Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

One-pot cascade reactions of 1-arylpenta-3,4-dien-2-ones leading to 2-arylphenols and dibenzopyroanones

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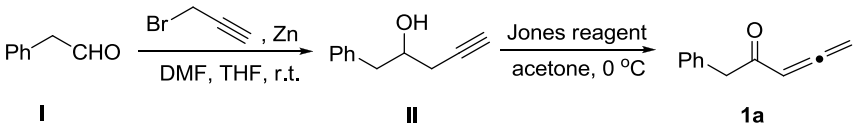
I. General Experimental Information

Unless otherwise noted, all commercial reagents were used without further purification. The solvents were dried prior to use. 1-Arylpenta-3,4-dien-2-ones (**1**) were synthesized through oxidation of the corresponding homopropargyl alcohols,[1] which were prepared through zinc promoted propargylation of the corresponding aldehydes.[2] All the activated ketones (**2**) are commercially available. Column chromatography was conducted with 200-300 mesh silica gel. Melting points were recorded with a micro melting point apparatus and uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on Bruker 400 MHz spectrometers. Chemical shifts were reported in ppm by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm, $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained by using a MicrOTOF mass spectrometer. All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (60 F254 0.25 mm) and components were visualized by observation under UV light (254 and 365 nm).

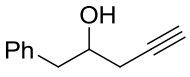
II. Experimental Procedures and Spectroscopic Data

1. Experimental procedures for the synthesis and spectroscopic data of 1-phenylpent-4-yn-2-ol (II)[1,3] and 1-phenyl-penta-3,4-dien-2-one (1a)[2]



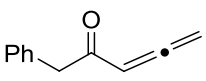
I II 1a

1-Phenylpent-4-yn-2-ol (II)



Typical procedure:[1] To a flask containing 2-phenylacetaldehyde (**I**, 240 mg, 2 mmol), THF (4 mL), and propargyl bromide (0.313 mL, 4 mmol) were added activated zinc dust (384 mg, 6 mmol) portion-wise with stirring. The mixture was then stirred at room temperature. Upon completion, it was diluted with saturated aqueous NH_4Cl (10 mL) and the excess zinc was filtered. The filtrate was concentrated and to the residue was added water. The aqueous phase was extracted with EtOAc (10 mL × 3). The combined organic phase was dried with anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) to afford 294 mg (92%) of **II**: yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.14 (s, 1H), 2.36-2.46 (m, 2H), 2.60 (br s, 1H), 2.83-2.98 (m, 2H), 3.92-4.06 (m, 1H), 7.27-7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.4, 42.4, 70.9, 71.3, 81.0, 126.7, 128.6, 129.6, 138.0; MS: m/z 161 $[MH]^+$.

1-Phenylpenta-3,4-dien-2-ones (1a)

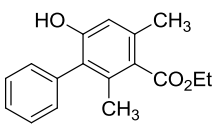


Typical procedure:[2] To a solution of 1-phenylpent-4-yn-2-ol (**II**, 160 mg, 1 mmol) in acetone (10 mL) cooled to 0 ℃ was added Jones reagent (0.44 mL, 1.2 mmol) in a drop-wise manner. Upon complete consumption of the starting material as monitored by TLC, the reaction mixture was quenched by addition of isopropanol. The resulting mixture was filtered and the filtrate was concentrated under vacuum. The residue were purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) to afford 142 mg (90%) of **1a**: yellow liquid; ^{1}H NMR (400

MHz, $CDCl_3$) δ: 3.93 (s, 2H), 5.32 (d, *J* = 6.8 Hz, 2H), 5.85 (t, *J* = 6.8 Hz, 1H), 7.25-7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 45.9, 80.0, 96.6, 126.9, 128.6, 129.5, 134.6, 197.8, 217.3; MS: m/z 159 $[MH]^+$.

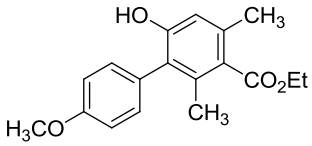
2. Experimental procedures for the synthesis and spectroscopic data of 3

Ethyl 6-hydroxy-2,4-dimethylbiphenyl-3-carboxylate (3a)



Typical procedure: To a flask containing 1-phenylpenta-3,4-dien-2-one (**1a**, 79 mg, 0.5 mmol) and ethyl 3-oxobutanoate (**2a**, 78 mg, 0.6 mmol) were added CH_3CN (5 mL) and Cs_2CO_3 (163 mg, 0.5 mmol). The mixture was stirred at 80 °C. Upon completion as monitored by TLC, the reaction was quenched with aqueous NH_4Cl. Then, the mixture was extracted with ethyl acetate (5 mL × 3). The combined organic layer was washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purified by chromatography on silica-gel (petroleum ether / ethyl acetate = 20:1) to afford 115 mg (85%) of **3a**: Yellow solid; Mp: 120-122 °C (ethanol); ^1H NMR (400 MHz, $CDCl_3$) δ: 1.37-1.40 (m, 3H), 2.02 (s, 3H), 2.33 (s, 3H), 4.36-4.41 (m, 2H), 4.89 (s, 1H), 6.71 (s, 1H), 7.24 (dd, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 2H), 7.40-7.44 (m, 1H), 7.48-7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 17.8, 19.7, 60.9, 114.3, 126.1, 127.2, 128.3, 129.5, 130.4, 134.3, 134.7, 136.0, 153.4, 170.3; MS: m/z 271 $[MH]^+$; HRMS calcd for $C_{17}H_{19}O_3$: 271.1334 [M+H], found: 271.1338.

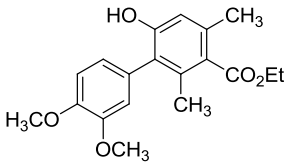
Ethyl 6-hydroxy-4'-methoxy-2,4-dimethylbiphenyl-3-carboxylate (3b)



The reaction of 1-(4-methoxyphenyl)penta-3,4-dien-2-one (**1b**, 94 mg, 0.5 mmol), ethyl 3-oxobutanoate (**2a**, 78 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 125 mg (83%) of **3b**: Eluent: ethyl acetate / petroleum ether (5%); Yellow solid; Mp: 92-94 ℃ (ethanol); ^1H NMR (400 MHz, $CDCl_3$) δ: 1.38 (t, *J* = 6.8 Hz, 3H), 2.03 (s, 3H), 2.31 (s, 3H), 3.83 (s, 3H), 4.37 (q, *J* = 7.6 Hz, 2H), 5.24 (s, 1H), 6.67 (s, 1H), 7.00 (dd, J_1 = 6.8 Hz,

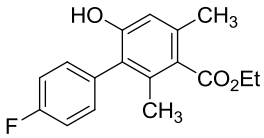
J_2 = 1.6 Hz, 2H), 7.14 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 17.9, 19.8, 55.2, 61.0, 114.3, 114.9, 125.9, 126.7, 127.1, 131.6, 134.8, 135.8, 153.9, 159.5, 170.5; MS: m/z 301 $[MH]^+$; HRMS calcd for $C_{18}H_{21}O_4$: 301.1440 [M+H], found: 301.1449.

Ethyl 6-hydroxy-3',4'-dimethoxy-2,4-dimethylbiphenyl-3-carboxylate (3c)



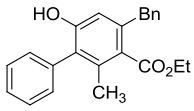
The reaction of 1-(3,4-dimethoxyphenyl)penta-3,4-dien-2-one (**1c**, 109 mg, 0.5 mmol), ethyl 3-oxobutanoate (**2a**, 78 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 135 mg (82%) of **3c**: Eluent: ethyl acetate / petroleum ether (20%); Yellow solid; Mp: 146-148 ℃ (ethanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.37 (t, J = 7.2 Hz, 3H), 2.03 (s, 3H), 2.30 (s, 3H), 3.84 (s, 3H), 3.91(s, 1H), 4.36 (q, J = 6.8 Hz, 2H), 5.08 (s, 1H), 6.68 (s, 1H), 6.72 (d, J = 1.2 Hz, 1H), 6.78 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 17.9, 19.8, 55.9, 61.0, 111.9, 113.2, 114.2, 122.6, 125.9, 126.8, 127.2, 134.7, 135.9, 149.0, 149.7, 153.7, 170.3; MS: m/z 331 $[MH]^{+;}$. HRMS calcd for $C_{19}H_{23}O_5$: 331.1545 [M+H], found: 331.1548.

Ethyl 4'-fluoro-6-hydroxy-2,4-dimethylbiphenyl-3-carboxylate (3d)



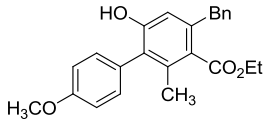
The reaction of 1-(4-fluorophenyl)penta-3,4-dien-2-one (**1d**, 88 mg, 0.5 mmol), ethyl 3-oxobutanoate (**2a**, 78 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 125 mg (87%) of **3d**: Eluent: ethyl acetate / petroleum ether (5%); Yellow solid; Mp: 87-89 ℃ (ethanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.38 (t, J = 7.2 Hz, 3H), 2.00 (s, 3H), 2.31 (s, 3H), 4.38 (q, J = 7.2 Hz, 2H), 5.10 (s, 1H), 6.67 (s, 1H), 7.15-7.20 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 17.9, 19.8, 61.0, 114.5, 116.5, 116.7, 125.1, 127.4, 130.5, 130.6, 132.3, 132.4, 134.6, 136.3, 153.5, 161.5, 163.9, 170.2; MS: m/z 289 $[MH]^+$; HRMS calcd for $C_{17}H_{18}FO_3$: 289.1240 [M+H], found: 289.1243.

Ethyl 4-benzyl-6-hydroxy-2-methylbiphenyl-3-carboxylate (3e)



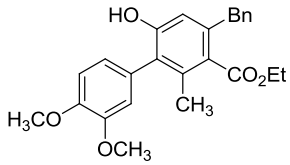
The reaction of 1,5-diphenylpenta-3,4-dien-2-one (**1e**, 117 mg, 0.5 mmol), ethyl 3-oxobutanoate (**2a**, 78 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 149 mg (86%) of **3e**: Eluent: ethyl acetate / petroleum ether (5%); Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.27 (t, *J* = 7.2 Hz, 3H), 2.03 (s, 3H), 4.01 (s, 2H), 4.26 (q, *J* = 7.6 Hz, 2H), 4.85 (s, 1H), 6.66 (s, 1H), 7.21-7.32 (m, 7H), 7.41-7.45 (m, 1H), 7.51 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 18.0, 39.4, 61.0, 114.4, 126.3, 126.7, 127.3, 128.5, 129.2, 129.6, 130.4, 130.5, 134.5, 134.6, 139.2, 139.9, 153.5, 170.2; MS: m/z 347 $[MH]^+$; HRMS calcd for $C_{23}H_{23}O_3$: 347.1647 [M+H], found: 347.1650.

Ethyl 4-benzyl-6-hydroxy-4'-methoxy-2-methylbiphenyl-3-carboxylate (3f)



The reaction of 1-(4-methoxyphenyl)-5-phenylpenta-3,4-dien-2-one (**1f**, 132 mg, 0.5 mmol), ethyl 3-oxobutanoate (**2a**, 78 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 158 mg (84%) of **3f**: Eluent: ethyl acetate / petroleum ether (5%); Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.28 (t, *J* = 6.8 Hz, 3H), 2.03 (s, 3H), 3.85 (s, 3H), 3.99 (s, 2H), 4.25 (q, *J* = 6.8 Hz, 2H), 4.94 (s, 1H), 6.64 (s, 1H), 7.01-7.03 (m, 3H), 7.15-7.23 (m, 4H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 17.9, 39.3, 55.3, 61.0, 114.17, 114.20, 115.0, 126.2, 126.3, 128.4, 129.1, 131.6, 134.9, 138.9, 139.9, 153.7, 153.8, 159.6, 170.2; MS: m/z 377 $[MH]^+$; HRMS calcd for $C_{24}H_{25}O_4$: 377.1753 [M+H], found: 377.1760.

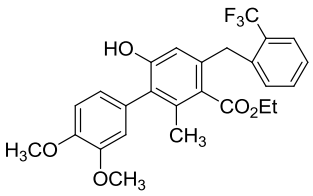
Ethyl 4-benzyl-6-hydroxy-3',4'-dimethoxy-2-methylbiphenyl-3-carboxylate (3g)



The reaction of 1-(3,4-dimethoxyphenyl)-5-phenylpenta-3,4-dien-2-one (**1g**, 147 mg, 0.5 mmol), ethyl 3-oxobutanoate (**2a**, 78 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 166 mg (82%) of **3g**: Eluent: ethyl acetate / petroleum ether (20%); Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.25 (t, *J* = 7.2 Hz, 3H), 2.04 (s, 3H), 3.86 (s, 3H), 3.93 (s, 3H), 3.99 (s, 2H), 4.24 (q, *J* = 6.8 Hz, 2H), 5.05 (s, 1H), 6.65 (s, 1H), 6.73 (s,

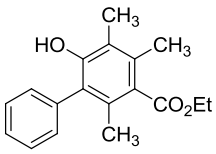
1H), 6.79-6.81 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 3H), 7.27 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 17.9, 39.3, 55.87, 55.90, 61.0, 111.9, 113.1, 114.2, 122.5, 126.2, 127.1, 128.4, 129.1, 134.8, 139.0, 139.9, 149.0, 149.7, 153.8, 170.2; MS: m/z 407 $[MH]^+$; HRMS calcd for $C_{25}H_{27}O_5$: 407.1858 [M+H], found: 407.1862.

Ethyl 6-hydroxy-3',4'-dimethoxy-2-methyl-4-(2-(trifluoromethyl)benzyl)biphenyl-3-carboxylate (3h)



The reaction of 1-(3,4-dimethoxyphenyl)-5-(4-trifluorophenyl)-penta-3,4-dien-2-one (**1h**, 181 mg, 0.5 mmol), ethyl 3-oxobutanoate (**2a**, 78 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 189 mg (80%) of **3h**: Eluent: ethyl acetate / petroleum ether (20%); Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.21 (t, *J* = 6.8 Hz, 3H), 2.08 (s, 3H), 3.86 (s, 3H), 3.92 (s, 3H), 4.18 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 5.08 (s, 1H), 6.48 (s, 1H), 6.75 (d, *J* = 2.0 Hz, 1H), 6.82 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 18.0, 35.2, 55.86, 55.91, 61.1, 111.9, 113.1, 114.3, 122.5, 125.7, 125.8, 126.3, 126.5, 126.7, 127.5, 131.6, 131.8, 135.0, 137.5, 138.4, 149.0, 149.7, 153.9, 170.0; MS: m/z 475 $[MH]^+$; HRMS calcd for $C_{26}H_{26}F_3O_5$: 475.1732 [M+H], found: 475.1739.

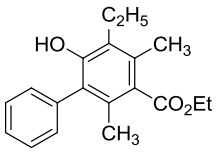
Ethyl 6-hydroxy-2,4,5-trimethylbiphenyl-3-carboxylate (3i)



The reaction of 3-methyl-1-phenylpenta-3,4-dien-2-one (**1i**, 86 mg, 0.5 mmol), ethyl 3-oxobutanoate (**2a**, 78 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 118 mg (83%) of **3i**: Eluent: ethyl acetate / petroleum ether (5%); Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.39 (t, *J* = 7.2 Hz, 3H), 1.97 (s, 3H), 2.19 (s, 3H), 2.27 (s, 3H), 4.39 (q, *J* = 7.2 Hz, 2H), 4.85 (s, 1H), 7.25 (dd, , J_1 = 8.0 Hz, J_2 = 1.2 Hz, 2H), 7.42-7.45 (m, 1H), 7.49-7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.9, 14.3, 17.0, 17.5, 61.0, 120.7, 125.7, 127.7, 128.4, 129.6, 130.2, 130.5,

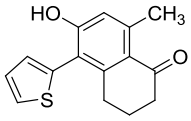
133.7, 135.2, 151.3, 171.0; MS: m/z 285 $[MH]^+$; HRMS calcd for $C_{18}H_{21}O_3$: 285.1491 [M+H], found: 285.1496.

Ethyl 5-ethyl-6-hydroxy-2,4-dimethylbiphenyl-3-carboxylate (3j)



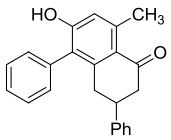
The reaction of 3-ethyl-1-phenylpenta-3,4-dien-2-one (**1j**, 93 mg, 0.5 mmol), ethyl 3-oxobutanoate (**2a**, 78 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 122 mg (82%) of **3j**: Eluent: ethyl acetate / petroleum ether (5%); Syrup; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (t, *J* = 7.6 Hz, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 2.01 (s, 3H), 2.34 (s, 3H), 2.74 (q, *J* = 7.6 Hz, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 4.87 (s, 1H), 7.30 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.4, 14.3, 16.1, 17.5, 19.7, 60.9, 125.9, 126.8, 127.9, 128.4, 129.6, 130.4, 130.6, 132.9, 135.1, 151.2, 171.0; MS: m/z 299 $[MH]^+$; HRMS calcd for $C_{19}H_{23}O_3$: 299.1647 [M+H], found: 299.1651.

6-Hydroxy-8-methyl-5-(thiophen-2-yl)-3,4-dihydronaphthalen-1(2*H*)-one (3k)



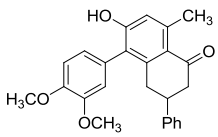
The reaction of 1-(thiophen-2-yl)penta-3,4-dien-2-one (**1k**, 82 mg, 0.5 mmol), cyclohexane-1,3-dione (**2b**, 67 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 101 mg (78%) of **3k**: Eluent: ethyl acetate / petroleum ether (10%); Yellow solid; Mp: 164-165 ℃ (ethanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.92-1.97 (m, 2H), 2.57 (t, *J* = 6.8 Hz, 2H), 2.66 (s, 3H), 2.70 (t, *J* = 6.4 Hz, 2H), 5.99 (s, 1H), 6.77 (s, 1H), 7.01 (d, *J* = 3.2 Hz, 1H), 7.18-7.20 (m, 1H), 7.52 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.6, 23.9, 29.4, 40.3, 117.0, 117.2, 125.1, 128.0, 128.3, 129.2, 134.3, 145.2, 147.8, 157.2, 199.3; MS: m/z 259 $[MH]^+$; HRMS calcd for $C_{15}H_{14}O_2S$: 259.0793 [M+H], found: 259.0798.

6-Hydroxy-8-methyl-3,5-diphenyl-3,4-dihydronaphthalen-1(2*H*)-one (3l)



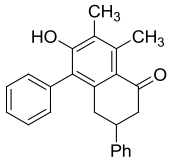
The reaction of 1-phenylpenta-3,4-dien-2-one (**1a**, 79 mg, 0.5 mmol), 5-phenyl cyclohexane-1,3-dione (**2c**, 113 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 133 mg (81%) of **3l**: Eluent: ethyl acetate / petroleum ether (20%); Yellow solid; Mp: 184-185 ℃ (ethanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.72 (s, 3H), 2.75-2.90 (m, 4H), 3.26-3.30 (m, 1H), 5.30 (s, 1H), 6.82 (s, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 2H), 7.26-7.31 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.47-7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.9, 37.0, 40.6, 47.4, 117.7, 124.5, 125.3, 126.8, 128.7, 129.7, 129.8, 129.9, 130.8, 134.2, 143.6, 144.2, 144.8, 156.4, 198.8; MS: m/z 329 $[MH]^+$; HRMS calcd for $C_{23}H_{21}O_2$: 329.1542 [M+H], found: 329.1549.

5-(3,4-Dimethoxyphenyl)-6-hydroxy-8-methyl-3-phenyl-3,4-dihydronaphthalen-1(2*H*)-one (3m)



The reaction of 1-(3,4-dimethoxyphenyl)penta-3,4-dien-2-one (**1c**, 109 mg, 0.5 mmol), 5-phenylcyclohexane-1,3-dione (**2c**, 113 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 149 mg (77%) of **3m**: Eluent: ethyl acetate / petroleum ether (20%); Yellow solid; Mp: 202-204 ℃ (ethanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.71 (s, 3H), 2.74-2.89 (m, 4H), 3.25-3.31 (m, 1H), 3.87 (s, 3H), 3.90 (s, 3H), 5.50 (d, *J* = 4.4 Hz, 1H), 6.68-6.84 (m, 3H), 6.96 (t, *J* = 7.6 Hz, 1H), 7.16-7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.9, 37.1, 40.5, 47.2, 55.9, 56.0, 112.2, 112.5, 113.4, 117.4, 122.1, 123.2, 124.5, 125.1, 125.9, 126.7, 128.7, 143.6, 144.1, 149.1, 149.9, 156.5, 198.7; MS: m/z 389 $[MH]^+$; HRMS calcd for $C_{25}H_{25}O_4$: 389.1753 [M+H], found: 389.1756.

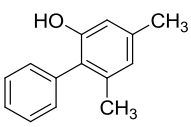
6-Hydroxy-7,8-dimethyl-3,5-diphenyl-3,4-dihydronaphthalen-1(2*H*)-one (3n)



The reaction of 3-methyl-1-phenylpenta-3,4-dien-2-one (**1i**, 86 mg, 0.5 mmol), 5-phenylcyclohexane-1,3-dione (**2c**, 113 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 138 mg (81%) of **3n**: Eluent: ethyl acetate / petroleum ether (5%); Yellow solid; Mp: 140-142 ℃ (ethanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.31 (s, 3H), 2.71 (s, 3H),

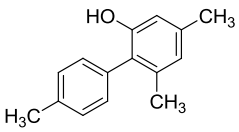
2.75-2.99 (m, 4H), 3.28-3.31 (m, 1H), 5.39 (s, 1H), 7.20-7.26 (m, 4H), 7.29-7.35 (m, 3H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.49-7.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.1, 18.2, 36.8, 40.7, 47.8, 123.2, 124.4, 125.2, 126.77, 126.80, 128.8, 129.99, 130.04, 131.1, 134.5, 141.2, 142.0, 143.8, 154.4, 199.3; MS: m/z 343 $[MH]^+$; HRMS calcd for $C_{24}H_{23}O_2$: 343.1698 [M+H], found: 343.1702.

4,6-Dimethylbiphenyl-2-ol (3o)



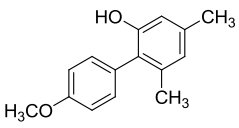
The reaction of 1-phenylpenta-3,4-dien-2-one (**1a**, 79 mg, 0.5 mmol), pentane-2,4-dione (**2d**, 60 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 79 mg (80%) of **3o**: Eluent: ethyl acetate / petroleum ether (5%); Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.06 (s, 3H), 2.34 (s, 3H), 4.75 (s, 1H), 6.71 (d, *J* = 2.8 Hz, 1H), 7.29-7.31 (m, 2H), 7.40-7.44 (m, 1H), 7.49-7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.3, 21.2, 113.3, 122.9, 125.3, 128.1, 129.4, 130.5, 135.4, 137.0, 138.6, 152.7; MS: m/z 199 $[MH]^+$; HRMS calcd for $C_{14}H_{15}O$: 199.1123 [M+H], found: 199.1127.

4,4',6-Trimethylbiphenyl-2-ol (3p)



The reaction of 1-*p*-tolylpenta-3,4-dien-2-one (**1l**, 86 mg, 0.5 mmol), pentane-2,4-dione (**2d**, 60 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 88 mg (83%) of **3p**: Eluent: ethyl acetate / petroleum ether (5%); Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.09 (s, 3H), 2.36 (s, 3H), 2.45 (s, 3H), 4.83 (s, 1H), 6.72 (s, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 21.26, 21.31, 113.2, 122.9, 125.3, 130.2, 130.4, 132.2, 137.1, 137.8, 138.4, 152.9; MS: m/z 213 $[MH]^+$; HRMS calcd for $C_{15}H_{17}O$: 213.1279 [M+H], found: 213.1286.

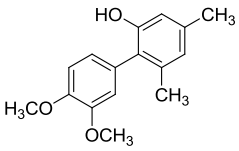
4'-Methoxy-4,6-dimethylbiphenyl-2-ol (3q)



The reaction of 1-(4-methoxyphenyl)penta-3,4-dien-2-one (**1b**, 94 mg, 0.5 mmol), pentane-2,4-dione (**2d**, 60 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in

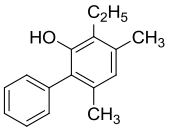
CH_3CN (5 mL) afforded 92 mg (81%) of **3q**: Eluent: ethyl acetate / petroleum ether (5%); Yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.08 (s, 3H), 2.35 (s, 3H), 3.87 (s, 3H), 4.98 (s, 1H), 6.71 (s, 2H), 7.03-7.05 (m, 2H), 7.22 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 21.2, 55.3, 113.2, 114.4, 114.8, 122.8, 125.0, 127.4, 131.6, 132.1, 137.3, 138.3, 153.1, 159.3; MS: m/z 229 $[MH]^+$; HRMS calcd for $C_{15}H_{17}O_2$: 229.1229 [M+H], found: 229.1233.

3',4'-Dimethoxy-4,6-dimethylbiphenyl-2-ol (3r)



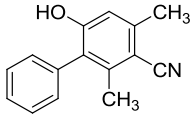
The reaction of 1-(3,4-dimethoxyphenyl)penta-3,4-dien-2-one (**1c**, 109 mg, 0.5 mmol), pentane-2,4-dione (**2d**, 60 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 102 mg (79%) of **3r**: Eluent: ethyl acetate / petroleum ether (5%); Yellow solid; Mp: 143-144 ℃ (ethanol); ^1H NMR (400 MHz, $CDCl_3$) δ: 2.06 (s, 3H), 2.31 (s, 3H), 3.86 (s, 3H), 3.92 (s, 3H), 4.94 (s, 1H), 6.67 (s, 2H), 6.77 (d, J = 1.2 Hz, 1H), 6.82 (dd, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.3, 21.2, 56.0, 56.2, 111.8, 113.1, 113.3, 122.6, 125.1, 127.0, 127.5, 137.2, 138.5, 148.7, 149.6, 153.0; MS: m/z 259 $[MH]^+$; HRMS calcd for $C_{16}H_{19}O_3$: 259.1334 [M+H], found: 259.1339.

3-Ethyl-4,6-dimethylbiphenyl-2-ol (3s)



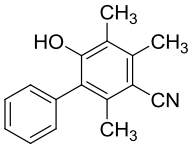
The reaction of 3-ethyl-1-phenylpenta-3,4-dien-2-one (**1j**, 93 mg, 0.5 mmol), pentane-2,4-dione (**2d**, 60 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 93 mg (82%) of **3s**: Eluent: ethyl acetate / petroleum ether (5%); Yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.31 (t, J = 7.2 Hz, 3H), 2.14 (s, 3H), 2.46 (s, 3H), 2.82 (q, J = 7.2 Hz, 2H), 4.87 (s, 1H), 6.82 (s, 1H), 7.42 (d, J = 7.2 Hz, 2H), 7.50-7.53 (m, 1H), 7.60 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 19.2, 19.9, 20.1, 123.5, 125.7, 126.3, 128.1, 129.5, 130.6, 133.6, 136.0, 136.4, 150.6; MS: m/z 227 $[MH]^+$; HRMS calcd for $C_{16}H_{19}O$: 227.1436 [M+H], found: 227.1439.

6-Hydroxy-2,4-dimethylbiphenyl-3-carbonitrile (3t)



The reaction of 1-phenylpenta-3,4-dien-2-one (**1a**, 79 mg, 0.5 mmol), 3-oxobutanenitrile (**2e**, 50 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 86 mg (78%) of **3t**: Eluent: ethyl acetate / petroleum ether (10%); Yellow solid; Mp: 219-220 ℃ (ethanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.24 (s, 3H), 2.52 (s, 3H), 6.78 (s, 1H), 7.23 (d, *J* = 8.0 Hz,, 2H), 7.46-7.53 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.3, 20.8, 105.8, 114.7, 118.0, 126.7, 128.9, 129.8, 130.3, 133.6, 142.0, 143.5, 156.2; MS: m/z 224 $[MH]^+$; HRMS calcd for $C_{15}H_{14}NO$: 224.1075 [M+H], found: 224.1078.

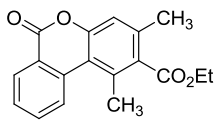
6-Hydroxy-2,4,5-trimethylbiphenyl-3-carbonitrile (3u)



The reaction of 3-methyl-1-phenylpenta-3,4-dien-2-one (**1i**, 86 mg, 0.5 mmol), 3-oxobutanenitrile (**2e**, 50 mg, 0.6 mmol) and Cs_2CO_3 (163 mg, 0.5 mmol) in CH_3CN (5 mL) afforded 101 mg (85%) of **3u**: Eluent: ethyl acetate / petroleum ether (5%); White solid; Mp: 142-143 ℃ (ethanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 2.22 (s, 3H), 2.52 (s, 3H), 5.25 (s, 1H), 7.23-7.28 (m, 2H), 7.48-7.56 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.1, 18.5, 19.1, 105.9, 118.7, 121.6, 126.3, 129.0, 129.9, 130.3, 134.0, 138.5, 141.5, 154.1; MS: m/z 238 $[MH]^+$; HRMS calcd for $C_{16}H_{16}NO$: 238.1232 [M+H], found: 238.1237.

3. Experimental procedures for the synthesis and spectroscopic data of 4

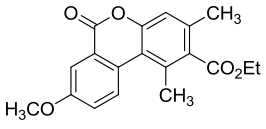
Ethyl 1,3-dimethyl-6-oxo-6*H*-benzo[*c*]chromene-2-carboxylate (4a)



Typical procedure: To a flask containing 1-phenylpenta-3,4-dien-2-one (**1a**, 32 mg, 0.2 mmol) and ethyl 3-oxobutanoate (**2a**, 31 mg, 0.24 mmol) were added CH_3CN (4 mL), Cs_2CO_3 (65 mg, 0.2 mmol), and anhydrous Na_2SO_4 (28 mg, 0.2 mmol). The mixture was stirred at 80 °C for 4 h. At this stage, $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) were added and the resulting mixture was stirred at 80 °C under CO (1atm). Upon completion as monitored by TLC,

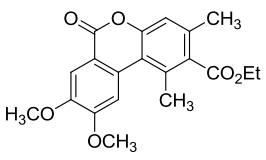
the reaction was quenched with aqueous NH_4Cl. The mixture was filtered on diatomite and the filtrate was extracted with ethyl acetate (5 mL × 3). The combined organic layer was washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purified by chromatography on silica-gel (petroleum ether / ethyl acetate = 20:1) to afford 40 mg (68%) of **4a**: Yellow solid; Mp: 145-147 °C (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.45 (t, *J* = 7.2 Hz, 3H), 2.40 (s, 3H), 2.79 (s, 3H), 4.47 (q, *J* = 7.2 Hz, 2H), 7.14 (s, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.81-7.85 (m, 1 H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.6, 21.8, 61.5, 115.7, 117.1, 122.2, 126.4, 128.2, 130.9, 132.8, 133.8, 134.2, 135.4, 136.8, 151.9, 161.0, 169.7; MS: m/z 297 $[MH]^+$; HRMS calcd for $C_{18}H_{17}O_4$: 297.1127 [M+H], found: 297.1131.

Ethyl 8-methoxy-1,3-dimethyl-6-oxo-6*H*-benzo[*c*]chromene-2-carboxylate (4b)



The reaction of 1-(4-methoxyphenyl)penta-3,4-dien-2-one (**1b**, 38 mg, 0.2 mmol), ethyl 3-oxobutanoate (**2a**, 31 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 48 mg (74%) of **4b**: Eluent: ethyl acetate / petroleum ether (10%); Yellow solid; Mp: 178-179 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.43 (t, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 2.75 (s, 3H), 3.94 (s, 3H), 4.45 (q, *J* = 7.2 Hz, 2H), 7.11 (s, 1H), 7.36-7.39 (m, 1H), 7.90 (d, *J* = 3.2 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.5, 21.8, 55.7, 61.5, 112.0, 115.7, 117.0, 122.9, 123.5, 127.9, 128.6, 131.9, 133.6, 135.5, 150.9, 159.0, 161.0, 169.7; MS: m/z 327 $[MH]^+$; HRMS calcd for $C_{19}H_{19}O_5$: 327.1232 [M+H], found: 327.1236.

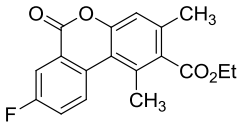
Ethyl 8,9-dimethoxy-1,3-dimethyl-6-oxo-6*H*-benzo[*c*]chromene-2-carboxylate (4c)



The reaction of 1-(3,4-dimethoxyphenyl)penta-3,4-dien-2-one (**1c**, 44 mg, 0.2 mmol), ethyl 3-oxobutanoate (**2a**, 31 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc

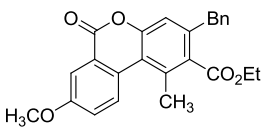
(100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 52 mg (73%) of **4c**: Eluent: ethyl acetate / petroleum ether (20%); Yellow solid; Mp: 200-201 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.43 (t, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 2.80 (s, 3H), 4.02 (s, 3H), 4.04 (s, 3H), 4.45 (q, *J* = 7.2 Hz, 2H), 7.11 (s, 1H), 7.71 (s, 1H), 7.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.5, 21.7, 56.11, 56.13, 61.5, 108.1, 110.8, 115.3, 115.5, 117.1, 130.3, 131.4, 133.6, 135.7, 148.9, 151.5, 153.8, 160.7, 169.7; MS: m/z 357 $[MH]^+$; HRMS calcd for $C_{20}H_{21}O_6$: 357.1338 [M+H], found: 357.1342.

Ethyl 8-fluoro-1,3-dimethyl-6-oxo-6*H*-benzo[*c*]chromene-2-carboxylate (4d)



The reaction of 1-(4-fluorophenyl)penta-3,4-dien-2-one (**1d**, 35 mg, 0.2 mmol), ethyl 3-oxobutanoate (**2a**, 31 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 36 mg (58%) of **4d**: Eluent: ethyl acetate / petroleum ether (10%); Yellow solid; Mp: 181-183 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.43 (t, *J* = 7.2 Hz, 3H), 2.39 (s, 3H), 2.75 (s, 3H), 4.46 (q, *J* = 7.2 Hz, 2H), 7.13 (s, 1H), 7.51-7.56 (m, 1H), 8.12-8.14 (m, 1H), 8.28-8.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 19.6, 21.8, 61.6, 115.1, 116.5, 116.8, 117.2, 122.0, 122.2, 124.3, 124.4, 128.7, 128.8, 131.9, 132.0, 132.4, 134.0, 136.8, 151.4, 160.09, 160.12, 160.4, 162.9, 169.6; MS: m/z 315 $[MH]^+$; HRMS calcd for $C_{18}H_{16}FO_4$: 315.1033 [M+H], found: 315.1036.

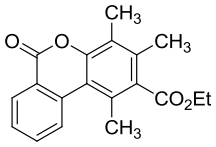
Ethyl 3-benzyl-8-methoxy-1-methyl-6-oxo-6*H*-benzo[*c*]chromene-2-carboxylate (4e)



The reaction of 1-(4-methoxyphenyl)-5-phenylpenta-3,4-dien-2-one (**1e**, 53 mg, 0.2 mmol), ethyl 3-oxobutanoate (**2a**, 31 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 60 mg (75%) of **4e**: Eluent: ethyl acetate / petroleum ether (10%); Yellow solid; Mp: 124-125 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.30 (t, *J* = 7.2 Hz, 3H), 2.76 (s, 3H), 3.95 (s, 3H), 4.04 (s, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 7.02 (s, 1H), 7.04-7.32 (m, 5H),

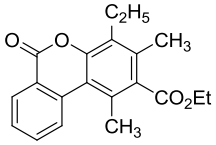
7.38 (dd, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 1H), 7.90 (d, J = 3.2 Hz, 1H), 8.23 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 21.9, 39.1, 55.8, 61.5, 112.1, 116.4, 117.1, 123.0, 123.7, 126.6, 128.2, 128.57, 128.63, 129.2, 132.3, 133.4, 138.85, 138.88, 151.2, 159.2, 161.0, 169.7; MS: m/z 403 $[MH]^+$; HRMS calcd for $C_{25}H_{23}O_5$: 403.1545 [M+H], found: 403.1548.

Ethyl 1,3,4-trimethyl-6-oxo-6*H*-benzo[*c*]chromene-2-carboxylate (4f)



The reaction of 3-methyl-1-phenylpenta-3,4-dien-2-one (**1i**, 34 mg, 0.2 mmol), ethyl 3-oxobutanoate (**2a**, 31 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 47 mg (76%) of **4f**: Eluent: ethyl acetate / petroleum ether (10%); White solid; Mp: 99-101 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.43 (t, J = 7.2 Hz, 3H), 2.31 (s, 3H), 2.41 (s, 3H), 2.72 (s, 3H), 4.46 (q, J = 7.2 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.45 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.2, 14.2, 17.3, 21.5, 61.5, 115.7, 122.1, 123.8, 126.7, 128.0, 129.0, 130.6, 133.8, 134.0, 134.9, 135.8, 150.0, 161.1, 170.4; MS: m/z 311 $[MH]^+$; HRMS calcd for $C_{19}H_{19}O_4$: 311.1283 [M+H], found: 311.1286.

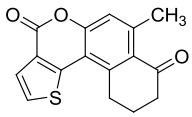
Ethyl 4-ethyl-1,3-dimethyl-6-oxo-6*H*-benzo[*c*]chromene-2-carboxylate (4g)



The reaction of 3-ethyl-1-phenylpenta-3,4-dien-2-one (**1j**, 37 mg, 0.2 mmol), ethyl 3-oxobutanoate (**2a**, 31 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 45 mg (70%) of **4g**: Eluent: ethyl acetate / petroleum ether (10%); White solid; Mp: 112-114 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.18 (t, J = 7.2 Hz, 3H), 1.42 (t, J = 7.6 Hz, 3H), 2.32 (s, 3H), 2.70 (s, 3H), 2.91 (q, J = 7.6 Hz, 2H), 4.44 (q, J = 7.2 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.42 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 14.3, 16.4, 19.7, 21.5, 61.5, 115.8, 122.1, 126.6, 128.0, 129.2, 129.6, 130.5, 134.0,

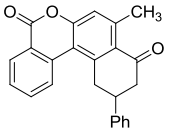
134.1, 134.2, 135.8, 149.8, 161.1, 170.4; MS: m/z 325 $[MH]^+$; HRMS calcd for $C_{20}H_{21}O_4$: 325.1440 [M+H], found: 325.1449.

7-Methyl-10,11-dihydro-4*H*-benzo[*f*]thieno[3,2-*c*]chromene-4,8(9*H*)-dione (4h)



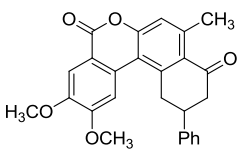
The reaction of 1-(thiophen-2-yl)penta-3,4-dien-2-one (**1k**, 33 mg, 0.2 mmol), cyclohexane-1,3-dione (**2b**, 27 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 39 mg (69%) of **4h**: Eluent: ethyl acetate / petroleum ether (10%); White solid; Mp: 125-127 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.30 (t, *J* = 6.8 Hz, 2H), 2.71-2.74 (m, 5H), 3.34 (t, *J* = 6.4 Hz, 2H), 7.23 (s, 1H), 7.55 (d, *J* = 5.6 Hz, 1H), 7.80 (d, *J* =5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.1, 23.9, 29.8, 39.7, 114.6, 119.5, 125.4, 126.7, 126.9, 128.8, 142.3, 144.2, 146.0, 153.3, 156.9, 198.6; MS: m/z 285 $[MH]^+$; HRMS calcd for $C_{16}H_{13}O_3S$: 285.0585 [M+H], found: 285.0591.

8-Methyl-11-phenyl-11,12-dihydro-5*H*-dibenzo[*c*,*f*]chromene-5,9(10*H*)-dione (4i)



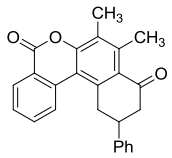
The reaction of 1-phenylpenta-3,4-dien-2-one (**1a**, 32 mg, 0.2 mmol), 5-phenylcyclohexane-1,3-dione (**2c**, 45 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 47 mg (66%) of **4i**: Eluent: ethyl acetate / petroleum ether (20%); Yellow solid; Mp: 158-160 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.76 (s, 3H), 2.99-3.02 (m, 2H), 3.25-3.28 (m, 1H), 3.52-3.58 (m, 1H), 3.74 (dd, J_1 = 15.2 Hz, J_2 = 1.6 Hz, 1H), 7.20 (s, 1H), 7.31-7.34 (m, 3H), 7.39-7.42 (m, 2H), 7.57-7.61 (m, 1H), 7.75-7.79 (m, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.6, 29.7, 41.2, 47.4, 119.8, 122.4, 126.7, 126.8, 126.88, 126.94, 128.9, 129.0, 129.3, 129.9, 130.9, 134.7, 142.9, 143.6, 144.2, 156.0, 160.7, 198.6; MS: m/z 355 $[MH]^+$; HRMS calcd for $C_{24}H_{19}O_3$: 355.1334 [M+H], found: 355.1338.

2,3-Dimethoxy-8-methyl-11-phenyl-11,12-dihydro-5*H*-dibenzo[*c*,*f*]chromene-5,9(10*H*)-dione (4j)



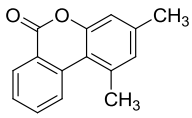
The reaction of 1-(3,4-dimethoxyphenyl)penta-3,4-dien-2-one (**1c**, 44 mg, 0.2 mmol), 5-phenylcyclohexane-1,3-dione (**2c**, 45 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 57 mg (69%) of **4j**: Eluent: ethyl acetate / petroleum ether (20%); White solid; Mp: 206-208 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.75 (s, 3H), 2.90-3.07 (m, 2H), 3.27-3.30 (m, 1H), 3.52-3.59 (m, 1H), 3.80-3.93 (m, 4H), 4.01 (s, 3H), 7.19 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 3H), 7.32-7.40 (m, 2H), 7.53 (s, 1H), 7.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.5, 40.4, 40.8, 46.3, 56.1, 56.3, 108.9, 111.1, 115.6, 115.8, 119.7, 126.5, 127.3, 129.0, 129.1, 129.7, 142.5, 142.9, 143.4, 149.3, 153.1, 153.8, 160.5, 198.5; MS: m/z 415 $[MH]^+$; HRMS calcd for $C_{26}H_{23}O_5$: 415.1545 [M+H], found: 415.1549.

7,8-Dimethyl-11-phenyl-11,12-dihydro-5*H*-dibenzo[*c*,*f*]chromene-5,9(10*H*)-dione (4k)



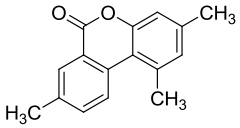
The reaction of 3-methyl-1-phenylpenta-3,4-dien-2-one (**1i**, 34 mg, 0.2 mmol), 5-phenylcyclohexane-1,3-dione (**2c**, 45 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 52 mg (71%) of **4k**: Eluent: ethyl acetate / petroleum ether (10%); White solid; Mp: 182-184 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.44 (s, 3H), 2.64 (s, 3H), 2.91-3.05 (m, 2H), 3.21 (t, *J* = 12.4 Hz, 1H), 3.45 (t, *J* = 12.4 Hz, 1H), 3.63 (t, *J* = 12.4 Hz, 1H), 7.26-7.41 (m, 5H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.3, 18.1, 40.0, 41.3, 46.5, 115.0, 122.2, 125.4, 126.9, 127.15, 127.21, 128.3, 128.9, 130.3, 130.5, 134.1, 134.9, 139.9, 141.9, 143.0, 151.6, 160.7, 199.7; MS: m/z 369 $[MH]^+$; HRMS calcd for $C_{25}H_{21}O_3$: 369.1491 [M+H], found: 369.1494.

1,3-Dimethyl-6*H*-benzo[*c*]chromen-6-one (4l)



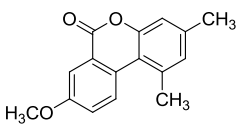
The reaction of 1-phenylpenta-3,4-dien-2-one (**1a**, 32 mg, 0.2 mmol), pentane-2,4-dione (**2d**, 24 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 32 mg (72%) of **4l**: Eluent: ethyl acetate / petroleum ether (5%); White solid; Mp: 137-139 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.41 (s, 3H), 2.86 (s, 3H), 7.00 (s, 1H), 7.09 (s, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 8.36 (d, *J* = 8.4 Hz., 1H), 8.49 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.0, 25.4, 114.8, 116.4, 121.7, 125.8, 127.6, 128.1, 130.0, 130.8, 134.2, 135.8, 136.3, 139.9, 152.2, 161.5; MS: m/z 225 $[MH]^+$; HRMS calcd for $C_{15}H_{13}O_2$: 225.0916 [M+H], found: 225.0919.

1,3,8-Trimethyl-6*H*-benzo[*c*]chromen-6-one (4m)



The reaction of 1-*p*-tolylpenta-3,4-dien-2-one (**1l**, 34 mg, 0.2 mmol), pentane-2,4-dione (**2d**, 24 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 31 mg (66%) of **4m**: Eluent: ethyl acetate / petroleum ether (5%); White solid; Mp: 170-171 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.41 (s, 3H), 2.50 (s, 3H), 2.84 (s, 3H), 6.98 (s, 1H), 7.08 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.0, 21.3, 25.4, 115.0, 116.3, 125.9, 128.9, 129.9, 130.1, 130.8, 133.7, 135.4, 137.8, 139.4, 152.0, 161.8; MS: m/z 239 $[MH]^+$; HRMS calcd for $C_{16}H_{15}O_2$: 239.1072 [M+H], found: 239.1077.

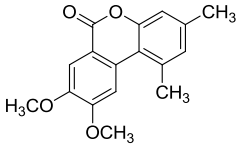
8-Methoxy-1,3-dimethyl-6*H*-benzo[*c*]chromen-6-one (4n)



The reaction of 1-(4-methoxyphenyl)penta-3,4-dien-2-one (**1b**, 38 mg, 0.2 mmol), pentane-2,4-dione (**2d**, 24 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN

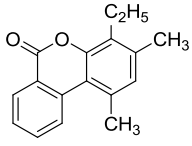
(4 mL) under CO (1atm) afforded 36 mg (70%) of **4n**: Eluent: ethyl acetate / petroleum ether (5%); White solid; Mp: 184-186 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 2.83 (s, 3H), 3.95 (s, 3H), 6.98 (s, 1H), 7.08 (s, 1H), 7.37 (dd, J_1 = 9.2 Hz, J_2 = 2.0 Hz, 1H), 7.92 (d, J = 2.0 Hz, 1H), 8.30 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.9, 21.2, 55.3, 113.0, 114.8, 122.8, 124.8, 127.1, 127.5, 129.9, 131.6, 134.9, 138.4, 153.0, 159.3, 161.6; MS: m/z 255 $[MH]^+$; HRMS calcd for $C_{16}H_{15}O_3$: 255.1021 [M+H], found: 255.1023.

8,9-Dimethoxy-1,3-dimethyl-6*H*-benzo[*c*]chromen-6-one (4o)



The reaction of 1-(3,4-dimethoxyphenyl)penta-3,4-dien-2-one (**1c**, 44 mg, 0.2 mmol), pentane-2,4-dione (**2d**, 24 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 40 mg (70%) of **4o**: Eluent: ethyl acetate / petroleum ether (10%); White solid; Mp: 211-213 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 2.87 (s, 3H), 4.02 (s, 3H), 4.06 (s, 3H), 6.97 (s, 1H), 7.08 (s, 1H), 7.80 (s, 1H), 7.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.0, 25.2, 56.1, 56.2, 107.7, 111.0, 114.9, 115.1, 116.5, 130.0, 131.5, 134.5, 139.1, 148.7, 152.0, 154.0 161.4; MS: m/z 285 $[MH]^+$; HRMS calcd for $C_{17}H_{17}O_4$: 285.1127 [M+H], found: 285.1132.

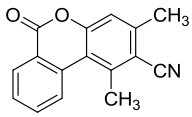
4-Ethyl-1,3-dimethyl-6*H*-benzo[*c*]chromen-6-one (4p)



The reaction of 3-ethyl-1-phenylpenta-3,4-dien-2-one (**1j**, 37 mg, 0.2 mmol), pentane-2,4-dione (**2d**, 24 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 35 mg (69%) of **4p**: Eluent: ethyl acetate / petroleum ether (10%); White solid; Mp: 158-160 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.22 (t, J = 7.2 Hz, 3H), 2.43 (s, 3H), 2.60 (s, 3H), 3.03 (q, J = 7.2 Hz, 1H), 7.26 (s, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.79 (t, J = 7.2 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.47 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.9, 20.2, 20.6,

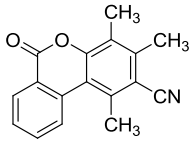
21.2, 116.4, 122.1, 124.9, 126.6, 128.0, 130.2, 130.6, 130.8, 133.9, 136.1, 145.2, 147.5, 161.4; MS: m/z 253 $[MH]^+$; HRMS calcd for $C_{17}H_{17}O_2$: 253.1229 [M+H], found: 253.1232.

1,3-Dimethyl-6-oxo-6*H*-benzo[*c*]chromene-2-carbonitrile (4q)



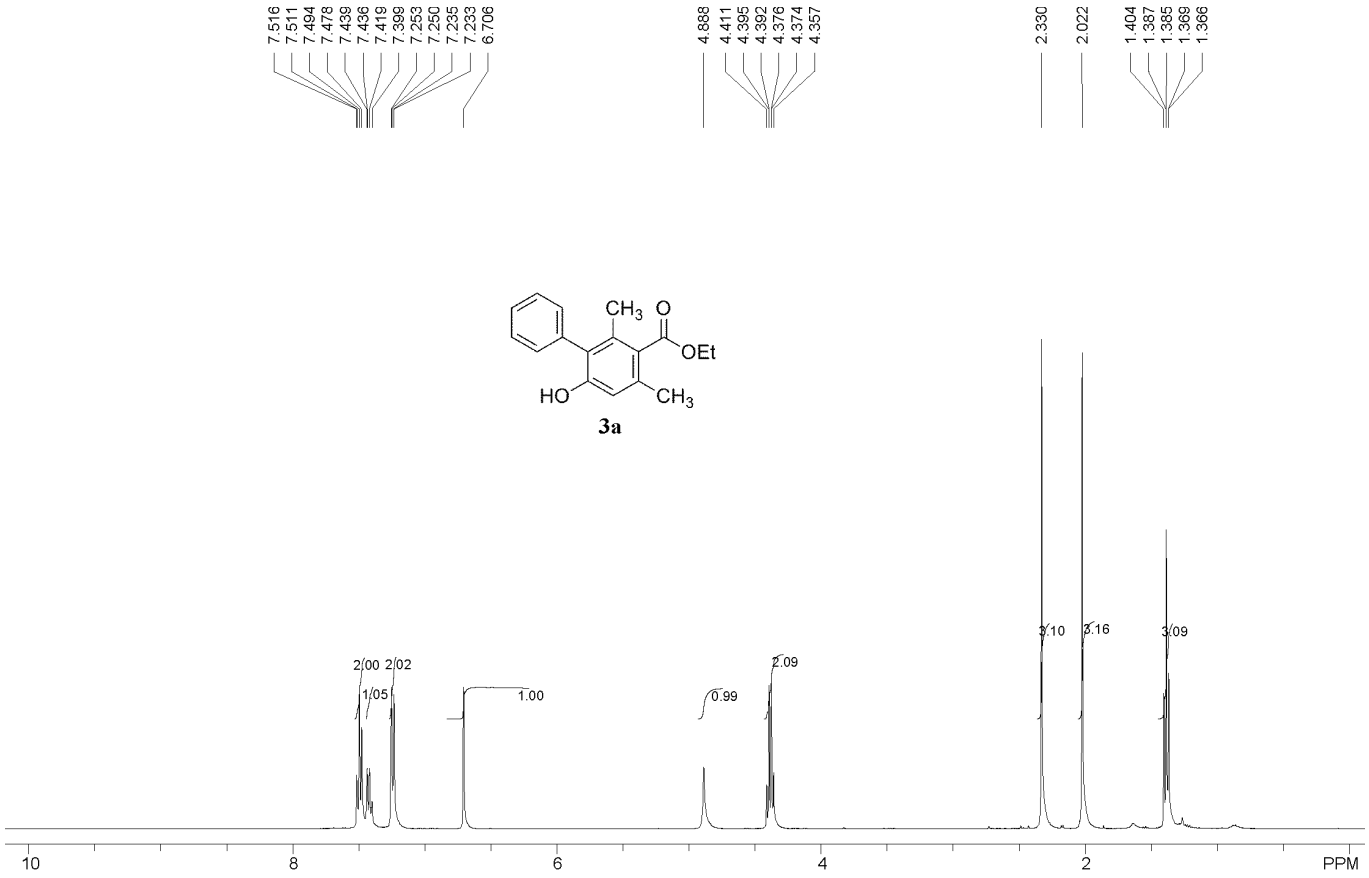
The reaction of 1-phenylpenta-3,4-dien-2-one (**1a**, 32 mg, 0.2 mmol), 3-oxobutanenitrile (**2e**, 20 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 33 mg (67%) of **4q**: Eluent: ethyl acetate / petroleum ether (10%); White solid; Mp: 257-259 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.62 (s, 3H), 3.08 (s, 3H), 7.19 (s, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.1, 23.4, 112.6, 116.5, 117.0, 117.6, 122.1, 126.4, 129.0, 131.1, 134.5, 134.7, 141.1, 143.9, 153.9, 160.3; MS: m/z 250 $[MH]^+$; HRMS calcd for $C_{16}H_{12}NO_2$: 250.0868 [M+H], found: 250.0881.

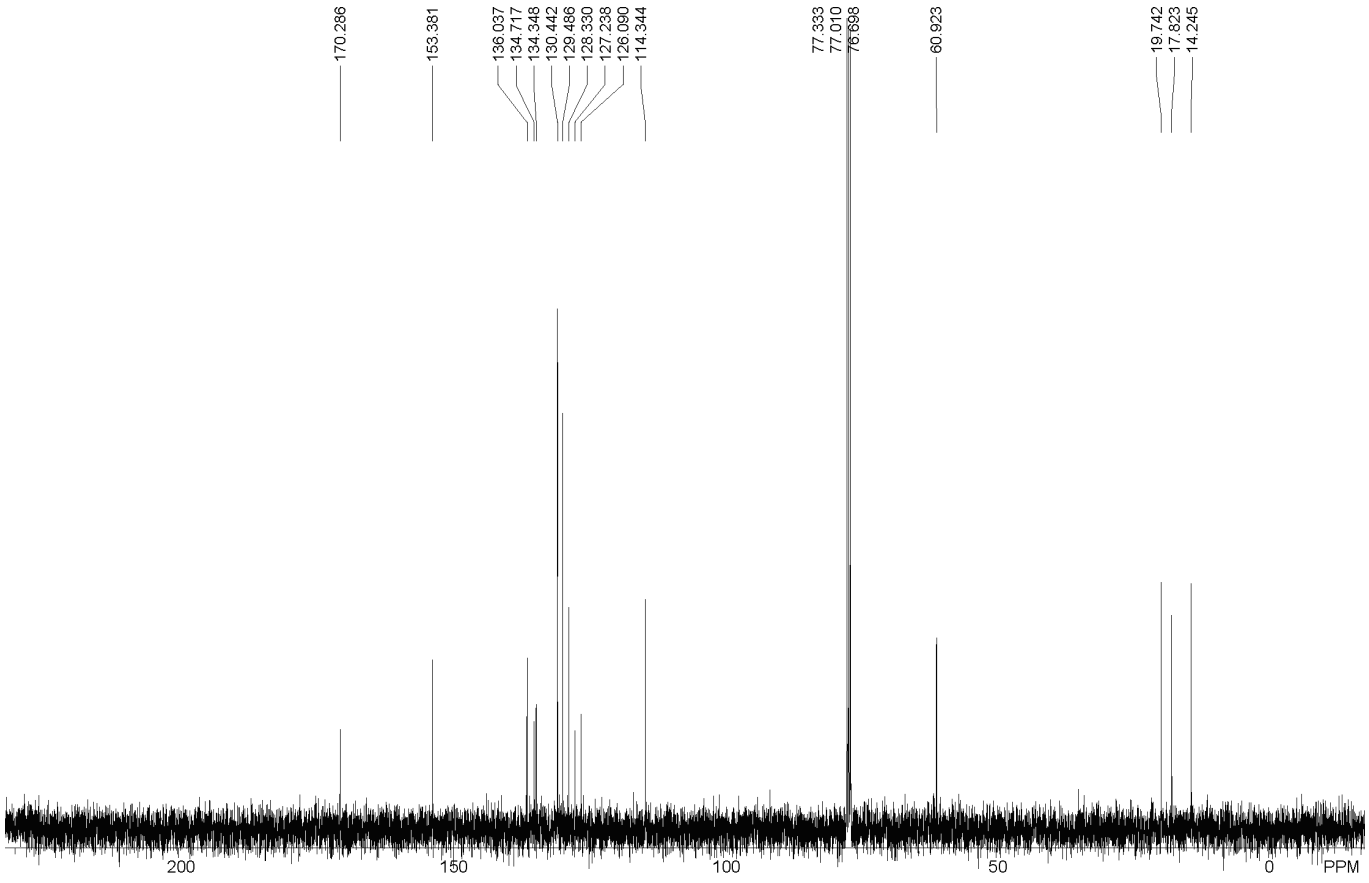
1,3,4-Trimethyl-6-oxo-6*H*-benzo[*c*]chromene-2-carbonitrile (4r)

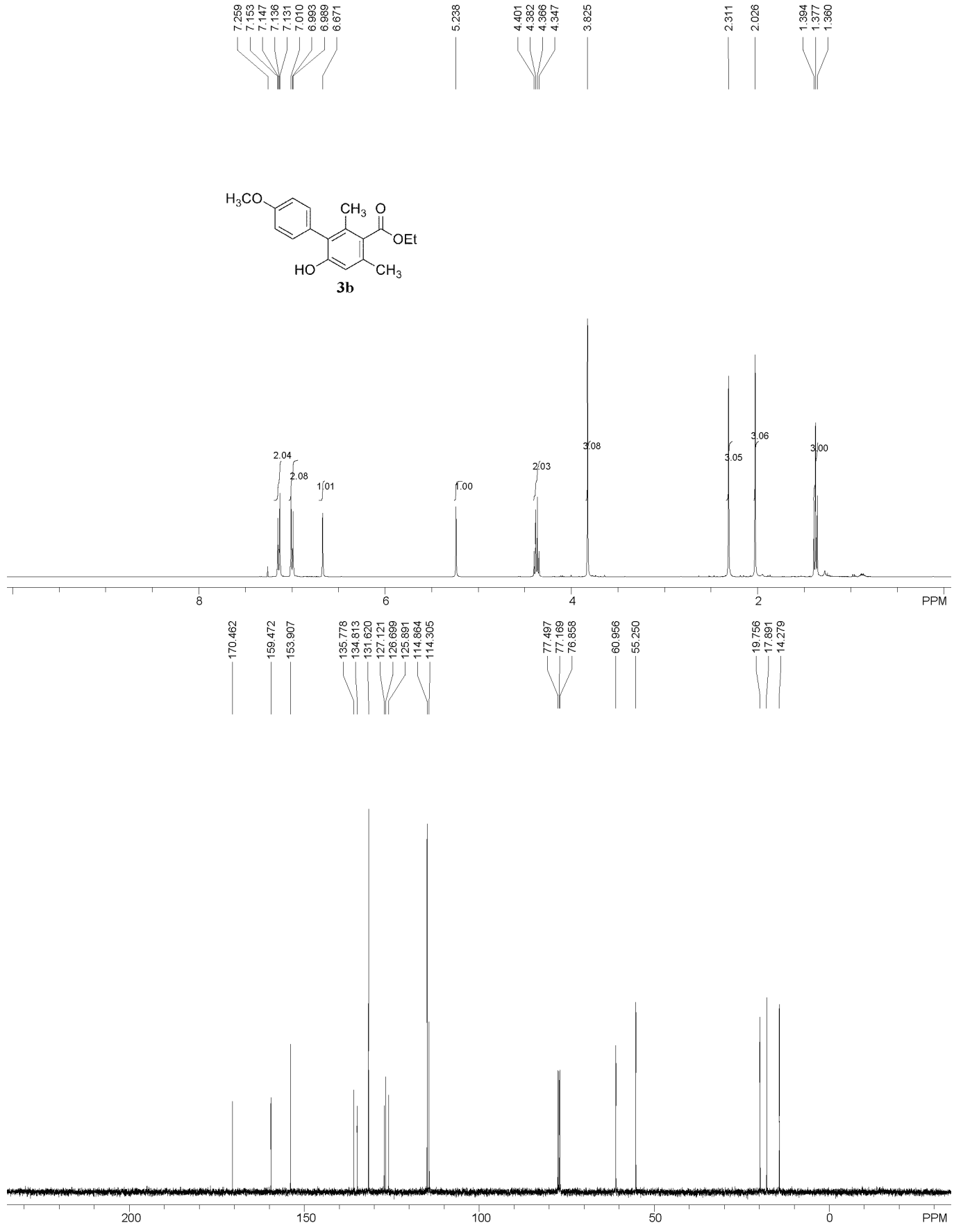


The reaction of 3-methyl-1-phenylpenta-3,4-dien-2-one (**1i**, 34 mg, 0.2 mmol), 3-oxobutanenitrile (**2e**, 20 mg, 0.24 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), anhydrous Na_2SO_4 (28 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and AgOAc (100 mg, 0.6 mmol) in CH_3CN (4 mL) under CO (1atm) afforded 42 mg (80%) of **4r**: Eluent: ethyl acetate / petroleum ether (10%); White solid; Mp: 225-226 ℃ (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.42 (s, 3H), 2.60 (s, 3H), 3.01 (s, 3H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.4, 19.0, 23.2, 112.5, 116.3, 117.7, 121.8, 124.7, 126.6, 128.8, 130.7, 134.5, 134.8, 137.6, 142.1, 152.0, 160.2; MS: m/z 264 $[MH]^+$; HRMS calcd for $C_{17}H_{14}NO_2$: 264.1025 [M+H], found: 264.1030.

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



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6.989
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4.366
4.347
3.825
2.311
2.026
1.394
1.377
1.360
H3CO
CH3
O
OEt
HO
CH3
3b
2.04
2.08
1.01
1.00
2.03
3.08
3.05
3.06
3.00
8
6
4
2
PPM
170.462
159.472
153.907
135.778
134.813
131.620
127.121
126.699
125.891
114.864
114.305
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76.858
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50
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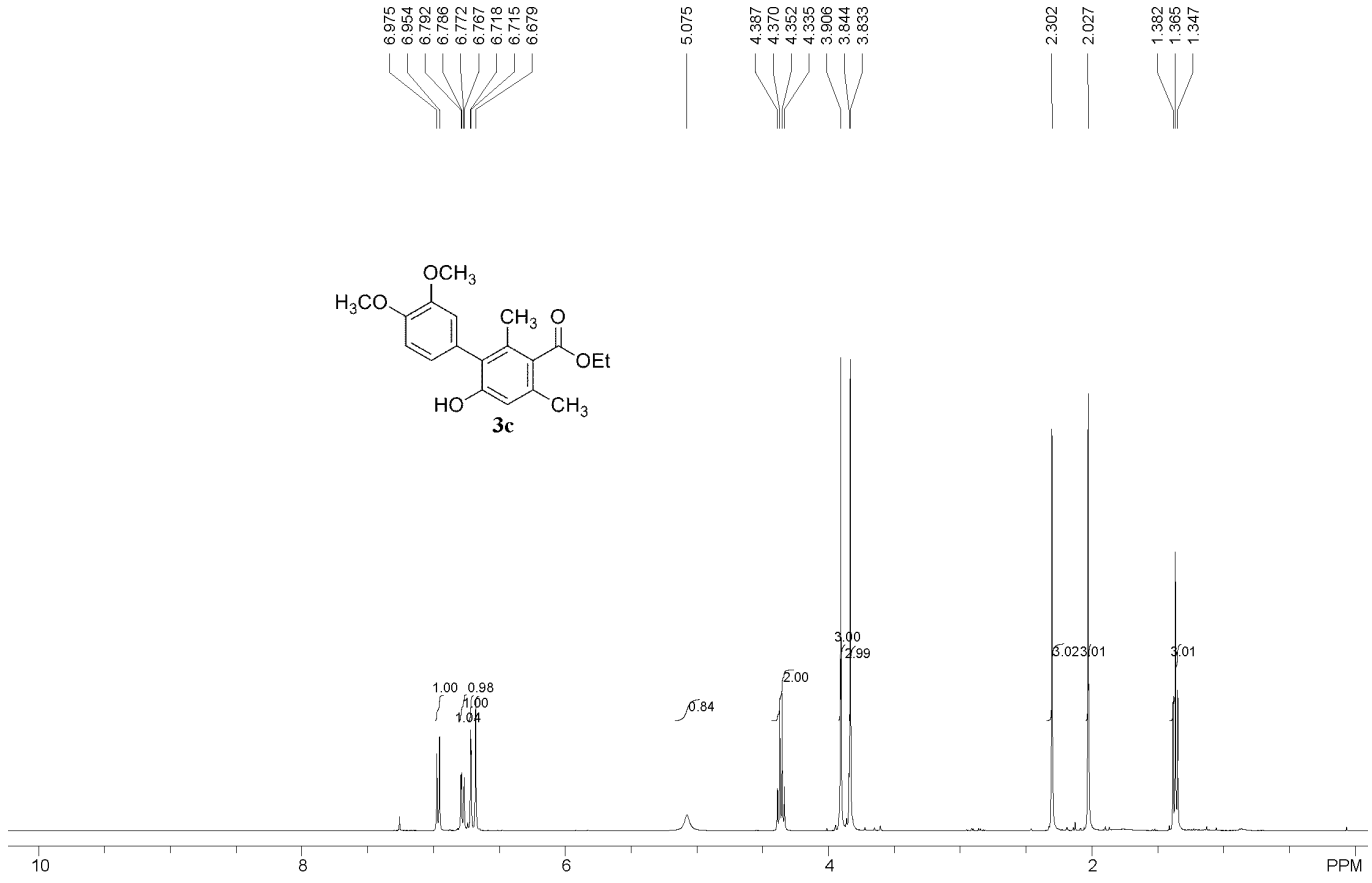
PPM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6.792
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6.718
6.715
6.679
5.075
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4.370
4.352
4.335
3.906
3.844
3.833
2.302
2.027
1.382
1.365
1.347
OCH3
H3CO
CH3
O
OEt
HO
CH3
3c
1.00
0.98
1.00
1.04
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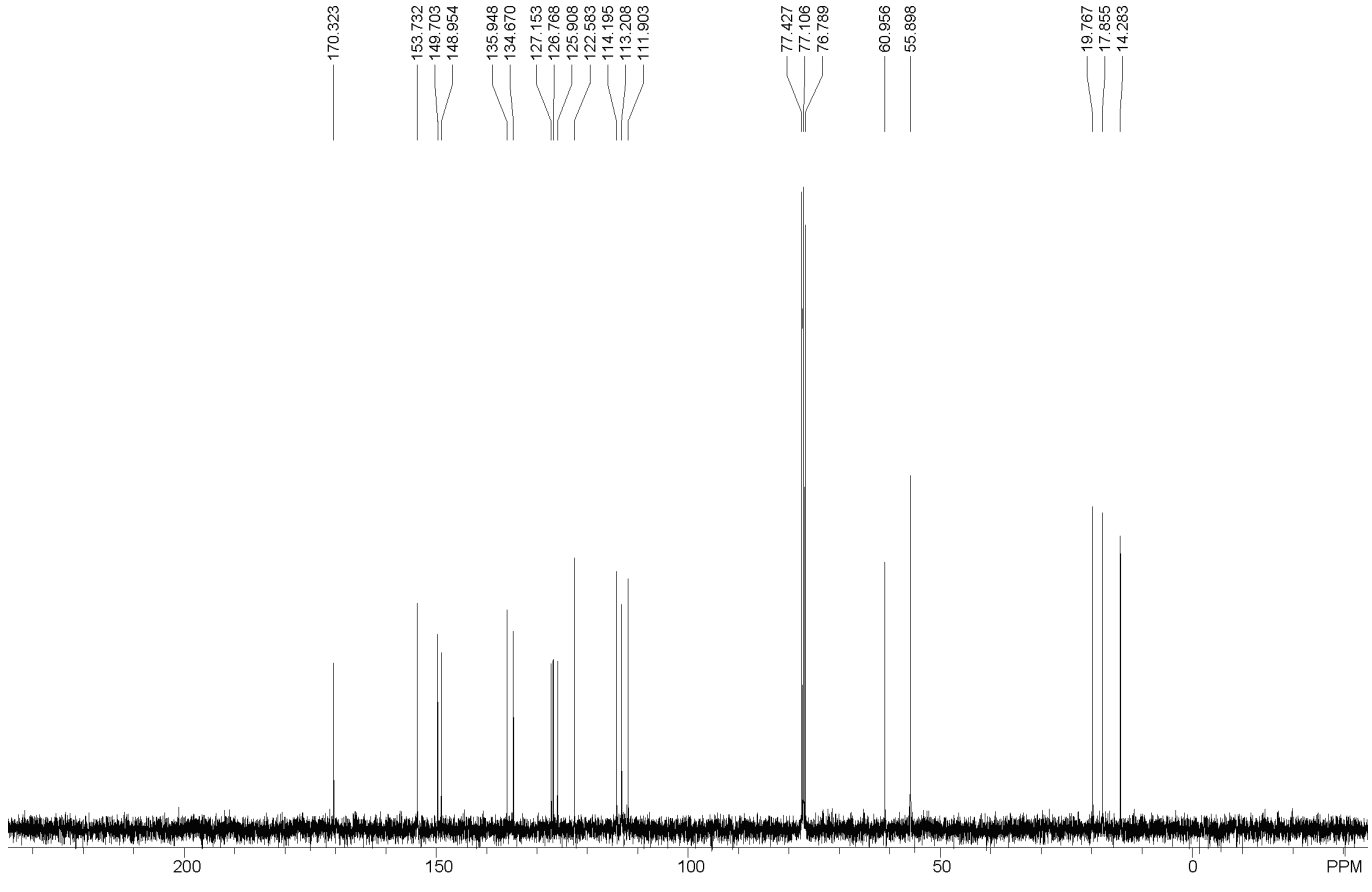
2.00
3.00
2.99
3.023.01
3.01
10
8
6
4
2
PPM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126.768
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122.583
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113.208
111.903
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100
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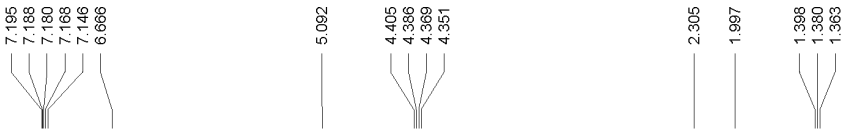
0
PPM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7.188
7.180
7.168
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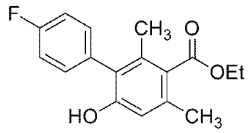
6.666
5.092
4.405
4.386
4.369
4.351
2.305
1.997
1.398
1.380
1.363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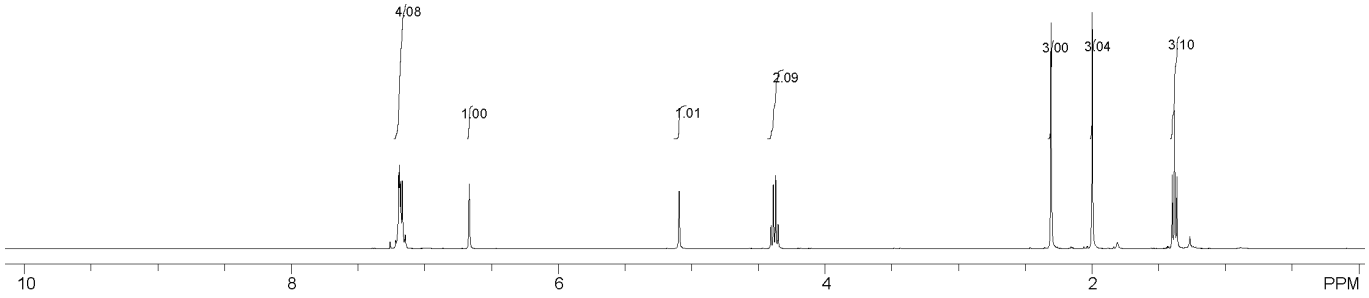
CH3
O
OEt
HO
CH3

3d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1.01
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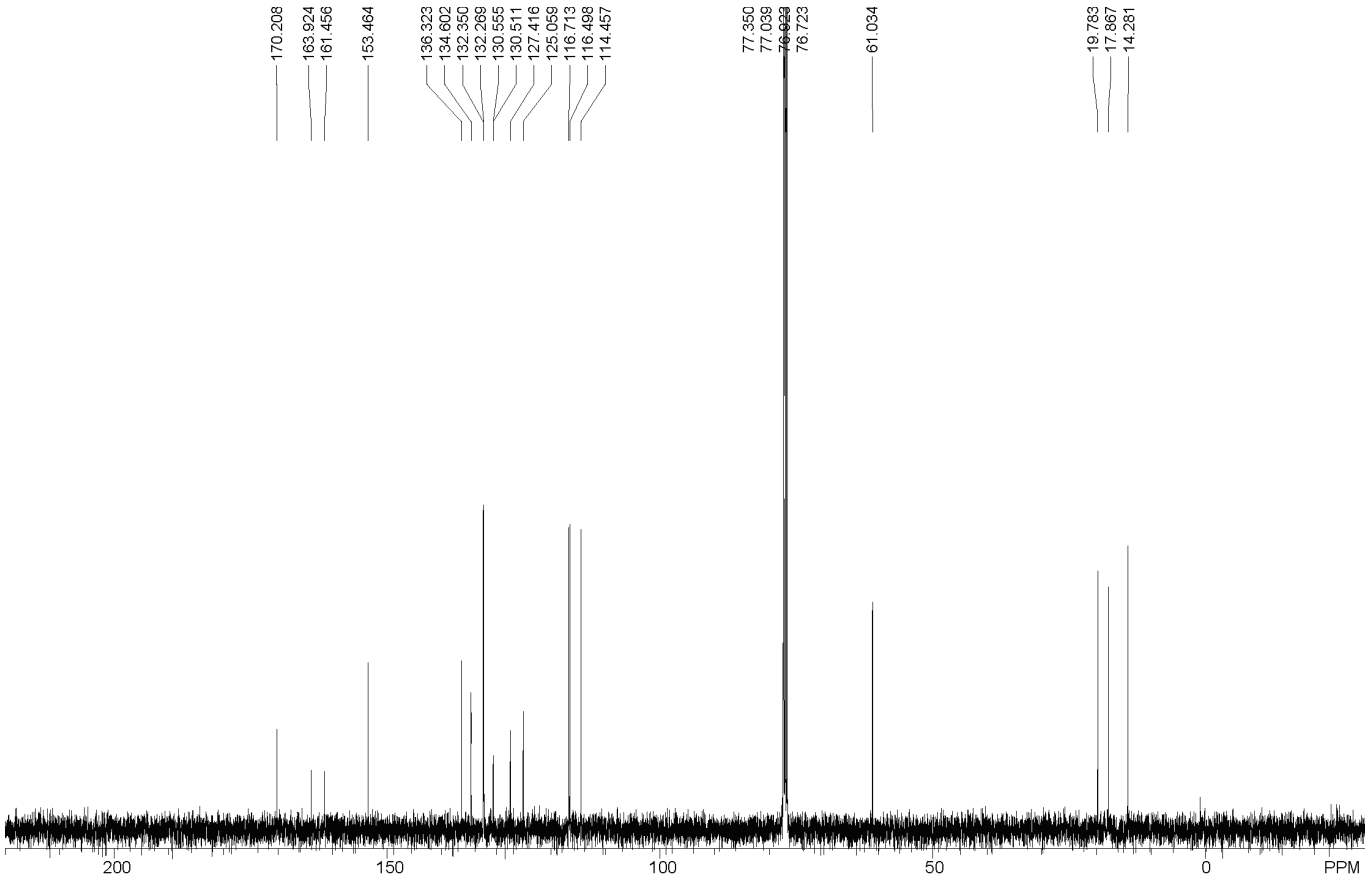
3.00
3.04
3.10
10
8
6
4
2
PPM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132.350
132.269
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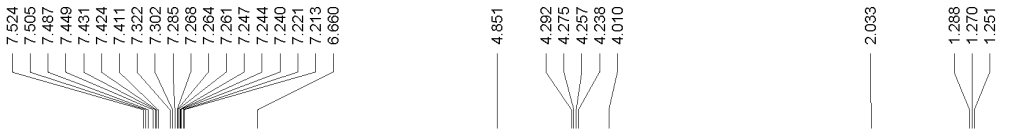
130.511
127.416
125.059
116.713
116.498
114.457
77.350
77.039
76.723
61.034
19.783
17.867
14.281
200
150
100
50
0
PPM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7.322
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7.268
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7.261
7.247
7.244
7.240
7.221
7.213
6.660
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4.275
4.257
4.238
4.010
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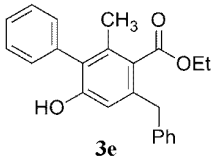
1.288
1.270
1.251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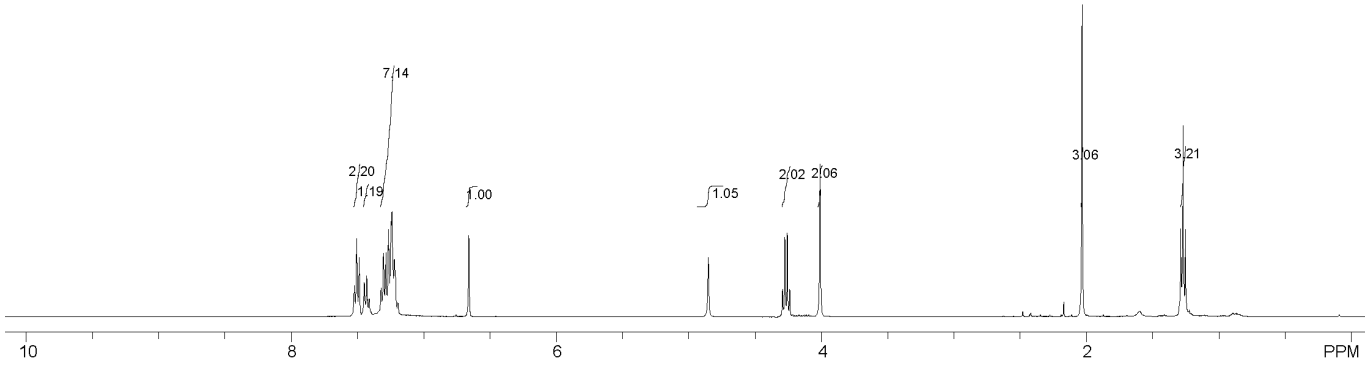
O
OEt
HO
Ph

3e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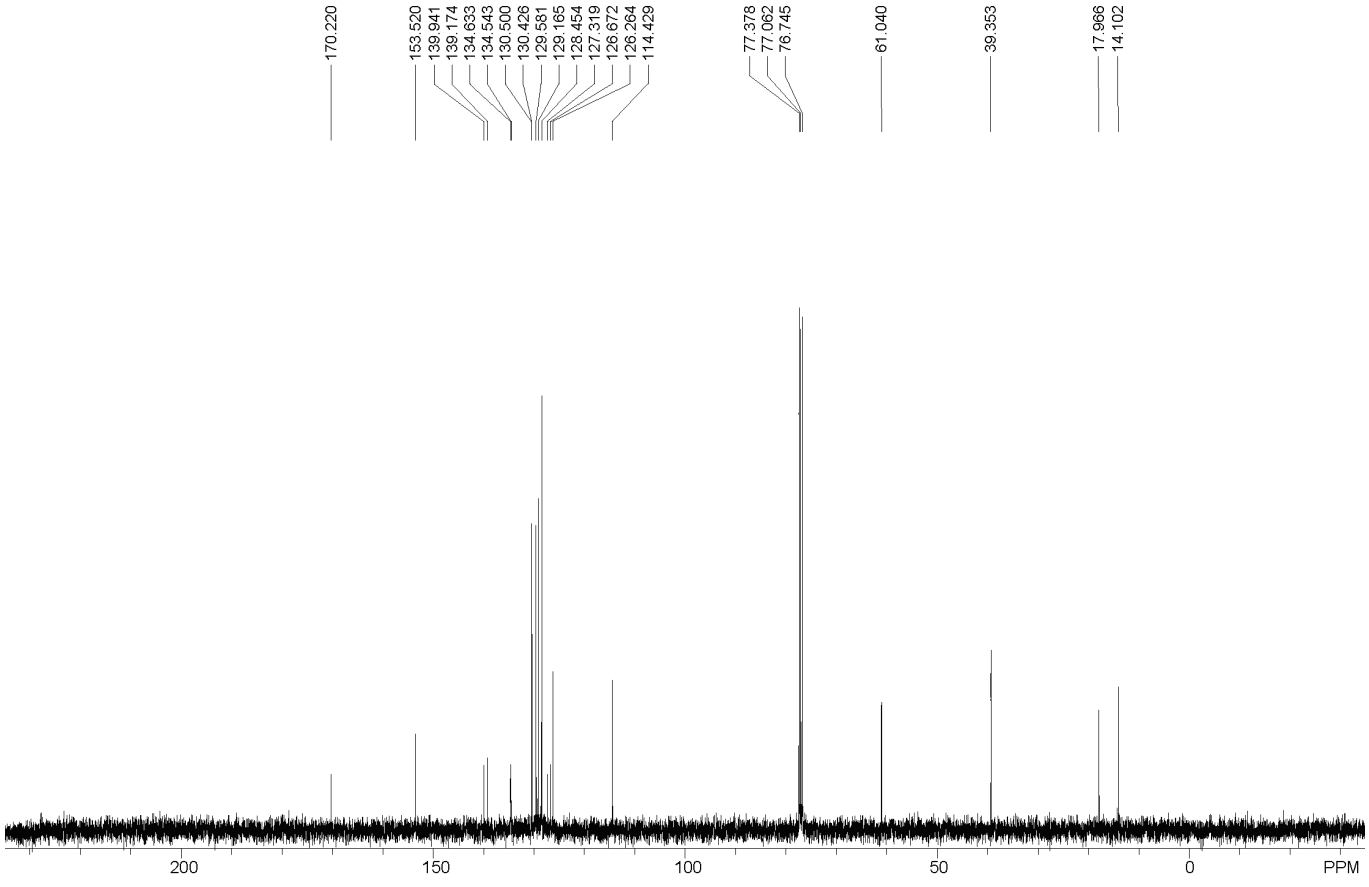
1.05
2.02
2.06
3.06
3.21
10
8
6
4
2
PPM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130.426
129.581
129.165
128.454
127.319
126.672
126.264
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77.062
76.745
61.040
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17.966
14.102
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100
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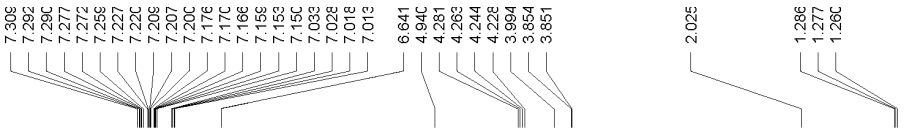
PPM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7.272
7.256
7.227
7.220
7.206
7.207
7.200
7.176
7.170
7.166
7.159
7.153
7.150
7.033
7.028
7.018
7.013
6.641
4.940
4.281
4.263
4.244
4.228
3.994
3.854
3.851
2.025
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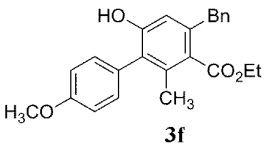
1.277
1.260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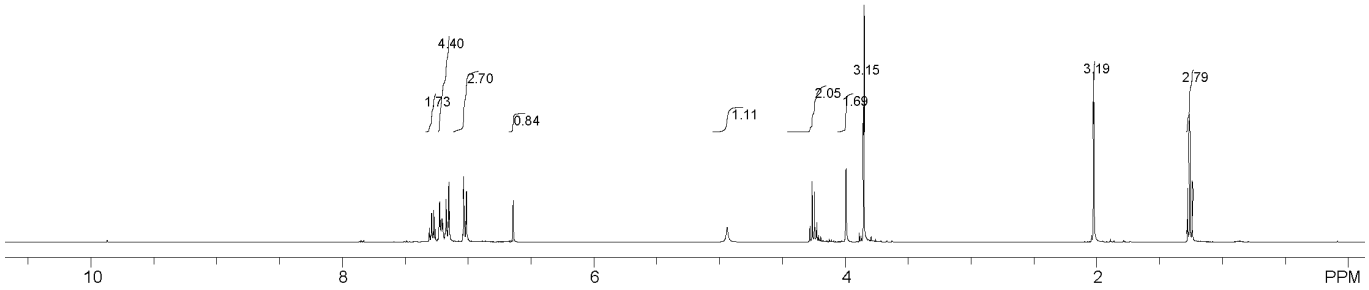
Bn
CO2Et
CH3
H3CO

3f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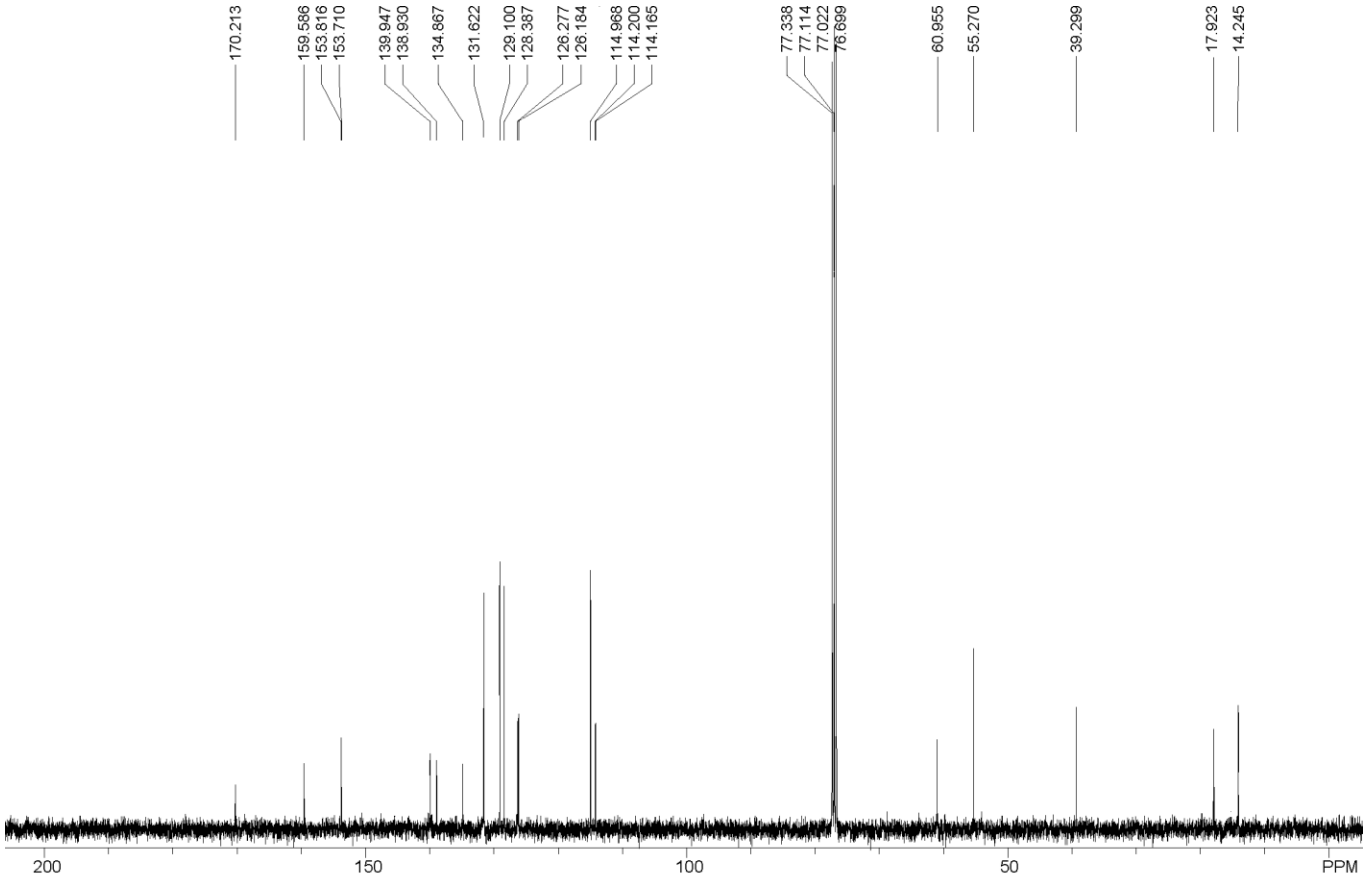
1.11
2.05
1.69
3.15
3.19
2.79
10
8
6
4
2
PPM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128.387
126.277
126.184
114.968
114.200
114.165
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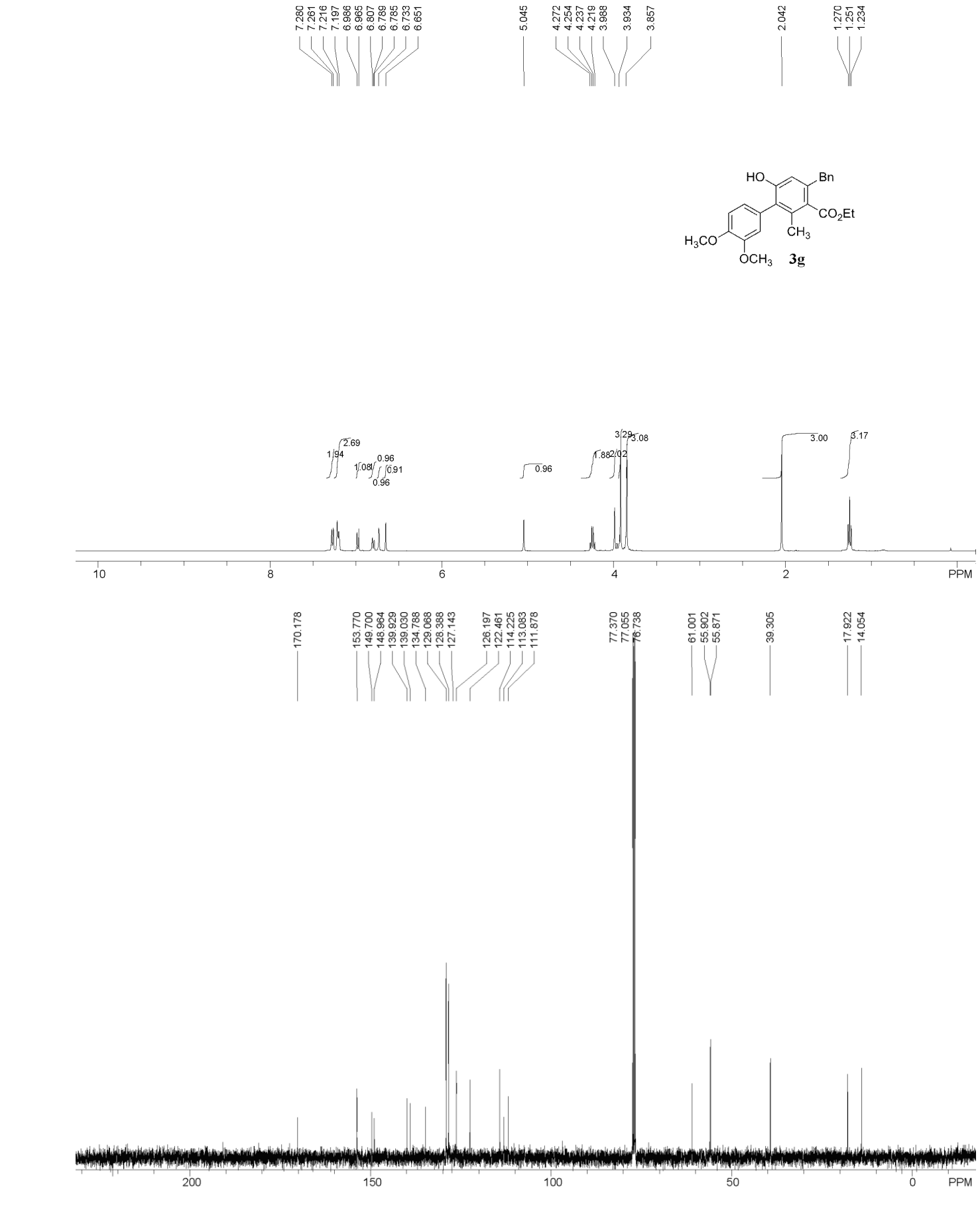
76.899
60.955
55.270
39.299
17.923
14.245
200
150
100
50
PPM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5.045
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4.254
4.237
4.219
3.988
3.934
3.857
2.042
1.270
1.251
1.234
HO
Bn
CO2Et
CH3
H3CO
OCH3
3g
2.69
1.94
1.08
0.96
0.91
0.96
0.96
1.88
2.02
3.29
3.08
3.00
3.17
10
8
6
4
2
PPM
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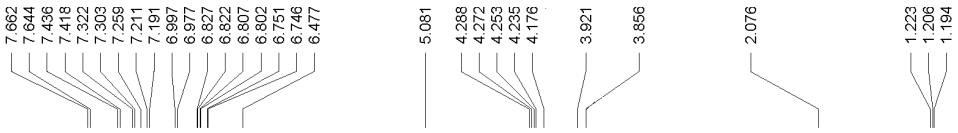
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6.807
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6.751
6.746
6.477
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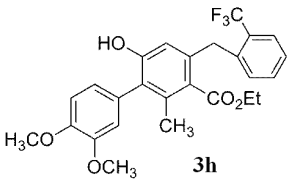
1.206
1.194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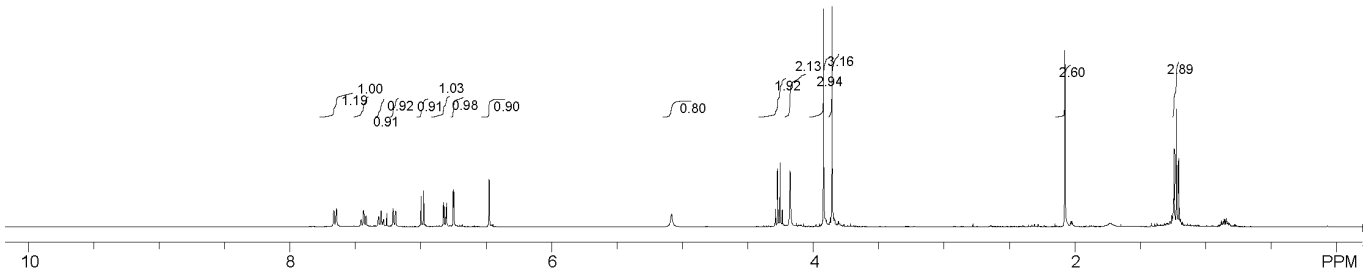
HO
CO2Et
CH3
H3CO
OCH3

3h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0.91
1.03
0.98
0.90
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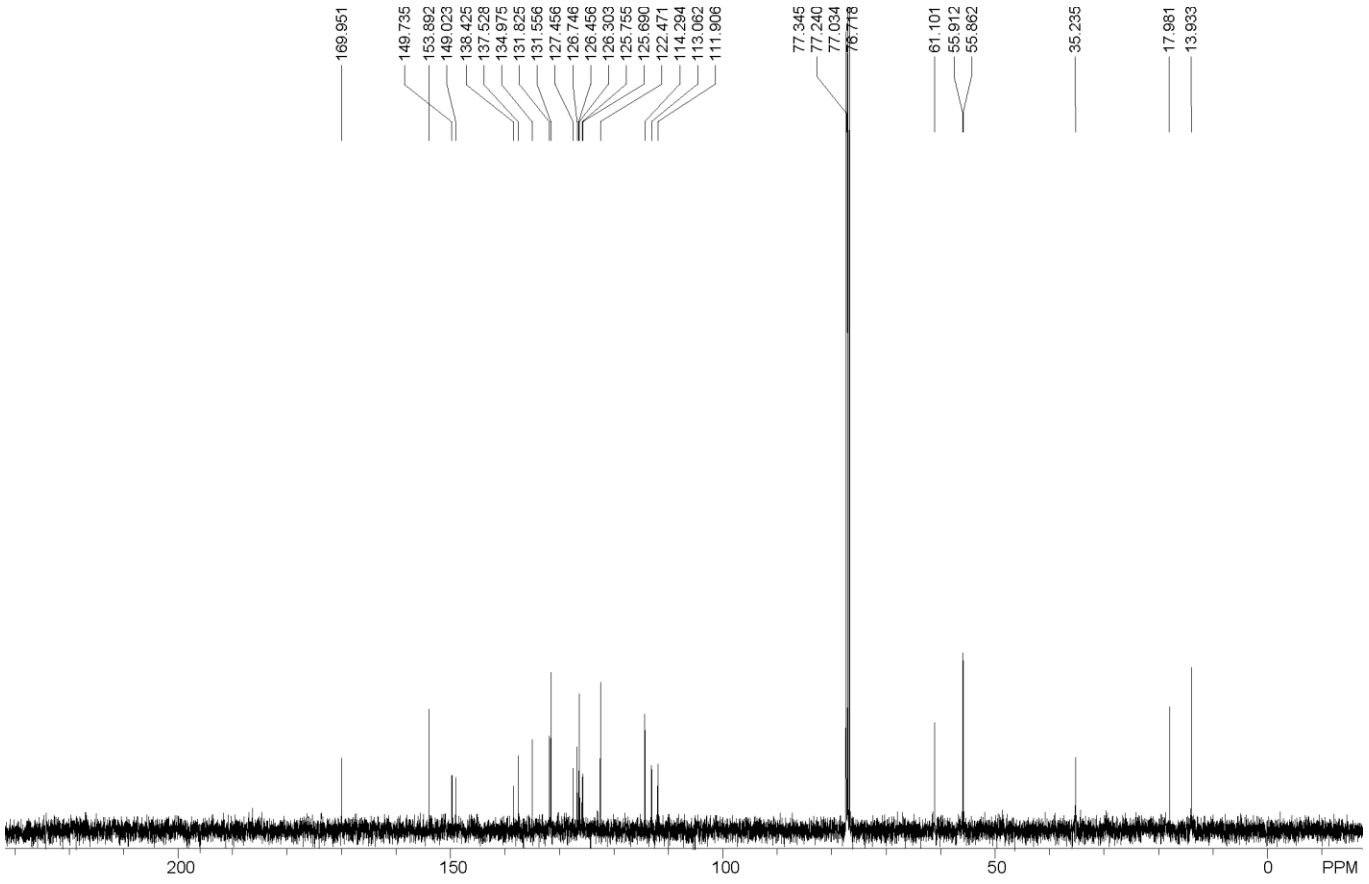
2.60
2.89
10
8
6
4
2
PPM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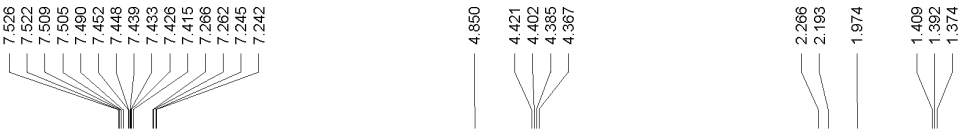
PPM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7.245
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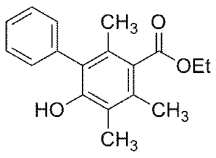
1.392
1.374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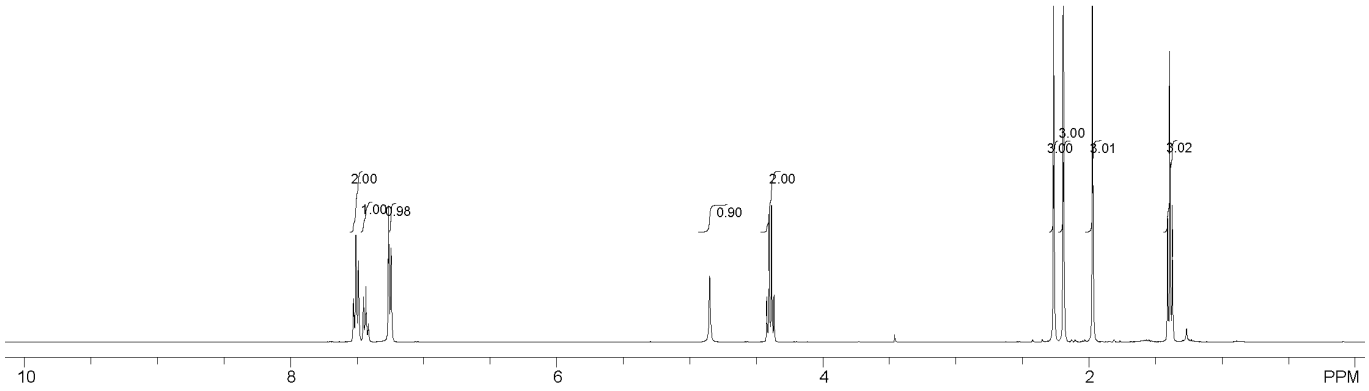
O
OEt
HO
CH3
CH3

3i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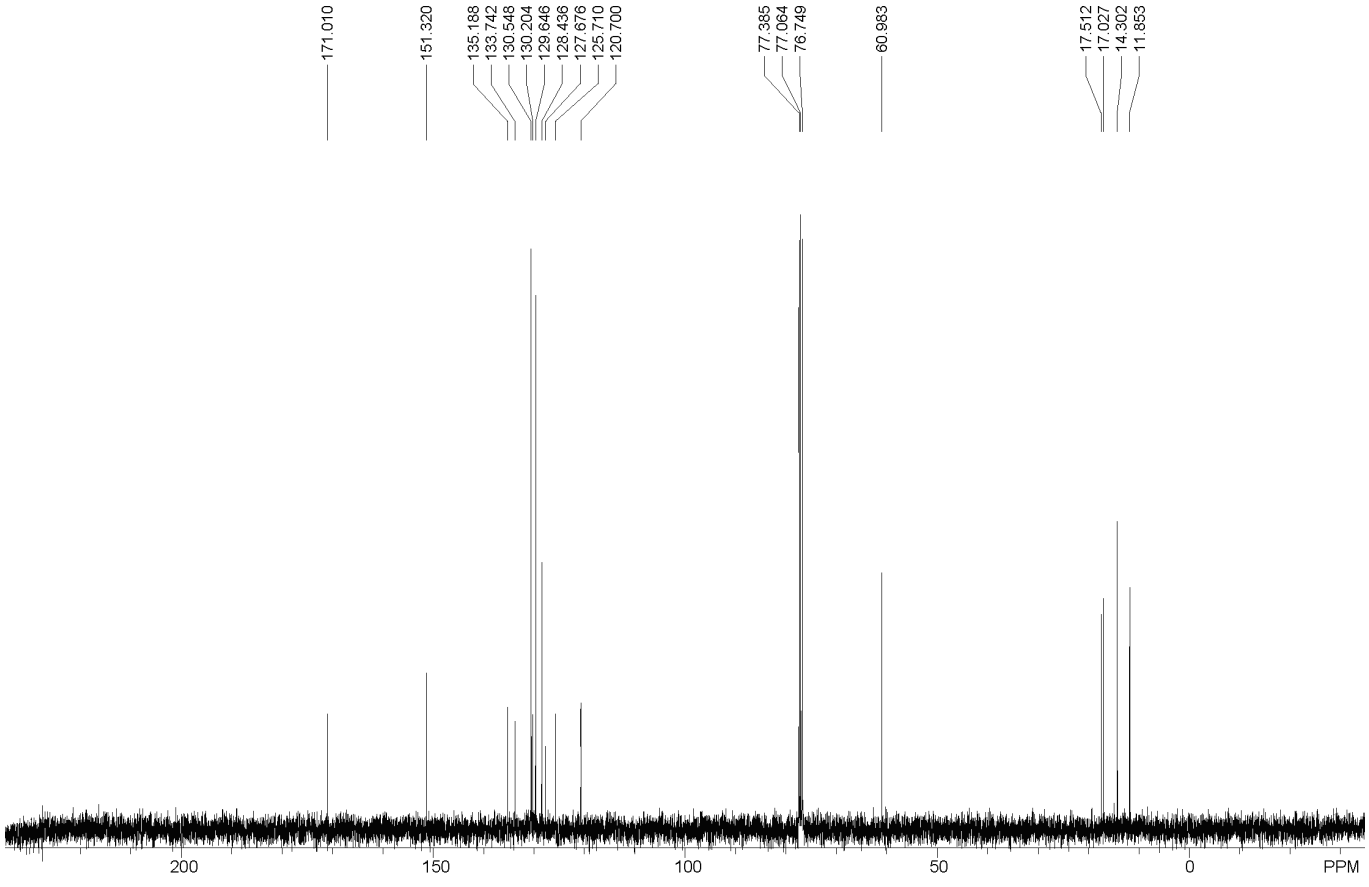
3.00
3.01
3.02
10
8
6
4
2
PPM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17.027
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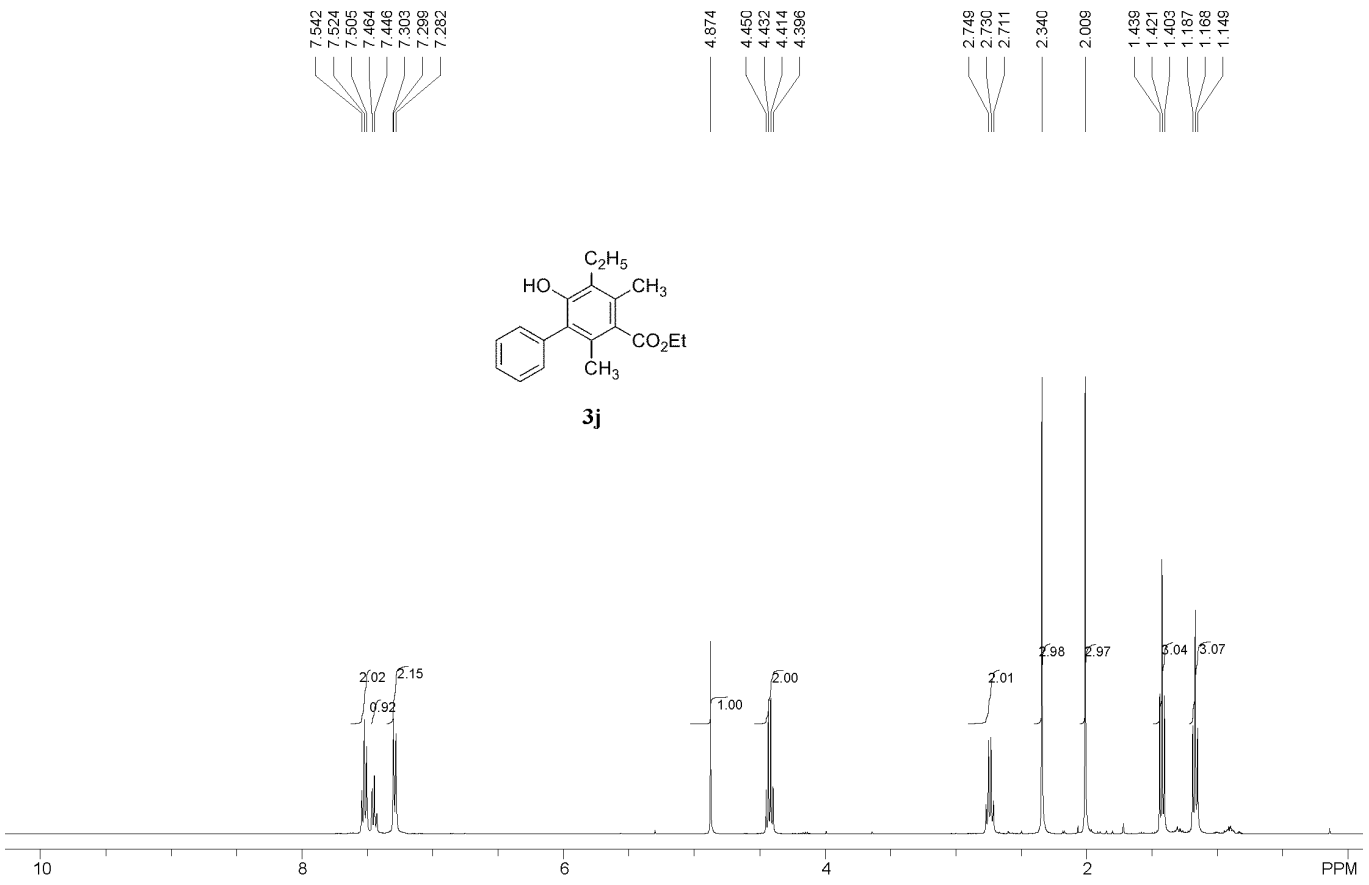
100
50
0
PPM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2.730
2.711
2.340
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1.421
1.403
1.187
1.168
1.149
C2H5
HO
CH3
CO2Et
CH3
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2.15
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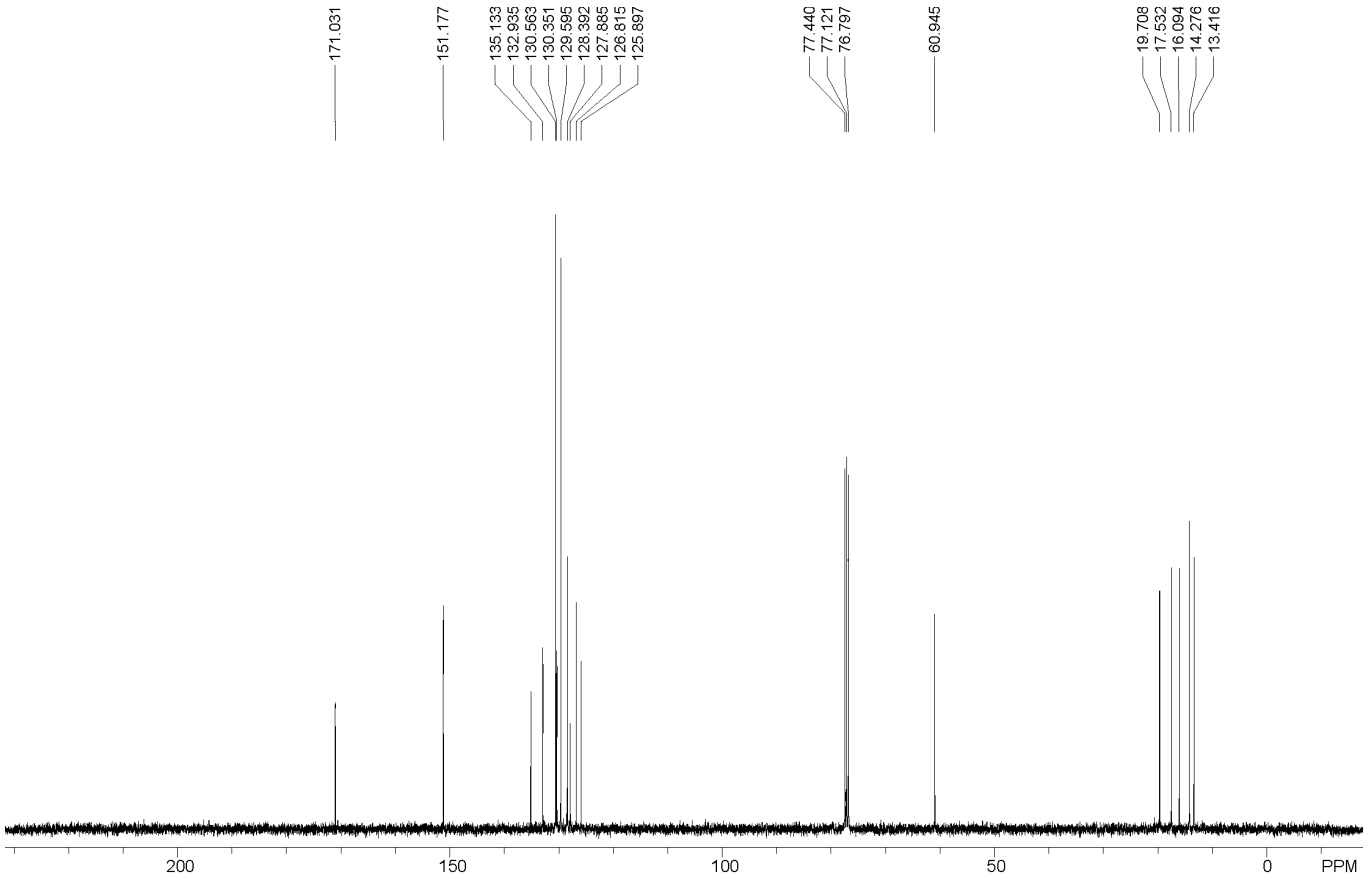
10
8
6
4
2
PPM

3j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13.416
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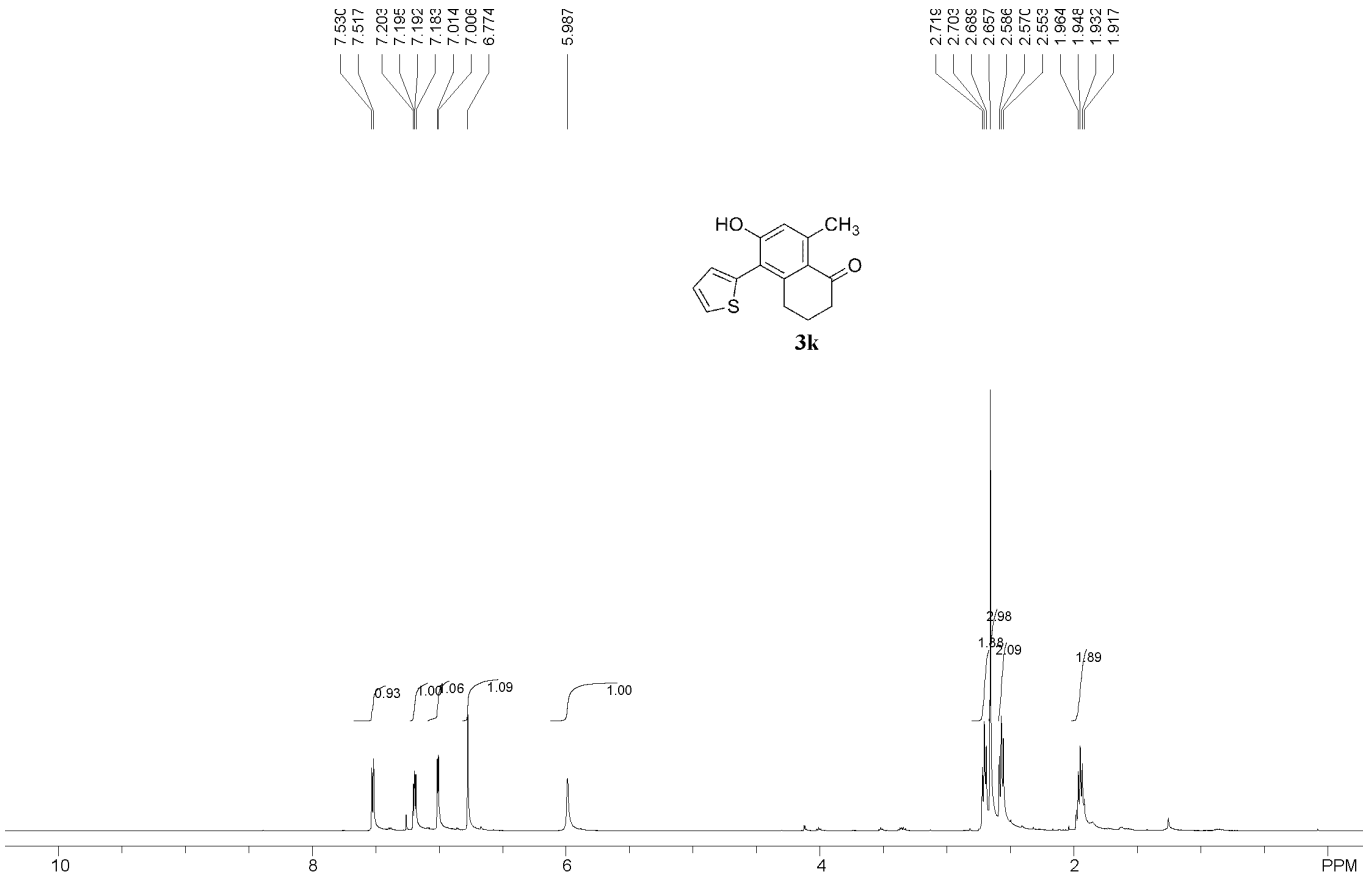
PPM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1.932
1.917
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CH3
O
S
0.93
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2.09
1.89
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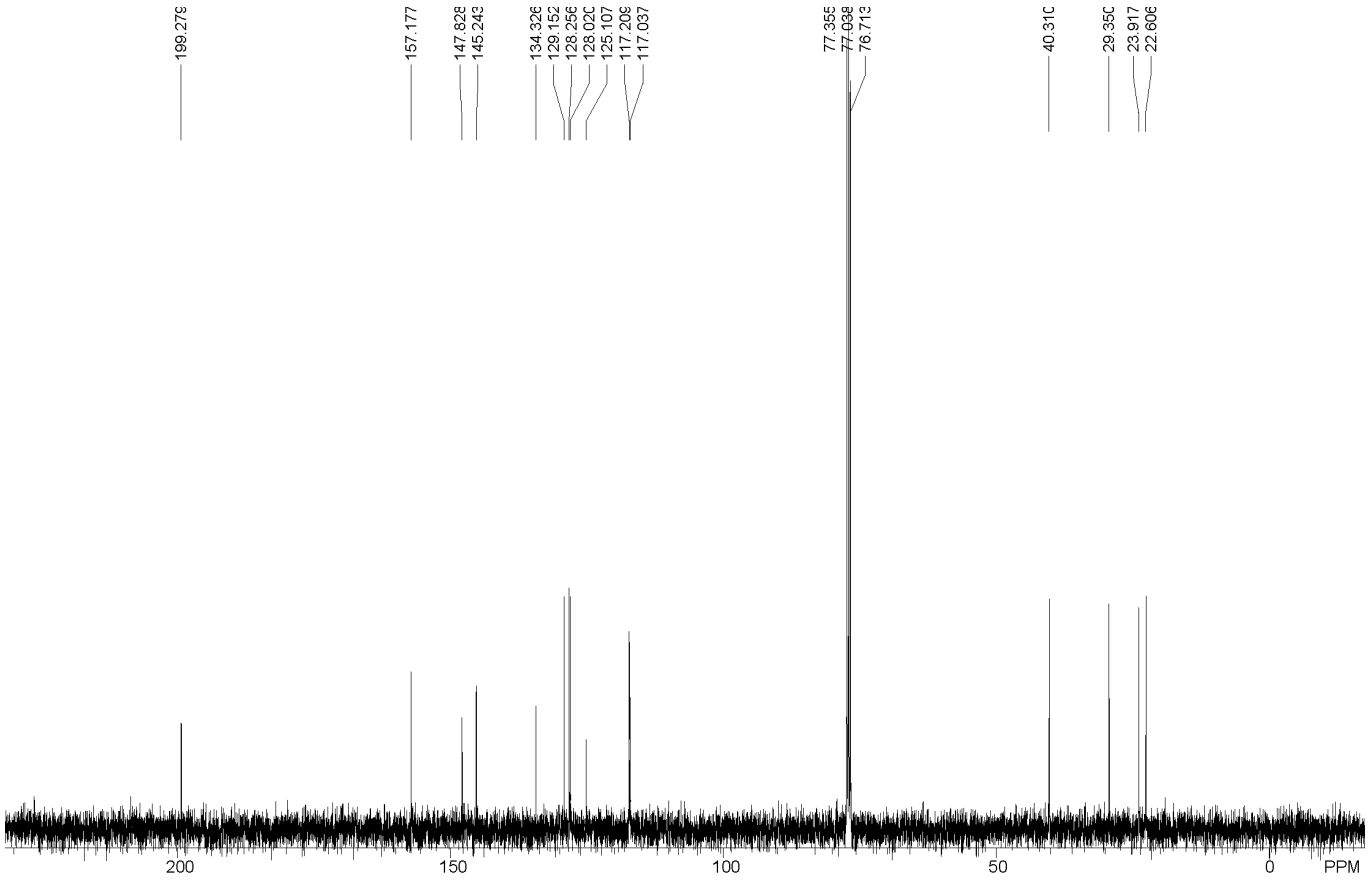
2
PPM

3k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128.022
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76.713
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29.350
23.917
22.606
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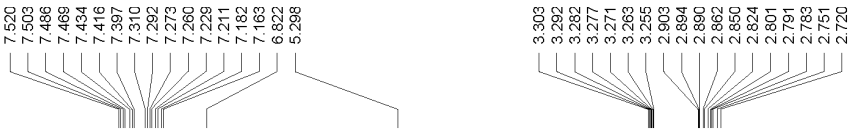
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7.310
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7.273
7.260
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7.211
7.182
7.163
6.822
5.298
3.303
3.292
3.282
3.277
3.271
3.263
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2.783
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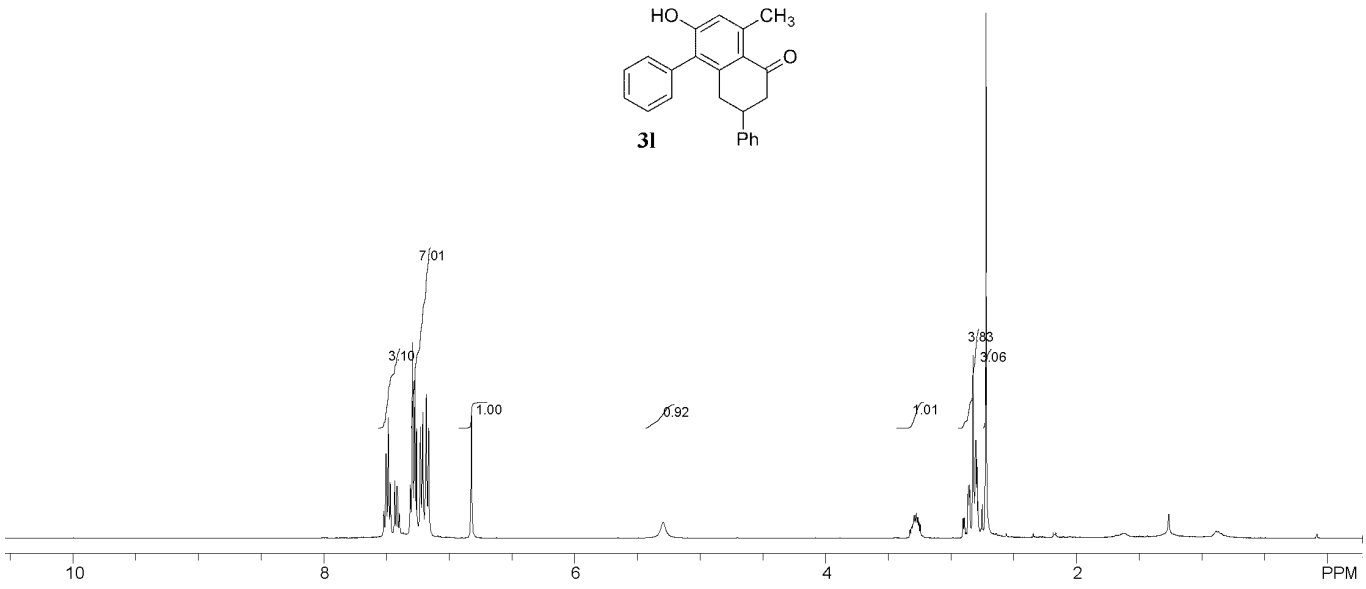
2.720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CH3
O
Ph
3l
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10
8
6
4
2
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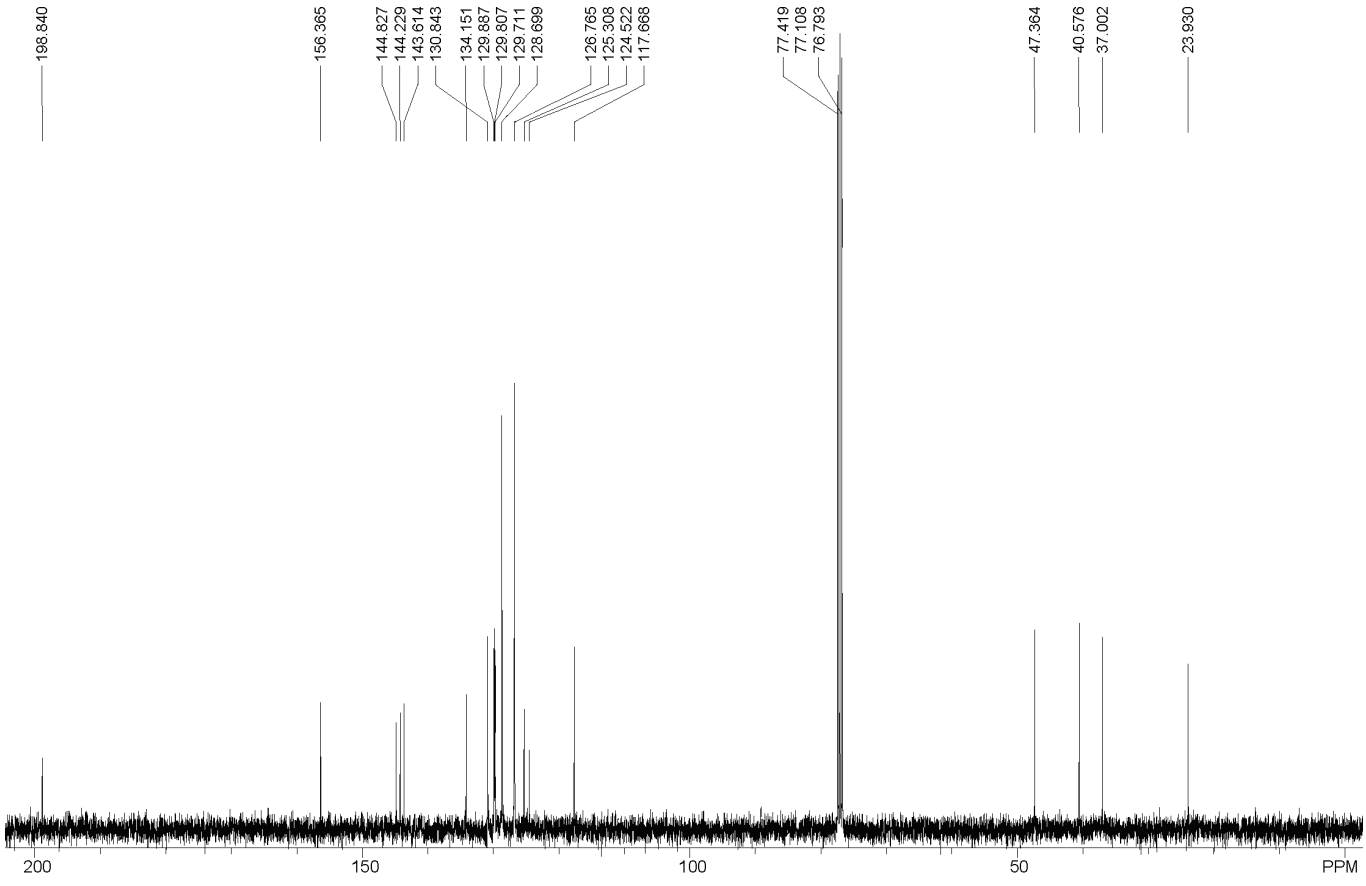
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125.308
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100
50
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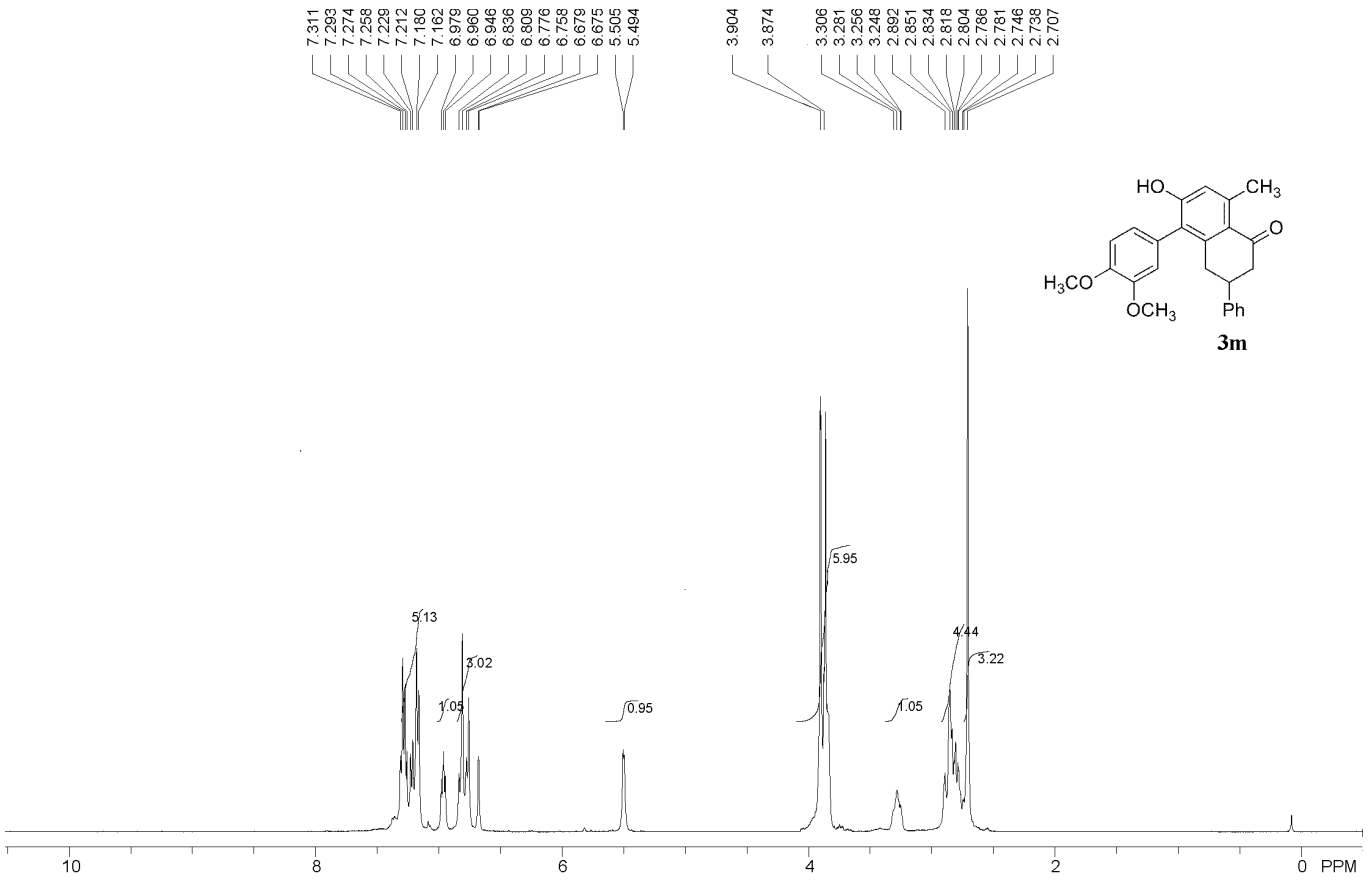
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6.809
6.776
6.758
6.679
6.675
5.505
5.494
3.904
3.874
3.306
3.281
3.256
3.248
2.892
2.851
2.834
2.818
2.804
2.786
2.781
2.746
2.738
2.707
HO
CH3
O
H3CO
OCH3
Ph
5.13
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5.95
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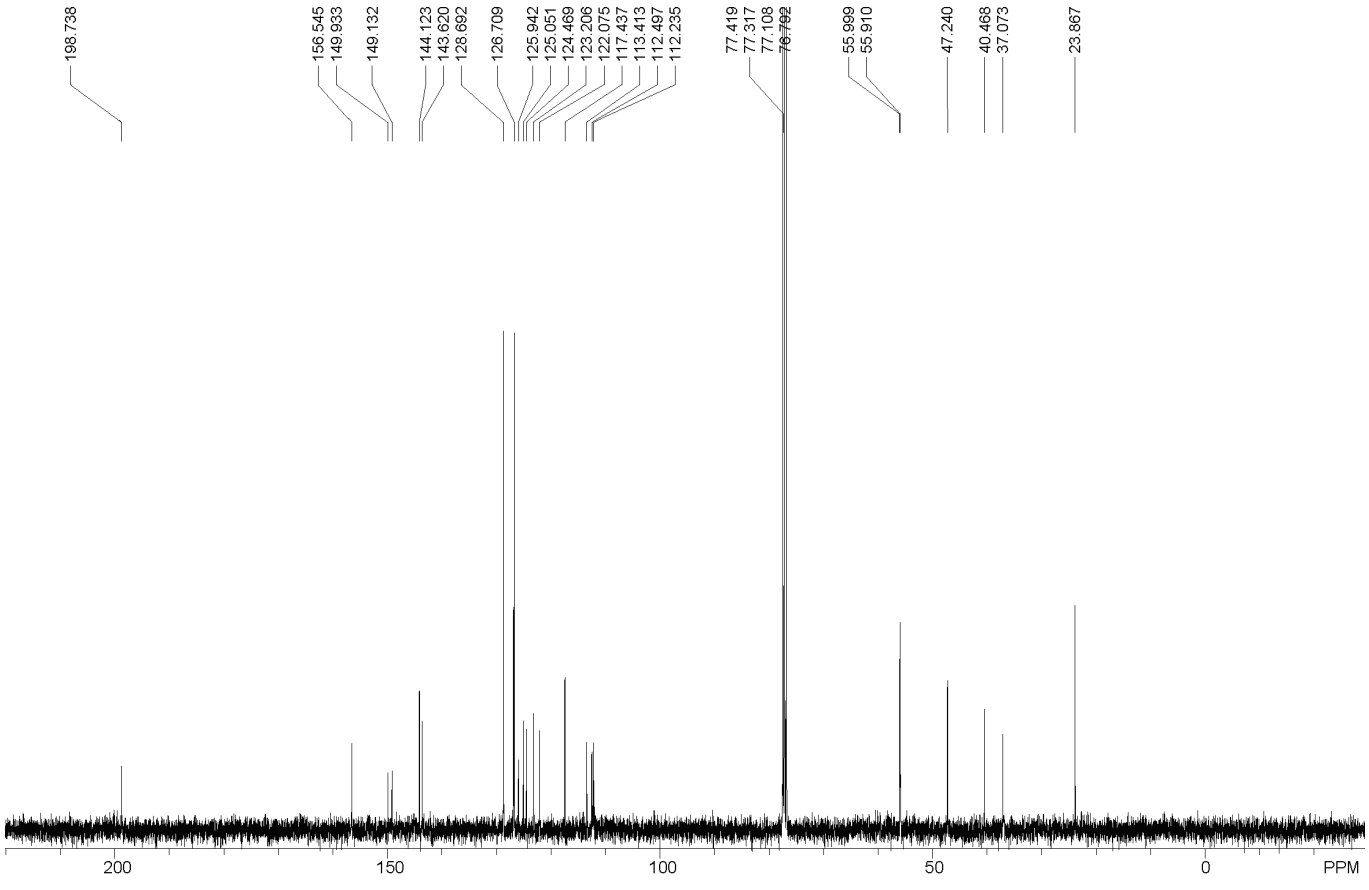
10
8
6
4
2
0 PPM

3m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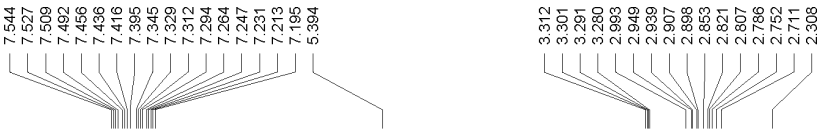
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7.247
7.231
7.213
7.195
5.394
3.312
3.301
3.291
3.280
2.993
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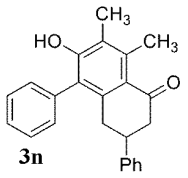
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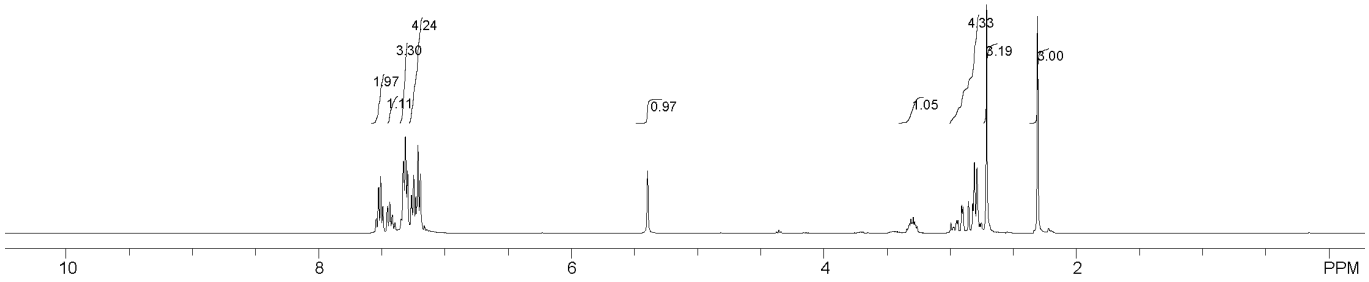
HO
CH3
O
Ph

3n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1.05
4.33
3.19
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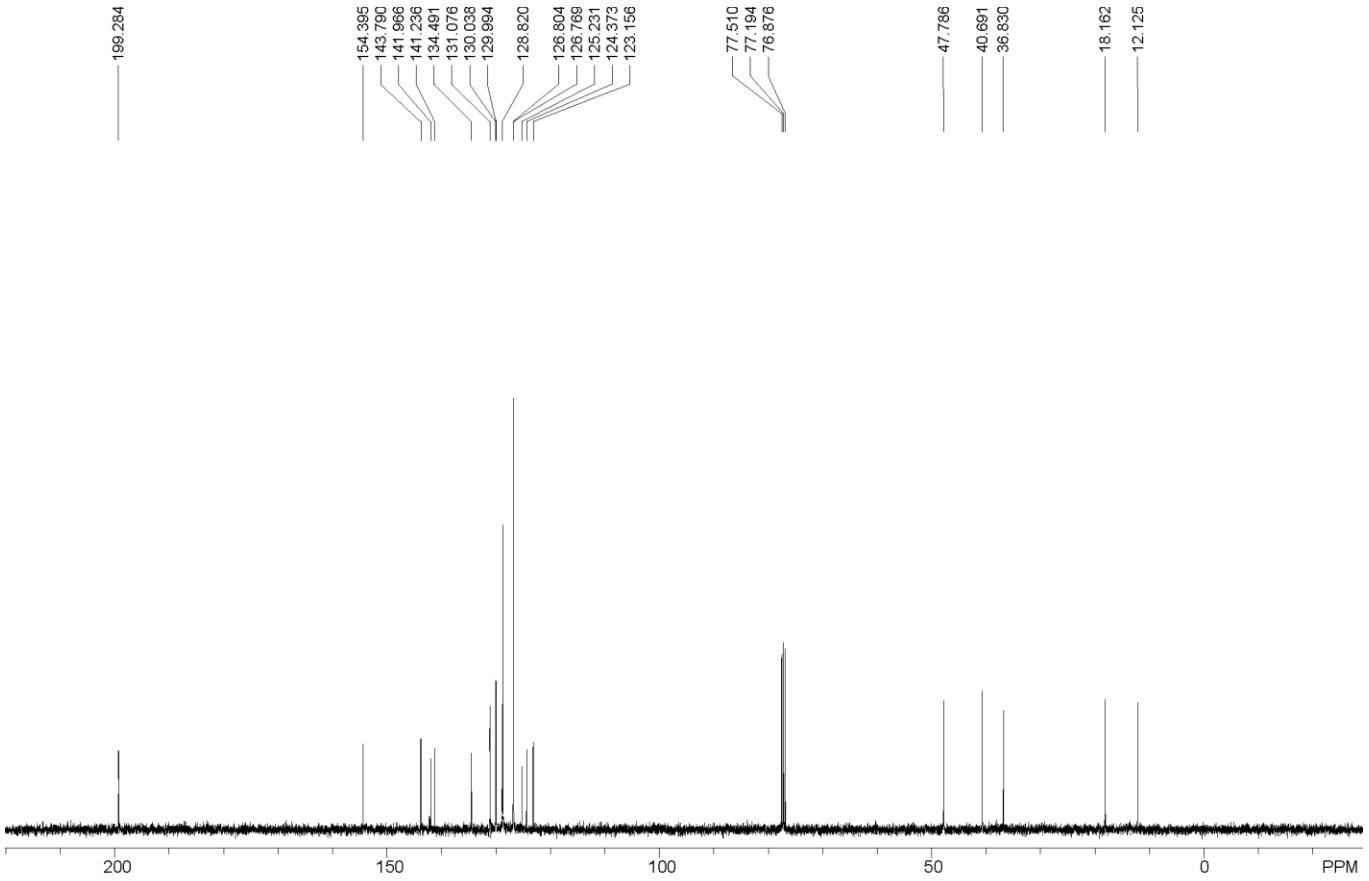
10
8
6
4
2
PPM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131.076
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128.820
126.804
126.769
125.231
124.373
123.156
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77.194
76.876
47.786
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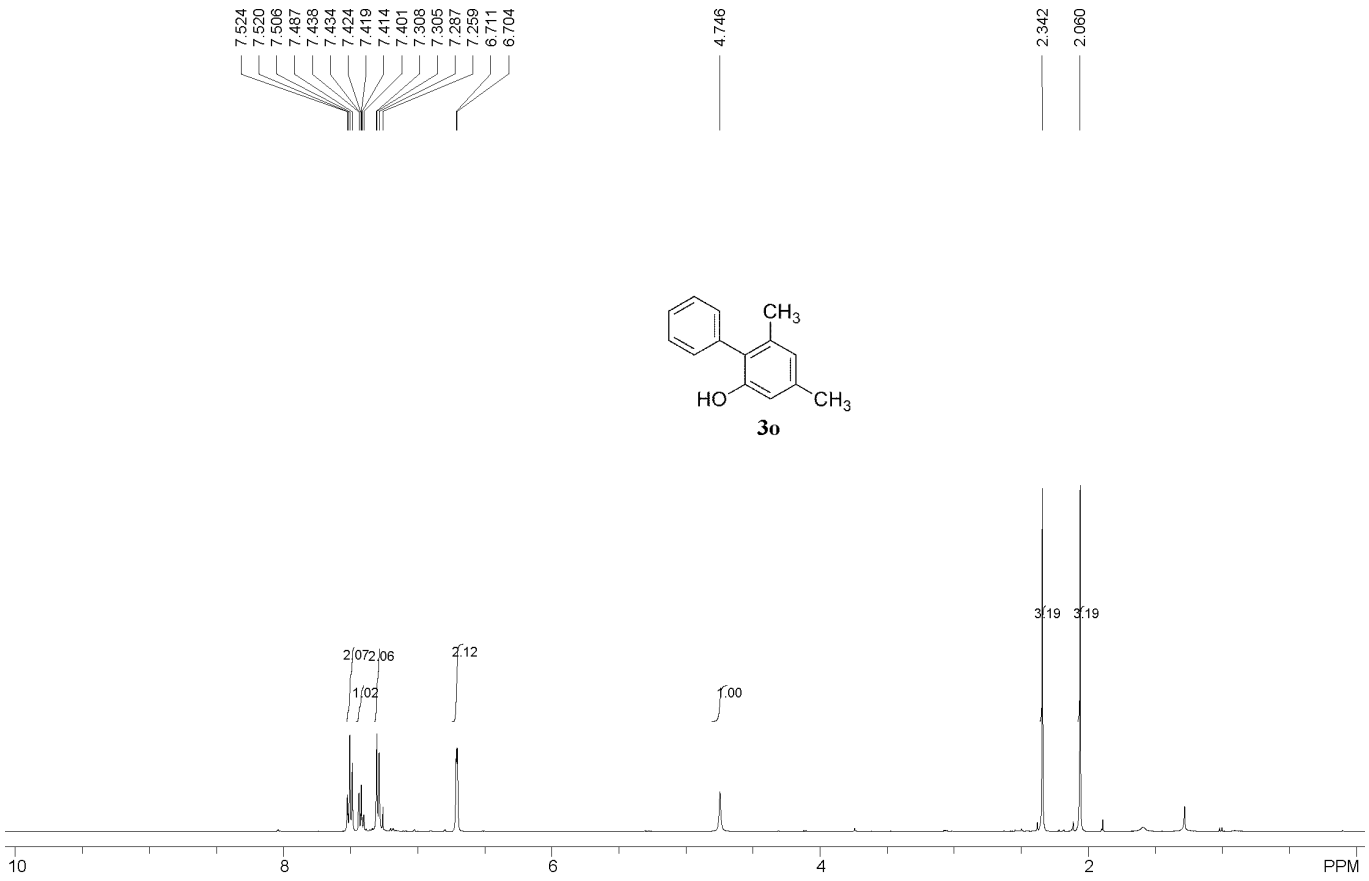
36.830
18.162
12.125
200
150
100
50
0
PPM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7.434
7.424
7.419
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7.401
7.308
7.305
7.287
7.259
6.711
6.704
4.746
2.342
2.060
CH3
HO
CH3
3o
2.07
2.06
1.02
2.12
1.00
3.19
3.19
10
8
6
4
2
PPM
152.712
138.619
136.954
135.421
130.499
129.406
128.054
125.294
122.931
113.264
77.382
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76.749
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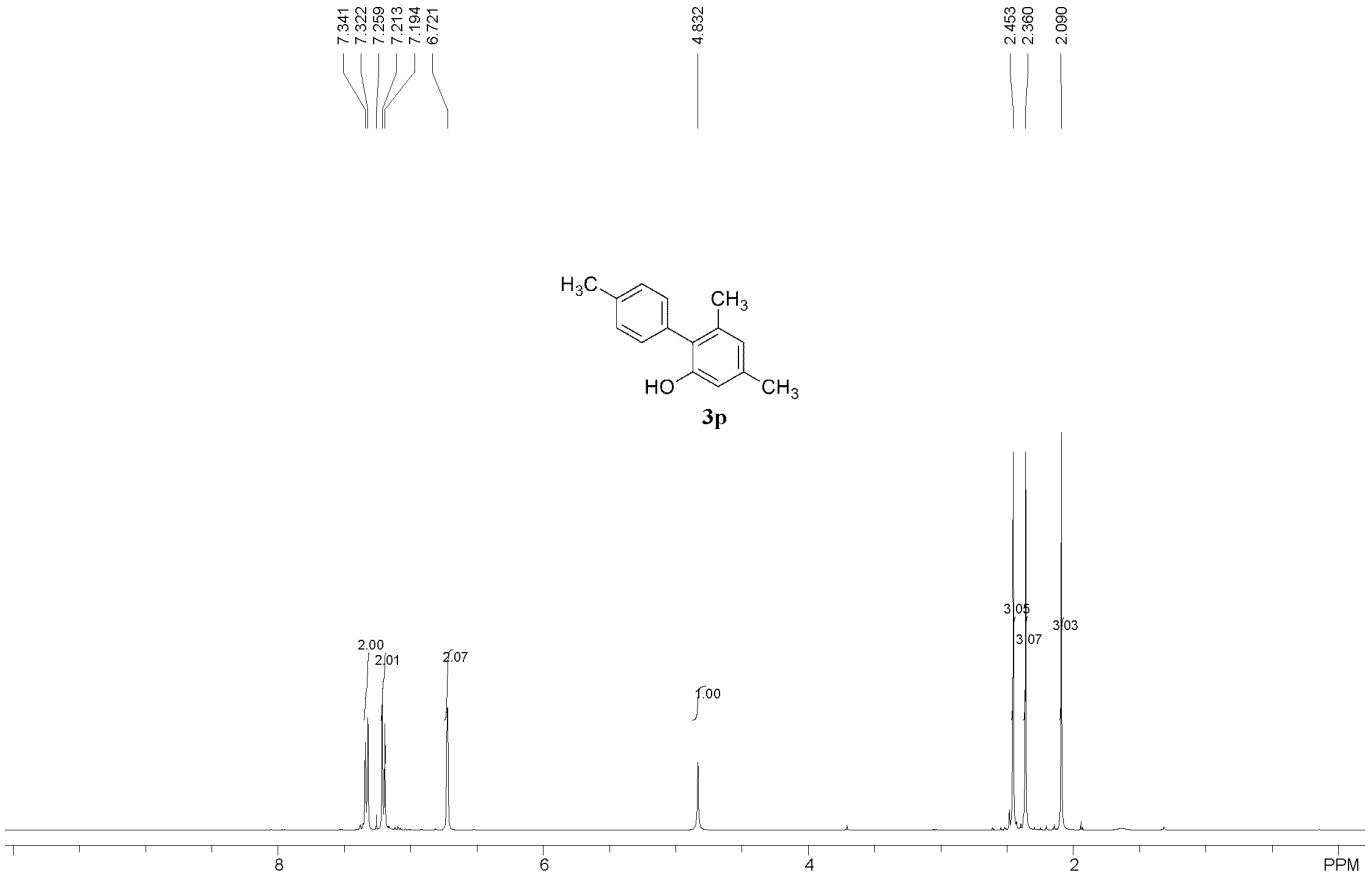
20.328
200
150
100
50
0
PPM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7.322
7.259
7.213
7.194
6.721
4.832
2.453
2.360
2.090
H3C
CH3
HO
CH3
3p
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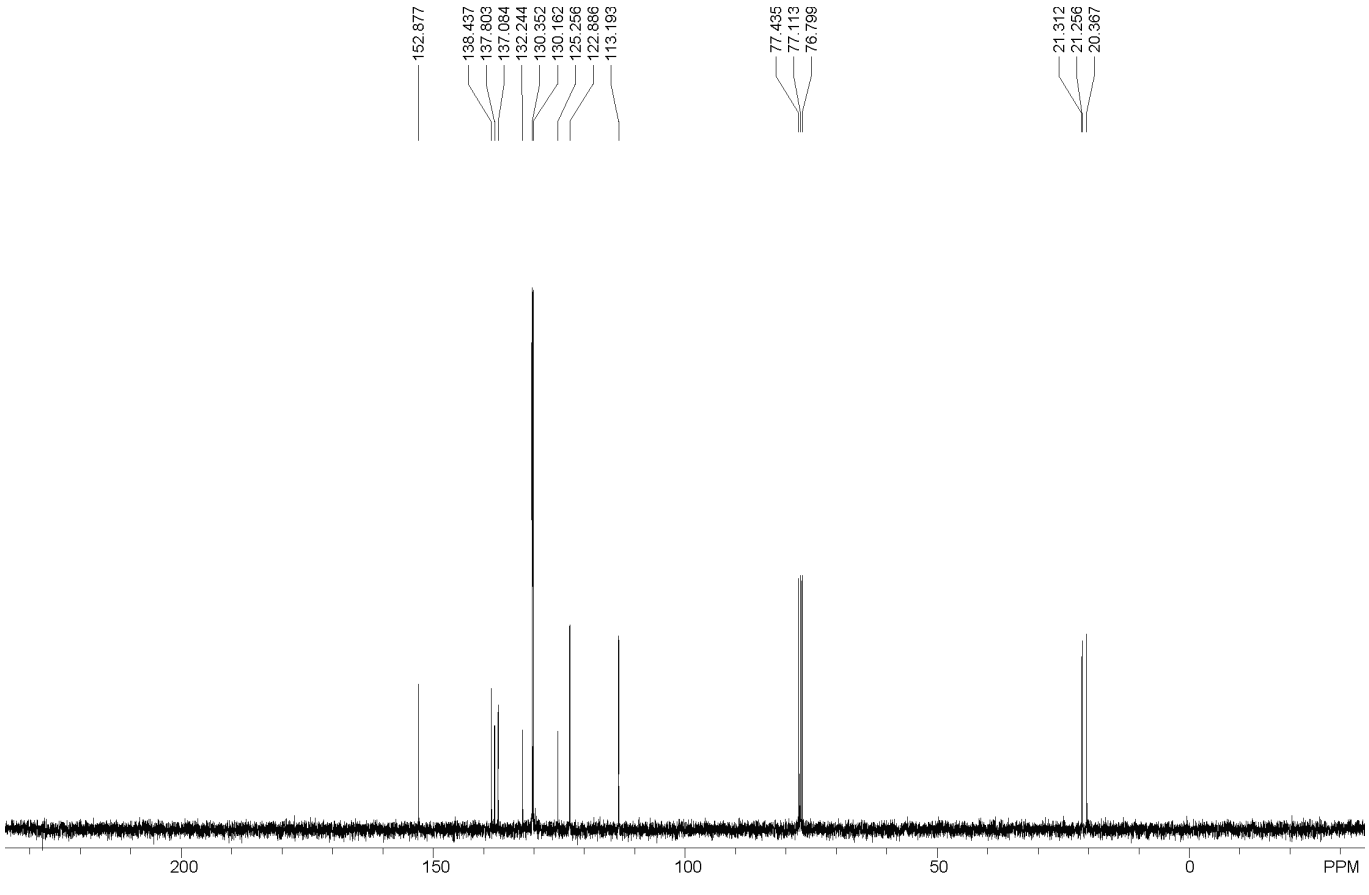
2.01
2.07
1.00
3.05
3.07
3.03
8
6
4
2
PPM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130.162
125.256
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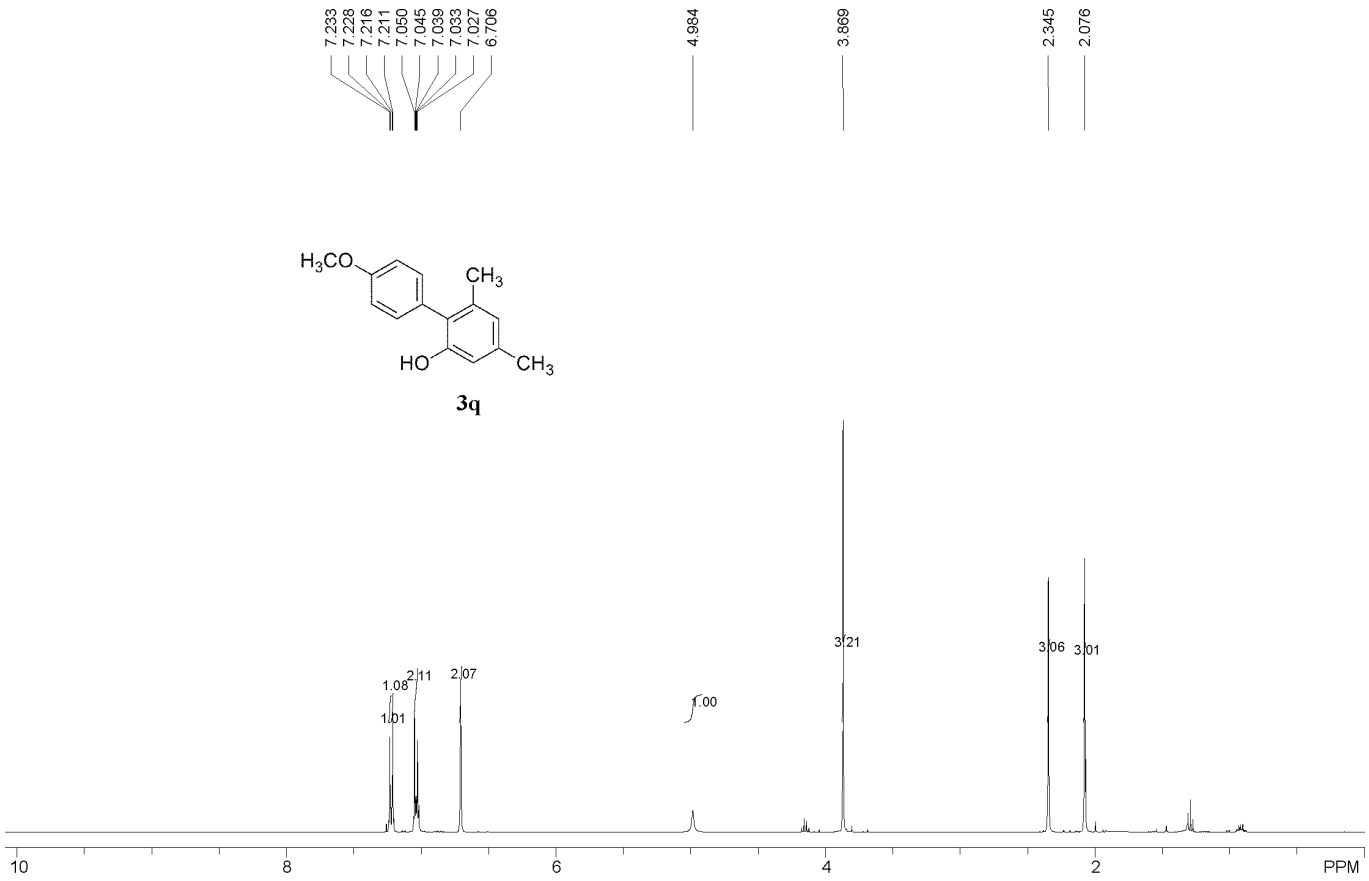
77.113
76.799
21.312
21.256
20.367
200
150
100
50
0
PPM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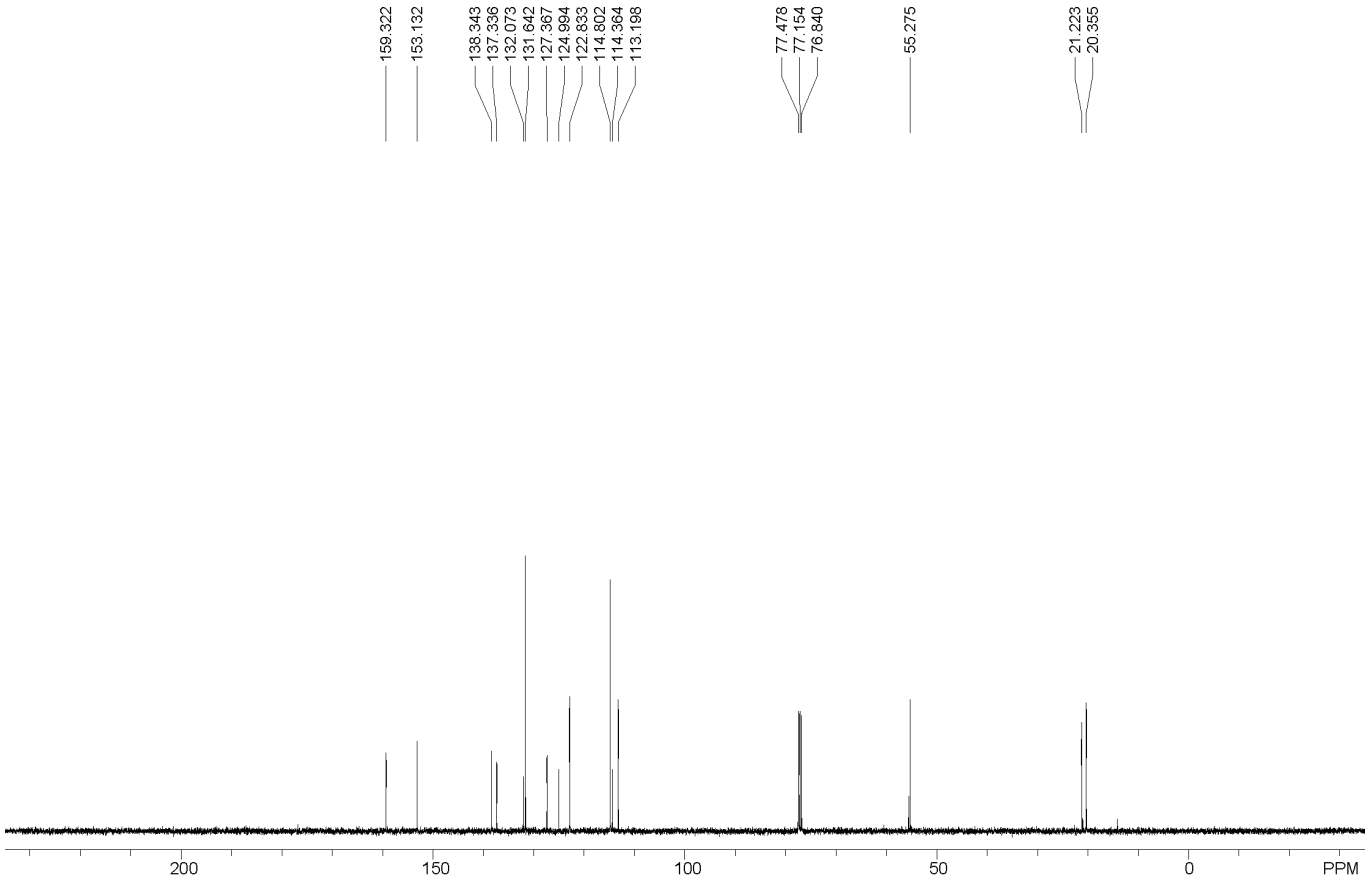
7.216
7.211
7.050
7.045
7.039
7.033
7.027
6.706
4.984
3.869
2.345
2.076
H3CO
CH3
HO
CH3
1.08
1.01
2.11
2.07
1.00
3.21
3.06
3.01
10
8
6
4
2
PPM

3q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77.478
77.154
76.840
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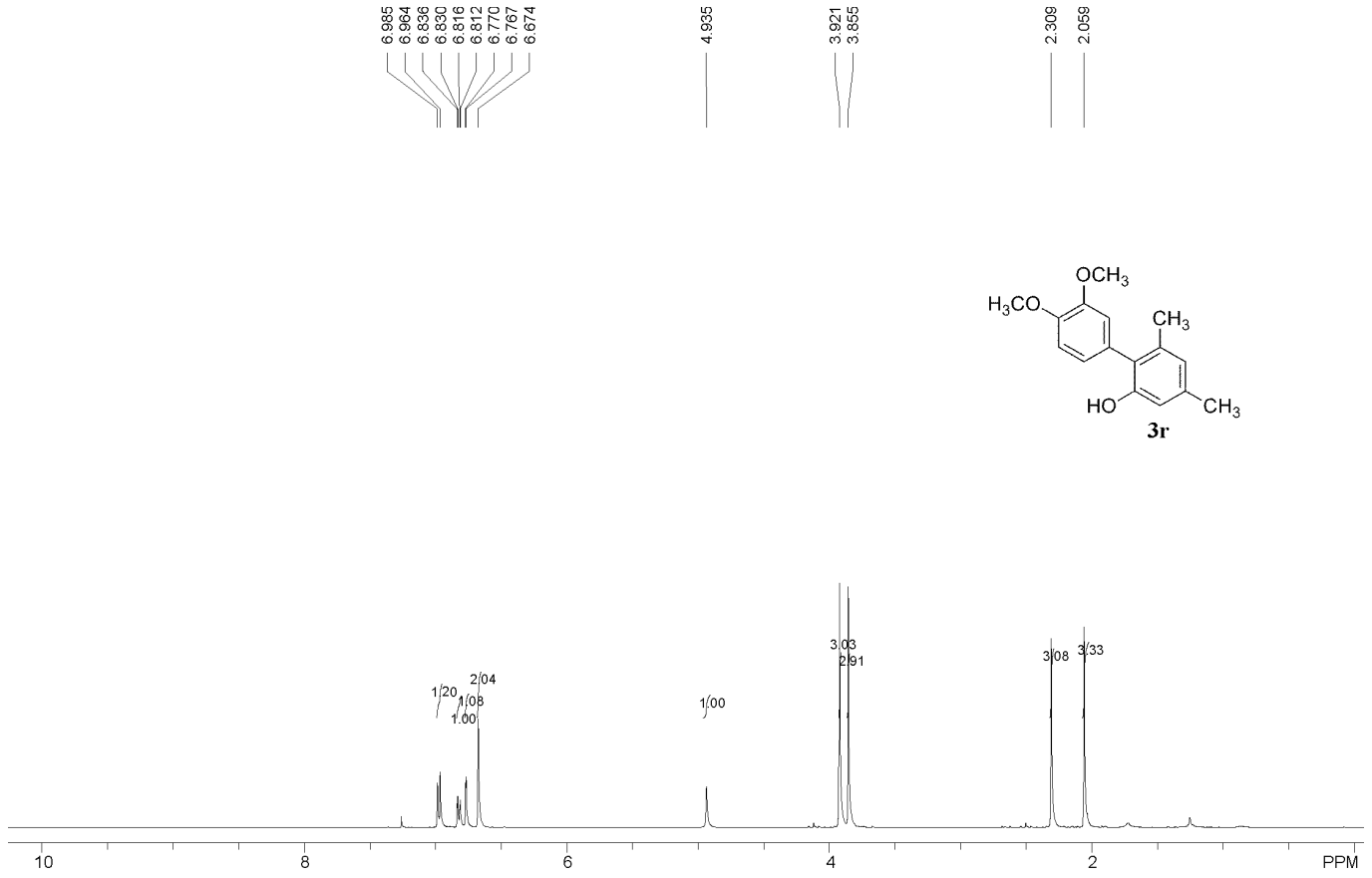
20.355
200
150
100
50
0
PPM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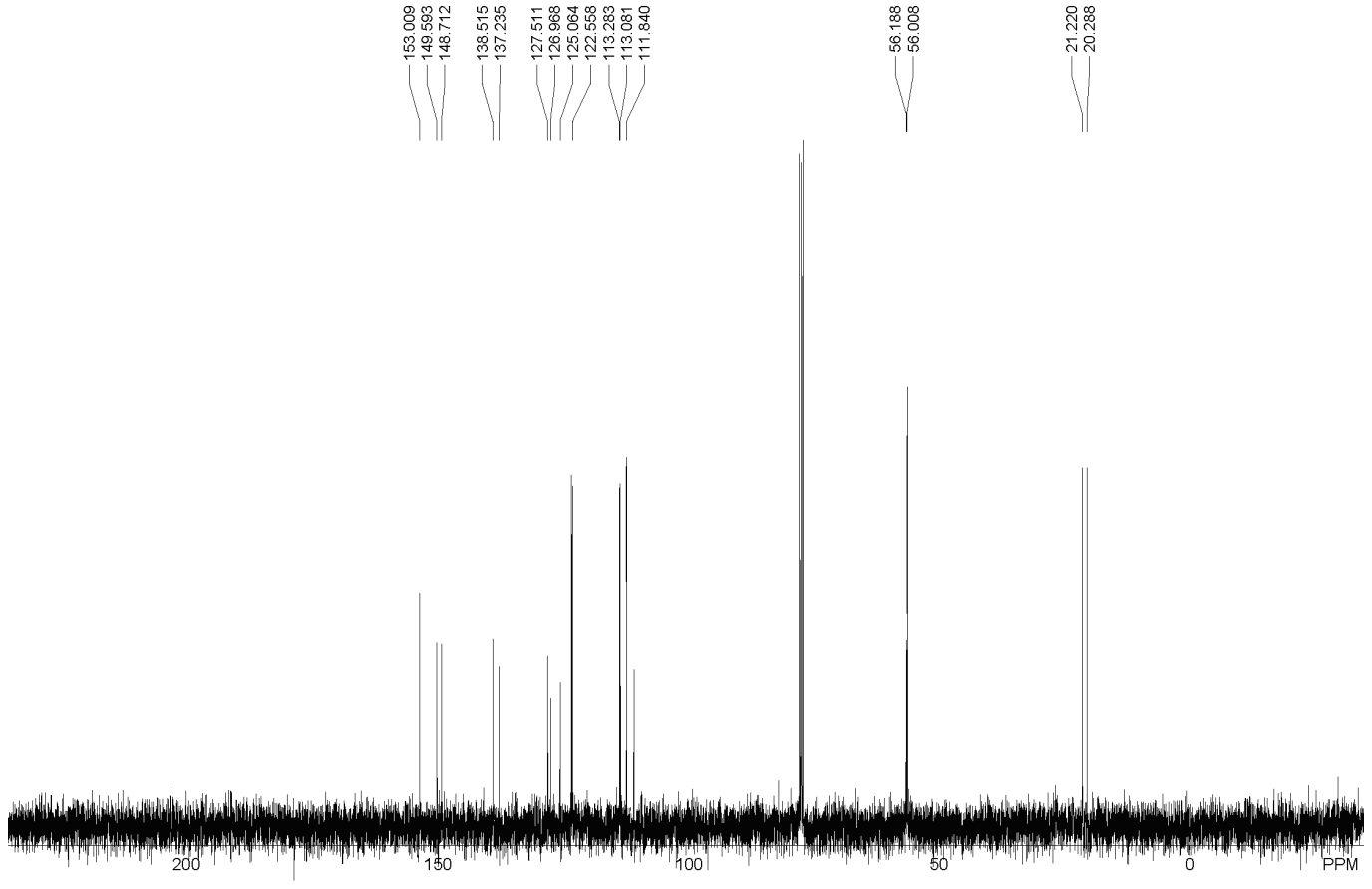
6.836
6.830
6.816
6.812
6.770
6.767
6.674
4.935
3.921
3.855
2.309
2.059
OCH3
H3CO
CH3
HO
CH3
3r
1.20
1.08
1.00
2.04
1.00
3.03
2.91
3.08
3.33
10
8
6
4
2
PPM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111.840
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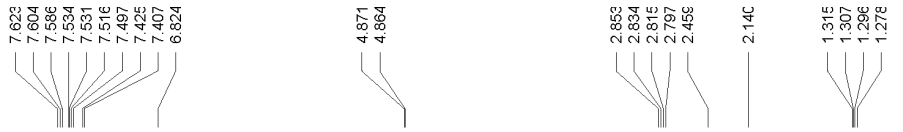
20.288
200
150
100
50
0
PPM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7.531
7.516
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7.425
7.407
6.824
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2.834
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2.797
2.456
2.140
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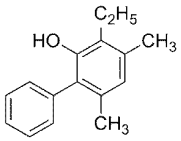
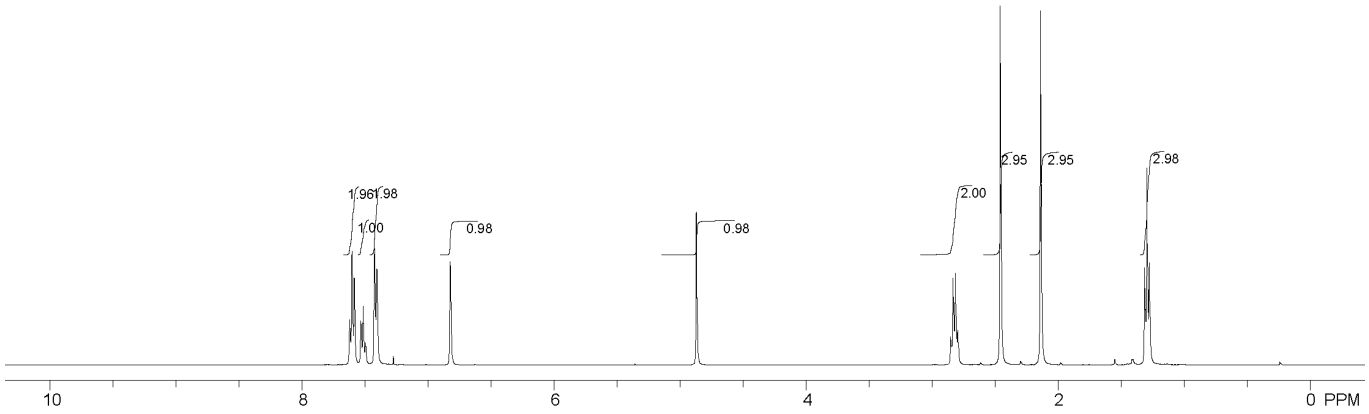
1.307
1.296
1.278


C_2H_5
HO
CH_3
CH_3

3s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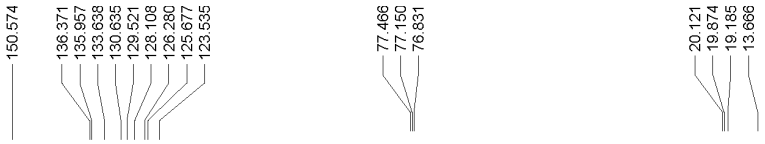
1.98
1.00
0.98
0.98
2.00
2.95
2.95
2.98
10
8
6
4
2
0 PPM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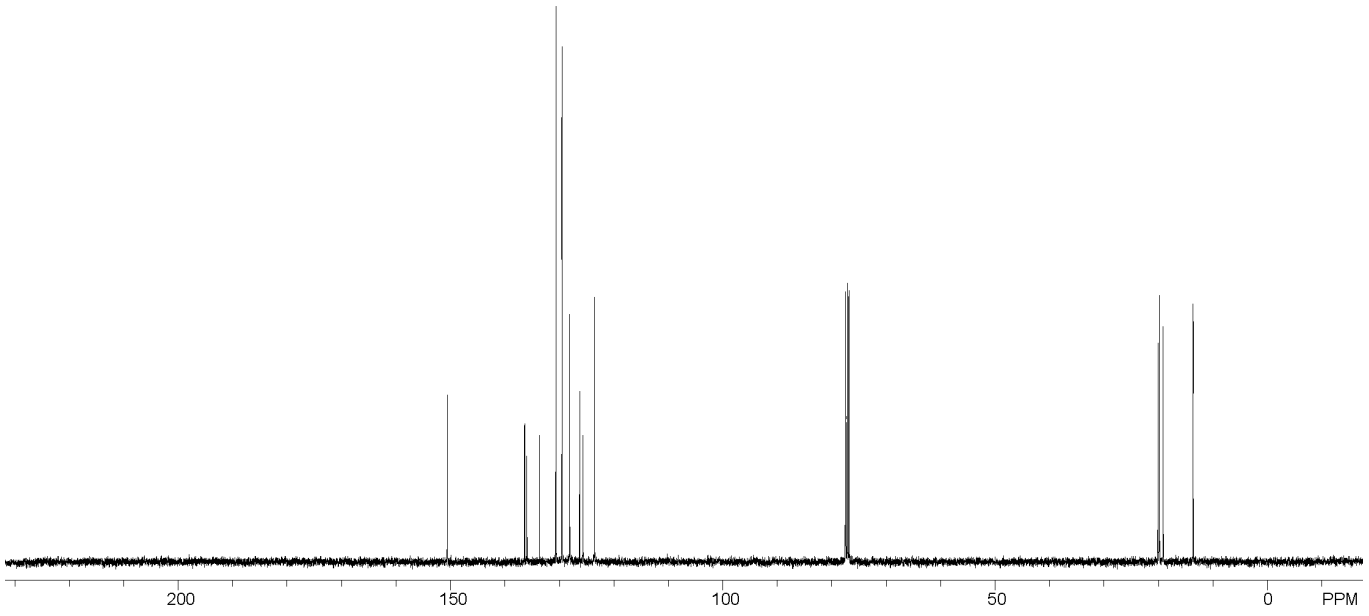
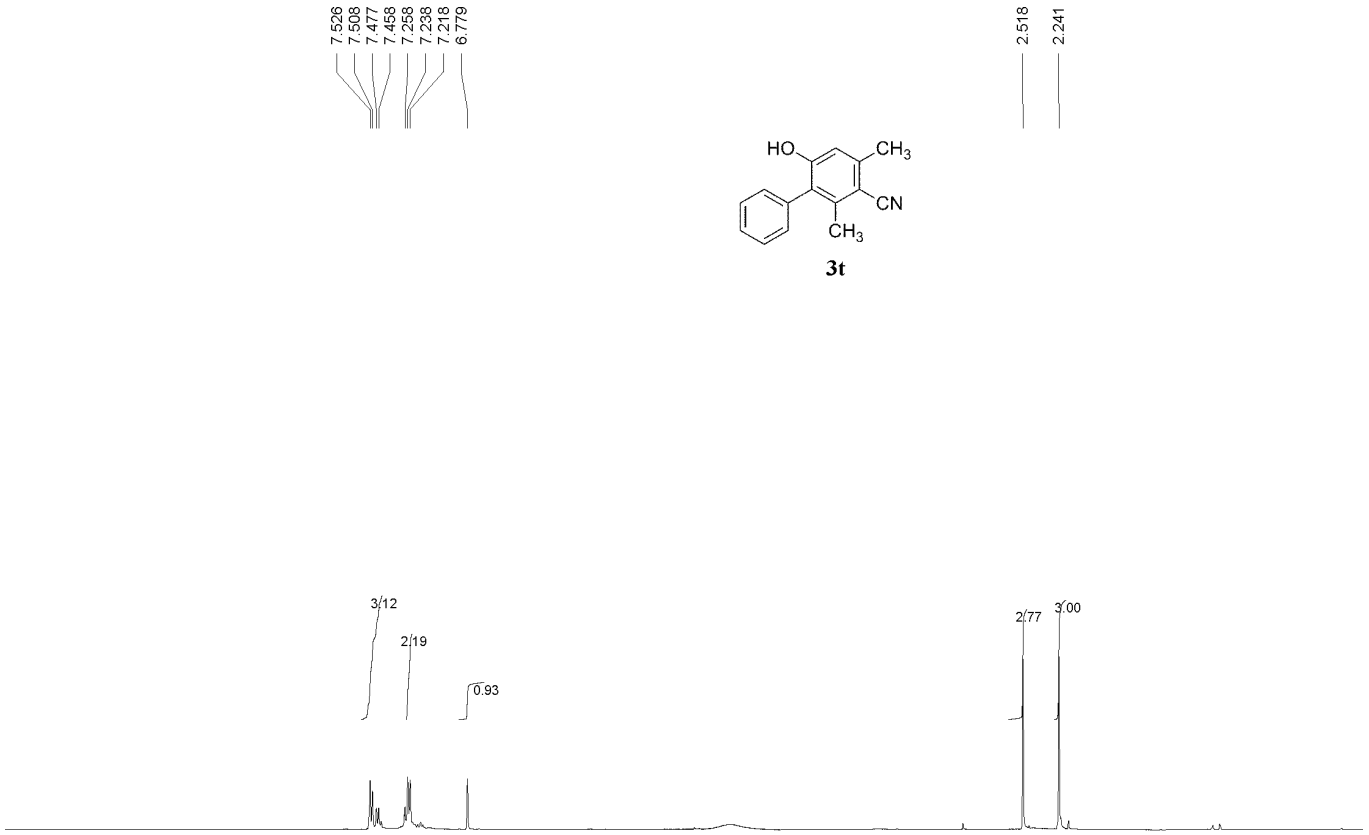
123.535
77.466
77.150
76.831
20.121
19.874
19.185
13.666


200
150
100
50
0 PPM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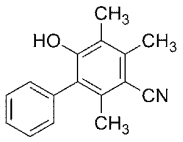
7.477
7.458
7.258
7.238
7.218
6.779
2.518
2.241
HO
CH3
CN
CH3
3t
3.12
2.19
0.93
2.77
3.00
10
8
6
4
2
PPM
156.169
143.530
142.006
133.558
130.252
129.779
128.894
126.696
118.033
114.690
105.786
77.358
77.047
76.731
20.836
19.274
200
150
100
50
0
PPM


7.562
7.545
7.526
7.495
7.477
7.275
7.271
7.249
7.232
5.253
2.518
2.218
2.207
1.269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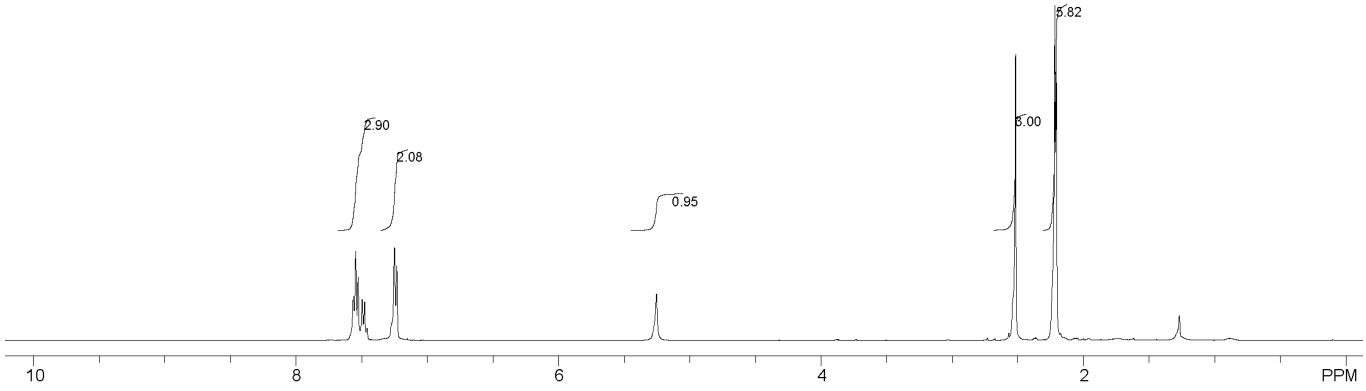
HO
CH3
CN
CH3

3u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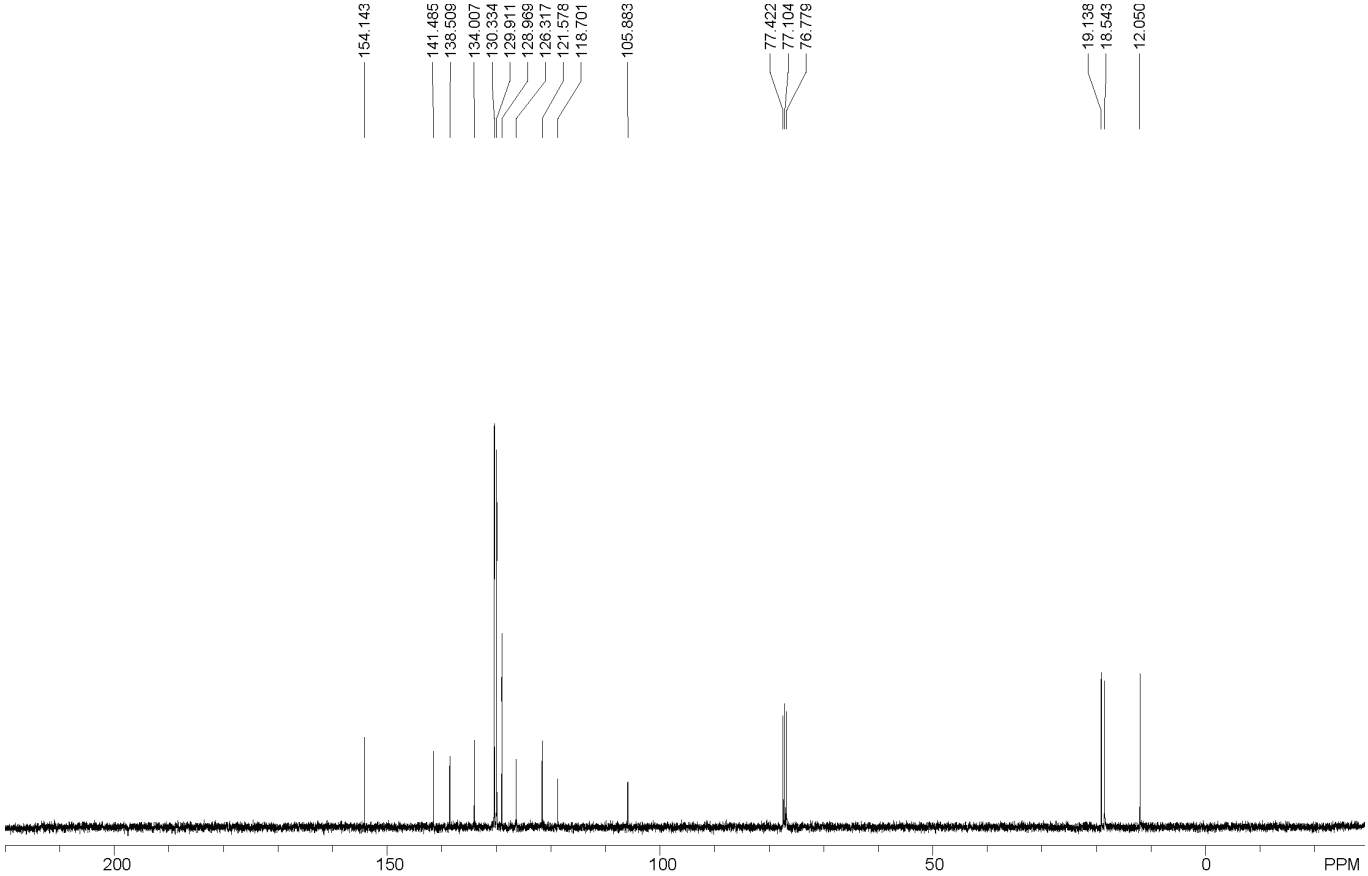
10
8
6
4
2
PPM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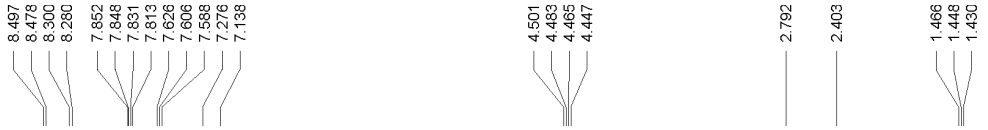
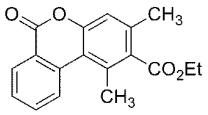
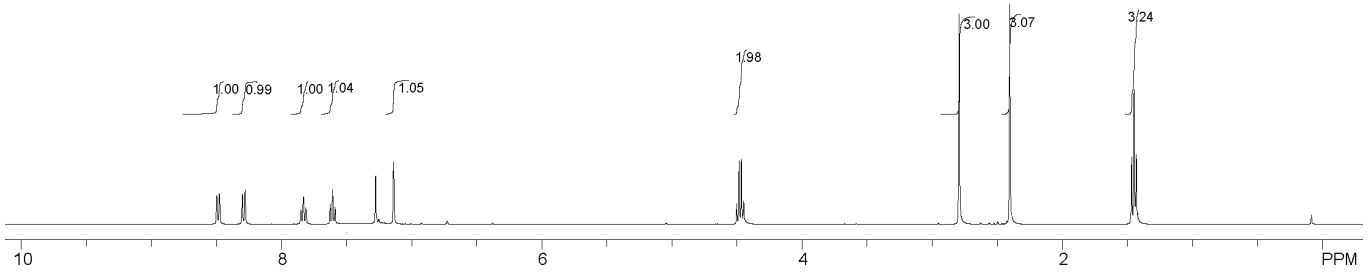
130.334
129.911
128.969
126.317
121.578
118.701
105.883
77.422
77.104
76.779
19.138
18.543
12.050
200
150
100
50
0
PPM

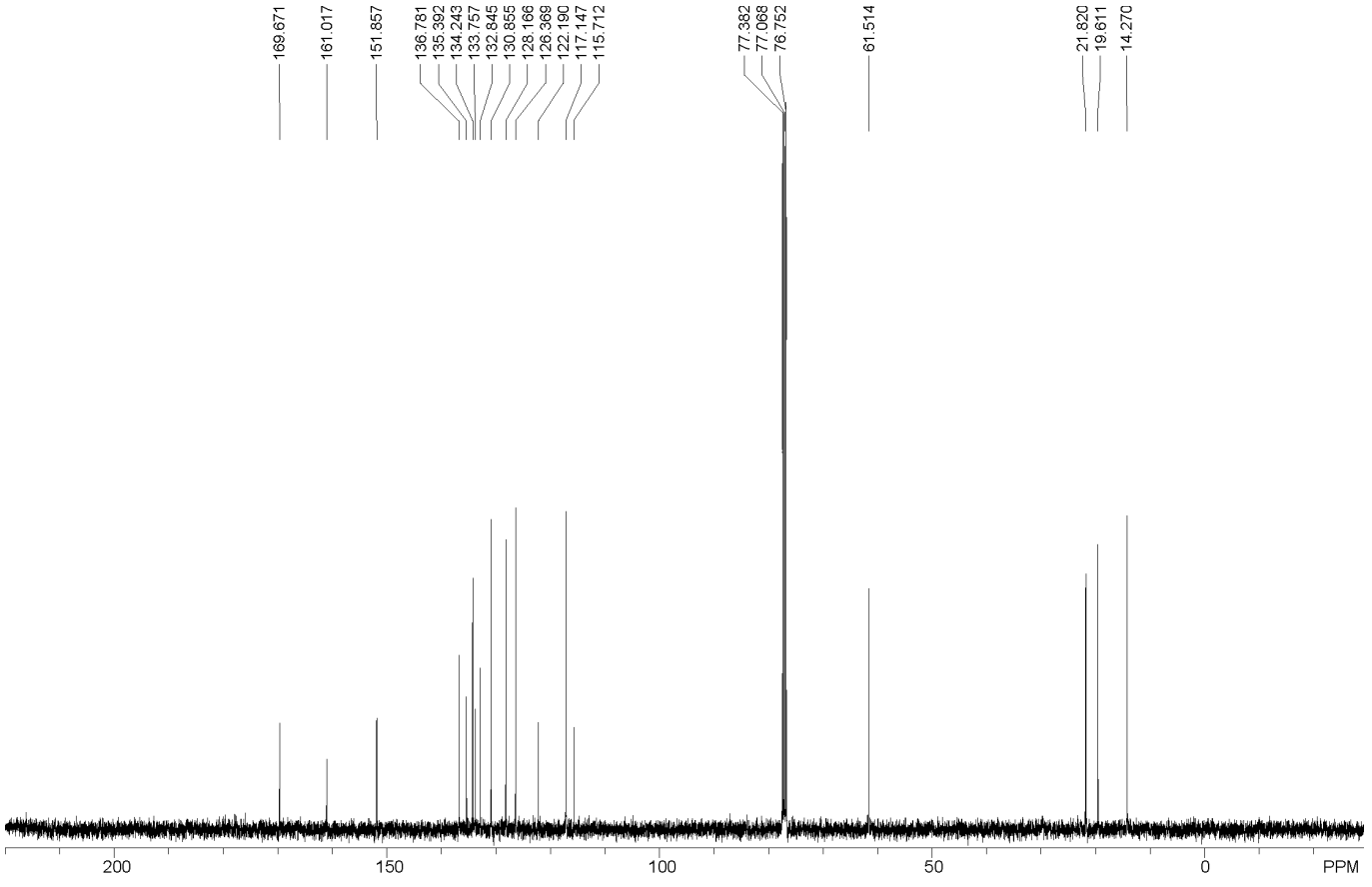
IV. Copies of ^{1}H and ^{13}C NMR spectra of 4a-4r

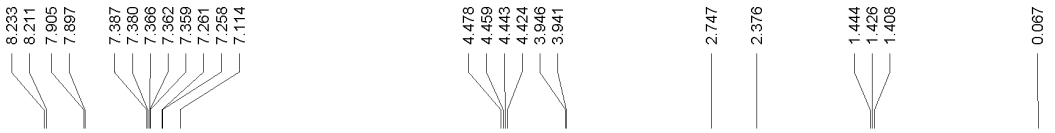




4a



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7.362
7.359
7.261
7.258
7.114
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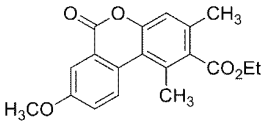
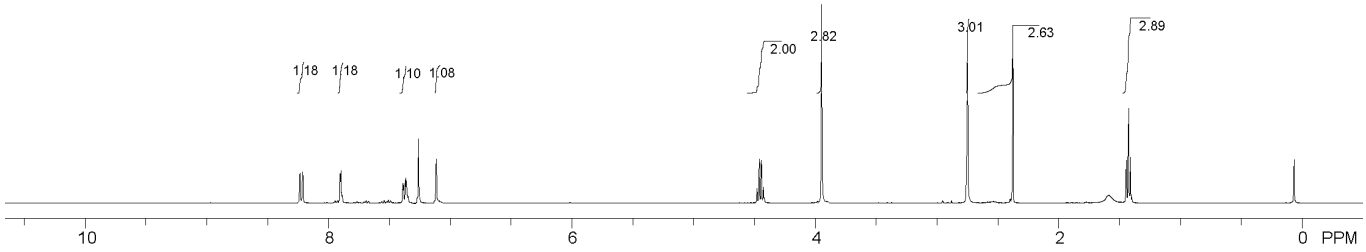
4.424
3.946
3.941
2.747
2.376
1.444
1.426
1.408
0.067


O
O
CH3
CO2Et
CH3
H3CO

4b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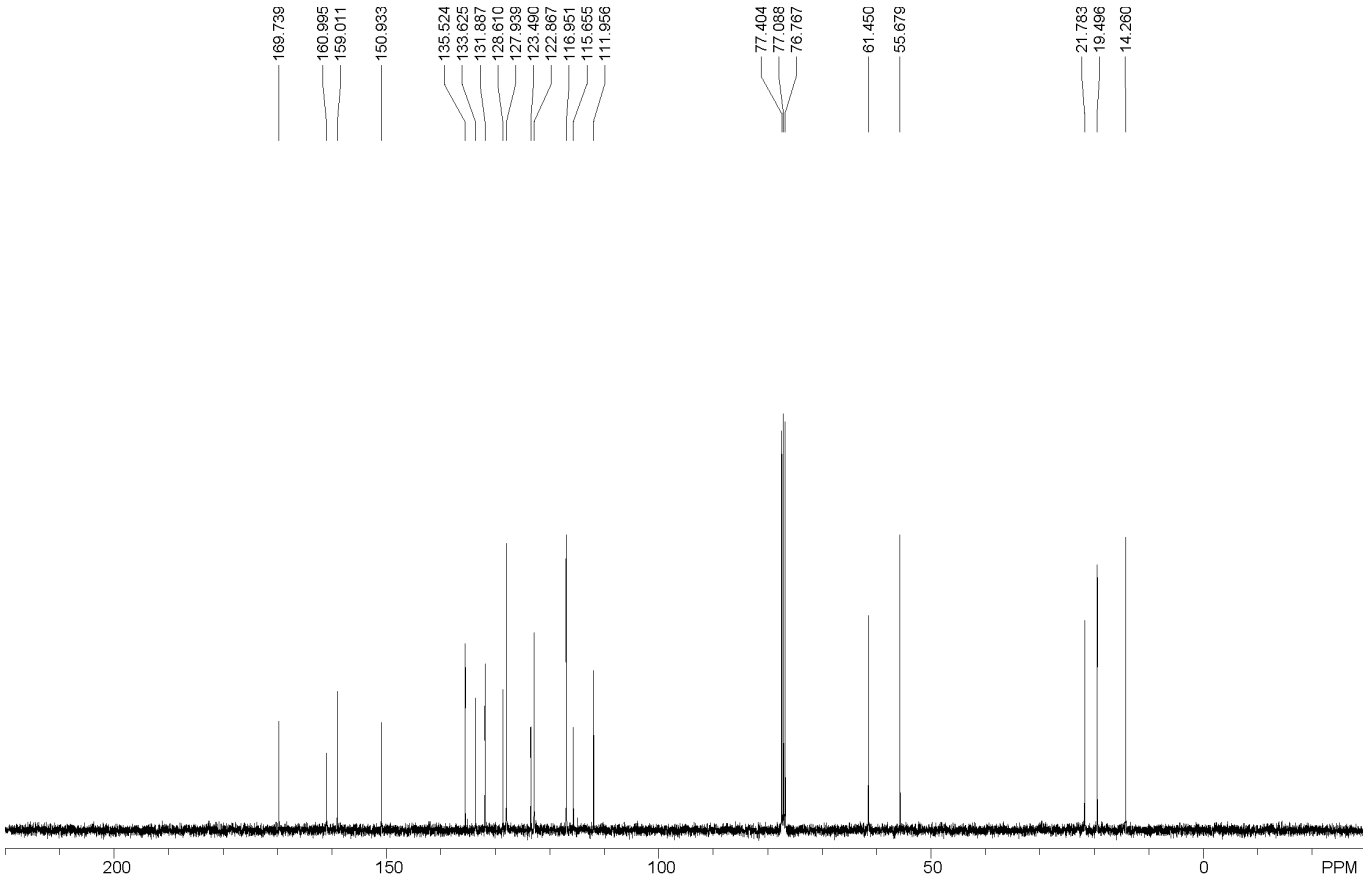
2.00
2.82
3.01
2.63
2.89
10
8
6
4
2
0
PPM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123.490
122.867
116.951
115.655
111.956
77.404
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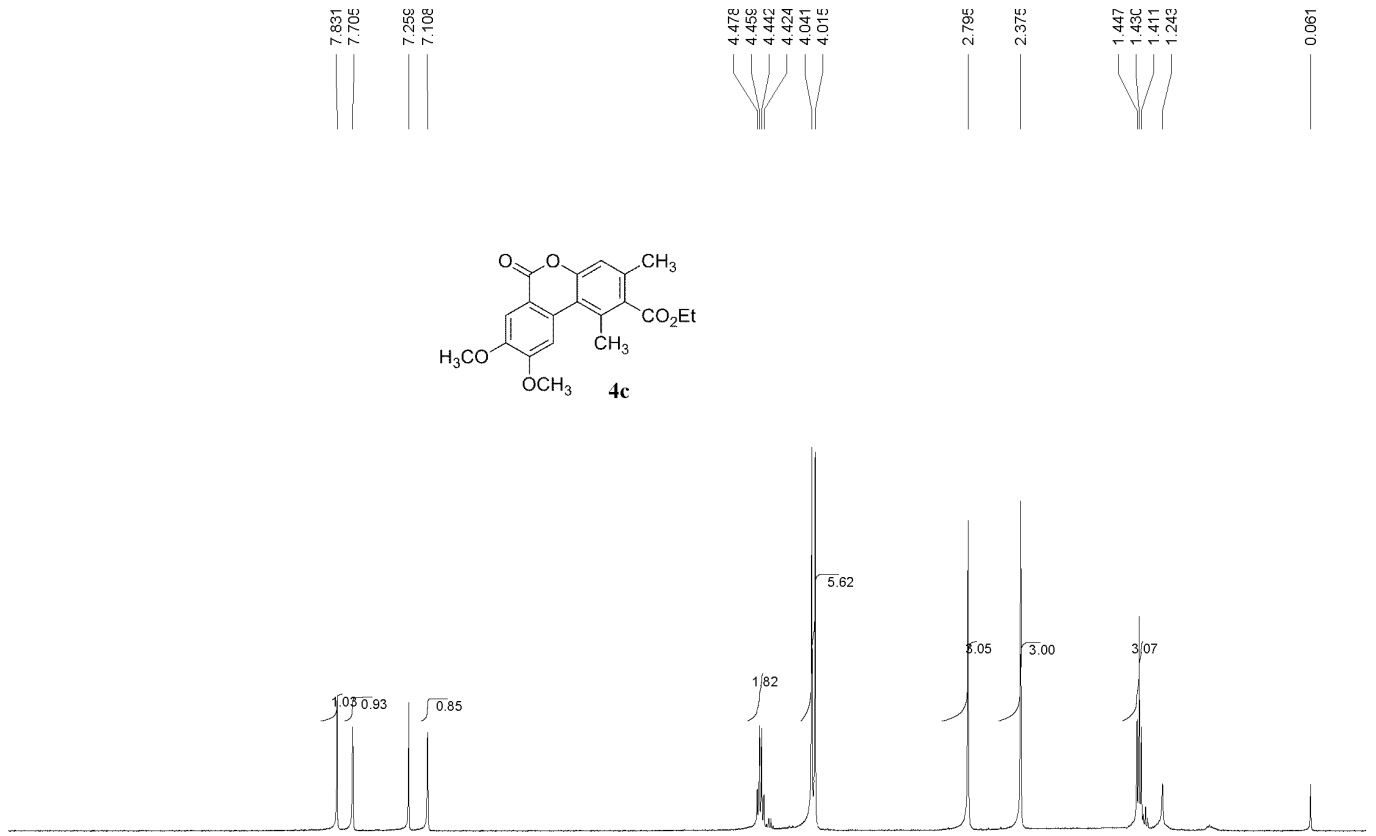
76.767
61.450
55.679
21.783
19.496
14.260
200
150
100
50
0
PPM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4.458
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1.411
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CH3
H3CO
OCH3
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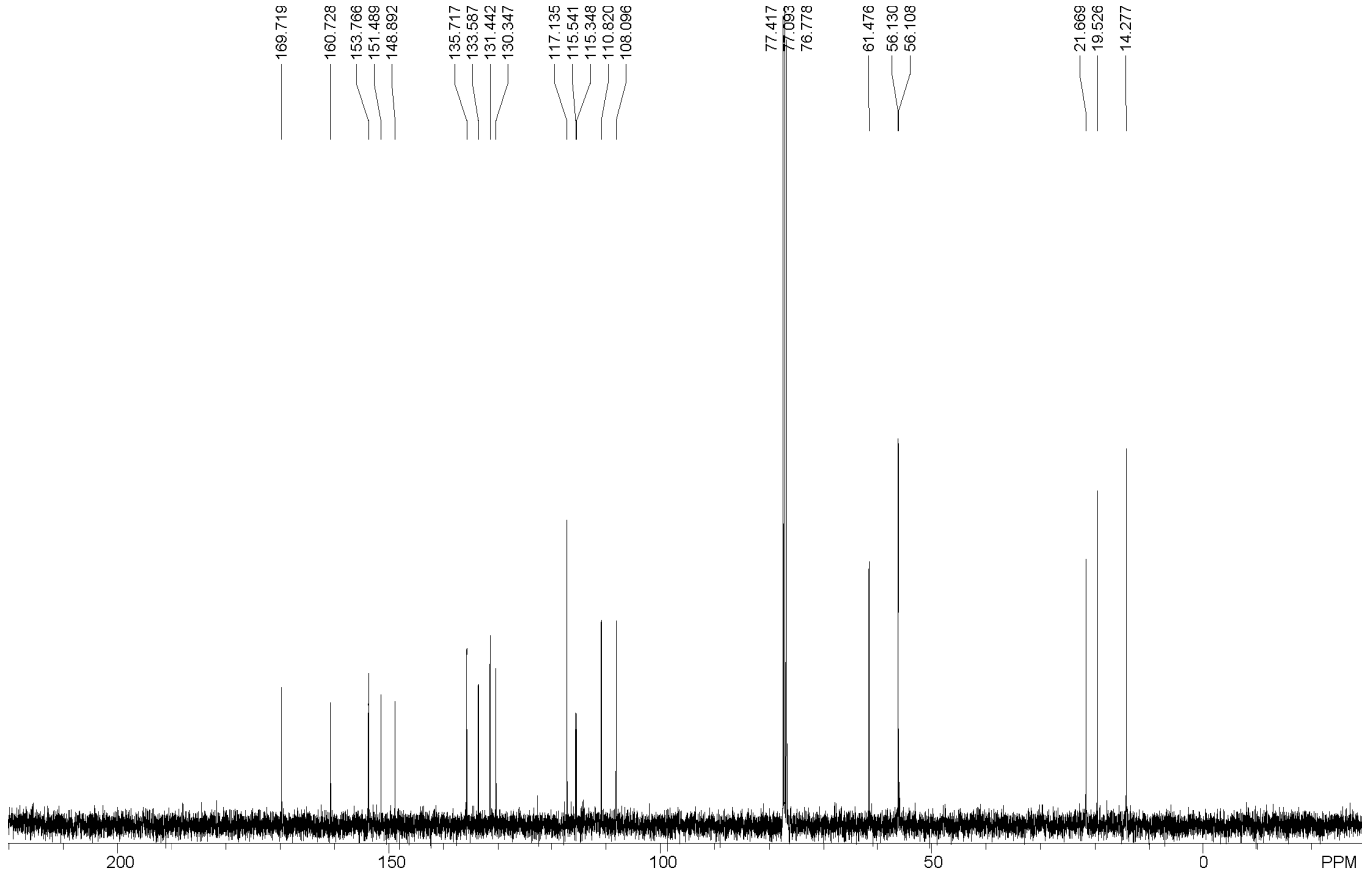
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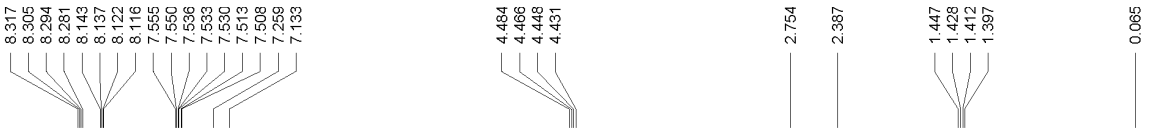
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7.513
7.508
7.259
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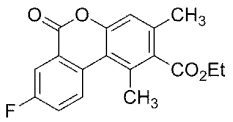
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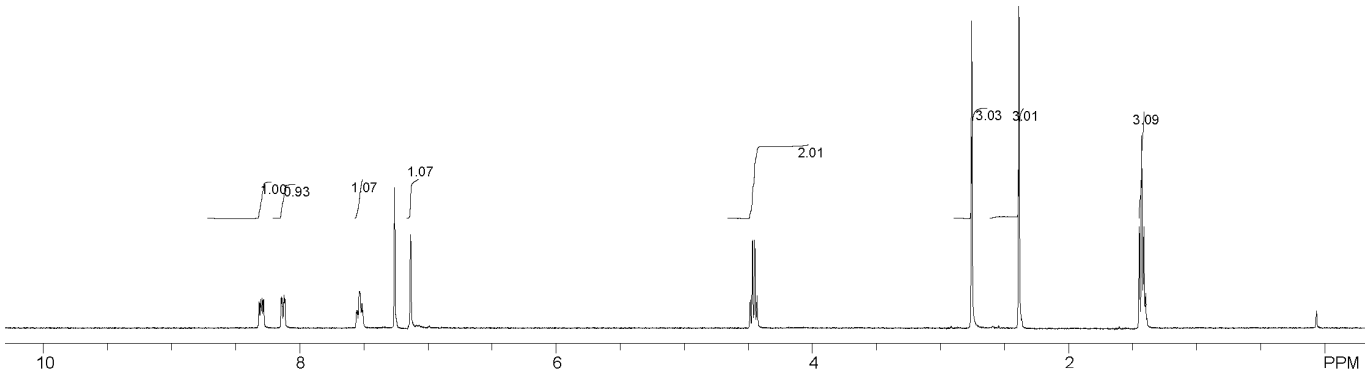
CO2Et
CH3
F

4d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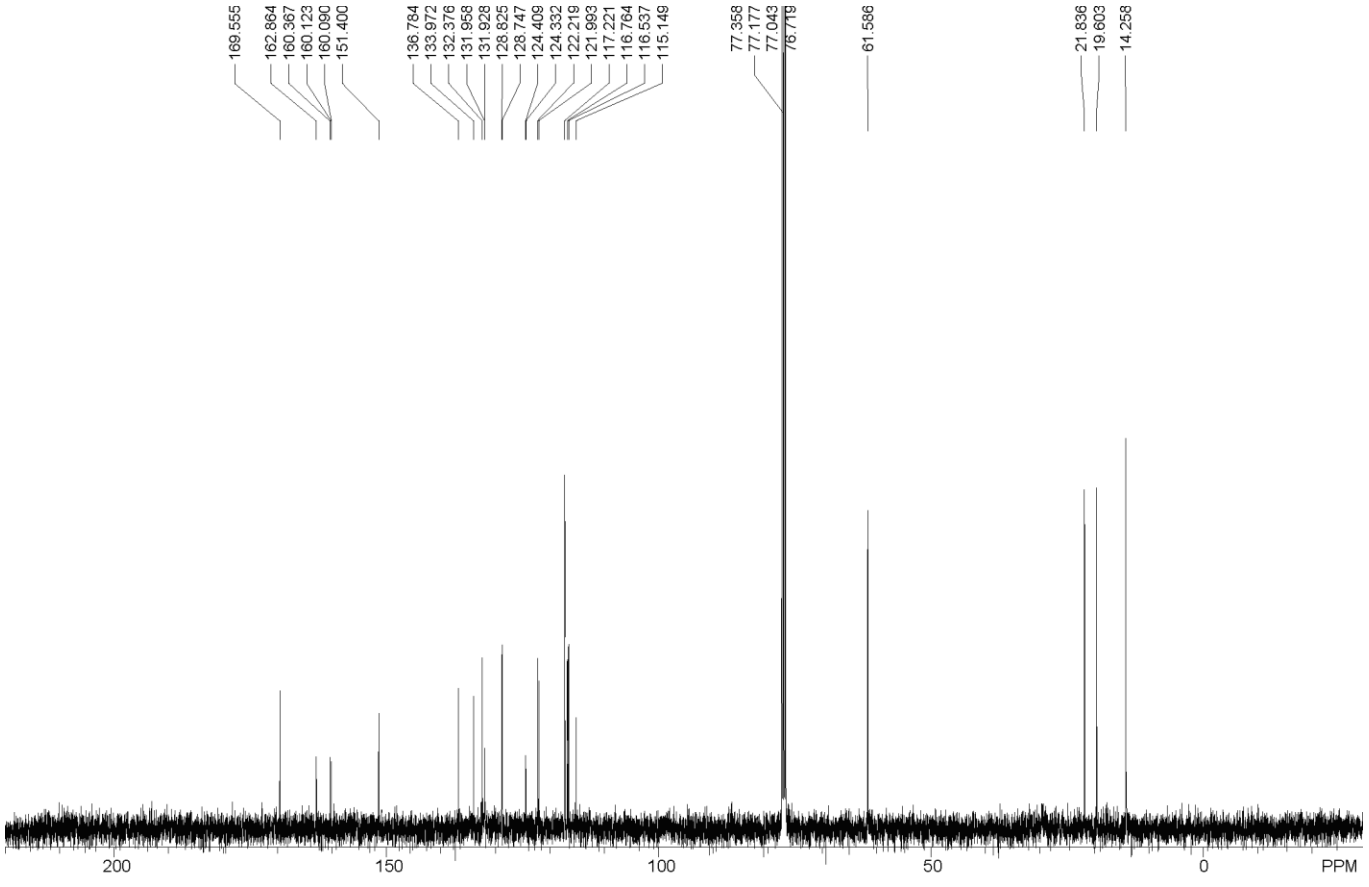
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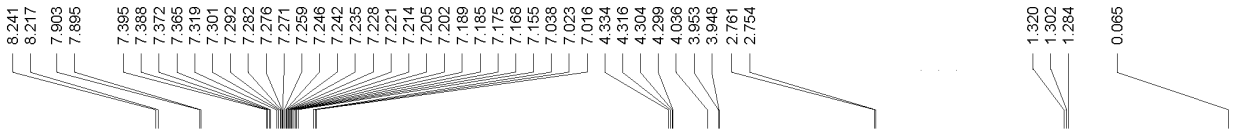
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7.016
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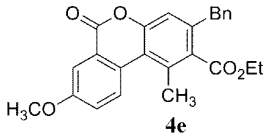
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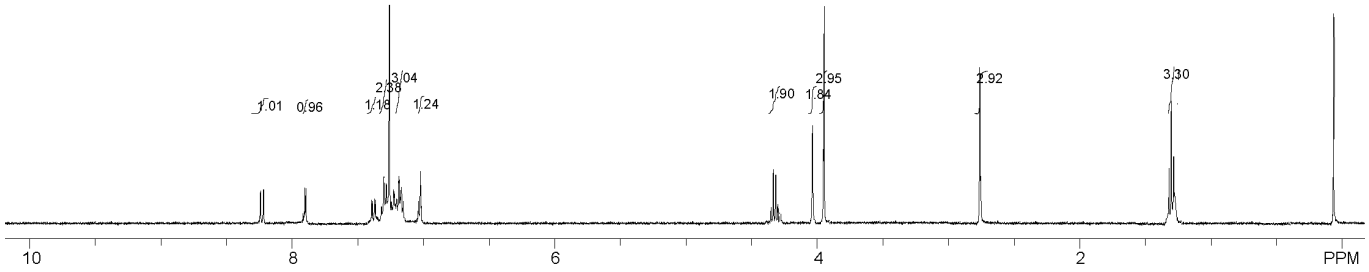
H3CO

4e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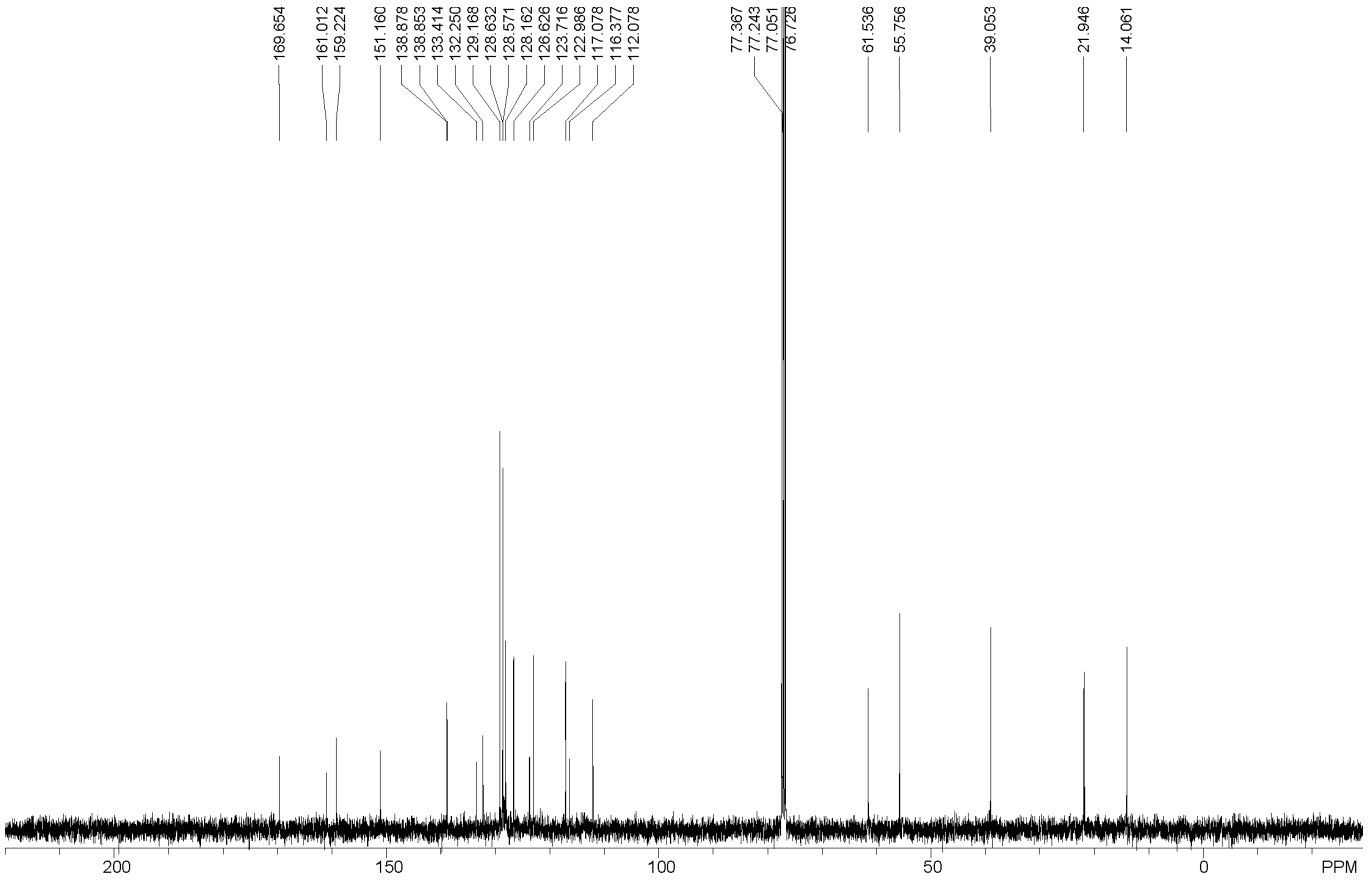
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126.626
123.716
122.986
117.078
116.377
112.078
77.367
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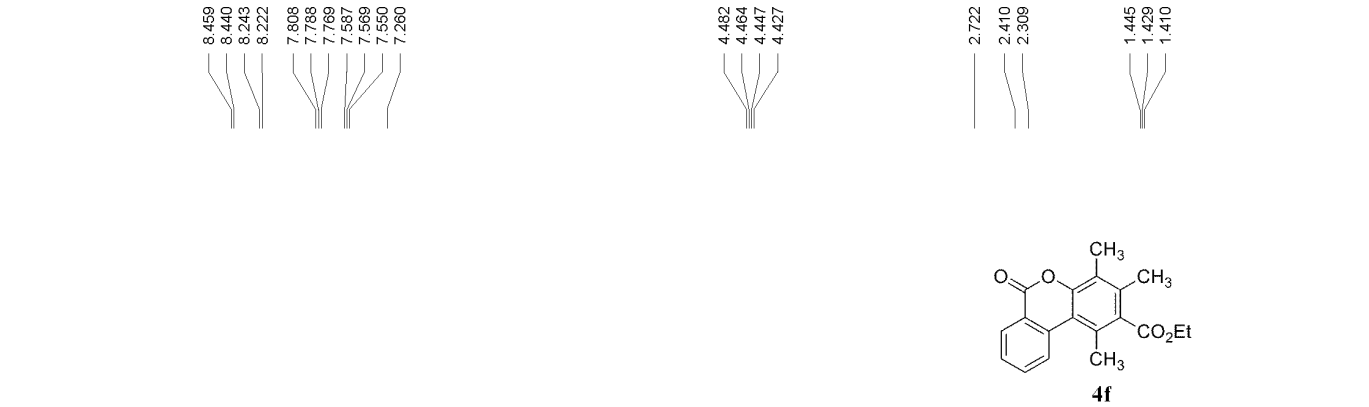
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7.550
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4.464
4.447
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2.309
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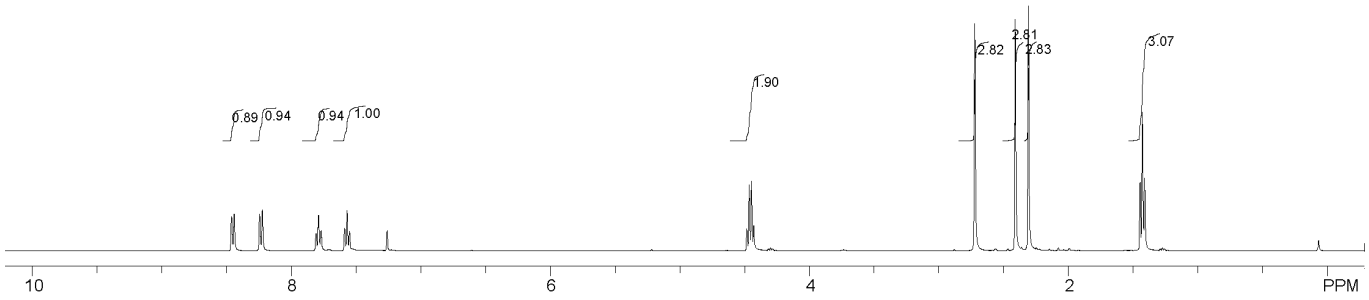
1.429
1.410

CH3
O
O
CH3
CO2Et
CH3

4f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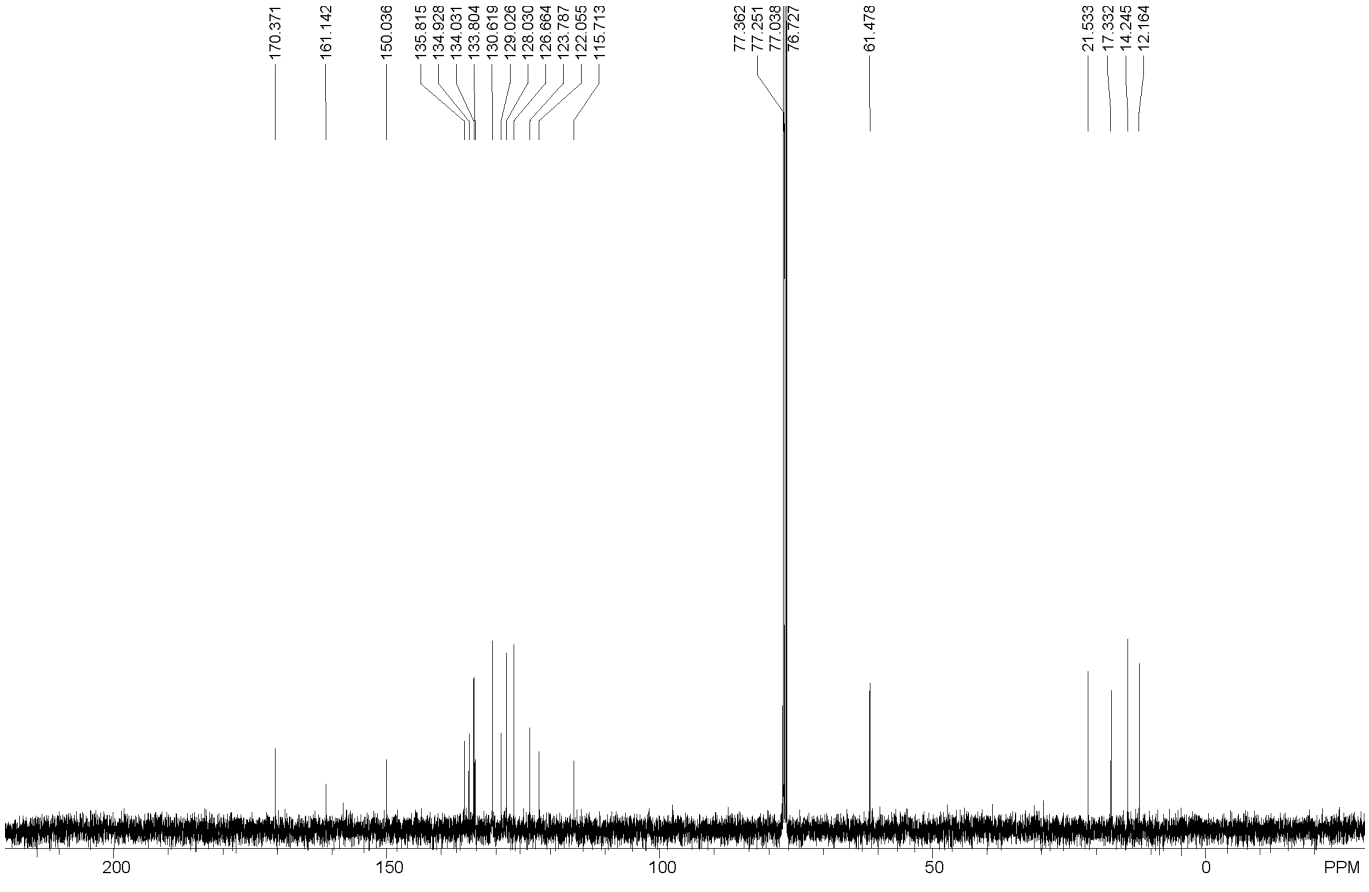
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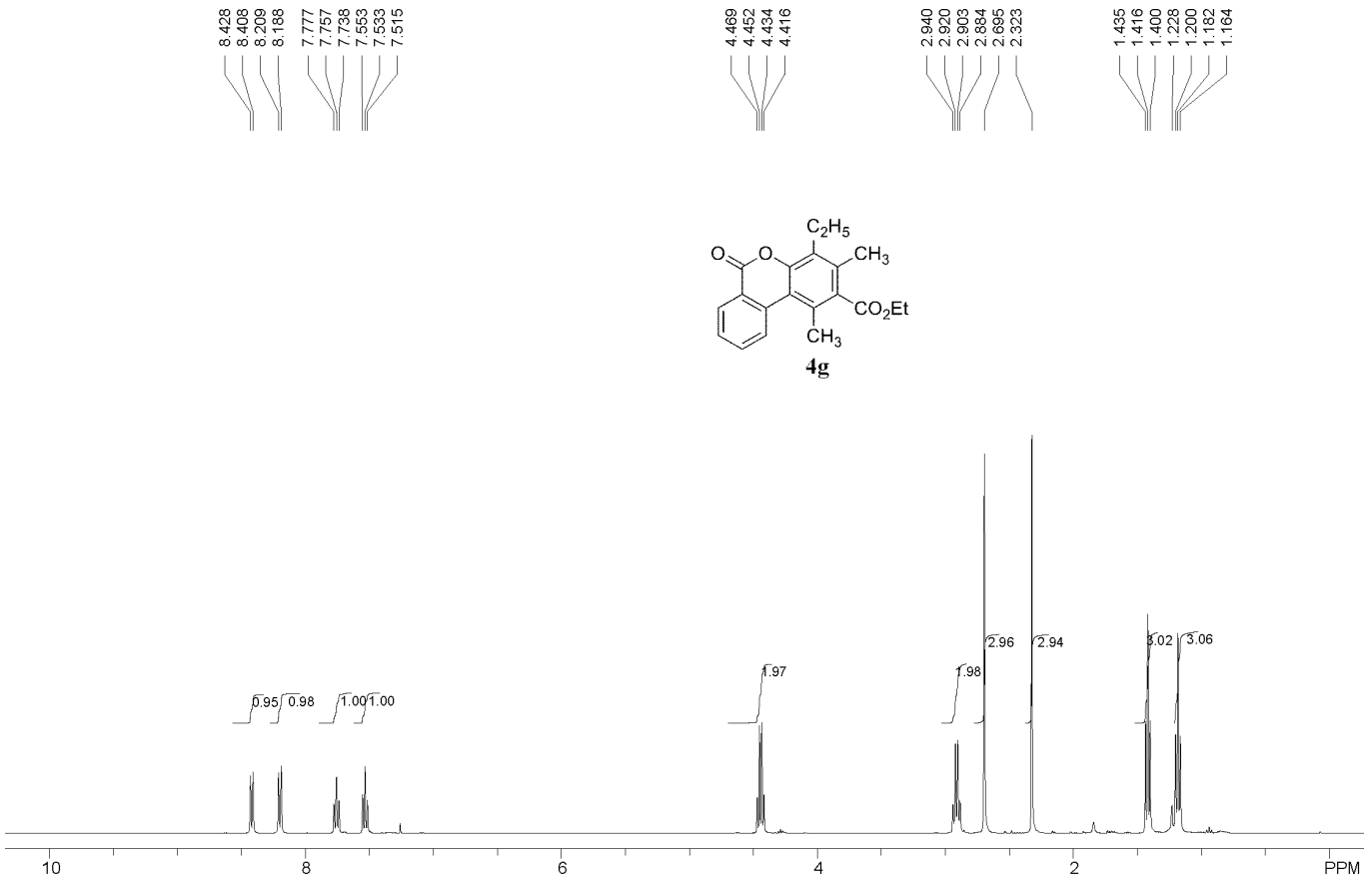
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4.416
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2.920
2.903
2.884
2.695
2.323
1.435
1.416
1.400
1.228
1.200
1.182
1.164
C2H5
CH3
CO2Et
CH3
4g
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0.98
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4
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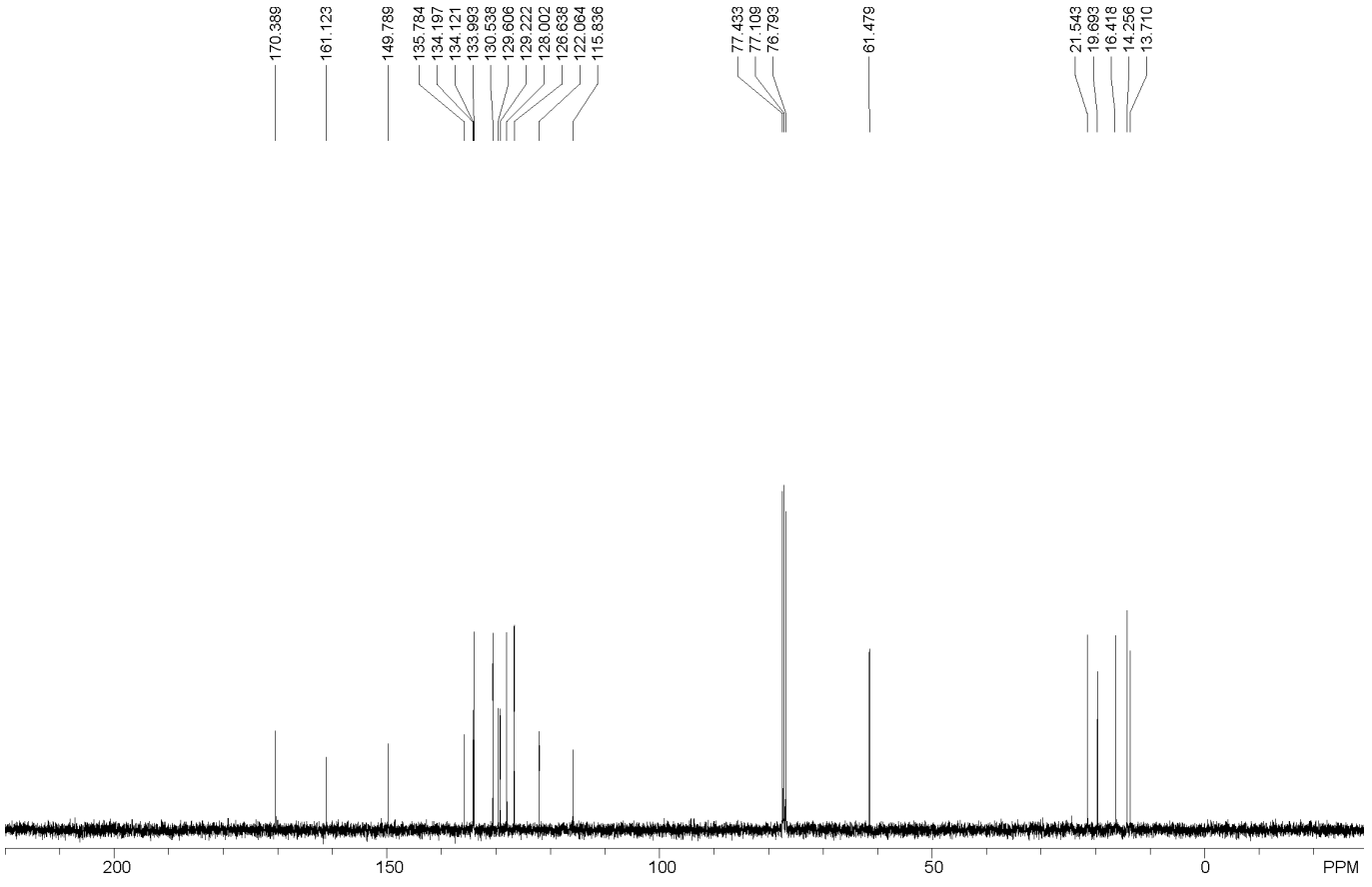
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77.433
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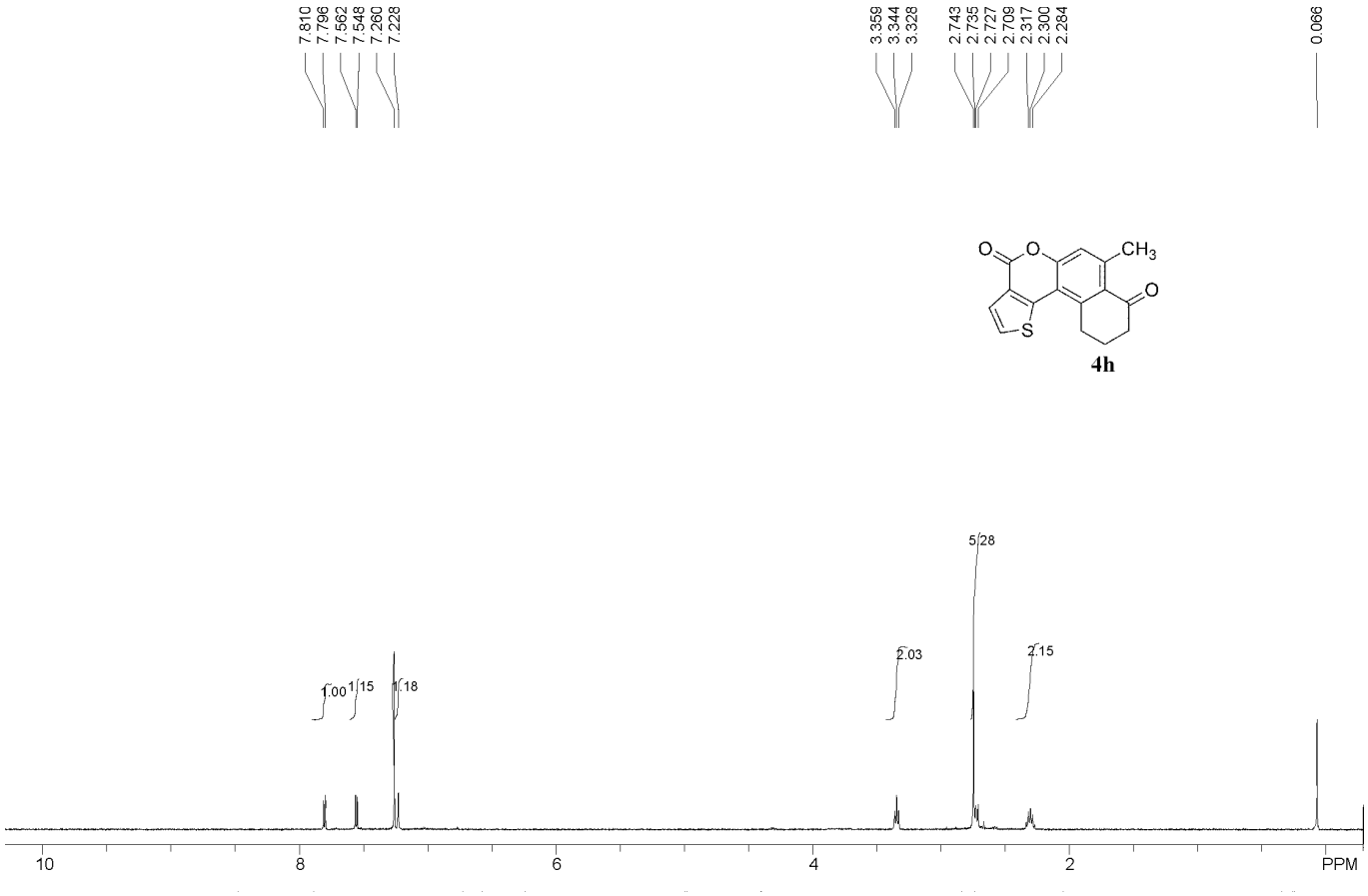
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2.727
2.709
2.317
2.300
2.284
0.066
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O
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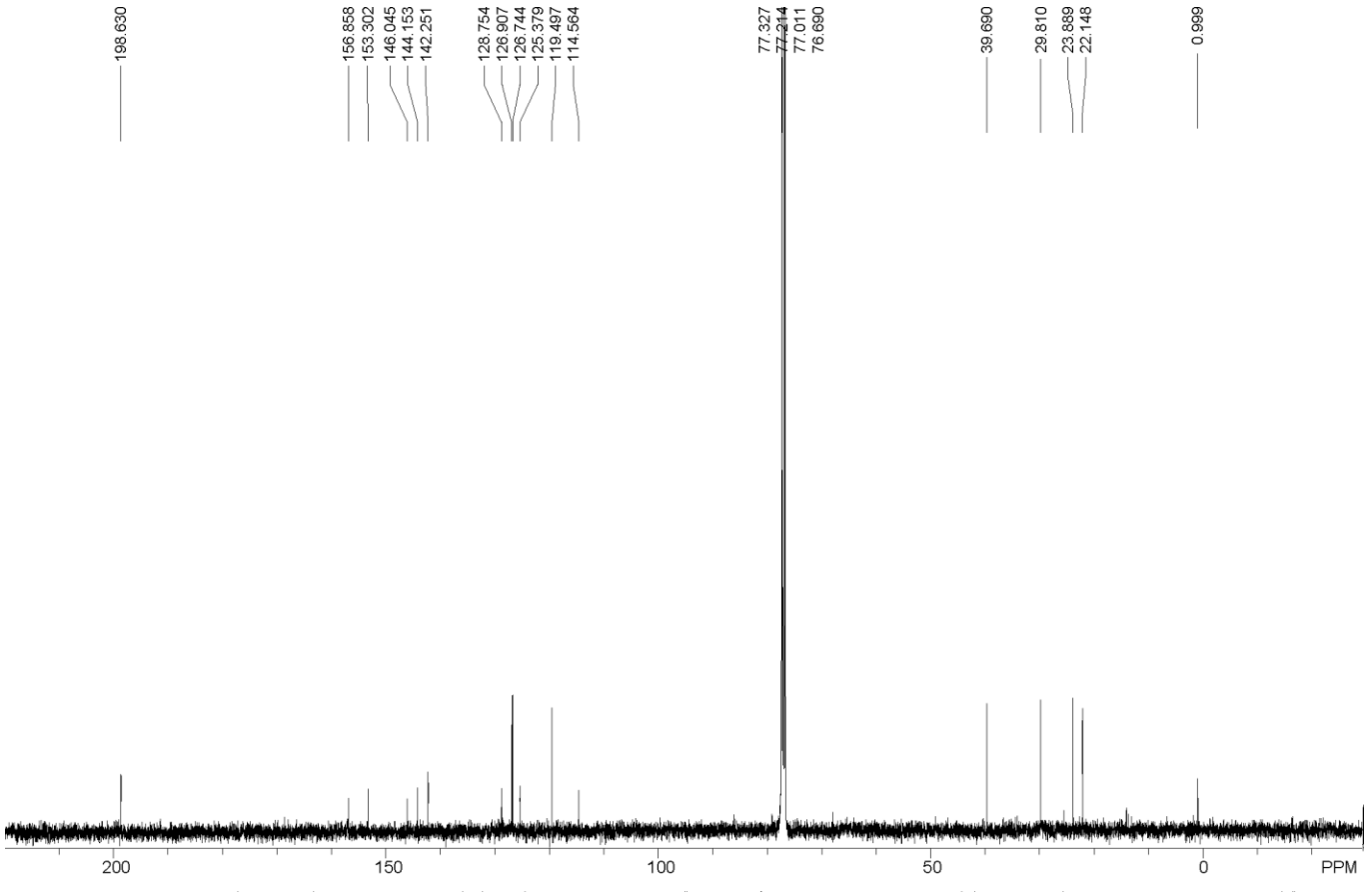
PPM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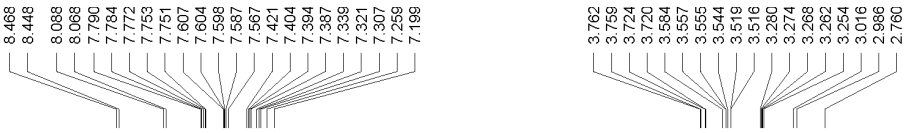
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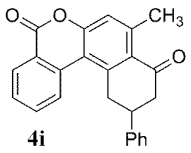
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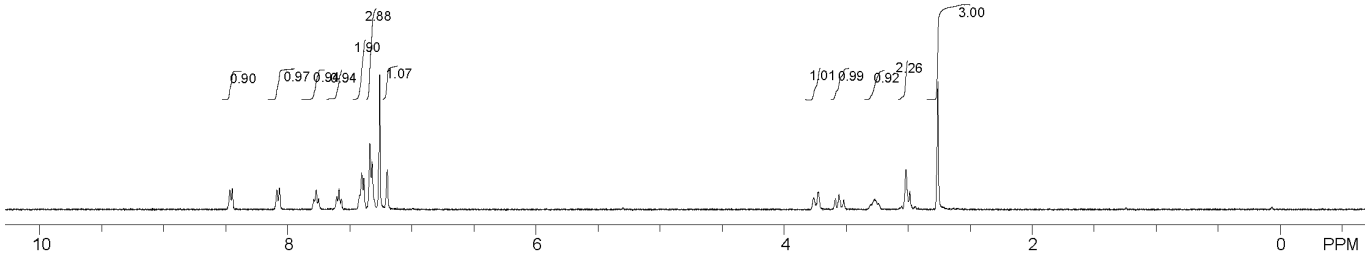
O
Ph

4i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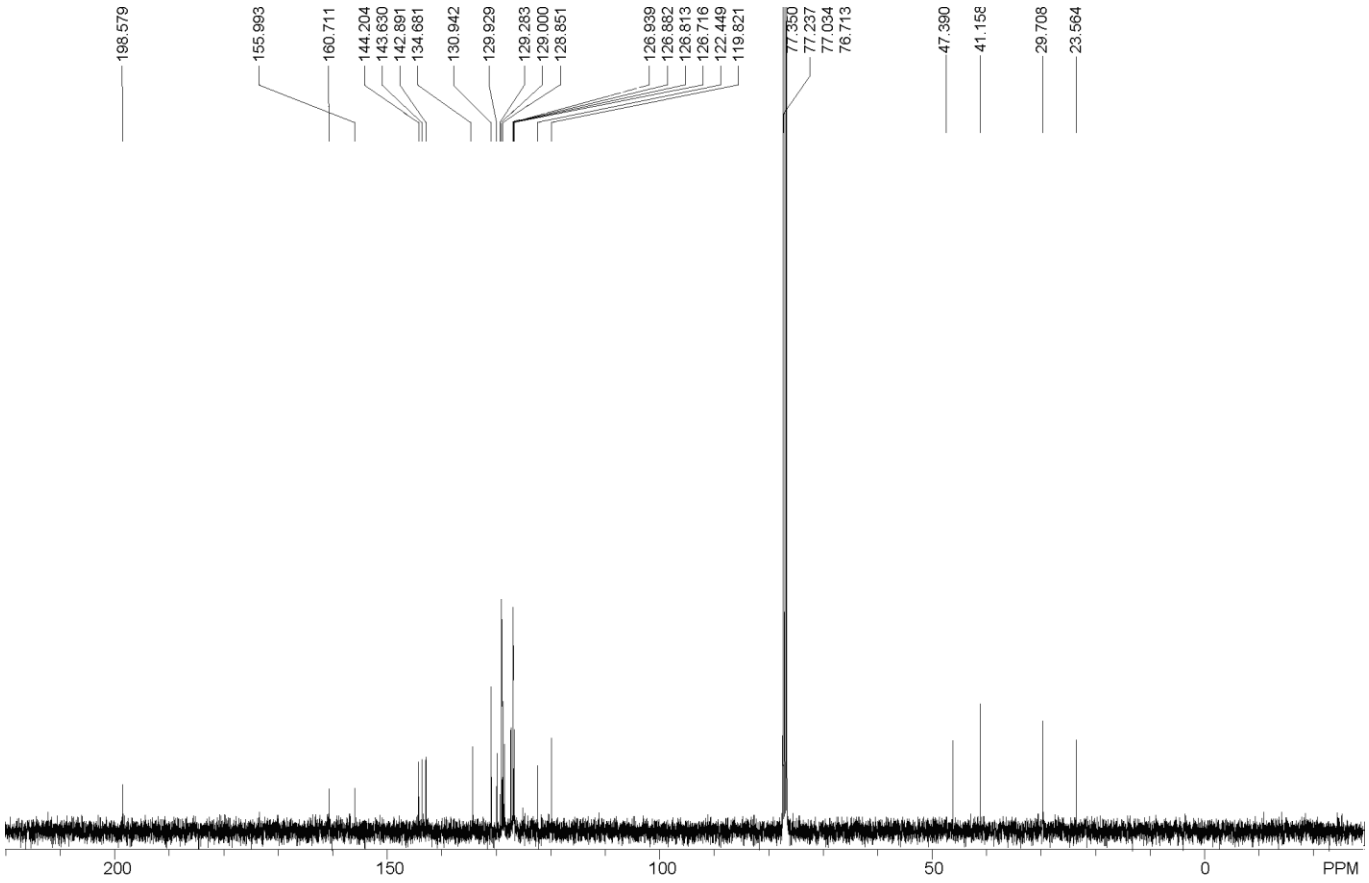
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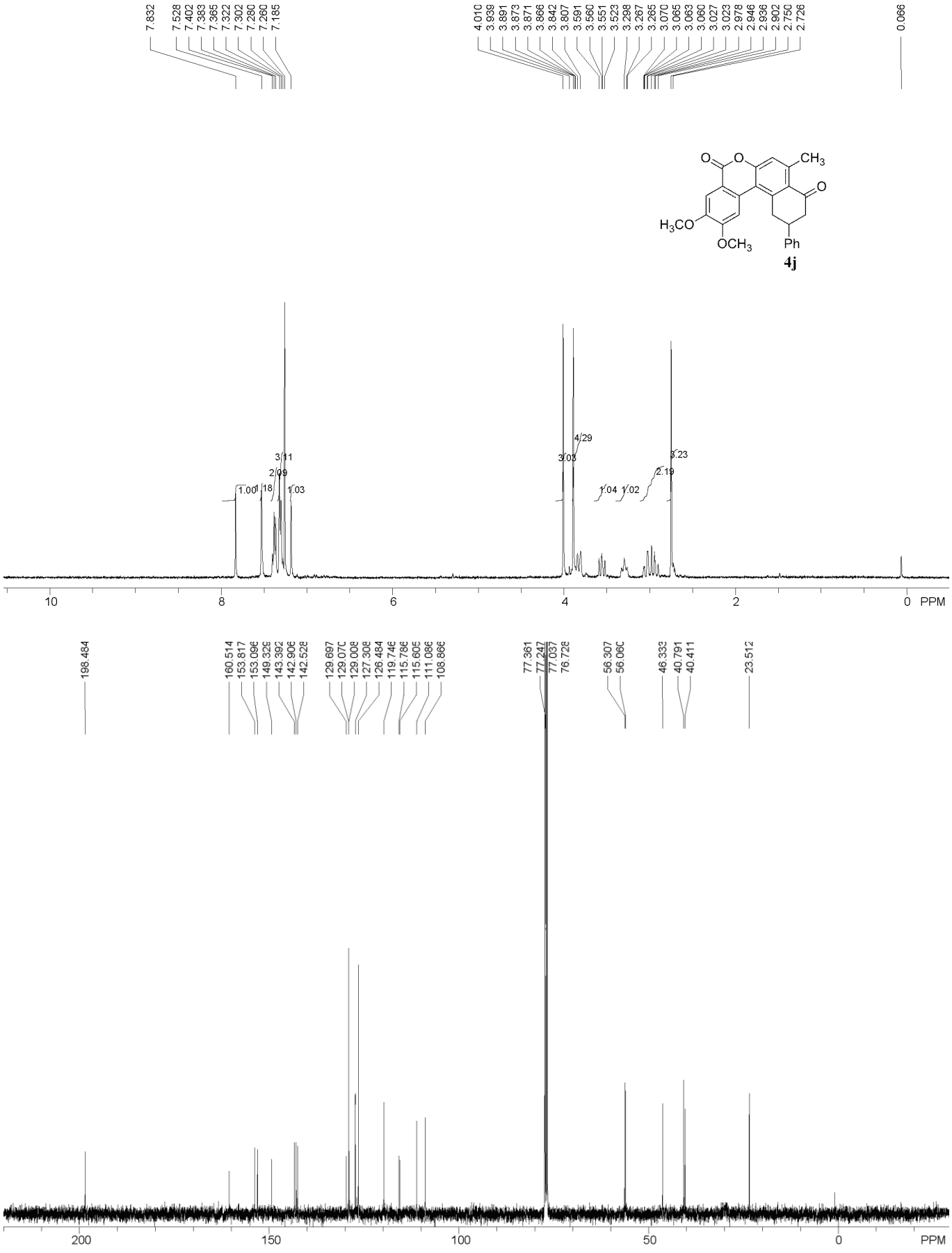
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O
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O
H3CO
OCH3
Ph
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1.18
3.11
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1.03
3.03
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1.04
1.02
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40.411
23.512
200
150
100
50
0 PPM


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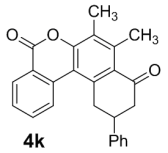
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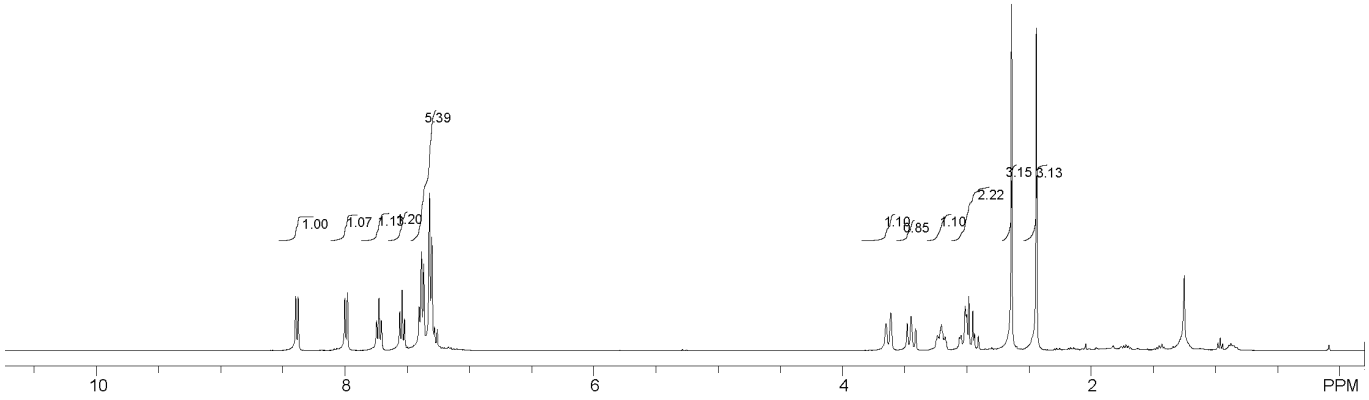
CH3
O
O
O
Ph

4k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10
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4
2
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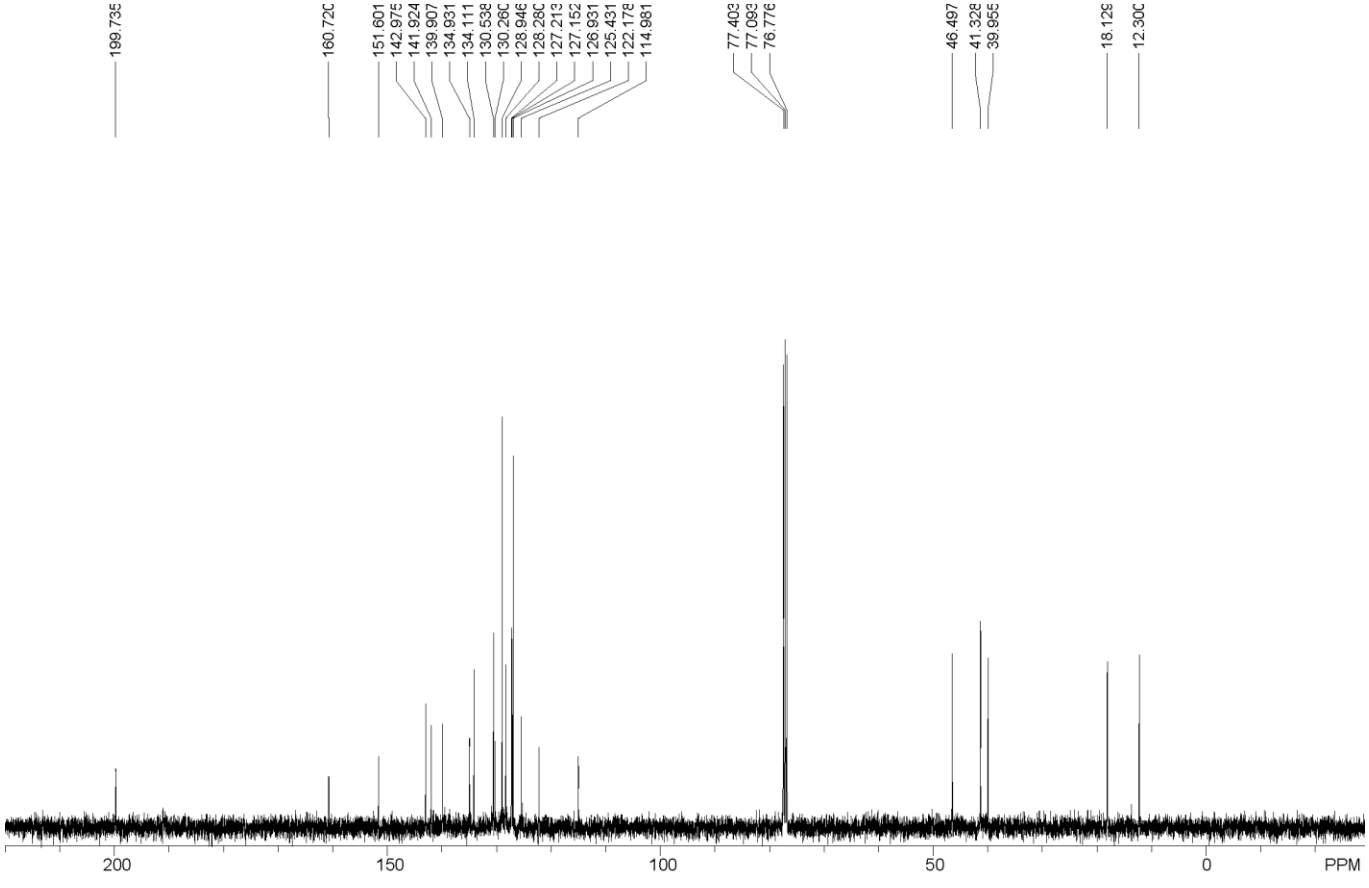
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127.213
127.152
126.931
125.431
122.178
114.981
77.403
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76.776
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41.328
39.955
18.128
12.300
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150
100
50
0
PPM


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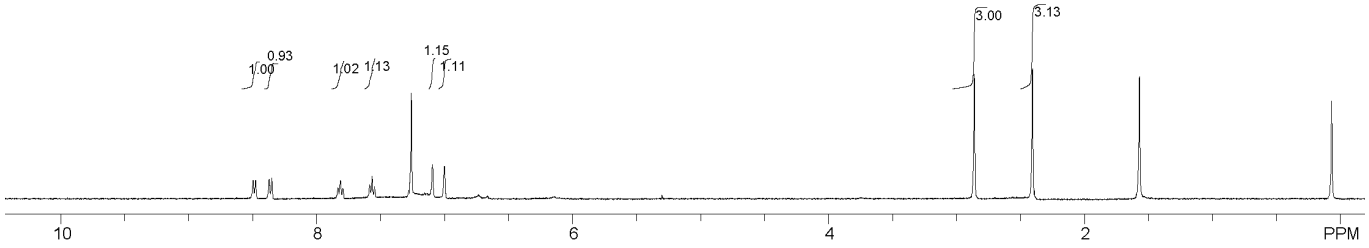
O
CH3
CH3

4l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6
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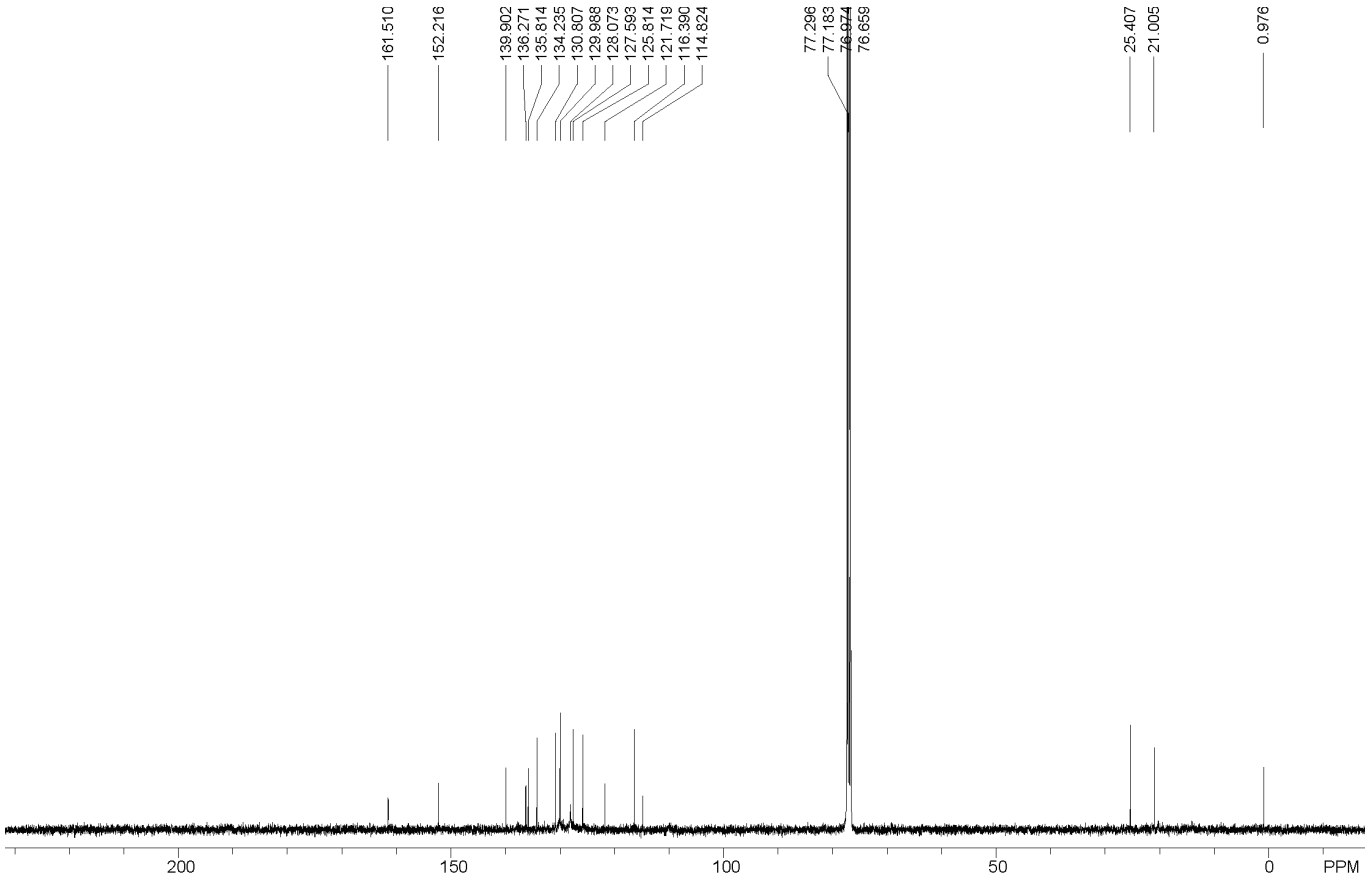
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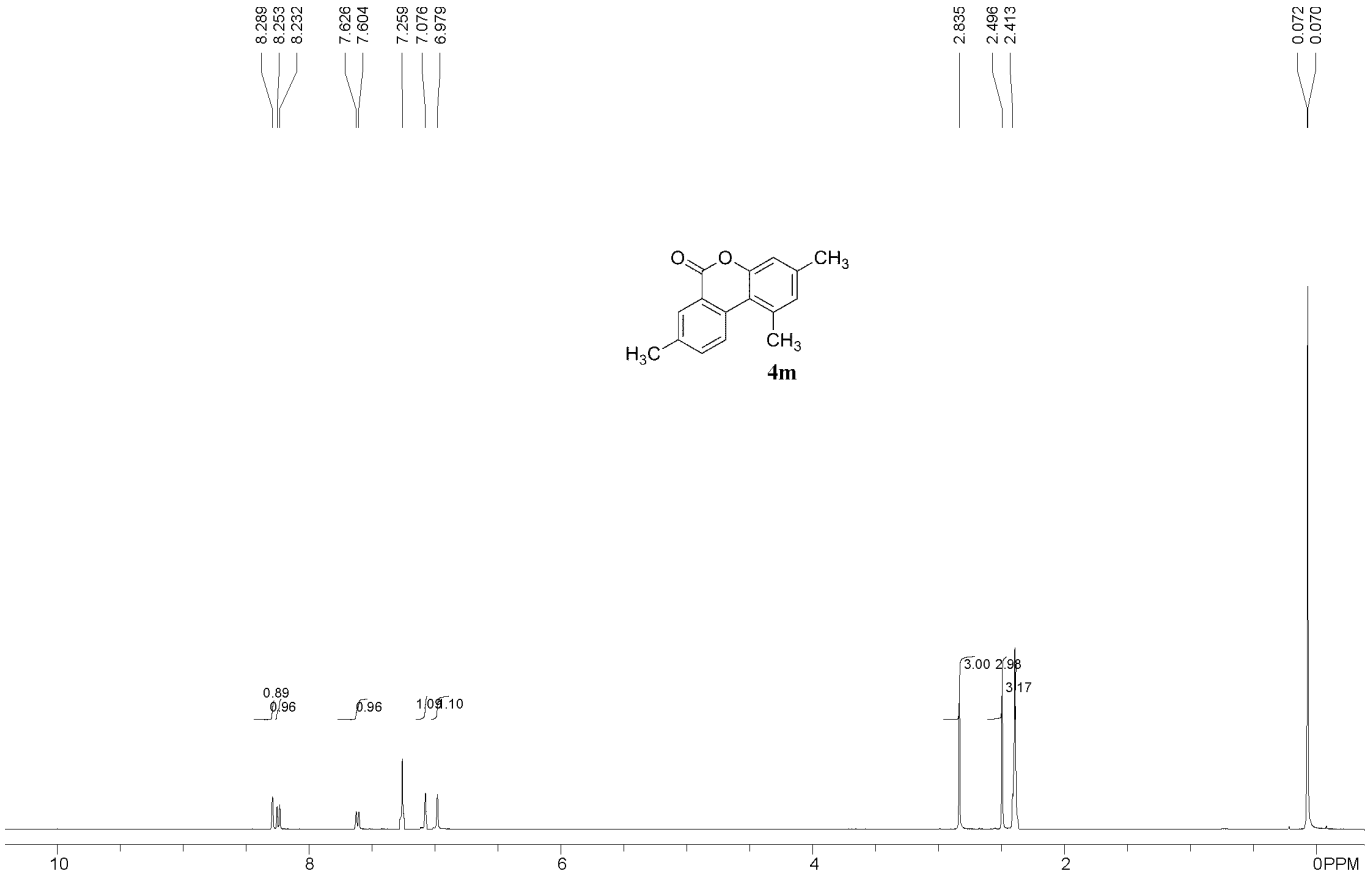
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0.070
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O
CH3
H3C
CH3
4m
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2
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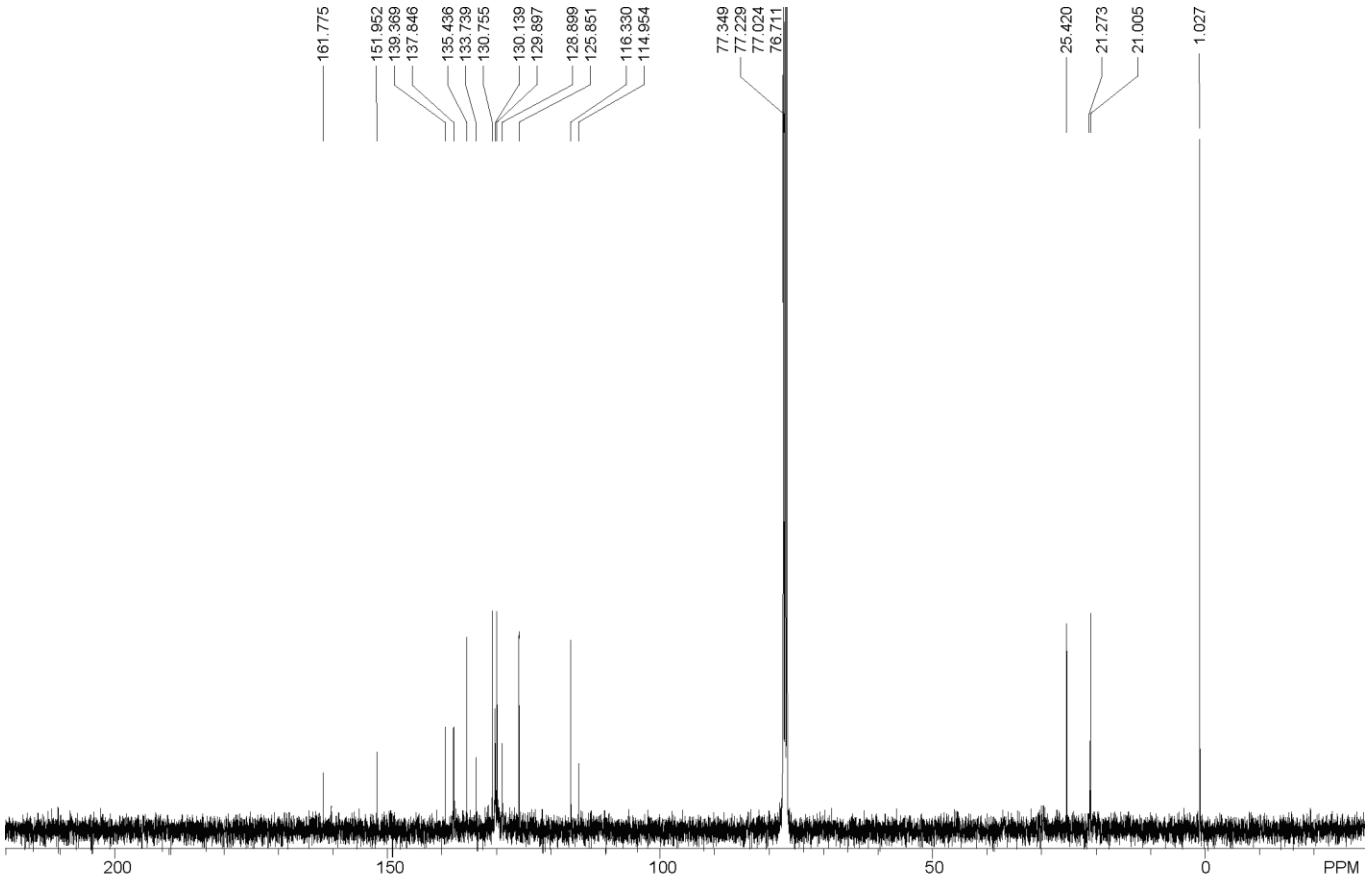
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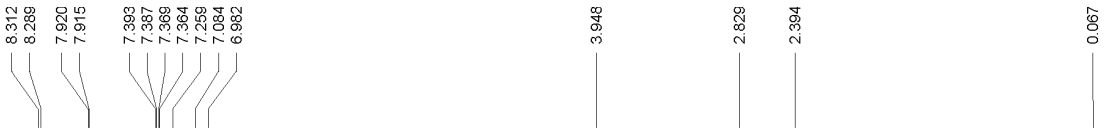
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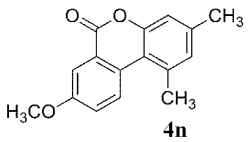
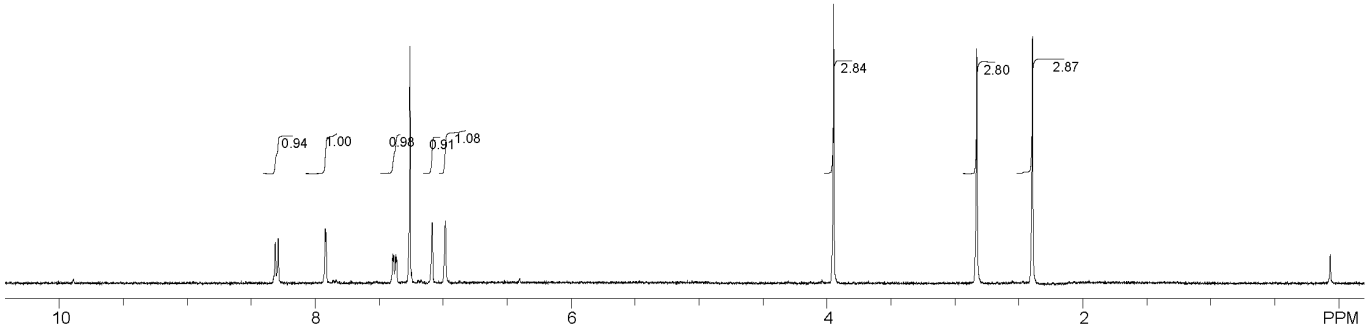

O
O
CH3
CH3
H3CO

4n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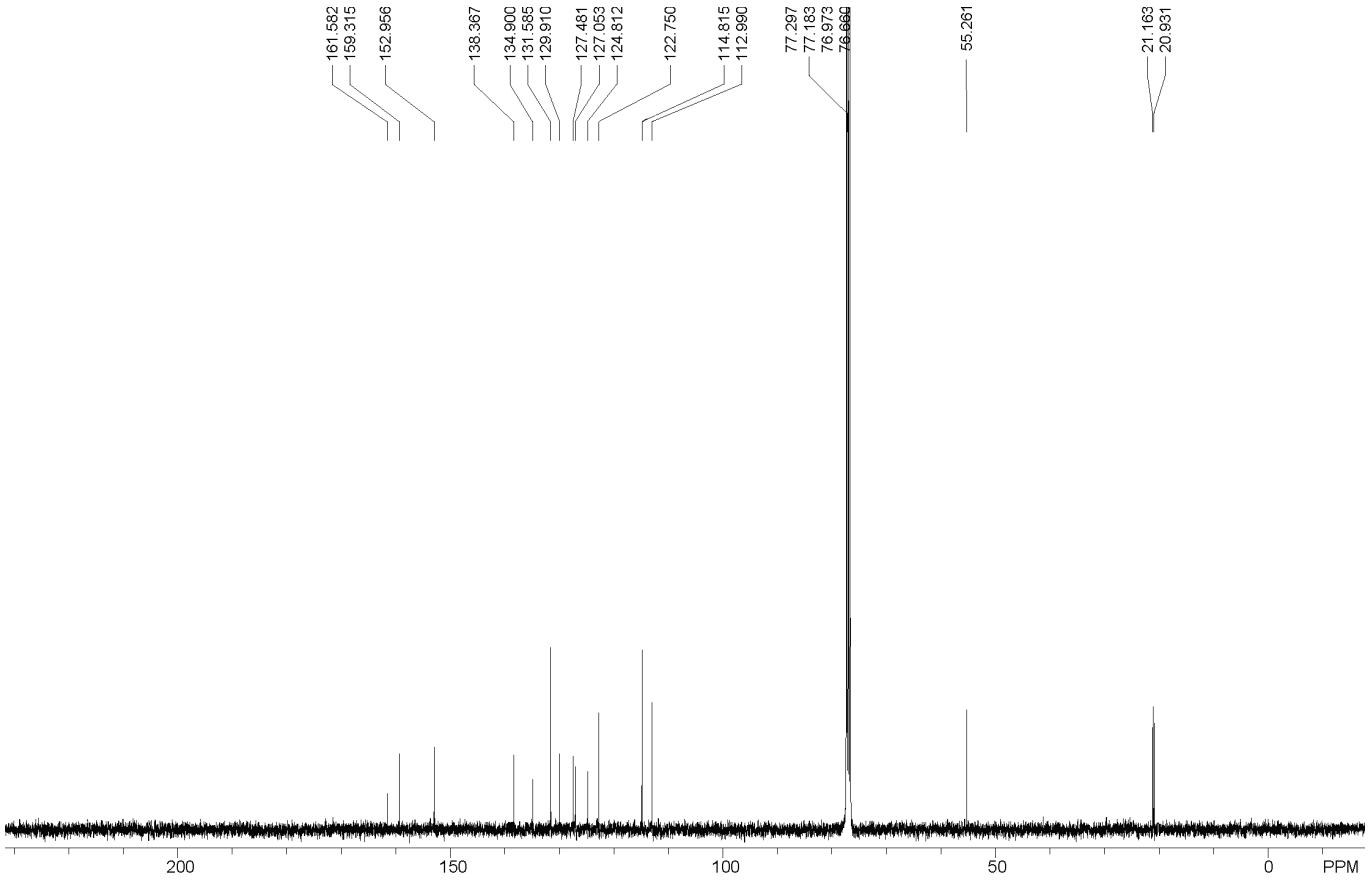
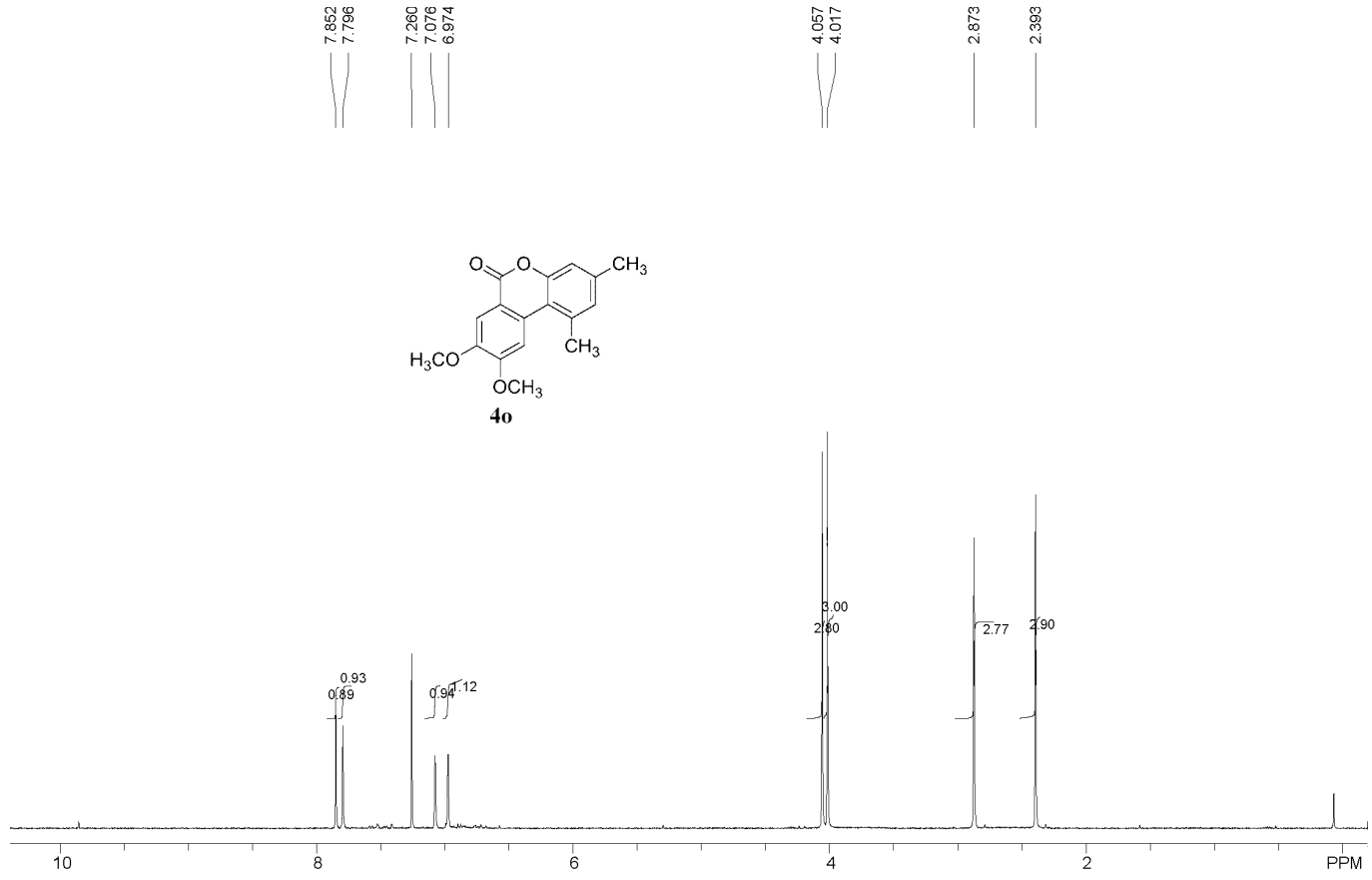
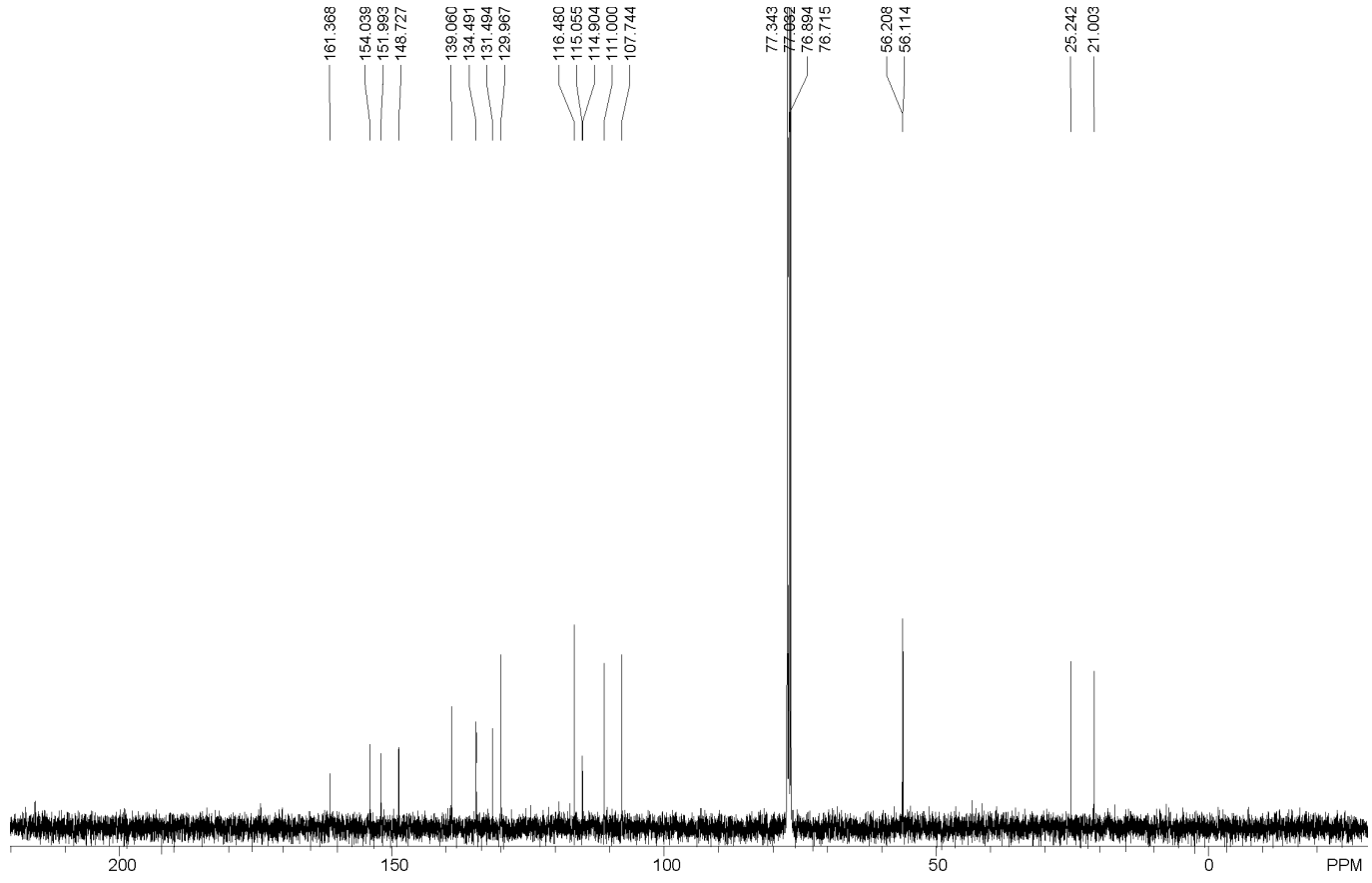
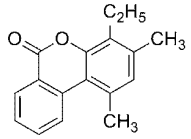
1.00
0.98
0.91
1.08
2.84
2.80
2.87
10
8
6
4
2
PPM


161.582
159.315
152.956
138.367
134.900
131.585
129.910
127.481
127.053
124.812
122.750
114.815
112.990
77.297
77.183
76.973
55.261
21.163
20.931
200
150
100
50
0
PPM

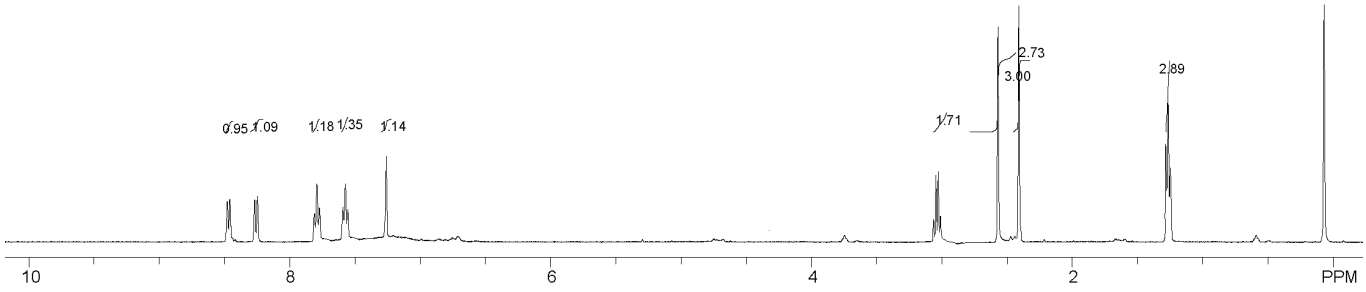

7.852
7.796
7.260
7.076
6.974
4.057
4.017
2.873
2.393
O
O
CH3
H3CO
CH3
OCH3
4o
3.00
2.80
2.77
2.90
0.93
0.89
0.94
1.12
10
8
6
4
2
PPM


161.368
154.039
151.993
148.727
139.060
134.491
131.494
129.967
116.480
115.055
114.904
111.000
107.744
77.343
76.894
76.715
56.208
56.114
25.242
21.003
200
150
100
50
0
PPM


8.479
8.459
8.269
8.248
7.809
7.791
7.773
7.593
7.572
7.554
7.260
3.061
3.043
3.025
3.003
2.595
2.426
1.234
1.215
1.197
0.070


C2H5
O
O
CH3
CH3

4p


0.95
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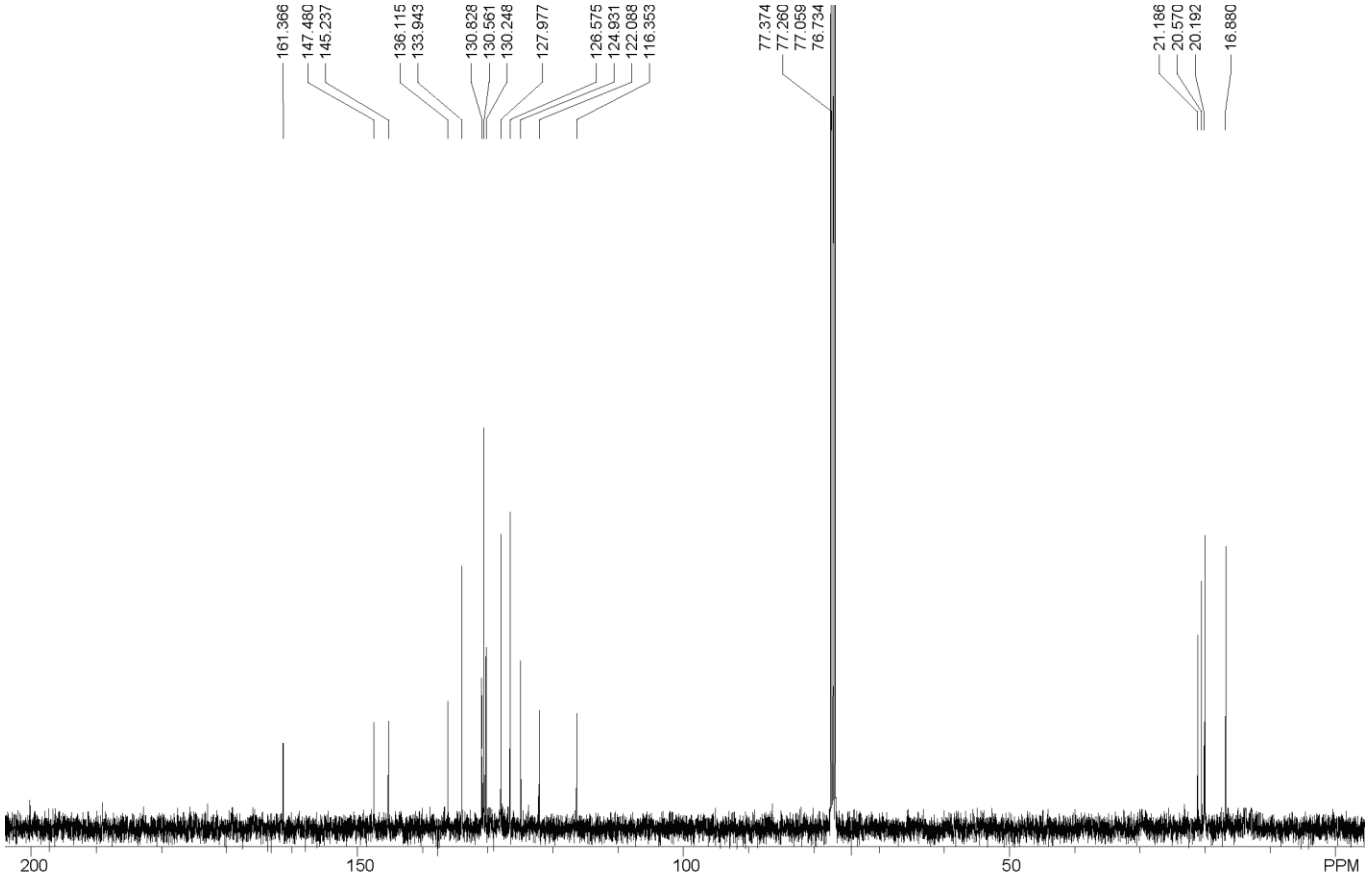
1.18
1.35
1.14
1.71
2.73
3.00
2.89
10
8
6
4
2
PPM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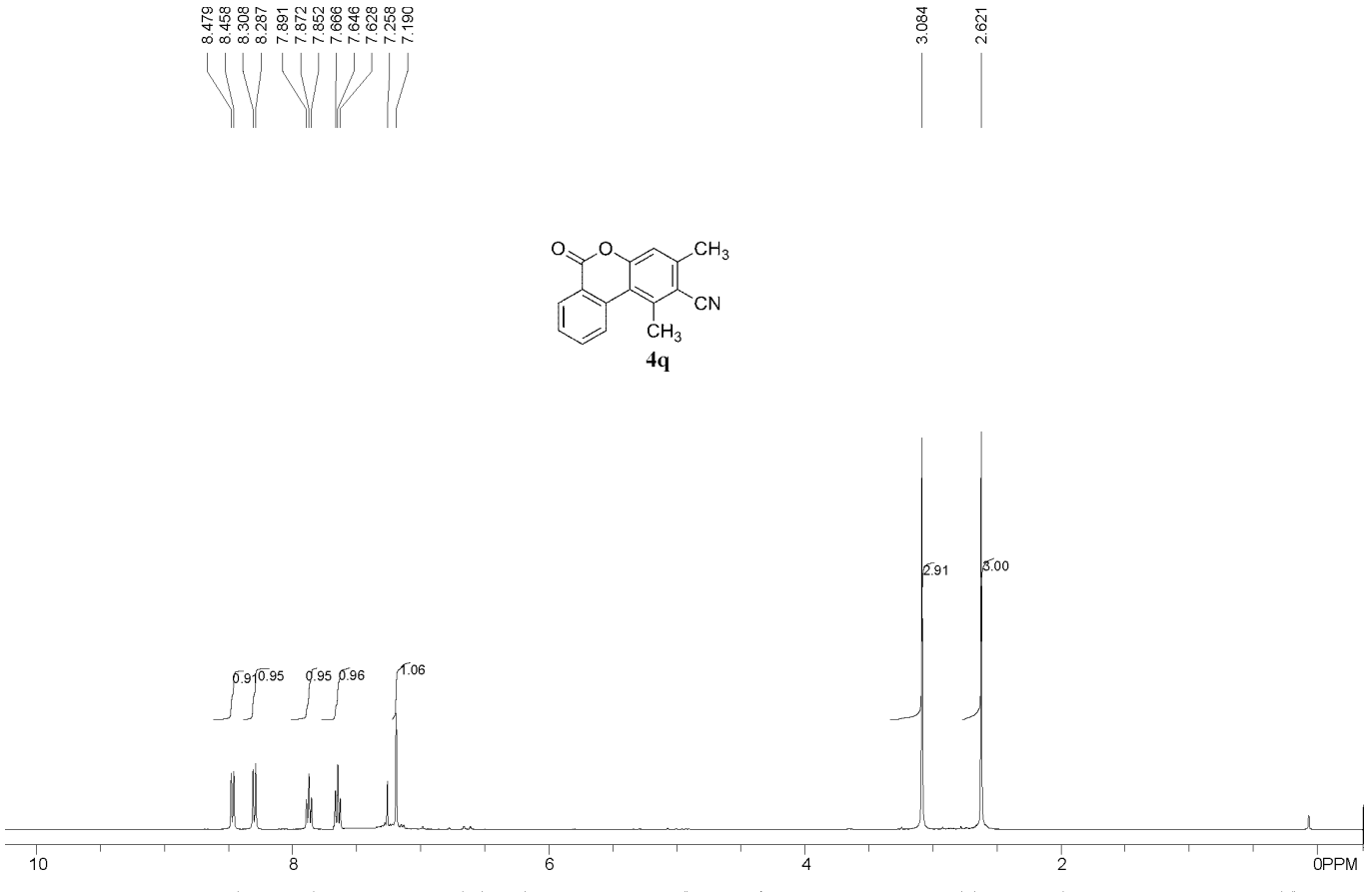
147.480
145.237
136.115
133.943
130.828
130.561
130.248
127.977
126.575
124.931
122.088
116.353
77.374
77.260
77.059
76.734
21.186
20.570
20.192
16.880
200
150
100
50
PPM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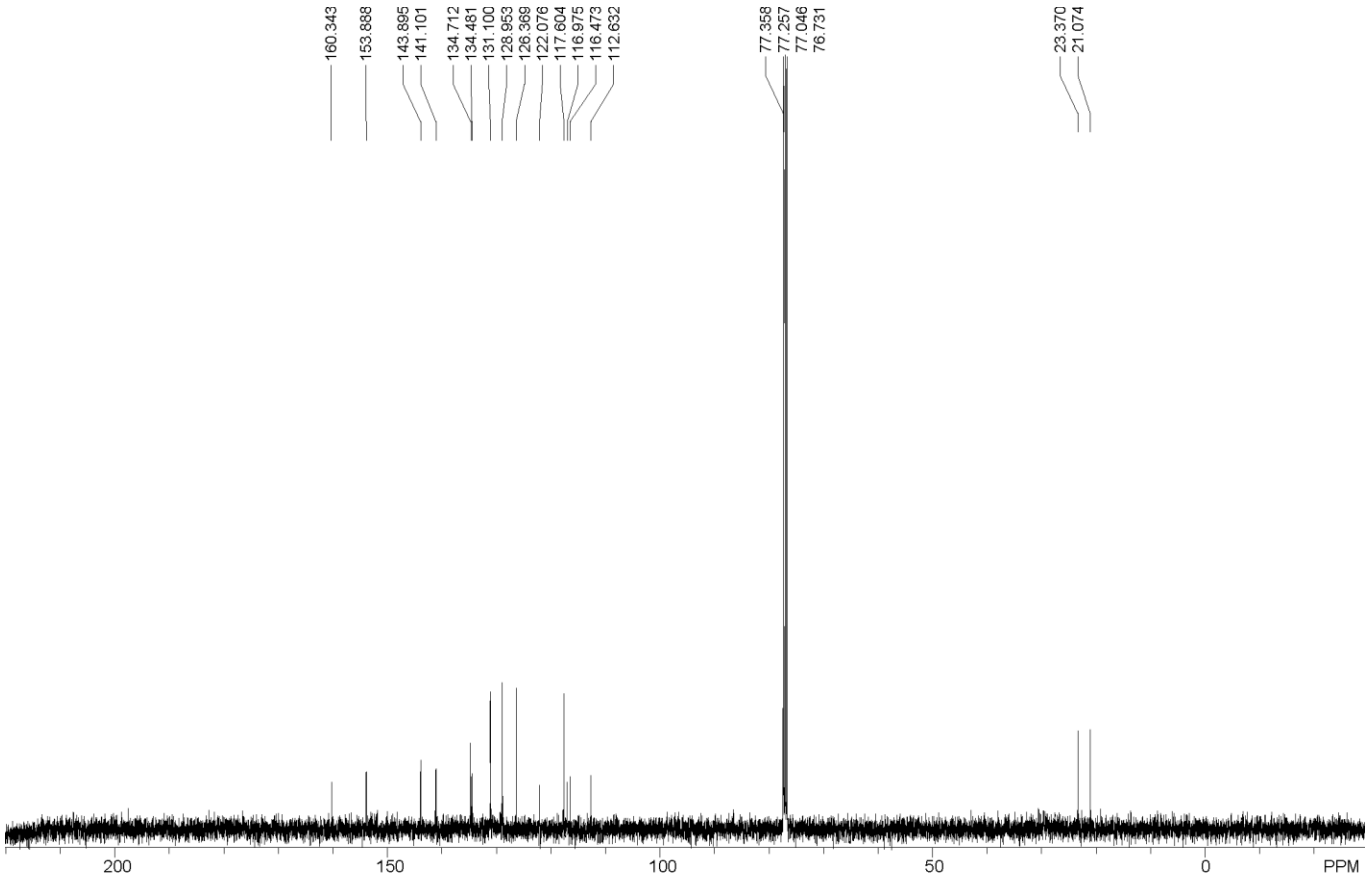
8.458
8.308
8.287
7.891
7.872
7.852
7.666
7.646
7.628
7.258
7.190
3.084
2.621
O
O
CH3
CN
CH3
4q
2.91
3.00
0.91
0.95
0.95
0.96
1.06
10
8
6
4
2
0PPM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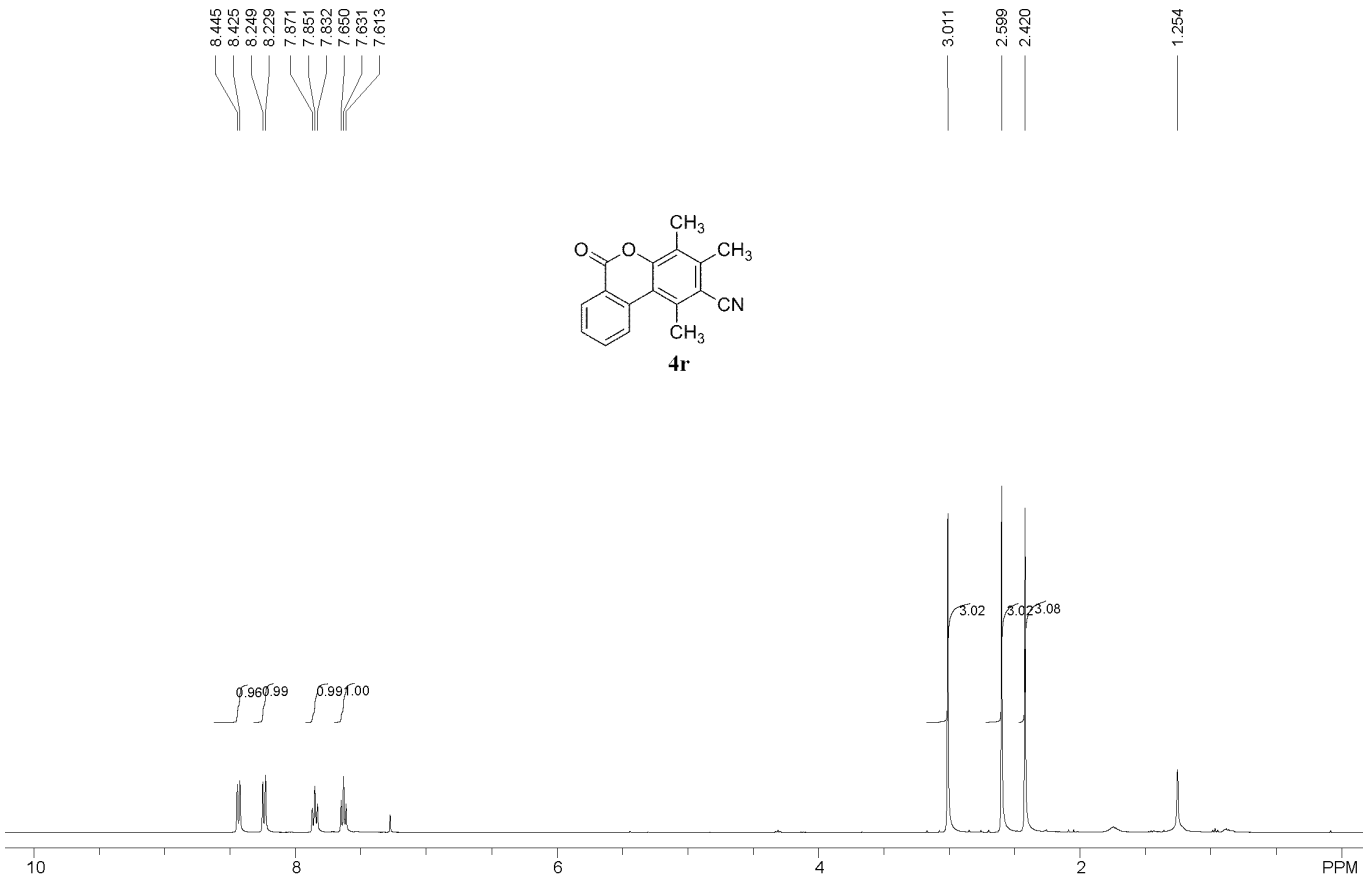
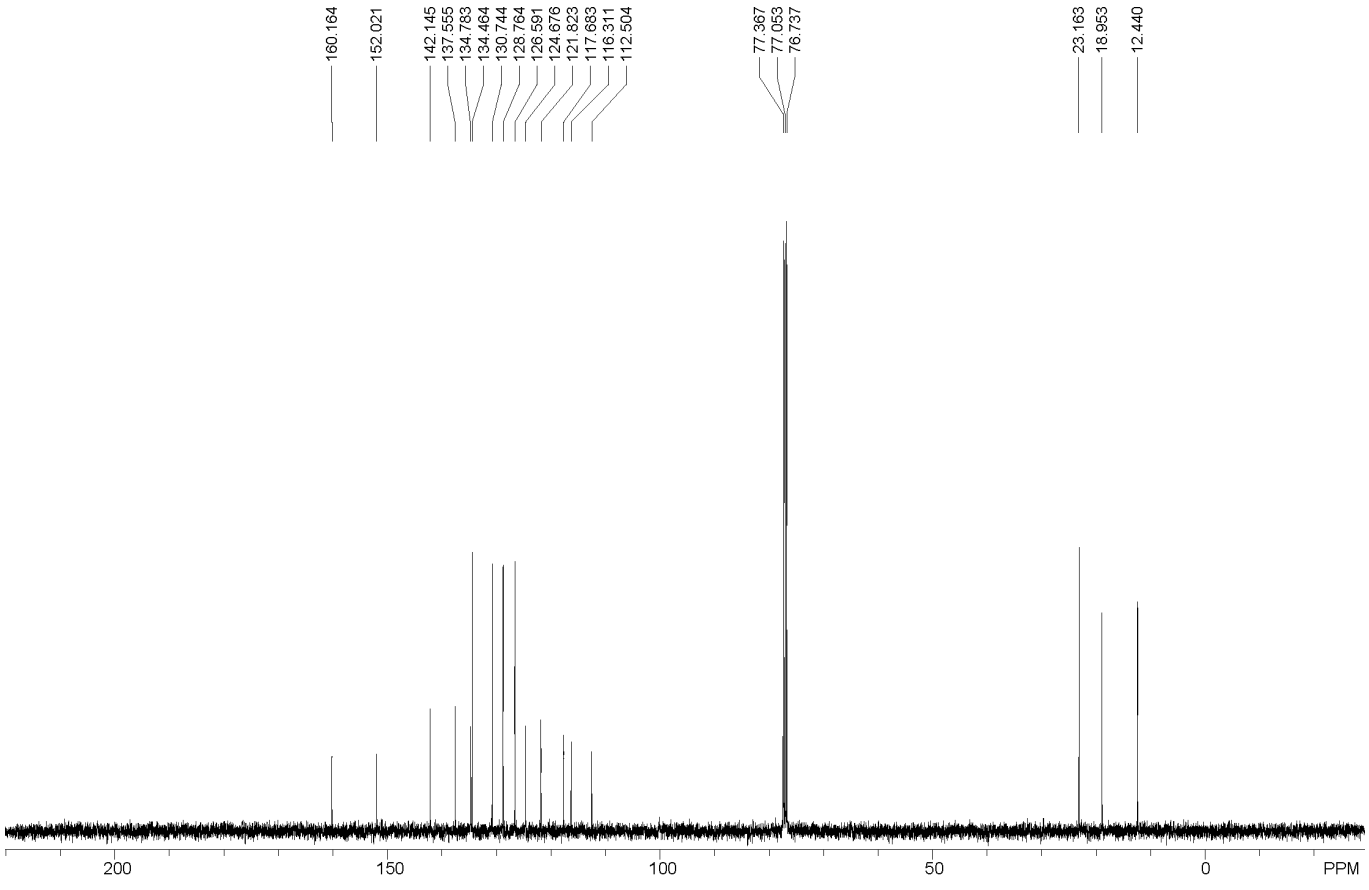
153.888
143.895
141.101
134.712
134.481
131.100
128.953
126.389
122.076
117.604
116.975
116.473
112.632
77.358
77.257
77.046
76.731
23.370
21.074
200
150
100
50
0
PPM


8.445
8.425
8.249
8.229
7.871
7.851
7.832
7.650
7.631
7.613
3.011
2.599
2.420
1.254
CH3
O
O
CH3
CN
CH3
4r
0.960.99
0.991.00
3.02
3.023.08
10
8
6
4
2
PPM


160.164
152.021
142.145
137.555
134.783
134.464
130.744
128.764
126.591
124.676
121.823
117.683
116.311
112.504
77.367
77.053
76.737
23.163
18.953
12.440
200
150
100
50
0
PPM

V. References

(1) A. Sniady, M. S. Morreale, R. Dembinski, *Org. Synth.*, 2007, **84**, 199.

(2) W. L. Wu, Z. J. Yao, Y. L. Li, J. C. Li, Y. Xia, Y. L. Wu, *J. Org. Chem*., 1995, **60**, 3257.

(3) Q. R. Li, C. Z. Gu, H. Yin, *Chin. J. Chem*., 2006, **24**, 72.