Supplementary Material (ESI) for Chemical Communications

Supporting Information

PPh_3-Catalyzed Unexpected α-Addition Reaction of 1-(*o*-Hydroxyaryl)-1,3-diketones to Terminal Alkynoates: A Straightforward Synthesis of Multifunctional Vinylesters

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General Remarks

All reactions were conducted in oven-dried glassware with magnetic stirring. Dichloromethane was dried and freshly distilled from calcium hydride under nitrogen atmosphere. Chromatographic purification was performed on silica gel (100~200 mesh) and analytical thin layer chromatography (TLC) on silica gel 60-F_{254} (Qindao), which was detected by fluorescence. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured with a Bruker AC 300 spectrometer using tetramethylsilane (TMS) as an internal standard. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (*J* are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), m (multiplet), and br (broad singlet). High resolution mass spectra were obtained with a Micromass GCT-TOF mass spectrometer. IR spectra were recorded as thin films or as solids in KBr pellets on a Perkin-Elmer FT210 spectrophotometer. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected.

General Procedure

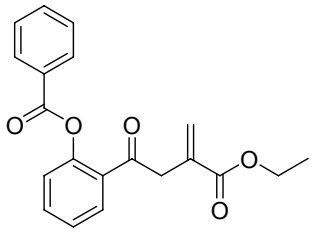
General procedure for the reaction of 1-(2-hydroxyphenyl)-3-aryl-1,3-diones with terminal alkynoates catalyzed by PPh_3 (Tables 2 and 3)

To a solution of 1-(2-hydroxyphenyl)-3-aryl-1,3-diones (0.3 mmol) and terminal alkynoates (0.33 mmol) in dry CH_2Cl_2 (2 mL) was added PPh_3 (24 mg, 0.09 mmol). The mixture was stirred at room temperature for 12 h. Then the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (10:1 petroleum ether/EtOAc) to give the desired product. (The **5b** and **5c** were purified by column chromatography on silica gel (2:1-5:1 dichloromethane/petroleum) to give the desired products.)

General procedure for the reaction of 1-(2-hydroxyphenyl)-3-alkyl-1,3-diones with terminal alkynoates catalyzed by PPh_3 (Table 4).

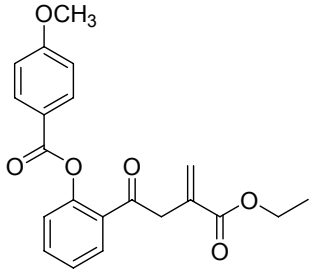
To a solution of 1-(2-hydroxyphenyl)-3-alkyl-1,3-diones (0.3 mmol) with terminal alkynoates (0.33 mmol) in dry CH_2Cl_2 (2 mL) was added PPh_3 (24 mg, 0.09 mmol) at 0 □. The resulting mixture was stirred at 0 □ for 24 h. Then the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (10:1 petroleum ether/EtOAc) to give the desired product.

Benzoic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-phenyl ester (3a)



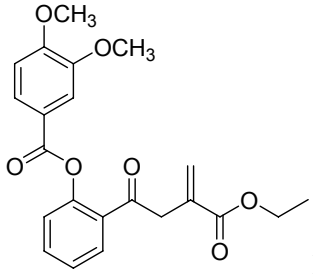
White solid. Mp: 79-81℃. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.20-8.17 (m, 2H), 7.89-7.86 (m, 1H), 7.63-7.47 (m, 4H), 7.39-7.34 (m, 1H), 7.26-7.23 (m, 1H), 6.32 (s, 1H), 5.60 (d, *J* = 0.9 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 196.9, 166.2, 165.1, 149.1, 134.6, 133.8, 133.2, 131.4, 130.4, 130.0, 129.3, 128.7, 126.2, 123.9, 61.0, 44.7, 14.1. IR (KBr) *v* 1735, 1719, 1699, 1638 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{18}O_5$ (M^+): 338.1154; Found: 338.1152.

4-Methoxy-benzoic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-phenyl ester (3b)



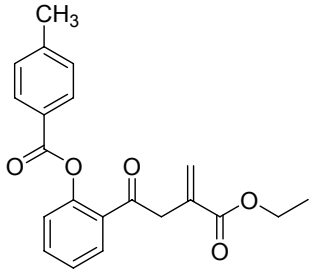
White solid. Mp: 78-79℃. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.16 (d, *J* = 8.7 Hz, 2H), 7.87-7.85 (m, 1H), 7.58-7.53 (m, 1H), 7.37-7.32 (m, 1H), 7.26-7.22 (m, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.32 (s, 1H), 5.59 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 2H), 3.87 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 197.0, 166.2, 164.7, 164.2, 149.3, 134.6, 133.1, 132.5, 131.5, 130.0, 128.6, 126.0, 123.9, 121.5, 114.0, 61.0, 55.6, 44.9, 14.1. IR (KBr) *v* 1732, 1716, 1699, 1637 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{20}O_6$ (M^+): 368.1260; Found: 368.1257.

3,4-Dimethoxy-benzoic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-phenyl ester (3c)



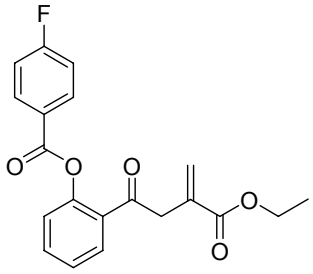
Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 7.88-7.85 (m, 2H), 7.67 (s, 1H), 7.59-7.54 (m, 1H), 7.38-7.33 (m, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.32 (s, 1H), 5.60 (s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 3.90 (s, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 196.9, 166.1, 164.6, 153.8, 149.2, 148.8, 134.5, 133.1, 131.4, 129.9, 128.5, 126.0, 124.6, 123.8, 121.5, 112.5, 110.5, 60.9, 56.1, 56.0, 44.8, 14.0. IR (neat) *v* 1725, 1691, 1638 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{22}O_7$ (M^+): 398.1366; Found: 398.1358.

4-Methyl-benzoic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-phenyl ester (3d)



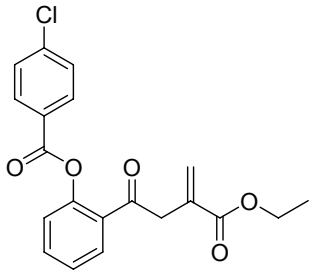
White solid. Mp: 106-108℃. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.09 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.59-7.53 (m, 1H), 7.37-7.22 (m, 4H), 6.31 (s, 1H), 5.58 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 2H), 2.43 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 197.0, 166.2, 165.1, 149.2, 144.8, 134.6, 133.2, 131.5, 130.4, 130.0, 129.5, 128.7, 126.5, 126.1, 123.9, 61.0, 44.9, 21.8, 14.1. IR (KBr) *v* 1734, 1715, 1686, 1637 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{20}O_5$ (M^+): 352.1311; Found: 352.1317.

4-Fluoro-benzoic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-phenyl ester (3e)



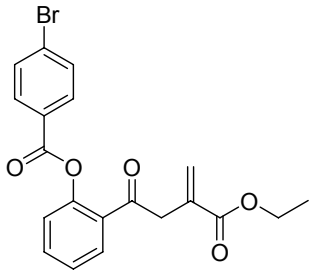
White solid. Mp: 84-86℃. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.23-8.18 (m, 2H), 7.90-7.87 (m, 1H), 7.60-7.55 (m, 1H), 7.40-7.35 (m, 1H), 7.26-7.14 (m, 3H), 6.33 (s, 1H), 5.62 (d, *J* = 0.9 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 196.8, 168.0, 166.3, 164.7, 149.1, 134.6, 133.3, 133.1, 131.2, 130.1, 128.8, 126.3, 125.7, 123.9, 116.1, 61.1, 44.6, 14.1. IR (KBr) *v* 1736, 1716, 1689, 1638 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{17}O_5F(M^+)$: 356.1060; Found: 356.1064.

4-Chloro-benzoic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-phenyl ester (3f)



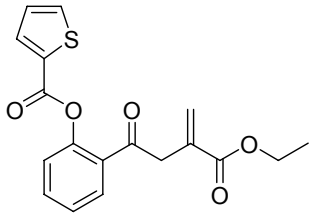
White solid. Mp: 110-112℃. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.13 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.60-7.55 (m, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.40-7.35 (m, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 6.33 (s, 1H), 5.61 (s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 2H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 196.8, 166.2, 164.4, 149.0, 140.4, 134.5, 133.4, 131.8, 131.1, 130.1, 129.1, 128.8, 127.8, 126.4, 123.9, 61.1, 44.5, 14.1. IR (KBr) *v* 1736, 1714, 1686, 1635 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{17}O_5{}^{35}Cl$ (M^+): 372.0765; Found: 372.0769.

4-Bromo-benzoic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-phenyl ester (3g)



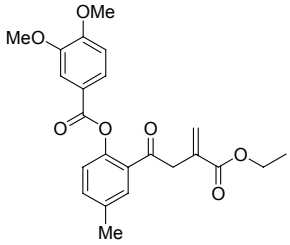
White solid. Mp: 124-126℃. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.05 (d, J = 8.4 Hz, 2H), 7.90-7.88 (m, 1H), 7.66-7.56 (m, 3H), 7.40-7.35 (m, 1H), 7.25 (d, J = 8.1 Hz, 1H), 6.33 (s, 1H), 5.62 (s, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.88 (s, 2H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 196.7, 166.2, 164.5, 149.0, 134.5, 133.4, 132.1, 131.9, 131.1, 130.1, 129.1, 128.8, 128.3, 126.4, 123.9, 61.1, 44.5, 14.1. IR (KBr) v 1736, 1711, 1686, 1636 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{17}O_5{}^{79}Br$ (M^+): 416.0259; Found: 416.0256.

Thiophene-2-carboxylic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-phenyl ester (3h)



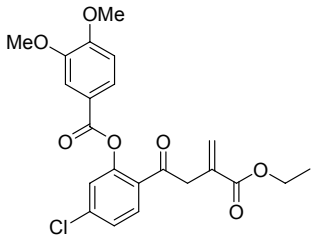
White solid. Mp: 87-90℃. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.00 (d, J = 3.3 Hz, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 4.8 Hz, 1H), 7.59-7.54 (m, 1H), 7.39-7.34 (m, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.19-7.17 (m, 1H), 6.35 (s, 1H), 5.63 (s, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.92 (s, 2H), 1.25 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 196.9, 166.3, 160.3, 148.7, 135.3, 134.6, 134.0, 133.2, 132.5, 131.4, 130.1, 128.8, 128.3, 126.4, 123.8, 61.1, 45.0, 14.2. IR (KBr) v 1719, 1714, 1691, 1636 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{16}O_5S$ (M^+): 344.0718; Found: 344.0720.

3,4-Dimethoxy-benzoic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-4-methyl-phenyl ester (5a)



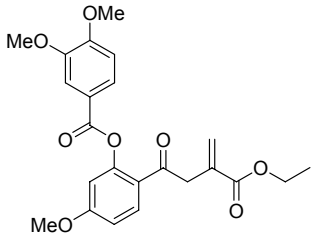
Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 7.84-7.82 (m, 1H), 7.65-7.63 (m, 2H), 7.35 (d, J = 8.1 Hz, 1H), 7.12 (d, J = 8.1 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.29 (s, 1H), 5.57 (s, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.94 (s, 3H), 3.93 (s, 3H), 3.86 (s, 2H), 2.39 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 197.1, 166.2, 164.9, 153.8, 148.9, 147.0, 135.8, 134.7, 133.8, 131.1, 130.3, 128.5, 124.6, 123.6, 121.7, 112.6, 110.5, 60.9, 56.1, 56.1, 44.9, 20.8, 14.1. IR (neat) v 1730, 1694, 1637 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{24}O_7$ (M^+): 412.1522; Found: 412.1516.

3,4-Dimethoxy-benzoic acid 5-chloro-2-(3-ethoxycarbonyl-but-3-enoyl)-phenyl ester (5b)



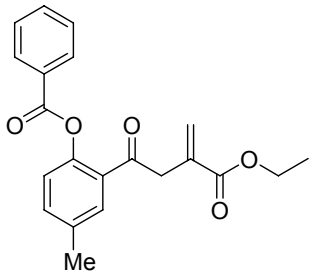
Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 7.87-7.83 (m, 2H), 7.66 (s, 1H), 7.37-7.28 (m, 2H), 6.98 (d, J = 8.7 Hz, 1H), 6.34 (s, 1H), 5.62 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.98 (s, 3H), 3.96 (s, 3H), 3.87 (s, 2H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 195.9, 166.2, 164.4, 154.1, 149.9, 149.0, 138.8, 134.4, 131.1, 129.9, 128.8, 126.4, 124.9, 124.4, 121.1, 112.6, 110.6, 61.1, 56.2, 56.1, 44.9, 14.1. IR (neat) v 1733, 1701, 1637 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{21}O_7{}^{35}Cl$ (M^+): 432.0976; Found: 432.0981.

3,4-Dimethoxy-benzoic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-5-methoxy-phenyl ester (5c)



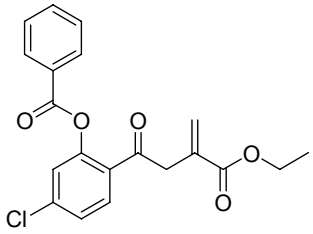
Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 7.93-7.85 (m, 2H), 7.67 (d, J = 1.8 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 6.89-7.85 (m, 1H), 6.74 (d, J = 2.4 Hz, 1H), 6.30 (s, 1H), 5.58 (s, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.97 (s, 3H), 3.95 (s, 3H), 3.86 (s, 3H), 3.86 (s, 2H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 195.0, 166.4, 164.7, 163.7, 153.9, 151.7, 149.0, 135.0, 132.2, 128.4, 124.8, 123.6, 121.7 112.7, 112.1, 110.6, 109.3, 61.0, 56.2, 56.2, 55.8, 44.5, 14.1. IR (neat) v 1730, 1684, 1636 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{24}O_8$ (M^+): 428.1471; Found: 428.1464..

Benzoic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-4-methyl-phenyl ester (5d)



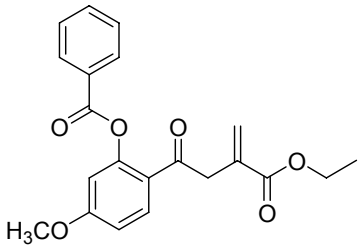
Coloress oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.20 (d, J = 7.5 Hz, 2H), 7.66-7.60 (m, 2H), 7.52-7.47 (m, 2H), 7.38 (d, J = 8.4 Hz, 1H), 7.13 (d, J = 8.1 Hz, 1H), 6.31 (s, 1H), 5.58 (s, 1H), 4.16 (q, J = 7.2 Hz, 2H), 3.88 (s, 2H), 2.41 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 197.1, 166.3, 165.3, 147.0, 136.0, 134.7, 133.9, 133.8, 131.1, 130.4, 129.4, 128.7, 128.6, 123.6, 61.0, 44.9, 20.9, 14.1. IR (neat) v 1740 cm^{-1}, 1724, 1695, 1638 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{20}O_5$ (M^+): 352.1311; Found: 352.1309

Benzoic acid 5-chloro-2-(3-ethoxycarbonyl-but-3-enoyl)-phenyl ester (5e)



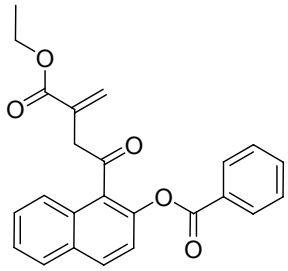
Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.19-8.16 (m, 2H), 7.86 (d, J = 8.4 Hz, 1H), 7.68-7.62 (m, 1H), 7.54-7.49 (m, 2H), 7.37-7.34 (m, 1H), 7.29 (d, J = 1.8 Hz, 1H), 6.32 (s, 1H), 5.61 (d, J = 0.9 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.85 (s, 2H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 195.8, 166.2, 164.8, 149.9, 138.9, 134.4, 134.1, 131.1, 130.5, 129.8, 129.2, 128.9, 128.8, 126.6, 124.5, 61.1, 44.8, 14.1. IR (neat) v 1745, 1717, 1697, 1639 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{17}O_5{}^{35}Cl$ (M^+): 372.0765; Found: 372.0762.

Benzoic acid 2-(3-ethoxycarbonyl-but-3-enoyl)-5-methoxy-phenyl ester (5f)



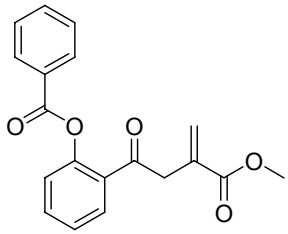
Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.20-8.18 (m, 2H), 7.93 (d, J = 8.7 Hz, 1H), 7.65-7.60 (m, 1H), 7.52-7.47 (m, 2H), 6.89-6.85 (m, 1H), 6.73 (d, J = 2.4 Hz, 1H), 6.30 (s, 1H), 5.57 (s, 1H), 4.16 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 2H), 1.23 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 194.9, 166.4, 165.1, 163.8, 151.6, 134.9, 133.8, 132.2, 130.4, 129.4, 128.7, 128.4, 123.5, 112.1, 109.4, 61.0, 55.8, 44.3, 14.1. IR (neat) v 1736, 1718, 1685, 1637 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{20}O_6$ (M^+): 368.1260; Found: 368.1263.

Benzoic acid 1-(3-ethoxycarbonyl-but-3-enoyl)-naphthalen-2-yl ester (5g)



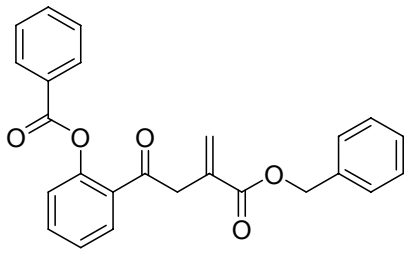
Coloress oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.22 (d, J = 7.5 Hz, 2H), 7.97-7.88 (m, 3H), 7.70-7.65 (m, 1H), 7.60-7.51 (m, 4H), 7.42 (d, J = 9.0 Hz, 1H), 6.32 (s, 1H), 5.52 (s, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.94 (s, 2H), 1.23 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 201.5, 166.2, 164.9, 144.8, 134.2, 133.9, 131.7, 131.1, 130.4, 130.3, 130.0, 129.1, 128.9, 128.4, 127.8, 126.4, 124.9, 121.4, 61.1, 48.2, 14.1. IR (neat) v 1736, 1718, 1708, 1638 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{20}O_5$ (M^+): 388.1311; Found: 388.1304.

Benzoic acid 2-(3-methoxycarbonyl-but-3-enoyl)-phenyl ester (5h)



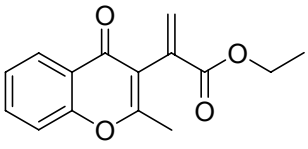
Coloress oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.20 (d, J = 8.1 Hz, 2H), 7.88 (d, J = 7.5 Hz, 1H), 7.66-7.48 (m, 4H), 7.39-7.34 (m, 1H), 7.26-7.23 (m, 1H), 6.32 (s, 1H), 5.61 (s, 1H), 3.90 (s, 2H), 3.66 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 196.9, 166.8, 165.1, 149.2, 134.3, 133.9, 133.3, 131.4, 130.4, 130.0, 129.3, 129.1, 128.8, 126.2, 123.9, 52.1, 44.8. IR (neat) v 1735, 1719, 1686, 1638 cm^{-1}. HRMS (EI) calcd for $C_{19}H_{16}O_5$ (M^+): 324.0998; Found: 324.1006.

Benzoic acid 2-(3-benzyloxycarbonyl-but-3-enoyl)-phenyl ester (5i)



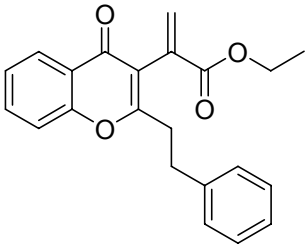
Coloress oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.19-8.16 (m, 2H), 7.82-7.79 (m, 1H), 7.64-7.45 (m, 4H), 7.34-7.22 (m, 7H), 6.37 (s, 1H), 5.63 (s, 1H), 5.11 (s, 2H), 3.90 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 196.8, 166.0, 165.1, 149.1, 135.8, 134.3, 133.8, 133.2, 131.3, 130.4, 130.0, 129.4, 128.7, 128.5, 128.2, 128.1, 126.2, 123.9, 66.8, 44.8. IR (neat) v 1735, 1719, 1691, 1638 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{20}O_5$ (M^+): 400.1311; Found: 400.1307.

Ethyl 2-(2-methyl-4-oxo-4H-chromen-3-yl)acrylate (7a)



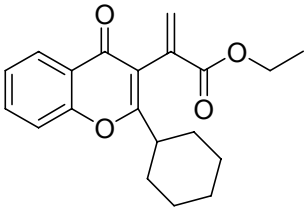
White solid. Mp: 68-71℃. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.19 (d, J = 7.8 Hz, 1H), 7.66-7.61 (m, 1H), 7.43-7.34 (m, 2H), 6.68 (s, 1H), 5.79 (s, 1H), 4.27 (q, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 176.4, 165.7, 163.7, 155.9, 134.2, 133.5, 130.9, 126.1, 124.9, 123.0, 120.1, 117.6, 61.2, 19.3, 14.2. IR (KBr) v 1719, 1644 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{14}O_4$ (M^+): 258.0892; Found: 258.0898.

Ethyl 2-(4-oxo-2-phenethyl-4H-chromen-3-yl)acrylate (7b)



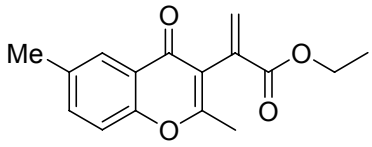
Pale yellow solid. Mp: 57-58□. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.20-8.17 (m, 1H), 7.69-7.63 (m, 1H), 7.45-7.35 (m, 2H), 7.30-7.14 (m, 5H), 6.57 (d, J = 1.2 Hz, 1H), 5.40 (d, J = 1.2 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 3.09-3.06 (m, 2H), 2.97-2.92 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 176.6, 165.7, 165.3, 155.9, 140.0, 133.8, 133.6, 131.0, 128.6, 128.4, 126.6, 126.2, 125.0, 123.1, 120.3, 117.7, 61.2, 34.6, 33.2, 14.2. IR (KBr) v 1720, 1645 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{20}O_4$ (M^+): 348.1362; Found: 348.1358.

Ethyl 2-(2-cyclohexyl-4-oxo-4H-chromen-3-yl)acrylate (7c)



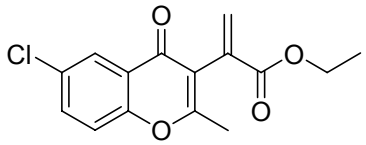
Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.20-8.16 (m, 1H), 7.67-7.61 (m, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.39-7.34 (m, 1H), 6.68 (d, J = 1.5 Hz, 1H), 5.75 (d, J = 1.5 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 2.76-2.69 (m, 1H), 1.85-1.72 (m, 7H), 1.30-1.24 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 176.9, 169.7, 166.0, 156.1, 134.1, 133.4, 130.7, 126.1, 124.9, 123.2, 118.6, 117.7, 61.2, 41.6, 29.9, 25.9, 25.7, 14.2. IR (neat) v 1721, 1646 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{22}O_4$ (M^+): 326.1518; Found: 326.1516.

Ethyl 2-(2,6-dimethyl-4-oxo-4H-chromen-3-yl)acrylate (7d)

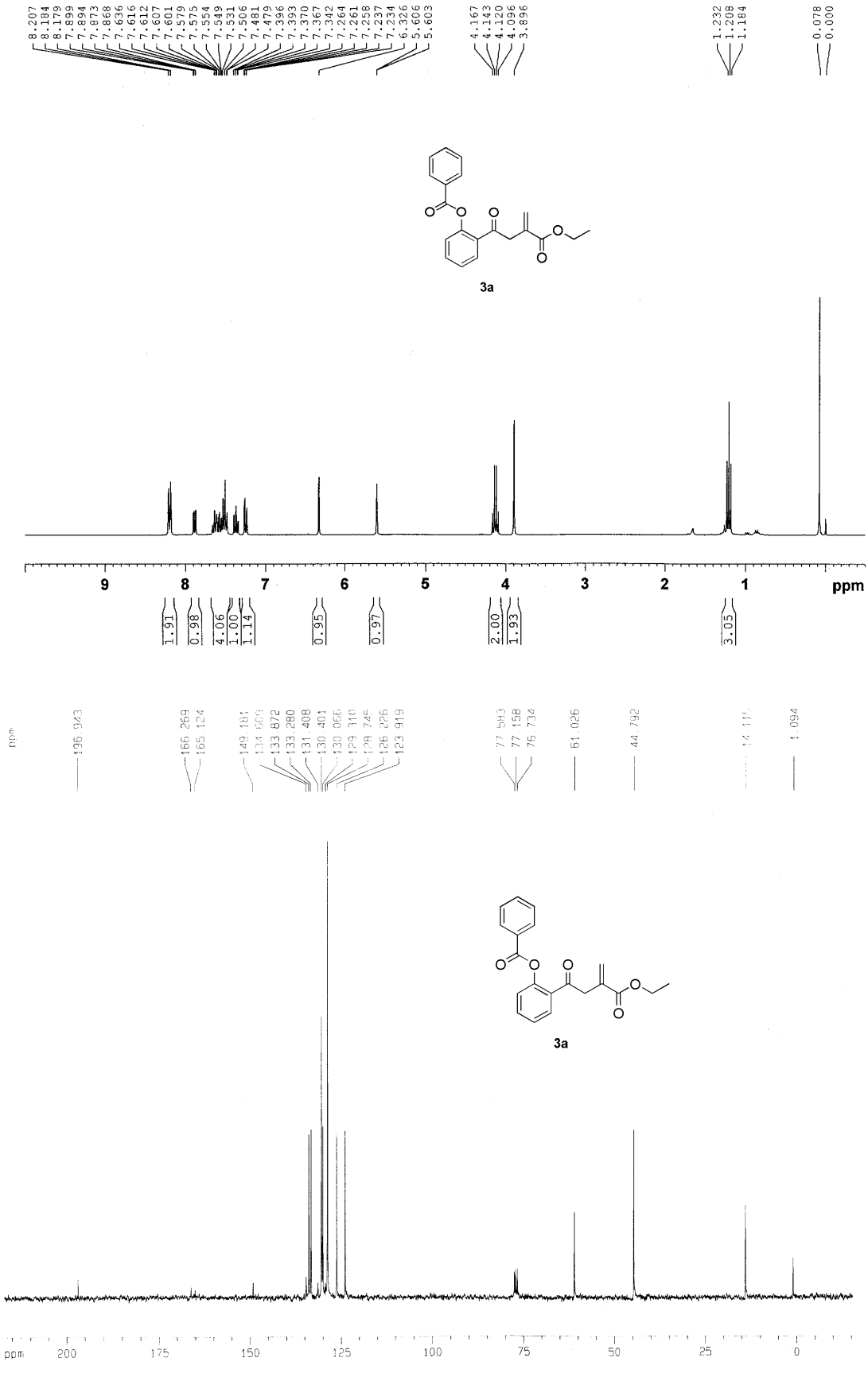


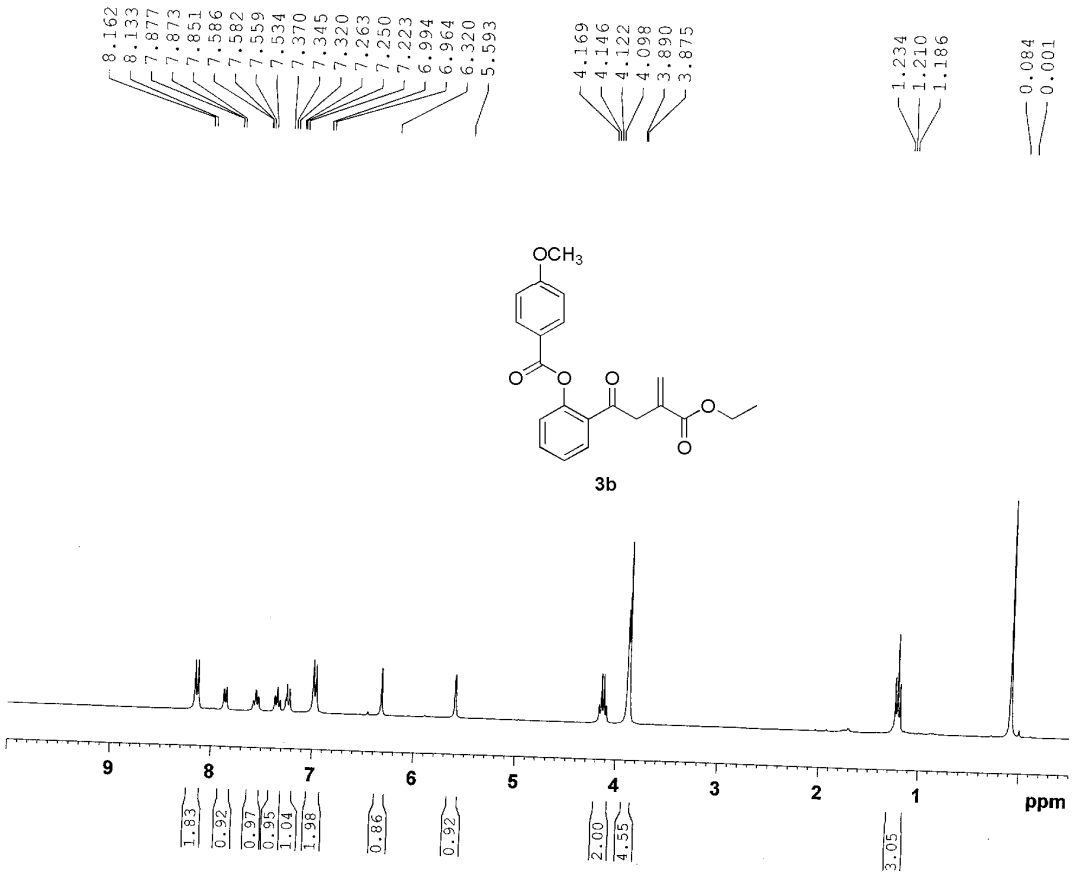
White solid. Mp: 74-76℃ ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 7.96 (s, 1H), 7.46-7.43 (m, 1H), 7.32-7.26 (m, 1H), 6.68 (d, *J* = 1.2 Hz, 1H), 5.78 (d, *J* = 1.2 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.36 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 176.5, 165.9, 163.5, 154.3, 134.9, 134.8, 134.4, 130.8, 125.5, 122.8, 120.0, 117.5, 61.3, 21.0, 19.3, 14.2. IR (KBr) *v* 1721, 1645 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{16}O_4$ (M^+): 272.1049; Found: 272.1045.

Ethyl 2-(6-chloro-2-methyl-4-oxo-4H-chromen-3-yl)acrylate (7e)



White solid. Mp: 103-105 ℃ ^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm, 8.14-8.13 (m, 1H), 7.60-7.56 (m, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 6.70 (s, 1H), 5.79 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ, ppm, 175.3, 165.6, 164.1, 154.3, 133.9, 133.8, 131.3, 131.0, 125.6, 124.1, 120.2, 119.5, 61.4, 19.3, 14.2. IR (KBr) *v* 1721, 1650 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{13}O_4{}^{35}Cl$ (M^+): 292.0502; Found: 292.0498.

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7.250
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6.964
6.320
5.593
4.169
4.146
4.122
4.098
3.890
3.875
1.234
1.210
1.186
0.084
0.001
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3b
9
8
7
6
5
4
3
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0.97
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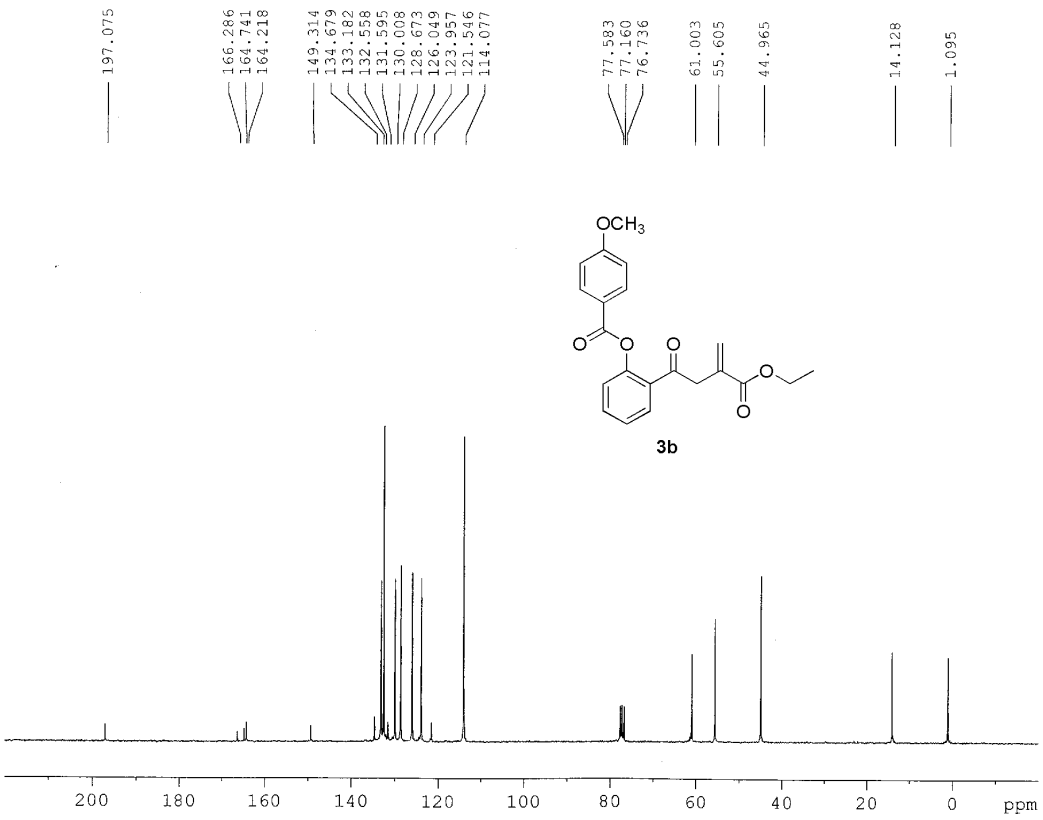
3.05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132.558
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123.957
121.546
114.077
77.583
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61.003
55.605
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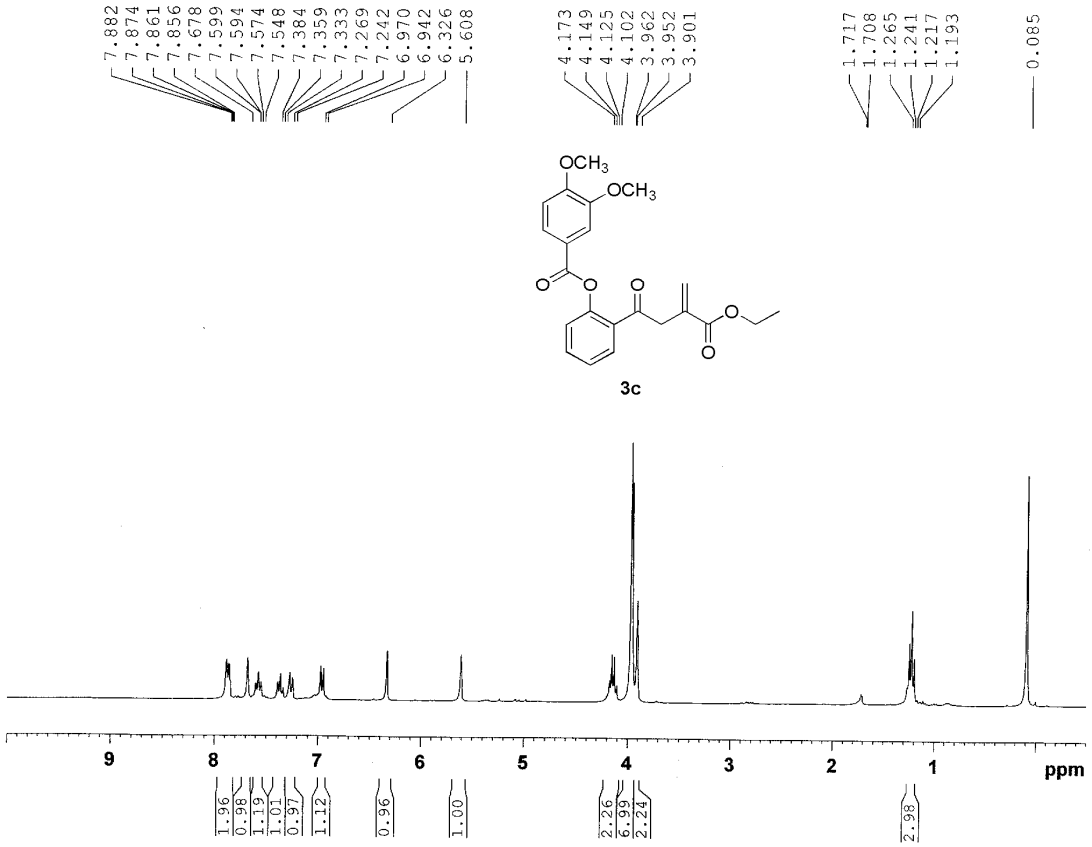
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6.970
6.942
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5
4
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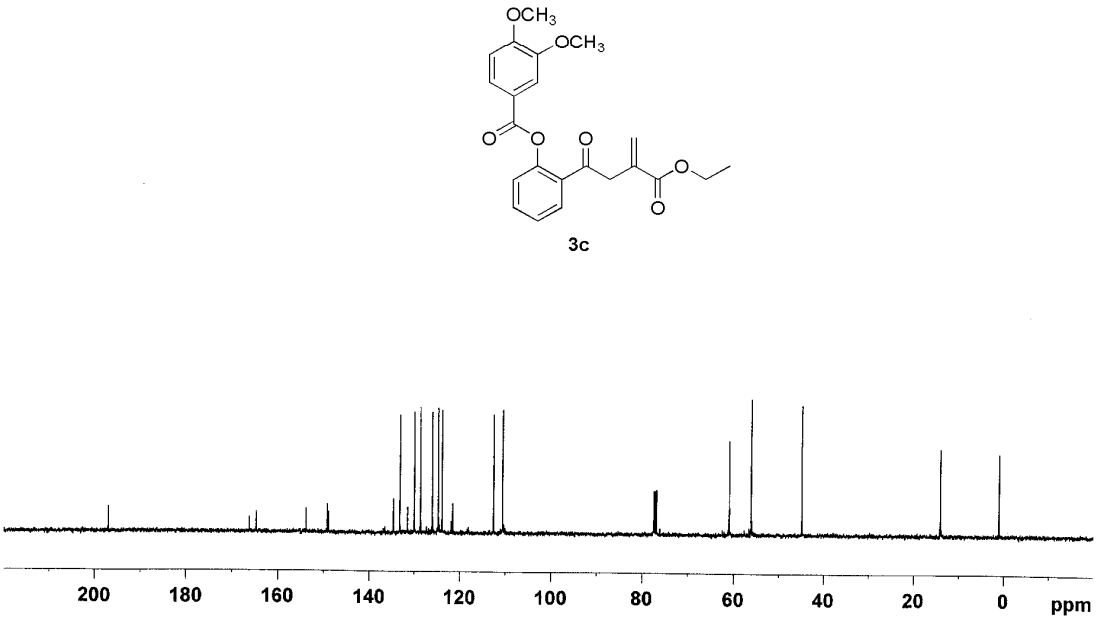
2.24
2.98

3c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123.858
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110.544
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77.099
76.781
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56.066
44.852
14.054
1.014
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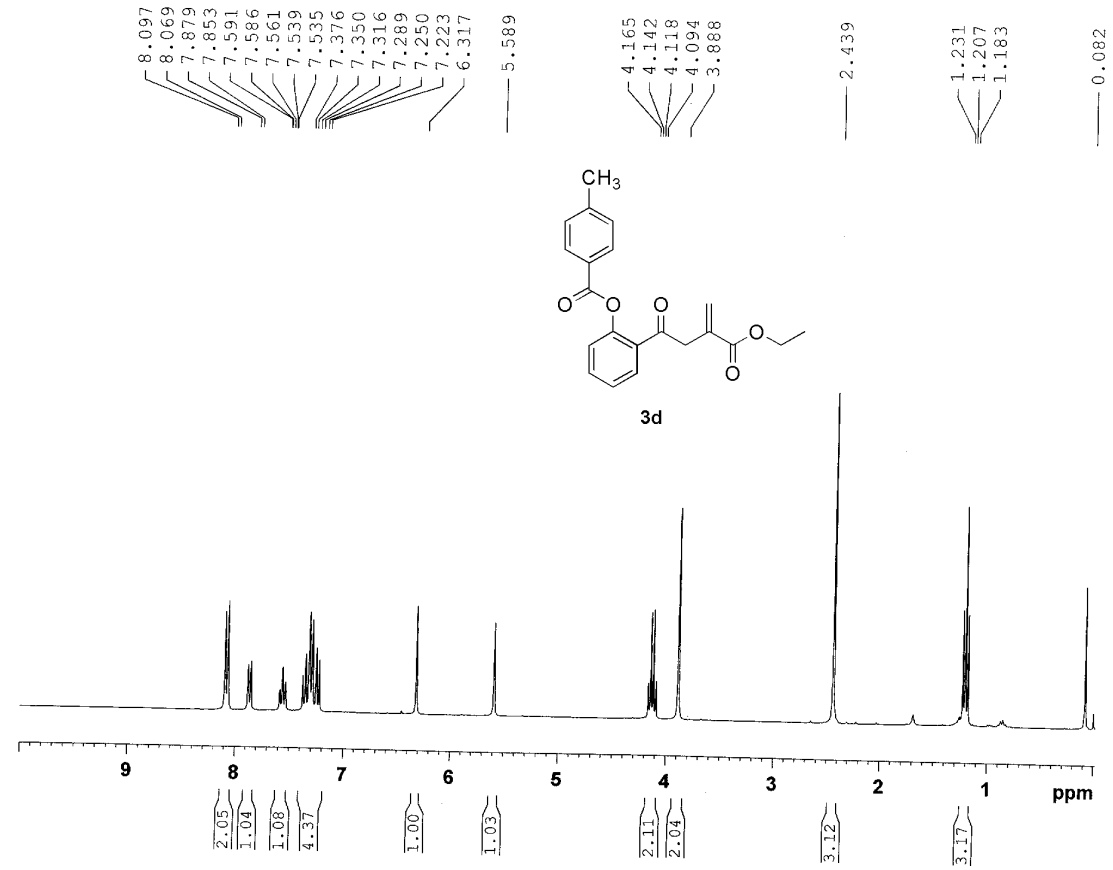
ppm

3c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7.289
7.250
7.223
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4.142
4.118
4.094
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2.439
1.231
1.207
1.183
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O
O
3d
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7
6
5
4
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1.03
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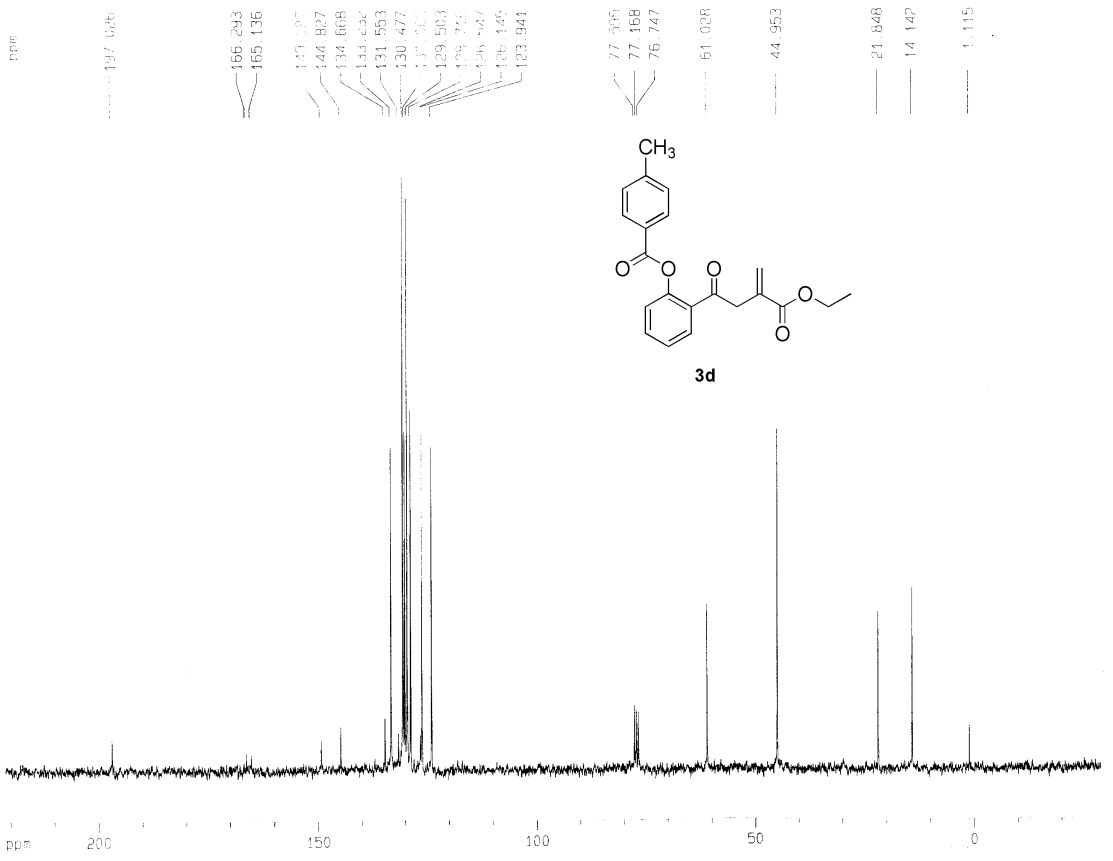
2.04
3.12
3.17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61.028
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21.848
14.142
1.115
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O
O
O
3d
ppm
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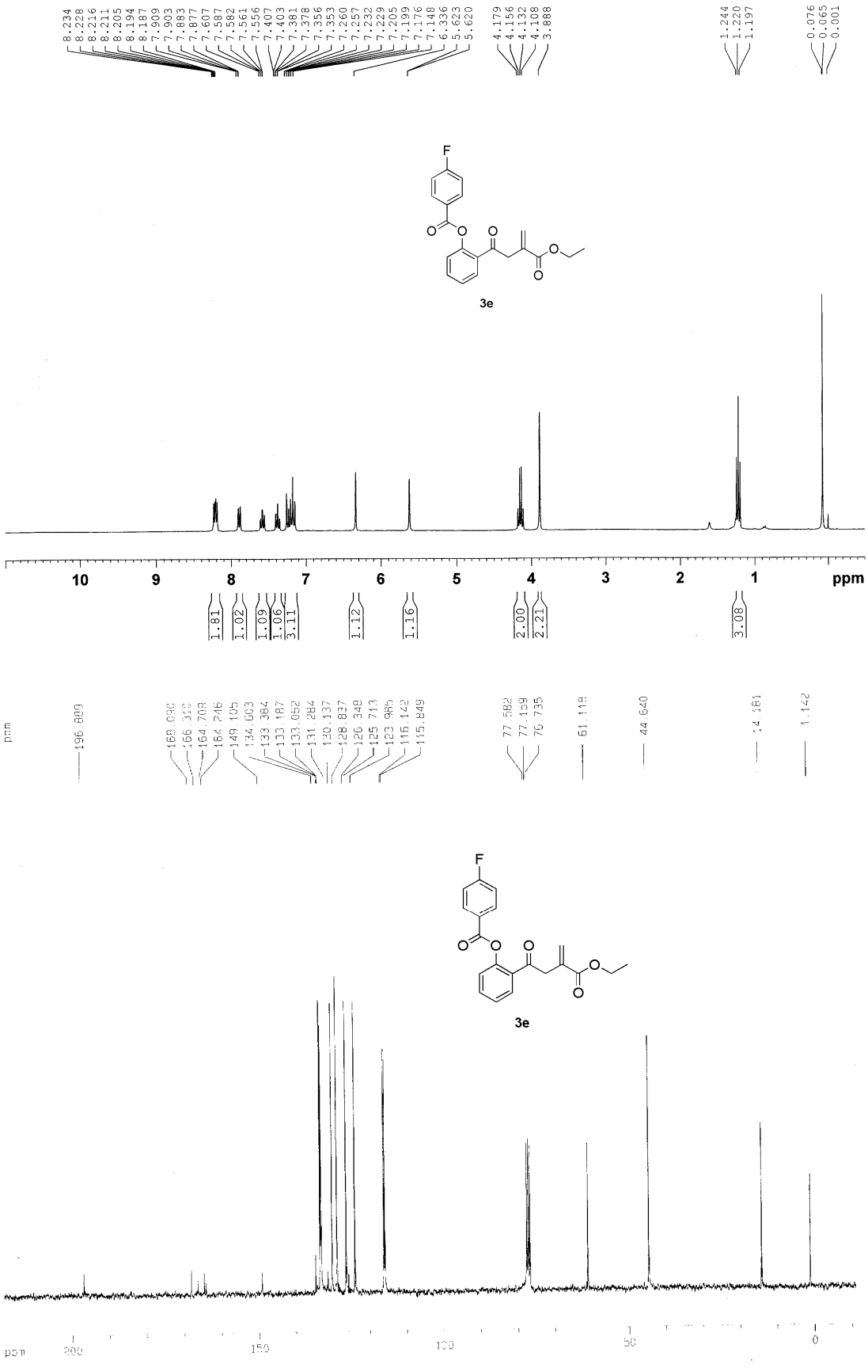
150
100
50
0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7.877
7.607
7.587
7.582
7.561
7.556
7.407
7.403
7.381
7.378
7.356
7.353
7.260
7.257
7.232
7.229
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7.199
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5.623
5.620
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4.156
4.132
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3.888
1.244
1.220
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0.065
0.001
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O
O
O
O
O
O
3e
10
9
8
7
6
5
4
3
2
1
ppm
1.81
1.02
1.09
1.06
3.11
1.12
1.16
2.00
2.21
3.08
ppm
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166.348
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77.159
76.735
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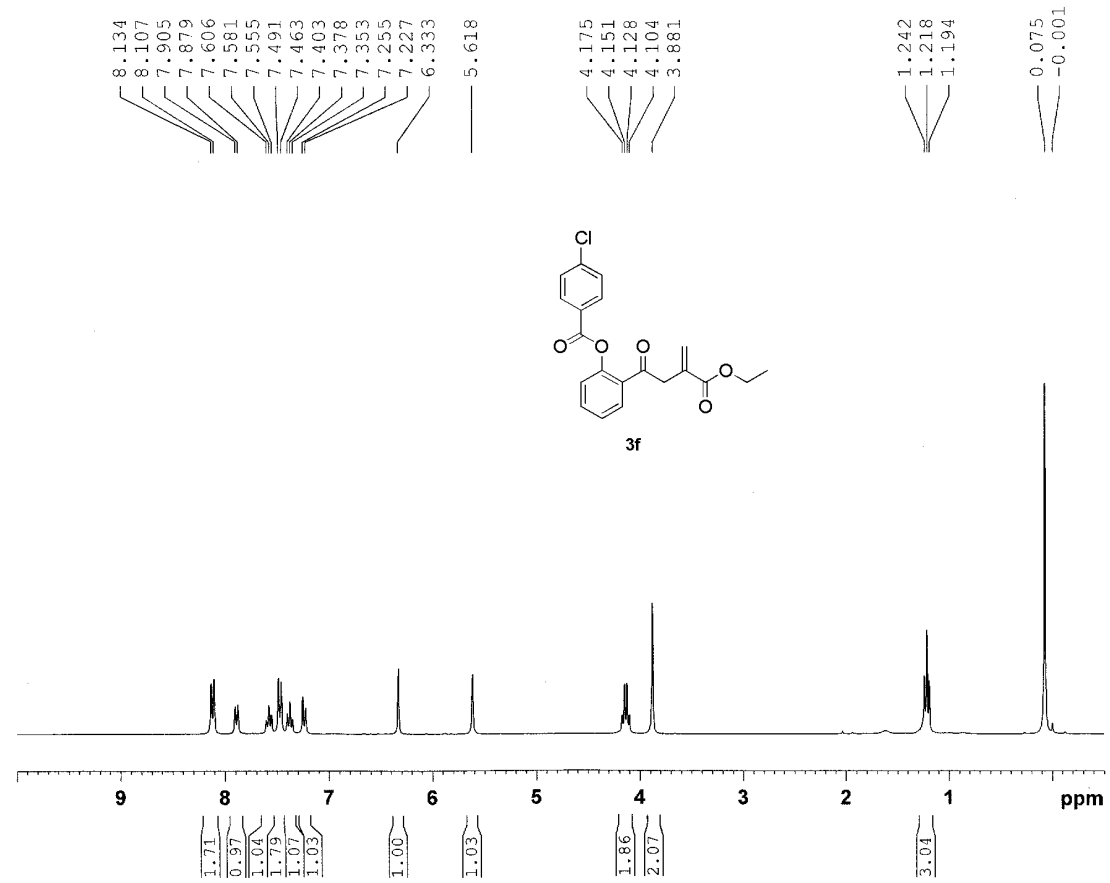
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7.463
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7.255
7.227
6.333
5.618
4.175
4.151
4.128
4.104
3.881
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1.194
0.075
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Cl
3f
9
8
7
6
5
4
3
2
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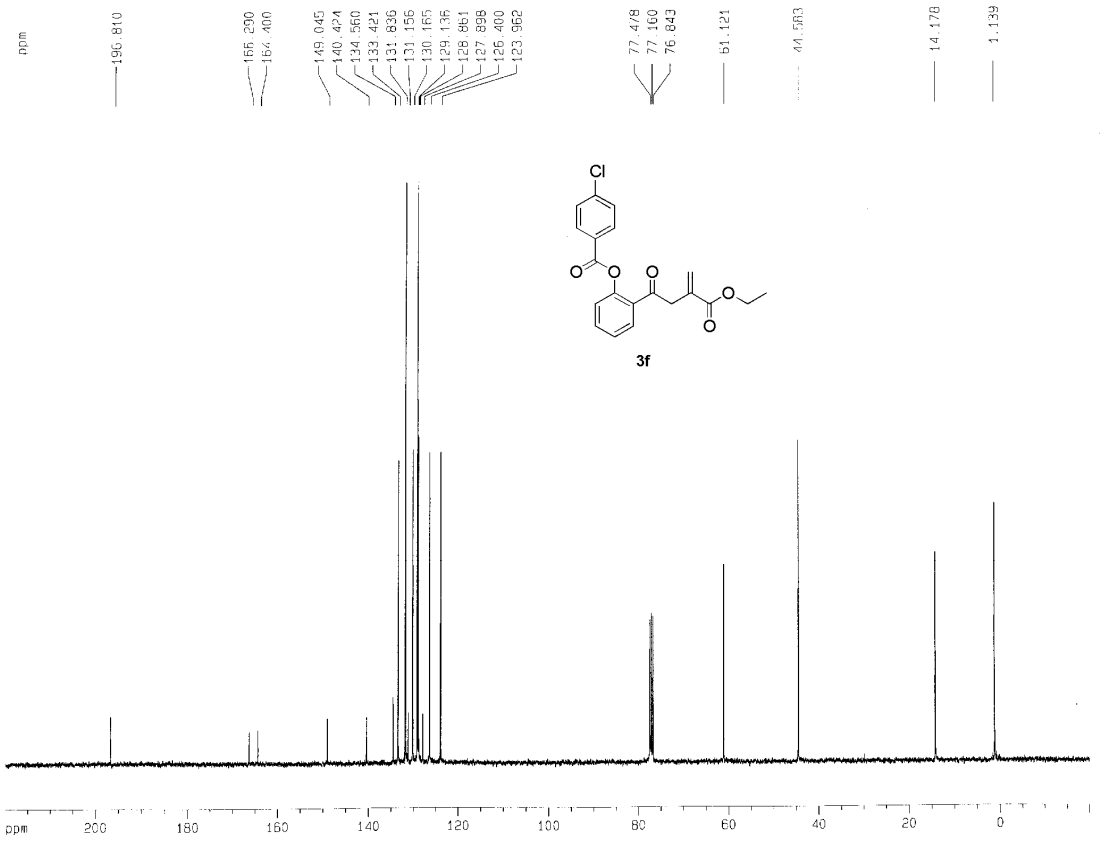
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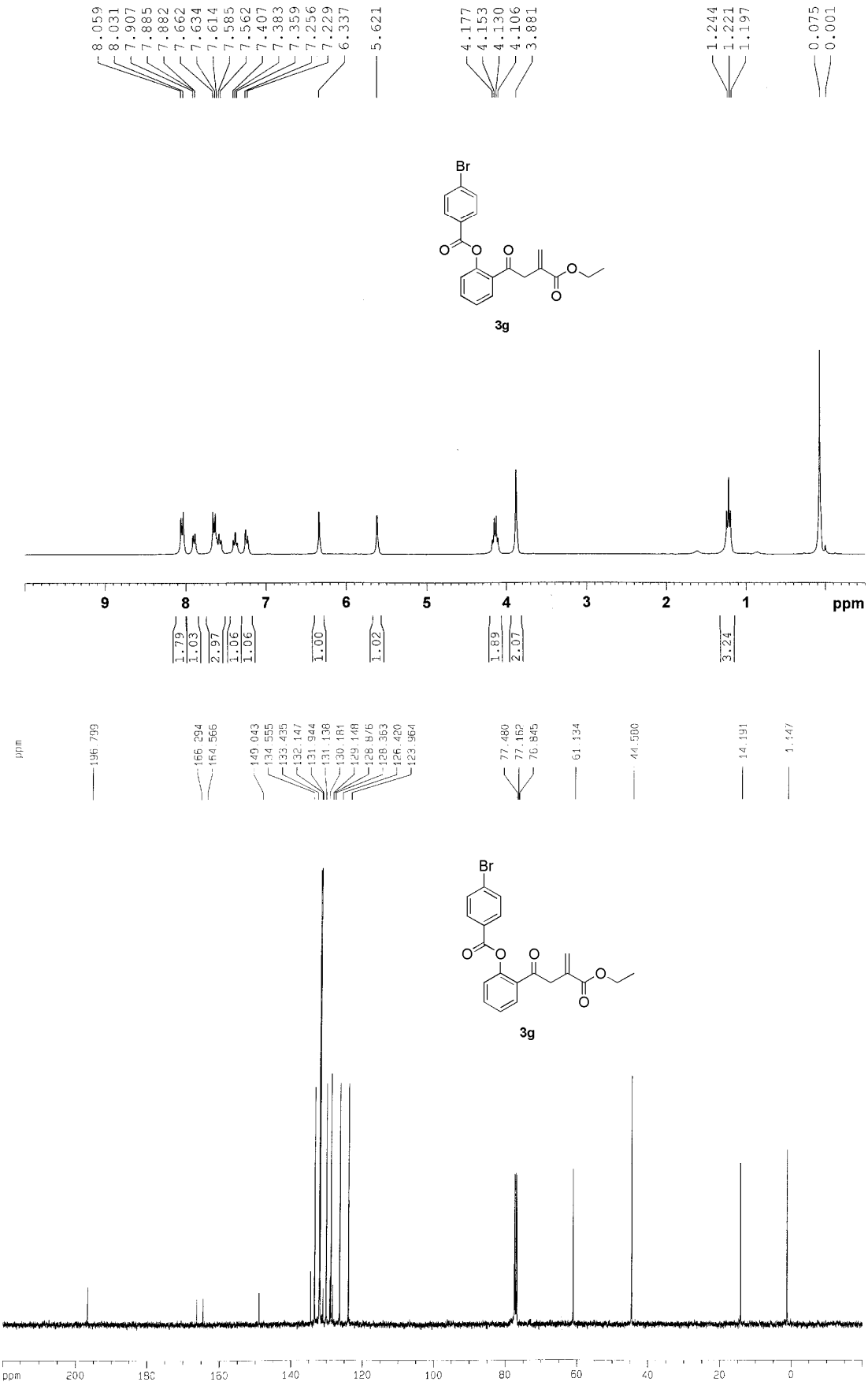
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7.229
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4.130
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6
5
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1.06
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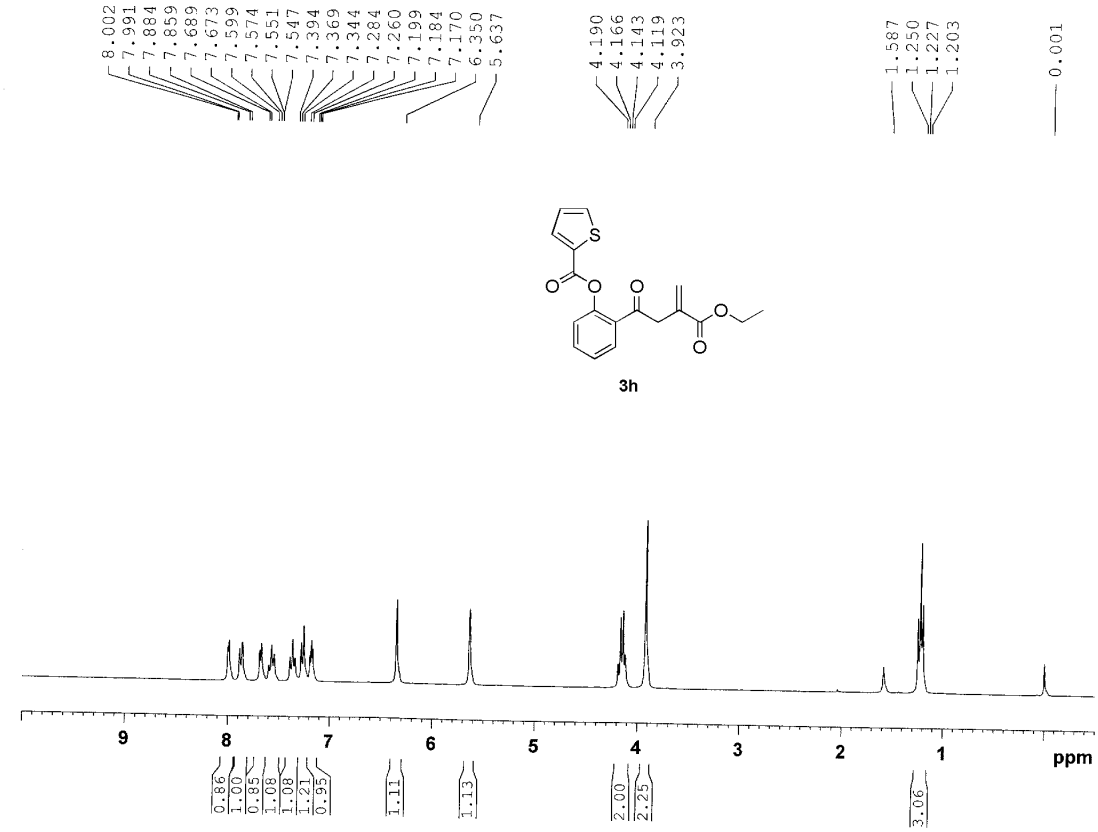
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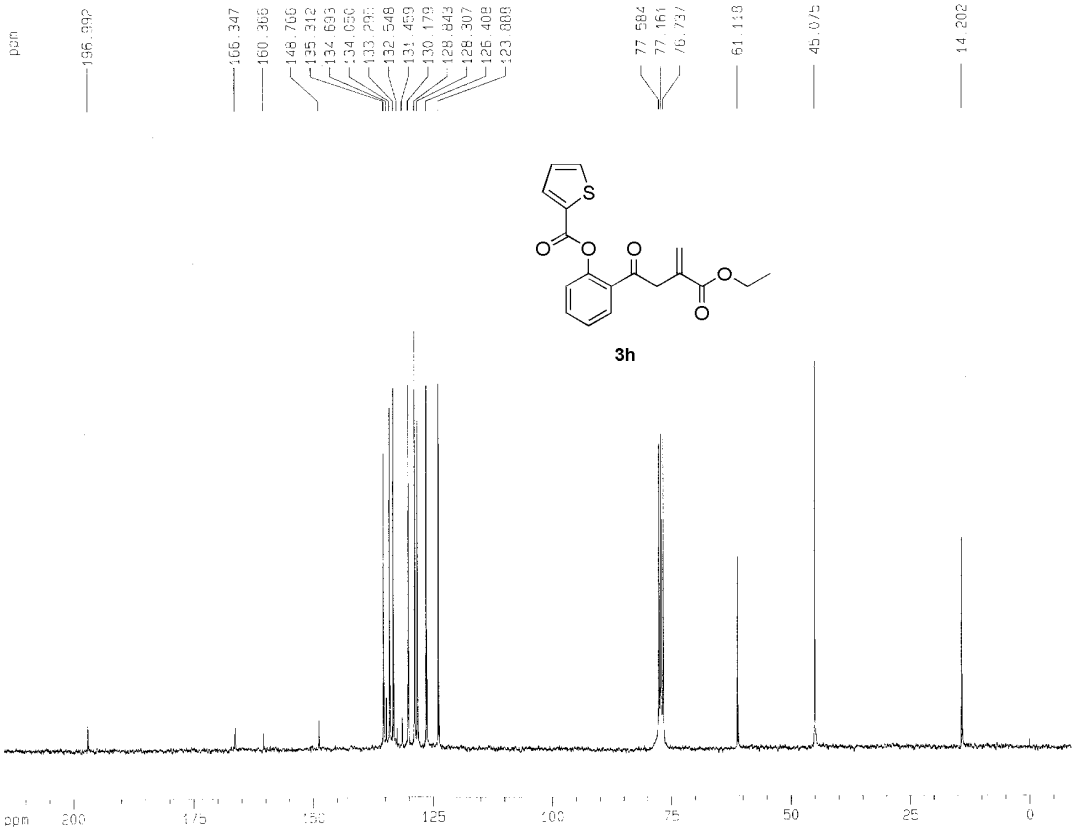
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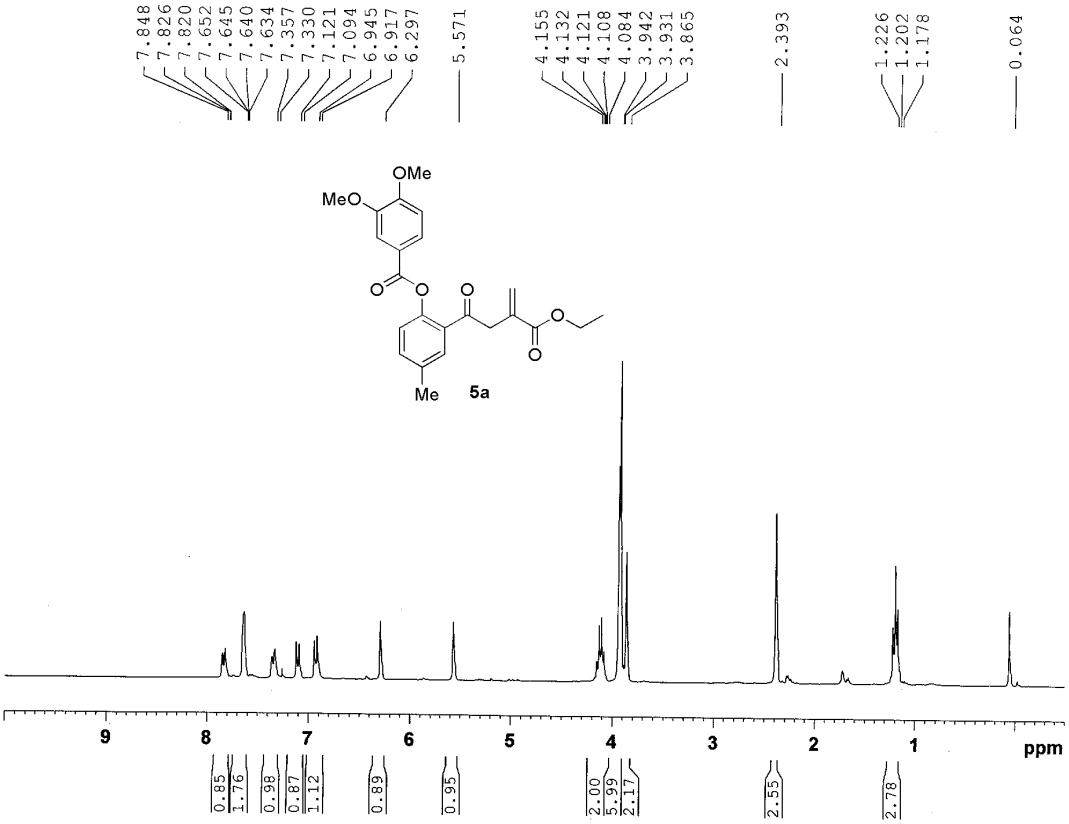
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4.108
4.084
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3.931
3.865
2.393
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1.202
1.178
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MeO
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O
O
O
O
Me
5a
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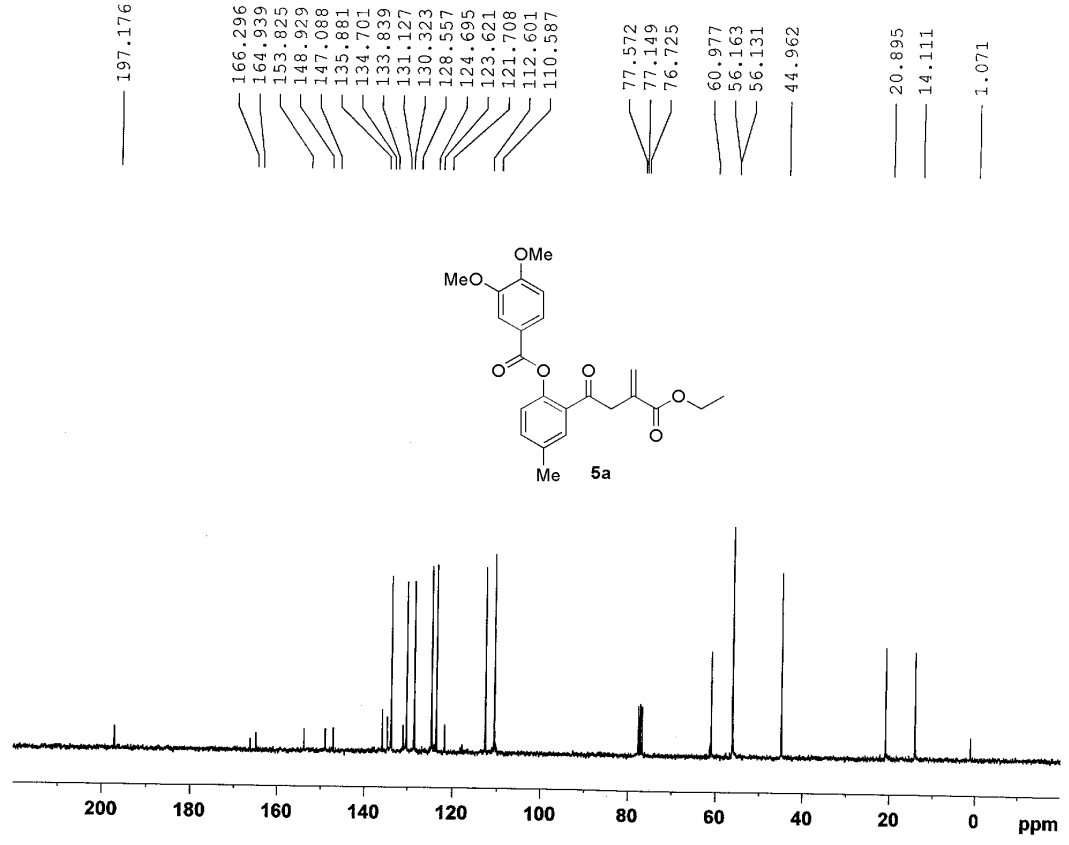
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77.149
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OMe
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Me
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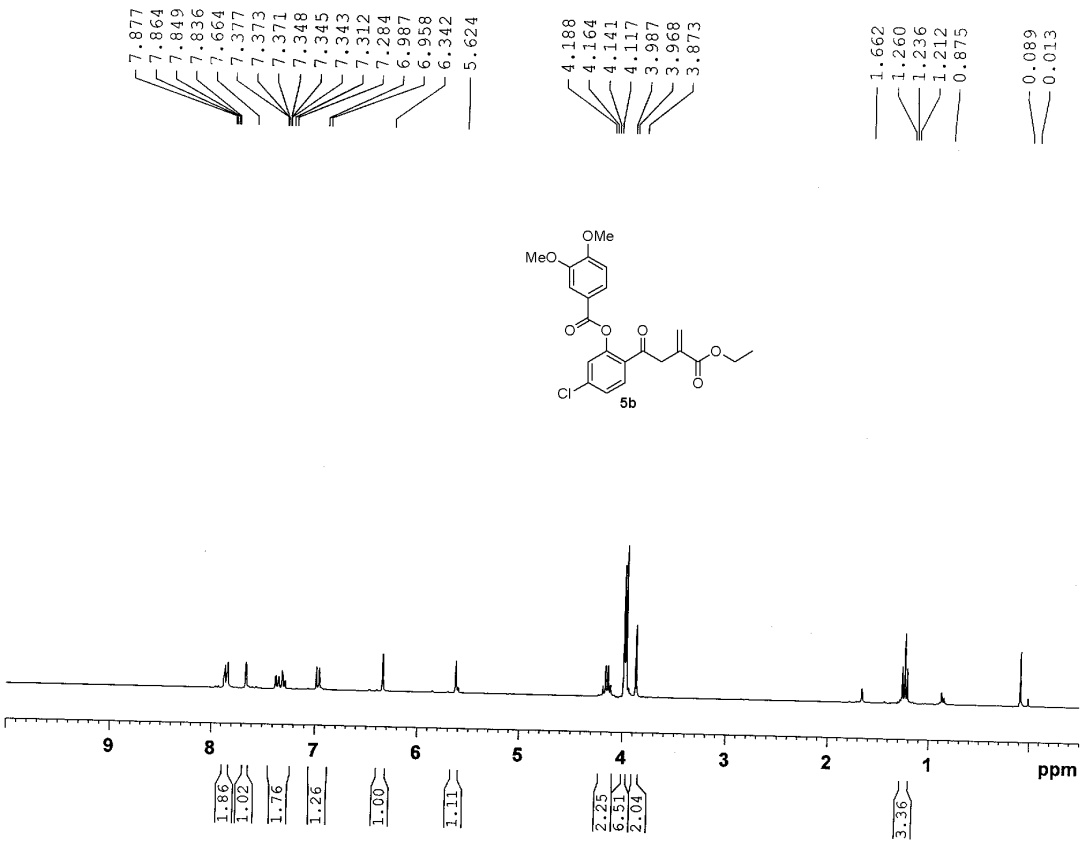

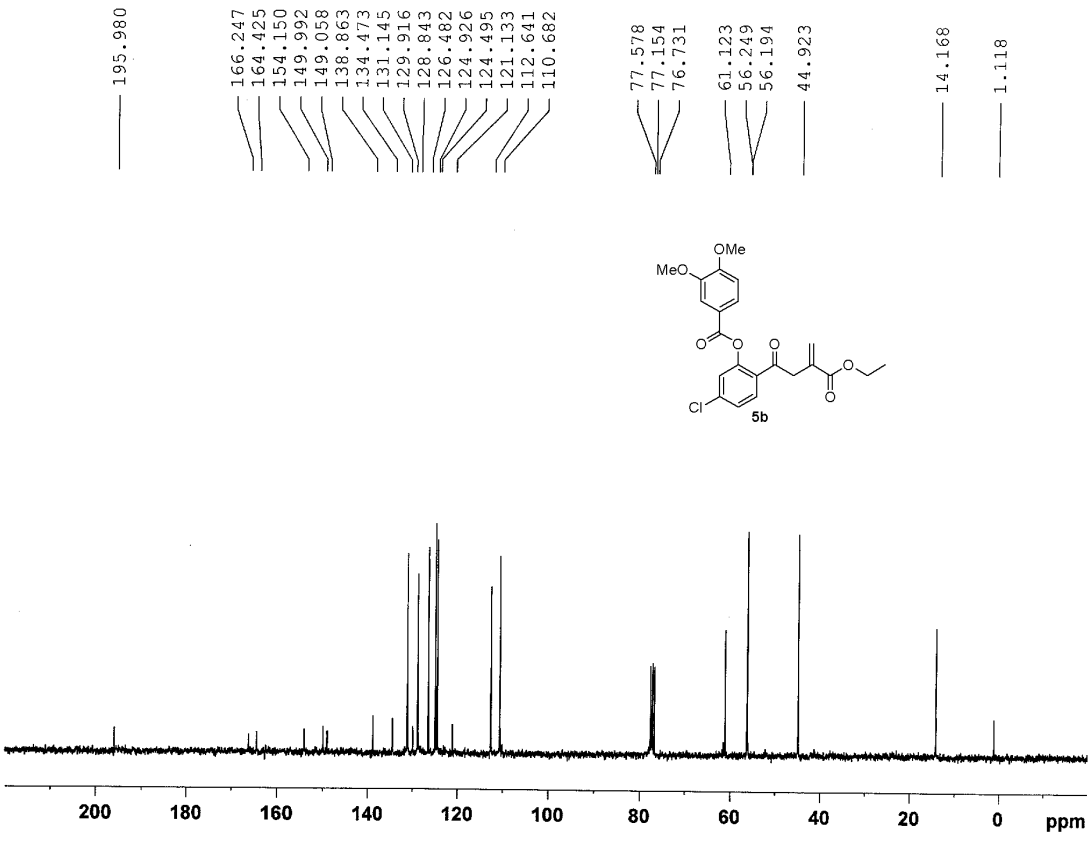

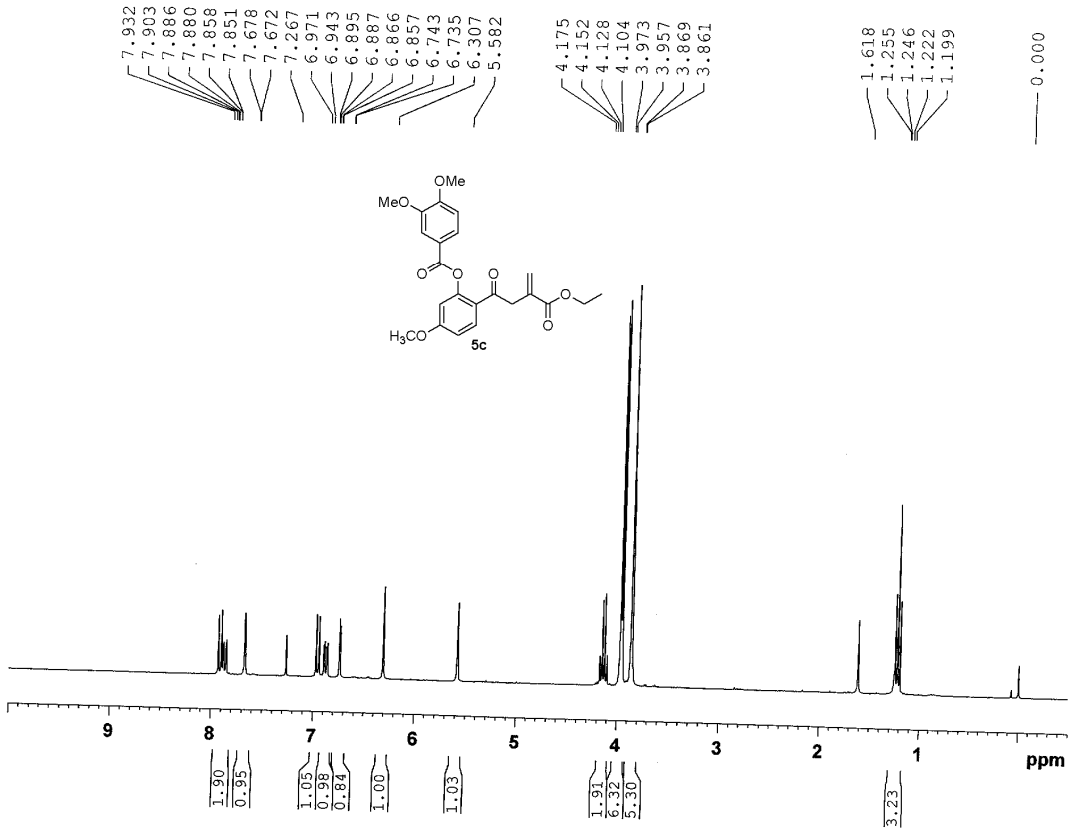

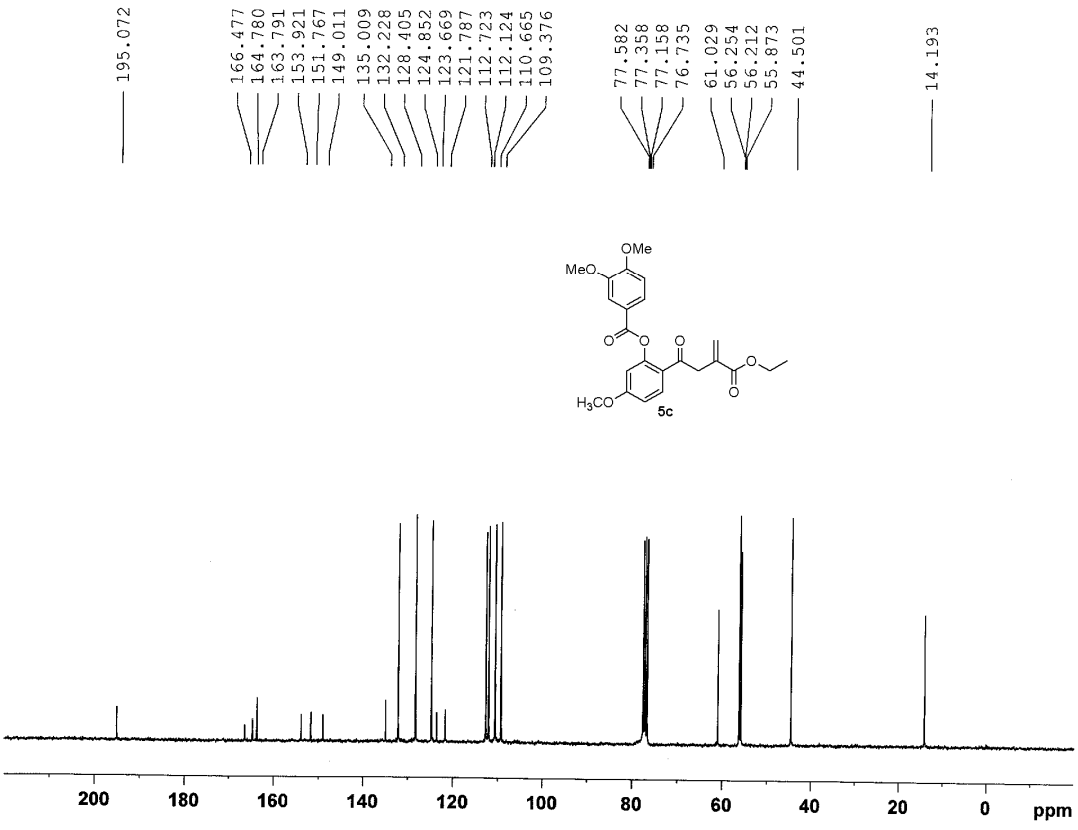

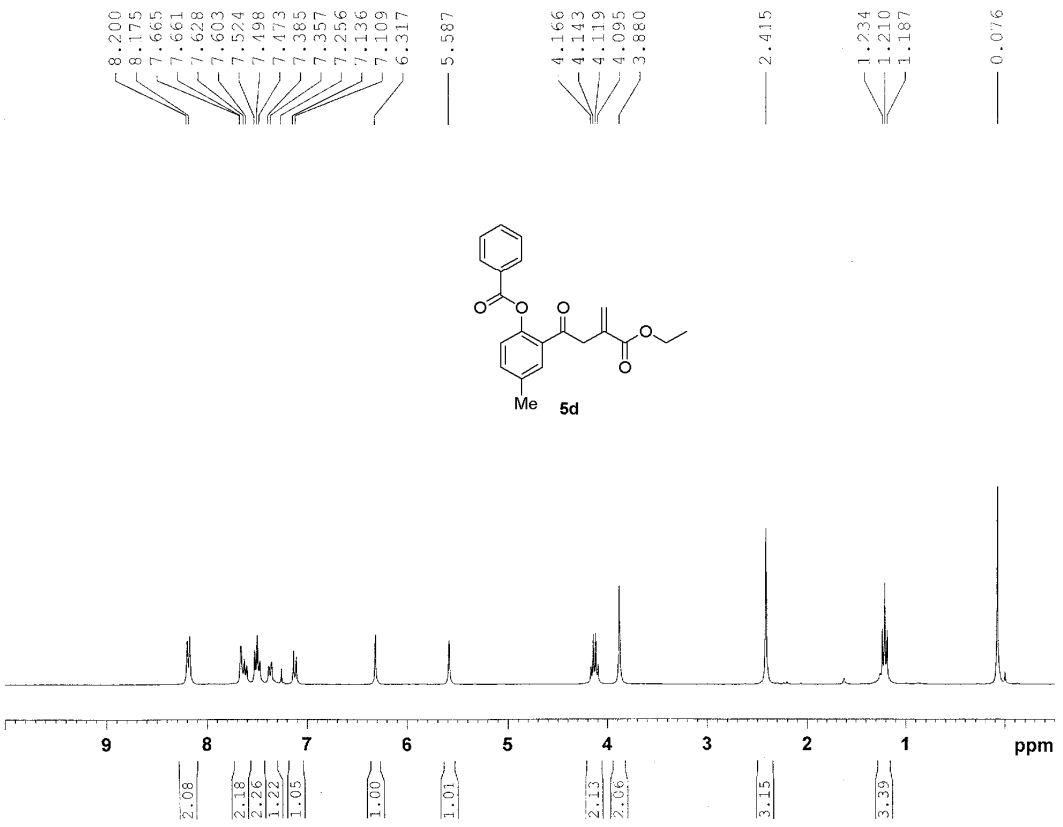

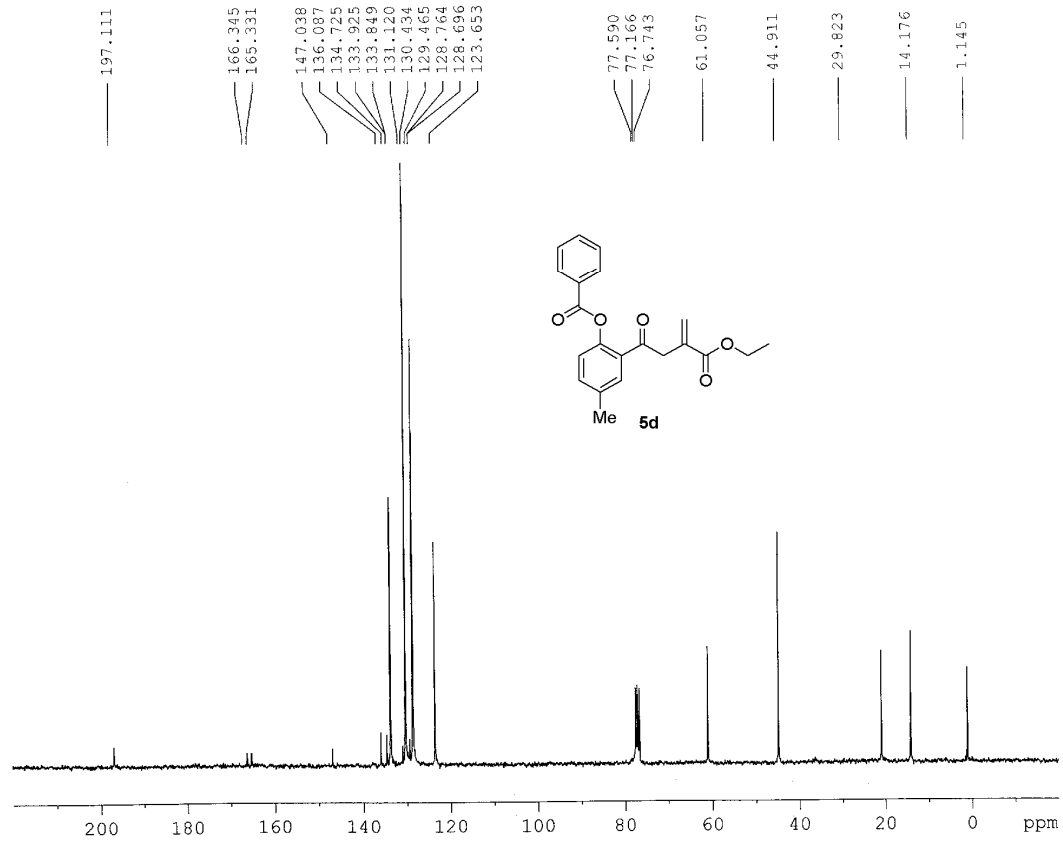

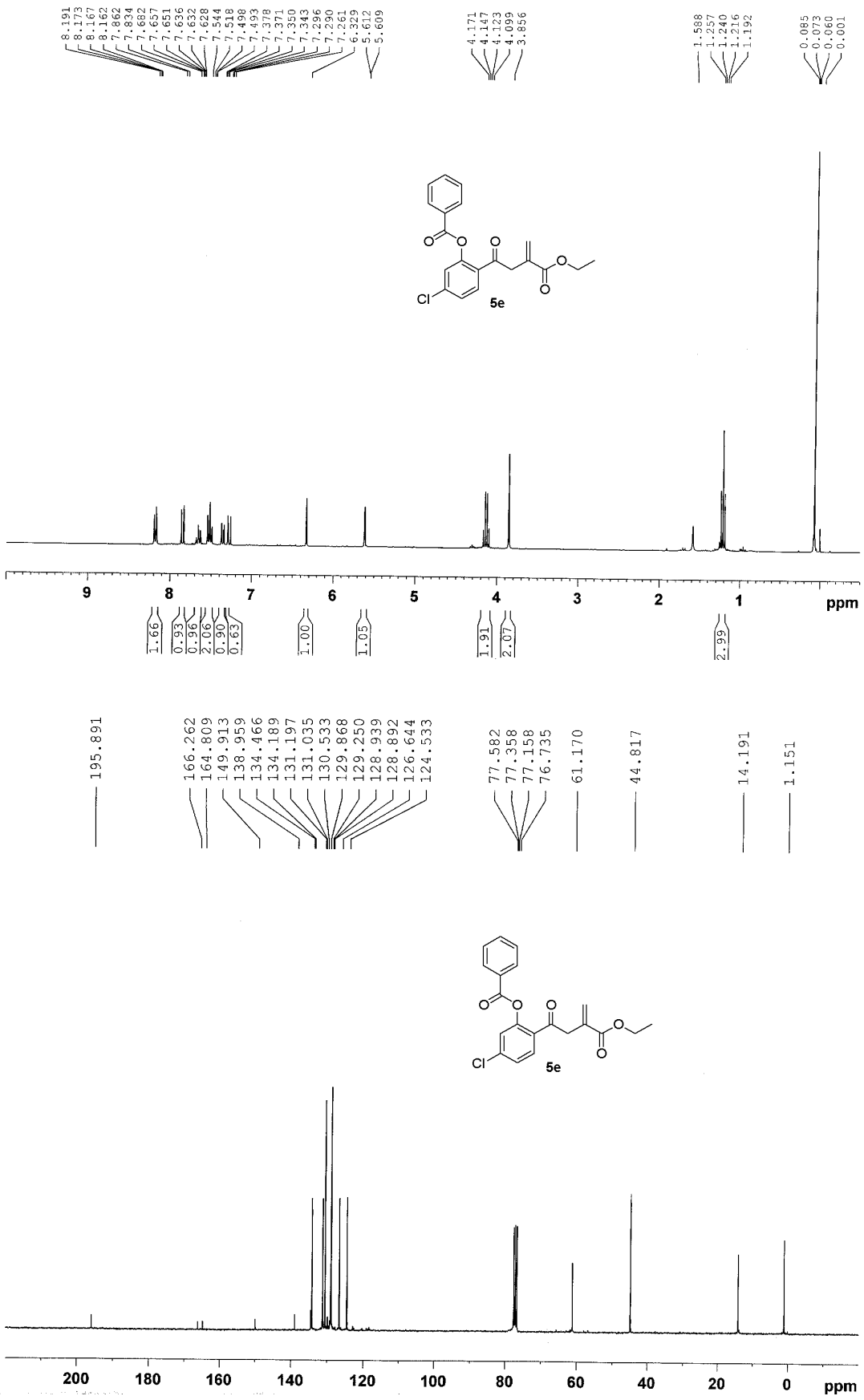
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7.632
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7.544
7.518
7.498
7.493
7.378
7.371
7.350
7.343
7.296
7.290
7.261
6.329
5.612
5.609
4.171
4.147
4.123
4.099
3.856
1.588
1.257
1.240
1.216
1.192
0.085
0.073
0.060
0.001
Cl
5e
9
8
7
6
5
4
3
2
1
ppm
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0.93
0.96
2.06
0.90
0.63
1.00
1.05
1.91
2.07
2.99
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166.262
164.809
149.913
138.959
134.466
134.189
131.197
131.035
130.533
129.868
129.250
128.939
128.892
126.644
124.533
77.582
77.358
77.158
76.735
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1.151
Cl
5e
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120
100
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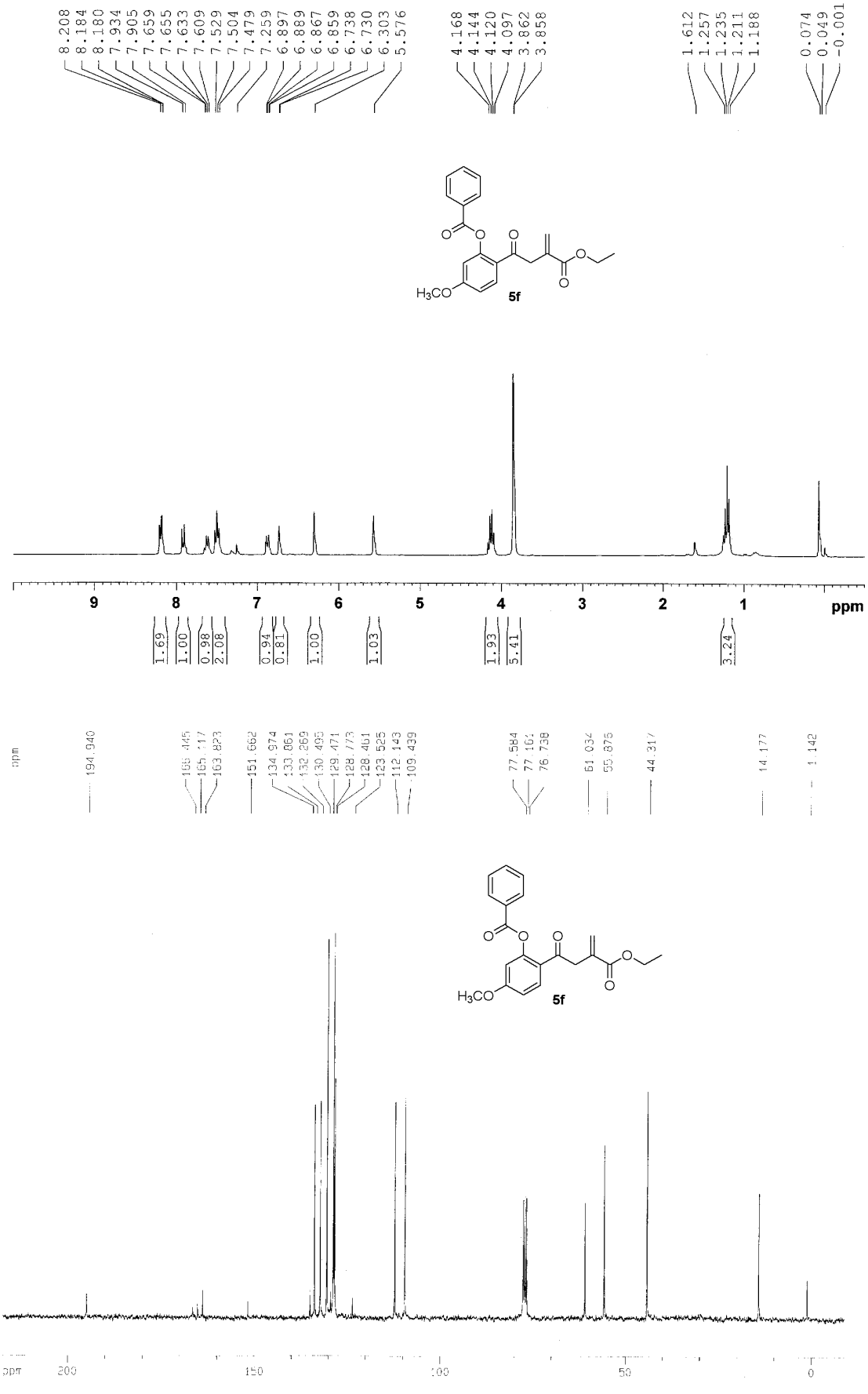
60
40
20
0
ppm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7.659
7.655
7.633
7.609
7.529
7.504
7.479
7.259
6.897
6.889
6.867
6.859
6.738
6.730
6.303
5.576
4.168
4.144
4.120
4.097
3.862
3.858
1.612
1.257
1.235
1.211
1.188
0.074
0.049
-0.001
H3CO
5f
9
8
7
6
5
4
3
2
1
ppm
1.69
1.00
0.98
2.08
0.94
0.81
1.00
1.03
1.93
5.41
3.24
ppm
194.940
151.662
134.974
133.061
129.471
128.401
123.525
112.143
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55.875
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14.177
1.142
H3CO
5f
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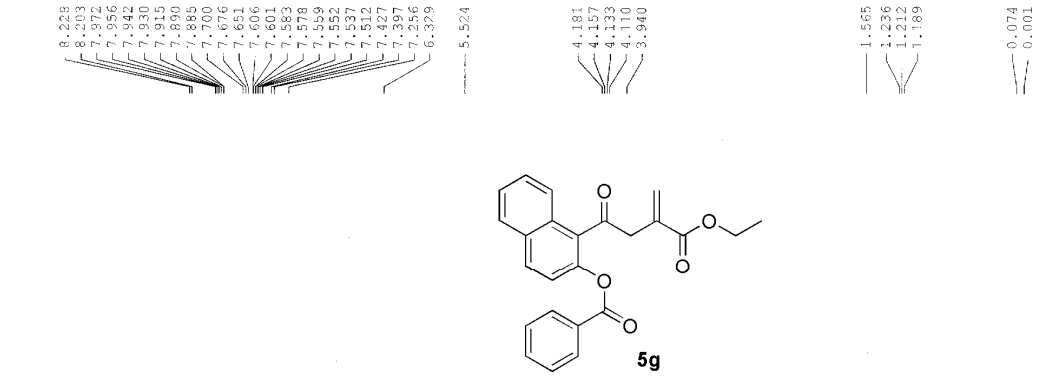
150
100
50
0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7.885
7.700
7.676
7.651
7.606
7.601
7.583
7.578
7.559
7.552
7.537
7.512
7.427
7.397
7.256
6.379
5.524
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4.133
4.110
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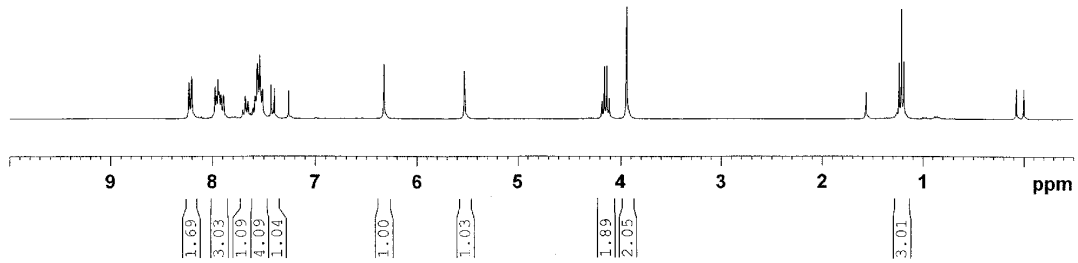
1.212
1.189
0.074
0.001

5g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6
5
4
3
2
1
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3.03
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4.09
1.04
1.00
1.03
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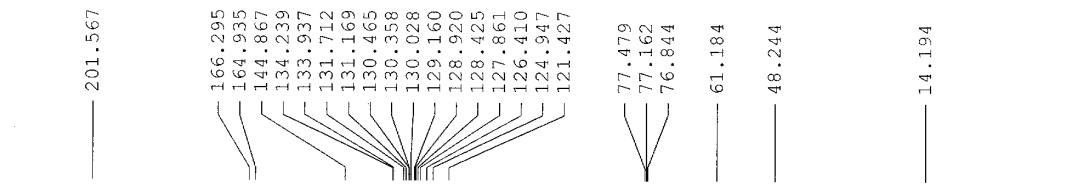
2.05
3.01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130.358
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129.160
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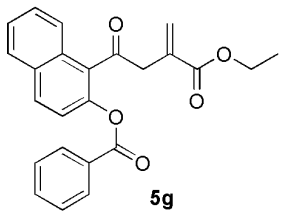
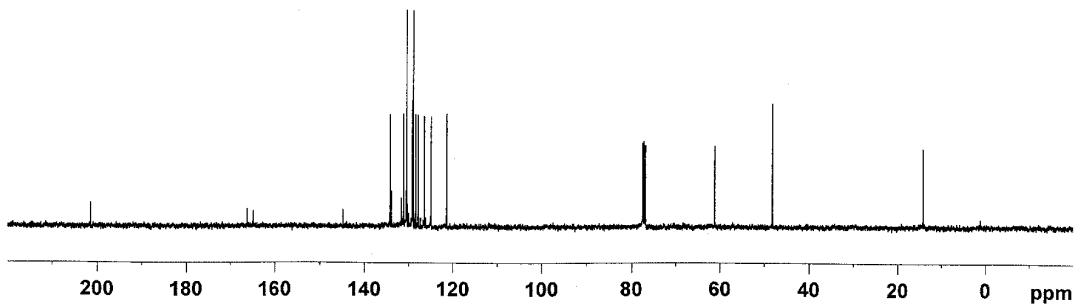
77.162
76.844
61.184
48.244
14.194


5g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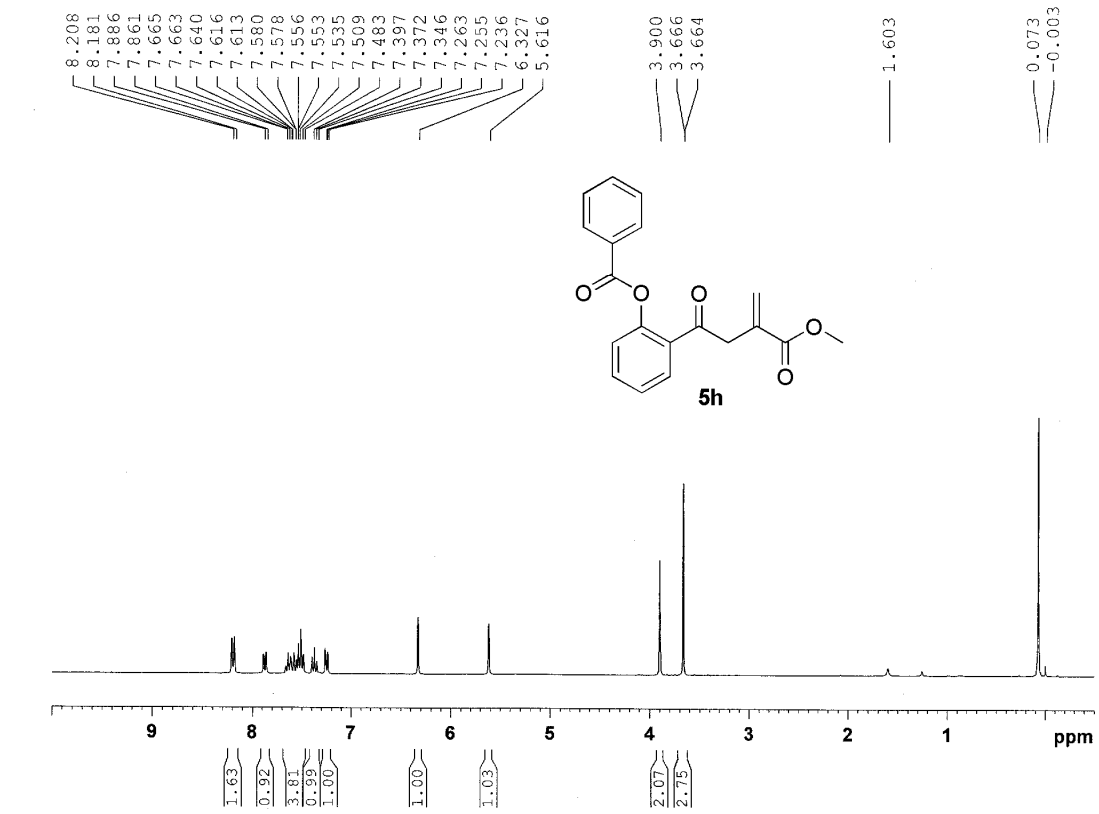
160
140
120
100
80
60
40
20
0
ppm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7.640
7.616
7.613
7.580
7.578
7.556
7.553
7.535
7.509
7.483
7.397
7.372
7.346
7.263
7.255
7.236
6.327
5.616
3.900
3.666
3.664
1.603
0.073
-0.003
5h
9
8
7
6
5
4
3
2
1
ppm
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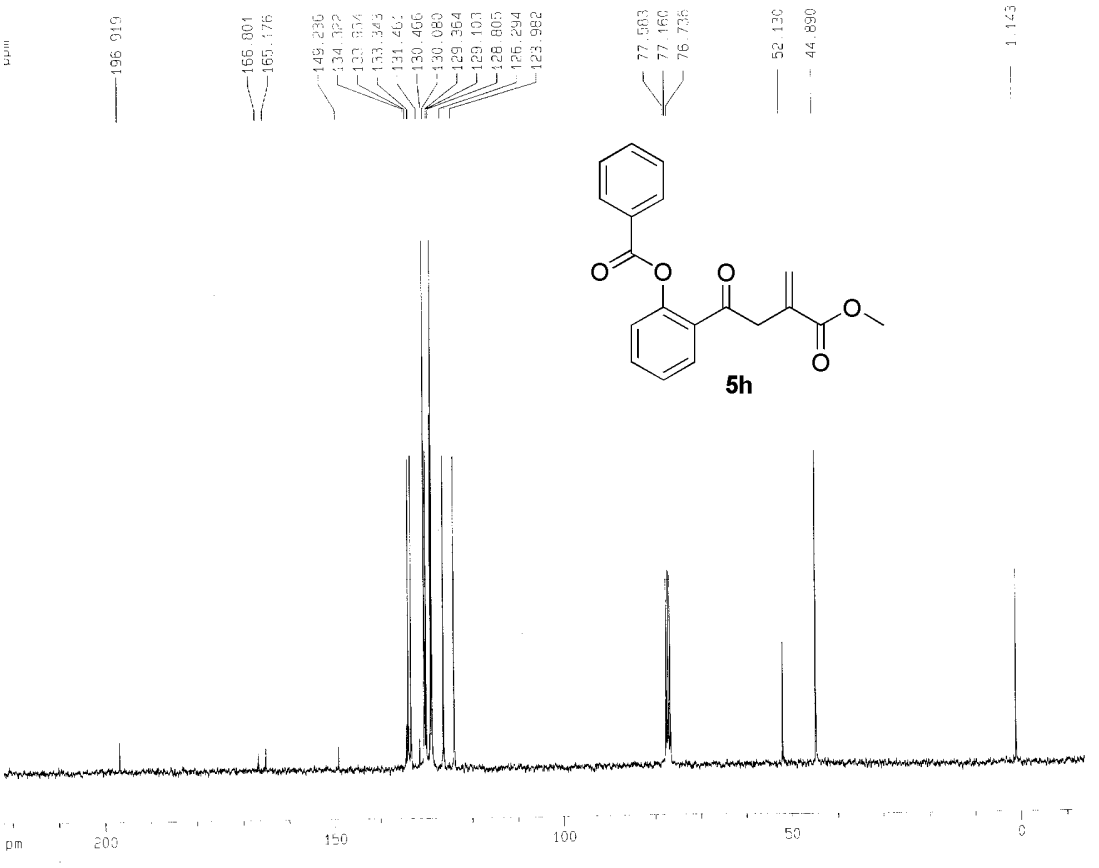
3.81
0.99
1.00
1.00
1.03
2.07
2.75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126.294
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77.160
76.736
52.130
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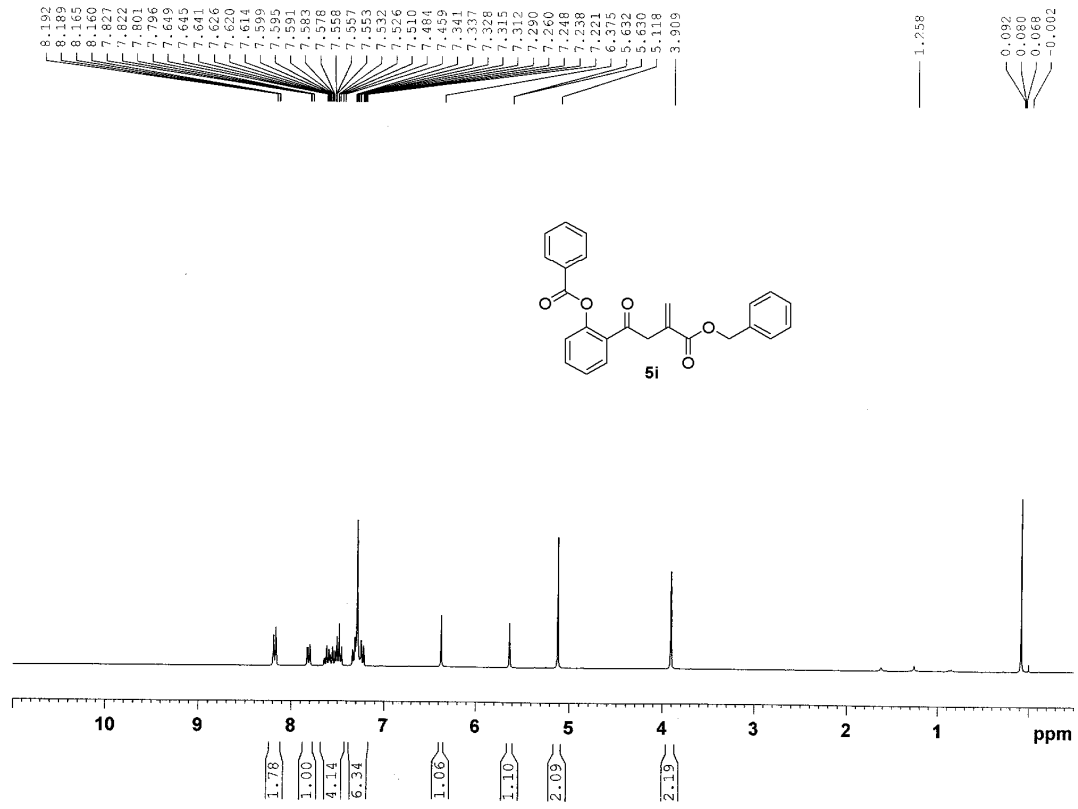
1.143
5h
ppm
200
150
100
50
0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7.645
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7.626
7.620
7.614
7.599
7.595
7.591
7.583
7.578
7.558
7.557
7.553
7.532
7.526
7.510
7.484
7.459
7.341
7.337
7.328
7.315
7.312
7.290
7.260
7.248
7.238
7.221
6.375
5.632
5.630
5.118
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0.080
0.068
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5i
10
9
8
7
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2
1
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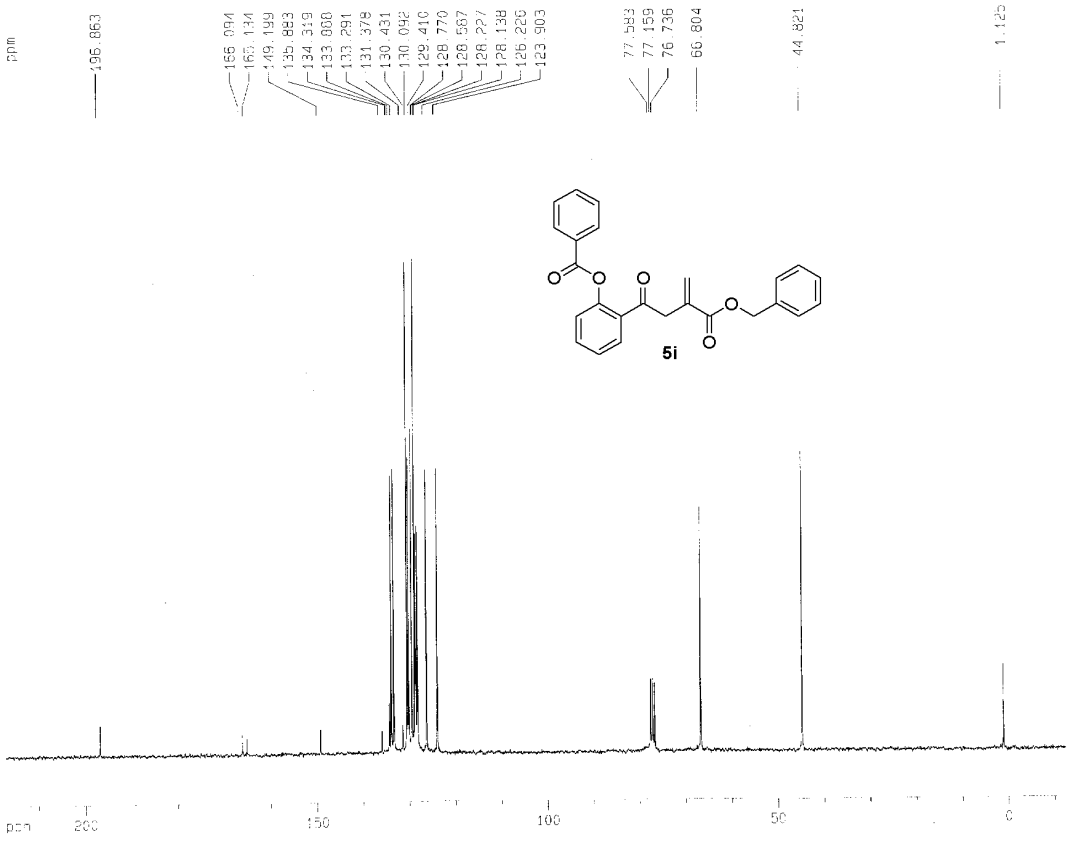
2.19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129.410
128.770
128.567
128.227
128.138
126.226
123.903
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77.159
76.736
66.804
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5i
ppm
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100
50
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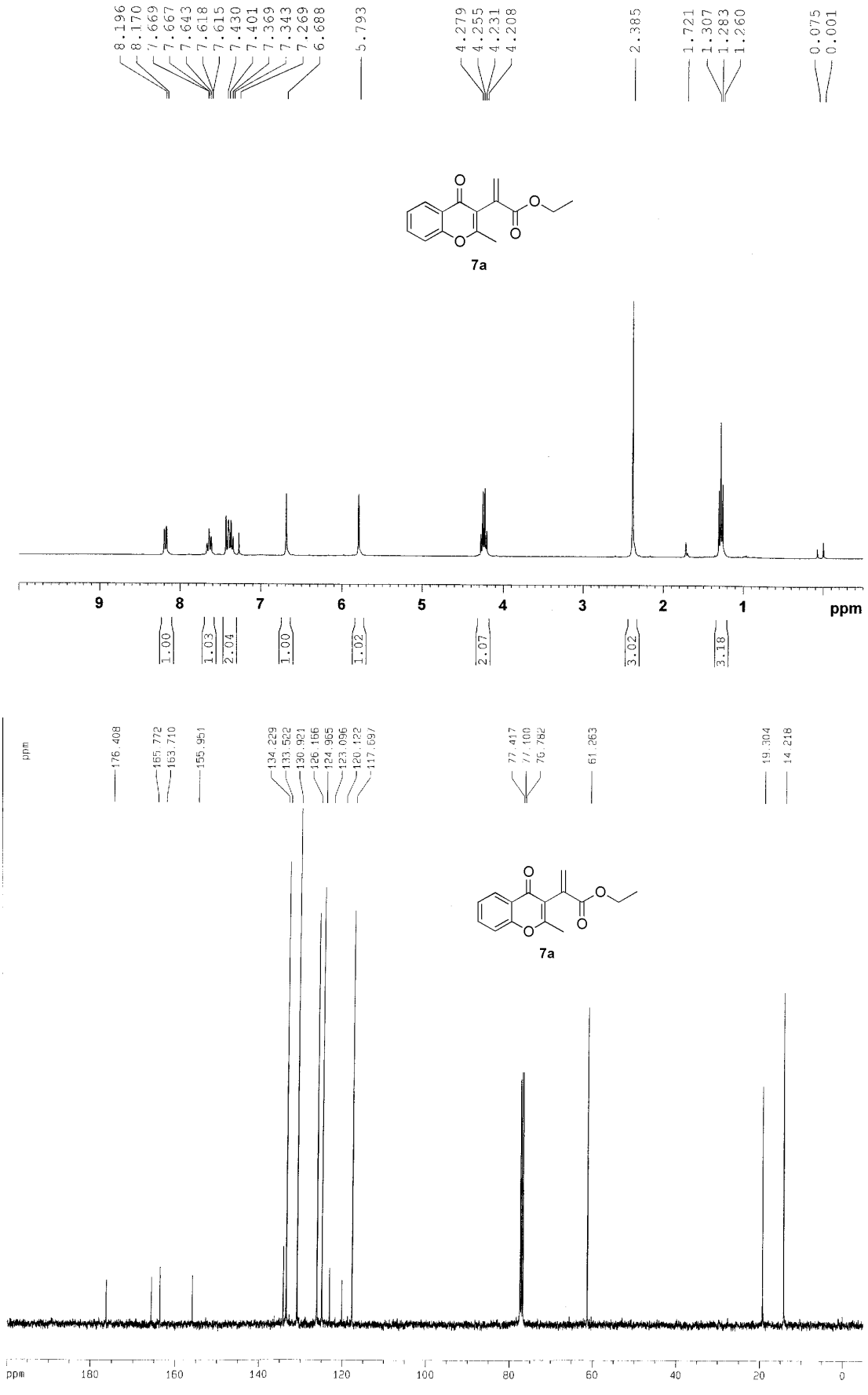
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7.369
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5.793
4.279
4.255
4.231
4.208
2.385
1.721
1.307
1.283
1.260
0.075
0.001
7a
9
8
7
6
5
4
3
2
1
ppm
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1.03
2.04
1.00
1.02
2.07
3.02
3.18
ppm
176.408
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163.710
155.951
134.229
133.522
130.921
126.166
124.965
123.096
120.122
117.697
77.417
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19.304
14.218
7a
ppm
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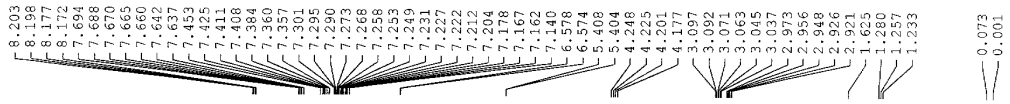
140
120
100
80
60
40
20
0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7.408
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7.360
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7.295
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7.273
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7.249
7.231
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7.178
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7.162
7.140
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4.177
3.097
3.092
3.071
3.063
3.045
3.037
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2.926
2.921
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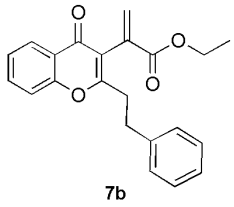
1.280
1.257
1.233
0.073
0.001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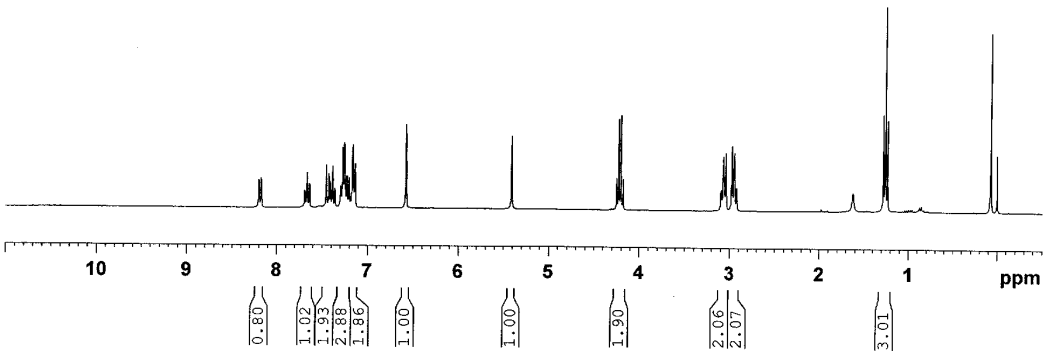
O
O
O

7b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9
8
7
6
5
4
3
2
1
ppm
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2.88
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1.00
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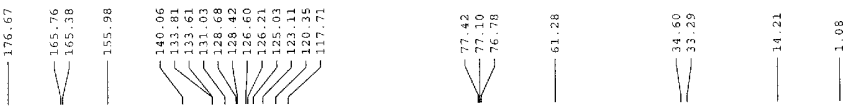
2.07
3.01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128.42
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126.21
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117.71
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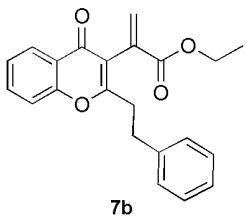
61.28
34.60
33.29
14.21
1.08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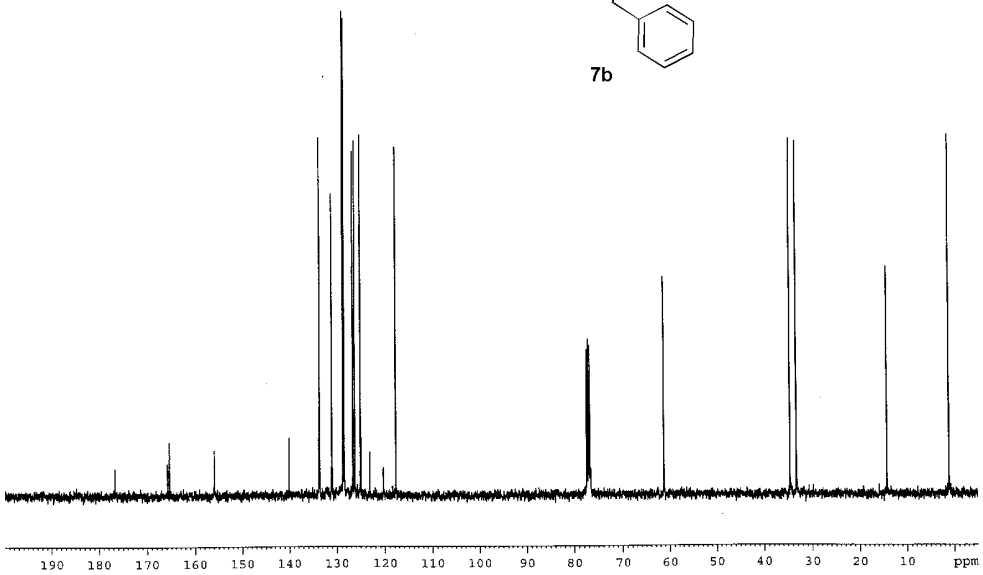
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130
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110
100
90
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70
60
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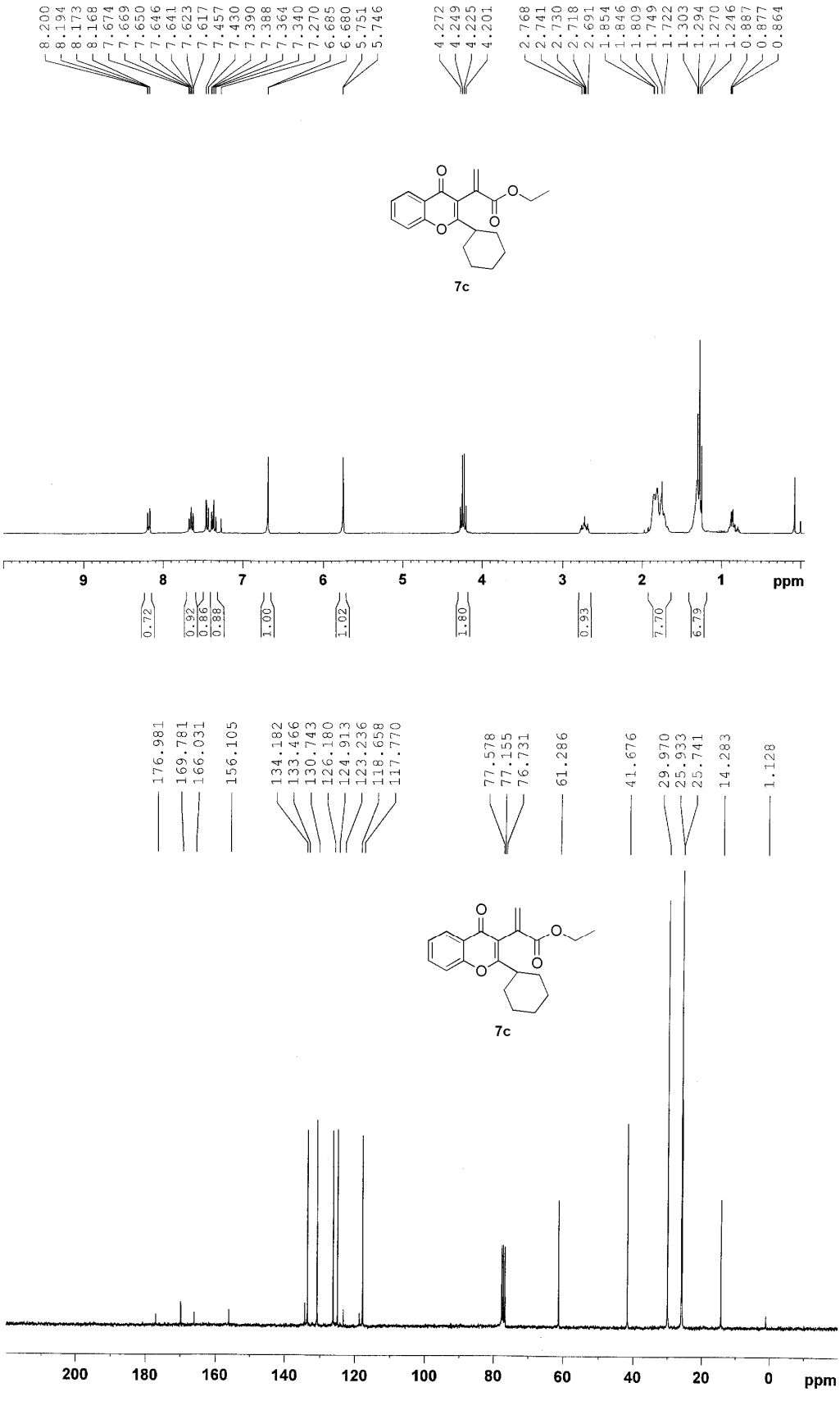
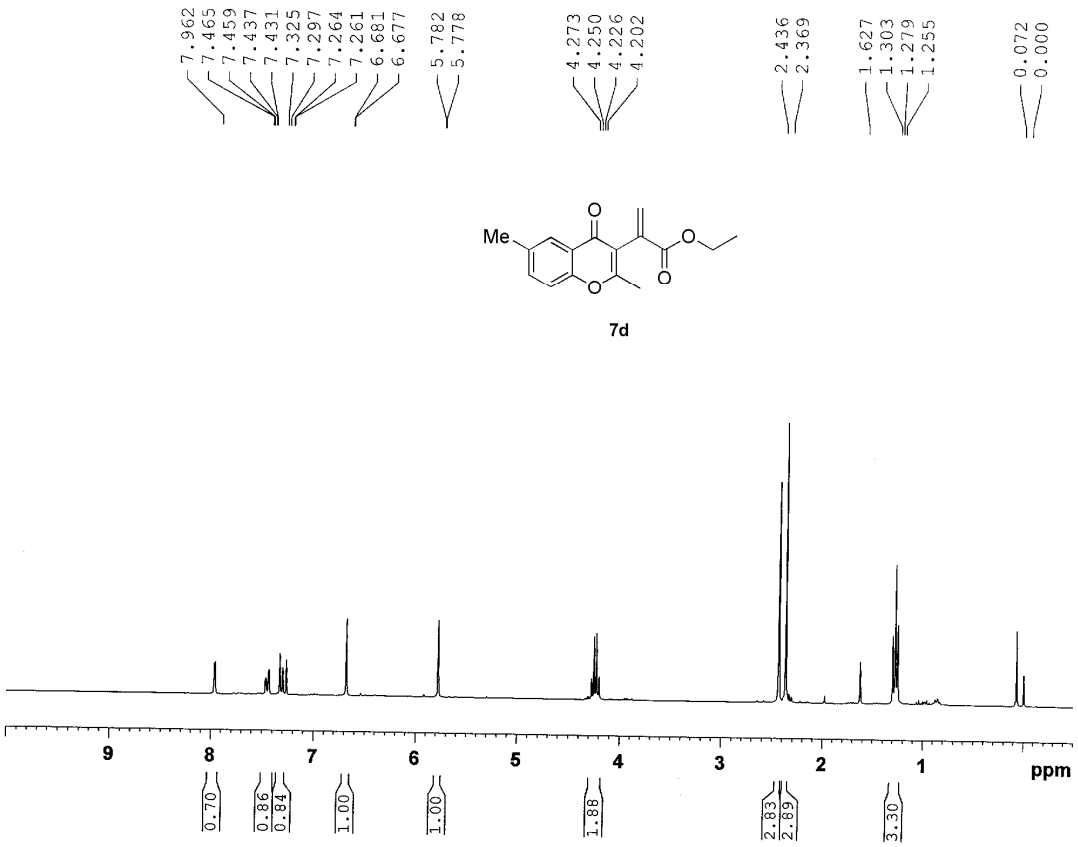
40
30
20
10
ppm

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7.264
7.261
6.681
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5.778
4.273
4.250
4.226
4.202
2.436
2.369
1.627
1.303
1.279
1.255
0.072
0.000
Me
O
O
O
O
9
8
7
6
5
4
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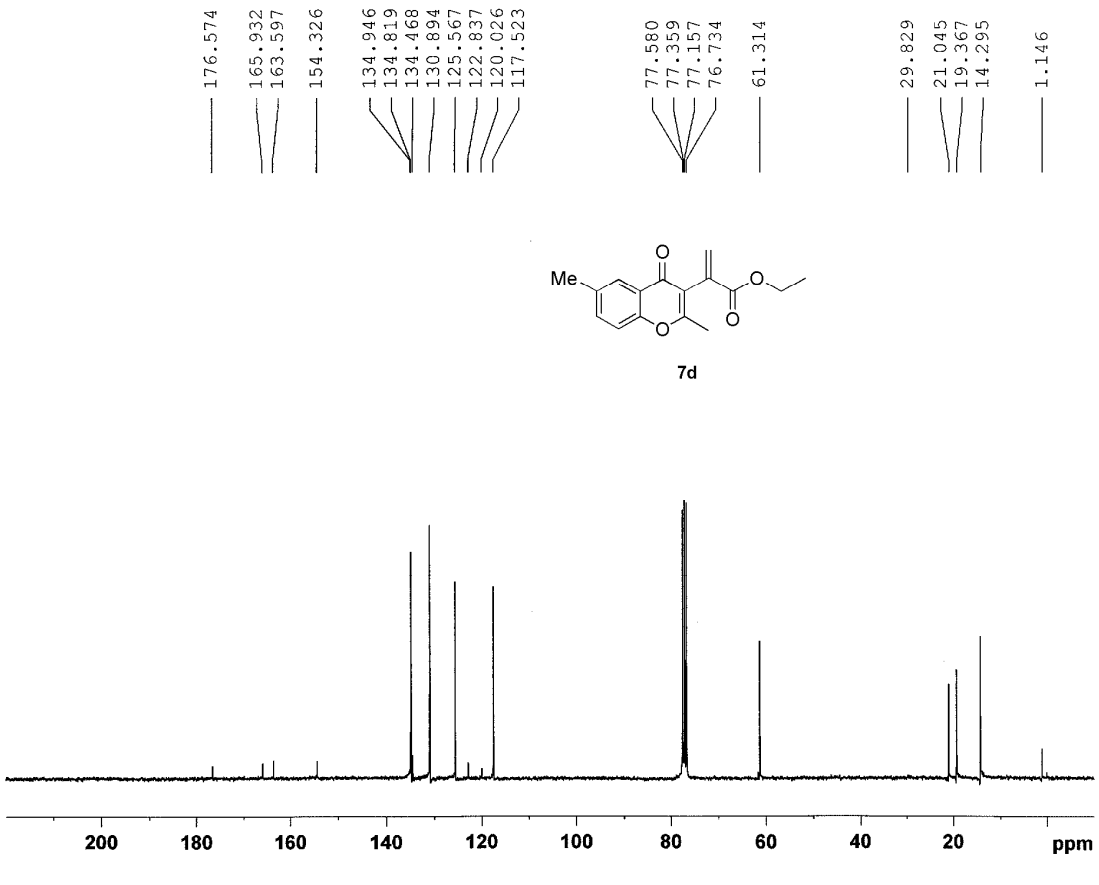
7d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130.894
125.567
122.837
120.026
117.523
77.580
77.359
77.157
76.734
61.314
29.829
21.045
19.367
14.295
1.146
Me
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O
O
O
200
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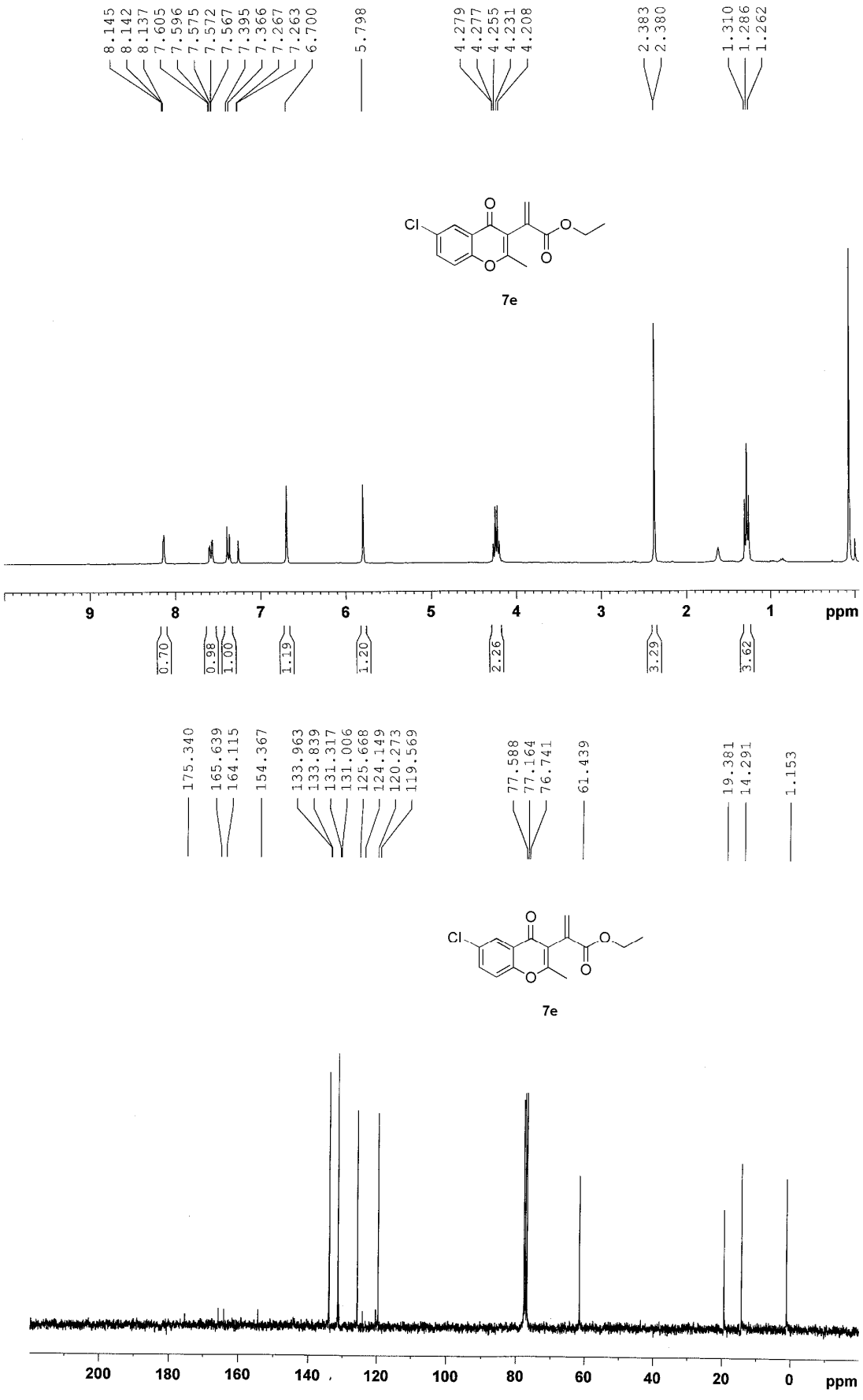
160
140
120
100
80
60
40
20
ppm

7d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7.267
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6.700
5.798
4.279
4.277
4.255
4.231
4.208
2.383
2.380
1.310
1.286
1.262
Cl
O
O
O
O
7e
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6
5
4
3
2
1
ppm
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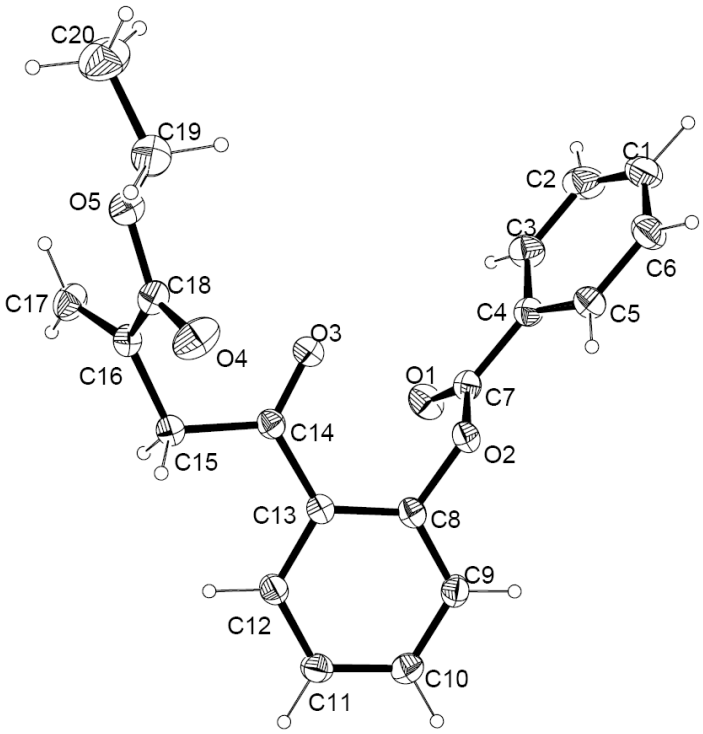
3.29
3.62
175.340
165.639
164.115
154.367
133.963
133.839
131.317
131.006
125.668
124.149
120.273
119.569
77.588
77.164
76.741
61.439
19.381
14.291
1.153
Cl
O
O
O
O
7e
200
180
160
140
120
100
80
60
40
20
0
ppm

Figure 1. X-ray crytal structure and data for compound 3a



The crystal data of 3a has been deposited in CCDC with number 711329. Empirical Formula: $C_{20}H_{18}O_5$; Formula Weight: 338.34; Crystal color, Habit: colorless, prismatic; Crystal Dimensions: 0.42 × 0.40 × 0.34 mm; Crystal System: monoclinic; Lattice Type: primitive; Lattice Parameters: a = 11.165(5)Å, b = 6.291(5)Å, c = 13.510 (5) Å, α = 90.000(5)°, β = 114.011(5)°, γ = 90.000(5)°, V= 866.8(9) Å^3; Space group: P 21; Z = 2; D_{calc} = 1.296 g/cm^3; F_{000} = 356 ; Diffractometer: Gemini s ultra oxford diffraction; Residuals: R; Rw: 0.0222, 0.0597.

Table 1. Crystal data and structure refinement for 081121-CU2.

Identification code	081121-cu2
Empirical formula	C20 H18 O5
Formula weight	338.34
Temperature	297(2) K
Wavelength	1.54184 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 11.165(5) A alpha = 90.000(5) deg. b = 6.291(5) A beta = 114.011(5) deg. c = 13.510(5) A gamma = 90.000(5) deg.
Volume	866.8(9) A^3
Z, Calculated density	2, 1.296 Mg/m^3
Absorption coefficient	0.768 mm^-1
F(000)	356
Crystal size	0.42 x 0.40 x 0.34 mm
Theta range for data collection	4.36 to 61.14 deg.
Limiting indices	-12<=h<=12, -6<=k<=6, -14<=l<=15
Reflections collected / unique	6079 / 2246 [R(int) = 0.0103]
Completeness to theta = 61.14	97.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7802 and 0.7385
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2246 / 1 / 298
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0222, wR2 = 0.0597
R indices (all data)	R1 = 0.0225, wR2 = 0.0600
Absolute structure parameter	-0.02(13)
Largest diff. peak and hole	0.078 and -0.080 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 081121-CU2.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(2)	3958(1)	4125(2)	6438(1)	49(1)
O(3)	2743(1)	7197(2)	7102(1)	61(1)
O(1)	5589(1)	6457(2)	7215(1)	68(1)
O(5)	21(1)	9239(2)	7957(1)	59(1)
C(13)	2734(1)	7121(2)	5340(1)	46(1)
C(15)	1388(1)	9821(3)	5904(1)	55(1)
C(14)	2329(1)	7956(2)	6197(1)	46(1)
O(4)	-307(1)	7321(2)	6487(1)	83(1)
C(5)	4940(1)	1433(3)	8180(1)	58(1)
C(10)	3407(1)	5611(3)	3686(1)	58(1)

C(4)	5466(1)	3429(2)	8223(1)	48(1)
C(3)	6452(2)	4112(4)	9184(1)	68(1)
C(9)	3841(1)	4559(2)	4667(1)	54(1)
C(8)	3515(1)	5323(2)	5479(1)	47(1)
C(7)	5044(1)	4867(2)	7275(1)	48(1)
C(12)	2314(1)	8151(2)	4337(1)	52(1)
C(16)	984(1)	10434(2)	6798(1)	51(1)
C(18)	170(1)	8836(2)	7045(1)	52(1)
C(1)	6348(2)	815(4)	10022(2)	83(1)
C(6)	5387(2)	126(3)	9075(1)	75(1)
C(17)	1281(2)	12264(3)	7305(2)	68(1)
C(19)	-749(2)	7739(3)	8261(2)	72(1)
C(2)	6883(2)	2780(5)	10082(1)	88(1)
C(20)	-893(3)	8637(5)	9224(2)	107(1)
C(11)	2655(1)	7413(3)	3522(1)	56(1)

Table 3. Bond lengths [A] and angles [deg] for 081121-CU2.

O(2)-C(7)	1.3604(16)
O(2)-C(8)	1.4035(16)
O(3)-C(14)	1.2152(16)
O(1)-C(7)	1.1906(19)
O(5)-C(18)	1.3333(17)
O(5)-C(19)	1.444(2)
C(13)-C(8)	1.393(2)
C(13)-C(12)	1.3997(19)
C(13)-C(14)	1.5001(18)
C(15)-C(16)	1.502(2)
C(15)-C(14)	1.516(2)
O(4)-C(18)	1.197(2)
C(5)-C(6)	1.376(2)
C(5)-C(4)	1.378(2)
C(10)-C(11)	1.374(2)
C(10)-C(9)	1.381(2)
C(4)-C(3)	1.385(2)
C(4)-C(7)	1.480(2)
C(3)-C(2)	1.390(3)
C(9)-C(8)	1.375(2)
C(12)-C(11)	1.383(2)
C(16)-C(17)	1.312(2)
C(16)-C(18)	1.481(2)
C(1)-C(2)	1.360(3)
C(1)-C(6)	1.364(3)
C(19)-C(20)	1.486(3)
C(7)-O(2)-C(8)	116.29(10)
C(18)-O(5)-C(19)	116.81(13)
C(8)-C(13)-C(12)	116.85(11)
C(8)-C(13)-C(14)	123.30(11)
C(12)-C(13)-C(14)	119.85(12)
C(16)-C(15)-C(14)	113.04(11)
O(3)-C(14)-C(13)	121.92(12)
O(3)-C(14)-C(15)	120.42(11)
C(13)-C(14)-C(15)	117.65(11)
C(6)-C(5)-C(4)	120.81(16)
C(11)-C(10)-C(9)	120.14(14)
C(5)-C(4)-C(3)	118.95(15)
C(5)-C(4)-C(7)	122.76(12)
C(3)-C(4)-C(7)	118.28(14)
C(4)-C(3)-C(2)	119.5(2)
C(8)-C(9)-C(10)	119.70(14)
C(9)-C(8)-C(13)	121.99(12)
C(9)-C(8)-O(2)	116.13(12)
C(13)-C(8)-O(2)	121.80(11)
O(1)-C(7)-O(2)	122.67(12)
O(1)-C(7)-C(4)	125.48(12)
O(2)-C(7)-C(4)	111.82(12)
C(11)-C(12)-C(13)	121.51(14)
C(17)-C(16)-C(18)	121.74(14)
C(17)-C(16)-C(15)	123.42(15)
C(18)-C(16)-C(15)	114.81(13)
O(4)-C(18)-O(5)	122.87(13)
O(4)-C(18)-C(16)	123.69(13)

O(5)-C(18)-C(16)	113.44(12)
C(2)-C(1)-C(6)	120.22(18)
C(1)-C(6)-C(5)	120.0(2)
O(5)-C(19)-C(20)	106.80(17)
C(1)-C(2)-C(3)	120.56(18)
C(10)-C(11)-C(12)	119.79(14)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 081121-CU2. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(2)	48(1)	41(1)	51(1)	6(1)	14(1)	0(1)
O(3)	72(1)	63(1)	50(1)	10(1)	26(1)	15(1)
O(1)	66(1)	58(1)	73(1)	7(1)	22(1)	-18(1)
O(5)	62(1)	56(1)	62(1)	-5(1)	29(1)	-8(1)
C(13)	44(1)	44(1)	47(1)	3(1)	17(1)	1(1)
C(15)	59(1)	53(1)	53(1)	7(1)	24(1)	11(1)
C(14)	47(1)	43(1)	47(1)	2(1)	18(1)	-1(1)
O(4)	88(1)	77(1)	95(1)	-40(1)	48(1)	-36(1)
C(5)	61(1)	56(1)	58(1)	6(1)	24(1)	-1(1)
C(10)	59(1)	63(1)	56(1)	-5(1)	29(1)	1(1)
C(4)	43(1)	53(1)	50(1)	0(1)	21(1)	2(1)
C(3)	56(1)	80(1)	59(1)	-4(1)	14(1)	-4(1)
C(9)	53(1)	49(1)	59(1)	-1(1)	22(1)	7(1)
C(8)	44(1)	43(1)	50(1)	4(1)	15(1)	-1(1)
C(7)	45(1)	45(1)	54(1)	-1(1)	21(1)	0(1)
C(12)	52(1)	52(1)	52(1)	7(1)	21(1)	8(1)
C(16)	49(1)	48(1)	55(1)	1(1)	20(1)	5(1)
C(18)	45(1)	52(1)	56(1)	-8(1)	18(1)	-1(1)
C(1)	86(1)	102(2)	65(1)	26(1)	37(1)	28(1)
C(6)	83(1)	73(1)	77(1)	25(1)	43(1)	13(1)
C(17)	79(1)	51(1)	85(1)	-10(1)	44(1)	-7(1)
C(19)	69(1)	68(1)	89(1)	4(1)	41(1)	-9(1)
C(2)	68(1)	130(2)	50(1)	-1(1)	9(1)	15(1)
C(20)	127(2)	108(2)	124(2)	-6(2)	90(2)	-17(2)
C(11)	60(1)	63(1)	47(1)	5(1)	23(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 081121-CU2.

	x	y	z	U(eq)
H(12)	1760(15)	9410(30)	4191(12)	56(4)
H(3)	6803(18)	5380(40)	9162(14)	71(5)
H(15B)	621(16)	9390(30)	5263(14)	70(5)
H(19B)	-250(19)	6420(40)	8498(15)	86(6)
H(10)	3612(15)	5060(30)	3130(13)	74(5)
H(5)	4250(17)	950(40)	7514(14)	79(5)
H(11)	2380(14)	8160(30)	2844(13)	59(4)
H(17B)	1729(18)	13330(40)	7087(14)	79(5)
H(1)	6706(19)	-170(40)	10673(18)	95(6)
H(15A)	1838(16)	11060(40)	5748(13)	72(5)
H(20A)	80(40)	8650(60)	9850(30)	143(11)
H(9)	4339(14)	3360(30)	4776(12)	58(4)
H(19A)	-1565(18)	7510(30)	7653(14)	71(5)
H(17A)	997(16)	12560(40)	7881(14)	75(5)
H(20B)	-1350(30)	7550(60)	9510(20)	140(10)
H(6)	4990(20)	-1230(50)	9057(18)	100(7)
H(2)	7500(30)	3360(50)	10680(20)	128(9)
H(20C)	-1350(30)	10040(60)	9030(20)	130(10)

Table 6. Torsion angles [deg] for 081121-CU2.

C(8)-C(13)-C(14)-O(3)	5.64(19)
C(12)-C(13)-C(14)-O(3)	-174.97(13)
C(8)-C(13)-C(14)-C(15)	-175.12(12)
C(12)-C(13)-C(14)-C(15)	4.28(18)
C(16)-C(15)-C(14)-O(3)	-4.4(2)
C(16)-C(15)-C(14)-C(13)	176.32(12)
C(6)-C(5)-C(4)-C(3)	-0.3(2)
C(6)-C(5)-C(4)-C(7)	178.26(13)
C(5)-C(4)-C(3)-C(2)	-0.3(2)
C(7)-C(4)-C(3)-C(2)	-178.94(14)
C(11)-C(10)-C(9)-C(8)	0.1(2)
C(10)-C(9)-C(8)-C(13)	1.1(2)
C(10)-C(9)-C(8)-O(2)	178.01(12)
C(12)-C(13)-C(8)-C(9)	-1.25(18)
C(14)-C(13)-C(8)-C(9)	178.16(12)
C(12)-C(13)-C(8)-O(2)	-177.95(11)
C(14)-C(13)-C(8)-O(2)	1.47(18)
C(7)-O(2)-C(8)-C(9)	100.88(14)
C(7)-O(2)-C(8)-C(13)	-82.23(14)
C(8)-O(2)-C(7)-O(1)	0.99(18)
C(8)-O(2)-C(7)-C(4)	-176.98(10)
C(5)-C(4)-C(7)-O(1)	-168.12(14)
C(3)-C(4)-C(7)-O(1)	10.5(2)
C(5)-C(4)-C(7)-O(2)	9.79(17)
C(3)-C(4)-C(7)-O(2)	-171.59(12)
C(8)-C(13)-C(12)-C(11)	0.17(19)
C(14)-C(13)-C(12)-C(11)	-179.26(12)
C(14)-C(15)-C(16)-C(17)	115.12(17)
C(14)-C(15)-C(16)-C(18)	-67.14(16)
C(19)-O(5)-C(18)-O(4)	0.3(2)
C(19)-O(5)-C(18)-C(16)	-179.32(13)
C(17)-C(16)-C(18)-O(4)	166.87(16)
C(15)-C(16)-C(18)-O(4)	-10.92(19)
C(17)-C(16)-C(18)-O(5)	-13.47(19)
C(15)-C(16)-C(18)-O(5)	168.75(11)
C(2)-C(1)-C(6)-C(5)	-1.0(3)
C(4)-C(5)-C(6)-C(1)	1.0(2)
C(18)-O(5)-C(19)-C(20)	-174.07(18)
C(6)-C(1)-C(2)-C(3)	0.4(3)
C(4)-C(3)-C(2)-C(1)	0.2(3)
C(9)-C(10)-C(11)-C(12)	-1.1(2)
C(13)-C(12)-C(11)-C(10)	1.0(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 081121-CU2 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)