Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Tandem reaction of 3-hydroxyhexa-4,5-allenic esters: a novel access to diversely substituted 2*H*-pyran-2-ones and indenes

Haiyun Xu, Xinying Zhang*, Yan He, Shenghai Guo, and Xuesen Fan*

I. General Experimental Information

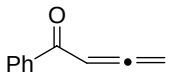
All the 3-hydroxyhexa-4,5-allenic ester substrates were prepared from the corresponding 1,2-allenic ketones and α-bromoacetates. The ^{1}H, ^{13}C NMR spectra were recorded at 400 MHz or 100 MHz, respectively. Chemical shifts were reported in ppm from tetramethylsilane (TMS) as internal standard in $CDCl_3$ solutions. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets); td (triplet of doublets); br s (broad singlet), etc. and coupling constants were given in Hz. The conversion of starting materials were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm) and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental Procedures and Spectroscopic Data

All the 3-hydroxyhexa-4,5-allenic ester substrates were prepared from the corresponding allenic ketones and α-bromoacetates with the promotion of zinc dust. 1-Aryl substituted allenic ketones were prepared through oxidation of the corresponding homopropargyl alcohols,[1] which were prepared through zinc promoted propargylation of aldehydes.[2] 1,4-Disubsituted allenic ketones were prepared from 1-(triphenylphosphoranylidene)-2-propanone or 2-(triphenyl phosphoranylidene)acetophenone with phenylacetyl chloride based on a literature procedure.[3]

1. Typical procedure for the preparation of 1-phenylbuta-2,3-dien-1-one (1a)

A solution of 1-phenylbut-3-yn-1-ol (1 mmol) in acetone (10 mL) was cooled to 0 °C. Jones reagent (0.42 mL, 3.0 M solution, 1.26 mmol) was added dropwise *via* syringe with stirring. Upon complete consumption of the starting material as monitored by TLC, the reaction was quenched by addition of isopropanol (0.2 mL). The mixture was filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (1:10) to give 1-phenylbuta-2,3-dien-1-one. Other 1-aryl substituted allenic ketones were obtained in a similar manner.



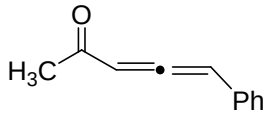
1-Phenylbuta-2,3-dien-1-one (1a)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.27 (d, J = 6.4 Hz, 2H), 6.46 (t, J = 6.4 Hz, 1H), 7.44-7.48 (m, 2H), 7.55-7.59 (m, 1H), 7.90-7.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 79.2, 93.2, 128.3, 128.7, 132.8, 137.4, 191.0, 217.1. MS: m/z 145 $[MH]^+$.

2. Typical procedure for the preparation of 5-phenylpenta-3,4-dien-2-one

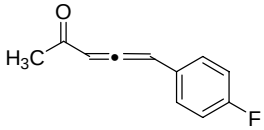
To an ice-cooled solution of 1-(triphenylphosphoranylidene)-2-propanone (0.637 g, 2 mmol) and Et_3N (0.202 g, 2 mmol) in CH_2Cl_2 (10 mL) being stirred under nitrogen was added dropwise a solution of phenylacetyl chloride (0.309 g, 2 mmol) in CH_2Cl_2 (2 mL). Upon completion,

approximately half of the solvent were removed, and diethyl ether was added to precipitate Ph_3PO. After filtration, silica gel was added to adsorb the reaction products and the solvent was evaporated in vacuo. Purification by column chromatography eluting with ethyl acetate/hexane (1:10) yielded 5-phenylpenta-3,4-dien-2-one as light yellow syrup. Other 1,4-disubstituted allenic ketones were obtained in a similar manner.



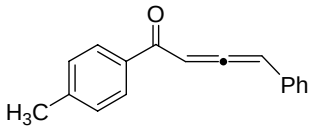
5-Phenylpenta-3,4-dien-2-one

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.26 (s, 3H), 6.14 (d, J = 6.0 Hz, 1H), 6.64 (d, J = 6.0 Hz, 1H), 7.27-7.38 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.8, 98.6, 101.1, 127.3, 128.3, 129.1, 130.9, 198.0, 215.9. MS: m/z 159 $[MH]^+$.



5-(4-Fluorophenyl)penta-3,4-dien-2-one

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.22 (s, 1H, CH_3), 6.09 (d, J = 6.0 Hz, 1H, CH), 6.59 (d, J = 6.0 Hz, 1H, CH), 6.98-7.02 (m, 2H, ArH), 7.23-7.26 (m, 2H, ArH). 13C NMR (100 MHz, $CDCl_3$) δ: 26.7, 97.6, 101.1, 115.9, 116.1, 127.0, 128.8, 128.9, 197.6, 215.4. MS: m/z 177 $[MH]^+$.



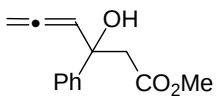
4-Phenyl-1-p-tolylbuta-2,3-dien-1-one

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.35 (s, 1H, CH_3), 6.64 (d, J = 6.4 Hz, 1H, CH), 6.78 (d, J = 6.4 Hz, 1H, CH), 7.18-7.35 (m, 7H, ArH), 7.89 (d, J = 7.6 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 97.4, 98.3, 127.5, 128.1, 128.9, 129.0, 129.2, 131.4, 134.9, 143.8, 190.1, 215.7. MS: m/z 235 $[MH]^+$.

3. Typical procedure for the preparation of 3-hydroxy-3-phenylhexa-4,5-dienoate (2a)

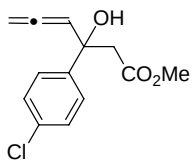
To a flask in an ice-water bath containing activated zinc dust (2 mmol) and THF (5 mL) was added a solution of methyl 2-bromoacetate (1.1 mmol) in THF (1 mL). The mixture was stirred at 0 °C for 15 min. To the mixture was added a solution of 1-phenylbuta-2,3-dien-1-one (1 mmol)

in THF (1 mL). The mixture was stirred at rt. 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 (10 mL). The aqueous phase was extracted with EtOAc (10 mL × 3). The combined organic phases were dried with anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel with EtOAc/hexane (0-3%) to give **2a**. Other 3-hydroxyhexa-4,5-dienoate derivatives were obtained in a similar manner.



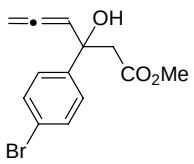
Methyl 3-hydroxy-3-phenylhexa-4,5-dienoate (2a)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.88 (d, *J* = 16.8 Hz, 1H), 2.99 (d, *J* = 16.4 Hz, 1H), 3.67 (s, 3H), 4.89-4.99 (m, 3H), 5.48 (t, *J* = 6.8 Hz, 1H), 7.25-7.28 (m, 1H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 44.7, 51.8, 73.4, 78.9, 98.3, 125.0, 127.3, 128.3, 144.9, 173.2, 206.0. MS: m/z 219 $[MH]^+$.



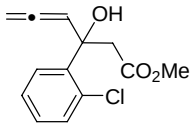
Methyl 3-(4-chlorophenyl)-3-hydroxyhexa-4,5-dienoate (2b)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.83 (d, *J* = 16.4 Hz, 1H), 2.96 (d, *J* = 16.0 Hz, 1H), 3.67 (s, 3H), 4.89-4.98 (m, 3H), 5.43 (t, *J* = 6.8 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 44.6, 51.9, 73.2, 79.1, 98.0, 126.6, 128.4, 133.2, 143.4, 173.0, 206.0. MS: m/z 253 $[MH]^+$.



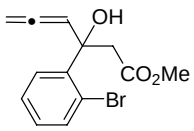
Methyl 3-(4-bromophenyl)-3-hydroxyhexa-4,5-dienoate (2c)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.83 (d, *J* = 16.8 Hz, 1H), 2.95 (d, *J* = 16.8 Hz, 1H), 3.67 (s, 3H), 4.89-4.99 (m, 3H), 5.43 (t, *J* = 6.8 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 44.5, 51.9, 73.2, 79.1, 97.9, 121.4, 127.0, 131.3, 144.0, 172.9, 206.0. MS: m/z 297 $[MH]^+$.



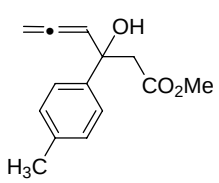
Methyl 3-(2-chlorophenyl)-3-hydroxyhexa-4,5-dienoate (2d)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.19 (d, *J* = 16.4 Hz, 1H), 3.36 (d, *J* = 16.4 Hz, 1H), 3.64 (s, 3H), 4.87-4.98 (m, 3H), 5.62 (t, *J* = 6.8 Hz, 1H), 7.20-7.35 (m, 3H), 7.90 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 41.7, 51.8, 73.1, 79.1, 96.1, 126.9, 128.0, 128.8, 131.1, 131.2, 140.9, 173.1, 207.3. MS: m/z 253 $[MH]^+$.



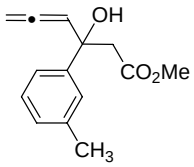
Methyl 3-(2-bromophenyl)-3-hydroxyhexa-4,5-dienoate (2e)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.24 (d, *J* = 16.4 Hz, 1H), 3.40 (d, *J* = 16.4 Hz, 1H), 3.65 (s, 3H), 4.87-4.98 (m, 3H), 5.62 (t, *J* = 6.8 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 41.6, 51.8, 73.7, 79.2, 96.1, 120.4, 127.5, 128.3, 129.1, 134.9, 142.3, 173.1, 207.6. MS: m/z 297 $[MH]^+$.



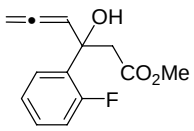
Methyl 3-hydroxy-3-(4-methylphenyl)hexa-4,5-dienoate (2f)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.34 (s, 3H), 2.87 (d, *J* = 16.4 Hz, 1H), 2.97 (d, *J* = 16.0 Hz, 1H), 3.67 (s, 3H), 4.82 (s, 1H), 4.87-4.98 (m, 2H), 5.46 (t, *J* = 6.8 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H). MS: m/z 233 $[MH]^+$.



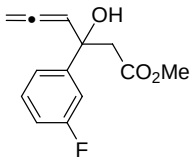
Methyl 3-hydroxy-3-(3-methylphenyl)hexa-4,5-dienoate (2g)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.37 (s, 3H), 2.87 (d, *J* = 16.8 Hz, 1H), 2.99 (d, *J* = 16.4 Hz, 1H), 3.68 (s, 3H), 4.90-5.01 (m, 3H), 5.47 (t, *J* = 6.8 Hz, 1H), 7.08 (d, *J* = 6.8 Hz, 1H), 7.22-7.28 (m, 2H), 7.34 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 44.7, 51.8, 73.3, 78.9, 98.3, 122.0, 125.7, 128.1, 128.2, 137.9, 144.8, 173.3, 205.9. MS: m/z 233 $[MH]^+$.



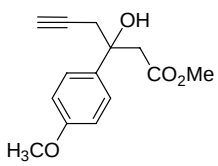
Methyl 3-(2-fluorophenyl)-3-hydroxyhexa-4,5-dienoate (2h)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.00 (d, *J* = 16.0 Hz, 1H), 3.12 (d, *J* = 16.4 Hz, 1H), 3.56 (s, 3H), 4.80-4.89 (m, 3H), 5.52 (t, *J* = 6.8 Hz, 1H), 6.91-6.96 (m, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.16-7.21 (m, 1H), 7.69 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 43.1, 51.7, 71.6, 79.1, 96.8, 115.6, 115.9, 124.0, 124.1, 127.4, 127.4, 129.2, 129.3, 172.9, 206.3. MS: m/z 237 $[MH]^+$.



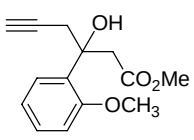
Methyl 3-(3-fluorophenyl)-3-hydroxyhexa-4,5-dienoate (2i)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.83 (d, *J* = 16.4 Hz, 1H), 2.97 (d, *J* = 16.0 Hz, 1H), 3.65 (s, 3H), 4.88-4.98 (m, 3H), 5.44 (t, *J* = 6.8 Hz, 1H), 6.91-6.95 (m, 1H), 7.22-7.31 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 44.5, 51.8, 73.1, 79.1, 98.0, 112.3, 112.5, 114.0, 114.2, 120.69, 120.72, 129.7, 129.8, 147.7, 147.8, 161.6, 164.0, 172.9, 206.0. MS: m/z 237 $[MH]^+$.



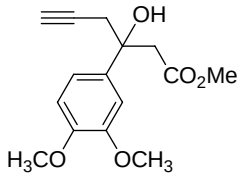
Methyl 3-hydroxy-3-(4-methoxyphenyl)hex-5-ynoate (2j)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.05 (s, 1H, CH), 2.61 (dd, *J1* = 16.4 Hz, *J2* = 2.4 Hz, 1H), 2.70 (dd, *J1* = 16.4 Hz, *J2* = 2.0 Hz, 1H), 3.01 (d, *J* = 16.0 Hz, 1H), 3.09 (d, *J* = 16.0 Hz, 1H), 3.56 (s, 3H), 3.74 (s, 3H), 4.37 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 33.9, 43.2, 51.8, 55.1, 71.6, 73.5, 80.2, 113.7, 126.2, 136.5, 158.8, 172.9. MS: m/z 249 $[MH]^+$.



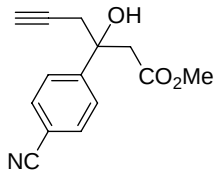
Methyl 3-hydroxy-3-(2-methoxyphenyl)hex-5-ynoate (2k)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.98 (s, 1 H), 2.79-3.37 (m, 4H), 3.48 (s, 3H), 3.80 (s, 3H), 4.61 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H). MS: m/z 249 $[MH]^+$.



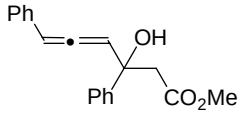
Methyl 3-hydroxy-3-(3,4-dimethoxyphenyl)hex-5-ynoate (2l)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.03 (s, 1H), 2.58 (d, *J* = 16.4 Hz, 1H), 2.69 (dd, *J1* = 16.4 Hz, *J2* = 1.6 Hz, 1H), 3.01 (d, *J* = 16.0 Hz, 1H), 3.09 (d, *J* = 16.0 Hz, 1H), 3.56 (s, 3H), 3.81 (s, 3H), 3.84 (s, 3H), 4.40 (s, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 7.07 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 33.9, 43.0, 51.8, 55.7, 55.8, 71.6, 73.6, 79.9, 108.7, 110.6, 117.0, 137.1, 148.2, 148.6, 172.9. MS: m/z 279 $[MH]^+$.



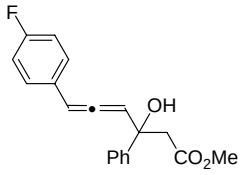
Methyl 3-(4-cyanophenyl)-3-hydroxyhex-5-ynoate (2m)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.05 (s, 1H), 2.61 (d, *J* = 16.8 Hz, 1H), 2.71 (d, *J* = 16.8 Hz, 1H), 3.03 (d, *J* = 16.4 Hz, 1H), 3.13 (d, *J* = 16.4 Hz, 1H), 3.59 (s, 3H), 4.52 (s, 1H), 7.59-7.63 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 33.5, 42.8, 52.1, 72.3, 73.7, 78.9, 111.4, 118.6, 126.0, 132.1, 149.6, 172.4. MS: m/z 244 $[MH]^+$.



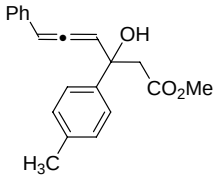
Methyl 3-hydroxy-3,6-diphenylhexa-4,5-dienoate (2n)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.83 (d, *J* = 16.8 Hz, 1H), 3.11 (d, *J* = 16.8 Hz, 1H), 3.29 (s, 3H), 5.43 (s, 1H), 5.93 (d, *J* = 6.0 Hz, 1H), 6.48 (d, *J* = 6.0 Hz, 1H), 7.27-7.44 (m, 8H), 7.63 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 44.2, 51.6, 74.8, 98.5, 102.8, 125.1, 127.2, 127.5, 128.2, 128.4, 128.6, 133.4, 145.0, 173.4, 202.6. MS: m/z 295 $[MH]^+$.



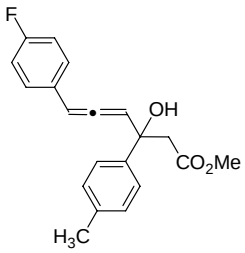
Methyl 6-(4-fluorophenyl)-3-hydroxy-3-phenylhexa-4,5-dienoate (2o)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.79 (d, *J* = 16.8 Hz, 1H), 3.04 (d, *J* = 16.4 Hz, 1H), 3.30 (s, 3H), 5.30 (s, 1H), 5.87 (d, *J* = 6.4 Hz, 1H), 6.41 (d, *J* = 6.4 Hz, 1H), 7.05 (t, *J* = 8.4 Hz, 2H), 7.26-7.31 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 44.2, 51.6, 74.6, 97.4, 102.9, 115.4, 115.6, 125.0, 127.4, 128.4, 128.56, 128.64, 129.1, 142.2, 173.3, 202.3. MS: m/z 313 $[MH]^+$.



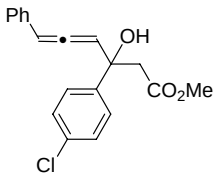
Methyl 3-hydroxy-6-phenyl-3-p-tolylhexa-4,5-dienoate (2p)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 2.82 (d, *J* = 16.4 Hz, 1H), 3.10 (d, *J* = 16.4 Hz, 1H), 3.30 (s, 3H), 5.37 (s, 1H), 5.92 (d, *J* = 6.4 Hz, 1H), 6.48 (d, *J* = 6.4 Hz, 1H), 7.23-7.36 (m, 7H), 7.51 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.1, 44.3, 51.5, 74.7, 98.4, 102.9, 125.0, 127.2, 127.5, 128.6, 129.1, 133.5, 137.1, 142.1, 173.4, 202.5. MS: m/z 309 $[MH]^+$.



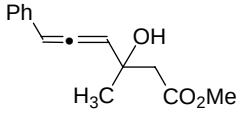
Methyl 6-(4-fluorophenyl)-3-hydroxy-3-p-tolylhexa-4,5-dienoate (2q)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.38 (s, 3H), 2.80 (d, *J* = 16.4 Hz, 1H), 3.06 (d, *J* = 16.4 Hz, 1H), 3.32 (s, 3H), 5.30 (s, 1H), 5.89 (d, *J* = 6.4 Hz, 1H), 6.42 (d, *J* = 6.4 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.0, 44.2, 51.6, 74.5, 97.4, 103.0, 115.4, 115.7, 125.0, 128.6, 128.7, 129.1, 129.5, 137.1, 142.0, 173.4, 202.3. MS: m/z 327 $[MH]^+$.



Methyl 3-(4-chlorophenyl)-3-hydroxy-6-phenylhexa-4,5-dienoate (2r)

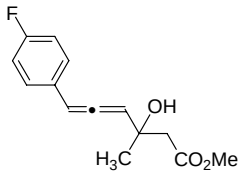
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.74 (d, *J* = 16.8 Hz, 1H), 3.02 (d, *J* = 16.8 Hz, 1H), 3.27 (s, 3H), 5.33 (s, 1H), 5.83 (d, *J* = 6.4 Hz, 1H), 6.44 (d, *J* = 6.4 Hz, 1H), 7.23-7.35 (m, 7H), 7.49 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 44.1, 51.6, 74.4, 98.6, 102.4, 126.6, 127.1, 127.5, 128.4, 128.6, 133.2, 143.4, 173.1, 202.6. MS: m/z 329 $[MH]^+$.



Methyl 3-hydroxy-3-methyl-6-phenylhexa-4,5-dienoate (2s)

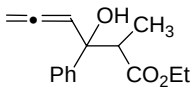
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.43 (s, 3H), 2.58 (d, *J* = 16.0 Hz, 1H), 2.75

(d, *J* = 16.0 Hz, 1H), 3.41 (s, 3H), 4.42 (s, 1H), 5.77 (d, *J* = 6.4 Hz, 1H), 6.29 (d, *J* = 6.4 Hz, 1H), 7.18-7.31 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.9, 44.1, 51.5, 70.7, 97.9, 102.8, 126.9, 127.2, 128.5, 133.6, 173.2, 201.9. MS: m/z 233$[MH]^+$.



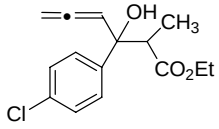
Methyl 6-(4-fluorophenyl)-3-hydroxy-3-methylhexa-4,5-dienoate (2t)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.41 (s, 3H), 2.57 (d, *J* = 16.0 Hz, 1H), 2.73 (d, *J* = 16.0 Hz, 1H), 3.42 (s, 3H), 4.40 (s, 1H), 5.75 (d, *J* = 6.4 Hz, 1H), 6.25 (d, *J* = 6.0 Hz, 1H), 6.96-7.00 (m, 2H), 7.20-7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.9, 44.0, 51.5, 70.6, 96.9, 103.0, 115.4, 115.6, 128.3, 128.4, 129.6, 173.2, 201.6. MS: m/z 251$[MH]^+$.



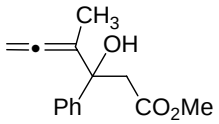
Ethyl 3-hydroxy-2-methyl-3-phenylhexa-4,5-dienoate (2u)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96-0.98 (m, 3H), 1.27-1.31 (m, 3H), 3.02-3.04 (m, 1H), 4.18-4.22 (m, 2H), 4.74 (s, 1H), 4.85-4.98 (m, 2H), 5.55 (t, *J* = 6.4 Hz, 1H), 7.24-7.49 (m, 5H). MS: m/z 247 $[MH]^+$.



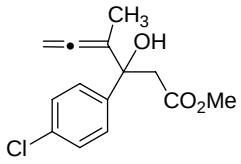
Ethyl 3-(4-chlorophenyl)-3-hydroxy-2-methylhexa-4,5-dienoate (2v)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.91-0.93 (m, 3H), 1.25-1.28 (m, 3H), 2.92-2.98 (m, 1H), 4.14-4.21 (m, 2H), 4.77 (s, 1H), 4.83-4.97 (m, 2H), 5.46 (t, *J* = 6.4 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.6, 14.1, 47.3, 60.9, 75.0, 79.1, 99.3, 127.0, 128.1, 132.8, 141.7, 177.1, 205.6. MS: m/z 281 $[MH]^+$.



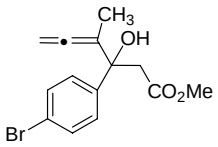
Methyl 3-hydroxy-4-methyl-3-phenylhexa-4,5-dienoate (2y)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.56 (t, *J* = 3.2 Hz, 3H), 2.79 (d, *J* = 16.0 Hz, 1H), 3.05 (d, *J* = 16.4 Hz, 1H), 3.66 (s, 3H), 4.78-4.91 (m, 2H), 5.00 (s, 1H), 7.23-7.50 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 45.1, 51.7, 75.3, 104.2, 125.2, 127.1, 128.2, 144.0, 173.9, 204.9. MS: m/z 233 $[MH]^+$.



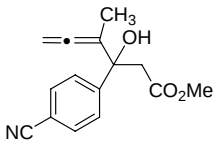
Methyl 3-(4-chlorophenyl)-3-hydroxy-4-methylhexa-4,5-dienoate (2z)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.51 (t, *J* = 3.2 Hz, 3H), 2.72 (d, *J* = 16.4 Hz, 1H), 3.00 (d, *J* = 16.4 Hz, 1H), 3.64 (s, 3H), 4.76-4.88 (m, 2H), 4.99 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 44.9, 51.8, 75.1, 103.9, 126.8, 128.3, 133.0, 142.7, 173.6, 204.8. MS: m/z 267 $[MH]^+$.



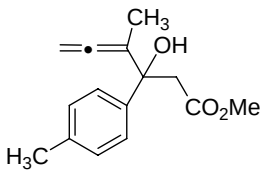
Methyl 3-(4-bromophenyl)-3-hydroxy-4-methylhexa-4,5-dienoate (2aa)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.51 (s, 3H), 2.71 (d, *J* = 16.8 Hz, 1H), 2.98 (d, *J* = 16.4 Hz, 1H), 3.64 (s, 3H), 4.76-4.79 (m, 1H), 4.85-4.88 (m, 1H), 4.99 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 44.9, 51.9, 75.1, 103.8, 121.2, 127.2, 131.2, 143.3, 173.6, 204.8. MS: m/z 311 $[MH]^+$.



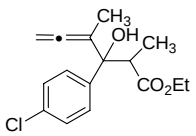
Methyl 3-(4-cyanophenyl)-3-hydroxy-4-methylhexa-4,5-dienoate (2ab)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.38 (t, *J* = 3.2 Hz, 3H), 2.64 (d, *J* = 16.8 Hz, 1H), 2.94 (d, *J* = 16.4 Hz, 1H), 3.56 (s, 3H), 4.70-4.83 (m, 2H), 4.96 (s, 1H), 7.50-7.55 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 28.7, 44.5, 51.8, 75.1, 103.4, 111.0, 118.6, 126.2, 132.0, 149.6, 173.2, 204.8. MS: m/z 258 $[MH]^+$.



Methyl 3-hydroxy-4-methyl-3-p-tolylhexa-4,5-dienoate (2ac)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.59 (s, 3H), 2.35 (s, 3H), 2.80 (d, *J* = 16.8 Hz, 1H), 3.06 (d, *J* = 16.8 Hz, 1H), 3.65 (s, 3H), 4.79-4.91 (m, 2H), 5.02 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.1, 21.0, 45.2, 51.6, 75.2, 104.3, 125.2, 128.9, 136.6, 141.2, 173.9, 204.9. MS: m/z 247 $[MH]^+$.



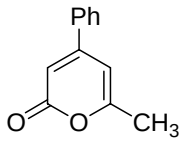
Ethyl 3-(4-chlorophenyl)-3-hydroxy-2,4-dimethylhexa-4,5-dienoate (2ad)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (d, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.47 (t, *J* = 3.2 Hz, 3H), 3.04-3.06 (m, 1H), 4.14-4.17 (m, 2H), 4.74-4.89 (m, 3H), 7.25 (d, *J* =

8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.1, 14.1, 14.5, 46.6, 60.7, 76.8, 105.7, 127.2, 128.1, 130.4, 132.7, 141.2, 178.1, 204.3. MS: m/z 295 $[MH]^+$.

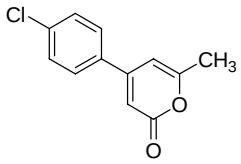
4. Typical procedure for the preparation of 6-methyl-4-phenyl-2*H*-pyran-2-one (3a)

To a flask containing 3-hydroxy-3-phenylhexa-4,5-dienoate (**2a**, 1 mmol) in CH_2Cl_2 (5 mL) were added H_2SO_4 (0.1 mmol). The solution was stirred at room temperature. Upon completion as monitored by TLC, the reaction was quenched with aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate (5 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluenting with ethyl acetate/hexane (1:10) to give 6-methyl-4-phenyl-2*H*-pyran-2-one (**3a**, 85%). Other 2*H*-pyran-2-one derivatives (**3b**-**3ad**) were obtained in a similar manner. It is noted that from the reactions of substrates **2y**-**2ad**, indene derivatives (**4a**-**4f**) were also obtained together with 2*H*-pyran-2-ones (**3y**-**3ad**).



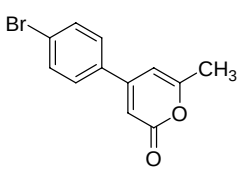
6-Methyl-4-phenyl-2*H*-pyran-2-one (3a)[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.32 (s, 3H), 6.30 (s, 1H), 6.36 (s, 1H), 7.45-7.47 (m, 3H), 7.55-7.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.2, 103.5, 108.1, 126.6, 129.1, 130.6, 135.8, 155.5, 162.1, 163.4. MS: m/z 187 $[MH]^+$.



4-(4-Chlorophenyl)-6-methyl-2*H*-pyran-2-one (3b)[4]

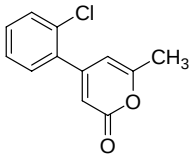
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.31 (s, 3H), 6.25 (s, 1H), 6.30 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.2, 103.1, 108.2, 127.9, 129.4, 134.2, 136.8, 154.2, 162.5, 163.1. MS: m/z 221 $[MH]^+$.



4-(4-Bromophenyl)-6-methyl-2*H*-pyran-2-one (3c)

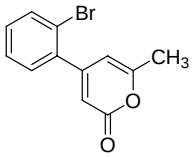
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.32 (s, 3H), 6.24 (s, 1H, CH), 6.32 (s, 1H, CH), 7.42 (d, *J* = 8.0 Hz, 2H,), 7.60 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100

MHz, $CDCl_3$) δ: 20.2, 103.0, 108.2, 125.1, 128.1, 132.4, 134.7, 154.3, 162.5, 163.1. MS: m/z 265 $[MH]^+$. HRMS (FAB) Calcd for $C_{12}H_{10}BrO_2$: 264.9865 [M+H], found: 264.9849.



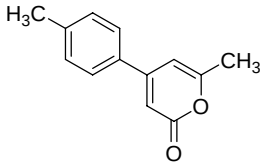
4-(2-Chlorophenyl)-6-methyl-2*H*-pyran-2-one (3d)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.25 (s, 3H), 6.11 (s, 1H), 6.13 (s, 1H), 7.23-7.34 (m, 3H), 7.41 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.0, 105.7, 112.0, 127.3, 129.7, 130.4, 130.6, 131.6, 135.9, 155.0, 161.4, 162.8. MS: m/z 221 $[MH]^+$. HRMS (FAB) Calcd for $C_{12}H_{10}ClO_2$: 221.037 [M+H], found: 221.0352.



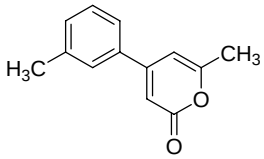
4-(2-Bromophenyl)-6-methyl-2*H*-pyran-2-one (3e)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.29 (s, 3H), 6.10 (s, 1H), 6.14 (s, 1H), 7.24-7.29 (m, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.0, 105.9, 112.1, 120.8, 127.8, 129.7, 130.7, 133.6, 138.1, 156.5, 161.4, 162.8. MS: m/z 265 $[MH]^+$. HRMS (FAB) Calcd for $C_{12}H_{10}BrO_2$: 264.9865 [M+H], found: 264.9856.



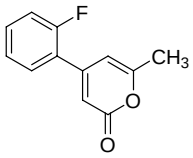
4-(4-Methylphenyl)-6-methyl-2*H*-pyran-2-one (3f)[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.30 (s, 3H), 2.39 (s, 3H), 6.29 (s, 1H), 6.32 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.1, 21.3, 103.3, 107.3, 126.5, 129.8, 132.8, 141.1, 155.3, 161.9, 163.5. MS: m/z 201 $[MH]^+$.



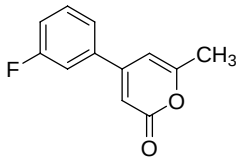
4-(3-Methylphenyl)-6-methyl-2*H*-pyran-2-one (3g)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.24 (s, 3H), 2.35 (s, 3H), 6.25 (s, 2H), 7.22-7.29 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.0, 21.3, 103.5, 107.8, 123.7, 127.2, 129.0, 131.3, 135.6, 138.8, 155.6, 162.0, 163.3. MS: m/z 201 $[MH]^+$. HRMS (FAB) Calcd for $C_{13}H_{13}O_2$: 201.0916 [M+H], found: 201.0911.



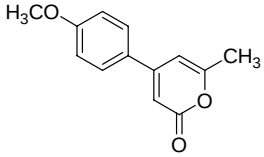
4-(2-Fluorophenyl)-6-methyl-2*H*-pyran-2-one (3h)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.19 (s, 3H), 6.17 (s, 1H), 6.21 (s, 1H), 7.05-7.16 (m, 2H), 7.31-7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.9, 104.7, 111.0, 116.4, 116.6, 124.7, 124.8, 129.4, 131.9, 132.0, 151.1, 158.5, 161.0, 161.6, 162.8. MS: m/z 205 $[MH]^+$. HRMS (FAB) Calcd for $C_{12}H_{10}FO_2$: 205.0666 [M+H], found: 205.0671.



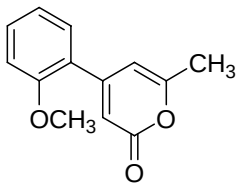
4-(3-Fluorophenyl)-6-methyl-2*H*-pyran-2-one (3i)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.29 (s, 3H), 6.24 (s, 1H), 6.28 (s, 1H), 7.11-7.16 (m, 1H), 7.22 (s, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.38-7.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.1, 103.1, 108.5, 113.5, 113.7, 117.3, 117.5, 122.3, 122.4, 130.8, 130.9, 137.9, 137.9, 154.1, 161.7, 162.5, 163.0, 164.2. MS: m/z 205 $[MH]^+$. HRMS (FAB) Calcd for $C_{12}H_{10}FO_2$: 205.0666 [M+H], found: 205.0668.



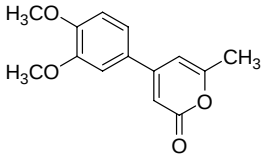
4-(4-Methoxyphenyl)-6-methyl-2*H*-pyran-2-one (3j)[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (s, 3H), 3.74 (s, 3H), 6.19 (s, 1H), 6.23 (s, 1H), 6.89 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.0, 55.4, 103.0, 106.1, 114.5, 127.5, 128.1, 154.7, 161.7, 161.8, 163.6. MS: m/z 217 $[MH]^+$.



4-(2-Methoxyphenyl)-6-methyl-2*H*-pyran-2-one (3k)

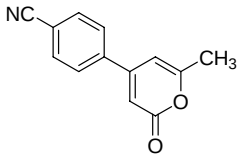
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.25 (s, 3H), 3.82 (s, 3H), 6.25 (s, 1H), 6.28 (s, 1H), 6.95-6.99 (m, 2H), 7.26-7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.0, 55.5, 105.9, 111.0, 111.4, 121.0, 125.5, 129.5, 131.4, 154.5, 156.7, 160.4, 163.6. MS: m/z 217 $[MH]^+$. HRMS (FAB) Calcd for $C_{13}H_{13}O_3$: 217.0865 [M+H], found: 217.0879.



4-(3,4-Dimethoxyphenyl)-6-methyl-2*H*-pyran-2-one (3l)

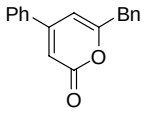
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.20 (s, 3H), 3.83 (s, 6H), 6.18 (s, 1H),

6.22 (s, 1H), 6.84 (d, J = 8.4 Hz, 2H), 6.98 (s, 1H), 7.09 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.0, 55.9, 103.1, 106.4, 109.3, 111.2, 119.9, 127.9, 149.3, 151.3, 154.8, 161.8, 163.4. MS: m/z 247 $[MH]^+$. HRMS (FAB) Calcd for $C_{14}H_{15}O_4$: 247.0971 [M+H], found: 247.0979.



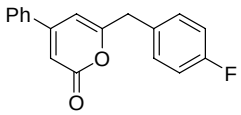
4-(4-Cyanophenyl)-6-methyl-2*H*-pyran-2-one (3m)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.30 (s, 3H), 6.25 (s, 1H), 6.32 (s, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.2, 102.8, 109.7, 126.0, 127.4, 132.1, 132.9, 140.2, 153.5, 162.6, 163.1. MS: m/z 212 $[MH]^+$. HRMS (FAB) Calcd for $C_{13}H_{10}NO_2$: 212.0712 [M+H], found: 212.0715.



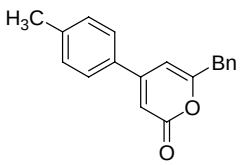
6-Benzyl-4-phenyl-2*H*-pyran-2-one (3n)[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.86 (s, 2H), 6.22 (s, 1H), 6.35 (s, 1H), 7.26-7.38 (m, 5H), 7.44-7.55 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 40.3, 103.5, 108.6, 126.7, 127.4, 128.9, 129.1, 129.3, 130.6, 135.1, 135.7, 155.3, 163.1, 164.4. MS: m/z 263 $[MH]^+$.



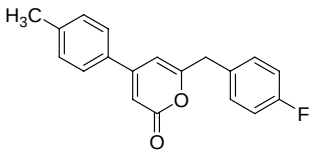
6-(4-Fluorobenzyl)-4-phenyl-2H-pyran-2-one (3o)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.84 (s, 2H), 6.20 (s, 1H), 6.36 (s, 1H), 7.04 (t, J = 8.0 Hz, 2H), 7.27-7.29 (m, 2H), 7.45-7.52 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 39.4, 103.5, 108.7, 115.7, 115.9, 126.6, 129.1, 130.7, 130.75, 130.82, 135.7, 155.3, 163.0, 164.0. MS: m/z 281 $[MH]^+$. HRMS (FAB) Calcd for $C_{18}H_{14}FO_2$: 281.0979 [M+H], found: 281.0983.



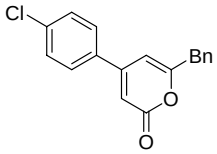
6-Benzyl-4-(4-methylphenyl)-2H-pyran-2-one (3p)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 3.86 (s, 2H), 6.22 (s, 1H), 6.34 (s, 1H), 7.24-7.43 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 40.3, 103.4, 107.8, 126.6, 127.3, 128.9, 129.2, 129.9, 132.7, 135.3, 141.2, 155.2, 163.3, 164.2. MS: m/z 277 $[MH]^+$. HRMS (FAB) Calcd for $C_{19}H_{17}O_2$: 277.1229 [M+H], found: 277.1221.



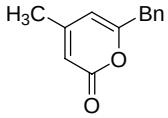
6-(4-Fluorobenzyl)-4-(4-methylphenyl)-2H-pyran-2-one (3q)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.38 (s, 3H), 3.81 (s, 2H), 6.22 (s, 1H), 6.32 (s, 1H), 7.02 (t, *J* = 8.0 Hz, 2H), 7.23-7.28 (m, 4H), 7.41 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 39.4, 103.4, 107.8, 115.6, 115.8, 126.5, 129.9, 130.7, 130.8, 131.0, 132.6, 141.2, 155.1, 160.8, 163.1, 163.3, 163.8. MS: m/z 295 $[MH]^+$. HRMS (FAB) Calcd for $C_{19}H_{16}FO_2$: 295.1135 [M+H], found: 295.1138.



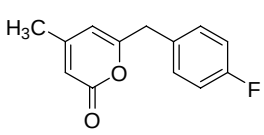
6-Benzyl-4-(4-chlorophenyl)-2H-pyran-2-one (3r)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.86 (s, 2H), 6.16 (s, 1H), 6.31 (s, 1H), 7.29-7.45 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 40.3, 103.1, 108.7, 127.4, 127.9, 128.9, 129.2, 129.4, 134.1, 135.0, 136.9, 154.0, 162.8, 164.7. MS: m/z 297 $[MH]^+$. HRMS (FAB) Calcd for $C_{18}H_{14}ClO_2$: 297.0683 [M+H], found: 297.0697.



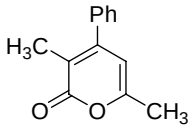
6-Benzyl-4-methyl-2H-pyran-2-one (3s)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.05 (s, 3H), 3.74 (s, 2H), 5.72 (s, 1H), 5.92 (s, 1H), 7.24-7.34 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.4, 39.9, 106.4, 110.9, 127.3, 128.8, 129.2, 135.2, 156.2, 162.9, 163.4. MS: m/z 201 $[MH]^+$. HRMS (FAB) Calcd for $C_{13}H_{13}O_2$: 201.0916 [M+H], found: 201.0931.



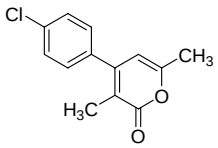
6-(4-Fluorobenzyl)-4-methyl-2*H*-pyran-2-one (3t)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.07 (s, 3H), 3.72 (s, 2H), 5.72 (s, 1H), 5.92 (s, 1H), 6.98-7.02 (m, 2H), 7.19-7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.4, 39.0, 106.3, 111.0, 115.5, 115.8, 130.7, 130.8, 130.9, 156.1, 162.7, 163.1. MS: m/z 219 $[MH]^+$. HRMS (FAB) Calcd for $C_{13}H_{12}FO_2$: 219.0822 [M+H], found: 219.0834.



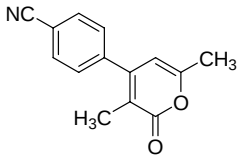
3,6-Dimethyl-4-phenyl-2H-pyran-2-one (3u)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.03 (s, 3H), 2.25 (s, 3H), 5.97 (s, 1H), 7.27-7.44 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 19.6, 106.6, 118.1, 127.8, 128.5, 128.7, 137.7, 152.0, 157.8, 164.8. MS: m/z 201 $[MH]^+$. HRMS (FAB) Calcd for $C_{13}H_{13}O_2$: 201.0916 [M+H], found: 201.0903.



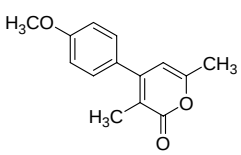
4-(4-Chlorophenyl)-3,6-dimethyl-2H-pyran-2-one (3v)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.97 (s, 3H), 2.21 (s, 3H), 5.90 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 19.5, 106.2, 118.3, 128.5, 129.3, 134.8, 136.0, 150.8, 158.1, 164.5. MS: m/z 235 $[MH]^+$. HRMS (FAB) Calcd for $C_{13}H_{12}ClO_2$: 235.0527 [M+H], found: 235.0518.



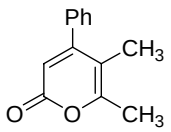
4-(3,6-Dimethyl-2-oxo-2H-pyran-4-yl)benzonitrile (3w)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.01 (s, 3H), 2.27 (s, 3H), 5.91 (s, 1H, CH), 7.41 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 19.6, 105.5, 112.7, 117.5, 119.0, 128.7, 132.4, 142.2, 148.5, 158.6, 164.1. MS: m/z 226 $[MH]^+$. HRMS (FAB) Calcd for $C_{14}H_{12}NO_2$: 226.0869 [M+H], found: 226.0882.



4-(4-Methoxyphenyl)-3,6-dimethyl-2*H*-pyran-2-one (3x)

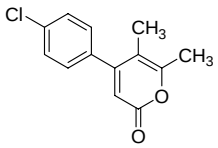
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.04 (s, 3H), 2.22 (s, 3H), 3.83 (s, 3H), 5.96 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 19.6, 55.3, 106.7, 113.9, 117.4, 129.5, 129.9, 151.7, 157.5, 159.9, 165.0. MS: m/z 231 $[MH]^+$. HRMS (FAB) Calcd for $C_{14}H_{15}O_3$: 231.1022 [M+H], found: 231.1009.



5,6-Dimethyl-4-phenyl-2H-pyran-2-one (3y)[5]

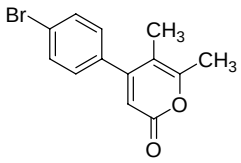
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.83 (s, 3H), 2.29 (s, 3H), 6.06 (s, 1H), 7.21-7.24 (m, 2H), 7.40-7.42 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 18.1, 110.2, 112.1, 127.6,

128.5, 128.9, 158.3, 160.2, 162.6. MS: m/z 201 $[MH]^+$. HRMS (FAB) Calcd for $C_{13}H_{13}O_2$: 201.0916 [M+H], found: 201.0928.



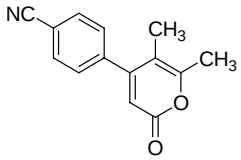
4-(4-Chlorophenyl)-5,6-dimethyl-2*H*-pyran-2-one (3z)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.81 (s, 3H), 2.28 (s, 3H), 6.02 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 18.1, 109.9, 112.2, 128.8, 129.0, 135.1, 135.7, 158.6, 158.9, 162.3. MS: m/z 235 $[MH]^+$. HRMS (FAB) Calcd for $C_{13}H_{12}ClO_2$: 235.0527 [M+H], found: 235.0538.



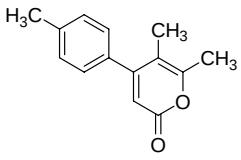
4-(4-Bromophenyl)-5,6-dimethyl-2*H*-pyran-2-one (3aa)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.82 (s, 3H), 2.29 (s, 3H), 6.03 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.8, 18.2, 109.8, 112.2, 123.3, 129.3, 129.3, 131.8, 136.1, 158.7, 158.9, 162.3. MS: m/z 279 $[MH]^+$. HRMS (FAB) Calcd for $C_{13}H_{12}BrO_2$: 279.0021 [M+H], found: 279.0036.



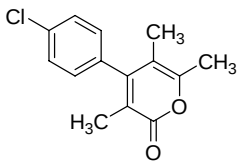
4-(5,6-Dimethyl-2-oxo-2H-pyran-4-yl)benzonitrile (3ab)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.80 (s, 3H), 2.30 (s, 3H), 6.04 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.7, 18.2, 109.3, 112.6, 112.9, 118.1, 128.4, 132.4, 141.8, 158.0, 159.2, 161.9. MS: m/z 226 $[MH]^+$. HRMS (FAB) Calcd for $C_{14}H_{12}NO_2$: 226.0869 [M+H], found: 226.0852.



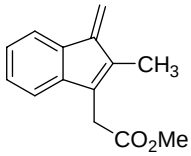
5,6-Dimethyl-4-p-tolyl-2*H*-pyran-2-one (3ac)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.83 (s, 3H), 2.27 (s, 3H), 2.37 (s, 3H), 6.03 (s, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9, 18.1, 21.2, 110.3, 111.9, 127.6, 129.1, 134.4, 138.9, 158.2, 160.2, 162.7. MS: m/z 215 $[MH]^+$. HRMS (FAB) Calcd for $C_{14}H_{15}O_2$: 215.1073 [M+H], found: 215.1086.



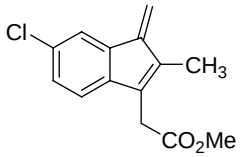
4-(4-Chlorophenyl)-3,5,6-trimethyl-2H-pyran-2-one (3ad)

^{1}H NMR (400 MHz, CDCl3) δ: 1.61 (s, 3H), 1.80 (s, 3H), 2.25 (s, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2, 14.4, 17.7, 110.4, 119.9, 128.8, 129.1, 134.1, 135.5, 154.1, 154.4, 163.9. MS: m/z 249 $[MH]^+$. HRMS (FAB) Calcd for $C_{14}H_{14}ClO_2$: 249.0683 [M+H], found: 249.0696.



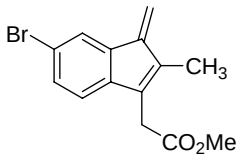
Methyl 2-(2-methyl-1-methylene-1H-inden-3-yl)acetate (4a)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.13 (s, 3H), 3.58 (s, 2H), 3.68 (s, 3H), 5.70 (s, 1H), 6.01 (s, 1H), 7.14-7.26 (m, 3H) 7.53 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 9.9, 31.6, 52.1, 110.5, 118.0, 119.2, 124.8, 128.1, 133.2, 134.9, 135.6, 143.0, 148.0, 171.0. MS: m/z 215 $[MH]^+$. HRMS (FAB) Calcd for $C_{14}H_{15}O_2$: 215.1073 [M+H], found: 215.1078.



Methyl 2-(6-chloro-2-methyl-1-methylene-1H-inden-3-yl)acetate (4b)

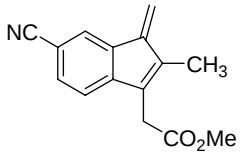
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.09 (s, 3H), 3.53 (s, 2H), 3.67 (s, 3H), 5.70 (d, *J* = 2.0 Hz, 1H), 5.96 (d, *J* = 2.0 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H)), 7.19-7.20 (m, 1H), 7.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 9.9, 31.5, 52.1, 111.8, 118.9, 119.8, 127.7, 130.8, 132.8, 135.3, 137.3, 141.4, 147.1, 170.7. MS: m/z 249 $[MH]^+$. HRMS (FAB) Calcd for $C_{14}H_{14}ClO_2$: 249.0683 [M+H], found: 249.0699.



Methyl 2-(6-bromo-2-methyl-1-methylene-1H-inden-3-yl)acetate (4c)

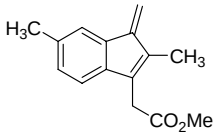
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.10 (s, 3H), 3.55 (s, 2H), 3.67 (s, 3H), 5.73 (s, 1H), 5.99 (s, 1H), 7.05 (d, *J* = 8.0 Hz, 1H)), 7.36 (d, *J* = 8.0 Hz, 1H),

7.61 (d, J = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 9.9, 31.6, 52.2, 111.9, 118.8, 119.4, 122.6, 130.6, 132.8, 135.3, 137.6, 141.8, 147.1, 170.8. MS: m/z 293 $[MH]^+$. HRMS (FAB) Calcd for $C_{14}H_{14}BrO_2$: 293.0178 [M+H], found: 293.0192.



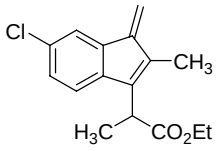
Methyl 2-(6-cyano-2-methyl-1-methylene-1H-inden-3-yl)acetate (4d)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.15 (s, 3H), 3.57 (s, 2H), 3.67 (s, 3H), 5.84 (s, 1H), 6.08 (s, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.70 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 10.1, 31.3, 52.2, 107.7, 113.7, 118.6, 119.8, 122.3, 132.4, 133.0, 136.0, 139.2, 146.2, 146.9, 170.4. MS: m/z 240 $[MH]^+$. HRMS (FAB) Calcd for $C_{15}H_{14}NO_2$: 240.1025 [M+H], found: 240.1018.



Methyl 2-(2,6-dimethyl-1-methylene-1H-inden-3-yl)acetate (4e)

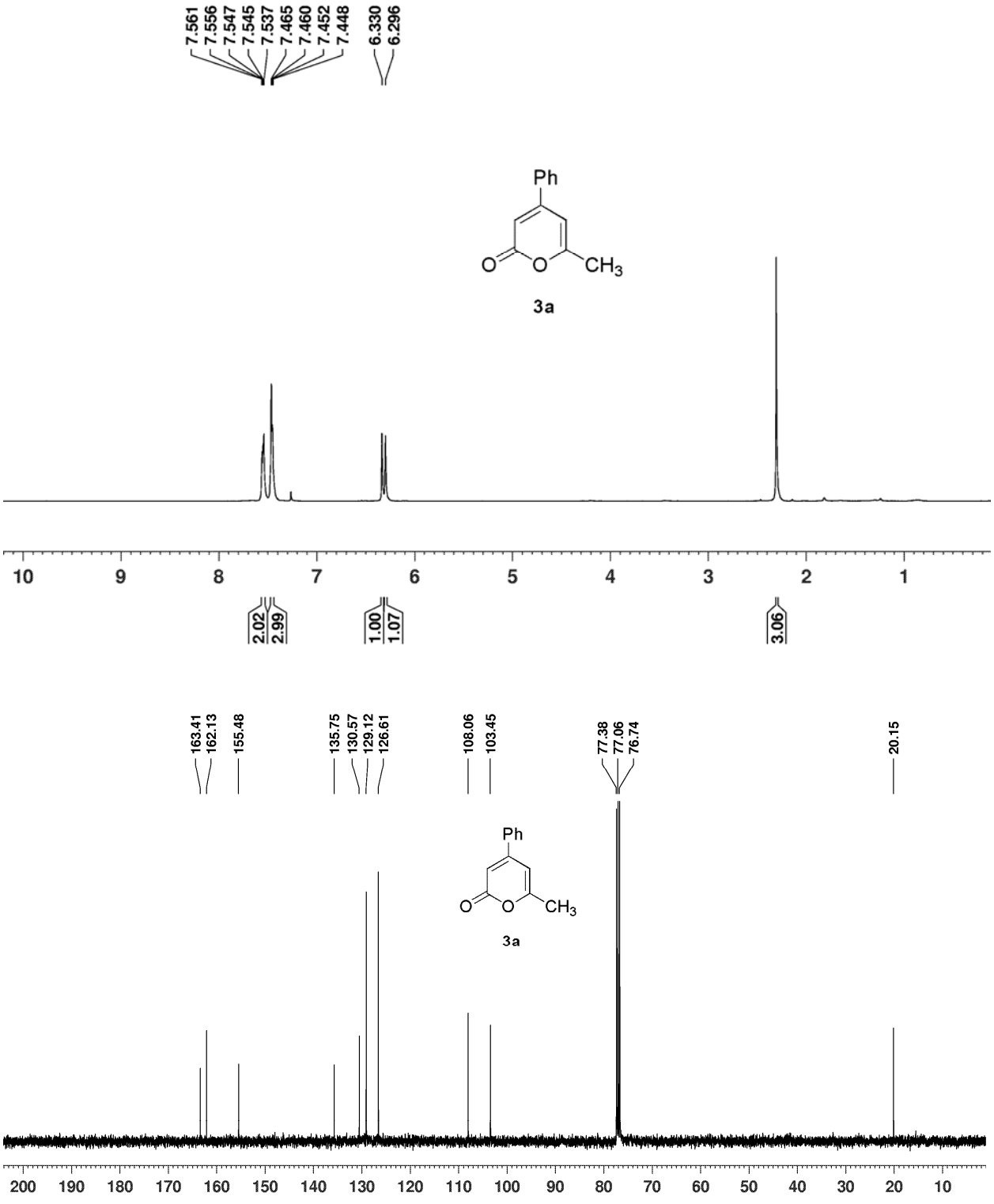
^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.16 (s, 3H), 2.44 (s, 3H), 3.60 (s, 2H), 3.71 (s, 3H), 5.68 (s, 1H), 6.00 (s, 1H), 7.11-7.17 (m, 2H), 7.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 9.8, 21.5, 31.7, 52.0, 109.9, 117.8, 120.3, 128.6, 133.3, 134.0, 136.0, 140.6, 148.2, 171.0. MS: m/z 229 $[MH]^+$. HRMS (FAB) Calcd for $C_{15}H_{17}O_2$: 229.1229 [M+H], found: 229.1242.

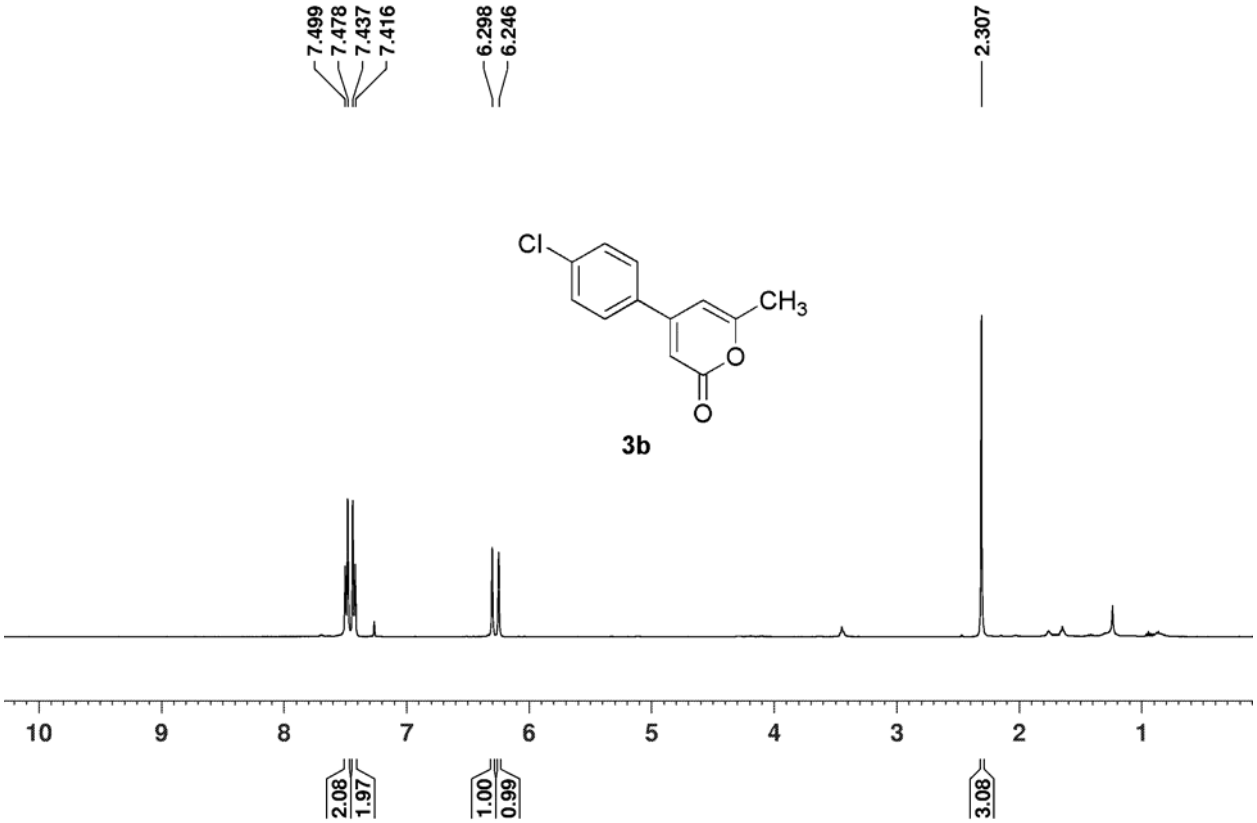


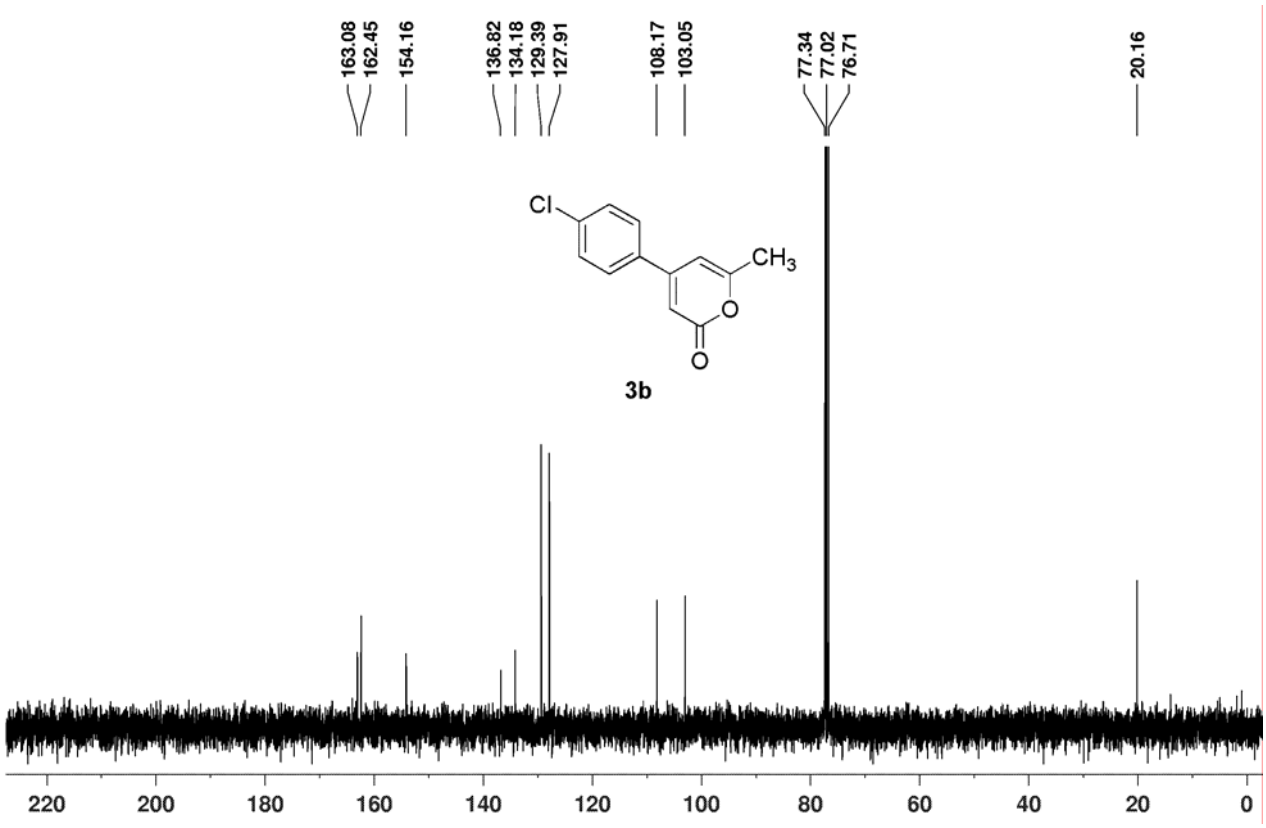
Ethyl 2-(6-chloro-2-methyl-1-methylene-1H-inden-3-yl)propanoate (4f)

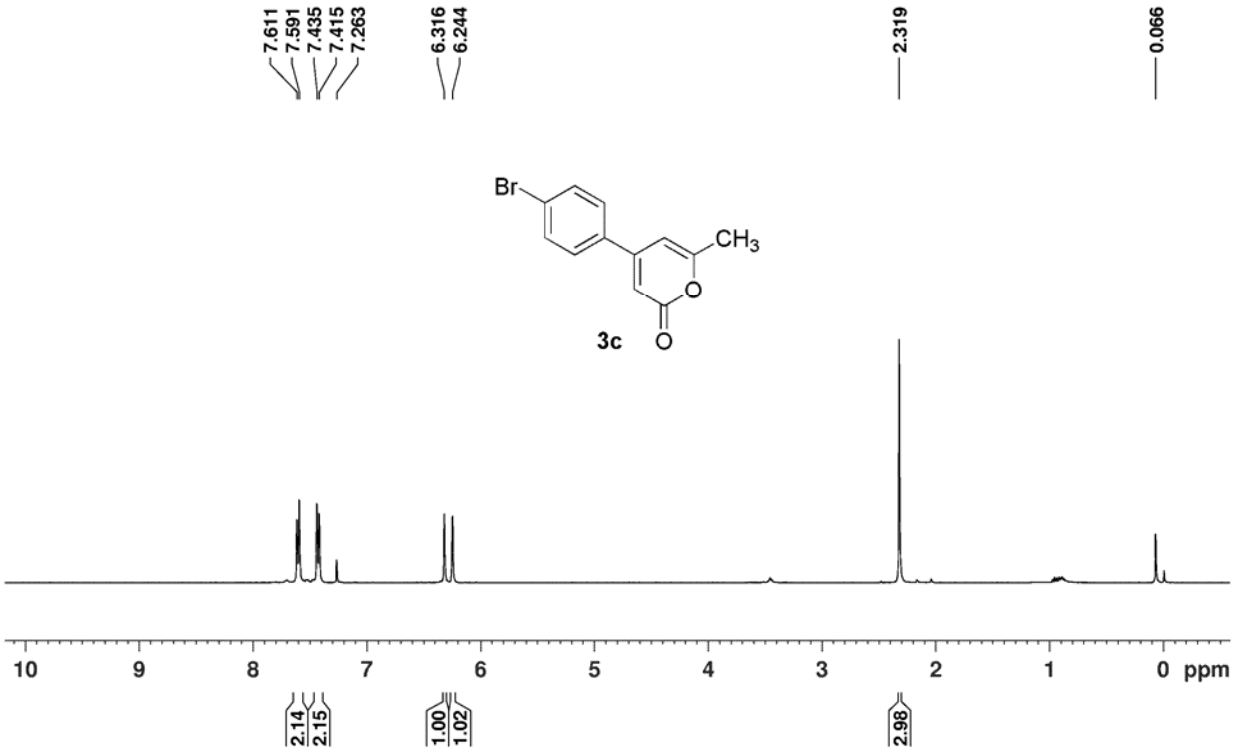
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.65 (t, J = 7.2 Hz, 3H), 1.47 (d, J = 7.2 Hz, 3H), 2.09 (s, 3H), 3.85-3.88 (m, 1H), 4.11-4.16 (m, 2H), 5.70 (s, 1H), 5.96 (s, 1H), 7.14-7.16 (m, 2H), 7.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 9.8, 14.1, 15.3, 37.4, 60.9, 111.4, 119.7, 119.8, 127.5, 130.6, 133.4, 137.8, 138.8, 140.1, 147.1, 173.7. MS: m/z 277 $[MH]^+$. HRMS (FAB) Calcd for $C_{16}H_{18}ClO_2$: 277.0996 [M+H], found: 277.0988.

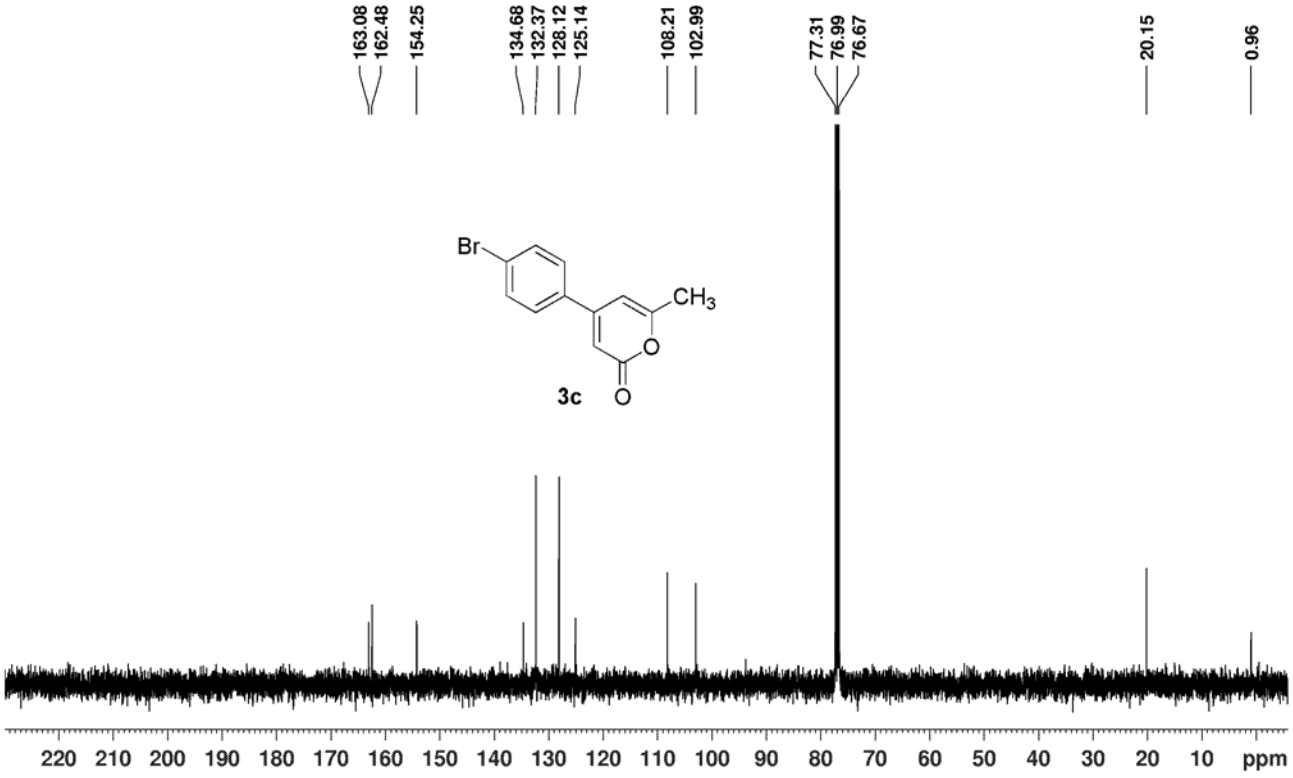
III. Copies of ^{1}H and ^{13}C NMR spectra of 3a-3ad, and 4a-4f

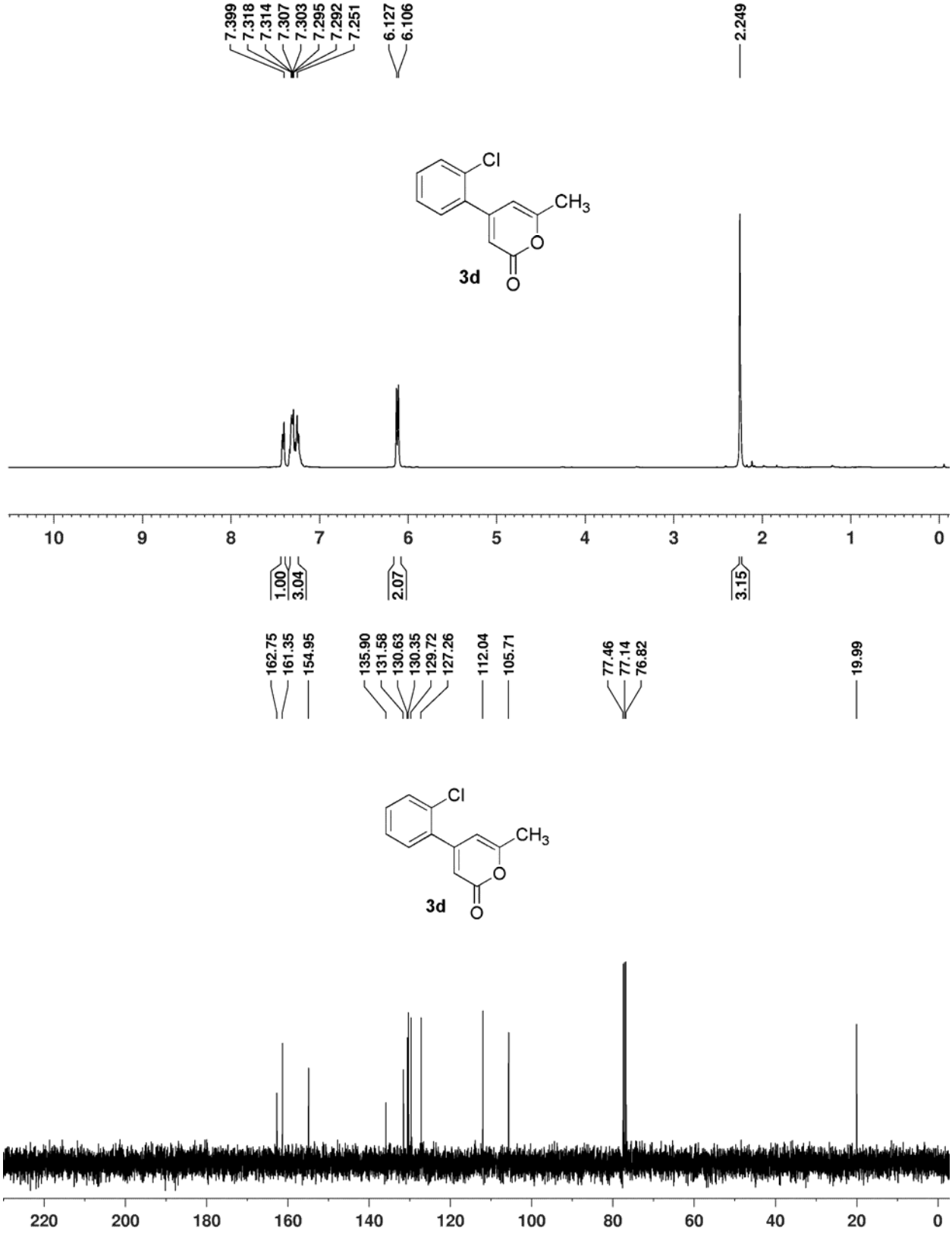


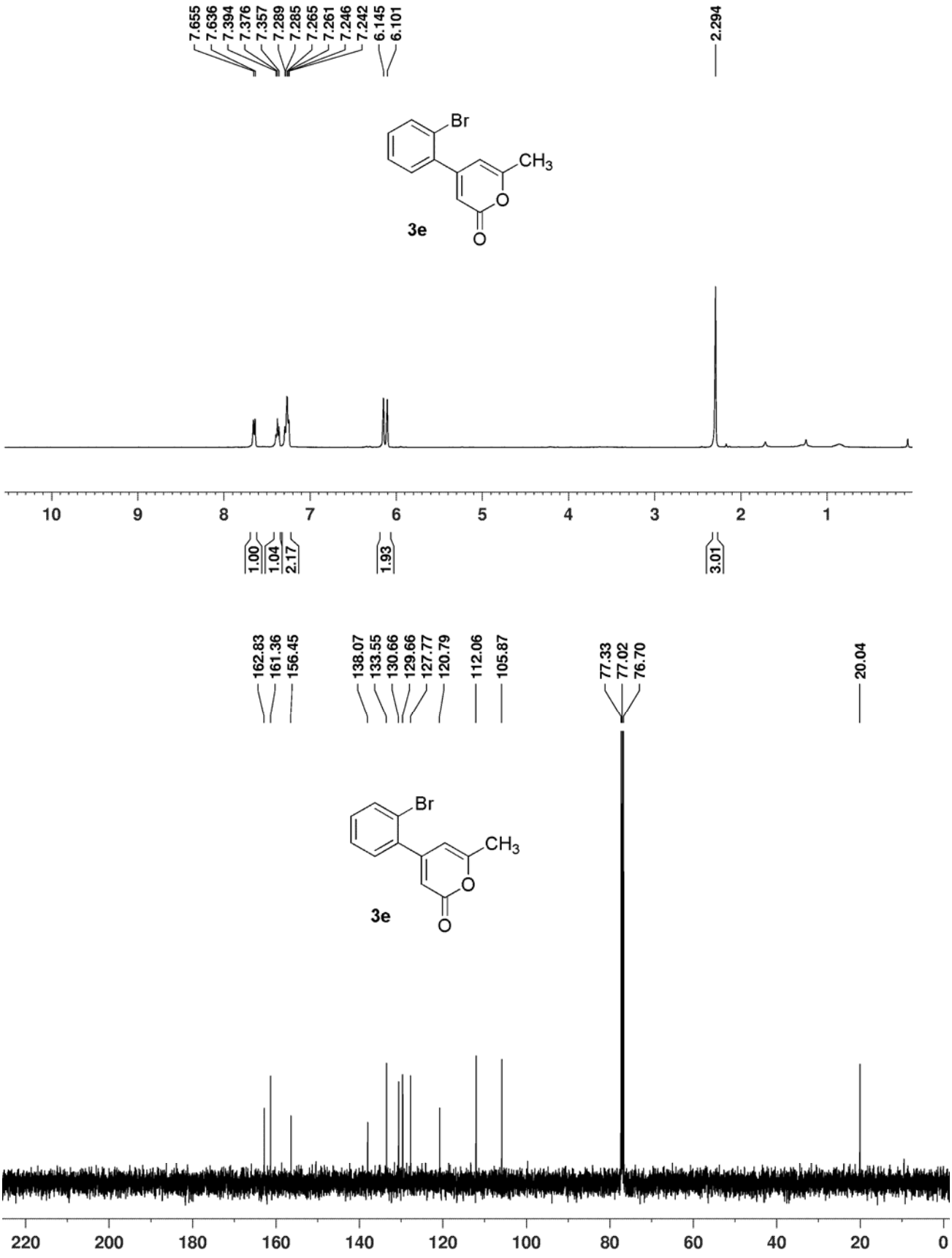


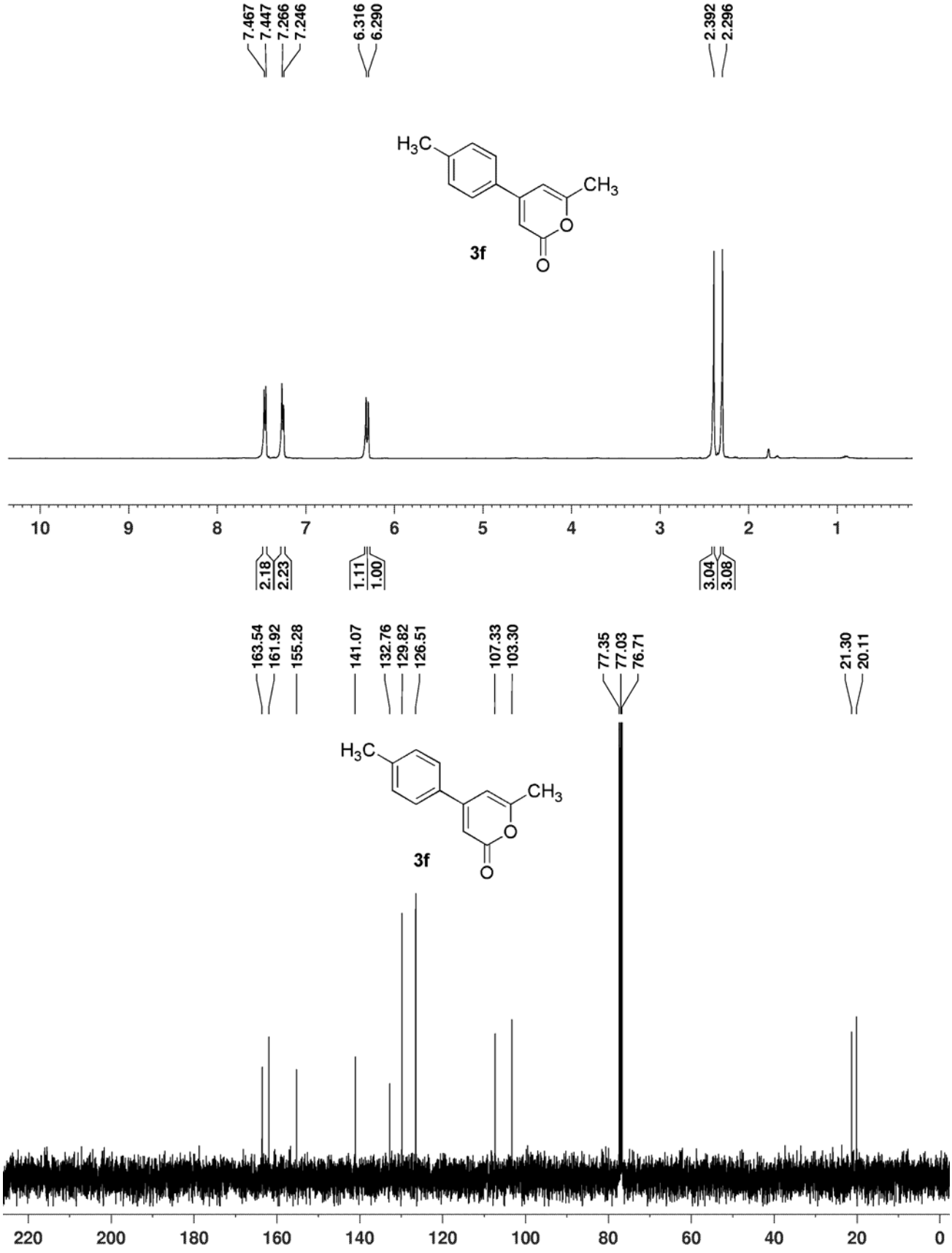


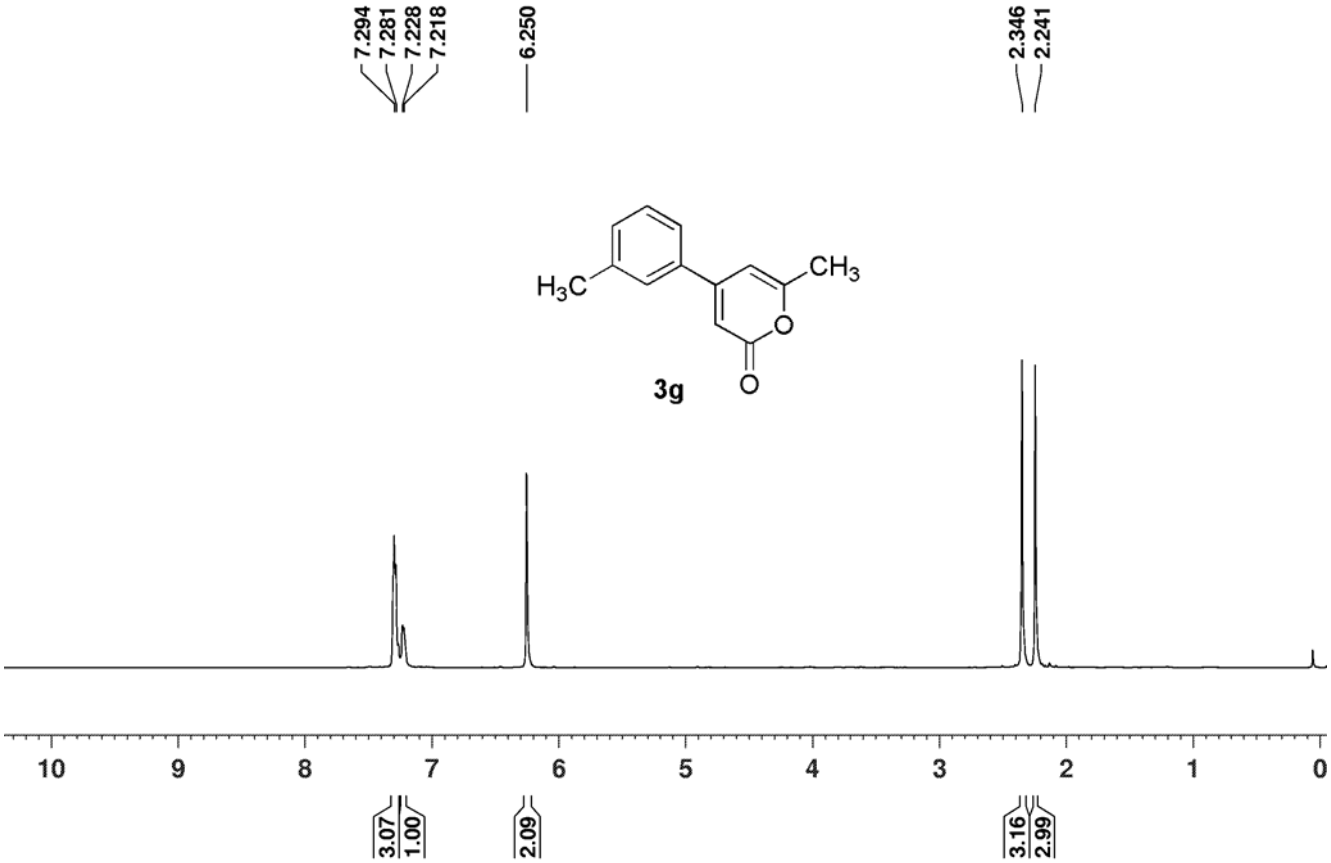


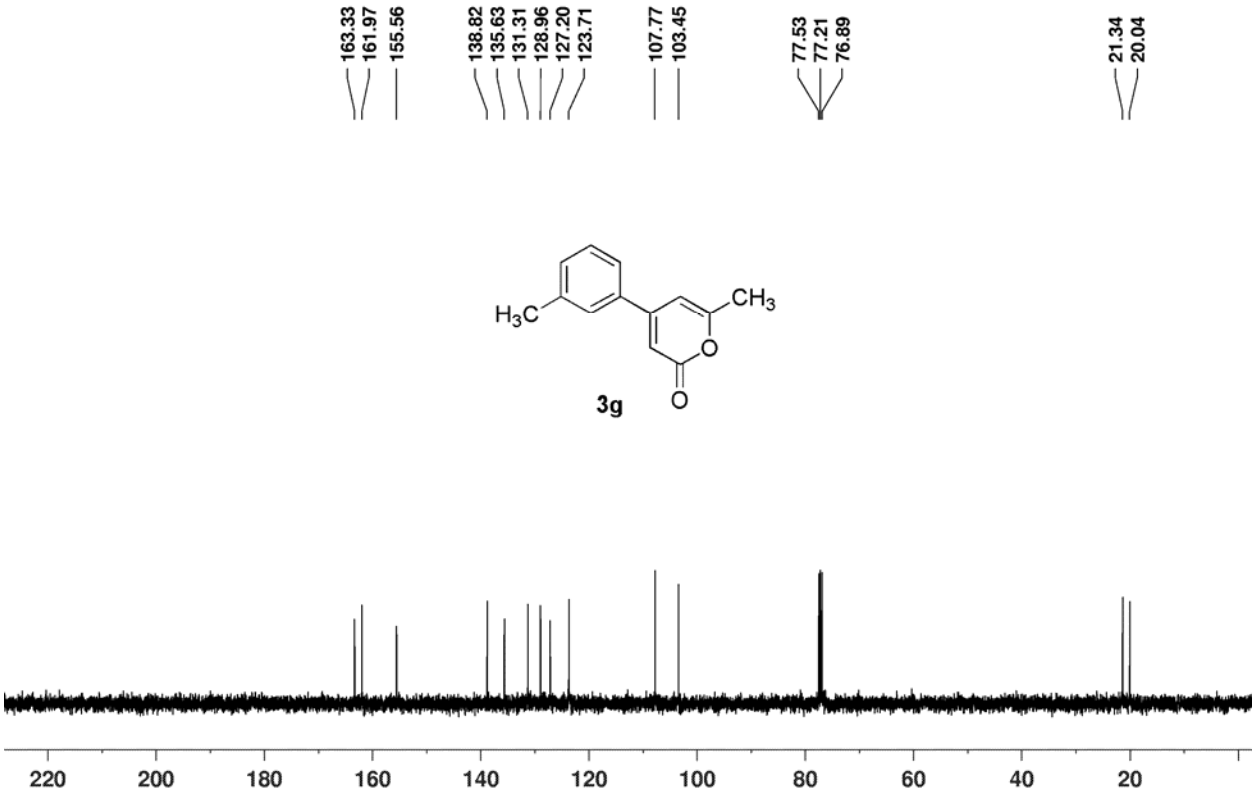


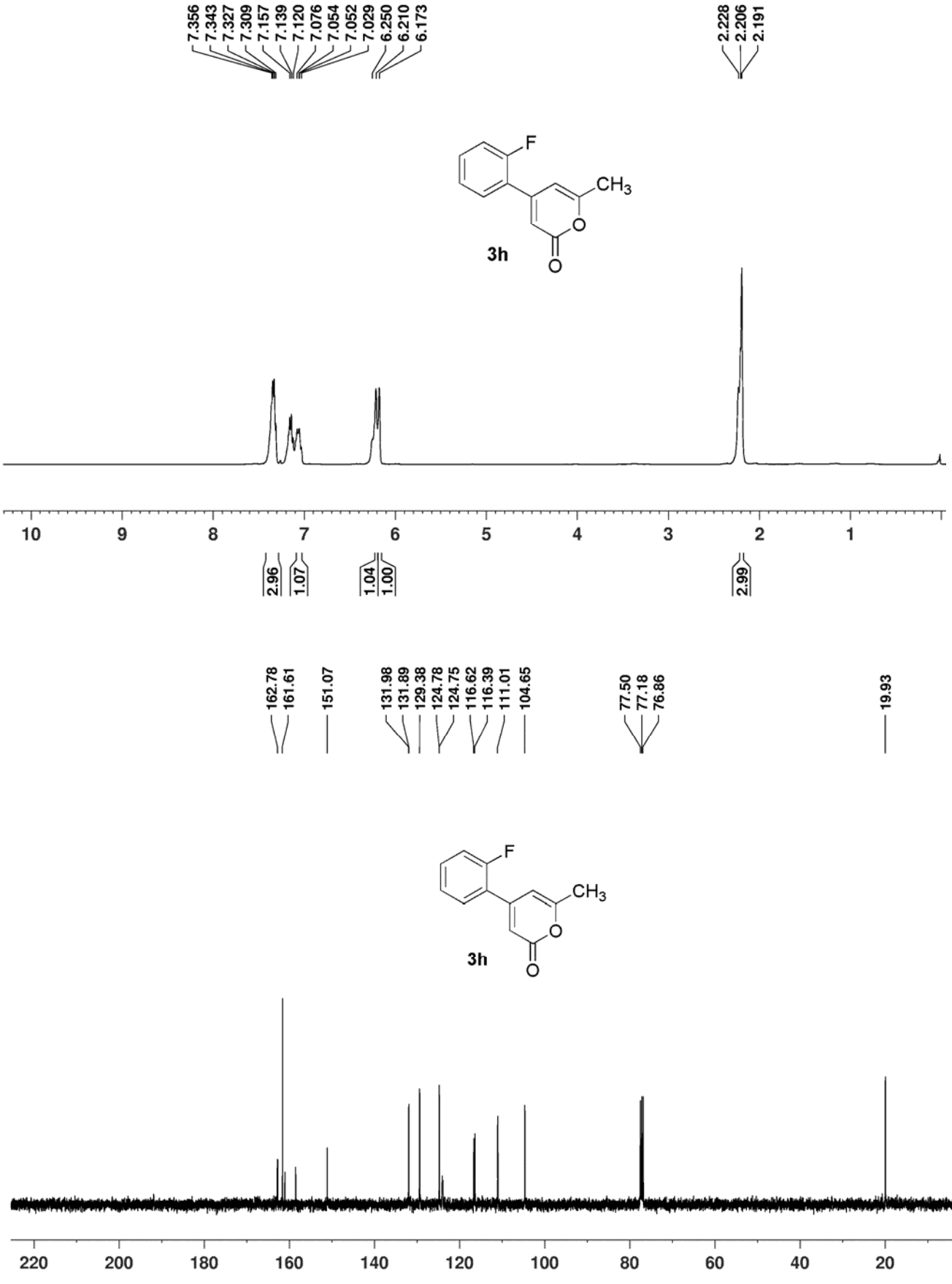


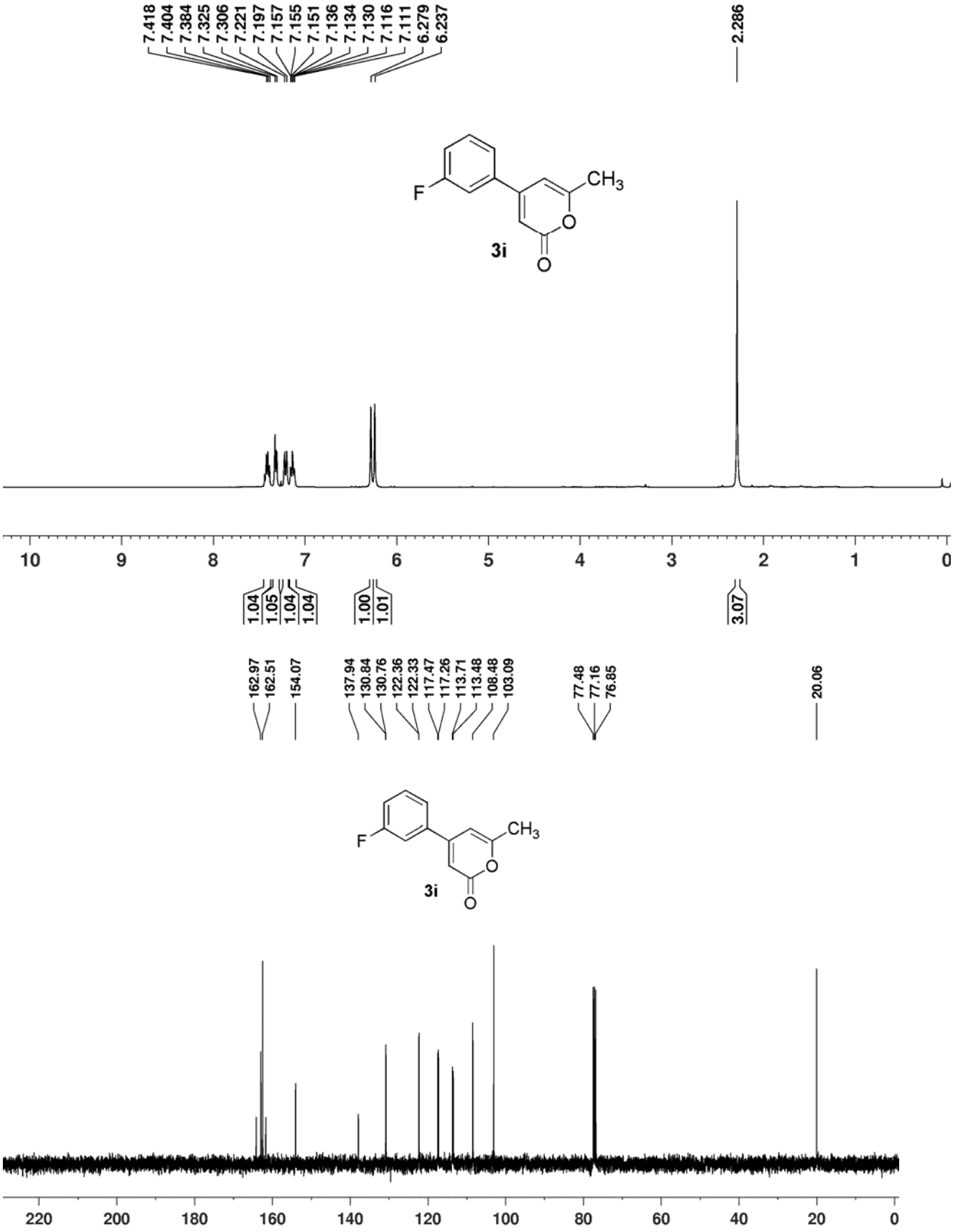


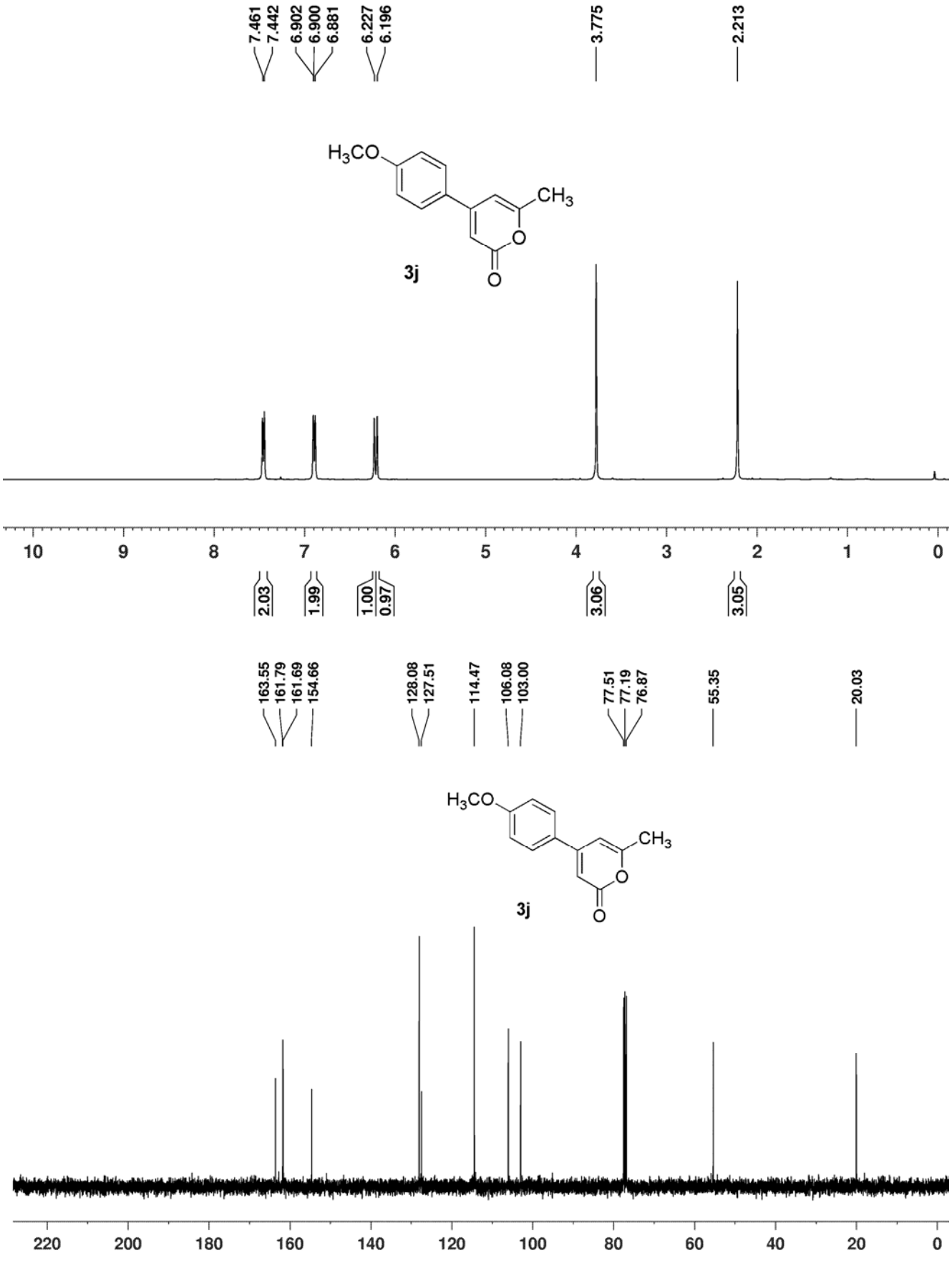


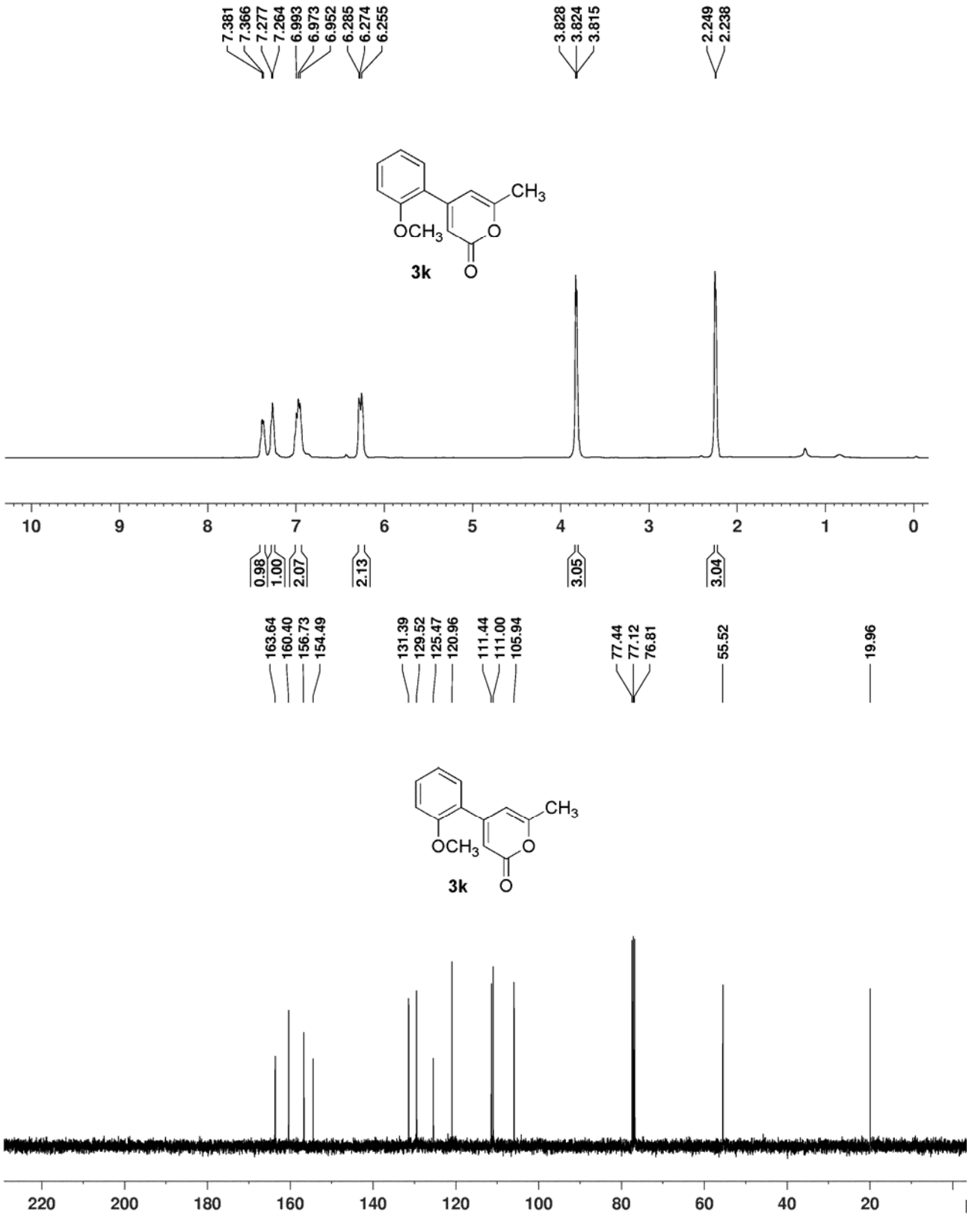


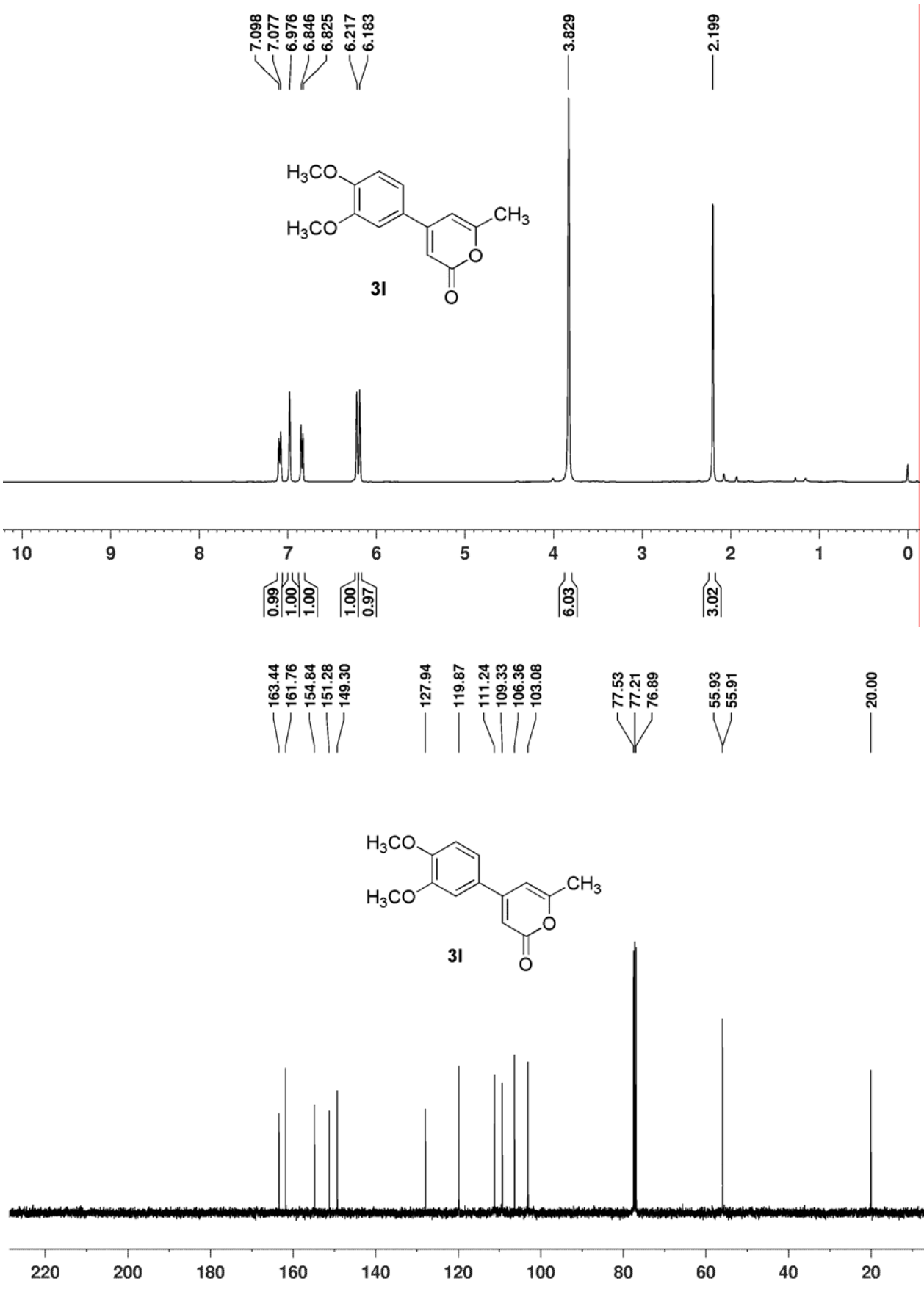


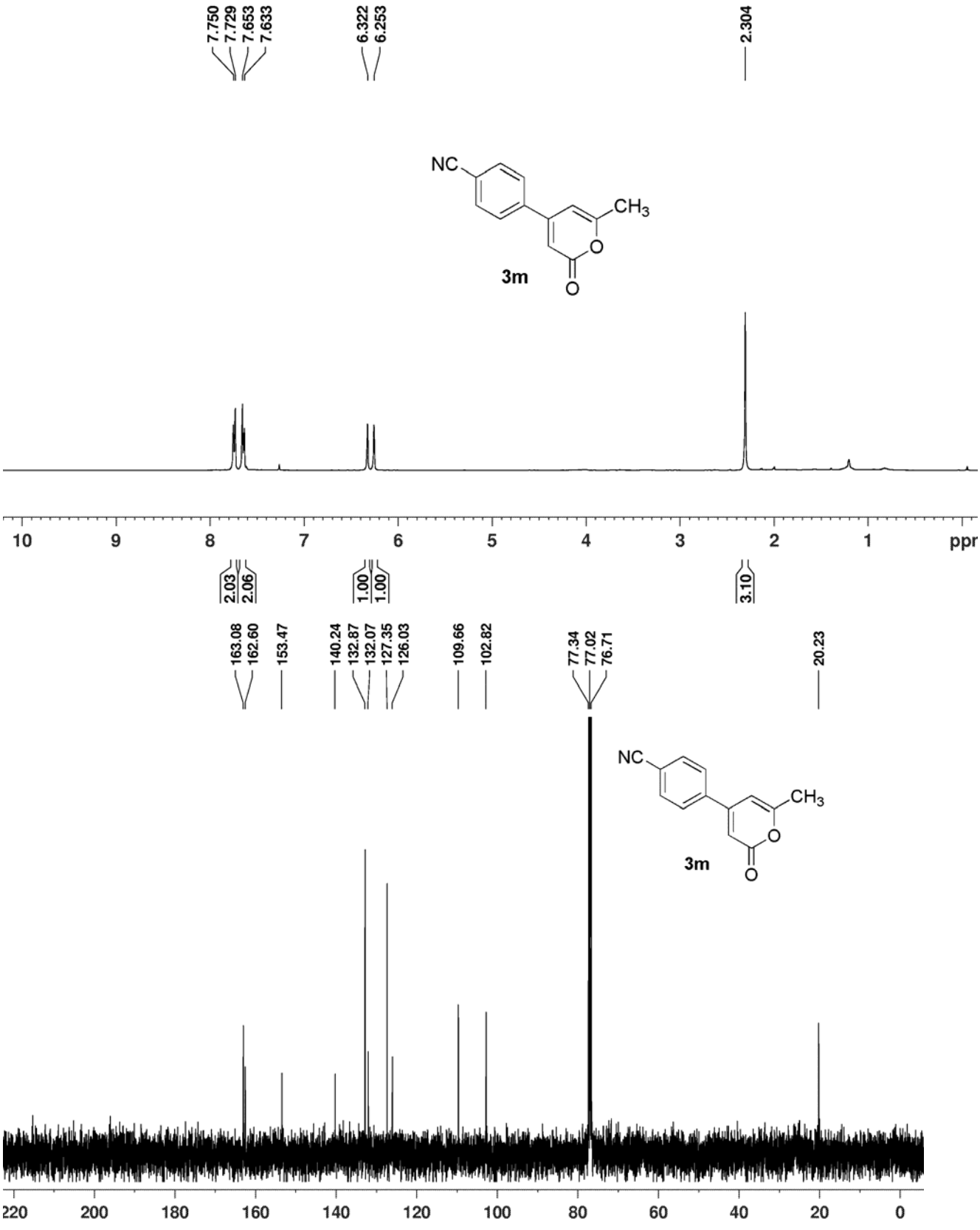


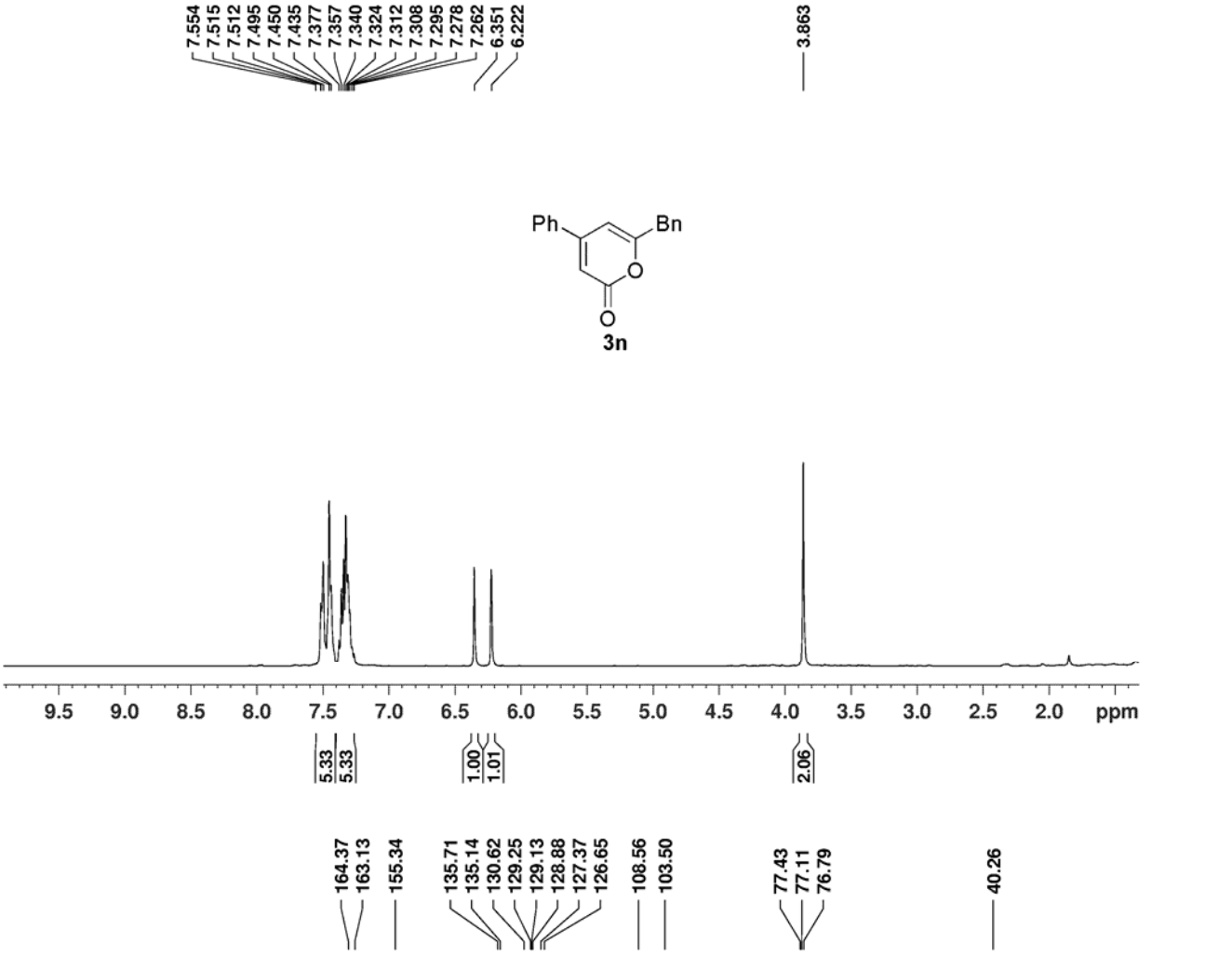


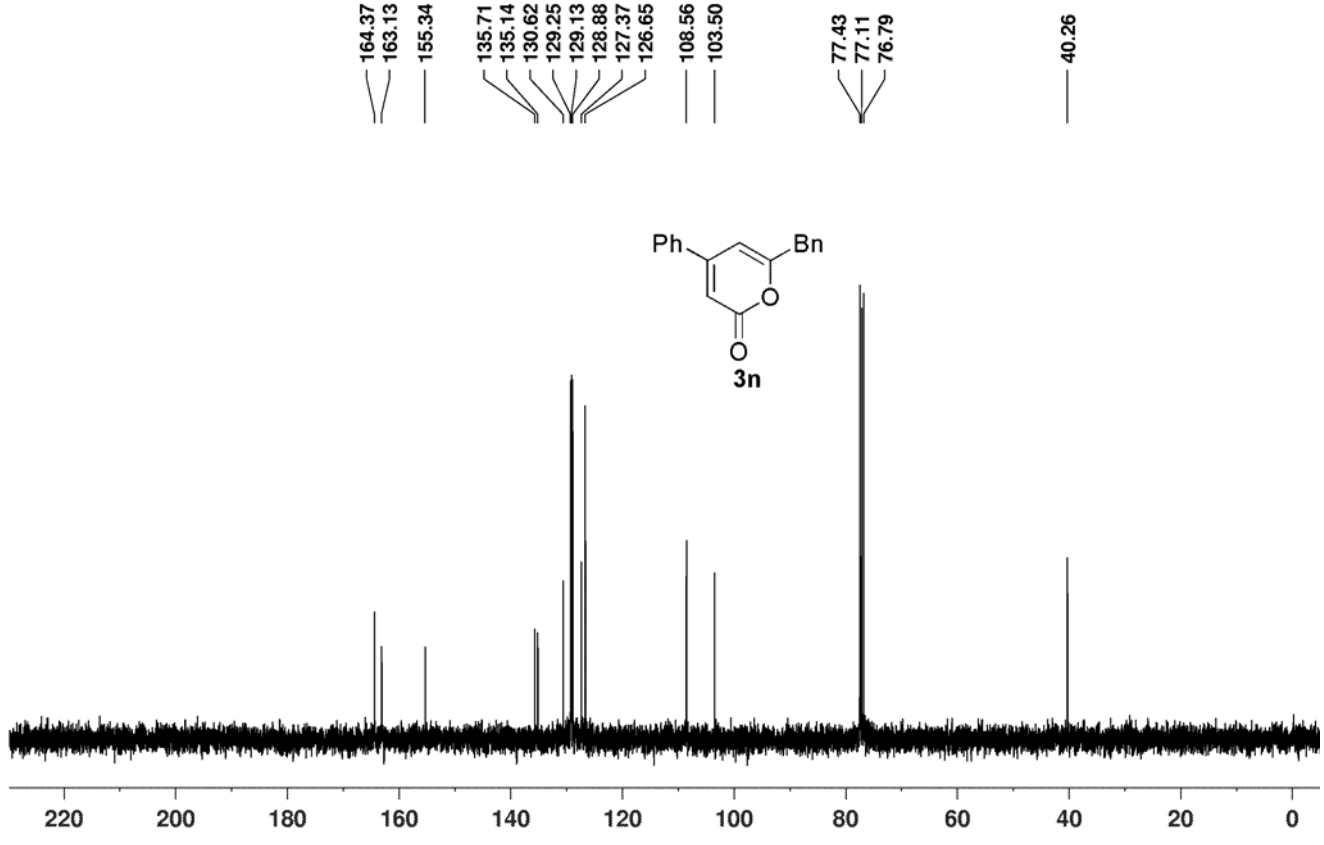


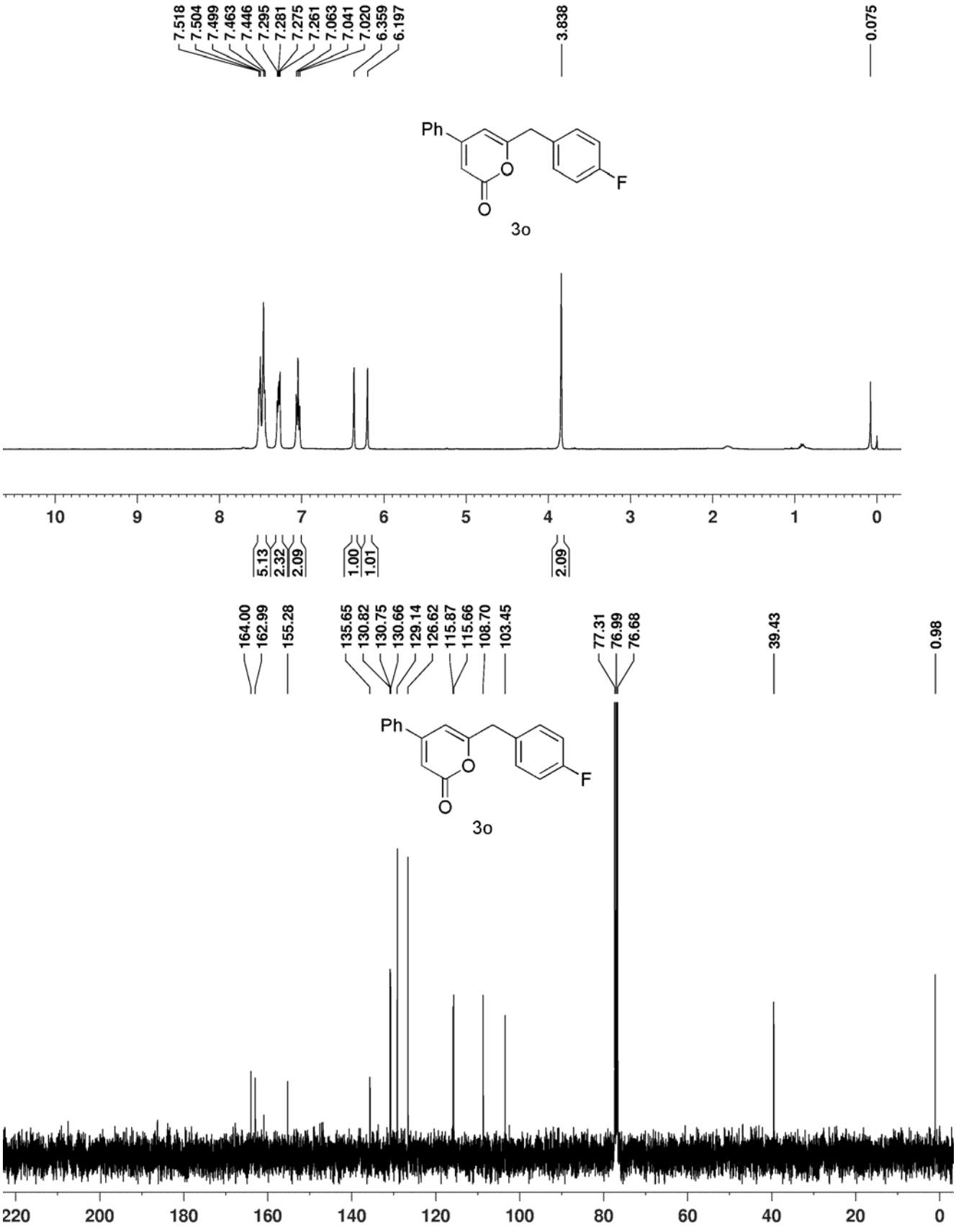


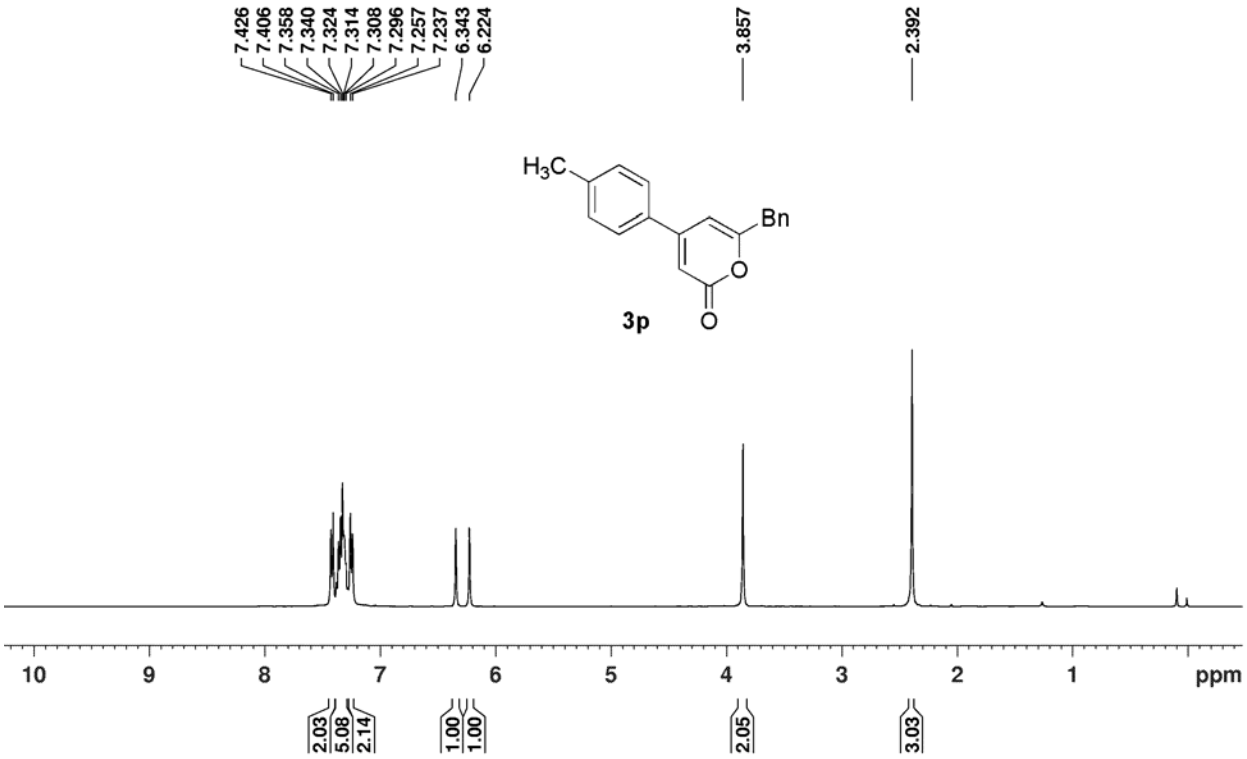


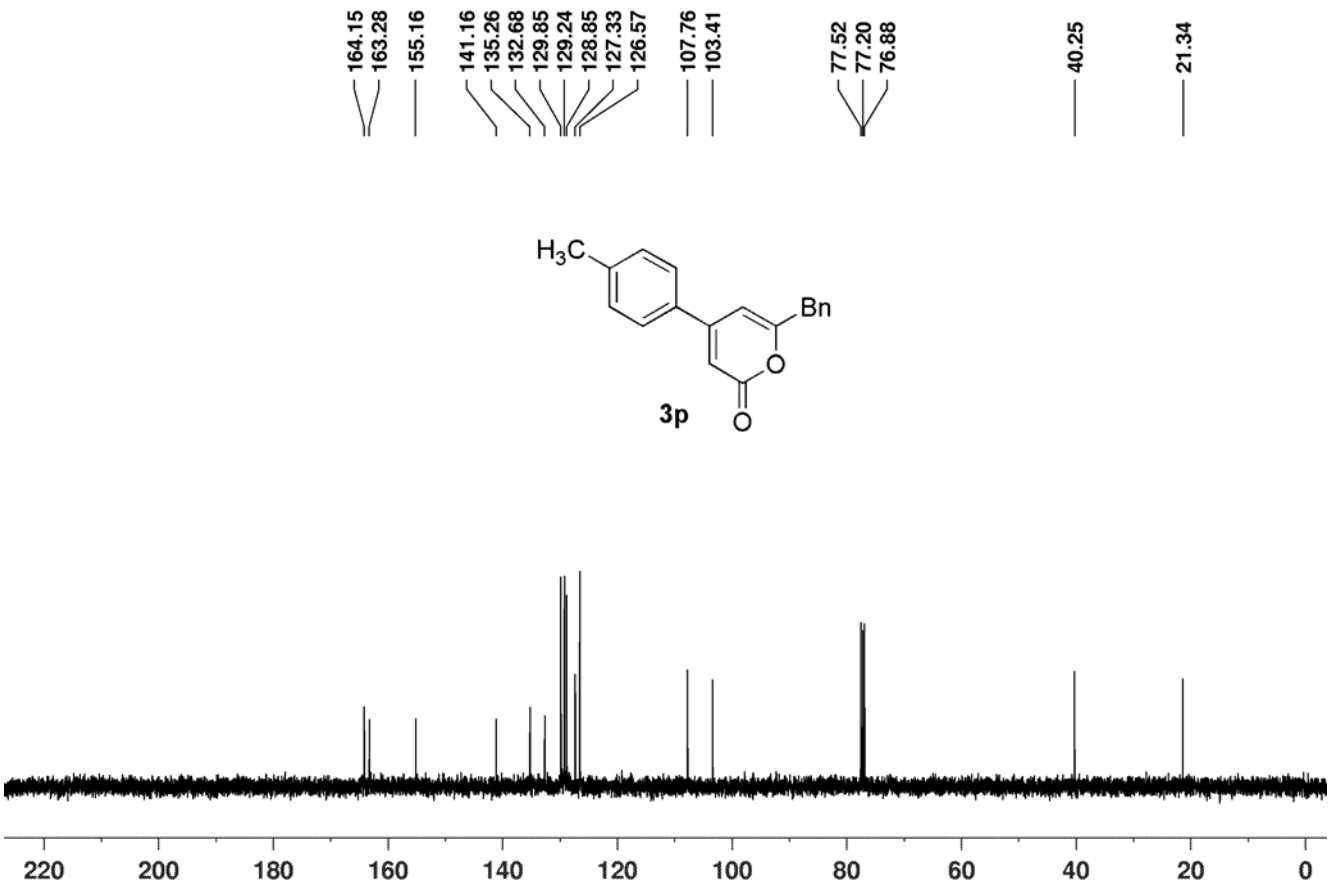


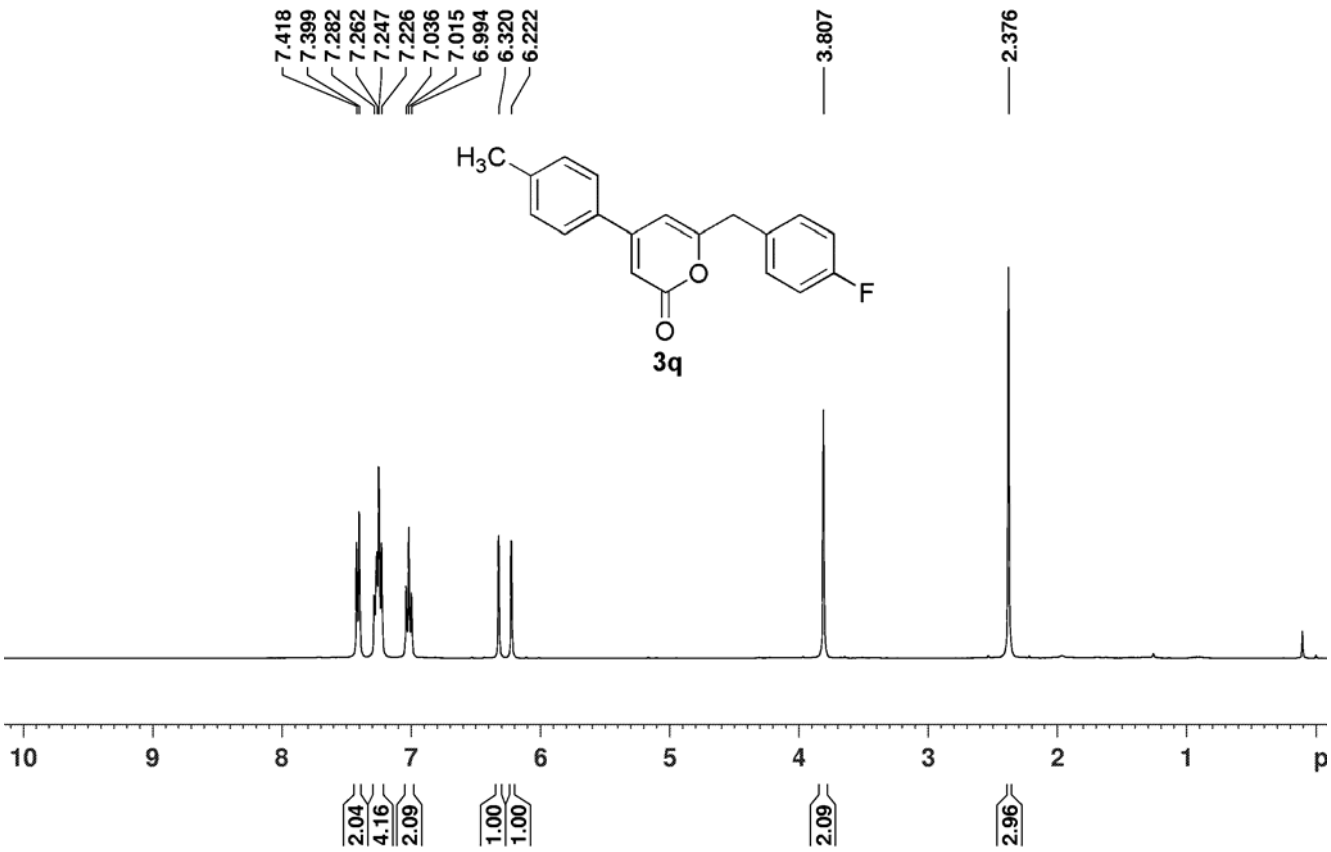


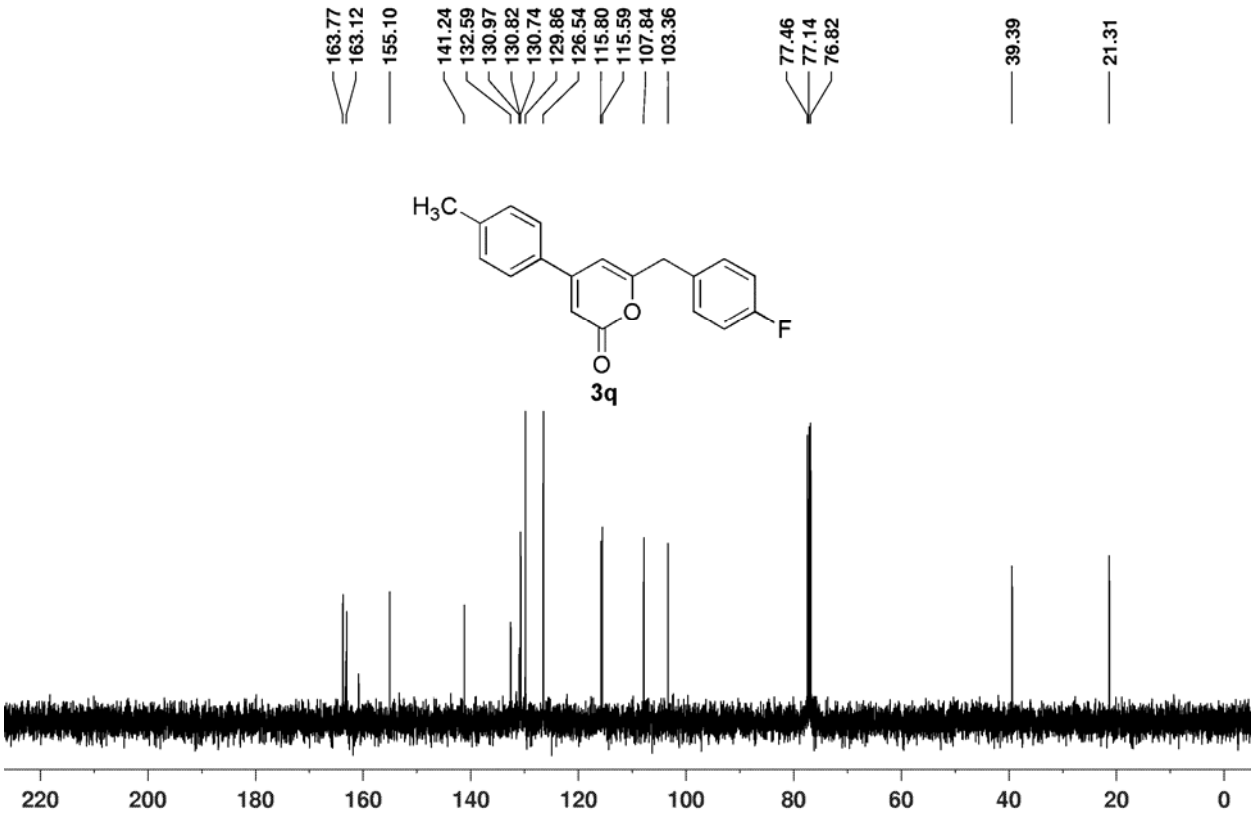


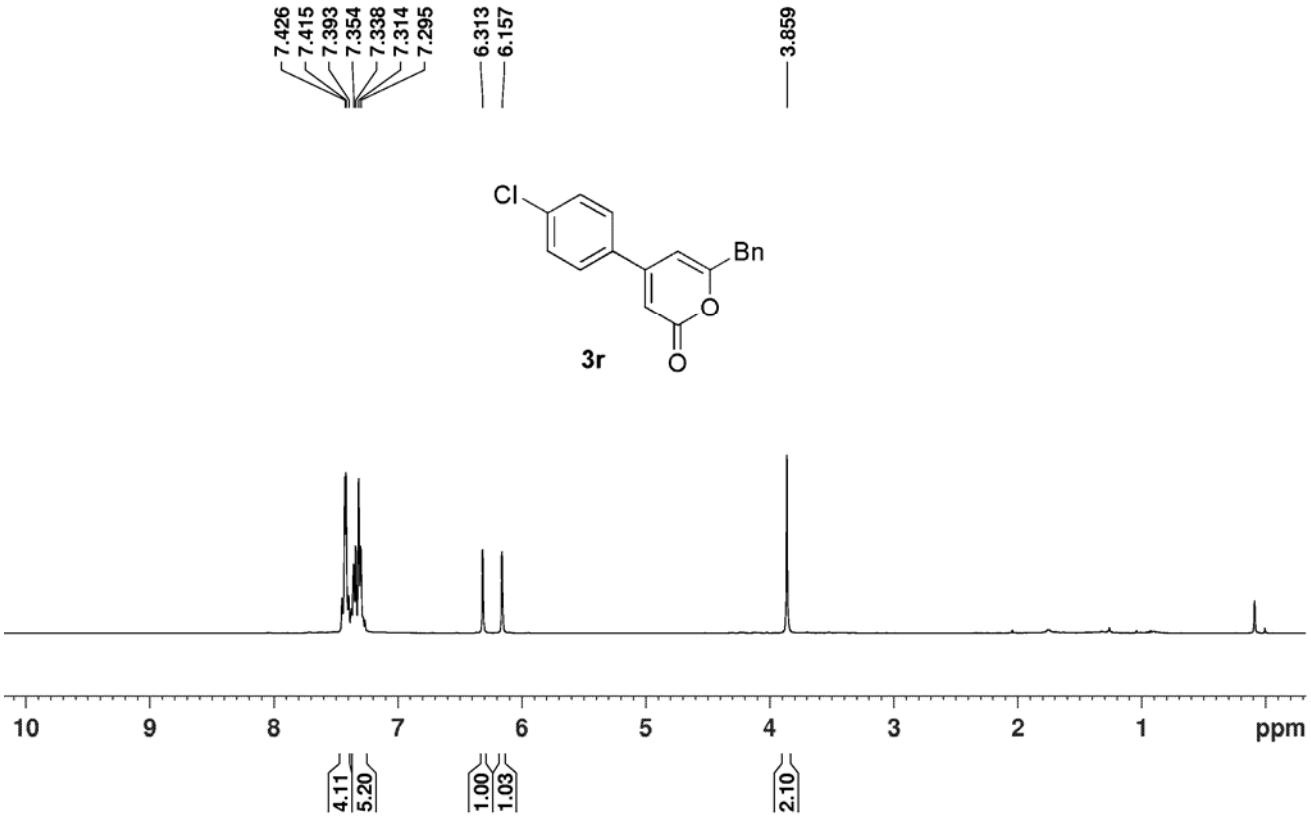


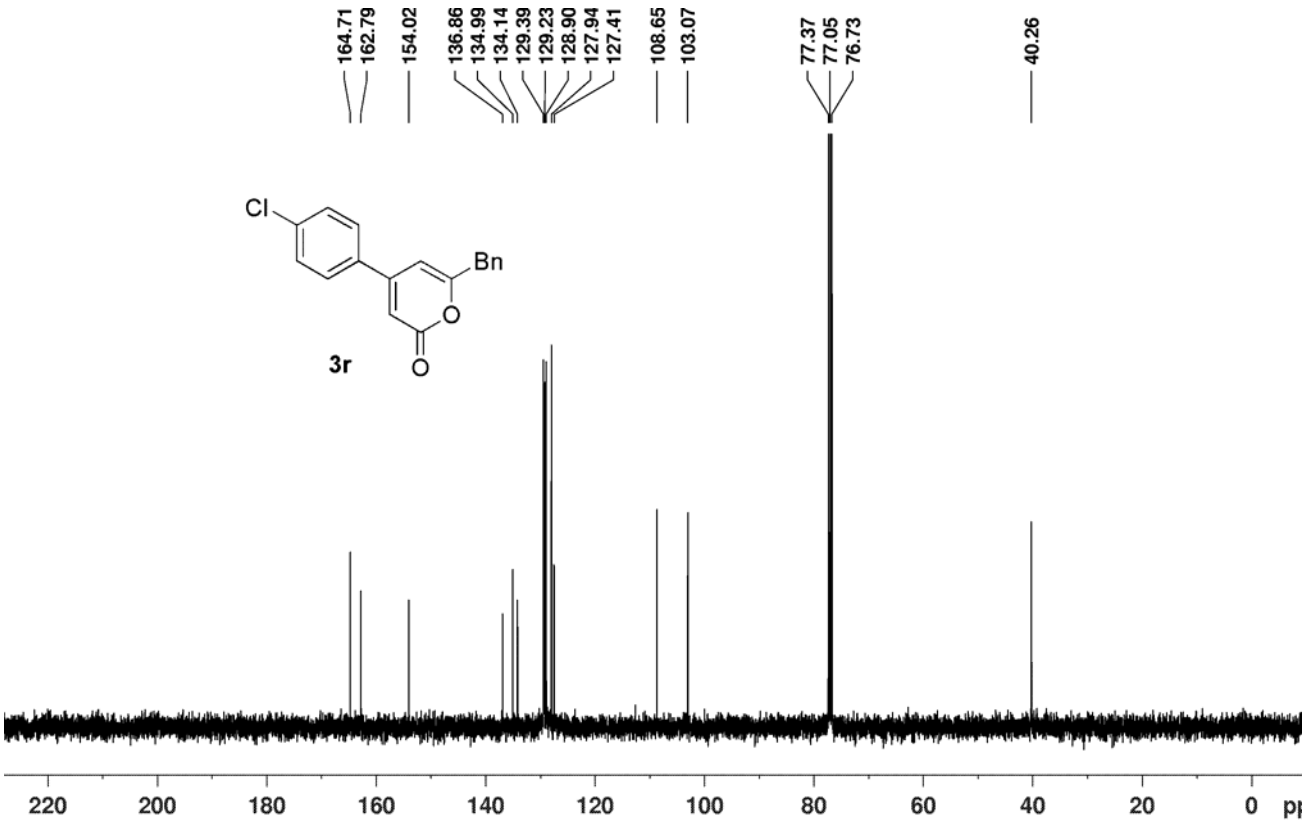


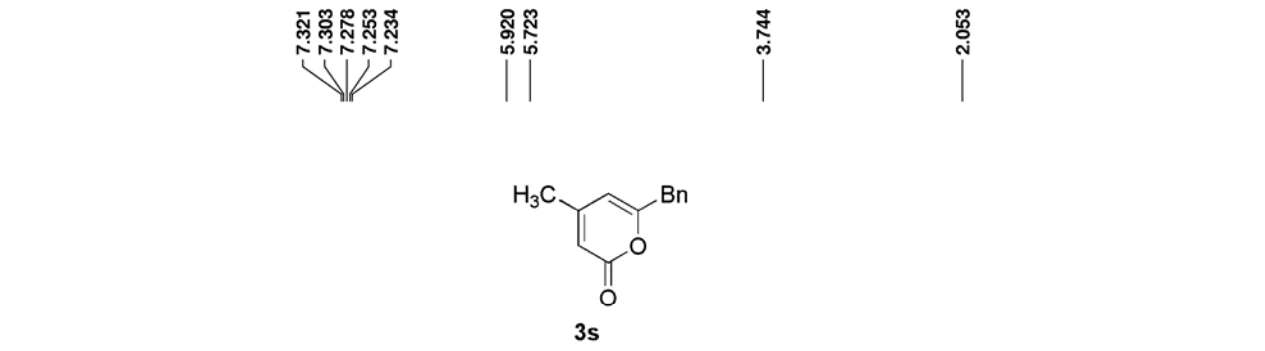






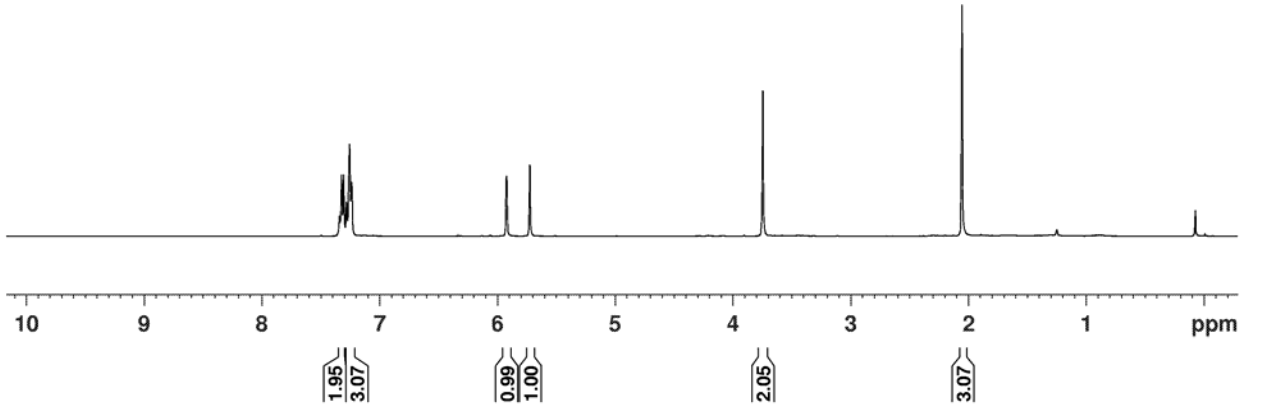


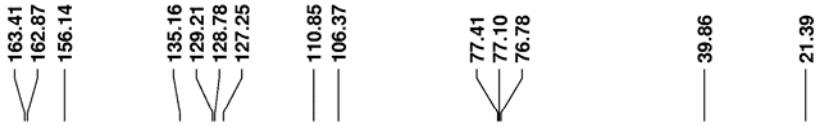


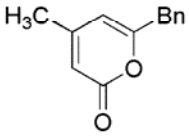

7.321
7.303
7.278
7.253
7.234
5.920
5.723
3.744
2.053

H3C
Bn
O
O

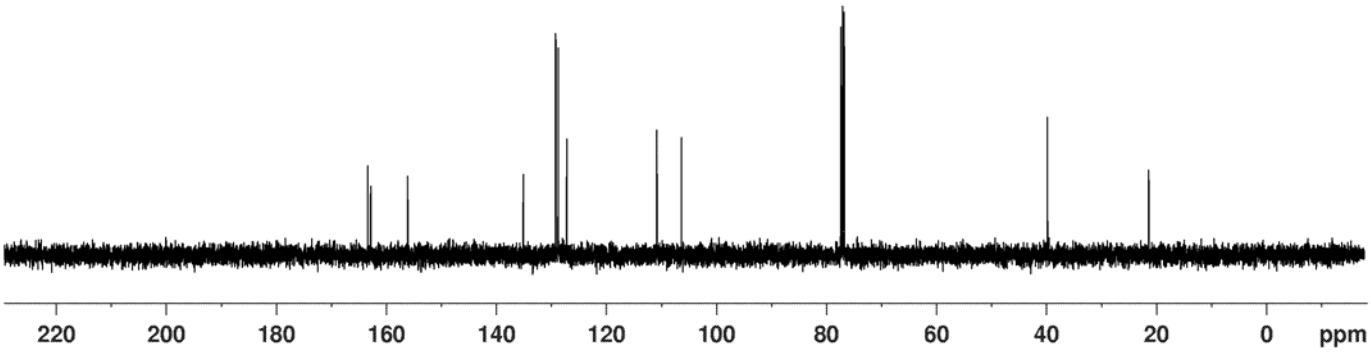
3s

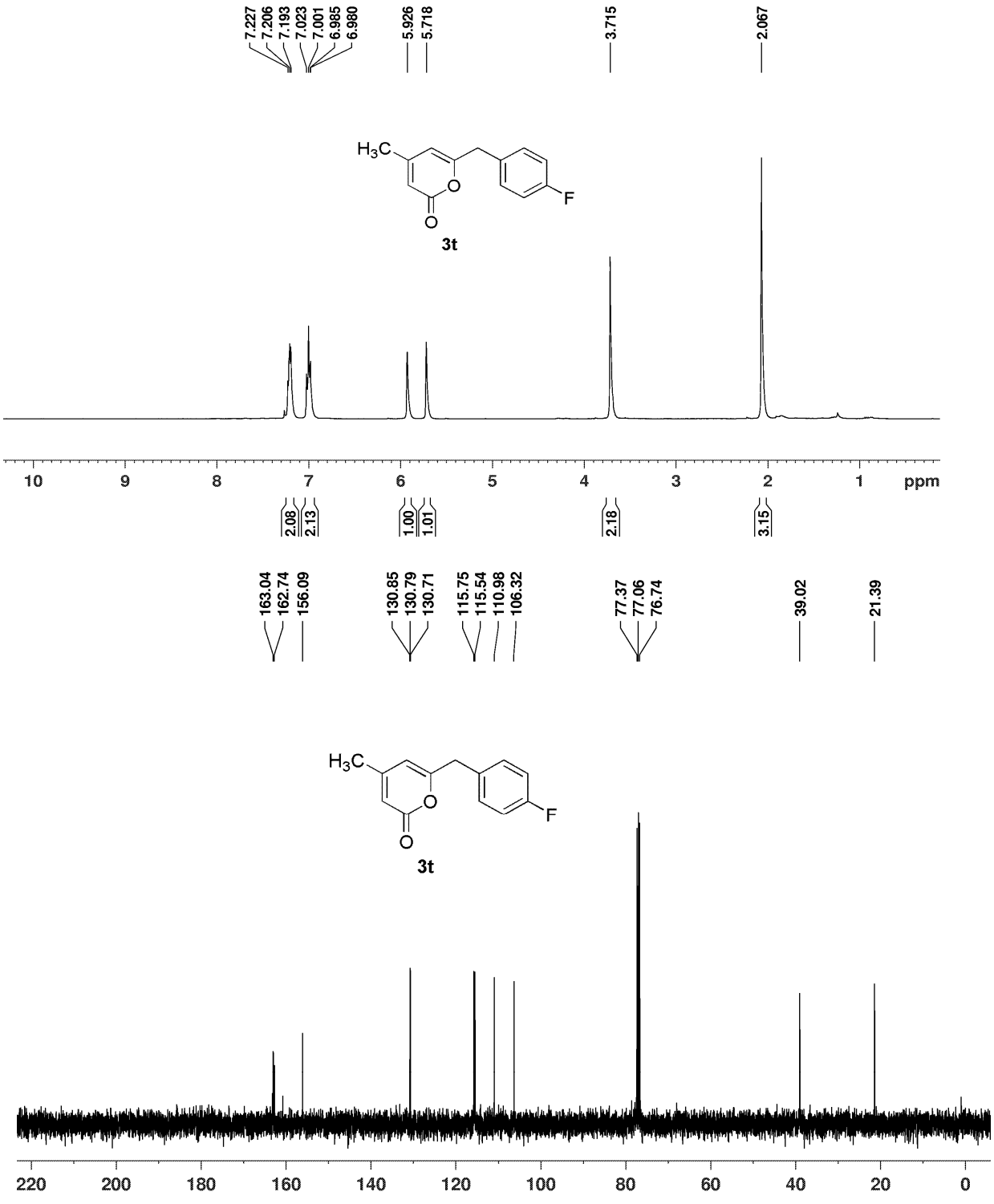

10
9
8
7
6
5
4
3
2
1
ppm
1.95
3.07
0.99
1.00
2.05
3.07

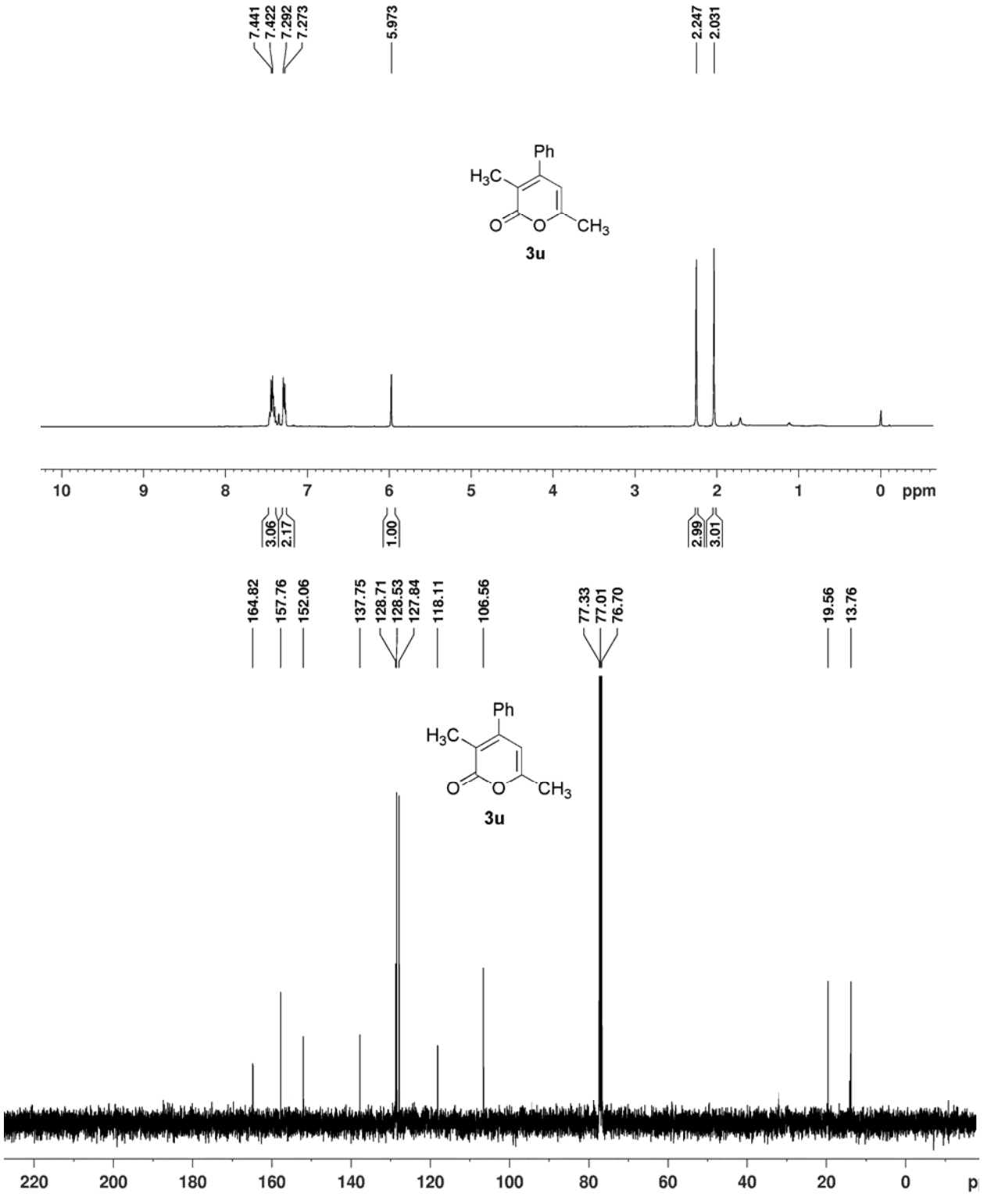

163.41
162.87
156.14
135.16
129.21
128.78
127.25
110.85
106.37
77.41
77.10
76.78
39.86
21.39

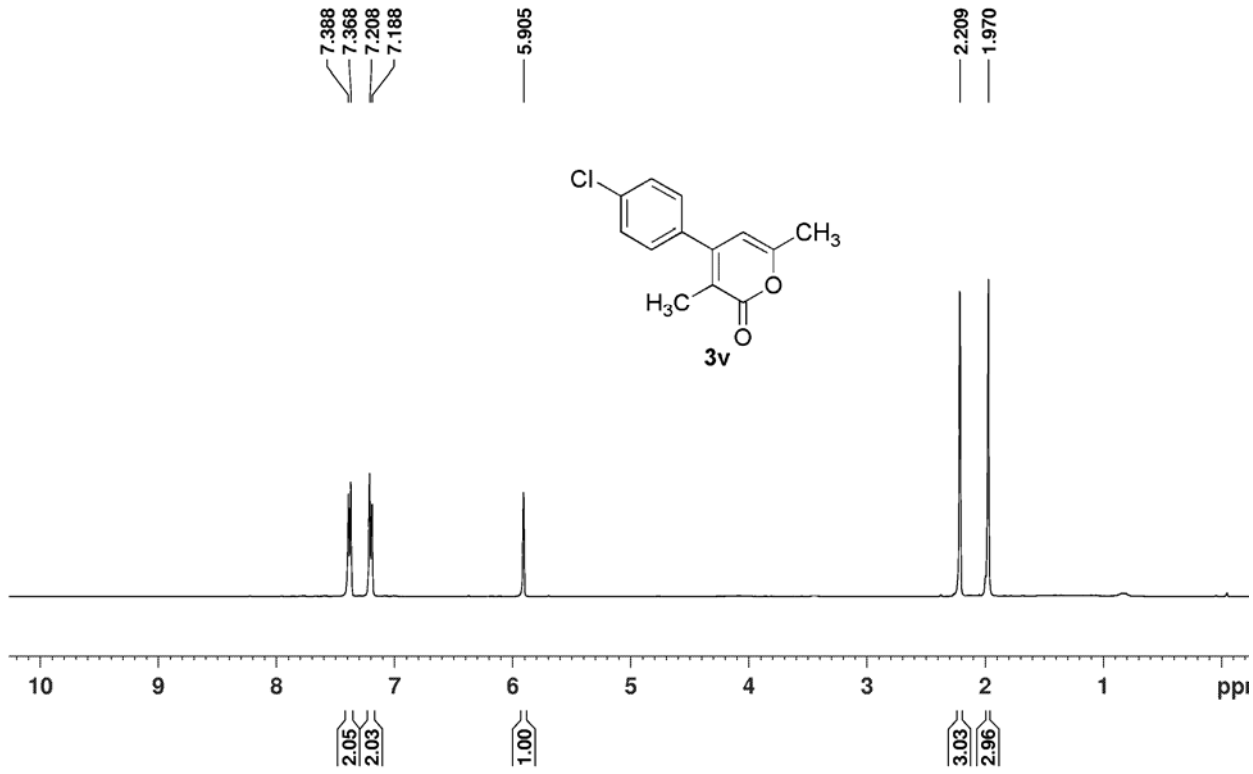

H3C
Bn
O
O

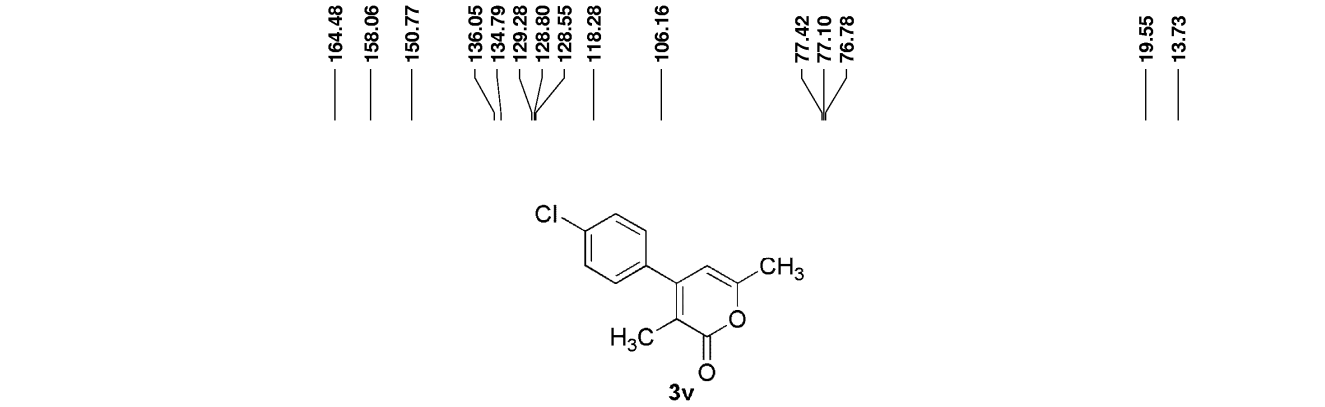
3s

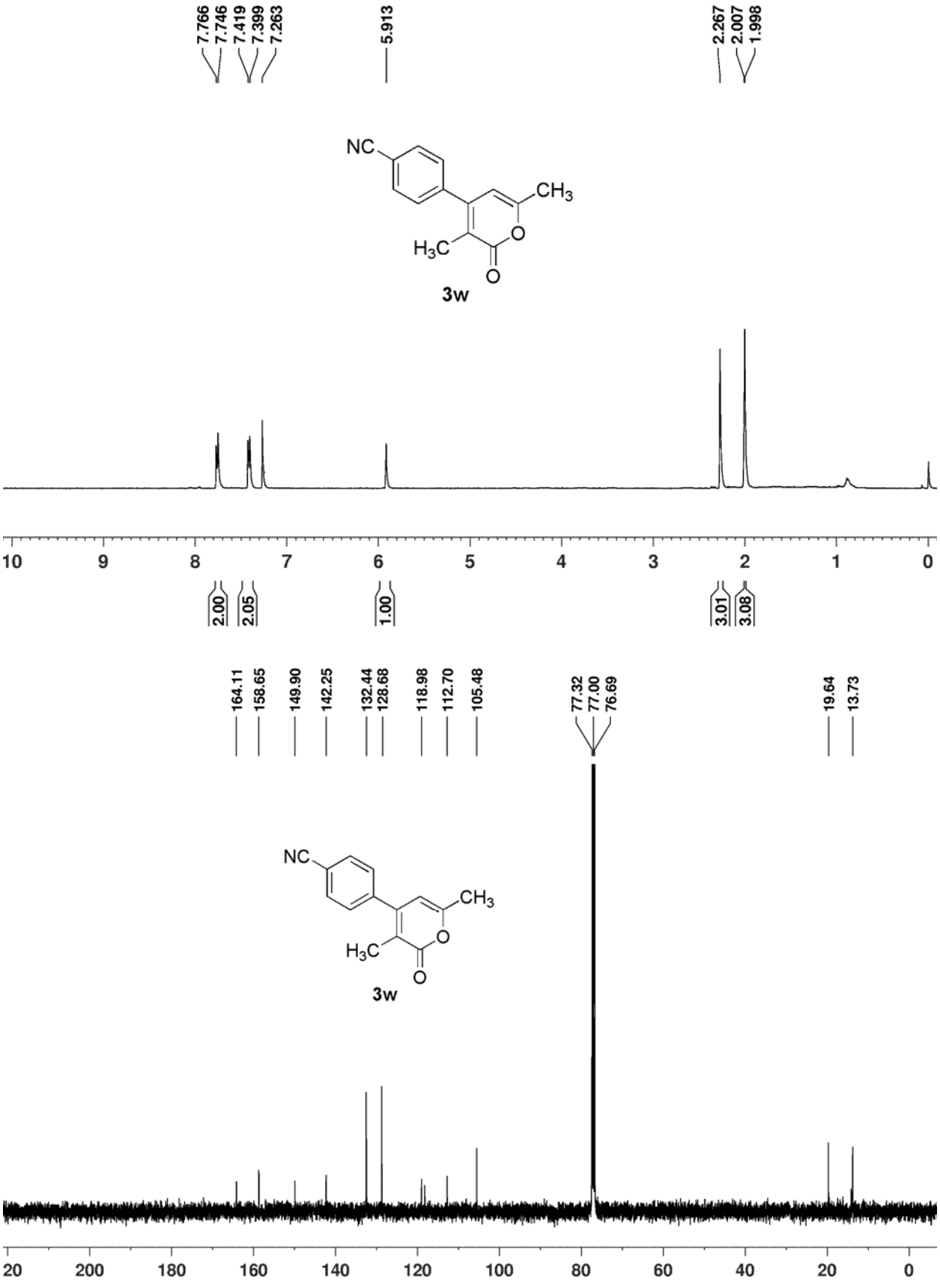

220
200
180
160
140
120
100
80
60
40
20
0
ppm

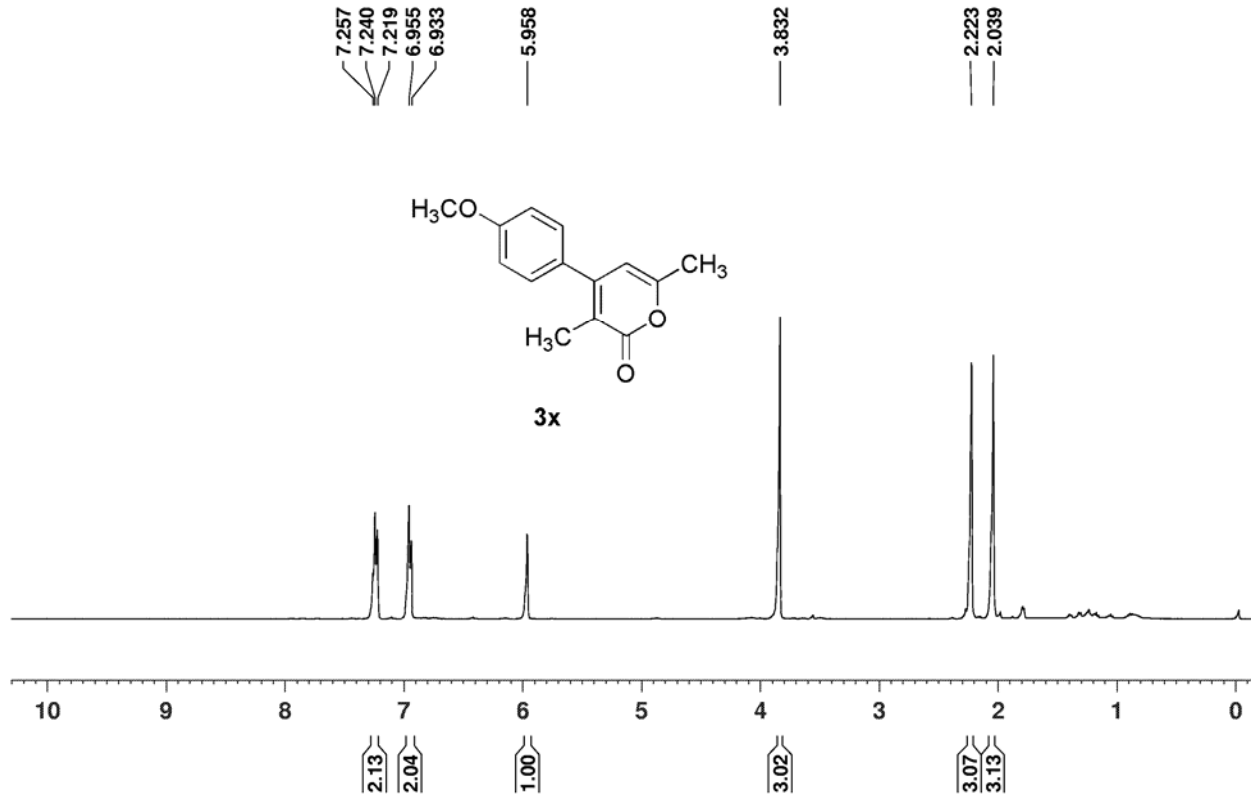


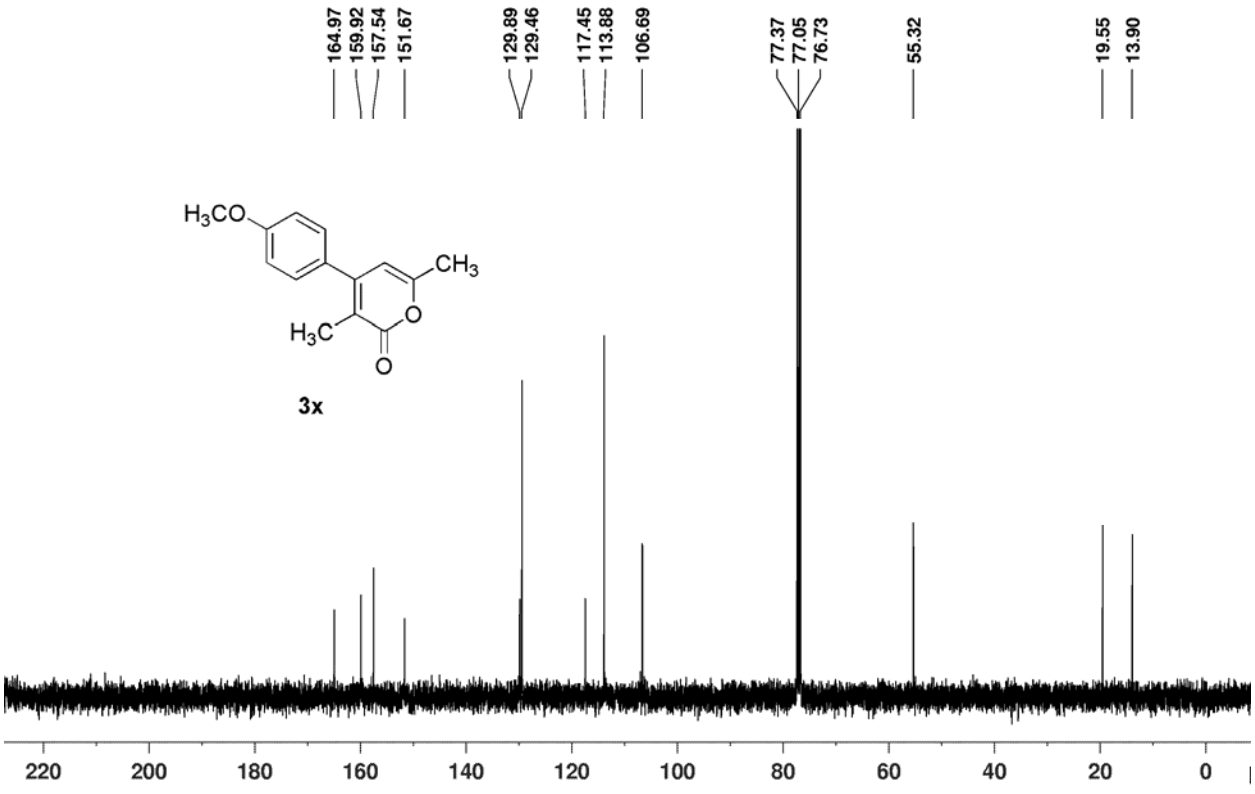


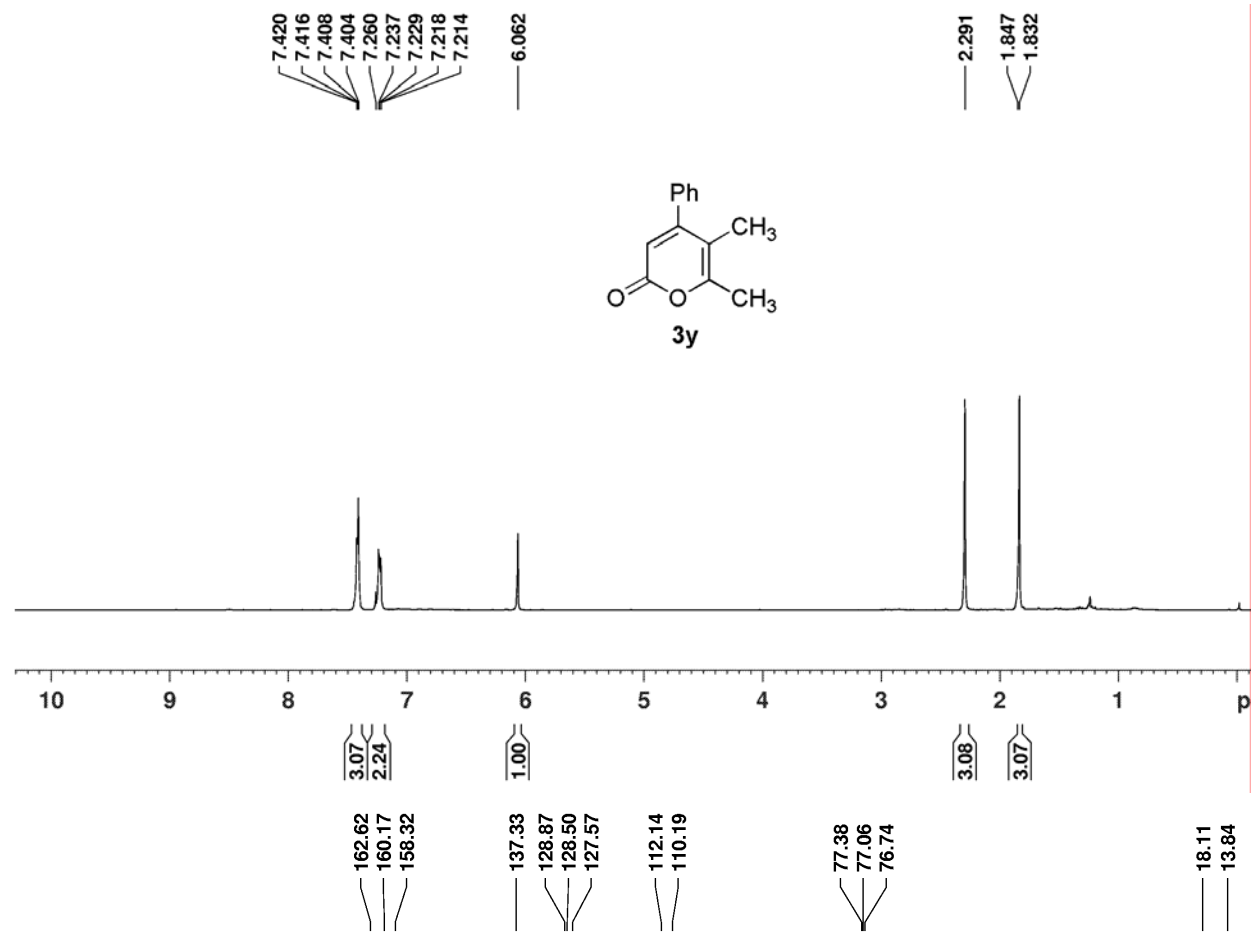


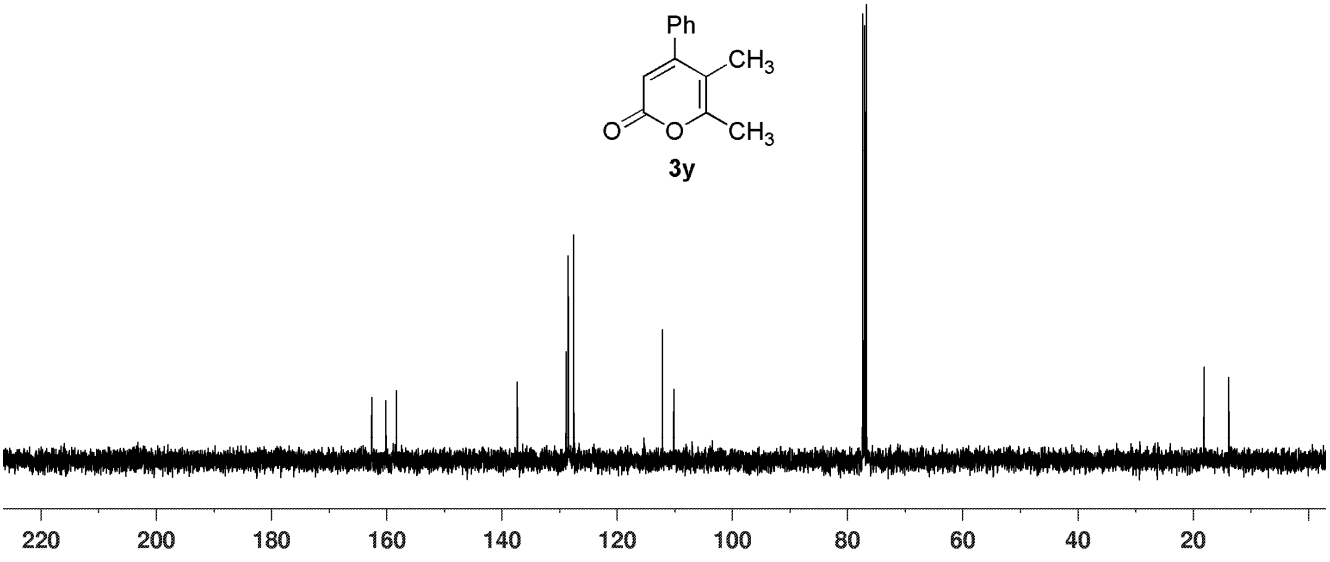


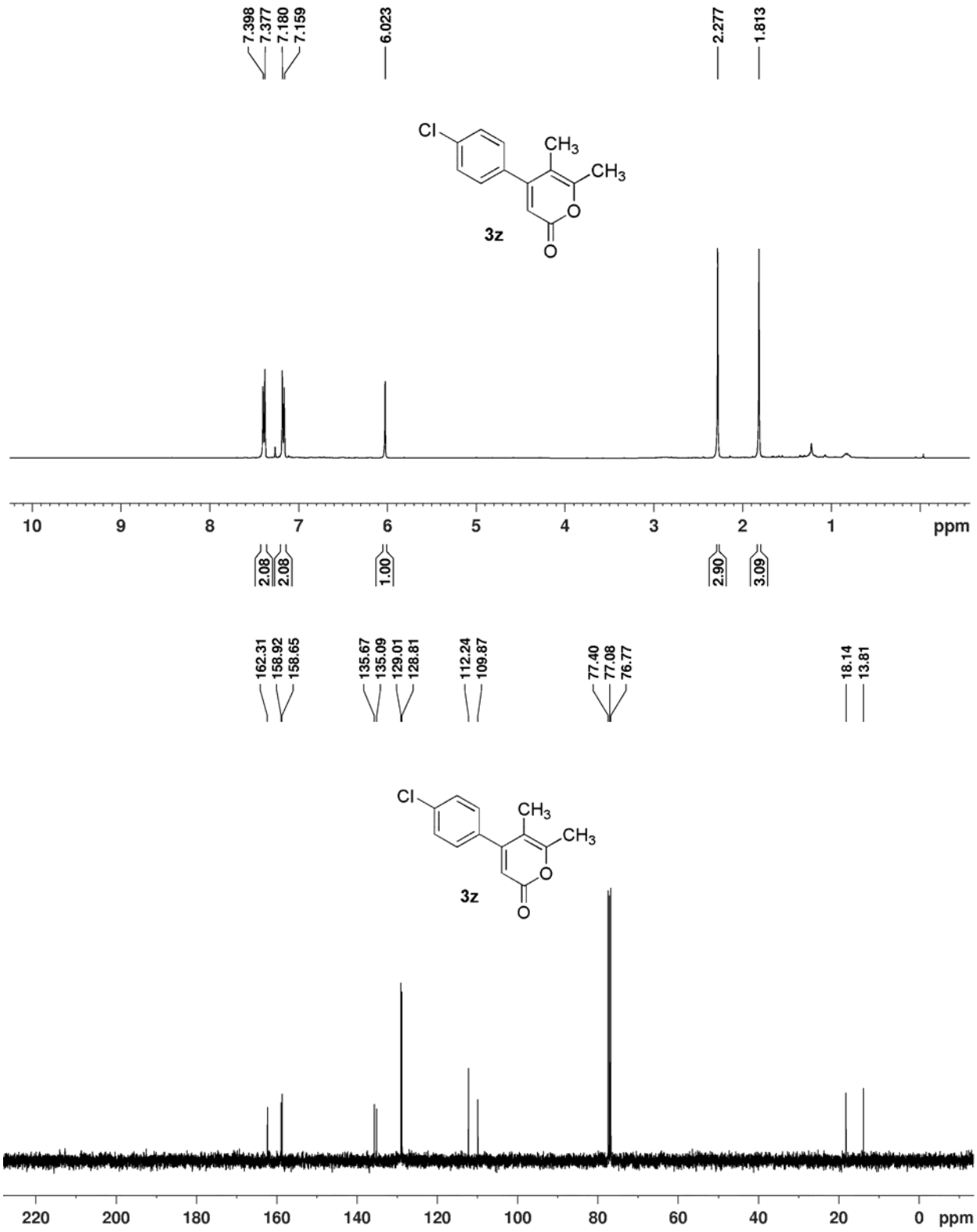


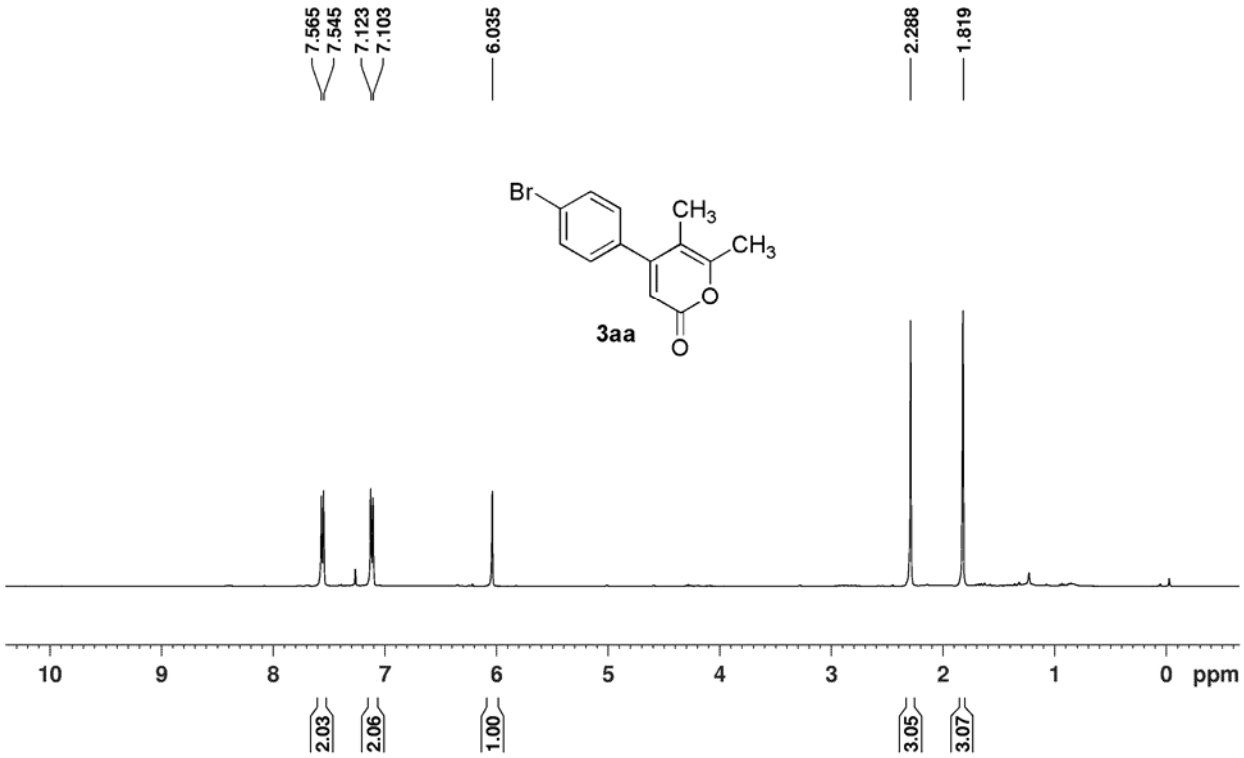


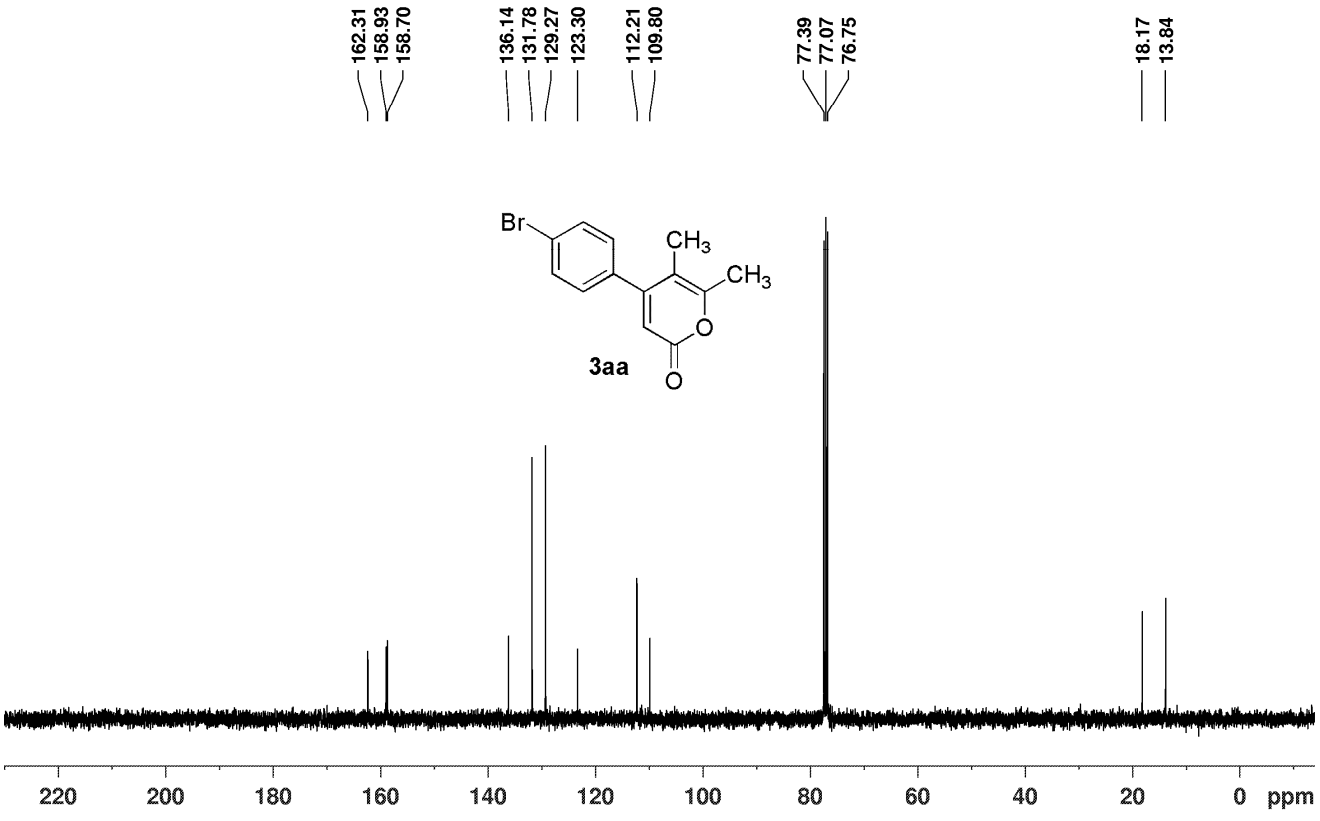


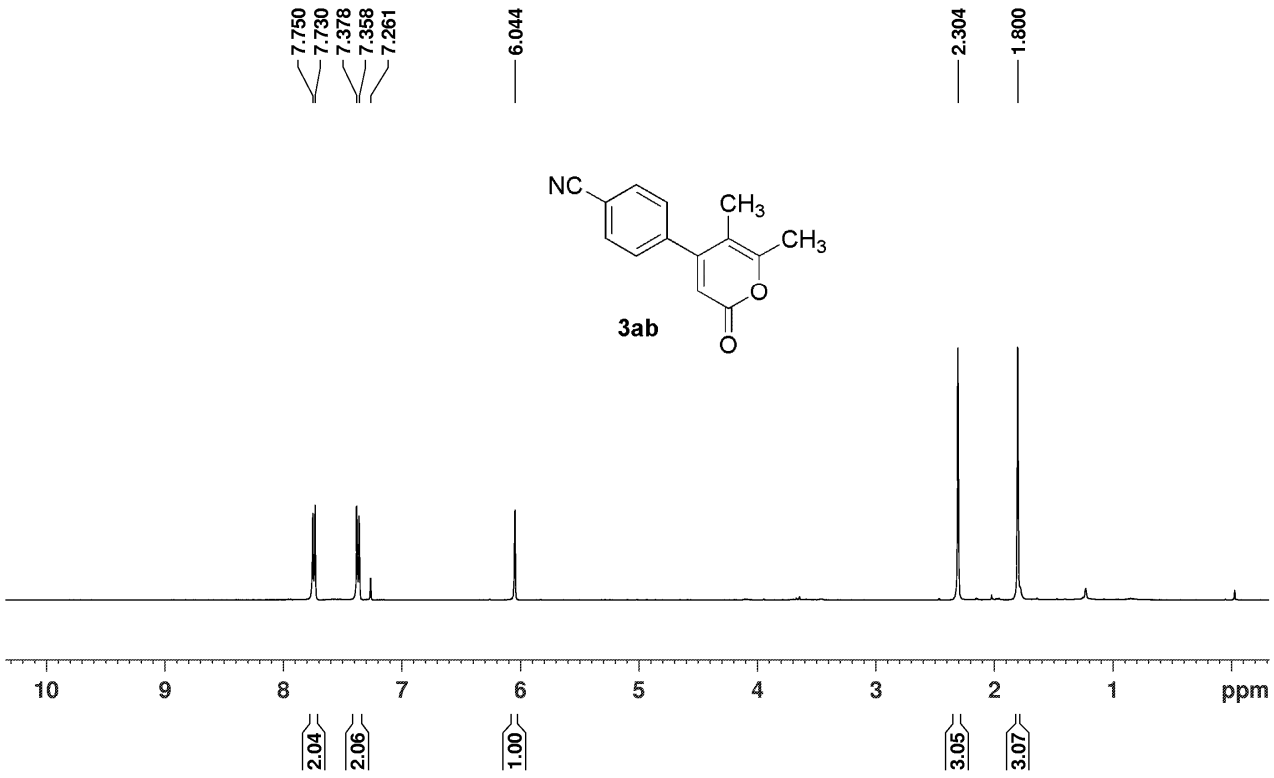


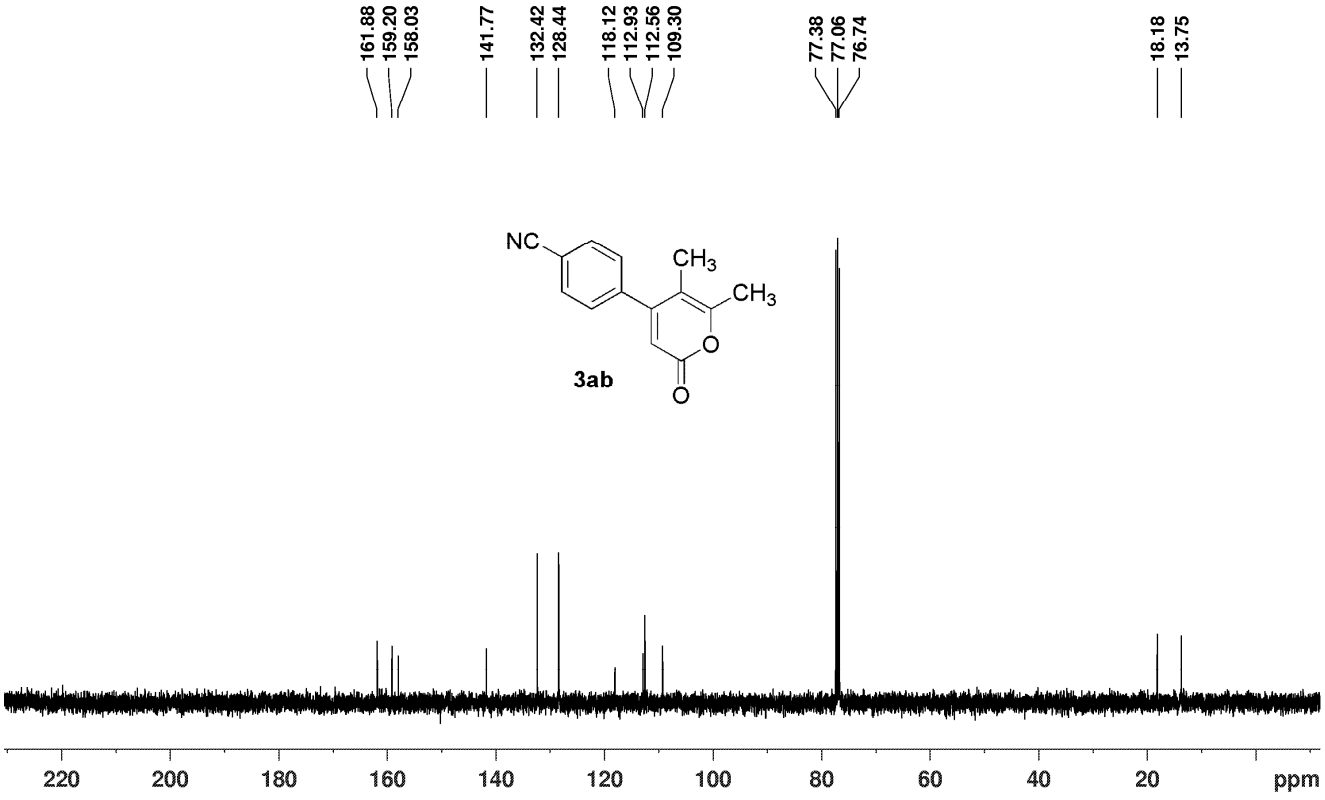


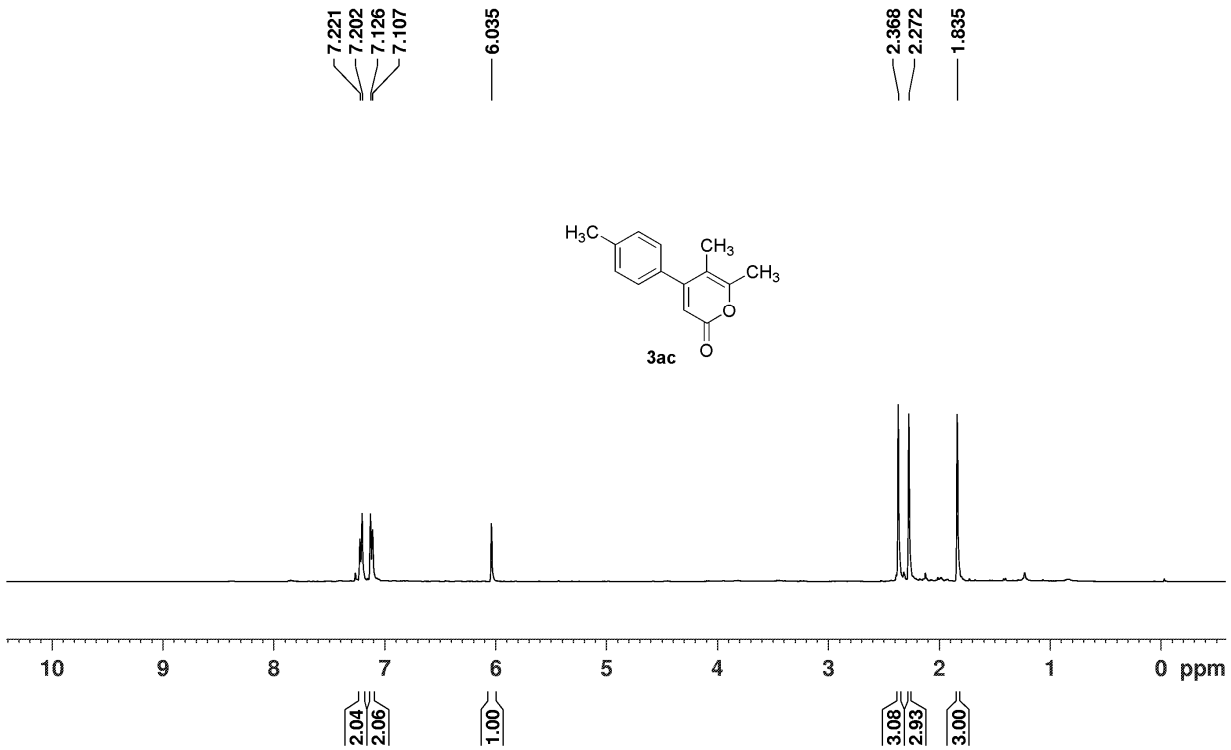


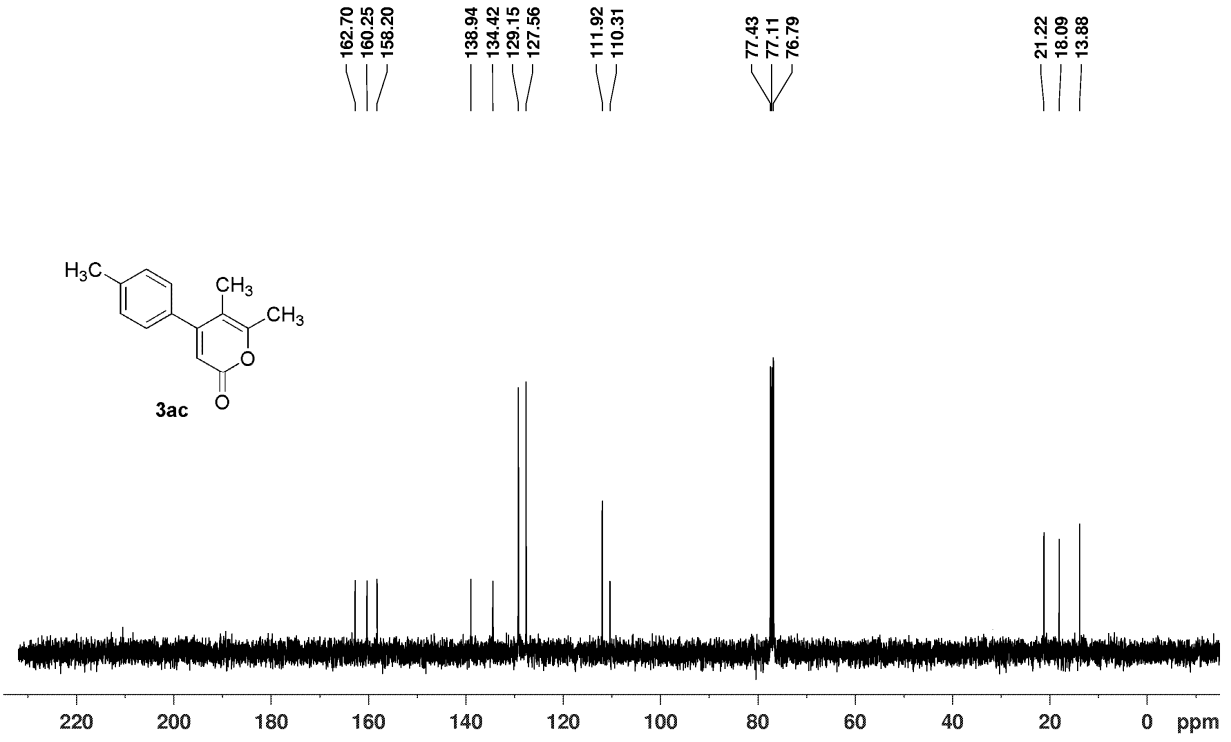


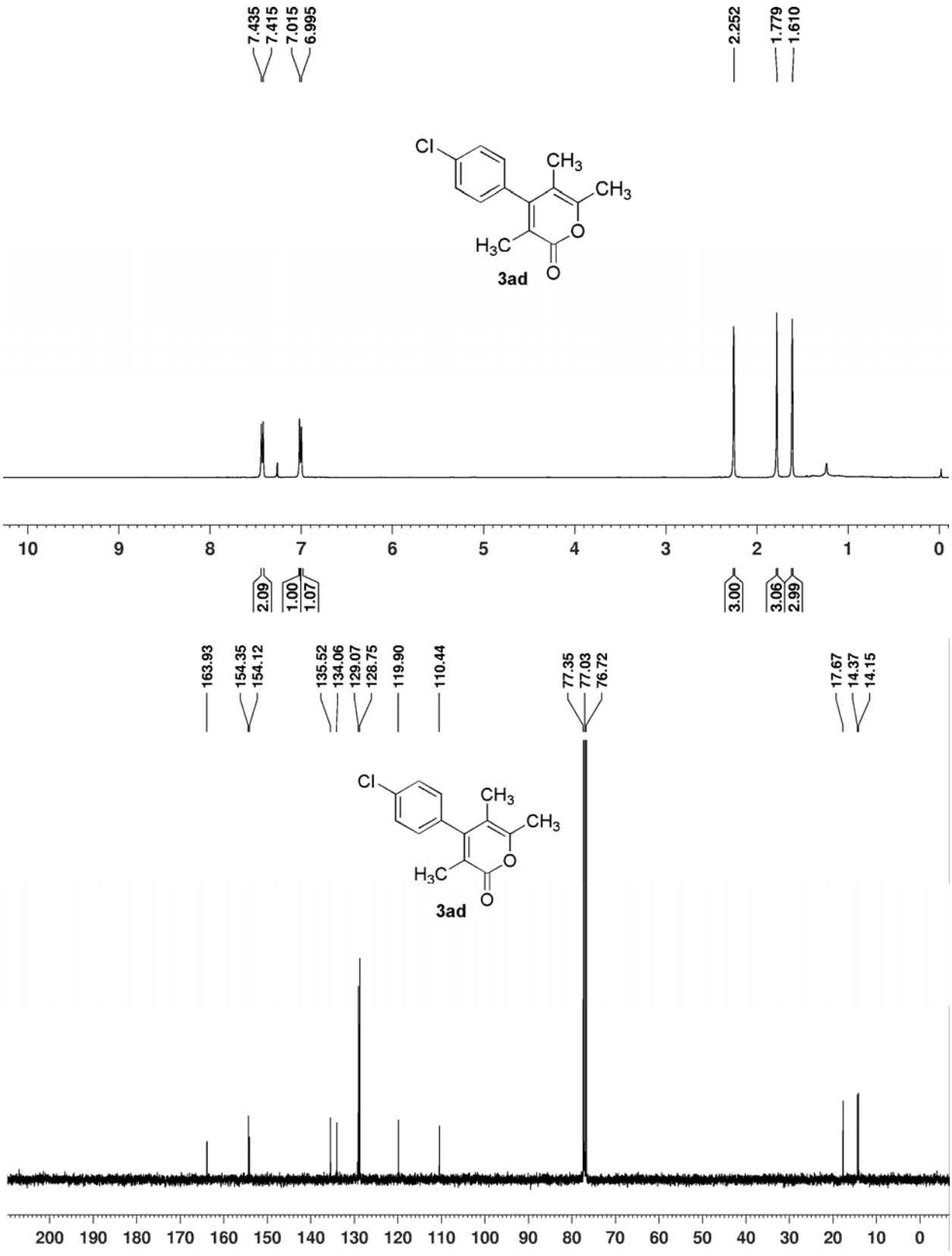


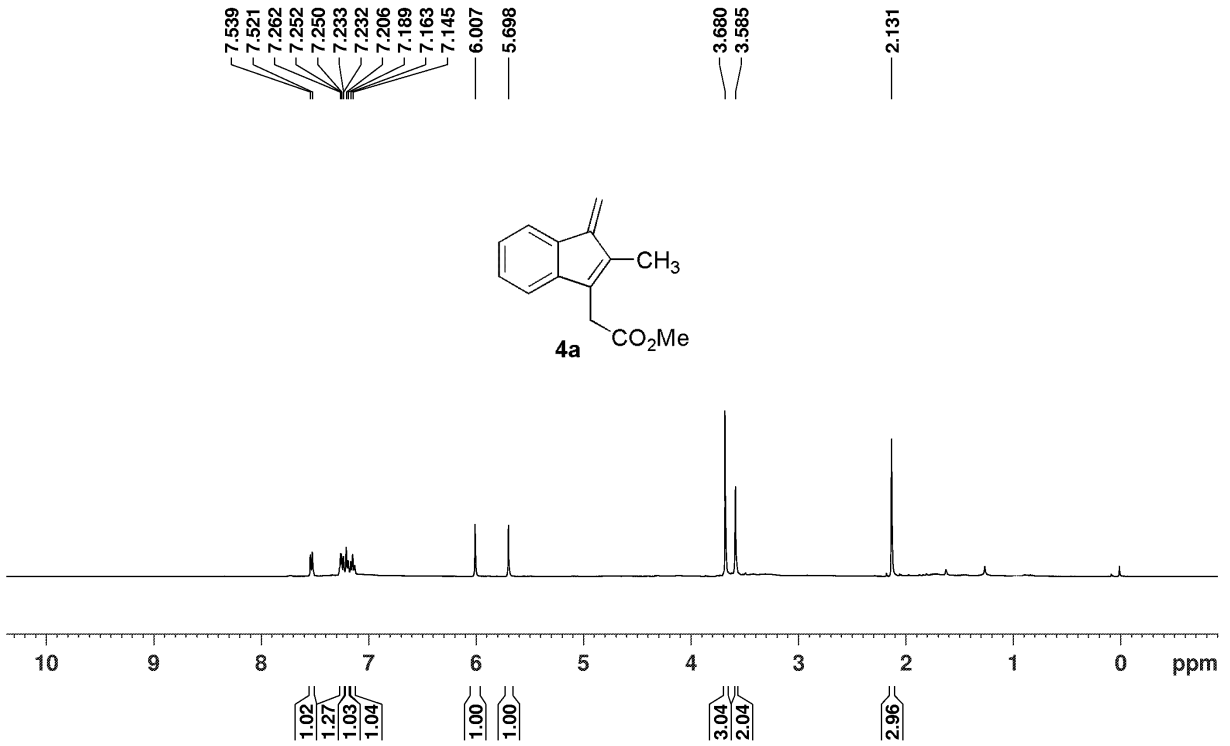


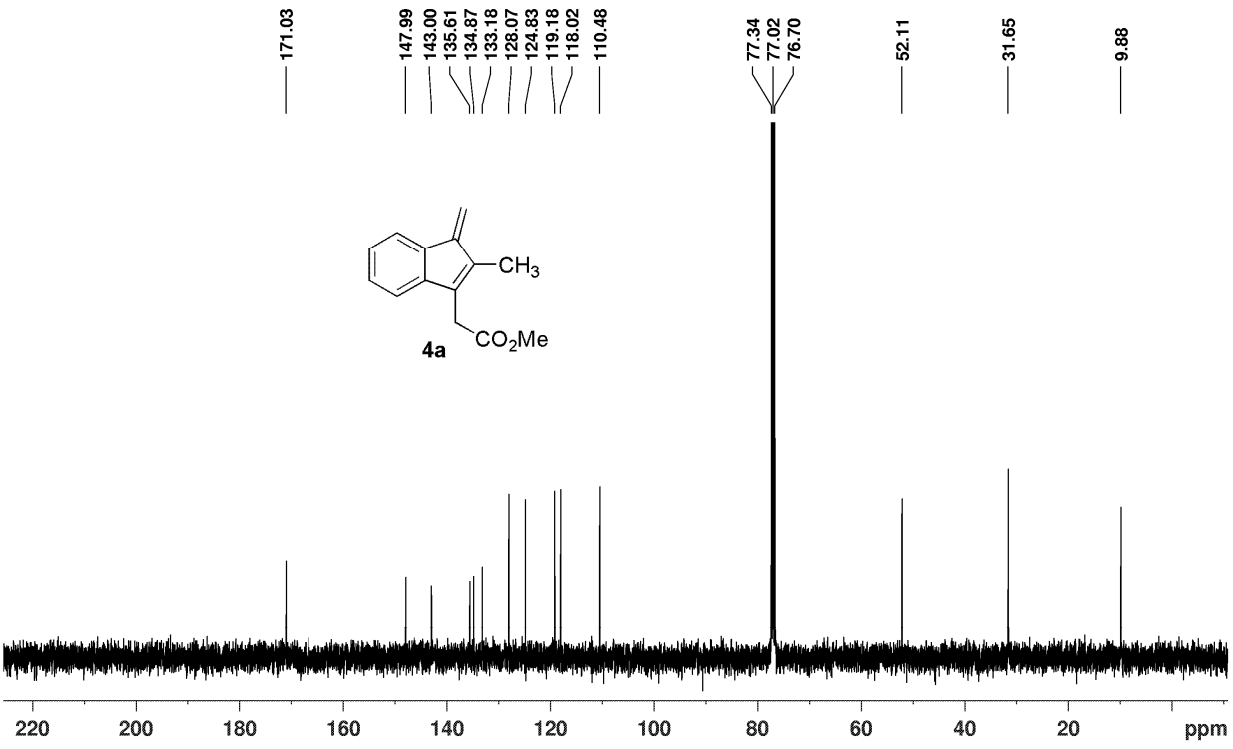


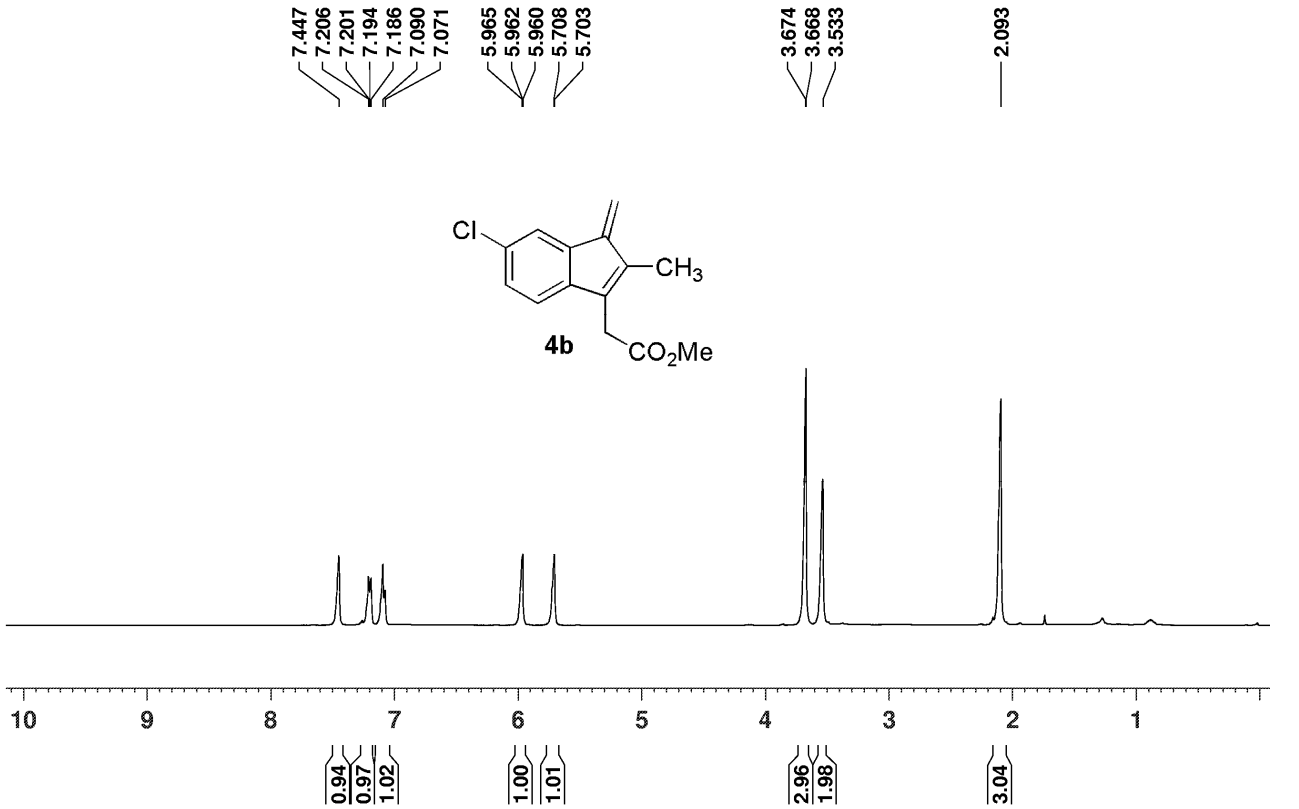


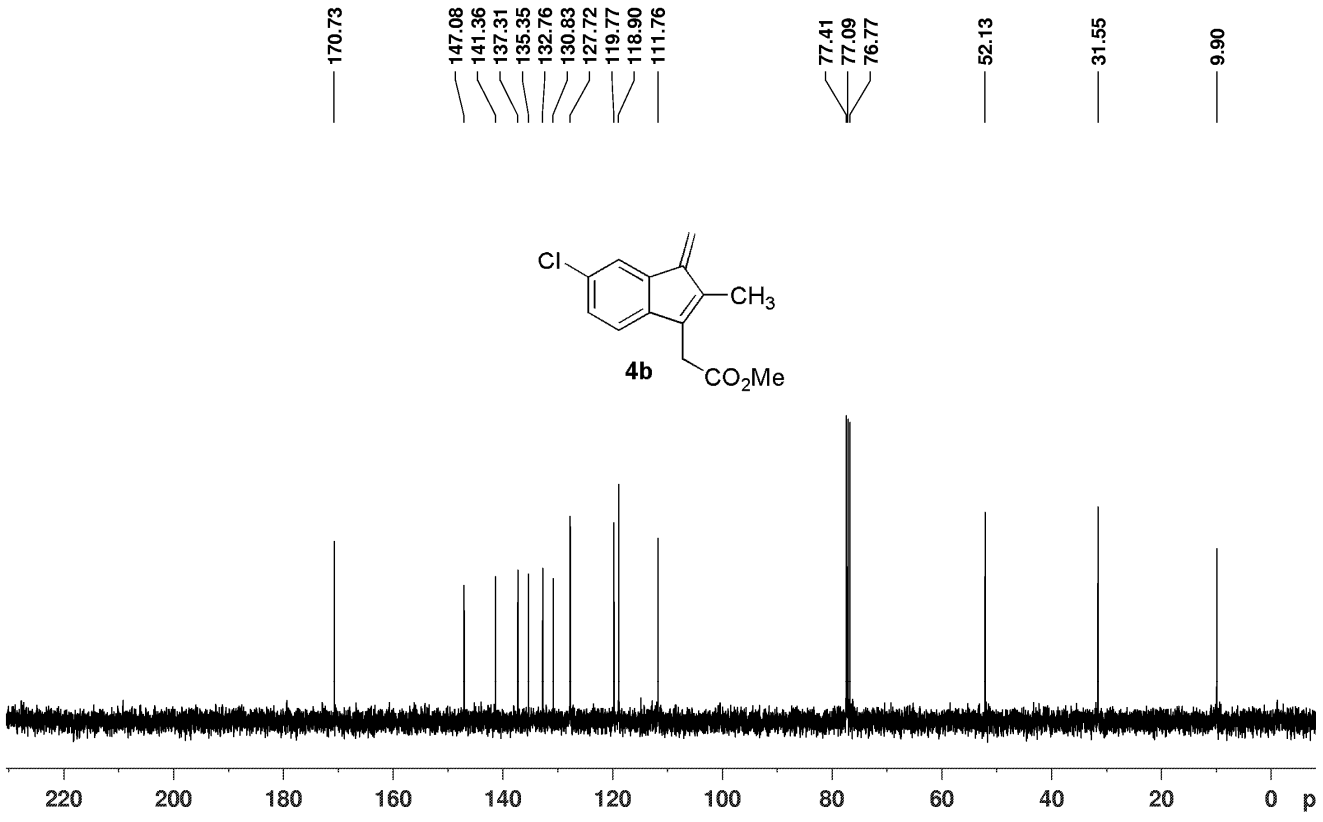


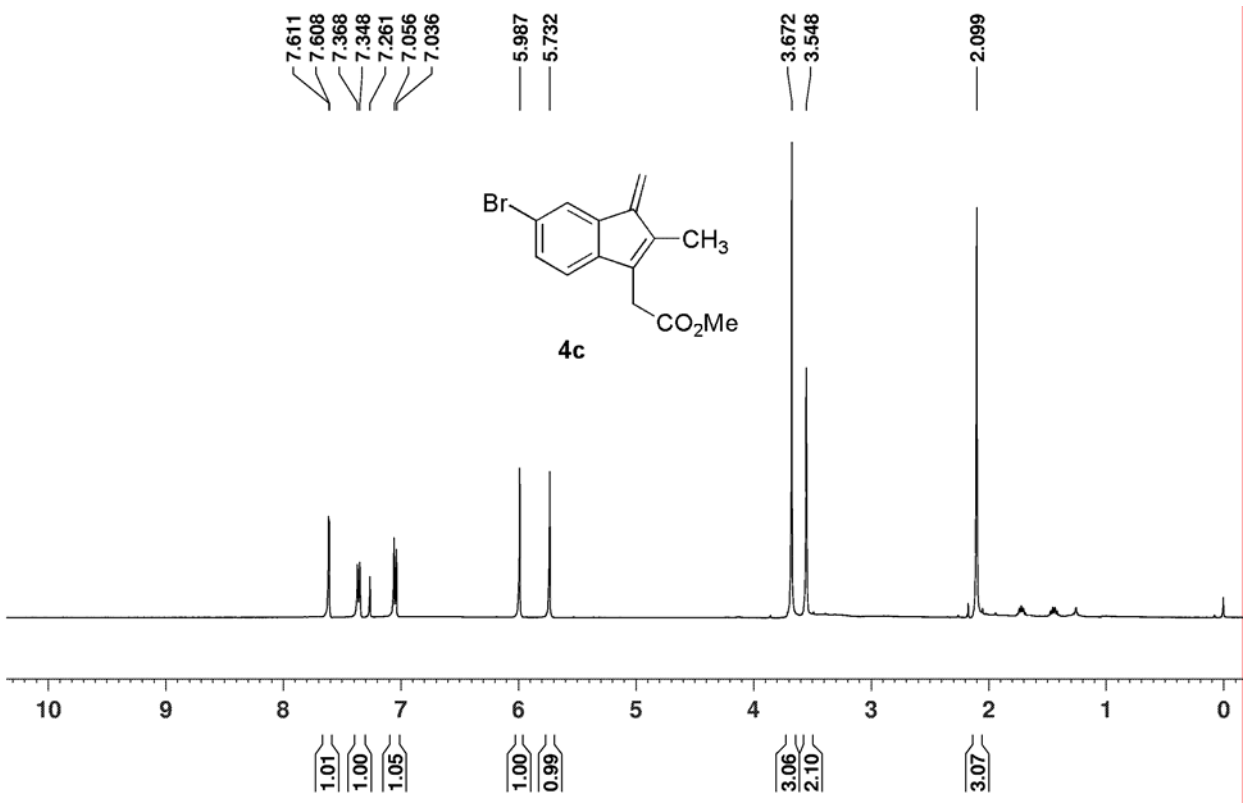


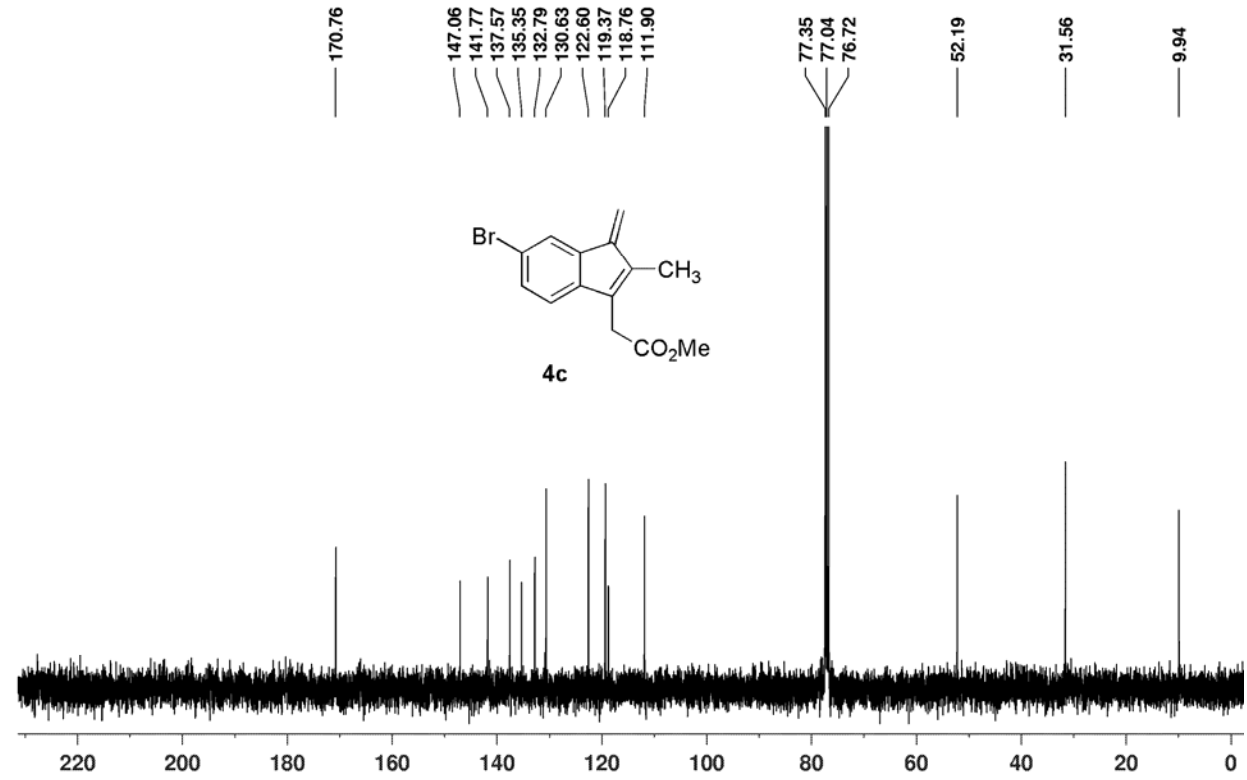

7.539
7.521
7.262
7.252
7.250
7.233
7.232
7.206
7.189
7.163
7.145
6.007
5.698
3.680
3.585
2.131
CH3
CO2Me
4a
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.27
1.03
1.04
1.00
1.00
3.04
2.04
2.96

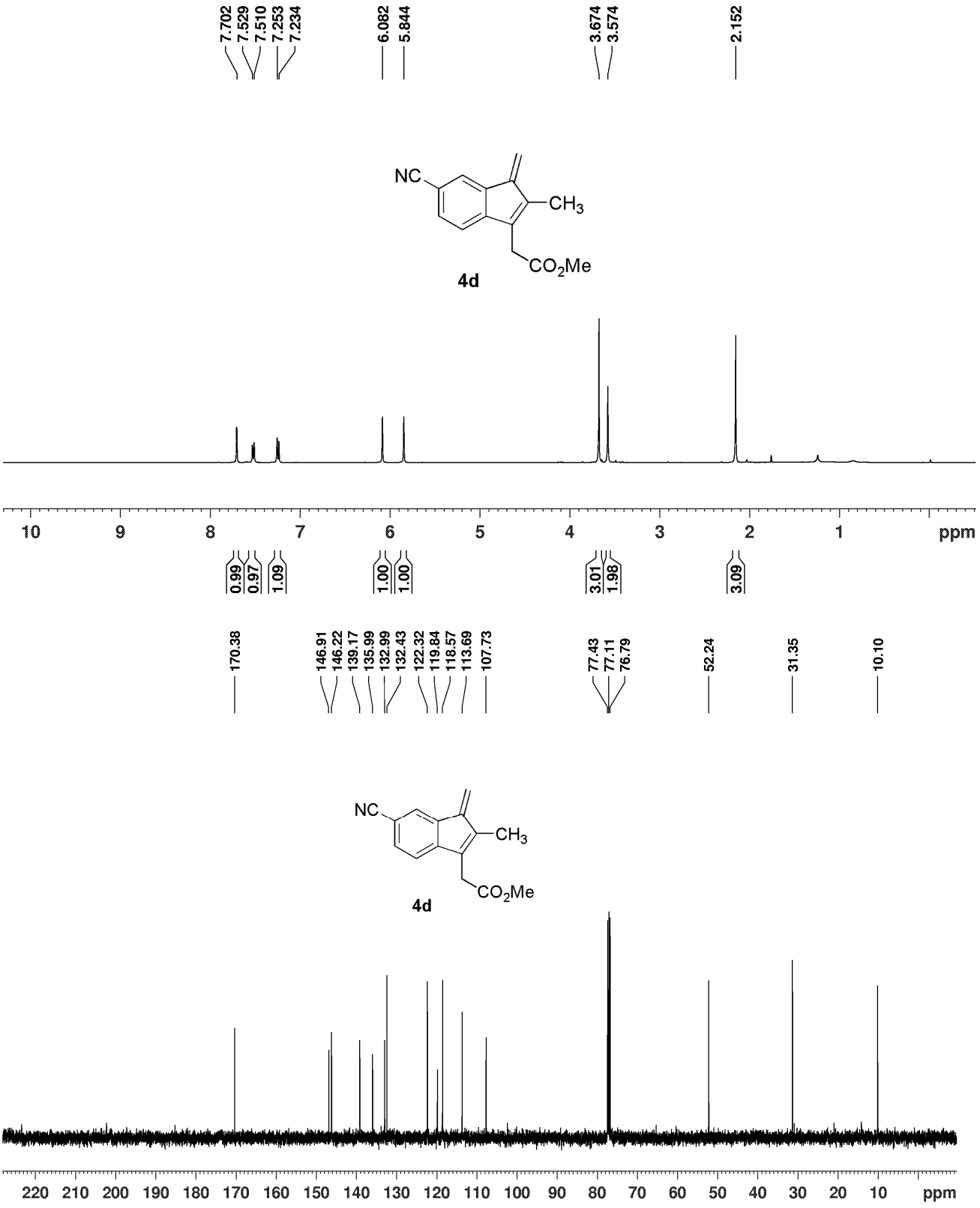

171.03
147.99
143.00
135.61
134.87
133.18
128.07
124.83
119.18
118.02
110.48
77.34
77.02
76.70
52.11
31.65
9.88
CH3
CO2Me
4a
220
200
180
160
140
120
100
80
60
40
20
ppm

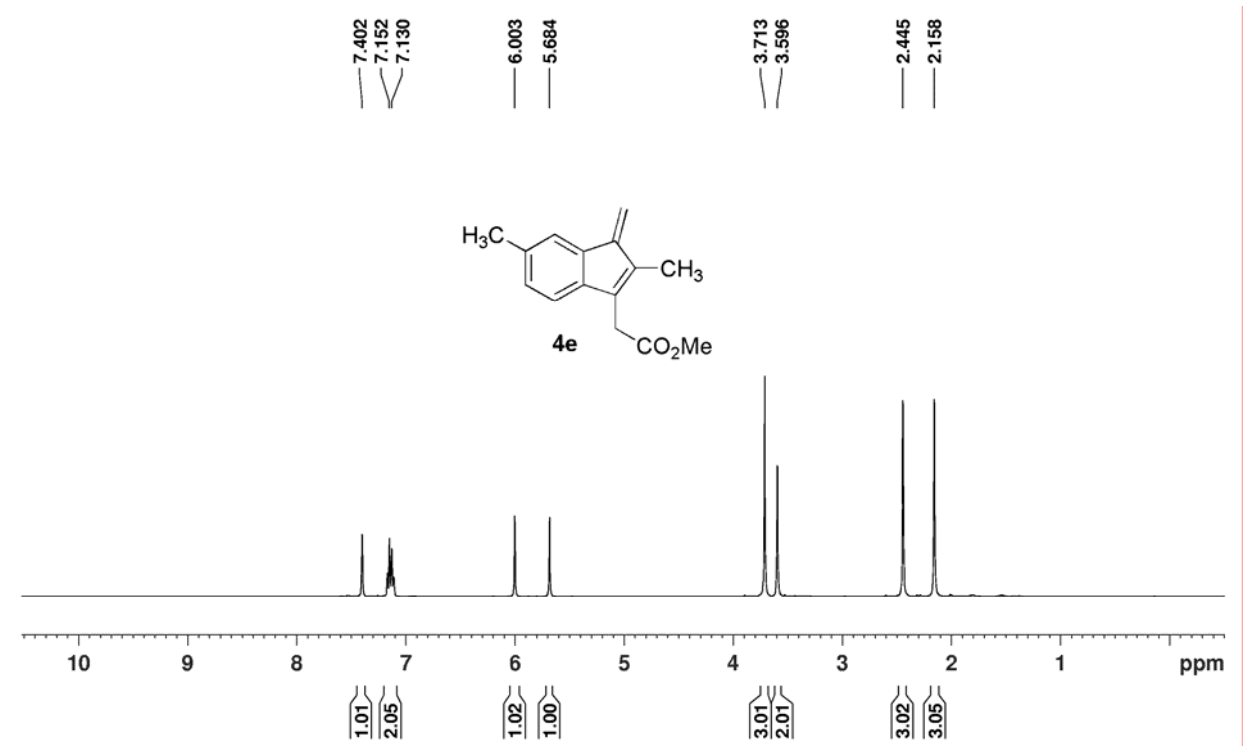


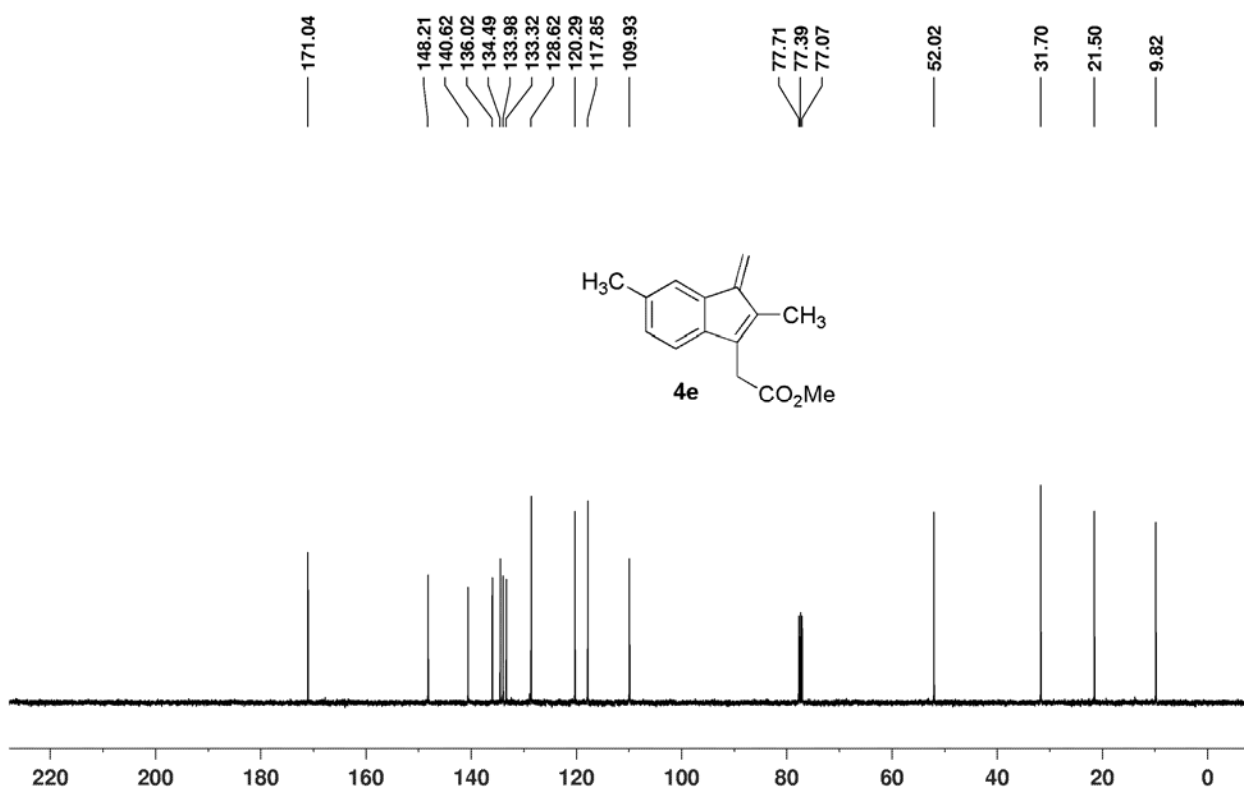


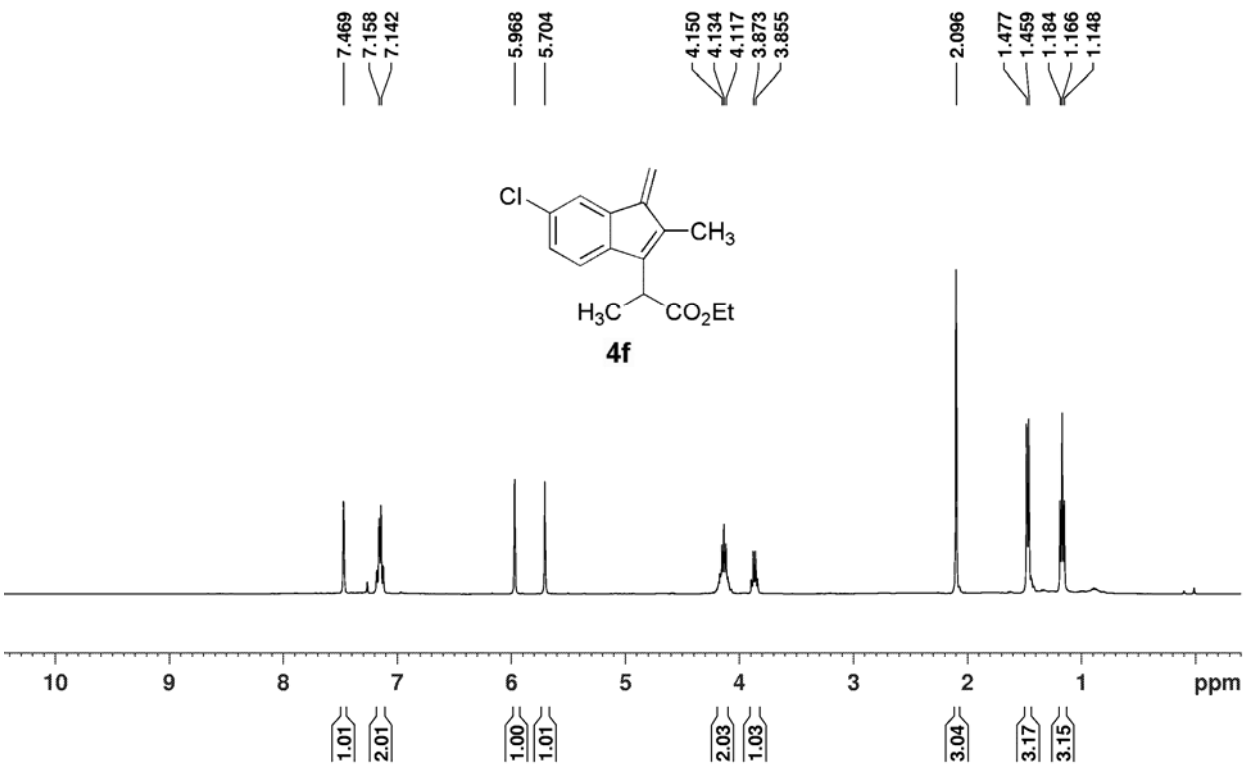


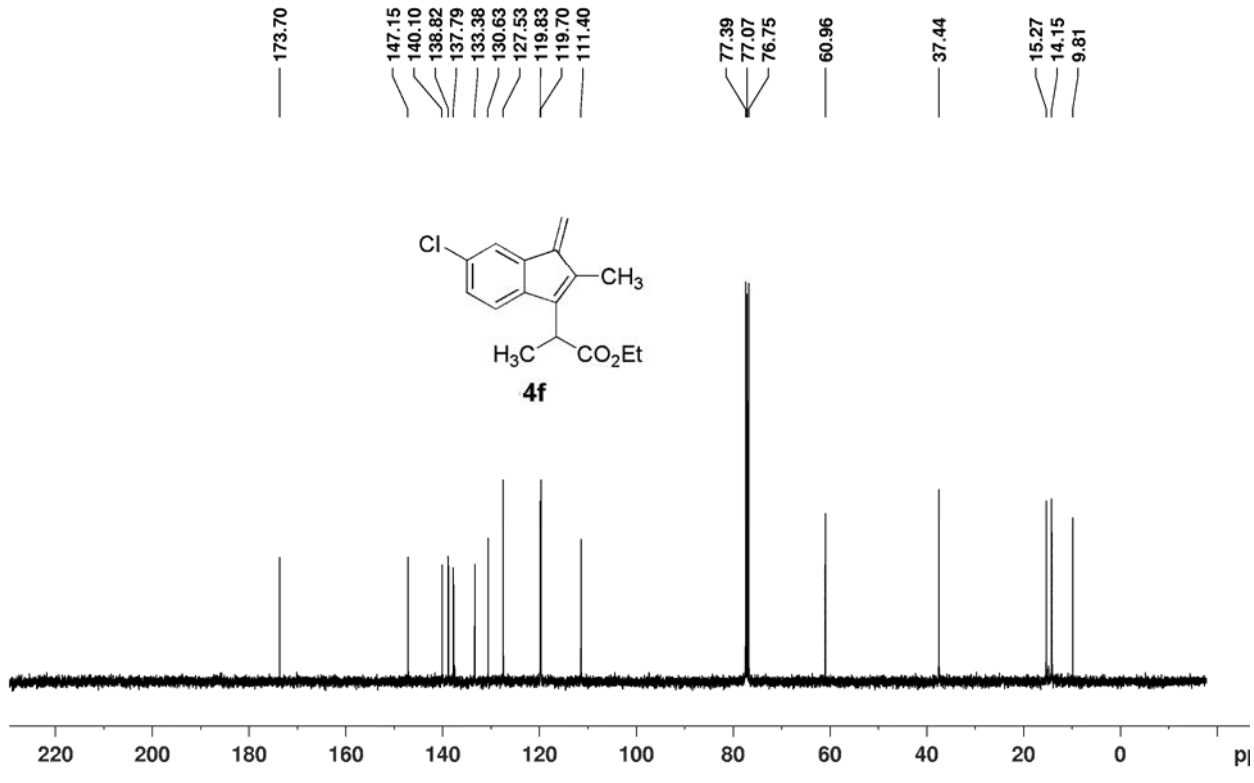




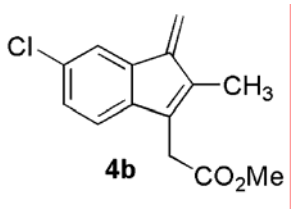


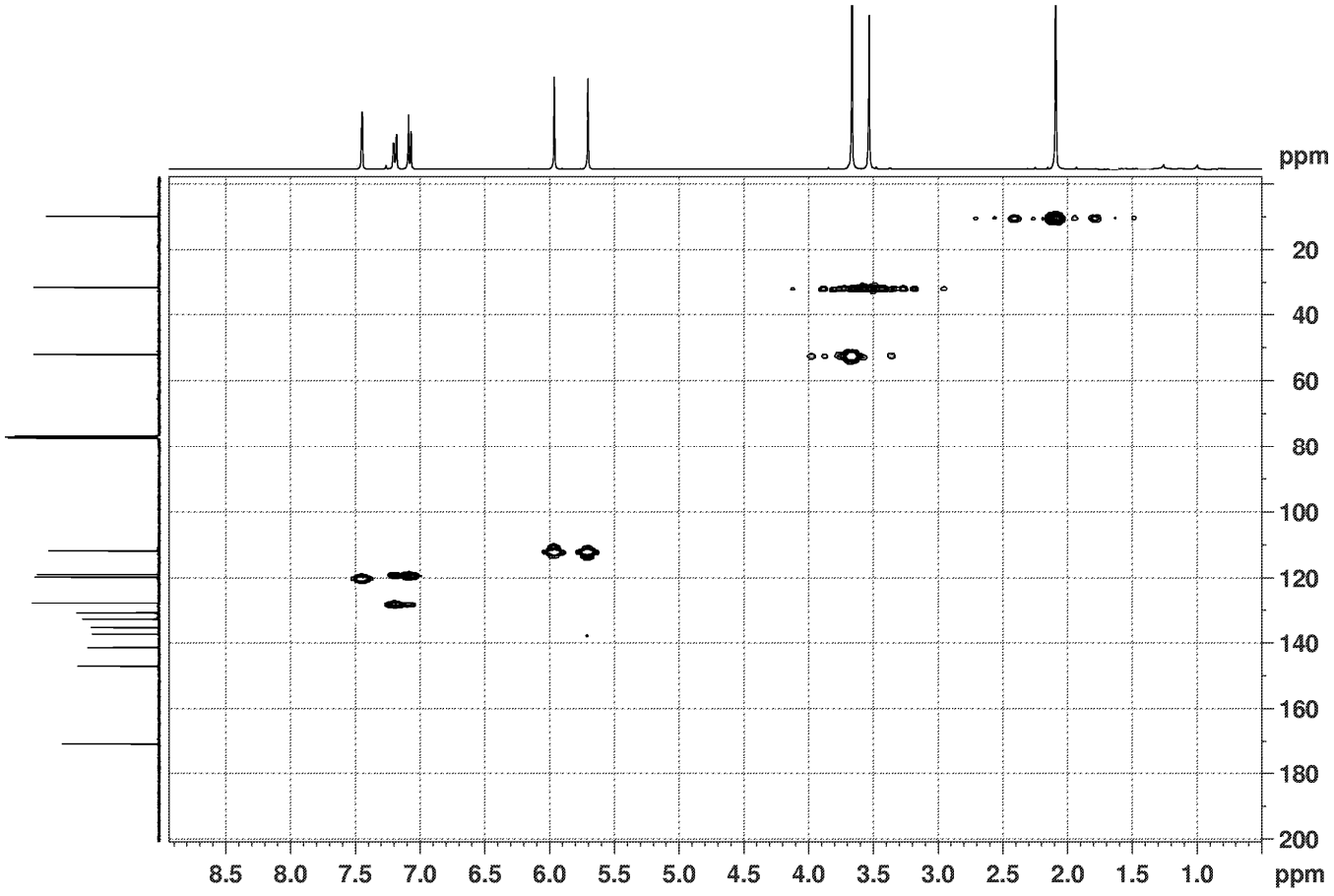






IV. Copy of HMQC spectrum of 4b





V. References

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

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

(3) N. A. Petasis and K. A. Teets, *J. Am. Chem. Soc.*, 1992, **114**, 10328.

(4) I. J. S. Fairlamb, L. R. Marrison, J. M. Dickinson, F.-J. Lu and J. P. Schmidt, *Bioorg. Med. Chem*., 2004, **12**, 4285.

(5) T. Luo, M. Dai, S.-L. Zheng and S. L. Schreiber, *Org. Lett*., 2011, **13**, 2834.