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Supporting Information

Selective syntheses of diversely substituted 2-hydroxy-4'-hydroxybenzophenones through [4+2] or [3+3] annulation of penta-3,4-dien-2-ones with 3-formylchromones

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I. General experimental information

Commercial reagents were used without further purification, and solvents were dried before using. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), br s (broad singlet), etc. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

1. Typical procedure for the synthesis of 3a and spectroscopic data of 3a-3o

To a reaction tube equipped with a stir bar were added 3-methyl-1-phenylpenta-3,4-dien-2-one (**1a**, 52 mg, 0.3 mmol), CH_3CN (2 mL), K_2CO_3 (41 mg, 0.3 mmol), and chromone-3-carboxaldehyde (**2a**, 52 mg, 0.3 mmol) with stirring. The mixture was then stirred at 80 ℃ for 1 h. Upon completion, it was added with brine (10 mL), and then extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (40:1) as the eluent to give **3a**. **3b**-**3o** were obtained in a similar manner.

(6-Hydroxy-4,5-dimethyl-[1,1'-biphenyl]-3-yl)(2-hydroxyphenyl)methanone (3a)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (66 mg, 69%), mp: 108-109 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.15 (s, 3H), 2.18 (s, 3H), 5.54 (s, 1H), 6.68-6.72 (m, 1H), 6.91-7.93 (m, 2H), 7.26-7.38 (m, 7H), 12.21 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 12.1, 17.4, 118.3, 118.8, 120.5, 124.7, 124.8, 127.1, 128.3, 129.2, 129.6, 131.0, 133.9, 136.0, 136.47, 136.55, 152.0, 163.3, 204.5. HRMS calcd for $C_{21}H_{18}NaO_3$: 341.1148 $[M+Na]^+$, found: 341.1151.

(6-Hydroxy-2',4,5-trimethyl-[1,1'-biphenyl]-3-yl)(2-hydroxyphenyl)methanone (3b)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (56 mg, 56%), mp: 103-104 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.20 (s, 3H), 2.28 (s, 3H), 2.29 (s, 3H), 5.09 (s, 1H), 6.80-6.84 (m, 1H), 6.93 (s, 1H), 7.03 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H), 7.27-7.31 (m, 1H), 7.33-7.34 (m, 2H), 7.43-7.47 (m, 2H), 12.34 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 12.0, 17.3, 19.9, 118.3, 118.7, 120.5, 124.2, 124.3, 126.7, 127.2, 128.9, 130.58, 130.61, 131.0, 133.8, 134.8, 136.1, 136.4, 137.6, 152.2, 163.3, 204.4. HRMS calcd for $C_{22}H_{20}NaO_3$: 355.1305 $[M+Na]^+$, found: 355.1303.

(6-Hydroxy-3',4,5-trimethyl-[1,1'-biphenyl]-3-yl)(2-hydroxyphenyl)methanone (3c)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (61 mg, 61%), mp: 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.25 (s, 3H), 2.28 (s, 3H), 2.39 (s, 3H), 5.68 (s, 1H), 6.79-6.83 (m, 1H), 7.02-7.04 (m, 2H), 7.20-7.24 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.43-7.49 (m, 2H), 12.35 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 12.1, 17.4, 21.5, 118.3, 118.8, 120.4, 124.6, 124.9, 126.1, 127.0, 129.1, 129.5, 129.8, 130.9, 134.0, 135.9, 136.3, 136.5, 139.5, 152.0, 163.3, 204.5. HRMS calcd for $C_{22}H_{20}NaO_3$: 355.1305 $[M+Na]^+$, found: 355.1313.

(6-Hydroxy-4,4',5-trimethyl-[1,1'-biphenyl]-3-yl)(2-hydroxyphenyl)methanone (3d)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (66 mg, 66%), mp: 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.31 (s, 3H), 2.35 (s, 3H), 2.44 (s, 3H), 5.78-5.81 (m, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 7.07-7.09 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.48-7.52 (m, 2H), 12.39 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 12.1, 17.4, 21.3, 118.3, 118.8, 120.5, 124.6, 124.9, 127.2, 129.0, 130.3, 130.9, 133.5, 134.0, 135.8, 136.5, 138.2, 152.2, 163.3, 204.5. HRMS calcd for $C_{22}H_{20}NaO_3$: 355.1305 $[M+Na]^+$, found: 355.1309.

(6-Hydroxy-4'-methoxy-4,5-dimethyl-[1,1'-biphenyl]-3-yl)(2-hydroxyphenyl)methanone (3e)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (68 mg, 65%), mp: 114-116 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.24 (s, 3H), 2.28 (s, 3H), 3.82 (s, 3H), 5.63 (s, 1H), 6.80 (t, *J* = 7.8 Hz, 1H), 6.98-7.01 (m, 3H), 7.02 (d, *J* = 9.0 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.43-7.47 (m, 2H), 12.33 (s, 1H). ^{13}C NMR(100 Hz, $CDCl_3$) δ: 12.1, 17.4, 55.4, 115.0, 118.2, 118.8, 120.4, 124.4, 124.5, 127.1, 128.4, 130.4, 130.9, 133.9, 135.7, 136.5, 152.1, 159.6, 163.2, 204.5. HRMS calcd for $C_{22}H_{21}O_4$: 349.1434 $[M+H]^+$, found: 349.1429.

(4-Hydroxy-2,3-dimethyl-5-(thiophen-2-yl)phenyl)(2-hydroxyphenyl)methanone (3f)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (53 mg, 54%), mp: 169-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.15 (s, 3H), 2.21 (s, 3H), 5.83 (s, 1H), 6.71-6.76 (m, 1H), 6.96 (dd, J_1 = 8.4 Hz, J_2 = 0.8

Hz, 1H), 7.05-7.07 (m, 1H), 7.09 (s, 1H), 7.13 (dd, J_1 = 3.6 Hz, J_2 = 1.2 Hz, 1H), 7.32-7.34 (m, 2H), 7.38-7.42 (m, 1H), 12.21 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 12.1, 17.4, 117.6, 118.3, 118.9, 120.4, 124.8, 126.4, 126.9, 127.1, 128.1, 131.0, 133.9, 136.5, 136.7, 138.0, 152.2, 163.3, 204.1. HRMS calcd for $C_{19}H_{17}O_3S$: 325.0893 $[M+H]^+$, found: 325.0858.

(5-Ethyl-6-hydroxy-4-methyl-[1,1'-biphenyl]-3-yl)(2-hydroxyphenyl)methanone (3g)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (62 mg, 62%), mp: 105-107 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.26 (t, J = 7.2 Hz, 3H), 2.34 (s, 3H), 2.86 (q, J = 7.2 Hz, 2H), 5.67 (br s, 1H), 6.86 (t, J = 7.8 Hz, 1H), 7.07-7.09 (m, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.48-7.53 (m, 6H), 12.38 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 13.3, 16.5, 19.9, 118.3, 118.8, 120.4, 125.0, 127.2, 128.3, 129.2, 129.6, 130.7, 131.2, 133.9, 135.2, 136.4, 136.6, 151.9, 163.3, 204.6. HRMS calcd for $C_{22}H_{20}NaO_3$: 355.1305 $[M+Na]^+$, found: 355.1271.

(3-Ethyl-4-hydroxy-2-methyl-5-(thiophen-2-yl)phenyl)(2-hydroxyphenyl)methanone (3h)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (52 mg, 51%), mp: 108-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.18 (t, J = 7.6 Hz, 3H), 2.26 (s, 3H), 2.78 (q, J = 7.6 Hz, 2H), 6.10 (s, 1H), 6.76-6.80 (m, 1H), 7.02 (d, J = 8.4 Hz, 1H), 7.07-7.09 (m, 1H), 7.15 (s, 1H), 7.20 (dd, J_1 = 3.6 Hz, J_2 = 1.2 Hz, 1H), 7.33 (dd, J_1 = 5.2 Hz, J_2 = 0.8 Hz, 1H), 7.40-7.46 (m, 2H), 12.32 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 13.3, 16.6, 20.0, 118.0, 118.4, 119.0, 120.4, 126.5, 126.9, 127.3, 128.1, 130.9, 131.2, 134.0, 135.6, 136.8, 138.0, 152.2, 163.3, 204.4. HRMS calcd for $C_{20}H_{18}NaO_3S$: 361.0869 $[M+Na]^+$, found: 361.0869.

(5-Ethyl-6-hydroxy-4'-methoxy-4-methyl-[1,1'-biphenyl]-3-yl)(2-hydroxyphenyl)methanone (3i)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (65 mg, 60%), mp: 117-118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.08 (t, J = 7.8 Hz, 3H), 2.16 (s, 3H), 2.68 (q, J = 7.2 Hz, 2H), 3.69 (s, 3H), 5.53 (s, 1H), 6.68 (t, J = 7.2 Hz, 1H), 6.85-6.88 (m, 3H), 6.90 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.32-7.34 (m, 2H), 12.22 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 13.3, 16.5, 19.9, 55.4, 115.0, 118.2, 118.8, 120.4,

124.7, 127.3, 128.4, 130.4, 130.5, 131.1, 134.0, 134.8, 136.5, 152.0, 159.6, 163.3, 204.7. HRMS calcd for $C_{23}H_{22}NaO_4$: 385.1410 $[M+Na]^+$, found: 385.1399.

(4-Benzyl-6-hydroxy-5-methyl-[1,1'-biphenyl]-3-yl)(2-hydroxyphenyl)methanone (3j)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (78 mg, 66%), mp: 108-109 ^oC. ^{1}HNMR (400 MHz, $CDCl_3$,) δ: 2.13 (s, 3H), 4.04 (s, 2H), 5.53 (s, 1H), 6.64-6.68 (m, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.98-7.03 (m, 4H), 7.10 (t, *J* = 7.2 Hz, 2H), 7.30-7.35 (m, 3H), 7.36-7.43 (m, 4H), 12.12 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 12.4, 36.1, 118.2, 118.6, 120.4, 125.3, 125.5, 126.0, 127.5, 128.3, 128.4, 128.5, 129.1, 129.7, 131.6, 133.9, 136.3, 136.5, 138.5, 139.9, 152.4, 163.3, 204.1. HRMS calcd for $C_{27}H_{22}NaO_3$: 417.1461 $[M+Na]^+$, found: 417.1483.

(6-Hydroxy-4,5-dimethyl-[1,1'-biphenyl]-3-yl)(2-hydroxy-5-methylphenyl)methanone (3k)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (67 mg, 67%), mp: 125-127 ^oC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 2.25 (s, 3H), 2.30 (s, 3H), 5.60 (s, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 7.03 (s, 1H), 7.21 (d, *J* = 1.6 Hz, 1H), 7.29 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.39-7.45 (m, 3H), 7.48-7.51 (m, 2H), 12.17 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 12.1, 17.4, 20.5, 118.0, 120.1, 124.6, 124.8, 126.9, 127.9, 128.3, 129.1, 129.6, 131.2, 133.4, 135.9, 136.5, 137.7, 151.9, 161.2, 204.4. HRMS calcd for $C_{22}H_{21}O_3$: 333.1485 $[M+H]^+$, found: 333.1484.

(5-Chloro-2-hydroxyphenyl)(6-hydroxy-4,5-dimethyl-[1,1'-biphenyl]-3-yl)methanone (3l)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (64 mg, 61%), mp: 93-94 ^oC. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.29 (s, 3H), 2.33 (s, 3H), 5.67 (br s, 1H), 7.03 (dd, J_1 = 7.8 Hz, J_2 = 2.4 Hz, 1H), 7.06 (s, 1H), 7.43-7.44 (m, 2H), 7.45-7.47 (m, 3H), 7.53 (t, *J* = 7.2 Hz, 2H), 12.24 (br s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 12.1, 17.4, 120.0, 121.1, 123.5, 124.9, 125.0, 127.0, 128.4, 129.1, 129.7, 130.2, 132.7, 136.16, 136.19, 136.4, 152.4, 161.7, 203.5. HRMS calcd for $C_{21}H_{18}ClO_3$: 353.0939 $[M+H]^+$, found: 353.0937.

(5-Ethyl-6-hydroxy-4-methyl-[1,1'-biphenyl]-3-yl)(5-fluoro-2-hydroxyphenyl)methanone (3m)

Eluent: petroleum ether-/ethyl acetate (40:1). Yellow solid (67 mg, 64%), mp: 107-108 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.24 (t, J = 7.2 Hz, 3H), 2.33 (s, 3H), 2.84 (q, J = 7.2 Hz, 2H), 5.65 (s, 1H), 7.03-7.05 (m, 1H), 7.06 (s, 1H), 7.16 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 7.24 (td, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.47 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.8 Hz, 2H), 12.08 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 13.2, 16.4, 19.9, 118.4 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 119.6 (d, $^{3}J_{C\text{-}F}$ = 6.5 Hz), 120.0 (d, $^{3}J_{C\text{-}F}$ = 6.6 Hz), 124.1 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 125.2, 127.1, 128.4, 129.2, 129.6, 130.6, 130.9, 135.3, 136.2, 152.2, 154.7 (d, $^{1}J_{C\text{-}F}$ = 236.3 Hz), 159.4, 203.6 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz). HRMS calcd for $C_{22}H_{19}FNaO_3$: 373.1210 $[M+Na]^+$, found: 373.1231.

(5-Chloro-2-hydroxyphenyl)(5-ethyl-6-hydroxy-4-methylbiphenyl-[1,1'-biphenyl]-3-yl)methanone (3n)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (60 mg, 54%), mp: 104-106 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.26 (t, J = 7.2Hz, 3H), 2.34 (s, 3H), 2.86 (q, J = 7.8 Hz, 2H), 5.69 (br s, 1H), 7.03 (d, J = 9.0 Hz, 1H), 7.06 (s, 1H), 7.43-7.47 (m, 3H), 7.48 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 7.8Hz, 2H), 12.26 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 13.3, 16.5, 19.9, 120.0, 121.1, 123.5, 125.2, 127.3, 128.4, 129.2, 129.7, 130.5, 131.0, 132.7, 135.4, 136.2, 136.4, 152.3, 161.8, 203.5. HRMS calcd for $C_{22}H_{19}ClNaO_3$: 389.0915 $[M+Na]^+$, found: 389.0940.

(5-Ethyl-6-hydroxy-4-methyl-[1,1'-biphenyl]-3-yl)(2-hydroxy-5-methylphenyl)methanone (3o)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (67 mg, 65%), mp: 129-130 ^{o}C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 1.27 (t, J = 7.2 Hz, 3H), 2.26 (s, 3H), 2.34 (s, 3H), 2.87 (q, J = 7.2 Hz, 2H), 5.67 (br s, 1H), 6.99 (d, J = 9.0 Hz, 1H), 7.08 (s, 1H), 7.27 (s, 1H), 7.33 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 7.49 (d, J = 7.2 Hz, 2H), 7.51-7.54 (m, 2H), 12.21 (s, 1H). ^{13}C NMR ($CDCl_3$, 150 Hz) δ: 13.3, 16.5, 19.9, 20.5, 118.1, 120.1, 125.0, 127.1, 128.0, 128.3, 129.2, 129.6, 130.7, 131.4, 133.4, 135.2, 136.5, 137.7, 151.8, 161.3, 204.6. HRMS calcd for $C_{23}H_{23}O_3$: 347.1642 $[M+H]^+$, found: 347.1647.

2. Typical procedure for the synthesis of 5a and spectroscopic data of 5a-5x

To a reaction tube equipped with a stir bar were added 1-phenylpenta-3,4-dien-2-one (**4a**, 48 mg, 0.3 mmol), chromone-3-carboxaldehyde (**2a**, 52 mg, 0.3 mmol), CH_3CN (2 mL) and an aqueous solution of sulfuric acid (4.74 M, 32 μL, 0.15 mmol). It was stirred at 70 ℃ for 2 h. To the resulting mixture were added H_2O (3 mL) and K_2CO_3 (62 mg, 0.45 mmol), and the stirring continued at 80 ℃ for 0.5 h. Upon completion, it was added with brine (10 mL), and then extracted with ethyl acetate (20 mL × 3). The organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (40:1) as eluent to give **5a**. **5b-5x** were obtained in a similar manner.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-[1,1'-biphenyl]-3-yl)ethan-1-one (5a)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (75 mg, 75%), mp: 106-107 ℃. ^{1}H NMR (600MHz, $CDCl_3$) δ: 2.73 (s, 3H), 6.92 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 1.8 Hz, 1H), 8.19 (d, *J* = 1.8 Hz, 1H), 11.80 (s, 1H), 13.30 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 27.0, 118.7, 118.9, 119.0, 119.4, 128.1, 128.4, 128.6, 129.4, 131.3, 132.4, 132.8, 135.8, 136.4, 137.9, 163.0, 163.1, 198.9, 205.0. HRMS calcd for $C_{21}H_{16}NaO_4$: 355.0941 $[M+Na]^+$, found: 355.0962.

1-(2'-Bromo-2-hydroxy-5-(2-hydroxy-5-methlbenzoyl)-[1,1'-biphenyl]-3-yl)ethan-1-one (5b)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (89 mg, 70%), mp: 160-161 ℃. ^{1}H NMR (600 MHz , $CDCl_3$) δ: 2.21 (s, 3H), 2.68 (s, 3H), 6.91 (d, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.25-7.28 (m, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.43 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.72 (s, 1H), 8.22 (s, 1H), 11.50 (s, 1H), 12.97 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 20.6, 26.9, 118.4, 118.7, 119.7, 123.8, 127.3, 128.1, 128.3, 129.8, 130.4, 131.7, 132.7, 132.8, 133.0, 136.7, 137.5, 138.8, 160.9, 162.7, 198.7, 204.7. HRMS calcd for $C_{22}H_{17}BrNaO_4$: 447.0202 $[M+Na]^+$, found: 447.0197.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-2'-methyl-[1,1'-biphenyl]-3-yl)ethan-1-one (5c)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (71 mg, 68%), mp: 118-121 ℃. ^{1}H NMR (400

MHz, $CDCl_3$) δ: 2.15 (s, 3H), 2.67 (s, 3H), 6.82-6.86 (m, 1H), 7.02 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.12-7.15 (m, 1H), 7.19-7.21 (m, 1H), 7.22-7.25 (m, 2H), 7.43-7.47 (m, 1H), 7.56 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.71 (d, J = 2.0 Hz, 1H), 8.17 (d, J = 2.4 Hz, 1H), 11.72 (s, 1H), 12.99 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 20.0, 27.0, 118.7, 118.9, 119.0, 119.2, 125.9, 128.37, 128.40, 130.0, 130.1, 131.9, 132.4, 132.7, 135.7, 136.4, 136.8, 138.3, 163.0, 163.1, 198.9, 204.8. HRMS calcd for $C_{22}H_{18}NaO_4$: 369.1097 $[M+Na]^+$, found: 369.1097.

1-(3'-Fluoro-2-hydroxy-5-(2-hydroxybenzoyl)-[1,1'-biphenyl]-3-yl)ethan-1-one (5d)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (68 mg, 65%), mp: 101-102 ℃. ^{1}H NMR (600 MHz , $CDCl_3$) δ: 2.72 (s, 3H), 6.93 (t, J = 7.8 Hz, 1H), 7.07-7.12 (m, 2H), 7.34-7.37 (m, 2H), 7.40-7.44 (m, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 0.6 Hz, 1H), 8.22 (d, J = 1.2 Hz, 1H), 11.77 (s, 1H), 13.34 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 27.0, 115.0 (d, $^2J_{C\text{-}F}$ = 20.9 Hz), 116.5 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 118.8, 118.9, 119.0, 119.5, 125.0 (d, $^4J_{C\text{-}F}$ = 2.1 Hz), 128.7, 129.86, 129.92, 130.0, 132.6 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 136.5, 137.7, 137.8 (d, $^3J_{C\text{-}F}$ = 8.9 Hz), 162.6 (d, $^1J_{C\text{-}F}$ = 243.9 Hz), 162.9, 163.1, 198.8, 204.9. HRMS calcd for $C_{21}H_{15}FNaO_4$: 373.0847 $[M+Na]^+$, found: 373.0879.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-3'-methyl-[1,1'-biphenyl]-3-yl)ethan-1-one (5e)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (81 mg, 78%), mp: 118-121 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.41 (s, 3H), 2.73 (s, 3H), 6.89-6.93 (m, 1H), 7.09 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.20 (d, J = 7.2 Hz, 1H), 7.32-7.39 (m, 3H), 7.50-7.55 (m, 1H), 7.63 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.91 (d, J = 1.6 Hz, 1H), 8.19 (d, J = 2.0 Hz, 1H), 11.83 (s, 1H), 13.29 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 21.5, 27.1, 118.7, 118.9, 119.0, 119.3, 126.5, 128.3, 128.5, 128.9, 130.0, 131.5, 132.2, 132.8, 135.7, 136.4, 137.9, 138.1, 163.05, 163.09, 199.0, 205.0. HRMS calcd for $C_{22}H_{19}O_4$: 347.1278 $[M+H]^+$, found: 347.1310.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-4'-methyl-[1,1'-biphenyl]-3-yl)ethan-1-one (5f)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (86 mg, 83%), mp: 96-97 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.31 (s, 3H), 2.63 (s, 3H), 6.80-6.84 (m, 1H), 7.01 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.39-7.41 (m, 2H), 7.43-7.45 (m, 1H), 7.55 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.82 (d, J = 2.0 Hz, 1H), 8.09 (d, J = 2.4 Hz, 1H), 11.73 (s, 1H), 13.19 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 21.3, 26.9, 27.0, 118.7, 118.9, 119.1, 119.4, 128.6, 129.1, 129.2, 131.4, 132.0, 132.82, 132.84, 136.4, 137.7, 138.0, 163.1, 199.0, 204.9. HRMS calcd for $C_{22}H_{18}NaO_4$: 369.1097 $[M+Na]^+$, found: 369.1098.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-4'-methoxy-[1,1'-biphenyl]-3-yl)ethan-1-one (5g)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (88 mg, 81%), mp: 121-122 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.64 (s, 3H), 3.76 (s, 3H), 6.83 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 1H), 7.42-7.46 (m, 3H), 7.55 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 8.07 (s, 1H), 11.73 (s, 1H), 13.22 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 26.0, 54.3, 112.8, 117.6, 117.8, 118.0, 118.3, 127.0, 127.5, 129.5, 130.0, 130.8, 131.8, 135.3, 136.4, 158.5, 161.99, 162.03, 198.0, 203.9. HRMS calcd for $C_{22}H_{18}NaO_5$: 385.1046 $[M+Na]^+$, found: 385.1062.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-3',4’dimethoxy-[1,1'-biphenyl]-3-yl)ethan-1-one (5h)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (100 mg, 85%), mp: 130-132 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.66 (s, 3H), 3.85 (d, J = 2.0 Hz, 6H), 6.82-6.86 (m, 1H), 6.88 (d, J = 8.4 Hz, 1H), 7.03 (dd, J_1 = 8.8 Hz, J_2 = 0.8 Hz, 1H), 7.07 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.10 (d, J = 1.6 Hz, 1H), 7.43-7.48 (m, 1H), 7.56 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.85 (d, J = 2.0 Hz, 1H), 8.09 (d, J = 2.0 Hz, 1H), 11.73 (s, 1H), 13.25 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 27.0, 55.97, 56.00, 111.1, 112.7, 118.7, 118.9, 119.1, 119.3, 121.9, 128.4, 128.6, 131.2, 131.9, 132.8, 136.4, 137.5, 148.7, 149.0, 163.0, 163.1, 199.1, 205.0. HRMS calcd for $C_{23}H_{20}NaO_6$: 415.1152 $[M+Na]^+$, found: 415.1155.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-3-(thiophen-2-yl)ethanone (5i)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (66 mg, 65%), mp: 138-140 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.74 (s, 3H), 6.92-6.96 (m, 1H), 7.11-7.15 (m, 2H), 7.41-7.43 (m, 1H), 7.54-7.58 (m, 1H), 7.63 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.65-7.66 (m, 1H), 8.13 (d, J = 2.0 Hz, 1H), 8.20 (d, J = 2.0 Hz, 1H), 11.81 (s, 1H), 13.74 (s, 1H). ^{13}C NMR (100 Hz , $CDCl_3$) δ: 27.0, 118.8, 118.9, 119.0, 119.5, 124.3, 126.7, 127.0, 127.3, 128.6, 131.4, 132.8, 135.3, 136.5, 136.7, 161.8, 163.1, 198.9, 205.0. HRMS calcd for $C_{19}H_{14}NaO_4S$: 361.0505 $[M+Na]^+$, found: 361.0541.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-4'-methoxy-[1,1'-biphenyl]-3-yl)propan-1-one (5j)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (93 mg, 82%), mp: 121-122 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.22 (t, J = 7.2 Hz, 3H), 3.06 (q, J = 7.2 Hz, 2H), 3.78 (s, 3H), 6.83-6.87 (m, 1H), 6.92 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 1H), 7.44-7.49 (m, 3H), 7.57 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.83 (d, J = 2.0 Hz, 1H), 8.12 (d, J = 2.0 Hz, 1H), 11.75 (s, 1H), 13.33 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 8.16, 40.0, 55.4, 113.9, 118.7, 118.8, 118.9, 119.1, 128.2, 128.5, 130.6, 131.0, 131.2, 132.8, 136.3, 137.2, 159.5, 163.06, 163.09, 199.2, 207.5. HRMS calcd for $C_{23}H_{20}NaO_5$: 399.1203 $[M+Na]^+$, found: 399.1191.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-3-(thiophen-2-yl)propan-1-one (5k)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (66 mg, 62%), mp: 110-112 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (t, J = 7.2 Hz, 3H), 3.02 (q, J = 7.2 Hz, 2H), 6.82-6.86 (m, 1H), 7.01-7.04 (m, 2H), 7.31 (dd, J_1 = 5.2 Hz, J_2 = 1.2 Hz, 1H), 7.45 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.52-7.56 (m, 2H), 8.05 (d, J = 2.0 Hz, 1H), 8.09 (d, J = 2.4 Hz, 1H), 11.71 (s, 1H), 13.73 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 8.1, 32.0, 118.8, 118.9, 118.96, 119.00, 124.4, 126.6, 126.9, 127.3, 128.5, 130.6, 132.8, 135.0, 136.4, 136.9, 161.9, 163.1, 198.9, 207.6. HRMS calcd for $C_{20}H_{16}NaO_4S$: 375.0662 $[M+Na]^+$, found: 375.0634.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-[1,1'-biphenyl]-3-yl)butan-1-one (5l)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (89 mg, 82%), mp: 118-119 ℃.[1] H NMR (600 MHz, $CDCl_3$) δ: 0.96 (t, *J* = 7.2 Hz, 3H), 1.71-1.77 (m, 2H), 2.97 (t, *J* = 7.2 Hz, 2H), 6.83 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.83 (s, 1H), 8.14 (s, 1H), 11.74 (s, 1H), 13.36 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 13.8, 17.9, 40.5, 118.7, 118.9, 119.0, 119.1, 128.1, 128.4 128.5, 129.4, 131.5, 131.6, 132.8, 135.9, 136.4, 137.6, 163.1, 163.2, 199.1, 207.2. HRMS calcd for $C_{23}H_{20}NaO_4$: 383.1254 $[M+Na]^+$, found: 383.1266.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-4'-methoxy-[1,1'-biphenyl]-3-yl)butan-1-one (5m)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (97 mg, 83%), mp: 120-122 ℃. ^1H NMR (600 MHz, $CDCl_3$) δ: 1.04 (t, *J* = 7.2 Hz, 3H), 1.79-1.85 (m, 2H), 3.05 (t, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 6.91 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.51-7.54 (m, 3H), 7.63 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.88 (d, *J* = 1.8 Hz, 1H), 8.18 (d, *J* = 1.8 Hz, 1H), 11.83 (s, 1H), 13.45 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 13.8, 17.9, 40.5, 55.3, 113.9, 118.7, 118.9, 119.0, 119.1, 128.2, 128.4, 130.6, 131.1, 131.2, 132.8, 136.3, 137.2, 159.5, 163.1, 163.2, 199.1, 207.2. HRMS calcd for $C_{24}H_{22}NaO_5$: 413.1359 $[M+Na]^+$, found: 413.1362.

1-(2-Hydroxy-5-(2-hydroxybenzoyl)-3-(thiophen-2-yl)phenyl)butan-1-one (5n)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (68 mg, 62%), mp: 90-94 ℃. ^1H NMR (600 MHz, $CDCl_3$) δ: 1.03 (t, *J* = 7.2 Hz, 3H), 1.77-1.84 (m, 2H), 3.02 (t, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 7.8 Hz, 1H), 7.08-7.11 (m, 2H), 7.37 (d, *J* = 4.8 Hz, 1H), 7.51-7.54 (m, 1H), 7.60-7.62 (m, 2H), 8.11 (d, *J* = 1.2 Hz, 1H), 8.15 (d, *J* = 1.8 Hz, 1H), 11.79 (s, 1H), 13.85 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 13.8, 17.9, 40.4,118.7, 118.9, 119.0, 119.1, 124.3, 126.6, 126.9, 127.3, 128.4, 130.8, 132.8, 135.0, 136.4, 136.9, 162.0, 163.1, 198.8, 207.3. HRMS calcd for $C_{21}H_{18}NaO_4S$: 389.0818 $[M+Na]^+$, found: 389.0829.

1-(5-(5-Fluoro-2-hydroxybenzoyl)-2-hydroxy-[1,1'-biphenyl]-3-yl)ethan-1-one (5o)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (82 mg, 78%), mp: 127-128 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.66 (s, 3H), 6.98-7.00 (m, 1H), 7.18-7.21 (m, 1H), 7.25 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.51 (d, J = 7.8 Hz, 2H), 7.84 (d, J = 1.8 Hz, 1H), 8.11 (d, J = 1.8 Hz, 1H), 11.42 (s, 1H), 13.25 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 27.0, 117.5 (d, $^{2}J_{C-F}$ = 23.1 Hz), 118.6 (d, $^{3}J_{C-F}$ =5.6 Hz), 119.4, 120.1 (d, $^{3}J_{C-F}$ = 6.6 Hz), 123.9 (d, $^{2}J_{C-F}$ = 23.0 Hz), 128.0, 128.2, 128.4, 129.4, 131.7, 132.2, 135.6, 137.6, 154.6 (d, $^{1}J_{C-F}$ = 238.5 Hz), 159.2, 163.3, 198.0, 204.9. HRMS calcd for $C_{21}H_{15}FNaO_4$: 373.0847 $[M+Na]^+$, found: 373.0877.

1-(5-(5-Fluoro-2-hydroxybenzoyl)-2-hydroxy-[1,1'-biphenyl]-3-yl)propan-1-one (5p)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (82 mg, 75%), mp: 131-133 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.30 (t, J = 7.2 Hz, 3H), 3.15 (q, J = 7.2 Hz, 2H), 7.06-7.09 (m, 1H), 7.26-7.28 (m, 1H), 7.33 (dd, J_1 = 8.4 Hz, J_2 = 3.0 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.91 (s, 1H), 8.22 (s, 1H), 11.51 (s, 1H), 13.43 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 8.11, 32.0, 117.6 (d, $^{2}J_{C-F}$ = 24.0), 118.6 (d, $^{3}J_{C-F}$ = 5.8 Hz), 118.9, 120.0 (d, $^{3}J_{C-F}$ = 7.2 Hz), 123.8 (d, $^{2}J_{C-F}$ = 23.3 Hz), 127.9, 128.1, 128.4, 129.4, 131.4, 131.8, 135.7, 137.3, 154.7 (d, $^{1}J_{C-F}$ = 237.8 Hz), 159.2 (d, $^{4}J_{C-F}$ = 1.5 Hz), 163.3, 198.0 (d, $^{4}J_{C-F}$ = 2.2 Hz), 207.4. HRMS calcd for $C_{22}H_{18}FO_4$: 365.1184 $[M+H]^+$, found: 365.1188.

1-(5-(5-Fluoro-2-hydroxybenzoyl)-2-hydroxy-[1,1'-biphenyl]-3-yl)butan-1-one (5q)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (80 mg, 70%), mp: 108-109 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.98 (t, J = 7.8 Hz, 3H), 1.73-1.79 (m, 2H), 2.99 (t, J = 7.2 Hz, 2H), 6.98-7.00 (m, 1H), 7.18-7.21 (m, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.31-7.33 (m, 1H), 7.38 (t, J = 7.2 Hz, 2H), 7.51 (d, J = 7.8 Hz, 2H), 7.83 (s, 1H), 8.14 (s, 1H), 11.43 (s, 1H), 13.40 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 13.8, 17.9, 40.5, 117.6 (d, $^{2}J_{C-F}$ = 24.0 Hz), 118.6 (d, $^{3}J_{C-F}$ = 6.5 Hz), 119.0, 120.0 (d, $^{3}J_{C-F}$ = 7.2 Hz), 123.8 (d, $^{2}J_{C-F}$ = 23.3 Hz), 127.9, 128.1, 128.4, 129.4, 131.5, 131.8, 135.7, 137.3, 154.7 (d, $^{1}J_{C-F}$ = 237.1 Hz), 159.2, 163.5,

198.0 (d, $^{4}J_{C\text{-}F}$ = 2.1 Hz), 207.1. HRMS calcd for $C_{23}H_{19}FNaO_4$: 401.1160 $[M+Na]^+$, found: 401.1174.

1-(5-(5-Chloro-2-hydroxybenzoyl)-2-hydroxy-[1,1'-biphenyl]-3-yl)ethanone (5r)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (85 mg, 77%), mp: 156-158 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.74 (s, 3H), 7.06 (d, *J* = 8.8 Hz, 1H), 7.38-7.41 (m, 1H), 7.44-7.49 m, 2H), 7.48 (d, *J* = 2.4 Hz, 1H), 7.58-7.60 (m, 2H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 8.17 (d, *J* = 2.4 Hz, 1H), 11.64 (s, 1H), 13.33 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 27.0, 119.4, 119.7, 120.4, 123.6, 127.9, 128.2, 128.4, 129.4, 131.7, 131.8, 132.3, 135.6, 136.2, 137.6, 161.5, 163.4, 197.9, 204.8. HRMS calcd for $C_{21}H_{15}ClNaO_4$: 389.0551 $[M+Na]^+$, found: 389.0558.

1-(5-(5-Chloro-2-hydroxybenzoyl)-2-hydroxy-[1,1'-biphenyl]-3-yl)propan-1-one (5s)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (91 mg, 80%), mp: 154-155 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.30 (t, *J* = 7.6 Hz, 3H), 3.13 (q, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 7.37-7.41 (m, 1H), 7.44-7.46 (m, 2H), 7.476-7.482 (m, 1H), 7.57-7.63 (m, 3H), 7.91 (d, *J* = 2.0 Hz, 1H), 8.19 (d, *J* = 2.0 Hz, 1H), 11.65 (s, 1H), 13.44 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 8.25, 32.1, 118.8, 119.7, 120.3, 123.6, 127.8, 128.2, 128.4, 129.4, 131.5, 131.8, 132.0, 135.7, 136.1, 137.3, 161.5, 163.4, 197.9, 207.4. HRMS calcd for $C_{22}H_{17}ClNaO_4$: 403.0708 $[M+Na]^+$, found: 403.0726.

1-(5-(5-Chloro-2-hydroxybenzoyl)-2-hydroxy-[1,1'-biphenyl]-3-yl)butan-1-one (5t)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (90 mg, 76%), mp: 141-142 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.97 (t, *J* = 7.6 Hz, 3H), 1.76 (q, *J* = 7.2 Hz, 2H), 1.72-1.81 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 1H), 7.31-7.33 (m, 1H), 7.36-7.40 (m, 3H), 7.50-7.52 (m, 2H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.83 (d, *J* = 2.4 Hz, 1H), 8.11 (d, *J* = 2.4 Hz, 1H), 11.57 (s, 1H), 13.41 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 13.8, 18.1, 40.6, 118.9, 119.7, 120.3, 123.6, 127.7, 128.2, 128.4, 129.4, 131.7, 131.8, 132.0, 135.7, 136.1, 137.4, 161.5, 163.6, 197.9, 207.2. HRMS calcd for $C_{23}H_{19}ClNaO_4$: 417.0864 $[M+Na]^+$, found: 417.0851.

1-(5-(5-hydroxy-5-(2-hydroxy-5-methylbenzoyl)-[1,1'-biphenyl]-3-yl)ethanone (5u)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (84 mg, 81%), mp: 163-164 ℃.^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.28 (s, 3H), 2.72 (s, 3H), 7.00 (d, J = 8.4 Hz, 1H), 7.34 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.38-7.40 (m, 1H), 7.42 (d, J = 1.6 Hz, 1H), 7.43-7.47 (m, 2H), 7.58-7.60 (m, 2H), 7.92 (d, J = 2.0 Hz, 1H), 8.17 (d, J = 2.0 Hz, 1H), 11.60 (s, 1H), 13.28 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 20.6, 27.0, 118.5, 118.8, 119.3, 128.0, 128.1, 128.4, 128.7, 129.4, 131.3, 132.2, 132.5, 135.8, 137.4, 137.8, 161.0, 162.9, 198.9, 204.9. HRMS calcd for $C_{22}H_{19}O_4$: 347.1278 $[M+H]^+$, found: 347.1318.

1-(2-Hydroxy-5-(2-hydroxy-5-methylbenzoyl)-[1,1'-biphenyl]-3-yl)propan-1-one (5v)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (86 mg, 79%), mp: 140-143 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.21 (t, J = 7.2 Hz, 3H), 2.21 (s, 3H), 3.04 (q, J = 7.2 Hz, 2H), 6.92 (d, J = 8.0 Hz, 1H), 7.26 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.30-7.33 (m, 1H), 7.34 (d, J = 1.6 Hz, 1H), 7.35-7.39 (m, 2H), 7.50-7.52 (m, 2H), 7.83 (d, J = 2.4 Hz, 1H), 8.12 (d, J = 2.4 Hz, 1H), 11.52 (s, 1H), 13.30 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 8.3, 20.6, 32.0, 118.5, 118.7, 118.8, 127.98, 128.05, 128.4, 128.6, 129.4, 131.4, 131.5, 132.5, 135.9, 137.4, 137.5, 161.0, 163.0, 199.0, 207.5. HRMS calcd for $C_{23}H_{20}NaO_4$: 383.1254 $[M+Na]^+$, found: 383.1228.

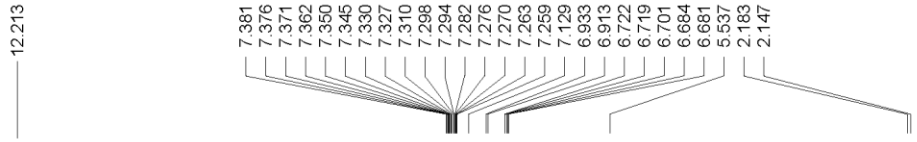
1-(2-Hydroxy-5-(2-hydroxy-5-methylbenzoyl)-[1,1'-biphenyl]-3-yl)butan-1-one (5w)

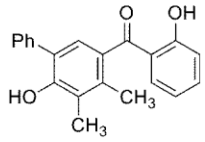
Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (92 mg, 82%), mp: 143-144 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.05 (t, J = 7.2 Hz, 3H), 1.80-1.89 (m, 2H), 2.29 (s, 3H), 3.05 (t, J = 7.2 Hz, 2H), 7.01 (d, J = 8.4 Hz, 1H), 7.35 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.40-7.41 (m, 1H), 7.42-7.48 (m, 3H), 7.59-7.61 (m, 2H), 7.92 (d, J = 2.4 Hz, 1H), 8.21 (d, J = 2.0 Hz, 1H), 11.61 (s, 1H), 13.43 (s, 1H). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 13.8, 18.1, 20.6, 40.6, 118.5, 118.8, 118.9, 127.97, 128.04, 128.4, 128.6, 129.4, 131.5, 131.6, 132.5, 135.9, 137.4, 137.6, 161.0, 163.1, 199.0, 207.2. HRMS calcd for $C_{24}H_{23}O_4$: 375.1591 $[M+H]^+$, found: 375.1590.

1-(3'-Fluoro-2-hydroxy-5-(2-hydroxy-5-methylbenzoyl)-[1,1'-biphenyl]-3-yl)ethanone (5x)

Eluent: petroleum ether/ethyl acetate (40:1). Yellow solid (79 mg, 72%), mp: 102-103 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.29 (s, 3H), 2.74 (s, 3H), 7.01 (d, *J* = 8.4 Hz, 1H), 7.08-7.11 (m, 1H), 7.34-7.37 (m, 3H), 7.40-7.42 (m, 2H), 7.92 (d, *J* = 1.8 Hz, 1H), 8.20 (d, *J* = 1.8 Hz,1H), 11.57 (s, 1H), 13.33 (s, 1H). ^{13}C NMR (150 Hz, $CDCl_3$) δ: 20.6, 27.0, 115.0 (d, $^{2}J_{C\text{-}F}$ = 20.9 Hz), 116.5 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 118.5, 118.7, 119.4, 125.0 (d, $^{4}J_{C\text{-}F}$ = 2.3 Hz), 128.1, 128.8, 129.9 (d, $^{3}J_{C\text{-}F}$ = 8.9 Hz), 130.0, 132.4, 132.5, 137.5, 137.7, 137.8 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 161.0, 162.6 (d, $^{1}J_{C\text{-}F}$ = 243.9 Hz), 162.8, 198.8, 204.9. HRMS calcd for $C_{22}H_{17}FNaO_4$: 387.1003 $[M+Na]^+$, found: 387.1021.

III. Copies of ^{1}H and ^{13}C NMR spectra of 3a-3o





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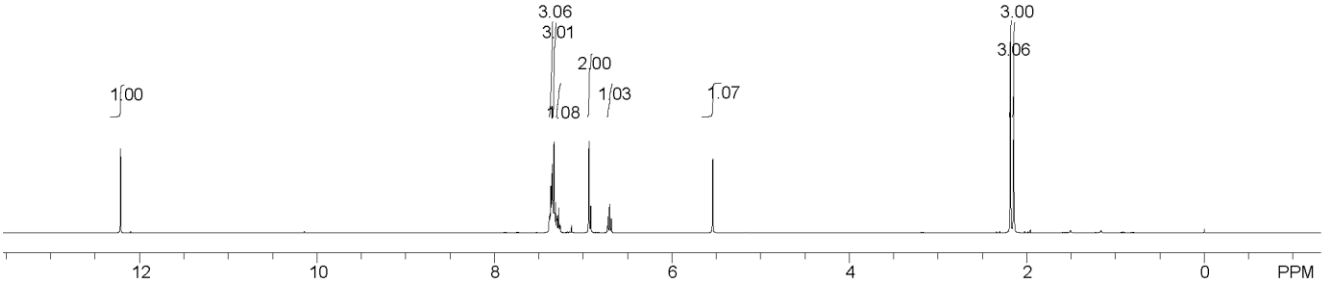

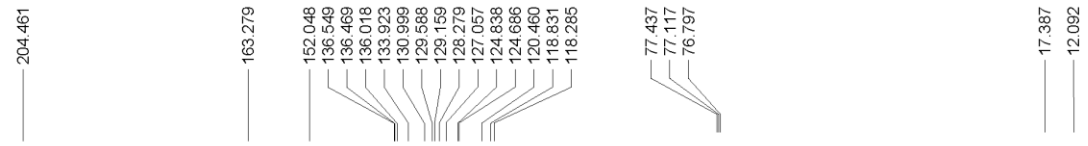

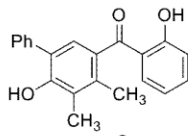

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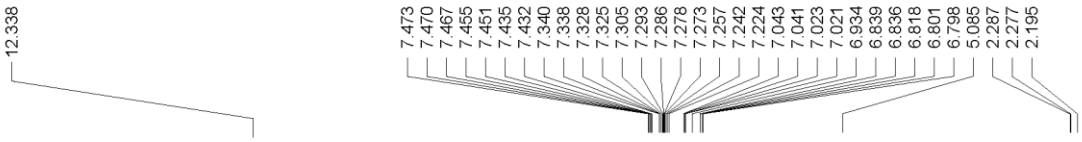
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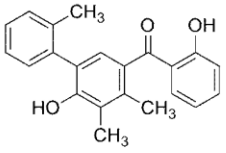
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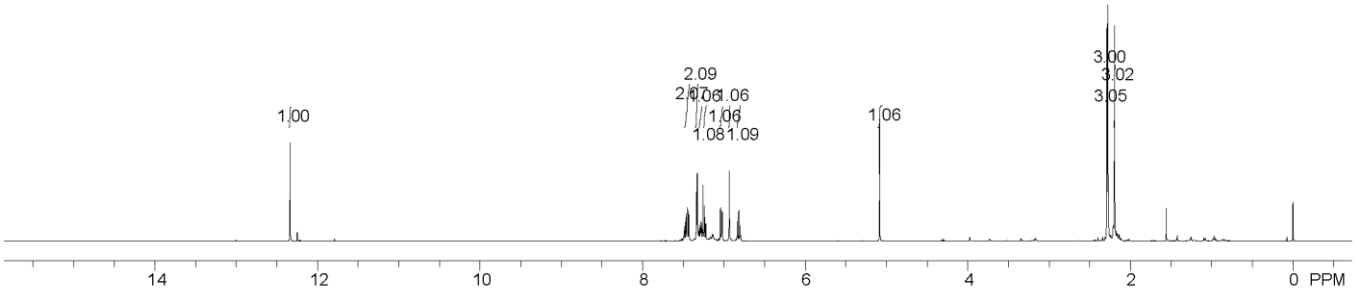
HO
CH3
CH3

3b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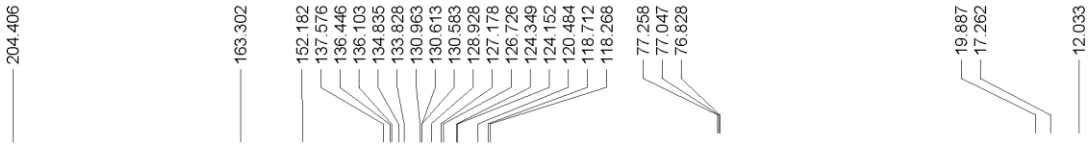
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127.178
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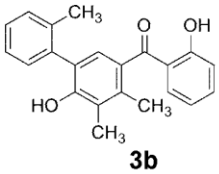
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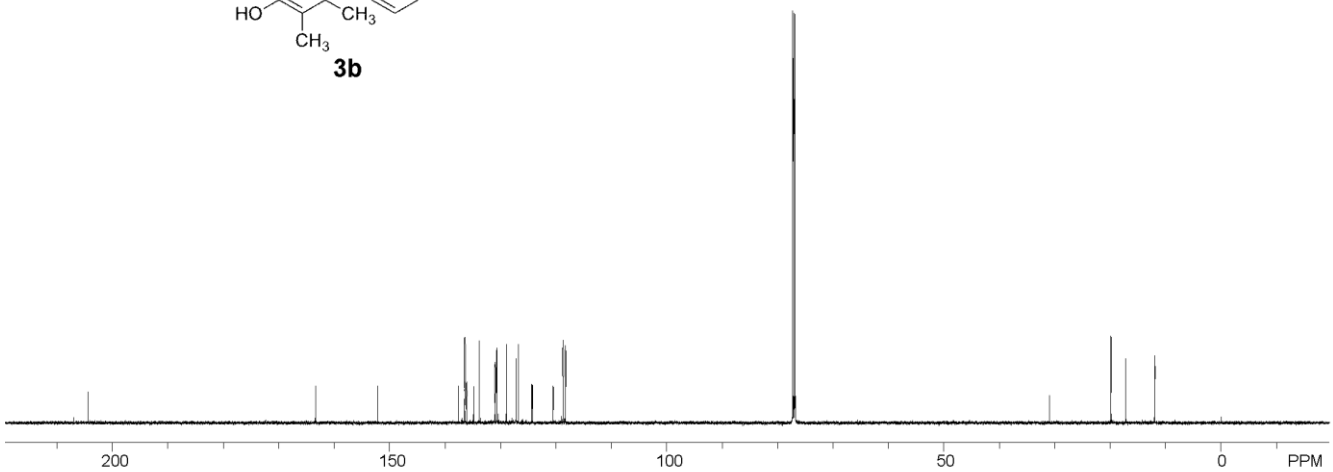
HO
CH3
CH3

3b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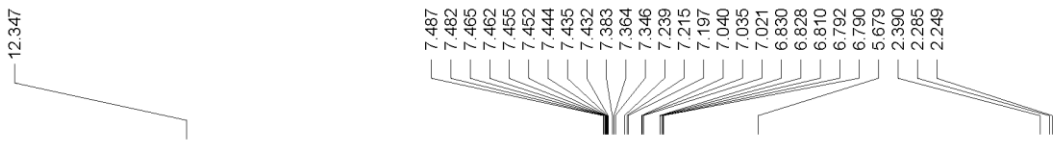
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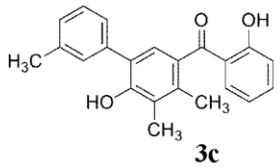
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OH
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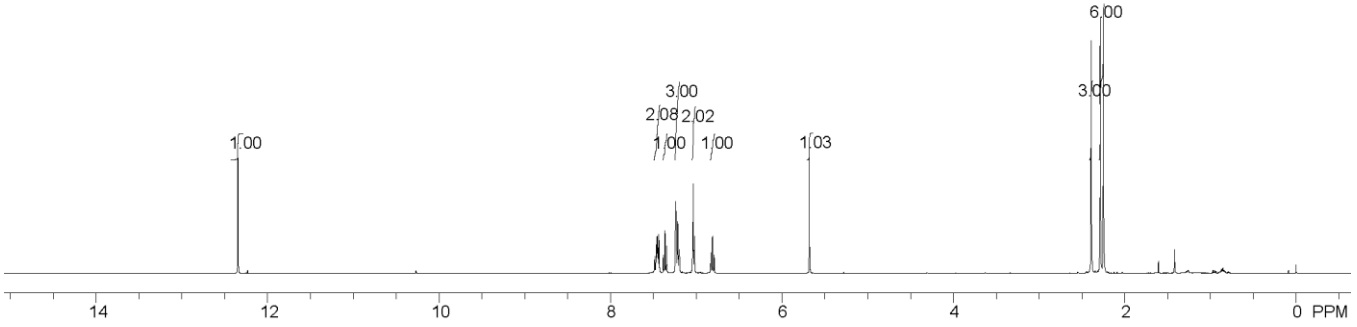
HO
CH3
CH3

3c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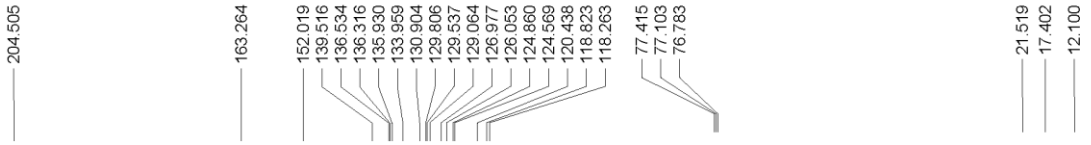
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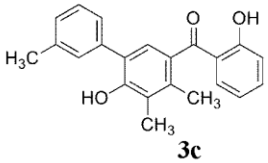
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HO
CH3
CH3

3c

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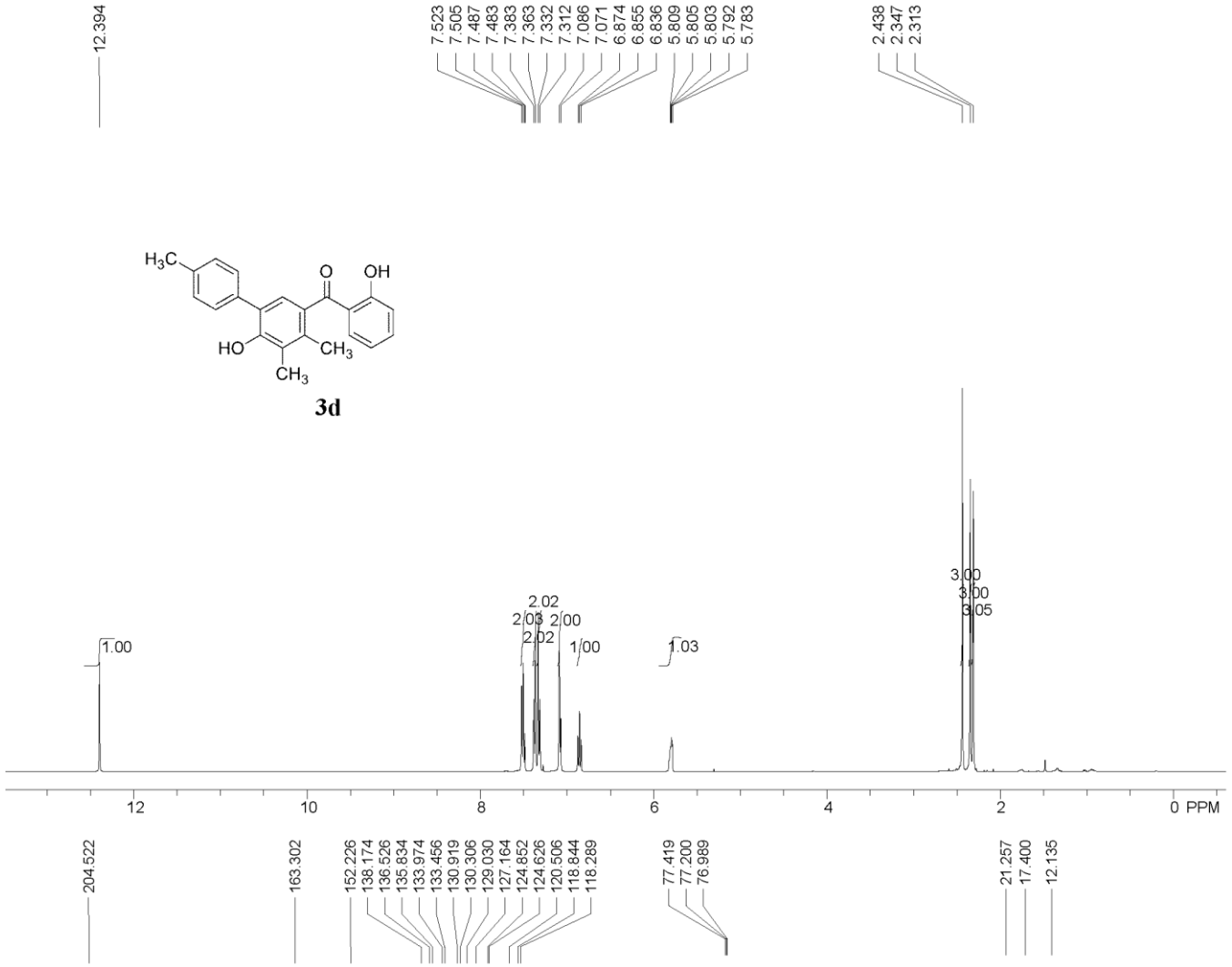
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HO
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CH3
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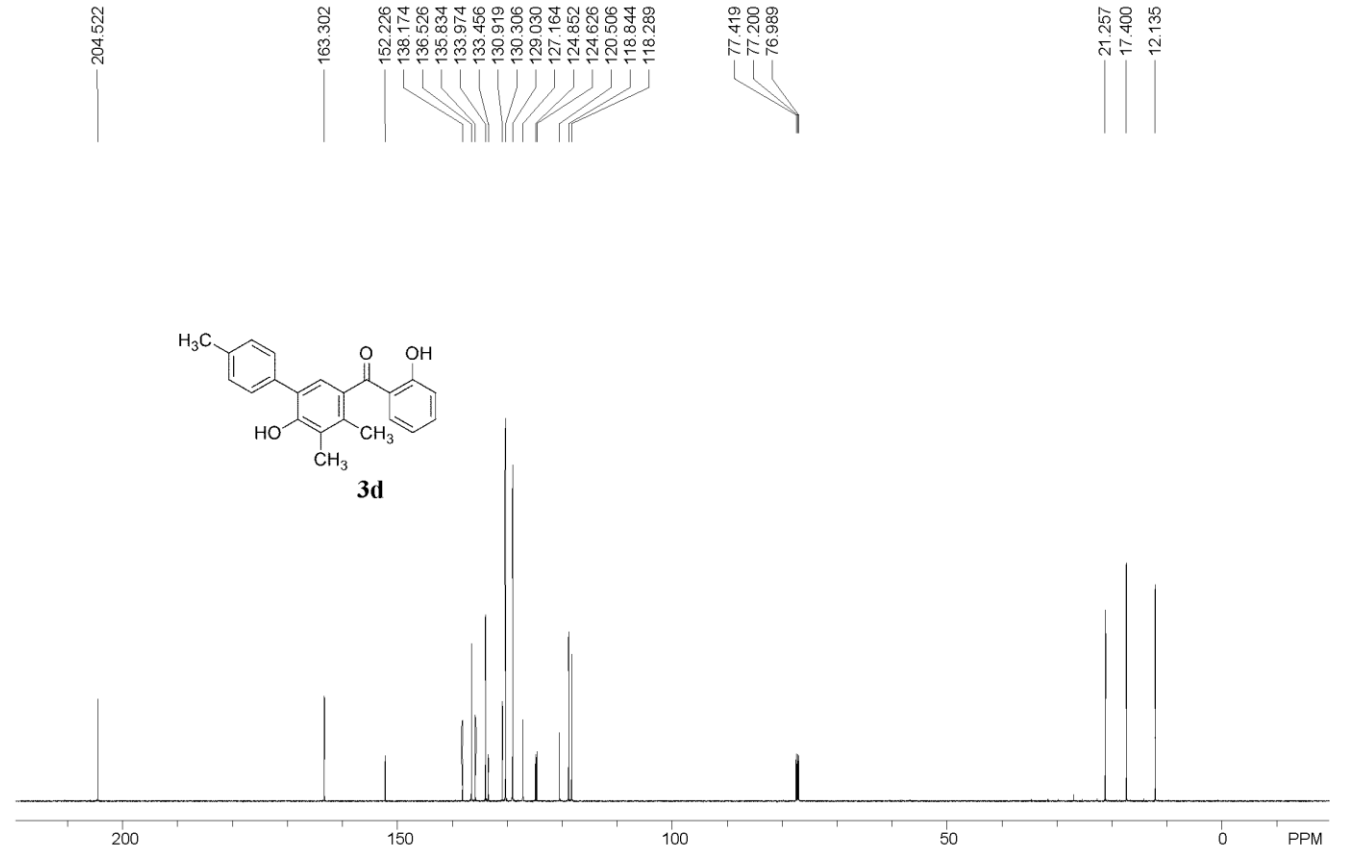
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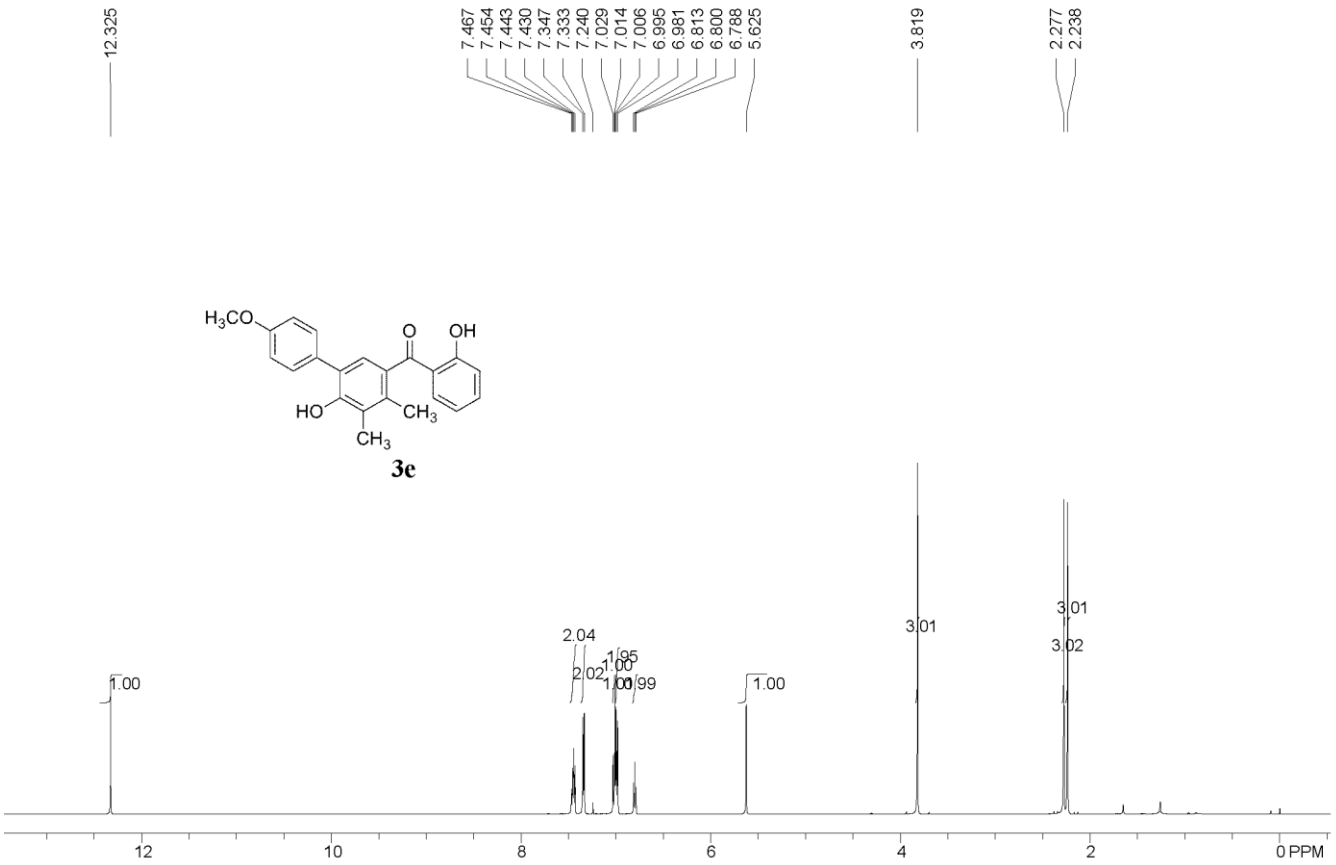
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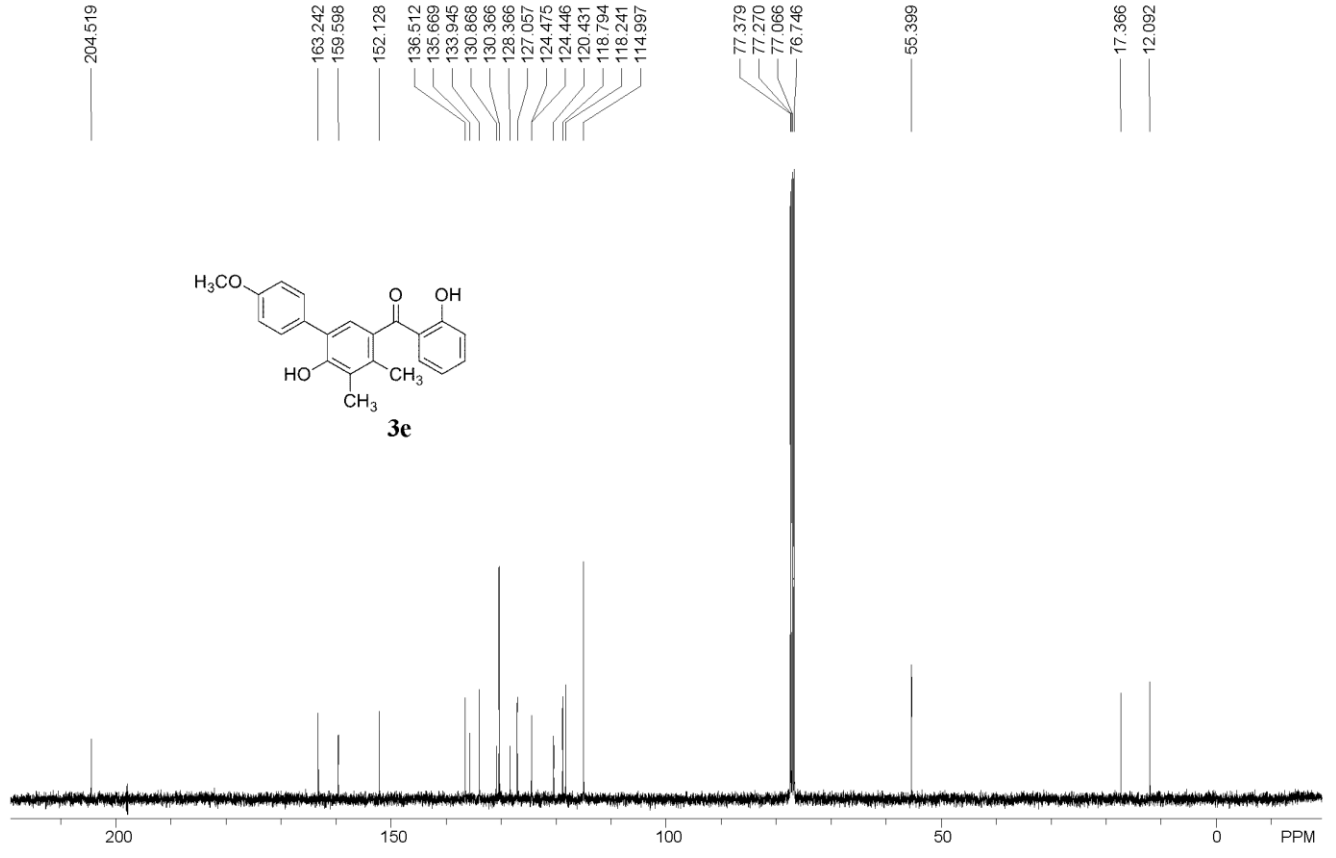
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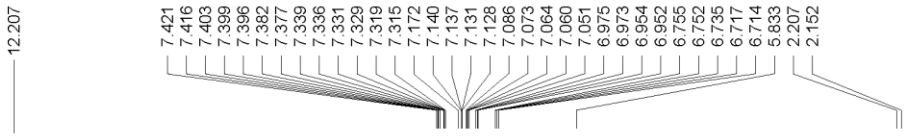
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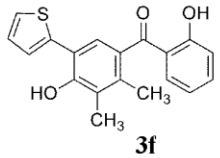
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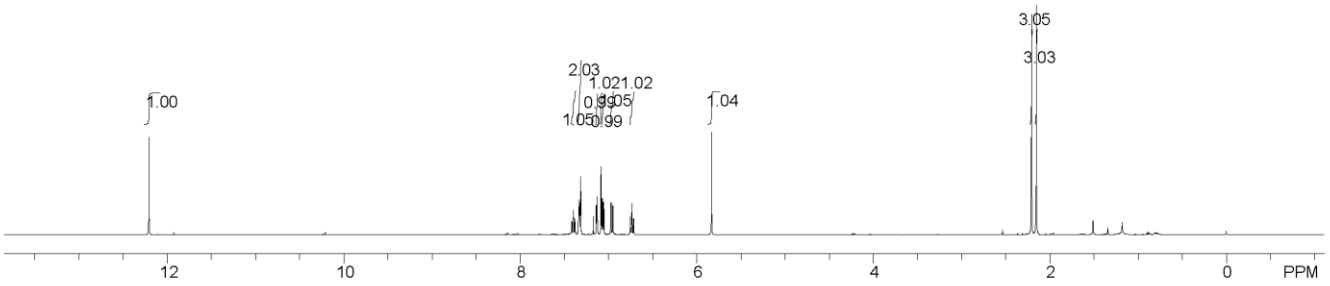
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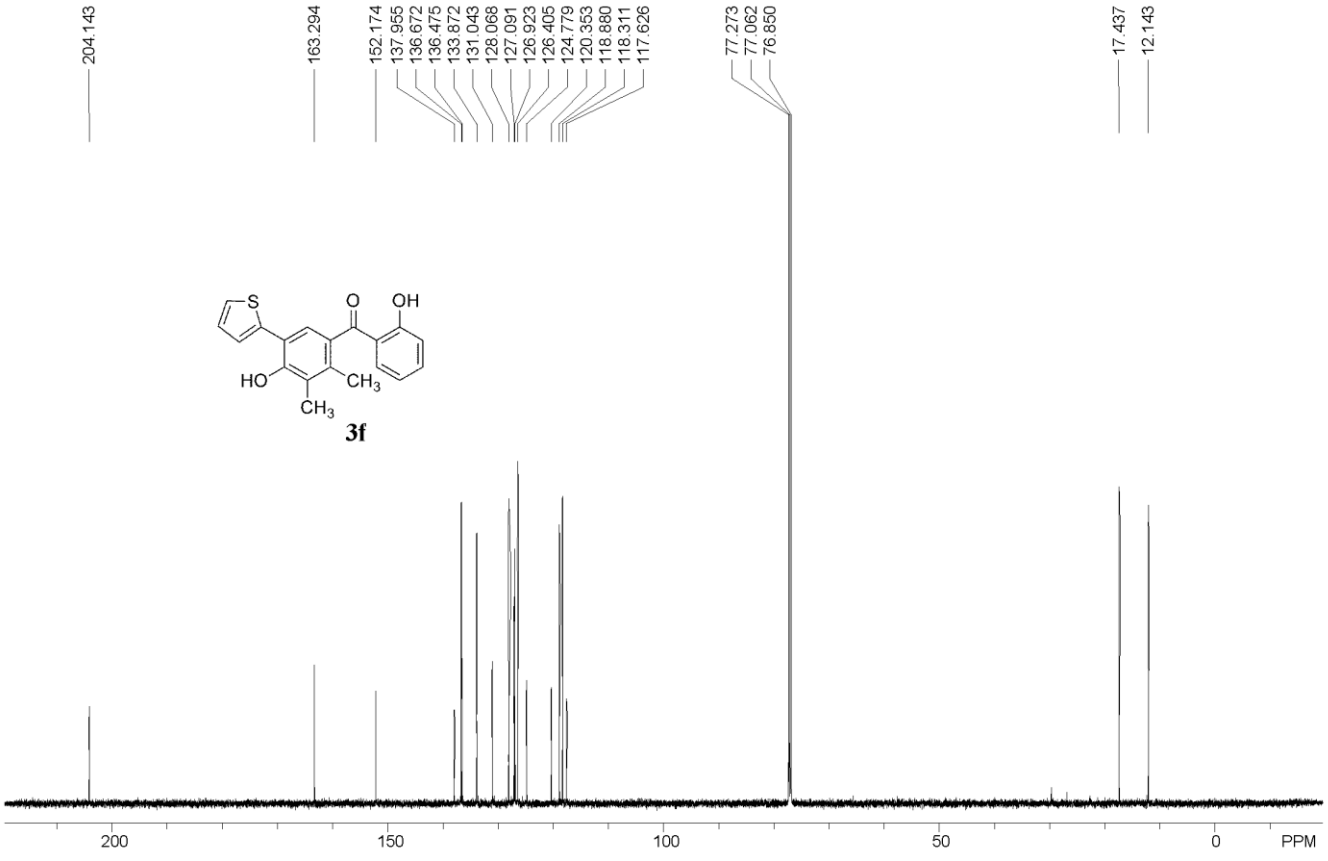
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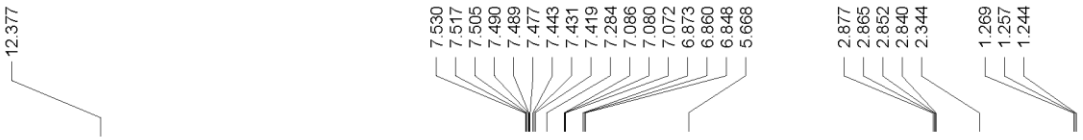
3f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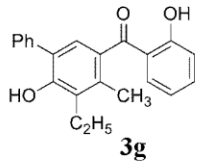
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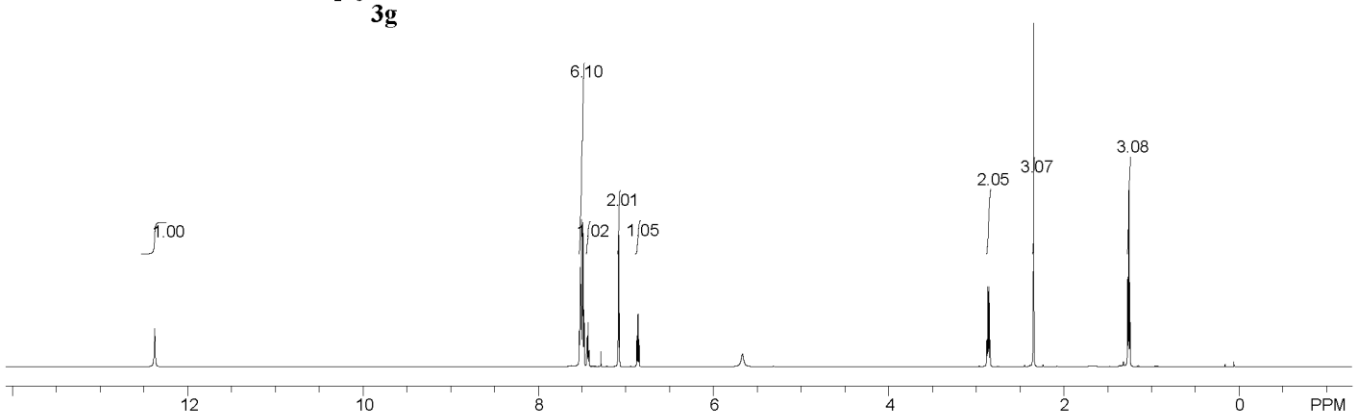
3g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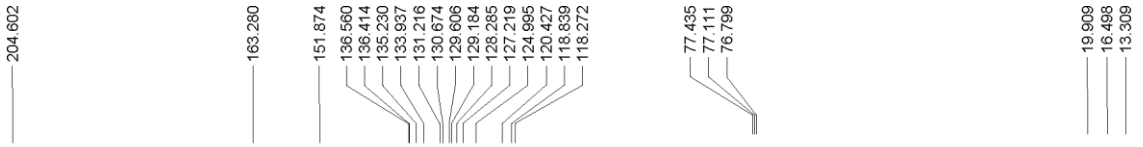
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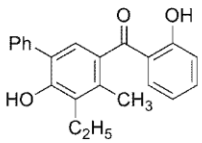
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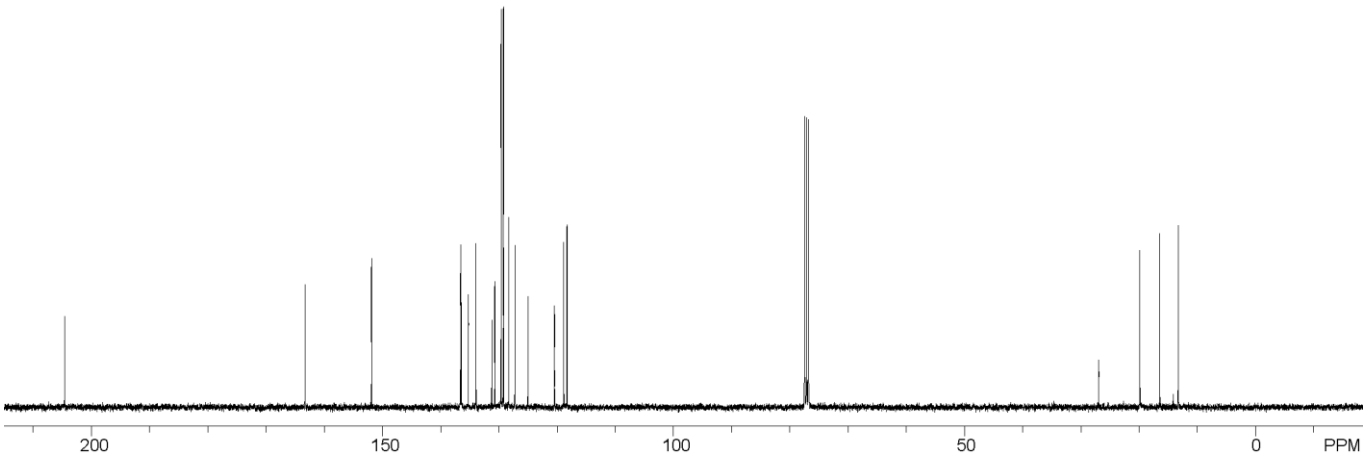
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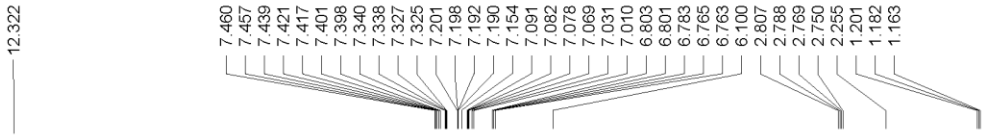
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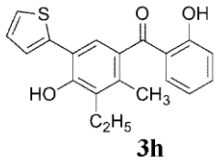
7.417
7.401
7.398
7.340
7.338
7.327
7.325
7.201
7.198
7.192
7.190
7.154
7.091
7.082
7.078
7.069
7.031
7.010
6.803
6.801
6.783
6.765
6.763
6.100
2.807
2.788
2.769
2.750
2.255
1.201
1.182
1.163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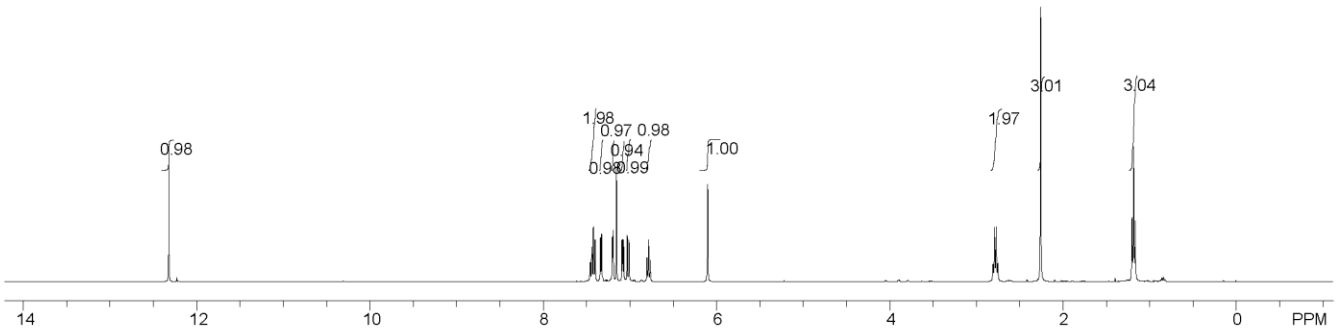
O
OH
HO
CH3
C2H5

3h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0.97
0.98
0.94
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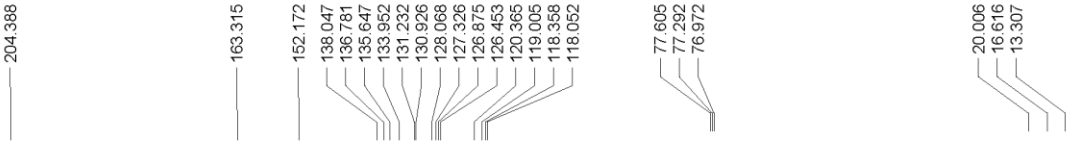
1.00
1.97
3.01
3.04
14
12
10
8
6
4
2
0
PPM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133.952
131.232
130.926
128.068
127.326
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119.005
118.358
118.052
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77.292
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20.006
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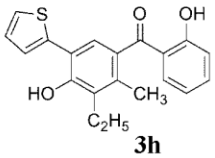
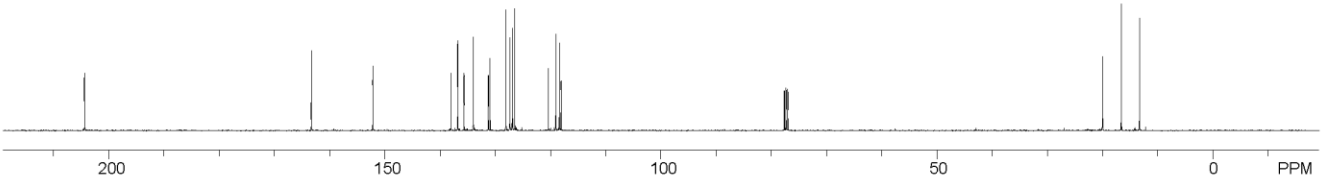
13.307


S
O
OH
HO
CH3
C2H5

3h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0
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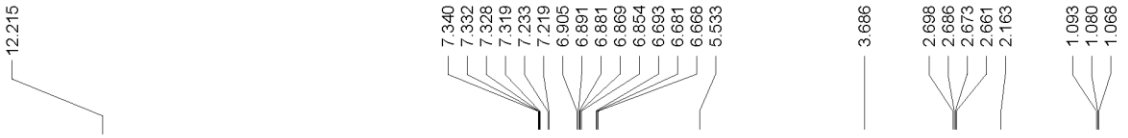
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7.332
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7.233
7.219
6.905
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6.881
6.869
6.854
6.693
6.681
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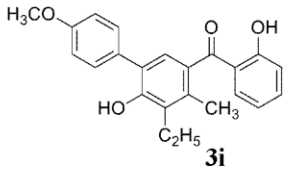
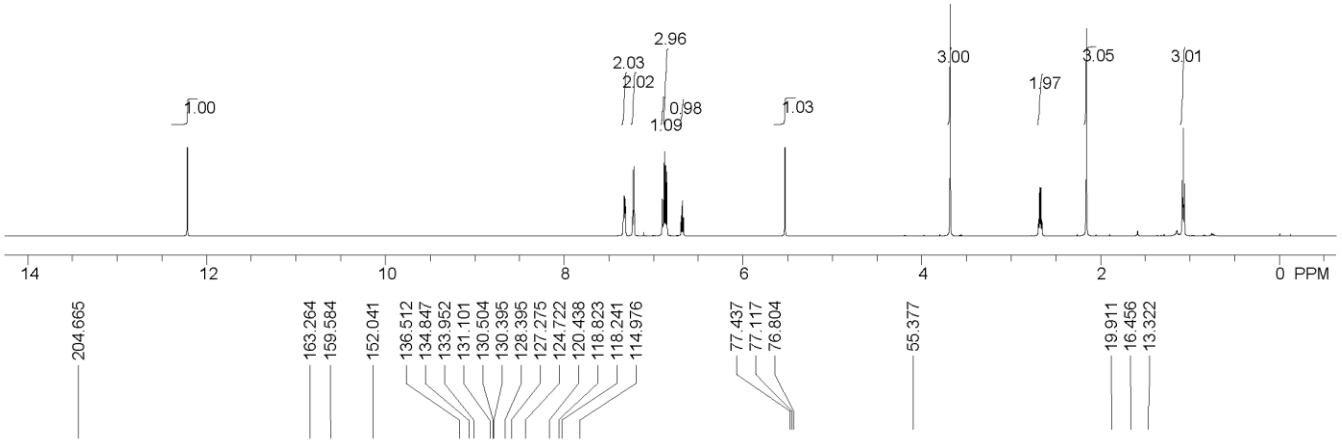
5.533
3.686
2.698
2.686
2.673
2.661
2.163
1.093
1.080
1.068


H3CO
O
OH
HO
CH3
C2H5

3i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2.02
2.96
0.98
1.09
1.03
3.00
1.97
3.05
3.01
14
12
10
8
6
4
2
0 PPM

204.665
163.264
159.584
152.041
136.512
134.847
133.952
131.101
130.504
130.395
128.395
127.275
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120.438
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118.241
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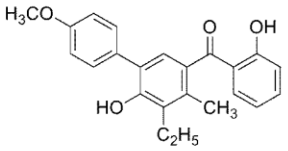
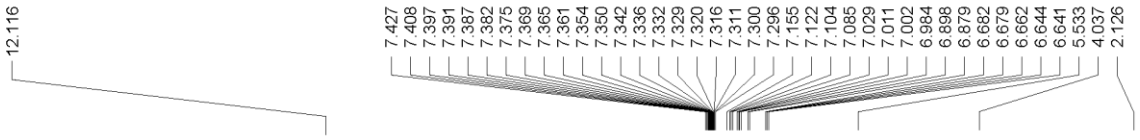
77.117
76.804
55.377
19.911
16.456
13.322


H3CO
O
OH
HO
CH3
C2H5

3i

200
150
100
50
0
PPM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7.375
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7.361
7.354
7.350
7.342
7.336
7.332
7.329
7.320
7.316
7.311
7.300
7.296
7.155
7.122
7.104
7.085
7.029
7.011
7.002
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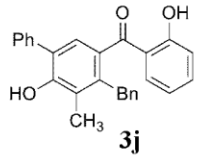
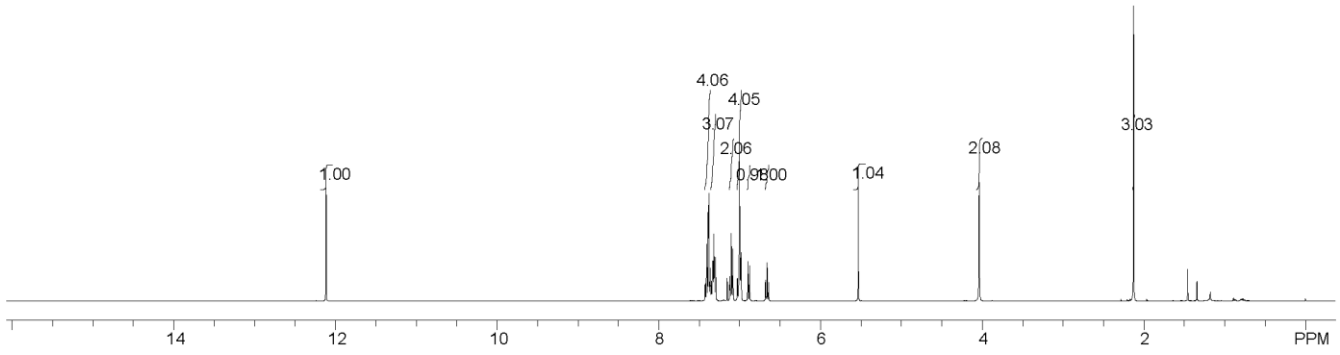
6.644
6.641
5.533
4.037
2.126


O
OH
Ph
HO
Bn
CH3

3j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4.05
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1.00
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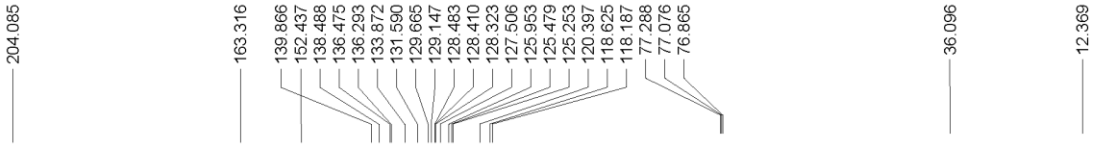
2.08
3.03
14
12
10
8
6
4
2
PPM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133.872
131.590
129.665
129.147
128.483
128.410
128.323
127.506
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125.479
125.253
120.397
118.625
118.187
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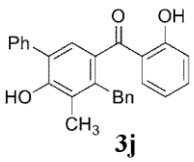
77.076
76.865
36.096
12.369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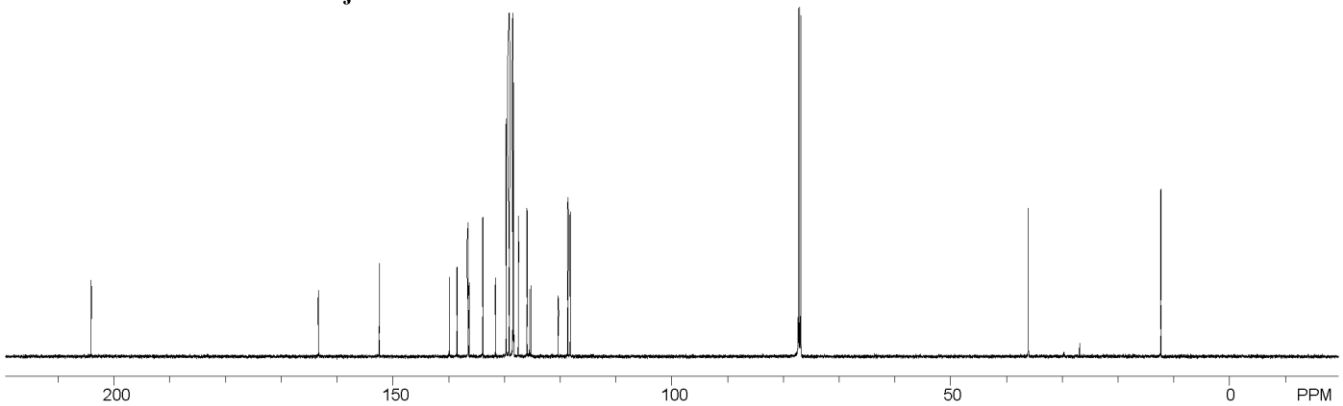
OH
Ph
HO
Bn
CH3

3j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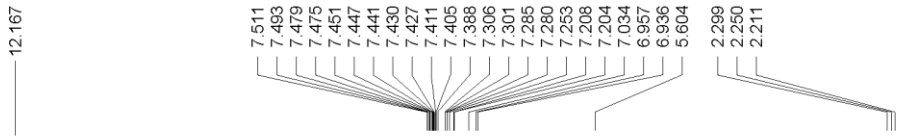
100
50
0
PPM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7.441
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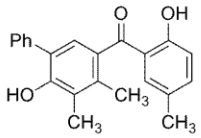
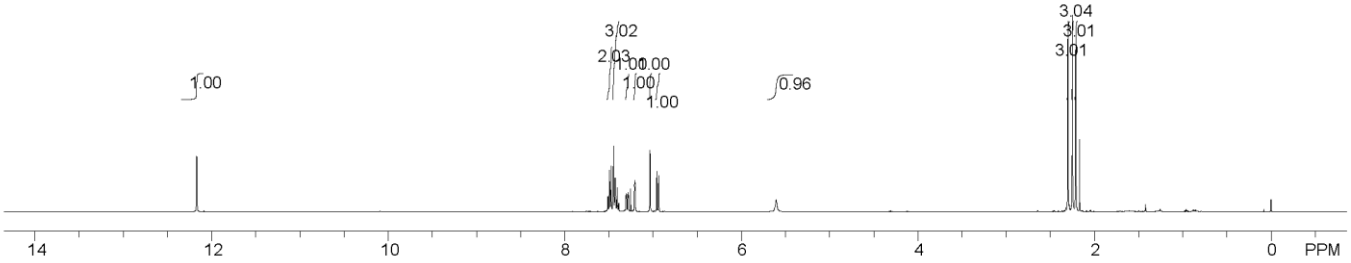
7.427
7.411
7.405
7.388
7.306
7.301
7.285
7.280
7.253
7.208
7.204
7.034
6.957
6.936
5.604
2.299
2.250
2.211


O
OH
Ph
HO
CH3
CH3
CH3

3k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1.00
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0.96
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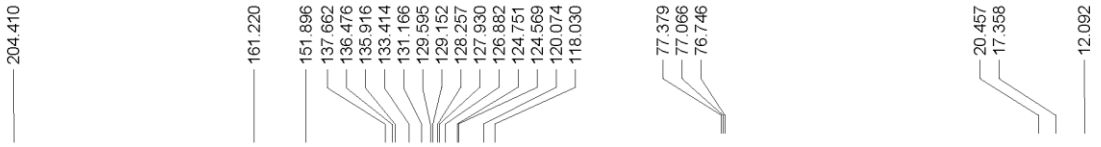
3.01
3.01
14
12
10
8
6
4
2
0
PPM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129.152
128.257
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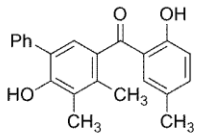
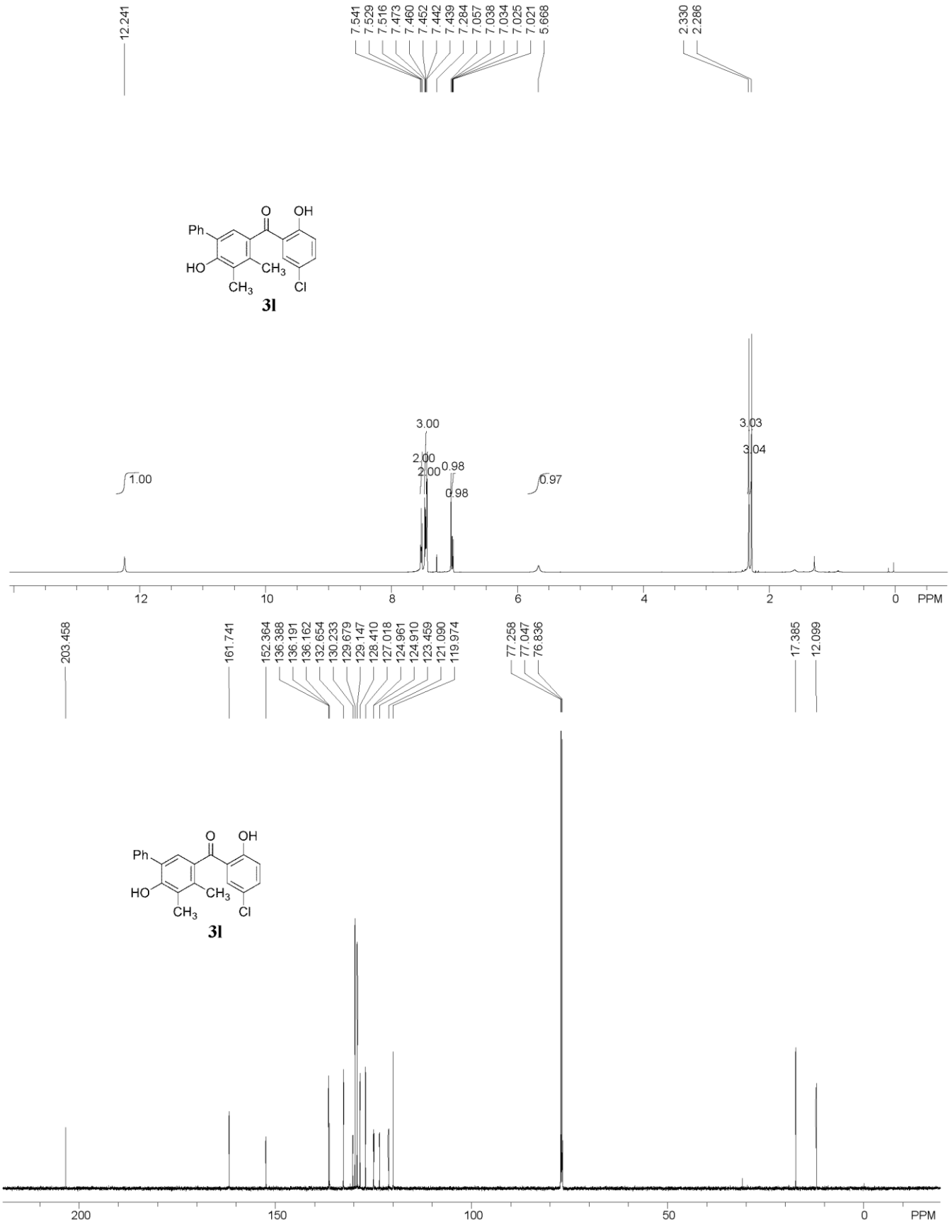
12.092


O
OH
Ph
HO
CH3
CH3
CH3

3k

200
150
100
50
0
PPM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7.025
7.021
5.668
2.330
2.286
Ph
O
OH
HO
CH3
CH3
Cl
3l
3.00
2.00
2.00
0.98
0.98
1.00
0.97
3.03
3.04
12
10
8
6
4
2
0
PPM
203.458
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128.410
127.018
124.961
124.910
123.459
121.090
119.974
77.258
77.047
76.836
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Ph
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HO
CH3
CH3
Cl
3l
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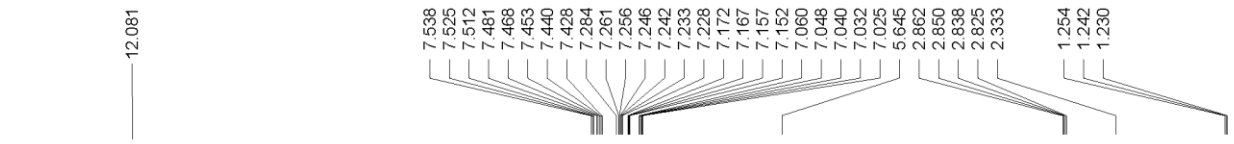
150
100
50
0
PPM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7.440
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7.284
7.261
7.256
7.246
7.242
7.233
7.228
7.172
7.167
7.157
7.152
7.060
7.048
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7.032
7.025
5.645
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2.825
2.333
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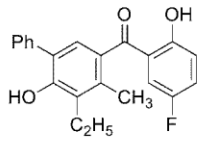
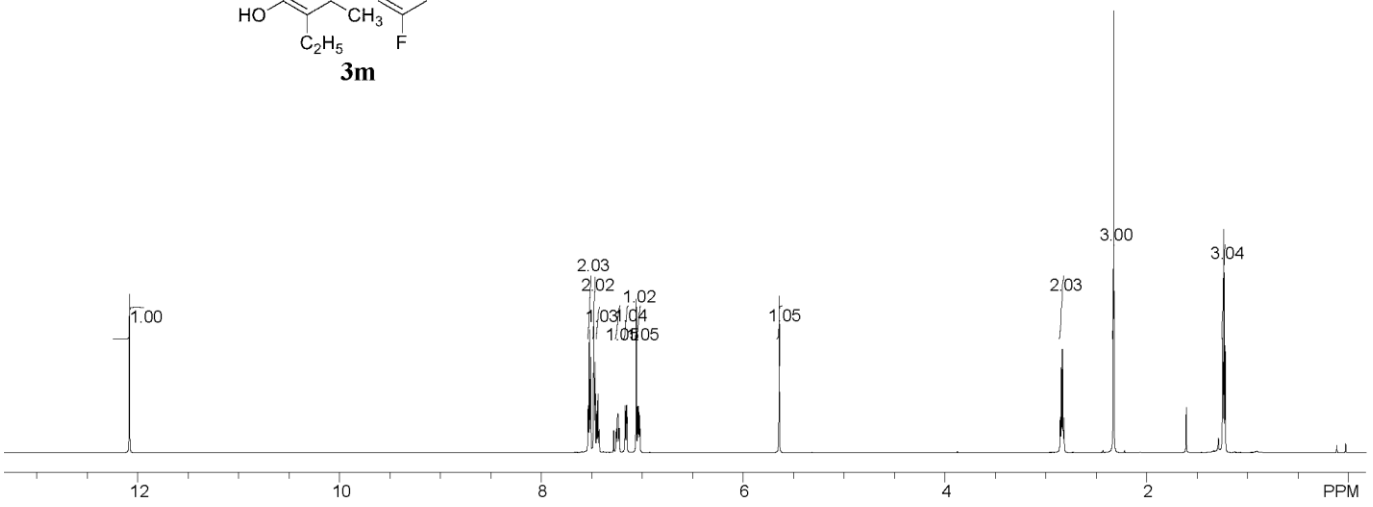
1.242
1.230


O
OH
Ph
HO
CH3
C2H5
F

3m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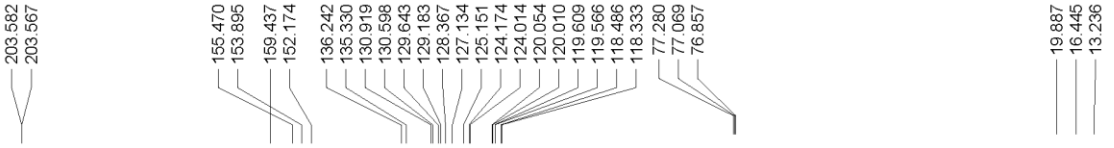
1.02
1.03
1.04
1.05
1.05
2.03
3.00
3.04
12
10
8
6
4
2
PPM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129.643
129.183
128.367
127.134
125.151
124.174
124.014
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120.010
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118.486
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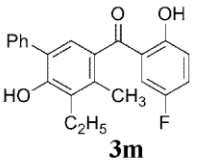
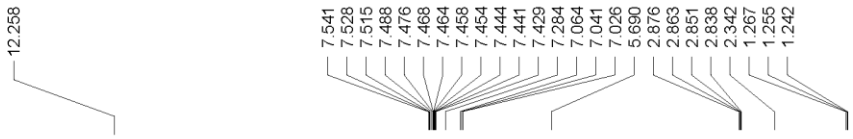
77.069
76.857
19.887
16.445
13.236


O
OH
Ph
HO
CH3
C2H5
F

3m

200
150
100
50
0
PPM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7.476
7.468
7.464
7.458
7.454
7.444
7.441
7.429
7.284
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7.026
5.690
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2.838
2.342
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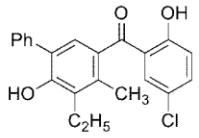
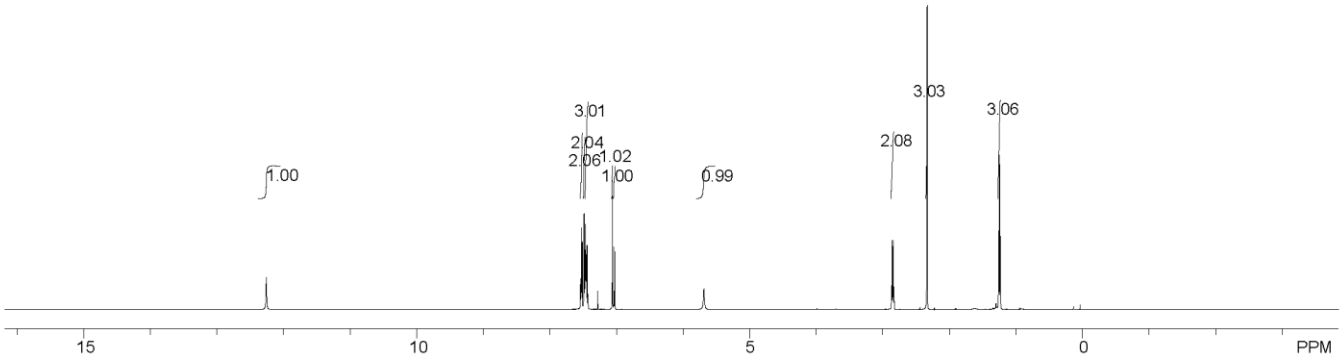
1.255
1.242


O
OH
Ph
HO
CH3
C2H5
Cl

3n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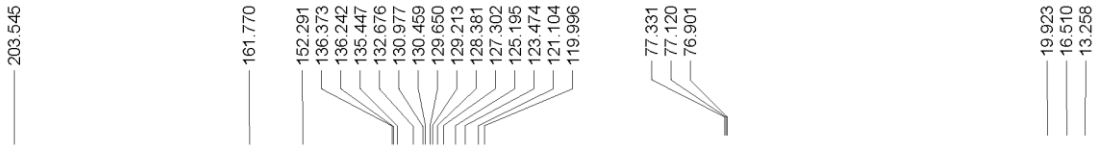
1.00
0.99
2.08
3.03
3.06
15
10
5
0
PPM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135.447
132.676
130.977
130.459
129.650
129.213
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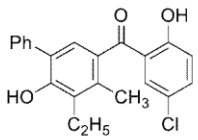
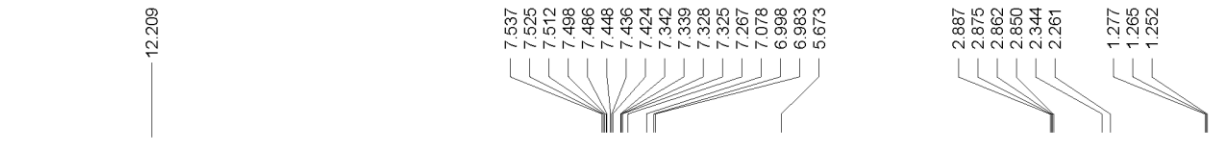
123.474
121.104
119.996
77.331
77.120
76.901
19.923
16.510
13.258


O
OH
Ph
HO
CH3
C2H5
Cl

3n

200
150
100
50
0
PPM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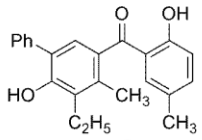
1.252


O
OH
Ph
HO
CH3
C2H5
CH3

3o

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1.01
1.01
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1.04
1.00
0.97
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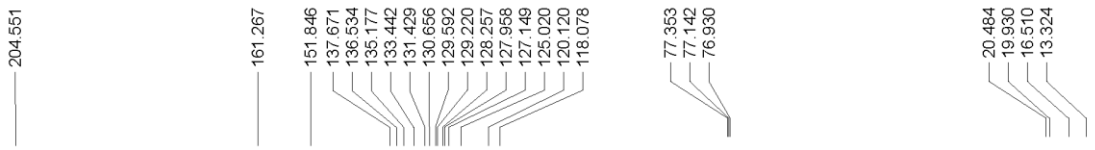
3.01
3.03
3.03
12
10
8
6
4
2
PPM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129.220
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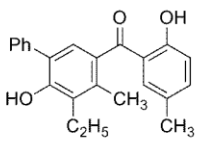
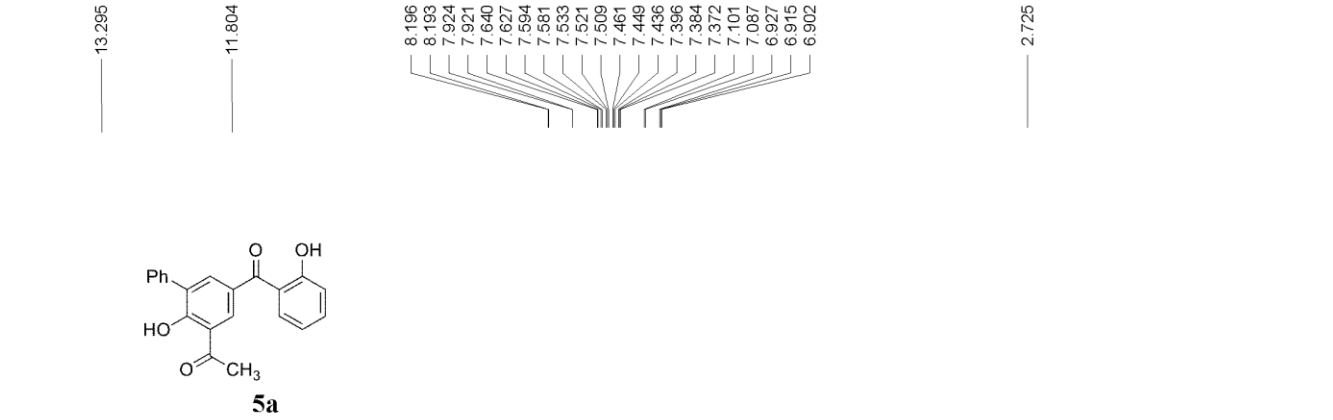
76.930
20.484
19.930
16.510
13.324


O
OH
Ph
HO
CH3
C2H5
CH3

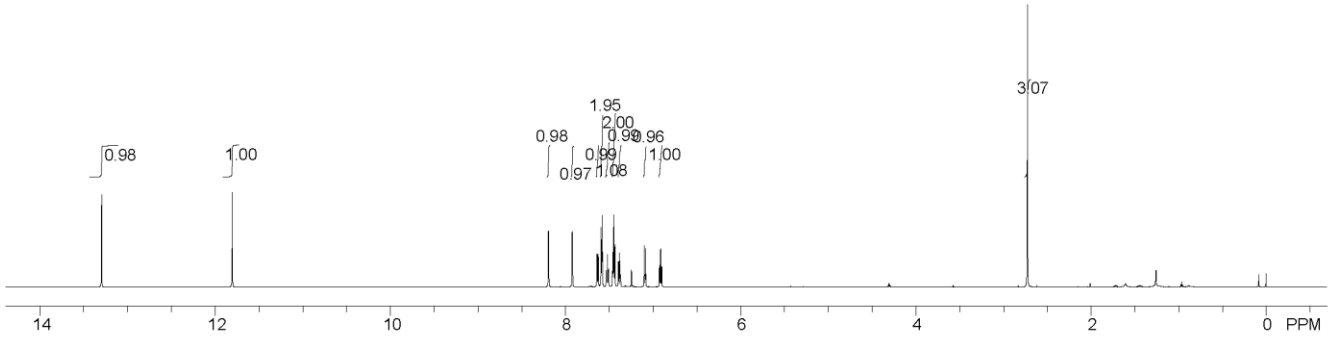
3o

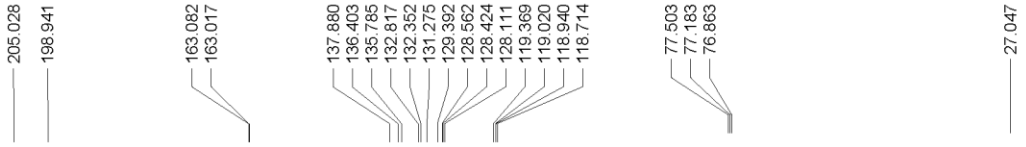
200
150
100
50
0
PPM

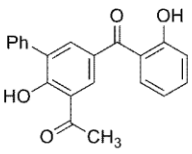
IV. Copies of ^{1}H and ^{13}C NMR spectra of 5a-5x



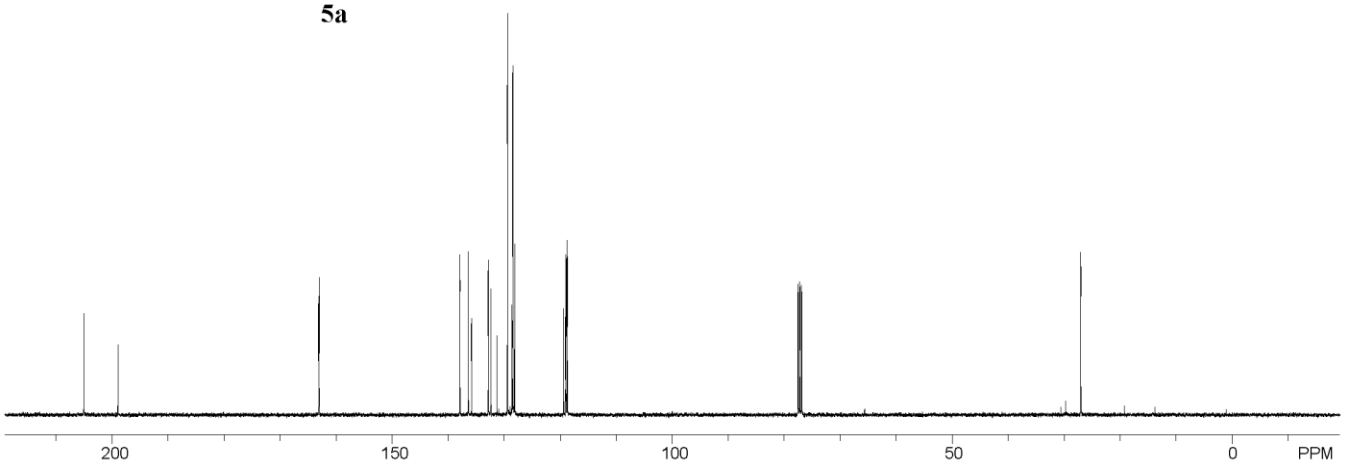
5a

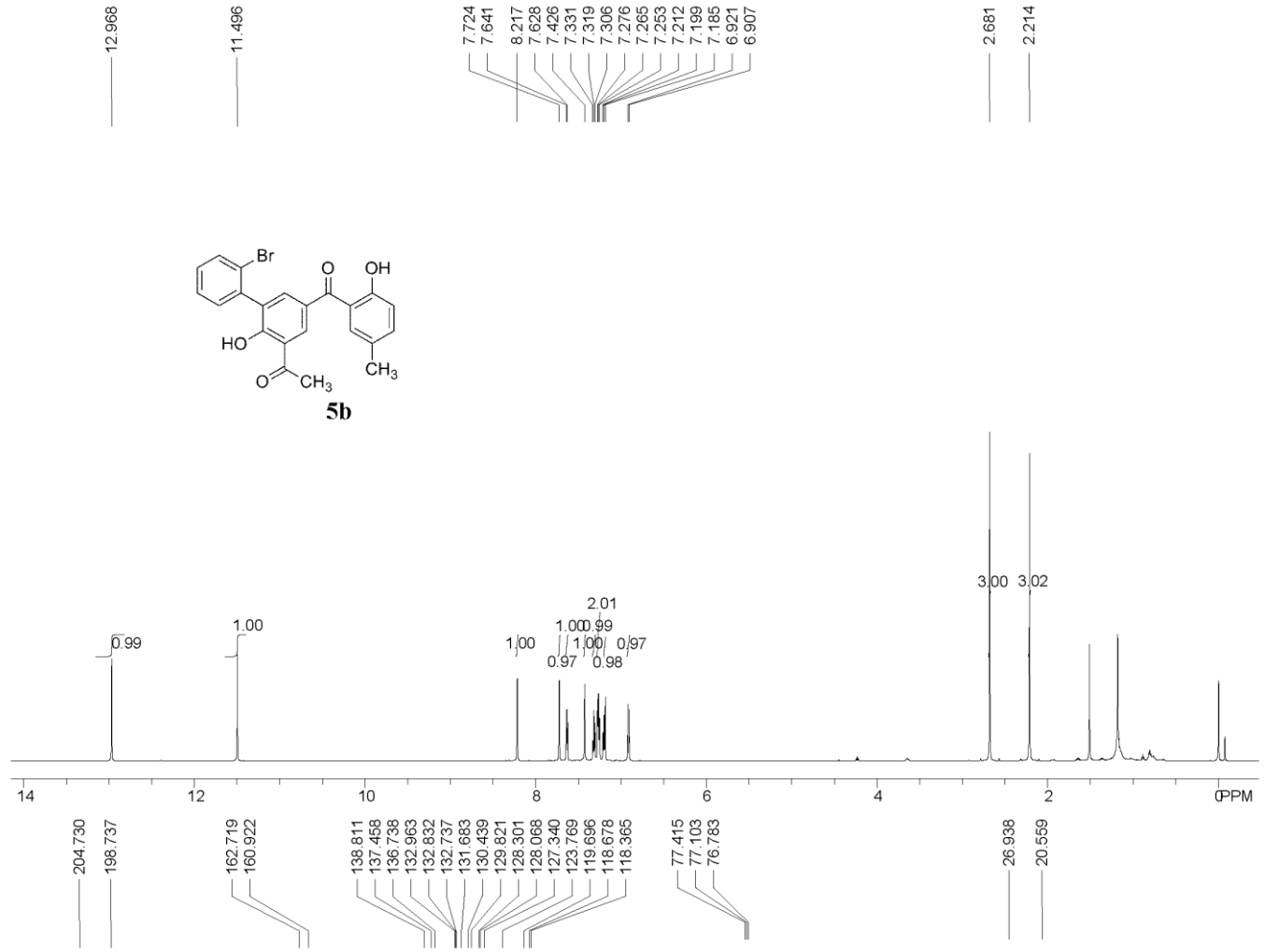






5a

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7.253
7.212
7.199
7.185
6.921
6.907
2.681
2.214
Br
O
OH
HO
O
CH3
CH3
5b
0.99
1.00
1.00
2.01
1.00
0.99
1.00
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3.00
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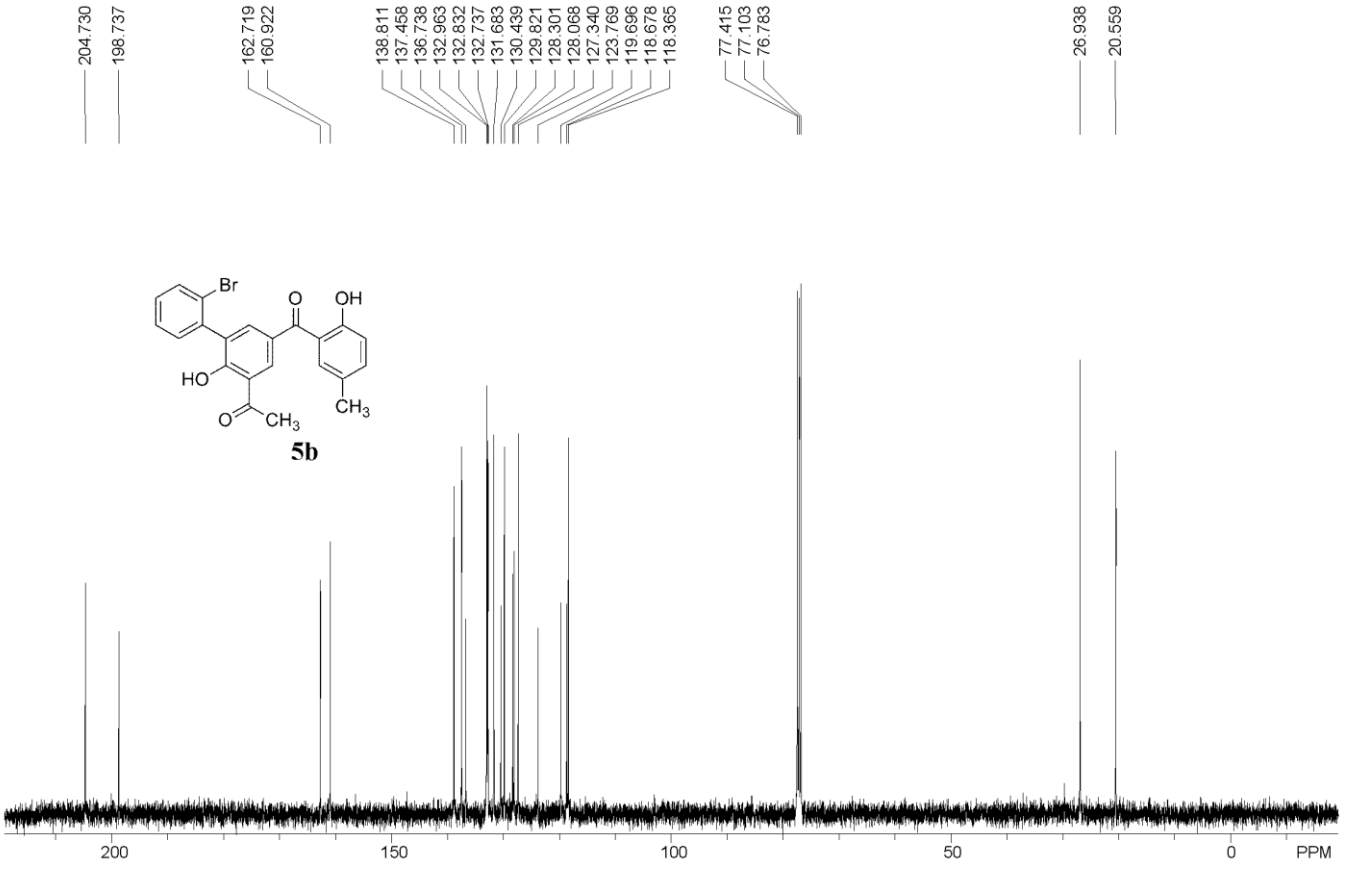
12
10
8
6
4
2
0
PPM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128.301
128.068
127.340
123.769
119.696
118.678
118.365
77.415
77.103
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Br
O
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HO
O
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CH3
5b
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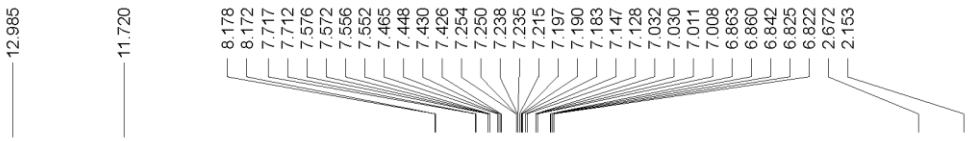
150
100
50
0
PPM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7.552
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7.448
7.430
7.426
7.254
7.250
7.238
7.235
7.215
7.197
7.190
7.183
7.147
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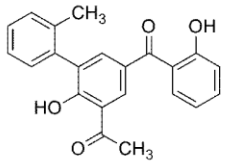
6.825
6.822
2.672
2.153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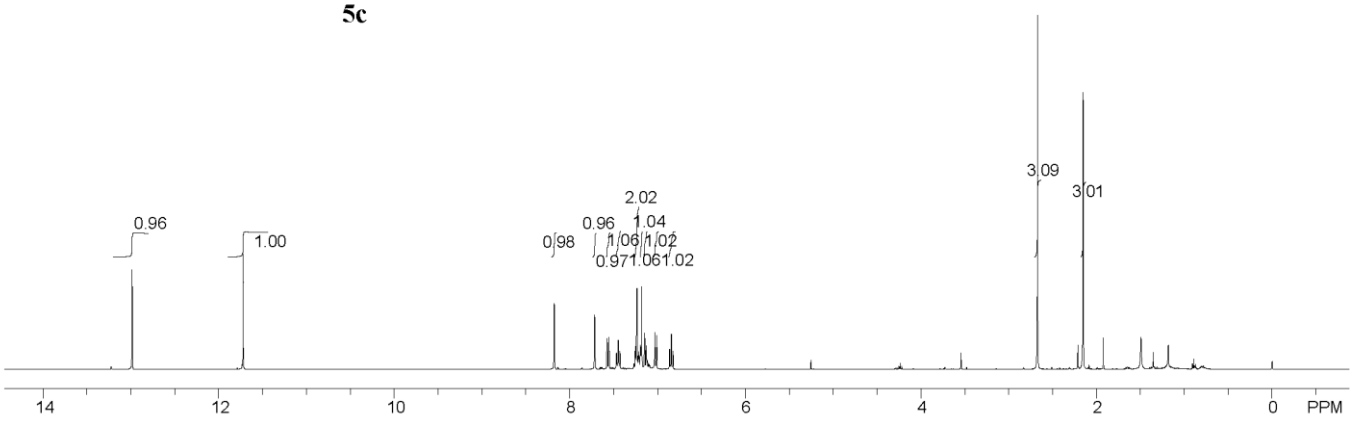
O
OH
HO
O
CH3

5c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3.01
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12
10
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2
0
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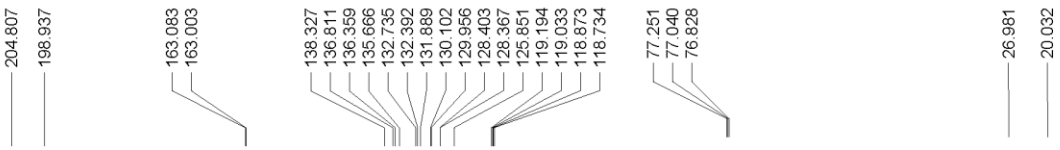
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135.666
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129.956
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119.194
119.033
118.873
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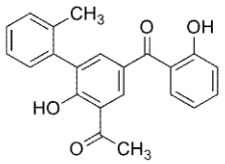
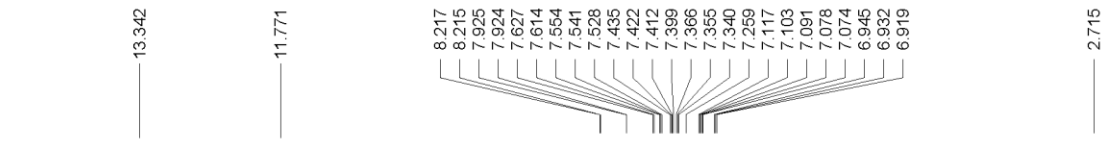
77.040
76.828
26.981
20.032


CH3
O
OH
HO
O
CH3

5c

200
150
100
50
0
PPM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7.614
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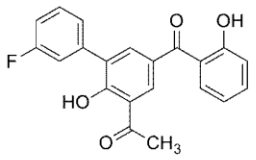
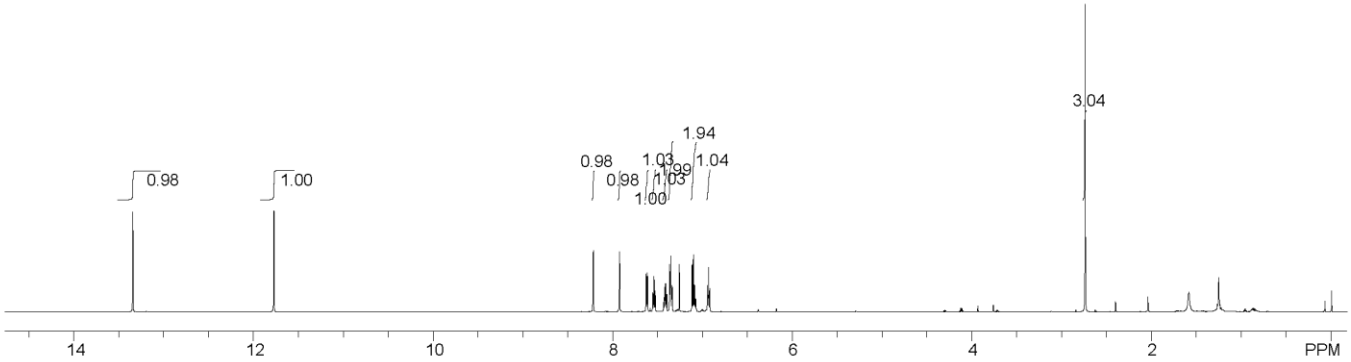
7.541
7.528
7.435
7.422
7.412
7.399
7.366
7.355
7.340
7.259
7.117
7.103
7.091
7.078
7.074
6.945
6.932
6.919
2.715


F
HO
O
OH
O
CH3

5d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12
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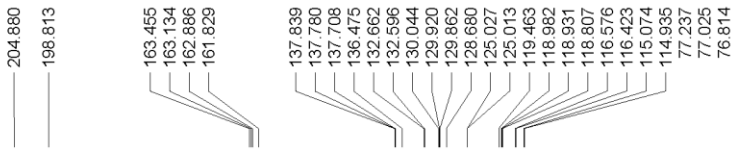
6
4
2
PPM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136.475
132.662
132.596
130.044
129.920
129.862
128.680
125.027
125.013
119.463
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118.807
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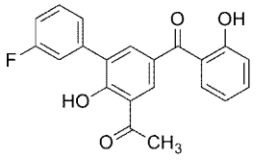
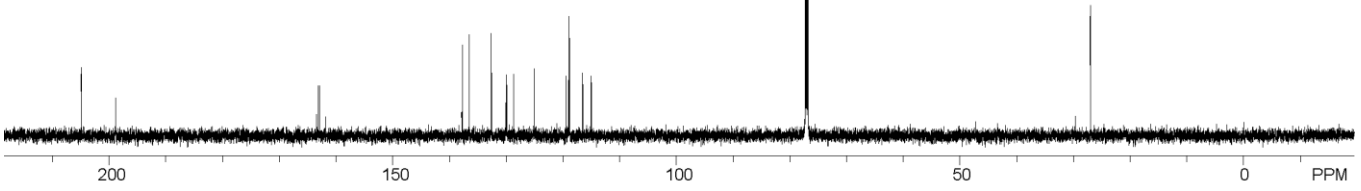
116.423
115.074
114.935
77.237
77.025
76.814
27.025


F
HO
O
OH
O
CH3

5d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100
50
0
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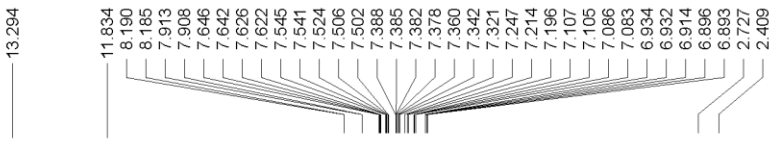
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7.642
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7.622
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7.541
7.524
7.506
7.502
7.388
7.385
7.382
7.378
7.360
7.342
7.321
7.247
7.214
7.196
7.107
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7.086
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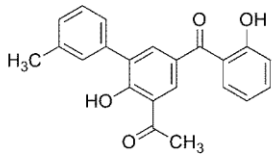
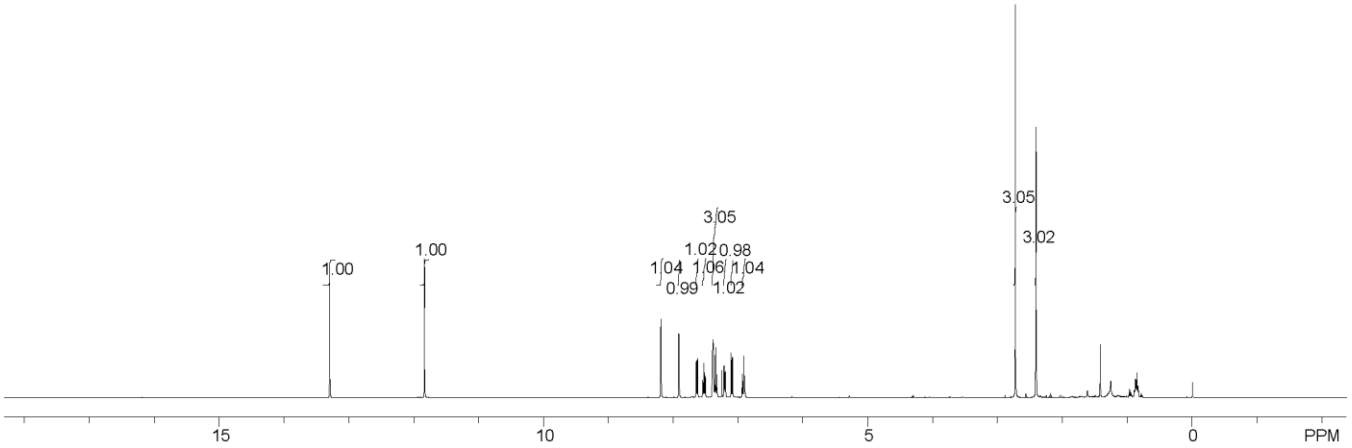
6.934
6.932
6.914
6.896
6.893
2.727
2.409


O
OH
H3C
HO
O
CH3

5e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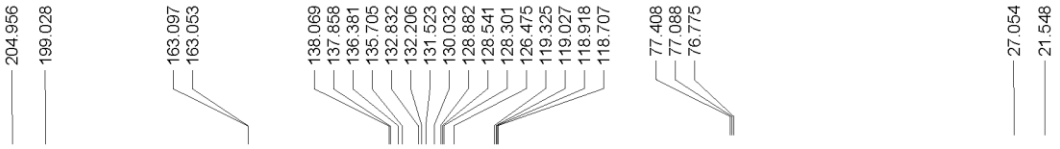
1.02
0.98
1.04
1.06
1.04
0.99
1.02
3.05
3.02
15
10
5
0
PPM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137.858
136.381
135.705
132.832
132.206
131.523
130.032
128.882
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118.918
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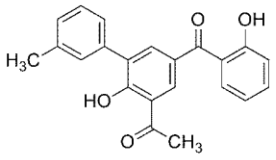
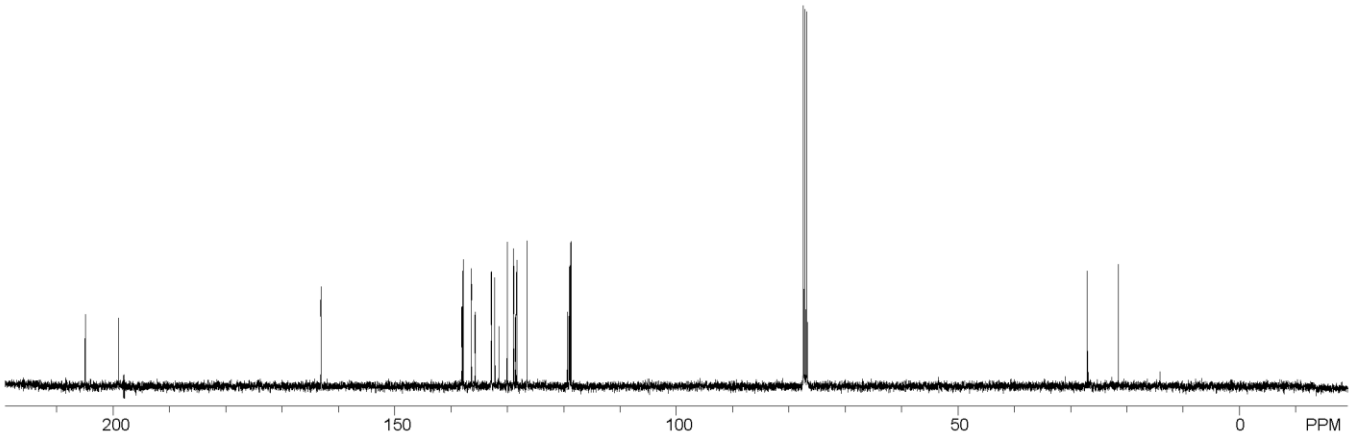
27.054
21.548


O
OH
H3C
HO
O
CH3

5e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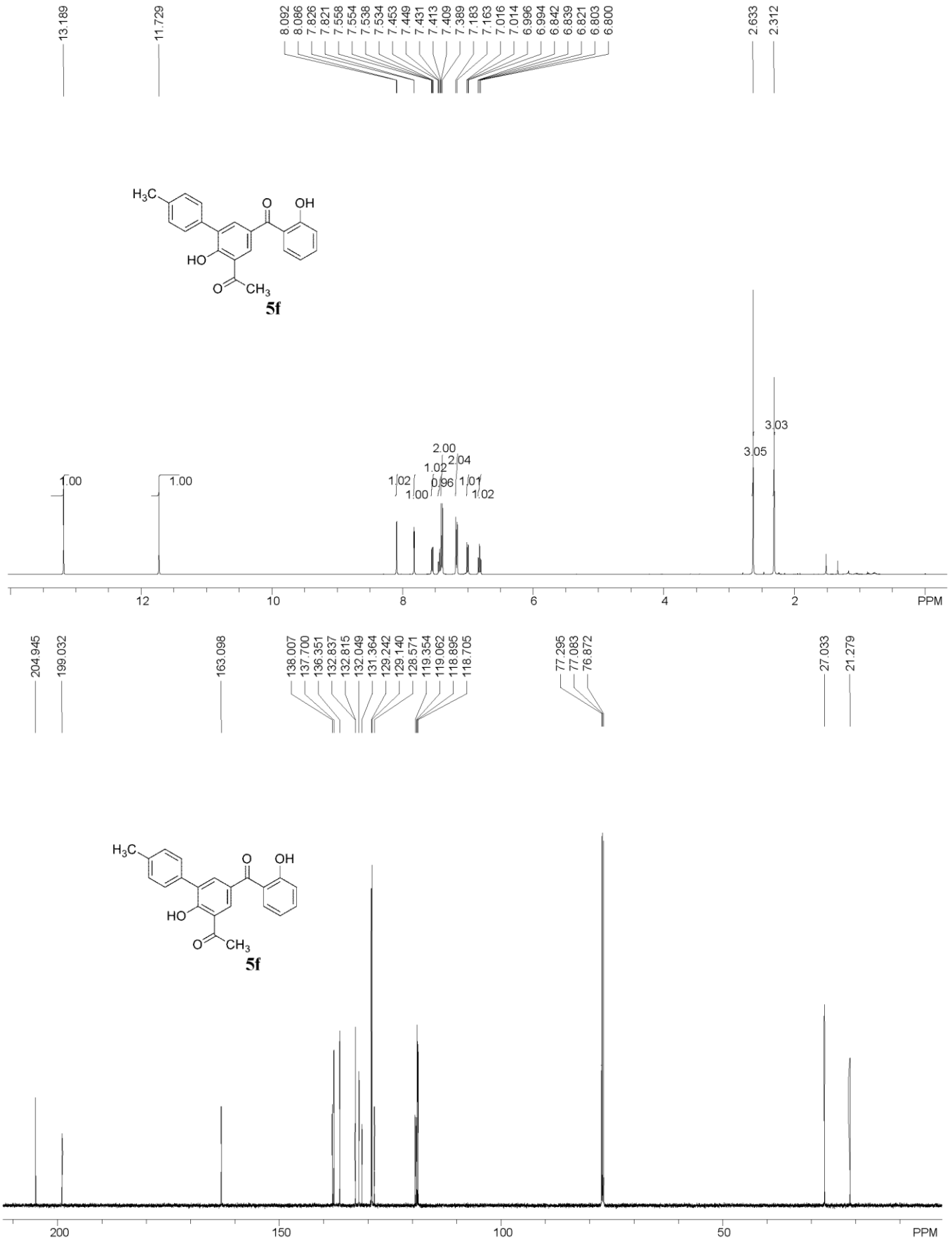
150
100
50
0
PPM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7.534
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7.449
7.431
7.413
7.409
7.389
7.183
7.163
7.016
7.014
6.996
6.994
6.842
6.839
6.821
6.803
6.800
2.633
2.312
H3C
O
OH
HO
O
CH3
5f
1.00
1.00
1.02
1.00
2.00
2.04
1.02
0.96
1.01
1.02
3.05
3.03
12
10
8
6
4
2
PPM
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118.705
77.295
77.083
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HO
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CH3
5f
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150
100
50
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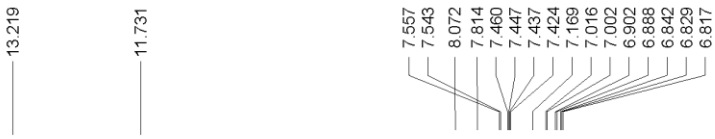
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7.814
7.460
7.447
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7.424
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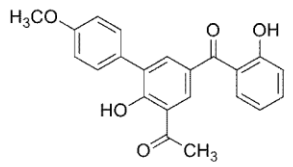
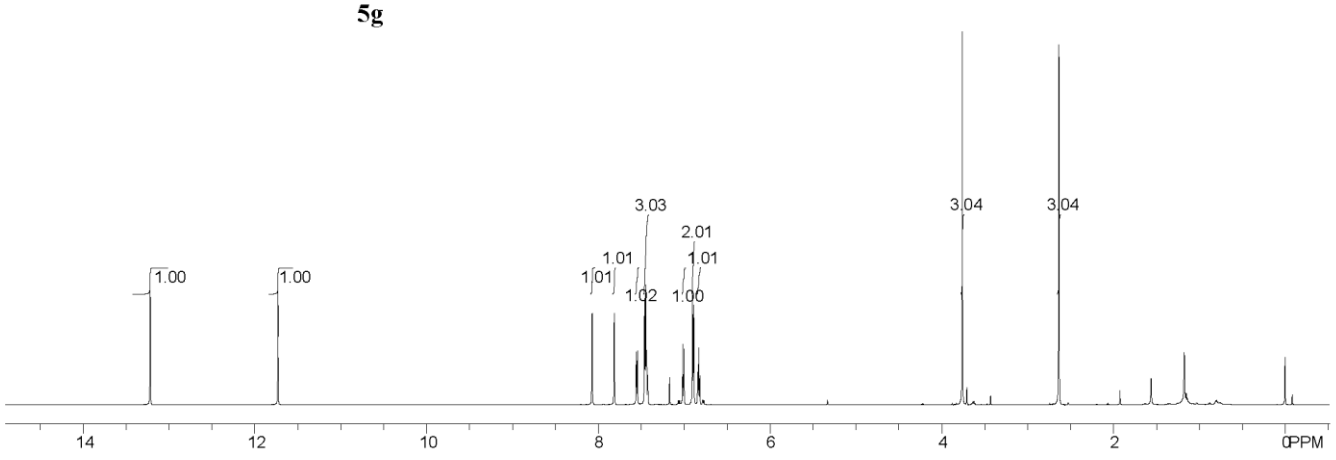
6.842
6.829
6.817
3.759
2.635


H3CO
O
OH
HO
O
CH3

5g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1.01
3.03
1.02
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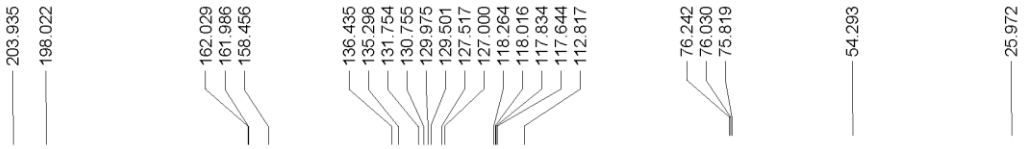
1.01
1.00
3.04
3.04
14
12
10
8
6
4
2
0PPM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76.242
76.030
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54.293
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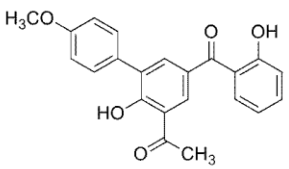
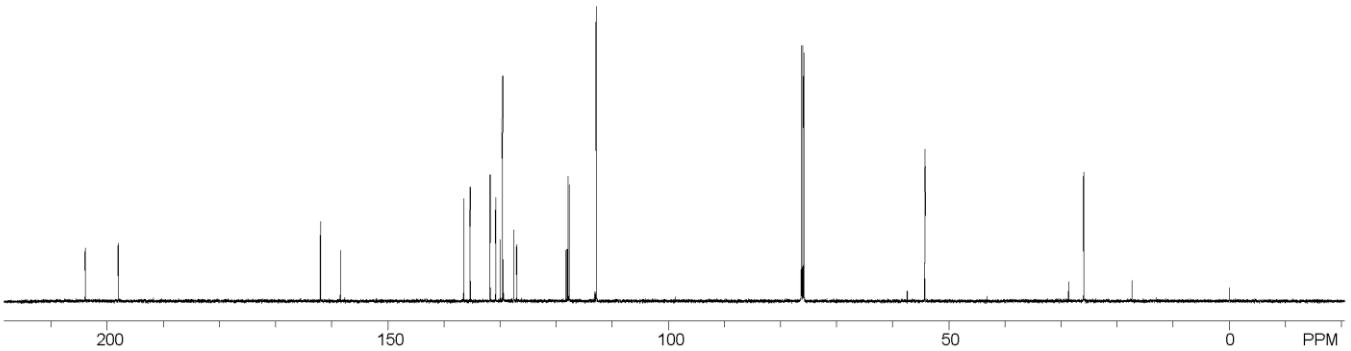
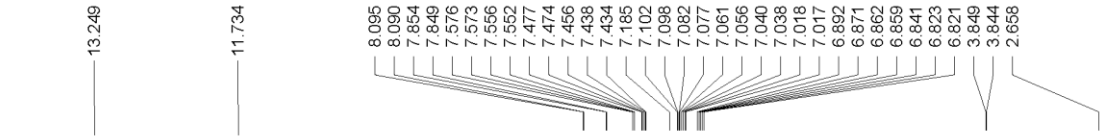

H3CO
O
OH
HO
O
CH3

5g


200
150
100
50
0
PPM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7.018
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3.844
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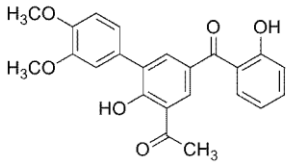
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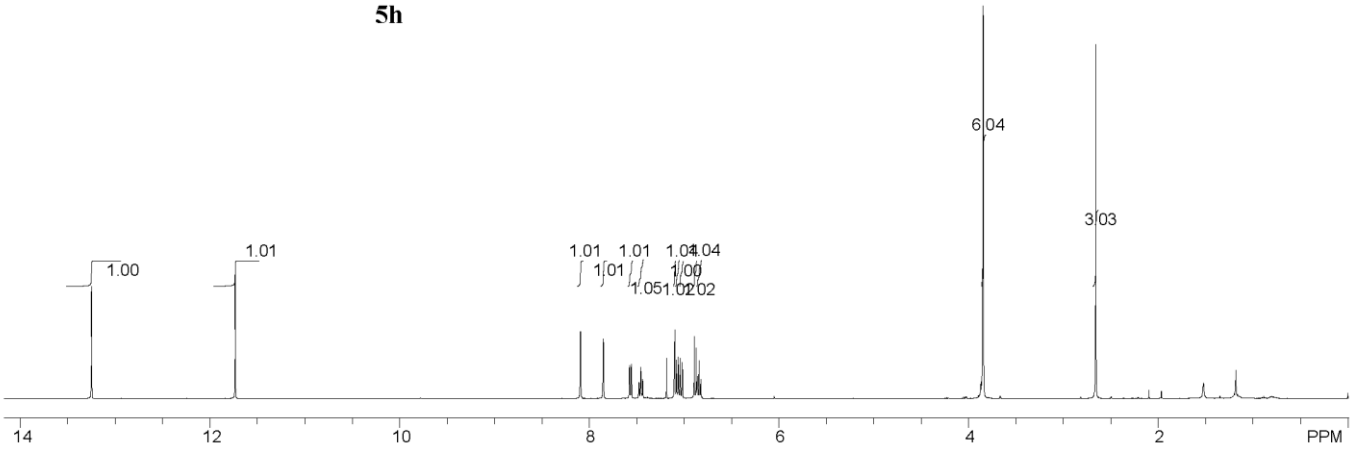
H3CO
HO
O
OH
O
CH3

5h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1.01
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1.00
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1.02
1.02
14
12
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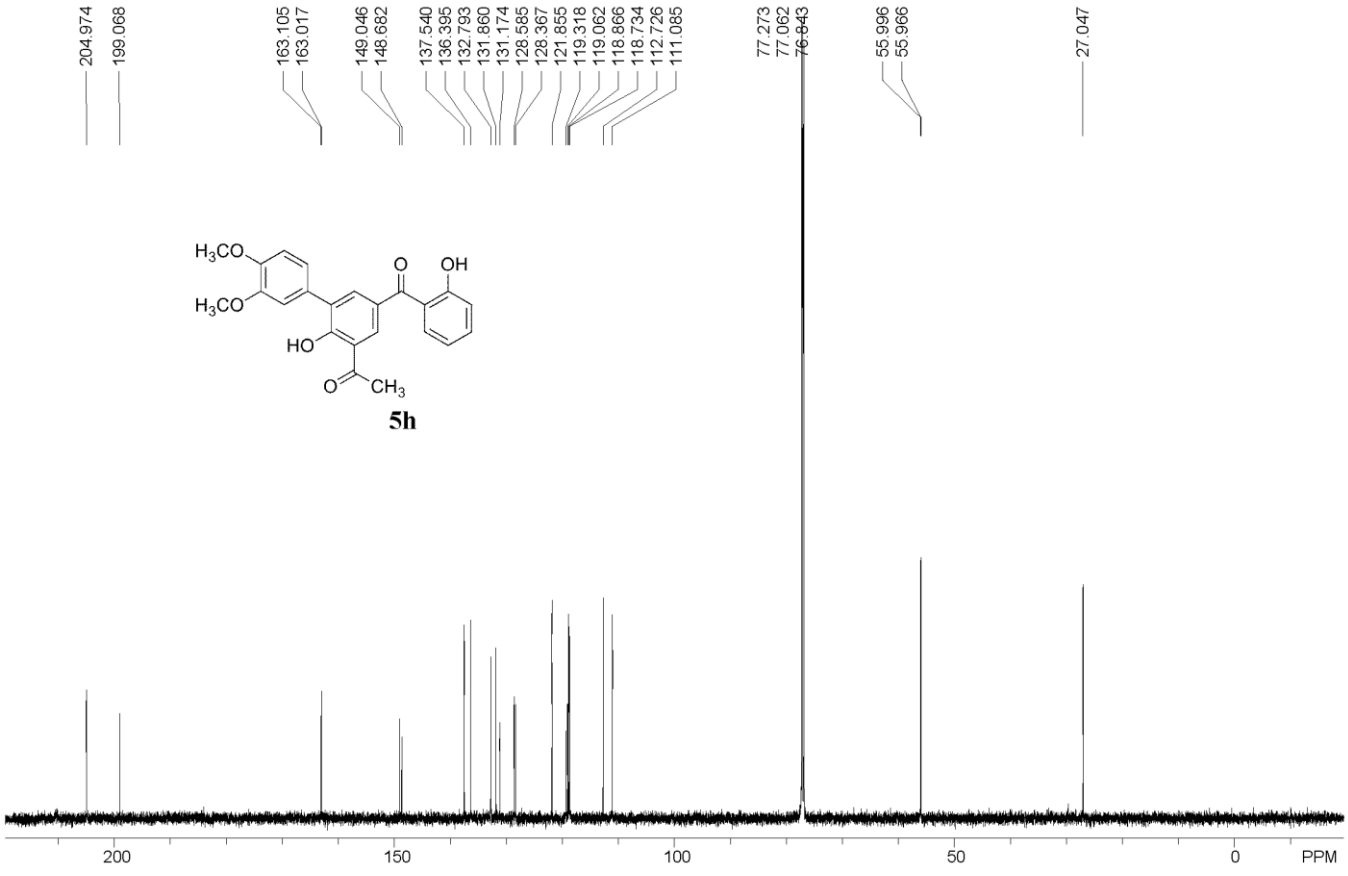
8
6
4
2
PPM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119.318
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111.085
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77.062
76.843
55.996
55.966
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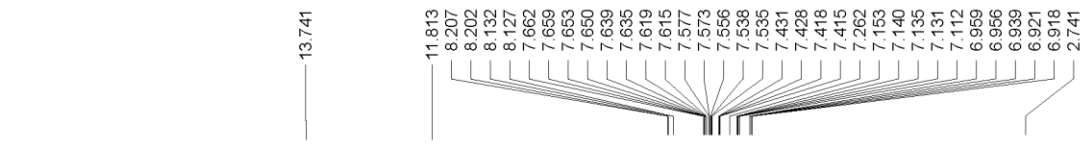
200
150
100
50
0
PPM

H3CO
H3CO
HO
O
OH
O
CH3

5h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7.535
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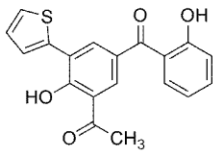
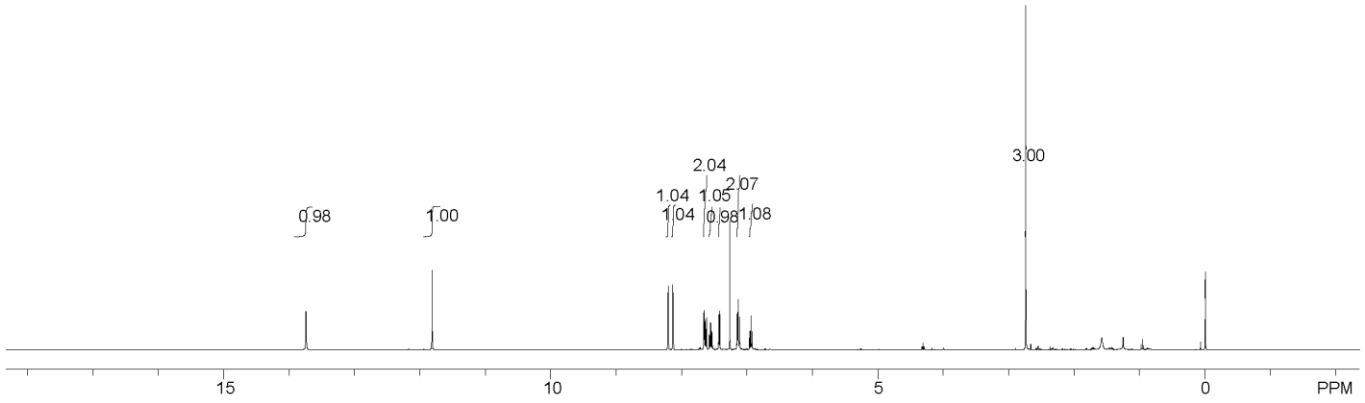

S
O
OH
HO
O
CH3

5i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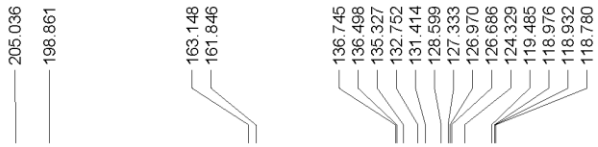
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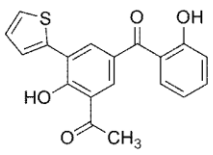
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OH
HO
O
CH3

5i

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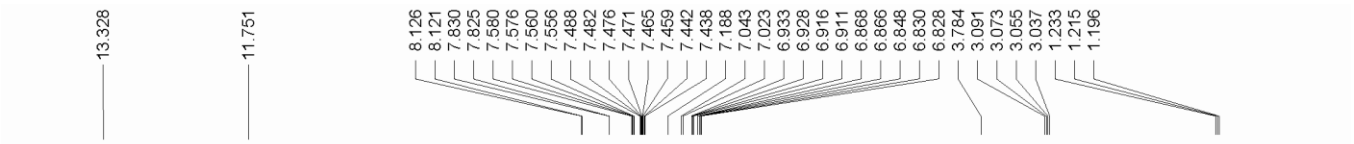
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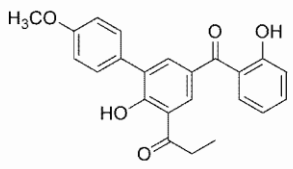
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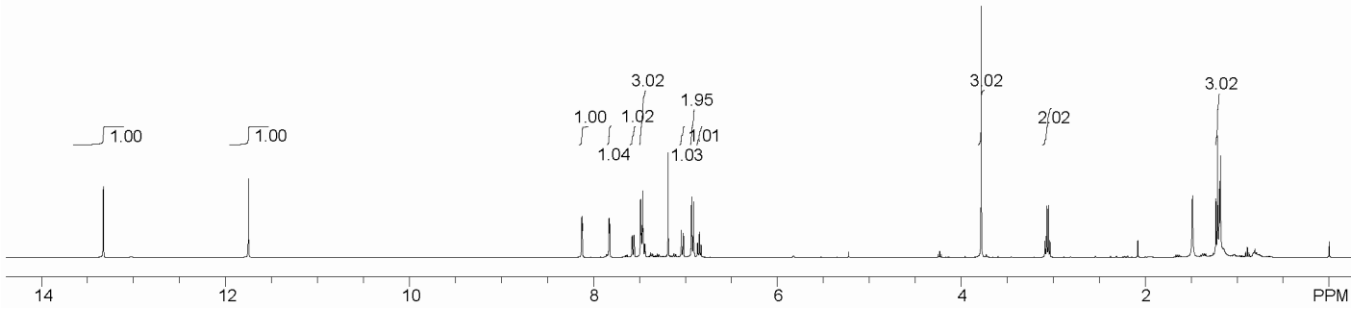
HO
O

5j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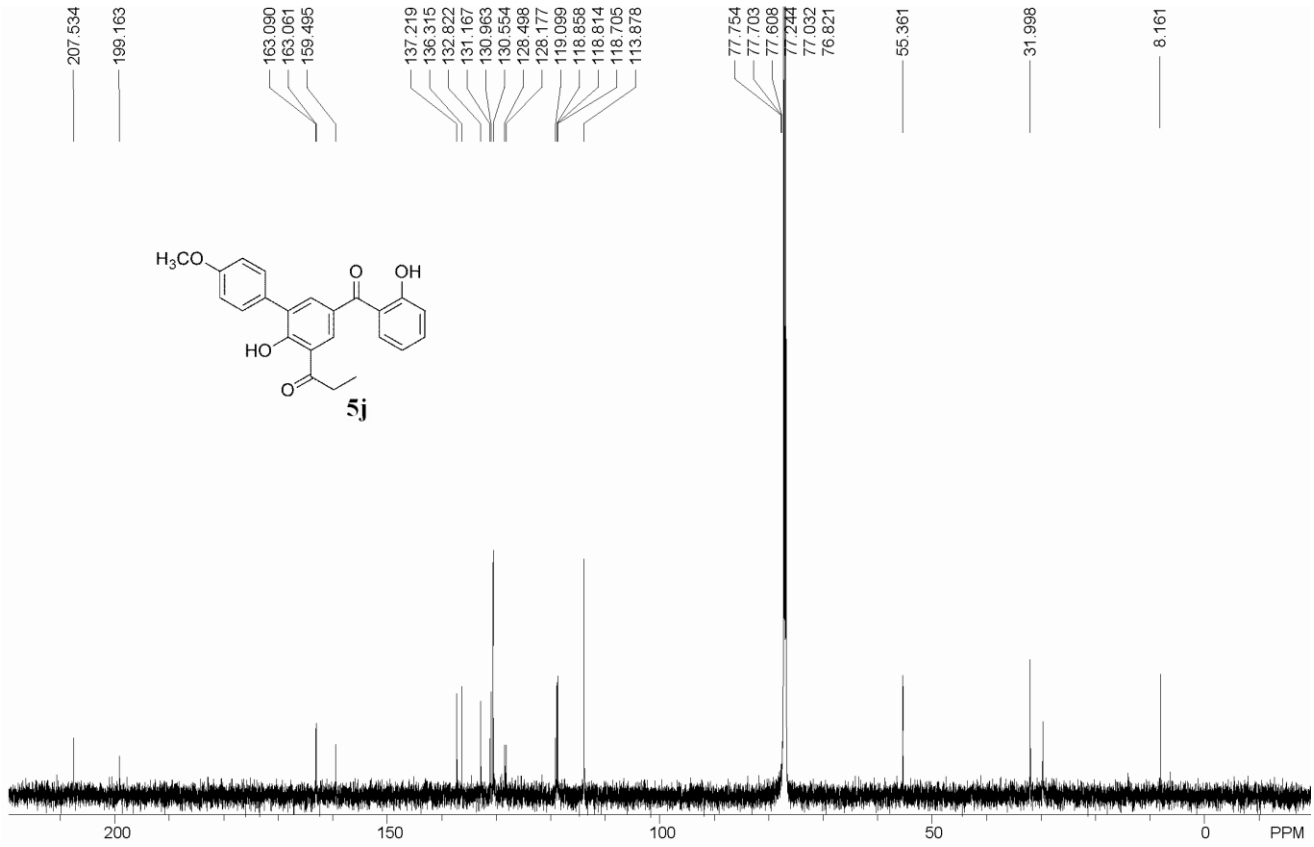
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H3CO
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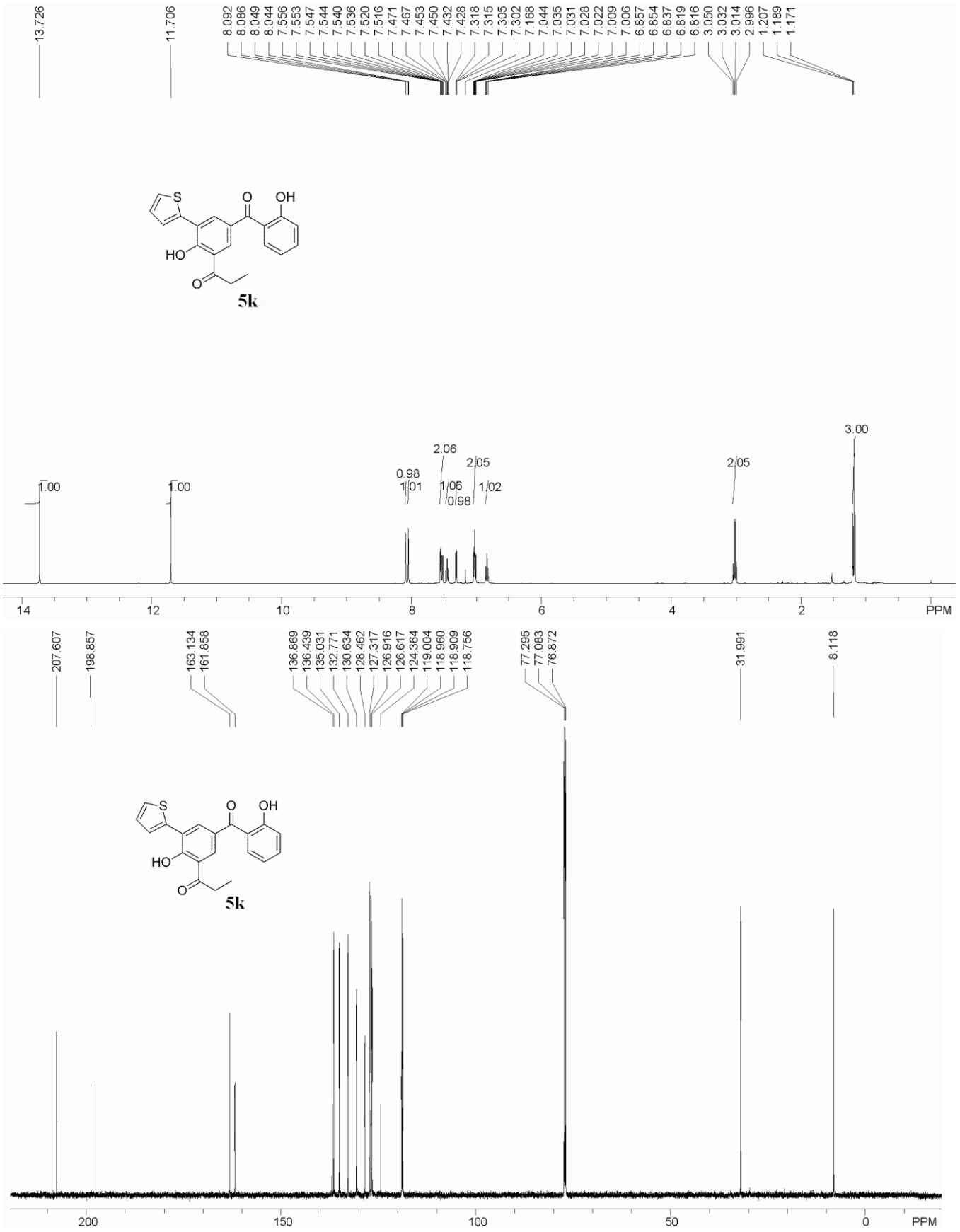
OH
HO
O

5j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7.516
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7.305
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O
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HO
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1.06
0.98
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1.02
2.05
3.00
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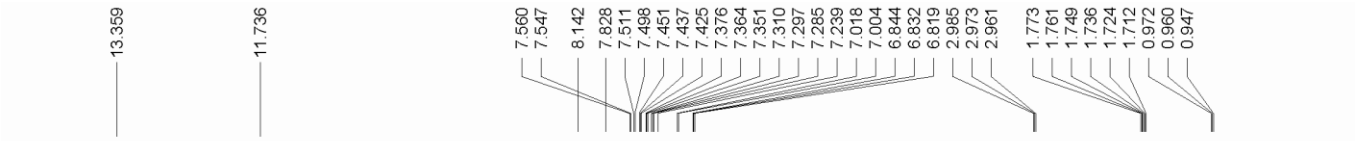
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7.239
7.018
7.004
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6.819
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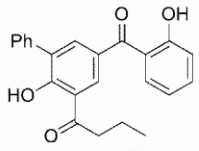
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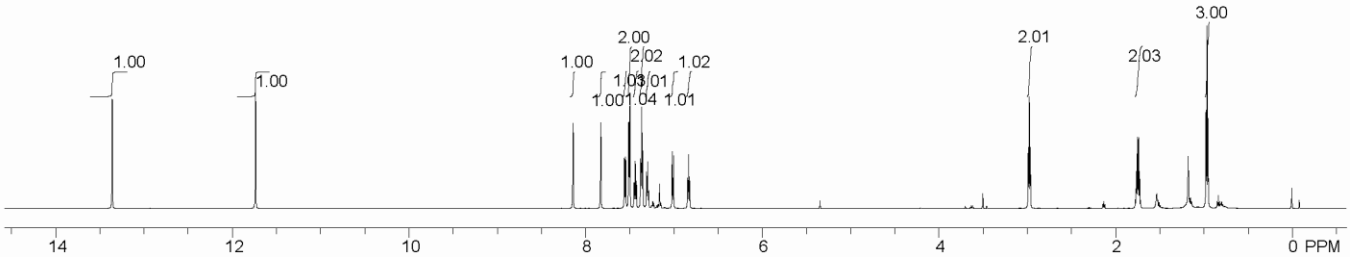
O

5l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12
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4
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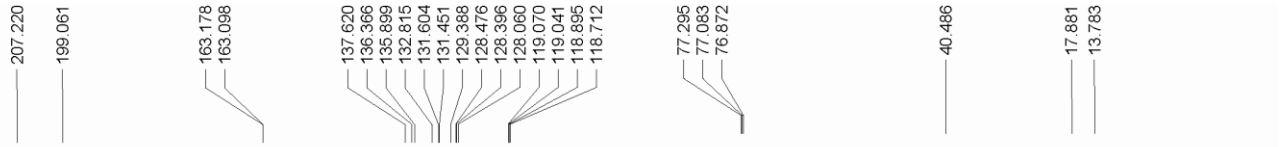
0 PPM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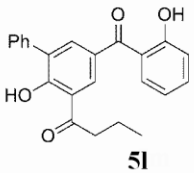
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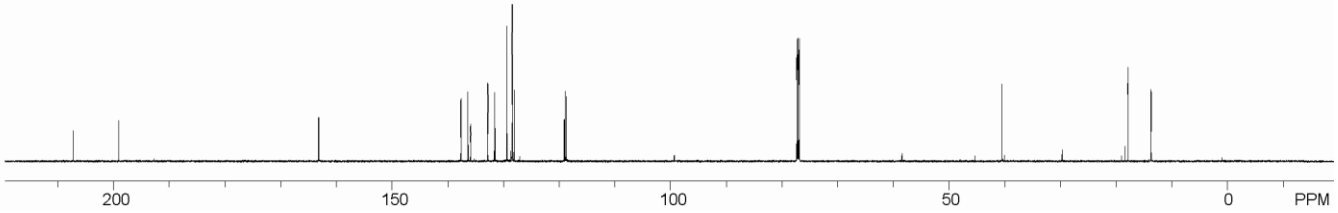
5l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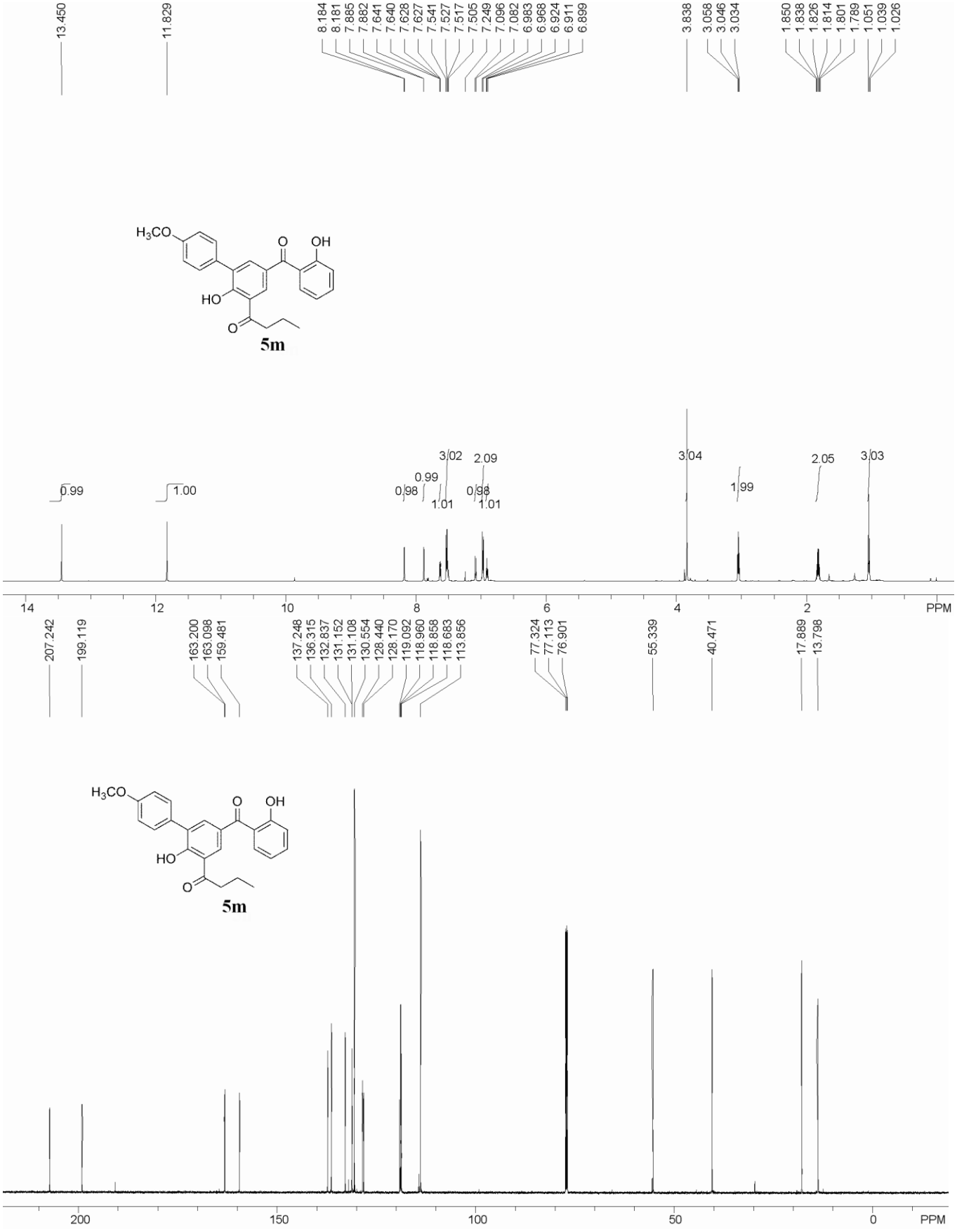
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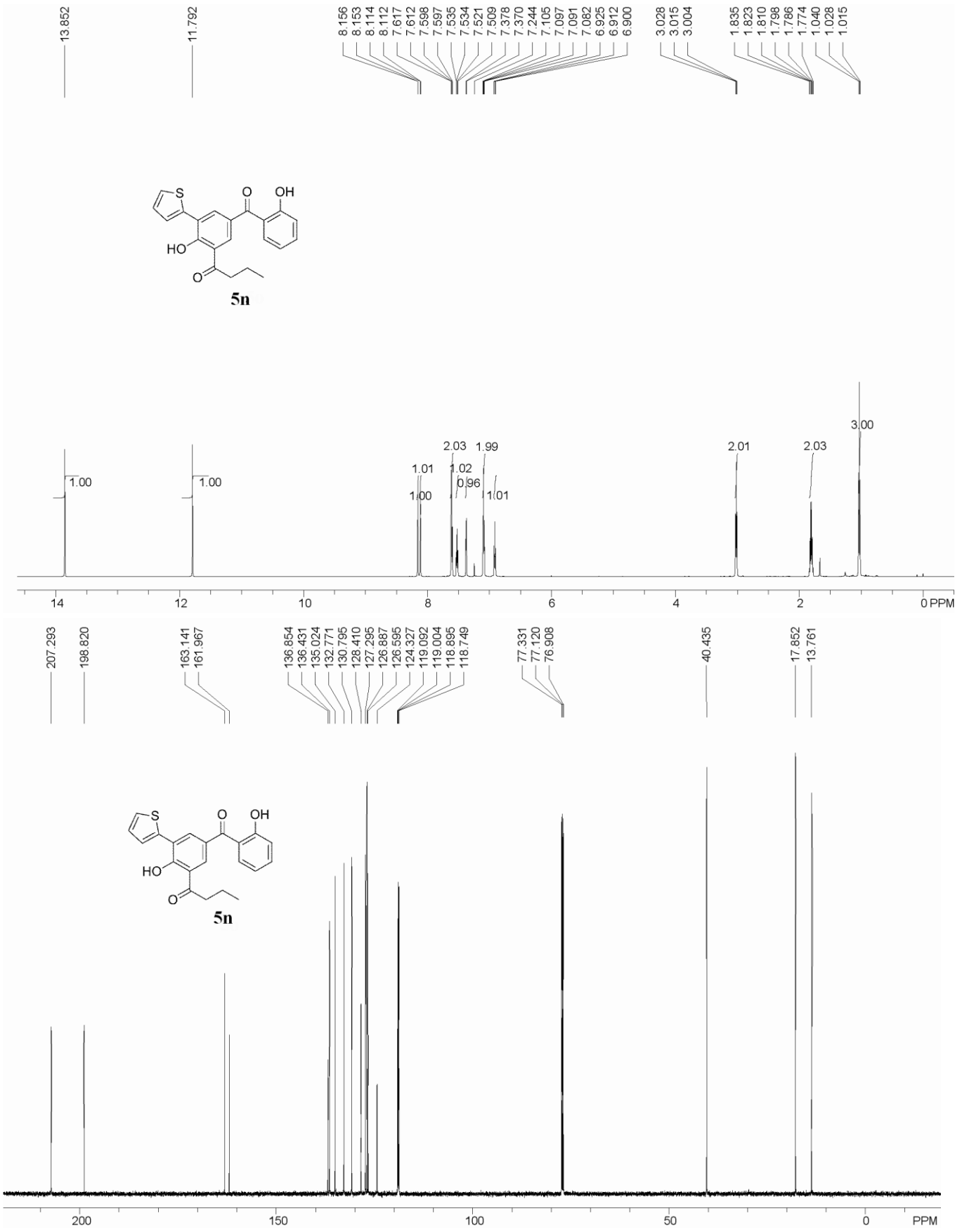
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HO
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1.00
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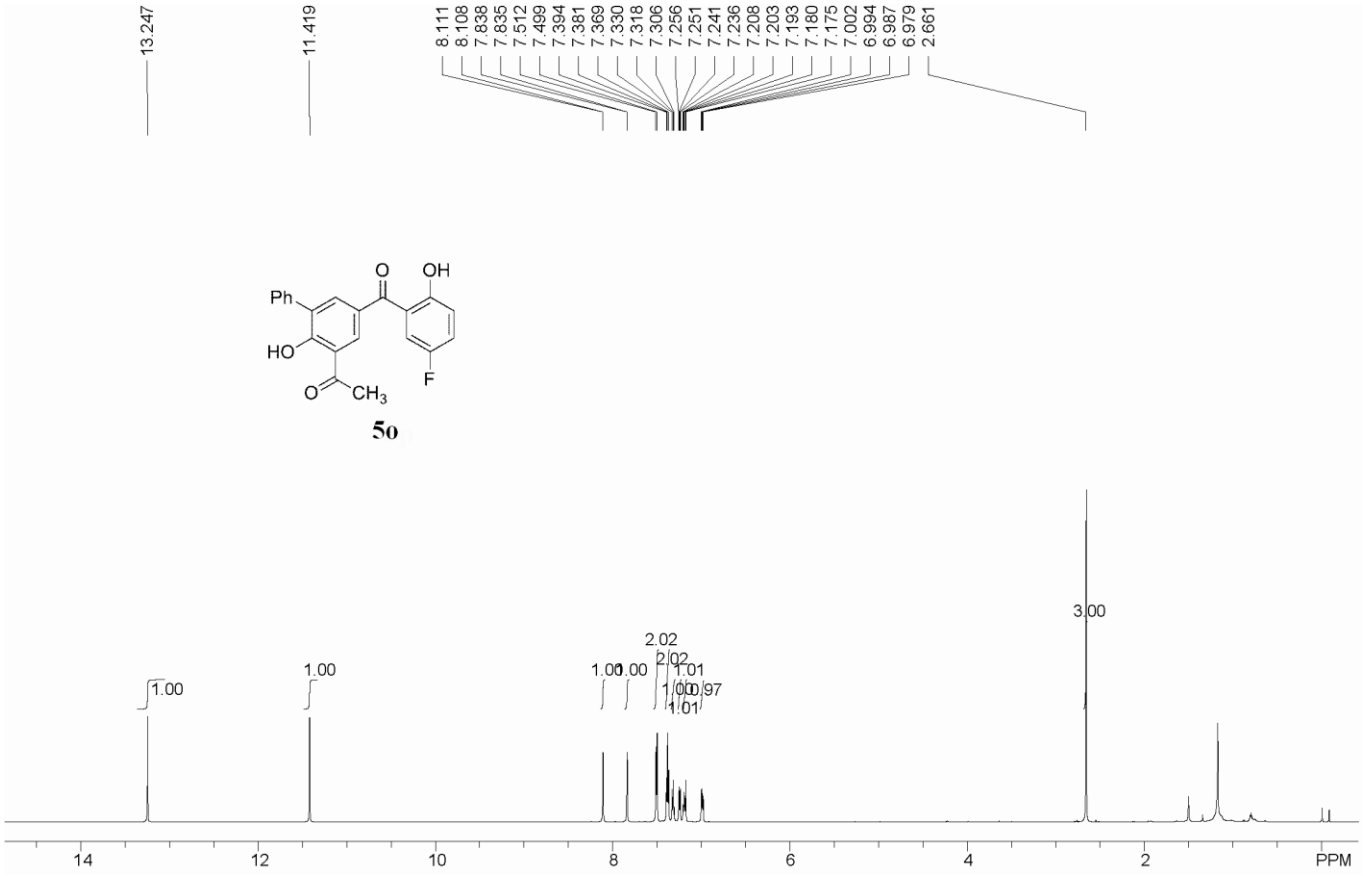
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O
OH
F
O
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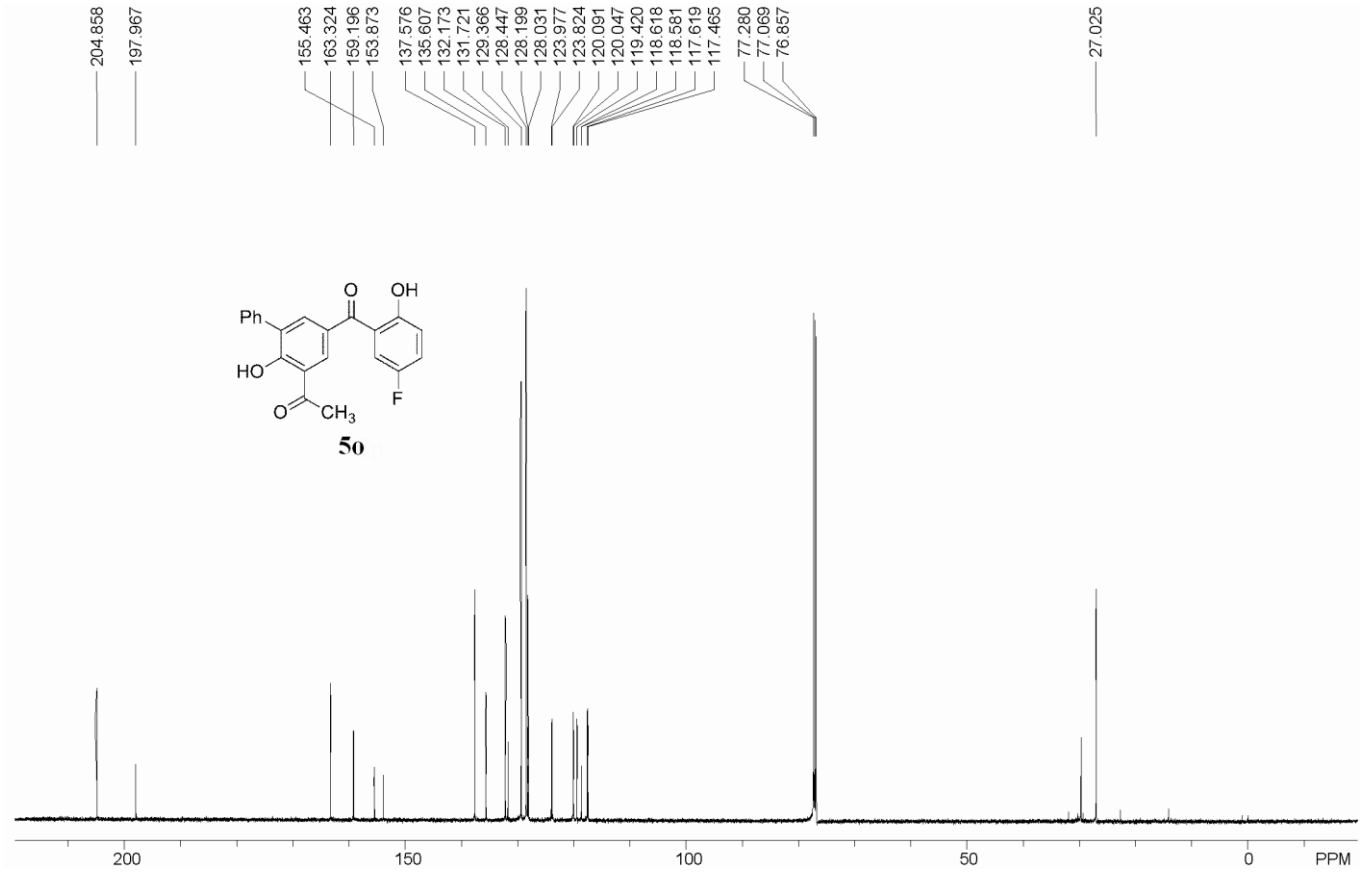
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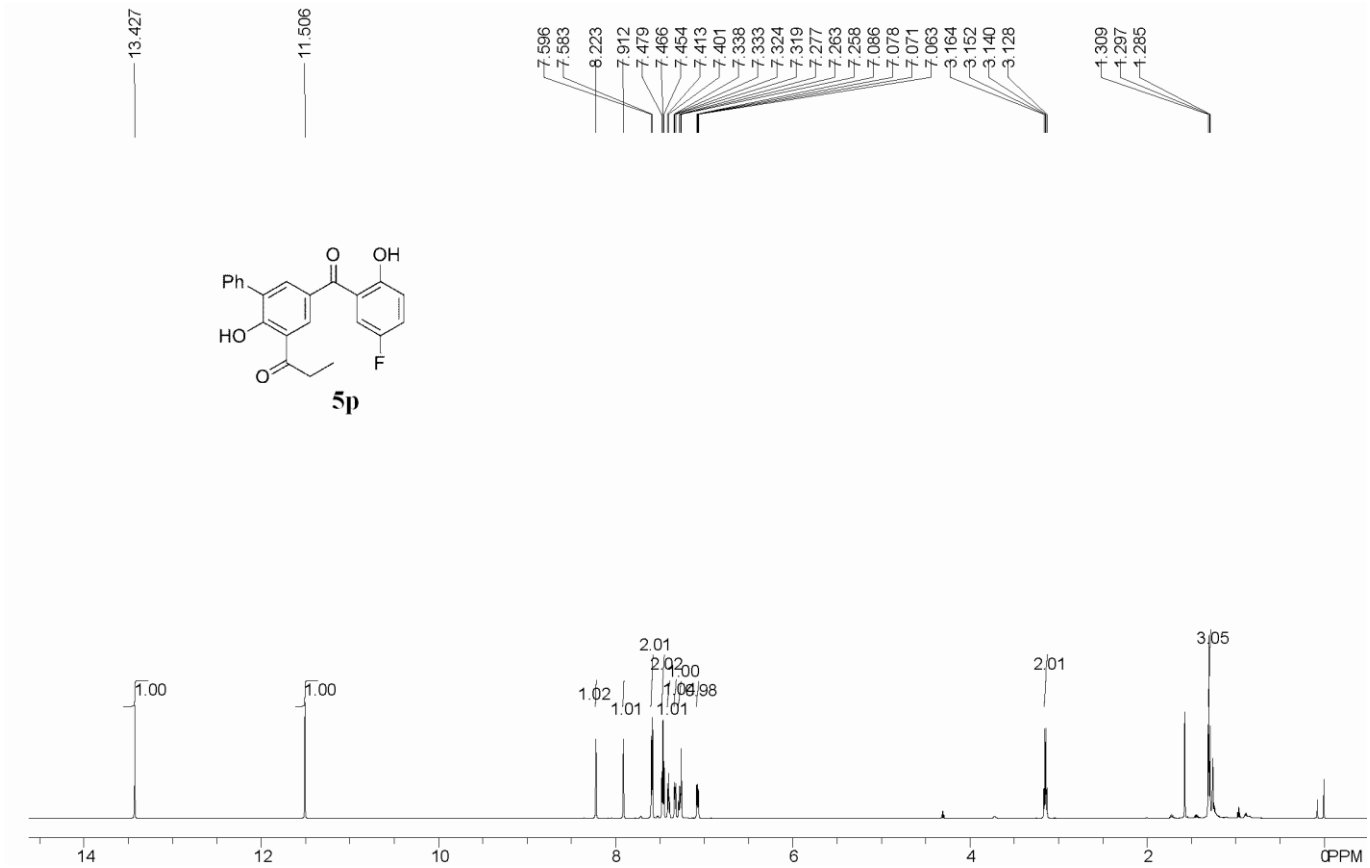
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HO
F
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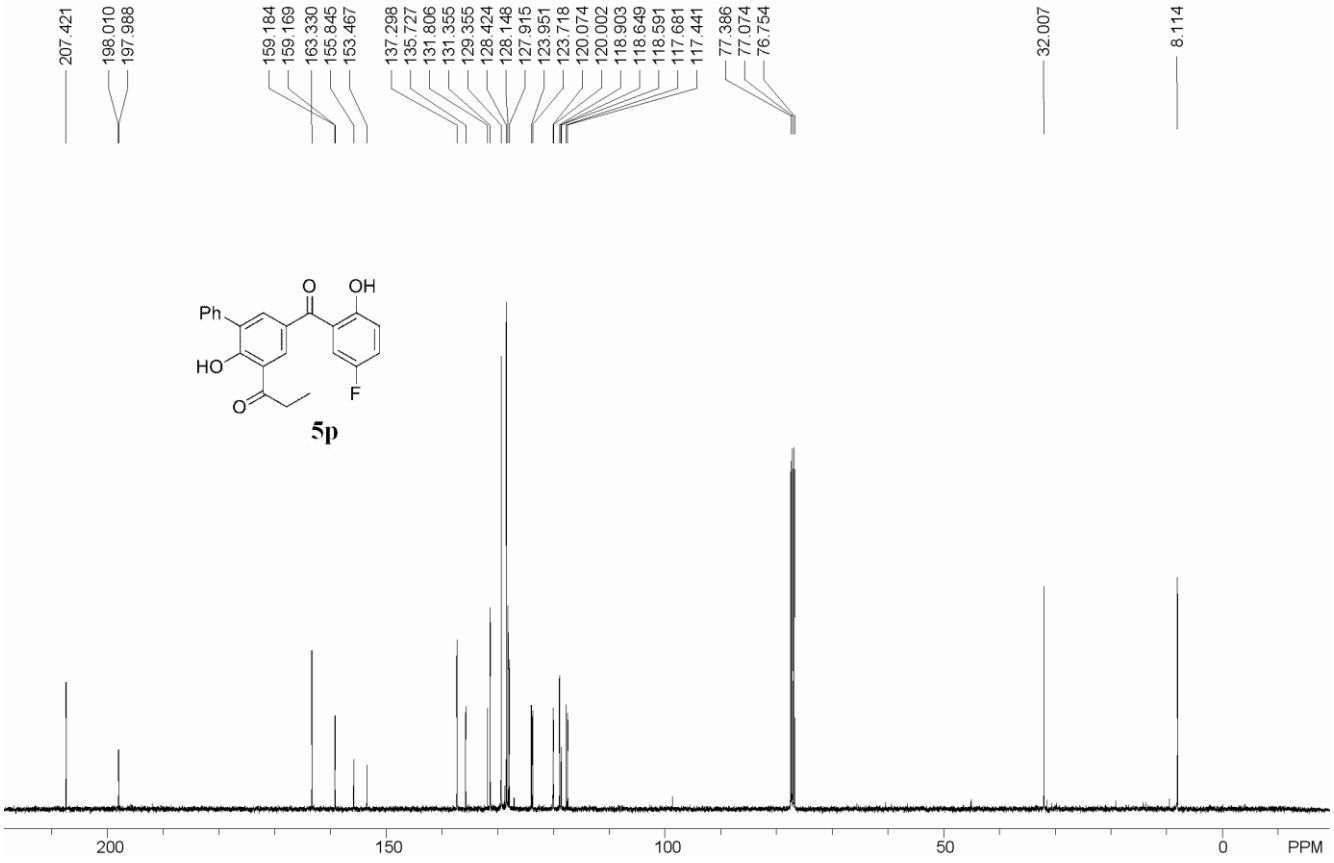
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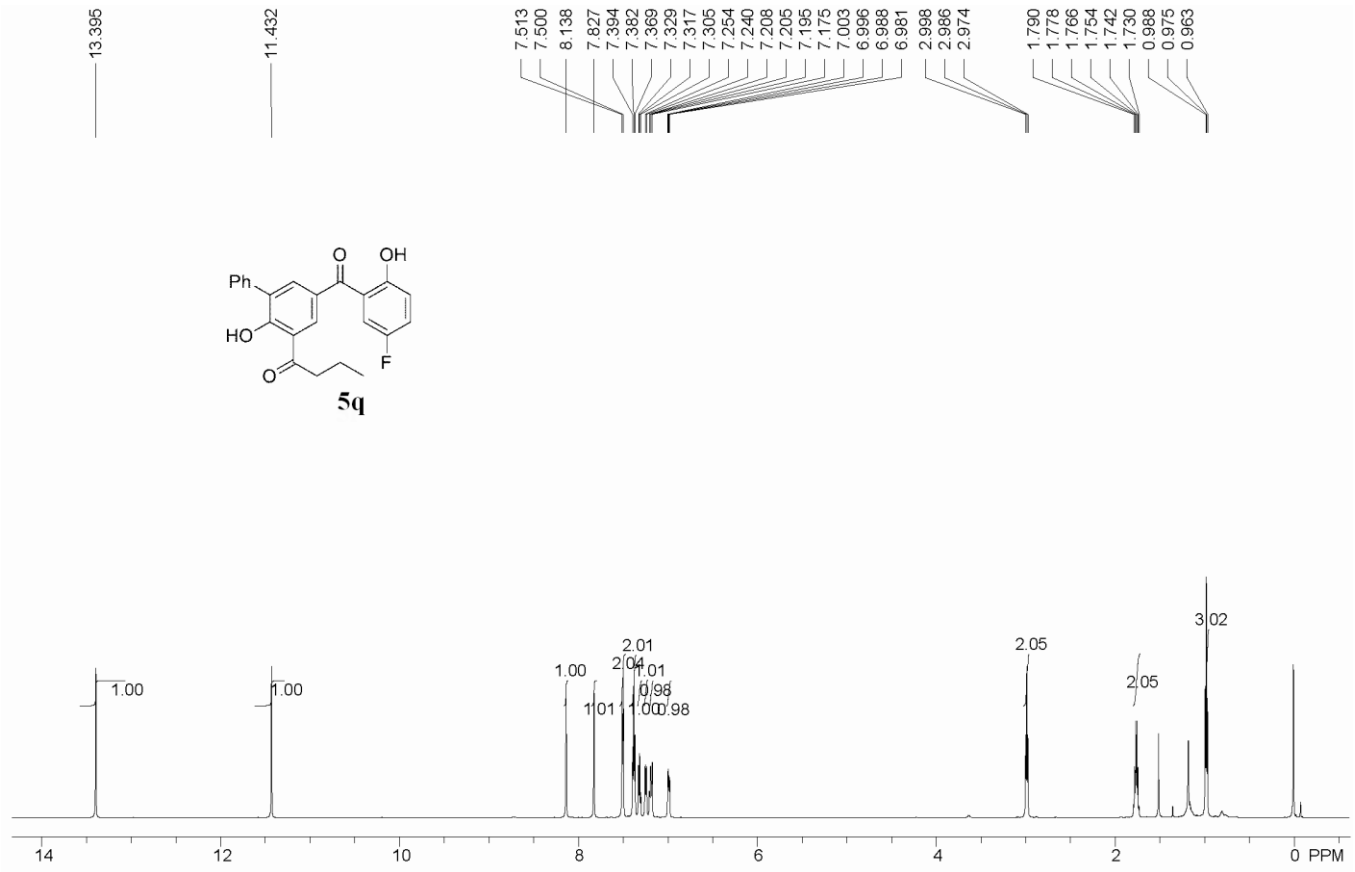
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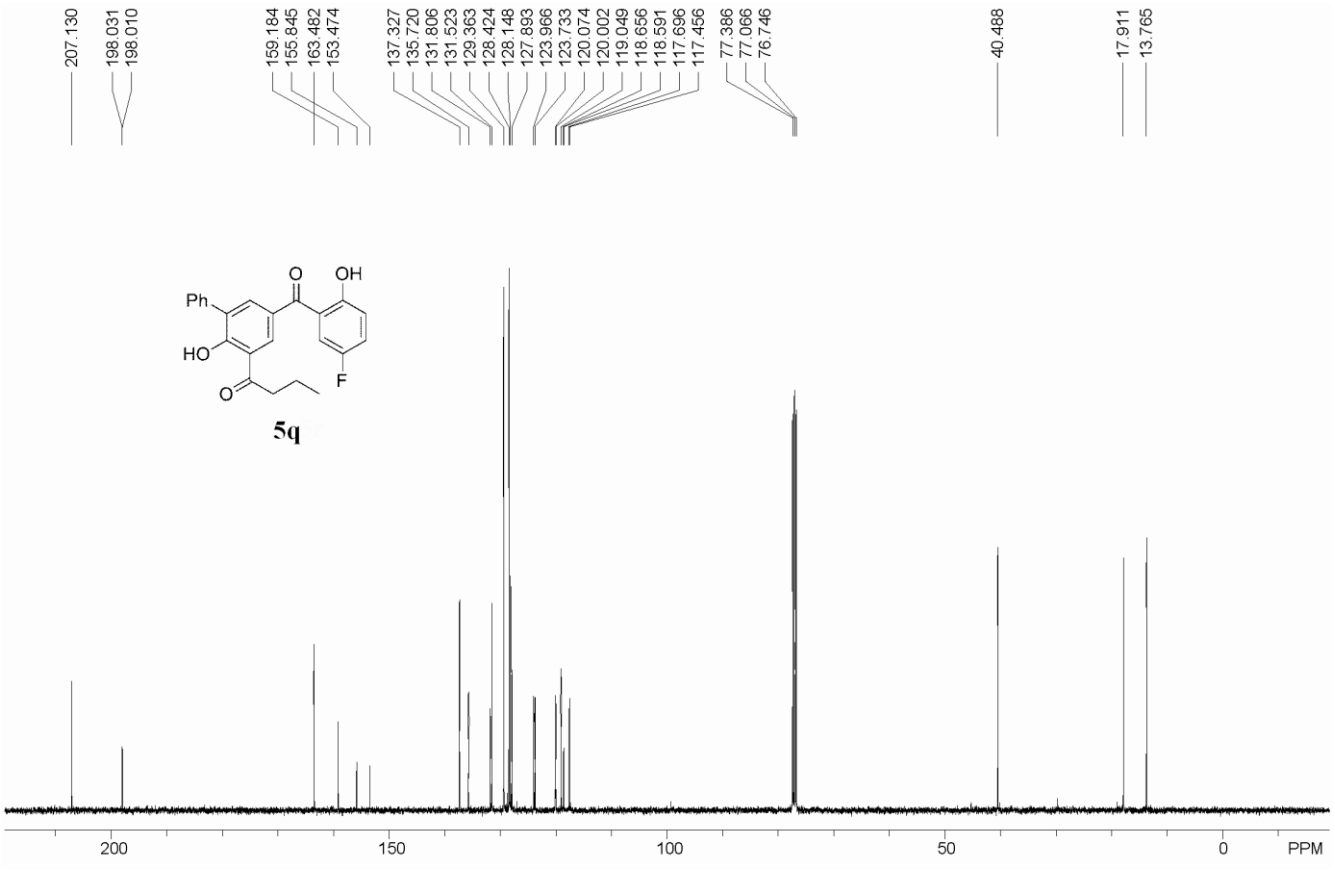
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HO
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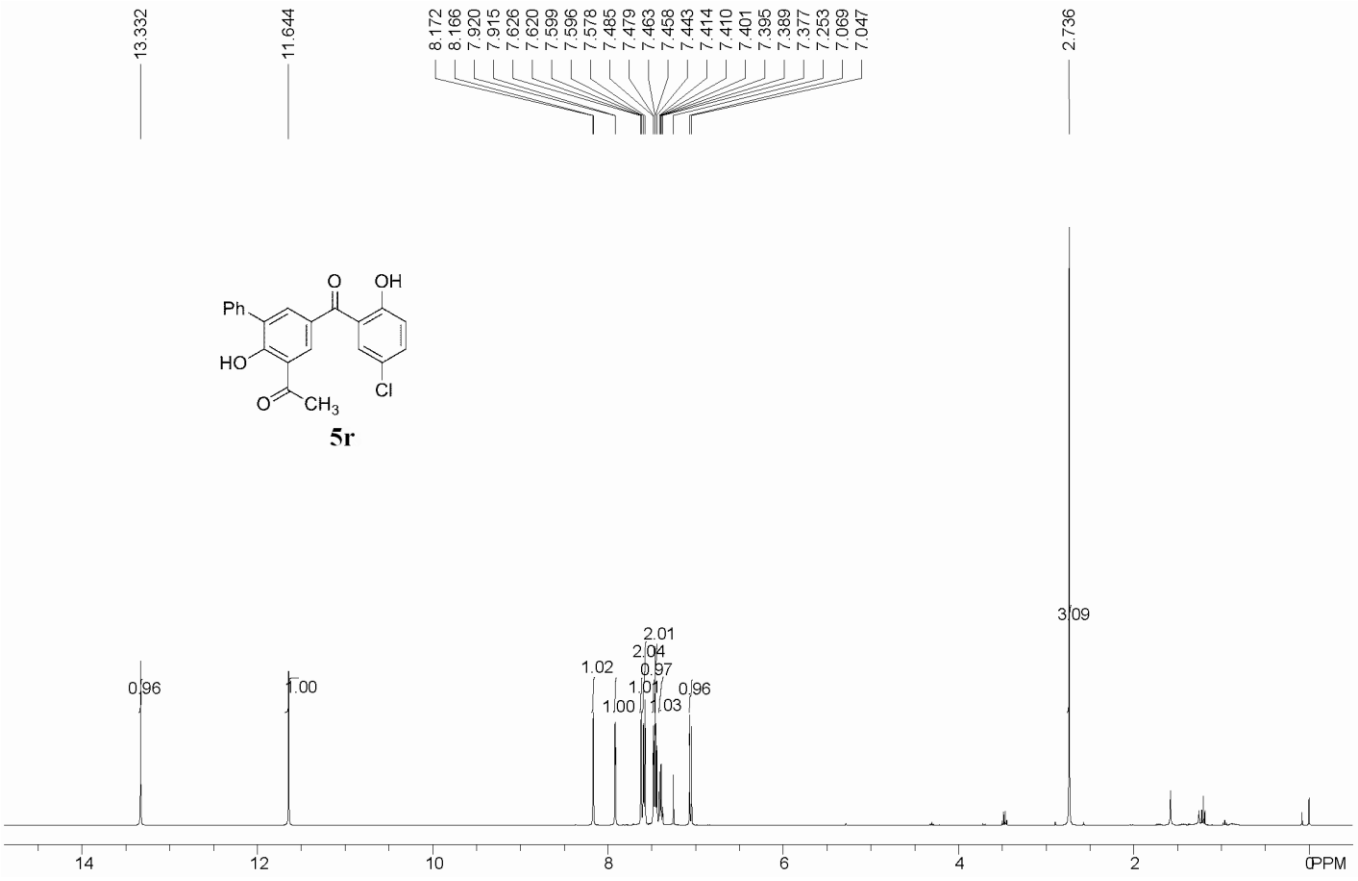
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Cl
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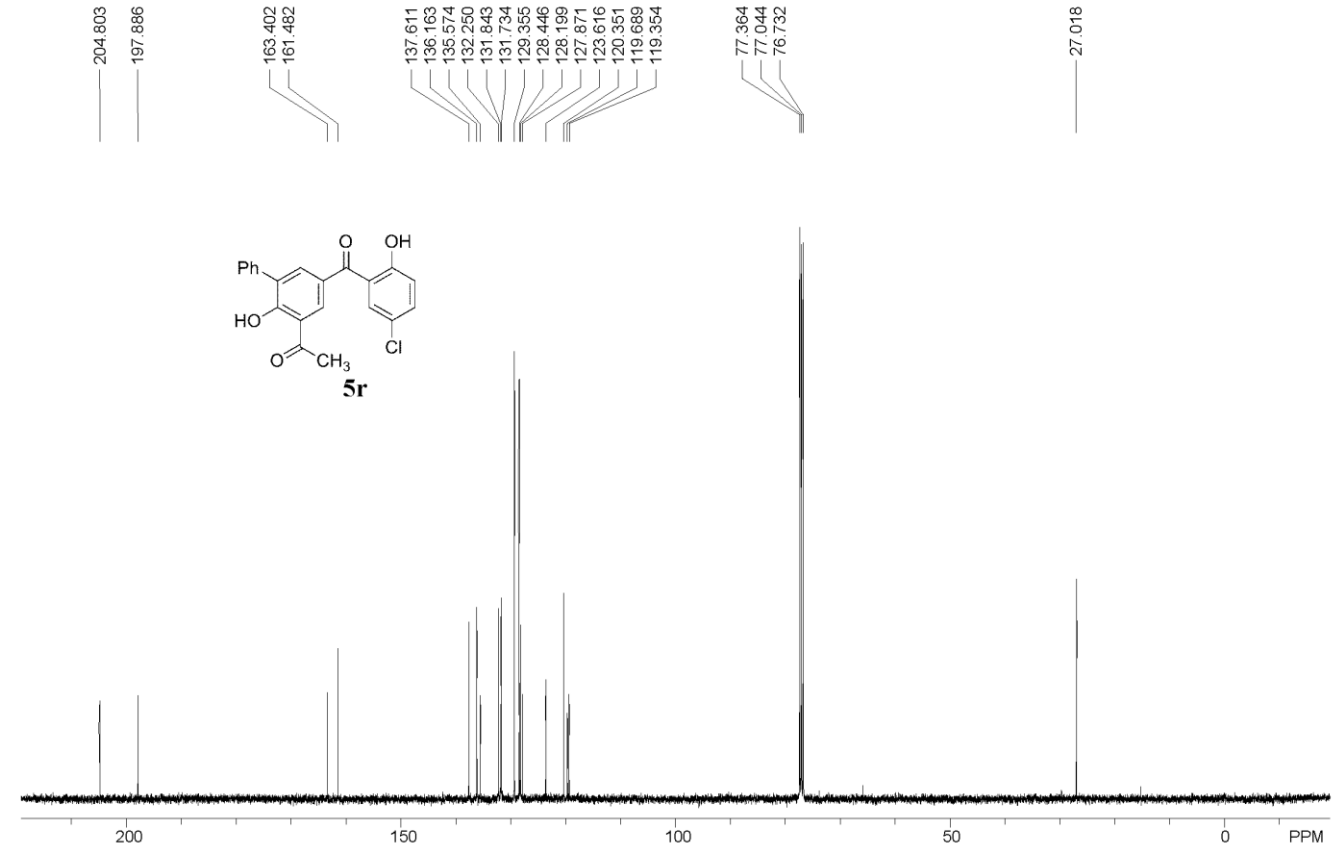
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OH
Cl
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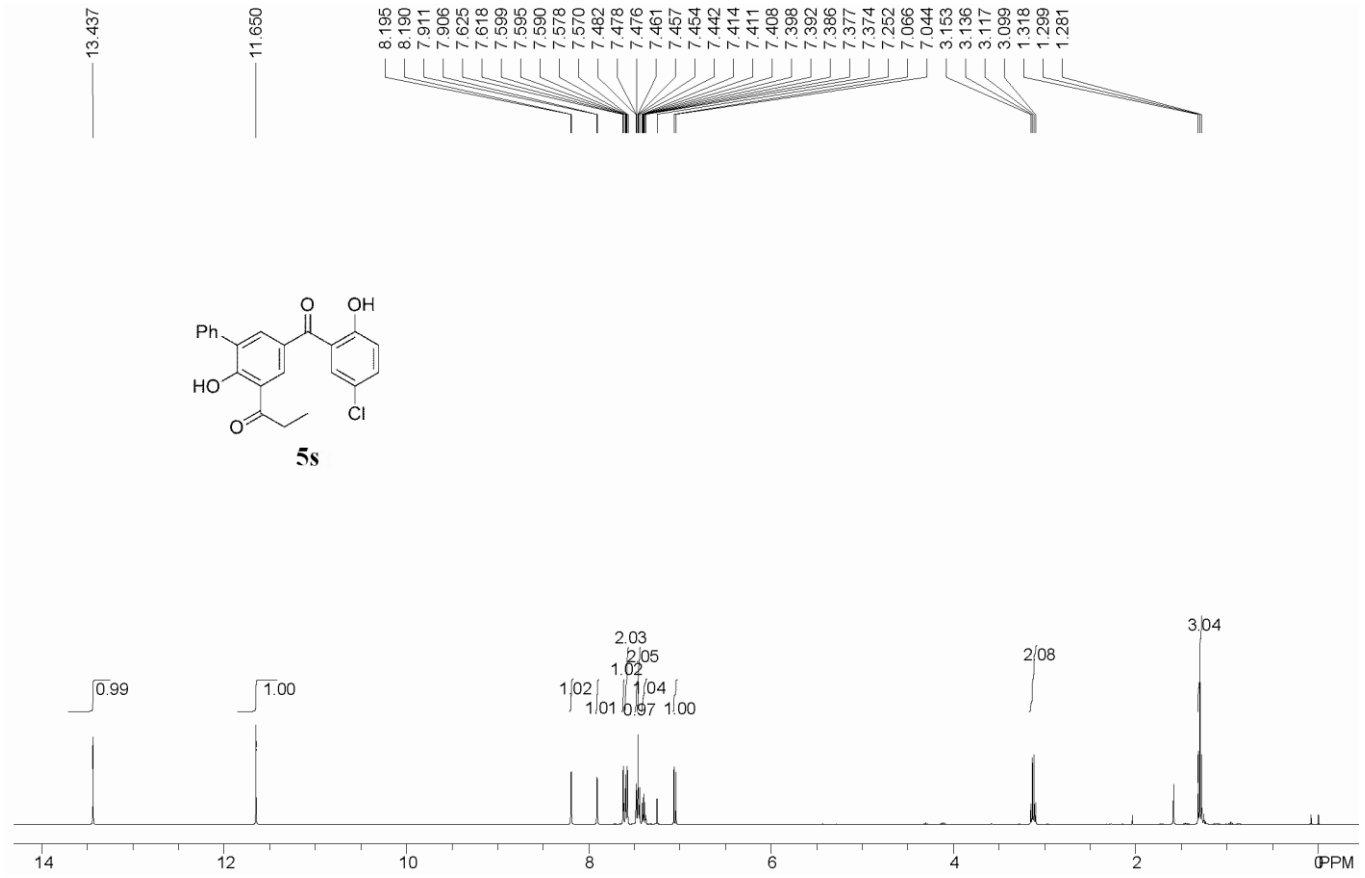
PPM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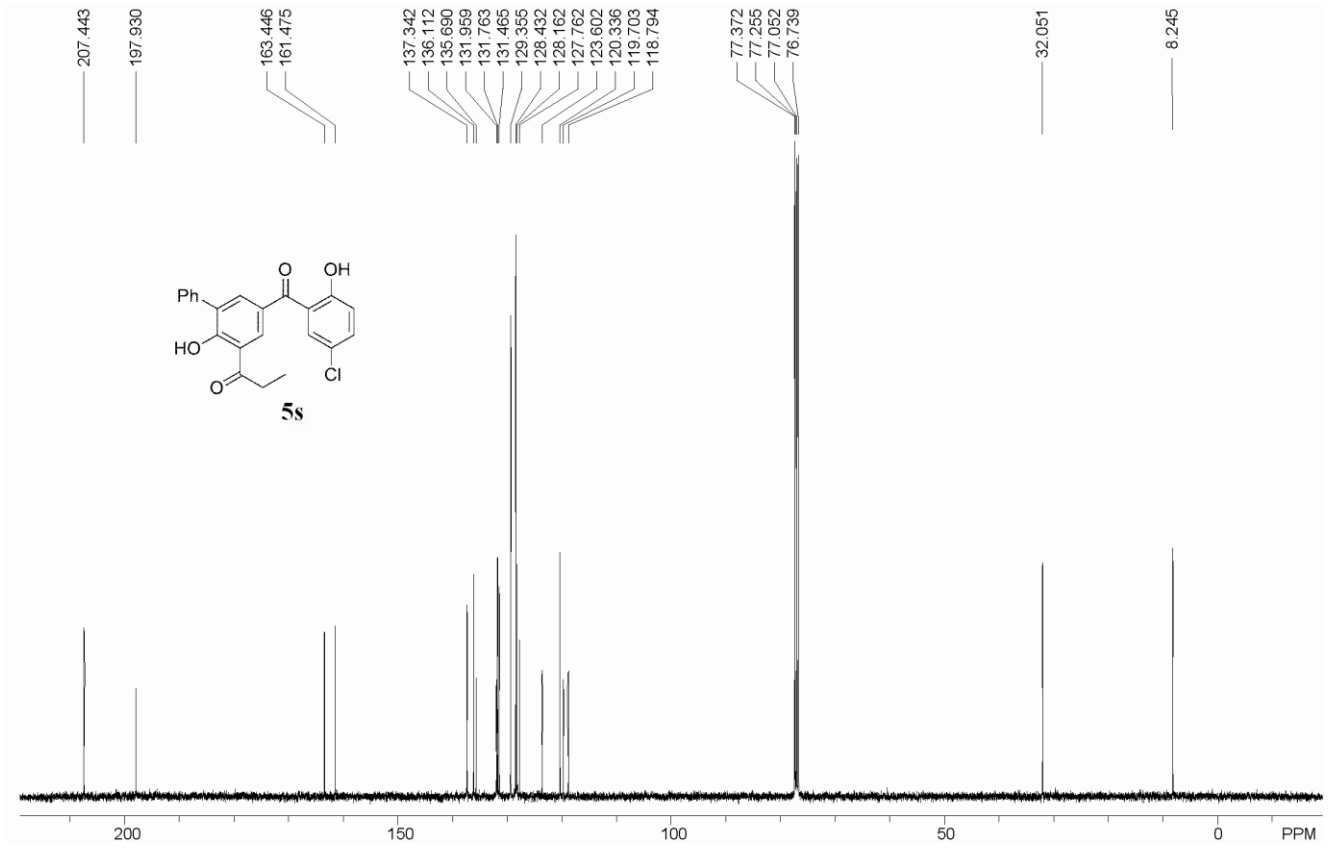
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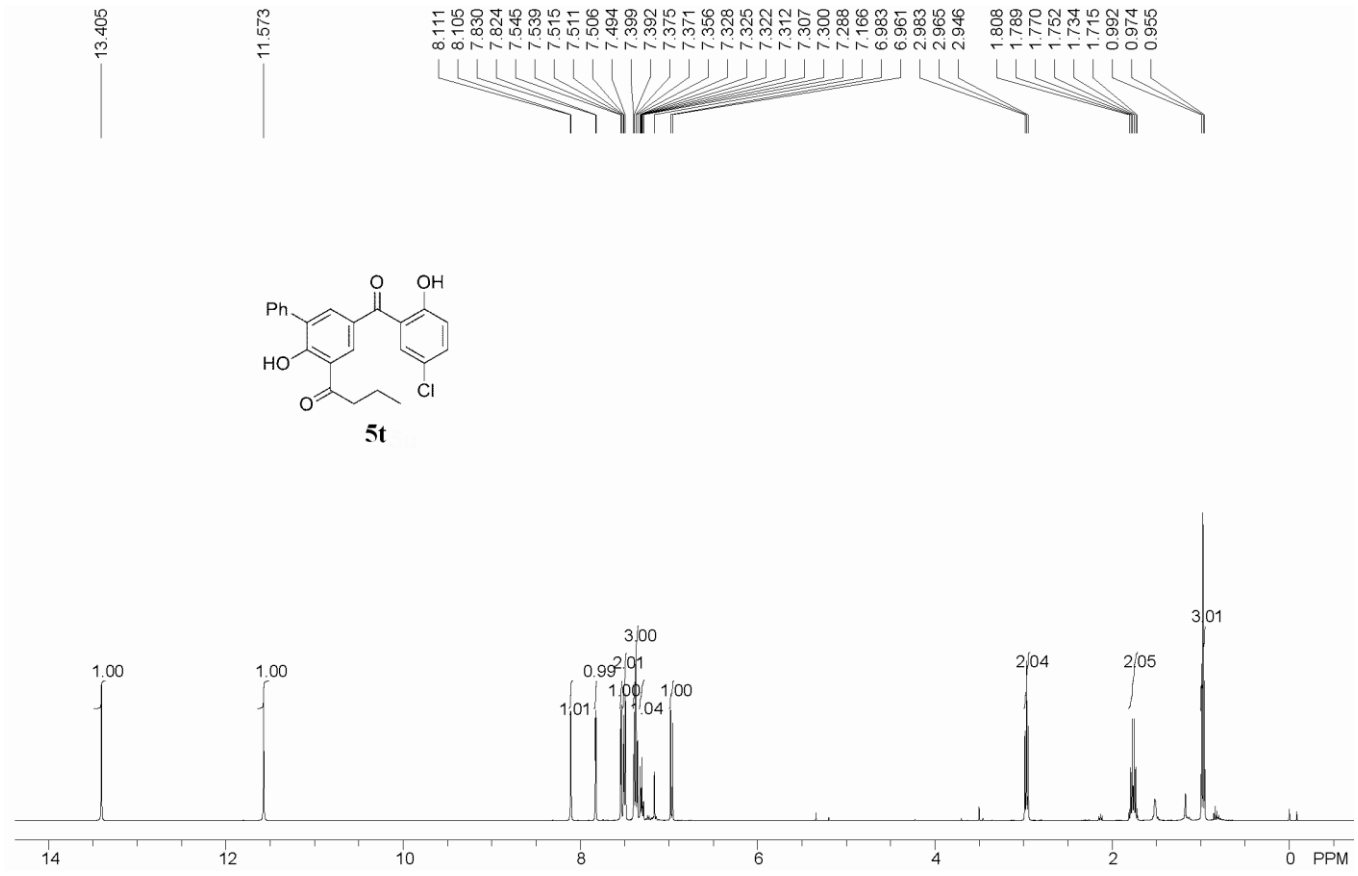
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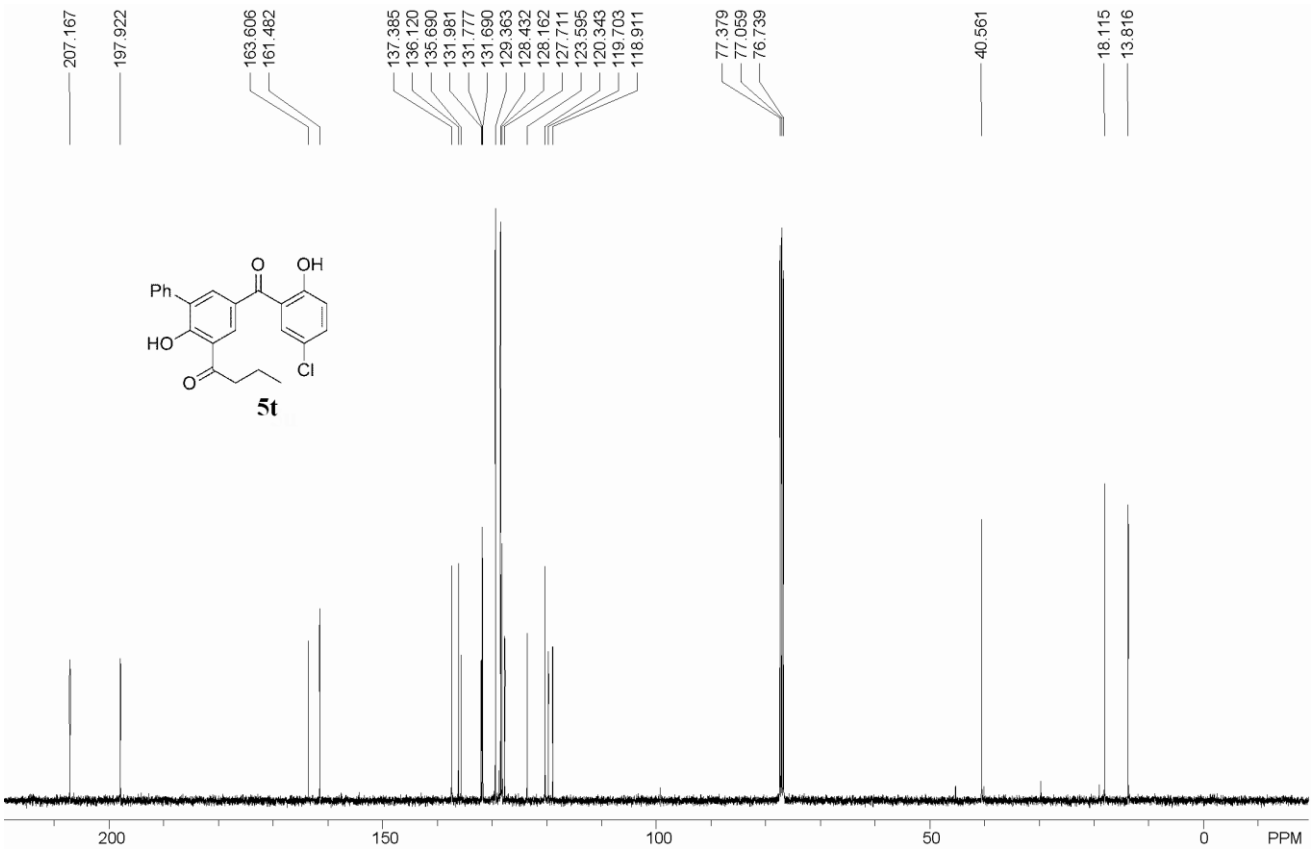
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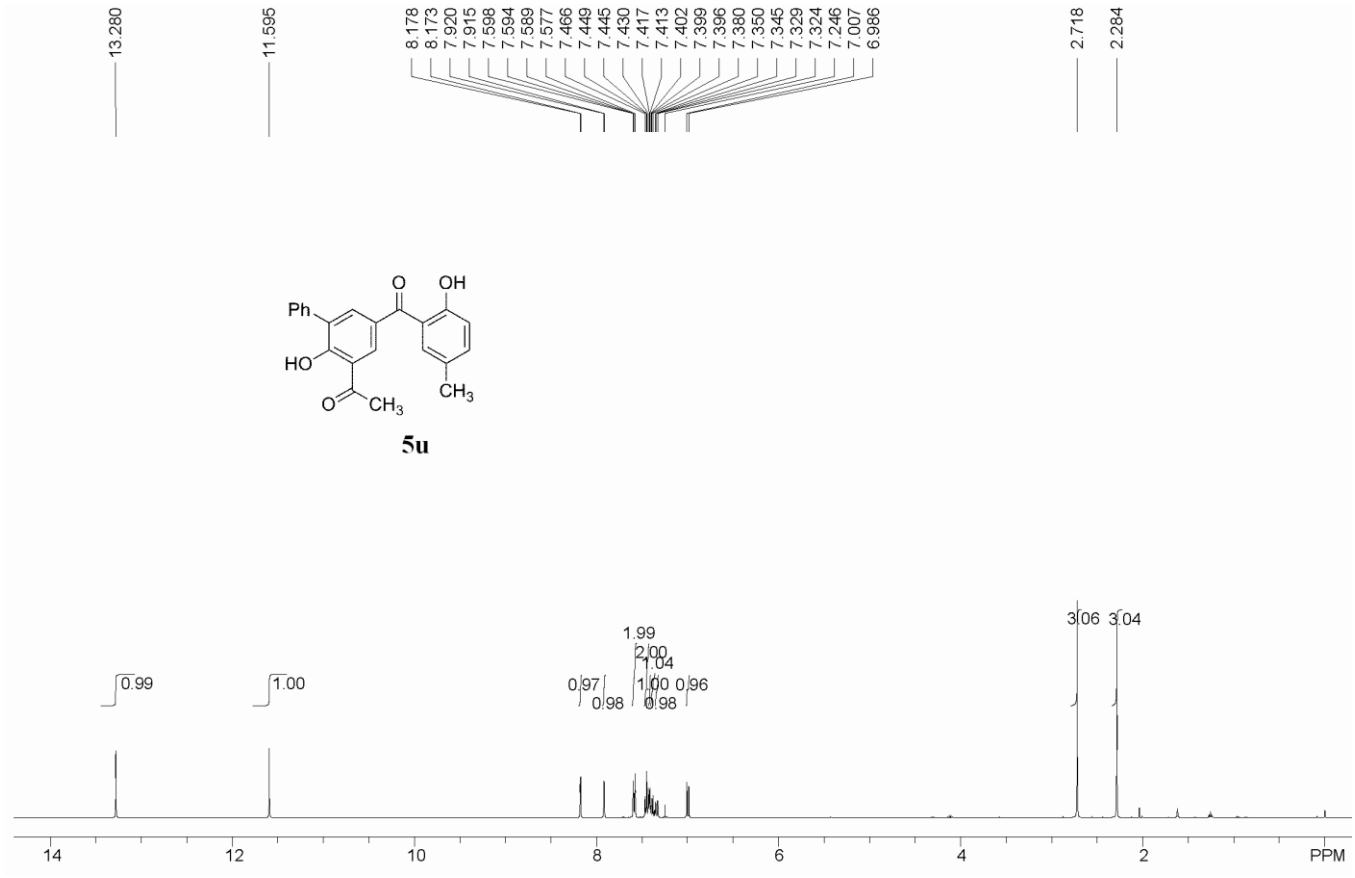
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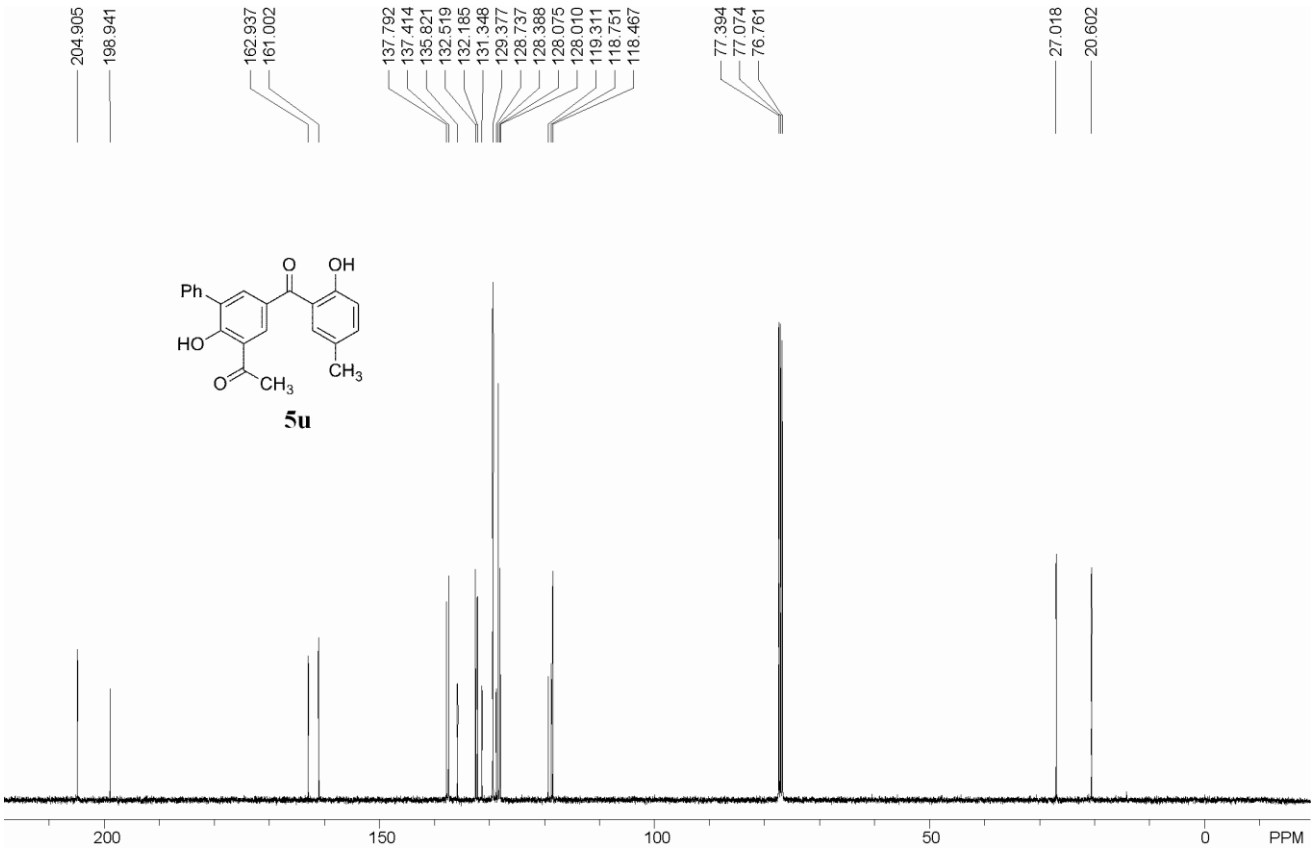
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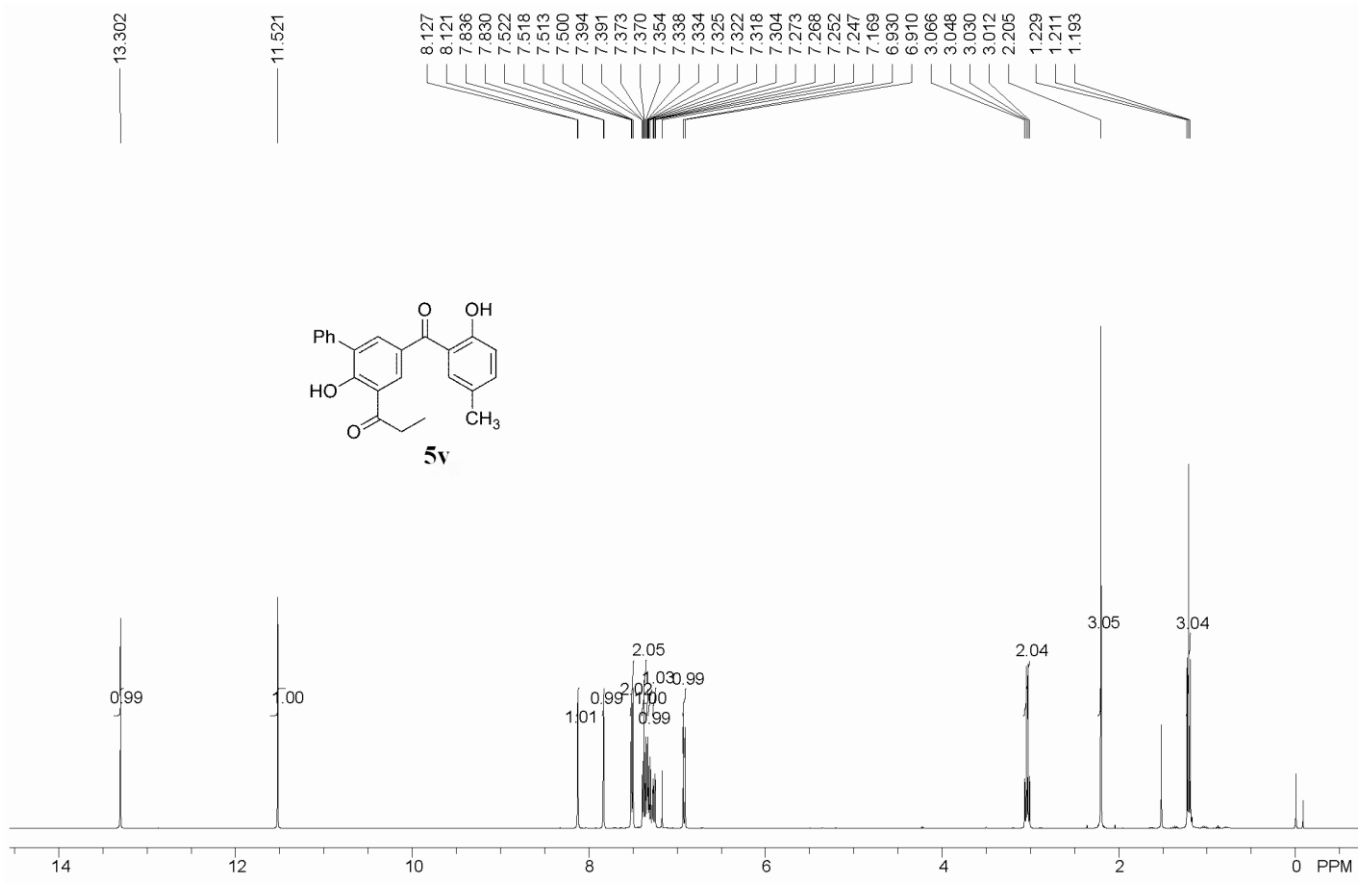
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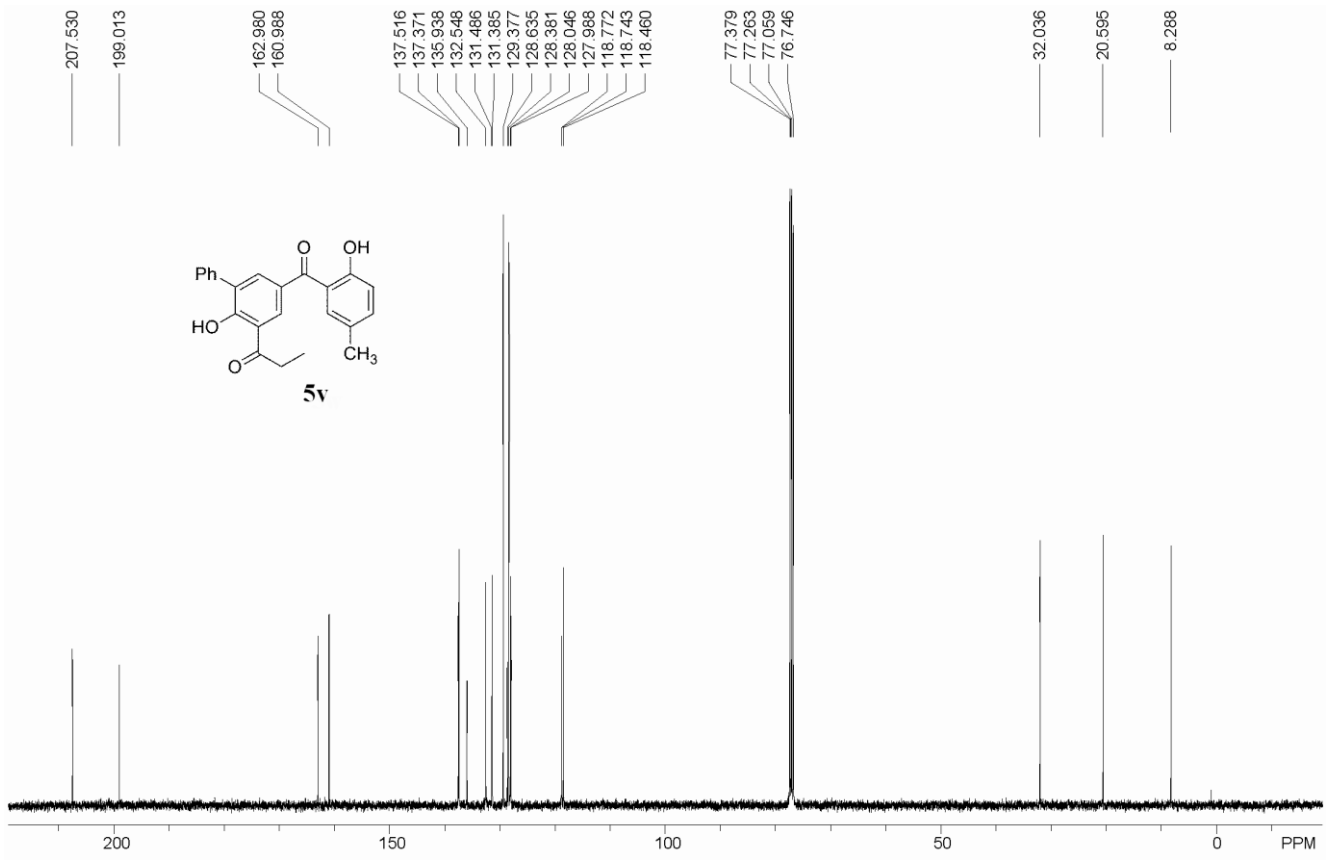
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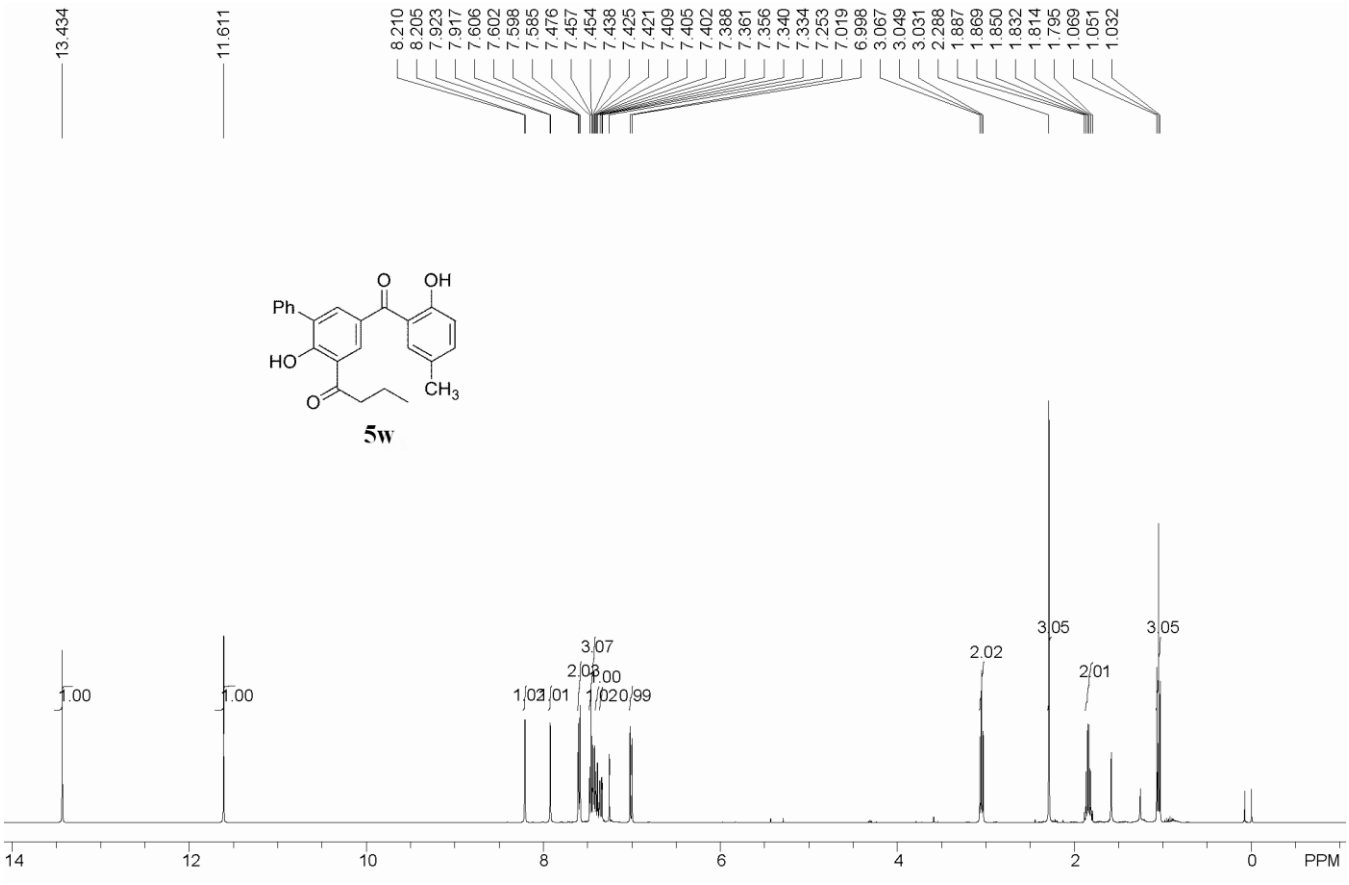
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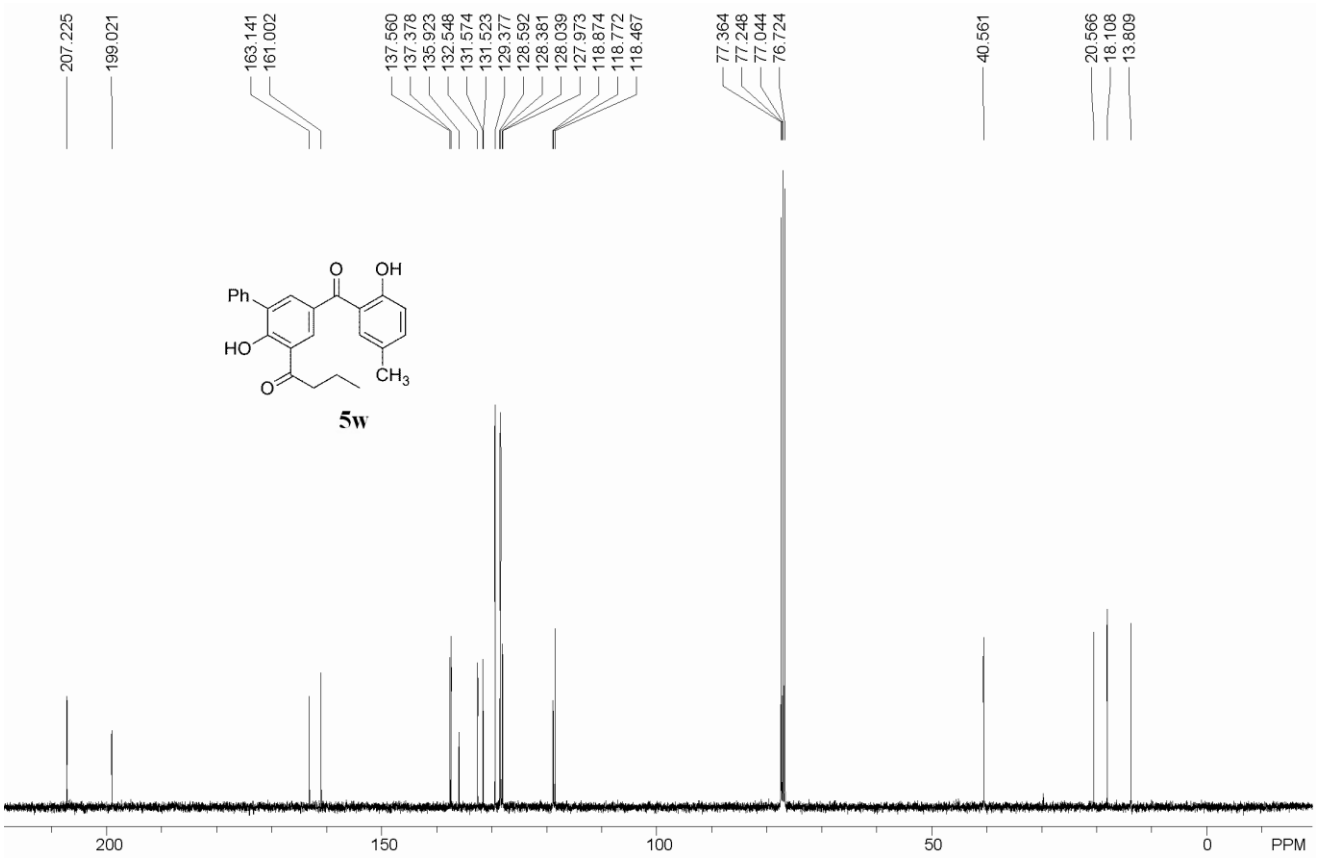
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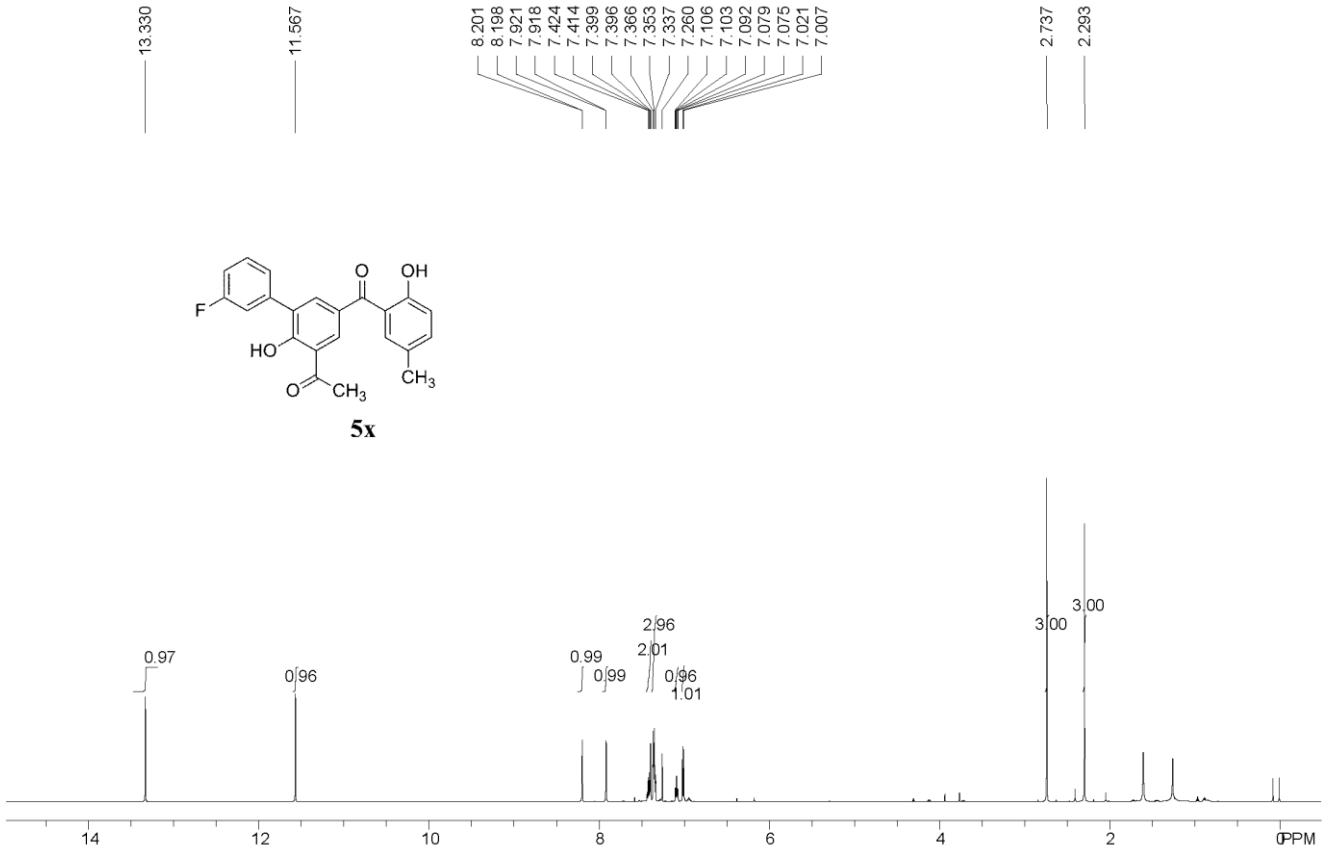
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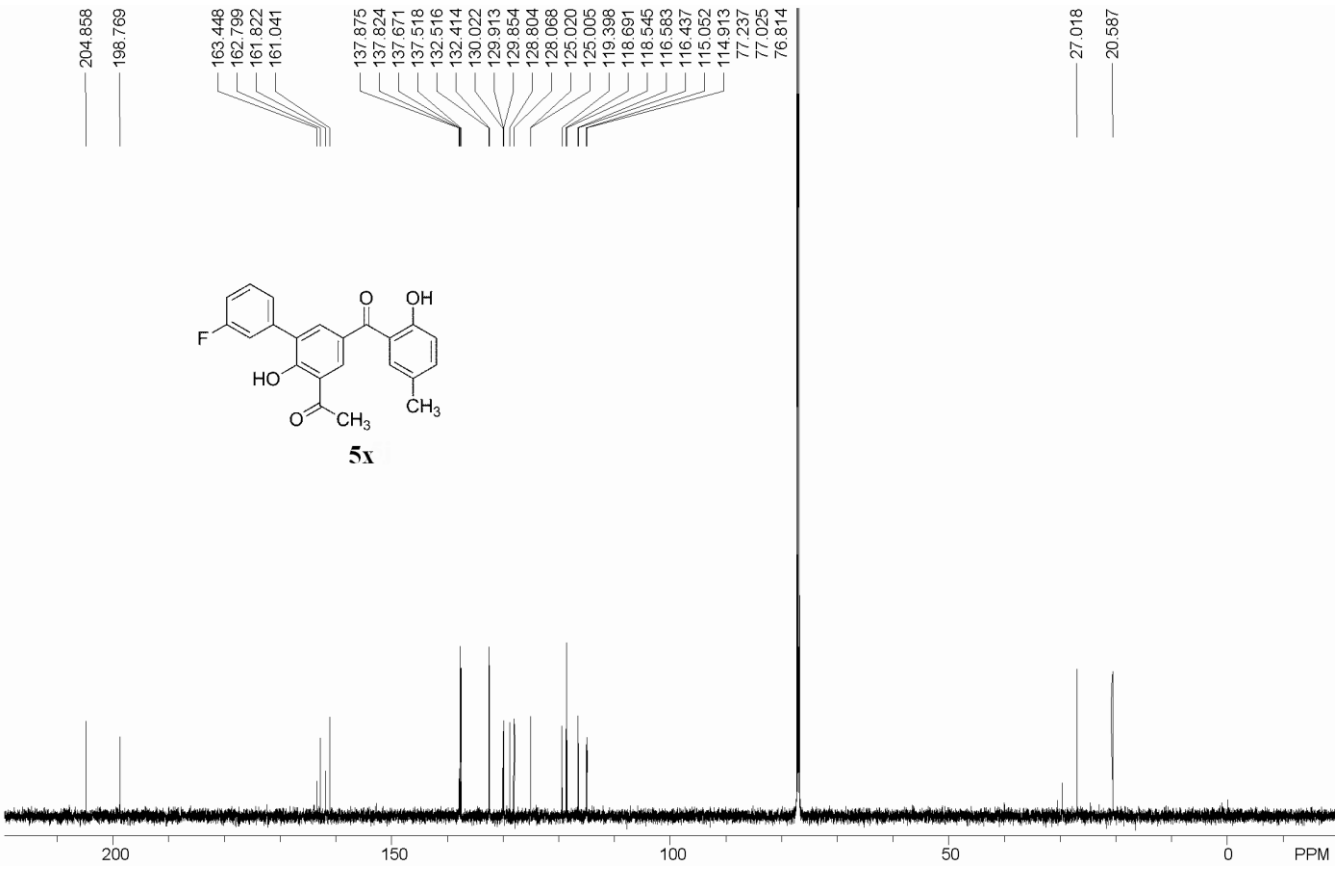
5x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CH3
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PPM

5x

V. X-ray crystal structure and data of 3k

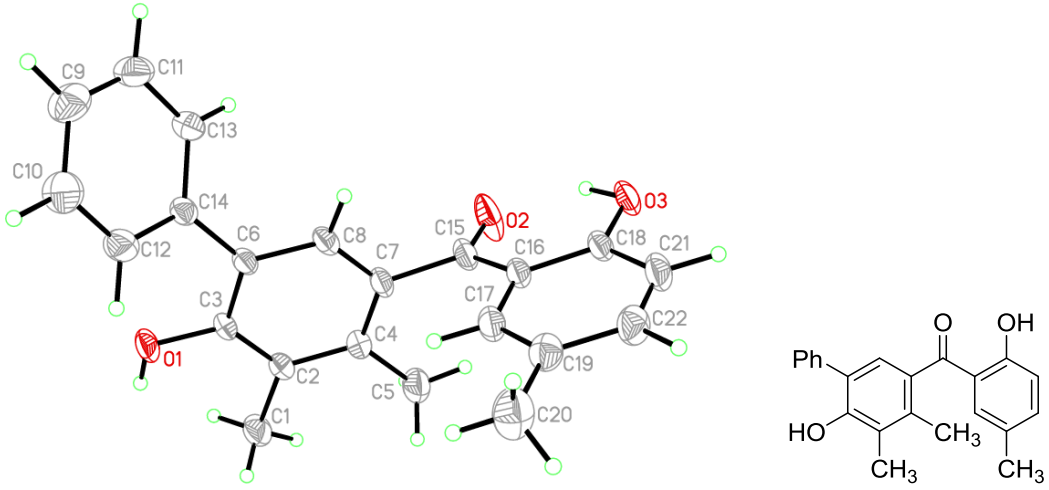

Fig 1. X-ray structure of **3k** with 30% ellipsoid probability

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a chloroform-petroleum ether (1:1 v/v) solution of **3k**. Crystal data collection and refinement parameters of **3k** are summarized in Table 1. Intensity data were collected at 296 K on a Bruker SMART 6000 CCD diffractometer using graphite-monochromated MoKα radiation, λ = 0.71073 Å. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model.

Table 1 Crystallographic data and structure refinement results of **3k**

Empirical formula	$C_{22}H_{20}O_3$
Formula weight	332.38
Temp, K	296.15
Crystal system	triclinic
Space group	P-1
a, Å	9.8395(17)
b, Å	10.7013(19)
c, Å	10.8636(19)
α (°)	114.335(2)
β (°)	94.477(2)
γ (°)	116.312(2)
Volume, Å^3	885.4(3)
Z	2
d_{calc}, g cm^{-3}	1.247
λ, Å	0.71073
μ, mm^{-1}	0.082
No. of data collected	7055
No. of unique data	3749
R_{int}	0.0185
Goodness-of-fit on F^2	1.029
R_1, wR_2 ($I > 2\sigma(I)$)	0.0473, 0.1274
R_1, wR_2 (all data)	0.0628, 0.1434