Electronic Supplementary Information (ESI)

Chiral Cobalt(II) Complex Catalyzed Friedel-Crafts-Aromatization for Synthesis of Axially Chiral Biaryldiols

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1. General information1.

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0).

Enantiomeric excess (e.e.) were determined by HPLC analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 ^{o}C.

Optical rotations were reported as follows: $[\alpha]_D^{25}$ (*c*: g/100 mL, in solvent).

HRMS was recorded on a commercial apparatus (ESI Source).

All catalytic reactions were run in dried glassware or test tube.

THF, toluene and diethyl ether (Et_2O) were distilled from sodium and benzophenone as indicator.

CH_3CN and CH_2Cl_2 was distilled over CaH_2.

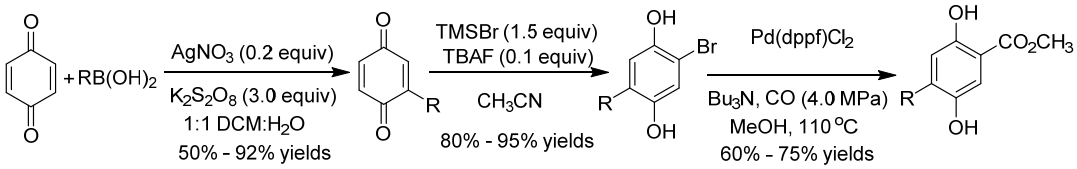
$Co(ClO_4)_2 \cdot 6H_2O$ (99%), Ag_2O were purchased from Alfa.

All racemic products (**3aa-3oa**) were obtained by using $Co(ClO_4)_2 \cdot 6H_2O$ (10 mol%) and racemic *N*,*N*'-dioxide ligand (***L*-RaPr$_2$** 10 mol%) as the catalyst according to general procedure for the catalytic enantioselective Friedel-Crafts- Aromatization reaction.

Quinone substrates (**1a-1k**) were synthesized by using the literature method (Chen, Y, H. Cheng, D, J. Zhang, J. Wang, Y. Liu, X, Y. Tan, B. *J. Am. Chem. Soc*. **2015**, *137*, 15062.).
Quinone substrates (**1m**, **1n, 1o**) were synthesized as follow method.

2-nathphol substrates (**2a-2e**) were purchased from commercial source.
2-nathphol substrates (**2f-2v**) were obtained by using the literature method as followed (Q. Yin, S. G. Wang, X. W. Liang, D. W. Gao, J. Zheng and S. L. You, *Chem. Sci.*, **2015**, *6*, 4179.).

2.The method for the synthesis of quinone substrates [1]

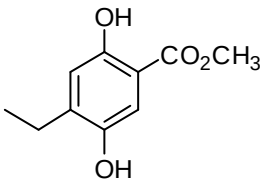


To a solution of benzoquinone (20 mmol, 1.0 equiv) in dichloromethane (100 mL) was added the corresponding boronic acid (30 mmol, 1.5 equiv), water (100 mL), and silver(I) nitrate (680 mg, 4.0 mmol, 0.2 equiv). Potassium persulfate (16.2 g, 60 mmol, 3.0 equiv) was then added and the solution was stirred vigorously at room temperature and monitored by thin-layer chromatography analysis of the organic layer. Upon consumption of quinone (3 – 24 h), the reaction was diluted with dichloromethane (50 mL). The layers were separated, and the aqueous layer was extracted with dichloromethane (3 x30 mL), dried over sodium sulfate, and evaporated in vacuo. The product was used for next step with silica gel quick purification.

To a solution of corresponding substituted benzoquinone in CH_3CN (30 mL), trimethylsilylbromide (TMSBr, 30 mmol, 4.0 mL) was added, and tetraethylammonium fluoroborate (TBAF, 1.0 M in THF, 1.5 mmol, 1.5 mL) in CH_3CN (10 mL) was carefully added, at which time the quinone color was disappeared. The reaction mixture was stirred for 2 hours at room temperature. After removal of solvent in vacuo, the resulted mixture was mixed with water (10 mL) and ethyl acetate (30 mL).The aqueous layer was separated and extracted with ethyl acetate twice (2 x 15 mL). The organic layers were combined and dried over sodiumsulfate, filtrated and removal of the solvent in vacuo. Purification was performed by silica gel chromatography to yield the pure product.

To a solution of the corresponding bromo-substituted benzene-1,4-diol (10 mmol) in DMF (15 mL), $Pd(dppf)Cl_2$ (0.75 g, 1.0 mmol), MeOH (6 mL), Bu_3N (2.74 mL, 14.8 mmol) was added in sequence. The vessel was purged and pressurized with CO (4.0 MPa) and stirred at 110 ^oC for 24 h. The reaction was cooled to room temperature, diluted with CH_2Cl_2 (50 mL), washed with 1N HCl (2 x 35 mL), brine/water (1:1, 35 mL), and brine (35 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to afford a dark purple oil. The residue was purified by flash chromatography (5-10% EtOAc/hexanes) to afford the titled compound as a white solid.

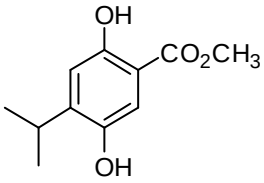
1.a) Y. Fujiwara, V. Domingo, I. B. Seiple, R.Gianatassio, M. D. Bel, and P. S. Baran, *J. Am. Chem. Soc.* **2011**, *133*, 3292-3295; b) M.Nakazaki, K.Naemura,*J. Org. Chem.* **1981**, *46*, 106-111; c) L. L. Miller, R. F. Stewart, *J. Org. Chem.* **1978**, *43*, 3078-3079; d) D. A. Evans, J. M. Wu, *J. Am. Chem. Soc.* **2003**, *125*, 10162-10163.



Methyl 4-ethyl-2,5-dihydroxybenzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 7.18 (s, 1H), 6.79 (s, 1H), 4.62 (s, 1H), 3.91 (s, 3H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.23 (td, *J* = 7.6, 1.6 Hz, 3H);

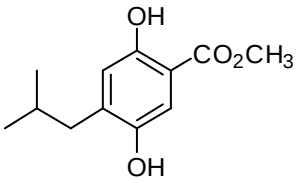
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 155.9, 145.9, 140.5, 117.7, 114.2, 109.6, 52.2, 23.4, 13.3.



Methyl 2,5-dihydroxy-4-isopropylbenzoate

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.18 (s, 1H), 6.84 (s, 1H), 4.49 (s, 1H), 3.92 (s, 3H), 3.42 – 3.05 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 6H);

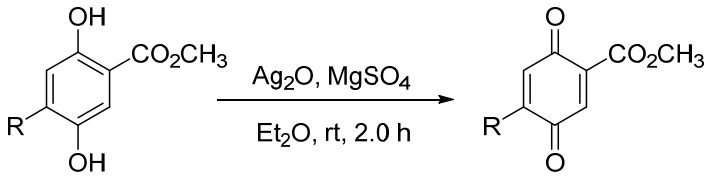
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 156.3, 145.3, 145.0, 115.3, 114.3, 109.5, 52.2, 27.6, 22.2.



Methyl 2,5-dihydroxy-4-isobutylbenzoate

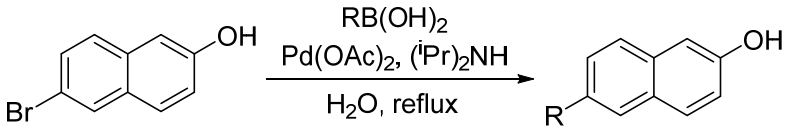
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.19 (s, 1H), 6.73 (s, 1H), 4.54 (s, 1H), 3.91 (s, 3H), 2.47 (d, *J* = 7.2 Hz, 2H), 2.0 –1.90 (m, 1H), 1.05 – 0.81 (m, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 155.6, 146.2, 138.2, 119.5, 114.4, 109.9, 52.2, 39.66, 28.6, 22.5.

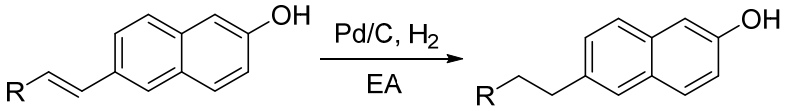


To a 25 mL round-bottom flask was added 2,5-dihydroxy-bznzoic acid methyl ester (1.0 mmol), $MgSO_4$ (dried at 300 ^{o}C for 2.0 h before use, 360 mg, 3 mmol), and Et_2O (dry, 20 mL). The solution was added Ag_2O (700 mg, 3.0 mmol), and then stirred for 2.0 h at room temperature. The reaction mixture was then filtered, washed with 10 mL of Et_2O (dry), and concentrated under reduced pressure at room temperature to afford the quinone product. The product was immediately used without further purification. (The product is sensitive to acid, H_2O and light, and stable at -20 ^{o}C for at least one week without any noticeable polymerization as judged by ^{1}H NMR spectroscopy)

3. The method for the synthesis of naphthalen-2-ol substrates [2]

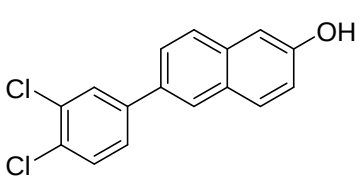


To a mixture of 6-bromonaphthalen-2-ol (1.1 g, 5 mmol, 1 eq), $RB(OH)_2$ (7.5 mmol, 1.5 eq) and $Pd(OAc)_2$ (45 mg, 0.2 mmol, 0.04 eq) in water (10 mL) was added diisopropylamine (1 mL). After heat to reflux for 10 hours, the mixture was then filtered and washed with 10 mL ethyl actate 3 times, The aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dry over Na_2SO_4, filtered and then concentrated. The residue was purified by silica gel column chromatograph (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product.



To a solution of 6-alkenylnaphthalen-2-ol (1 mmol, 1 eq) in ethyl acetate (3 mL), 10% Pd/C (20 mg) was added under N_2 atmosphere. Then the reaction was charged with 1 atm of hydrogen and stirred at room temperature for 17 hours. The reaction mixture was filtered and washed with ethyl acetate. The filtrate was concentrated under reduce pressure. The crude product was purified by silica gel column (ethyl acetate/petroleum ether = 1/30, v/v) to afford the product.

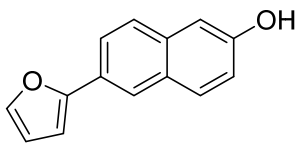
2. Q. Yin, S. G.. Wang, X. W. Liang, D. W. Gao, J. Zheng and S. L. You, *Chem. Sci.*, **2015**, *6*, 4179.



6-(3,4-dichlorophenyl)naphthalen-2-ol

^{1}H NMR (400 MHz, DMSO) δ 9.92 (s, 1H), 8.17 (s, 1H), 8.03 (d, J = 2.0 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.82 – 7.66 (m, 4H), 7.20 – 7.17 (m, 1H), 7.16 (dd, J = 8.8, 2.3 Hz, 1H).

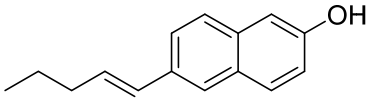
^{13}C NMR (101 MHz, DMSO) δ 156.0, 140.9, 134.3, 131.7, 131.5, 130.9, 130.0, 129.6, 128.2, 127.8, 126.9, 126.6, 125.7, 124.8, 119.3, 108.5 .



6-(furan-2-yl)naphthalen-2-ol

^{1}H NMR (400 MHz, DMSO) δ 9.84 (s, 1H), 8.09 (s, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 10.6 Hz, 3H), 7.12 (dd, J = 11.2, 1.7 Hz, 2H), 6.97 (d, J = 3.2 Hz, 1H), 6.64 – 6.56 (m, 1H).

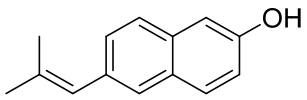
^{13}C NMR (101 MHz, DMSO) δ 155.6, 153.5, 142.5, 133.8, 129.7, 127.6, 126.7, 124.8, 122.4, 121.5, 119.2, 112.1, 108.8, 105.2 .



(E)-6-(pent-1-en-1-yl)naphthalen-2-ol

^{1}H NMR (400 MHz, DMSO) δ 9.71 (s, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.53 (d, J = 8.4 Hz, 1H), 7.07 (dd, J = 8.4, 7.2 Hz, 2H), 6.48 (d, J = 16.0 Hz, 1H), 6.43 – 6.15 (m, 1H), 2.19 (dd, J = 14.4, 7.0 Hz, 2H), 1.48 (dd, J = 14.4, 7.2 Hz, 2H), 0.94 (t, J = 7.2 Hz, 3H).

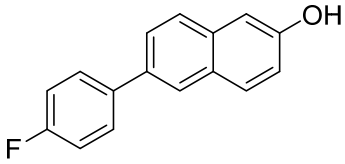
^{13}C NMR (101 MHz, DMSO) δ 155.2, 133.8, 131.8, 130.0, 129.4, 129.2, 127.8, 126.3, 125.0, 123.7, 118.7, 108.7, 34.6, 22.1, 13.6.



6-(2-methylprop-1-en-1-yl)naphthalen-2-ol

^{1}H NMR (400 MHz, DMSO) δ9.70 (s, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.28 (d, J = 8.8 Hz, 1H), 7.12 – 7.01 (m, 2H), 6.35 (s, 1H), 1.90 (d, J = 6.8 Hz, 6H).

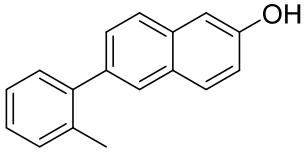
^{13}C NMR (101 MHz, DMSO) δ 155.10, 134.22, 132.90, 132.36, 129.21, 127.5, 127.6, 126.58, 125.65, 125.01, 118.67, 108.45, 26.73, 19.36.



6-(4-fluorophenyl)naphthalen-2-ol

^{1}H NMR (400 MHz, DMSO) δ 9.85 (s, 1H), 8.08 (s, 1H), 7.88 – 7.76 (m, 4H), 7.72 (d, J = 8.8 Hz, 1H), 7.33 (t, J = 8.8 Hz, 2H), 7.22 – 7.11 (m, 2H).

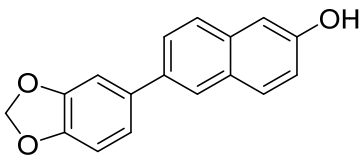
^{13}C NMR (101 MHz, DMSO) δ 155.56, 136.74 (d, J = 3.1 Hz), 133.77, 133.26, 129.76, 128.49 (d, J = 8.1 Hz), 127.91, 126.72, 125.1, 125.0, 119.10, 115.77, 115.56, 108.43.



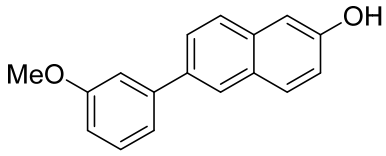
6-(o-tolyl)naphthalen-2-ol

^{1}H NMR (400 MHz, DMSO) δ 9.80 (s, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 9.6 Hz, 2H), 7.39 (d, J = 8.4 Hz, 1H), 7.29 (dd, J = 10.8, 1.2 Hz, 4H), 7.19 (s, 1H), 7.14 (d, J = 8.8 Hz, 1H), 2.28 (s, 3H).

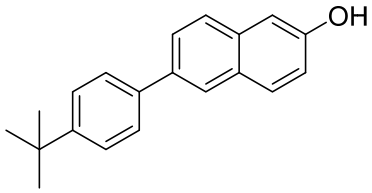
^{13}C NMR (101 MHz, DMSO) δ 155.5, 141.4, 135.5, 134.9, 133.4, 130.3, 129.7, 129.5, 127.6, 127.3, 127.1, 125.9, 125.7, 118.9, 108.4, 20.3 .



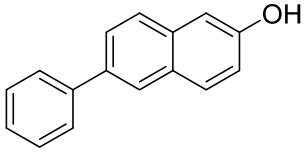
6-(benzo[d][1,3]dioxol-5-yl)naphthalen-2-ol
^{1}H NMR (400 MHz, DMSO) δ 9.79 (s, 1H), 8.01 (s, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.35 (s, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.12 (dd, J = 12.4, 3.6 Hz, 2H), 7.02 (d, J = 8.0 Hz, 1H), 6.08 (s, 2H).
^{13}C NMR (101 MHz, DMSO) δ 155.4, 148.0, 146.5, 134.6, 134.1, 133.6, 129.7, 128.0, 126.5, 125.2, 124.6, 120.1, 119.0, 108.7, 108.4, 107.0, 101.1 .



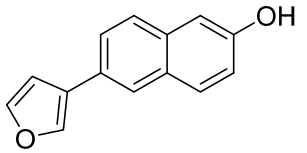
6-(3-methoxyphenyl)naphthalen-2-ol
^{1}H NMR (400 MHz, DMSO) δ 9.84 (s, 1H), 8.10 (s, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.75 (dt, J = 8.8, 5.2 Hz, 2H), 7.40 (t, J = 7.6 Hz, 1H), 7.32 (dd, J = 9.6, 5.2 Hz, 2H), 7.19 – 7.11 (m, 2H), 6.94 (dd, J = 8.0, 2.4 Hz, 1H), 3.85 (s, 3H).
^{13}C NMR (101 MHz, DMSO) δ 159.8, 155.6, 141.8, 134.2, 134.0, 129.9, 129.8, 127.9, 126.6, 125.3, 125.2, 119.0, 112.62, 112.1, 108.4, 55.1 .



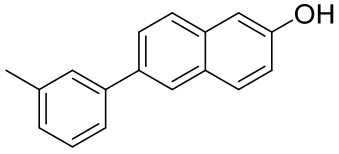
6-(4-(tert-butyl)phenyl)naphthalen-2-ol
^{1}H NMR (400 MHz, DMSO) δ 9.80 (s, 1H), 8.04 (s, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.73 – 7.62 (m, 3H), 7.48 (d, J = 8.0 Hz, 2H), 7.13 (dd, J = 13.6, 4.8 Hz, 2H), 1.32 (s, 9H).
^{13}C NMR (101 MHz, DMSO) δ 155.4, 149.4, 137.4, 134.2, 133.7, 129.7, 128.0, 126.62 (s), 126.2, 125.7, 125.2, 124.7, 119.0, 108.5, 34.2, 31.1 .



6-phenylnaphthalen-2-ol
^{1}H NMR (400 MHz, DMSO) δ 9.83 (s, 1H), 8.08 (s, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.81 – 7.66 (m, 4H), 7.49 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.23 – 7.05 (m, 2H).
^{13}C NMR (101 MHz, DMSO) δ 155.6, 140.3, 134.3, 133.9, 129.8, 128.9, 128.0, 127.0, 126.7, 126.6, 125.2, 125.1 119.1, 108.4 .

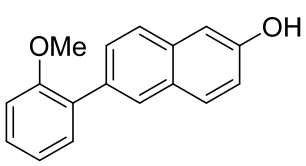


6-(furan-3-yl)naphthalen-2-ol
^{1}H NMR (400 MHz, DMSO) δ9.76 (s, 1H), 8.24 (s, 1H), 7.99 (s, 1H), 7.76 (t, J = 5.2 Hz, 2H), 7.72 – 7.64 (m, 2H), 7.15 – 7.07 (m, 2H), 7.07 – 7.01 (m, 1H).
^{13}C NMR (101 MHz, DMSO) δ 155.2, 144.2, 139.0, 133.6, 129.2, 127.9, 126.5, 126.2, 126.0, 124.5, 123.4, 119.0, 108.7 .

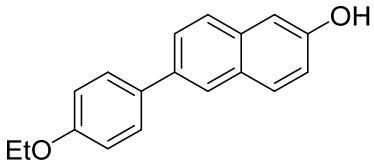


6-(m-tolyl)naphthalen-2-ol
^{1}H NMR (400 MHz, DMSO) δ 9.80 (s, 1H), 8.07 (s, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.73 (dt, J = 8.8, 5.2 Hz, 2H), 7.59 (s, 1H),

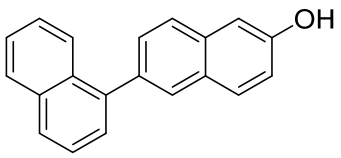
7.54 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.22 – 7.06 (m, 3H), 2.40 (s, 3H).
^{13}C NMR (101 MHz, DMSO) δ 160.7, 145.5, 143.3, 139.6, 139.1, 135.0, 134.1, 133.2, 132.9, 132.5, 131.9, 130.5, 130.3, 130.2, 129.0, 124.2, 113.7, 26.4 .



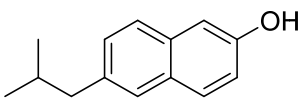
6-(2-methoxyphenyl)naphthalen-2-ol
^{1}H NMR (400 MHz, DMSO) δ 9.77 (s, 1H), 7.84 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.53 (dd, J = 8.8, 1.6 Hz, 1H), 7.39 – 7.30 (m, 2H), 7.15 (d, J = 2.4 Hz, 1H), 7.14 – 7.08 (m, 2H), 7.05 (td, J = 7.6, 0.8 Hz, 1H), 3.77 (s, 3H).
^{13}C NMR (101 MHz, DMSO) δ 156.3, 155.4, 133.5, 132.6, 130.5, 130.0, 129.6, 128.6, 128.1, 127.6, 127.5, 125.3, 120.8, 118.7, 111.7, 108.4, 55.5 .



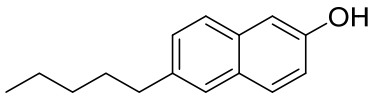
6-(4-ethoxyphenyl)naphthalen-2-ol
^{1}H NMR (400 MHz, DMSO) δ9.79 (s, 1H), 8.04 (d, J = 1.2 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.74 (dd, J = 23.2, 8.8 Hz, 4H), 7.19 – 7.10 (m, 2H), 7.06 (d, J = 8.8 Hz, 2H), 5.80 (s, 1H), 4.11 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, DMSO) δ 163.1, 160.5, 139.3, 138.7, 137.7, 134.8, 133.3, 132.9, 131.8, 130.3, 129.4, 124.2, 120.1, 113.7, 68.3, 19.9 .



[1,2'-binaphthalen]-6'-ol
^{1}H NMR (400 MHz, DMSO) δ10.00 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.95 (dd, J = 8.0, 4.4 Hz, 2H), 7.91 (s, 1H), 7.86 (dd, J = 8.4, 2.8 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.53 (ddd, J = 8.4, 5.2, 1.3 Hz, 3H), 7.50 – 7.43 (m, 1H), 7.37 (d, J = 2.4 Hz, 1H), 7.27 (dd, J = 8.8, 2.4 Hz, 1H).
^{13}C NMR (101 MHz, DMSO) δ 155.7, 139.7, 134.3, 133.8, 133.5, 131.1, 129.6, 128.3, 128.2, 127.8, 127.4, 127.1, 126.2, 126.0, 125.8, 125.5, 119.15, 108.66 .



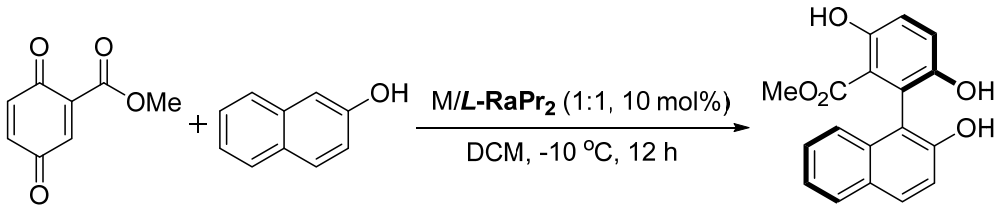
6-isobutylnaphthalen-2-ol
^{1}H NMR (400 MHz, DMSO) δ 9.64 (s, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.53 (s, 1H), 7.25 (dd, J = 8.4, 1.6 Hz, 1H), 7.12 (d, J = 2.4 Hz, 1H), 7.09 (dd, J = 8.8, 2.4 Hz, 1H), 2.57 (d, J = 7.2 Hz, 2H), 1.93 (dt, J = 13.6, 6.8 Hz, 1H), 0.92 (d, J = 6.8 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 140.5, 138.2, 134.0, 133.2, 133.0, 131.9, 131.0, 123.7, 113.7, 49.8, 34.9, 27.4.



6-pentylnaphthalen-2-ol
^{1}H NMR (400 MHz, DMSO) δ 9.62 (s, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.55 (s, 1H), 7.27 (dd, J = 8.4, 1.6 Hz, 1H), 7.10 (d, J = 2.4 Hz, 1H), 7.07 (dd, J = 8.8, 2.4 Hz, 1H), 2.75 – 2.64 (m, 2H), 1.71 – 1.60 (m, 2H), 1.33 (dd, J = 6.8, 3.6 Hz, 4H), 0.89 (t, J = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, DMSO) δ 159.9, 141.7, 138.2, 133.9, 133.1, 132.7, 131.1, 123.69 (s), 113.7, 40.3, 36.2, 35.9, 27.2, 19.2 .

4. Optimization of the reaction conditions

Table 1: Screening the metal salts of the reaction

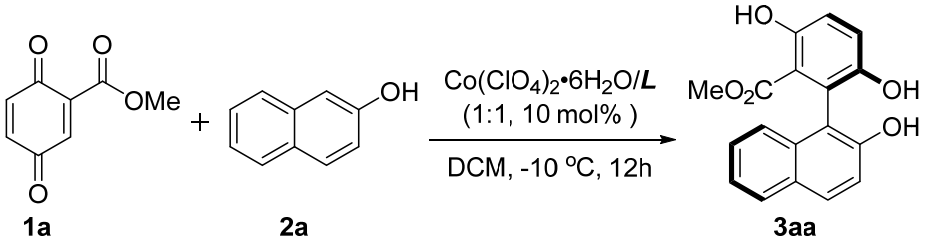


1a 2a 3aa

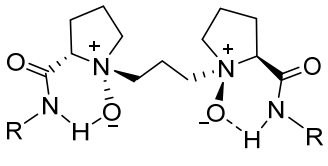
Entry[a]	Matel salt	3aa	
		Yield (%)[b]	Ee (%)[c]
1	$Cu(OTf)_2$	87	Race
2	$Mg(OTf)_2$	62	Race
3	$Ni(OTf)_2$	58	Race
4	$Zn(OTf)_2$	91	42
5	$In(OTf)_3$	59	40
6	$Y(OTf)_3$	75	7
7	$Er(OTf)_3$	71	15
8	$Sc(OTf)_3$	89	26
9	$Yb(OTf)_3$	70	17
10	$Co(ClO_4)_2 \cdot 6H_2O$	90	64
11	$Co(BF_4)_2 \cdot 6H_2O$	90	60
12	$Co(OAc)_2$	86	Race
13	$CoBr_2$	42	Race

[a] All reactions were carried out with 2-methoxycarbonyl-1,4-benzoquinone (**1a**, 0.1 mmol), 2-naphthol (**2a**, 0.1 mmol), and Ligand/Matel salt (10 mol% : 10 mol%) in 2.5 mL of DCM under N_2, unless noted otherwise. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

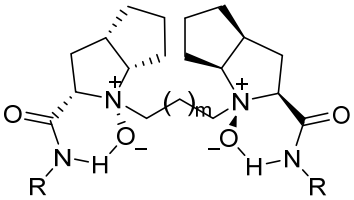
Table 2: Screening the ligands of the reaction



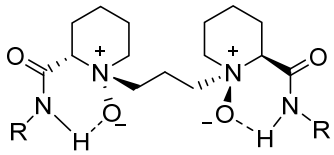
1a 2a 3aa



***L*-PrPr$_2$**: R = 2,6-*i*-$Pr_2C_6H_3$



***L*-RaPr$_2$**: R = 2,6-*i*-$Pr_2C_6H_3$, m = 1
***L*-RaPr$_3$**: R = 2,4,6-*i*-$Pr_3C_6H_2$, m = 1
***L*-RaPh**: R = C_6H_5, m = 1
***L*-RaMe2:** R = 2,6-$Me_2C_6H_3$, m = 1
***L*-RaEt2**: R = 2,6-$Et_2C_6H_3$, m = 1
***L*-Rao^{t}Bu**:R = 2-^{t}BuC_6H_4, m = 1
***L*$_2$-RaPr$_2$**: R = 2,6-*i*-$Pr_2C_6H_3$, m = 0

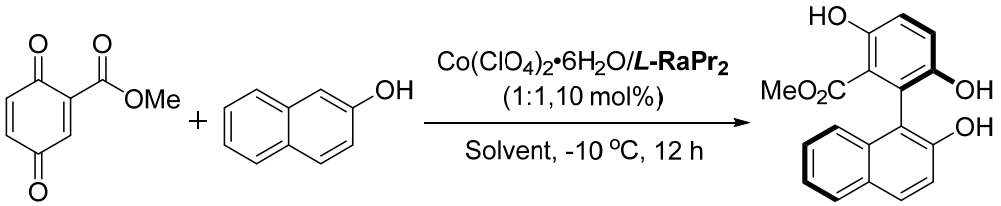


***L*-PiPr$_2$**: R = 2,6-*i*-$Pr_2C_6H_3$

Entry[a]	Ligand	3aa	
		Yield (%)[b]	Ee (%)[c]
1	***L*-PrPr$_2$**	92	44
2	***L*-PiPr$_2$**	92	20
3	***L*-RaPr$_2$**	90	64
4	***L*-RaPr$_3$**	87	47
5	***L*-RaPh**	60	Race
6	***L*-RaMe$_2$**	96	20
7	***L*-RaEt$_2$**	94	42
8	***L*-Rao^{t}Bu**	89	60
9	***L*$_2$-RaPr$_2$**	80	31

[a] All reactions were carried out with 2-methoxycarbonyl-1,4-benzoquinone (**1a**, 0.1 mmol), 2-naphthol (**2a**, 0.1 mmol), and Ligand/Matel salt (10 mol% : 10 mol%) in 2.5 mL of DCM under N_2, unless noted otherwise. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

Table 3: Screening the solvents of the reaction



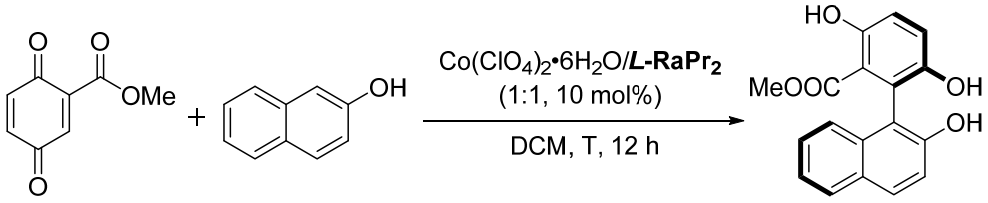
1a **2a** **3aa**

Entry[a]	Solvent	3aa	
		Yield (%)[b]	Ee (%)[c]
1	toluene	96	Race
2	Et_2O	26	Race
3	THF	17	Race
4	EA	51	Race
5	MeCN	5	Race
6	CH_2Cl_2	90	64

7	$CHCl_3$	90	20
8	1,2-dichloroethane	93	20
9	1,1,2-trichloroethane	90	28
10	1,1,2,2-tetrachloroethane	89	31
11	1,1,1-trichloroethane	95	Race

[a] All reactions were carried out with 2-methoxycarbonyl-1,4-benzoquinone (**1a**, 0.1 mmol), 2-naphthol (**2a**, 0.1 mmol), and Ligand/Matel salt (10 mol% : 10 mol%) in 2.5 mL of solvent under N_2, unless noted otherwise. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. EA = ethyl acetate, THF = tetrahydrofuran

Table 4: Screening the temperature of the reaction

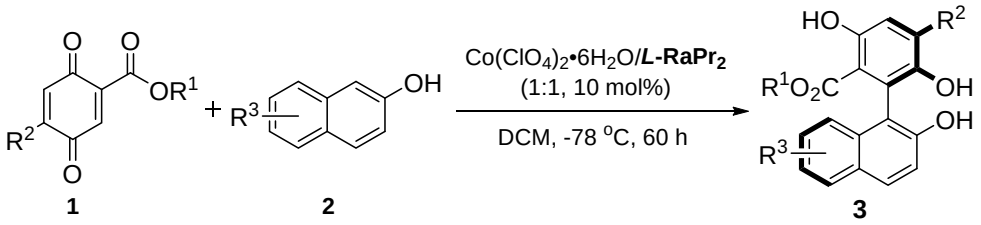


1a **2a** **3aa**

Entry[a]	**T (°C)**	**3aa**	
		Yield (%)[b]	**Ee (%)**[c]
1	-10	90	64
2	-30	86	66
4[d]	-50	90	71
5[e]	-60	89	80
6[f]	-78	91	83

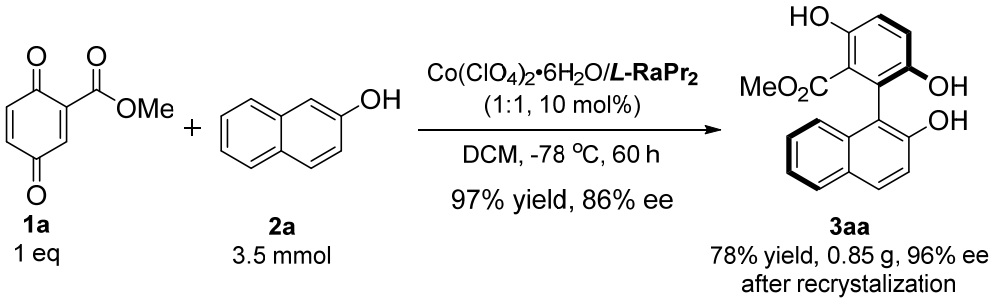
[a] All reactions were carried out with 2-methoxycarbonyl-1,4-benzoquinone (**1a**, 0.1 mmol), 2-naphthol (**2a**, 0.1 mmol), and Ligand/Matel salt (10 mol% : 10 mol%) in 2.5 mL of solvent under N_2, unless noted otherwise. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Reaction at -50 °C for 24 h. [e] Reaction at -60 °C for 48 h. [f] Reaction at -78 °C for 60 h.

5. General procedure for the catalytic enantioselective Friedel-Crafts-Aromatization reaction



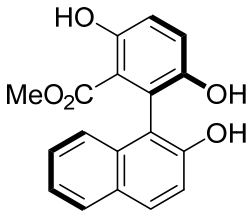
In an oven dried test tube with a magnetic stirring bar, naphthalen-2-ol (0.1 mmol), *N*,*N*'-dioxide ***L*-RaPr$_2$** (0.01 mmol) and $Co(ClO_4)_2 \cdot 6H_2O$ (0.01 mmol) in CH_2Cl_2 (2.0 mL) were stirred at 35 °C for 1h. Then the mixture was cooled to -78 °C, and the quinone (0.1 mmol) dissolved in 0.5 mL DCM was added. The mixture was stirred at -78 °C for 60 h. The reaction mixture was detected by TLC. After completion, 0.8 mg $NaBH_4$ in 0.2 mL MeOH was added to quench the reaction. Then flash column chromatography was carried out to provide the desired product. The products was used immediately for HPLC and NMR analysis.

6. Gram-scale synthesis of the product 3aa



To an oven dried 100 mL round-bottomtest flask with a magnetic stirring bar were sequentially added naphthalen-2-ol (3.5 mmol), *N*,*N*'-dioxide-metal complex ***L*-RaPr$_2$/** $Co(ClO_4)_2 \cdot 6H_2O$ (1:1, 0.35 mmol) and CH_2Cl_2 (60 mL) under N_2 atmosphere. After stirring at 35 °C for 1h, the mixture was cooled to -78 °C, and the quinone (3.5 mmol) dissolved in 20 mL DCM was added. The mixture was stirred at -78 °C for 60 h. The reaction mixture was detected by TLC. After completion, 28 mg $NaBH_4$ in 10 mL MeOH was added, followed by poured into 50 mL of water. The mixture was extract by DCM, and the aqueous layer was washed with DCM (2 x 10 mL). The combined organic phases was washed with brine (20 mL), and dried over Na_2SO_4. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with DCM/EA = 20:1. The products was used immediately for HPLC and NMR analysis.

7. The analytical and spectral characterization data of the products



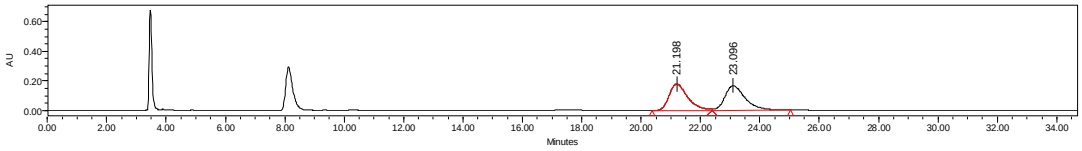
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate

white solid; 91% yield, 95:5 e.r.; $[\alpha]_D^{25}$ = −22.4 (c 0.54, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 20.97 min,t_2 = 22.87 min];

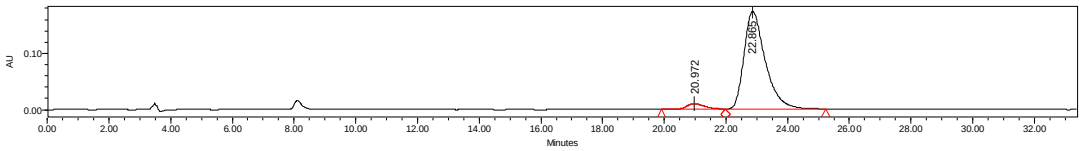
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 7.85 (d, J = 9.2 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.38 – 7.33 (m, 2H), 7.26 (s, 2H), 7.17 (dd, J = 6.0, 3.6 Hz, 1H), 7.12 (d, J = 9.2 Hz, 1H), 5.13 (s, 1H), 4.63 (s, 1H), 3.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.1, 151.1, 147.3, 133.0, 130.7, 129.1, 128.2, 127.4, 124.0, 123.9, 123.5, 120.5, 117.9, 117.5, 113.7, 112.6, 52.2.

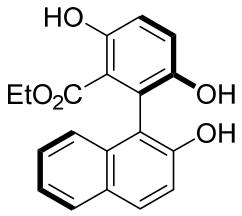
HRMS (ESI) calcd for $[M+H]^+$, $C_{18}H_{15}O_5^+$, m/z: 311.0919, observed: 311.0919.



	Retention Time	Area	% Area
1	21.198	7773590	49.56
2	23.096	7911641	50.44



	Retention Time	Area	% Area
1	20.972	436363	4.97
2	22.865	8339474	95.03



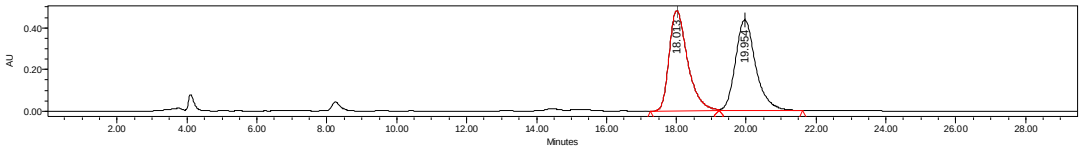
ethyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate

white solid; 82% yield, 96:4 e.r.; $[\alpha]_D^{25}$ = -46.3 (c 0.366, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 17.51 min,t_2 = 19.40 min];

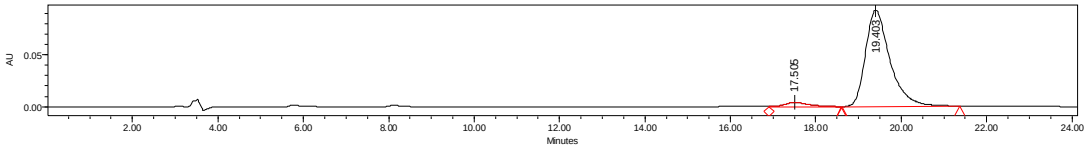
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.81 (dd, J = 5.6, 4.0 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.29 – 7.23 (m, 2H), 7.19 (dd, J = 5.6, 4.0 Hz, 1H), 7.13 (d, J = 9.2 Hz, 1H), 5.07 (s, 1H), 4.64 (s, 1H), 3.85 – 3.58 (m, 2H), 0.30 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 157.4, 151.1, 147.3, 133.3, 130.6, 129.2, 128.1, 127.4, 123.9, 123.9, 123.6, 120.5, 117.8, 117.6, 114.0, 112.6, 61.1, 12.5.

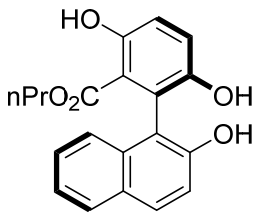
HRMS (ESI) calcd for $[M+H]^+$, $C_{19}H_{17}O_5^+$, m/z: 325.1076, observed: 325.1080.



	Retention Time	Area	% Area
1	18.013	17652586	50.16
2	19.954	17543244	49.84



	Retention Time	Area	% Area
1	17.505	153689	4.00
2	19.403	3692686	96.00

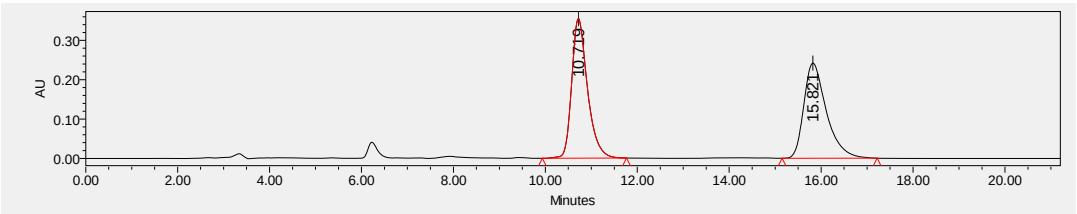


propyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate white solid; 80% yield, 95:5 e.r.; $[\alpha]_D^{25}$ = -32.1 (c 0.320, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t_1 = 10.74 min,t_2 = 15.85 min];

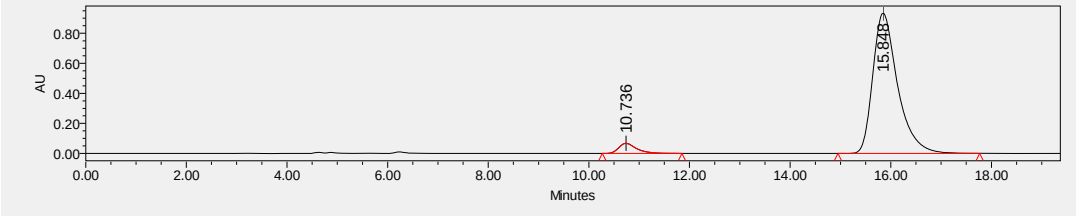
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.05 (s, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.82 (dd, J = 6.4, 3.2 Hz, 1H), 7.41 – 7.31 (m, 2H), 7.27 (dd, J = 17.2, 7.6 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.15 (d, J = 9.2 Hz, 1H), 4.99 (s, 1H), 4.57 (s, 1H), 3.82 – 3.53 (m, 2H), 0.69 (ddt, J = 26.4, 14.0, 7.2 Hz, 2H), 0.26 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) 170.3, 157.5, 151.0, 147.2, 133.1, 130.7, 129.3, 128.2, 127.4, 123.9, 123.9, 123.6, 120.6, 117.6, 113.9, 112.6, 67.2, 20.7, 9.8 .

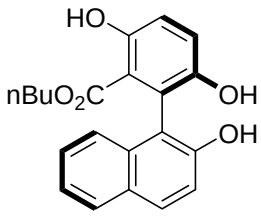
HRMS (ESI) calcd for $[M+H]^+$, $C_{20}H_{19}O_5^+$, m/z: 339.1232, observed: 339.1238.



	Retention Time	Area	% Area
1	10.719	8426134	50.71
2	15.821	8191077	49.29



	Retention Time	Area	% Area
1	10.736	1625576	4.85
2	15.848	31861316	95.15



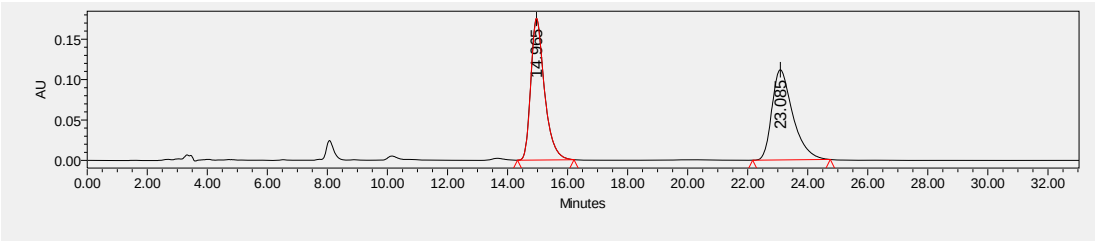
butyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate

white solid; 83% yield, 95:5 e.r.; $[\alpha]_D^{25}$ = -36.6 (c 0.204, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 14.91 min,t_2 = 22.95 min];

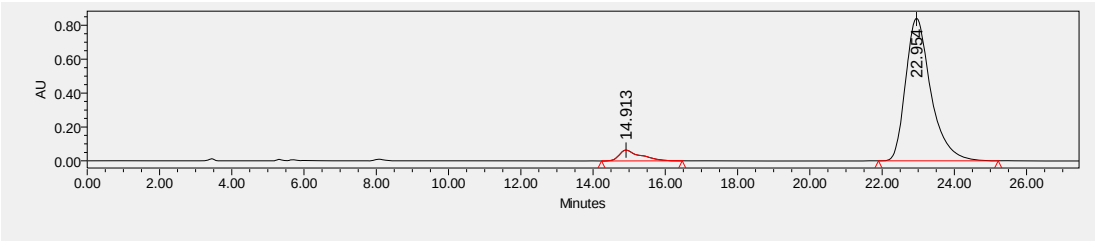
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.07 (s, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.82 (dd, J = 5.6, 4.0 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.31 – 7.24 (m, 2H), 7.20 (dd, J = 5.6, 4.0 Hz, 1H), 7.14 (d, J = 9.2 Hz, 1H), 5.05 (s, 1H), 4.58 (s, 1H), 3.73 (td, J = 5.6, 2.4 Hz, 2H), 0.71 – 0.40 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.5, 151.0, 147.2, 133.1, 130.6, 129.2, 128.2, 127.4, 124.0, 123.6, 120.6, 117.6, 117.6, 113.9, 112.6, 65.5, 29.5, 18.6, 13.5 .

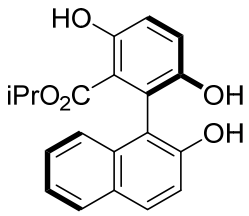
HRMS (ESI) calcd for $[M+H]^+$, $C_{21}H_{21}O_5^+$, m/z: 353.1389, observed: 353.1389.



	Retention Time	Area	% Area
1	14.965	5527342	50.67
2	23.085	5382163	49.33



	Retention Time	Area	% Area
1	14.913	2146606	5.02
2	22.954	40634230	94.98

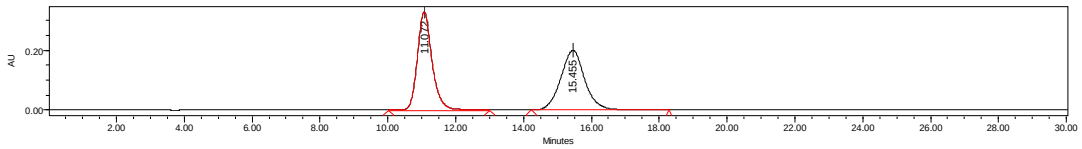


isopropyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate

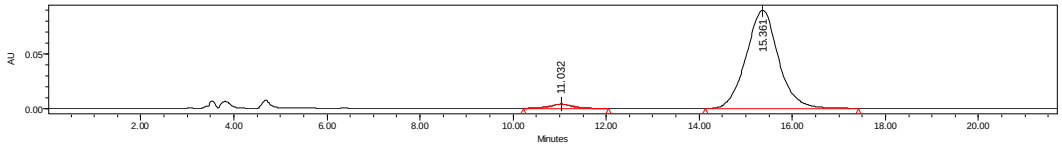
white solid; 60% yield, 97:3 e.r.; $[\alpha]_D^{25}$ = -60.5 (c 0.376, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t_1 = 11.03 min,t_2 = 15.36 min];

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.39 – 7.32 (m, 2H), 7.26 (d, J = 9.2 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.13 (d, J = 9.2 Hz, 1H), 5.03 (s, 1H), 4.75 (dt, J = 12.4, 6.2 Hz, 1H), 4.64 (s, 1H), 0.65 (d, J = 6.4 Hz, 3H), 0.19 (d, J = 6.4 Hz, 3H).

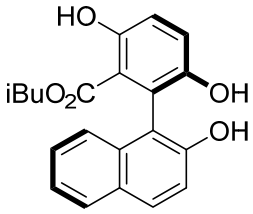
^{13}C NMR (101 MHz, $CDCl_3$) 169.4, 157.4, 151.1, 147.2, 133.5, 130.6, 129.2, 128.1, 127.3, 124.06 – 123.61, 120.5, 117.7, 117.6, 114.2, 113.0, 68.8, 20.8, 20.2 .
HRMS (ESI) calcd for $[M+H]^+$, $C_{20}H_{19}O_5^+$, m/z: 339.1232, observed: 339.1232.



	Retention Time	Area	% Area
1	11.072	9930868	50.35
2	15.455	9794589	49.65

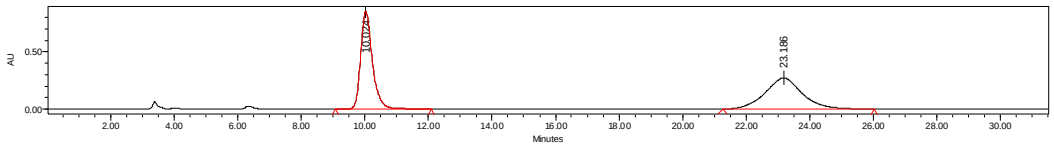


	Retention Time	Area	% Area
1	11.032	133874	3.00
2	15.361	4334500	97.00

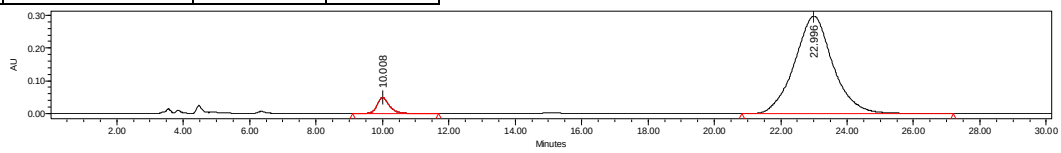


isobutyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate white solid; 80% yield, 95:5 e.r.; $[\alpha]_D^{25}$ = -30.7 (c 0.502, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t_1 = 10.01 min,t_2 = 23.00 min];

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H), 7.85 (d, J = 9.2 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.38 – 7.32 (m, 2H), 7.27 (s, 2H), 7.21 (dd, J = 5.6, 4.0 Hz, 1H), 7.14 (d, J = 9.2 Hz, 1H), 5.07 (s, 1H), 4.55 (s, 1H), 3.52 (ddd, J = 29.6, 10.8, 6.8 Hz, 2H), 0.87 (dd, J = 13.6, 6.8 Hz, 1H), 0.38 (d, J = 6.8 Hz, 3H), 0.18 (d, J = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.5, 151.0, 147.2 , 133.0, 130.7, 129.3, 128.2, 127.5, 124.0, 124.0, 123.6, 120.6, 117.7, 117.6, 113.9, 112.6, 72.1, 26.8, 18.6, 18.4 .
HRMS (ESI) calcd for $[M+H]^+$, $C_{21}H_{21}O_5^+$, m/z: 353.1389, observed: 353.1386.

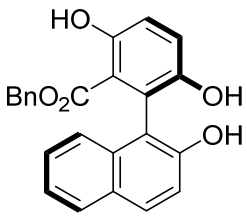


	Retention Time	Area	% Area
1	10.024	21725540	49.94
2	23.186	21782070	50.06



	Retention Time	Area	% Area

1	10.008	1253306	5.01
2	22.996	23758399	94.99



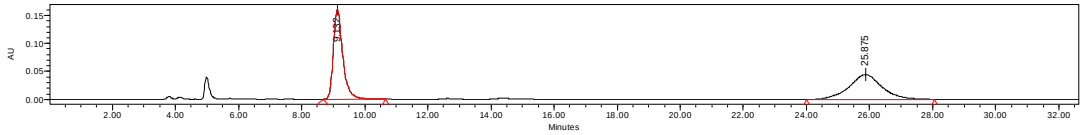
benzyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate

white solid; 96% yield, 90:10 e.r.; $[\alpha]_D^{25}$ = -20.5 (c 0.650, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_1 = 9.08 min,t_2 = 25.38 min];

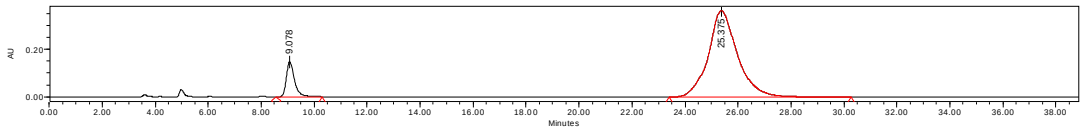
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.95 (s, 1H), 7.71 (dd, J = 7.6, 2.0 Hz, 1H), 7.59 (d, J = 9.2 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.23 (s, 1H), 7.15 (d, J = 9.2 Hz, 2H), 7.09 (d, J = 9.2 Hz, 1H), 7.04 (t, J = 7.6 Hz, 2H), 7.00 (d, J = 9.2 Hz, 1H), 6.56 – 6.37 (m, 2H), 5.06 (s, 1H), 4.73 – 4.63 (m, 2H), 4.57 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 157.5, 151.0, 147.3, 133.7, 133.0, 130.7, 129.1, 128.4, 128.4, 128.3, 128.2, 128.2, 127.3, 124.1, 123.8, 123.5, 120.5, 117.9, 117.4, 113.6, 112.4, 67.5 .

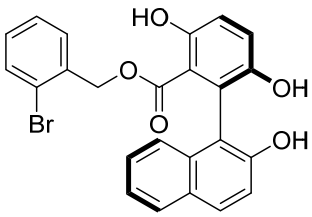
HRMS (ESI) calcd for $[M+H]^+$, $C_{24}H_{19}O_5^+$, m/z: 387.1232, observed: 387.1231.



	Retention Time	Area	% Area
1	9.132	3333626	50.86
2	25.875	3221510	49.14



	Retention Time	Area	% Area
1	9.078	3070727	10.05
2	25.375	27472489	89.95



2-brombenzyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl) benzoate

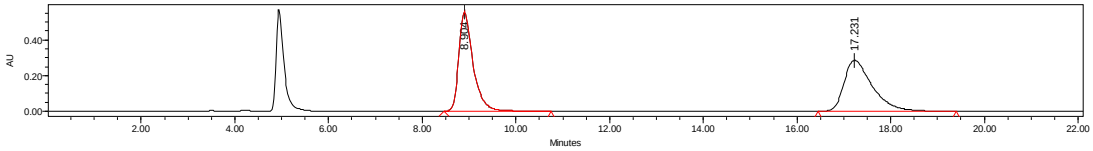
white solid; 70% yield, 93:7 e.r.; $[\alpha]_D^{25}$ = 5.1 (c 0.652, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_1 = 8.89 min,t_2 = 17.22 min];

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.97 (s, 1H), 7.62 – 7.57 (m, 1H), 7.43 (d, J = 9.2 Hz, 1H), 7.35 – 7.26 (m, 4H), 7.18 – 7.12 (m, 2H), 7.07 (td, J = 7.6, 1.6 Hz, 1H), 6.94 (ddd, J = 9.2, 6.8, 2.8 Hz, 2H), 6.32 (dd, J = 7.6, 1.6 Hz, 1H), 5.05 – 4.52 (m, 4H).

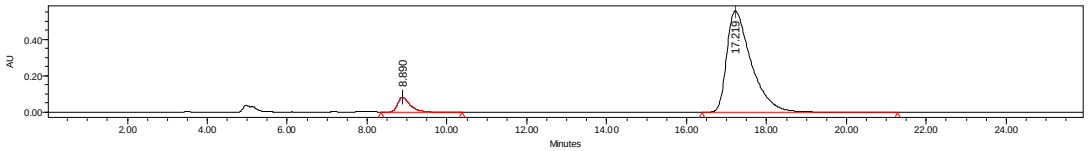
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 157.7, 150.9, 147.3, 133.1, 132.8, 132.5, 130.6, 130.3, 129.7, 129.0, 128.3, 127.3, 127.2, 124.2, 123.9, 123.7, 123.5, 120.6, 118.0, 117.3, 113.4, 112.1, 67.0 .

HRMS (ESI) calcd for $[M+Na]^+$, $C_{24}H_{17}O_5BrNa^+$, m/z:487.0157, 489.0137, observed:

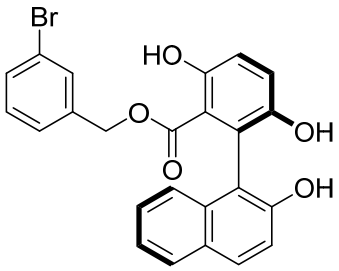
487.0157, 489.0132.



	Retention Time	Area	% Area
1	8.904	11755873	49.94
2	17.231	11784240	50.06



	Retention Time	Area	% Area
1	8.890	1733359	6.85
2	17.219	23584060	93.15



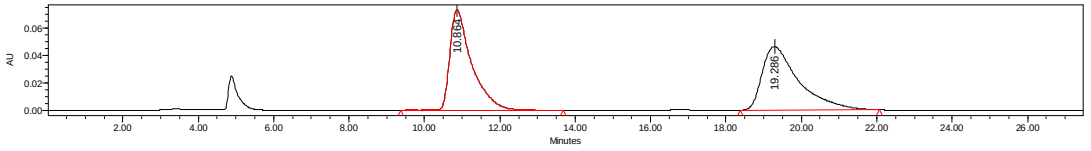
3-bromobenzyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate

white solid; 92% yield, 92.5:7.5 e.r.; $[\alpha]_D^{25}$ = -35.9 (c 0.674, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_1 = 10.83 min,t_2 = 19.20 min];

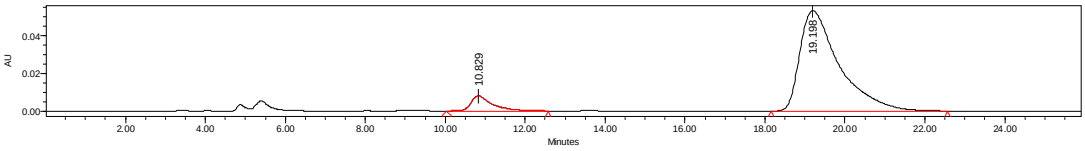
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.87 (s, 1H), 7.74 – 7.67 (m, 1H), 7.62 (d, J = 9.2 Hz, 1H), 7.31 (ddd, J = 6.8, 2.8, 2.0 Hz, 3H), 7.25 (s, 1H), 7.11 (d, J = 9.2 Hz, 2H), 7.02 (d, J = 9.2 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.66 (t, J = 1.6 Hz, 1H), 6.43 (d, J = 7.6 Hz, 1H), 5.14 – 4.96 (m, 1H), 4.61 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 157.5, 150.9, 147.3, 135.7, 132.9, 131.6, 131.4, 130.7, 129.8, 129.0, 128.3, 127.4, 127.2, 124.3, 123.9, 123.4, 122.2, 120.5, 118.0, 117.3, 113.5, 112.2, 66.5 .

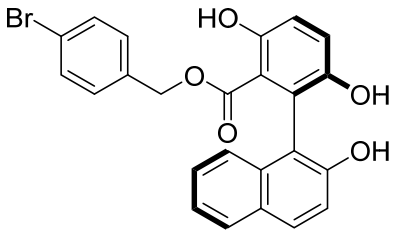
HRMS (ESI) calcd for $[M+Na]^+$, $C_{24}H_{17}O_5BrNa^+$, m/z:487.0157, 489.0137, observed: 487.0162, 489.0148.



	Retention Time	Area	% Area
1	10.864	2913334	48.35
2	19.286	3112103	51.65



	Retention Time	Area	% Area
1	10.829	295953	7.56
2	19.198	3618016	92.44



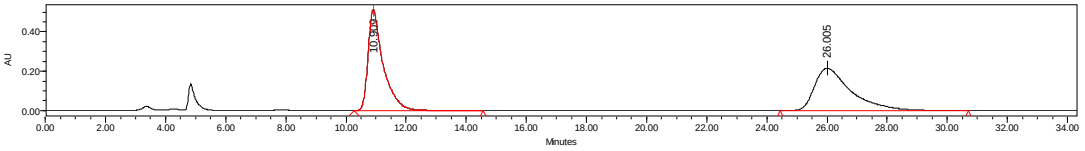
4-bromobenzyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate

white solid; 93% yield, 92:8 e.r.; $[\alpha]_D^{25}$ = -44.5 (c 0.802, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_1 = 10.97 min,t_2 = 26.31 min];

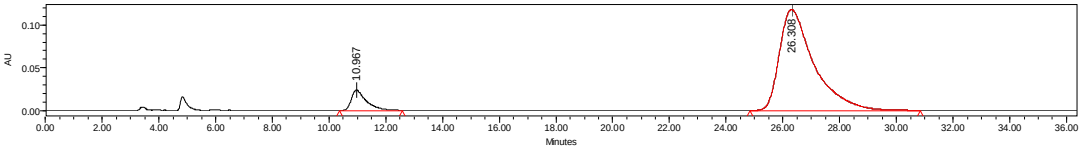
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.89 (s, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 9.2 Hz, 1H), 7.31 (td, J = 7.2, 1.6 Hz, 2H), 7.25 (d, J = 2.8 Hz, 1H), 7.12 (dd, J = 12.0, 8.8 Hz, 4H), 7.01 (d, J = 9.2 Hz, 1H), 6.29 (d, J = 8.4 Hz, 2H), 5.03 (s, 1H), 4.72 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 12.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 157.6, 150.9, 147.3, 132.9, 132.6, 131.4, 130.6, 130.0, 129.1, 128.4, 127.4, 124.3, 123.9, 123.5, 122.3, 120.6, 117.8, 117.4, 113.6, 112.2, 66.6 .

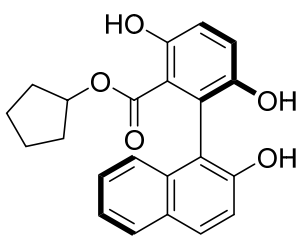
HRMS (ESI) calcd for $[M+Na]^+$, $C_{24}H_{17}O_5BrNa^+$, m/z:487.0157, 489.0137, observed: 487.0153, 489.0150.



	Retention Time	Area	% Area
1	10.909	17903616	49.72
2	26.005	18105270	50.28



	Retention Time	Area	% Area
1	10.967	866122	8.03
2	26.308	9926117	91.97



cyclopentyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate

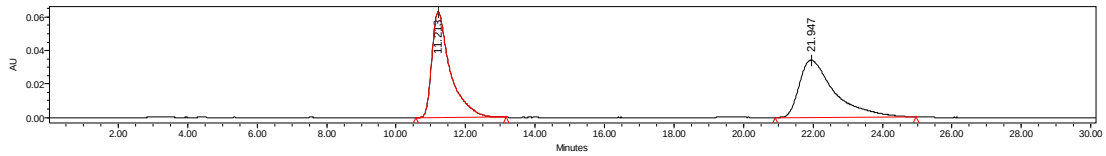
white solid; 55% yield, 98:2 e.r.; $[\alpha]_D^{25}$ = -53.7 (c 0.264, CH_2Cl_2);

Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t_1 = 11.23 min,t_2 = 22.06 min];

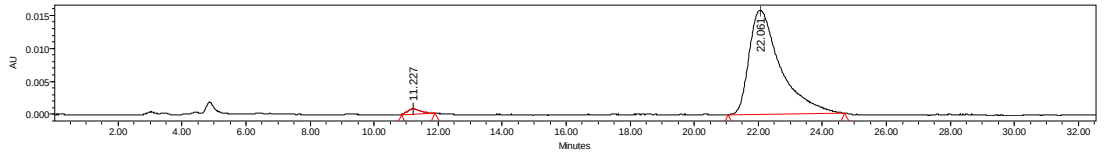
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.36 (dd, J = 6.0, 3.2 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 1H), 7.14 (d, J = 9.2 Hz, 1H), 4.95 (dd, J = 5.6, 3.2 Hz, 3H), 1.52 – 1.30 (m, 2H), 1.05 (ddd, J = 46.8, 13.6, 6.8 Hz, 4H), 0.81 (dd, J = 9.6, 4.4 Hz, 2H), 0.56 (ddd, J = 17.6, 13.6, 6.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 157.5, 150.9, 147.2, 133.2, 130.6, 129.3, 128.2, 127.4, 124.1, 123.8, 123.7, 120.6, 117.6, 117.5, 114.1, 112.8, 78.8, 31.9, 31.8, 23.3, 23.2 .

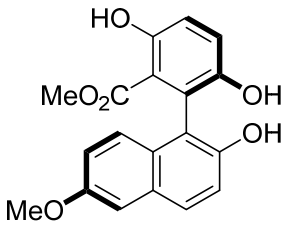
HRMS (ESI) calcd for $[M+Na]^+$, $C_{22}H_{20}O_5Na^+$, m/z: 387.1208, observed: 387.1214.



	Retention Time	Area	% Area
1	11.213	2307823	49.16
2	21.947	2386784	50.84



	Retention Time	Area	% Area
1	11.227	21862	2.00
2	22.061	1072517	98.00



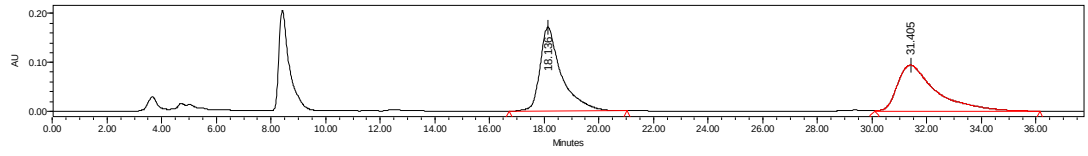
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxy-6-methoxynaphthalen-1-yl)benzoate

white solid; 91% yield, 95.5:4.5 e.r.; $[\alpha]_D^{25}$ = -63.4 (c 0.404, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t_1 = 18.43 min,t_2 = 31.43 min];

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.75 (s, 1H), 7.75 (d, J = 9.2 Hz, 1H), 7.26 (d, J = 10.4 Hz, 2H), 7.18 – 7.07 (m, 3H), 7.03 (dd, J = 9.2, 2.4 Hz, 1H), 4.68 (s, 2H), 3.90 (s, 3H), 3.24 (s, 3H).

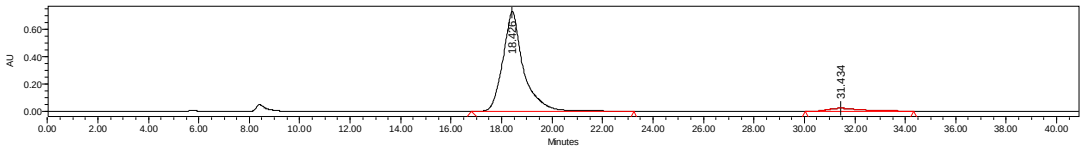
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.1, 156.3, 149.4, 147.3, 130.1, 129.4, 128.1, 125.1, 123.9, 120.5, 119.7, 118.0, 117.9, 114.0, 112.5, 106.7. 55.4, 52.2 .

HRMS (ESI) calcd for $[M+H]^+$, $C_{19}H_{17}O_6^+$, m/z: 341.1025, observed: 341.1024.

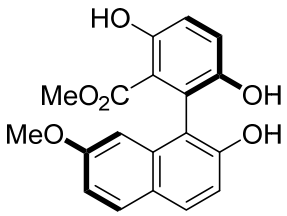


	Retention Time	Area	% Area

1	18.136	9325552	50.31
2	31.405	9209128	49.69



	Retention Time	Area	% Area
1	18.426	40593991	95.57
2	31.434	1880726	4.43



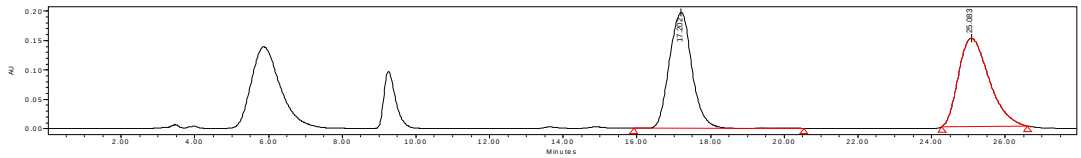
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxy-7-methoxynaphthalen-1-yl)benzoate

white solid; 89% yield, 90.5:9.5 e.r.; $[\alpha]_D^{25}$ = -90.8 (c 0.254, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 17.31 min,t_2 = 25.58 min];

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.75 (s, 1H), 7.72 (dd, J = 15.6, 9.2 Hz, 2H), 7.29 (s, 1H), 7.09 (dd, J = 13.6, 9.2 Hz, 2H), 7.00 (dd, J = 9.2, 2.4 Hz, 1H), 6.44 (d, J = 2.4 Hz, 1H), 5.07 (s, 1H), 4.77 (s, 1H), 3.68 (s, 3H), 3.24 (s, 3H).

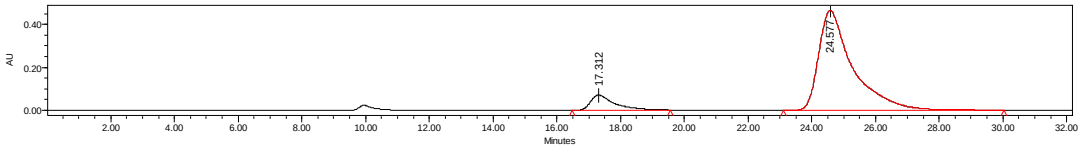
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 159.0, 157.0, 151.7, 147.3, 134.4, 130.4, 129.8, 124.5, 123.9, 120.4, 118.2, 115.9, 114.9, 112.9, 112.5, 102.5, 55.2, 52.2 .

HRMS (ESI) calcd for $[M+Na]^+$, $C_{19}H_{16}O_6Na^+$, m/z: 363.0845, observed: 363.0842

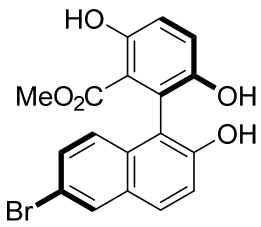


	Retention Time	Area	% Area
1	17.202	8339921	49.17
2	25.083	8621700	50.83

.



	Retention Time	Area	% Area
1	17.312	3606329	9.53
2	24.577	34227781	90.47



methyl (a*R*)-2-(6-bromo-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate

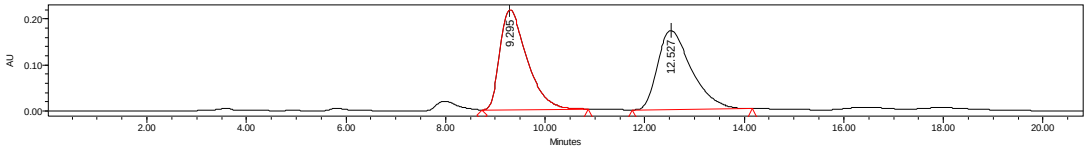
white solid; 71% yield, 97.5:2.5 e.r.; $[\alpha]_D^{25}$ = -44.8 (c 0.358, CH_2Cl_2);

Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 9.38 min,t_2 = 12.58 min];

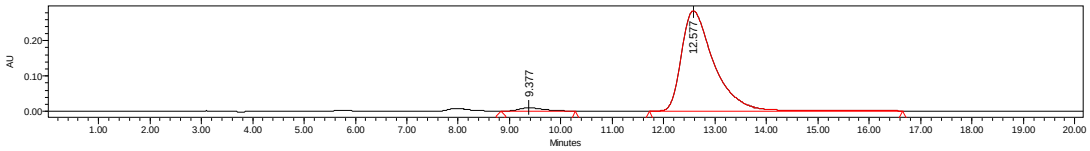
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.78 (s, 1H), 7.98 (d, J = 1.6 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H), 7.42 (dd, J = 9.2, 1.6 Hz, 1H), 7.29 (dd, J = 9.2, 1.6 Hz, 2H), 7.15 (d, J = 9.2 Hz, 1H), 7.06 (d, J = 9.2 Hz, 1H), 5.09 (s, 1H), 4.53 (s, 1H), 3.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 157.3, 151.3, 147.3, 131.6, 130.6, 130.2, 129.7, 125.4, 124.2, 120.9, 118.7, 117.7, 117.1, 114.2, 112.4, 52.3 .

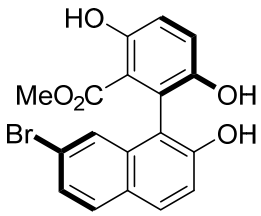
HRMS (ESI) calcd for $[M+K]^+$,$C_{18}H_{13}O_5BrK$, m/z:426.9583, 428.9563, observed: 426.9584, 428.9570.



	Retention Time	Area	% Area
1	9.295	8191451	50.37
2	12.527	8071518	49.63



	Retention Time	Area	% Area
1	9.377	330733	2.59
2	12.577	12415415	97.41



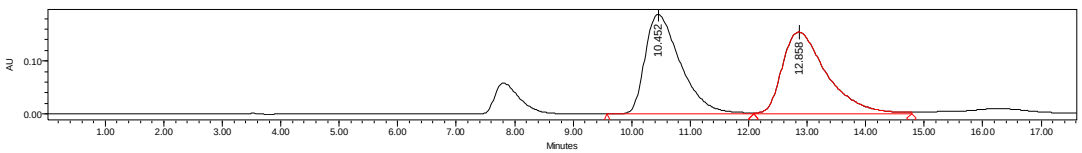
methyl (a*R*)-2-(7-bromo-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate

white solid; 53% yield, 96.5:3.5 e.r.; $[\alpha]_D^{25}$ = -25.7 (c 0.384, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 10.60 min,t_2 = 12.92 min];

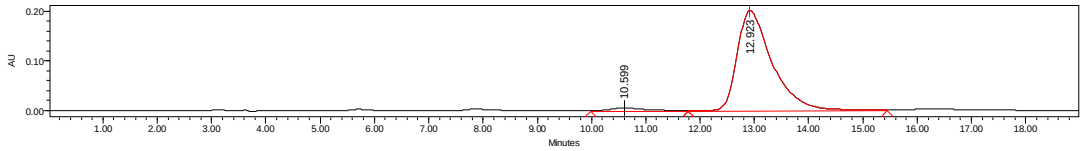
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.83 (s, 1H), 7.82 (d, J = 9.2 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.43 (dd, J = 8.8, 1.8 Hz, 1H), 7.31 (s, 1H), 7.27 (dd, J = 9.2, 3.6 Hz, 2H), 7.15 (d, J = 9.2 Hz, 1H), 5.14 (s, 1H), 4.56 (s, 1H), 3.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 157.4, 151.9, 147.3, 134.3, 130.6, 129.9, 127.5, 127.4, 125.6, 124.3, 122.0, 121.0, 118.0, 116.9, 113.3, 112.2, 52.3 .

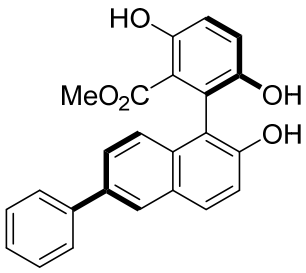
HRMS (ESI) calcd for $[M+K]^+$,$C_{18}H_{13}O_5BrK$, m/z:426.9583, 428.9563, observed: 426.9585, 428.9570.



	Retention Time	Area	% Area
1	10.452	7875402	49.24
2	12.858	8119639	50.76



	Retention Time	Area	% Area
1	10.599	334100	3.49
2	12.923	9235864	96.51



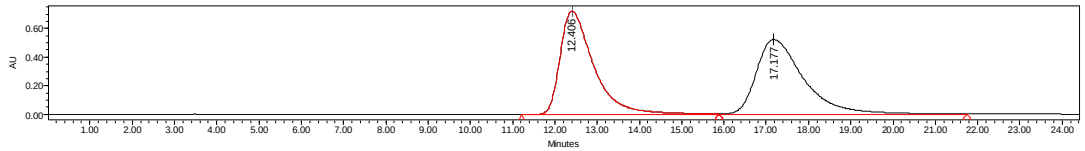
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxy-6-methoxynaphthalen-1-yl)benzoate

white solid; 74% yield, 96.5:3.5 e.r.; $[\alpha]_D^{25}$ = -74.6 (c 0.556, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 12.76 min,t_2 = 17.23 min];

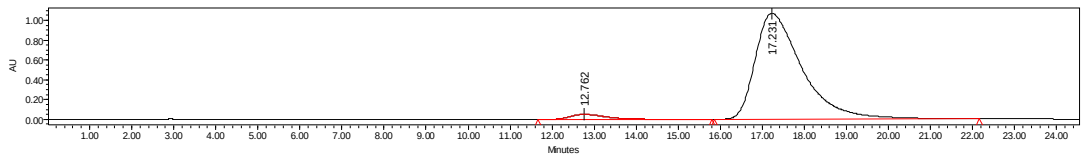
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.02 (d, J = 1.6 Hz, 1H), 7.90 (d, J = 9.2 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.62 (dd, J = 8.8, 1.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 7.6 Hz, 1H), 7.27 (dd, J = 8.8, 3.2 Hz, 3H), 7.14 (d, J = 9.2 Hz, 1H), 4.97 (d, J = 74.8 Hz, 2H), 3.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.1, 151.2, 147.4, 140.7, 136.6, 132.2, 131.0, 129.4, 128.9, 127.3, 127.2, 127.0, 126.1, 124.1, 124.1, 120.6, 118.0, 118.0, 113.8, 112.6, 52.3 .

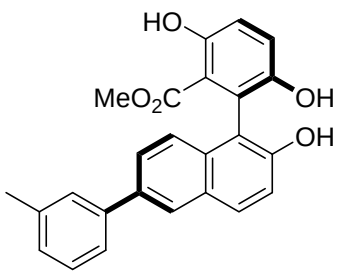
HRMS (ESI) calcd for $[M+Na]^+$, $C_{24}H_{18}O_5Na^+$, m/z: 409.1052, observed: 409.1054.



	Retention Time	Area	% Area
1	12.406	39952163	49.38
2	17.177	40963218	50.62



	Retention Time	Area	% Area
1	12.762	3004629	3.52
2	17.231	82382598	96.48



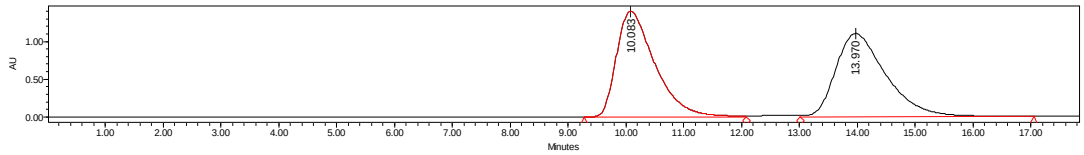
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxy-6-(m-tolyl)naphthalen-1-yl)benzoate

white solid; 88% yield, 93.5:6.5 e.r.; $[\alpha]_D^{25}$ = -74.0 (c 0.602, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 10.19min,t_2 = 13.88 min];

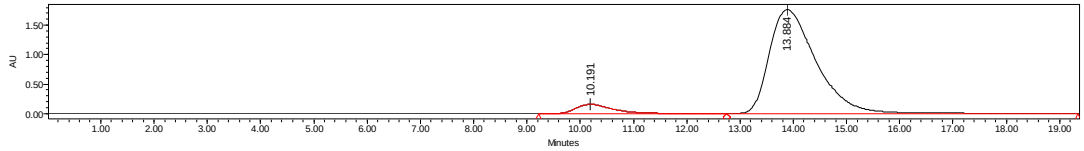
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.01 (d, J = 1.6 Hz, 1H), 7.89 (d, J = 9.2 Hz, 1H), 7.61 (dd, J = 8.8, 2.0 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.28 (dd, J = 9.2, 7.6 Hz, 2H), 7.22 (s, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.13 (d, J = 9.2 Hz, 1H), 5.16 (s, 1H), 4.67 (s, 1H), 3.25 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.1, 151.1, 147.4, 140.7, 138.5, 136.8, 132.1, 131.0, 129.4, 128.8, 128.1, 128.0, 127.1, 126.1, 124.3, 124.1, 120.6, 118.0, 117.9, 113.7, 112.6, 52.3, 21.6 .

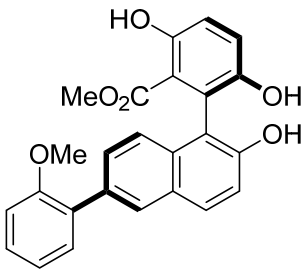
HRMS (ESI) calcd for $[M+K]^+$, $C_{25}H_{20}O_5K^+$, m/z: 439.0948, observed: 439.0948.



	Retention Time	Area	% Area
1	10.083	64457782	49.33
2	13.970	66212951	50.67



	Retention Time	Area	% Area
1	10.191	7392799	6.43
2	13.884	107578958	93.57



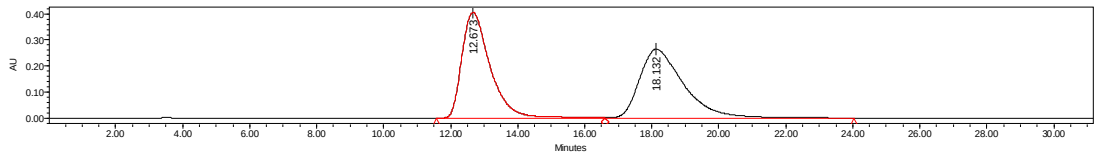
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxy-6-(2-methoxyphenyl)naphthaen-1- yl)benzoate

white solid; 90% yield, 92:8 e.r.; $[\alpha]_D^{25}$ = -52.9 (c 0.648, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 12.59 min,t_2 = 17.77 min];

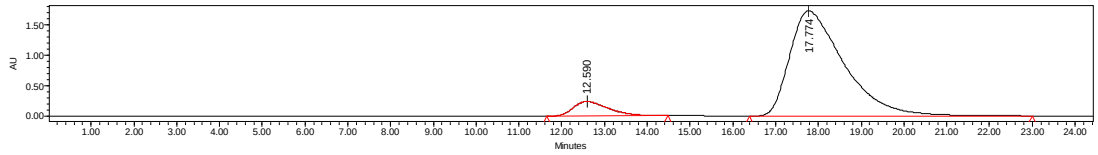
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.95 (d, J = 1.6 Hz, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.57 (dd, J = 8.8, 1.6 Hz, 1H), 7.40 (dd, J = 7.6, 1.6 Hz, 1H), 7.34 (td, J = 8.0, 1.6 Hz, 1H), 7.26 (s, 2H), 7.18 (d, J = 8.8 Hz, 1H), 7.12 (d, J = 9.2 Hz, 1H), 7.06 (td, J = 7.6, 0.8 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 5.17 (s, 1H), 4.66 (s, 1H), 3.82 (s, 3H), 3.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 157.1, 156.6, 151.2, 147.4, 134.3, 131.8, 131.0, 131.0, 130.2, 129.6, 129.2, 128.8, 128.5, 124.0, 123.0, 121.0, 120.5, 118.1, 117.6, 113.6, 112.6, 111.3, 55.6, 52.4.

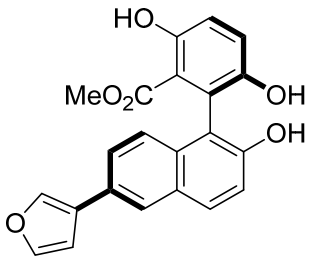
HRMS (ESI) calcd for $[M+Na]^+$, $C_{25}H_{20}O_6Na^+$, m/z: 439.1158, observed: 439.1159.



	Retention Time	Area	% Area
1	12.673	23834340	49.88
2	18.132	23951236	50.12



	Retention Time	Area	% Area
1	12.590	13482376	8.16
2	17.774	151744434	91.84



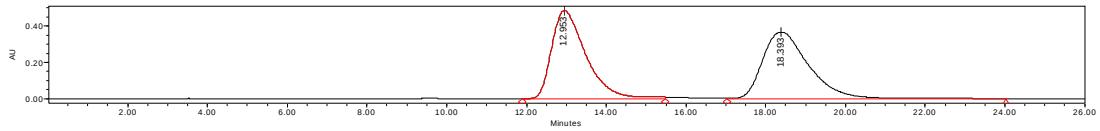
methyl (a*R*)-2-(6-(furan-3-yl)-2-hydroxynaphthalen-1-yl)-3,6-di hydroxybenzoate

white solid; 88% yield, 94.5:5.5 e.r.; $[\alpha]_D^{25}$ = -134.7 (c 0.284, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 12.91 min,t_2 = 18.02 min];

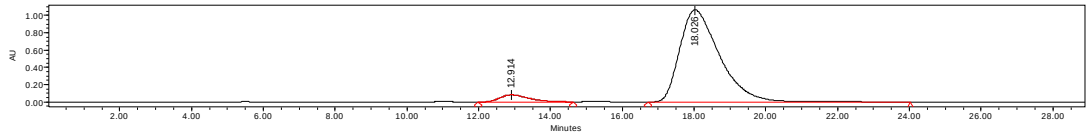
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 7.84 (dd, J = 24.8, 16.0 Hz, 3H), 7.49 (dd, J = 11.2, 1.2 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.15 (dd, J = 18.0, 9.2 Hz, 2H), 6.79 (s, 1H), 5.14 (s, 1H), 4.66 (s, 1H), 3.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.1, 151.0, 147.3, 143.9, 138.7, 132.0, 130.6, 129.4, 128.0, 126.2, 1256.0, 124.5, 124.2, 124.0, 120.6, 118.1, 117.8, 113.9, 112.5, 108.8, 52.3 .

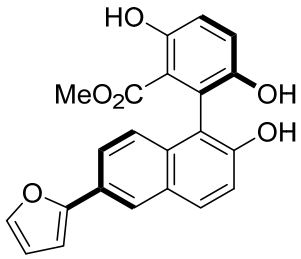
HRMS (ESI) calcd for $[M+Na]^+$, $C_{22}H_{16}O_6Na^+$, m/z: 399.0845, observed: 399.0845.



	Retention Time	Area	% Area
1	12.953	28872604	49.60
2	18.393	29333438	50.40



	Retention Time	Area	% Area
1	12.914	4789161	5.51
2	18.026	82096744	94.49



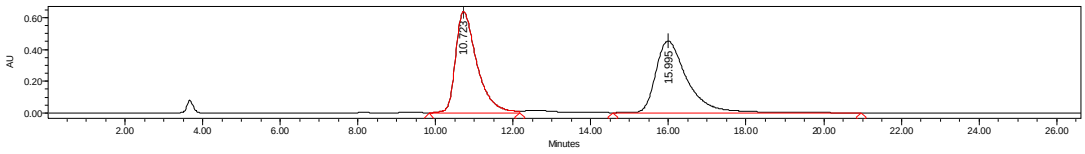
methyl (a*R*)-2-(6-(furan-2-yl)-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate

white solid; 84% yield, 96:4 e.r.; $[\alpha]_D^{25}$ = -83.6 (c 0.560, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 11.00 min,t_2 = 16.04 min];

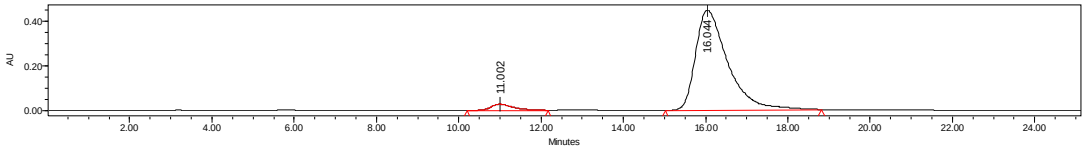
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.12 (d, J = 1.6 Hz, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.63 (dd, J = 8.8, 1.6 Hz, 1H), 7.50 (d, J = 1.2 Hz, 1H), 7.27 (d, J = 2.0 Hz, 2H), 7.18 (d, J = 8.8 Hz, 1H), 7.13 (d, J = 9.2 Hz, 1H), 6.70 (dd, J = 3.2, 0.4 Hz, 1H), 6.50 (dd, J = 3.2, 1.6 Hz, 1H), 5.16 (s, 1H), 4.67 (s, 1H), 3.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.1, 153.8, 151.2, 147.3, 142.2, 132.2, 130.9, 129.2, 126.6, 124.1, 124.0, 123.9, 122.5, 120.6, 118.2, 117.8, 114.1, 112.5, 111.8, 105.3, 52.3 .

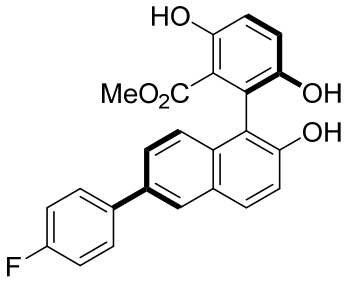
HRMS (ESI) calcd for $[M+K]^+$, $C_{22}H_{16}O_6K^+$, m/z: 415.0584, observed: 415.0586.



	Retention Time	Area	% Area
1	10.723	24473579	49.00
2	15.995	25476456	51.00



	Retention Time	Area	% Area
1	11.002	1035280	4.06
2	16.044	24447844	95.94



methyl (a*R*)-2-(6-(4-fluorophenyl)-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate

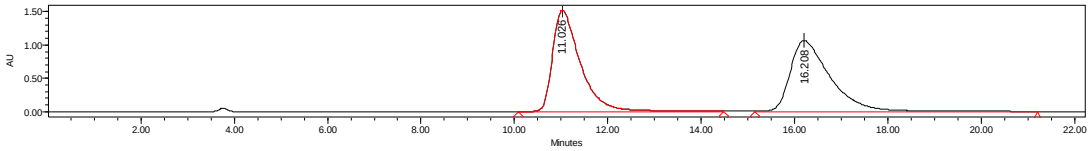
white solid; 63% yield, 97:3 e.r.; $[\alpha]_D^{25}$ = -102.0 (c 0.278, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 11.09 min,t_2 = 16.05 min];

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.97 (d, J = 1.6 Hz, 1H), 7.90 (d, J = 9.2 Hz, 1H), 7.63 (dd, J = 8.8, 5.2 Hz, 2H), 7.57 (dd, J = 8.8, 1.6 Hz, 1H), 7.30 (dd, J = 9.2, 4.0 Hz, 2H), 7.23 (s, 1H), 7.19 – 7.12 (m, 3H), 5.13 (s, 1H), 4.63 (s, 1H), 3.26 (s, 3H).

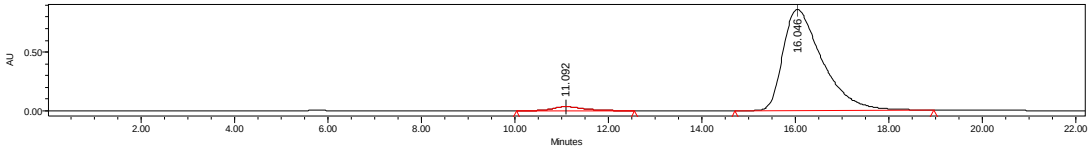
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 163.7, 161.3, 157.2, 151.2, 147.3, 136.8, 136.8, 135.7, 132.1, 130.9, 129.4, 128.8, 128.7, 126.8, 126.0, 124.2, 124.1, 120.7, 118.1, 117.7, 115.9,

115.7, 113.8, 112.5, 52.3.

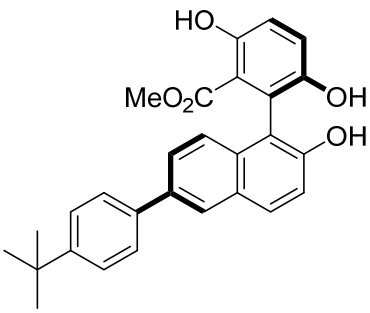
HRMS (ESI) calcd for $[M+K]^+$, $C_{24}H_{17}O_5FK^+$, m/z: 443.0697, observed: 443.0693.



	Retention Time	Area	% Area
1	11.026	63059499	49.88
2	16.208	63372476	50.12



	Retention Time	Area	% Area
1	11.092	1509581	2.92
2	16.046	50104848	97.08



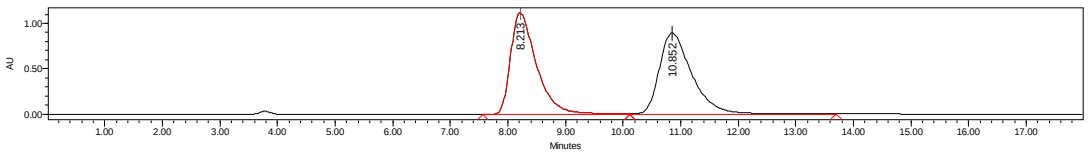
methyl (a*R*)-2-(6-(4-(tert-butyl)phenyl)-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate

white solid; 95% yield, 95:5 e.r.; $[\alpha]_D^{25}$ = -60.8 (c 0.522, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 8.21 min,t_2 = 10.72 min];

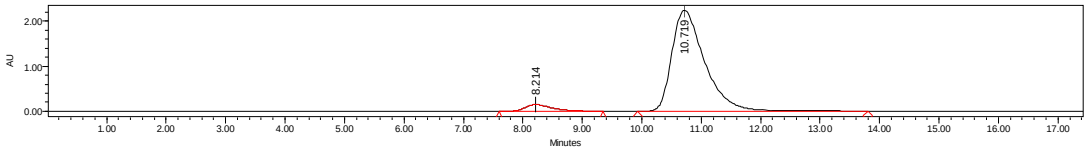
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.01 (d, J = 1.6 Hz, 1H), 7.89 (d, J = 9.2 Hz, 1H), 7.62 (d, J = 8.4 Hz, 3H), 7.50 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 9.2 Hz, 1H), 7.27 (d, J = 9.2 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 9.2 Hz, 1H), 5.09 (s, 1H), 4.65 (s, 1H), 3.25 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.2, 151.1, 150.4, 147.4, 137.8, 136.5, 132.0, 131.0, 129.5, 127.0, 126.8, 125.9, 125.8, 124.0, 120.6, 117.9, 117.9, 113.7, 112.5, 52.3, 34.6, 31.4, 29.7 .

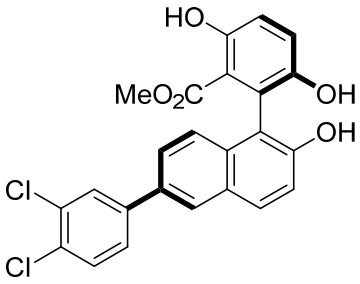
HRMS (ESI) calcd for $[M+K]^+$, $C_{28}H_{26}O_5K^+$, m/z: 481.1417, observed: 481.1412.



	Retention Time	Area	% Area
1	8.213	34950623	49.60
2	10.852	35515492	50.40



	Retention Time	Area	% Area
1	8.214	4556482	5.03
2	10.719	85997639	94.97



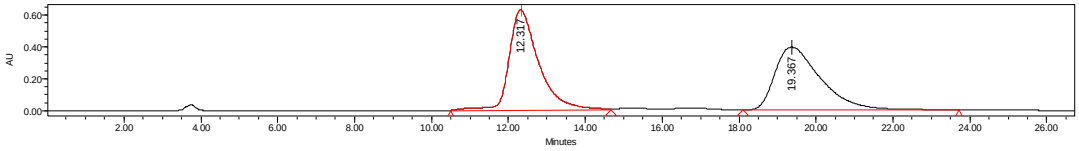
methyl (a*R*)-2-(6-(3,4-dichlorophenyl)-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate

white solid; 80% yield, 95:5 e.r.; $[\alpha]_D^{25}$ = -73.7 (c 0.590, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 12.51min,t_2 = 19.16 min];

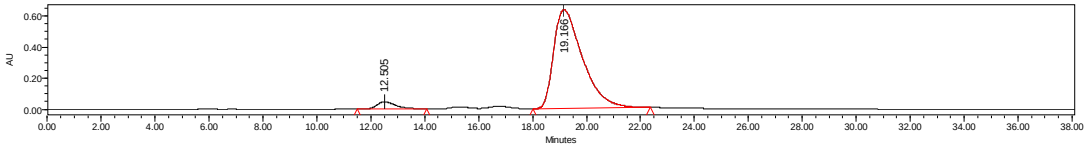
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 7.90 (s, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.67 (s, 1H), 7.43 (dd, J = 11.2, 5.2 Hz, 3H), 7.22 (dd, J = 9.2, 4.4 Hz, 3H), 7.06 (d, J = 9.2 Hz, 1H), 4.83 (s, 2H), 3.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 157.2, 151.6, 147.3, 140.8, 134.2, 133.0, 132.5, 131.4, 131.0, 130.8, 129.2, 129.0, 126.4, 126.3, 126.3, 124.5, 124.1, 120.8, 118.4, 117.5, 113.9, 112.5, 52.3 .

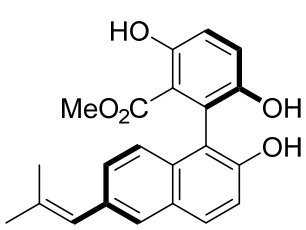
HRMS (ESI) calcd for $[M+K]^+$, $C_{24}H_{16}O_5Cl_2K^+$, m/z: 493.0012, 494.9982, observed: 493.0010, 494.9998.



	Retention Time	Area	% Area
1	12.317	33861332	50.82
2	19.367	32763952	49.18



	Retention Time	Area	% Area
1	12.505	2272256	4.58
2	19.166	47287780	95.42



methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxy-6-(2-methylprop-1-en-1-yl)naphthalen-1-yl)benzoate

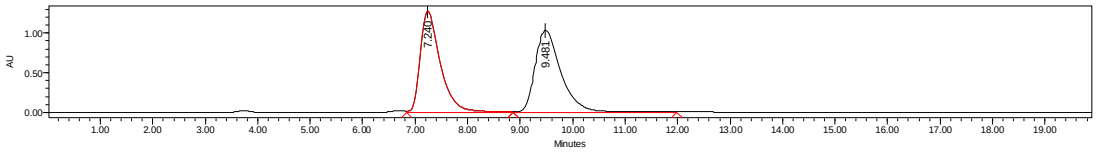
white solid; 88% yield, 95:5 e.r.; $[\alpha]_D^{25}$ = -79.4 (c 0.478, CH_2Cl_2);

Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 7.26 min,t_2 = 9.42 min];

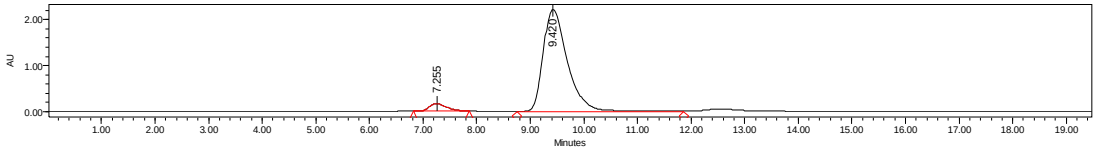
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.78 (s, 1H), 7.79 (d, J = 9.2 Hz, 1H), 7.64 (s, 1H), 7.25 (dd, J = 4.8, 1.6 Hz, 2H), 7.22 (d, J = 9.2 Hz, 1H), 7.11 (dd, J = 8.8, 5.2 Hz, 2H), 6.35 (s, 1H), 5.07 (s, 1H), 4.68 (s, 1H), 3.23 (s, 3H), 1.93 (dd, J = 8.4, 0.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.1, 150.8, 147.3, 135.9, 134.4, 131.2, 130.6, 129.1, 129.0, 127.4, 124.7, 123.9, 123.1, 120.4, 118.0, 117.6, 113.6, 112.6, 52.2, 27.0, 19.6 .

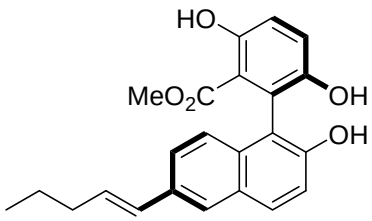
HRMS (ESI) calcd for $[M+K]^+$, $C_{22}H_{20}O_5K^+$, m/z: 403.0948, observed: 403.0948.



	Retention Time	Area	% Area
1	7.240	34027152	49.48
2	9.481	34740062	50.52



	Retention Time	Area	% Area
1	7.255	3669042	4.97
2	9.420	70201573	95.03



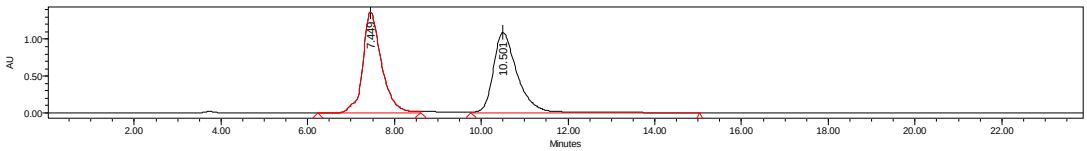
methyl (a*R*)-(E)-3,6-dihydroxy-2-(2-hydroxy-6-(pent-1-en-1-yl)naphthalen-1-yl)benzoate

white solid; 86% yield, 93:7 e.r.; $[\alpha]_D^{25}$ = -81.5 (c 0.464, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 7.45 min,t_2 = 10.42 min];

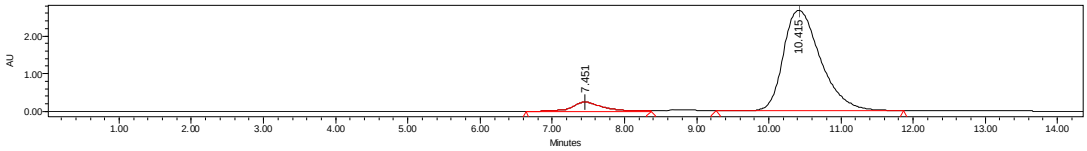
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 7.78 (d, J = 9.2 Hz, 1H), 7.66 (d, J = 1.2 Hz, 1H), 7.44 (dd, J = 8.8, 1.6 Hz, 1H), 7.27 (d, J = 9.2 Hz, 1H), 7.21 (d, J = 9.2 Hz, 1H), 7.11 (dd, J = 10.4, 9.2 Hz, 2H), 6.50 (d, J = 15.6 Hz, 1H), 6.29 (dt, J = 15.6, 6.8 Hz, 1H), 5.05 (s, 1H), 4.63 (s, 1H), 3.22 (s, 3H), 2.22 (td, J = 8.0, 1.2 Hz, 2H), 1.52 (dd, J = 14.8, 7.6 Hz, 2H), 0.97 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.1, 150.8, 147.3, 133.6, 132.0, 131.2, 130.6, 129.6, 129.4, 125.6, 125.2, 124.0, 123.7, 120.5, 117.9, 117.7, 113.9, 112.5, 52.2, 35.2, 22.6, 13.8 .

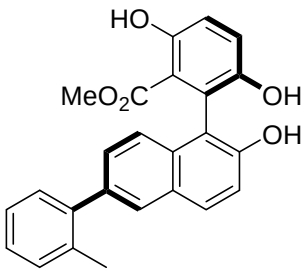
HRMS (ESI) calcd for $[M+K]^+$, $C_{23}H_{22}O_5K^+$, m/z: 417.1104, observed: 417.1102.



	Retention Time	Area	% Area
1	7.449	40940718	49.38
2	10.501	41966539	50.62



	Retention Time	Area	% Area
1	7.451	6881799	6.70
2	10.415	95789254	93.30



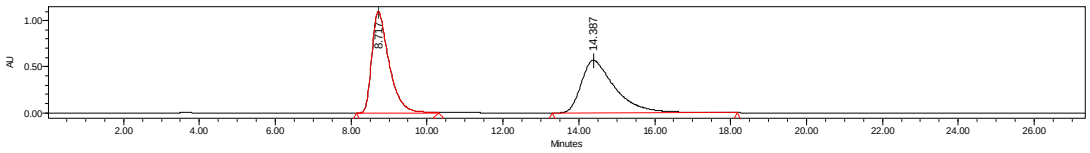
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxy-6-(o-tolyl)naphthalen-1-yl)benzoate

white solid; 94% yield, 94:6 e.r.; $[\alpha]_D^{25}$ = -79.3 (c 0.440, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 8.68 min,t_2 = 14.37 min];

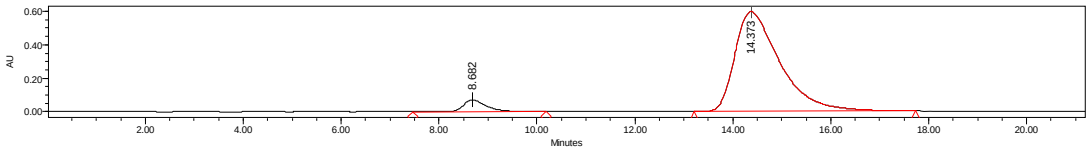
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.75 (d, J = 1.6 Hz, 1H), 7.35 (dd, J = 8.8, 1.6 Hz, 1H), 7.29 (dd, J = 6.0, 3.2 Hz, 5H), 7.24 (d, J = 7.6 Hz, 1H), 7.20 (d, J = 8.8 Hz, 1H), 7.13 (d, J = 9.2 Hz, 1H), 5.17 (s, 1H), 4.70 (s, 1H), 3.27 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.1, 151.1, 147.4, 141.5, 137.6, 135.6, 131.8, 130.8, 130.4, 130.0, 129.2, 129.0, 128.1, 127.4, 125.9, 124.0, 123.2, 120.6, 118.0, 117.9, 113.7, 112.6, 52.3, 20.6 .

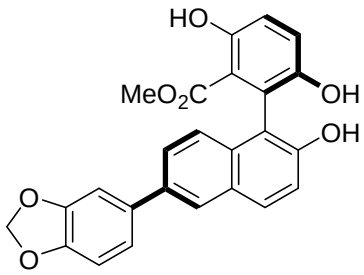
HRMS (ESI) calcd for $[M+Na]^+$, $C_{25}H_{20}O_5Na^+$, m/z: 423.1208, observed: 423.1208.



	Retention Time	Area	% Area
1	8.717	34554653	49.59
2	14.387	35121195	50.41



	Retention Time	Area	% Area
1	8.682	2401669	5.92
2	14.373	38165920	94.08



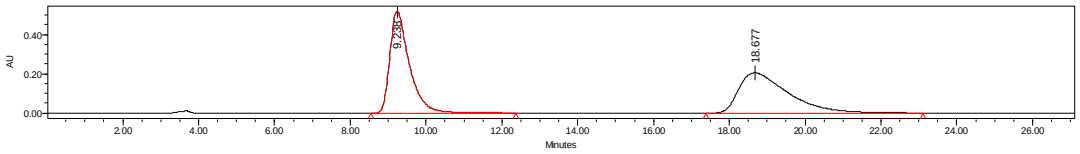
methyl (a*R*)-2-(6-(benzo[d][1,3]dioxol-5-yl)-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate

white solid; 93% yield, 95:5 e.r.; $[\alpha]_D^{25}$ = -127.8 (c 0.352, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 75/25, 1.0 mL/min, λ = 254 nm, t_1 = 9.28 min,t_2 = 18.35 min];

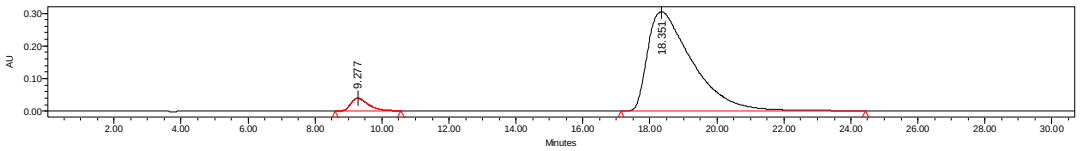
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 7.92 (d, J = 1.6 Hz, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.53 (dd, J = 8.8, 2.0 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.8 Hz, 1H), 7.17 – 7.09 (m, 3H), 6.90 (d, J = 8.4 Hz, 1H), 5.99 (s, 2H), 5.13 (s, 1H), 4.66 (s, 1H), 3.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.1, 151.1, 148.2, 147.3, 147.1, 136.4, 135.1, 131.9, 130.9, 129.4, 126.9, 125.6, 124.1, 124.1, 120.7, 120.6, 118.0, 117.9, 113.7, 112.5, 108.7, 107.6, 101.2, 52.3 .

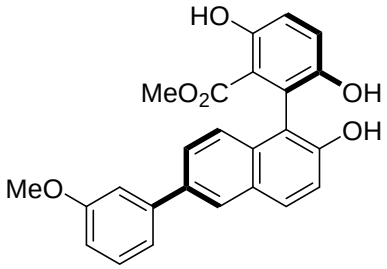
HRMS (ESI) calcd for $[M+K]^+$, $C_{25}H_{18}O_7K^+$, m/z: 469.0690, observed: 469.0687.



	Retention Time	Area	% Area
1	9.238	18625424	50.05
2	18.677	18585251	49.95



	Retention Time	Area	% Area
1	9.277	1477093	4.96
2	18.351	28331083	95.04



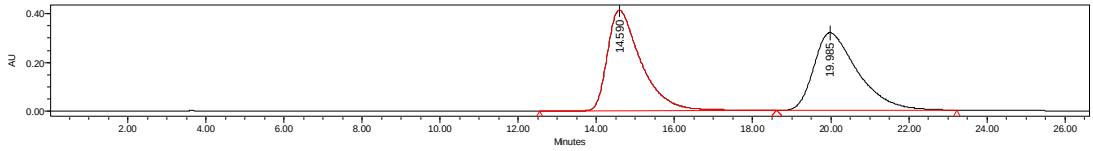
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxy-6-(3-methoxyphenyl)naphthalen-1-yl)benzoate

white solid; 91% yield, 95.5:4.5 e.r.; $[\alpha]_D^{25}$ = -73.0 (c 0.634, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 14.82 min,t_2 = 19.89 min];

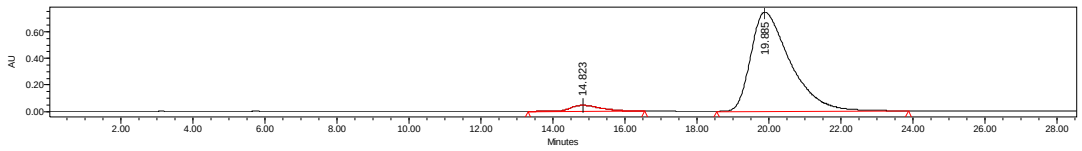
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.01 (d, J = 1.2 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.61 (dd, J = 8.8, 1.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.26 (dd, J = 13.2, 8.8 Hz, 4H), 7.20 (s, 1H), 7.13 (d, J = 9.2 Hz, 1H), 6.91 (dd, J = 8.0, 2.4 Hz, 1H), 4.88 (s, 2H), 3.87 (s, 3H), 3.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 160.0, 157.2, 151.2, 147.4, 142.2, 136.5, 132.2, 131.0, 129.9, 129.4, 127.0, 126.2, 124.1, 124.1, 120.6, 119.7, 118.0, 117.8, 113.8, 113.0, 112.7, 112.5, 55.4, 52.3 .

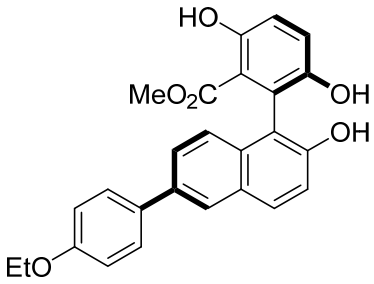
HRMS (ESI) calcd for $[M+K]^+$, $C_{25}H_{20}O_6K^+$, m/z: 455.0897, observed: 455.0891.



	Retention Time	Area	% Area
1	14.590	24931539	50.02
2	19.985	24916121	49.98



	Retention Time	Area	% Area
1	14.823	2683931	4.53
2	19.885	56603414	95.47



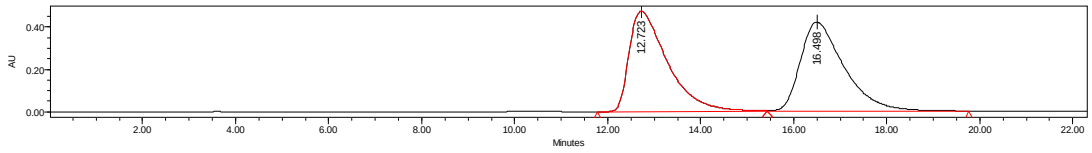
methyl (a*R*)-2-(6-(4-ethoxyphenyl)-2-hydroxynaphthalen-1-yl)-3,6-dihydroxybenzoate

white solid; 33% yield, 96.5:3.5 e.r.; $[\alpha]_D^{25}$ = -107.1 (c 0.160, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 13.50 min,t_2 = 16.14 min];

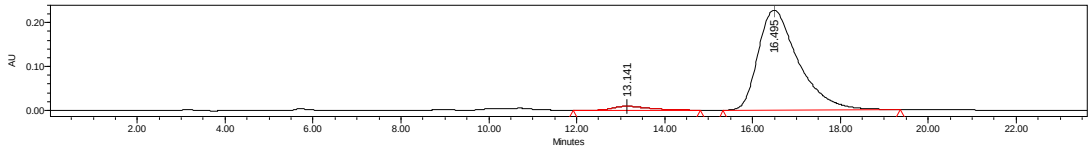
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 7.97 (d, J = 1.6 Hz, 1H), 7.89 (d, J = 9.2 Hz, 1H), 7.69 – 7.51 (m, 3H), 7.29 (dd, J = 13.6, 9.2 Hz, 2H), 7.22 (d, J = 8.8 Hz, 1H), 7.16 (d, J = 9.2 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 5.03 (s, 1H), 4.63 (s, 1H), 4.09 (q, J = 7.2 Hz, 2H), 3.26 (s, 3H), 1.45 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 158.6, 157.2, 150.9, 147.3, 136.3, 133.0, 131.7, 130.9, 129.5, 128.2, 126.8, 125.3, 124.0, 120.6, 117.9, 117.8, 114.9, 113.6, 112.5, 63.6, 52.3, 14.9 .

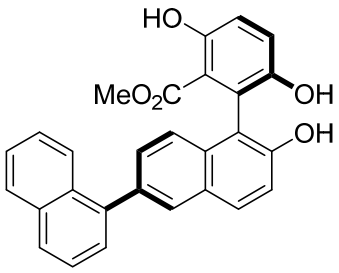
HRMS (ESI) calcd for $[M+K]^+$, $C_{26}H_{22}O_6K^+$, m/z: 469.1053, observed: 469.1055.



	Retention Time	Area	% Area
1	12.723	27322366	49.83
2	16.498	27508209	50.17



	Retention Time	Area	% Area
1	13.141	525530	3.52
2	16.495	14423843	96.48



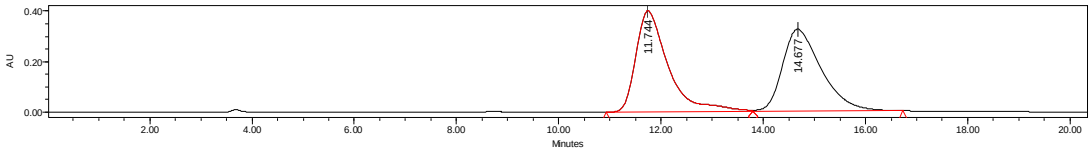
methyl (a*R*)-3,6-dihydroxy-2-(6'-hydroxy-[1,2'-binaphthalen]-5'-yl)benzoate

white solid; 98% yield, 94:6 e.r.; $[\alpha]_D^{25}$ = -68.4 (c 0.886, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 12.39 min,t_2 = 15.17 min];

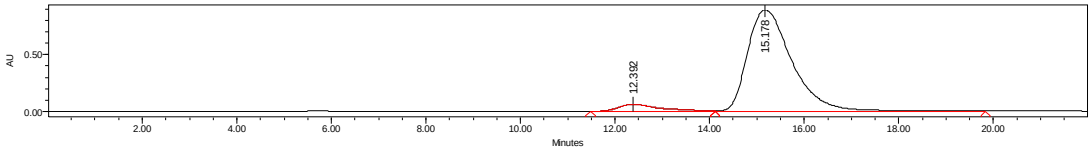
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.74 (s, 1H), 7.90 – 7.75 (m, 5H), 7.48 – 7.39 (m, 4H), 7.36 – 7.31 (m, 1H), 7.23 (dd, J = 9.2, 1.2 Hz, 3H), 7.16 (s, 1H), 7.07 (d, J = 9.2 Hz, 1H), 5.20 (s, 2H), 3.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 157.2, 151.3, 147.4, 139.8, 136.4, 133.9, 132.1, 131.7, 130.9, 130.0, 129.2, 129.1, 128.4, 127.8, 127.3, 126.2, 126.0, 125.9, 125.5, 124.1, 123.4, 120.6, 118.0, 118.0, 113.8, 112.6, 52.4 .

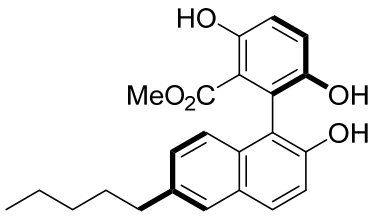
HRMS (ESI) calcd for $[M+K]^+$, $C_{28}H_{20}O_5K^+$, m/z: 475.0948, observed: 475.0949.



	Retention Time	Area	% Area
1	11.744	17725251	50.67
2	14.677	17253255	49.33



	Retention Time	Area	% Area
1	12.392	3751004	6.05
2	15.178	58244228	93.95



methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxy-6-pentylnaphthalen-1-yl)benzoate

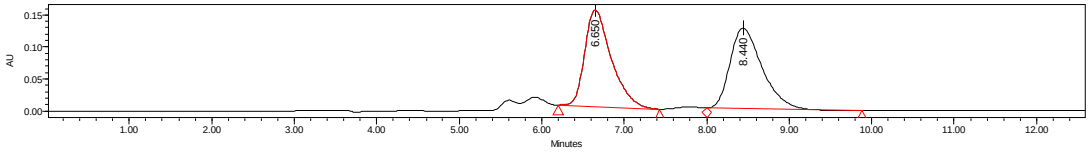
white solid; 80% yield, 95.5:4.5 e.r.; $[\alpha]_D^{25}$ = -37.7 (c 0.718, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 6.70 min,t_2 = 8.44 min];

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.77 (s, 1H), 7.77 (d, J = 9.2 Hz, 1H), 7.58 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.11 (d, J = 9.2 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H), 5.04 (s, 1H), 4.63 (s, 1H), 3.22 (s, 3H), 2.79 – 2.64 (m, 2H), 1.75 – 1.62 (m, 2H), 1.40 – 1.29 (m, 4H),

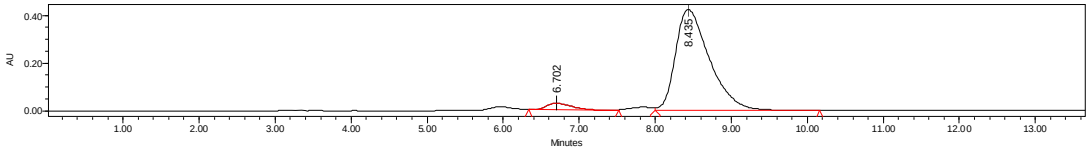
0.89 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 157.0, 150.4, 147.3, 138.5, 131.3, 130.2, 129.3, 128.9, 126.7, 123.9, 123.4, 120.4, 118.2, 117.4, 113.6, 112.6, 52.2, 35.7, 31.6, 31.0, 22.6, 14.1 .

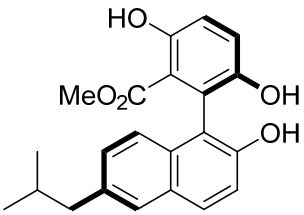
HRMS (ESI) calcd for $[M+K]^+$, $C_{23}H_{24}O_5K^+$, m/z: 419.1261, observed: 419.1260.



	Retention Time	Area	% Area
1	6.650	3356553	49.90
2	8.440	3370092	50.10



	Retention Time	Area	% Area
1	6.702	635443	4.59
2	8.435	13220497	95.41



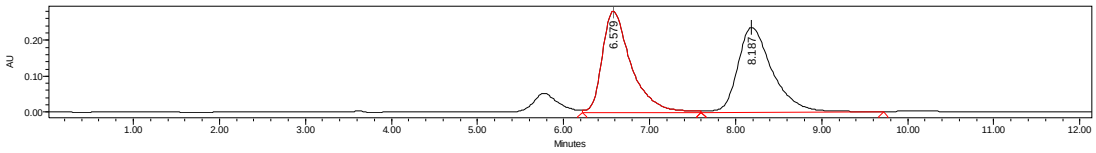
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxy-6-isobutylnaphthalen-1-yl)benzoate

white solid; 86% yield, 95.5:4.5 e.r.; $[\alpha]_D^{25}$ = -48.1 (c 0.606, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 6.64 min,t_2 = 8.20 min];

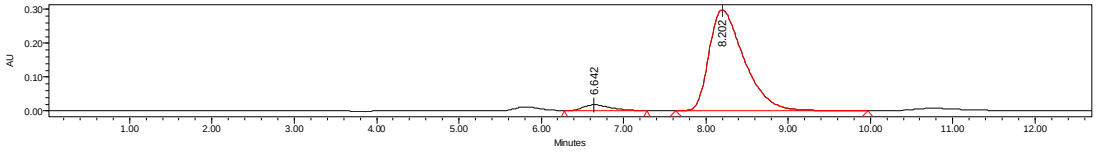
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.77 (s, 1H), 7.78 (d, J = 9.2 Hz, 1H), 7.55 (s, 1H), 7.27 (d, J = 9.2 Hz, 1H), 7.22 (d, J = 9.2 Hz, 1H), 7.17 (dd, J = 8.8, 1.6 Hz, 1H), 7.12 (d, J = 9.2 Hz, 1H), 7.08 (d, J = 8.8 Hz, 1H), 5.03 (s, 1H), 4.65 (s, 1H), 3.21 (s, 3H), 2.59 (d, J = 7.2 Hz, 2H), 1.93 (dt, J = 13.6, 6.8 Hz, 1H), 0.92 (dd, J = 6.8, 0.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 157.0, 150.4, 147.3, 137.3, 131.4, 130.2, 129.4, 129.2, 127.6, 123.9, 123.2, 120.4, 118.2, 117.4, 113.5, 112.6, 52.2, 45.2, 30.2, 22.5, 22.4.

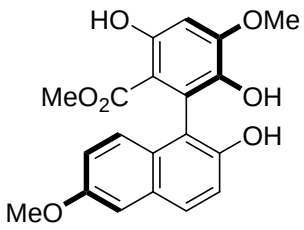
HRMS (ESI) calcd for $[M+K]^+$, $C_{22}H_{22}O_5K^+$, m/z: 405.1104, observed: 405.1107.



	Retention Time	Area	% Area
1	6.579	6549990	49.67
2	8.187	6636025	50.33



	Retention Time	Area	% Area
1	6.642	394811	4.25
2	8.202	8891802	95.75



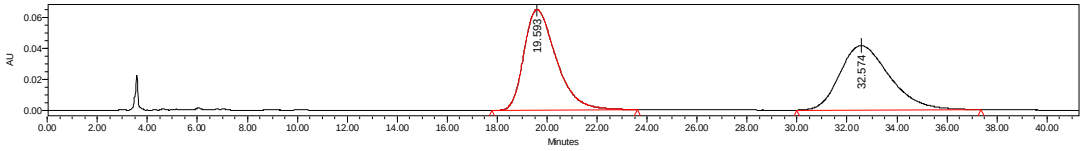
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxy-6-methoxynaphthalen-1-yl)-4-methoxybenzoate

white solid; 84% yield, 92.5:7.5 e.r.; $[\alpha]_D^{25}$ = -4.0 (c 0.602, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakODH, n-hexane/ i-PrOH = 75/25, 1.0 mL/min, λ = 254 nm, t_1 = 19.38 min,t_2 = 32.00 min];

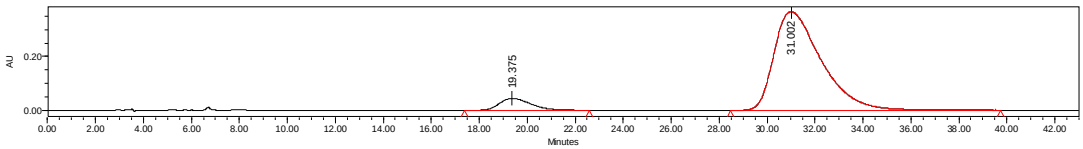
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.40 (s, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.99 (dd, J = 9.2, 2.8 Hz, 1H), 6.65 (s, 1H), 5.14 (s, 2H), 3.95 (s, 3H), 3.88 (s, 3H), 3.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 158.9, 155.8, 153.1, 148.6, 137.6, 129.8, 128.3, 125.4, 119.1, 118.9, 117.9, 116.2, 106.5, 104.7, 100.6, 56.3, 55.3, 51.9 .

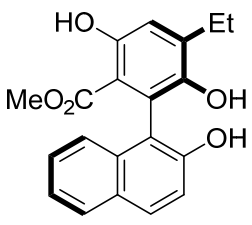
HRMS (ESI) calcd for $[M+K]^+$, $C_{20}H_{18}O_7K^+$, m/z: 409.0690, observed: 409.0691.



	Retention Time	Area	% Area
1	19.593	5818302	50.44
2	32.574	5717782	49.56



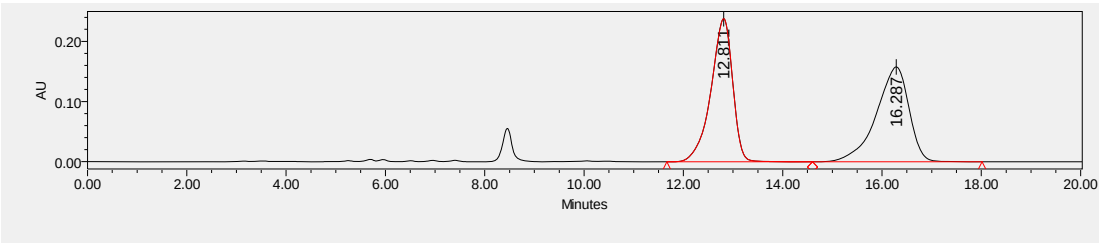
	Retention Time	Area	% Area
1	19.375	4089713	7.55
2	31.002	50048532	92.45



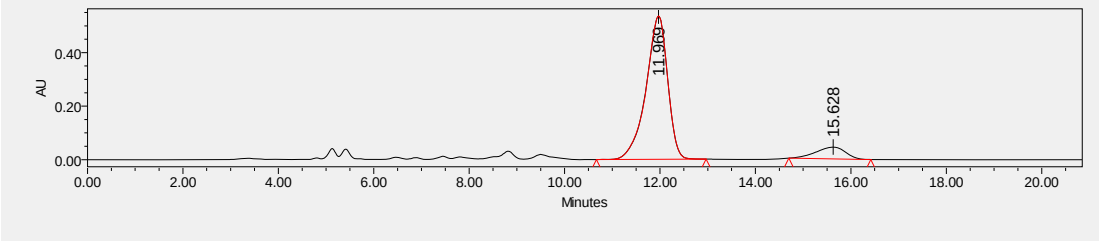
methyl (a*R*)-4-ethyl-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)benzoate

white solid; 71% yield, 90:10 e.r.; $[\alpha]_D^{25}$ = 9.8 (c 0.430, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 11.97 min,t_2 = 15.63 min];

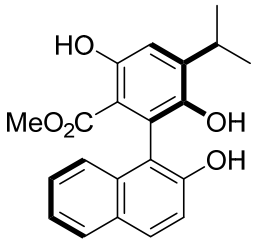
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.88 (s, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.40 – 7.31 (m, 2H), 7.27 (d, J = 9.2 Hz, 1H), 7.21 – 7.14 (m, 1H), 7.04 (s, 1H), 4.64 (d, J = 98.4 Hz, 2H), 3.19 (s, 3H), 2.73 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 157.2, 151.2, 145.5, 140.8, 133.1, 130.7, 129.1, 128.2, 127.3, 123.9, 123.6, 119.4, 117.5, 116.7, 114.0, 109.8, 52.0, 23.8, 13.1 .
HRMS (ESI) calcd for $[M+K]^+$, $C_{20}H_{18}O_5K^+$, m/z: 377.0791, observed: 377.0789.



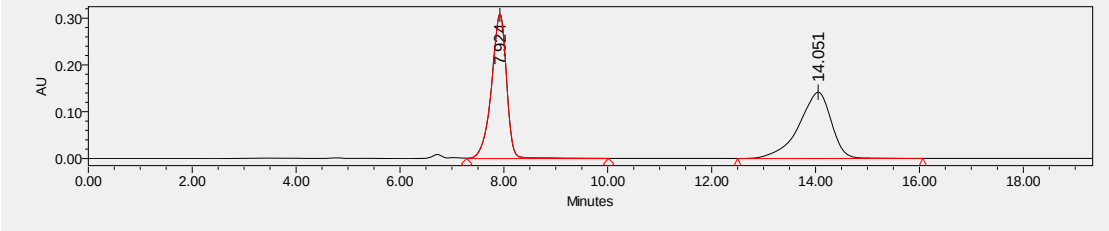
	Retention Time	Area	% Area
1	12.811	7199059	50.02
2	16.287	7193502	49.98



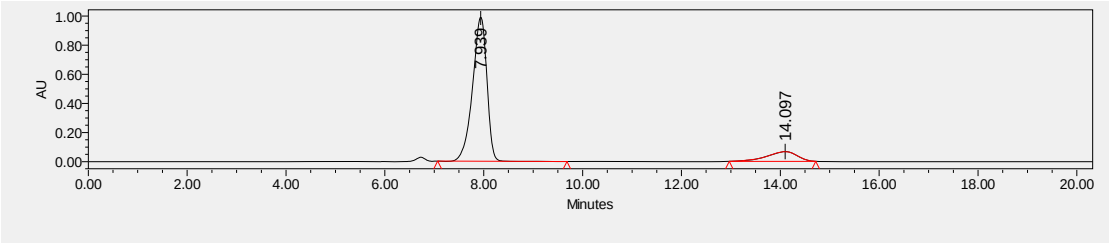
	Retention Time	Area	% Area
1	11.969	16806170	89.88
2	15.628	1892032	10.12



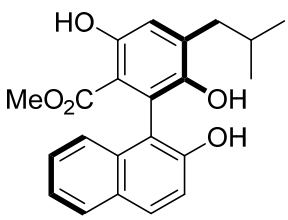
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)-4-isopropylbenzoate
white solid; 47% yield, 87.5:12.5 e.r.; $[\alpha]_D^{25}$ = 18.3 (c 0.284, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 7.94 min,t_2 = 14.10 min];
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.87 (s, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.83 (dd, J = 5.6, 3.6 Hz, 1H), 7.36 (dd, J = 5.6, 3.6 Hz, 2H), 7.28 (d, J = 9.2 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.09 (s, 1H), 5.02 (s, 1H), 4.66 (s, 1H), 3.33 (dt, J = 13.6, 6.8 Hz, 1H), 3.19 (s, 3H), 1.28 (d, J = 6.8 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 157.4, 151.2, 145.3, 145.0, 133.1, 130.7, 129.2, 128.2, 127.4, 123.9, 123.6, 117.4, 117.1, 116.8, 114.0, 109.7, 52.0, 28.0, 22.1.
HRMS (ESI) calcd for $[M+K]^+$, $C_{21}H_{20}O_5K^+$, m/z: 391.0948, observed: 391.0948.



	Retention Time	Area	% Area
1	7.924	6166832	50.10
2	14.051	6141711	49.90



	Retention Time	Area	% Area
1	7.939	19850973	87.48
2	14.097	2841016	12.52



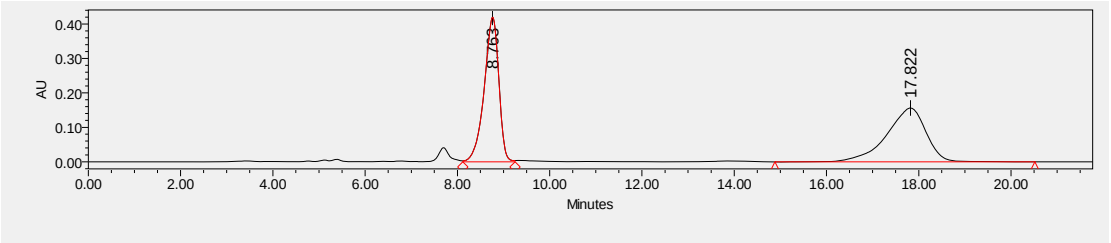
methyl (a*R*)-3,6-dihydroxy-2-(2-hydroxynaphthalen-1-yl)-4-isobutylbenzoate

white solid; 92% yield, 91.5:8.5 e.r.; $[\alpha]_D^{25}$ = 20.7 (c 0.702, CH_2Cl_2); Determined by HPLC analysis[Daicel chiralpakADH, n-hexane/ i-PrOH = 85/15, 1.0 mL/min, λ = 254 nm, t_1 = 8.81 min,t_2 = 18.10 min];

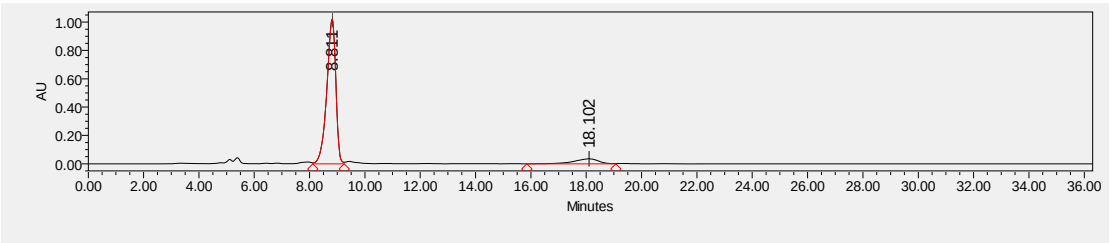
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.83 (s, 1H), 7.85 (d, J = 9.2 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.39 – 7.31 (m, 2H), 7.26 (d, J = 9.2 Hz, 1H), 7.16 (dd, J = 5.2, 4.4 Hz, 1H), 6.98 (s, 1H), 5.29 – 4.03 (m, 2H), 3.19 (s, 3H), 2.58 (dd, J = 9.2, 7.2 Hz, 2H), 2.01 (dt, J = 13.6, 6.8 Hz, 1H), 0.95 (dd, J = 6.8, 4.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 156.8, 151.2, 145.9, 138.6, 133.0, 130.7, 129.2, 128.2, 127.3, 123.9, 123.5, 121.2, 117.5, 116.9, 114.1, 110.1, 52.0, 39.9, 28.6, 22.6, 22.5 .

HRMS (ESI) calcd for $[M+K]^+$, $C_{22}H_{22}O_5K^+$, m/z: 405.1104, observed: 405.1106.



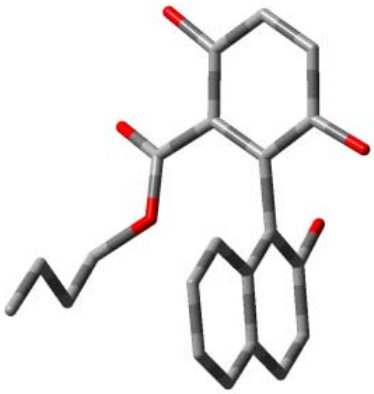
	Retention Time	Area	% Area
1	8.763	9199086	49.95
2	17.822	9218337	50.05



	Retention Time	Area	% Area
1	8.811	23003154	91.54
2	18.102	2125508	8.46

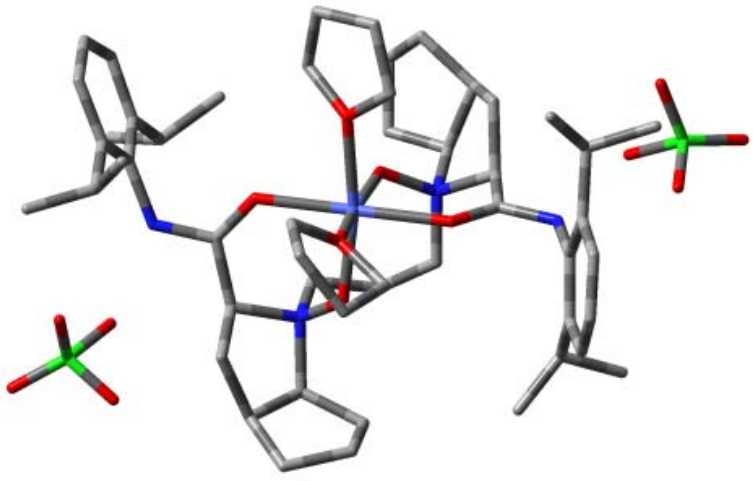
8. X-ray crystals structure of the product 3da:

Empirical formula	$C_{21}H_{20}O_5$
Formula weight	352.37
Temperature/K	290.64(10)
Crystal system	monoclinic
Space group	P21
a/Å	8.0345(2)
b/Å	12.6015(4)
c/Å	9.2114(3)
α/°	90
β/°	107.576(3)
γ/°	90
Volume/Å3	889.10(5)
Z	2
ρcalcg/cm3	1.316
μ/mm-1	0.770
F(000)	372.0
Crystal size/mm3	0.6 × 0.6 × 0.5
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.072 to 134.048
Index ranges	-8 ≤ h ≤ 9, -15 ≤ k ≤ 13, -10 ≤ l ≤ 11
Reflections collected	8560
Independent reflections	2889 [Rint = 0.0347, Rsigma = 0.0282]
Data/restraints/parameters	2889/1/239
Goodness-of-fit on F2	1.043
Final R indexes [I>=2σ (I)]	R1 = 0.0513, wR2 = 0.1314
Final R indexes [all data]	R1 = 0.0521, wR2 = 0.1330
Largest diff. peak/hole / e Å-3	0.52/-0.46
Flack parameter	-0.06(13)

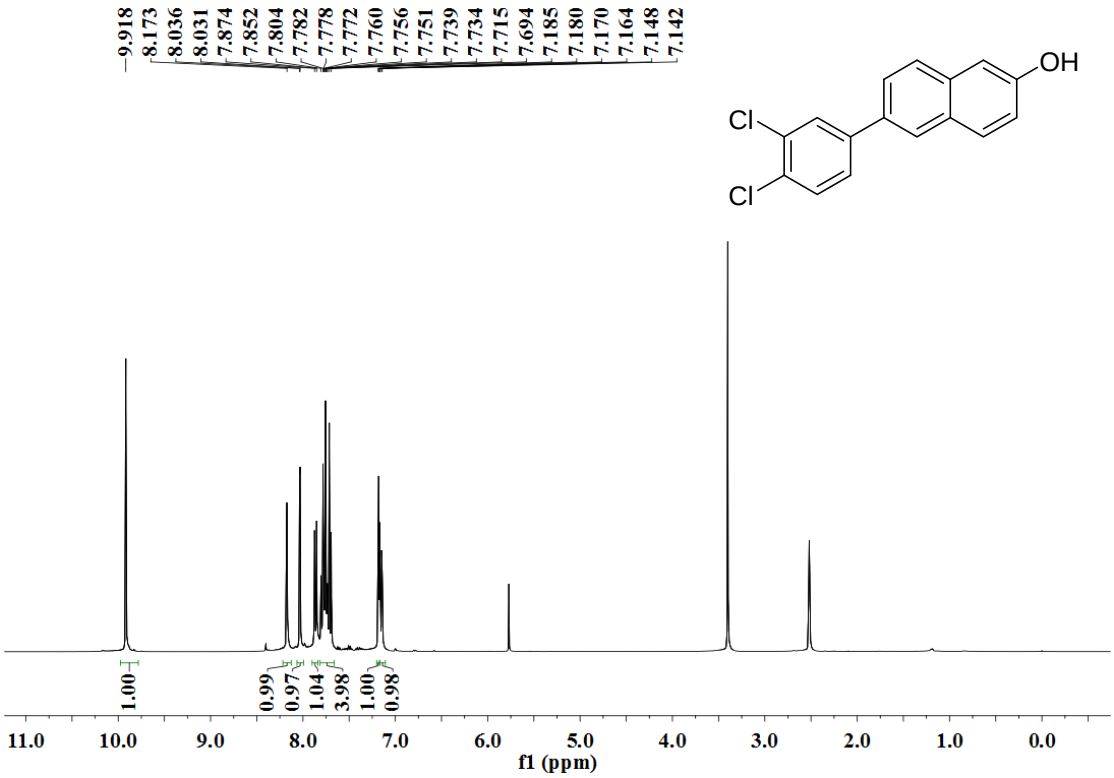


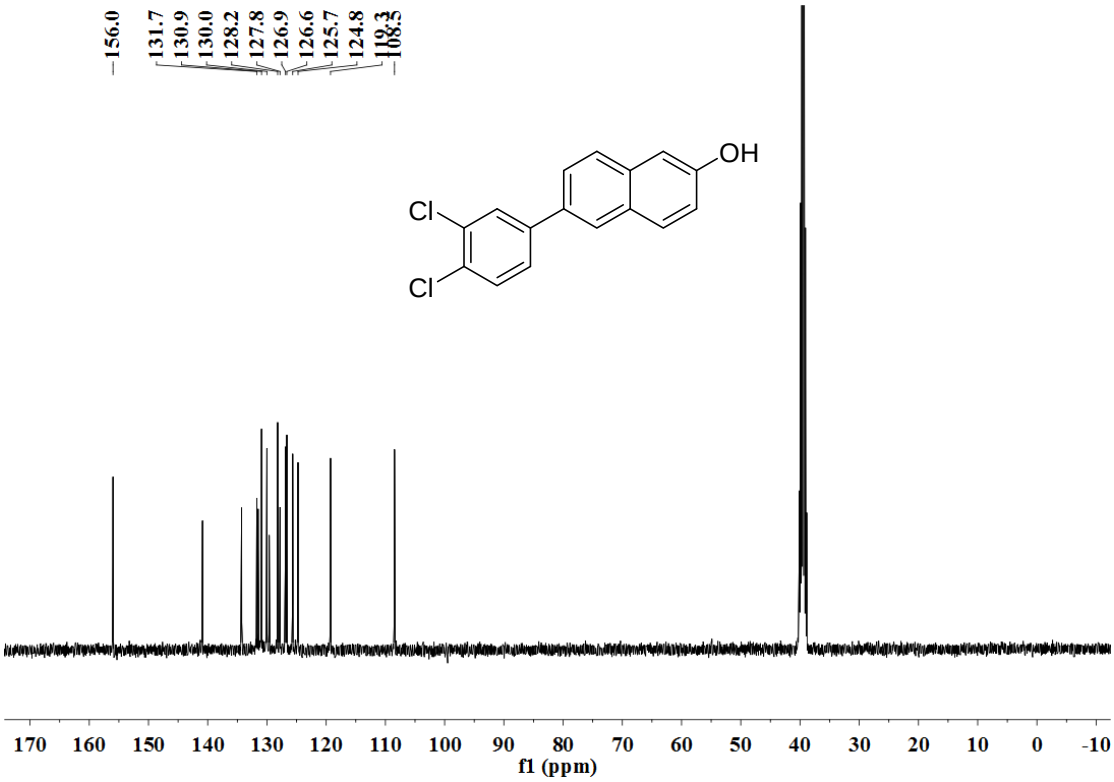
9. X-ray crystal structure of *L*-RaPr$_2$/Co(ClO$_4$)$_2$ complex.

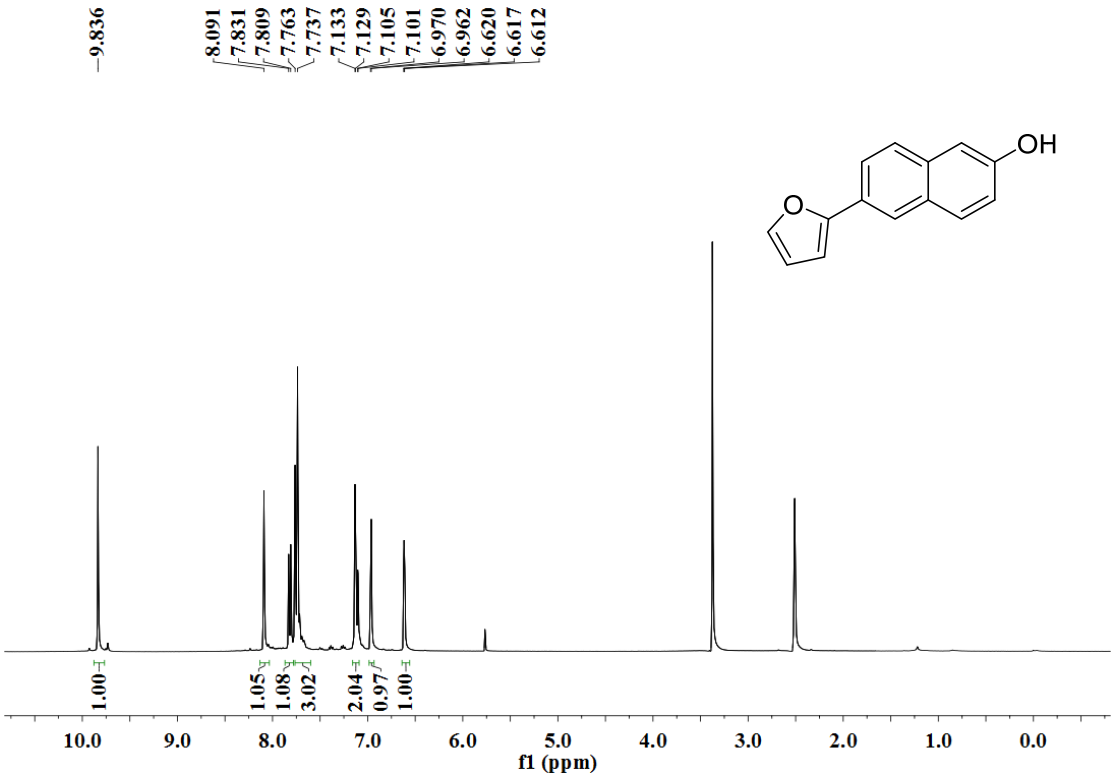
Empirical formula	C51H80Cl2CoN4O14
Formula weight	1103.02
Temperature/K	143.00(10)
Crystal system	monoclinic
Space group	P21
a/Å	12.6288(8)
b/Å	16.6036(7)
c/Å	13.9577(8)
α/°	90
β/°	90.375(5)
γ/°	90
Volume/Å3	2926.6(3)
Z	2
ρcalcg/cm3	1.252
μ/mm-1	0.447
F(000)	1174.0
Crystal size/mm3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.872 to 52.74
Index ranges	-15 ≤ h ≤ 15, -20 ≤ k ≤ 20, -17 ≤ l ≤ 17
Reflections collected	28110
Independent reflections	11959 [Rint = 0.0310, Rsigma = 0.0576]
Data/restraints/parameters	11959/2/639
Goodness-of-fit on F2	0.990
Final R indexes [I>=2σ (I)]	R1 = 0.0698, wR2 = 0.1768
Final R indexes [all data]	R1 = 0.0991, wR2 = 0.1959
Largest diff. peak/hole / e Å-3	0.94/-0.44
Flack parameter	0.020(7)



10. NMR spectra



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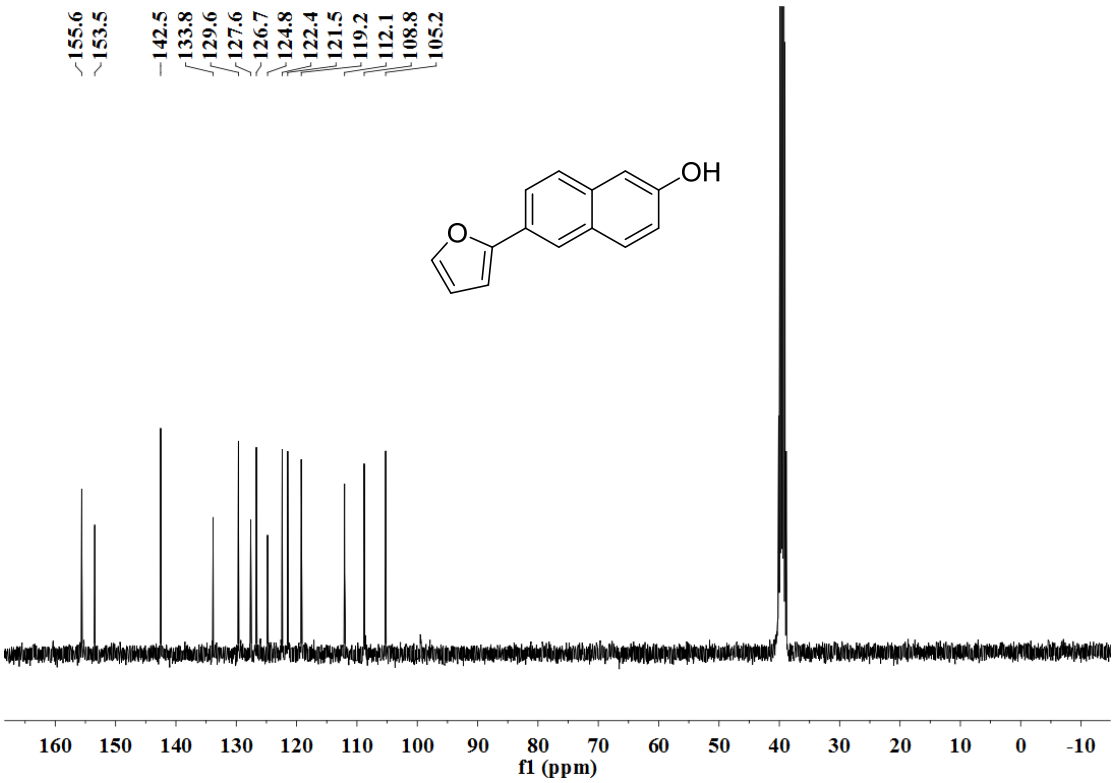
7.831
7.809
7.763
7.737
7.133
7.129
7.105
7.101
6.970
6.962
6.620
6.617
6.612
OH
O
1.00
1.05
1.08
3.02
2.04
0.97
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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153.5
142.5
133.8
129.6
127.6
126.7
124.8
122.4
121.5
119.2
112.1
108.8
105.2
OH
O
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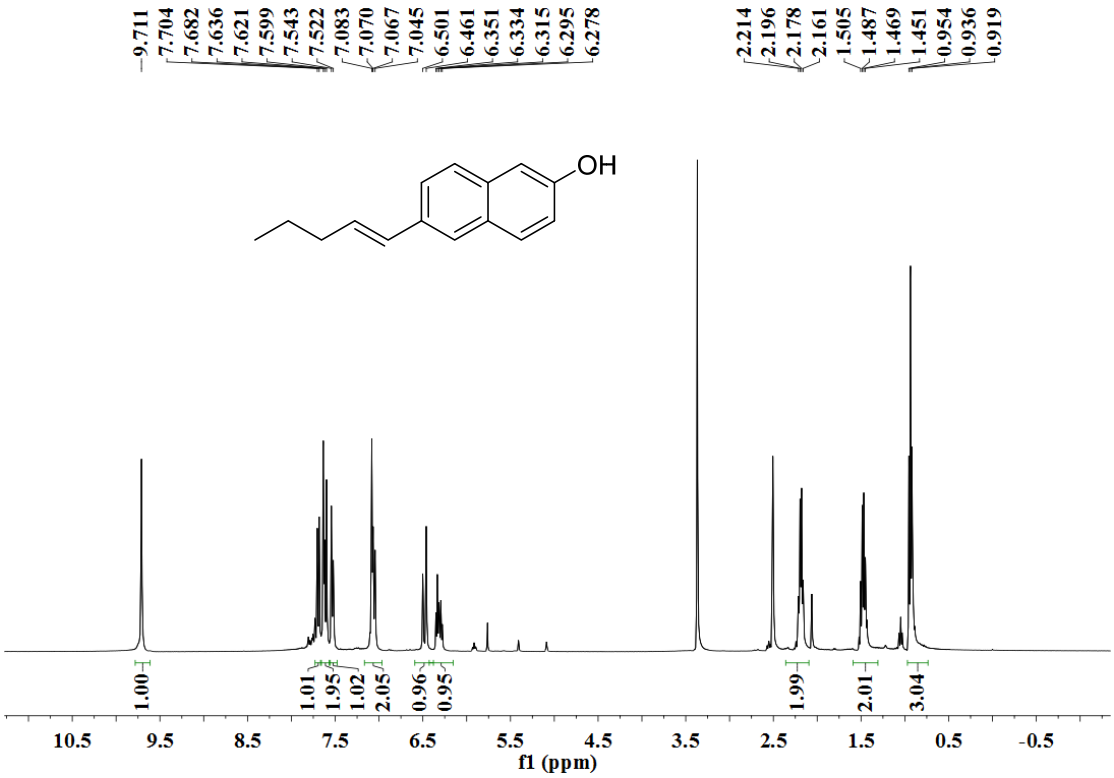
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.543
7.522
7.083
7.070
7.067
7.045
6.501
6.461
6.351
6.334
6.315
6.295
6.278
2.214
2.196
2.178
2.161
1.505
1.487
1.469
1.451
0.954
0.936
0.919
OH
1.00
1.01
1.95
1.02
2.05
0.96
0.95
1.99
2.01
3.04
10.5
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7.5
6.5
5.5
4.5
3.5
2.5
1.5
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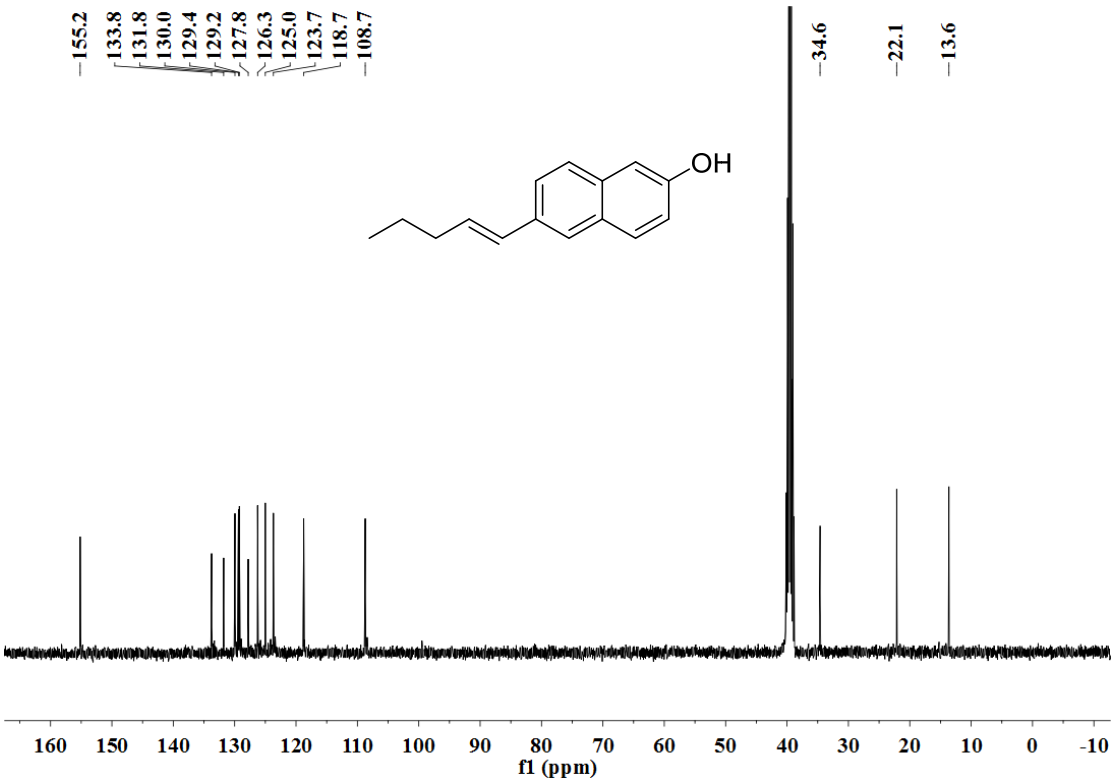
f1 (ppm)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133.8
131.8
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129.4
129.2
127.8
126.3
125.0
123.7
118.7
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34.6
22.1
13.6
OH
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140
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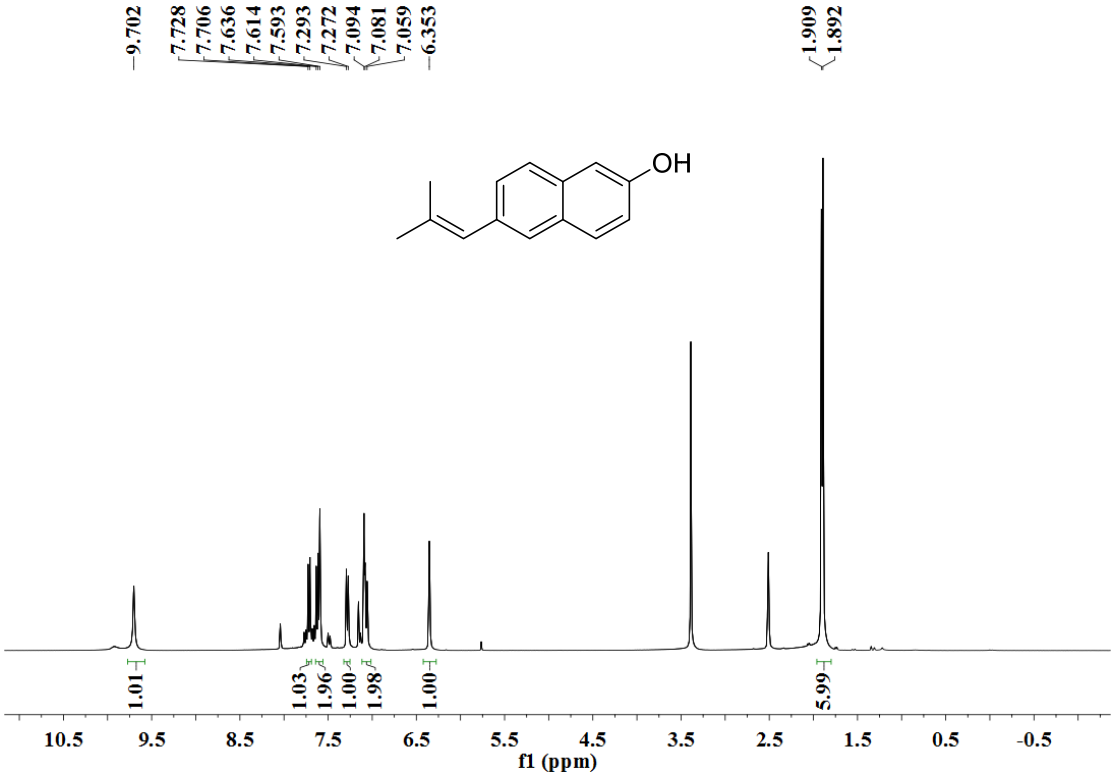
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.706
7.636
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7.593
7.293
7.272
7.094
7.081
7.059
6.353
1.909
1.892
OH
1.01
1.03
1.96
1.00
1.98
1.00
5.99
10.5
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6.5
5.5
4.5
3.5
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1.5
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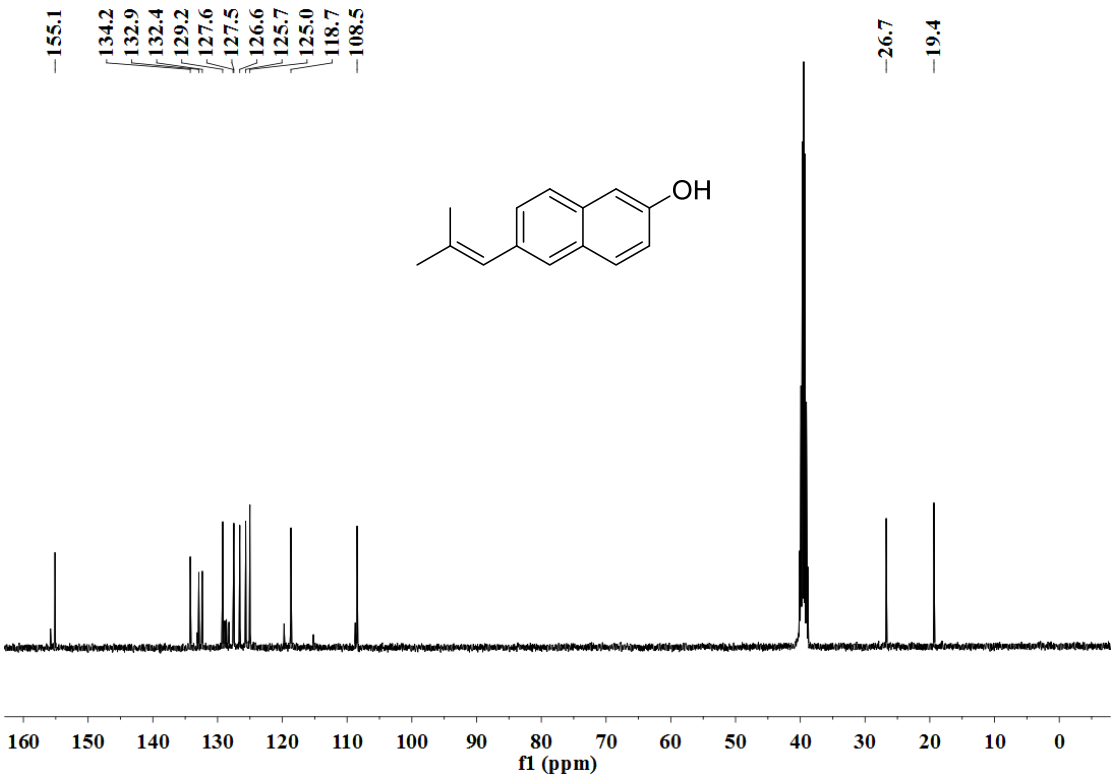
f1 (ppm)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132.9
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129.2
127.6
127.5
126.6
125.7
125.0
118.7
108.5
26.7
19.4
OH
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150
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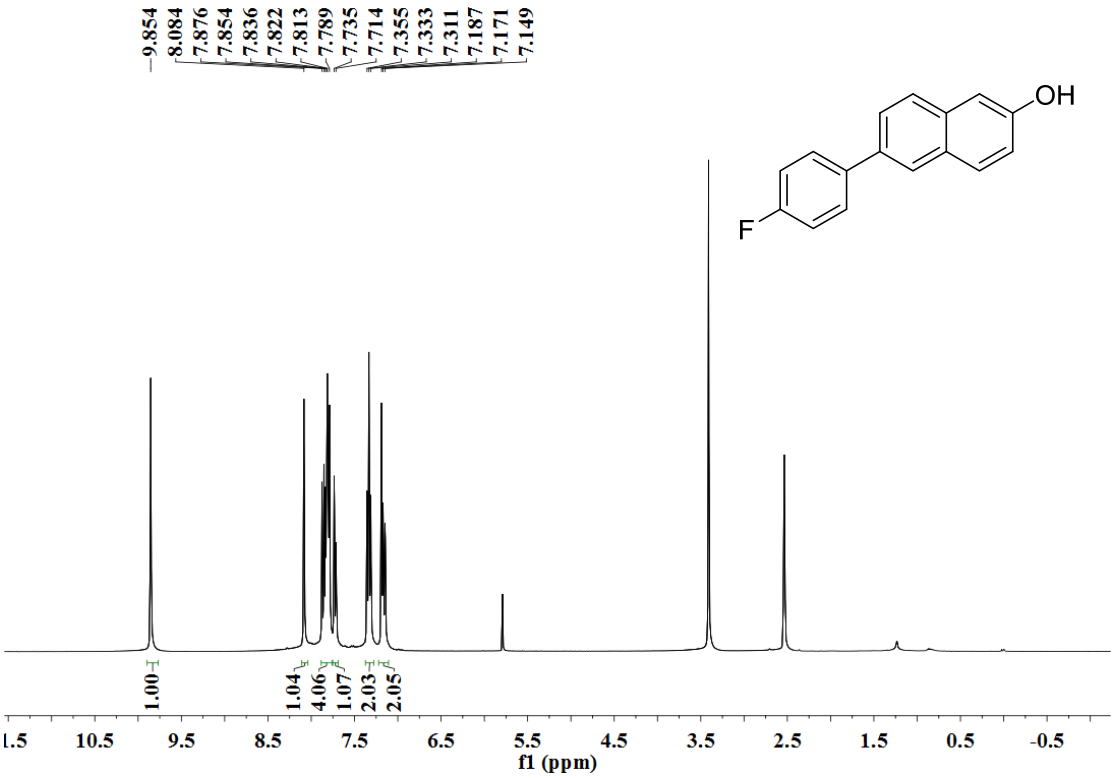
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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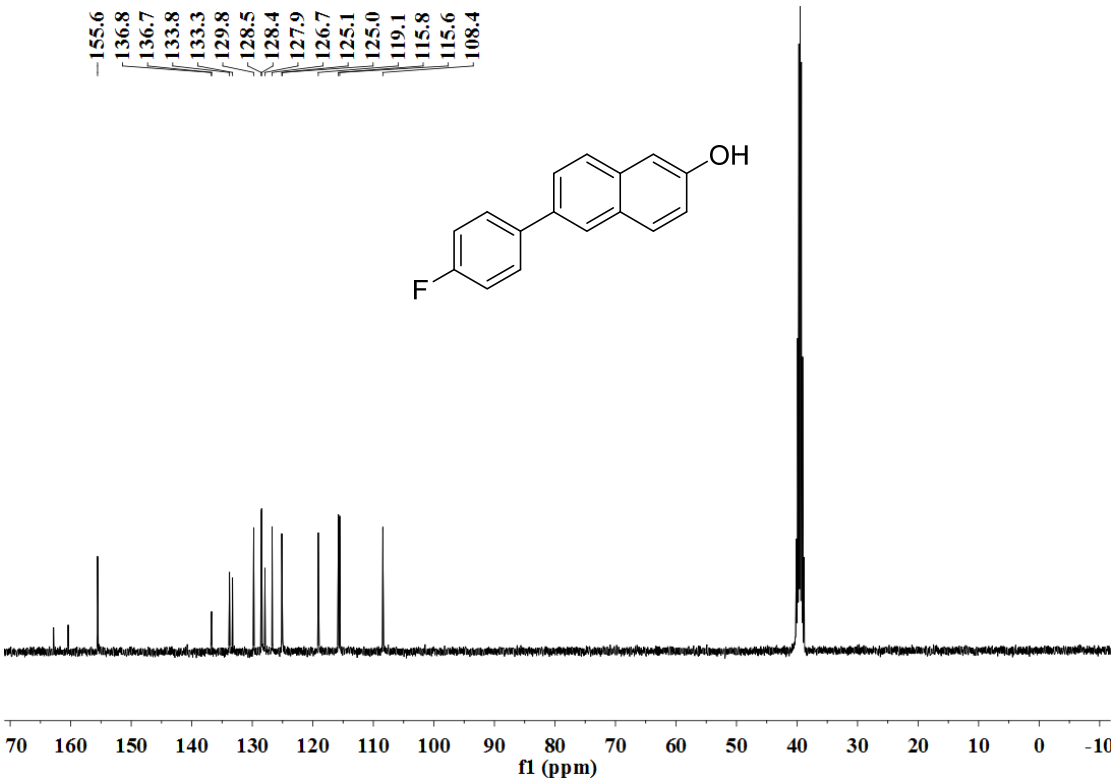
7.876
7.854
7.836
7.822
7.813
7.789
7.735
7.714
7.355
7.333
7.311
7.187
7.171
7.149
OH
F
1.00
1.04
4.06
1.07
2.03
2.05
f1 (ppm)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136.8
136.7
133.8
133.3
129.8
128.5
128.4
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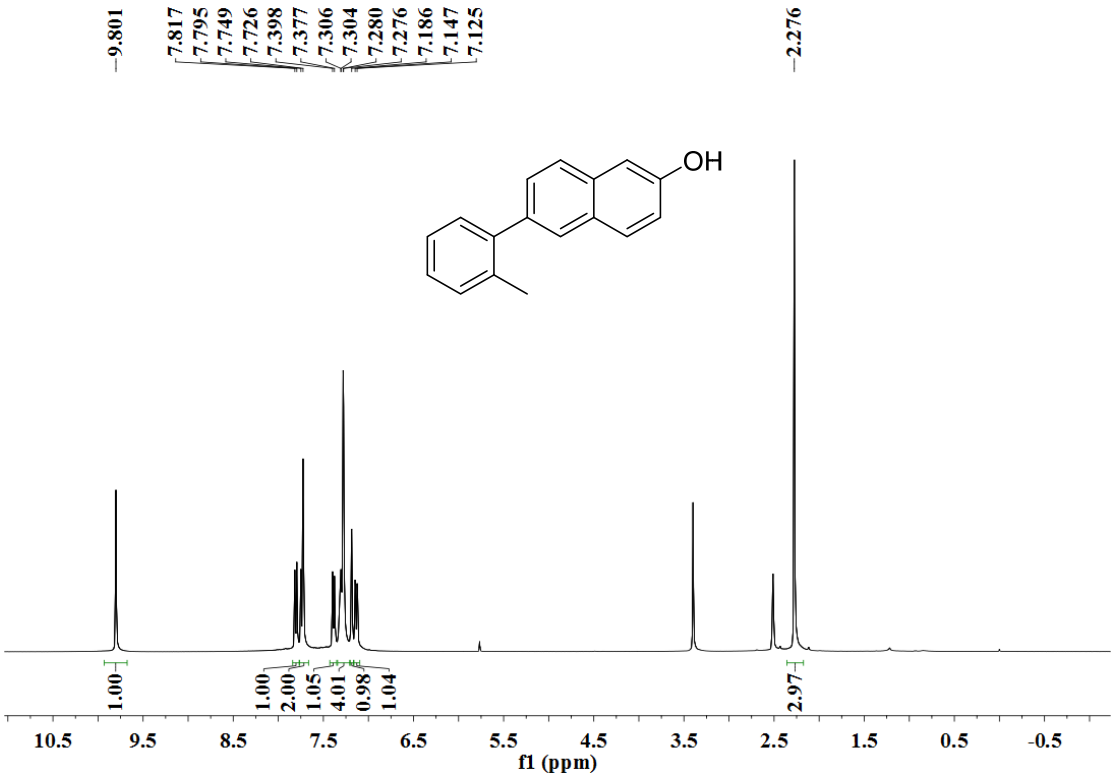
126.7
125.1
125.0
119.1
115.8
115.6
108.4
OH
F
f1 (ppm)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7.795
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7.726
7.398
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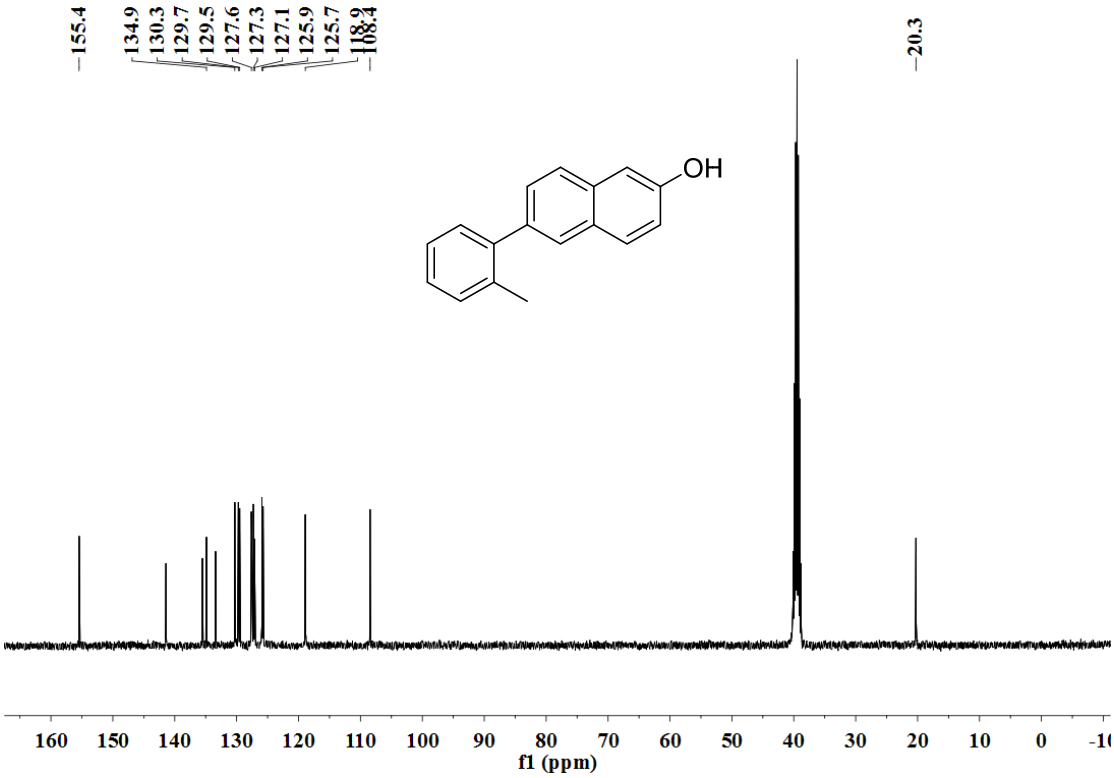
7.306
7.304
7.280
7.276
7.186
7.147
7.125
2.276
OH
1.00
1.00
2.00
1.05
4.01
0.98
1.04
2.97
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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134.9
130.3
129.7
129.5
127.6
127.3
127.1
125.9
125.7
118.9
108.4
20.3
OH
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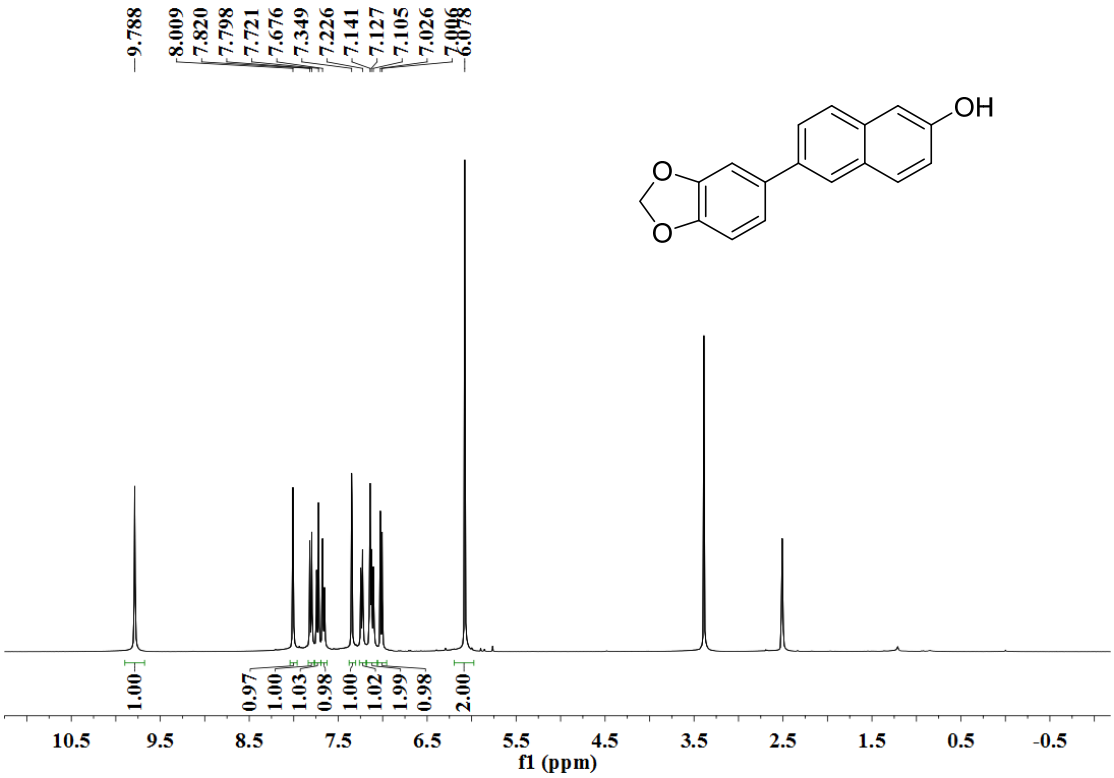
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.820
7.798
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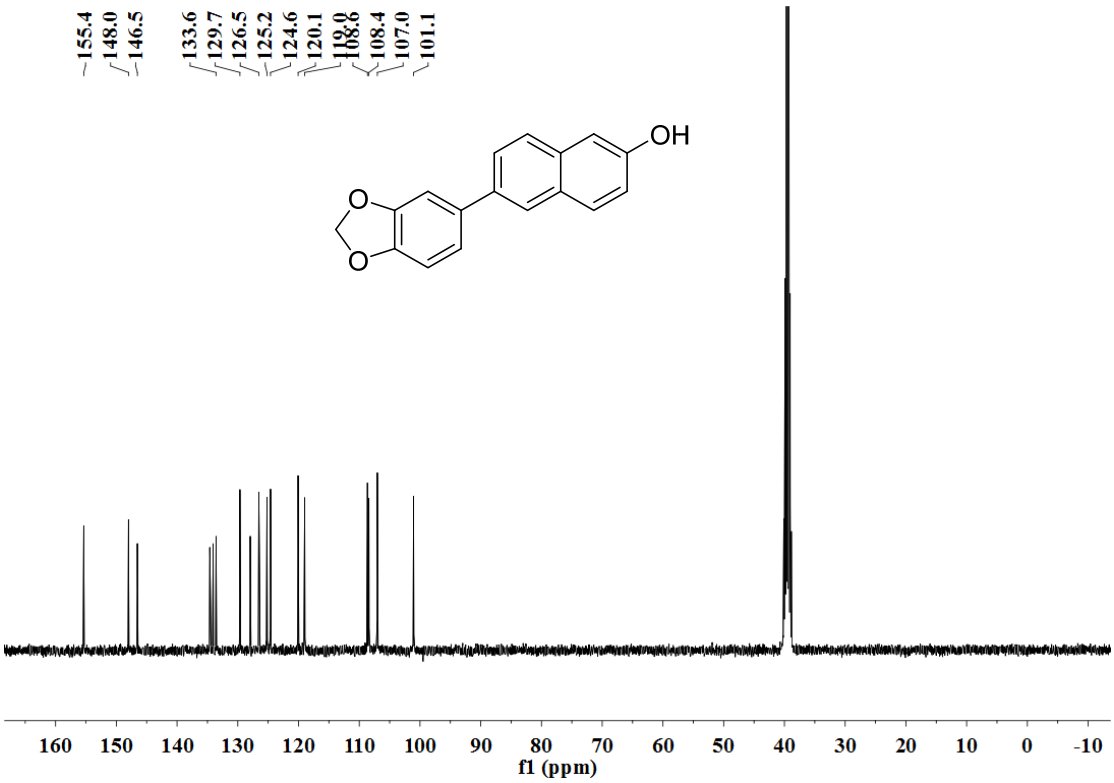
7.676
7.349
7.226
7.141
7.127
7.105
7.026
7.006
6.978
OH
O
O
1.00
0.97
1.00
1.03
0.98
1.00
1.02
1.99
0.98
2.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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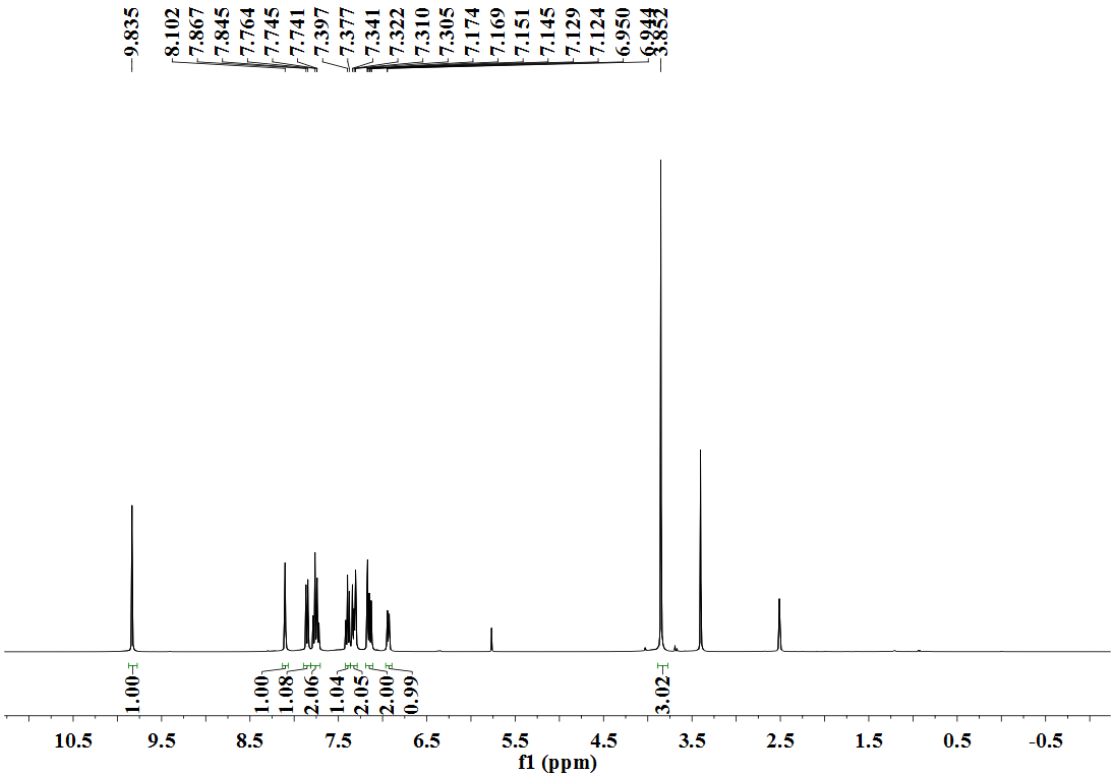
146.5
133.6
129.7
126.5
125.2
124.6
120.1
118.0
108.8
108.4
107.0
101.1
OH
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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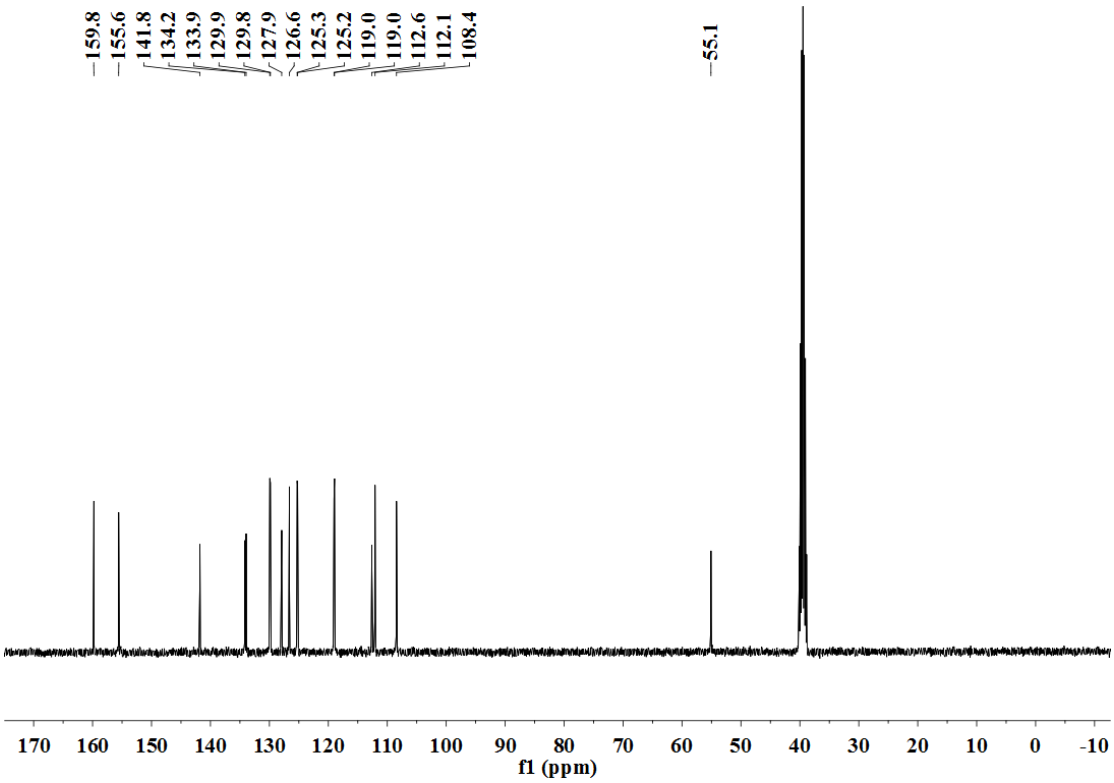
7.745
7.741
7.397
7.377
7.341
7.322
7.310
7.305
7.174
7.169
7.151
7.145
7.129
7.124
6.950
6.944
3.852
1.00
1.00
1.08
2.06
1.04
2.05
2.00
0.99
3.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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155.6
141.8
134.2
133.9
129.9
129.8
127.9
126.6
125.3
125.2
119.0
119.0
112.6
112.1
108.4
55.1
170
160
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140
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120
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100
90
80
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60
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30
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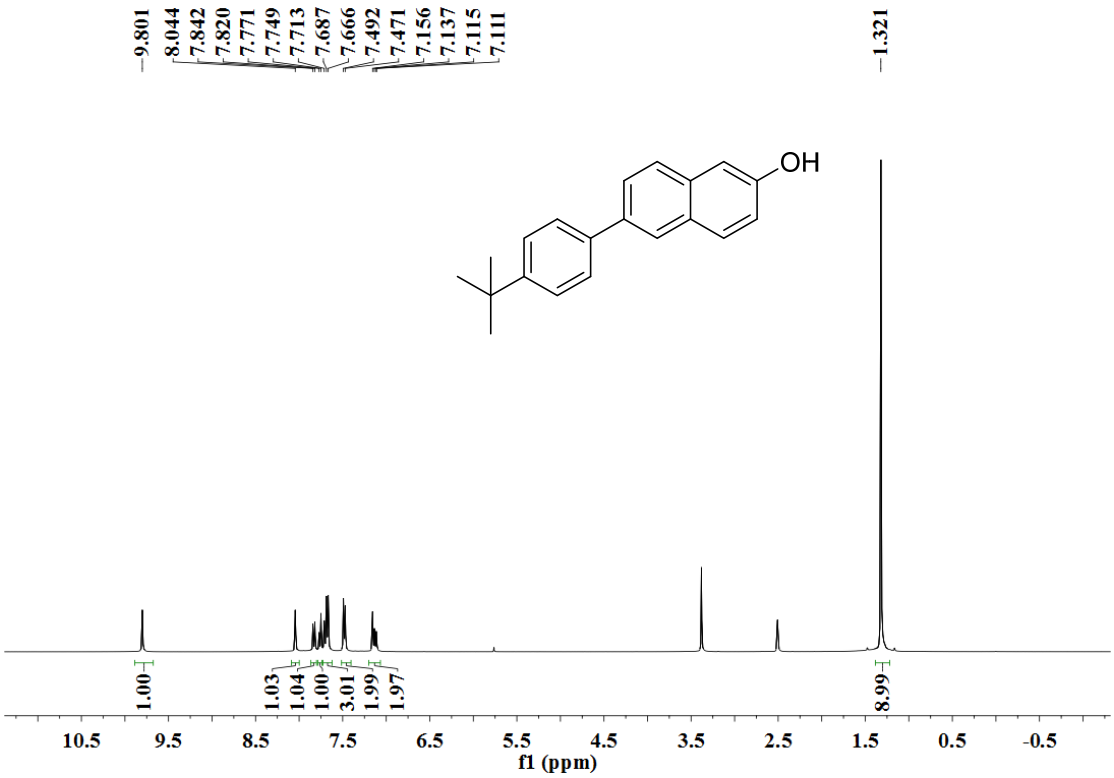
-10
f1 (ppm)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7.137
7.115
7.111
1.321
OH
1.00
1.03
1.04
1.00
3.01
1.99
1.97
8.99
10.5
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8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
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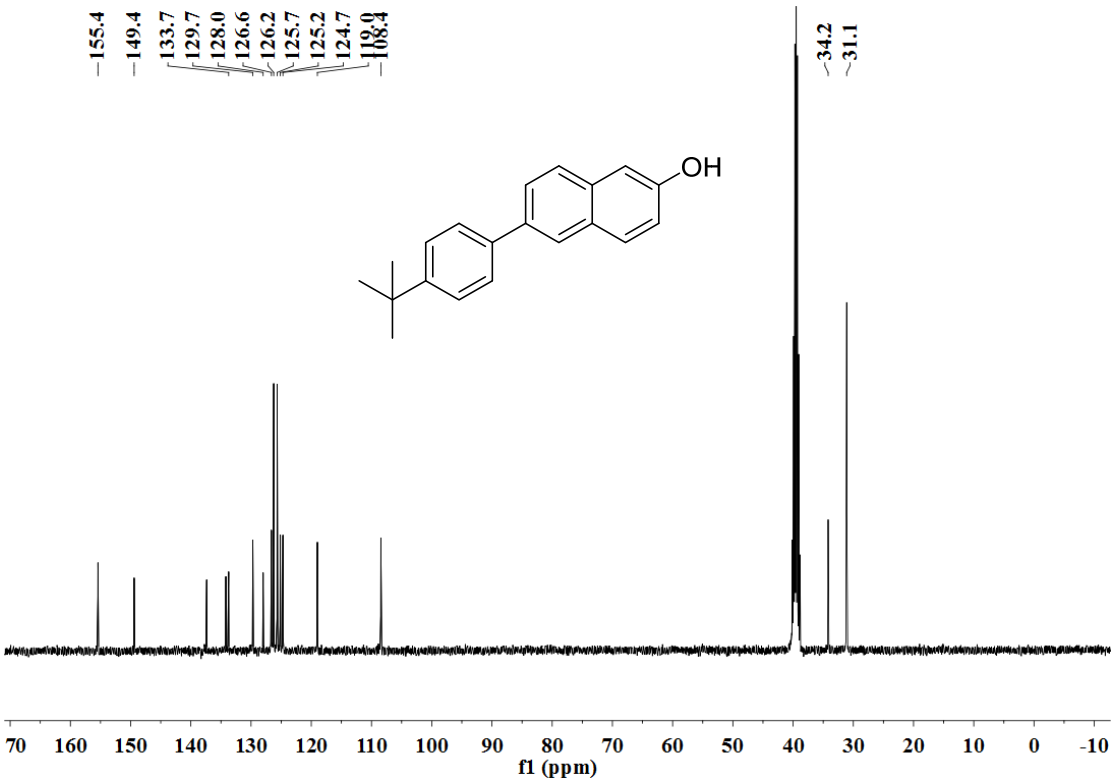
f1 (ppm)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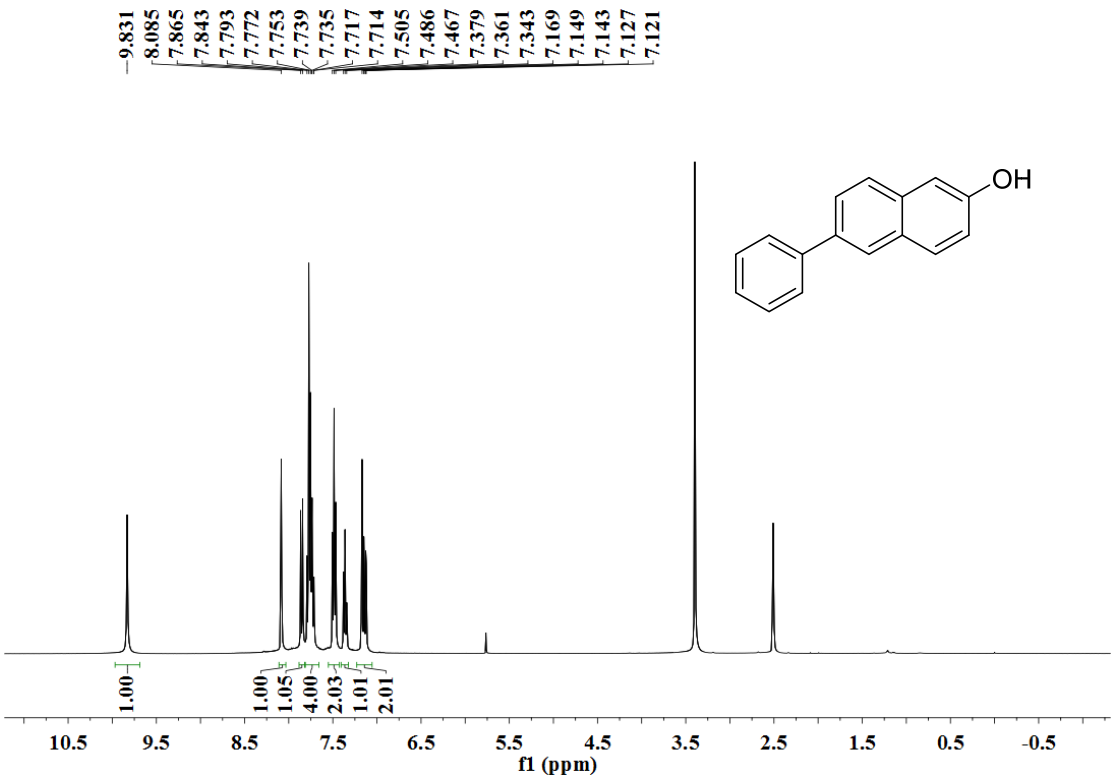
133.7
129.7
128.0
126.6
126.2
125.7
125.2
124.7
119.0
108.4
34.2
31.1
OH
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.505
7.486
7.467
7.379
7.361
7.343
7.169
7.149
7.143
7.127
7.121
OH
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1.00
1.05
4.00
2.03
1.01
2.01
10.5
9.5
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7.5
6.5
5.5
4.5
3.5
2.5
1.5
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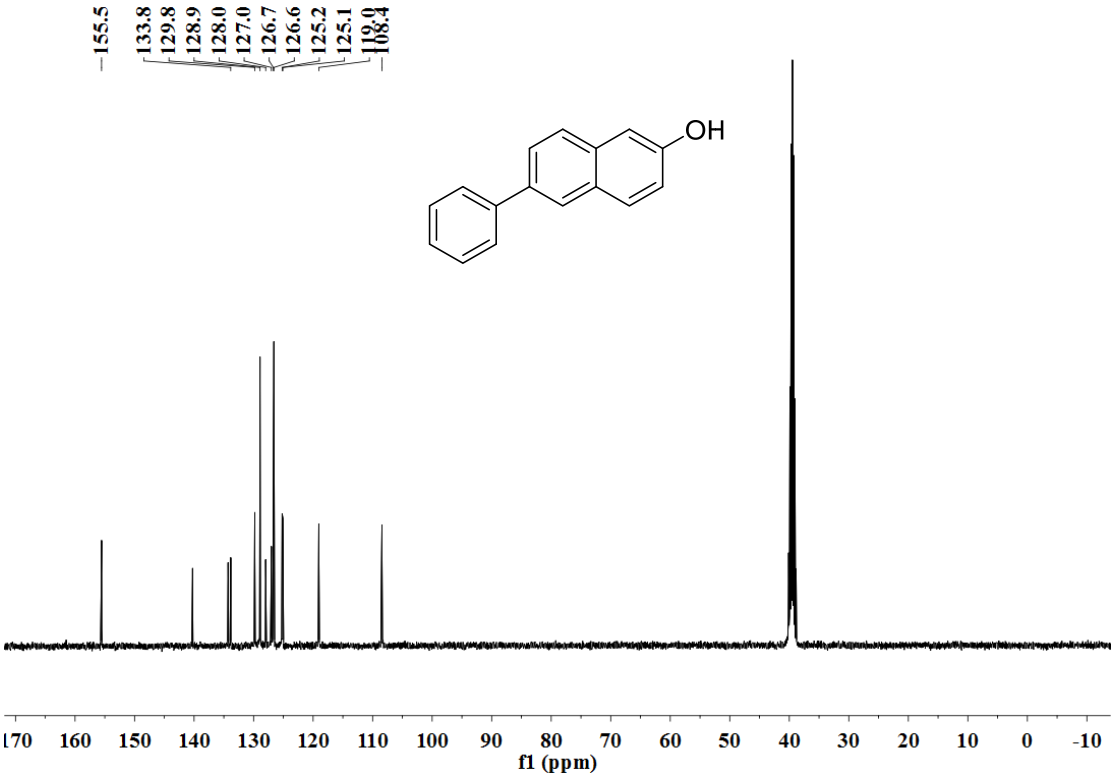
f1 (ppm)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129.8
128.9
128.0
127.0
126.7
126.6
125.2
125.1
118.0
108.4
OH
170
160
150
140
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120
110
100
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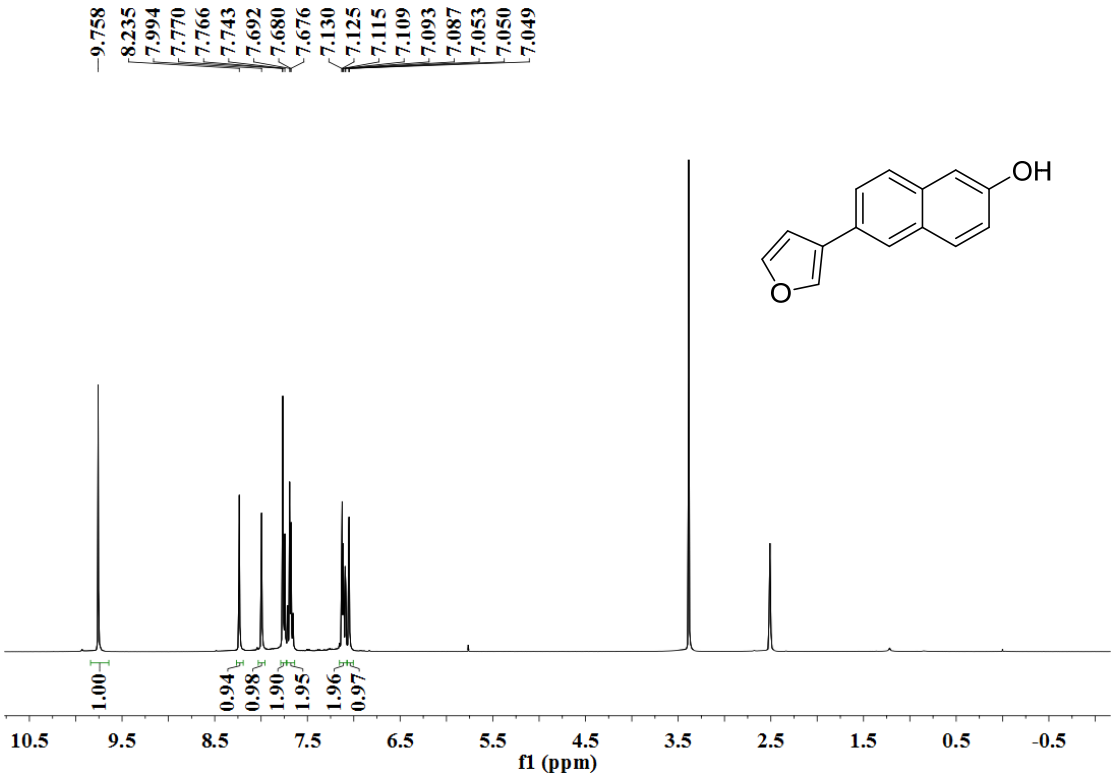
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.109
7.093
7.087
7.053
7.050
7.049
OH
O
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0.94
0.98
1.90
1.95
1.96
0.97
10.5
9.5
8.5
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6.5
5.5
4.5
3.5
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1.5
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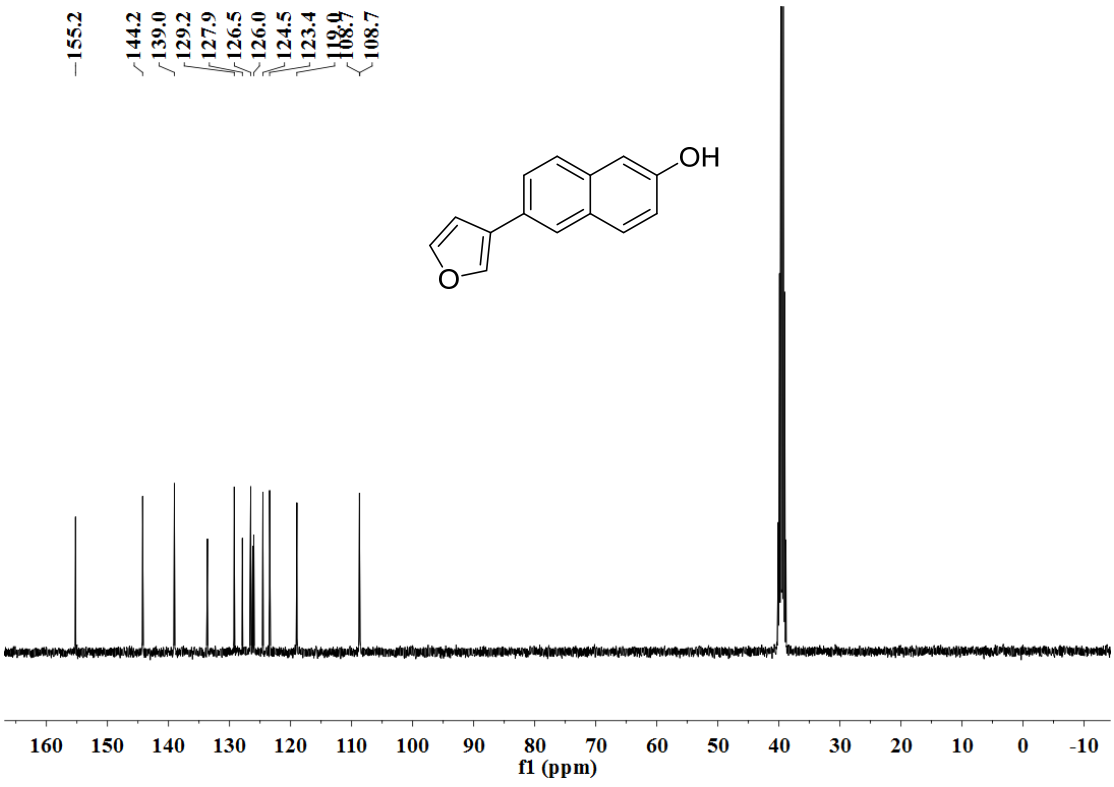
f1 (ppm)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126.5
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124.5
123.4
119.0
108.7
108.7
OH
O
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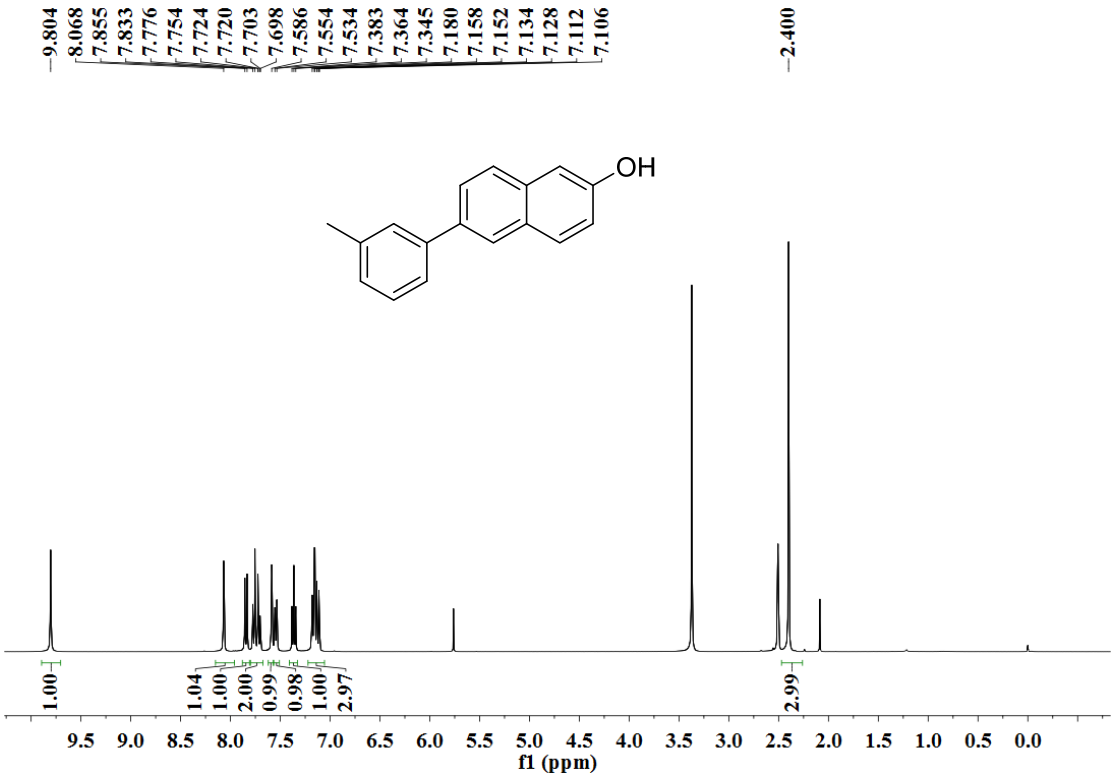
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.554
7.534
7.383
7.364
7.345
7.180
7.158
7.152
7.134
7.128
7.112
7.106
2.400
OH
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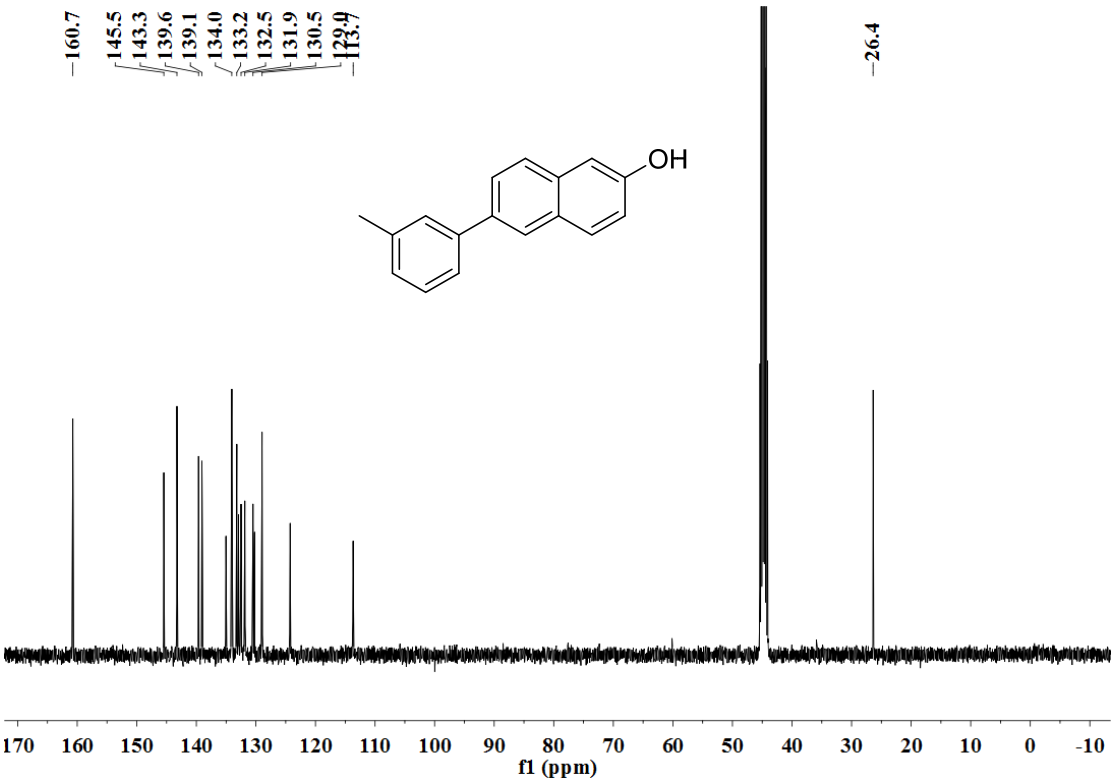
1.04
1.00
2.00
0.99
0.98
1.00
2.97
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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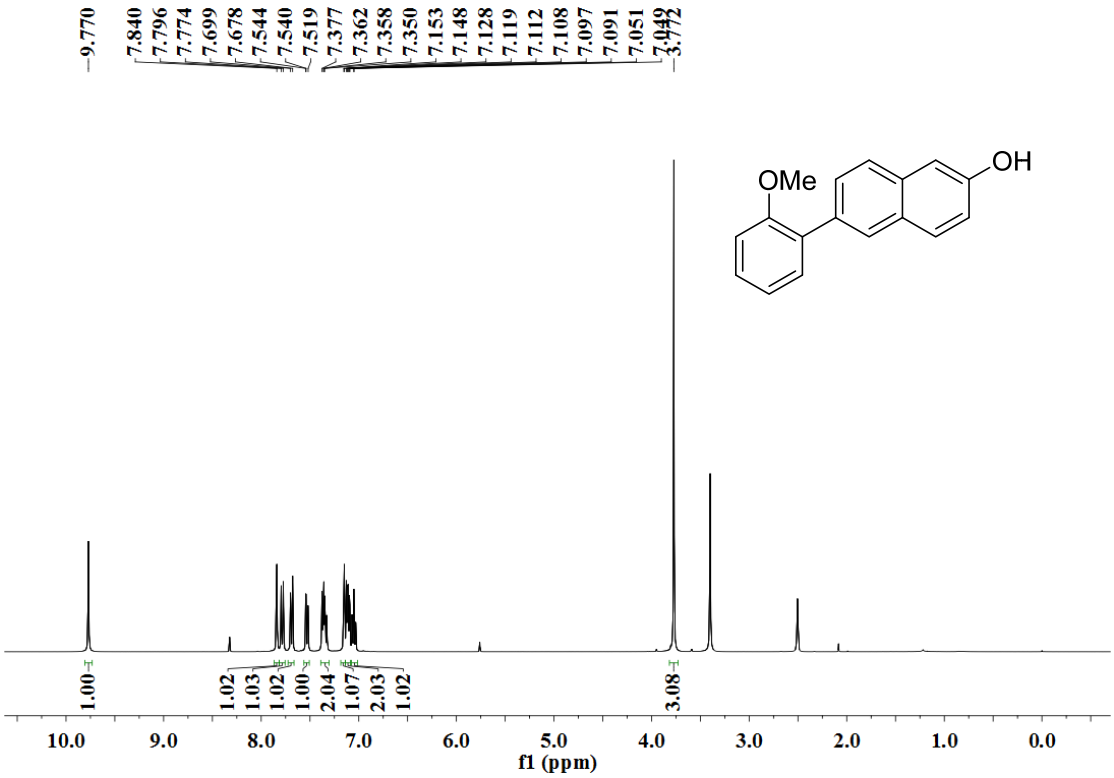
139.6
139.1
134.0
133.2
132.5
131.9
130.5
129.4
113.7
26.4
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.358
7.350
7.153
7.148
7.128
7.119
7.112
7.108
7.097
7.091
7.051
7.049
3.772
OMe
OH
1.00
1.02
1.03
1.02
1.00
2.04
1.07
2.03
1.02
3.08
10.0
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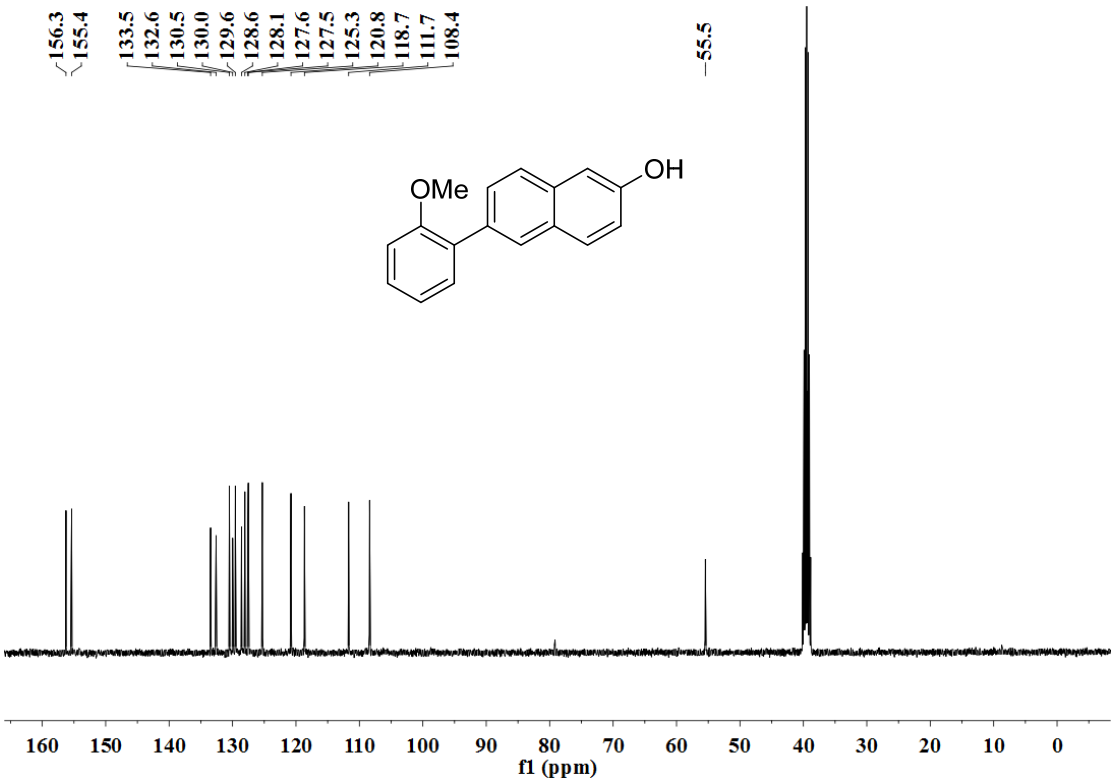
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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155.4
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132.6
130.5
130.0
129.6
128.6
128.1
127.6
127.5
125.3
120.8
118.7
111.7
108.4
55.5
OMe
OH
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110
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50
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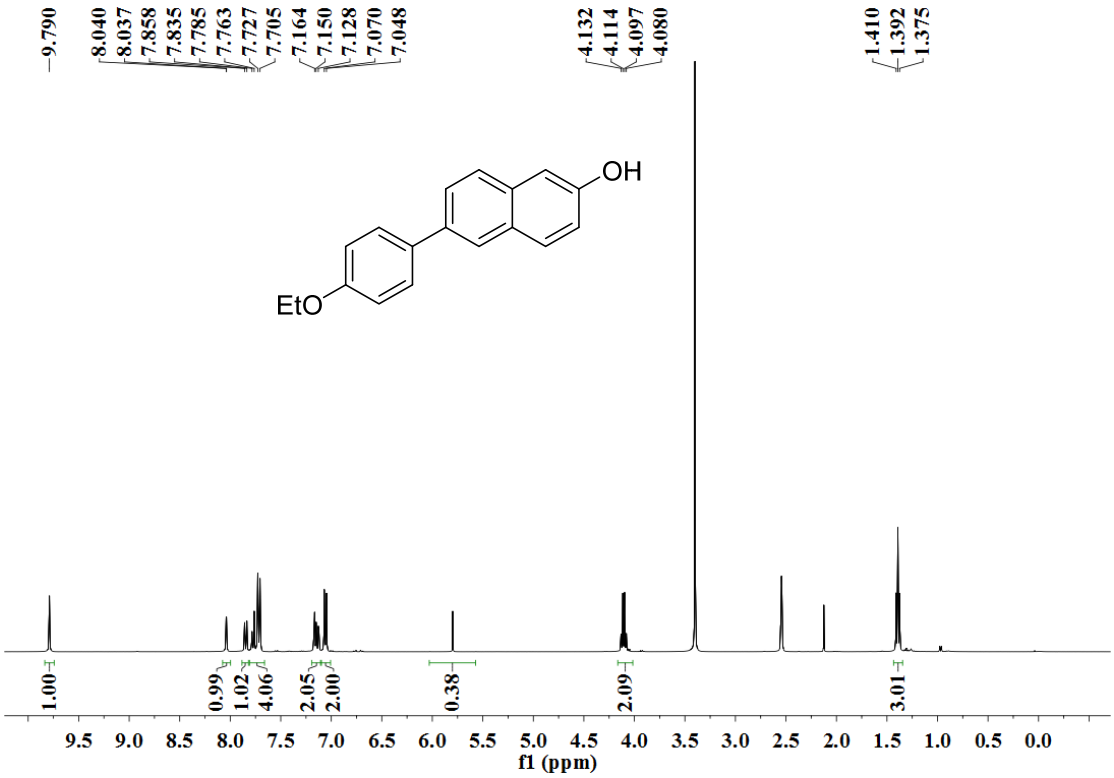
20
10
0
f1 (ppm)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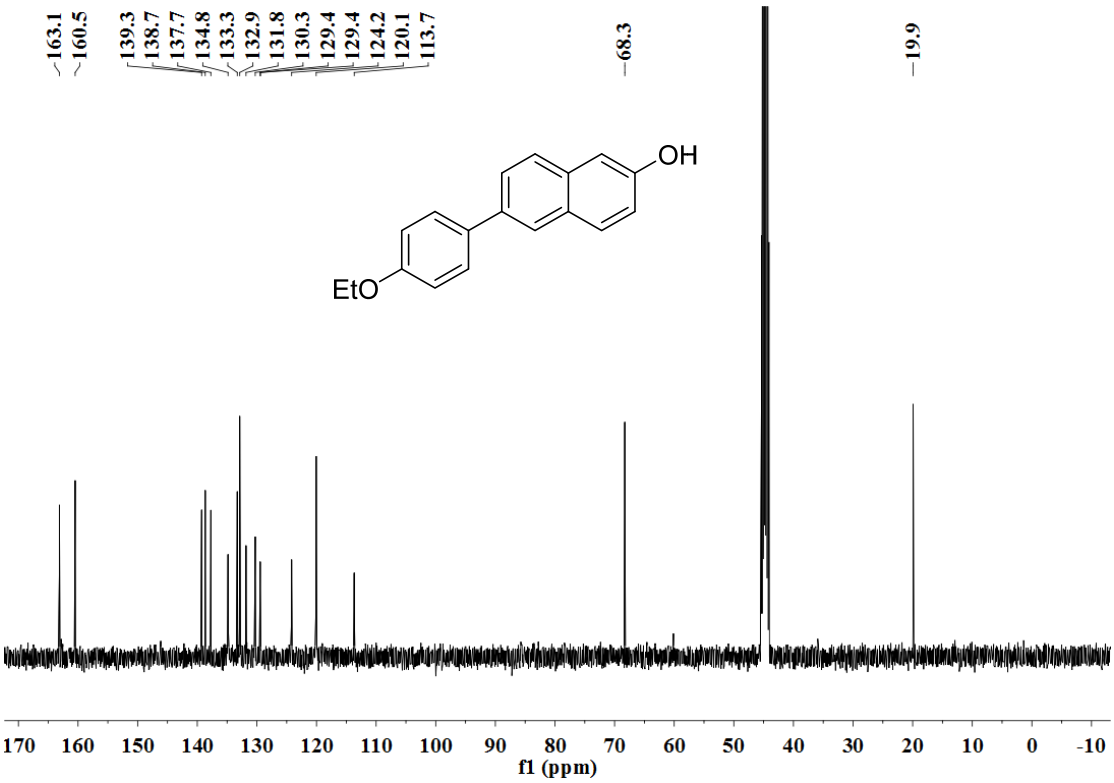
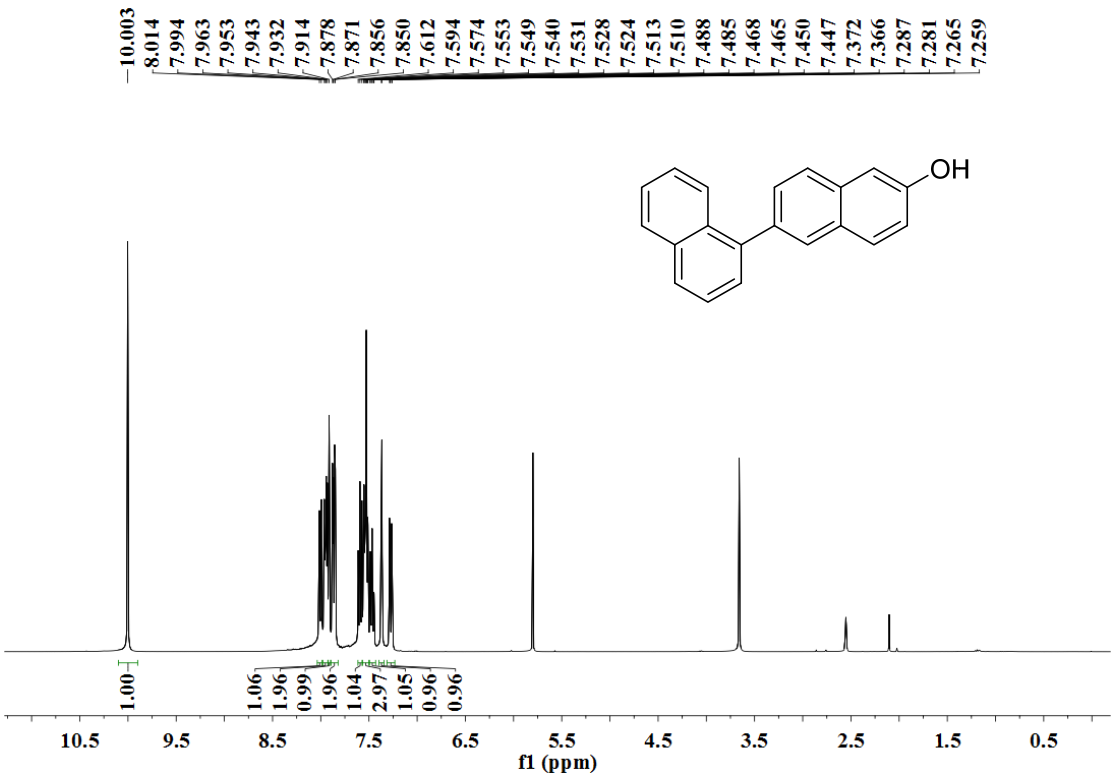
7.128
7.070
7.048
4.132
4.114
4.097
4.080
1.410
1.392
1.375
OH
EtO
1.00
0.99
1.02
4.06
2.05
2.00
0.38
2.09
3.01
f1 (ppm)


163.1
160.5
139.3
138.7
137.7
134.8
133.3
132.9
131.8
130.3
129.4
129.4
124.2
120.1
113.7
68.3
19.9
OH
EtO
f1 (ppm)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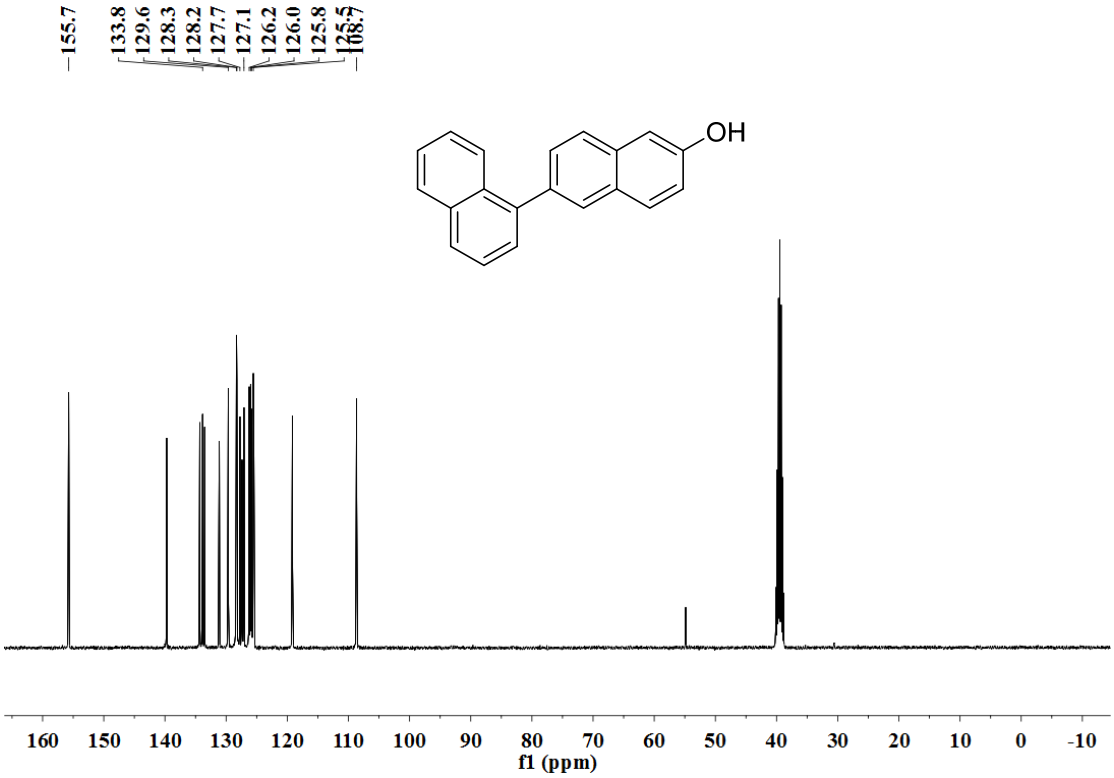
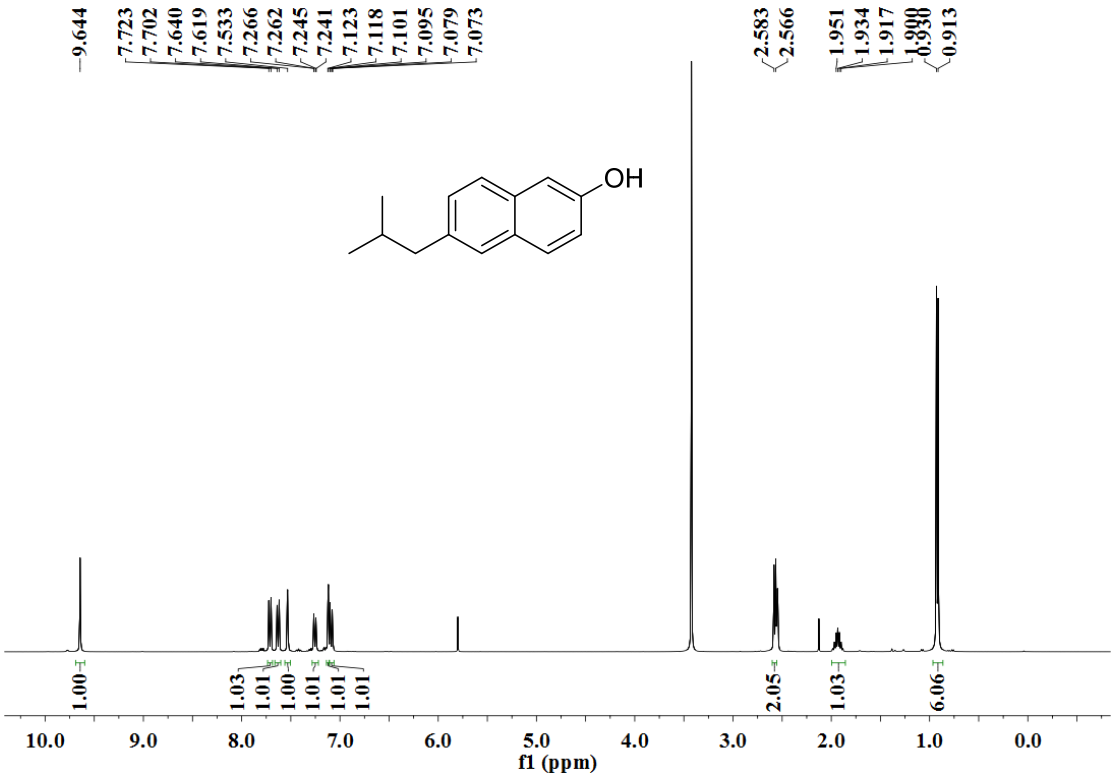
7.994
7.963
7.953
7.943
7.932
7.914
7.878
7.871
7.856
7.850
7.612
7.594
7.574
7.553
7.549
7.540
7.531
7.528
7.524
7.513
7.510
7.488
7.485
7.468
7.465
7.450
7.447
7.372
7.366
7.287
7.281
7.265
7.259
OH
1.00
1.06
1.96
0.99
1.96
1.04
2.97
1.05
0.96
0.96
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


155.7
133.8
129.6
128.3
128.2
127.7
127.1
126.2
126.0
125.8
125.5
108.7
OH
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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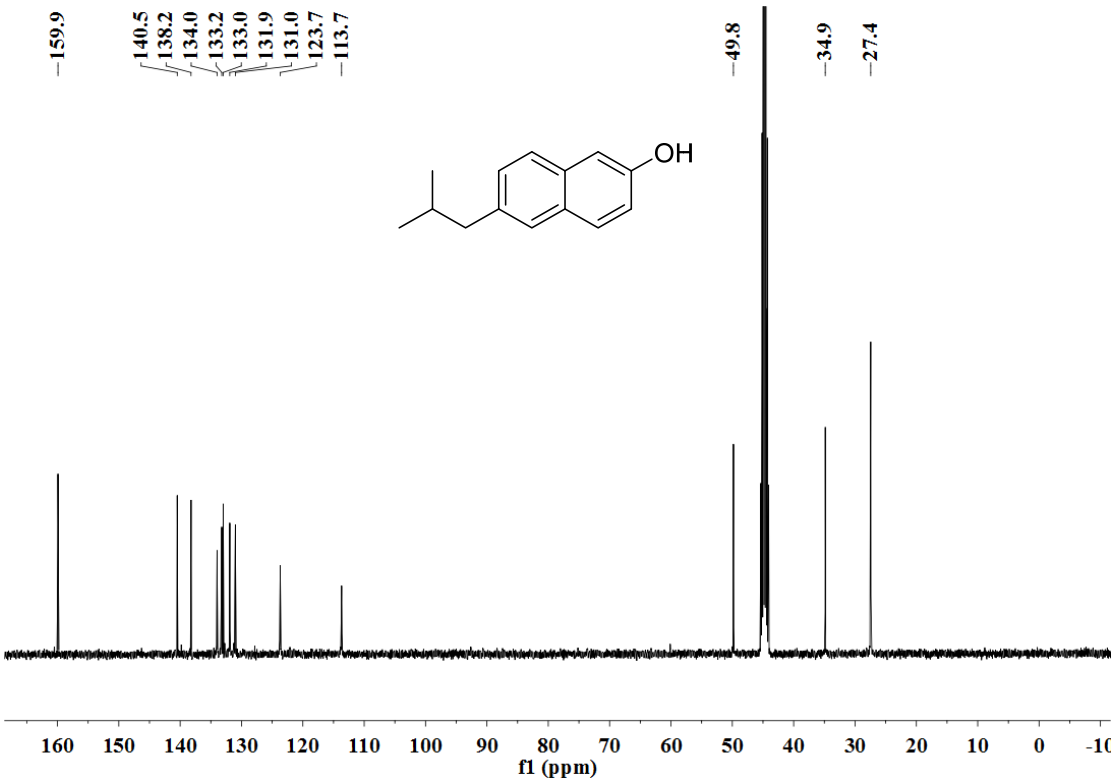
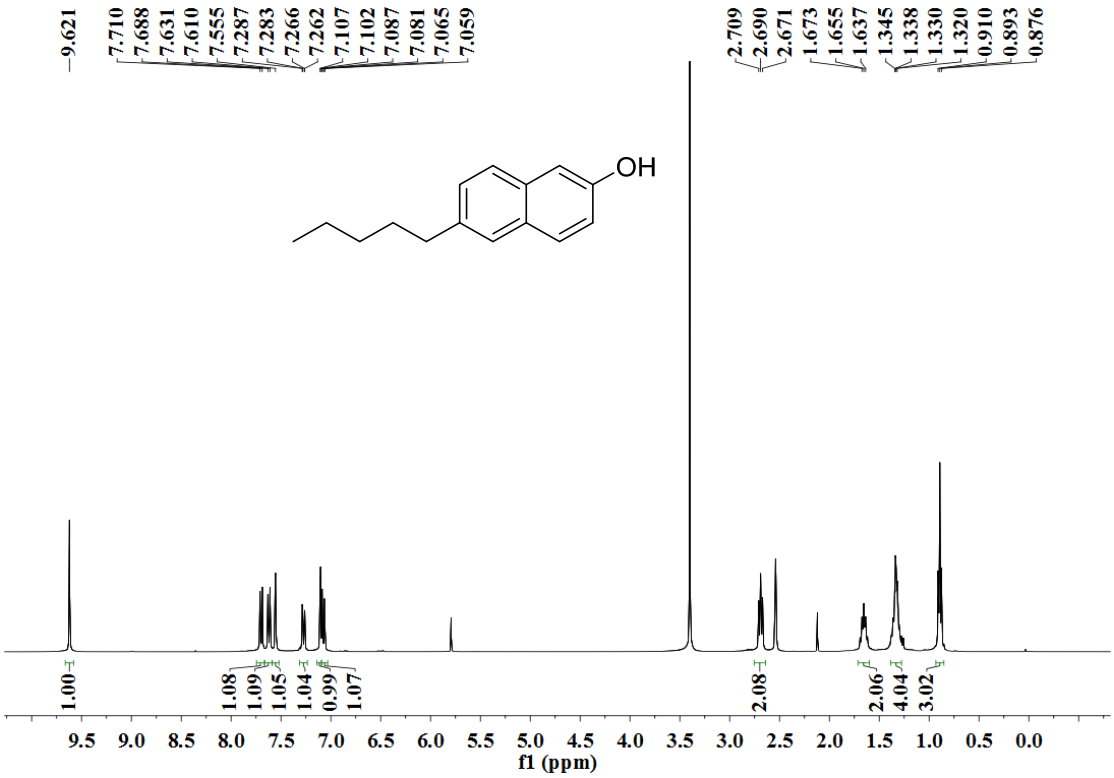
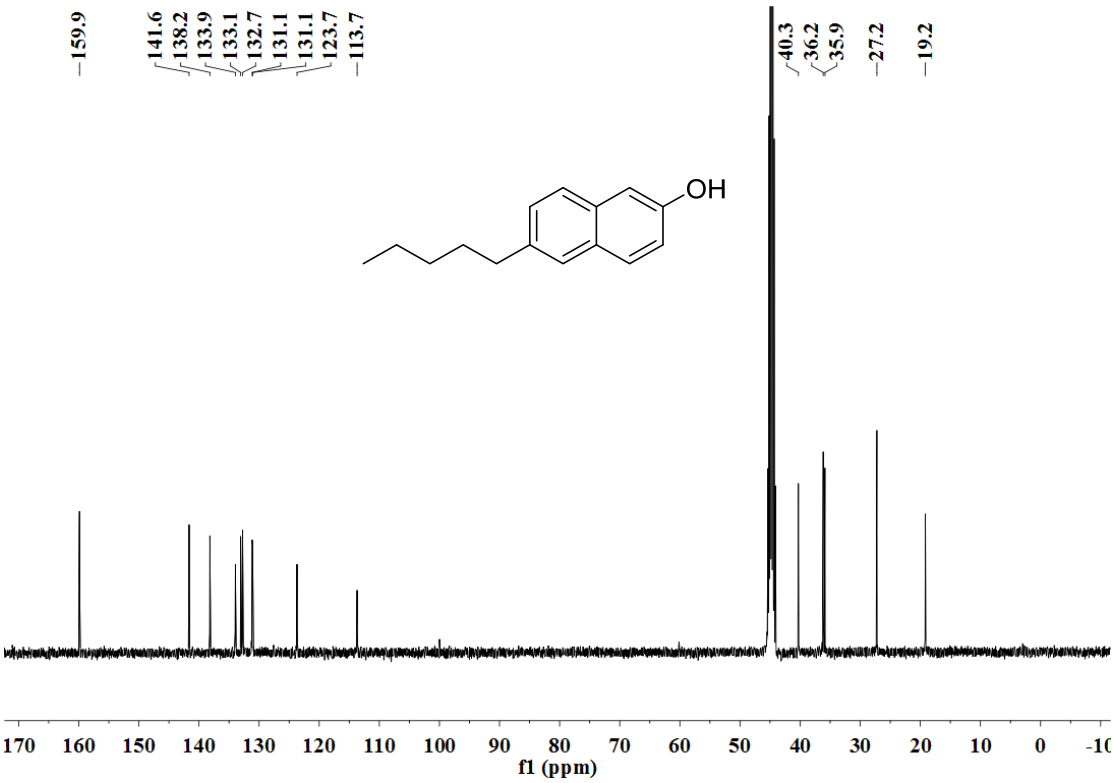
7.723
7.702
7.640
7.619
7.533
7.266
7.262
7.245
7.241
7.123
7.118
7.101
7.095
7.079
7.073
2.583
2.566
1.951
1.934
1.917
0.930
0.913
OH
1.00
1.03
1.01
1.00
1.01
1.01
1.01
2.05
1.03
6.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


159.9
140.5
138.2
134.0
133.2
133.0
131.9
131.0
123.7
113.7
49.8
34.9
27.4
OH
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.621
7.710
7.688
7.631
7.610
7.555
7.287
7.283
7.266
7.262
7.107
7.102
7.087
7.081
7.065
7.059
2.709
2.690
2.671
1.673
1.655
1.637
1.345
1.338
1.330
1.320
0.910
0.893
0.876
OH
1.00
1.08
1.09
1.05
1.04
0.99
1.07
2.08
2.06
4.04
3.02
f1 (ppm)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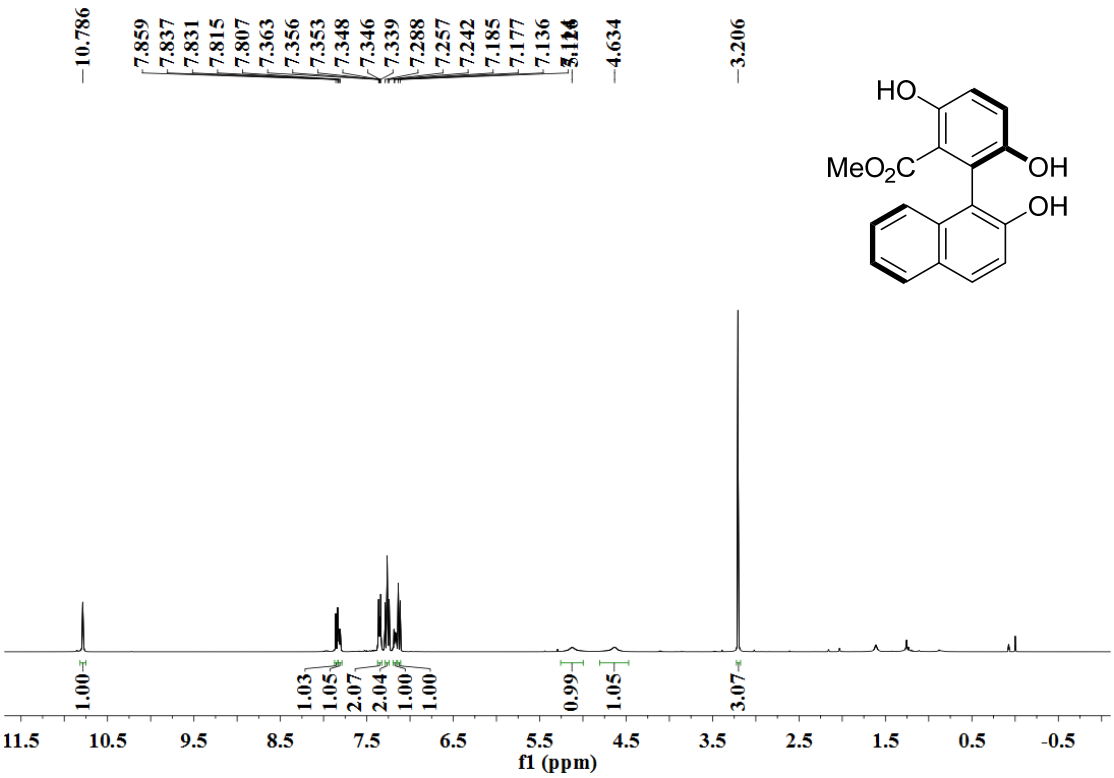
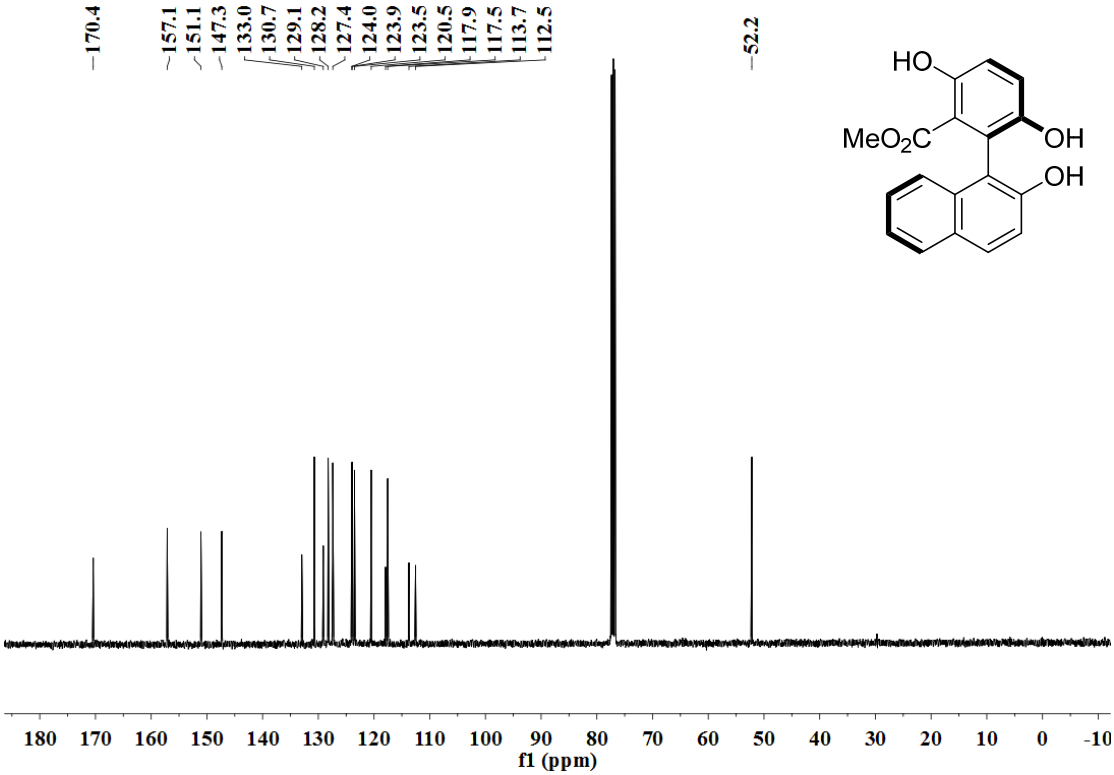
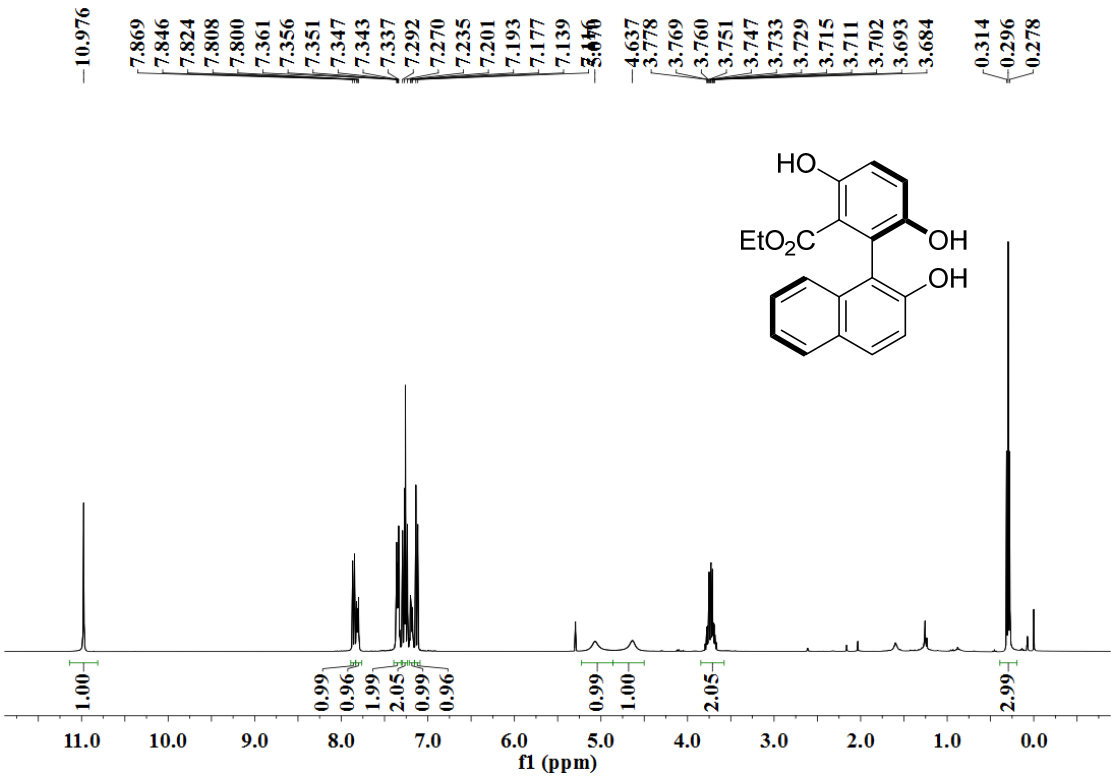
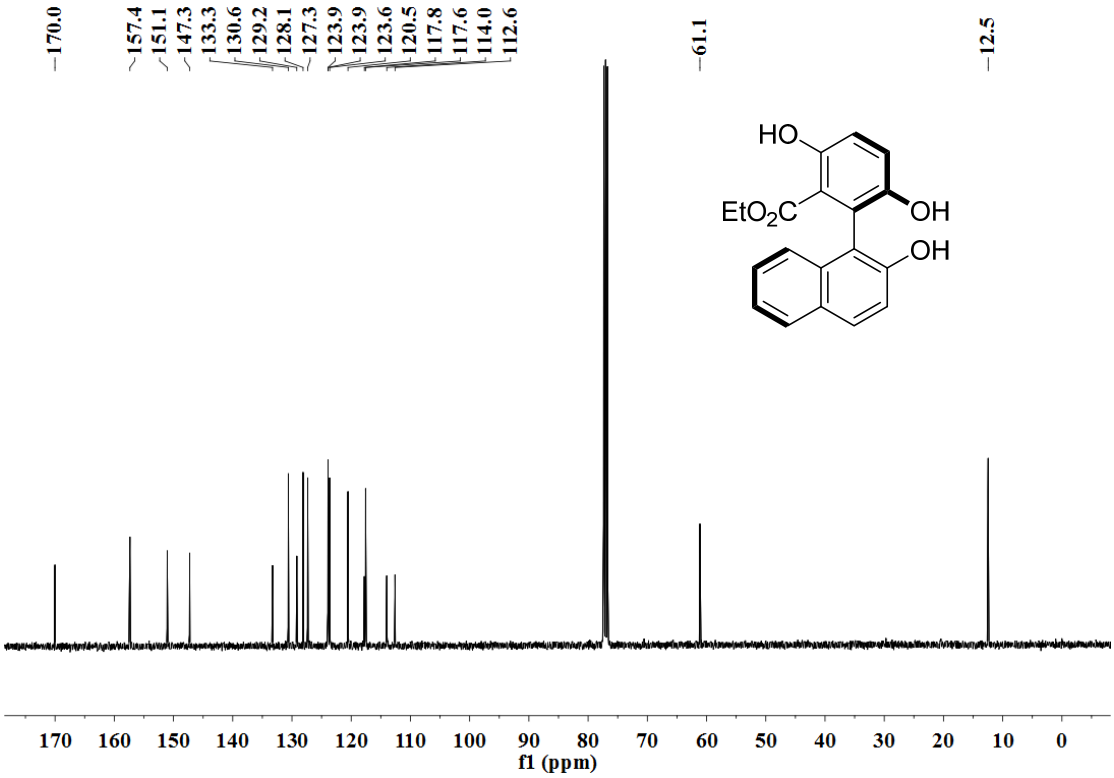
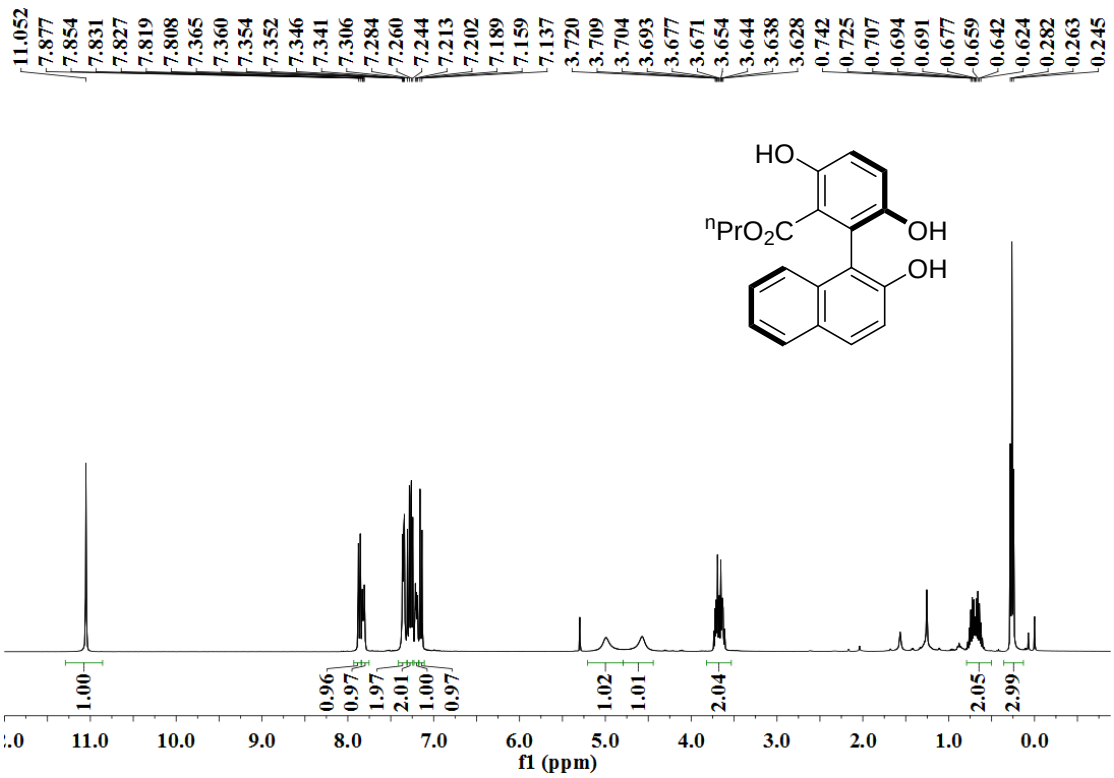
141.6
138.2
133.9
133.1
132.7
131.1
131.1
123.7
113.7
40.3
36.2
35.9
27.2
19.2
OH
f1 (ppm)


10.786
7.859
7.837
7.831
7.815
7.807
7.363
7.356
7.353
7.348
7.346
7.339
7.288
7.257
7.242
7.185
7.177
7.136
4.634
3.206
HO
MeO2C
OH
OH
1.00
1.03
1.05
2.07
2.04
1.00
1.00
0.99
1.05
3.07
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


170.4
157.1
151.1
147.3
133.0
130.7
129.1
128.2
127.4
124.0
123.9
123.5
120.5
117.9
117.5
113.7
112.5
52.2
HO
MeO2C
OH
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


10.976
7.869
7.846
7.824
7.808
7.800
7.361
7.356
7.351
7.347
7.343
7.337
7.292
7.270
7.235
7.201
7.193
7.177
7.139
4.637
3.778
3.769
3.760
3.751
3.747
3.733
3.729
3.715
3.711
3.702
3.693
3.684
0.314
0.296
0.278
HO
EtO2C
OH
OH
1.00
0.99
0.96
1.99
2.05
0.99
0.96
0.99
1.00
2.05
2.99
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


170.0
157.4
151.1
147.3
133.3
130.6
129.2
128.1
127.3
123.9
123.9
123.6
120.5
117.8
117.6
114.0
112.6
61.1
12.5
HO
EtO2C
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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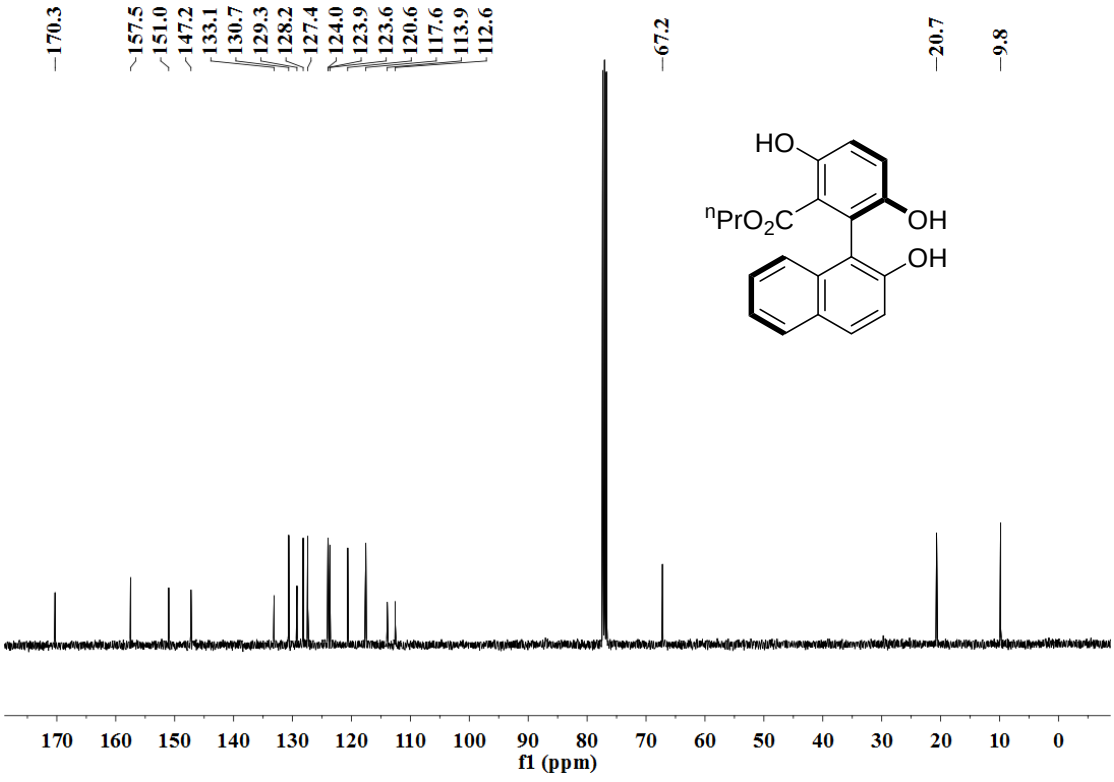
7.877
7.854
7.831
7.827
7.819
7.808
7.365
7.360
7.354
7.352
7.346
7.341
7.306
7.284
7.260
7.244
7.213
7.202
7.189
7.159
7.137
3.720
3.709
3.704
3.693
3.677
3.671
3.654
3.644
3.638
3.628
0.742
0.725
0.707
0.694
0.691
0.677
0.659
0.642
0.624
0.282
0.263
0.245
HO
nPrO2C
OH
OH
1.00
0.96
0.97
1.97
2.01
1.00
0.97
1.02
1.01
2.04
2.05
2.99
f1 (ppm)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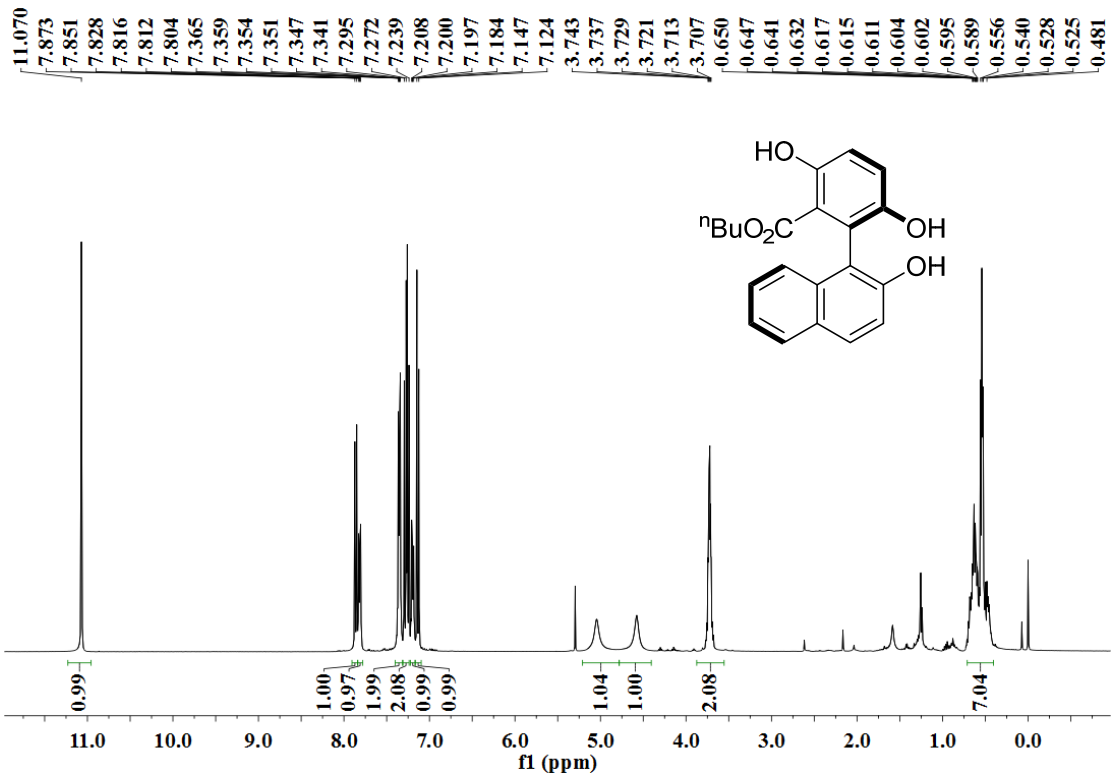
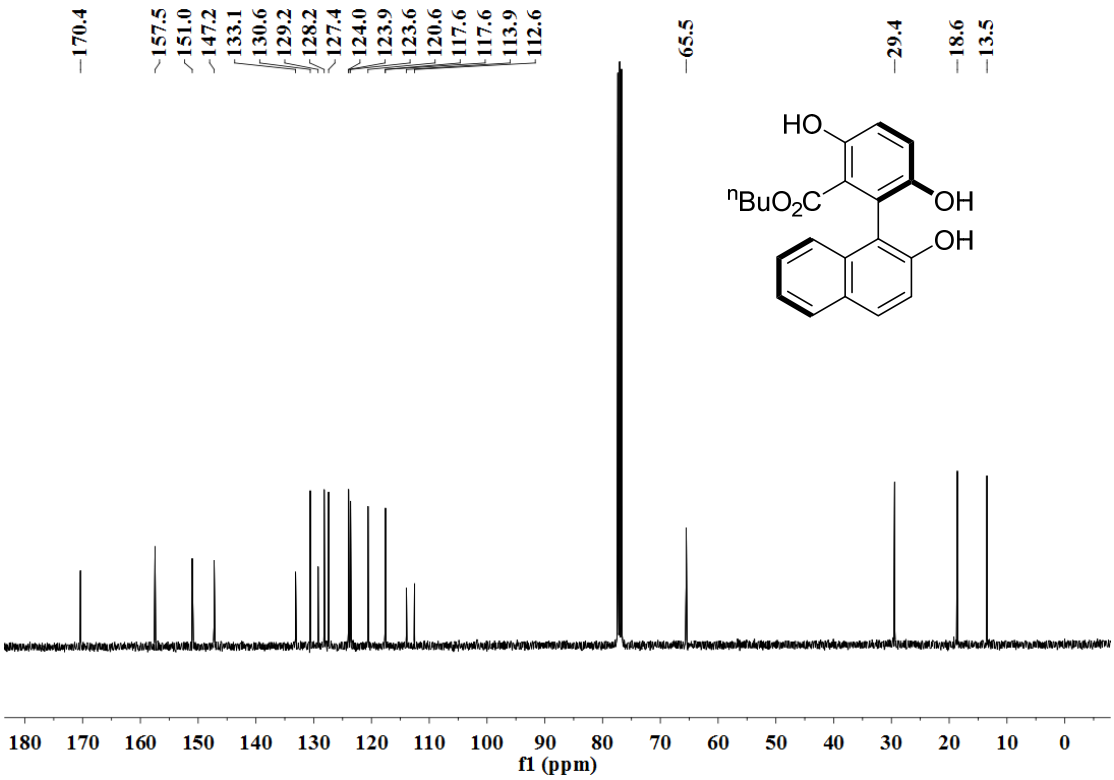
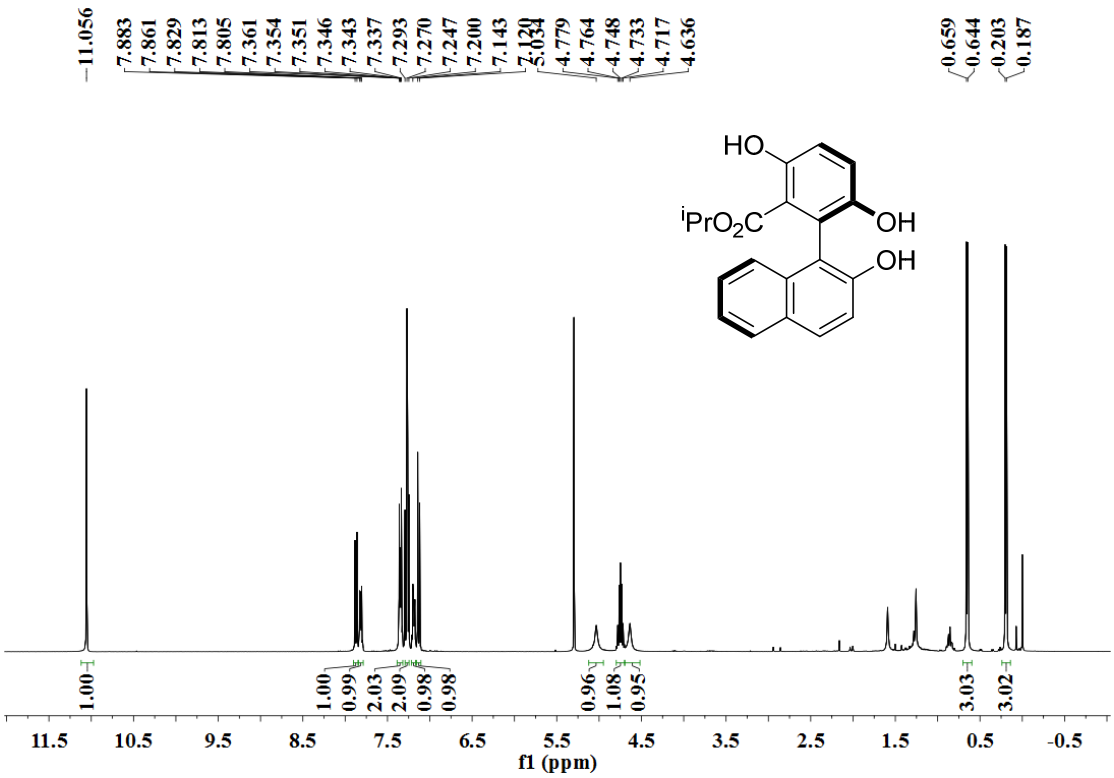
157.5
151.0
147.2
133.1
130.7
129.3
128.2
127.4
124.0
123.9
123.6
120.6
117.6
113.9
112.6
67.2
20.7
9.8
HO
nPrO2C
OH
OH
f1 (ppm)


11.070
7.873
7.851
7.828
7.816
7.812
7.804
7.365
7.359
7.354
7.351
7.347
7.341
7.295
7.272
7.239
7.208
7.200
7.197
7.184
7.147
7.124
3.743
3.737
3.729
3.721
3.713
3.707
0.650
0.647
0.641
0.632
0.617
0.615
0.611
0.604
0.602
0.595
0.589
0.556
0.540
0.528
0.525
0.481
HO
nBuO2C
OH
OH
0.99
1.00
0.97
1.99
2.08
0.99
0.99
1.04
1.00
2.08
7.04
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


170.4
157.5
151.0
147.2
133.1
130.6
129.2
128.2
127.4
124.0
123.9
123.6
120.6
117.6
117.6
113.9
112.6
65.5
29.4
18.6
13.5
HO
nBuO2C
OH
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.861
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7.813
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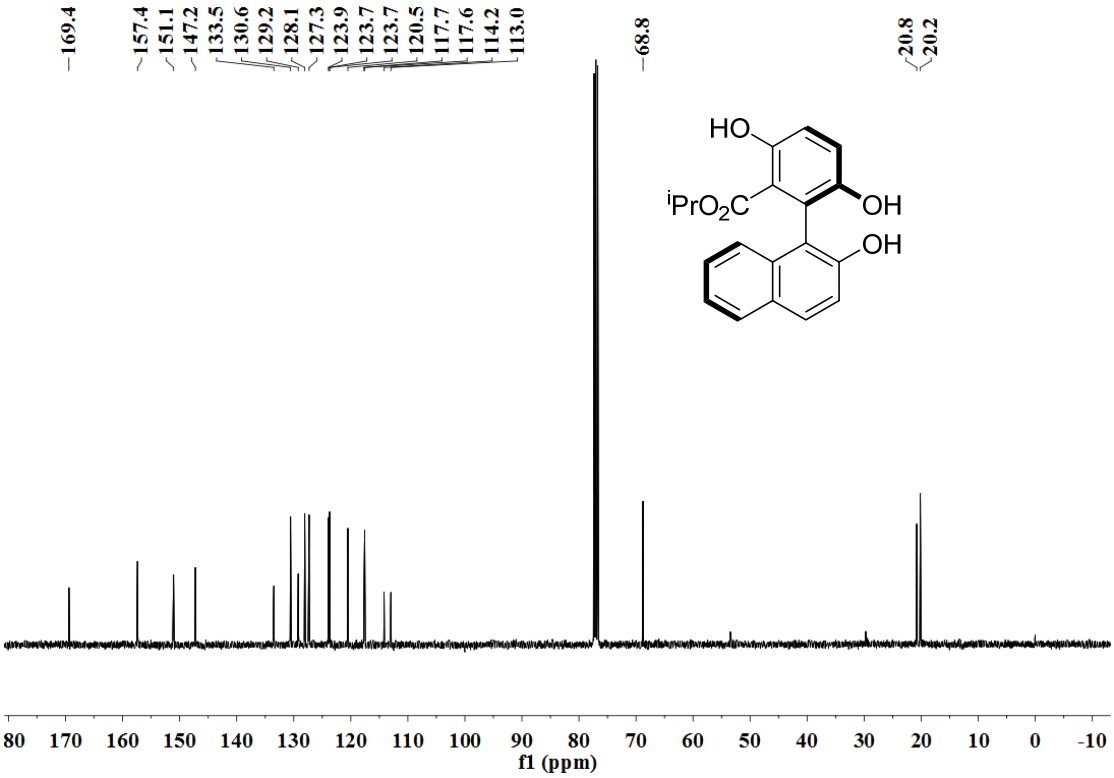
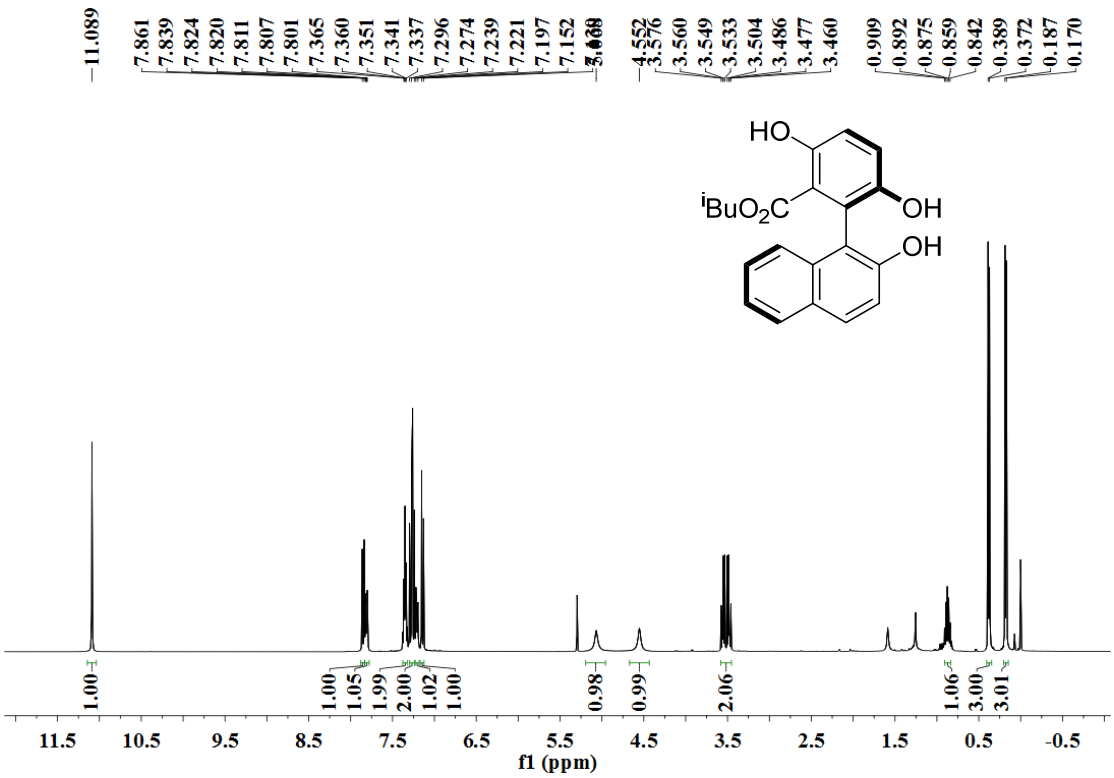
7.361
7.354
7.351
7.346
7.343
7.337
7.293
7.270
7.247
7.200
7.143
5.034
4.779
4.764
4.748
4.733
4.717
4.636
0.659
0.644
0.203
0.187
HO
iPrO2C
OH
OH
1.00
1.00
0.99
2.03
2.09
0.98
0.98
0.96
1.08
0.95
3.03
3.02
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


169.4
157.4
151.1
147.2
133.5
130.6
129.2
128.1
127.3
123.9
123.7
123.7
120.5
117.7
117.6
114.2
113.0
68.8
20.8
20.2
HO
iPrO2C
OH
OH
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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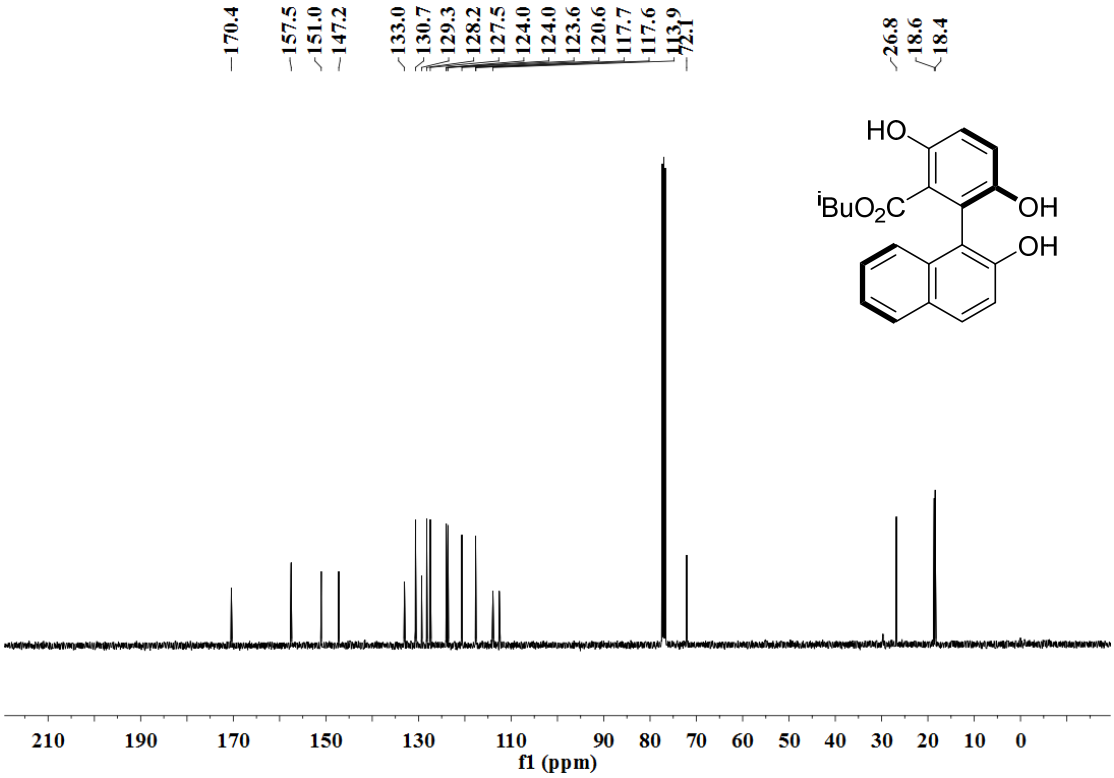
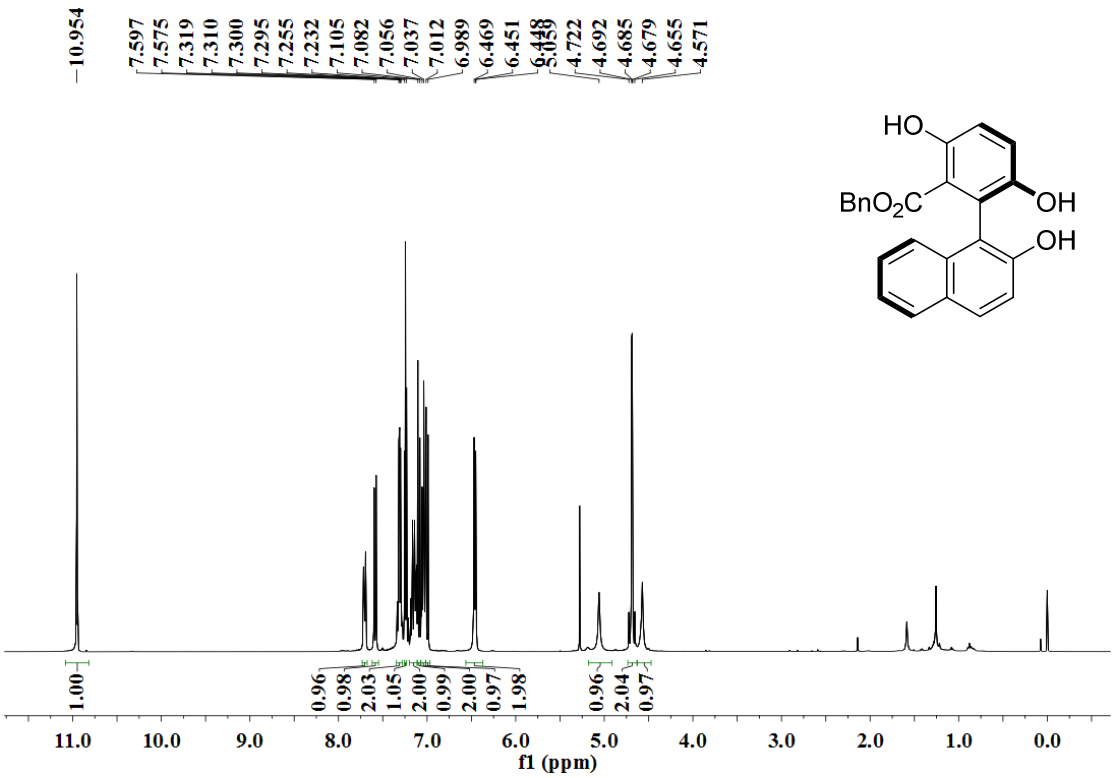
7.839
7.824
7.820
7.811
7.807
7.801
7.365
7.360
7.351
7.341
7.337
7.296
7.274
7.239
7.221
7.197
7.152
4.552
3.576
3.560
3.549
3.533
3.504
3.486
3.477
3.460
0.909
0.892
0.875
0.859
0.842
0.389
0.372
0.187
0.170
HO
iBuO2C
OH
OH
1.00
1.00
1.05
1.99
2.00
1.02
1.00
0.98
0.99
2.06
1.06
3.00
3.01
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


170.4
157.5
151.0
147.2
133.0
130.7
129.3
128.2
127.5
124.0
124.0
123.6
120.6
117.7
117.6
113.9
72.1
26.8
18.6
18.4
HO
iBuO2C
OH
OH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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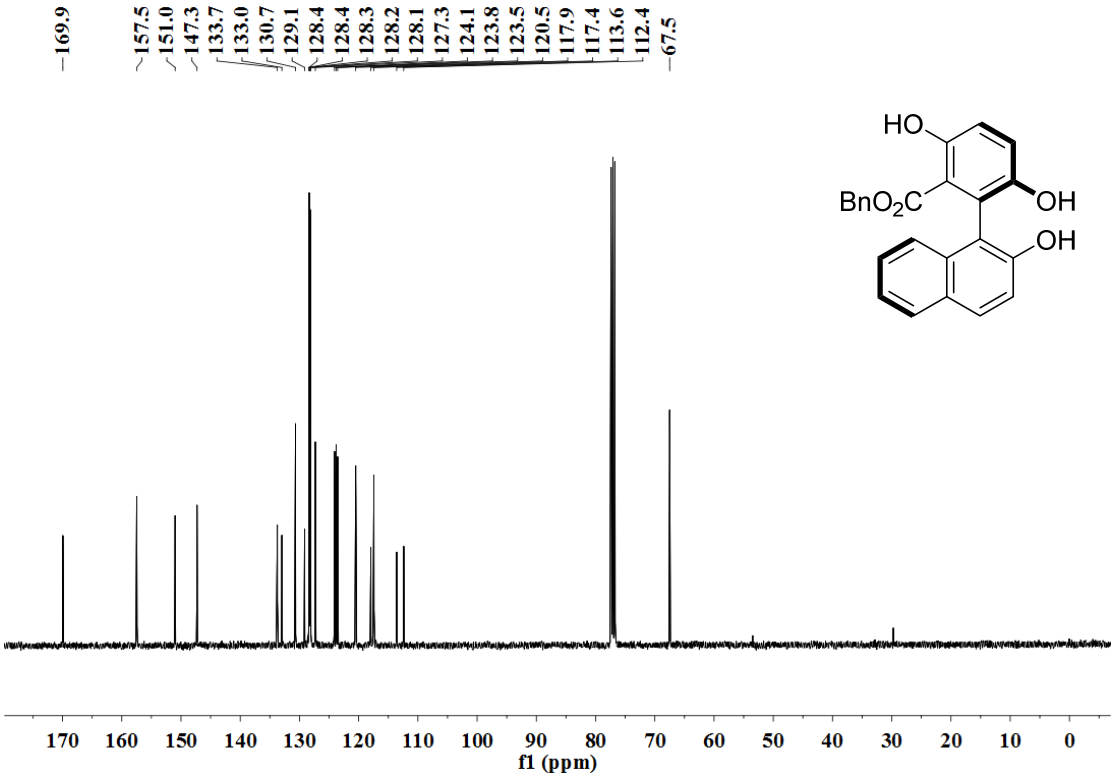
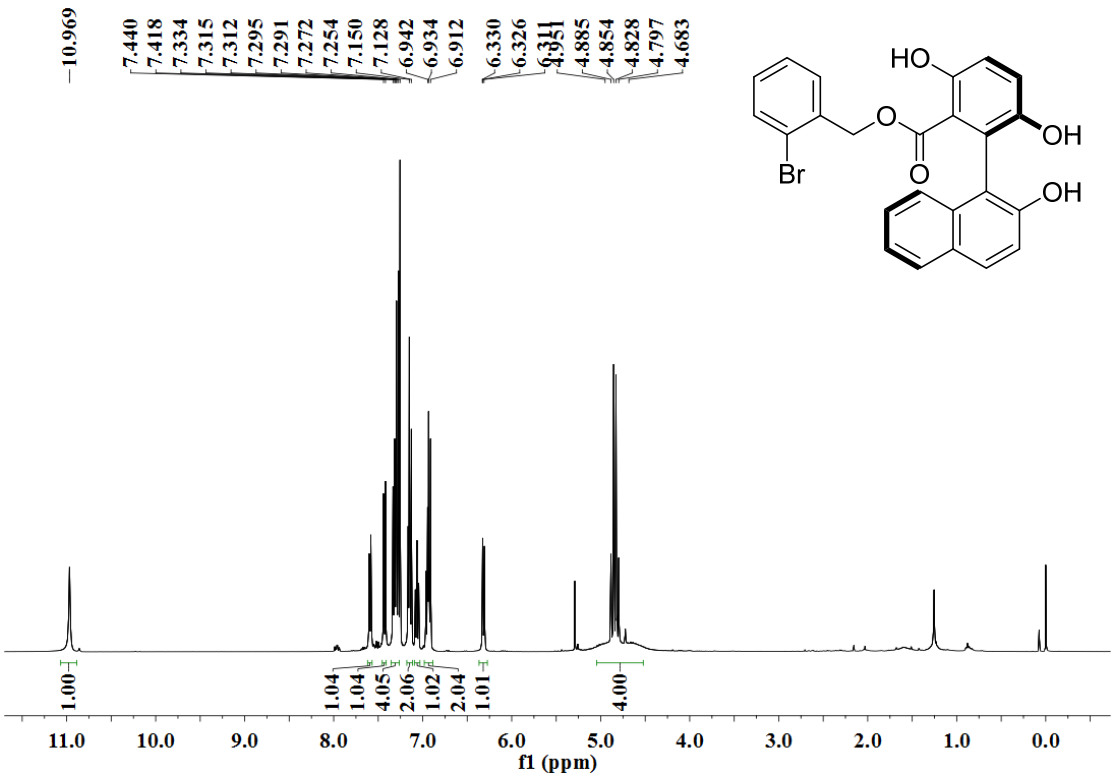
7.575
7.319
7.310
7.300
7.295
7.255
7.232
7.105
7.082
7.056
7.037
7.012
6.989
6.469
6.451
4.722
4.692
4.685
4.679
4.655
4.571
HO
BnO2C
OH
OH
1.00
0.96
0.98
2.03
1.05
2.00
0.99
2.00
0.97
1.98
0.96
2.04
0.97
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


169.9
157.5
151.0
147.3
133.7
133.0
130.7
129.1
128.4
128.4
128.3
128.2
128.1
127.3
124.1
123.8
123.5
120.5
117.9
117.4
113.6
112.4
67.5
HO
BnO2C
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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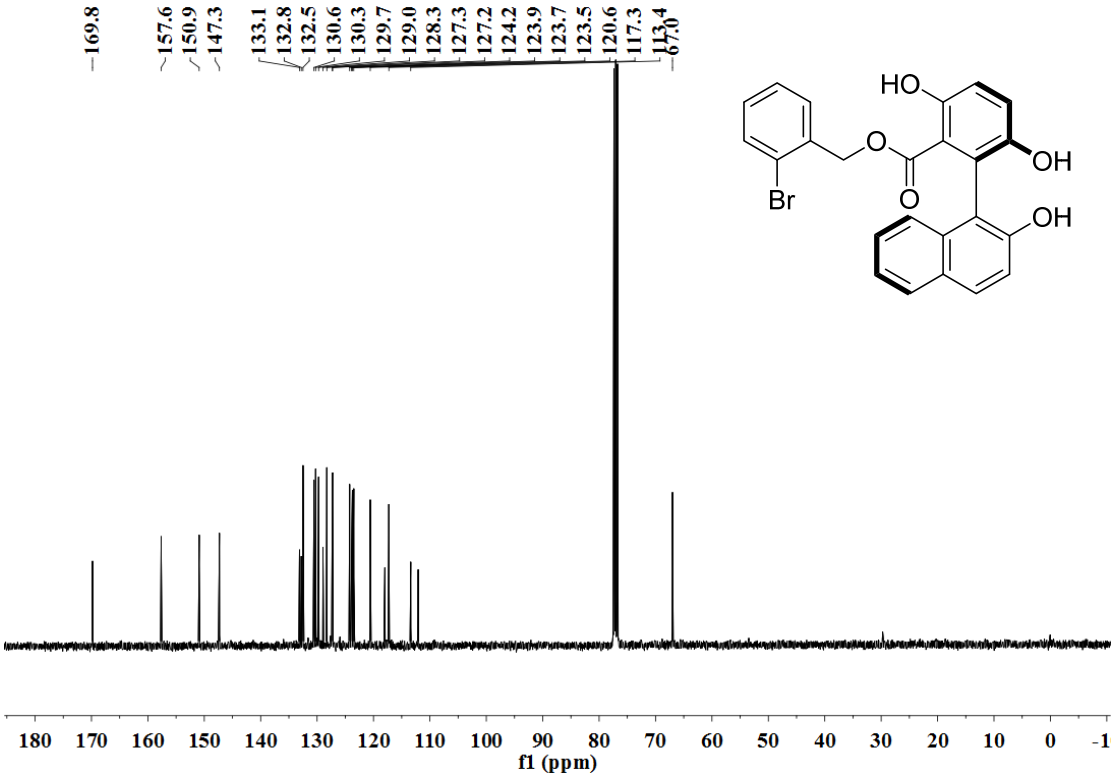
7.315
7.312
7.295
7.291
7.272
7.254
7.150
7.128
6.942
6.934
6.912
6.330
6.326
6.311
4.885
4.854
4.828
4.797
4.683
HO
OH
OH
O
O
Br
1.00
1.04
1.04
4.05
2.06
1.02
2.04
1.01
4.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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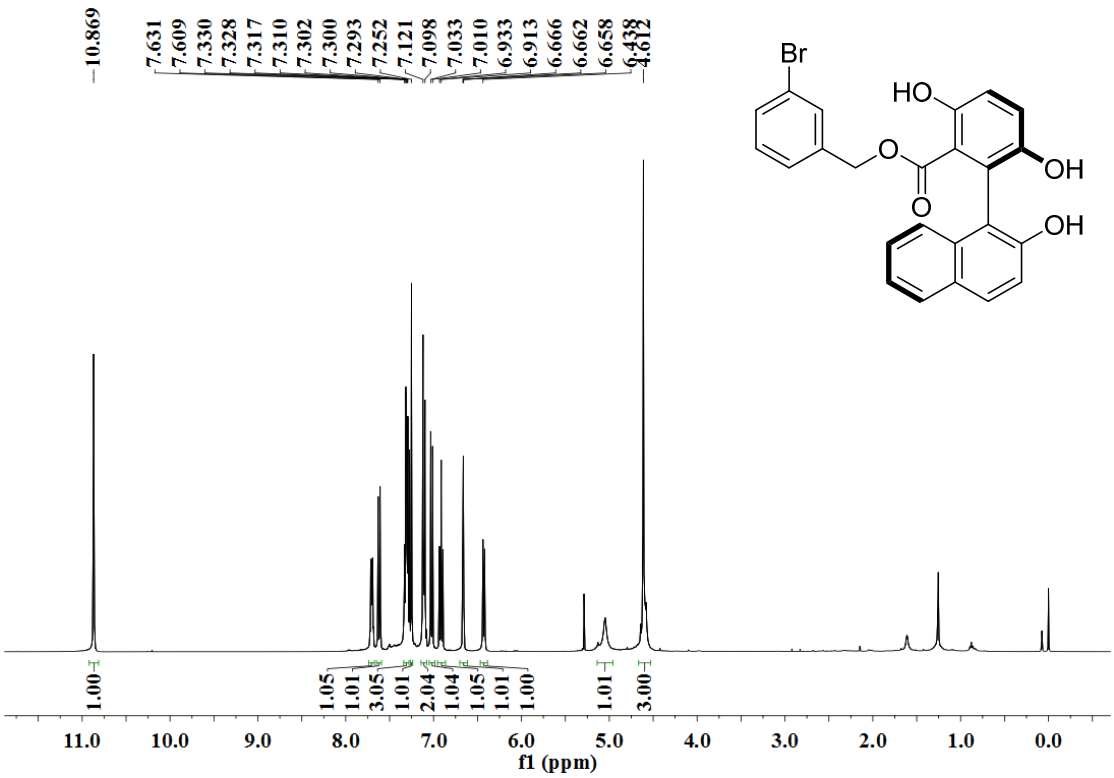
150.9
147.3
133.1
132.8
132.5
130.6
130.3
129.7
129.0
128.3
127.3
127.2
124.2
123.9
123.7
123.5
120.6
117.3
113.4
67.0
HO
OH
OH
O
O
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


10.869
7.631
7.609
7.330
7.328
7.317
7.310
7.302
7.300
7.293
7.252
7.121
7.098
7.033
7.010
6.933
6.913
6.666
6.662
6.658
6.438
4.612
Br
HO
O
O
OH
OH
1.00
1.05
1.01
3.05
1.01
2.04
1.04
1.05
1.01
1.00
1.01
3.00
11.0
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5.0
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3.0
2.0
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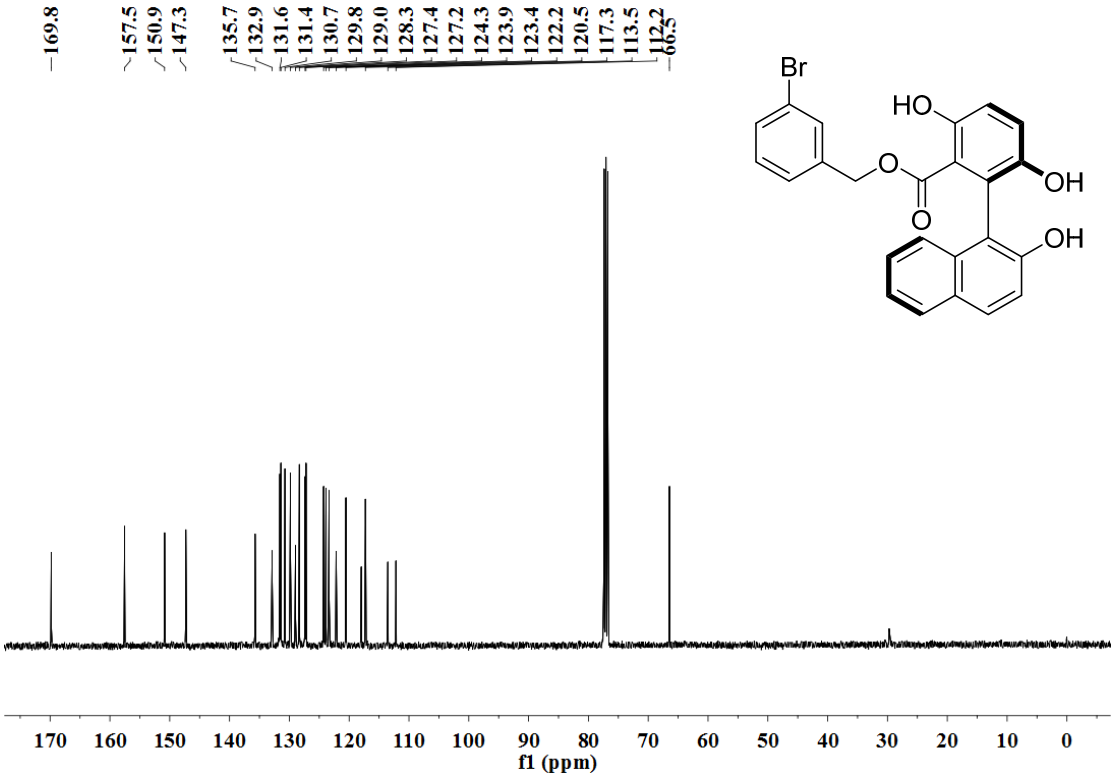
0.0
f1 (ppm)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150.9
147.3
135.7
132.9
131.6
131.4
130.7
129.8
129.0
128.3
127.4
127.2
124.3
123.9
123.4
122.2
120.5
117.3
113.5
112.2
66.5
Br
HO
O
O
OH
OH
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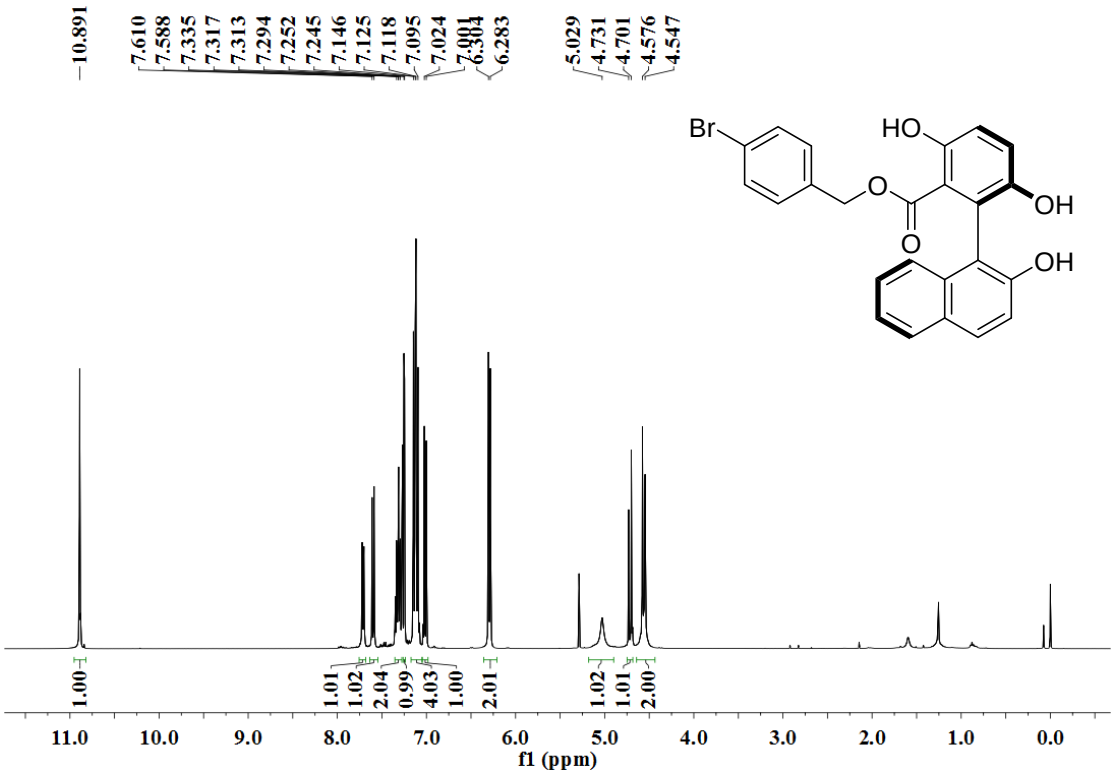
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.252
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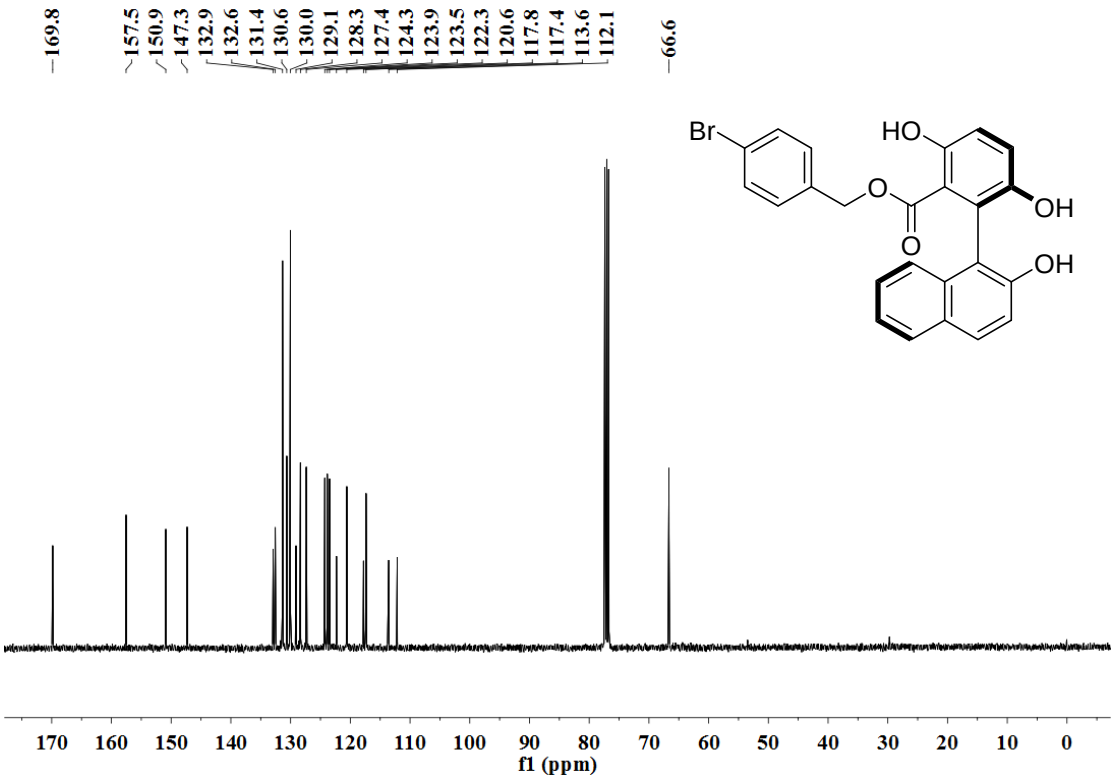
7.118
7.095
7.024
7.001
6.304
6.283
5.029
4.731
4.701
4.576
4.547
Br
HO
O
OH
O
OH
1.00
1.01
1.02
2.04
0.99
4.03
1.00
2.01
1.02
1.01
2.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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150.9
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130.6
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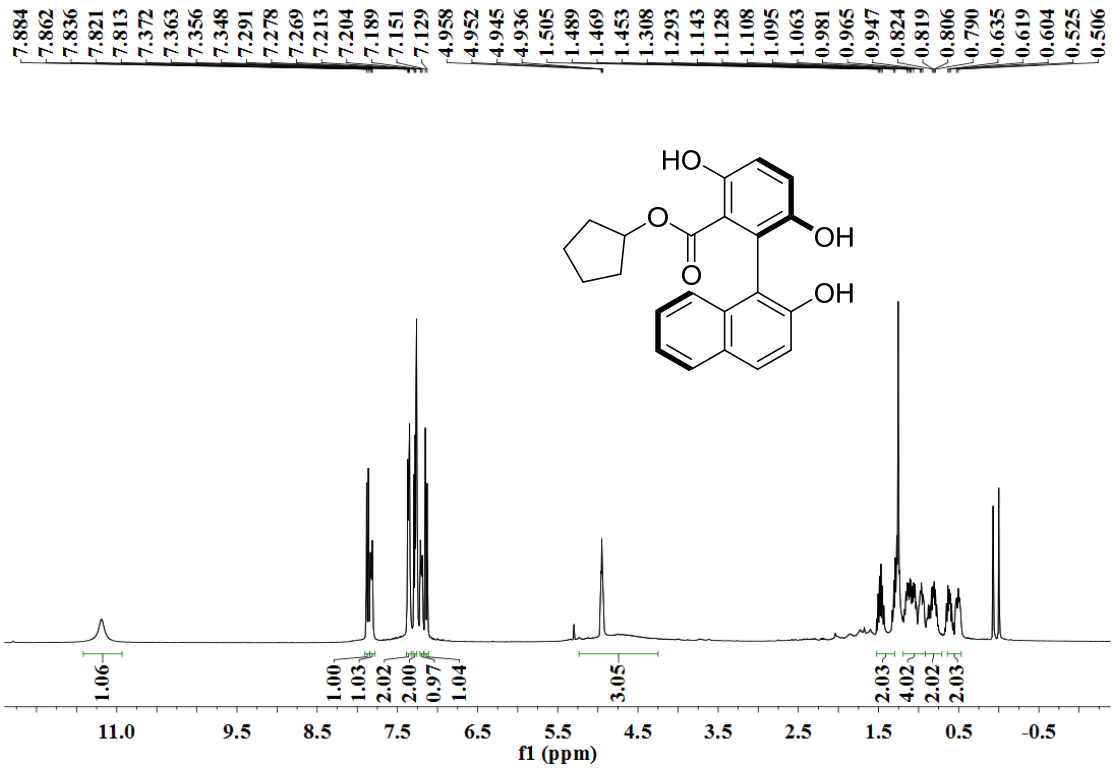
129.1
128.3
127.4
124.3
123.9
123.5
122.3
120.6
117.8
117.4
113.6
112.1
66.6
Br
HO
O
OH
O
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.813
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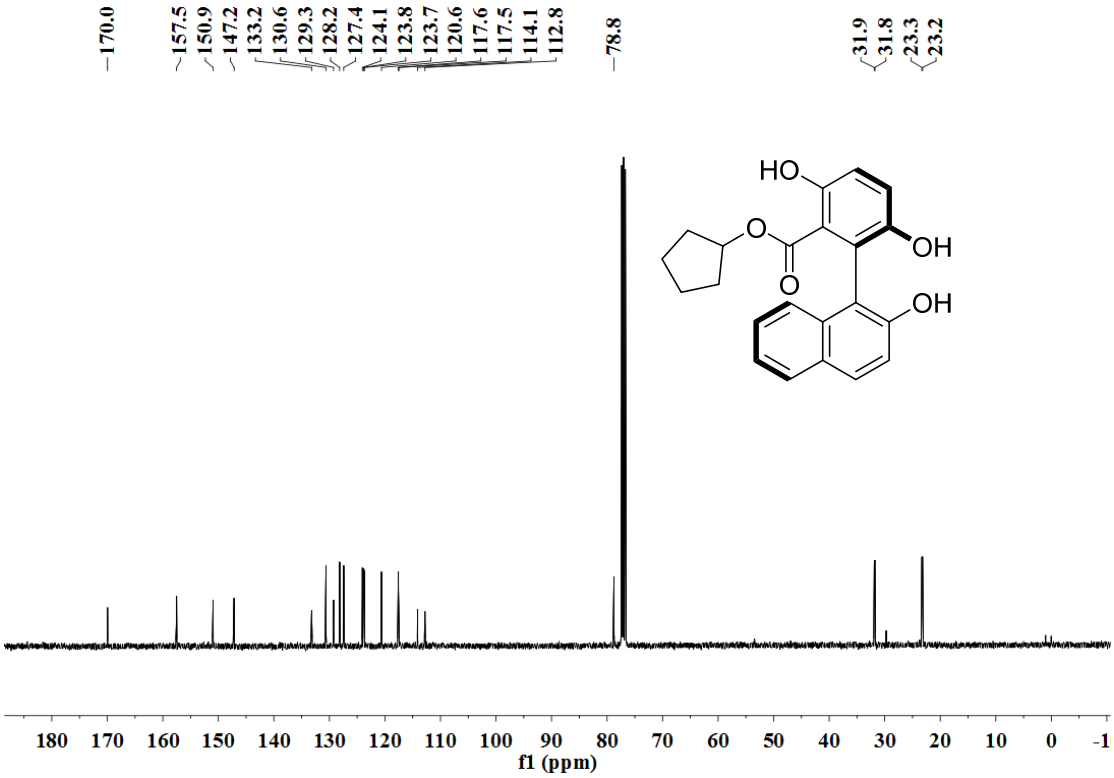
7.356
7.348
7.291
7.278
7.269
7.213
7.204
7.189
7.151
7.129
4.958
4.952
4.945
4.936
1.505
1.489
1.469
1.453
1.308
1.293
1.143
1.128
1.108
1.095
1.063
0.981
0.965
0.947
0.824
0.819
0.806
0.790
0.635
0.619
0.604
0.525
0.506
HO
O
O
OH
OH
1.06
1.00
1.03
2.02
2.00
0.97
1.04
3.05
2.03
4.02
2.02
2.03
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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150.9
147.2
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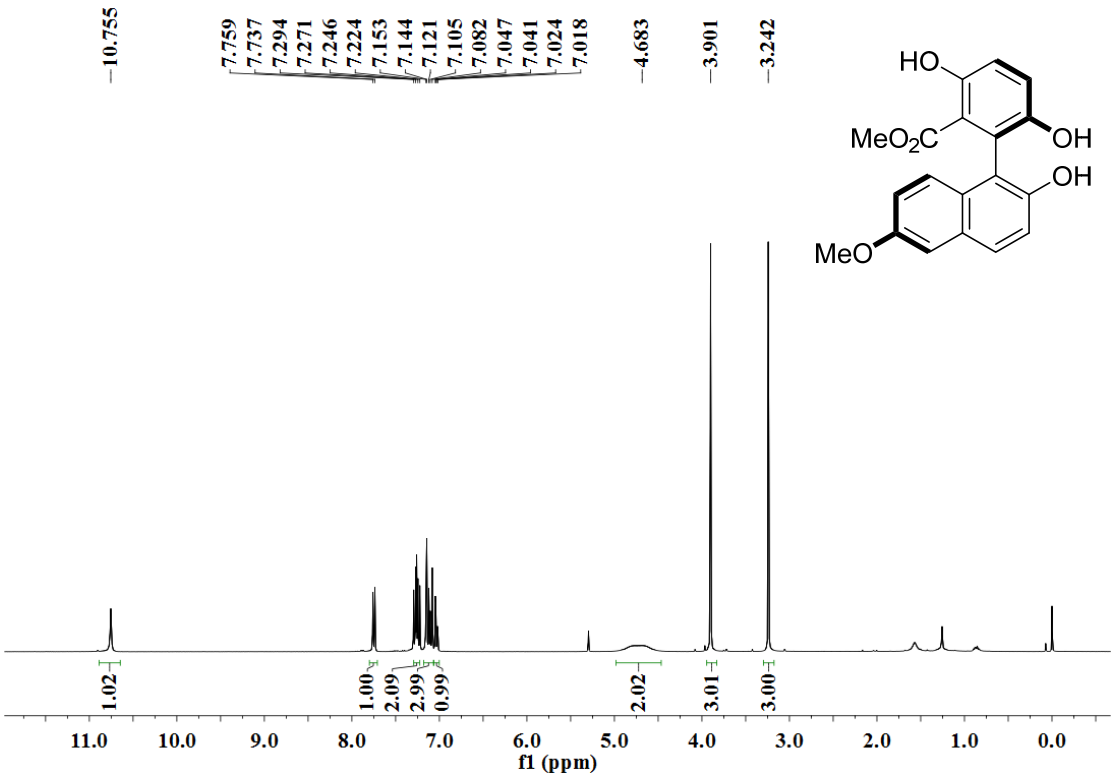
130.6
129.3
128.2
127.4
124.1
123.8
123.7
120.6
117.6
117.5
114.1
112.8
78.8
31.9
31.8
23.3
23.2
HO
O
O
OH
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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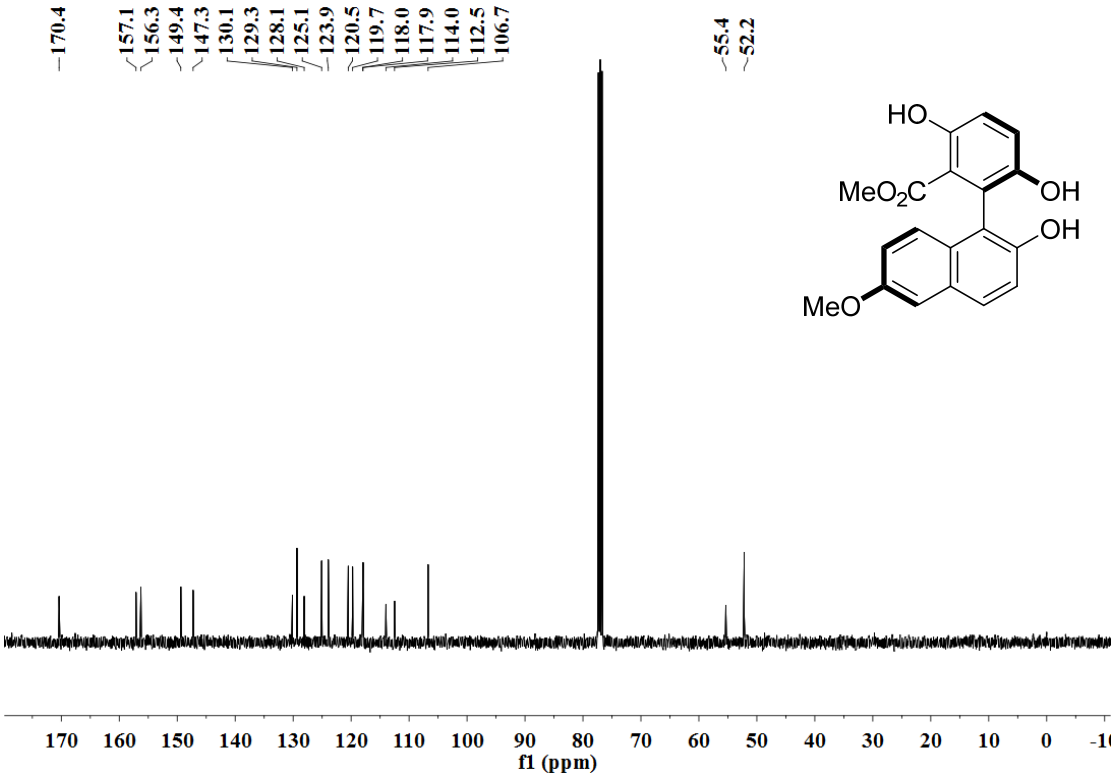
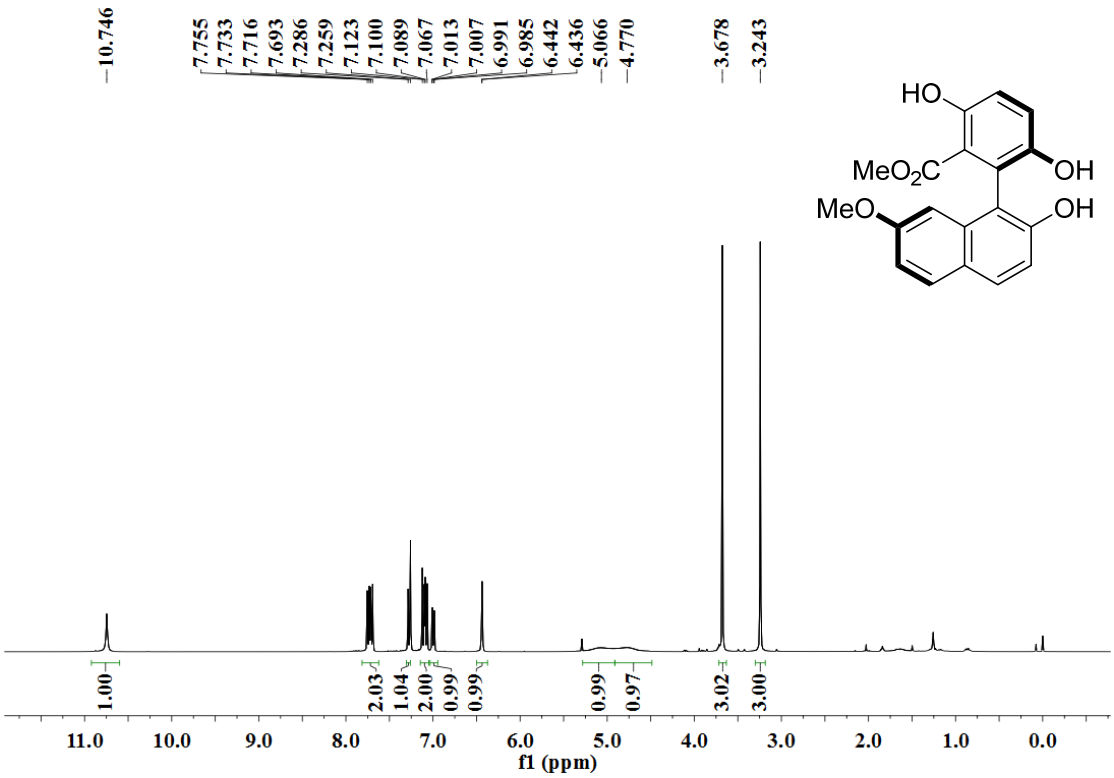
7.759
7.737
7.294
7.271
7.246
7.224
7.153
7.144
7.121
7.105
7.082
7.047
7.041
7.024
7.018
4.683
3.901
3.242
HO
MeO2C
OH
OH
MeO
1.02
1.00
2.09
2.99
0.99
2.02
3.01
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


170.4
157.1
156.3
149.4
147.3
130.1
129.3
128.1
125.1
123.9
120.5
119.7
118.0
117.9
114.0
112.5
106.7
55.4
52.2
HO
MeO2C
OH
OH
MeO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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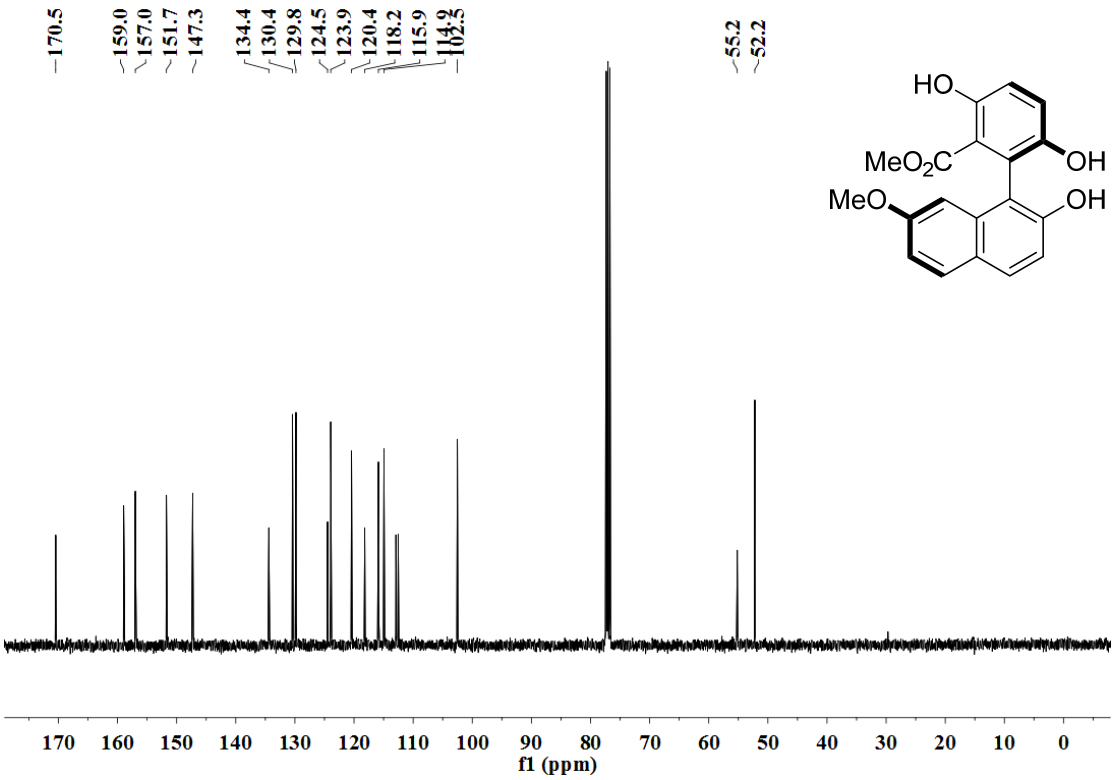
7.733
7.716
7.693
7.286
7.259
7.123
7.100
7.089
7.067
7.013
7.007
6.991
6.985
6.442
6.436
5.066
4.770
3.678
3.243
HO
MeO2C
OH
MeO
OH
1.00
2.03
1.04
2.00
0.99
0.99
0.99
0.97
3.02
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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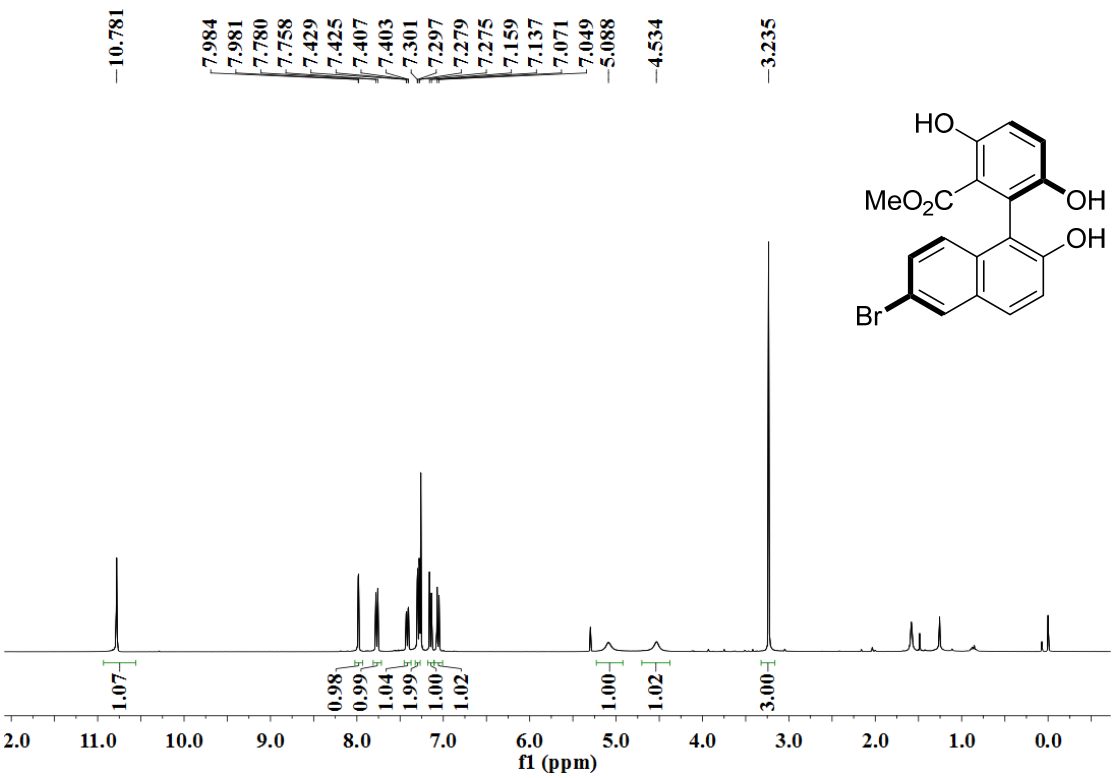
159.0
157.0
151.7
147.3
134.4
130.4
129.8
124.5
123.9
120.4
118.2
115.9
55.2
52.2
HO
MeO2C
OH
MeO
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.981
7.780
7.758
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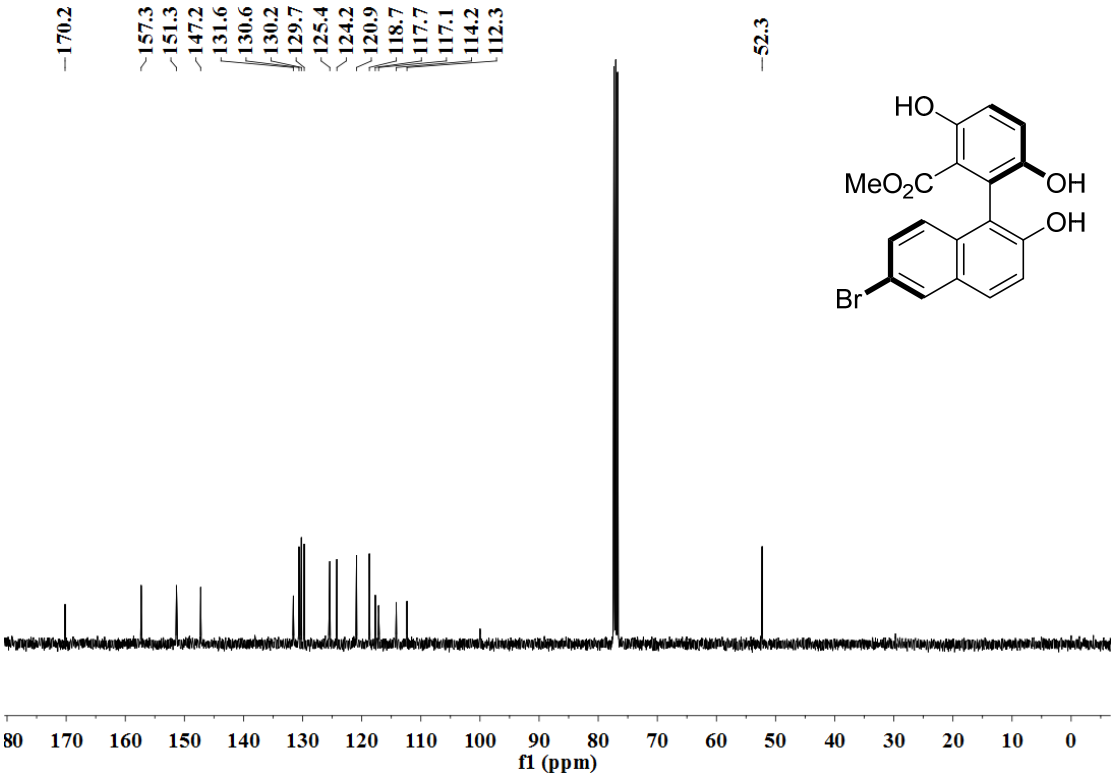
7.425
7.407
7.403
7.301
7.297
7.279
7.275
7.159
7.137
7.071
7.049
5.088
4.534
3.235
HO
MeO2C
OH
OH
Br
1.07
0.98
0.99
1.04
1.99
1.00
1.02
1.00
1.02
3.00
f1 (ppm)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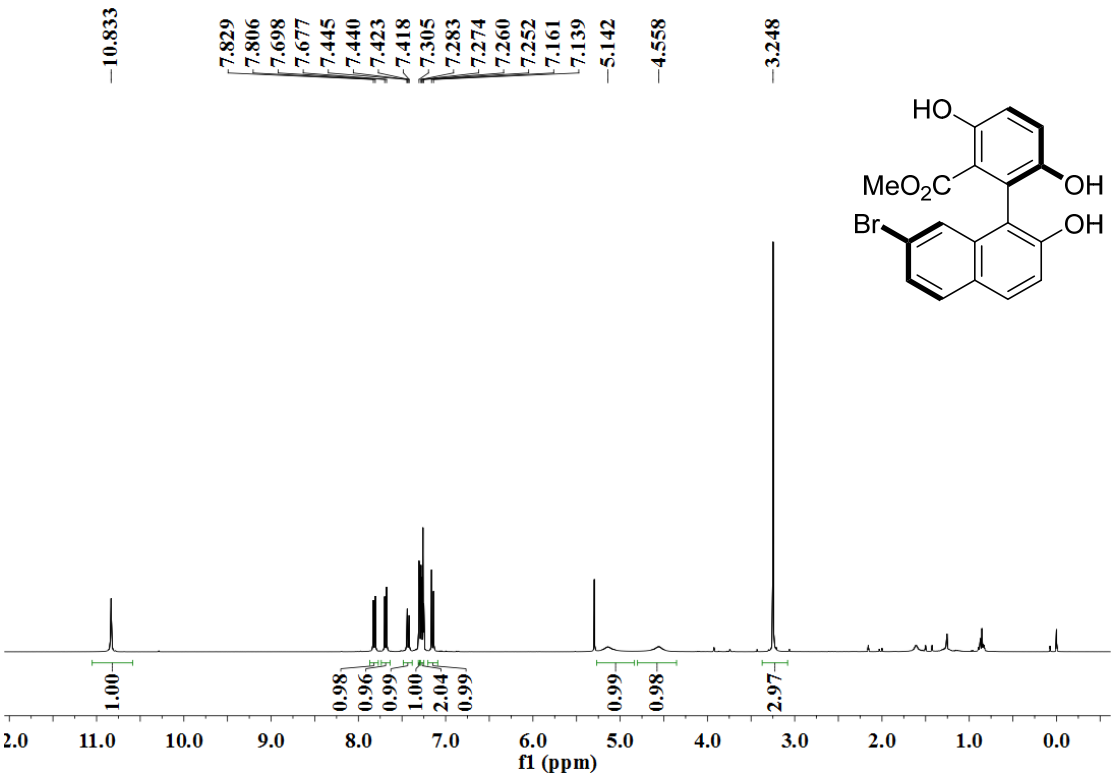
157.3
151.3
147.2
131.6
130.6
130.2
129.7
125.4
124.2
120.9
118.7
117.7
117.1
114.2
112.3
52.3
HO
MeO2C
OH
OH
Br
f1 (ppm)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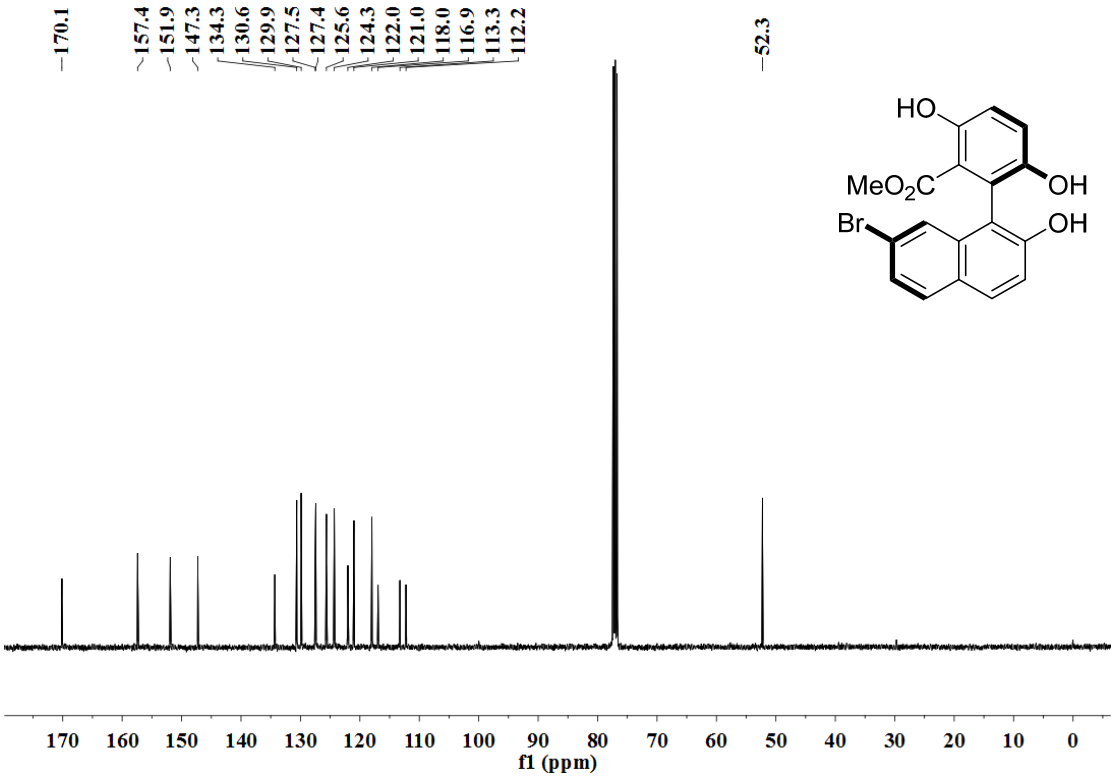
7.829
7.806
7.698
7.677
7.445
7.440
7.423
7.418
7.305
7.283
7.274
7.260
7.252
7.161
7.139
5.142
4.558
3.248
HO
MeO2C
OH
Br
OH
1.00
0.98
0.96
0.99
1.00
2.04
0.99
0.99
0.98
2.97
f1 (ppm)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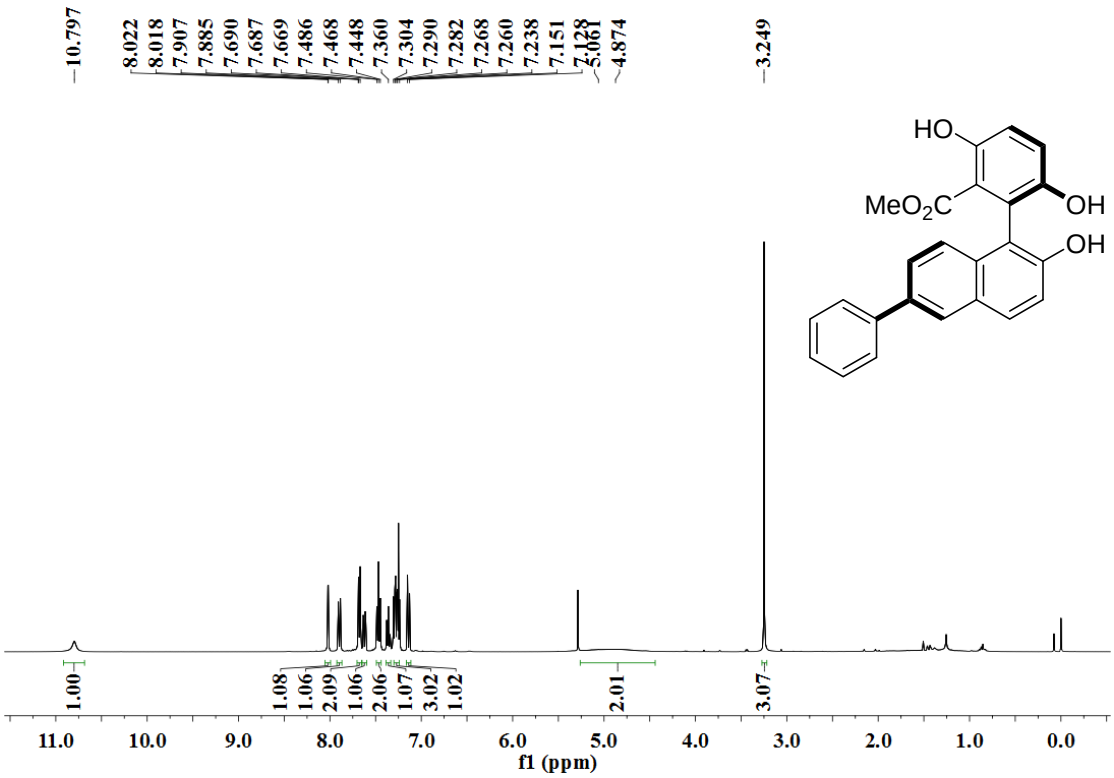
157.4
151.9
147.3
134.3
130.6
129.9
127.5
127.4
125.6
124.3
122.0
121.0
118.0
116.9
113.3
112.2
52.3
HO
MeO2C
OH
Br
OH
f1 (ppm)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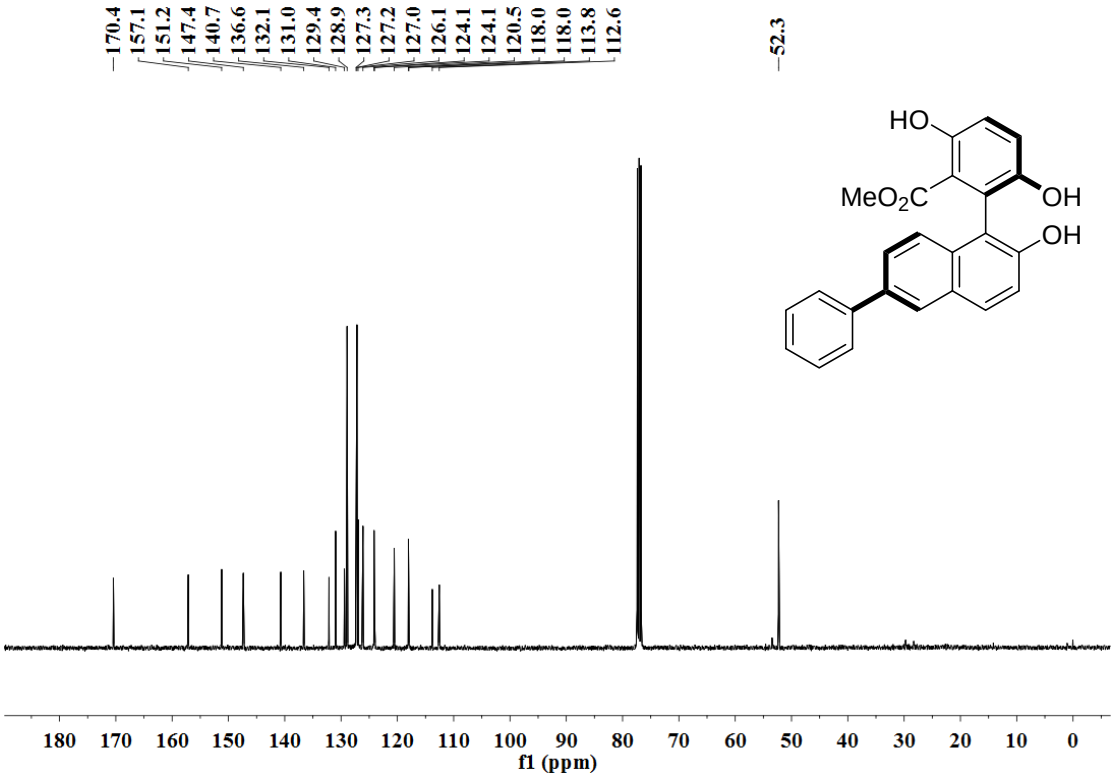
8.018
7.907
7.885
7.690
7.687
7.669
7.486
7.468
7.448
7.360
7.304
7.290
7.282
7.268
7.260
7.238
7.151
7.128
5.061
4.874
3.249
HO
MeO2C
OH
OH
1.00
1.08
1.06
2.09
1.06
2.06
1.07
3.02
1.02
2.01
3.07
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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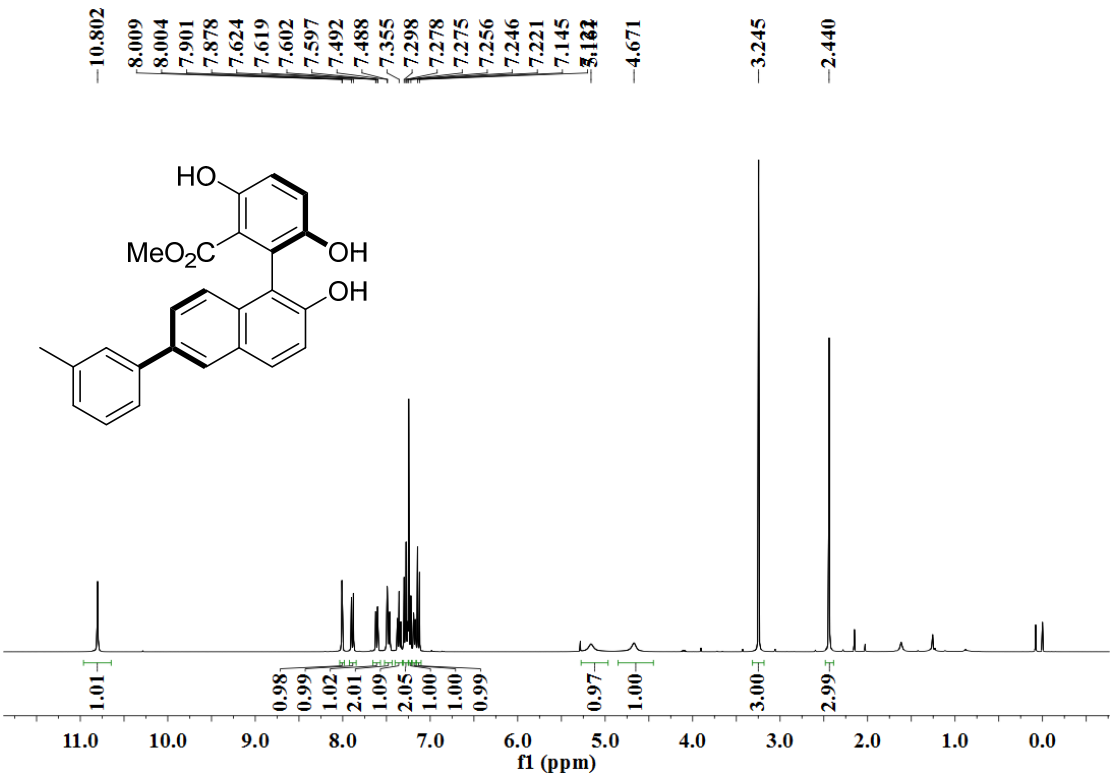
157.1
151.2
147.4
140.7
136.6
132.1
131.0
129.4
128.9
127.3
127.2
127.0
126.1
124.1
124.1
120.5
118.0
118.0
113.8
112.6
52.3
HO
MeO2C
OH
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.004
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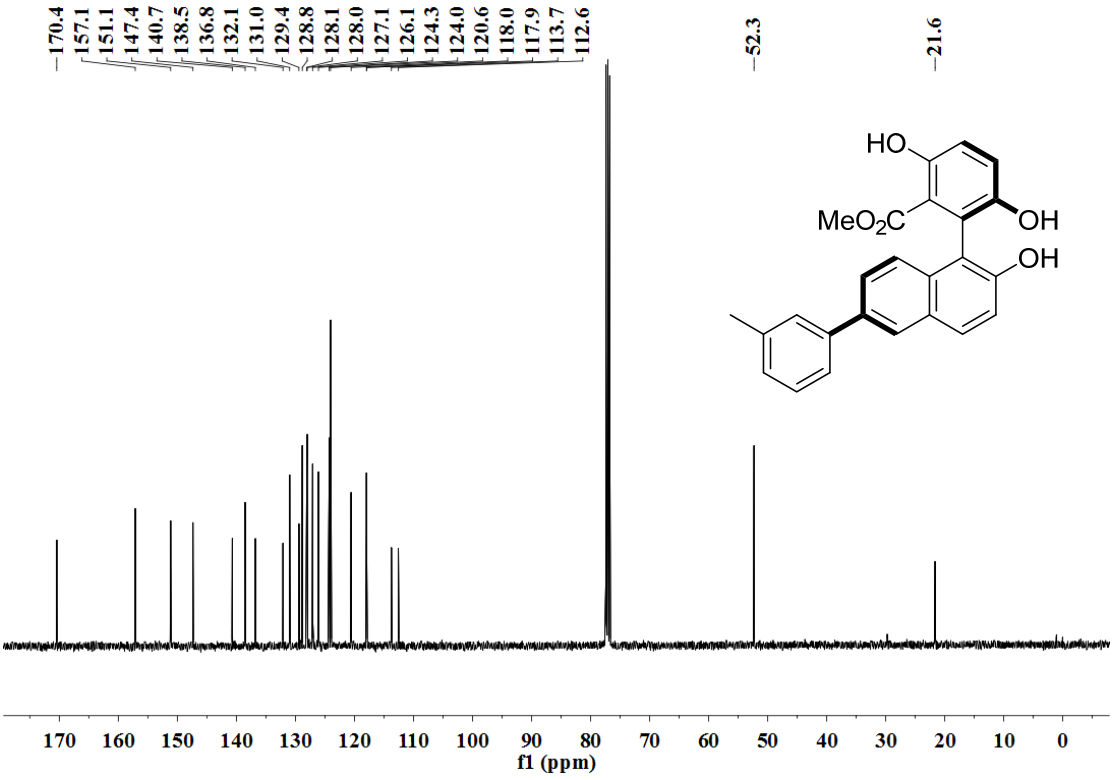
7.878
7.624
7.619
7.602
7.597
7.492
7.488
7.355
7.298
7.278
7.275
7.256
7.246
7.221
7.145
4.671
3.245
2.440
HO
MeO2C
OH
OH
1.01
0.98
0.99
1.02
2.01
1.09
2.05
1.00
1.00
0.99
0.97
1.00
3.00
2.99
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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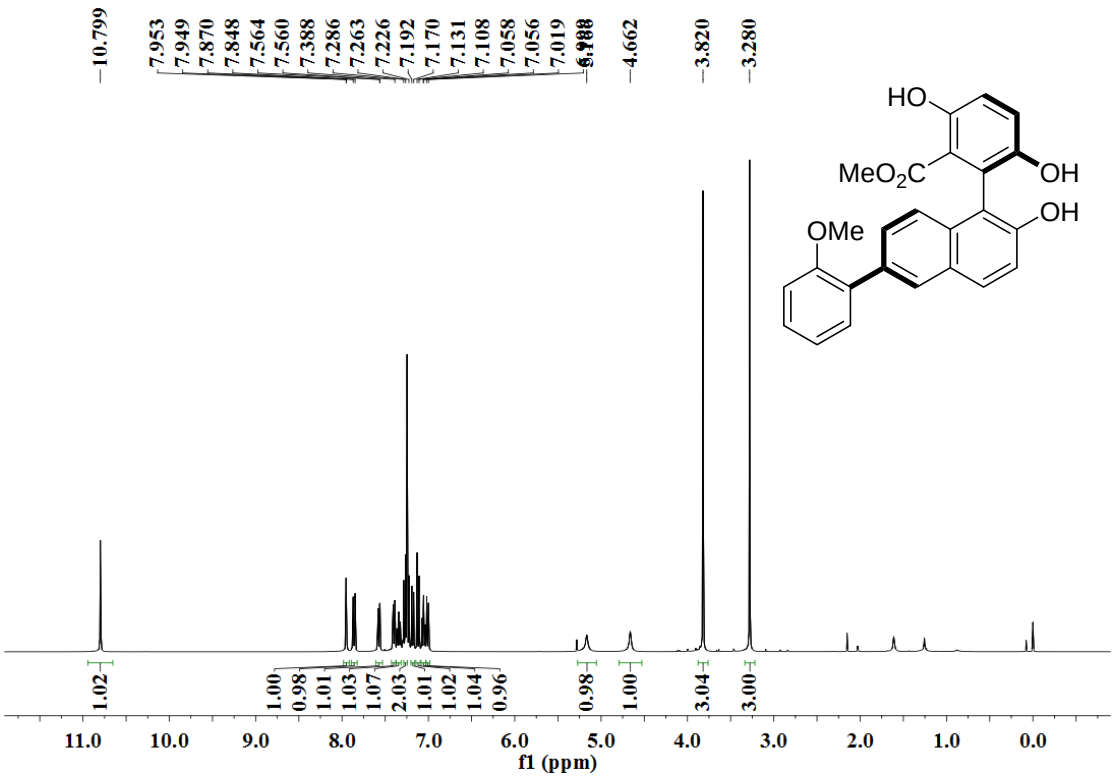
157.1
151.1
147.4
140.7
138.5
136.8
132.1
131.0
129.4
128.8
128.1
128.0
127.1
126.1
124.3
124.0
120.6
118.0
117.9
113.7
112.6
52.3
21.6
HO
MeO2C
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.870
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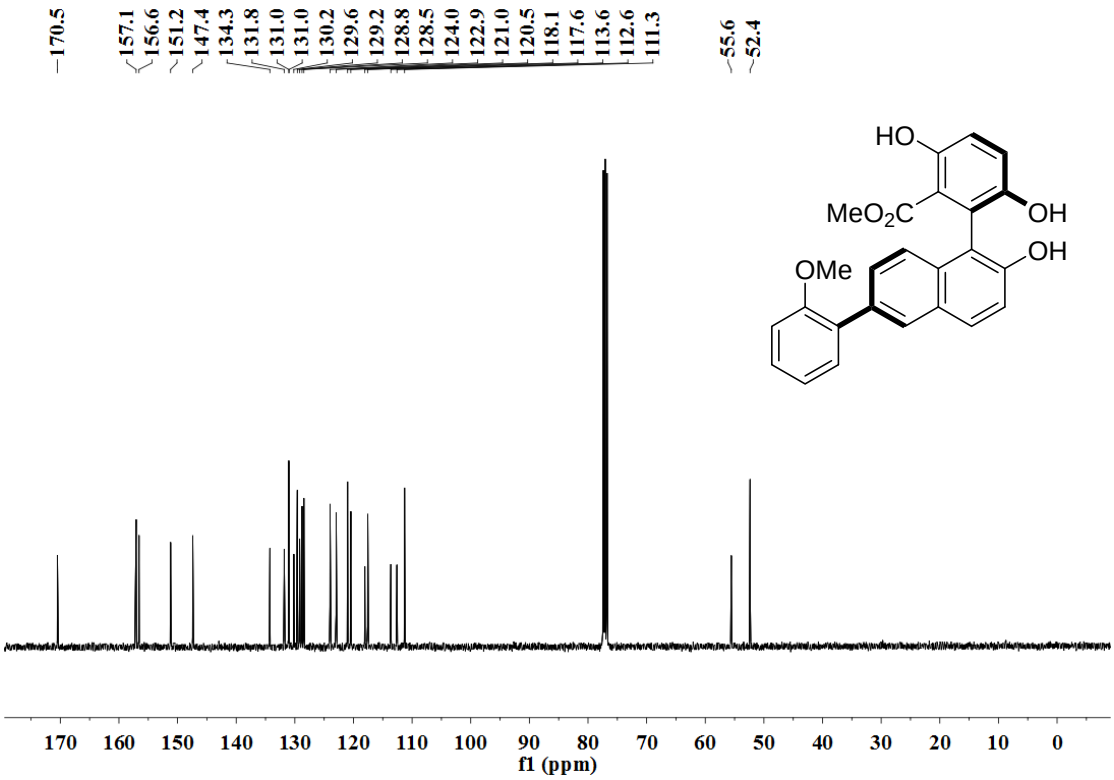
7.564
7.560
7.388
7.286
7.263
7.226
7.192
7.170
7.131
7.108
7.058
7.056
7.019
4.662
3.820
3.280
HO
MeO2C
OH
OH
OMe
1.02
1.00
0.98
1.01
1.03
1.07
2.03
1.01
1.02
1.04
0.96
0.98
1.00
3.04
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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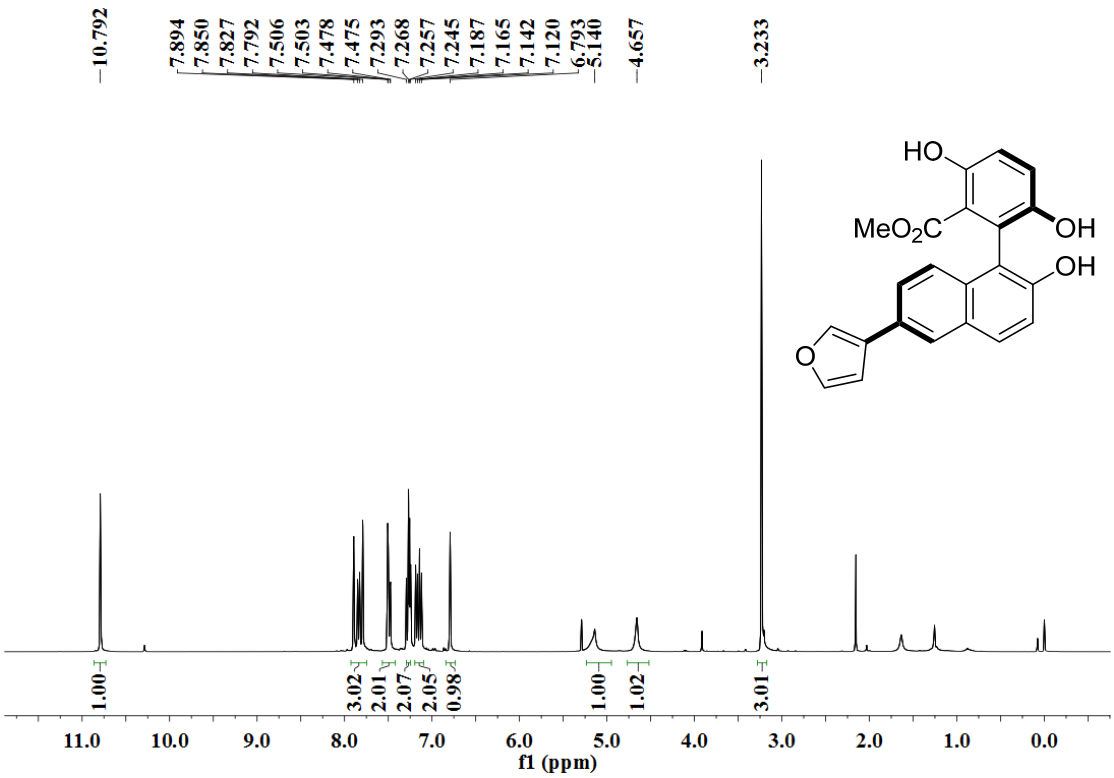
157.1
156.6
151.2
147.4
134.3
131.8
131.0
131.0
130.2
129.6
129.2
128.8
128.5
124.0
122.9
121.0
120.5
118.1
117.6
113.6
112.6
111.3
55.6
52.4
HO
MeO2C
OH
OH
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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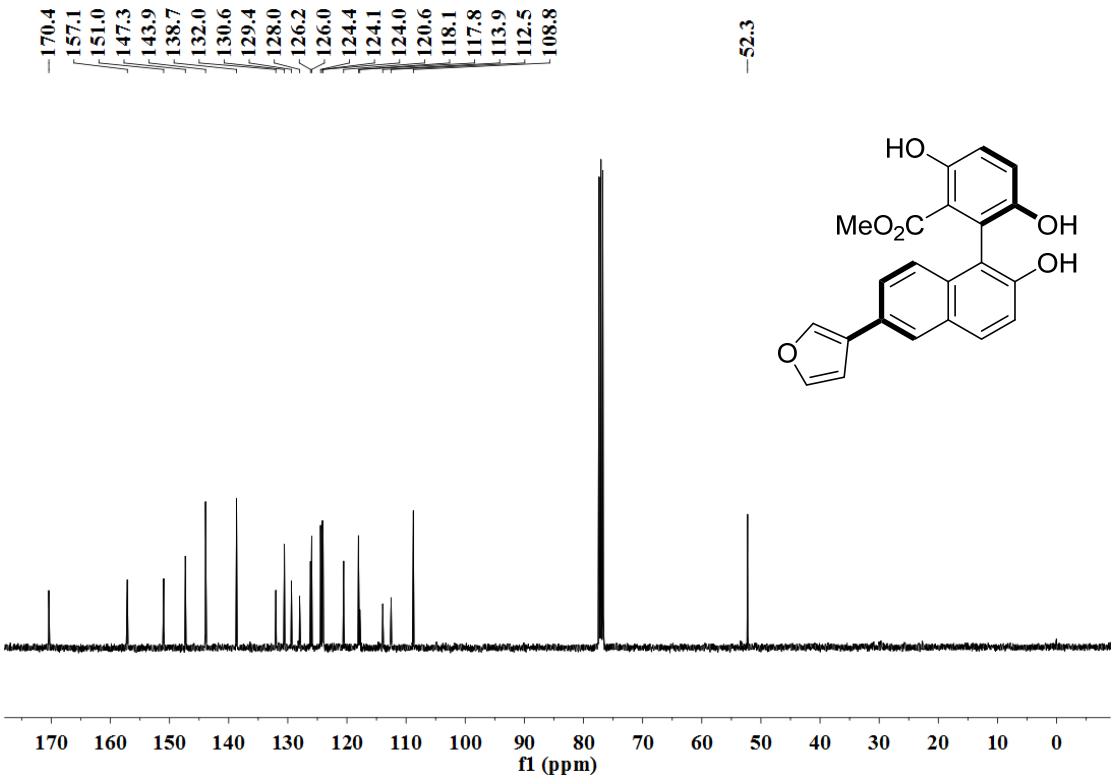
7.503
7.478
7.475
7.293
7.268
7.257
7.245
7.187
7.165
7.142
7.120
6.793
5.140
4.657
3.233
HO
MeO2C
OH
OH
O
1.00
3.02
2.01
2.07
2.05
0.98
1.00
1.02
3.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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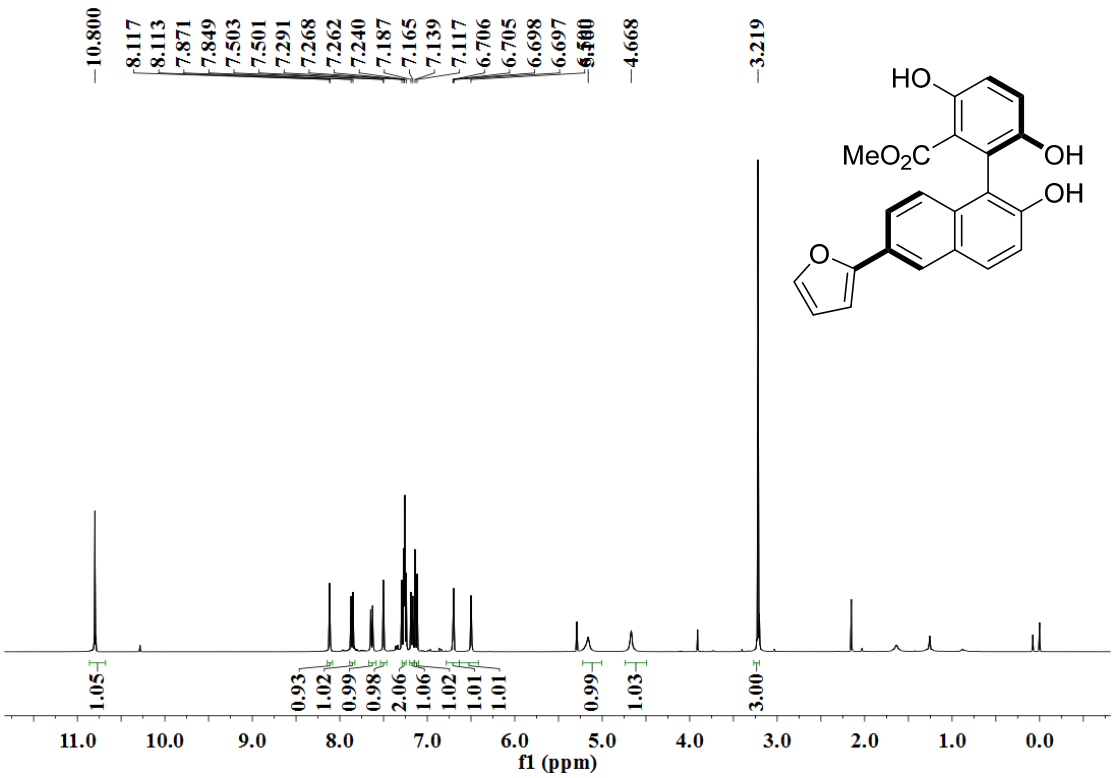
157.1
151.0
147.3
143.9
138.7
132.0
130.6
129.4
128.0
126.2
126.0
124.4
124.1
124.0
120.6
118.1
117.8
113.9
112.5
108.8
52.3
HO
MeO2C
OH
OH
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.113
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7.849
7.503
7.501
7.291
7.268
7.262
7.240
7.187
7.165
7.139
7.117
6.706
6.705
6.698
6.697
4.668
3.219
HO
MeO2C
OH
OH
O
1.05
0.93
1.02
0.99
0.98
2.06
1.06
1.02
1.01
1.01
0.99
1.03
3.00
11.0
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9.0
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7.0
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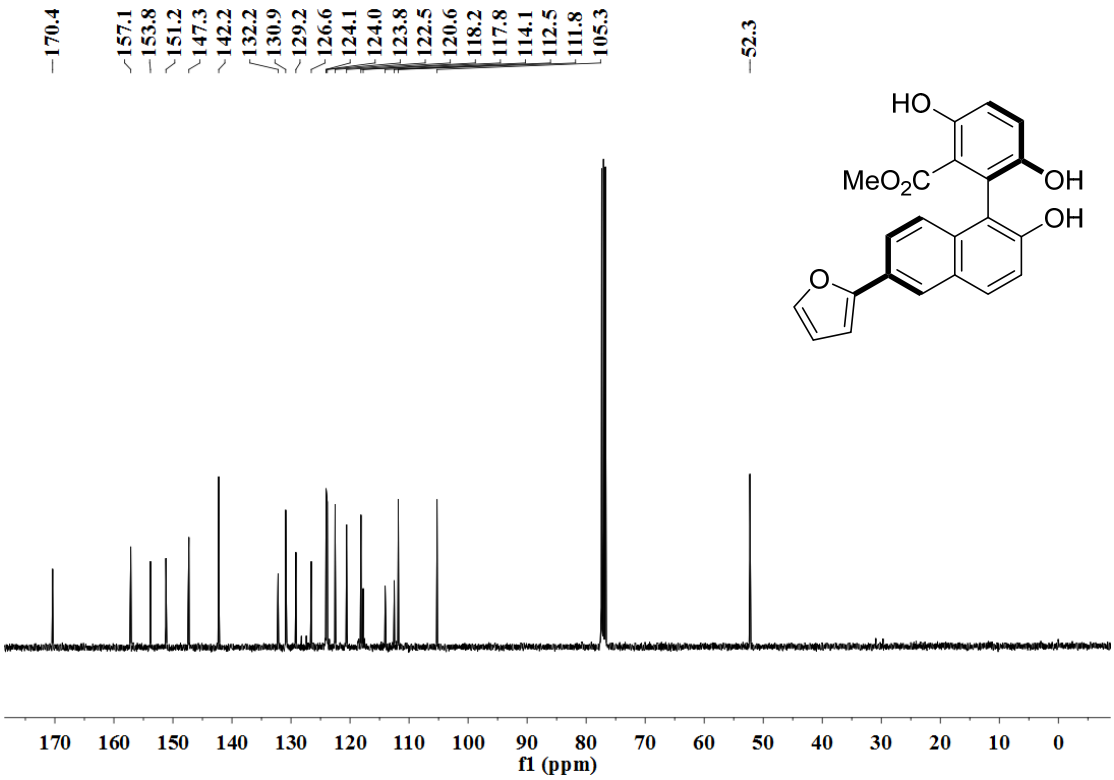
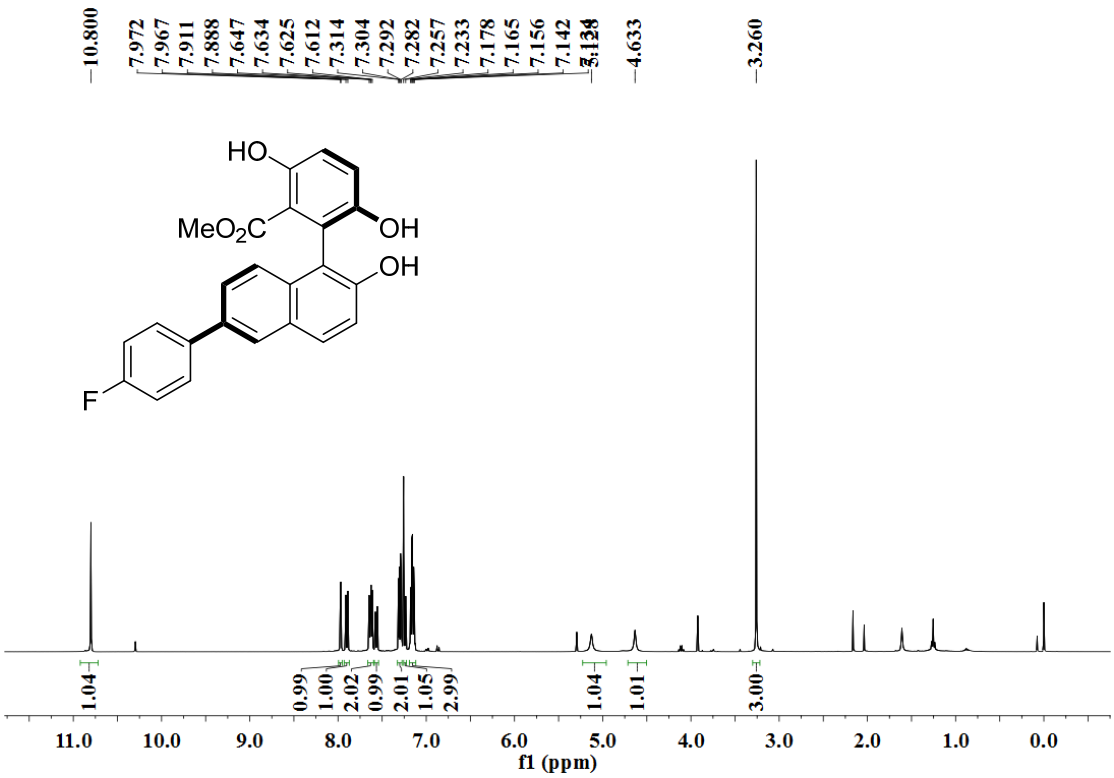
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


170.4
157.1
153.8
151.2
147.3
142.2
132.2
130.9
129.2
126.6
124.1
124.0
123.8
122.5
120.6
118.2
117.8
114.1
112.5
111.8
105.3
52.3
HO
MeO2C
OH
OH
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.625
7.612
7.314
7.304
7.292
7.282
7.257
7.233
7.178
7.165
7.156
7.142
4.633
3.260
HO
MeO2C
OH
OH
F
1.04
0.99
1.00
2.02
0.99
2.01
1.05
2.99
1.04
1.01
3.00
11.0
10.0
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5.0
4.0
3.0
2.0
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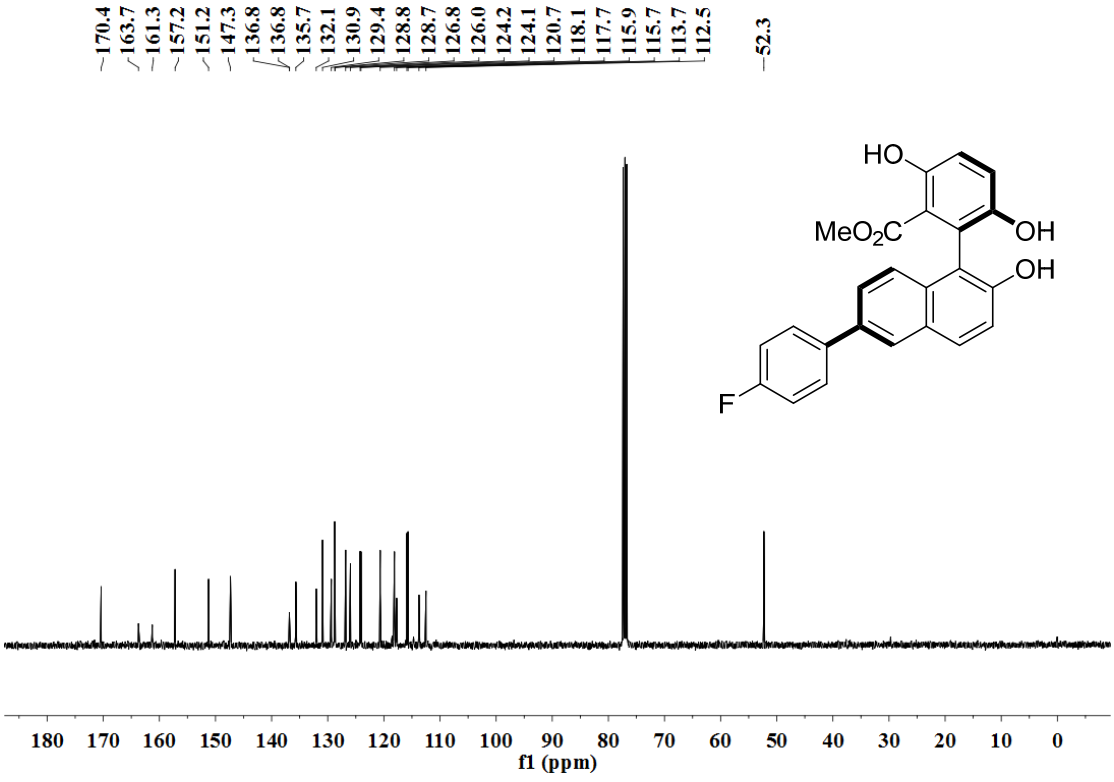
0.0
f1 (ppm)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147.3
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136.8
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132.1
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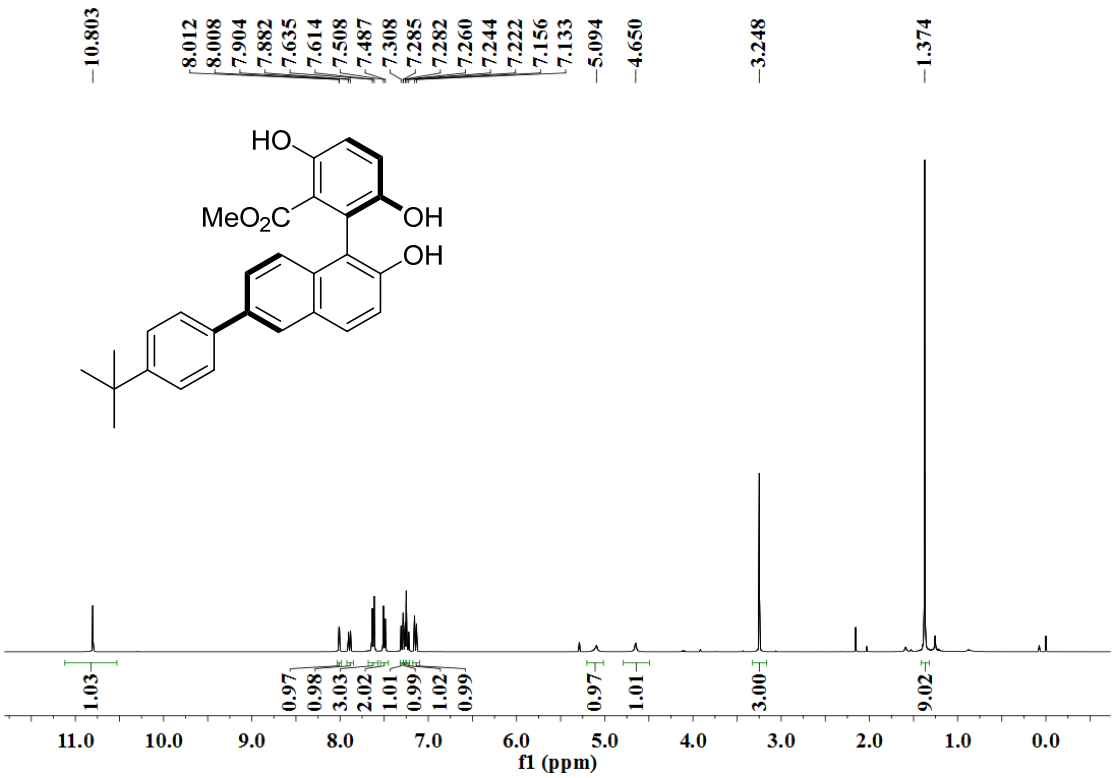
129.4
128.8
128.7
126.8
126.0
124.2
124.1
120.7
118.1
117.7
115.9
115.7
113.7
112.5
52.3
HO
MeO2C
OH
OH
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.508
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7.260
7.244
7.222
7.156
7.133
5.094
4.650
3.248
1.374
HO
MeO2C
OH
OH
1.03
0.97
0.98
3.03
2.02
1.01
0.99
1.02
0.99
0.97
1.01
3.00
9.02
11.0
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5.0
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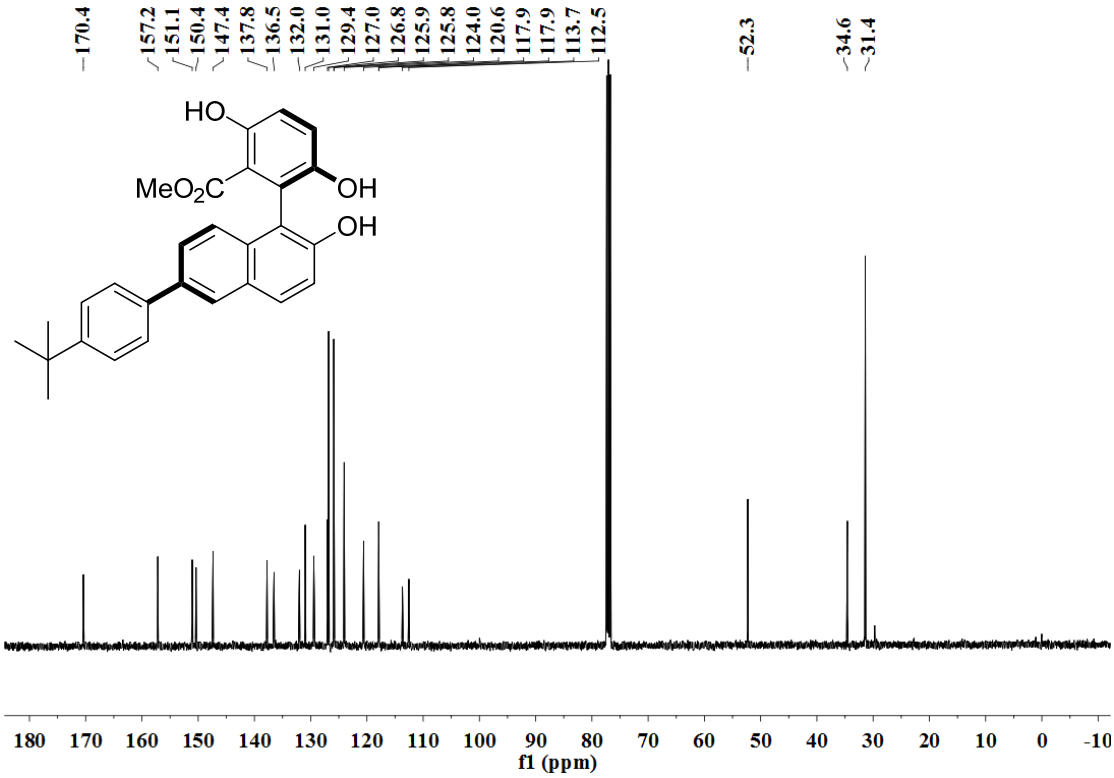
f1 (ppm)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132.0
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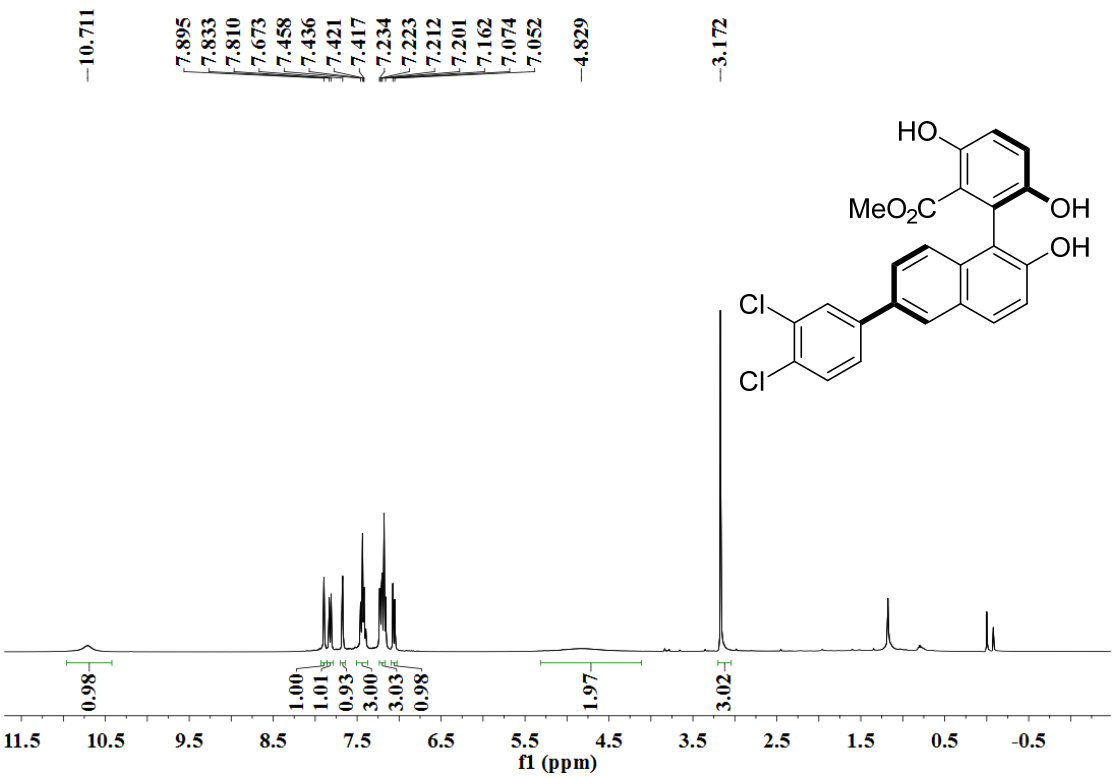
129.4
127.0
126.8
125.9
125.8
124.0
120.6
117.9
117.9
113.7
112.5
52.3
34.6
31.4
HO
MeO2C
OH
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.421
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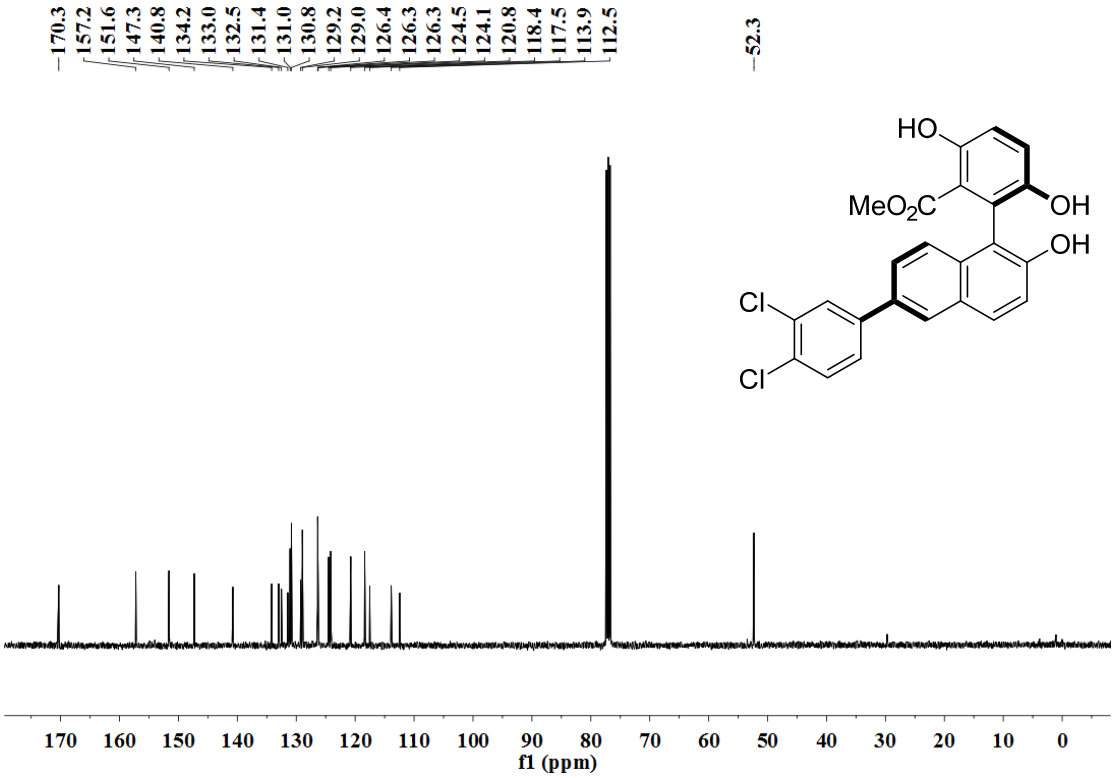
7.234
7.223
7.212
7.201
7.162
7.074
7.052
4.829
3.172
HO
MeO2C
OH
OH
Cl
Cl
0.98
1.00
1.01
0.93
3.00
3.03
0.98
1.97
3.02
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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157.2
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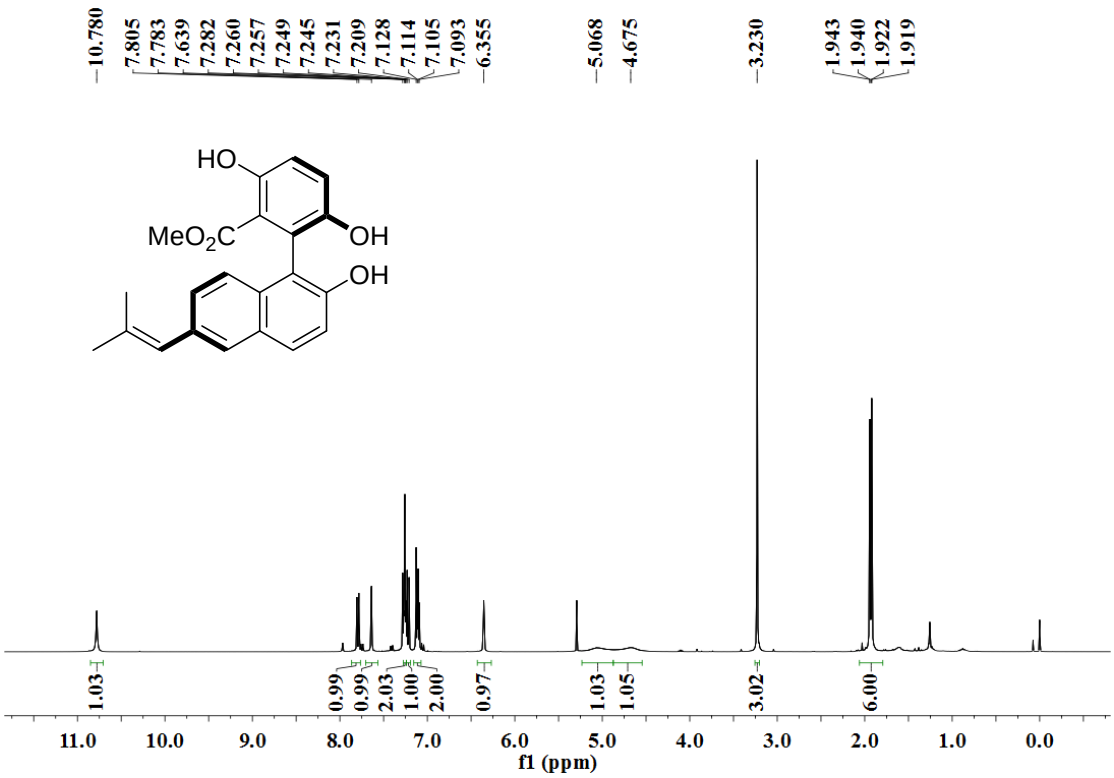
147.3
140.8
134.2
133.0
132.5
131.4
131.0
130.8
129.2
129.0
126.4
126.3
126.3
124.5
124.1
120.8
118.4
117.5
113.9
112.5
52.3
HO
MeO2C
OH
OH
Cl
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.783
7.639
7.282
7.260
7.257
7.249
7.245
7.231
7.209
7.128
7.114
7.105
7.093
6.355
5.068
4.675
3.230
1.943
1.940
1.922
1.919
HO
MeO2C
OH
OH
1.03
0.99
0.99
2.03
1.00
2.00
0.97
1.03
1.05
3.02
6.00
11.0
10.0
9.0
8.0
7.0
6.0
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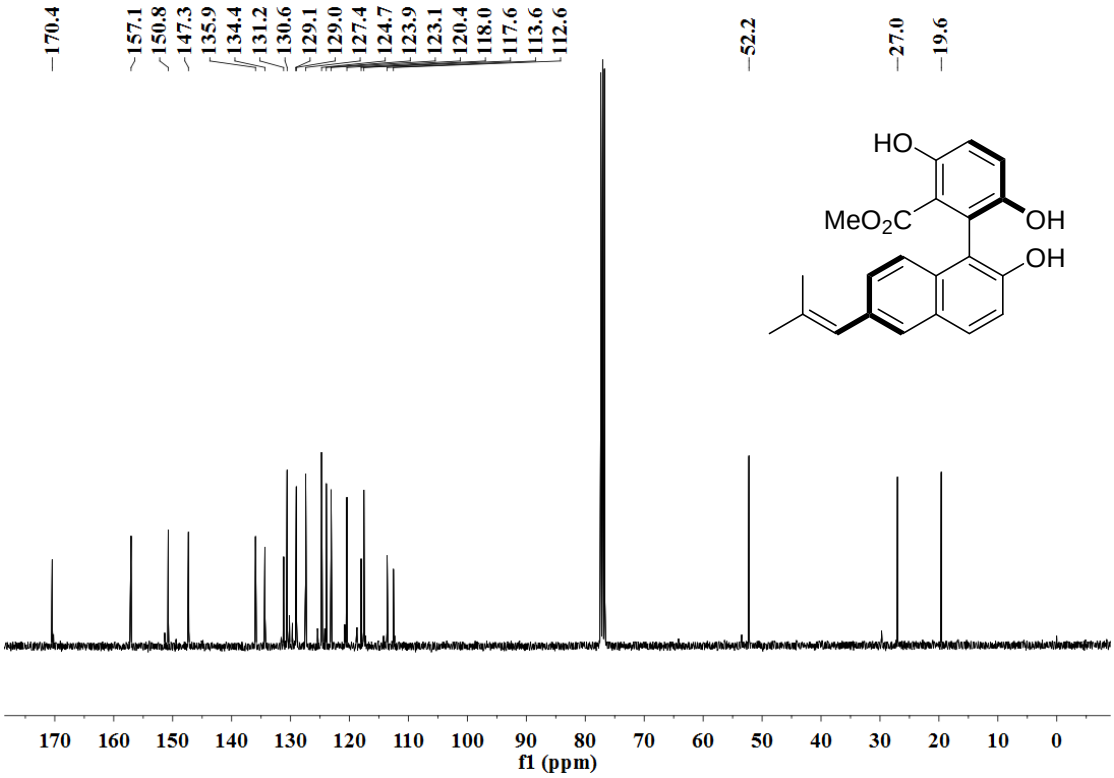
3.0
2.0
1.0
0.0
f1 (ppm)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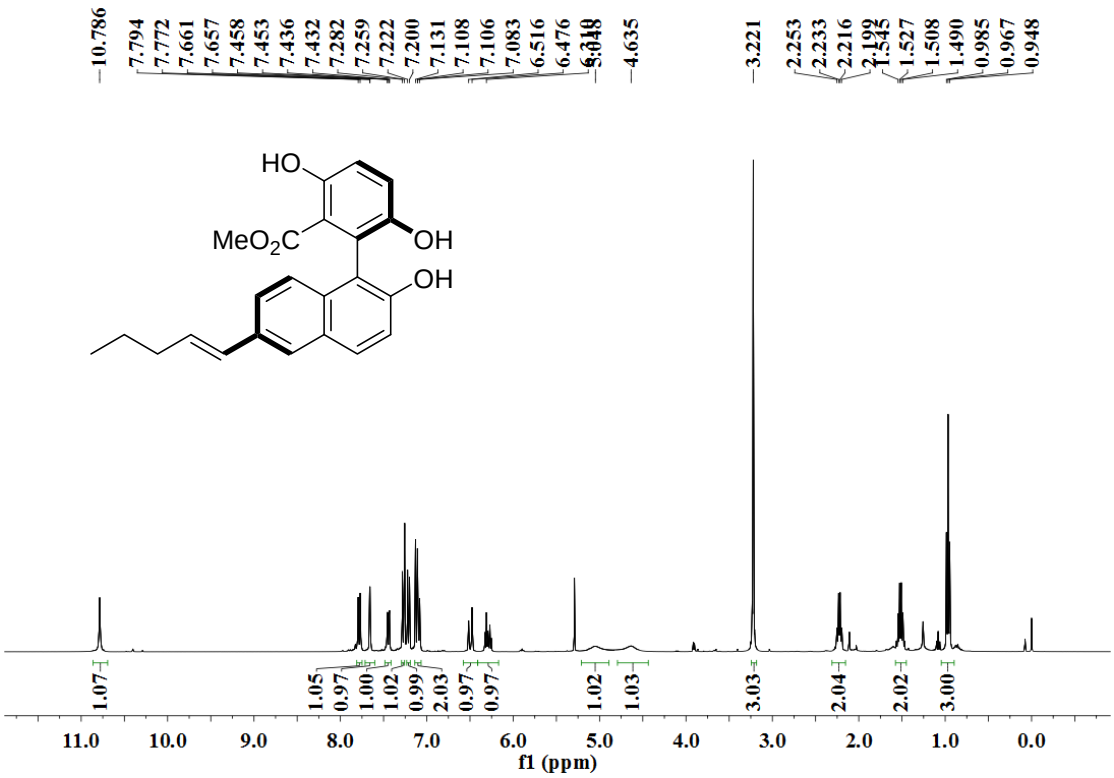
150.8
147.3
135.9
134.4
131.2
130.6
129.1
129.0
127.4
124.7
123.9
123.1
120.4
118.0
117.6
113.6
112.6
52.2
27.0
19.6
HO
MeO2C
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.772
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7.657
7.458
7.453
7.436
7.432
7.282
7.259
7.222
7.200
7.131
7.108
7.106
7.083
6.516
6.476
4.635
3.221
2.253
2.233
2.216
1.527
1.508
1.490
0.985
0.967
0.948
HO
MeO2C
OH
OH
1.07
1.05
0.97
1.00
1.02
0.99
2.03
0.97
0.97
1.02
1.03
3.03
2.04
2.02
3.00
11.0
10.0
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7.0
6.0
5.0
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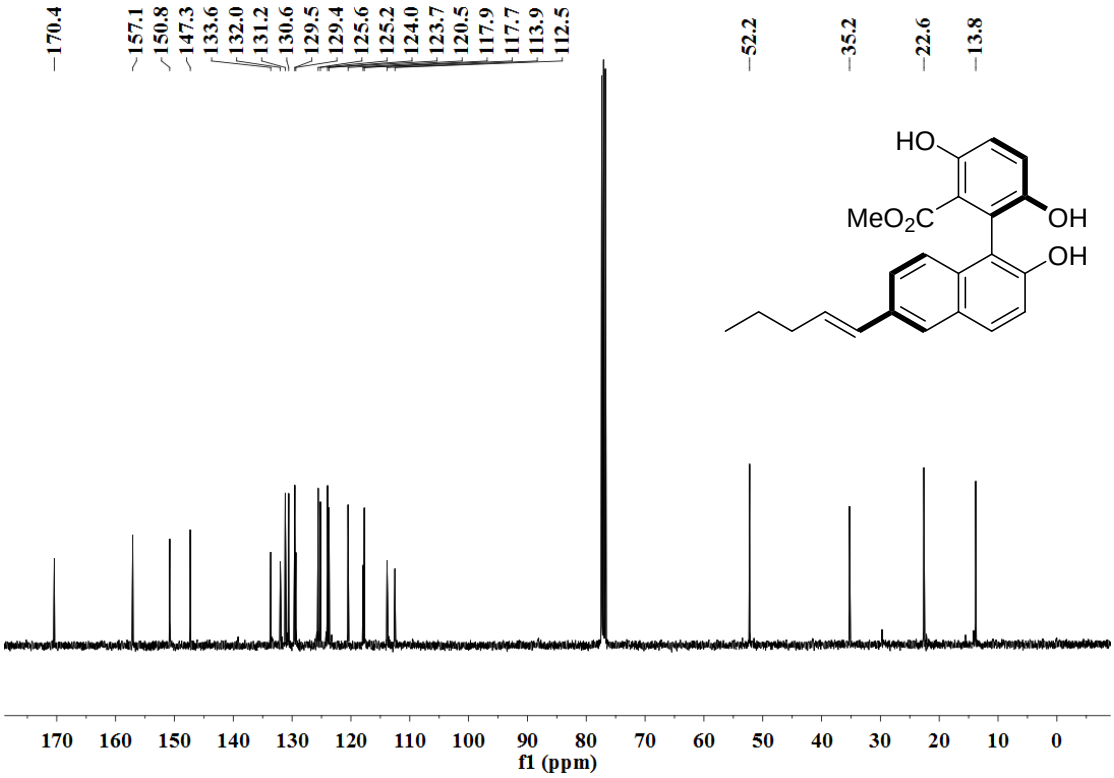
3.0
2.0
1.0
0.0
f1 (ppm)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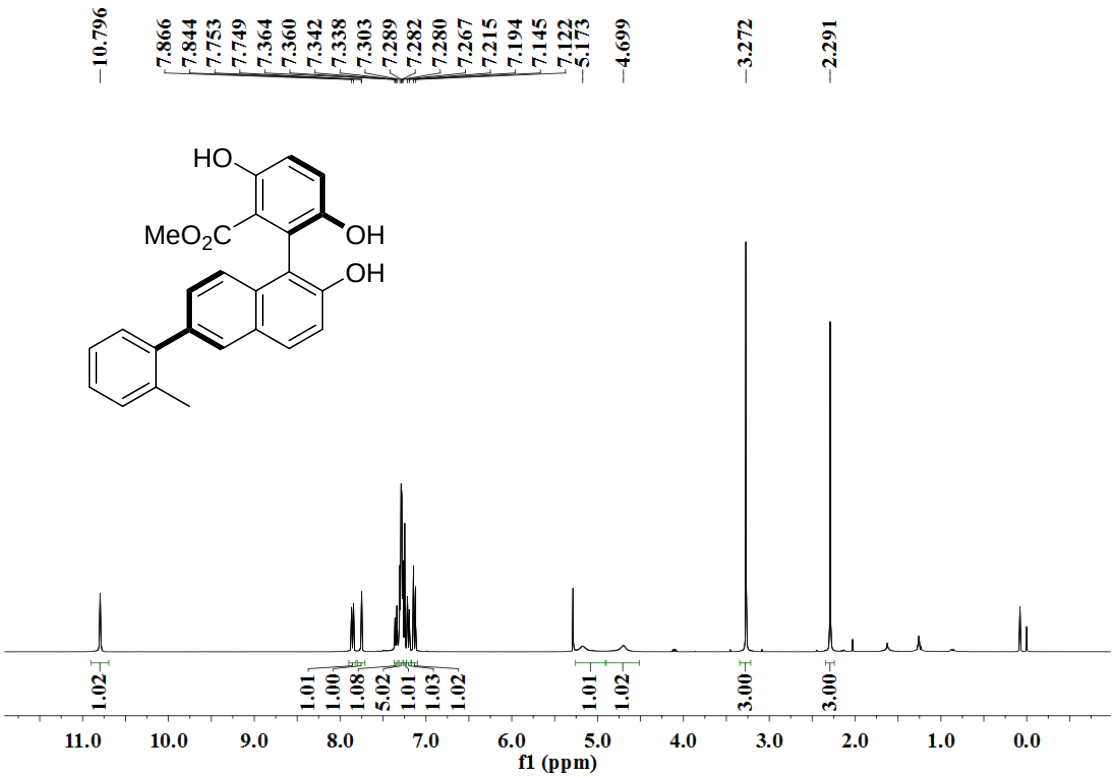
157.1
150.8
147.3
133.6
132.0
131.2
130.6
129.5
129.4
125.6
125.2
124.0
123.7
120.5
117.9
117.7
113.9
112.5
52.2
35.2
22.6
13.8
HO
MeO2C
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.289
7.282
7.280
7.267
7.215
7.194
7.145
7.122
5.173
4.699
3.272
2.291
HO
MeO2C
OH
OH
1.02
1.01
1.00
1.08
5.02
1.01
1.03
1.02
1.01
1.02
3.00
3.00
11.0
10.0
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7.0
6.0
5.0
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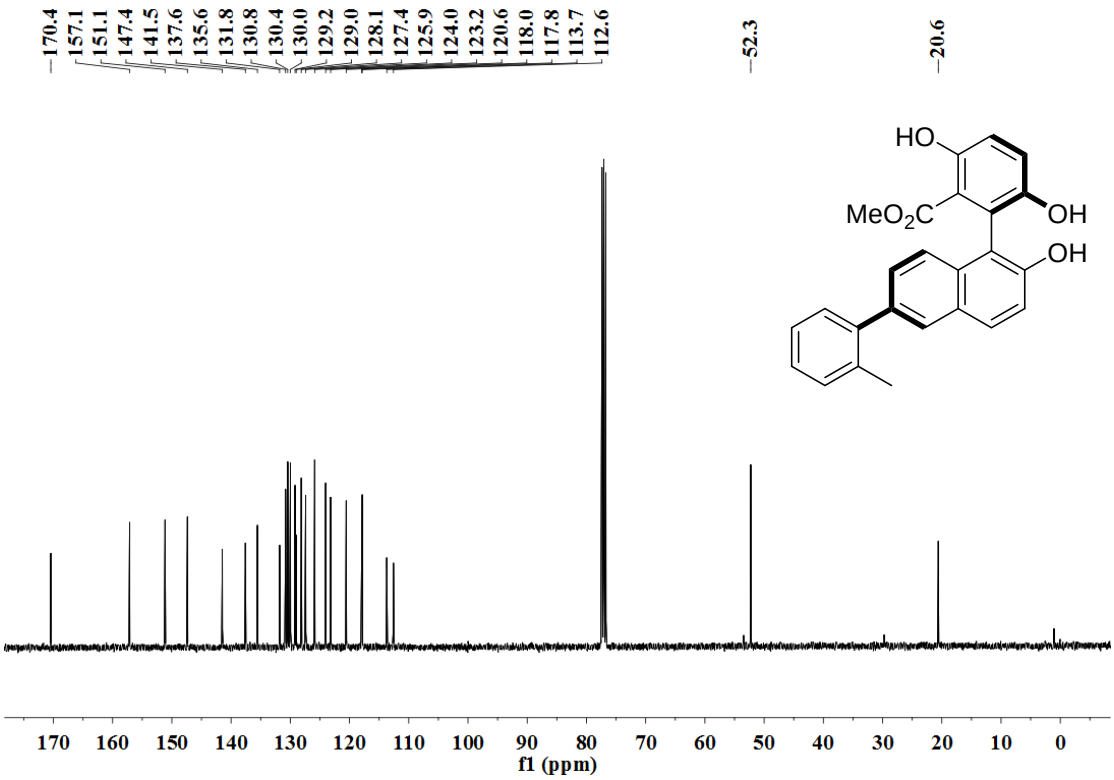
3.0
2.0
1.0
0.0
f1 (ppm)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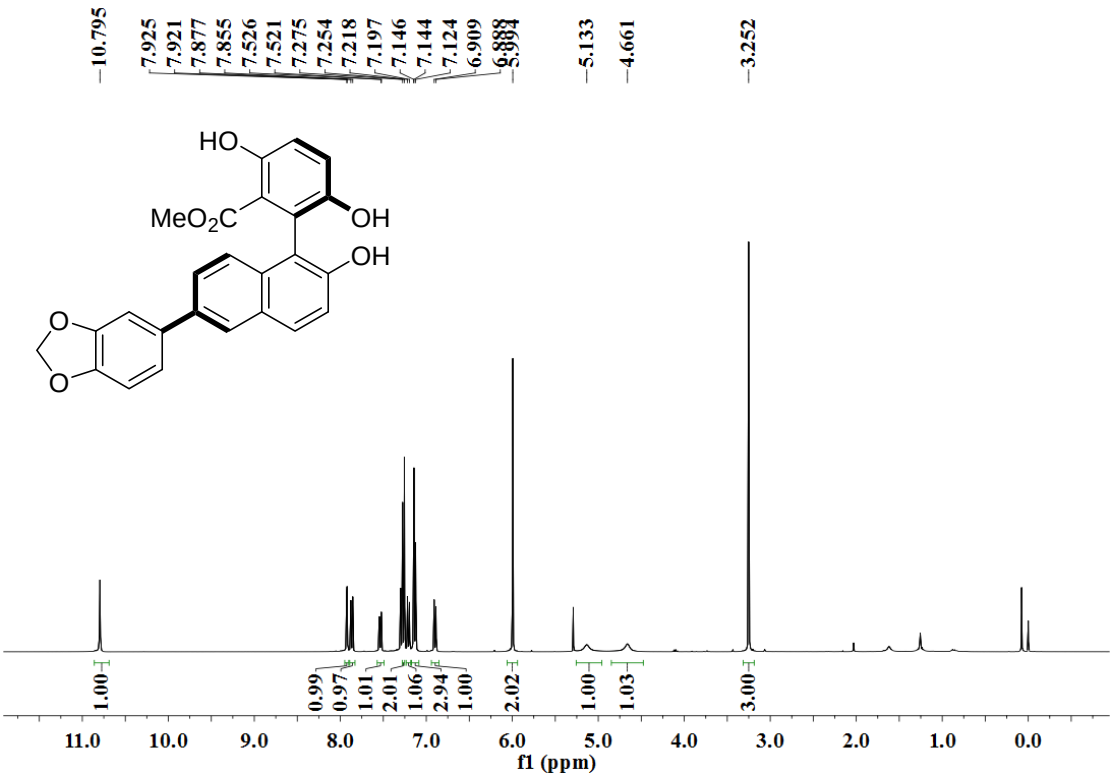
157.1
151.1
147.4
141.5
137.6
135.6
131.8
130.8
130.4
130.0
129.2
129.0
128.1
127.4
125.9
124.0
123.2
120.6
118.0
117.8
113.7
112.6
52.3
20.6
HO
MeO2C
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.197
7.146
7.144
7.124
6.909
5.133
4.661
3.252
HO
MeO2C
OH
OH
O
O
1.00
0.99
0.97
1.01
2.01
1.06
2.94
1.00
2.02
1.00
1.03
3.00
11.0
10.0
9.0
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7.0
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5.0
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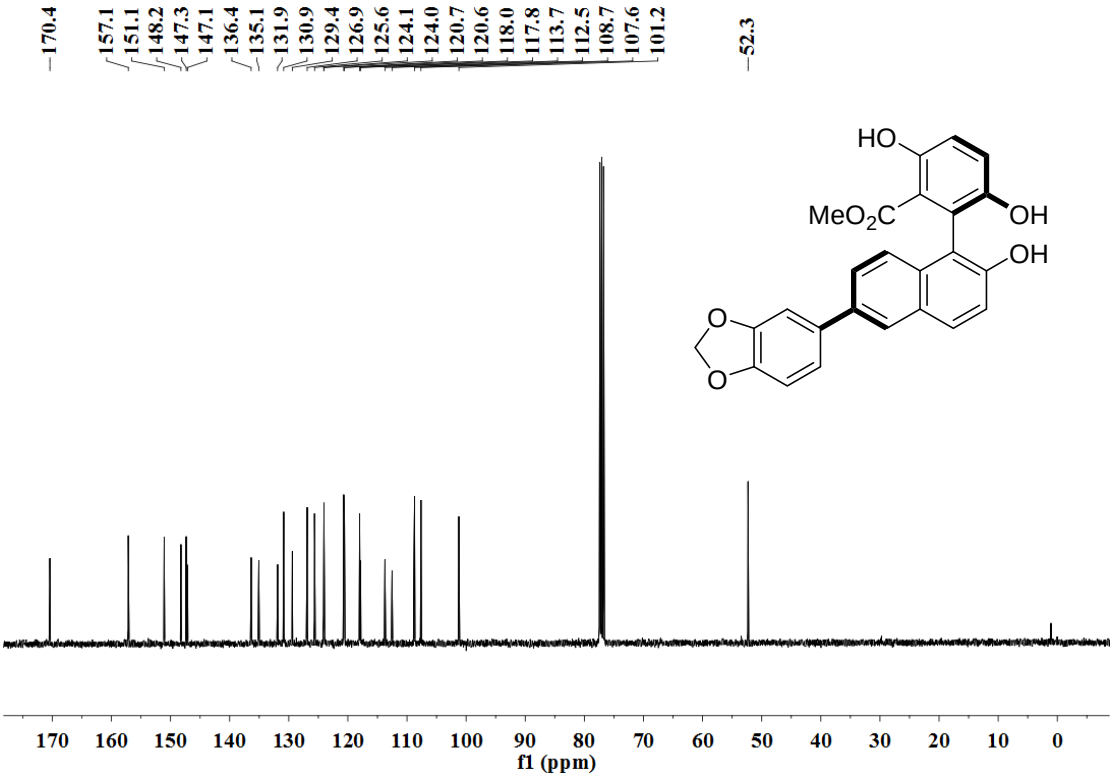
2.0
1.0
0.0
f1 (ppm)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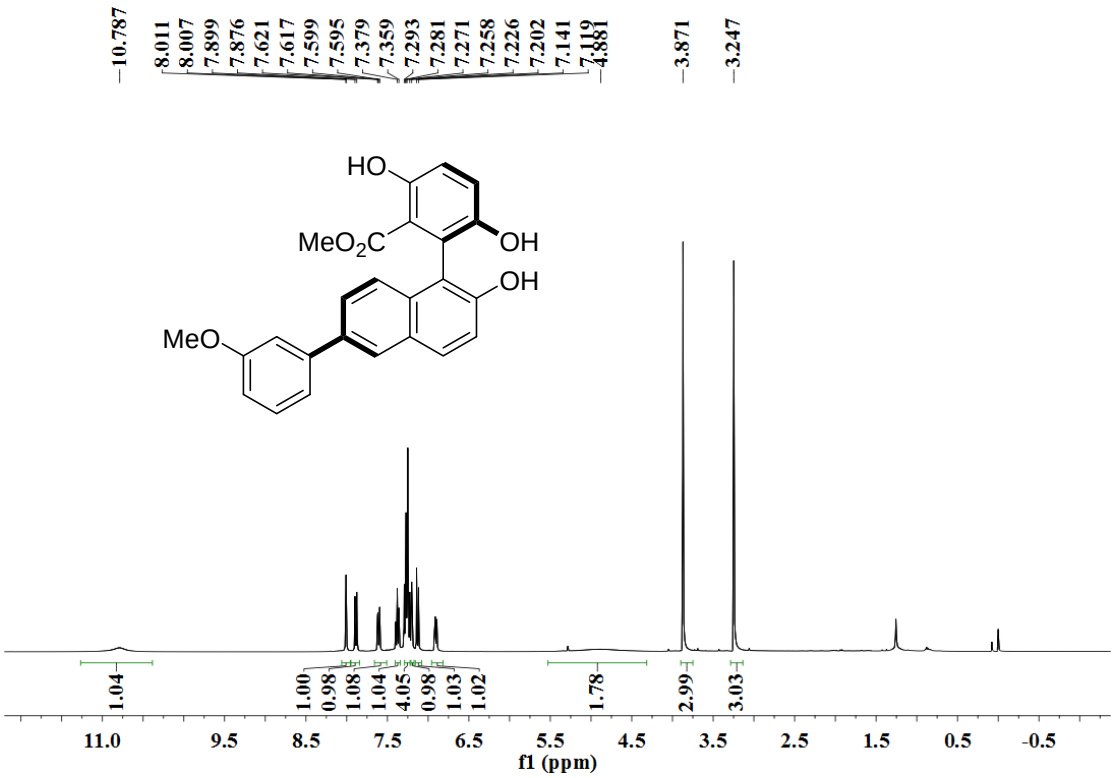
151.1
148.2
147.3
147.1
136.4
135.1
131.9
130.9
129.4
126.9
125.6
124.1
124.0
120.7
120.6
118.0
117.8
113.7
112.5
108.7
107.6
101.2
52.3
HO
MeO2C
OH
OH
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.359
7.293
7.281
7.271
7.258
7.226
7.202
7.141
7.119
4.881
3.871
3.247
HO
MeO2C
OH
OH
MeO
1.04
1.00
0.98
1.08
1.04
4.05
0.98
1.03
1.02
1.78
2.99
3.03
11.0
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6.5
5.5
4.5
3.5
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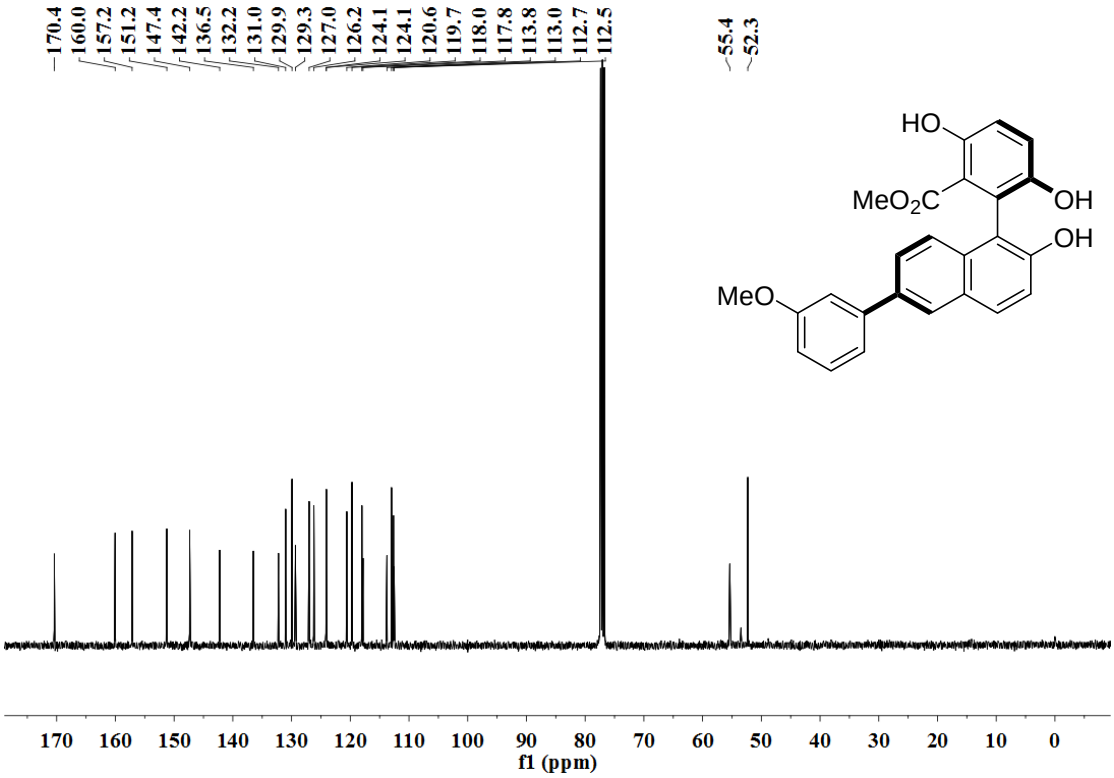
1.5
0.5
-0.5
f1 (ppm)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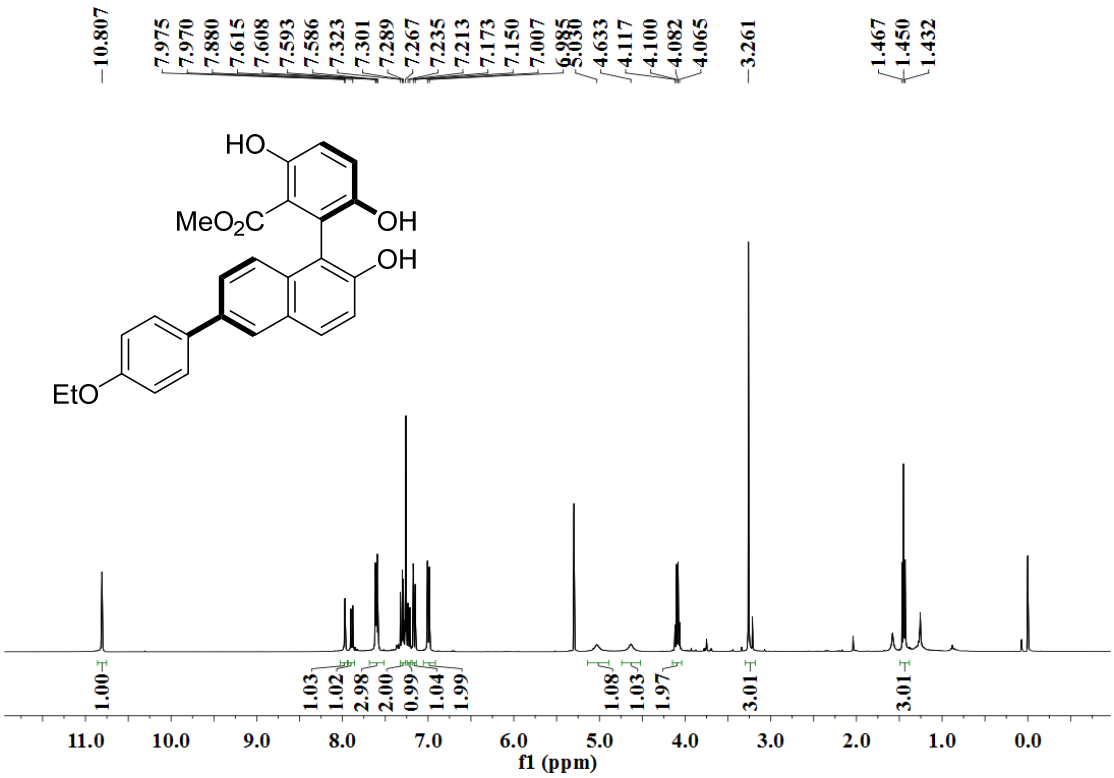
157.2
151.2
147.4
142.2
136.5
132.2
131.0
129.9
129.3
127.0
126.2
124.1
124.1
120.6
119.7
118.0
117.8
113.8
113.0
112.7
112.5
55.4
52.3
HO
MeO2C
OH
OH
MeO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.586
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7.301
7.289
7.267
7.235
7.213
7.173
7.150
7.007
6.985
5.030
4.633
4.117
4.100
4.082
4.065
3.261
1.467
1.450
1.432
HO
MeO2C
OH
OH
EtO
1.00
1.03
1.02
2.98
2.00
0.99
1.04
1.99
1.08
1.03
1.97
3.01
3.01
11.0
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7.0
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2.0
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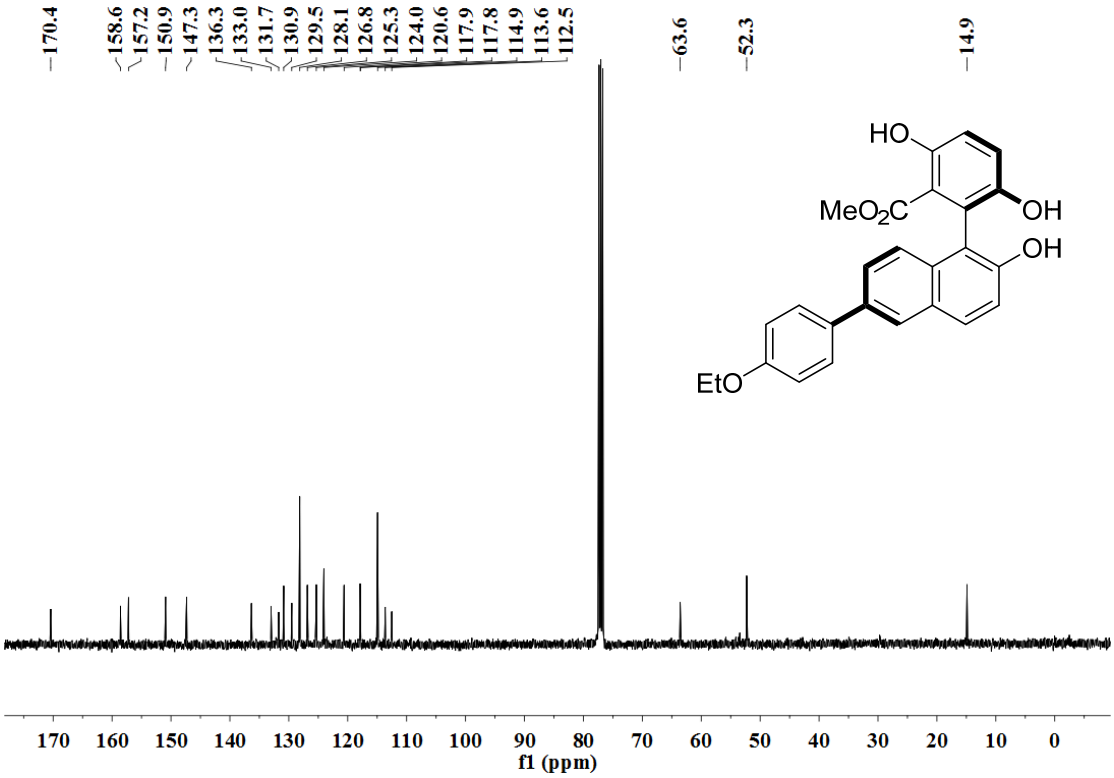
0.0
f1 (ppm)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157.2
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133.0
131.7
130.9
129.5
128.1
126.8
125.3
124.0
120.6
117.9
117.8
114.9
113.6
112.5
63.6
52.3
14.9
HO
MeO2C
OH
OH
EtO
170
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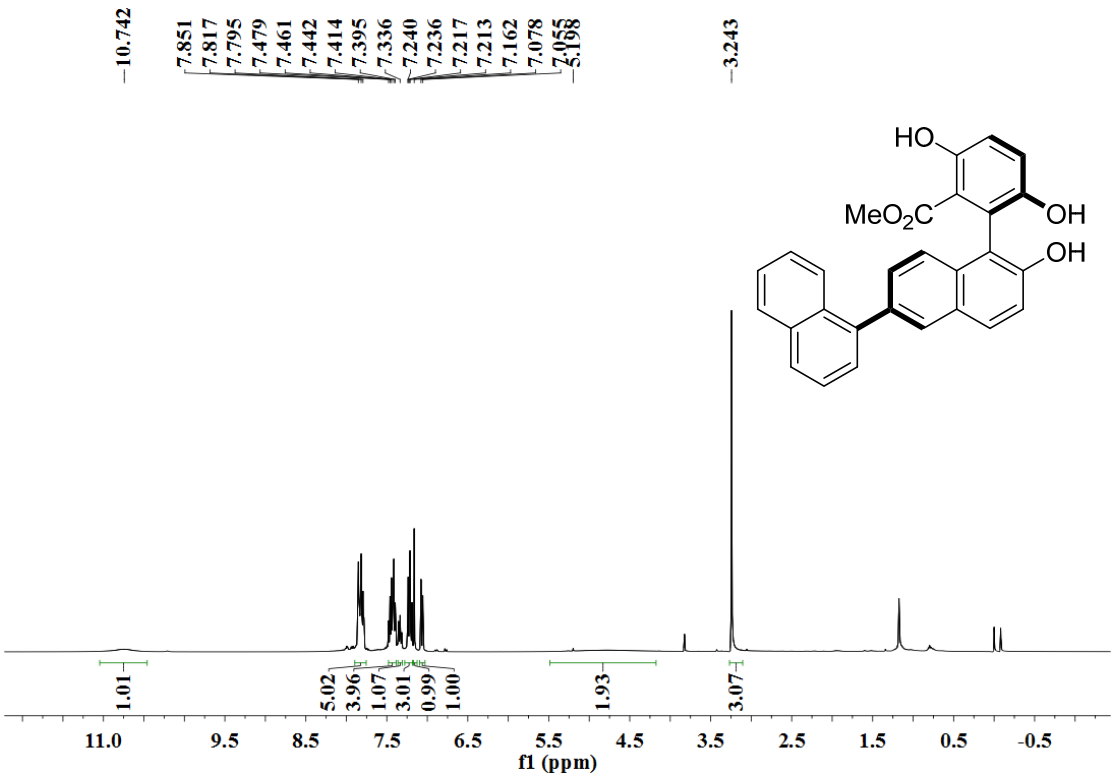
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.461
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7.414
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7.240
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7.217
7.213
7.162
7.078
7.055
7.038
3.243
HO
MeO2C
OH
OH
1.01
5.02
3.96
1.07
3.01
0.99
1.00
1.93
3.07
11.0
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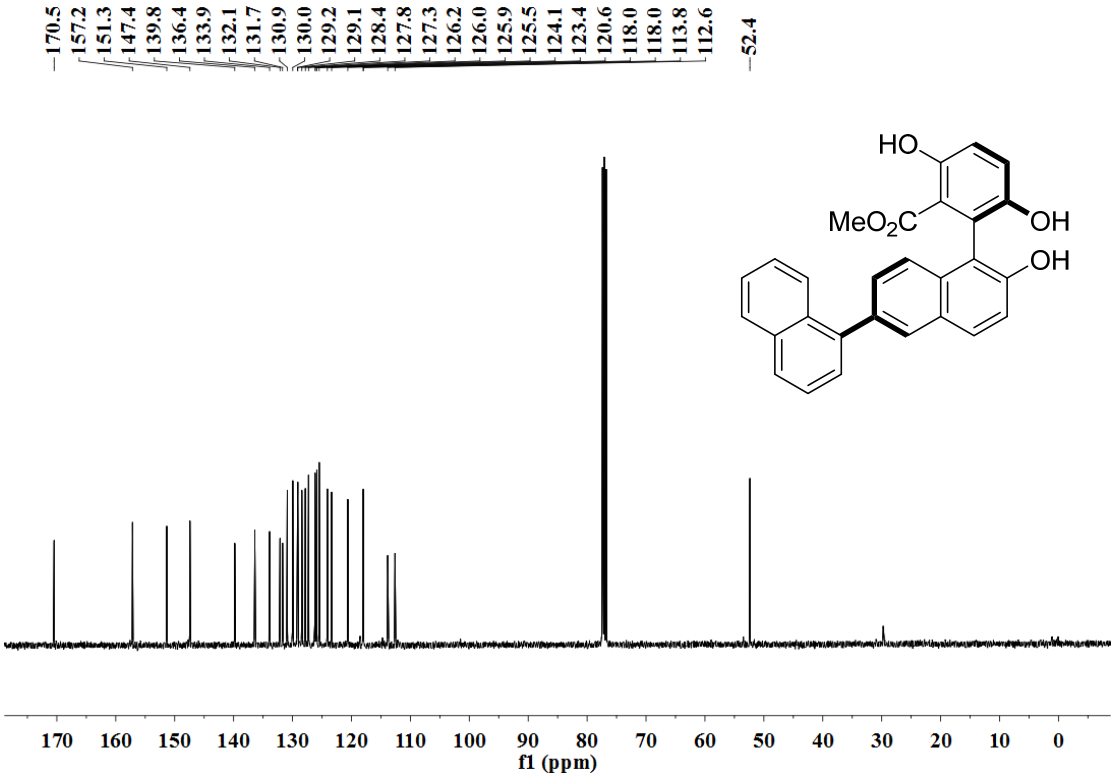
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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157.2
151.3
147.4
139.8
136.4
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132.1
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130.9
130.0
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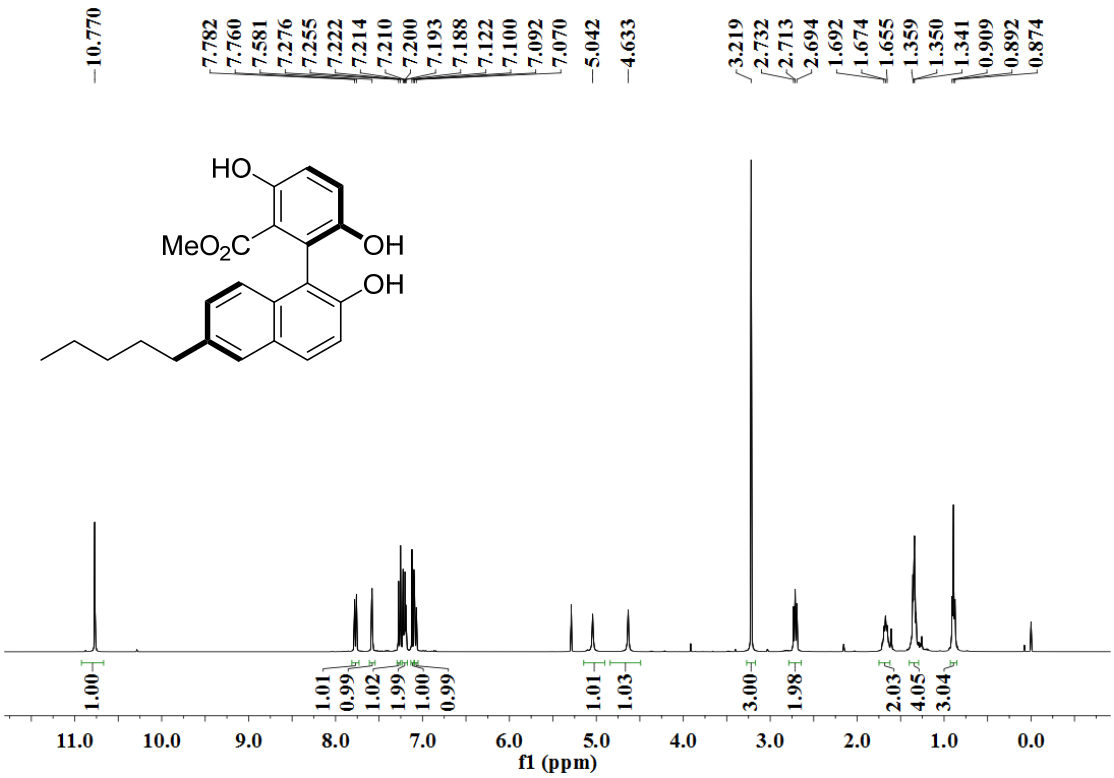
129.1
128.4
127.8
127.3
126.2
126.0
125.9
125.5
124.1
123.4
120.6
118.0
118.0
113.8
112.6
52.4
HO
MeO2C
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.581
7.276
7.255
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7.214
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7.200
7.193
7.188
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7.100
7.092
7.070
5.042
4.633
3.219
2.732
2.713
2.694
1.692
1.674
1.655
1.359
1.350
1.341
0.909
0.892
0.874
HO
MeO2C
OH
OH
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1.01
0.99
1.02
1.99
1.00
0.99
1.01
1.03
3.00
1.98
2.03
4.05
3.04
11.0
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5.0
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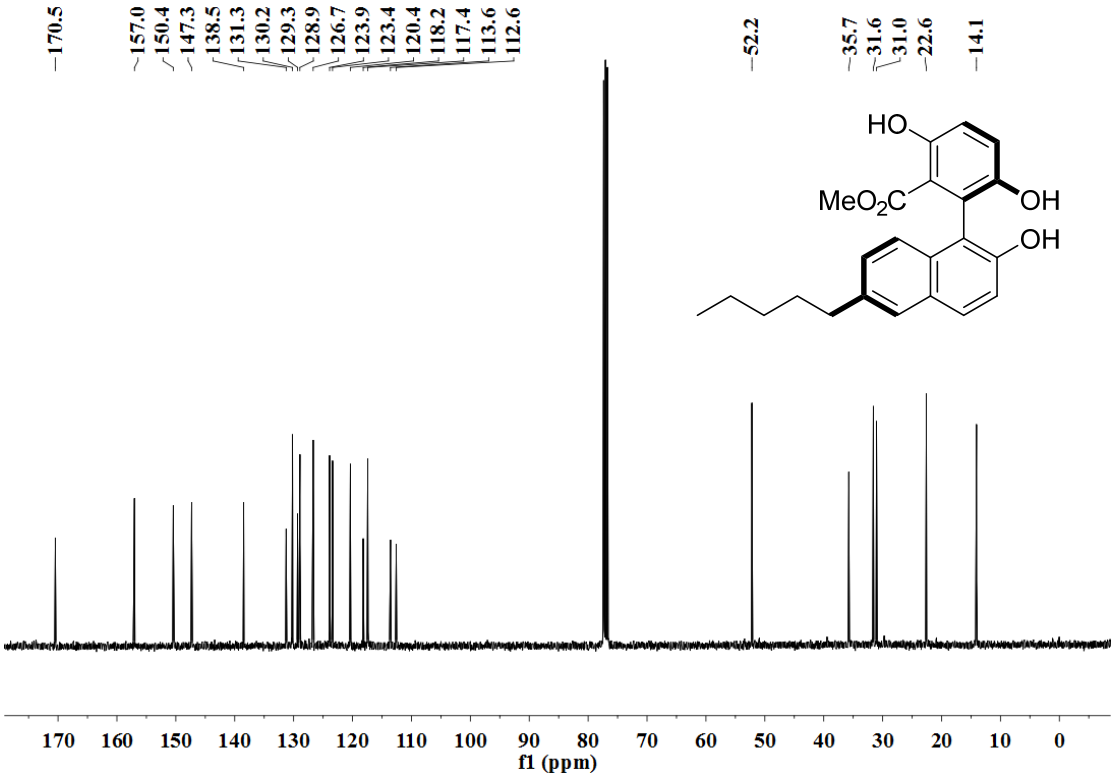
0.0
f1 (ppm)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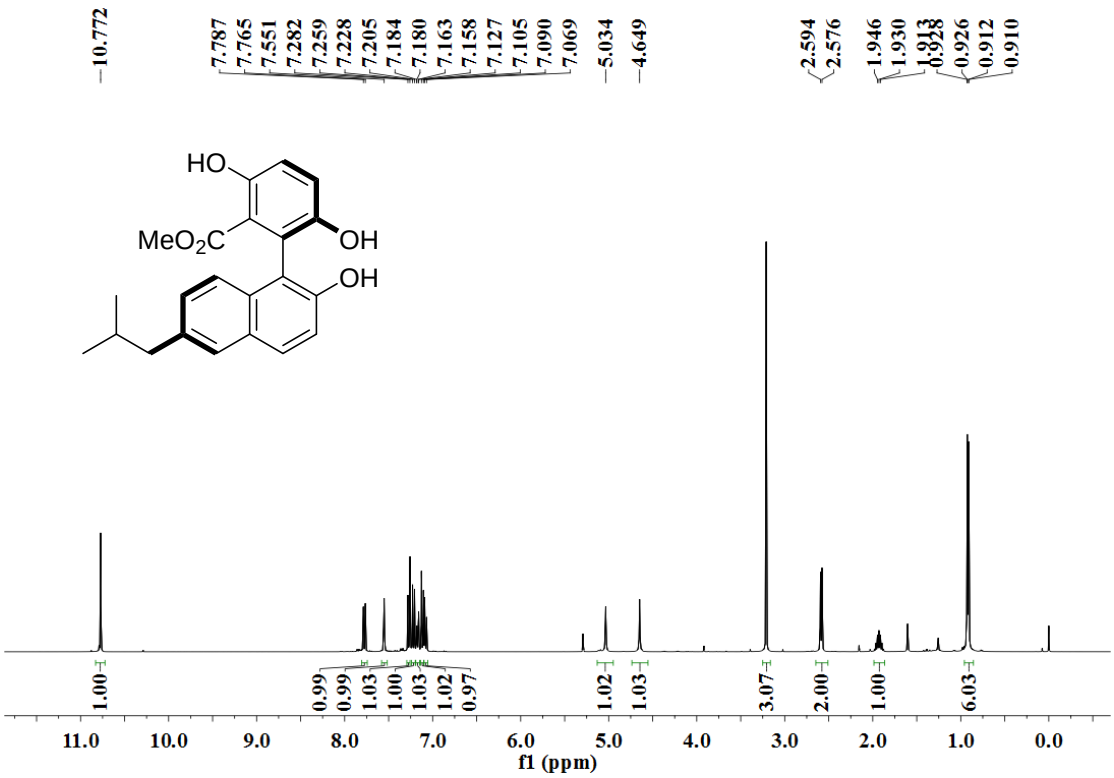
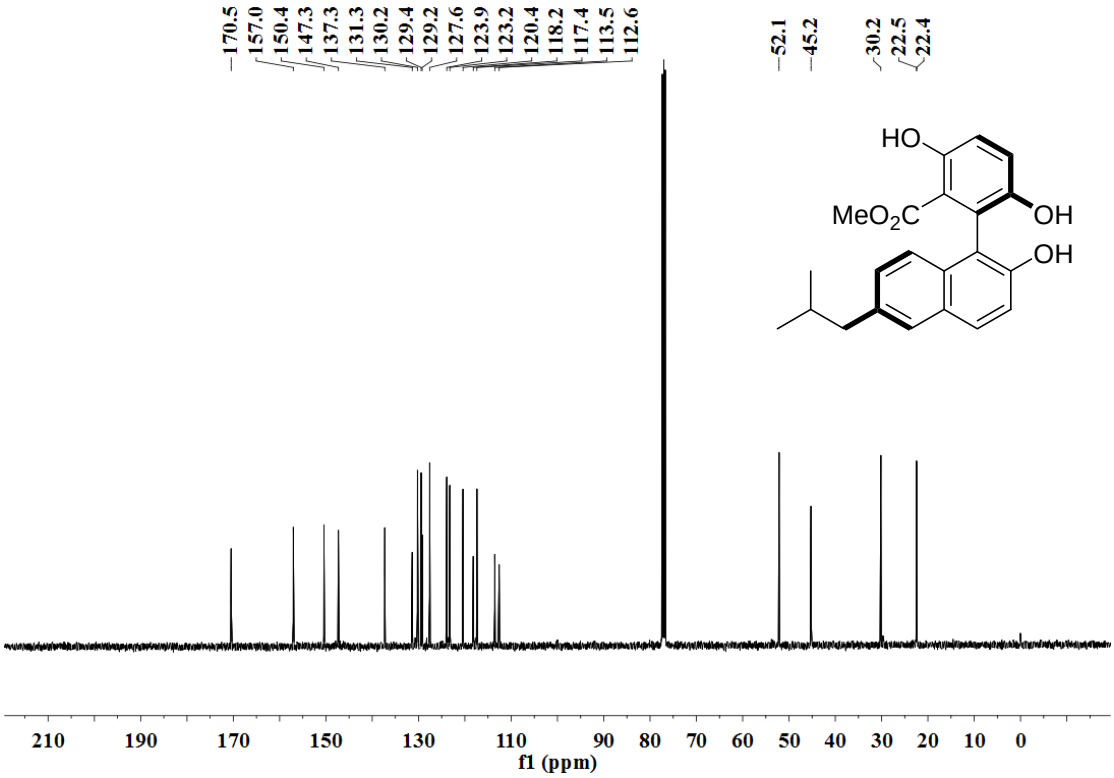
157.0
150.4
147.3
138.5
131.3
130.2
129.3
128.9
126.7
123.9
123.4
120.4
118.2
117.4
113.6
112.6
52.2
35.7
31.6
31.0
22.6
14.1
HO
MeO2C
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.772
7.787
7.765
7.551
7.282
7.259
7.228
7.205
7.184
7.180
7.163
7.158
7.127
7.105
7.090
7.069
5.034
4.649
2.594
2.576
1.946
1.930
1.913
1.928
0.926
0.912
0.910
HO
MeO2C
OH
OH
1.00
0.99
0.99
1.03
1.00
1.03
1.02
0.97
1.02
1.03
3.07
2.00
1.00
6.03
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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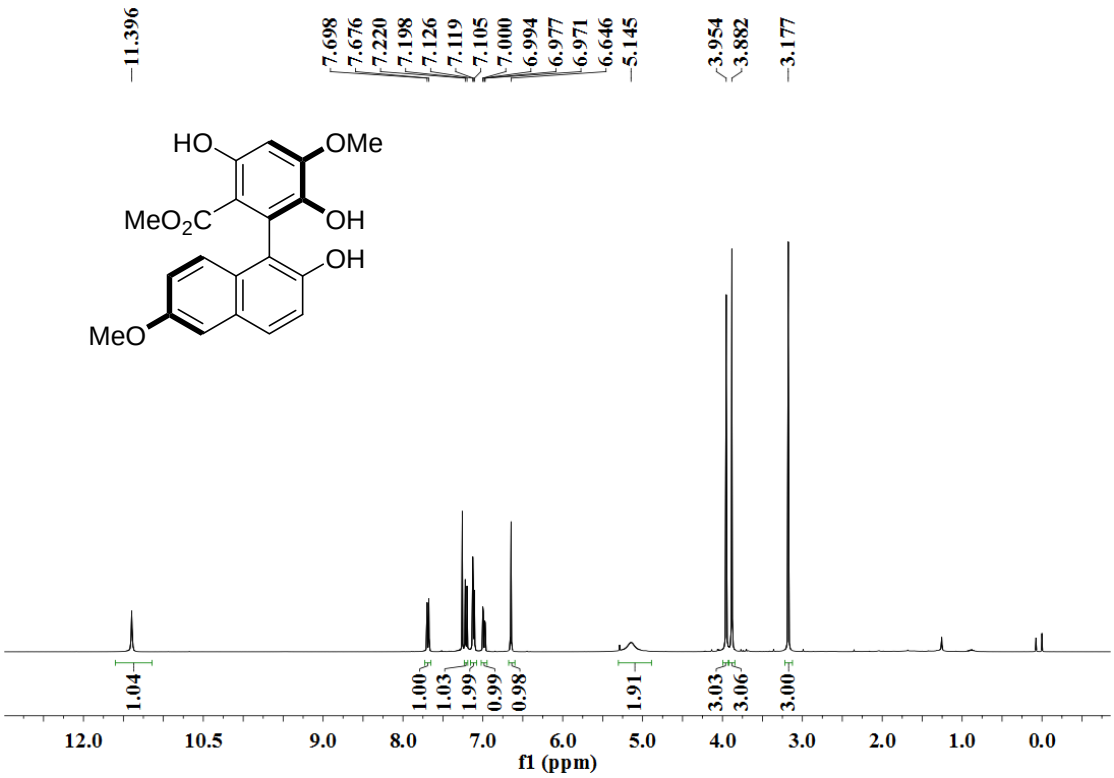
157.0
150.4
147.3
137.3
131.3
130.2
129.4
129.2
127.6
123.9
123.2
120.4
118.2
117.4
113.5
112.6
52.1
45.2
30.2
22.5
22.4
HO
MeO2C
OH
OH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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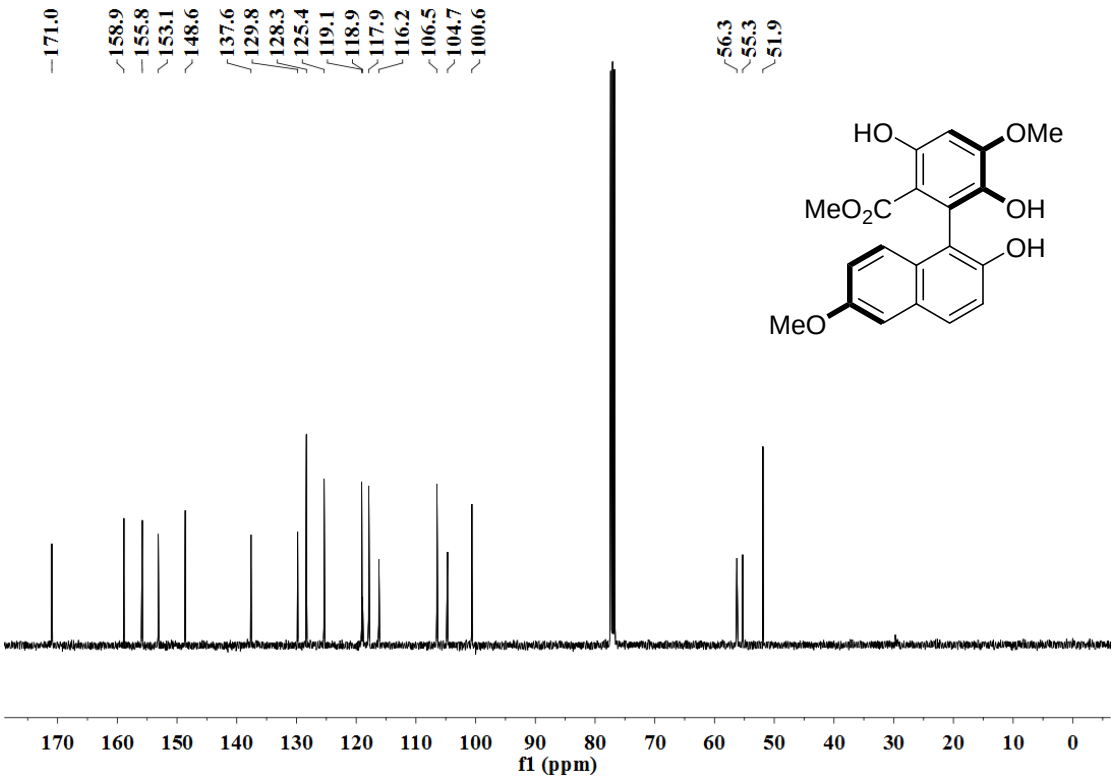
7.676
7.220
7.198
7.126
7.119
7.105
7.000
6.994
6.977
6.971
6.646
5.145
3.954
3.882
3.177
HO
OMe
MeO2C
OH
OH
MeO
1.04
1.00
1.03
1.99
0.99
0.98
1.91
3.03
3.06
3.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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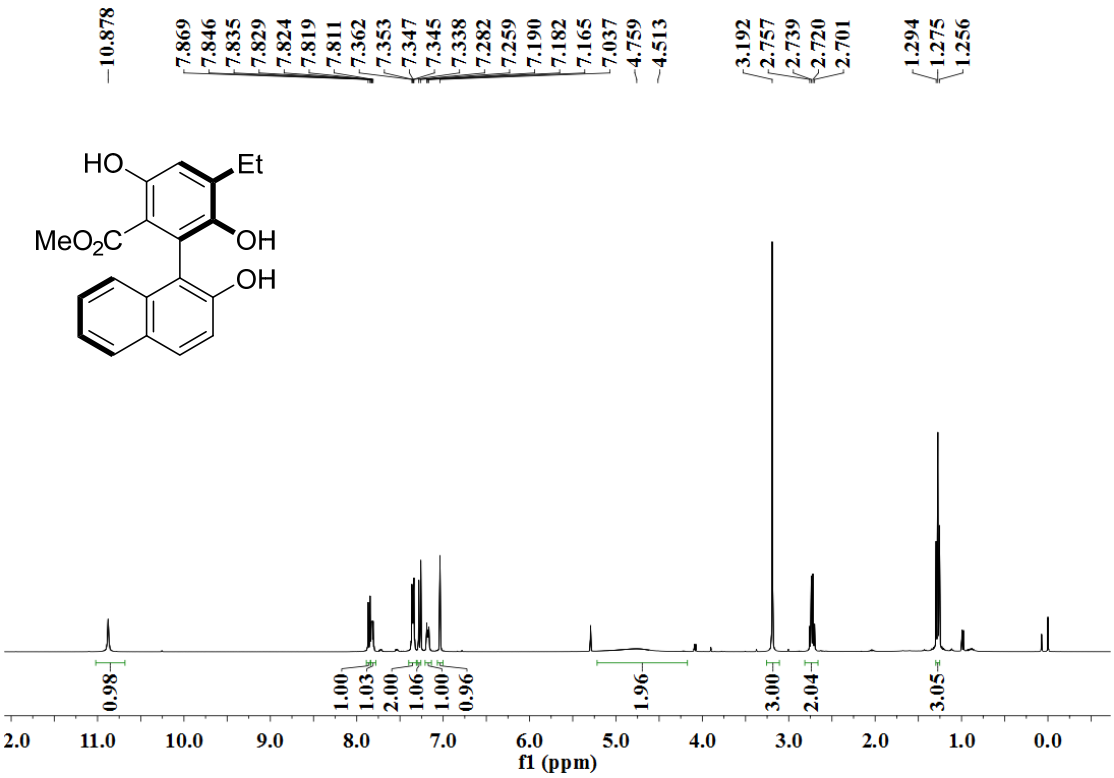
158.9
155.8
153.1
148.6
137.6
129.8
128.3
125.4
119.1
118.9
117.9
116.2
106.5
104.7
100.6
56.3
55.3
51.9
HO
OMe
MeO2C
OH
OH
MeO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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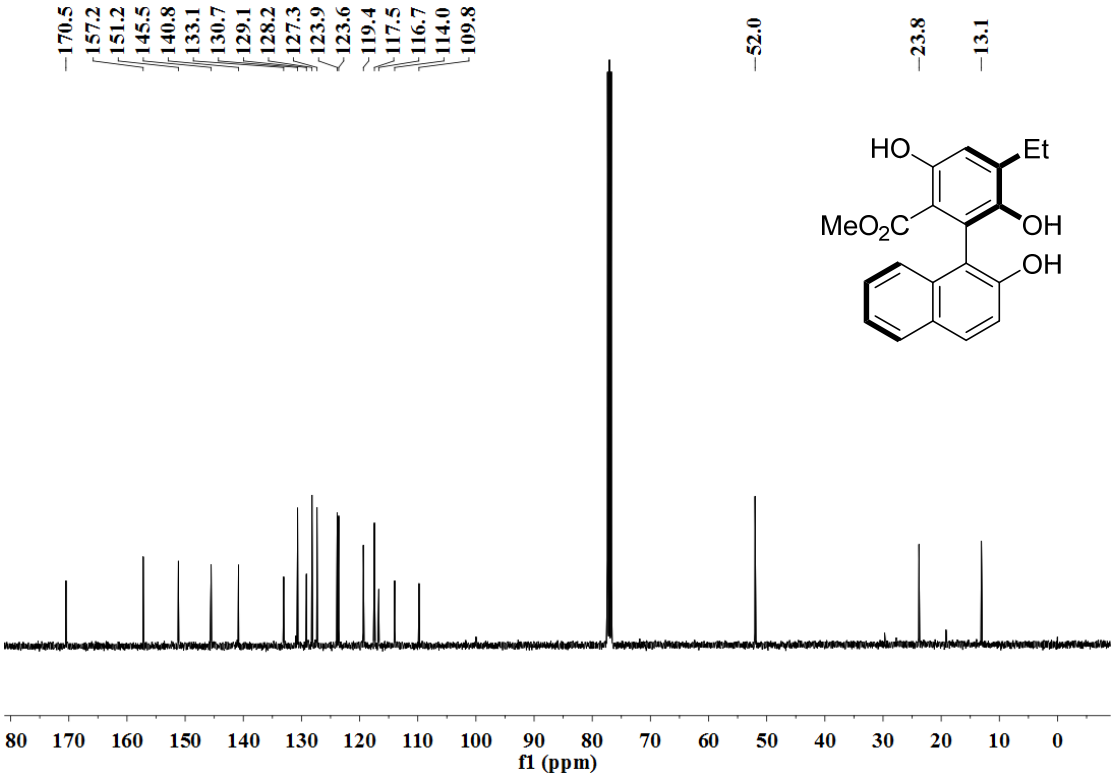
7.869
7.846
7.835
7.829
7.824
7.819
7.811
7.362
7.353
7.347
7.345
7.338
7.282
7.259
7.190
7.182
7.165
7.037
4.759
4.513
3.192
2.757
2.739
2.720
2.701
1.294
1.275
1.256
HO
Et
MeO2C
OH
OH
0.98
1.00
1.03
2.00
1.06
1.00
0.96
1.96
3.00
2.04
3.05
2.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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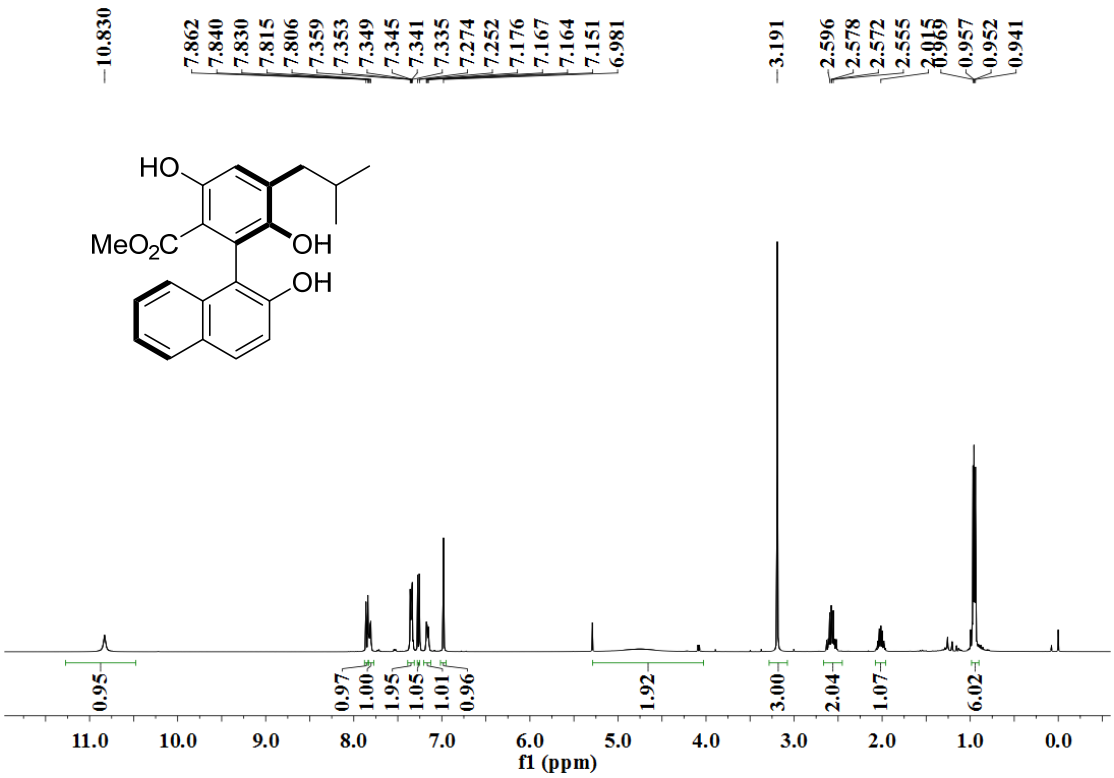
157.2
151.2
145.5
140.8
133.1
130.7
129.1
128.2
127.3
123.9
123.6
119.4
117.5
116.7
114.0
109.8
52.0
23.8
13.1
HO
Et
MeO2C
OH
OH
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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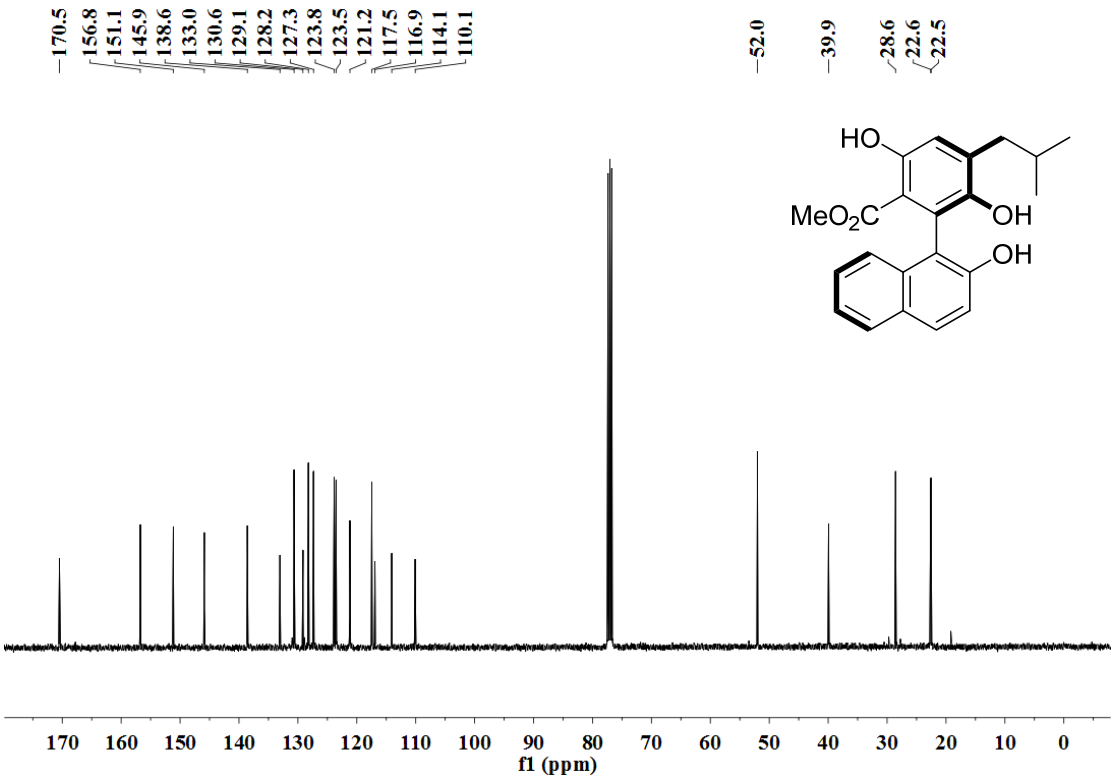
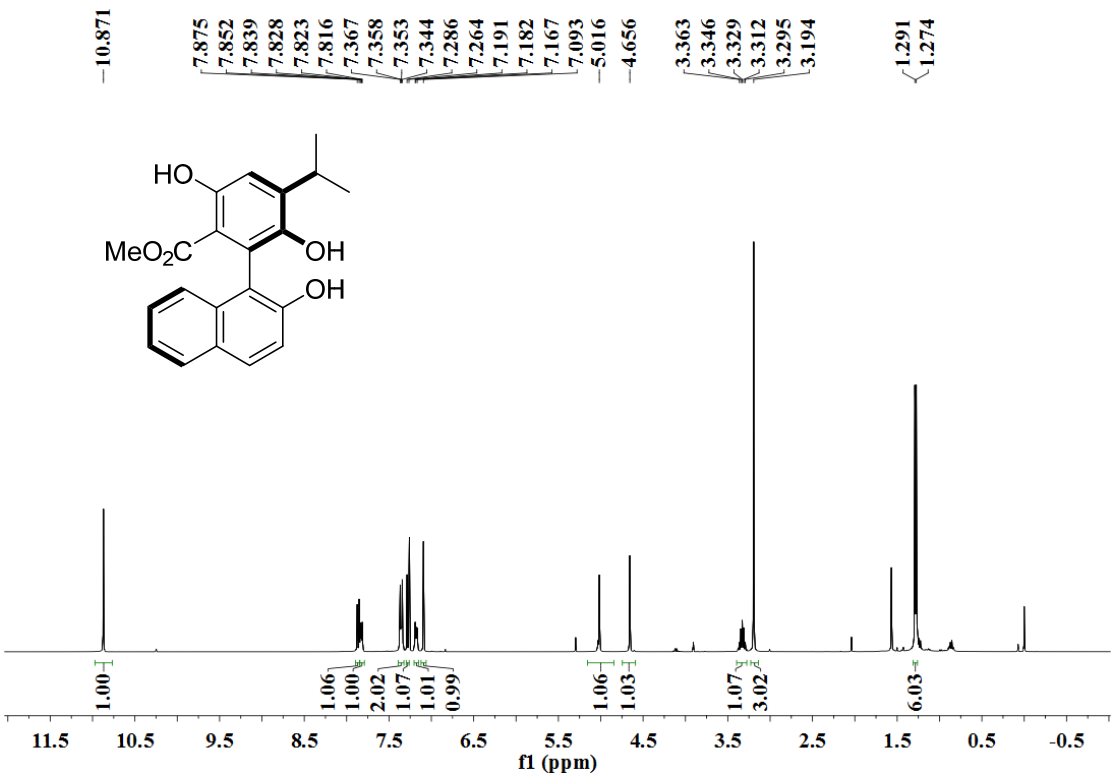
7.862
7.840
7.830
7.815
7.806
7.359
7.353
7.349
7.345
7.341
7.335
7.274
7.252
7.176
7.167
7.164
7.151
6.981
3.191
2.596
2.578
2.572
2.555
2.015
0.969
0.957
0.952
0.941
HO
MeO2C
OH
OH
0.95
0.97
1.00
1.95
1.05
1.01
0.96
1.92
3.00
2.04
1.07
6.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


170.5
156.8
151.1
145.9
138.6
133.0
130.6
129.1
128.2
127.3
123.8
123.5
121.2
117.5
116.9
114.1
110.1
52.0
39.9
28.6
22.6
22.5
HO
MeO2C
OH
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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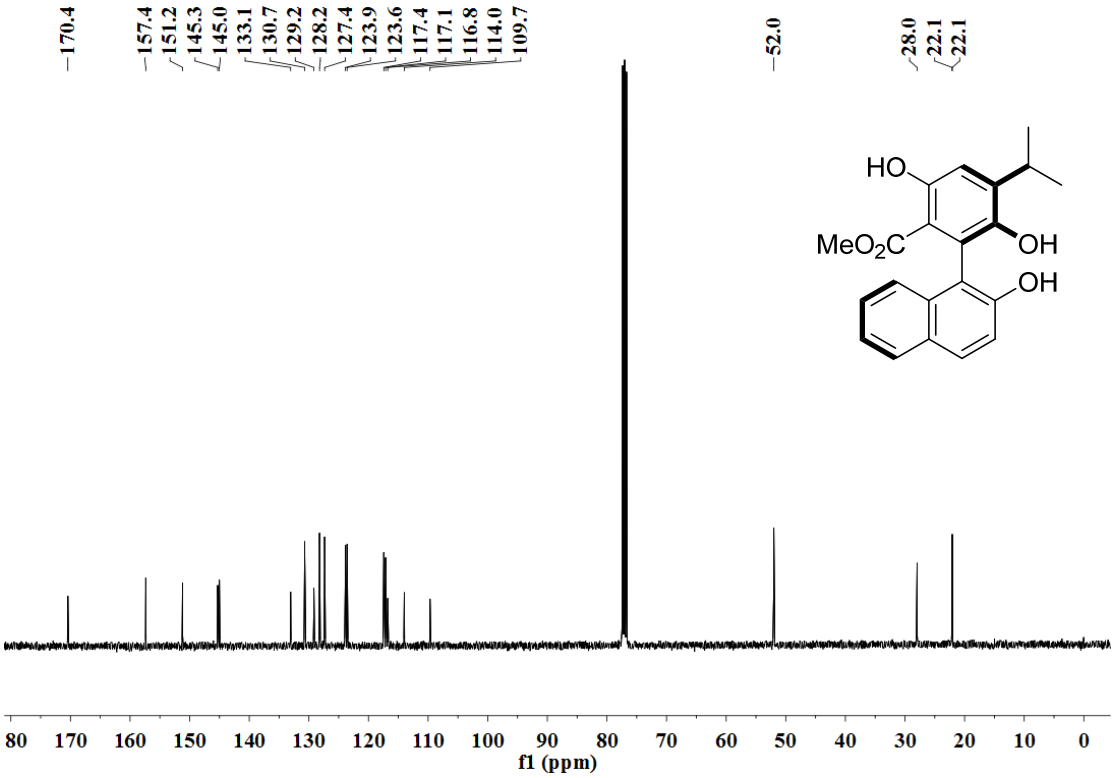
7.852
7.839
7.828
7.823
7.816
7.367
7.358
7.353
7.344
7.286
7.264
7.191
7.182
7.167
7.093
5.016
4.656
3.363
3.346
3.329
3.312
3.295
3.194
1.291
1.274
HO
MeO2C
OH
OH
1.00
1.06
1.00
2.02
1.07
1.01
0.99
1.06
1.03
1.07
3.02
6.03
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


170.4
157.4
151.2
145.3
145.0
133.1
130.7
129.2
128.2
127.4
123.9
123.6
117.4
117.1
116.8
114.0
109.7
52.0
28.0
22.1
22.1
HO
MeO2C
OH
OH
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)