

Ruthenium-Catalyzed Decarbonylative Addition Reaction of Anhydrides to Alkynes: A Facile Synthesis of Isocoumarins and α -Pyrone

Rashmi Prakash, Kommuri Shekarrao, Sanjib Gogoi,* and Romesh C Boruah*

*Corresponding author, Tel.: +913762372948; Fax: +913762370011;
Email: skgogoi1@gmail.com; rc_boruah@yahoo.co.in

Medicinal Chemistry Division, CSIR-North East Institute of Science and Technology,
Jorhat 785006, India

SUPPORTING INFORMATION

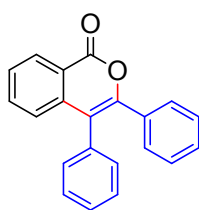
Table of Contents	Page
General Experimental	3
Experimental Procedures	3
Spectral and Analytical data	4-11
NMR spectra for compounds 3a-o, 4a-j	12-63

General Experimental:

Melting points were measured with a Buchi B-540 melting point apparatus and are uncorrected. IR spectra were recorded on Elmer FT-IR-2000 spectrometer on a thin film using chloroform. NMR spectra were recorded on Bruker Avance III 500 MHz FT-NMR spectrometer using tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on Trace DSQ GCMS instrument. All the commercially available reagents were used as received. All experiments were monitored by thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (Merck). Column chromatography was performed on silica gel (100-200 mesh, Merck).

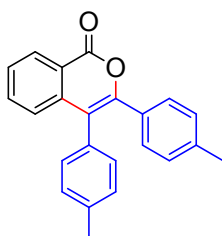
General procedure for the synthesis of Synthesis of isocoumarins 3a-o and α -pyrones 4a-j: A solution of anhydride **1** (1.0 mmol), alkyne **2** (1.0 mmol) and $[\text{RuCl}_2(p\text{-cymene})]_2$ (2.5 mol %) in *tert*-amyl alcohol (3.0 mL) was heated at 100 °C under air for 24 hours. After completion of the reaction, the solvent was removed under vacuo. The crude reaction mixture was poured into water and extracted with ethyl acetate. The ethyl acetate layer was then washed with brine and water. Finally, it was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuo. The crude product obtained was purified by column chromatography over silica gel (100-200 mesh) using EtOAc/Hexane (1:9) as the eluant. Following this general procedure, compounds **3a-o** and **4a-j** were synthesized.

Spectral and Analytical data:



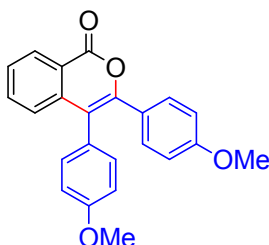
3a

3,4-Diphenyl-1*H*-isochromen-1-one (3a): White solid, m.p. 171 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.16-7.27 (m, 6H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.41- 7.43 (m, 3H), 7.50-7.54 (m, 1H), 7.6-7.65 (m, 1H), 8.41 (d, *J* = 7.5 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 116.8, 120.3, 125.2, 127.7, 127.9, 128.1, 128.8, 128.9, 129.1, 129.5, 131.1, 132.8, 134.2, 134.5, 138.8, 150.8, 162.2. IR (CHCl₃, cm⁻¹): 2925, 1737, 1604, 763. MS (EI, m/z): 298. Anal. calcd. for C₂₁H₁₄O₂: C, 84.54; H, 4.73; Found: C, 84.45; H, 4.63.



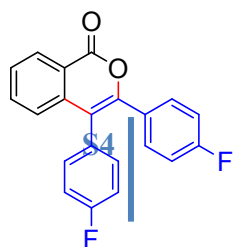
3b

3,4-Di-*p*-tolyl-1*H*-isochromen-1-one (3b): White solid, m.p. 168 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.28 (s, 3H), 2.41 (s, 3H), 7.01 (d, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.18-7.25 (m, 5H), 7.48-7.52 (m, 1H), 7.60-7.64 (m, 1H), 8.39 (d, *J* = 7.6 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 21.2, 21.3, 116.2, 120.2, 125.2, 127.7, 128.5, 128.9, 129.3, 129.7, 130.1, 130.9, 131.3, 134.4, 137.7, 138.9, 139.1, 150.8, 162.4. IR (CHCl₃, cm⁻¹): 2923, 1736, 1023, 773. MS (EI, m/z): 326. Anal. calcd. for C₂₃H₁₈O₂: C, 84.64; H, 5.56; Found: C, 84.79; H, 5.54.



3c

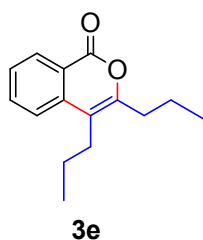
3,4-bis(4-Methoxyphenyl)-1*H*-isochromen-1-one (3c): Yellow solid, m.p. 159 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.78 (s, 3H), 3.87 (s, 3H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.47-7.51 (m, 1H), 7.61-7.63 (m, 1H), 8.39 (d, *J* = 7.5 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 55.1, 55.2, 113.2, 114.5, 115.4, 120.1, 125.1, 125.5, 126.7, 127.6, 129.4, 130.5, 132.2, 134.4, 139.6, 150.9, 159.4, 159.9, 162.6. IR (CHCl₃, cm⁻¹): 2924, 1730, 1603, 1219, 772. MS (EI, m/z): 358. Anal. calcd. for C₂₃H₁₈O₄: C, 77.08; H, 5.06; Found: C, 77.15; H, 4.95.



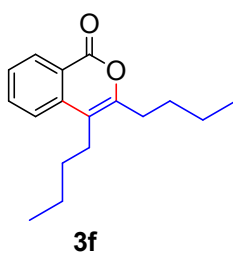
3d

3,4-bis(4-Fluorophenyl)-1*H*-isochromen-1-one (3d): Yellow solid, m.p. 167 °C. ¹H NMR (500 MHz, CDCl₃): δ 6.91 (d, *J* = 8.5 Hz, 2H), 7.12-7.18 (m, 4H), 7.21- 7.25 (m, 1H), 7.29-7.32 (m, 2H), 7.53-7.56 (m, 1H), 7.65-7.68 (m, 1H), 8.41 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 116.2, 116.4, 120.3, 124.9,

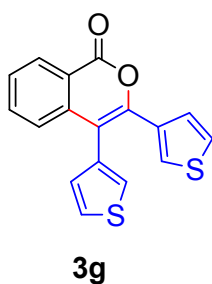
128.2, 128.8, 129.6, 129.7, 129.9, 131.1, 131.2, 132.7, 132.8, 134.7, 138.5, 150.2, 161.7, 163.4. IR (CHCl₃, cm⁻¹): 2923, 1738, 1505, 1232, 665. IR (CHCl₃, cm⁻¹): 2924, 1732, 1638, 1219, 772. MS (EI, m/z): 334. Anal. calcd. for C₂₁H₁₂F₂O₂: C, 75.45; H, 3.62; Found: C, 75.67; H, 3.70.



3,4-Dipropyl-1H-isochromen-1-one (3e): Oil. ¹H NMR (500 MHz, CDCl₃): δ 1.01 (t, *J* = 7.5 Hz, 3H), 1.04 (t, *J* = 7.4 Hz, 3H), 1.58-1.77 (m, 4H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 7.46 Hz (ddd, *J* = 8.0 Hz, 7.3 Hz, 1.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.74 (ddd, *J* = 8.0 Hz, 7.3 Hz, 1.5 Hz, 1H), 8.32 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 13.7, 14.1, 21.1, 22.8, 28.1, 32.6, 112.1, 120.7, 122.6, 126.9, 129.7, 134.4, 137.9, 154.1, 162.9. IR (CHCl₃, cm⁻¹): 2952, 1734, 1647, 1242, 775. MS (EI, m/z): 230. Anal. calcd. for C₁₅H₁₈O₂: C, 78.23; H, 7.88; Found: C, 78.42; H, 7.81.



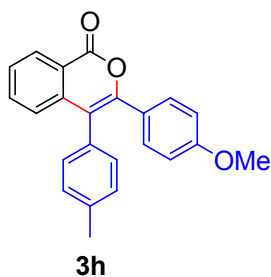
3,4-Dibutyl-1H-isochromen-1-one (3f): Oil. ¹H NMR (500 MHz, CDCl₃): δ 0.94-1.0 (m, 6H), 1.37-1.55 (m, 6H), 1.66-1.73 (m, 2H), 2.57-2.62 (m, 4H), 7.43-7.48 (m, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.71-7.75 (m, 1H), 8.31 (dd, *J* = 7.5 Hz, 1.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 13.7, 13.9, 22.4, 22.7, 25.8, 29.9, 30.4, 31.7, 112.1, 120.6, 122.5, 126.9, 129.7, 134.4, 137.9, 154.1, 162.8. IR (CHCl₃, cm⁻¹): 2959, 1732, 1640, 1258, 771. MS (EI, m/z): 258. Anal. calcd. for C₁₇H₂₂O₂: C, 79.03; H, 8.58; Found: C, 78.83; H, 8.41.



3,4-Di(thiophen-3-yl)-1H-isochromen-1-one (3g): Yellow solid, m.p. 163 °C; ¹H NMR (500 MHz, CDCl₃): δ 6.76 (d, *J* = 4.0 Hz, 1H), 7.07 (d, *J* = 3.5 Hz, 1H), 7.14 - 7.16 (m, 2H), 7.25-7.28 (m, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.51 (s, 1H), 7.56-7.58 (m, 1H), 7.62-7.66 (m, 1H), 8.36 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 110.3, 119.9, 125.1, 125.8, 126.7, 126.8, 127.3, 127.4, 127.8, 129.3, 129.4, 133.8, 134.1, 134.7, 139.1, 147.3, 161.8. IR (CHCl₃, cm⁻¹): 2923, 1738, 1479, 1023, 770. MS (EI, m/z): 310. Anal. calcd. for C₁₇H₁₀O₂ S₂: C, 65.78; H, 3.25;

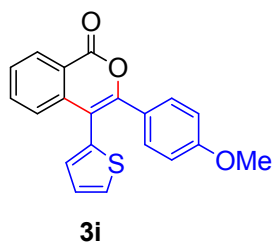
Found: C, 65.90; H, 3.15.

3-(4-Methoxyphenyl)-4-(*p*-tolyl)-1*H*-isochromen-1-one and 4-(4-methoxyphenyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one (1:1 mixture, 3h):



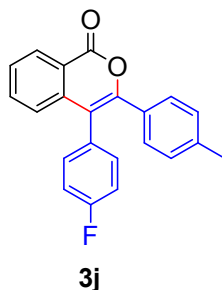
Yellow solid, m.p. 168 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.41 (s, 3H), 3.85 (s, 3H), 6.71 (d, *J* = 7.0 Hz, 1H), 6.95 (d, *J* = 6.5 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.13-7.21 (m, 3H), 7.22-7.25 (m, 2H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.43-7.50 (m, 1H), 7.58-7.63 (m, 1H), 8.38 (d, *J* = 8.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 21.3, 55.2, 113.2, 114.4, 115.6, 115.8, 125.1, 127.7, 128.6, 128.9, 129.3, 129.7, 130.6, 130.9, 132.2, 134.5, 139.2, 150.6, 159.2, 162.4. IR (CHCl₃, cm⁻¹): 2930, 1733, 1508, 1248, 773. MS (EI, *m/z*): 342. Anal. calcd. for C₂₃H₁₈O₃ : C, 80.68; H, 5.30; Found: C, 80.74; H, 5.36.

3-(4-Methoxyphenyl)-4-(thiophen-2-yl)-1*H*-isochromen-1-one and 4-(4-methoxyphenyl)-3-(thiophen-2-yl)-1*H*-isochromen-1-one (1:1 mixture, 3i):



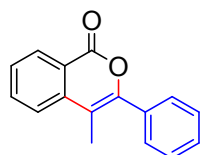
White solid, m.p. 128 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.77 (s, 1.5H), 3.90 (s, 1.5H), 6.70-6.78 (m, 1.5H), 6.96-7.13 (m, 3H), 7.14-7.35 (m, 3H), 7.42-7.52 (m, 1.5H), 7.61 (t, *J* = 7.0 Hz, 0.5 H), 7.64 (t, *J* = 7.0 Hz, 0.5 H), 8.34 (d, *J* = 4.0 Hz, 0.5 H), 8.36 (d, *J* = 4.0 Hz, 0.5 H). ¹³C NMR (125 MHz, CDCl₃): δ 14.1, 29.6, 29.9, 31.8, 55.1, 55.2, 110.6, 113.2, 114.9, 115.0, 119.9, 120.1, 124.9, 125.3, 125.7, 126.7, 127.1, 127.7, 129.3, 130.2, 131.9, 134.5, 134.6, 139.5, 146.9, 151.2, 159.7, 159.9, 161.9, 162.2. IR (CHCl₃, cm⁻¹): 2978, 1722, 1023, 770. MS (EI, *m/z*): 334. Anal. calcd. for C₂₀H₁₄O₃S : C, 71.84; H, 4.22; Found: C, 71.70; H, 4.08.

4-(4-Fluorophenyl)-3-(*p*-tolyl)-1*H*-isochromen-1-one and 3-(4-fluorophenyl)-4-(*p*-tolyl)-1*H*-isochromen-1-one (1:1 mixture, 3j):



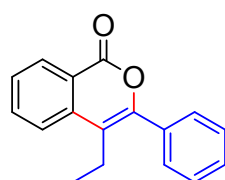
White solid, m.p. 144 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.29 (s, 1.5H), 2.42 (s, 1.5H), 6.85 (t, *J* = 9.0 Hz, 1H), 6.97-7.03 (m, 1H), 6.80-7.38 (m, 7H), 7.48-7.55 (m, 1H), 7.60-7.67 (m, 1H), 8.35-8.43 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 21.2, 21.3, 114.8, 115.0, 116.0, 116.2, 125.3, 128.0, 128.6, 128.9, 129.4,

129.8, 130.8, 131.1, 132.8, 132.9, 134.5, 137.9, 138.7, 149.7, 151.3, 161.4, 161.6, 162.1, 163.6. IR (CHCl₃, cm⁻¹): 2924, 1720, 1029, 771. MS (EI, m/z): 330. Anal. calcd. for C₂₂H₁₅FO₂ : C, 79.99; H, 4.58; Found: C, 80.16; H, 4.56.



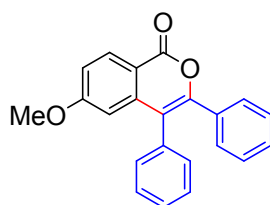
3k

4-Methyl-3-phenyl-1H-isochromen-1-one (3k): Pale yellow solid, m.p. 115 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.32 (s, 3H), 7.43-7.49 (m, 3H), 7.53-7.61 (m, 3H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.78-7.83 (m, 1H), 8.38 (d, *J* = 8.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 13.5, 109.1, 120.7, 123.3, 127.8, 128.2, 129.2, 129.4, 129.6, 133.1, 134.7, 138.7, 151.1, 162.4. IR (CHCl₃, cm⁻¹): 2978, 1722, 1029, 772. MS (EI, m/z): 236. Anal. calcd. for C₁₆H₁₂O₂ : C, 81.34; H, 5.12; Found: C, 81.47; H, 5.03.



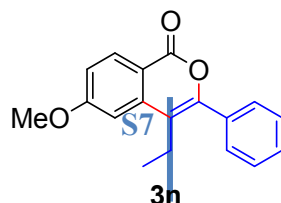
3l

3-Ethyl-4-phenyl-1H-isochromen-1-one (3l): Yellow solid, m.p. 133 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.29 (t, *J* = 5.0 Hz, 3H), 2.73 (q, *J* = 5.0 Hz, 2H), 7.45-7.48 (m, 3H), 7.53-7.60 (m, 3H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.78 -7.81 (m, 1H), 8.39 (dd, *J* = 7.6 Hz, 1.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 14.7, 20.1, 115.1, 121.2, 123.3, 127.8, 128.3, 128.8, 129.3, 129.9, 133.3, 134.6, 137.6, 151.2, 162.4. IR (CHCl₃, cm⁻¹): 2973, 1727, 1019, 765. MS (EI, m/z): 250. Anal. calcd. for C₁₇H₁₄O₂ : C, 81.58; H, 5.64; Found: C, 81.69; H, 5.71.



3m

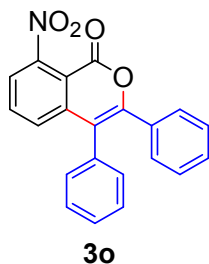
6-Methoxy-3,4-diphenyl-1H-isochromen-1-one (3m): Yellow solid, m.p.: 173 °C. ¹H NMR (500 MHz, CDCl₃): δ 3.75 (s, 3H), 6.58 (d, *J* = 2.1 Hz, 1H), 7.07 (dd, *J* = 8.7 Hz, 2.4 Hz, 1H), 7.19-7.27 (m, 5H), 7.31-7.34 (m, 2H), 7.38-7.44 (m, 3H), 8.35 (d, *J* = 8.7 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 55.4, 108.4, 113.6, 115.5, 116.7, 127.7, 127.9, 128.8, 128.9, 129.1, 131.1, 131.8, 132.9, 134.3, 141.1, 151.4, 161.9, 164.5. IR (CHCl₃, cm⁻¹): 2924, 1729, 1604, 767. MS (EI, m/z): 328. Anal. calcd. for C₂₂H₁₆O₃ : C, 80.47; H, 4.91; Found: C, 80.56; H, 4.89..



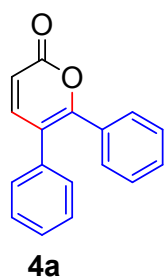
3n

3-Ethyl-6-methoxy-4-phenyl-1H-isochromen-1-one (3n): Yellow solid, m.p. 136 °C; ¹H NMR (500 MHz, CDCl₃): δ 1.25 (t, *J* = 5.0 Hz, 3H), 2.64-2.71 (m, 2H), 3.96 (s, 3H), 7.07 (d, *J* = 2.0 Hz, 1H),

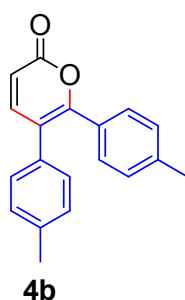
7.42-7.50 (m, 4H), 7.51-7.57 (m, 2H), 8.33 (d, $J = 8.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 14.5, 20.1, 55.5, 106.8, 114.4, 114.8, 114.9, 128.2, 128.8, 129.3, 132.3, 133.4, 139.8, 151.8, 162.1, 164.6. IR (CHCl_3 , cm^{-1}): 2971, 1735, 1219, 765. MS (EI, m/z): 280. Anal. calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_3$: C, 77.12; H, 5.75; Found: C, 77.19; H, 5.75.



8-nitro-3,4-diphenyl-1H-isochromen-1-one (3o): Brown solid, m.p. 162 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.11-7.27 (m, 10H), 7.64-7.67 (m, 1H), 7.86 (d, $J = 7.5$ Hz, 1H), 8.63 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 113.2, 122.5, 127.7, 128.1, 128.3, 128.5, 129.4, 130.4, 130.5, 130.6, 132.3, 132.5, 133.1, 147.8, 154.4, 160.0. IR (CHCl_3 , cm^{-1}): 2925, 1737, 1604, 763. MS (EI, m/z): 343. Anal. calcd. for $\text{C}_{21}\text{H}_{13}\text{NO}_4$: C, 73.46; H, 3.82; Found: C, 73.56; H, 3.71.

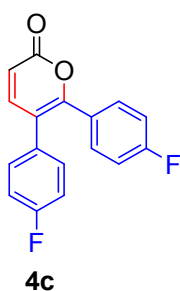


5,6-Diphenyl-2H-pyran-2-one (4a): White solid, m.p. 87 °C. ^1H NMR (500 MHz, CDCl_3): δ 6.38 (d, $J = 9.5$ Hz, 1H), 7.17- 7.19 (m, 2H), 7.23-7.26 (m, 2H), 7.31-7.33 (m, 4H), 7.35-7.37 (m, 2H) 7.47 (d, $J = 9.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 113.9, 117.8, 127.8, 128.1, 128.9, 129.1, 129.2, 129.9, 131.9, 136.1, 147.8, 157.9, 161.8. IR (CHCl_3 , cm^{-1}): 2924, 1739, 1535, 763. MS (EI, m/z): 248. Anal. calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_2$: C, 82.24; H, 4.87; Found: C, 82.02; H, 4.73.

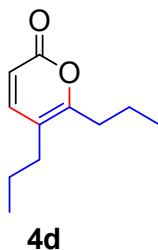


5,6-di-*p*-Tolyl-2H-pyran-2-one (4b): Brown solid, mp: 96 °C. ^1H NMR (500 MHz, CDCl_3): δ 2.23 (s, 3H), 2.27 (s, 3H), 6.24 (d, $J = 9.5$ Hz, 1H), 6.95-6.99 (m, 4H), 7.04 (d, $J = 7.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 9.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 21.1, 21.3, 113.4, 117.3, 128.8, 128.9, 129.0, 129.2, 129.6, 133.3, 137.6, 140.1, 148.1, 157.9, 161.9. IR (CHCl_3 , cm^{-1}): 2925, 1734, 1219, 771. MS (EI, m/z): 276. Anal. calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_2$: C, 82.58; H, 5.84; Found: C, 82.70; H, 5.81.

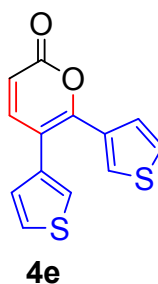
5,6-bis(4-Fluorophenyl)-2H-pyran-2-one (4c): Brown solid, mp: 92 °C. ^1H NMR (500 MHz, CDCl_3): δ 6.38 (d, $J = 9.5$ Hz, 1H), 6.94-6.98 (m, 2H), 7.03-7.06 (m, 2H), 7.13-7.16 (m, 2H), 7.33-7.37



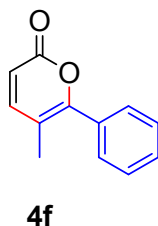
(m, 2H), 7.43 (d, $J = 9.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 114.3, 115.5, 115.7, 116.2, 116.4, 116.8, 130.9, 131.3, 131.4, 147.6, 157.2, 161.5, 162.5. IR (CHCl_3 , cm^{-1}): 2925, 1737, 1604, 772. MS (EI, m/z): 284. Anal. calcd. for $\text{C}_{17}\text{H}_{10}\text{O}_2\text{F}_2$: C, 71.83; H, 3.55; Found: C, 71.65; H, 3.65.



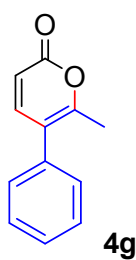
5,6-Dipropyl-2H-pyran-2-one (4d): Gum. ^1H NMR (500 MHz, CDCl_3): δ 0.85-0.91 (m, 6H), 1.41-1.46 (m, 2H), 1.60-1.65 (m, 2H), 2.21 (t, $J = 7.5$ Hz, 2H), 2.4 (t, $J = 7.5$ Hz, 2H), 6.08 (d, $J = 9.5$ Hz, 1H), 7.11 (d, $J = 9.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 13.5, 13.6, 20.8, 23.2, 30.9, 32.4, 113.2, 114.9, 146.9, 161.7, 162.9. IR (CHCl_3 , cm^{-1}): 2925, 1734, 1219, 771. MS (EI, m/z): 180. Anal. calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 77.40; H, 8.95; Found: C, 77.62; H, 8.97.



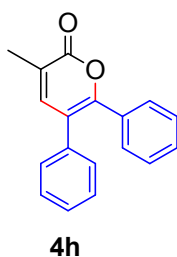
5,6-di(Thiophen-3-yl)-2H-pyran-2-one (4e): Pale yellow solid, m.p. 87 °C. ^1H NMR (500 MHz, CDCl_3): δ 6.29 (d, $J = 9.5$, 1H), 6.88 (d, $J = 5.0$ Hz, 1H), 6.94 (d, $J = 5.0$ Hz, 1H), 7.17-7.18 (m, 1H), 7.24 (d, $J = 1.5$, 1H), 7.37-7.40 (m, 2H), 7.52 (d, $J = 9.5$, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 111.9, 113.2, 124.1, 125.5, 126.7, 126.8, 128.1, 128.2, 133.2, 136.1, 147.8, 153.8, 161.3. IR (CHCl_3 , cm^{-1}): 2924, 1729, 1219, 763. MS (EI, m/z): 260. Anal. calcd. for $\text{C}_{13}\text{H}_8\text{O}_2\text{S}_2$: C, 59.98; H, 3.10; Found: C, 59.89; H, 3.15.



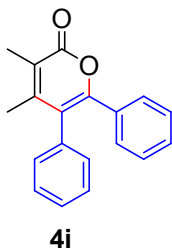
5-Methyl-6-phenyl-2H-pyran-2-one (4f): Brown solid, mp: 94 °C. ^1H NMR (500 MHz, CDCl_3): δ 2.09 (s, 3H), 6.19 (d, $J = 9.0$ Hz, 1H), 7.22 (d, $J = 9.5$ Hz, 1H), 7.36-7.37 (m, 3H), 7.48-7.50 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 16.6, 111.9, 114.1, 128.1, 129.7, 132.3, 146.8, 148.6, 157.3, 162.2. IR (CHCl_3 , cm^{-1}): 2924, 1734, 1019, 763. MS (EI, m/z): 186. Anal. calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_2$: C, 77.40; H, 5.41; Found: C, 77.36; H, 5.49.



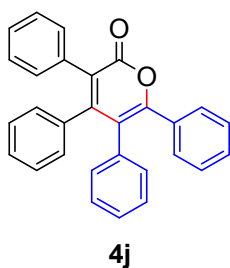
6-Methyl-5-phenyl-2H-pyran-2-one (4g): White solid, m.p. 67 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.19 (s, 3H), 6.17 (d, *J* = 10.0 Hz, 1H), 7.12-7.33 (m, 4H), 7.35 (t, *J* = 5.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 18.4, 113.0, 117.8, 127.8, 128.7, 135.6, 146.7, 159.4, 162.2. IR (CHCl₃, cm⁻¹): 2923, 1734, 1219, 757. MS (EI, m/z): 186. Anal. calcd. for C₁₂H₁₀O₂: C, 77.40; H, 5.41; Found: C, 77.58; H, 5.27.



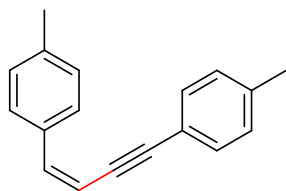
3-Methyl-5,6-diphenyl-2H-pyran-2-one (4h): White solid, m.p. 92 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.12 (s, 3H), 7.09- 7.16 (m, 6H), 7.19-7.28 (m, 5H), ¹³C NMR (125 MHz, CDCl₃): δ 16.4, 117.9, 123.5, 127.7, 127.9, 128.0, 128.8, 128.9, 129.4, 132.1, 136.4, 144.1, 155.3, 163.1, IR (CHCl₃, cm⁻¹): 2925, 1737, 1604, 772. MS (EI, m/z): 262. Anal. calcd. for C₁₈H₁₄O₂: C, 82.42; H, 5.38; Found: C, 82.71; H, 5.19.



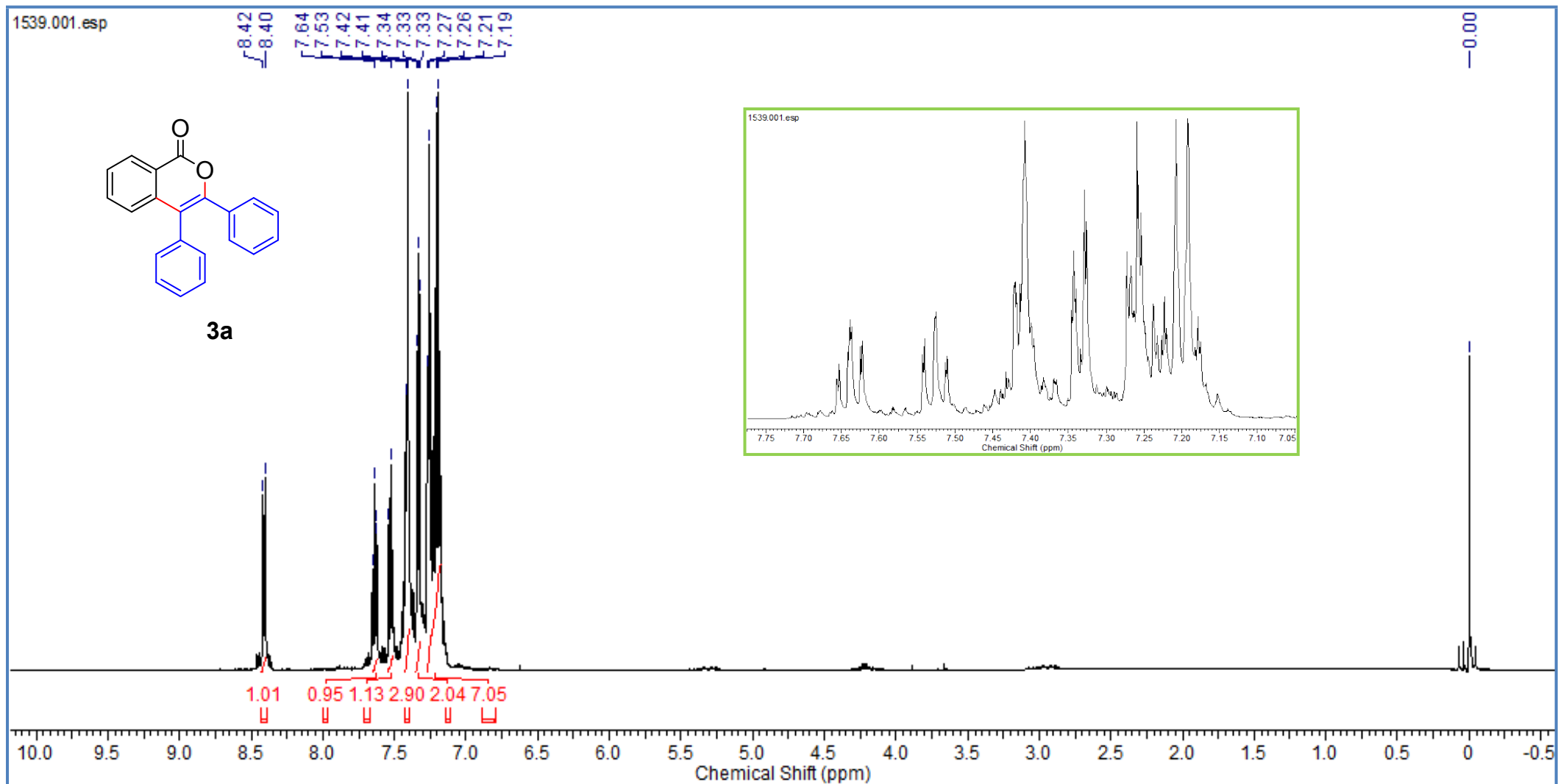
3,4-Dimethyl-5,6-diphenyl-2H-pyran-2-one (4i): Pale yellow solid. mp: 119 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.92 (s, 3H), 2.18 (s, 3H) 7.10-7.23 (m, 7H), 7.33-7.35 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 13.1, 18.1, 120.9, 127.7, 127.8, 128.8, 128.9, 130.6, 132.6, 135.5, 140.7, 150.8, 153.8, 163.1. IR (CHCl₃, cm⁻¹): 2923, 1702, 1019, 757. MS (EI, m/z): 276. Anal. calcd. for C₁₉H₁₆O₂: C, 82.58; H, 5.84; Found: C, 82.54; H, 5.88.



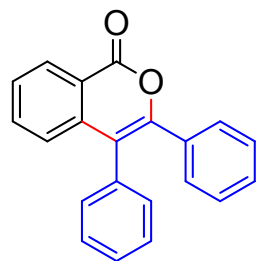
3,4,5,6-Tetraphenyl-2H-pyran-2-one (4j): White solid, m.p. 92 °C. ¹H NMR (500 MHz, CDCl₃): δ 6.68 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.0 Hz, 1H), 6.90-7.48 (m, 17H), 7.54 (d, *J* = 8.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 119.5, 127.1, 128.0, 128.8, 128.9, 129.3, 129.6, 130.5, 131.1, 131.3, 134.1, 136.0, 138.1, 147.9, 155.3, 156.5, 162.3. IR (CHCl₃, cm⁻¹): 2925, 1737, 1604, 763. MS (EI, m/z): 400. Anal. calcd. for C₂₉H₂₀O₂: C, 86.98; H, 5.03; Found: C, 86.84; H, 5.12.



(Z)-1,4-di-*p*-Tolylbut-1-en-3-yne: Yellow solid, m.p. 63 °C. ¹H NMR (500 MHz, CDCl₃): δ 2.38 (s, 6H), 5.85 (d, *J* = 12 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 7.11-7.22 (m, 4H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 21.3, 21.4, 87.8, 95.8, 106.4, 120.4, 126.6, 128.6, 128.9, 129.1, 131.2, 133.8, 138.1, 138.4. IR (CHCl₃, cm⁻¹): 2925, 1640, 763. MS (EI, m/z): 232. Anal. calcd. for C₁₈H₁₆: C, 93.06; H, 6.94; Found: C, 93.13; H, 6.90.



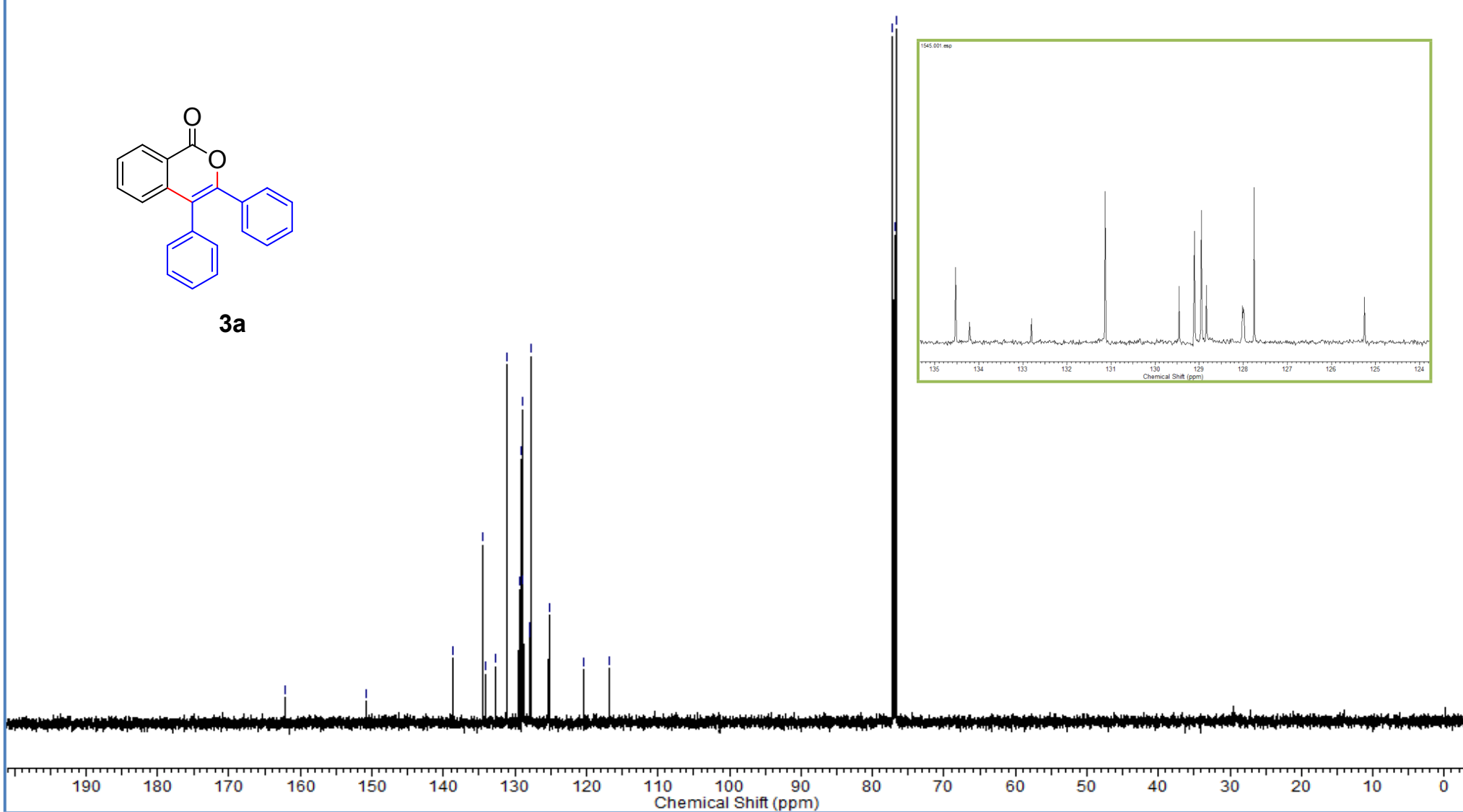
1545.001.esp

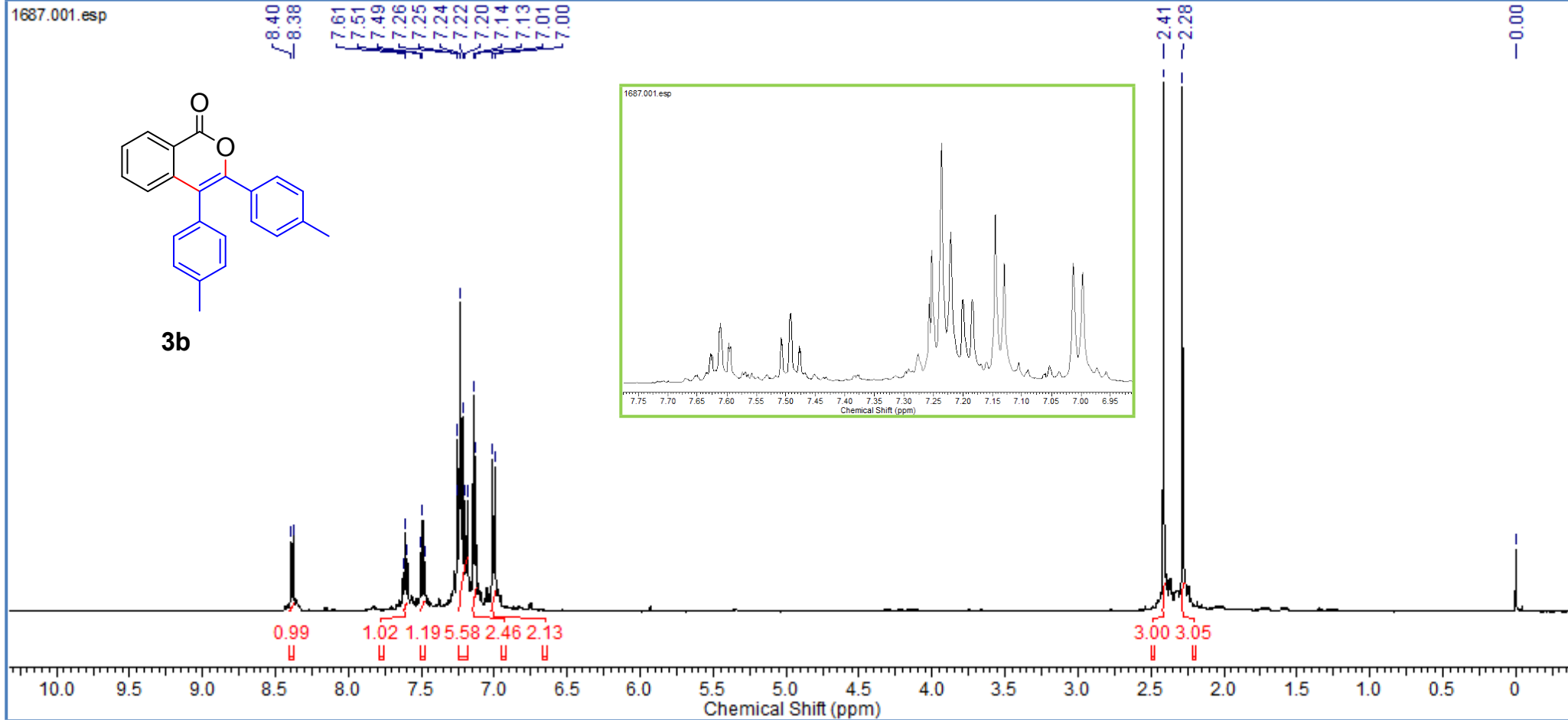


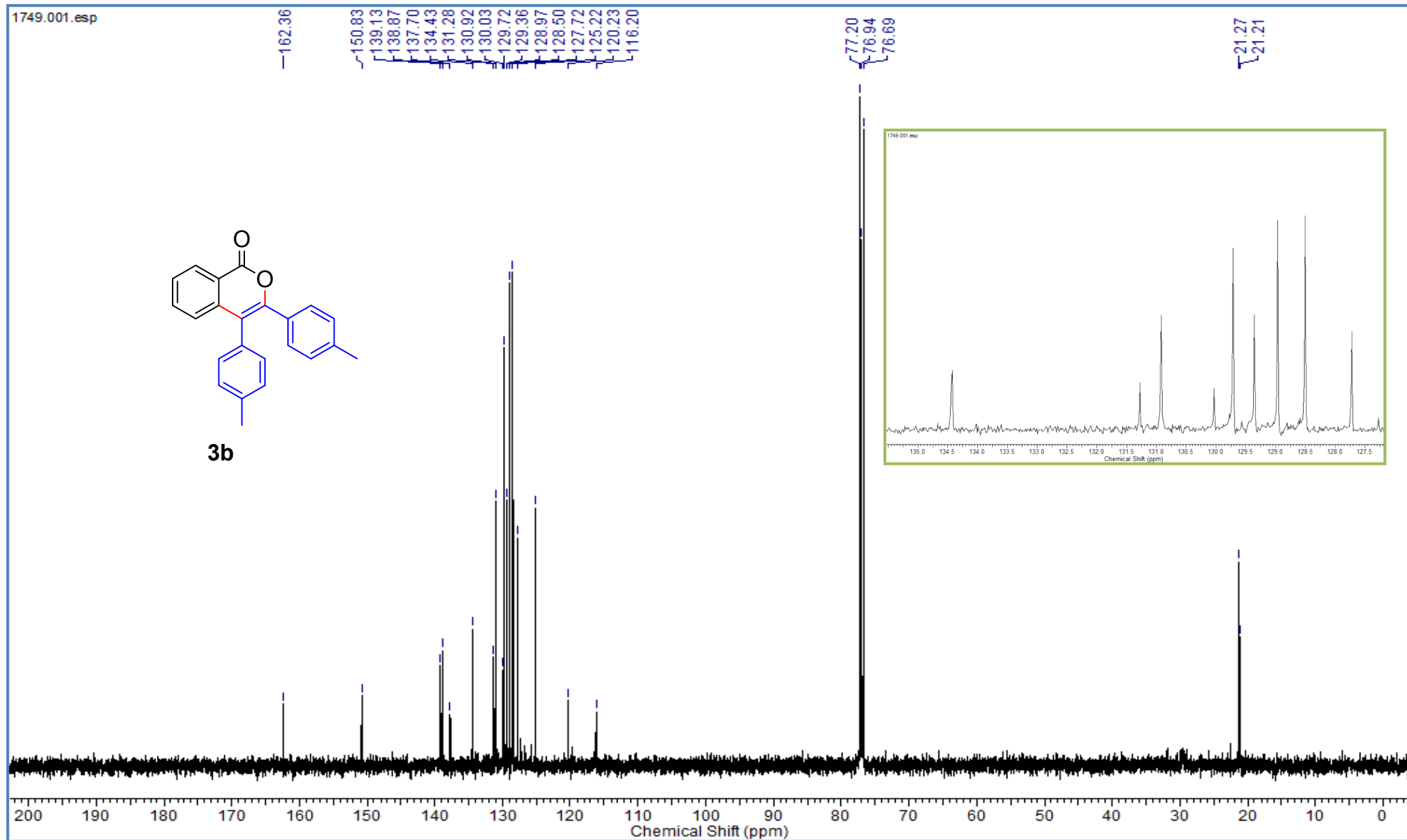
3a

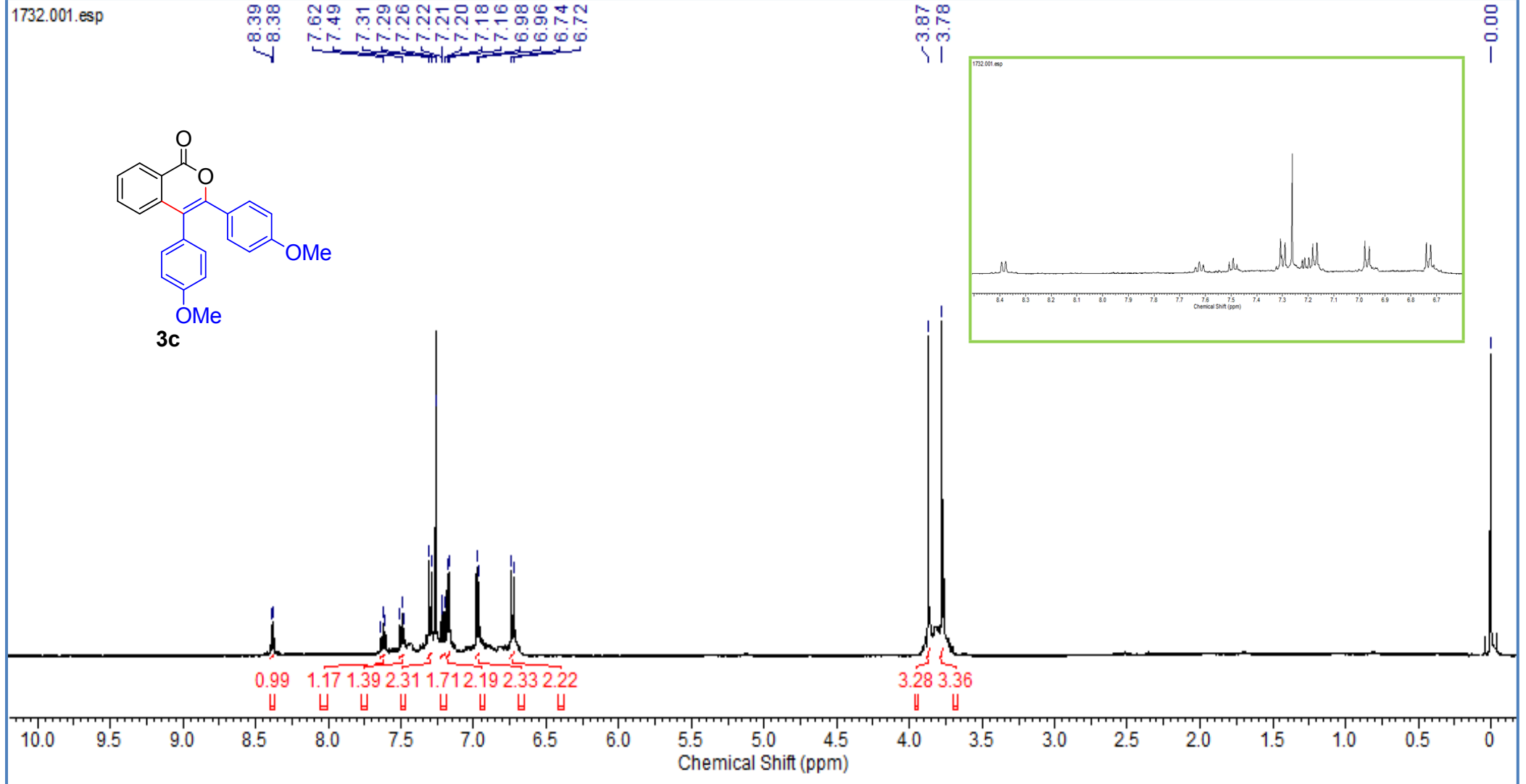
162.17
150.85
138.76
134.53
132.81
131.13
129.46
129.11
128.95
128.84
128.03
128.00
127.75
125.25
120.34
116.79

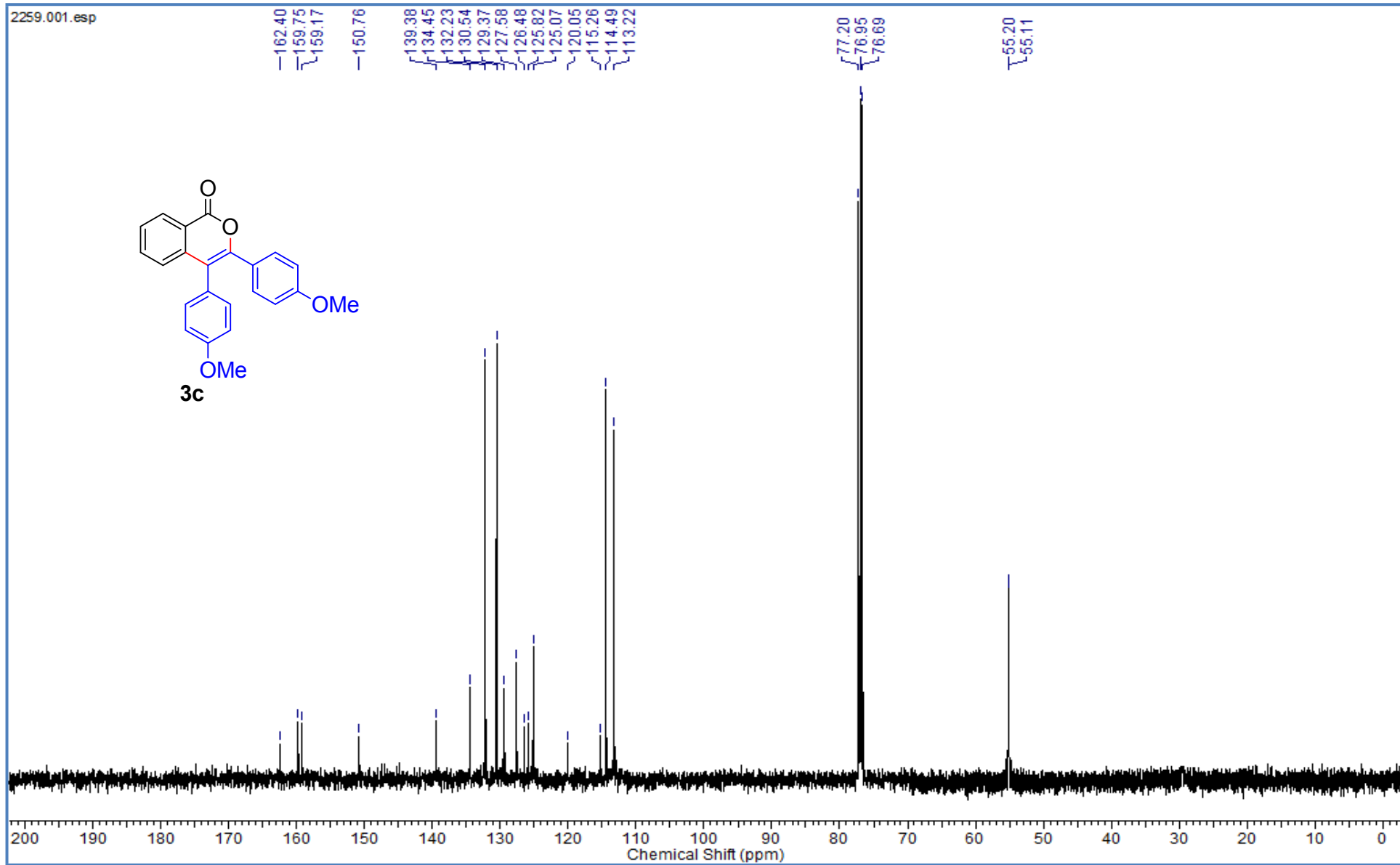
77.17
76.92
76.66

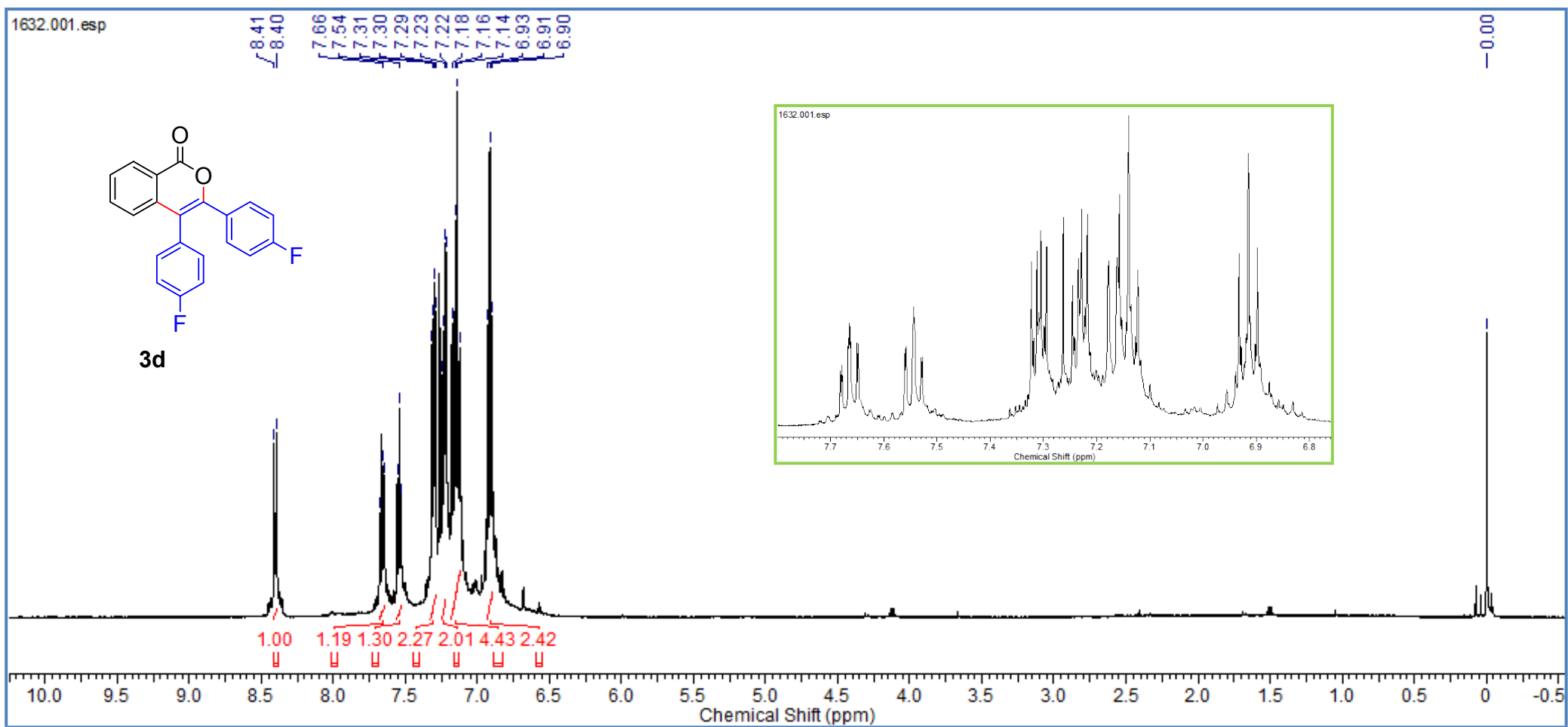


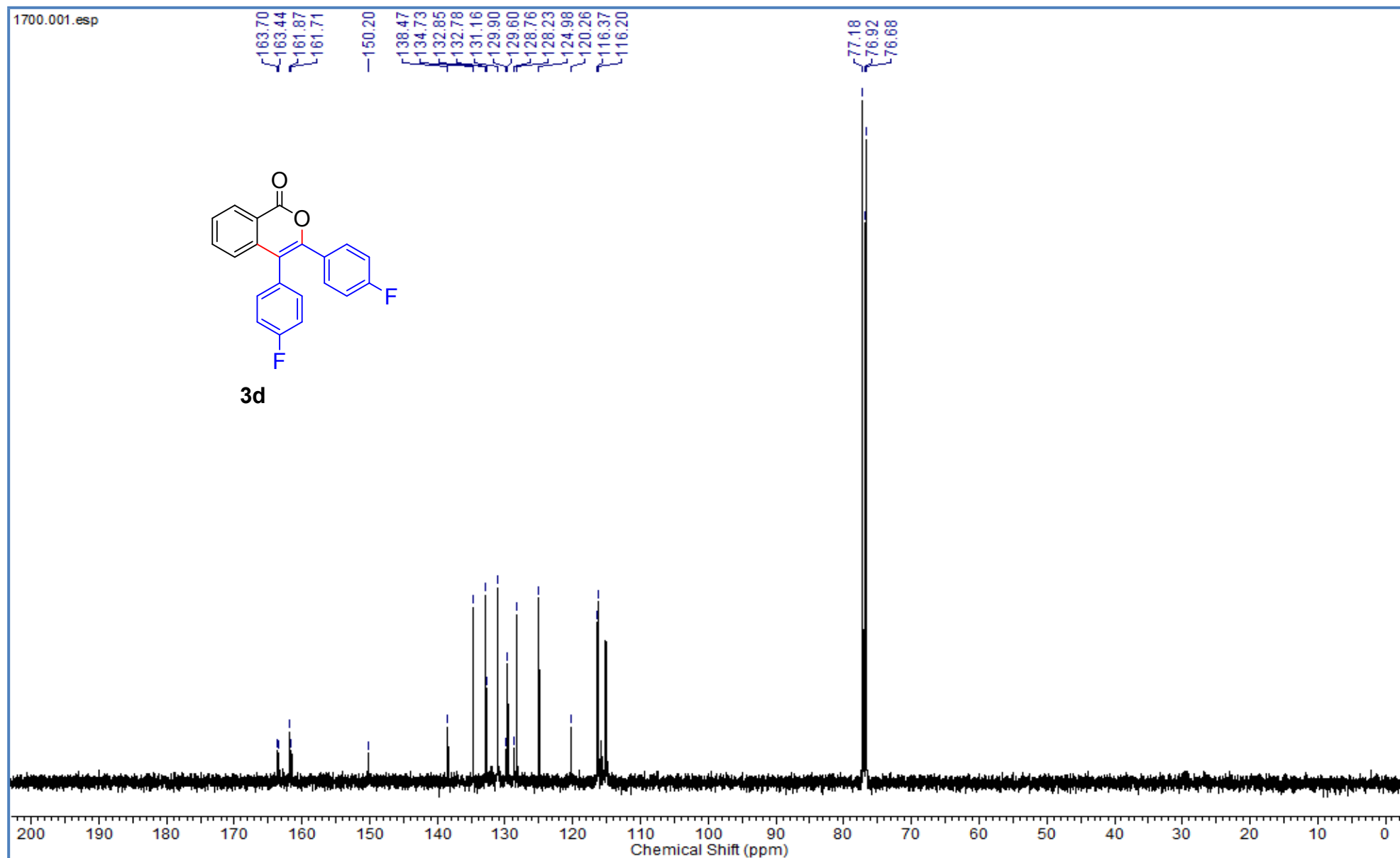


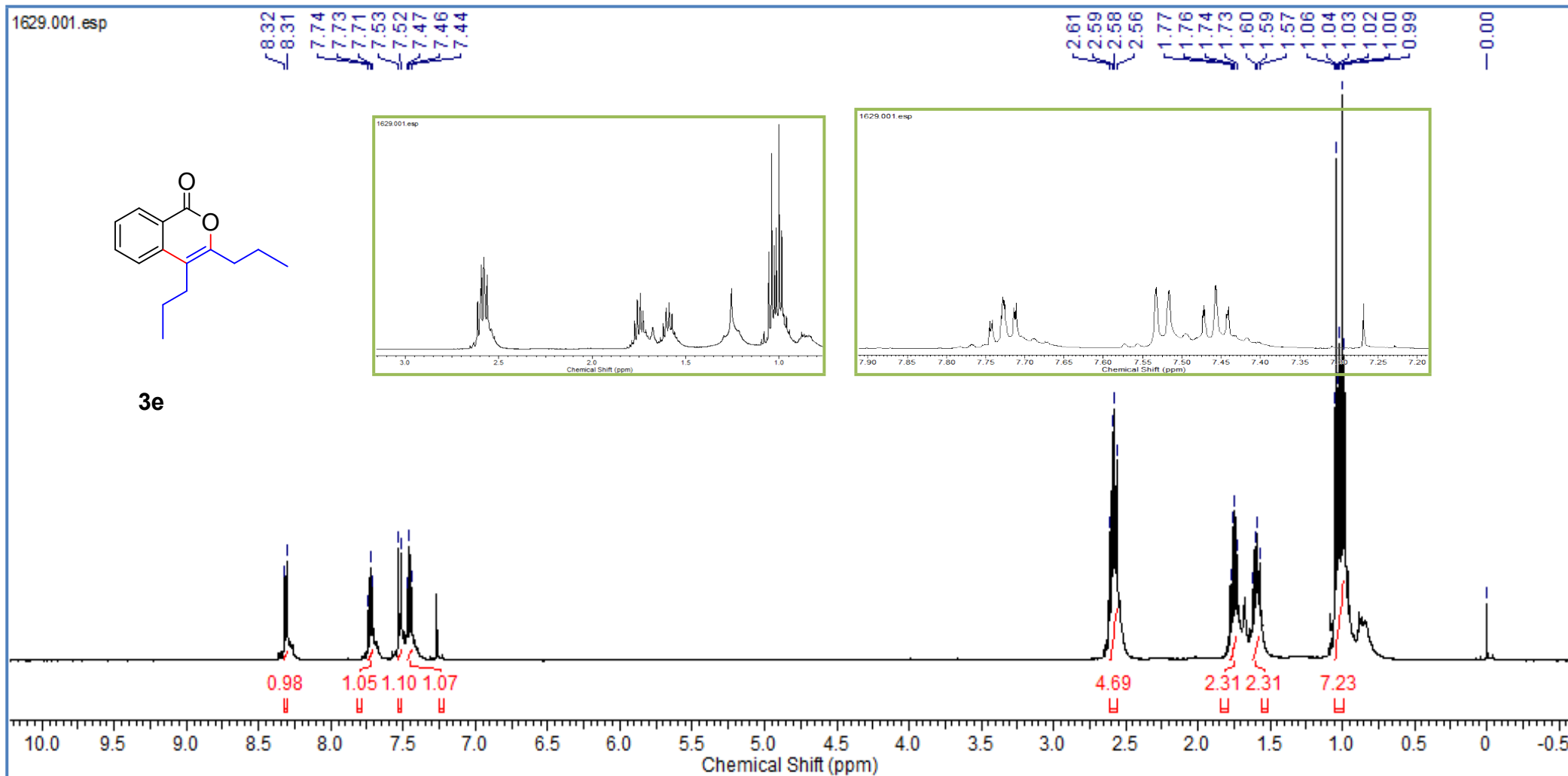


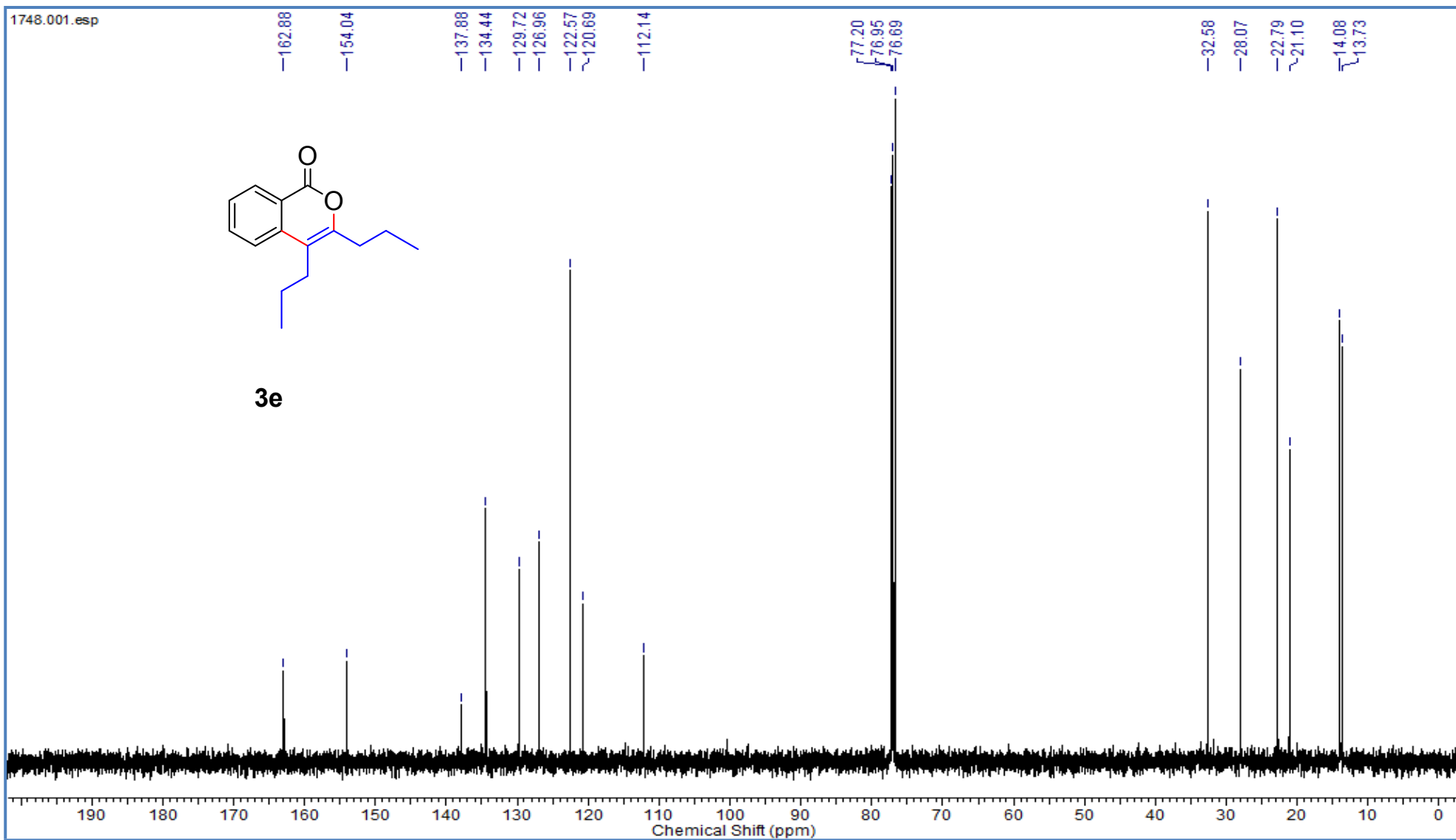


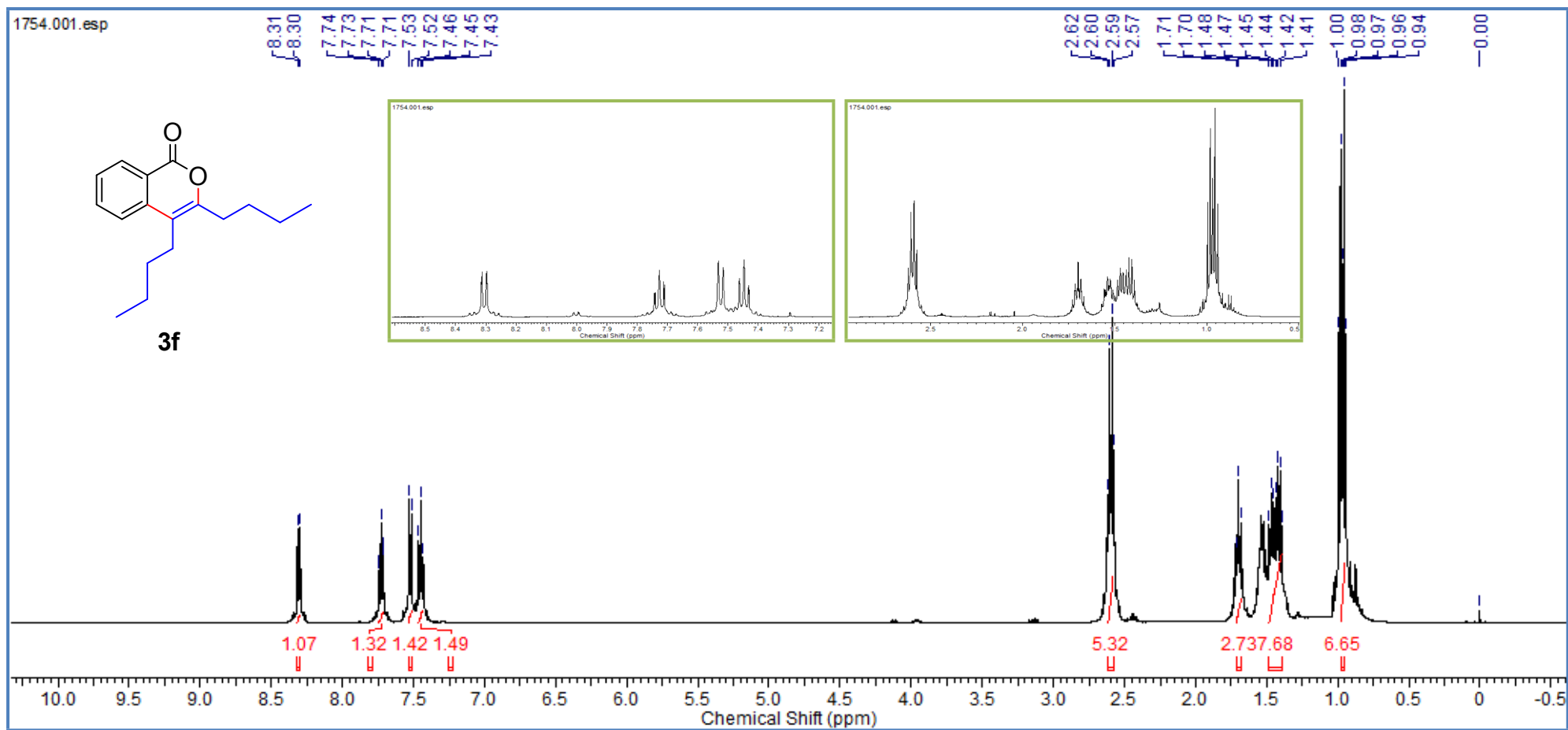


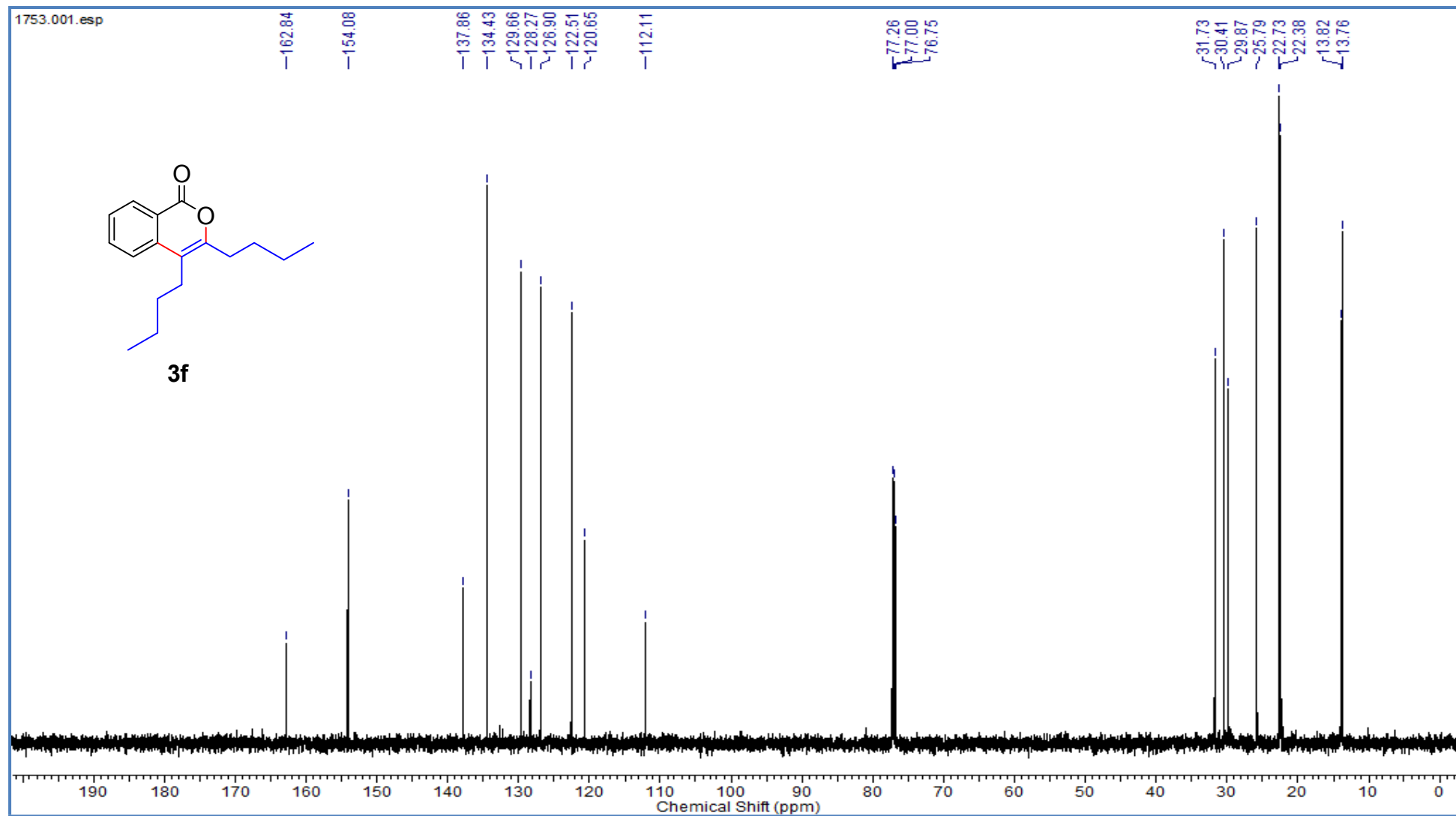


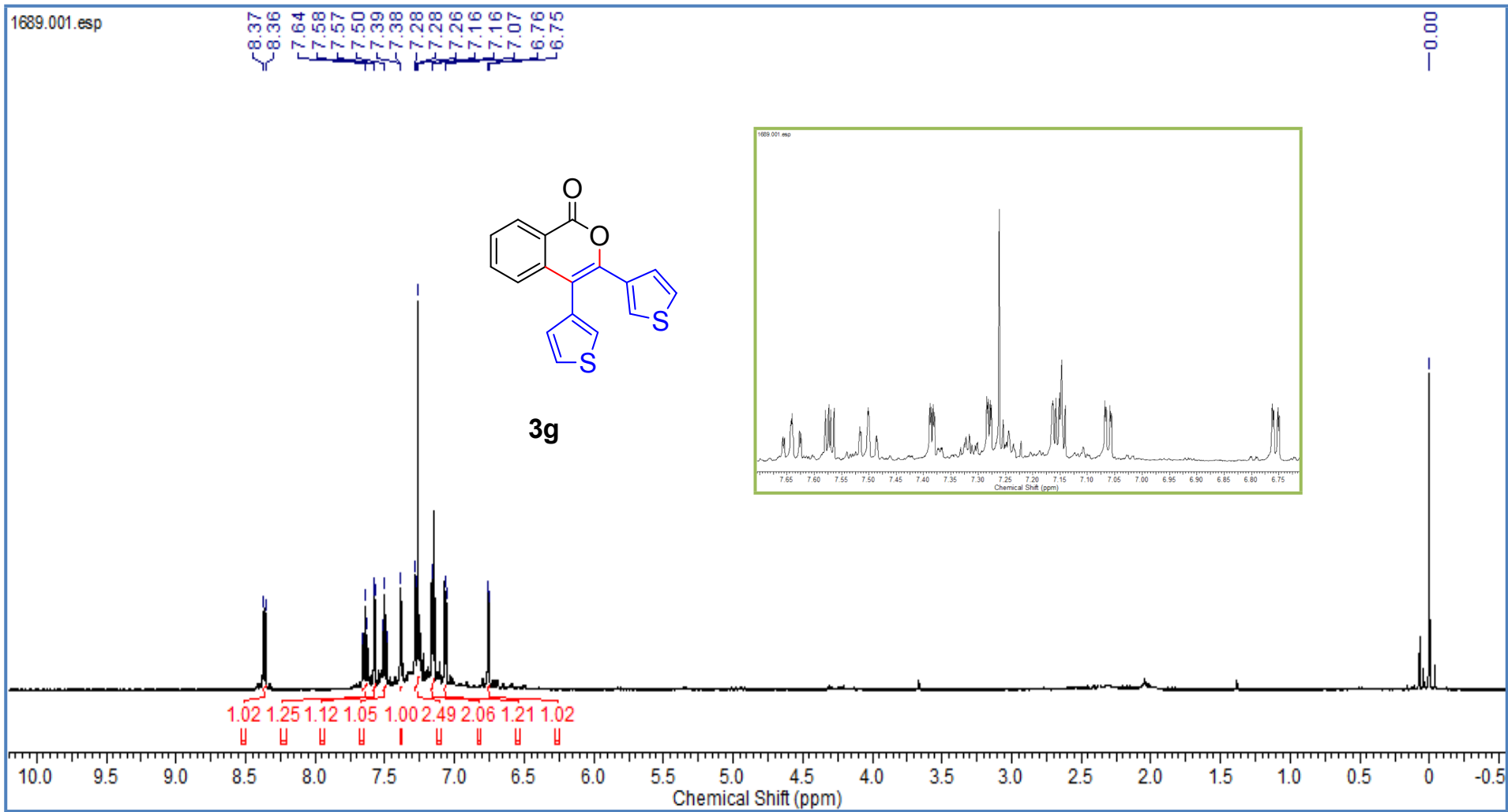


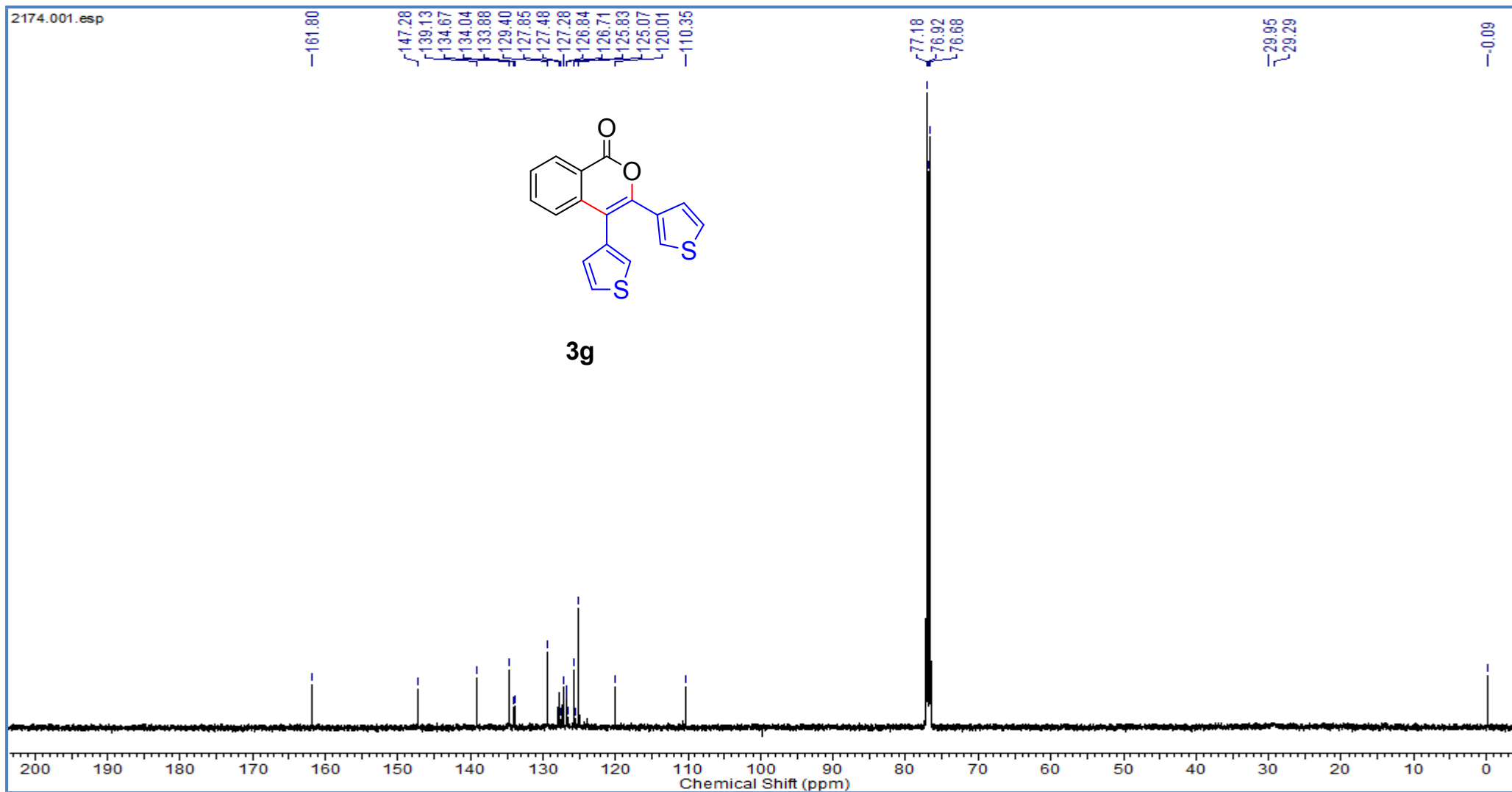


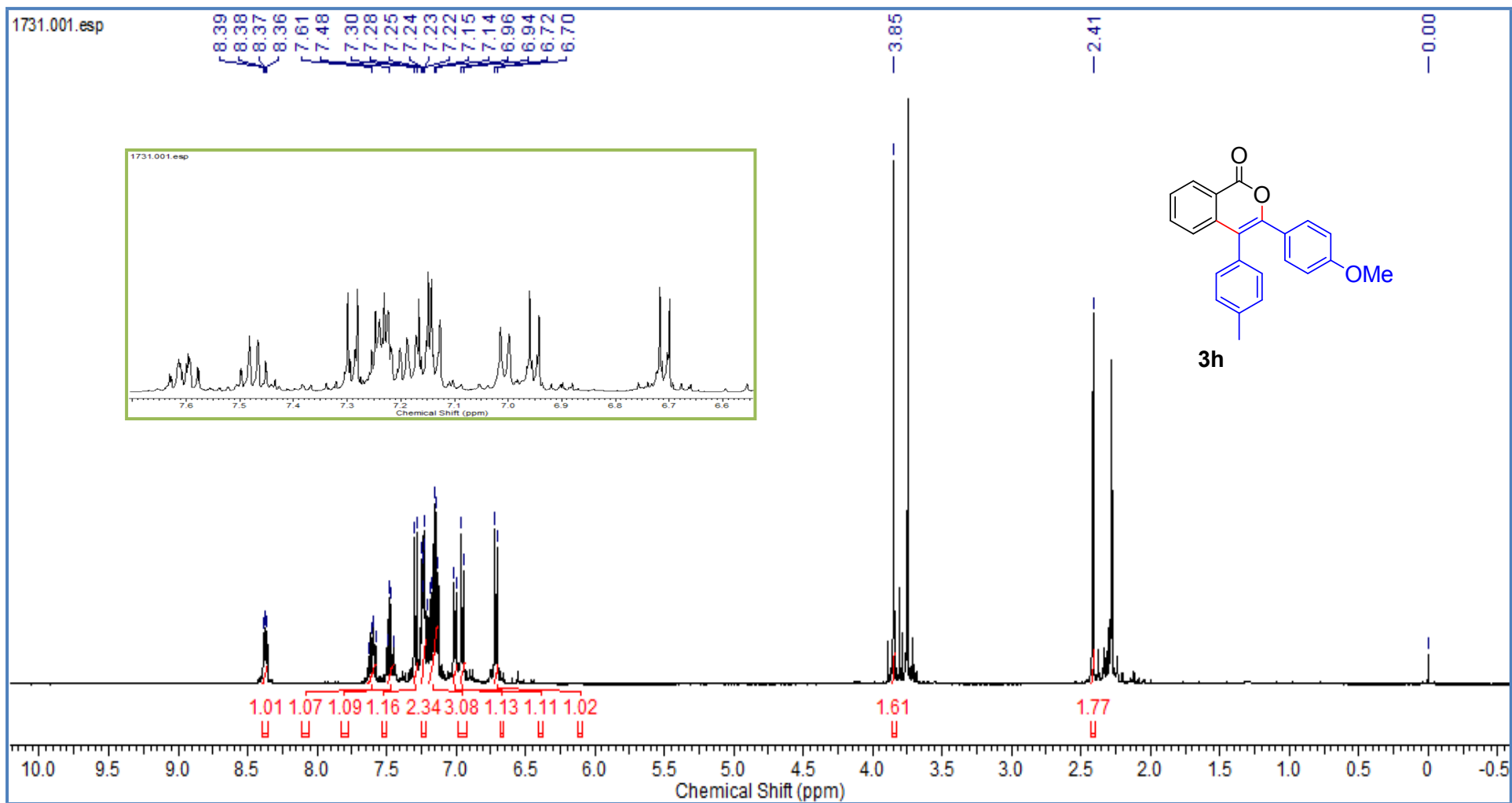


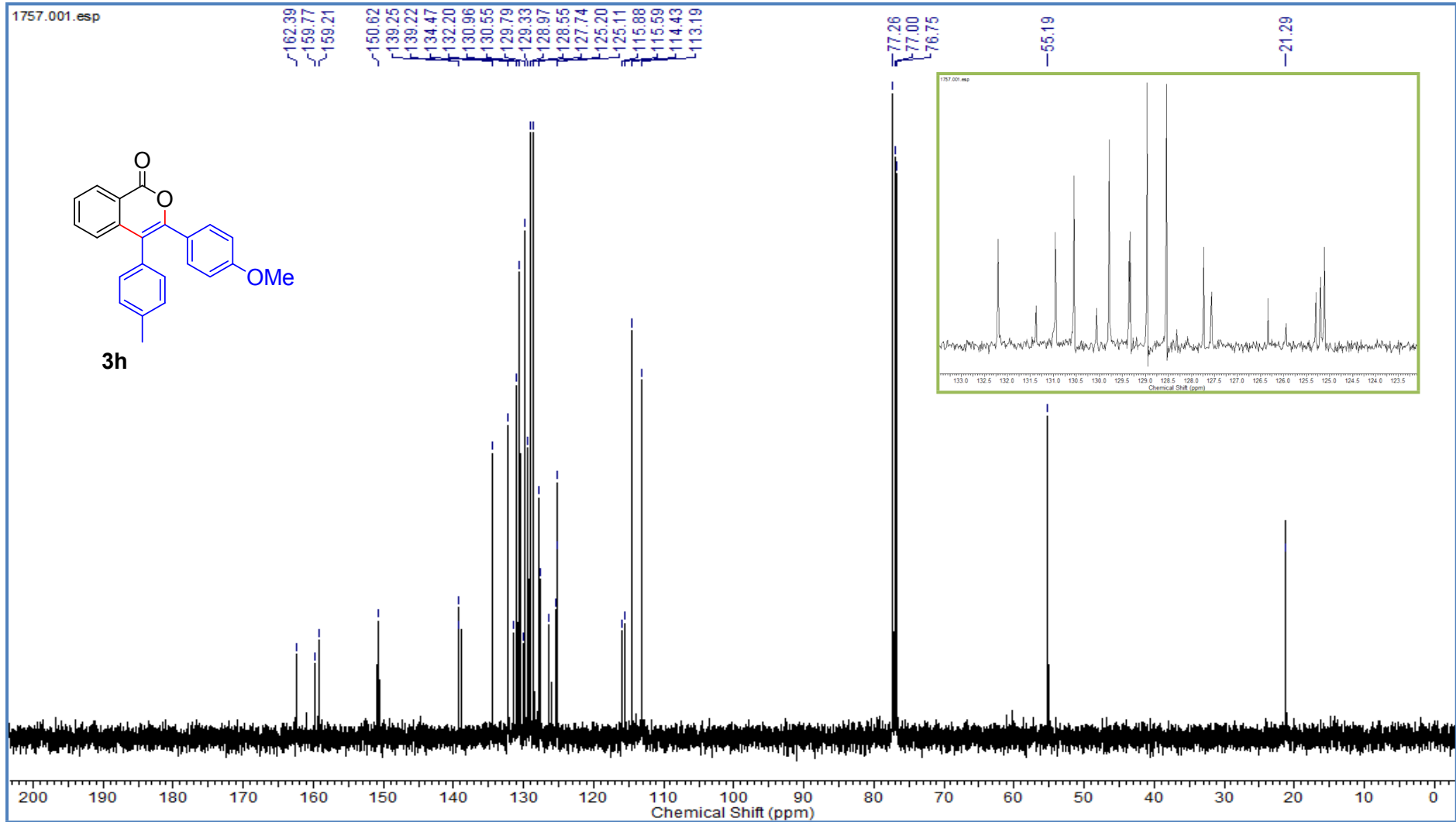


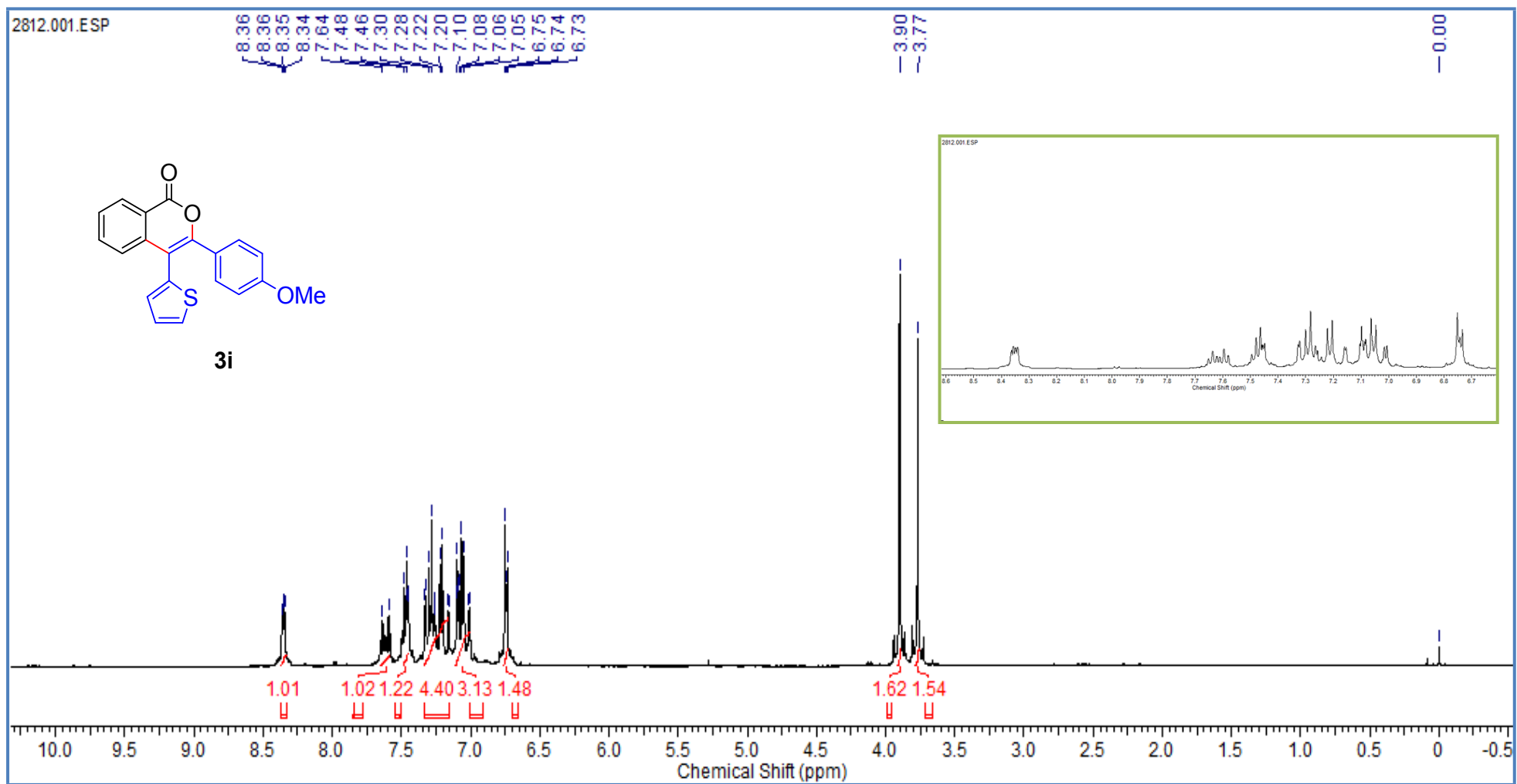


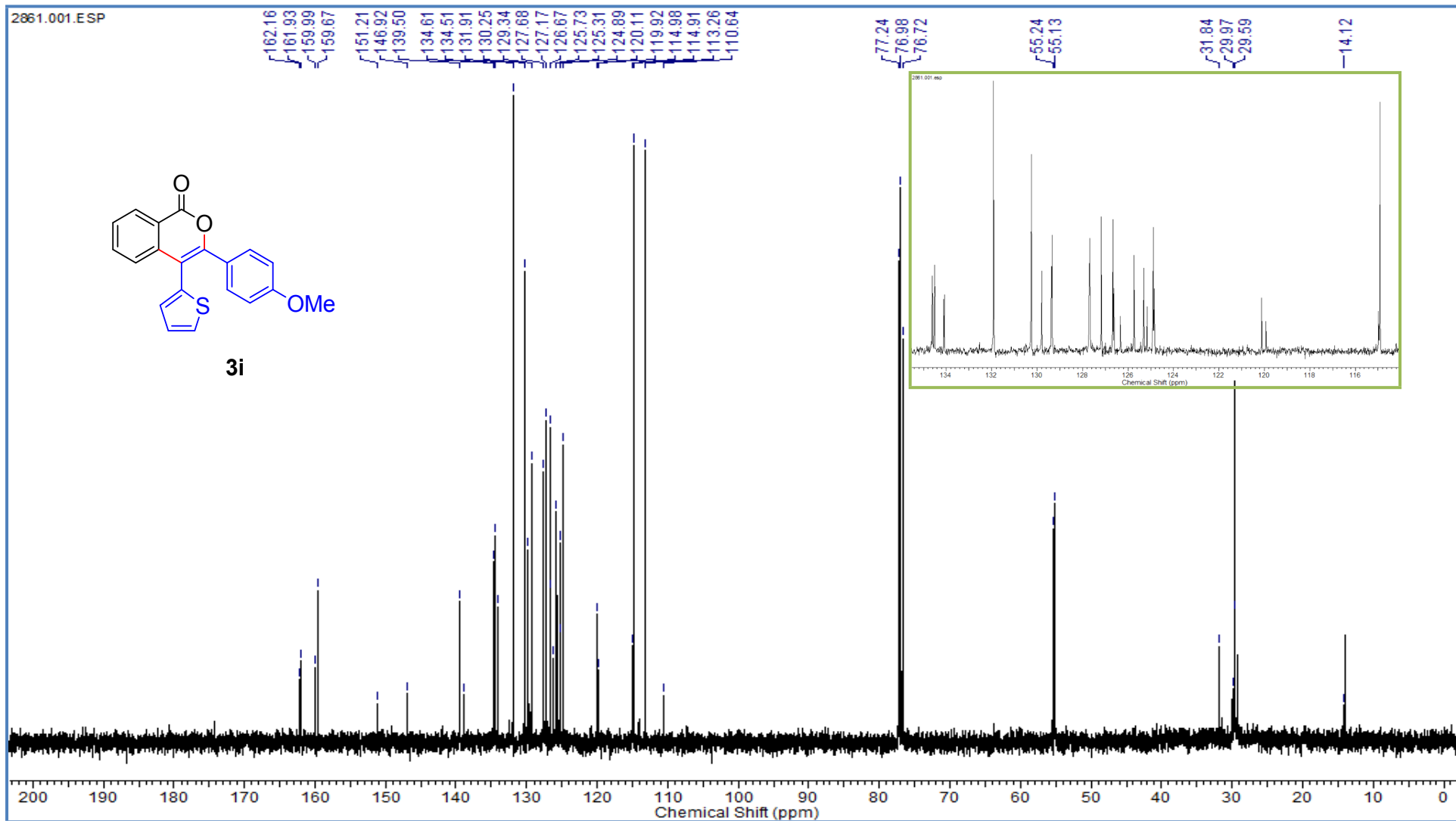


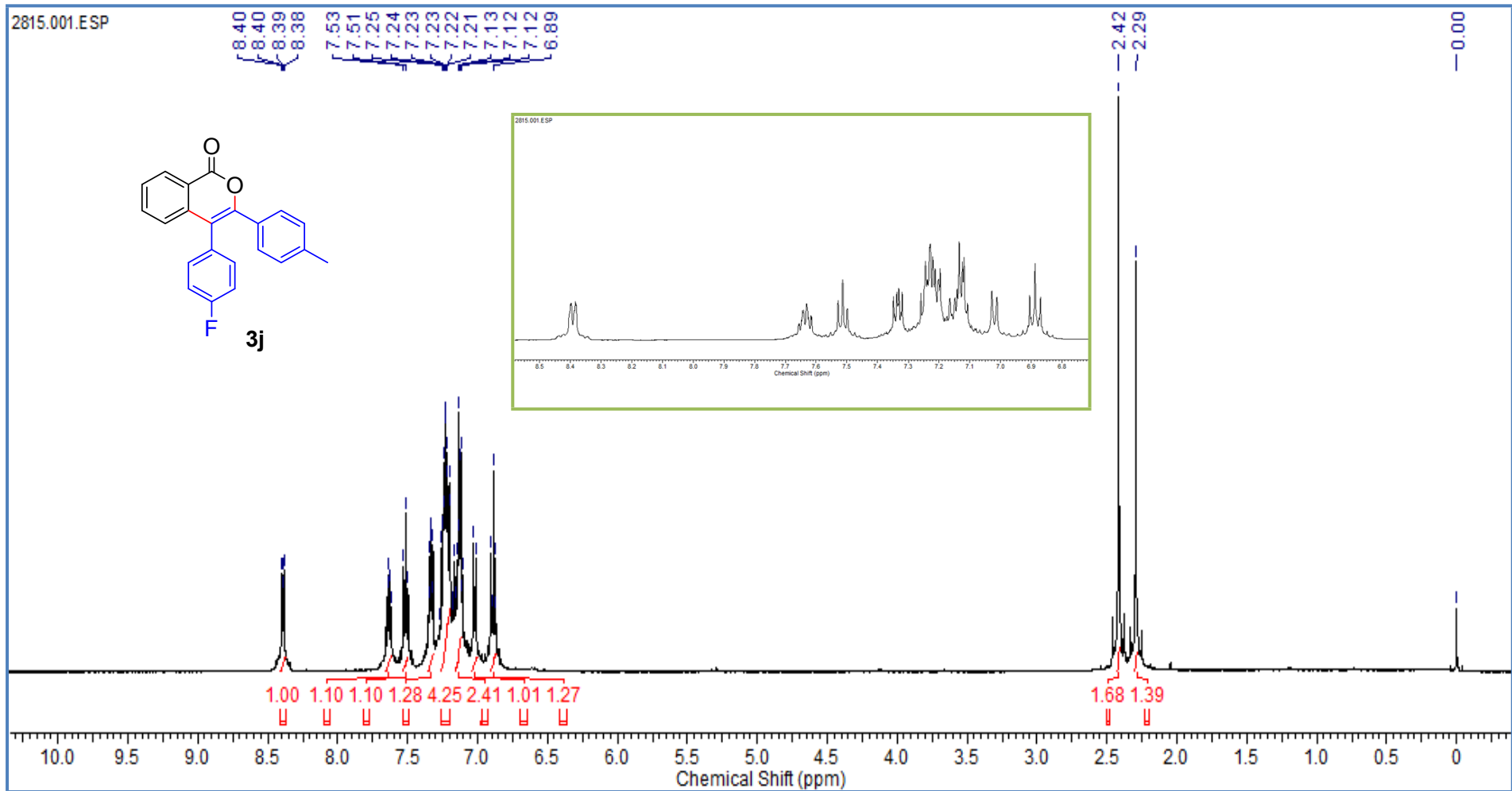


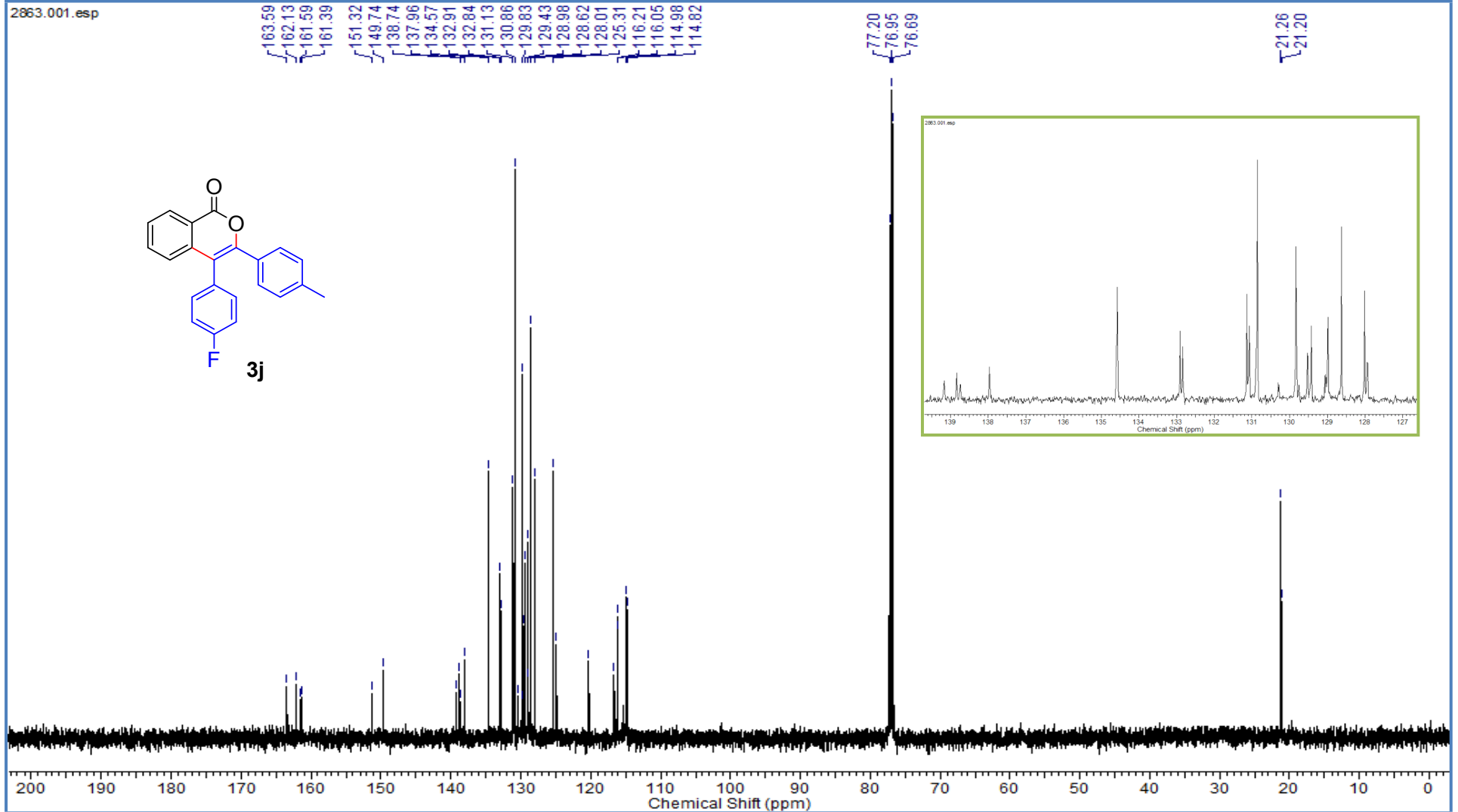


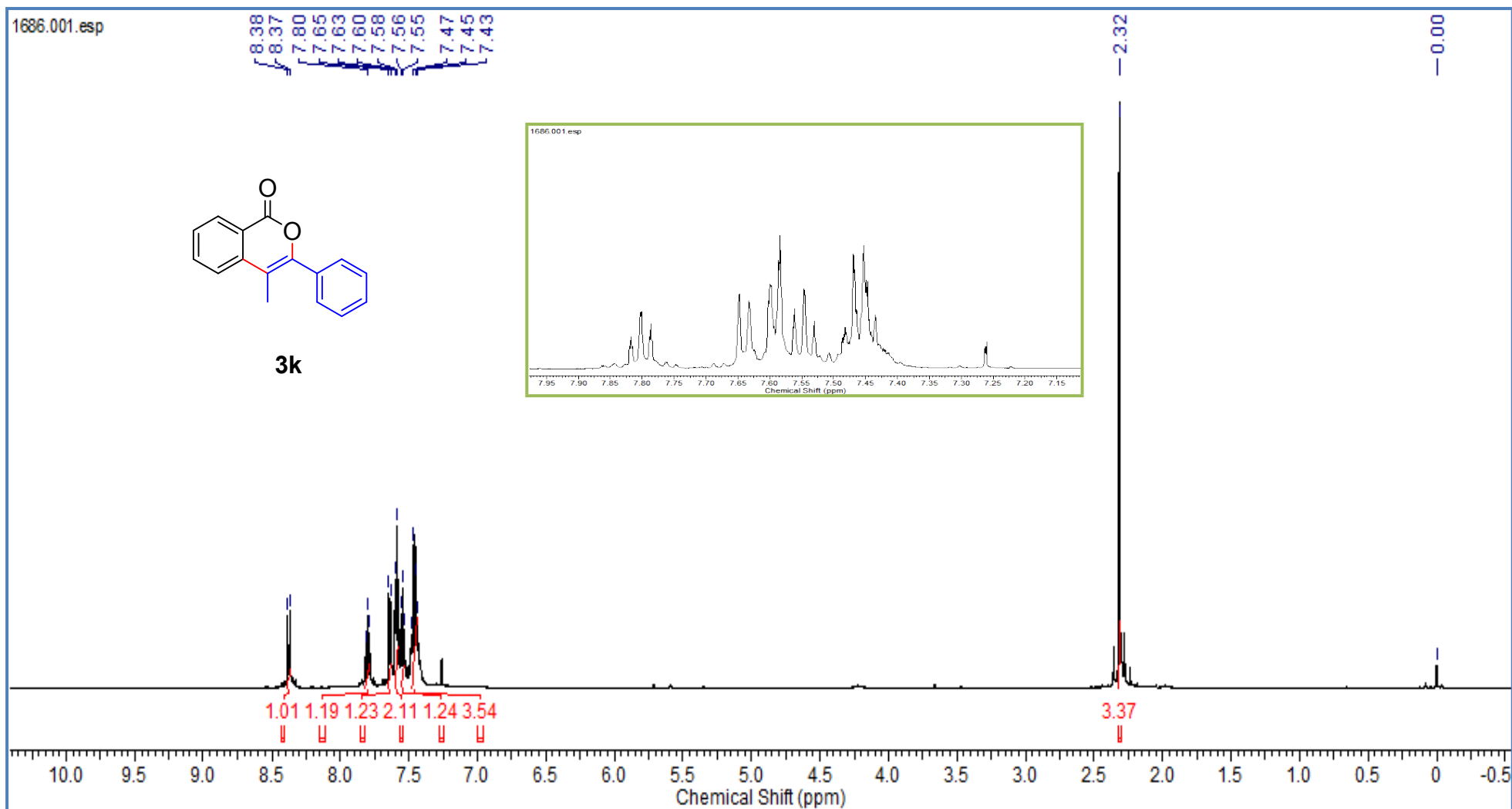


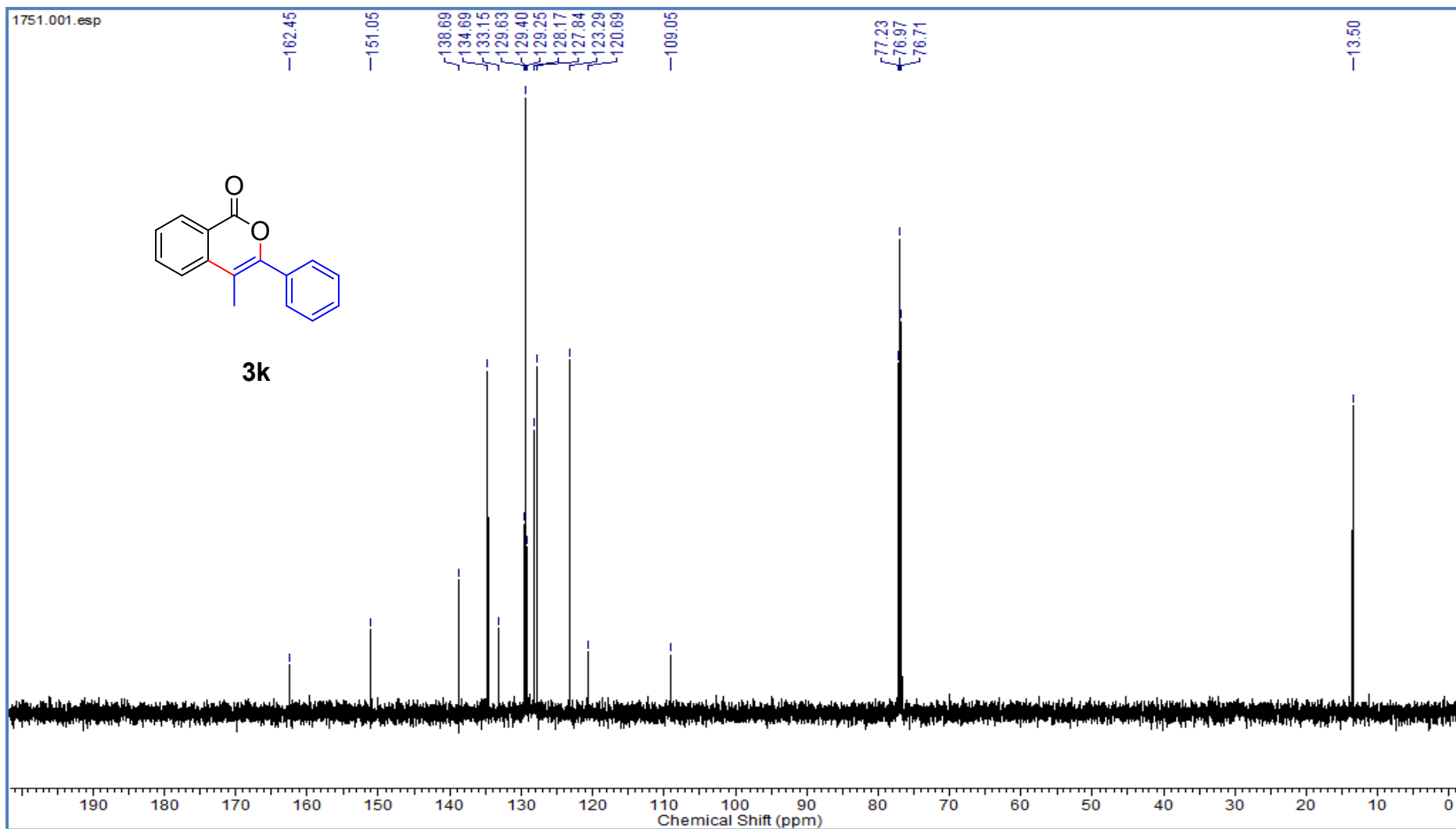


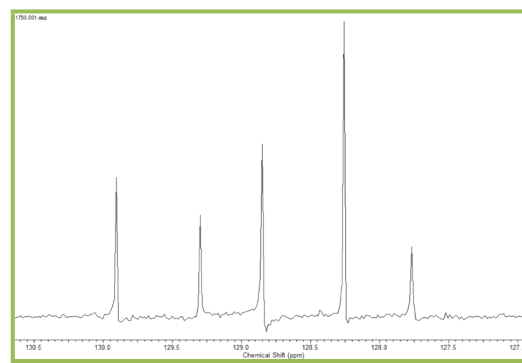
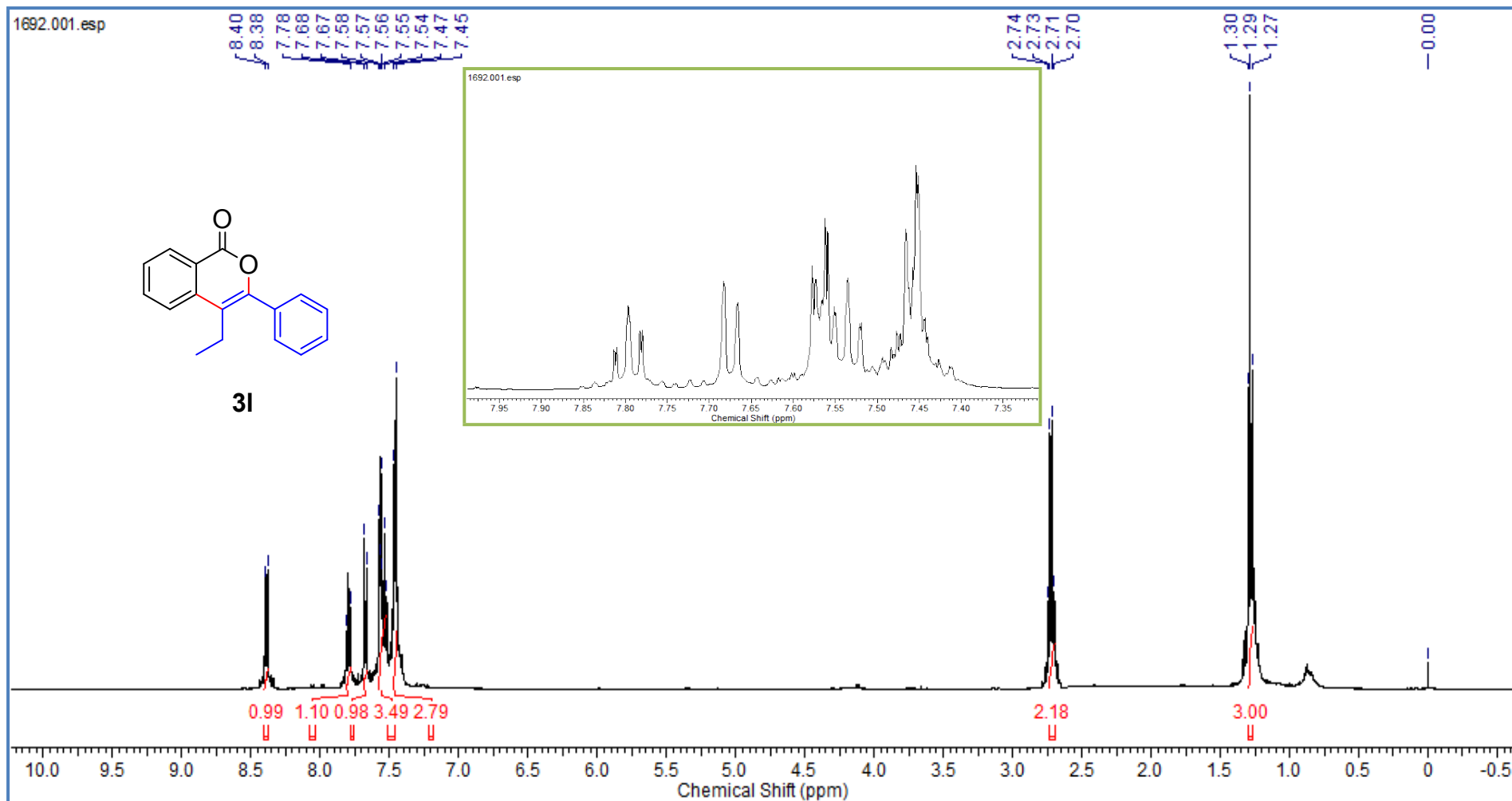


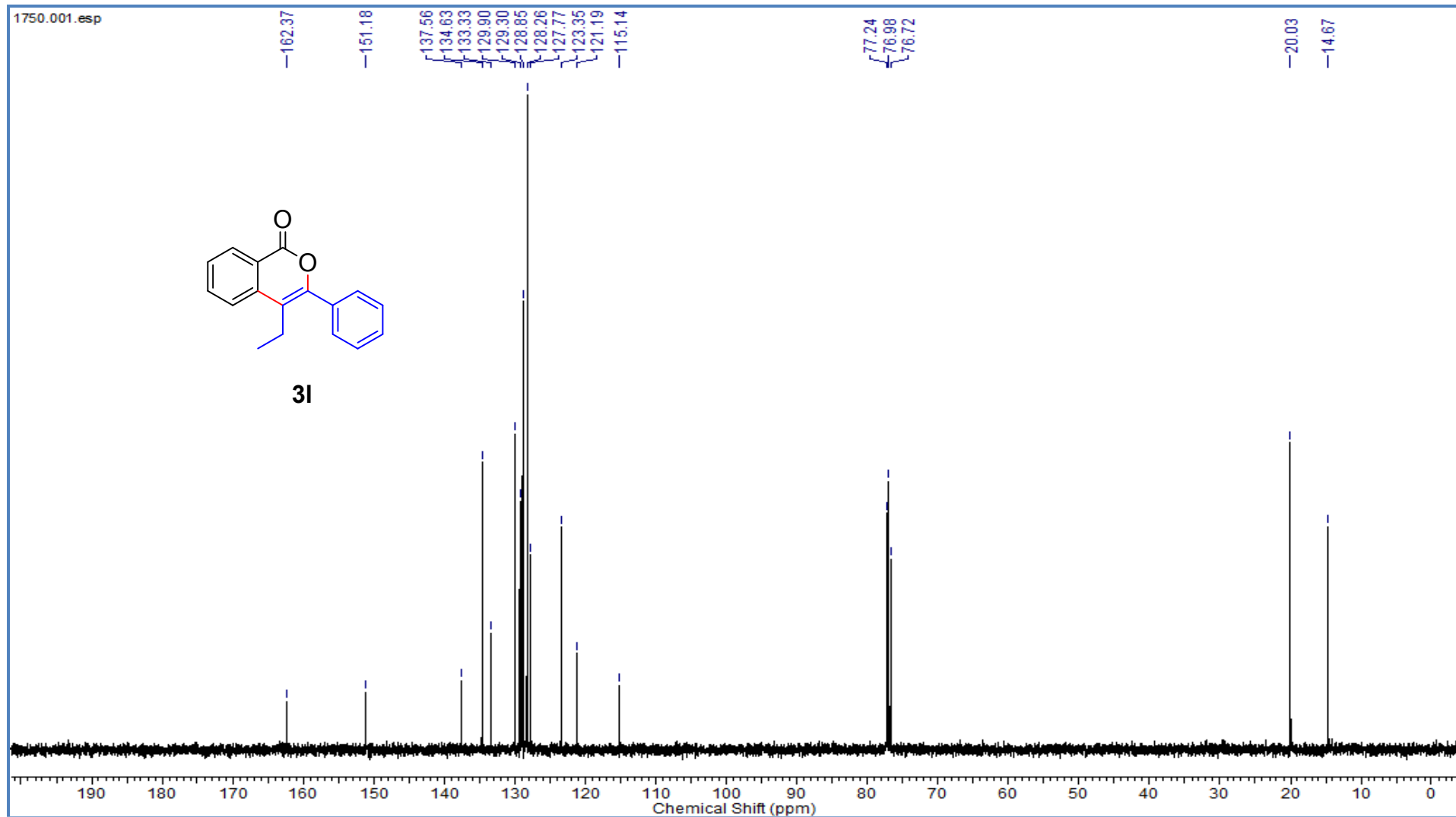


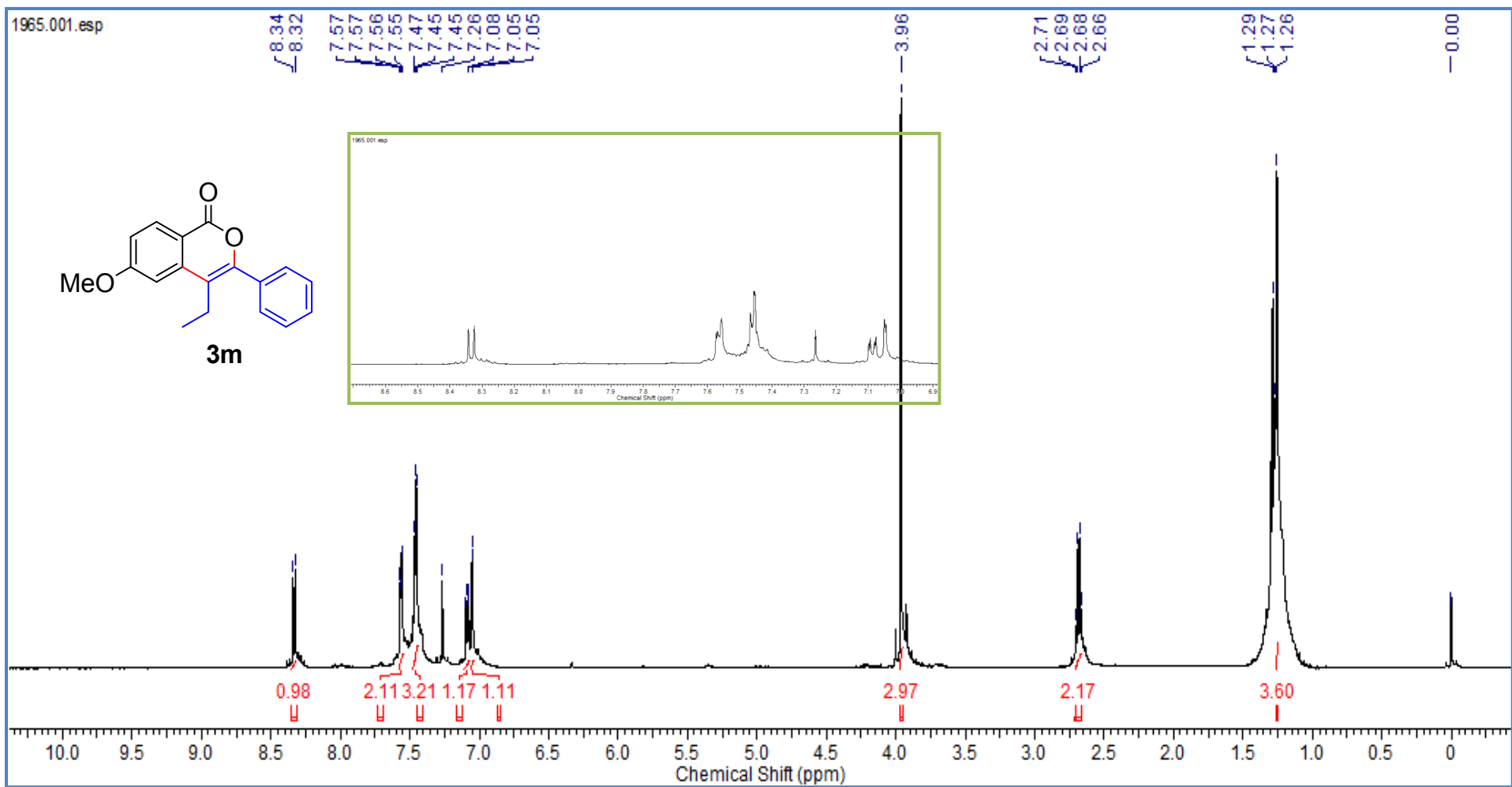


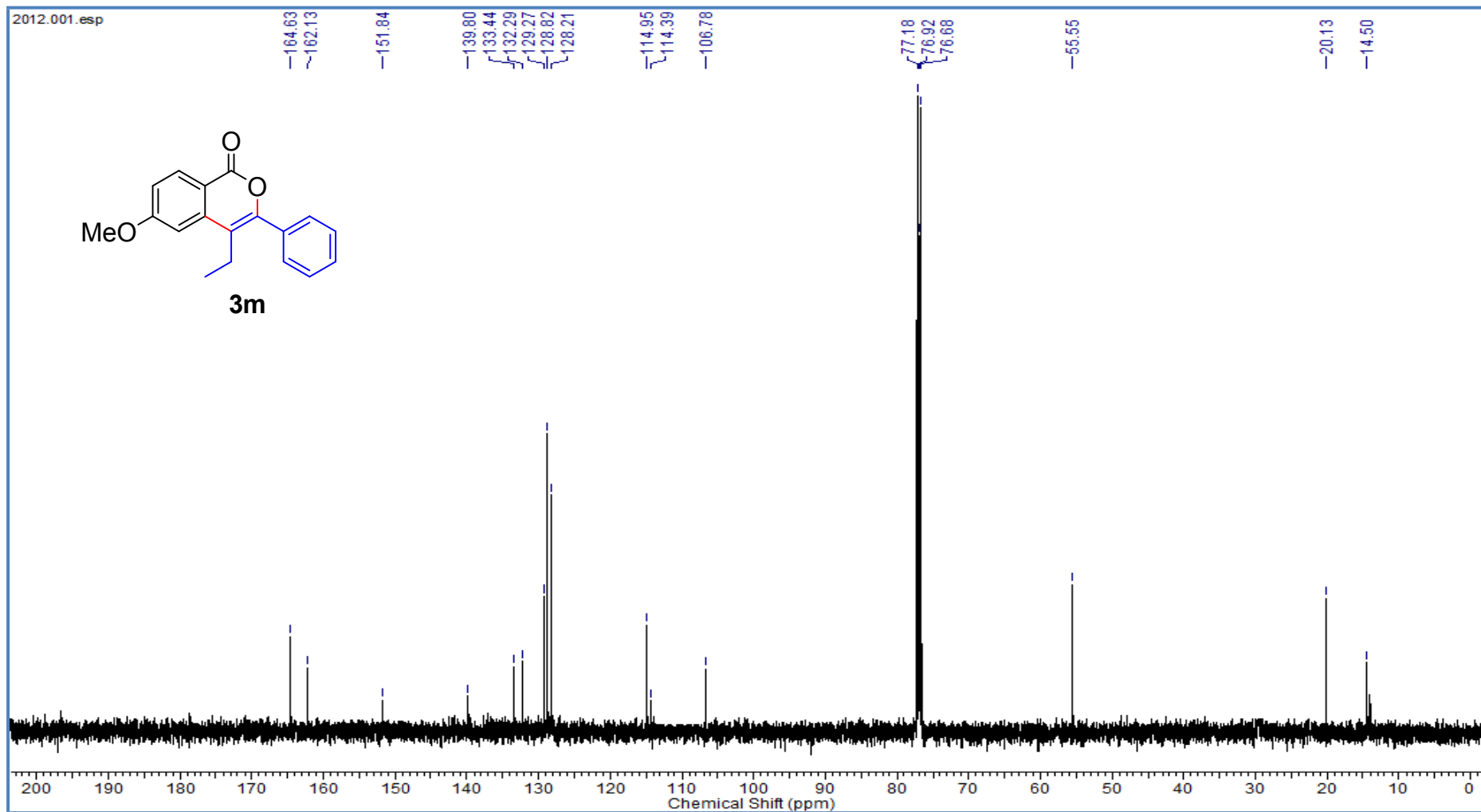


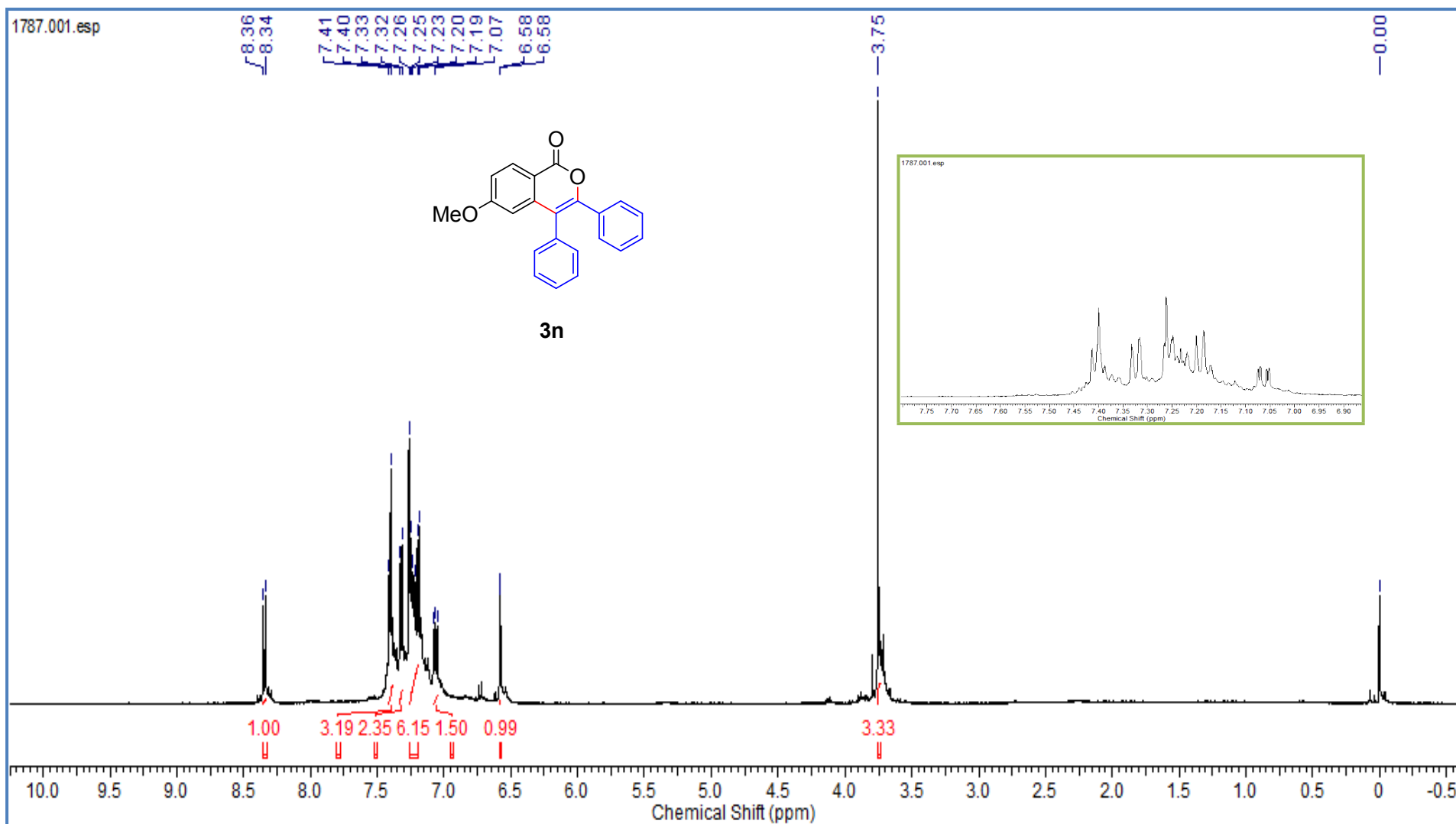


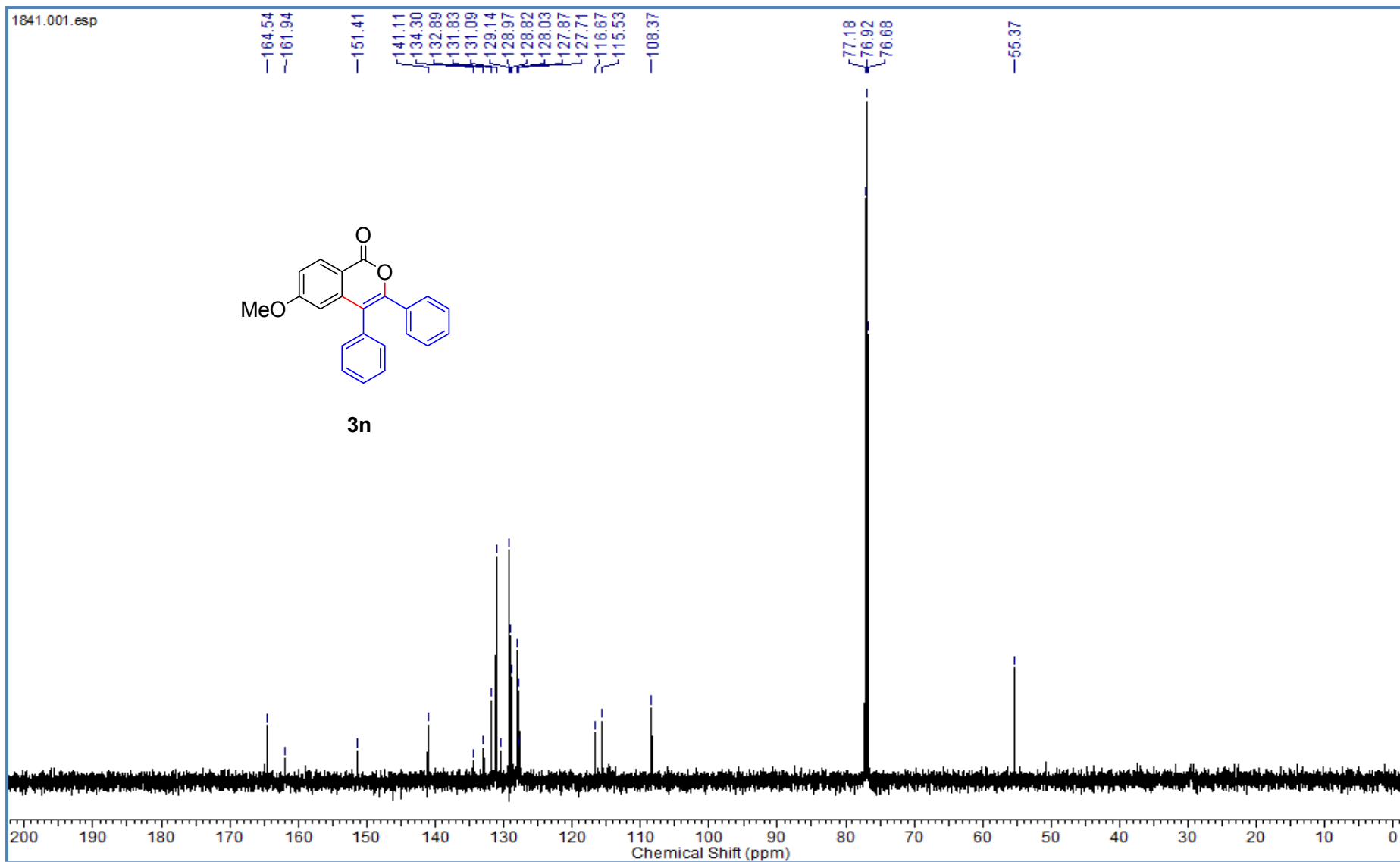


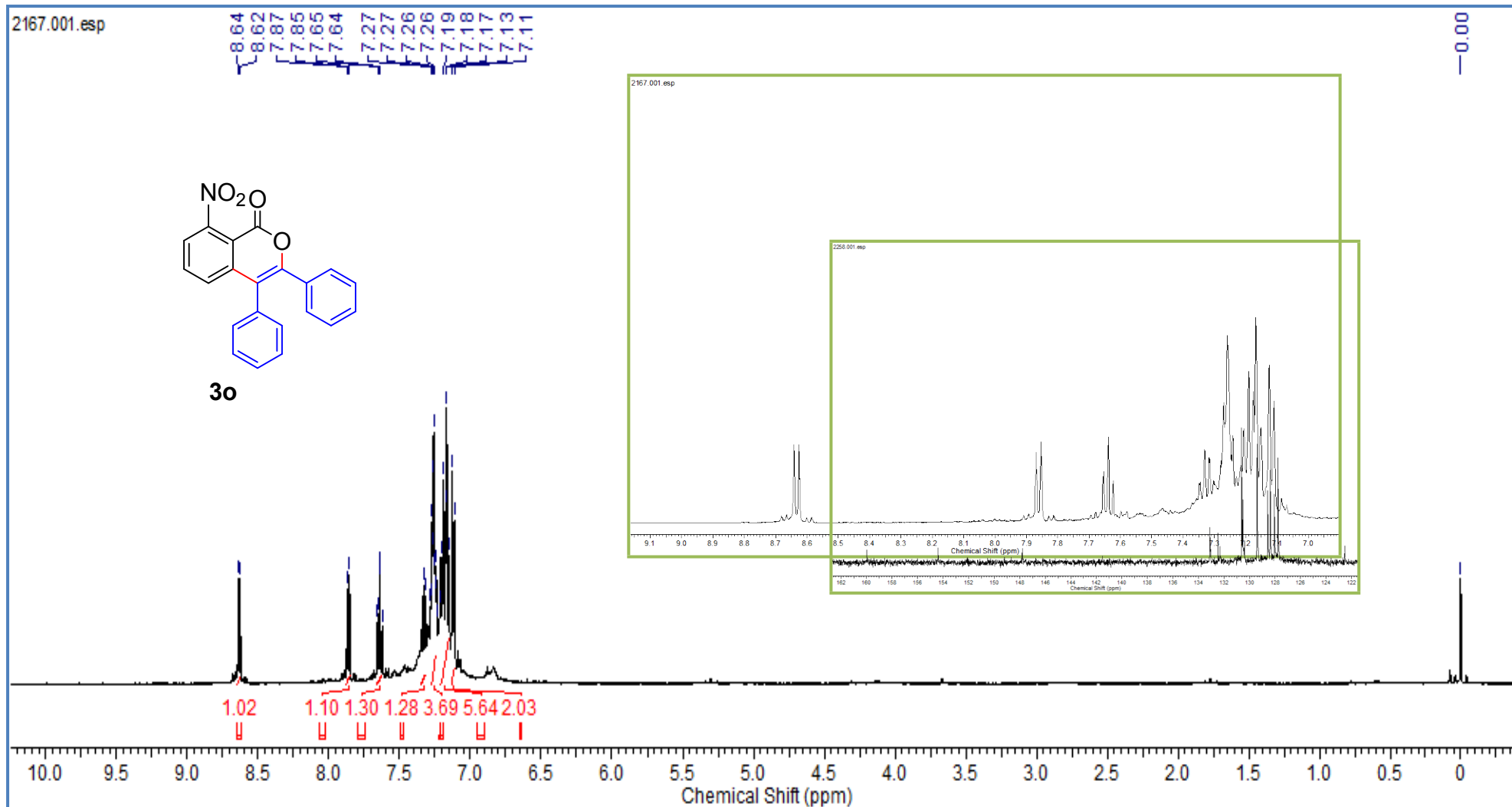


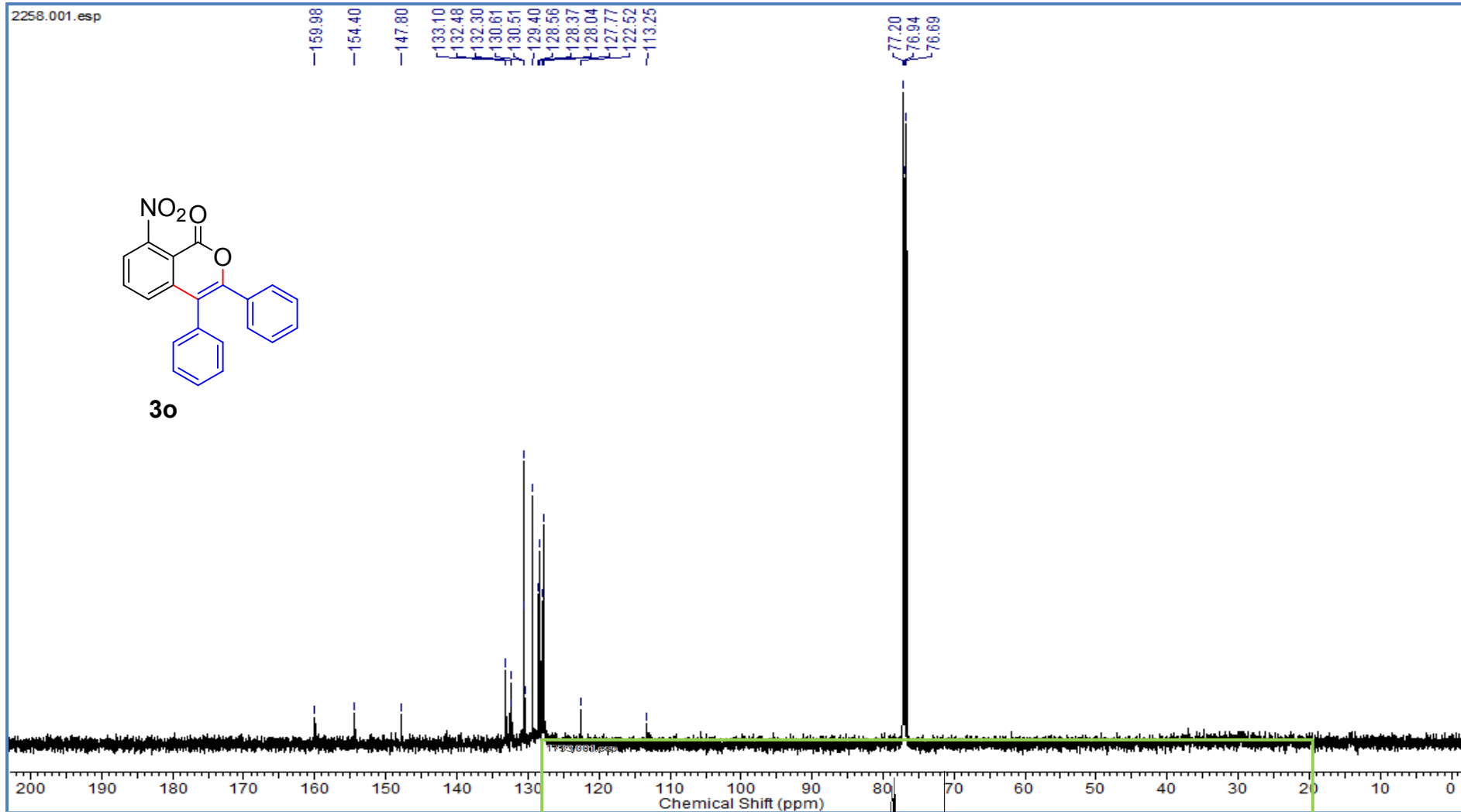




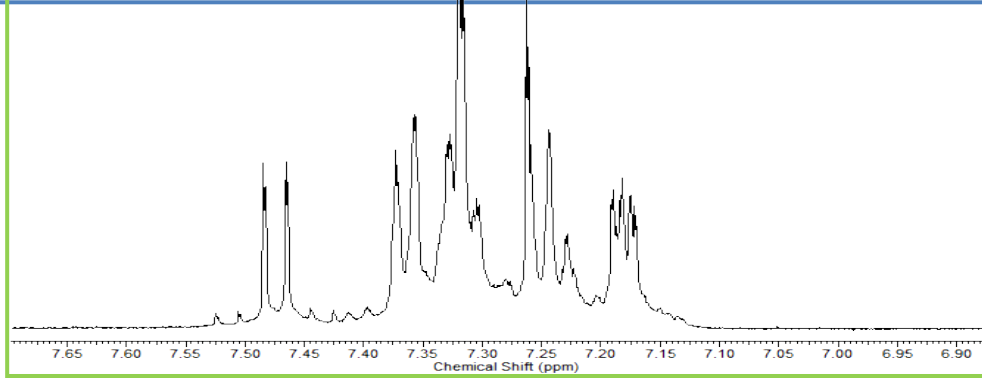


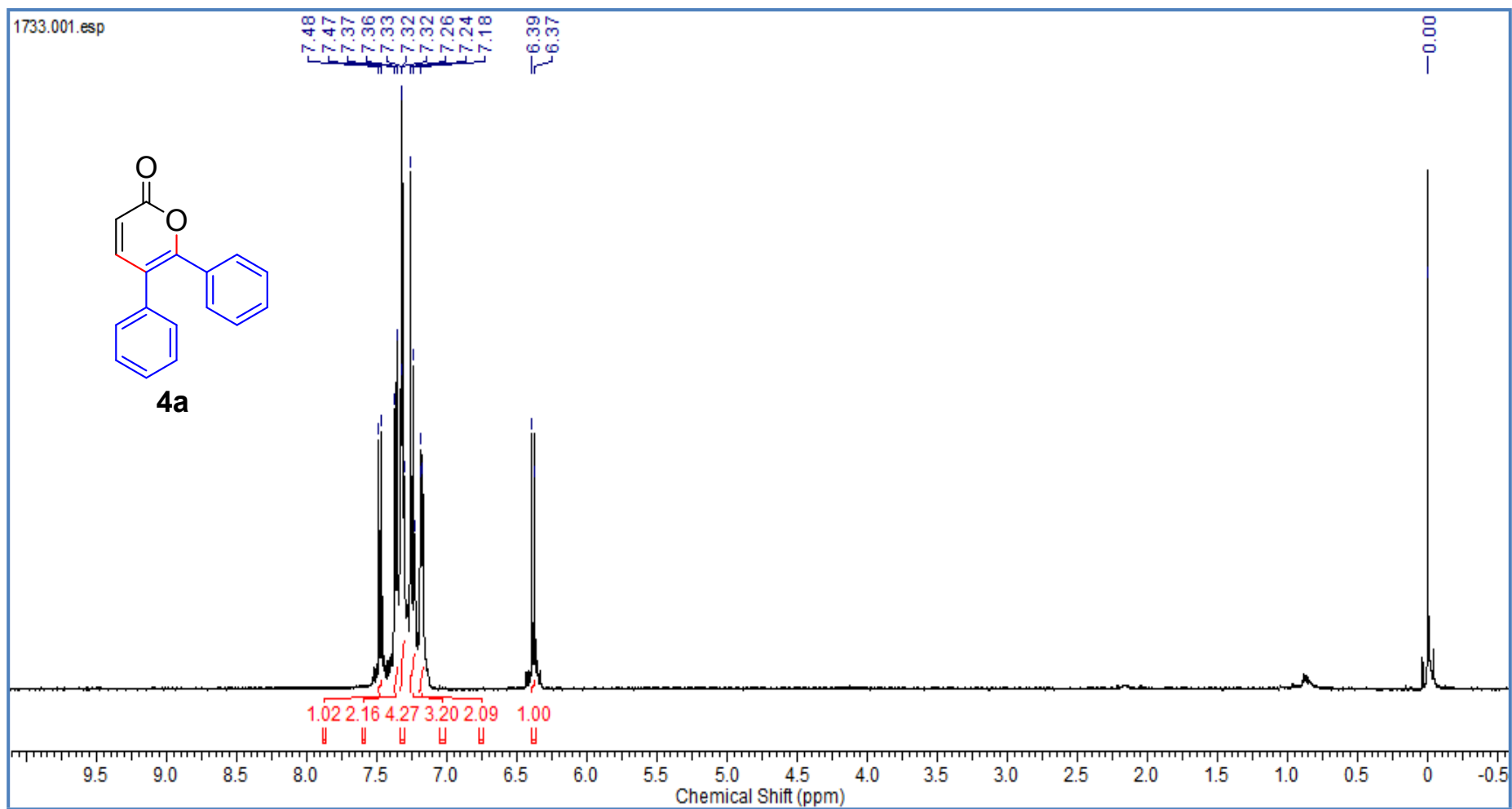


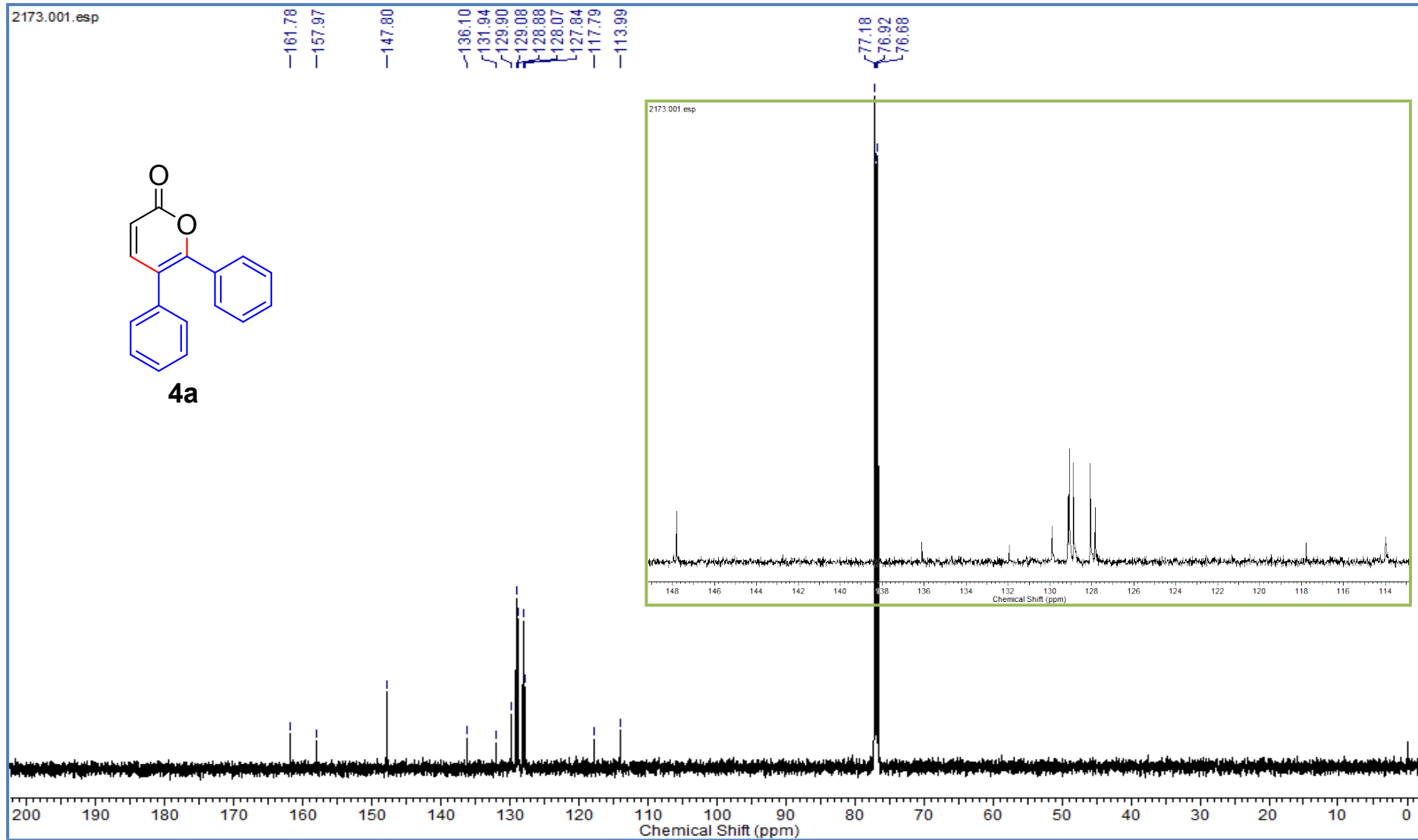


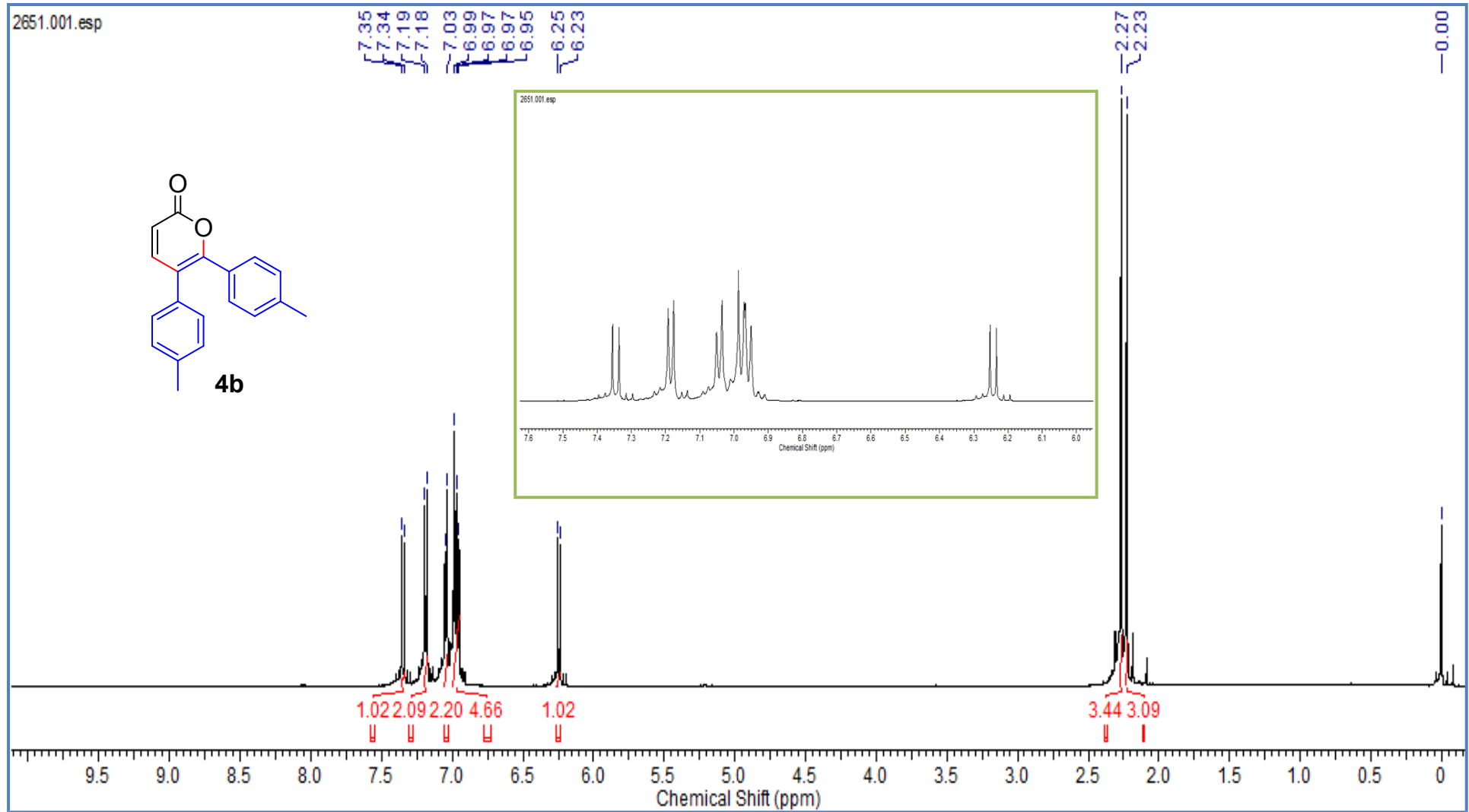


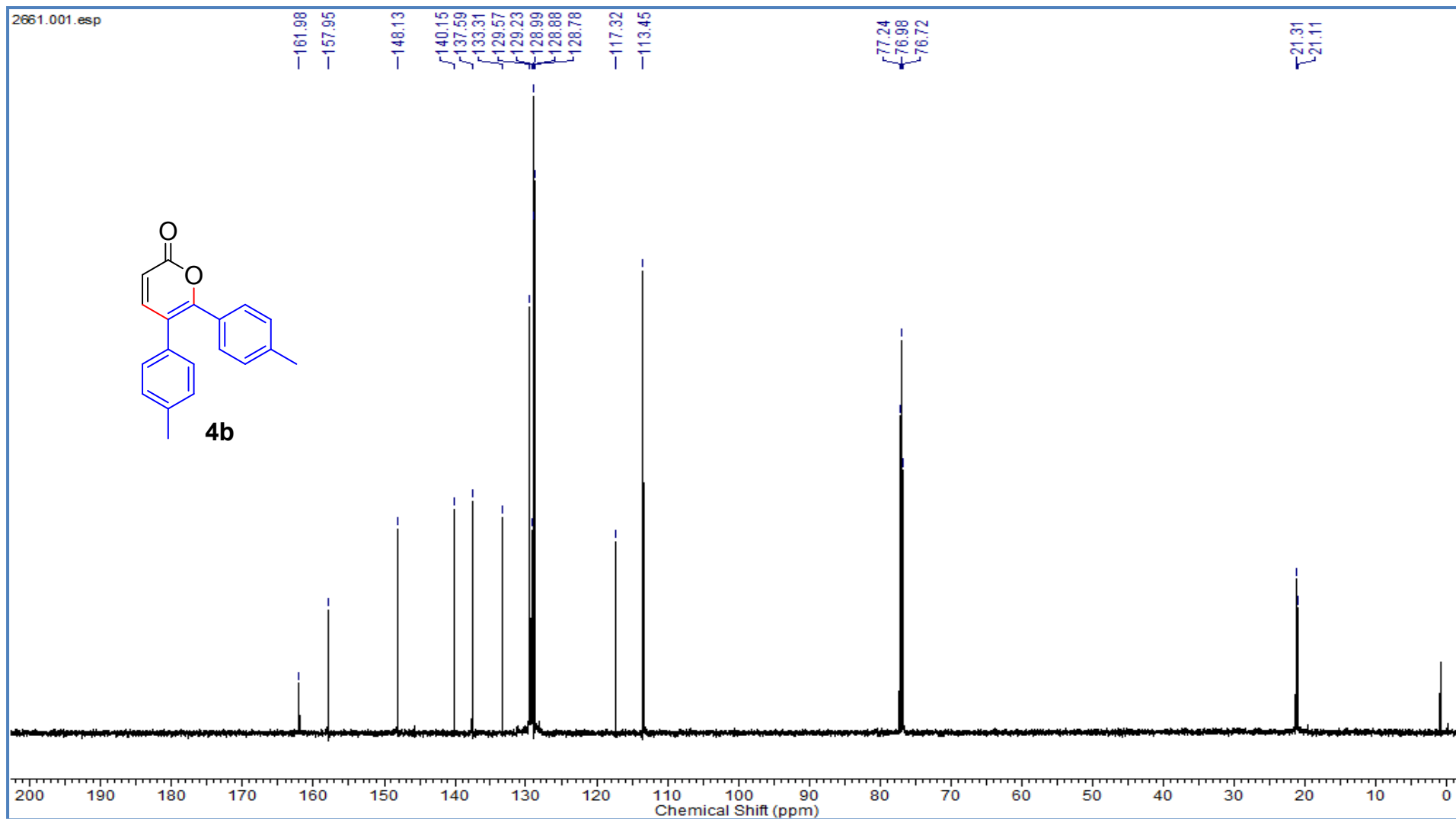
S41

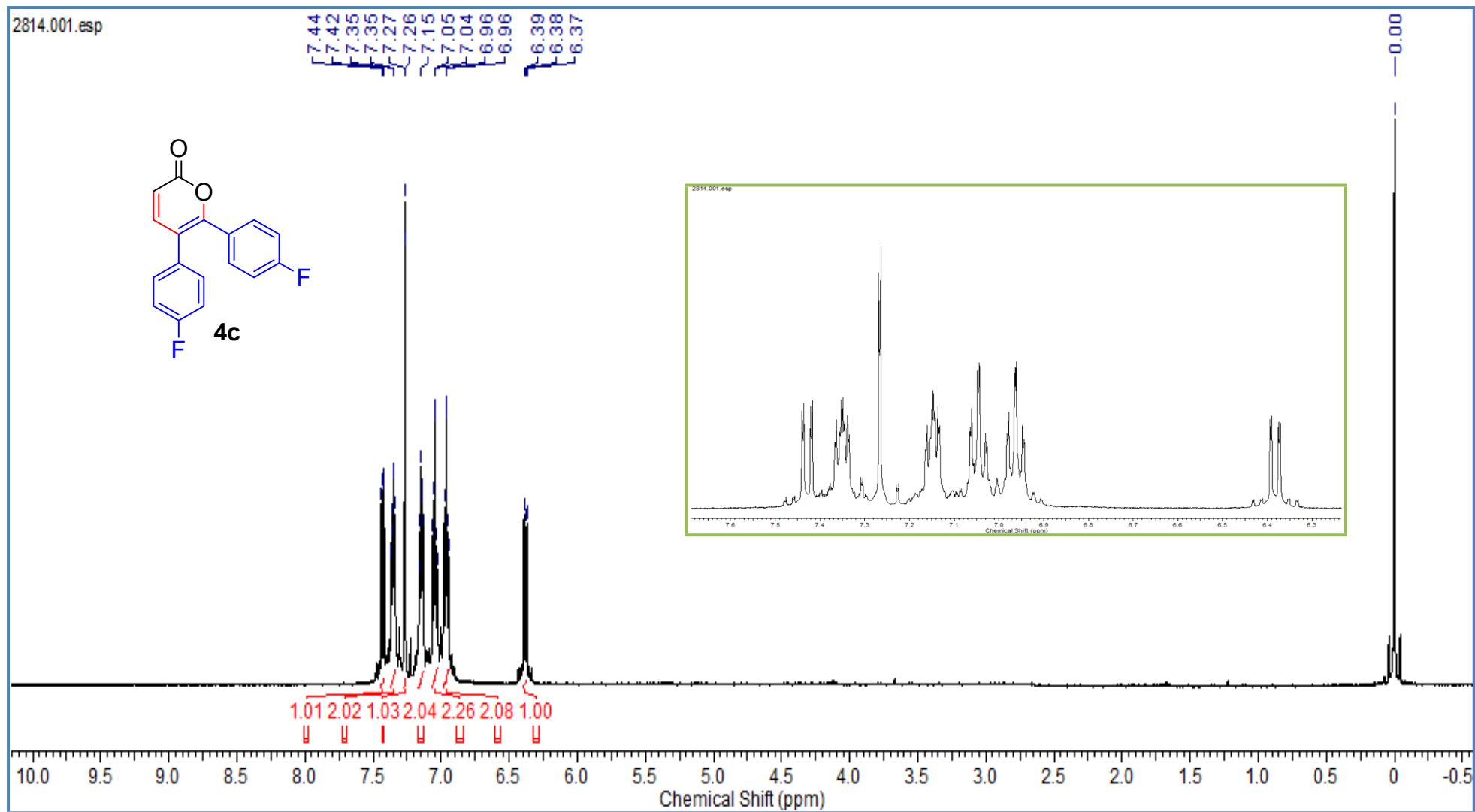


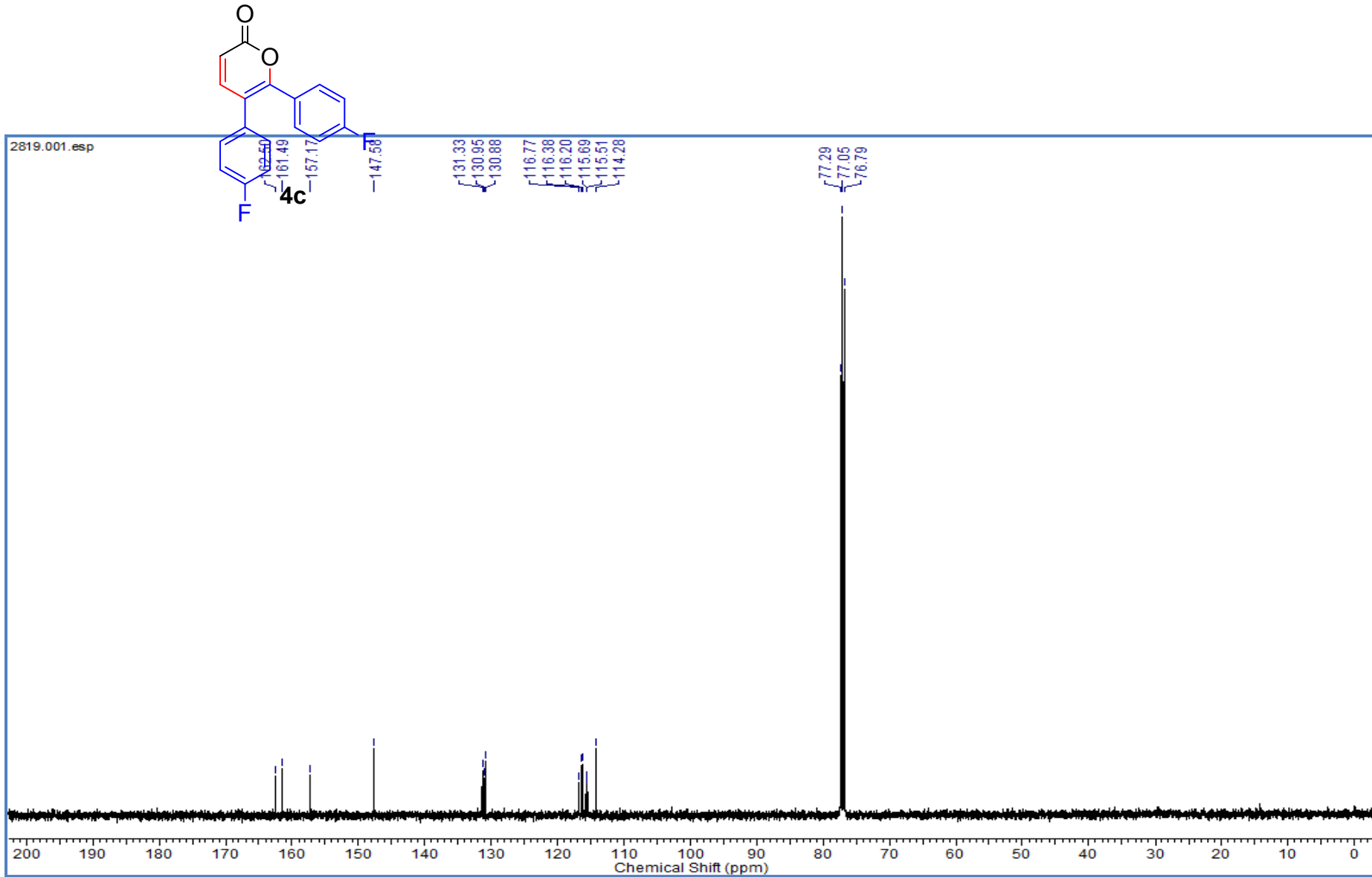


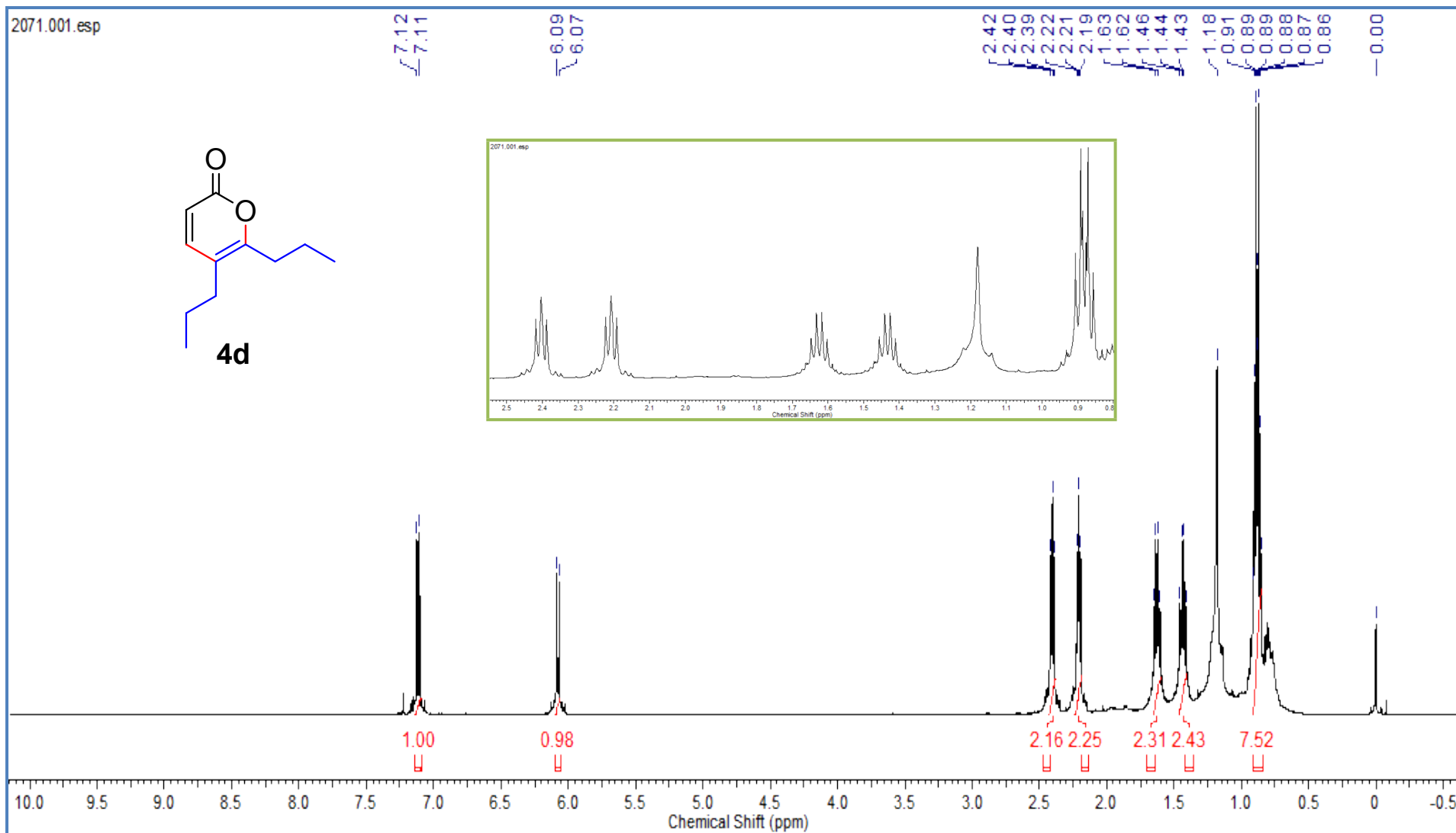


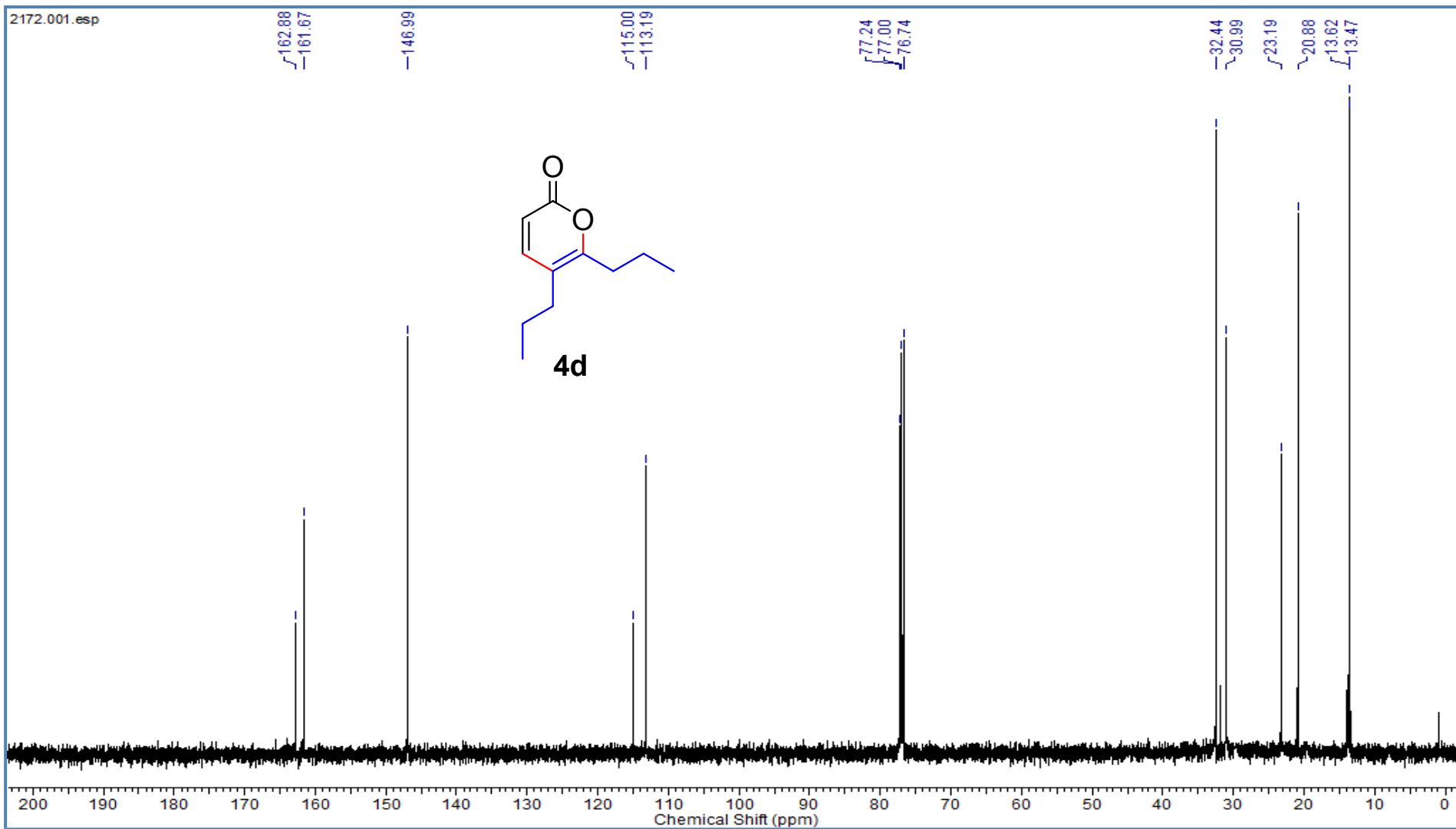




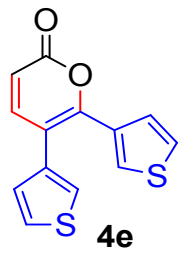






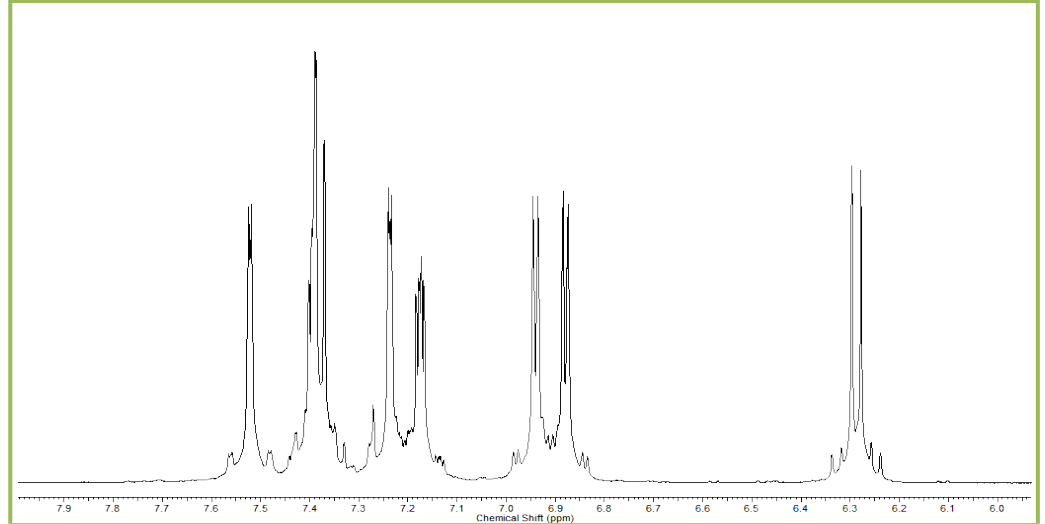


2813.001.esp



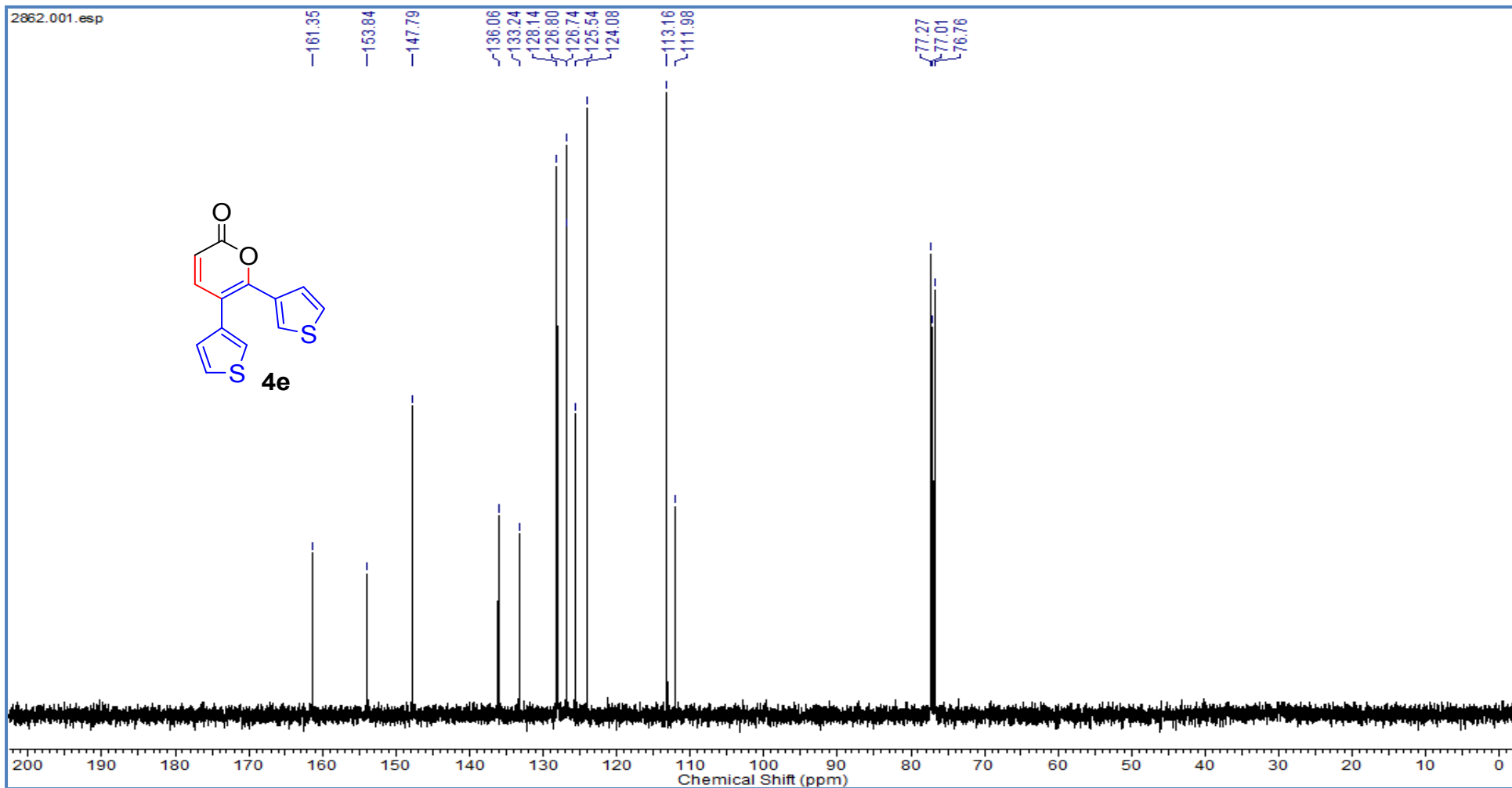
7.52
7.52
7.40
7.39
7.39
7.37
7.24
7.23
6.94
6.94
6.88
6.87
6.30
6.28

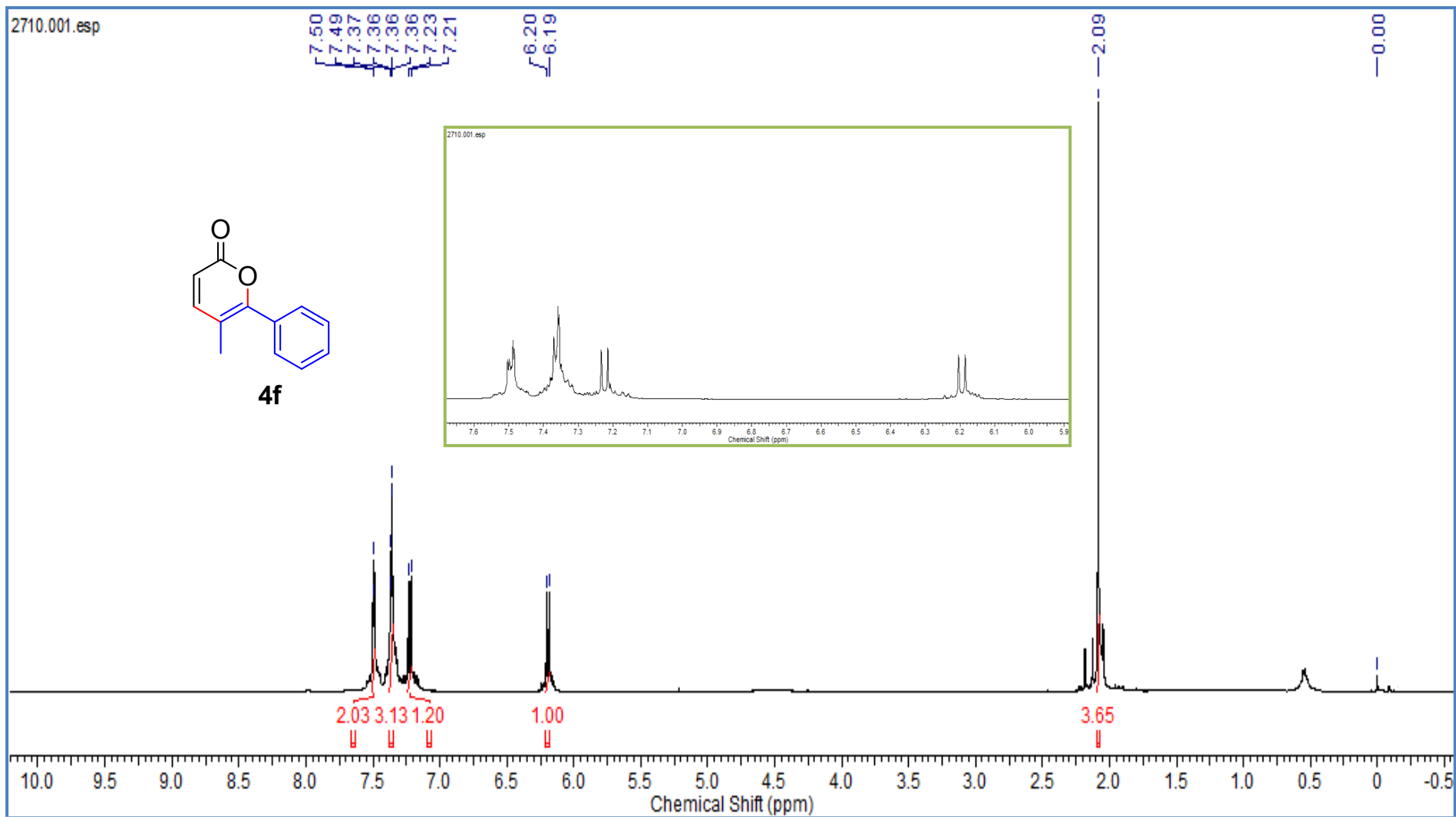
-0.00

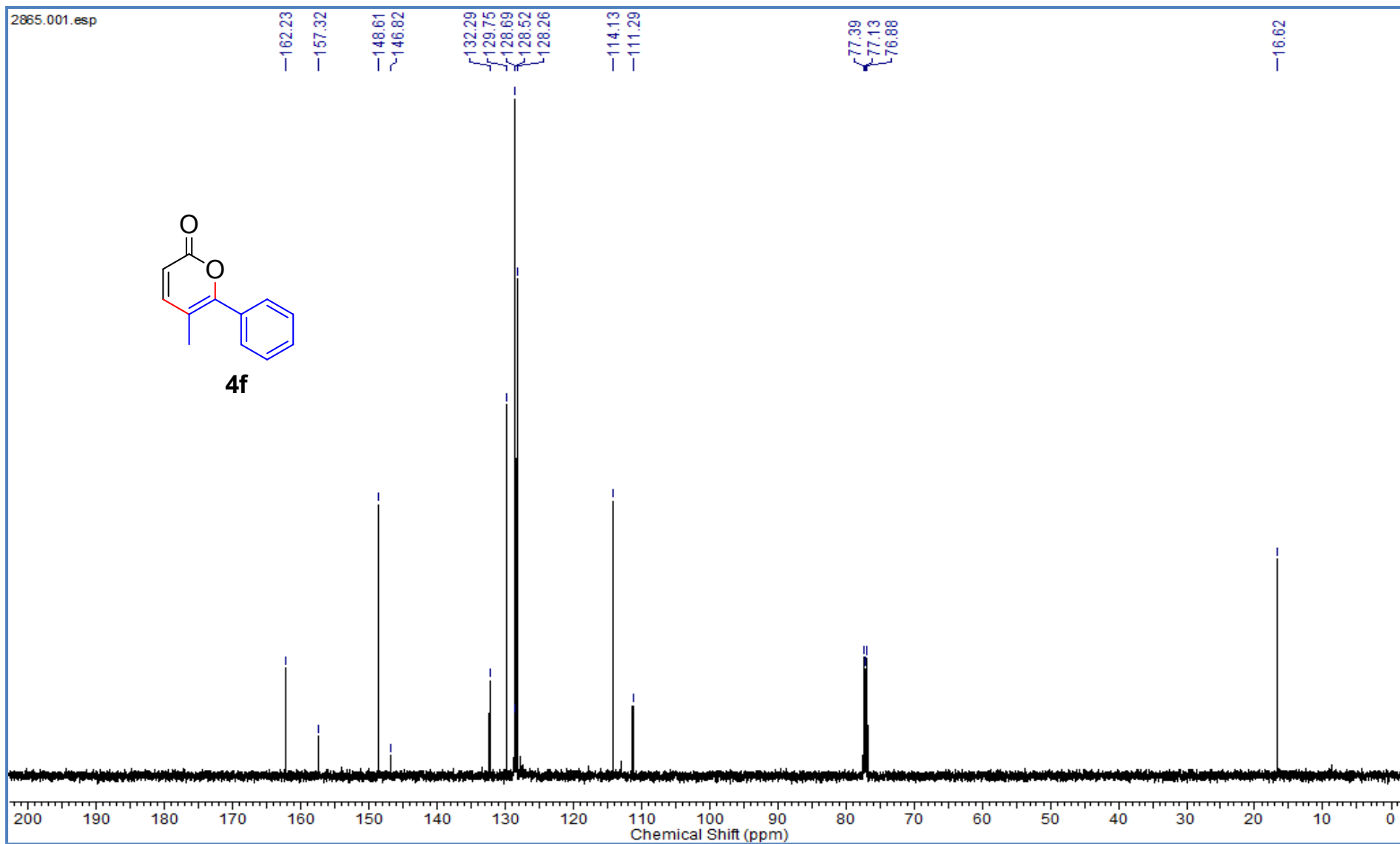


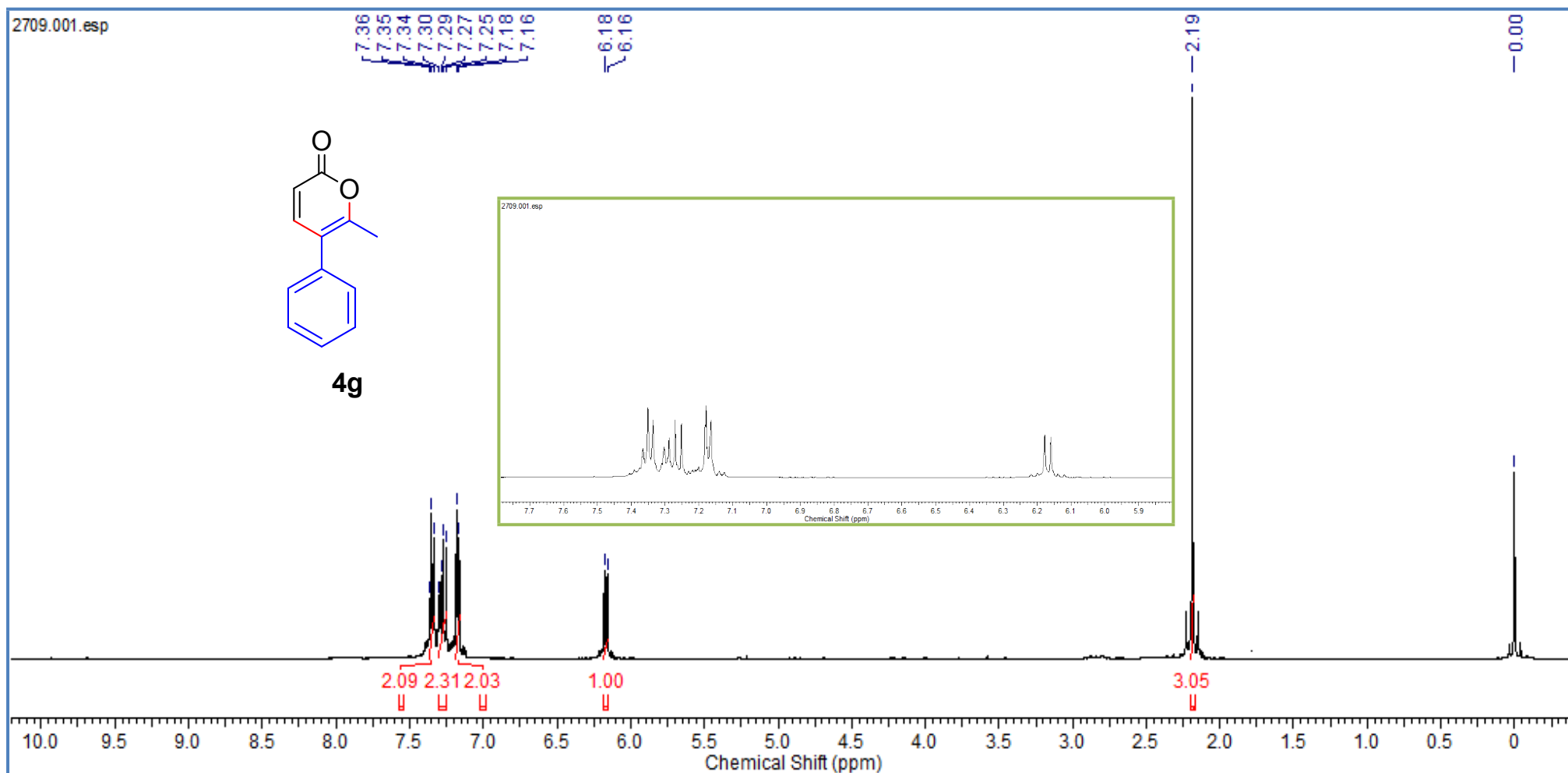
1.00 2.53 1.00 1.18 1.16 1.02 1.13

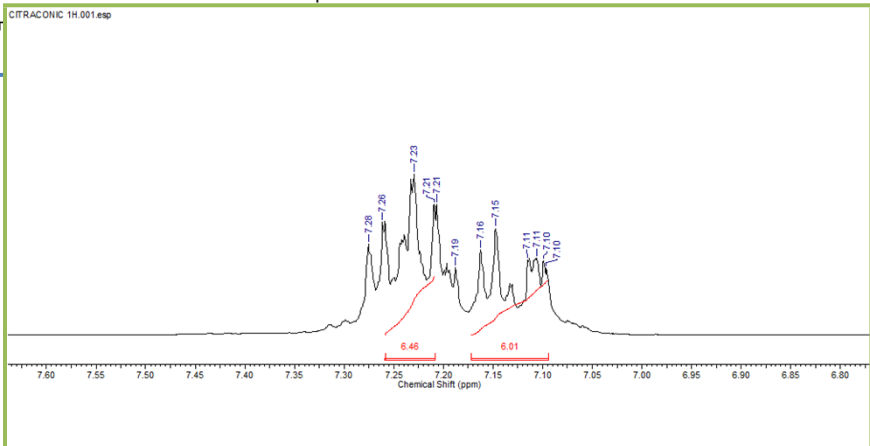
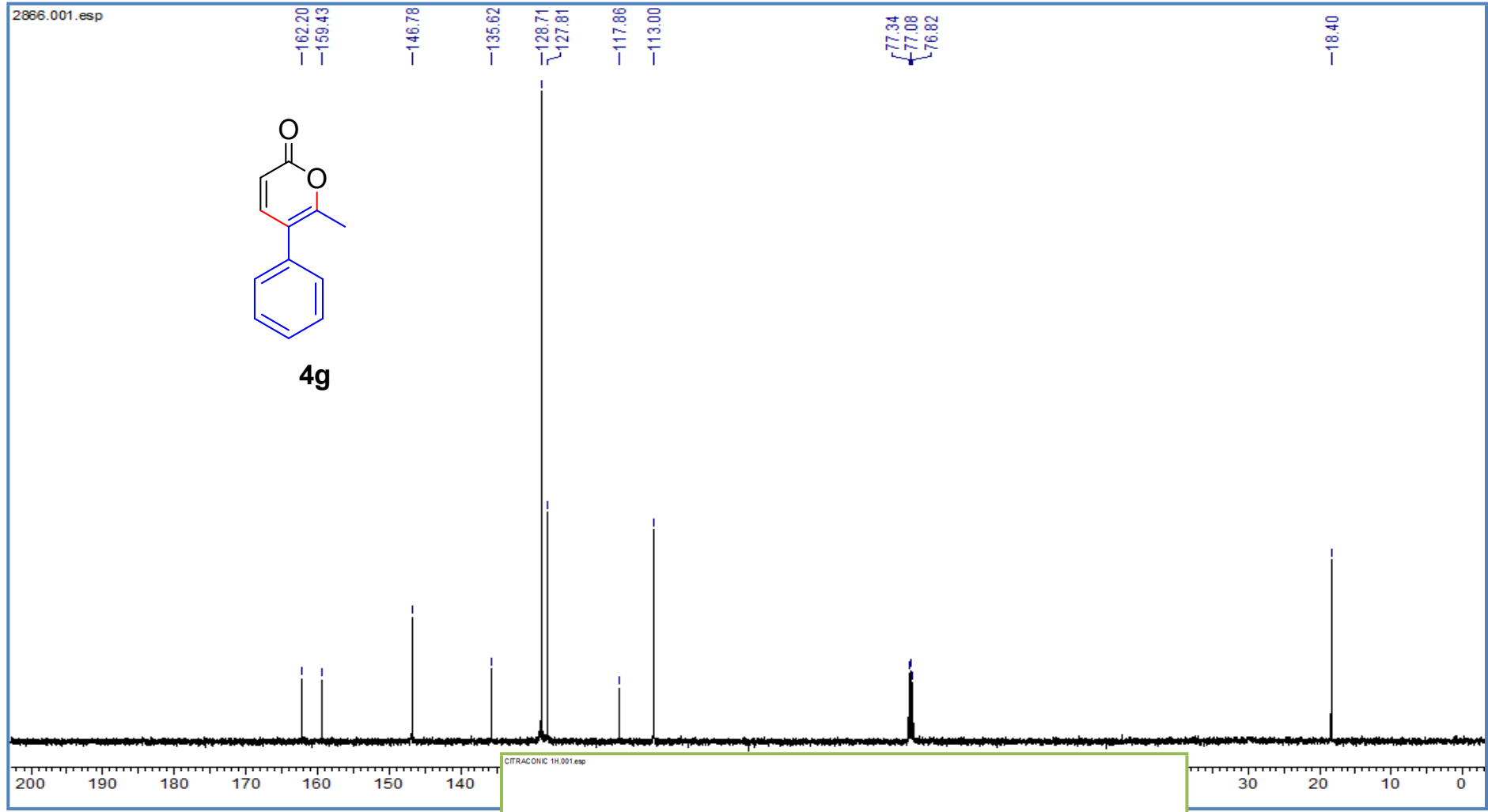
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)

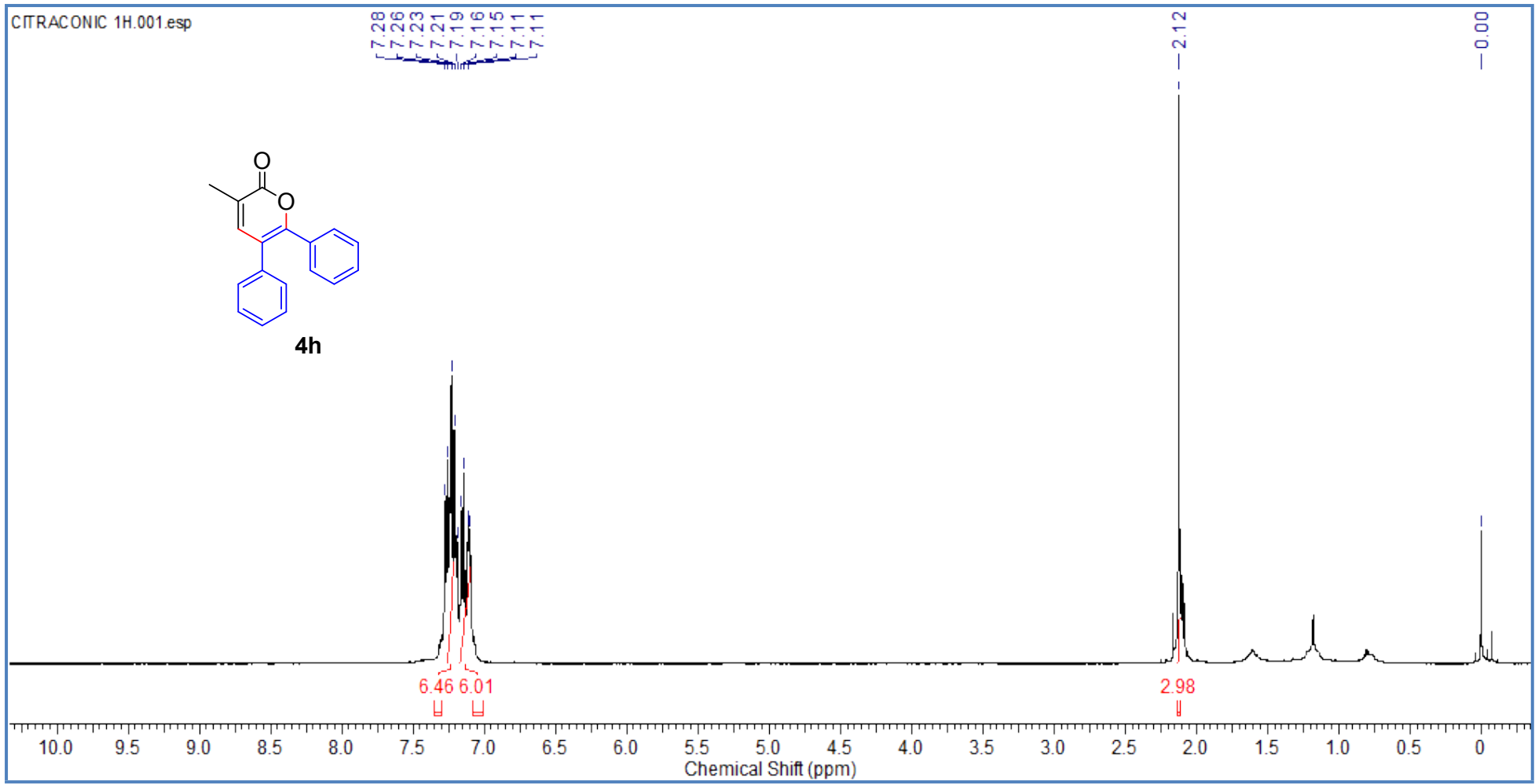


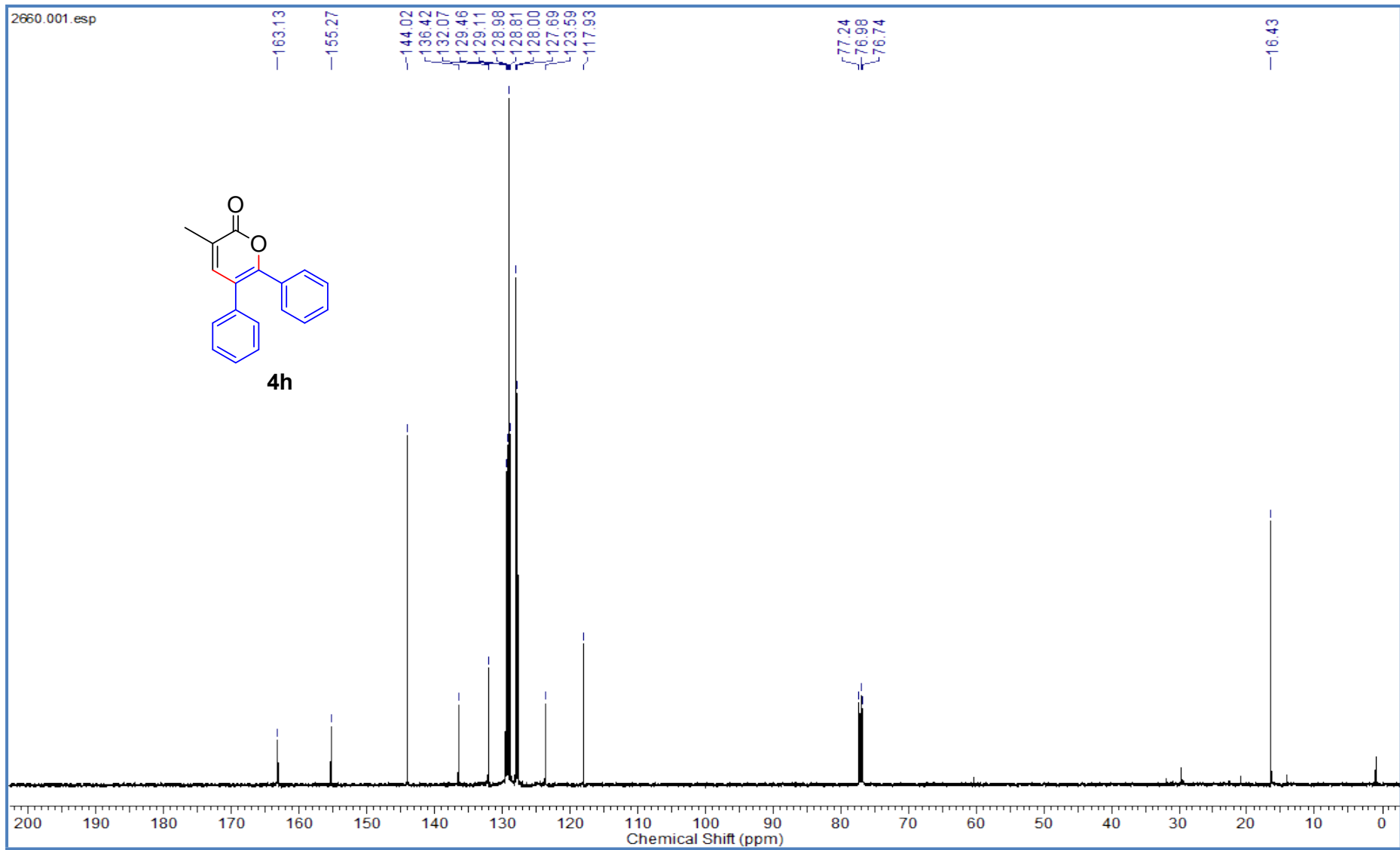


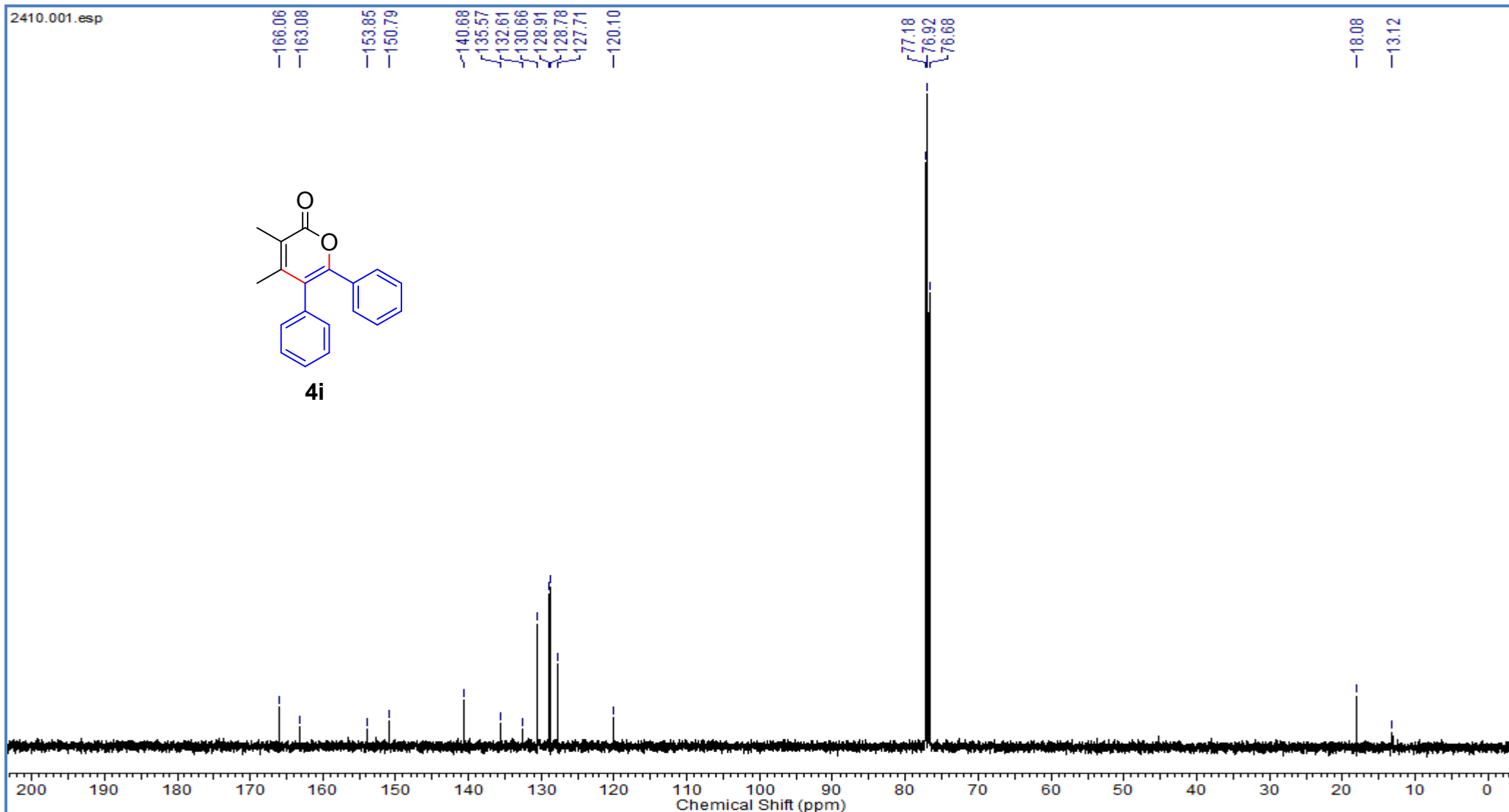


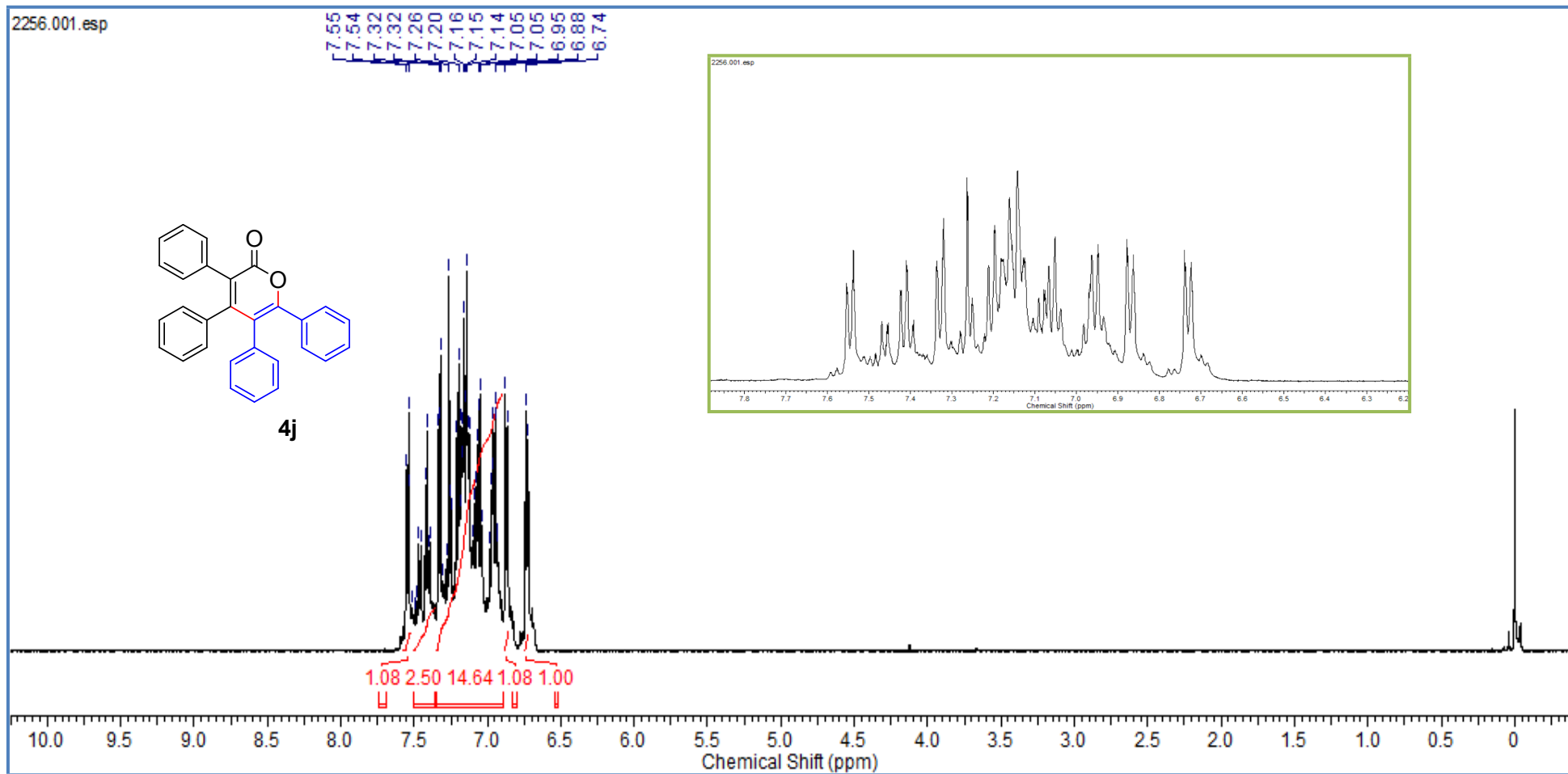








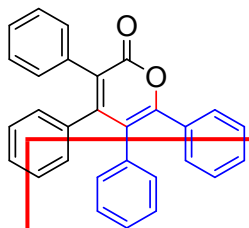




2411.001.esp

162.29
156.50
155.30
147.93
138.07
136.03
134.06
131.26
131.07
130.54
129.60
129.33
128.85
128.79
128.03
127.13
119.56

77.20
76.94
76.68



4j

