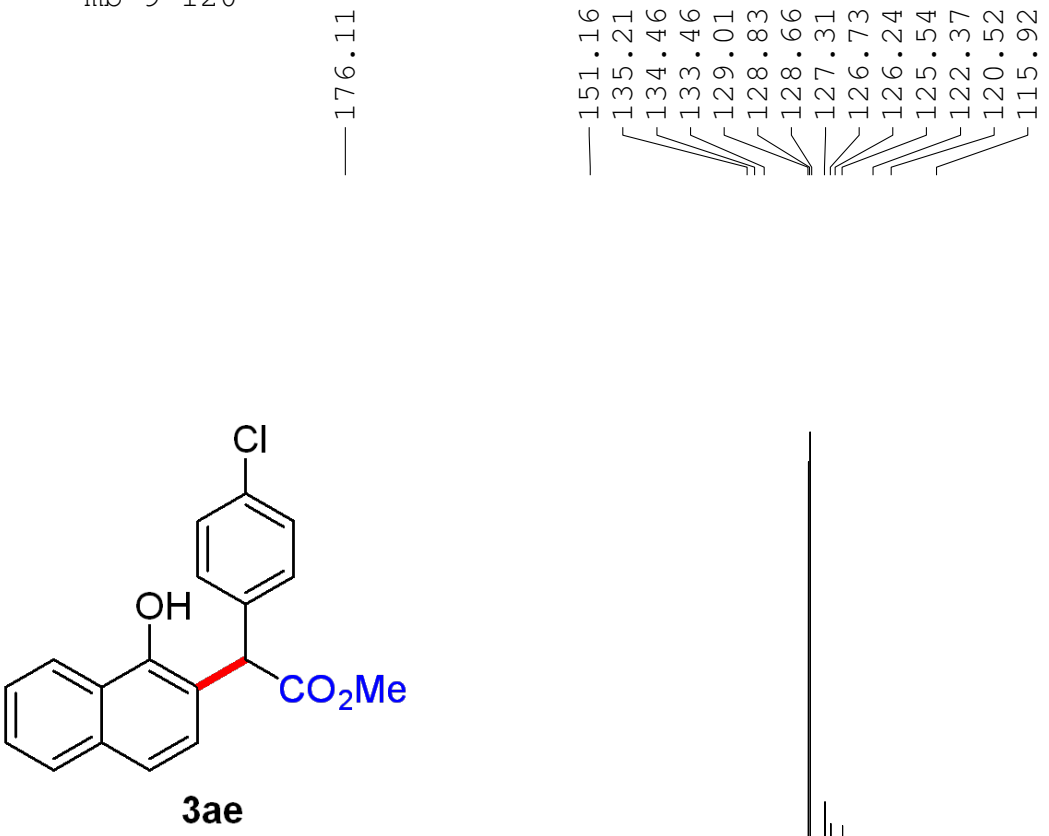
5.165

3.853



3ae

mb-9-120


Cl
OH
CO2Me

3ae

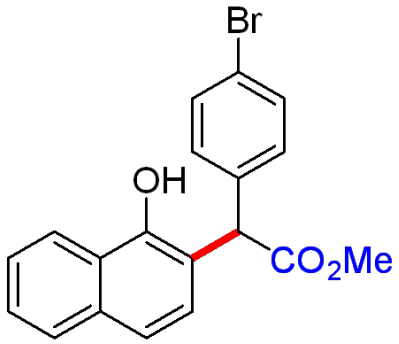
176.11
151.16
135.21
134.46
133.46
129.01
128.83
128.66
127.31
126.73
126.24
125.54
122.37
120.52
115.92
77.32
77.00
76.68
54.95
53.32
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

mb-9-140-2

8.570
8.269
8.256
8.245
7.765
7.759
7.755
7.742
7.470
7.467
7.457
7.446
7.444
7.398
7.393
7.377
7.372
7.185
7.164
7.107
7.086

5.141

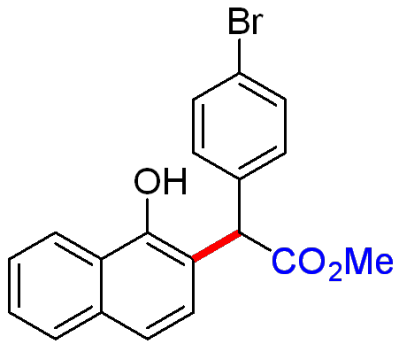
3.817



3af

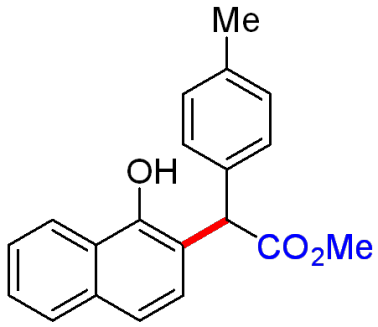
mb-9-140-2

176.00
151.10
135.74
134.43
131.76
129.35
128.61
127.30
126.71
126.18
125.52
122.32
121.56
120.52
115.88
77.32
77.00
76.68
54.94
53.33



3af

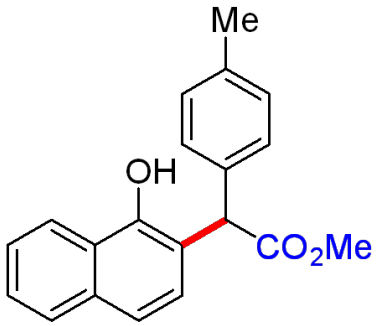
mb-9-121-1_500M



3ag

mb-9-121-1 500M

176.63
151.19
137.19
134.32
133.61
129.38
128.92
127.37
127.18
126.49
126.23
125.29
122.46
120.19
116.31
77.25
77.00
76.74
55.35
53.12
20.92



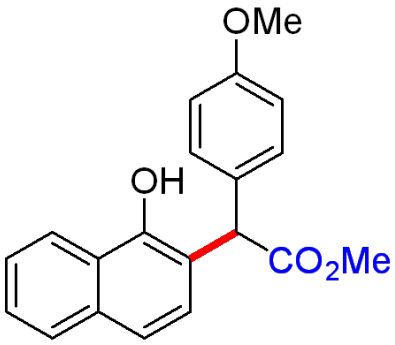
3ag

mb-9-121-1

8.760
8.306
8.292
8.282
7.766
7.755
7.742
7.467
7.462
7.457
7.454
7.448
7.443
7.392
7.371
7.205
7.184
7.169
7.148
6.817
6.795

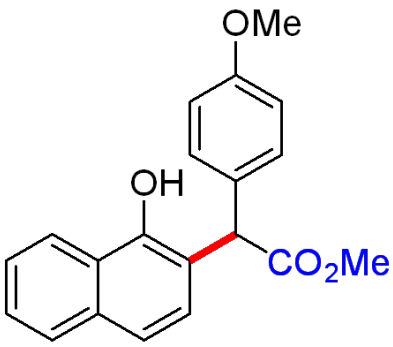
5.150

3.821
3.724



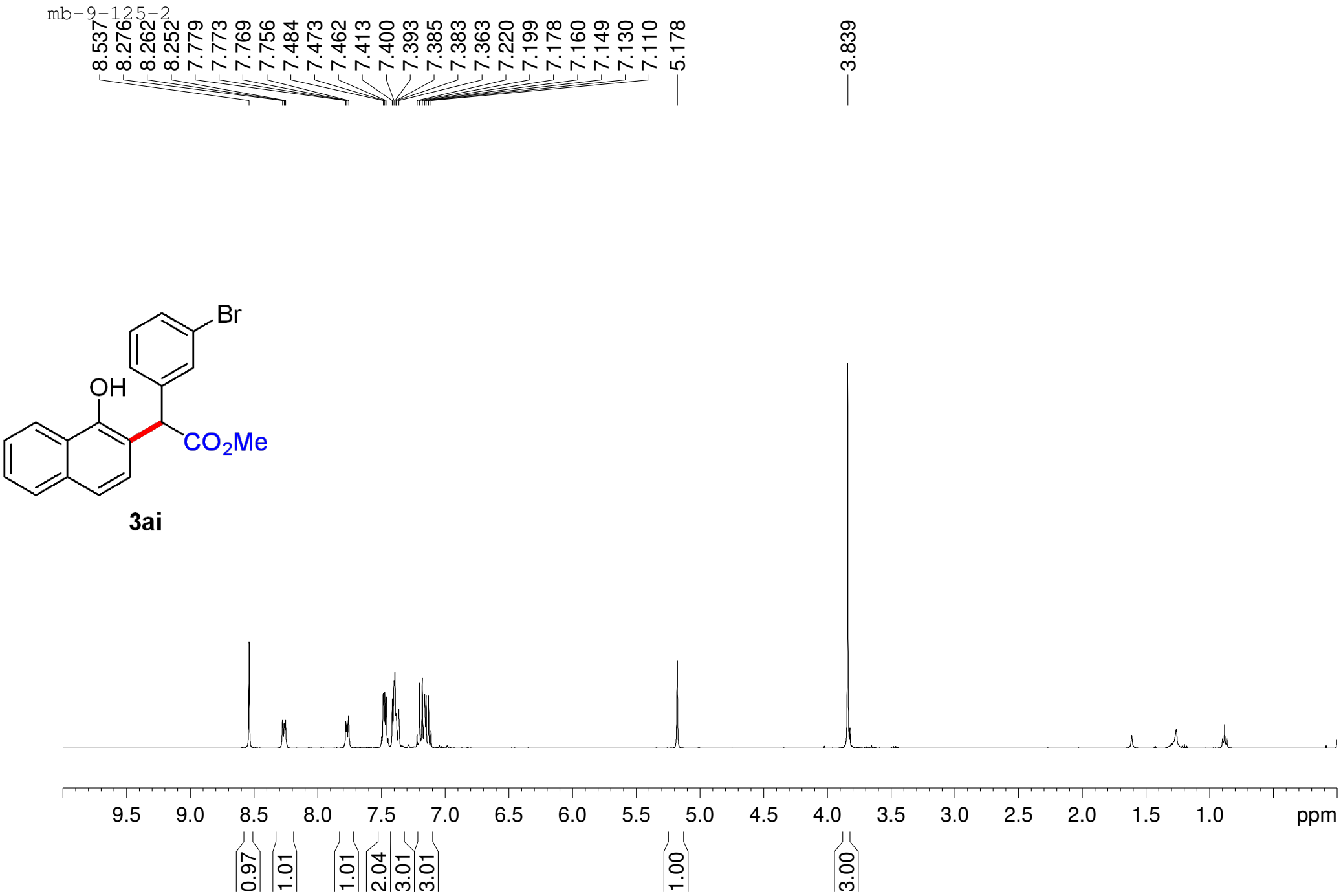
3ah

mb-9-134-2


OMe
OH
CO2Me

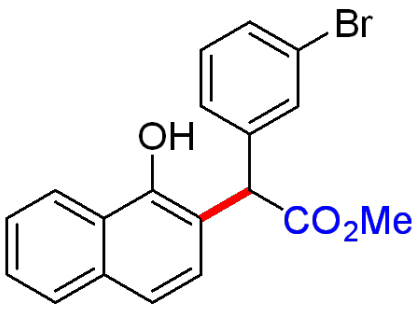
3ah

176.69
158.92
151.22
134.36
128.91
128.69
128.64
127.21
126.54
126.28
125.34
122.50
120.23
116.37
114.12
77.32
77.00
76.68
55.19
55.06
53.17
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

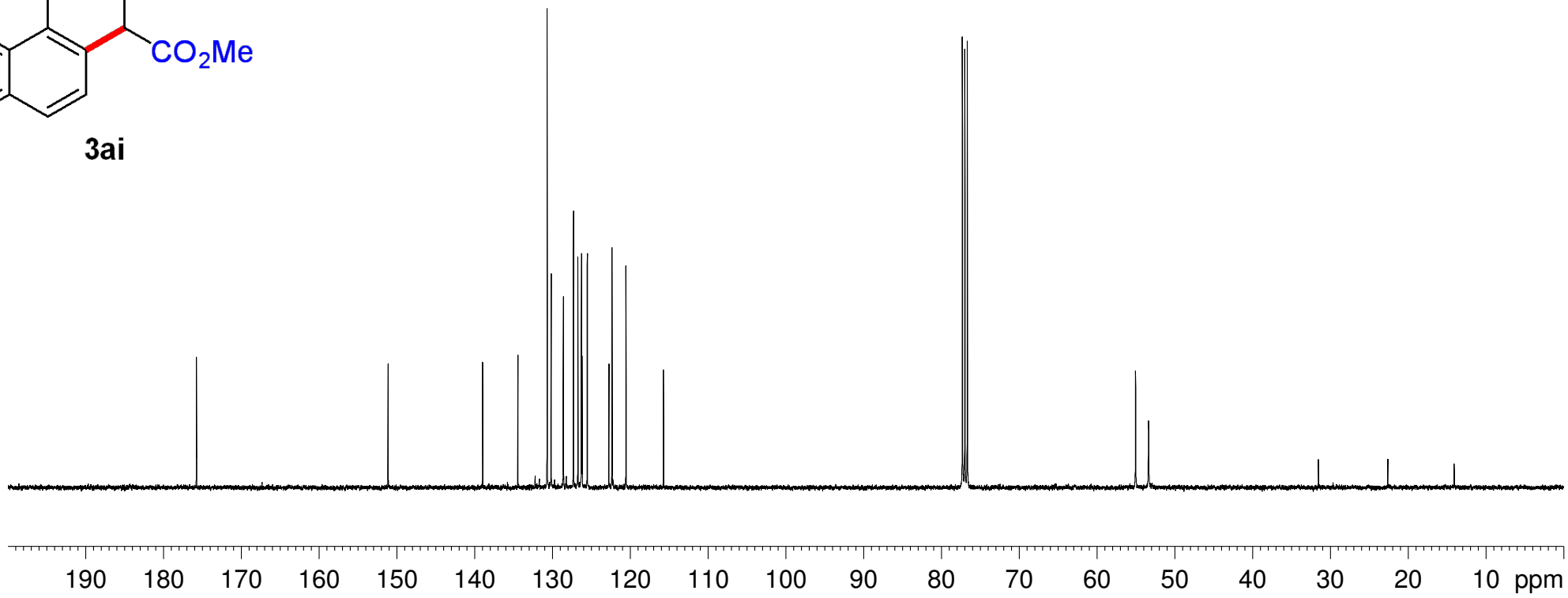

mb-9-125-2
8.537
8.276
8.262
8.252
7.779
7.773
7.769
7.756
7.484
7.473
7.462
7.413
7.400
7.393
7.385
7.383
7.363
7.220
7.199
7.178
7.160
7.149
7.130
7.110
5.178
3.839
Br
OH
CO2Me
3ai
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.97
1.01
1.01
2.04
3.01
3.01
1.00
3.00

mb-9-125-2

175.79
151.15
139.01
134.47
130.71
130.20
128.62
127.33
126.75
126.30
126.22
125.55
122.78
122.36
120.57
115.75
77.32
77.00
76.69
55.06
53.40

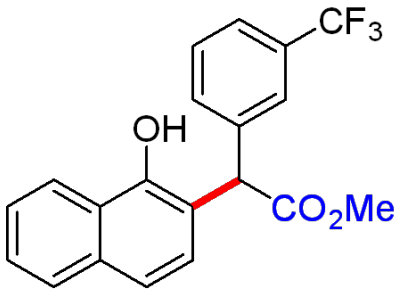


3ai



mb-9-121-2

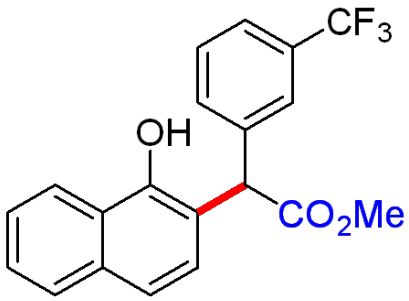
8.461
8.263
8.248
8.239
7.785
7.775
7.762
7.541
7.497
7.489
7.486
7.476
7.466
7.427
7.421
7.407
7.394
7.375
7.221
7.200
5.268
3.848



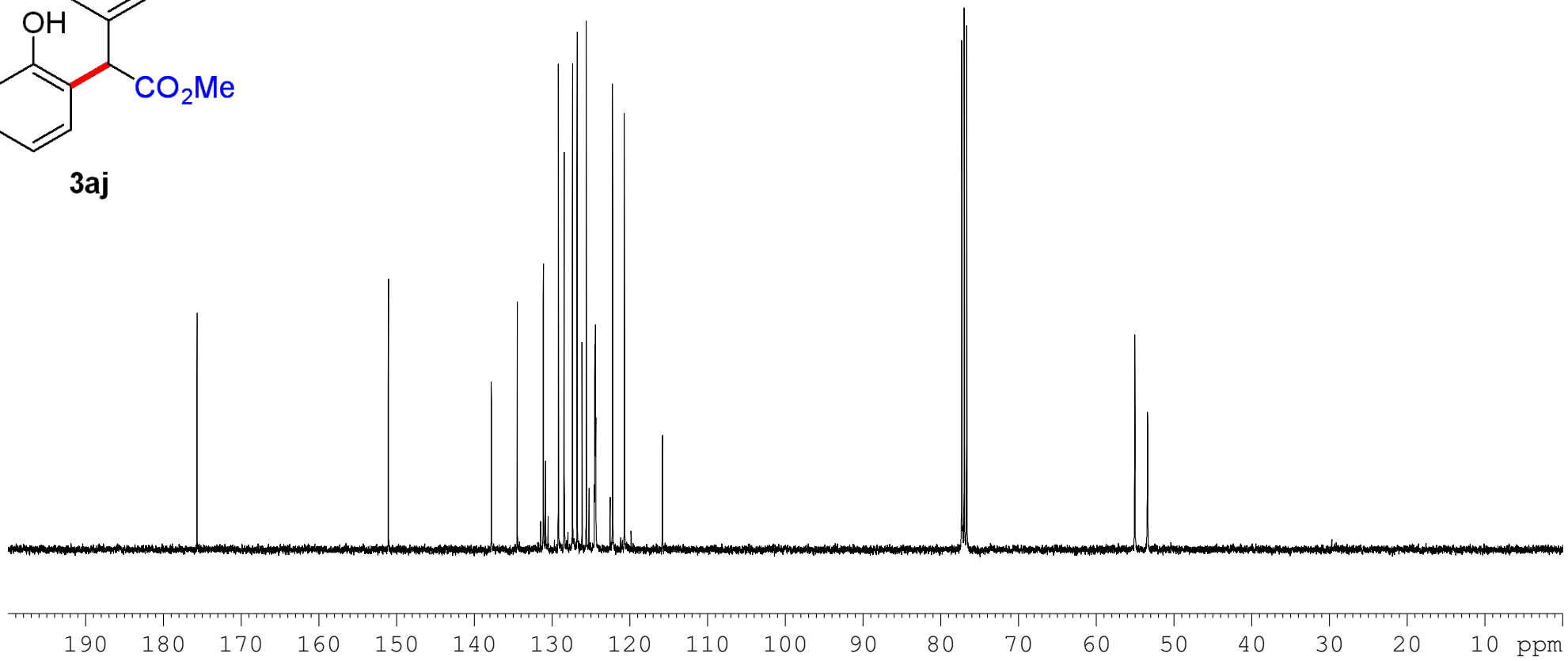
3aj

mb-9-121-2

175.71
151.09
137.85
134.51
131.51
131.15
130.86
130.54
129.22
128.47
127.99
127.40
126.81
126.18
125.63
125.28
124.55
124.51
124.46
124.42
122.57
122.25
120.73
119.86
115.83
77.32
77.00
76.68
55.06
53.43

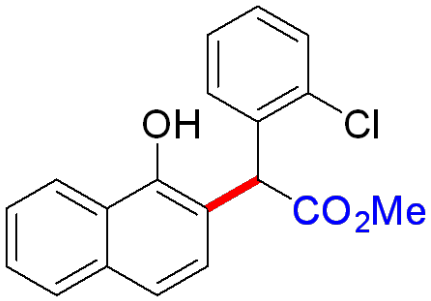


3aj



mb-9-125-1

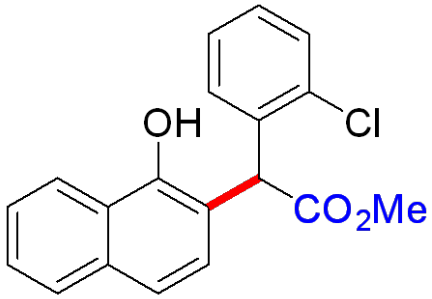
8.266
8.250
8.242
7.786
7.778
7.774
7.762
7.493
7.487
7.484
7.479
7.476
7.469
7.427
7.415
7.411
7.406
7.395
7.393
7.242
7.224
7.215
7.212
7.204
7.192
7.174
7.171
7.155
7.152
5.507
3.796



3ak

mb-9-125-1

174.98
151.14
134.43
134.16
133.99
130.03
129.85
129.07
128.60
127.44
127.08
126.72
125.83
125.59
122.13
120.78
114.74
77.32
77.00
76.68
53.27
52.87

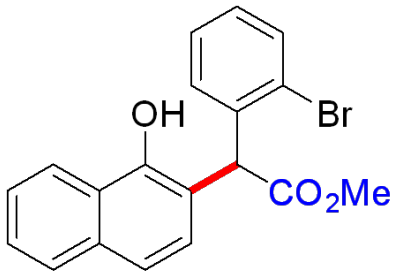


3ak

mb-9-134-1

8.207
7.776
7.767
7.757
7.752
7.599
7.596
7.579
7.576
7.551
7.480
7.473
7.470
7.466
7.462
7.456
7.416
7.395
7.277
7.274
7.258
7.255
7.216
7.195
7.131
7.127
7.112
7.108
7.093
7.089
5.550

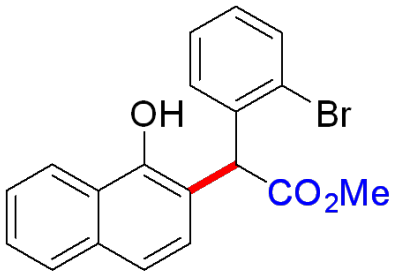
3.785



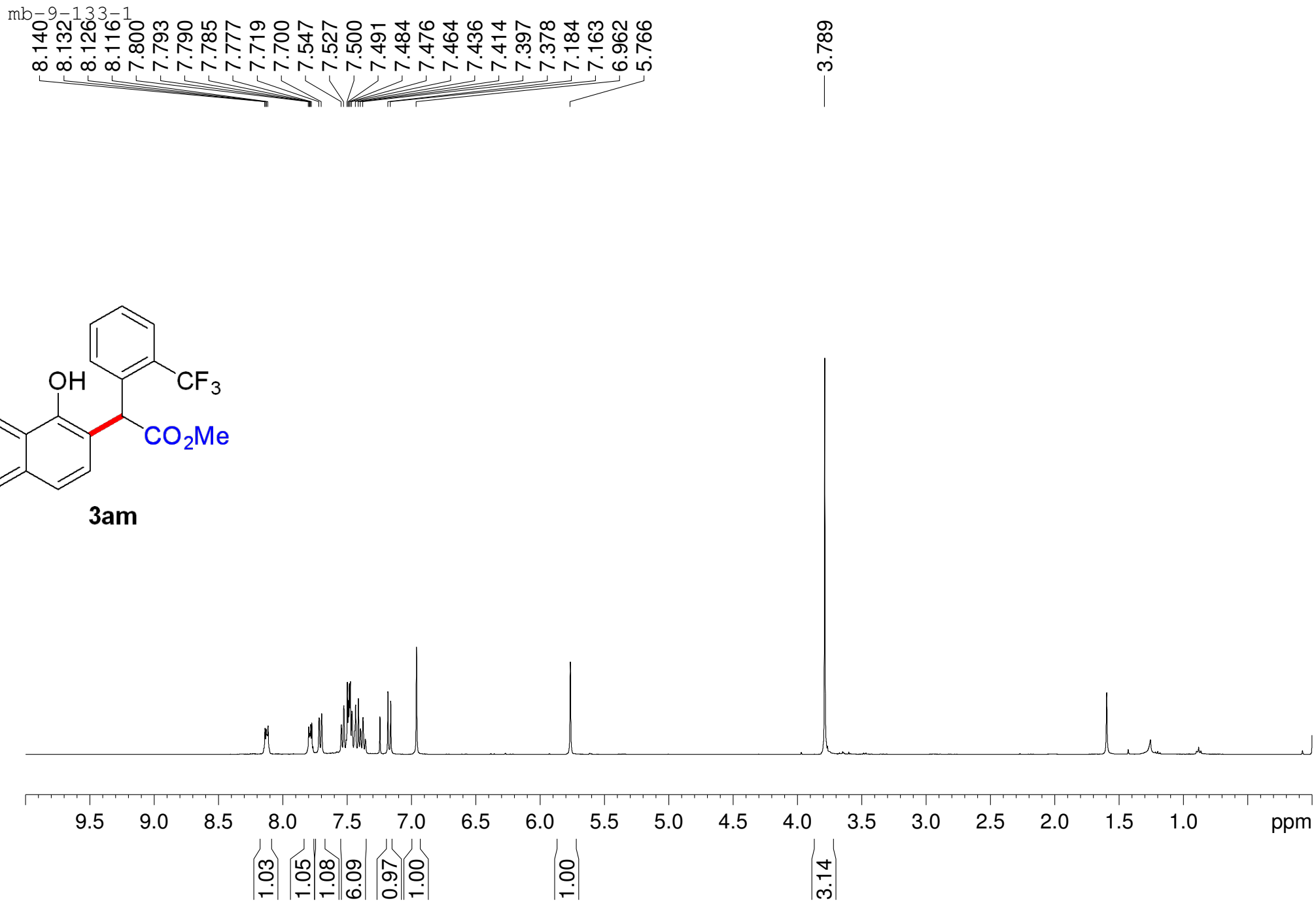
3al

mb-9-134-1

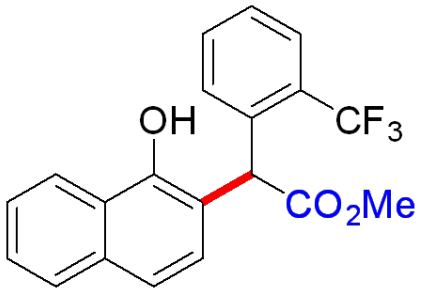
174.64
150.80
135.86
134.34
133.22
130.31
129.26
128.32
127.69
127.49
126.66
125.70
125.59
124.78
121.94
120.80
115.42
77.32
77.00
76.68
54.79
53.21



3al

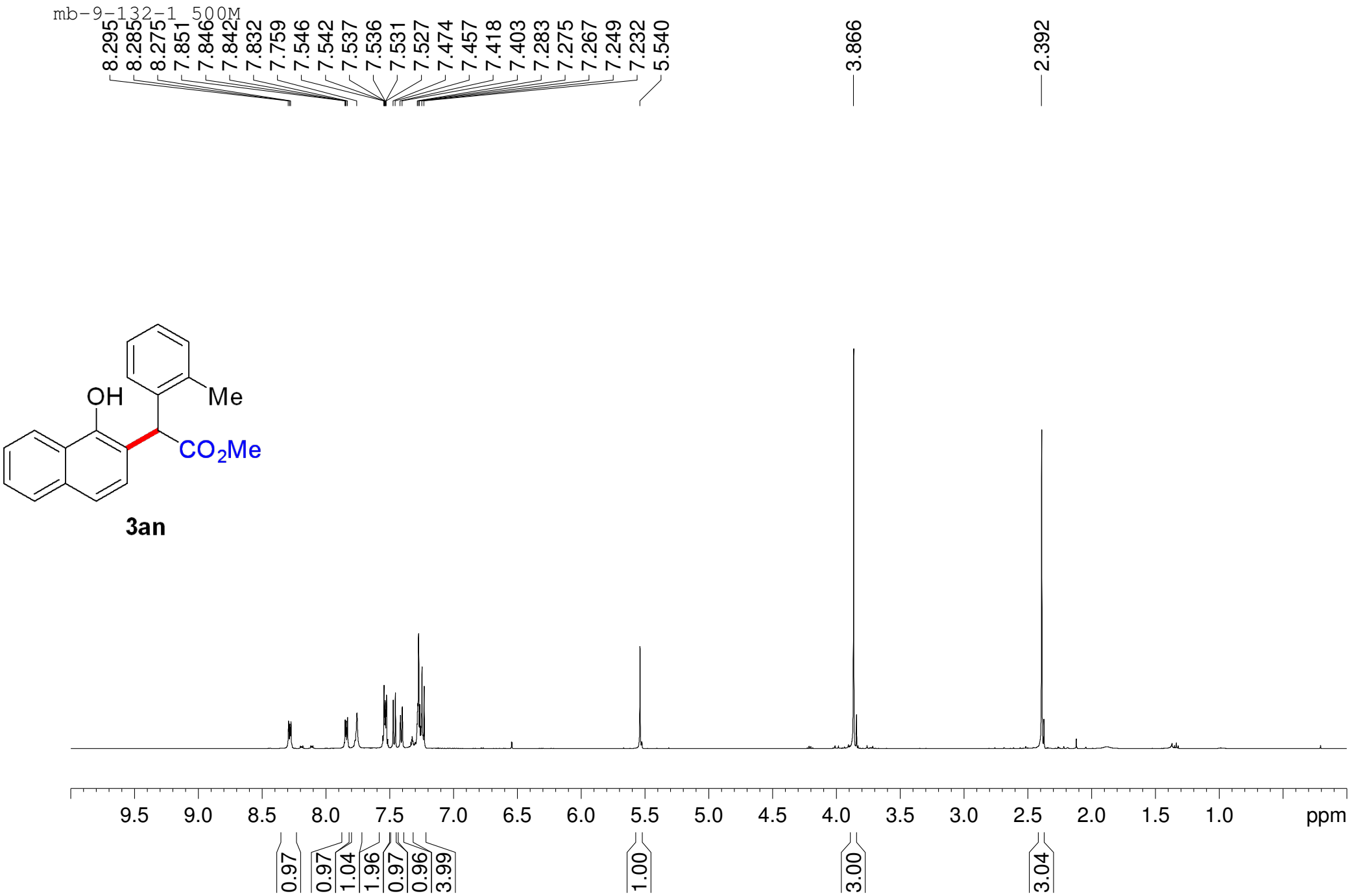

mb-9-133-1
8.140
8.132
8.126
8.116
7.800
7.793
7.790
7.785
7.777
7.719
7.700
7.547
7.527
7.500
7.491
7.484
7.476
7.464
7.436
7.414
7.397
7.378
7.184
7.163
6.962
5.766
3.789
OH
CF3
CO2Me
3am
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.03
1.05
1.08
6.09
0.97
1.00
1.00
3.14

mb-9-133-1


OH
CF3
CO2Me

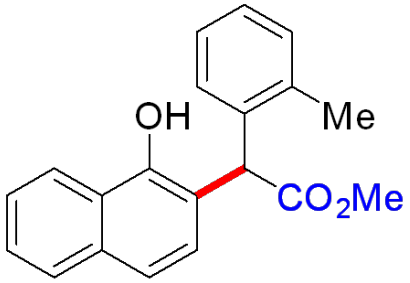
3am

174.15
149.81
135.59
134.16
132.29
131.28
128.90
128.60
128.30
128.01
127.76
127.73
127.45
126.60
126.37
126.31
126.25
126.19
125.77
125.41
123.09
121.28
120.90
117.21
77.32
77.00
76.68
53.08
49.74
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

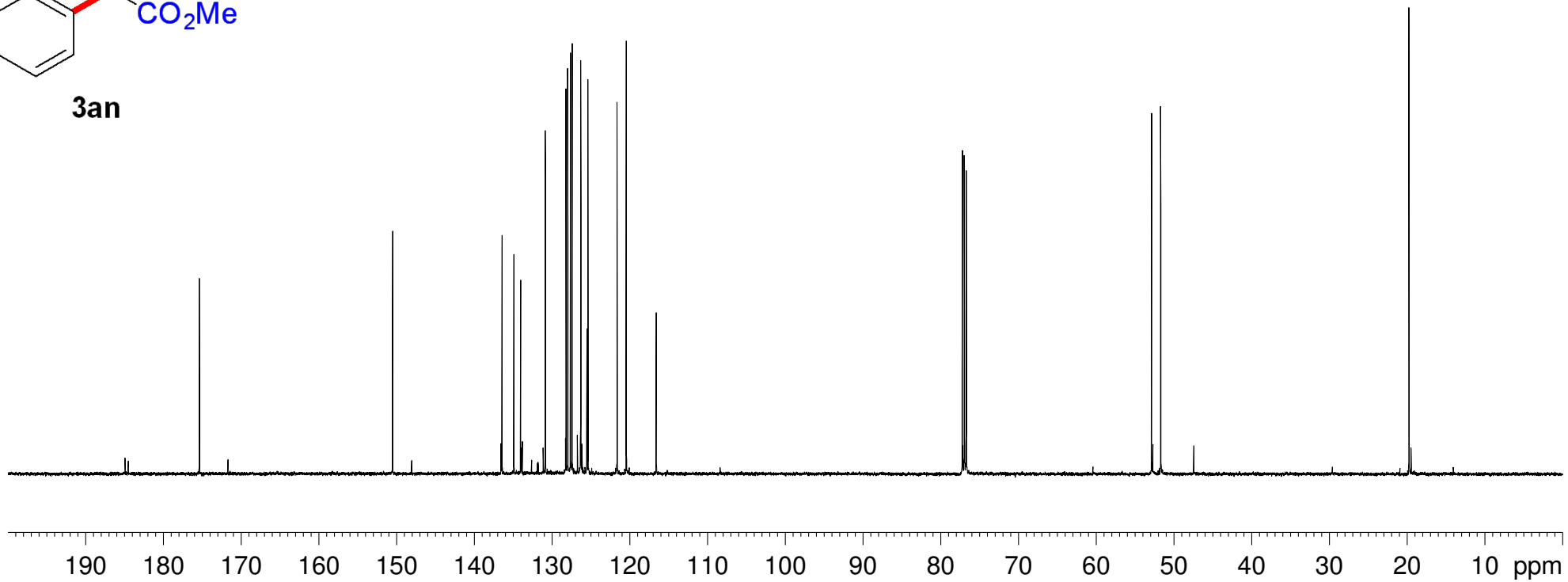

mb-9-132-1_500M
8.295
8.285
8.275
7.851
7.846
7.842
7.832
7.759
7.546
7.542
7.537
7.536
7.531
7.527
7.474
7.457
7.418
7.403
7.283
7.275
7.267
7.249
7.232
5.540
3.866
2.392
OH
Me
CO2Me
3an
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.97
0.97
1.04
1.96
0.97
0.96
3.99
1.00
3.00
3.04

mb-9-132-1 500M

175.35
150.50
136.47
134.94
134.08
130.89
128.24
128.02
127.67
127.46
126.36
126.33
125.56
125.42
121.67
120.49
116.63
77.25
77.00
76.74
52.91
51.73
19.80

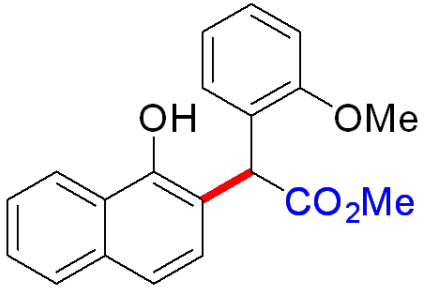


3an

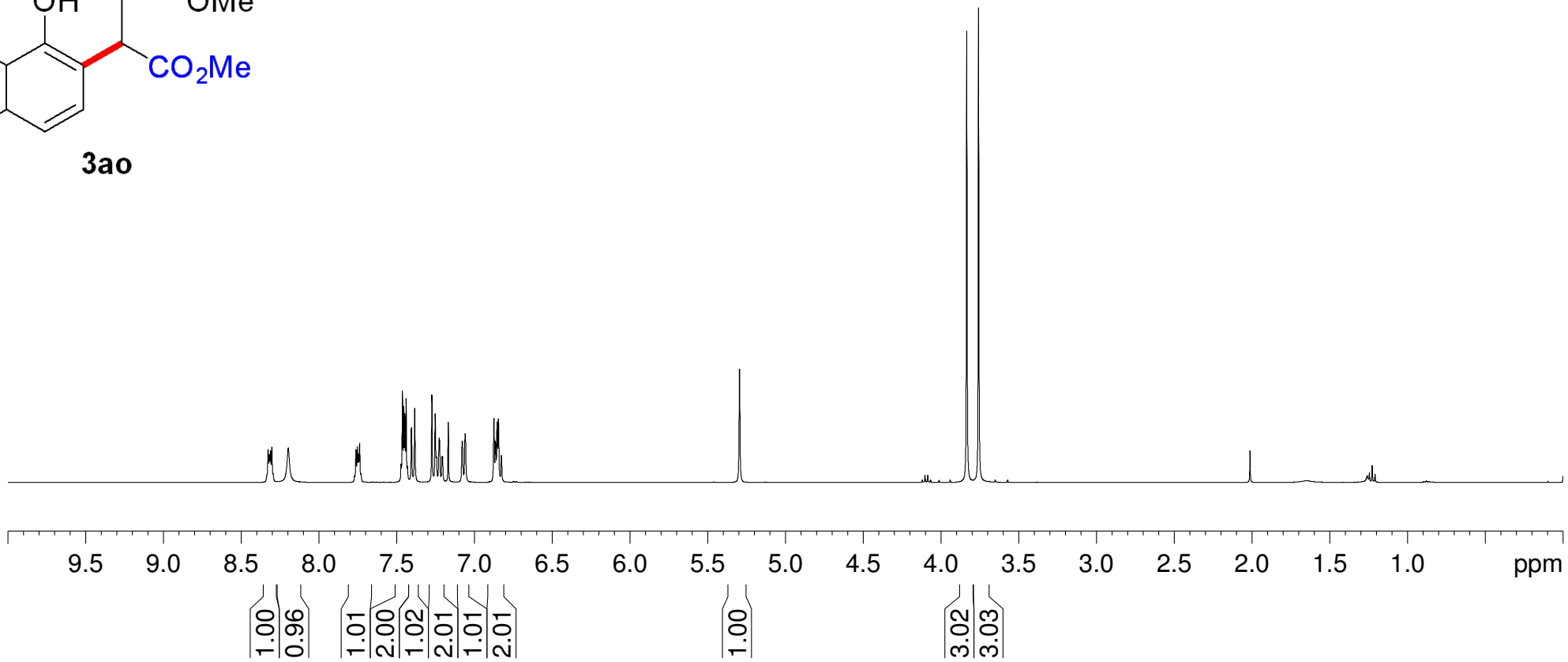


mb-9-145-1

8.313
8.304
8.199
7.763
7.755
7.749
7.747
7.740
7.465
7.457
7.449
7.441
7.407
7.386
7.275
7.254
7.246
7.227
7.210
7.207
7.080
7.061
6.876
6.866
6.855
6.848
6.829
5.297
3.835
3.759

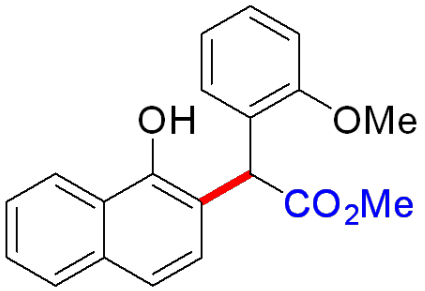


3ao

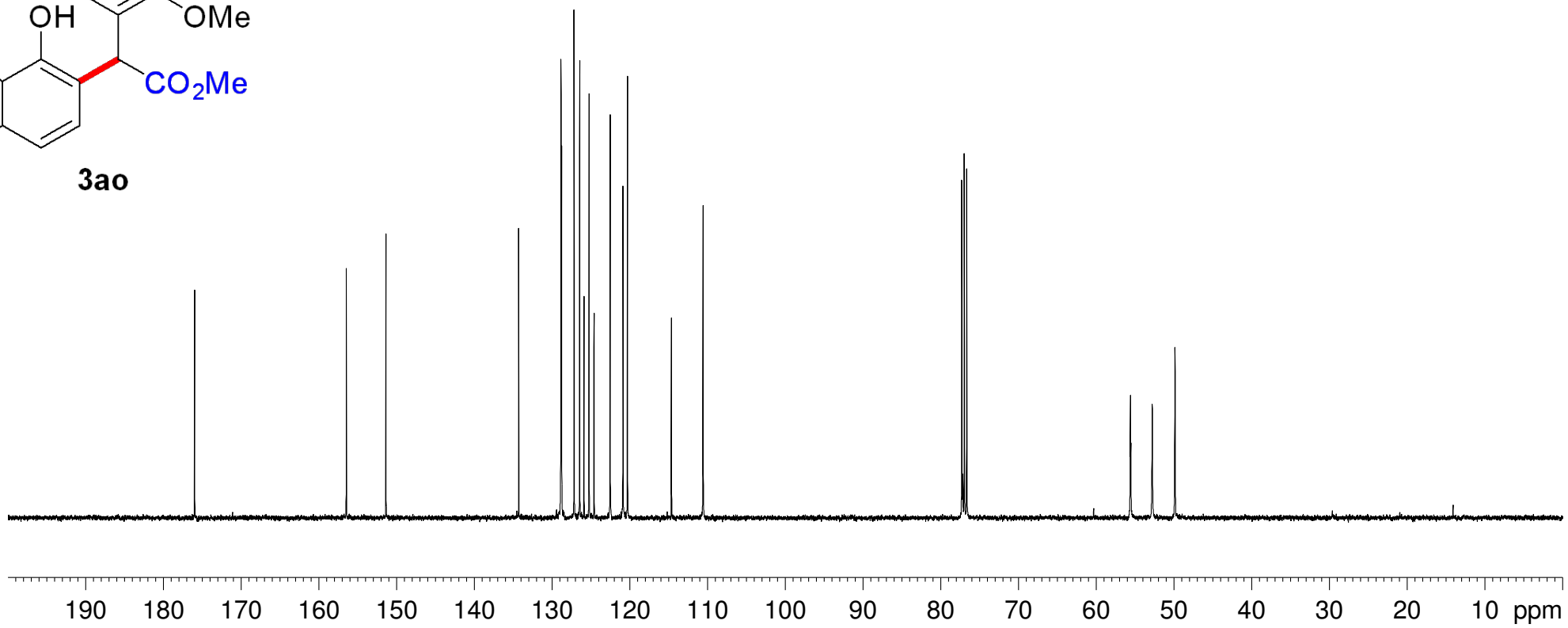


mb-9-145-1

176.01
156.50
151.40
134.32
128.89
128.87
128.80
127.19
126.48
125.92
125.27
124.64
122.55
120.91
120.33
114.68
110.60
77.32
77.00
76.68
55.62
52.84
49.90

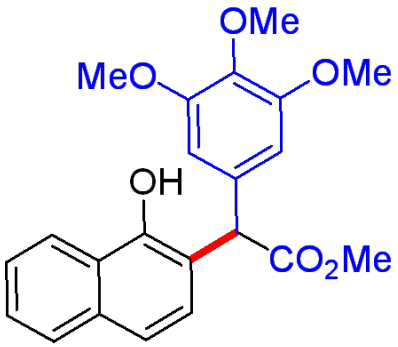


3ao



mb-9-136-2

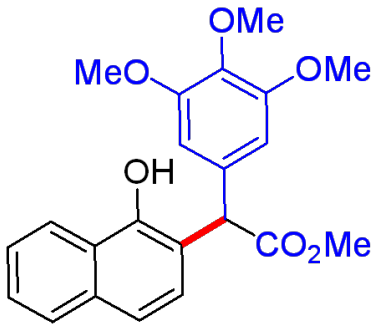
8.603
8.291
8.278
8.267
7.775
7.765
7.752
7.477
7.471
7.466
7.457
7.453
7.407
7.386
7.238
7.222
7.201
6.543
5.178
3.836
3.808
3.748



3ap

mb-9-136-2 C

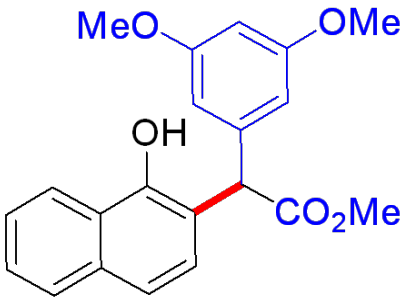
175.92
153.30
150.96
137.47
134.30
132.32
128.56
127.27
126.54
126.08
125.39
122.26
120.35
116.37
105.15
77.32
77.00
76.68
60.73
56.08
55.41
53.17



3ap

mb-9-132-2

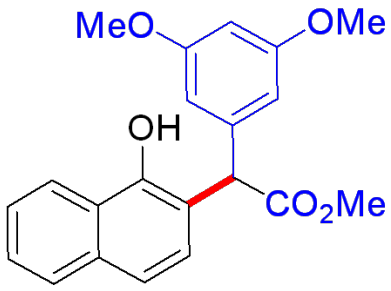
8.642
8.289
8.275
8.265
7.764
7.757
7.753
7.741
7.467
7.465
7.463
7.455
7.444
7.390
7.369
7.210
7.189
6.426
6.422
6.353
6.348
6.343
5.148
3.830
3.692



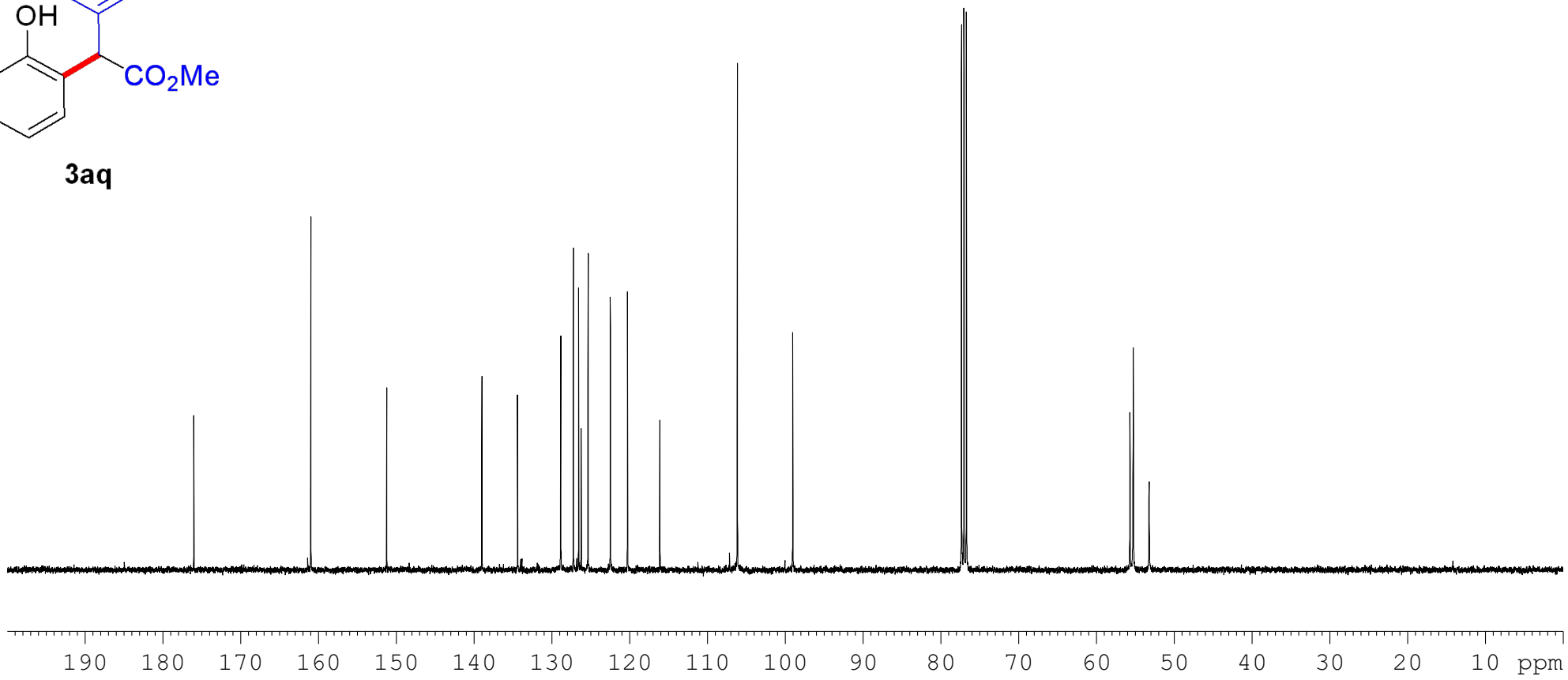
3aq

mb-9-132-2

176.01
160.97
151.21
138.98
134.39
128.84
127.22
126.54
126.22
125.33
122.46
120.25
116.09
106.14
99.01
77.32
77.00
76.68
55.66
55.24
55.22
53.20

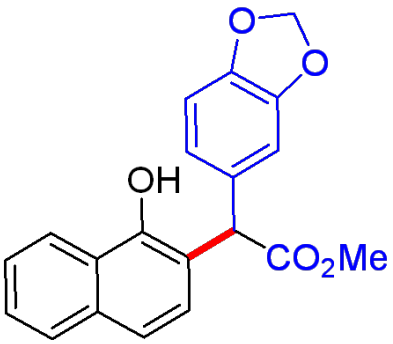


3aq



mb-9-145-2_H

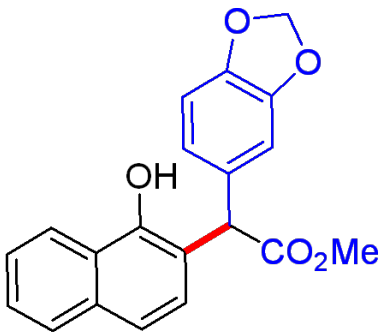
8.680
8.290
8.277
8.274
8.265
7.761
7.750
7.742
7.737
7.465
7.459
7.454
7.451
7.446
7.441
7.388
7.367
7.204
7.190
7.169
6.733
6.705
6.703
5.866
5.116
3.813



3ar

mb-9-145-2 C

176.38
151.12
148.00
146.98
134.36
130.42
128.74
127.23
126.58
126.22
125.39
122.41
120.83
120.31
116.31
108.26
101.12
77.32
77.00
76.68
55.27
53.21

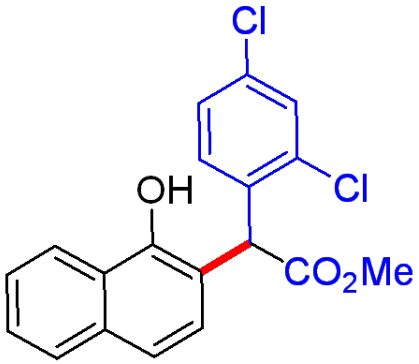


3ar

mb-9-134-2

8.206
8.190
8.182
7.777
7.770
7.767
7.753
7.627
7.481
7.478
7.468
7.458
7.454
7.420
7.407
7.402
7.198
7.189
7.168
7.150
7.129
7.114
7.109
5.479

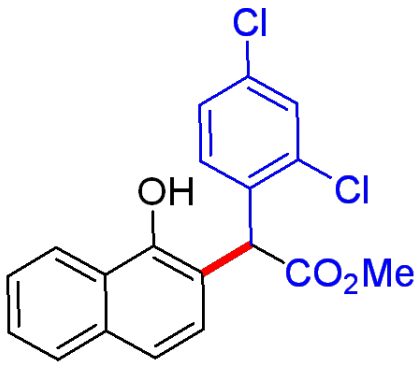
3.781



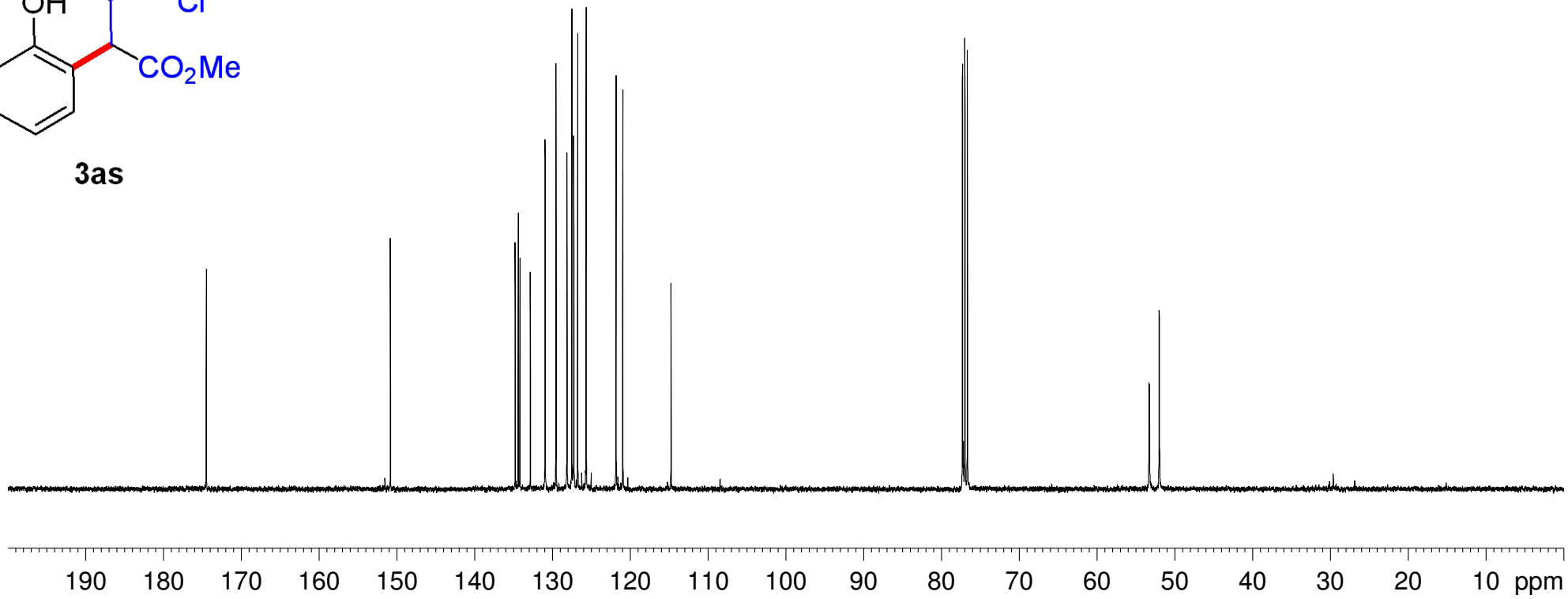
3as

mb-9-134-2

174.53
150.86
134.81
134.42
134.20
132.87
130.97
129.57
128.16
127.54
127.28
126.78
125.70
125.69
121.85
120.98
114.79
77.32
77.00
76.68
53.32
52.02



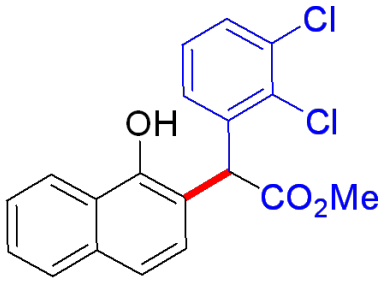
3as



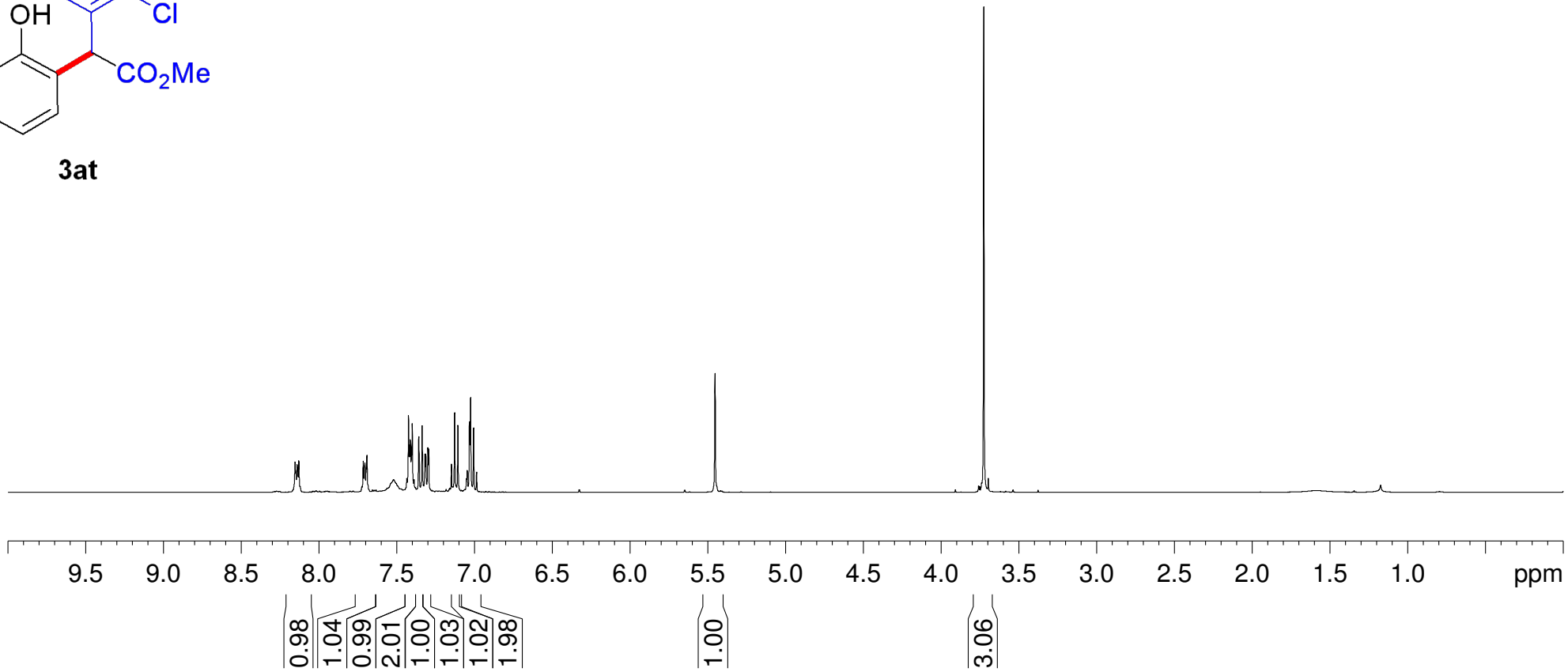
mb-9-133-2

8.143
8.140
8.131
7.717
7.706
7.698
7.693
7.521
7.426
7.420
7.415
7.413
7.407
7.402
7.360
7.338
7.320
7.315
7.302
7.297
7.130
7.108
7.049
7.034
7.027
7.008
6.988
5.455

3.727

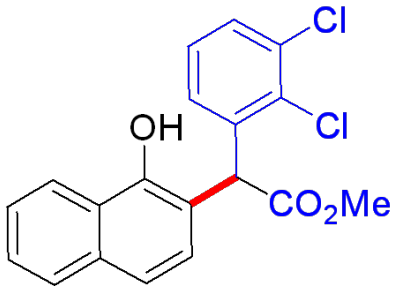


3at



mb-9-133-2
MB-9-133-2

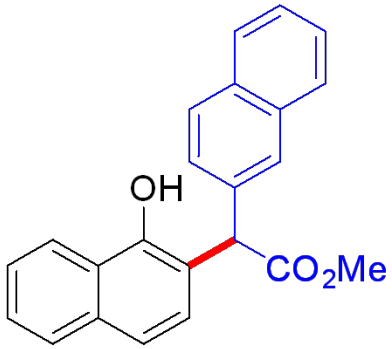
174.54
151.01
136.42
134.47
133.54
132.52
129.84
128.36
128.29
127.53
127.36
126.84
125.72
121.94
120.96
114.65
77.32
77.00
76.68
53.50
53.37



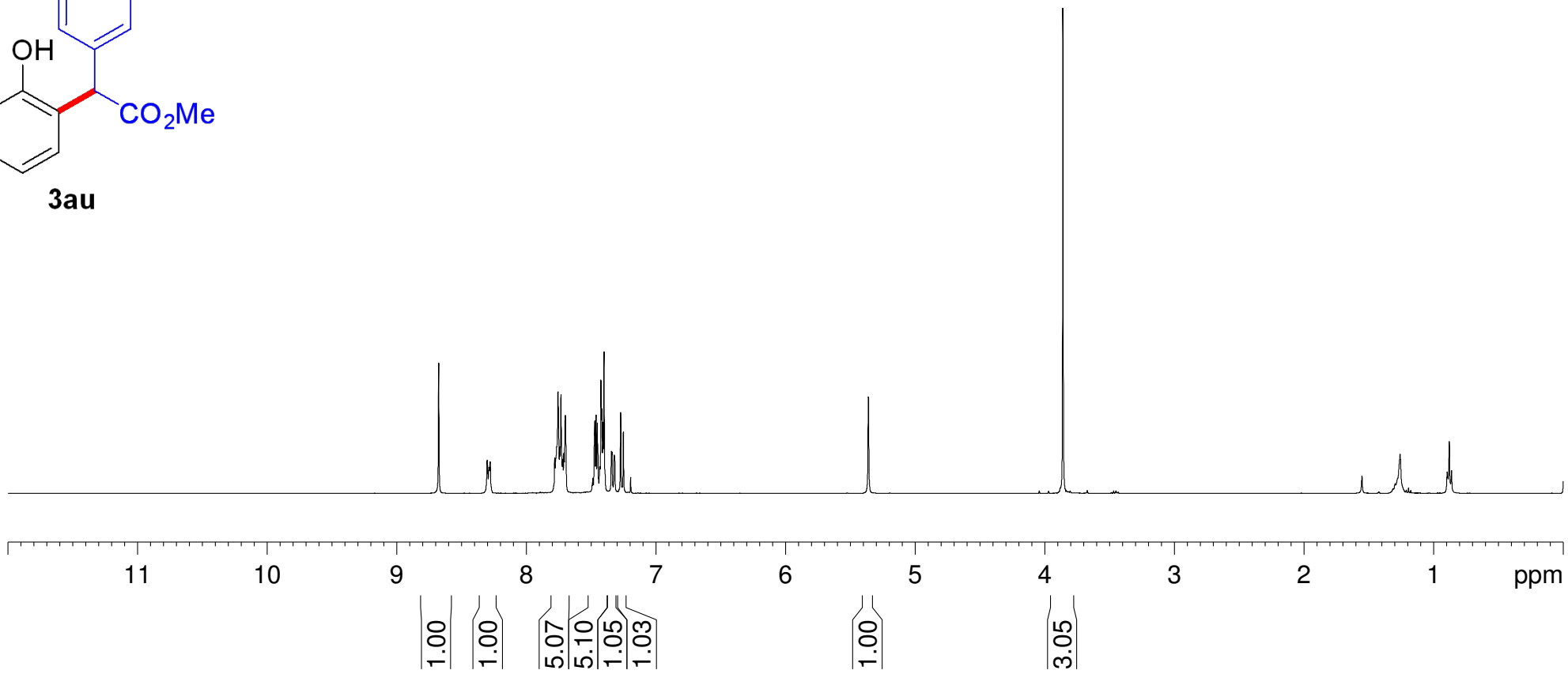
3at

mb-9-124-1

8.678
8.304
8.288
8.280
7.783
7.776
7.773
7.767
7.758
7.743
7.735
7.721
7.712
7.701
7.477
7.473
7.464
7.454
7.450
7.426
7.418
7.411
7.402
7.345
7.341
7.324
7.320
7.274
7.253
5.362
3.861

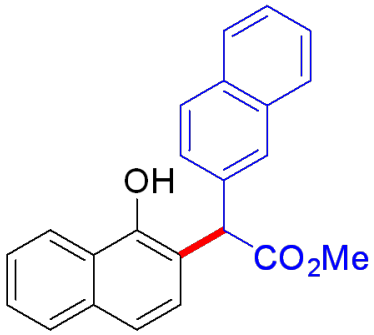


3au

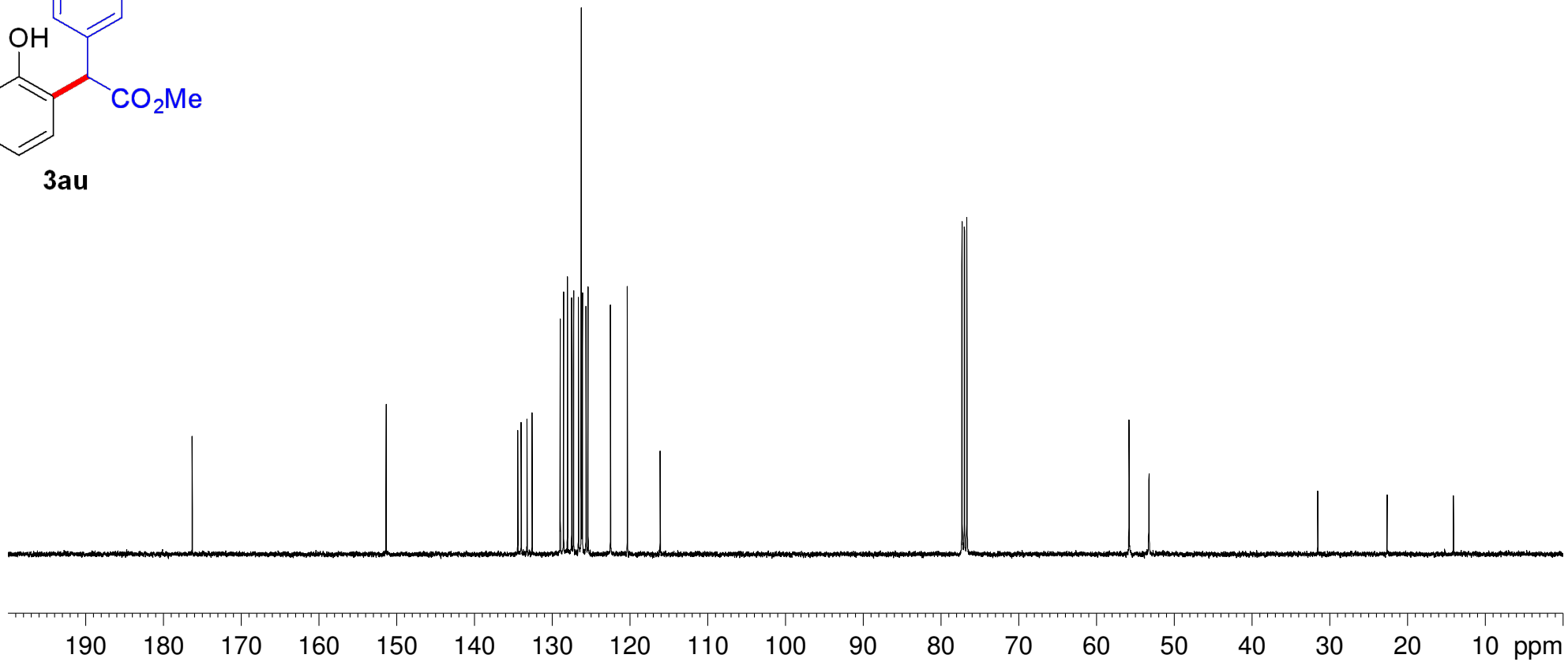


mb-9-124-1

176.33
151.39
134.46
134.01
133.26
132.60
128.99
128.56
128.05
127.52
127.28
126.64
126.28
126.14
125.66
125.42
122.53
120.36
116.14
77.32
77.00
76.68
55.82
53.26

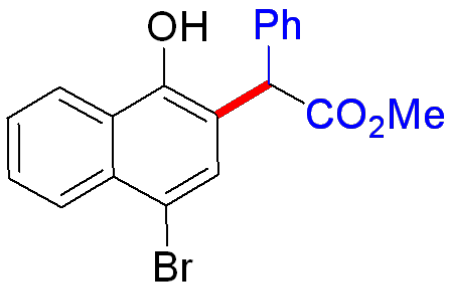


3au



mb-9-150-1

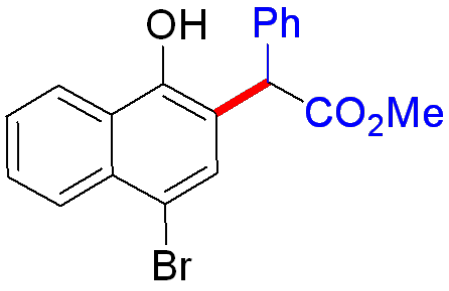
9.027
8.326
8.305
8.119
8.098
7.593
7.590
7.575
7.573
7.555
7.552
7.522
7.514
7.494
7.476
7.285
7.280
7.268
7.254
7.242
7.223
5.124
3.841



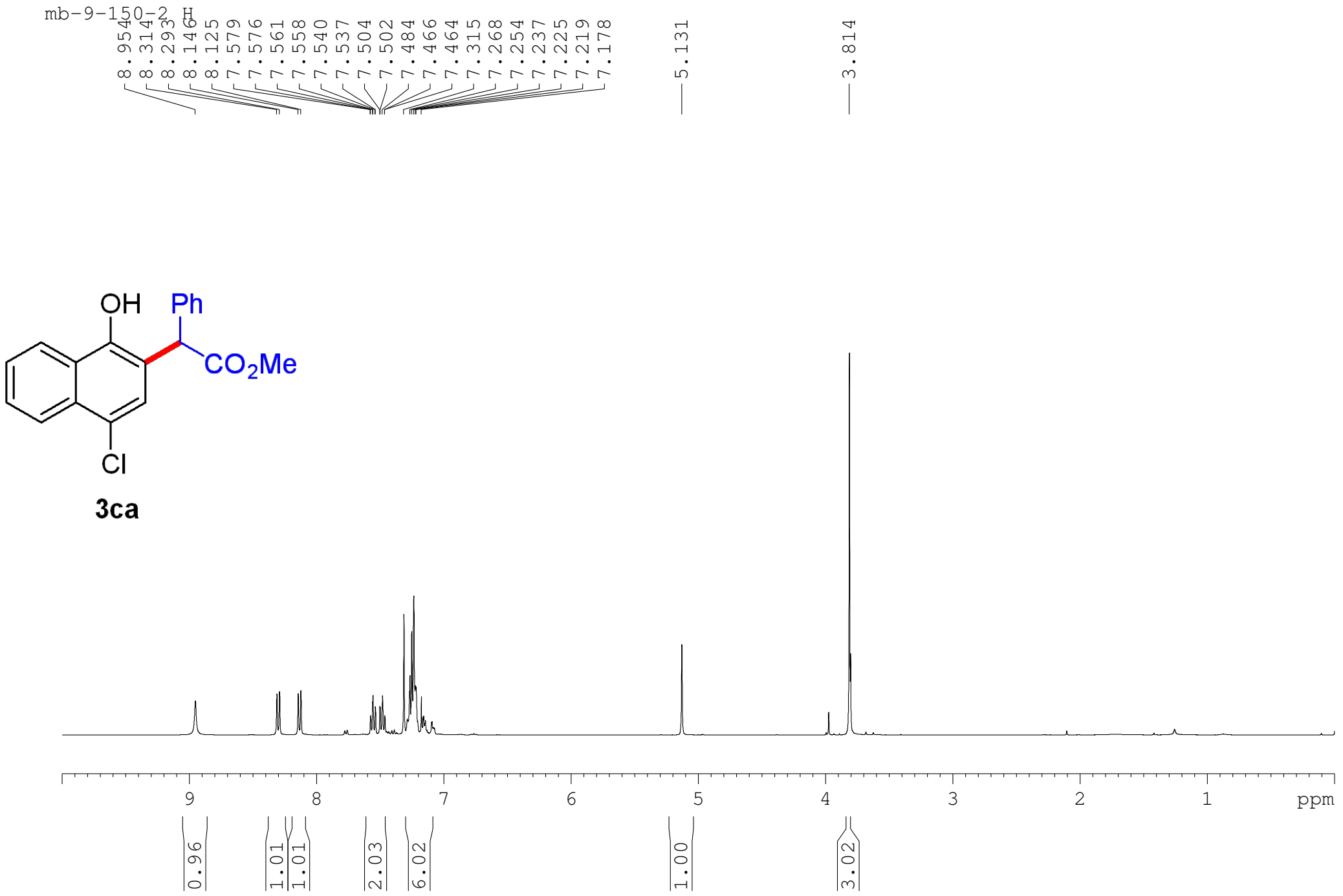
3ba

mb-9-150-1

176.39
151.37
136.08
132.46
132.16
128.85
127.97
127.76
127.59
127.43
126.60
126.11
123.12
116.94
112.95
77.32
77.00
76.69
55.60
53.44

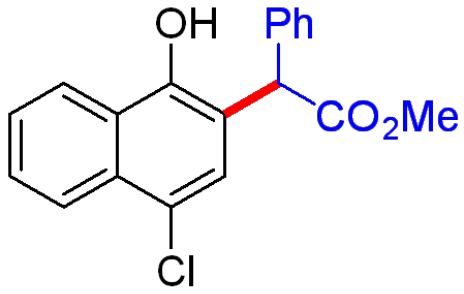


3ba


mb-9-150-2 H
8.954
8.314
8.293
8.146
8.125
7.579
7.576
7.561
7.558
7.540
7.537
7.504
7.502
7.484
7.466
7.464
7.315
7.268
7.254
7.237
7.225
7.219
7.178
5.131
3.814
OH
Ph
CO2Me
Cl
3ca
9
8
7
6
5
4
3
2
1
ppm
0.96
1.01
1.01
2.03
6.02
1.00
3.02

mb-9-150-2 C

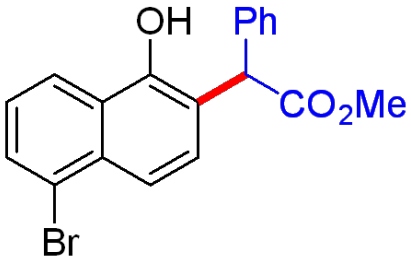
176.26
150.52
136.10
131.17
129.61
128.80
128.50
127.71
127.61
127.45
127.32
126.07
123.95
122.99
116.47
77.32
77.00
76.68
55.43
53.33



3ca

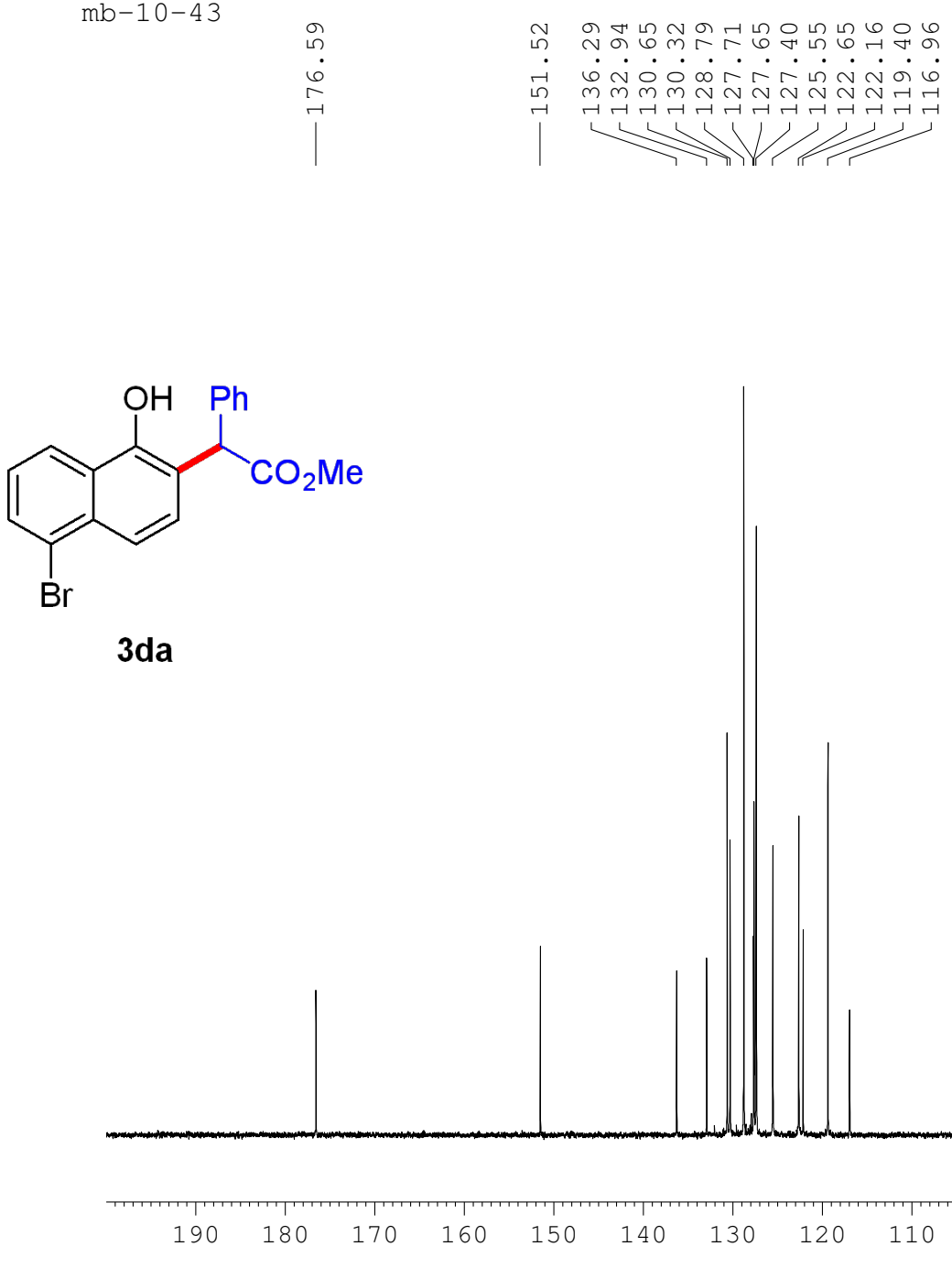
mb-10-43

8.999
8.218
8.197
7.688
7.667
7.648
7.646
7.227
7.205
7.190
7.171
7.162
7.158
7.150
7.145
7.136
7.133
7.117
5.112
3.756



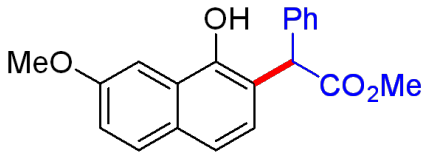
3da

mb-10-43

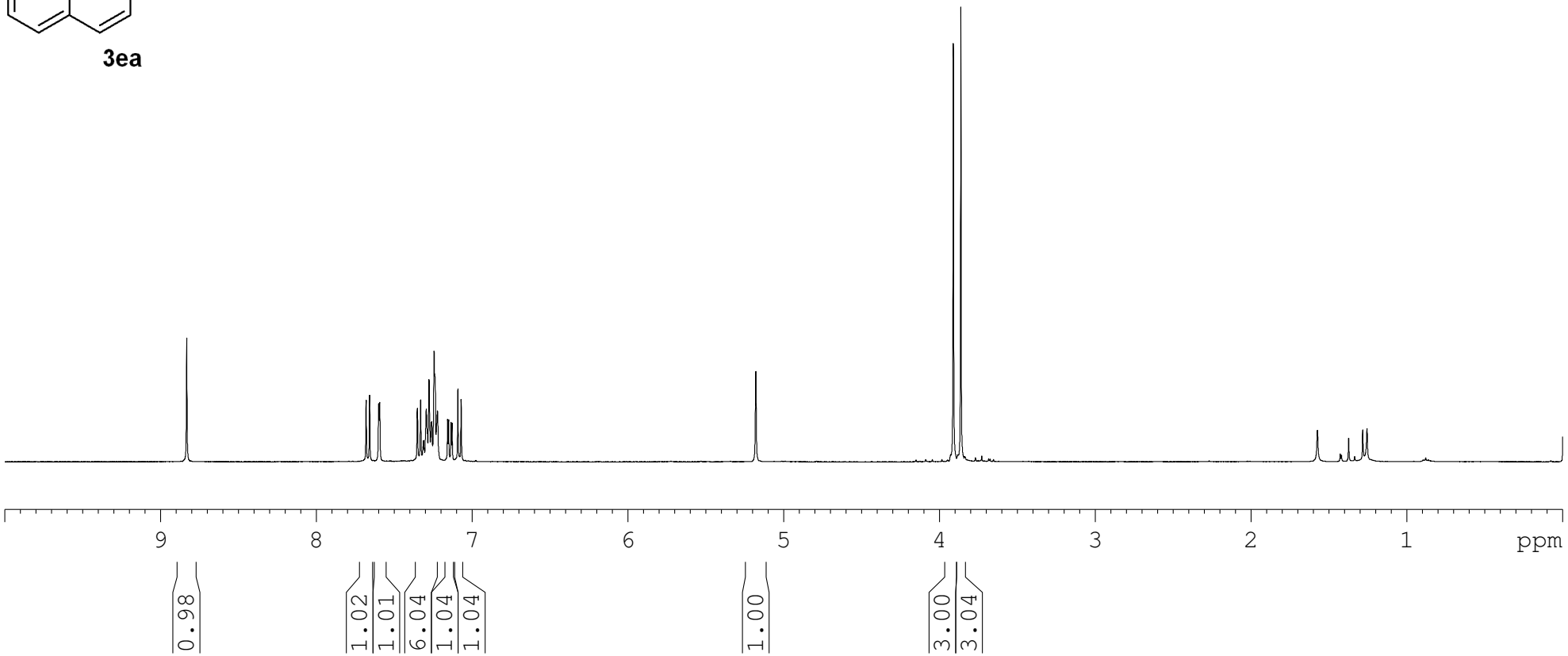

176.59
151.52
136.29
132.94
130.65
130.32
128.79
127.71
127.65
127.40
125.55
122.65
122.16
119.40
116.96
77.32
77.00
76.68
55.92
53.40
OH
Ph
CO2Me
Br
3da
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

mb-10-17-1

8.834
7.682
7.660
7.601
7.595
7.353
7.332
7.313
7.296
7.289
7.278
7.263
7.260
7.246
7.224
7.159
7.152
7.137
7.130
7.093
7.072
5.181
3.912
3.864

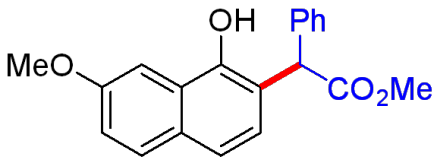


3ea



mb-10-17-1

176.78
157.60
150.41
136.63
129.96
128.80
128.74
127.53
127.45
126.70
120.11
119.60
116.60
100.69
77.32
77.00
76.68
56.13
55.33
53.30

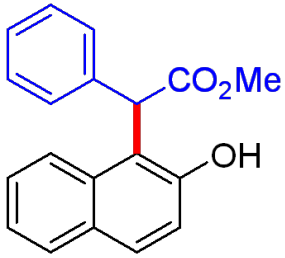


3ea

mb-9-80

8.062
7.982
7.960
7.799
7.779
7.734
7.712
7.491
7.488
7.473
7.470
7.452
7.450
7.351
7.332
7.314
7.244
7.217
7.209
7.142
7.120
5.970

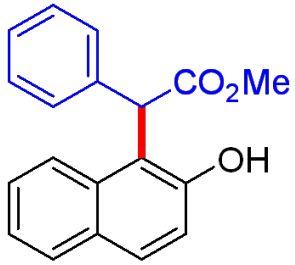
3.796



8aa

mb-9-80

176.39
153.62
136.58
133.21
130.27
129.41
128.90
128.55
127.75
127.30
127.13
123.24
121.79
120.11
114.95
77.31
77.00
76.68
53.06
48.30

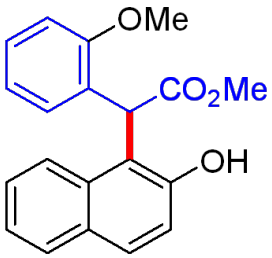


8aa

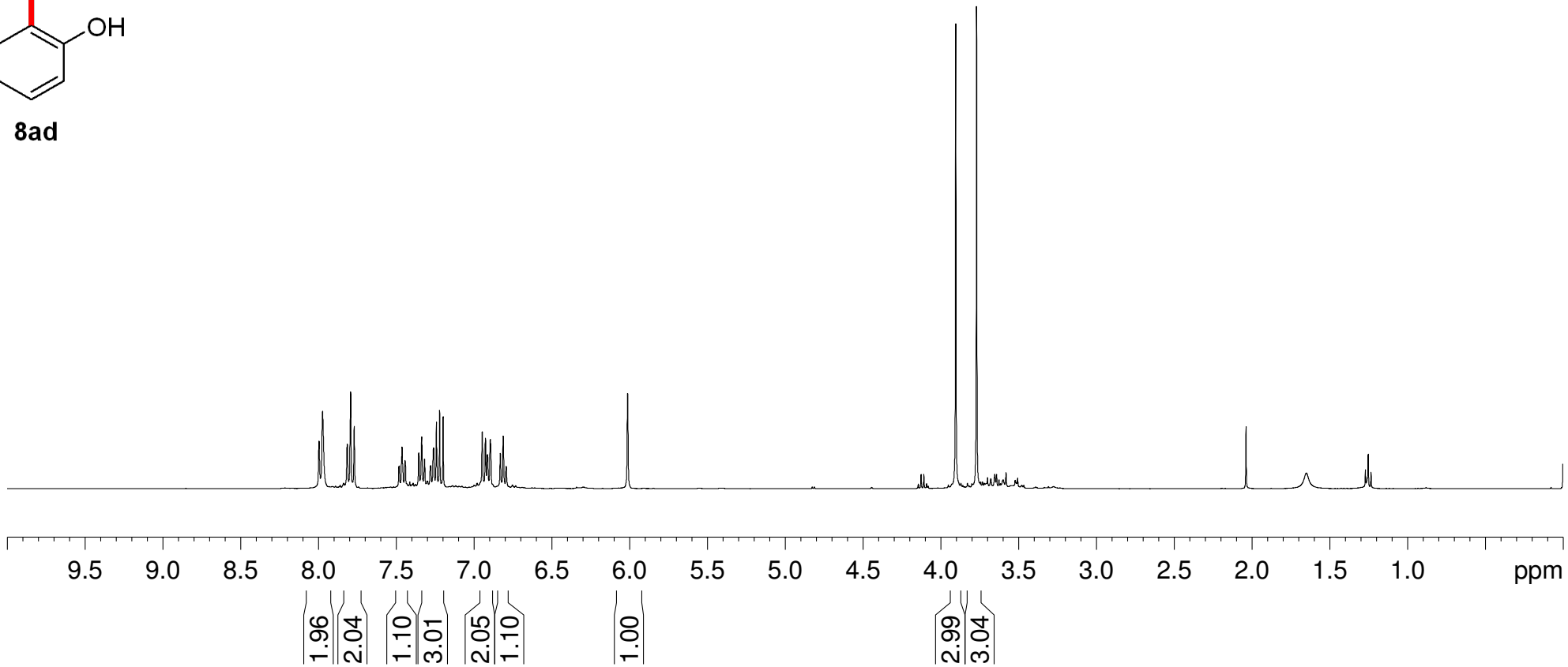
mb-10-10-1

7.996 7.973 7.814 7.792 7.769 7.482 7.479 7.465 7.462 7.444 7.441 7.355 7.335 7.318 7.281 7.277 7.260 7.241 7.221 7.198 6.946 6.926 6.913 6.894 6.831 6.812 6.793 6.012

3.903 3.769

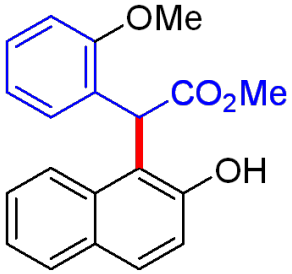


8ad



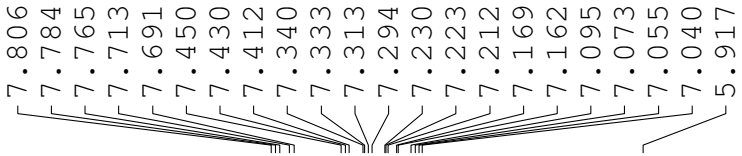
mb-10-10-1

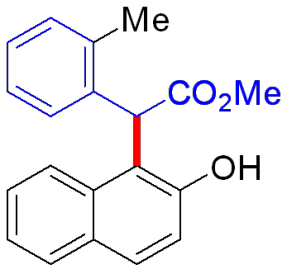
176.67
157.30
154.49
133.36
130.37
129.59
128.94
128.84
127.00
123.85
123.23
122.00
120.75
120.16
112.35
110.58
77.32
77.00
76.68
55.67
52.93
44.07



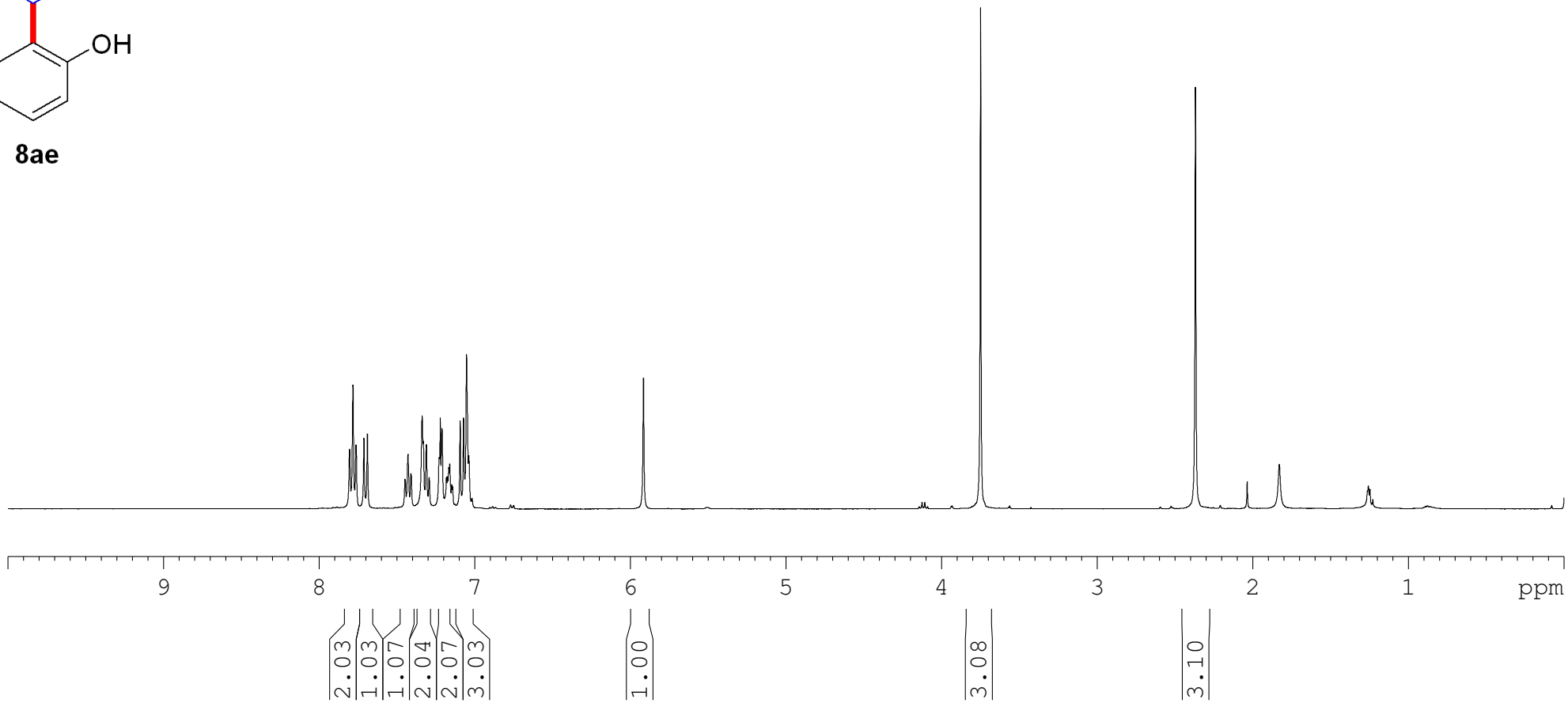
8ad

mb-10-9-2

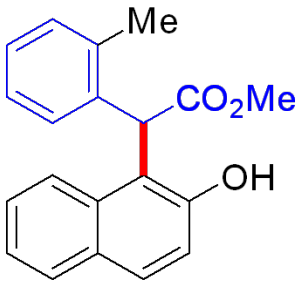

7.806
7.784
7.765
7.713
7.691
7.450
7.430
7.412
7.340
7.333
7.313
7.294
7.230
7.223
7.212
7.169
7.162
7.095
7.073
7.055
7.040
5.917
3.750
2.369


Me
CO2Me
OH

8ae


9
8
7
6
5
4
3
2
1
ppm
2.03
1.03
1.07
2.04
2.07
3.03
1.00
3.08
3.10

mb-10-9-2


Me
CO2Me
OH

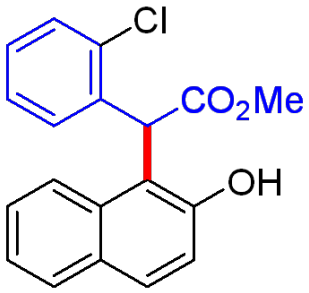
8ae

175.65
153.41
136.78
134.42
133.16
130.78
130.13
129.46
128.87
128.01
127.64
127.09
126.28
123.23
121.97
119.50
114.63
77.32
77.00
76.68
52.93
46.92
19.90
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

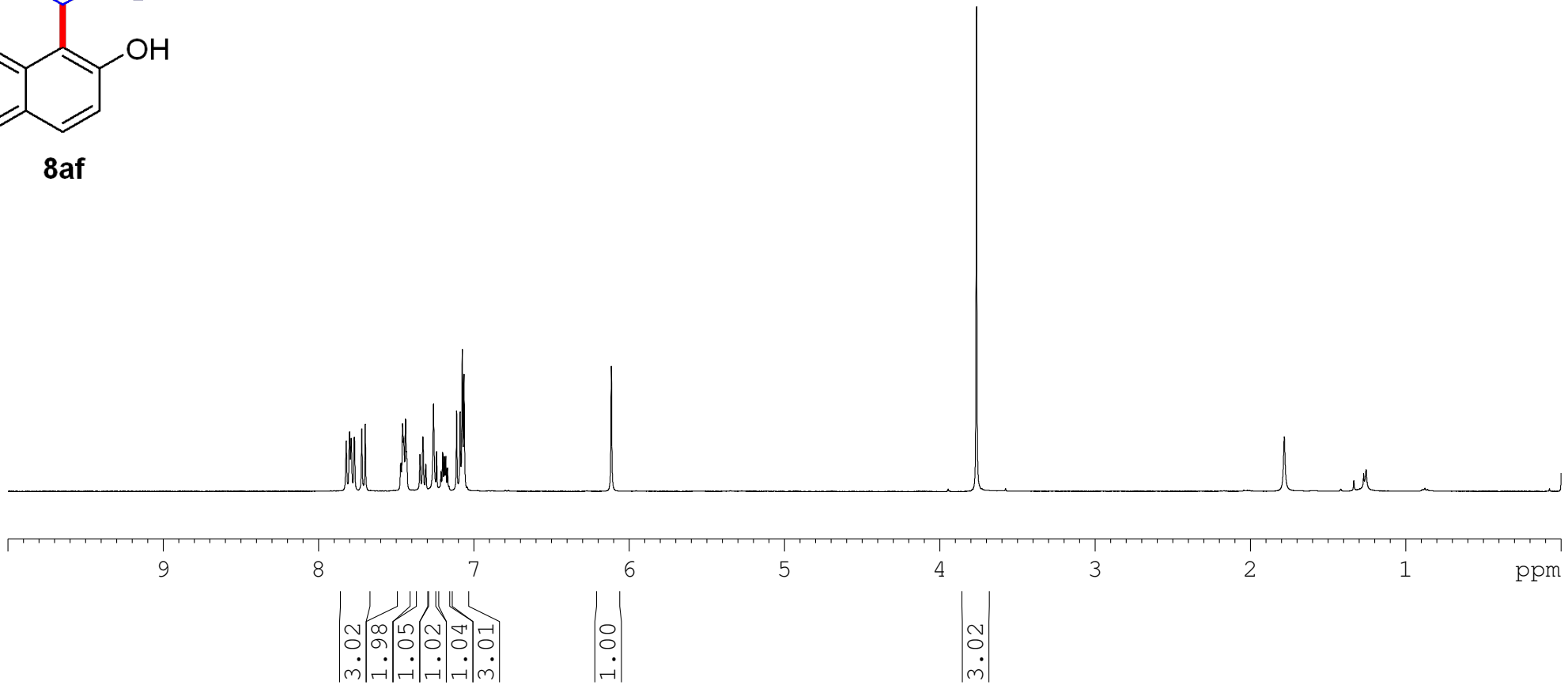
mb-10-8-1

7.824
7.802
7.792
7.771
7.724
7.701
7.461
7.453
7.441
7.436
7.349
7.330
7.312
7.261
7.213
7.202
7.191
7.182
7.171
7.112
7.090
7.076
7.065
6.116

3.765

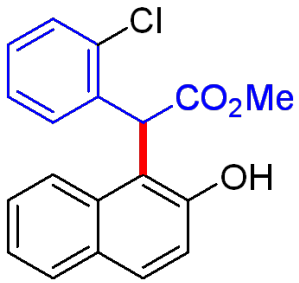


8af

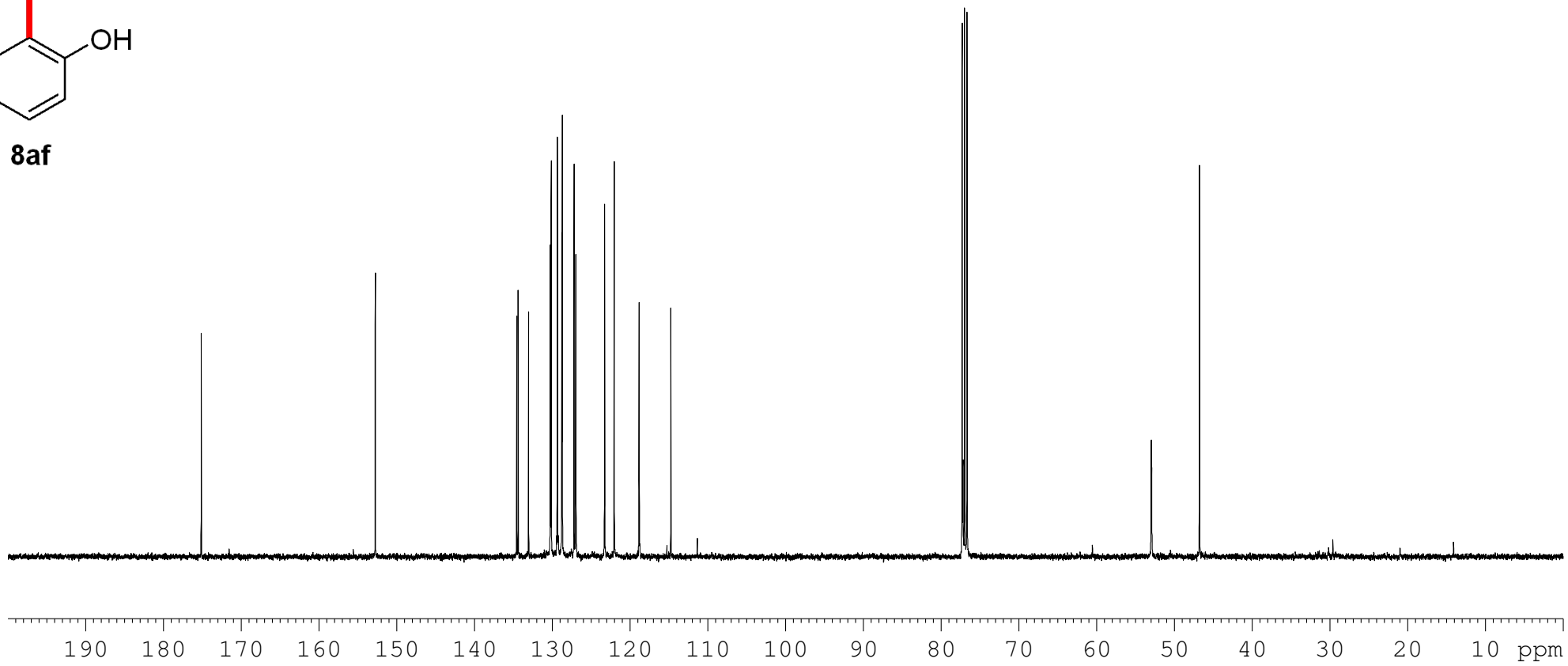


mb-10-8-1

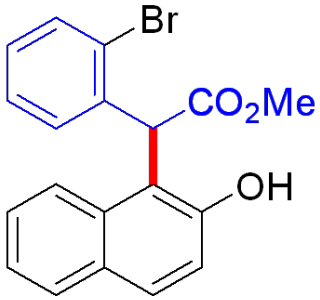
175.17
152.79
134.60
134.43
133.07
130.28
130.16
129.38
129.33
128.79
128.74
127.23
126.99
123.30
122.06
118.85
114.78
77.32
77.00
76.68
52.99
46.79



8af



mb-10-15-1

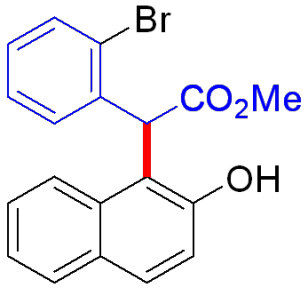

Br
CO2Me
OH

8ag

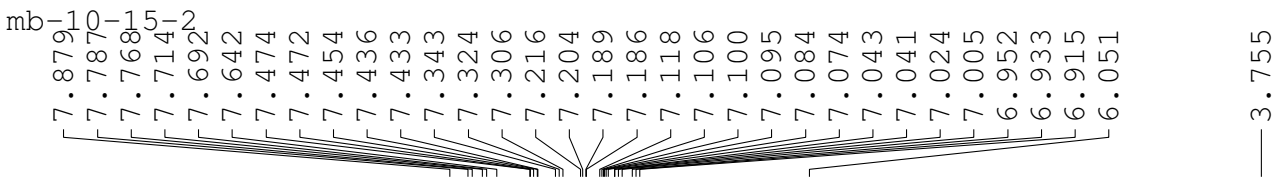
7.753
7.735
7.718
7.641
7.634
7.627
7.620
7.442
7.440
7.422
7.403
7.401
7.339
7.316
7.296
7.278
7.067
7.061
7.031
7.009
6.068
3.735
9
8
7
6
5
4
3
2
1
ppm
2.07
2.00
1.06
1.01
1.13
4.06
1.02
3.12

mb-10-15-1

175.10
152.59
136.21
133.09
132.73
130.50
130.15
129.33
129.04
128.73
127.65
127.27
125.52
123.32
122.18
118.78
115.27
77.32
77.00
76.68
53.00
49.54



8ag


mb-10-15-2
7.879
7.787
7.768
7.714
7.692
7.642
7.474
7.472
7.454
7.436
7.433
7.343
7.324
7.306
7.216
7.204
7.189
7.186
7.118
7.106
7.100
7.095
7.084
7.074
7.043
7.041
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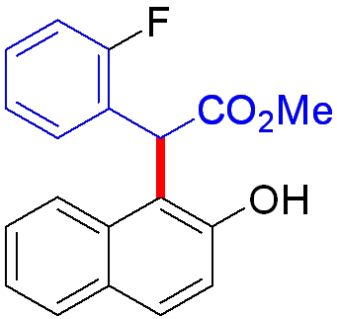
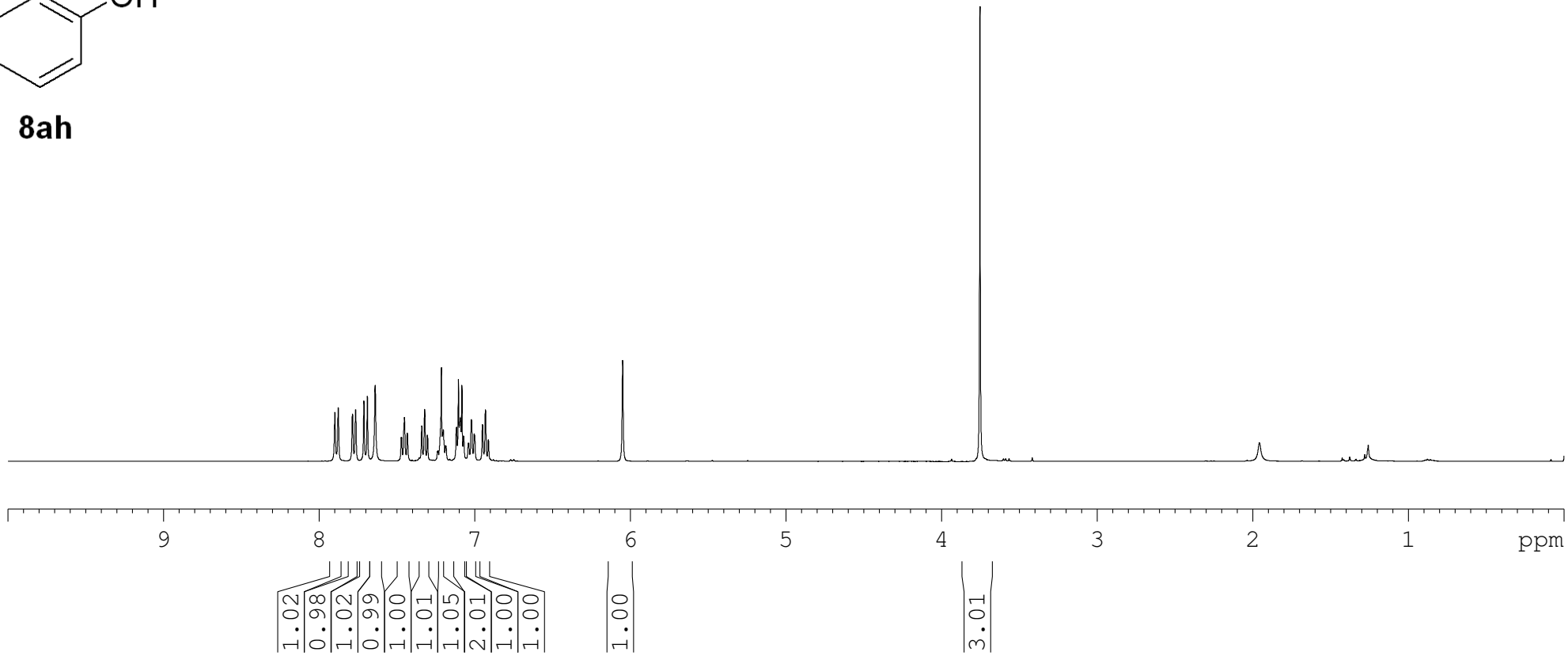
7.005
6.952
6.933
6.915
6.051
3.755

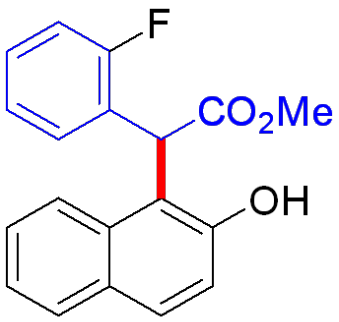

F
CO2Me
OH

8ah

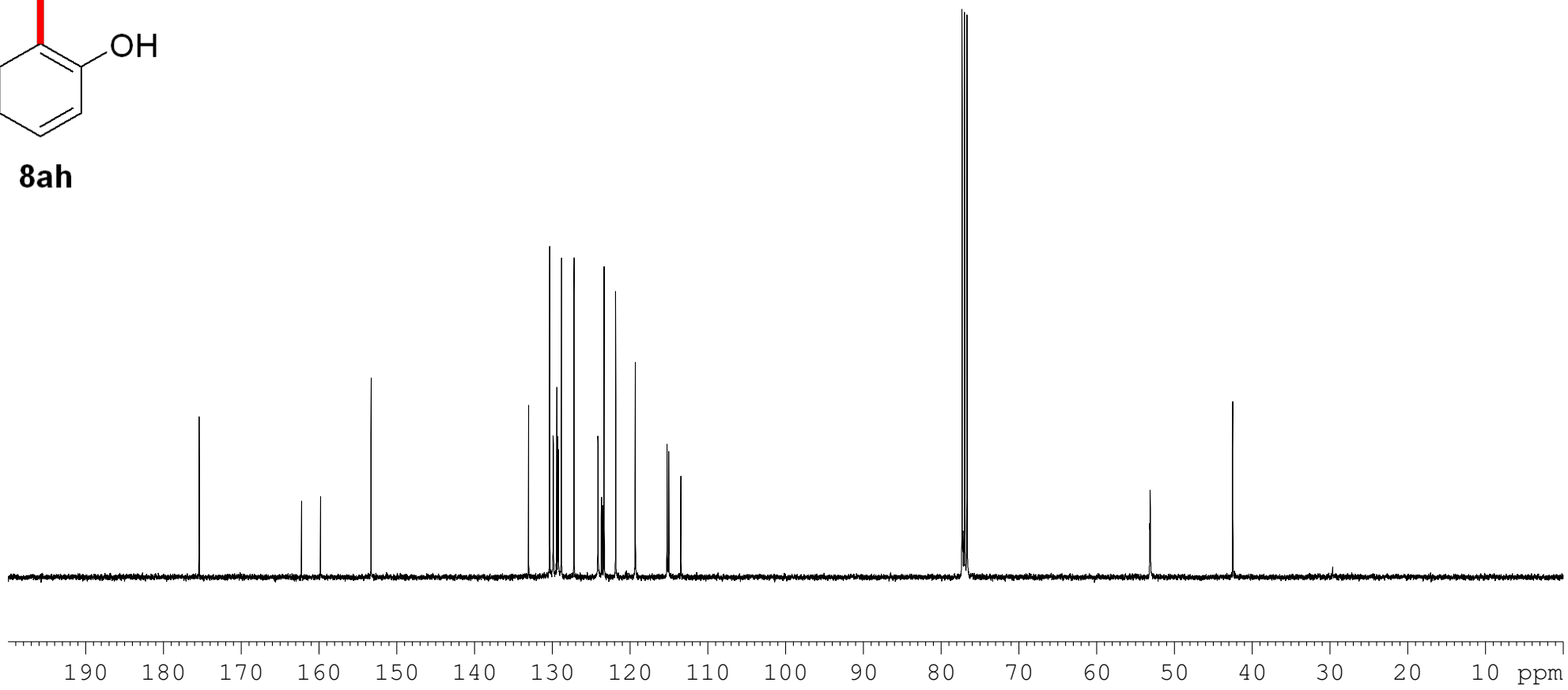

9
8
7
6
5
4
3
2
1
ppm
1.02
0.98
1.02
0.99
1.00
1.01
1.05
2.01
1.00
1.00
1.00
3.01

mb-10-15-2

175.44
162.28
159.84
153.33
133.08
130.36
129.91
129.88
129.44
129.31
129.23
128.86
127.23
124.17
124.13
123.71
123.57
123.36
121.87
119.35
115.27
115.05
113.48
77.32
77.00
76.68
53.16
42.53

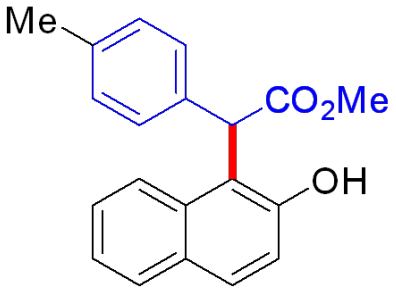


8ah

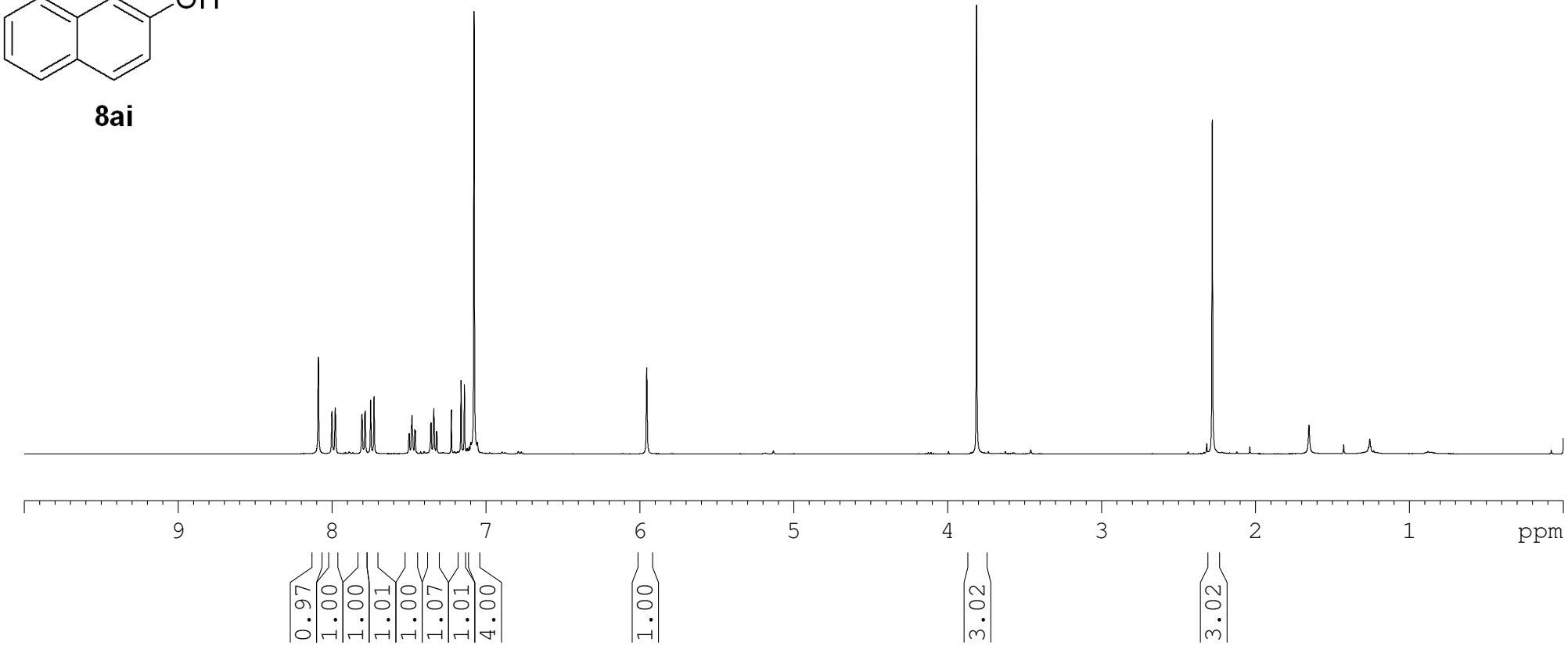


mb-10-22-2

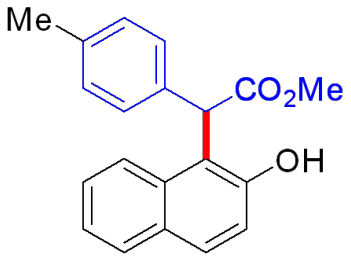
8.091
8.002
7.981
7.807
7.787
7.751
7.729
7.503
7.500
7.485
7.482
7.464
7.461
7.359
7.358
7.340
7.322
7.164
7.142
7.079
5.957
3.813
2.281



8ai



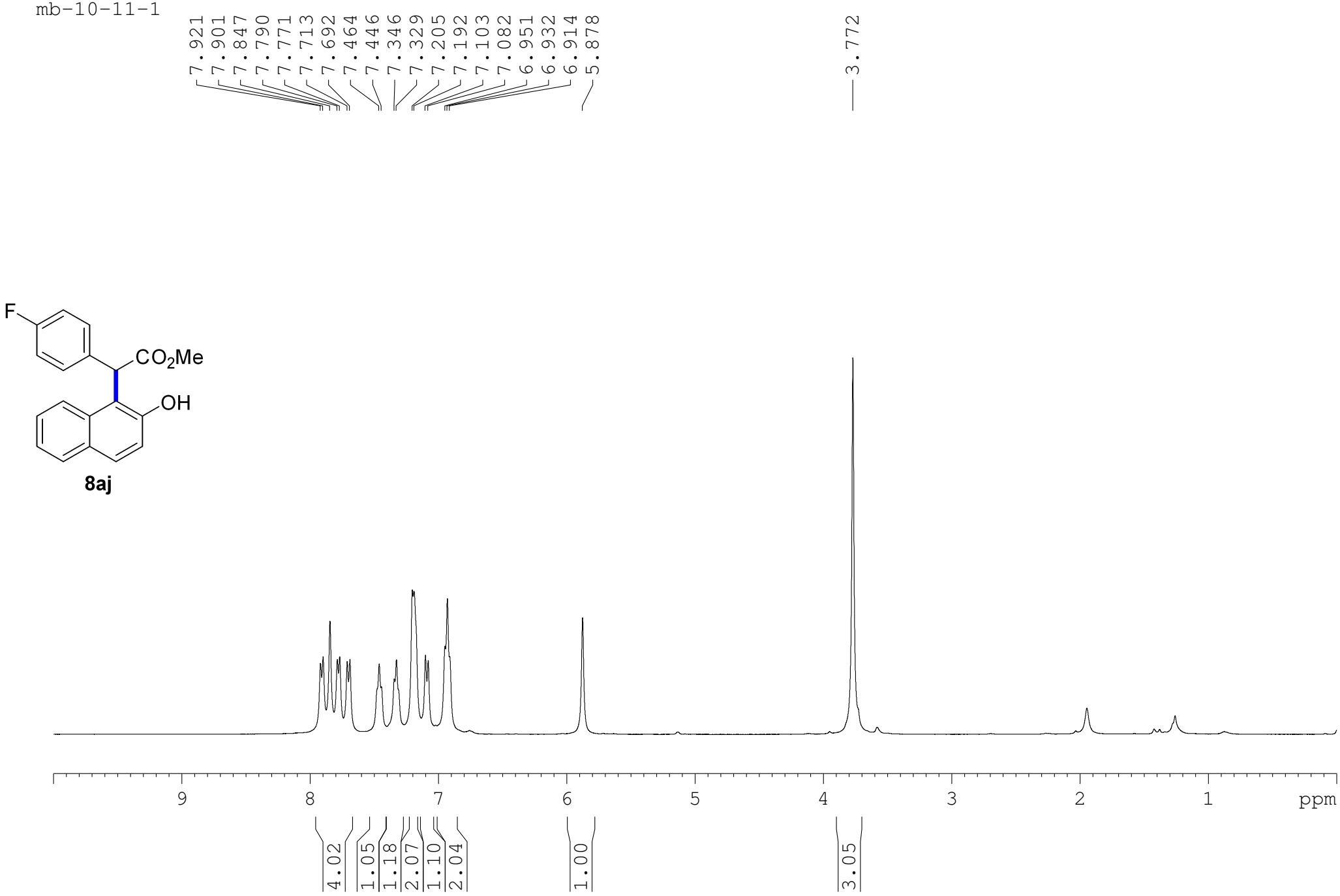
mb-10-22-2


Me
CO2Me
OH

8ai

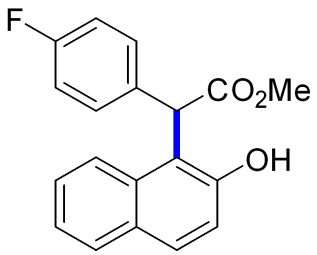
176.56
153.83
137.03
133.46
133.26
130.26
129.44
129.31
128.91
127.50
127.13
123.23
121.76
120.35
114.89
77.32
77.00
76.68
53.12
47.98
20.98
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

mb-10-11-1


7.921
7.901
7.847
7.790
7.771
7.713
7.692
7.464
7.446
7.346
7.329
7.205
7.192
7.103
7.082
6.951
6.932
6.914
5.878
3.772
F
CO2Me
OH
8aj
9
8
7
6
5
4
3
2
1
ppm
4.02
1.05
1.18
2.07
1.10
2.04
1.00
3.05

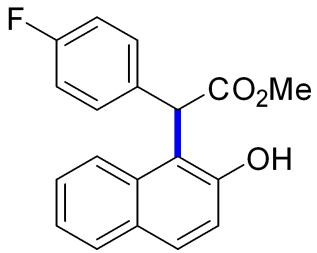
mb-10-11-1

176.20
163.14
160.70
153.12
133.01
132.46
132.42
130.30
129.73
129.65
129.42
128.94
127.22
123.34
121.76
119.72
115.45
115.26
115.23
77.32
77.00
76.68
53.06
47.61



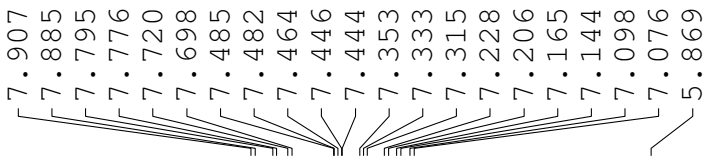
8aj

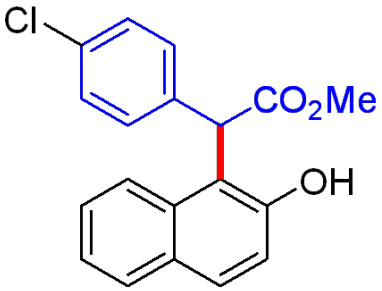
mb-10-11-1 f
mb-10-11-1 f



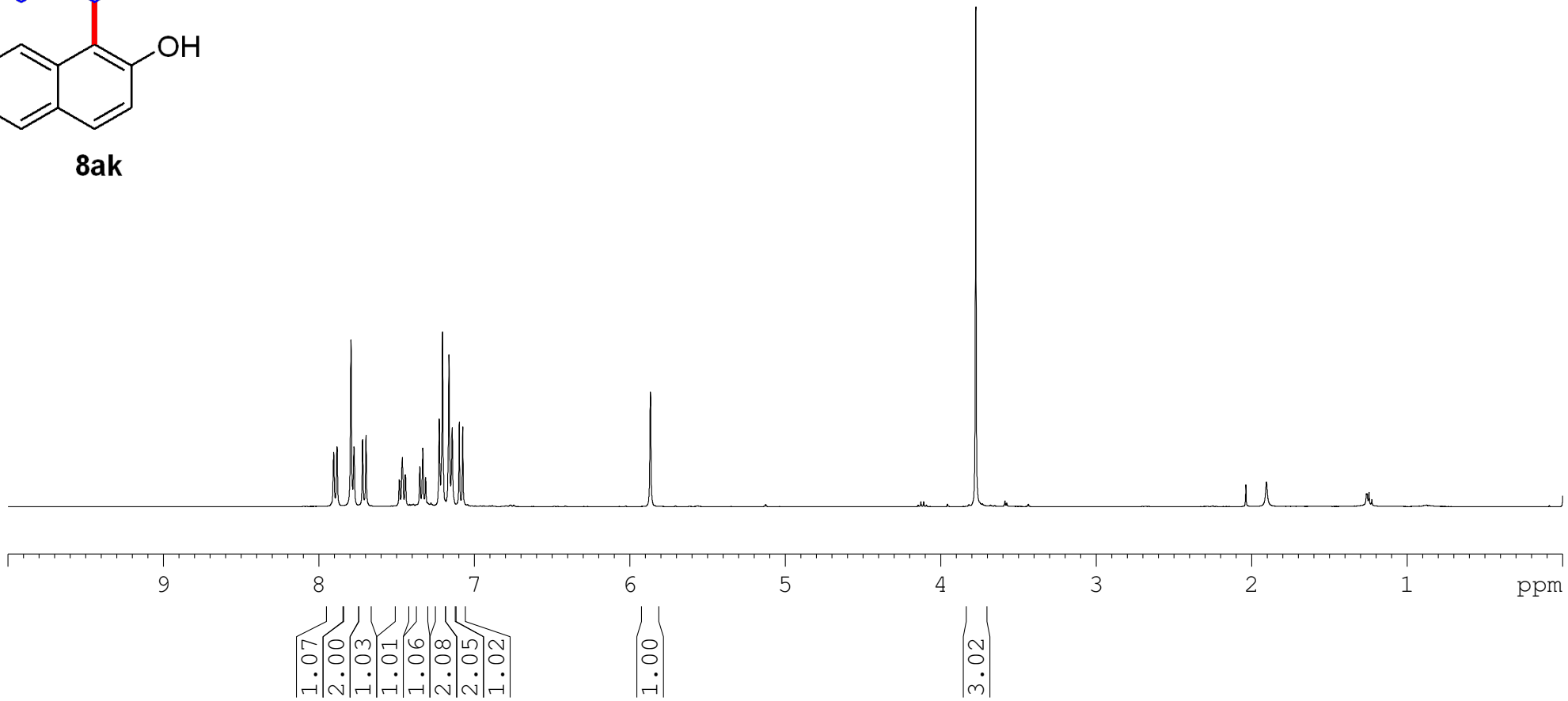
8aj

mb-10-8-2


7.907
7.885
7.795
7.776
7.720
7.698
7.485
7.482
7.464
7.446
7.444
7.353
7.333
7.315
7.228
7.206
7.165
7.144
7.098
7.076
5.869
3.776

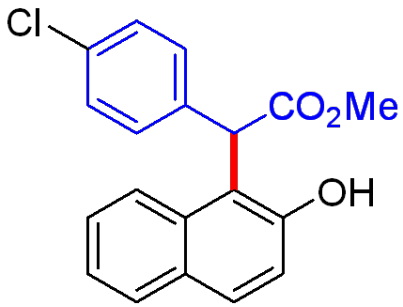

Cl
CO2Me
OH

8ak

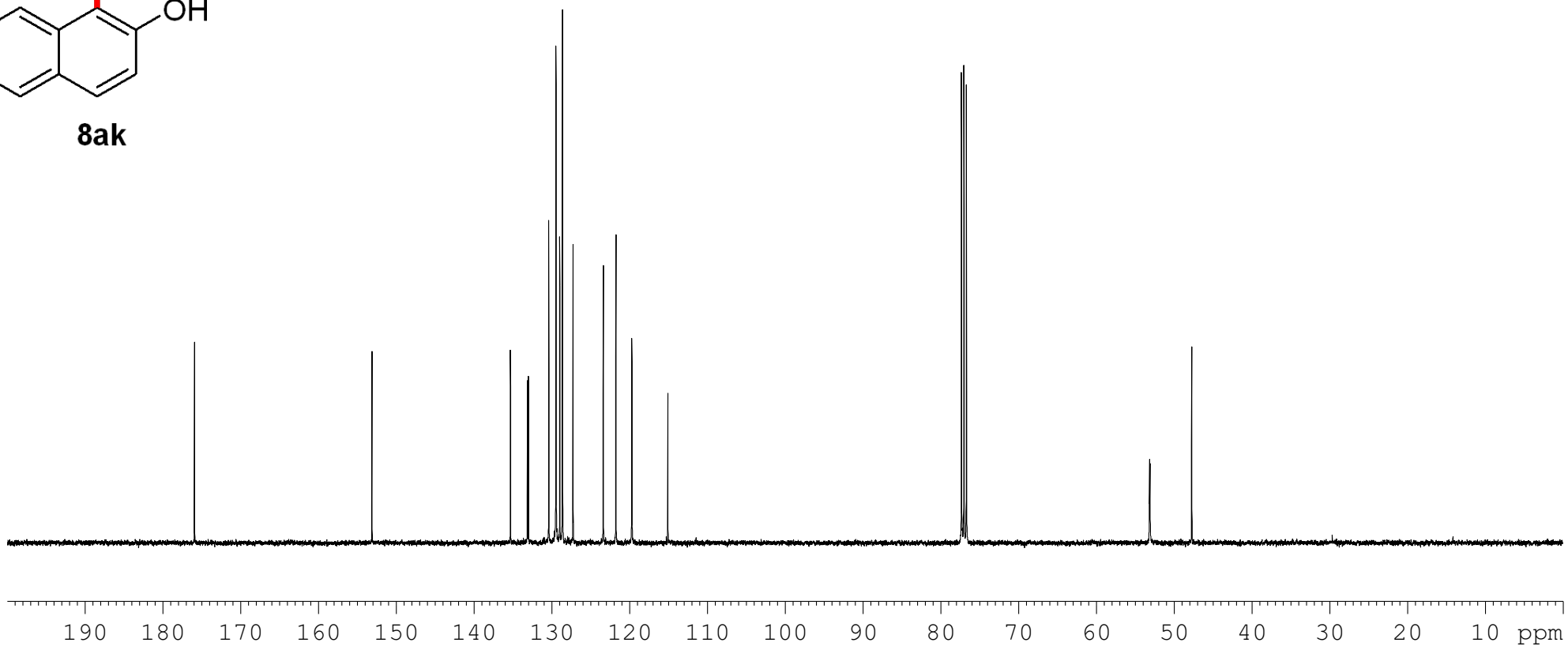

9
8
7
6
5
4
3
2
1
ppm
1.07
2.00
1.03
1.01
1.06
2.08
2.05
1.02
1.00
3.02

mb-10-8-2

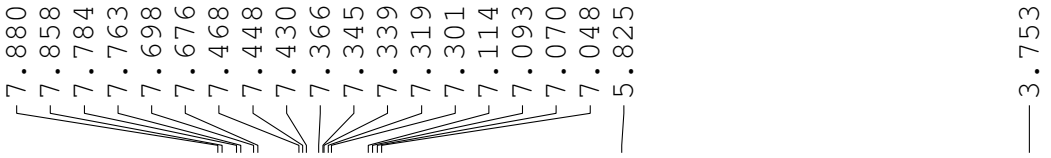
175.92
153.11
135.30
133.12
132.99
130.37
129.45
129.43
128.96
128.62
127.25
123.37
121.75
119.70
115.06
77.32
77.00
76.68
53.13
47.72

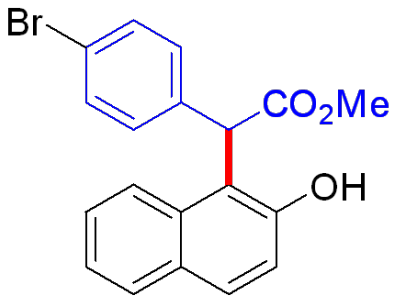


8ak

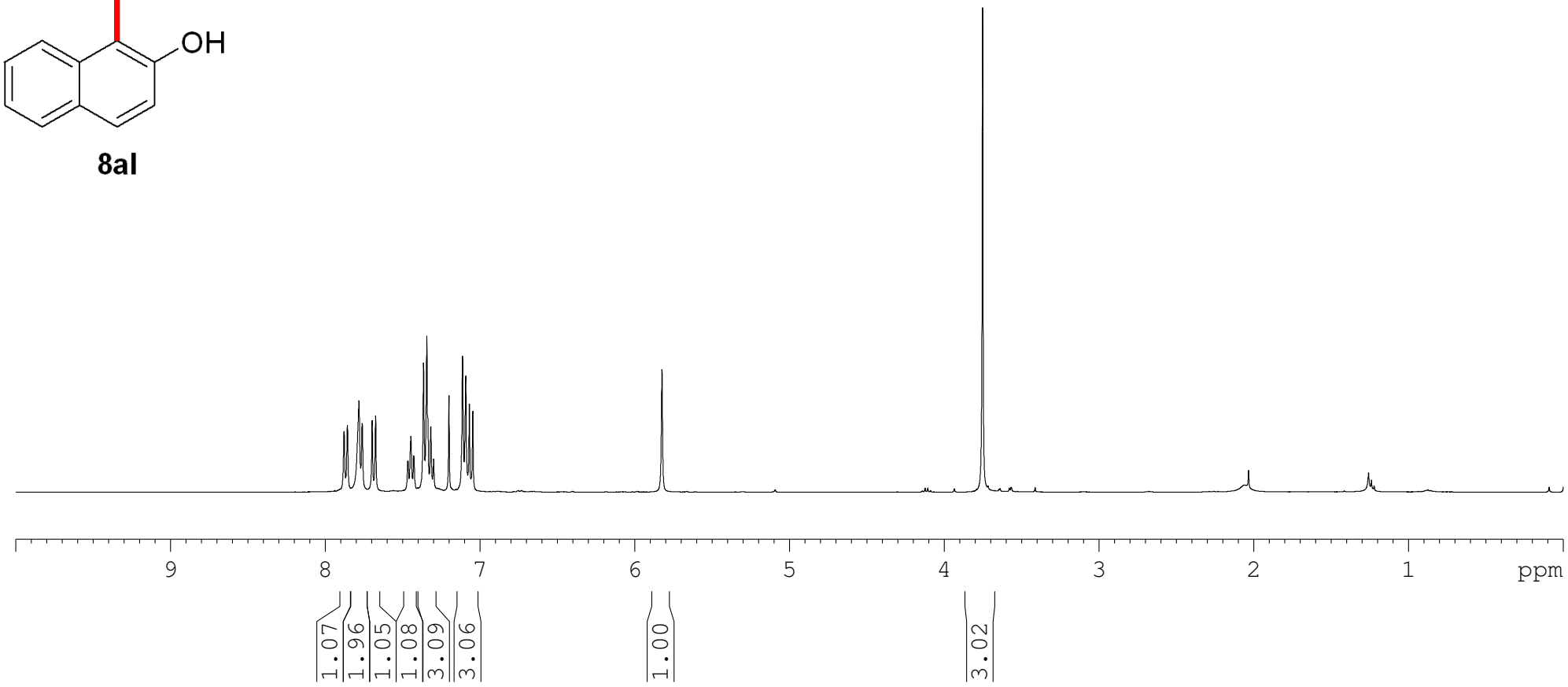


mb-10-11-2


7.880
7.858
7.784
7.763
7.698
7.676
7.468
7.448
7.430
7.366
7.345
7.339
7.319
7.301
7.114
7.093
7.070
7.048
5.825
3.753

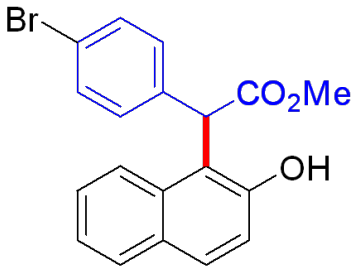

Br
CO2Me
OH

8al


9
8
7
6
5
4
3
2
1
ppm
1.07
1.96
1.05
1.08
3.09
3.06
1.00
3.02

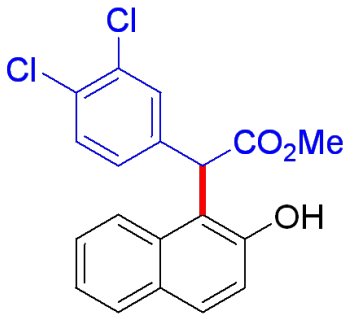
mb-10-11-2

175.80
152.92
135.91
132.94
131.52
130.31
129.91
129.38
128.94
127.22
123.34
121.77
121.22
119.50
115.14
77.32
77.00
76.68
53.05
47.79



8al

mb-10-14-2

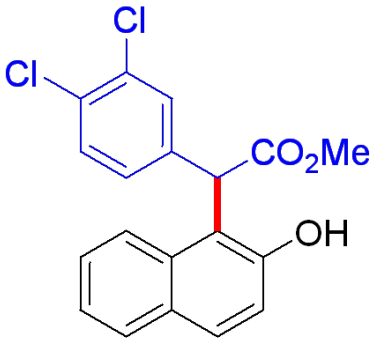

Cl
Cl
CO2Me
OH

8am

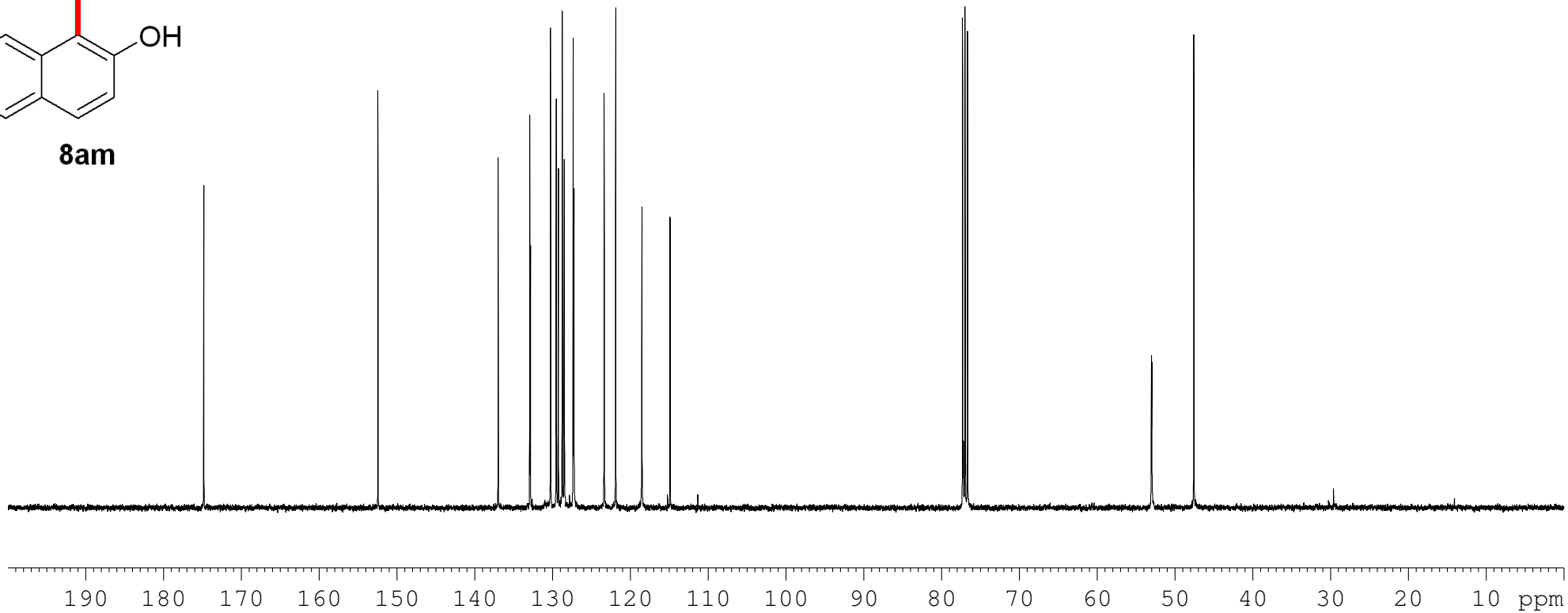
7.743
7.723
7.666
7.645
7.614
7.592
7.426
7.408
7.389
7.342
7.307
7.288
7.271
6.968
6.946
6.930
6.927
6.907
6.887
6.868
6.115
3.705
9
8
7
6
5
4
3
2
1
ppm
1.00
1.99
1.01
0.97
2.02
3.00
1.00
2.99

mb-10-14-2

174.85
152.47
137.02
132.97
132.95
132.87
130.28
129.55
129.27
128.78
128.52
127.37
127.28
123.39
121.91
118.54
114.92
77.32
77.00
76.68
53.04
47.59



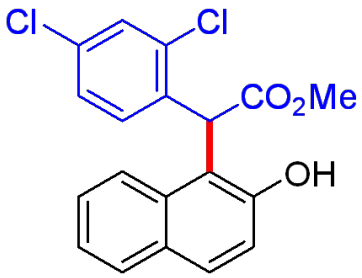
8am



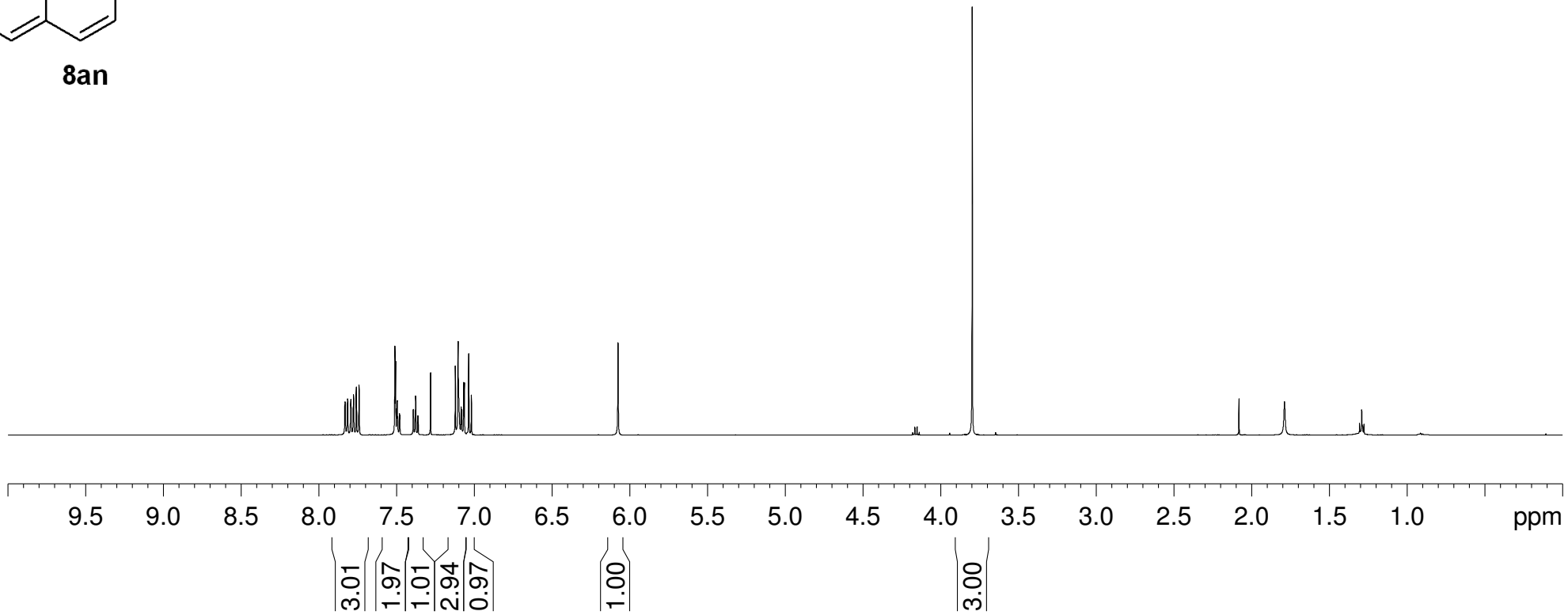
mb-10-10-2

7.833 7.817 7.796 7.779 7.761 7.743 7.512 7.508 7.501 7.498 7.495 7.484 7.481 7.395 7.393 7.379 7.365 7.363 7.124 7.106 7.087 7.082 7.070 7.066 7.038 7.021 6.077

3.799

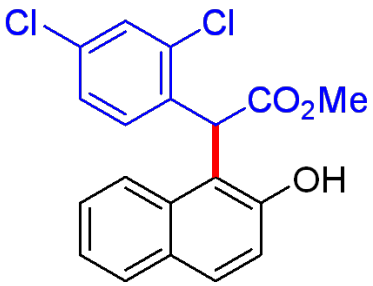


8an



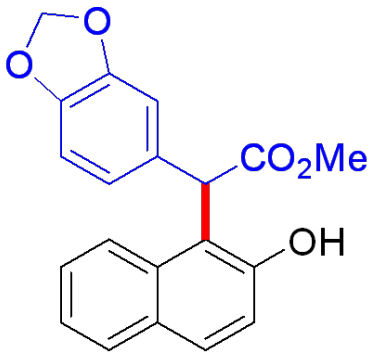
mb-10-10-2

174.63
152.77
135.24
133.99
132.95
131.16
130.56
129.47
129.30
128.90
127.47
127.33
123.58
121.88
118.96
114.14
77.26
77.00
76.75
53.15
46.38



8an

mb-10-16-1

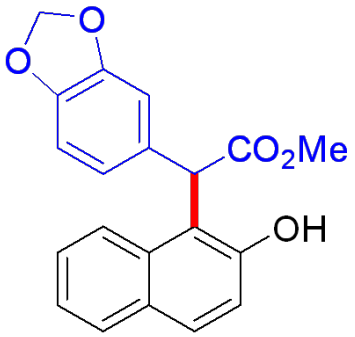

O
O
CO2Me
OH

8ao

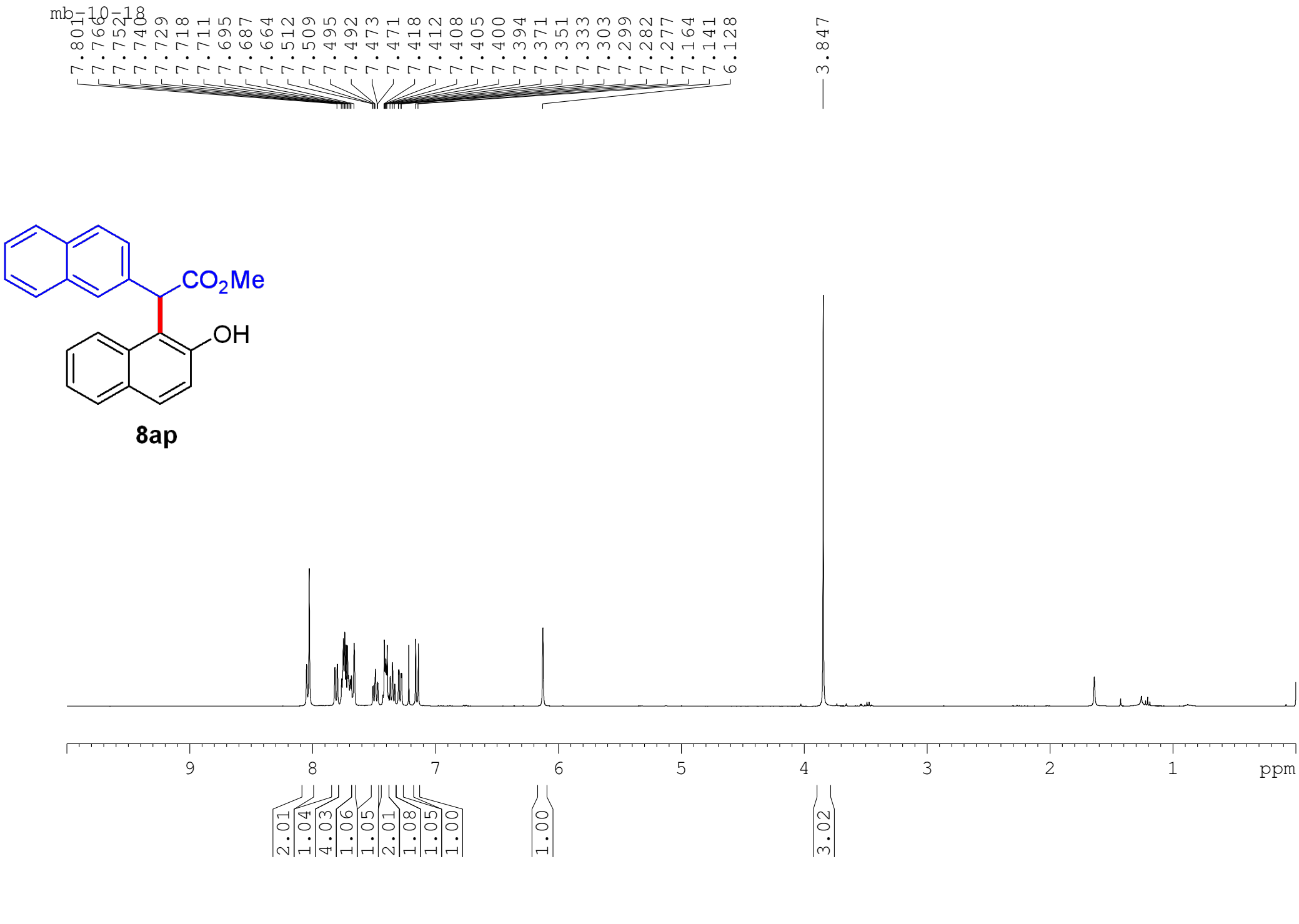
7.947
7.928
7.789
7.769
7.720
7.697
7.490
7.487
7.473
7.469
7.451
7.448
7.347
7.346
7.328
7.310
7.122
7.100
6.712
6.703
5.849
5.841
3.782
9
8
7
6
5
4
3
2
1
ppm
1.97
0.97
0.99
0.99
1.00
0.99
2.97
1.95
1.08
3.00

mb-10-16-1

176.32
153.33
147.90
146.79
133.09
130.43
130.24
129.41
128.91
127.16
123.25
121.74
121.12
119.95
115.21
108.60
108.14
101.04
77.32
77.00
76.69
53.09
48.07



8ao


mb-10-18
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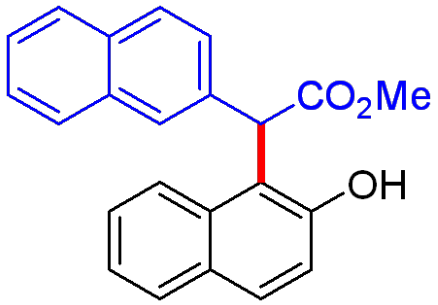
7.766
7.752
7.740
7.729
7.718
7.711
7.695
7.687
7.664
7.512
7.509
7.495
7.492
7.473
7.471
7.418
7.412
7.408
7.405
7.400
7.394
7.371
7.351
7.333
7.303
7.299
7.282
7.277
7.164
7.141
6.128
3.847
CO2Me
OH
8ap
9
8
7
6
5
4
3
2
1
ppm
2.01
1.04
4.03
1.06
1.05
2.01
1.08
1.05
1.00
1.00
3.02

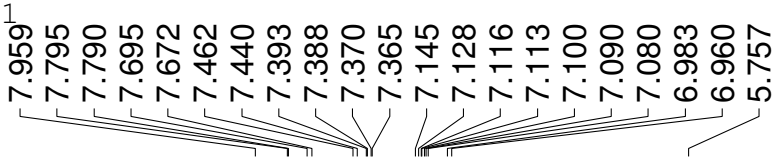
mb-10-18

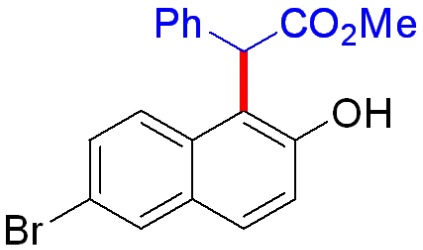
176.28
153.87
133.93
133.29
133.24
132.57
130.43
129.49
128.96
128.39
128.00
127.51
127.24
126.33
126.15
126.01
125.90
123.31
121.82
120.27
114.78
77.32
77.00
76.68
53.16
48.48



8ap

mb-10-24-1


7.959
7.795
7.790
7.695
7.672
7.462
7.440
7.393
7.388
7.370
7.365
7.145
7.128
7.116
7.113
7.100
7.090
7.080
6.983
6.960
5.757
3.667

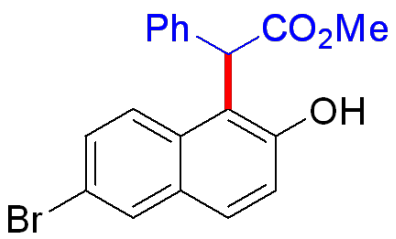

Ph
CO2Me
OH
Br

8ba

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.07
0.99
1.10
1.01
0.99
5.04
1.02
1.00
3.01

mb-10-24-1

176.06
153.52
136.39
131.72
130.66
130.52
130.16
129.18
128.56
127.87
127.37
123.88
120.89
116.86
115.58
77.32
77.00
76.68
53.07
48.37



8ba

mb-10-12

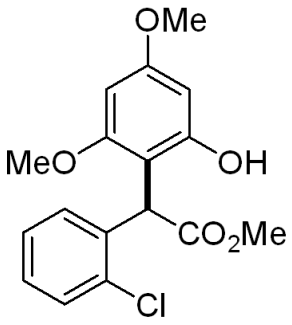
9.620

7.193
7.191
7.172
6.986
6.982
6.967
6.963
6.947
6.854
6.835

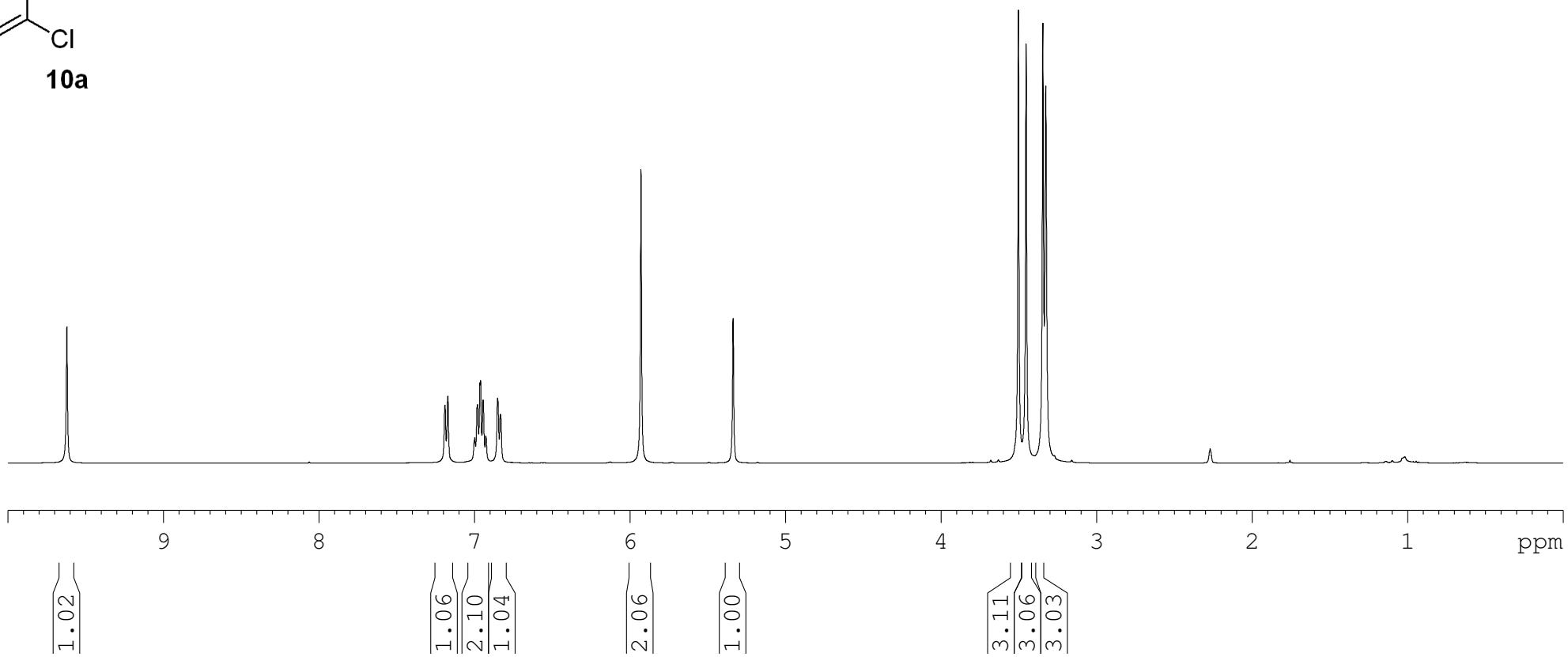
5.931

5.339

3.504
3.455
3.347
3.328



10a



1.02

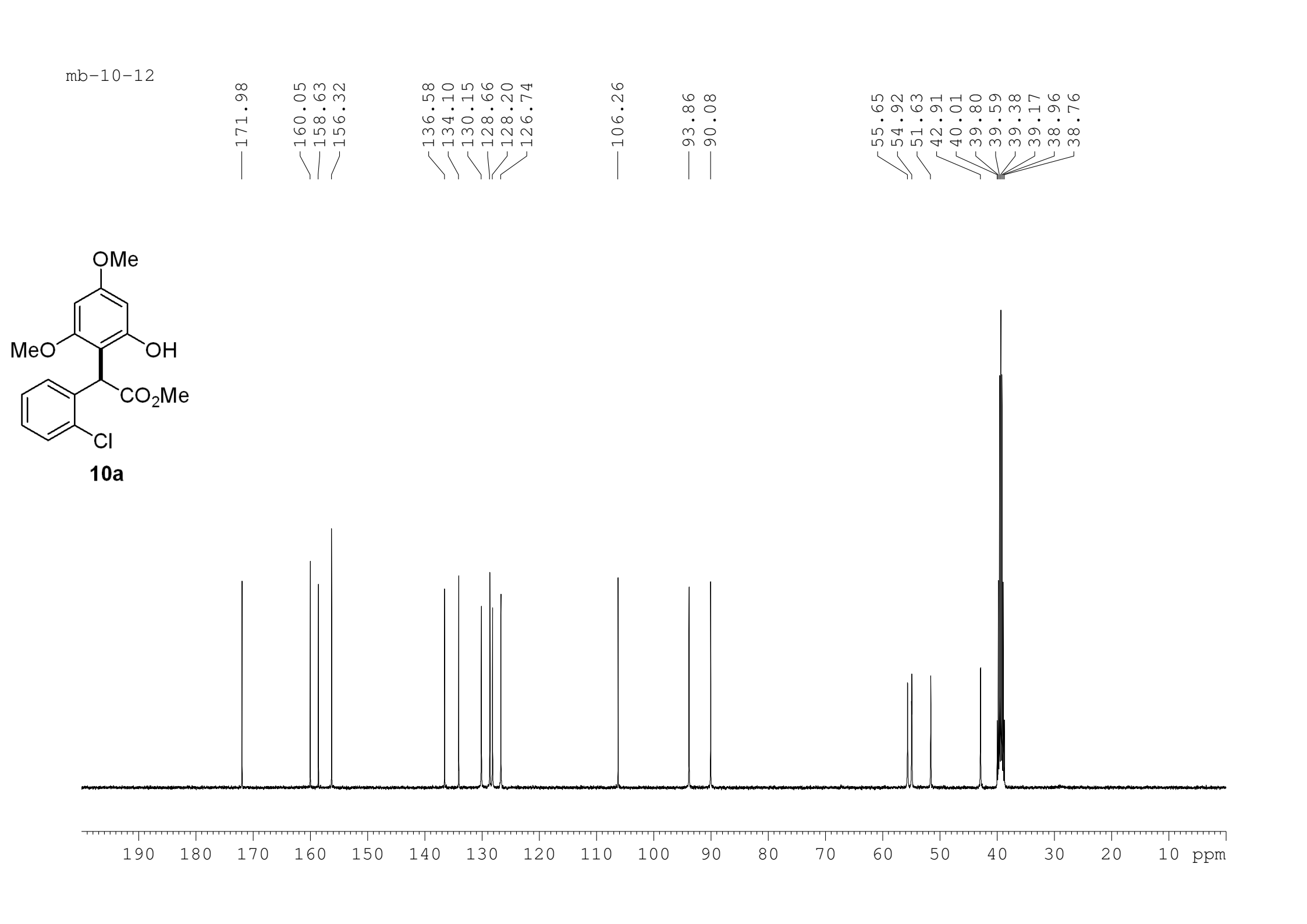
1.06
2.10
1.04

2.06

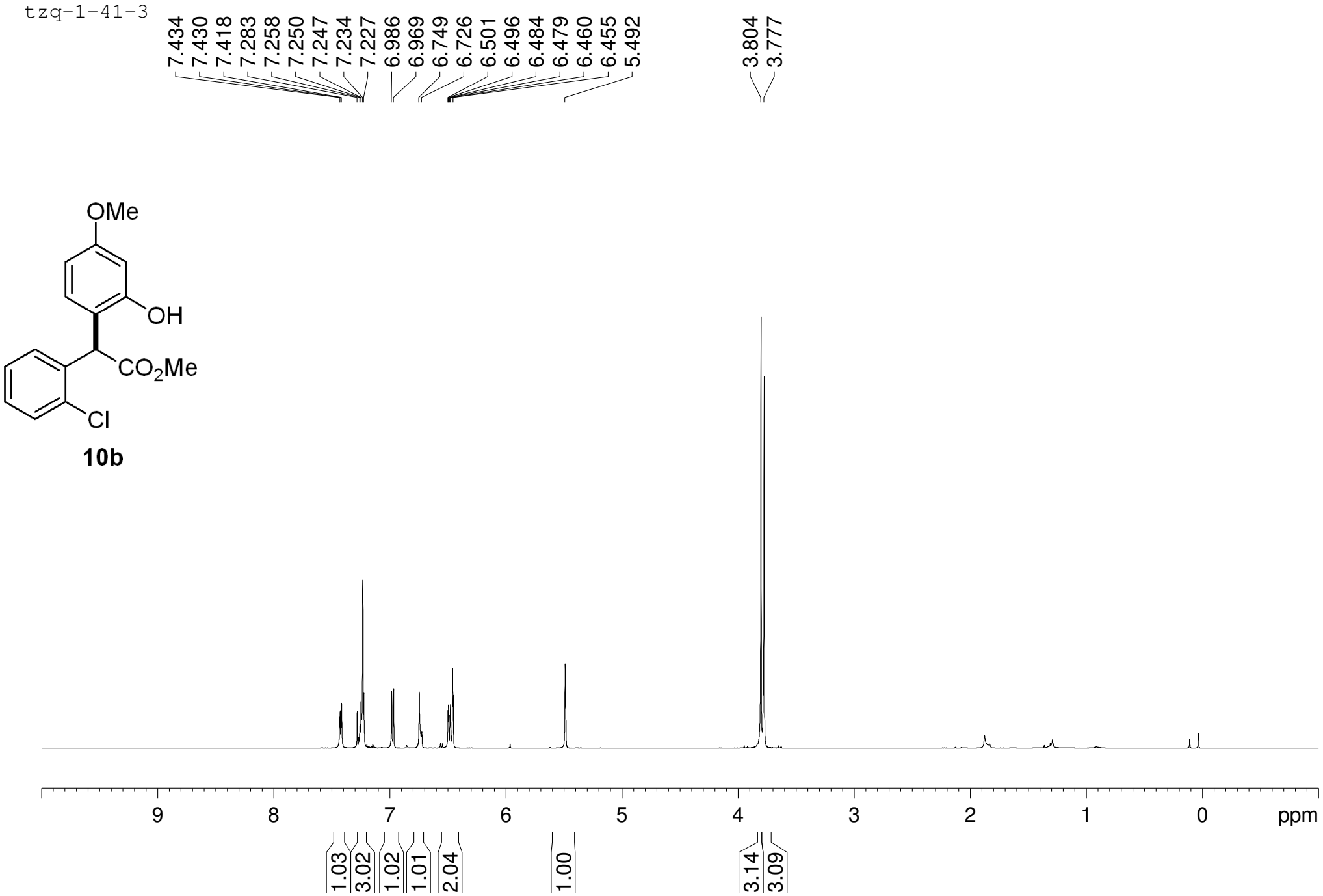
1.00

3.11
3.06
3.03

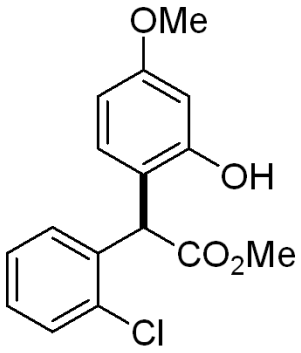
mb-10-12


171.98
160.05
158.63
156.32
136.58
134.10
130.15
128.66
128.20
126.74
106.26
93.86
90.08
55.65
54.92
51.63
42.91
40.01
39.80
39.59
39.38
39.17
38.96
38.76
OMe
MeO
OH
CO2Me
Cl
10a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

tzq-1-41-3


7.434
7.430
7.418
7.283
7.258
7.250
7.247
7.234
7.227
6.986
6.969
6.749
6.726
6.501
6.496
6.484
6.479
6.460
6.455
5.492
3.804
3.777
OMe
OH
CO2Me
Cl
10b
9
8
7
6
5
4
3
2
1
0
ppm
1.03
3.02
1.02
1.01
2.04
1.00
3.14
3.09

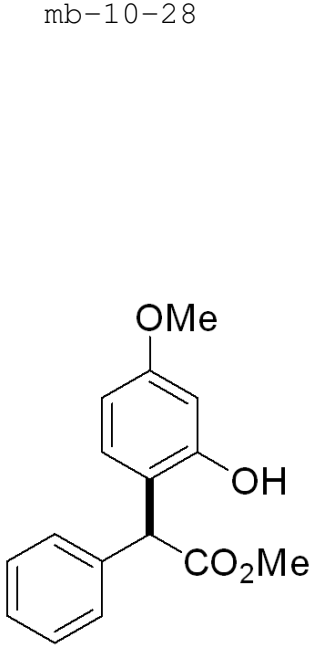
mb-10-28


OMe
OH
CO2Me
Cl

10b

175.62
160.32
155.43
137.25
131.14
128.57
128.02
127.26
116.78
106.19
102.90
77.32
77.00
76.68
55.16
52.97
52.74
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

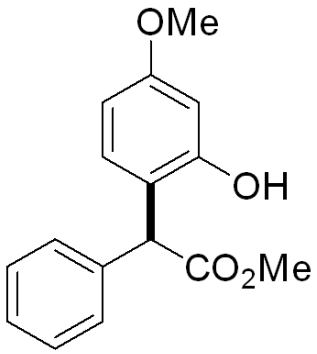
mb-10-28


OMe
OH
CO2Me

10c

7.410
7.221
7.199
7.194
7.184
7.156
7.148
7.141
6.862
6.855
6.846
6.839
6.331
6.325
6.315
6.309
5.031
3.661
3.590
9
8
7
6
5
4
3
2
1
ppm
1.02
5.05
1.01
2.02
1.00
3.09
3.04

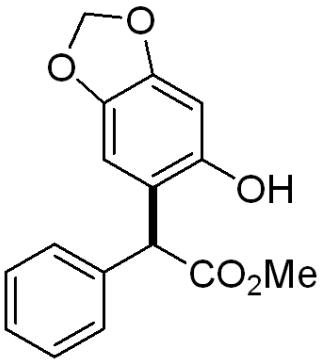
mb-10-28


OMe
OH
CO2Me

10c

175.62
160.32
155.43
137.25
131.14
128.57
128.02
127.26
116.78
106.19
102.90
77.32
77.00
76.68
55.16
52.97
52.74
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

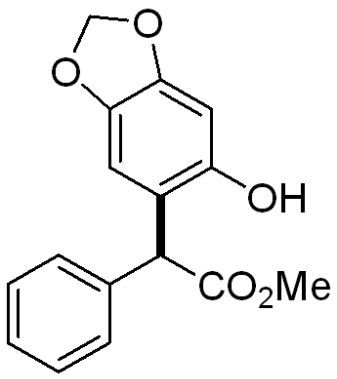
mb-10-30


O
O
OH
CO2Me

10d

7.247
7.232
7.229
7.220
7.211
7.184
7.173
7.168
7.155
7.147
6.837
6.454
6.295
5.751
5.031
3.681
9
8
7
6
5
4
3
2
1
ppm
5.01
0.91
0.99
1.00
2.04
1.00
3.02

mb-10-30

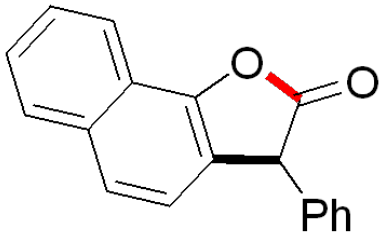

O
O
OH
CO2Me

10d

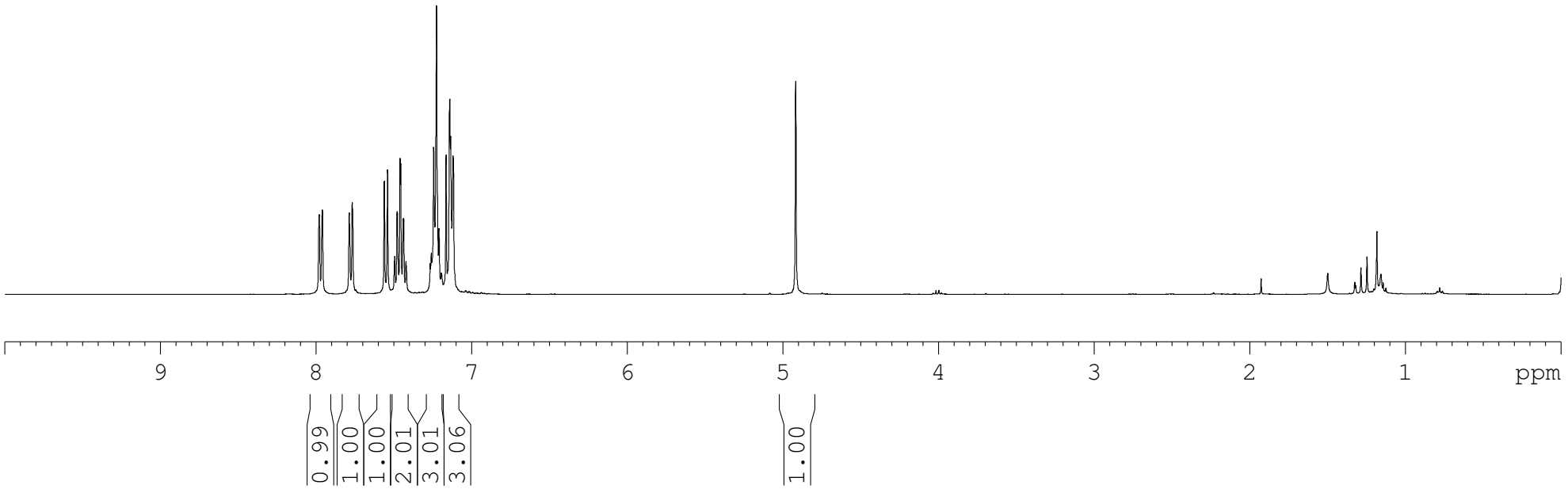
175.18
149.15
147.55
141.35
137.12
128.65
128.12
127.37
116.33
109.51
101.12
99.31
77.32
77.00
76.68
52.75
52.70
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

mb-9-106

7.978
7.959
7.785
7.766
7.563
7.542
7.498
7.496
7.481
7.479
7.462
7.457
7.441
7.438
7.424
7.421
7.261
7.256
7.246
7.238
7.227
7.223
7.213
7.166
7.144
7.142
7.136
7.121
4.919

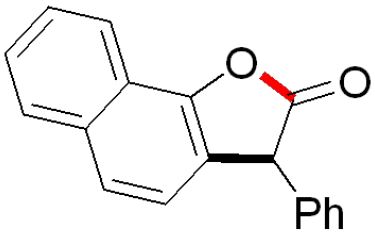


11



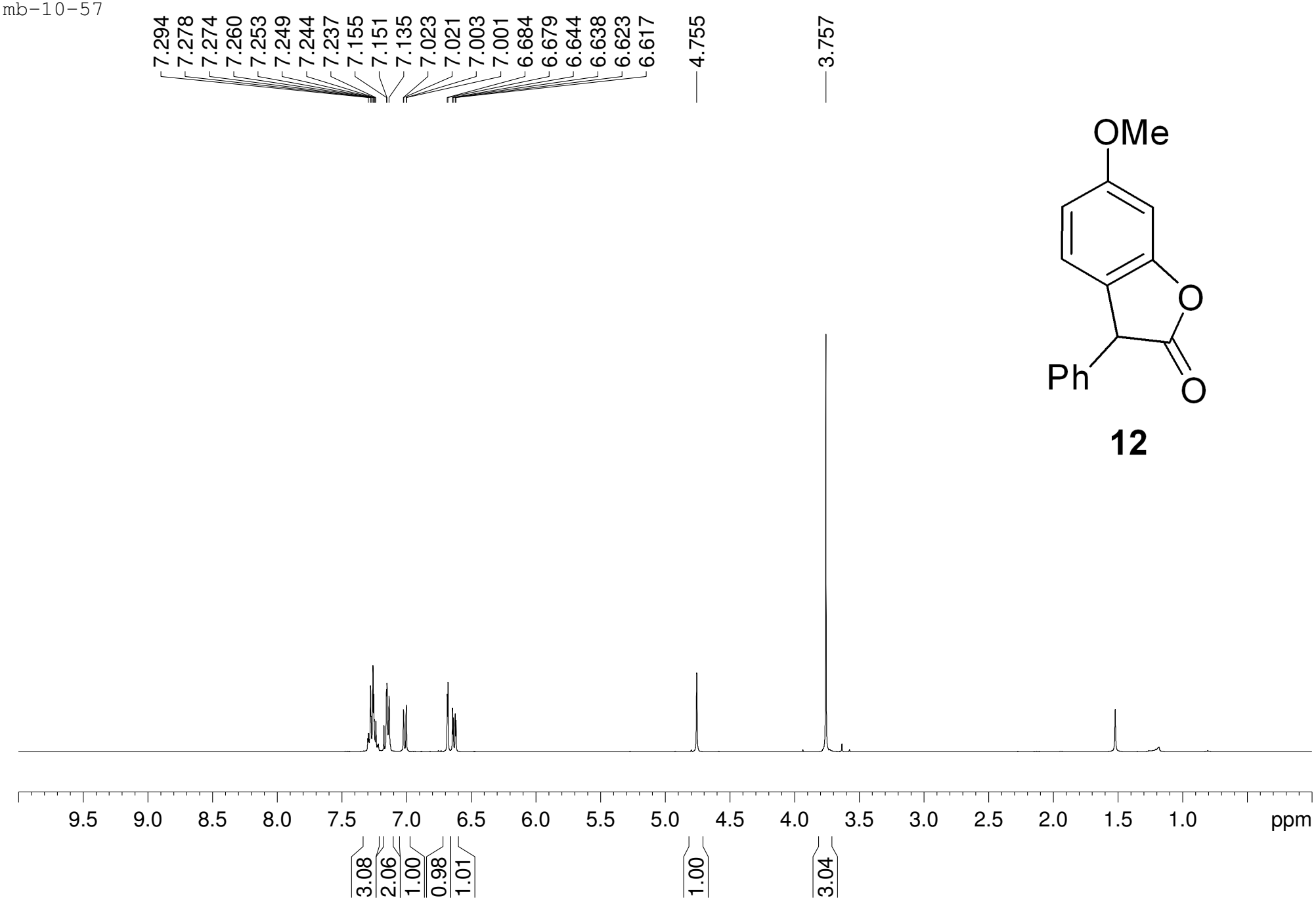
mb-9-108

175.55
151.94
134.83
131.03
130.69
129.37
129.24
129.19
128.32
128.28
127.62
124.86
123.25
119.37
111.45
77.32
77.00
76.68
49.79



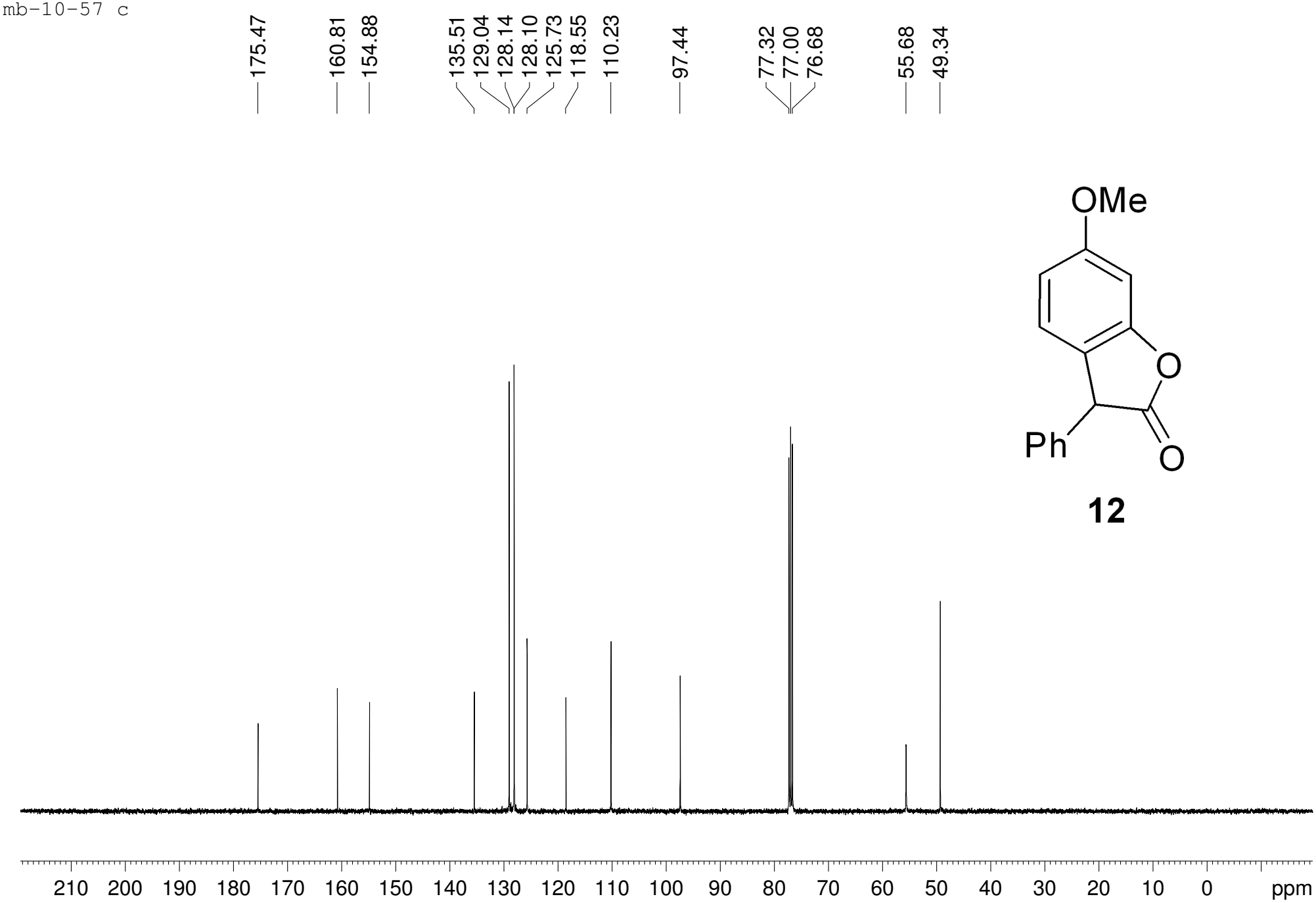
11

mb-10-57


7.294
7.278
7.274
7.260
7.253
7.249
7.244
7.237
7.155
7.151
7.135
7.023
7.021
7.003
7.001
6.684
6.679
6.644
6.638
6.623
6.617
4.755
3.757
OMe
O
Ph
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.08
2.06
1.00
0.98
1.01
1.00
3.04

12

mb-10-57 c


175.47
160.81
154.88
135.51
129.04
128.14
128.10
125.73
118.55
110.23
97.44
77.32
77.00
76.68
55.68
49.34
OMe
O
Ph
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

12