Accessing polysubstituted 2-cyclopentenones *via* base mediated annulation of β-keto esters and phenacyl bromides

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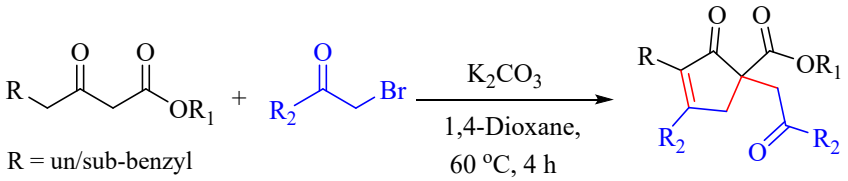
1. General Information

All reactions were performed under argon atmosphere with oven or flame dried glassware with septum sealed. Anhydrous Acetonitrile, 1,4-Dioxane, Ethanol, Methanol were purchased from commercial sources and used as such while performing the reactions. Chromatography was performed on silica gel (100-200 mesh) by standard techniques eluting with solvents as indicated. Visualization was accomplished with short UV light, anisaldehyde staining solutions followed by heating. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 400 and 500 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ H = 7.27 ppm, δ C = 77.00 ppm), the following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; td, triplet doublet; and br, broad. HRMS data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump, FT-IR instrument (Bruker Alpha Model) at normal temperature with a NaCl pellet (IR grade).

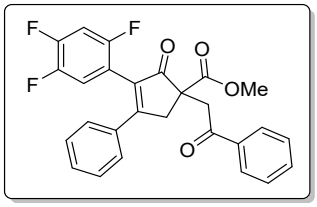
2. General procedure for the Synthesis Of Highly Functionalized Cyclopent-2-Enones (A):



R = un/sub-benzyl
R_1= Me, Et
R_2= un/sub-benzyl, Naphthyl

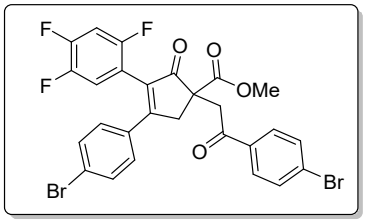
To a solution of aryl β-Keto ester (**1**, 1 equiv) in 4 mL of 1,4-Dioxane, phenacyl bromide (**2**, 2 equiv) and K_2CO_3 (2 equiv) were added in a dry 25 mL single neck round bottom flask under the argon atmosphere and the mixture was stirred for 4-7 h at 60 °C. After completion of the reaction, ethyl acetate (20 mL) and water (20 mL) were added. The two phases were separated, and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (100-200 mesh size) using petroleum ether/ethyl acetate as eluting system to obtain cyclopent-2-enones derivatives in 41-93% yields.

3. Characterization of the Products.



3a

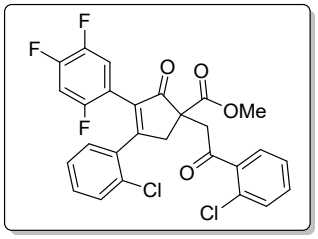
Methyl 2-oxo-1-(2-oxo-2-phenylethyl)-4-phenyl-3-(2,4,5-trifluorophenyl) cyclopent-3-ene-1-carboxylate (3a). Following the general procedure **A**, **3a** was prepared from methyl 3-oxo-4-(2,4,5-trifluorophenyl)butanoate **1a** (0.200 g, 0.813 mmol), 2-bromo-1-phenylethan-1-one **2a** (0.323 g, 1.626 mmol), and K_2CO_3 (0.224 g, 1.626 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.306 g (81%); *Rf*: 0.5 (Ethyl acetate: pet ether 1:10), **M.P:** 109-111 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.89 – 7.98 (m, 2H), 7.48 – 7.58 (m, 1H), 7.39 – 7.45 (m, 2H), 7.24 – 7.39 (m, 5H), 7.05 (ddd, *J* = 10.07, 8.88, 6.44 Hz, 1H), 6.87 (td, *J* = 9.44, 6.63 Hz, 1H), 4.19 (d, *J* = 18.39 Hz, 1H), 4.06 (d, *J* = 18.76 Hz, 1H), 3.67 (s, 3H), 3.30 (d, *J* = 18.39 Hz, 1H), 3.04 (d, *J* = 18.76 Hz, 1H); **^{13}C NMR** (100 MHz, CDCl3): δ ppm 200.2, 195.9, 170.0, 168.8, 155.4 – 152.9 (ddd, *J* = 249.67, 11.16, 2.29 Hz), 150.4 – 147.8 (ddd, *J* = 253.30, 12.30, 2.29 Hz), 147.1 – 144.7 (ddd, *J* = 255.19, 12.82, 2.29 Hz), 135.1, 133.3, 132.7, 130.2, 128.5, 127.7 (2C), 127.7 (2C), 127.1 (2C), 126.7 (2C), 118.1 (dd, *J* = 18.31, 3.82 Hz), 115.5 (dd, *J* = 17.31, 3.62 Hz), 105.1 (dd, *J* = 27.47, 20.60 Hz), 55.6, 52.2, 43.0, 40.6 ; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.27 (dd, *J* =15.78 Hz), −132.41 (dd, *J* = 23.68 Hz), −142.0 (dd, *J* = 23.68 Hz); **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{20}O_4F_3^+$, 465.1308, found, 465.1303.



3b

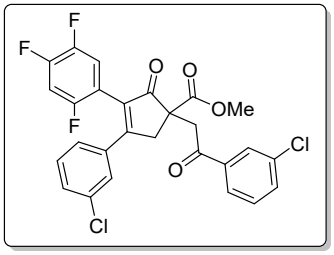
methyl 4-(4-bromophenyl)-1-(2-(4-bromophenyl)-2-oxoethyl)-2-oxo-3-(2,4,5-trifluorophenyl) cyclo - pent-3-ene-1-carboxylate (3b). Following the general procedure **A**, **3b** was prepared from methyl 3-oxo-4-(2,4,5-tri fluorophenyl)butanoate **1b** (0.200 g, 0.813 mmol), 2-bromo-1-(4-bromophenyl)ethan-1-one **2b** (0.452 g, 1.626 mmol), and K_2CO_3 (0.224 g, 1.626 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.389 g (77%); *Rf*: 0.5 (Ethyl acetate: pet ether 1:10), **M.P:** 160 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.73 – 7.83 (m, 2H), 7.53 – 7.60 (m, 2H), 7.38 – 7.46 (m, 2H), 7.15 – 7.22 (m, 2H), 7.04 (ddd, *J* = 10.1, 8.8, 6.4 Hz, 1H), 6.88 (ddd, *J* = 9.8, 9.0, 6.6 Hz, 1H), 4.12 (d, *J* = 18.4 Hz, 1H), 3.96 (d, *J* = 18.6 Hz, 1H), 3.66 (s, 3H), 3.26 (d, *J* = 18.4 Hz, 1H), 3.01 ppm (d, *J* = 18.6 Hz, 1H); **^{13}C NMR** (100 MHz, CDCl3): δ

ppm 199.3, 194.5, 168.2, 166.9, 155.1 – 152.6 (ddd, *J* = 246.67, 9.96, 2.29 Hz), 150.9 – 148.4 (ddd, *J* = 254.82, 14.50, 12.21 Hz), 149.7, 147.2 – 144.8 (ddd, *J* = 246.19, 12.21, 2.29 Hz), 147.8, 139.6, 139.2, 131.1, 128.2 (2C), 127.3 (2C), 123.0 (2C), 118.0 (dd, *J* = 19.84, 4.58 Hz), 113.9 (dd, *J* = 19.31, 4.58 Hz) , 106.3, 105.5 (dd, *J* = 28.23, 21.36 Hz), 55.6, 52.5, 42.9, 40.5; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.10 (dd, *J* =15.26 Hz), −131.70 (dd, *J* = 20.81 Hz), −141.52 (dd, J = 20.81 Hz); **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{18}O_4Br^{81}BrF_3^+$, 622.9539, found, 622.9553.



3c

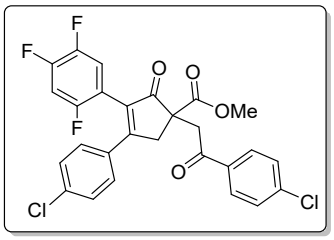
methyl 4-(2-chlorophenyl)-1-(2-(2-chlorophenyl)-2-oxoethyl)-2-oxo-3-(2,4,5-trifluorophenyl) cyclo -pent-3-ene-1-carboxylate (3c). Following the general procedure **A**, **3c** was prepared from methyl 3-oxo-4-(2,4,5-tri fluorophenyl)butanoate **1c** (0.200 g, 0.813 mmol), 2-bromo-1-(2-chlorophenyl)ethan-1-one **2c** (0.379 g, 1.626 mmol), and K_2CO_3 (0.224 g, 1.626 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.178 g (41%); *Rf*: 0.4 (Ethyl acetate: pet ether 1:10), **M.P:** 62 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.56 – 7.61 (m, 1H), 7.39 – 7.44 (m, 3H), 7.31 – 7.38 (m, 2H), 7.26 – 7.30 (m, 1H), 7.17 – 7.22 (m, 1H), 7.02 (ddd, *J* = 10.32, 8.82, 6.38 Hz, 1H), 6.82 (td, *J* = 9.54, 6.57 Hz, 1H), 4.12 (d, *J* = 18.64 Hz, 1H), 3.96 (d, *J* = 19.14 Hz, 1H), 3.45 (d, *J* = 18.64 Hz, 1H), 3.23 (d, *J* = 19.14 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 199.5, 198.7, 171.0, 168.5, 155.4 – 152.9 (ddd, *J* = 248.72, 11.44, 1.53 Hz), 150.4 – 147.9 (ddd, *J* = 254.90, 12.97, 3.05 Hz), 146.7 – 144.3 (ddd, *J* = 245.67, 12.21, 3.05 Hz), 137.2, 133.7, 132.5, 131.2, 130.2, 130.0, 129.7, 129.6, 129.2, 128.1, 127.5, 126.1, 126.0, 117.7 (dd, *J* = 19.84, 5.34 Hz), 114.1 (dd, *J* = 19.07, 6.87 Hz), 104.8 (dd, *J* = 27.47, 20.60 Hz), 56.2, 52.3, 46.3, 42.0; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.14 (dd, *J* =15.78 Hz), −132.22 (dd, *J* = 15.79 Hz), −142.51 (dd, *J* = 19.73 Hz); **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{18}O_4Cl_2F_3^+$, 533.0529, found, 533.0528.



3d

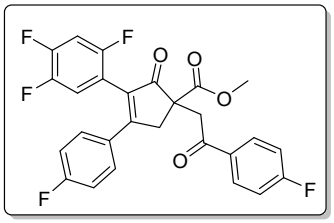
methyl 4-(3-chlorophenyl)-1-(2-(3-chlorophenyl)-2-oxoethyl)-2-oxo-3-(2,4,5-trifluorophenyl) cyclo -pent-3-ene-1-carboxylate (3d). Following the general procedure **A**, **3d** was prepared from methyl 3-oxo-4-(2,4,5-tri fluorophenyl)butanoate **1d** (0.200 g, 0.813 mmol), 2-bromo-1-(3-chlorophenyl)ethan-1-one **2d**

(0.379 g, 1.626 mmol), and K_2CO_3 (0.224 g, 1.626 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.277 g (64%); *Rf*: 0.5 (Ethyl acetate: pet ether 1:10), **M.P:** 98 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.96 (t, *J* = 1.69 Hz, 1H), 7.87 (d, *J* = 7.75 Hz, 1H), 7.55 – 7.60 (m, 1H), 7.37 – 7.47 (m, 3H), 7.20 – 7.29 (m, 2H), 7.13 (ddd, *J* = 10.01, 8.88, 6.38 Hz, 1H), 6.95 (td, *J* = 9.41, 6.57 Hz, 1H), 4.19 (d, *J* = 18.51 Hz, 1H), 4.02 (d, *J* = 18.64 Hz, 1H), 3.74 (s, 3H), 3.37 (d, *J* = 18.51 Hz, 1H), 3.09 (d, *J* = 18.64 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 199.7, 194.7, 168.5, 168.1, 155.3 – 152.8 (ddd, *J* = 249.72, 9.44, 2.29 Hz), 150.7 – 148.2 (ddd, *J* = 254.72, 12.44, 2.29 Hz), 147.1 – 144.7 (ddd, *J* = 242.72, 12.44, 3.81 Hz), 136.5, 135.1, 134.1, 133.9, 132.6, 130.0, 129.1, 129.0, 127.3, 126.5, 125.2, 124.7, 118.1 (dd, *J* = 19.84, 3.05 Hz), 114.7 (dd, *J* = 18.31, 3.82 Hz), 105.3 (dd, *J* = 27.47, 20.60 Hz), 55.5, 52.3, 42.8, 40.5; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.1 (dd, *J* =19.73 Hz), −131.61 (dd, *J* = 19.73 Hz), −141.57 (dd, *J* = 23.67 Hz); **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{18}O_4Cl_2F_3^+$, 533.0529, found, 533.0529.



3e

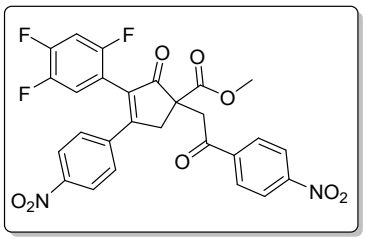
methyl 4-(4-chlorophenyl)-1-(2-(4-chlorophenyl)-2-oxoethyl)-2-oxo-3-(2,4,5-trifluorophenyl) cyclo -pent-3-ene-1-carboxylate (3e). Following the general procedure **A**, **3e** was prepared from methyl 3-oxo-4-(2,4,5-tri fluorophenyl)butanoate **1e** (0.200 g, 0.813 mmol), 2-bromo-1-(4-chlorophenyl)ethan-1-one **2e** (0.379 g, 1.626 mmol), and K_2CO_3 (0.224 g, 1.626 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.325 g (75%); *Rf*: 0.5 (Ethyl acetate: pet ether 1:10), **M.P:** 162-164 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 9.40 (br. s., 1H), 7.11 – 7.03 (m, 1H), 6.95 (td, *J* = 9.47, 2.88 Hz, 1H), 5.57 (br. s., 1H), 4.00 (s, 2H), 3.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 199.8, 194.7, 168.6, 168.3, 155.0 – 153.0 (ddd, *J* = 247.96, 9.63, 2.29 Hz), 150.3 – 148.3 (ddd, *J* = 253.68, 13.35, 3.86 Hz), 146.9 – 145.0 (ddd, *J* = 243.19, 9.54, 2.86 Hz), 139.2, 136.4, 133.3, 131.7, 128.8, 128.5 (2C), 128.1 (2C), 128.1 (2C), 127.9 (2C), 118.1 (dd, *J* = 19.83, 3.05 Hz), 114.9 (dd, *J* = 18.31, 3.82 Hz), 105.3 (dd, *J* = 27.45, 20.55 Hz) , 55.5, 52.3, 42.7, 40.4 ; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.10 (dd, *J* =15.79 Hz), −131.76 (dd, *J* = 23.67 Hz), −141.55 (dd, *J* = 23.67 Hz); HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{18}O_4Cl_2F_3^+$, 533.0529, found, 533.0526.



(3f)

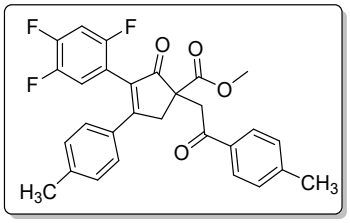
methyl 4-(4-fluorophenyl)-1-(2-(4-fluorophenyl)-2-oxoethyl)-2-oxo-3-(2,4,5-trifluorophenyl) cyclo -pent-3-ene-1-carboxylate (3f). Following the general procedure **A**, **3f** was prepared from methyl 3-oxo-4-

(2,4,5-tri fluorophenyl)butanoate **1f** (0.200 g, 0.813 mmol), 2-bromo-1-(4-fluorophenyl)ethan-1-one **2f** (0.353 g, 1.626 mmol), and K_2CO_3 (0.224 g, 1.626 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.301 g (74%); *Rf*: 0.3 (Ethyl acetate: pet ether 1:10), **M.P:** 130-132 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.98 – 8.07 (m, 2H), 7.35 – 7.49 (m, 2H), 7.13 – 7.18 (m, 2H), 7.08 – 7.13 (m, 1H), 7.01 – 7.07 (m, 2H), 6.95 (ddd, *J* = 9.9, 9.0, 6.6 Hz, 1H), 4.21 (d, *J* = 18.3 Hz, 1H), 4.07 (d, *J* = 18.5 Hz, 1H), 3.74 (s, 3H), 3.34 (d, *J* = 18.4 Hz, 1H), 3.11 ppm (d, *J* = 18.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 199.9, 194.4, 168.7, 168.4, 166.3 – 163.8 (d, *J* = 253.30 Hz), 164.5 − 161.9 (d, *J* = 254.06 Hz), 155.3 – 152.8 (ddd, *J* = 248.72, 9.92, 3.05 Hz), 150.6 – 148.0 (ddd, *J* = 253.30, 12.21, 2.27 Hz), 147.2 – 144.8 (ddd, *J* = 246.43, 12.21, 3.81 Hz), 131.5 (2C), 129.8 (2C), 129.4 (2C), 128.9 (2C), 128.3, 118.1 (dd, *J* = 19.84, 3.82 Hz), 115.1 (dd, *J* = 21.36, 16.02 Hz), 105.5 (dd, *J* = 27.47, 20.60 Hz), 55.5, 52.2, 42.8, 40.5; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −103.96, −107.28, −113.19 (dd, *J* =15.78 Hz), −131.96 (dd, *J* = 23.67 Hz), −141.67 (dd, *J* = 19.73 Hz); **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{17}O_4F_5Na^+$, 523.0939, found, 523.0938.



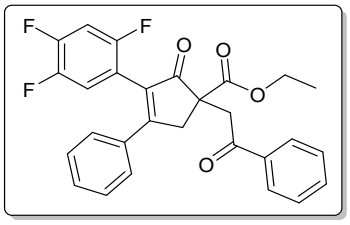
(3g)

methyl 4-(4-nitrophenyl)-1-(2-(4-nitrophenyl)-2-oxoethyl)-2-oxo-3-(2,4,5-trifluorophenyl)cyclopent-3-ene-1-carboxylate (3g). Following the general procedure **A**, **3g** was prepared from methyl 3-oxo-4-(2,4,5-tri fluorophenyl)butanoate **1g** (0.200 g, 0.813 mmol), 2-bromo-1-(4-nitrophenyl)ethan-1-one **2g** (0.397 g, 1.626 mmol), and K_2CO_3 (0.224 g, 1.626 mmol) in 1,4 dioxane at 60 °C as a yellow solid. Yield: 0.365 g (81%); *Rf*: 0.3 (Ethyl acetate: pet ether 2:10), **M.P:** 96-98 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.34 (d, *J* = 8.4 Hz, 2H), 8.21 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.11 – 7.24 (m, 1H), 6.88 – 7.04 (m, 1H), 4.26 (d, *J* = 18.5 Hz, 1H), 4.03 (d, *J* = 18.6 Hz, 1H), 3.77 (s, 3H), 3.52 (d, *J* = 18.5 Hz, 1H), 3.20 ppm (d, *J* = 18.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 199.3, 194.5, 168.2, 166.9, 155.1 – 152.6 (ddd, *J* = 249.72, 9.15, 3.05 Hz), 150.9 – 148.4 (ddd, *J* = 255.58, 14.50, 12.21 Hz), 149.7, 147.3 – 144.8 (ddd, *J* = 247.19, 12.97, 3.81 Hz), 147.7, 139.6, 139.2 (2C), 131.1, 128.2 (2C), 127.3 (2C), 122.9 (2C), 118.0 (dd, *J* = 19.84, 3.82 Hz), 114.1, 113.9 (dd, *J* = 18.31, 4.58 Hz), 105.5 (dd, *J* = 27.47, 20.60 Hz), 55.6, 52.6, 42.9, 40.5; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.03 (dd, *J* =15.26 Hz), −130.58 (dd, *J* = 20.81 Hz), −140.99 (dd, *J* = 22.19 Hz); **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{17}O_8N_2F_3Na^+$, 577.0829; found, 577.0829.



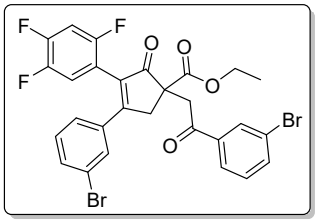
(3h)

methyl 2-oxo-1-(2-oxo-2-(p-tolyl)ethyl)-4-(p-tolyl)-3-(2,4,5-trifluorophenyl) cyclopent-3-ene-1-carboxylate (3h). Following the general procedure **A**, **3h** was prepared from methyl 3-oxo-4-(2,4,5-tri fluorophenyl)butanoate **1h** (0.200 g, 0.813 mmol), 2-bromo-1-(p-tolyl)ethan-1-one **2h** (0.346 g, 1.626 mmol), and K_2CO_3 (0.224 g, 1.626 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.260 g (65%); *Rf*: 0.3 (Ethyl acetate: pet ether 2:10), **M.P:** 163-165 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.81 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 8.1 Hz, 4H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.98 – 7.04 (m, 1H), 6.87 (td, *J* = 9.4, 6.6 Hz, 1H), 4.15 (d, *J* = 18.3 Hz, 1H), 4.04 (d, *J* = 18.6 Hz, 1H), 3.65 (s, 3H), 3.24 (d, *J* = 18.3 Hz, 1H), 3.01 (d, *J* = 18.8 Hz, 1H), 2.34 (s, 3H), 2.28 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.3, 195.6, 169.9, 168.9, 155.3 – 152.9 (ddd, *J* = 251.01, 9.16, 2.29 Hz), 150.3 – 147.8 (ddd, *J* = 252.53, 12.21, 3.86), 147.1 – 144.7 (ddd, *J* = 249.48, 9.54, 2.86 Hz), 143.6, 140.9, 132.6, 130.3, 128.5 (2C), 128.4 (2C), 127.5, 127.2 (2C), 126.8 (2C), 118.2 (dd, *J* = 19.76, 3.13 Hz), 115.7 (dd, J = 18.26, 3.82 Hz), 105.1 (dd, *J* = 28.45, 21.55 Hz), 55.5, 52.1, 43.0, 40.4, 20.7, 20.5; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.25 (dd, *J* =15.26 Hz), −132.65 (dd, *J* = 20.81 Hz), −142.10 (dd, *J* = 20.81 Hz); **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{24}O_4F_3^+$, 493.1621, found, 493.1616.



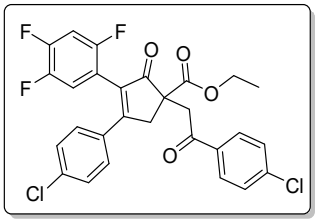
(3i)

Ethyl 2-oxo-1-(2-oxo-2-phenylethyl)-4-phenyl-3-(2,4,5-trifluorophenyl) cyclopent-3-ene-1-carboxylate (3i). Following the general procedure **A**, **3i** was prepared from ethyl 3-oxo-4-(2,4,5-tri fluorophenyl)butanoate **1i** (0.200 g, 0.769 mmol), 2-bromo-1-phenylethan-1-one **2i** (0.306 g, 1.538 mmol), and K_2CO_3 (0.212 g, 1.538 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.295 g (80%); *Rf*: 0.6 (Ethyl acetate: pet ether 1:10), **M.P:** 124-126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.96 – 8.06 (m, 2H), 7.57 – 7.63 (m, 1H), 7.45 – 7.51 (m, 2H), 7.37 – 7.44 (m, 3H), 7.31 – 7.37 (m, 2H), 7.10 (ddd, *J* = 10.2, 8.8, 6.4 Hz, 1H), 6.94 (ddd, *J* = 10.0, 8.9, 6.6 Hz, 1H), 4.14 – 4.30 (m, 3H), 4.09 (d, *J* = 18.6 Hz, 1H), 3.36 (d, *J* = 18.3 Hz, 1H), 3.13 (d, *J* = 18.6 Hz, 1H), 1.20 ppm (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.3, 196.0, 169.9, 168.3, 155.4 – 152.9 (ddd, *J* = 249.06, 11.23, 2.29 Hz), 150.4 – 147.9 (ddd, *J* = 252.56. 11.53, 3.84 Hz), 147.1 –144.7 (ddd, *J* = 249.36, 10.21, 2.89 Hz), 135.2, 133.3, 132.6, 130.1, 128.6, 127.7 (2C), 127.7 (2C), 127.1 (2C), 126.7 (2C), 118.1 (dd, *J* = 19.33, 3.25 Hz), 115.5 (dd, *J* = 18.65, 3.55 Hz), 105.1 (dd, *J* = 27.25, 21.46 Hz), 61.1, 55.7, 42.8, 40.6, 12.9; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.27 (dd, *J* =15.78 Hz), −132.41 (dd, *J* = 23.68 Hz), −142.0 (dd, *J* = 23.68 Hz); **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{22}O_4F_3^+$, 479.1465, found, 479.1460.



(3j)

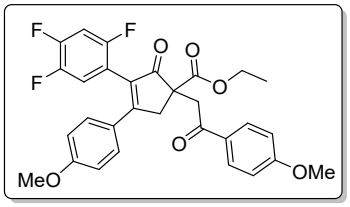
Ethyl 4-(3-bromophenyl)-1-(2-(3-bromophenyl)-2-oxoethyl)-2-oxo-3-(2,4,5-trifluorophenyl) cyclo -pent-3-ene-1-carboxylate (3j). Following the general procedure **A**, **3j** was prepared from ethyl 3-oxo-4-(2,4,5-tri fluorophenyl)butanoate **1j** (0.200 g, 0.769 mmol), 2-bromo-1-(3-bromophenyl)ethan-1-one **2j** (0.427 g, 1.538 mmol), and K_2CO_3 (0.212 g, 1.538 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.328 g (67%); *Rf*: 0.4 (Ethyl acetate: pet ether 1:10), **M.P:** 65 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.12 (t, *J* = 1.63 Hz, 1H), 7.91 (d, *J* = 7.88 Hz, 1H), 7.70 – 7.75 (m, 1H), 7.51 – 7.58 (m, 2H), 7.37 (t, *J* = 7.88 Hz, 1H), 7.25 – 7.30 (m, 1H), 7.17 – 7.24 (m, 1H), 7.10 (ddd, *J* = 10.07, 8.82, 6.38 Hz, 1H), 6.95 (td, *J* = 9.41, 6.57 Hz, 1H), 4.10 – 4.27 (m, 3H), 3.98 (d, *J* = 18.51 Hz, 1H), 3.36 (d, *J* = 18.39 Hz, 1H), 3.09 (d, *J* = 18.64 Hz, 1H), 1.21 (t, *J* = 7.07 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.8, 195.7, 168.9, 168.9, 156.4 – 153.9 (ddd, *J* = 254.09, 9.15, 2.29 Hz), 151.7 – 149.2 (ddd, *J* = 245.09, 12.21, 2.29 Hz), 148.2 – 145.8 (ddd, *J* = 246.43, 12.97, 3.05 Hz), 137.9, 136.5, 136.5, 133.9, 131.2, 130.8, 130.4, 130.3, 130.3, 126.7, 126.1, 123.1, 123.0, 119.1 (dd, *J* = 18.93, 3.29 Hz), 115.9 (dd, *J* = 18.25, 3.87 Hz), 106.3 (dd, *J* = 27.25, 21.46 Hz), 62.3, 56.7, 43.5, 41.6, 13.9; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.16 (dd, *J* =15.26 Hz), −131.65 (dd, *J* = 20.81 Hz), −141.57 (dd, *J* = 22.19 Hz); **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{20}O_4Br^{81}BrF_3^+$, 636.9654, found, 636.9623.



(3k)

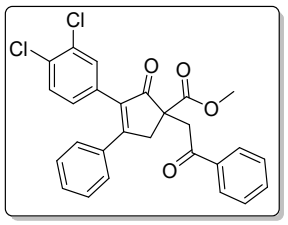
Ethyl 4-(4-chlorophenyl)-1-(2-(4-chlorophenyl)-2-oxoethyl)-2-oxo-3-(2,4,5-trifluorophenyl) cyclo -pent-3-ene-1-carboxylate (3k). Following the general procedure **A**, **3k** was prepared from ethyl 3-oxo-4-(2,4,5-tri fluorophenyl)butanoate **1k** (0.200 g, 0.769 mmol), 2-bromo-1-(4-chlorophenyl)ethan-1-one **2k** (0.452 g, 1.538 mmol), and K_2CO_3 (0.212 g, 1.538 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.332 g (79%); *Rf*: 0.5 (Ethyl acetate: pet ether 1:10), **M.P:** 69 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.90 – 7.98 (m, 2H), 7.42 – 7.49 (m, 2H), 7.33 (s, 4H), 7.10 (ddd, *J* = 10.1, 8.8, 6.4 Hz, 1H), 6.95 (ddd, *J* = 9.9, 8.9, 6.5 Hz, 1H), 4.11 – 4.28 (m, 3H), 4.02 (d, *J* = 18.5 Hz, 1H), 3.33 (d, *J* = 18.4 Hz, 1H), 3.10 (d, *J* = 18.5 Hz, 1H), 1.19 ppm (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.0, 194.8, 168.3, 168.0, 155.3 – 152.8 (ddd, *J* = 248.72, 9.15, 2.29 Hz), 150.5 – 148.1 (ddd, *J* = 253.30, 12.21, 2.29 Hz), 147.1 – 144.8 (ddd, *J* = 246.43, 12.93, 3.05 Hz), 139.2, 136.3, 133.5, 131.8, 129.0, 128.5, 128.1, 128.1, 127.9, 118.1 (dd, *J* = 19.84, 3.81 Hz), 115.0 (dd, *J* = 18.73, 3.85 Hz), 105.3 (dd, *J* = 27.22, 20.49 Hz), 61.2, 55.7,

42.5, 40.5, 12.9; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.34 (dd, *J* =15.78 Hz), −132.49 (dd, *J* = 20.81 Hz), −142..06 (dd, *J* = 23.67 Hz); **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{20}O_4Br^{81}BrF_3^+$, 636.9654; found, 636.9668.



(3l)

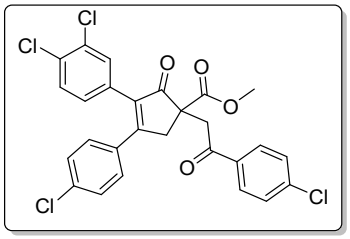
Ethyl 4-(4-methoxyphenyl)-1-(2-(4-methoxyphenyl)-2-oxoethyl)-2-oxo-3-(2,4,5-trifluorophenyl) cyclopent-3-ene-1-carboxylate (3l). Following the general procedure **A**, **3l** was prepared from ethyl 3-oxo-4-(2,4,5-tri fluorophenyl)butanoate **1l** (0.200 g, 0.789 mmol), 2-bromo-1-(4-methoxyphenyl)ethan-1-one **2l** (0.352 g, 1.538 mmol), and K_2CO_3 (0.212 g, 1.538 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.277 g (67%); *Rf*: 0.2 (Ethyl acetate: pet ether 1:10), **M.P:** 137 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.90 (d, *J* = 8.88 Hz, 2H), 7.25 – 7.36 (m, 2H), 7.02 (ddd, *J* = 10.19, 8.88, 6.44 Hz, 1H), 6.82 – 6.94 (m, 3H), 6.71 – 6.82 (m, 2H), 3.97 – 4.19 (m, 4H), 3.81 (s, 3H), 3.75 (s, 3H), 3.19 (d, *J* = 18.14 Hz, 1H), 3.03 (d, *J* = 18.51 Hz, 1H), 1.12 (t, *J* = 7.13 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.3, 194.6, 169.0, 168.5, 162.8, 161.0, 155.5 – 153.0 (ddd, *J* = 248.19, 9.15, 2.29 Hz), 150.4 – 147.2 (ddd, *J* = 245.46, 12.59, 2.29 Hz), 145.4 – 143.9 (ddd, *J* = 246.47, 12.25, 3.05 Hz), 129.4, 128.8, 128.4, 126.6, 125.6, 118.2 (dd, *J* = 18.58, 3.29 Hz), 116.1 (dd, *J* = 19.29, 3.47 Hz), 113.1, 112.8, 105.1 (dd, *J* = 27.57, 21.99 Hz), 60.9, 55.6, 54.5, 54.4, 42.7, 40.4, 12.9; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.34 (dd, *J* = 15.78 Hz), −132.82 (dd, *J* = 20.81 Hz), −140.7 (dd, *J* = 20.81 Hz); **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{30}H_{25}O_6F_3Na^+$, 561.1495, found, 561.1492.



(3m)

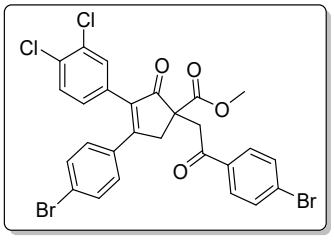
Methyl 3-(3,4-dichlorophenyl)-2-oxo-1-(2-oxo-2-phenylethyl)-4-phenylcyclopent-3-ene-1-carboxylate (3m). Following the general procedure **A**, **3m** was prepared from methyl 4-(3,4-dichlorophenyl)-3-oxobutanoate **1m** (0.200 g, 0.766 mmol), 2-bromo-1-phenylethan-1-one **2m** (0.305 g, 1.532 mmol), and K_2CO_3 (0.212 g, 1.532 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.301 g (82%); *Rf*: 0.5 (Ethyl acetate: pet ether 1:10), **M.P:** 164 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.95 – 8.02 (m, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.44 (m, 5H), 7.30 – 7.37 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 1H), 4.24 (d, *J* = 18.3 Hz, 1H), 4.05 (d, *J* = 18.8 Hz, 1H), 3.73 (s, 3H), 3.39 (d, *J* = 18.3 Hz, 1H), 3.04 ppm (d, *J* = 18.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.6, 195.9, 168.9, 168.6, 135.1, 133.3, 133.2, 132.6, 131.7, 131.3, 130.8, 130.4, 129.9, 129.5, 127.9 (2C), 127.7 (2C), 127.3

(2C), 127.1 (2C), 55.6, 52.2, 43.0, 40.7; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{21}O_4Cl_2^+$, 479.0811; found, 479.0813.



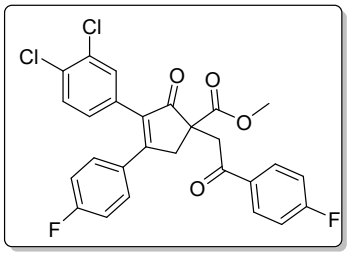
(3n)

Methyl 4-(4-chlorophenyl)-1-(2-(4-chlorophenyl)-2-oxoethyl)-3-(3,4-dichlorophenyl)-2-oxocyclopent -3-ene-1-carboxylate (3n). Following the general procedure **A**, **3n** was prepared from methyl 4-(3,4-dichlorophenyl)-3-oxobutanoate **1n** (0.200 g, 0.766 mmol), 2-bromo-1-(4-chlorophenyl)ethan-1-one **2n** (0.358 g, 1.532 mmol), and K_2CO_3 (0.212 g, 1.532 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.390 g (93%); *Rf*: 0.4 (Ethyl acetate: pet ether 1:10), **M.P:** 188 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.92 (d, *J* = 8.25 Hz, 2H), 7.37 – 7.51 (m, 4H), 7.32 (s, 4H), 7.06 (d, *J* = 8.25 Hz, 1H), 4.18 (d, *J* = 18.26 Hz, 1H), 3.98 (d, *J* = 18.64 Hz, 1H), 3.73 (s, 3H), 3.36 (d, *J* = 18.26 Hz, 1H), 3.02 (d, *J* = 18.64 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.2, 194.7, 168.7, 166.7, 139.2, 136.1, 133.7, 133.3, 131.9, 131.6, 131.5, 130.5, 130.3, 129.7, 128.6 (2C), 128.5 (2C), 128.1 (2C), 128.1 (2C), 127.8, 55.5, 52.3, 42.8, 40.5; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{19}O_4Cl_3{}^{37}Cl^+$, 549.0002; found, 549.0013.



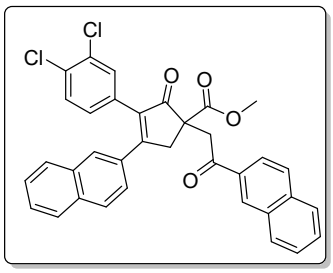
(3o)

Methyl 4-(4-bromophenyl)-1-(2-(4-bromophenyl)-2-oxoethyl)-3-(3,4-dichlorophenyl) -2-oxocyclo -pent-3-ene-1-carboxylate (3o). Following the general procedure **A**, **3o** was prepared from methyl 4-(3,4-dichlorophenyl)-3-oxobutanoate **1o** (0.200 g, 0.766 mmol), 2-bromo-1-(4-bromophenyl)ethan-1-one **2o** (0.426 g, 1.532 mmol), and K_2CO_3 (0.212 g, 1.532 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.444 g (91%); *Rf*: 0.5 (Ethyl acetate: pet ether 1:10), **M.P:** 147 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.77 (m, *J* = 8.63 Hz, 2H), 7.56 (m, *J* = 8.63 Hz, 2H), 7.38 – 7.46 (m, 2H), 7.30 – 7.38 (m, 2H), 7.12 – 7.24 (m, 3H), 6.98 (dd, *J* = 8.25, 2.00 Hz, 1H), 4.10 (d, *J* = 18.26 Hz, 1H), 3.90 (d, *J* = 18.64 Hz, 1H), 3.66 (s, 3 H), 3.28 (d, *J* = 18.39 Hz, 1H), 2.94 (d, *J* = 18.64 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.2, 194.9, 168.7, 166.8, 133.8, 133.7, 132.0, 131.9, 131.7, 131.1 (2C), 130.4, 130.3 (2C), 129.7, 128.7 (2C), 128.6 (2C), 128.0, 127.8, 124.5, 55.5, 52.3, 42.7, 40.4; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{19}O_4Br^{81}BrCl_2^+$, 636.9001; found, 636.9009.



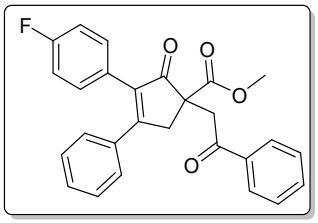
(3p)

Methyl 3-(3,4-dichlorophenyl)-4-(4-fluorophenyl)-1-(2-(4-fluorophenyl)-2-oxoethyl)-2-oxocyclopent-3-ene-1-carboxylate (3p). Following the general procedure **A**, **3p** was prepared from methyl 4-(3,4-dichlorophenyl)-3-oxobutanoate **1p** (0.200 g, 0.766 mmol), 2-bromo-1-(4-fluorophenyl)ethan-1-one **2p** (0.332 g, 1.532 mmol), and K_2CO_3 (0.212 g, 1.532 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.343 g (87%); *Rf*: 0.3 (Ethyl acetate: pet ether 1:10), **M.P:** 164 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.95 – 7.95 (m, 2H), 7.33 – 7.37 (m, 4H), 7.09 – 7.11 (m, 2H), 6.98 – 7.07 (m, 3H), 4.15 (d, *J* = 18.26 Hz, 1H), 3.95 (d, *J* = 18.64 Hz, 1H), 3.68 (s, 3H), 3.30 (d, *J* = 18.26 Hz, 1H), 2.98 (d, *J* = 18.64 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.3, 194.4, 168.8, 166.9, 166.3 – 163.8 (d, *J* = 255.58 Hz), 164.2 – 161.7 (d, *J* = 253.30 Hz), 133.2, 131.8, 131.5, 131.5, 130.7, 130.3, 129.9, 129.8, 129.6, 129.6, 129.5, 129.3, 129.2, 127.9, 115.1, 114.9, 114.9, 114.8, 55.6, 52.2, 42.8, 40.6; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −103.99, −107.20; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{19}O_4Cl_2F_2^+$, 515.0623, found, 515.0625.



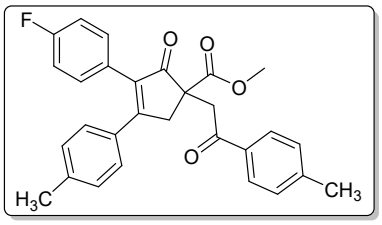
(3q)

Methyl 3-(3,4-dichlorophenyl)-4-(naphthalen-2-yl)-1-(2-(naphthalen-2-yl) -2-oxoethyl)-2-oxocyclo -pent-3-ene-1-carboxylate (3q). Following the general procedure **A**, **3q** was prepared from methyl 4-(3,4-dichlorophenyl)-3-oxobutanoate **1q** (0.200 g, 0.766 mmol), 2-bromo-1-(naphthalen-2-yl)ethan-1-one **2q** (0.381 g, 1.532 mmol), and K_2CO_3 (0.212 g, 1.532 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.333 g (75%); *Rf*: 0.4 (Ethyl acetate: pet ether 1:10), M.P: 91 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.46 (s, 1H), 7.93 – 8.00 (m, 2H), 7.88 (d, *J* = 7.88 Hz, 1H), 7.76 – 7.85 (m, 2H), 7.72 (d, *J* = 7.88 Hz, 2H), 7.63 (d, *J* = 8.75 Hz, 1H), 7.39 – 7.58 (m, 5H), 7.30 (d, *J* = 8.25 Hz, 1H), 7.24 (dd, *J* = 8.69, 1.69 Hz, 1H), 7.04 (dd, *J* = 8.32, 1.94 Hz, 1H), 4.35 (d, *J* = 18.14 Hz, 1H), 4.15 (d, *J* = 18.64 Hz, 1H), 3.68 (s, 3H), 3.48 (d, *J* = 18.26 Hz, 1H), 3.15 (d, *J* = 18.64 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.7, 195.9, 169.0, 168.3, 134.8, 133.4, 133.2, 132.4, 131.9, 131.7, 131.4, 131.4, 130.9, 130.7, 130.5, 129.5, 129.2, 128.6, 128.1, 127.8, 127.8, 127.7, 127.6, 127.2, 126.9, 126.8, 126.7, 125.9, 125.9, 124.2, 122.5, 55.8, 52.2, 43.2, 40.8; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{35}H_{25}O_4Cl_2^+$, 579.1124; found, 579.1127.



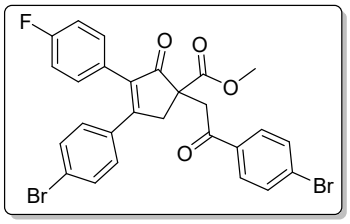
(3r)

Methyl 3-(4-fluorophenyl)-2-oxo-1- (2-oxo-2-phenylethyl)-4-phenylcyclopent-3-ene-1-carboxylate (3r). Following the general procedure **A**, **3r** was prepared from methyl 4-(4-fluorophenyl)-3-oxobutanoate **1r** (0.200 g, 0.951 mmol), 2-bromo-1-phenylethan-1-one **2r** (0.379 g, 1.904 mmol), and K_2CO_3 (0.263 g, 1.904 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.257 g (63%); *Rf*: 0.3 (Ethyl acetate: pet ether 1:10), **M.P:** 85 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.96 – 8.03 (m, 2H), 7.59 (t, *J* = 7.38 Hz, 1H), 7.48 (t, *J* = 7.69 Hz, 2H), 7.33 – 7.41 (m, 3H), 7.28 – 7.33 (m, 2H), 7.22 – 7.28 (m, 2H), 7.03 (t, *J* = 8.76 Hz, 2H), 4.26 (d, *J* = 18.39 Hz, 1H), 4.07 (d, *J* = 18.76 Hz, 1H), 3.73 (s, 3H), 3.35 (d, *J* = 18.39 Hz, 1H), 3.03 (d, *J* = 18.64 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 201.2, 196.1, 169.1, 167.5, 161.5 (d, *J* = 247.95 Hz), 135.2, 134.5, 133.7, 132.6, 130.4 (d, *J* = 8.39 Hz), 129.5, 127.7, 127.6, 127.3, 127.1, 126.7, 126.7, 114.6 (d, *J* = 22.12 Hz), 55.5, 52.1, 43.2, 40.6; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.14; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{22}O_4F^+$, 429.1497; found, 429.1496.



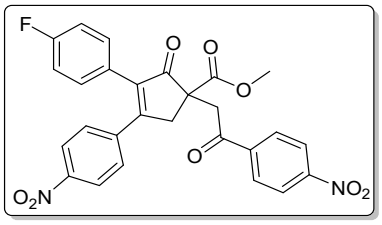
(3s)

Methyl 3-(4-fluorophenyl)-2-oxo-1-(2-oxo-2-(p-tolyl)ethyl)-4-(p-tolyl)cyclopent-3-ene-1-carboxylate (3s). Following the general procedure **A**, **3s** was prepared from methyl 4-(4-fluorophenyl)-3-oxobutanoate **1s** (0.200 g, 0.951 mmol), 2-bromo-1-(p-tolyl)ethan-1-one **2s** (0.405 g, 1.904 mmol), and K_2CO_3 (0.263 g, 1.904 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.321 g (74%); *Rf*: 0.4 (Ethyl acetate: pet ether 1:10), **M.P:** 180 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.81 – 7.92 (m, *J* = 7.9 Hz, 2H), 7.27 – 7.35 (m, 4H), 7.23 – 7.26 (m, 4H), 6.97 – 7.12 (m, *J* = 7.9 Hz, 2H), 4.22 (d, *J* = 18.3 Hz, 1H), 4.05 (d, *J* = 18.8 Hz, 1H), 3.68 (s, 3H), 3.25 (d, *J* = 18.3 Hz, 1H), 2.98 (d, *J* = 18.6 Hz, 1H), 2.38 (s, 3H), 2.30 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 202.3, 196.8, 170.3, 168.2, 161.5 (d, *J* = 247.95 Hz), 144.4, 141.0, 135.9, 133.8, 131.0 (d, *J* = 8.39 Hz), 129.6, 129.4, 129.2, 128.5, 128.3, 128.0, 114.6 (d, *J* = 22.12 Hz), 56.6, 53.0, 44.3, 41.5, 21.7, 21.5; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −113.65; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{26}O_4F^+$, 457.1810, found, 457.1808.



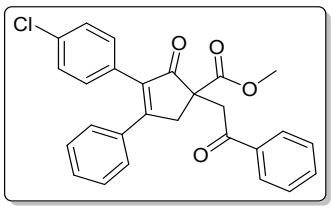
(3t)

Methyl 4-(4-bromophenyl)-1-(2-(4-bromophenyl)-2-oxoethyl)-3-(4-fluorophenyl)-2-oxocyclopent-3-ene-1-carboxylate (3t). Following the general procedure **A**, **3t** was prepared from methyl 4-(4-fluorophenyl)-3-oxobutanoate **1t** (0.200 g, 0.951 mmol), 2-bromo-1-(4-bromophenyl)ethan-1-one **2t** (0.529 g, 1.904 mmol), and K_2CO_3 (0.263 g, 1.904 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.352 g (63%); *Rf*: 0.5 (Ethyl acetate: pet ether 1:10), **M.P:** 200 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.71 – 7.84 (m, 2H), 7.49 – 7.60 (m, 2H), 7.31 – 7.44 (m, 2H), 7.11 – 7.19 (m, 4H), 6.98 (t, *J* = 8.7 Hz, 2H), 4.13 (d, *J* = 18.4 Hz, 1H), 3.92 (d, *J* = 18.5 Hz, 1H), 3.65 (s, 3H), 3.24 (d, *J* = 18.4 Hz, 1H), 2.92 ppm (d, *J* = 18.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 201.8, 196.1, 169.9, 166.7, 162.7 (d, *J* = 248.72 Hz), 136.1, 136.0, 134.9, 134.8, 133.5, 133.5, 132.1, 131.9, 131.3 (d, *J* = 8.39 Hz), 129.9, 129.8, 129.6, 129.0, 127.3, 125.1, 115.8 (d, *J* = 21.36 Hz), 56.5, 53.2, 43.9, 41.3; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −112.55; **HRMS** (ESI) m/z: $[M-H]^-$ calcd for $C_{27}H_{18}O_4Br^{81}BrF^-$, 584.9530, found, 584.9557.



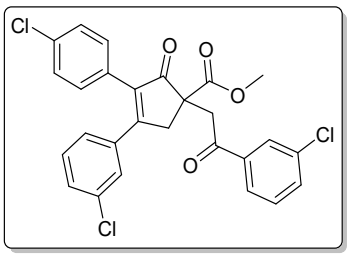
(3u)

Methyl 3-(4-fluorophenyl)-4-(4-nitrophenyl)-1-(2-(4-nitrophenyl)-2-oxoethyl)-2-oxocyclopent-3-ene-1-carboxylate (3u). Following the general procedure **A**, **3u** was prepared from methyl 4-(4-fluorophenyl)-3-oxobutanoate **1u** (0.200 g, 0.951 mmol), 2-bromo-1-(4-nitrophenyl)ethan-1-one **2u** (0.464 g, 1.904 mmol), and K_2CO_3 (0.263 g, 1.904 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.355 g (72%); *Rf*: 0.5 (Ethyl acetate: pet ether 2:10), **M.P:** 201 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.34 (m, *J* = 8.38 Hz, 2H), 8.17 (t, *J* = 8.76 Hz, 4H), 7.55 (m, *J* = 8.50 Hz, 2H), 7.16 – 7.32 (m, 2H), 7.07 (t, *J* = 8.44 Hz, 2H), 4.27 (d, *J* = 18.51 Hz, 1H), 3.99 (d, *J* = 18.64 Hz, 1H), 3.76 (s, 3H), 3.48 (d, *J* = 18.64 Hz, 1H), 3.10 (d, *J* = 18.51 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 199.8, 194.1, 167.9, 163.4, 161.5 (d, *J* = 249.48 Hz), 149.2, 147.0, 139.6, 138.8, 136.8, 129.8 (d, *J* = 8.39 Hz), 127.7, 127.7, 124.9, 124.8, 122.5, 122.4, 114.5 (d, *J* = 21.36 Hz), 55.1, 52.0, 42.6, 39.9; **^{19}F NMR** (376 MHz, CDCl3): δ ppm −111.42; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{20}O_8N_2F^+$, 519.1198; found, 519.1199.



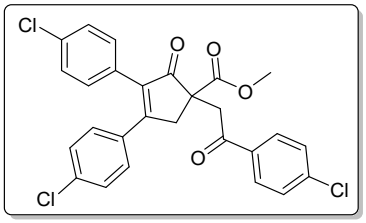
(3v)

Methyl 3-(4-chlorophenyl)-2-oxo-1-(2-oxo-2-phenylethyl)-4-phenylcyclopent-3-ene-1-carboxylate (3v). Following the general procedure **A**, **3v** was prepared from methyl 4-(4-chlorophenyl)-3-oxobutanoate **1v** (0.200 g, 0.882 mmol), 2-bromo-1-phenylethan-1-one **2v** (0.351 g, 1.725 mmol), and K_2CO_3 (0.243 g, 1.725 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.321 g (82%); *Rf*: 0.5 (Ethyl acetate: pet ether 2:10), **M.P:** 122 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.95 – 8.03 (m, 2H), 7.59 (t, *J* = 7.44 Hz, 1H), 7.47 (t, *J* = 7.69 Hz, 2H), 7.34 – 7.42 (m, 3H), 7.27 – 7.34 (m, 4H), 7.18 – 7.24 (m, 2H), 4.26 (d, *J* = 18.26 Hz, 1H), 4.06 (d, *J* = 18.64 Hz, 1H), 3.73 (s, 3H), 3.36 (d, *J* = 18.39 Hz, 1H), 3.03 (d, *J* = 18.76 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 201.9, 197.0, 170.1, 168.8, 136.2, 135.4, 134.6, 134.1, 133.6, 130.9 (2C), 130.6, 130.2, 128.8 (2C), 128.7 (2C), 128.6 (2C), 128.3 (2C), 128.1 (2C), 56.6, 53.1, 44.2, 41.7; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{22}O_4Cl^+$, 445.1201, found, 445.1201.



(3w)

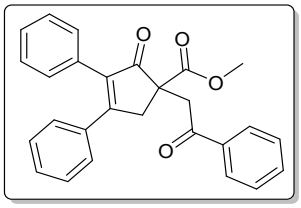
Methyl 4-(3-chlorophenyl)-3-(4-chlorophenyl)-1-(2-(3-chlorophenyl)-2-oxoethyl)-2-oxocyclopent-3-ene-1-carboxylate (3w). Following the general procedure **A**, **3w** was prepared from methyl 4-(4-chlorophenyl)-3-oxobutanoate **1w** (0.200 g, 0.882 mmol), 2-bromo-1-(3-chlorophenyl)ethan-1-one **2w** (0.412 g, 1.765 mmol), and K_2CO_3 (0.244 g, 1.765 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.308 g (68%); *Rf*: 0.5 (Ethyl acetate: pet ether 1:10), **M.P:** 136 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.96 (s, 1H), 7.86 (d, *J* = 7.75 Hz, 1H), 7.57 (d, *J* = 8.00 Hz, 1H), 7.39 – 7.46 (m, 2H), 7.30 – 7.37 (m, 3H), 7.17 – 7.25 (m, 4H), 4.20 (d, *J* = 18.39 Hz, 1H), 3.97 (d, *J* = 18.64 Hz, 1H), 3.73 (s, 3H), 3.35 (d, *J* = 18.51 Hz, 1H), 3.00 (d, *J* = 18.64 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 201.6, 195.8, 169.7, 166.8, 137.6, 136.4, 135.1, 134.8, 134.5, 133.6, 130.8 (2C), 130.5, 130.1, 129.9, 129.5, 128.9 (2C), 128.3, 128.1, 126.5, 126.2, 56.5, 53.3, 43.9, 41.6; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{20}O_4Cl_3^+$, 513.0422, found, 513.0423.



(3x)

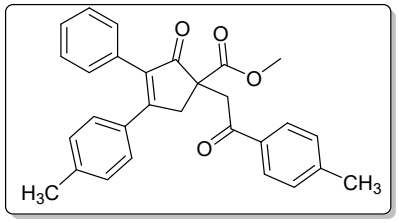
Methyl 3,4-bis(4-chlorophenyl)-1-(2-(4-chlorophenyl)-2-oxoethyl)-2-oxocyclopent-3-ene-1-carboxylate (3x). Following the general procedure **A**, **3x** was prepared from methyl 4-(4-chlorophenyl)-3-

oxobutanoate **1x** (0.200 g, 0.882 mmol), 2-bromo-1-(4-chlorophenyl)ethan-1-one **2x** (0.412 g, 1.765 mmol), and K_2CO_3 (0.244 g, 1.765 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.408 g (90%); *Rf*: 0.4 (Ethyl acetate: pet ether 1:10), **M.P:** 189 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.82 – 7.88 (m, *J* = 8.5 Hz, 2H), 7.36 – 7.41 (m, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.25 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.13 (d, *J* = 18.4 Hz, 1H), 3.92 (d, *J* = 18.5 Hz, 1H), 3.65 (s, 3H), 3.25 (d, *J* = 18.3 Hz, 1H), 2.93 ppm (d, *J* = 18.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.6, 194.8, 168.8, 166.0, 139.2, 135.8, 134.8, 133.4, 133.4, 131.9, 129.8 (2C), 128.8 (2C), 128.6 (2C), 128.5 (2C), 128.1 (2C), 127.9 (2C), 55.5, 52.2, 42.9, 40.4; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{20}O_4Cl_3^+$, 513.0422, found, 513.0425.



(3y)

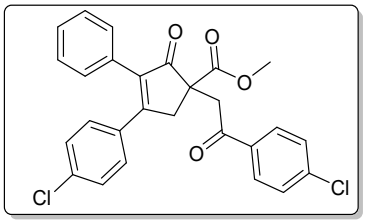
Methyl 2-oxo-1-(2-oxo-2-phenylethyl)-3,4-diphenylcyclopent-3-ene-1-carboxylate (3y). Following the general procedure **A**, **3y** was prepared from methyl 3-oxo-4-phenylbutanoate **1y** (0.200 g, 1.040 mmol), 2-bromo-1-phenylethan-1-one **2y** (0.414 g, 2.081 mmol), and K_2CO_3 (0.288 g, 2.081 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.265 g (62 %); *Rf*: 0.4 (Ethyl acetate: pet ether 1:10), **M.P:** 83 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.92 (d, *J* = 7.75 Hz, 2H), 7.51 (t, *J* = 7.32 Hz, 1H), 7.40 (t, *J* = 7.63 Hz, 2H), 7.32 (d, *J* = 7.63 Hz, 2H), 7.23 – 7.30 (m, 4H), 7.15 – 7.23 (m, 4H), 4.21 (d, *J* = 18.39 Hz, 1H), 4.02 (d, *J* = 18.76 Hz, 1H), 3.65 (s, 3H), 3.25 (d, *J* = 18.39 Hz, 1H), 2.95 (d, *J* = 18.64 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 202.3, 197.2, 170.2, 168.3, 136.5, 136.2, 134.8, 133.6, 131.9, 130.5 (2C), 129.6 (2C), 128.7 (2C), 128.6 (2C), 128.5 (2C), 128.2 (2C), 56.6, 53.2, 44.4, 41.6; **HRMS** (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{23}O_4^+$, 407.1642, found, 407.1638.



(3z)

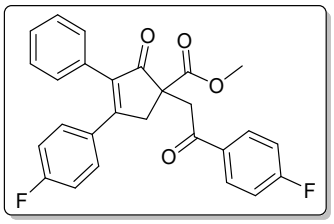
Methyl 2-oxo-1-(2-oxo-2-(p-tolyl)ethyl)-3-phenyl-4-(p-tolyl) cyclopent-3-ene-1-carboxylate (3z). Following the general procedure **A**, **3z** was prepared from methyl 3-oxo-4-phenylbutanoate **1z** (0.200 g, 1.040 mmol), 2-bromo-1-(p-tolyl)ethan-1-one **2z** (0.443 g, 2.081 mmol), and K_2CO_3 (0.288 g, 2.081 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.319 g (70 %); *Rf*: 0.4 (Ethyl acetate: pet ether 1:10), **M.P:** 85 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.86 – 7.91 (m, *J* = 7.8 Hz, 2H), 7.30 – 7.38 (m, 4H), 7.25 – 7.29 (m, 5H), 7.05 – 7.11 (m, *J* = 7.9 Hz, 2H), 4.25 (d, *J* = 18.3 Hz, 1H), 4.08 (d, *J* = 18.6 Hz, 1H), 3.72 (s, 3H), 3.28 (d, *J* = 18.3 Hz, 1H), 3.01 ppm (d, *J* = 18.6 Hz, 1H), 2.41 (s, 3 H), 2.33 ppm (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 202.3, 196.8, 170.3, 168.2, 144.4, 140.9, 135.9, 133.8, 132.2, 131.9, 129.6 (2C),

129.3 (2C), 129.2 (2C), 128.5 (2C), 128.3 (2C), 128.0 (2C), 56.5, 53.0, 44.3, 41.5, 21.7, 21.5; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{27}O_4^+$, 438.1831, found, 438.1826.



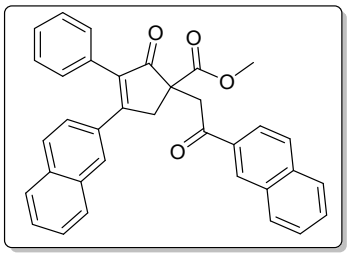
(3aa)

Methyl 4-(4-chlorophenyl)-1-(2-(4-chlorophenyl)-2-oxoethyl)-2-oxo-3-phenyl cyclopent-3-ene-1-carboxylate (3aa). Following the general procedure, **3aa** was prepared from methyl 3-oxo-4-phenylbutanoate **1aa** (0.200 g, 1.040 mmol), 2-bromo-1-(4-chlorophenyl)ethan-1-one **2aa** (0.486 g, 2.081 mmol), and K_2CO_3 (0.288 g, 2.081 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.264 g (53 %); *Rf*: 0.4 (Ethyl acetate: pet ether 1:10), **M.P:** 131 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ ppm 7.83 – 7.90 (m, *J* = 8.6 Hz, 2H), 7.35 – 7.41 (m, *J* = 8.5 Hz, 2H), 7.27 – 7.31 (m, 3H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.13 – 7.21 (m, 4H), 4.15 (d, *J* = 18.4 Hz, 1H), 3.95 (d, *J* = 18.5 Hz, 1H), 3.65 (s, 3H), 3.22 (d, *J* = 18.3 Hz, 1H), 2.94 ppm (d, *J* = 18.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.8, 194.9, 168.9, 165.4, 139.1, 136.0, 135.5, 133.5, 132.1, 130.4, 128.7 (2C), 128.5 (2C), 128.4 (2C), 128.0 (2C), 127.8 (2C), 127.7 (2C), 127.4, 55.5, 52.2, 43.0, 40.3; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{21}O_4Cl_2^+$, 479.0811; found, 479.0815.



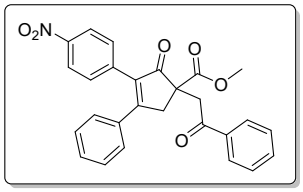
(3ab)

Methyl 4-(4-fluorophenyl)-1-(2-(4-fluorophenyl)-2-oxoethyl)-2-oxo-3-phenylcyclopent-3-ene-1-carboxylate (3ab). Following the general procedure, **3ab** was prepared from methyl 3-oxo-4-phenylbutanoate **1ab** (0.200 g, 1.040 mmol), 2-bromo-1-(4-fluorophenyl)ethan-1-one **2ab** (0.452 g, 2.081 mmol), and K_2CO_3 (0.288 g, 2.081 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.325 g (70 %); *Rf*: 0.3 (Ethyl acetate: pet ether 1:10), **M.P:** 144 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.95 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.33 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.24 – 7.30 (m, 3H), 7.13 – 7.21 (m, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.90 (t, *J* = 8.6 Hz, 2H), 4.17 (d, *J* = 18.3 Hz, 1H), 3.97 (d, *J* = 18.5 Hz, 1H), 3.65 (s, 3H), 3.22 (d, *J* = 18.3 Hz, 1H), 2.94 ppm (d, *J* = 18.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 201.9, 195.6, 170.0, 166.6, 166.1 (d, *J* = 255.59 Hz), 163.8 (d, *J* = 252.53 Hz), 136.6, 132.7, 132.7, 131.7, 130.6 (d, *J* = 8.39 Hz), 130.8 (d, *J* = 9.15 Hz), 129.5, 128.7, 128.3, 115.7 (d, *J* = 22.12 Hz), 115.8 (d, *J* = 21.36 Hz), 56.6, 53.1, 44.1, 41.5; **^{19}F NMR** (376 MHz, $CDCl_3$): δ ppm −104.15, −108.66; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{21}O_4F_2^+$, 447.1402, found, 447.1400.



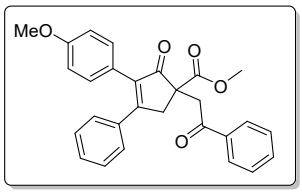
(3ac)

Methyl 4-(naphthalen-2-yl)-1-(2-(naphthalen-2-yl)-2-oxoethyl)-2-oxo-3-phenylcyclopent-3-ene-1-carboxylate (3ac). Following the general procedure **A**, **3ac** was prepared from methyl 3-oxo-4-phenylbutanoate **1ac** (0.200 g, 1.040 mmol), 2-bromo-1-phenylethan-1-one **2ac** (0.518 g, 2.081 mmol), and K_2CO_3 (0.288 g, 2.081 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.388 g (73 %); *Rf*: 0.4 (Ethyl acetate: pet ether 1:10), **M.P:** 194 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.48 (s, 1H), 7.93 – 8.00 (m, 2H), 7.88 (d, *J* = 7.88 Hz, 1H), 7.77 – 7.85 (m, 2H), 7.69 (d, *J* = 8.00 Hz, 2H), 7.47 – 7.60 (m, 3H), 7.41 (quind, *J* = 7.29, 7.29, 7.29, 7.29, 1.13 Hz, 2H), 7.22 – 7.29 (m, 6H), 4.40 (d, *J* = 18.26 Hz, 1H), 4.19 (d, *J* = 18.64 Hz, 1H), 3.68 (s, 3H), 3.43 (d, *J* = 18.26 Hz, 1H), 3.15 (d, *J* = 18.51 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 202.3, 197.2, 170.3, 168.0, 136.8, 135.8, 134.1, 133.6, 132.9, 132.5, 132.4, 131.9, 130.2, 129.7 (2C), 129.6, 128.8, 128.8, 128.7, 128.6, 128.5 (2C), 128.3, 127.8, 127.7, 127.6, 126.9, 126.7, 125.6, 123.6, 56.8, 53.2, 44.5, 41.7; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{35}H_{27}O_4^+$, 511.1904, found, 511.1900.



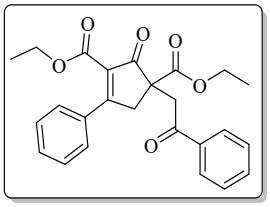
(3ad)

methyl 3-(4-nitrophenyl)-2-oxo-1-(2-oxo-2-phenylethyl)-4-phenylcyclopent-3-ene-1-carboxylate (3ad). Following the general procedure **A**, **3ad** was prepared from methyl 4-(4-nitrophenyl)-3-oxobutanoate **1ad** (0.200 g, 0.843 mmol), 2-bromo-1-phenylethan-1-one **2ad** (0.336 g, 1.690 mmol), and K_2CO_3 (0.233 g, 1.690 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.345 g (90 %); *Rf*: 0.5 (Ethyl acetate: pet ether 2:10), **M.P:** 125-128 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.19 (d, *J* = 8.9 Hz, 2H), 7.97 – 8.02 (m, 2H), 7.54 – 7.63 (m, 2H), 7.44 – 7.50 (m, 4H), 7.31 – 7.37 (m, 4H), 4.25 (d, *J* = 18.4 Hz, 1H), 4.08 (d, *J* = 18.9 Hz, 1H), 3.75 (s, 3H), 3.45 ppm (d, *J* = 18.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.3, 195.9, 169.9, 168.9, 146.4, 137.8, 135.0, 133.6, 133.1, 132.7, 130.1, 129.6, 127.8 (2C), 127.7 (2C), 127.3 (2C), 127.1 (2C), 122.6, 76.3, 76.0, 75.7, 55.8, 52.3, 43.0, 40.9; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{22}O_6N^+$, 456.1442, found, 456.1435.



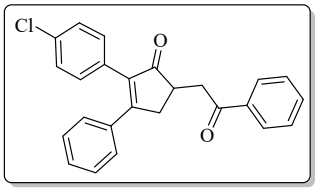
(3ae)

methyl 3-(4-methoxyphenyl)-2-oxo-1-(2-oxo-2-phenylethyl)-4-phenylcyclopent-3-ene-1-carboxylate (3ae). Following the general procedure **A**, **3ae** was prepared from methyl 4-(4-methoxyphenyl)-3-oxobutanoate **1ae** (0.200 g, 0.899 mmol), 2-bromo-1-phenylethan-1-one **2ae** (0.358 g, 1.801 mmol), and K_2CO_3 (0.249 g, 1.801 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.258 g (65 %); *Rf*: 0.5 (Ethyl acetate: pet ether 2:10), **M.P:** 101-103 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.92 – 8.01 (m, 4H), 7.40 – 7.50 (m, 6H), 7.21 (d, *J* = 8.8 Hz, 2H), 6.88 (s, 2H), 4.27 (d, *J* = 18.4 Hz, 1H), 4.03 (d, *J* = 11.1 Hz, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.31 (d, *J* = 18.4 Hz, 1H), 3.01 ppm (d, *J* = 18.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 201.5, 196.2, 169.2, 158.4, 135.2, 135.0, 134.1, 132.5, 129.8, 129.2, 127.7 (2C), 127.4 (2C), 127.3 (2C), 127.1 (2C), 113.0, 55.5, 54.2, 52.0, 43.3, 40.5; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{25}O_5^+$, 441.1697, found, 441.1690.



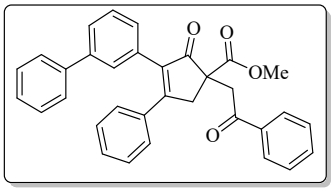
(5)

Diethyl 2-oxo-1-(2-oxo-2-phenylethyl)-4-phenylcyclopent-3-ene-1,3-dicarboxylate (5). Following the general procedure , **5** was prepared from diethyl 3-oxopentanedioate **4** (0.200 g, 0.989 mmol), 2-bromo-1-phenylethan-1-one **2a** (0.394 g, 1.978 mmol), and K_2CO_3 (0.273 g, 1.978 mmol) in 1,4 dioxane at 60 °C as a white solid. Yield: 0.283 g (68%); *Rf*: 0.5 (Ethyl acetate: pet ether 1:10), **M.P:** 101 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.94 – 8.00 (m, 2H), 7.56 – 7.62 (m, 3H), 7.42 – 7.53 (m, 5H), 4.28 – 4.35 (m, 2H), 4.25 (d, *J* = 18.26 Hz, 1H), 4.16 – 4.22 (m, 2H), 4.13 (d, *J* = 19.01 Hz, 1H), 3.25 (d, *J* = 18.39 Hz, 1H), 3.03 (d, *J* = 19.01 Hz, 1H), 1.26 (t, 3H), 1.19 (t, *J* = 7.13 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 198.8, 196.9, 173.5, 168.7, 164.3, 136.1, 133.7 (2C), 133.4, 131.8, 130.3, 128.7 (2C), 128.1 (2C), 127.9 (2C), 62.2, 61.6, 57.3, 43.9, 41.7, 13.9 (2C); **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{25}O_6^+$, 421.1646, found, 421.1664.



(6)

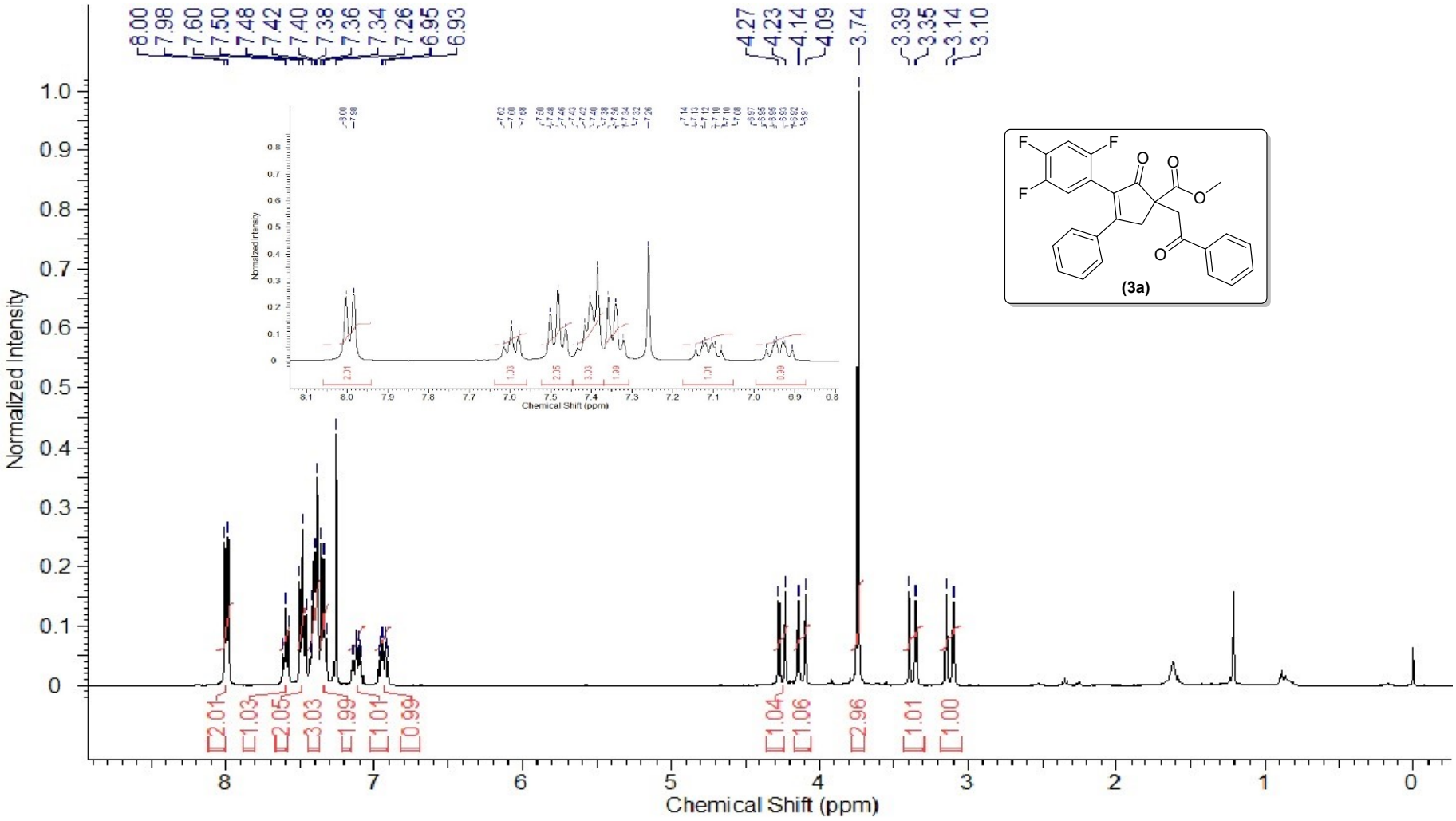
2-(4-chlorophenyl)-5-(2-oxo-2-phenylethyl)-3-phenylcyclopent-2-en-1-one (6). A 25 mL round-bottom flask was stirred with a Teflon-coated magnetic stir bar. methyl 3-(4-chlorophenyl)-2-oxo-1-(2-oxo-2-phenylethyl)-4-phenylcyclopent-3-ene-1-carboxylate **3w** (0.1 g, 0.2248 mmol, 1.0 equiv) and sodium methoxide (0.024 g, 0.4495 mmol, 2 equiv) were stirred in 4 mL of methanol at room temperature for 30 min. The reaction was monitored by TLC in a 10% ethyl acetate + pet ether system, and upon the completion of the reaction, the solvent was carefully removed by vacuum. Then, the residue was purified by silica gel (230−400 mesh) column chromatography to give the desired solid product (6) as a white solid. Yield: 0.061 g (70 %); *Rf*: 0.5 (Ethyl acetate: pet ether 1:10), **M.P:** 61 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.97 – 8.04 (m, 2H), 7.59 (t, *J* = 7.32 Hz, 1H), 7.48 (t, *J* = 7.63 Hz, 2H), 7.35 (d, *J* = 2.00 Hz, 1H), 7.24 – 7.31 (m, 4H), 7.21 (d, *J* = 8.50 Hz, 2H), 3.72 – 3.84 (m, 1H), 3.47 (dd, *J* = 18.39, 6.13 Hz, 1H), 3.20 – 3.27 (m, 2H), 2.79 (dd, *J* = 18.39, 2.50 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 207.2, 197.1, 166.4, 136.7, 135.5, 134.2, 132.8, 132.4, 129.9 (2C), 129.7, 129.1, 127.7 (2C), 127.7 (2C), 127.5 (2C), 127.1 (2C), 127.1 (2C), 40.5, 39.4, 36.4; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{20}O_2Cl^+$, 387.1146, found, 387.1139.



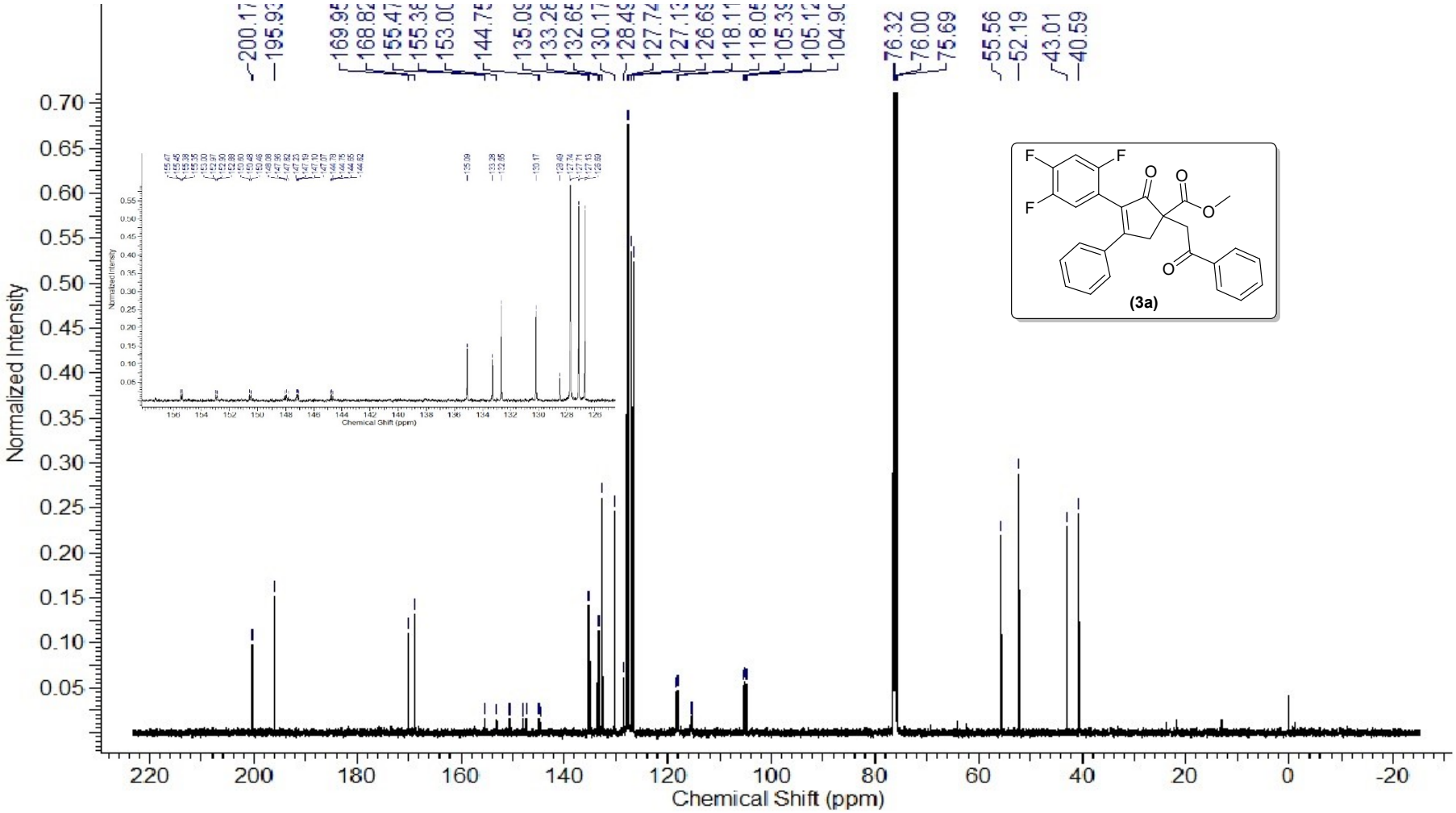
(8)

Methyl 3-([1,1'-biphenyl]-3-yl)-2-oxo-1-(2-oxo-2-phenylethyl)-4-phenyl cyclopent-3-ene-1-carboxylate (8). A 25 mL round-bottom flask was stirred with a Teflon-coated magnetic stir bar. methyl 3-(3-bromophenyl)-2-oxo-1-(2-oxo-2-phenylethyl)-4-phenylcyclopent-3-ene-1-carboxylate **7** (0.1 g, 0.2043 mmol, 1.0 eq.), phenyl boronic acid (0.025 g, 0.2043 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (0.007 g, 0.0061 mmol, 0.03 eq.) and sodium carbonate (0.022 g, 0.2043 mmol, 1 eq.) were stirred in 4 mL of toluene at 85 ^{o}C for 5 h. The reaction was monitored by TLC in a 10% ethyl acetate + pet ether system, and upon the completion of the reaction, the solvent was carefully removed by vacuum. Then, the residue was purified by silica gel (100−200 mesh) column chromatography to give the desired solid product (8) as a white solid. Yield: 0.075 g (76 %); *Rf*: 0.4 (Ethyl acetate: pet ether 1:10), **M.P:** 59 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.91 – 8.04 (m, 3H), 7.54 – 7.65 (m, 2H), 7.43 – 7.53 (m, 5H), 7.39 (d, *J* = 7.75 Hz, 4H), 7.28 – 7.35 (m, 2H), 7.20 (q, *J* = 8.80 Hz, 3H), 4.26 (d, *J* = 18.26 Hz, 1H), 4.07 (d, *J* = 18.89 Hz, 1H), 3.74 (s, 3H), 3.36 (d, *J* = 18.26 Hz, 1H), 3.05 (d, *J* = 18.64 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ ppm 200.8, 196.0, 169.0, 168.1, 135.1, 134.1, 133.3, 133.0, 132.6, 131.9, 131.4, 130.2, 129.7, 129.2, 129.0 (2C), 127.7 (2C), 127.6 (2C), 127.4 (2C), 127.2 (2C), 127.1 (2C), 121.5 , 55.6, 52.1, 43.1, 40.6; **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{35}H_{27}O_4^+$, 511.1904, found, 511.1900.

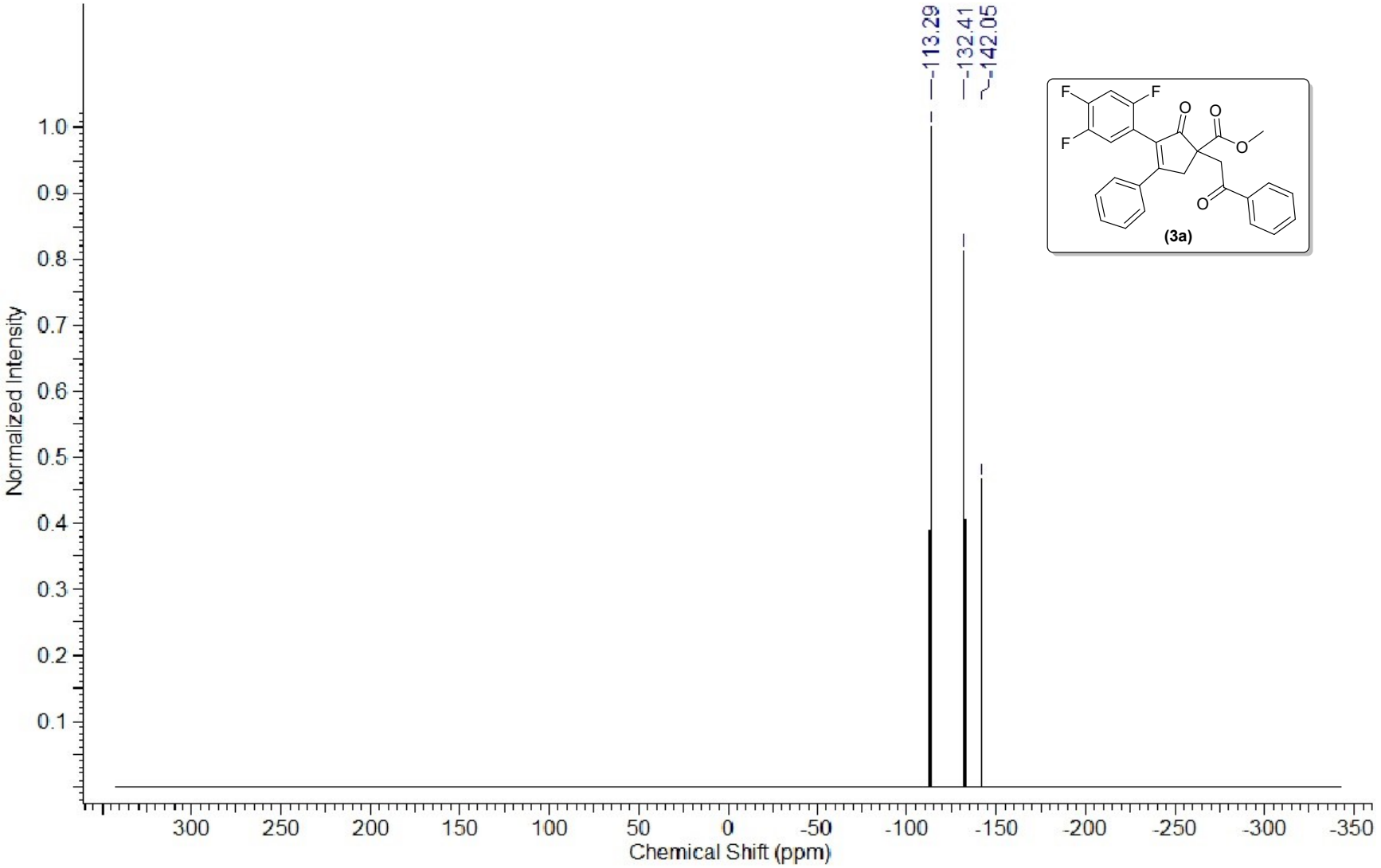
4. NMR Spectrum



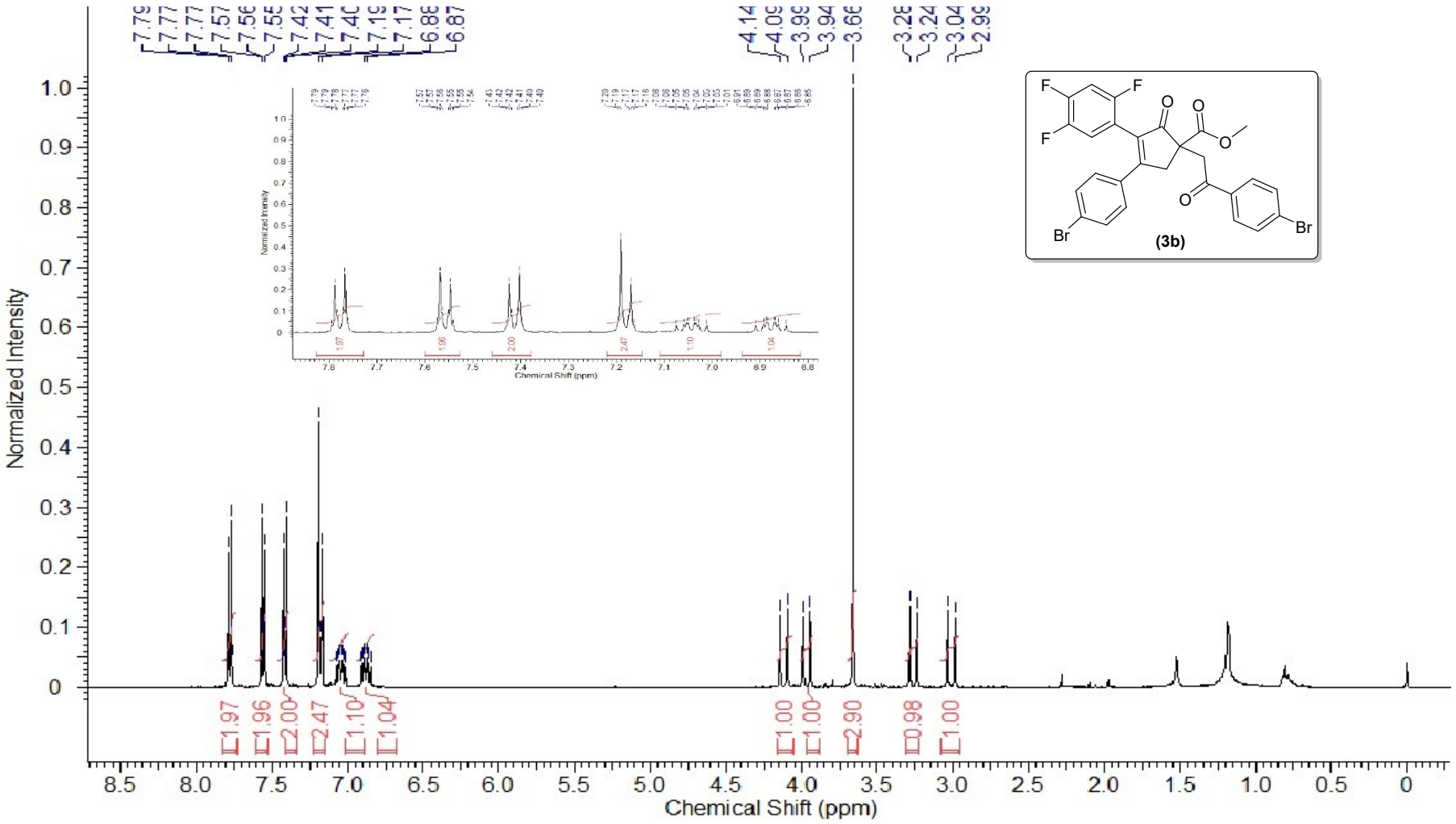
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3a



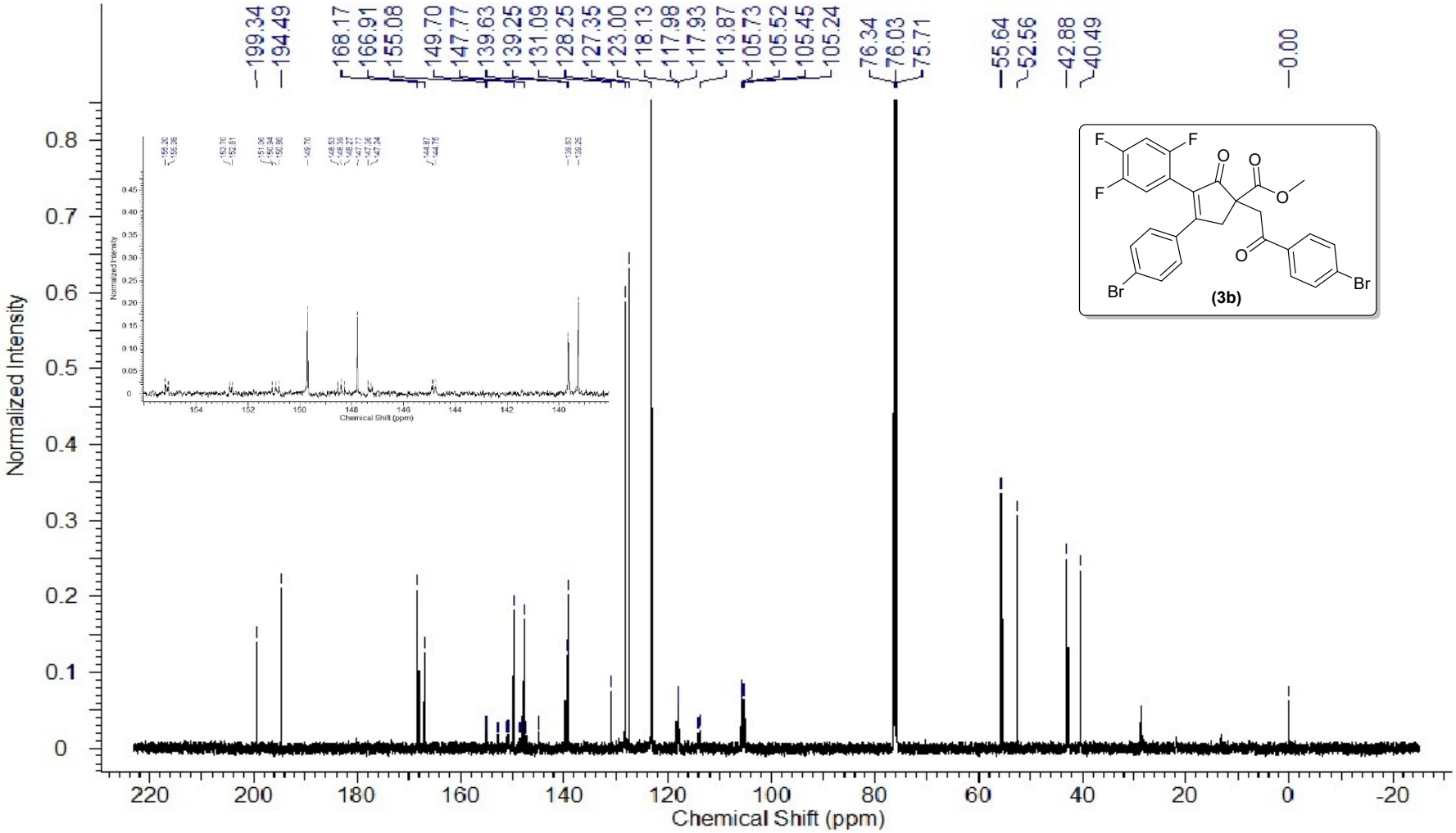
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3a



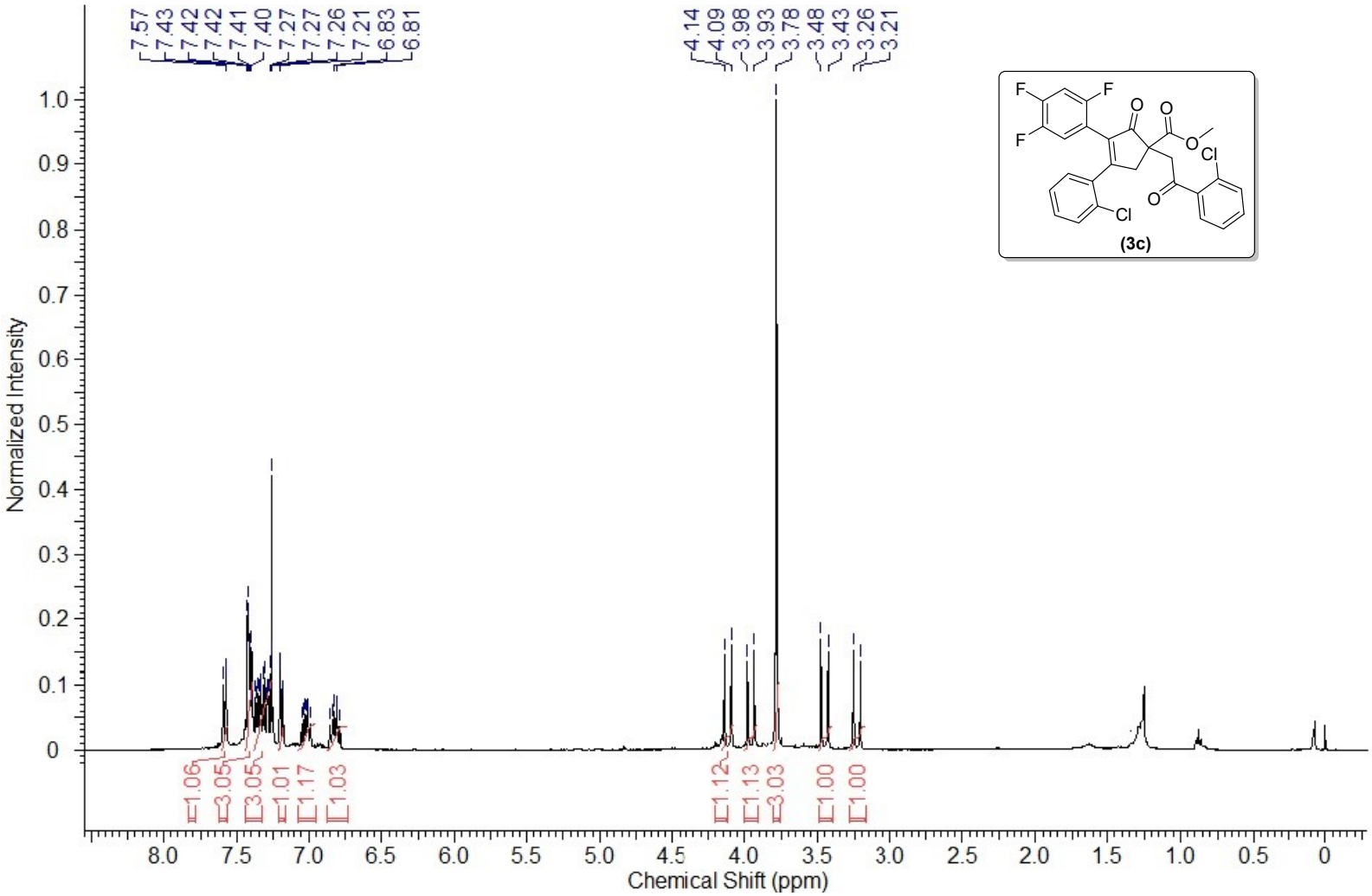
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3a



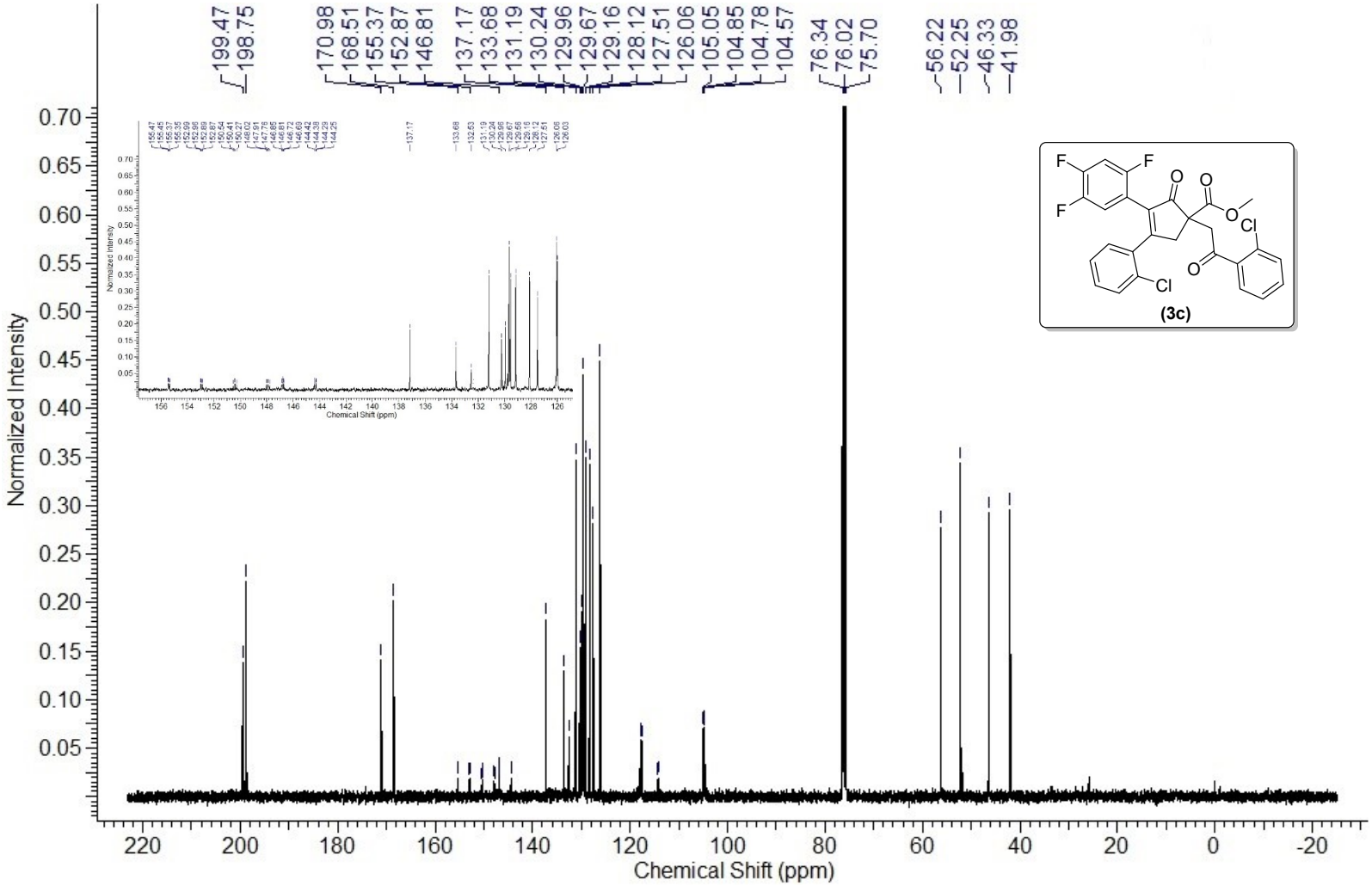
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3b



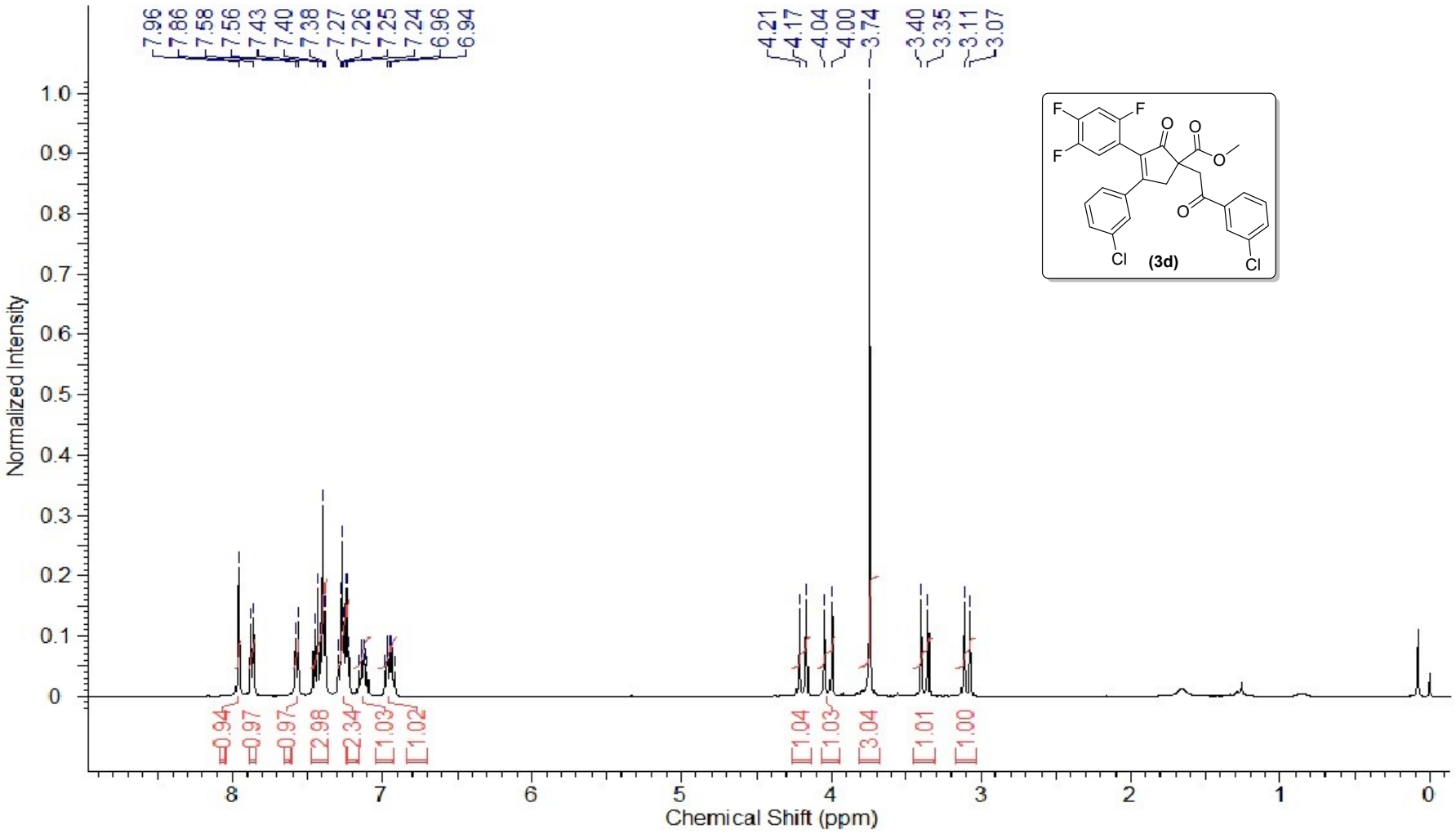
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3b



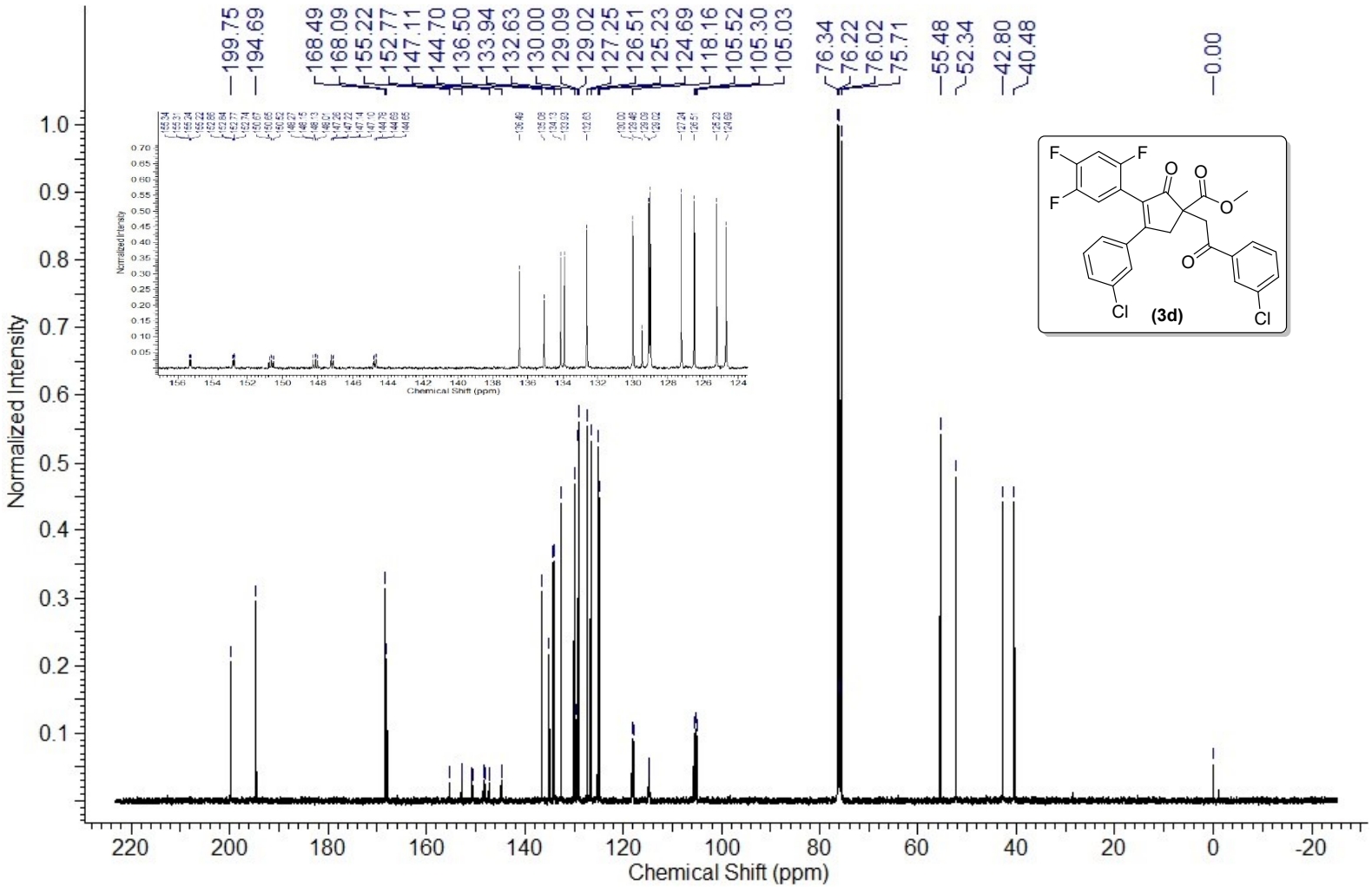
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3c



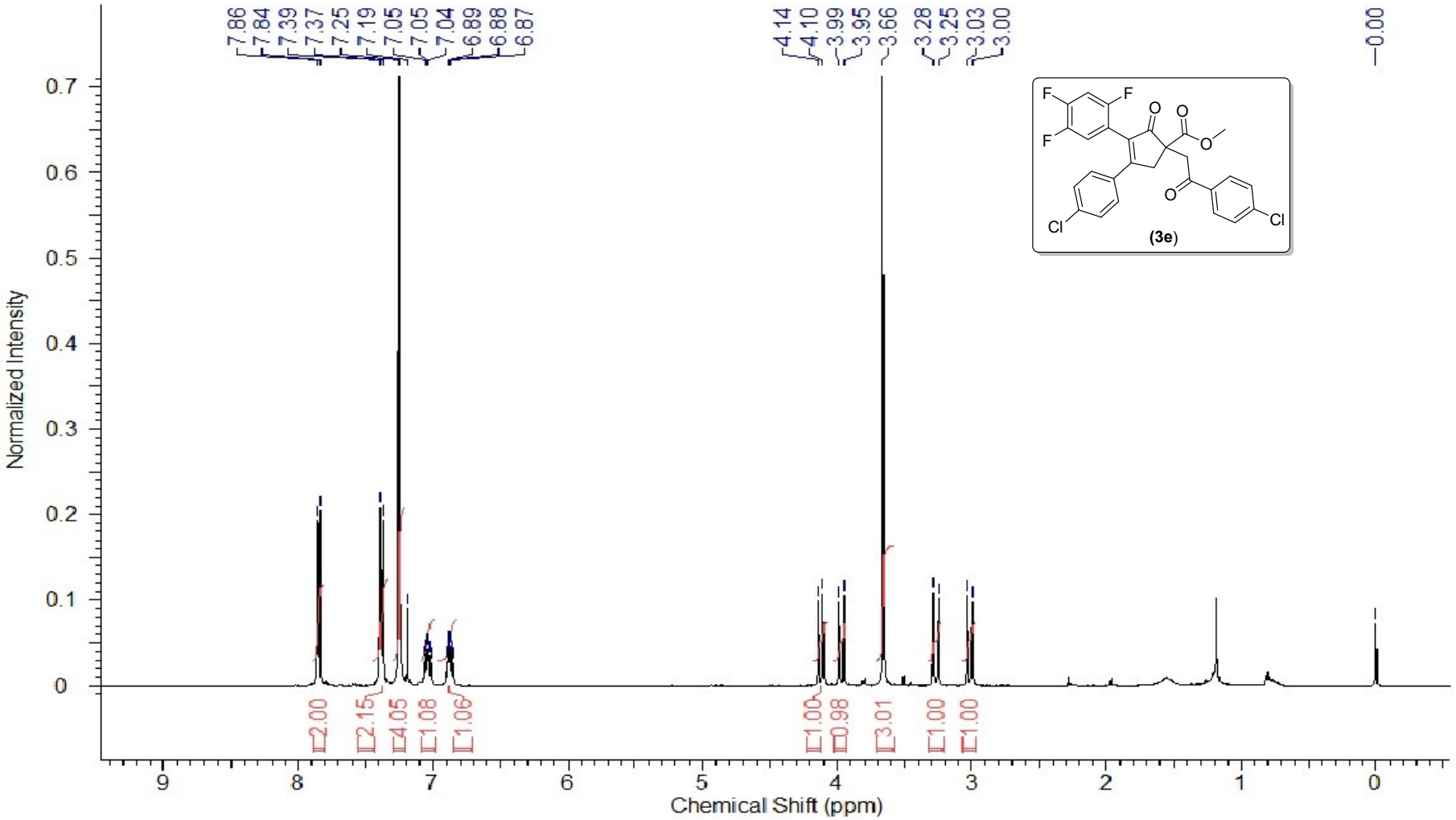
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3c



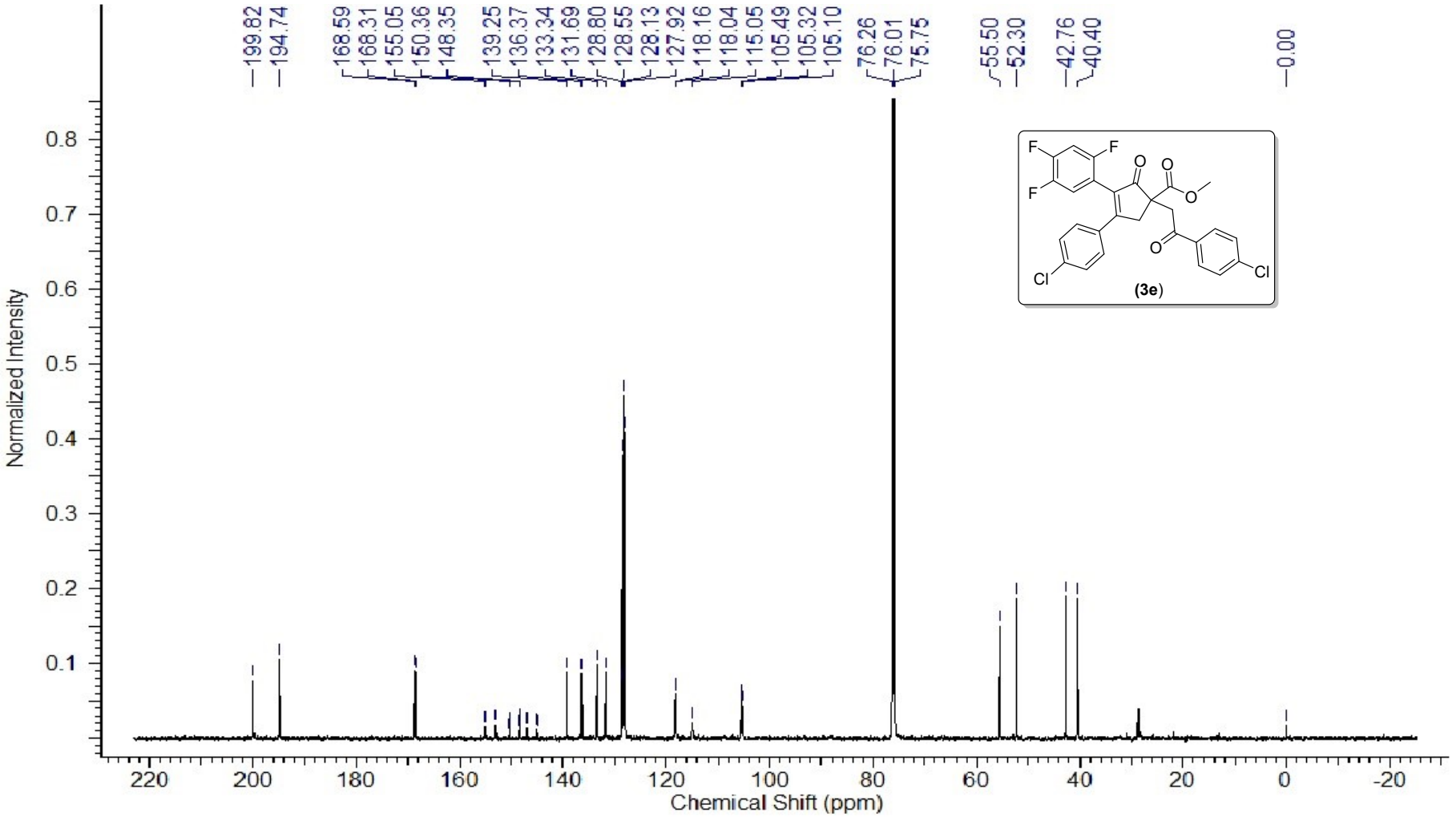
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3d



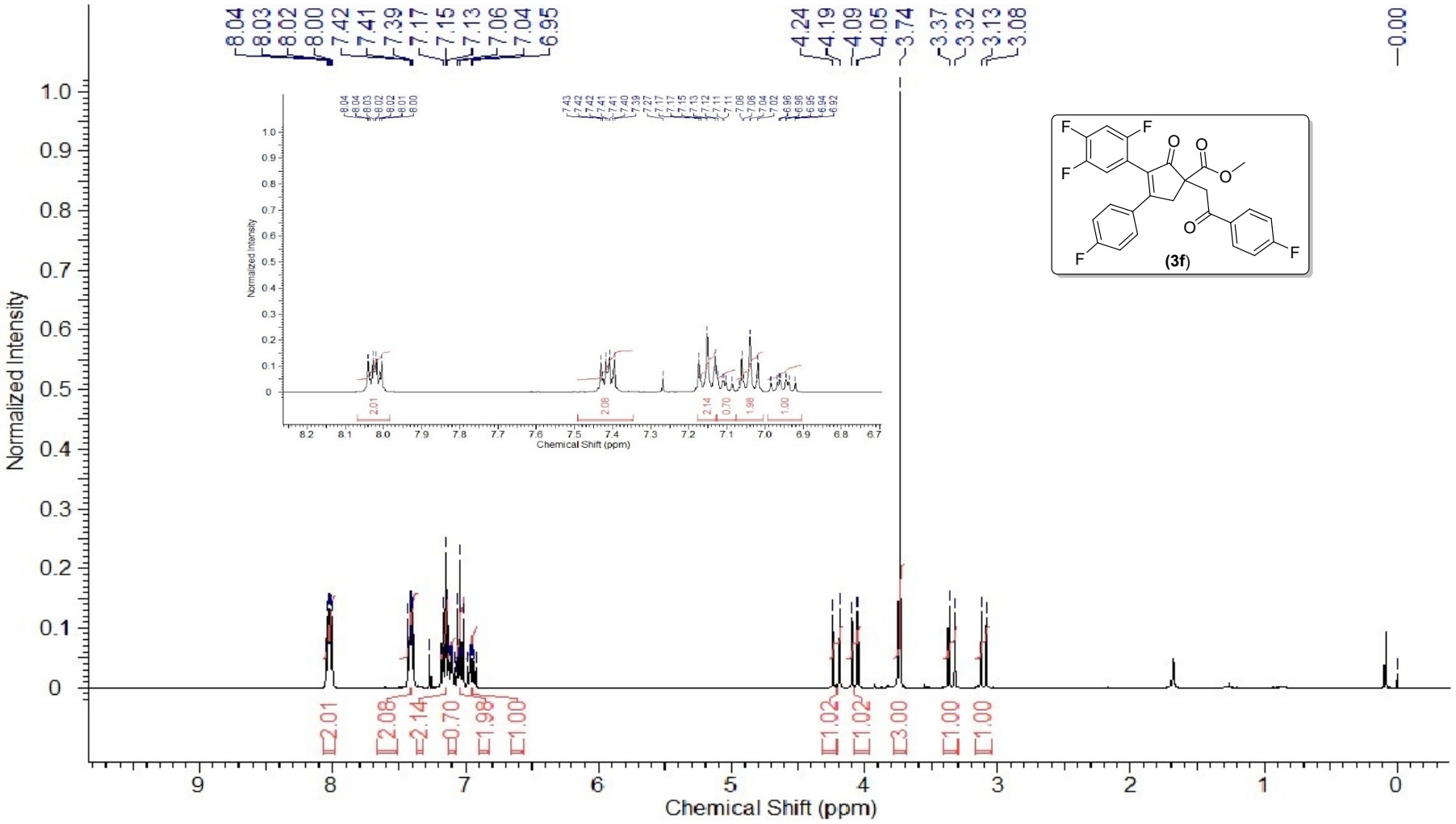
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3d



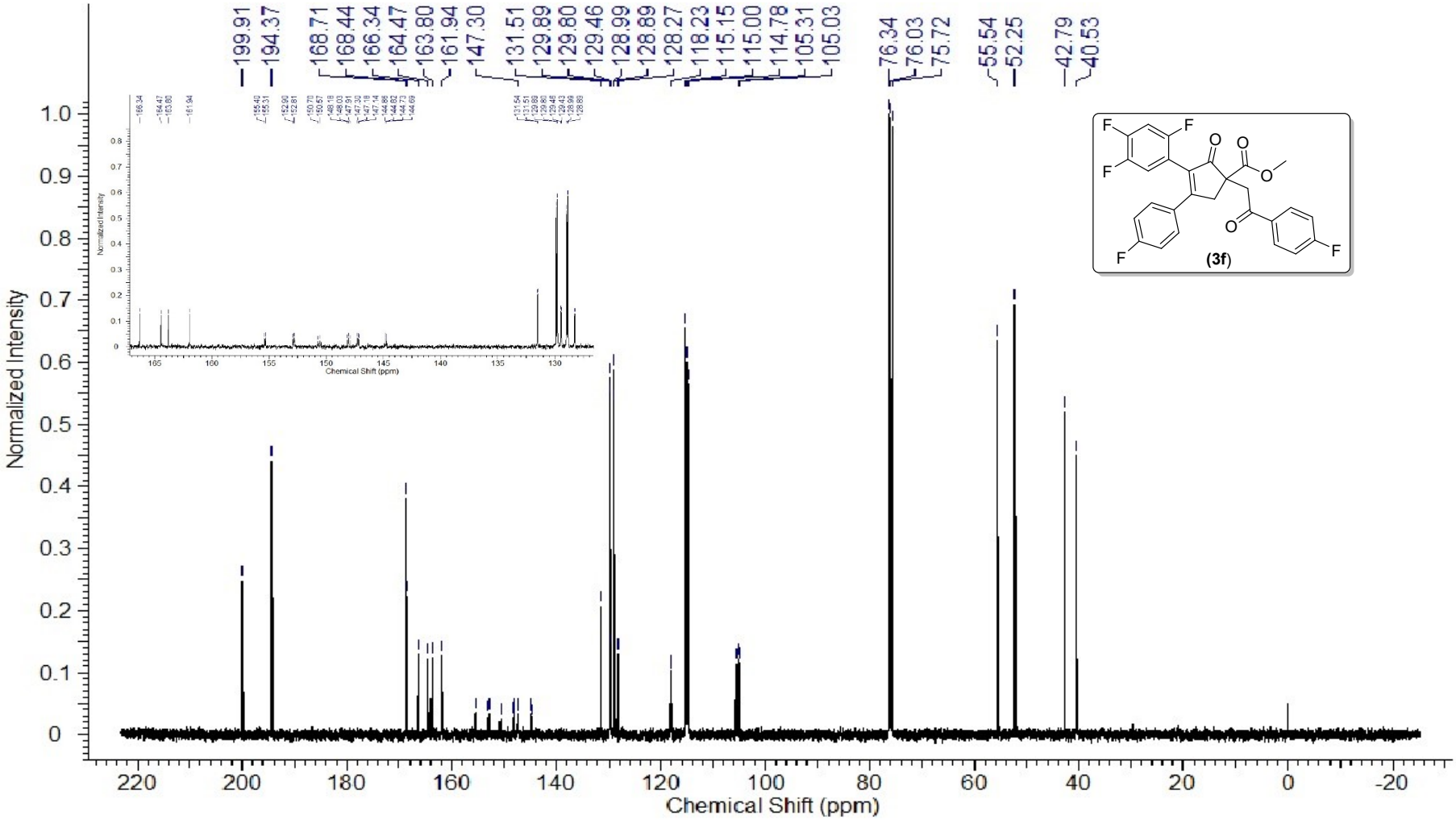
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3e



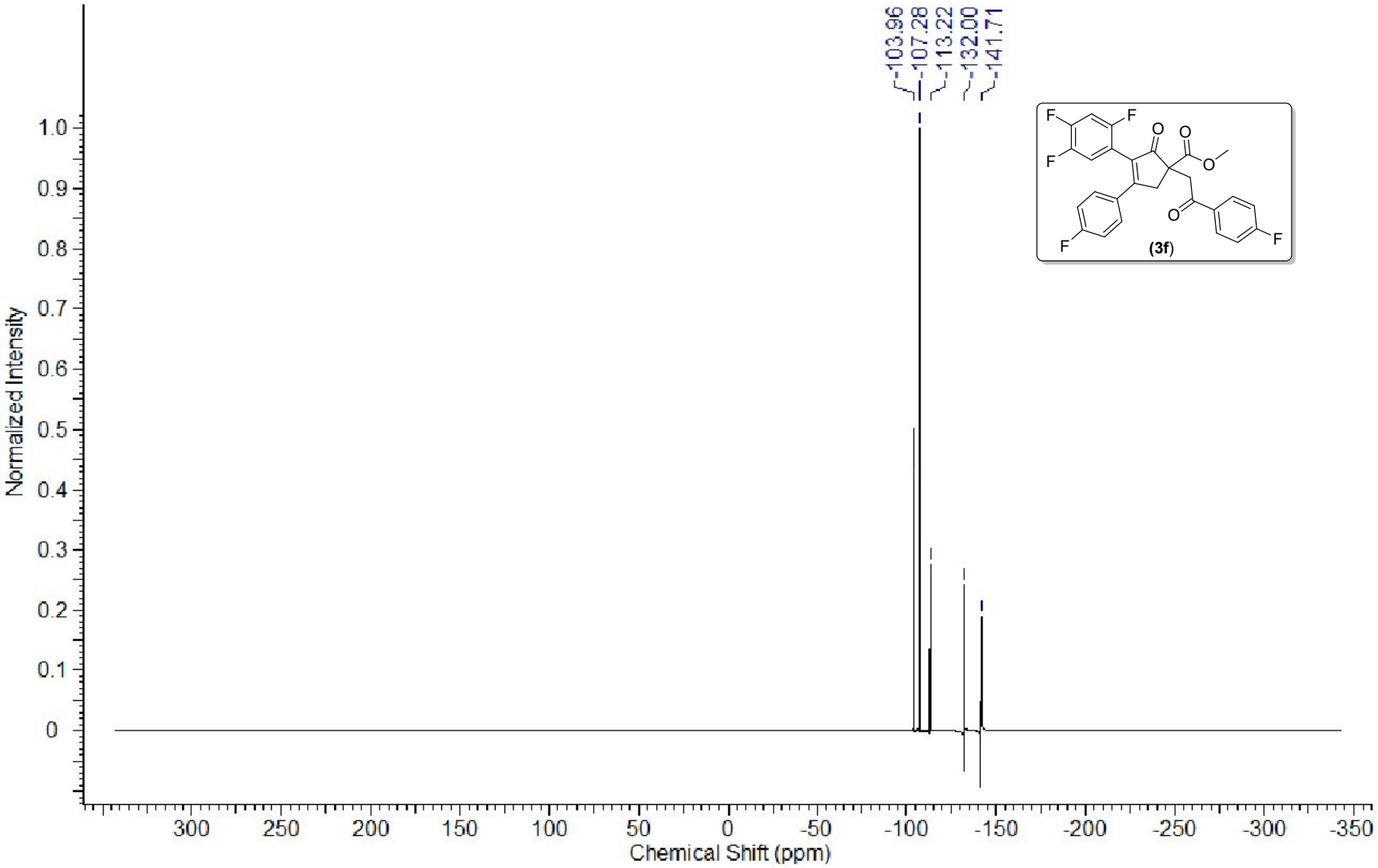
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3e



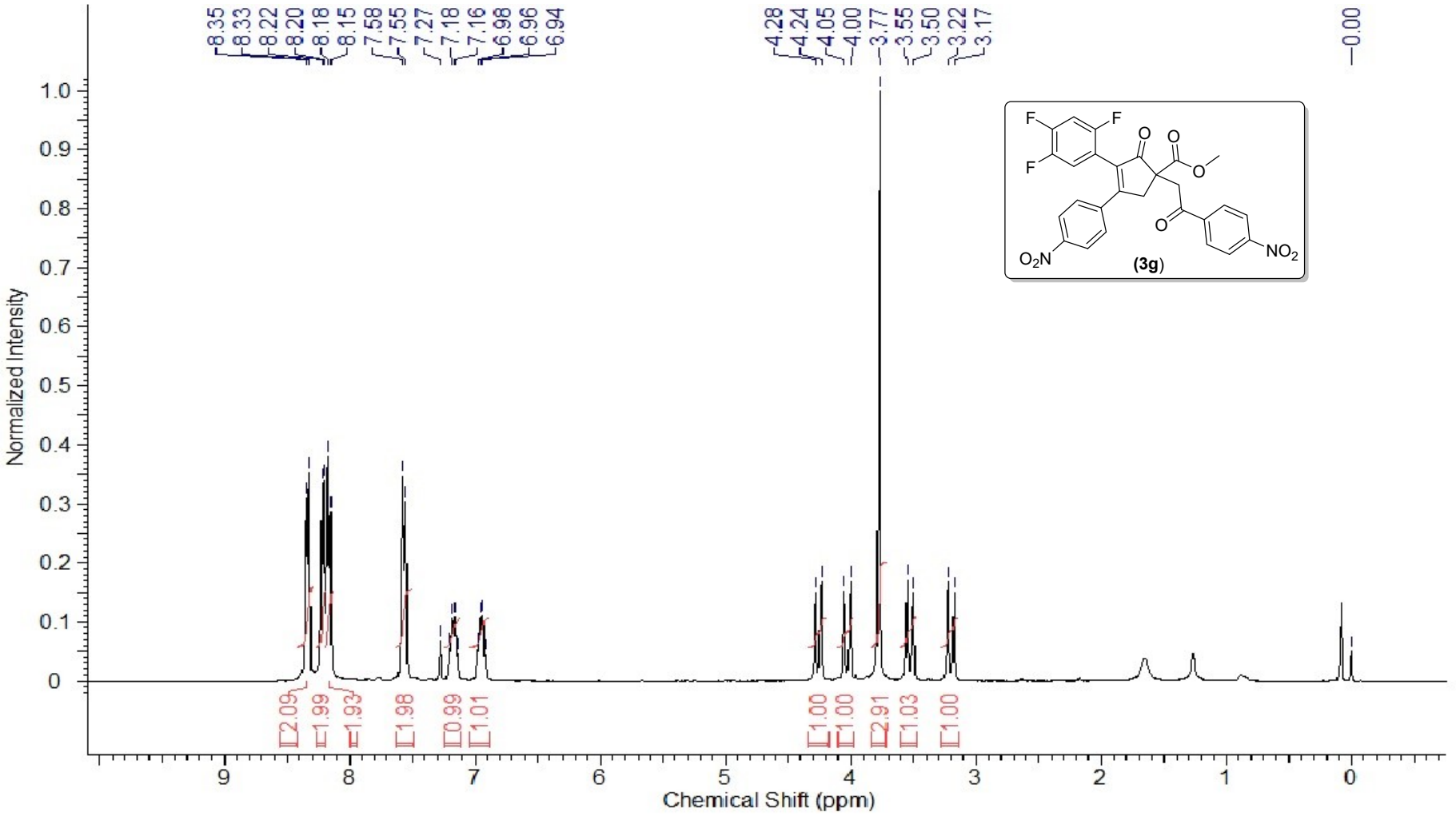
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3f



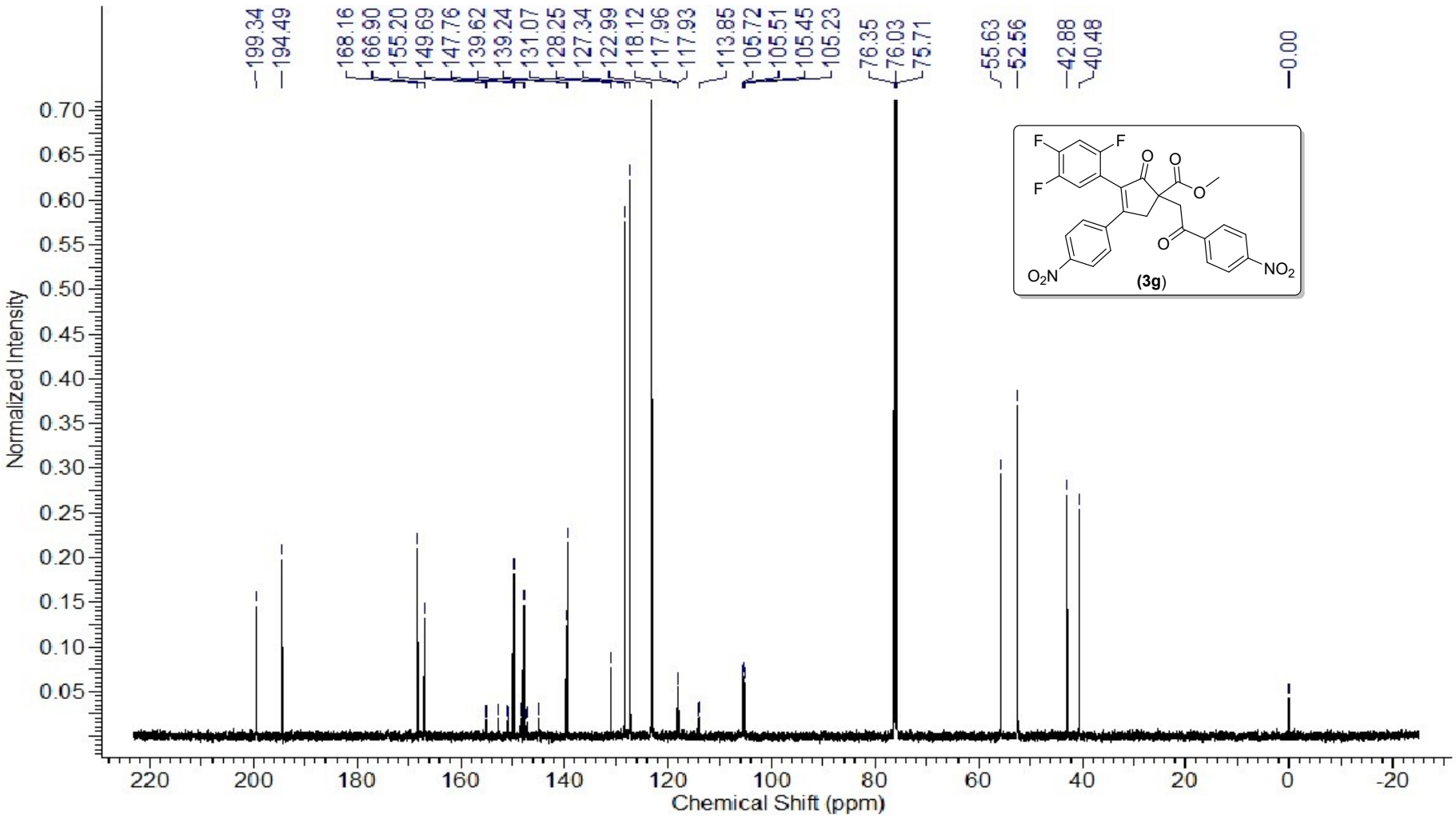
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3f



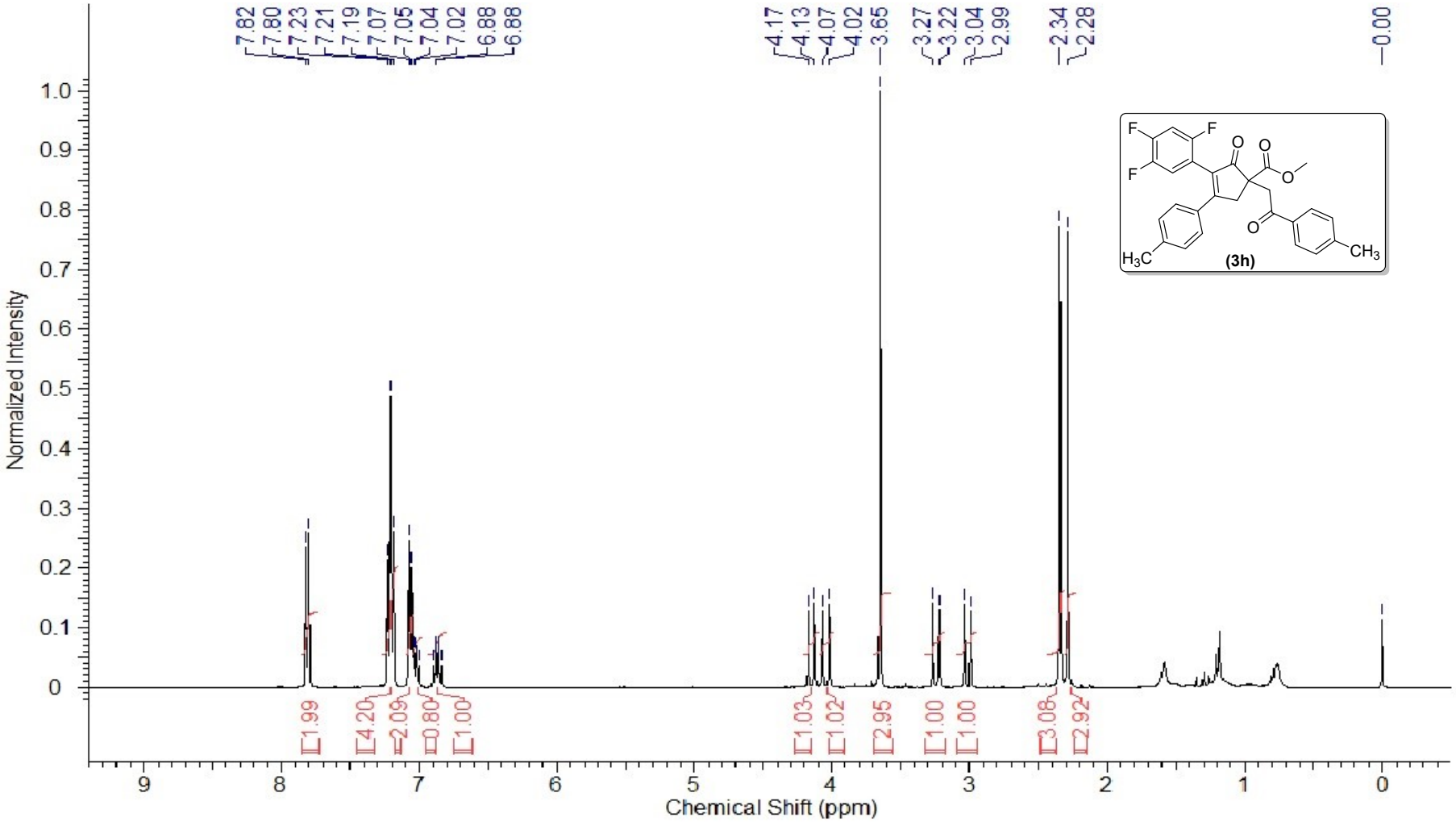
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3f



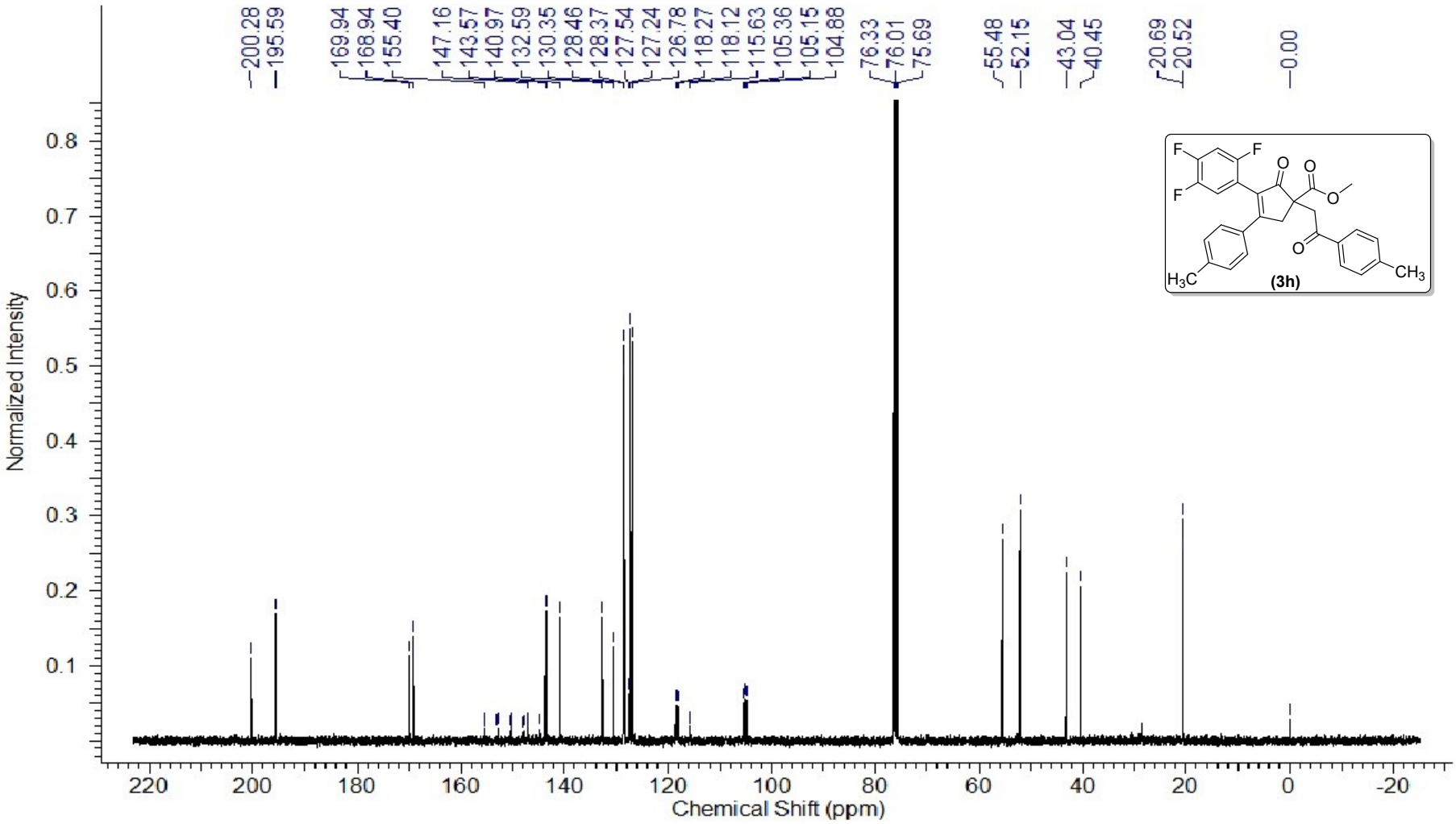
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3g



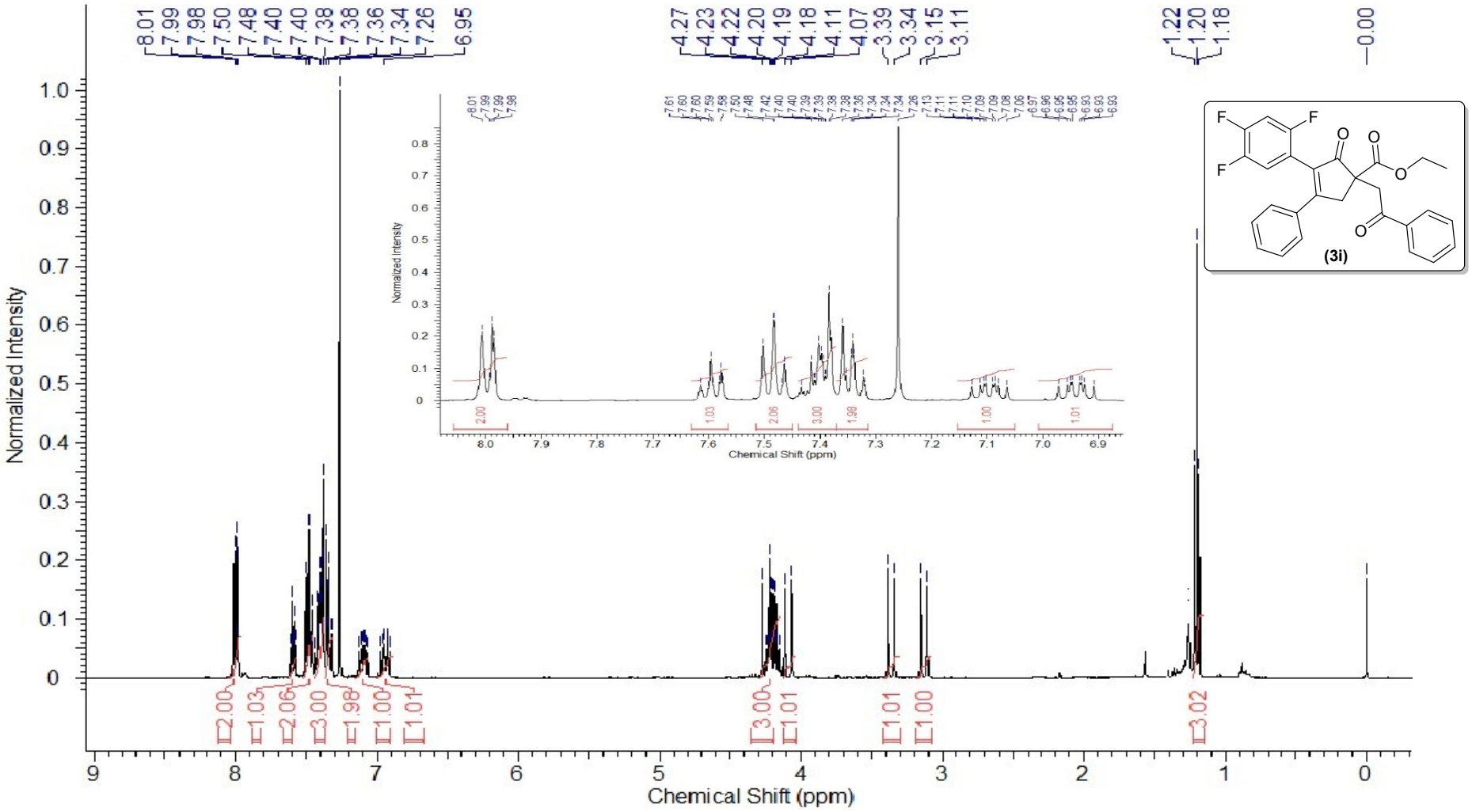
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3g



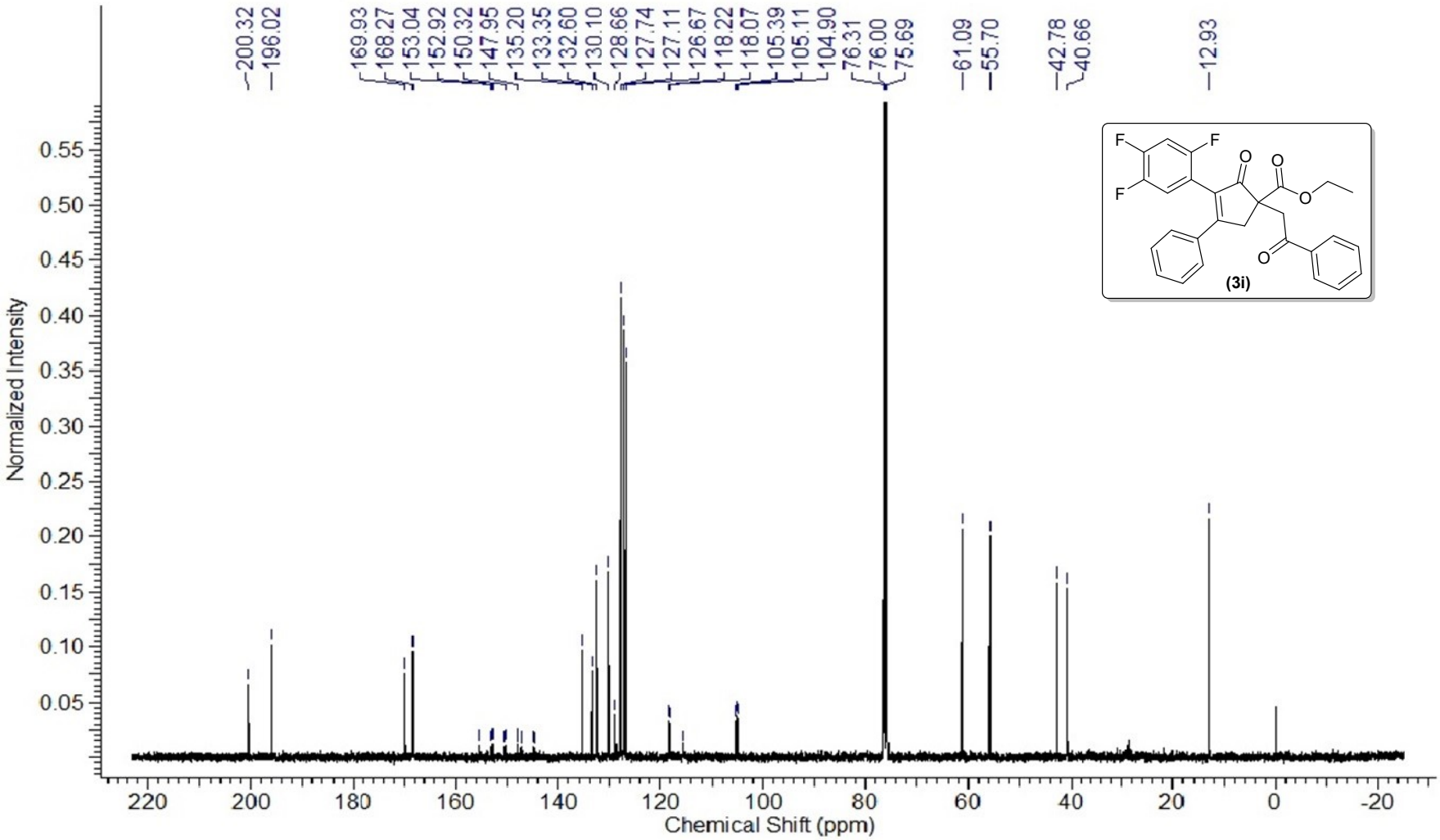
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3h



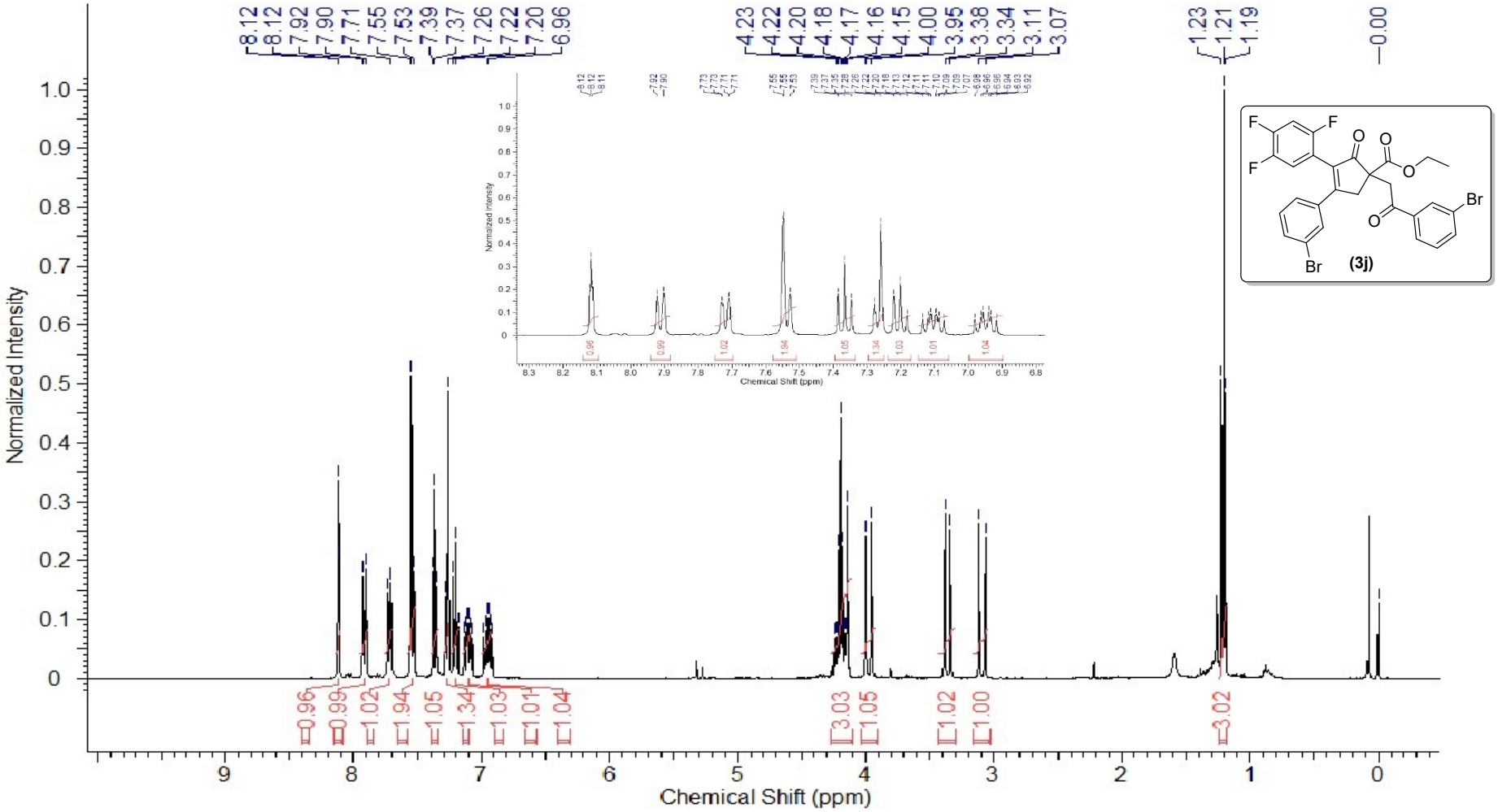
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3h



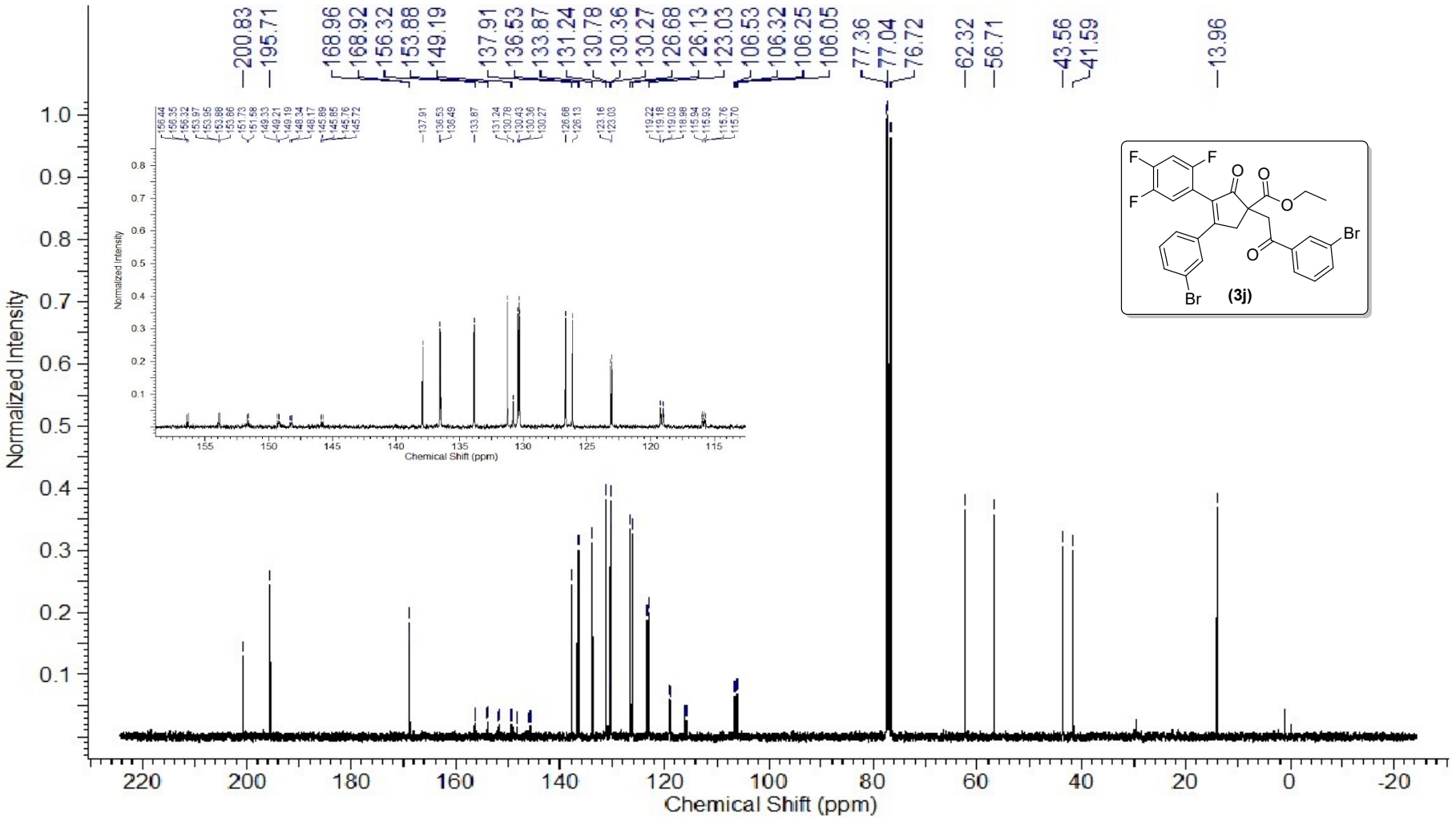
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3i



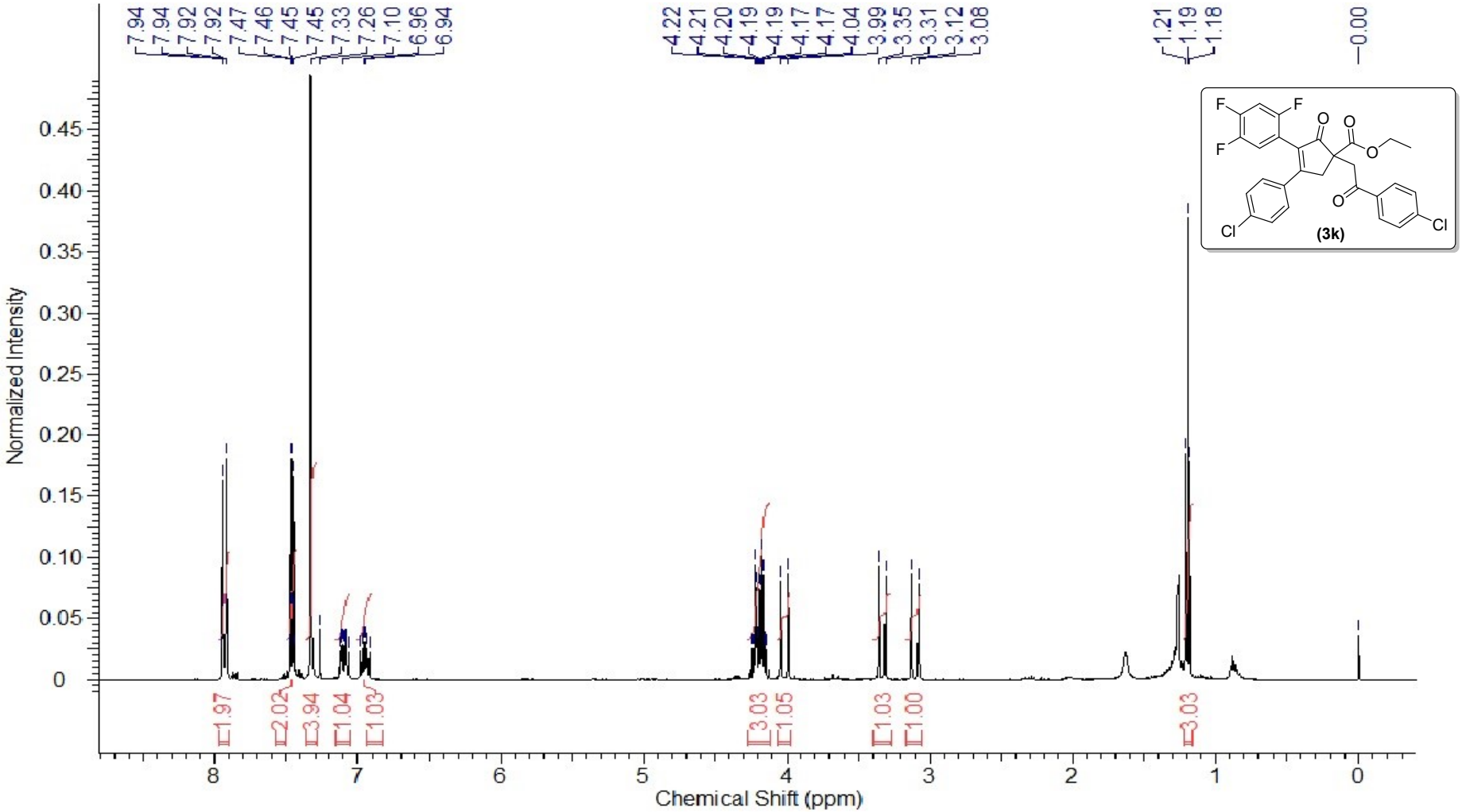
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3i



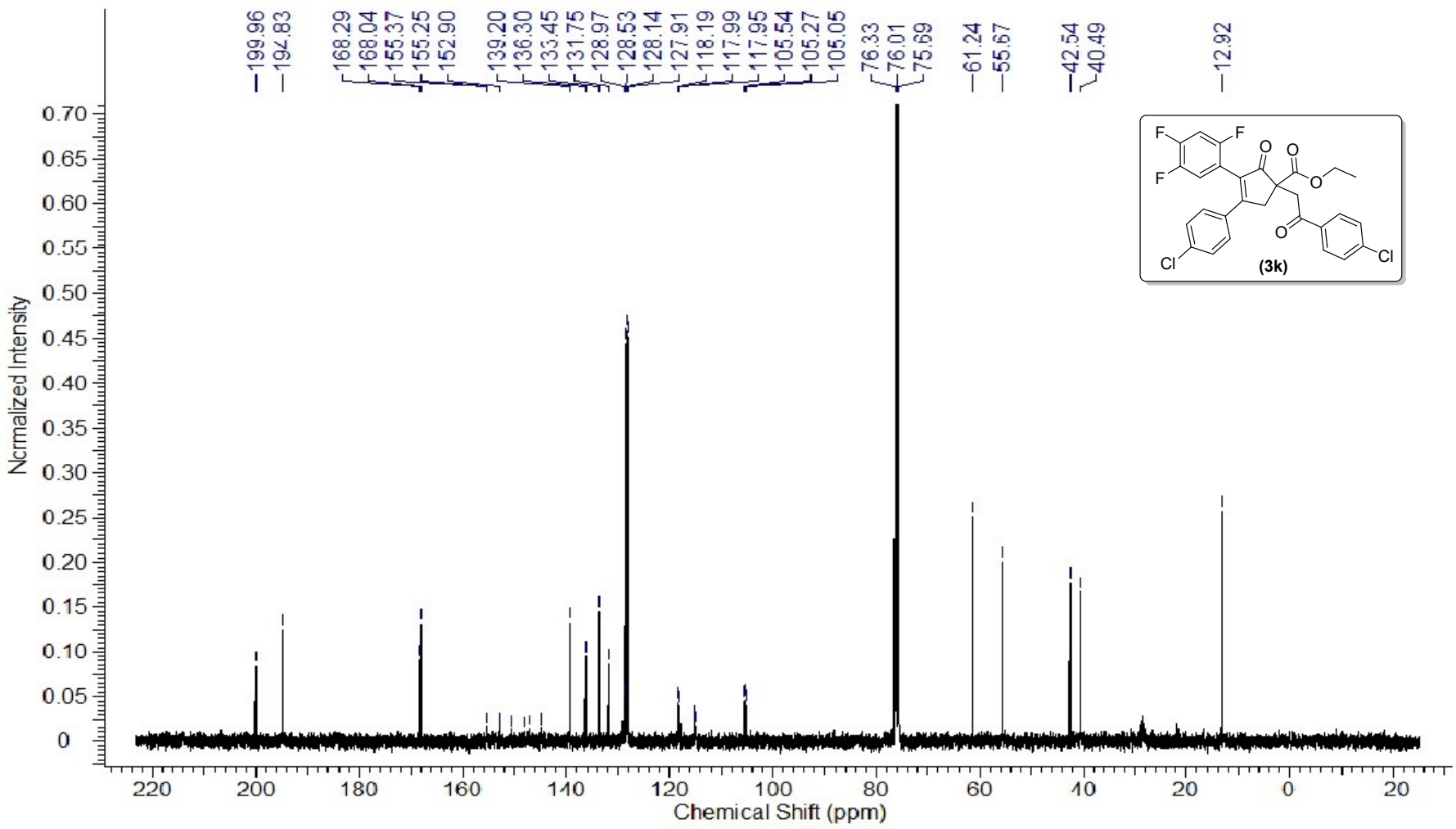
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3j



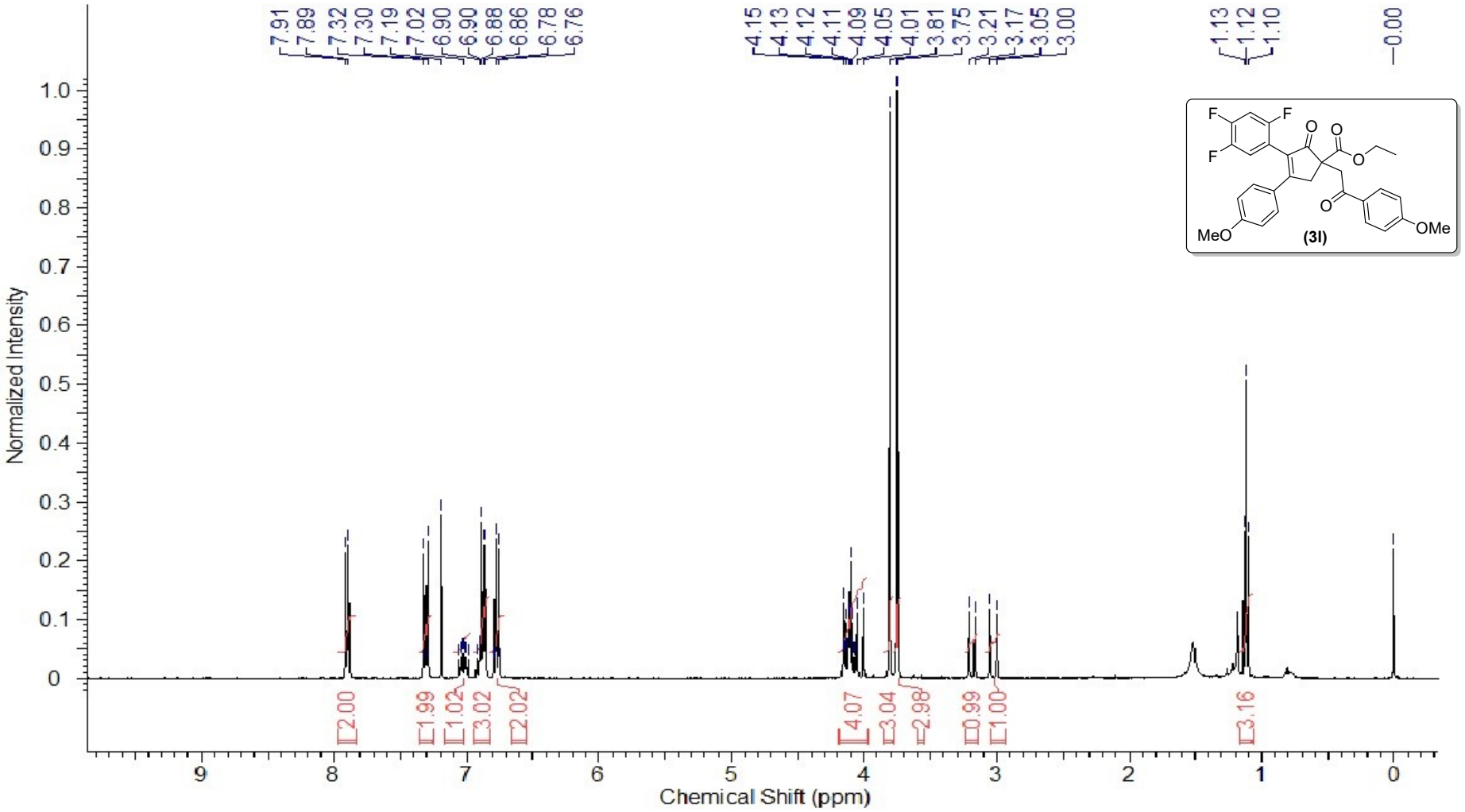
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3j



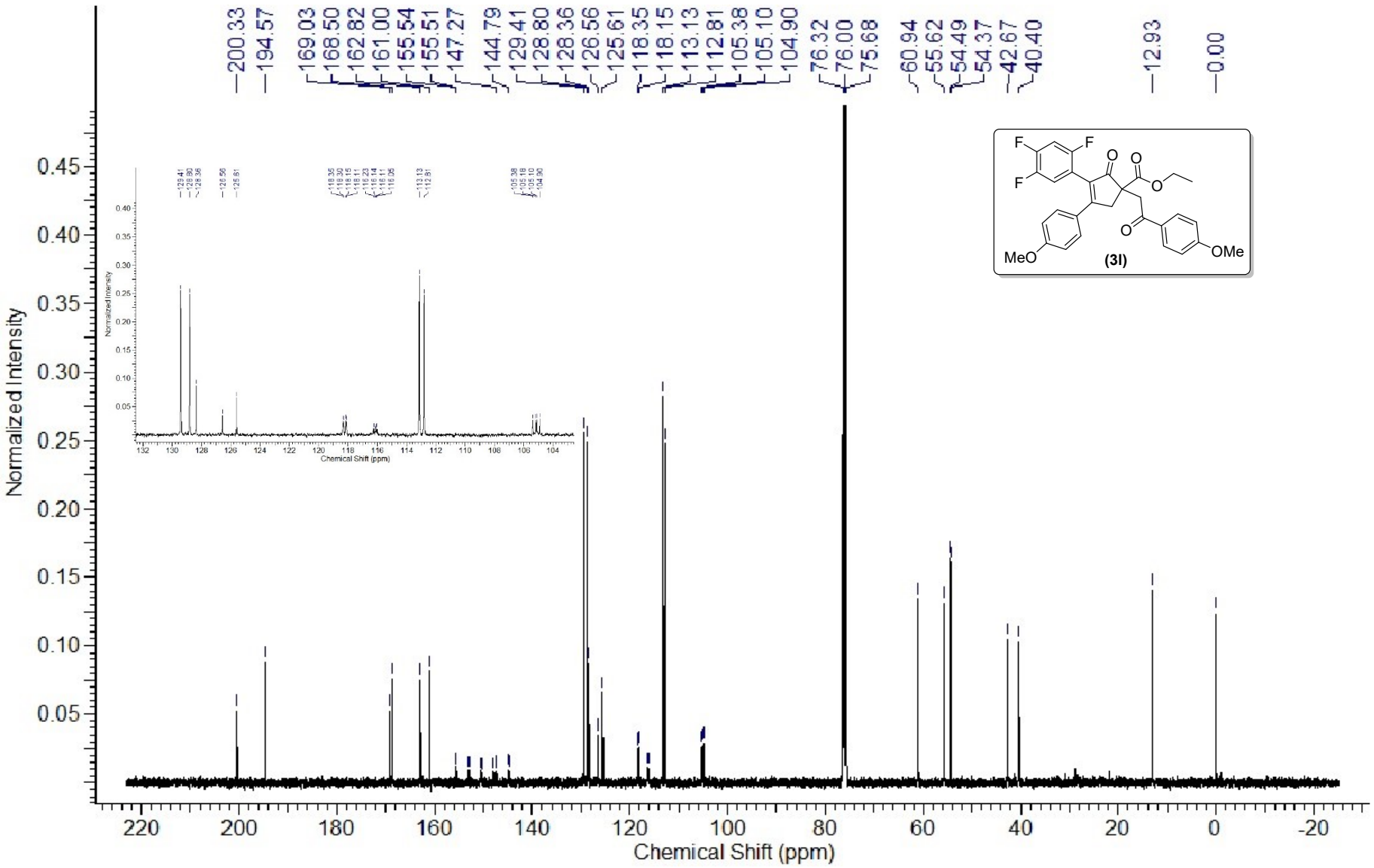
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3k



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3k



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3l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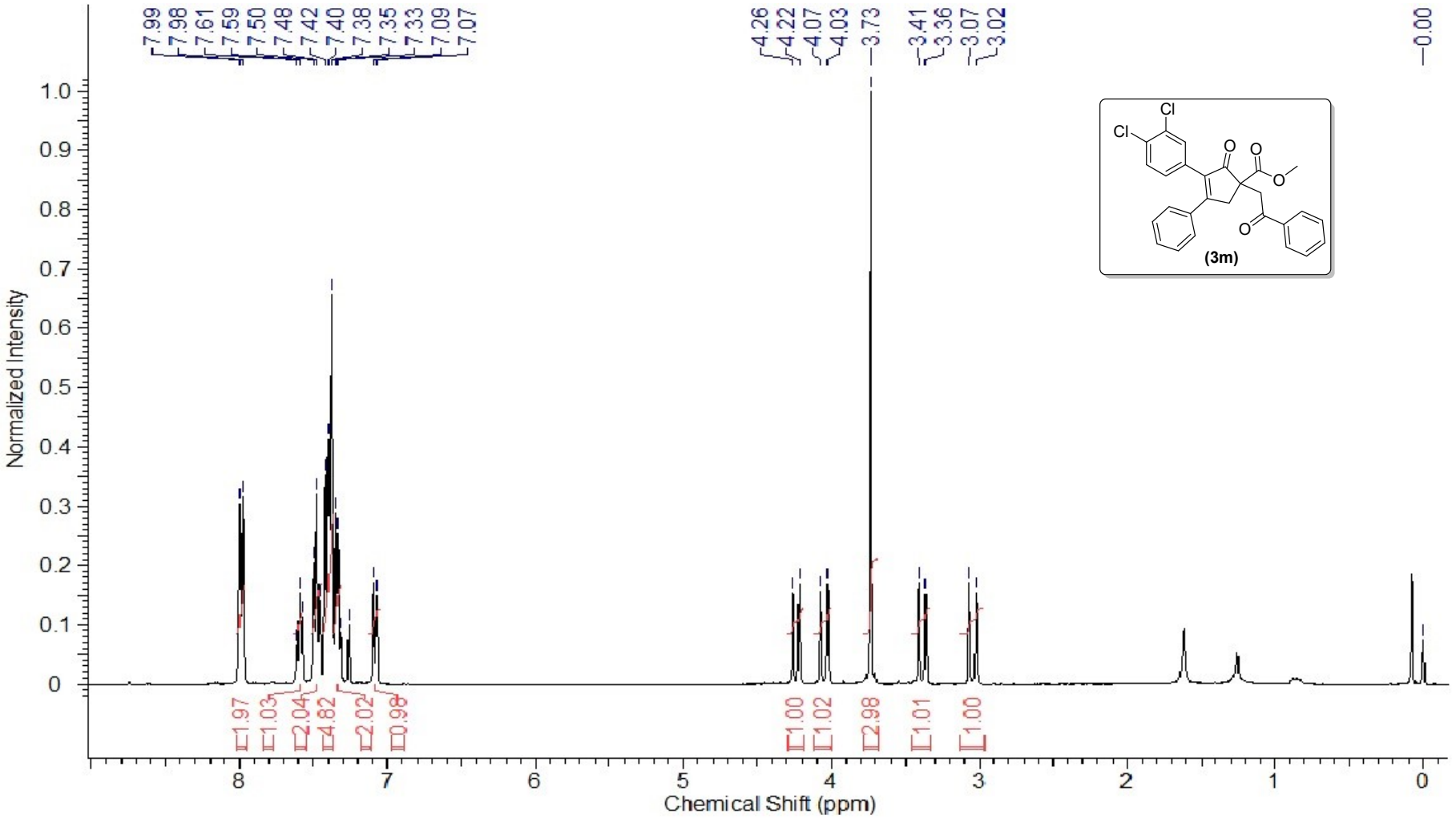
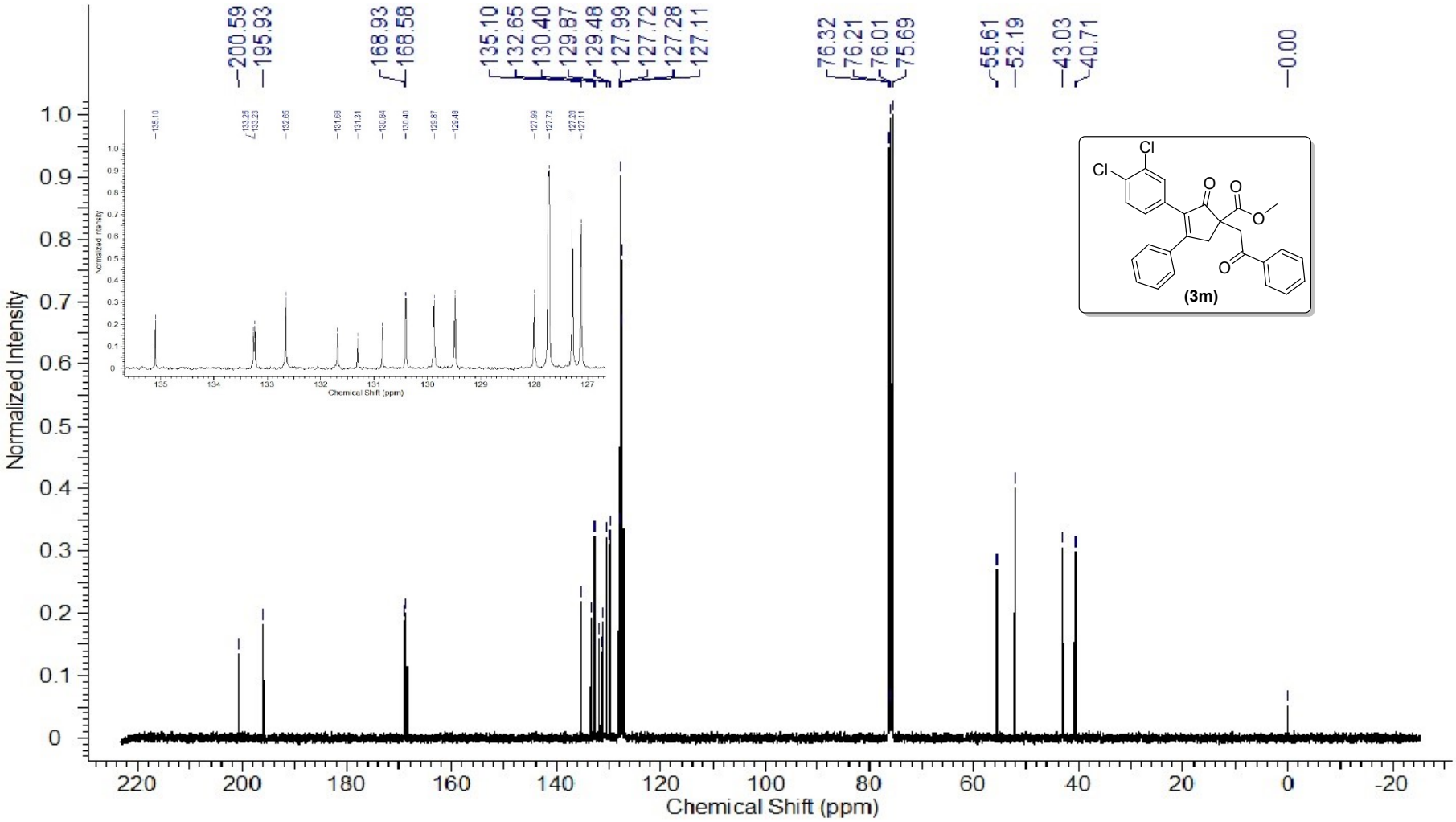
168.50
162.82
161.00
155.54
155.51
147.27
144.79
129.41
128.80
128.36
126.56
125.61
118.35
118.15
113.13
112.81
105.38
105.10
76.32
76.00
75.68
60.94
55.62
54.49
54.37
42.67
40.40
12.93
0.00
Normalized Intensity
Chemical Shift (ppm)
F
F
F
O
O
O
O
MeO
OMe
(3l)

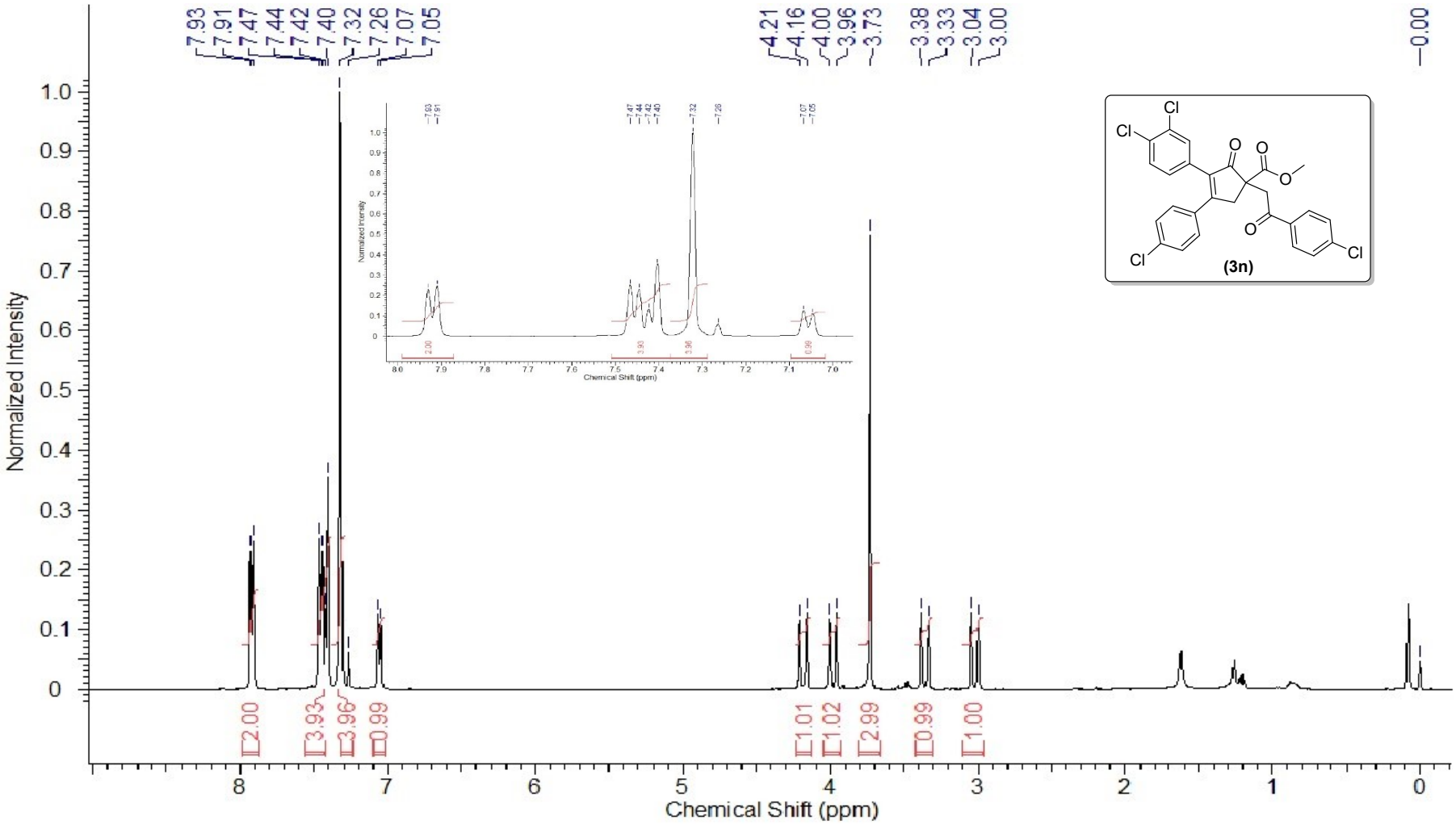
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3l



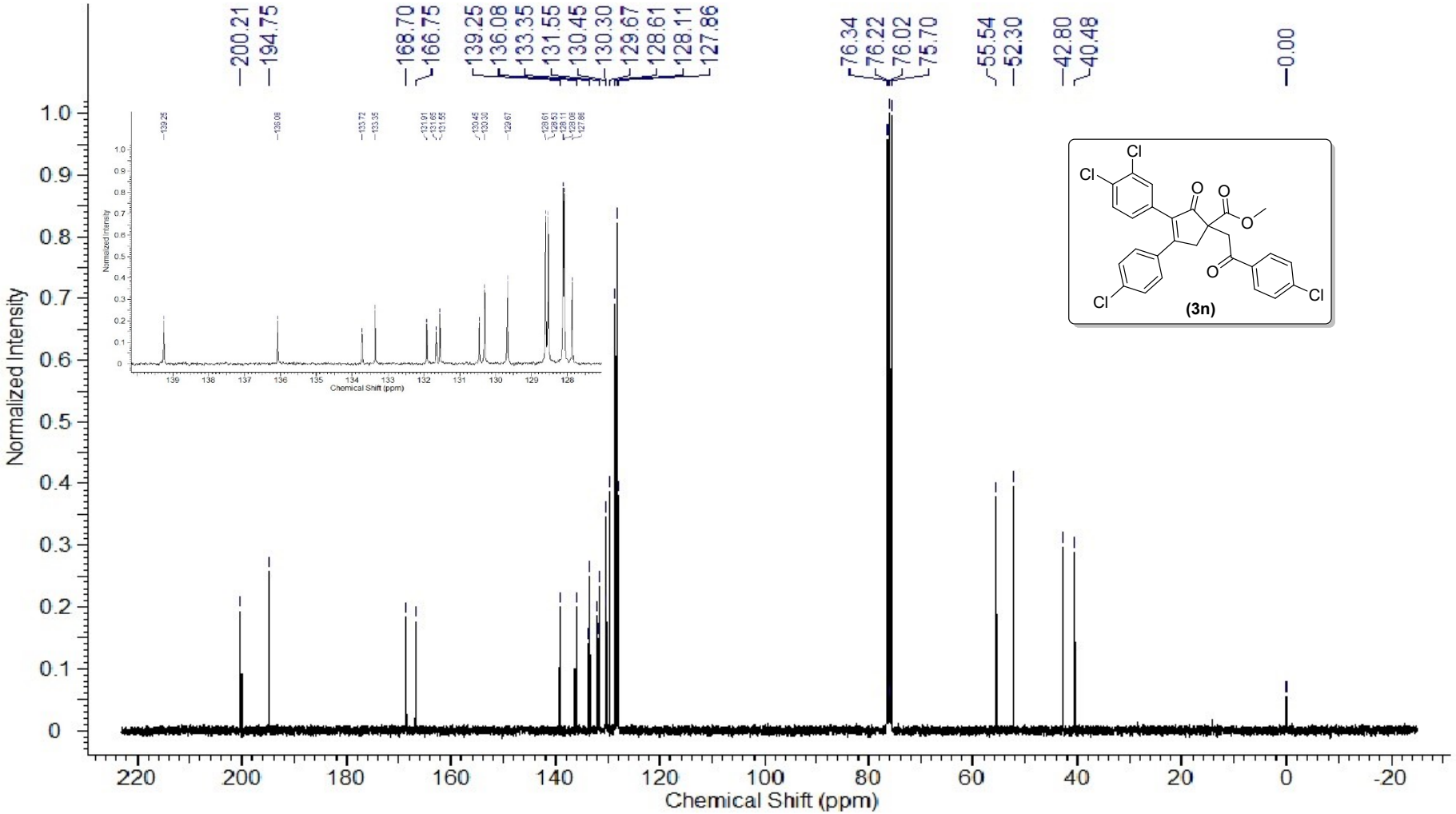
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3m



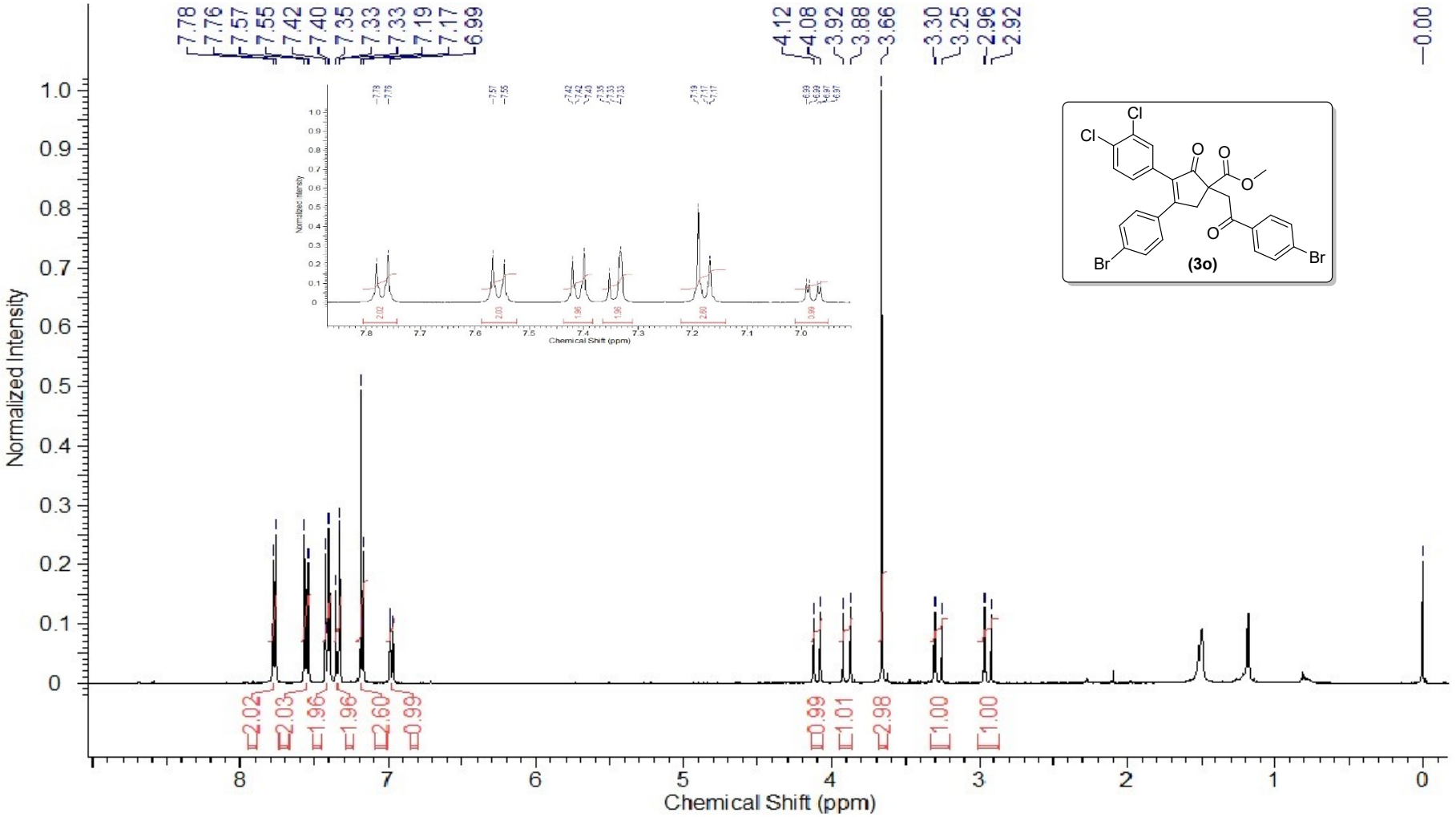
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3m



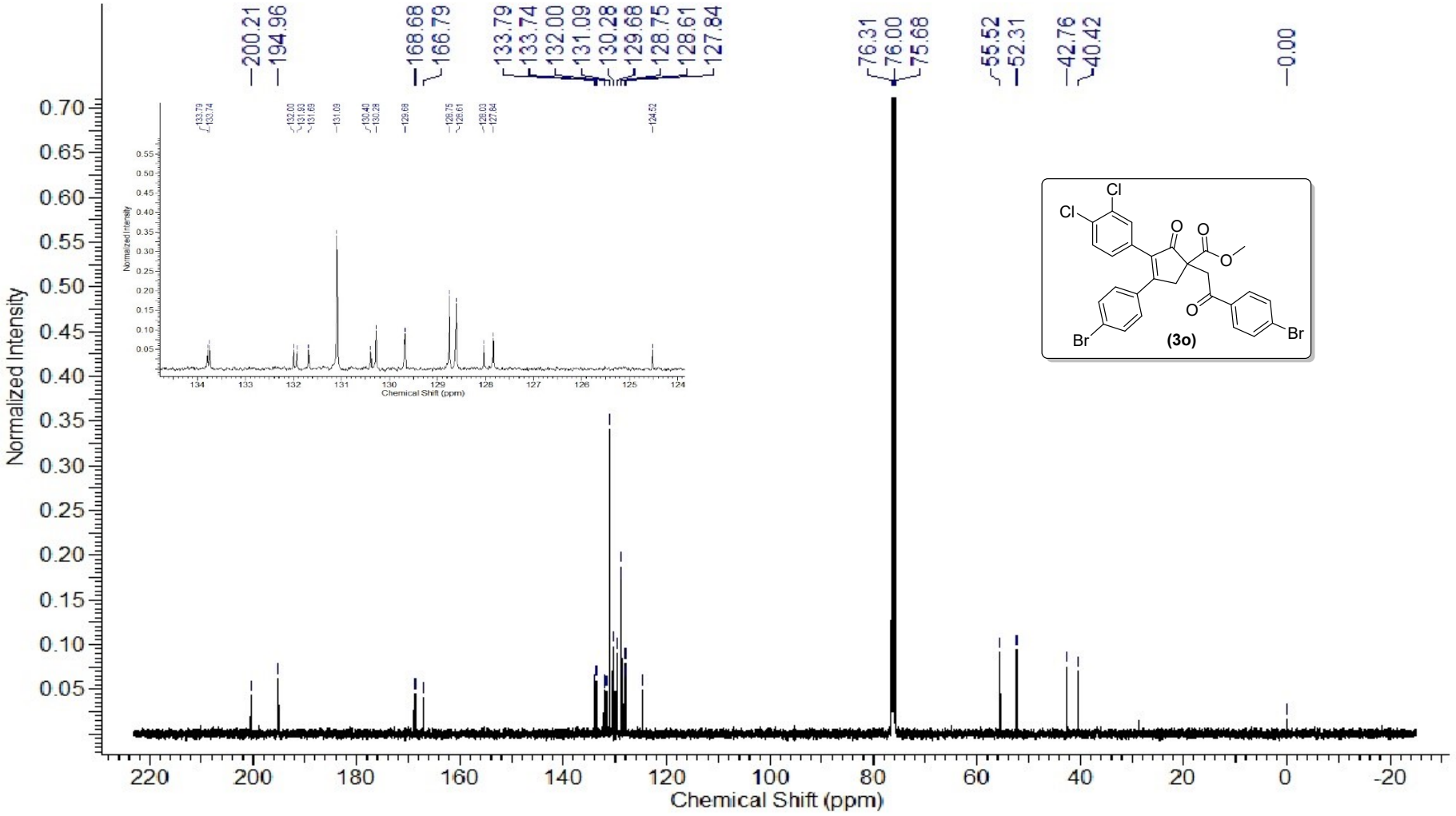
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3n



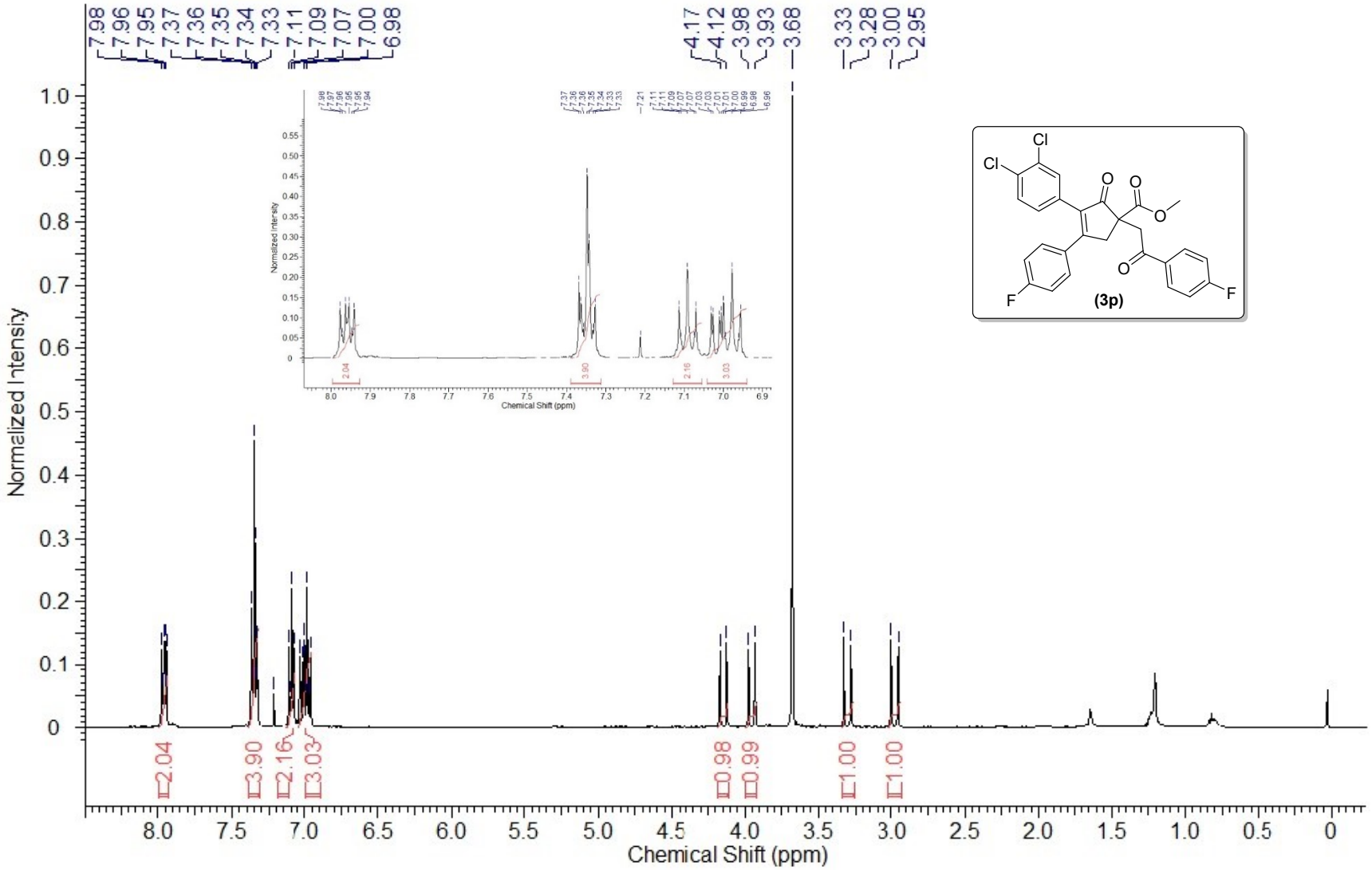
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3n



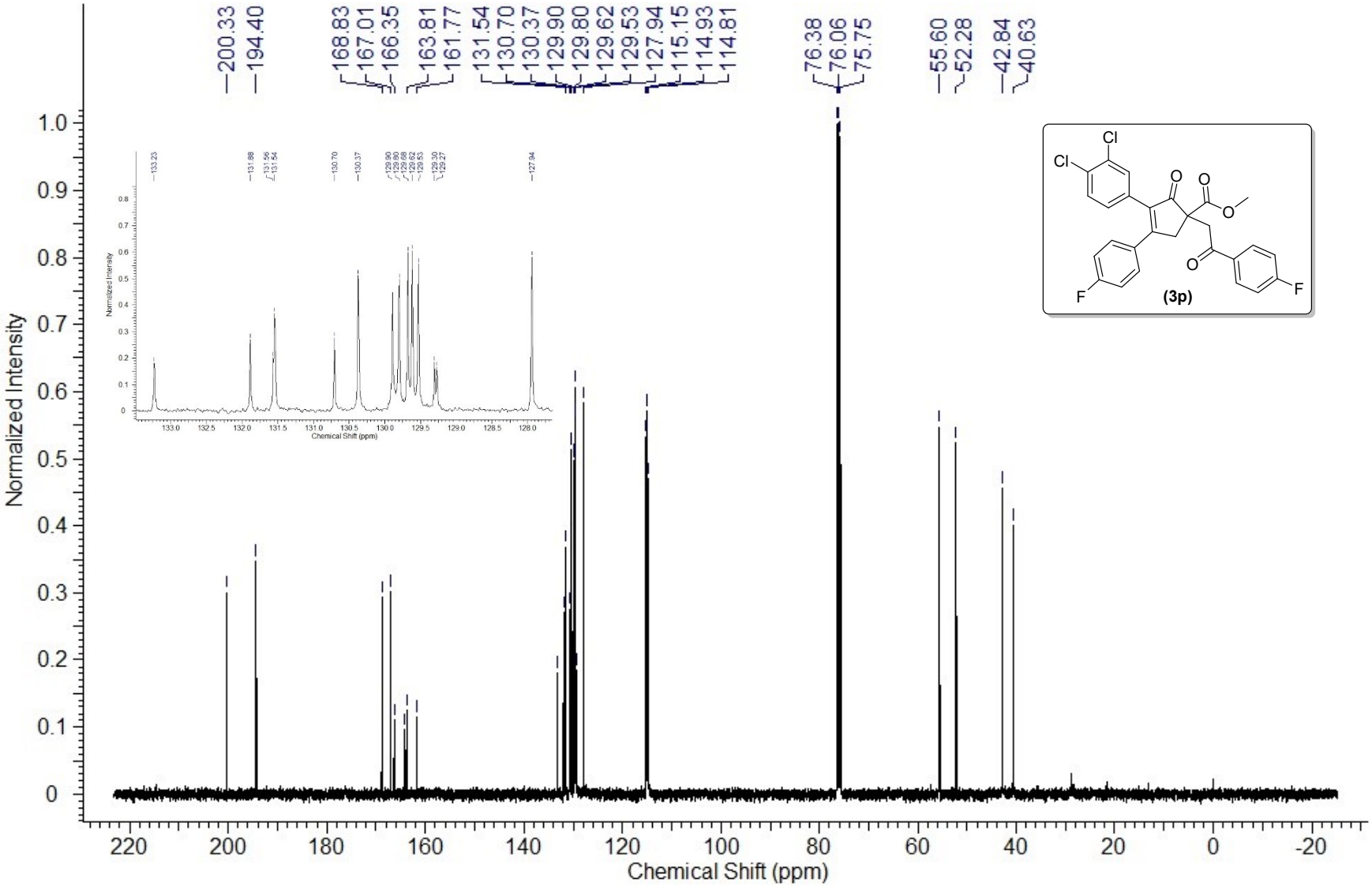
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3o



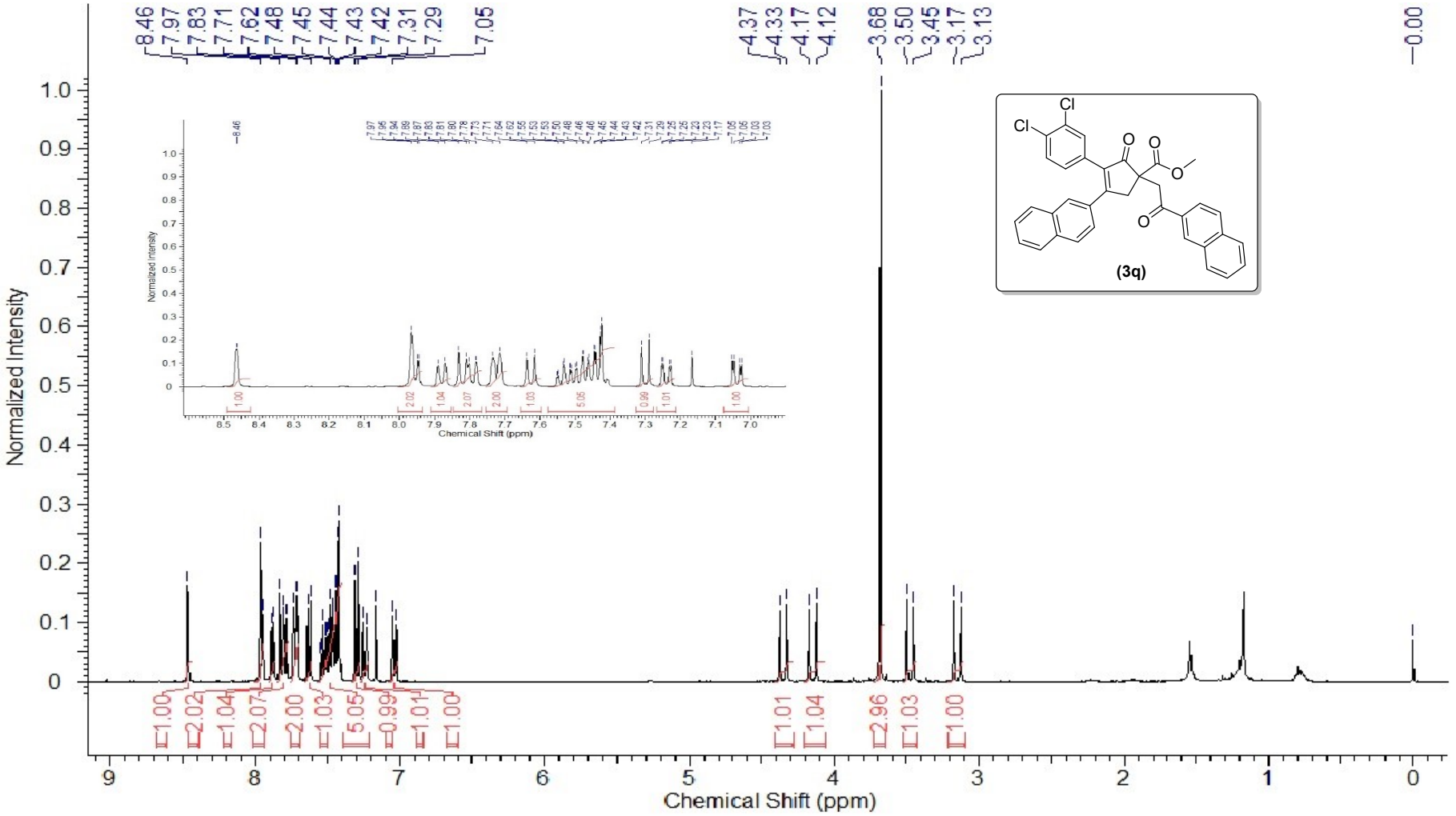
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3o



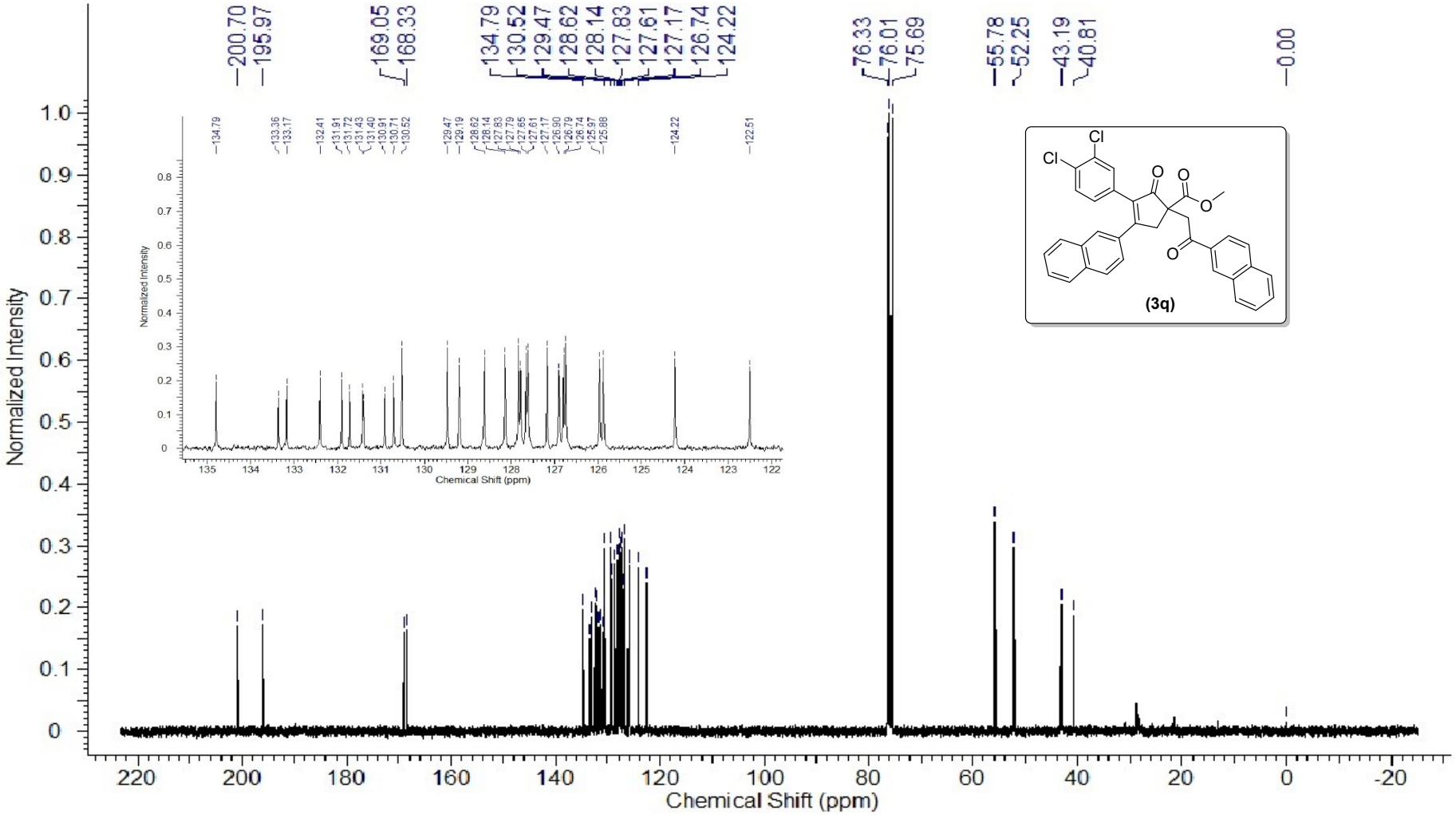
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3p



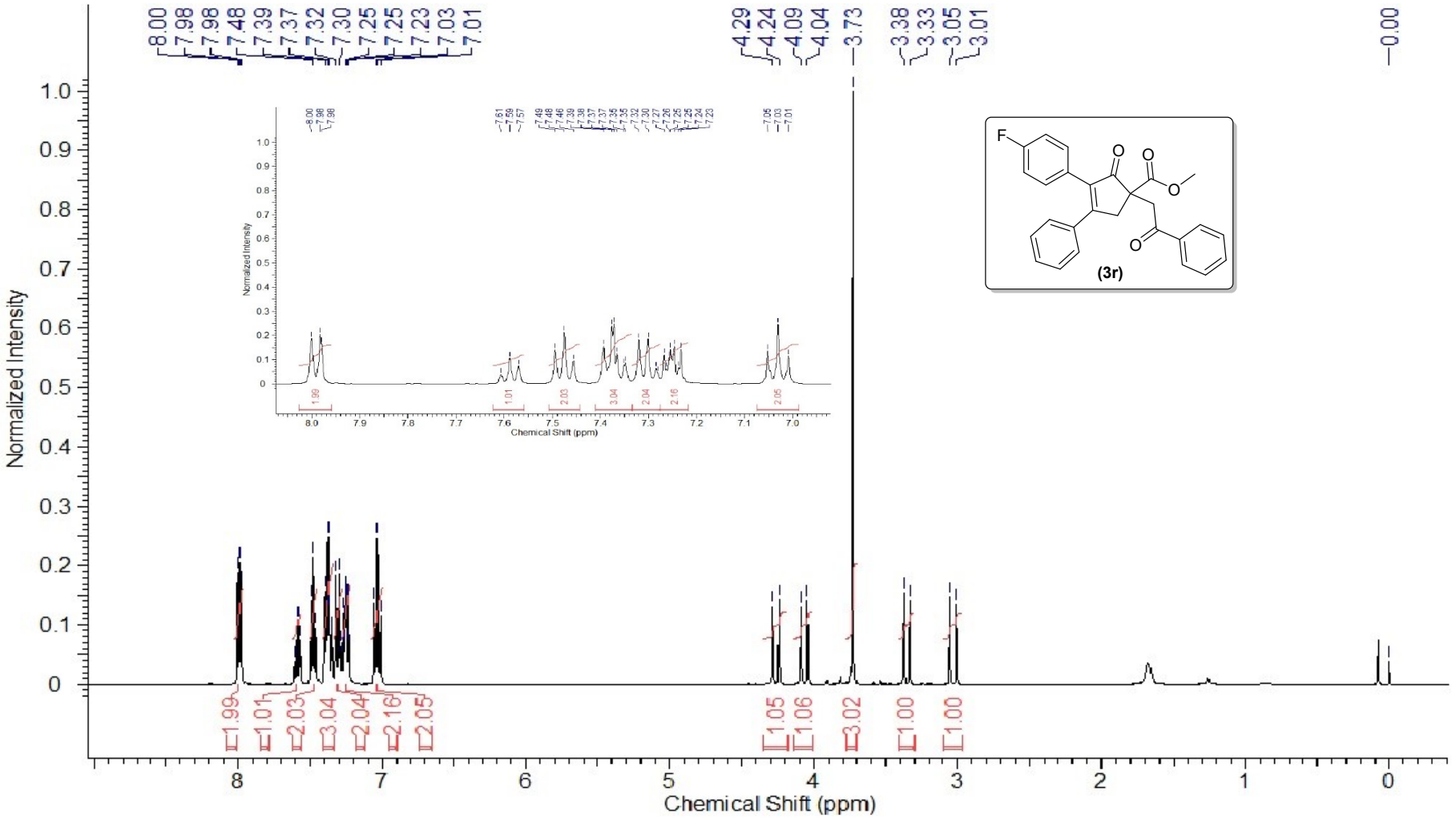
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3p



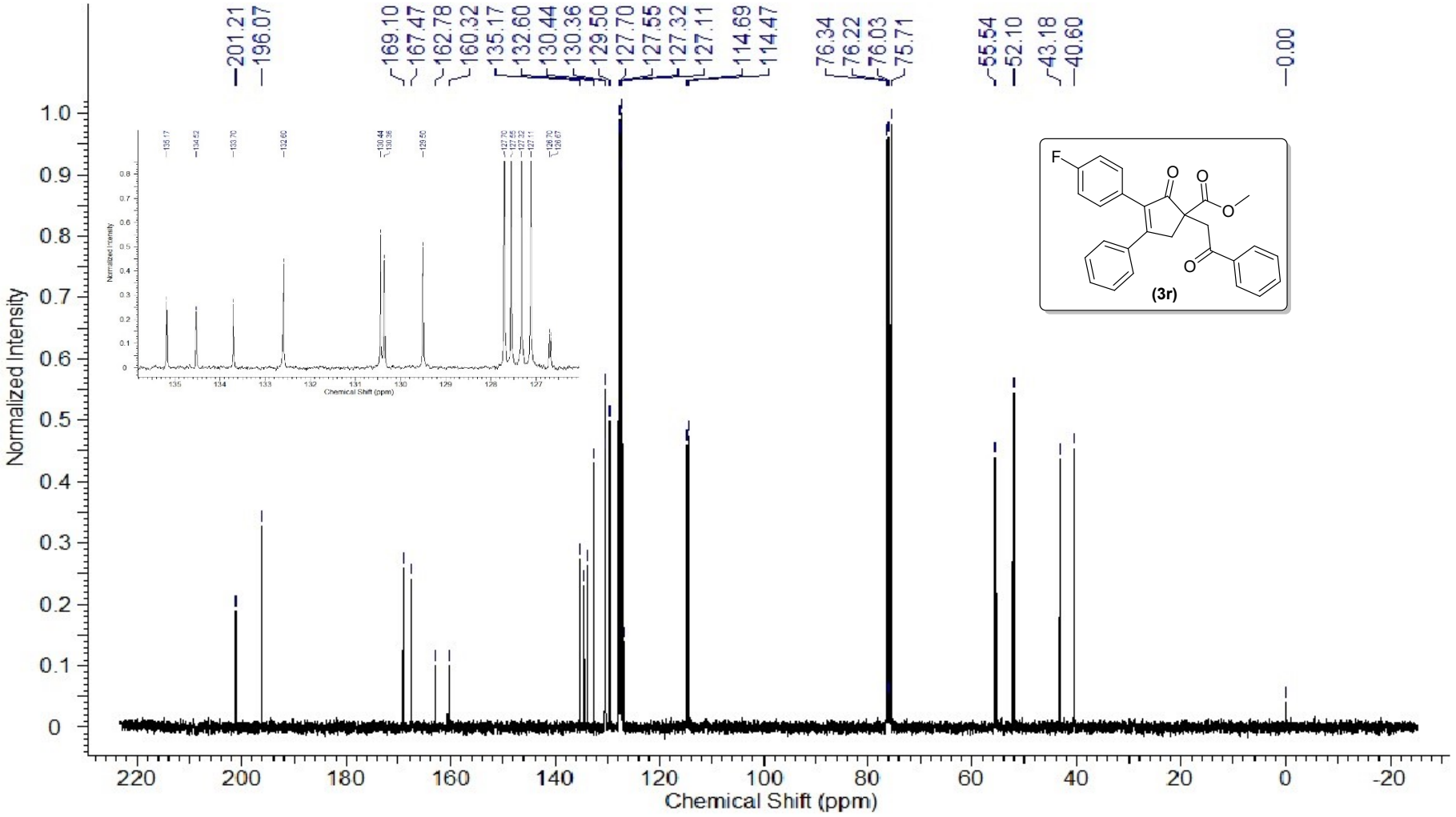
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3q



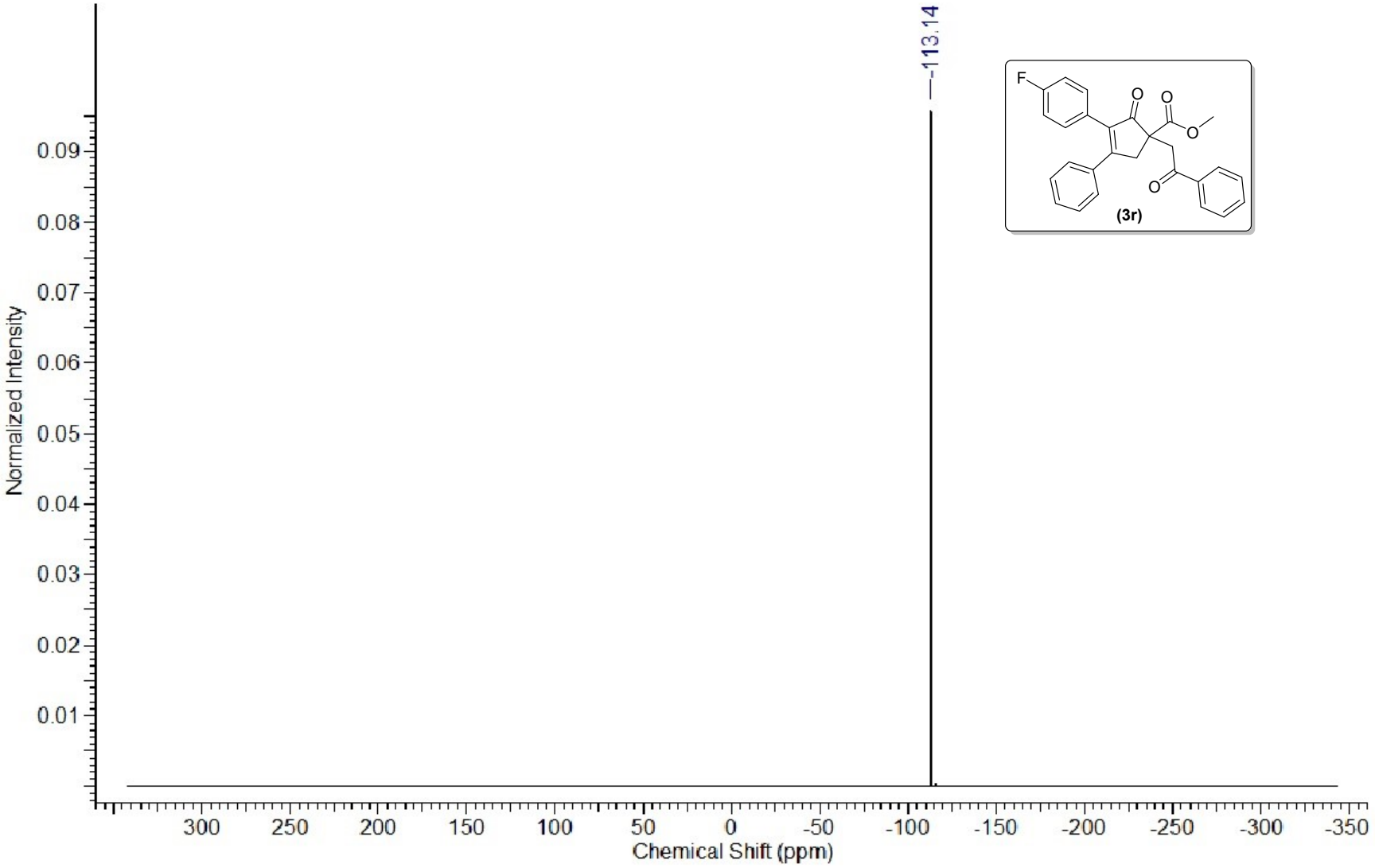
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3q



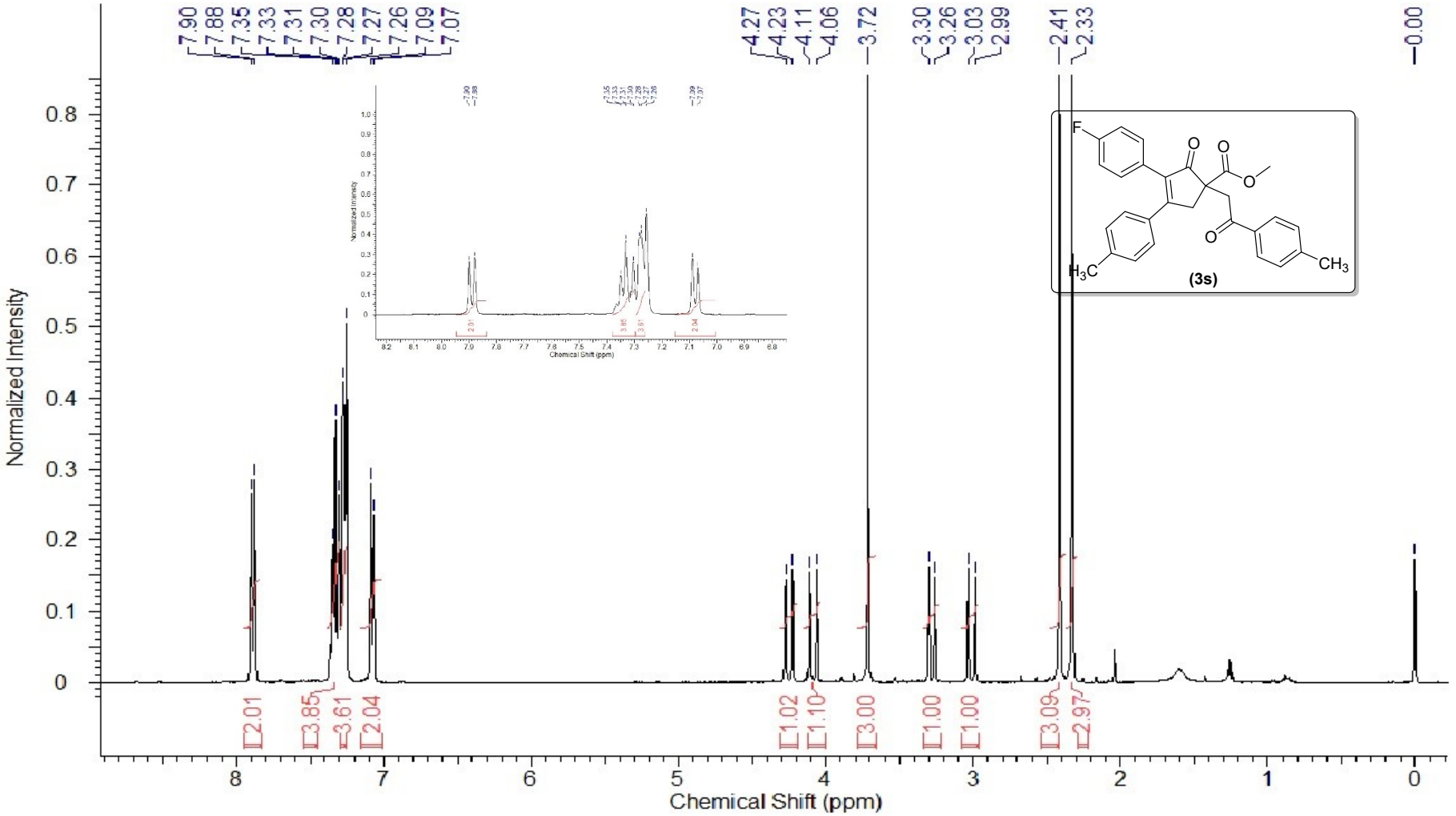
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3r



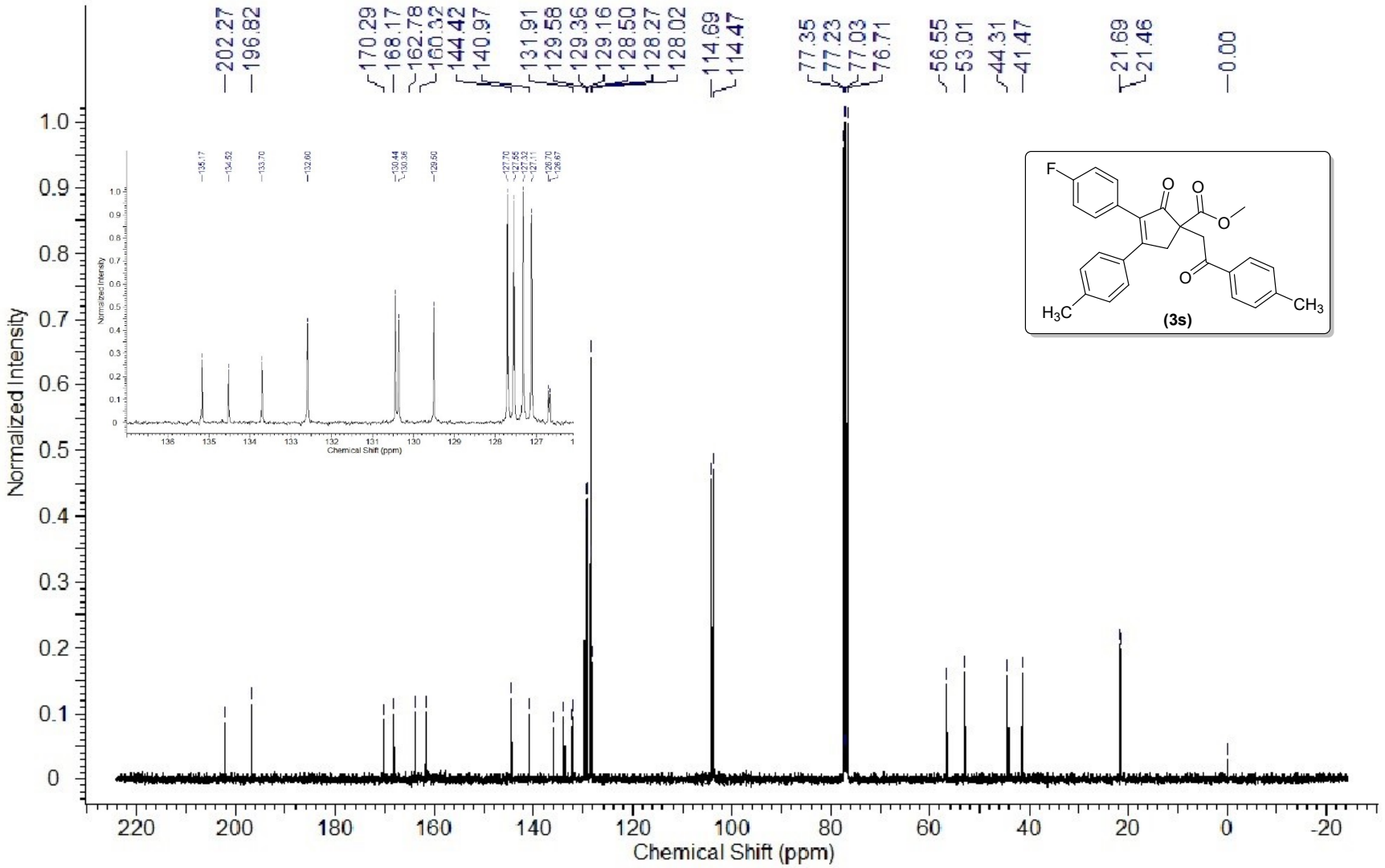
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3r



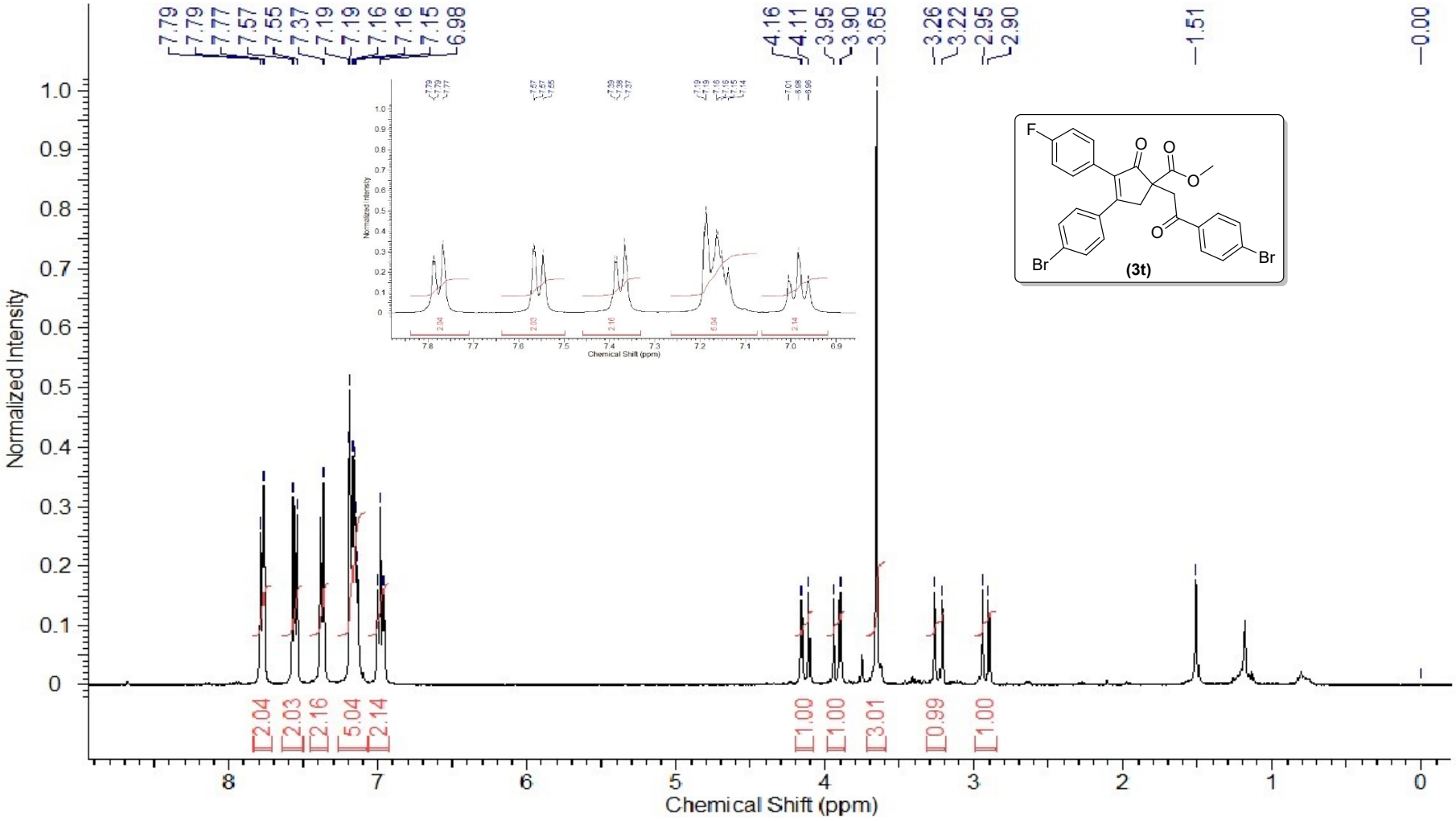
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3r



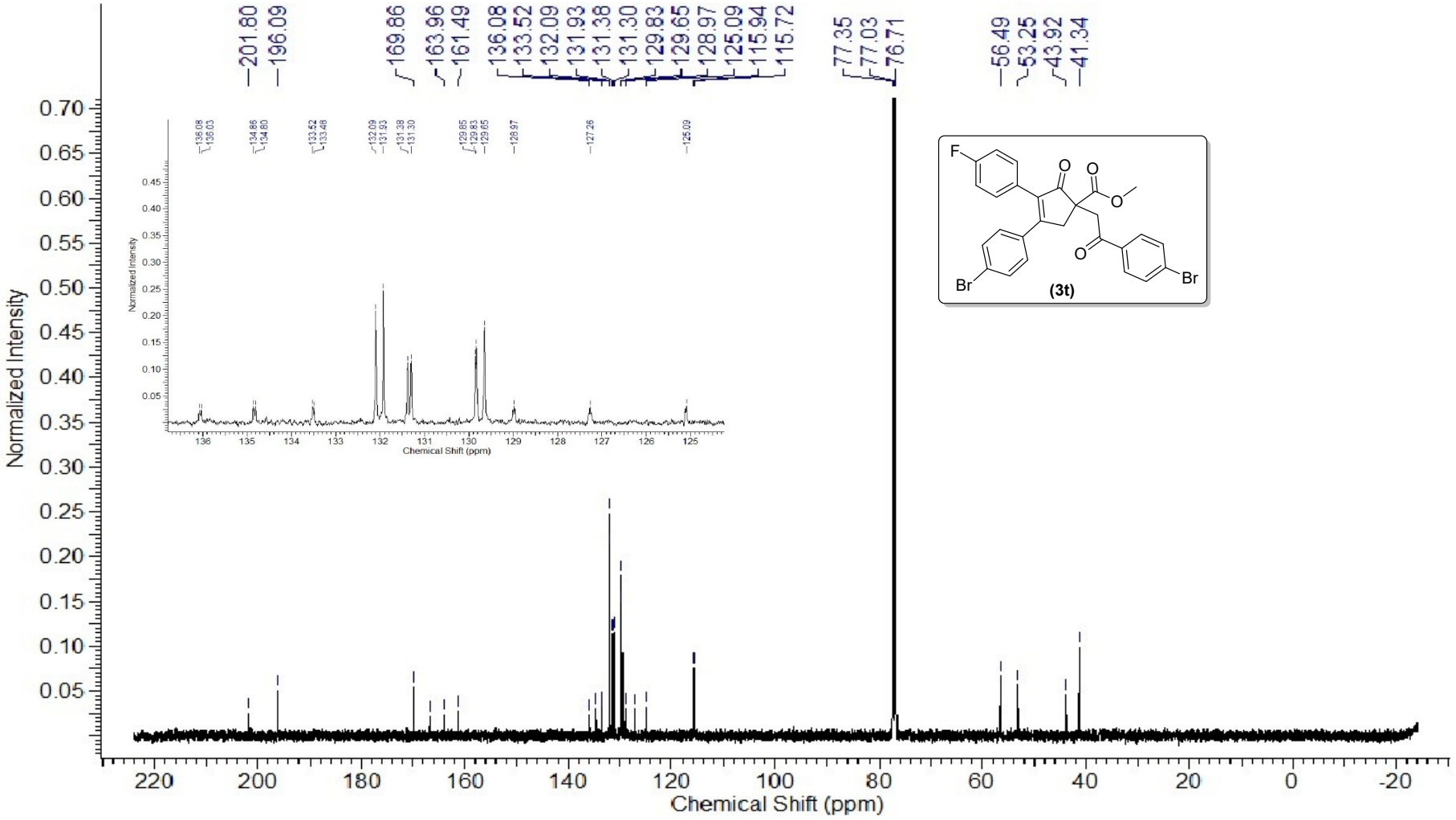
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3s



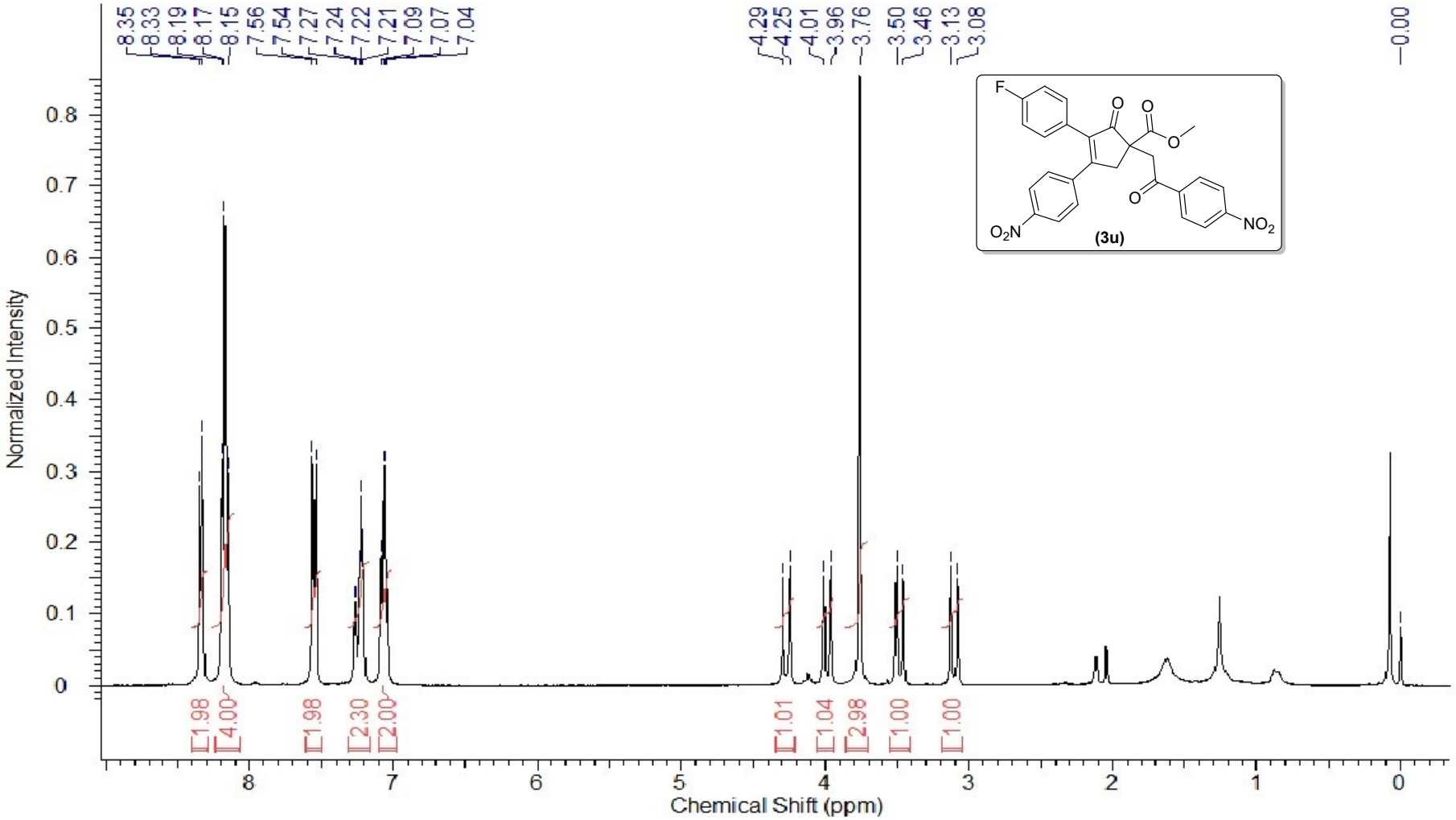
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3s



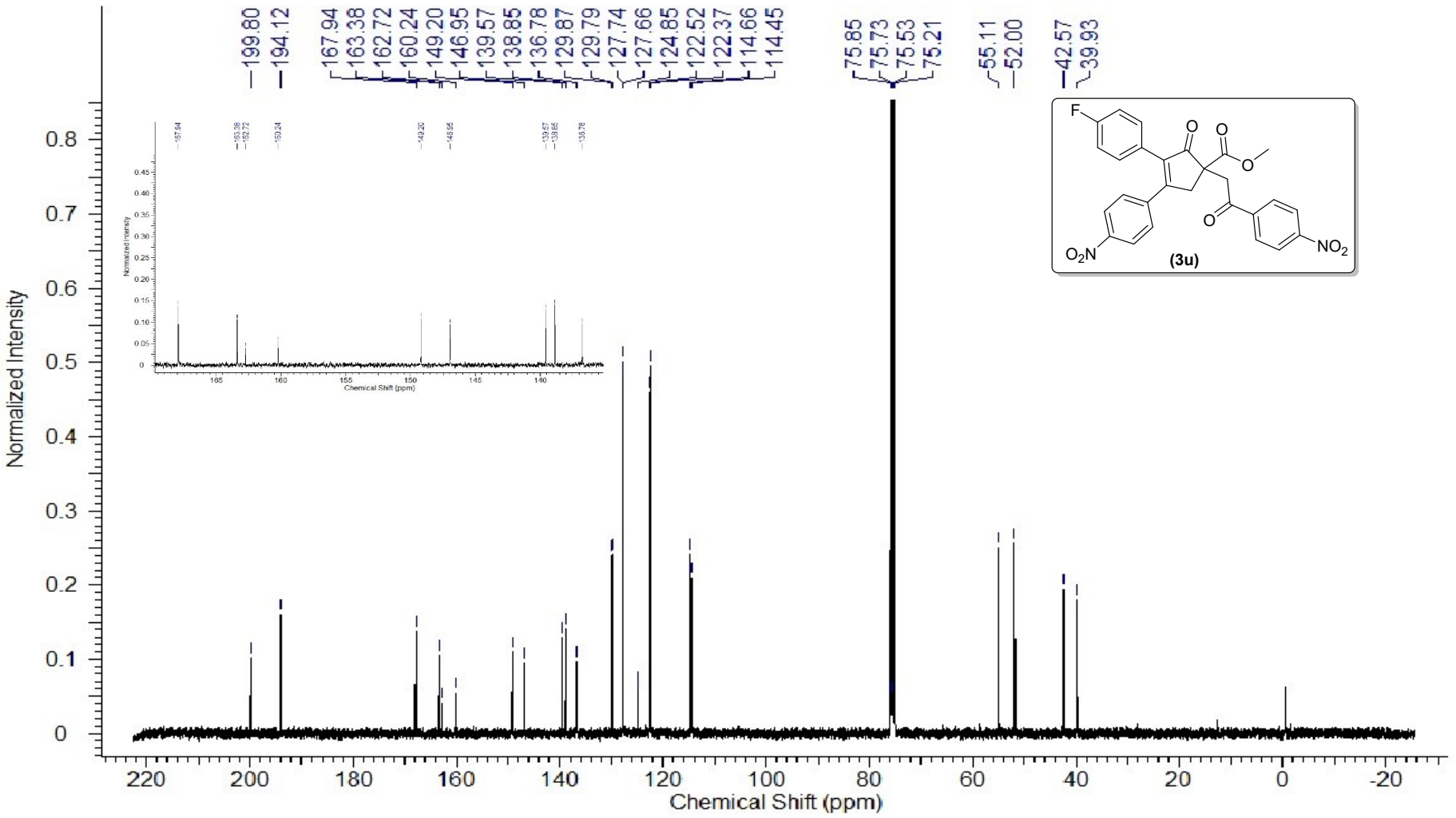
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3t



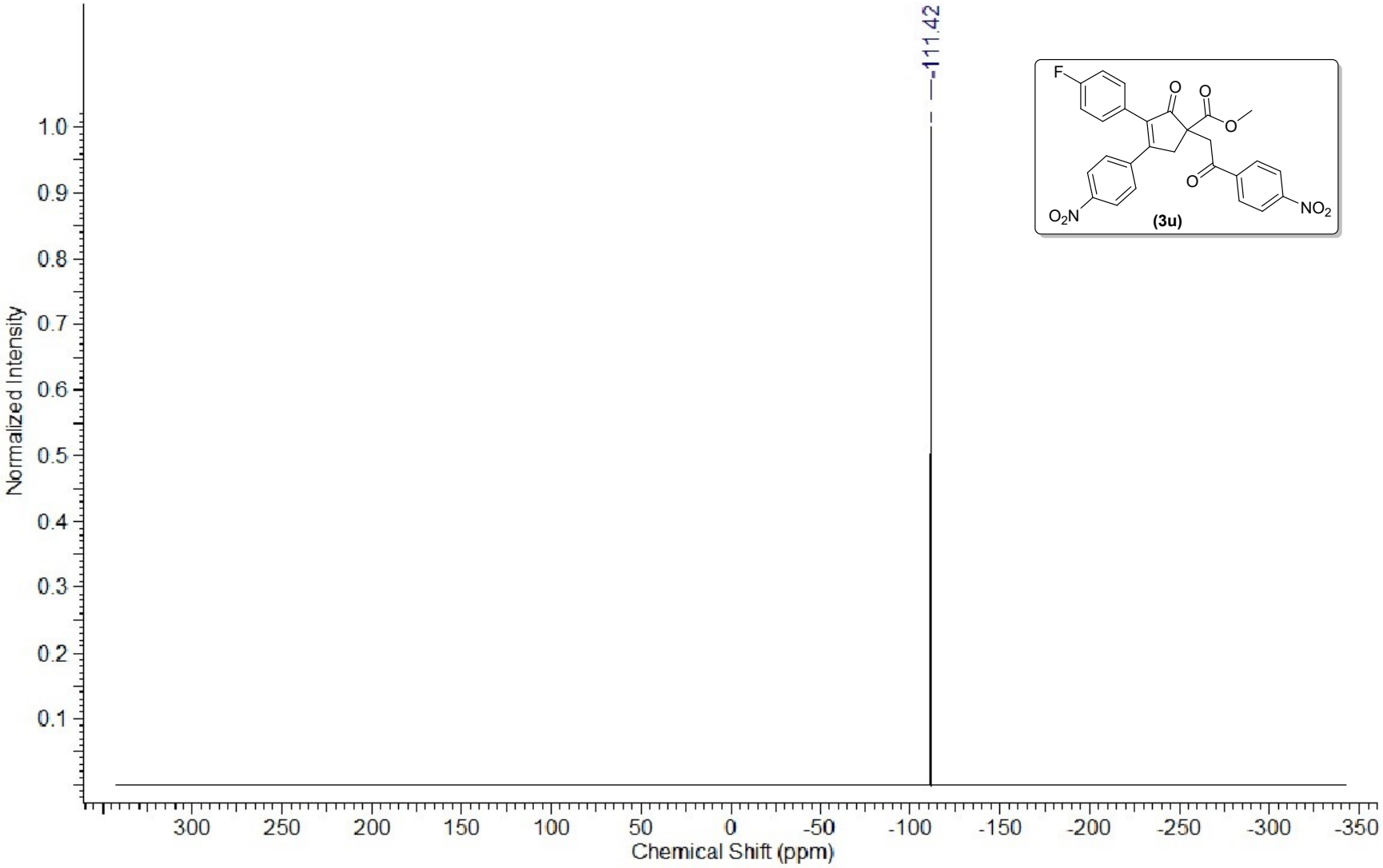
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3t



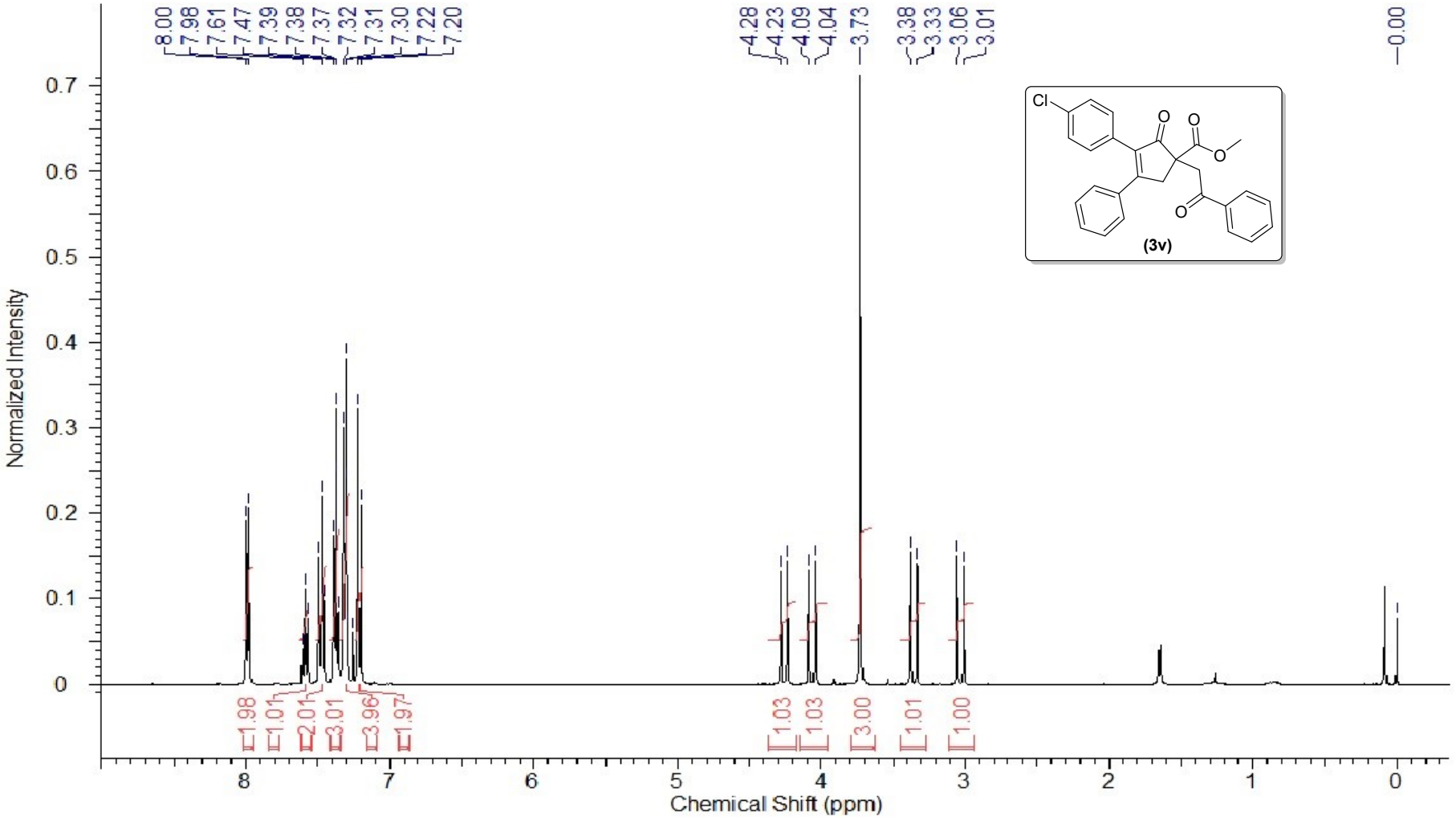
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3u



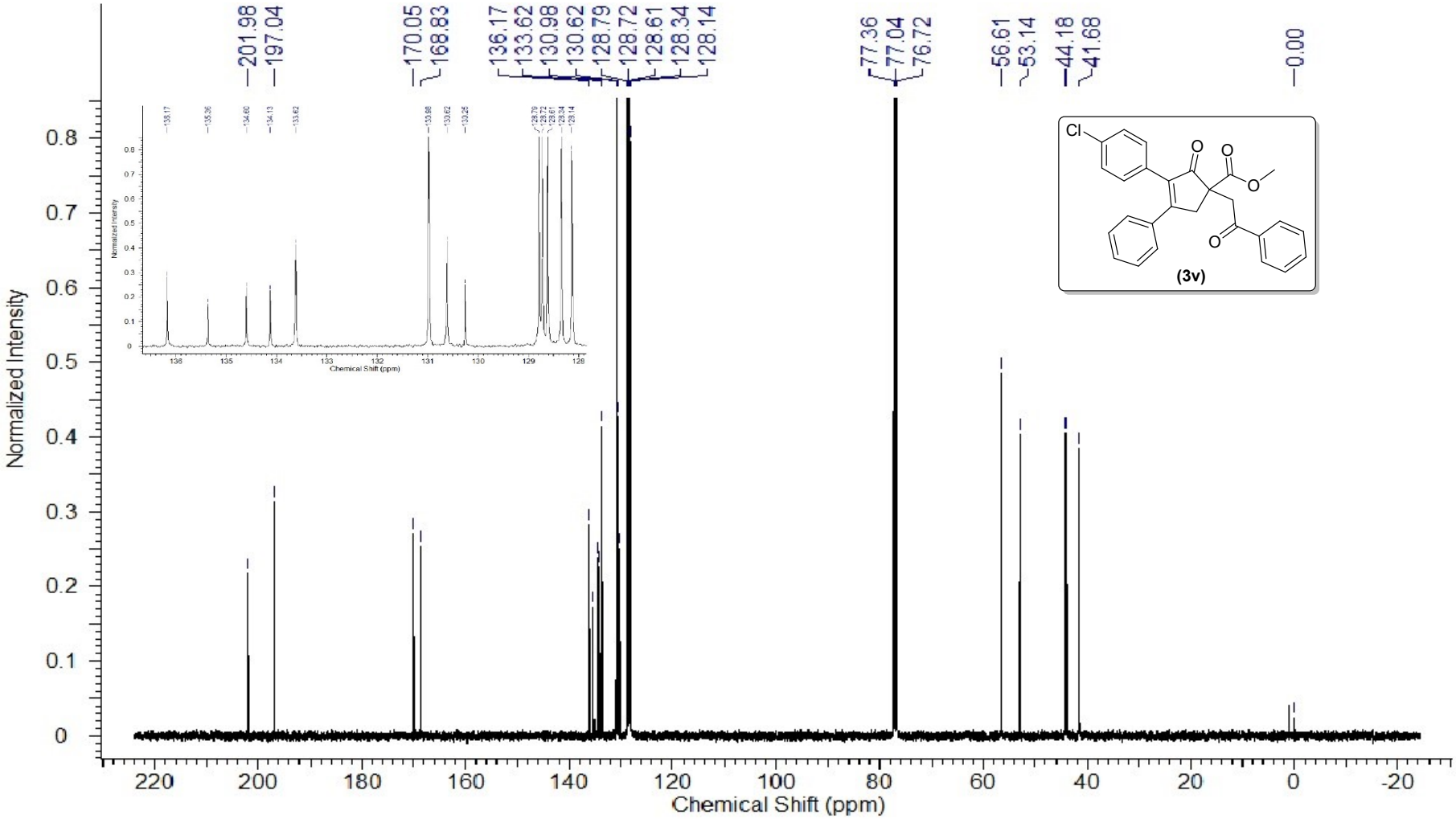
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3u



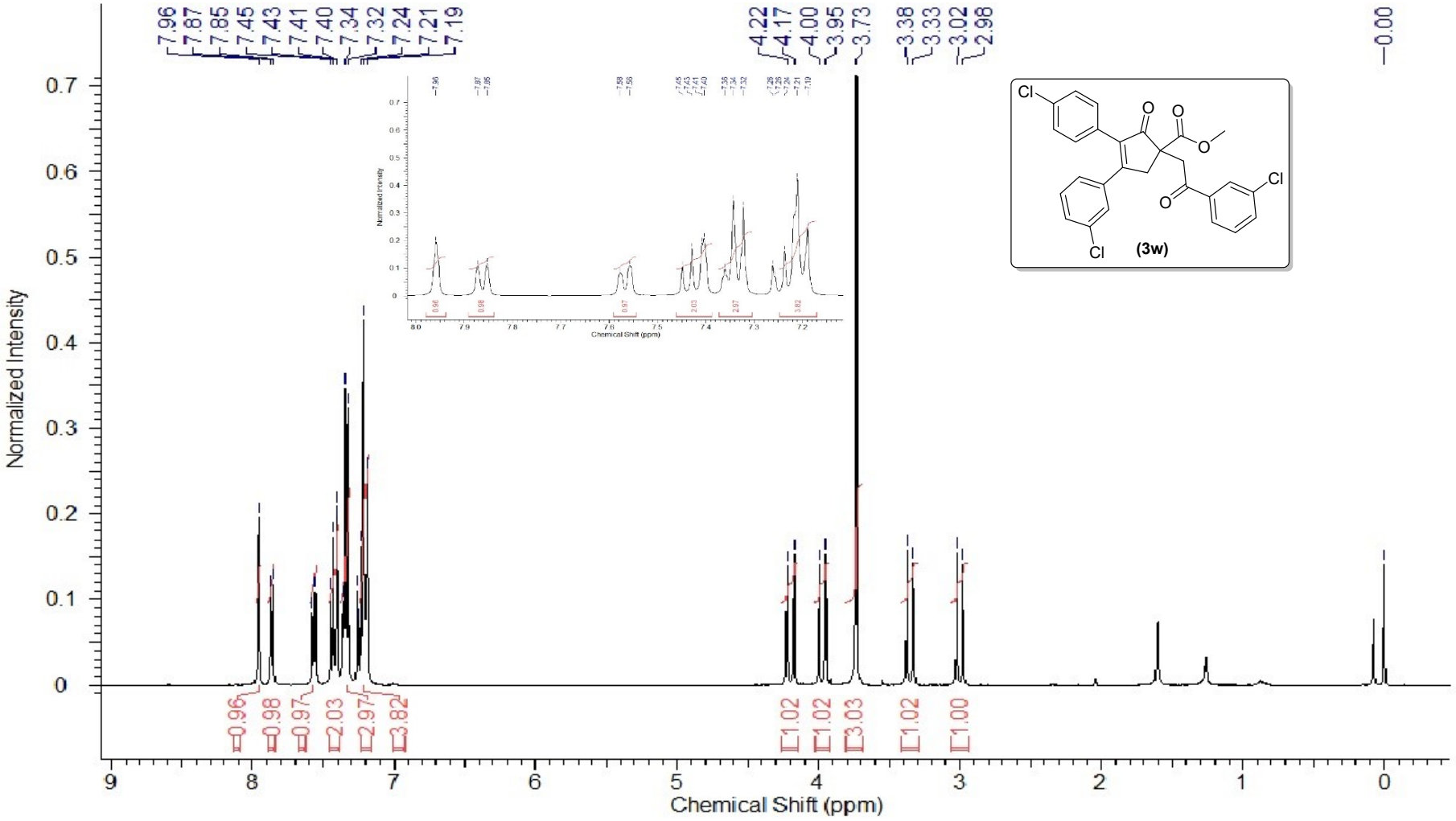
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3u



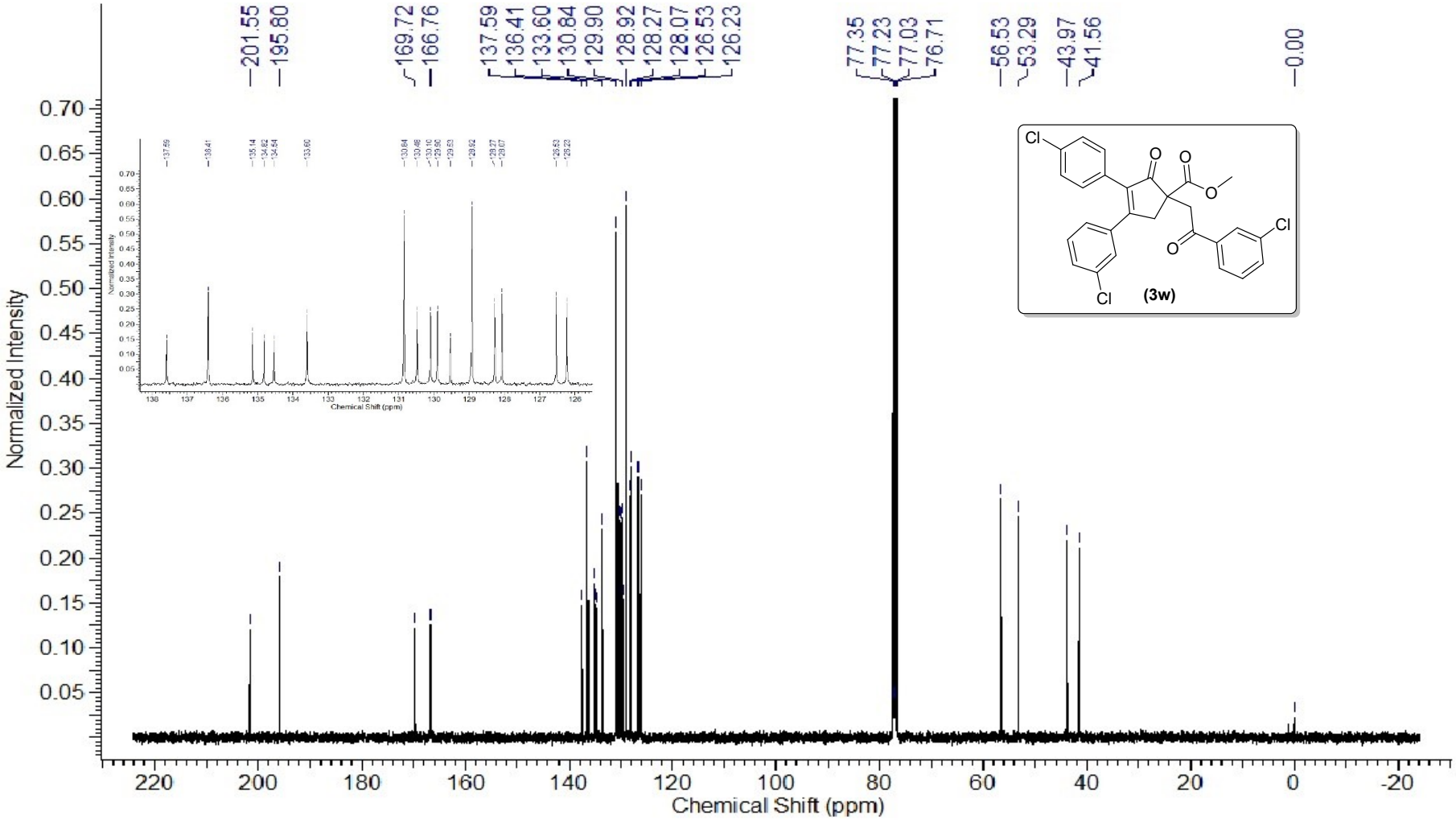
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3v



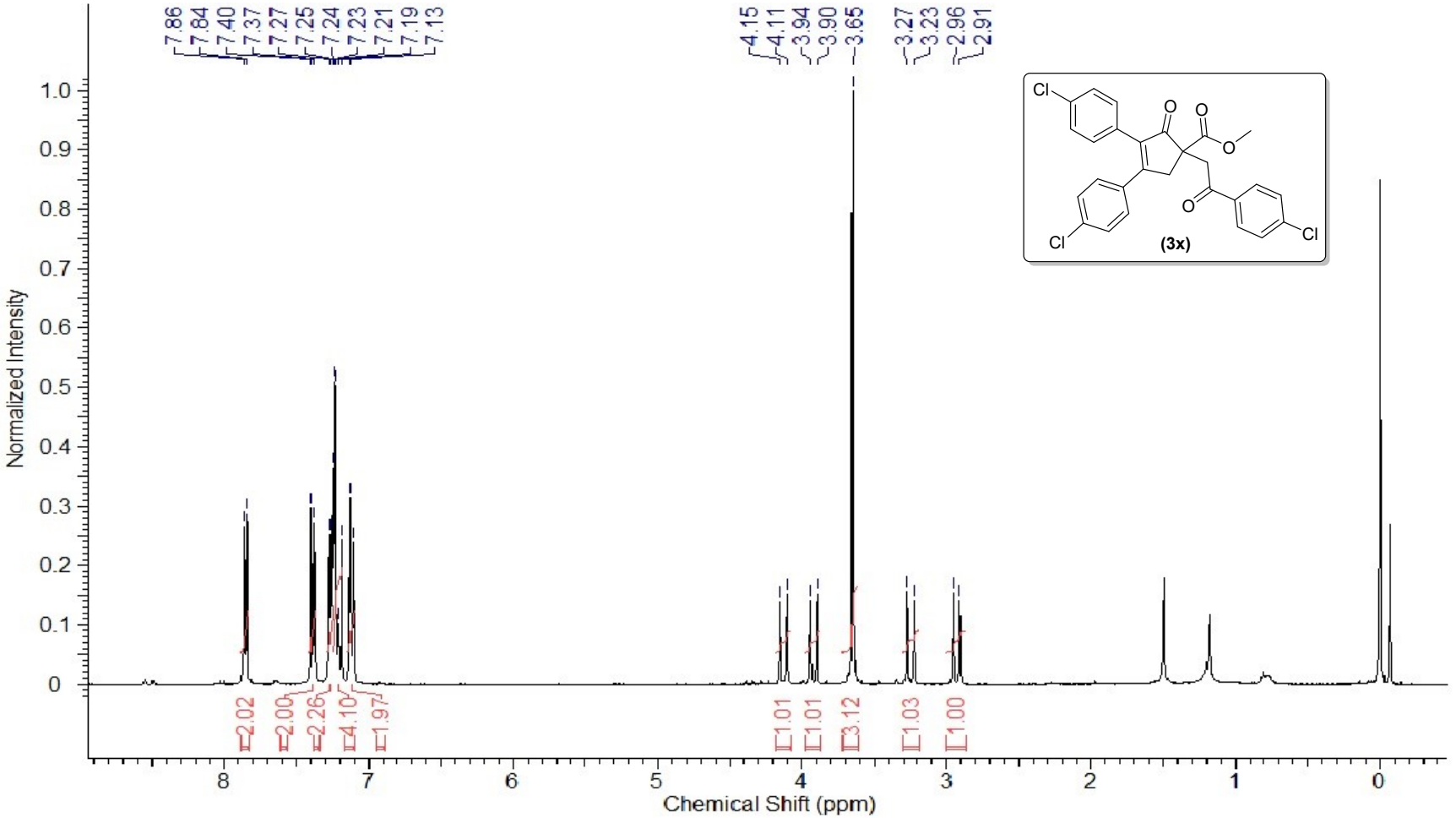
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3v



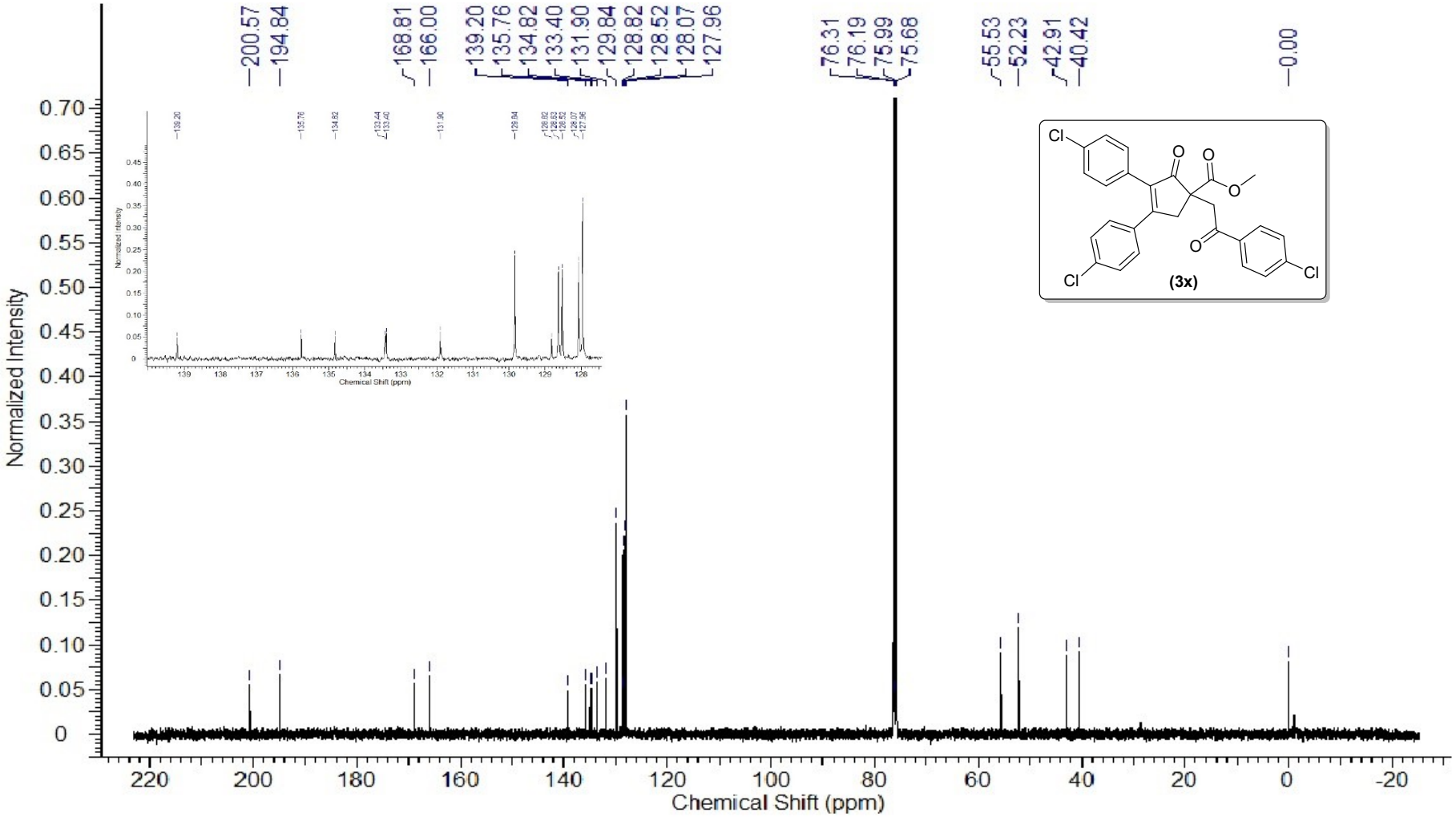
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3w



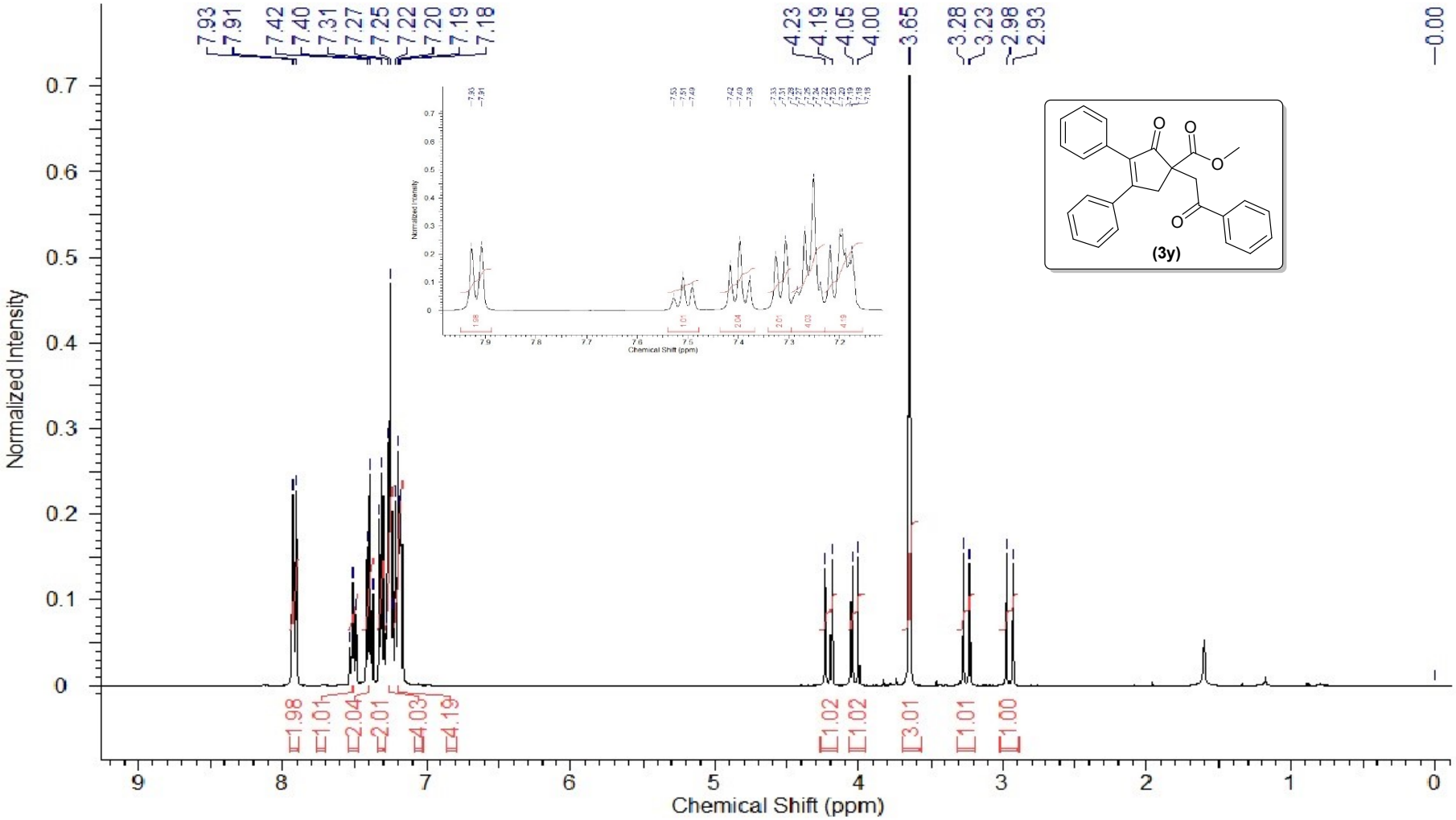
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3w



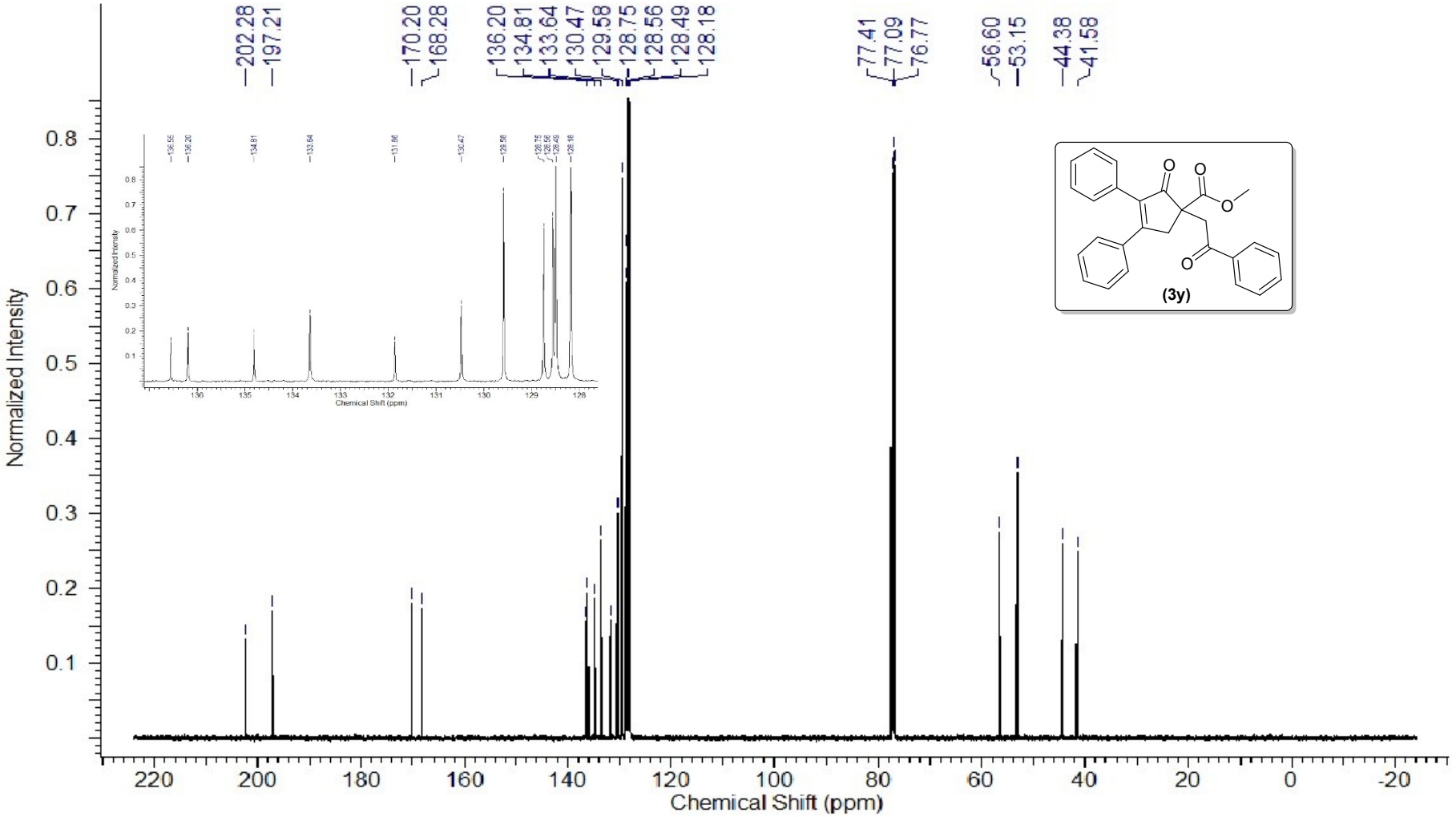
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3x



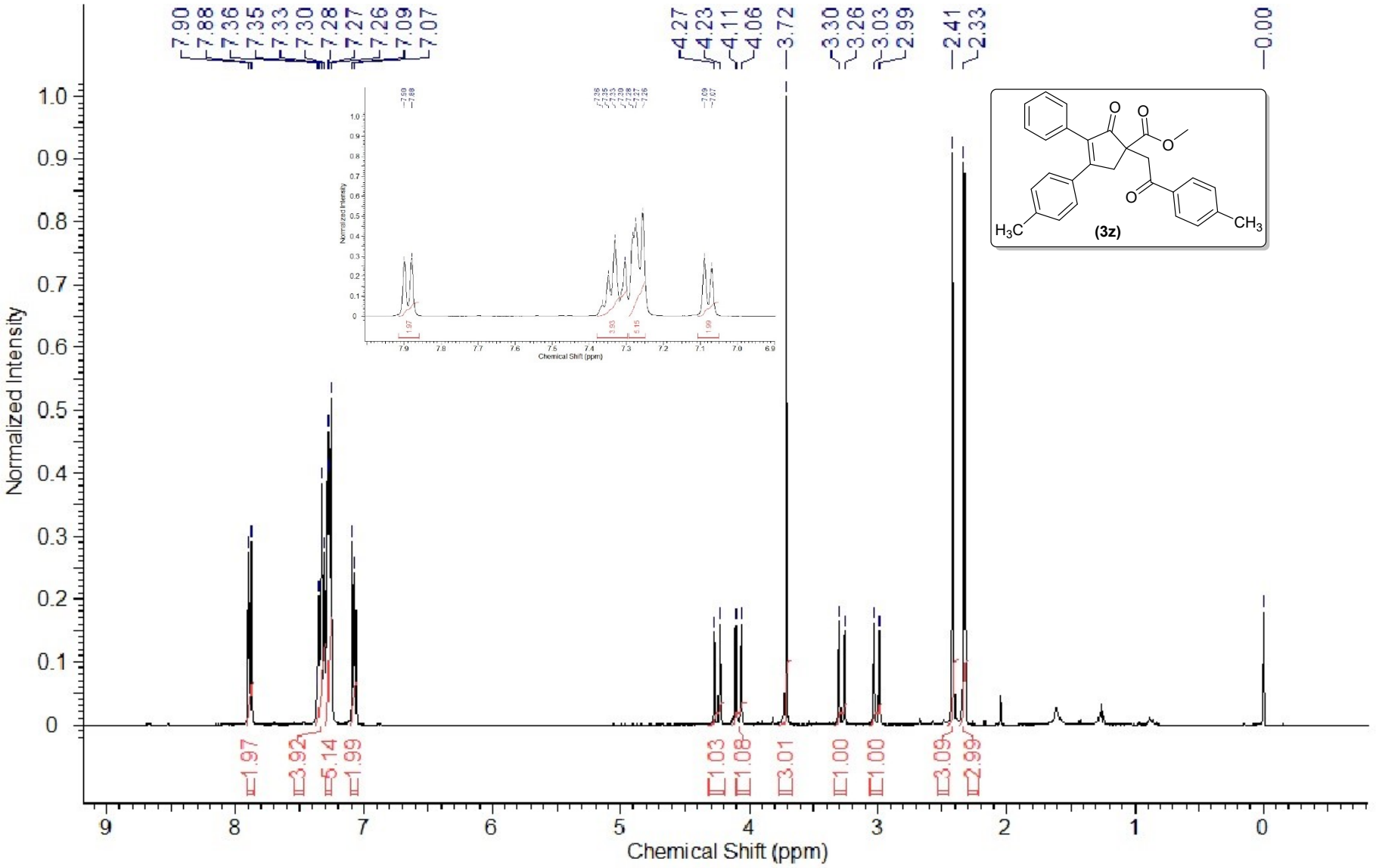
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3x



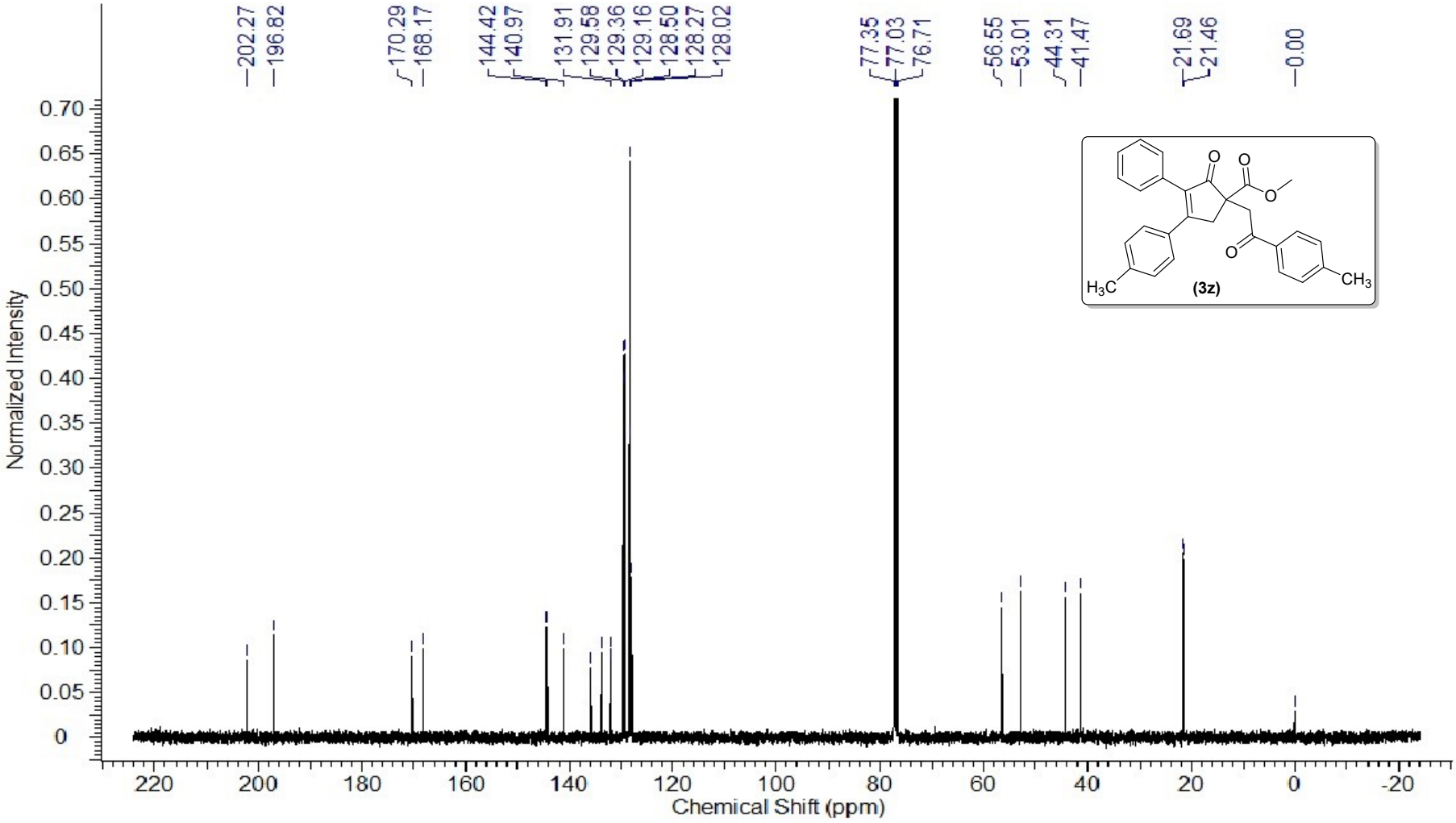
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3y



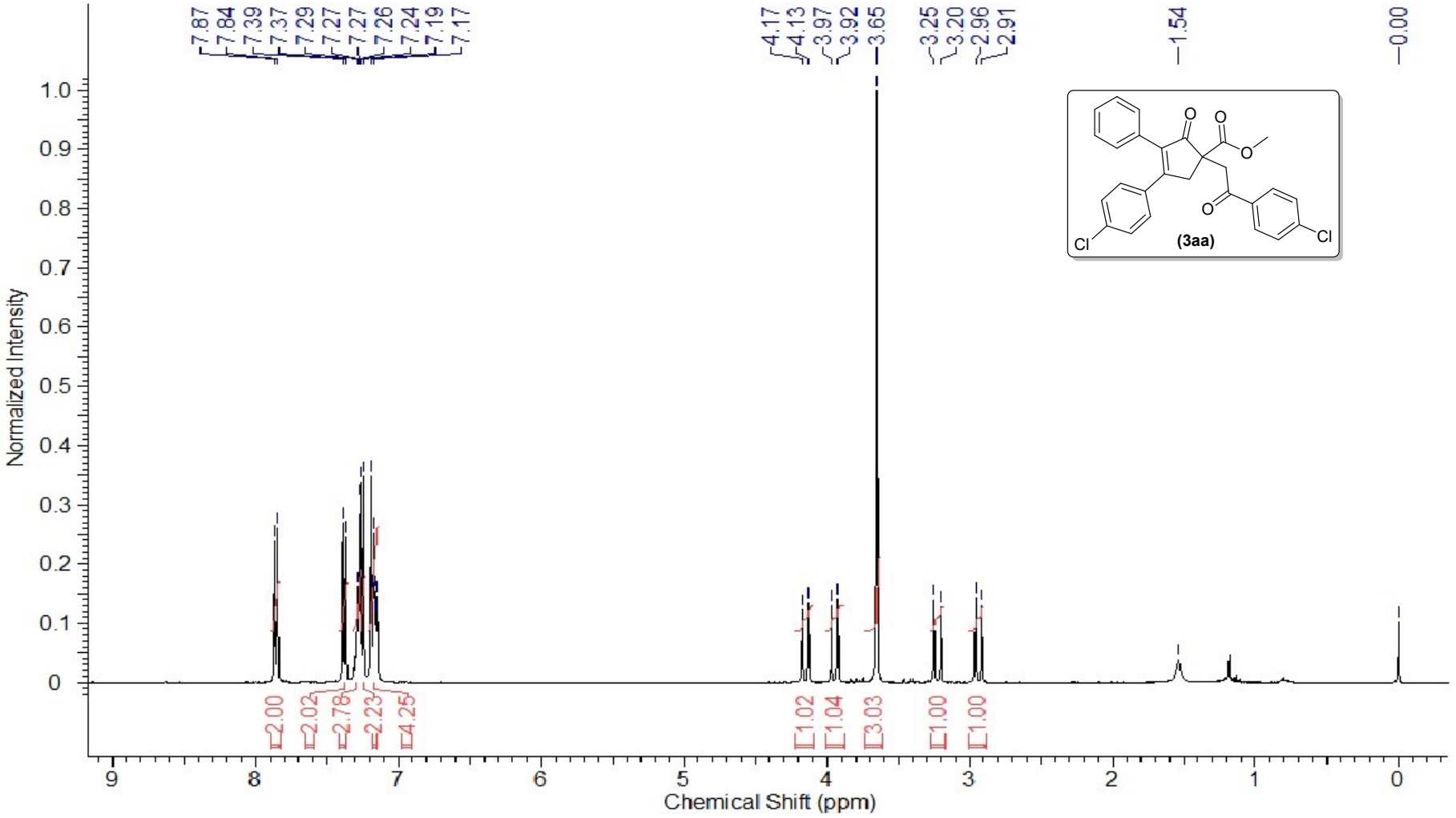
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3y



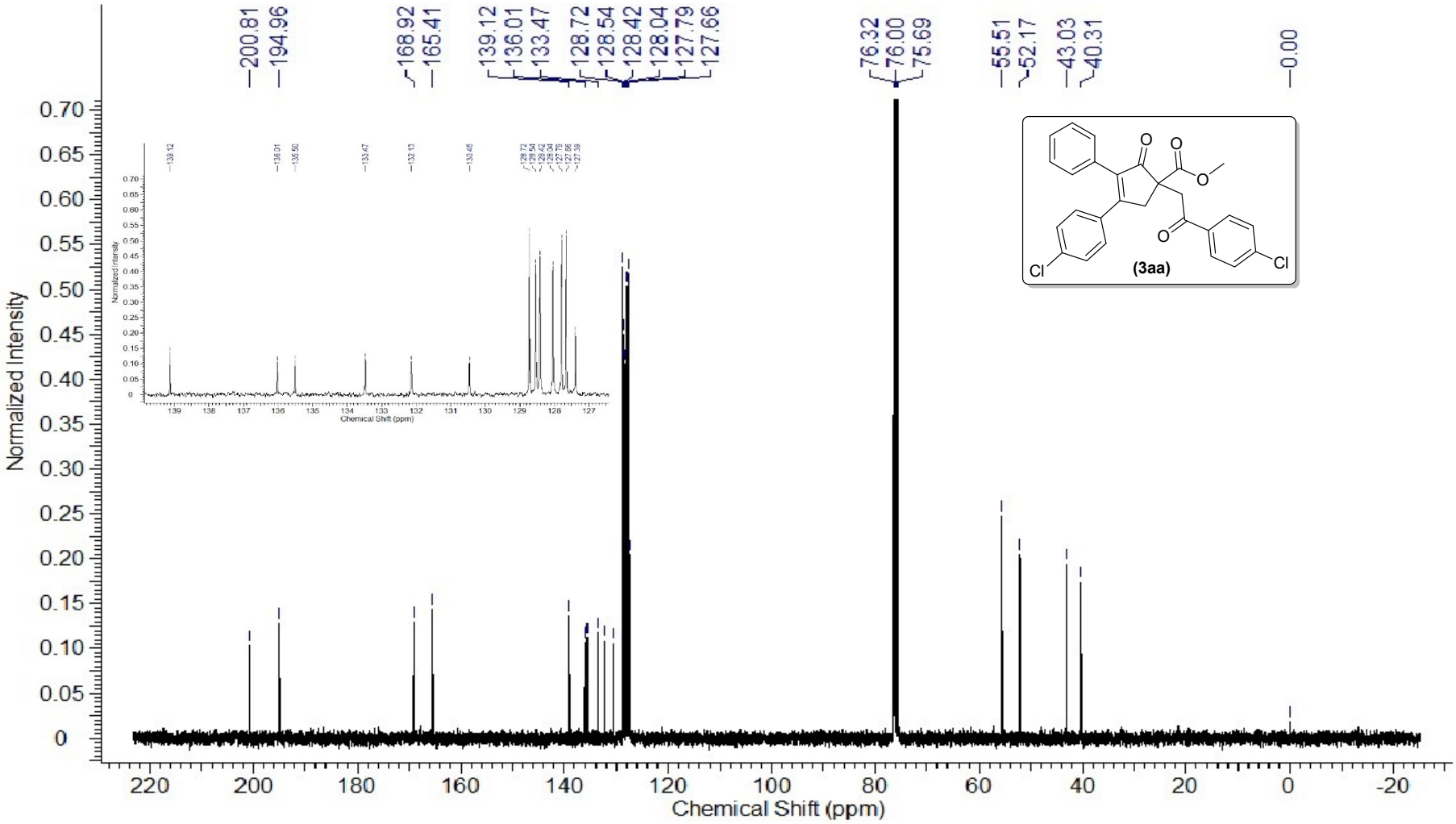
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3z



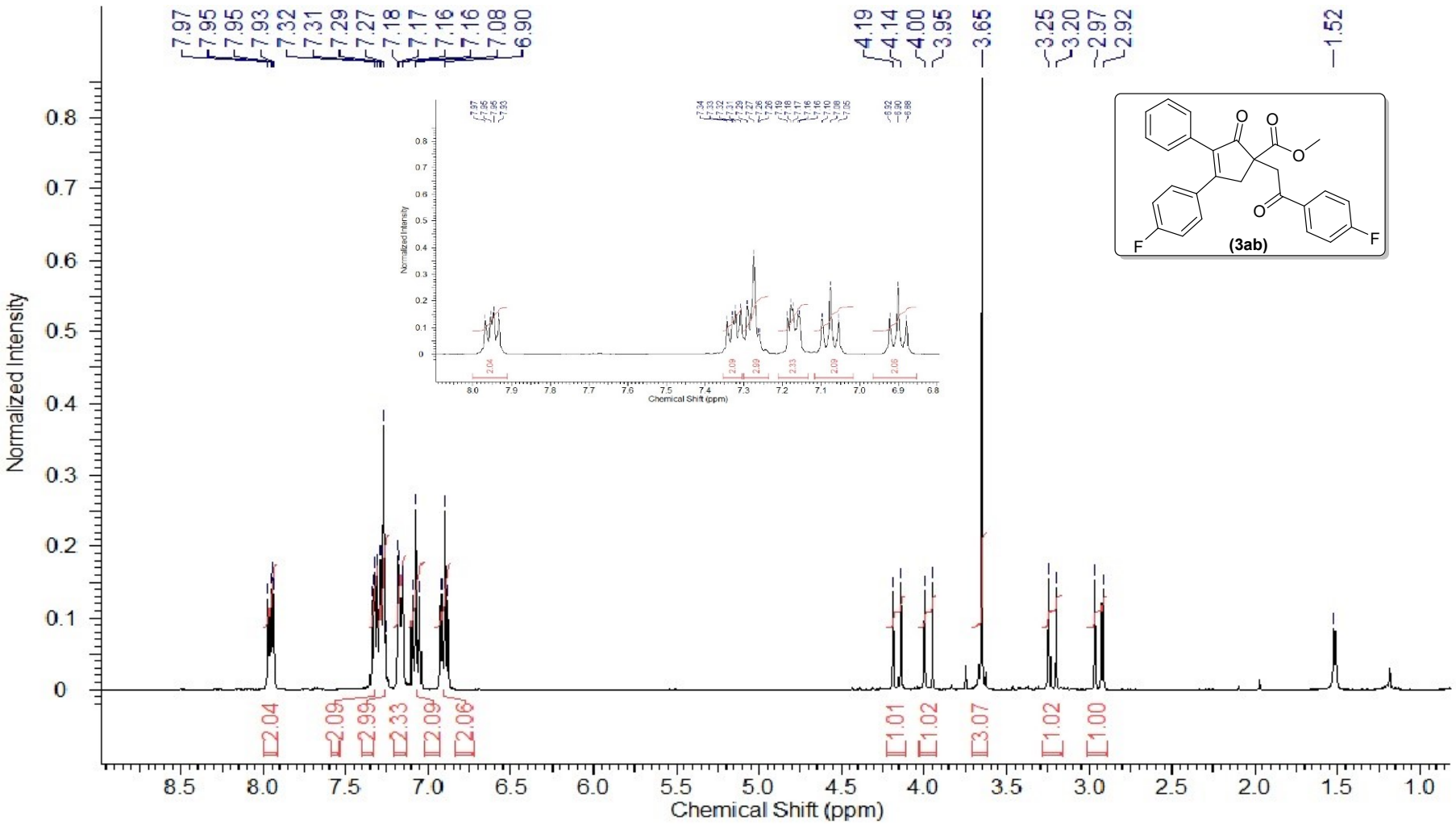
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3z



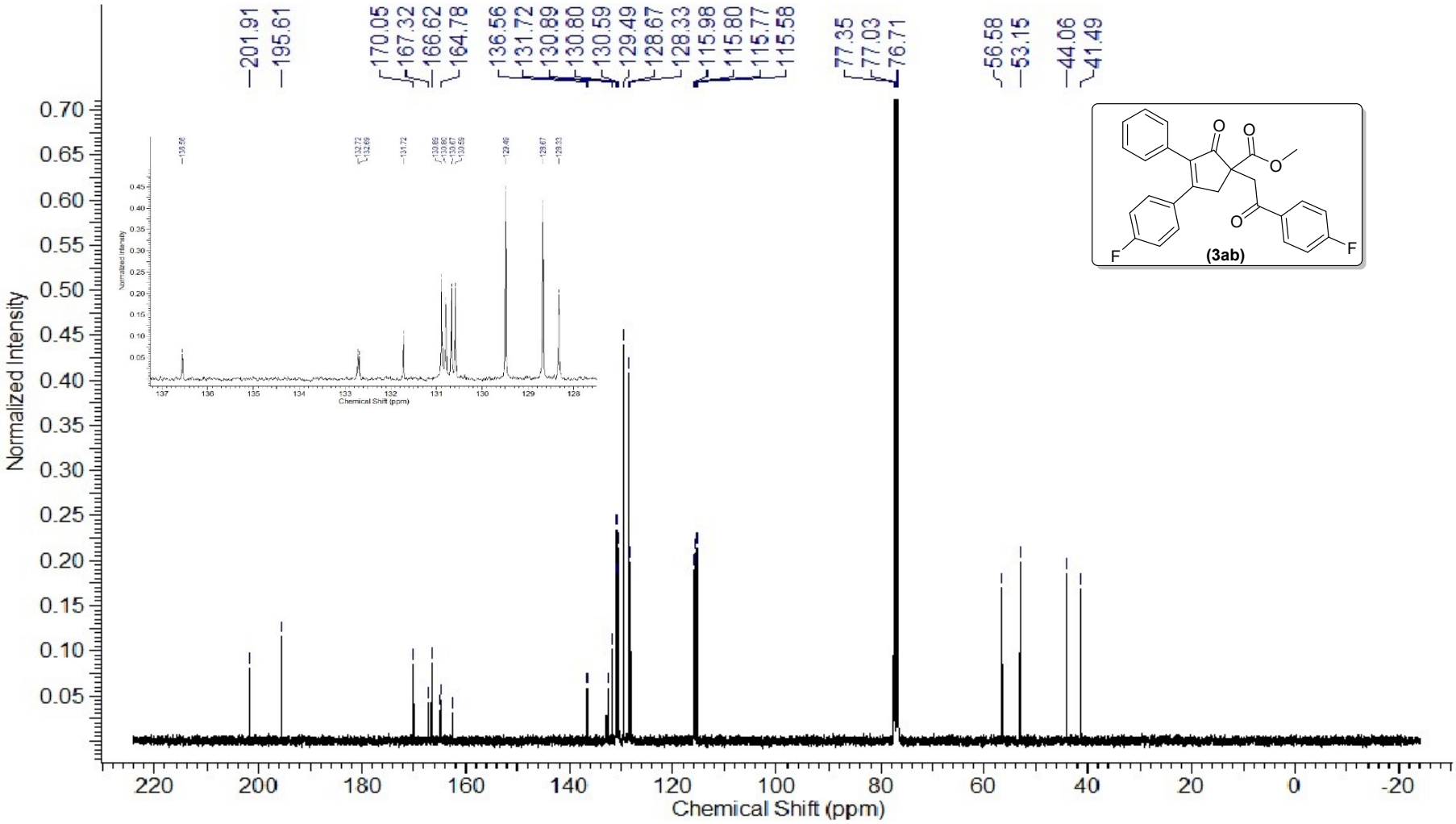
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3aa



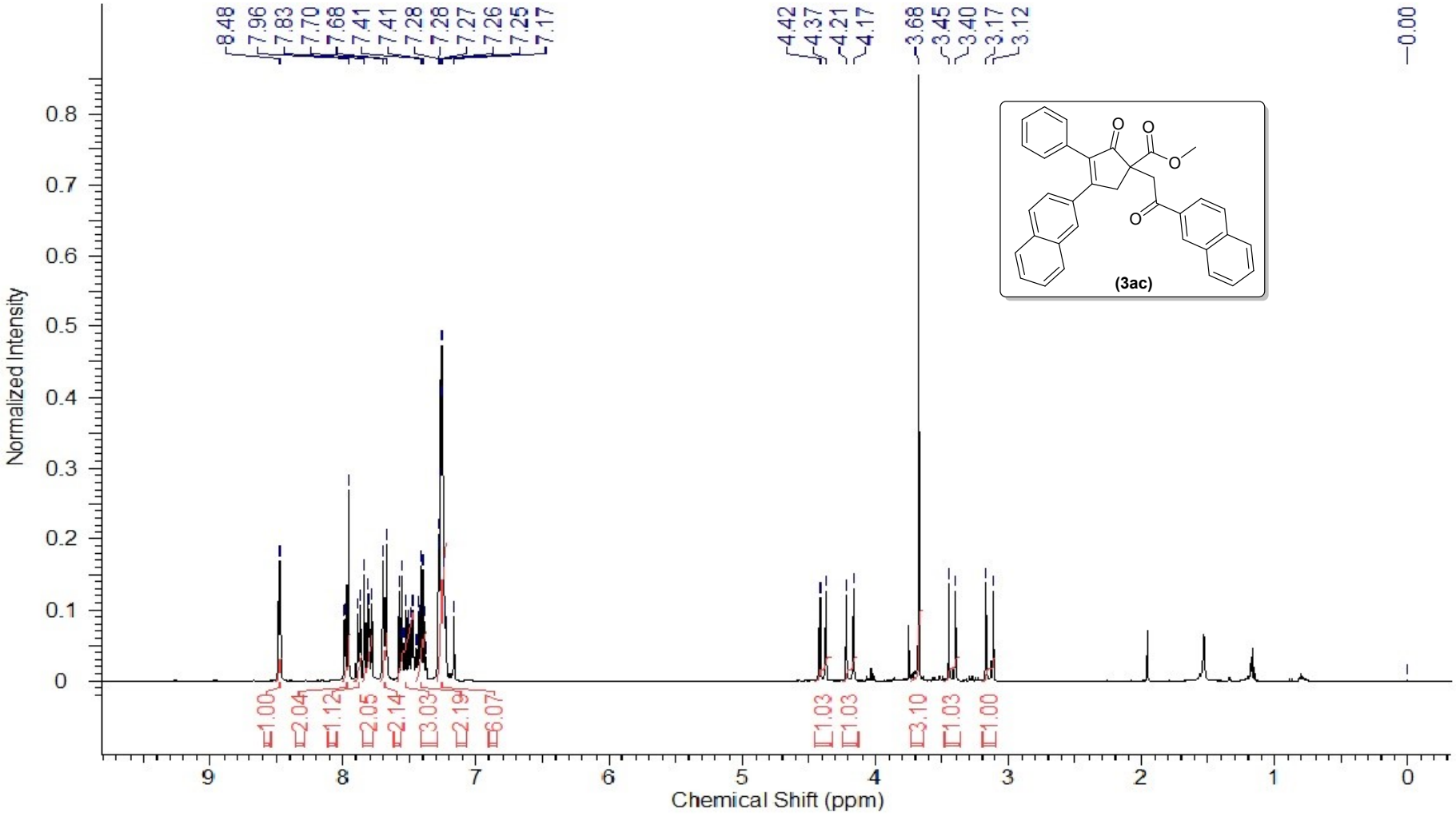
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3aa



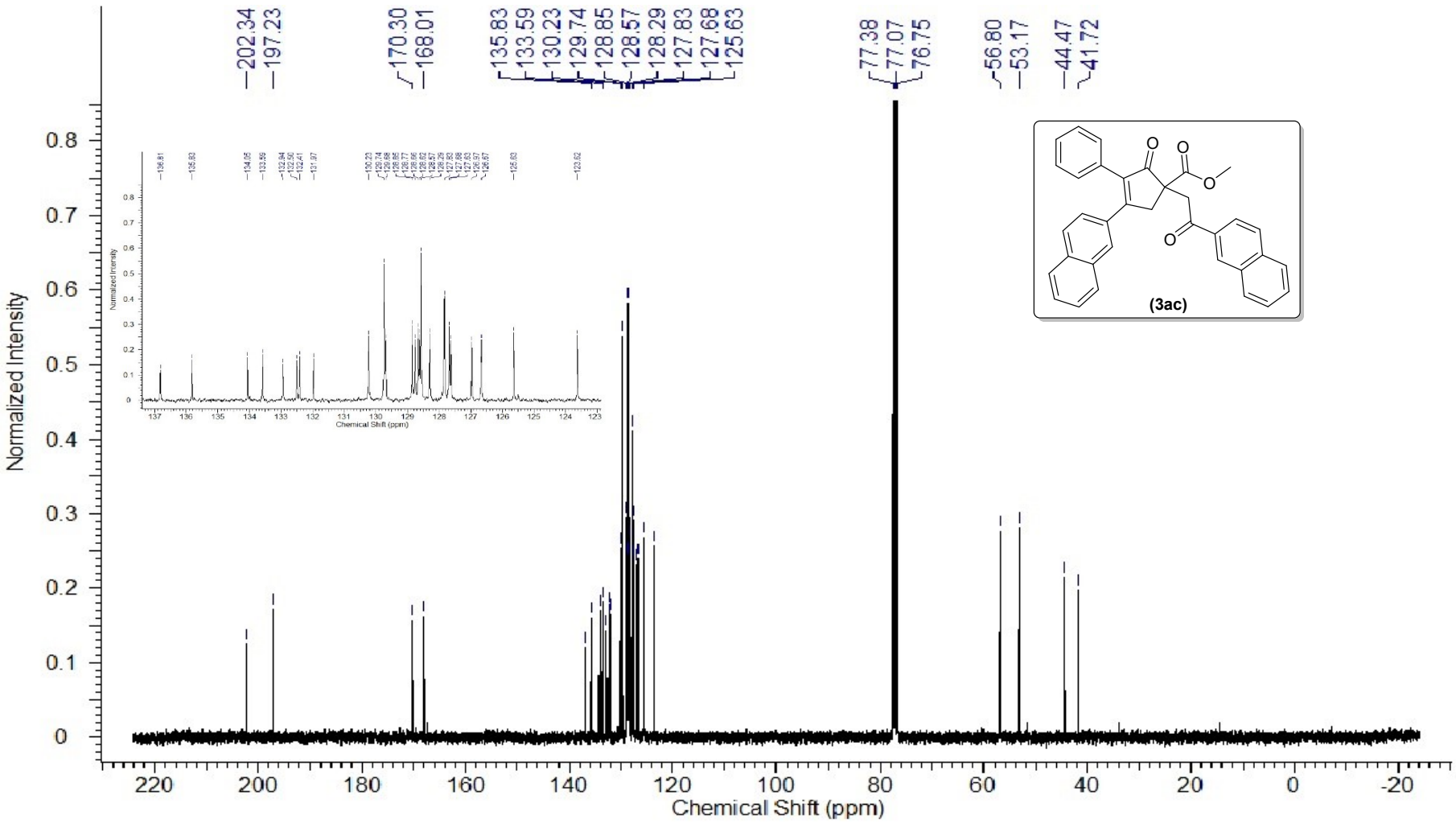
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ab



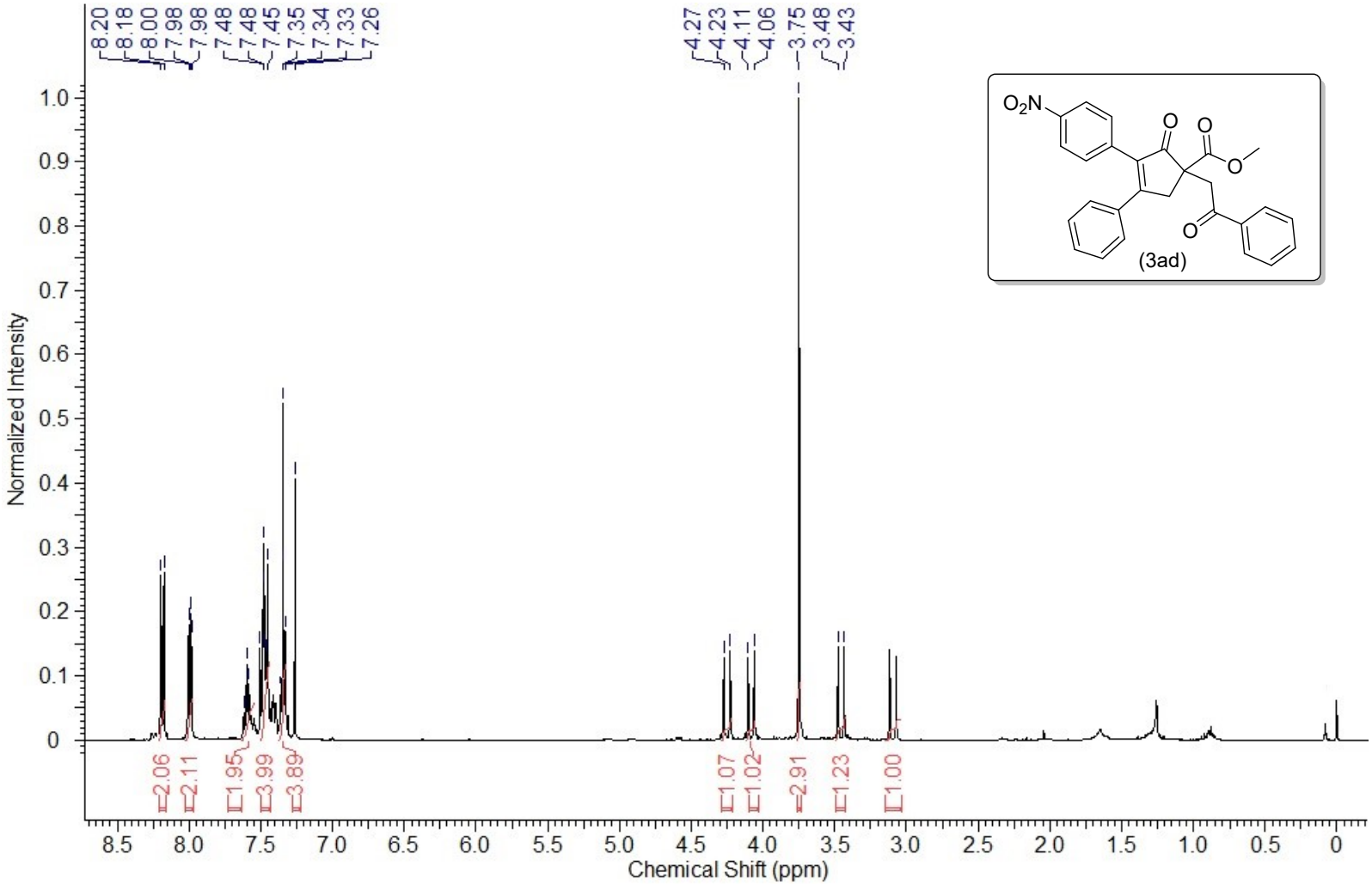
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ab



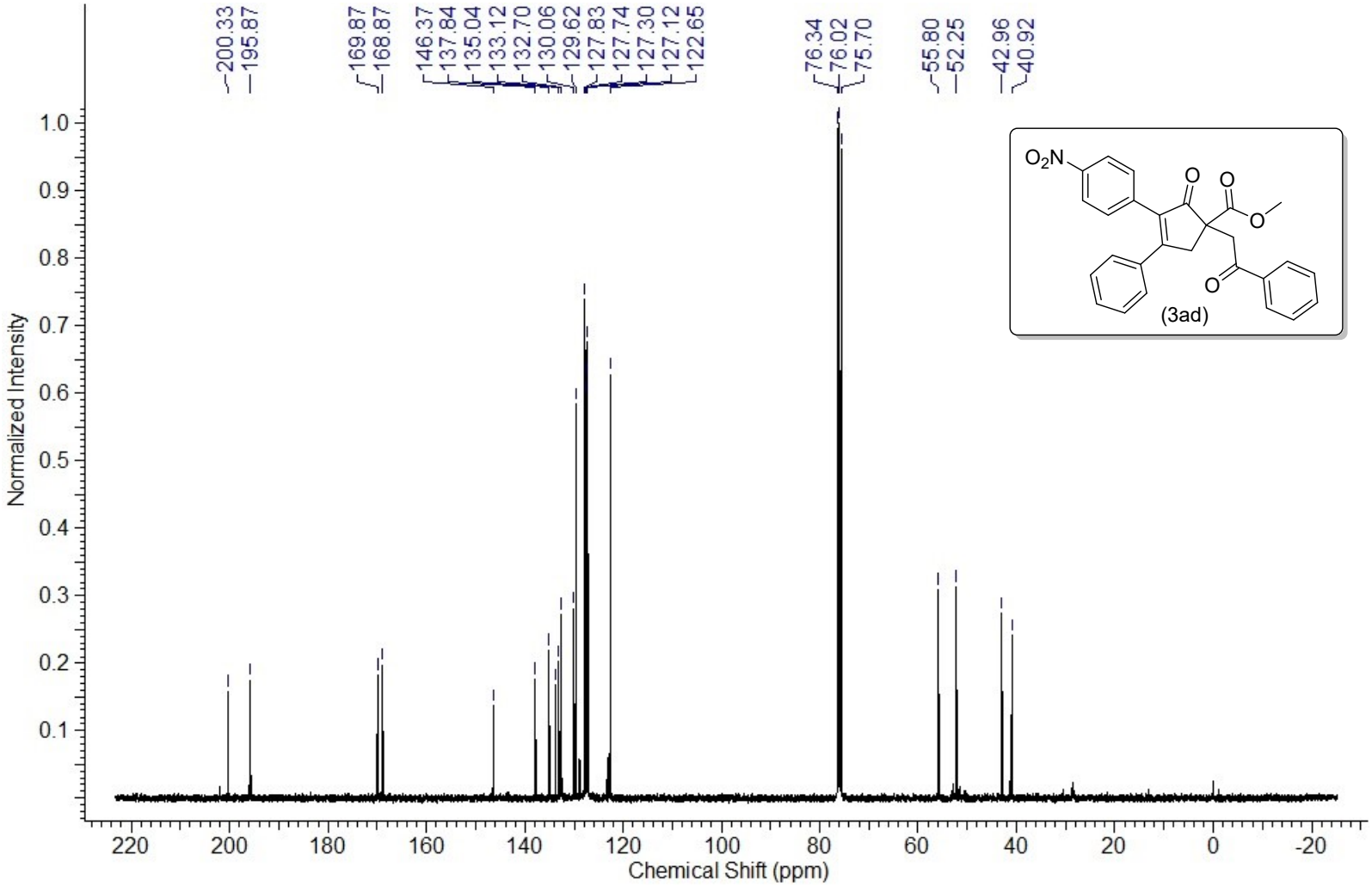
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ac



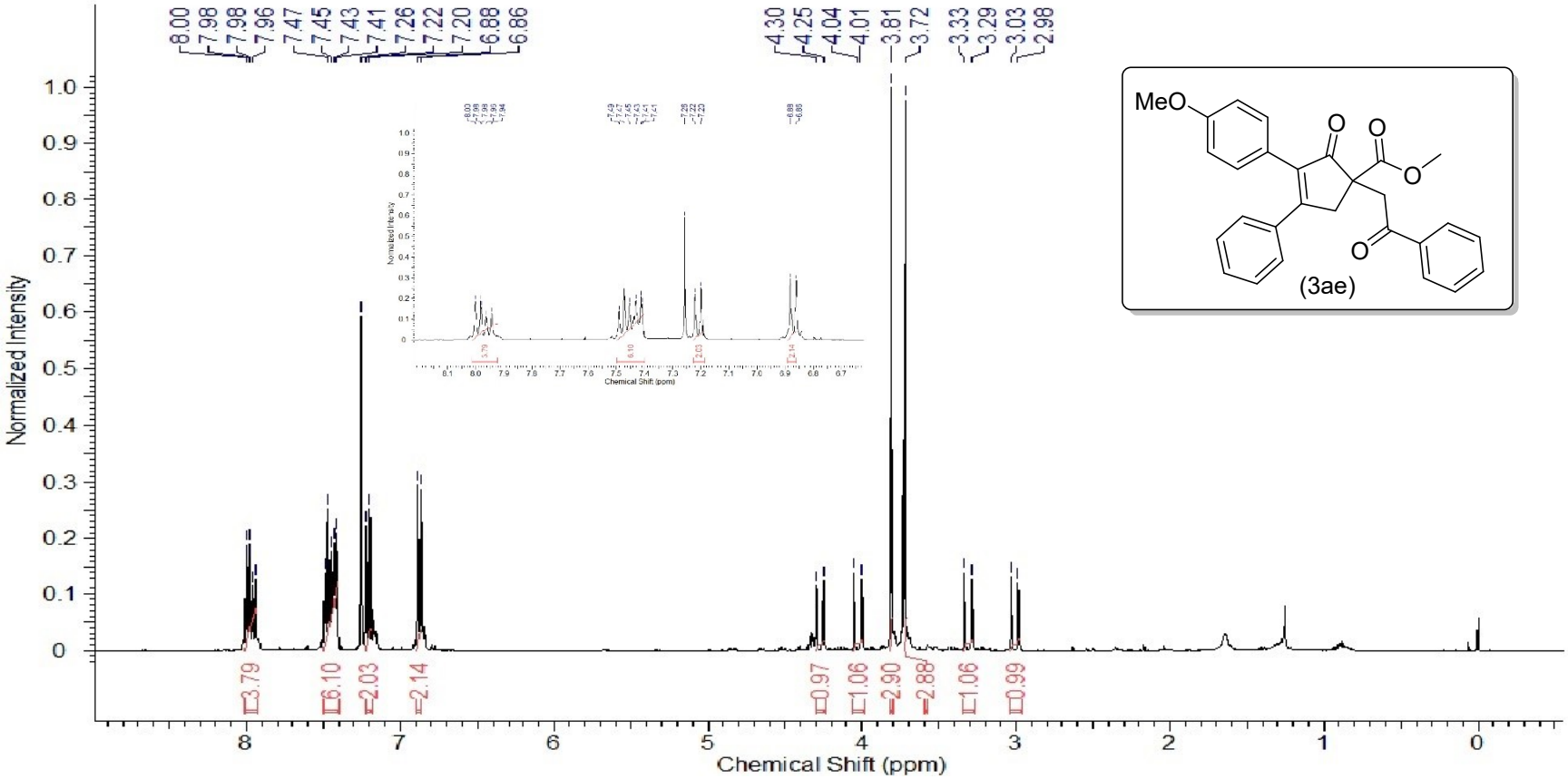
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ac



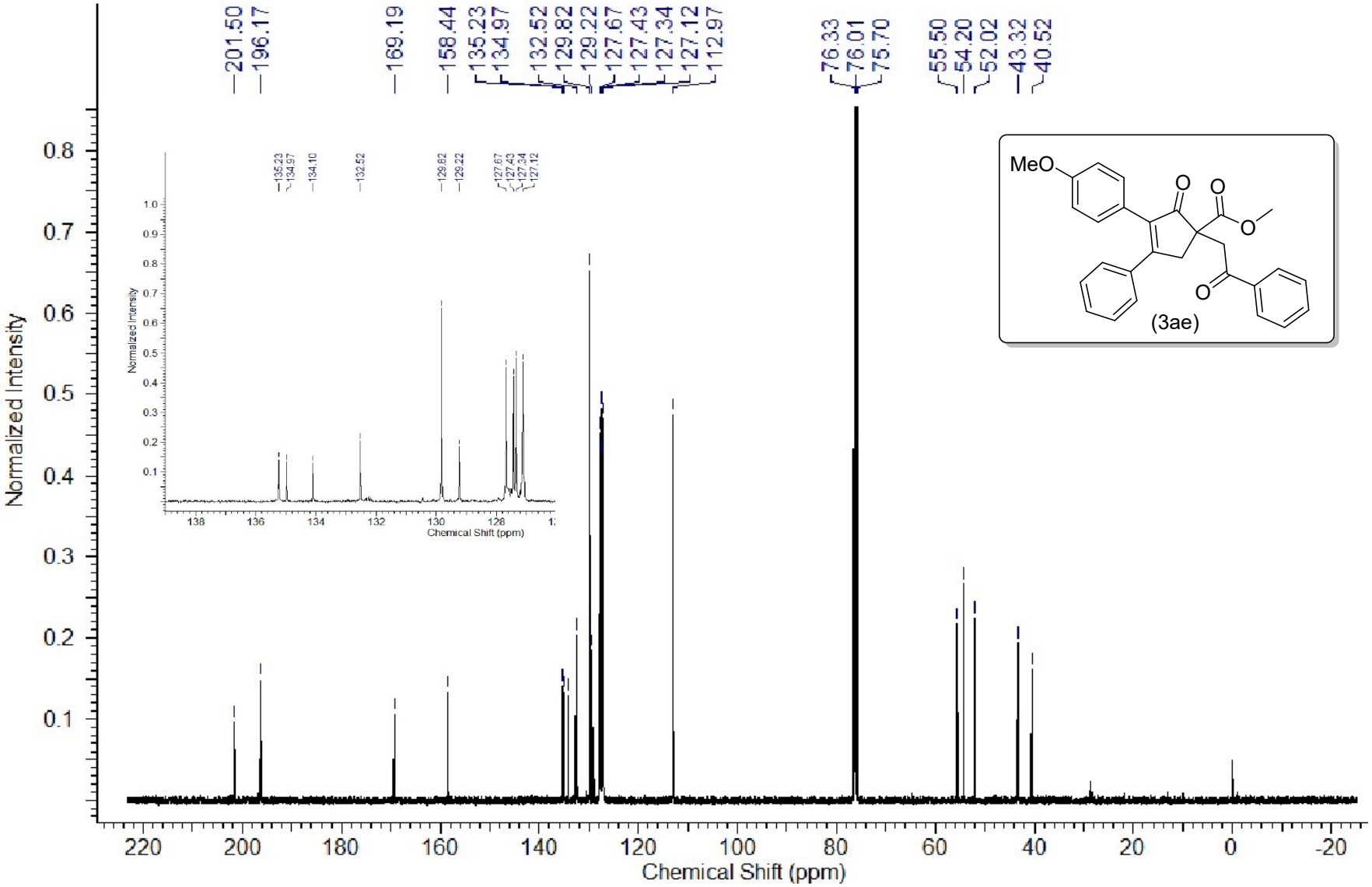
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ad



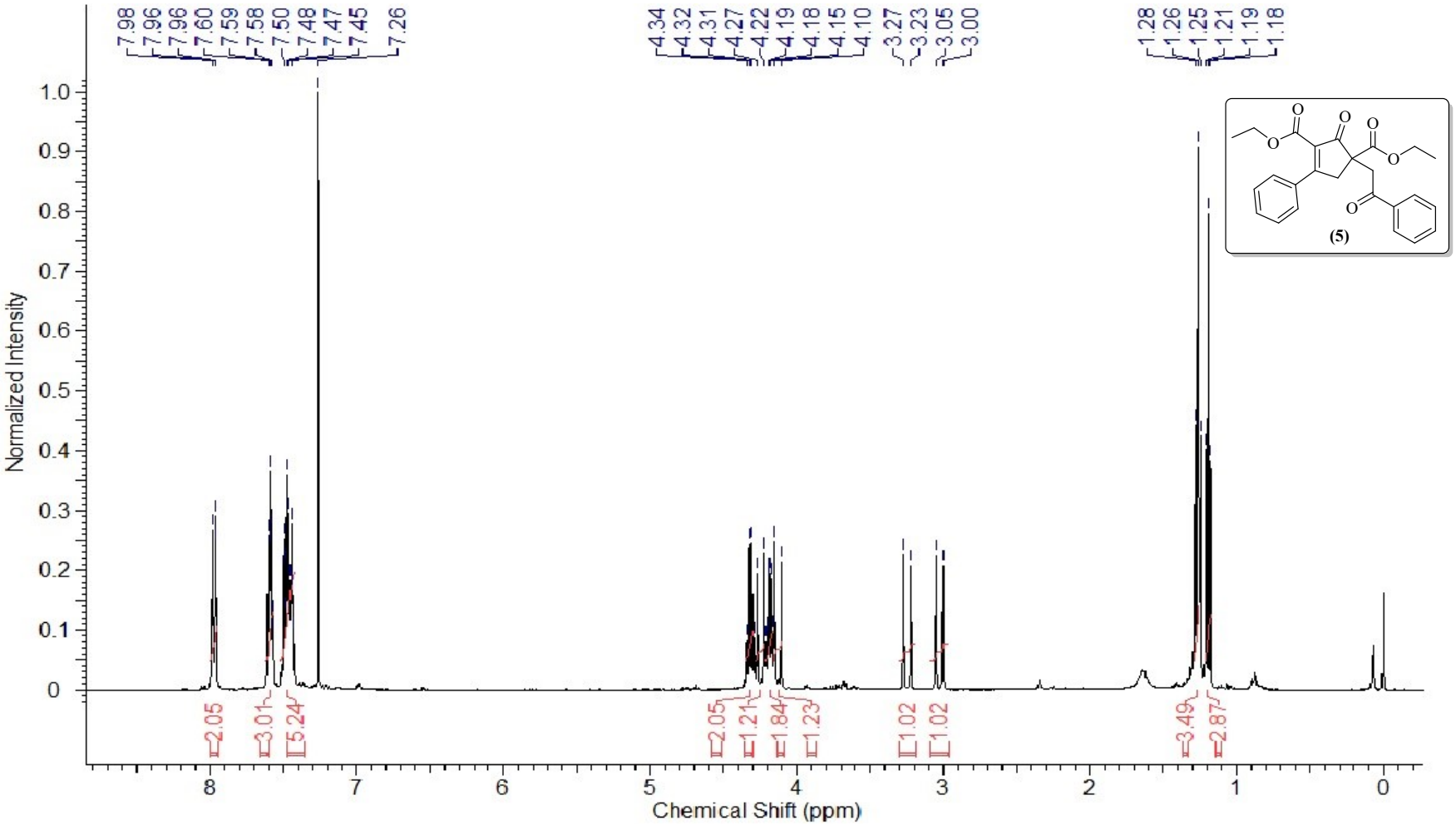
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ad



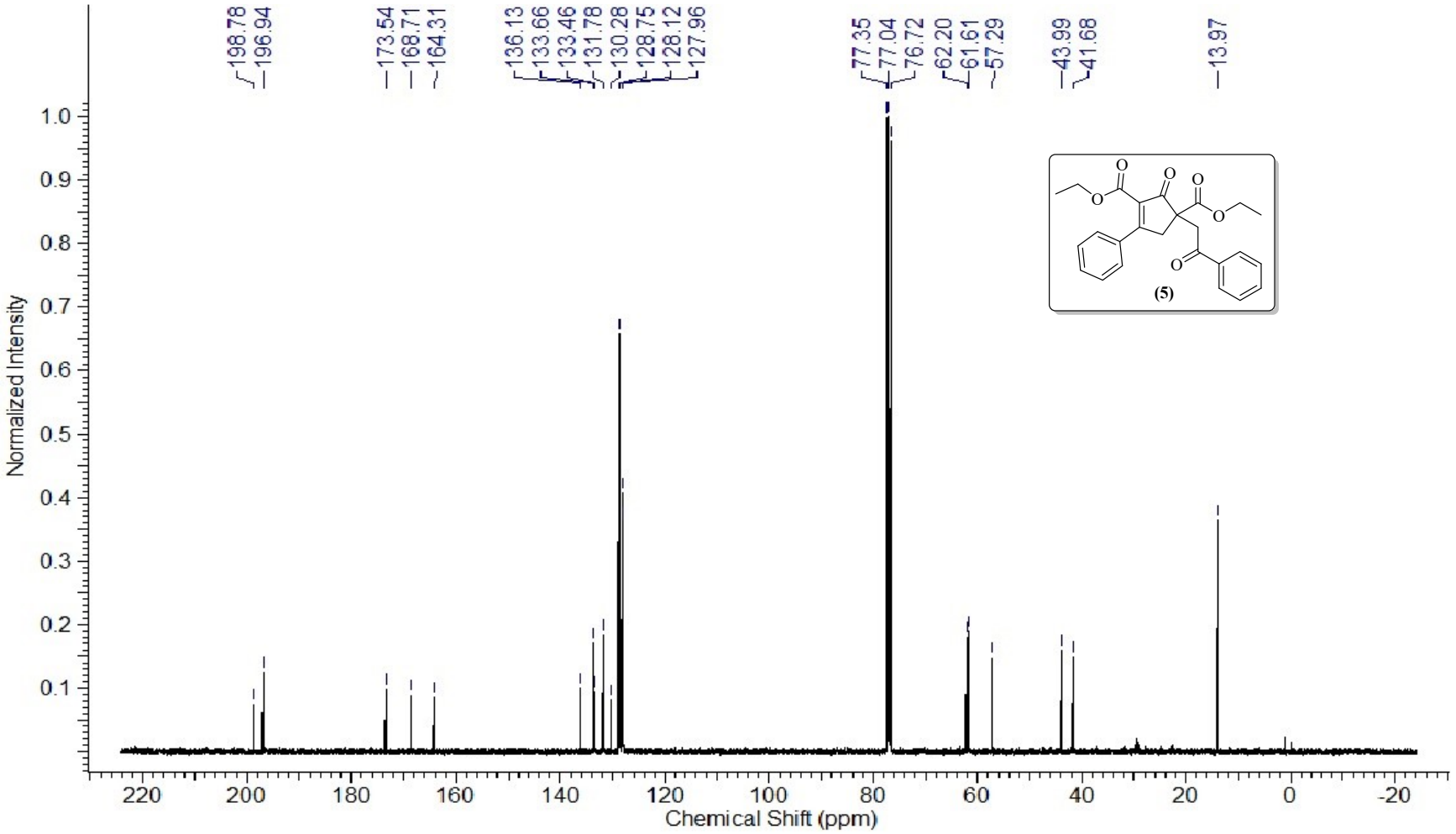
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3ae



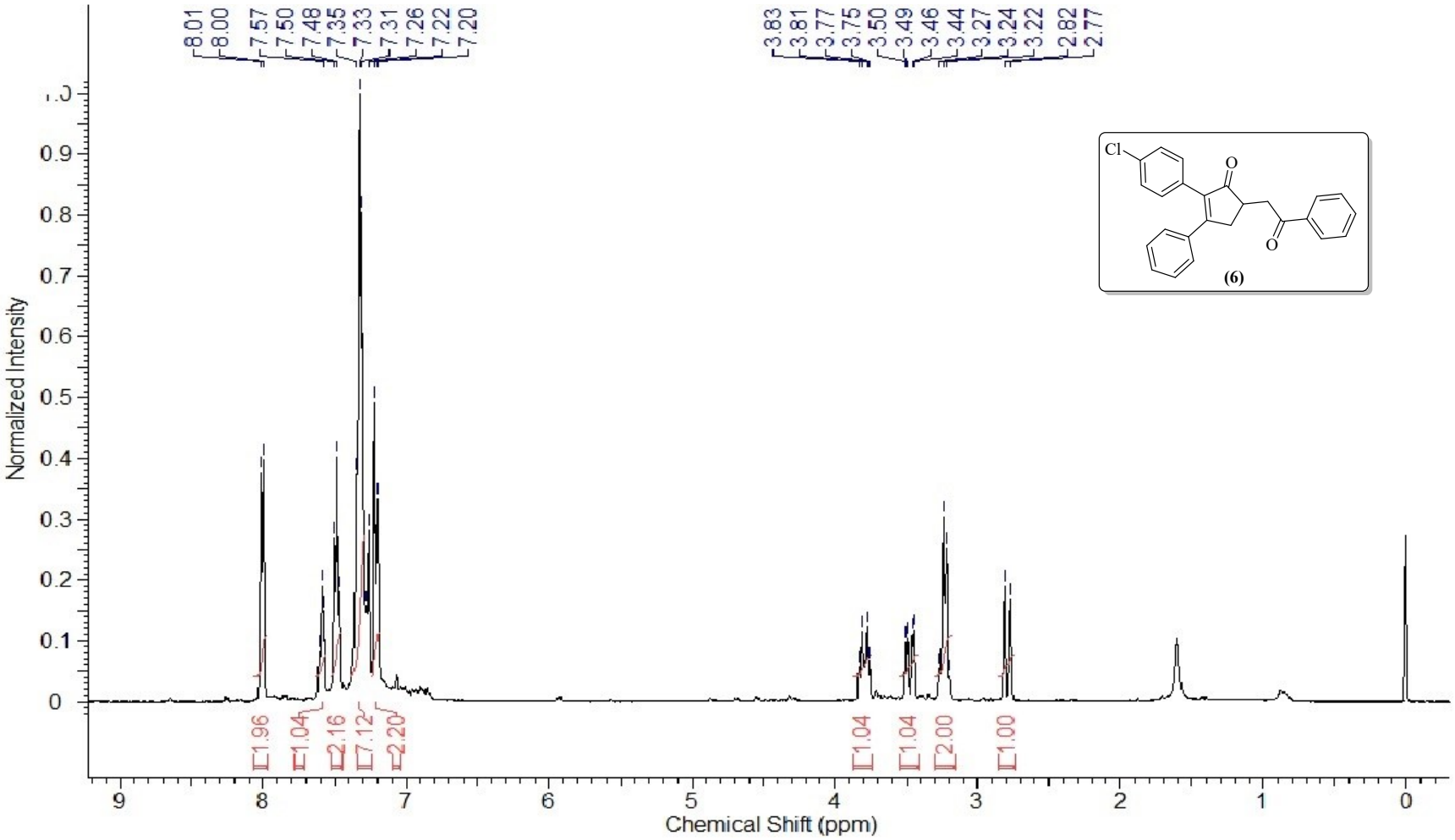
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3ae



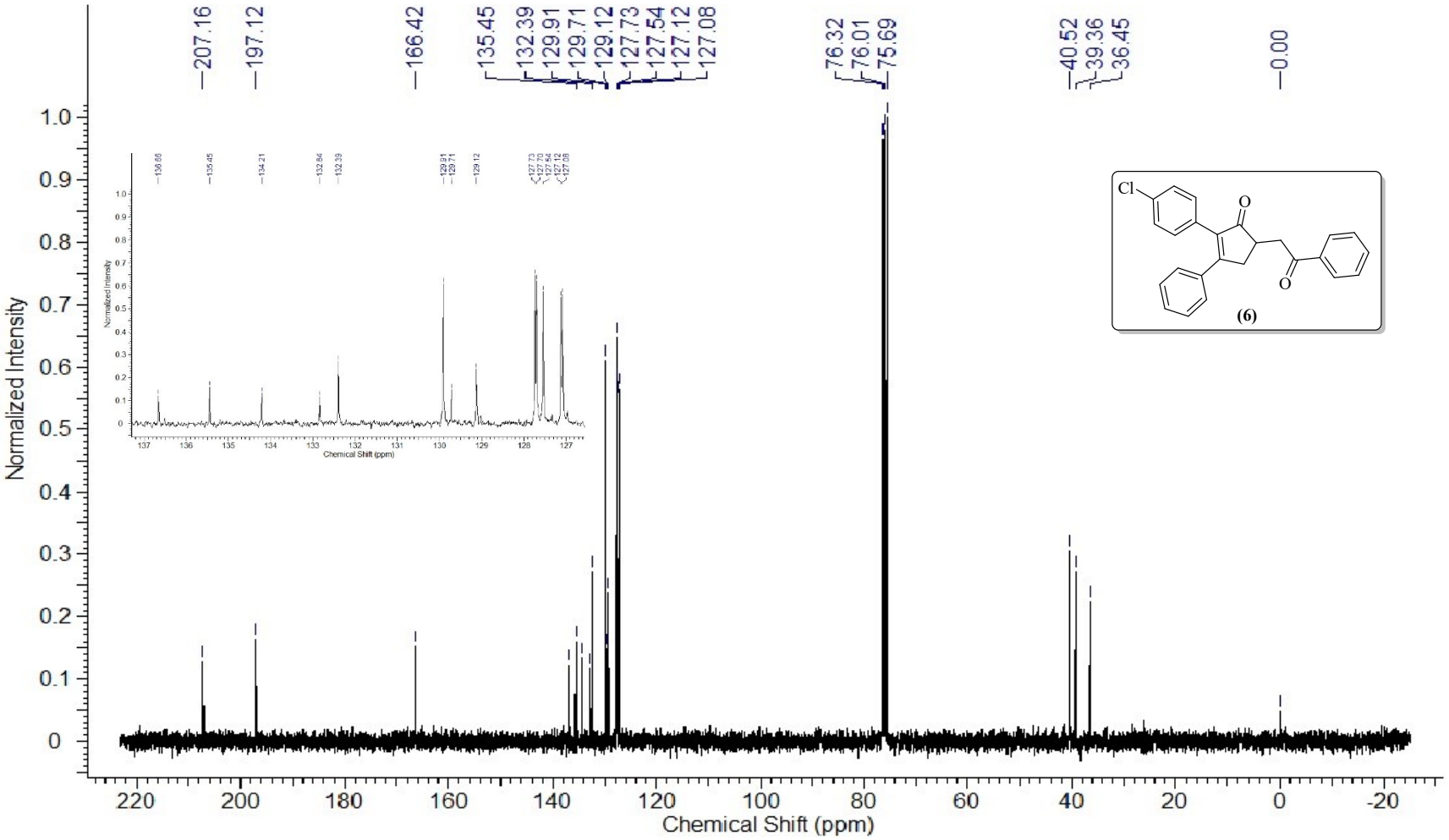
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5



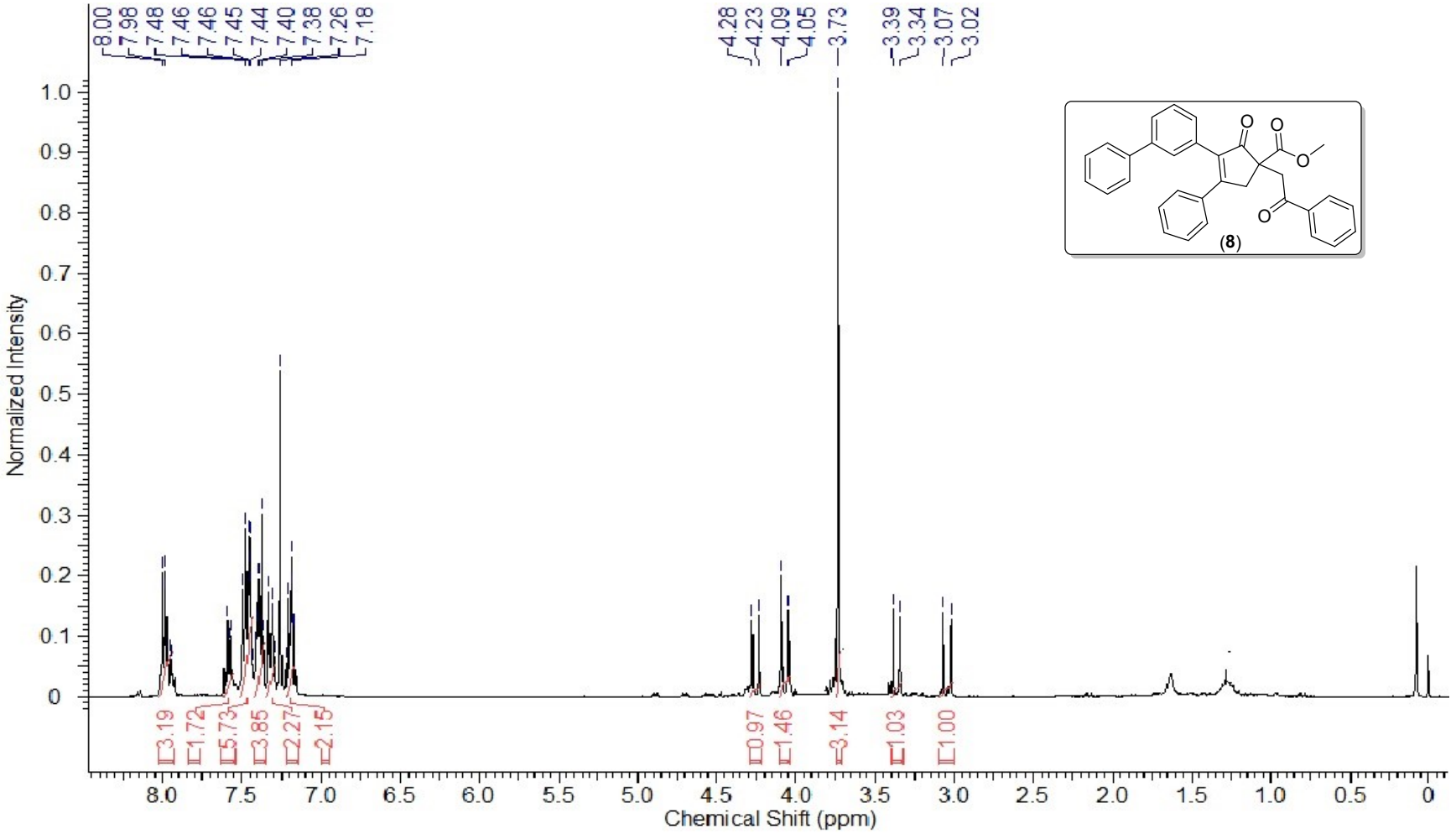
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5



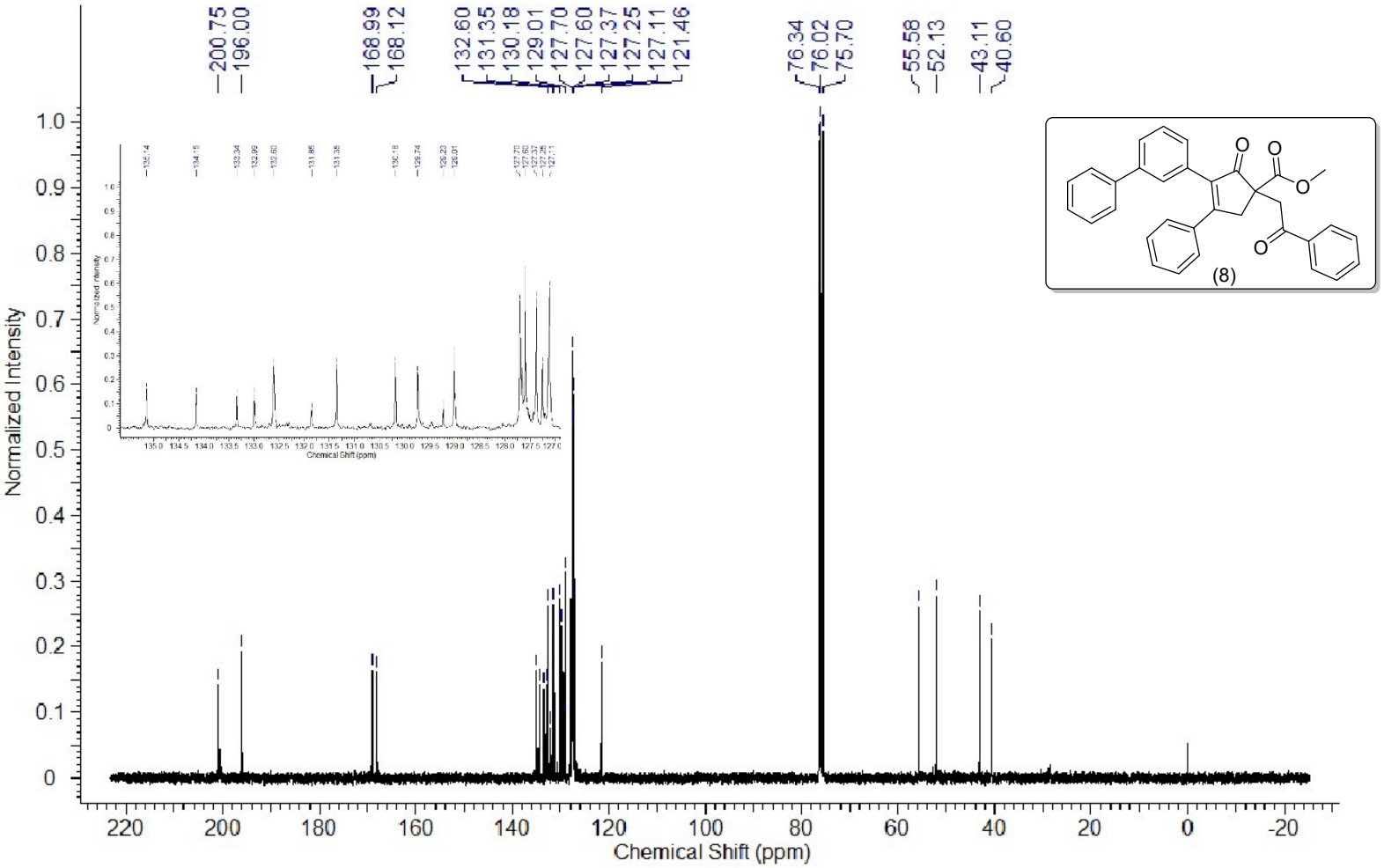
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 6

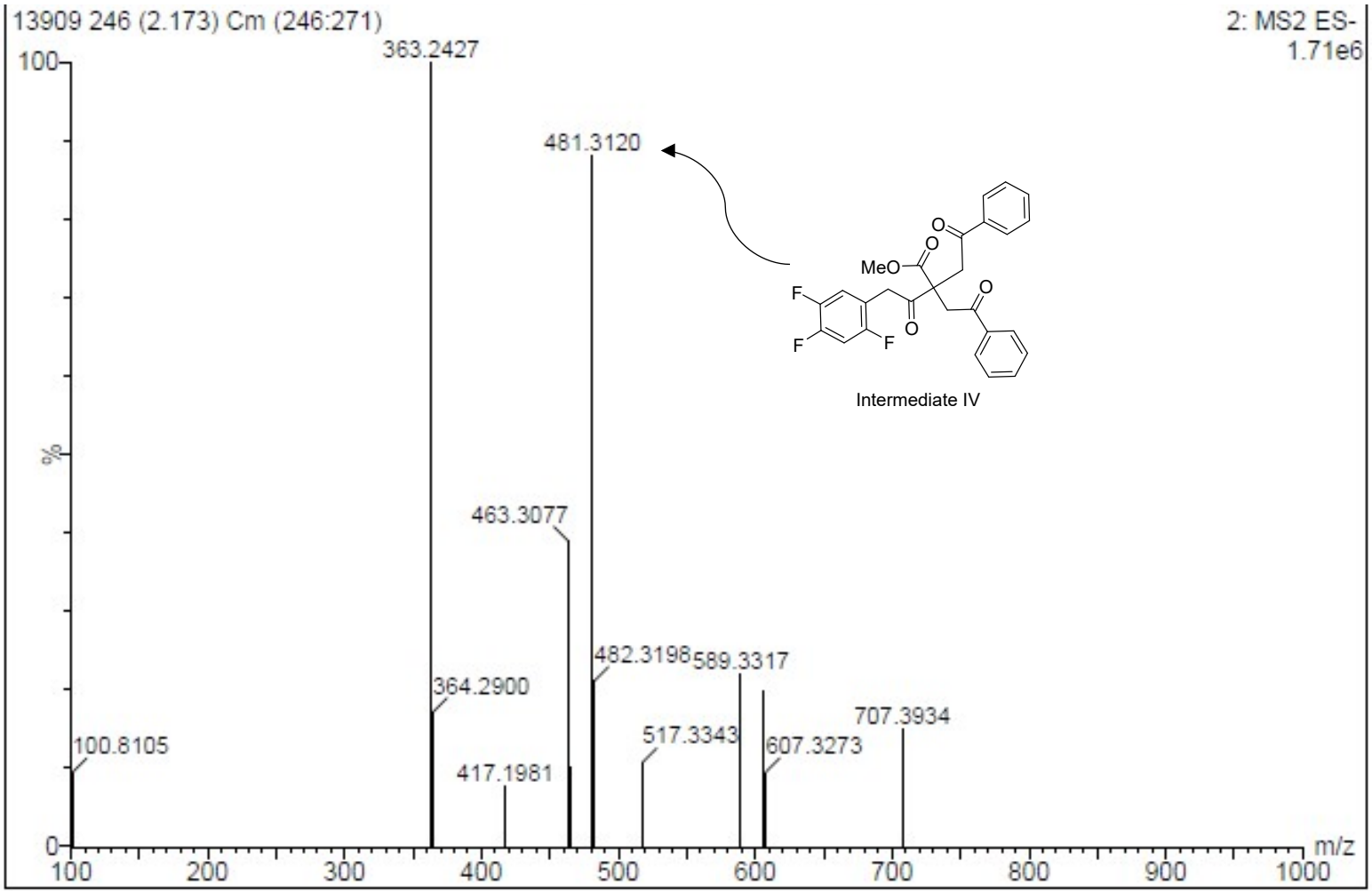


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 8

5. LC-MS spectrum of intermediate IV



Intermediate IV

6. X-ray crystallographic data

SC-XRD: The single crystals of intermediate **IIIA**, **IIIB** and **3e** were obtained from the ethyl acetate solvent by the slow evaporation method. The single crystal X-ray diffraction measurements were performed to determine the crystal structure at 100 K using APEX3 (Bruker, 2016; Bruker D8 VENTURE Kappa Duo PHOTON II CPAD) diffractometer having graphite-monochromatized (MoKα (0.71073)). The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of unit cell parameters and an orientation matrix were calculated from 36 frames, and the cell refinement was performed by SAINT-Plus (Bruker, 2016). An optimized strategy used for data collection consisted of different sets of φ and ω scans with 0.5^{o} steps φ/ω. The data were collected with a time frame of 10 sec by setting the sample to detector distance fixed at 40 cm. All the data points were corrected for Lorentzian, polarization, and absorption effects using SAINT-Plus and SADABS programs (Bruker, 2016). SHELXS-97 (Sheldrick, 2008) was used for structure solution, and full-matrix least-squares refinement on F^2.[1, 2] The molecular graphics of ORTEP diagrams were performed by Mercury software. The crystal symmetry of the components was cross-checked by running the cif files through PLATON (Spek, 2020) software and notified that no additional symmetry was observed. The Encifer software was used to correct the cif files.

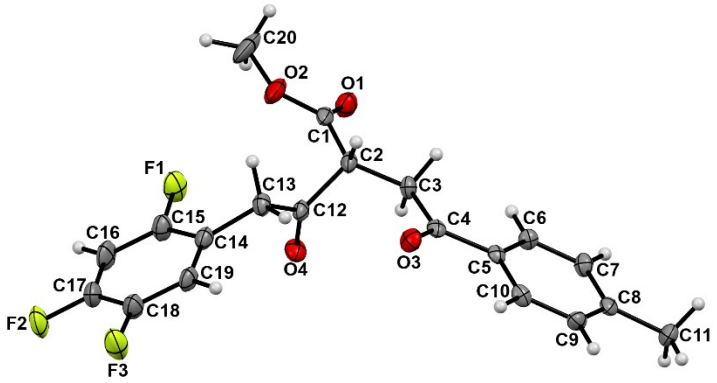


Figure 1. ORTEP diagram of compound **IIIA**, the asymmetric unit contains one molecule of **IIIA**. Herein, the ellipsoids are drawn with a 50% probability.

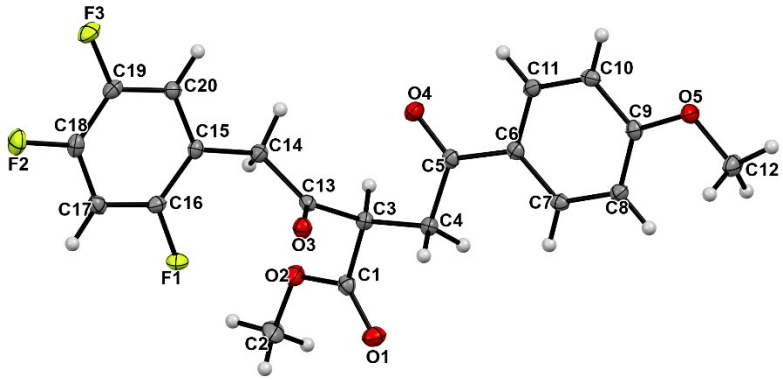


Figure 2. ORTEP diagram of compound **IIIB**, the asymmetric unit contains one molecule of **IIIB**. Herein, the ellipsoids are drawn with a 50% probability.

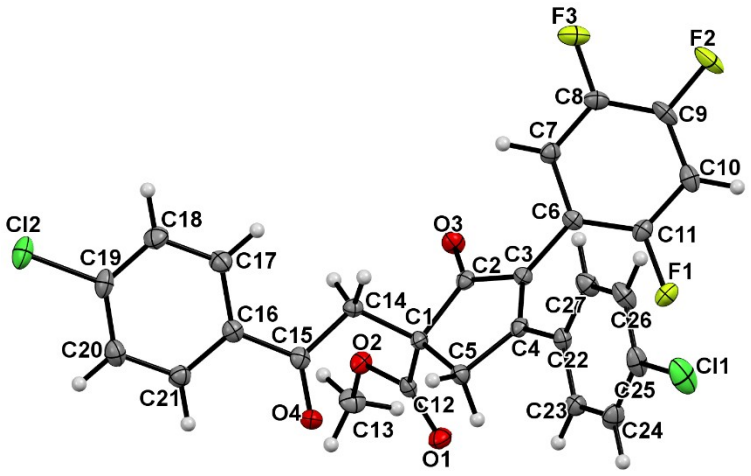


Figure 3. ORTEP diagram of compound **3e**, the asymmetric unit contains one molecule of **3e**. Herein, the ellipsoids are drawn with a 50% probability.

Table 1. Crystallographic information details of compounds, **IIIA, IIIB** and **3e**.

Crystal data	**IIIA**	**IIIB**	**3e**
Chemical formula	$C_{20}H_{17}F_3O_4$	$2(C_{20}H_{17}F_3O_5)$	$C_{27}H_{17}Cl_2F_3O_4$
Formula weight (M_r)	378.33	788.67	533.31
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C*$_2$/*c*	*P-1*	*P*2$_1$/*c*
Temperature T (K)	100	100	100
a (Å)	38.220 (9)	5.5852 (10)	6.2659 (9)
b (Å)	5.6457 (12)	8.4012 (14)	14.989 (2)
c (Å)	16.281 (4)	18.790 (3)	24.786 (3)
α (°)	90	83.603 (6)	90
β (°)	99.503 (8)	82.238 (6)	94.532 (5)
γ (°)	90	89.317 (7)	90
Z	8	1	4
Volume (Å^3)	3464.8 (14)	868.2 (3)	2320.7 (6)
Source of radiation	Mo*K*α (0.71073)	Mo*K*α (0.71073)	Mo*K*α (0.71073)
D_{calc} (g cm^{-3})	1.451	1.509	1.526
Crystal size (mm)	0.21×0.1×0.09	0.19×0.1×0.08	0.24×0.11×0.09
μ (mm^{-1})	0.12	0.13	0.34
Data collection			
Diffractometer	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II

			CPAD
Absorption correction	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)
No. of measured, independent and observed [I > 2σ(I)] reflections	73737, 3776, 3121	31105, 3759, 3473	35836, 5037, 3549
Theta range (°)	2.537-26.992	2.30- 27.46	2.82- 26.86
R_{int}	0.177	0.048	0.103
Refinement			
R[F^2 > 2σ (F^2)], wR(F^2)	0.098, 0.201	0.032, 0.084	0.045, 0.108
GOF on F^2	1.24	1.03	1.01
No. of independent reflections	3776	3759	5037
No. of parameters	247	256	327
F_000	1568	408	1088
No. of restraints	0	0	0
H-atom treatment	Constr	Constr	Constr
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $A^{\circ -3}$)	0.31, −0.30	0.33, −0.18	0.34, −0.29
CCDC number	2284904	2284905	2303221

Table 2. Hydrogen-bond geometry (A˚, °) of **IIIA, IIIB** and **3e** are given as below.

Name of the compound	*D*–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
IIIA	C7−H7•••O1	0.9500	2.4200	3.2571(8)	147
	C16−H16•••F1	0.9500	2.4000	3.3228(8)	163
	C20−H20B•••F3	0.9800	2.3200	3.1400(8)	141
IIIB	C12−H12C•••O1	0.9800	2.4800	3.3593(6)	149
	C17−H17•••F1	0.9500	2.4000	3.3020(6)	159
	C20−H20•••O3	0.9500	2.5800	3.4566(6)	154
3e	C5−H5A•••F2	0.990	2.550	3.290(3)	132

	C5−H5B•••O1	0.990	2.360	2.837(3)	108
	C7−H7•••O1	0.950	2.390	3.275(3)	155
	C10−H10•••O4	0.950	2.430	3.371(3)	169
	C14−H14A•••O1	0.990	2.560	3.233(3)	125
	C14−H14A•••F2	0.990	2.480	3.240(3)	133

7. References

1. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Cryst*. (2015). C71, 3–8.
2. G. M. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination, *Acta Cryst*. (2015). A71, 3–8.