Pd-Catalyzed arylative annulation of alkynyl nitriles with boronic acids to functionalized cyclopentene-3-ones/2-indenones

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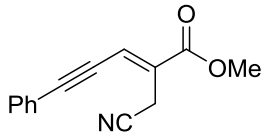
1. General information:

All the reactions were performed in an oven-dried glass apparatus, the air and moisture sensitive reactions were carried out under inert atmosphere (nitrogen) using freshly distilled anhydrous solvents. Commercially available reagents were used as such without further purification. All reactions were monitored by thin-layer chromatography carried out on silica plates using UV-light and anisaldehyde for visualization. Column chromatography was performed on silica gel (100-200 mesh) using hexane and ethyl acetate as eluent. ^{1}H NMR was recorded in $CDCl_3$ on 500 MHz, 400 MHz and 300 MHz and ^{13}C NMR was recorded on 125 MHz, 101 MHz and 176 MHz. δ 7.26 and δ 77 are corresponding to $CDCl_3$ in ^{1}H NMR and ^{13}C NMR respectively, δ 1.56 is related to moisture present in $CDCl_3$. ^{19}F NMR was recorded in $CDCl_3$ on 471 MHz and 377 MHz. Chemical shifts were reported in δ (ppm) relative to TMS as an internal standard and *J* values were given in Hz (hertz). Multiplicity is indicated as, s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. High resolution mass spectra (HRMS) [ESI^+] were obtain using either a TOF or a double focusing spectrometer. Chemical nomenclature was generated using ChemDraw 21.0. Melting points were determined using a digital melting point apparatus (MP-97). All the 2-en-4-ynyl cyanides and 2-(2-(phenylethynyl)phenyl)acetonitrile were synthesized by using previous report.[1]

2. Structures of starting materials:



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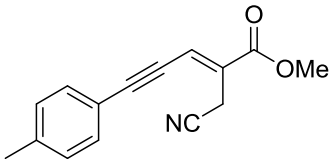

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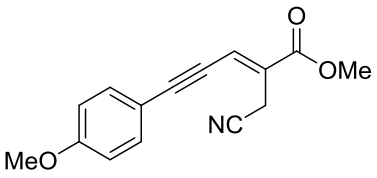

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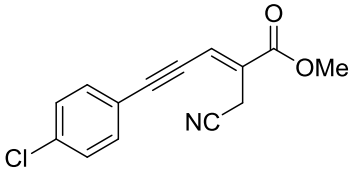

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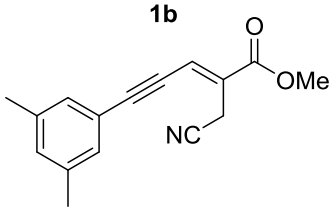

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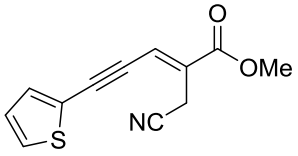

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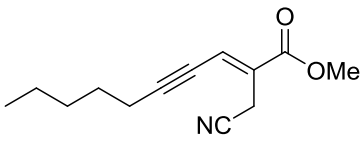

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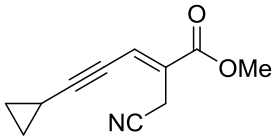

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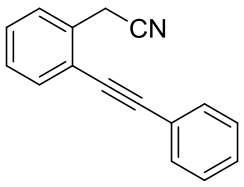

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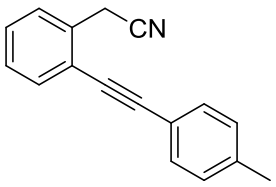

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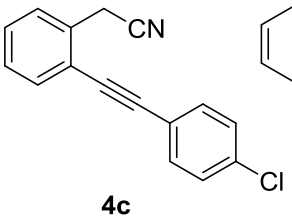

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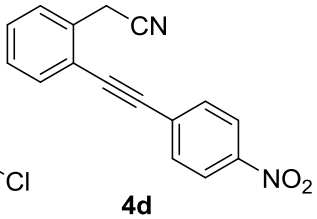

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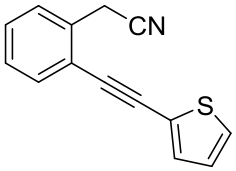

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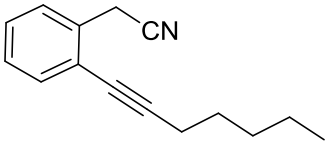

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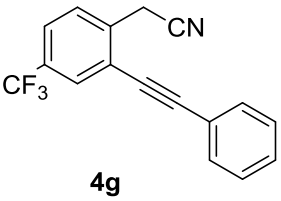

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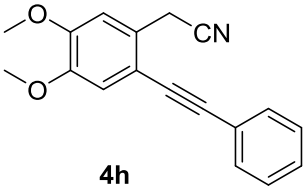

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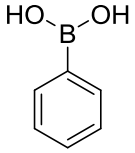
Boronic acids **2a** to **2l** are commercially available.



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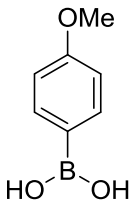

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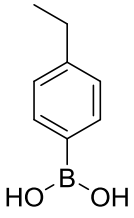

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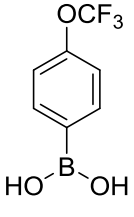

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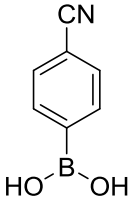

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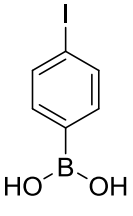

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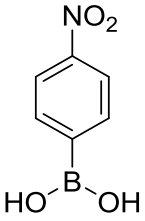

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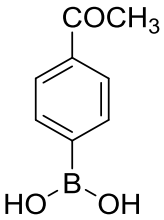

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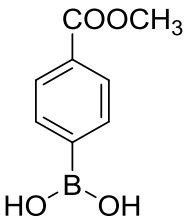

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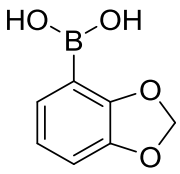

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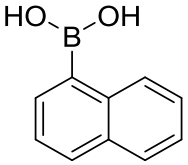

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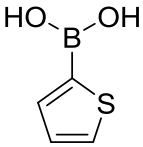
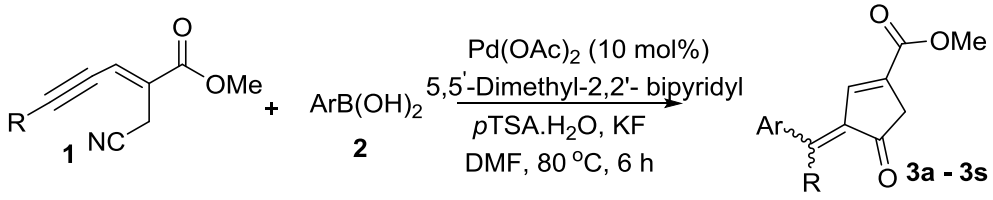


2l

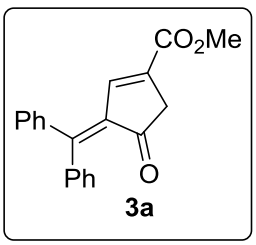
3. General reaction and characterization data of compounds

A) General procedure for the preparation of diphenyl methylene oxo-cyclopentene carboxylate: (3a - 3m):

To a stirred solution of corresponding enynyl nitriles **1** (0.3 mmol, 1 equiv.), and aryl boronic acid **2** (0.45 mmol, 1.5 equiv.) in 3 mL of DMF, was added 5,5'-Dimethyl-2,2'- bipyridyl (L2) (20 mol%), *p*-TSA (1.2 mmol, 4 equiv.), KF (0.6 mmol, 2 equiv.) and $Pd(OAc)_2$ (10 mol %) at room temperature. The reaction mixture was stirred at 80 ^oC (oil-bath temperature) for given time. After the completion of reaction (monitored by TLC), saturated $NaHCO_3$ aqueous solution (2 mL) was added to the reaction mixture and extracted with EtOAc (2×10 mL), the residue was purified and washed with brine (2×10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel (5% EtOAc in petroleum ether) to afford the corresponding **3**.



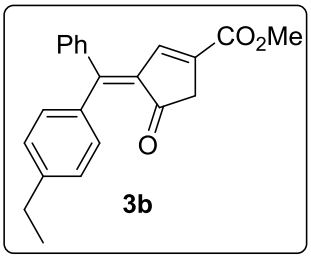
Methyl 3-(diphenylmethylene)-4-oxocyclopent-1-ene-1-carboxylate (3a):



Yellow solid, 77 mg, 84% yield, mp: 110 - 112 °C, R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, J = 1.8 Hz, 1H), 7.44 – 7.37 (m, 4H), 7.37 – 7.33 (m, 2H),

7.24 – 7.18 (m, 4H), 3.79 (s, 3H), 3.28 (d, J = 1.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 200.7, 165.0, 153.2, 143.8, 142.0, 138.3, 134.4, 131.9, 130.8, 130.7, 129.7, 129.7, 128.4, 127.8, 52.0, 43.0; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{20}H_{17}O_3$ 305.1172; Found 305.1174.

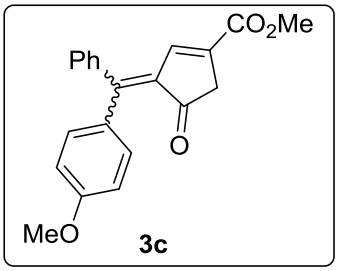
Methyl (*Z*)-3-((4-ethylphenyl)(phenyl)methylene)-4-oxocyclopent-1-ene-1-carboxylate (3b):



3b

Yellow solid, 81 mg, 81% yield, mp: 115 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.45 – 7.35 (m, 3H), 7.24 – 7.10 (m, 6H), 3.79 (d, J = 4.1 Hz, 3H), 3.28 (d, J = 1.4 Hz, 2H), 2.70 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 200.7, 165.0, 153.7, 146.3, 144.2, 141.2, 135.5, 134.2, 131.1, 130.9, 130.8, 129.6, 128.4, 127.2, 51.9, 43.1, 28.8, 15.1; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{22}H_{21}O_3$ 333.1485; Found 333.1489.

Methyl(*Z*)-3-((4-methoxyphenyl)(phenyl)methylene)-4-oxocyclopent-1-ene-carboxylate (3c): (*E/Z* : 4:6)

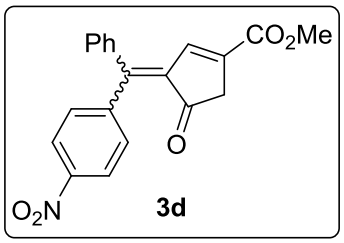


3c

Brown solid, 85 mg, 85% yield, mp: 120 - 122 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) (*E/Z* 4:6) ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.53 (m, 1H) (both isomers), 7.47 – 7.32 (m, 3H) (both isomers), 7.29 – 7.13 (m, 4H) (both isomers), 6.96 – 6.82 (m, 2H) (both isomers), 3.86 (d, J = 4.6 Hz, 3H) (both isomers), 3.79 (d, J = 7.2 Hz, 3H) (both isomers), 3.28 (d, J = 11.3 Hz, 2H) (both isomers); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 200.8, 165.1, 161.2, 161.1, 153.5, 153.2, 144.5, 144.2, 141.3, 138.6, 133.6, 133.5, 133.2, 133.1, 132.7, 131.1, 131.0,

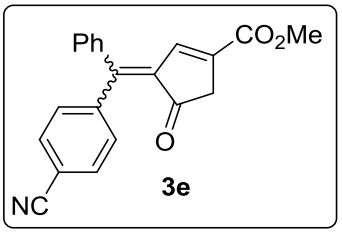
130.9, 130.4, 129.7, 128.4, 127.7, 115.3, 113.9, 113.1, 55.4, 55.3, 51.9, 51.8, 43.2, 43.0; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{24}H_{19}O_4$ 335.1283; Found 335.1283.

Methyl(*Z*)-3-((4-nitrophenyl)(phenyl)methylene)-4-oxocyclopent-1-ene-1-carboxylate (3d): (E/Z : 2:8)



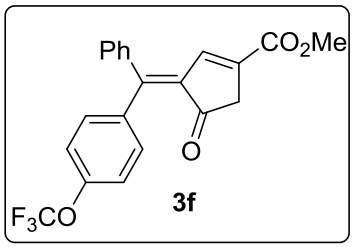
Yellow solid, 73 mg, 70% yield, mp: 160 - 162 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ {8.21 (major) 8.26 (minor) (d, J = 8.5 Hz, 2H)}, 7.65 (s, 1H), 7.49 – 7.40 (m, 3H), 7.38 (d, J = 8.4 Hz, 2H), {7.18 (major) 6.89 (minor) (d, J = 7.6 Hz, 2H)}, 3.82 (s, 3H), 3.29 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)(both isomers) δ 200.5, 199.8, 164.6, 149.2, 148.0, 145.1, 142.4, 139.6, 135.7, 134.3, 131.3, 130.6, 130.4, 130.2, 128.8, 128.1, 126.2, 123.7, 123.1, 119.7, 115.6, 52.1, 42.7; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{20}H_{16}NO_5$ 350.1023; Found 350.1017.

Methyl (*Z*)-3-((4-cyanophenyl)(phenyl)methylene)-4-oxocyclopent-1-ene-1-carboxylate (3e): (E/Z :1:9)



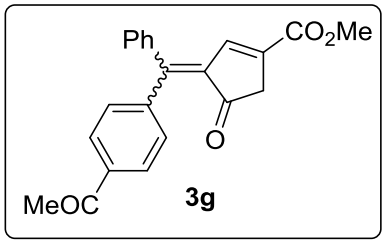
Yellow solid, 71 mg, 72% yield, mp: 135 - 137 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 1H), 7.64 (d, J = 8.2 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.32 (d, J = 7.9 Hz, 2H), 7.17 (t, J = 7.5 Hz, 2H), 3.81 (s, 3H), 3.29 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$)(both isomers) δ 200.4, 200.4, 164.6, 149.7, 149.6, 143.1, 142.6, 142.1, 139.8, 135.5, 134.0, 132.2, 131.6, 131.1, 130.6, 130.4, 130.1, 128.8, 128.1, 118.7, 112.8, 52.1, 42.7; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{21}H_{16}NO_3$ 330.1133; Found 330.1133.

Methyl (*Z*)-4-oxo-3-(phenyl(4-(trifluoromethoxy)phenyl)methylene)cyclopent-1-ene-1-carboxylate (3f):



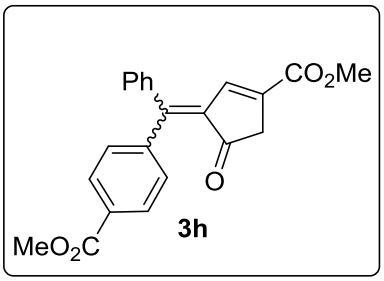
Yellow solid, 88 mg, 76% yield, mp: 119 - 121 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1 ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 1H), 7.44 – 7.42 (m, 1H), 7.42 – 7.40 (m, 1H), 7.28 – 7.26 (m, 1H), 7.26 – 7.23 (m, 2H), 7.20 – 7.15 (m, 4H), 3.80 (s, 3H), 3.29 (d, J = 1.9 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.6, 164.8, 151.2, 150.0, 143.3, 140.6, 136.6, 134.8, 132.46 (2C), 130.6, 129.9, 128.6, 119.8, 52.0, 42.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.57; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{21}H_{16}F_3O_4$ 389.0995; Found 389.0997.

Methyl (*Z*)-3-((4-acetylphenyl)(phenyl)methylene)-4-oxocyclopent-1-ene-1-carboxylate (3g): (*E/Z* : 4:6)



Yellow solid, 81 mg, 78% yield, mp: 125 - 127 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ {7.99 – 7.96 (minor) 7.95 – 7.92 (major) (m, 2H)}, {7.64 (major) 7.53 (minor) (t, *J* = 1.9 Hz, 1H)}, 7.46 – 7.35 (m, 3H) (both isomers), 7.34 – 7.29 (m, 2H), 7.24 – 7.16 (m, 2H) (both isomers), {3.81 (major) 3.80 (minor) (s, 3H)}, 3.29 (dd, *J* = 2.9, 2.0 Hz, 2H) (both isomers), {2.64 (minor) 2.63 (major) (s, 3H)}; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) (both isomers)) δ 200.5, 200.2, 197.6, 197.4, 164.8, 151.3, 151.1, 145.5, 143.3, 143.0, 142.8, 140.2, 137.5, 137.4, 135.2, 133.2, 133.1, 130.8, 130.8, 130.7, 130.5, 129.9, 129.9, 128.6, 128.4, 127.9, 127.8, 52.0, 42.8, 42.8, 26.7; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{22}H_{19}O_4$ 347.1277; Found 347.1271.

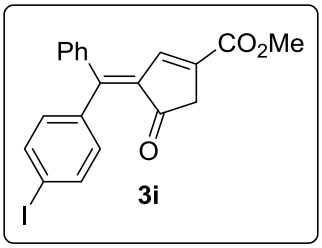
Methyl (*Z*)-4-oxo-3-(phenyl(thiophen-3-yl)methylene)cyclopent-1-ene-1-carboxylate (3h): (*E/Z*: 3:7)



3h

Yellow solid, 87 mg, 80% yield, mp: 142 - 144 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (400 MHz, CDCl3) δ 8.10 – 7.93 (m, 2H)(both isomer), {7.63 (major) 7.52 (minor) (t, *J* = 44.4, 1.9 Hz, 1H)}, 7.49 – 7.35 (m, 3H)(both isomer), 7.31 – 7.27 (m, 2H)(both isomer), 7.22 – 7.15 (m, 2H)(both isomer), 3.94 (d, *J* = 8.2 Hz, 3H)(both isomer), 3.80 (d, *J* = 3.2 Hz, 3H)(both isomer), {3.29 (minor) 3.28 (major) (dd, *J* = 3.8, 1.9 Hz, 2H)}; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.5, 200.2, 166.7, 164.81, 158.2, 151.3, 145.4, 143.1, 143.0, 142.9, 140.3, 137.6, 135.1, 133.1, 133.0, 131.9, 130.9, 130.7, 130.5, 129.9, 129.6, 129.1, 128.8, 128.6, 128.0, 127.3, 115.2, 52.2, 52.0, 42.9, 42.8; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{22}H_{19}O_5$ 363.1227; Found 363.1229.

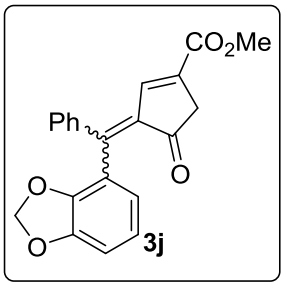
Methyl(*Z*)-3-((4-iodophenyl)(phenyl)methylene)-4-oxocyclopent-1-ene-1-carboxylate (3i):



3i

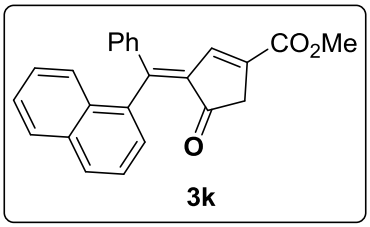
Yellow solid, 98 mg, 76% yield, mp: 150 - 152 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.58 (s, 1H), 7.45 – 7.38 (m, 3H), 7.18 (d, *J* = 6.6 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 3H), 3.28 (d, *J* = 1.5 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.5, 164.8, 151.6, 143.4, 140.5, 137.7, 137.0, 134.6, 132.5, 132.4, 130.7, 129.9, 128.6, 96.4, 52.0, 42.9; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{20}H_{16}IO_3$ 431.0138; Found 431.0143.

Methyl(*Z*)-3-(benzo[d][1,3]dioxol-4-yl(phenyl)methylene)-4-oxocyclopent-1-ene-1-carboxylate (3j): (*E/Z* : 3:7)



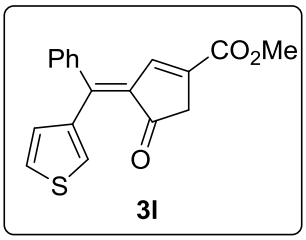
Yellow solid, 83 mg, 80% yield, mp: 156 - 158 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ {7.68 (minor) 7.53 (major) (t, J = 1.7 Hz, 1H)}, 7.46 – 7.32 (m, 3H) (both isomers), 7.24 – 7.18 (m, 2H) (both isomers), 6.85 – 6.61 (m, 3H) (both isomers), 6.02 (d, J = 7.3 Hz, 2H) (both isomers), {3.80 (minor) 3.78 (major) (s, 3H)}, {3.29 (major) 3.26 (minor) (d, J = 1.8 Hz, 2H)}.; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.6, 165.0, 153.0, 152.9, 149.3, 149.2, 147.2, 144.2, 143.9, 141.0, 134.0, 132.0, 130.9, 130.8, 129.8, 129.7, 128.4, 127.8, 126.2, 125.8, 111.5, 111.0, 108.3, 107.7, 101.7, 101.5, 51.9, 43.1, 43.0.; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{21}H_{17}O_5$ 349.1070; Found 349.1072.

Methyl(*Z*)-3-(naphthalen-1-yl(phenyl)methylene)-4-oxocyclopent-1-ene-1-carboxylate (3k):



Yellow solid, 80 mg, 75% yield, mp: 162 - 164 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.83 (m, 3H), 7.65 (d, J = 8.2 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.45 – 7.41 (m, 1H), 7.39 – 7.29 (m, 7H), 3.83 (s, 3H), 3.19 (d, J = 1.5 Hz, 2H).; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 200.2, 165.0, 150.3, 142.3, 140.4, 137.2, 136.2, 133.7, 133.6, 131.7, 129.8, 129.7, 129.0, 128.6, 128.6, 126.9, 126.4, 125.8, 125.2, 124.9, 52.0, 42.4; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{24}H_{19}O_3$ 355.1328; Found 355.1320.

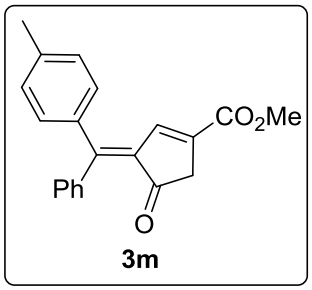
Methyl(*Z*)-4-oxo-3-(phenyl(thiophen-3-yl)methylene)cyclopent-1-ene-1-carboxylate (3l):



3l

Voilet solid, 67 mg, 72% yield, mp: 158 - 160 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.72 (d, J = 5.4 Hz, 1H), 7.61 (s, 1H), 7.52 (d, J = 5.4 Hz, 1H), 7.30 (t, J = 7.2 Hz, 2H), 7.24 (d, J = 7.2 Hz, 1H), 7.18 (d, J = 7.3 Hz, 2H), 4.33 (s, 2H), 3.95 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 180.4, 167.8, 152.8, 143.3, 141.3, 138.7, 136.0, 134.4, 134.3, 130.0, 129.0, 128.4, 127.7, 127.0, 53.5, 45.4; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{18}H_{15}O_3S$ 311.0736; Found 311.0735.

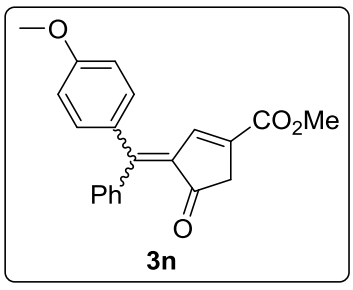
Methyl (*E*)-4-oxo-3-(phenyl(p-tolyl)methylene)cyclopent-1-ene-1-carboxylate (3m):



3m

Yellow solid, 76 mg, 80% yield, mp: 150 - 152 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (m, 1H), 7.46 – 7.32 (m, 3H), 7.23 – 7.07 (m, 6H), 3.79 (s, 3H), 3.28 (s, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 200.7, 165.0, 153.4, 144.0, 140.2, 138.5, 138.2, 134.1, 131.4, 130.8, 129.6, 129.1, 128.4, 127.7, 51.9, 43.0, 21.5; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{21}H_{19}O_3$ 319.1328; Found 319.1332.

Methyl(*E*)-3-((4-methoxyphenyl)(phenyl)methylene)-4-oxocyclopent-1-ene-1-carboxylate (3n): (E/Z : 7:3)

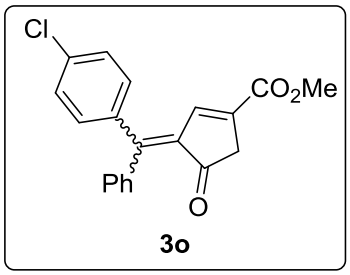


3n

Red solid, 83 mg, 83% yield, mp: 125 - 127 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1 ^{1}H NMR (400 MHz, CDCl3) δ {7.69 (major), 7.53 (minor) (t, J = 1.6 Hz, 2H)}, 7.61 (dt, J = 61.7, 1.7 Hz, 1H) (both isomers), 7.44 – 7.32 (m, 3H) (both isomers), 7.24 – 7.12 (m, 4H) (both isomers), 6.93 – 6.81 (m, 2H) (both isomers), 3.85 (d, J = 4.8 Hz, 3H) (both isomers),

3.79 (d, *J* = 7.4 Hz, 3H) (both isomers),{3.29 (major), 3.27 (minor) (d, *J* = 1.7 Hz, 2H)}.$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 200.8, 165.0, 165.01, 161.3, 161.1, 153.5, 153.2, 144.5, 144.2, 141.4, 138.6, 133.6, 133.5, 133.2, 132.7, 131.0, 130.9, 130.4, 130.3, 129.7, 129.7, 128.4, 127.7, 113.9, 113.1, 55.5, 55.3, 51.9, 51.8, 43.2, 43.0. HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{21}H_{19}O_4$ 335.1277; Found 335.1279.

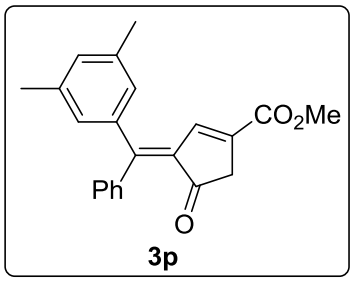
Methyl(*E*)-3-((4-chlorophenyl)(phenyl)methylene)-4-oxocyclopent-1-ene-1-carboxylate (3o): (E/Z : 8:2)



3o

Yellow solid, 73 mg, 72% yield, mp: 140 - 142 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^1H NMR (400 MHz, $CDCl_3$) δ {7.57 (major) 7.59 (minor) (d, *J* = 8.0 Hz, 1H)}, 7.47 – 7.36 (m, 3H), 7.36 – 7.28 (m, 2H), 7.23 – 7.10 (m, 4H), 3.79 (s, 3H), 3.28 (s, 2H); $13C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 200.6, 200.3, 164.8, 151.5, 143.4, 143.1, 140.6, 139.4, 137.9, 136.6, 135.8, 134.7, 132.3, 132.2, 131.9, 130.8, 130.7, 129.9, 128.8, 128.6, 128.1, 127.9, 52.0, 43.0; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{20}H_{16}ClO_3$ 339.0782; Found 339.0783.

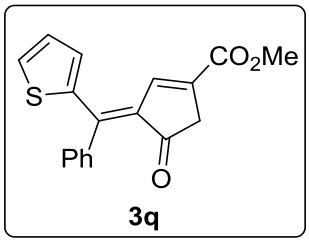
Methyl (*E*)-3-((3,5-dimethylphenyl)(phenyl)methylene)-4-oxocyclopent-1-ene-carboxylate (3p):



3p

Yellow solid, 77 mg, 78% yield, mp: 146 - 148 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1 ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.46 – 7.31 (m, 3H), 7.25 – 7.16 (m, 2H), 7.05 (s, 1H), 6.81 (d, *J* = 14.3 Hz, 2H), 3.79 (s, 3H), 3.27 (s, 2H), 2.30 (d, *J* = 8.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 200.7, 165.02, 153.8, 144.1, 143.9, 141.01, 138.0, 137.2, 131.4, 130.7, 129.6, 128.4, 128.3, 127.7, 51.8, 43.0, 21.3; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{22}H_{21}O_3$ 333.1485; Found 333.1486.

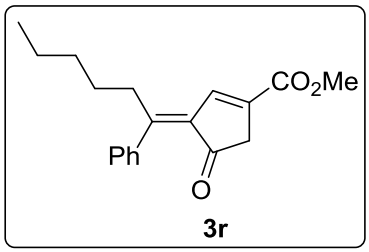
Methyl(*E*)-4-oxo-3-(phenyl(thiophen-2-yl)methylene)cyclopent-1-ene-1-carboxylate (3q):



3q

Brown solid, 67 mg, 72% yield, mp: 123 - 125 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 3.5 Hz, 1H), 7.56 (d, J = 5.0 Hz, 1H), 7.45 (d, J = 6.8 Hz, 3H), 7.28 (s, 2H), 7.19 (s, 1H), 7.08 (t, 1H), 3.75 (s, 3H), 3.34 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 200.5, 167.2, 144.6, 141.2, 141.2, 135.5, 132.3, 130.1, 129.9, 129.8, 129.3, 129.2, 128.4, 127.3, 51.8, 43.2; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{18}H_{15}O_3S$ 311.0736; Found 311.0738.

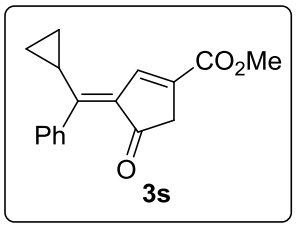
Methyl (*Z*)-4-oxo-3-(1-phenylhexylidene)cyclopent-1-ene-1-carboxylate (3r):



3r

Red solid, 65 mg, 75% yield, mp: 118 - 120 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 1H), 7.42 – 7.37 (m, 2H), 7.36 (t, J = 1.9 Hz, 1H), 7.26 (s, 1H), 7.25 (t, J = 1.4 Hz, 1H), 3.75 (s, 3H), 3.23 (d, J = 1.9 Hz, 2H), 3.17 – 3.09 (m, 2H), 1.37 – 1.23 (m, 6H), 0.83 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 203.2, 165.1, 158.9, 142.6, 140.7, 134.2, 130.3, 128.8, 128.6, 128.0, 51.8, 42.9, 33.0, 31.8, 28.4, 22.4, 14.0; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{19}H_{23}O_3$: 299.1642, Found 299.1645.

Methyl (*Z*)-3-(cyclopropyl(phenyl)methylene)-4-oxocyclopent-1-ene-1-carboxylate (3s):

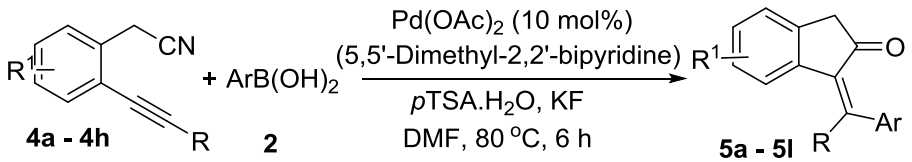


3s

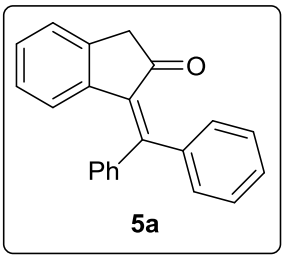
White solid, 59 mg, 73% yield, mp: 115 - 117 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 3H), 7.03 – 7.01 (m, 1H), 7.01 – 7.00 (m, 1H), 6.88 (t, *J* = 1.9 Hz, 1H), 3.71 (s, 3H), 3.68 – 3.62 (m, 1H), 3.25 (d, *J* = 1.9 Hz, 2H), 0.99 (dd, *J* = 8.3, 2.6 Hz, 2H), 0.58 (dd, *J* = 5.1, 2.6 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 203.9, 165.1, 161.3, 142.6, 135.2, 135.0, 128.3, 128.2(2C), 128.0, 51.7, 43.3, 14.3, 8.5; HRMS (ESI) m/z : $(M+H)^+$ Calcd for $C_{17}H_{17}O_3$ 269.1172; found 269.1167.

B) General procedure for the preparation of diphenyl methylene dihydroindenone: (5a – 5l):

To a stirred solution of corresponding 2-ethynylphenylacetonitrile **4**(0.3 mmol, 1 equiv.), and aryl boronic acid **2** (0.45 mmol, 1.5 equiv.) in 3 mL of DMF, was added 5,5'-dimethyl bipyridyl (L2) (20 mol%), *p*-TSA (1.2 mmol, 4 equiv.), KF (0.6 mmol, 2 equiv.) and $Pd(OAc)_2$ (10 mol%) at room temperature. The reaction mixture was stirred at 80 ^{o}C (oil-bath temperature) for given time. After the completion of reaction (monitored by TLC), saturated $NaHCO_3$ aqueous solution (2 mL) was added to the reaction mixture and extracted with EtOAc (2×10 mL), the residue was purified and washed with brine (2×10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel (5% EtOAc in petroleum ether) to afford the corresponding product **5**.



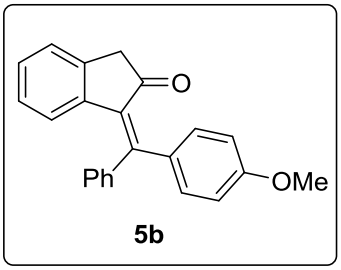
1-(Diphenylmethylene)-1,3-dihydro-2*H*-inden-2-one(5a):



5a

Yellow solid, 74 mg, 84% yield, mp: 148 - 150 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 3H), 7.37 – 7.31 (m, 3H), 7.30 – 7.27 (m, 3H), 7.25 – 7.21 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 3.55 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 202.5, 150.3, 141.6, 140.5, 140.4, 137.9, 132.2, 130.2, 129.2, 129.0, 128.9, 128.8, 128.3, 127.7, 126.7, 125.1, 124.2, 42.8; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{22}H_{17}O$ 297.1273; Found 297.1270.

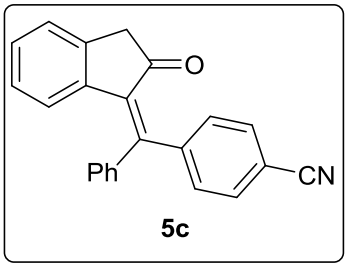
(*Z*)-1-((4-Methoxyphenyl)(phenyl)methylene)-1,3-dihydro-2*H*-inden-2-one(5b):



5b

Red solid, 83 mg, 85% yield, mp: 122 - 124 °C; R_f = 0.5 (hexanes : ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 3H) (both isomers), 7.29 – 7.25 (m, 3H) (both isomers), 7.22 – 7.18 (m, 2H) (both isomers), 7.14 (td, *J* = 7.5, 0.8 Hz, 1H) (both isomers), 6.90 (t, *J* = 7.2 Hz, 1H) (both isomers), 6.87 – 6.82 (m, 2H) (both isomers), 6.46 (d, *J* = 8.0 Hz, 1H) (both isomers), 3.83 (s, 3H) (both isomers), 3.56 (s, 2H) (both isomers). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) (both isomers) δ 202.4, 160.6, 150.6, 141.9, 141.1, 137.5, 132.7, 132.4, 129.7, 129.0, 128.9 127.8, 126.58, 124.9, 123.9, 113.0, 55.2, 42.9; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{23}H_{19}O_2$ 327.1379; Found 327.1375.

(*Z*)-4-((2-Oxo-2,3-dihydro-1*H*-inden-1-ylidene)(phenyl)methyl)benzonitrile (5c):

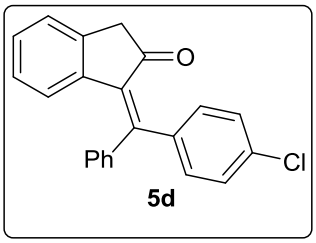


5c

Yellow solid, 81 mg, 84% yield, mp: 144 - 146 °C; R_f = 0.5 (hexanes : ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 3.4 Hz, 3H), 7.37 – 7.29 (m,

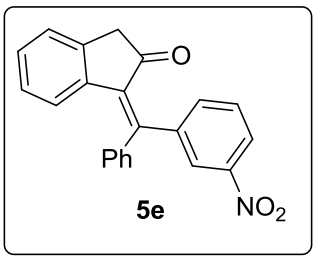
3H), 7.29 – 7.16 (m, 3H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 3.56 (s, 2H); $^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ 202.6, 146.9, 145.5, 140.4, 139.4, 138.4, 133.3, 131.6, 130.6, 129.4, 129.2, 129.0, 127.0, 125.3, 124.4, 118.9, 111.9, 42.5.; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{23}H_{16}NO$ 322.1205; Found 321.1232.

(*Z*)-1-((4-Chlorophenyl)(phenyl)methylene)-1,3-dihydro-2*H*-inden-2-one (5d):



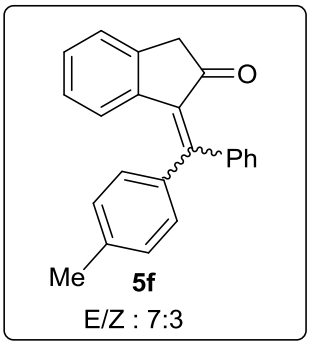
Yellow solid, 81 mg, 82% yield, mp: 128 - 130 °C; R_f = 0.5 (hexanes : ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 3H), 7.31 – 7.26 (m, 4H), 7.25 (s, 1H), 7.22 – 7.15 (m, 3H), 6.93 (t, *J* = 7.7 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 3.56 (s, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 202.5, 148.6, 141.2, 140.1, 138.8, 138.0, 134.8, 132.5, 131.7, 129.3, 129.2, 128.6, 128.0, 127.8, 126.7, 125.1, 124.2, 42.7; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{22}H_{16}ClO$ 331.0884; Found 331.0880.

(*Z*)-1-((4-Nitrophenyl)(phenyl)methylene)-1,3-dihydro-2*H*-inden-2-one(5e):



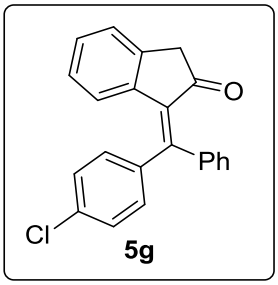
Yellow solid, 82 mg, 80% yield, mp: 165 - 167 °C; R_f = 0.5 (hexane : ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.18 (m, 1H), 8.09 (t, *J* = 1.9 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.46 – 7.42 (m, 3H), 7.34 – 7.27 (m, 3H), 7.25 – 7.20 (m, 1H), 7.00 – 6.93 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 3.58 – 3.56 (m, 2H); $^{13}C\{^{1}H\}$NMR (176 MHz, $CDCl_3$) δ 202.6, 147.9, 146.2, 142.1, 140.3, 139.4, 138.3, 136.1, 133.5, 129.5, 129.5, 129.2, 129.0, 128.6, 126.9, 125.3, 125.0, 124.4, 123.3, 42.5; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{22}H_{16}NO_3$ 342.1124; Found 342.1122.

(*Z*)-1-(Phenyl(p-tolyl)methylene)-1,3-dihydro-2*H*-inden-2-one (5f): (E/Z : 7:3)



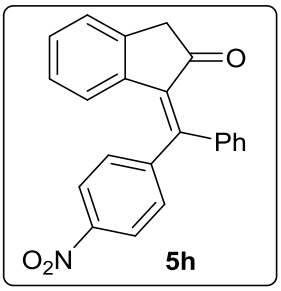
Yellow solid, 70 mg, 75% yield, mp: 144 - 146 °C; R_f = 0.5 (hexanes : ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 1H) (both isomers) , 7.37 – 7.31 (m, 2H) (both isomers), 7.31 – 7.27 (m, 2H) (both isomers), 7.25 – 7.16 (m, 5H) (both isomers), 7.14 (s, 1H) (both isomers), 6.99 – 6.90 (m, 1H) (both isomers), 6.60 (dd, J = 67.3, 8.0 Hz, 1H) (both isomers), 3.55 (d, J = 4.3 Hz, 2H) (both isomers), 2.40 (d, J = 16.1 Hz, 3H) (both isomers); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) (both isomers) δ 202.6, 202.5, 150.6, 140.8, 140.7, 139.1, 138.7, 137.8, 131.9, 130.5, 130.3, 129.7, 129.3, 129.0, 128.9, 128.8, 128.4, 128.2, 128.1, 127.7, 126.6, 125.0, 124.0, 42.8, 42.8, 21.5, 21.5; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{23}H_{199}O$ 311.1430; Found 311.1428.

(*E*)-1-((4-Chlorophenyl)(phenyl)methylene)-1,3-dihydro-2*H*-inden-2-one (5g):



Yellow solid, 75 mg, 76% yield, mp: 150 - 152 °C; R_f = 0.5 (hexanes : ethyl acetate = 9:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.36 – 7.28 (m, 4H), 7.25 – 7.19 (m, 5H), 6.99 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 3.55 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.2, 148.6, 140.1, 140.1, 140.0, 138.1, 135.0, 132.5, 130.9, 130.3, 129.3, 129.0, 128.6, 127.8, 126.8, 125.2, 124.1, 42.7; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{20}H_{16}ClO_3$ 331.0884; Found 331.0880.

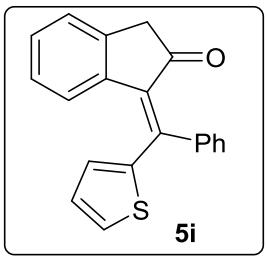
(*E*)-1-((4-Nitrophenyl)(phenyl)methylene)-1,3-dihydro-2*H*-inden-2-one (5h):



5h

Yellow solid, 80 mg, 78% yield, mp: 144 - 146 °C; R_f = 0.5 (hexanes : ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 3H), 7.31 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 7.20 – 7.14 (m, 3H), 6.93 (t, J = 7.7 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 3.56 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 201.8, 148.2, 147.9, 146.5, 139.2, 139.2, 138.5, 133.2, 130.4, 130.1, 129.3, 128.1, 127.0, 125.5, 124.4, 124.2, 123.1, 42.6; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{22}H_{16}NO_3$ 342.1124; Found 342.1124.

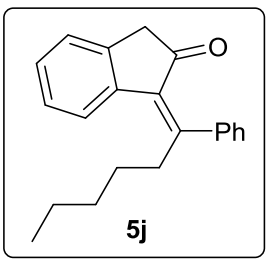
(*E*)-1-(Phenyl(thiophen-2-yl)methylene)-1,3-dihydro-2*H*-inden-2-one (5i):



5i

Yellow solid, 67 mg, 74% yield, mp: 138 - 140 °C; R_f = 0.5 (hexanes : ethyl acetate = 9:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 4H), 7.41 (dd, J = 3.8, 1.1 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.27 – 7.24 (m, 1H), 7.16 – 7.10 (m, 1H), 7.09 – 7.00 (m, 1H), 6.91 – 6.81 (m, 1H), 6.12 (d, J = 8.1 Hz, 1H), 3.60 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.0, 142.2, 141.9, 141.8, 140.9, 137.5, 133.6, 131.3, 130.3, 129.4, 129.1, 129.1, 127.9, 126.8, 126.7, 124.8, 124.4, 42.8; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{20}H_{15}OS$ 303.0838; Found 303.0834.

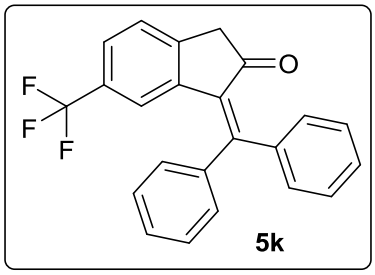
(*Z*)-1-(1-Phenylhexylidene)-1,3-dihydro-2*H*-inden-2-one (5j):



5j

Yellow solid, 65 mg, 75% yield, mp: 113 - 115 °C; R_f = 0.5 (hexanes : ethyl acetate = 9:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 7.8 Hz, 1H), 7.40 – 7.36 (m, 3H), 7.36 – 7.28 (m, 3H), 7.20 – 7.16 (m, 2H), 3.43 (s, 2H), 2.86 – 2.79 (m, 2H), 1.61 – 1.54 (m, 2H), 1.44 – 1.37 (m, 2H), 1.37 – 1.30 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.2, 153.4, 142.2, 140.0, 138.0, 131.4, 128.0, 127.9, 127.6, 127.6, 127.3, 125.3, 124.2, 42.7, 37.6, 32.1, 26.5, 22.5, 14.0; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{21}H_{23}O$ 291.1744; Found 291.1747.

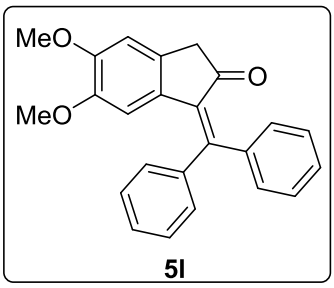
1-(Diphenylmethylene)-6-(trifluoromethyl)-1,3-dihydro-2*H*-inden-2-one (5k):



5k

Yellow solid, 78 mg, 70% yield, mp: 98 - 100 °C; R_f = 0.5 (hexanes: ethyl acetate = 9:1) ^{1}H NMR (500 MHz, CDCl3) δ 7.49 – 7.43 (m, 3H), 7.43 – 7.38 (m, 3H), 7.36 - 7.33(m, 3H), 7.27 - 7.29 (m, 3H), 6.70 (s, 1H), 3.59 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 152.8, 141.2, 141.0, 140.8, 139.7, 131.2, 130.3, 129.5, 129.4, 129.3, 128.9, 127.8, 125.3, 124.7, 124.6, 121.1, 121.0, 42.7: ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.10; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{23}H_{16}F_3O$ 365.1147; Found 365.1142.

1-(Diphenylmethylene)-5,6-dimethoxy-1,3-dihydro-2*H*-inden-2-one (5l):



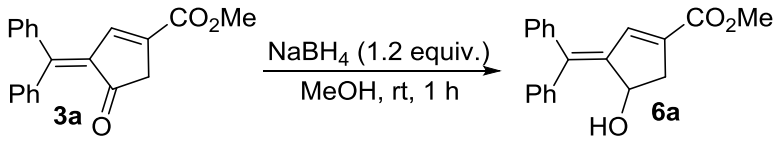
5l

Orange solid, 83 mg, 75% yield, mp: 130 - 132 °C; R_f = 0.5 (hexanes : ethyl acetate = 9:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.39 – 7.35 (m, 1H), 7.32 (m, 5H), 7.28 – 7.26 (m, 1H), 7.26 – 7.25 (m, 1H), 6.77 (s, 1H), 6.03 (s, 1H), 3.88 (s, 3H), 3.48 (s, 2H), 3.35 (s, 3H).: ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.8, 149.9, 147.8, 146.4, 141.8, 140.4, 133.2, 132.3, 131.1, 130.2, 129.5, 129.0, 128.5, 128.5, 127.7, 107.2, 107.1, 56.0, 55.1, 42.4; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{24}H_{21}O_3$ 357.1491; Found 357.1491.

Gram scale synthesis (3a):

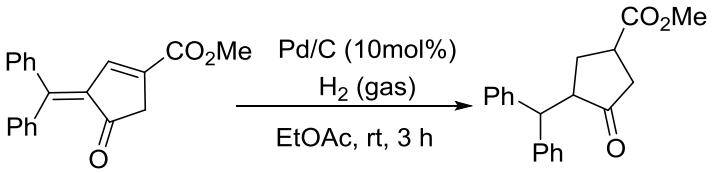
To a stirred solution of corresponding methyl (E)-2-(cyanomethyl)-5-phenylpent-2-en-4-ynoate **1a** (1.25 g, 3 mmol, 1 equiv.), phenyl boronic acid (894 mg, 4.5 mmol, 1.5 equiv.), in 20 mL of DMF, was added KF (567 mg, 6 mmol, 2 equiv.), PTSA (3.3 g, 12 mmol, 4 equiv.) L2 (179 g, 0.6 mmol, 0.2 equiv.) and $Pd(OAC)_2$ (110 mg, 0.3 mmol, 0.1 equiv.) at room temperature. The reaction mixture was stirred at 80 ^oC (oil-bath temperature) for 6 h. After the completion of reaction (monitored by TLC), saturated $NaHCO_3$ aqueous solution (10 mL) was added to the reaction mixture and extracted with EtOAc (3×10 mL), the residue was purified and washed with brine (2×10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (EtOAc: hexanes in 10:90) to afford the corresponding **3a** compound as yellow solid in 83% of yield.

Methyl 3-(diphenylmethylene)-4-hydroxycyclopent-1-ene-1-carboxylate (6a):



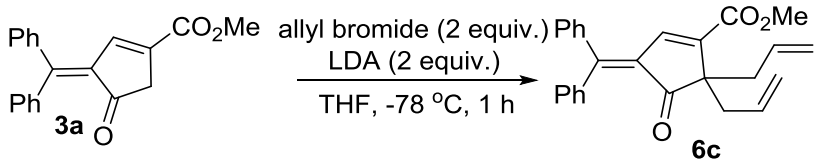
In a reaction vial, compound **3a** (50 mg, 0.16 mmol, 1 equiv.) was dissolved in 3 mL methanol. To it, sodium borohydride (12 mg, 0.19 mmol, 1.2 equiv.) was added (by maintaining 0 ^oC), and allowed to stir to rt for 1 hour. The formation of product was observed by TLC and upon completion, the reaction mass was quenched with saturated solution of aqueous $NaHCO_3$, evaporated under reduced pressure (methanol) extracted using ethyl acetate (10 mLX3). The combined organic layers were dried over Na_2SO_4, and the solvent evaporated and purified by using the column chromatography to afford **6a** as white solid, 82 mg, 90% yield, mp: 88 - 90 °C; R_f = 0.5 (hexanes : ethyl acetate = 9:1) ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 4H), 7.40 – 7.30 (m, 5H), 7.22 – 7.17 (m, 2H), 5.09 (d, J = 5.5 Hz, 1H), 3.91 – 3.71 (m, 3H), 3.19 – 3.03 (m, 1H), 2.82 – 2.64 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.9, 145.7, 143.2, 141.4, 140.6, 140.2, 137.0, 129.9, 129.4, 128.6, 128.2, 128.1, 127.9, 71.8, 51.7, 40.8; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{20}H_{19}O_3$ 307.3678; Found 307.3675.

Methyl 3-benzhydryl-4-oxocyclopentane-1-carboxylate (6b):



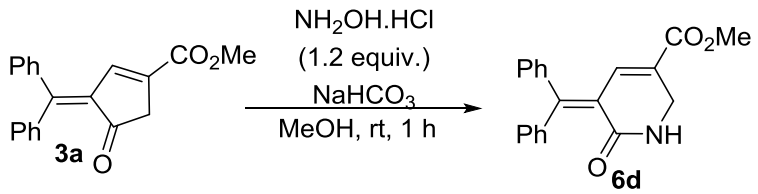
In a 10 ml round bottomed flask, Compound **3a** (50 mg, 0.16 mmol, 1 equiv.) was dissolved in 3 mL EtOAc at kept under hydrogen atmosphere (hydrogen bladder). To it, Pd/C (10 mol%) (17 mg, 0.001 mmol, 0.01 equiv.) was added and allowed to stir at r.t for 3 hours. Upon completion, the reaction mass was filtered using celite pad (later celite pad quenched with 1N HCl solution). The filtrate was evaporated under reduced pressure and purified by using the column chromatography to afford **6b as** white solid, 80 mg, 87% yield, mp: 96 - 98 °C; R_f = 0.5 (hexanes : ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 7.25 – 7.14 (m, 4H), 7.08 (dd, *J* = 7.1, 1.4 Hz, 2H), 4.59 (d, *J* = 5.6 Hz, 1H), 3.67 (d, *J* = 2.8 Hz, 3H), 3.13 – 2.95 (m, 2H), 2.59 – 2.47 (m, 2H), 2.34 (dd, *J* = 18.8, 11.4 Hz, 1H), 1.77 (dd, *J* = 24.5, 12.5 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 214.7, 174.2, 142.9, 142.0, 129.0, 128.5, 128.2, 126.6, 126.5, 53.8, 52.2, 50.1, 41.2, 38.8, 31.4; HRMS (ESI) m/z: $(M+H)^+$Calcd for $C_{20}H_{21}O_3$ 309.1446; Found 309.1448.

Methyl 5,5-diallyl-3-(diphenylmethylene)-4-oxocyclopent-1-ene-1-carboxylate (6c):



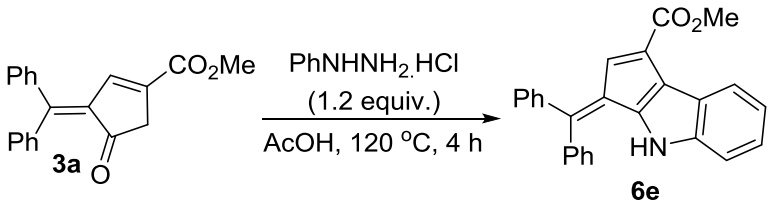
In a 25 ml round bottomed flask equipped with magnetic stirrer, Compound **3a** (50 mg, 0.16 mmol, 1 equiv.) was dissolved in 5 mL THF and placed at -78 °C under N_2 atmosphere. To it, 2M LDA in hexane/THF (0.04 ml, 0.3 mmol, 2 equiv.) was added dropwise and allowed to stir at the same temperature for 30 mins. Then allyl bromide (0.02ml, 0.3 mmol, 2 equiv.) was added and allowed to stir to for 30 min. The completion of reaction was observed by TLC and the reaction mass was quenched with saturated solution of aqueous NH_4Cl, and extracted using ethyl acetate (10 mLX3). The combined organic layers were dried over Na_2SO_4, and the solvent evaporated and purified by using the column chromatography to afford **6c** as yellow solid, 93 mg, 81% yield, mp: 90 - 92 °C; Rf = 0.5 (hexanes/ethyl acetate = 9:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.43 – 7.37 (m, 4H), 7.36 – 7.32 (m, 2H), 7.19 – 7.16 (m, 4H), 5.58 – 5.54 (m, 1H), 5.54 – 5.50 (m, 1H), 5.03 – 5.01 (m, *J* = 2.3, 1.2 Hz, 1H), 5.00 – 4.98 (m, 2H), 4.98 – 4.97 (m, 1H), 3.79 (s, 3H), 2.67 (dd, *J* = 13.4, 7.6 Hz, 2H), 2.51 (dd, *J* = 13.4, 7.4 Hz, 2H): ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.7, 164.7, 153.0, 144.4, 141.0, 138.5, 136.3, 133.8, 133.3, 131.0, 130.9, 129.7, 128.4, 127.7, 118.1, 59.3, 51.6, 40.4; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{26}H_{25}O_3$ 385.1798; Found 385.1791.

Methyl 5-(diphenylmethylene)-6-oxo-1,2,5,6-tetrahydropyridine-3-carboxylate (6d):



In a 25 ml round bottomed flask, Compound **3a** (50 mg, 0.16 mmol, 1 equiv.) was dissolved in 3 mL methanol. To it, hydroxylamine hydrochloride (13 mg, 0.19 mmol, 1.2 equiv.) was added (by maintaining the temperature 0 ^{o}C), and allowed to stir to rt for 1 hour. The formation of product was observed by TLC and upon completion, the reaction mass was quenched with saturated solution of aqueous $NaHCO_3$, evaporated under reduced pressure extracted using ethyl acetate (10 mLX3). The combined organic layers were dried over Na_2SO_4, and the solvent evaporated and purified by using the column chromatography to afford **6e** as pale green solid, 82 mg, 86% yield, mp: 194 - 196 °C; R_f = 0.5 (hexanes/ethyl acetate = 9:1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.38 – 7.28 (m, 7H), 7.25 – 7.22 (m, 2H), 7.18 – 7.10 (m, 2H), 3.78 (d, J = 7.7 Hz, 3H), 3.51 (d, J = 1.0 Hz, 2H): ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ δ 165.3, 158.7, 145.4, 143.4, 142.9, 141.1, 134.4, 133.3, 130.3, 129.9, 128.5, 128.3, 128.3, 128.1, 51.8, 33.7; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{20}H_{18}NO_3$ 320.1281; Found 320.1278.

Methyl 3-(diphenylmethylene)-3,4-dihydrocyclopenta[b]indole-1-carboxylate (6e):



In a 25 ml round bottomed flask, Compound **3a** (50 mg, 0.16 mmol, 1 equiv.) was dissolved in 3 mL AcOH. To it, phenylhydrazine hydrochloride (28 mg, 0.19 mmol, 1.2 equiv.) was added at room temperature. The reaction mixture was stirred at 120 ^{o}C for 4 hours. The formation of product was observed by TLC and upon completion, the reaction mass was quenched with saturated solution of aqueous $NaHCO_3$, evaporated under reduced pressure extracted using ethyl acetate (10 mLX3). The combined organic layers were dried over Na_2SO_4, and the solvent evaporated and purified by using the column chromatography to afford **6f** as yellow solid, 84 mg, 88% yield, mp: 202-204 °C; R_f = 0.5 (hexanes/ethyl acetate = 9:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 1H), 7.60 – 7.51 (m, 5H), 7.46 – 7.38

(m, 4H), 7.36 – 7.31 (m, 2H), 7.14 – 7.07 (m, 3H), 6.80 (s, 1H), 3.96 (s, 3H): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.4, 152.2, 140.8, 140.1, 139.79, 137.7, 132.4, 131.8, 130.5, 130.4, 130.1, 129.8, 129.5, 129.2, 128.2, 123.0, 122.3, 121.7, 121.0, 120.6, 111.6, 51.7; HRMS (ESI) m/z: $(M+H)^+$ Calcd for $C_{26}H_{20}NO_2$ 377.1490; Found 377.1494.

X-ray Crystallography:

Crystal Growth: Compound was dissolved in acetonitrile in a culture vial. The vial was covered with aluminum foil having small holes and left at room temperature for 2 days for crystal growth. After slow evaporation of the solvent, colorless crystals are appeared on the walls of the culture vial. The crystals were examined under X-Ray crystallographic studies.

X-ray data for the compound was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. The N-H and O-H atoms were located in the difference Fourier map and their positions and isotropic displacement parameters were refined. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

Crystal structure determination of 3p:

Crystal Data for $C_{22}H_{20}O_3$ (M =332.38 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 7.4256(12) Å, b = 28.847(5) Å, c = 8.6123(14) Å, β = 105.576(7)°, V = 1777.0(5) $Å^3$, Z = 4, T = 294.15 K, μ(MoKα) = 0.082 mm^{-1}, $Dcalc$ = 1.242 g/cm^3, 20484 reflections measured (5.696° ≤ 2Θ ≤ 61.05°), 5048 unique (R_{int} = 0.0422, R_{sigma} = 0.0325) which were used in all calculations. The final R_1 was 0.0480 (I > 2σ(I)) and wR_2 was 0.1449 (all data). **CCDC 2404673** deposition number contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

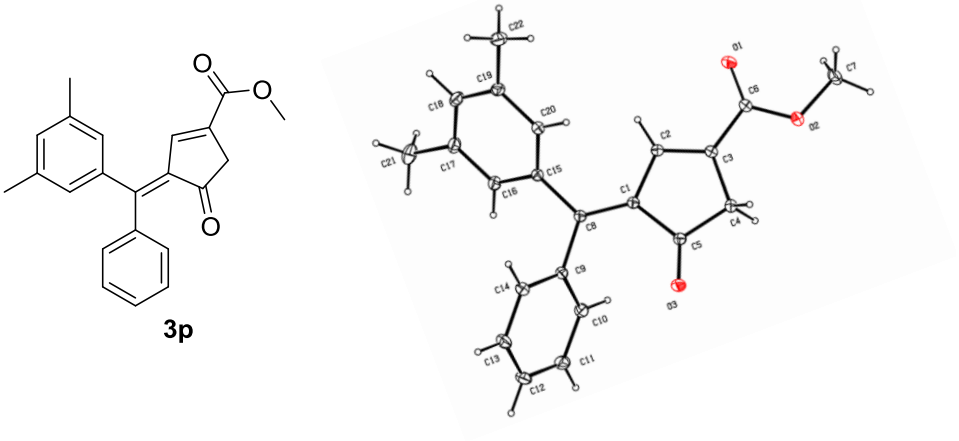


Figure S1: ORTEP diagram of **3p** compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal structure determination of 5e:

Crystal Data for $C_{22}H_{15}NO_3$ (*M* =341.35 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.2385(13) Å, *b* = 9.7060(12) Å, *c* = 10.2025(13) Å, α = 94.316(4)°, β = 109.438(4)°, γ = 95.638(4)°, *V* = 852.83(19) Å^3, *Z* = 2, *T* = 294.15 K, μ(MoKα) = 0.089 mm^{-1}, *Dcalc* = 1.329 g/cm^3, 16655 reflections measured (4.716° ≤ 2Θ ≤ 56.712°), 4226 unique (R_{int} = 0.0340, R_{sigma} = 0.0341) which were used in all calculations. The final R_1 was 0.0436 (I > 2σ(I)) and wR_2 was 0.1206 (all data). **CCDC 2404674** deposition number contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

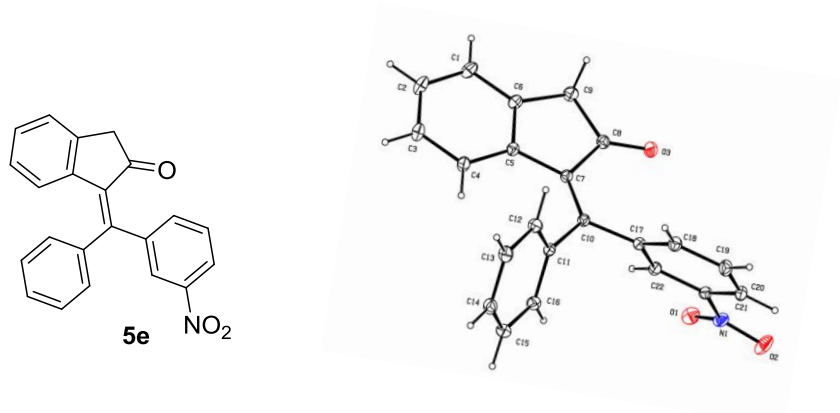


Figure S2: ORTEP diagram of **5e** compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystal structure determination of 6b:

Crystal Data for $C_{20}H_{20}O_3$ (M =308.36 g/mol): monoclinic, space group P2 1 /n (no. 14), a =13.7298(16) Å, b = 8.6498(10) Å, c = 14.4582(15) Å, β = 97.461(3)°, V = 1702.5(3) $Å^3$, Z =4, T = 294.15 K, μ(MoKα) = 0.080 mm -1 , Dcalc = 1.203 g/cm^3 , 26306 reflections measured (5.5°≤ 2Θ ≤ 56.668°), 4229 unique (R_{int} = 0.0409, R_{sigma} = 0.0374) which were used in all calculations. The final R_1 was 0.0461 (I > 2σ(I)) and wR_2 was 0.1541 (all data). **CCDC 2404675** deposition number contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

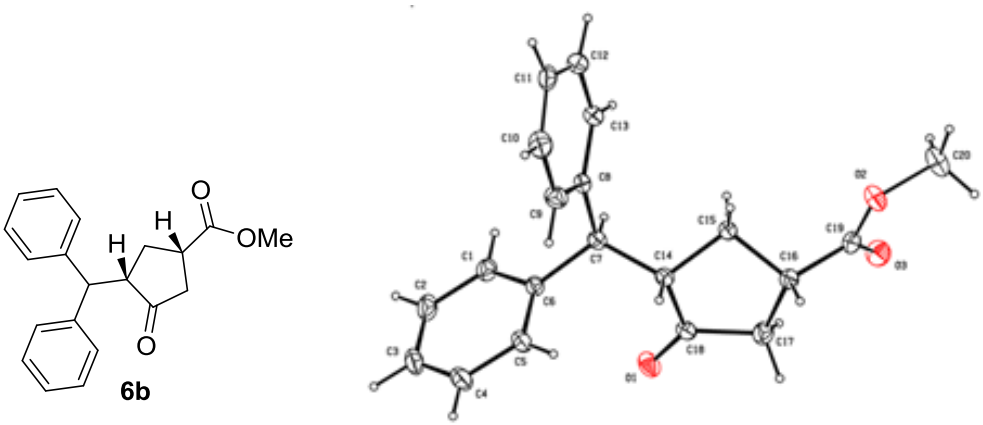


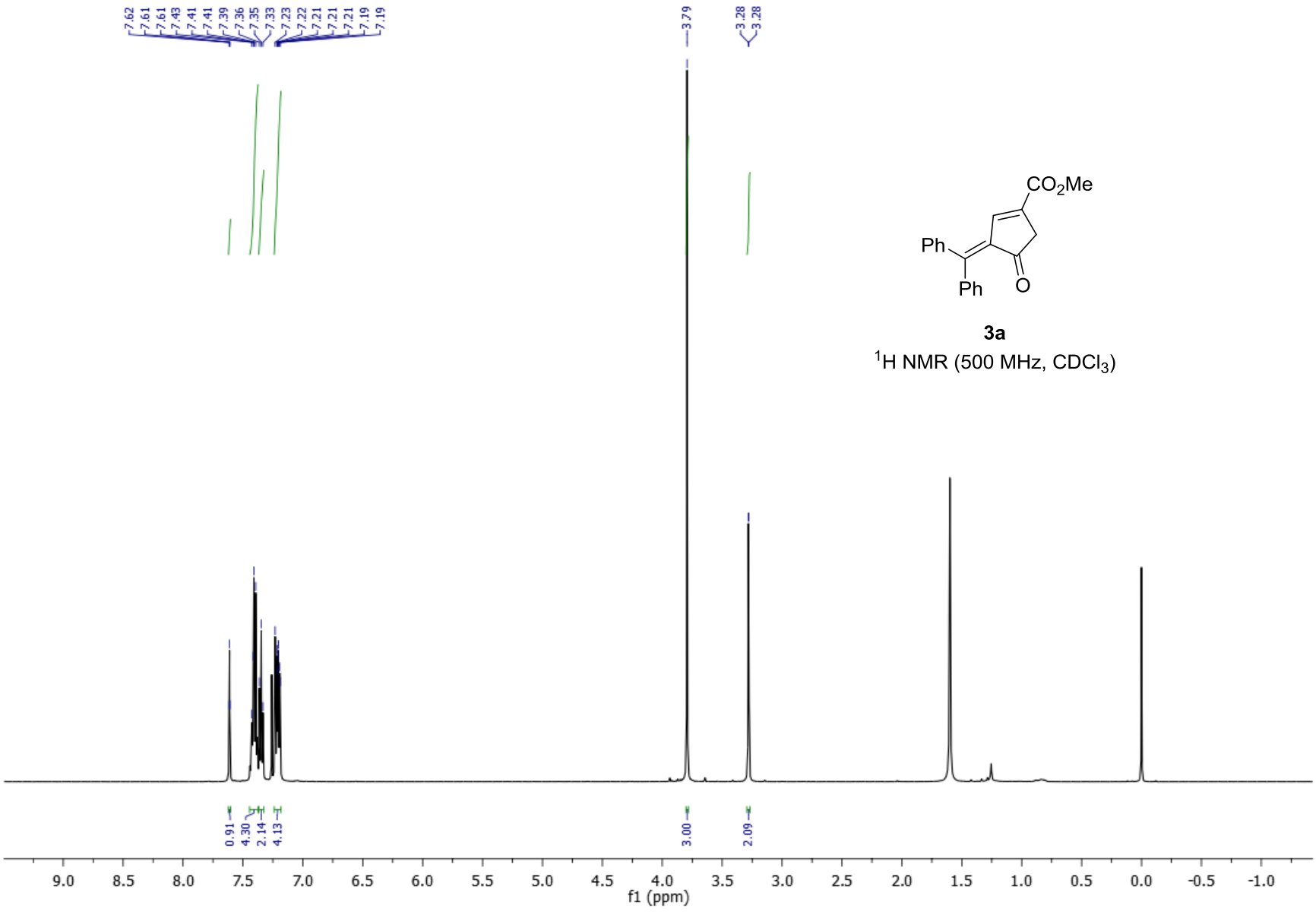
Figure S3: ORTEP diagram of **6b** compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

References:

1) a) C. R. Reddy, V. Ganesh and N. Punna, *J. Org. Chem.*, 2022, **87**, 11547. b) C. R. Reddy, V. Ganesh and N. Punna, *Chem. Commun.*, 2023,**59**, 8600.

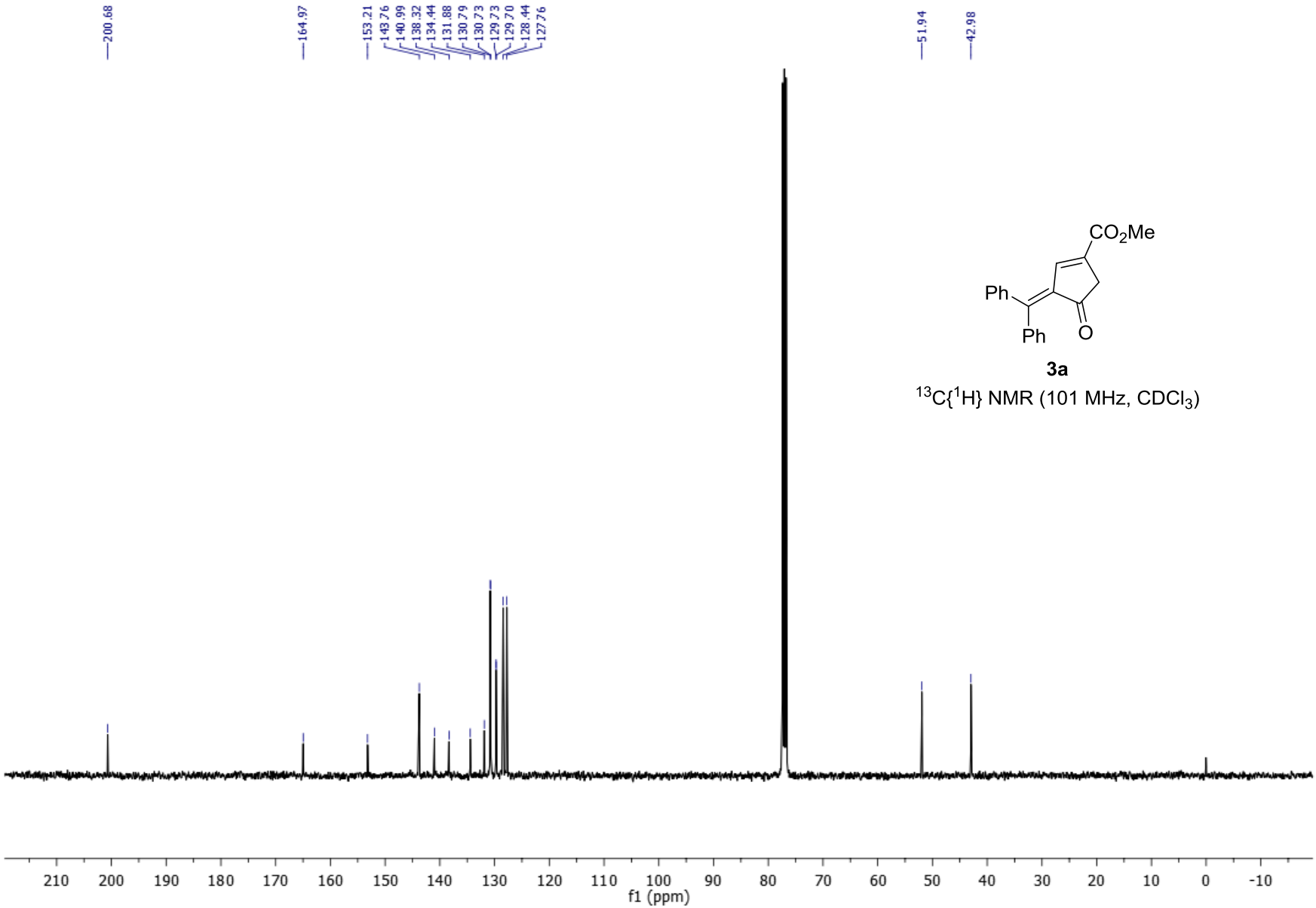
2) Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.

3) Sheldrick G. M. (2015).Acta Crystallogr C71: 3-8.



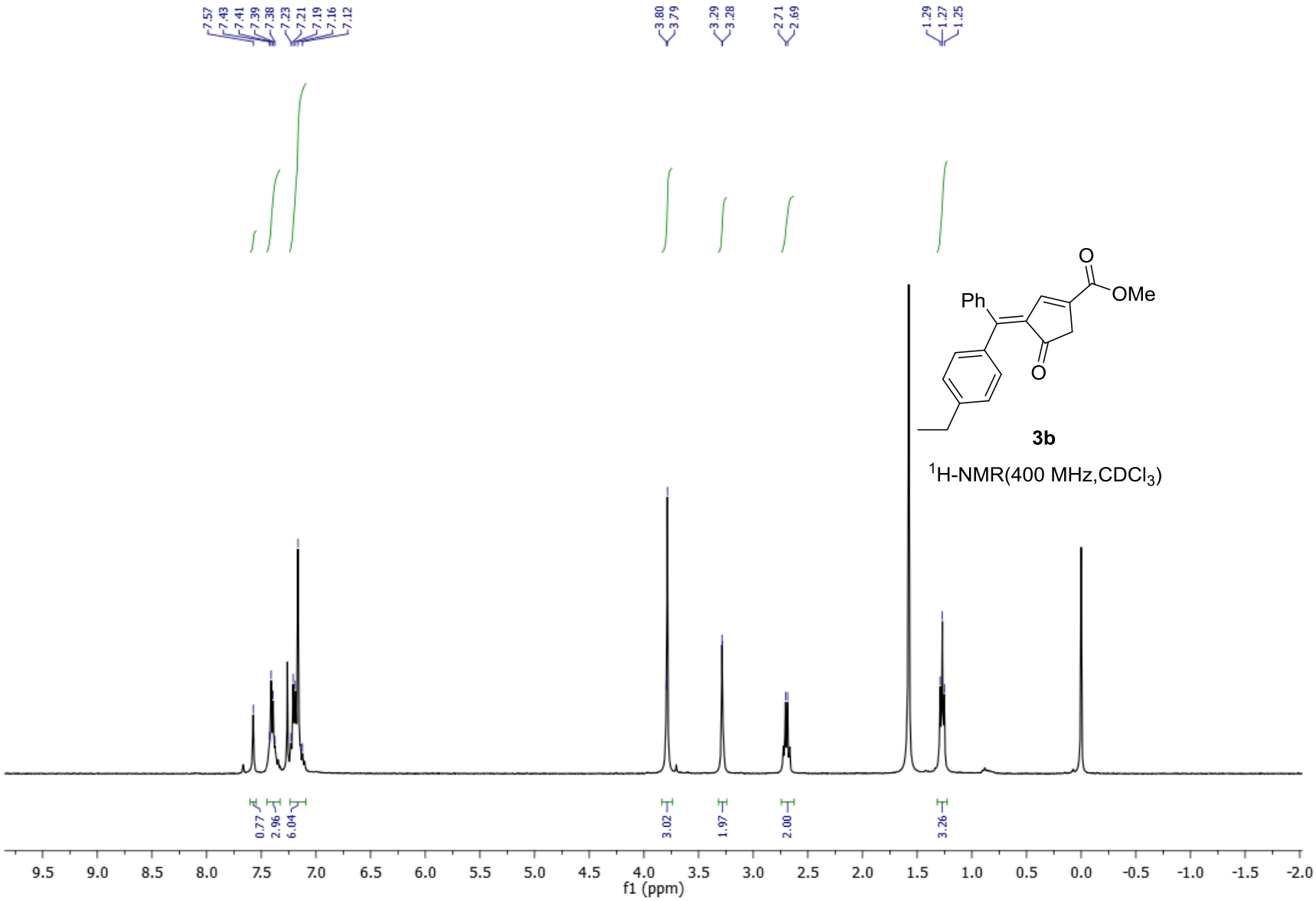
3a

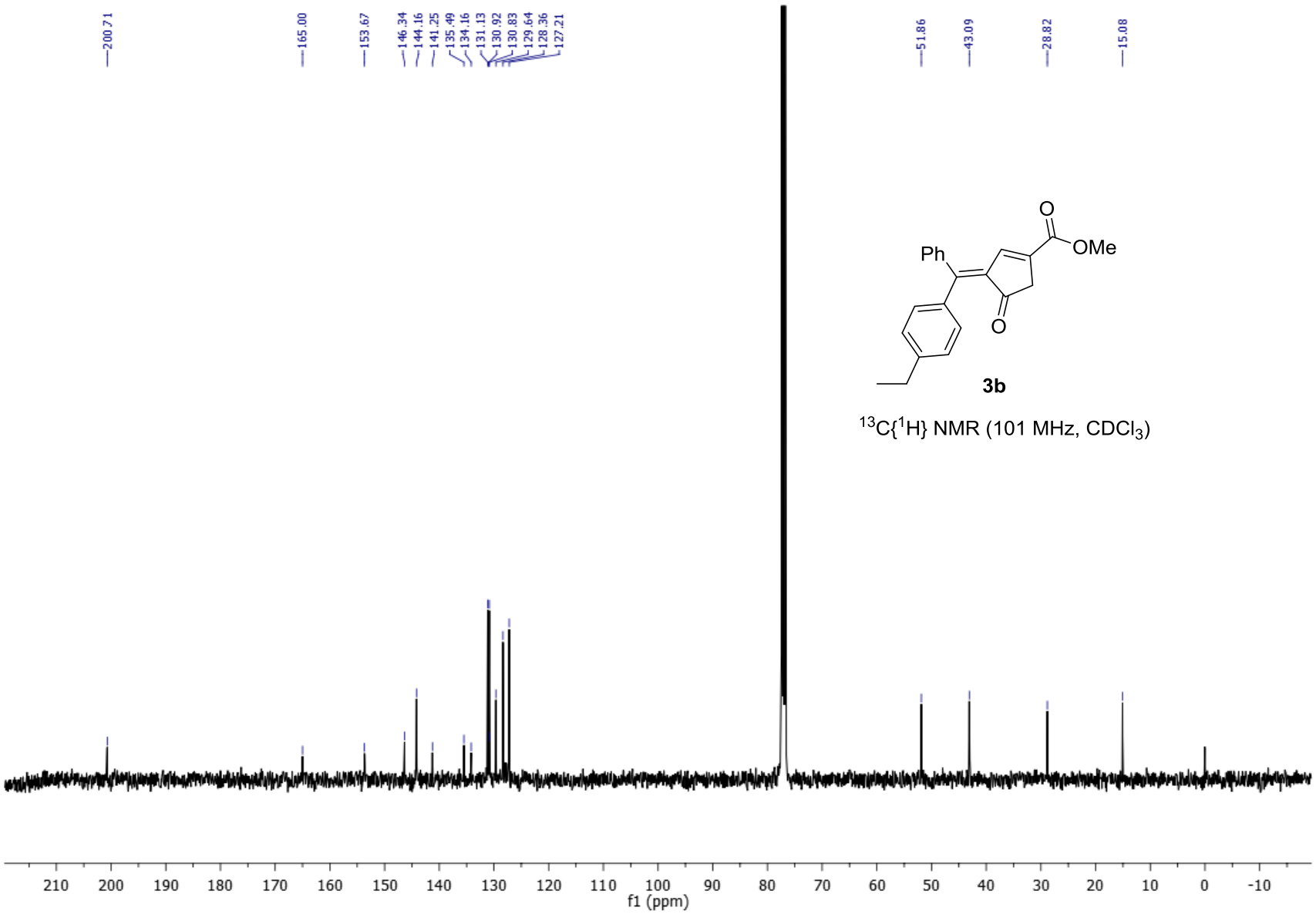
^{1}H NMR (500 MHz, $CDCl_3$)

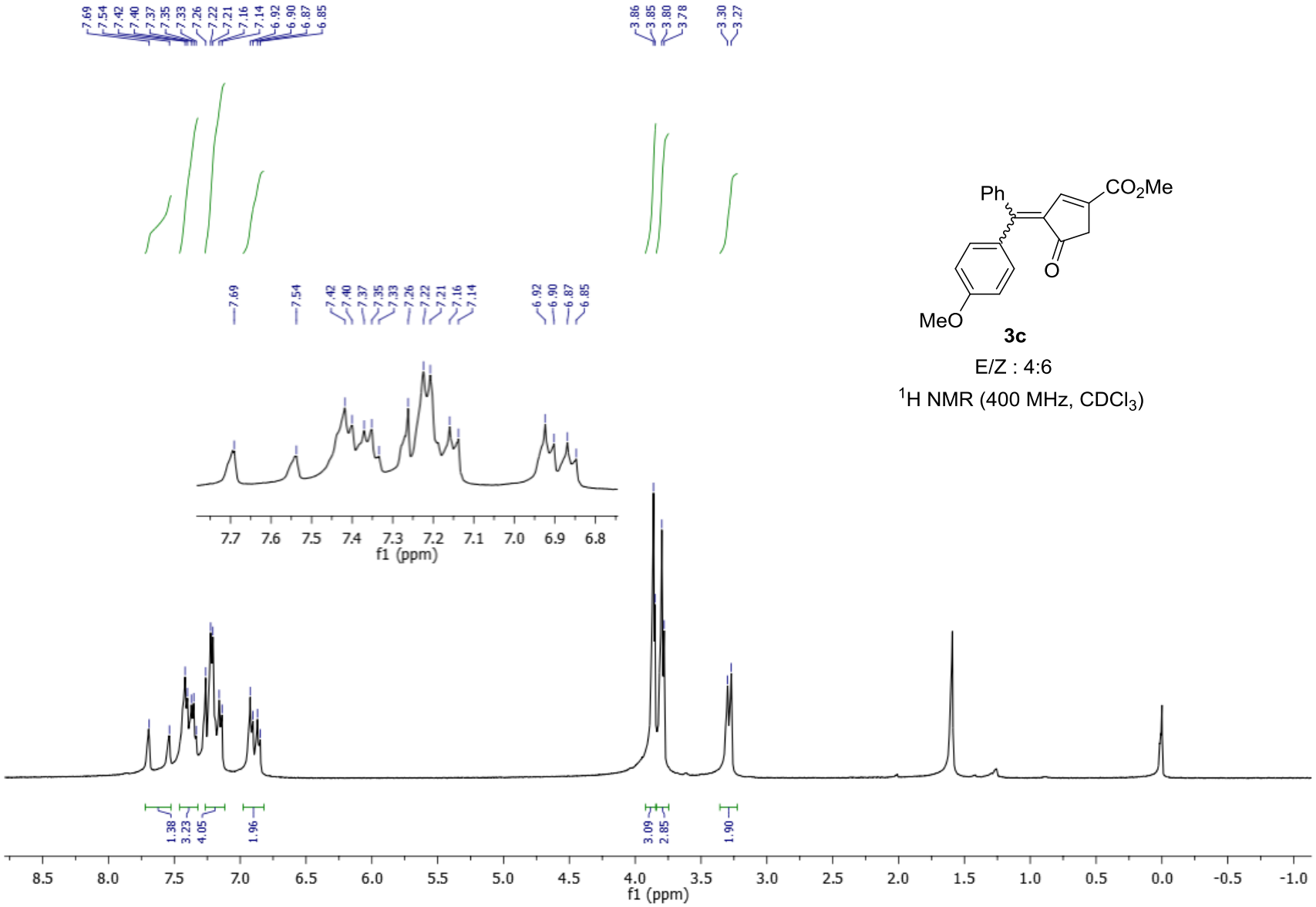


3a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)


7.57
7.43
7.41
7.39
7.38
7.23
7.21
7.19
7.16
7.12
3.80
3.79
3.29
3.28
2.71
2.69
1.29
1.27
1.25
O
OMe
Ph
O
3b
1H-NMR(400 MHz,CDCl3)
0.77
2.96
6.04
3.02
1.97
2.00
3.26
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 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

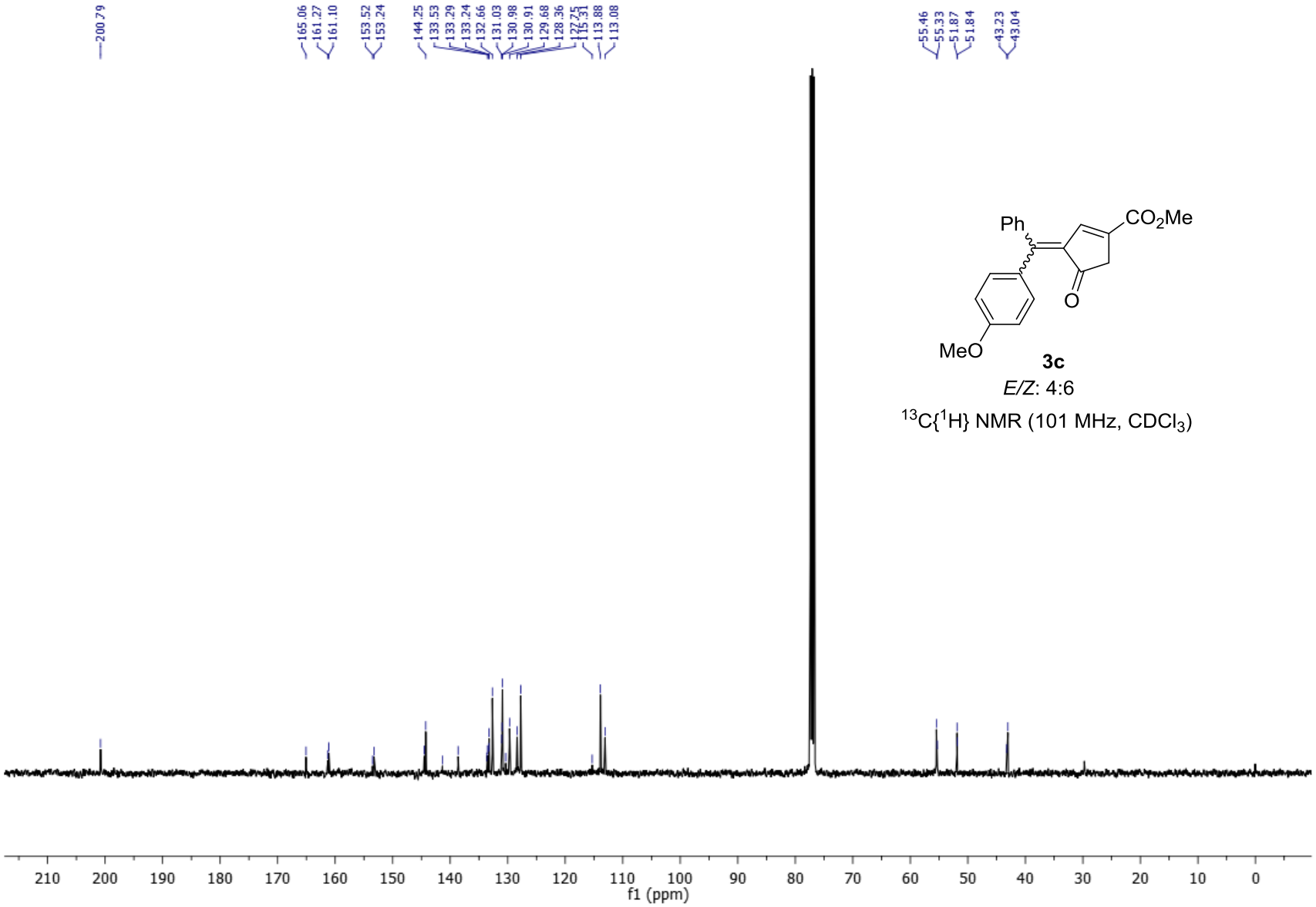

200.71
165.00
153.67
146.34
144.16
141.25
135.49
134.16
131.13
130.92
130.83
129.64
128.36
127.21
51.86
43.09
28.82
15.08
O
OMe
Ph
O
3b
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3c

E/Z : 4:6

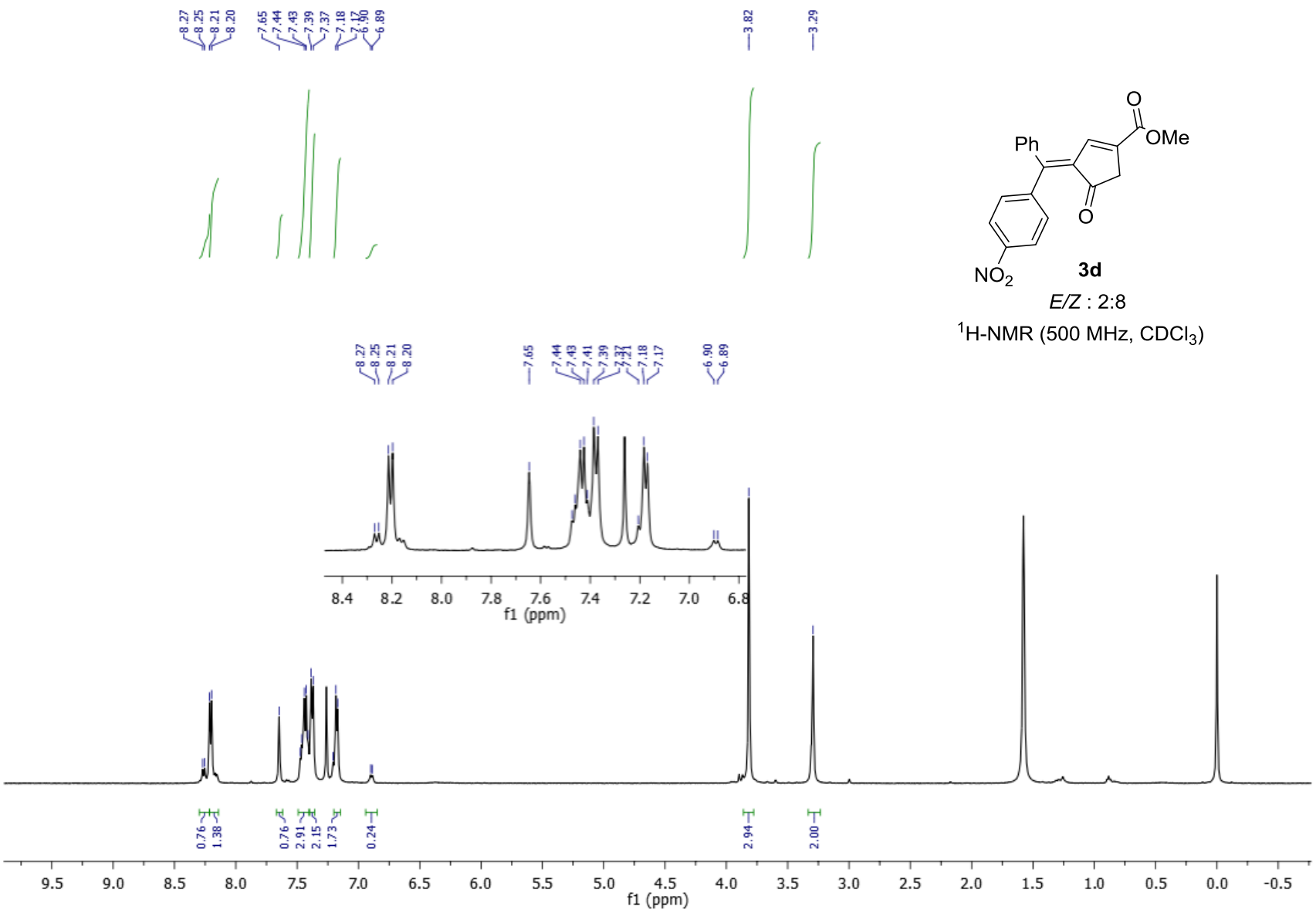
^{1}H NMR (400 MHz, $CDCl_3$)



3c

E/*Z*: 4:6

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

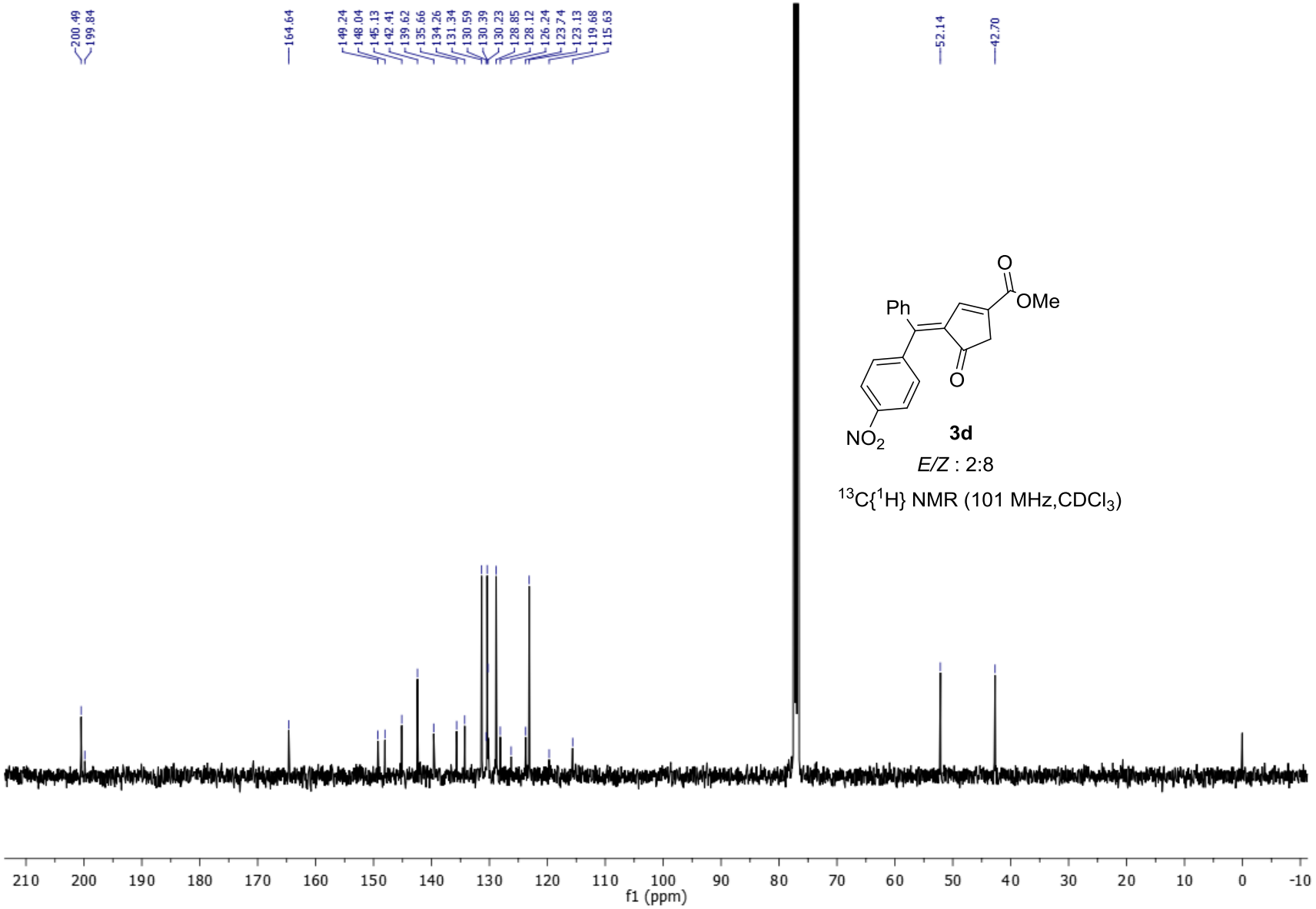


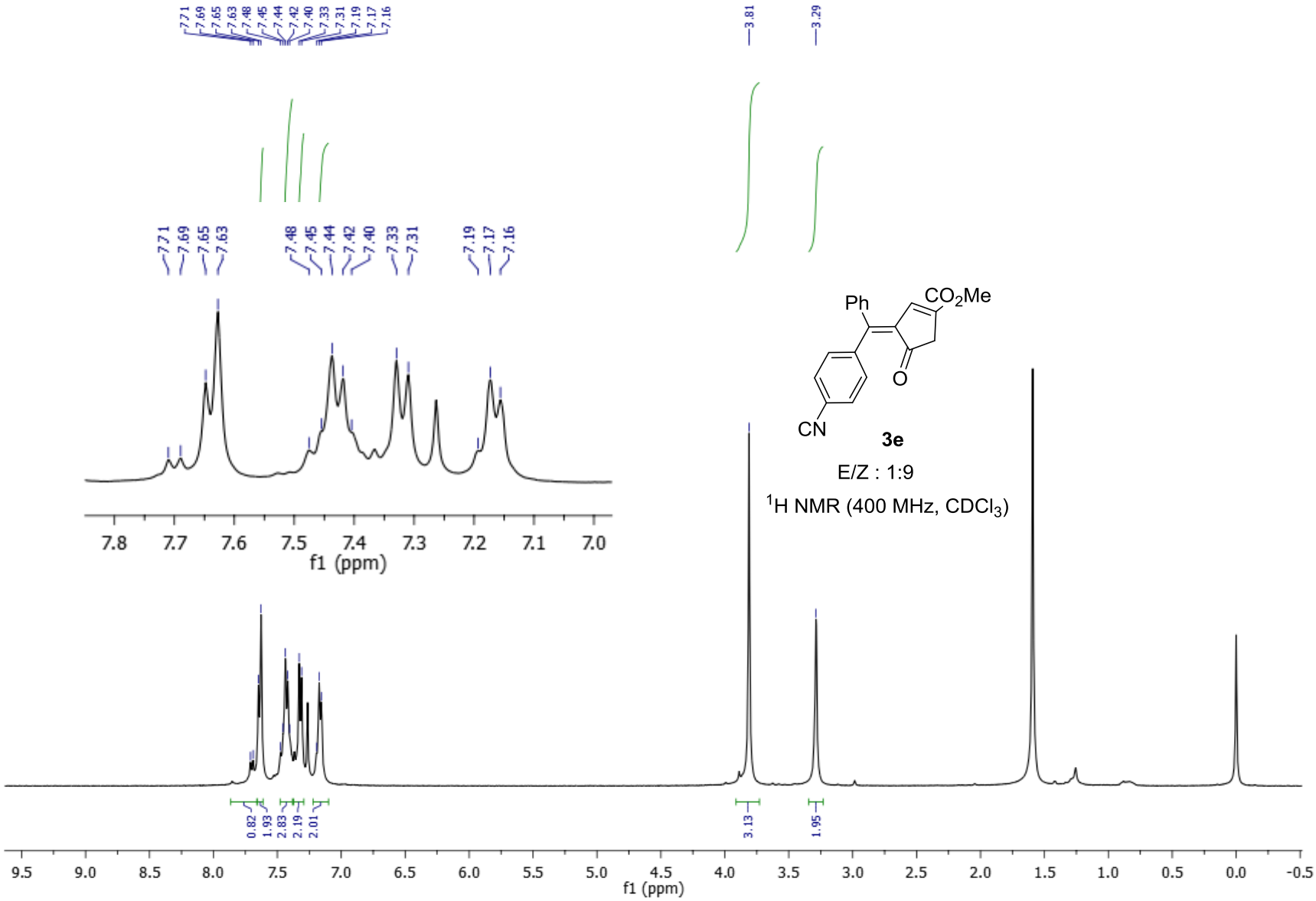
3d

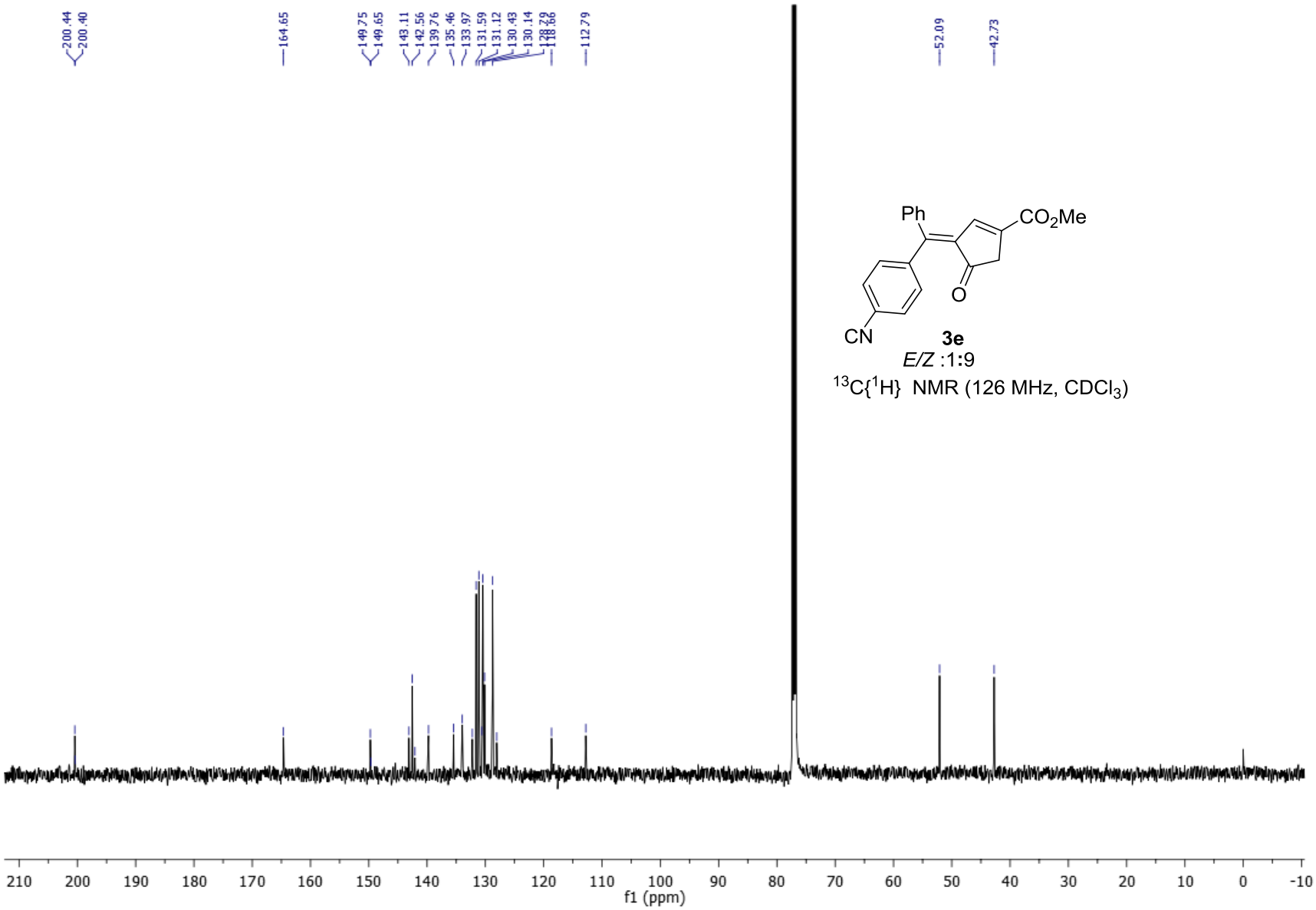
E/Z : 2:8

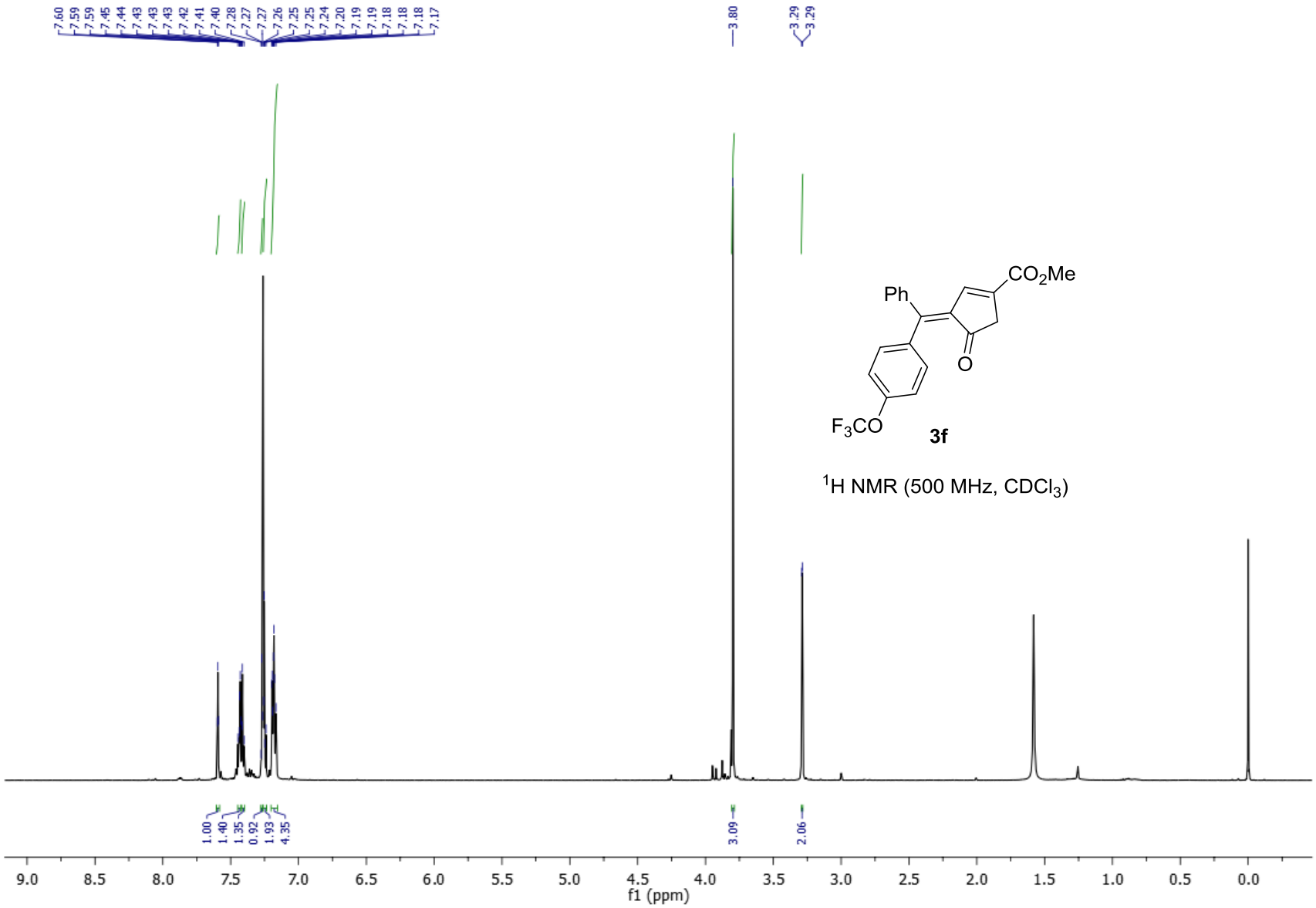
^{1}H-NMR (500 MHz, $CDCl_3$)

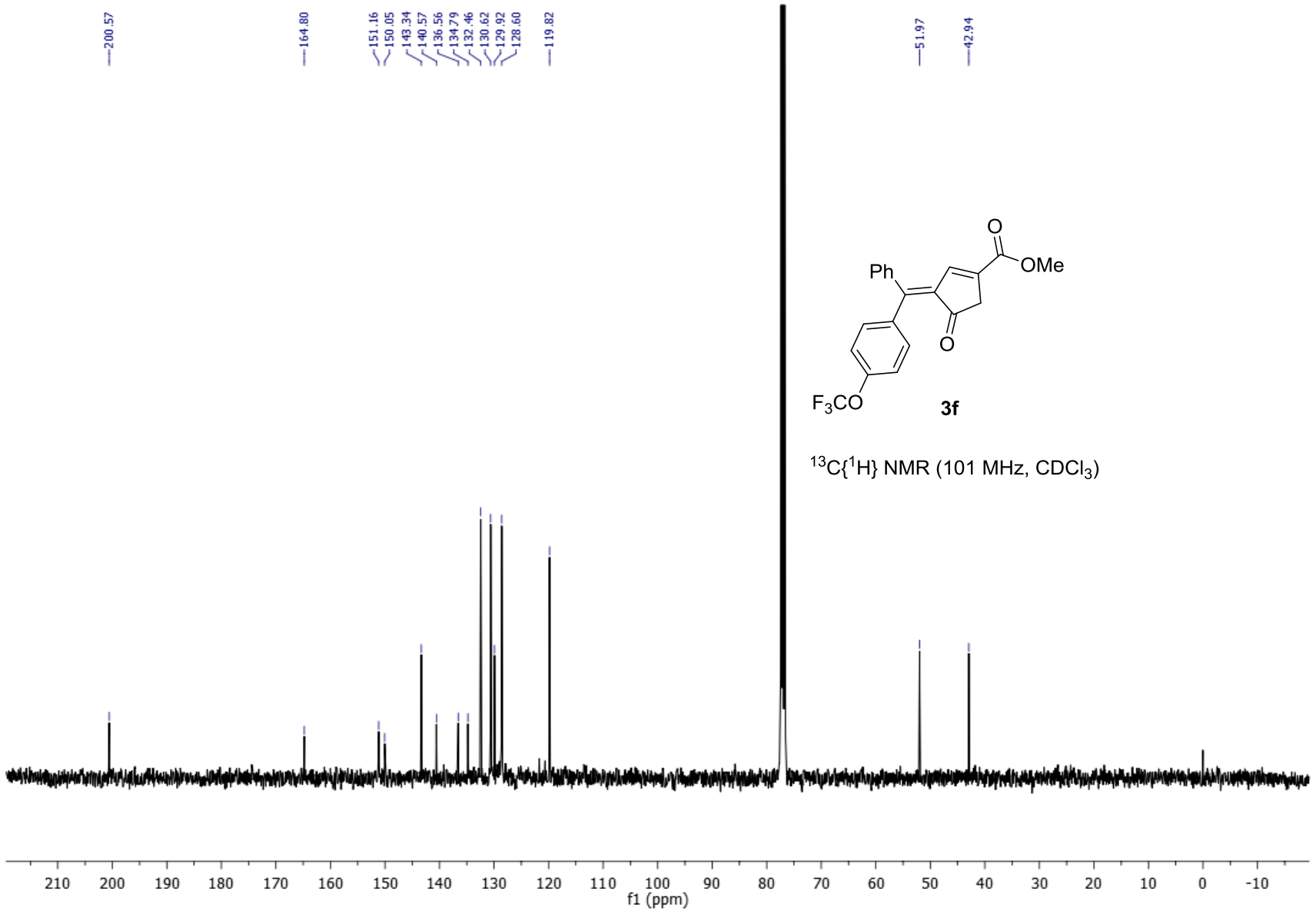
i

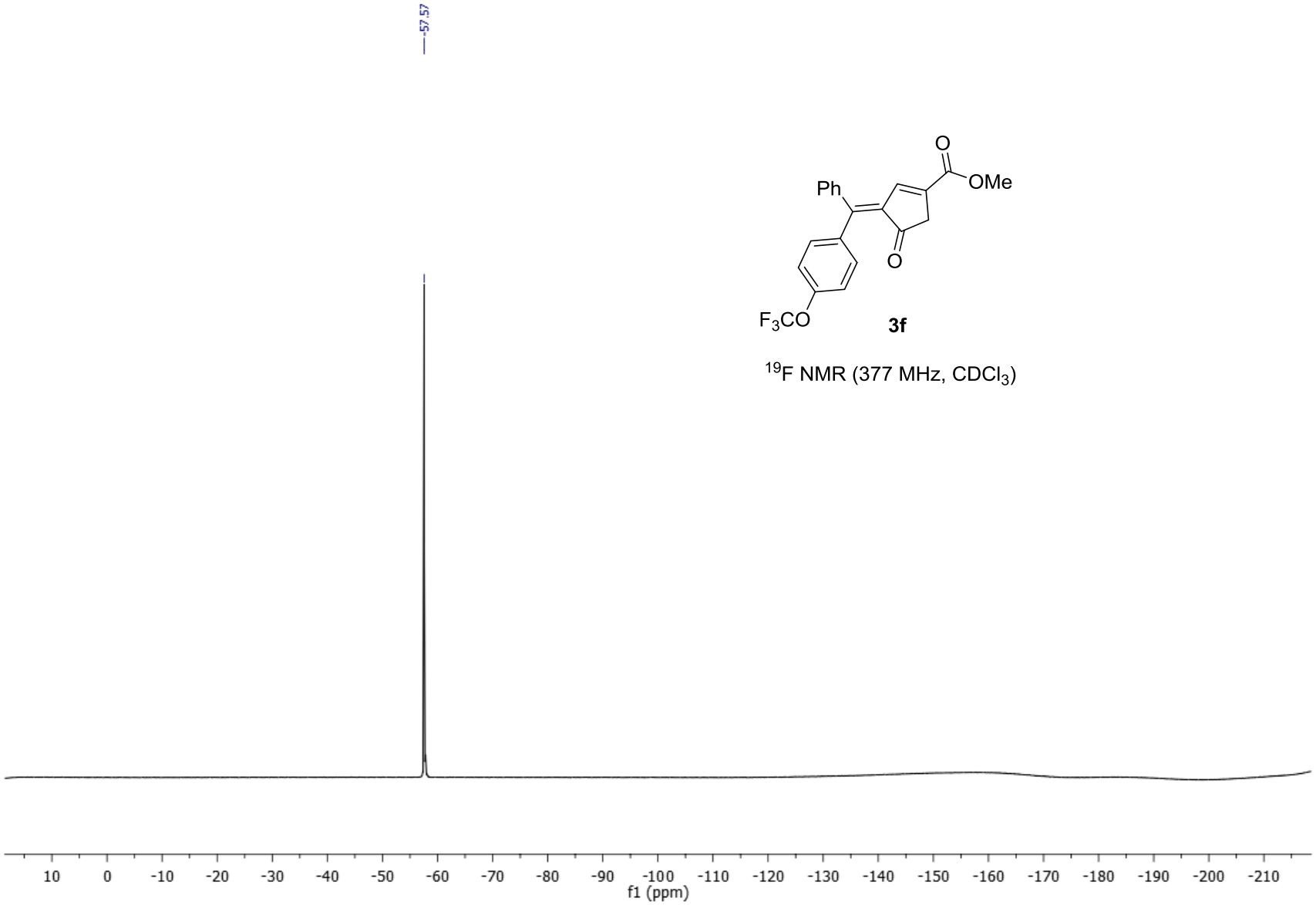

200.49
199.84
164.64
149.24
148.04
145.13
142.41
139.62
135.66
134.26
131.34
130.59
130.39
130.23
128.85
128.12
126.24
123.74
123.13
119.68
115.63
52.14
42.70
O
OMe
Ph
O
NO2
3d
E/Z : 2:8
13C{1H} NMR (101 MHz,CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.71
7.69
7.65
7.63
7.48
7.45
7.44
7.42
7.40
7.33
7.31
7.19
7.17
7.16
3.81
3.29
Ph
CO2Me
O
CN
3e
E/Z : 1:9
1H NMR (400 MHz, CDCl3)
f1 (ppm)
0.82
1.93
2.83
2.19
2.01
3.13
1.95


200.44
200.40
164.65
149.75
149.65
143.11
142.56
139.76
135.46
133.97
131.59
131.12
130.43
130.14
128.29
128.02
118.66
112.79
52.09
42.73
Ph
CO2Me
O
CN
3e
E/Z :1:9
13C{1H} NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

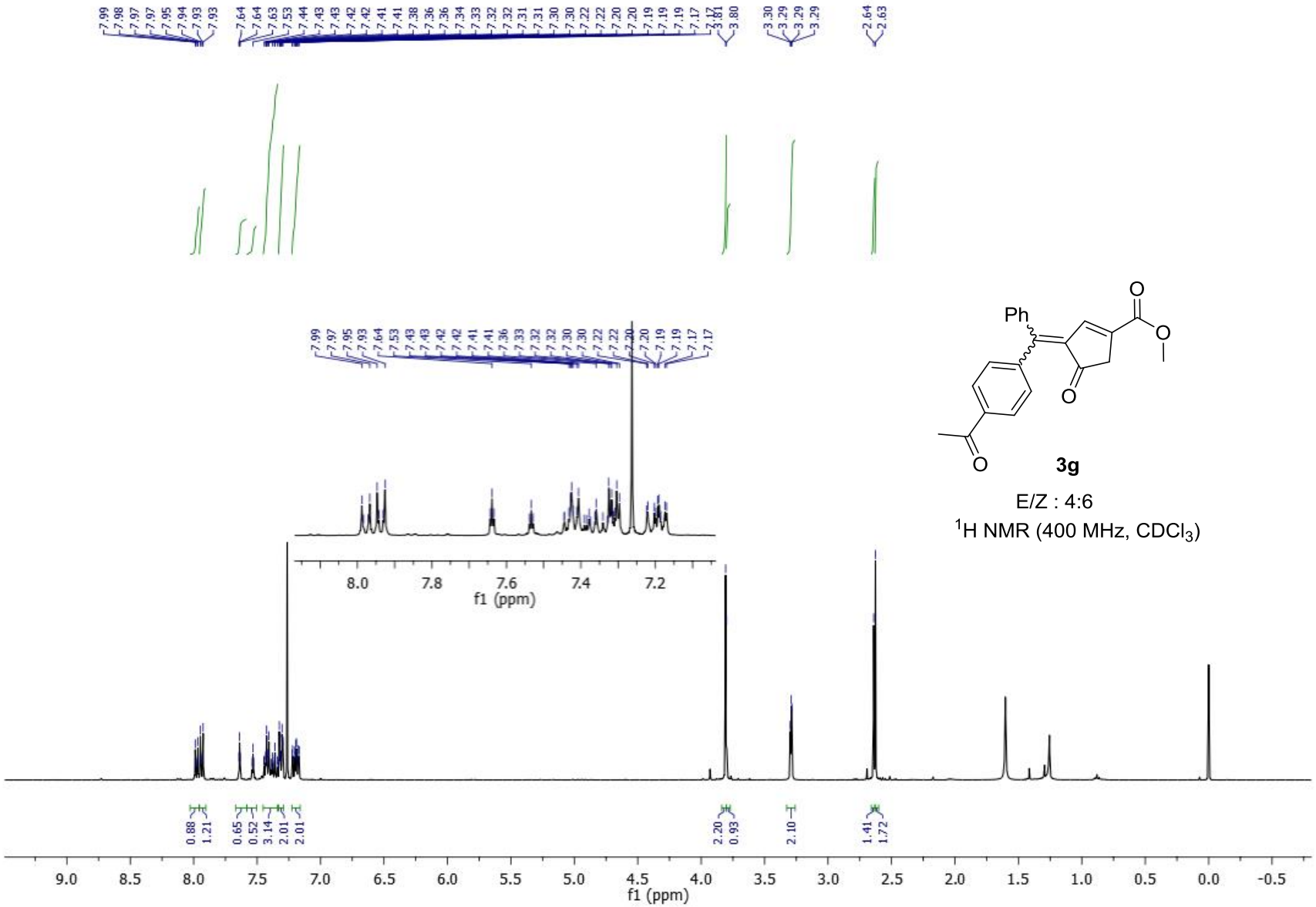

7.60
7.59
7.59
7.45
7.44
7.43
7.43
7.43
7.42
7.41
7.40
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.20
7.19
7.19
7.18
7.18
7.17
3.80
3.29
3.29
CO2Me
Ph
O
F3CO
3f
1H NMR (500 MHz, CDCl3)
1.00
1.40
1.35
0.92
1.93
4.35
3.09
2.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


200.57
164.80
151.16
150.05
143.34
140.57
136.56
134.79
132.46
130.62
129.92
128.60
119.82
51.97
42.94
Ph
O
OMe
O
F3CO
3f
13C{1H} NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3f

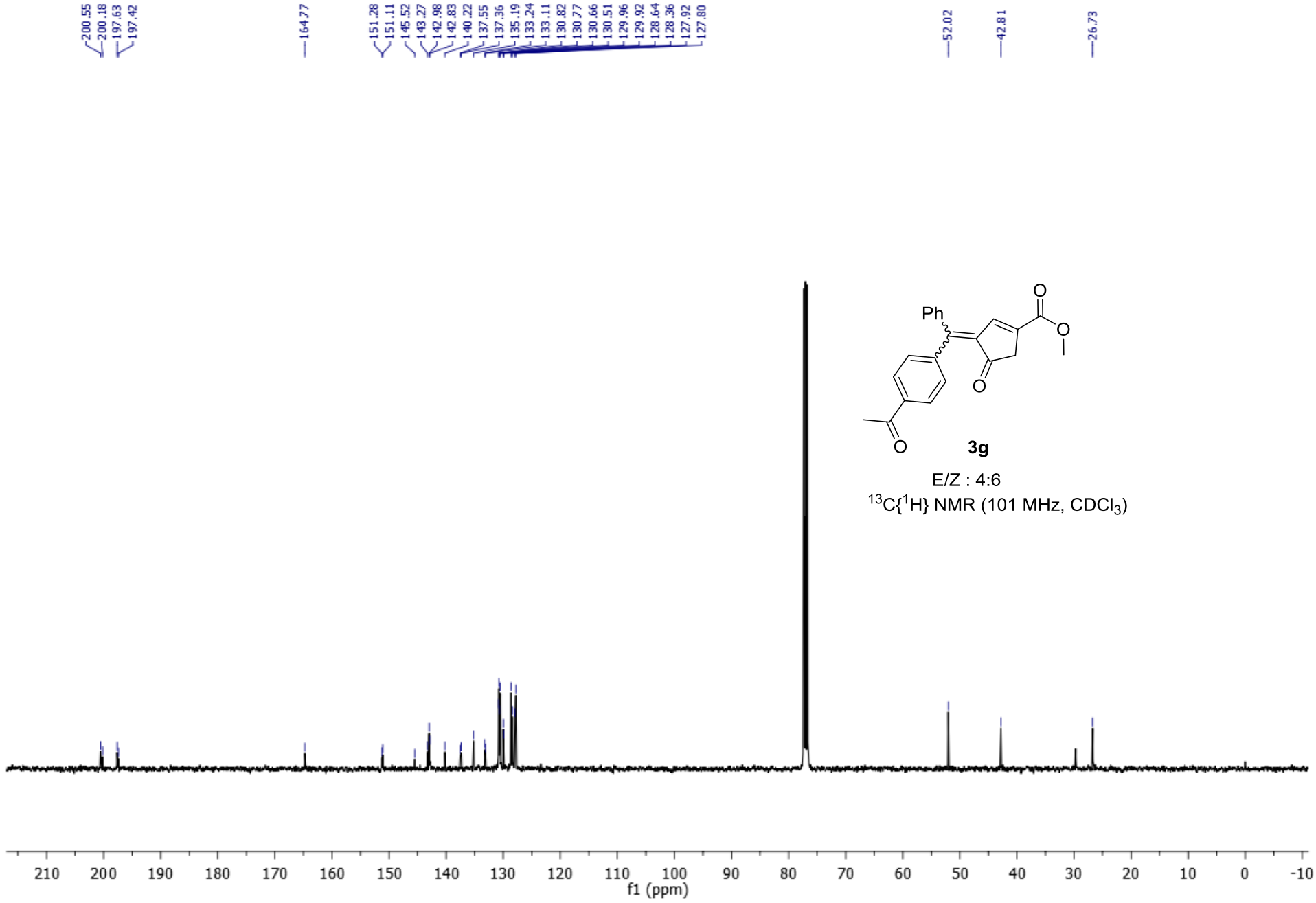
^{19}F NMR (377 MHz, $CDCl_3$)

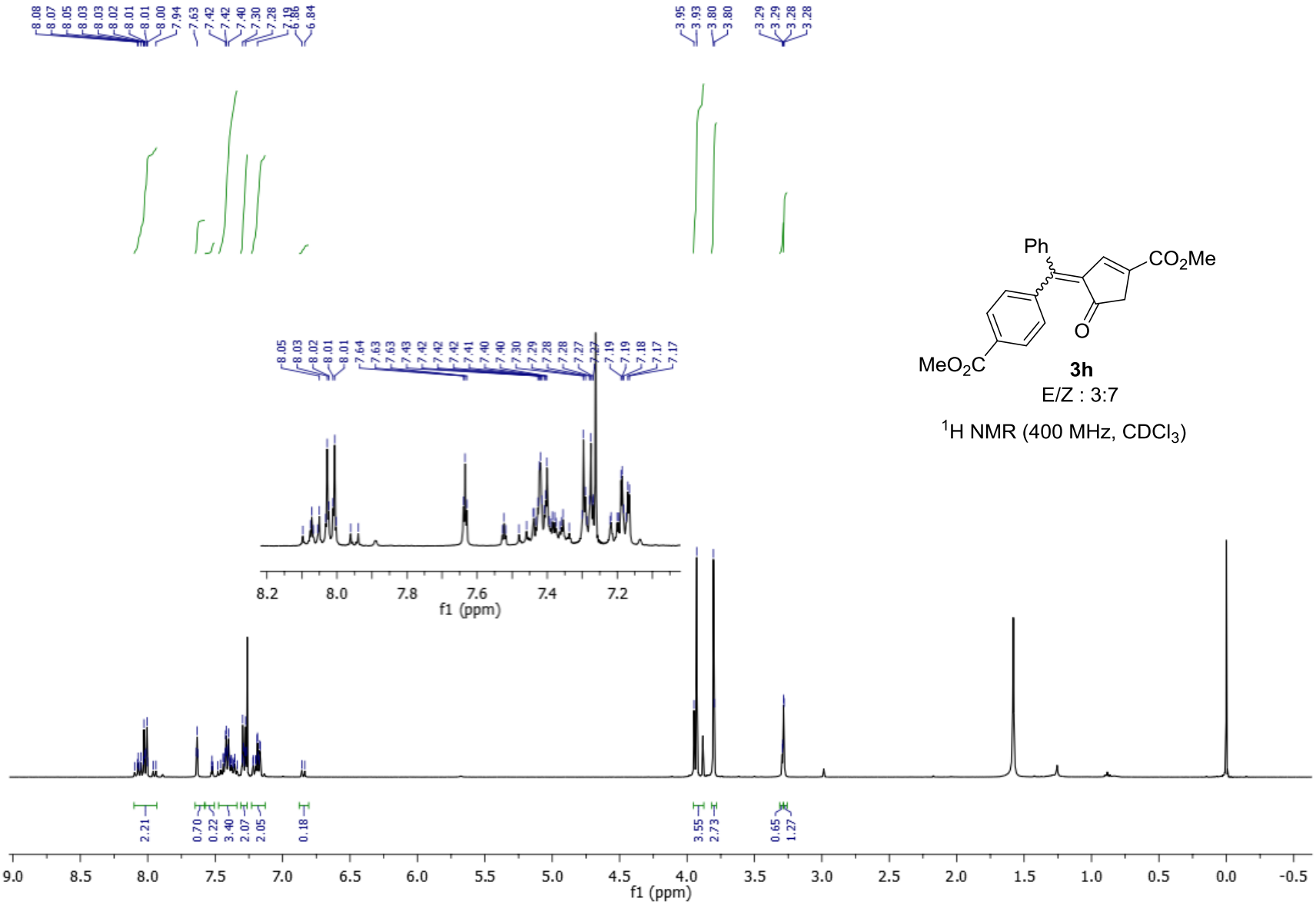


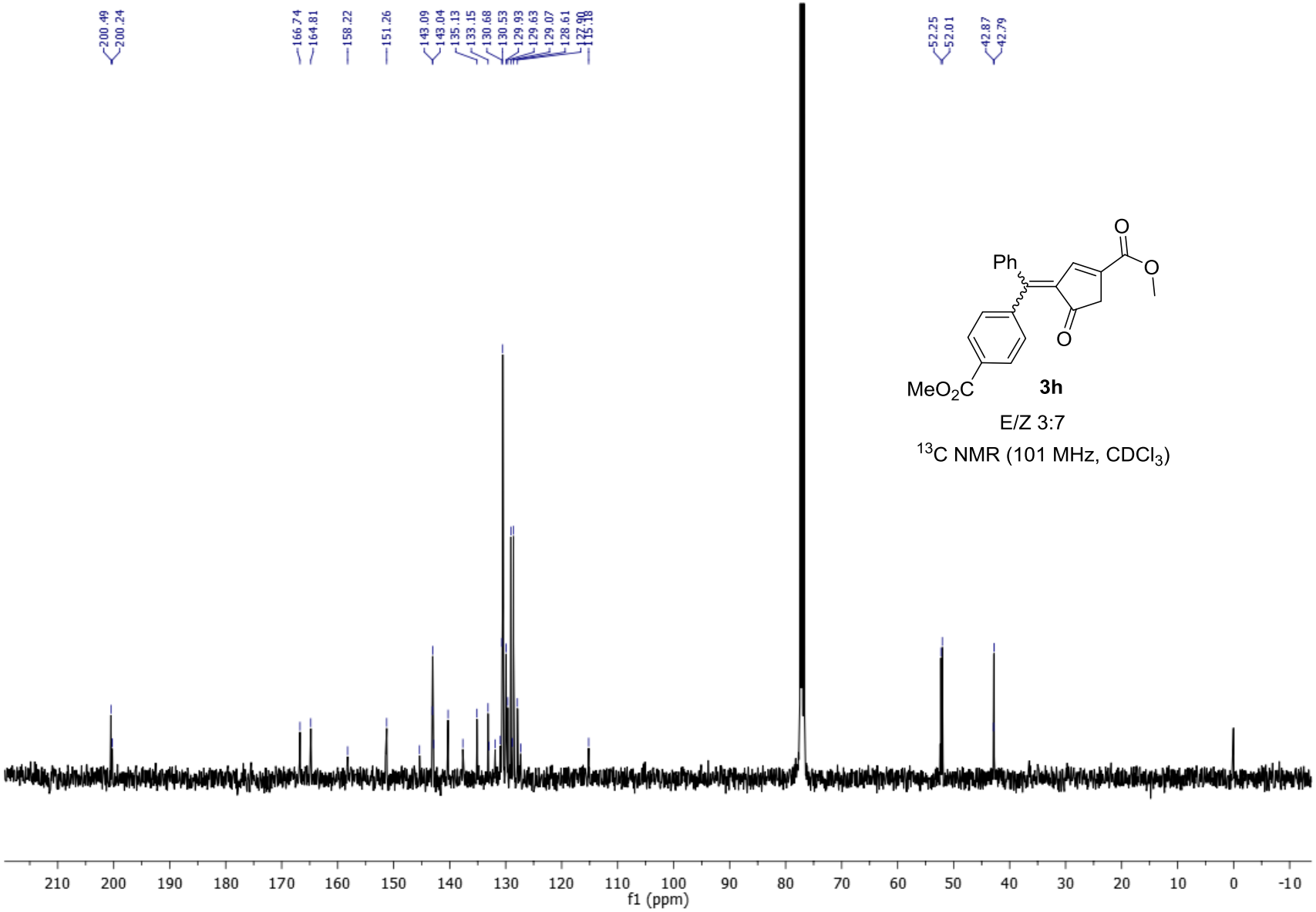
3g

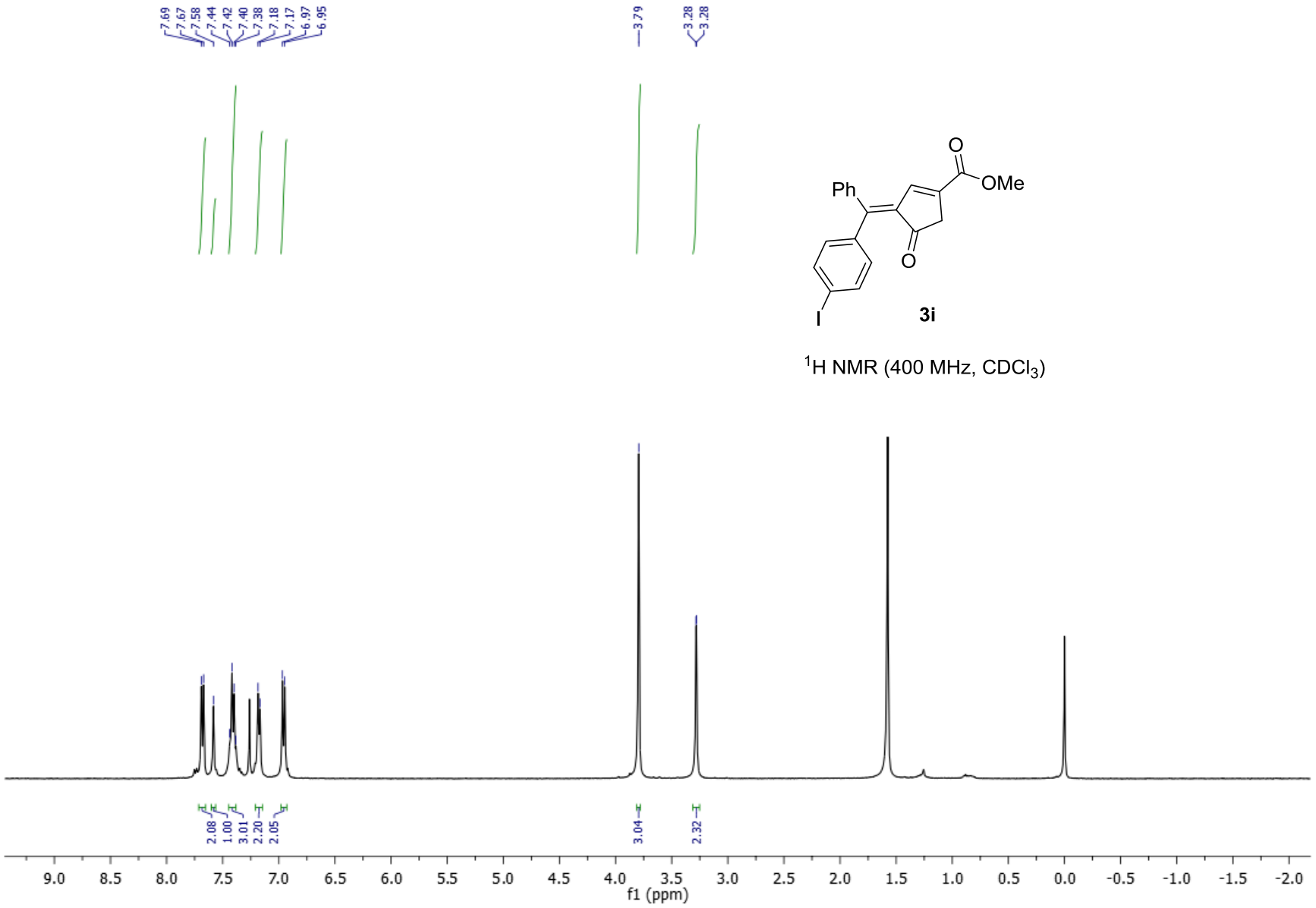
E/Z : 4:6

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

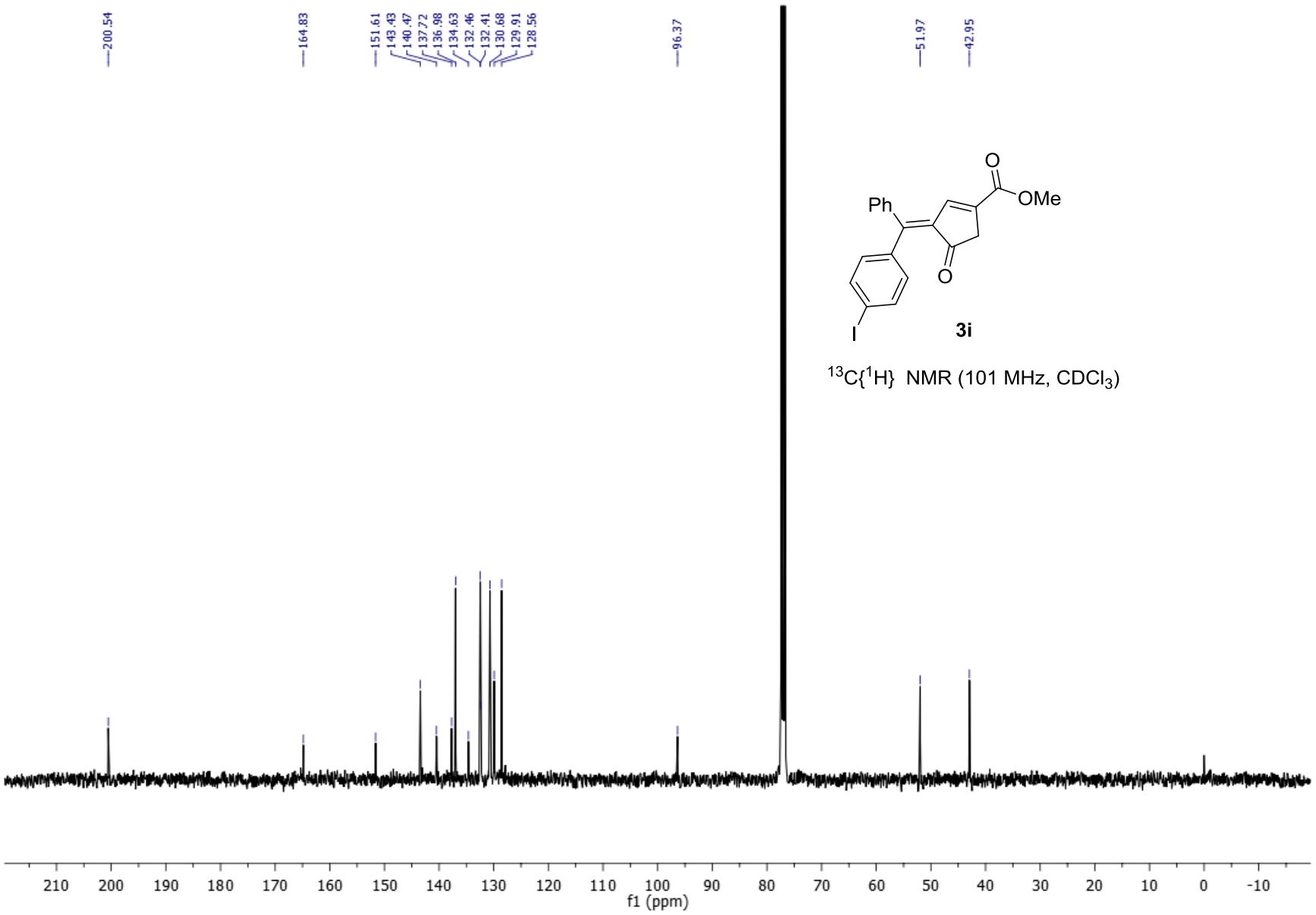

200.55
200.18
197.63
197.42
164.77
151.28
151.11
145.52
143.27
142.98
142.83
140.22
137.55
137.36
135.19
133.24
133.11
130.82
130.77
130.66
130.51
129.96
129.92
128.64
128.36
127.92
127.80
52.02
42.81
26.73
Ph
O
O
O
O
3g
E/Z : 4:6
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

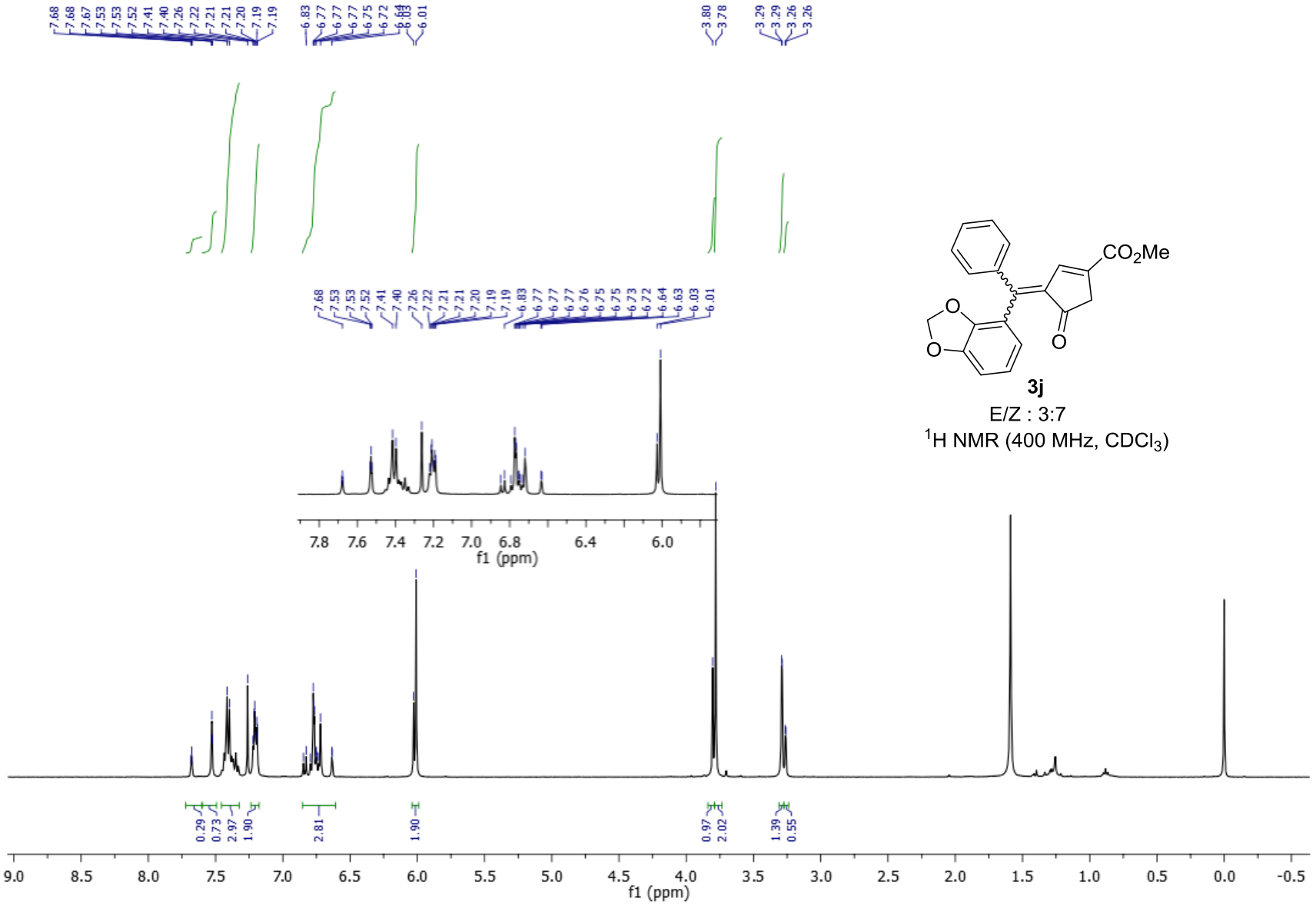

Ph
CO2Me
O
MeO2C
3h
E/Z : 3:7
1H NMR (400 MHz, CDCl3)
f1 (ppm)


200.49
200.24
166.74
164.81
158.22
151.26
143.09
143.04
135.13
133.15
130.68
130.53
129.93
129.63
129.07
128.61
52.25
52.01
42.87
42.79
Ph
O
O
O
MeO2C
3h
E/Z 3:7
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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


200.54
164.83
151.61
143.43
140.47
137.72
136.98
134.63
132.46
132.41
130.68
129.91
128.56
96.37
51.97
42.95
O
OMe
Ph
O
I
3i
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

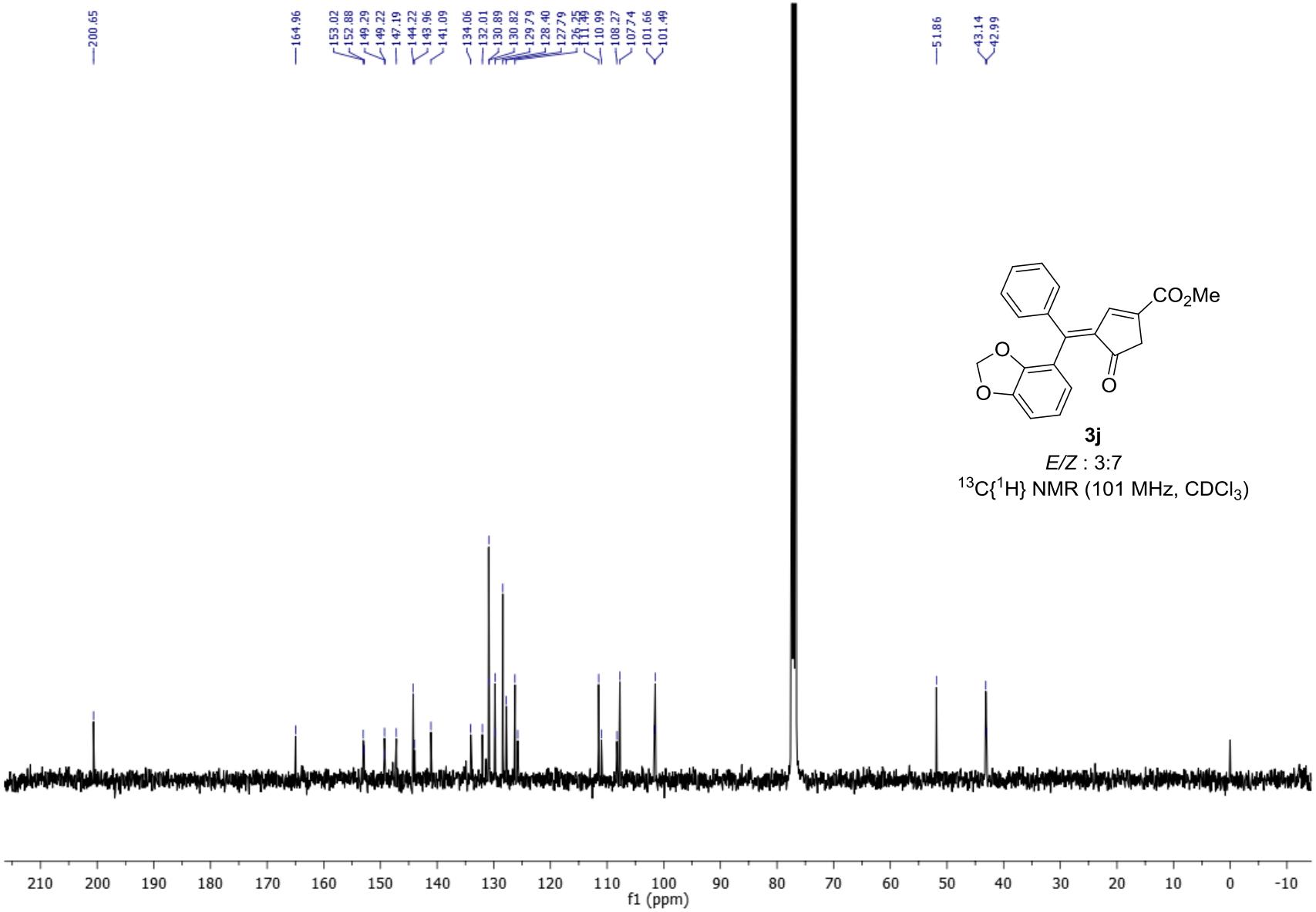


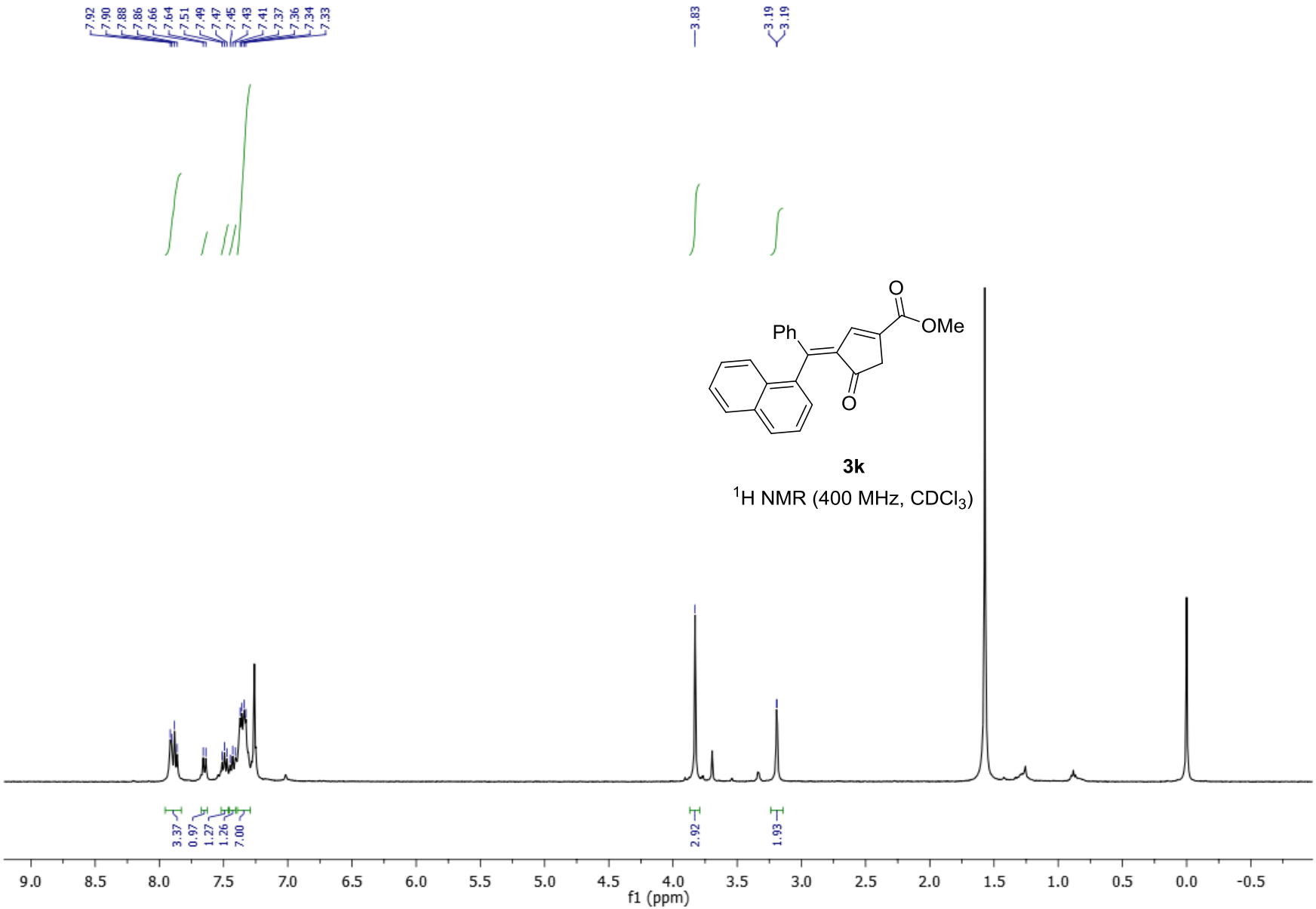
3j

E/Z : 3:7

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

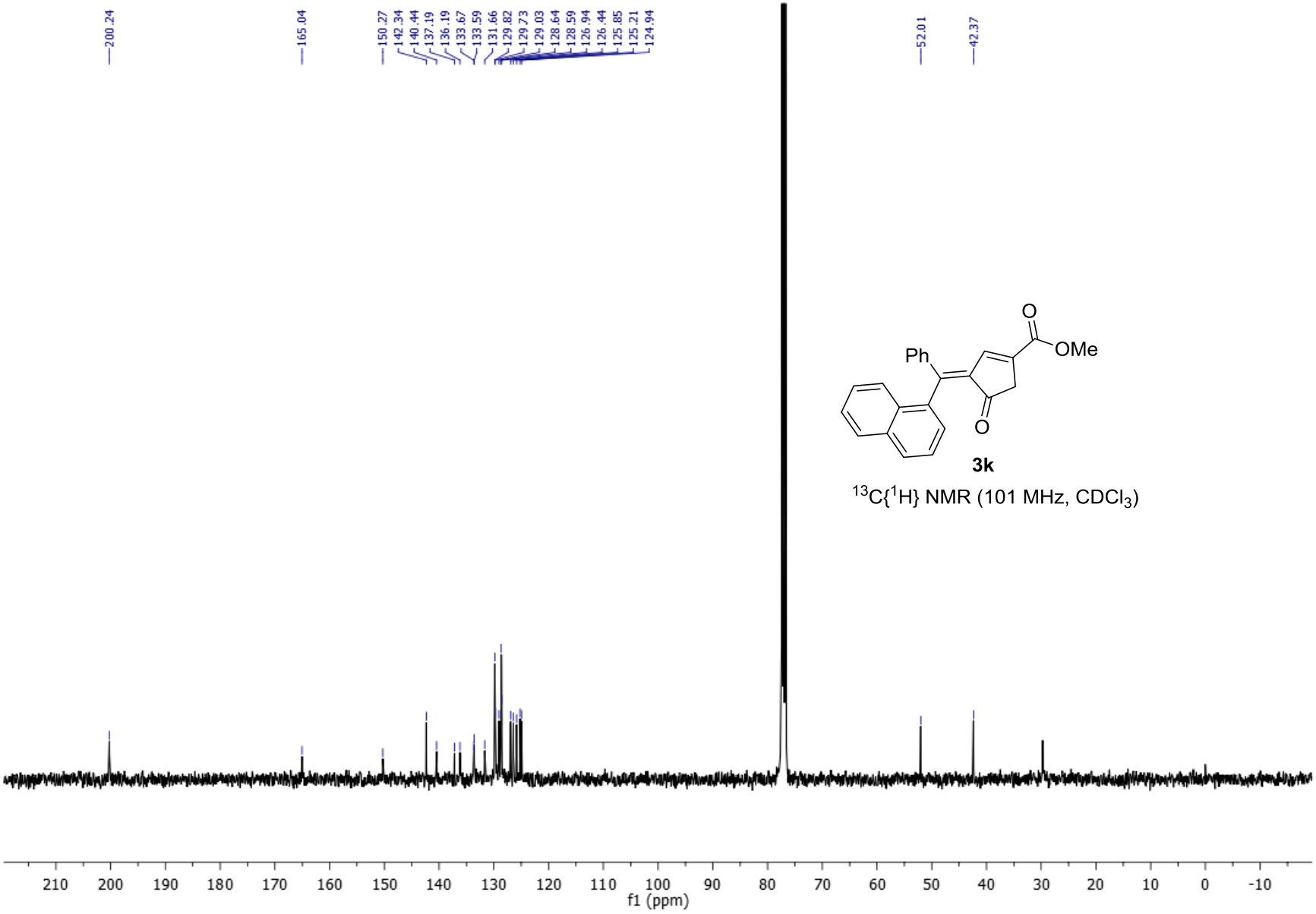
s


200.65
164.96
153.02
152.88
149.29
149.22
147.19
144.22
143.96
141.09
134.06
132.01
130.89
130.82
129.79
128.40
127.79
110.99
108.27
107.74
101.66
101.49
51.86
43.14
42.99
CO2Me
O
O
O
3j
E/Z : 3:7
13C{1H} NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



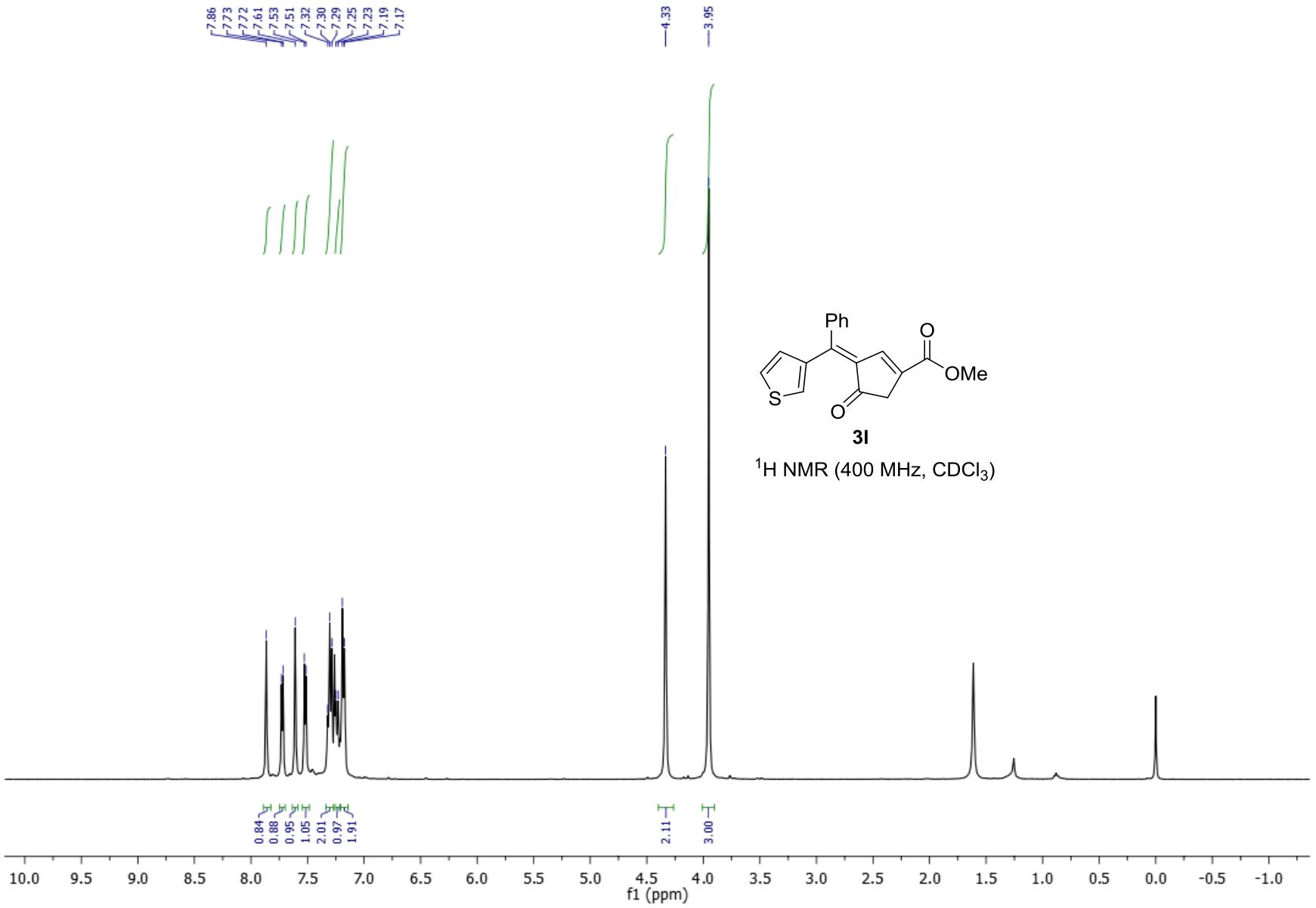
3k

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



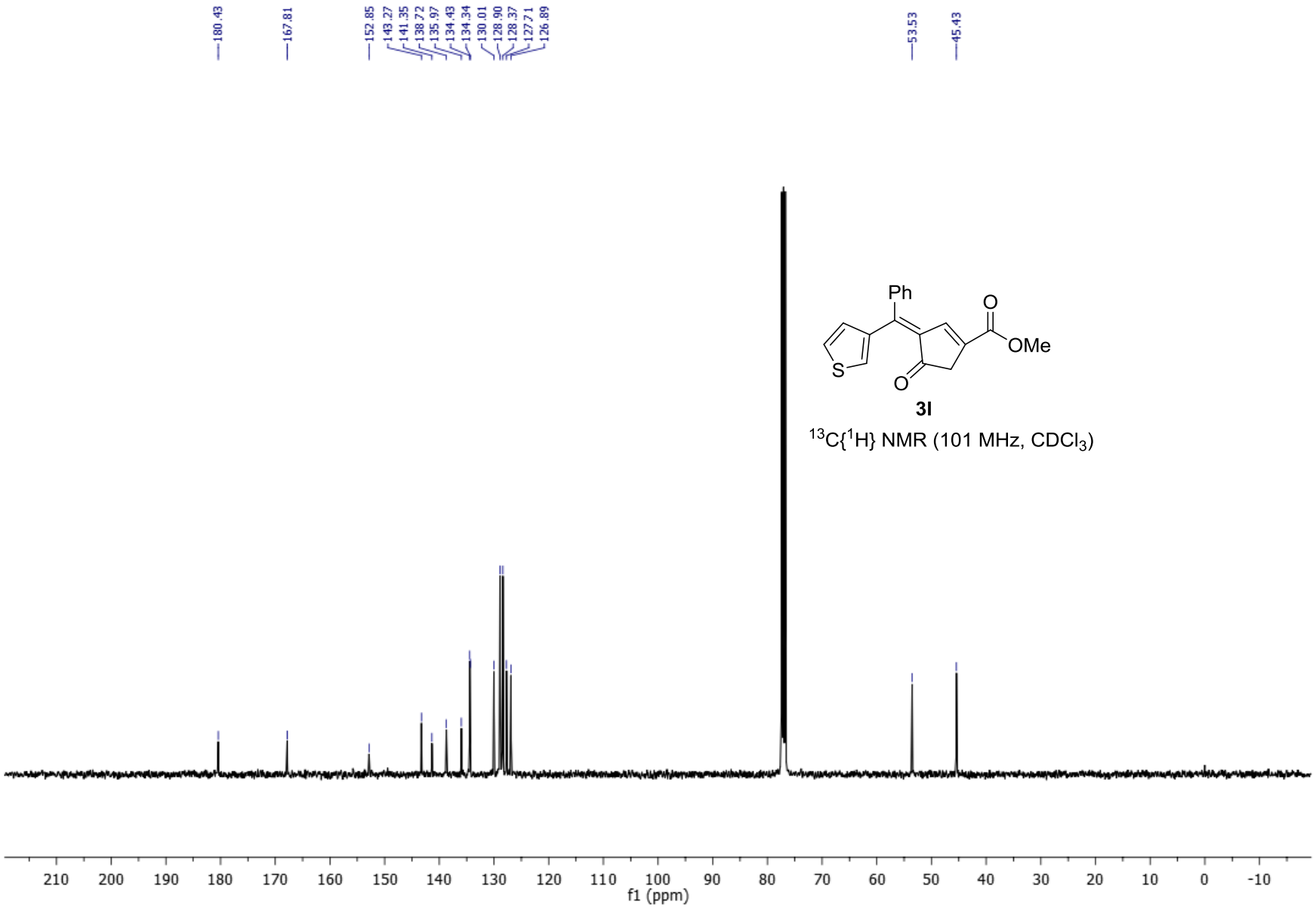
3k

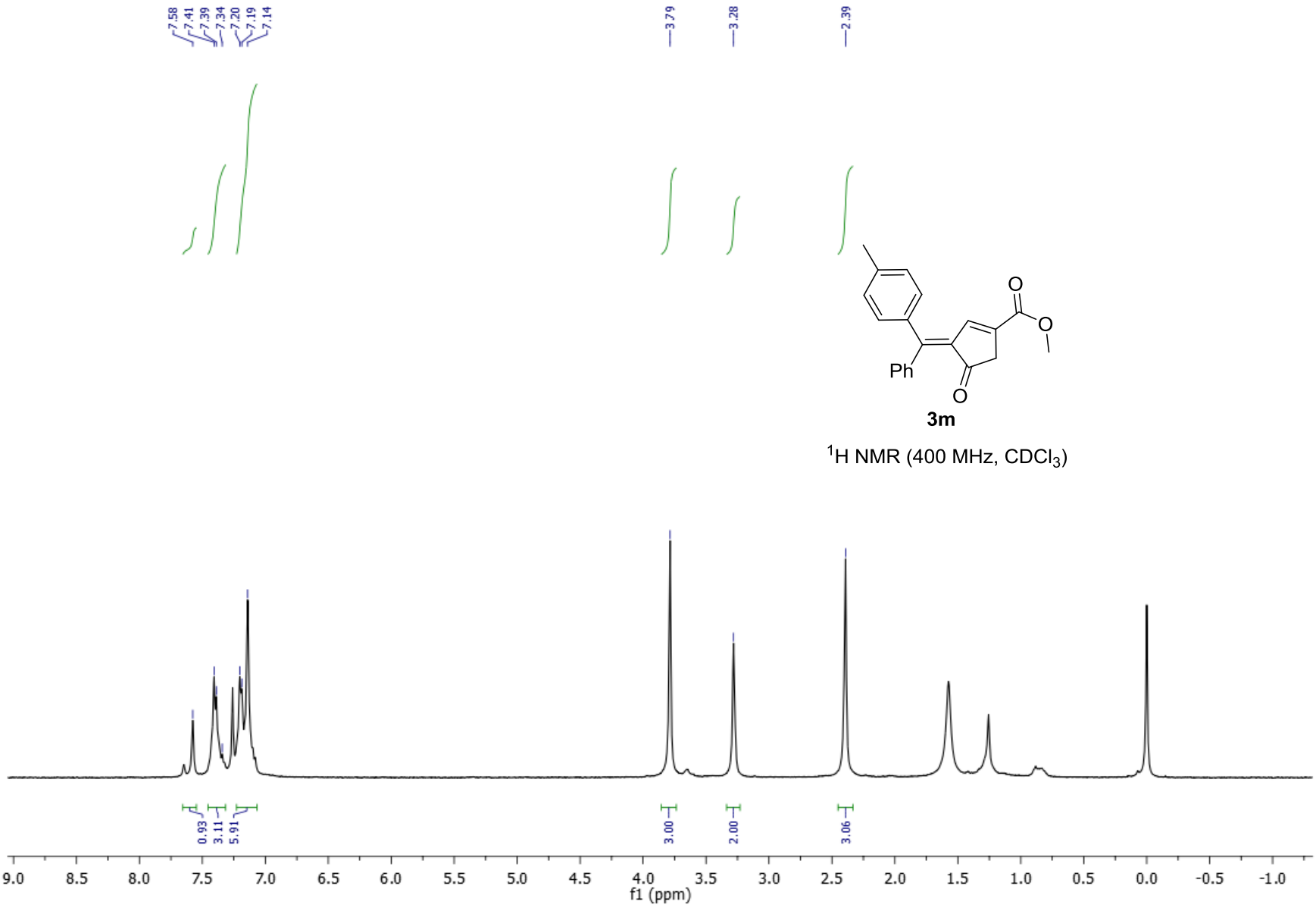
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



3l

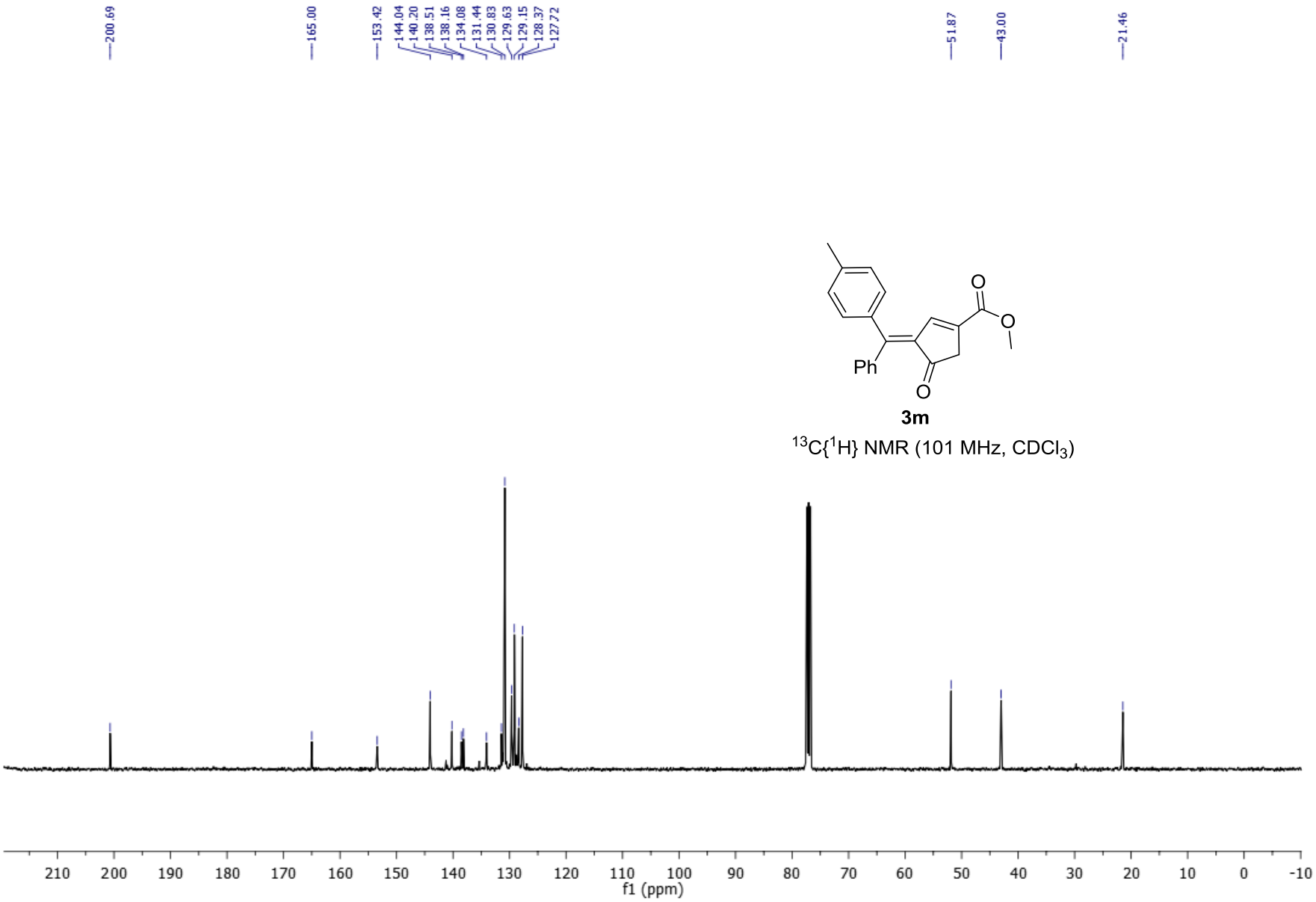
^{1}H NMR (400 MHz, $CDCl_3$)

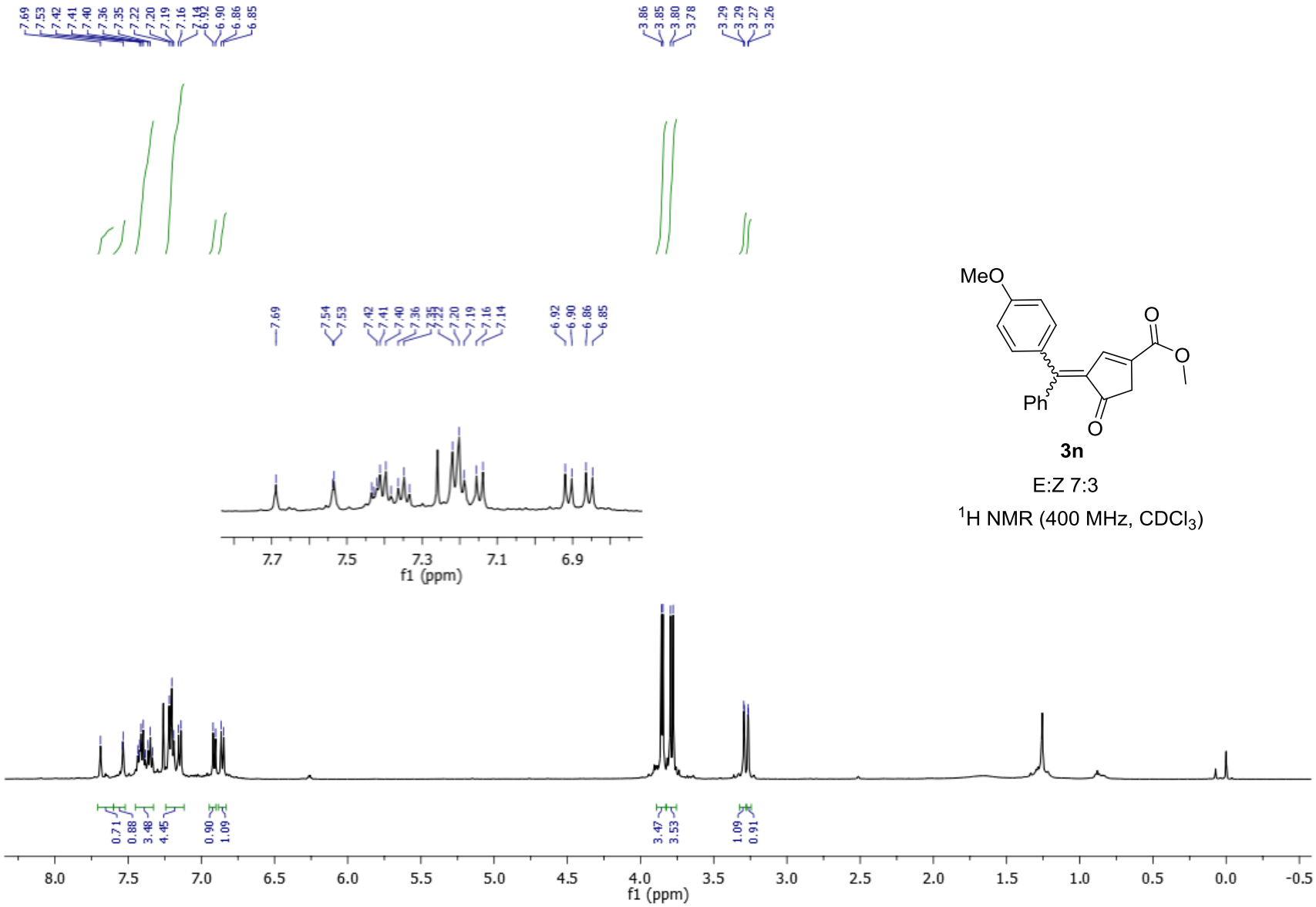

180.43
167.81
152.85
143.27
141.35
138.72
135.97
134.43
134.34
130.01
128.90
128.37
127.71
126.89
53.53
45.43
Ph
O
OMe
S
O
3l
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3m

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

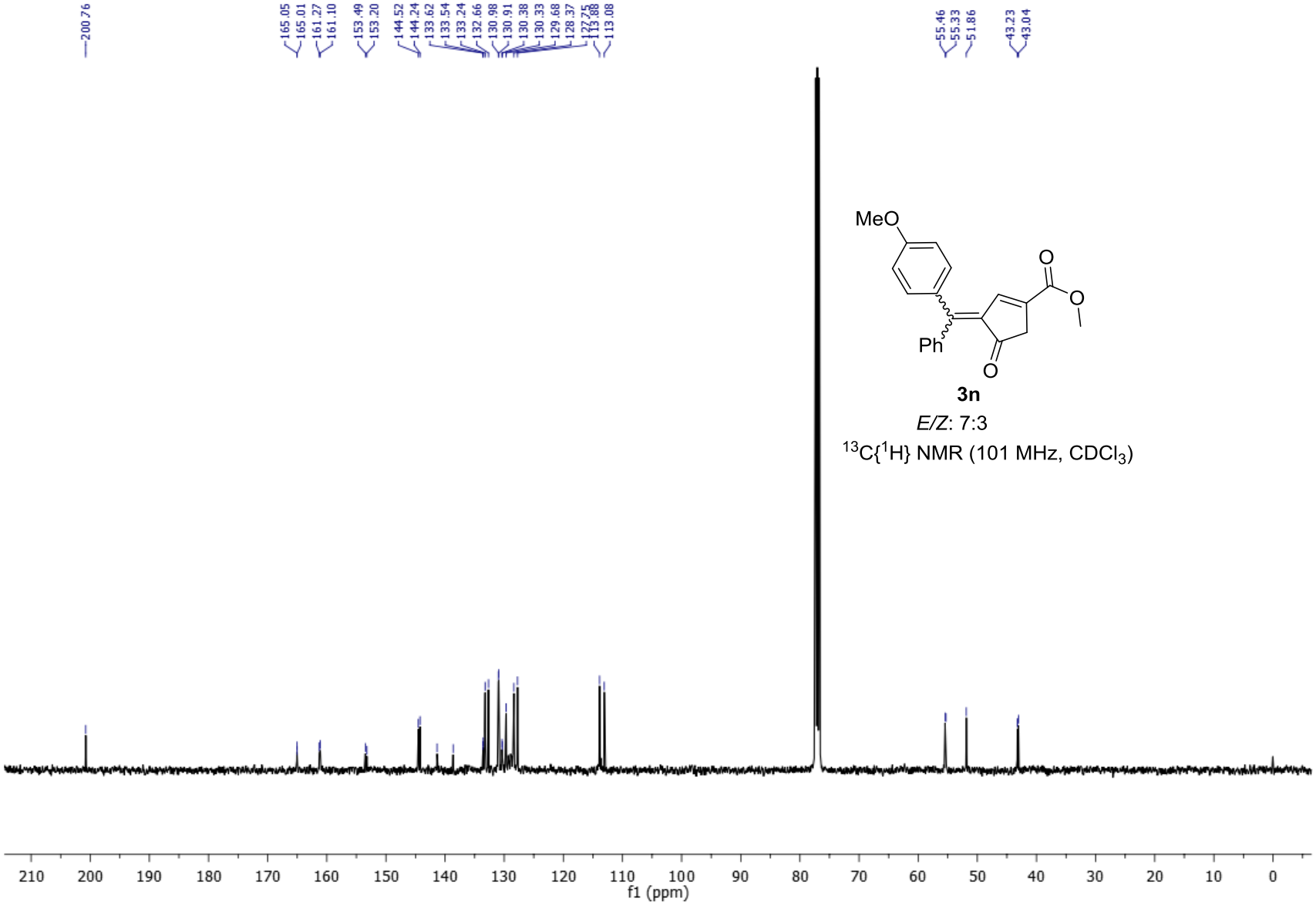

200.69
165.00
153.42
144.04
140.20
138.51
138.16
134.08
131.44
130.83
129.63
129.15
128.37
127.72
51.87
43.00
21.46
O
O
Ph
O
3m
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3n

E:Z 7:3

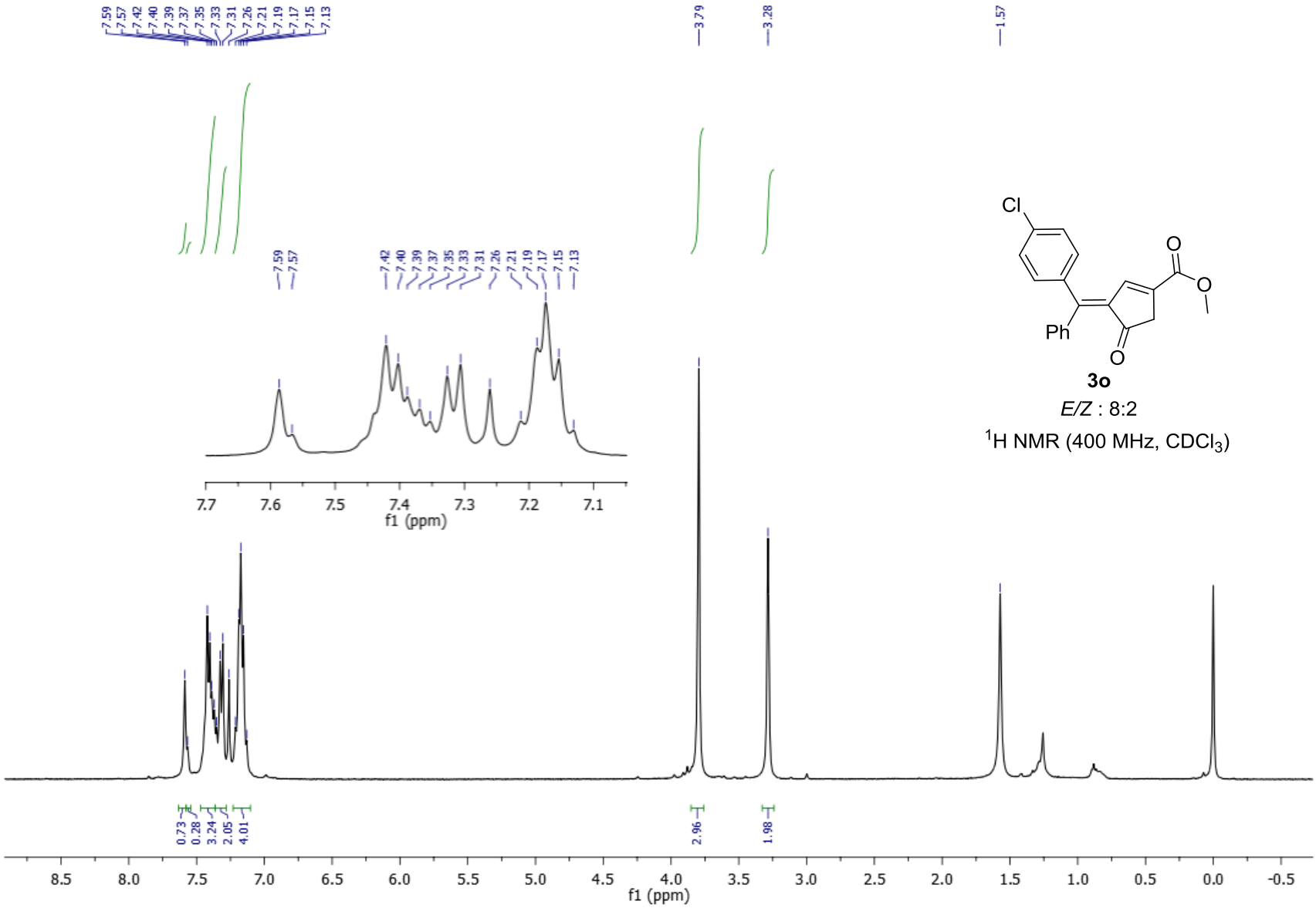
^{1}H NMR (400 MHz, $CDCl_3$)



3n

E/*Z*: 7:3

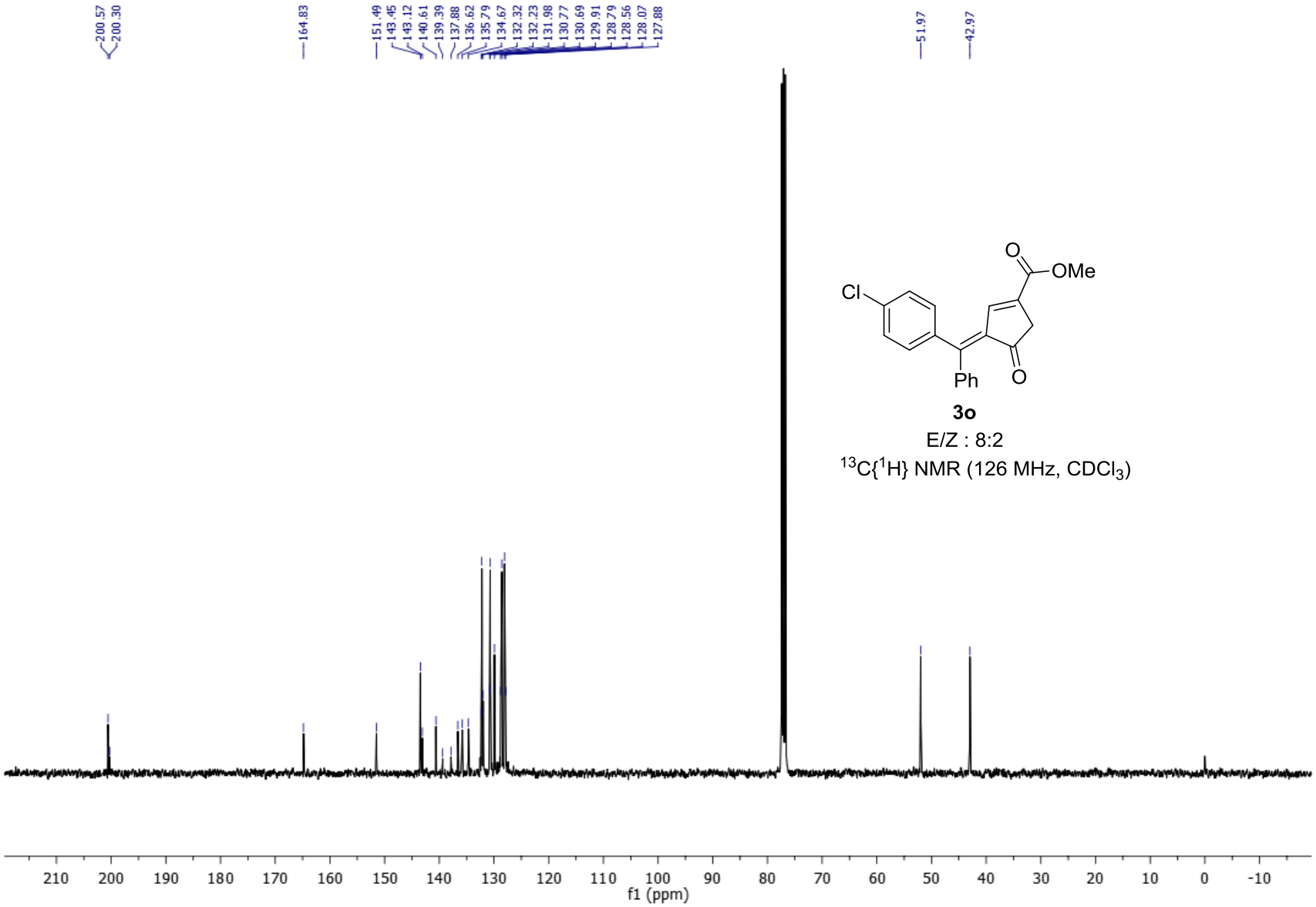
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

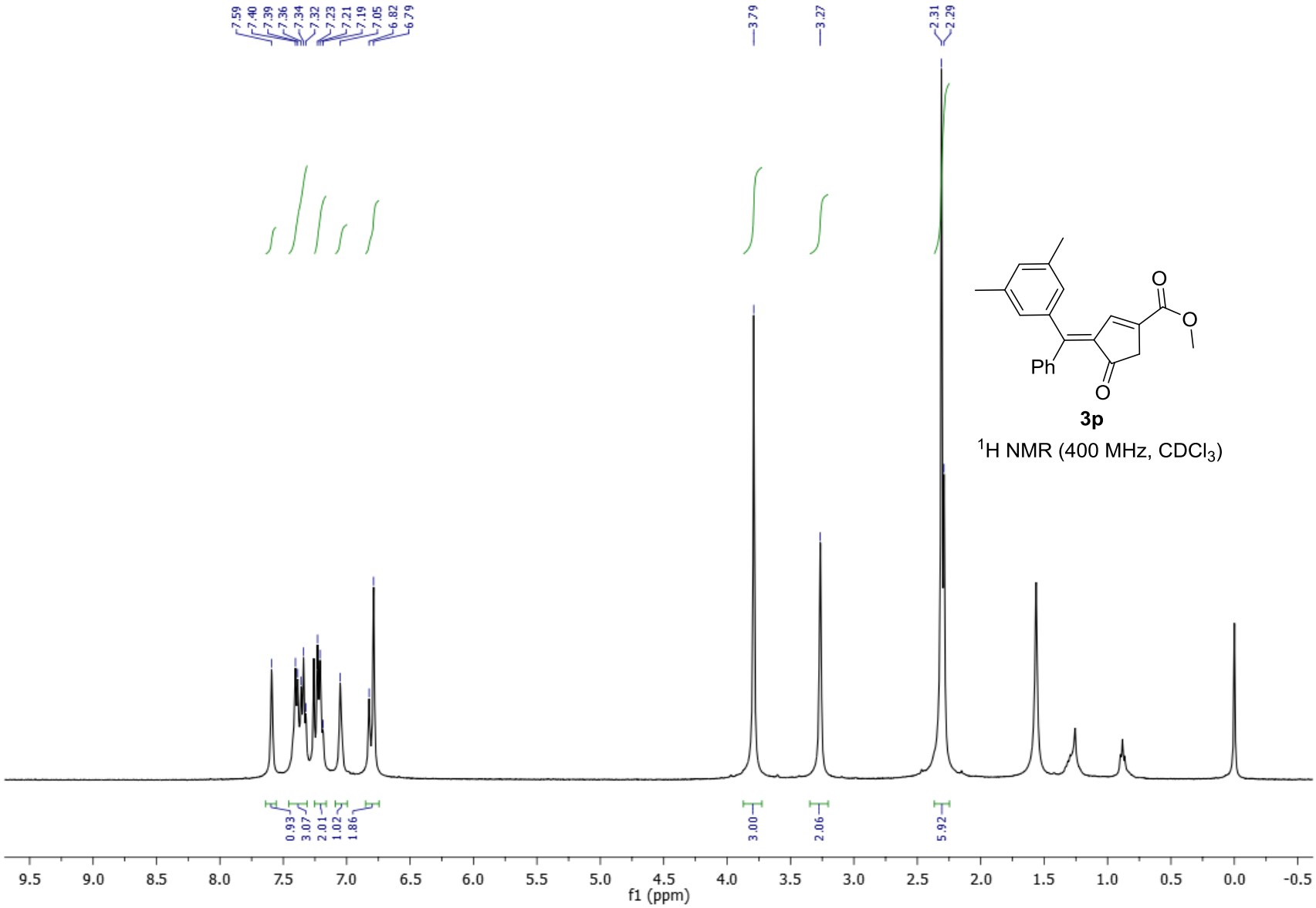


3o

E/*Z* : 8:2

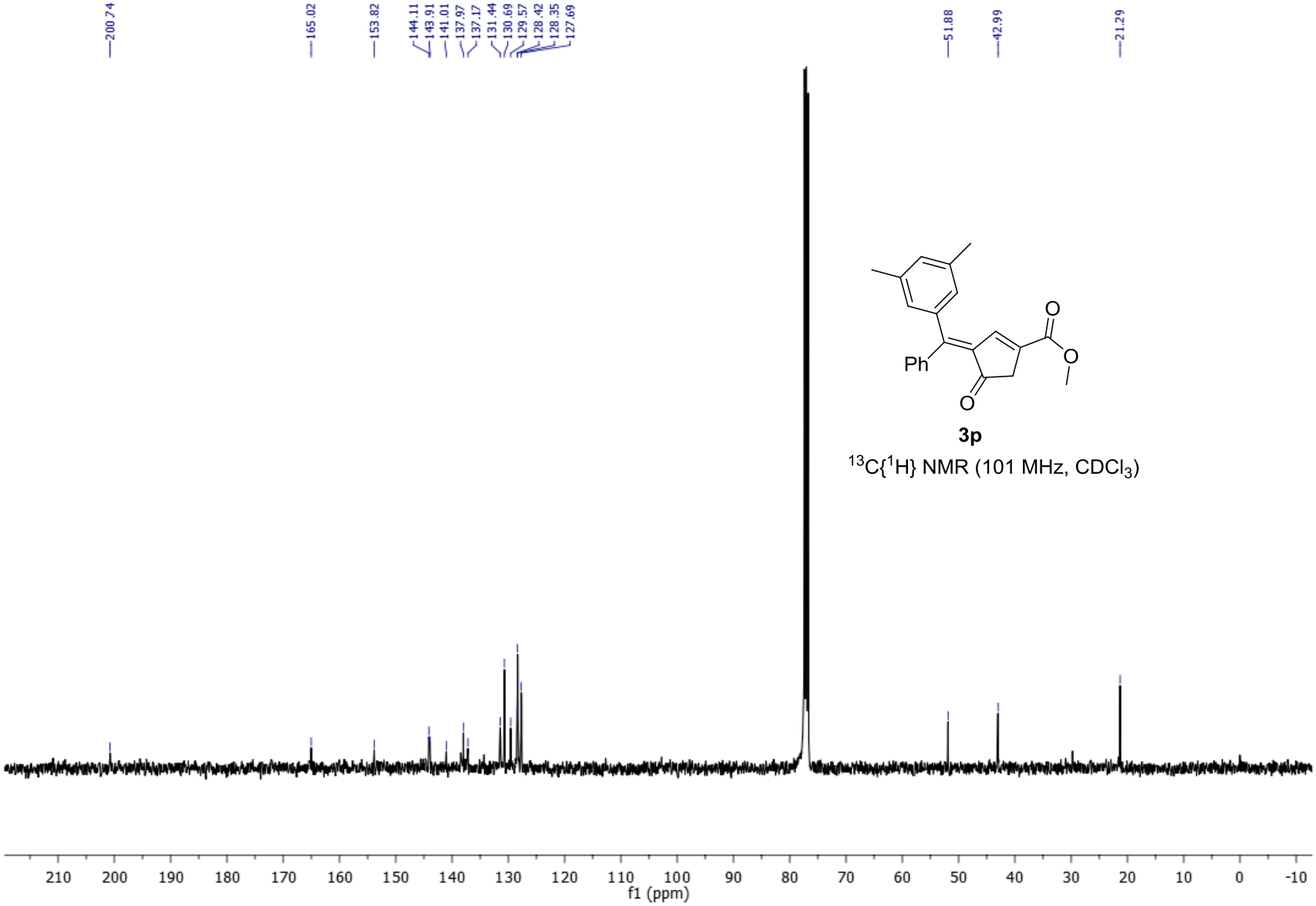
^{1}H NMR (400 MHz, $CDCl_3$)


200.57
200.30
164.83
151.49
143.45
143.12
140.61
139.39
137.88
136.62
135.79
134.67
132.32
132.23
131.98
130.77
130.69
129.91
128.79
128.56
128.07
127.88
51.97
42.97
Cl
O
OMe
O
Ph
3o
E/Z : 8:2
13C{1H} NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



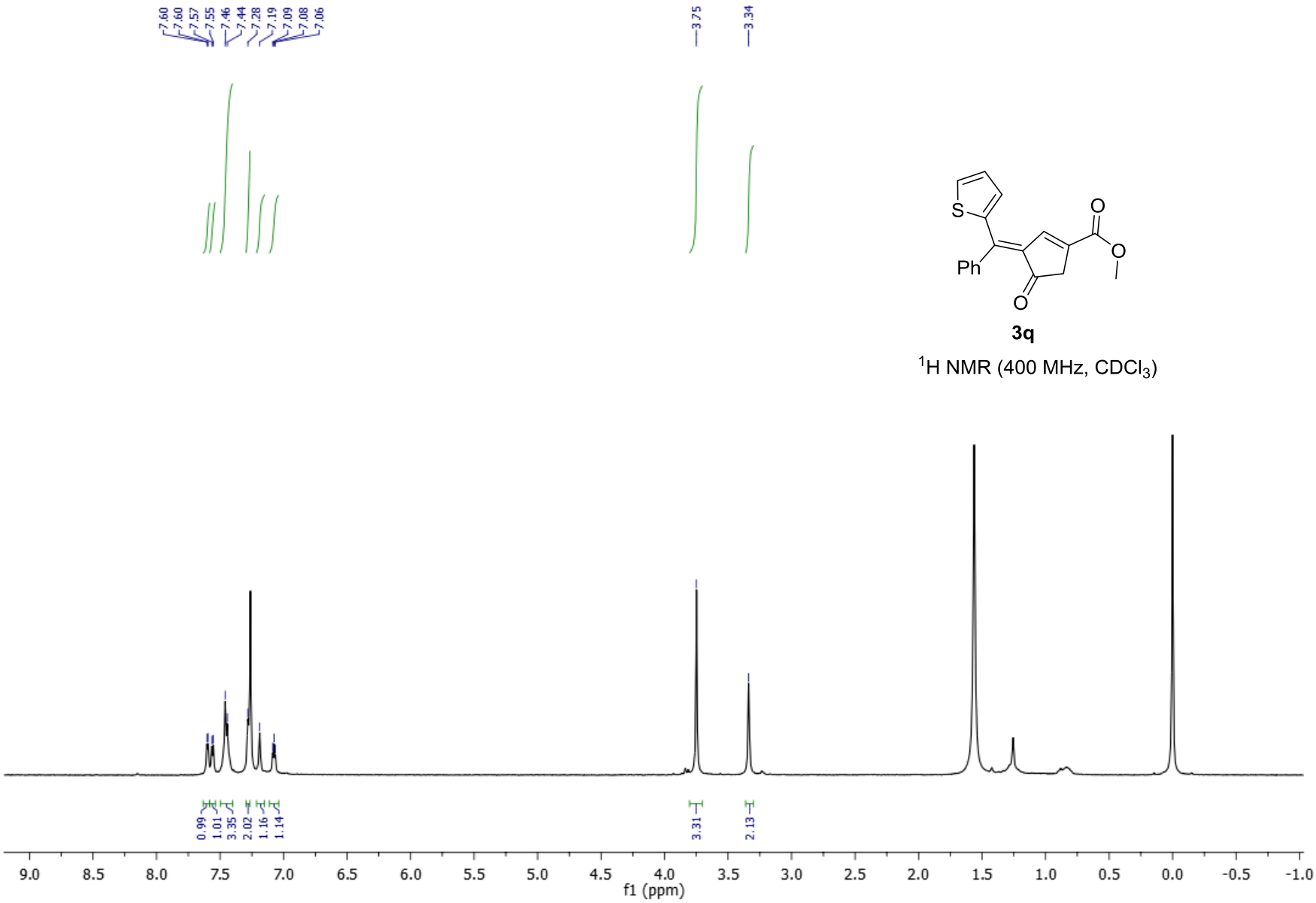
3p

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



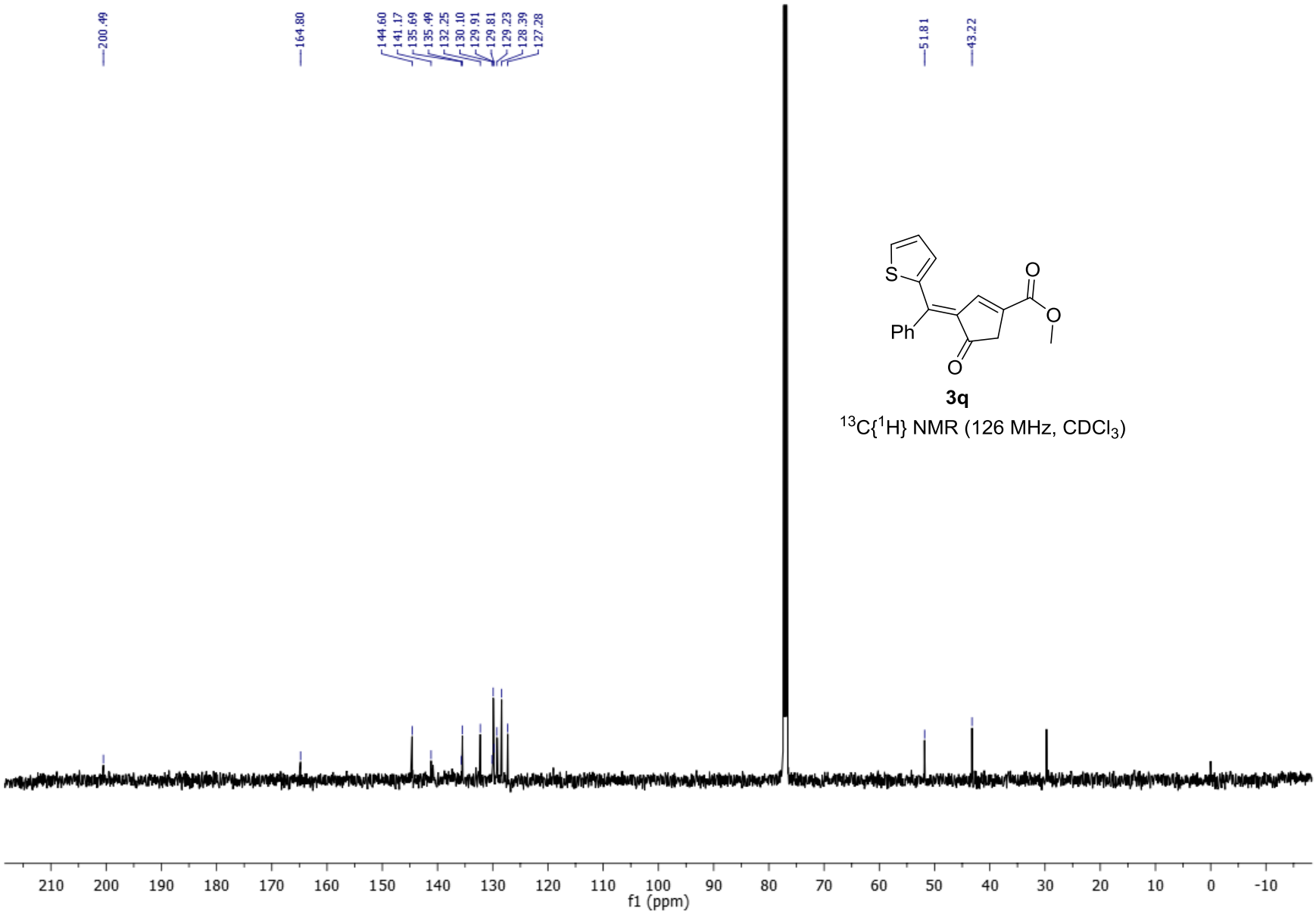
3p

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



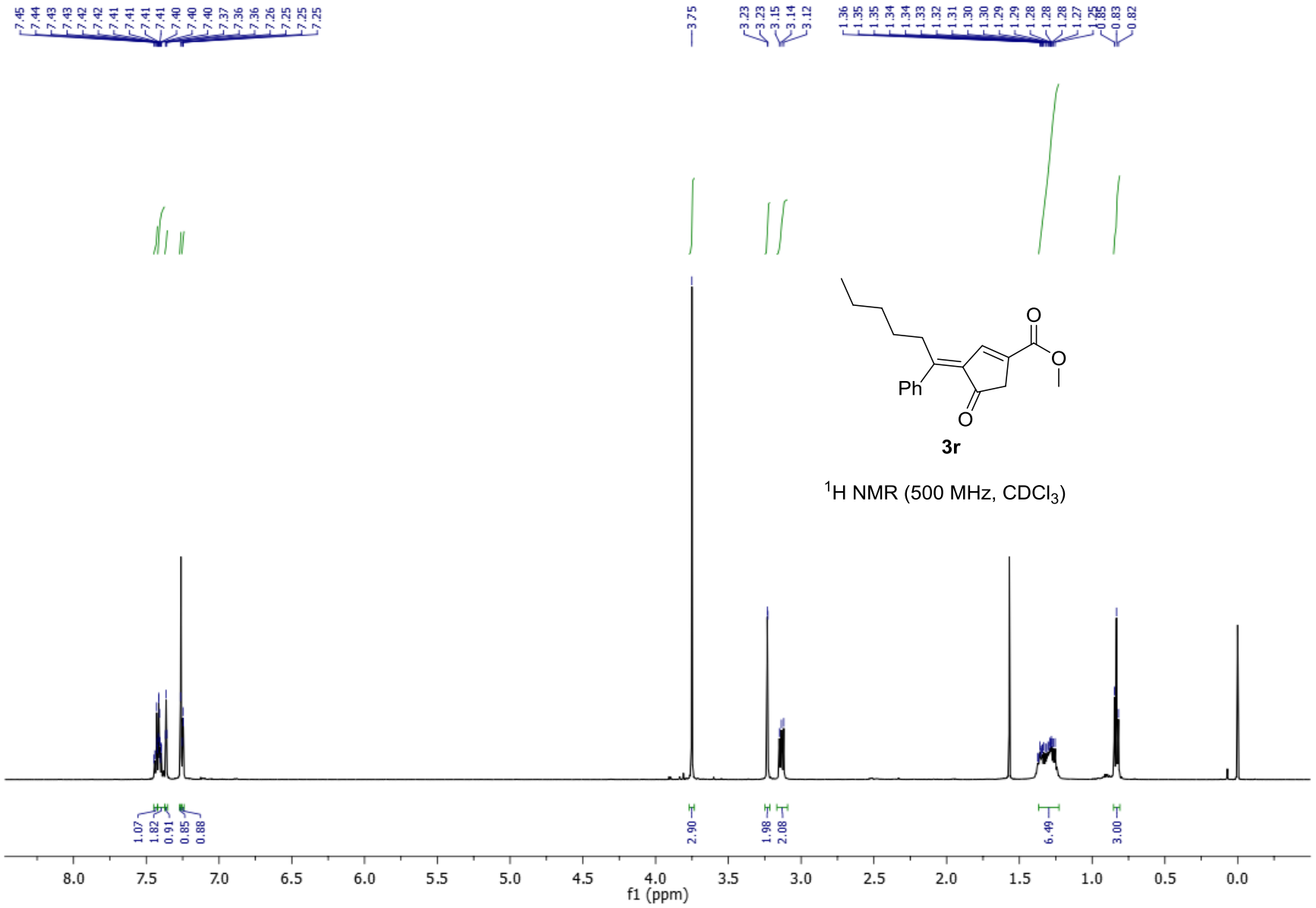
3q

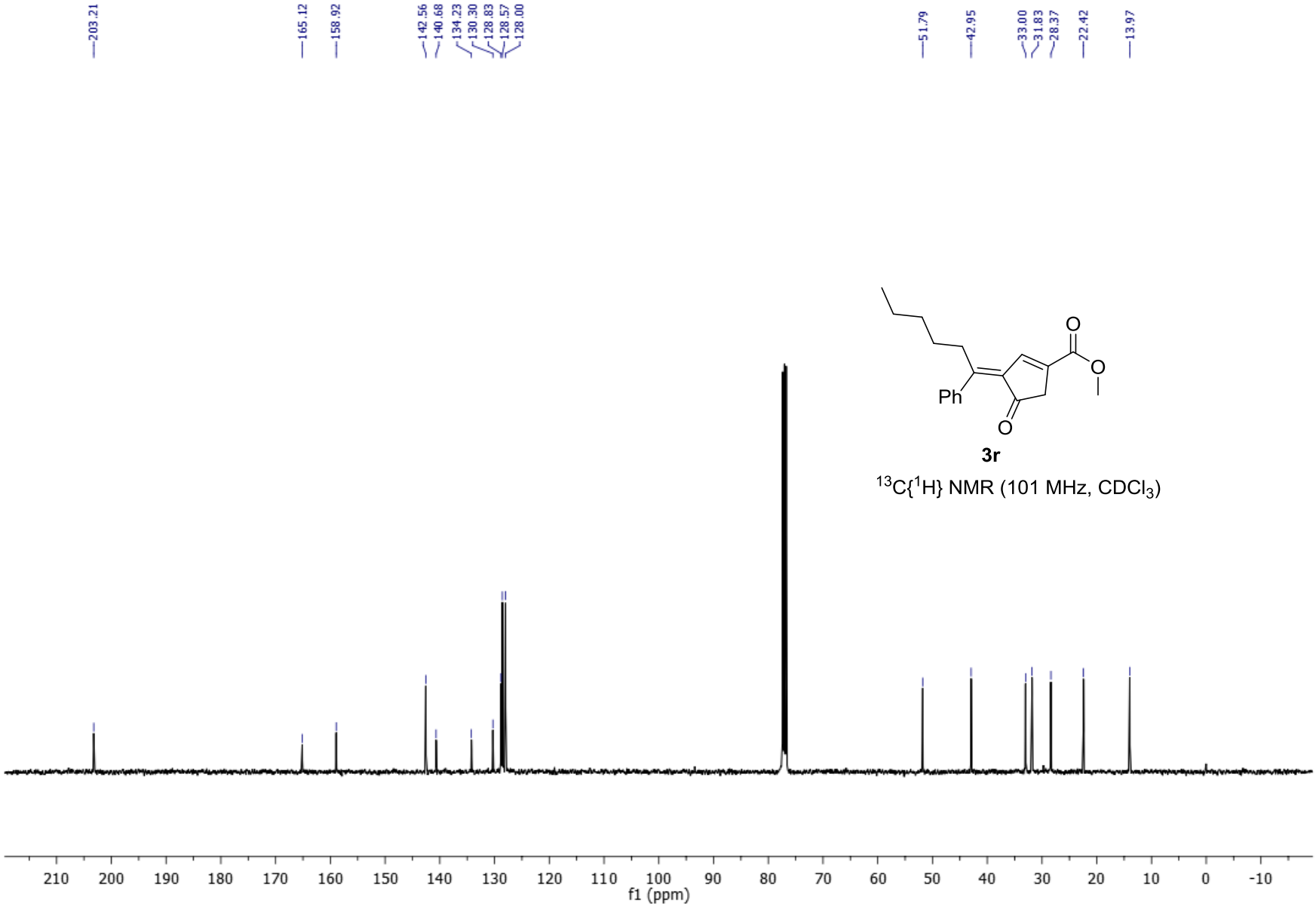
^{1}H NMR (400 MHz, $CDCl_3$)



3q

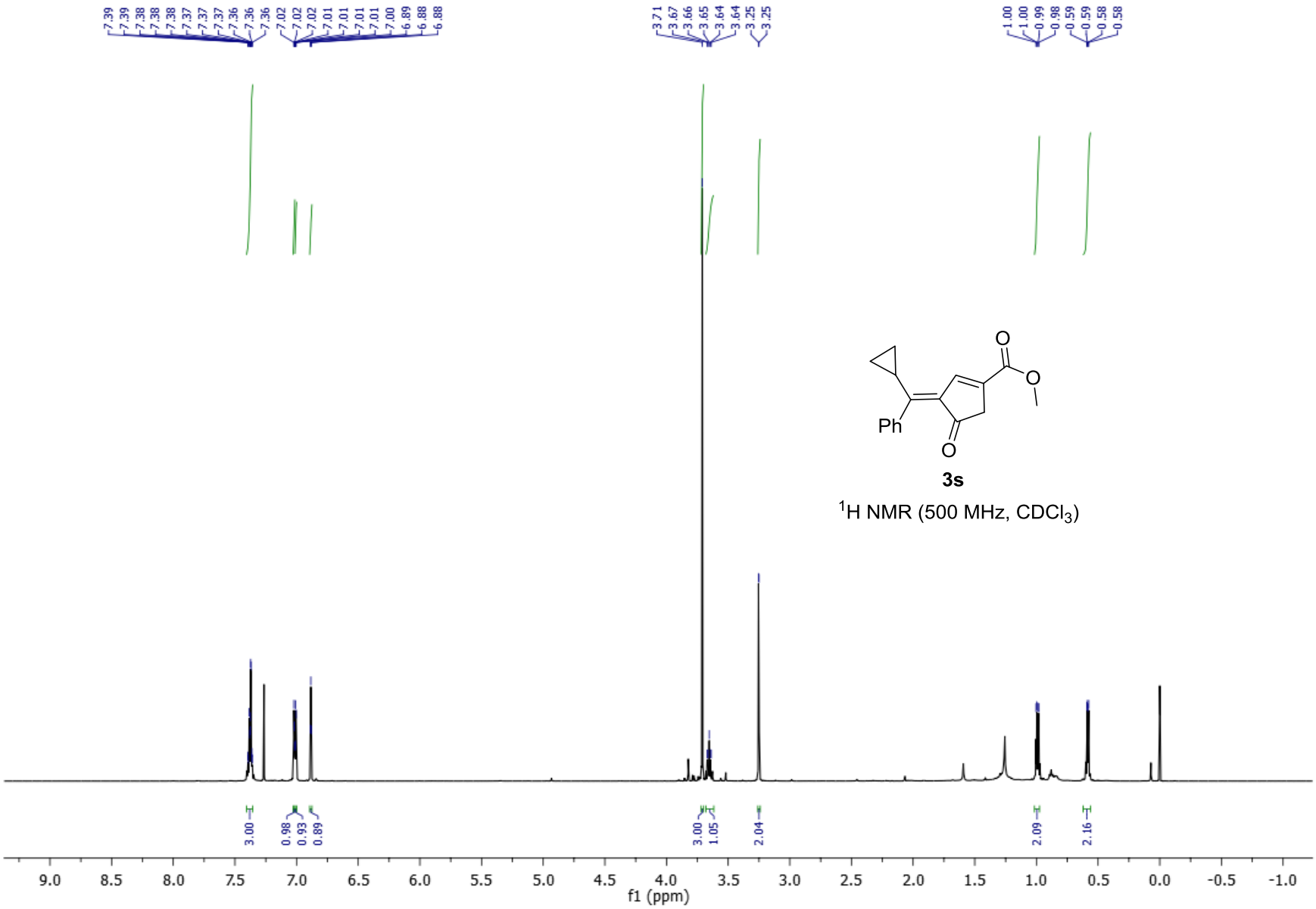
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)


7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.41
7.40
7.40
7.40
7.37
7.36
7.36
7.26
7.25
7.25
7.25
3.75
3.23
3.23
3.15
3.14
3.12
1.36
1.35
1.35
1.34
1.34
1.33
1.32
1.31
1.30
1.30
1.29
1.29
1.28
1.28
1.27
0.85
0.83
0.82
O
O
Ph
O
3r
1H NMR (500 MHz, CDCl3)
1.07
1.82
0.91
0.85
0.88
2.90
1.98
2.08
6.49
3.00
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)



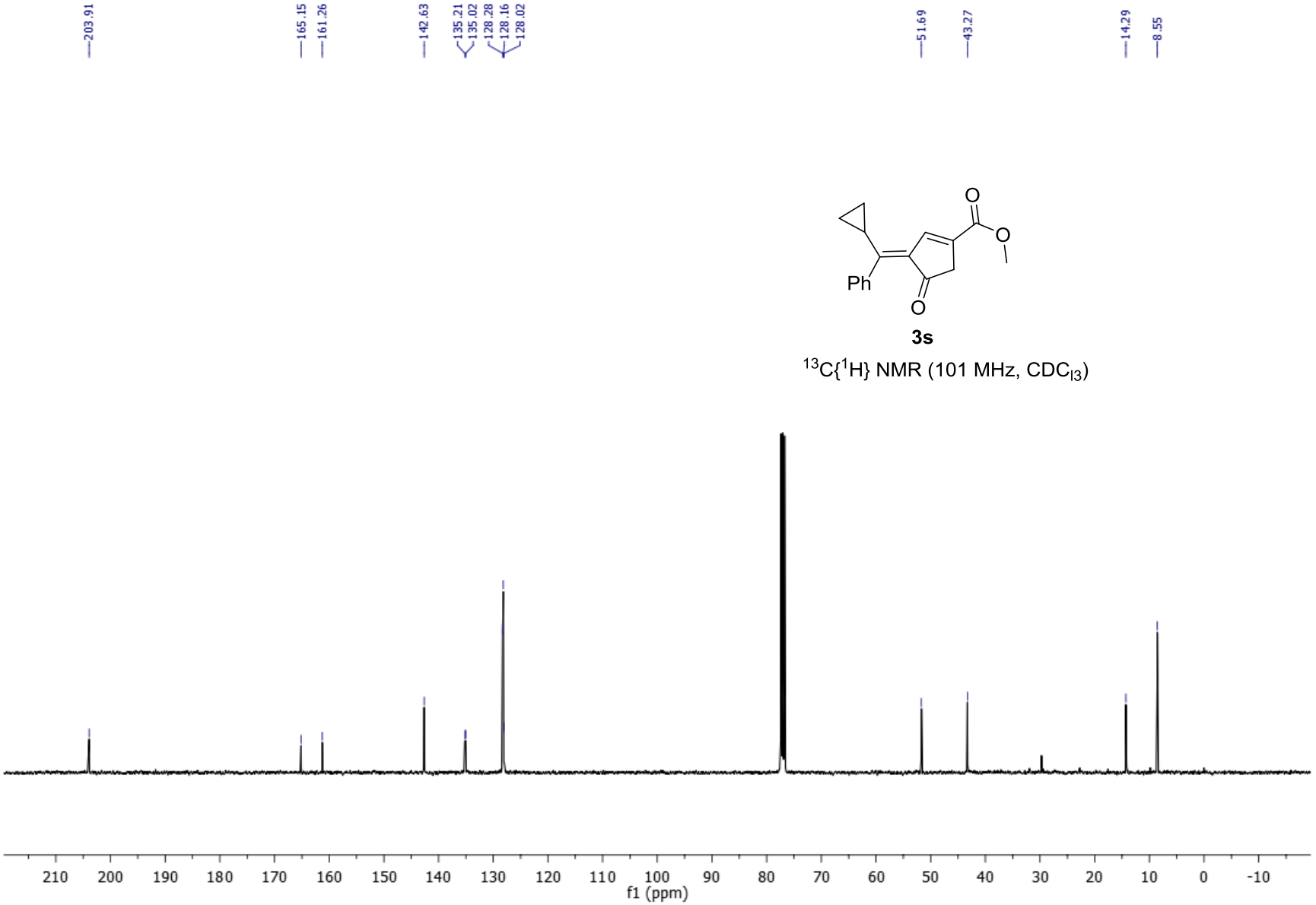
3r

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



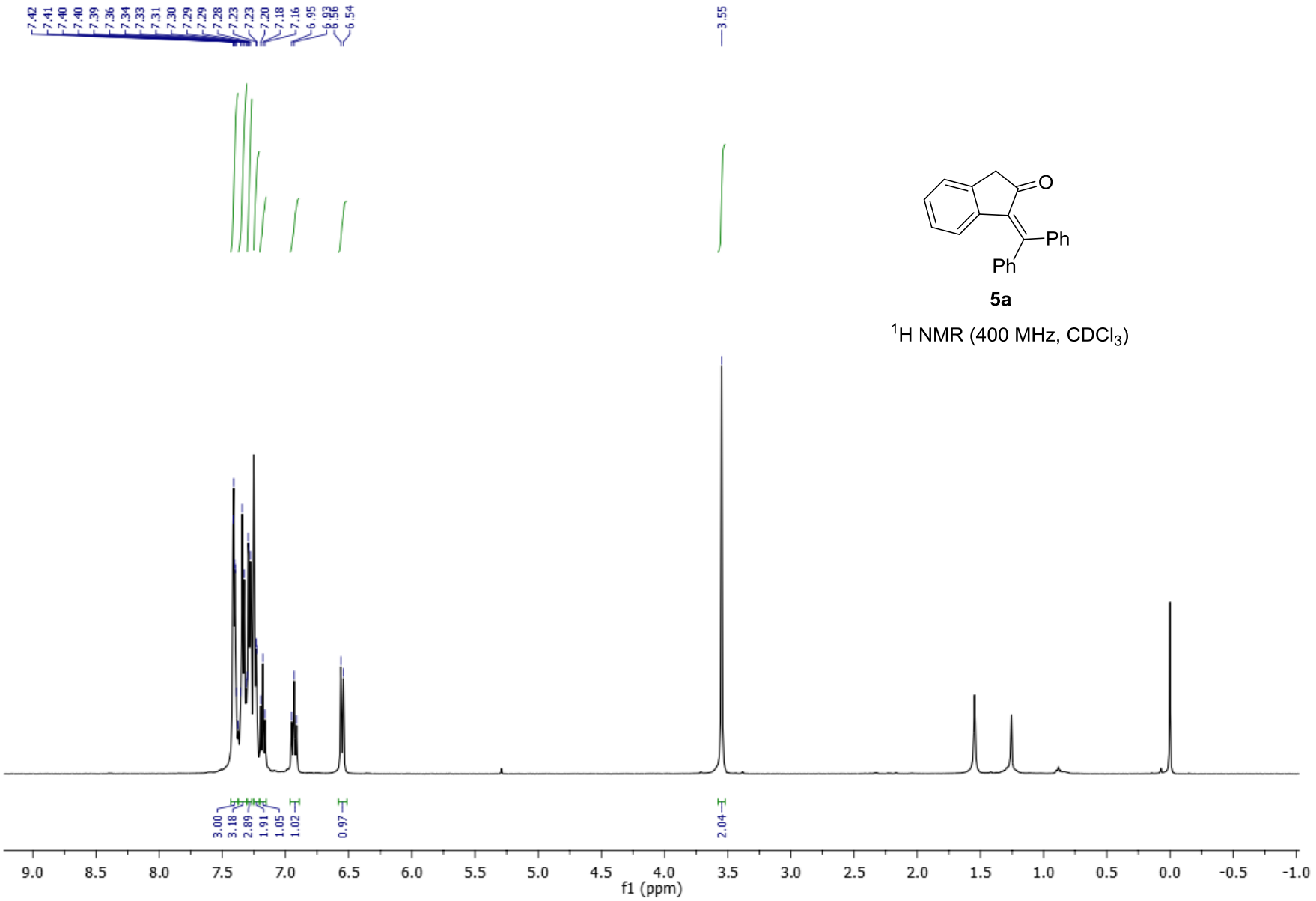
3s

^{1}H NMR (500 MHz, $CDCl_3$)



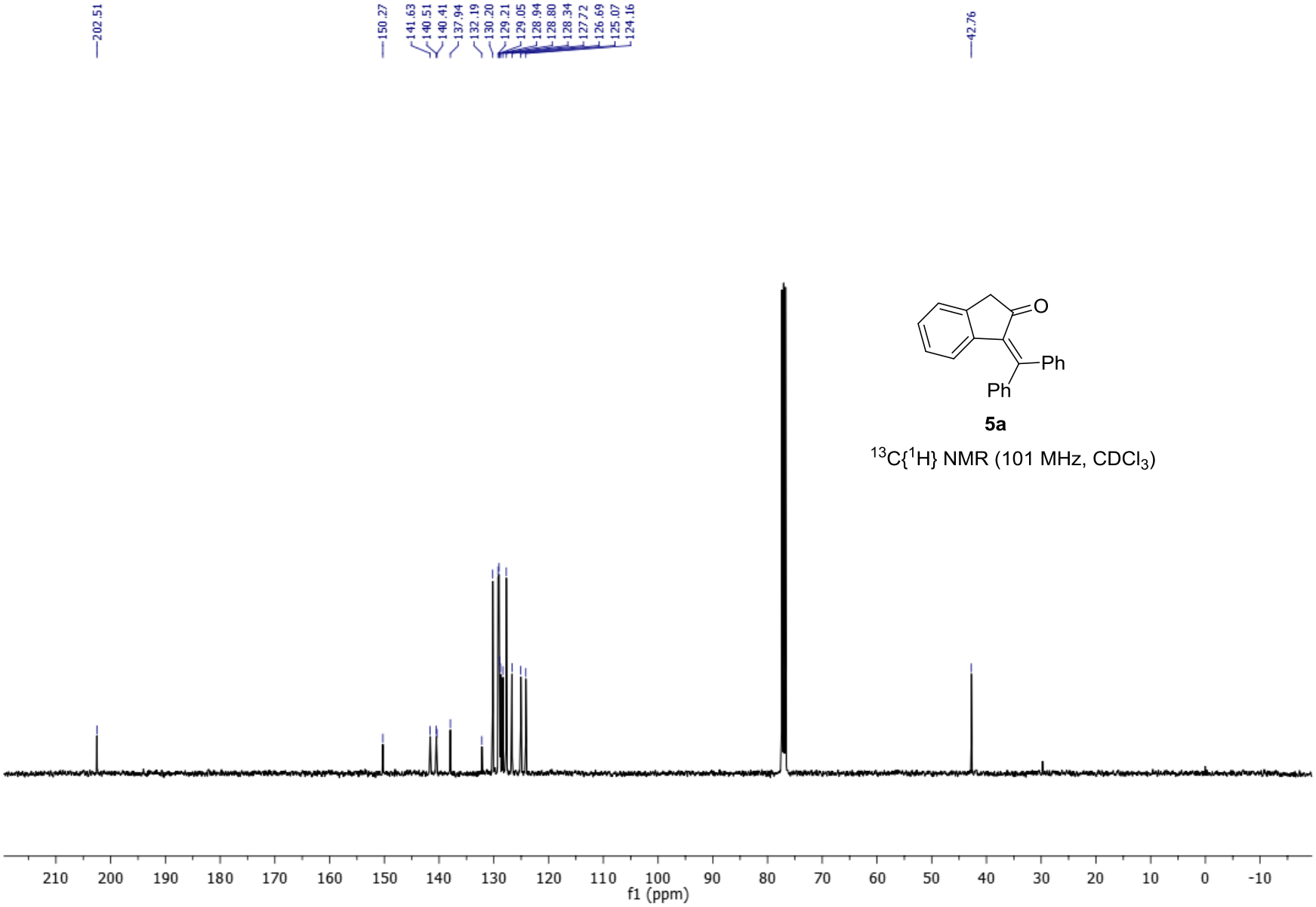
3s

$^{13}C\{^{1}H\}$ NMR (101 MHz, CDC_{l3})



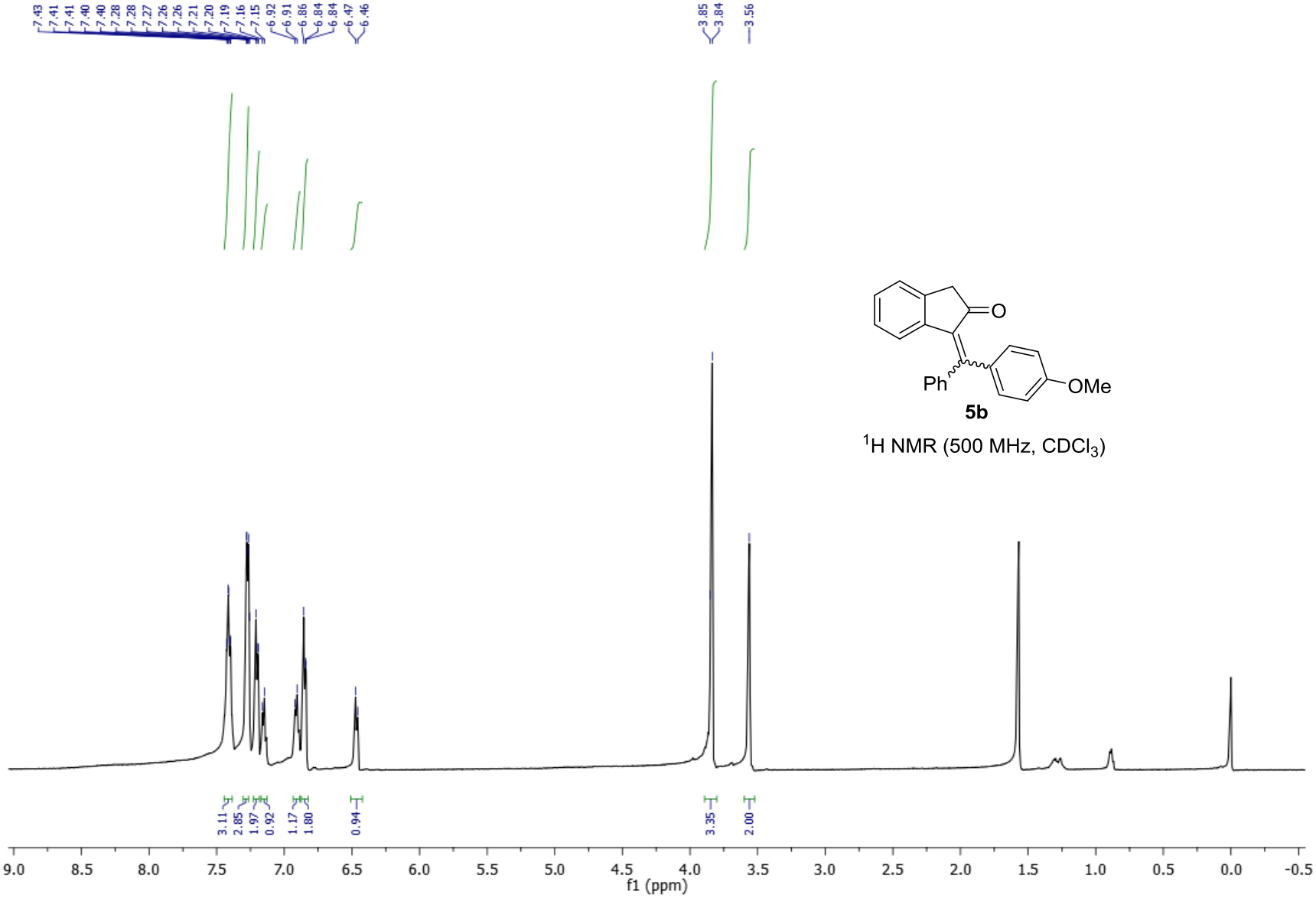
5a

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



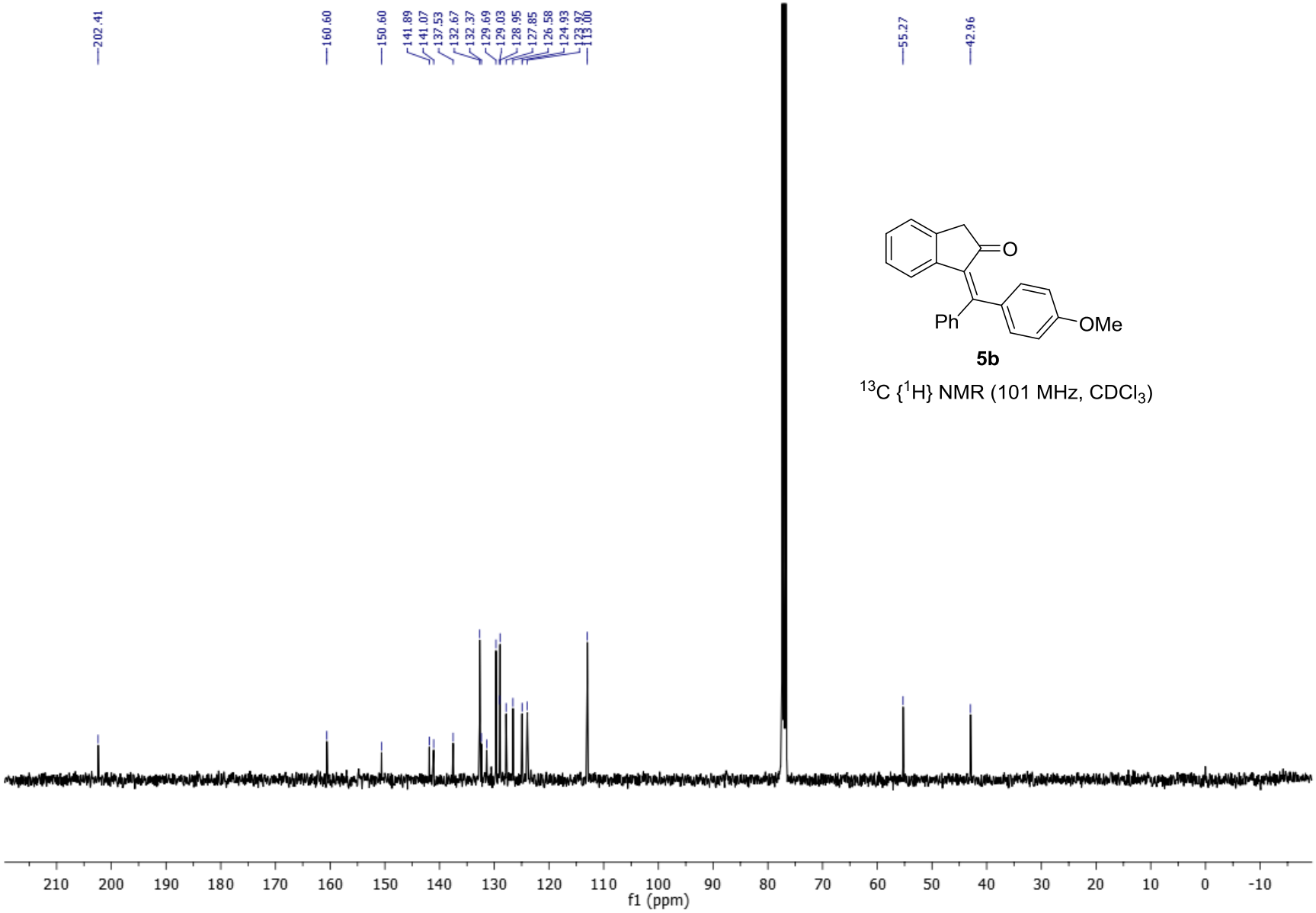
5a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



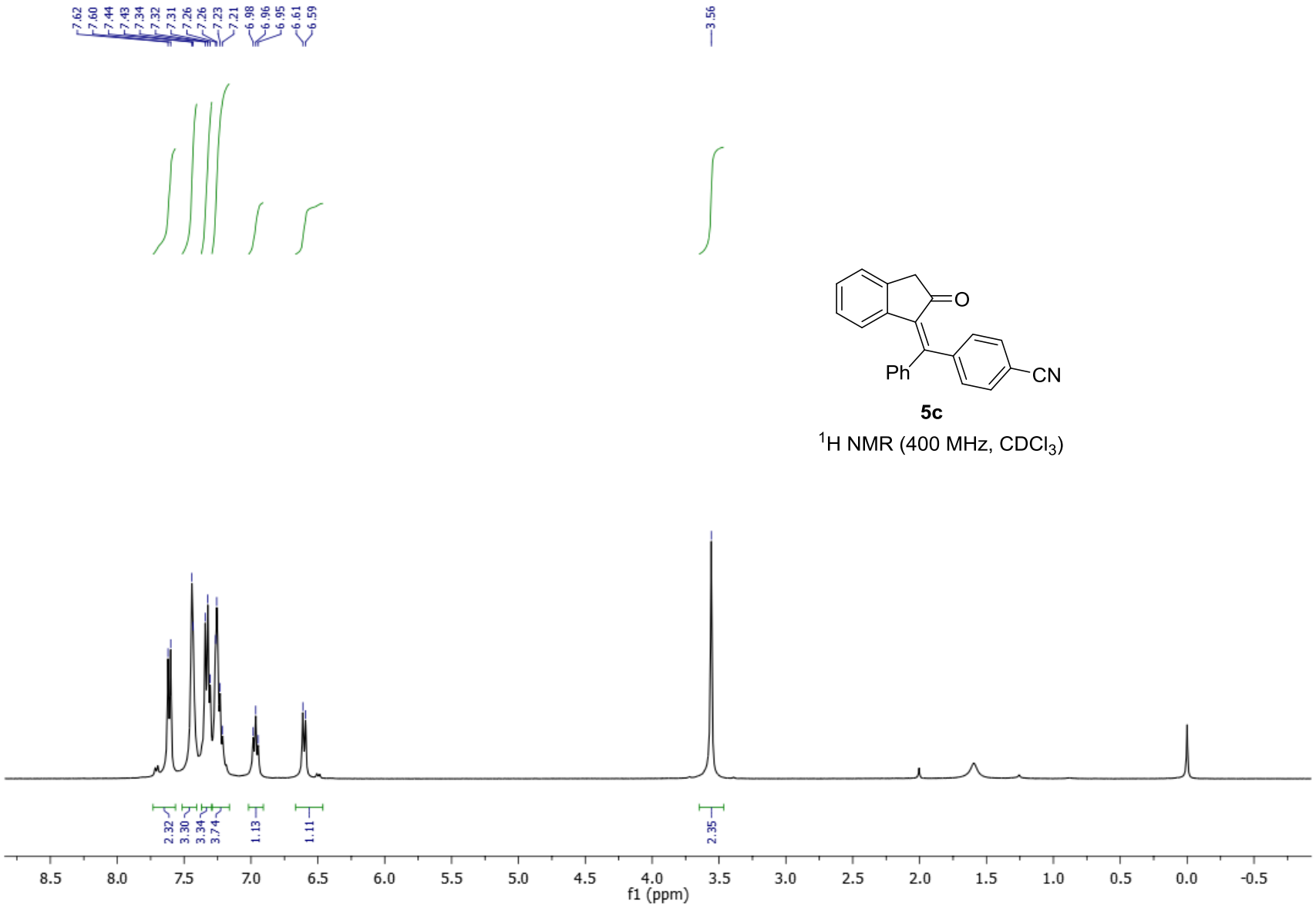
5b

^{1}H NMR (500 MHz, $CDCl_3$)



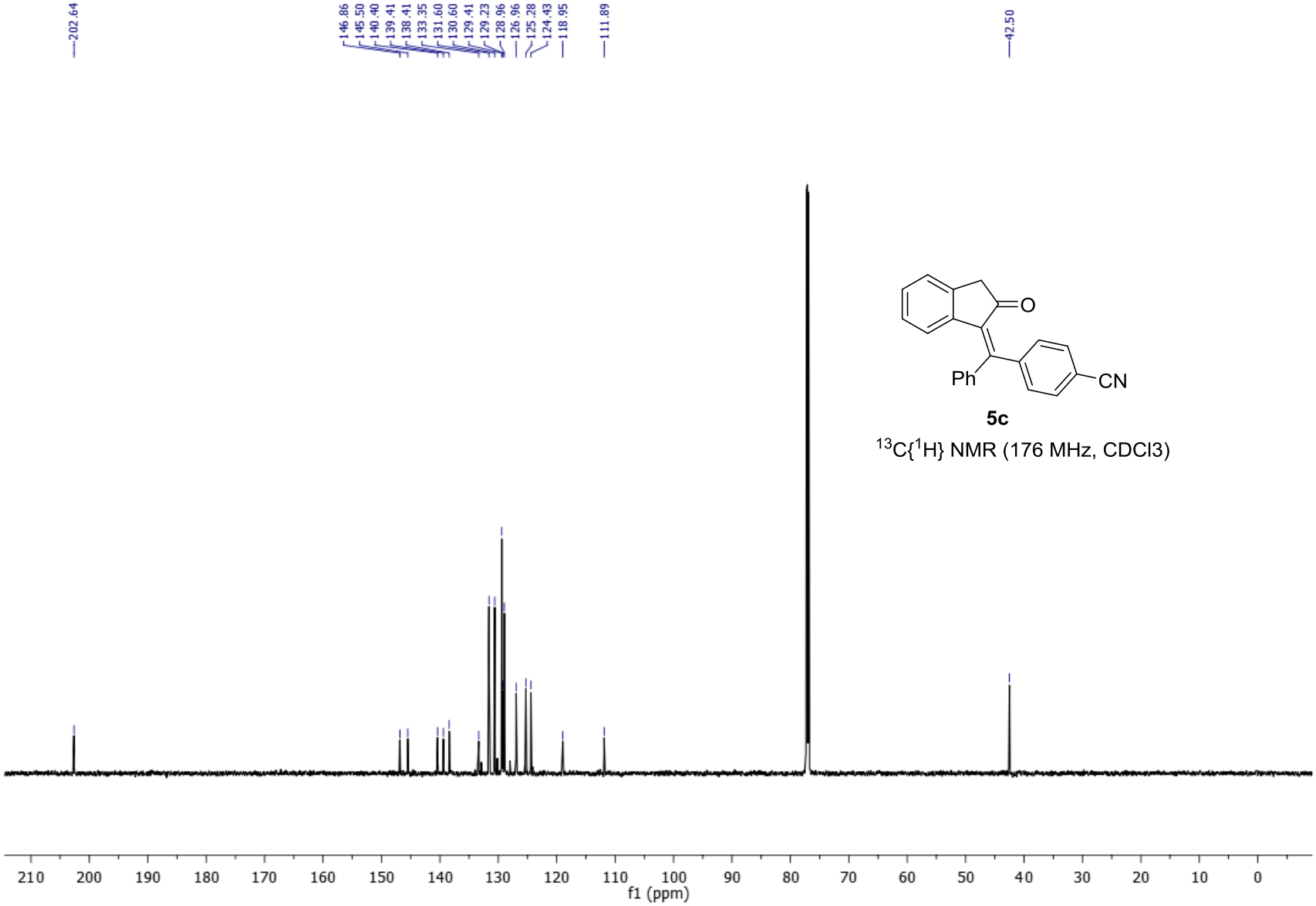
5b

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)



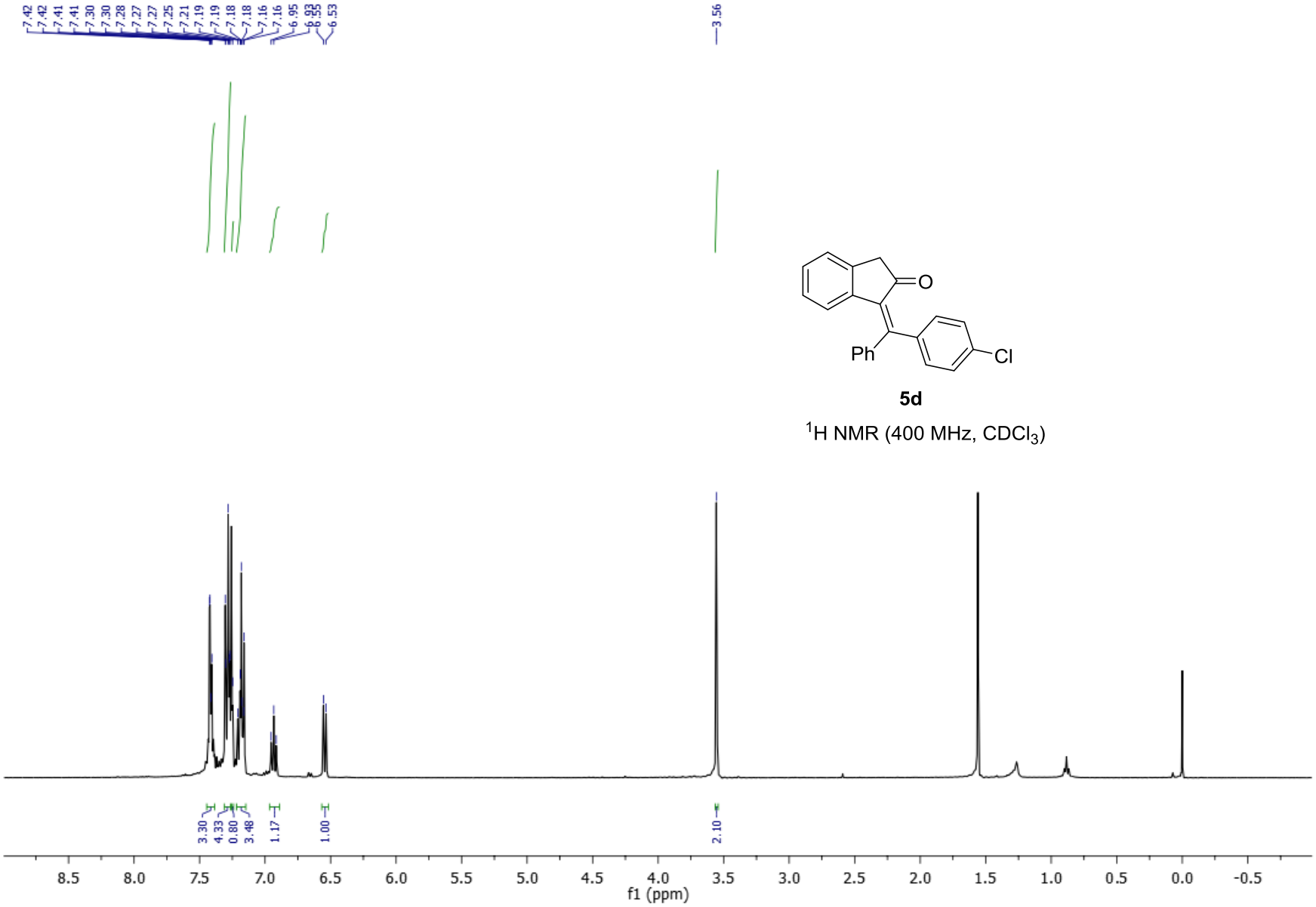
5c

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



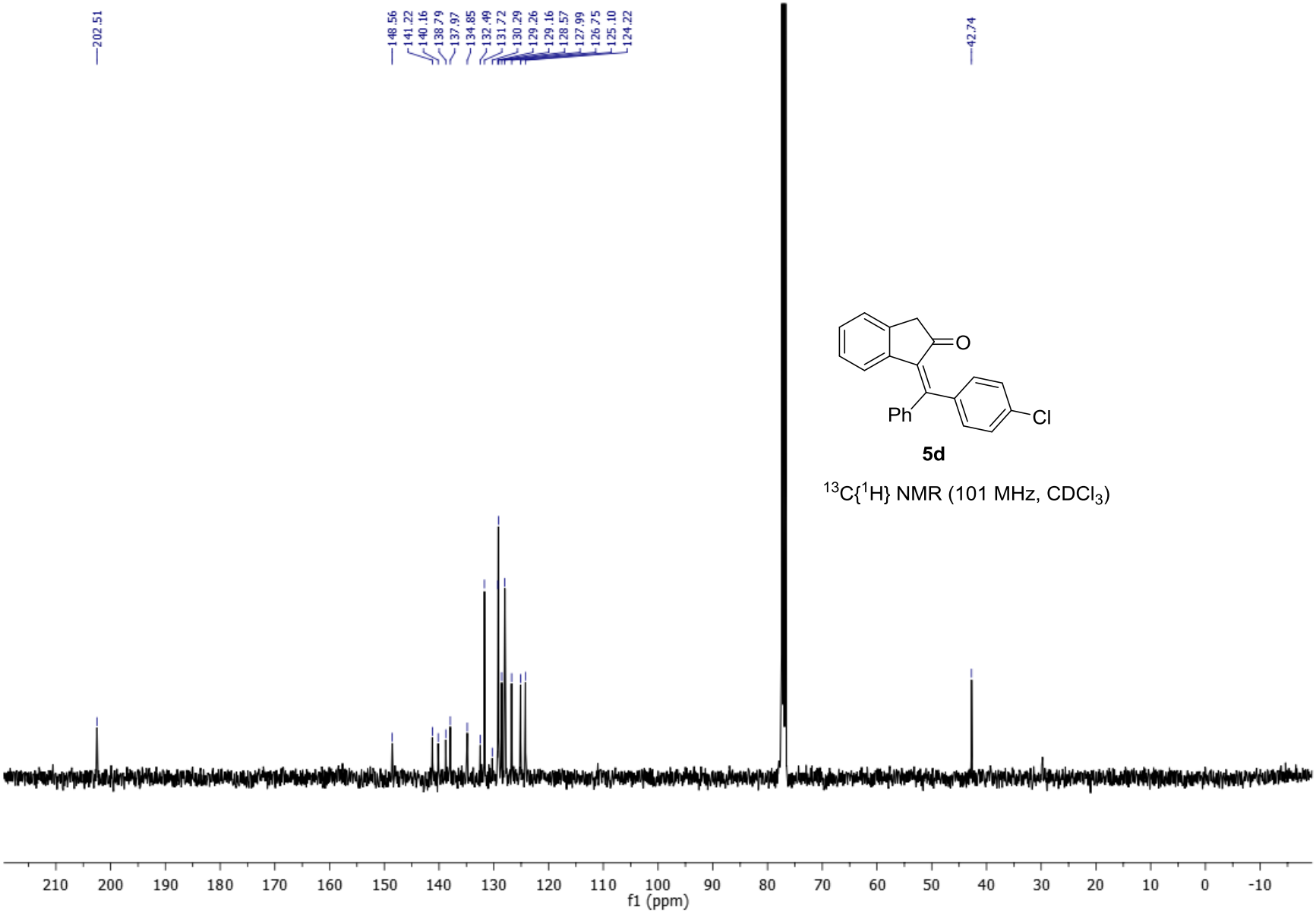
5c

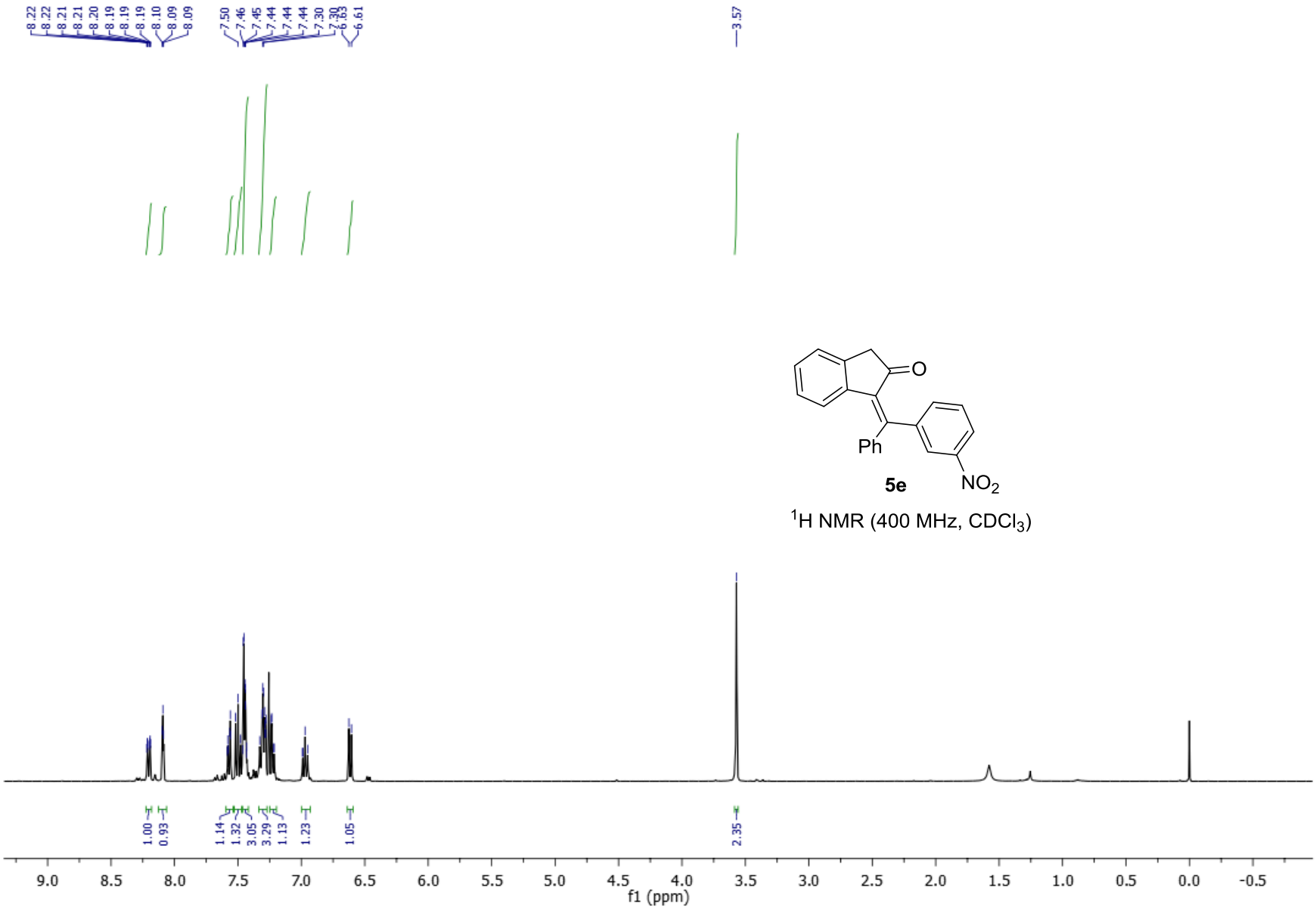
$^{13}C\{^{1}H\}$ NMR (176 MHz, CDCl3)



5d

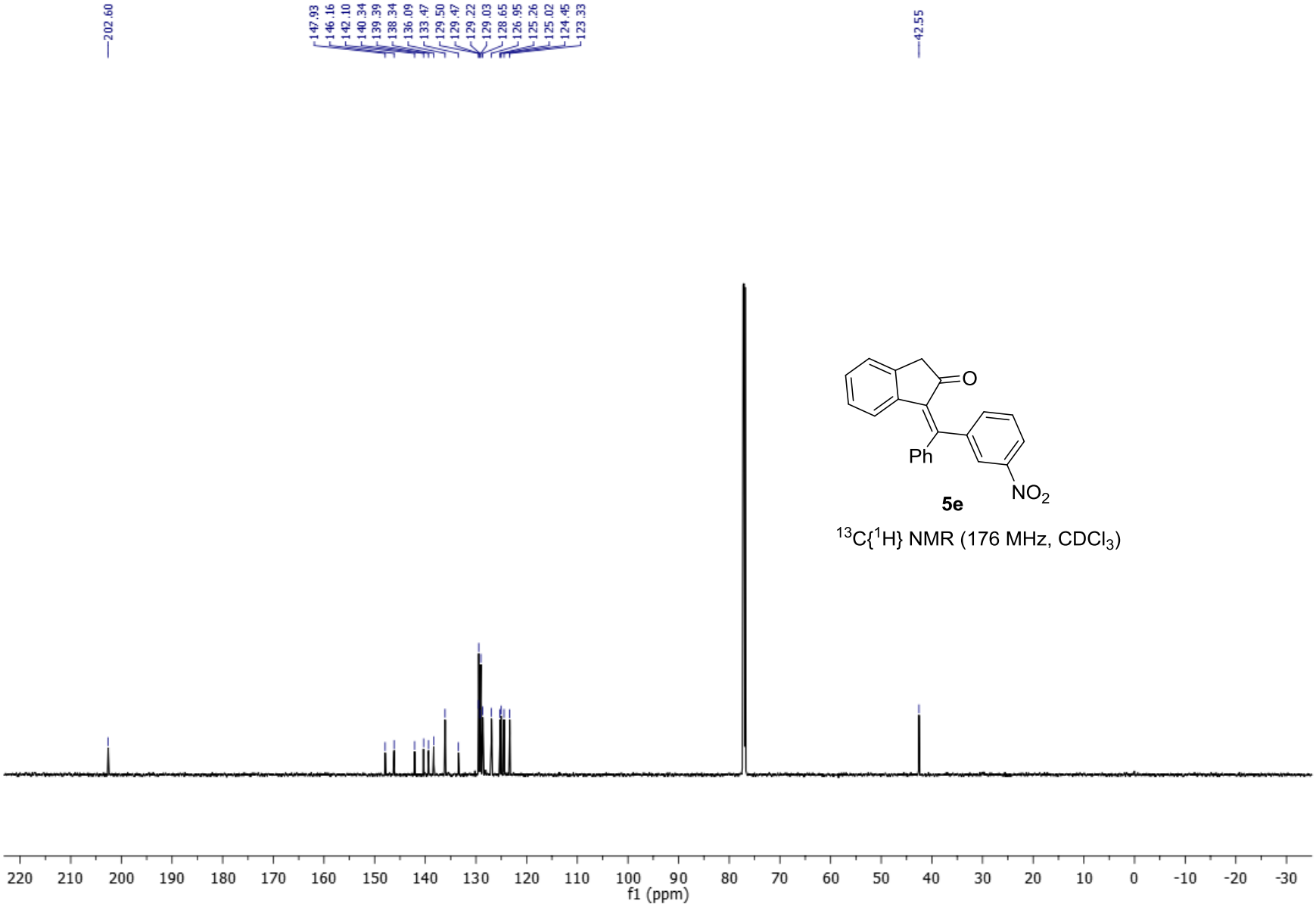
^{1}H NMR (400 MHz, $CDCl_3$)


202.51
148.56
141.22
140.16
138.79
137.97
134.85
132.49
131.72
130.29
129.26
129.16
128.57
127.99
126.75
125.10
124.22
42.74
O
Ph
Cl
5d
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



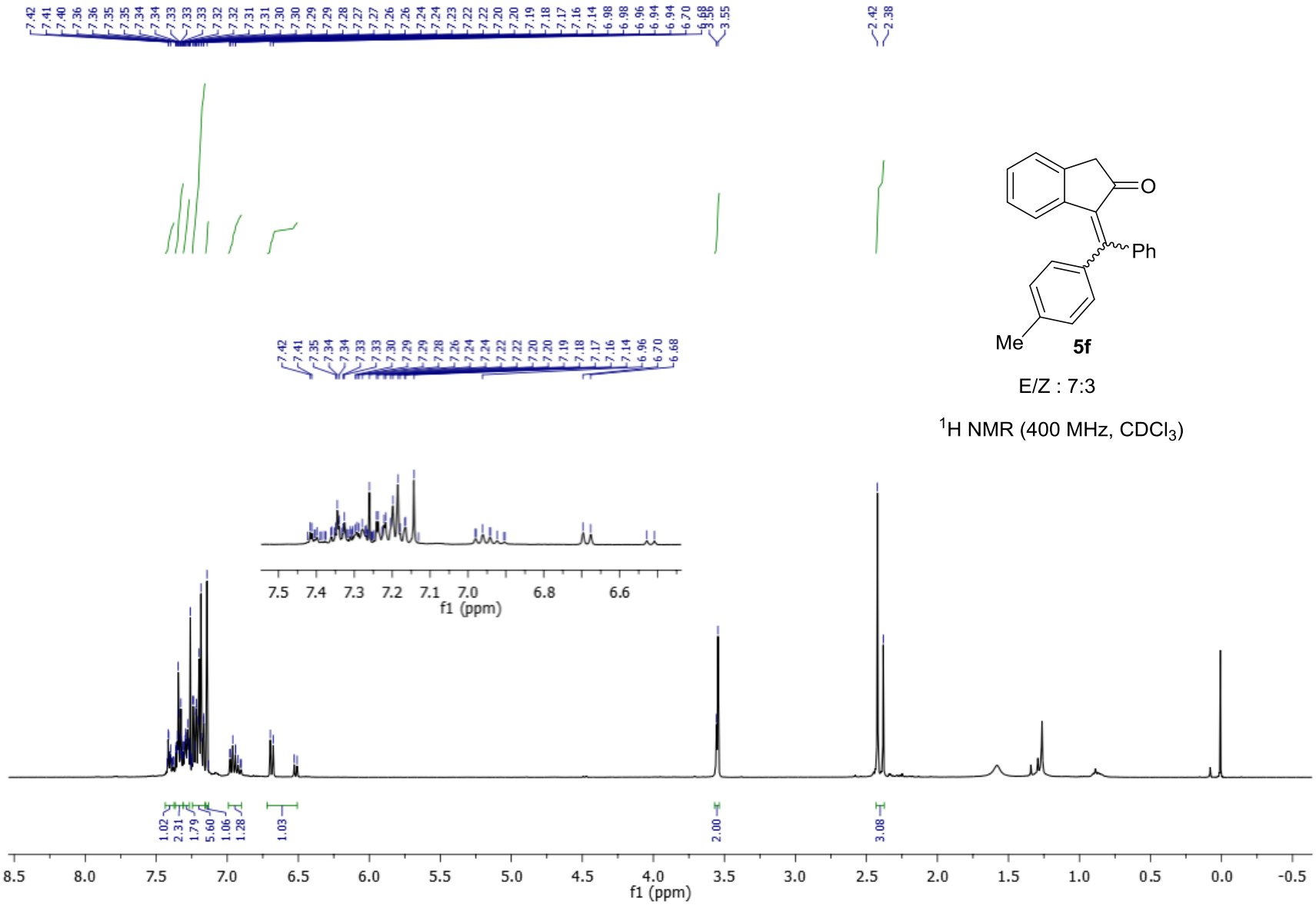
5e

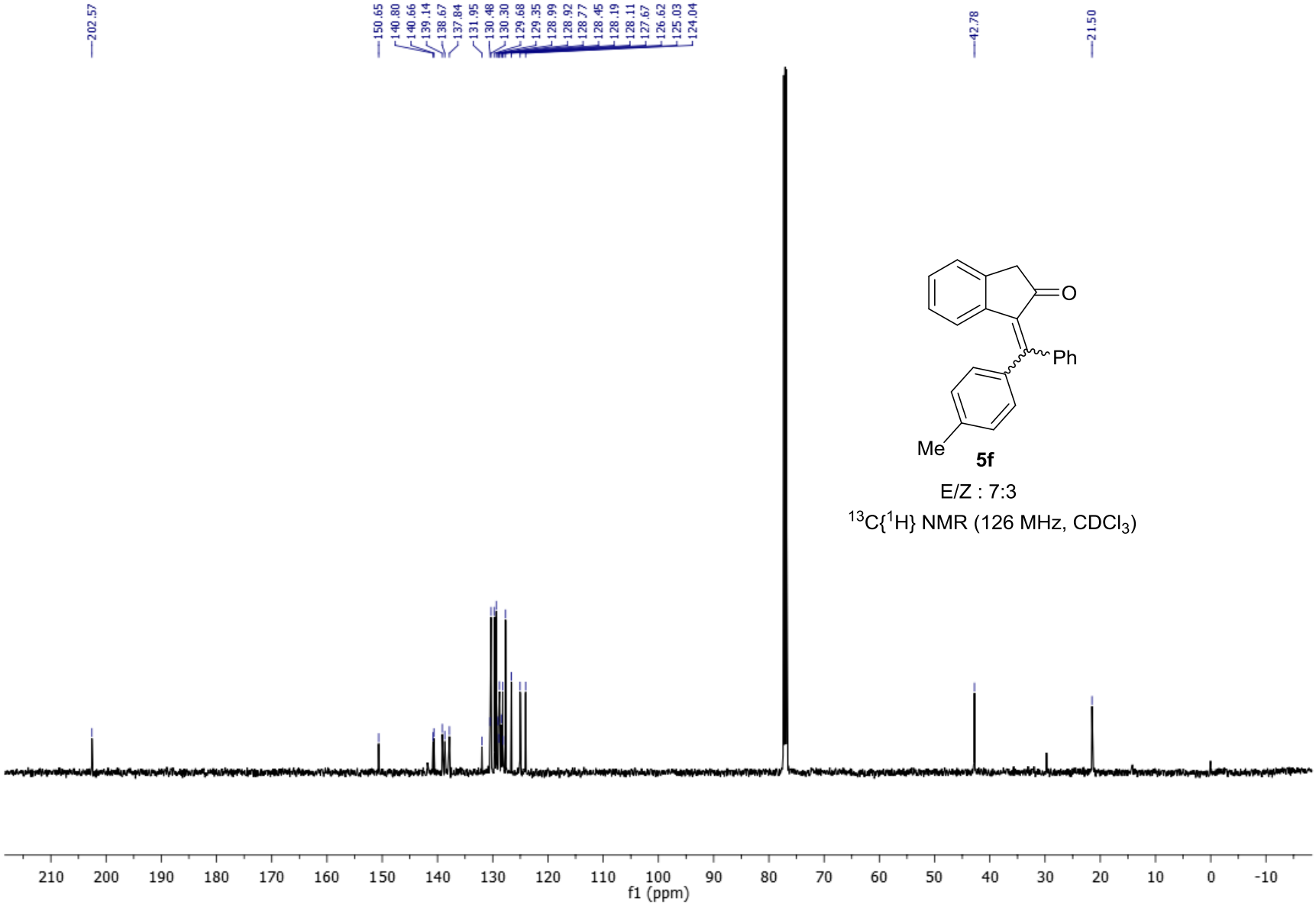
^{1}H NMR (400 MHz, $CDCl_3$)



5e

$^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$)

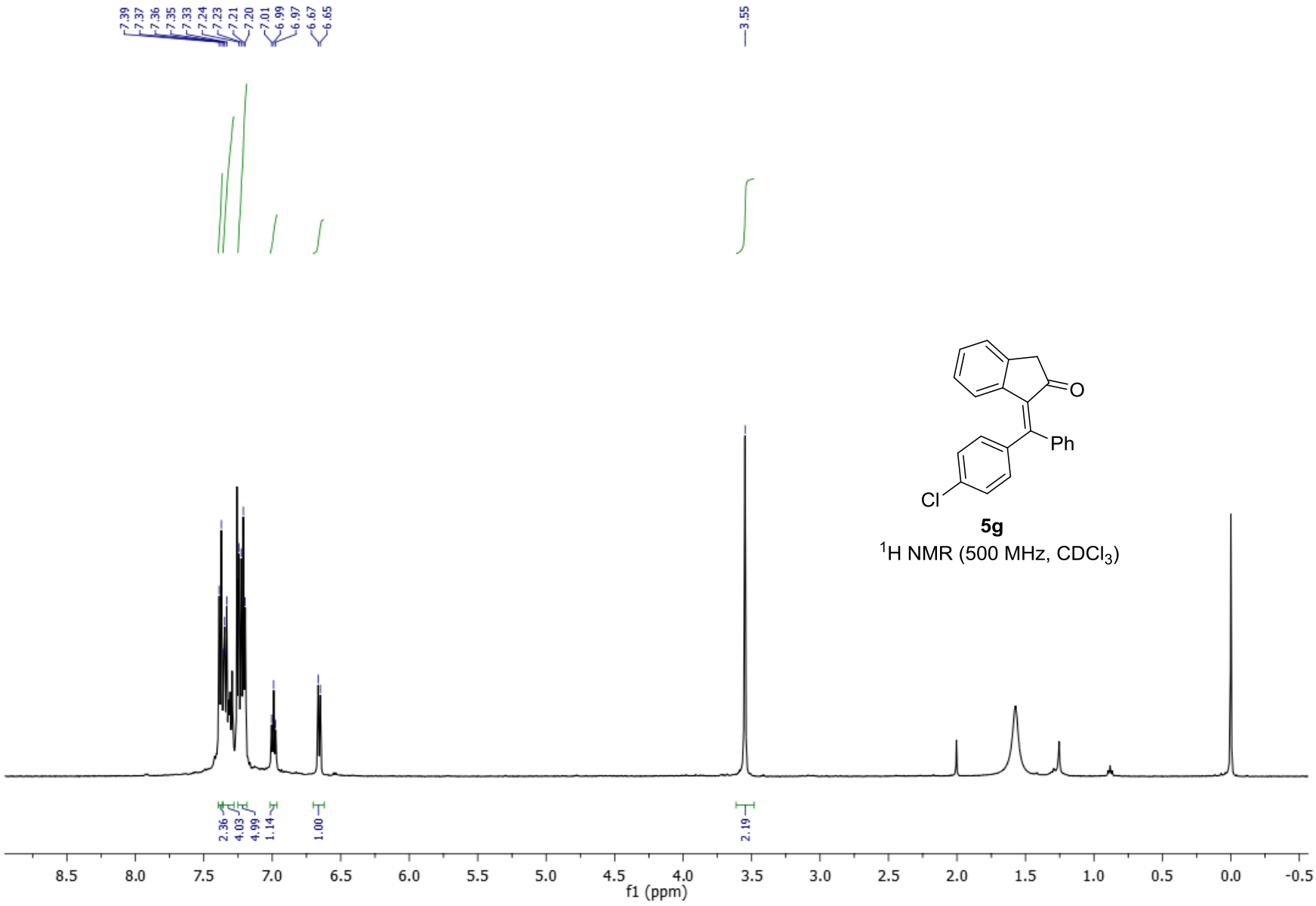

7.42 7.41 7.40 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.24 7.24 7.23 7.22 7.22 7.20 7.20 7.19 7.18 7.17 7.16 7.14 6.98 6.98 6.96 6.94 6.94 6.70 6.68 3.58 3.55
2.42 2.38
O
Ph
Me
5f
E/Z : 7:3
1H NMR (400 MHz, CDCl3)
7.42 7.41 7.35 7.34 7.34 7.33 7.30 7.29 7.29 7.28 7.26 7.24 7.24 7.22 7.22 7.20 7.20 7.19 7.18 7.17 7.16 7.14 6.96 6.70 6.68
7.5 7.4 7.3 7.2 7.1 7.0 6.8 6.6
f1 (ppm)
1.02 2.31 1.79 5.60 1.06 1.28 1.03 2.00 3.08
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 -0.5
f1 (ppm)



5f

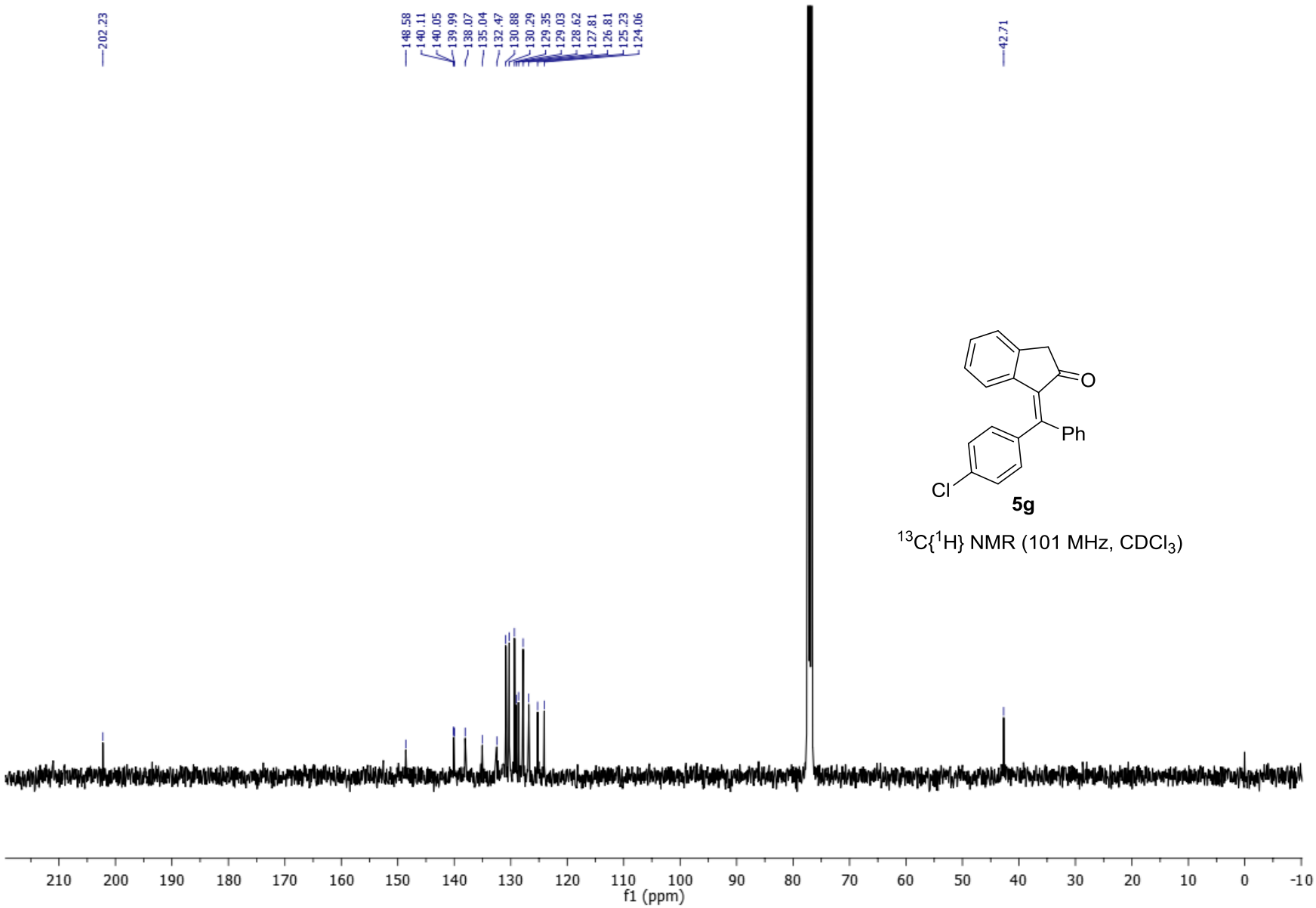
E/Z : 7:3

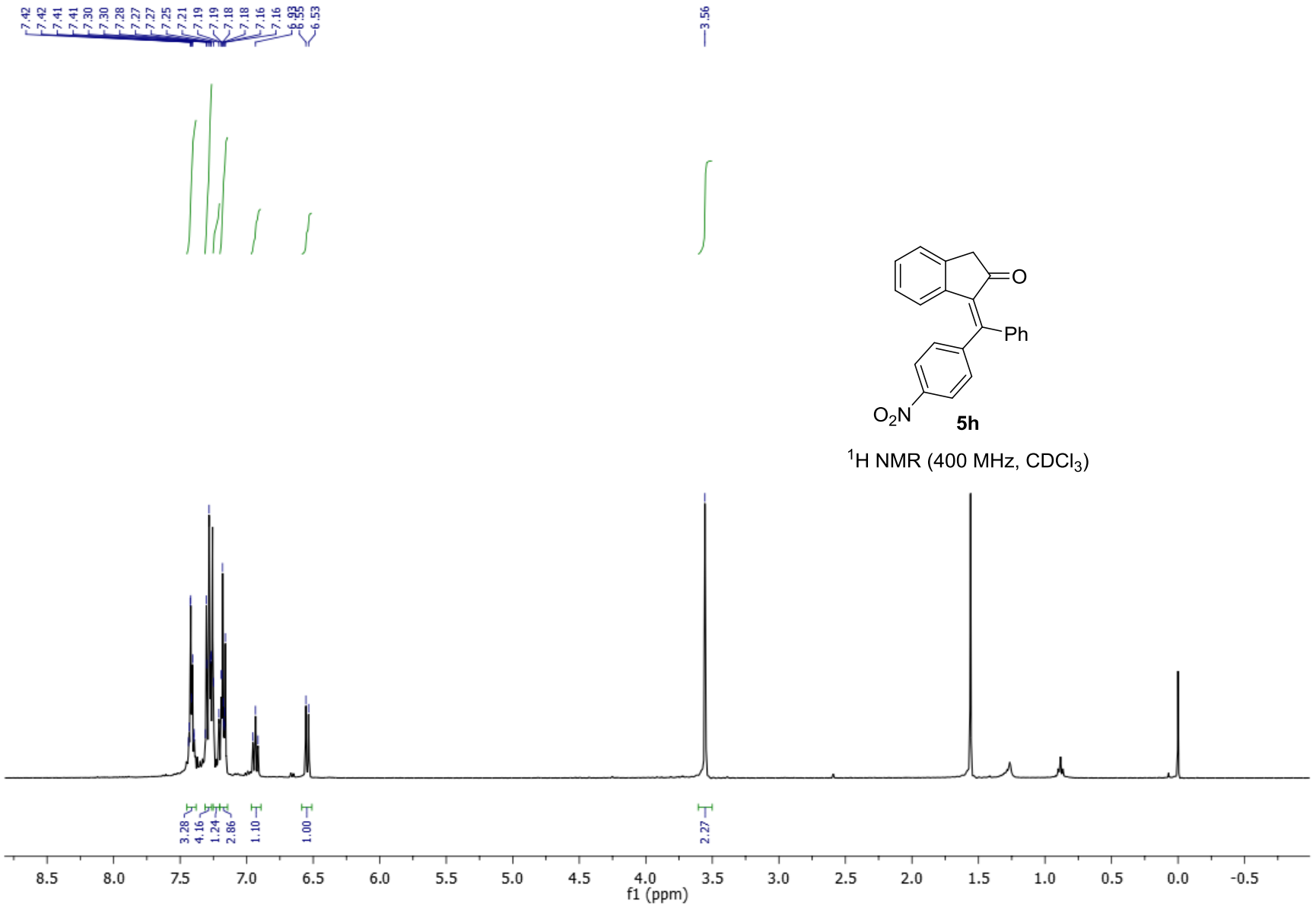
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

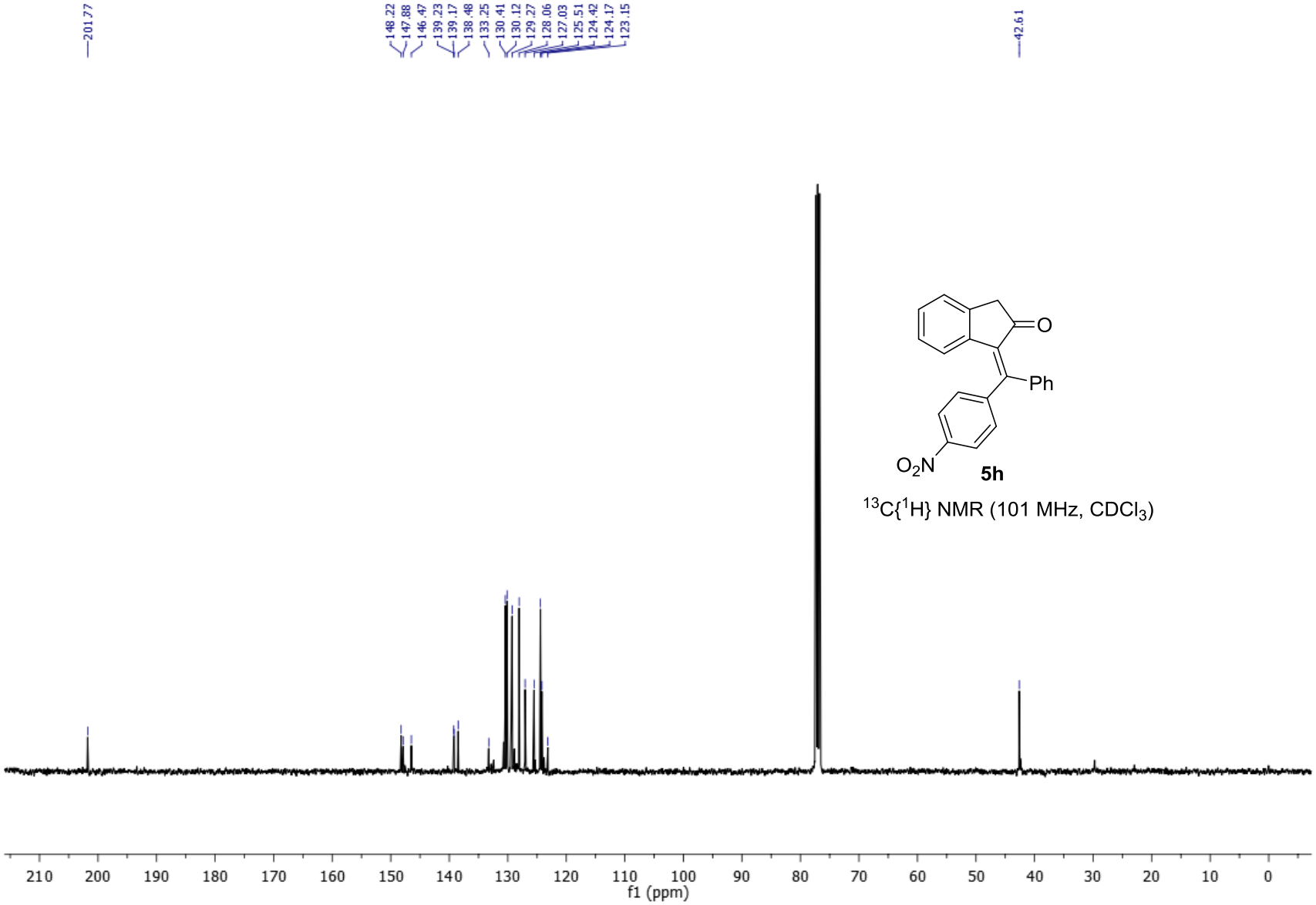


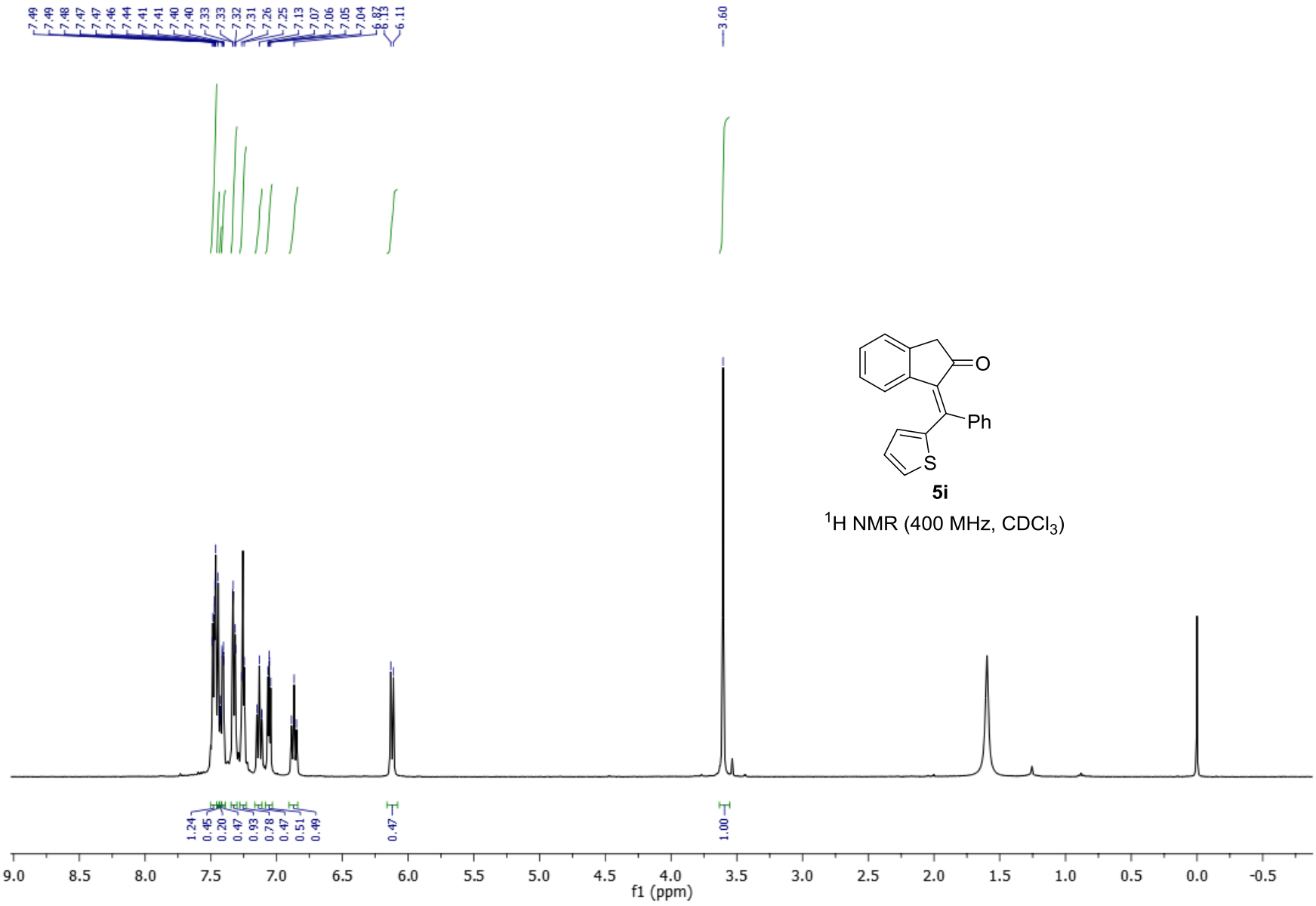
5g

^{1}H NMR (500 MHz, $CDCl_3$)


202.23
148.58
140.11
140.05
139.99
138.07
135.04
132.47
130.88
130.29
129.35
129.03
128.62
127.81
126.81
125.23
124.06
42.71
O
Ph
Cl
5g
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

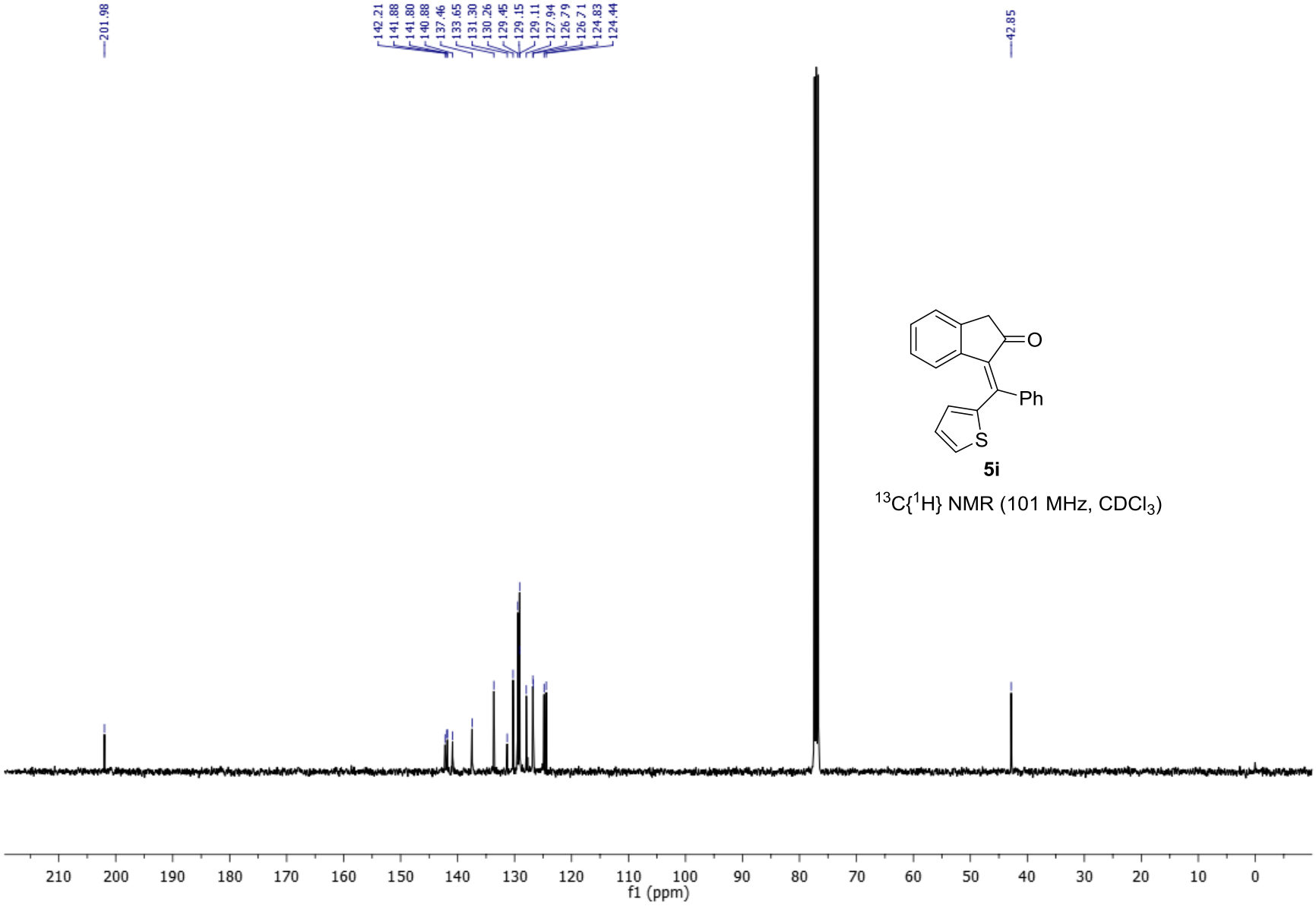

7.42
7.42
7.41
7.41
7.30
7.30
7.28
7.27
7.27
7.25
7.21
7.19
7.19
7.18
7.18
7.16
7.16
6.53
3.56
O
Ph
O2N
5h
1H NMR (400 MHz, CDCl3)
3.28
4.16
1.24
2.86
1.10
1.00
2.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


201.77
148.22
147.88
146.47
139.23
139.17
138.48
133.25
130.41
130.12
129.27
128.06
127.03
125.51
124.42
124.17
123.15
42.61
O
Ph
O2N
5h
13C{1H} NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



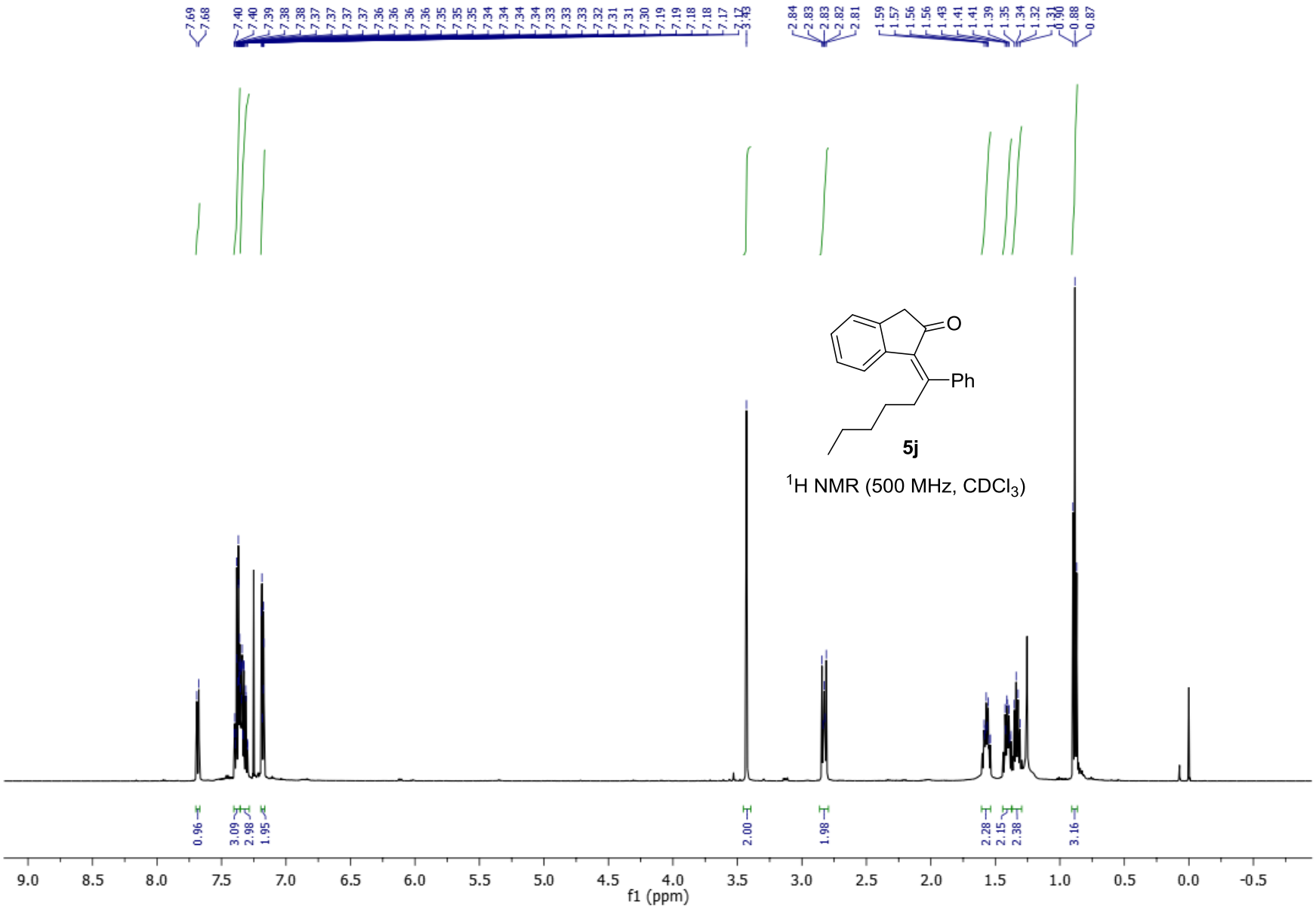
5i

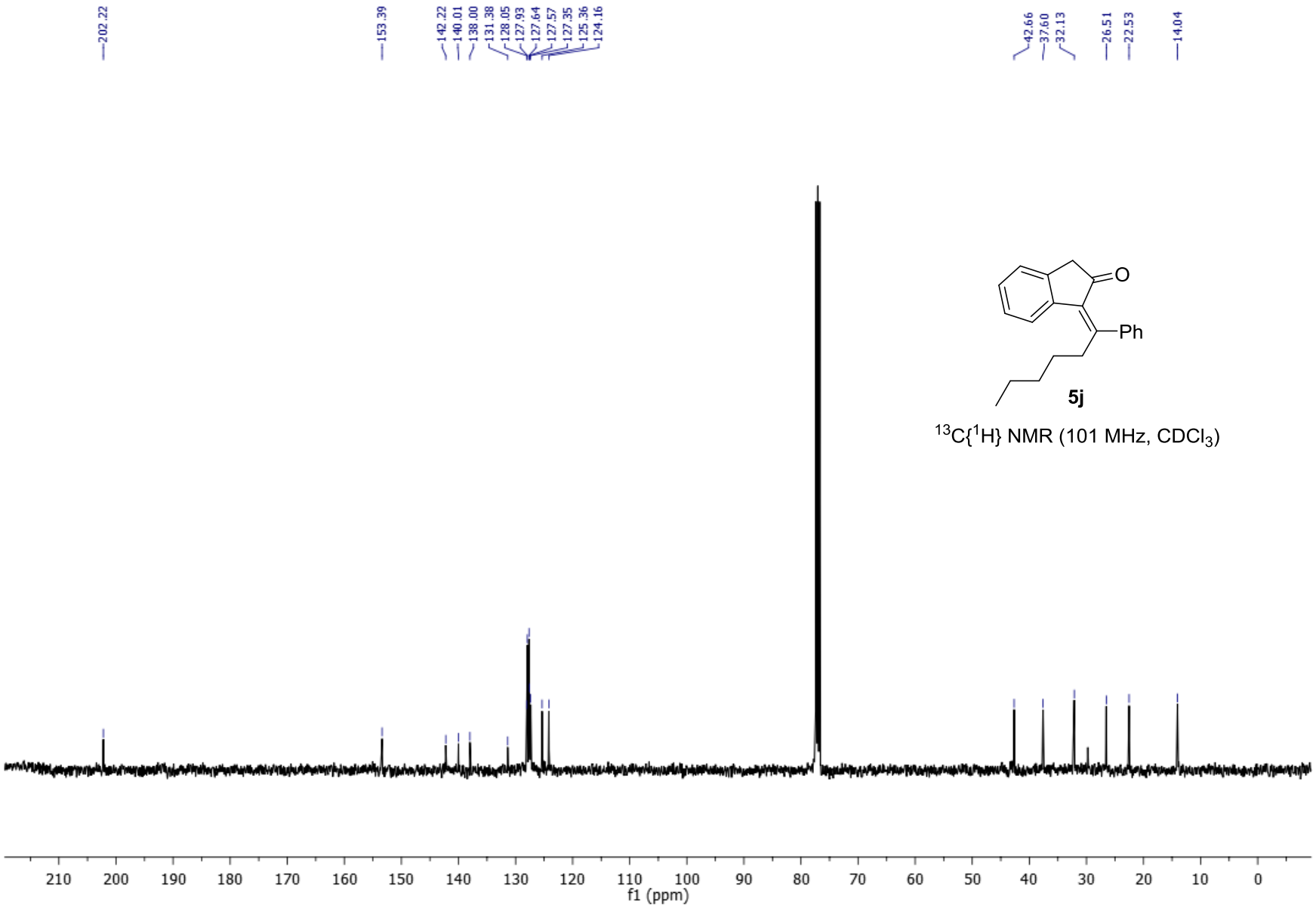
^{1}H NMR (400 MHz, $CDCl_3$)



5i

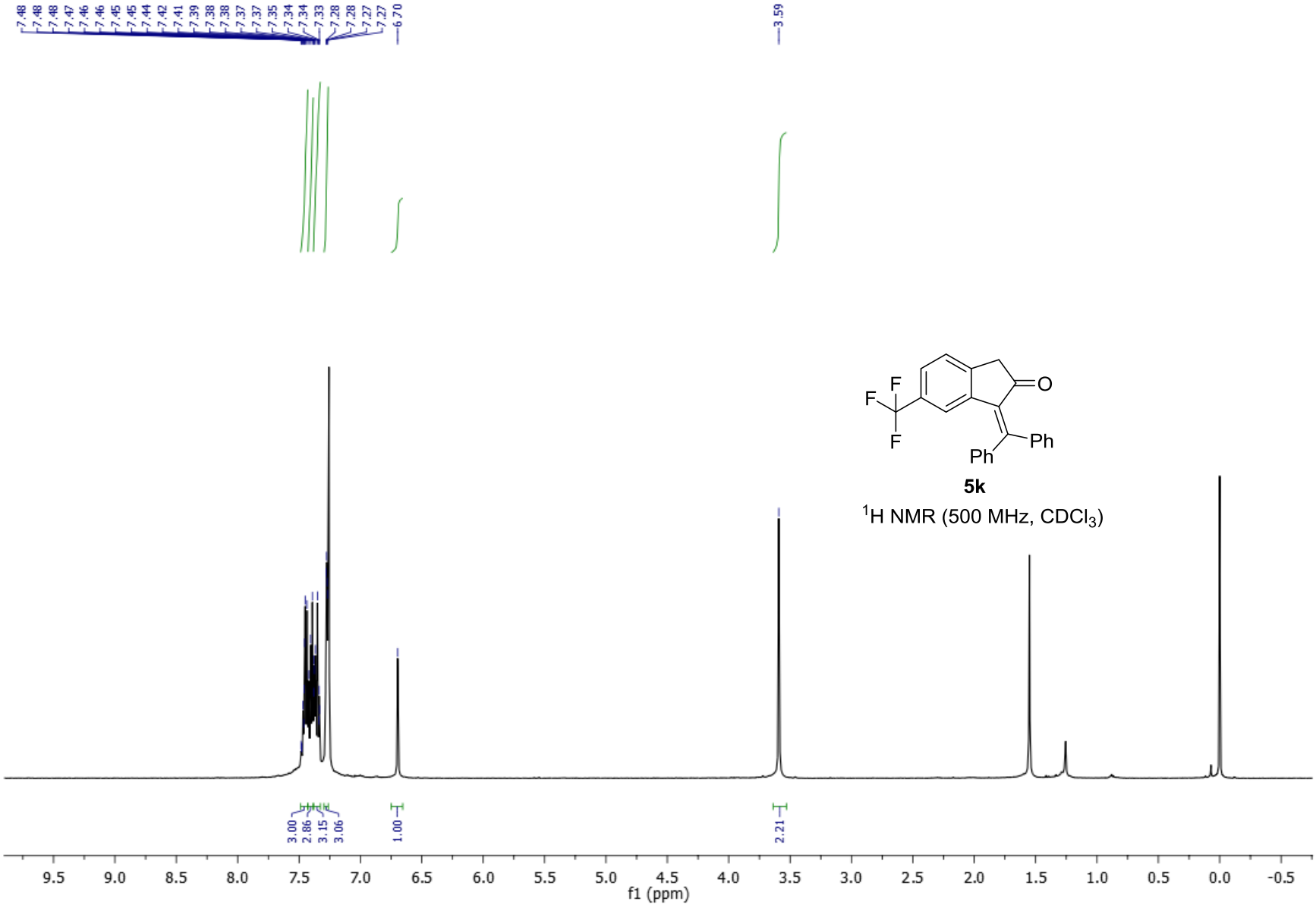
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)


O
Ph
5j
^{1}H NMR (500 MHz, $CDCl_3$)
f1 (ppm)



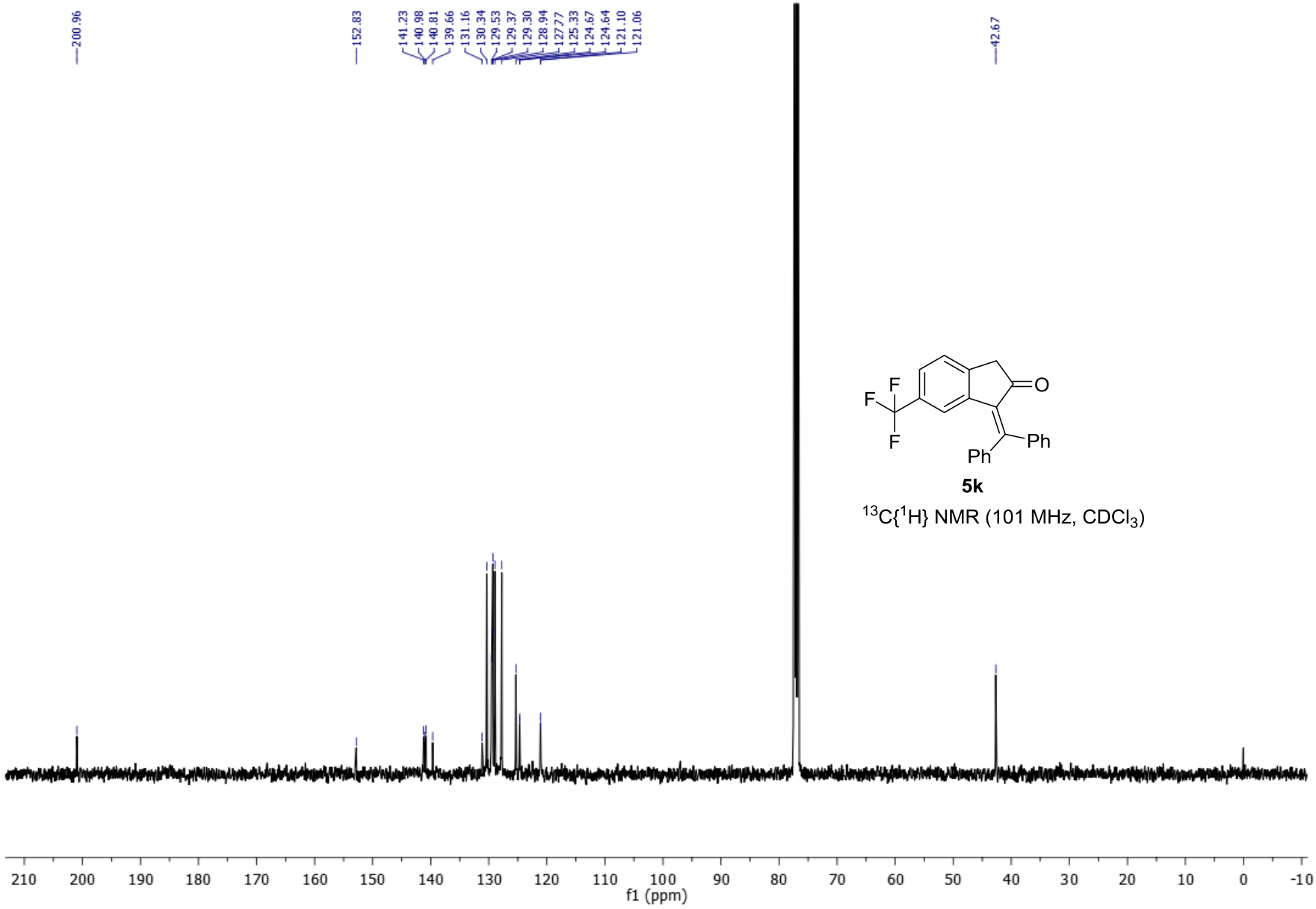
5j

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



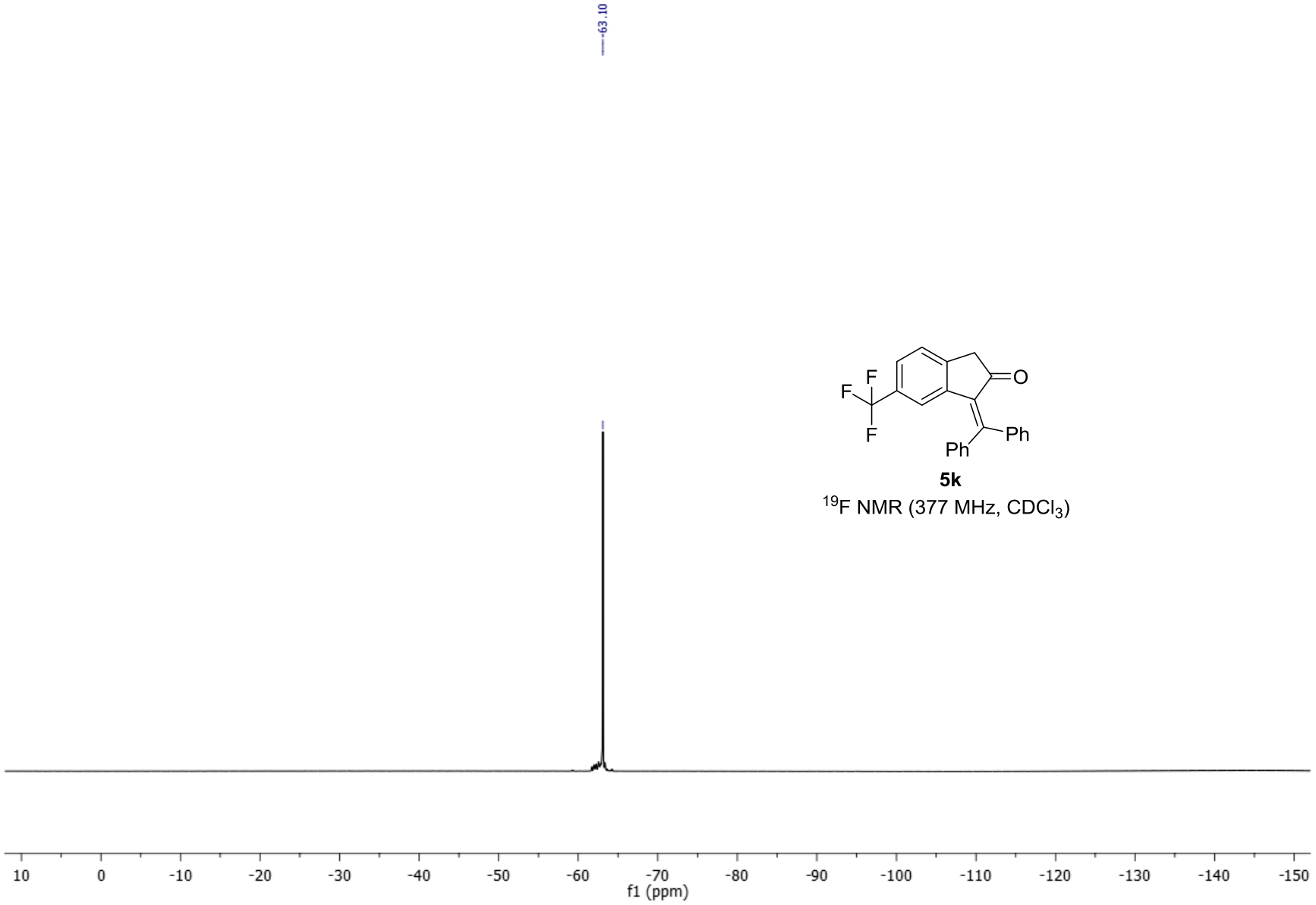
5k

^{1}H NMR (500 MHz, $CDCl_3$)



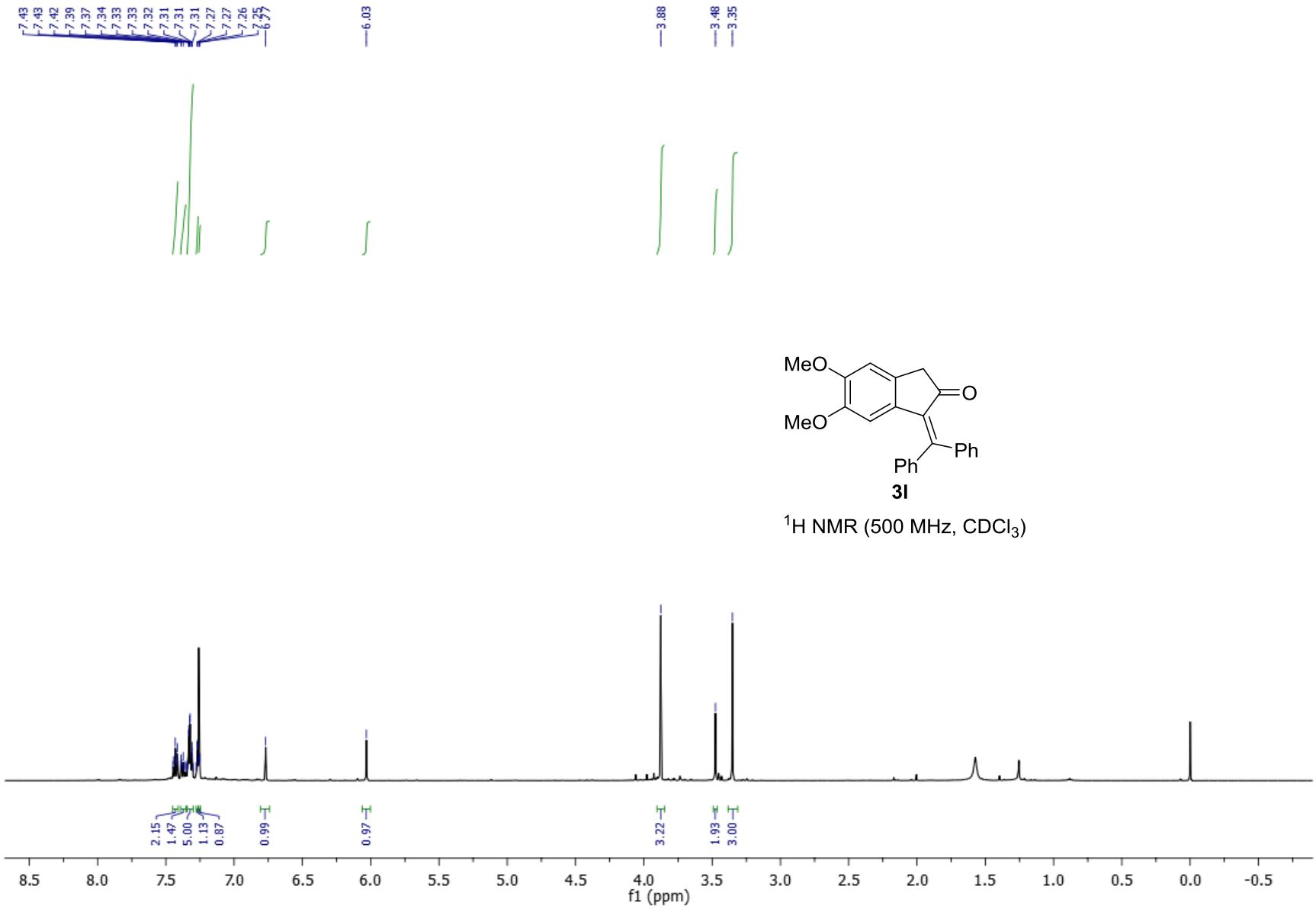
5k

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



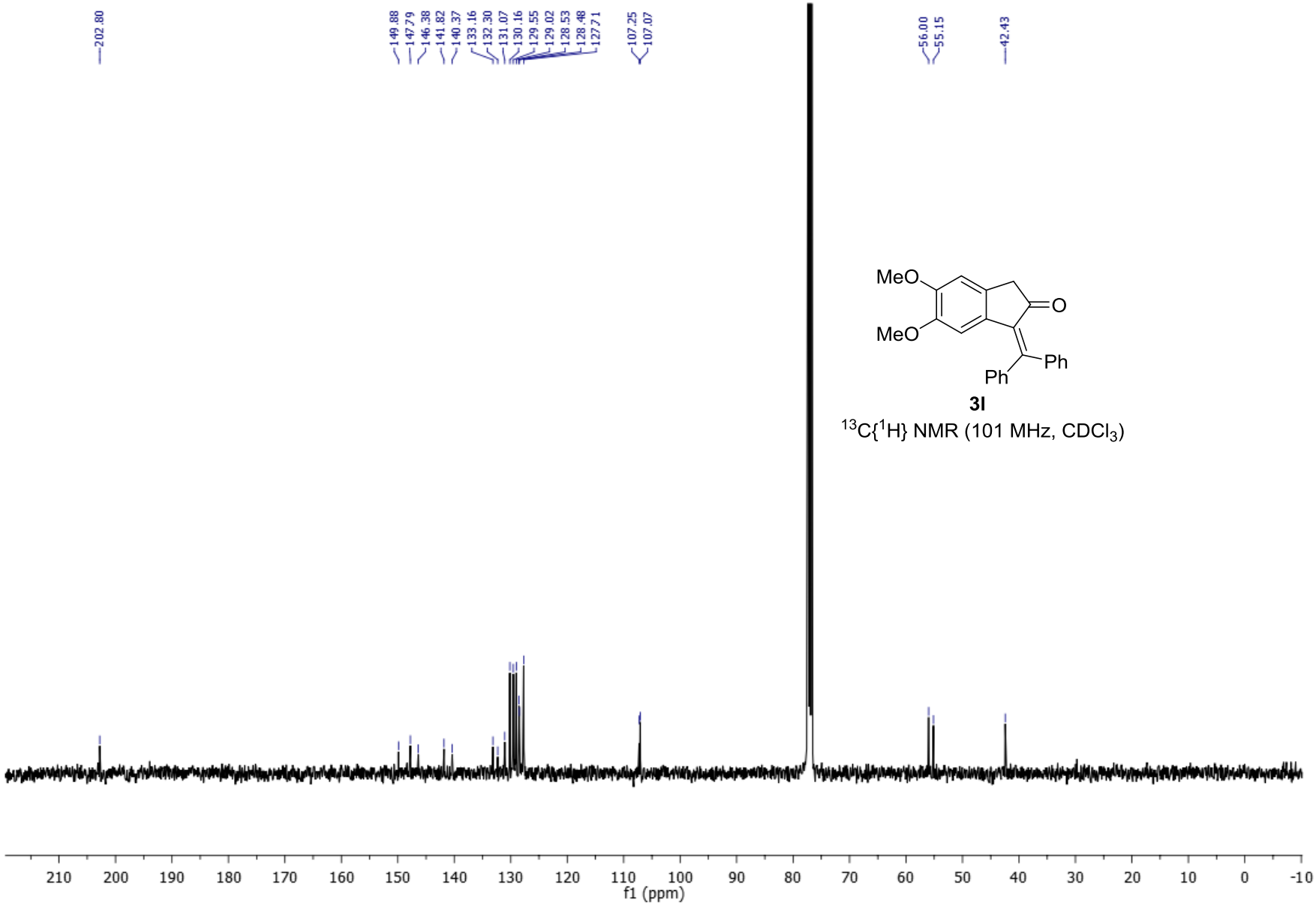
5k

^{19}F NMR (377 MHz, $CDCl_3$)



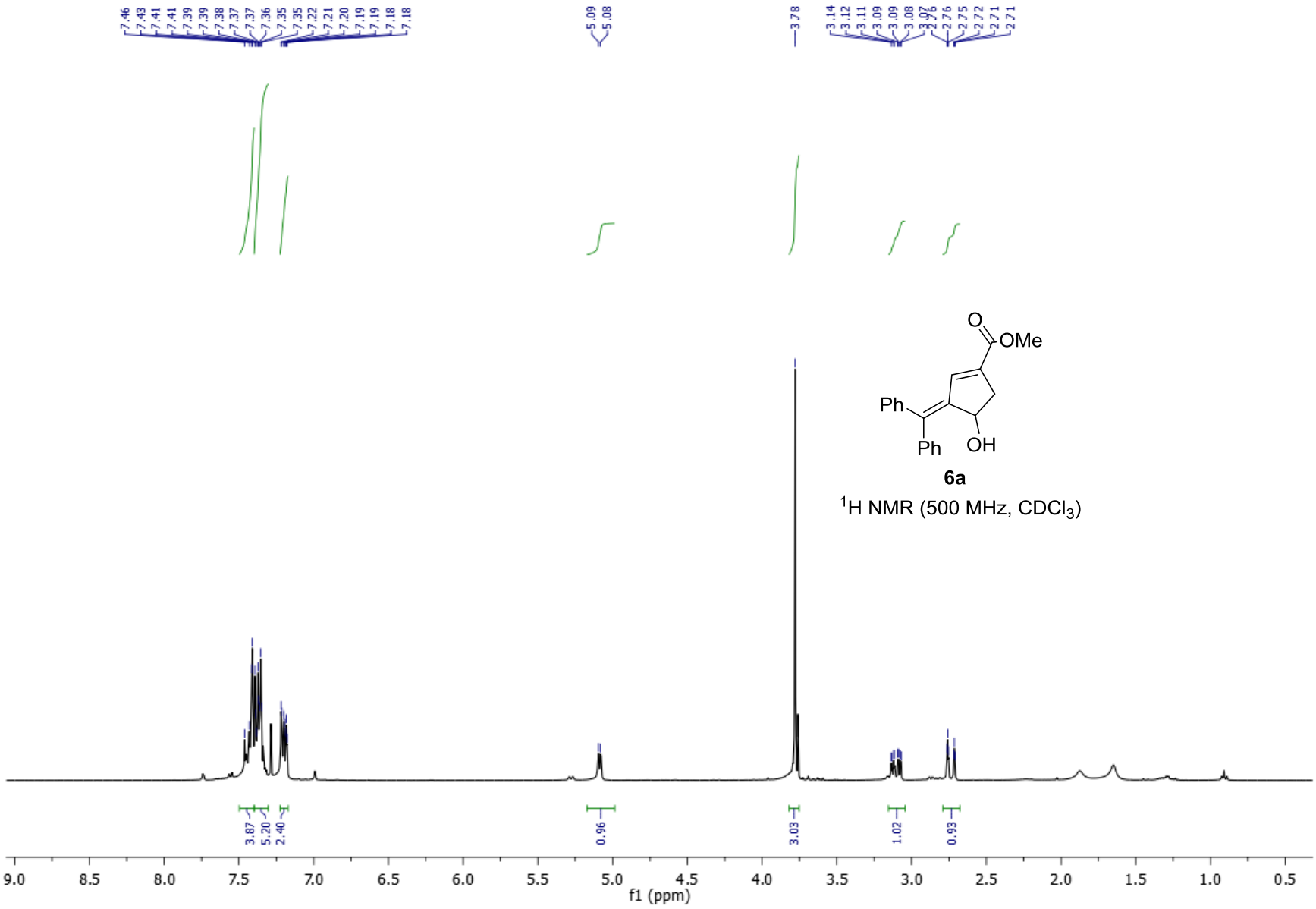
3l

^{1}H NMR (500 MHz, $CDCl_3$)



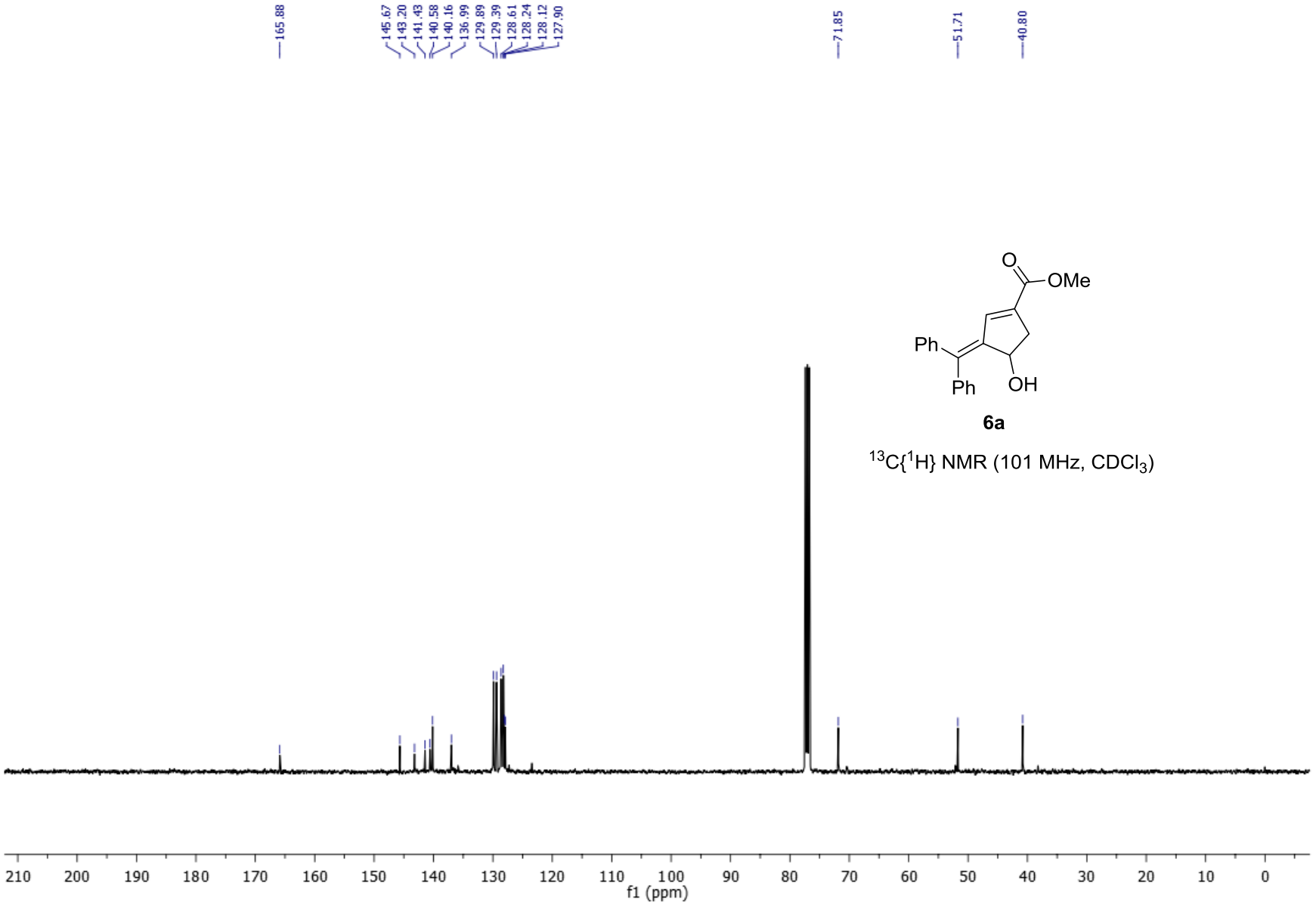
3l

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



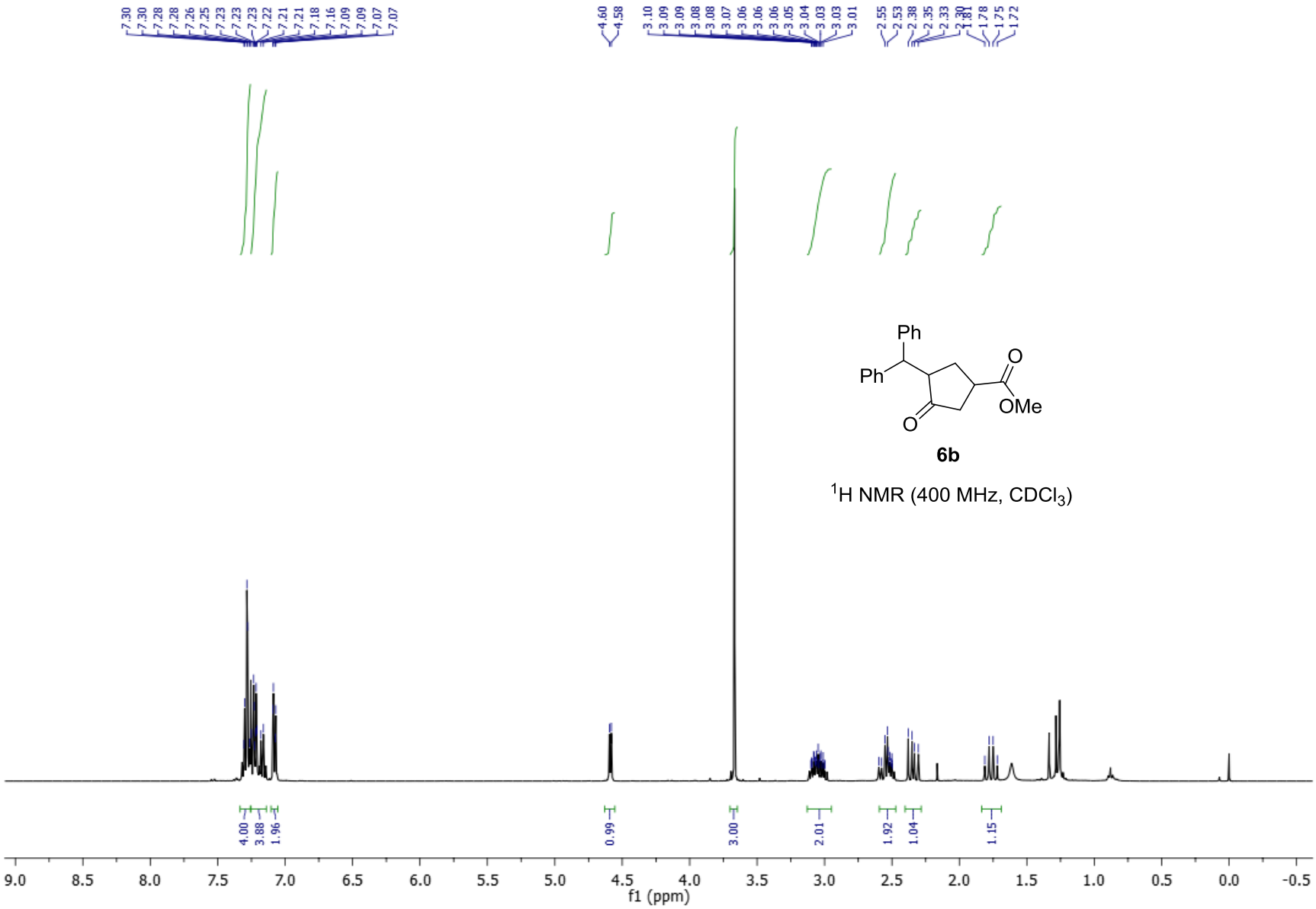
6a

^{1}H NMR (500 MHz, $CDCl_3$)



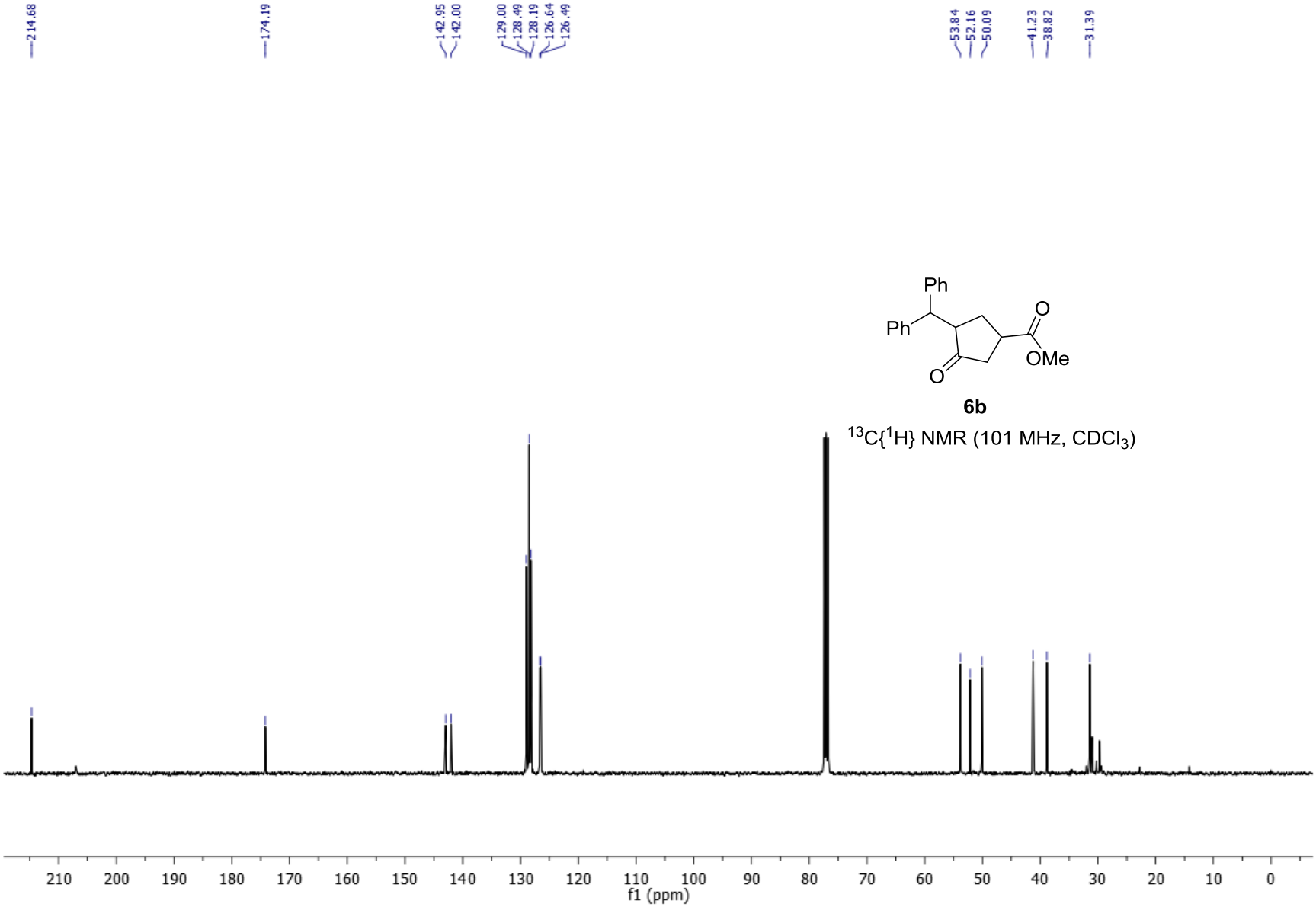
6a

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



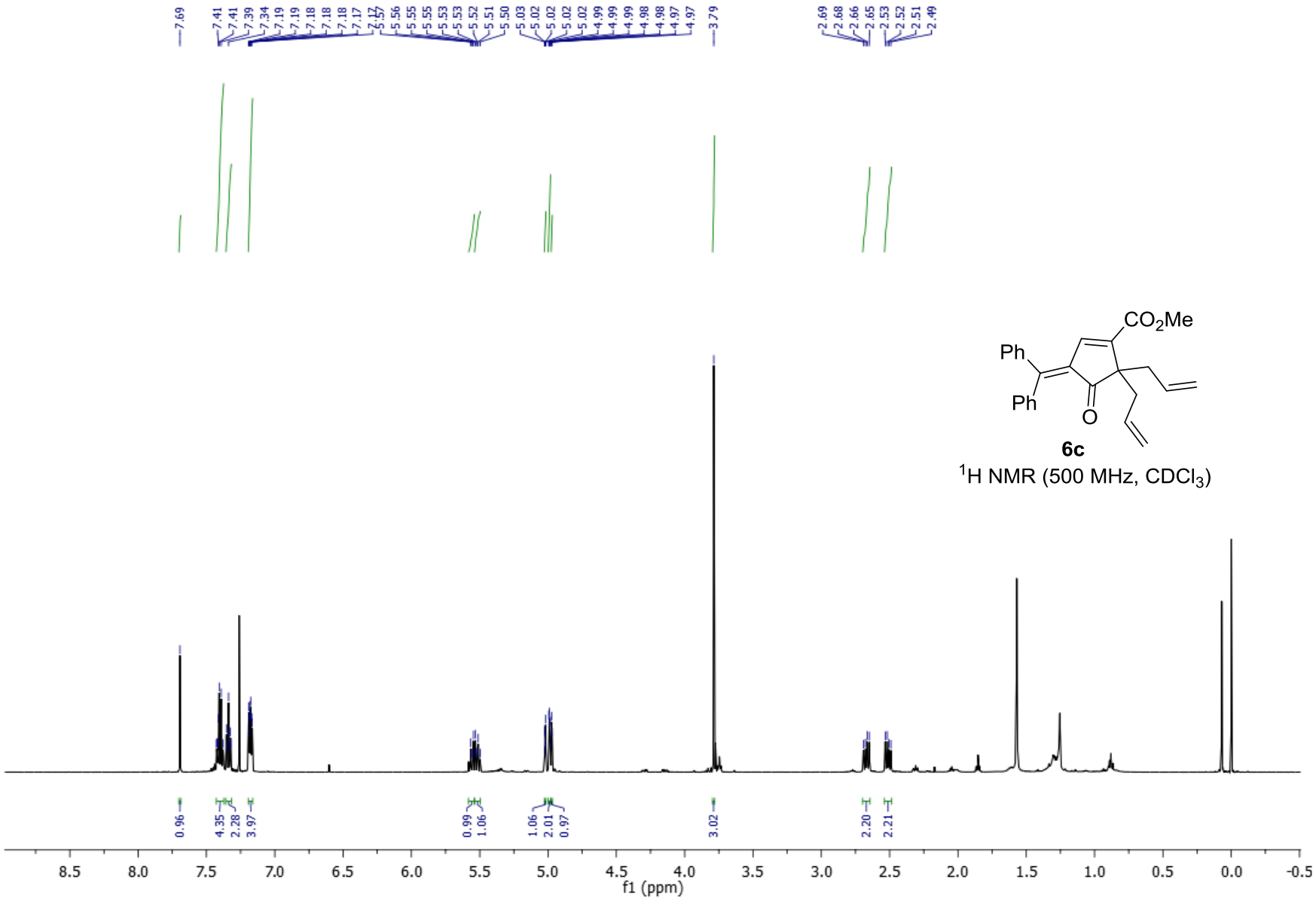
6b

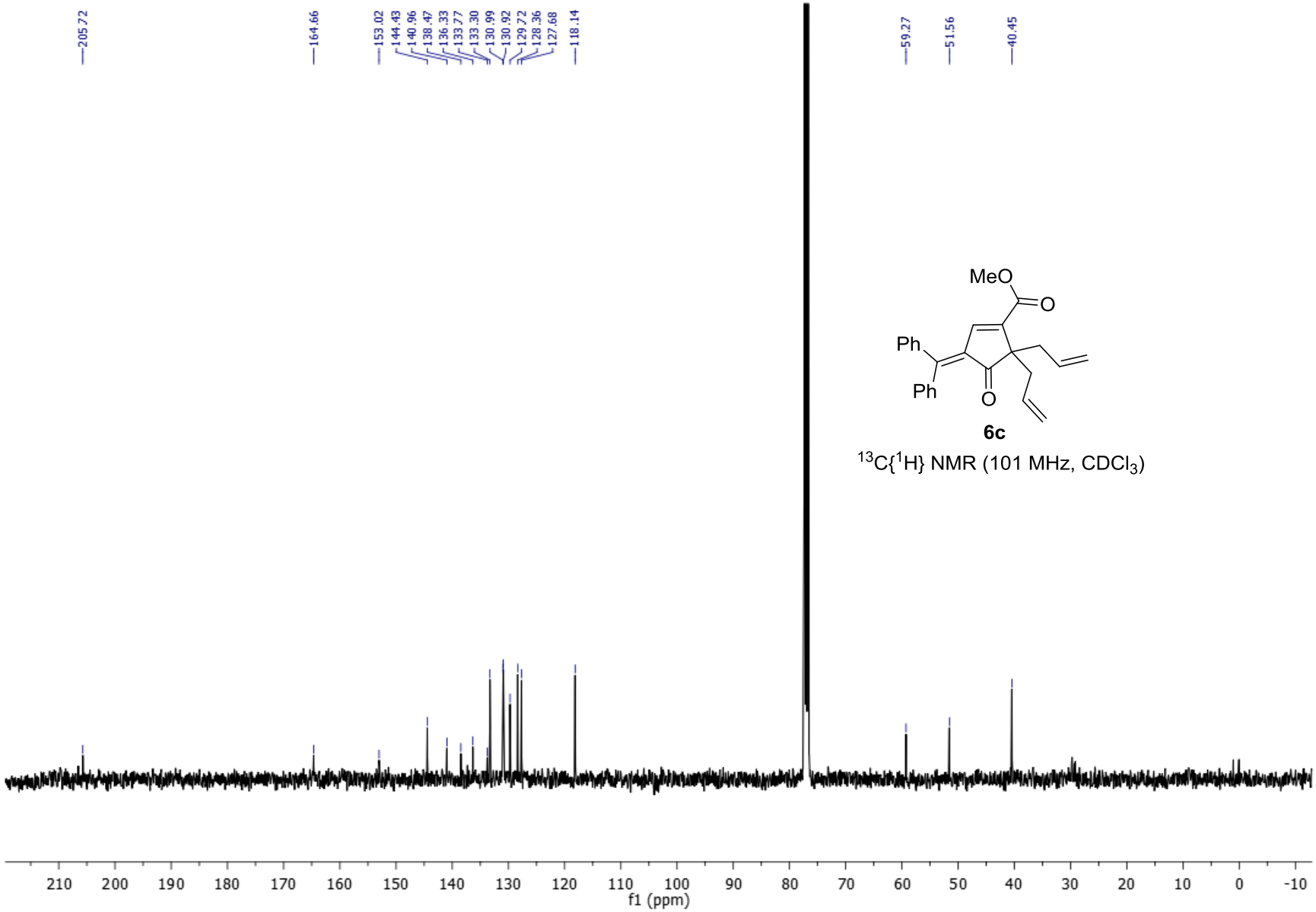
^{1}H NMR (400 MHz, $CDCl_3$)



6b

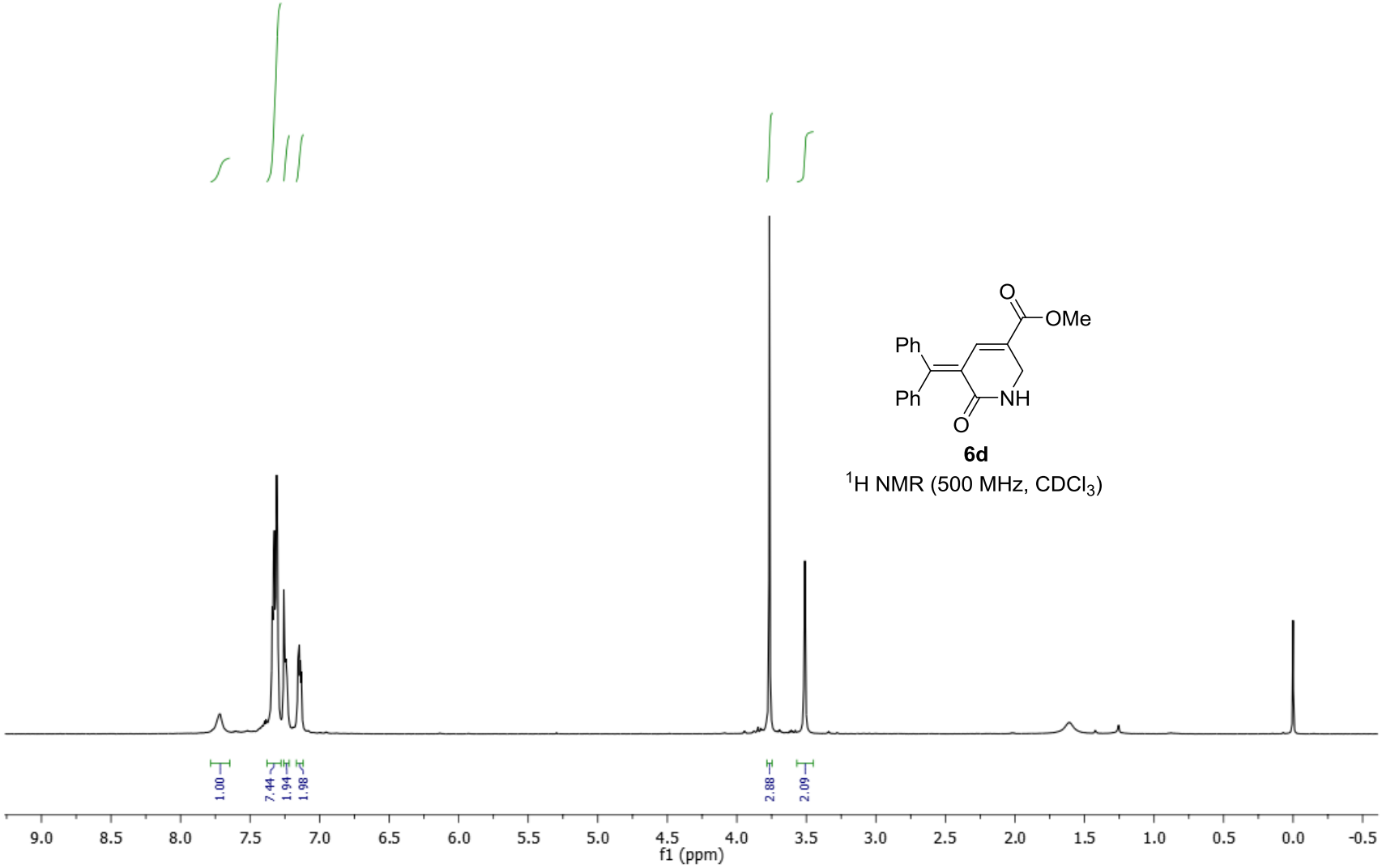
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)


7.69
7.41
7.41
7.39
7.34
7.19
7.19
7.18
7.18
7.17
5.56
5.55
5.55
5.53
5.53
5.52
5.51
5.50
5.03
5.02
5.02
5.02
5.02
4.99
4.99
4.99
4.98
4.98
4.97
4.97
3.79
2.69
2.68
2.66
2.65
2.53
2.52
2.51
2.49
CO2Me
Ph
Ph
O
6c
1H NMR (500 MHz, CDCl3)
0.96
4.35
2.28
3.97
0.99
1.06
1.06
2.01
0.97
3.02
2.20
2.21
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
-0.5
f1 (ppm)



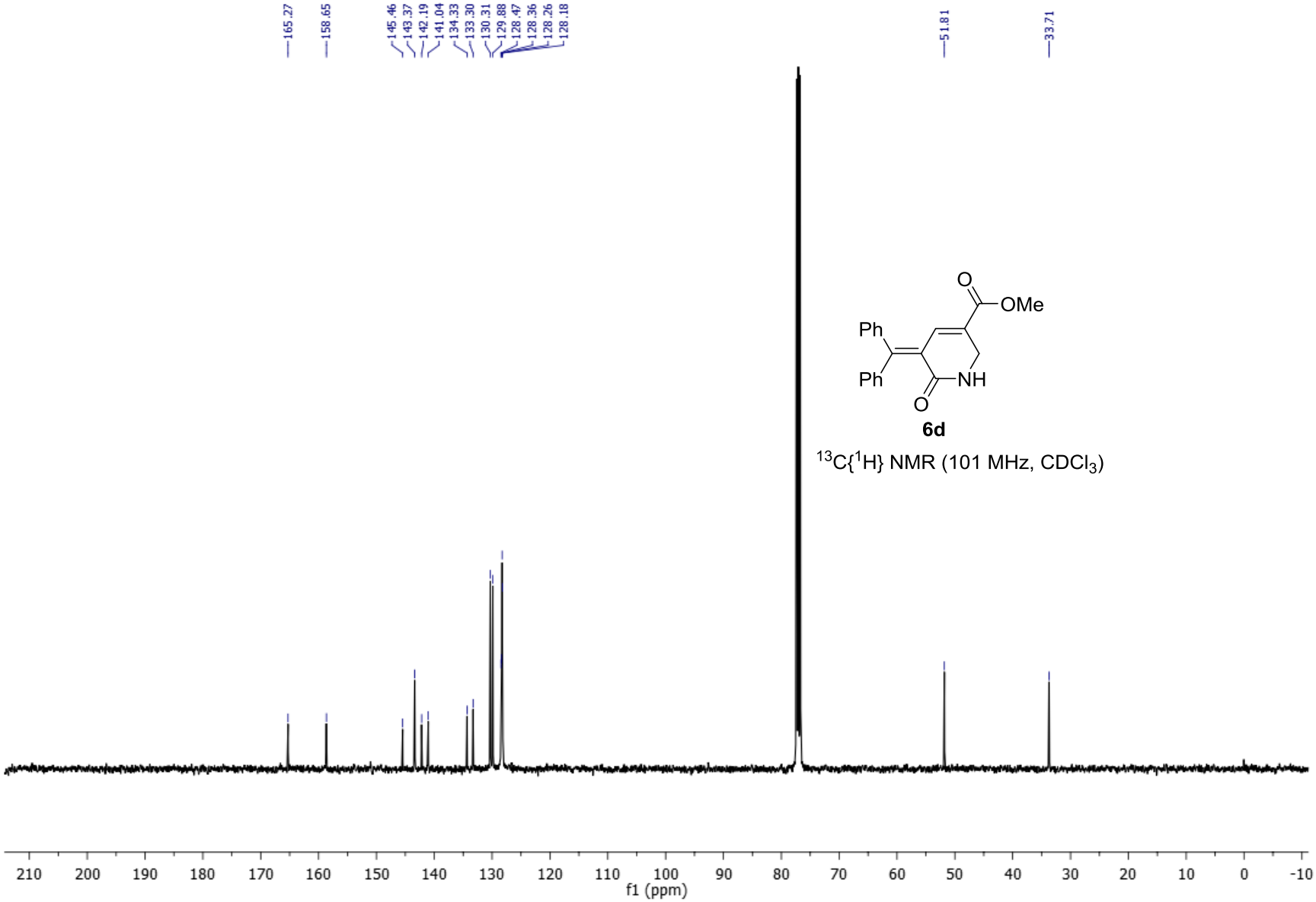
6c

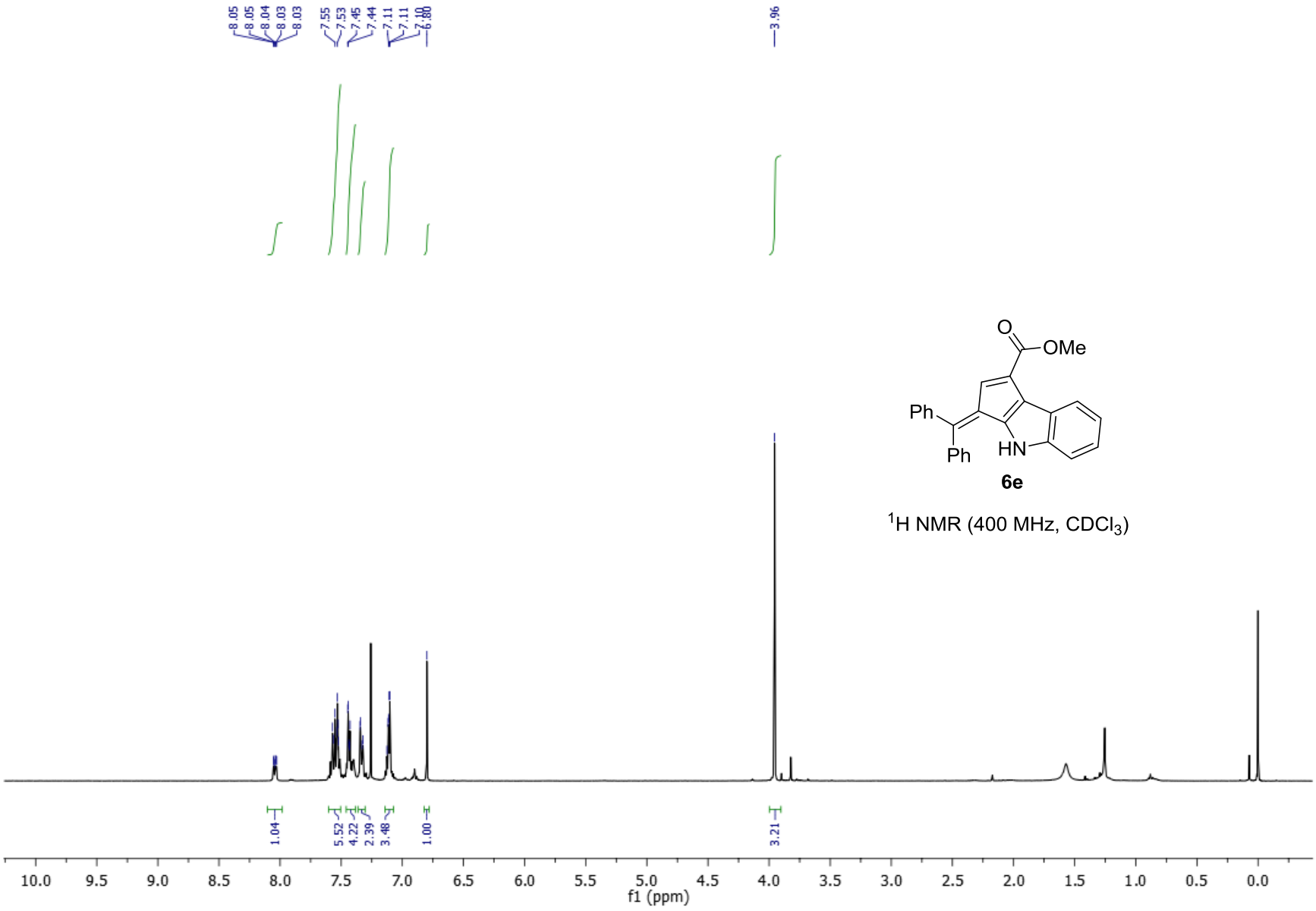
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

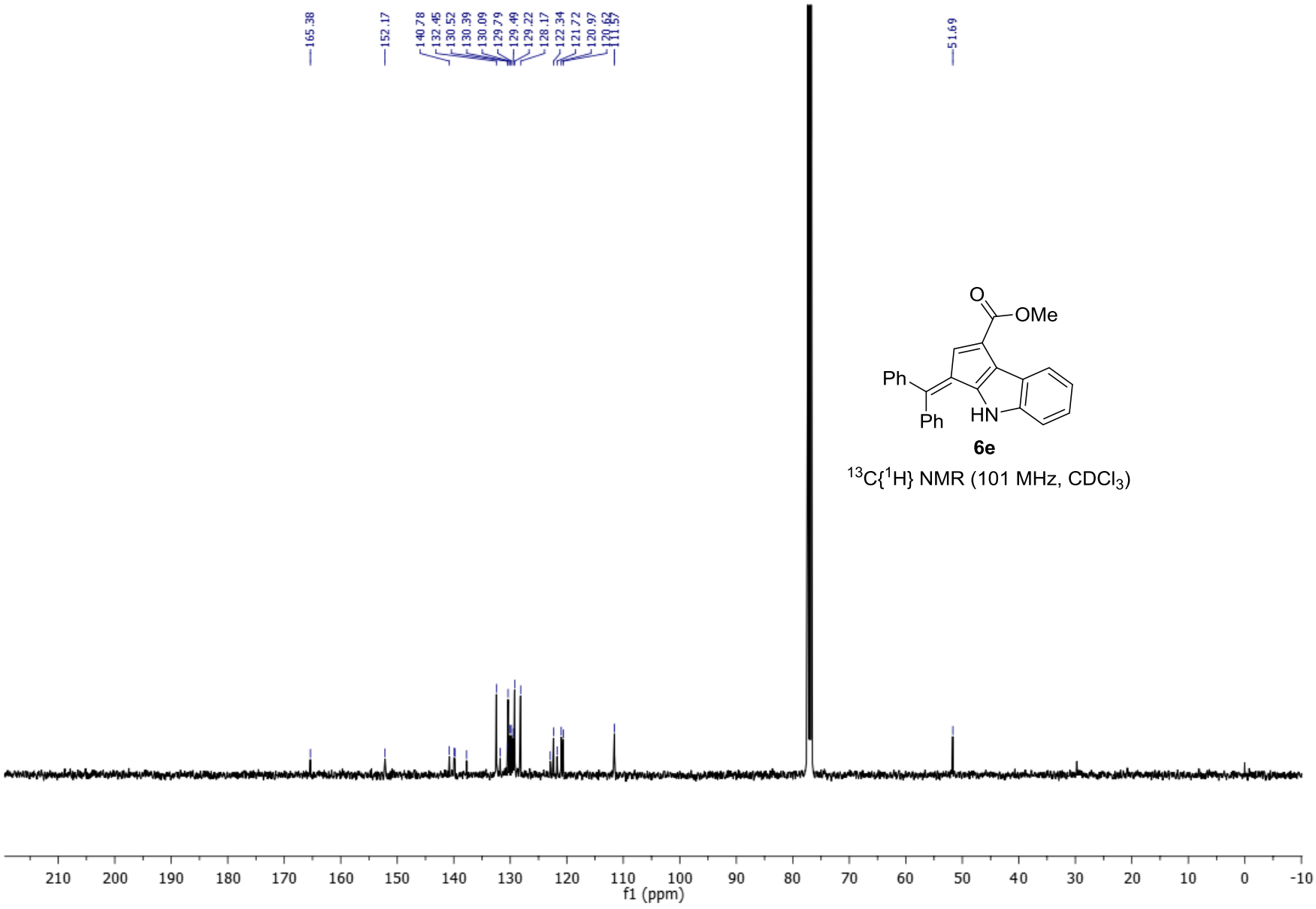


6d

^{1}H NMR (500 MHz, $CDCl_3$)


165.27
158.65
145.46
143.37
142.19
141.04
134.33
133.30
130.31
129.88
128.47
128.36
128.26
128.18
51.81
33.71
O
OMe
Ph
Ph
NH
O
6d
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.05
8.05
8.04
8.03
8.03
7.55
7.53
7.45
7.44
7.11
7.11
7.10
6.80
3.96
O
OMe
Ph
Ph
HN
6e
1H NMR (400 MHz, CDCl3)
1.04
5.52
4.22
2.39
3.48
1.00
3.21
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
f1 (ppm)



6e

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)