Advanced Synthesis & Catalysis

Supporting Information

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# Total synthesis of viniferifuran, resveratrol-piceatannol hybrid, anigopreissin A and analogues – Investigation of demethylation strategies

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## General

LC-MS analysis was carried out on a Waters LC system equipped with an Xterra MS C18 18.5 µm 4.6 × 50 mm column and an eluent system consisting of MeCN in water, both of which contained 0.2 % formic acid. Detection was performed at 214 and 254 nm. Mass spectra were obtained by use of a Waters micromass ZG 2000, using both positive and negative electrospray ionization (ESI). $^{1}$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DRX-400 spectrometer in $CDCl_3$ solution [residual $CHCl_3$ (δH 7.26 ppm, δC 77.16 ppm) as internal standard] or in $SO(CD_3)_2$ solution [residual $SO(CD_3)(CD_2H)$ (δH 2.50 ppm, δC 39.52 ppm) as internal standard] or in $CO(CD_3)_2$ solution [residual $CO(CD_3)(CD_2H)$ (δH 2.05 ppm, δC 29.84 ppm) as internal standard] or in $CD_3OD$ solution [residual $CD_2HOH$ (δH 3.31 ppm, δC 49.00 ppm) as internal standard]. A Biotage Initiator 400W was used for microwave heating. TLC analysis was carried out using TLC Aluminum Sheets from EMD/Merck KGaA (mfr. no. Merck, 1.05554.0001). Product purification was done using Biotage flash chromatography (FC) with cartridge or ultra cartridge of 10 g, 25 g, 50 g or 100 g of silica gel. HPLC purification was carried out on a Gilson system equipped with a Macherey-Nagel Nucleodur C18 HTEC 5 µm 21 × 250 mm column. All eluents contained 0.005 % formic acid and the flowrate was set to 20 mL/minute for $CH_3CN$ and 15 mL/minute for MeOH (method A: $H_2O$/MeOH 80/20 to 0/100 over 30 min; method B: $H_2O$/ $CH_3CN$ 80/20 to 0/100 over 30 min).

## Abbreviations

$Ac_2O$ = acetic anhydride, $Bi(OTf)_3$ = bismuth(III) trifluoromethanesulfonate, DCM = dichloromethane, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DMA = dimethylacetamide, DME = dimethoxyethane, DMF = dimethylformamide, dppp = 1,4-bis(diphenylphosphino)propane, FC = flash chromatography, LAH = lithium aluminium hydride, MWI = microwave irradiation, NBS = N-bromosuccinimide, NIS = N-iodosuccinimide, $PCy_3{\cdot}HBF_4$ = tricyclohexylphosphine tetrafluoroborate, $PdCl(C_3H_5)$dppb = 1,4-bis(diphenylphosphino)butane-palladium(II) allyl chloride, $PdCl_2$(dppf)·DCM = 1,1'-bis(diphenylphosphino)ferrocene-palladium(II) dichloride dichloromethane complex, PivOH = pivalic acid, pTsOH = p-toluenesulfonic acid, TBAI = tetrabutylammonium idodide, $Tf_2O$ = triflic anhydride, THF = tetrahydrofuran.

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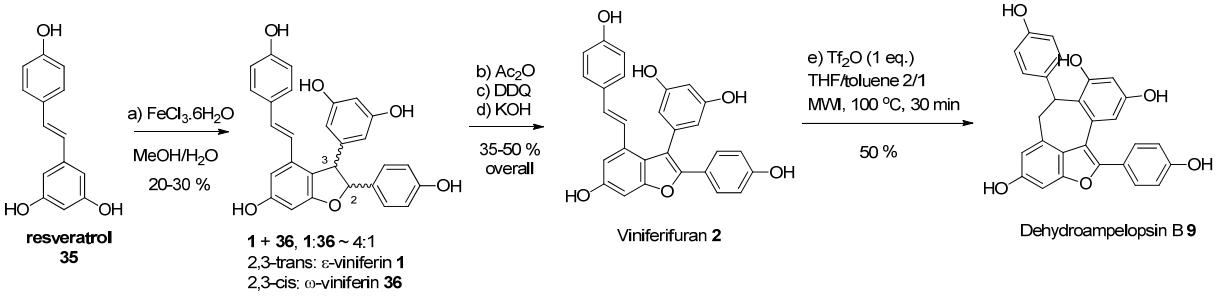
**SI-1. Biomimetic approach to viniferifuran 2 and dehydroampelopsin B 9**[1-3]

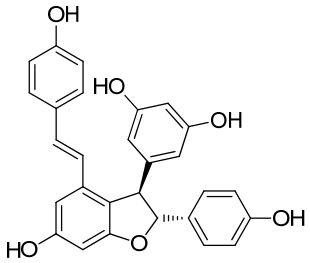



**Scheme S1.**

Reagents and conditions: a) $FeCl_3.6H_2O$ (1 eq.), $MeOH/H_2O$, rt, 48 h, 20-30 % (**1** + **36**). b) $Ac_2O$, THF, $Et_3N$, rt, overnight. c) DDQ, DCM, reflux, 48 h. d) KOH, MeOH, 0 °C, 30 min, 35-50 % overall 3 steps. e) $Tf_2O$ (1 eq.), THF/toluene 2/1, MWI, 100 °C, 30 min, 50 %.

Step a: Dimerization of resveratrol[1]

To a solution of resveratrol (12.36 g, 54.15 mmol, 1 eq.) in a mixture of MeOH-$H_2O$ (1/1, v/v, 400 mL) at rt, was added $FeCl_3.6H_2O$ (14.88 g, 1 eq.). The mixture was stirred at rt for 48 h. MeOH was evaporated and the mixture was extracted with EtOAc (300 mL). The organic phase was dried with $Na_2SO_4$ and concentrated. FC (heptane:acetone 2:1) gave mixture of **1** + **36** (**1**:**36** = 4:1) as yellow solid. Yield: 2.58 g (21 %). The major product ε-vinferin **1** (rac) could be separated using HPLC method A.



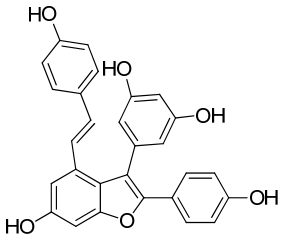
$^1$H NMR (400 MHz, $CD_3OD$) $\delta$ (ppm): 7.15 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 16.3 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 2.0 Hz, 1H), 6.57 (d, *J* = 16.3 Hz, 1H), 6.26 (d, *J* = 2.0 Hz, 1H), 6.19 (t, *J* = 2.1 Hz, 1H), 6.17 (d, *J* = 2.1 Hz, 2H), 5.37 (d, *J* = 6.6 Hz, 1H), 4.35 (d, *J* = 6.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CD_3OD$) $\delta$ (ppm): 162.8, 160.1, 159.8, 159.7, 158.5, 158.4, 147.4, 137.0, 136.9, 133.9, 130.5, 130.4, 128.8, 128.2, 123.8, 123.7, 120.1, 116.4, 116.3, 107.5, 104.4, 102.2, 96.9, 94.9, 58.3; ESIMS m/z $[M-H]^-$ calcd. 453.13; found 453.06. Analytical data are in agreement with those reported in the literature.[1]

Step b-d: Biomimetic synthesis of viniferifuran **2**[2-3]

To a solution of **1**/**36** (1.77 g, 3.9 mmol, 1 eq.) in THF (200 mL) at 0 °C, was added $Ac_2O$ (3.67 mL, 39 mmol, 10 eq.) and $Et_3N$ (3.26 mL, 23.4 mmol, 6 eq.). The mixture was allowed to reach rt and stirred for overnight. Solvent was evaporated and the residue was purified by FC (heptane:EtOAc 3:2) to afford desired product as white solid. Yield: 1.95 g (75 %).

Next, to a solution of the above obtained acetylated product (1.95 g, 2.93 mmol, 1 eq.) in DCM (150 mL) at rt was added DDQ (13.3 g, 58.6 mmol, 20 eq.). The mixture was stirred under reflux for 48 h. After cooling the mixture was filtered on celite and then concentrated under reduced pressure. FC (heptane:EtOAc 6:4) gave desired product as white solid. This material was used as such for the next step.

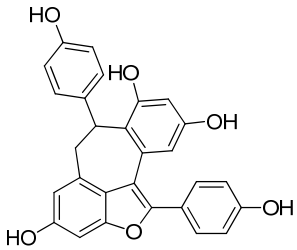
To a solution of the obtained acetylated benzofuran derivative (2.93 mmol, 1 eq., expected) in MeOH at 0 °C was added KOH (1.61 g, 29.3 mmol, 10 eq.). The mixture was stirred at 0 °C for 30 min and then acidified with 1N HCl until pH = 1. The mixture was diluted with EtOAc (150 mL), washed with $H_2O$ (30 mL) and brine (30 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (DCM:MeOH 9:1) gave desired product viniferifuran **2** as yellow solid. Yield: 920 mg (69 %, 2 steps, 90-95 % pure). > 98 % pure product could be obtained using HPLC method A.




$^1$H NMR (400 MHz, $CD_3OD$) $\delta$ (ppm): 7.43 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 16.3 Hz, 1H), 6.85 (d, *J* = 16.3 Hz, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.48 (t, *J* = 2.2 Hz, 1H), 6.41 (d, *J* = 2.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CD_3OD$) $\delta$ (ppm): 160.7, 158.5, 158.2, 156.6, 156.4, 150.6, 138.7, 133.3, 130.7, 129.3, 128.8, 128.5, 123.9, 123.3, 122.5, 117.4, 116.4, 116.2, 110.2, 107.4, 103.1, 97.4; ESIMS m/z $[M-H]^-$ calcd. 451.12; found 451.05. Analytical data are in agreement with those reported in the literature.[2-3]

Step e: Synthesis of dehydroampelopsin B **9** (rac)

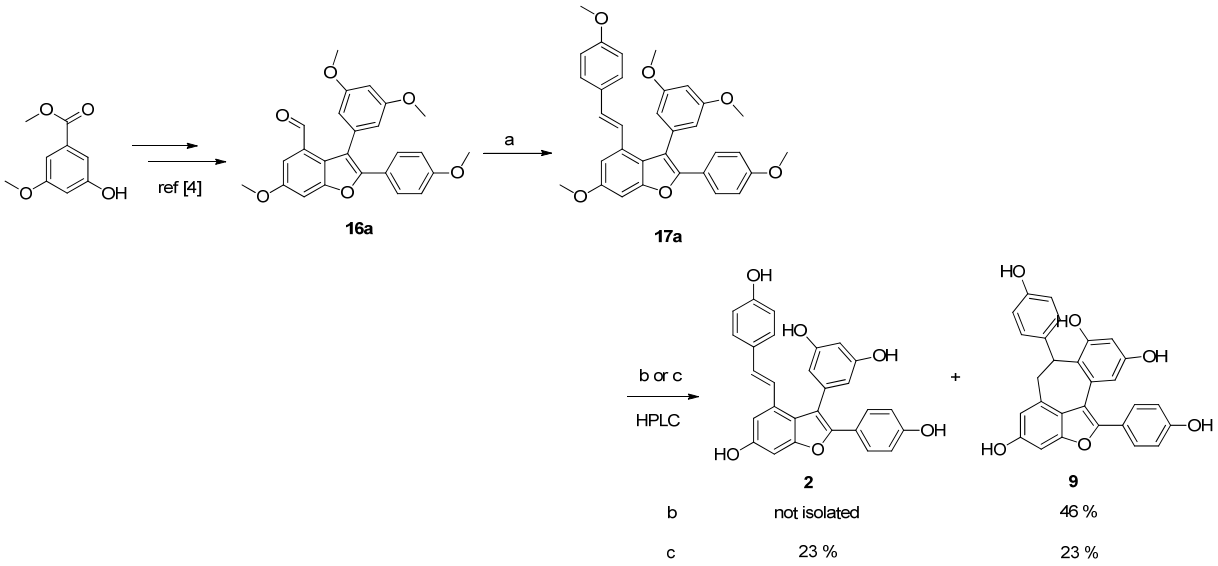
To a solution of viniferifuran **2** (30 mg, 0.066 mmol, 1 eq.) in a mixture of THF/toluene (2/1, v/v, 3 mL) in a microwave vial, was added a 0.1 M solution of $Tf_2O$ in DCM (0.3 mL, 1 eq.). The mixture was heated at 100 °C under MWI for 30 min. After cooling down, the mixture was diluted with EtOAc (25 mL), washed with saturated $NaHCO_3$ solution (5 mL), $H_2O$ (5 mL) and brine (5 mL). ). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (DCM:MeOH 93:7) gave desired product dehydroampelopsin B **9** as yellow solid. Yield: 15 mg (50 %).




$^1$H NMR (400M Hz, acetone-d6) $\delta$ (ppm): 8.68 (s, 1H), 8.34 (s, 1H), 8.23 (s, 1H), 8.06 (s, 1H), 7.74 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.99 (dd, *J* = 8.7, 0.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.65-6.64 (m, 1H), 6.62 (d, *J* = 2.5 Hz, 1H), 6.59 (dd, *J* = 1.9, 0.6 Hz, 1H), 6.48 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 2.6 Hz, 1H), 5.44 (d, *J* = 4.9 Hz, 1H), 3.69 (d, *J* = 16.3, 6.1 Hz, 1H), 3.39 (d, *J* = 16.3 Hz, 1H); $^{13}$C NMR (100 MHz, acetone-d6) $\delta$ (ppm):

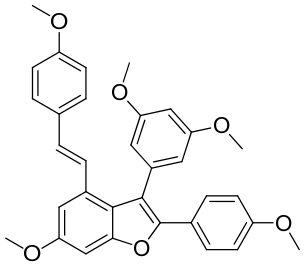
159.6, 157.9, 157.7, 156.9, 156.4, 156.1, 151.9, 137.0, 136.8, 135.5, 131.7, 130.2, 125.4, 123.4, 121.8, 117.9, 117.3, 116.1, 114.5, 111.0, 103.3, 96.5, 38.9, 38.8; ESIMS m/z $[M-H]^-$ calcd. 451.12; found 451.00.

**SI-2. Synthesis of permethylated viniferifuran described by Kim and Choi [4] and final demethylation by $BBr_3$ and $BCl_3$/TBAI**




**Scheme S2.** Reagents and conditions: a) diethyl 4-methoxybenzylphosphonate (1.5 eq.), NaH (3 eq.), THF, 120 °C, MWI, 30 min, 80 %. g) $BBr_3$ (1M in DCM), 0 °C - rt, 6 h, HPLC purification. c) $BCl_3$ (1M in DCM), TBAI, DCM, 0 °C - rt, 6 h, HPLC purification.

The mixture of **16a** (100 mg, 0.24 mmol. 1 eq.), 60 % NaH (28.8 mg, 0.72 mmol, 3 eq.) and diethyl 4-methoxybenzylphosphonate (92.6 mg, 0.36 mmol, 1.5 eq.) in THF (3 mL) in a MW vial was closed and heated at 120 °C under MWI for 30 min. After cooling, sat. $NH_4Cl$ (1 mL) was added and the mixture was extracted with EtOAc (25 mL): The organic phase was washed with $H_2O$ (5 mL) and brine (5 mL), dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane: EA 4:1) gave **17a** as yellow solid. Yield: 100 mg (80 %).



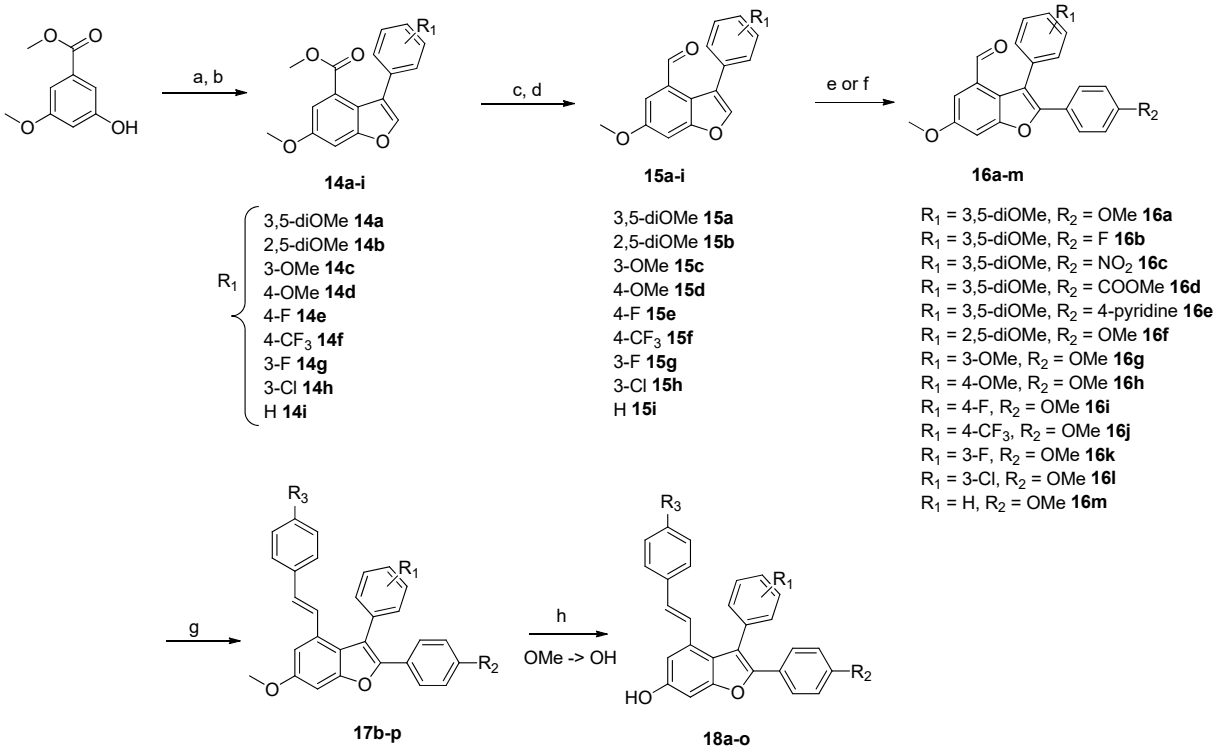
**17a**: $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm): 7.53 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 1.6 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 1.6 Hz, 1H), 6.88 (d, *J* = 16.3 Hz, 1H), 6.85 (d, *J* = 16.3 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.66 (d, *J* = 1.9 Hz, 2H), 6.63 (t, *J* = 1.9 Hz, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.74 (s, 6H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm): 161.4, 159.2, 159.1, 158.0, 154.9, 149.7, 136.9, 132.1, 130.2, 128.5, 127.6, 127.5, 123.5, 123.1, 122.0, 116.3, 113.9, 113.8, 108.5, 106.6, 100.4, 94.9. ESIMS m/z $[M+H]^+$ calcd. 523.21; found 523.07. Analytical data are in agreement with those reported in the literature.[4]

To a stirred solution of **17a** (25 mg, 0.048 mmol, 1 eq.) at 0 °C in DCM (3 mL) under nitrogen atmosphere was added 1 M $BBr_3$ solution in DCM (0.72 mL, 0.72 mmol, 15 eq.). The mixture was allowed to warm up

and stirred at rt for 6 h. The reaction was quenched with $H_2O$ (1 mL) at 0 °C. The mixture was diluted with EtOAc (25 mL), washed with $H_2O$ (5 mL) and brine (5 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (DCM:MeOH 9:1) followed by HPLC method A gave dehydroampelopsin B **9** as yellow solid. Yield: 10 mg (46 %).

To a stirred solution of **17a** (25 mg, 0.048 mmol, 1 eq.), TBAI (265 mg, 0.72 mmol, 15 eq.) at 0 °C in DCM (3 mL) under nitrogen atmosphere was added 1 M $BCl_3$ solution in DCM (0.72 mL, 0.72 mmol, 15 eq.). The mixture was stirred at rt for 6 h. The reaction was quenched with $H_2O$ (1 mL) at 0 °C. The mixture was diluted with EtOAc (25 mL), washed with 10 % $Na_2S_2O_3$ solution (5 mL), $H_2O$ (5 mL) and brine (5 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (DCM:MeOH 9:1) afforded a 1:1 mixture of **2** and **9** that was purified using HPLC method A to give viniferifuran **2** (5 mg, 23 %) and dehydroampelopsin B **9** (5 mg 23 %) as yellow solids.

**SI-3. Synthetic procedures for viniferifuran analogues using final demethylation by $BCl_3$/TBAI**




**Scheme S3.** Reagents and conditions: a) bromoacetophenone derivatives (1 eq.), $K_2CO_3$, acetone, 70 °C, 2 h, 80-90 %. b) $Bi(OTf)_3$ (0.2 eq.), DCM, reflux, 20 h, 70-90 %. c) LAH (3 eq.), THF, 0 °C, 10 min. d) Dess-Martin periodinane (1.2 eq.), DCM, 0 °C, 1 h, 80-90 %, 2 steps. e) ArBr or ArI (1.5-2 eq.), $Pd(OAc)_2$ (0.1 eq.), $PCy_3 \cdot HBF_4$ (0.2 eq.), $K_2CO_3$ (1.5 eq.), PivOH (3 eq.), 100 °C, 20 h, 35-74 %. f) ArBr (1.5-2 eq.), $PdCl(C_3H_5)$dppb, KOAc (2 eq.), DMA, 150 °C, 20 h, 47-60 %. g) phosphonate derivatives (1.5 eq.), NaH (3 eq.), THF, 120 °C, MWI, 30 min, 52-82 %. h) $BCl_3$, TBAI, DCM, 0 °C - rt, 6 h.

**A) General procedure for alkylation of bromoacetophenone derivatives with phenols[4] (Exampliefied by methyl 3-(2-(3,5-dimethoxyphenyl)-2-oxoethoxy)-5-methoxy-benzoate)**

The mixture of methyl 3-hydroxy-5-methoxybenzoate (2.72 g, 14.94 mmol. 1 eq.), 3,5-dimethoxybromoacetophenone (3.87 g, 1 eq.) and $K_2CO_3$ (6.19 g, 44.81 mmol, 3 eq.) in acetone (150 mL) was stirred under reflux for 2 h. After cooling down, the mixture was filtered off $K_2CO_3$ and concentrated under reduced pressure. FC (heptane:EtOAc 85:15) gave as pale yellow solid. Yield: 5.38 g (94 %).

**B) General procedure for sequence one pot cyclization-dehydratation to form 3-arylbenzofuran catalyzed by $Bi(OTf)_3$ from aryloxy ketone[4] (Examplified by 14a)**

The mixture of aryloxy ketone above (1.55 g, 4.29 mmol. 1 eq.), $Bi(OTf)_3$ (563 mg, 0.86 mmol, 0.2 eq.) in DCM (100 mL) was stirred under reflux for 20 h. After cooling, the mixture was filtered on celite and

concentrated under reduced pressure. FC (heptane:DCM:EtOAc 7:3:1) gave **14a** as pale yellow solid. Yield: 1.14 g (78 %).

**C) General procedure for transformation of ester to aldehyde (Examplified with 15a)**

Step 1: to a solution of **14a** (1.81 g, 5.31 mmol, 1 eq.) in THF (50 mL) at 0 °C, was added LAH (605 mg, 3 eq.). The reaction was stirred at 0 °C for 10 min then quenched with 1N HCl (50 mL) and extract with EtOAc (50 mL x 3). The collected organic phases were dried with $Na_2SO_4$ and concentrated under reduced pressure to give a crude alcohol that was used as such for the next step.

Step 2: to a solution of the above obtained alcohol (5.31 mmol, 1 eq. expected) in DCM (30 mL) at 0 °C was added Dess-Martin periodinane reagent (3.02 g, 6.91 mmol, 1.3 eq.). The reaction was stirred at rt for 1 h. The mixture was then filtered using DCM as washing solvent. The organic phase was concentrated to give a crude which was purified by FC (heptane:EtOAc 85:15) to give **15a** as yellow solid. Yield: 1.09 g (87 %, 2 steps).

**D) General procedure for direct arylation with $Pd(OAc)_2$[5-6] (Examplified with 16a)**

The mixture of **15a** (400 mg, 1.28 mmol, 1 eq.), 4-bromoanisole (0.32 mL, 2.56 mmol, 2 eq.), $Pd(OAc)_2$ (28.8 mg, 0.128 mmol, 0.1 eq.), $PCy_3 \cdot HBF_4$ (94.4 mg, 0.256 mmol, 0.2 eq.), $K_2CO_3$ (266 mg, 1.92 mmol, 1.5 eq.), PivOH (392 mg, 3.84 mmol, 3 eq.) in DMA (5 mL) was closed and degassed then heated at 100 °C for 20 h. After cooling down, the mixture was diluted with EtOAc (100 mL), washed with $H_2O$ (50 x 3 mL) and brine (50 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane:EtOAc 85:15) gave **16a** as yellow solid. Yield: 400 mg (74 %).

**D') General procedure for direct arylation with $PdCl(C_3H_5)$dppb[7] (Examplified with 16a)**

The mixture of **15a** (50 mg, 0.16 mmol, 1 eq.), 4-bromoanisole (0.03 mL, 0.24 mmol, 1.5 eq.), $PdCl(C_3H_5)$dppb (4.9 mg, 0.008 mmol, 0.05 eq.), KOAc (47 mg, 0.48 mmol, 3 eq.) in dimethylacetamide (DMA) (2 mL) was closed and degassed then heated at 150 °C for 20 h. After cooling down, the mixture was diluted with EtOAc (25 mL), washed with $H_2O$ (10 x 3 mL) and brine (10 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane:EtOAc 85:15) gave **16a** as yellow solid. Yield: 40 mg (60 %).

**E) General procedure for Wittig-Horner olefination using MWI (Examplified with 17a)**

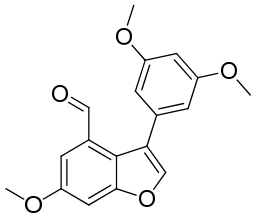
The mixture of **16a** (100 mg, 0.24 mmol. 1 eq.), 60 % NaH (28.8 mg, 0.72 mmol, 3 eq.) and diethyl 4-methoxybenzylphosphonate (92.6 mg, 0.36 mmol, 1.5 eq.) in THF (3 mL) in a MW vial was closed and heated at 120 °C under MWI for 30 min. After cooling down, sat. $NH_4Cl$ (1 mL) was added and the mixture was extracted with EtOAc (25 mL): The organic phase was washed with $H_2O$ (5 mL) and brine (5 mL), dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane:EtOAc 4:1) gave **17a** as yellow solid. Yield: 100 mg (80 %).

**F) General procedure for demethylation with $BBr_3$ (Examplified with dehydroampelopsin B, 9)**

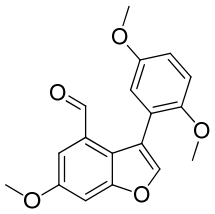
To a stirred solution of **17a** (25 mg, 0.048 mmol, 1 eq.) at 0 °C in DCM (3 mL) under nitrogen atmosphere was added 1 M $BBr_3$ solution in DCM (0.72 mL, 0.72 mmol, 15 eq.). The mixture was allowed to warm up and stirred at rt for 6 h. The reaction was quenched with $H_2O$ (1 mL) at 0 °C. The mixture was diluted with EtOAc (25 mL), washed with $H_2O$ (5 mL) and brine (5 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (DCM:MeOH 9:1) afforded a mixture that was purified using HPLC method A to give dehydroampelopsin B **9** as yellow solid. Yield: 10 mg (46 %).

**F') General procedure for demethylation with $BCl_3$/TBAI (Examplified with dehydroampelopsin B, 9 and viniferifuran, 2)**

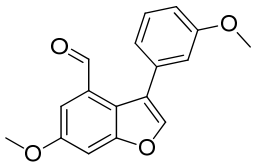
To a stirred solution of **17a** (25 mg, 0.048 mmol, 1 eq.), TBAI (265 mg, 0.72 mmol, 15 eq.) at 0 °C in DCM (3 mL) under nitrogen atmosphere was added 1 M $BCl_3$ solution in DCM (0.72 mL, 0.72 mmol, 15 eq.). The mixture was stirred at rt for 6 h. The reaction was quenched with $H_2O$ (1 mL) at 0 °C. The mixture was diluted with EtOAc (25 mL), washed with 10 % $Na_2S_2O_3$ solution (5 mL), $H_2O$ (5 mL) and brine (5 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (DCM:MeOH 9:1) afforded a 1:1 mixture of **2** and **9** that was purified using HPLC method A to give viniferifuran **2** (5 mg, 23 %) and dehydroampelopsin B **9** (5 mg, 23 %) as yellow solids.



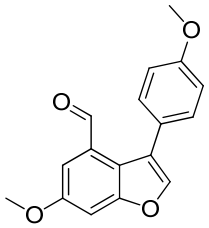
**15a:** Yield: 1.09 g (65 %, 4 steps from methyl 3-hydroxy-5-methoxybenzoate using procedure A, B and C). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 10.21 (s, 1H), 7.64 (s, 1H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.32 (d, *J* = 1.6 Hz, 1H), 6.62 (d, *J* = 1.5 Hz, 2H), 6.51 (t, *J* = 1.5 Hz, 1H), 3.91 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.8, 161.1, 157.8, 157.1, 143.5, 134.5, 129.8, 122.6, 121.9, 108.7, 103.3, 100.2, 56.1, 55.4; ESIMS m/z $[M+H]^+$ calcd. 313.11; found 313.04.



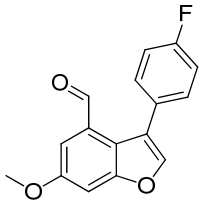
**15b:** Yield: 120 mg (42 %, 4 steps from methyl 3-hydroxy-5-methoxybenzoate using procedure A, B and C). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.93 (s, 1H), 7.64 (s, 1H), 7.49 (d, *J* = 1.8 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 1H), 7.03-6.83 (m, 3H), 3.91 (s, 3H), 3.82 (s, 3H), 3.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 190.5, 157.6, 157.0, 153.9, 151.2, 143.9, 130.4, 122.2, 118.7, 117.2, 114.0, 111.5, 108.3, 103.1, 56.1, 55.8, 55.5; ESIMS m/z $[M+H]^+$ calcd. 313.11; found 313.04.



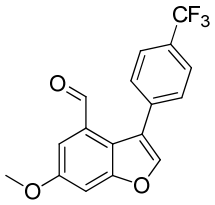
**15c:** Yield: 174 mg (57 %, 4 steps from methyl 3-hydroxy-5-methoxybenzoate using procedure A, B and C). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 10.17 (s, 1H), 7.64 (s, 1H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 2.2 Hz, 1H), 6.96 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.92 (s, 3H), 3.83 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.6, 159.9, 157.8, 157.2, 143.6, 134.0, 130.0, 129.9, 122.6, 121.9, 121.7, 114.9, 113.8, 108.8, 103.4, 56.1, 55.3; ESIMS m/z $[M+H]^+$ calcd. 283.10; found 283.04.



**15d:** Yield: 170 mg (58 %, 4 steps from methyl 3-hydroxy-5-methoxybenzoate using procedure A, B and C).$^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 10.16 (s, 1H), 7.60 (s, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 2.3 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 3H), 3.86 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.6, 159.6, 157.7, 157.2, 143.5, 130.5, 130.0, 124.7, 123.1, 121.6, 114.4, 108.6, 103.4, 56.1, 55.4; ESIMS m/z $[M+H]^+$ calcd. 283.10; found 283.04.

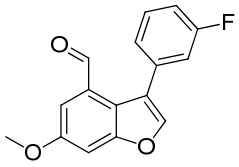


**15e:** Yield: 620 mg (83 %, 4 steps from methyl 3-hydroxy-5-methoxybenzoate using procedure A, B and C). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 10.10 (s, 1H), 7.62 (s, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 7.44 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.16 (t, *J* = 8.5 Hz, 2H), 3.92 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.2, 162.7 (d, *J* = 247.9 Hz), 157.9, 157.2, 143.8, 131.0 (d, *J* = 8.1 Hz), 130.0, 128.6 (d, *J* = 3.5 Hz), 122.4, 121.1, 115.9 (d, *J* = 21.6 Hz), 109.5, 103.3, 56.1; ESIMS m/z $[M+H]^+$ calcd. 271.08; found 271.00.

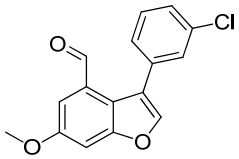


**15f:** Yield: 46 mg (67 %, 4 steps from methyl 3-hydroxy-5-methoxybenzoate using procedure A, B and C). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 10.09 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.68 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.36 (d, *J* = 2.3 Hz, 1H), 3.93 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.0,

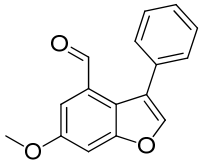
158.1, 157.4, 144.1, 136.7, 130.4 (q, *J* = 32.7 Hz), 129.7, 125.7 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.2 Hz), 121.4, 121.1, 110.5, 103.3, 56.1; ESIMS m/z $[M+H]^+$ calcd. 321.07; found 321.01.



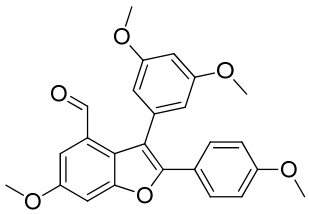
**15g:** Yield: 88 mg (41 %, 4 steps from methyl 3-hydroxy-5-methoxybenzoate using procedure A, B and C). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 10.13 (s, 1H), 7.65 (s, 1H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.42 (td, *J* = 7.9, 6.0 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.26 (dt, *J* = 8.8, 1.2 Hz, 1H), 7.19 (dt, *J* = 11.7, 2.4 Hz, 1H), 7.13 (ddd, *J* = 8.6, 2.6, 0.9 Hz, 1H), 3.92 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.1, 162.8 (d, *J* = 247.5 Hz), 158.0, 157.3, 143.9, 134.9 (d, *J* = 8.1 Hz), 130.4 (d, *J* = 8.6 Hz), 129.9, 125.1 (d, *J* = 2.9 Hz), 121.9, 121.1, 116.4 (d, *J* = 21.9 Hz), 115.2 (d, *J* = 20.8 Hz), 109.7, 103.3, 56.1; ESIMS m/z $[M+H]^+$ calcd. 271.08; found 271.00.



**15h:** Yield: 131 mg (51 %, 4 steps from methyl 3-hydroxy-5-methoxybenzoate using procedure A, B and C). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 10.12 (s, 1H), 7.65 (s, 1H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.49-7.47 (m, 1H), 7.42-7.34 (m, 3H), 7.34 (d, *J* = 2.4 Hz, 1H), 3.92 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.1, 158.0, 157.3, 144.0, 134.7, 134.6, 130.0, 129.9, 129.4, 128.4, 127.5, 121.8, 121.0, 109.8, 103.3, 56.1; ESIMS m/z $[M+H]^+$ calcd. 287.05; found 287.00.

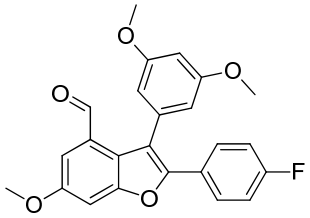


**15i:** Yield: 168 mg (63 %, 4 steps from methyl 3-hydroxy-5-methoxybenzoate using procedure A, B and C). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 10.14 (s, 1H), 7.64 (s, 1H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.52-7.40 (m, 5H), 7.34 (d, *J* = 2.1 Hz, 1H), 3.92 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.5, 157.8, 157.3, 143.7, 132.7, 129.9, 129.3, 128.9, 128.3, 122.6, 122.1, 108.9, 103.4, 56.1; ESIMS m/z $[M+H]^+$ calcd. 253.09; found 253.03.

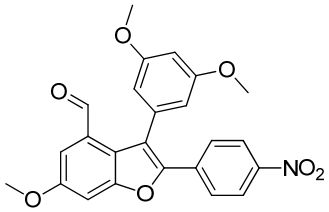


**16a:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.78 (s, 1H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 2.3 Hz, 1H), 7.32 (d, *J* = 2.3 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 2.3 Hz, 2H), 6.56 (t, *J* = 2.3 Hz, 1H), 4.45 (s, 2H), 3.91 (s, 3H), 3.80 (s, 3H), 3.79 (s, 6H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm): 189.7, 161.9, 159.9, 157.4, 155.2,

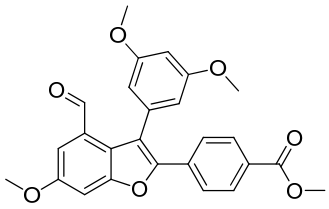
152.2, 136.4, 129.4, 128.0, 126.8, 122.6, 114.9, 114.0, 107.8, 107.4, 103.2, 100.6, 56.1, 56.4, 55.3; ESIMS m/z $[M+H]^+$ calcd. 419.15; found 419.08.



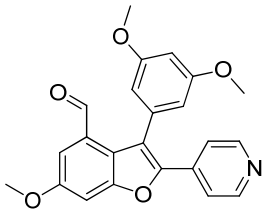
**16b:** Application of **procedure D** for direct arylation of **15a** (200 mg, 0.64 mmol, 1 eq.). FC (heptane:EtOAc 85:15) gave **16b** as yellow solid. Yield: 156 mg (60 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.78 (s, 1H), 7.57 (dd, *J* = 9.0, 5.4 Hz, 2H), 7.48 (d, *J* = 2.4 Hz, 1H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.00 (t, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 2.3 Hz, 2H), 6.82 (t, *J* = 2.3 Hz, 1H), 3.93 (s, 3H), 3.79 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm): 189.5, 162.7 (d, *J* = 249.9 Hz), 162.0, 157.8, 155.3, 151.1, 135.9, 129.7, 128.3 (d, *J* = 8.0 Hz), 126.2, 126.1 (d, *J* = 3.3 Hz), 116.2, +115.7 (d, *J* = 21.8 Hz), 108.0, 107.7, 103.1, 100.6, 56.1, 55.4; ESIMS m/z $[M+H]^+$ calcd. 407.13; found 407.06.



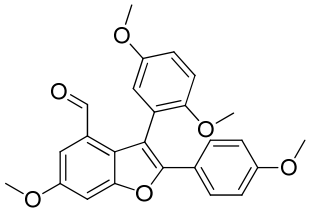
**16c:** Application of **procedure D** for direct arylation of **15a** (200 mg, 0.64 mmol). FC (heptane:EtOAc 85:15) gave desired product **16c** as yellow solid. Yield: 160 mg (58 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.77 (s, 1H), 8.15 (d, *J* = 9.1 Hz, 2H), 7.73 (d, *J* = 9.1 Hz, 2H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.36 (d, *J* = 2.3 Hz, 1H), 6.63-6.57 (m, 3H), 3.94 (s, 3H), 3.81 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.1, 162.2, 158.8, 155.8, 149.2, 146.9, 135.9, 135.2, 130.4, 126.6, 125.3, 123.9, 120.2, 109.3, 107.3, 102.7, 100.8, 56.2, 55.5; ESIMS m/z $[M+H]^+$ calcd. 434.12; found 434.05.



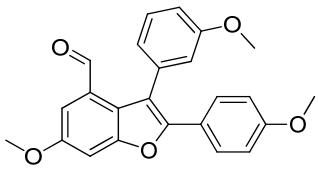
**16d:** Application of **procedure D'** for direct arylation of **15a** (165 mg, 0.53 mmol). FC (heptane:EtOAc 7:3) gave **16d** as yellow solid. Yield: 111 mg (47 %).$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.78 (s, 1H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 2.3 Hz, 1H), 7.36 (d, *J* = 2.3 Hz, 1H), 6.60 (d, *J* = 2.2 Hz, 1H), 6.58 (d, *J* = 2.2 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.79 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.4, 165.6, 162.0, 158.3, 155.6, 150.6, 135.7, 134.0, 130.1, 129.8, 129.5, 126.0, 125.8, 118.6, 108.6, 107.5, 102.9, 100.8, 56.1, 55.5, 52.2; ESIMS m/z $[M+H]^+$ calcd. 447.14; found 447.07.



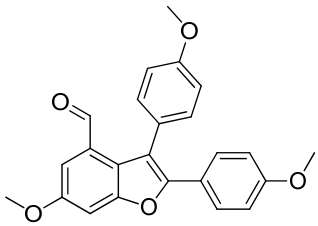
**16e:** Application of **procedure D** for direct arylation of **15a** (50 mg, 0.16 mmol). FC (heptane:EtOAc 7:3) gave **16e** as yellow solid. Yield: 30 mg (48 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.76 (s, 1H), 8.54 (d, $J$ = 6.3 Hz, 2H), 7.51 (d, $J$ = 2.3 Hz, 1H), 7.41 (d, $J$ = 6.3 Hz, 2H), 7.36 (d, $J$ = 2.3 Hz, 1H), 6.64-6.56 (m, 3H), 3.94 (s, 3H), 3.81 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.2, 162.1, 158.8, 155.7, 150.1, 148.7, 136.9, 135.1, 130.4, 125.2, 120.4, 119.7, 109.2, 107.3, 102.7, 100.9, 56.2, 55.5; ESIMS m/z $[M+H]^+$ calcd. 390.13; found 390.05.



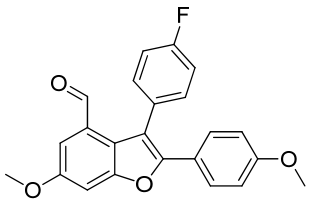
**16f:** Application of **procedure D** for direct arylation of **15b** (110 mg, 0.35 mmol). FC (heptane:EtOAc 4:1) gave **16f** as yellow solid. Yield: 95 mg (64 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.76 (s, 1H), 7.48 (d, $J$ = 9.0 Hz, 2H), 7.44 (d, $J$ = 2.3 Hz, 1H), 7.33 (d, $J$ = 2.3 Hz, 1H), 6.98 (d, $J$ = 1.6 Hz, 2H), 6.88 (t, $J$ = 1.5 Hz, 1H), 6.82 (d, $J$ = 9.0 Hz, 2H), 3.92 (s, 3H), 3.80 (s, 3H), 3.72 (s, 3H), 3.68 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 190.0, 159.8, 157.2, 155.5, 154.1, 152.8, 151.9, 129.7, 128.1, 126.1, 123.7, 122.8, 117.3, 115.0, 113.9, 112.6, 111.3, 107.2, 103.2, 56.1, 56.0, 55.8, 55.2; ESIMS m/z $[M+H]^+$ calcd. 419.15; found 419.08.



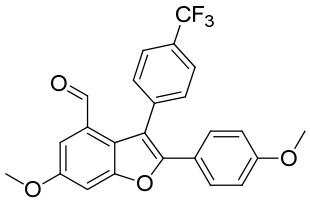
**16g:** Application of **procedure D** for direct arylation of **15c** (80 mg, 0.28 mmol). FC (heptane:EtOAc 4:1) gave **16g** as yellow solid. Yield: 61 mg (55 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.74 (s, 1H), 7.48 (d, $J$ = 9.0 Hz, 2H), 7.46 (d, $J$ = 2.4 Hz, 1H), 7.42 (td, $J$ = 8.0, 0.7 Hz, 1H), 7.33 (d, $J$ = 2.4 Hz, 1H), 7.05 (dt, $J$ = 7.5, 1.1 Hz, 1H), 7.03-6.99 (m, 2H), 6.82 (d, $J$ = 9.0 Hz, 2H), 3.92 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.5, 160.6, 159.8, 157.4, 155.3, 152.4, 135.8, 130.9, 129.4, 128.0, 126.8, 122.6, 122.3, 115.4, 114.2, 114.0, 107.5, 103.2, 56.1, 55.3, 55.2; ESIMS m/z $[M+H]^+$ calcd. 389.14; found 389.07.



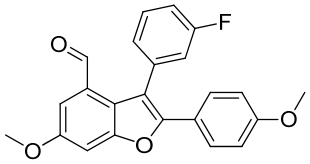
**16h:** Application of **procedure D** for direct arylation of **15d** (160 mg, 0.56 mmol). FC (heptane:EtOAc 4:1) gave **16h** as yellow solid. Yield: 76 mg (35 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.78 (s, 1H), 7.47 (d, $J$ = 9.0 Hz, 2H), 7.45 (d, $J$ = 2.4 Hz, 1H), 7.36 (d, $J$ = 8.7 Hz, 2H), 7.32 (d, $J$ = 2.4 Hz, 1H), 7.04 (d, $J$ = 8.7 Hz, 2H), 6.82 (d, $J$ = 9.0 Hz, 2H), 3.92 (s, 3H), 3.90 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.5, 159.8, 159.7, 157.3, 155.3, 152.6, 131.2, 129.5, 128.0, 127.1, 126.2, 122.8, 115.2, 114.7, 114.0, 107.4, 103.2, 56.1, 55.3, 55.2; ESIMS m/z $[M+H]^+$ calcd. 389.14; found 389.07.



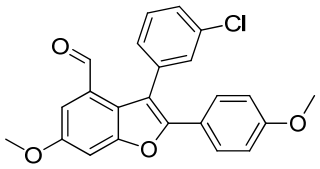

**16i:** Application of **procedure D** for direct arylation of **15e** (40 mg, 0.15 mmol). FC (heptane:EtOAc 4:1) gave **16i** as yellow solid. Yield: 33 mg (59 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.76 (s, 1H), 7.48-7.39 (m, 5H), 7.34 (d, $J$ = 2.3 Hz, 1H), 7.22 (t, $J$ = 8.6 Hz, 2H), 6.82 (d, $J$ = 8.9 Hz, 2H), 3.92 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.0, 162.8 (d, $J$ = 248.8 Hz), 160.0, 157.5, 155.4, 152.8, 132.0 (d, $J$ = 8.0 Hz), 130.4 (d, $J$ = 3.6 Hz), 129.5, 128.1, 126.5, 122.5, 116.9 (d, $J$ = 21.5 Hz), 114.0, 108.0, 103.2, 56.1, 55.3; ESIMS m/z $[M+H]^+$ calcd. 377.12; found 377.05.



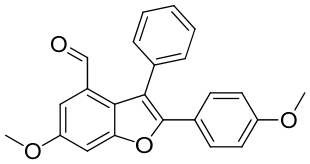

**16:j** Application of **procedure D** for direct arylation of **15f** (40 mg, 0.125 mmol). FC (heptane:EtOAc 8:2) gave **16j** as yellow solid. Yield: 27 mg (51 %). $^{1}$H NMR (400MHz, $CDCl_3$) $\delta$ (ppm): 9.71 (s, 1H), 7.77 (d, $J$ = 8.0 Hz, 2H), 7.61 (d, $J$ = 8.0 Hz, 2H), 7.47 (d, $J$ = 2.4 Hz, 1H), 7.38 (d, $J$ = 9.0 Hz, 2H), 7.36 (d, $J$ = 2.4 Hz, 1H), 6.83 (d, $J$ = 9.0 Hz, 2H), 3.93 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (100MHz, $CDCl_3$) $\delta$ (ppm): 188.7, 160.1, 157.6, 155.5, 153.0, 138.7, 130.8, 129.4, 128.2, 126.6 (q, $J$ = 3.7 Hz), 125.7, 123.4 (q, $J$ = 272.8 Hz), 122.1, 114.1, 113.8, 108.7, 103.2, 56.1, 55.3; ESIMS m/z [M+H]+ calcd. 427.11; found 427.05.



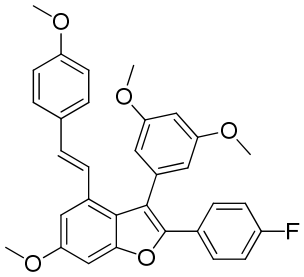

**16k:** Application of **procedure D** for direct arylation of **15g** (80 mg, 0.30 mmol). FC (heptane:EtOAc 4:1) gave **16k** as yellow solid. Yield: 65 mg (58 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.74 (s, 1H), 7.65 (s, 1H), 7.52-7.46 (m, 1H), 7.46 (d, $J$ = 2.3 Hz, 1H), 7.43 (d, $J$ = 9.0 Hz, 2H), 7.27 (d, $J$ = 7.9 Hz, 1H), 7.20-7.17 (m, 2H), 6.82 (d, $J$ = 9.0 Hz, 2H), 3.92 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.0, 163.4 (d, $J$ = 248.7 Hz), 160.0, 157.5, 155.4, 152.8, 136.8 (d, $J$ = 8.1 Hz), 131.9 (d, $J$ = 8.6 Hz), 129.4, 128.1, 126.2, 126.1 (d, $J$ = 2.9 Hz), 122.3, 117.3 (d, $J$ = 21.2 Hz), 115.6 (d, $J$ = 20.8 Hz), 114.1, 113.8 (d, $J$ = 1.9 Hz), 108.1, 103.2, 56.1, 55.3; ESIMS m/z $[M+H]^+$ calcd. 377.12; found 377.05.



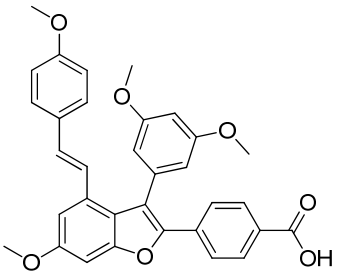

**16l:** Application of **procedure D** for direct arylation of **15h** (130 mg, 0.45 mmol). FC (heptane:EtOAc 4:1) gave **16l** as yellow solid. Yield: 74 mg (41 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.74 (s, 1H), 7.52-7.43 (m, 4H), 7.42 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 2.3 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 188.9, 160.0, 157.5, 155.4, 152.8, 136.5, 135.5, 131.0, 130.3, 129.4, 128.8, 128.5, 128.1, 126.1, 122.2, 114.1, 113.7, 108.2, 103.2, 56.1, 55.3; ESIMS m/z $[M+H]^+$ calcd. 393.09; found 393.02.



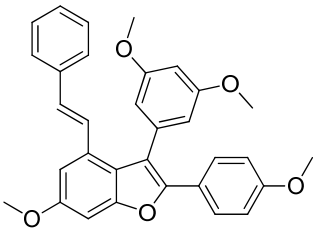

**16m:** Application of **procedure D** for direct arylation of **15i** (160 mg, 0.63 mmol). FC (heptane:EtOAc 4:1) gave **16m** as yellow solid. Yield: 172 mg (76%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.72 (s, 1H), 7.57-7.44 (m, 5H), 7.46 (d, *J* = 2.3 Hz, 1H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 2.3 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H), 3.79 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 189.4, 159.8, 157.4, 155.4, 152.5, 134.5, 130.2, 129.7, 129.5, 128.5, 128.0, 126.8, 122.7, 115.1, 114.0, 107.6, 103.2, 56.1, 55.2; ESIMS m/z $[M+H]^+$ calcd. 359.13; found 359.06.



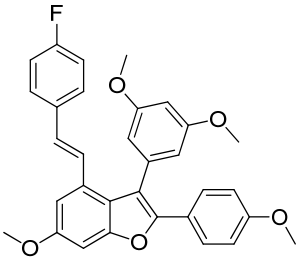

**17b:** Application of **procedure E** for Wittig-Horner olefination of **16b** (50 mg, 0.12 mmol). FC (heptane: EtOAc 8:2) gave desired product **17b** as yellow solid. Yield: 34 mg (54 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.57 (dd, *J* = 9.0, 5.4 Hz, 2H), 7.12 (d, *J* = 2.1 Hz, 1H), 7.04-6.95 (m, 5H), 6.90 (d, *J* = 16.3 Hz, 1H), 6.84 (d, *J* = 16.3 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.67-6.65 (m, 3H), 3.92 (s, 3H), 3.81 (s, 3H), 3.75 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 162.2 (d, *J* = 248.3 Hz), 161.5, 159.3, 158.3, 155.1, 148.7, 136.6, 132.5 130.1, 128.8, 127.9 (d, *J* = 8.0 Hz), 127.6, 127.0, 122.9, 121.7, 117.6, 115.5 (d, *J* = 21.8 Hz), 113.9, 108.5, 107.0, 100.5, 94.8, 55.9, 55.5, 55.3; ESIMS m/z $[M+H]^+$ calcd. 511.19; found 511.12.



**17c:** Application of **procedure E** for Wittig-Horner olefination of **16d** (30 mg, 0.067 mmol). FC (DCM:MeOH 95:5) gave a mixture. Repurified by HPLC (method B) gave **17c** as yellow solid. Yield: 8 mg (22 %). $^{1}$H NMR (600 MHz, $CDCl_3$ + DMSO-d6) $\delta$ (ppm): 7.93 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 1.6 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 1.6 Hz, 1H), 6.87 (d, *J* = 16.2 Hz, 1H), 6.80 (d, *J* = 16.2 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 2H), 6.63-6.62 (m, 3H), 3.90 (s, 3H), 3.79 (s, 3H), 3.72 (s, 3H), 3.74 (s, 6H); $^{13}$C NMR (150 MHz, $CDCl_3$ + DMSO-d6) $\delta$ (ppm): 168.4, 161.5, 159.2, 158.8, 155.4, 148.3, 136.2, 134.9, 132.9, 130.0, 129.9, 129.0, 128.7, 127.6, 125.5, 122.6, 121.5, 120.2, 113.9, 108.2, 107.2, 100.6, 94.6, 55.8, 55.4, 55.3; ESIMS m/z $[M-H]^-$ calcd. 535.17; found 535.12.

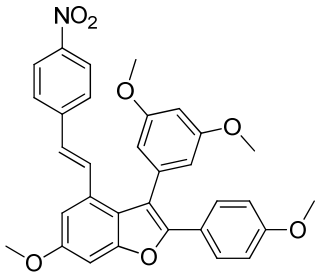


**17d:** Application of **procedure E** for Wittig olefination of **16a** (50 mg, 0.12 mmol). FC (heptane:EtOAc 4:1) gave **17d** as yellow solid. Yield: 48 mg (82 %).$^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.54 (d, *J* = 8.9 Hz, 2H), 7.27-7.14 (m, 3H), 7.14 (d, *J* = 2.1 Hz, 1H), 7.10-7.07 (m, 2H), 7.03 (d, *J* = 2.1 Hz, 1H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 16.3 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 2.2 Hz, 2H), 6.64 (t, *J* = 2.2 Hz, 1H), 3.93 (s, 3H), 3.80 (s, 3H), 3.74 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 161.5, 159.3, 157.9, 154.9, 149.8, 137.3, 136.8, 131.7, 129.0, 128.4, 127.5, 127.4, 126.4, 125.2, 123.4, 122.2, 116.3, 113.9, 108.5, 107.0, 100.4, 95.2, 55.9, 55.5, 55.2; ESIMS m/z $[M+H]^+$ calcd. 493.20; found 493.10.

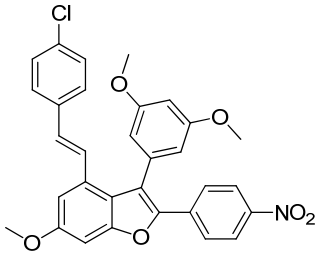


**17e:** Application of **procedure E** for Wittig-Horner olefination of **16a** (50 mg, 0.12 mmol.). FC (heptane:EtOAc 4:1) gave **17e** as yellow solid. Yield: 50 mg (82 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.53 (d, *J* = 9.0 Hz, 2H), 7.10 (d, *J* = 2.2 Hz, 1H), 7.04 (d, *J* = 8.8, 5.5 Hz, 2H), 7.02 (d, *J* = 2.2 Hz, 1H), 6.96-6.81 (m, 6H), 6.65 (d, *J* = 2.3 Hz, 2H), 6.62 (t, *J* = 2.3 Hz, 1H), 3.92 (s, 3H), 3.80 (s, 3H), 3.74 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 162.3 (d, *J* = 224.2 Hz), 161.5, 159.3, 158.0, 154.9, 149.9, 136.9, 133.5 (d, *J* = 3.1 Hz),

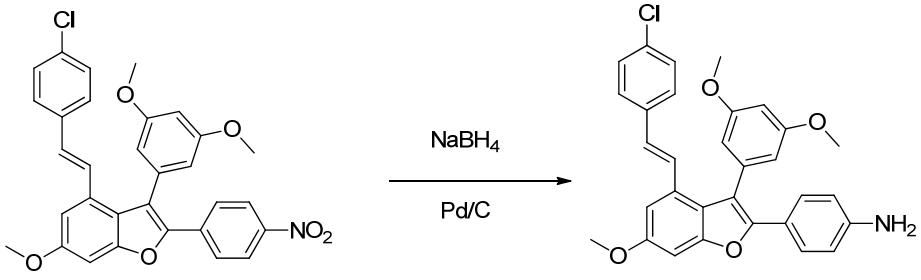
131.5, 127.8 (d, *J* = 8.2 Hz), 127.5, 125.0, 123.4, 122.2, 116.2, 115.3 (d, *J* = 21.5 Hz), 113.9, 113.8, 108.6, 107.0, 100.3, 95.2, 55.9, 55.5, 55.2; ESIMS m/z $[M+H]^+$ calcd. 511.19; found 511.12.



**17f:** Application of **procedure E** for Wittig-Horner olefination of **16a** (50 mg, 0.12 mmol). FC (heptane:EtOAc 4:1) gave **17f** as yellow solid. Yield: 40 mg (62 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 8.09 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 2H), 7.18 (d, *J* = 16.3 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 2.1 Hz, 1H), 7.08 (d, *J* = 2.1 Hz, 1H), 6.94 (d, *J* = 16.3 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.67-6.63 (m, 3H), 3.93 (s, 3H), 3.81 (s, 3H), 3.76 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 161.7, 159.5, 157.9, 154.9, 150.4, 146.5, 144.0, 136.8, 130.2, 129.9, 127.5, 126.6, 123.9, 123.1, 122.8, 115.9, 113.9, 108.5, 107.3, 100.1, 96.4, 55.9, 55.5, 55.3; ESIMS m/z $[M+H]^+$ calcd. 538.19; found 538.12.



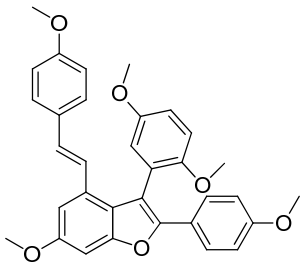
**17g:** Application of **procedure E** for Wittig-Horner olefination of **16c** (50 mg, 0.12 mmol). FC (heptane:EtOAc 4:1) gave **17g** as yellow solid. Yield: 35 mg (56 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 8.13 (d, *J* = 9.1 Hz, 2H), 7.72 (d, *J* = 9.1 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 2.1 Hz, 1H), 7.04 (d, *J* = 2.1 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 16.3 Hz, 1H), 6.87 (d, *J* = 16.3 Hz, 1H), 6.67 (t, *J* = 2.3 Hz, 1H), 6.63 (d, *J* = 2.3 Hz, 2H), 3.94 (s, 3H), 3.77 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 161.8, 159.3, 155.7, 147.2, 146.4, 136.6, 135.7, 135.6, 133.3, 132.6, 128.6, 128.5, 127.5, 126.0, 123.8, 121.8, 121.6, 108.1, 108.0, 100.5, 95.1, 55.9, 55.5. ESIMS m/z $[M+H]^+$ calcd. 542.14; found 542.07.



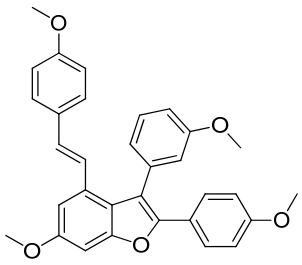

**17g** **17h**

**17h:** To a solution of **17g** (18 mg, 0.033 mmol, 1 eq.) in a 1/1 mixture of DCM/MeOH (4 mL, v/v) at 0 °C, was added 10 % Pd/C (5 mg, 0.016 mmol, 0.5 eq.) $NaBH_4$ (6.2 mg, 0.165 mmol, 5 eq.). The reaction was

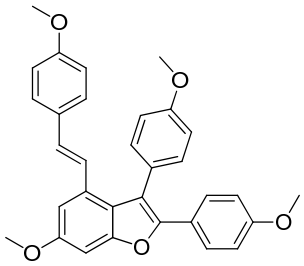
stirred for 30 min at 0 °C then filtered on celite. The organic phase was evaporated then the residue was purified by silicagel flash chromatography (heptane:EtOAc 7:3) to give **17h** as yellow solid. Yield: 8 mg (47 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.40 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 2.1 Hz, 1H), 7.01 (d, *J* = 2.1 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 16.3 Hz, 1H), 6.84 (d, *J* = 16.3 Hz, 1H), 6.64 (d, *J* = 2.3 Hz, 2H), 6.61 (t, *J* = 2.3 Hz, 1H), 6.59 (d, *J* = 8.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 161.4, 157.7, 154.7, 150.6, 146.2, 137.1, 135.9, 132.8, 131.0, 128.6, 127.5, 127.4, 126.0, 122.5, 121.1, 115.1, 114.8, 108.6, 106.8, 100.2, 95.5; ESIMS m/z $[M+H]^+$ calcd. 512.16; found 516.10.



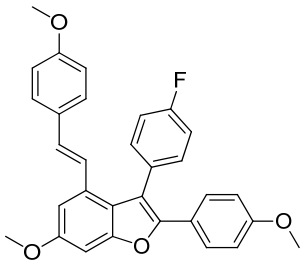
**17i:** Application of **procedure E** for Wittig-Horner olefination of **16f** (50 mg, 0.12 mmol). FC (heptane:EtOAc 4:1) gave **17i** as yellow solid. Yield: 42 mg (66 %). $^{1}$H NMR (400MHz, $CDCl_3$) $\delta$ (ppm): ): 7.50 (d, *J* = 9.0 Hz, 2H), 7.09 (d, *J* = 2.1 Hz, 1H), 7.06 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.04-6.99 (m, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 3.0 Hz, 1H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 16.2 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.72 (s, 3H), 3.60 (s, 3H); $^{13}$C NMR (100MHz, $CDCl_3$) $\delta$ (ppm): 159.1, 159.0, 157.8, 155.1, 154.1, 152.5, 150.1, 132.2, 130.2, 127.6, 127.3, 124.7, 123.8, 122.7, 117.5, 113.9, 113.8, 112.8, 112.4, 106.5, 95.0, 56.3, 55.8, 55.3, 55.2; ESIMS m/z [M+H]+ calcd. 523.21; found 523.07.



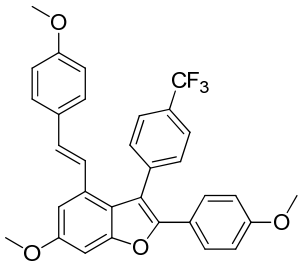
**17j:** Application of **procedure E** for Wittig-Horner olefination of **16g** (50 mg, 0.13 mmol). FC (heptane:EtOAc 85:15) gave **17j** as yellow solid. Yield: 40 mg (63 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.48 (d, *J* = 9.0 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.10-7.02 (m, 4H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 16.2 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 16.2 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.75 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 160.3, 159.2, 159.1, 158.0, 154.9, 149.8, 136.4, 132.1, 130.2, 130.1, 128.5, 127.6, 127.5, 123.6, 122.9, 122.1, 116.3, 115.8, 113.9, 113.8, 106.6, 94.9, 55.8, 55.3, 55.2; ESIMS m/z $[M+H]^+$ calcd. 493.20; found 493.10.



**17k:** Application of **procedure E** for Wittig-Horner olefination of **16h** (69 mg, 0.18 mmol). FC (heptane:EtOAc 85:15) gave **17k** as yellow solid. Yield: 72 mg (82 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.51 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 2.1 Hz, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 16.2 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 16.2 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 159.4, 159.1, 157.9, 154.9, 149.9, 132.0, 131.9, 130.1, 128.3, 127.6, 127.4, 126.9, 123.7, 122.9, 122.4, 116.0, 114.6, 113.8, 106.6, 94.8, 55.8, 55.4, 55.2, 55.1; ESIMS m/z $[M+H]^+$ calcd. 493.20; found 493.10.

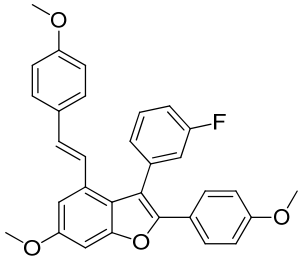


**17l:** Application of **procedure E** for Wittig-Horner olefination of **16i** (30 mg, 0.08 mmol). FC (heptane:EtOAc 85:15) gave **17l** as yellow solid. Yield: 20 mg (52 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.45 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.22 (t, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 2.0 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 16.2 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 16.2 Hz, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 162.6 (d, *J* = 247.2 Hz), 159.3, 158.0, 154.9, 150.2, 132.6 (d, *J* = 7.9 Hz), 132.1, 130.9 (d, *J* = 3.5 Hz), 129.9, 128.8, 127.6, 127.5, 123.4, 122.6, 122.0, 116.1, (d, *J* = 21.3 Hz), 115.3, 114.0, 113.9, 106.9, 94.9, 55.8, 55.3, 55.2; ESIMS m/z $[M+H]^+$ calcd. 481.18; found 481.12.

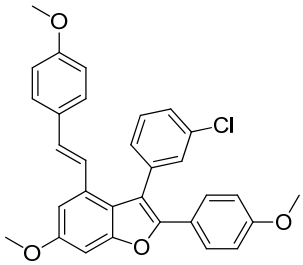


**17m:** Application of **procedure E** for Wittig-Horner olefination of **16j** (25 mg, 0.06 mmol). FC (heptane:EtOAc 85:15) gave desired product **17m** as yellow solid. Yield: 23 mg (72 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.79 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 0.9 Hz, 1H), 7.02 (d, *J* = 0.9 Hz, 1H), 6.91-6.70 (m, 7H), 6.50 (d, *J* = 16.2 Hz, 1H), 3.92 (s, 3H), 3.80 (s, 6H); $^{13}$C NMR

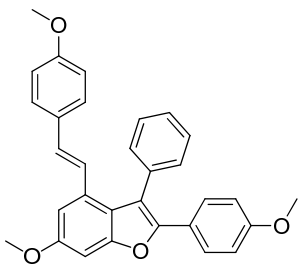
(100 MHz, $CDCl_3$) $\delta$ (ppm): 159.5, 159.3, 158.1, 155.0, 150.1, 139.4, 131.9, 131.4, 129.7, 129.0, 127.6, 127.4, 127.0 (q, *J* = 272.1 Hz), 126.0 (q, *J* = 3.7 Hz), 123.0, 122.4, 121.7, 115.0, 114.0, 113.9, 107.0, 94.9, 55.8, 55.2; ESIMS m/z $[M+H]^+$ calcd. 531.18; found 531.12.



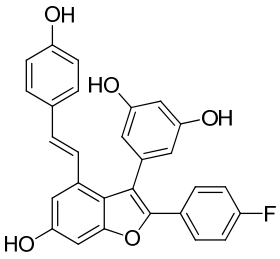

**17n:** Application of **procedure E** for Wittig-Horner olefination of **16k** (50 mg, 0.13 mmol). FC (heptane:EtOAc 85:15) gave desired product **17n** as yellow solid. Yield: 38 mg (59 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.49 (qt, *J* = 7.5, 1.3 Hz, 1H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.29 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.25-7.19 (m, 2H), 7.10 (d, *J* = 2.1 Hz, 1H), 7.01 (d, *J* = 2.1 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 16.2 Hz, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 163.2 (d, *J* = 247.7 Hz), 159.4, 159.2, 154.9, 150.1, 137.4 (d, *J* = 8.1 Hz), 132.0, 130.6 (d, *J* = 8.6 Hz), 129.9, 128.9, 127.6, 127.5, 126.8 (d, *J* = 2.9 Hz), 123.2, 122.6, 121.7, 117.9 (d, *J* = 21.1 Hz), 115.2 (d, *J* = 1.7 Hz), 114.7 (d, *J* = 20.8 Hz), 113.9, 106.9, 94.9, 55.8, 55.3, 55.2; ESIMS m/z $[M+H]^+$ calcd. 481.18; found 481.12.



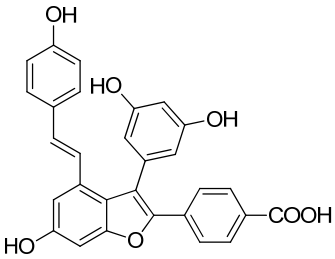

**17o:** Application of **procedure E** for Wittig-Horner olefination of **16l** (60 mg, 0.15 mmol). FC (heptane:EtOAc 85:15) gave **17o** as yellow solid. Yield: 57 mg (75 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.54-7.44 (m, 2H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.37 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 16.2 Hz, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 159.4, 159.2, 158.0, 150.2, 137.1, 134.9, 132.0, 131.0, 130.4, 129.9, 129.3, 129.0, 127.9, 127.7, 127.5, 123.1, 122.6, 121.6, 115.0, 113.9, 107.0, 94.9, 55.8, 55.3, 55.2; ESIMS m/z $[M+H]^+$ calcd. 497.15; found 497.10.



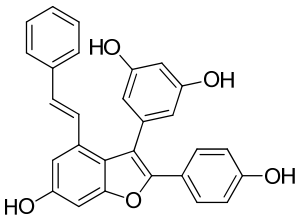
**17p:** Application of **procedure E** for Wittig-Horner olefination of **16m** (164 mg, 0.46 mmol). FC (heptane:EtOAc 85:15) gave **17p** as yellow solid. Yield: 115 mg (54 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.59-7.46 (m, 5H), 7.45 (d, *J* = 8.9 Hz, 2H), 7.10 (d, *J* = 1.9 Hz, 1H), 7.01 (d, *J* = 1.9 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 16.3 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 16.3 Hz, 1H), 3.92 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 159.2, 159.1, 157.9, 154.9, 149.9, 135.1, 132.1, 130.8, 130.0, 129.1, 128.5, 127.7, 127.5, 123.6, 122.8, 116.5, 113.8, 106.6, 94.9, 55.8, 55.3, 55.2; ESIMS m/z $[M+H]^+$ calcd. 463.19; found 463.12.




**18a:** Application of **procedure F'** for demethylation of **17c** (20 mg, 0.039 mmol). FC (DCM:MeOH 9:1) followed by HPLC method A **18a** as yellow solid. Yield: 1.5 mg (8 %). $^{1}$H NMR (60 0MHz, $CD_3OD$) $\delta$ (ppm): 7.61 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.05-7.01 (m, 3H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 16.3 Hz, 1H), 6.88 (d, *J* = 16.3 Hz, 1H), 6.84 (d, *J* = 2.0 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.49 (t, *J* = 2.2 Hz, 1H), 6.41 (d, *J* = 2.2 Hz, 2H); ESIMS m/z $[M-H]^-$ calcd. 453.11; found 453.06.

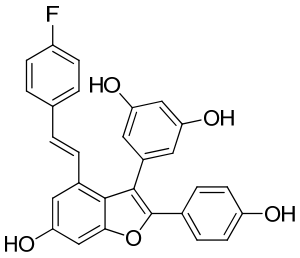



**18b:** Application of **procedure F'** for demethylation of **17c** (6 mg, 0.011 mmol). FC (DCM:MeOH 9:1) followed by HPLC method A gave **18b** as yellow solid. Yield: 0.5 mg (9 %).$^{1}$H NMR (400 MHz, acetone-d6) $\delta$ (ppm): 7.98 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 2.0 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 16.2 Hz, 1H), 6.98 (d, *J* = 16.2 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.64 (t, *J* = 2.2 Hz, 1H), 6.52 (d, *J* = 2.2 Hz, 2H); ESIMS m/z $[M-H]^-$ calcd. 479.11; found 479.00.

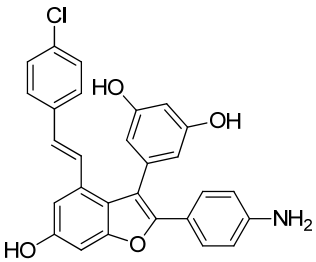



**18c:** Application of **procedure F'** for demethylation of **17d** (25 mg, 0.051 mmol). FC (DCM:MeOH 9:1) gave **18c** as yellow solid. Yield: 11 mg (50 %). $^{1}$H NMR (400 MHz, acetone-d6) $\delta$ (ppm): 8.68-8.34 (m, 4H), 7.50 (d, *J* = 8.9 Hz, 2H), 7.30-7.18 (m, 6H), 7.17 (d, *J* = 2.0 Hz, 1H), 7.04 (d, *J* = 16.3 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.61 (t, *J* = 2.2 Hz, 1H), 6.51 (d, *J* = 2.2 Hz, 2H); $^{13}$C NMR (100 MHz, acetone-d6) $\delta$ (ppm): 161.5, 161.4, 159.3, 157.4, 156.8, 151.3, 139.5, 139.0, 138.9, 133.3, 130.3, 130.1, 129.3,

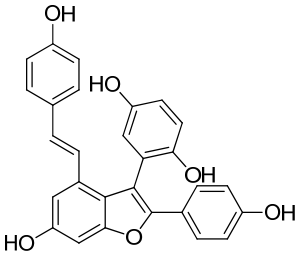
129.2, 128.3, 126.7, 124.3, 123.4, 118.0, 117.2, 110.8, 108.9, 104.2, 98.9; ESIMS m/z $[M-H]^-$ calcd. 435.12; found 435.05.




**18d:** Application of **procedure F** for demethylation of **17e** (40 mg, 0.078 mmol). FC (DCM:MeOH 9:1) gave **18d** as yellow solid. Yield: 4 mg (11 %). Application of **procedure F'** for demethylation of **17e** (20 mg, 0.039 mmol). FC (DCM:MeOH 9:1) followed by HPLC method A gave **18d** as yellow solid. Yield: 9 mg (51 %). $^1$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 8.69-8.45 (m, 4H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.23 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.14 (d, *J* = 2.1 Hz, 1H), 7.12 (d, *J* = 16.3 Hz, 1H), 7.03 (d, *J* = 16.3 Hz, 1H), 7.02 (t, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 1.1 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.61 (t, *J* = 2.2 Hz, 1H), 6.50 (d, *J* = 2.2 Hz, 2H); $^{13}$C NMR (150 MHz, acetone-d6) $\delta$ (ppm): 164.0 (d, *J* = 245.3 Hz), 161.5, 159.3, 157.5, 156.8, 151.3, 139.0, 136.1 (d, *J* = 3.2 Hz), 133.1, 129.9 (d, *J* = 8.0 Hz), 129.3, 128.8, 126.8, 126.7, 124.3, 123.4, 117.9, 117.6, 117.2, 117.1 (d, *J* = 21.7 Hz), 110.9, 108.9, 104.2, 99.0; ESIMS m/z $[M-H]^-$ calcd. 453.11; found 453.06.

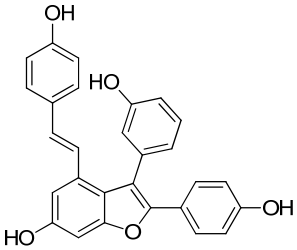



**18g:** Application of **procedure F** for demethylation of **17h** (3 mg, 0.006 mmol). FC (DCM:MeOH 9:1) followed HPLC method A gave **18g** as yellow solid. Yield: 0.5 mg (18 %). $^1$H NMR (400 MHz, acetone-d6) $\delta$ (ppm): 8.52 (br s, 2H), 8.49 (br s, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 16.3 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 16.3 Hz, 1H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.61 (d, *J* = 8.6 Hz, 2H), 6.60 (t, *J* = 2.2 Hz, 1H), 6.49 (d, *J* = 2.2 Hz, 2H), 4.91 (br s, 2H); ESIMS m/z $[M-H]^-$ calcd. 468.10; found 468.00.

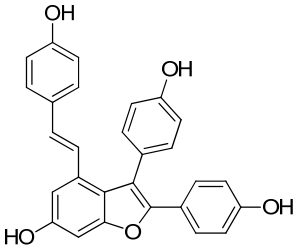



**18h:** Application of **procedure F'** for demethylation of **17i** (30 mg, 0.057 mmol). FC (DCM:MeOH 9:1) gave **18h** as yellow solid. Yield: 12 mg (46 %). $^1$H NMR (400 MHz, acetone-d6) $\delta$ (ppm): 8.74-8.26 (m, 4H), 7.92 (br s, 1H), 7.57 (br s, 1H), 7.50 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.03-6.93 (m, 6H), 6.90 (d, *J* = 2.0

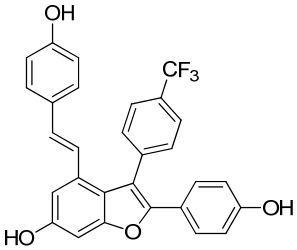
Hz, 1H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 16.3 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR (100 MHz, acetone-d6) *δ* (ppm): 159.2, 159.0, 157.3, 157.1, 152.9, 152.2, 150.9, 134.1, 131.2, 130.1, 129.7, 129.2, 124.7, 12.9, 123.4, 123.3, 119.7, 118.8, 118.3, 117.2, 117.1, 113.4, 108.2, 98.3; ESIMS m/z [M-H]$^-$ calcd. 451.12; found 451.05.




**18i:** Application of **procedure F'** for demethylation of **17j** (30 mg, 0.061 mmol). FC (DCM:MeOH 9:1) followed by HPLC method A gave **18i** as yellow solid. Yield: 5 mg (24 %). $^1$H NMR (400 MHz, acetone-d6) *δ* (ppm): 8.74-8.26 (m, 4H), 7.47-7.38 (m, 3H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.08 (ddd, *J* = 8.2, 2.4, 1.0 Hz, 1H), 6.99-6.90 (m, 6H), 6.84 (d, *J* = 16.3 Hz, 1H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR (100 MHz, acetone-d6) *δ* (ppm): 160.2, 159.2, 159.1, 157.5, 156.9, 151.3, 138.6, 133.9, 132.3, 131.0, 130.2, 129.6, 124.4, 123.7, 123.6, 123.1, 119.3, 118.0, 117.2, 117.1, 116.8, 108.6, 98.4; ESIMS m/z [M-H]$^-$ calcd. 435.12; found 435.05.

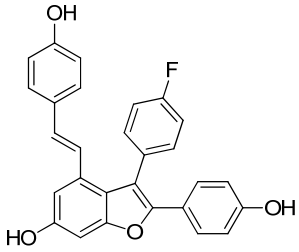



**18j:** Application of **procedure F'** for demethylation of **17k** (115 mg, 0.061 mmol). FC (DCM:MeOH 9:1) gave **18j** as yellow solid. Yield: 4 mg (19 %). $^1$H NMR (400 MHz, acetone-d6) *δ* (ppm): 8.71 (s, 1H), 8.59 (s, 1H), 8.45 (s, 1H), 8.41 (s, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 2.0 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 16.3 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 16.3 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR (100 MHz, acetone-d6) *δ* (ppm): 159.4, 159.1, 159.0, 157.4, 156.9, 151.5, 134.0, 133.7, 130.1, 129.6, 129.2, 127.7, 124.6, 123.7, 123.5, 118.0, 117.9, 117.3, 117.1, 108.6, 98.3; ESIMS m/z [M-H]$^-$ calcd. 435.12; found 435.05.

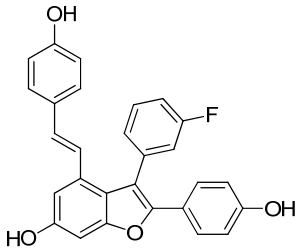



**18k:** Application of **procedure F'** for demethylation of **17l** (20 mg, 0.038 mmol). FC (heptane:EtOAc 3:2) gave **18k** as yellow solid. Yield: 10 mg (54 %).$^1$H NMR (400 MHz, acetone-d6) *δ* (ppm): 8.70 (s, 1H), 8.59 (s, 1H), 8.46 (s, 1H), 7.95 (d, *J* = 7.9 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 2.0 Hz,

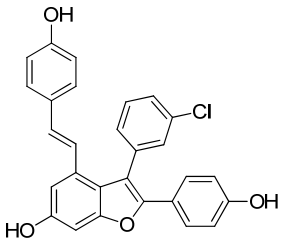
1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 16.2 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.6 Hz, 2H), 6.50 (d, *J* = 16.2 Hz, 1H); $^{13}$C NMR (100 MHz, acetone-d6) *δ* (ppm): 159., 159.3, 157.7, 157.0, 151.8, 142.0, 133.8, 133.7, 131.5, 131.2, 130.8, 130.7, 129.6, 129.4, 127.9 (d, *J* = 3.8 Hz), 125.2, 123.8, 123.2, 122.7, 117.4, 117.2, 116.6, 109.1, 98.5; ESIMS m/z [M-H]$^-$ calcd. 487.11; found 487.01.



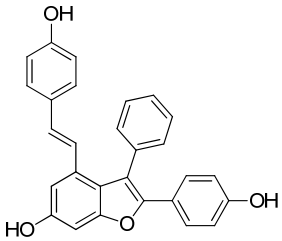

**18l:** Application of **procedure F** for demethylation of **17m** (29 mg, 0.06 mmol). FC (DCM:MeOH 99:1 to 9/1) gave impure **18l** (8 mg) and a mixture of dimers (16 mg). Purification of by HPLC method A gave gave pure **18l** as yellow solid. Yield: 4 mg (16 %). Application of **procedure F'** for demethylation of **17m** (35 mg, 0.073 mmol). FC (heptane:EtOAc 3:2) gave **18l** as yellow solid. Yield: 17 mg (53 %).$^1$H NMR (400 MHz acetone-d6) *δ* (ppm): 8.53 (br s, 3H), 7.54 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.37 (t, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.9 Hz, 2H), 7.10 (d, *J* = 1.9 Hz, 1H), 6.97-6.87 (m, 4H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 16.3 Hz, 1H); $^{13}$C NMR (100 MHz, acetone-d6) *δ* (ppm): 164.6 (d, *J* = 245.3 Hz), 159.4, 159.2, 157.6, 156.9, 151.8, 134.7 (d, *J* = 8.1 Hz), 133.9, 133.4, (d, *J* = 3.2 Hz), 130.9, 130.6, 129.5, 129.4, 124.1, 123.5, 123.0, 117.9 (d, *J* = 21.7 Hz), 117.3, 116.9, 109.0, 98.4; ESIMS m/z [M-H]$^-$ calcd. 437.12; found 437.05.




**18m:** Application of **procedure F'** for demethylation of **17n** (30 mg, 0.062 mmol). FC (heptane:EtOAc 3:2) gave **18m** as yellow solid. Yield: 15 mg (55 %). $^1$H NMR (400 MHz, acetone-d6) *δ* (ppm): 8.66 (s, 1H), 8.55 (s, 1H), 8.46 (s, 1H), 7.64 (td, *J* = 7.8, 6.2 Hz, 1H), 7.40-7.25 (m, 5H), 7.11 (d, *J* = 2.0 Hz, 1H), 6.97-6.91 (m, 4H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 16.3 Hz, 1H); $^{13}$C NMR (100 MHz, acetone-d6) *δ* (ppm): 165.2 (d, *J* = 245.8 Hz), 159.5, 159.2, 157.6, 156.9, 151.8, 139.7 (d, *J* = 8.2 Hz), 134.0, 133.0 (d, *J* = 8.7 Hz), 130.8, 130.7, 129.5, 129.4, 128.9 (d, *J* = 2.7 Hz), 123.9, 123.4, 122.7, 119.5 (d, *J* = 21.2 Hz), 117.3, 116.7 (d, *J* = 2.1 Hz), 116.6 (d, *J* = 20.9 Hz), 109.1, 98.4; ESIMS m/z [M-H]$^-$ calcd. 437.12; found 437.05.

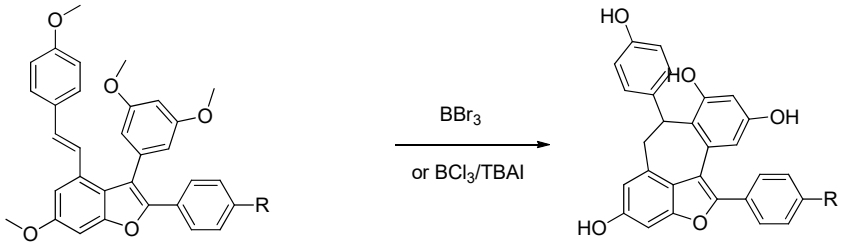


**18n:** Application of **procedure F'** for demethylation of **17o** (30 mg, 0.060 mmol). FC (heptane:EtOAc 3:2) gave **18n** as yellow solid. Yield: 15 mg (55 %).$^{1}$H NMR (400 MHz, acetone-d6) $\delta$ (ppm): 8.66-8.41 (m, 3H), 7.66-7.56 (m, 3H), 7.47 (ddd, *J* = 6.7, 2.0, 1.7 Hz, 1H), 7.36 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 1.9 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 1.9 Hz, 1H), 6.94 (d, *J* = 16.3 Hz, 1H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 16.3 Hz, 1H); $^{13}$C NMR (100 MHz, acetone-d6) $\delta$ (ppm): 159.5, 159.2, 157.6, 157.0, 151.9, 139.5, 136.4, 133.9, 132.7, 132.6, 131.5, 130.9, 130.8, 129.8, 129.6, 129.5, 123.9, 123.4, 122.6, 117.3, 116.6, 109.1, 98.5; ESIMS m/z [M-H]- calcd. 453.09; found 453.03.




**18o:** Application of **procedure F'** for demethylation of **17p** (104 mg, 0.225 mmol). FC (heptane:EtOAc 3:2) gave **18o** as yellow solid. Yield: 50 mg (53 %). $^{1}$H NMR (400M Hz, acetone-d6) $\delta$ (ppm): 8.58 (s, 1H), 8.48 (s, 1H), 8.41 (s, 1H), 7.36 (d, *J* = 8.9 Hz, 2H), 7.10 (d, *J* = 1.9 Hz, 1H), 6.93 (d, *J* = 1.9 Hz, 1H), 6.91 (d, *J* = 16.3 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 16.3 Hz, 1H); $^{13}$C NMR (100 MHz, acetone-d6) $\delta$ (ppm): 159.2, 159.1, 157.5, 156.9, 151.5, 137.3, 134.0, 132.7, 131.1, 130.9, 130.4, 129.7, 129.6, 129.4, 124.3, 123.5, 123.1, 118.0, 117.2, 108.8, 98.4; ESIMS m/z $[M-H]^-$ calcd. 419.13; found 419.06.

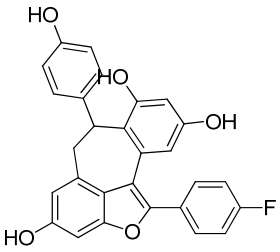
**SI-4. Representative examples of the formation of cyclized products during demethylation**



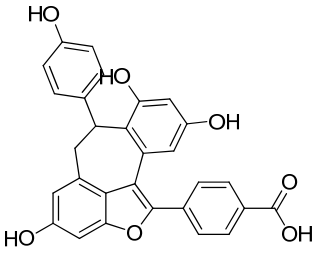

**17b** R = F
**17c** R = COOH

**37** R = F
**38** R = COOH

major products



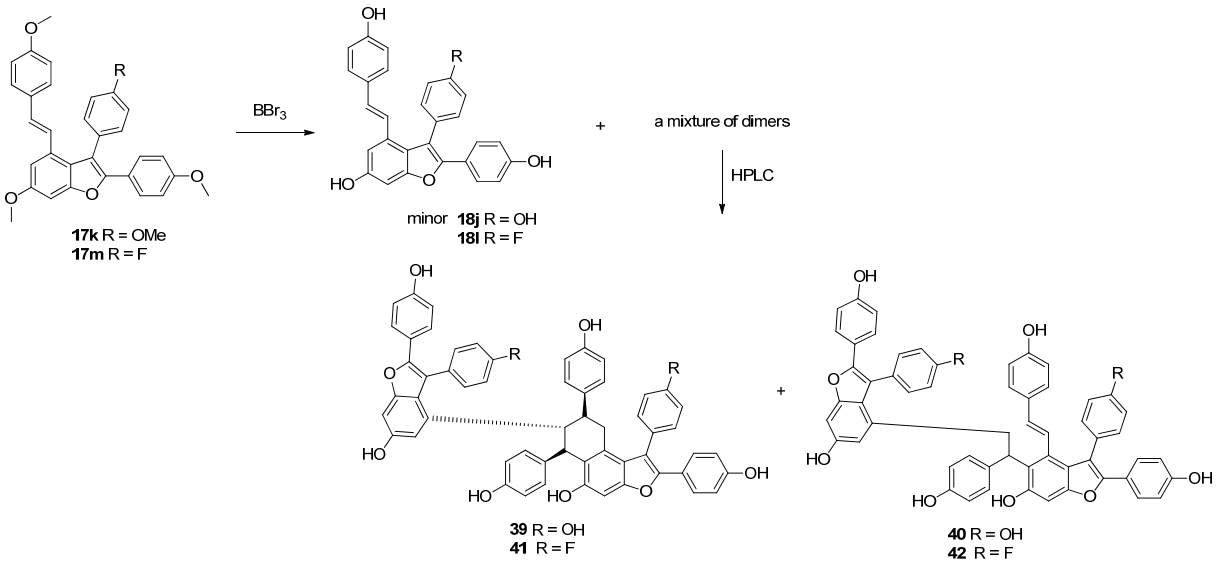

**37:** Application of **procedure F** (**SI-3**) for demethylation of **17b** (30 mg, 0.06 mmol). FC (DCM:MeOH 95:5) gave **37** and **18b** (15 mg, 49 %) as a 85:15 mixture ($^1$H NMR). HPLC method A furnished pure **18b**. Yield: 10 mg (37 %). $^1$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 8.44 (s, 1H), 8.33 (s, 1H), 8.05 (s, 1H), 7.75 (s, 1H), 7.71 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 1.4 Hz, 1H), 6.62 (d, *J* = 1.4 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 6.49-6.45 (m, 3H), 5.44 (d, *J* = 5.6 Hz, 1H), 3.71 (d, *J* = 16.3, 6.1 Hz, 1H), 3.40 (d, *J* = 16.3 Hz, 1H); $^{13}$C NMR (150 MHz, acetone-d6) $\delta$ (ppm): 164.4 (d, *J* = 246.5 Hz), 158.1, 157.8, 157.4, 156.5, 156.4, 150.2, 137.5, 136.2, 135.4, 132.3 (d, *J* = 8.3 Hz), 130.5 (d, *J* = 3.3 Hz), 130.2, 123.6, 121.5, 119.6, 117.4 (d, *J* = 21.9 Hz), 116.2, 114.8, 111.1, 103.6, 96.6, 38.9, 38.8; ESIMS m/z $[M-H]^-$ calcd. 453.11; found 453.01.



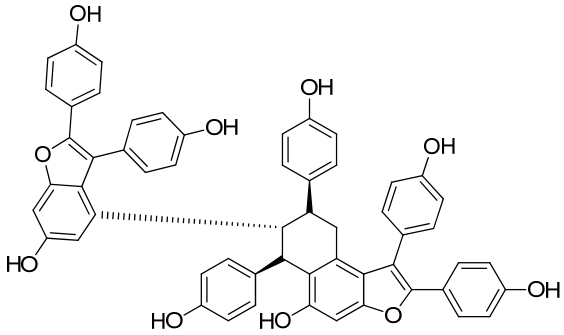

**38:** Application of **procedure F'** (**SI-3**) for demethylation of **17c** (6 mg, 0.011 mmol). FC (DCM:MeOH 85:15) followed by HPLC method A gave **38** as yellow solid. Yield: 2 mg (37 %). This product gradually decomposed in NMR tube. $^1$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 8.07 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.00 (dd, *J* = 8.7, 0.7 Hz, 2H), 6.70 (s, 1H), 6.65 (d, *J* = 1.5 Hz, 1H), 6.61 (d, *J* = 2.4 Hz, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 6.49 (d, *J* = 8.7 Hz, 2H),), 5.45 (d, *J* = 5.0 Hz, 1H), 3.73 (d, *J* = 16.3, 6.1 Hz, 1H), 3.41 (d, *J* = 16.3 Hz, 1H); ESIMS m/z [M-H]- calcd. 479.11; found 479.01.

**SI-5. Representative exemples of dimerization during $BBr_3$ mediated demethylation**

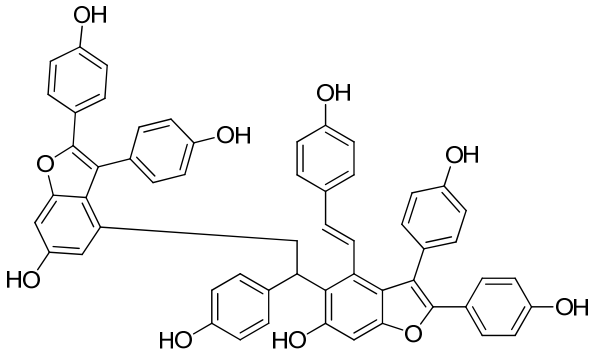
The structures of the major formed dimers are proposed based on previously described cationic mechanisms of acid-catalyzed dimerization of stilbenes[8] and analysis of $^1$H NMR data.




Application of **procedure F** (**SI-3**) for demethylation of **17k** (16 mg, 0.032 mmol). FC (DCM:MeOH 85:15) followed by HPLC method A gave **39** (2 mg, 14 %) and **40** (1 mg, 7 %).

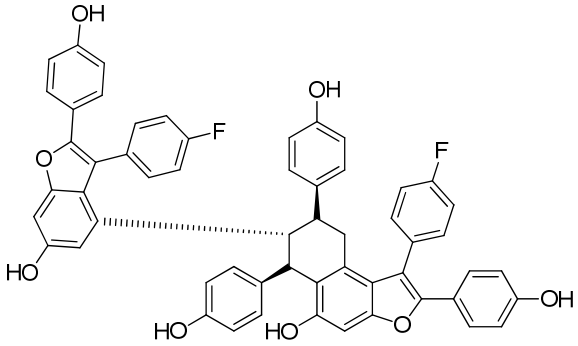


**39:** $^1$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 8.60-7.69 (br, OHs), 7.33 (d, *J* = 8.9 Hz, 2H), 7.26-7.12 (m, 2H), 7.04 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 2.1 Hz, 1H), 6.85 (s, 1H), 6.83 (dd, *J* = 8.2, 2.7 Hz, 1H), 6.76-6.72 (m, 1H), 6.75 (d, *J* = 2.1 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 2H), 6.68-6.60 (m, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 8.6 Hz, 2H), 6.48-6.46 (m, 1H), 6.47 (d, *J* = 8.6 Hz, 2H), 6.39-6.36 (m, 4H), 5.87 (dd, *J* = 8.2, 2.1 Hz, 1H), 4.72 (d, *J* = 7.6 Hz, 1H), 3.38 (dd, *J* = 11.0, 7.7 Hz, 1H), 2.86 (td, *J* = 11.9, 2.7 Hz, 1H), 2.64 (dd, *J* = 15.9, 3.0 Hz, 1H), 2.50 (dd, *J* = 15.9, 12.2 Hz, 1H). ESIMS m/z $[M-H]^-$ calcd. 871.25; found 871.15.

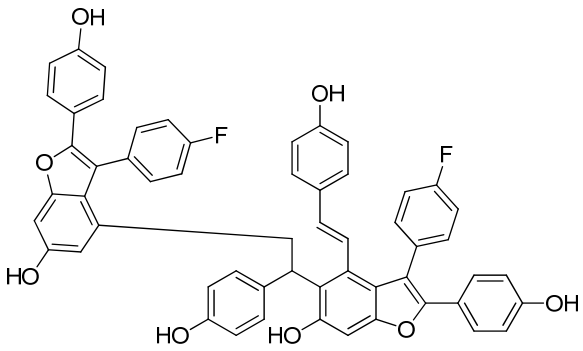



**40:** $^1$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 8.78-7.78 (br, OHs), 7.44 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 7.06-7.03 (m, 3H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.88-6.84 (m, 2H), 6.76-6.66 (m, 9H), 6.65 (d, *J* = 8.6 Hz, 2H), 6.54 (d, *J* = 1.8 Hz, 1H), 4.84 (dd, *J* = 9.3, 6.5 Hz, 1H), 3.78 (dd, *J* = 14.0, 9.3 Hz, 1H), 3.56 (dd, *J* = 14.0, 6.5 Hz, 1H). ESIMS m/z $[M-H]^-$ calcd. 871.25; found 871.15.

Application of **procedure F** (**SI-3**) for demethylation of **17m** (29 mg, 0.060 mmol). FC (DCM:MeOH 9:1) afforded a mixture of dimers (16 mg, by LCMS) that were purified by HPLC method A to give **41** (3 mg, 11 %) and **42** (2 mg, 8 %).

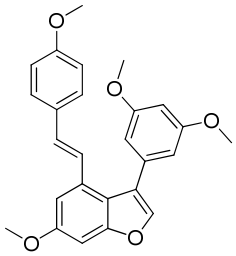



**41:** $^1$H NMR (600MHz, acetone-d6) $\delta$ (ppm): 8.66-7.77 (br, OHs), 7.52-7.37 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.11 (td, *J* = 8.7, 2.7 Hz, 1H), 7.03 (d, *J* = 2.1 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.87 (s, 1H), 6.82 (td, *J* = 8.7, 2.7 Hz, 1H), 6.81 (d, *J* = 2.1 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.74-6.66 (m, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 6.61-6.57 (m, 1H), 6.49 (d, *J* = 8.6 Hz, 2H), 6.42 (d, *J* = 8.6 Hz, 2H), 6.34 (d, *J* = 8.6 Hz, 2H), 5.99-5.96 (m, 1H), 4.75 (d, *J* = 7.6 Hz, 1H), 3.14 (dd, *J* = 11.3, 7.6 Hz, 1H), 2.91-2.85 (m, 1H), 2.56-2.47 (m, 2H). ESIMS m/z $[M-H]^-$ calcd. 875.24; found 875.13.

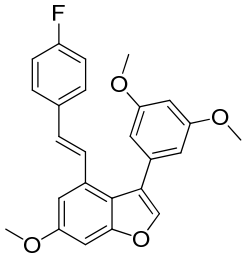


**42:** $^{1}$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 8.70-7.93 (br, OHs), 7.54-7.45 (m, 4H), 7.38-7.32 (m, 4H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.02 (s, 1H), 7.00-6.90 (m, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 2.1 Hz, 1H), 6.74 (d, *J* = 16.3 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 16.3 Hz, 1H), 6.42 (d, *J* = 2.1 Hz, 1H), 4.71 (t, *J* = 7.5 Hz, 1H), 3.63 (dd, *J* = 14.0, 7.5 Hz, 1H), 3.54 (dd, *J* = 14.0, 7.5 Hz, 1H). ESIMS m/z $[M-H]^-$ calcd. 875.24; found 875.13.

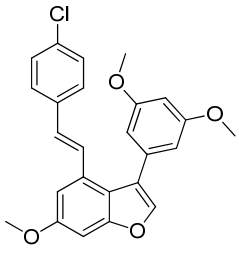
**SI-6. Alternatives routes toward viniferifuran and analogues**



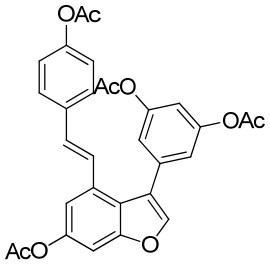
**20a**: Application of **procedure E** (**SI-3**) on **15a** (400 mg, 1.28 mmol). FC (heptane:EtOAc 4:1) gave **20a** as yellow solid. Yield: 400 mg (75 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.54 (s, 1H), 7.20 (d, $J$ = 16.3 Hz, 1H), 7.16 (d, $J$ = 2.1 Hz, 1H), 7.15 (d, $J$ = 8.7 Hz, 2H), 6.99 (d, $J$ = 2.1 Hz, 1H), 6.94 (d, $J$ = 16.3 Hz, 1H), 6.82 (d, $J$ = 8.7 Hz, 2H), 6.68 (d, $J$ = 2.3 Hz, 2H), 6.55 (t, $J$ = 2.3 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H), 3.73 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 160.6, 159.3, 158.2, 156.8, 141.3, 134.8, 132.5, 130.0, 129.1, 127.6, 123.9, 123.1, 118.6, 114.0, 107.8, 107.5, 100.1, 95.1, 55.8, 55.3; ESIMS m/z $[M+H]^+$ calcd. 417.17; found 417.07.



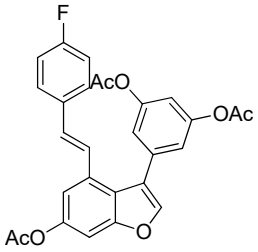
**20b:** Application of **procedure E** (**SI-3**) on **15a** (200 mg, 0.64 mmol). FC (heptane:EtOAc 4:1) gave **20b** as white solid. Yield: 200 mg (77 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.55 (s, 1H), 7.23 (d, $J$ = 16.3 Hz, 1H), 7.16 (dd, $J$ = 8.7, 5.4 Hz, 2H), 7.14 (d, $J$ = 2.2 Hz, 1H), 6.96 (t, $J$ = 8.7 Hz, 2H), 7.01 (d, $J$ = 2.1 Hz, 1H), 6.92 (d, $J$ = 16.3 Hz, 1H), 6.66 (d, $J$ = 2.3 Hz, 2H), 6.54 (t, $J$ = 2.3 Hz, 1H), 3.91 (s, 3H), 3.72 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 162.3 (d, $J$ = 247.7 Hz), 161.1, 158.2, 156.8, 141.4, 134.8, 133.4 (d, $J$ = 3.4 Hz), 131.9, 128.3, 127.9 (d, $J$ = 8.0 Hz), 125.8, 123.0, 118.8, 115.5 (d, $J$ = 21.5 Hz), 107.9, 100.0, 95.5, 55.8, 55.3; ESIMS m/z $[M+H]^+$ calcd. 405.15; found 405.10.



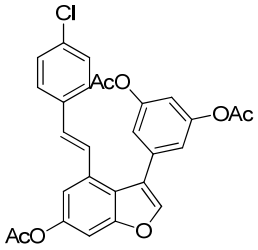
**20c:** Application of **procedure E** (**SI-3**) on **15a** (200 mg, 0.64 mmol). FC (heptane:EtOAc 4:1) gave **20c** as white solid. Yield: 200 mg (74 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.55 (s, 1H), 7.29 (d, $J$ = 16.1 Hz, 1H), 7.23 (d, $J$ = 8.5 Hz, 2H), 7.15 (d, $J$ = 2.1 Hz, 1H), 7.11 (d, $J$ = 8.5 Hz, 2H), 7.01 (d, $J$ = 2.1 Hz, 1H), 6.91 (d, $J$ = 16.1 Hz, 1H), 6.65 (d, $J$ = 2.3 Hz, 2H), 6.54 (t, $J$ = 2.3 Hz, 1H), 3.91 (s, 3H), 3.73 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 160.7, 158.2, 156.8, 141.5, 135.7, 134.7, 133.2, 131.7, 128.7, 128.1, 127.5, 126.6, 123.0, 118.9, 107.9, 100.0, 95.7, 55.8, 55.3; ESIMS m/z $[M+H]^+$ calcd. 421.12; found 421.02.



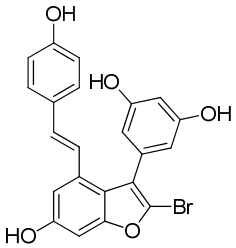

**21a:** Step 1: Application of **procedure F** (**SI-3**) for demethylation of **20a** (200 mg, 0.48 mmol). FC (DCM:MeOH 9:1) afforded a mixture containing **21a** as major product according to $^{1}$H NMR and was used as such in the next step. ESIMS m/z $[M-H]^-$ calcd. 359.09; found 359.02. Step 2: To a solution of this mixture (0.48 mmol, 1 eq., expected) in THF (5 mL) at 0 °C, was added $Ac_2O$ (0.54 mL, 5.76 mmol, 12 eq.) and $Et_3N$ (0.33 mL, 2.4 mmol, 5 eq.). The mixture was allowed to reach rt and was stirred for overnight. The solvent was evaporated and the residue was purified by FC (DCM:heptane:EtOAc 7:3:2) to afford **21a** as white solid. Yield: 100 mg (39 %, 2 steps). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.66 (s, 1H), 7.30-7.20 (m, 5H), 7.19 (d, $J$ = 16.2 Hz, 1H), 7.13 (d, $J$ = 2.0 Hz, 2H), ), 7.06 (t, $J$ = 2.0 Hz, 1H), 7.01 (d, $J$ = 8.5 Hz, 2H), 6.94 (d, $J$ = 16.2 Hz, 1H), 2.37 (s, 3H), 2.29 (s, 3H), 2.23 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 169.7, 169.4, 168.8, 155.6, 150.9, 150.3, 148.4, 143.7, 134.5, 134.4, 132.3, 130.1, 127.5, 124.8, 122.4, 121.8, 121.6, 120.2, 115.1, 113.7, 104.6, 21.2, 21.1, 21.0. ESIMS m/z $[M+H]^+$ calcd. 529.15; found 529.02.



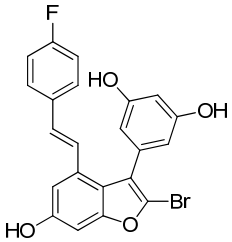

**21b:** Step 1: Application of **procedure F** (**SI-3**) for demethylation of **20b** (200 mg, 0.49 mmol). FC (heptane:EtOAc 3:2) afforded the phenolic product as yellow solid. Yield: 115 mg (64 %). ESIMS m/z $[M-H]^-$ calcd. 361.09; found 360.99. Step 2: To a solution of phenolic intermediate (115 mg, 0.32 mmol, 1 eq.) in THF (5 mL) at 0 °C, was added $Ac_2O$ (0.27 mL, 2.9 mmol, 9 eq.) and $Et_3N$ (0.18 mL, 1.27 mmol, 4 eq.). The mixture was allowed to reach rt and was stirred overnight. The solvent was evaporated and the residue was purified by FC (heptane:EtOAc 7:3) to afford **21b** as white solid. Yield: 118 mg (76 %). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.65 (s, 1H), 7.26 (d, $J$ = 1.9 Hz, 1H), 7.23 (d, $J$ = 1.9 Hz, 1H), 7.18 (dd, $J$ = 8.5, 5.4 Hz, 2H), 7.13 (d, $J$ = 16.2 Hz, 1H), 7.12 (d, $J$ = 2.1 Hz, 2H), 7.06 (t, $J$ = 2.1 Hz, 1H), 6.97 (d, $J$ = 8.7 Hz, 2H), 6.92 (d, $J$ = 16.2 Hz, 1H), 2.37 (s, 3H), 2.23 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 169.7, 168.7, 162.5 (d, $J$ = 247.7 Hz), 155.6, 150.9, 148.4, 143.7, 134.6, 132.9 (d, $J$ = 3.2 Hz), 132.3, 129.9, 128.2 (d, $J$ = 8.1 Hz), 124.4 (d, $J$ = 2.4 Hz), 122.4, 121.6, 120.3, 115.6 (d, $J$ = 21.7 Hz), 115.2, 113.6, 104.5, 21.2, 21.0. ESIMS m/z $[M+H]^+$ calcd. 489.13; found 489.02.



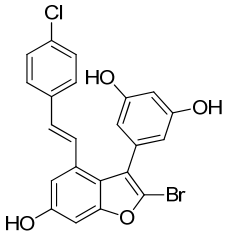

**21c:** Step 1: Application of **procedure F** (**SI-3**) for demethylation of **20c** (200 mg, 0.48 mmol). FC (heptane:EtOAc 3:2) afforded the phenolic product as yellow solid. Yield: 151 mg (84 %). ESIMS m/z $[M-H]^-$ calcd. 377.06; found 376.95. Step 2: To a solution of the phenolic intermediate (151 mg, 0.4 mmol, 1 eq.) in THF (5 mL) at 0 °C, was added $Ac_2O$ (0.34 mL, 3.6 mmol, 9 eq.) and $Et_3N$ (0.22 mL, 1.6 mmol, 4 eq.). The mixture was allowed to reach rt and was stirred overnight. The solvent was evaporated and the residue was purified by FC (heptane:EtOAc 7:3) to afford **21c** as white solid. Yield: 148 mg (74 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.66 (s, 1H), 7.27-7.23 (m, 4H), 7.19 (d, $J$ = 16.2 Hz, 1H), 7.13 (d, $J$ = 9.0 Hz, 2H), 7.12 (d, $J$ = 2.1 Hz, 2H), 7.06 (t, $J$ = 2.1 Hz, 1H), 6.90 (d, $J$ = 16.2 Hz, 1H), 2.36 (s, 3H), 2.23 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 169.7, 168.7, 155.6, 151.0, 148.4, 143.7, 135.2, 134.5, 133.5, 132.1, 129.8 128.8, 127.8, 125.2, 122.5, 115.2, 113.7, 104.7, 21.1, 21.0. ESIMS m/z $[M+H]^+$ calcd. 505.10; found 504.99.




**22a:** Step 1: To a mixture of **21a** (20 mg, 0.04 mmol, 1 eq.), pTsOH (7.2 mg, 0.04 mmol, 1 eq.) in DCM (2 mL) at rt was added NBS (20.2 mg, 0.12 mmol, 3 eq.). The mixture was stirred at rt overnight. The mixture was then diluted with DCM (25 mL) and washed with saturated $NaHCO_3$ solution (5 mL), $H_2O$ (5 mL), and brine (5 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane:DCM:EtOAc 7:3:1.5) gave the acetyl protected brominated product as pale yellow solid. Yield: 17 mg (74 %). ESIMS m/z $[M+H]^+$ calcd. 607.06; found 606.91. Step 2: To a solution of the brominated product (13 mg, 0.021 mmol, 1 eq.) in MeOH/THF/$H_2O$ (6 mL, v/v/v, 1/1/1) at 0 °C was added KOH (12 mg, 0.21 mmol, 10 eq.). The mixture was stirred at 0 °C for 30 min and then acidified with 1N HCl until pH = 1. The mixture was diluted with EtOAc (25 mL), washed with $H_2O$ (5 mL) and brine (5 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (DCM:MeOH 9:1) gave **22a** as yellow solid. Yield: 4.5 mg (48 %). $^1$H NMR (400 MHz, $CD_3OD$) $\delta$ (ppm): 7.04 (d, $J$ = 2.0 Hz, 1H), 7.01 (d, $J$ = 8.6 Hz, 2H), 6.98 (d, $J$ = 16.3 Hz, 1H), 6.89 (d, $J$ = 16.3 Hz, 1H), 6.78 (d, $J$ = 2.0 Hz, 1H), 6.43 (t, $J$ = 2.2 Hz, 1H), 6.36 (d, $J$ = 2.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CD_3OD$) $\delta$ (ppm): 160.0, 158.5, 158.0, 157.0, 135.8, 133.0, 130.4, 130.2, 128.9, 125.5, 123.3, 122.8, 120.3, 116.4, 110.0, 108.2, 103.4, 97.4; ESIMS m/z $[M-H]^-$ calcd. 437.00; found 436.90.



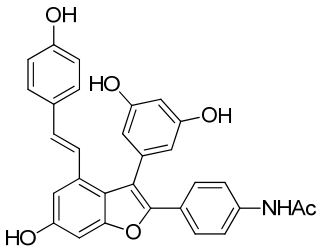

**22b:** Step 1: To a mixture of **21b** (20 mg, 0.041 mmol, 1 eq.), pTsOH (8 mg, 0.041 mmol, 1 eq.) in DCM (2 mL) at rt was added NBS (22 mg, 0.123 mmol, 3 eq.). The mixture was stirred at rt for 48 h. After cooling down, the mixture was diluted with DCM (25 mL) and washed with saturated $NaHCO_3$ solution (5 mL), $H_2O$ (5 mL), and brine (5 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane:EtOAc 7:3) gave the acetyla protected brominated product as pale yellow solid. Yield: 16 mg (70 %). ESIMS m/z [M+H]+ calcd. 567.04; found 566.92. Step 2: To a solution of the brominated product (30 mg, 0.053 mmol, 1 eq.) in MeOH/THF/$H_2O$ (6 mL, v/v/v, 1/1/1) at 0 °C was added KOH (30 mg, 0.53 mmol, 10 eq.). The mixture was stirred at 0 °C for 30 min and then acidified with 1N HCl until pH = 1. The mixture was diluted with EtOAc (25 mL), washed with $H_2O$ (5 mL) and brine (5 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (dichloromethane:MeOH 95:5) gave **22b** as yellow solid. Yield: 20 mg (84 %). The product **22b** is unstable and was therefore directly used in the subsequent Susuzki coupling. ESIMS m/z $[M-H]^-$ calcd. 439.00; found 438.90.



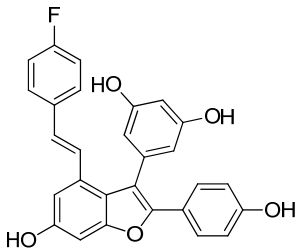

**22c:** Step 1: To a mixture of **21c** (20 mg, 0.041 mmol, 1 eq.), pTsOH (8 mg, 0.041 mmol, 1 eq.) in DCM (2 mL) at rt was added NBS (22 mg, 0.123 mmol, 3 eq.). The mixture was stirred at rt for 48 h. After cooling down, the mixture was diluted with DCM (25 mL) and washed with saturated $NaHCO_3$ solution (5 mL), $H_2O$ (5 mL), and brine (5 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane:EtOAc 7:3) gave desired acetyl protected brominated product as pale yellow solid. Yield: 16 mg (70 %). ESIMS m/z [M+H]+ calcd. 583.01; found 582.90. Step 2: To a solution of the brominated product (70 mg, 0.12 mmol, 1 eq.) in MeOH/THF/$H_2O$ (6 mL, v/v/v, 1/1/1) at 0 °C was added KOH (67 mg, 1.2 mmol, 10 eq.). The mixture was stirred at 0 °C for 30 min and then acidified with 1N HCl until pH = 1. The mixture was diluted with EtOAc (25 mL), washed with $H_2O$ (5 mL) and brine (5 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (DCM:MeOH 95:5) gave desired product **22c** as yellow solid. Yield: 51 mg (92 %). The product **22c** is unstable and was therefore directly used in the subsequent Susuzki coupling. ESIMS m/z $[M-H]^-$ calcd. 454.97; found 454.90.

**G) General procedure for Suzuki coupling using MWI (Examplified with 18p)**

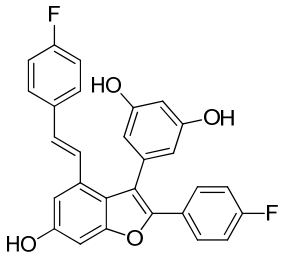
A mixture of **22a** (7 mg, 0.016 mmol. 1 eq.), 4-acetamidophenylboronic acid (4.3 mg, 0.024 mmol, 1.5 eq.), $PdCl_2$(dppf)·DCM (0.7 mg, 0.0008 mmol, 0.05 eq.) and $Na_2CO_3$ (5.1 mg, 0.05 mmol, 3 eq.) in a 1/1 mixture of DME/$H_2O$ (2 mL) was heated at 70 °C for 30 min under MWI. After cooling down, the mixture was diluted with EtOAc (15 mL), washed with water (5 mL) and brine (5 mL). The crude was purified by FC (DCM:MeOH 9:1) afforded desired product **18p** as a yellow solid. Yield: 6 mg (76 %).




$^1$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 9.25 (s, 1H), 8.68-8.32 (m, 4H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 1.9 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.96 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 1.9 Hz, 1H), 6.74 (d, *J* = 8.5 Hz, 2H), 6.60 (t, *J* = 2.1 Hz, 1H), 6.50 (d, *J* = 2.1 Hz, 2H), 2.88 (s, 3H); $^{13}$C NMR (150 MHz, acetone-d6) $\delta$ (ppm): 169.9, 161.5, 159.1, 157.8, 157.0, 150.5, 141.1, 138.8, 136.7, 134.2, 131.1, 130.3, 129.7, 128.1, 127.6, 123.7, 122.9, 120.6, 119.3, 117.3, 110.8, 108.6, 104.2, 98.3, 25.3; ESIMS m/z $[M-H]^-$ calcd. 492.14; found 492.04.

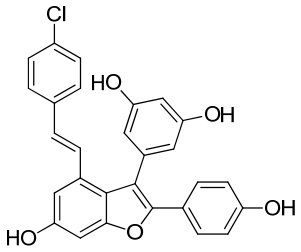



**18d:** Application of **procedure G** on **22b** (4 mg, 0.009 mmol FC (DCM:MeOH 92:8) gave **18d** as a yellow solid. Yield: 2 mg (50 %). NMR and MS data are given in **SI-3**.

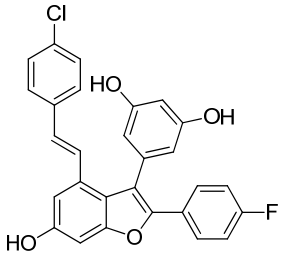



**18q:** Application of **procedure G** on **22b** (7 mg, 0.016 mmol). FC (DCM:MeOH 9:1) gave **18r** as a yellow solid. Yield: 4 mg (55 %). $^1$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 8.65 (br s, 1H), 8.60 (br s, 2H), 7.67 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.24 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.17 (d, *J* = 1.9 Hz, 1H), 7.13 (t, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 16.3 Hz, 1H), 7.05 (d, *J* = 16.3 Hz, 1H), 7.02 (t, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 1.9 Hz, 1H), 6.63 (t, *J* = 2.2 Hz, 1H), 6.51 (d, *J* = 2.2 Hz, 2H); $^{13}$C NMR (150 MHz, acetone-d6) $\delta$ (ppm): 164.1 (d, *J* = 246.6 Hz), 164.0 (d, *J* = 245.5

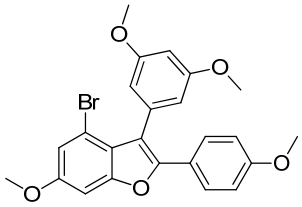
Hz), 161.6, 158.0, 157.1, 149.8, 138.5, 138.4, 138.3, 135.9 (d, *J* = 3.2 Hz), 133.7, 130.0 (d, *J* = 8.0 Hz), 129.7 (d, *J* = 8.0 Hz), 129.3, 129.2 (d, *J* = 3.3 Hz), 126.5, 126.4, 123.0, 120.0, 117.2 (d, *J* = 22.0 Hz), 117.1 (d, *J* = 21.8 Hz), 116.2, 116.0, 110.6, 109.3, 104.4, 99.0; ESIMS m/z $[M-H]^-$ calcd. 455.11; found 455.01.




**18r:** Application of **procedure G** on **22c** (12 mg, 0.026 mmol). FC (DCM:MeOH 9:1) gave **18r** as a yellow solid. Yield: 5 mg (41 %). $^1$H NMR (400 MHz, acetone-d6) $\delta$ (ppm): 8.70-8.43 (m, 4H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 16.3 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.62 (t, *J* = 2.2 Hz, 1H), 6.50 (d, *J* = 2.2 Hz, 2H); $^{13}$C NMR (100 MHz, acetone-d6) $\delta$ (ppm): 161.5, 159.4, 157.5, 156.8, 151.4, 139.0, 138.5, 134.1, 132.9, 130.4, 139.7, 129.3, 128.6, 127.7, 124.2, 123.6, 117.9, 117.2, 110.9, 109.0, 104.2, 99.2; ESIMS m/z $[M-H]^-$ calcd. 469.08; found 469.01.

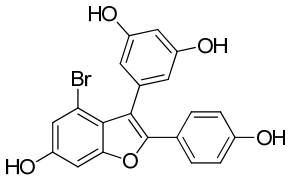



**18s:** Application of **procedure G** on **22c** (7 mg, 0.015 mmol). FC (DCM:MeOH 9:1) gave **18s** as a yellow solid. Yield: 3 mg (41 %). $^1$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 8.66 (br s, 1H), 8.60 (br s, 2H), 7.67 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 1.9 Hz, 1H), 7.17 (d, *J* = 16.3 Hz, 1H), 7.14 (t, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 16.3 Hz, 1H), 7.00 (d, *J* = 1.9 Hz, 1H), 6.65 (t, *J* = 2.2 Hz, 1H), 6.51 (d, *J* = 2.2 Hz, 2H); $^{13}$C NMR (150 MHz, acetone-d6) $\delta$ (ppm): 164.1 (d, *J* = 246.6 Hz), 161.7, 158.0, 157.1, 149.9, 138.4 (d, *J* = 9.3 Hz), 134.3, 133.4, 130.4, 129.7, 129.6, 129.2 (d, *J* = 3.3 Hz), 129.1, 127.4, 123.2, 119.9, 117.3 (d, *J* = 21.9 Hz), 110.6, 109.4, 104.4, 99.2; ESIMS m/z [M-H]- calcd. 471.08; found 470.99.




**23:** Application of **procedure D** (**SI-3**) on **19**[6] (2 g, 5.5 mmol). FC (heptane:EtOAc 85:15) gave **23** as white solid. Yield: 920 mg (36 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.48 (d, *J* = 9.0 Hz, 2H), 7.04 (d, *J* = 2.1 Hz, 1H), 7.02 (d, *J* = 2.1 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 2.3 Hz, 2H), 6.50 (t, *J* = 2.3 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 6H), 3.79 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 160.7, 159.5, 157.9, 154.6, 150.8, 134.5,

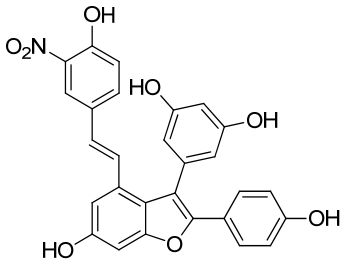
127.7, 123.0, 122.6, 116.0, 115.9, 113.9, 113.5, 109.5, 100.5, 95.5, 56.0, 55.4, 55.2. ESIMS m/z $[M+H]^+$ calcd. 469.06; found 468.95.




**24:** Application of **procedure F** (**SI-3**) for demethylation of **23** (485 mg, 1.03 mmol). FC (DCM:MeOH 92:8) afforded desired product as white solid. Yield: 410 mg (96 %). $^1$H NMR (400 MHz, DMSO-d6) $\delta$ (ppm): 10.08-9.12 (br, OHs), 7.30 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 2.0 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.20 (t, *J* = 2.2 Hz, 1H), 6.26 (d, *J* = 2.2 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ (ppm): 158.2, 157.6, 155.7, 154.2, 149.6, 133.7, 127.2, 120.7, 120.6, 116.2, 115.3, 115.2, 112.2, 109.0, 102.3, 97.2. ESIMS m/z $[M-H]^-$ calcd. 410.99; found 410.90.

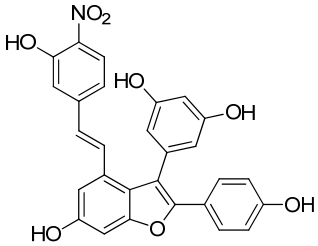
**H) General procedure for Heck coupling (Examplified with viniferifuran, 2)**

A mixture of **24** (10 mg, 0.024 mmol, 1 eq.), 4-hydroxystyrene (3.5 mg, 0.029 mmol, 1.2 eq.), $Pd(OAc)_2$ (0.54 mg, 0.0024 mmol, 0.1 eq.), dppp (1 mg, 0.0024 mmol, 0.1 eq.), $Et_3N$ (6.7 µL, 0.048 mmol, 2 eq.) in DMF (1 mL) was closed and degassed then heated at 120 °C for 20 h. After cooling down, the mixture was diluted with EtOAc (25 mL), washed with $H_2O$ (10 x 3 mL) and brine (10 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (DCM:MeOH 9:1) gave **2** as yellow solid. Yield: 7 mg (64 %). NMR and MS data are given in **SI-1**.

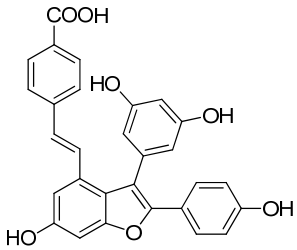



**18t:** Application of **procedure H** on **24** (10 mg, 0.024 mmol) with 3-nitro-4-hdroxystyrene. FC (DCM:MeOH 93:7) followed by HPLC method A gave **18t** as an orange solid. Yield: 3 mg (25 %).

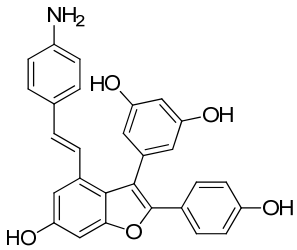
$^1$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 9.11-8.17 (br, OHs), 7.93 (d, *J* = 2.2 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.44 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.16 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 16.3 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 7.06 (d, *J* = 16.3 Hz, 1H), 6.97 (dd, *J* = 2.0 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.64 (t, *J* = 2.2 Hz, 1H), 6.50 (d, *J* = 2.2 Hz, 2H); $^{13}$C NMR (150 MHz, acetone-d6) $\delta$ (ppm): 161.5, 159.4, 157.5, 156.8, 155.9, 151.4, 138.8, 136.1, 136.0, 132.8, 132.2, 129.3, 127.6, 127.3, 124.3, 124.2, 123.5, 122.0, 117.9, 117.2, 110.8, 109.1, 104.4, 99.2. ESIMS m/z $[M-H]^-$ calcd. 496.10; found 495.95.



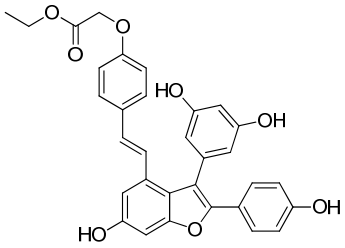

**18u:** Application of **procedure H** on **24** (10 mg, 0.024 mmol) with 3-hydroxy-4-nitrostyrene. FC (DCM:MeOH 93:7) followed by HPLC method A gave **18u** as an orange solid. Yield: 7 mg (58 %). $^{1}$H NMR (400 MHz, acetone-d6) $\delta$ (ppm): 9.30-8.24 (m, 4H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.52 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 16.3 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 16.3 Hz, 1H), 7.04 (d, *J* = 2.0 Hz, 1H), 7.00 (d, *J* = 1.7 Hz, 1H), 6.82 (d, *J* = 8.9 Hz, 2H), 6.82 (dd, *J* = 8.9, 1.7 Hz, 1H), 6.67 (t, *J* = 2.2 Hz, 1H), 6.51 (d, *J* = 2.2 Hz, 2H); $^{13}$C NMR (100 MHz, acetone-d6) $\delta$ (ppm): 161.6, 159.5, 157.5, 157.2, 156.8, 151.8, 149.1, 138.8, 134.3, 132.3, 131.9, 129.4, 127.7, 127.0, 124.2, 124.1, 119.1, 117.8, 117.2, 110.8, 109.5, 104.5, 100.3; ESIMS m/z $[M-H]^-$ calcd. 496.10; found 495.95.




**18v:** Application of **procedure H** on **24** (10 mg, 0.024 mmol) with4-carboxystyrene. FC (DCM:MeOH 8:2) gave **18v** as yellow solid. Yield: 7 mg (60 %). $^{1}$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 9.85-8.15 (m, 4H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 16.3 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 1.8 Hz, 1H), 7.11 (d, *J* = 16.3 Hz, 1H), 6.99 (d, *J* = 1.8 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.68 (t, *J* = 2.1 Hz, 1H), 6.52 (d, *J* = 2.1 Hz, 2H); $^{13}$C NMR (150 MHz, acetone-d6) $\delta$ (ppm): 161.6, 159.4, 157.5, 156.8, 151.5, 139.0, 132.6, 131.8, 129.4, 129.3, 128.9, 128.1, 124.2, 123.8, 117.9, 117.2, 110.9, 109.1, 104.3, 99.5; ESIMS m/z $[M-H]^-$ calcd. 479.11; found 479.01.



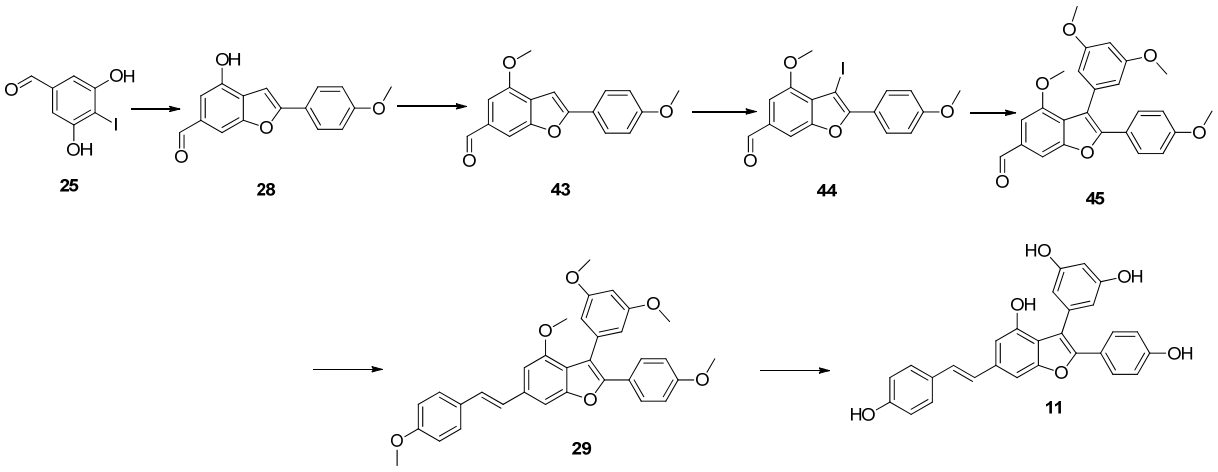

**18w:** Application of **procedure H** on **24** (10 mg, 0.024 mmol) with 4-aminostyrene. FC (DCM:MeOH 8:2) gave **18w** as yellow solid. Yield: 7 mg (64 %). $^{1}$H NMR (400 MHz, acetone-d6) $\delta$ (ppm): 8.67-8.30 (m, 4H), 7.47 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 2.0 Hz, 1H), 6.95 (d, *J* = 16.3 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 16.3 Hz, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.57 (t, *J* = 2.2 Hz, 1H), 6.56 (d, *J* = 8.5 Hz, 2H), 6.49 (d, *J* = 2.2 Hz, 2H), 4.76 (br s, 2H); This compound is not stable and gradually decomposed in acetone-d6 after a few day of stock in freeze. ESIMS m/z $[M-H]^-$ calcd. 450.13; found 450.01.

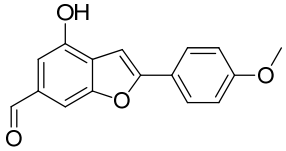


**18x:** Application of **procedure H** on **24** (10 mg, 0.024 mmol, 1 eq.) with 4-ethyoxycarbonylmethoxystyrene. FC (DCM:MeOH 4:1) gave **18x** as yellow solid. Yield: 7 mg (54 %). $^{1}$H NMR (400 MHz, acetone-d6) $\delta$ (ppm): 8.68-8.35 (br, OHs), 7.49 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 2.0 Hz, 1H), 7.08 (d, *J* = 16.3 Hz, 1H), 6.98 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.61 (t, *J* = 2.2 Hz, 1H), 6.50 (d, *J* = 2.2 Hz, 2H), 4.72 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, acetone-d6) $\delta$ (ppm): 170.3, 161.5, 159.6, 159.2, 157.5, 156.9, 151.2, 139.0, 133.6, 133.0, 129.6, 129.5, 129.3, 125.0, 124.4, 123.2, 118.0, 117.2, 116.5, 110.9, 108.6, 104.2, 98.6, 66.8, 62.5, 15.5. ESIMS m/z $[M-H]^-$ calcd. 537.15; found 537.05.

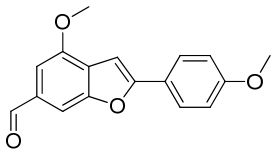
**SI-7. Synthetic procedures for total synthesis of anigopreissin A 11, resveratrol-piceatannol 12 and dehydro-δ-viniferin 4**

Synthesis of anigopreissin A, **11**



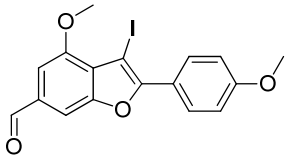



**28:** A mixture of **25** (400 mg, 1.51 mmol, 1 eq.), 4-ethynylanisole (240 mg, 1.82 mmol, 1.2 eq.), $PdCl_2(PPh_3)_2$ (53.2 mg, 0.076 mmol, 0.05 eq.), CuI (8.66 mg, 0.045 mmol, 0.03 eq.), $Et_3N$ (4.2 mL, 30.2 mmol, 20 eq.), THF (4 mL) in a microwave vial was closed and degassed then heated at 40 °C under MWI for 30 min. Then, $CH_3CN$ (8 mL) was added and the mixture was heated at 100 °C for 30 min. After cooling down and evaporation of the solvent, the residue was purified by FC (heptane:EtOAc 7:3) to afford **28** as yellow solid. Yield: 300 mg (74 %). $^1$H NMR (600 MHz, acetone-d6) $\delta$ (ppm): 9.99 (s, 1H), 9.35 (s, 1H, OH), 7.92 (d, $J$ = 8.6 Hz, 2H), 7.65 (s, 1H), 7.28 (s, 1H), 7.24 (s, 1H), 7.09 (d, $J$ = 8.6 Hz, 2H), 3.88 (s, 3H). $^{13}$C NMR (150 MHz, acetone-d6) $\delta$ (ppm): 192.9, 162.7, 160.1, 157.6, 153.0, 136.2, 128.6, 126.7, 124.3, 116.4, 109.0, 107.8, 99.5, 56.8. ESIMS m/z $[M+H]^+$ calcd. 269.08; found 268.98.

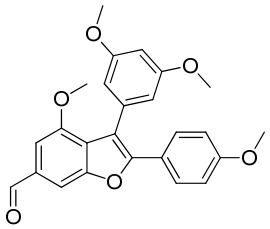


**43:** To a mixture of phenol intermediate **28** (300 mg, 1.1 mmol, 1 eq.) in DMF (5 mL) at rt, was added $K_2CO_3$ (232 mg, 1.67 mmol, 1.5 eq.) and MeI (105 µL, 1.67 mmol, 1.5 eq.). The mixture was stirred at rt for overnight. EtOAc (50 mL) was added and the organic phase was washed with $H_2O$ (20 mL x 3) and brine (20 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane:DCM:EtOAc 7:3:1.5) gave **43** as yellow solid. Yield: 242 mg (77 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.99 (s, 1H), 7.81 (d, $J$ = 8.9 Hz, 2H), 7.63 (t, $J$ = 0.8 Hz, 1H), 7.22 (d, $J$ = 0.8 Hz, 1H), 7.03 (d, $J$ = 0.8 Hz, 1H), 6.99 (d, $J$ = 8.6 Hz, 2H),

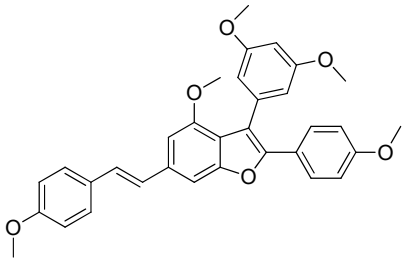
4.02 (s, 3H), 3.87 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 191.4, 160.6, 158.7, 155.0, 153.4, 133.6, 126.8, 126.1, 122.5, 114.4, 109.0, 102.0, 97.7, 55.8, 55.4. ESIMS m/z [M+H]+ calcd. 283.10; found 283.00.



**44:** To a mixture of **43** (95 mg, 0.336 mmol, 1 eq.) in $CH_3CN$ (10 mL) at rt was added NIS (75.7 mg, 0.336 mmol, 1 eq.), pTsOH (64 mg, 0.336 mmol, 1 eq.). The mixture was stirred at rt for overnight. After that, the mixture was diluted with EtOAc (25 mL) and washed with saturated $NaHCO_3$ solution (5 mL), 10 % $Na_2S_2O_3$ solution (5 mL), and brine (5 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was then dissolved in 1/1/1 mixture of DCM/MeOH/acetone (30 mL). FC (heptane:DCM:EtOAc 7:3:0.5) gave **44** as pale yellow solid. Yield: 81 mg (59 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.98 (s, 1H), 8.11 (d, *J* = 9.0 Hz, 2H), 7.62 (d, *J* = 0.9 Hz, 1H), 7.23 (d, *J* = 0.9 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 2H), 4.02 (s, 3H), 3.89 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 191.2, 160.8, 156.3, 154.5, 154.2, 133.9, 129.7, 125.7, 124.0, 122.0, 113.9, 108.5, 102.7, 55.8, 55.4. ESIMS m/z $[M+H]^+$ calcd. 408.99; found 408.90.

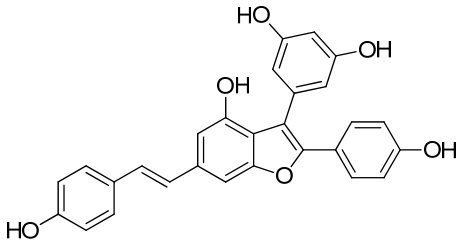


**45:** A mixture of **44** (57 mg, 0.14 mmol, 1 eq.), 3,5-dimethoxyphenylboronic acid (35.6 mg, 0.2 mmol, 1.4 eq.), $PdCl_2$(dppf).DCM (5.81 mg, 0.007 mmol, 0.05 eq.) and $K_2CO_3$ (58 mg, 0.42 mmol, 3 eq.) in a 1/1 mixture of THF/$H_2O$ (6 mL) was heated at 70 °C for 30 min under MWI. After cooling down, the mixture was diluted with EtOAc (25 mL), washed with water (5 mL) and brine (5 mL). FC (heptane:EtOAc 4:1) gave **45** as yellow solid. Yield: 53 mg (91 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 9.98 (s, 1H), 7.63 (d, *J* = 0.9 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 2H), 7.19 (d, *J* = 0.9 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 2.3 Hz, 2H), 6.52 (t, *J* = 2.3 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.78 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 191.4, 160.4, 160.0, 154.6, 154.1, 153.7, 134.7, 133.6, 128.6, 124.9, 122.4, 116.1, 113.9, 108.7, 108.6, 102.3, 100.1, 55.7, 55.3, 55.2. ESIMS m/z $[M+H]^+$ calcd. 419.15; found 419.05.



**29:** A mixture of **45** (40 mg, 0.096 mmol. 1 eq.), 60 % NaH (11.5 mg, 0.29 mmol, 3 eq.) and diethyl 4-methoxybenzylphosphonate (37 mg, 0.143 mmol, 1.5 eq.) in THF (3 mL) in a MW vial was closed and heated at 140 °C under MWI for 30 min. After cooling down, sat. $NH_4Cl$ (1 mL) was added and the mixture was extracted with EA (25 mL). The organic phase was washed with $H_2O$ (5 mL) and brine (5 mL), dried

with $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane:EtOAc 75:25) gave **29** as yellow solid. Yield: 29 mg (58 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.52 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 0.9 Hz, 1H), 7.11 (d, *J* = 16.2 Hz, 1H), 7.06 (d, *J* = 16.2 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 0.9 Hz, 1H), 6.67 (d, *J* = 2.3 Hz, 2H), 6.51 (t, *J* = 2.3 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.78 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 160.3, 159.4, 159.2, 155.4, 154.2, 150.3, 135.6, 135.1, 130.1, 128.3, 127.6, 127.1, 123.3, 118.8, 116.0, 114.1, 113.8, 108.7, 102.4, 102.3, 100.0, 55.6, 55.4, 55.3, 55.2. ESIMS m/z $[M+H]^+$ calcd. 523.21; found 523.07.



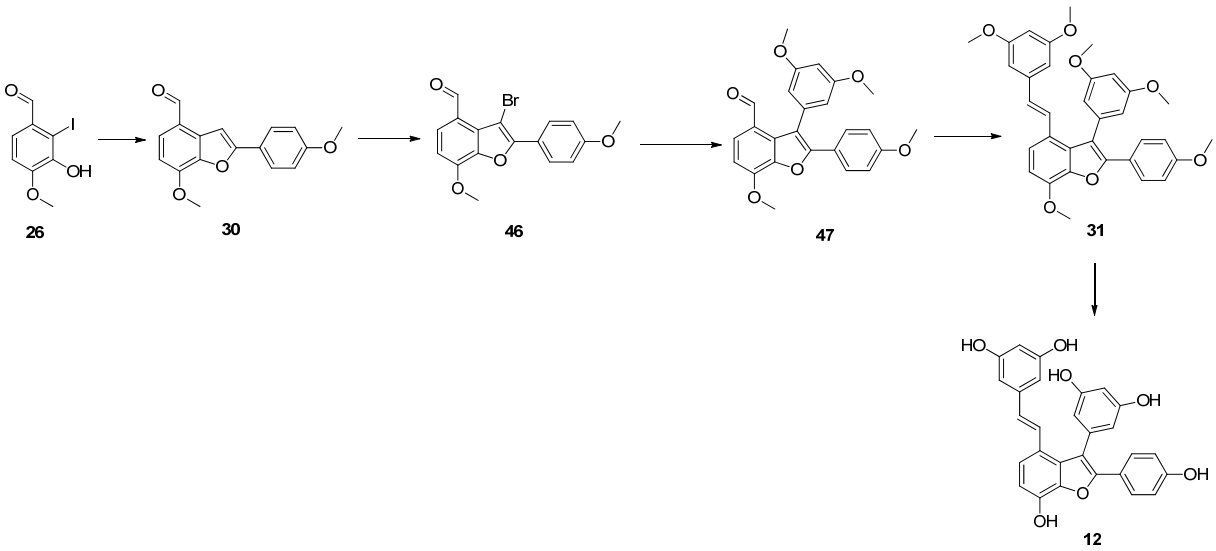

Anigopreissin A **11**

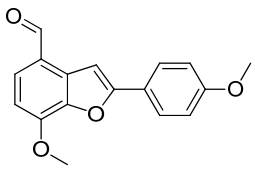
Table S1. NMR data comparison of our synthetic anigopreisin A **11** with literature[9] (natural product isolation)

| $^1$H | | $^{13}$C | |
|---|---|---|---|
| Our data<br>$CD_3OD$, 400MHz | Ref 9a<br>Acetone-d6, 500MHz | Our data<br>$CD_3OD$, 400MHz | Ref 9a<br>Acetone-d6, 500MHz |
| 7.44-7.35<br>(m, 4H) | 7.46<br>(d, *J* = 8.8 Hz, 2H) | 159.5 | 159.5 |
| | 7.45<br>(d, *J* = 8.5 Hz, 2H) | 158.7 | 158.4 |
| 7.15<br>(d, *J* = 0.9 Hz, 1H) | 7.25<br>(d, *J* = 0.8 Hz, 1H) | 158.4 | 158.1 |
| 7.06<br>(d, *J* = 16.2 Hz, 1H) | 7.13<br>(d, *J* = 16.3 Hz, 1H) | 157.2 | 156.5 |
| 6.98<br>(d, *J* = 16.2 Hz, 1H) | 7.06<br>(d, *J* = 16.3 Hz, 1H) | 153.0 | 152.4 |
| 6.78<br>(d, *J* = 8.6 Hz, 2H) | 6.85<br>(d, *J* = 8.5 Hz, 2H) | 151.2 | 150.6 |
| 6.76<br>(d, *J* = 0.9 Hz, 1H) | 6.87<br>(d, *J* = 0.8 Hz, 1H) | 137.2 | 136.5 |
| 6.71<br>(d, *J* = 8.8 Hz, 2H) | 6.80<br>(d, *J* = 8.8 Hz, 2H) | 136.8 | 136.4 |
| 6.42<br>(d, *J* = 2.2 Hz, 2H) | 6.49<br>(d, *J* = 2.2 Hz, 2H) | 130.7 | 130.0 |
| 6.31<br>(t, *J* = 2.2 Hz, 1H) | 6.41<br>(d, *J* = 2.2 Hz, 1H) | 129.3 | 128.9 |
| | | 128.9 | 128.7 |
| | | 128.8 | 128.6 |
| | | 127.3 | 126.8 |
| | | 123.7 | 123.0 |
| | | 119.1 | 118.6 |
| | | 116.8 | 116.4 |
| | | 116.6 | 116.3 |

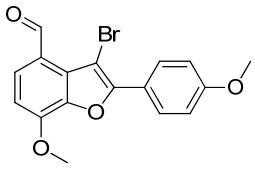
| | | | |
|---|---|---|---|
| | | 116.2 | 116.1 |
| | | 110.3 | 109.7 |
| | | 107.2 | 107.4 |
| | | 102.8 | 102.9 |
| | | 101.7 | 101.4 |

Synthesis of resveratrol-piceatannol hybrid, **12**

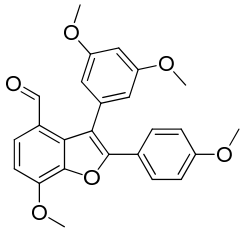


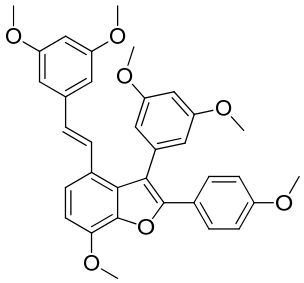
**30:** A mixture of **26** (500 mg, 1.8 mmol, 1 eq.), 4-ethynylanisole (285 mg, 2.2 mmol, 1.2 eq.), $PdCl_2(PPh_3)_2$ (63.1 mg, 0.09 mmol, 0.05 eq.), CuI (10.3 mg, 0.054 mmol, 0.03 eq.), $Et_3N$ (5 mL, 36.1 mmol, 20 eq.), THF (5 mL) in a MW vial was closed and degassed then heated at 40 °C under MWI for 30 min. Then, $CH_3CN$ (10 mL) was added and the mixture was heated at 100 °C for 30 min. After cooling down and evaporation of the solvent FC (heptane:DCM:EtOAc 7:3:1) gave **30** as yellow solid. Yield: 459 mg (90 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 10.05 (s, 1H), 7.88 (d, $J$ = 9.0 Hz, 2H), 7.66 (s, 1H), 7.65 (d, $J$ = 8.3 Hz, 1H), 6.98 (d, $J$ = 9.0 Hz, 2H), 6.86 (d, $J$ = 8.3 Hz, 1H), 4.13 (s, 3H), 3.87 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 190.8, 160.6, 159.2, 149.6, 143.7, 131.8, 130.3, 127.0, 122.7, 122.5, 114.3, 105.7, 100.4, 56.4, 55.4; ESIMS m/z $[M+H]^+$ calcd. 283.10; found 282.95.



**46:** To a mixture of **30** (1.03 g, 3.64 mmol, 1 eq.) in DCM (200 mL) at rt was added NBS (712 mg, 4.0 mmol, 1.1 eq.). The mixture was stirred at rt for overnight. After that, the mixture was washed with saturated $NaHCO_3$ solution (50 mL), $H_2O$ (50 mL), and brine (50 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was then redissolved in 1/1/1 mixture of DCM/MeOH/acetone (30 mL). The solid was filtered and washed with heptane (30 mL) and then dried under vacuum to give a yellow solid. Yield: 788 mg (60 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 11.20 (s, 1H), 8.11 (d, $J$ = 9.0 Hz, 2H), 7.99 (d, $J$ = 8.6 Hz, 1H), 7.03 (d, $J$ = 9.0 Hz, 2H), 6.91 (d, $J$ = 8.6 Hz, 1H), 4.10 (s, 3H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 187.6, 160.8, 153.6, 149.5, 142.5, 130.9, 129.4, 125.7, 123.1, 121.2, 114.1, 106.9, 89.8, 56.4, 55.4; ESIMS m/z [M+H]+ calcd. 361.00; found 360.90.



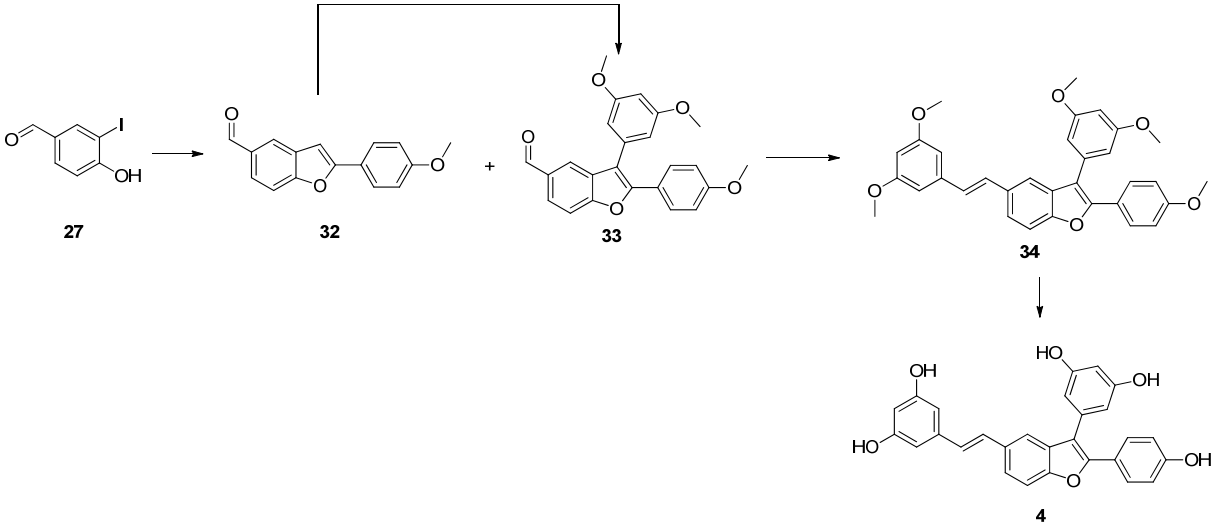
**47:** A mixture of **46** (150 mg, 0.414 mmol. 1 eq.), 3,5-dimethoxyphenylboronic acid (90.6 mg, 0.498 mmol, 1.2 eq.), $PdCl_2$(dppf)·DCM (17.3 mg, 0.021 mmol, 0.05 eq.) and $K_2CO_3$ (169 mg, 1.24 mmol, 3 eq.) in a 1/1 mixture of THF/$H_2O$ (12 mL) was heated at 100 °C for 30 min under MWI. After cooling down, the mixture was diluted with EtOAc (25 mL), washed with water (5 mL) and brine (5 mL). FC (heptane:EtOAc 75:25) gave **47** as a white solid. Yield: 144 mg (83 %). $^1$H NMR (400M Hz, $CDCl_3$) $\delta$ (ppm): 9.67 (s, 1H), 7.90 (d, $J$ = 8.5 Hz, 1H), 7.58 (d, $J$ = 9.0 Hz, 2H), 6.90 (d, $J$ = 8.5 Hz, 1H), 6.83 (d, $J$ = 9.0 Hz, 2H), 6.61 (d, $J$ = 2.3 Hz, 2H), 6.55 (t, $J$ = 2.3 Hz, 1H), 4.14 (s, 3H), 3.80 (s, 3H), 3.79 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 188.9, 161.8, 160.1, 152.8, 149.5, 142.4, 136.2, 133.7, 128.4, 124.7, 123.2, 122.3, 115.6, 114.0, 107.9, 106.6, 100.6, 56.4, 55.4, 55.3. ESIMS m/z $[M+H]^+$ calcd. 419.15; found 419.05.



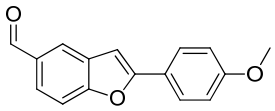
**31:** A mixture of **47** (100 mg, 0.24 mmol. 1 eq.), 60 % NaH (28.8 mg, 0.72 mmol, 3 eq.) and diethyl 3,5-dimethoxybenzylphosphonate (103 mg, 0.36 mmol, 1.5 eq.) in THF (5 mL) in a MW vial was closed and heated at 120 °C under MWI for 30 min. After cooling down, sat. $NH_4Cl$ (1 mL) was added and the mixture was extracted with EA (25 mL). The organic phase was washed with $H_2O$ (5 mL) and brine (5 mL), dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane:DCM:EtOAc 7:3:1) gave **31** as white solid. Yield: 80 mg (61 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.57 (d, $J$ = 8.9 Hz, 2H), 7.47 (d, $J$ = 8.4 Hz, 1H), 6.97 (d, $J$ = 16.2 Hz, 1H), 6.84 (d, $J$ = 8.9 Hz, 2H), 6.82 (d, $J$ = 8.4 Hz, 1H), 6.80 (d, $J$ = 16.2 Hz, 1H), 6.67 (d, $J$ = 2.2 Hz, 2H), 6.56 (t, $J$ = 2.2 Hz, 1H), 6.31 (t, $J$ = 2.1 Hz, 1H), 6.26 (d, $J$ = 2.1 Hz, 2H), 4.09 (s, 3H), 3.80 (s, 3H), 3.77 (s, 6H), 3.74 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 161.2, 160.8, 159.6, 151.1, 144.7,

142.7, 139.7, 136.5, 129.5, 128.1, 127.0, 125.3, 124.1, 123.0, 119.8, 116.7, 113.8, 108.4, 107.2, 103.8, 100.9, 99.9, 56.3, 55.4, 55.2; ESIMS m/z $[M+H]^+$ calcd. 553.22; found 553.07.

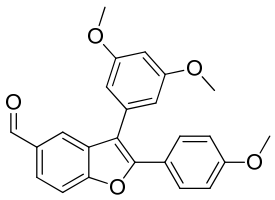
Synthesis of dehydro-δ-viniferin, **4**




A mixture of **27** (100 mg, 0.4 mmol, 1 eq.), 4-ethynylanisole (64 mg, 0.48 mmol, 1.2 eq.), $PdCl_2(PPh_3)_2$ (14.2 mg, 0.02 mmol, 0.05 eq.), CuI (2.2 mg, 0.012 mmol, 0.03 eq.), $Et_3N$ (1.12 mL, 8.0 mmol, 20 eq.), THF (1 mL) in a MW vial was closed and degassed then heated at 40 °C under MWI for 30 min. Then, 1-iodo-3,5-dimethoxybenzene (128 mg, 0.48 mmol, 1.2 eq.) and $CH_3CN$ (2 mL) were added and the mixture was heated at 100 °C for 30 min. After cooling down and evaporation of the solvent FC (heptane:EtOAc 4:1) gave **33** as yellow solid (40 mg, 26 %) and **32** as yellow solid (60 mg, 60 %).



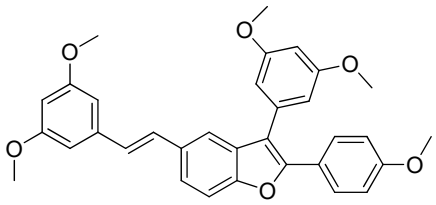
**32:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 10.05 (s, 1H), 8.02 (d, $J$ = 1.5 Hz, 1H), 8.08 (d, $J$ = 1.2 Hz, 1H), 7.83-7.78 (m, 3H), 7.60 (d, $J$ = 8.4 Hz, 1H), 7.00 (d, $J$ = 8.9 Hz, 2H), 6.97 (s, 1H), 3.87 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 191.8, 160.5, 158.1, 132.3, 130.1, 126.7, 125.6, 123.5, 122.4, 114.4, 111.6, 99.8, 55.4; ESIMS m/z $[M+H]^+$ calcd. 253.08; found 253.01.



**33:** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 10.02 (s, 1H), 8.02 (d, $J$ = 1.5 Hz, 1H), 7.86 (dd, $J$ = 8.5, 1.5 Hz, 1H), 7.65 (d, $J$ = 8.9 Hz, 2H), 7.61 (d, $J$ = 8.5 Hz, 1H), 6.87 (d, $J$ = 8.9 Hz, 2H), 6.64 (d, $J$ = 2.3 Hz, 2H), 6.55 (t, $J$ = 2.3 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 191.7, 161.3, 160.1, 157.1, 152.5,

133.8, 132.3, 131.1, 128.5, 125.7, 123.1, 122.2, 116.1, 114.0, 111.6, 107.6, 100.0, 55.4, 55.2. ESIMS m/z $[M+H]^+$ calcd. 389.14; found 389.01.

A mixture of **32** (12 mg, 0.05 mmol, 1 eq.), 1-bromo-3,5-dimethoxybenzene (15.5 mg, 0.071 mmol, 1.5 eq.), $PdCl(C_3H_5)$dppb (1.5 mg, 0.0024 mmol, 0.05 eq.), KOAc (14 mg, 0.14 mmol, 3 eq.) in DMA (1 mL) was closed and degassed then heated at 150 °C for 20 h. After cooling down, the mixture was diluted with EtOAc (25 mL), washed with $H_2O$ (10 x 3 mL) and brine (5 mL). The organic phase was dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane:EtOAc 4:1) gave **33** as yellow solid. Yield: 11 mg (60 %).



**34:** A mixture of **33** (40 mg, 0.103 mmol. 1 eq.), 60 % NaH (12.4 mg, 0.31 mmol, 3 eq.) and diethyl 3,5-dimethoxybenzylphosphonate (44.5 mg, 0.154 mmol, 1.5 eq.) in THF (3 mL) in a MW vial was closed and heated at 120 °C under MWI for 30 min. After cooling down, sat. $NH_4Cl$ (1 mL) was added and the mixture was extracted with EtOAc (25 mL). The organic phase was washed with $H_2O$ (5 mL) and brine (5 mL), dried with $Na_2SO_4$ and concentrated under reduced pressure. FC (heptane:EtOAc 3:1) gave **34** as yellow solid. Yield: 45 mg (84 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm): 7.65 (d, *J* = 8.9 Hz, 2H), 7.60 (s, 1H), 7.50 (d, *J* = 1.0 Hz, 2H), 7.18 (d, *J* = 16.2 Hz, 1H), 7.01 (d, *J* = 16.2 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.68 (d, *J* = 2.2 Hz, 4H), 6.56 (t, *J* = 2.2 Hz, 1H), 6.40 (t, *J* = 2.2 Hz, 1H), 3.84 (s, 6H), 3.83 (s, 3H), 3.81 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ (ppm): 161.2, 160.9, 159.8, 153.5, 151.3, 139.5, 134.8, 132.4, 130.8, 129.5, 128.4, 127.5, 123.0, 122.9, 117.8, 115.9, 113.9, 111.1, 107.7, 104.3, 99.9, 99.8, 55.4, 55.3, 55.2. ESIMS m/z $[M+H]^+$ calcd. 523.21; found 523.07.

**SI-8. References**


[1] G.-W. Wang, H.-L. Wang, D. A. Capretto, Q. Han, R.-B. Hu, S.-D. Yang, *Tetrahedron* **2012**, *68*, 5216.

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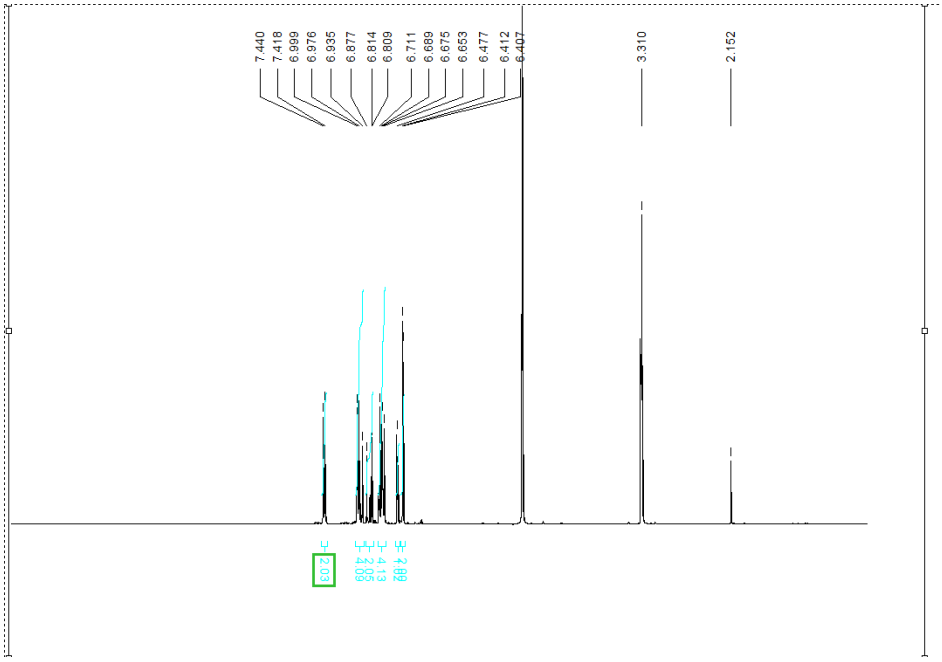
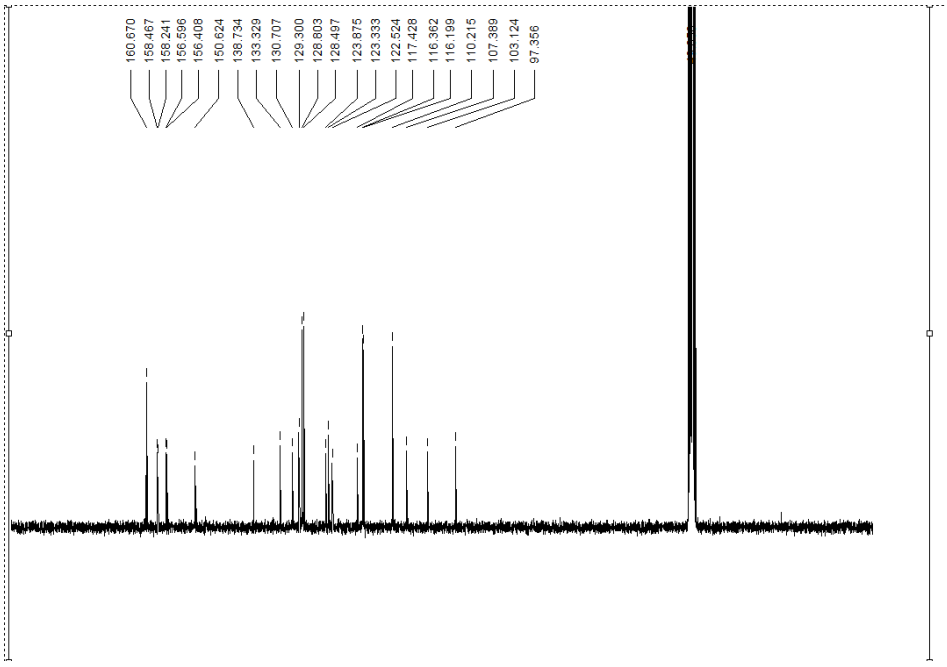
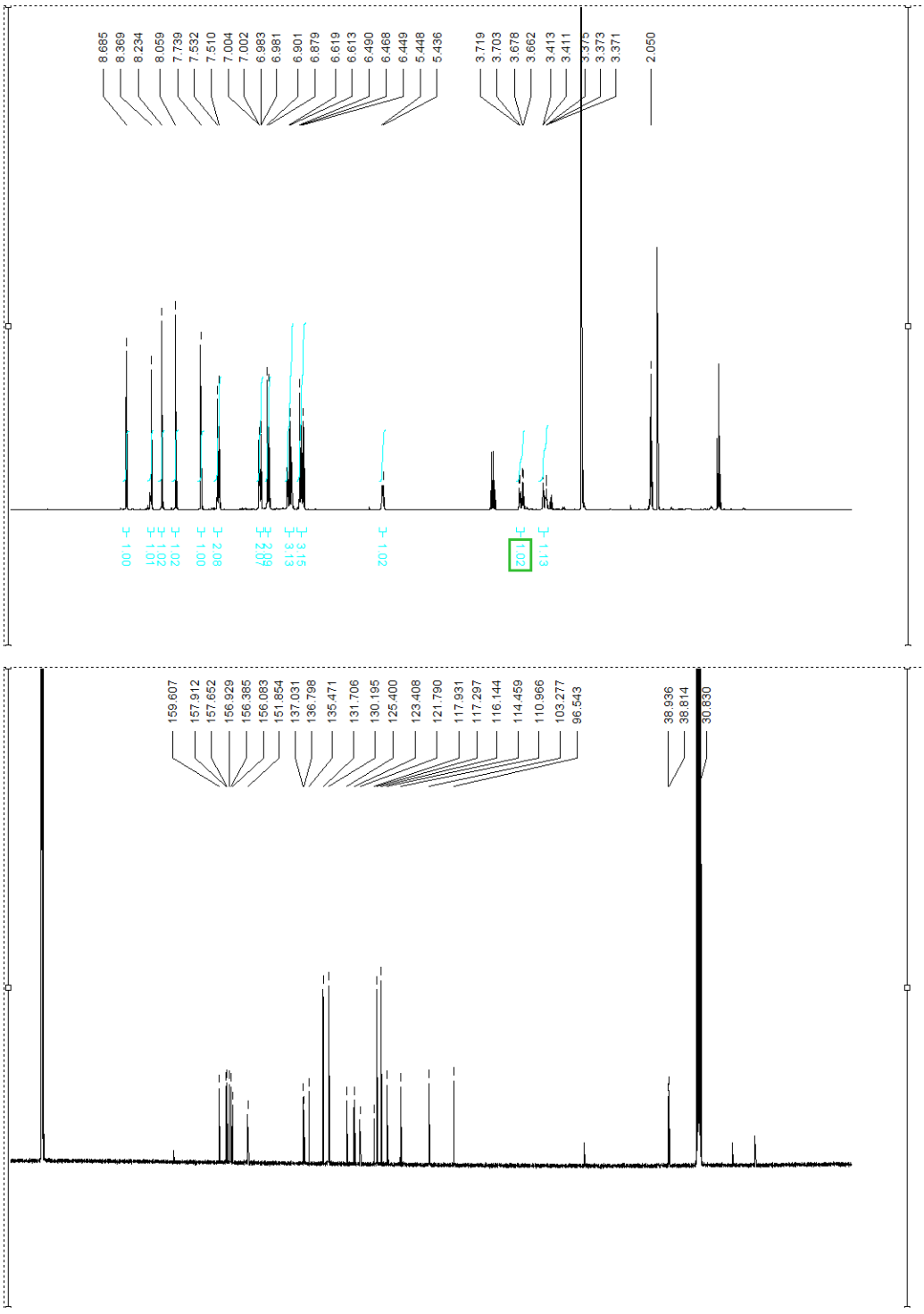
**SI-9. NMR spectra of final compounds**

Viniferifuran **2**

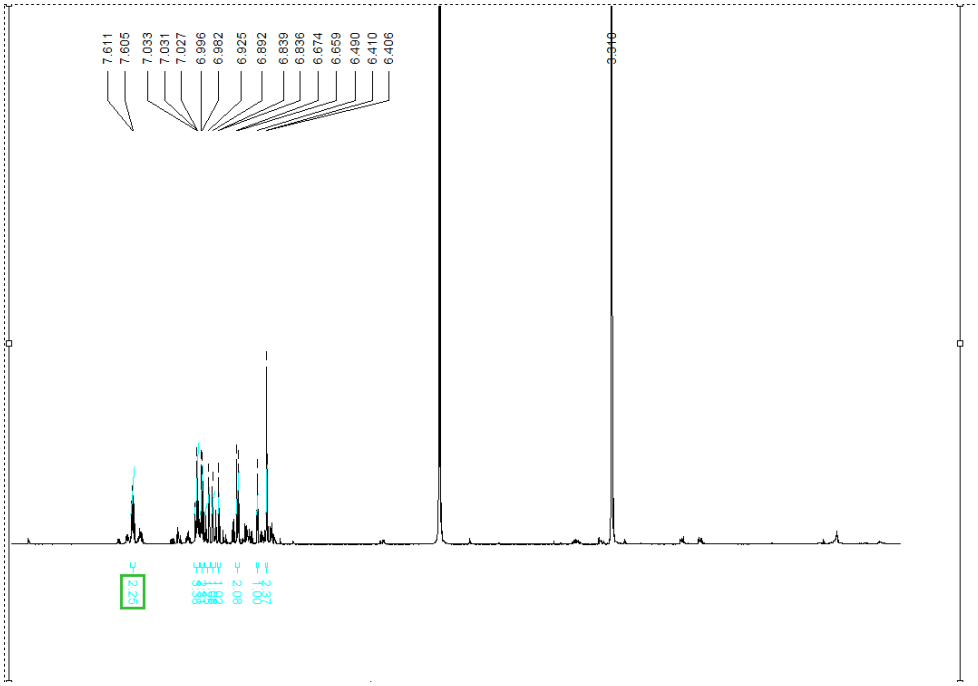


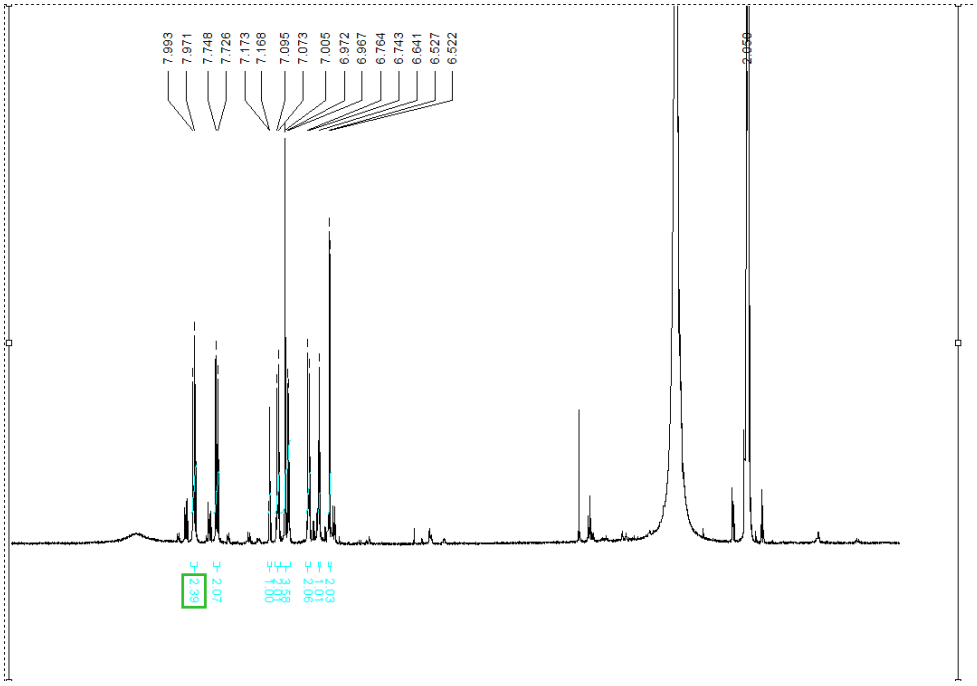
Dehydroampelopsin **9**



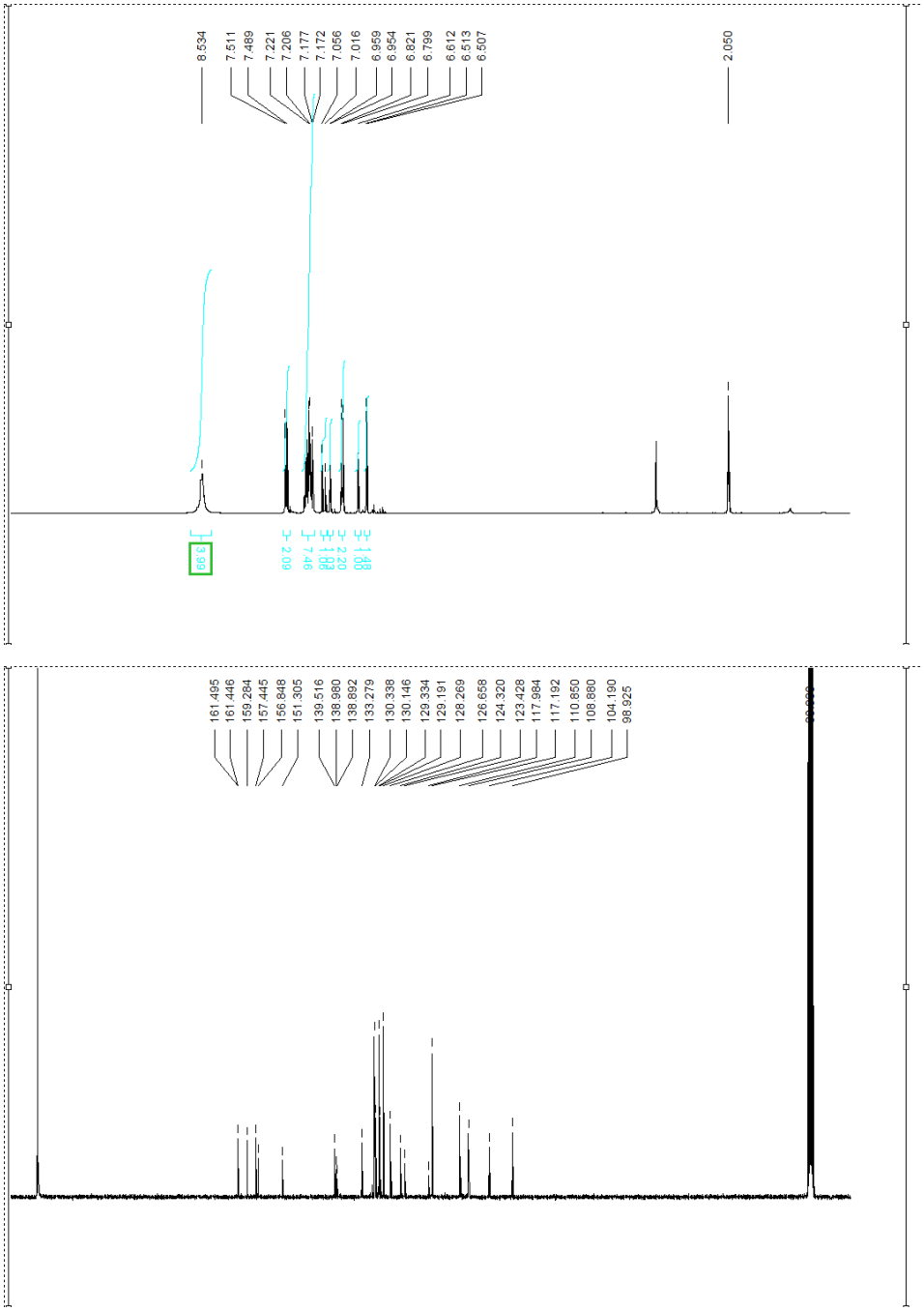
Compound **18a**



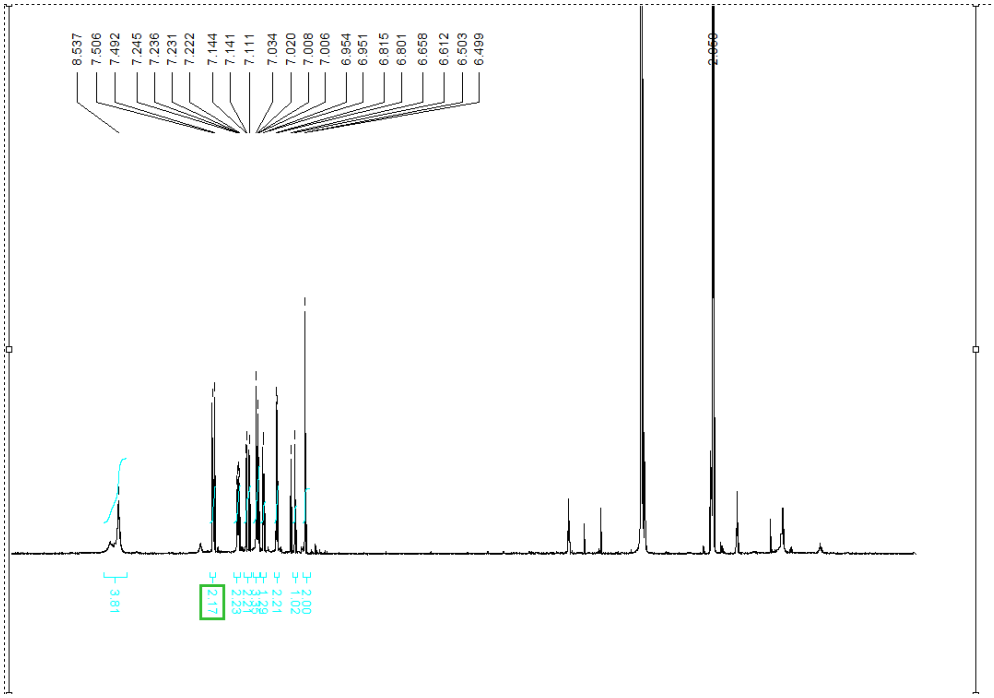
Compound **18b**

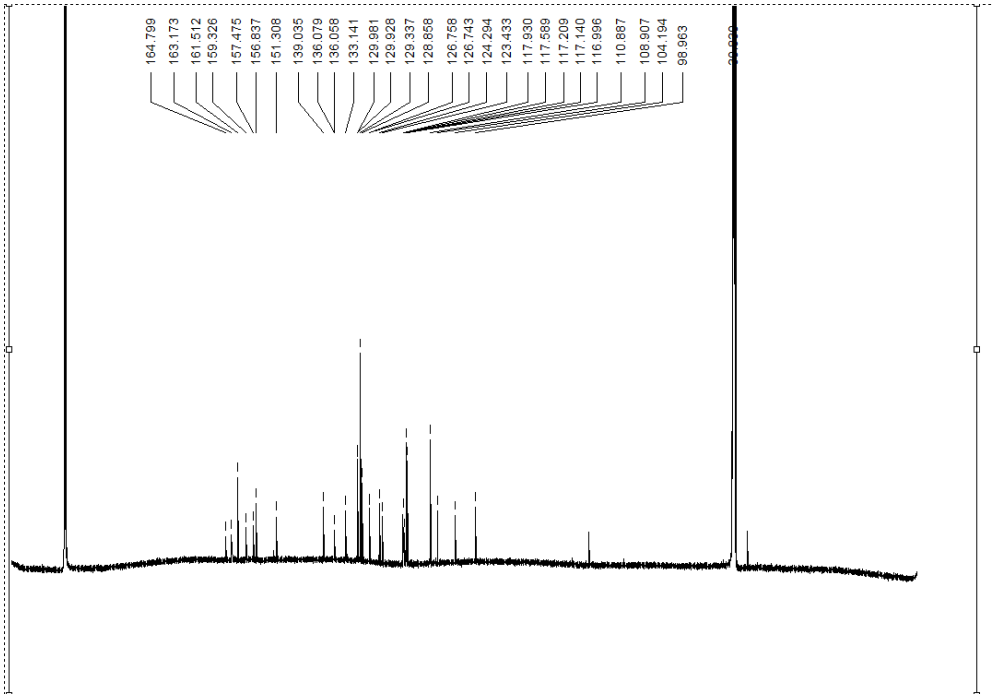


Compound **18c**

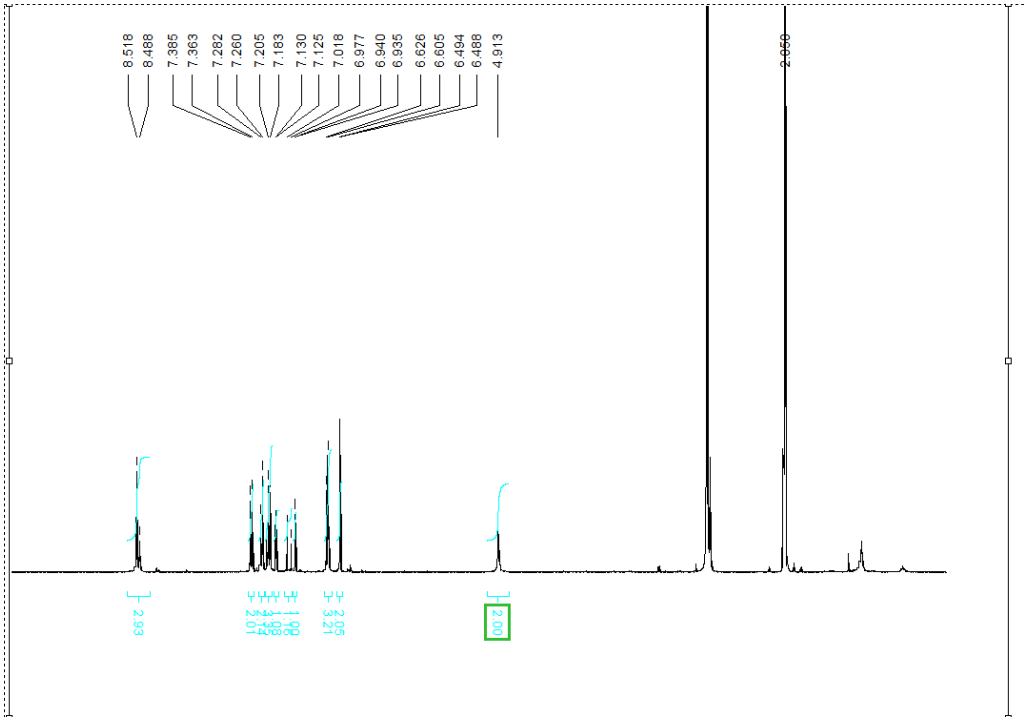


Compound **18d**

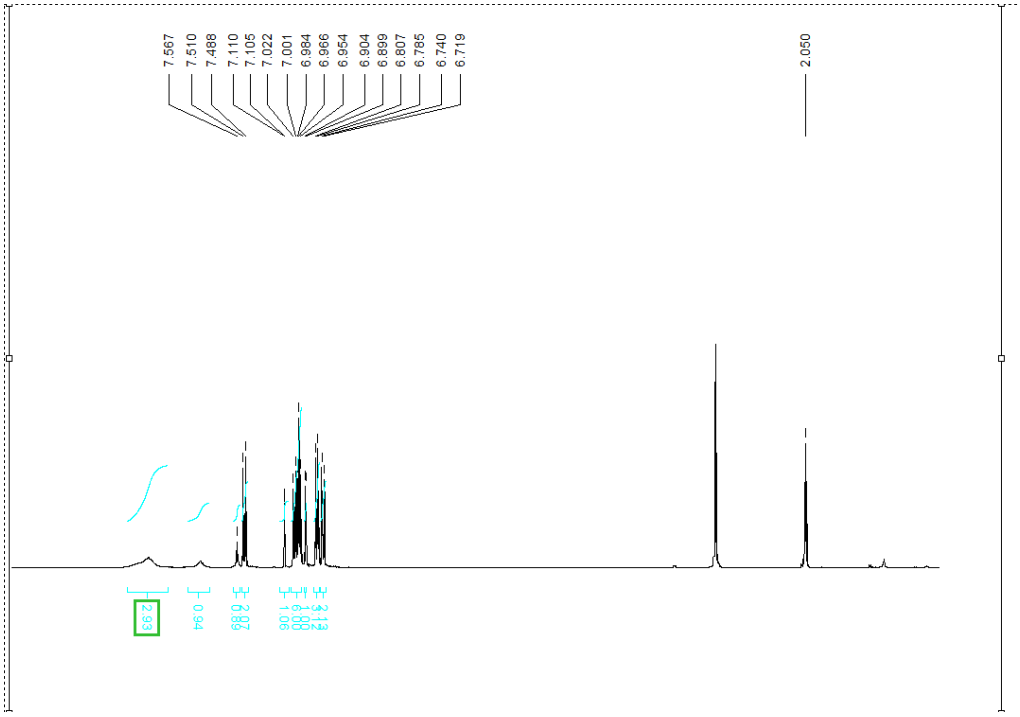


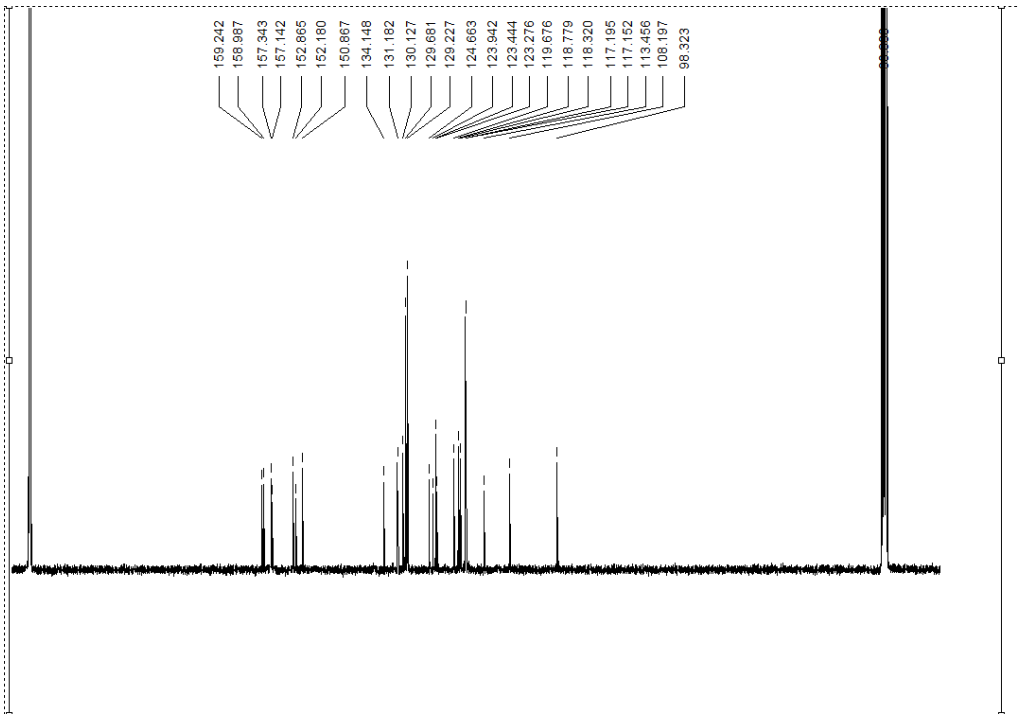



Compound **18g**

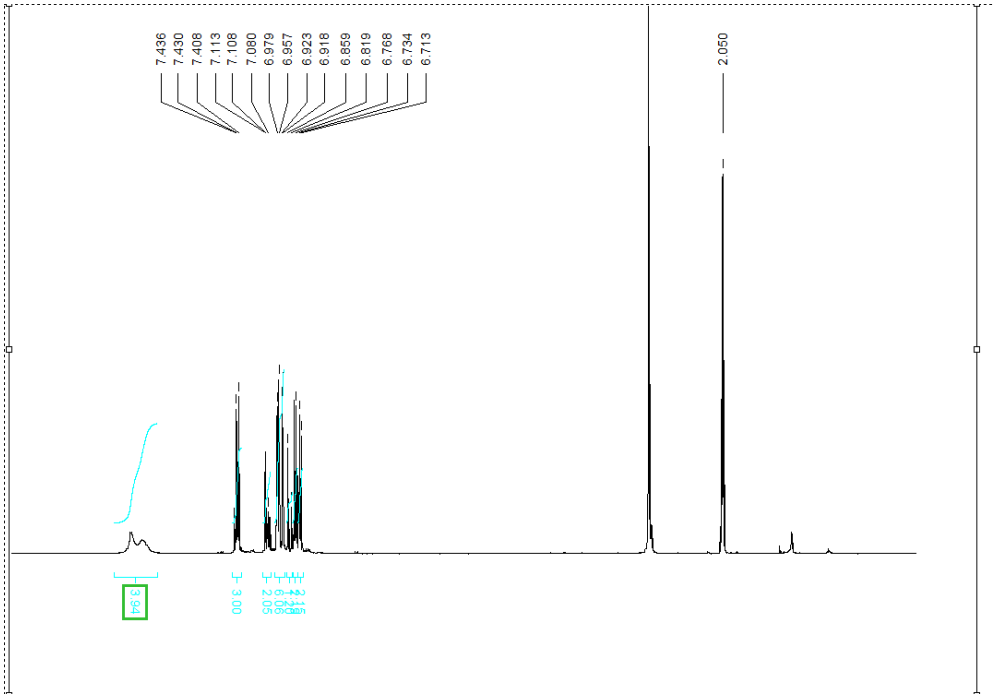


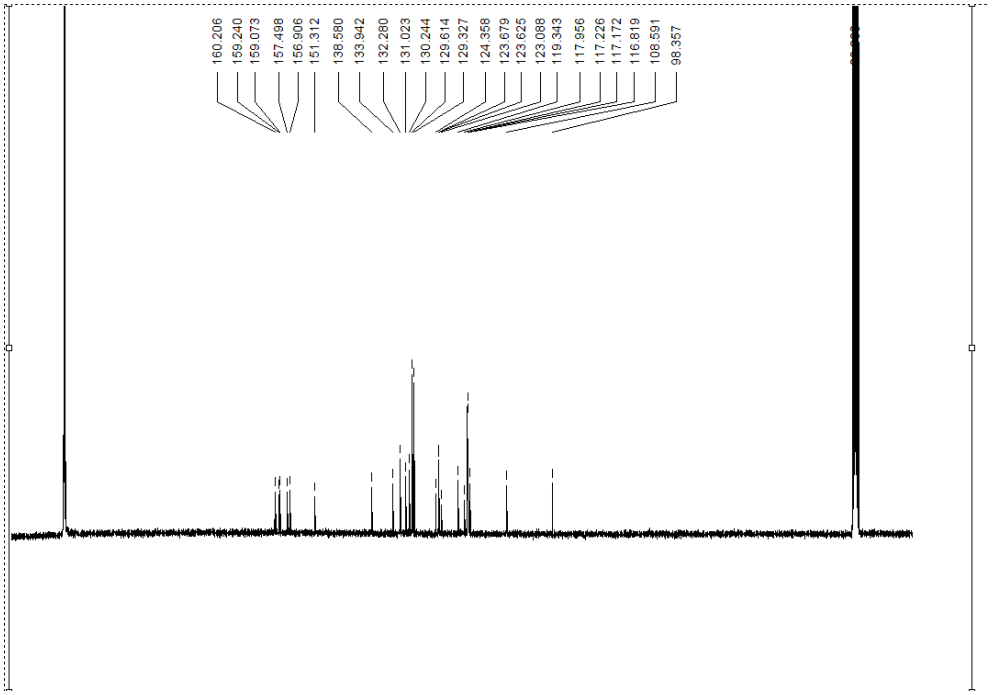
Compound **18h**



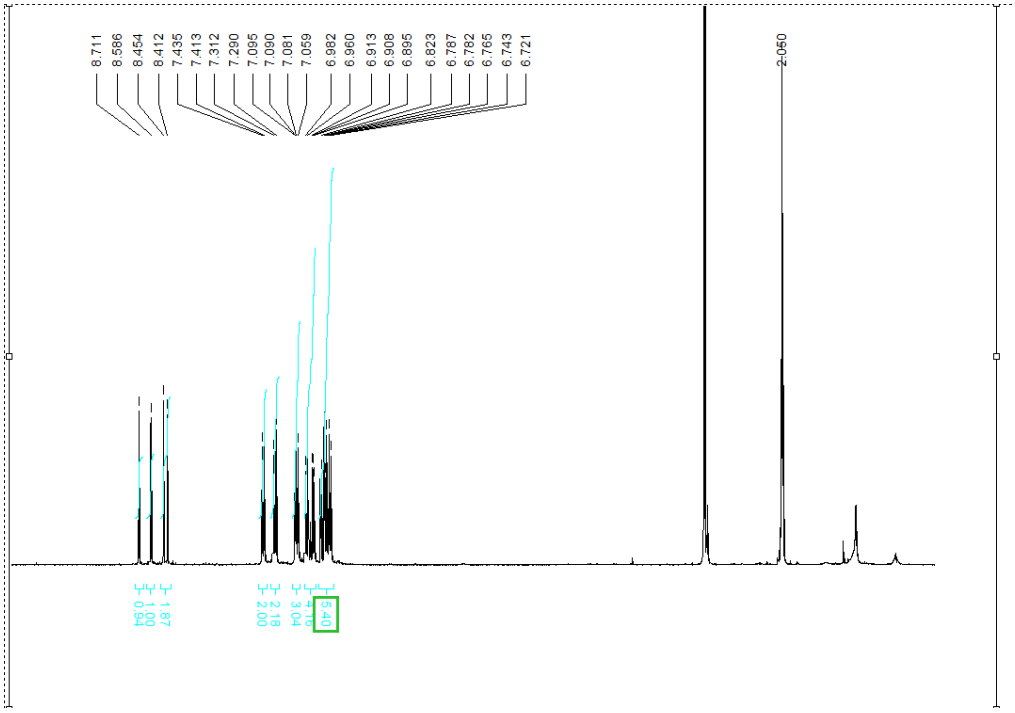



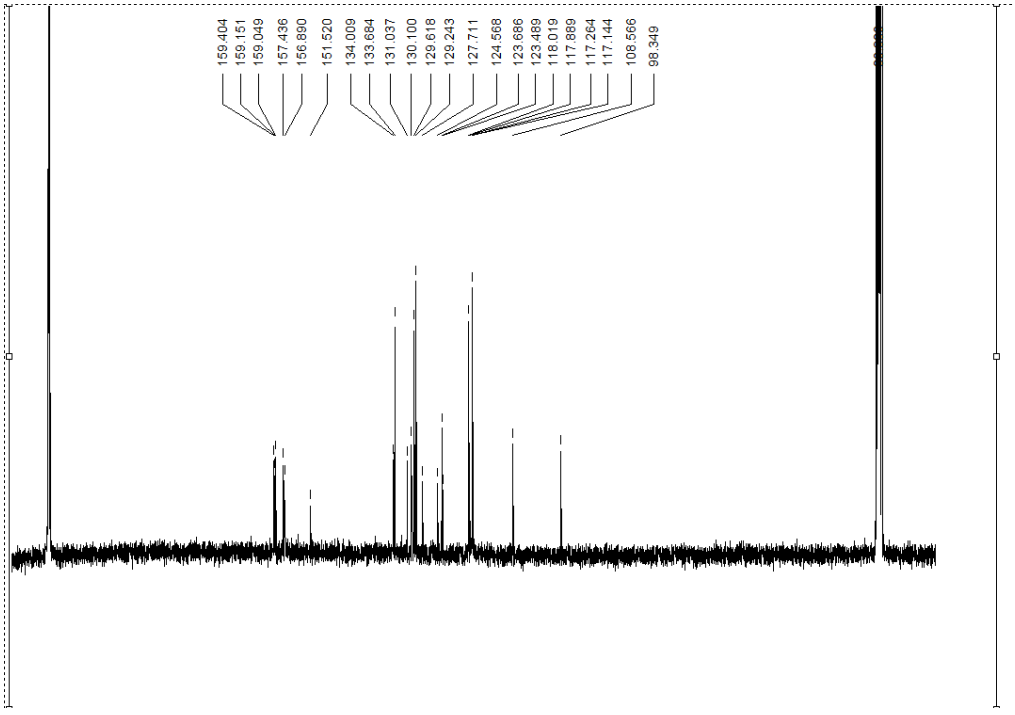
Compound **18i**



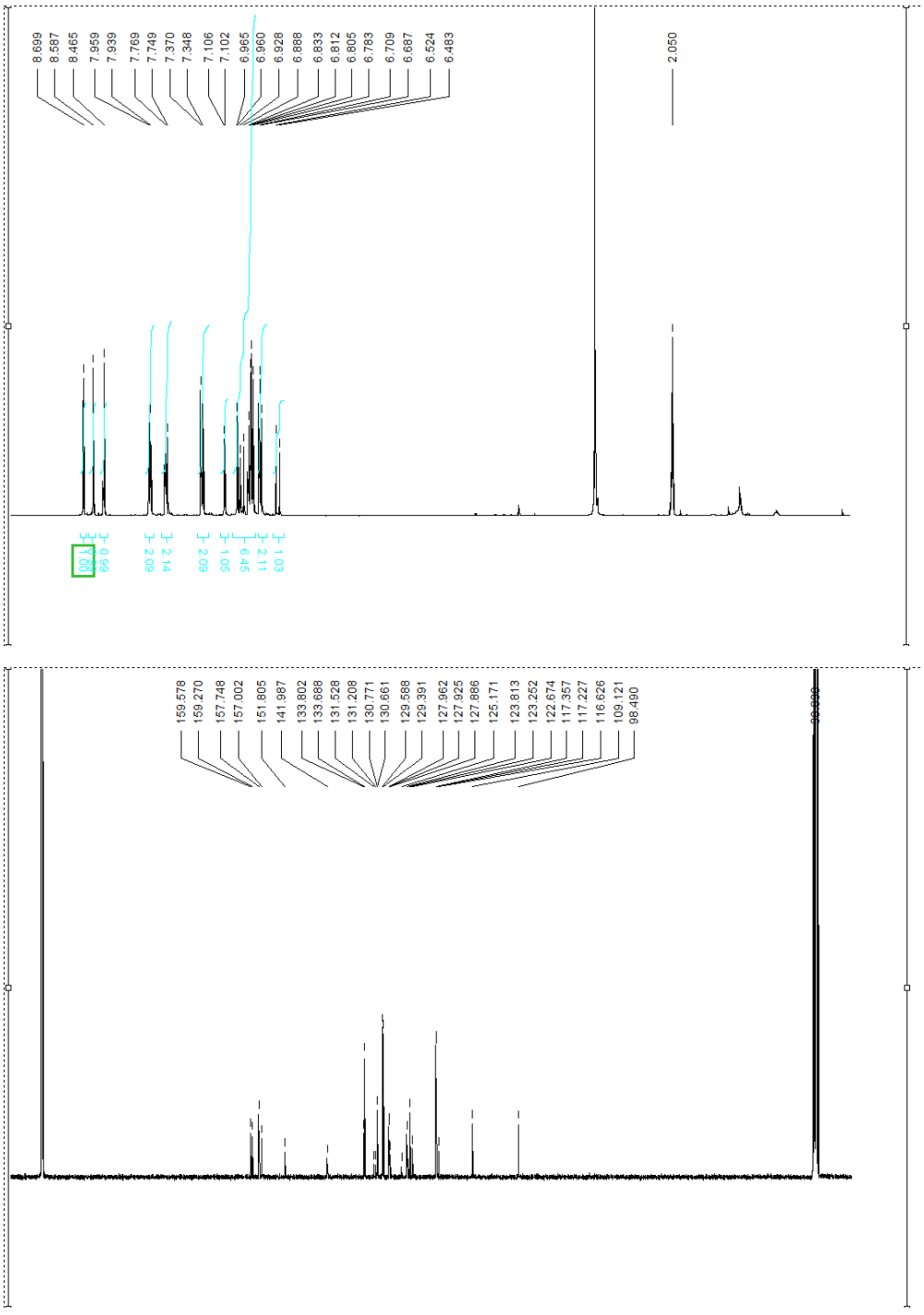



Compound **18j**

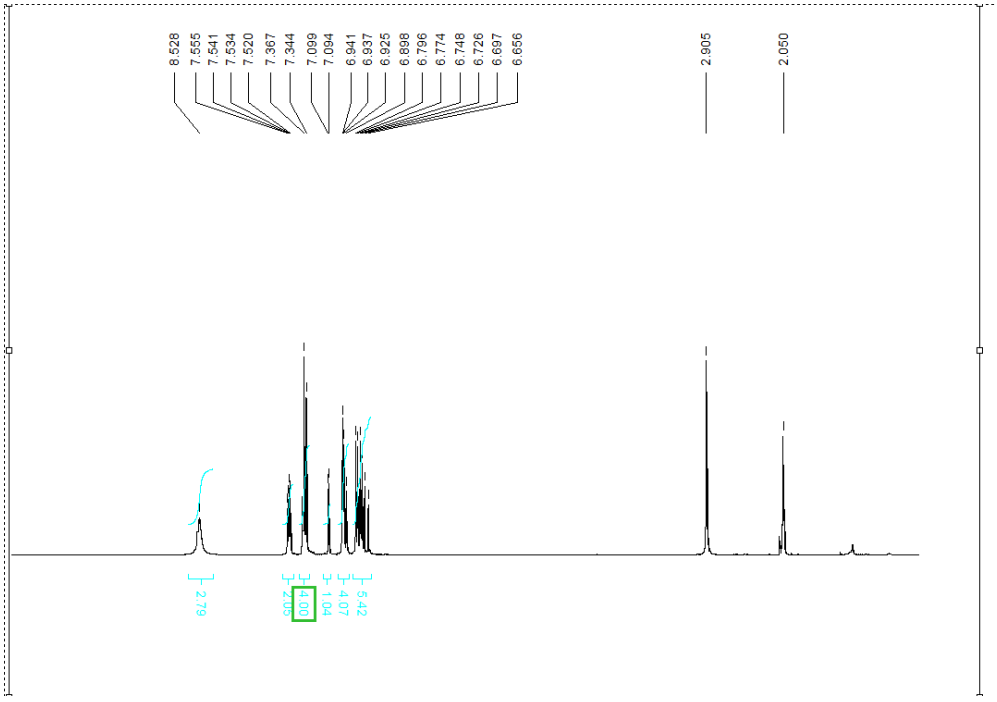


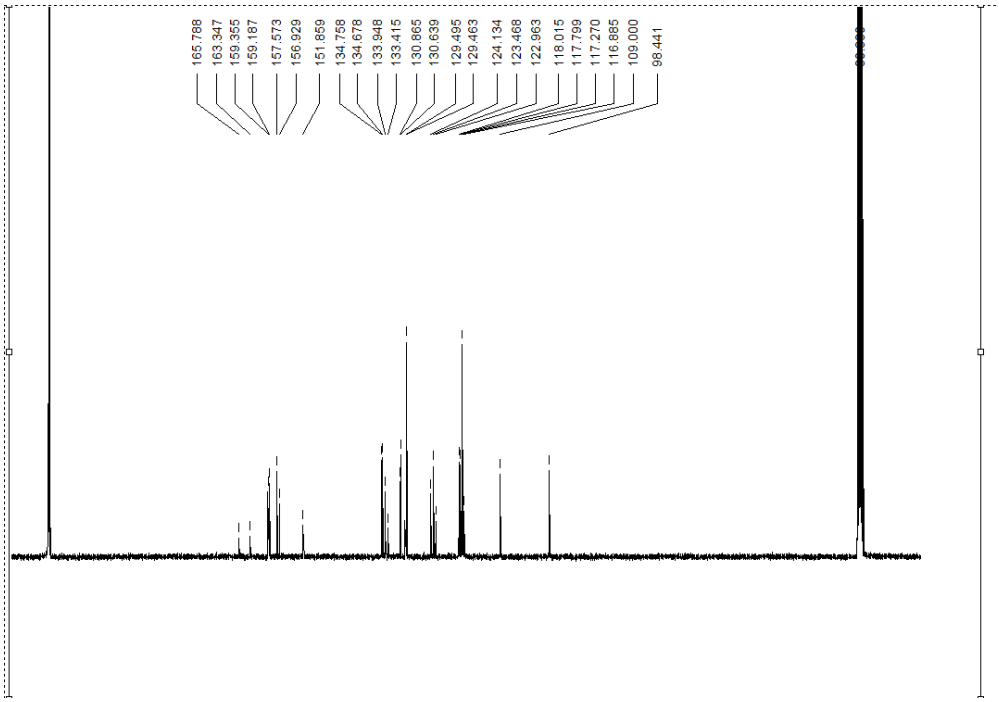



Compound **18k**

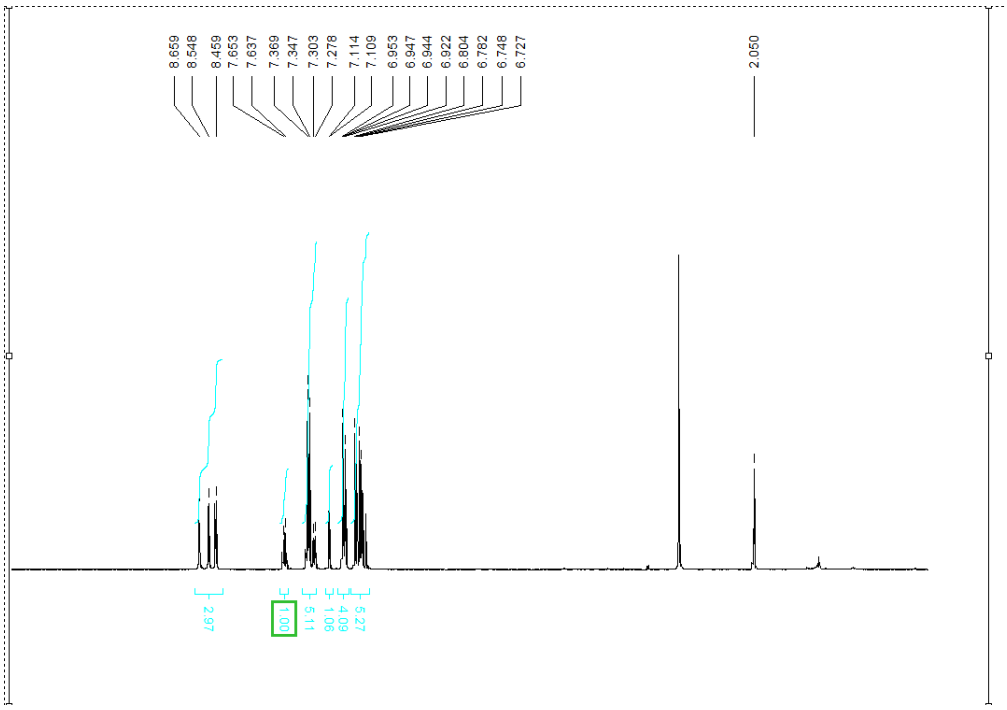


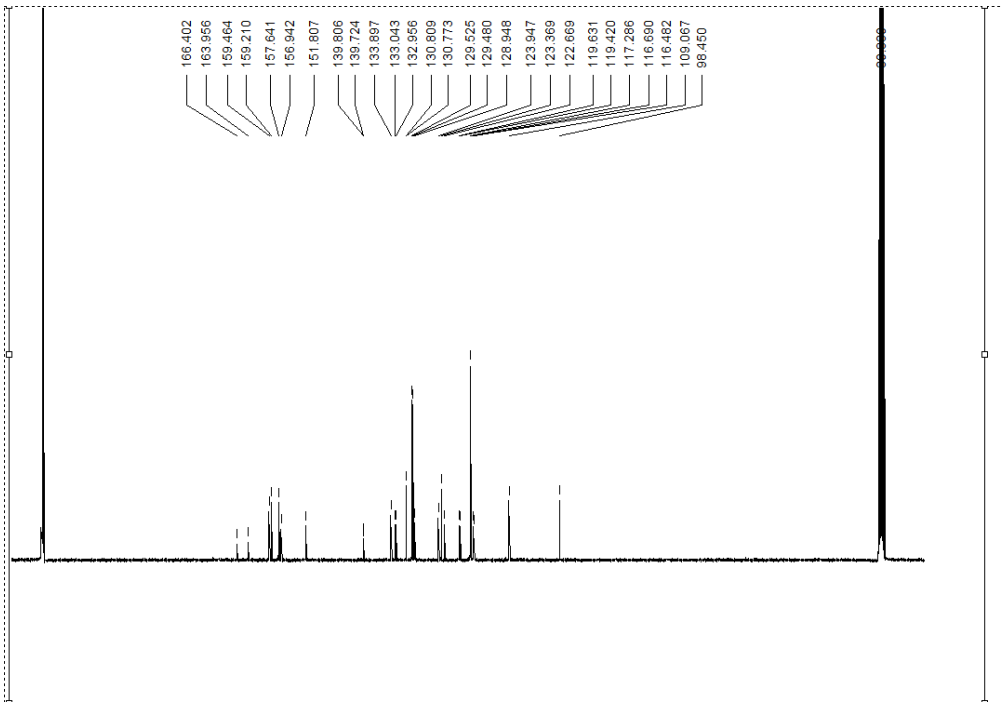
Compound **18l**



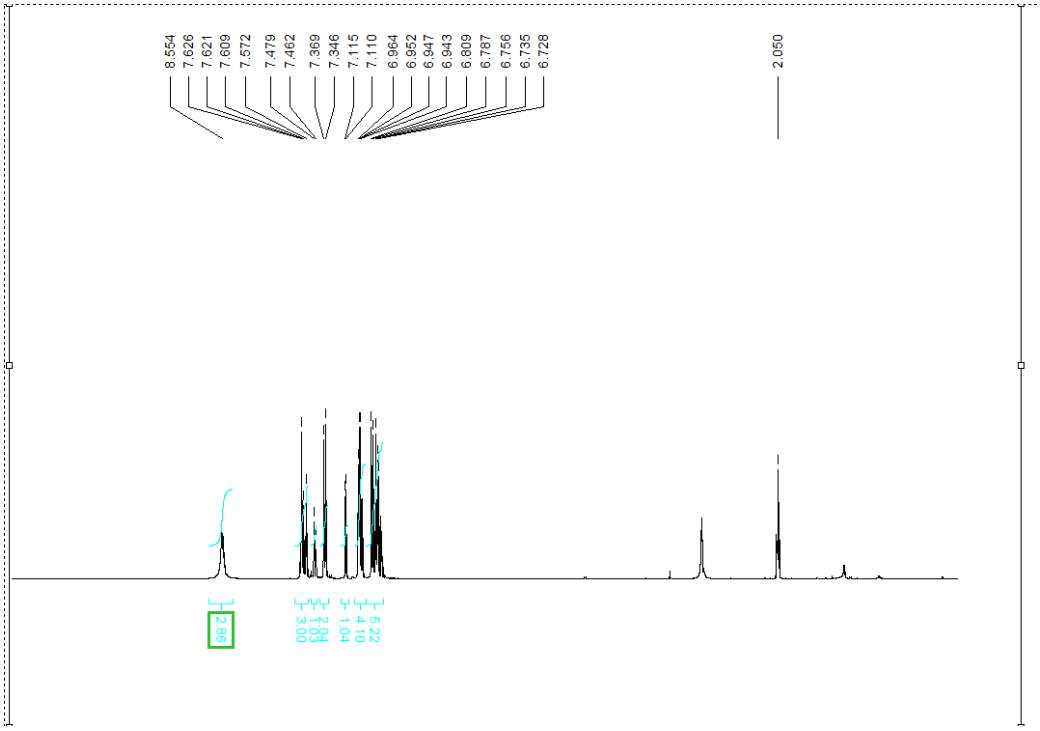



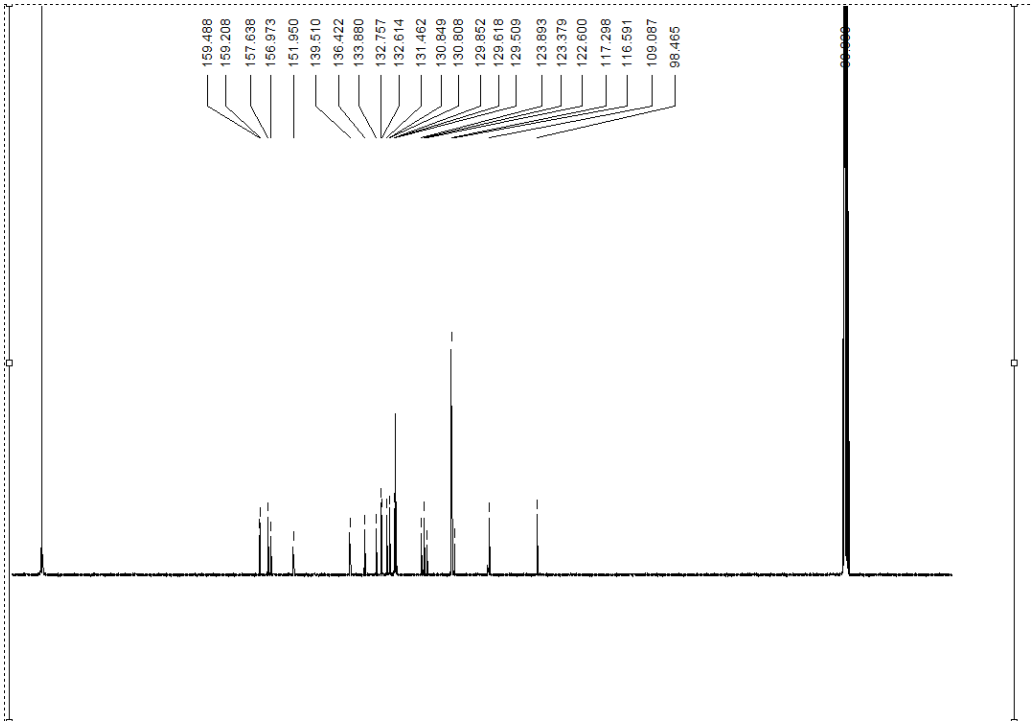
Compound **18m**



Compound **18n**



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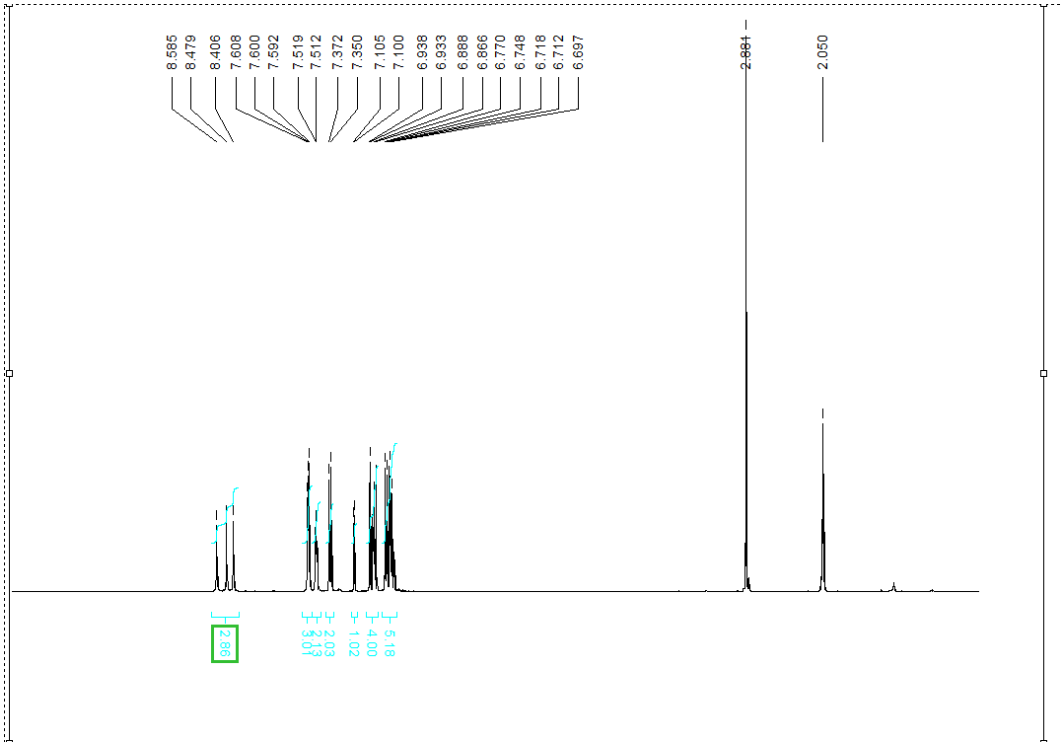
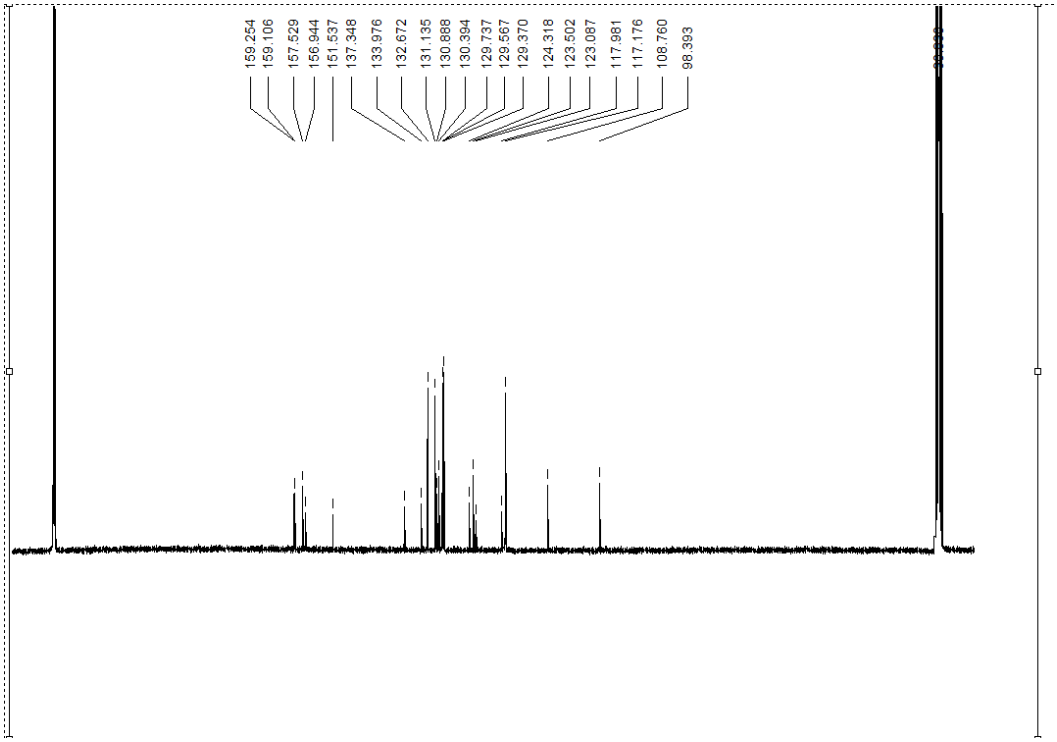
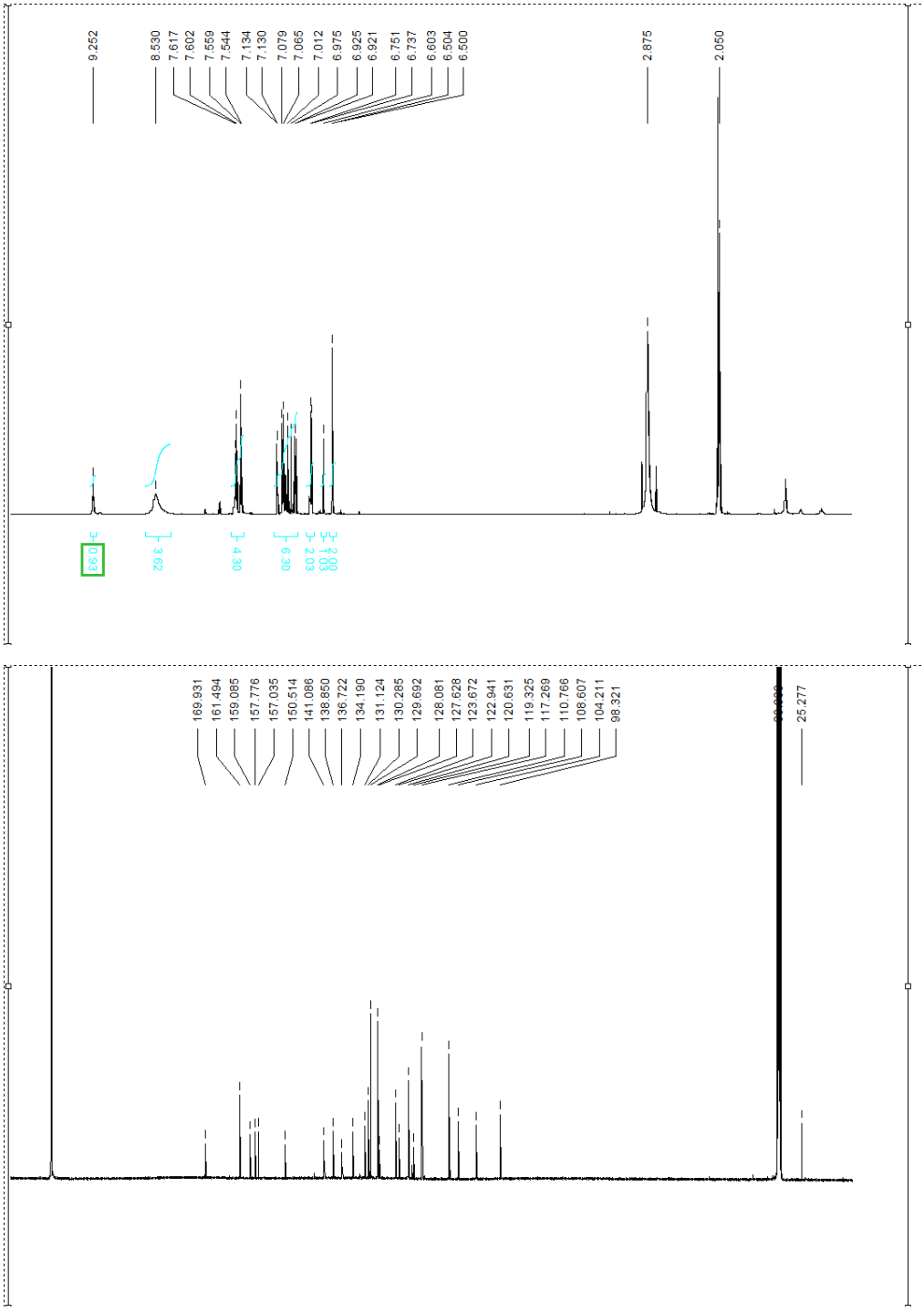
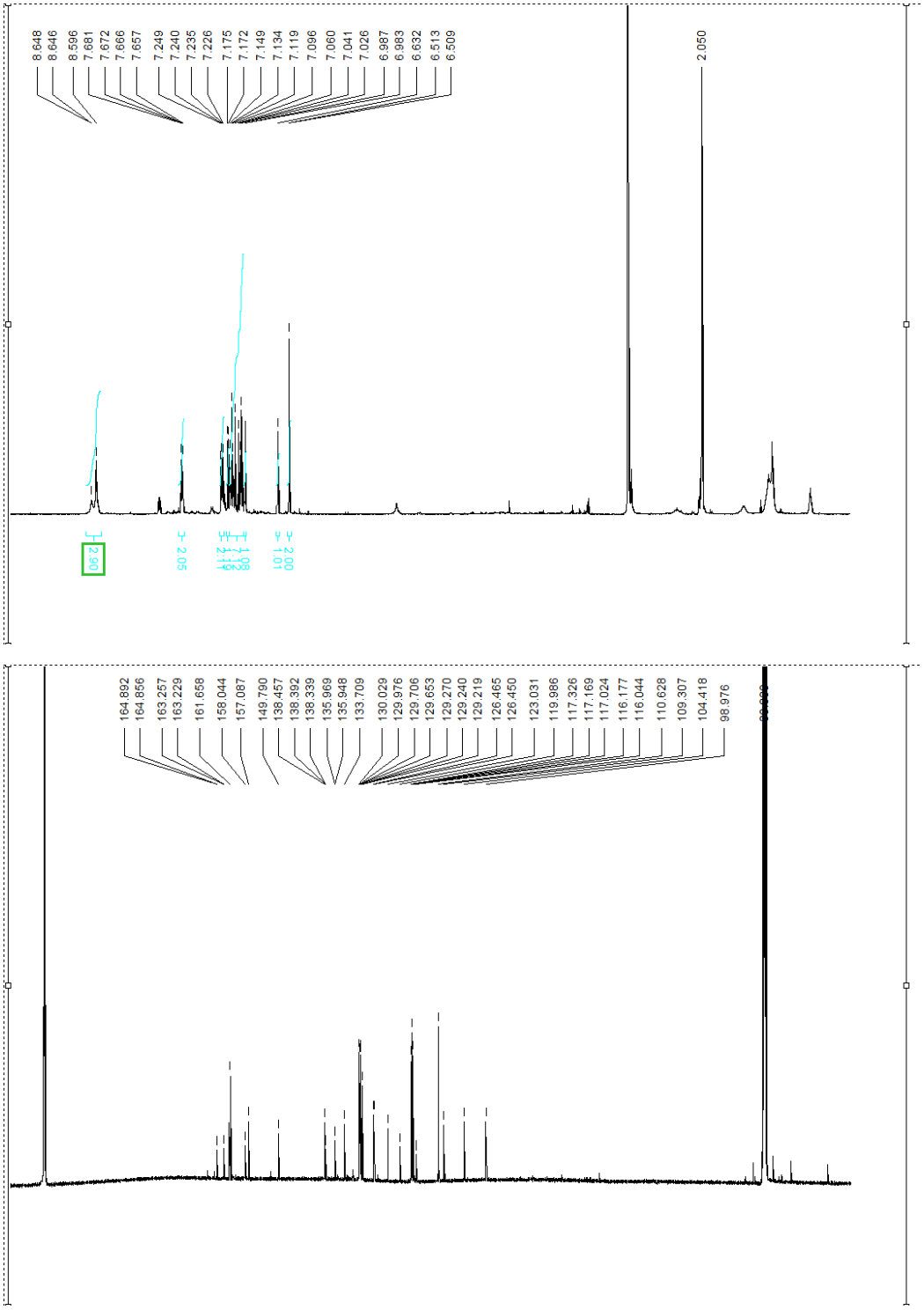


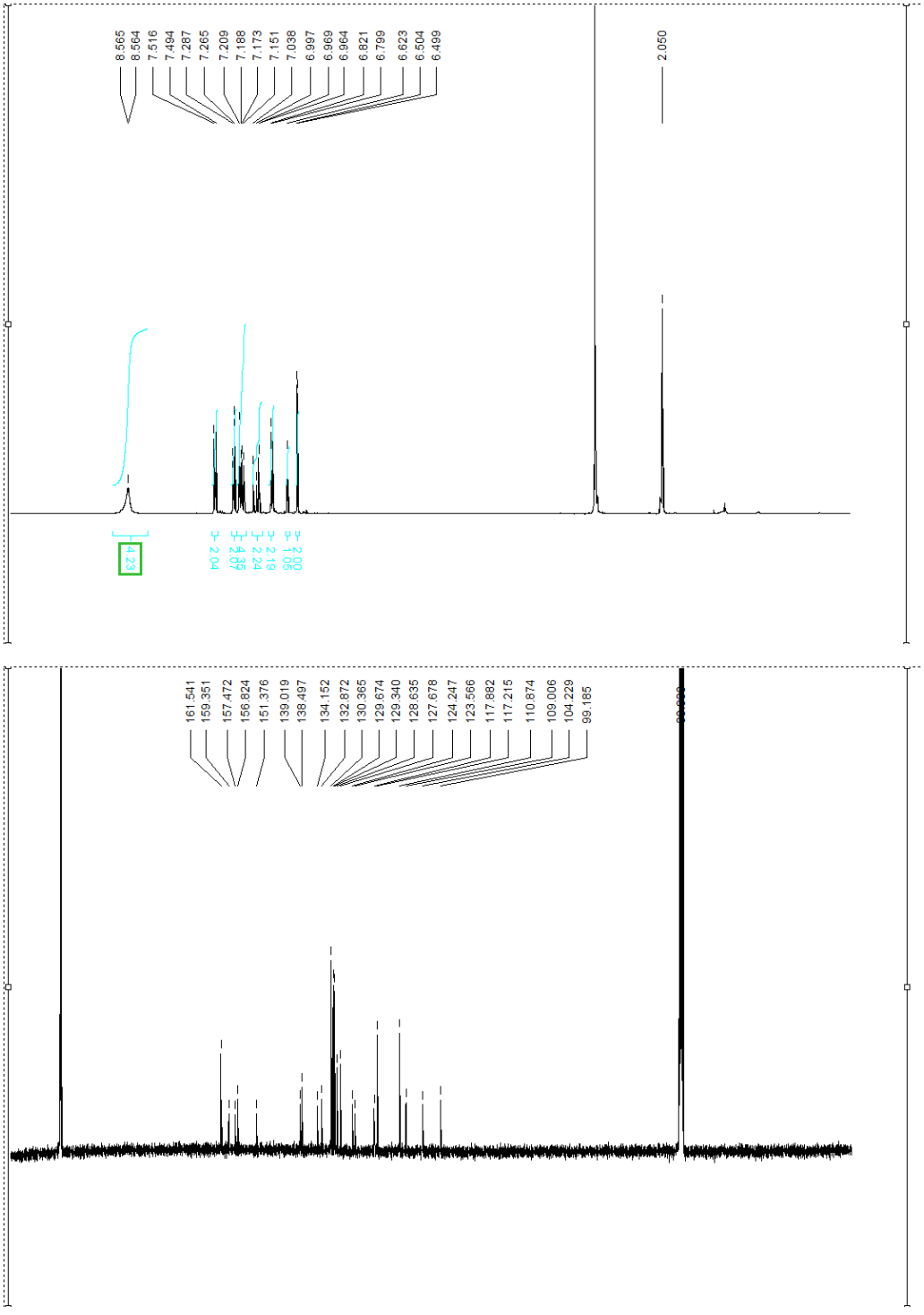
Compound **18p**



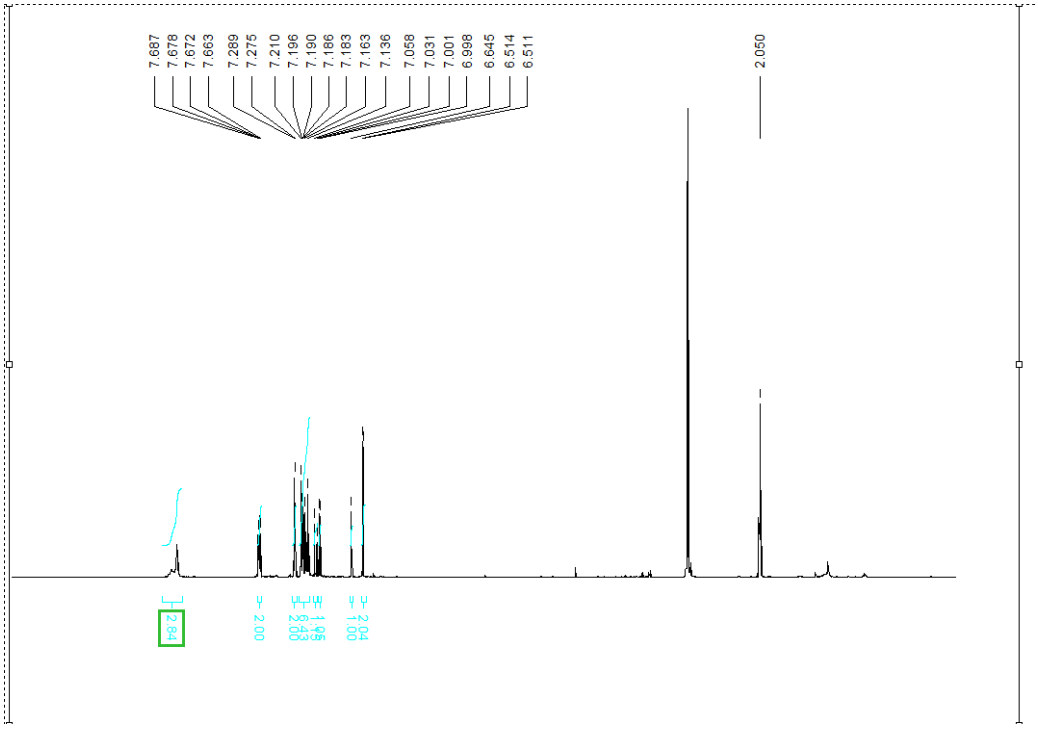
Compound **18q**

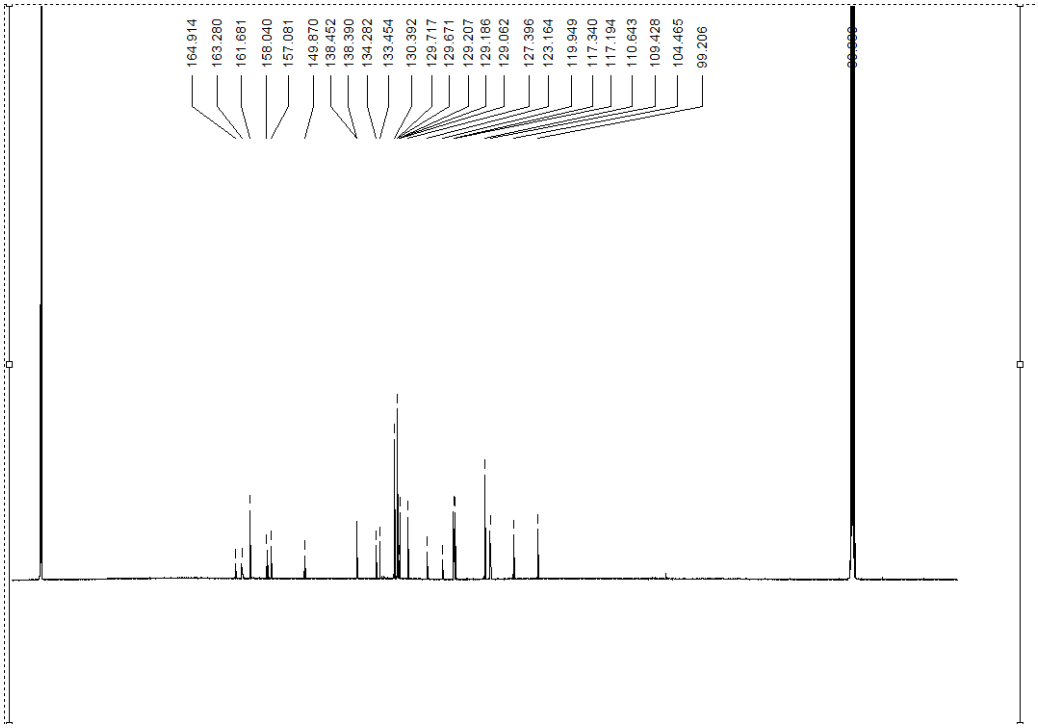


Compound **18r**

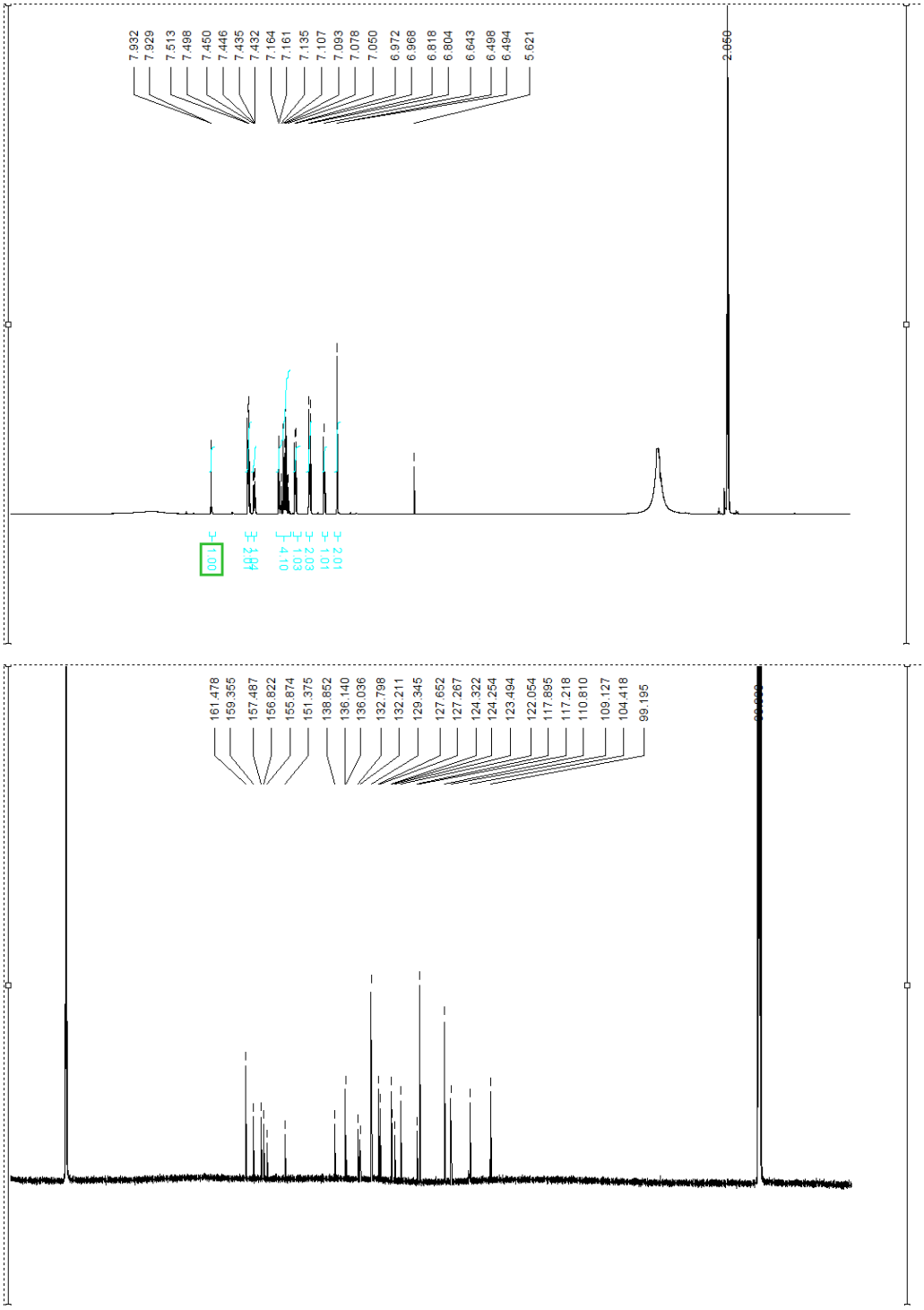


Compound **18s**

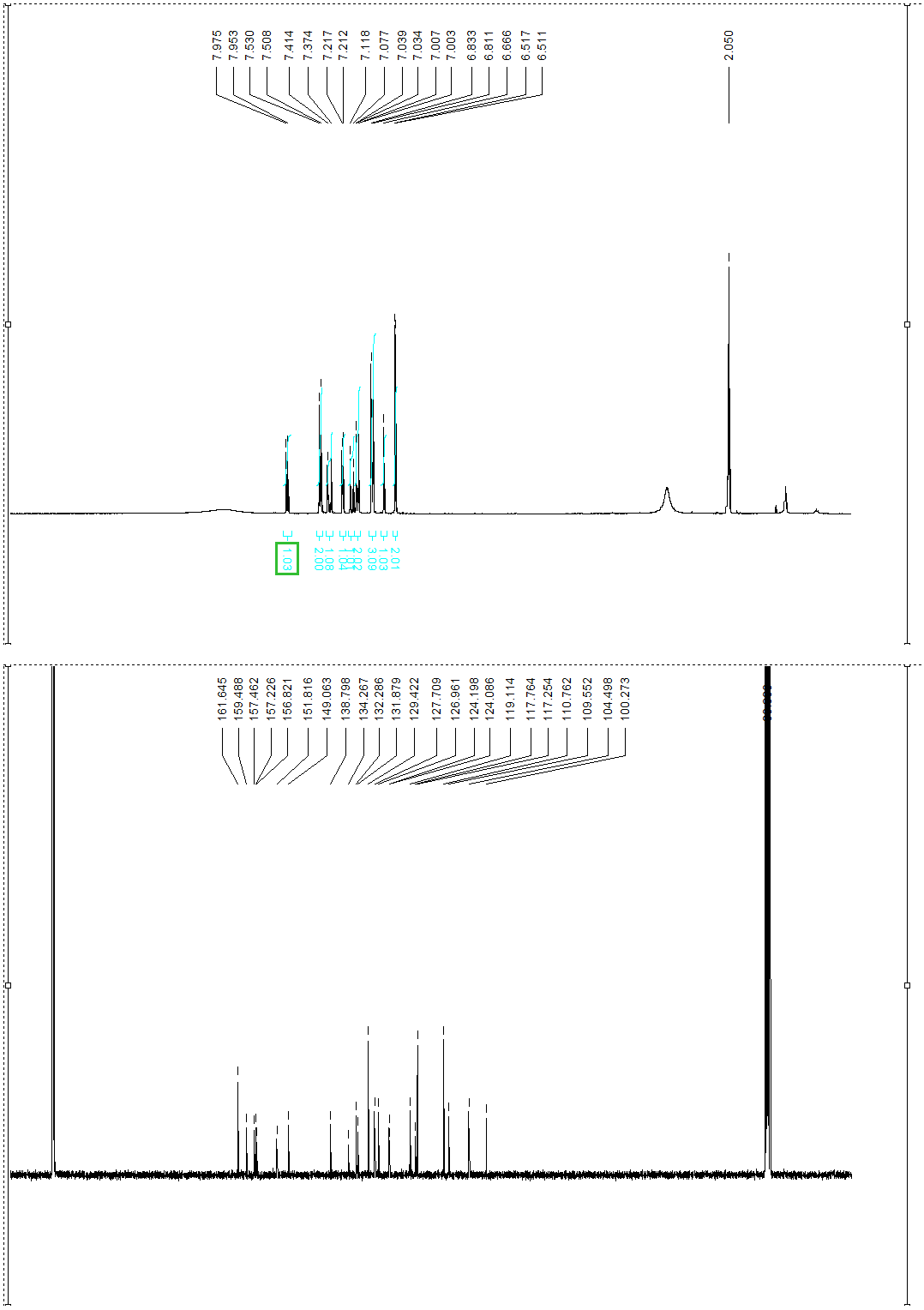


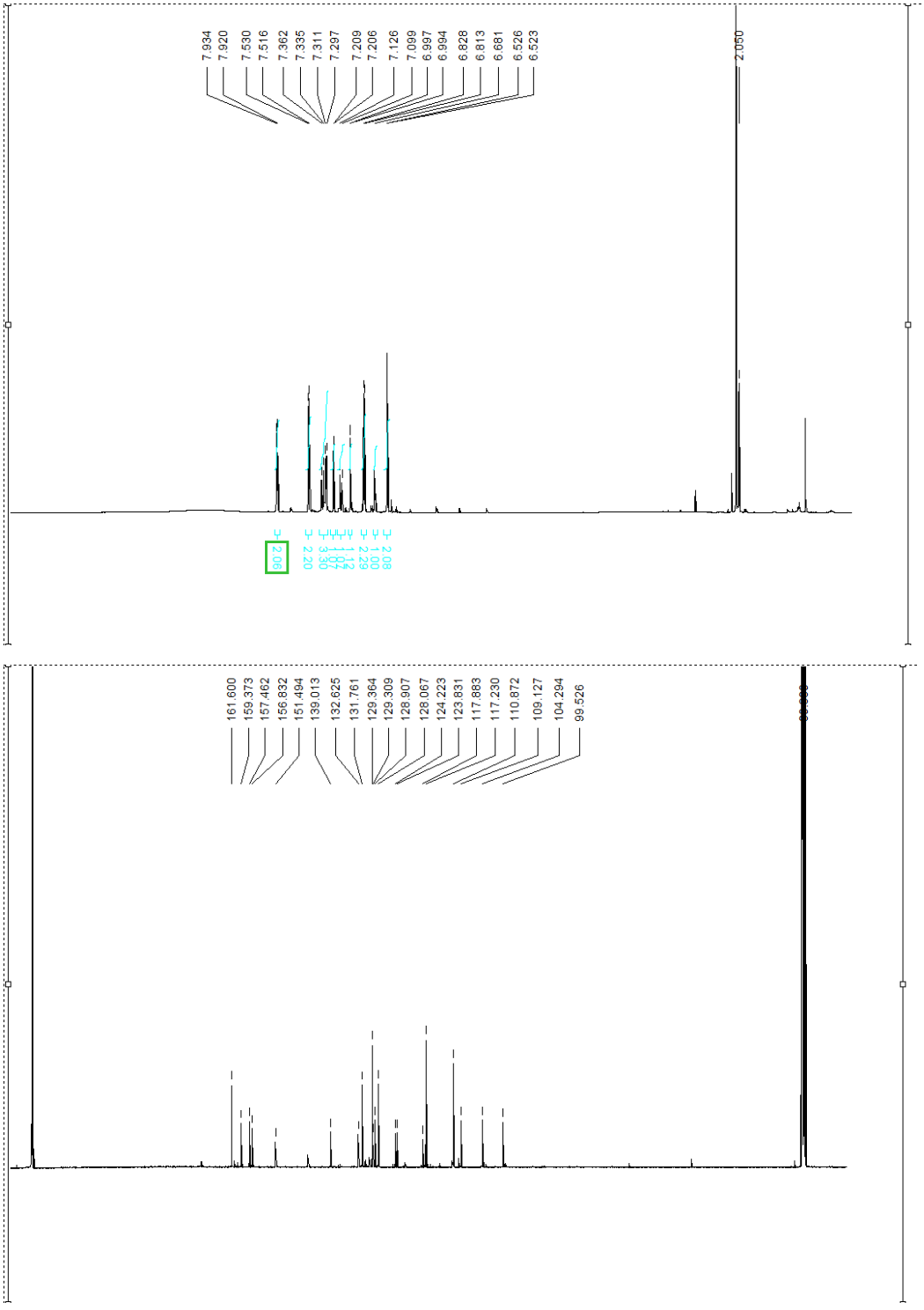
Compound **18t**



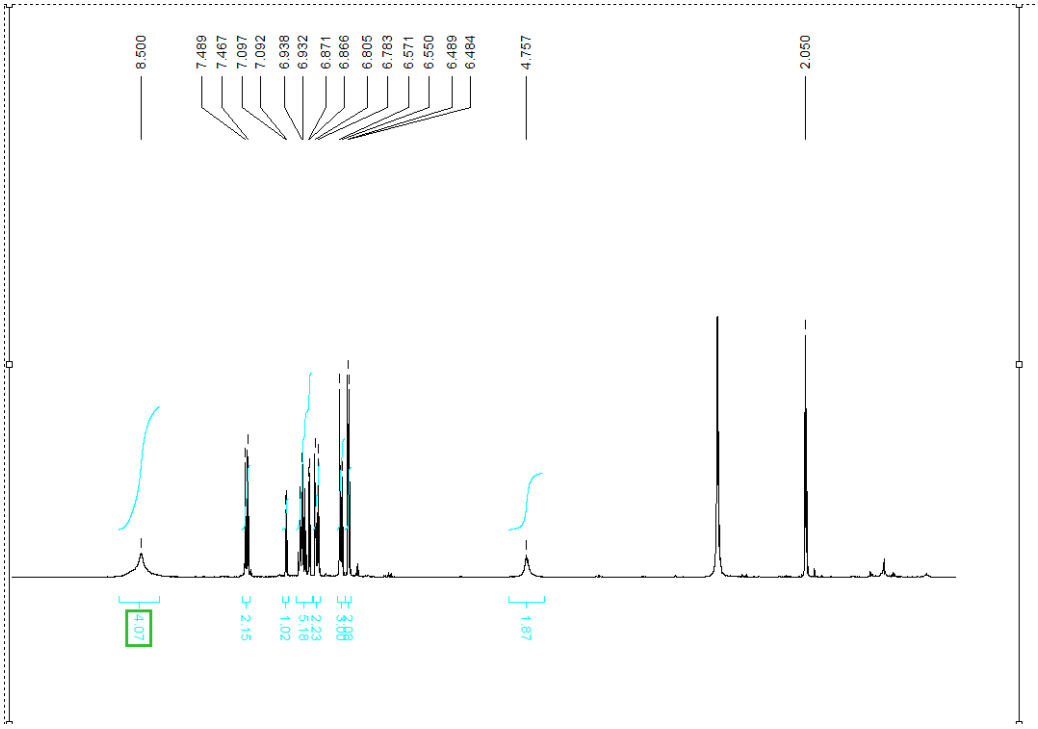
Compound **18u**



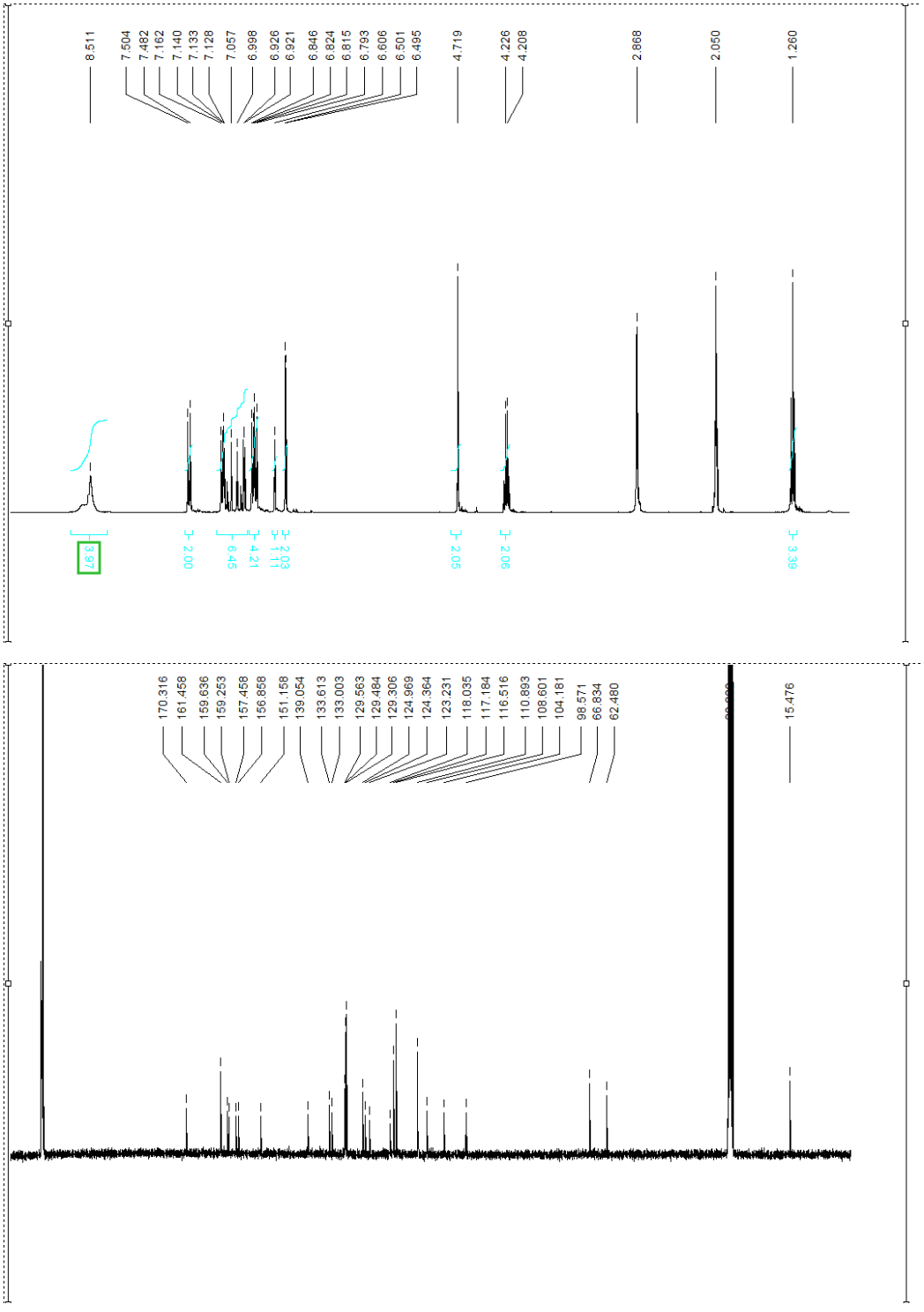
Compound **18v**



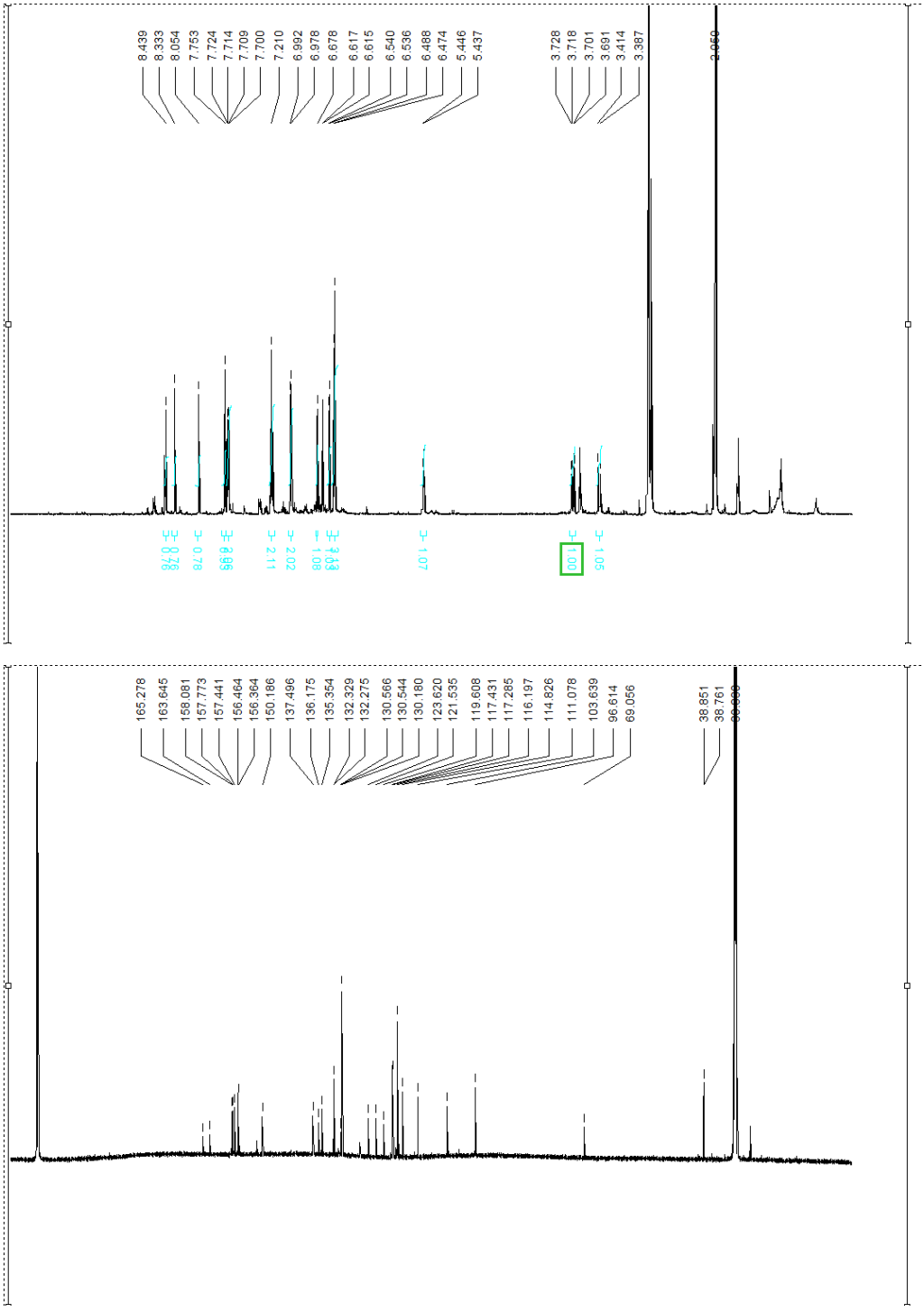
Compound **18w**



Compound **18x**



Compound **37**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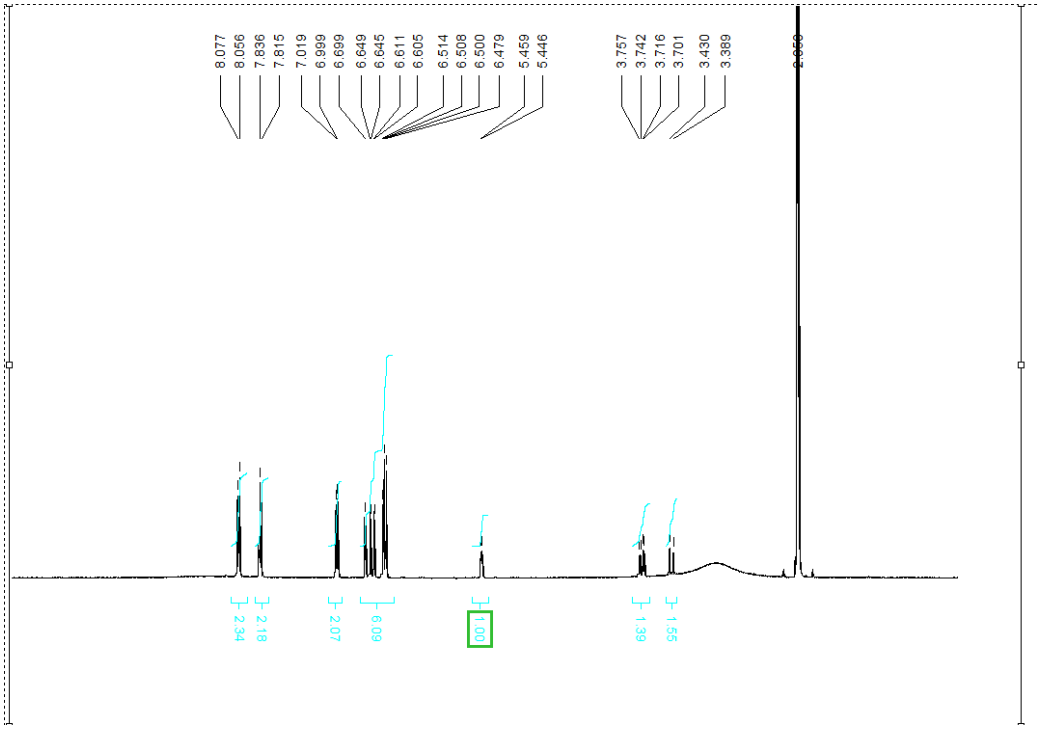
8.333
8.054
7.753
7.724
7.714
7.709
7.700
7.210
6.992
6.978
6.678
6.617
6.615
6.540
6.536
6.488
6.474
5.446
5.437
3.728
3.718
3.701
3.691
3.414
3.387
3.060
0.78
0.78
0.78
0.96
2.11
2.02
1.08
1.07
1.00
1.05
165.278
163.645
158.081
157.773
157.441
156.464
156.364
150.186
137.496
136.175
135.354
132.329
132.275
130.566
130.544
130.180
123.620
121.535
119.608
117.431
117.285
116.197
114.826
111.078
103.639
96.614
69.056
38.851
38.761

Compound **38**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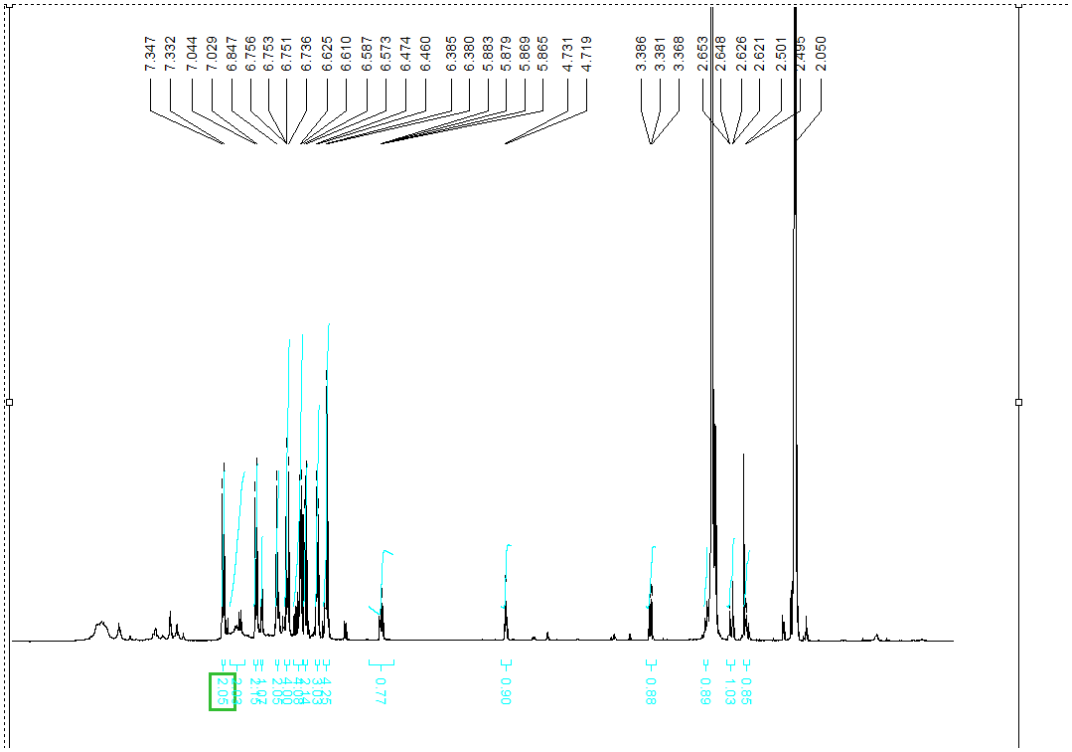
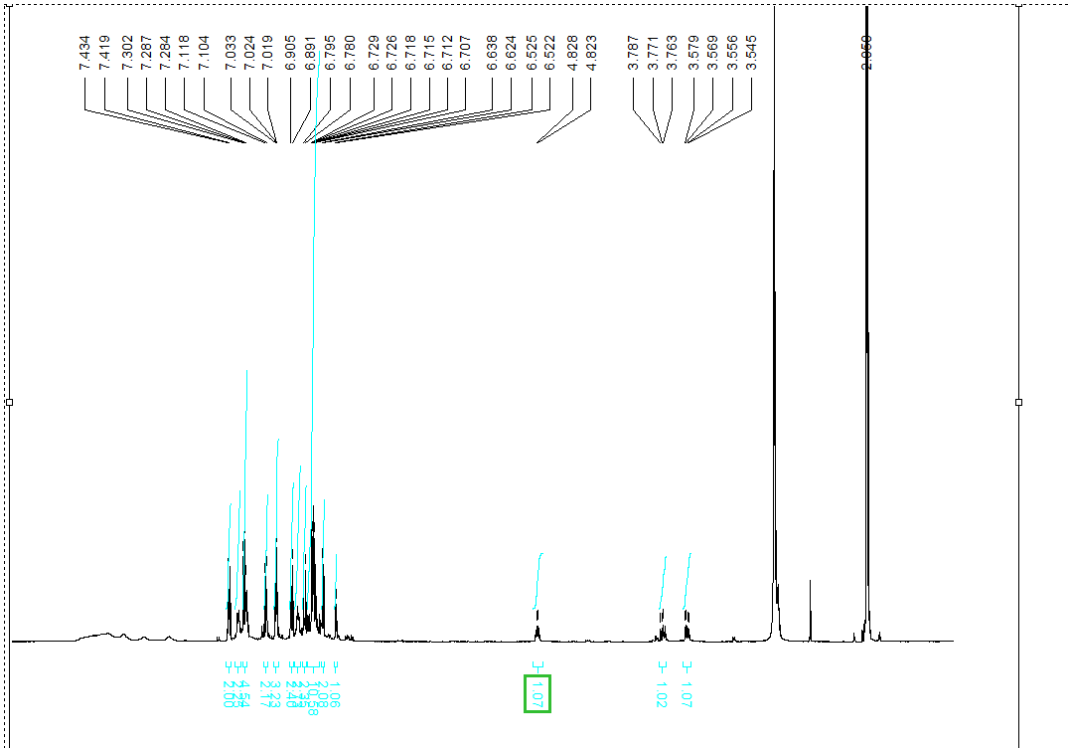
8.056
7.836
7.815
7.019
6.999
6.699
6.649
6.645
6.611
6.605
6.514
6.508
6.500
6.479
5.459
5.446
3.757
3.742
3.716
3.701
3.430
3.389
2.050
2.34
2.18
2.07
6.09
1.00
1.39
1.55

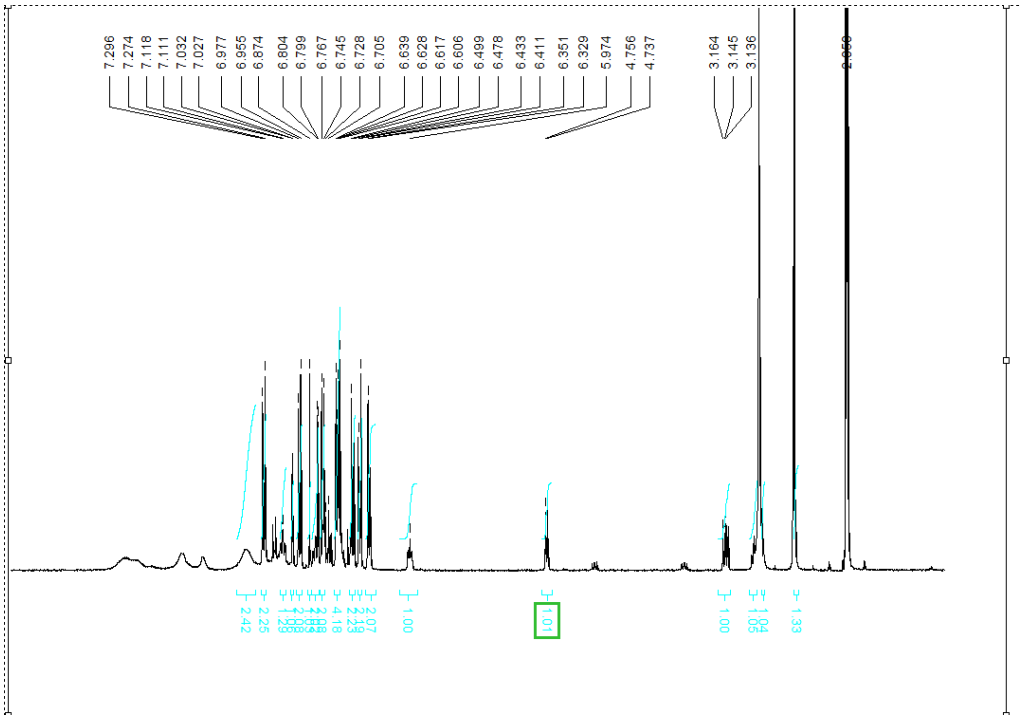
Compound **39**



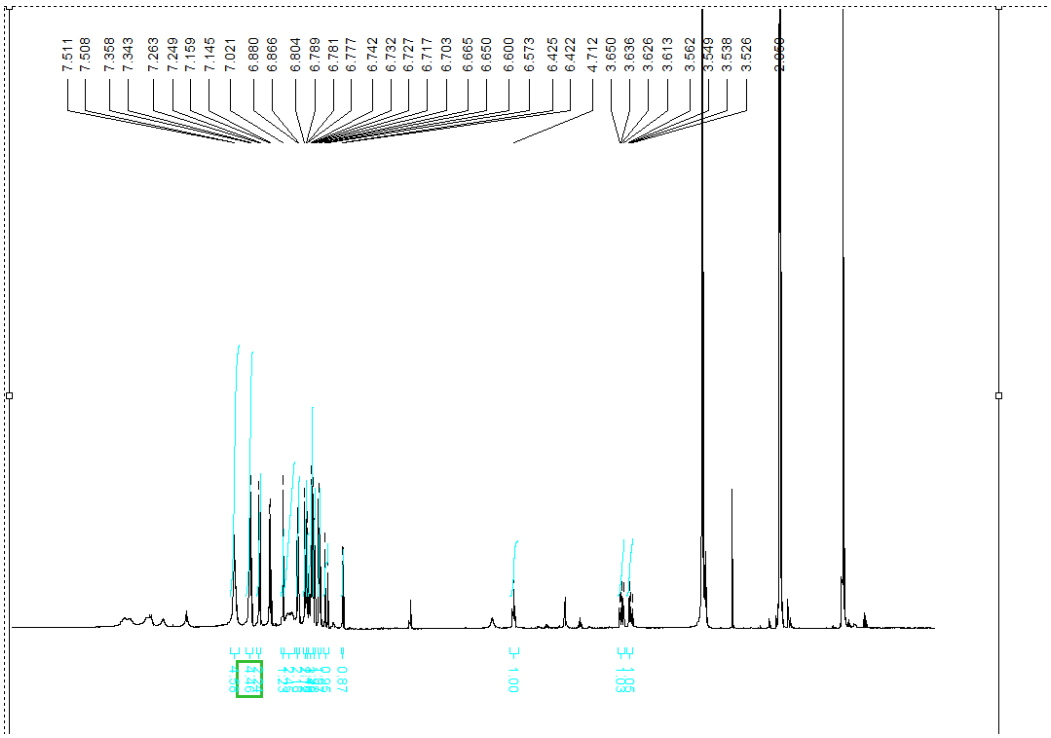

Compound **40**



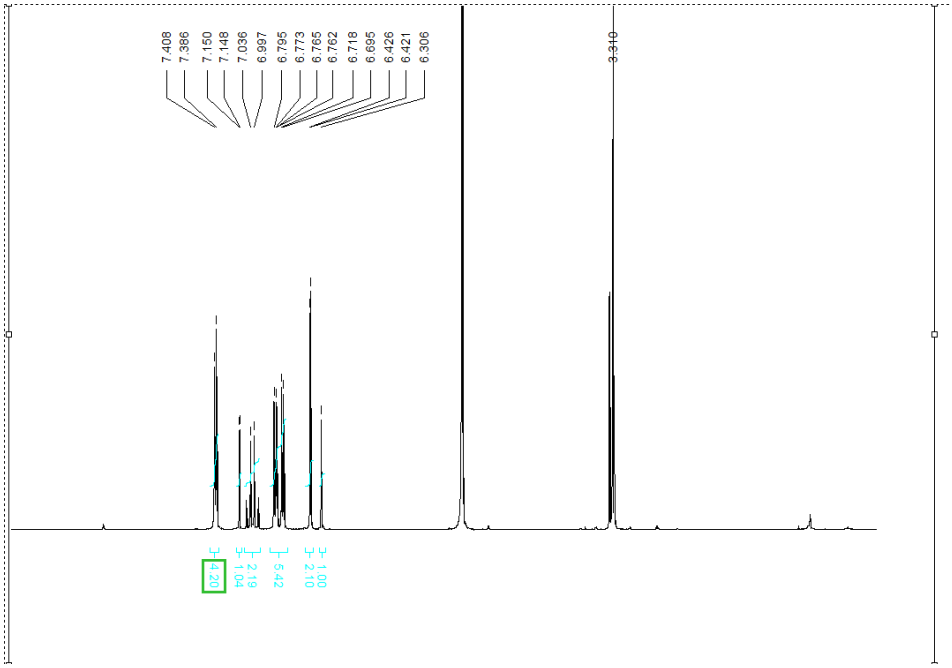
Compound **41**

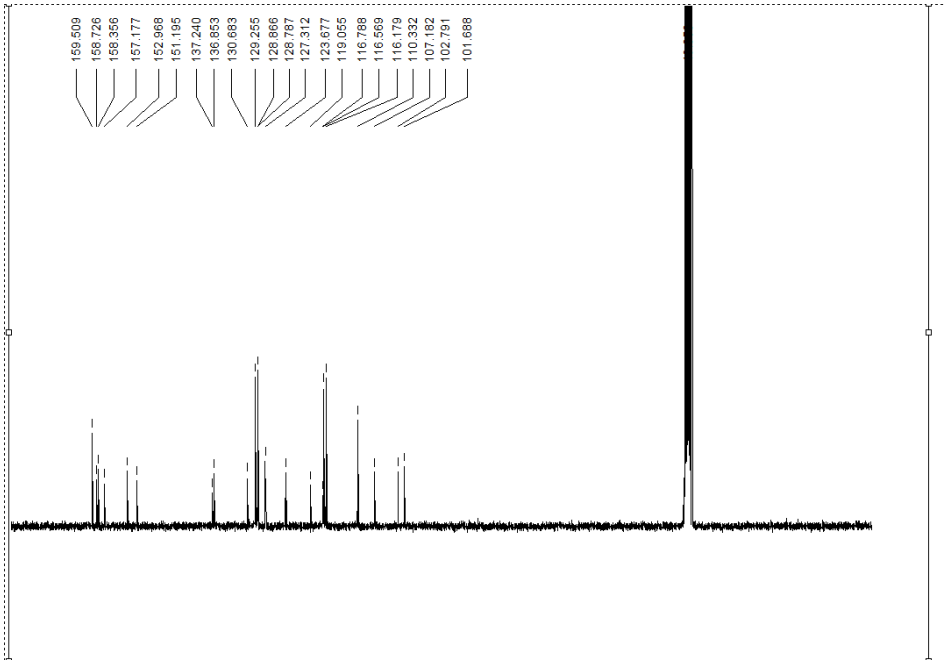



Compound **42**

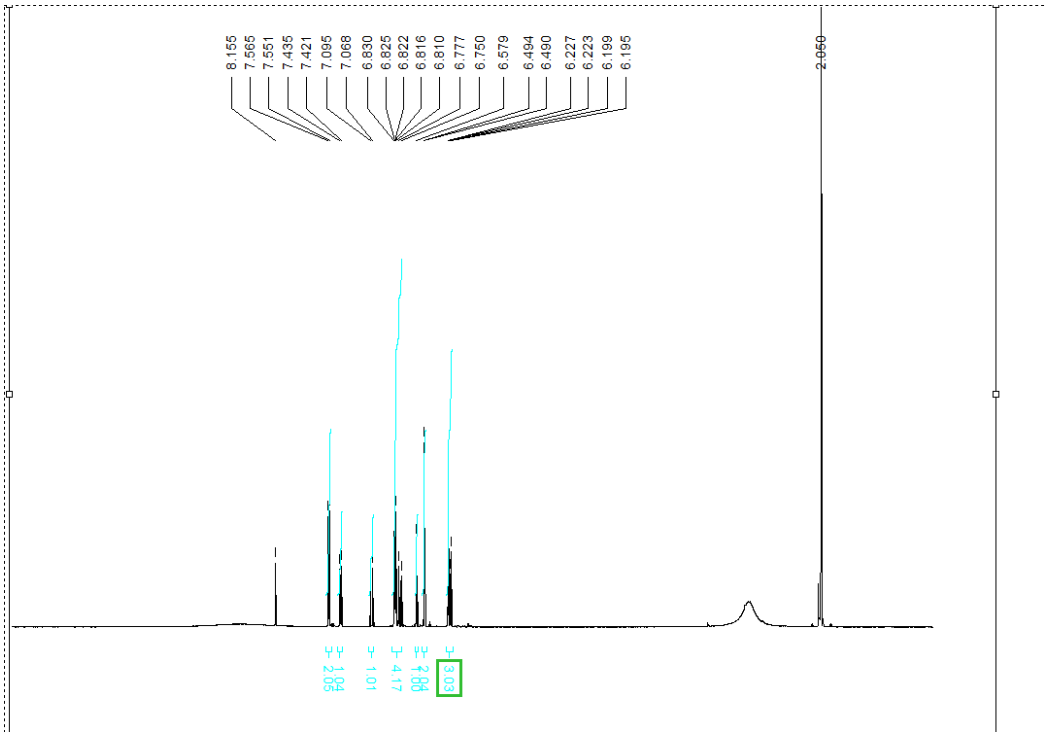


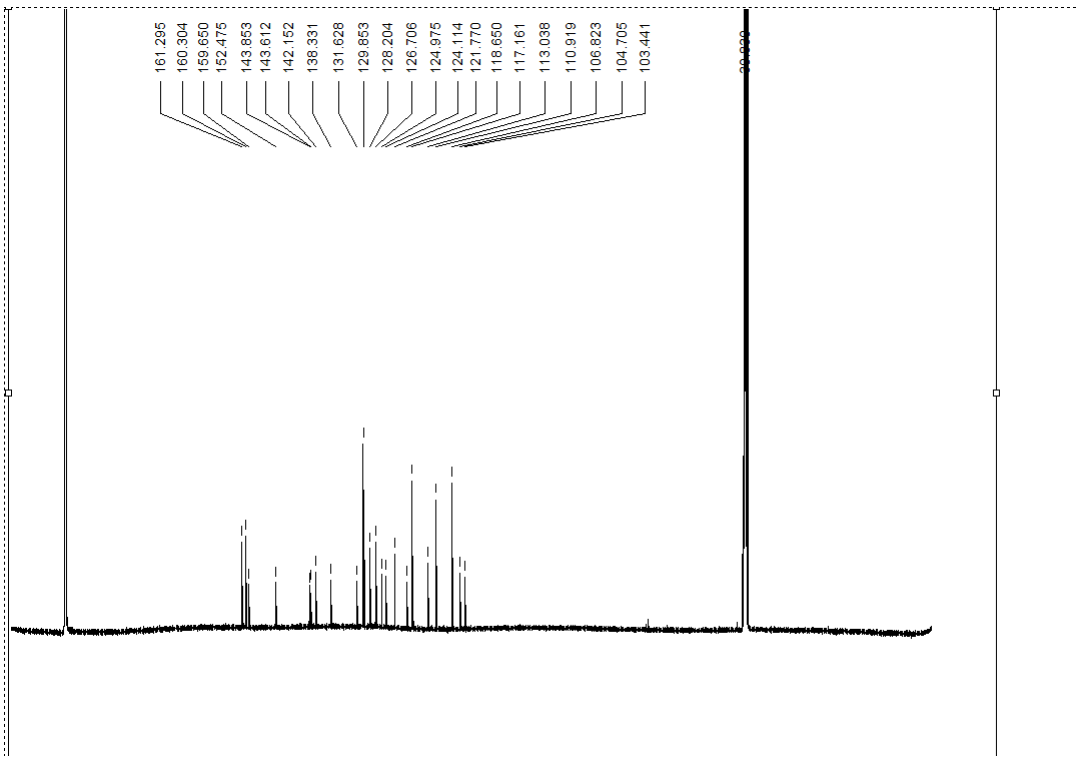
Anigopreissin A **11**



Resveratrol-piceatannol hybrid **12**



Dehydro-δ-viniferin **4**