Ruthenium(II)-Catalyzed Alkene C-H Bond Functionalization on Cinnamic Acids: A Facile Synthesis of Versatile *α*-Pyrones

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SUPPORTING INFORMATION

Table of Contents **Page**

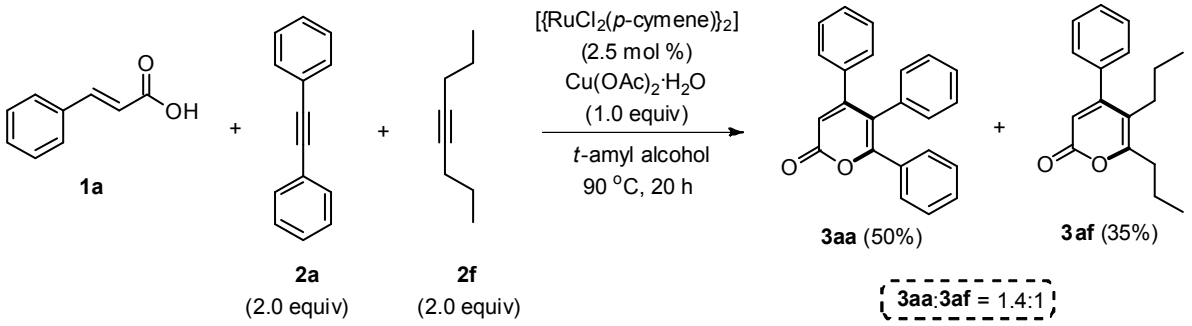
General Experimental	**3**
Experimental Procedures	**3-6**
Spectral and Analytical data	**6-18**
References	**19**
NMR spectra	**20-87**

1. 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 regents 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).

2. General procedure for the synthesis of *α*-pyrones 3aa-3ao, 3ba-3oa: A solution of acid **1** (1.0 mmol), alkyne **2** (1.0 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %) and $Cu(OAc)_2.H_2O$ (1.0 mmol) in *tert*-amyl alcohol (5.0 mL) was heated at 90 ^oC under air for 20 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 silica gel (100-200 mesh) column chromatography using EtOAc/Hexane (1:9) as the eluant.

3. Substrate Competition Experiments:

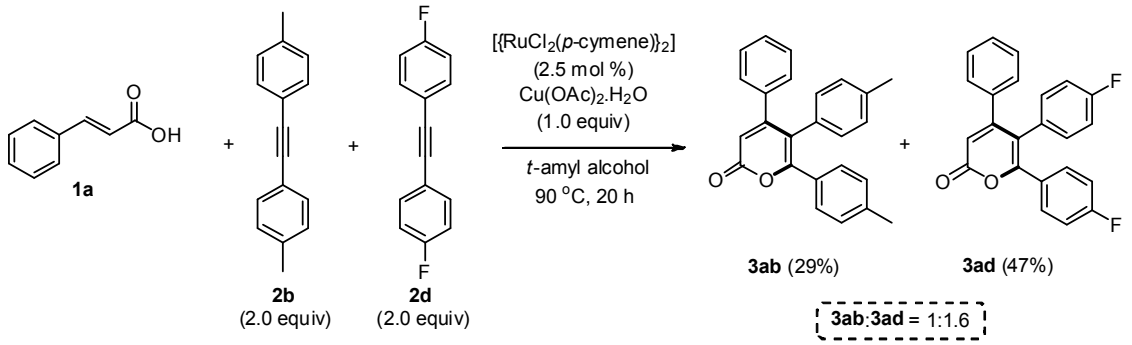
(a)



A solution of acid **1a** (148 mg, 1.0 mmol), alkyne **2a** (356 mg, 2.0 mmol), alkyne **2f** (220 mg, 2.0 mmol), $[RuCl_2(p\text{-cymene})]_2$ (15 mg, 2.5 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (200 mg, 1.0 mmol) in *tert*-amyl alcohol (6.0 mL) was heated at 90 ^oC under air for 20 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.

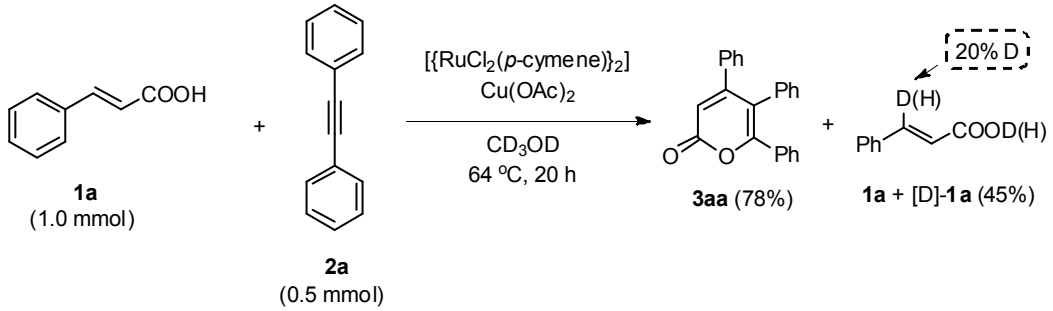
The crude product obtained was purified by silica gel (100-200 mesh) column chromatography using EtOAc/Hexane (1:9) as the eluant to afford the desired products **3aa** (162 mg, 50%) and **3af** (90 mg, 35%).

(b)



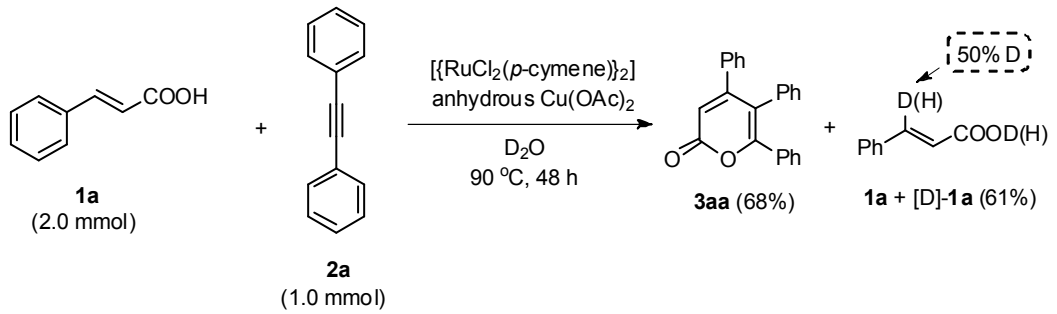
A solution of acid **1a** (148 mg, 1.0 mmol), alkyne **2b** (412 mg, 2.0 mmol), alkyne **2d** (428 mg, 2.0 mmol), $[RuCl_2(p\text{-cymene})]_2$ (15 mg, 2.5 mol %) and $Cu(OAc)_2.H_2O$ (200 mg, 1.0 mmol) in *tert*-amyl alcohol (6.0 mL) was heated at 90 ^oC under air for 20 hours. The solvent was removed under vacuo and the crude reaction mixture was poured into water and extracted with ethyl acetate. The ethyl acetate layer was then washed with brine, water and dried over anhydrous Na_2SO_4. The crude product obtained was purified by silica gel (100-200 mesh) column chromatography using EtOAc/Hexane (1:9) as the eluant to afford the desired products **3ab** (102 mg, 29%) and **3ad** (169 mg, 47%).

4. Isotopically Labelled Experiments



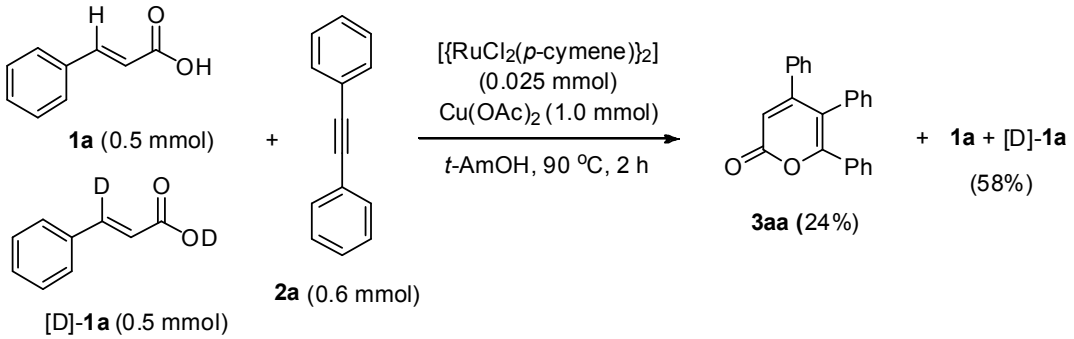
A solution of acid **1a** (148 mg, 1.0 mmol), alkyne **2a** (89 mg, 0.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (15 mg, 0.025 mmol) and anhydrous $Cu(OAc)_2$ (182 mg, 1.0 mmol) in CD_3OD (4.0 mL) was heated at 64 ^oC under nitrogen for 20 hours. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using EtOAc/Hexane (1:9) as the eluant to afford **3aa** (126 mg, 78%) and **1a** + D-**1a** (67 mg, 45%). The deuterium incorporation in **1a** + D-**1a** was estimated to be 20% by ^1H NMR spectroscopy.

When the same reaction was performed for 2 hours, deuterium incorporation in **1a** + D-**1a** was estimated to be only 2% by ^{1}H NMR spectroscopy.



A solution of acid **1a** (296 mg, 2.0 mmol), alkyne **2a** (178 mg, 1.0 mmol), $[RuCl_2(p\text{-cymene})]_2$ (30 mg, 0.05 mmol) and anhydrous $Cu(OAc)_2$ (364 mg, 2.0 mmol) in D_2O (7.0 mL) was heated at 90 ^oC under nitrogen for 48 hours. The solvent was removed under vacuo and the crude product obtained was purified by silica gel (100-200 mesh) column chromatography using EtOAc/Hexane (1:9) as the eluant to afford the **3aa** (220 mg, 68%) and **1a** + D-**1a** (182 mg, 61%). The deuterium incorporation in **1a** + D-**1a** was estimated to be 50% by ^{1}H NMR spectroscopy.

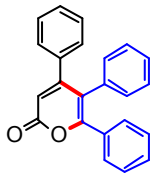
5. Intermolecular competition experiment between substrates 1a and [D]-1a



A 1:1 mixture of acids **1a** (74 mg, 0.5 mmol) and [D]-**1a** (75 mg, 0.5 mmol), alkyne **2a** (107 mg, 0.6 mmol), $[RuCl_2(p\text{-cymene})]_2$ (15 mg, 0.025 mmol) and $Cu(OAc)_2$ (182 mg, 1.0 mmol) in *tert*-amyl alcohol (5.0 mL) was heated at 90 ^oC for two hours. The solvent was removed under vacuo and 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 silica gel (100-200 mesh) column chromatography using EtOAc/Hexane (1:9) as the eluant to obtain **3aa** (47 mg, 24%) and unreacted acids **1a** + [D]-**1a** (86 mg, 58%). The ratio of the unreacted

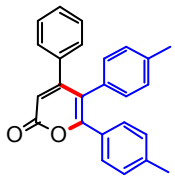
cinnamic acids was determined by ^{1}H NMR integration method to be 1:1. However, in the above isotopically labelled experiment (Experiment 4), we found that the *β*-hydrogen atom of cinnamic acid showed 2% exchange with the deuterium of the solvent CD_3OD (2 hours). Therefore, **1a** reacted with **2a** slightly faster than [D]-**1a** and the ratio of the recovered cinnamic acids (**1a**:[D]-**1a**) reached up to 1:1 after the hydrogen exchange with *t*-AmOH, as a result $k_H/k_D > 1.0$.

6. Spectral and Analytical Data:



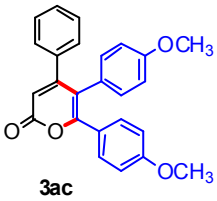
3aa

4,5,6-Triphenyl-2*H*-pyran-2-one[1] **(3aa):** Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (285 mg, 88%), m.p. 222 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.39 (s, 1H), 6.89 (d, J = 6.5 Hz, 2H), 7.00 (d, J = 7.0 Hz, 2H), 7.01-7.29 (m, 11H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 113.3, 118.4, 127.4, 127.8, 128.2, 128.5, 129.3, 129.5, 131.3, 132.6, 134.2, 136.8, 158.3, 159.1, 161.8. IR ($CHCl_3$, cm^{-1}): 2924, 1716, 1445, 775. MS (EI, m/z): 324. Anal. calcd. for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 85.10; H, 4.89.



3ab

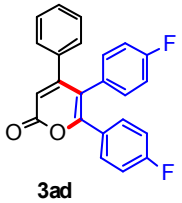
4-Phenyl-5,6-di-*p*-tolyl-2*H*-pyran-2-one (3ab): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (324 mg, 92%), m.p. 172 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.25 (s, 3H), 2.29 (s, 3H), 6.33 (s, 1H), 6.75 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 4H), 7.16-7.27 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.1, 21.3, 112.9, 117.9, 127.8, 128.2, 128.4, 128.5, 128.9, 129.2, 129.8, 131.1, 131.3, 137.1, 139.6, 158.3, 159.4, 161.9. IR ($CHCl_3$, cm^{-1}): 2924, 1639, 1498, 772. MS (EI, m/z): 352. Anal. calcd. for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. Found: C, 85.08; H, 5.67.



3ac

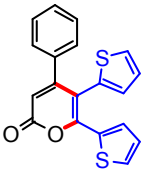
5,6-bis(4-Methoxyphenyl)-4-phenyl-2*H*-pyran-2-one (3ac): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (4:1) as an eluent. White solid (303 mg, 79%), m.p. 152 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.72(s, 3H), 3.75 (s, 3H), 6.31 (s, 1H), 6.67 (d, J = 8.5 Hz, 2H), 6.71 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 7.18-7.24 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.0, 55.1, 112.5, 113.3, 113.8, 117.1, 125.1, 126.6, 127.8, 128.2, 128.3, 128.8, 130.5,

130.9, 132.3, 137.1, 158.1, 158.7, 159.6, 160.3, 162.1. IR ($CHCl_3$, cm^{-1}): 2924, 1718, 1498, 772. MS (EI, m/z): 384. Anal. calcd. for $C_{25}H_{20}O_4$: C, 78.11; H, 5.24. Found: C, 78.33; H, 5.22.



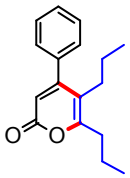
3ad

5, 6-bis (4-Fluorophenyl)-4-phenyl-2*H*-pyran-2-one (3ad): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (274 mg, 76%), m.p. 105 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.37 (s, 1H), 6.83 (d, *J* =7.0 Hz, 4H), 6.89-6.93(m, 2H), 6.97 (d, *J* = 7.0 Hz, 2H), 7.18-7.29 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 113.4, 115.1, 115.3, 115.5, 115.7, 128.0, 128.1, 128.2, 128.7, 131.3, 131.4, 132.8, 132.9, 136.5, 157.4, 158.9, 161.0, 162.9, 164.1. IR ($CHCl_3$, cm^{-1}): 2924, 1734, 1378, 772. MS (EI, m/z): 360. Anal. calcd. for $C_{23}H_{14}F_2O_2$: C, 76.66; H, 3.92. Found: C, 76.61; H, 3.88.



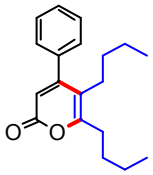
3ae

4-Phenyl-5,6-di(thiophen-2-yl)-2*H*-pyran-2-one (3ae): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Brown solid (225 mg, 67%), m.p. 132 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.30 (s, 1H), 6.69 (d, *J* = 5.0 Hz, 1H), 6.77 (d, *J* = 5.0 Hz, 1H), 6.88 (d, *J* = 3.0 Hz, 1H), 7.04-7.05 (m, 2H), 7.13-7.15 (m, 1H), 7.21-7.28 (m, 4H), 7.38 (d, *J* = 3.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 112.4, 125.2, 125.9, 126.3, 127.1, 127.8, 127.9, 128.3, 128.6, 129.4, 133.6, 134.1, 136.8, 154.1, 159.4, 161.4. IR ($CHCl_3$, cm^{-1}): 2924, 1639, 1464, 771. MS (EI, m/z): 336. Anal. calcd. for $C_{19}H_{12}O_2S_2$: C, 67.83; H, 3.60. Found: C, 67.95; H, 3.56.



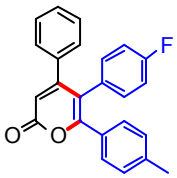
3af

4-Phenyl-5,6-dipropyl-2*H*-pyran-2-one (3af): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (195 mg, 76%), m.p. 84 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.70 (t, J = 7.5 Hz, 3H), 1.01 (t, J = 7.0 Hz, 3H), 1.17-1.22 (m, 2H), 1.73-1.79 (m, 2H), 2.23 (t, J = 5.5 Hz, 2H), 2.55 (t, J =7.5 Hz, 2H), 6.04 (s, 1H), 7.23-7.25 (m, 2H), 7.42-7.43 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.7, 21.1, 23.5, 28.5, 33.1, 112.8, 115.1, 127.3, 128.3, 128.5, 137.6, 160.2, 162.1, 162.5. IR ($CHCl_3$, cm^{-1}): 2928, 1638, 1388, 771. MS (EI, m/z): 256. Anal. calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.51; H, 7.89.



3ag

5,6-Dibutyl-4-phenyl-2*H*-pyran-2-one (3ag): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Oil (227 mg, 80%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.69 (t, J = 7.5 Hz, 3H), 0.96 (t, J = 7.5 Hz, 3H), 1.07-1.15 (m, 4H), 1.40-1.45 (m, 2H), 1.69-1.73 (m, 2H), 2.25 (t, J = 7.5 Hz, 2H), 2.57 (t, J = 8.0 Hz, 2H), 6.04 (s, 1H), 7.23-7.25 (m, 2H), 7.40-7.44 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.3, 13.7, 22.1, 22.4, 26.1, 29.8, 30.9, 32.3, 112.7, 115.1, 127.3, 128.3, 128.5, 137.5, 160.2, 162.1, 162.5. IR ($CHCl_3$, cm^{-1}): 2928, 1639, 1387, 771. MS (EI, m/z): 284. Anal. calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.47; H, 8.44.

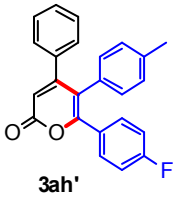


3ah

5-(4-Fluorophenyl)-4-phenyl-6-(*p*-tolyl)-2*H*-pyran-2-one (3ah): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Yellow solid (160 mg, 45%), m.p. 182 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.26 (s, 3H), 6.35 (s, 1H), 6.73 (d, J = 8.0 Hz, 2H), 6.87-6.93 (m, 4H), 6.99 (d, J = 8.0 Hz, 2H), 7.18-7.27 (m, 5H). ^{13}C NMR (125

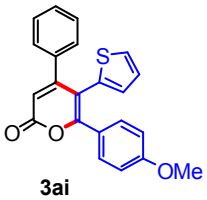
MHz, $CDCl_3$): δ 21.1, 113.3, 114.9, 115.1, 125.5, 127.5, 127.8, 128.2, 128.6, 129.1, 130.9, 131.4, 133.3, 136.8, 137.3, 157.1, 159.2, 161.7, 163.7. IR ($CHCl_3$, cm^{-1}): 2924, 1720, 1229, 771. MS (EI, m/z): 356. Anal. calcd. for $C_{24}H_{17}FO_2$: C, 80.88; H, 4.81. Found: C, 80.98; H, 5.05.

6-(4-Fluorophenyl)-4-phenyl-5-(*p*-tolyl)-2*H*-pyran-2-one (3ah′): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Yellow solid (106 mg, 30%), m.p. 185 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.23 (s, 3H), 6.27 (s, 1H), 6.70-6.80 (m, 3H), 6.91 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.5 Hz, 2H), 7.10-7.21 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.2, 113, 115.1, 115.3, 125.5, 127.5, 128.0, 128.2, 128.6, 128.7, 129.2, 131.1, 132.9, 133.0, 136.8, 139.9, 158.7, 159.0, 160.9, 161.7. IR ($CHCl_3$, cm^{-1}): 2924, 1720, 1229, 771. MS (EI, m/z): 356. Anal. calcd. for $C_{24}H_{17}FO_2$: C, 80.88; H, 4.81. Found: C, 80.81; H, 4.79.



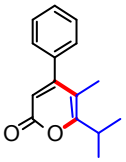
3ah'

6-(4-Methoxyphenyl)-4-phenyl-5-(thiophen-2-yl)-2*H*-pyran-2-one and 5-(4-methoxyphenyl)-4-phenyl-6-(thiophen-2-yl)-2*H*-pyran-2-one (1:1 mixture, 3ai): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (6:1) as an eluent. Oil (256 mg, 71%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.78 (s, 1.5H), 3.79 (s, 1.5H), 6.30 (s, 1H), 6.53-6.55 (m, 0.5H), 6.72-6.78 (m, 3H), 6.89-6.92 (m, 1H), 7.01-7.05 (m, 1.5H), 7.06-7.15 (m, 1H), 7.15-7.35 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.1, 55.2, 112.3, 112.5, 113.3, 113.8, 114.2, 117.1, 124.9, 125.7, 125.7, 127.2, 127.4, 127.8, 127.9, 128.2, 128.23, 128.4, 128.42, 128.6, 128.9, 129.4, 129.6, 130.6, 132.1, 133.8, 133.9, 134.2, 136.9, 137.0, 158.4, 159.2, 159.4, 159.7, 160.6, 161.7, 162.0. IR ($CHCl_3$, cm^{-1}): 2978, 1722, 1023, 770. MS (EI, m/z): 360. Anal. calcd. for $C_{22}H_{16}O_3S$: C, 73.31;

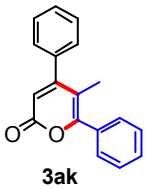


3ai

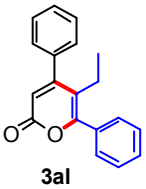
H, 4.47. Found: C, 73.08; H, 4.40.


3aj

6-Isopropyl-5-methyl-4-phenyl-2*H*-pyran-2-one (6.2:1 mixture, 3aj): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Oil (140 mg, 61%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.18-1.26 (m, 6H), 1.86 (s, 2.6H), 1.93 (s, 0.4H), 3.01-3.20 (m, 1H), 6.07 (s, 0.86H), 6.16 (s, 0.14H), 7.22–7.32 (m, 2H), 7.42-7.48 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 6.2:1 mixture): δ 13.1, 15.7, 19.7, 20.9, 29.6, 29.8, 108.2, 112.2, 113.3, 127.5, 128.0, 128.4, 128.5, 128.7, 128.8, 137.5, 146.3, 160.4, 162.7, 165.4. IR ($CHCl_3$, cm^{-1}): 2922, 1639, 1387, 771. MS (EI, m/z): 228. Anal. calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.88; H, 6.99.


3ak

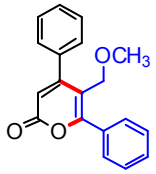
5-Methyl-4,6-diphenyl-2*H*-pyran-2-one (3ak): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Yellow oil (204 mg, 78%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.98 (s, 3H), 6.25 (s, 1H), 7.34-7.35 (m, 2H), 7.35-7.46 (m, 6H), 7.47-7.63 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.8, 111.1, 113.4, 127.6, 127.9, 128.2, 128.5, 128.9, 129.1, 129.8, 130.6, 132.7, 137.3, 157.9, 160.6, 162.1. IR ($CHCl_3$, cm^{-1}): 2922, 1708, 1489, 771. MS (EI, m/z): 262. Anal. calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.49; H, 5.24.


3al

5-Ethyl-4,6-diphenyl-2*H*-pyran-2-one (3al): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Oil (213 mg, 77%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.71 (t, J = 7.5 Hz, 3H), 2.45 (q, J = 7.5 Hz, 2H), 6.22 (s, 1H), 7.35-7.36 (m, 2H), 7.47-7.48 (m, 6H), 7.57-7.59 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.4, 20.4, 114.5, 117.6, 127.4, 128.2, 128.3, 128.4, 128.7, 128.8, 129.7, 130.5, 137.3,

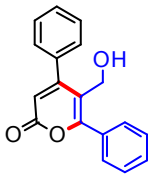
158.3, 160.1, 161.9. IR ($CHCl_3$, cm^{-1}): 2924, 1727, 1219, 765. MS (EI, m/z): 276. Anal. calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.52; H, 5.71.

5-(Methoxymethyl)-4,6-diphenyl-2*H*-pyran-2-one (3am): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (4:1) as an eluent. White solid (242 mg, 83%), m.p. 132 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.22 (s, 3H), 3.82 (s, 2H), 6.27 (s, 1H), 7.47–7.52 (m, 8H), 7.85 (dd, J = 8.0 Hz & 1.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 57.3, 67.9, 112.7, 113.2, 128.1, 128.3, 128.4, 128.9, 129.3, 130.6, 132.1, 136.7, 160.7, 161.6, 162.9 .IR ($CHCl_3$, cm^{-1}): 2923, 1722, 1076, 772. MS (EI, m/z): 292. Anal. calcd. for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.89; H, 5.48.



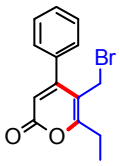
3am

5-(Hydroxymethyl)-4,6-diphenyl-2*H*-pyran-2-one (3an): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (4:1) as an eluent. Yellow solid (195 mg, 70%), m.p. 117 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.31 (s, 2H), 6.80 (s, 1H), 7.10 (d, J = 10.5 Hz, 2H), 7.19-7.47 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 67.2, 115.7, 128.6, 128.7, 129.1, 129.9, 130.7, 136.0, 136.8, 138.7, 156.1, 164.1, 167.7. IR ($CHCl_3$, cm^{-1}): 3428, 2925, 1719, 1261, 698. MS (EI, m/z): 278. Anal. calcd. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.60; H, 4.92.



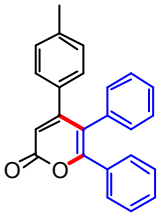
3an

5-(Bromomethyl)-6-ethyl-4-phenyl-2*H*-pyran-2-one and 6-(bromomethyl)-5-ethyl-4-phenyl-2H-pyran-2-one (4:3 mixture, 3ao): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Oil (178 mg, 61%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.85 (t, J = 7.5 Hz, 1.7H),



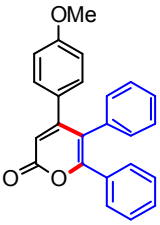
3ao

0.93 (t, J = 7.5 Hz, 1.3H), 2.39 (q, J = 7.5 Hz, 0.8H), 2.69 (q, J = 7.5 Hz, 1.2H), 3.95 (s, 0.8H), 4.24 (s, 1.2H), 6.14 (s, 0.6H), 6.13 (s, 0.4H), 7.36-7.49 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 8.3, 12.2, 14.9, 19.6, 32.6, 33.3, 112.1, 115.1, 127.3, 127.9, 128.1, 128.4, 128.6, 129.0, 136.7, 137.0, 159.8, 160.2, 167.2. IR ($CHCl_3$, cm^{-1}): 2923, 1725, 1072, 770. MS (EI, m/z): 292. Anal. calcd. for $C_{14}H_{13}BrO_2$: C, 57.36; H, 4.47. Found: C, 57.48; H, 4.34.



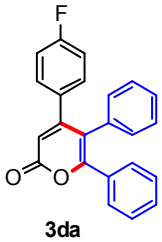
3ba

5,6-Diphenyl-4-(*p*-tolyl)-2*H*-pyran-2-one (3ba): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (301 mg, 89%), m.p. 169 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.28 (s, 3H), 6.36 (s, 1H), 6.88-6.89 (m, 4H), 6.98-7.0 (m, 2H), 7.10-7.13 (m, 3H), 7.16-7.25 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.6, 113.1, 118.4, 127.4, 127.8, 128.2, 128.6, 129.3, 131.3, 132.7, 133.9, 134.4, 138.7, 158.2, 159.1, 161.9. IR ($CHCl_3$, cm^{-1}): 2924, 1727, 1459, 697. MS (EI, m/z): 338. Anal. calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.01; H, 5.27.



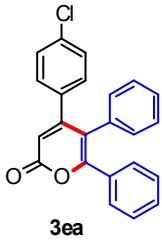
3ca

4-(4-Methoxyphenyl)-5,6-diphenyl-2*H*-pyran-2-one (3ca): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Yellow solid (269 mg, 76%), m.p. 155 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.76 (s, 3H), 6.35 (s, 1H), 6.70 (d, J = 9.0 Hz, 2H), 6.91-6.93 (m, 4H), 7.13-7.24 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.1, 112.7, 113.3, 127.4, 127.8, 128.2, 129.3, 129.8, 131.4, 132.7, 134.5, 158.2, 158.6, 159.8, 161.9. IR ($CHCl_3$, cm^{-1}): 2924, 1639, 1377, 771. MS (EI, m/z): 354. Anal. calcd. for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.30; H, 5.04.



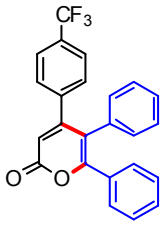
3da

4-(4-Fluorophenyl)-5,6-diphenyl-2*H*-pyran-2-one (3da): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Brown solid (277 mg, 81%), m.p. 166 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.36 (m, 1H), 6.84-6.90 (m, 4H), 6.96-6.99 (m, 2H), 7.10-7.27 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 113.3, 115.0, 115.2, 118.2, 127.6, 127.8, 128.4, 129.3, 129.5, 130.1, 130.2, 131.2, 132.4, 134.1, 157.9, 158.4, 161.5, 163.7. IR ($CHCl_3$, cm^{-1}): 2922, 1731, 1367, 698. MS (EI, m/z): 342. Anal. calcd. for $C_{23}H_{15}FO_2$: C, 80.69; H, 4.42. Found: C, 80.88; H, 4.36.



3ea

4-(4-Chlorophenyl)-5,6-diphenyl-2*H*-pyran-2-one (3ea): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Yellow solid (286 mg, 80%), m.p. 153 ^{o}C. ^{1}H NMR ($CDCl_3$,500 MHz): δ 6.35 (s, 1H), 6.88 (d, J = 7.0 Hz, 2H), 6.94 (d, J = 7.5 Hz, 2H), 7.12-7.21 (m, 8H), 7.25- 7.27 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 113.4, 118.1, 127.6, 127.8, 128.2, 128.4, 129.3, 129.6, 131.2, 132.4, 133.9, 134.8, 135.2, 157.8, 158.5, 161.5. IR ($CHCl_3$, cm^{-1}): 2924, 1727, 1488, 770. MS (EI, m/z): 358. Anal. calcd. for $C_{23}H_{15}ClO_2$: C, 76.99; H, 4.21. Found: C, 76.92; H, 4.17.

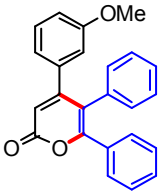


3fa

5,6-Diphenyl-4-(4-(trifluoromethyl)phenyl)-2*H*-pyran-2-one (3fa): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Yellow solid (321 mg, 82%), m.p. 190 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.37 (s, 1H), 6.88 (d, J = 7.0 Hz, 2H), 7.10-7.28 (m, 10H), 7.46 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 113.7, 117.8, 124.8, 124.9, 127.7, 127.9, 128.5, 128.6, 129.3, 129.7, 131.1, 132.3, 133.7, 140.4, 157.5, 158.7, 161.3. IR ($CHCl_3$, cm^{-1}): 2925, 1727, 1324, 695.

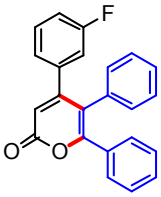
MS (EI, m/z): 392. Anal. calcd. for $C_{24}H_{15}F_3O_2$: C, 73.47; H, 3.85. Found: C, 73.41; H, 3.80.

4-(3-Methoxyphenyl)-5,6-diphenyl-2*H*-pyran-2-one (3ga): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Yellow solid (258 mg, 73%), m.p. 162 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.54 (s, 3H), 6.39 (s, 1H), 6.45 (s, 1H), 6.64 (d, J = 7.5 Hz, 1H), 6.78 (dd, J = 8.5 Hz & 2.5 Hz, 1H), 6.90 (d, J = 7.0 Hz, 2H), 7.10-7.28 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.1, 113.2, 113.4, 114.9, 118.3, 120.7, 127.4, 127.8, 128.3, 129.1, 129.3, 129.5, 131.2, 132.6, 134.4, 138.1, 158.3, 158.8, 161.8. IR ($CHCl_3$, cm^{-1}): 2925, 1639, 1377, 767. MS (EI, m/z): 354. Anal. calcd. for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.38; H, 5.04.



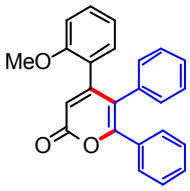
3ga

4-(3-Fluorophenyl)-5,6-diphenyl-2*H*-pyran-2-one (3ha): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (263 mg, 77%), m.p. 215 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.30 (s, 1H), 6.70 (d, J = 7.5 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.87-6.89 (m, 2H), 6.92-6.95 (dt, J = 8.5 Hz & 1.5 Hz, 1H), 7.12-7.38 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 113.5, 115.3, 115.4, 115.5, 115.6, 118.1, 124.1, 127.7, 127.9, 128.4, 129.3, 129.6, 129.7, 131.1, 132.4, 133.9, 138.9, 157.7, 158.5, 161.0, 161.4, 162.9. IR ($CHCl_3$, cm^{-1}): 2923, 1718, 1448, 764. MS (EI, m/z): 342. Anal. calcd. for $C_{23}H_{15}FO_2$: C, 80.69; H, 4.42. Found: C, 80.51; H, 4.54.



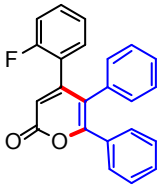
3ha

4-(2-Methoxyphenyl)-5,6-diphenyl-2*H*-pyran-2-one (3ia): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (248 mg, 70%), m.p. 167 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.35 (s,



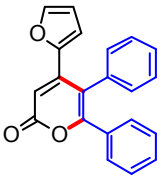
3ia

3H), 6.34 (s, 1H), 6.57 (d, J = 8.5 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 7.00-7.07 (m, 3H), 7.12-7.19 (m, 4H), 7.22-7.28 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 54.7, 110.2, 114.1, 119.5, 120.3, 126.3, 126.9, 127.4, 127.7, 128.1, 129.3, 130.3, 132.7, 134.7, 155.2, 157.3, 158.1, 161.9. IR ($CHCl_3$, cm^{-1}): 2924, 1641, 1462, 1012, 698. MS (EI, m/z): 354. Anal. calcd. for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.29; H, 5.04.



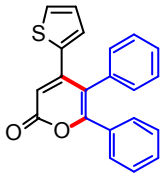
3ja

4-(2-Fluorophenyl)-5,6-diphenyl-2*H*-pyran-2-one (3ja): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (260 mg, 76%), m.p. 190 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.36 (s, 1H), 6.73 (d, J = 10.5 Hz, 1H), 6.79 (d, J = 7.5 Hz, 1H), 6.88-6.90 (m, 2H), 6.93-6.97 (m, 1H), 7.13-7.28 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 113.5, 115.3, 115.5, 115.6, 118.1, 124.1, 127.6, 127.8, 128.4, 129.3, 129.6, 131.1, 132.4, 133.9, 138.9, 157.7, 158.5, 161.1, 161.4, 162.9. IR ($CHCl_3$, cm^{-1}): 2925, 1642, 1463, 699. MS (EI, m/z): 342. Anal. calcd. for $C_{23}H_{15}FO_2$: C, 80.69; H, 4.42. Found: C, 80.81; H, 4.38.



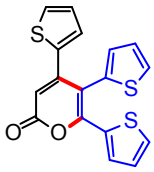
3ka

4-(Furan-2-yl)-5,6-diphenyl-2*H*-pyran-2-one (3ka): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Gum (267 mg, 85%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.21 (dd, J = 3.5 Hz & 1.5 Hz, 1H), 6.84 (s, 1H), 7.12-7.40 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 107.3, 112.2, 116.1, 127.7, 128.1, 128.5, 128.8, 129.1, 129.3, 129.6, 132.5, 134.6, 144.5, 145.1, 148.2, 158.1, 162.3. IR ($CHCl_3$, cm^{-1}): 2924, 1705, 1447, 770. MS (EI, m/z): 314. Anal. calcd. for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49. Found: C, 80.45; H, 4.18.



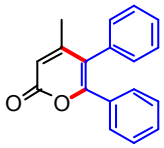
3la

5,6-Diphenyl-4-(thiophen-2-yl)-2*H*-pyran-2-one (3la): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. Yellow solid (277 mg, 84%), m.p. 235 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.55 (s, 1H), 6.65 (d, J = 4.0 Hz, 1H), 6.85-6.86 (m, 1H), 7.07-7.09 (m, 2H), 7.13 (d, J = 7.5 Hz, 1H), 7.16-7.31 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 111.6, 117.5, 127.6, 127.8, 128.0, 128.2, 128.6, 129.2, 129.4, 129.8, 131.6, 134.2, 137.9, 151.1, 158.4, 161.6. IR ($CHCl_3$, cm^{-1}): 2924, 1708, 1447, 771. MS (EI, m/z): 330. Anal. calcd. for $C_{21}H_{14}O_2S$: C, 76.34; H, 4.27. Found: C, 76.20; H, 4.22.



3lm

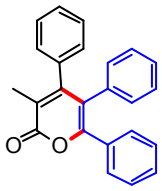
4,5,6-Tri(thiophen-2-yl)-2*H*-pyran-2-one (3lm): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (280 mg, 82%), m.p. 185 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.51 (s. 1H), 6.80 (dd, J = 5.5 Hz & 1.5 Hz, 1H), 6.86 (dd, J = 4.0 Hz & 1.0 Hz, 1H), 6.88-6.93 (m, 2H), 7.10-7.16 (m, 2H) 7.31 (dd, J = 3.0 Hz &1.3 Hz, 1H), 7.36 (dd, J = 5.1 Hz & 1.1 Hz, 1H), 7.44 (dd, J = 4.9 Hz & 3.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 110.2, 110.9, 125.2, 126.9, 127.0, 127.3, 128.3, 129.5, 129.7, 129.9, 134.0, 137.8, 151.2, 154.2, 161.3. IR ($CHCl_3$, cm^{-1}): 2924, 1639, 1467, 772. MS (EI, m/z): 342. Anal. calcd. for $C_{17}H_{10}O_2S_3$: C, 59.62; H, 2.94. Found: C, 59.90; H, 2.93.



3ma

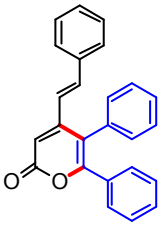
4-Methyl-5,6-diphenyl-2*H*-pyran-2-one (3ma): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (186 mg, 71%), m.p. 110 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.95 (s, 3H), 6.24 (s, 1H), 7.12-7.17 (m, 4H), 7.22-7.27 (m, 3H), 7.34-7.35 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.5, 112.4, 119.7, 127.8, 127.9, 128.8,

129.1, 129.4, 130.4, 132.2, 134.5, 156.9, 157.4, 162.1. IR ($CHCl_3$, cm^{-1}): 2918, 1719, 1216, 756. MS (EI, m/z): 262. Anal. calcd. for $C_{18}H_{14}O_2$: C 82.42; H, 5.38. Found: C, 82.36; H, 5.30.



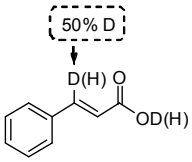
3na

4-Methyl-3,5,6-triphenyl-2*H*-pyran-2-one[2] **(3na):** Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (291 mg, 86%), m.p. 152 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.99 (s, 3H), 6.83 (d, *J* = 7.0 Hz, 2H), 6.91(d, *J* = 7.0 Hz, 2H), 7.02-7.04 (m, 2H), 7.16-7.28 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.6, 119.3, 121.1, 127.0, 127.5, 127.8, 127.9, 128.2, 129.1, 131.1, 132.6, 135.1, 136.5, 154.5, 163.4. IR ($CHCl_3$, cm^{-1}): 2922, 1720, 1216, 771. MS (EI, m/z): 338. Anal. calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 84.99; H, 5.31.



3oa

(*E*)-5,6-Diphenyl-4-styryl-2*H*-pyran-2-one (3oa): Prepared according to the above general procedure. The crude reaction mixture was purified on a silica gel (100-200 mesh) column chromatography using Hexane/EtOAc (9:1) as an eluent. White solid (312 mg, 89%), m.p. 115 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.50 (d, *J* = 16.0 Hz, 1H), 6.60 (s, 1H), 7.17-7.37 (m, 16H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 107.2, 118.3, 123.5, 127.3, 127.8, 128.1, 128.7, 128.8, 129.2, 129.4, 131.0, 132.5, 134, 135.6, 136.2, 154.1, 157.7, 162.3. IR ($CHCl_3$, cm^{-1}): 2924, 1721, 1385, 692. MS (EI, m/z): 350. Anal. calcd. for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.62; H, 5.04.

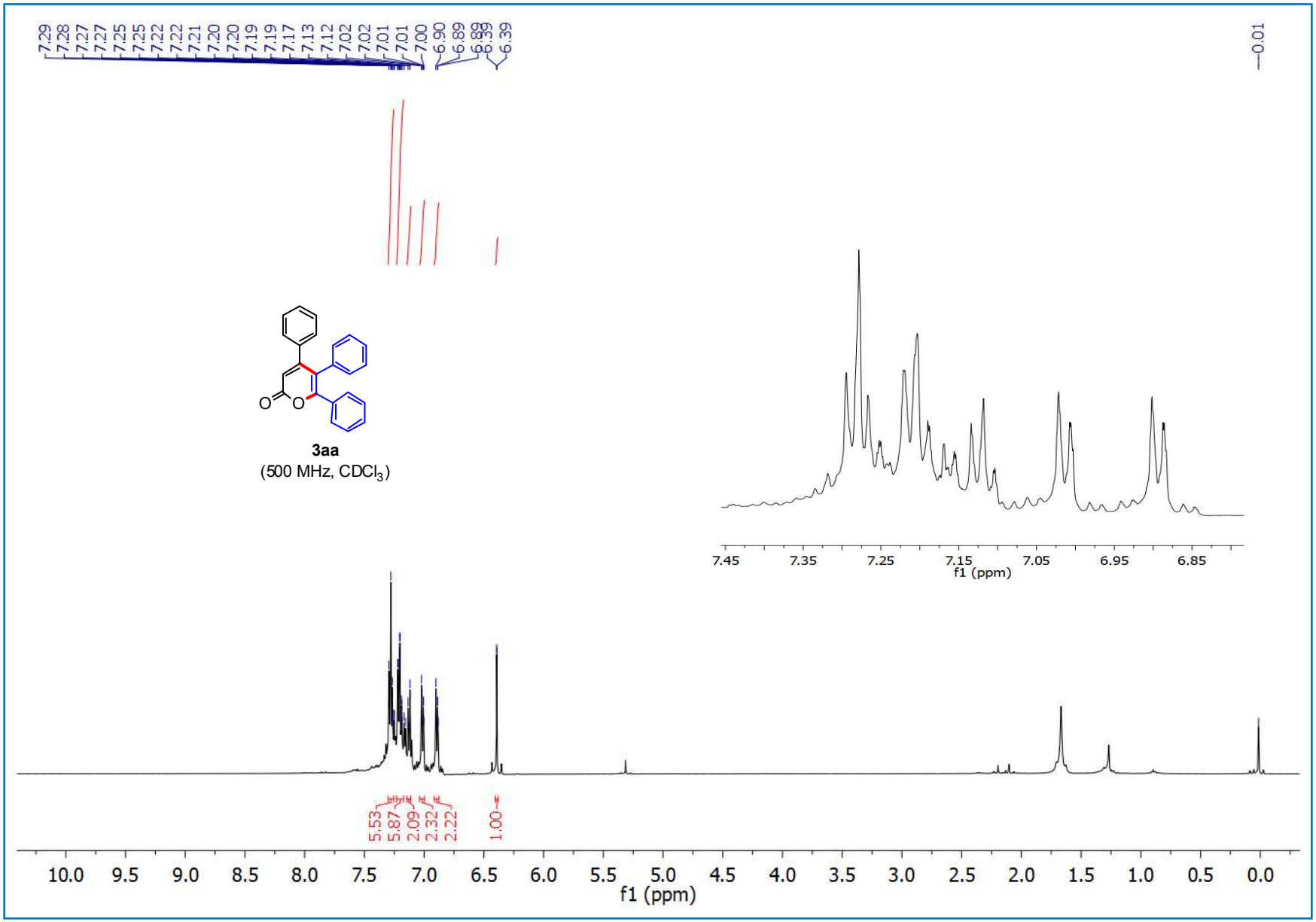


1a + [D]-1a

Cinnamic acid (1a) + Cinnamic acid-d$_2$ (1a + [D]-1a): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.46 (s, 0.5H), 6.47 (d, *J* = 16.0 Hz, 0.5H), 7.35-7.45 (m, 3H), 7.50-7.60 (m, 2H), 7.81 (d, *J* = 16.0 Hz, 0.5H). IR ($CHCl_3$, cm^{-1}): 3067, 2977, 2720, 1686, 1288, 987. MS (EI, m/z): 148, 150.

References:

1. El-Kholy, I. E.-S.; Mishrikey, M. M.; Abdoul-Ela, S. L. *J. Heterocyclic Chem.* **1982**, *19*, 1329-1334.
2. Kuninobu, Y.; Kawata, A.; Nishi, M.; Takata, H.; Takai, K. *Chem. Commun.* **2008**, 6360-6362.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7.27
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7.22
7.22
7.21
7.20
7.20
7.19
7.19
7.17
7.13
7.12
7.02
7.02
7.01
7.01
7.00
6.90
6.89
6.39
6.39
0.01
O
O
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(500 MHz, CDCl3)
7.45
7.35
7.25
7.15
7.05
6.95
6.85
f1 (ppm)
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5.87
2.09
2.32
2.22
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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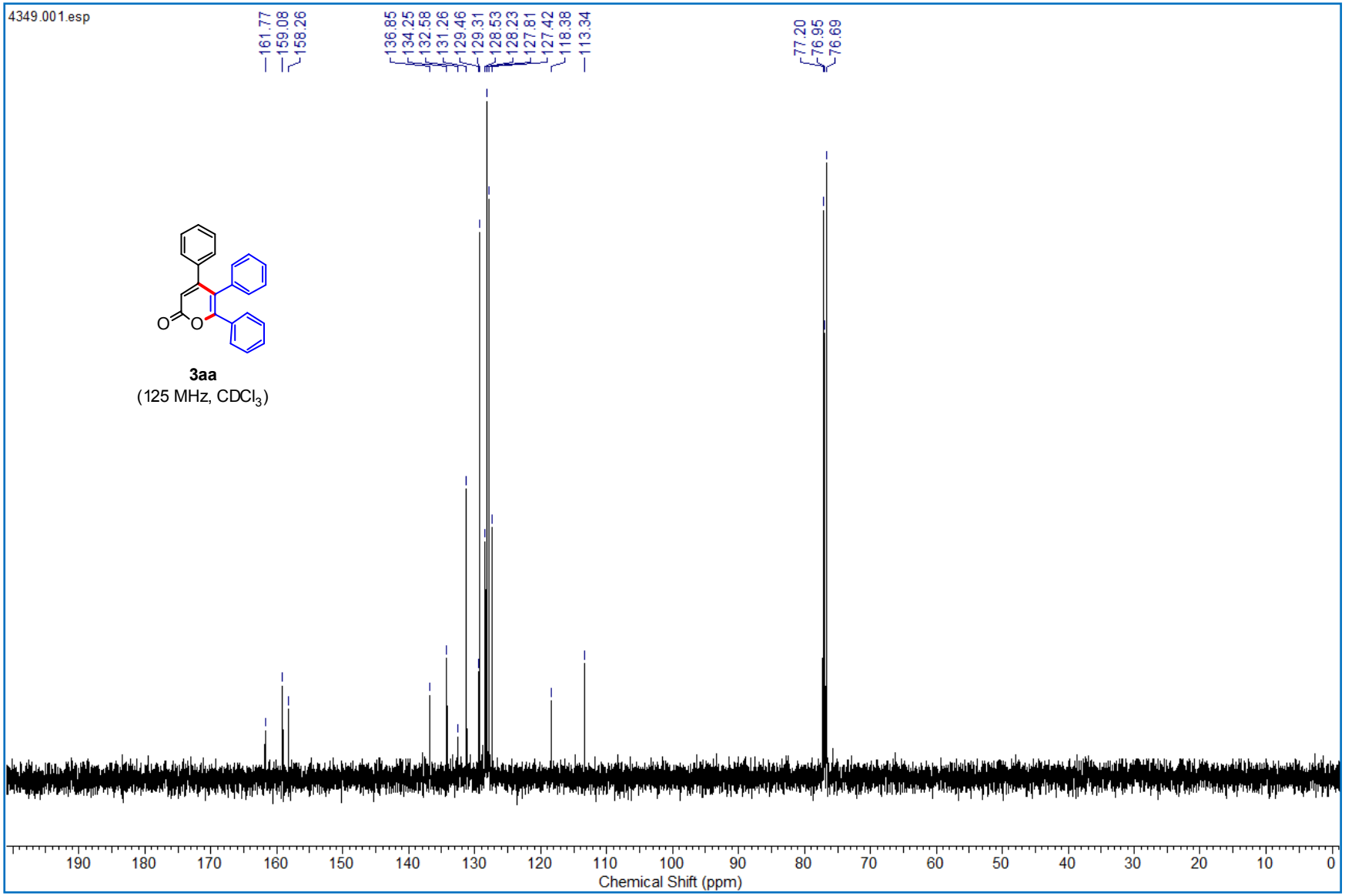
0.0
f1 (ppm)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129.31
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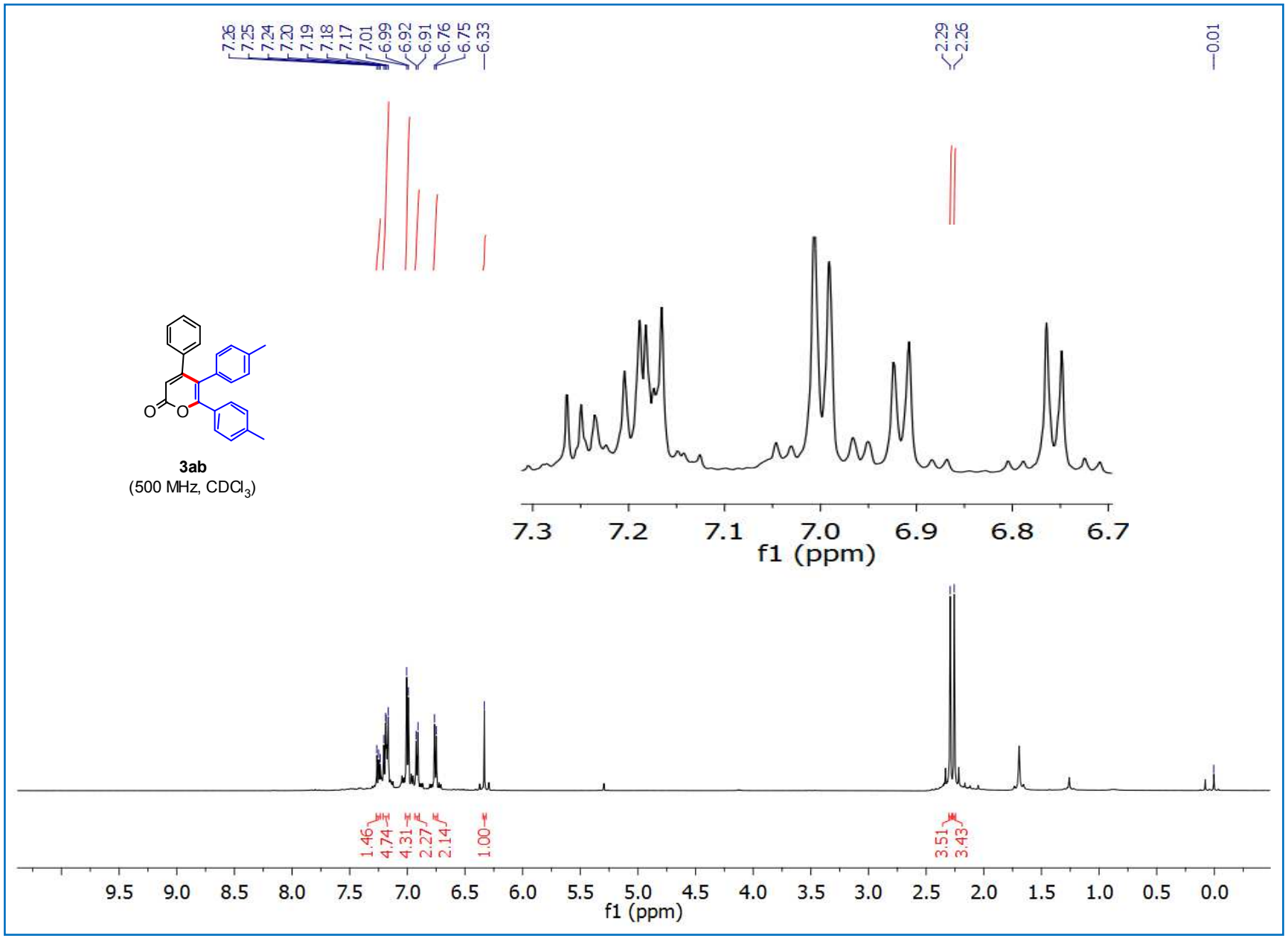
127.81
127.42
118.38
113.34
77.20
76.95
76.69
O
O
3aa
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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7.18
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7.01
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6.91
6.76
6.75
6.33
2.29
2.26
0.01
3ab
(500 MHz, CDCl3)
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
1.46
4.74
4.31
2.27
2.14
1.00
3.51
3.43
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
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2.5
2.0
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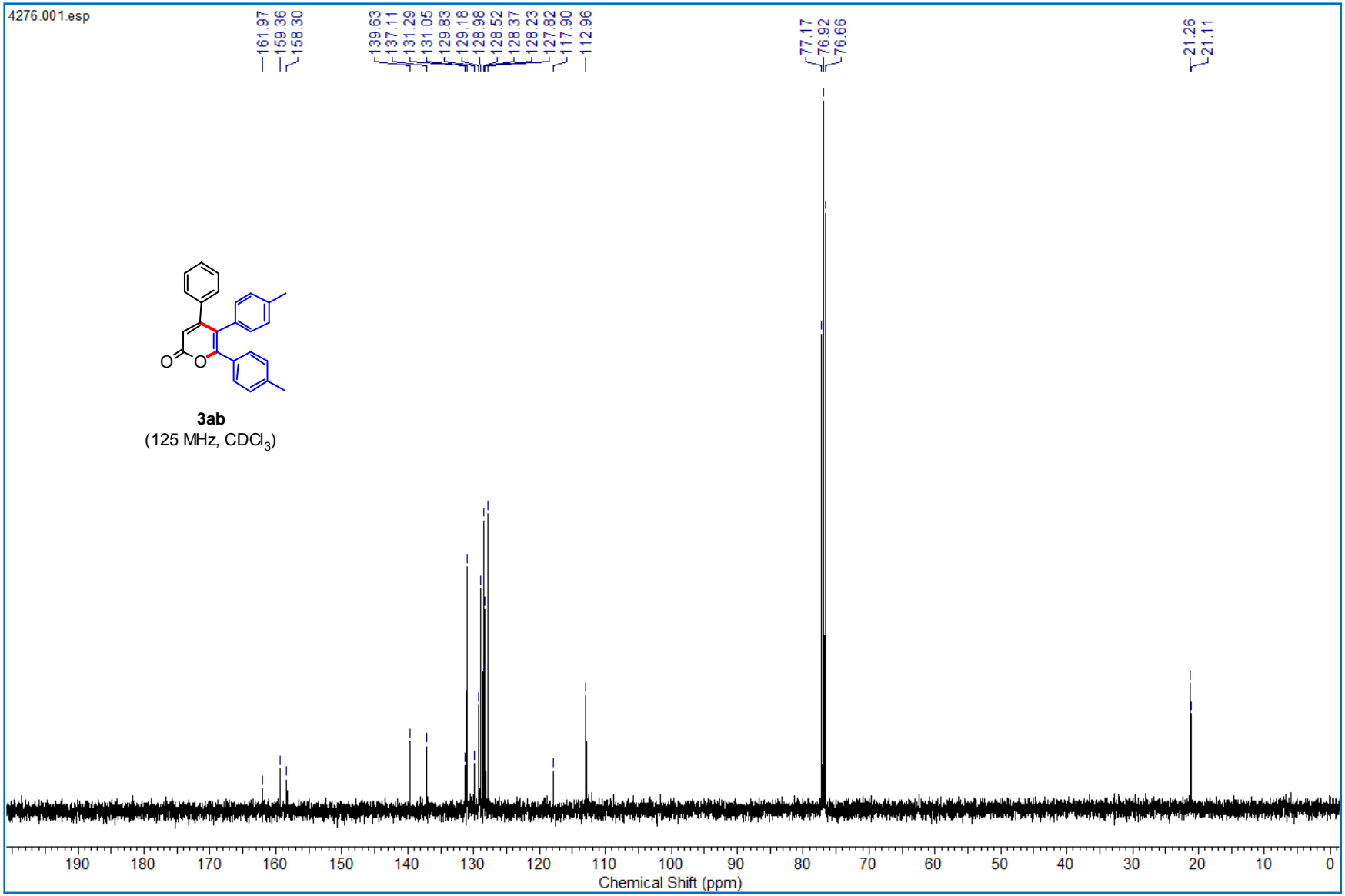
0.0
f1 (ppm)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128.98
128.52
128.37
128.23
127.82
117.90
112.96
77.17
76.92
76.66
21.26
21.11
O
O
3ab
(125 MHz, CDCl3)
190
180
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150
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30
20
10
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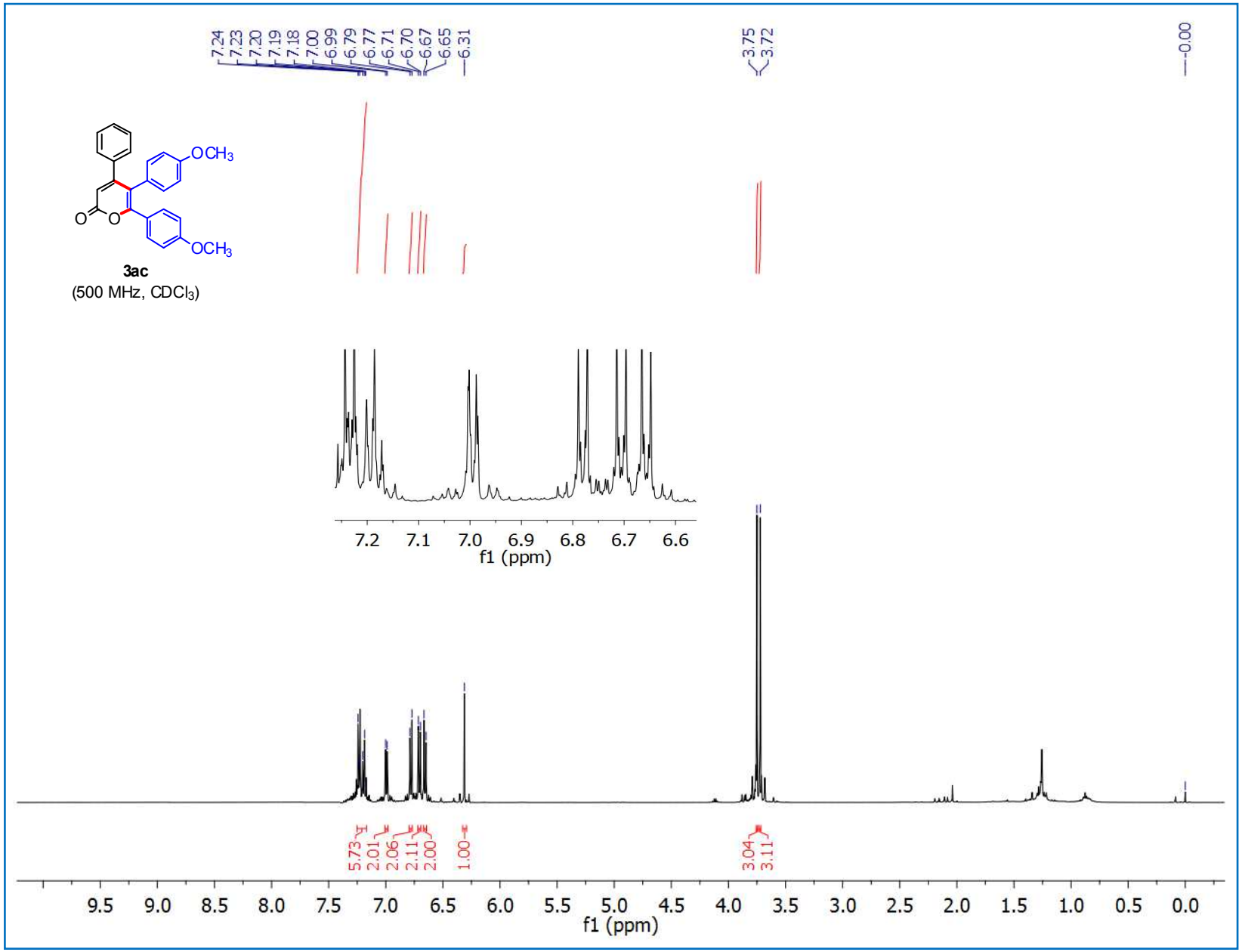
Chemical Shift (ppm)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6.71
6.70
6.67
6.65
6.31
3.75
3.72
0.00
OCH3
OCH3
O
O
3ac
(500 MHz, CDCl3)
7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
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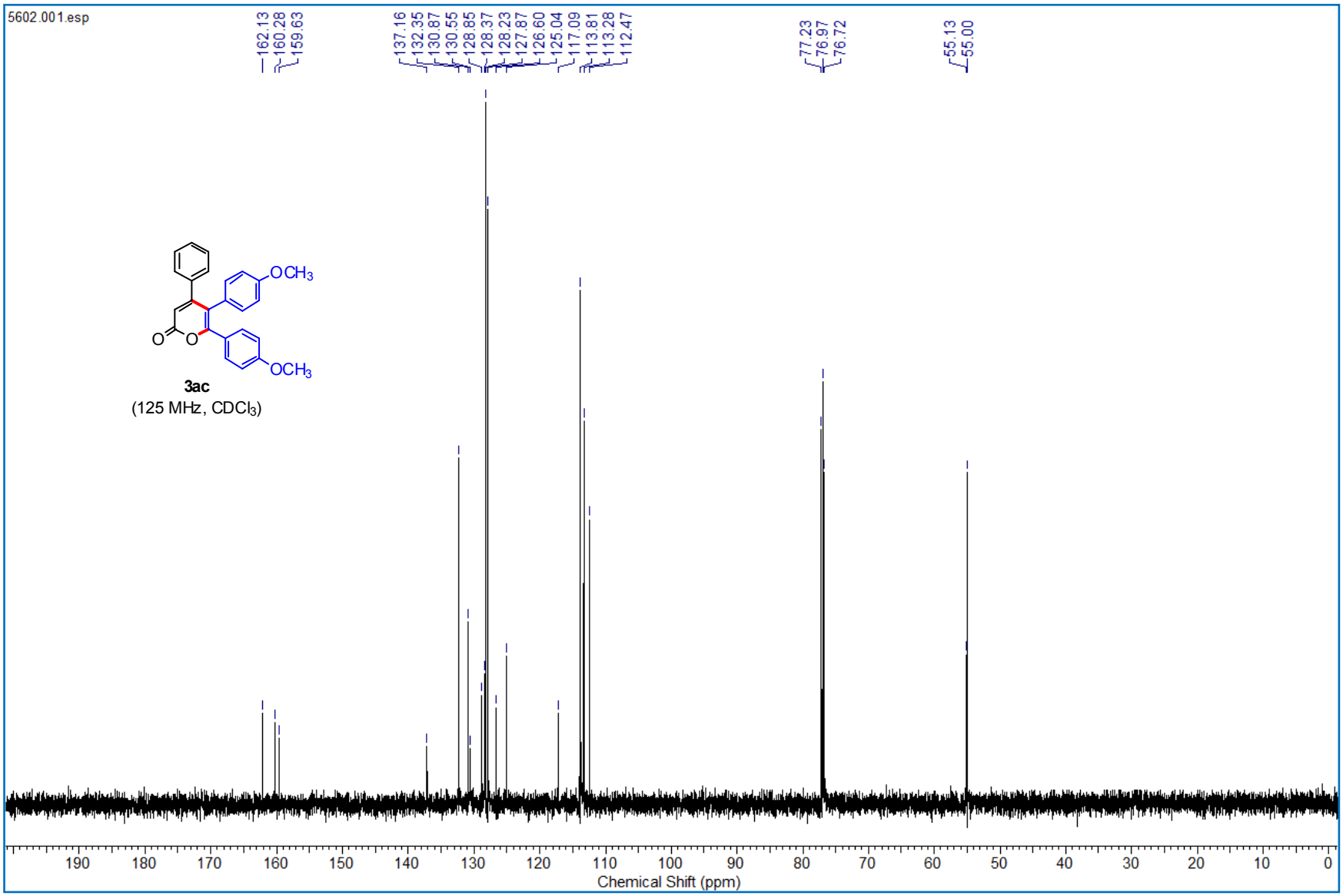
2.01
2.06
2.11
2.00
1.00
3.04
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.87
126.60
125.04
117.09
113.81
113.28
112.47
77.23
76.97
76.72
55.13
55.00
OCH3
OCH3
O
O
3ac
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
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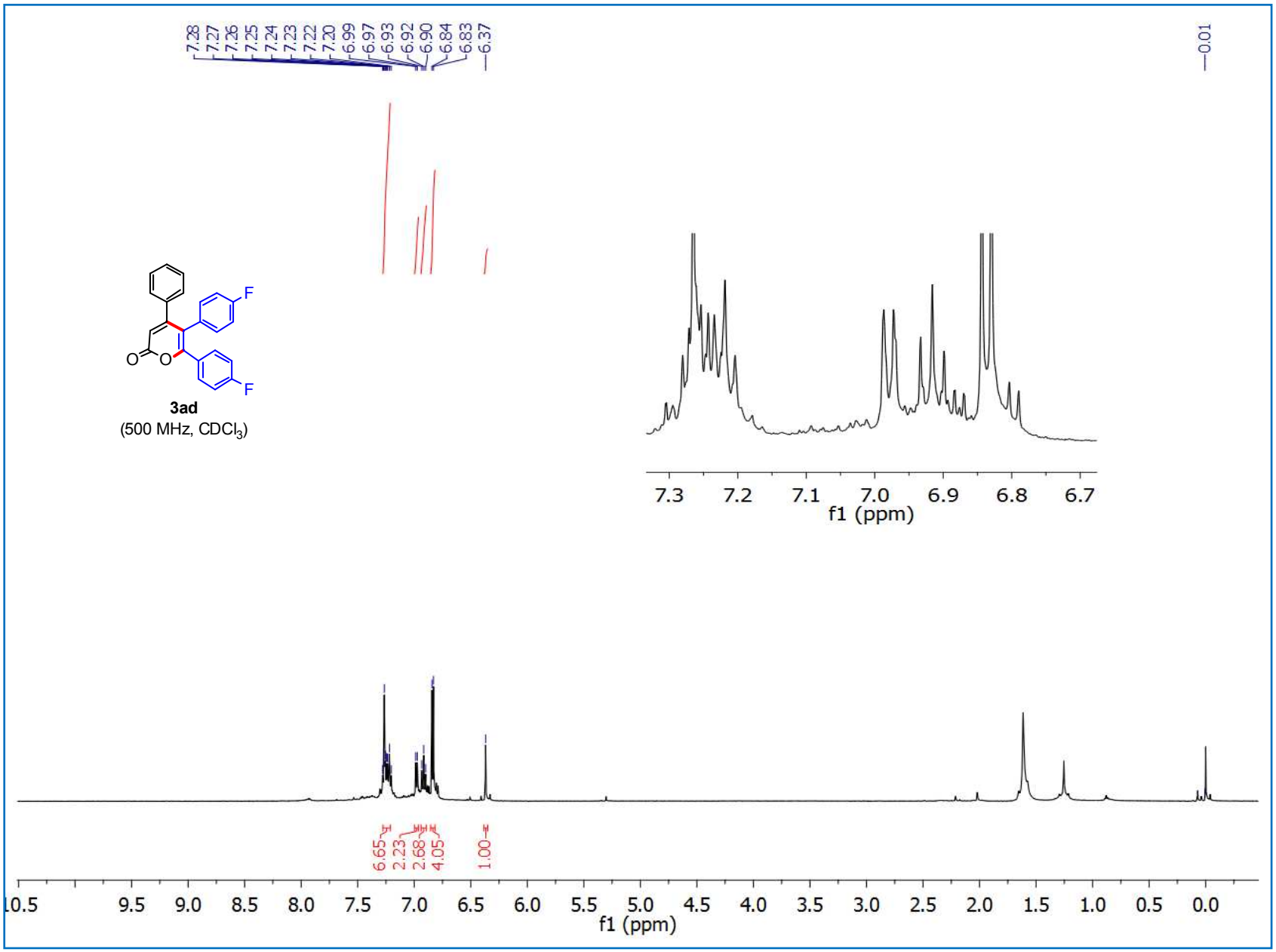
50
40
30
20
10
0
Chemical Shift (ppm)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7.22
7.20
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6.92
6.90
6.84
6.83
6.37
0.01
F
F
O
O
3ad
(500 MHz, CDCl3)
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
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2.23
2.68
4.05
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10.5
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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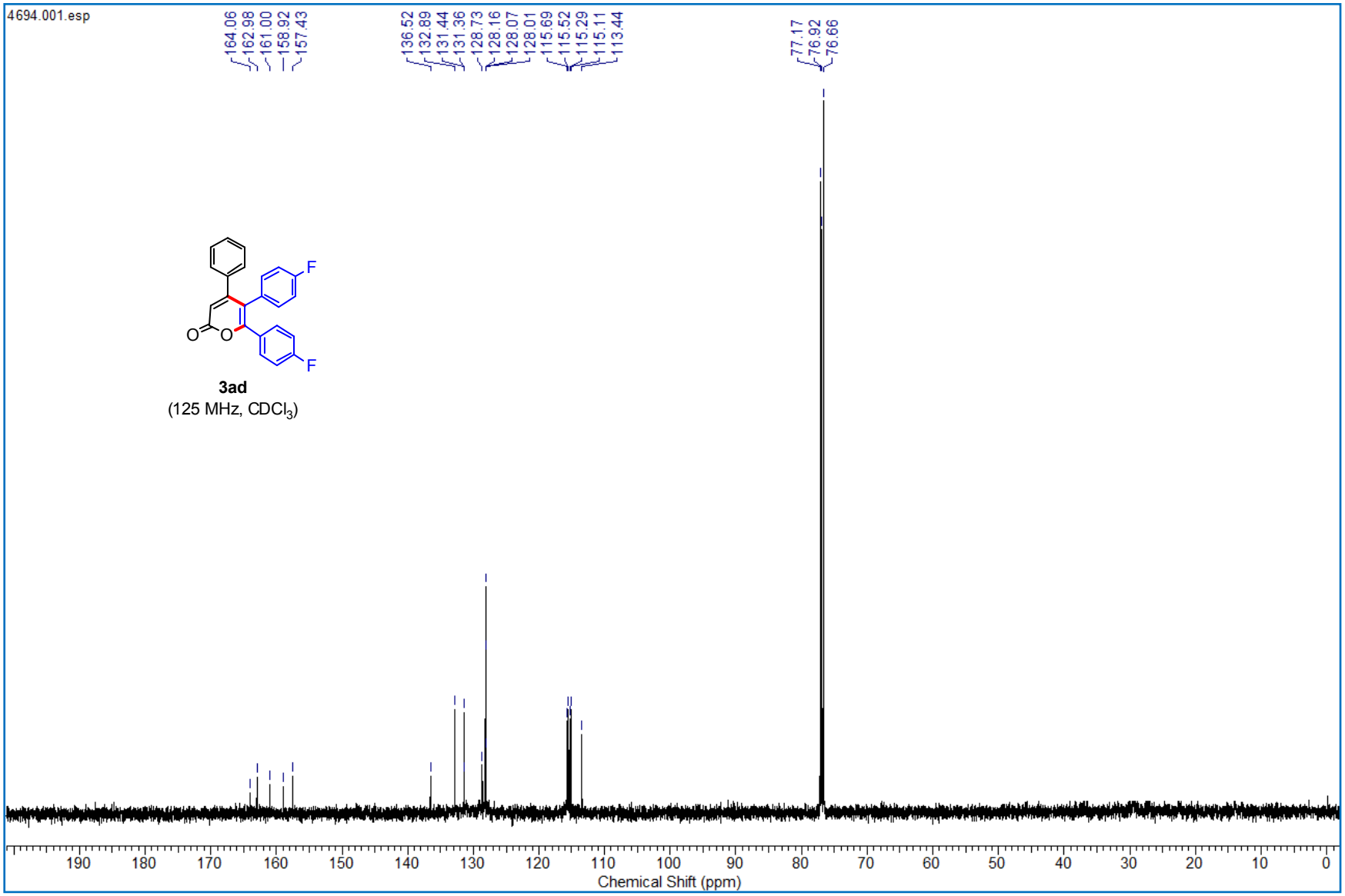
1.0
0.5
0.0
f1 (ppm)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128.07
128.01
115.69
115.52
115.29
115.11
113.44
77.17
76.92
76.66
F
F
O
O
3ad
(125 MHz, CDCl3)
190
180
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120
110
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90
80
70
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40
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10
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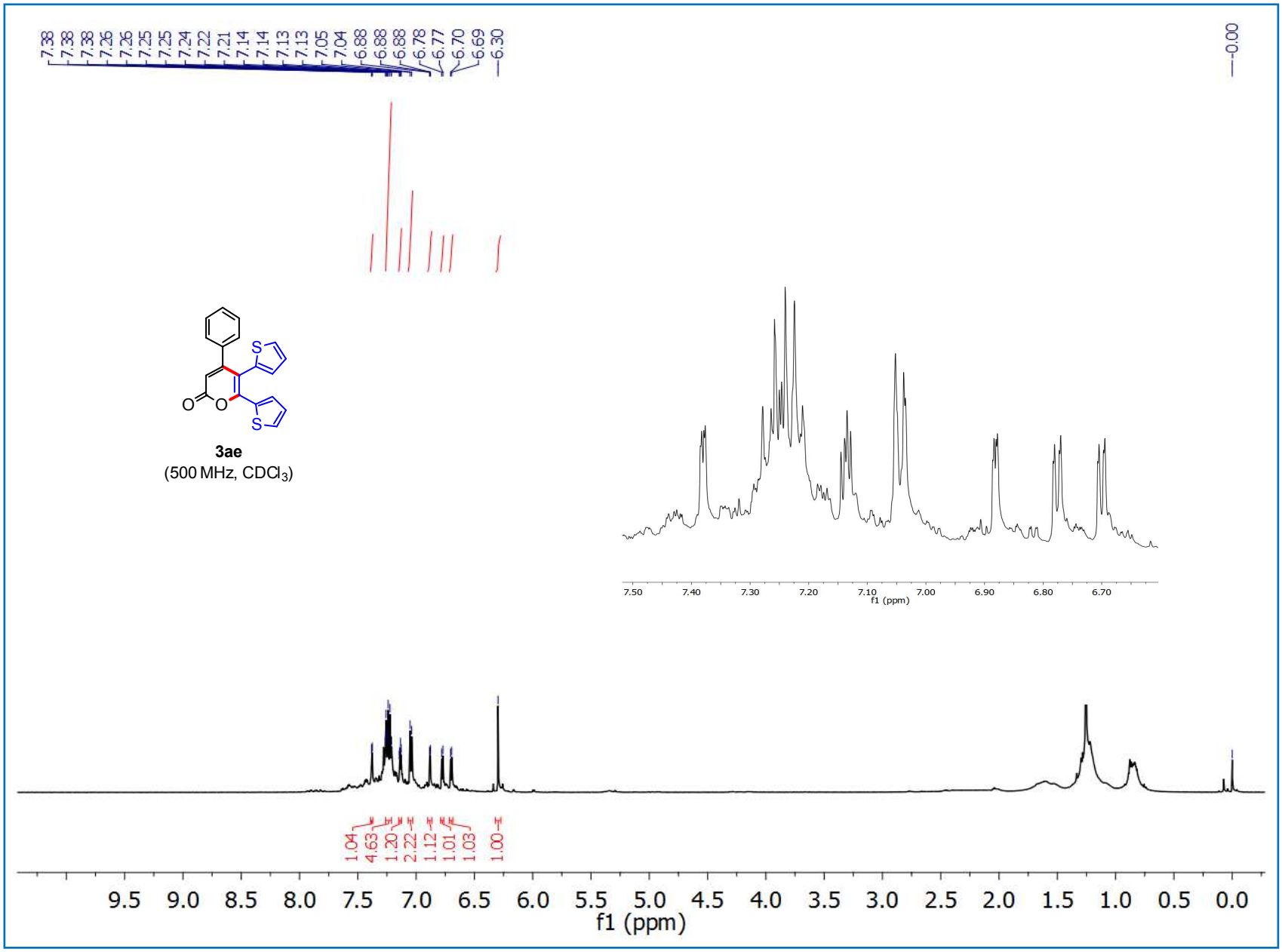
Chemical Shift (ppm)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7.13
7.13
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6.77
6.70
6.69
6.30
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S
S
O
O
3ae
(500 MHz, CDCl3)
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7.40
7.30
7.20
7.10
7.00
6.90
6.80
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f1 (ppm)
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4.63
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2.22
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1.00
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8.0
7.5
7.0
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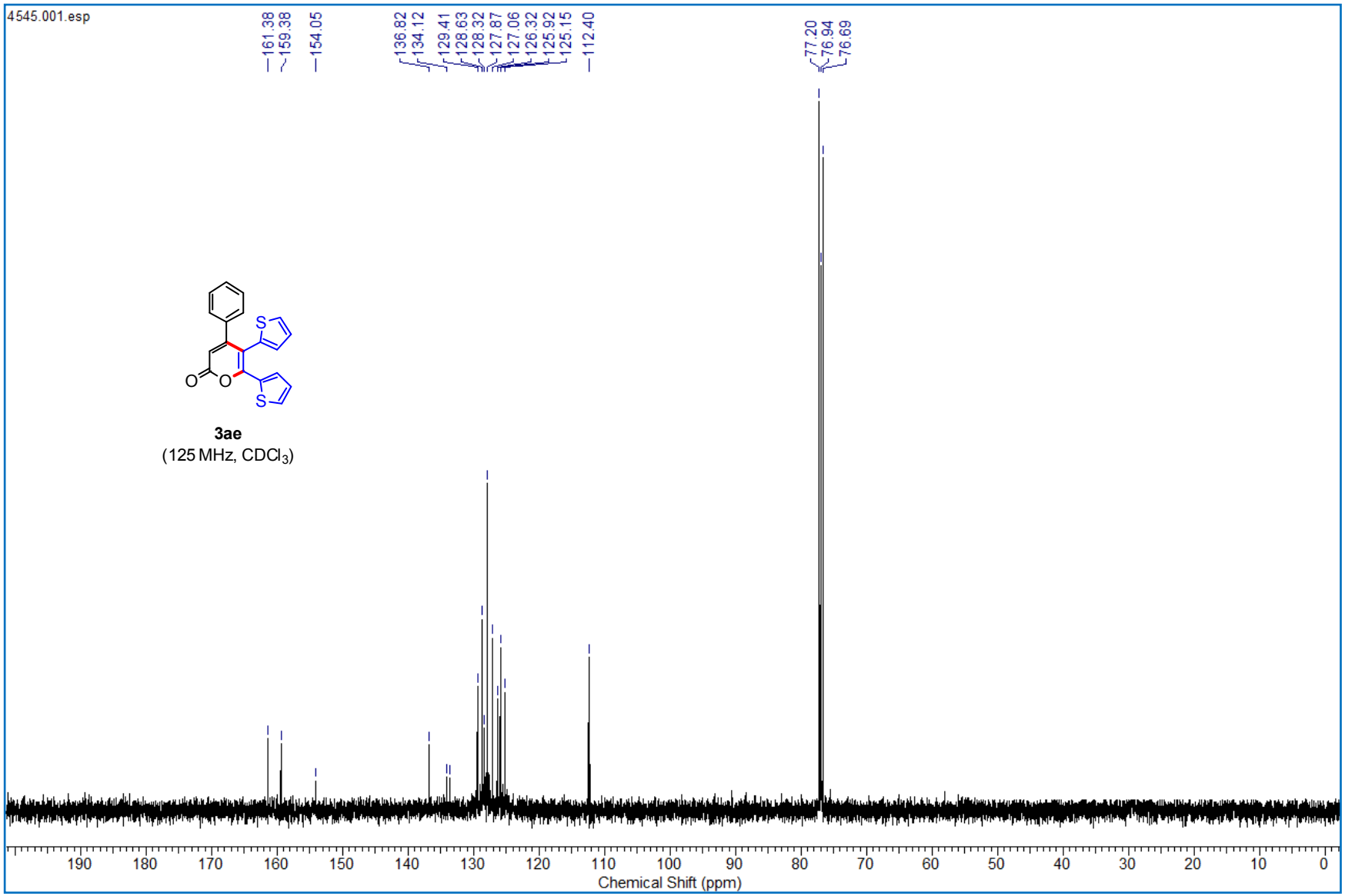
0.0
f1 (ppm)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112.40
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76.94
76.69
S
S
O
O
3ae
(125 MHz, CDCl3)
190
180
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90
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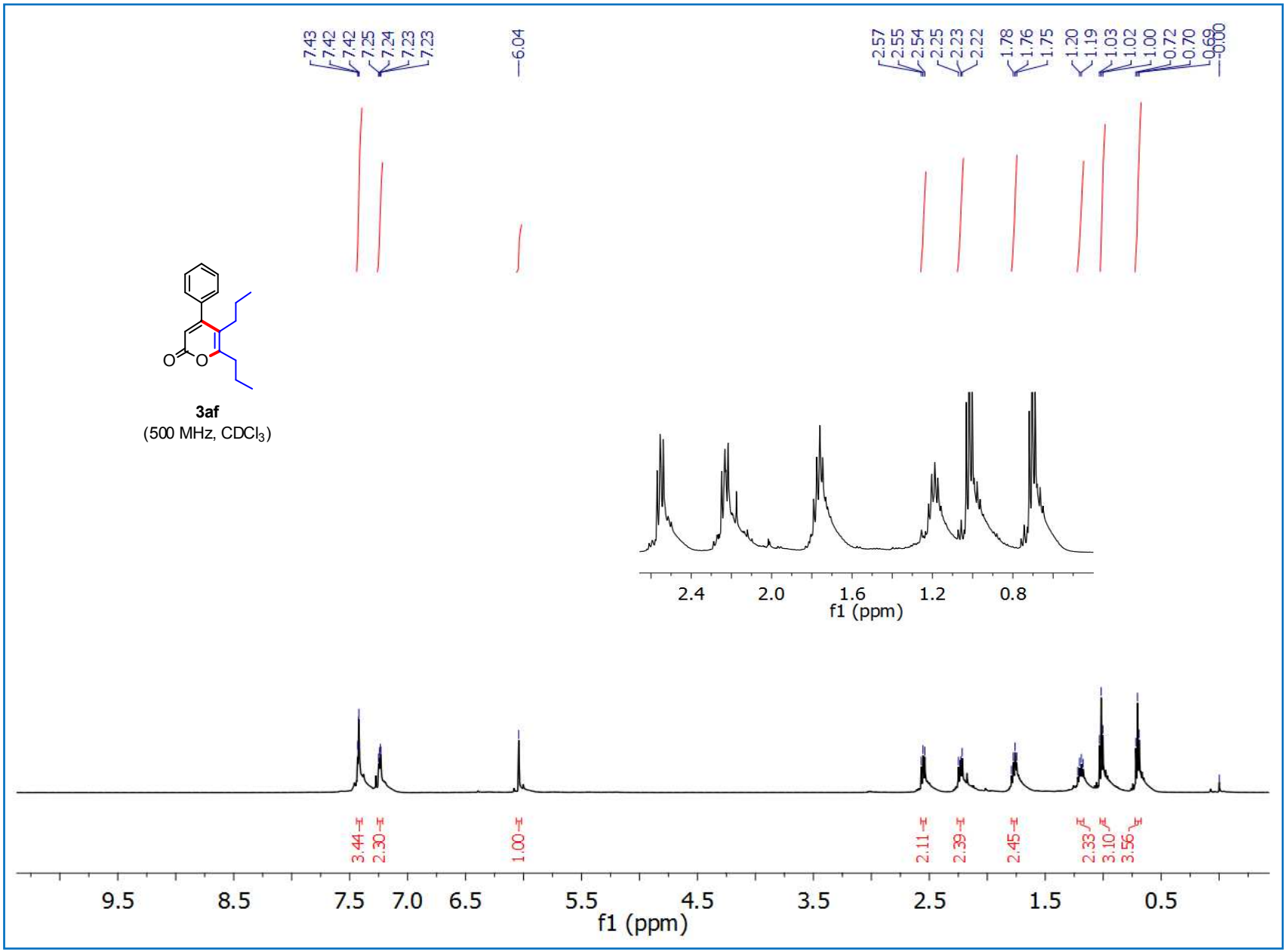
Chemical Shift (ppm)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2.22
1.78
1.76
1.75
1.20
1.19
1.03
1.02
1.00
0.72
0.70
0.69
0.00
3af
(500 MHz, CDCl3)
2.4
2.0
1.6
1.2
0.8
f1 (ppm)
3.44
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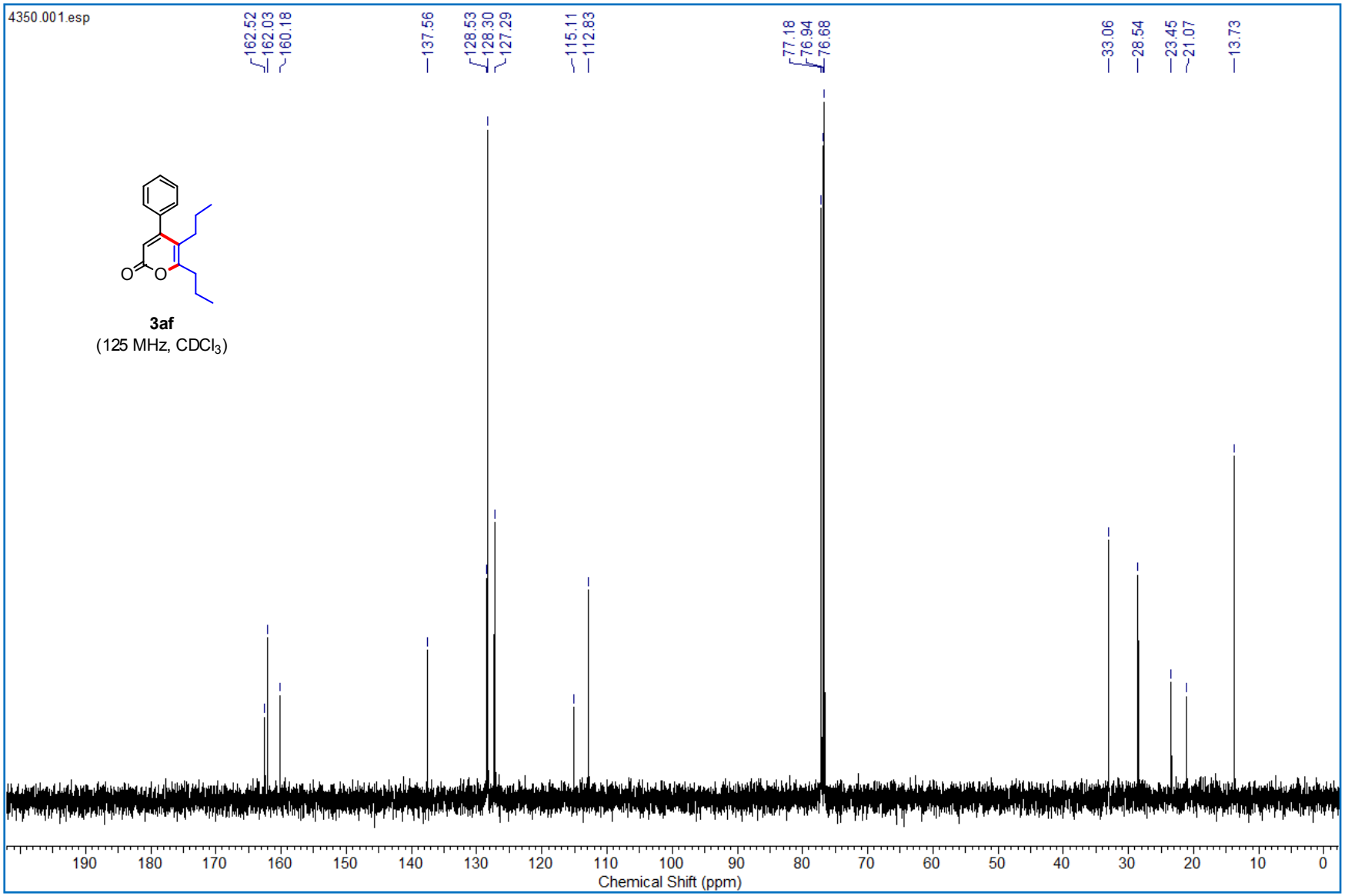
f1 (ppm)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76.68
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28.54
23.45
21.07
13.73
O
O
3af
(125 MHz, CDCl3)
190
180
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110
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40
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20
10
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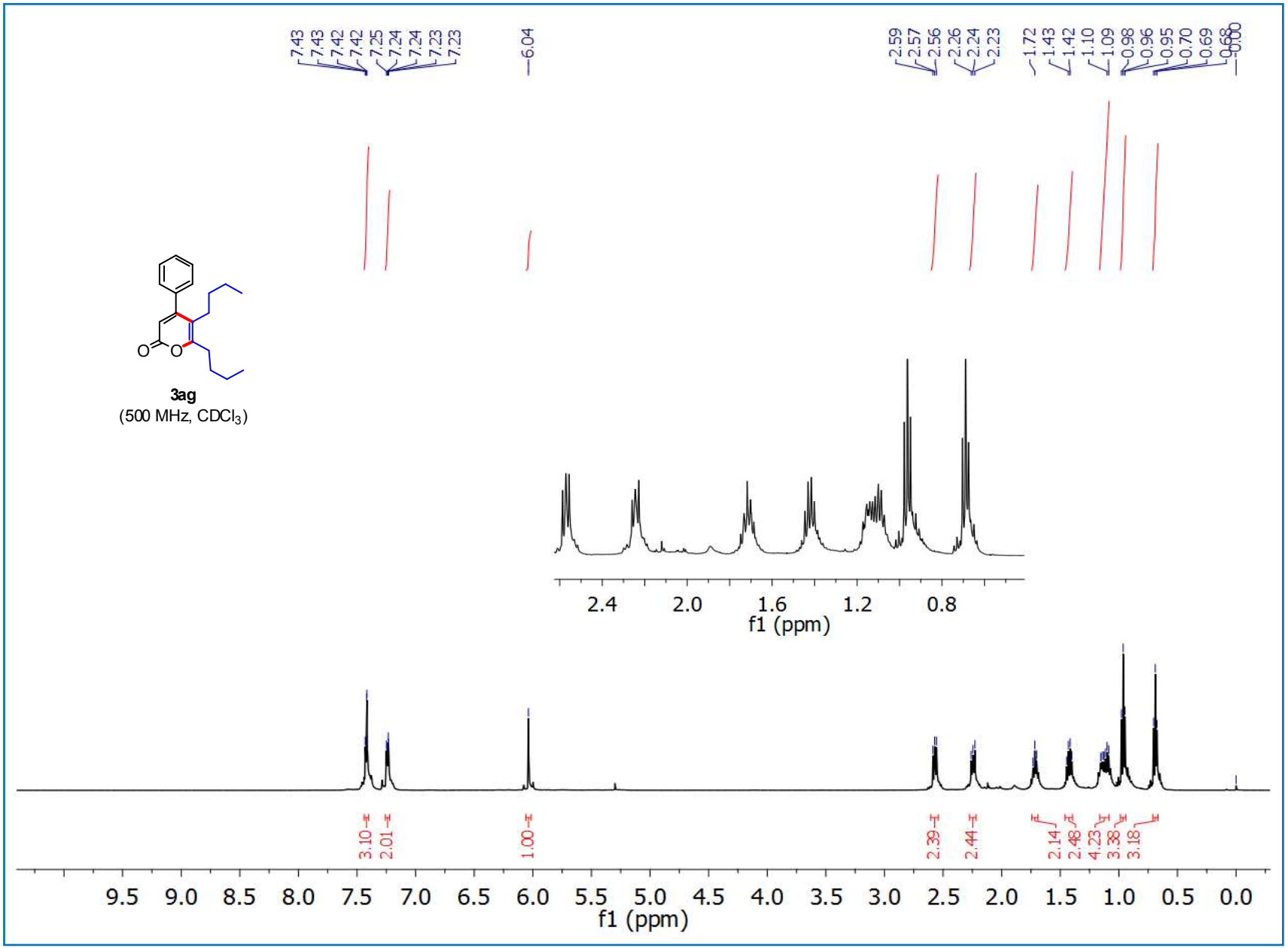
Chemical Shift (ppm)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7.23
6.04
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2.56
2.26
2.24
2.23
1.72
1.43
1.42
1.10
1.09
0.98
0.96
0.95
0.70
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0.68
0.00
O
O
3ag
(500 MHz, CDCl3)
2.4
2.0
1.6
1.2
0.8
f1 (ppm)
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2.01
1.00
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1.0
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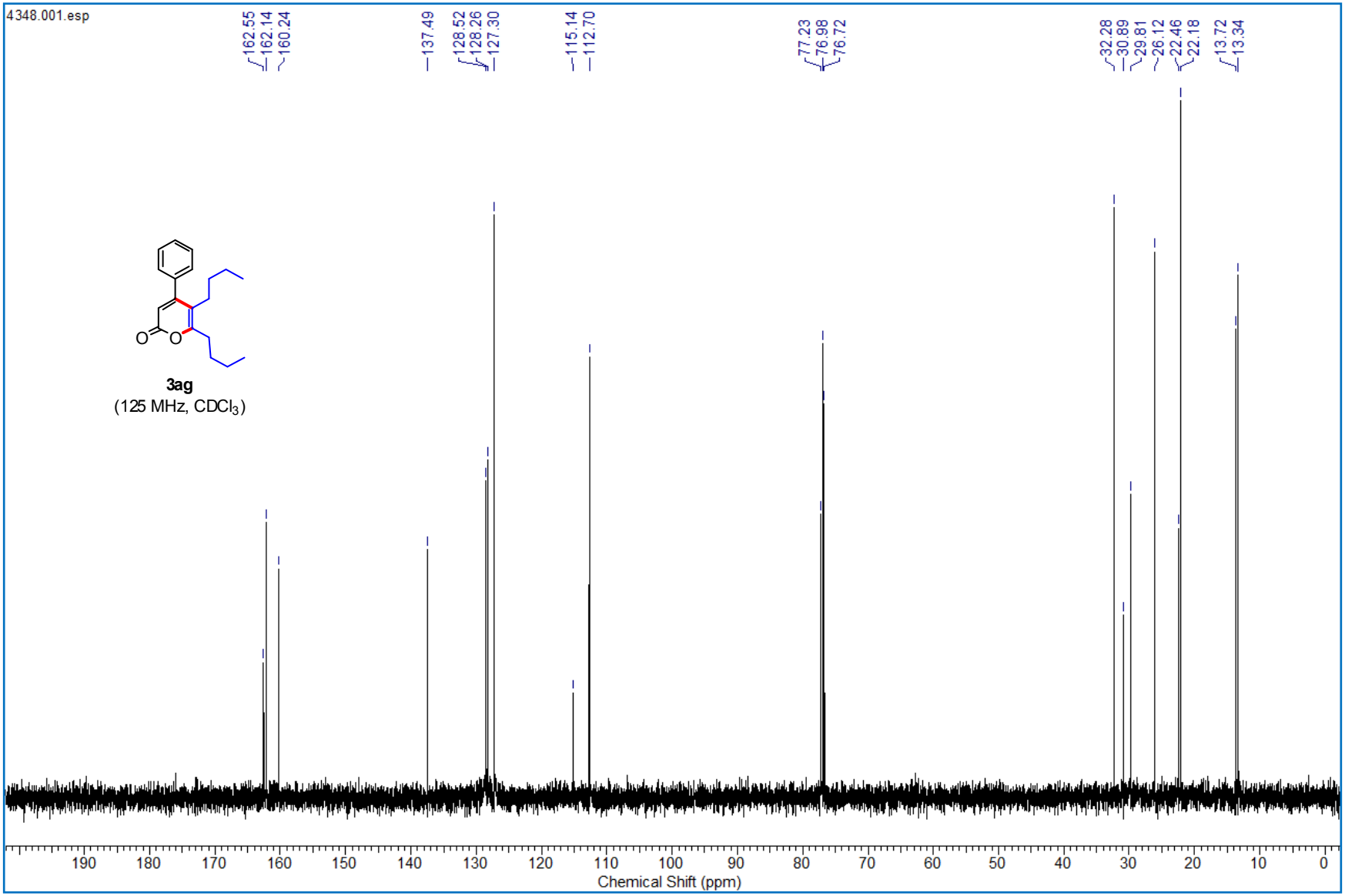
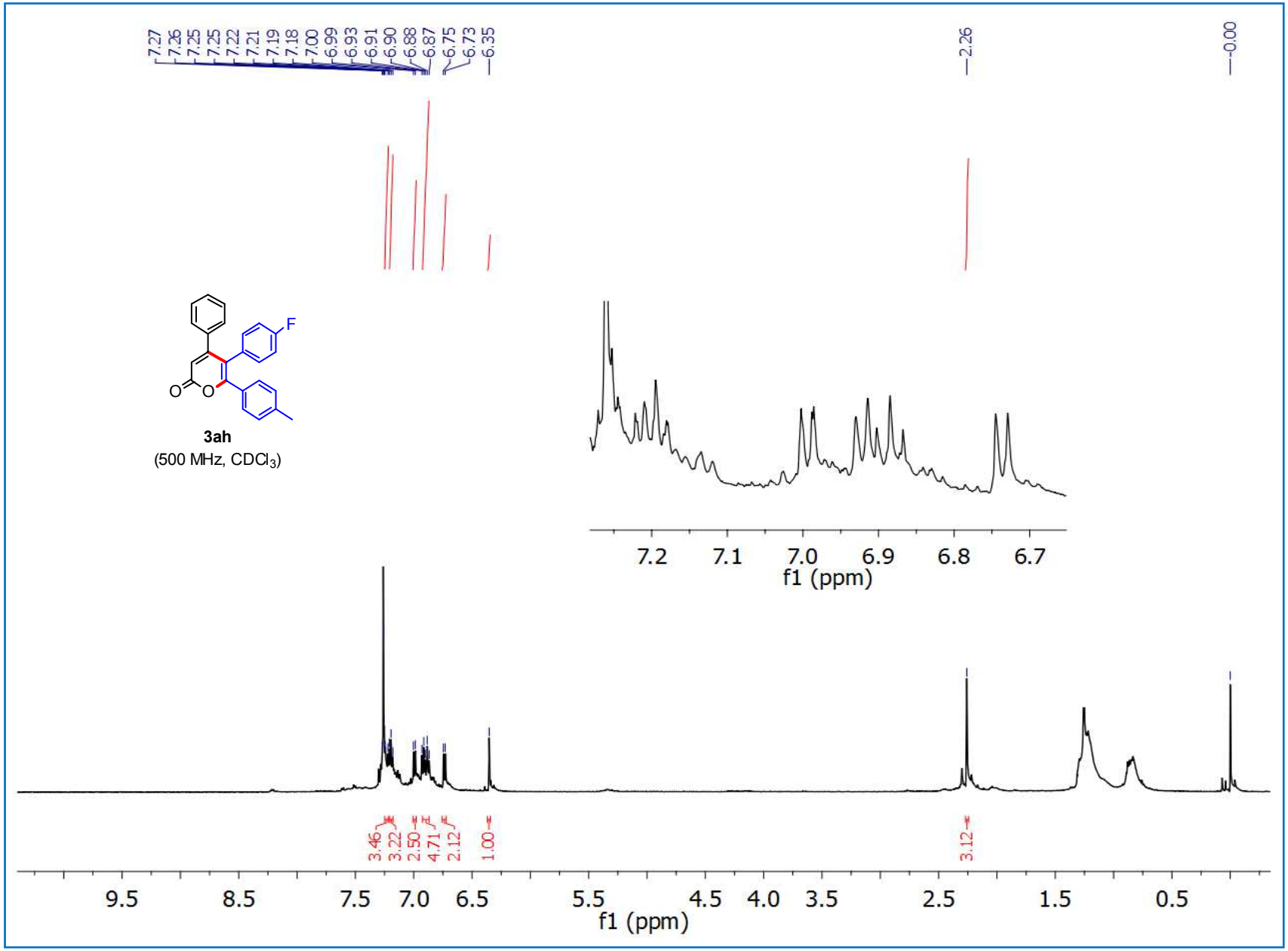
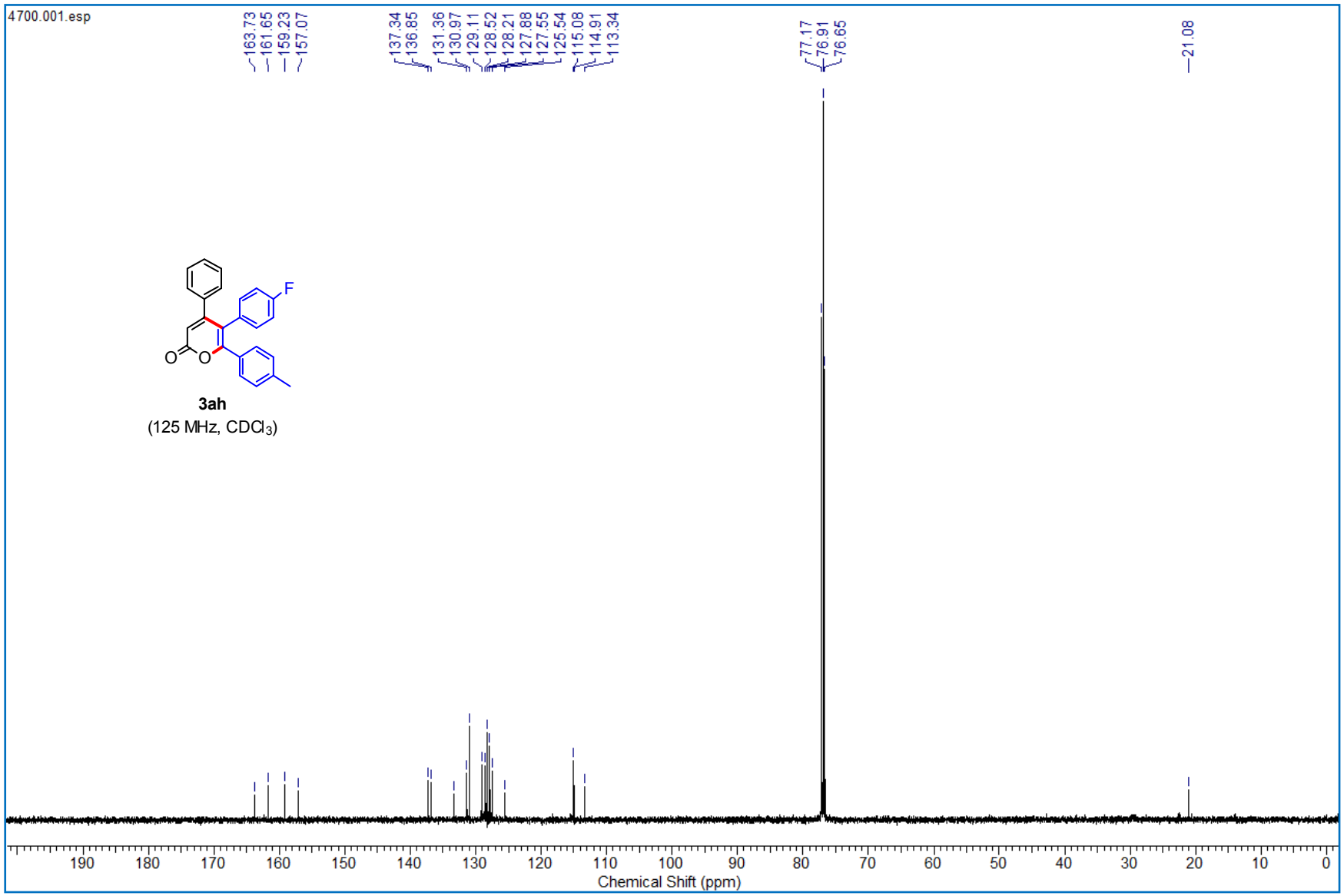
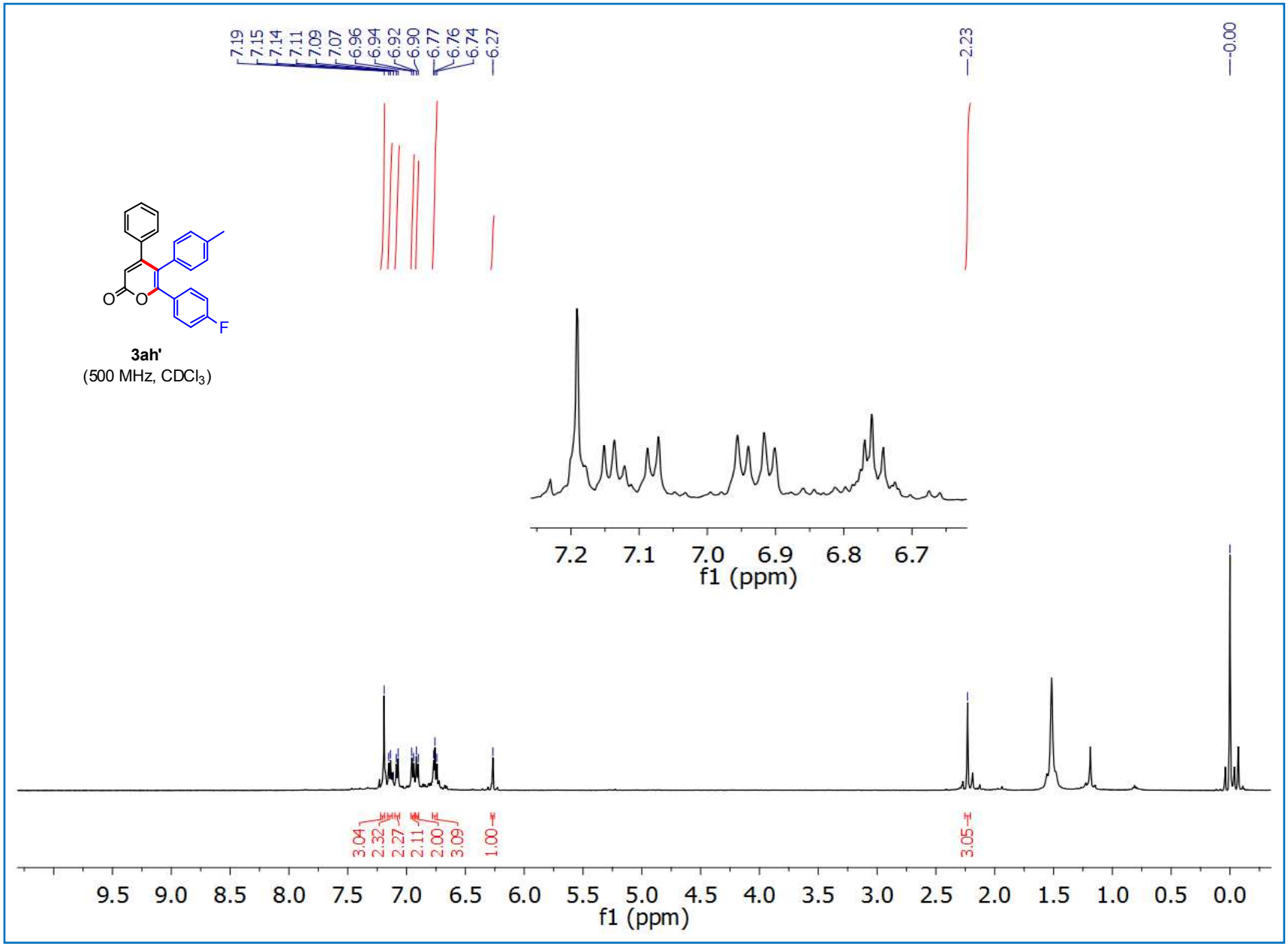
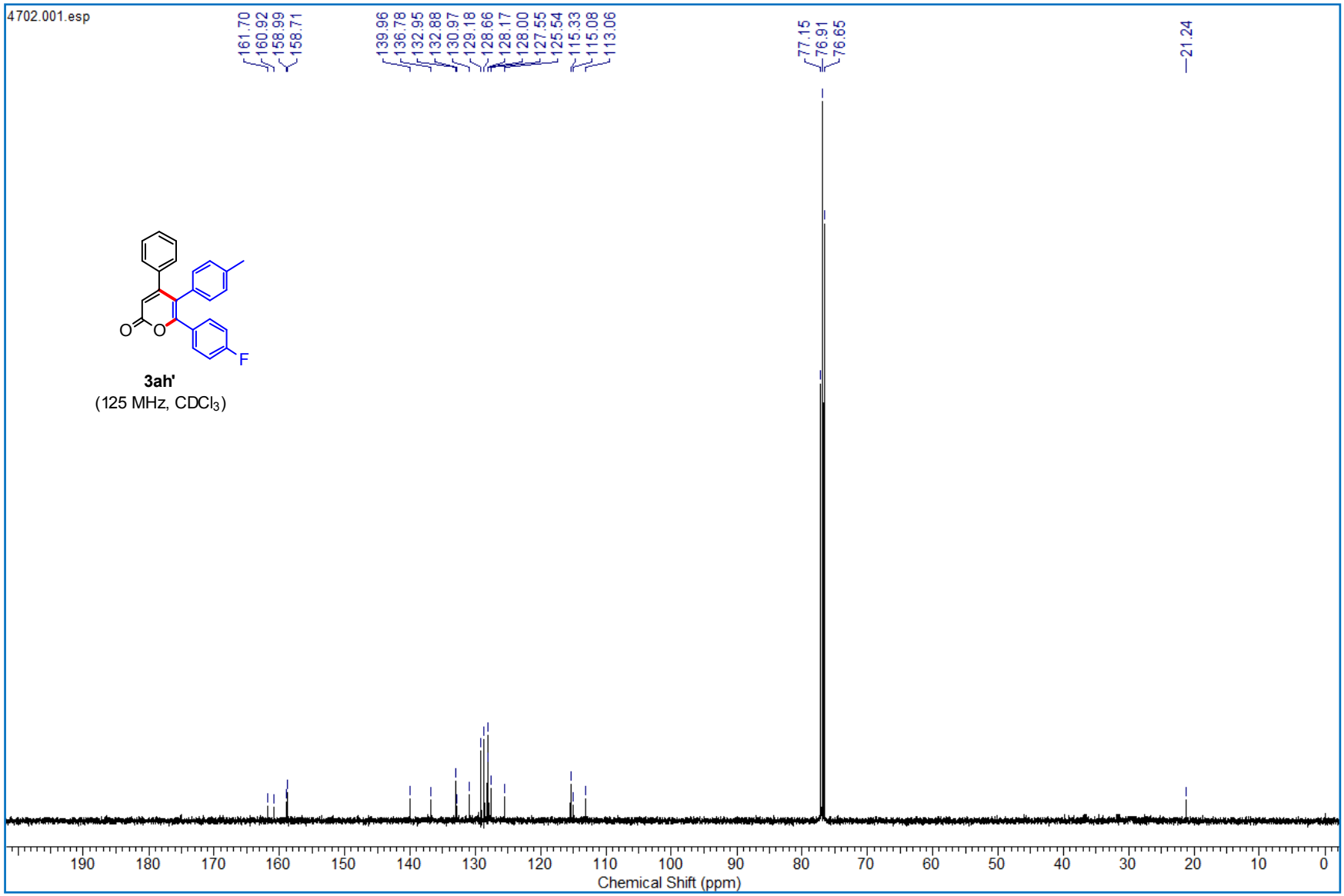
0.0
f1 (ppm)

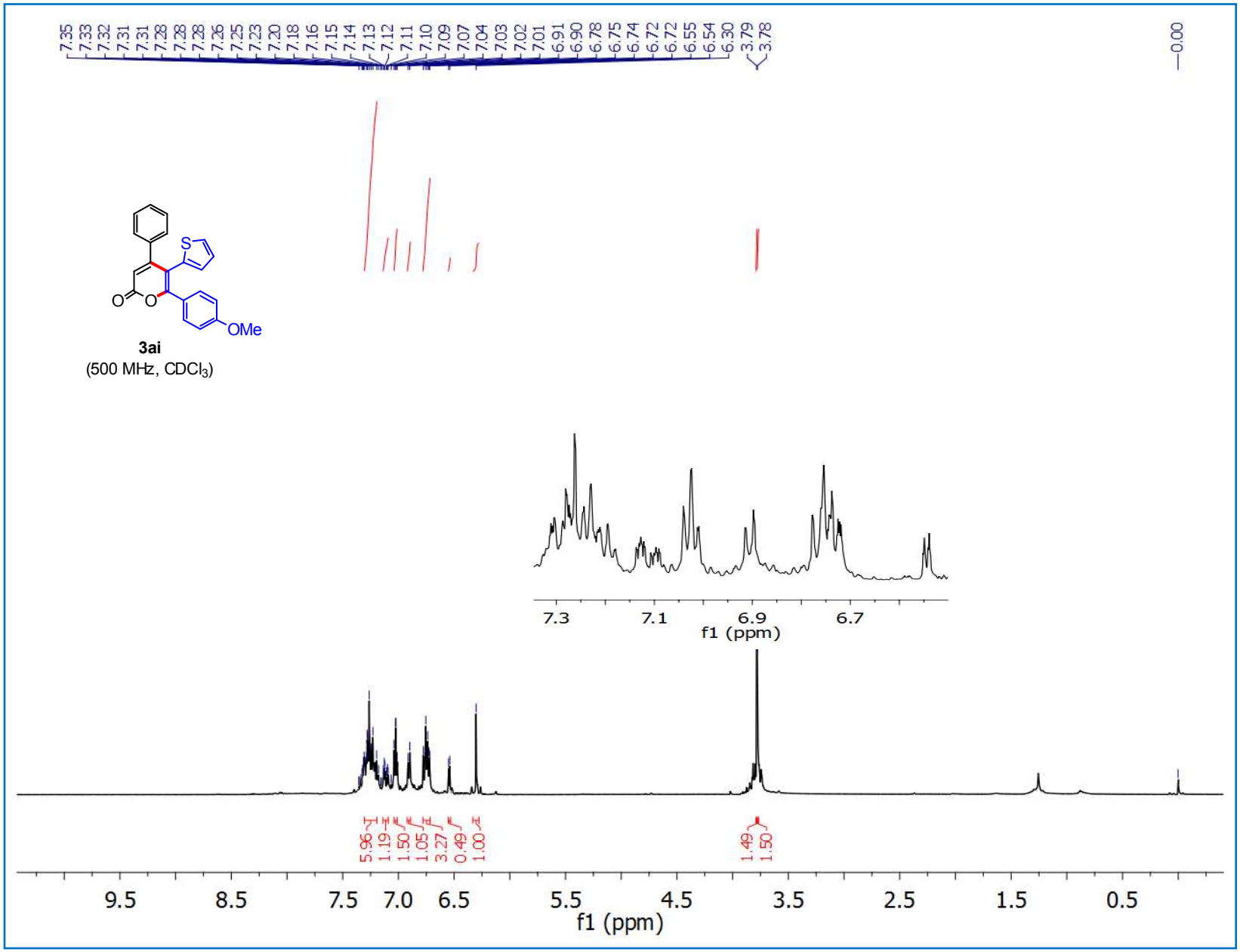

4348.001.esp
162.55
162.14
160.24
137.49
128.52
128.26
127.30
115.14
112.70
77.23
76.98
76.72
32.28
30.89
29.81
26.12
22.46
22.18
13.72
13.34
O
O
3ag
(125 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

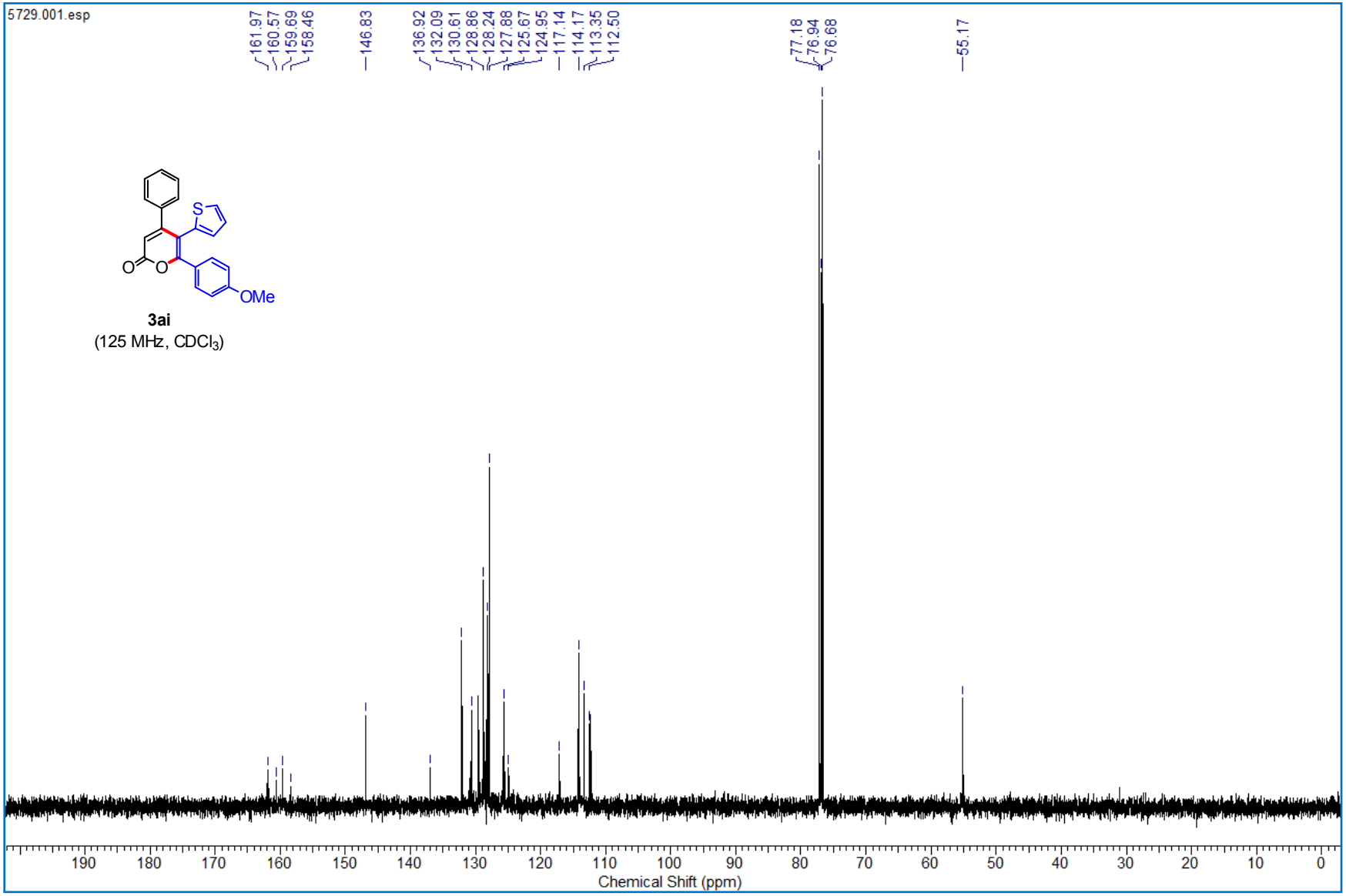

7.27
7.26
7.25
7.25
7.22
7.21
7.19
7.18
7.00
6.99
6.93
6.91
6.90
6.88
6.87
6.75
6.73
6.35
2.26
0.00
F
O
O
3ah
(500 MHz, CDCl3)
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
3.46
3.22
2.50
4.71
2.12
1.00
3.12
9.5
8.5
7.5
7.0
6.5
5.5
4.5
4.0
3.5
2.5
1.5
0.5
f1 (ppm)


4700.001.esp
163.73
161.65
159.23
157.07
137.34
136.85
131.36
130.97
129.11
128.52
128.21
127.88
127.55
125.54
115.08
114.91
113.34
77.17
76.91
76.65
21.08
F
O
O
3ah
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

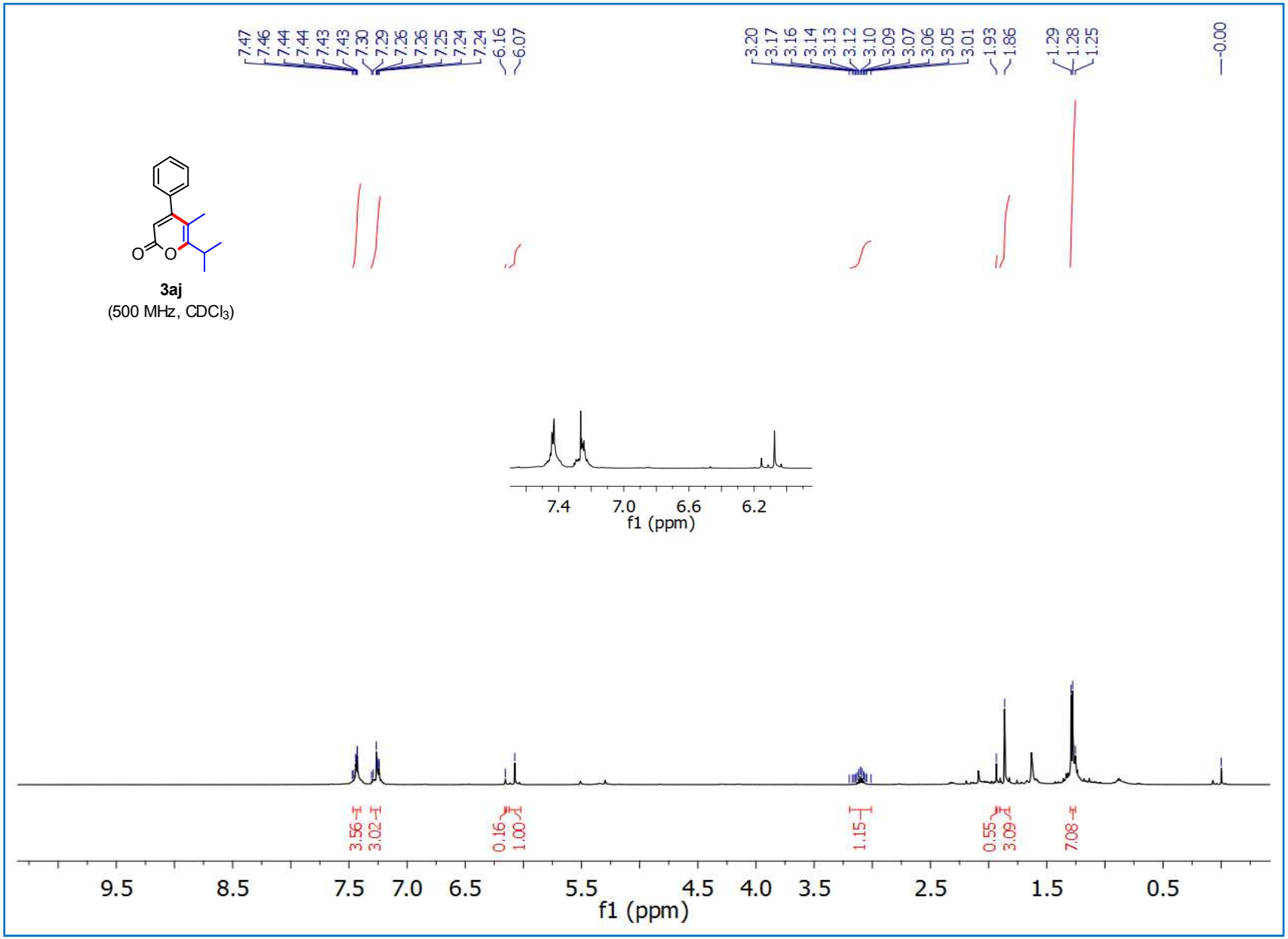

7.19
7.15
7.14
7.11
7.09
7.07
6.96
6.94
6.92
6.90
6.77
6.76
6.74
6.27
2.23
-0.00
O
O
F
3ah'
(500 MHz, CDCl3)
7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
3.04
2.32
2.27
2.11
2.00
3.09
1.00
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

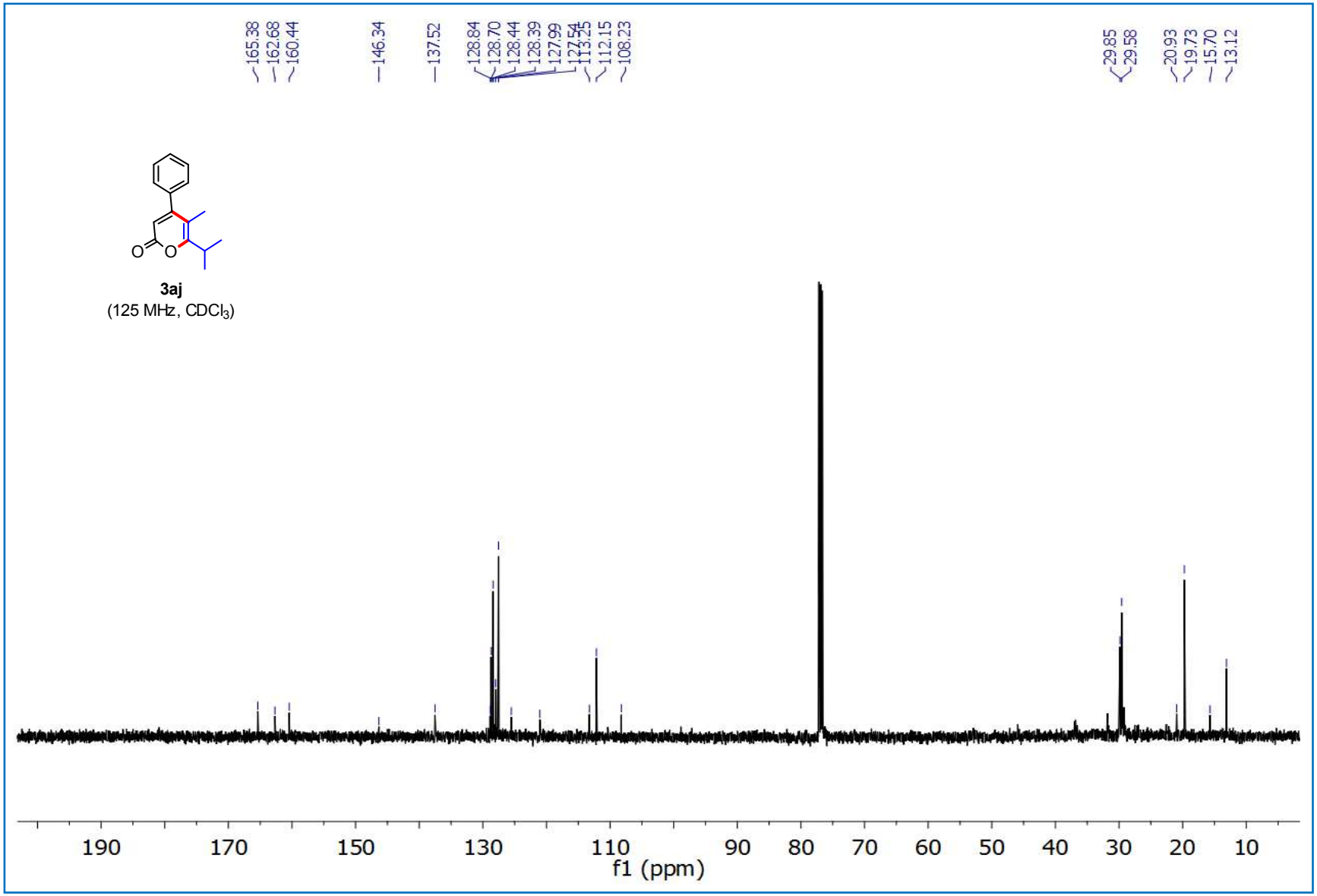

4702.001.esp
161.70
160.92
158.99
158.71
139.96
136.78
132.95
132.88
130.97
129.18
128.66
128.17
128.00
127.55
125.54
115.33
115.08
113.06
77.15
76.91
76.65
21.24
O
O
F
3ah'
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

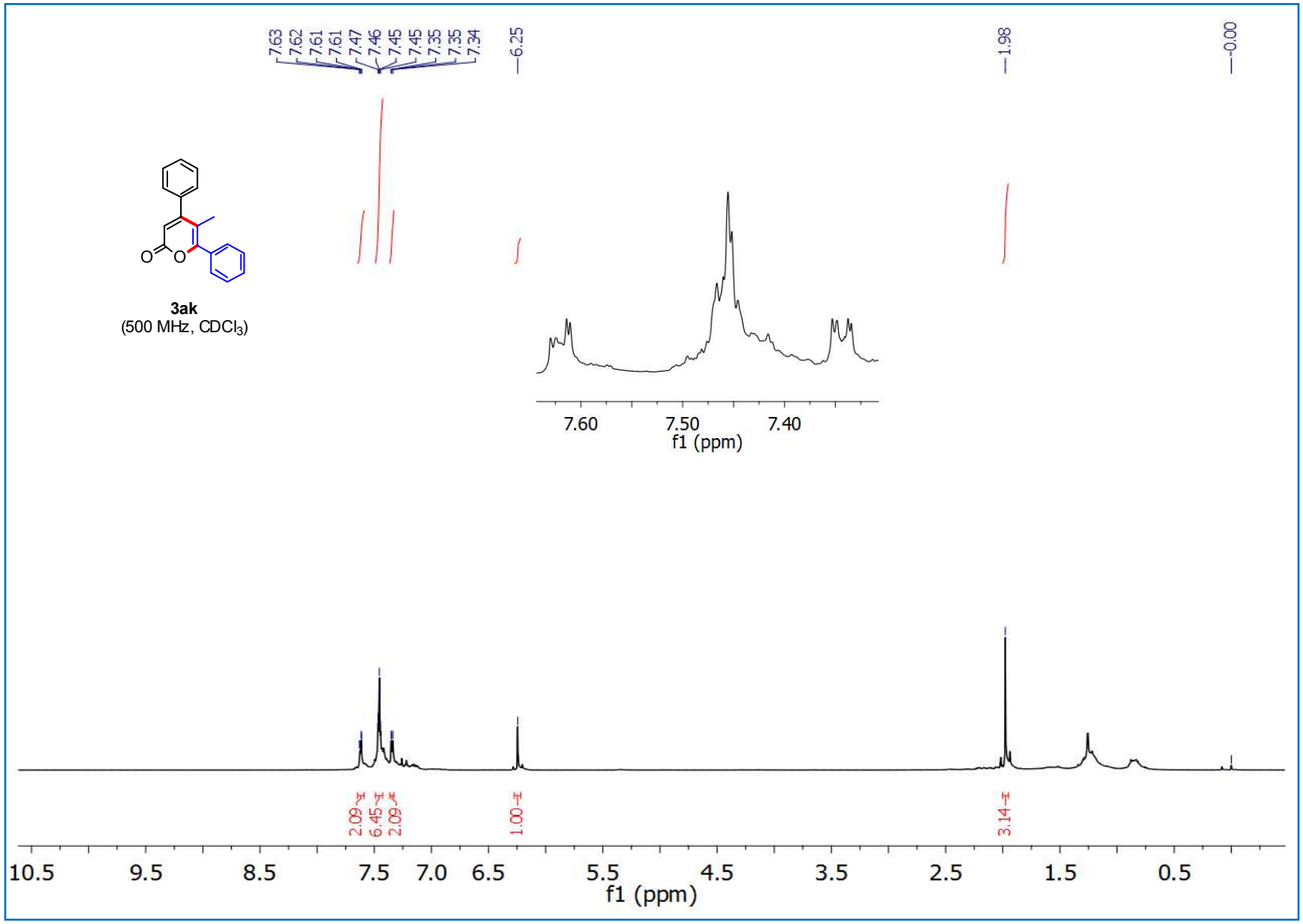

7.35 7.33 7.32 7.31 7.31 7.28 7.28 7.28 7.26 7.25 7.23 7.20 7.18 7.16 7.15 7.14 7.13 7.12 7.11 7.10 7.09 7.07 7.04 7.03 7.02 7.01 6.91 6.90 6.78 6.75 6.74 6.72 6.72 6.55 6.54 6.30 3.79 3.78
0.00
S
O
O
OMe
3ai
(500 MHz, CDCl3)
7.3 7.1 6.9 6.7
f1 (ppm)
5.96 1.19 1.50 1.05 3.27 0.49 1.00
1.49 1.50
9.5 8.5 7.5 7.0 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

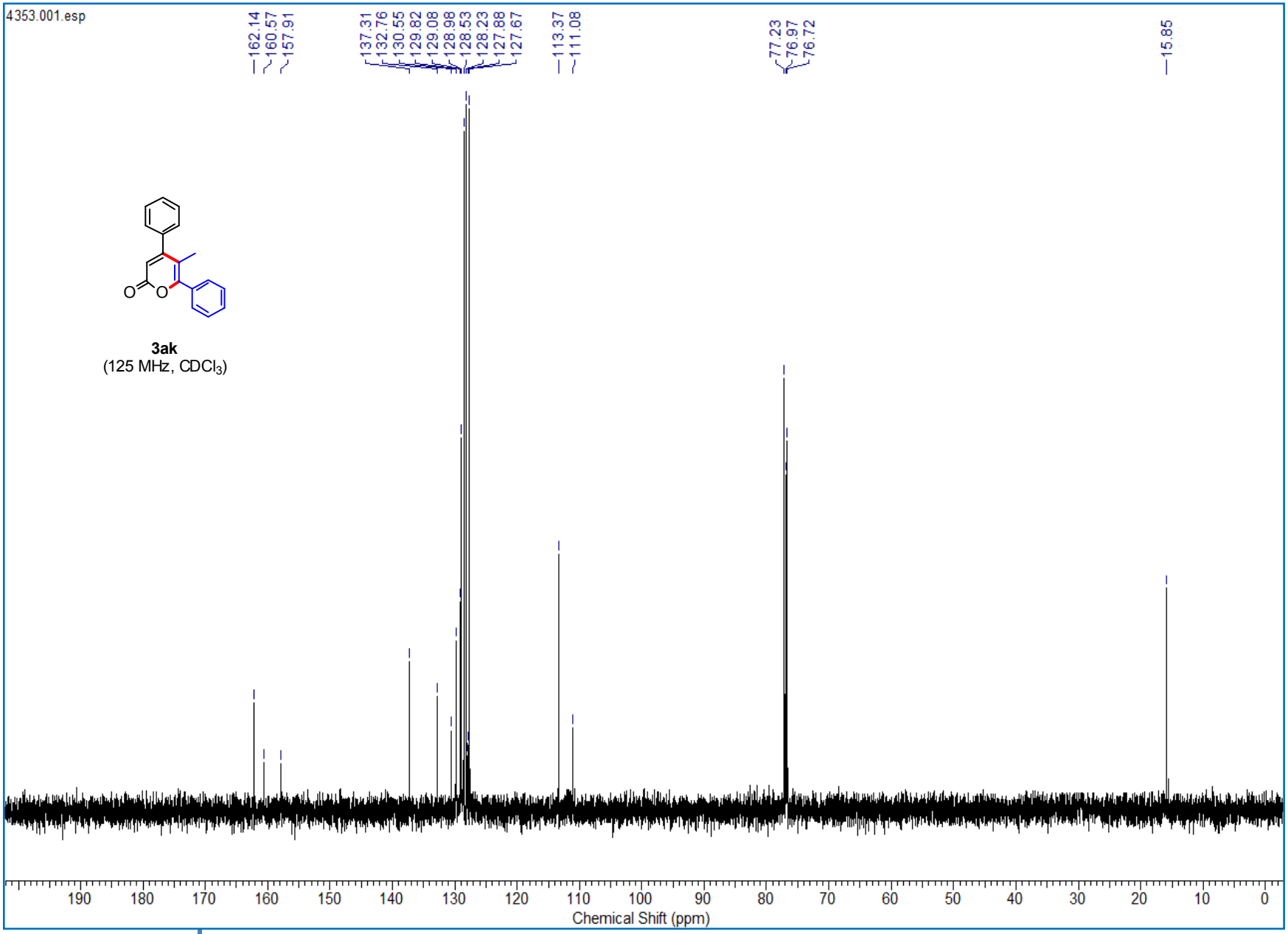


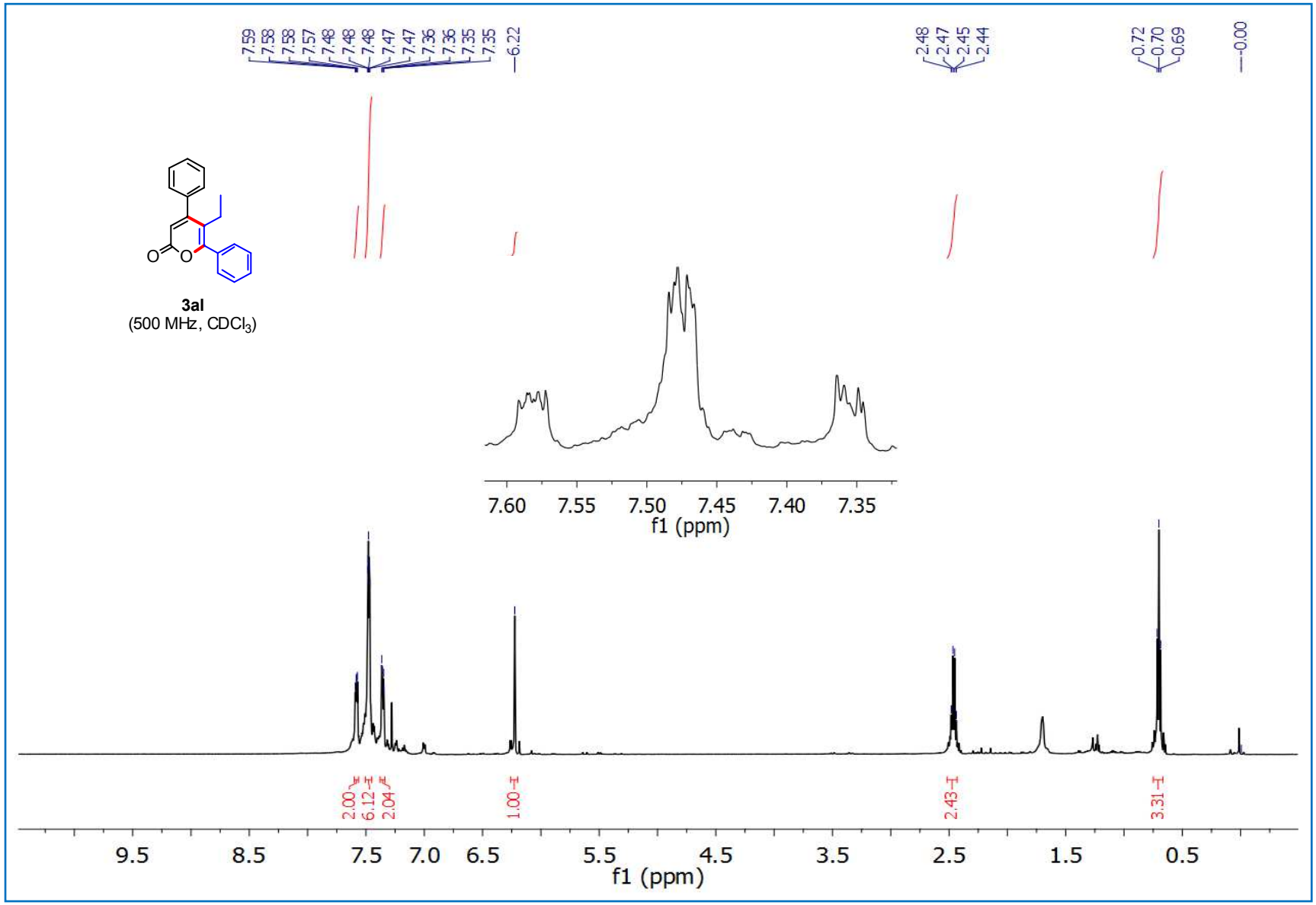
3ai
(125 MHz, $CDCl_3$)

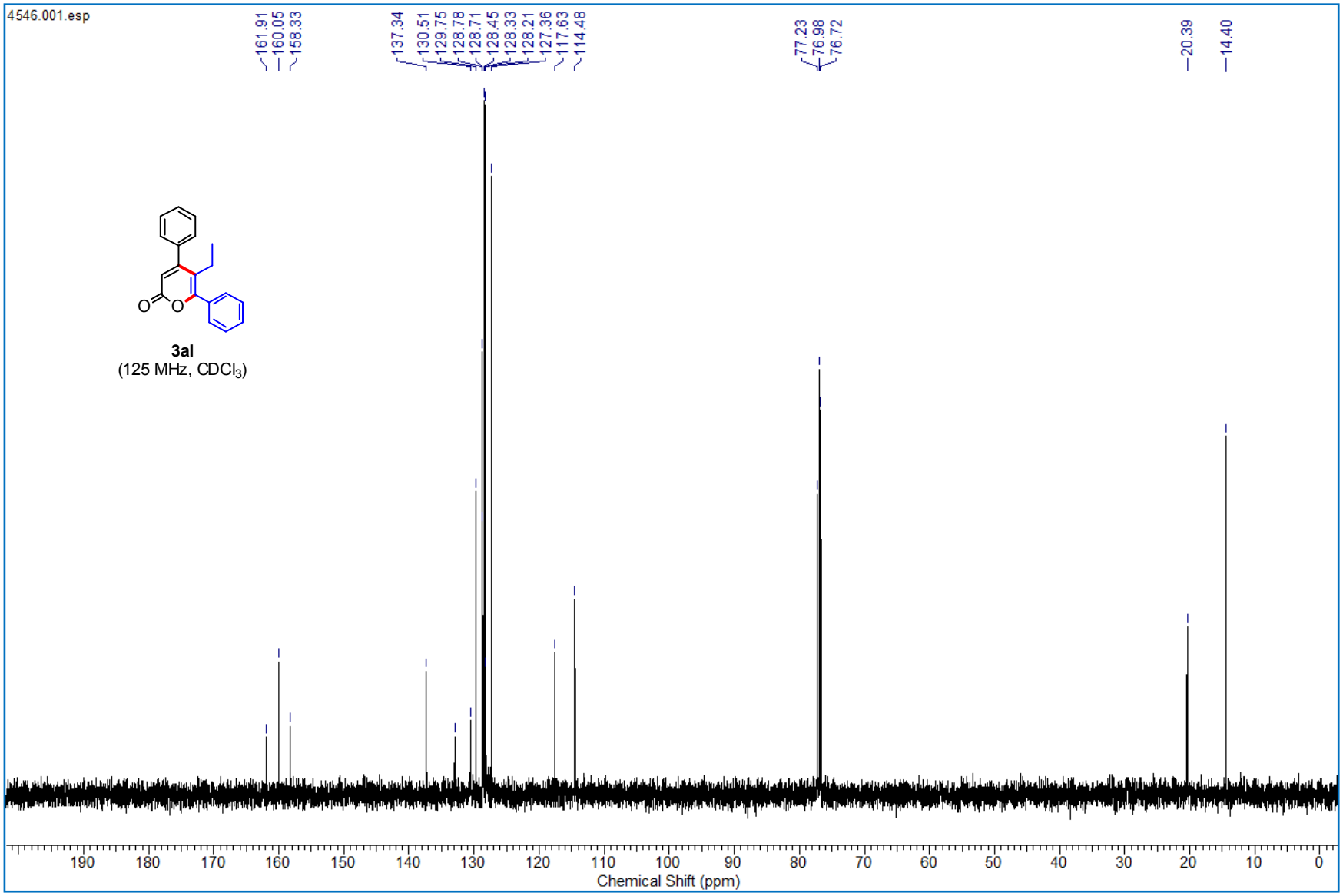

7.47
7.46
7.44
7.44
7.43
7.43
7.30
7.29
7.26
7.26
7.25
7.24
7.24
6.16
6.07
3.20
3.17
3.16
3.14
3.13
3.12
3.10
3.09
3.07
3.06
3.05
3.01
1.93
1.86
1.29
1.28
1.25
0.00
3aj
(500 MHz, CDCl3)
7.4
7.0
6.6
6.2
f1 (ppm)
3.56
3.02
0.16
1.00
1.15
0.55
3.09
7.08
9.5
8.5
7.5
7.0
6.5
5.5
4.5
4.0
3.5
2.5
1.5
0.5
f1 (ppm)

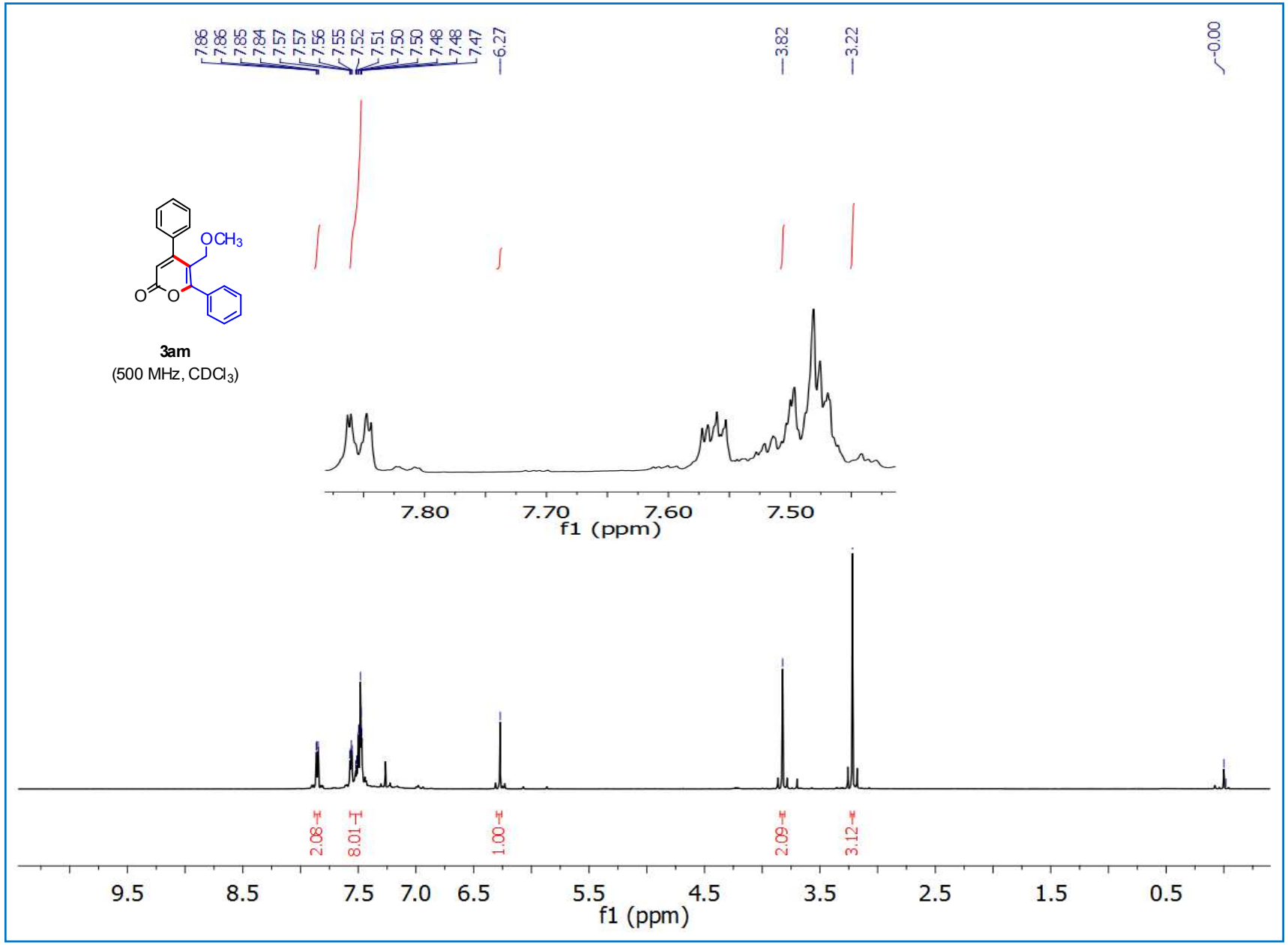

165.38
162.68
160.44
146.34
137.52
128.84
128.70
128.44
128.39
127.99
127.54
113.25
112.15
108.23
29.85
29.58
20.93
19.73
15.70
13.12
O
O
3aj
(125 MHz, CDCl3)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

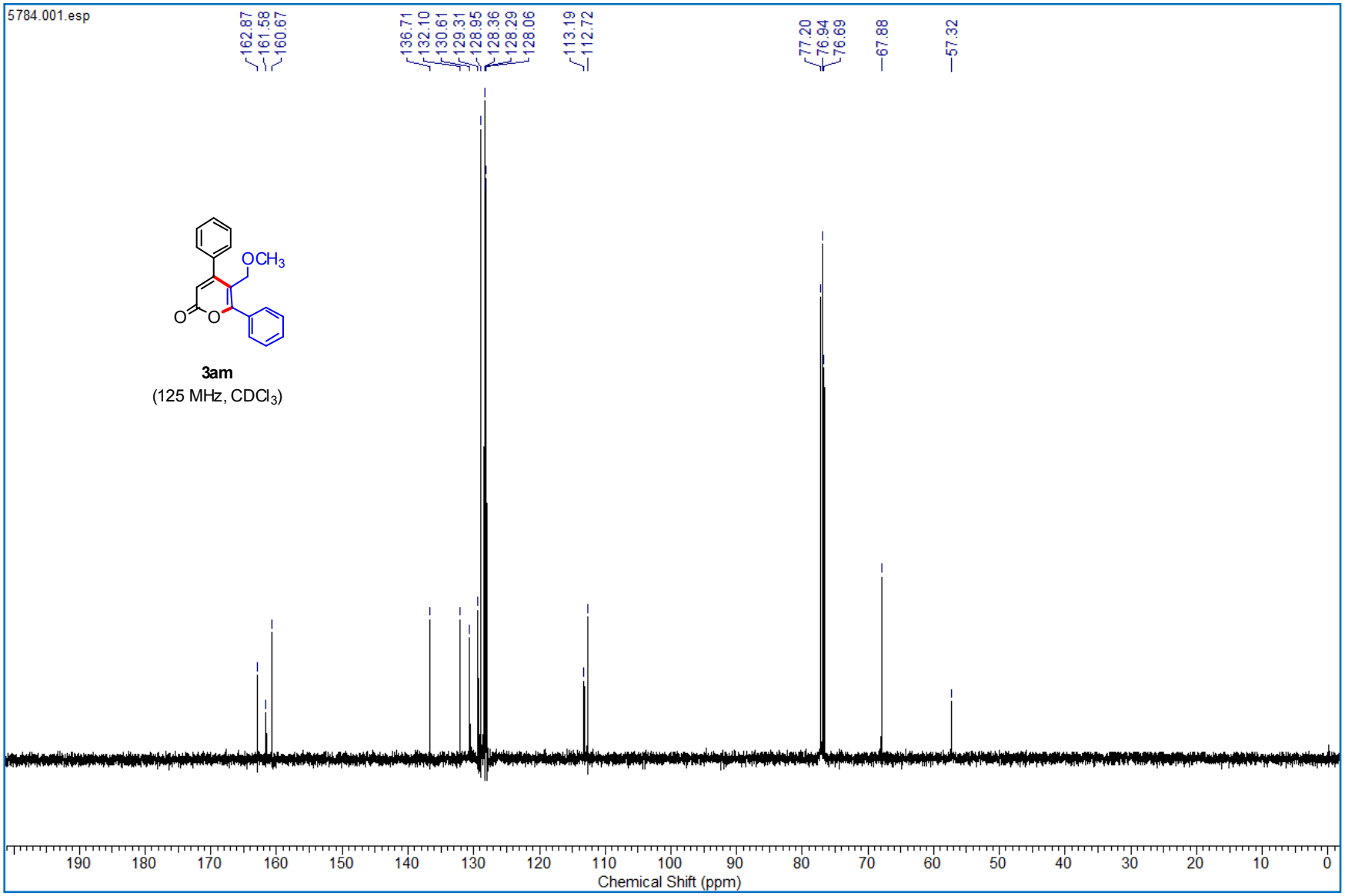

7.63
7.62
7.61
7.61
7.47
7.46
7.45
7.45
7.35
7.35
7.34
6.25
1.98
0.00
3ak
(500 MHz, CDCl3)
7.60
7.50
7.40
f1 (ppm)
2.09
6.45
2.09
1.00
3.14
10.5
9.5
8.5
7.5
7.0
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

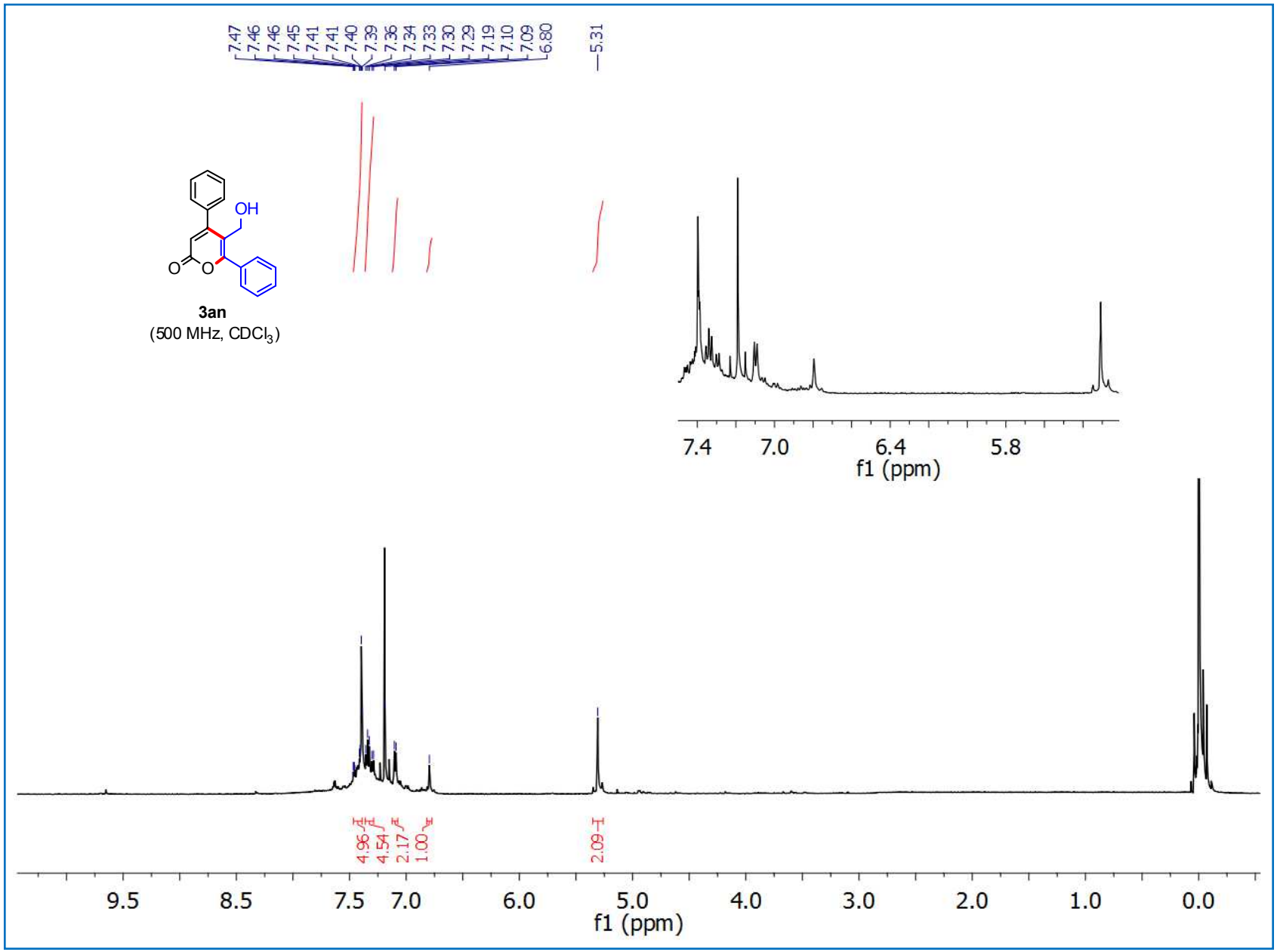

4353.001.esp
162.14
160.57
157.91
137.31
132.76
130.55
129.82
129.08
128.98
128.53
128.23
127.88
127.67
113.37
111.08
77.23
76.97
76.72
15.85
O
O
3ak
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

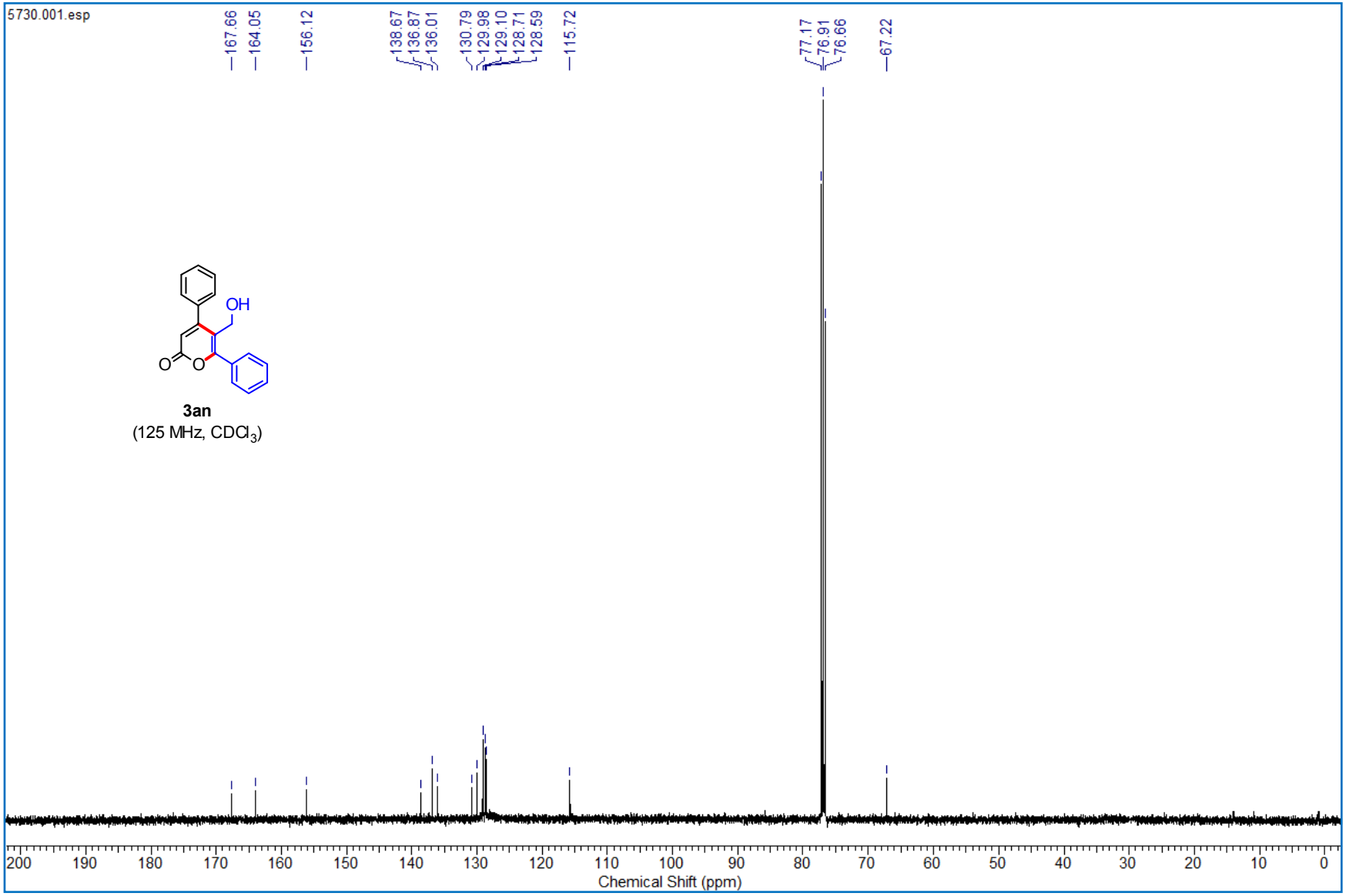

7.59
7.58
7.58
7.57
7.48
7.48
7.48
7.47
7.47
7.36
7.36
7.35
7.35
6.22
2.48
2.47
2.45
2.44
0.72
0.70
0.69
-0.00
O
O
3al
(500 MHz, CDCl3)
7.60
7.55
7.50
7.45
7.40
7.35
f1 (ppm)
2.00
6.12
2.04
1.00
2.43
3.31
9.5
8.5
7.5
7.0
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

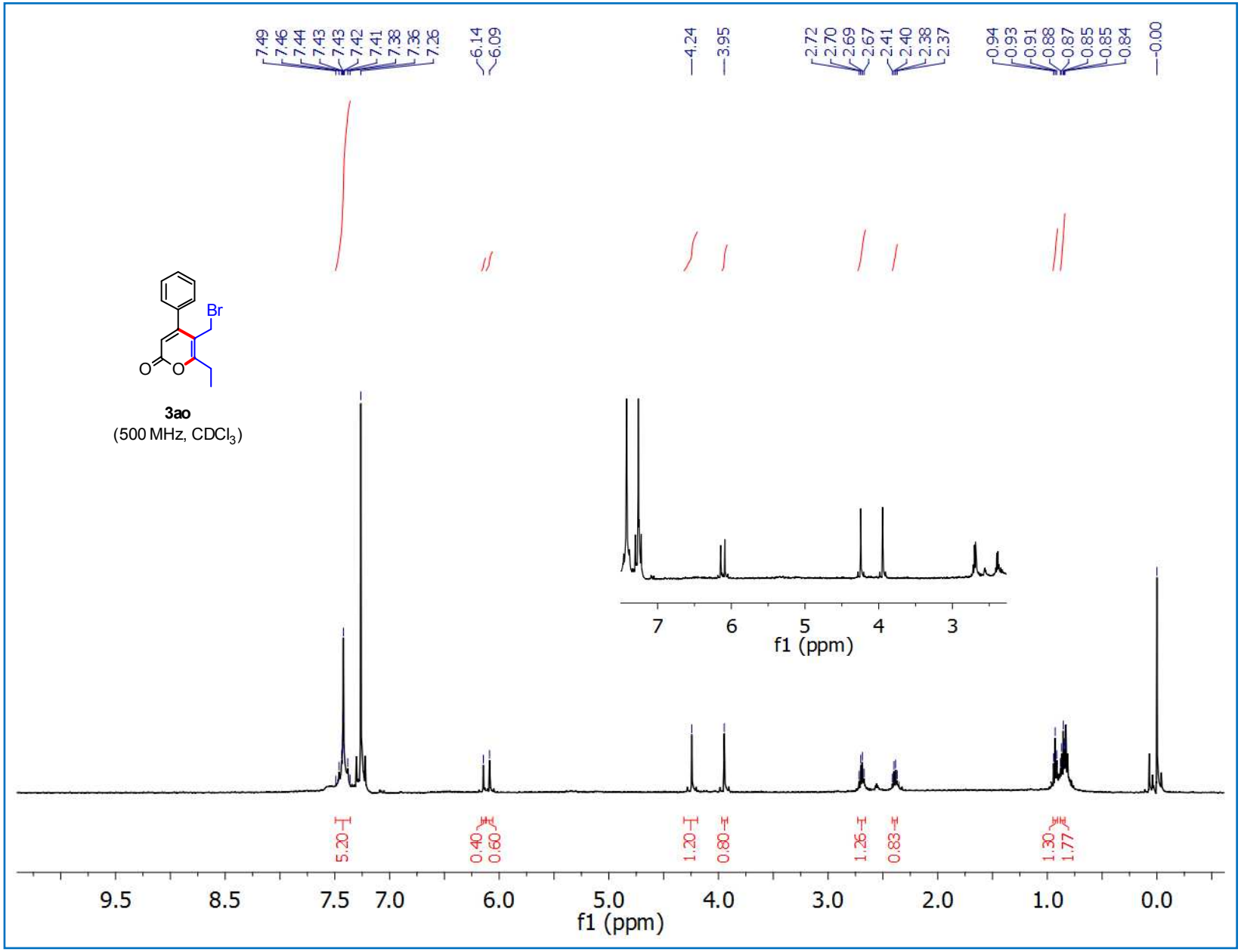

4546.001.esp
161.91
160.05
158.33
137.34
130.51
129.75
128.78
128.71
128.45
128.33
128.21
127.36
117.63
114.48
77.23
76.98
76.72
20.39
14.40
O
O
3al
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

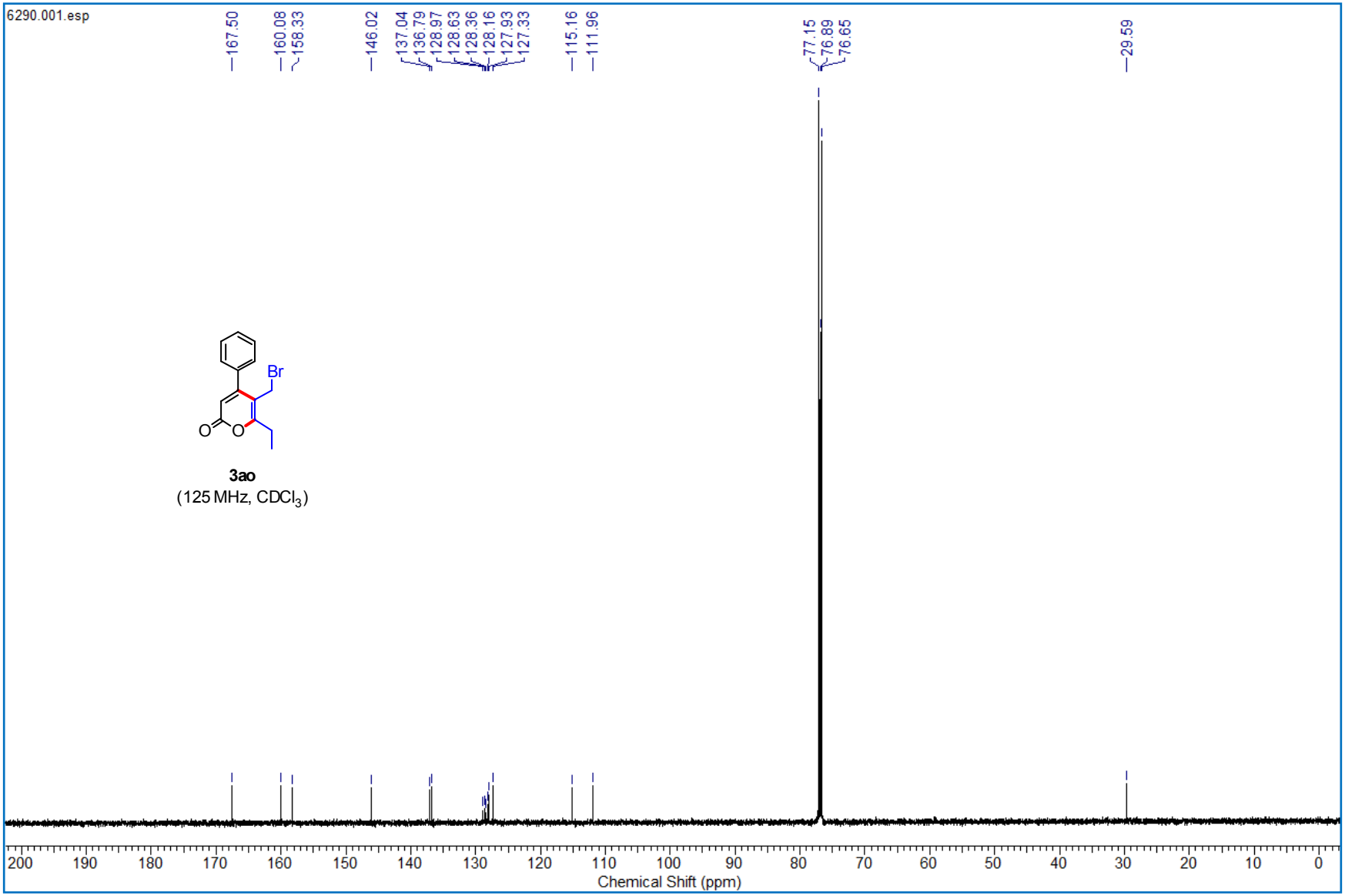

7.86
7.86
7.85
7.84
7.57
7.57
7.56
7.55
7.52
7.51
7.50
7.50
7.48
7.48
7.47
6.27
3.82
3.22
0.00
OCH3
O
O
3am
(500 MHz, CDCl3)
7.80
7.70
7.60
7.50
f1 (ppm)
2.08
8.01
1.00
2.09
3.12
9.5
8.5
7.5
7.0
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

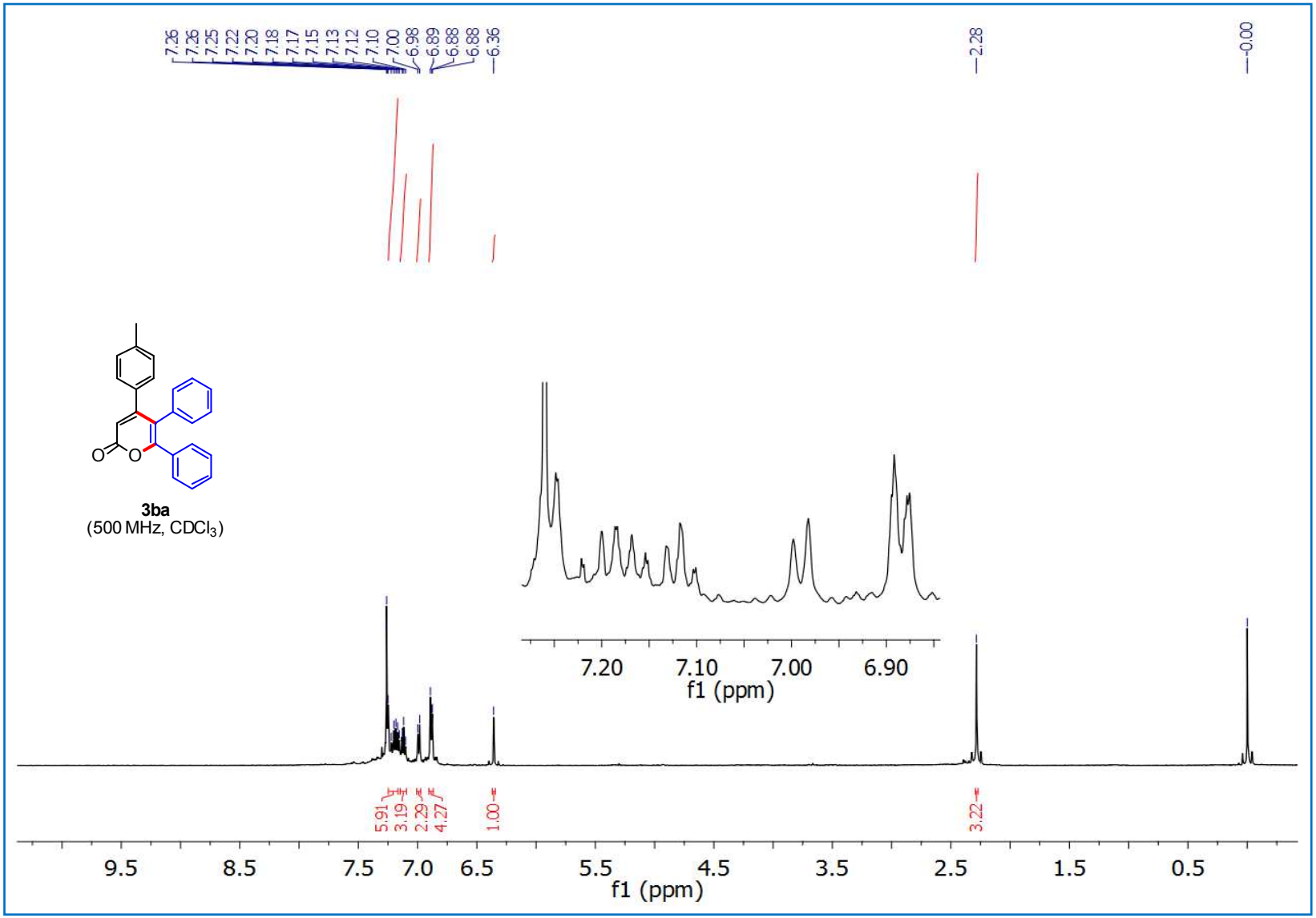

5784.001.esp
162.87
161.58
160.67
136.71
132.10
130.61
129.31
128.95
128.36
128.29
128.06
113.19
112.72
77.20
76.94
76.69
67.88
57.32
OCH3
O
O
3am
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

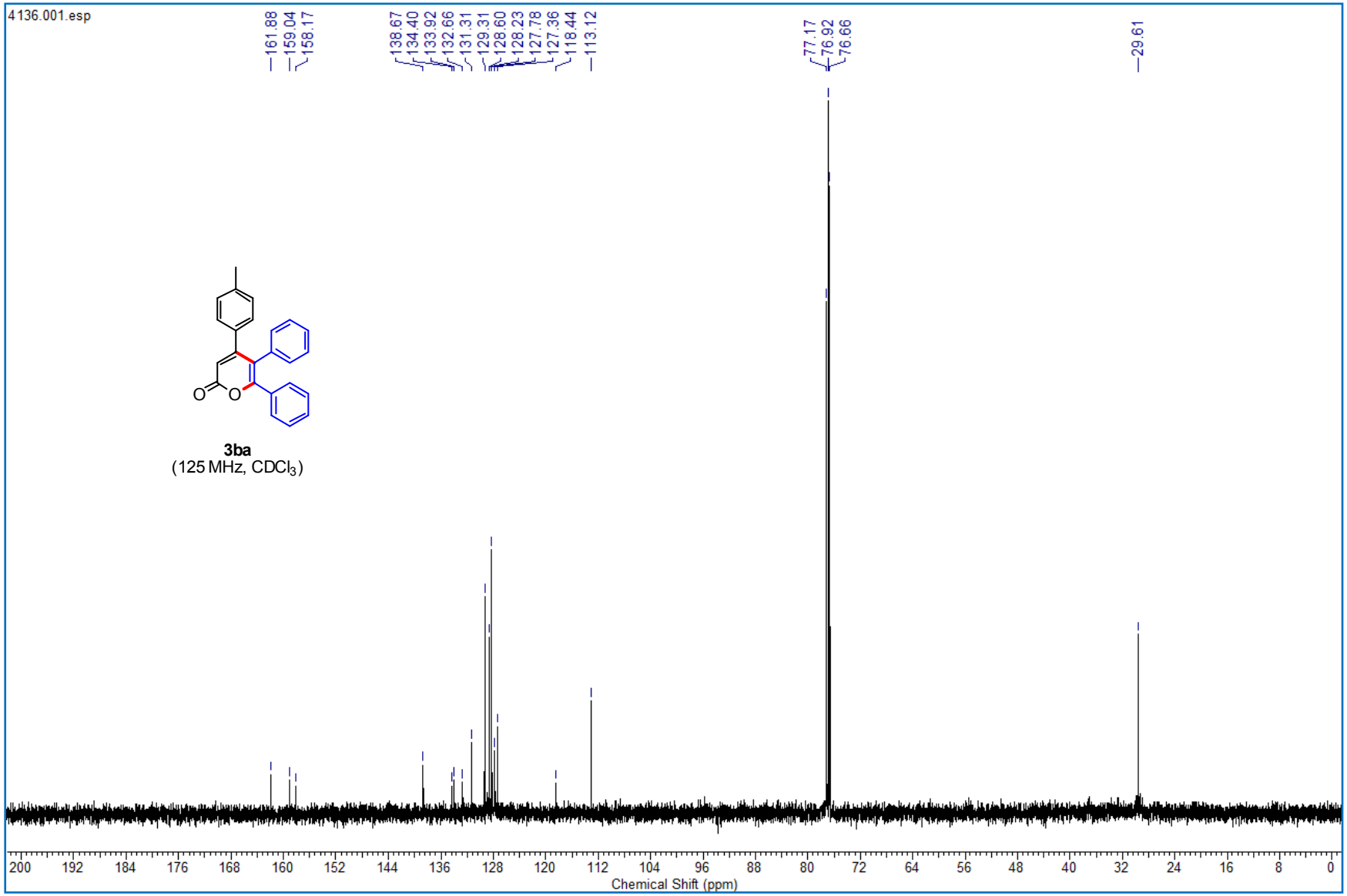

7.47
7.46
7.46
7.45
7.41
7.41
7.40
7.39
7.36
7.34
7.33
7.30
7.29
7.19
7.10
7.09
6.80
5.31
OH
O
O
3an
(500 MHz, CDCl3)
7.4
7.0
6.4
5.8
f1 (ppm)
4.96
4.54
2.17
1.00
2.09
9.5
8.5
7.5
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

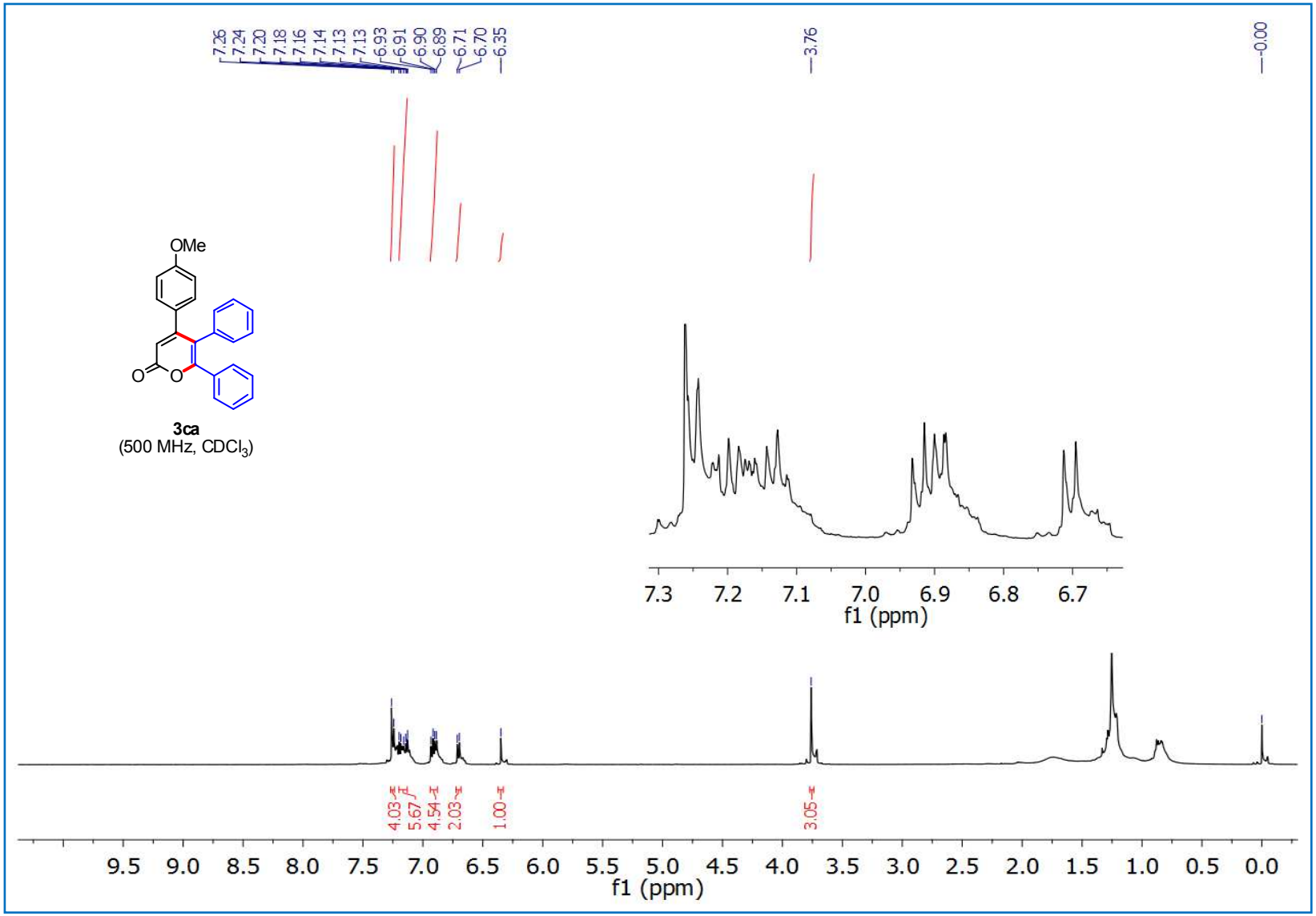

5730.001.esp
167.66
164.05
156.12
138.67
136.87
136.01
130.79
129.98
129.10
128.71
128.59
115.72
77.17
76.91
76.66
67.22
OH
O
O
3an
(125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

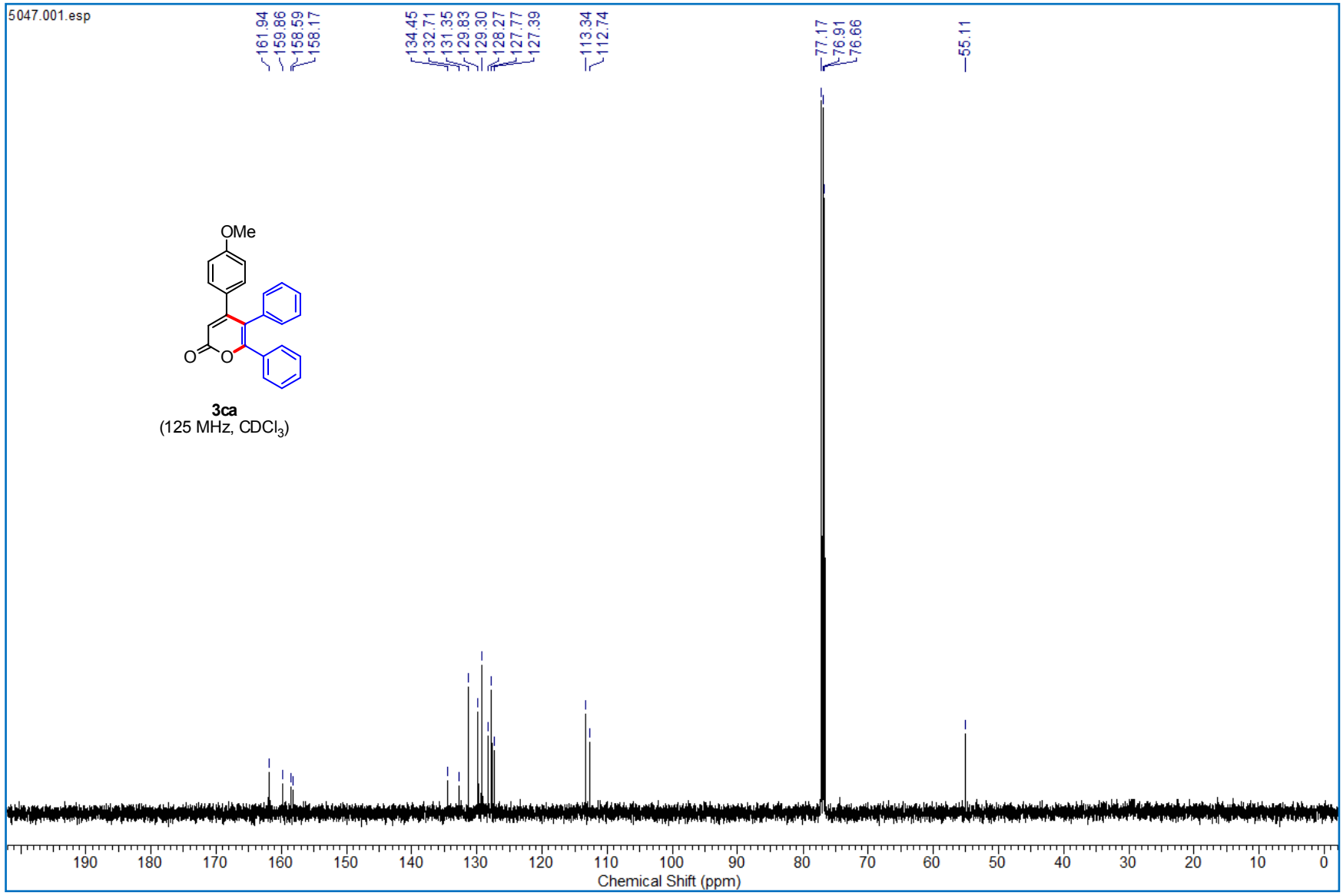

7.49
7.46
7.44
7.43
7.43
7.42
7.41
7.38
7.36
7.26
6.14
6.09
4.24
3.95
2.72
2.70
2.69
2.67
2.41
2.40
2.38
2.37
0.94
0.93
0.91
0.88
0.87
0.85
0.85
0.84
-0.00
Br
O
O
3ao
(500 MHz, CDCl3)
5.20
0.40
0.60
1.20
0.80
1.26
0.83
1.30
1.77
9.5
8.5
7.5
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
7
6
5
4
3
f1 (ppm)

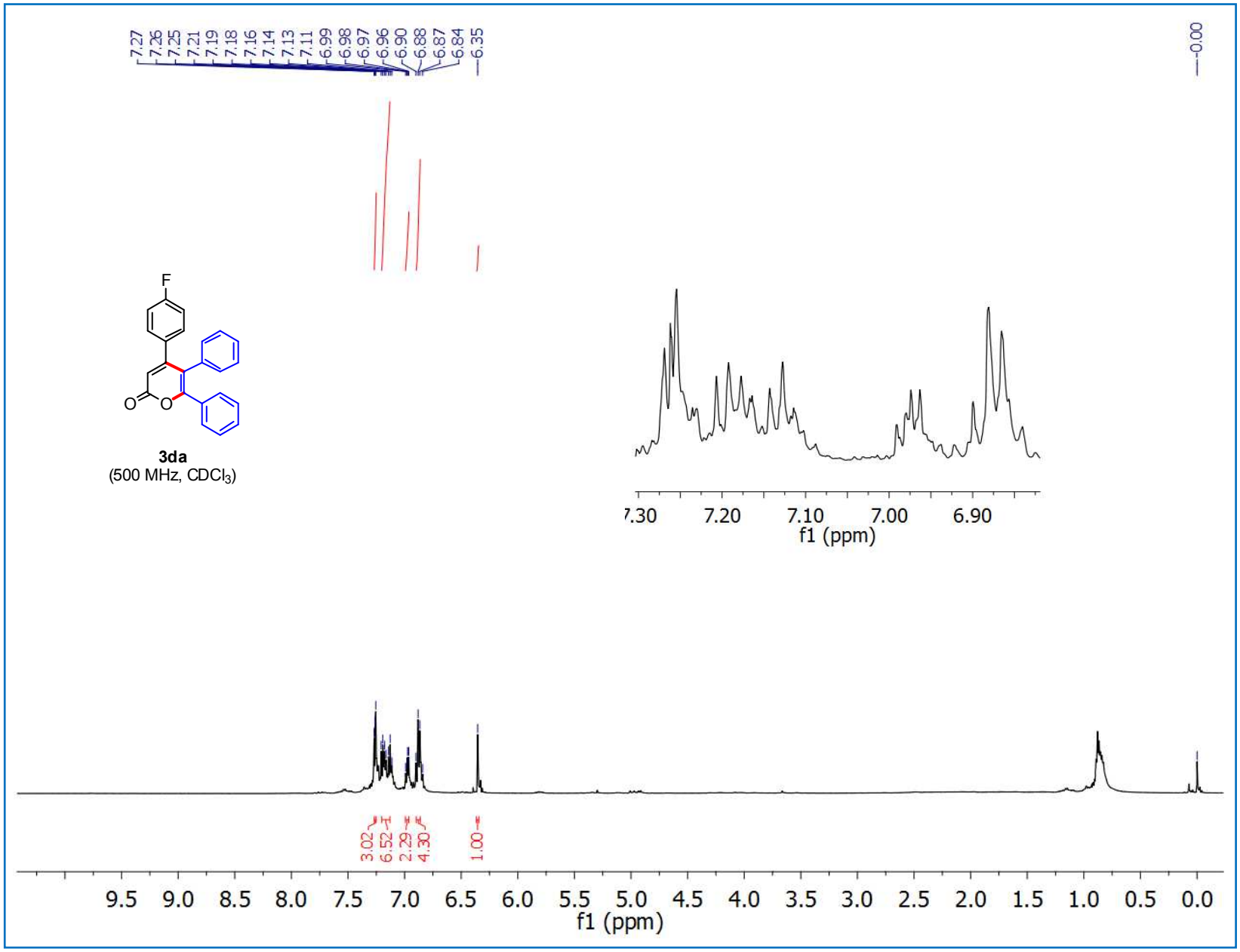

6290.001.esp
167.50
160.08
158.33
146.02
137.04
136.79
128.97
128.63
128.36
128.16
127.93
127.33
115.16
111.96
77.15
76.89
76.65
29.59
Br
O
O
3ao
(125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

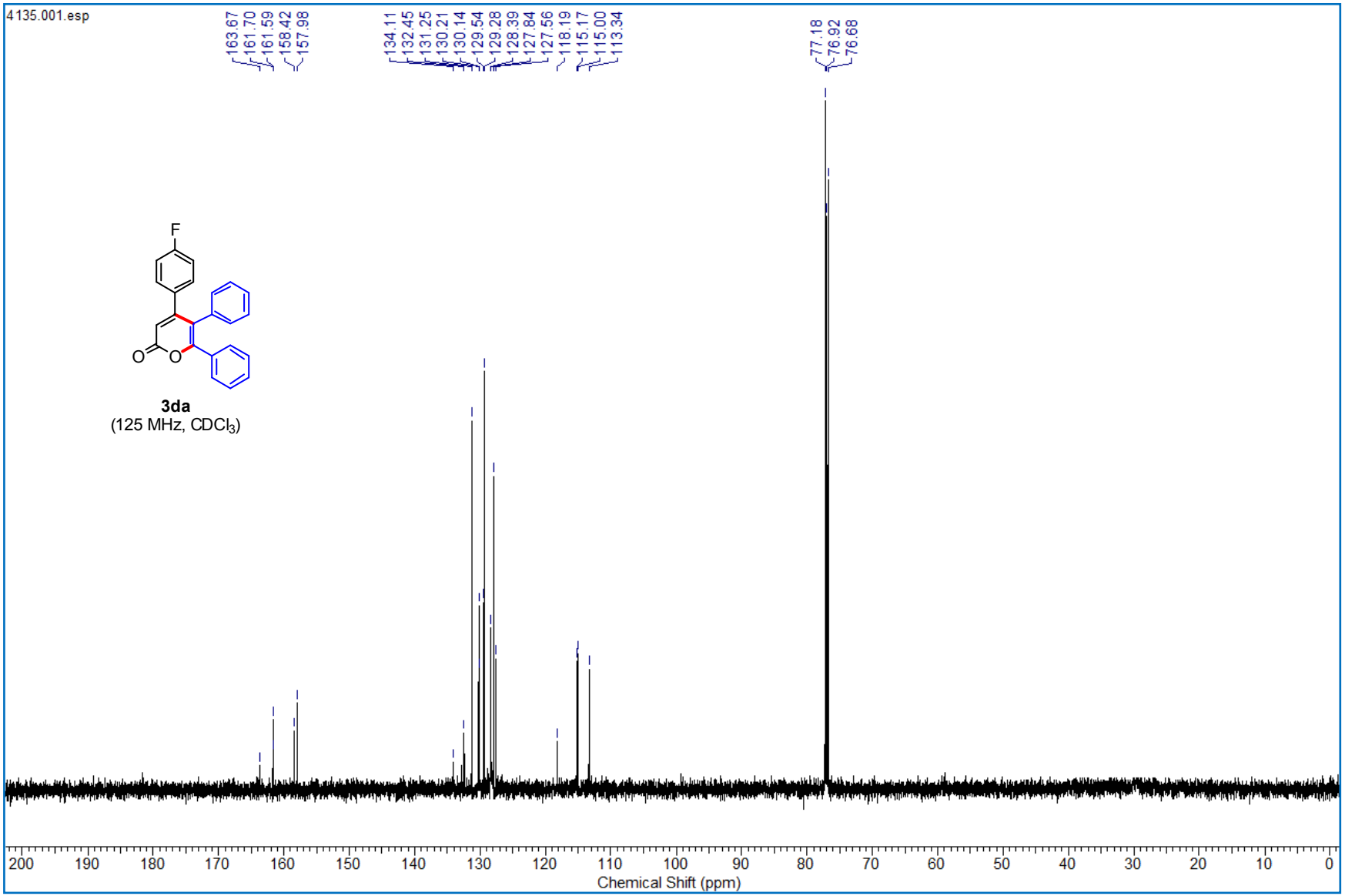

7.26
7.26
7.25
7.22
7.20
7.18
7.17
7.15
7.13
7.12
7.10
7.00
6.98
6.89
6.88
6.88
6.36
2.28
0.00
3ba
(500 MHz, CDCl3)
7.20
7.10
7.00
6.90
f1 (ppm)
5.91
3.19
2.29
4.27
1.00
3.22
9.5
8.5
7.5
7.0
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

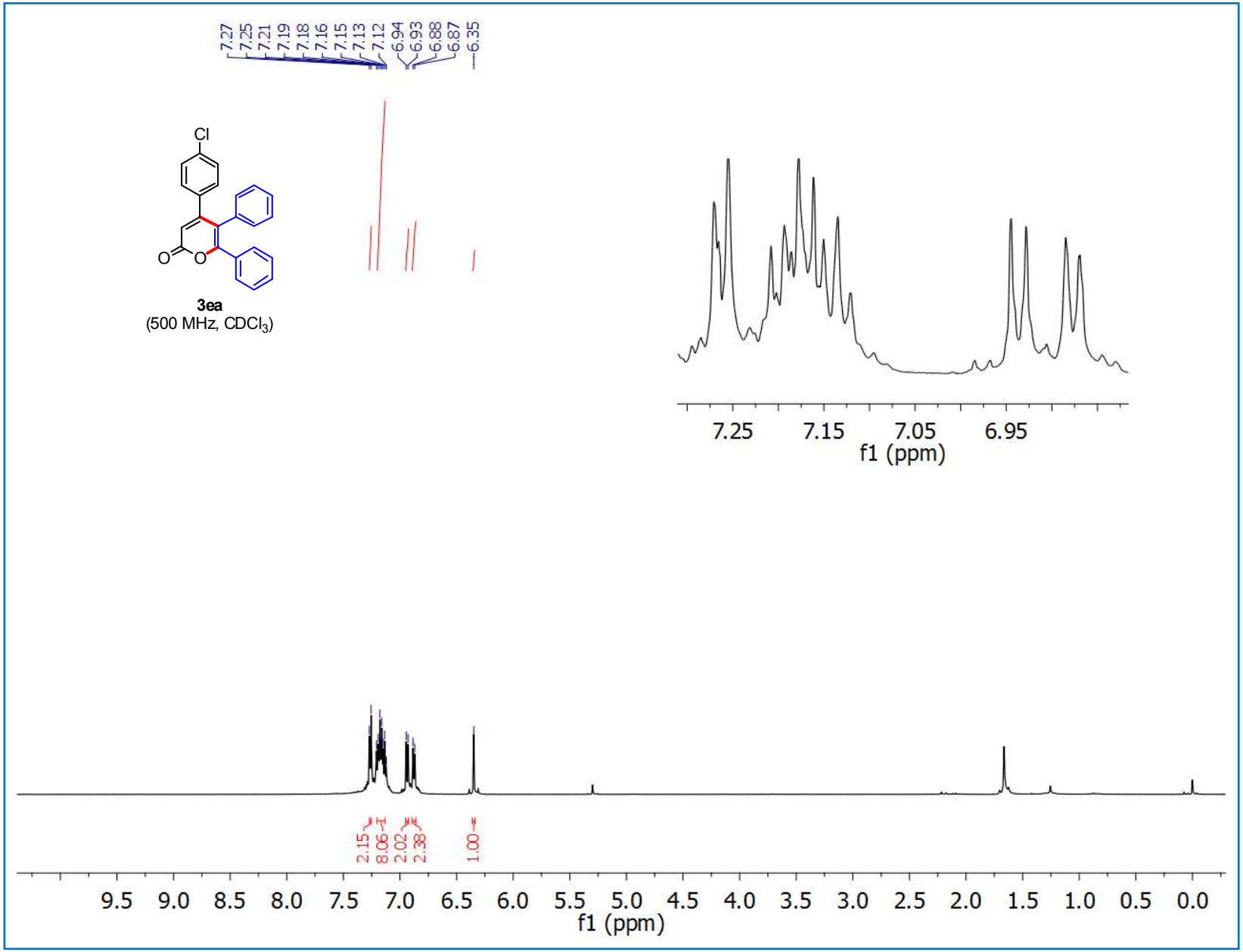

4136.001.esp
161.88
159.04
158.17
138.67
134.40
133.92
132.66
131.31
129.31
128.60
128.23
127.78
127.36
118.44
113.12
77.17
76.92
76.66
29.61
O
O
3ba
(125 MHz, CDCl3)
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

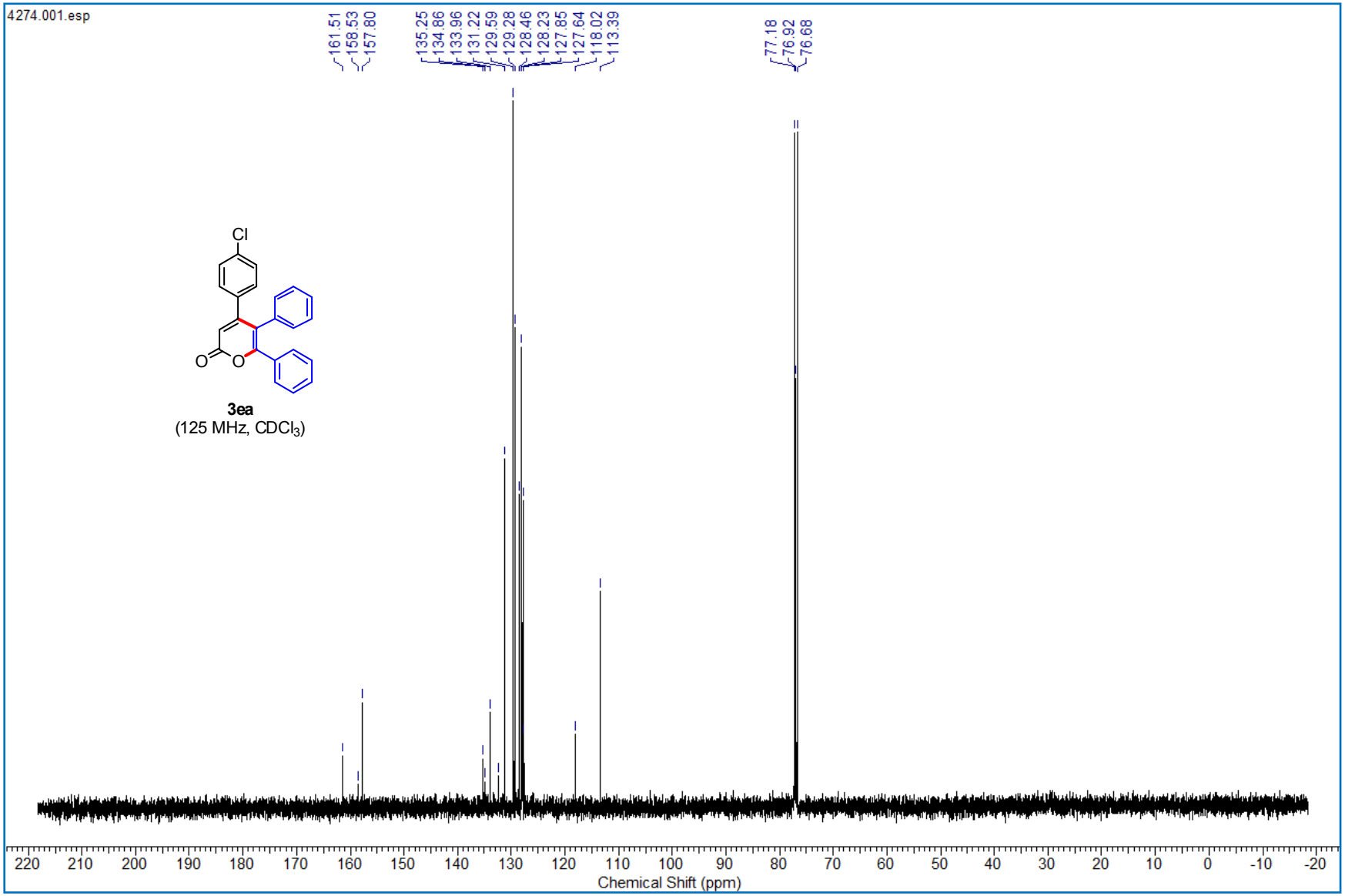

7.26
7.24
7.20
7.18
7.16
7.14
7.13
7.13
6.93
6.91
6.90
6.89
6.71
6.70
6.35
3.76
0.00
OMe
O
O
3ca
(500 MHz, CDCl3)
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
4.03
5.67
4.54
2.03
1.00
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

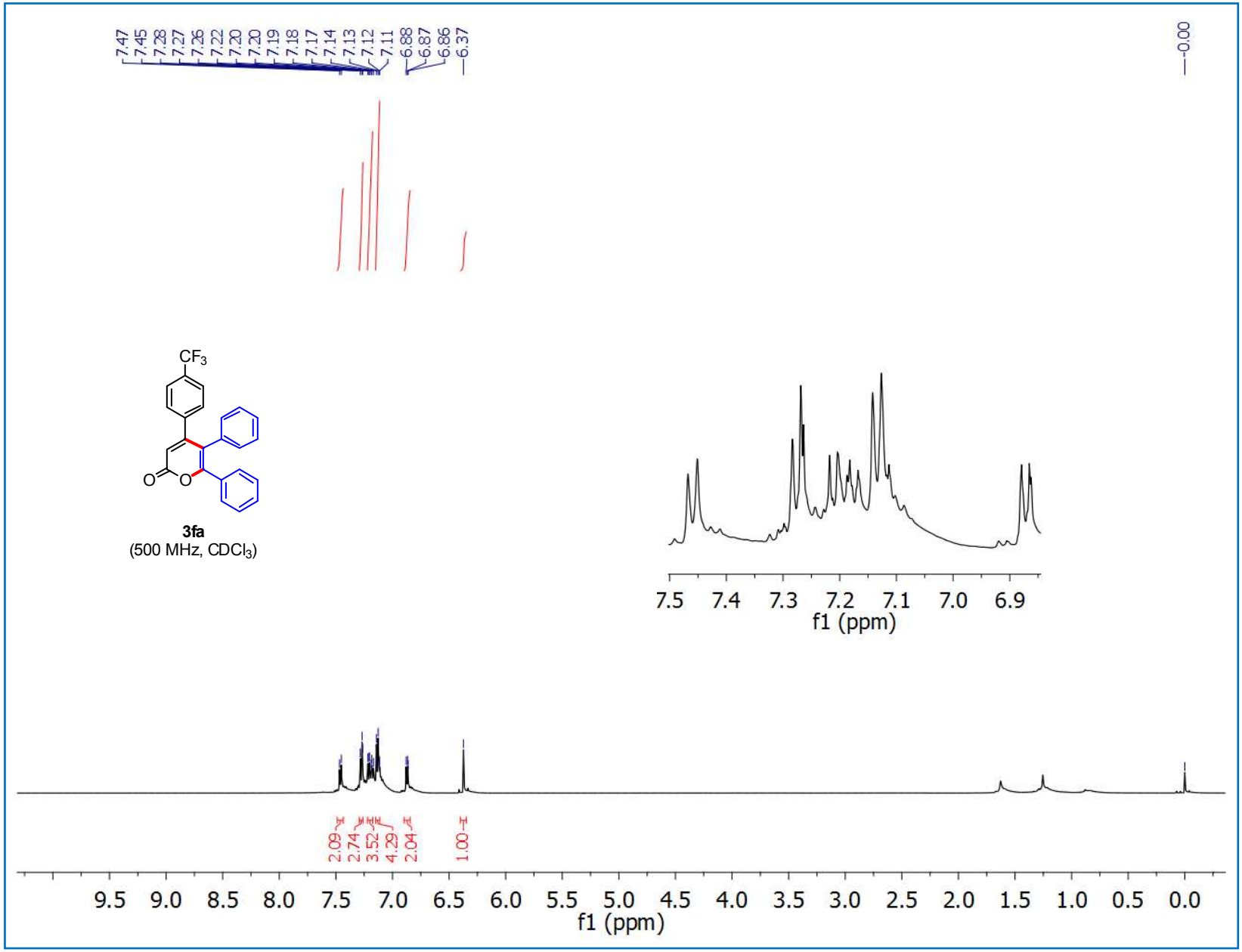

5047.001.esp
161.94
159.86
158.59
158.17
134.45
132.71
131.35
129.83
129.30
128.27
127.77
127.39
113.34
112.74
77.17
76.91
76.66
55.11
OMe
O
O
3ca
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

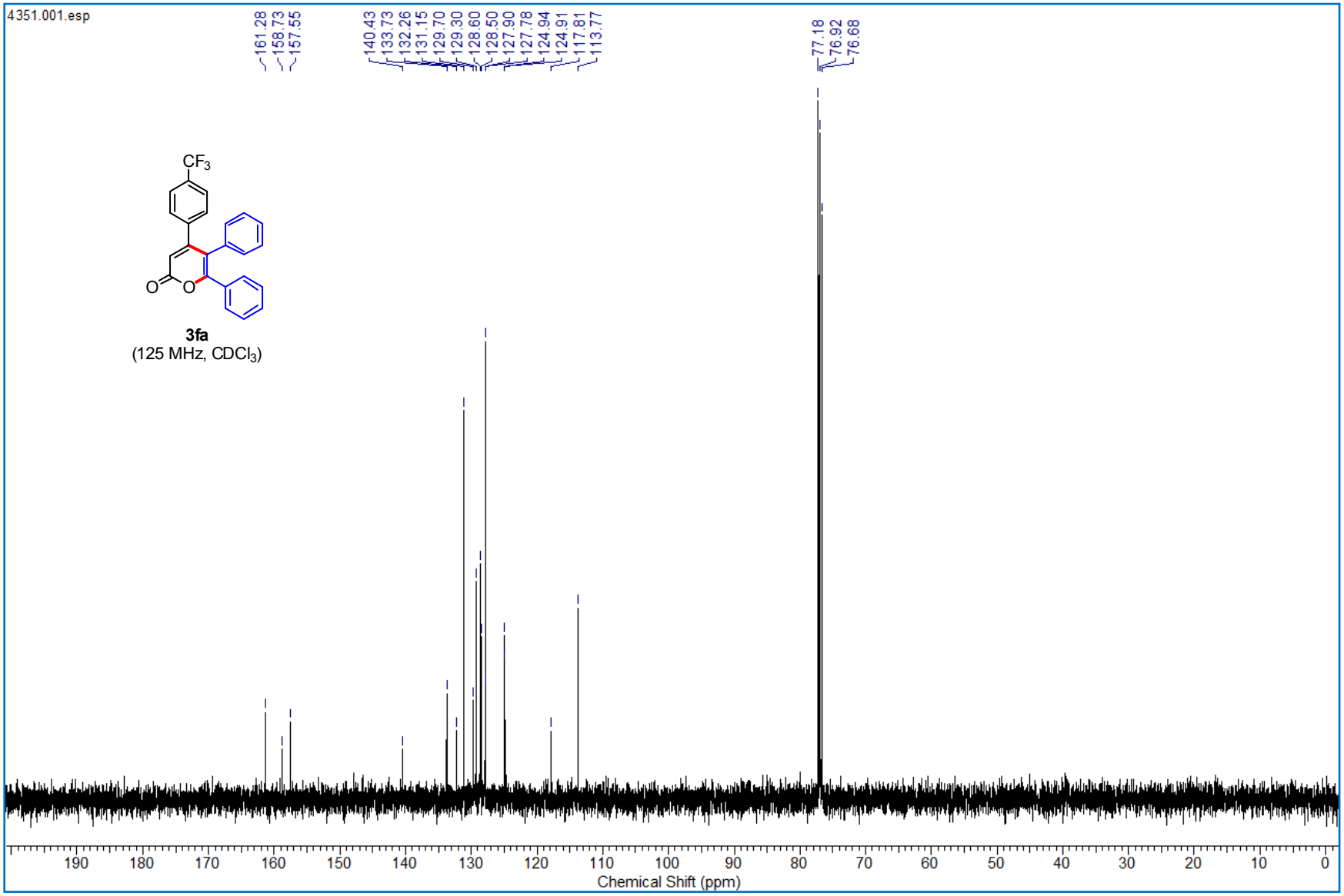

7.27
7.26
7.25
7.21
7.19
7.18
7.16
7.14
7.13
7.11
6.99
6.98
6.97
6.96
6.90
6.88
6.87
6.84
6.35
0.00
F
O
O
3da
(500 MHz, CDCl3)
7.30
7.20
7.10
7.00
6.90
f1 (ppm)
3.02
6.52
2.29
4.30
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

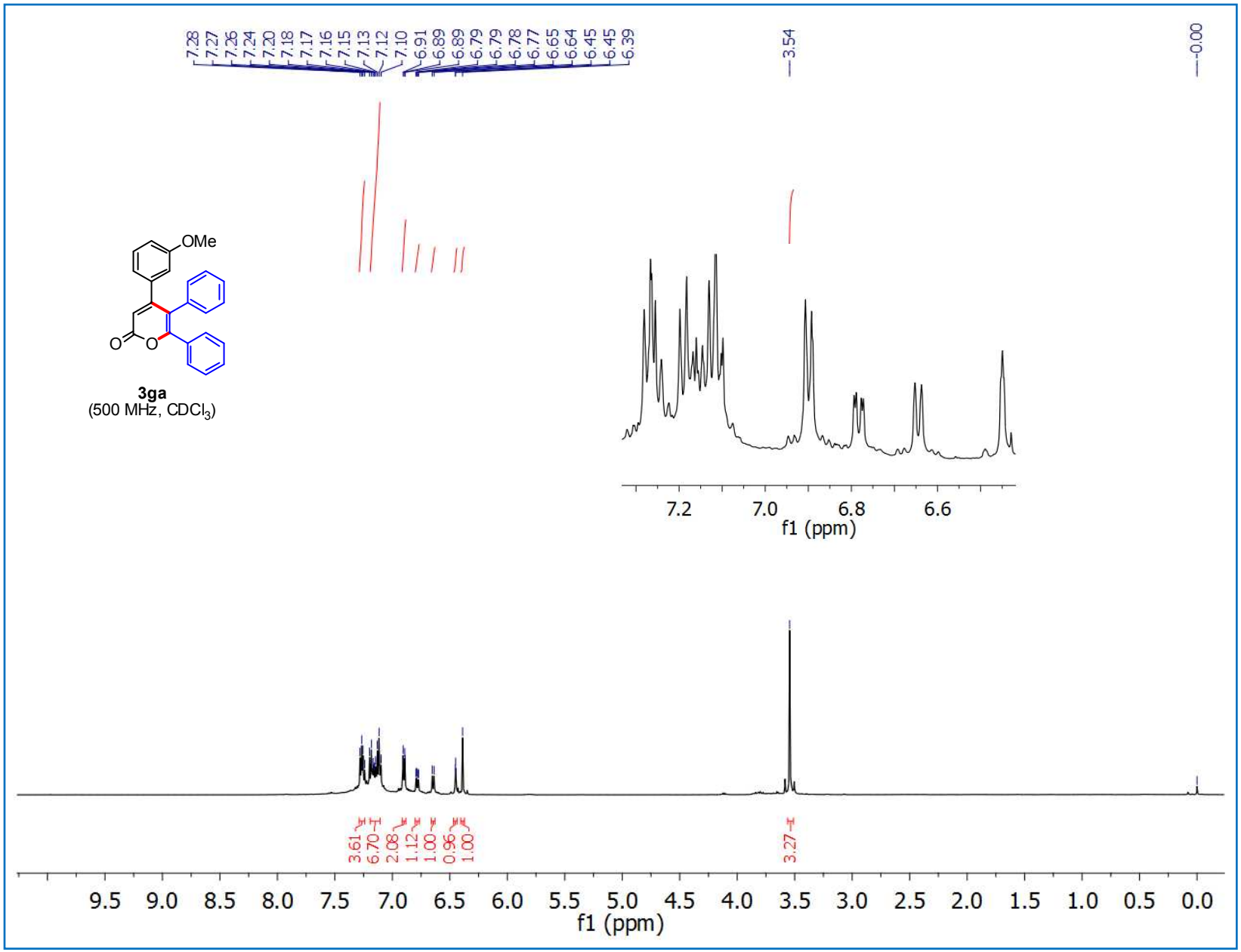

4135.001.esp
163.67
161.70
161.59
158.42
157.98
134.11
132.45
131.25
130.21
130.14
129.54
129.28
128.39
127.84
127.56
118.19
115.17
115.00
113.34
77.18
76.92
76.68
F
O
O
3da
(125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

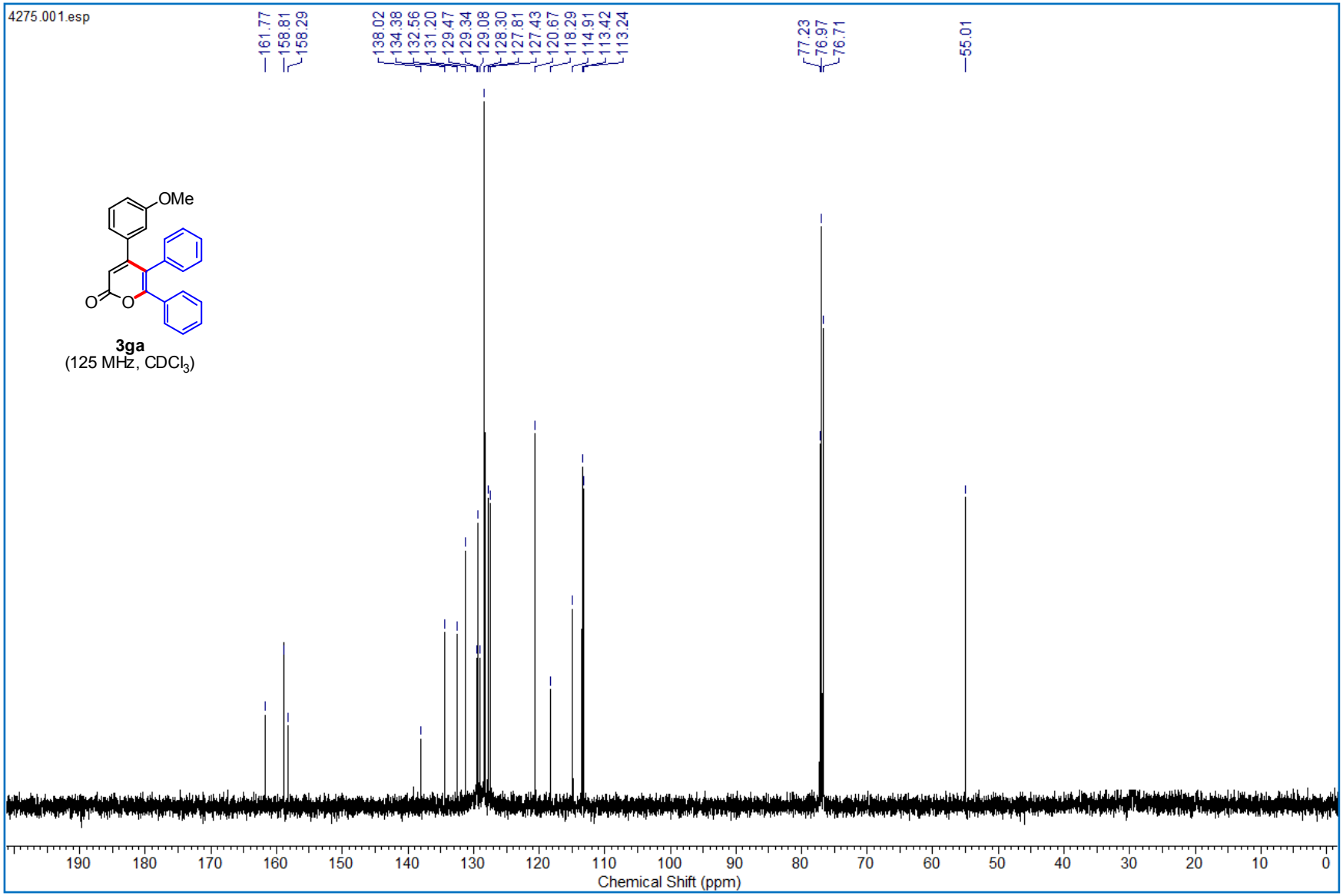

7.27
7.25
7.21
7.19
7.18
7.16
7.15
7.13
7.12
6.94
6.93
6.88
6.87
6.35
Cl
O
O
3ea
(500 MHz, CDCl3)
7.25
7.15
7.05
6.95
f1 (ppm)
2.15
8.06
2.02
2.38
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

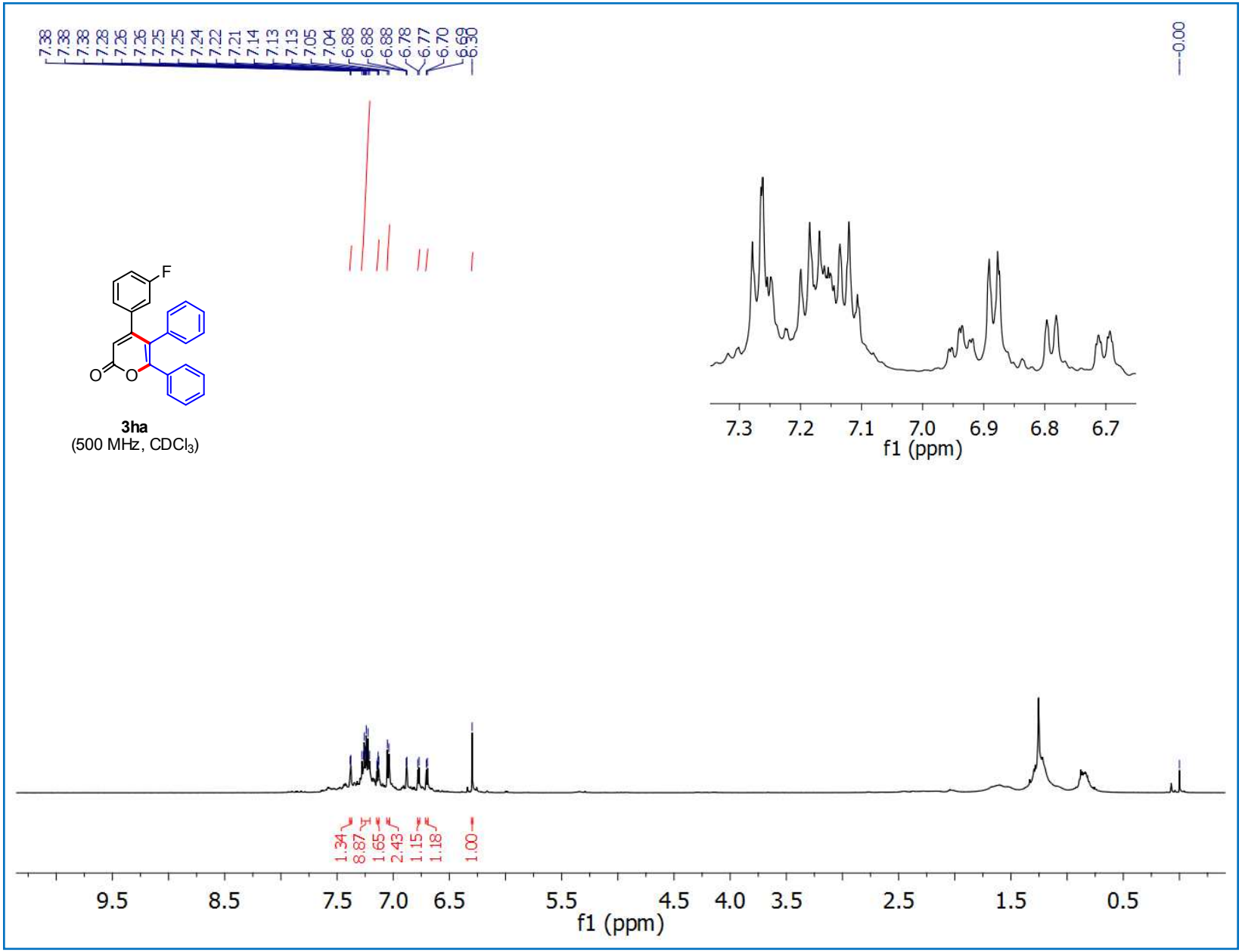

4274.001.esp
161.51
158.53
157.80
135.25
134.86
133.96
131.22
129.59
129.28
128.46
128.23
127.85
127.64
118.02
113.39
77.18
76.92
76.68
Cl
O
O
3ea
(125 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
Chemical Shift (ppm)

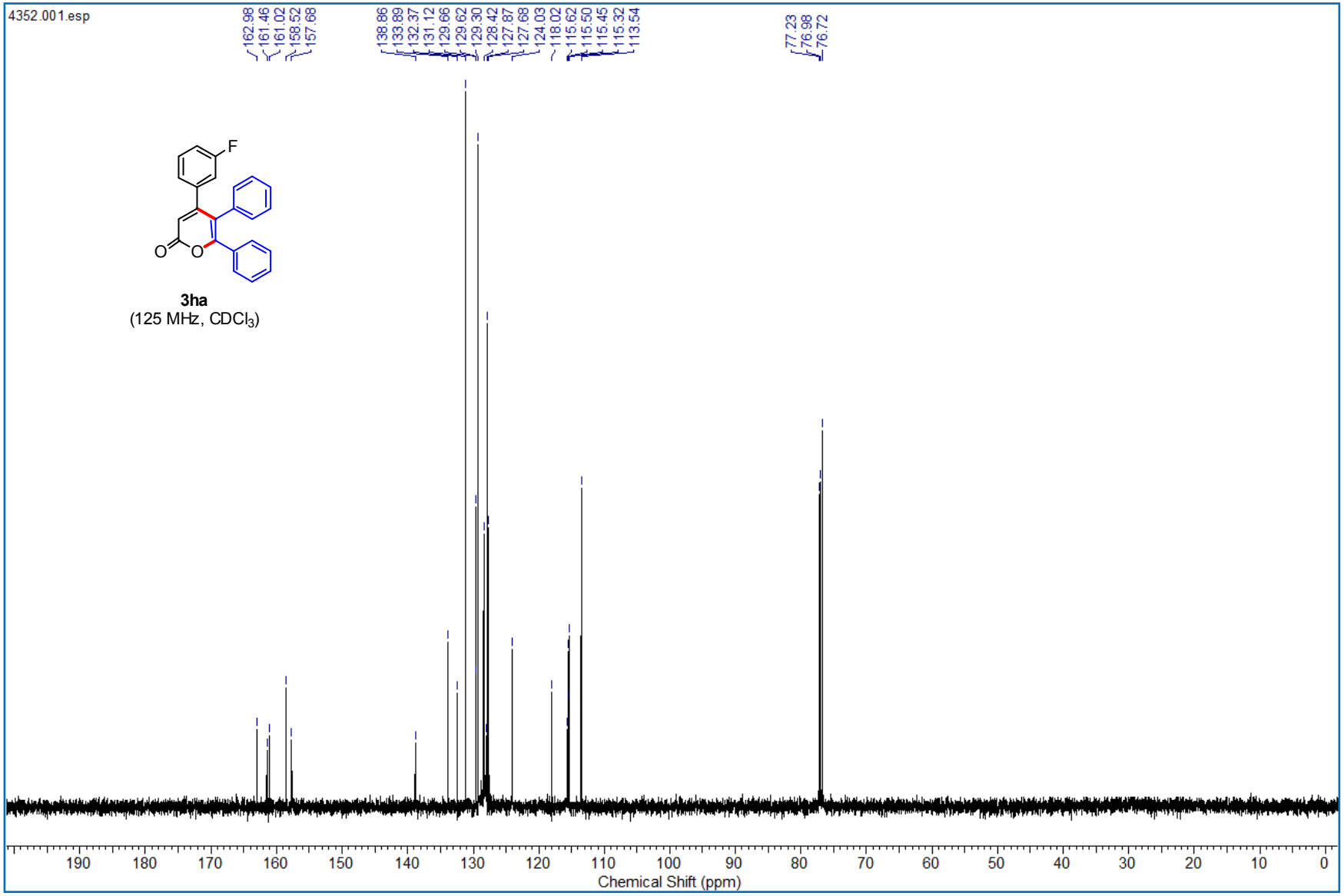

7.47
7.45
7.28
7.27
7.26
7.22
7.20
7.20
7.19
7.18
7.17
7.14
7.13
7.12
7.11
6.88
6.87
6.86
6.37
0.00
CF3
O
O
3fa
(500 MHz, CDCl3)
7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
2.09
2.74
3.52
4.29
2.04
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

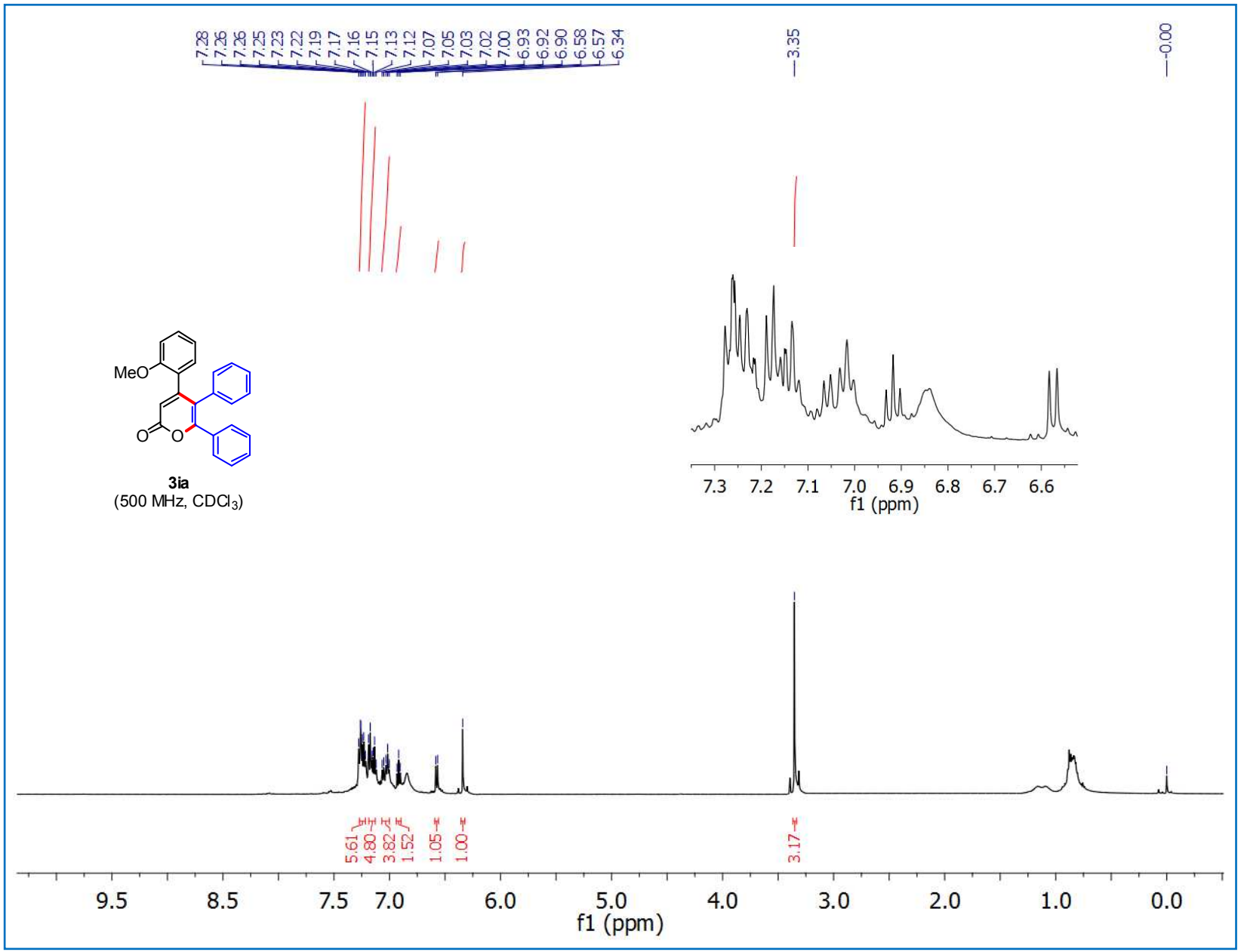

4351.001.esp
161.28
158.73
157.55
140.43
133.73
132.26
131.15
129.70
129.30
128.60
128.50
127.90
127.78
124.94
124.91
117.81
113.77
77.18
76.92
76.68
CF3
O
O
3fa
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

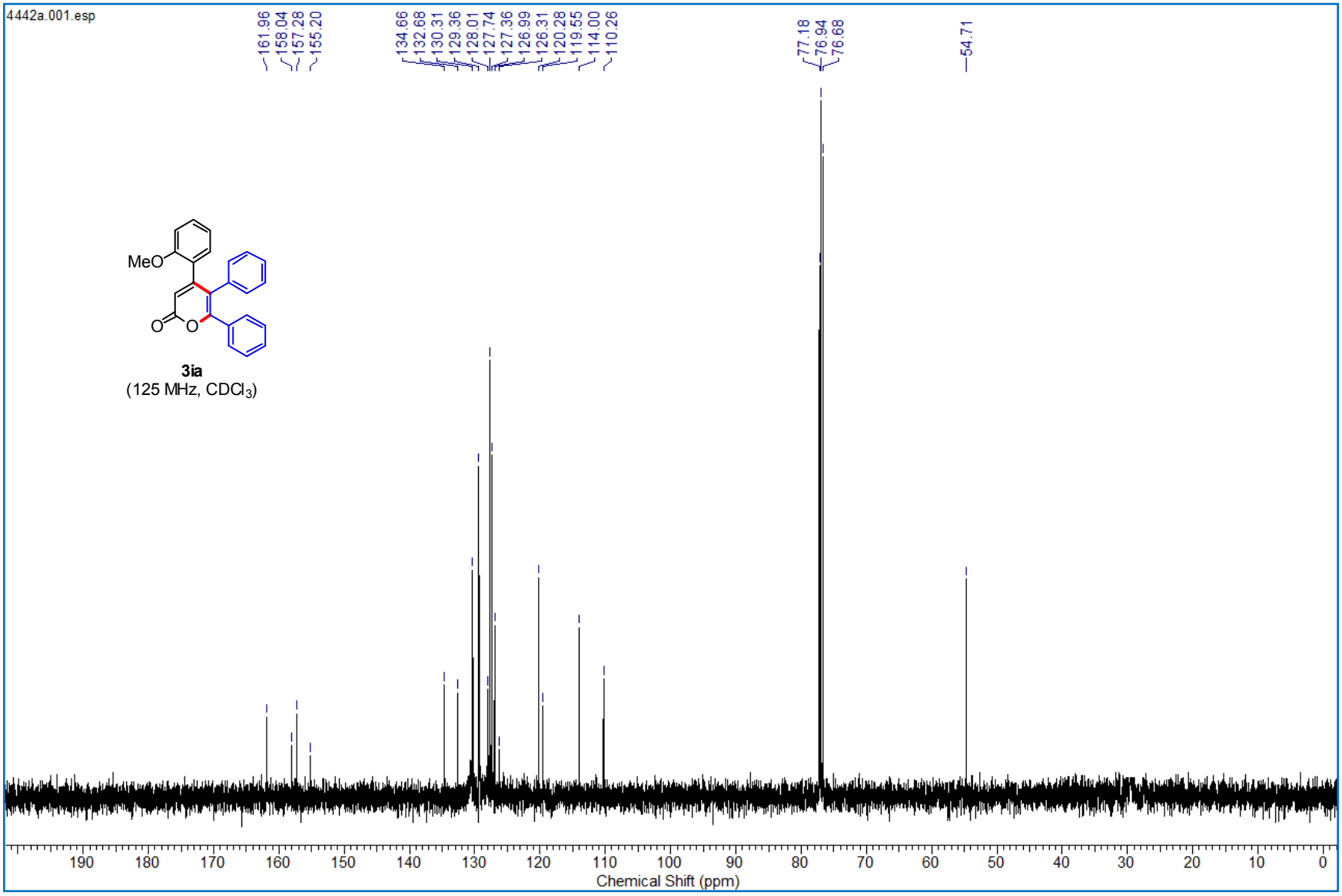

7.28
7.27
7.26
7.24
7.20
7.18
7.17
7.16
7.15
7.13
7.12
7.10
6.91
6.89
6.89
6.79
6.79
6.78
6.77
6.65
6.64
6.45
6.45
6.39
3.54
0.00
OMe
O
O
3ga
(500 MHz, CDCl3)
7.2
7.0
6.8
6.6
f1 (ppm)
3.61
6.70
2.08
1.12
1.00
0.96
1.00
3.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

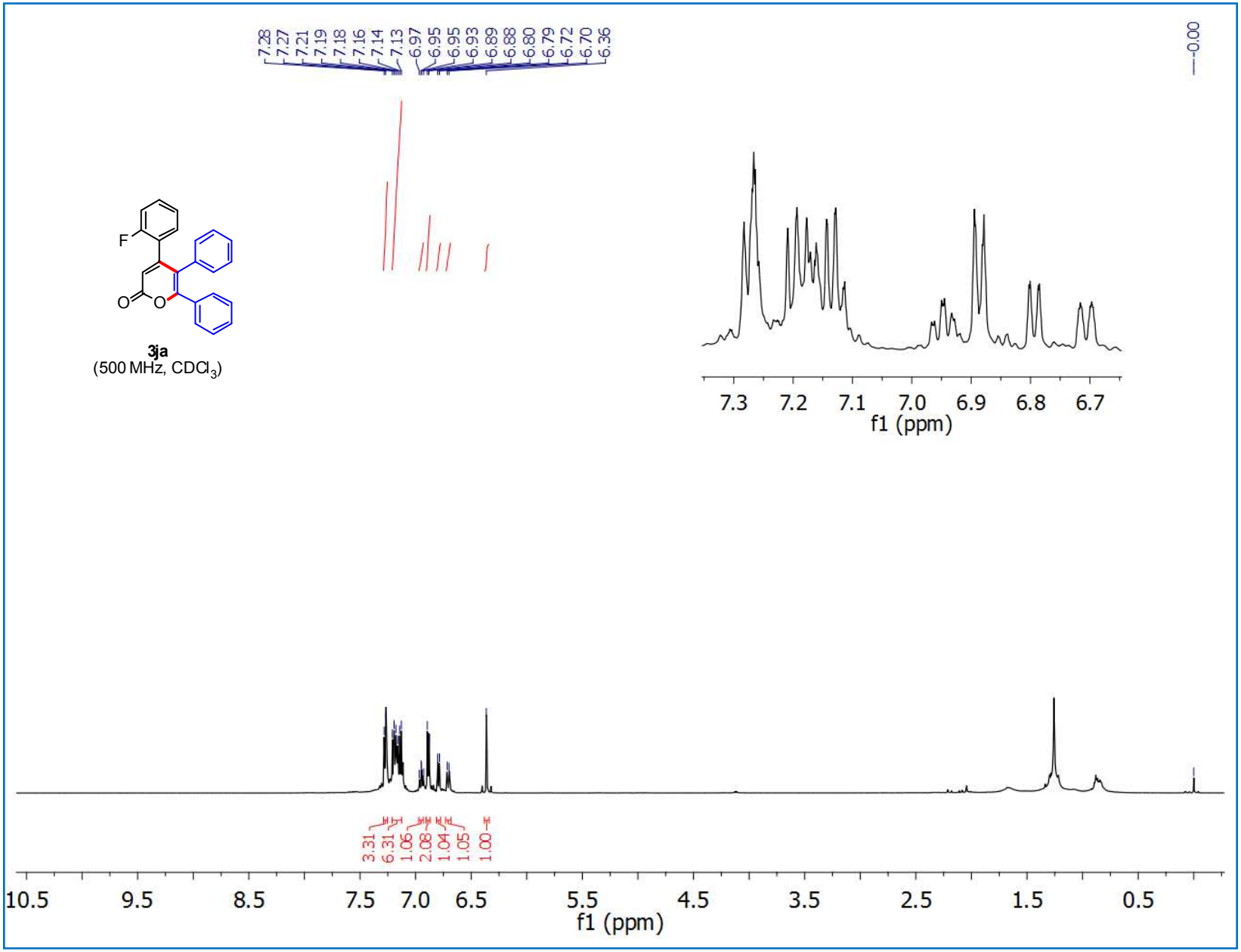

4275.001.esp
161.77
158.81
158.29
138.02
134.38
132.56
131.20
129.47
129.34
129.08
128.30
127.81
127.43
120.67
118.29
114.91
113.42
113.24
77.23
76.97
76.71
55.01
OMe
O
O
3ga
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

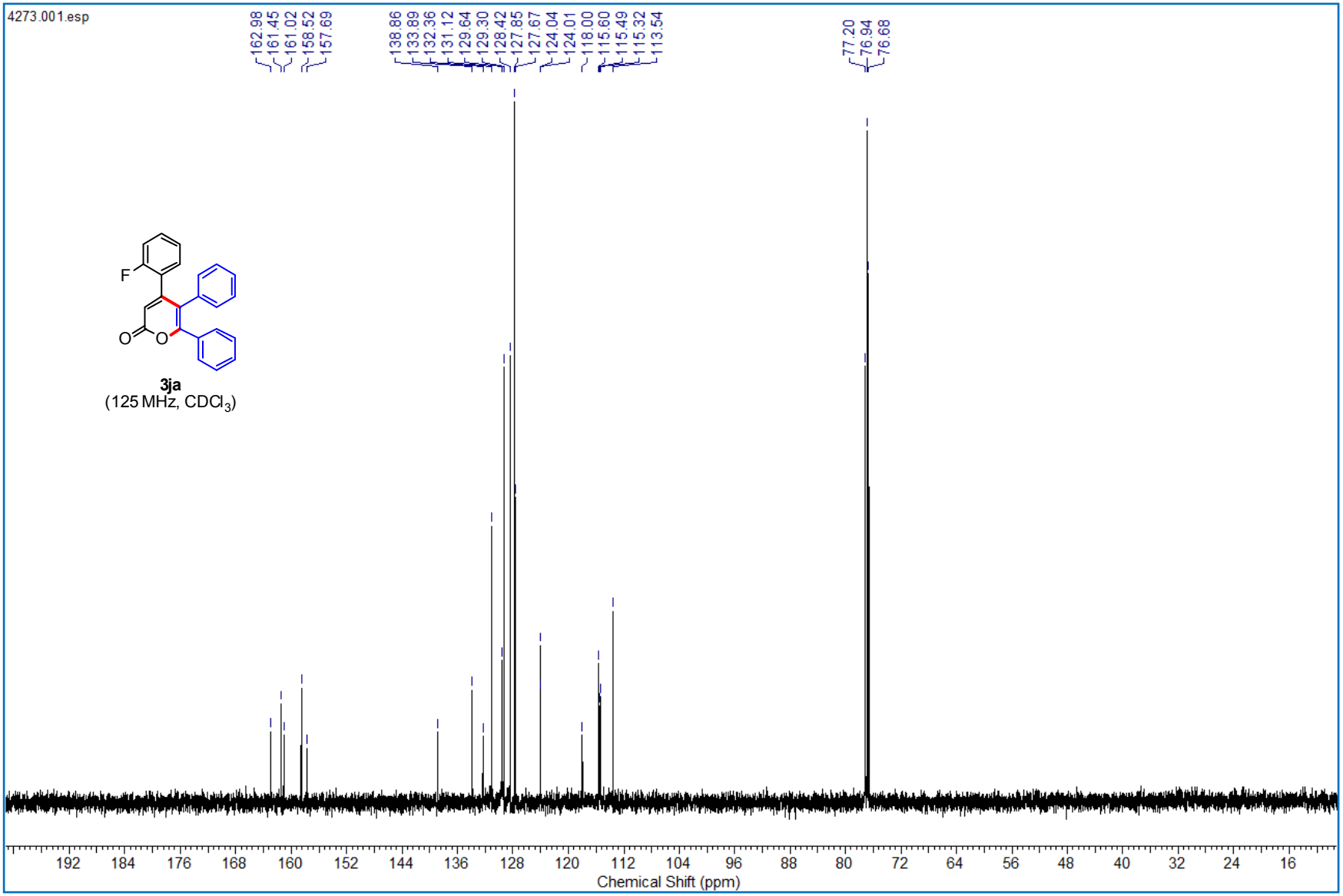

7.38
7.38
7.38
7.28
7.26
7.26
7.25
7.25
7.24
7.22
7.21
7.14
7.13
7.13
7.05
7.04
6.88
6.88
6.88
6.78
6.77
6.70
6.69
6.30
0.00
F
O
O
3ha
(500 MHz, CDCl3)
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
1.34
8.87
1.65
2.43
1.15
1.18
1.00
9.5
8.5
7.5
7.0
6.5
5.5
4.5
4.0
3.5
2.5
1.5
0.5
f1 (ppm)

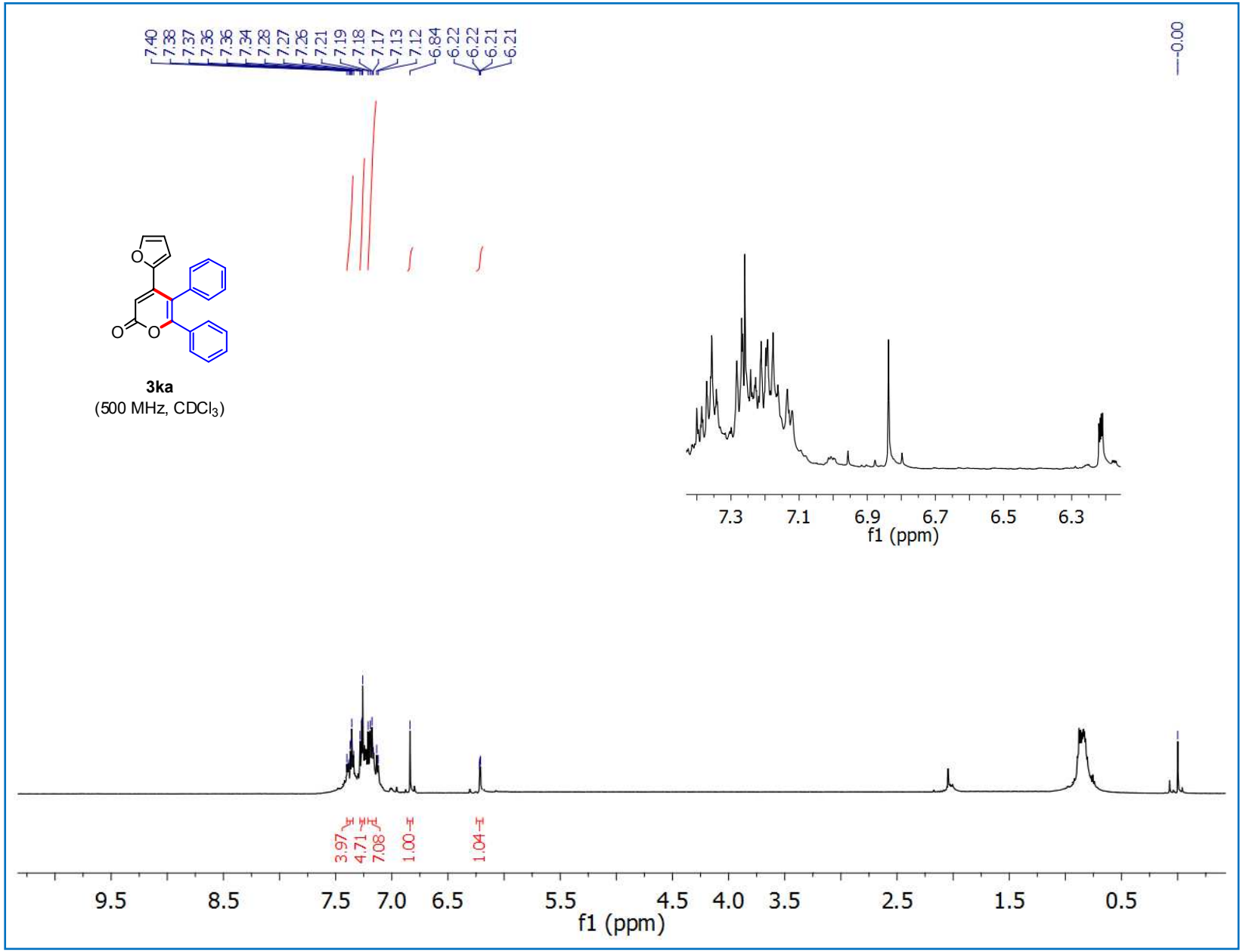

4352.001.esp
162.98
161.46
161.02
158.52
157.68
138.86
133.89
132.37
131.12
129.66
129.62
129.30
128.42
127.87
127.68
124.03
118.02
115.62
115.50
115.45
115.32
113.54
77.23
76.98
76.72
F
O
O
3ha
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

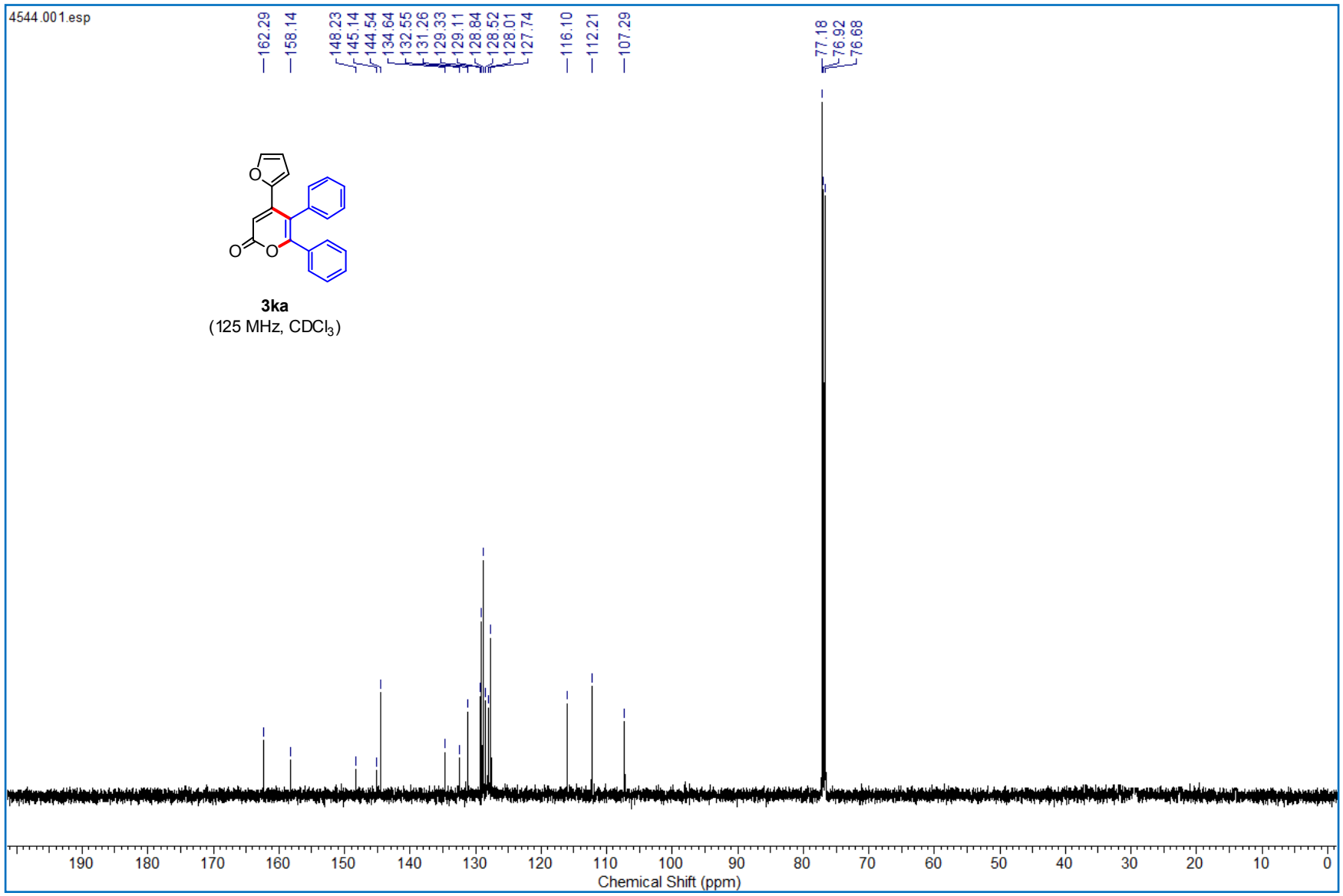

7.28
7.26
7.26
7.25
7.23
7.22
7.19
7.17
7.16
7.15
7.13
7.12
7.07
7.05
7.03
7.02
7.00
6.93
6.92
6.90
6.58
6.57
6.34
3.35
0.00
MeO
O
O
3ia
(500 MHz, CDCl3)
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
f1 (ppm)
5.61
4.80
3.82
1.52
1.05
1.00
3.17
9.5
8.5
7.5
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

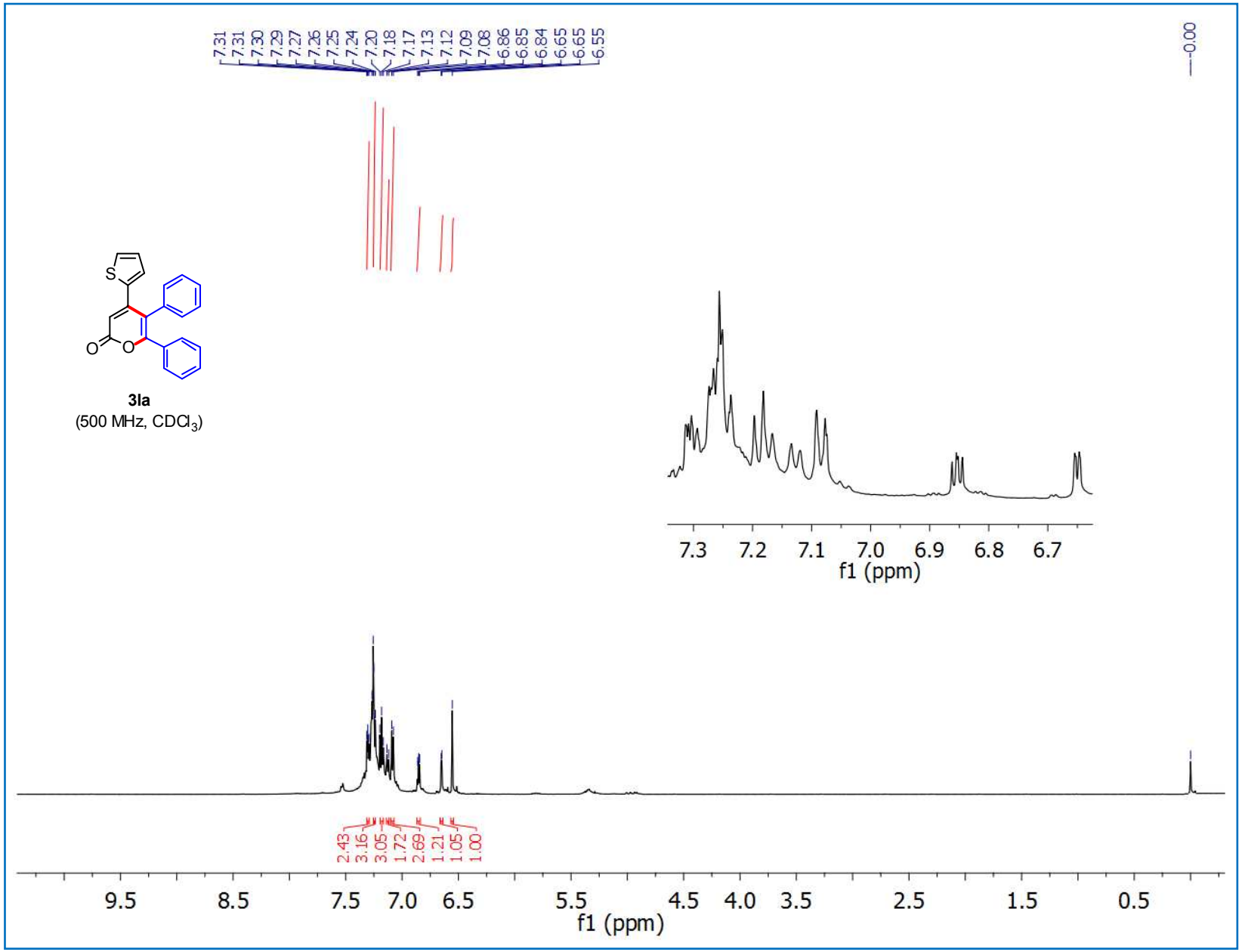

4442a.001.esp
161.96
158.04
157.28
155.20
134.66
132.68
130.31
129.36
128.01
127.74
127.36
126.99
126.31
120.28
119.55
114.00
110.26
77.18
76.94
76.68
54.71
MeO
O
O
3ia
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

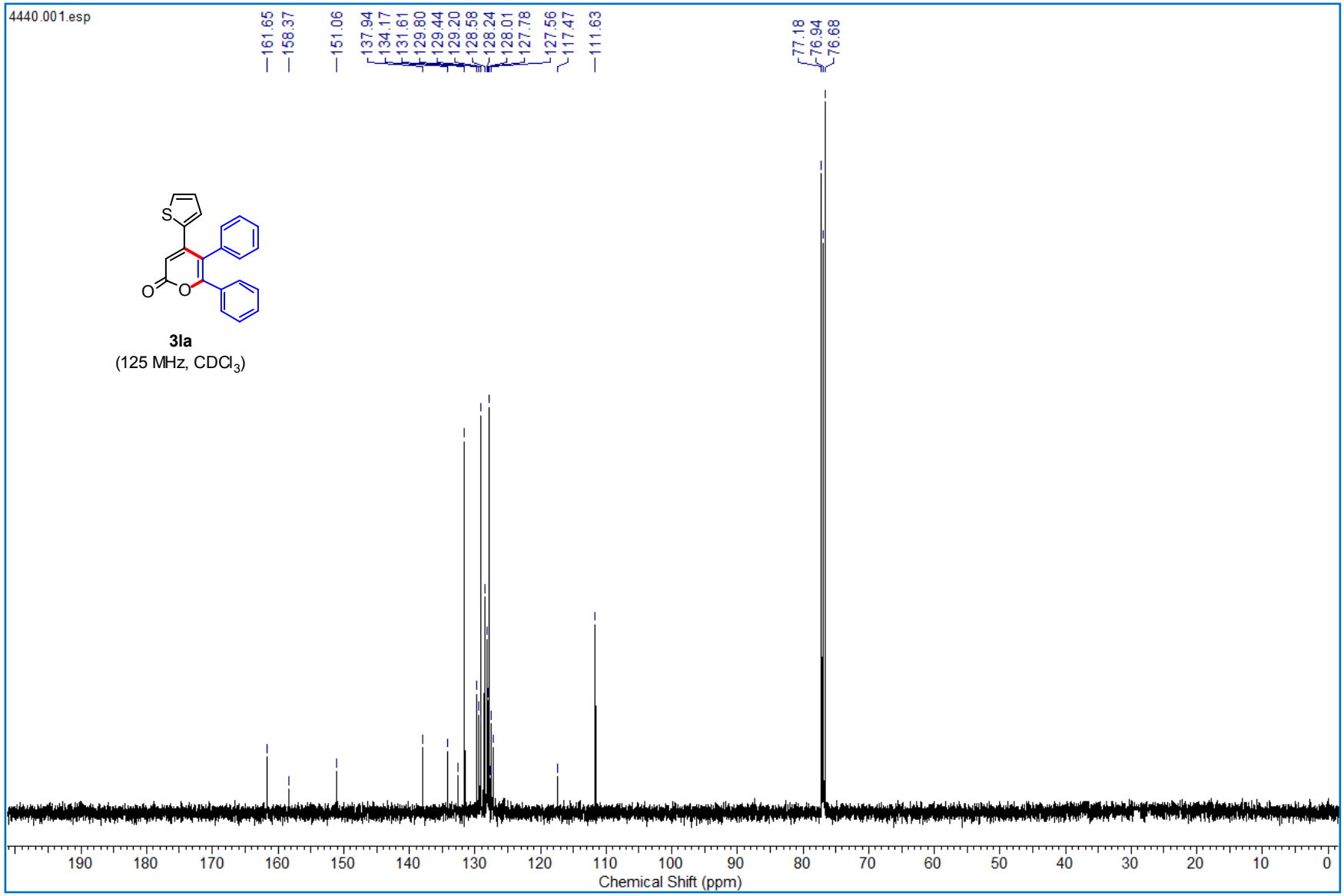

7.28
7.27
7.21
7.19
7.18
7.16
7.14
7.13
6.97
6.95
6.95
6.93
6.89
6.88
6.80
6.79
6.72
6.70
6.36
0.00
F
O
O
3ja
(500 MHz, CDCl3)
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
3.31
6.31
1.06
2.08
1.04
1.05
1.00
10.5
9.5
8.5
7.5
7.0
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


4273.001.esp
162.98
161.45
161.02
158.52
157.69
138.86
133.89
132.36
131.12
129.64
129.30
128.42
127.85
127.67
124.04
124.01
118.00
115.60
115.49
115.32
113.54
77.20
76.94
76.68
F
O
O
3ja
(125 MHz, CDCl3)
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

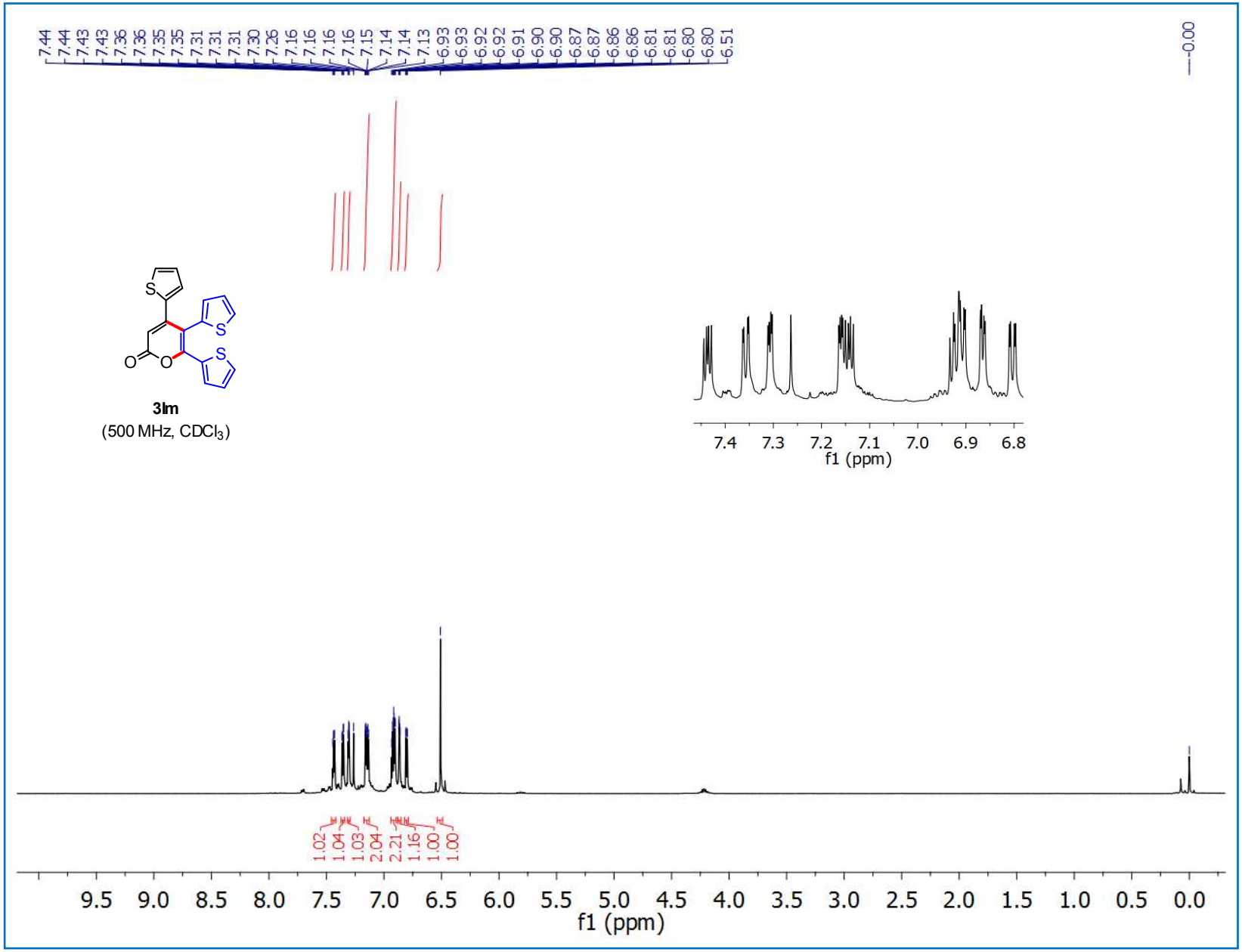

7.40
7.38
7.37
7.36
7.36
7.34
7.28
7.27
7.26
7.21
7.19
7.18
7.17
7.13
7.12
6.84
6.22
6.22
6.21
6.21
0.00
3ka
(500 MHz, CDCl3)
7.3
7.1
6.9
6.7
6.5
6.3
f1 (ppm)
3.97
4.71
7.08
1.00
1.04
9.5
8.5
7.5
7.0
6.5
5.5
4.5
4.0
3.5
2.5
1.5
0.5
f1 (ppm)

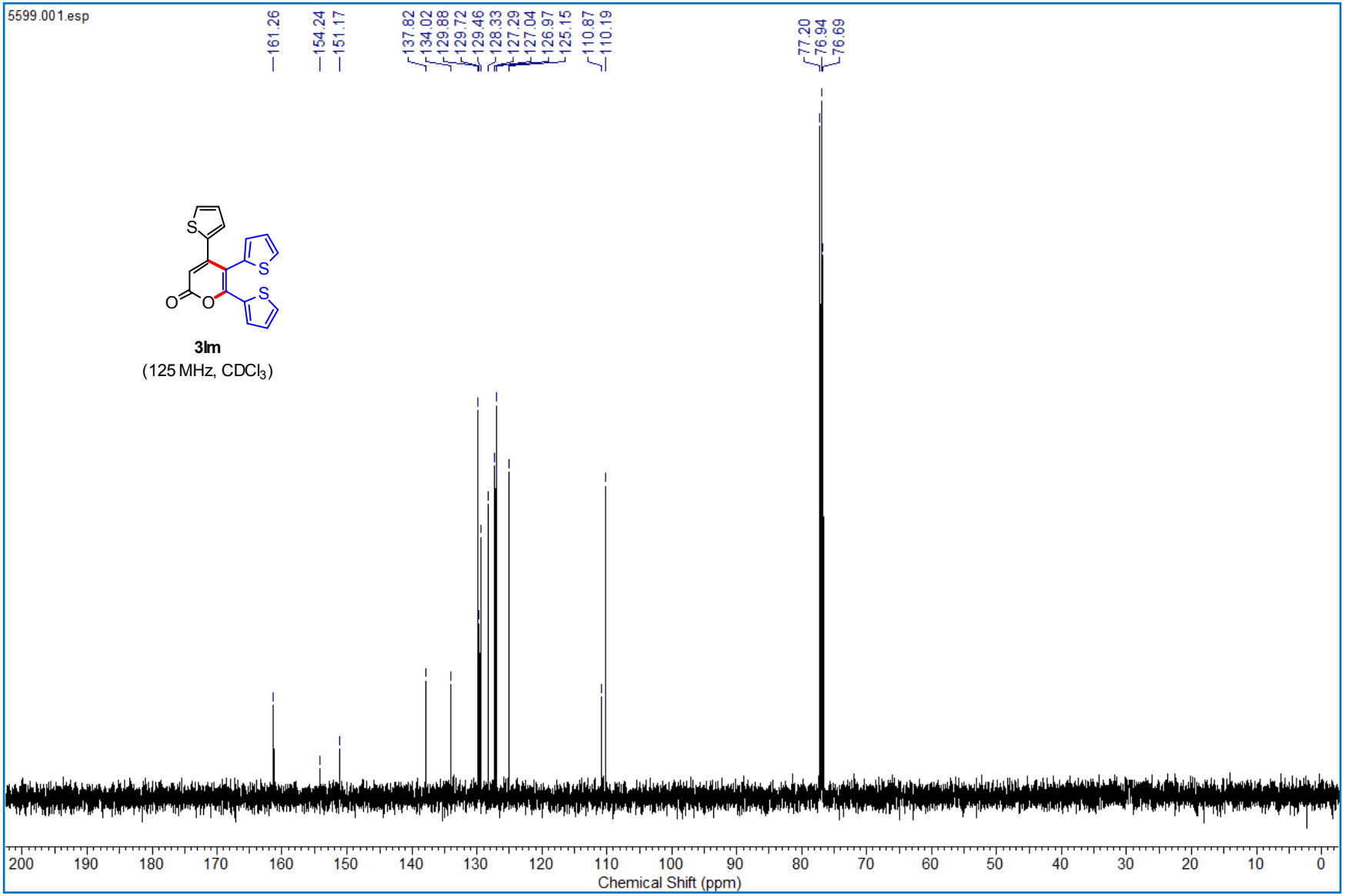

4544.001.esp
162.29
158.14
148.23
145.14
144.54
134.64
132.55
131.26
129.33
129.11
128.84
128.52
128.01
127.74
116.10
112.21
107.29
77.18
76.92
76.68
O
O
O
3ka
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

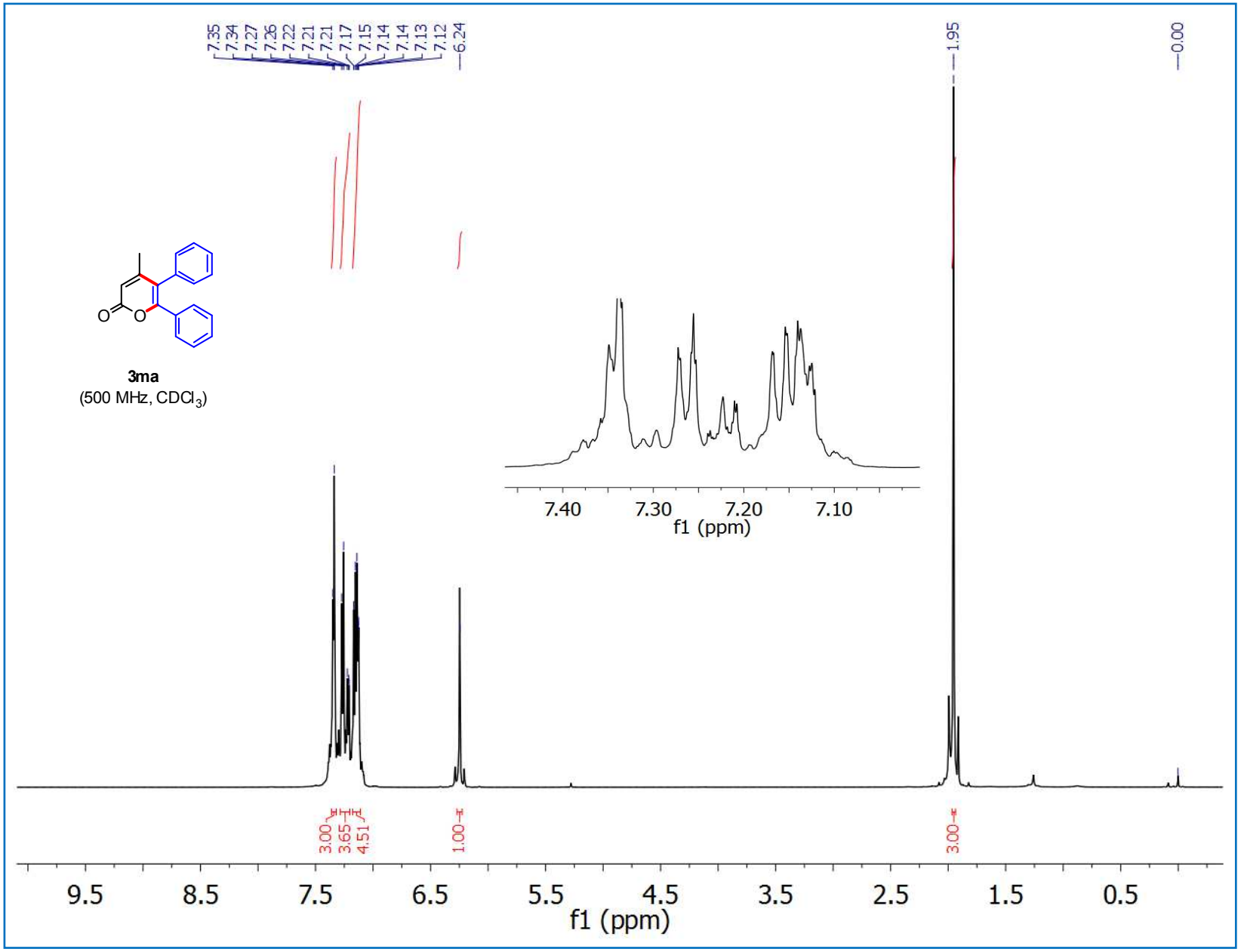

7.31
7.31
7.30
7.29
7.27
7.26
7.25
7.24
7.20
7.18
7.17
7.13
7.12
7.09
7.08
6.86
6.85
6.84
6.65
6.65
6.55
0.00
S
O
O
3la
(500 MHz, CDCl3)
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
2.43
3.16
3.05
1.72
2.69
1.21
1.05
1.00
9.5
8.5
7.5
7.0
6.5
5.5
4.5
4.0
3.5
2.5
1.5
0.5
f1 (ppm)

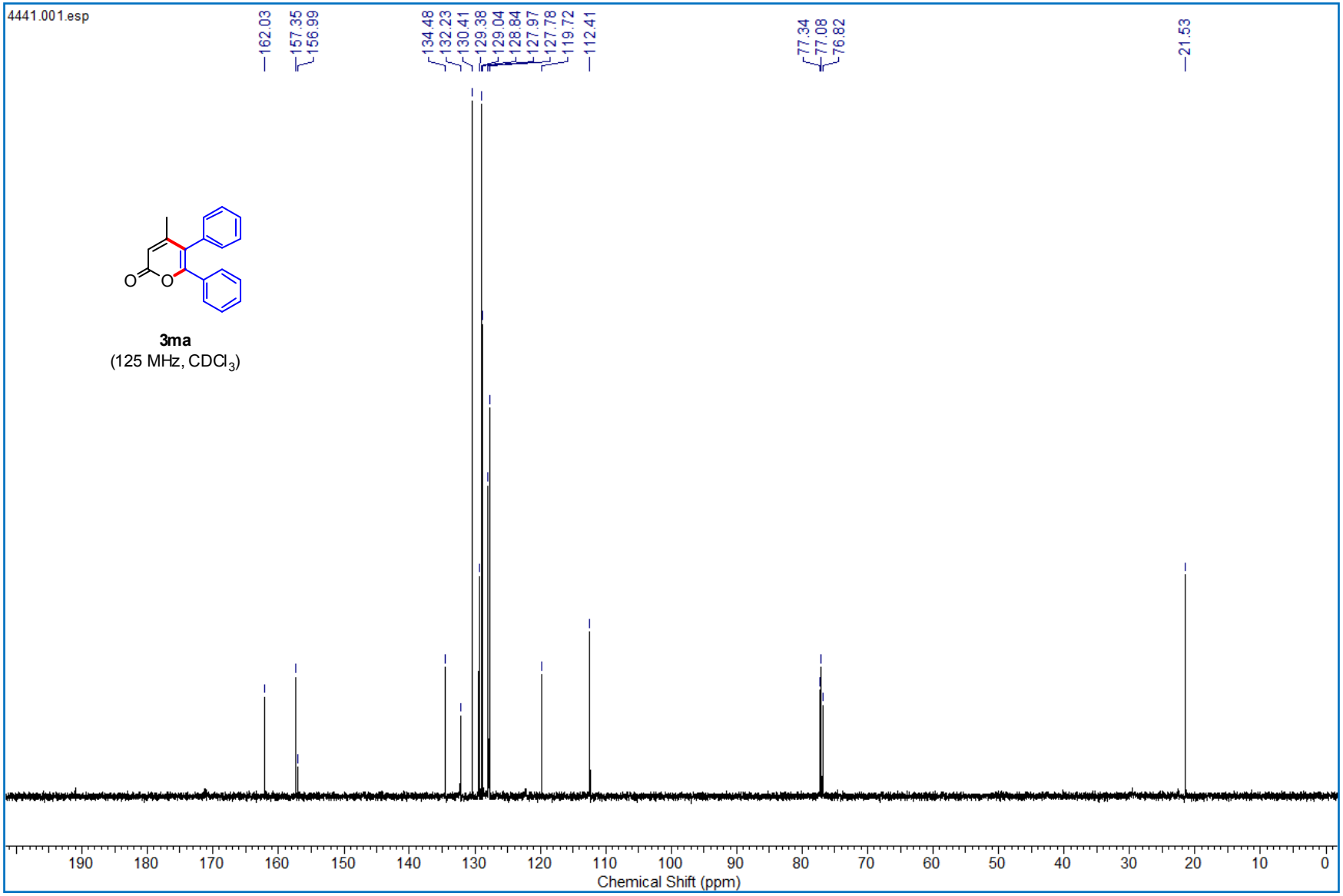


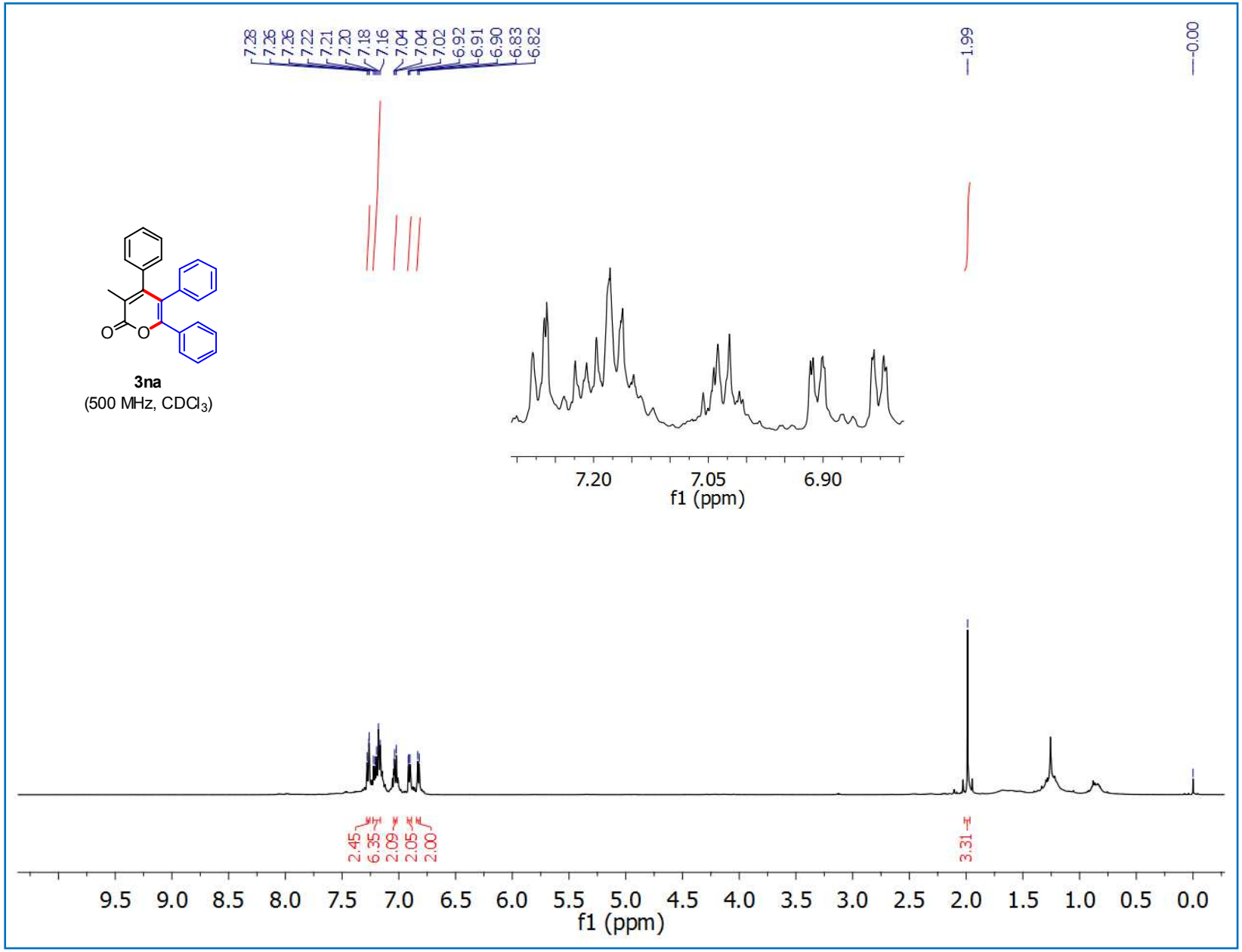
3la
(125 MHz, $CDCl_3$)

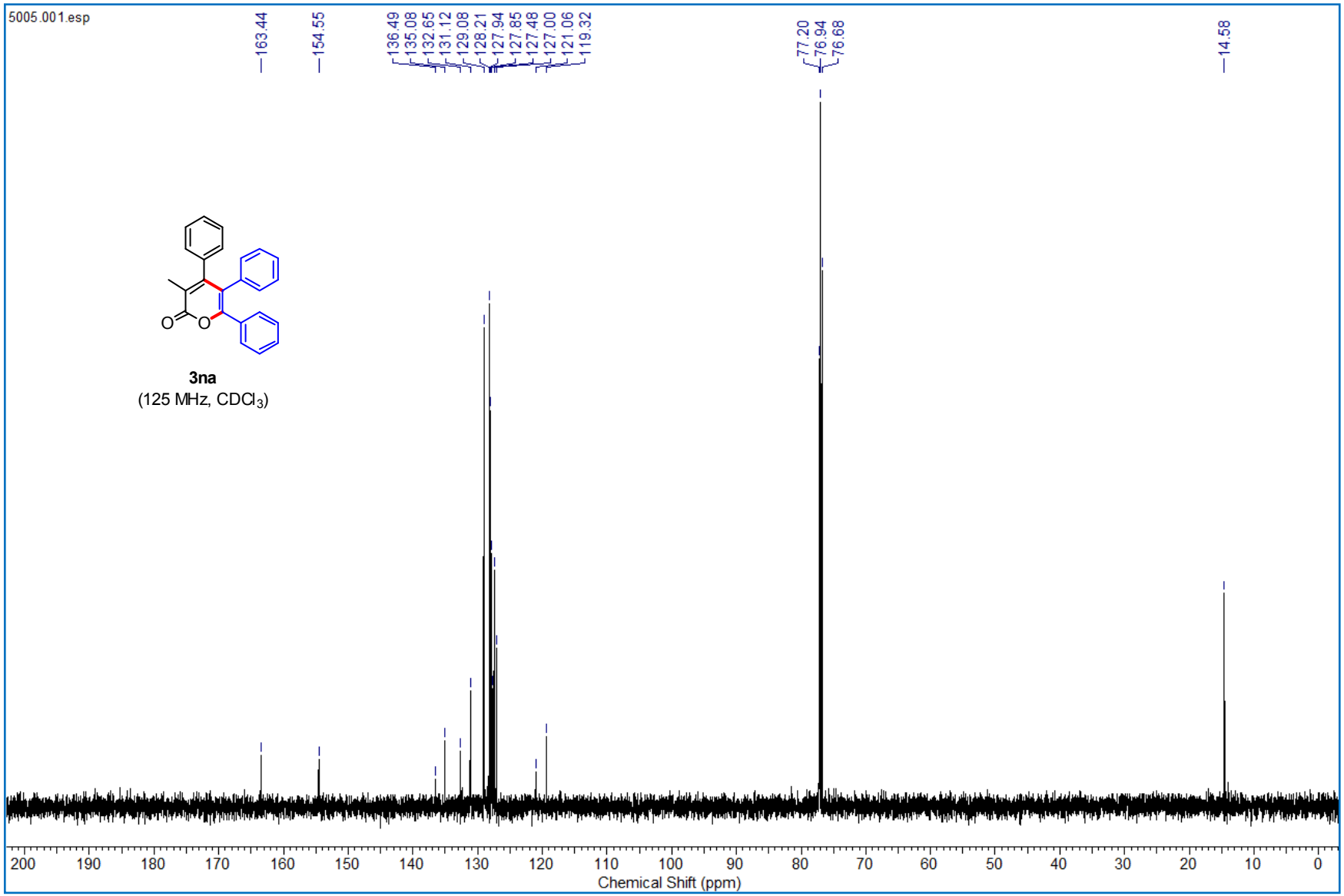

7.44 7.44 7.43 7.43 7.36 7.36 7.35 7.35 7.31 7.31 7.31 7.30 7.26 7.16 7.16 7.16 7.15 7.14 7.14 7.13 6.93 6.93 6.92 6.92 6.91 6.90 6.90 6.87 6.87 6.86 6.86 6.81 6.81 6.80 6.80 6.51
0.00
S
S
S
O
O
3lm
(500 MHz, CDCl3)
7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.02 1.04 1.03 2.04 2.21 1.16 1.00 1.00
9.5 9.0 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
f1 (ppm)

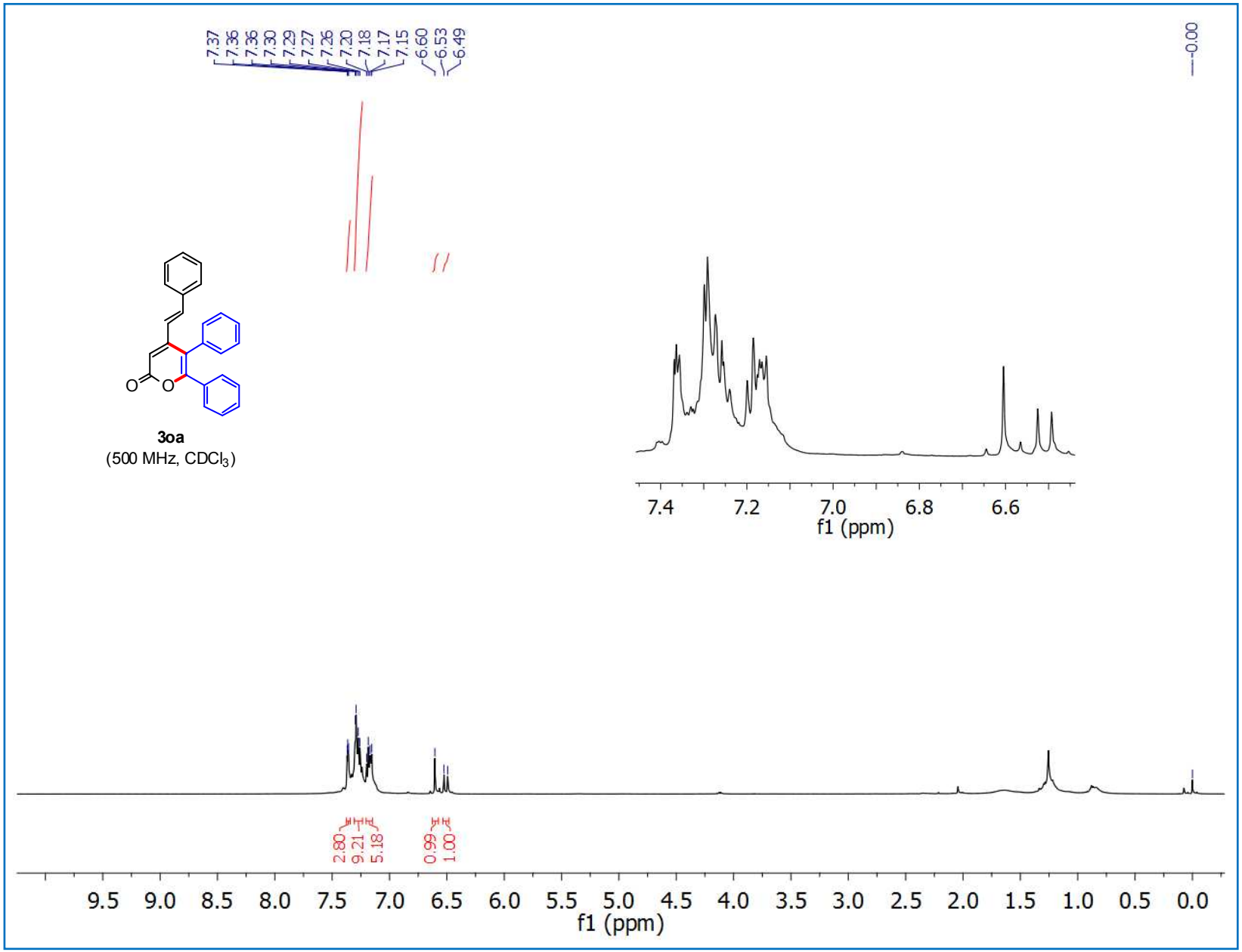

5599.001.esp
161.26
154.24
151.17
137.82
134.02
129.88
129.72
129.46
128.33
127.29
127.04
126.97
125.15
110.87
110.19
77.20
76.94
76.69
S
S
S
O
O
3lm
(125 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

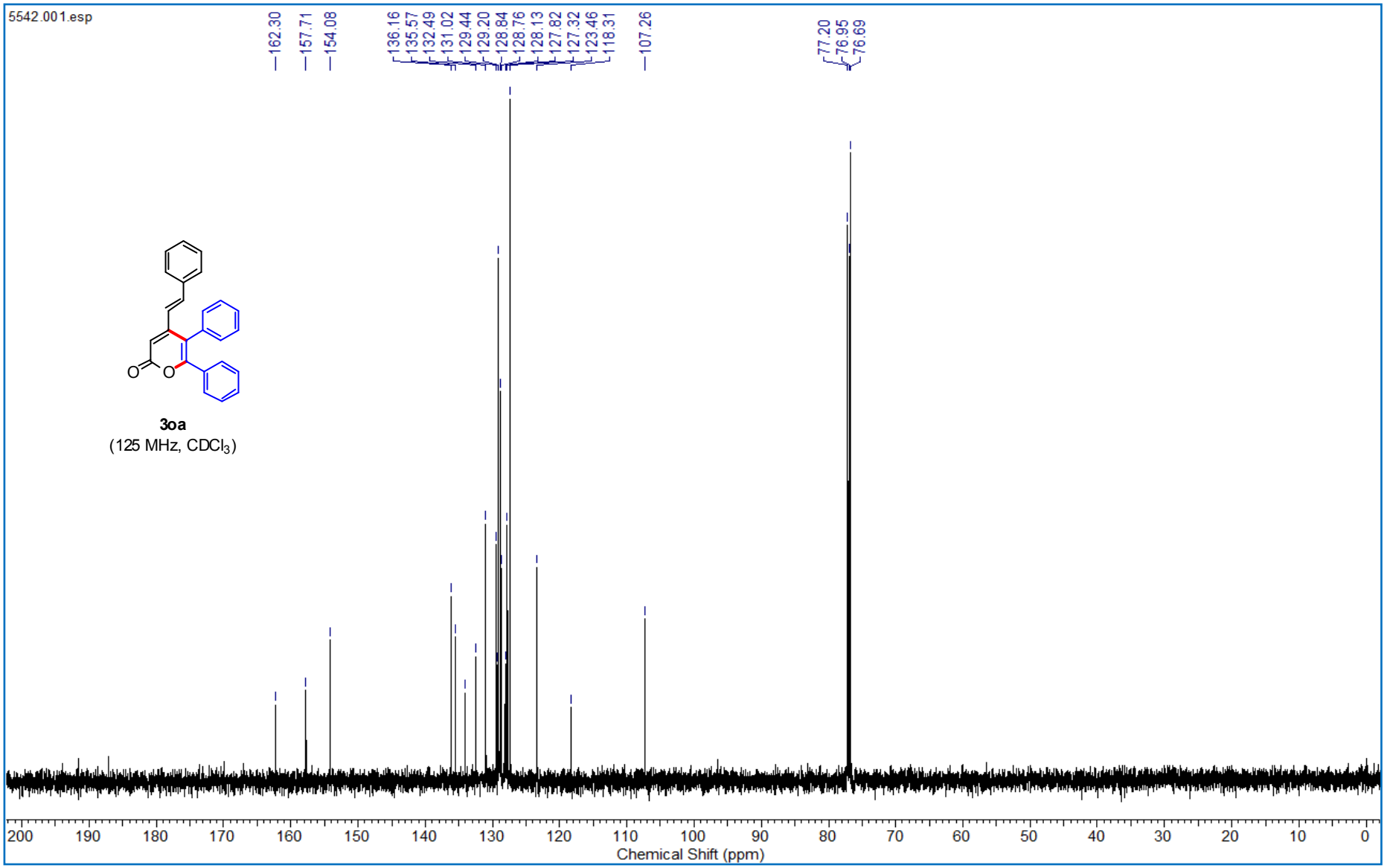

7.35
7.34
7.27
7.26
7.22
7.21
7.21
7.17
7.15
7.14
7.14
7.13
7.12
6.24
1.95
0.00
O
O
3ma
(500 MHz, CDCl3)
7.40
7.30
7.20
7.10
f1 (ppm)
3.00
3.65
4.51
1.00
3.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

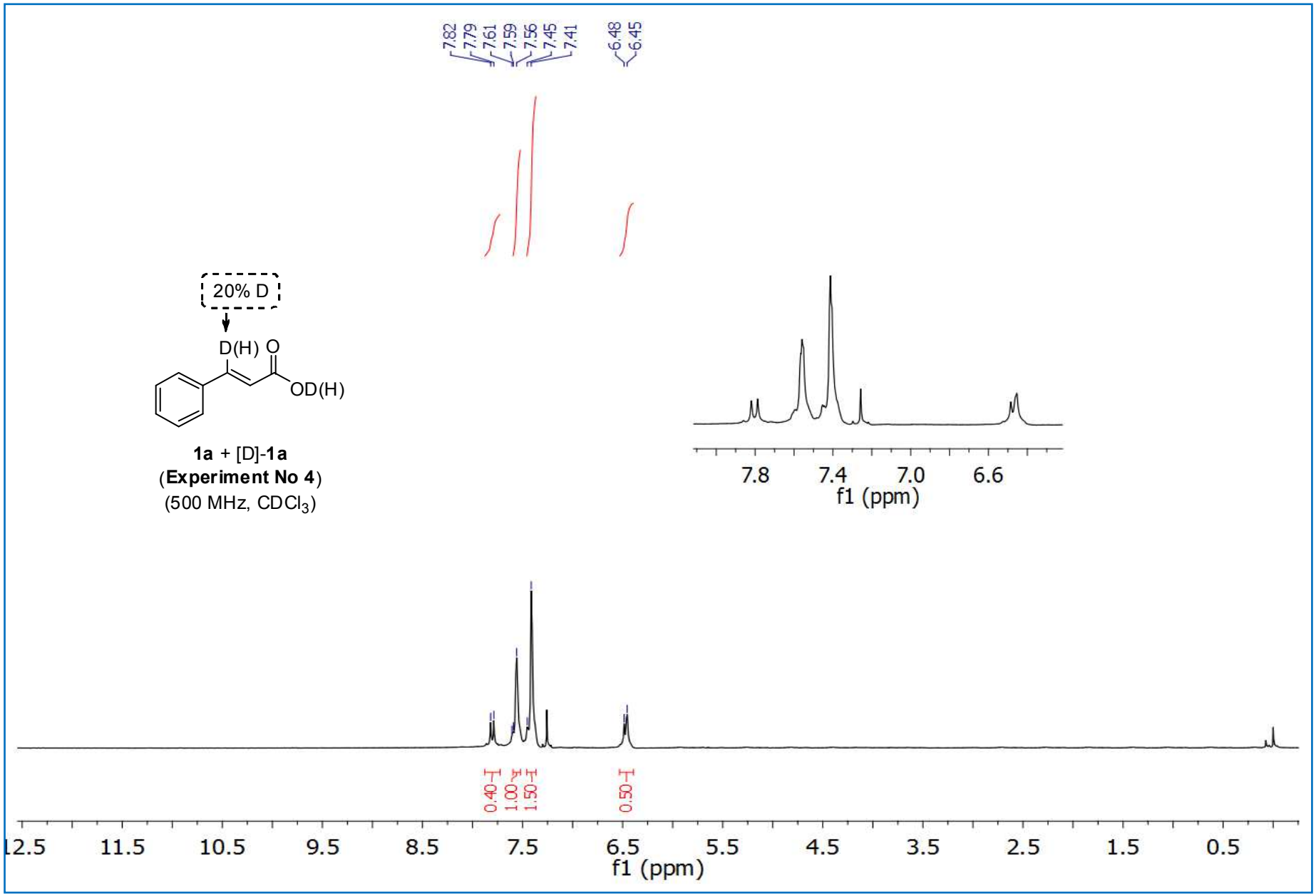

4441.001.esp
162.03
157.35
156.99
134.48
132.23
130.41
129.38
129.04
128.84
127.97
127.78
119.72
112.41
77.34
77.08
76.82
21.53
O
O
3ma
(125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

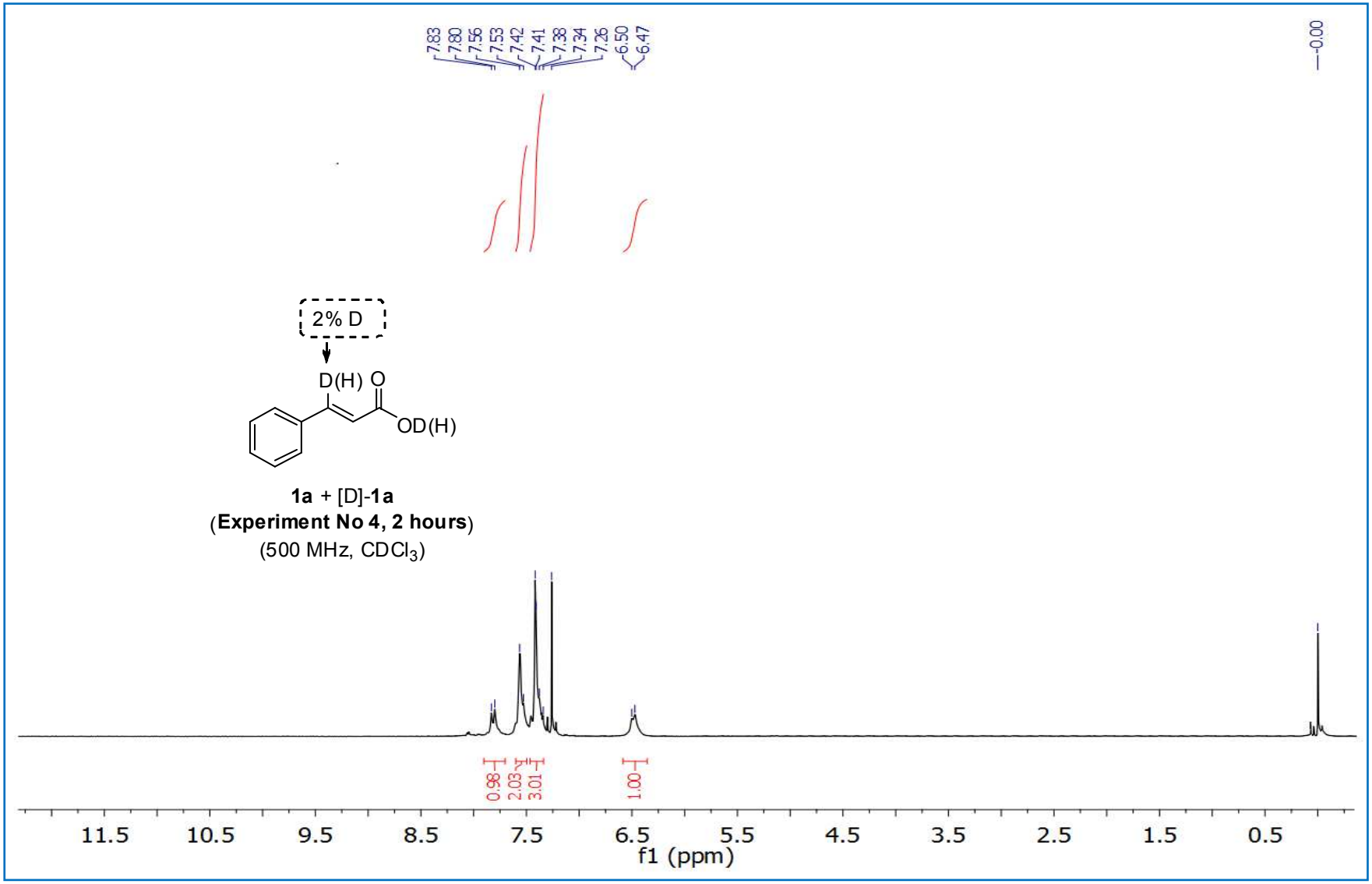

7.28
7.26
7.26
7.22
7.21
7.20
7.18
7.16
7.04
7.04
7.02
6.92
6.91
6.90
6.83
6.82
1.99
0.00
O
O
3na
(500 MHz, CDCl3)
7.20
7.05
6.90
f1 (ppm)
2.45
6.35
2.09
2.05
2.00
3.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


5005.001.esp
163.44
154.55
136.49
135.08
132.65
131.12
129.08
128.21
127.94
127.85
127.48
127.00
121.06
119.32
77.20
76.94
76.68
14.58
O
O
3na
(125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

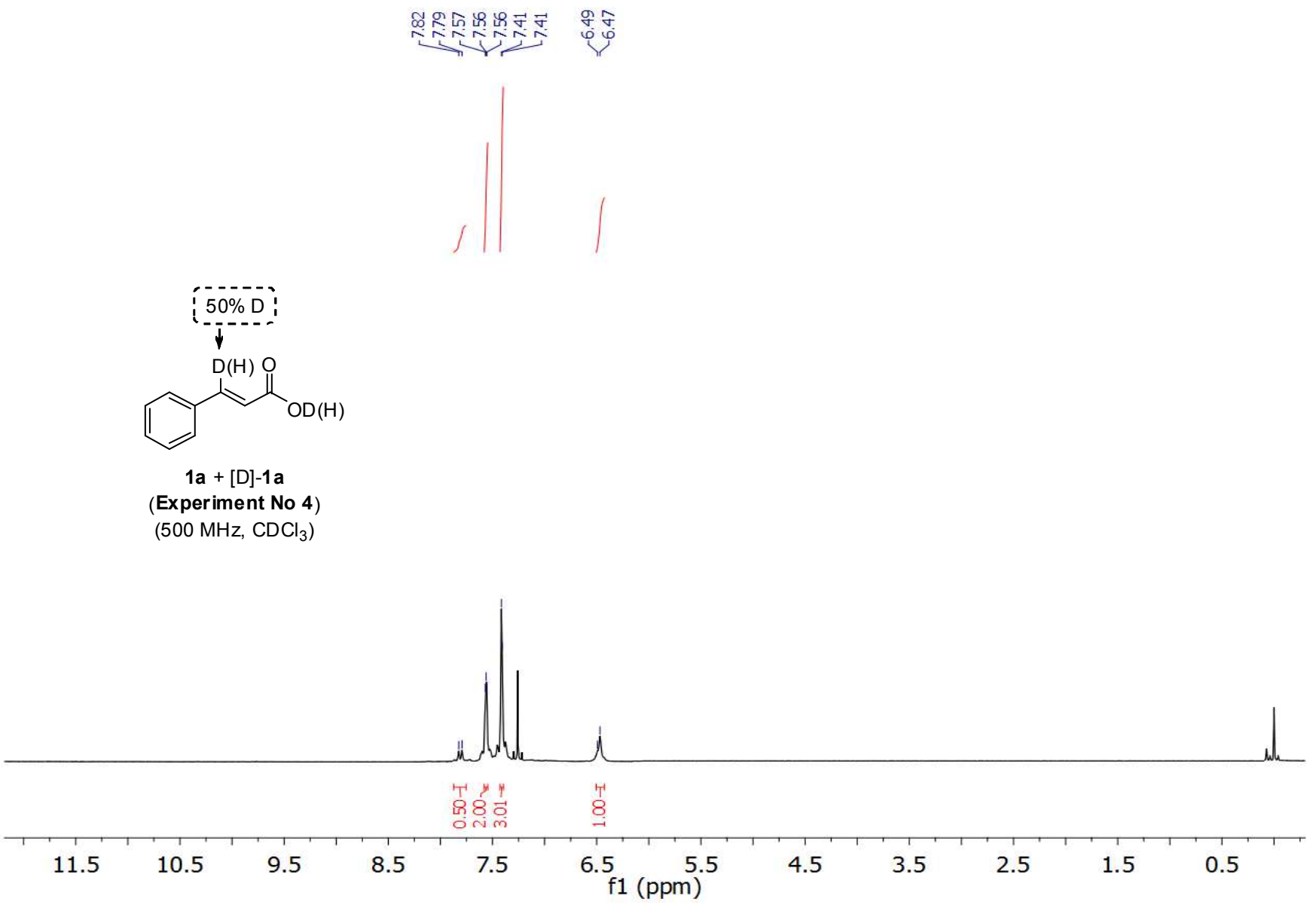

7.37
7.36
7.36
7.30
7.29
7.27
7.26
7.20
7.18
7.17
7.15
6.60
6.53
6.49
0.00
O
O
3oa
(500 MHz, CDCl3)
7.4
7.2
7.0
6.8
6.6
f1 (ppm)
2.80
9.21
5.18
0.99
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


5542.001.esp
162.30
157.71
154.08
136.16
135.57
132.49
131.02
129.44
129.20
128.84
128.76
128.13
127.82
127.32
123.46
118.31
107.26
77.20
76.95
76.69
O
O
3oa
(125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

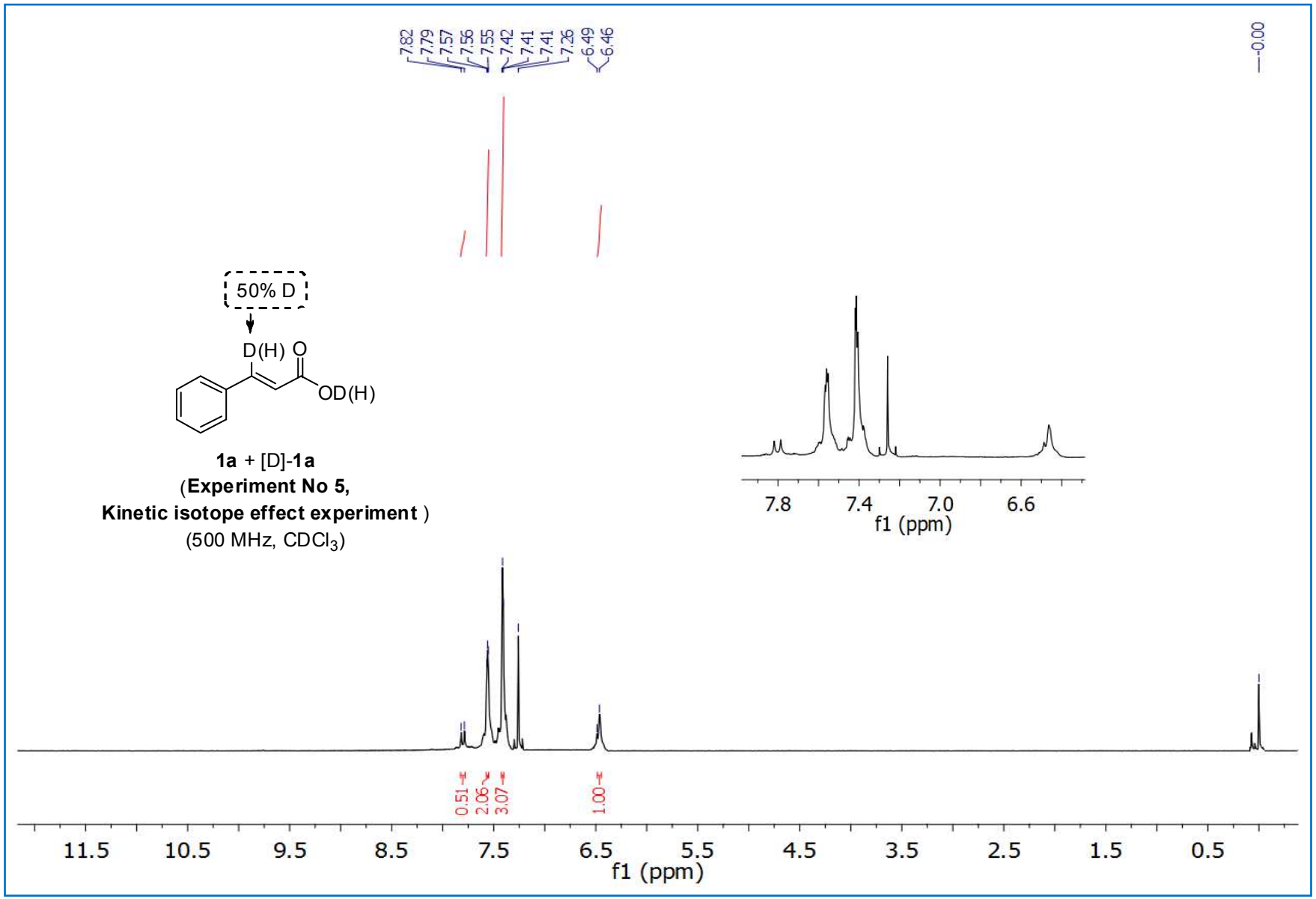

7.82
7.79
7.61
7.59
7.56
7.45
7.41
6.48
6.45
20% D
D(H) O
OD(H)
1a + [D]-1a
(Experiment No 4)
(500 MHz, CDCl3)
7.8
7.4
7.0
6.6
f1 (ppm)
0.40
1.00
1.50
0.50
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

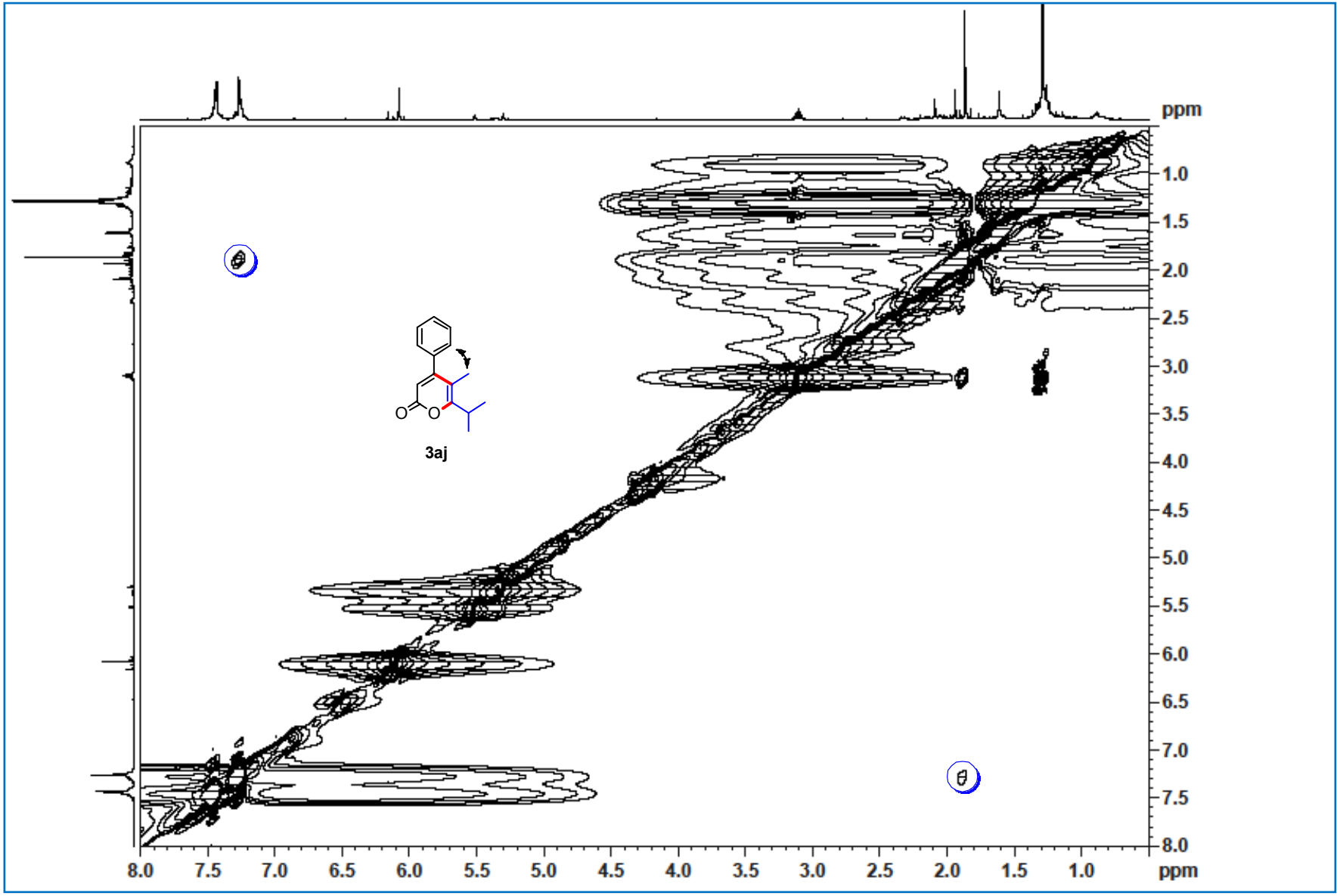


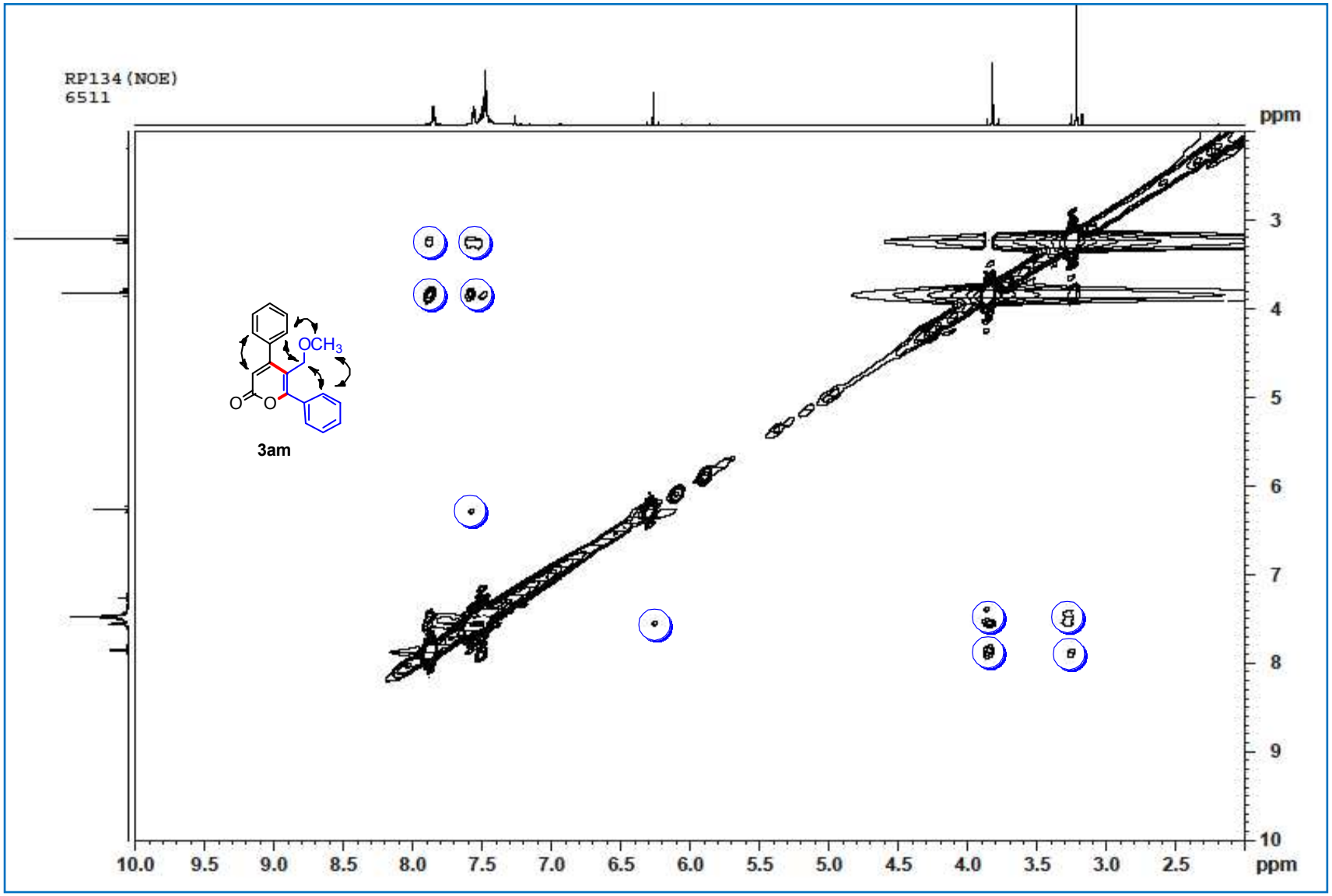
1a + [D]-**1a**
(**Experiment No 4, 2 hours**)
(500 MHz, $CDCl_3$)



1a + [D]-**1a**
(**Experiment No 4**)
(500 MHz, $CDCl_3$)


7.82
7.79
7.57
7.56
7.55
7.42
7.41
7.41
7.26
6.49
6.46
-0.00
50% D
D(H)
O
OD(H)
1a + [D]-1a
(Experiment No 5,
Kinetic isotope effect experiment)
(500 MHz, CDCl3)
7.8
7.4
7.0
6.6
f1 (ppm)
0.51
2.06
3.07
1.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
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
ppm
O
O
3aj


RP134 (NOE)
6511
OCH3
O
O
3am
ppm
3
4
5
6
7
8
9
10
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
ppm