Electronic Supplementary Material (ESI) for ChemComm.

Oxa-[3+3] Annulation of MBH-Carbonates of Propiolaldehydes with α-Nitro/Bromo Ketones to Access 2*H*-Pyrans

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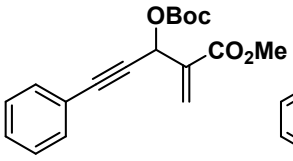
1. General information:

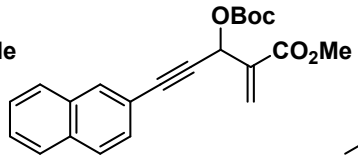
All the reactions were performed in oven-dried glass apparatus, the air and moisture sensitive reactions were carried out under inert atmosphere (nitrogen) using reagent grade solvents. Commercially available reagents were used as such without any further purification. All reactions were monitored by thin-layer chromatography carried out on silica plates using UV-light, anisaldehyde and β- naphthol for visualization. Column chromatography was performed on silica gel (100–200 mesh) using hexanes and ethyl acetate as eluent. ^{1}H NMR was recorded in $CDCl_3$ on 500 MHz, 400 MHz and 300 MHz instruments and ^{13}C NMR was recorded on 126 MHz, 101 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 $CDCl_3$. 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); td (tiplet of doublets), etc. Specific rotation was recorded on anton-paar polarimeter, FTIR spectra were recorded on Alpha (Bruker) infrared Spectrophotometer. High resolution mass spectra (HRMS) [ESI+] were obtained using either a TOF or a double focusing spectrometer.

The MBH Carbonates (**1a, 1c, 1d, 1e, 1g, 1h 1i, 1l, 1m)**,[1] (**1f, 1k**),[2] **7**,[5] **8**[6] and Benzoylnitromethanes **2a-2f**[7,8] were prepared based on literature reports. Compounds **5a** to **5d** were commercially available.

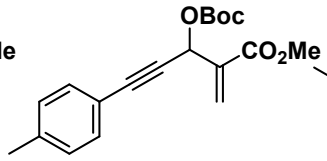
2. Structures of MBH Carbonates:



1a



1b



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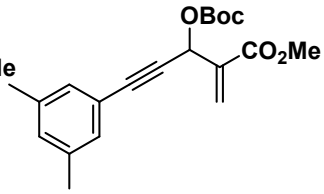

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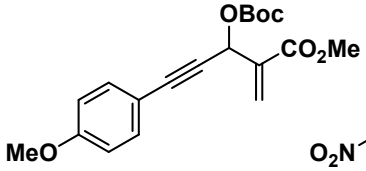

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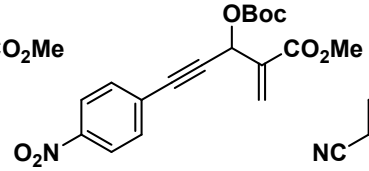

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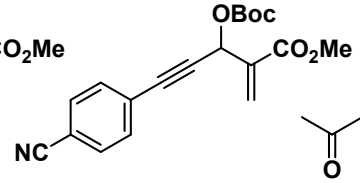

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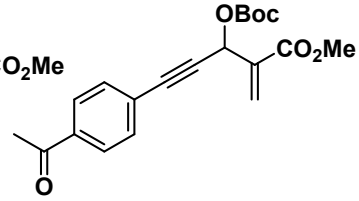

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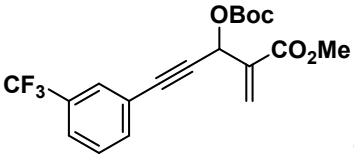
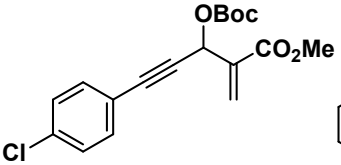


1i



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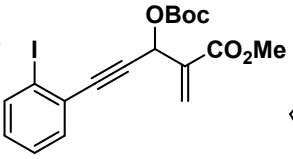

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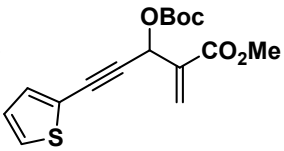
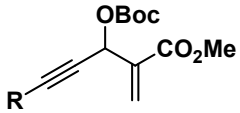
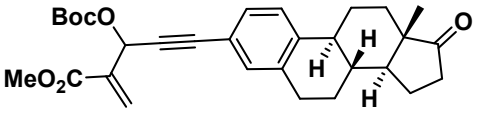


1l

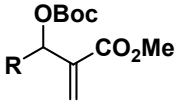


R= C_3H_7, 1m

R= C_4H_9, 1n



1o

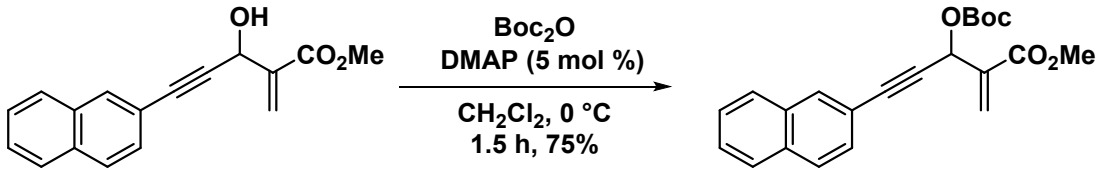


R= Ph, 7

R=H, 8

3. Experimental procedures and characterization data of new starting compounds:

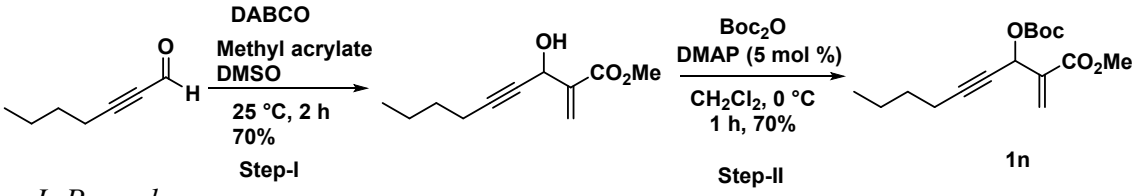
A) Procedure for Methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-(naphthalen-2-yl) pent-4-ynoate (1b):



1b

Methyl 3-hydroxy-2-methylene-5-(naphthalen-2-yl) pent-4-ynoate[3 & 4] (2 g, 7.52 mmol) was dissolved in 23 mL dichloromethane and cooled to 0 °C. DMAP (5 mol %) followed by Di-*tert*-butyl dicarbonate (1.97 g, 9.02 mmol) added drop by drop within 5 min. The reaction mixture was stirred for 1.5 h at 0 °C. After completion of the reaction, reaction mixture was diluted by 38 mL water and extracted with dichloromethane (2 x 38 mL). Combined organic layer and dried over anhydrous Na_2SO_4. Organic layer was concentrated under reduced pressure at 40 °C. Obtained crude oil was purified by column chromatography on silica gel (10% Ethyl acetate in hexanes) to afford the estrone MBH carbonate (**1o**) (2.06 g, 75%) as colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, J = 8.1, 0.8 Hz, 1H), 7.86–7.84 (m, 2H), 7.70 (dd, J = 7.1, 1.1 Hz, 1H), 7.58–750 (m, 2H), 7.42 (dd, J = 8.3, 7.2 Hz, 1H), 6.58 (s, 1H), 6.51 (d, J = 0.7 Hz, 1H), 6.45 (s, 1H), 3.85 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 152.3, 136.5, 133.4, 133.1, 130.9, 129.6, 129.4, 128.3, 127.0, 126.5, 126.1, 125.1, 119.6, 88.5, 85.9, 83.3, 65.2, 52.4, 27.8; IR (neat): 2950, 2229, 1746, 1439, 1253, 862, 753 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 367.12; HRMS: calcd. For $C_{22}H_{22}O_5Na$ $[M + Na]^+$ 389.1365, found 389.1367.

B) Procedure for methyl 3-((tert-butoxycarbonyl)oxy)-2-methylenenon-4-ynoate (1n):



Step I; Procedure:

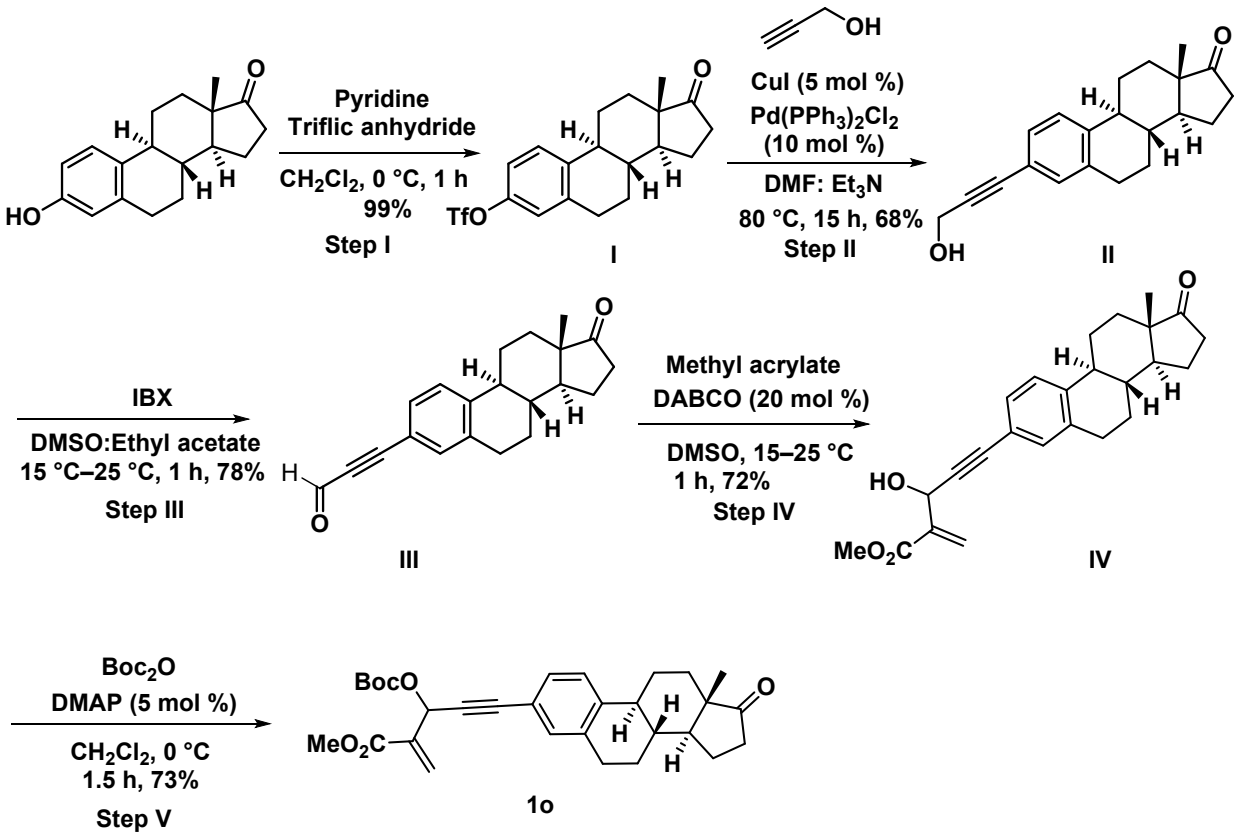
Hept-2-ynal (2 g, 18.15 mmol) was allowed to react with methyl acrylate (1.87 g, 21.79 mmol) in presence of DABCO (0.407 g, 3.63 mmol) in DMSO (20 mL) for 2 h at 25 °C. After completion, the reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 x 30 mL). Combined organic layers were washed with water (2 x 30 mL) and saturated brine solution (2 x 30 mL). Organic layer was separated, dried over sodium sulphate and evaporated under reduced pressure at 40 °C. Obtained crude oil was purified by column chromatography on silica gel (10% ethyl acetate in hexanes) to afford the methyl 3-hydroxy-2-methylenenon-4-ynoate (2.5 g, 70%) as yellow liquid; *Rf* = 0.3 (*n*-hexane: ethyl acetate = 8:2)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (s, 1H), 6.13 (s, 1H), 5.22 (d, *J* = 5Hz, 1H), 3.82 (s, 3H), 3.02 (d, *J* = 6.2 Hz, 1H), 2.25 (td, *J* = 7.0, 2.0 Hz, 2H), 1.55–148 (m, 2H), 1.45–1.36 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H)**;** ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 139.6, 126.7, 87.9, 77.7, 62.4, 52.2, 30.6, 21.9, 18.5, 13.6; IR (neat): 3491, 2948, 1717, 1442, 1260, 1143, 1016, 152 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 219.10; HRMS: calcd. For $C_{11}H_{16}O_3Na$ $[M + Na]^+$ 219.0997, found 219.1002.

Step II; procedure:

Methyl 3-hydroxy-2-methylenenon-4-ynoate (from step-I) (1.5 g, 7.65 mmol) was dissolved in dichloromethane (23 mL) and cooled to 0 °C. DMAP (5 mol %) followed by Di-*tert*-butyl dicarbonate (2 g, 9.18 mmol) added drop by drop within 5 min. The reaction mixture was stirred for 1 h at 0 °C. After completion, the reaction mixture was diluted with water (38 mL) and extracted with dichloromethane (2 x 38 mL). Combined organic layers were dried over

anhydrous Na_2SO_4 and concentrated under reduced pressure at 40 °C. The crude oil was purified by column chromatography on silica gel (5% ethyl acetate in hexanes) to afford the methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylenenon-4-ynoate (**1n**) (1.59 g, 70%) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.45 (s, 1H), 6.26 (t, J = 1.0 Hz, 1H), 6.12 (dd, J = 2.8, 2.0 Hz, 1H), 3.79 (s, 3H), 2.27–2.23 (m, 2H), 1.50 (s, 9H), 1.49–1.34 (m, 4H), 0.90 (t, J = 9.1 Hz, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 152.3, 136.9, 129.1, 89.1, 85.2, 82.9, 74.8, 64.9, 52.2, 30.4, 27.8, 27.4, 21.9, 18.5, 13.6; IR (neat): 2948, 1740, 1258, 1145, 955, 852 cm^{-1}; *m/z* (ESI): [M + Na]$^+$ 319.15; HRMS: calcd. For $C_{16}H_{24}O_5Na$ [M + Na]$^+$ 319.1521, found 319.1535.

C) Procedure for estrone MBH carbonate (1o):



Step I; Procedure for estrone triflate (I):

Estrone (10 g, 37 mmol) was dissolved in dichloromethane (200 mL), cooled to 0 °C and pyridine (7.32 g, 92.6 mmol) was added. Triflic anhydride (12.52 g,44.38 mmol) was added to it

drop wise within 10 min. Reaction mixture was stirred for 1 h at 0 °C. After completion of the reaction, water (100 mL) was added. Organic layer was separated and washed by 2N HCl (100 mL). Organic layer separated and washed by sat. brine solution (100 mL). Organic layer dried over sodium sulphate and evaporated under reduced pressure at 40 °C. Crude residue purified by column chromatography on silica gel (40% ethyl acetate in hexanes) to afford estrone triflate (**I**) (14.74 g, 99%) as white solid. *Rf* = 0.5 (*n*-hexane: ethyl acetate = 7:3)**;** mp: 88 °C–89 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.6 Hz, 1H), 7.05–7.00 (m, 2H), 2.97–2.93 (3, 2H), 2.57–2.48 (m, 1H), 2.44–2.26 (m, 2H), 2.22–1.97 (m, 4H), 1.71–1.64 (m, 1H), 1.58–1.40 (m, 5H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.42, 147.61, 140.30, 139.32, 127.2, 121.3, 118.8 (q, *J* = 321.0 Hz) 118.3, 50.4, 47.9, 44.1, 37.8, 35.8, 31.5, 29.4, 26.1, 25.7, 21.6, 13.8. IR (KBr): 2934, 1737, 1417, 1208, 920, 834, 754; *m/z* (ESI): $[M + H]^+$ 403.07; HRMS: calcd. For $C_{19}H_{22}F_3O_4S$ $[M + H]^+$ 403.1191, found 403.1194.

Step II; procedure for estrone propargyl alcohol (II):

Estrone triflate (**I**) (10 g, 24.8 mmol) was taken into round bottom flask and DMF (50 mL) and triethyl amine (20 mL) was added. Nitrogen gas purged for 30 min continuously and propargyl alcohol (1.8 g, 32.24 mmol) was added. Nitrogen gas purged for 20 min followed by $Pd(PPh_3)_2Cl_2$ (10 mol %) and CuI (5 mol %) was added. Reaction mass was heated to 80 °C and stirred for 15 h at 80 °C, water (50 mL) and ethyl acetate (100 mL) was added. Reaction mixture was filtered through celite and filtrate washed saturated brine (50 mL). Organic layer was dried over sodium sulphate and evaporated under reduced pressure at 45 °C. Crude compound was purified by column chromatography on silica gel to afford estrone propargyl alcohol (**II**) (5.2 g, 68%) as white solid; *Rf* = 0.3 (*n*-hexane: Ethyl acetate = 7:3)**;** mp: 182 °C–184 °C**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 2H), 7.18 (s, 1H), 5.54–4.47 (s, 2H), 2.89–2.86 (m, 2H), 2.51 (m,

1H), 2.42–2.37 (m, 1H), 2.26 (td, J = 10.7, 4.3 Hz, 1H), 2.20–1.95 (m, 5H), 1.65–1.53 (m, 3H), 1.52–1.48 (m, 2H), 1.46–1.40 (m, 1H), 0.91 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.9, 140.5, 136.6, 132.2, 129.0, 125.4, 119.9, 86.7, 85.7, 51.7, 50.5, 47.9, 44.4, 37.9, 35.9, 31.6, 29.1, 26.3, 25.6, 21.6, 13.9; IR (KBr): 3383, 2926, 1729,1449, 1259, 1031 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 309.20; HRMS: calcd. For $C_{21}H_{25}O_2$ $[M + H]^+$ 309.1855, found 309.1857.

Step III; procedure for estrone propiolaldehyde (III):

IBX (3.54 g, 12.65 mmol) was taken into round bottom flask containing DMSO (50 mL) at 15 °C. Reaction mass was stirred for 10 min to get clear solution followed by estrone propargyl alcohol (**II**) (3 g, 9.73 mmol) dissolved in ethyl acetate (20 mL) was added slowly. The reaction mixture stirred for 1 h at 25 °C. After completion of the reaction, water (100 mL) and ethyl acetate (50 mL) was added. Reaction mixture was filtered through celite and washed with ethyl acetate (50 mL). Filtrate washed saturated brine solution (3 x30 mL). Combined organic layer were dried over sodium sulphate and evaporated under reduced pressure. Crude compound was purified by column chromatography on silica gel to afford estrone propiolaldehyde (**III**) (2.32 g, 78%) as white solid; *Rf* = 0.5 (*n*-hexane: ethyl acetate = 8: 2)**;** mp: 174 °C–176 °C **;** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.41–7.37 (m, 1H), 7.37–7.31 (m, 2H), 3.00–2.86 (m, 2H), 2.55–2.49 (m, 1H), 2.44–2.40 (m, 1H), 2.33 (td, J = 10.8, 3.8 Hz, 1H), 2.20–2.11 (m, 1H), 2.11–2.02 (m, 2H), 2.01–1.96 (m, 1H), 1.67–1.52 (m, 4H), 1.51–1.42 (m, 2H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.4, 176.8, 143.9, 137.3, 133.9, 130.7, 125.9, 116.7, 95.9, 88.4, 50.5, 47.9, 44.7, 37.8, 35.8, 31.5, 29.0, 26.2, 25.5, 21.6, 13.8; IR (KBr): 2935, 2181, 1730, 1654, 1259, 1002, 760 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 307.20; HRMS: calcd. For $C_{21}H_{23}O_2$ $[M + H]^+$ 307.1698, found 307.1705.

Step IV; procedure for estrone MBH alcohol (IV):

Estrone propiolaldehyde (**III**) (2 g, 6.5359 mmol) was allowed to react with methyl acrylate (0.674 g, 7.843 mmol) in presence of DABCO (0.146 g, 1.3072 mmol) in 20 mL DMSO for 1 h at 25 °C. The reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 x 30 mL). Combined organic layer was washed with water (2 x 30 mL) and saturated brine (2 x 30 mL). Organic layer was separated, dried over sodium sulphate and evaporated under reduced pressure at 40 °C. The residue was purified by column chromatography on silica gel (15 % ethyl acetate in hexanes) to afford the estrone MBH alcohol (**IV**) (1.84 g, 72%) as white solid; *Rf* = 0.3 (*n*-hexane: ethyl acetate = 8:2)**;** mp: 88 °C–90 °C**; [**α**]**$^{20}_{D}$ +118.69 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 1.0 Hz, 2H), 7.21 (s, 1H), 6.36 (s, 1H), 6.21 (t, *J* = 0.9 Hz, 1H), 5.45 (d, *J* = 6.4 Hz, 1H), 3.84 (s, 3H), 3.16 (d, *J* = 6.7 Hz, 1H), 2.88 (dd, *J* = 8.7, 4.1 Hz, 2H), 2.54–2.48 (m, 1H), 2.4–2.38 (m, 1H), 2.29 (td, *J* = 10.7, 4.3 Hz, 1H), 2.19–2.10 (m, 1H), 2.09–2.00 (m, 2H), 1.99–1.93 (m, 1H), 1.66–1.62 (m, 1H), 1.58– 1.41 (m, 5H), 0.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.7, 166.4, 140.7, 139.2, 136.6, 132.3, 129.1, 127.0, 125.4, 119.6, 86.9, 85.98, 62.7, 52.3, 50.5, 47.9, 44.5, 37.9, 35.9, 31.6, 29.1, 26.3, 25.6, 21.6, 13.9; IR (KBr): 2930, 1724, 1438, 1259, 1146, 1048 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 393.20; HRMS: calcd. For $C_{25}H_{28}O_4Na$ $[M + Na]^+$ 415.1885, found 415.1890.

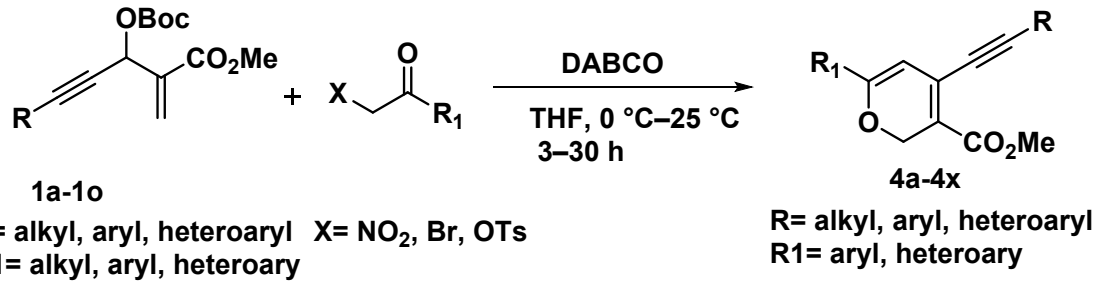
Step V; procedure for estrone MBH carbonate (1o)

Estrone MBH alcohol (**IV**) (1.8 g, 4.59 mmol) was dissolved in dichloromethane (14 mL) and cooled to 0 °C. DMAP (5 mol %) followed by Di-*tert*-butyl dicarbonate (1.2 g, 5.51 mmol) added drop by drop within 5 min. The reaction mixture was stirred for 1.5 h at 0 °C. After completion of the reaction (showed by TLC), the reaction mixture was diluted with water (23 mL) and extracted with dichloromethane (2 x 23 mL). Combined organic layer and dried over anhydrous Na_2SO_4. Organic layer was concentrated under reduced pressure at 40 °C. Obtained

crude oil was purified by column chromatography on silica gel (10% ethyl acetate in hexanes) to afford the estrone MBH carbonate (**1o**) (1.65 g, 73%) as colourless liquid; *Rf* = 0.7 (*n*-hexane: ethyl acetate = 8: 2); **[**α**]**$^{20}_{D}$ + 48.20 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 2H), 7.21 (s, 1H), 6.51 (s, 1H), 6.36 (s, 1H), 6.34 (d, *J* = 0.8 Hz, 1H), 3.81 (s, 3H), 2.88 (dd, *J* = 8.7, 4.1 Hz, 2H), 2.54-2.48 (m, 1H), 2.43–2.38 (m, 1H), 2.33–2.26 (m, 1H), 2.19–1.95 (m, 5H), 1.68–1.62 (m, 1H), 1.61–1.58 (m, 3H), 1.56–1.54 (m, 1H), 1.51 (m, 9H), 0.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.7, 164.9, 152.2, 140.9, 136.7, 136.6, 132.4, 129.4, 129.3, 125.4, 119.3, 87.9, 83.1, 82.9, 64.9, 52.3, 50.5, 47.9, 44.5, 37.9, 35.9, 31.6, 29.1, 27.8, 26.3, 25.6, 21.6, 13.9; IR (neat): 2928, 2333, 1739, 1450, 1262, 846, 758 cm^{-1} ; *m/z* (ESI): [M + Na]$^{+}$ 515.45 ; HRMS: calcd. For $C_{30}H_{36}O_6Na$ [M + Na]$^{+}$ 515.2410, found 515.2418.

4. Experimental procedures and characterization data of compounds:

A) General procedure for the synthesis of 2*H*-pyran:



1a-1o

R= alkyl, aryl, heteroaryl X= NO_2, Br, OTs
R1= alkyl, aryl, heteroary

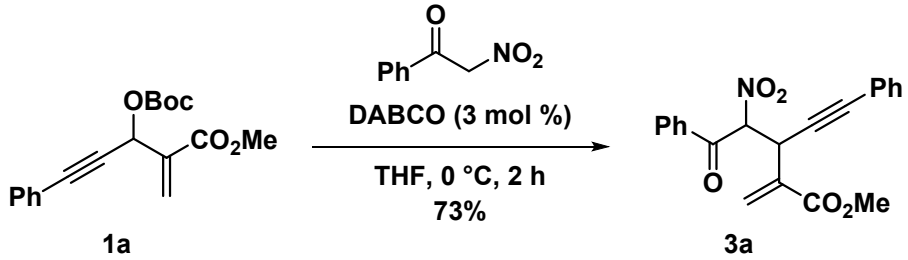
4a-4x

R= alkyl, aryl, heteroaryl
R1= aryl, heteroary

The mixture of MBH-carbonate (0.3 mmol, 1 equiv.) and Benzoylnitromethane or active methylene compound (0.36 mmol, 1.2 equiv.) in 3 mL THF. The reaction mixture was cooled to 0 °C. DABCO (0.009 mmol, 0.03 equiv.) was added to the reaction mixture and stirred for 2 h at 0 °C. Temperature of the reaction mixture rose to 25 °C and stirred for 1 h-30 h. The reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (2 x 3 mL). Combined organic layer and dried over anhydrous Na_2SO_4. Organic layer was concentrated under reduced pressure at 40 °C. Obtained crude oil was purified by column chromatography on silica gel (5%

Ethyl acetate in hexanes) to afford the yellow oil or solid.

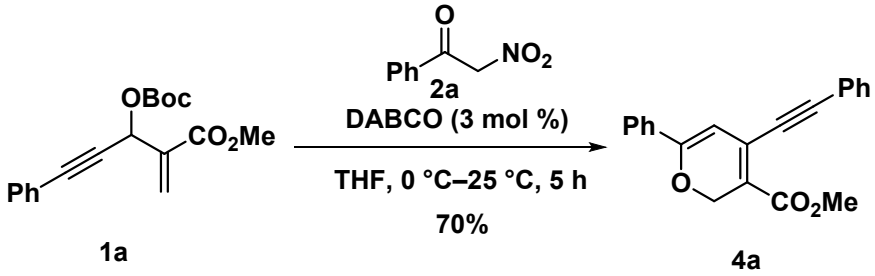
Methyl 2-methylene-3-(1-nitro-2-oxo-2-phenylethyl)-5-(4-nitrophenyl)pent-4- ynoate (3a):



1a **3a**

Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl pent-4-ynoate (**1a**) (95 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in THF (3 mL) for 2 h at 0 °C. After work-up, the residue was purified by column chromatography on silica gel (5 % ethyl acetate in hexanes) to afford methyl 2-methylene-3-(1-nitro-2-oxo-2-phenylethyl)-5-(4-nitrophenyl)pent-4-ynoate (**3a**) (79 mg, 73%) as white solid; *Rf* = 0.4 (*n*-hexane: ethyl acetate = 9.5:0.5); mp: 126–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.14 (m, 2H), 7.68–7.64 (m, 1H), 7.56–7.52 (m, 2H), 7.24–7.20 (m, 1H), 7.17–7.13 (m, 2H), 7.01-6.97(m, 3H), 6.43 (s, 1H), 6.08 (s, 1H), 4.86 (d, *J* = 9.6 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 165.4, 135.1, 134.8, 134.5, 131.5(2C), 131.4, 129.6(2C), 129.1(2C), 128.6, 128.1(2C), 121.9, 87.7, 86.9, 82.8, 52.5, 38.2; IR (KBr): 2921, 1708, 1563, 1337, 1244, 763 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 386.20 ; HRMS: calcd. For $C_{21}H_{17}NO_5Na$ $[M + Na]^+$ 386.1004, found 386.1004.

Methyl 6-phenyl-4-(phenylethynyl)-2*H*-pyran-3-carboxylate *(4a):*

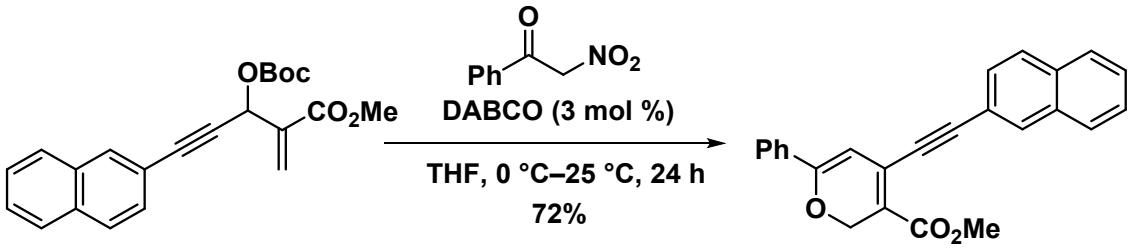


1a **4a**

Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl

pent-4-ynoate **(1a)** (95 mg, 0.3 mmol) was allowed to react with benzoylnitromethane **(2a)** (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 5 h. After the work-up, the residue was purified by column chromatography on silica gel (3% ethyl acetate in hexanes) to afford the methyl 6-phenyl-4-(phenylethynyl)-2*H*-pyran-3-carboxylate ***(4a)*** (67 mg, 70%) as yellow solid; *Rf* = 0.7 (*n*-hexane: Ethyl acetate = 9.5:0.5); mp: 92–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 5.8, 2.1 Hz, 2H), 7.58 (dd, *J* = 5.9, 2.2 Hz, 2H), 7.427.40 (m,3H), 7.39 – 7.37 (m, 3H), 6.21 (s, 1H), 5.01 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 158.9, 132.4, 132.1(2C), 130.4, 129.1, 128.6 (3C), 128.4 (2C), 126.0 (2C), 122.8, 115.4, 102.8, 98.5, 87.1, 66.2, 51.7; IR (KBr): 3376, 2925, 2351, 2213, 1702, 1624, 1550, 1372, 1255, 1107, 809, 768 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 317.20; HRMS:calcd. For $C_{21}H_{17}O_3$ $[M + H]^+$ 317.1178, found 317.1185.

Methyl 4-(naphthalen-2-ylethynyl)-6-phenyl-2*H*-pyran-3-carboxylate (*4b*):

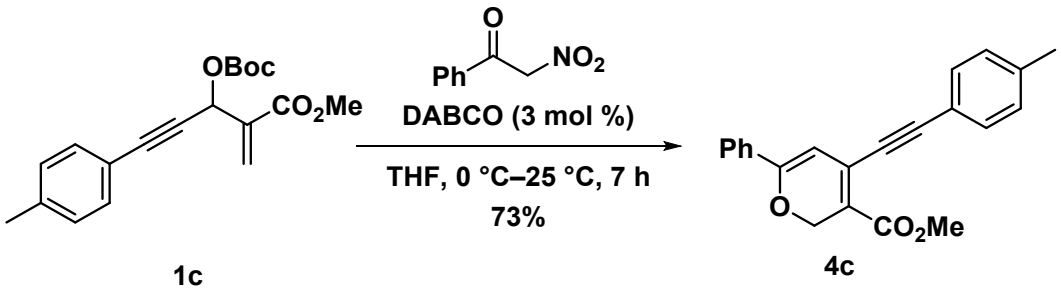


1b **4b**

Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-(naphtha len-2-yl) pent-4-ynoate (**1b**) ((110 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**) (69 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in THF (3 mL) for 24 h. After work-up, the residue was purified by column chromatography on silica gel (3% ethyl acetate in hexanes) to afford the methyl 4-(naphthalen-2-ylethynyl)-6-phenyl-2*H*-pyran-3-carbox ylate (**4b**) (79 mg, 72 %) as yellow Solid; *Rf* = 0.6 (*n*-hexane: ethyl acetate = 9.5:0.5); mp: 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.3 Hz, 1H), 7.9–7.87(m, 2H), 7.82 (dd, *J* = 7.1, 0.9 Hz, 1H), 7.79–7.75 (m, 2H), 7.66–7.62 (m, 1H), 7.57–7.53 (m, 1H), 7.48 (dd, *J*

= 8.1, 7.3 Hz, 1H), 7.44-7.42 (m,3H), 6.31 (s, 1H), 5.13 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 158.9, 133.7, 133.1, 132.4, 131.5, 130.5, 129.8, 128.6 (2C), 128.6 128.3, 127.1, 126.6, 126.4, 126.1 (2C), 125.2, 120.5, 115.2, 103.0, 96.8, 91.9, 66.3, 51.8; IR (KBr): 3376, 2958, 2203, 1699, 1620, 1548, 1397, 1255, 1104, 807, 772 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 367.30; HRMS: calcd. for $C_{25}H_{19}O_3$ $[M + H]^+$ 367.1334, found 367.1335.

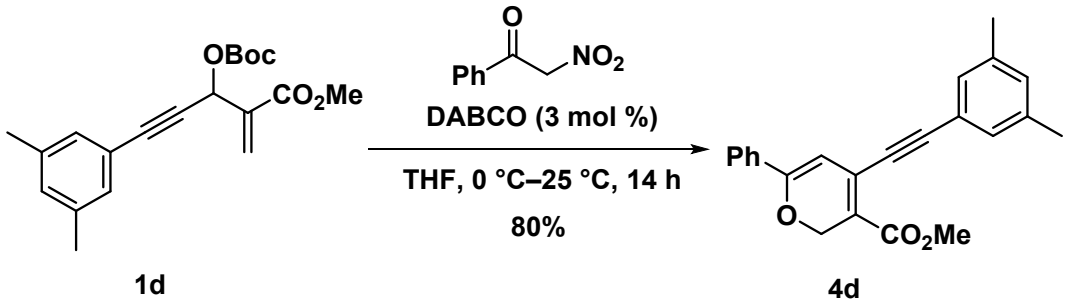
Methyl 6-phenyl-4-(*p*-tolylethynyl)-2*H*-pyran-3-carboxylate (4c):



1c 4c

Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene -5-(p-tolyl) pent-4-ynoateate (**1c**) (99 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 7 h. After the work-up, the residue was purified by column chromatography on silica gel (3% Ethyl acetate in hexanes) to afford the methyl 6-phenyl-4-(*p*-tolylethynyl)-2*H*-pyran-3-carboxylate (**4c)** (72 mg, 73%) as yellow liquid; *Rf* = 0.5 (n-hexane: Ethyl acetate = 9.5:0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.71 (m, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.42–7.39 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.20 (s, 1H), 5.07 (s, 2H), 3.85 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 158.8, 139.5, 132.4, 132.0 (2C), 130.4, 129.2 (2C), 128.8, 128.5 (2C), 126.1 (2C), 119.7, 115.0, 102.9, 98.9, 86.7, 66.2, 51.6, 21.7; IR (neat): 3393, 2927, 2208,1696, 1617, 1548, 1446, 1773, 1254, 1107, 818, 771 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 353.20; HRMS: calcd. For $C_{22}H_{19}O_3$ $[M + H]^+$ 331.1334, found 331.1337.

Methyl 4-((3,5-dimethylphenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate (4d):

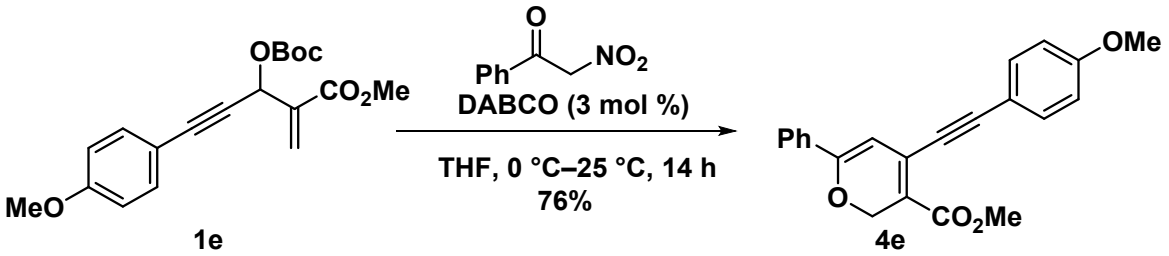


1d **4d**

Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-5-(3,5-dimethylphenyl) -2-methylenepent-4-ynoate (**1d**) (103 mg, 0.3 mmol) was allowed to react with benzoylnitro methane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 14 h. After work-up, the residue was purified by column chromatography on silica gel (4% Ethyl acetate in hexanes) to afford the methyl 4-((3,5-dimethylphenyl)ethynyl)-6-phenyl-2*H*-pyran -3-carboxylate **(4d)** (82 mg, 80%) as yellow liquid; *Rf* = 0.5 (*n*-hexane: Ethyl acetate = 9.5:0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.71 (m, 2H), 7.42–7.39 (m, 3H), 7.21 (s, 2H), 7.01 (s, 1H), 6.19 (s, 1H), 5.07 (s, 2H), 3.86 (s, 3H), 2.32 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 158.8, 138.0 (2C),

132.4, 131.1, 130.3, 129.8 (2C), 128.8, 128.5 (2C), 126.1 (2C), 122.4, 115.1, 103.0, 99.1, 86.5, 66.2, 51.6, 21.1 (2C); IR (neat): 2922, 2854, 2203, 1716, 1687, 1543, 1444, 1251, 805 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 345.30; HRMS: calcd. For $C_{23}H_{21}O_3$ $[M + H]^+$ 345.1491, found 345.1497.

Methyl 4-((4-methoxyphenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate (4e):

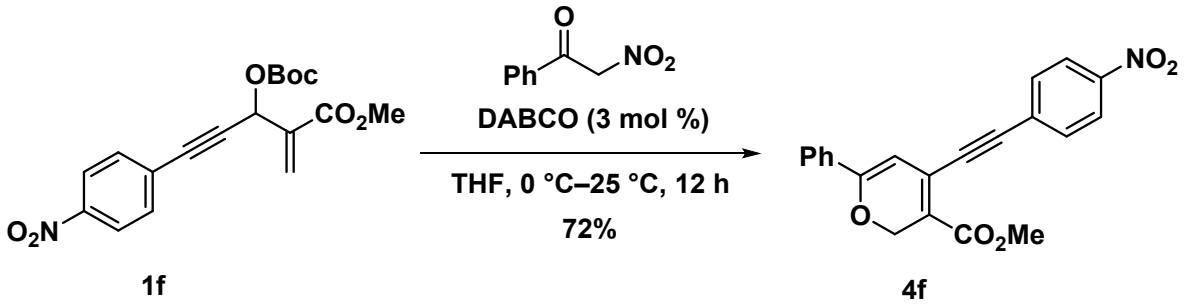


1e **4e**

Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-5-(4-methoxyphenyl)-

2- methylenepent-4-ynoate (**1e**) (104 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in THF (3 mL) for 14 h. After the work-up, the residue was purified by column chromatography on silica gel (4% Ethyl acetate in hexanes) to afford the methyl 4-((4-methoxyphenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate (**4e)** (79 mg, 76%) as yellow Solid; *Rf* = 0.4 (*n*-hexane: Ethyl acetate = 9.5:0.5); mp: 88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.71 (m, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.42–7.39 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.20 (s, 1H), 5.07 (s, 2H), 3.85 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 160.4, 158.8, 133.8 (2C), 132.4, 130.4, 128.9, 128.5 (2C), 126.0 (2C), 114.8, 114.6, 114.1 (2C), 102.9, 99.1, 86.4, 66.2, 55.4, 51.6; IR (KBr): 3375, 2923, 2400–2200, 1693, 1609, 1373, 1253, 1107, 836, 773 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 369.20 ; HRMS: calcd. For $C_{22}H_{19}O_4$ $[M + H]^+$ 347.1283, found 347.1288.

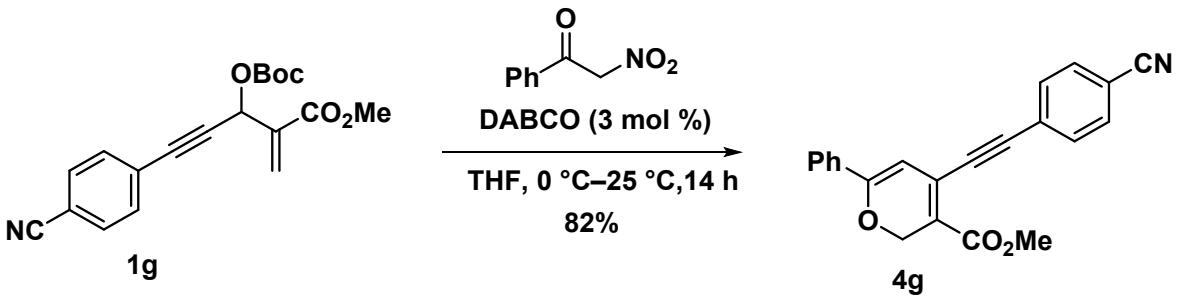
Methyl 4-((4-nitrophenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate (4f):



Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-(4-nitro phenyl)pent-4-ynoate (**1f**) (108 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 12 h. After the work-up, the residue was purified by column chromatography on silica gel (8% Ethyl acetate in hexanes) to afford the methyl 4-((4-nitrophenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate **(4f)** (78 mg, 72%) as yellow Solid; *Rf* = 0.3 (*n*-hexane: Ethyl acetate = 9:1); mp: 138–140 °C; ^{1}H

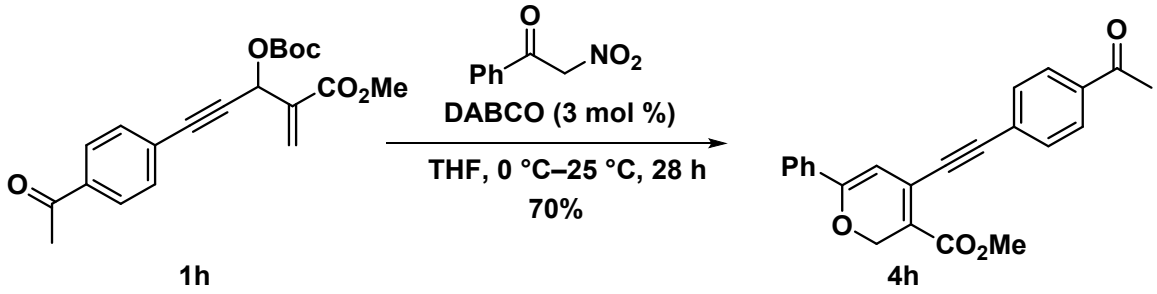
NMR (500 MHz, $CDCl_3$) δ 8.25–8.23 (m, 2H), 7.73–7.71 (m, 4H), 7.45–7.40 (m, 3H), 6.19 (s, 1H), 5.09 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz,$CDCl_3$) δ 164.0, 159.3, 147.5, 132.8 (2C), 132.0, 130.7, 129.60, 128.6 (2C), 127.7, 126.1 (2C), 123.7 (2C), 116.8, 102.1, 95.5, 91.6, 66.0, 51.8 ; IR (KBr): 3366, 2978, 2343, 2217, 1704, 1607, 1565, 1353, 1254, 817, 772 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 384.15; HRMS: calcd. For $C_{21}H_{16}NO_5$ $[M + H]^+$ 362.1028, found 362.1017.

Methyl 4-((4-cyanophenyl)ethynyl)-6-phenyl-2H-pyran-3-carboxylate (4g):



Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-(4-cyano phenyl)pent-4-ynoate (**1g**) (102 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 14 h. After the work-up, the residue was purified by column chromatography on silica gel (8% Ethyl acetate in hexanes) to afford the methyl 4-((4-cyanophenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate **(4g)** (84 mg, 82%) as yellow Solid; *Rf* = 0.6 (*n*-hexane: Ethyl acetate = 9.5:0.5); mp: 146–148 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75–7.72 (m, 2H), 7.66 (s, 4H), 7.43–7.38 (m, 3H), 6.19 (s, 1H), 5.09 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 159.3, 132.5 (2C), 132.1 (3C) , 130.7, 128.6 (2C) , 127.7, 127.6, 126.1 (2C) , 118.4, 116.6, 112.3, 102.1, 95.8, 90.9, 66.1, 51.8; IR (KBr): 2922, 2228, 1680, 1541, 1439, 1239, 836 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 342.25 ; HRMS: calcd. For $C_{22}H_{16}NO_3$ $[M + H]^+$ 342.1130, found 342.1128.

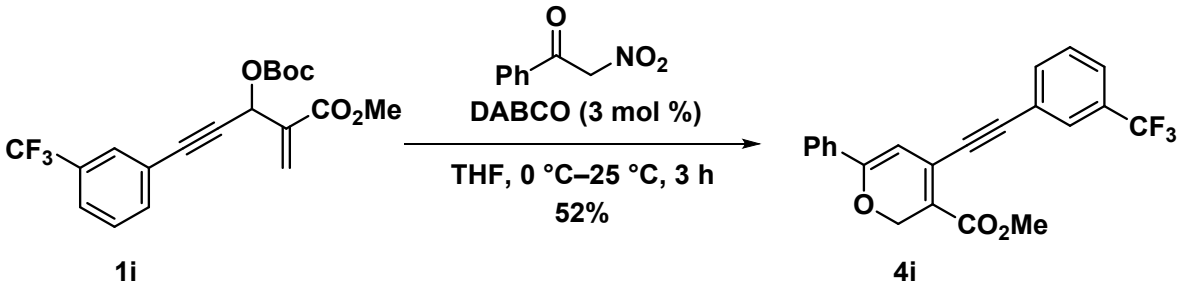
Methyl 4-((4-acetylphenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate (4h):



1h **4h**

Following the general procedure **A**, methyl 5-(4-acetylphenyl)-3-((*tert*-butoxycarbonyl)oxy)-2-methylenepent-4-ynoate (**1h**) (107 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 28 h. After the work-up, the residue was purified by column chromatography on silica gel (7% Ethyl acetate in hexanes) to afford the methyl 4-((4-acetylphenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate (**4h)** (75 mg, 70%) as yellow liquid; *Rf* = 0.4 (*n*-hexane: ethyl acetate = 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.5 Hz, 2H), 7.75–7.73 (m, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.44–7.39 (m, 3H), 6.22–6.18 (m, 1H), 5.08 (s, 2H), 3.86 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 164.3, 159.1, 136.9, 132.2 (3C), 130.6, 128.6 (2C), 128.3 (2C), 128.1, 127.6, 126.1 (2C), 116.2, 102.5, 97.0, 89.9, 66.1, 51.7, 26.7; IR (neat): 3375, 2957, 1689, 1612, 1549, 1367, 1262, 1108, 841, 772 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 381.25; HRMS: calcd. For $C_{23}H_{19}O_4$ $[M + H]^+$ 359.1283, found 359.1275.

Methyl 6-phenyl-4-((3-(trifluoromethyl)phenyl)ethynyl)-2*H*-pyran-3-carboxylate (*4i*):

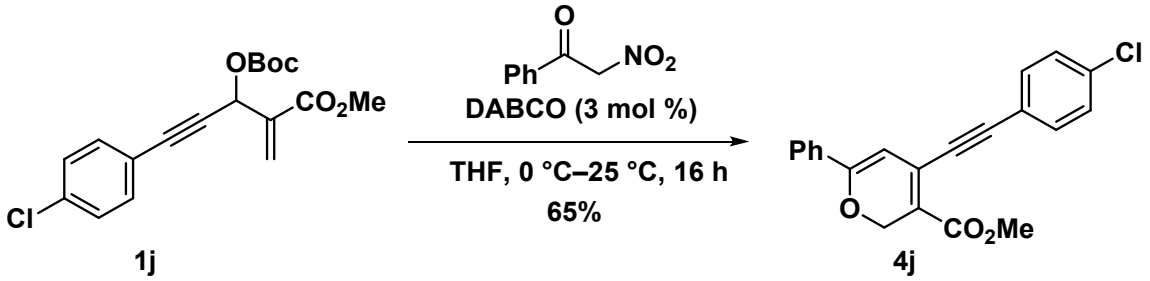


1i **4i**

Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-(3-(triflu oromethyl)phenyl)pent-4-ynoate (**1i**) (115 mg, 0.3 mmol) was allowed to react with

benzoyl nitromethane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 3 h. After the work-up, the residue was purified by column chromatography on silica gel (4% Ethyl acetate in hexanes) to afford the methyl 6-phenyl-4-((3-(trifluoromethyl)phenyl) ethynyl)-2*H* -pyran-3-carboxylate (**4i)** (60 mg, 52%) as yellow Solid; *Rf* = 0.5 (n-hexane: Ethyl acetate = 9.5: 0.5); mp: 82–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.75-7.73 (m, 3H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.43–7.4 (m, 3H), 6.20 (s, 1H), 5.08 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3, 159.1, 135.1, 132.2, 130.6, 129.0, 128.8 (2C), 128.6 (2C), 128.0, 126.1 (2C), 125.6, 125.6, 123.7, 116.1, 102.5, 96.3, 88.3, 66.1, 51.7; IR (KBr): 3198, 2957, 2350, 2216, 1723, 1621, 1547, 1443, 1372, 1257, 1130, 807, 770 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 385.25; HRMS: calcd. For $C_{22}H_{16}O_3F_3$ $[M + H]^+$ 385.1052, found 385.1048.

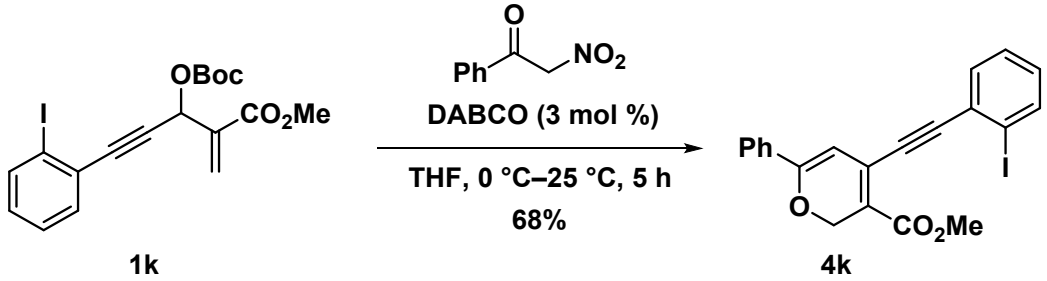
Methyl 4-((4-chlorophenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate (4j):



Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-5-(4-chlorophenyl)-2-methylenepent-4-ynoate (**1j**) (105 mg, 0.286 mmol) was allowed to react with benzoylnitro methane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 16 h. After the work-up, the residue was purified by column chromatography on silica gel (4% ethyl acetate in hexanes) to afford the methyl 4-((4-chlorophenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate (**4j)** (68 mg, 65%) as yellow Solid; *Rf* = 0.6 (*n*-hexane: Ethyl acetate = 9.5:0.5); mp: 84–86 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 7.75–7.71 (m, 2H), 7.51(d, *J* = 8.6 Hz, 2H), 7.43–7.39 (m, 3H), 7.35 (d, *J* = 8.6 Hz, 2H), 6.19 (s, 1H), 5.07 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 159.0, 135.3, 133.3 (2C), 132.3, 130.5, 128.8 (2C), 128.6(2C), 128.3, 126.0

(2C), 121.3, 115.7, 102.6, 97.1, 88.0, 66.1, 51.7; IR (KBr): 3376, 2954, 2350, 2213, 1699, 1622, 1546, 1371, 1255, 1102, 831, 770 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 373.15; HRMS: calcd. For $C_{21}H_{16}O_3Cl$ $[M + H]^+$ 351.0788, found 351.0791.

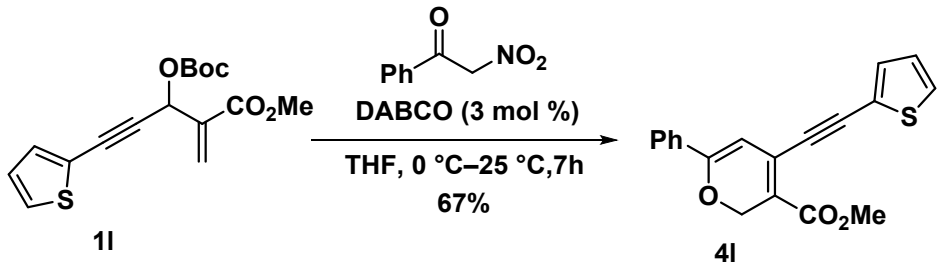
Methyl 4-((2-iodophenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate *(*4k*):*



1k **4k**

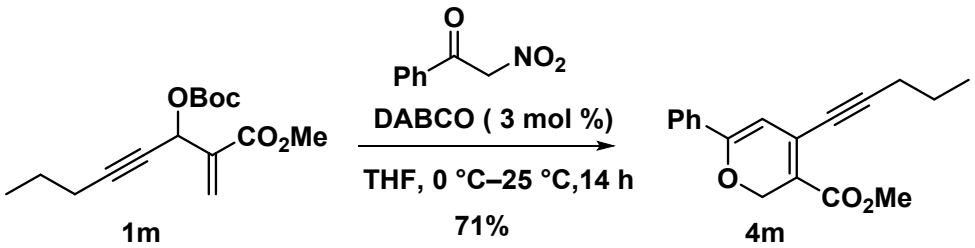
Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl pent-4-ynoate (**1k**) (133 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in THF (3 mL) for 5 h. After the work-up, the residue was purified by column chromatography on silica gel (4% ethyl acetate in hexanes) to afford the methyl 4-((2-iodophenyl)ethynyl)-6-phenyl-2*H*-pyran-3-carboxylate *(***4k***)* (90 mg, 68%) as yellow liquid; *Rf* = 0.6 (*n*-hexane: ethyl acetate = 9.5:0.5); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.75–7.72 (m, 2H), 7.59 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.43–7.40 (m, 3H), 7.36 (td, *J* = 7.6, 1.2 Hz, 1H), 7.06 (td, *J* = 7.8, 1.6 Hz, 1H), 6.31 (s, 1H), 5.09 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 158.9, 138.8, 133.4, 132.3, 130.5, 130.2, 129.3, 128.6 (2C), 128.2, 127.9, 126.1 (2C), 115.5, 102.6, 101.0, 100.0, 90.4, 66.1, 51.8; IR (neat): 3375, 2958, 2342, 2215, 1722, 1617, 1550, 1370, 1256, 1102, 808, 765 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 465.05; HRMS: calcd. For $C_{21}H_{16}IO_3$ $[M + H]^+$ 443.0144, found 443.0147.

Methyl 6-phenyl-4-(thiophen-2-ylethynyl)-2*H*-pyran-3-carboxylate (4l):



Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-(thiophen-2-yl)pent-4-ynoate (**1k**) (97 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in THF (3 mL) for 7 h. After the work-up, the residue was purified by column chromatography on silica gel (4% Ethylacetate in hexanes) to afford the methyl 6-phenyl-4-(thiophen-2-ylethynyl)-2*H*-pyran -3-carboxylate (**4k)** (65 mg, 67%) as yellow solid; *Rf* = 0.6 (*n*-hexane: ethyl acetate = 9.5:0.5); mp: 87–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.71 (m, 2H), 7.43–7.37 (m, 5H), 7.05 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.18 (s, 1H), 5.07 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 158.9, 133.4, 132.3, 130.5, 129.0, 128.5, 128.1, 127.4 (2C), 126.1 (2C), 122.8, 115.0, 102.3, 91.8, 91.4, 66.1, 51.7; IR (KBr): 3365, 2925, 2198, 1694, 1619, 1552, 1378, 1255, 1106, 809, 771 cm^{-1}; *m/z* (ESI):$[M + Na]^+$ 345.15; HRMS: calcd. For $C_{19}H_{15}O_3S$ $[M + H]^+$ 323.0742, found 323.0745.

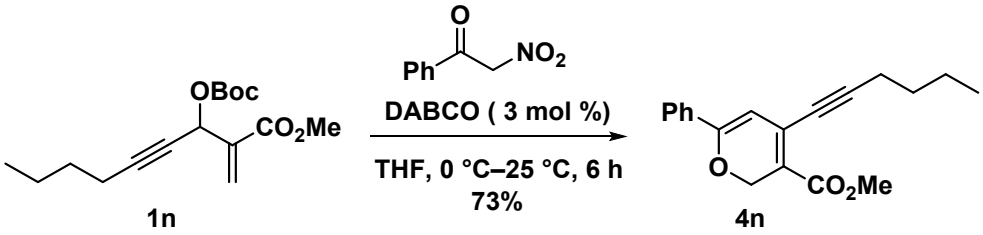
Methyl 4-(pent-1-yn-1-yl)-6-phenyl-2*H*-pyran-3-carboxylate (4m):



Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methyleneoct-4-ynoate (**1m**) (85 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**) (59 mg,

0.36 mmol) and DABCO (1 mg, 0.009 mmol) in THF (3 mL) for 14 h. After the work-up, the residue was purified by column chromatography on silica gel (4% ethyl acetate in hexanes) to afford the methyl 4-(pent-1-yn-1-yl)-6-phenyl-*2H*-pyran-3-carboxylate **(4m)** (60 mg, 71%) as yellow liquid; *Rf* = 0.6 (*n*-hexane: ethyl acetate = 9.5:0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.67 (m, 2H), 7.40–7.37 (m, 3H), 6.08 (s, 1H), 5.01 (s, 2H), 3.80 (s, 3H), 2.47 (t, *J* = 7.0 Hz, 2H), 1.71–1.62 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 160.7, 158.6, 132.4, 130.3, 129.4, 128.5 (2C), 126.0 (2C), 114.7, 103.6, 101.0, 78.7, 51.5, 22.0 (2C), 13.6; IR (neat): 3369, 2927, 1600-1800, 1454, 1250, 1107, 809,773 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 305.20; HRMS: calcd. For $C_{18}H_{19}O_3$ $[M + H]^+$ 283.1334, found 283.1331.

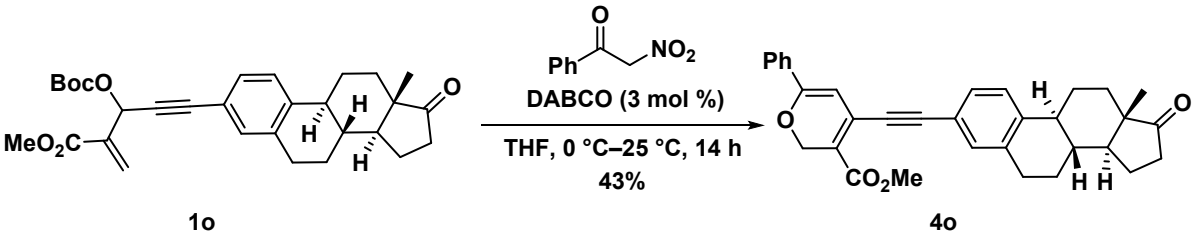
Methyl 4-(hex-1-yn-1-yl)-6-phenyl-2H-pyran-3-carboxylate (4n):



Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylenenon-4-ynoate (**1n**) (89 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**)(59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in THF (3 mL) for 6 h. After the work-up, the residue was purified by column chromatography on silica gel (3% ethyl acetate in hexanes) to afford the methyl 4-(hex-1-yn-1-yl)-6-phenyl-*2H*-pyran-3-carboxylate **(4n)** (65 mg, 73%) as yellow liquid; *Rf* = 0.6 (*n*-hexane: ethyl acetate = 9.5:0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.68 (m, 2H), 7.41–7.37 (m, 3H), 6.08 (s, 1H), 5.01 (s, 2H), 3.80 (s, 3H), 2.50 (t, *J* = 7.0 Hz, 2H), 1.67–1.59 (m, 2H), 1.55–1.48 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 156.0, 129.9, 127.7, 126.9, 125.9 (2C), 123.5 (2C), 112.1, 101.0, 98.7, 75.9, 63.6, 48.9, 28.1, 19.5, 17.2, 11.1; IR (neat): 3367, 2931, 2200–2400, 1694, 1624, 1551, 1370, 1255, 1105, 809,

774 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 297.25; HRMS: calcd. For $C_{19}H_{21}O_3$ $[M + H]^+$ 297.1491, found 297.1484.

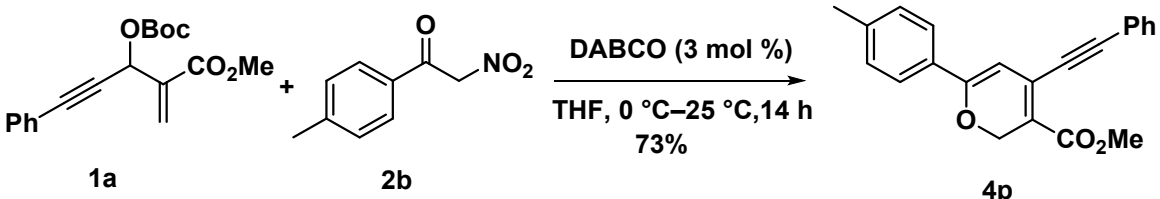
Estrone-2*H*-pyran-3-carboxylate (4o):



1o **4o**

Following the general procedure **A**, Boc-estrone MBH carbonate (**1o**) (148 mg, 0.3 mmol) was allowed to react with benzoylnitromethane (**2a**) (59 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in THF (3 mL) for 14 h. After the work-up, the residue was purified by column chromatography on silica gel (10 % ethyl acetate in hexanes) to afford the methyl estrone-2*H*-pyran-3-carboxylate (**4o**) (64 mg, 43%) as yellow liquid; *Rf* = 0.5 (*n*-hexane: Ethyl acetate = 9:1); $[\alpha]^{20}_D$ +52.58 (*c* 0.58, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.74–7.72 (m, 2H), 7.42–7.39 (m, 3H), 7.37–7.28 (m, 3H), 6.20 (s, 1H), 5.07 (s, 2H), 3.85 (s, 3H), 2.94–2.91 (m, 2H), 2.55–2.49 (m, 1H), 2.45–2.41 (m, 1H), 2.36–2.30 (m, 1H), 2.23–1.97 (m, 5 H), 1.67–1.59 (m, 2H), 1.56–1.42 (m, 4H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.7, 164.6, 158.8, 141.4, 136.8, 132.6, 132.4, 130.4, 129.5, 128.8, 128.6 (2C), 126.1 (2C), 125.5, 120.1, 115.1, 102.9, 98.9, 86.7, 66.2, 51.6, 50.6, 47.9, 44.5, 37.9, 35.9, 31.6, 29.1, 26.4, 25.6, 21.6, 13.9; IR (neat): 2934, 2192, 1738, 1261, 842, 759 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 493.29; HRMS: calcd. For $C_{33}H_{33}O_4$ $[M + H]^+$ 493.2379, found 493.2377.

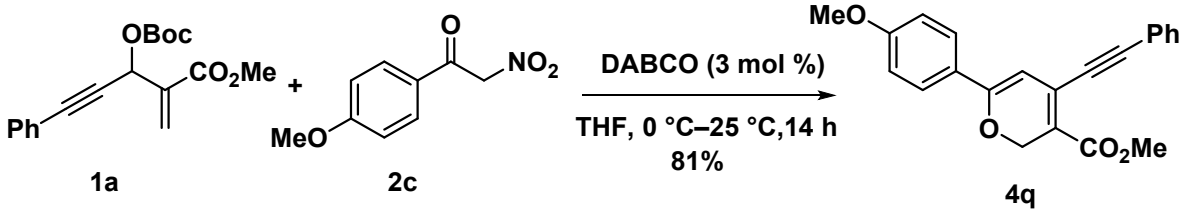
Methyl 4-(phenylethynyl)-6-(p-tolyl)-2*H*-pyran-3-carboxylate (4p)



1a **2b** **4p**

Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl pent-4-ynoate (**1a**) (95 mg, 0.3 mmol) was allowed to react with 4-methyl benzoylnitromethane (**2b**) (65 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in THF (3 mL) for 14 h. After the work-up, the residue was purified by column chromatography on silica gel (4% ethyl acetate in hexanes) to afford the methyl 4-(phenylethynyl)-6-(p-tolyl)-2*H*-pyran-3-carboxylate (**4p**) (72 mg, 73%) as yellow liquid; *Rf* = 0.5 (n-hexane: ethyl acetate = 9.5:0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.62 (m,2H), 7.60–7.56 (m, 2H), 7.39–7.35 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.17 (s, 1H), 5.06 (s, 2H), 3.85 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 159.1, 140.9, 132.1 (2C), 129.5, 129.3 (2C), 129.1, 128.8, 128.5 (2C), 126.1 (2C), 122.8, 114.9, 102.2, 98.3, 87.2, 66.2, 51.7, 21.5; IR (neat): 2924, 2858, 2209, 1718, 1443, 1251, 1110, 799 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 353.30; HRMS: calcd. For $C_{22}H_{19}O_3$ $[M + H]^+$ 331.1334, found 331.1324.

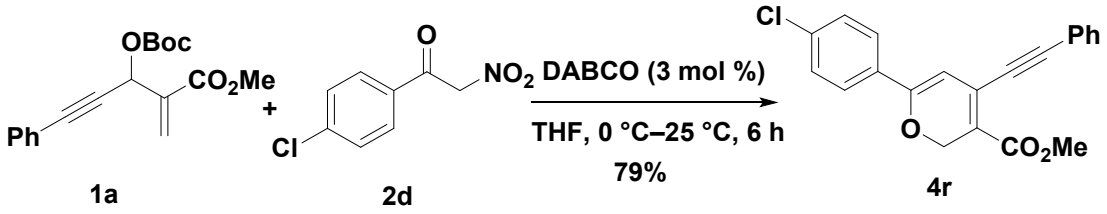
Methyl 6-(4-methoxyphenyl)-4-(phenylethynyl)-2*H*-pyran-3-carboxylate (4q):



Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl pent-4-ynoate (**1a**) (95 mg, 0.3 mmol) was allowed to react with 4-methoxy benzoylnitromethane (**2c**) (70 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 14 h. After the work-up, the residue was purified by column chromatography on silica gel (4% ethyl acetate in hexanes) to afford the methyl 6-(4-methoxyphenyl)-4-(phenylethynyl)-2*H*-pyran-3-carboxylate **(4q) (**84 mg, 81%) as yellow solid; *Rf* = 0.3 (n-hexane: ethyl acetate = 9.5:0.5); mp: 122–124 °C;

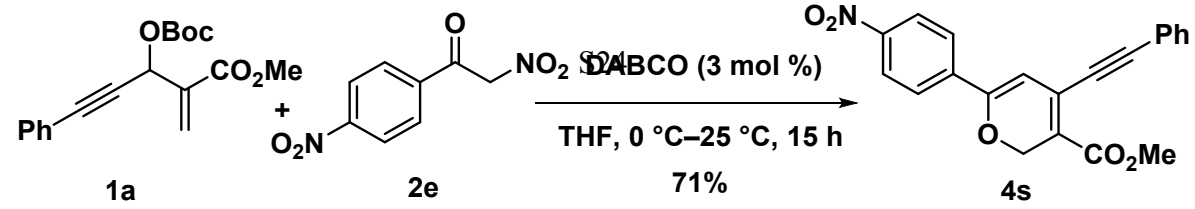
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 9.0 Hz, 2H), 7.59–7.57 (m, 2H), 7.39–7.35 (m, 3H), 6.92 (d, J = 9.0 Hz, 2H), 6.11 (s, 1H), 5.05 (s, 2H), 3.85 (d, J = 1.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 161.6, 159.0, 132.1 (2C), 129.1, 129.0, 128.4 (2C), 127.9 (2C), 124.8, 122.9, 114.3, 113.9 (2C), 101.4, 98.2, 87.3, 66.2, 55.4, 51.6; IR (KBr): 2953, 2866, 2210, 1715, 1688, 1506, 1256, 799 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 369.25; HRMS: calcd. For $C_{22}H_{19}O_4$ $[M + H]^+$ 347.1283, found 347.1278.

Methyl 4-(hex-1-yn-1-yl)-6-phenyl-*2H*-pyran-3-carboxylate (4r):



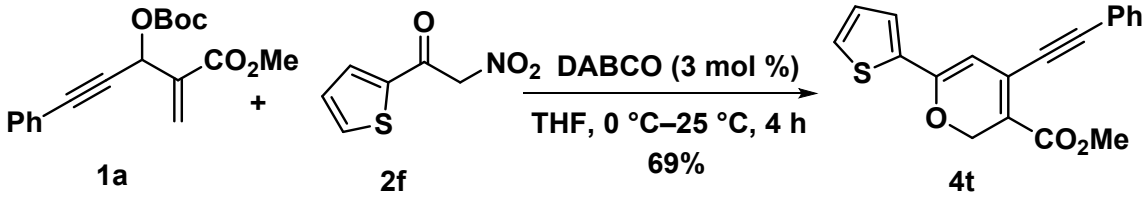
Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl pent-4-ynoate (**1a**) (95 mg, 0.3 mmol) was allowed to react with 4-Chloro benzoylnitromethane (**2d**) (72 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 6 h. After the work-up, the residue was purified by column chromatography on silica gel (4% ethyl acetate in hexanes) to afford the methyl 6-(4-chlorophenyl)-4-(phenylethynyl)-*2H*-pyran -3-carboxylate **(4r) (**84 mg, 79%) as yellow liquid, *Rf* = 0.5 (n-hexane: ethyl acetate = 9.5:0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.7 Hz, 2H), 7..59–7.56 (m, 2H), 7.39–7.36 (m, 5H), 6.17 (s, 1H), 5.07 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.42, 157.64, 136.4, 132.1 (2C), 130.8, 129.3, 128.8 (2C), 128.4 (2C), 128.2, 127.3 (2C) , 122.7, 115.7, 103.0, 98.7, 86.9, 66.2, 51.7; IR (neat): 2927, 2858, 2346, 2203, 1722, 1261, 812 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 351.25 ; HRMS: calcd. For $C_{21}H_{16}O_3Cl$ $[M + H]^+$ 351.0788, found 351.0791.

Methyl 6-(4-nitrophenyl)-4-(phenylethynyl)-2*H*-pyran-3-carboxylate (4s):



Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl pent-4-ynoate (**1a**) (95 mg, 0.3 mmol) was allowed to react with 4-nitro benzoylnitromethane (**2e**) (76 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 15 h. After the work-up, the residue was purified by column chromatography on silica gel (5 % ethyl acetate in hexanes) to afford the methyl 6-(4-nitrophenyl)-4-(phenylethynyl)-2*H*-pyran-3-carboxylate **(4s)** (77 mg, 71%) as yellow solid; *Rf* = 0.3 (n-hexane: ethyl acetate = 9:1); mp: 148–150 °C**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.59–7.57 (m, 2H), 7.41–7.36 (m, 3H), 6.33 (s, 1H), 5.12 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 155.8, 148.5, 138.4, 132.1 (2C), 129.4, 128.5 (2C), 127.42, 126.5 (2C), 123.8 (2C), 122.5, 117.5, 105.8, 99.2, 86.6, 66.3, 51.9; IR (KBr): 2923, 2862, 2209, 1716, 1691, 1554, 1345, 1253, 856 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 384.15 ; HRMS: calcd. For $C_{21}H_{16}NO_5$ $[M + H]^+$ 362.1028, found 362.1020.

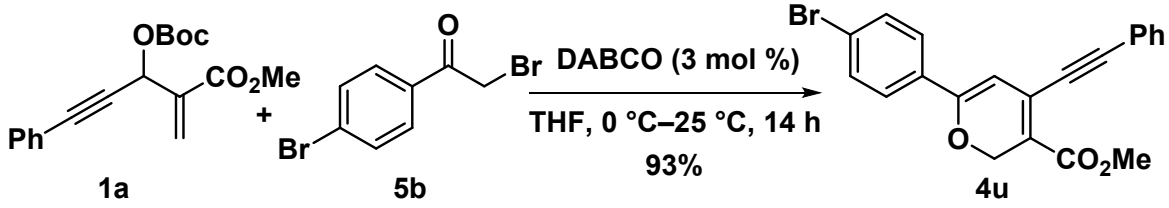
Methyl 4-(phenylethynyl)-6-(thiophen-2-yl)-2*H*-pyran-3-carboxylate (4t):



Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl pent-4-ynoate (**1a**) (95 mg, 0.3 mmol) was allowed to react with 2-nitro-1-(thiophen-2-yl) ethanone (**2f**) (62 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 4 h. After the work-up, the residue was purified by column chromatography on silica gel (4% ethyl acetate in hexanes) to afford the methyl 4-(phenylethynyl)-6-(thiophen-2-yl)-2H-pyran-3-carboxylate

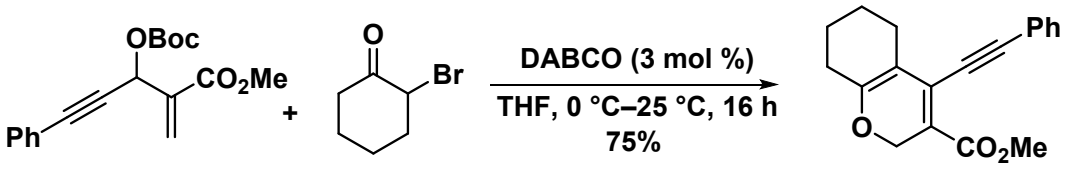
(4t) (67 mg, 69%) as yellow liquid; *Rf* = 0.6 (n-hexane: ethyl acetate = 9.5:0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.56 (m, 2H), 7.47 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.42 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.39–7.36 (m, 3H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.09 (s, 1H), 5.05 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 154.2, 136.4, 132.1 (2C), 129.2, 128.6 (2C) , 128.4 (2C) , 128.0, 127.2, 122.7, 115.2, 102.0, 98.6, 86.9, 66.4, 51.7; IR (neat): 2930, 2866, 2208, 1719, 1684, 1547, 1369, 1248, 850 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 323.15; HRMS: calcd. For $C_{19}H_{15}O_3S$ $[M + H]^+$ 323.0742, found 323.0822.

Methyl 6-(4-bromophenyl)-4-(phenylethynyl)-2*H*-pyran-3-carboxylate (4u):



Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl pent-4-ynoate (**1a**) (95 mg, 0.3 mmol) was allowed to react with 2-bromo-1-(4-bromophenyl) ethan-1-one (**5b**) (100 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in THF (3 mL) for 14 h. After the work-up, the residue was purified by column chromatography on silica gel (5% Ethyl acetate in hexanes) to afford the methyl 6-(4-bromophenyl)-4-(phenylethynyl)-2*H*-pyran -3-carboxylate **(4u) (** 109 mg, 93%) as yellow liquid; *Rf* = 0.6 (n-hexane: Ethyl acetate = 9.5:0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.56 (m, 4H), 7.55–7.52 (m, 2H), 7.39–7.36 (m, 3H), 6.18 (s, 1H), 5.06 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 156.6, 131.0 (2C), 130.7 (2C) , 130.2, 128.2, 127.4 (2C), 127.2, 126.4 (2C), 123.7, 121.6, 114.8, 102.0, 97.7, 85.9, 65.2, 50.7; IR (neat): 2926, 2853, 2208, 1715, 1689, 1252, 762, 692 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 395.02 ; HRMS: calcd. For $C_{21}H_{16}BrO_3$ $[M + H]^+$ 395.0283, found 395.0270.

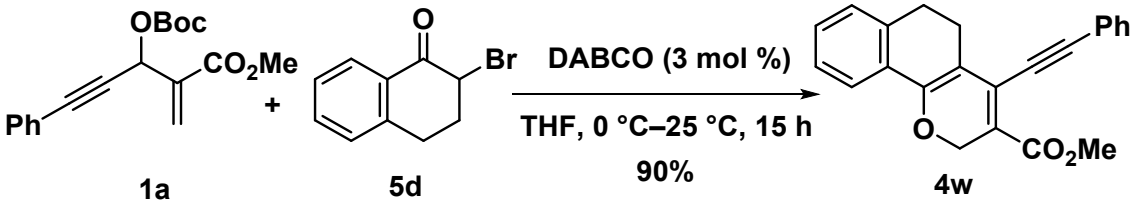
Methyl 4-(phenylethynyl)-5,6,7,8-tetrahydro-2*H*-chromene-3-carboxylate (4v):



1a 5c 4v

Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl pent-4-ynoate (**1a**) (95 mg, 0.3 mmol) was allowed to react with 2-bromocyclohexan-1-one (**5c**) (64 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 16 h. After the work-up, the residue was purified by column chromatography on silica gel (5% ethyl acetate in hexanes) to afford the methyl 4-(phenylethynyl)-5,6,7,8-tetrahydro-*2H*-chromene-3-carboxylate **(4v) (**69 mg, 75%) as yellow liquid; *Rf* = 0.5 (n-hexane: ethyl acetate = 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.53 (m, 2H), 7.37–7.34 (m, 3H), 4.80 (s, 2H), 3.82 (s, 3H), 2.47–245 (m, 2H), 2.22–2.20 (m, 2H), 1.72–1.69 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 158.1, 131.9 (2C), 130.1, 129.0, 128.4 (2C), 123.0, 115.2, 110.3, 101.7, 85.2, 64.8, 51.5, 27.3, 24.8, 22.7, 22.1 ; IR (neat): 2923, 2855, 2200, 1728, 1449, 1248, 1166, 757, 697 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 295.25; HRMS: calcd. For $C_{19}H_{19}O_3$ $[M + H]^+$ 295.1334, found 295.1311.

Methyl 4-(phenylethynyl)-5,6-dihydro-*2H*-benzo[*h*]chromene-3-carboxylate (4w):

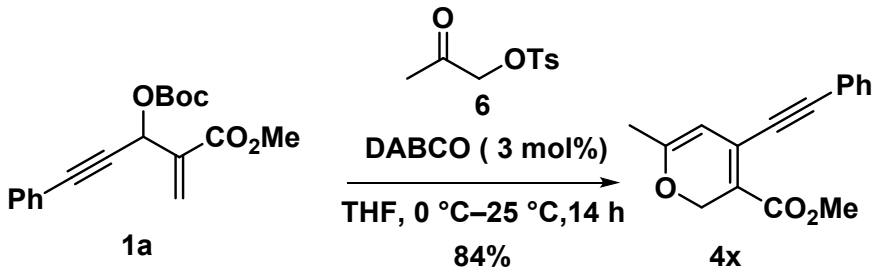


1a 5d 4w

Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl pent-4-ynoate (**1a**) (95 mg, 0.3 mmol) was allowed to react with 2-bromotetral-1-one (**5d**) (81 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in 3 mL THF for 15 h. After the work-up, the residue was purified by column chromatography on silica gel (5% ethyl acetate in hexanes) to afford the methyl 4-(phenylethynyl)-5,6-dihydro-*2H*-benzo[h]chromene-3-carboxylate **(4w) (**97

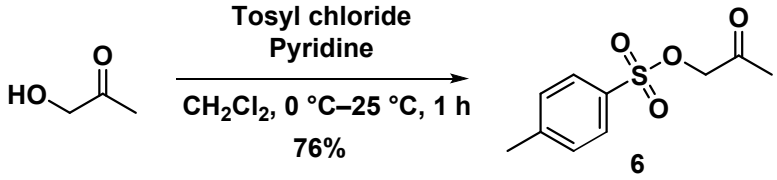
mg, 90%) as yellow solid; *Rf* = 0.5 (n-hexane: ethyl acetate = 9.5:0.5); mp: 78–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.55 (m, 3H), 7.39–7.36 (m, 3H), 7.30–7.23 (m, 3H), 7.20–7.18 (m, 1H), 5.01 (s, 2H), 3.86 (s, 3H), 2.94-2.90 (m, 2H), 2.81–2.77 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 153.5, 137.8, 132.0 (2C), 130.0, 129.5 (2C), 129.2, 128.5 (2C) , 127.4, 126.6, 122.9, 122.4, 116.0, 111.9, 101.8, 84.9, 65.3, 51.6, 27.9, 23.4; IR (KBr): 2947, 2203,1716, 1442, 1251, 759, 694 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 343.30 ; HRMS: calcd. For $C_{23}H_{19}O_3$ $[M + H]^+$ 343.1334, found 343.1331.

Methyl 6-methyl-4-(phenylethynyl)-2*H*-pyran-3-carboxylate (4x):



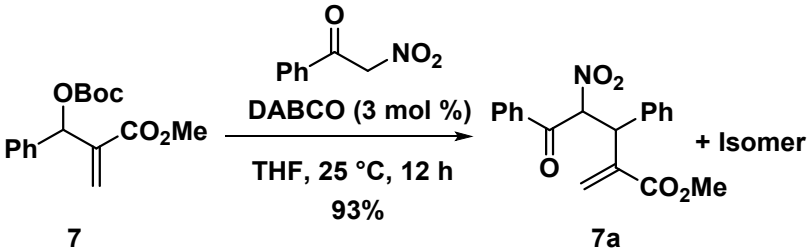
Following the general procedure **A**, methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenyl pent-4-ynoate (**1a**) (95 mg, 0.3 mmol) was allowed to react with 2-oxopropyl 4-methylbenzene sulfonate (**6**) (82 mg, 0.36 mmol) and DABCO (1 mg, 0.009 mmol) in THF (3 mL) for 14 h. After the work-up, the residue was purified by column chromatography on silica gel (5% ethyl acetate in hexanes) to afford the methyl 6-methyl-4-(phenylethynyl)-2*H*-pyran-3-carboxylate **(4x) (**67 mg, 84%) as yellow solid; *Rf* = 0.6 (n-hexane: ethyl acetate = 9.5:0.5); mp: 48–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.37–7.33 (m, 3H), 5.42 (d, *J* = 0.9 Hz, 1H), 4.90 (s, 2H), 3.81 (s, 3H), 1.94 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 161.3, 132.1 (2C), 129.1, 128.4, 128.5 (2C), 122.8, 113.6, 103.9, 98.2, 87.0, 65.8, 51.5, 19.3; IR (KBr): 2950, 2843, 2207, 1692, 1559, 1441, 1256, 762 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 255.21 ; HRMS: calcd. For $C_{16}H_{15}O_3$ $[M + H]^+$ 255.1021, found 255.1024.

2-Oxopropyl 4-methylcyclohexa-1,2,3,5-tetraene-1-sulfonate (6):



1-Hydroxypropan-2-one (1.5 g, 20.27 mmol) was dissolved in 30 mL dichloromethane and cooled to 0 °C. Pyridine (2.4 g, 30.40 mmol) was added to it. Tosyl chloride (4.6 g, 24.32 mmol) was added to reaction mixture at 0 °C. Reaction mixture stirred for 1 h at 25 °C. After completion showed by TLC. Reaction mixture was diluted with 15 mL water and adjusted pH to 2 by using aqueous solution of 2N HCl. Organic layer was separated and washed by 15 mL saturated brine two times. Organic layer dried over sodium sulphate and evapourated under reduced pressure at 40 °C. Crude oil purified by using column chromatography on silica gel (2% Ethyl acetate in hexanes) to afford 2-oxopropyl 4-methylcyclohexa-1,2,3,5-tetraene-1-sulfonate (**6)** (3.5 g, 76%) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 4.48 (s, 2H), 2.46 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 145.6, 132.3, 130.1, 128.1, 72.1, 26.6, 21.7; IR (neat): 2932, 1738, 1356, 1175, 1024, 808, 768 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 241.10; HRMS: calcd. For $C_{10}H_{12}SO_4$ $[M + H]^+$ 229.0535, found 229.0535.

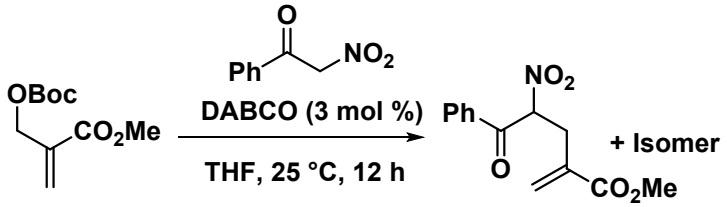
Methyl 2-methylene-4-nitro-5-oxo-3, 5-diphenylpentanoate (7a):



Methyl 2-(((tert-butoxycarbonyl)oxy)(phenyl)methyl)acrylate (**7**) (88 mg, 0.30 mmol) was taken to round bottom flask and 3 mL THF was added at 25 °C. Benzoylnitromethane (**2a**) (59 mg,

0.32 mmol) was added to it. DABCO (1mg, 0.009 mmol) was added to it. Reaction mixture was stirred for 12 h at 25 °C. After completion of the reaction, water (10 mL) was added to the reaction mixture. Reaction mixture extracted with ethyl acetate (10 mL). Organic layer was separated, dried over sodium sulphate and concentrated under vacuum at 45 °C. Crude residue was purified by column chromatography on silica gel (5%, 7% ethyl acetate in hexanes) to afford methyl 2-methylene-4-nitro-5-oxo-3,5-diphenylpentanoate with inseparable mixture of isomers (**7a**) (100 mg, 93 % yield) as white solid; *Rf* = 0.5 (n-hexane: ethyl acetate= 9:1)**;** mp: 98 °C-100 °C **;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–8.11 (m, 2H), 7.86–7.84 (m, 2H), 7.69–7.65 (m, 1H), 7.58–7.52 (m, 3H), 7.42–7.38 (m, 4H), 7.35–7.27 (m, 3H), 7.23–7.20 (m, 2H), 7.17–7.11 (m, 3H), 7.10–7.06 (m, 2H), 6.40 (s, 1H), 6.18 (s, 1H), 6.00 (d, *J* = 0.7 Hz, 1H), 5.73 (d, *J* = 0.5 Hz, 1H), 5.12 (dd, *J* = 11.7, 7.7 Hz, 2H), 3.73 (s, 3H), 3.61 (s, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.5, 187.1, 166.0, 165.9, 138.5, 138.4, 136.5, 134.9, 134.9, 134.6, 129.4, 129.2, 129.0, 128.9, 128.8, 128.8, 128.2, 128.1, 127.9, 127.7, 126.7, 90.0, 88.6, 52.3, 49.3, 49.3; IR (KBr): 2964, 1715, 1562, 1359, 1257, 802, 764 cm^{-1}; *m/z* (ESI): $[M + Na]^+$ 362.15 ; HRMS: calcd. For $C_{19}H_{17}NO_5Na$ $[M + Na]^+$ 362.1004, found 362.0990.

Methyl 2-methylene- 4-nitro- 5-oxo-5-phenylpentanoate (8a):

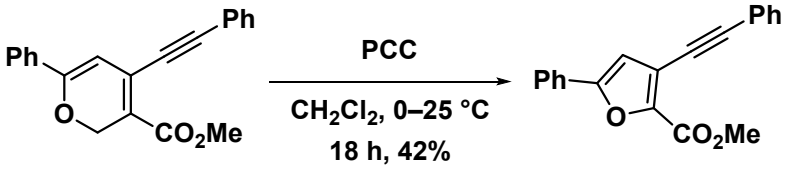


8 **8a**

Methyl 2-(((*tert*-butoxycarbonyl)oxy)methyl)acrylate (**8**) (65 mg, 0.3 mmol) was taken to round bottom flask and 3 mL THF was added at 25 °C. Benzoyl nitromethane (**2a**) (60 mg, 0.36 mmol) was added to it. DABCO (1 mg, 0.009 mmol) was added to it. Reaction mixture was stirred for 12 h at 25 °C. After completion of the reaction, water (10 mL) was added to the reaction mixture.

Reaction mixture extracted with ethyl acetate (10 mL). Organic layer was separated, dried over sodium sulphate, concentrated under vacuum at 45 °C. Crude residue was purified by column chromatography on silica gel (5%, ethyl acetate in hexanes) to afford methyl 2-methylene-4-nitro-5-oxo-5-phenylpentanoate with inseparable mixture of isomers (**8a**) (69 mg, 87%) as colorless liquid; *Rf* = 0.6 (*n*-hexane: ethyl acetate = 9:1)**;** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.03 (m, 2H), 7.63–7.59 (m, 1H), 7.51–7.46 (m, 2 H), 6.45 (dd, *J* = 9.8, 4.5 Hz, 1H), 6.28 (s, 1H), 6.24 (s, 1H), 5.82 (d, *J* = 1.0 Hz, 1H), 5.67 (dd, *J* = 2.0, 1.0 Hz, 1H), 4.51 (dd, *J* = 8.5, 5.1 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 2 H), 3.20–3.09 (m, 2H), 2.93 (td, *J* = 6.8, 1.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.6, 170.3, 165.7, 165.3, 133.9, 133.6, 132.7, 132.4, 132.1, 130.4, 129.2, 128.2, 128.1, 127.5, 88.0, 73.2, 51.4, 51.2, 33.1, 29.3; IR (neat): 3391, 2924, 1705, 1555, 1151, 957 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 263.95 ; HRMS: calcd. For $C_{13}H_{14}NO_5$ $[M + H]^+$ 264.0872, found 264.0873.

Methyl 5-phenyl-3-(phenylethynyl)furan-2-carboxylate (9):

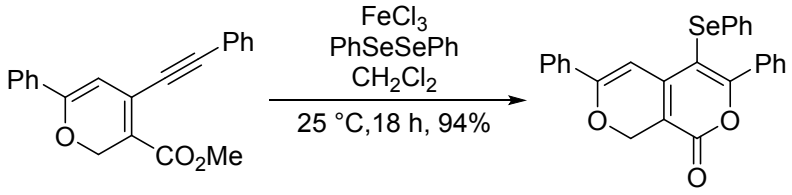


4a **9**

Methyl 6-phenyl-4-(phenylethynyl)-2*H*-pyran-3-carboxylate *(***4a)** (95 mg, 0.3 mmol) was added to round bottom flask containing dichloromethane (3 mL). Reaction mixture allowed cooling to 0 °C. PCC (22 mg, 3.0 mmol) was added to it and stirred reaction mixture for 18 h at 25 °C**.** After completion, reaction mixture was concentrated and purified by column chromatography on silica gel (2% ethyl acetate in hexanes) to afford methyl 5-phenyl-3-(phenylethynyl) furan -2-carboxylate (**9**) **(** 38 mg, 42 %) as colorless liquid ; *Rf* = 0.6 (*n*-hexane: ethyl acetate = 9.5:0.5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.77 (m, 2H), 7.59–7.56 (m, 2H), 7.46–7.42 (m, 2H), 7.40–

7.36 (m, 4H), 6.87 (s, 1H), 3.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.7, 156.6, 143.97, 131.8 (2C), 129.4, 128.9 (3C), 128.9, 128.4 (2C), 125.0 (2C) , 122.7, 116.9, 109.9, 96.6, 80.4, 52.0; IR (neat): 3057, 2943, 1722, 1294, 1084, 767, 697 cm^{-1}; *m/z* (ESI): $[M+H]^+$ 303.20; HRMS: calcd. For $C_{20}H_{15}O_3$ $[M + H]^+$ 303.1021, found 303.1035.

3,6-Diphenyl-4-(phenylselanyl)-1*H*,8*H*-pyrano[3,4-c]pyran-1-one (10):

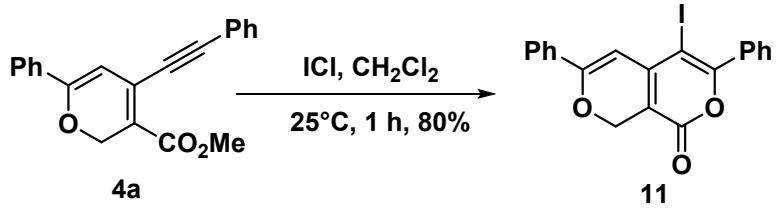


4a **10**

Diphenyl diselenide (48 mg, 0.1533 mmol) was added to 3 mL dichloromethane and $FeCl_3$ (73 mg, 0.45 mmol) was added to it. Reaction mixture was stirred for 15 min at 25 °C. Methyl 6-phenyl-4-(phenylethynyl)-2*H*-pyran-3-carboxylate (**4a**) (95 mg, 0.3 mmol) was dissolved in dichloromethane (2 mL) and added to the reaction mixture and stirred for 18 h at 25 °C. After completion of reaction, reaction mixture diluted with dichloromethane (20 mL) and quenched by saturated ammonium chloride. Organic layer was separated and washed by saturated brine soln. Organic layer was dried over sodium sulphate and evaporated under reduced pressure at 45 °C. Crude residue was purified by column chromatography on silica gel (5% ethyl acetate in hexanes) to afford 3,6-diphenyl-4- (phenylselanyl)-1*H*,8*H*-pyrano[3,4-c]pyran-1-one (**10**) (88 mg, 94%) as yellow solid; *Rf* = 0.3 (*n*-hexane: ethyl acetate = 9:1)**;** mp:145 °C–148 °C **;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.62 (m, 2H), 7.52–7.50 (m, 2H), 7.47–7.33 (m, 7H), 7.25 (d, *J* = 2.7 Hz, 2H), 7.23–7.16 (m, 2H), 6.63 (s, 1H), 5.26 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 161.99, 158.3, 147.8, 132.6, 131.5, 130.9, 130.0, 129.5, 128.7 (2C), 128.5 (2C), 127.99 (2C), 127.5 (2C), 126.9 (2C), 125.8, 125.7 (2C), 102.8, 102.2, 98.2, 63.3; IR (KBr): 2921, 2848,

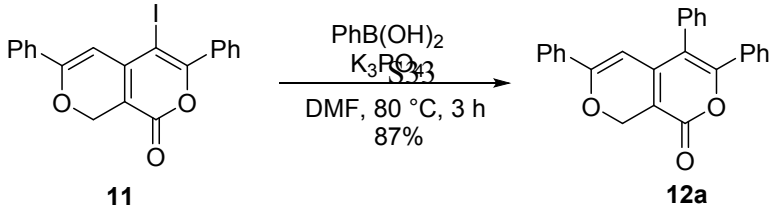
1709, 1552, 1263, 803, 767 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 459.15; HRMS: calcd. For $C_{26}H_{19}O_3Se$ $[M + H]^+$ 459.0499, found 459.0500.

4-Iodo-3,6-diphenyl-1*H*,8*H*-pyrano[3,4-c]pyran-1-one (11):



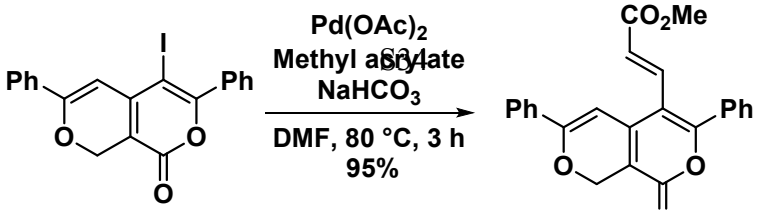
Methyl 6-Phenyl-4-(phenylethynyl)-2*H*-pyran-3-carboxylate (**4a)** (500 mg, 1.58 mmol) was added to round bottom flask containing 7 mL dichloromethane. Reaction mixture allow to cool 0 °C. Iodine monochloride (308 mg, 1.9 mmol) was added and stirred for 1 h at 25 °C. After completion of the reaction (monitored by TLC, reaction mixture quenched by sat. sodium thiosulphate solution and extracted with diluted with 20 mL diethyl ether. Organic layer washed by 20 mL sat. brine. Organic layer was separated and dried over sodium sulphate and concentrated under reduced pressure at 35 °C. Crude residue purified by column chromatography on silica gel (5% ethyl acetate in hexanes) to afford 4-iodo-3,6-diphenyl-*1H,8H*-pyrano[3,4-c]pyran-1-one (**11**) **(** 542 mg, 80 % yield) as yellow Solid; *Rf* = 0.4 (n-hexane: ethyl acetate = 9.5:0.5); mp : 194–196 °C**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.73 (m, 2H), 7.61–7.58 (m, 2H), 7.43–7.36 (m, 6H), 6.49 (s, 1H), 5.19 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 160.8, 159.3, 147.8, 134.8, 132.3, 131.4, 130.6, 129.6 (2C) , 128.7 (2C), 128.2 (2C), 126.6 (2C), 103.4, 102.5, 73.2, 64.6; IR (KBr): 3638, 2927, 2853, 1711, 1558, 1454, 1278, 767 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 429.10 ; HRMS: calcd. For $C_{20}H_{14}O_3I$ $[M + H]^+$ 428.9988, found 428.9996.

3,4,6-Triphenyl-1*H*,8*H*-pyrano[*3,4-c*]pyran-1-one(12a):



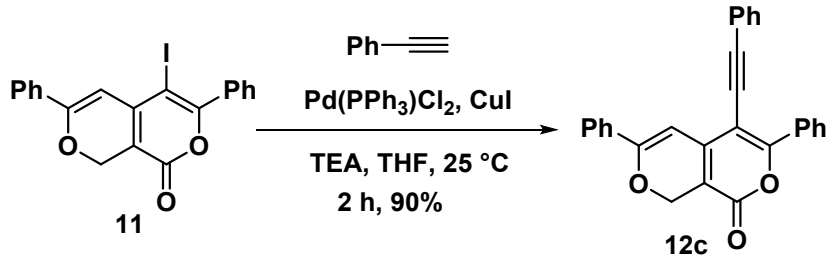
4-Iodo-3,6-diphenyl-*1H,8H*-pyrano[3,4-c]pyran-1-one (**11**) (130 mg, 0.3 mmol) was added to DMF (3 mL). Tripotassium phosphate (129 mg, 0.6 mmol) was added to the reaction mass and nitrogen gas was purged for 10 min. Tetrakis(triphenylphosphine)palladium(0) (10 mol %) followed by phenylboronic acid (55 mg, 0.45 mmol) was added to it. Reaction mixture was stirred for 3 h at 80 °C. After completion of reaction, reaction mixture was cooled to 25 °C and diluted with diethyl ether (10 mL) and water (10 mL). Organic layer separated and aqueous layer was extracted with diethyl ether (10 mL). Combined organic layers were washed with water (10 mL) and sat. brine (10 mL). Organic layer was separated, dried over sodium sulphate and concentrated under reduced pressure. Crude residue was purified by column chromatography on silica gel (5%, 10% ethyl acetate in hexanes) to afford 3,4,6-triphenyl-1*H*,8*H*- pyrano[*3,4-c*]pyran-1-one (**12a**) (100 mg, 87 %) as yellow solid; *Rf* = 0.4 (n-hexane: ethyl acetate = 8.5:1.5); mp: 172 °C–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.54 (m, 2H), 7.44–7.32 (m, 6H), 7.30–7.28 (m, 2H), 7.25–7.17 (m, 5H), 5.87 (s, 1H), 5.31 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 159.9, 157.3, 146.8, 133.6, 132.7, 132.6, 130.9 (2C), 130.8, 129.5, 129.2 (2C), 129.0 (2C), 128.6 (2C), 128.3, 127.9 (2C), 126.3 (2C), 115.9, 103.5, 96.5, 64.4; IR (KBr): 2925, 2853, 2331, 1702, 1566, 1447, 1224, 877 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 379.25; HRMS: calcd. For $C_{26}H_{19}O_3$ $[M + H]^+$ 379.1334, found 379.1324.

Methyl(*E*)-3-(1-oxo-3,6-diphenyl-*1H,8H*-pyrano[*3,4-c*]pyran-4-yl)acrylate (12b):



4-Iodo-3,6-diphenyl-*1H,8H*-pyrano[3,4-c]pyran-1-one (**11**) (129 mg, 0.3014 mmol) was added to DMF (3 mL). Sodium bicarbonate (19 mg, 0.9042 mmol) followed by methyl acrylate (20 mg, 0.4521 mmol) was added to the reaction mass and nitrogen gas was purged for 10 min. Palladium (II) acetate (10 mol %) was added to it. Reaction mixture was heated to 80 °C and stirred for 3 h at 80 °C. After completion of the reaction, reaction mass was cooled to 25 °C and diluted with water (5 mL) and extracted with diethyl ether (2 x 5 mL). Combined organic layers were washed with water (4 x 5 mL). Organic layer was separated, dried over sodium sulphate and concentrated under reduced pressure at 45 °C. Obtained crude was purified by column chromatography on silica gel (5%, 10% ethyl acetate in hexanes) to afford methyl (*E*)-3-(1-oxo-3,6-diphenyl-*1H,8H*-pyrano -[*3,4-c*] -pyran-4-yl)acrylate (111 mg, 95 % yield) as yellow solid; *Rf* = 0.3 (n-hexane: ethyl acetate = 9:1); mp 164°C–166°C**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.74 (m, 2H), 7.59–7.57 (m, 2H), 7.52 (d, J = 16.3 Hz, 1H), 7.48–7.42 (m, 6H), 6.45 (s, 1H), 6.17 (d, J = 16.3 Hz, 1H), 5.28 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 163.0, 160.1, 158.9, 144.98, 137.8, 132.5, 132.0, 131.2, 130.9, 129.6 (2C), 128.7 (2C), 128.5 (2C), 126.5 (2C), 124.9, 109.9, 104.1, 95.6, 64.3, 52.0; IR (KBr): 2948, 2852, 2333, 1713, 1559, 1447, 769, 694 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 387.25; HRMS: calcd. For $C_{24}H_{19}O_5$ $[M + H]^+$ 387.1232, found 387.1224.

3,6-Diphenyl-4-(phenylethynyl)-1*H*,8*H*-pyrano[3,4-c]pyran-1-one (12c):



4-Iodo-3,6-diphenyl-*1H,8H*-pyrano[3,4-c]pyran-1-one (**11**) (130 mg, 0.3 mmol) was added to triethyl amine (3 mL) and THF (3 mL). Nitrogen gas was purged for 10 min. Phenyl acetylene (61 mg, 0.4673 mmol) was added to it. Bis(triphenylphosphine)palladium (II) chloride (10 mol %) followed by copper iodide (5 mol %) was added. Reaction mixture was stirred for 2 h at 25°C. After completion of reaction, reaction mixture diluted with diethyl ether (10 mL) and water (10 mL). Organic layer washed by 1N HCl solution and brine. Organic layer separated, dried over sodium sulphate and concentrated under reduced pressure at 35 °C. Crude residue purified by column chromatography on silica gel (5%, 10% ethyl acetate in hexanes) to afford 3,6-diphenyl-4-(phenylethynyl)-1*H*,8*H*-pyrano[3,4-c]pyran-1-one (**12c**) **(** 110 mg, 90%) as yellow Solid; *Rf* = 0.3 (*n*-hexane: ethyl acetate = 9:1); mp: 176–178 °C**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.18 (m, 2H), 7.82–7.80 (m, 2H), 7.52–7.49 (m ,5H), 7.48–7.45 (m, 3H), 7.42–7.39 (m, 3H), 6.74 (s, 1H), 5.29 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 162.4, 158.6, 146.6, 132.6, 132.1, 131.3(2C), 131.2, 131.0, 128.9 (2C), 128.8 (2C), 128.8 (2C), 128.7 (2C), 128.3 (2C), 126.5, 122.7, 102.7, 98.6, 97.5, 96.4, 82.1, 64.2; IR (KBr): 2925, 2858, 2258, 1712, 1562, 1225, 807 cm^{-1}; *m/z* (ESI): $[M + H]^+$ 403.25; HRMS: calcd. For $C_{28}H_{19}O_3$ $[M + H]^+$ 403.1334, found 403.1342.

5. Gram scale reaction procedure for 4a.

The mixture of methyl 3-((*tert*-butoxycarbonyl)oxy)-2-methylene-5-phenylpent -4-ynoate **(1a)** (1.9 g, 6.0 mmol) was taken to rallowed to react with benzoyl nitromethane **(2a)** (1.19 g, 7.2 mmol) in THF (60 mL). The reaction mixture was cooled to 0 °C and DABCO (20 mg, 0.18

mmol) was added to the reaction mixture and stirred for 2 h at 0 °C. Temperature of the reaction mixture rose to 25°C and stirred for 3 h. The reaction mixture was diluted with water (60 mL) and extracted with ethyl acetate (2 x 60 mL). Combined organic layer and dried over anhydrous Na_2SO_4. Organic layer was concentrated under reduced pressure at 40 °C. Obtained crude oil was purified by column chromatography on silica gel (ethyl acetate:hexanes) to afford the methyl 6-phenyl -4-(phenylethynyl)-2*H*-pyran-3-carboxylate (**4a)** (1.33 g, 70% yield).

6. References:

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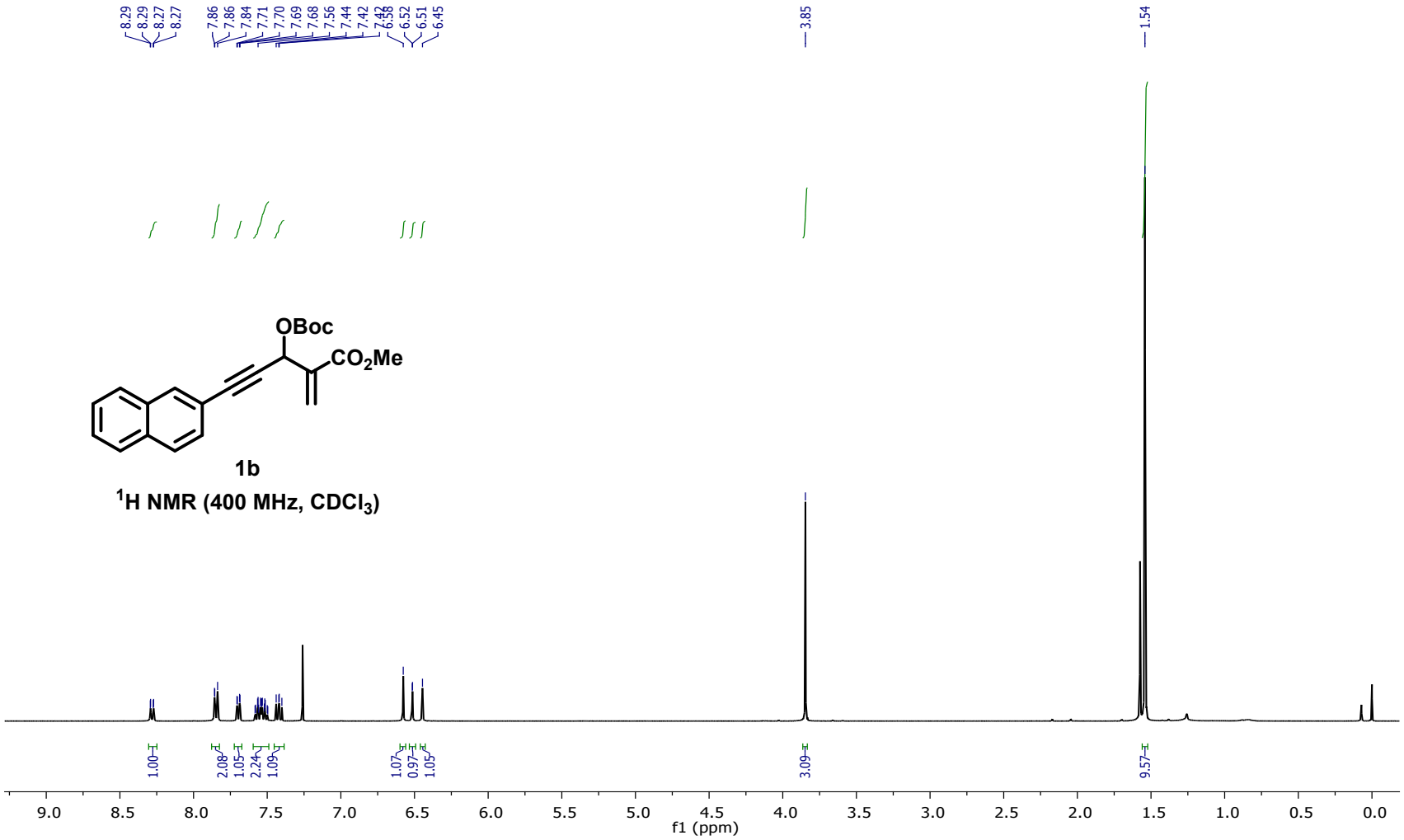
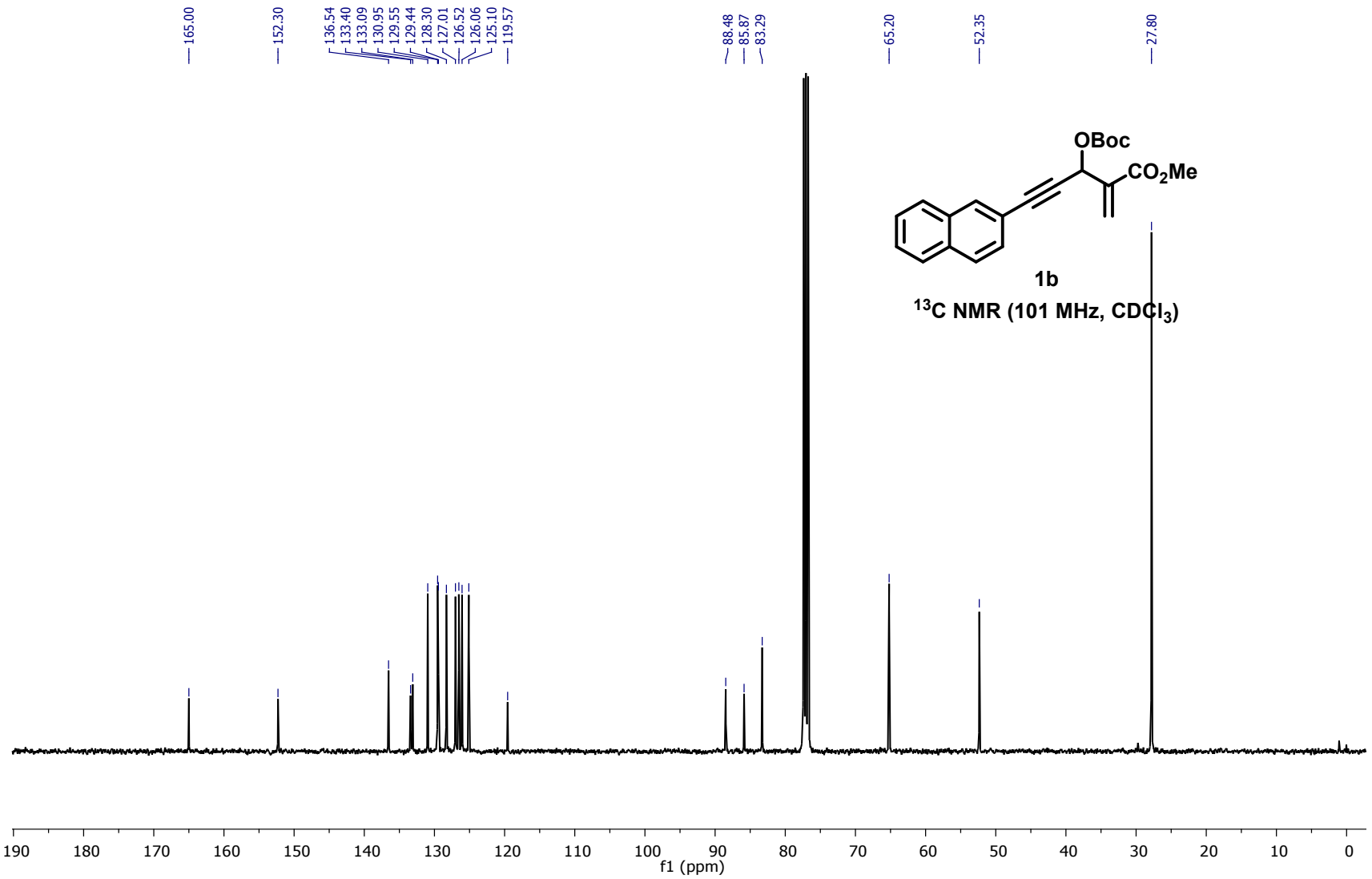
7. ^{1}H NMR and ^{13}C NMR Spectral Copies of compounds:

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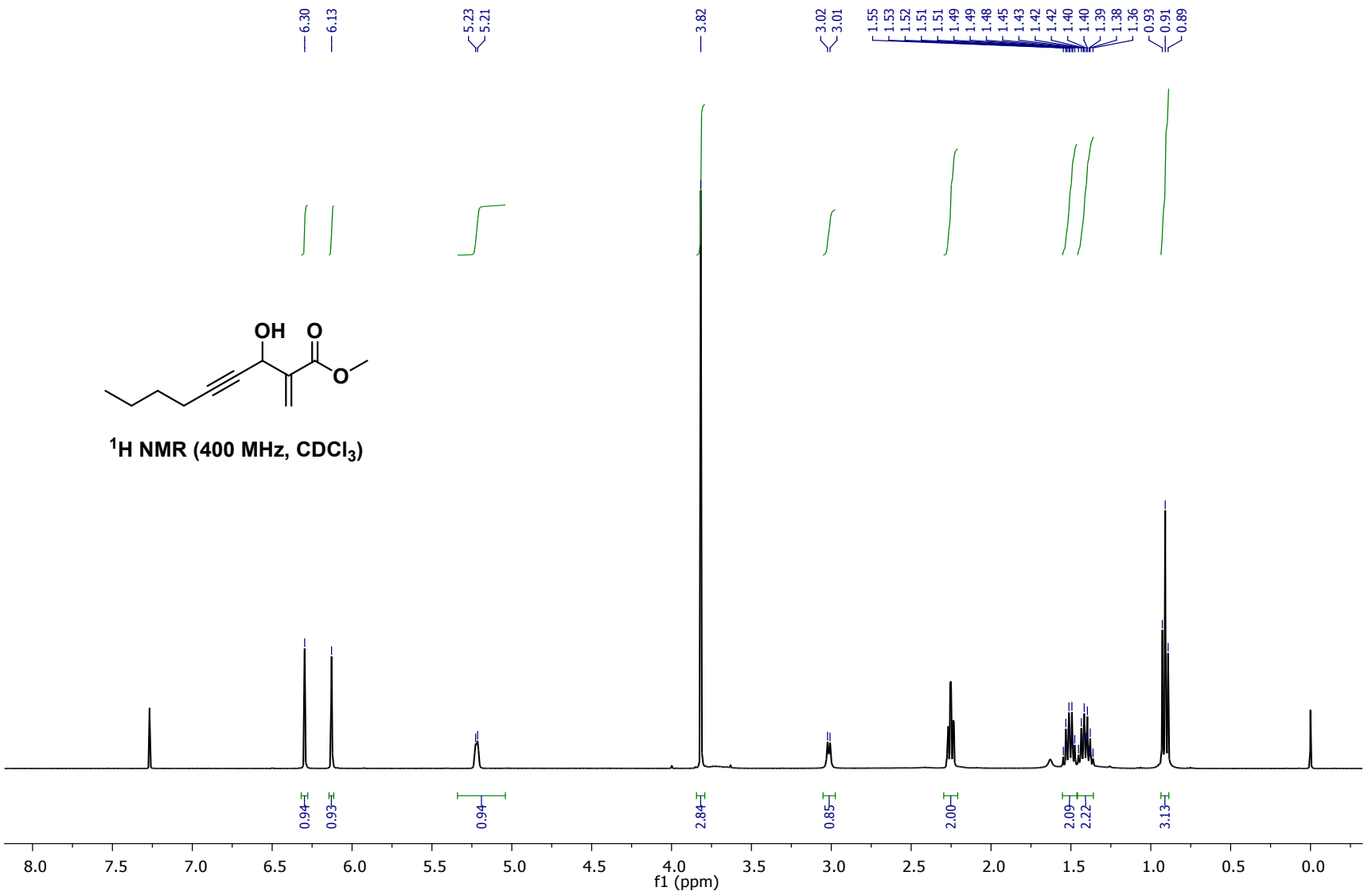
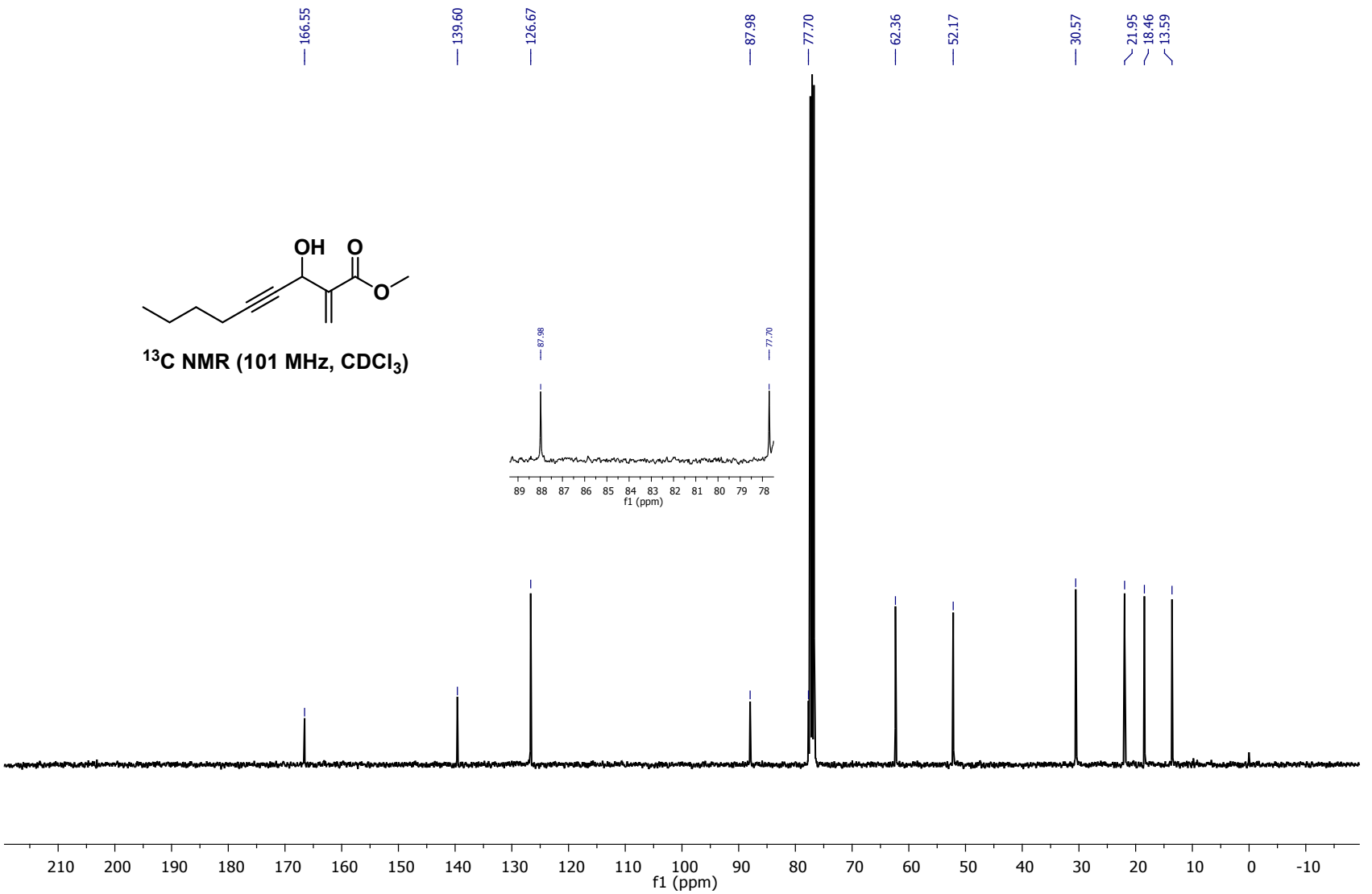
152.30
136.54
133.40
133.09
130.95
129.55
129.44
128.30
127.01
126.52
126.06
125.10
119.57
88.48
85.87
83.29
65.20
52.35
27.80
OBoc
CO2Me
1b
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)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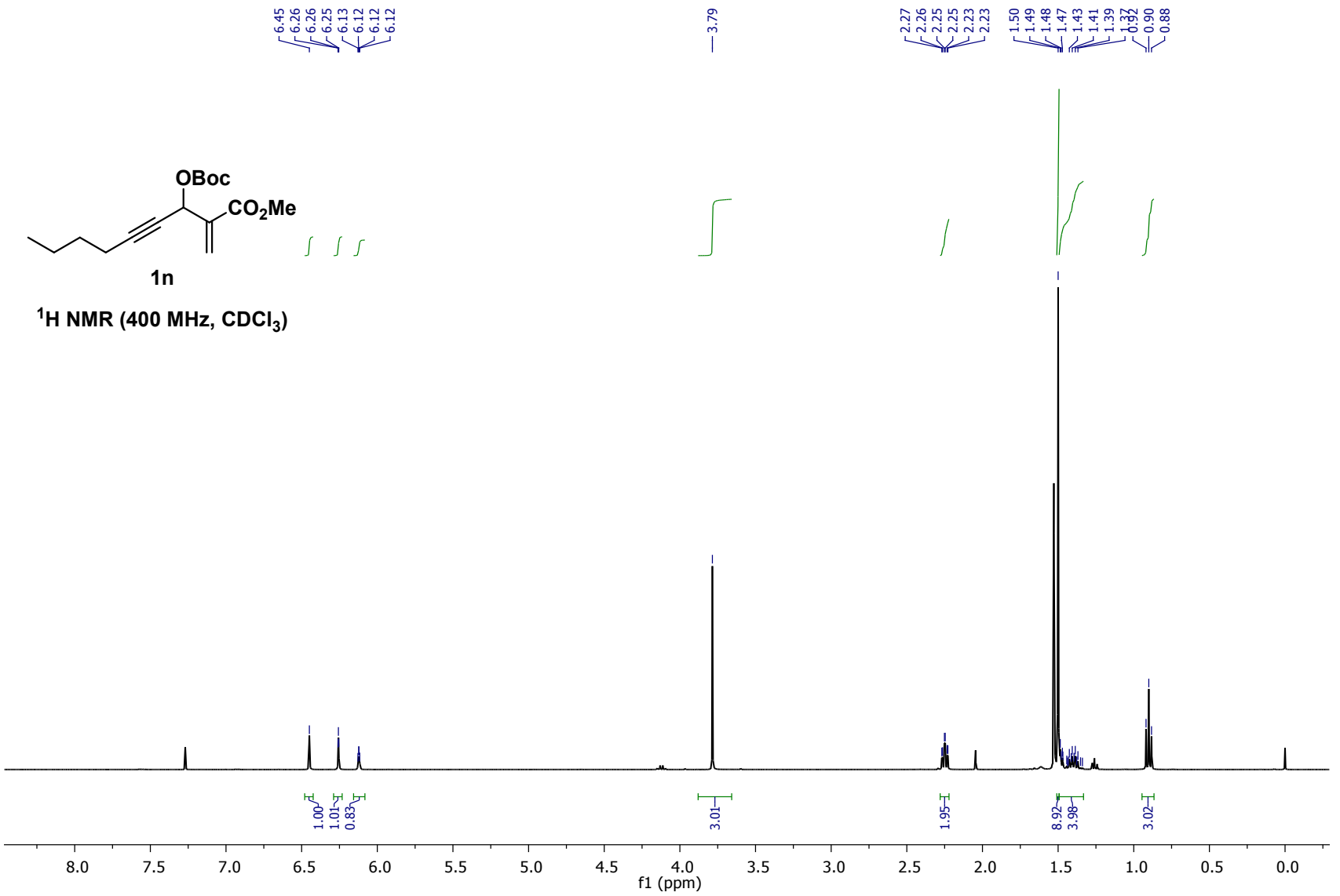
139.60
126.67
87.98
77.70
62.36
52.17
30.57
21.95
18.46
13.59
OH
O
O
13C NMR (101 MHz, CDCl3)
87.98
77.70
89 88 87 86 85 84 83 82 81 80 79 78
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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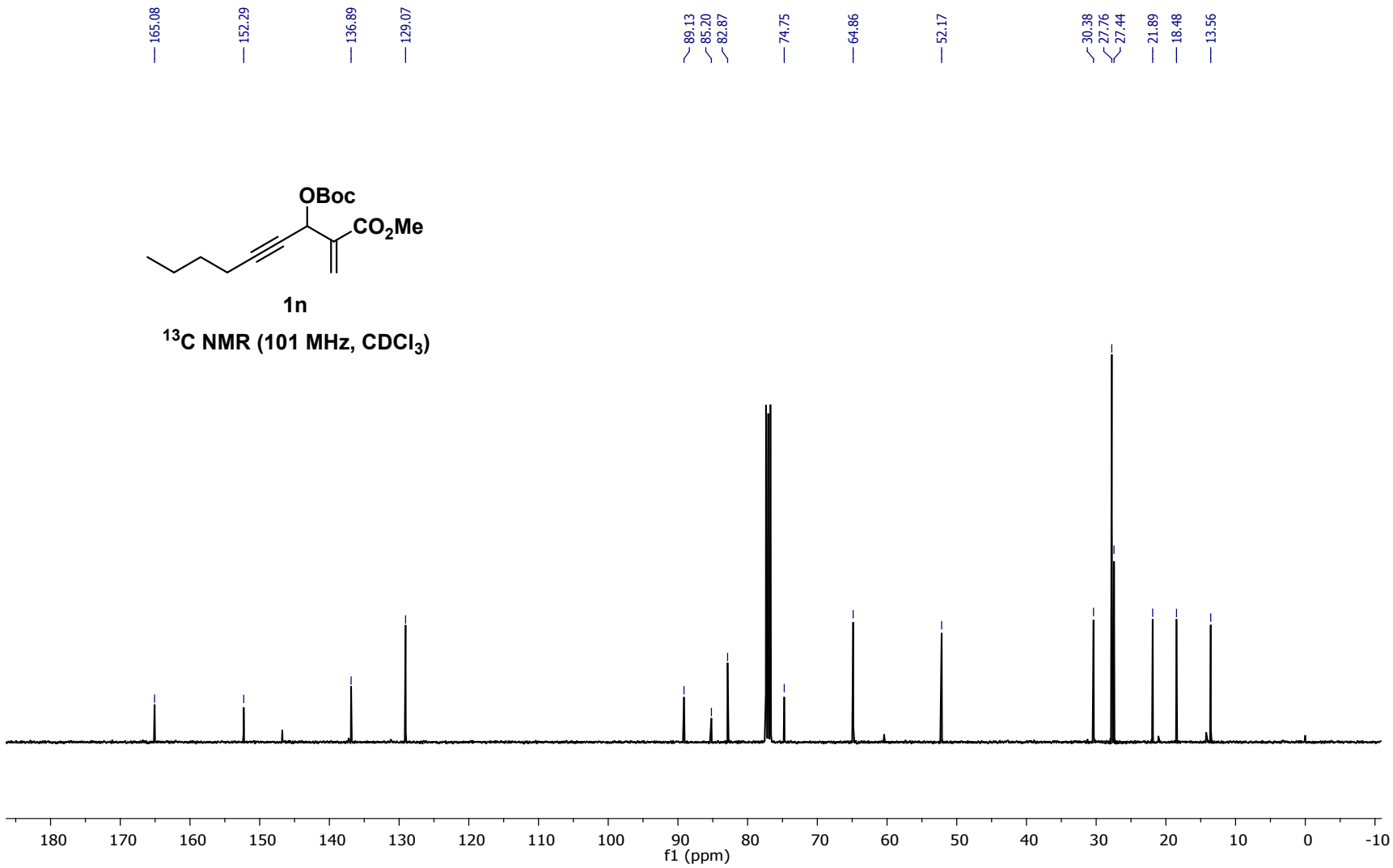
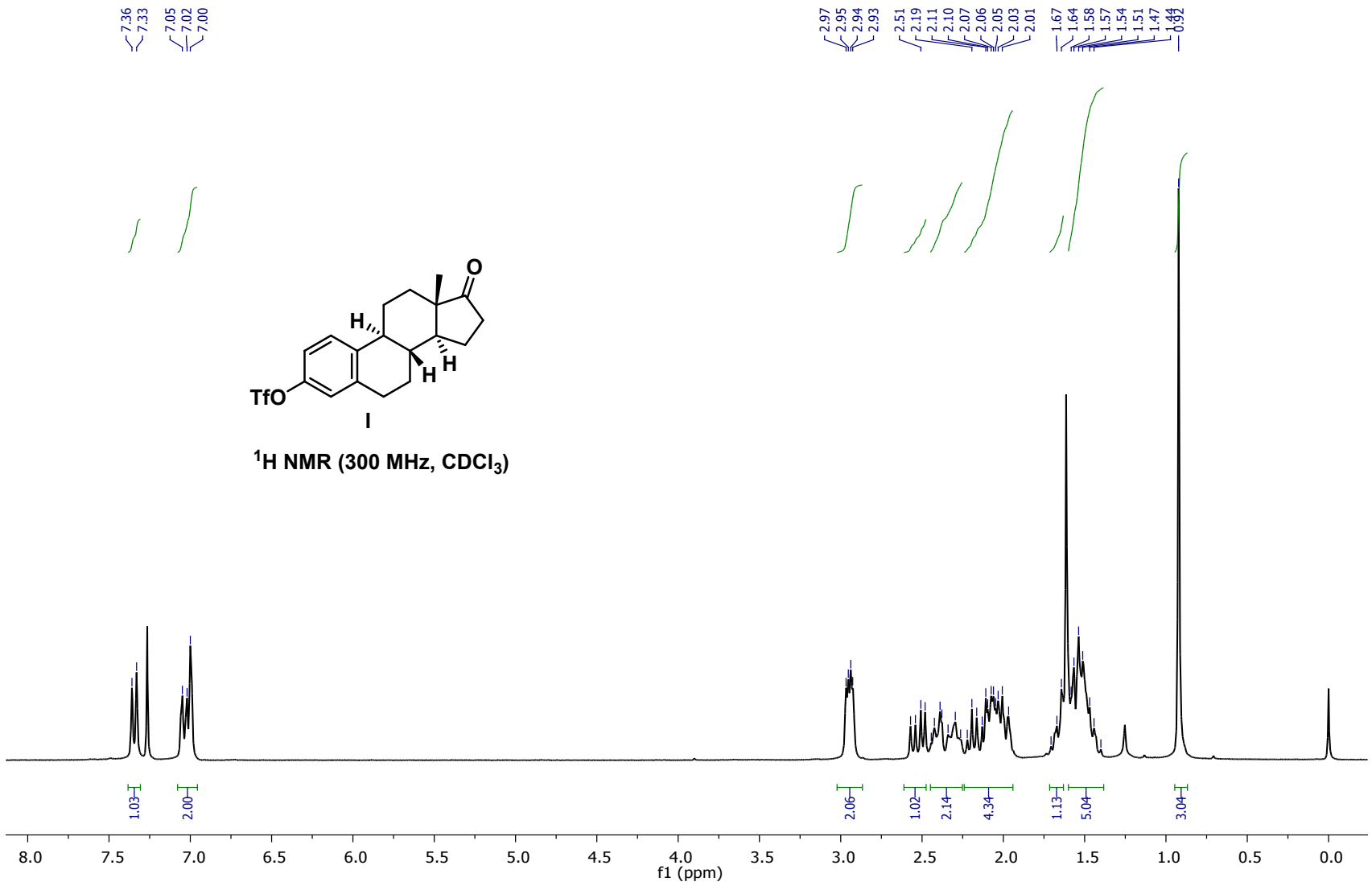
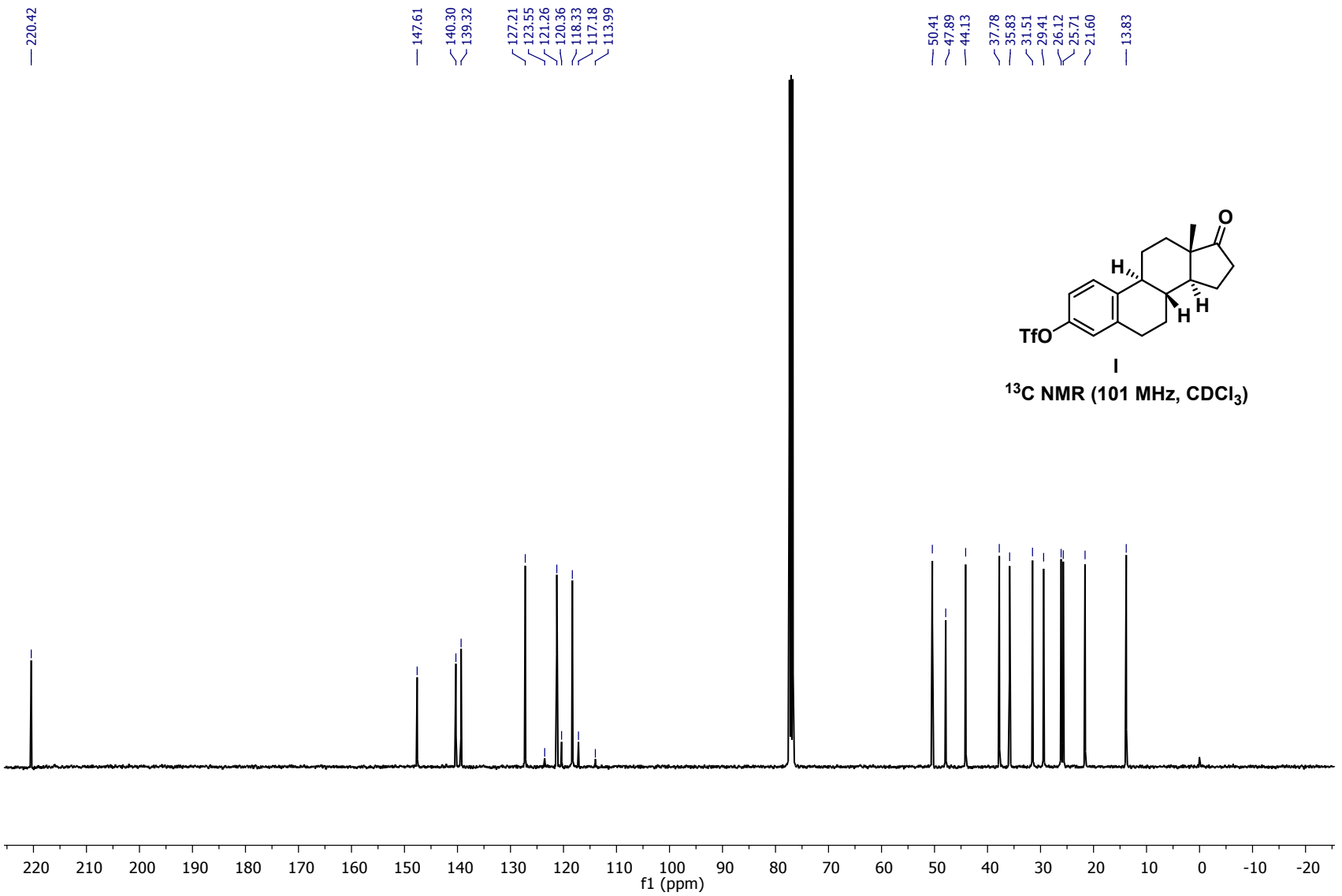
6.26
6.26
6.25
6.13
6.12
6.12
6.12
3.79
2.27
2.26
2.25
2.25
2.23
2.23
1.50
1.49
1.48
1.47
1.43
1.41
1.39
1.37
0.92
0.90
0.88
OBoc
CO2Me
1n
1H NMR (400 MHz, CDCl3)
1.00
1.01
0.83
3.01
1.95
8.92
3.98
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.08
152.29
136.89
129.07
89.13
85.20
82.87
74.75
64.86
52.17
30.38
27.76
27.44
21.89
18.48
13.56
OBoc
CO2Me
1n
13C NMR (101 MHz, CDCl3)
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 (300 MHz, $CDCl_3$)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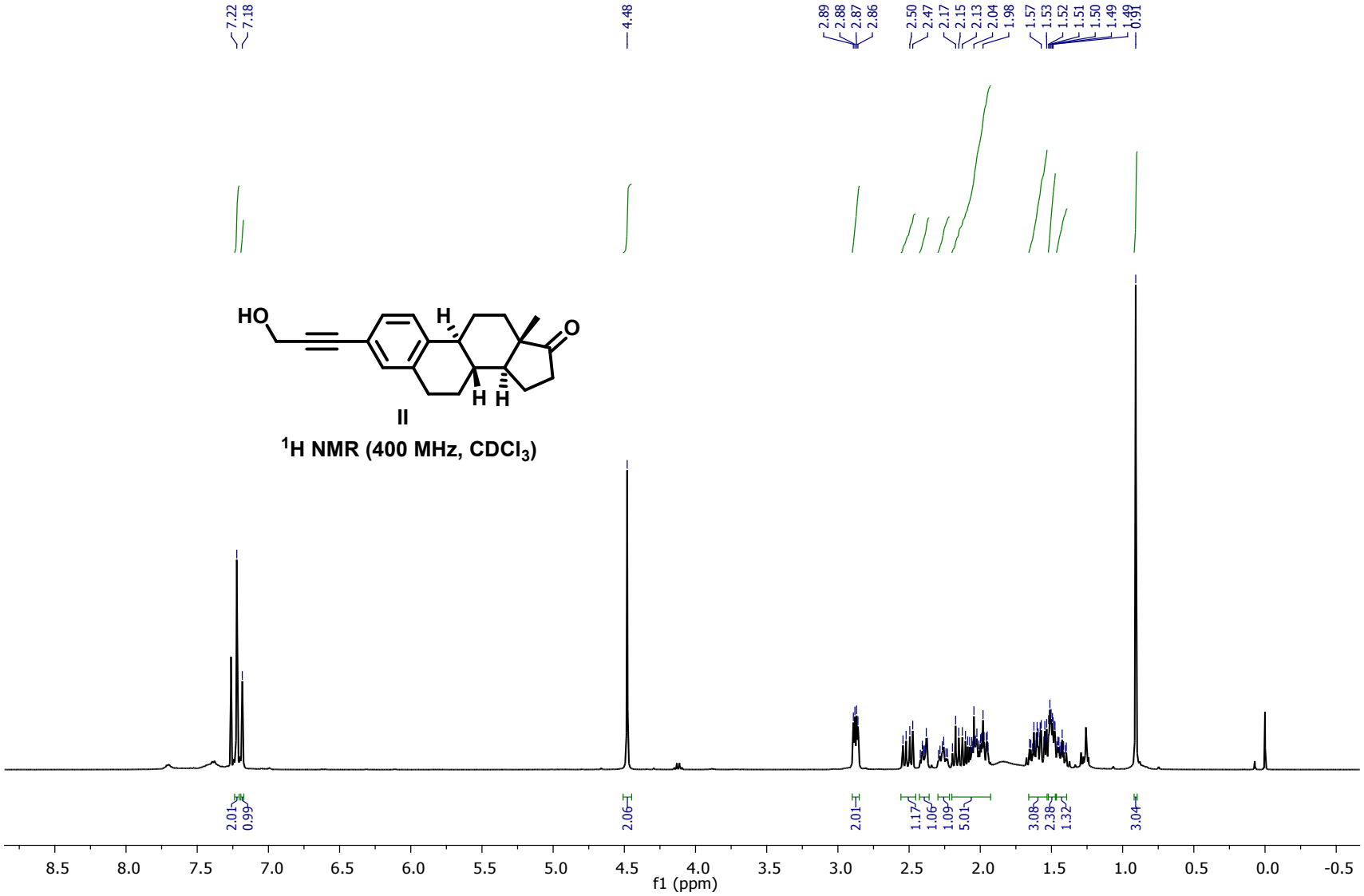
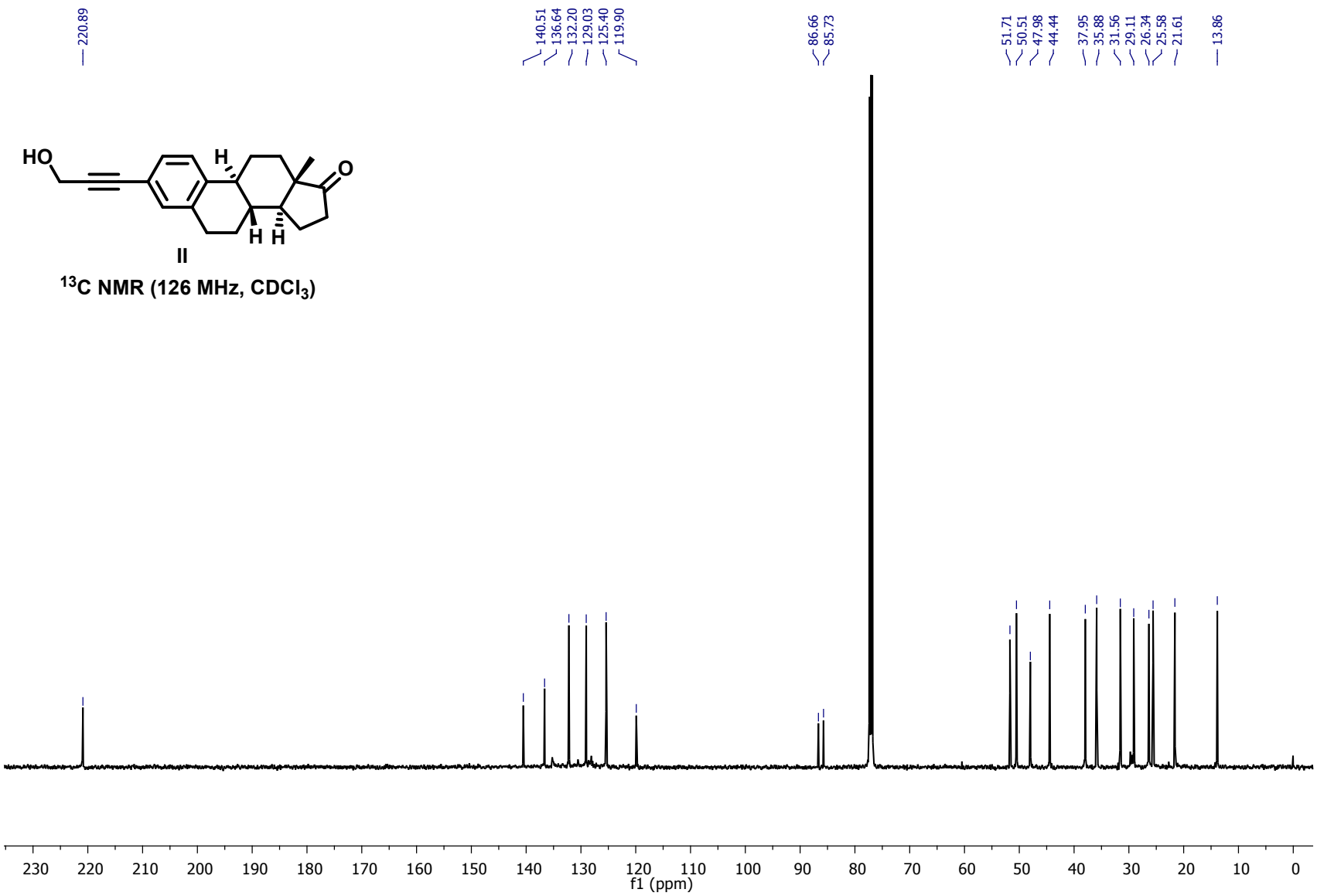
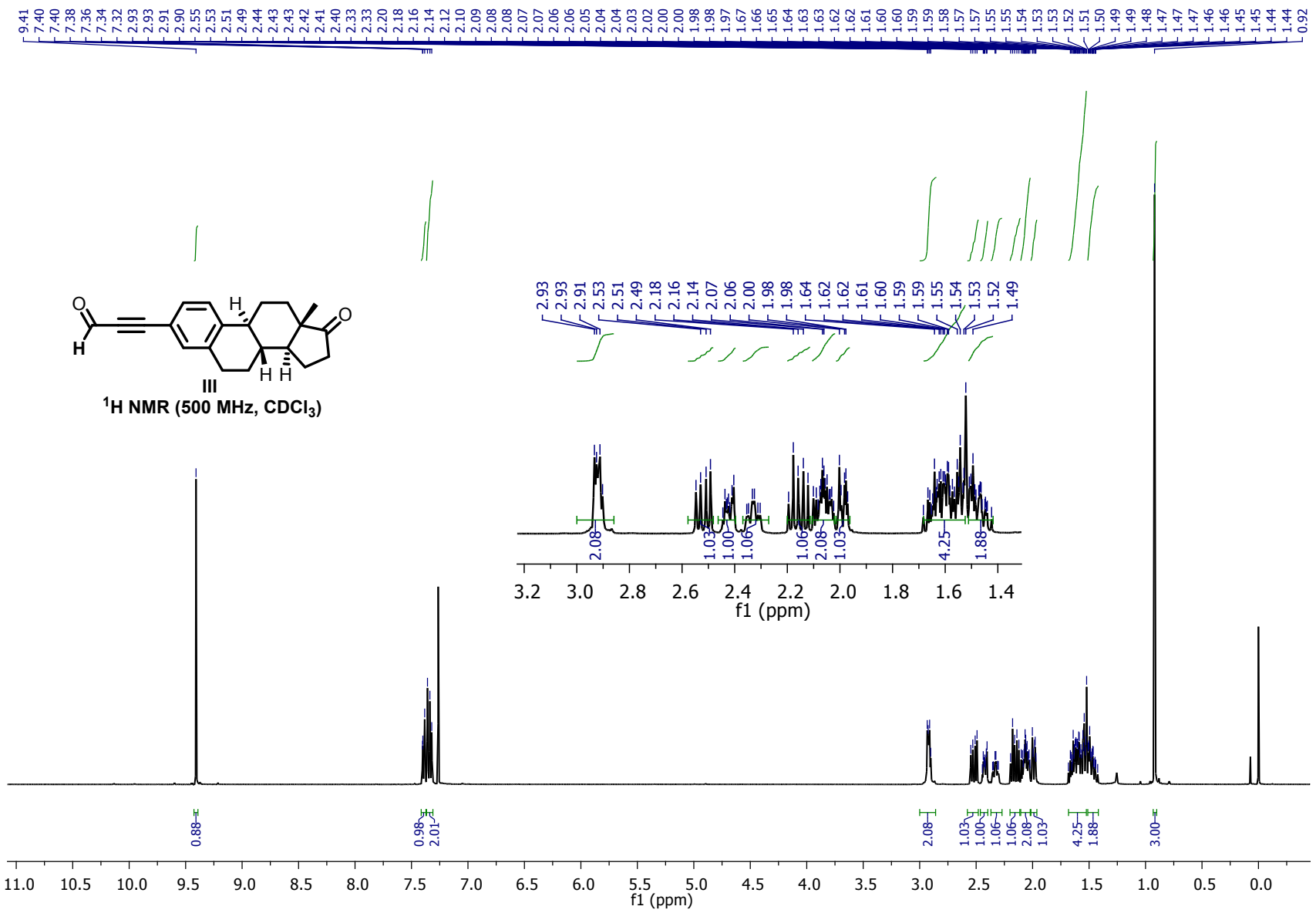
140.30
139.32
127.21
123.55
121.26
120.36
118.33
117.18
113.99
50.41
47.89
44.13
37.78
35.83
31.51
29.41
26.12
25.71
21.60
13.83
O
H
H
H
TfO
I
13C NMR (101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

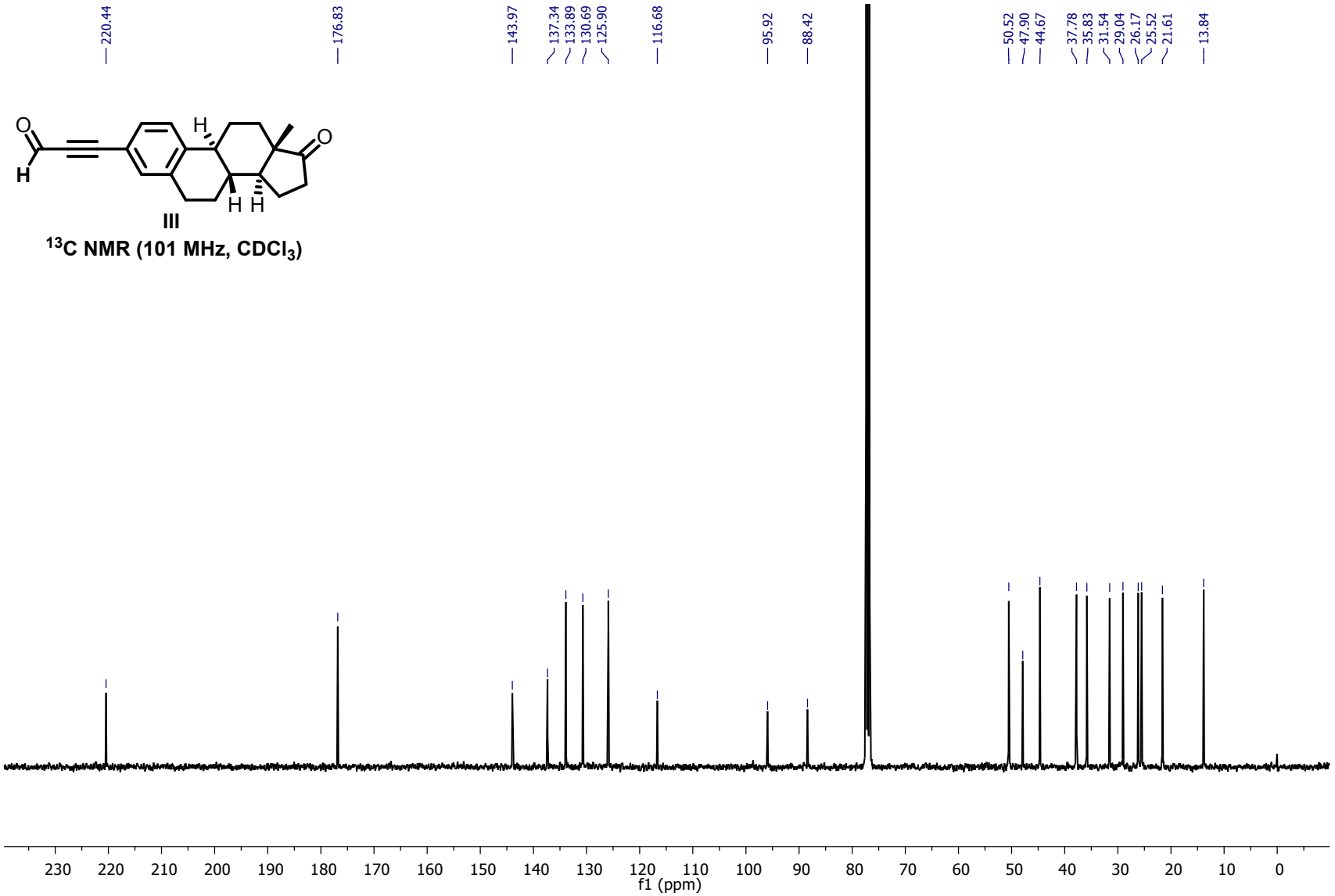

7.22
7.18
4.48
2.89
2.88
2.87
2.86
2.50
2.47
2.17
2.15
2.13
2.04
1.98
1.57
1.53
1.52
1.51
1.50
1.49
0.91
HO
H
O
H H
II
^{1}H NMR (400 MHz, CDCl$_3$)
2.01
0.99
2.06
2.01
1.17
1.06
1.09
5.01
3.08
2.38
1.32
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



II

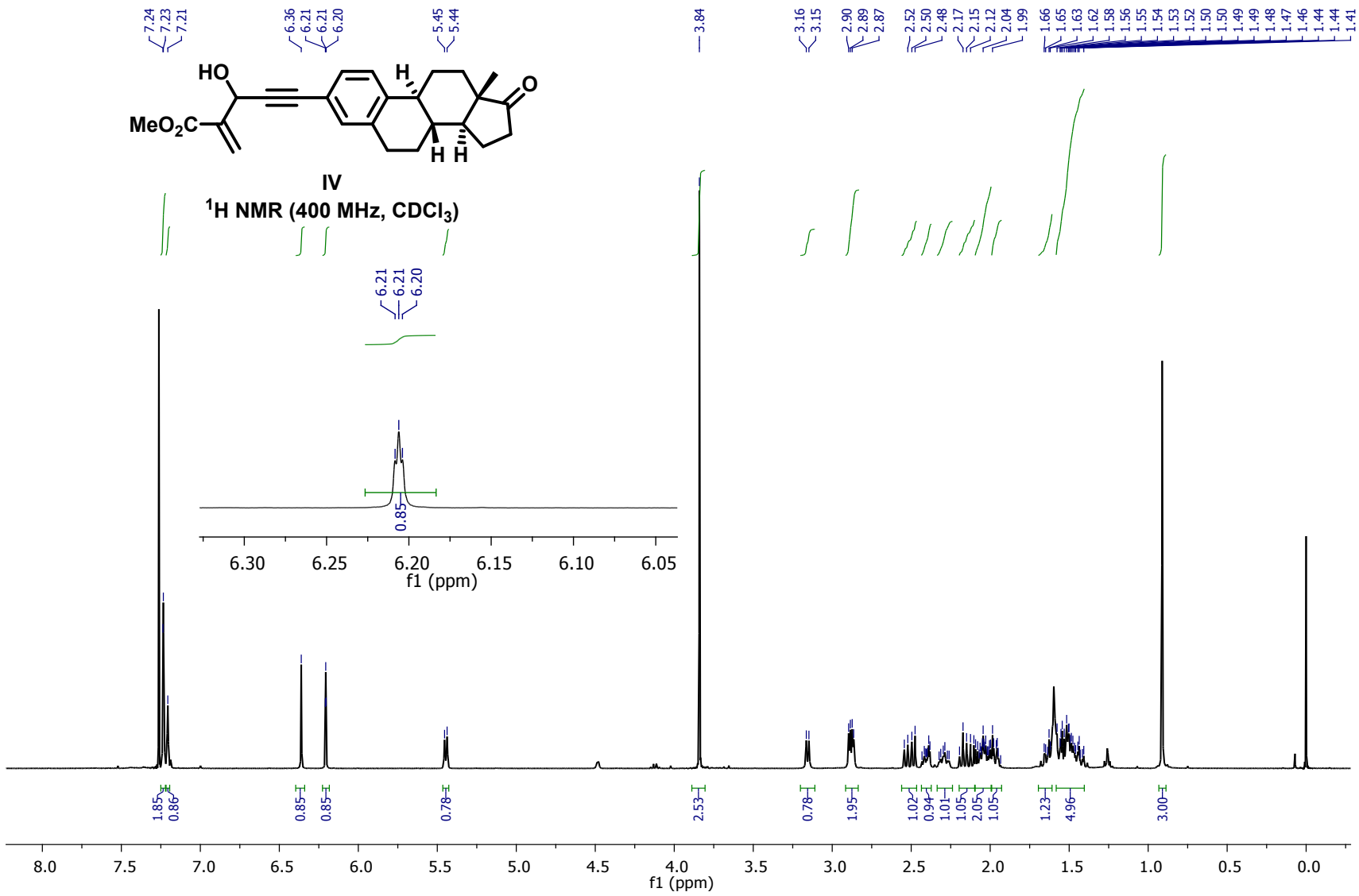
^{13}C NMR (126 MHz, $CDCl_3$)

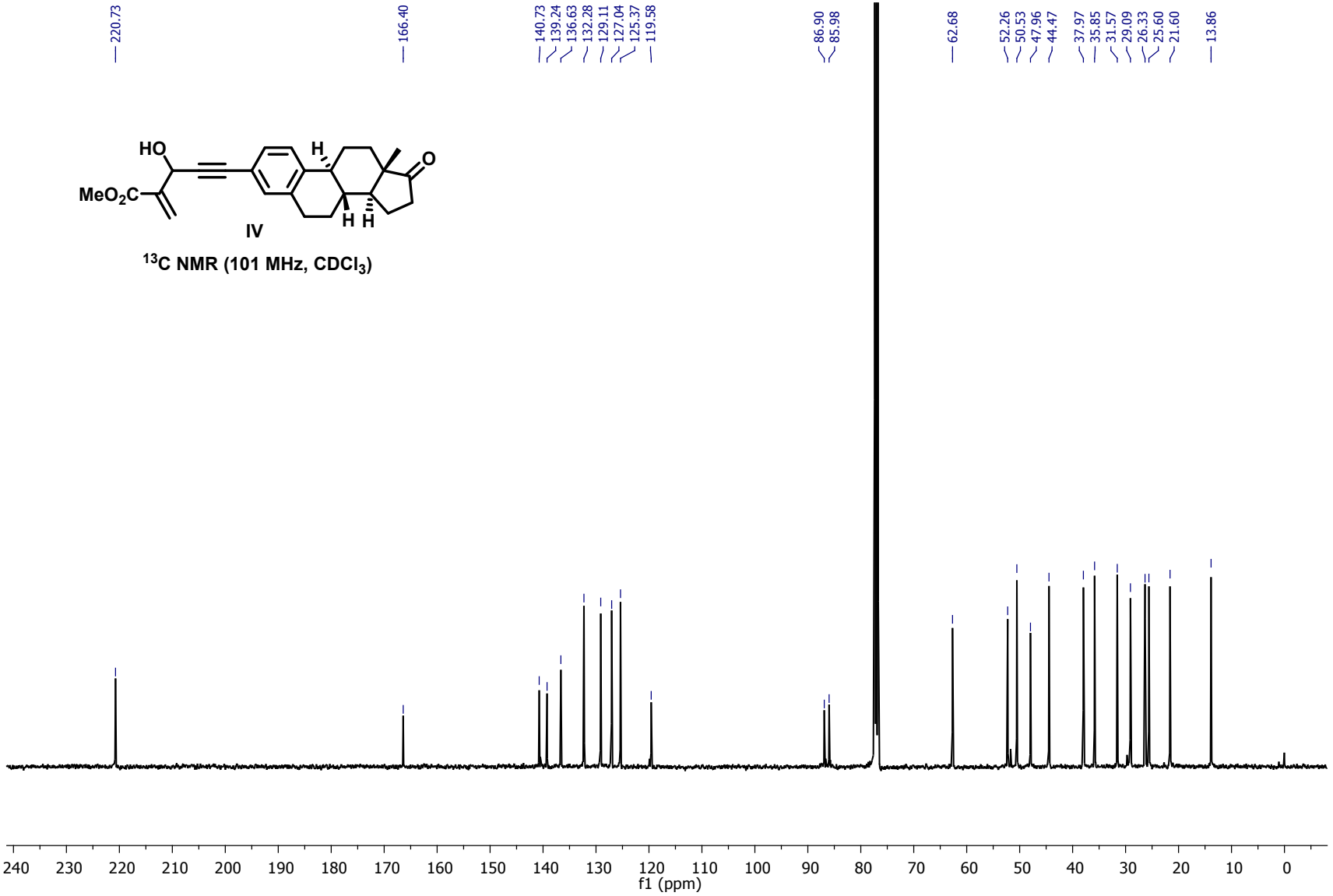

III
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)
f1 (ppm)

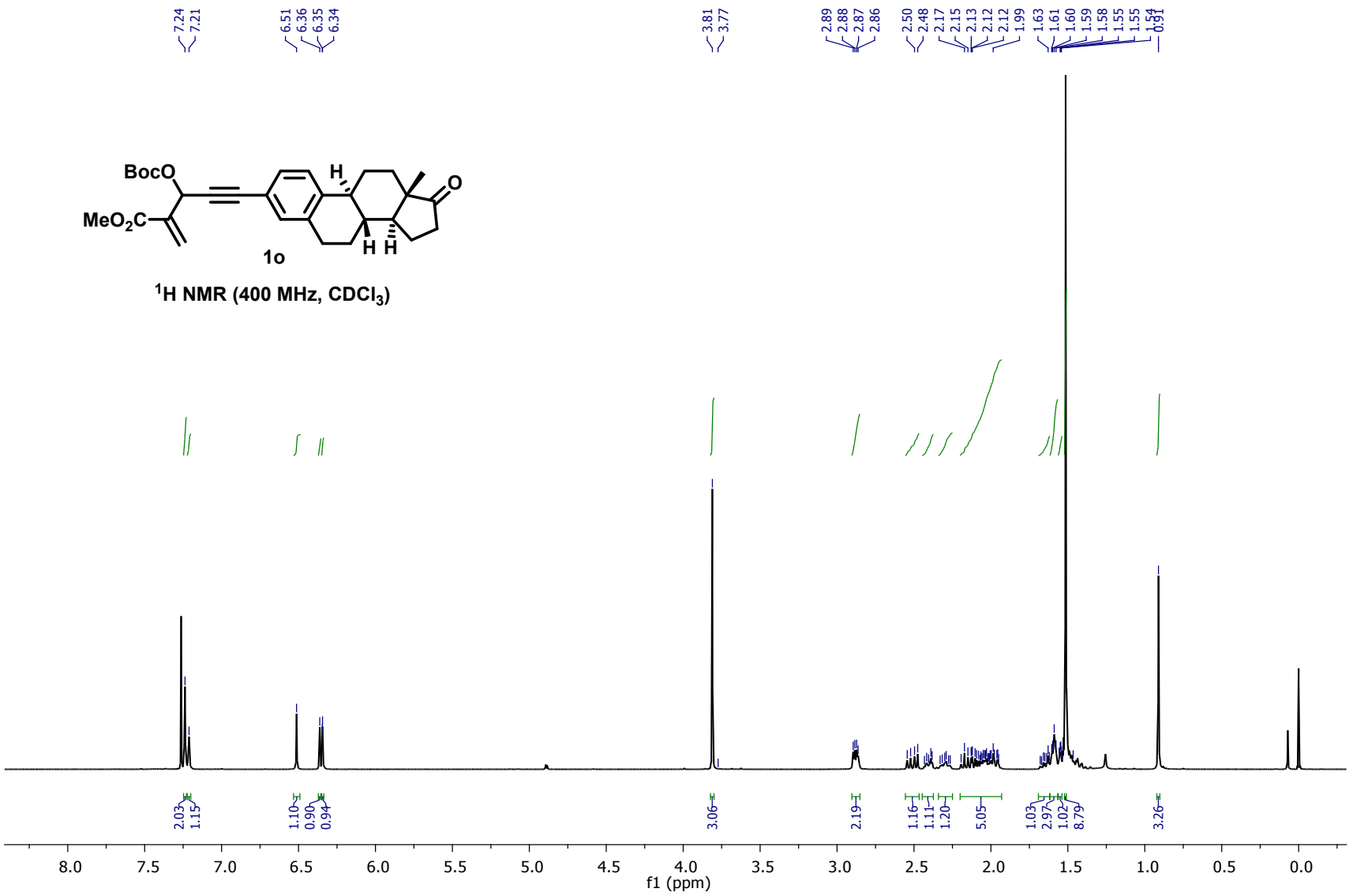


III

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


HO
MeO2C
H
O
H H
IV
1H NMR (400 MHz, CDCl3)
f1 (ppm)
f1 (ppm)


220.73
166.40
140.73
139.24
136.63
132.28
129.11
127.04
125.37
119.58
86.90
85.98
62.68
52.26
50.53
47.96
44.47
37.97
35.85
31.57
29.09
26.33
25.60
21.60
13.86
HO
H
O
MeO2C
H H
IV
13C NMR (101 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


BocO
MeO2C
H
O
H H
1o
1H NMR (400 MHz, CDCl3)
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7.21
6.51
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6.35
6.34
3.81
3.77
2.89
2.88
2.87
2.86
2.50
2.48
2.17
2.15
2.13
2.12
2.12
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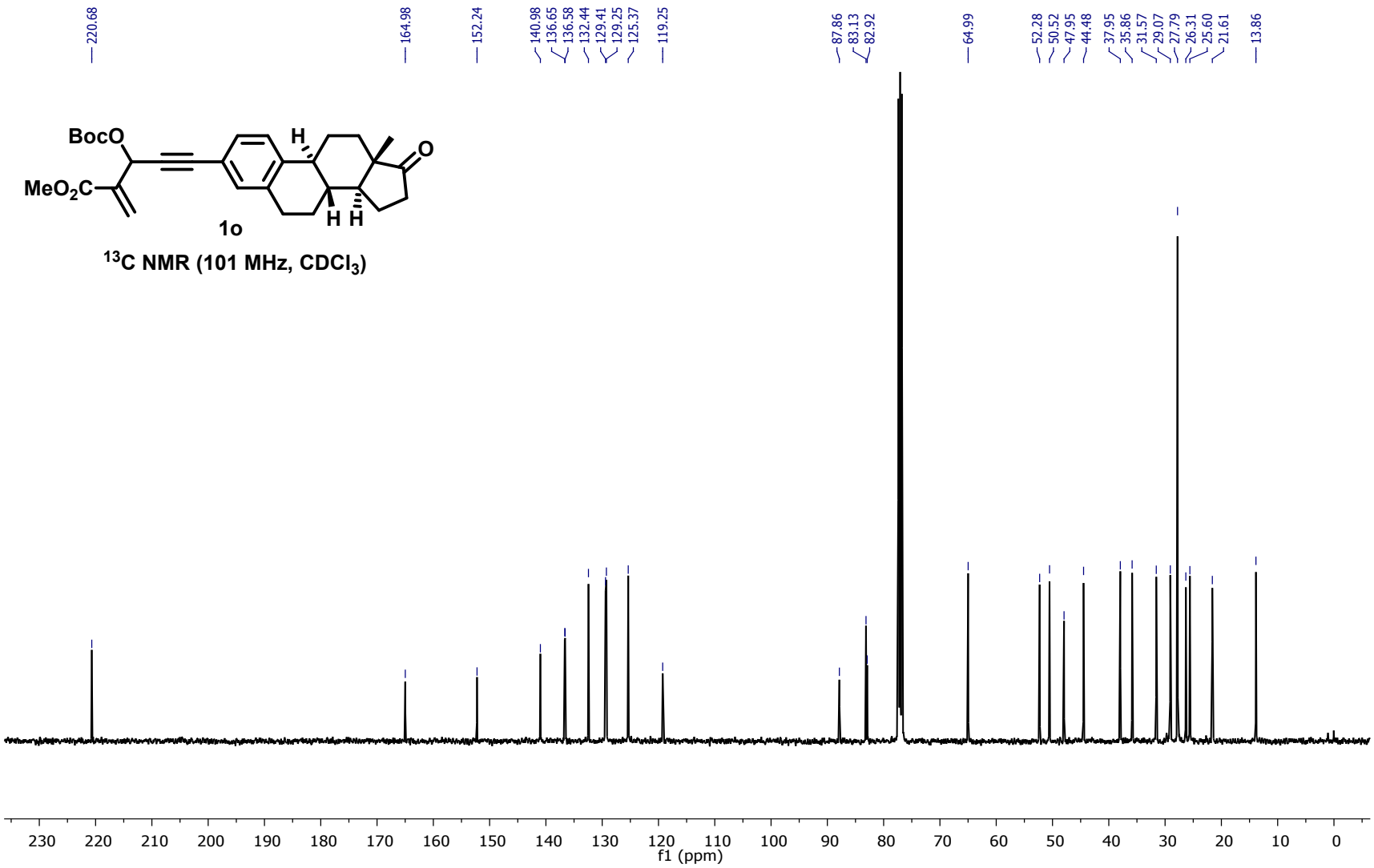
1.63
1.61
1.60
1.59
1.58
1.55
1.55
1.54
0.91
2.03
1.15
1.10
0.90
0.94
3.06
2.19
1.16
1.11
1.20
5.05
1.03
2.97
1.02
8.79
3.26
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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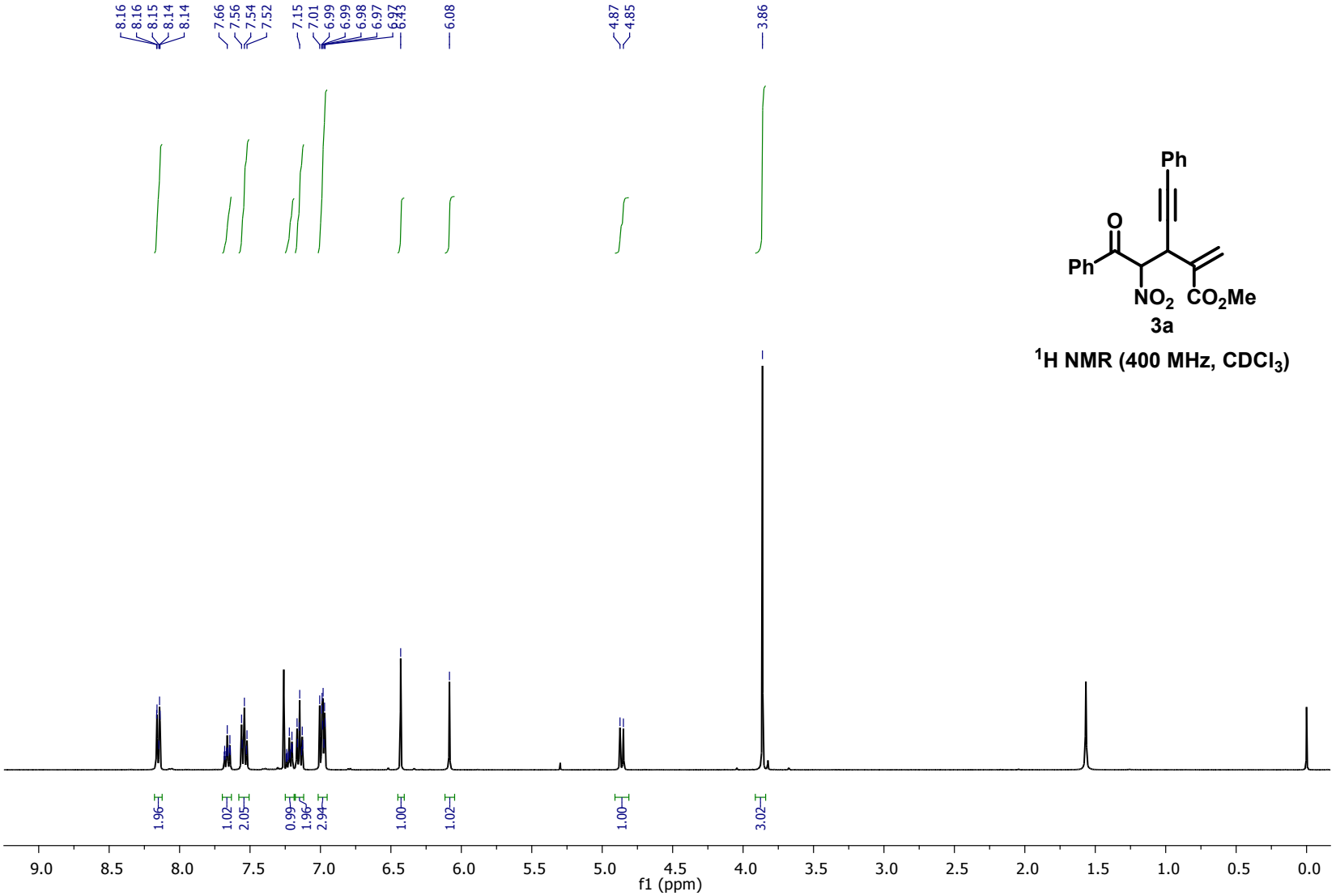
152.24
140.98
136.65
136.58
132.44
129.41
129.25
125.37
119.25
87.86
83.13
82.92
64.99
52.28
50.52
47.95
44.48
37.95
35.86
31.57
29.07
27.79
26.31
25.60
21.61
13.86
BocO
MeO2C
H
O
H H
1o
13C NMR (101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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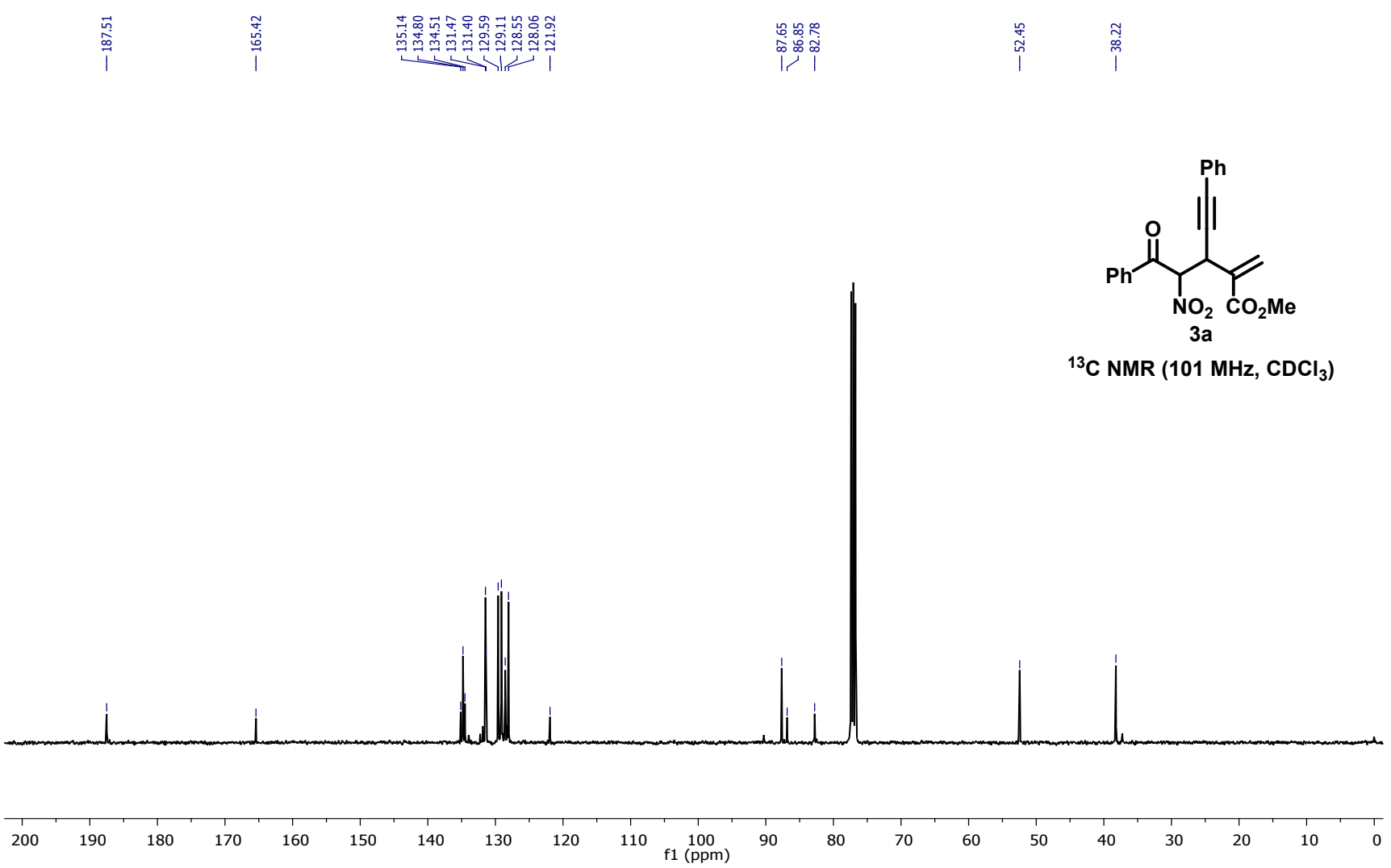
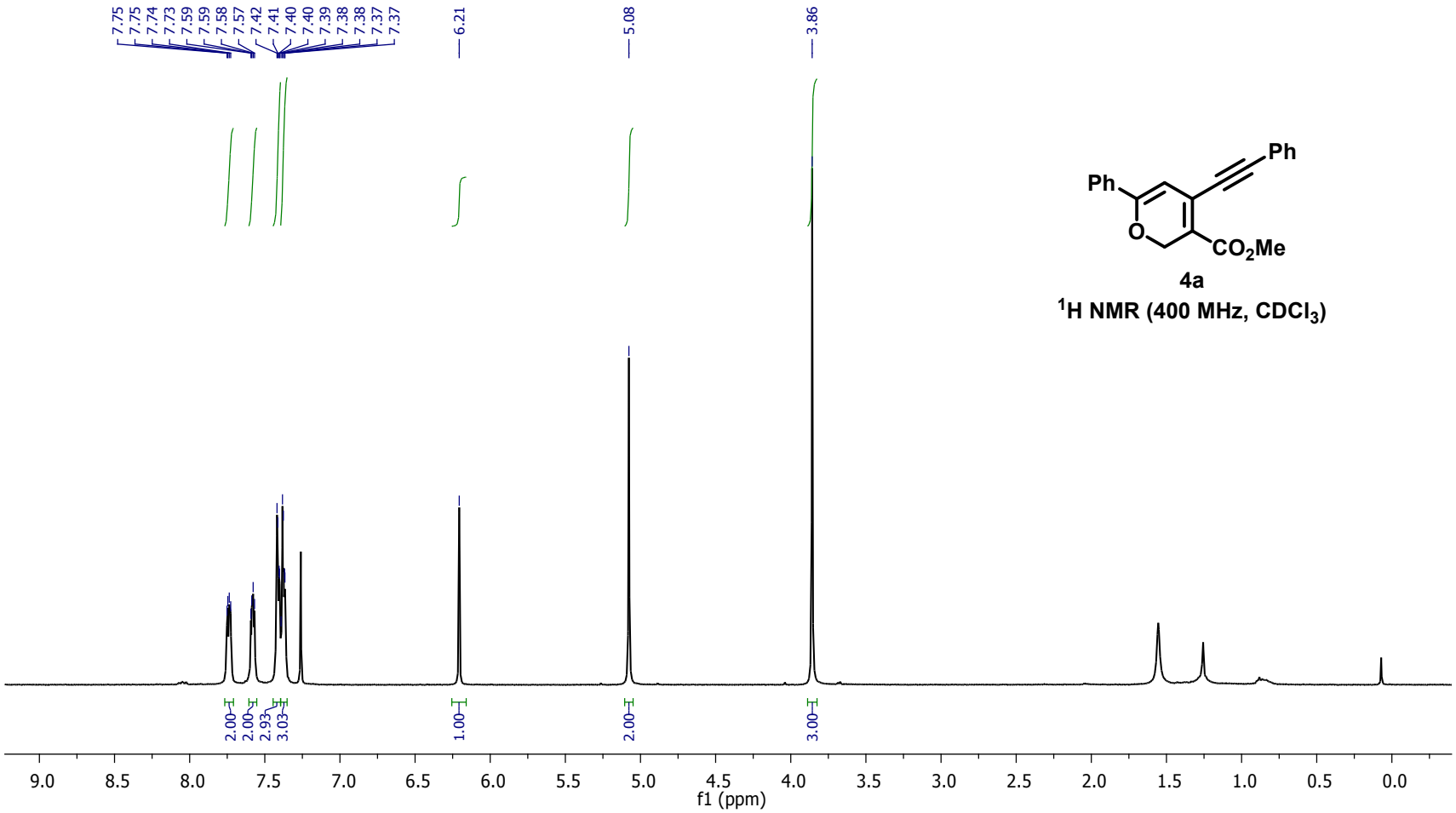
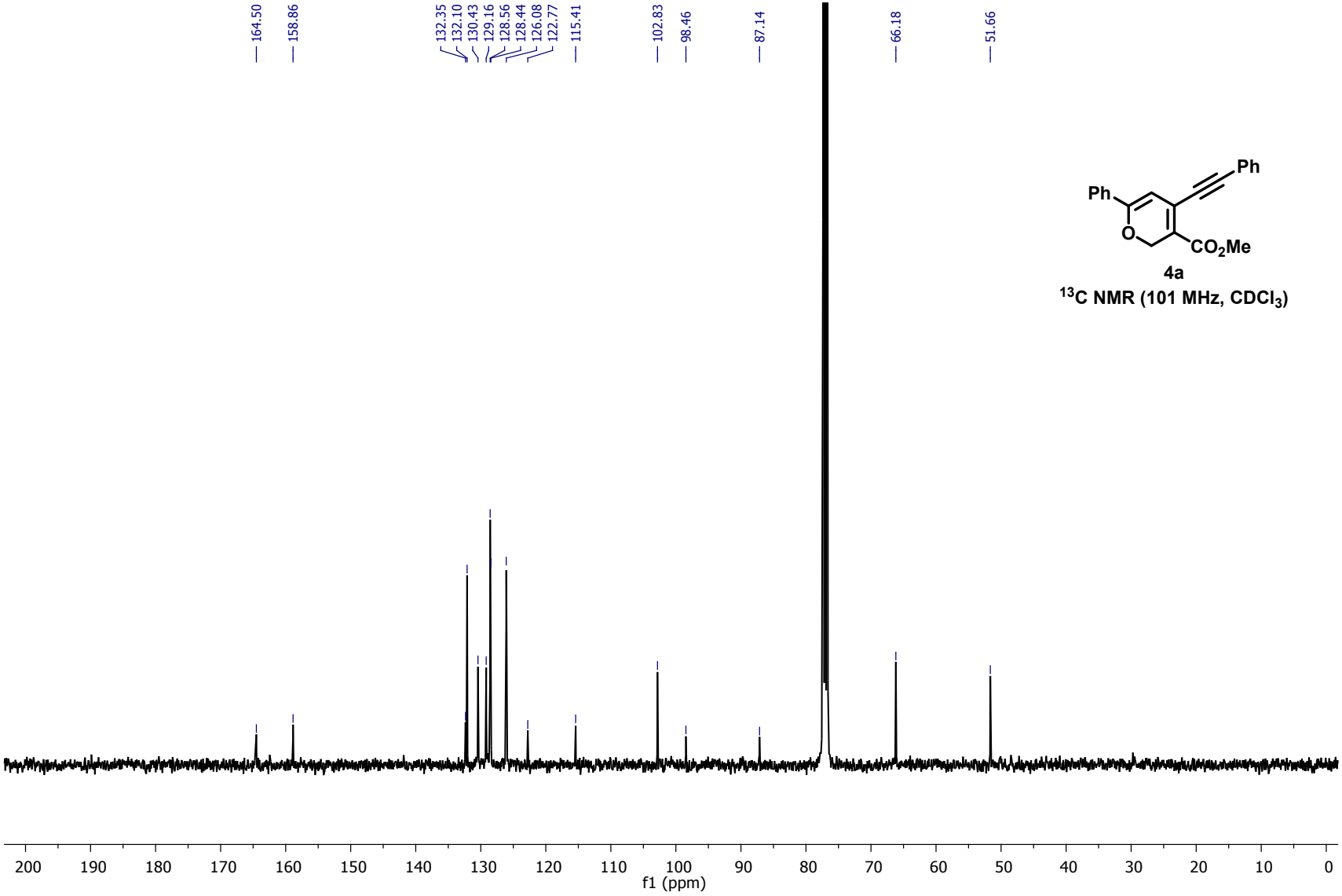
8.16
8.15
8.14
8.14
7.66
7.56
7.54
7.52
7.15
7.01
6.99
6.99
6.98
6.97
6.97
6.43
6.08
4.87
4.85
3.86
Ph
O
Ph
NO2
CO2Me
3a
1H NMR (400 MHz, CDCl3)
1.96
1.02
2.05
0.99
1.96
2.94
1.00
1.02
1.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


187.51
165.42
135.14
134.80
134.51
131.47
131.40
129.59
129.11
128.55
128.06
121.92
87.65
86.85
82.78
52.45
38.22
Ph
O
Ph
NO2
CO2Me
3a
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4a

^{1}H NMR (400 MHz, $CDCl_3$)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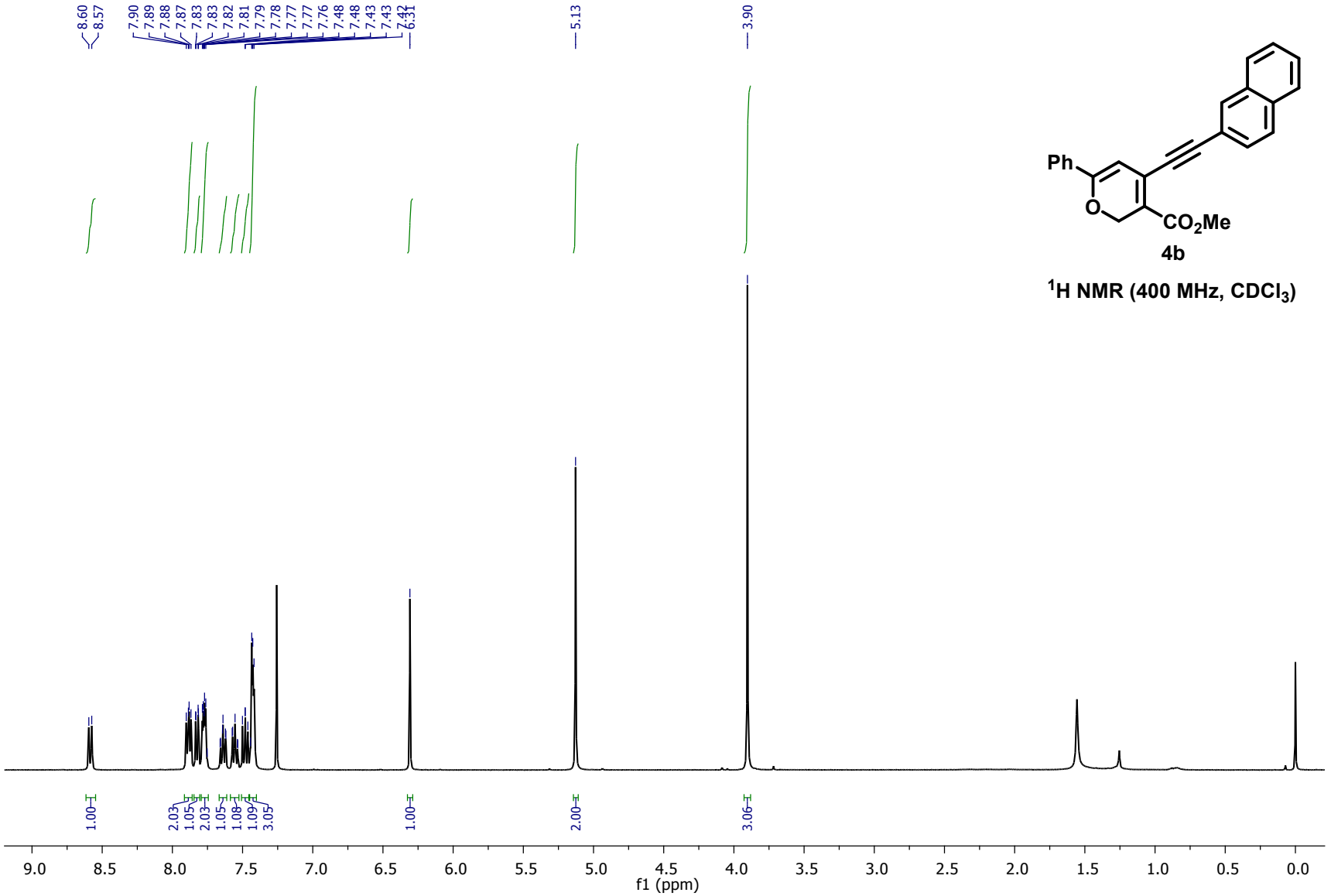
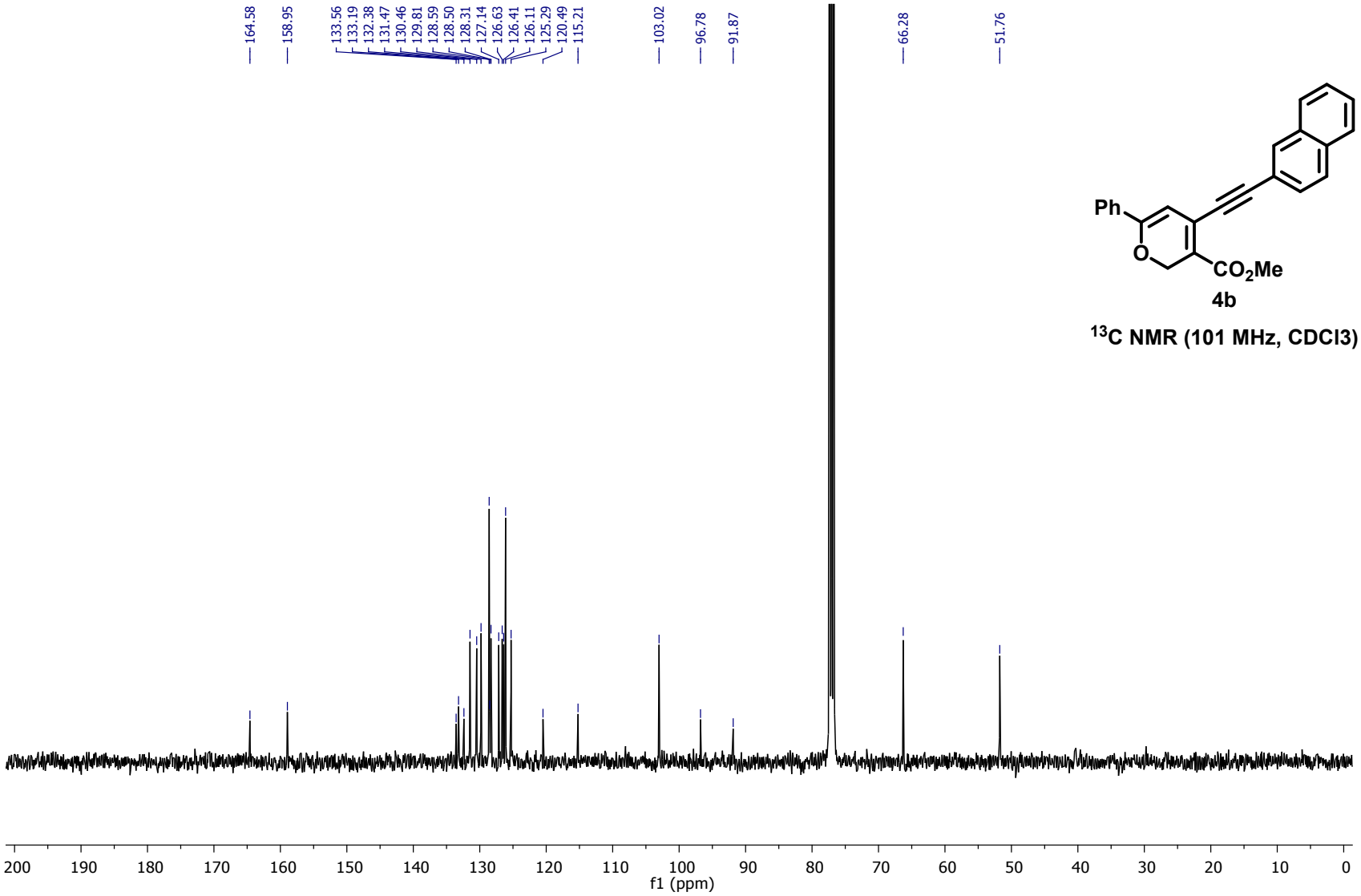
132.10
130.43
129.16
128.56
128.44
126.08
122.77
115.41
102.83
98.46
87.14
66.18
51.66
Ph
Ph
O
CO2Me
4a
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.60
8.57
7.90
7.89
7.88
7.87
7.83
7.83
7.82
7.81
7.79
7.78
7.77
7.77
7.76
7.48
7.48
7.43
7.43
7.42
7.31
5.13
3.90
Ph
O
CO2Me
4b
1H NMR (400 MHz, CDCl3)
1.00
2.03
1.05
2.03
1.05
1.08
1.09
3.05
1.00
2.00
3.06
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)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132.38
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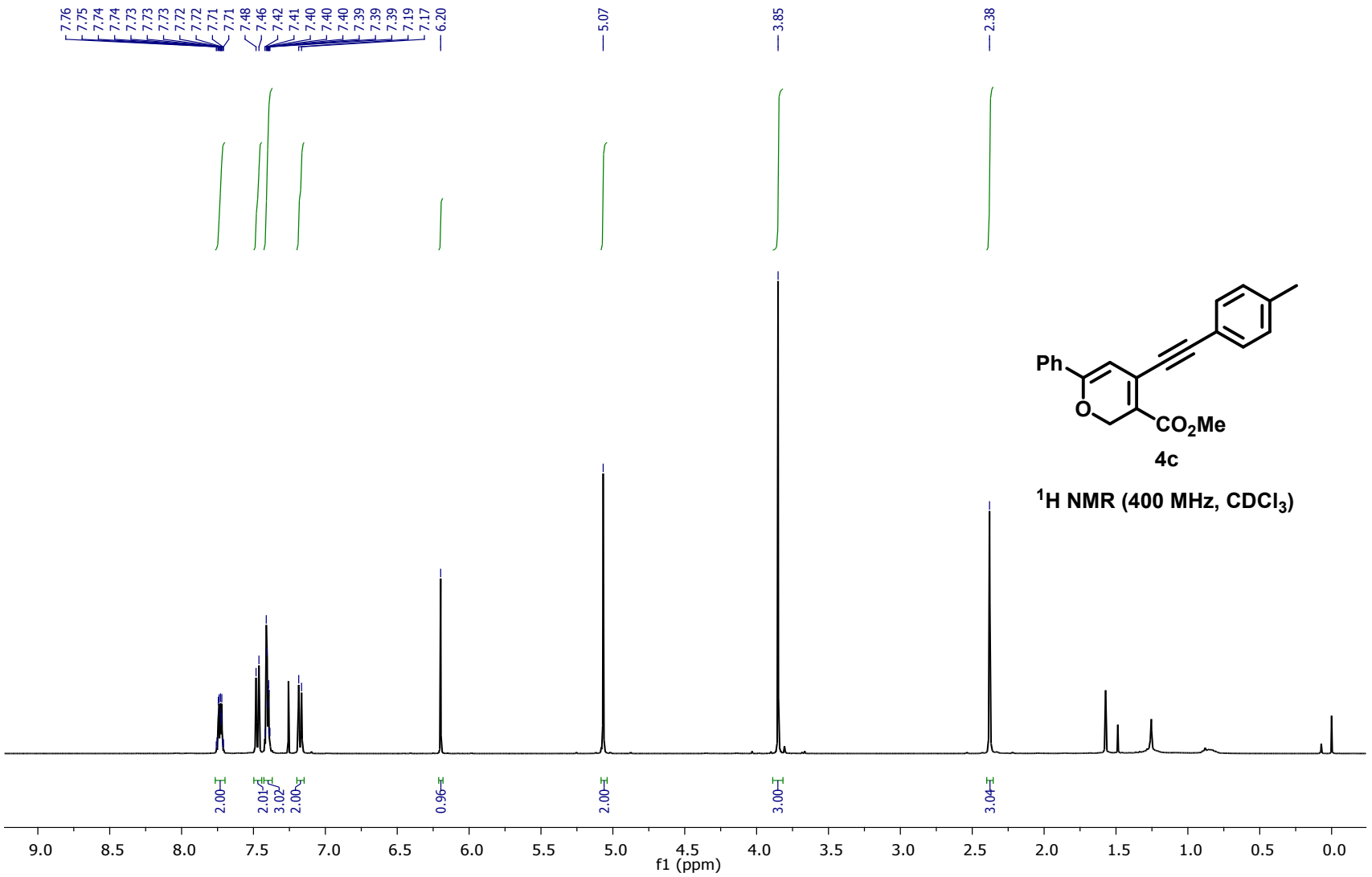
129.81
128.59
128.50
128.31
127.14
126.63
126.41
126.11
125.29
120.49
115.21
103.02
96.78
91.87
66.28
51.76
Ph
O
CO2Me
4b
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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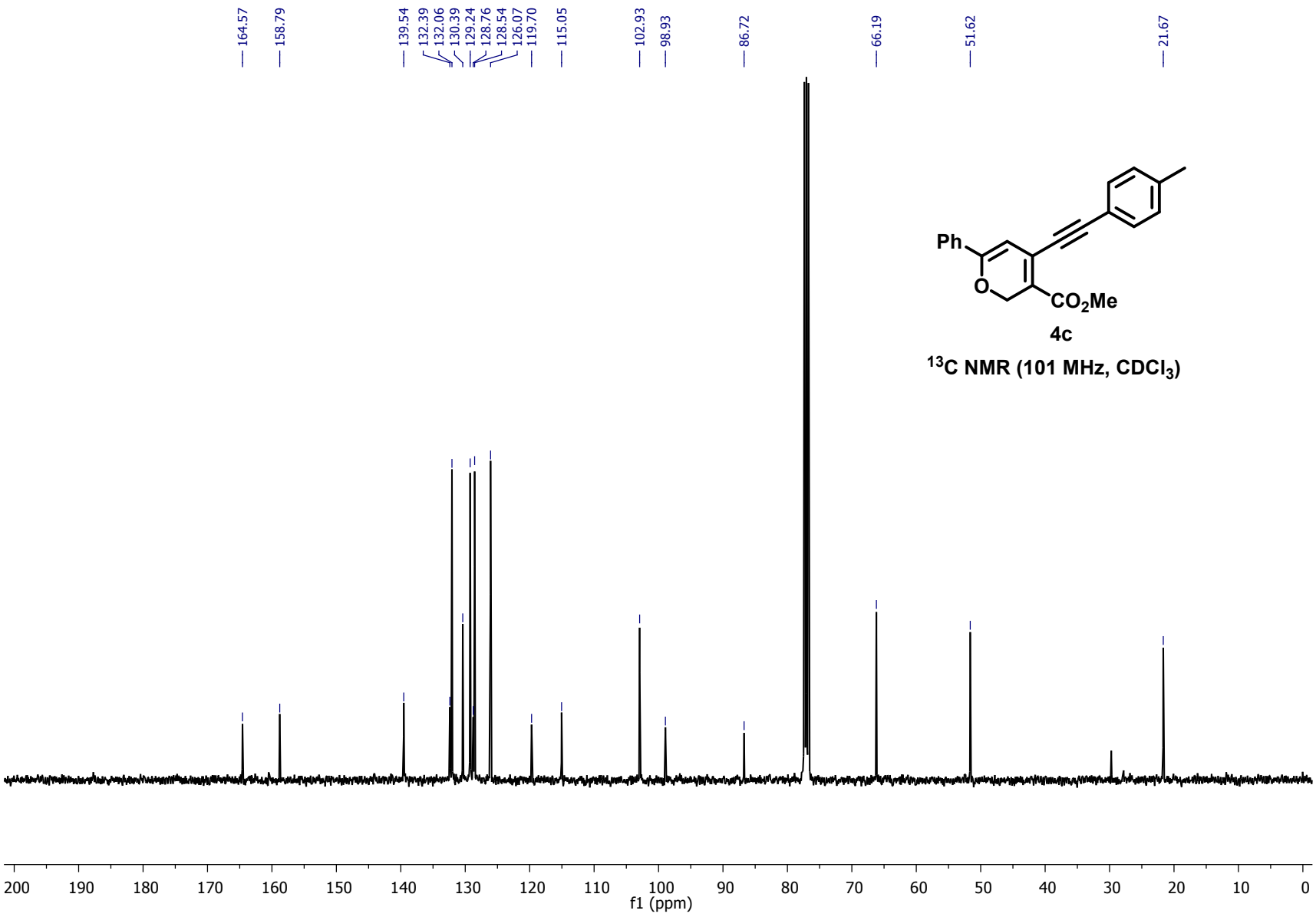
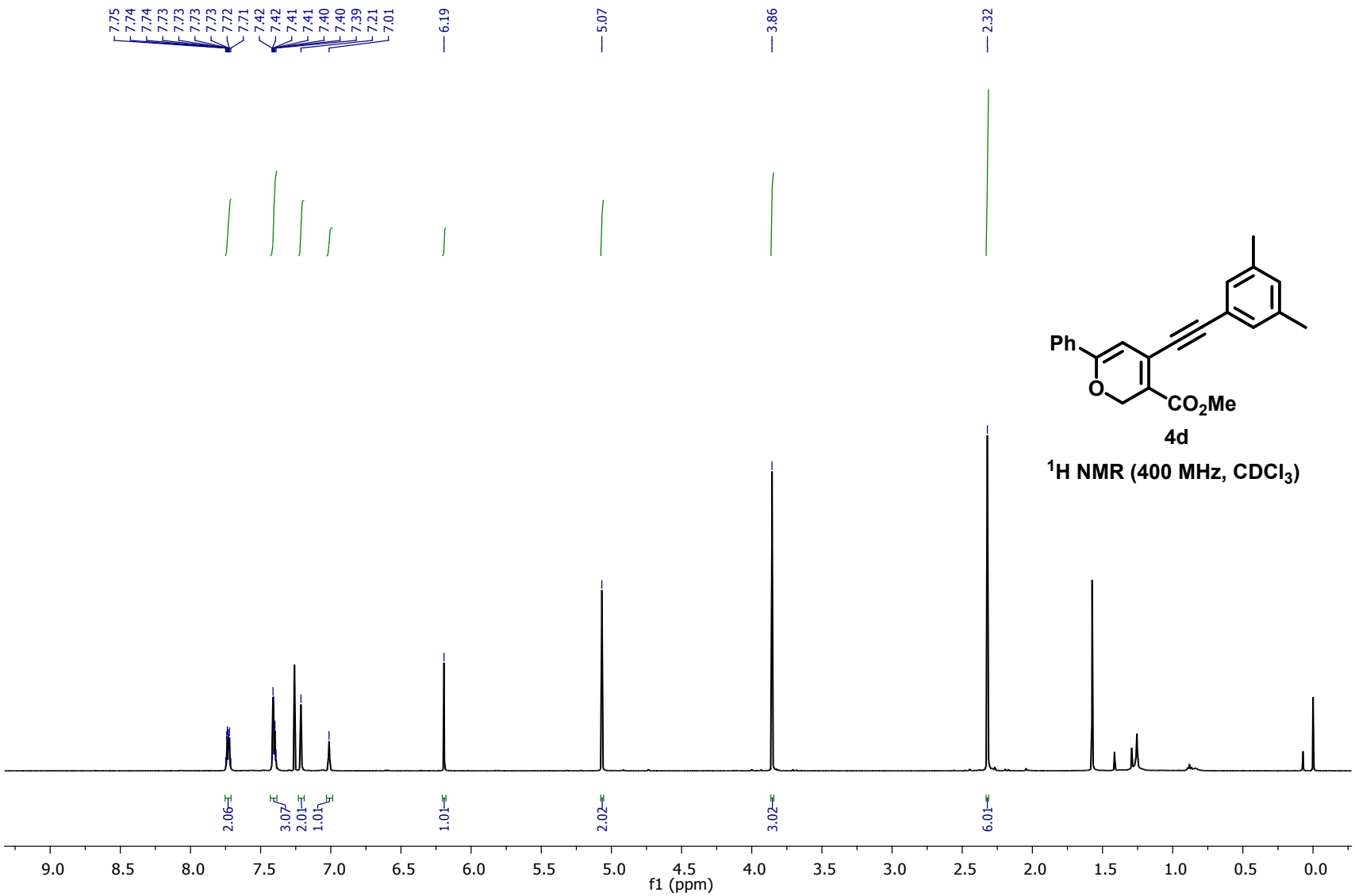
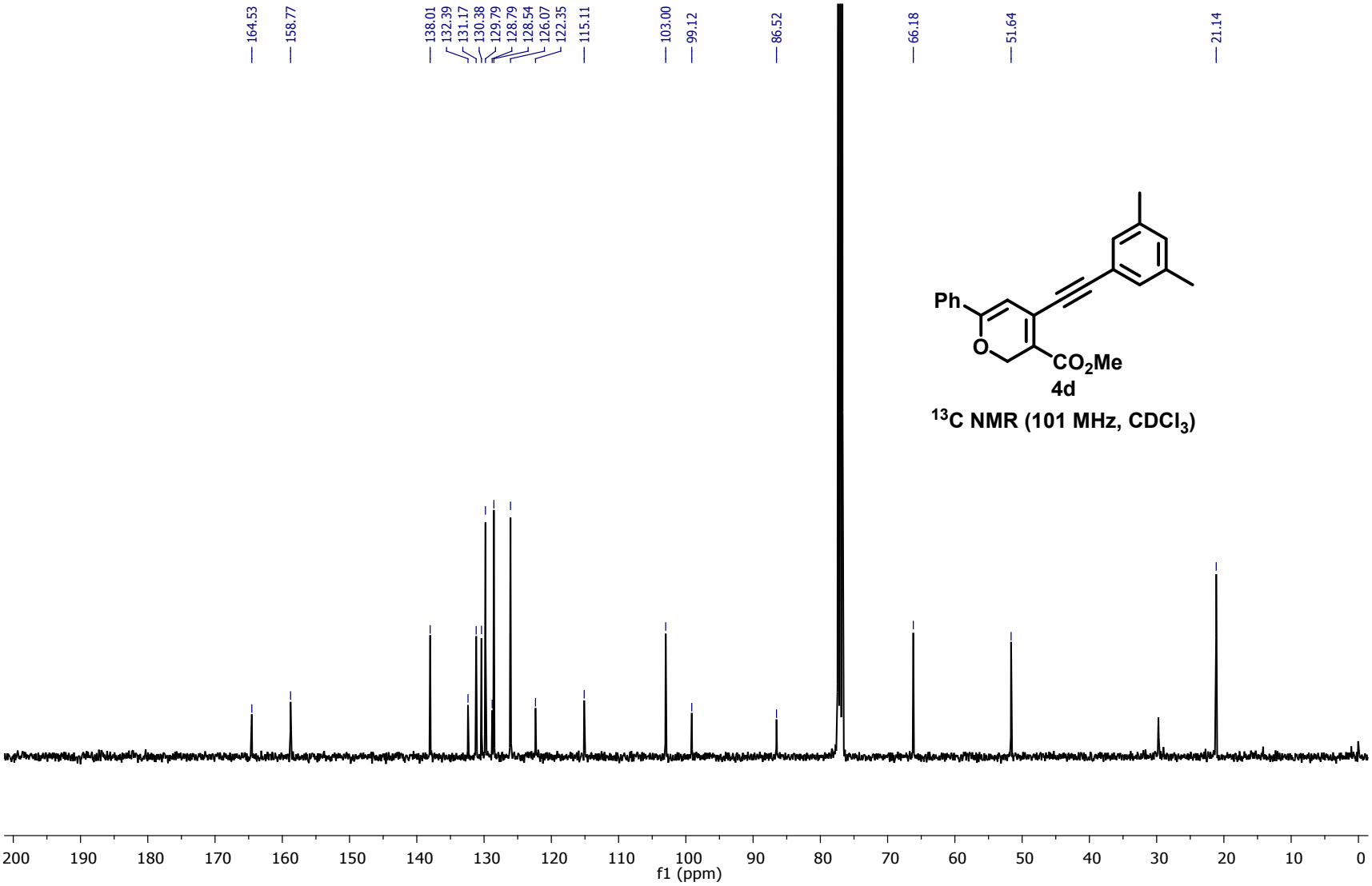
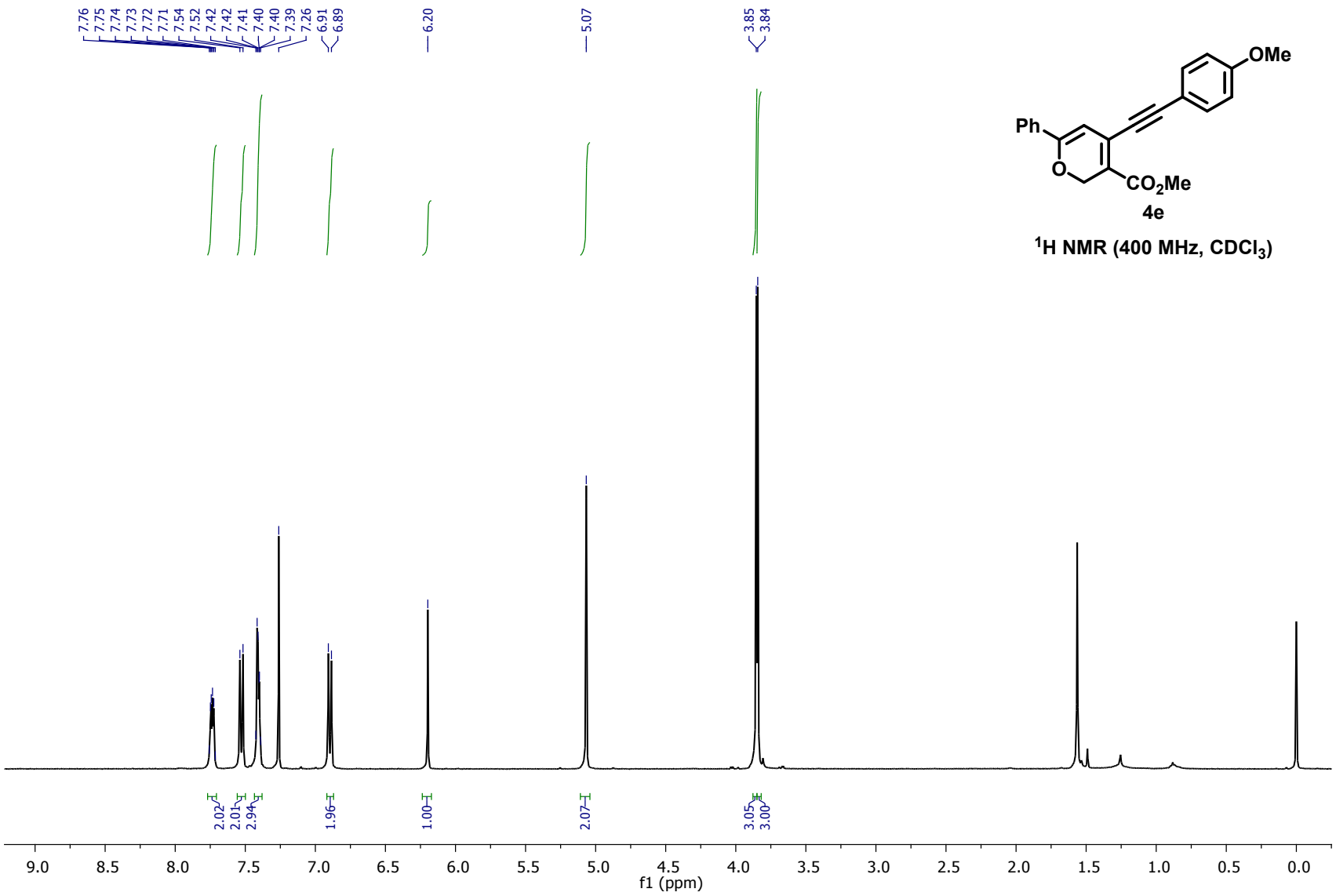
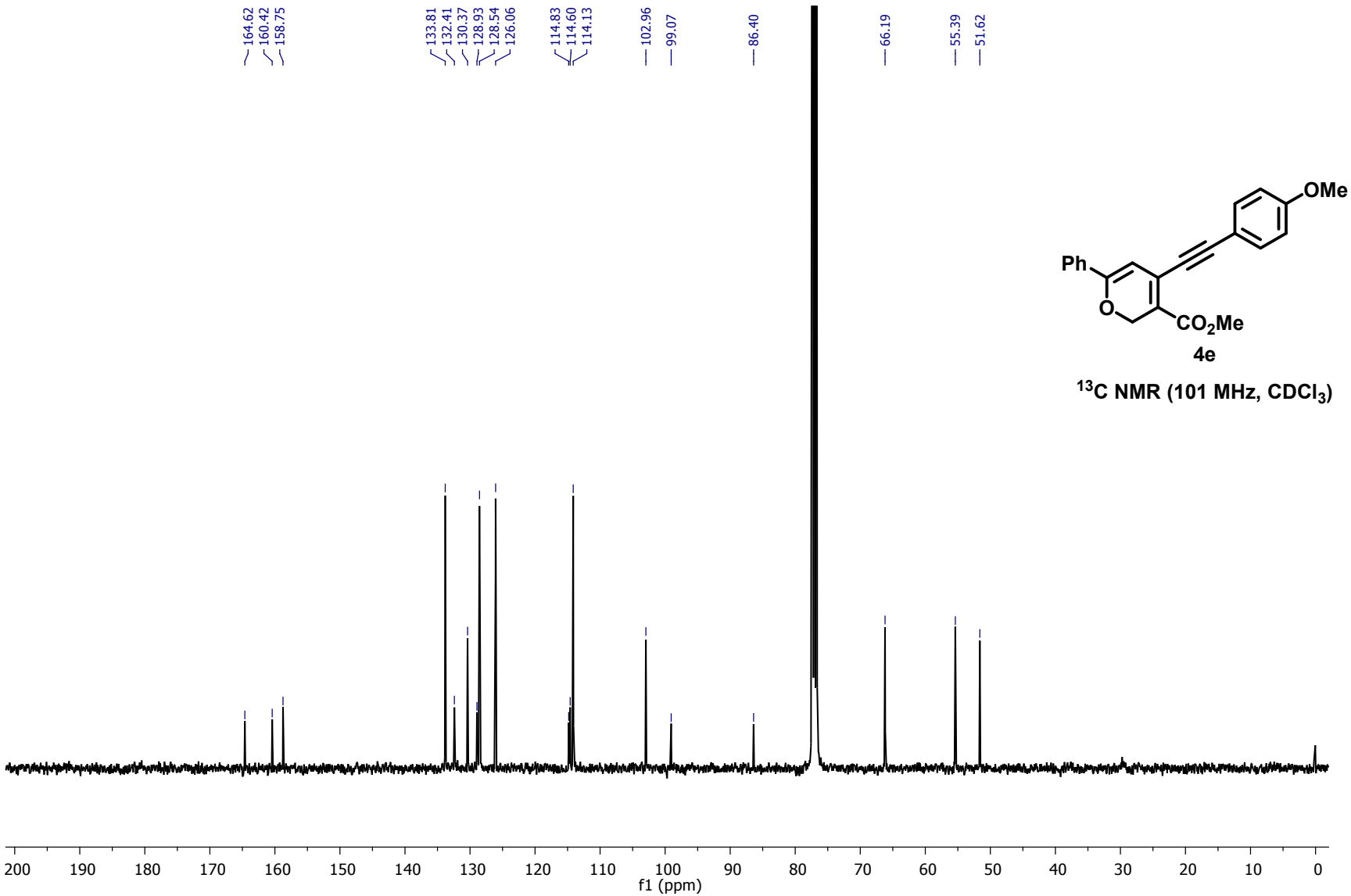
7.75
7.74
7.74
7.73
7.73
7.73
7.72
7.72
7.71
7.71
7.48
7.46
7.42
7.41
7.40
7.40
7.40
7.39
7.39
7.39
7.19
7.17
6.20
5.07
3.85
2.38
Ph
O
CO2Me
4c
1H NMR (400 MHz, CDCl3)
2.00
2.01
3.02
2.00
0.96
2.00
3.00
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

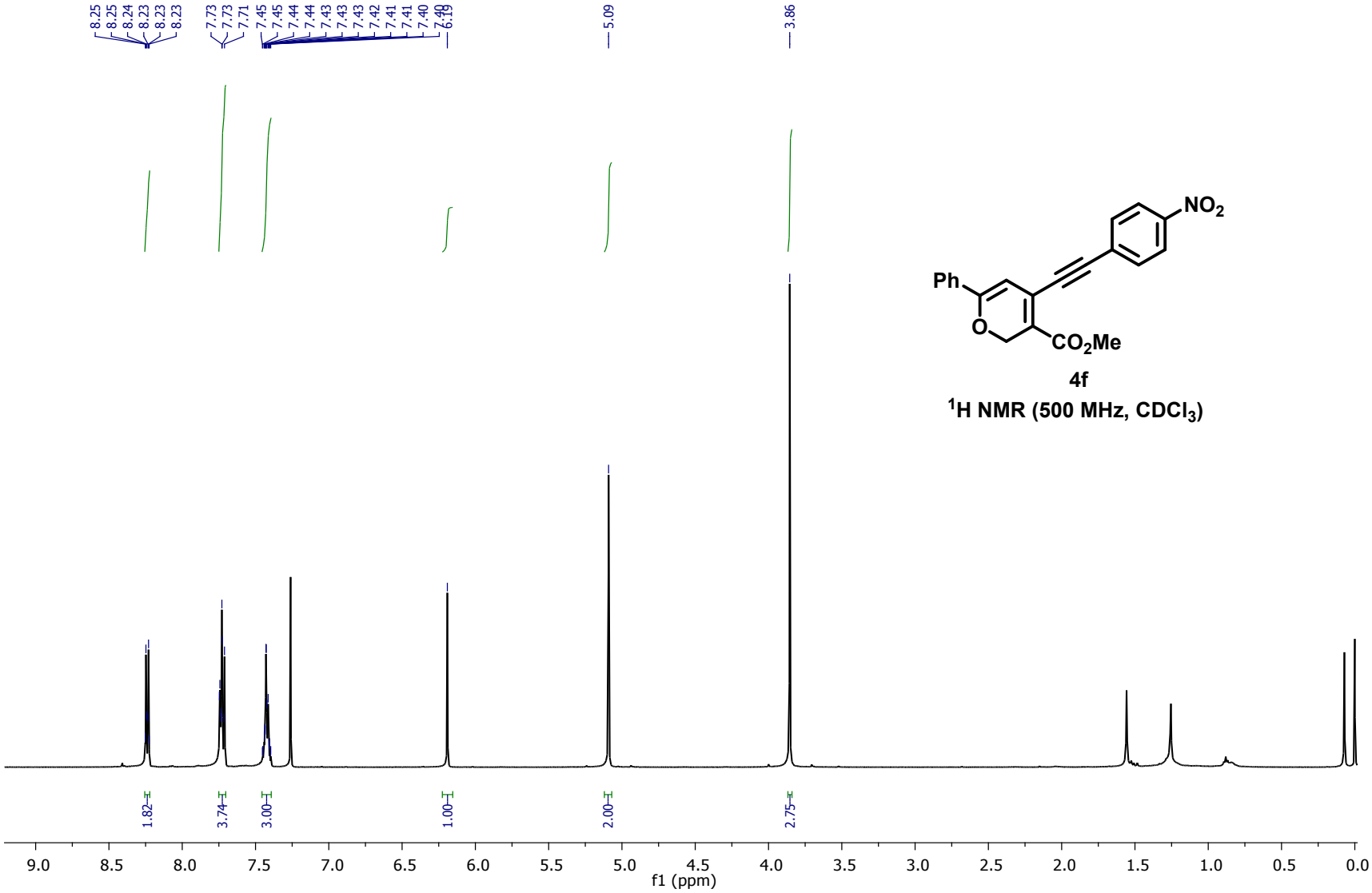

164.57
158.79
139.54
132.39
132.06
130.39
129.24
128.76
128.54
126.07
119.70
115.05
102.93
98.93
86.72
66.19
51.62
21.67
Ph
O
CO2Me
4c
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.75
7.74
7.74
7.73
7.73
7.73
7.73
7.72
7.71
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.21
7.01
6.19
5.07
3.86
2.32
Ph
O
CO2Me
4d
1H NMR (400 MHz, CDCl3)
2.06
3.07
2.01
1.01
1.01
2.02
3.02
6.01
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)


164.53
158.77
138.01
132.39
131.17
130.38
129.79
128.79
128.54
126.07
122.35
115.11
103.00
99.12
86.52
66.18
51.64
21.14
Ph
O
CO2Me
4d
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

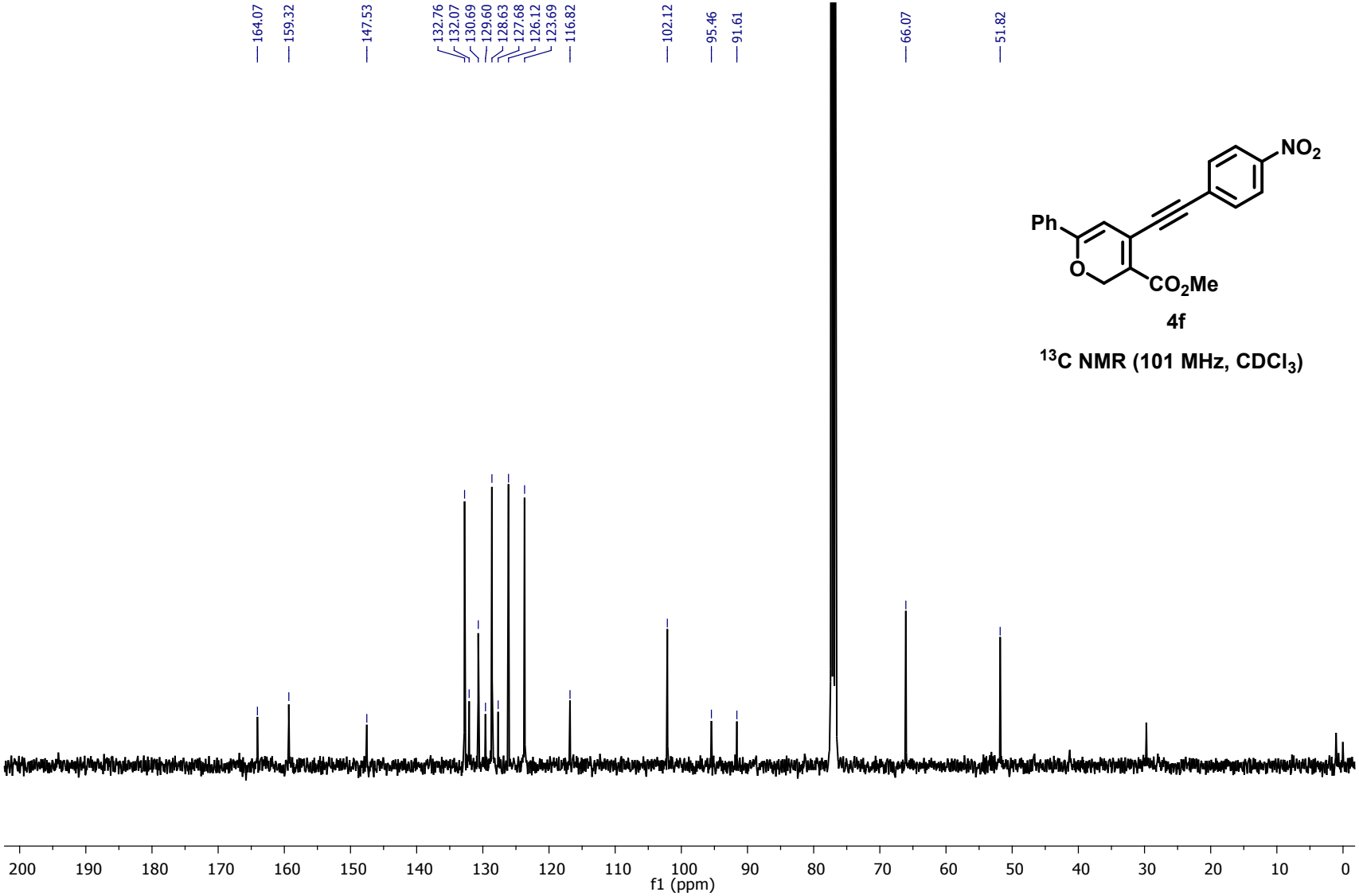

7.76
7.75
7.74
7.73
7.72
7.71
7.54
7.52
7.42
7.42
7.41
7.40
7.40
7.39
7.26
6.91
6.89
6.20
5.07
3.85
3.84
OMe
Ph
O
CO2Me
4e
1H NMR (400 MHz, CDCl3)
2.02
2.01
2.94
1.96
1.00
2.07
3.05
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

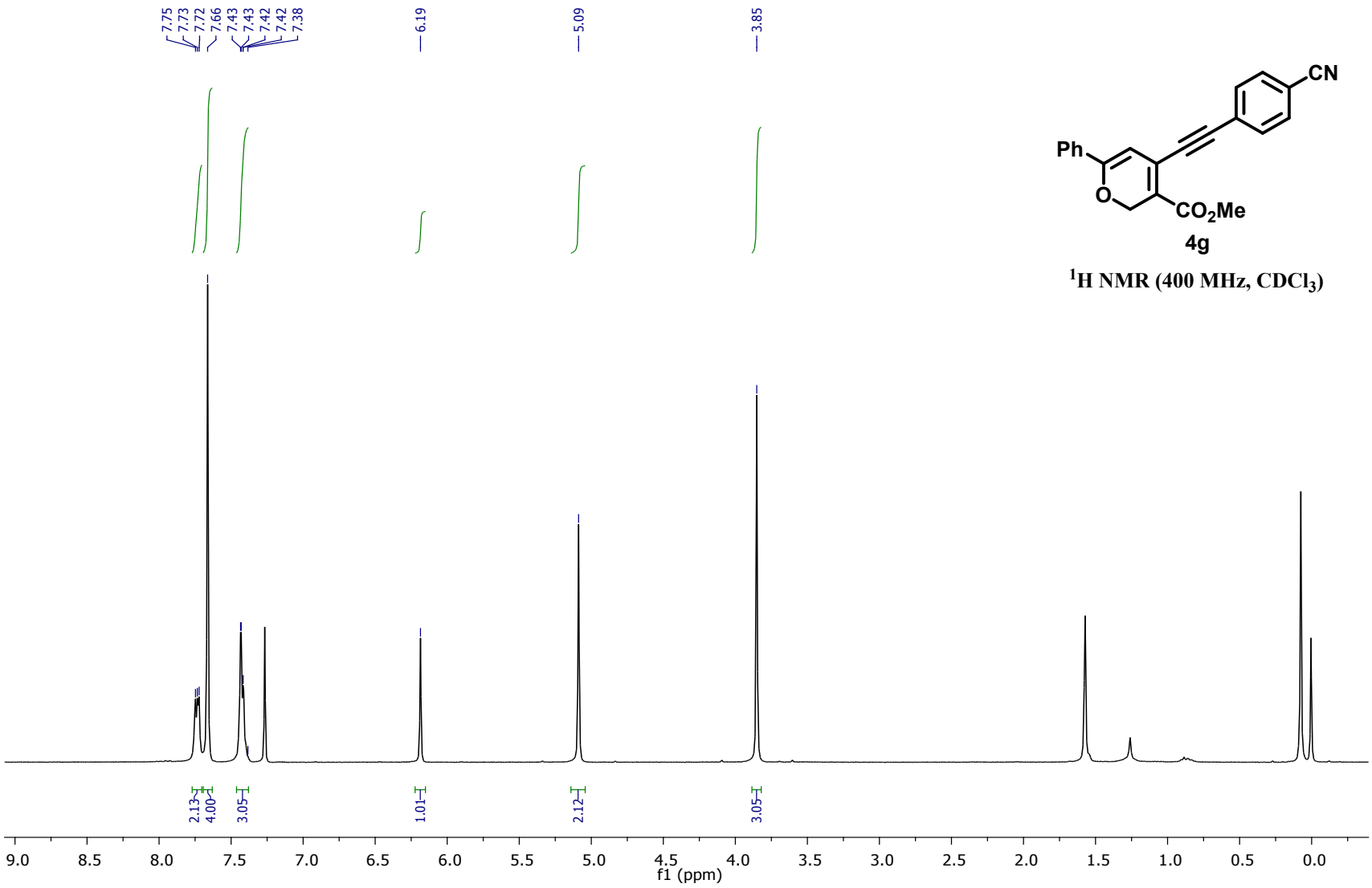

164.62
160.42
158.75
133.81
132.41
130.37
128.93
128.54
126.06
114.83
114.60
114.13
102.96
99.07
86.40
66.19
55.39
51.62
OMe
Ph
O
CO2Me
4e
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4f

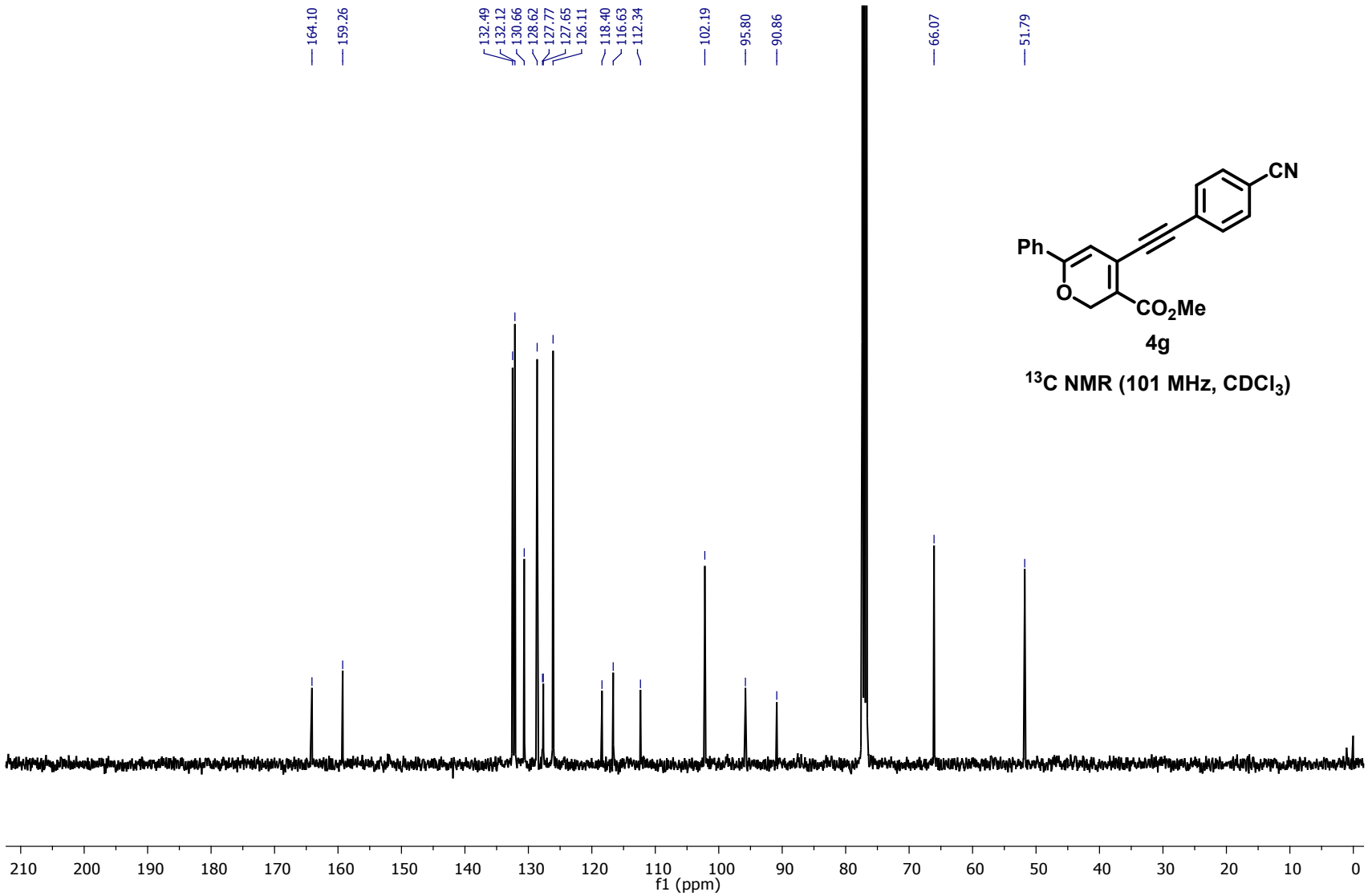
^{1}H NMR (500 MHz, $CDCl_3$)

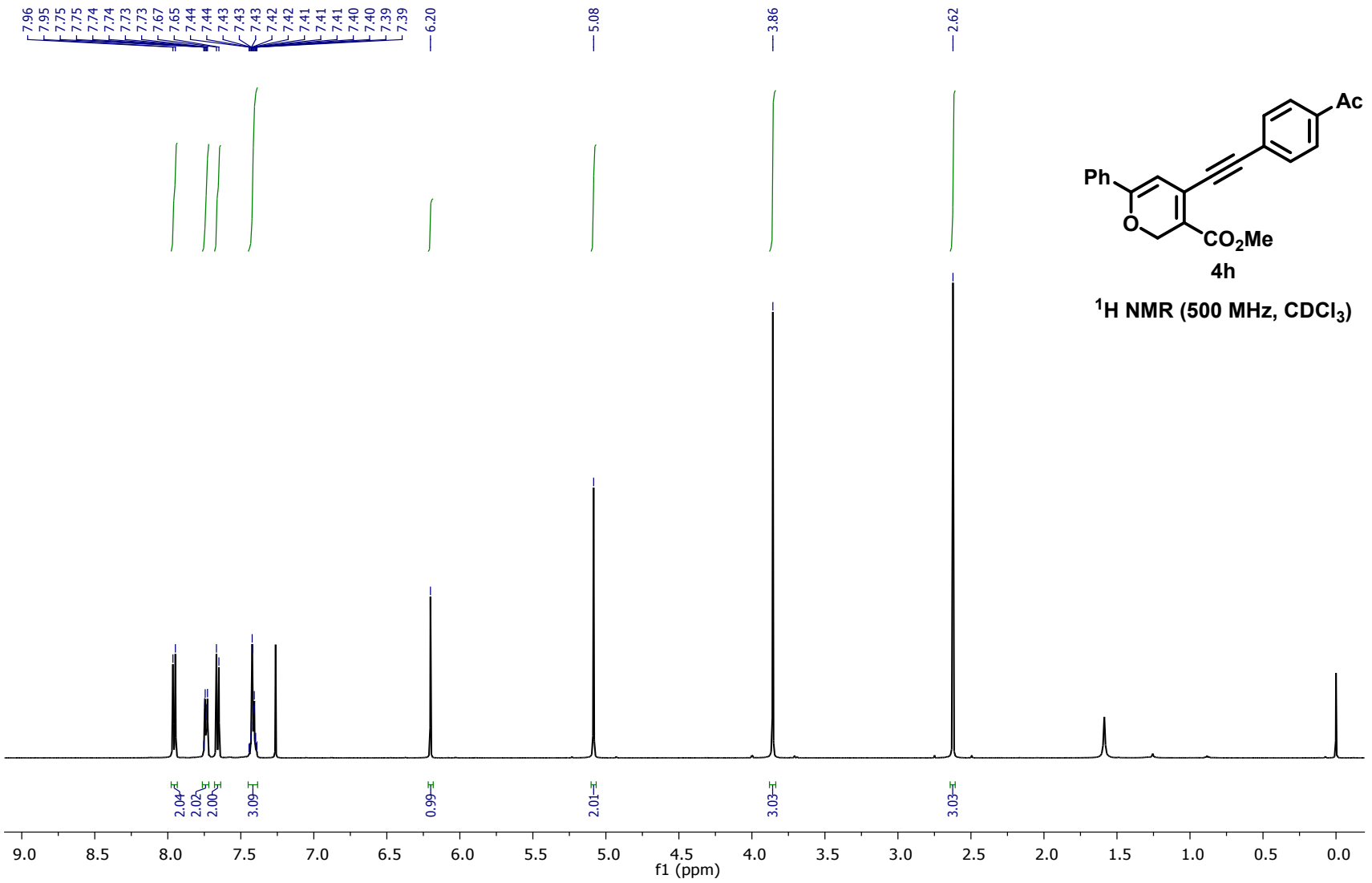

164.07
159.32
147.53
132.76
132.07
130.69
129.60
128.63
127.68
126.12
123.69
116.82
102.12
95.46
91.61
66.07
51.82
NO2
Ph
O
CO2Me
4f
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

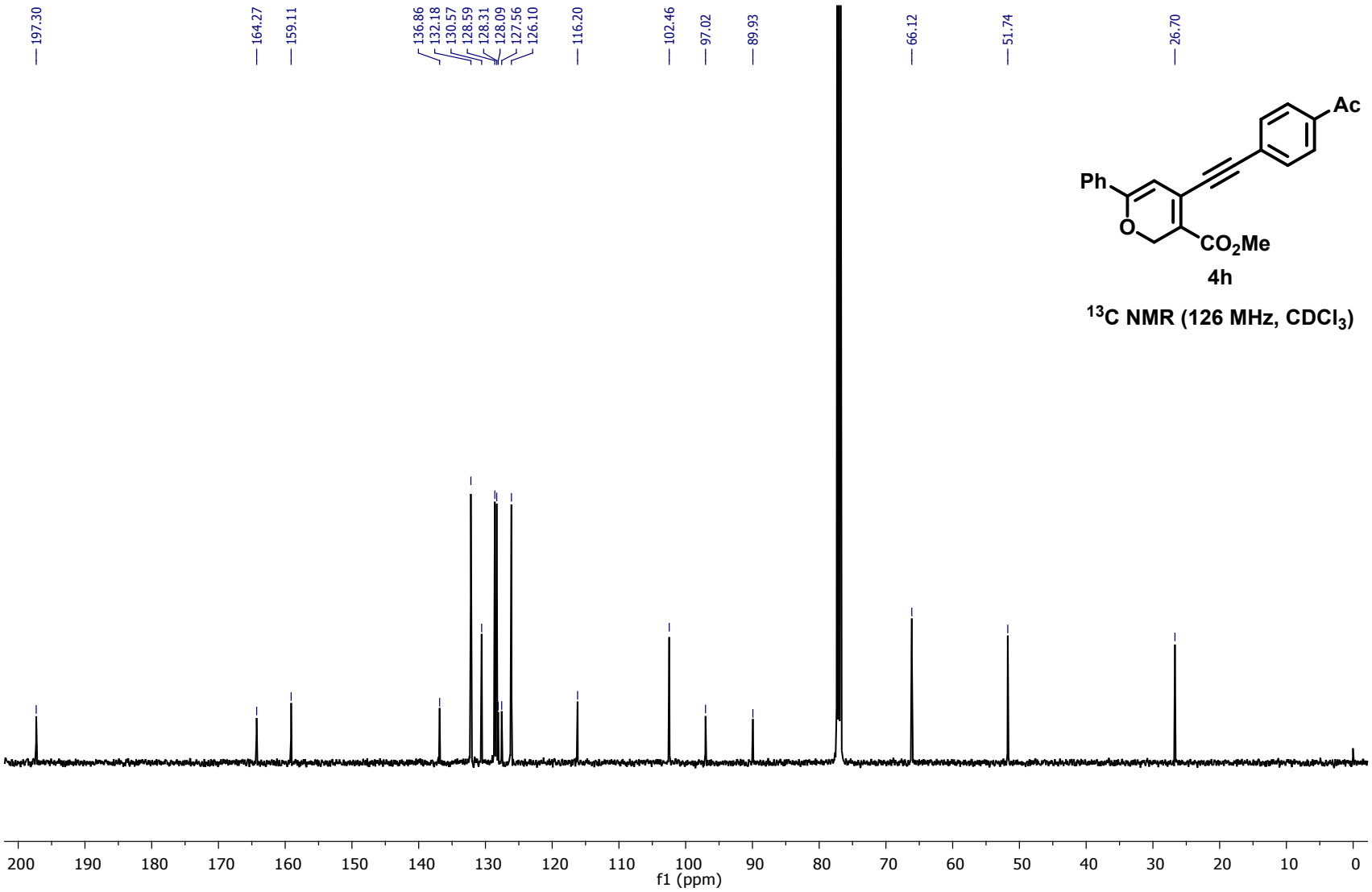


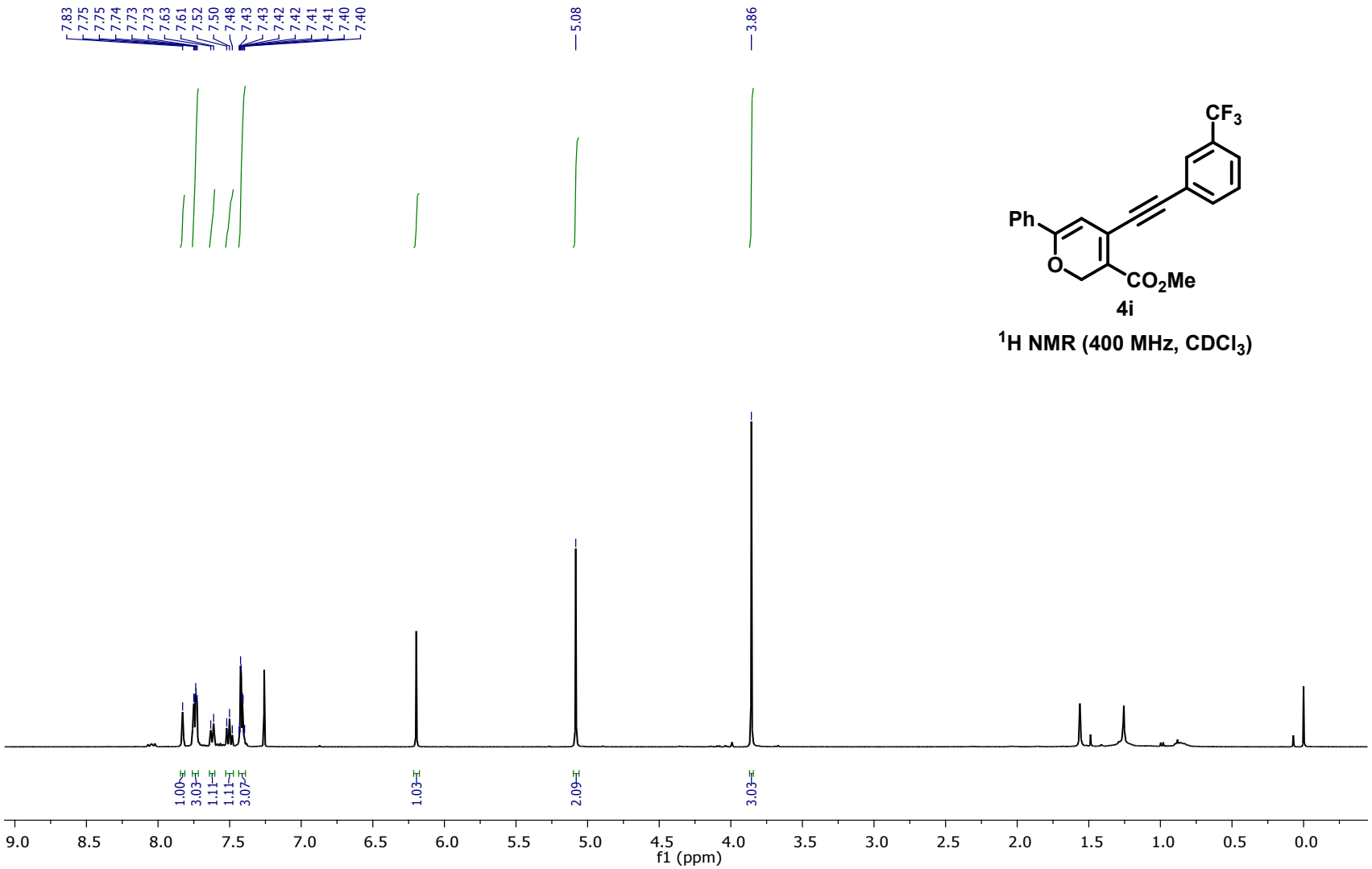
4g

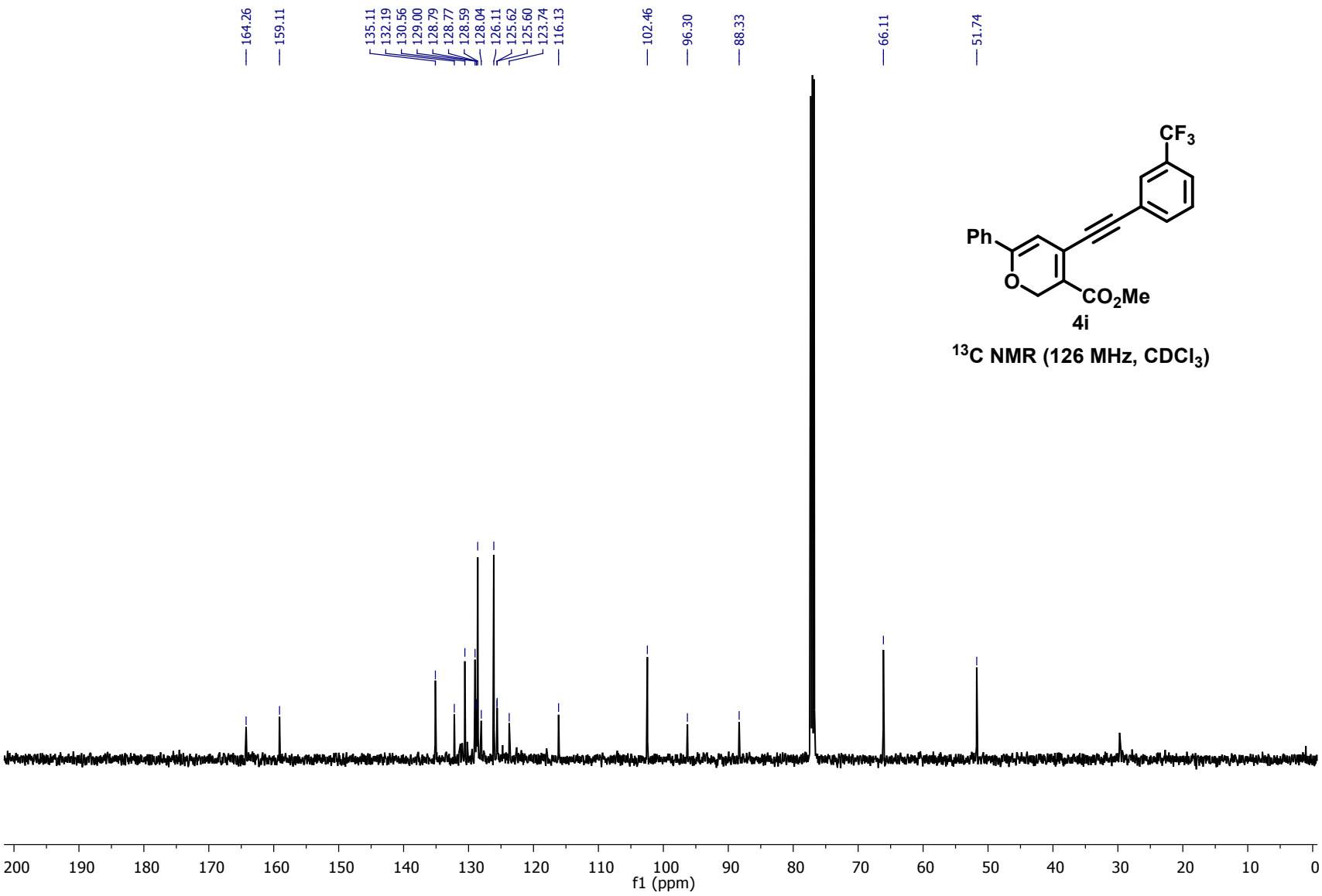
^{1}H NMR (400 MHz, $CDCl_3$)

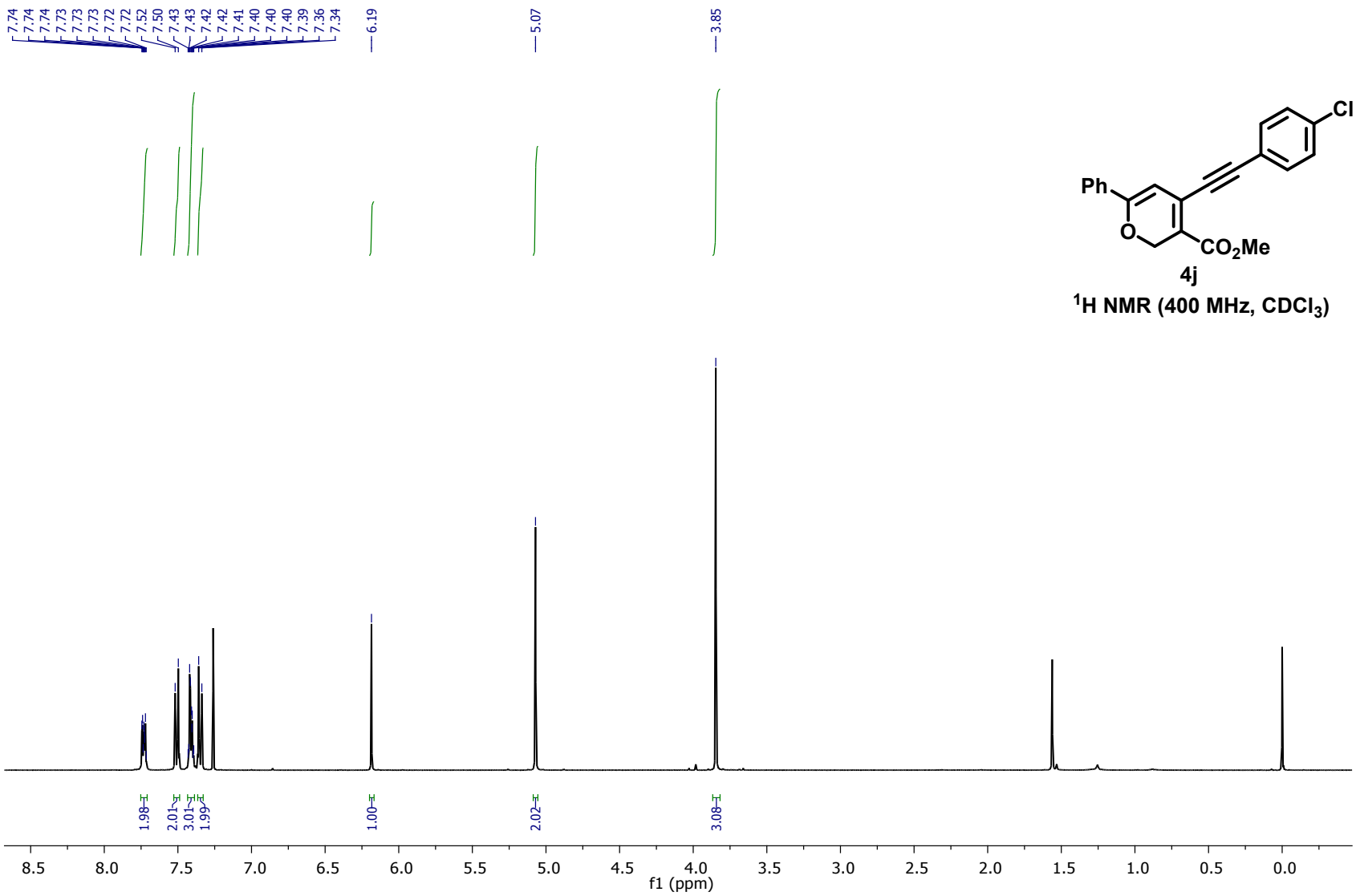

164.10
159.26
132.49
132.12
130.66
128.62
127.77
127.65
126.11
118.40
116.63
112.34
102.19
95.80
90.86
66.07
51.79
CN
Ph
O
CO2Me
4g
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

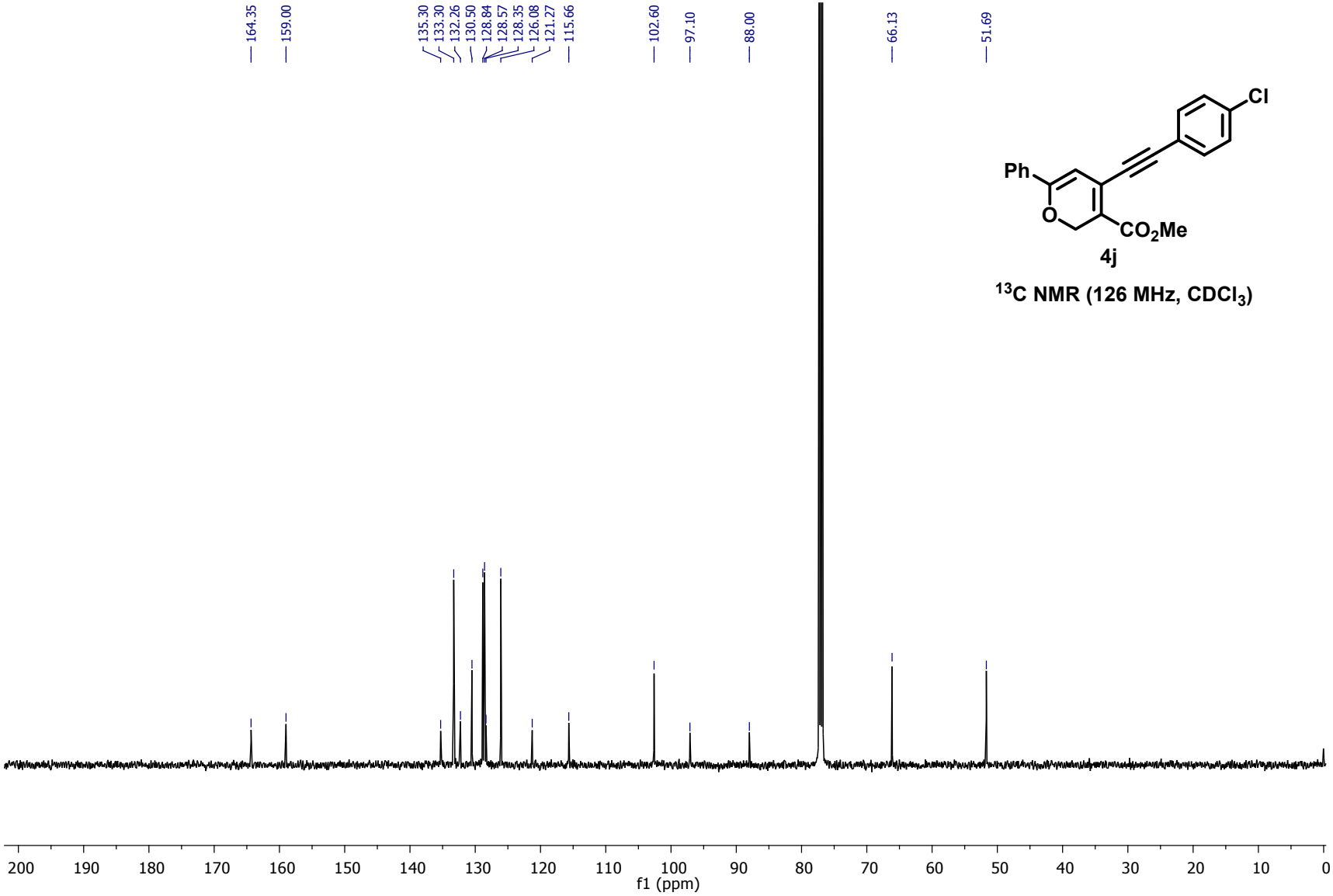

7.96
7.95
7.75
7.75
7.74
7.74
7.73
7.73
7.67
7.65
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.39
6.20
5.08
3.86
2.62
Ac
Ph
O
CO2Me
4h
1H NMR (500 MHz, CDCl3)
2.04
2.02
2.00
3.09
0.99
2.01
3.03
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

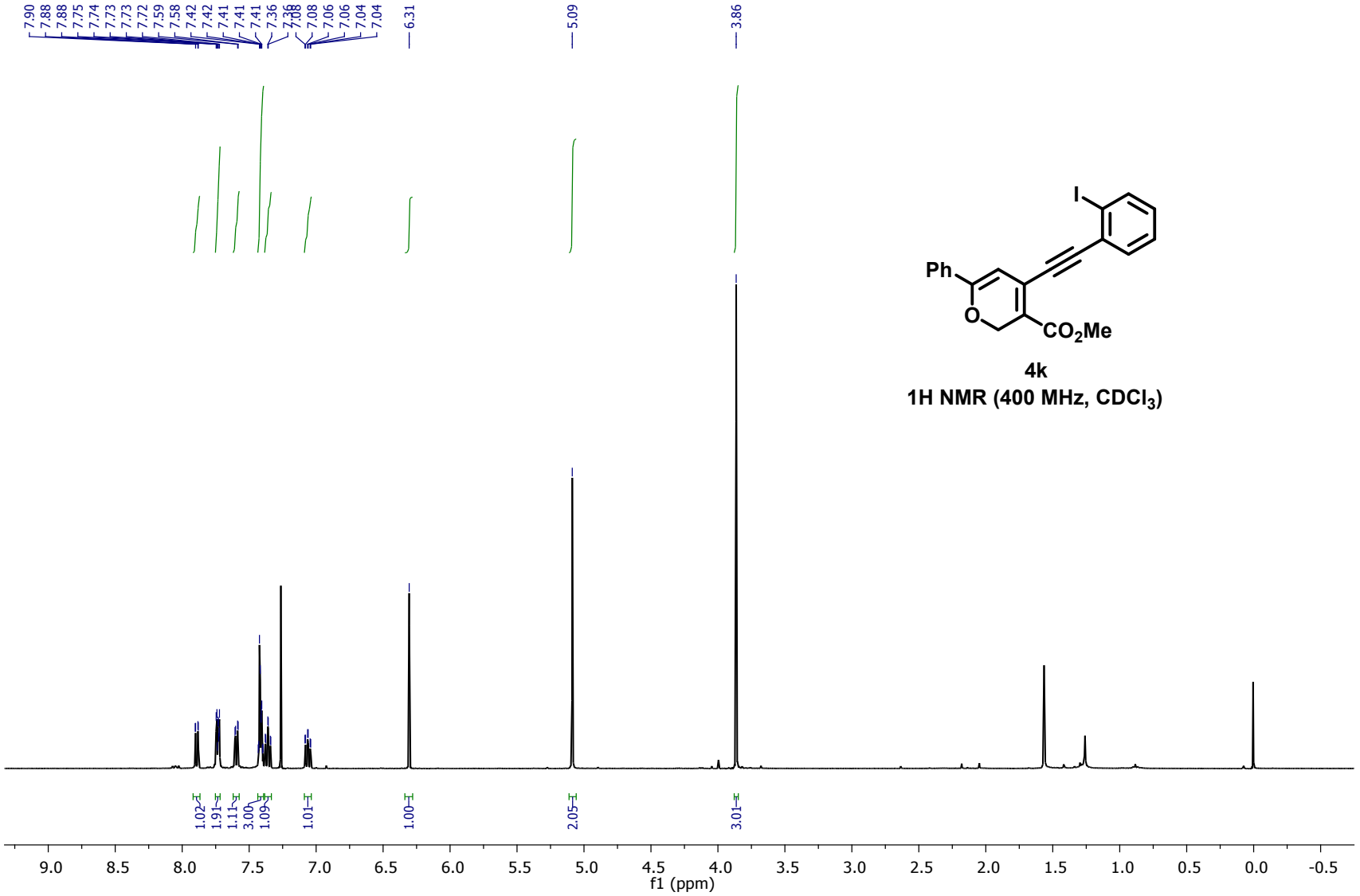

197.30
164.27
159.11
136.86
132.18
130.57
128.59
128.31
128.09
127.56
126.10
116.20
102.46
97.02
89.93
66.12
51.74
26.70
Ac
Ph
O
CO2Me
4h
13C NMR (126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.83
7.75
7.75
7.74
7.73
7.73
7.63
7.61
7.52
7.50
7.48
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
5.08
3.86
CF3
Ph
O
CO2Me
4i
1H NMR (400 MHz, CDCl3)
1.00
3.03
1.11
1.11
3.07
1.03
2.09
3.03
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)


164.26
159.11
135.11
132.19
130.56
129.00
128.79
128.77
128.59
128.04
126.11
125.62
125.60
123.74
116.13
102.46
96.30
88.33
66.11
51.74
CF3
Ph
O
CO2Me
4i
13C NMR (126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

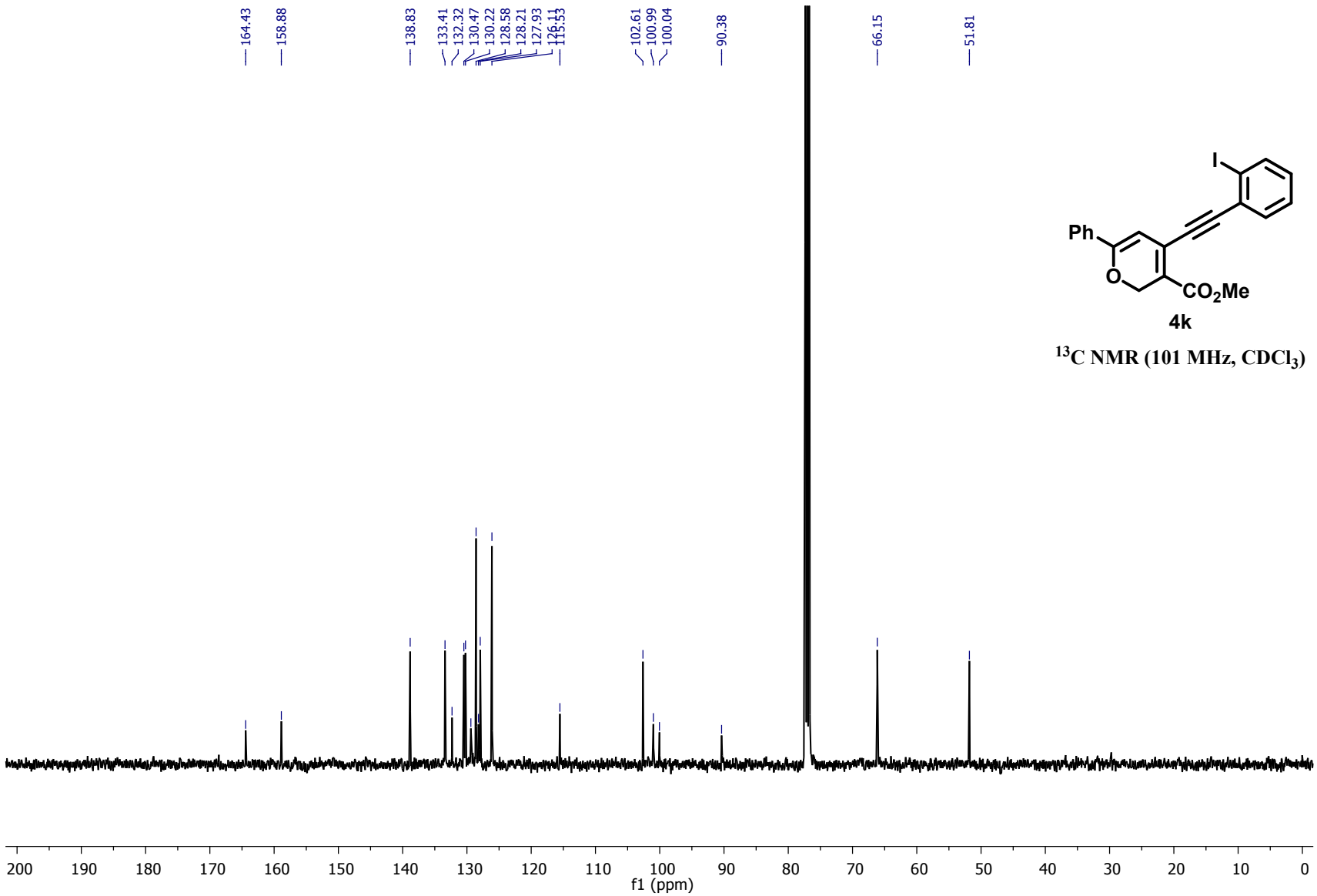

7.74
7.74
7.74
7.73
7.73
7.73
7.72
7.72
7.52
7.50
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.40
7.39
7.36
7.34
6.19
5.07
3.85
Cl
Ph
O
CO2Me
4j
1H NMR (400 MHz, CDCl3)
1.98
2.01
3.01
1.99
1.00
2.02
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

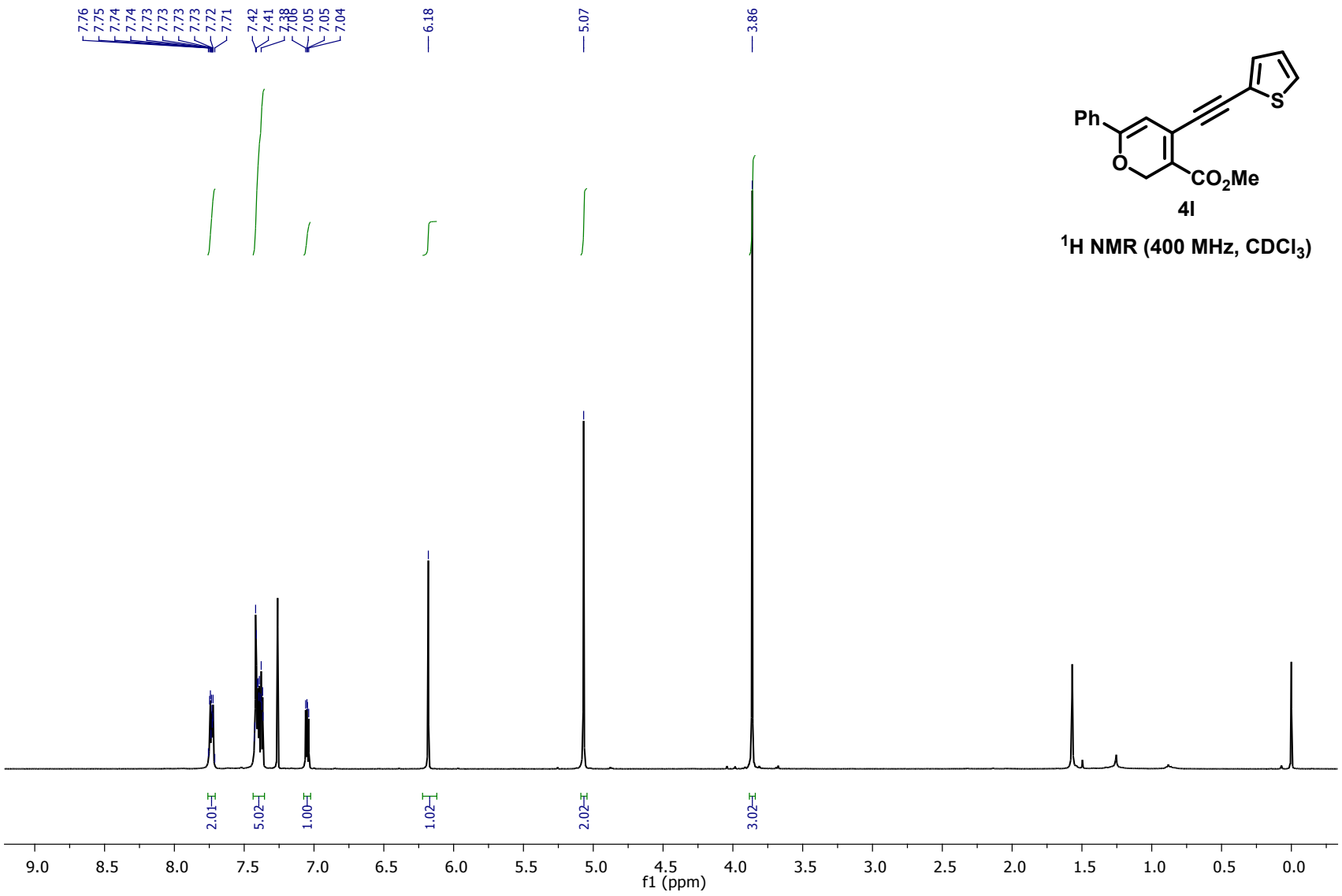

164.35
159.00
135.30
133.30
132.26
130.50
128.84
128.57
128.35
126.08
121.27
115.66
102.60
97.10
88.00
66.13
51.69
Cl
Ph
O
CO2Me
4j
13C NMR (126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

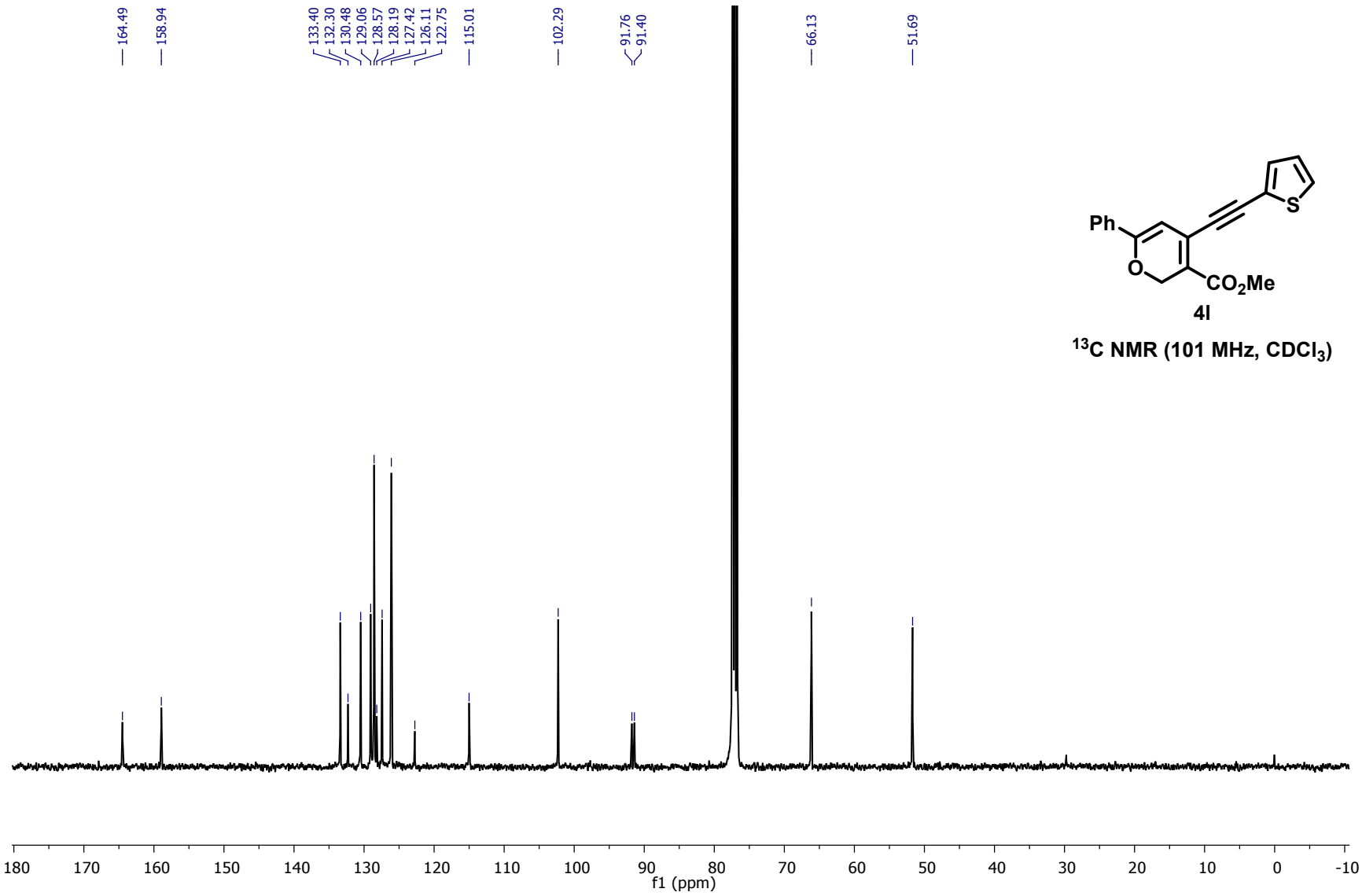


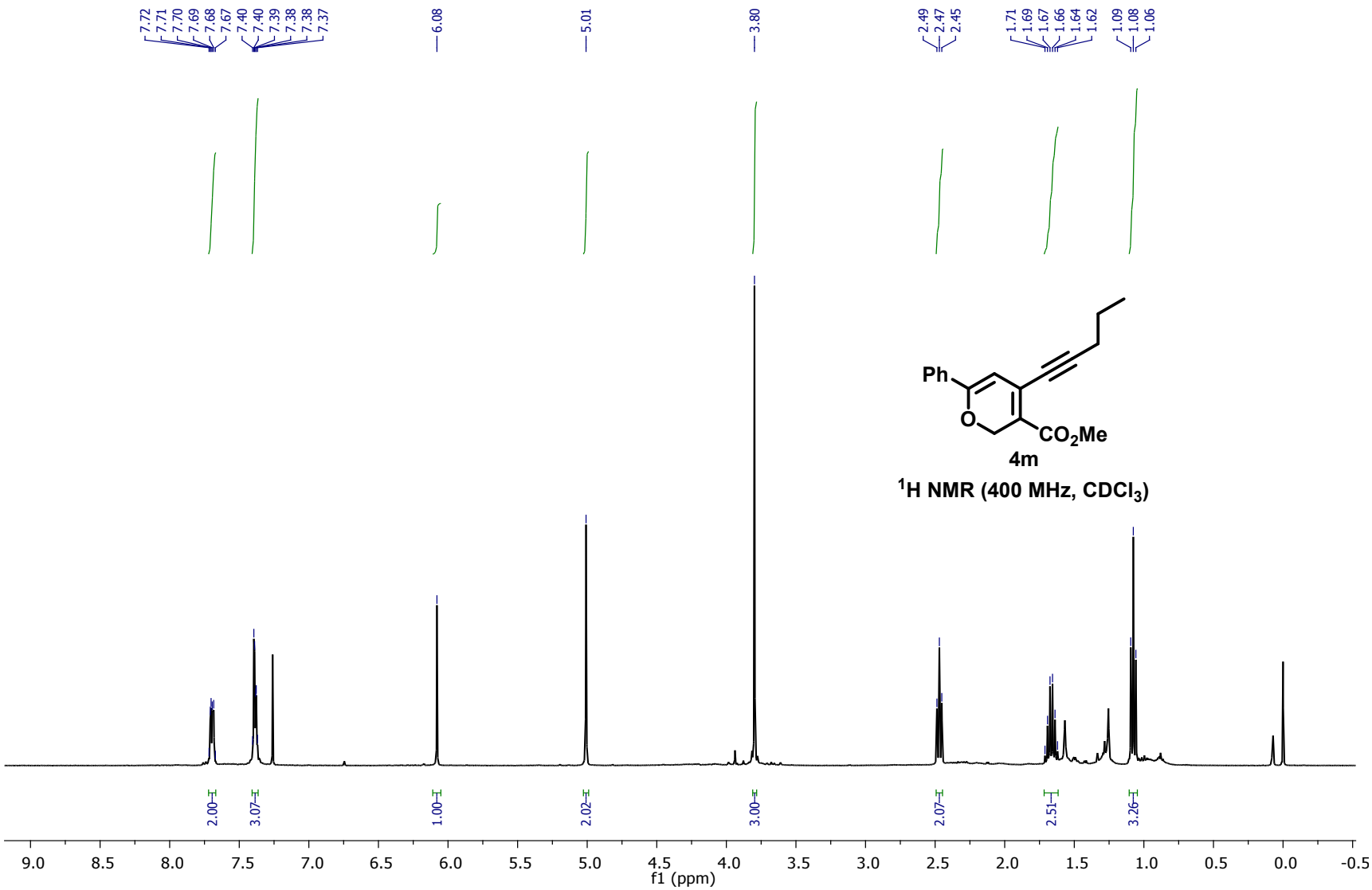
4k

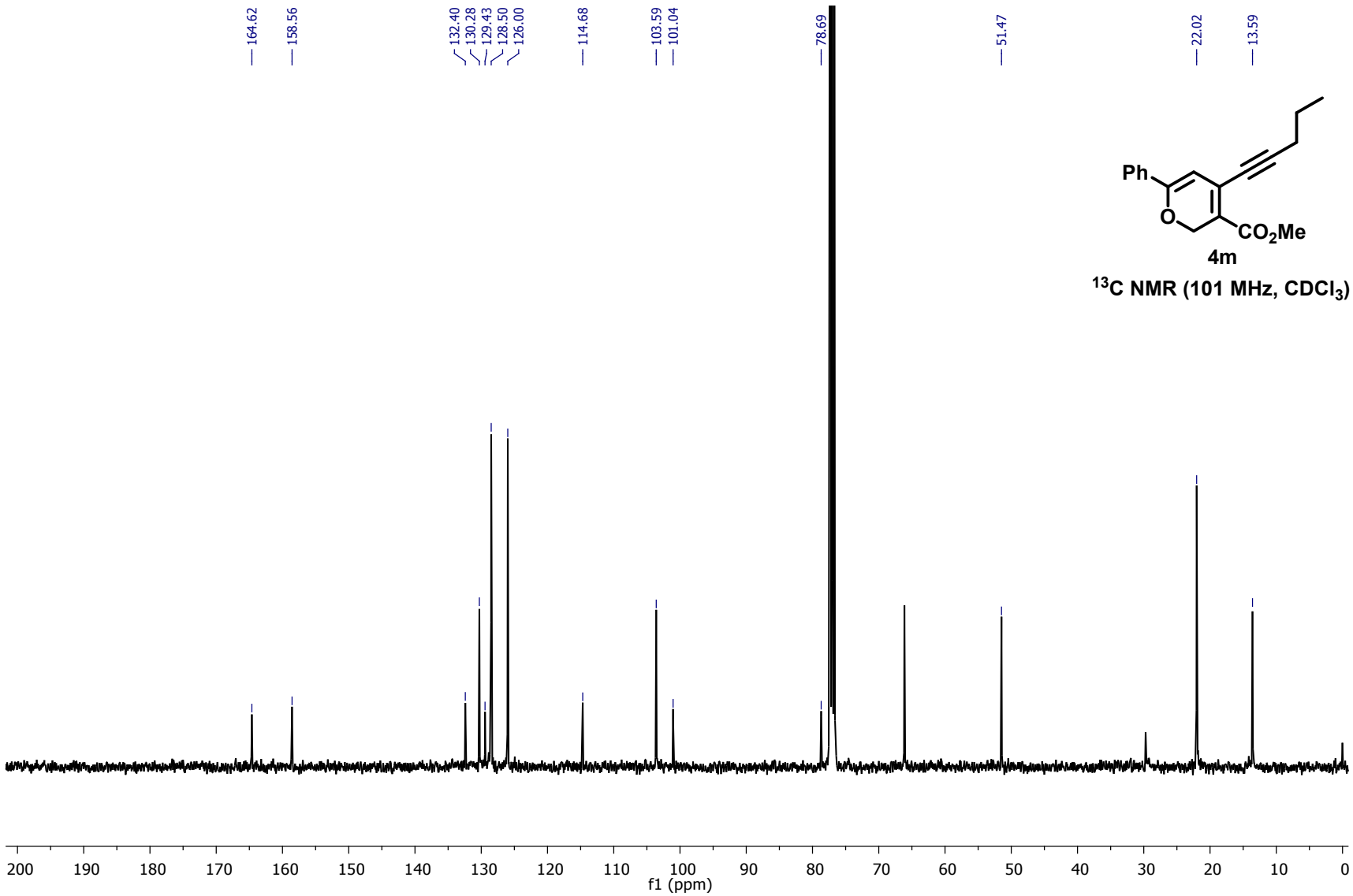
1H NMR (400 MHz, $CDCl_3$)

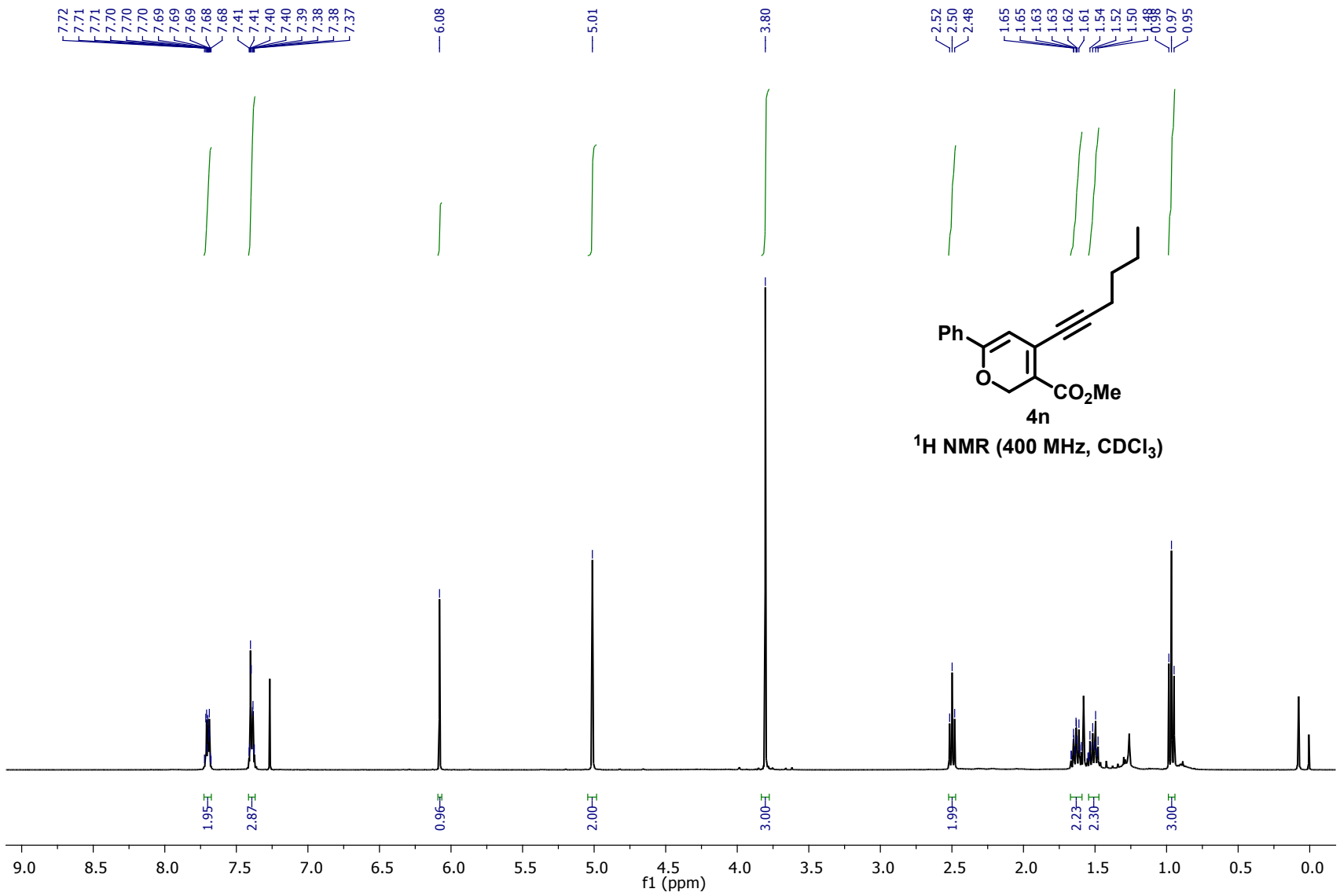

164.43
158.88
138.83
133.41
132.32
130.47
130.22
128.58
128.21
127.93
126.11
115.53
102.61
100.99
100.04
90.38
66.15
51.81
I
Ph
O
CO2Me
4k
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

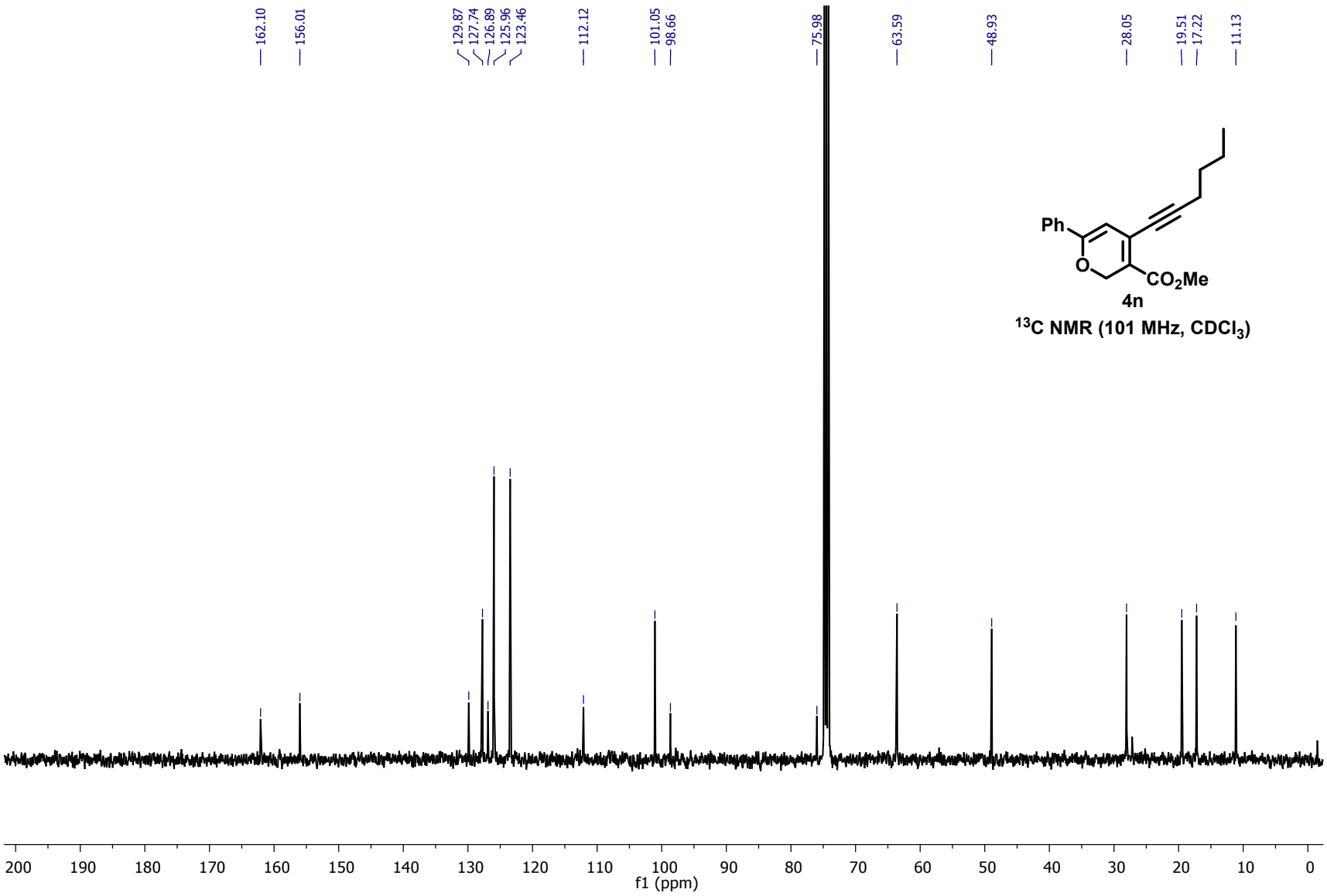

7.76
7.75
7.74
7.74
7.73
7.73
7.73
7.73
7.72
7.71
7.42
7.41
7.08
7.06
7.05
7.05
7.04
6.18
5.07
3.86
Ph
O
S
CO2Me
4l
1H NMR (400 MHz, CDCl3)
2.01
5.02
1.00
1.02
2.02
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

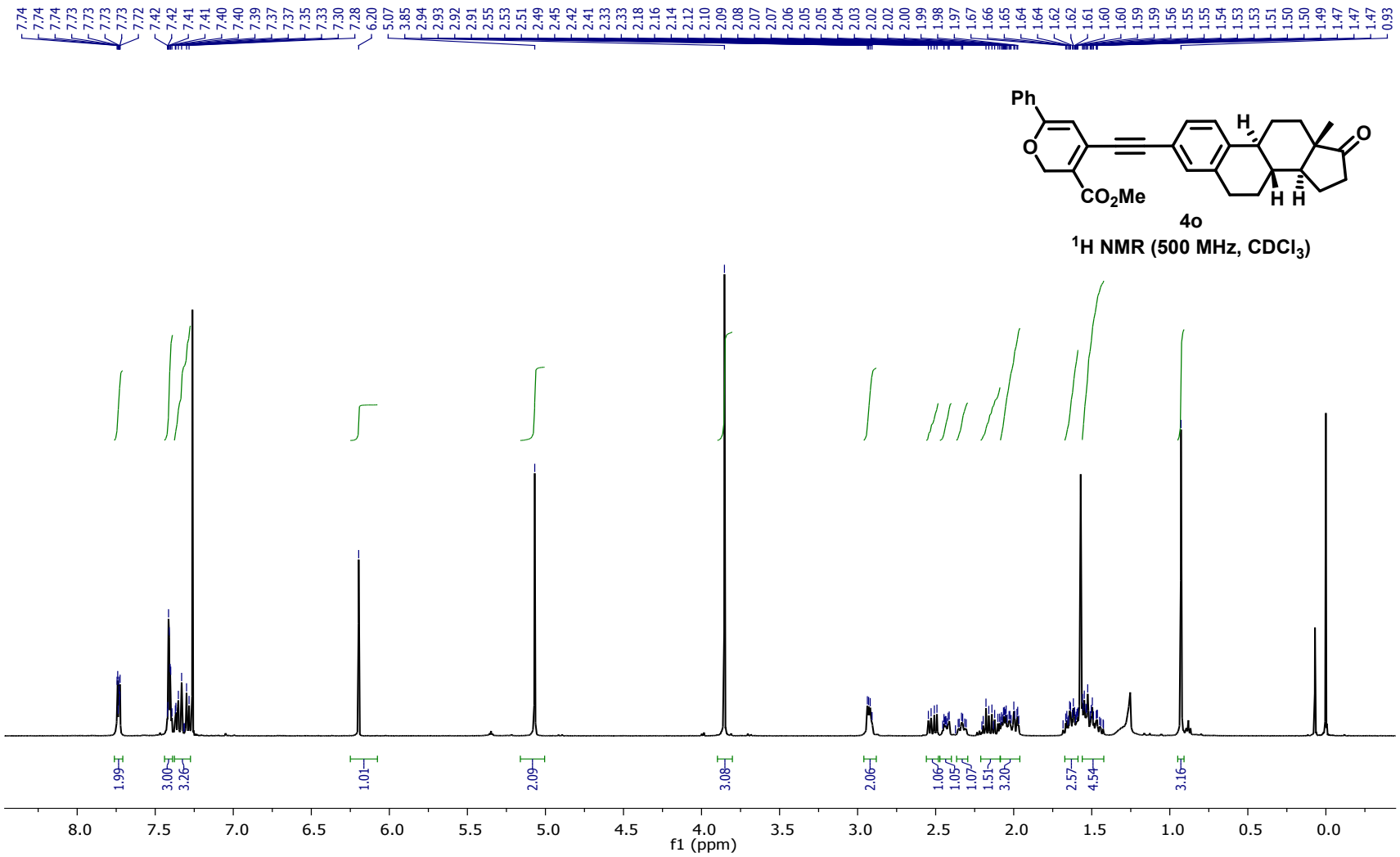

164.49
158.94
133.40
132.30
130.48
129.06
128.57
128.19
127.42
126.11
122.75
115.01
102.29
91.76
91.40
66.13
51.69
Ph
O
S
CO2Me
4l
13C NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

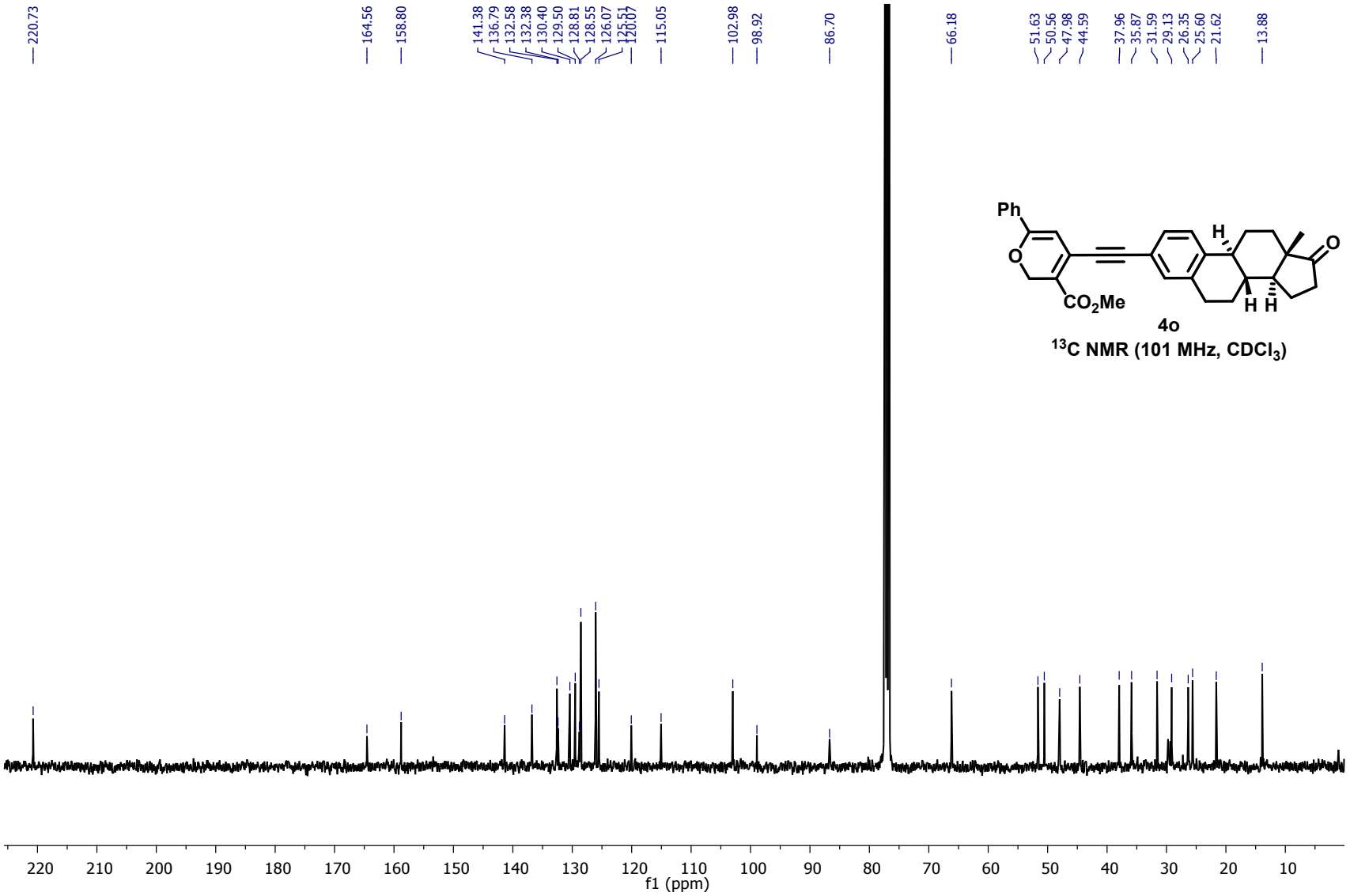

7.72
7.71
7.70
7.69
7.68
7.67
7.40
7.40
7.39
7.38
7.38
7.37
6.08
5.01
3.80
2.49
2.47
2.45
1.71
1.69
1.67
1.66
1.64
1.62
1.09
1.08
1.06
Ph
O
CO2Me
4m
1H NMR (400 MHz, CDCl3)
2.00
3.07
1.00
2.02
3.00
2.07
2.51
3.26
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

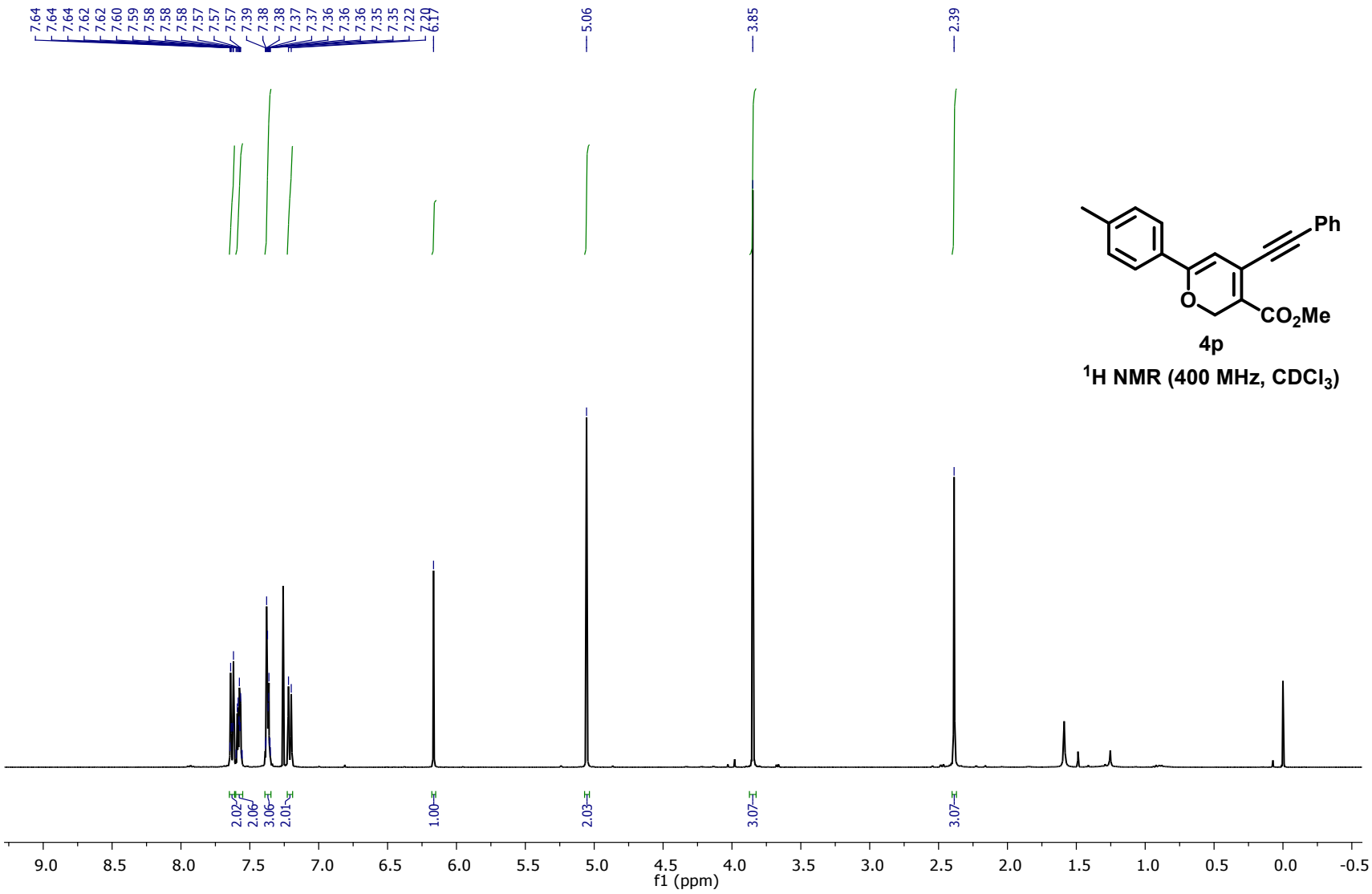

164.62
158.56
132.40
130.28
129.43
128.50
126.00
114.68
103.59
101.04
78.69
51.47
22.02
13.59
Ph
O
CO2Me
4m
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

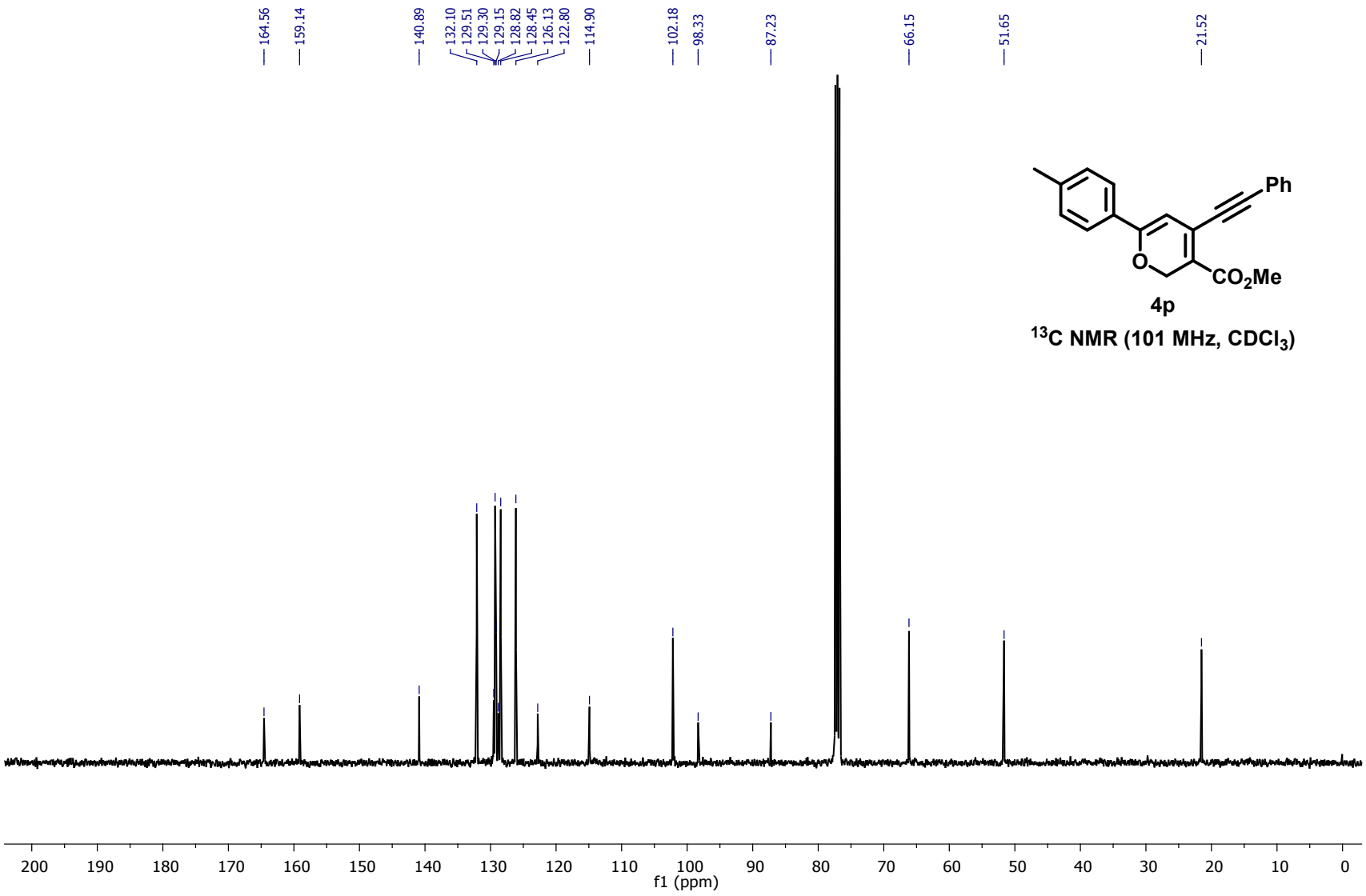

7.72
7.71
7.71
7.70
7.70
7.70
7.69
7.69
7.69
7.68
7.68
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
6.08
5.01
3.80
2.52
2.50
2.48
1.65
1.65
1.63
1.63
1.62
1.61
1.54
1.52
1.50
0.98
0.97
0.95
Ph
O
CO2Me
4n
1H NMR (400 MHz, CDCl3)
1.95
2.87
0.96
2.00
3.00
1.99
2.23
2.30
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

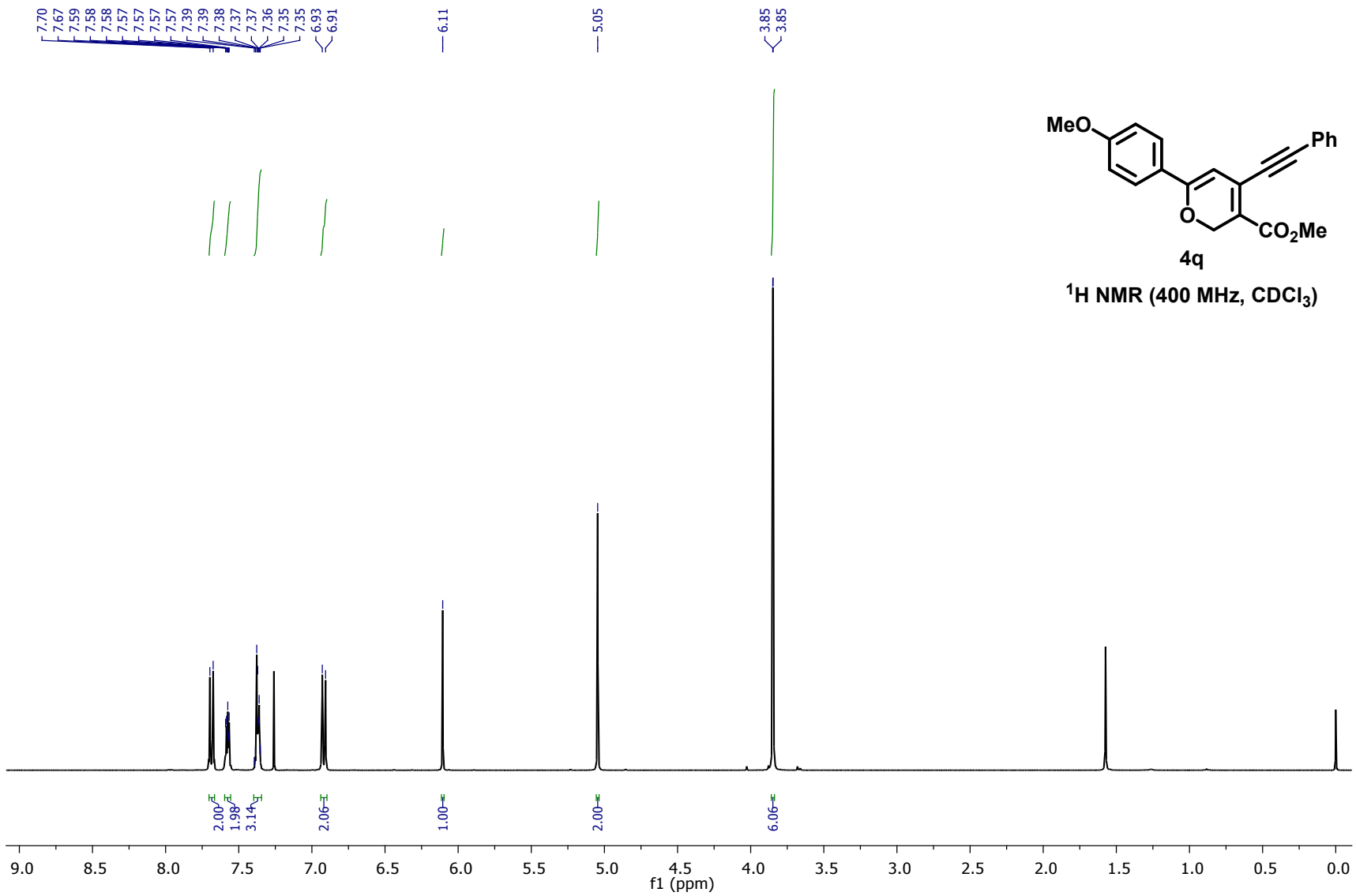

162.10
156.01
129.87
127.74
126.89
125.96
123.46
112.12
101.05
98.66
75.98
63.59
48.93
28.05
19.51
17.22
11.13
Ph
O
CO2Me
4n
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

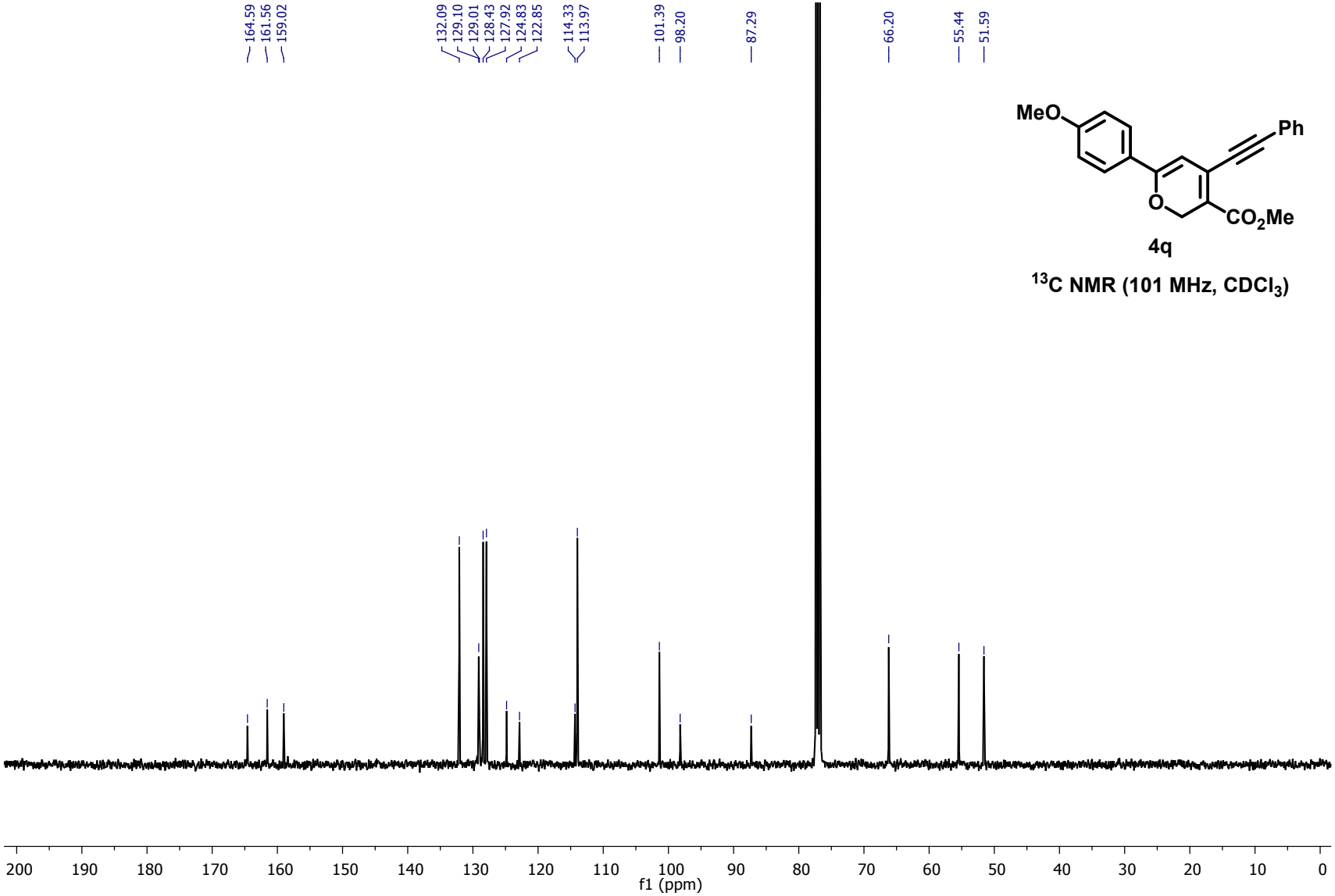

Ph
O
CO2Me
H
O
H H
4o
1H NMR (500 MHz, CDCl3)
f1 (ppm)

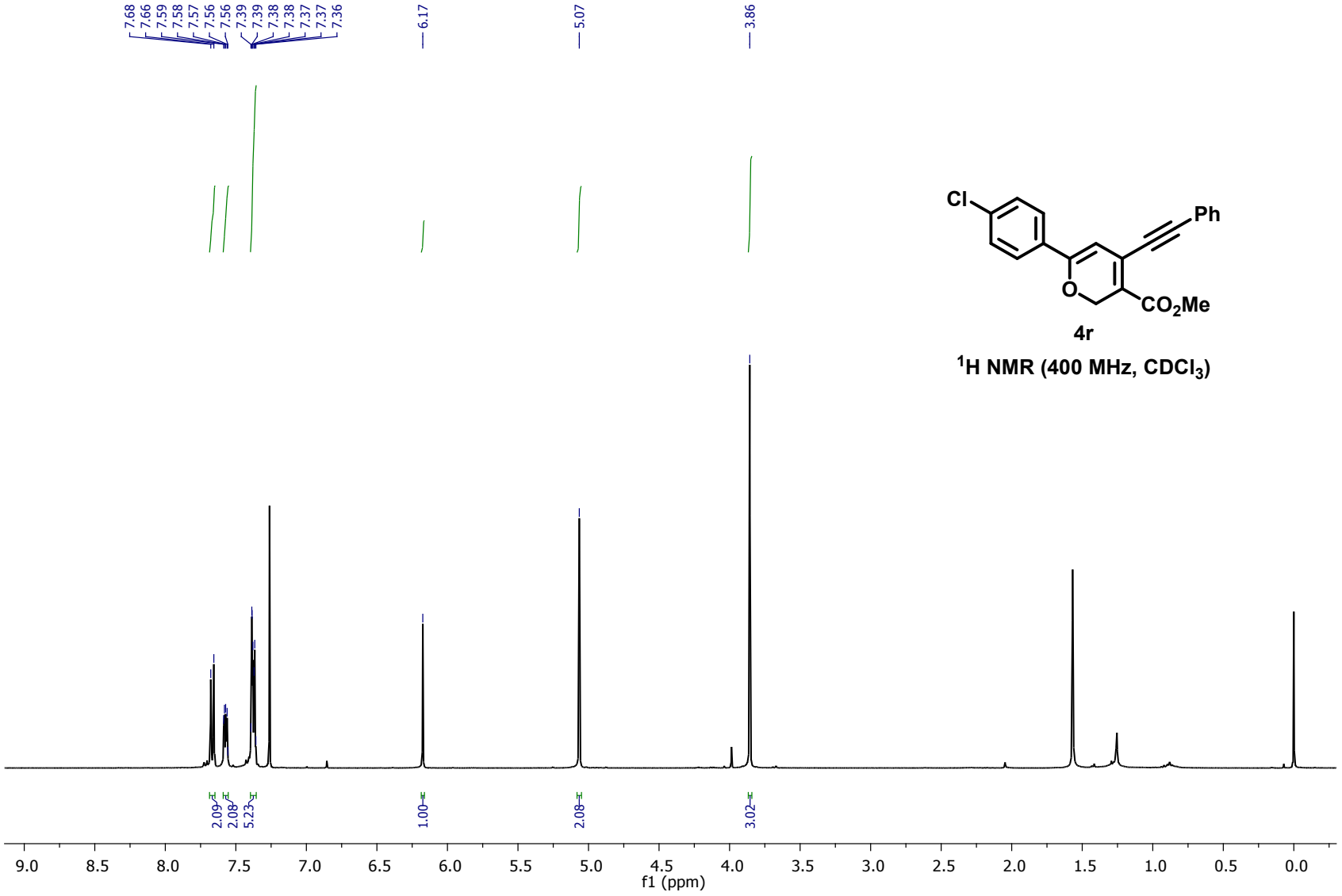

220.73
164.56
158.80
141.38
136.79
132.58
132.38
130.40
129.50
128.81
128.55
126.07
125.51
120.07
115.05
102.98
98.92
86.70
66.18
51.63
50.56
47.98
44.59
37.96
35.87
31.59
29.13
26.35
25.60
21.62
13.88
Ph
O
CO2Me
H
H H
O
4o
13C NMR (101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

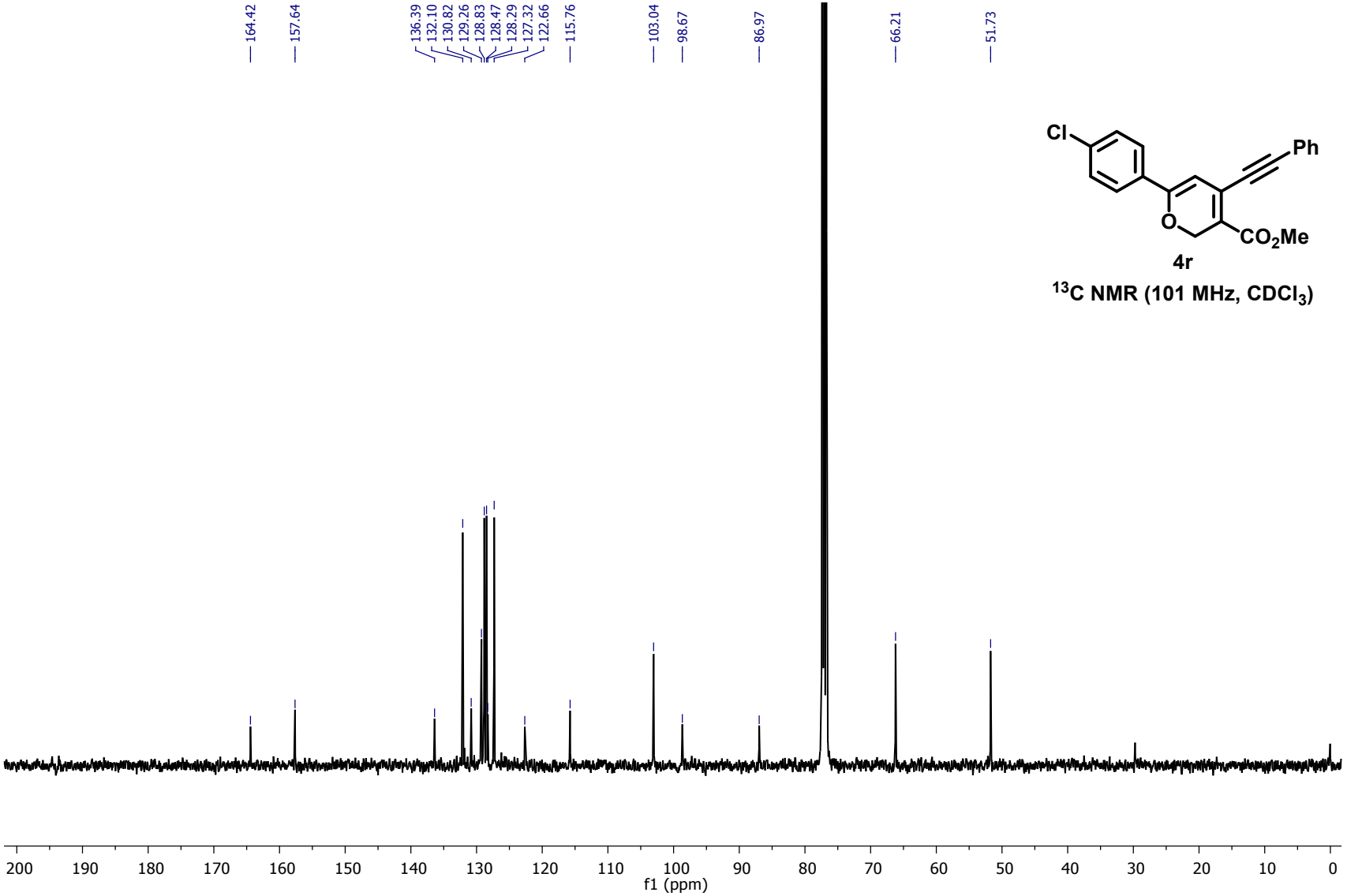

7.64
7.64
7.64
7.62
7.62
7.60
7.59
7.58
7.58
7.58
7.57
7.57
7.57
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.22
7.20
6.17
5.06
3.85
2.39
Ph
O
CO2Me
4p
1H NMR (400 MHz, CDCl3)
2.02
2.06
3.06
2.01
1.00
2.03
3.07
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

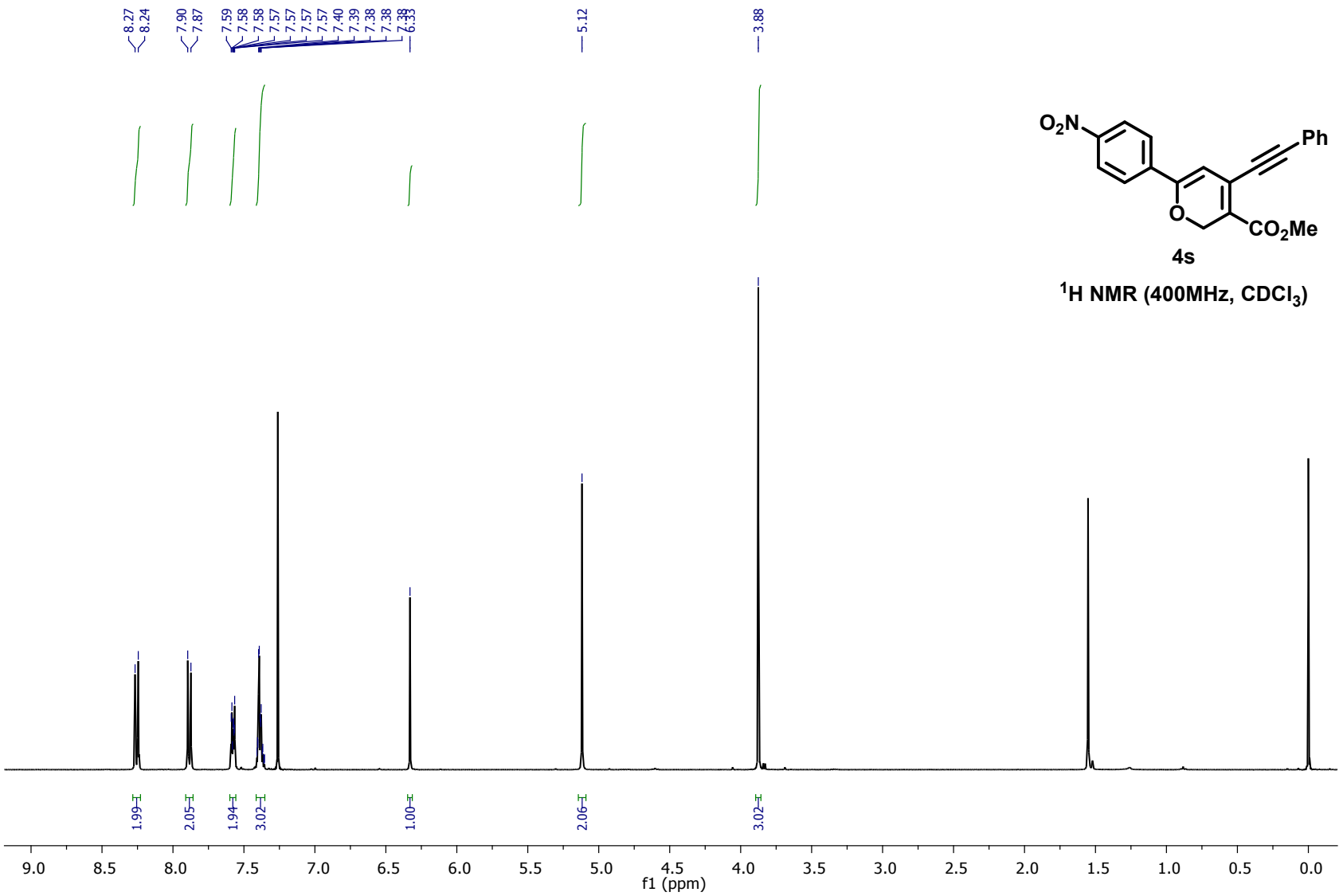

164.56
159.14
140.89
132.10
129.51
129.30
129.15
128.82
128.45
126.13
122.80
114.90
102.18
98.33
87.23
66.15
51.65
21.52
Ph
O
CO2Me
4p
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.70
7.67
7.59
7.58
7.58
7.57
7.57
7.57
7.57
7.39
7.39
7.38
7.37
7.37
7.36
7.35
7.35
6.93
6.91
6.11
5.05
3.85
3.85
MeO
Ph
O
CO2Me
4q
1H NMR (400 MHz, CDCl3)
2.00
1.98
3.14
2.06
1.00
2.00
6.06
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)


164.59
161.56
159.02
132.09
129.10
129.01
128.43
127.92
124.83
122.85
114.33
113.97
101.39
98.20
87.29
66.20
55.44
51.59
MeO
Ph
O
CO2Me
4q
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

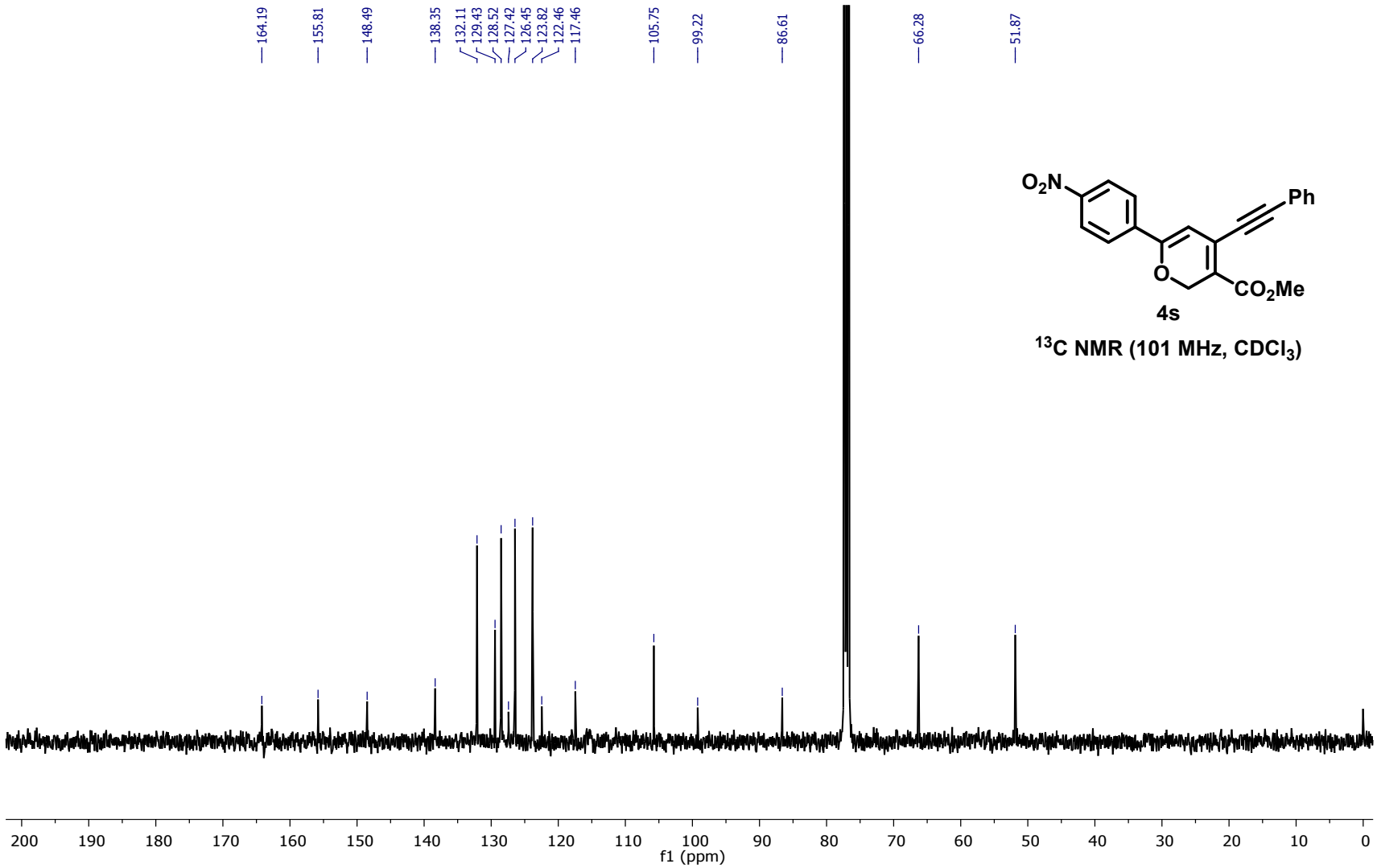

7.68
7.66
7.59
7.58
7.57
7.56
7.56
7.39
7.39
7.38
7.38
7.37
7.37
7.36
6.17
5.07
3.86
Cl
Ph
O
CO2Me
4r
1H NMR (400 MHz, CDCl3)
2.09
2.08
5.23
1.00
2.08
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

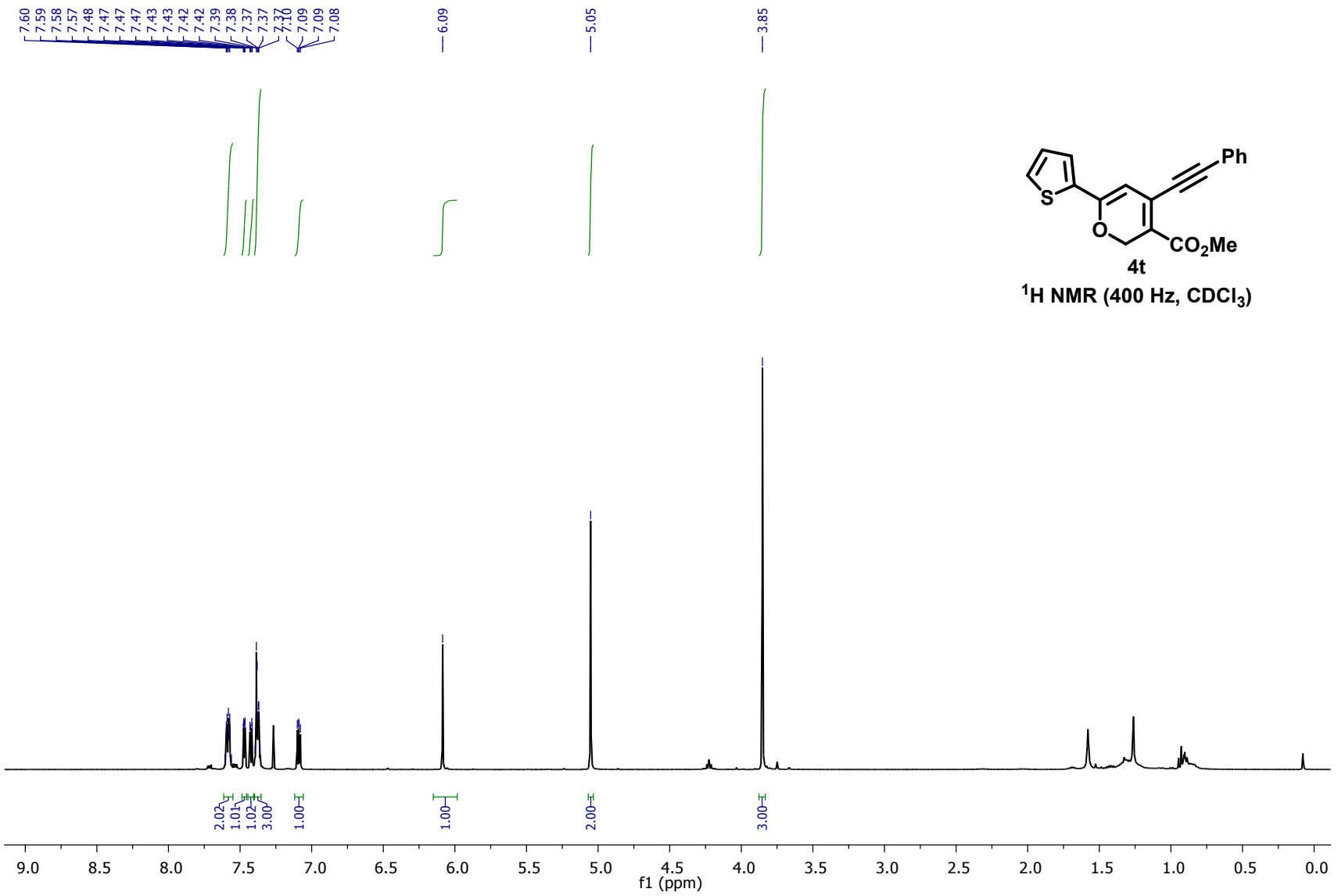

164.42
157.64
136.39
132.10
130.82
129.26
128.83
128.47
128.29
127.32
122.66
115.76
103.04
98.67
86.97
66.21
51.73
Cl
Ph
O
CO2Me
4r
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

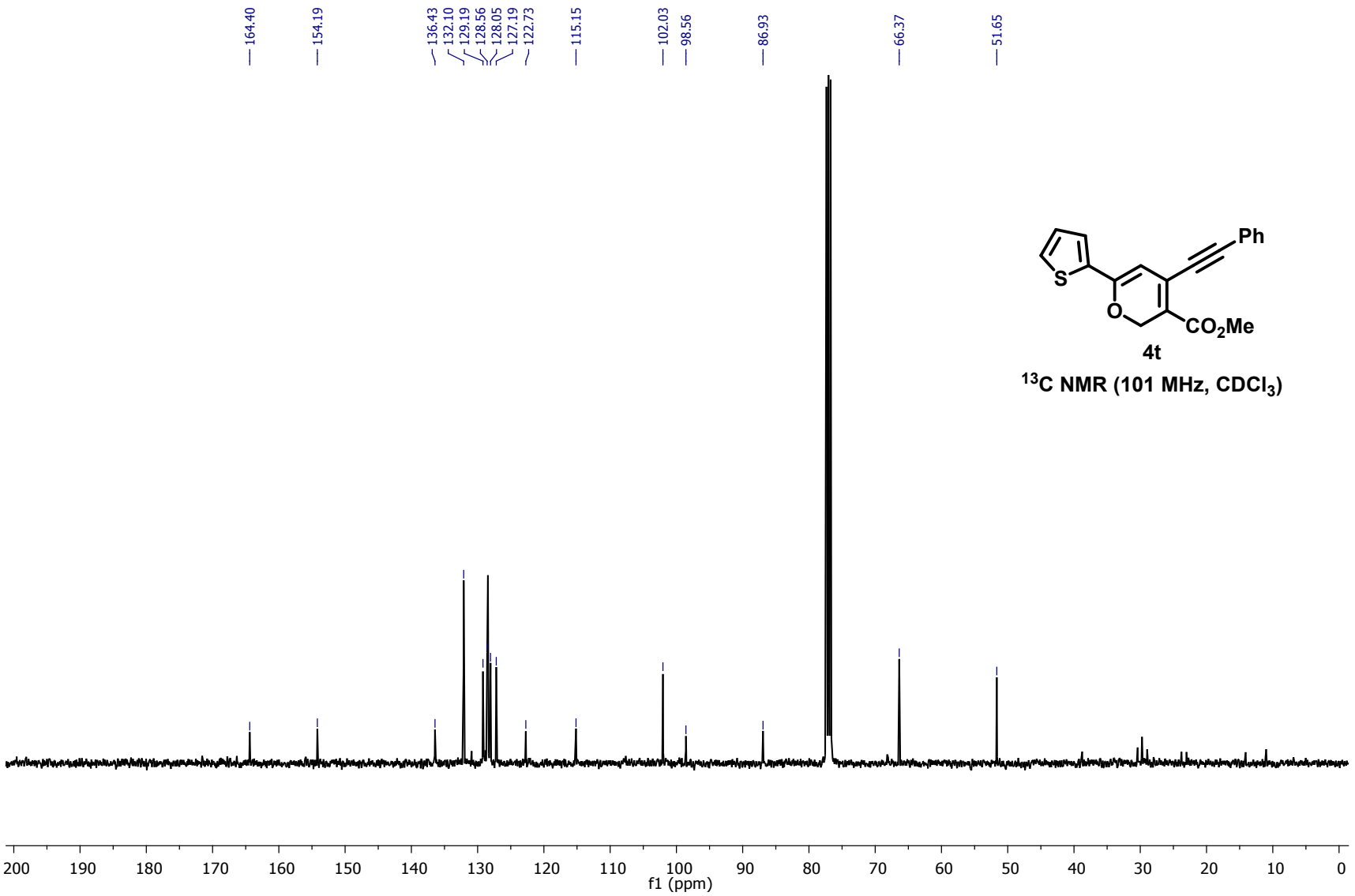


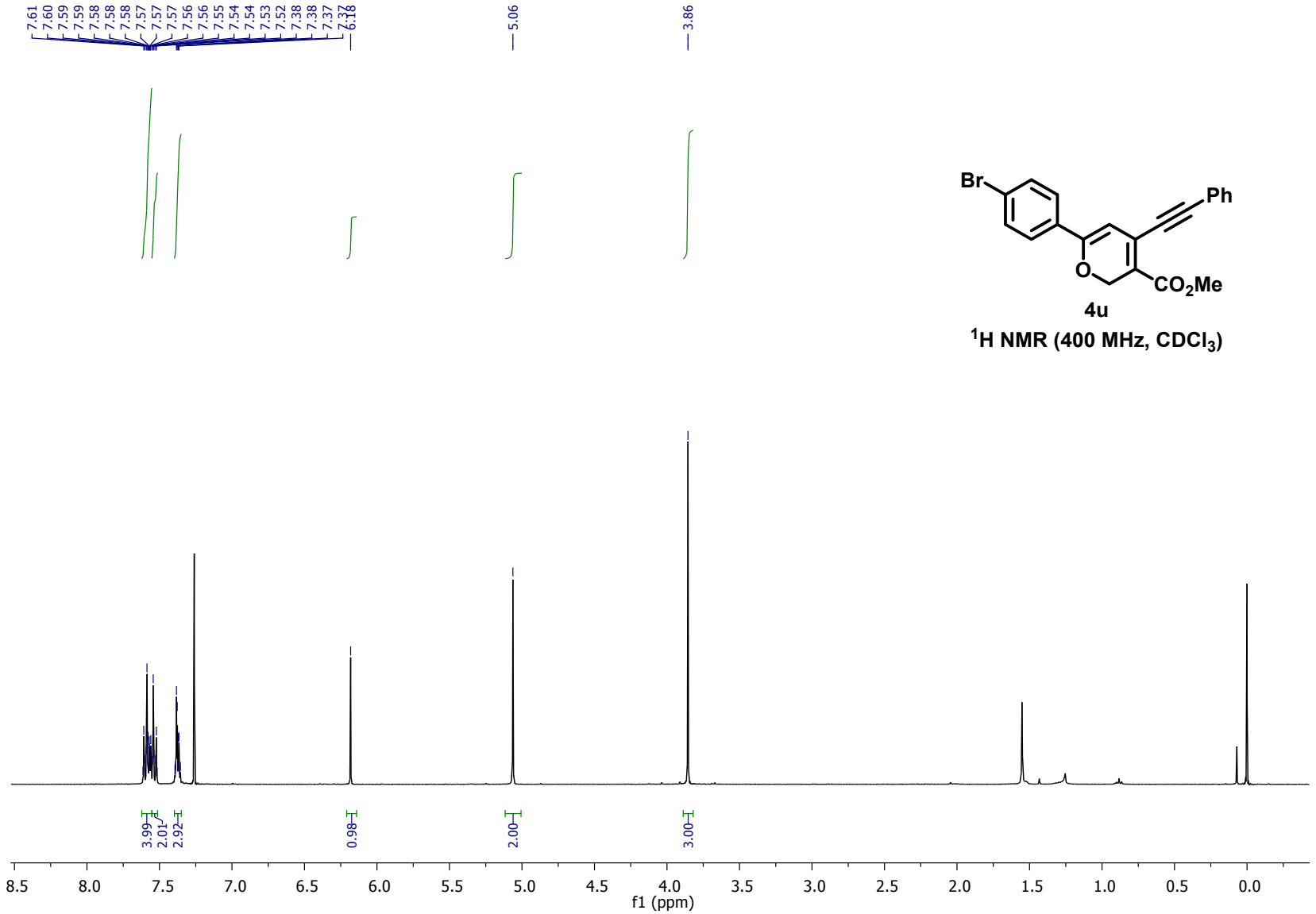
4s

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


164.19
155.81
148.49
138.35
132.11
129.43
128.52
127.42
126.45
123.82
122.46
117.46
105.75
99.22
86.61
66.28
51.87
O2N
Ph
O
CO2Me
4s
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

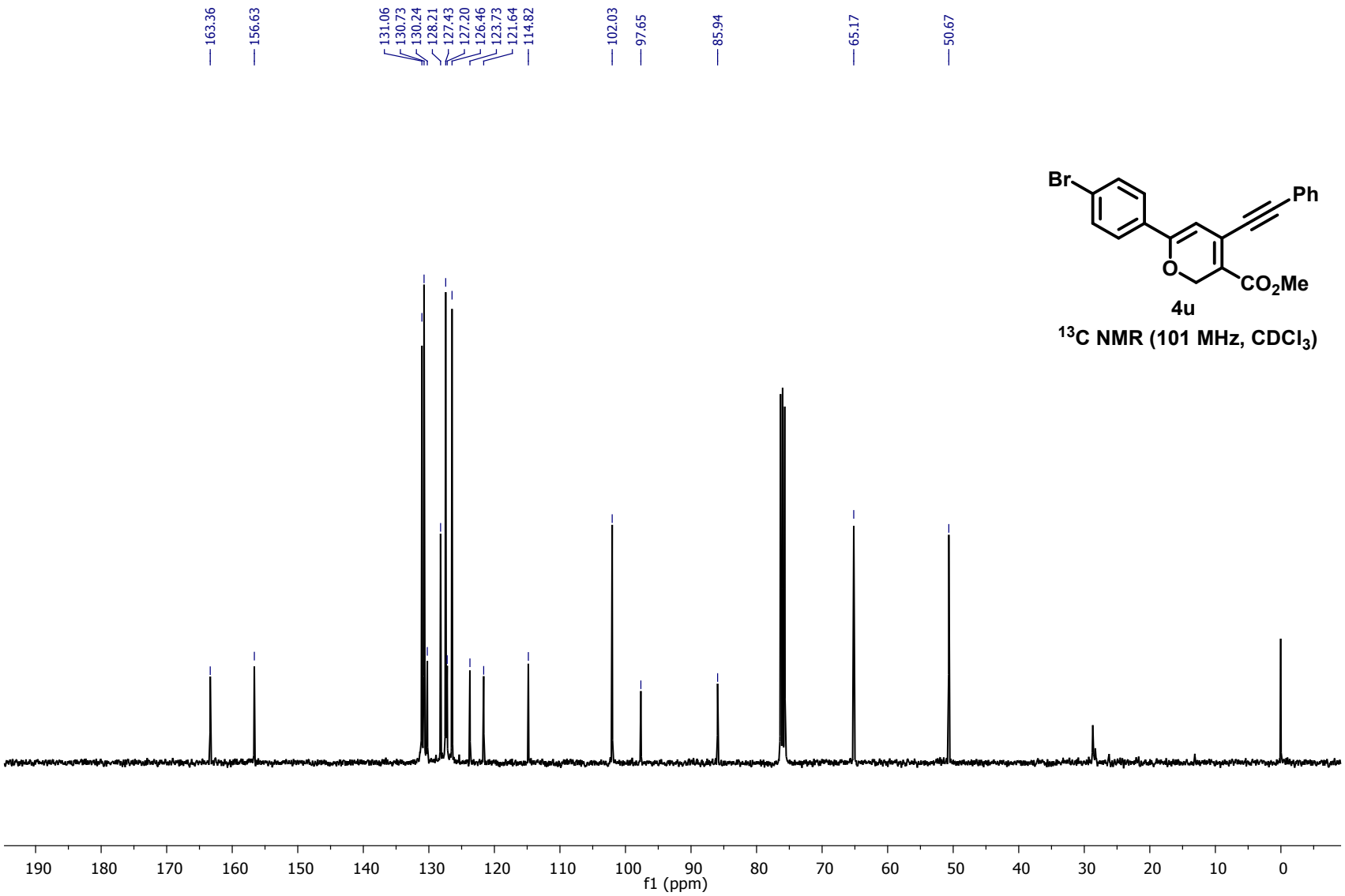

7.60
7.59
7.58
7.57
7.48
7.47
7.47
7.47
7.43
7.42
7.42
7.39
7.38
7.37
7.37
7.10
7.09
7.09
7.08
6.09
5.05
3.85
Ph
S
O
CO2Me
4t
1H NMR (400 Hz, CDCl3)
2.02
1.01
1.02
3.00
1.00
1.00
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

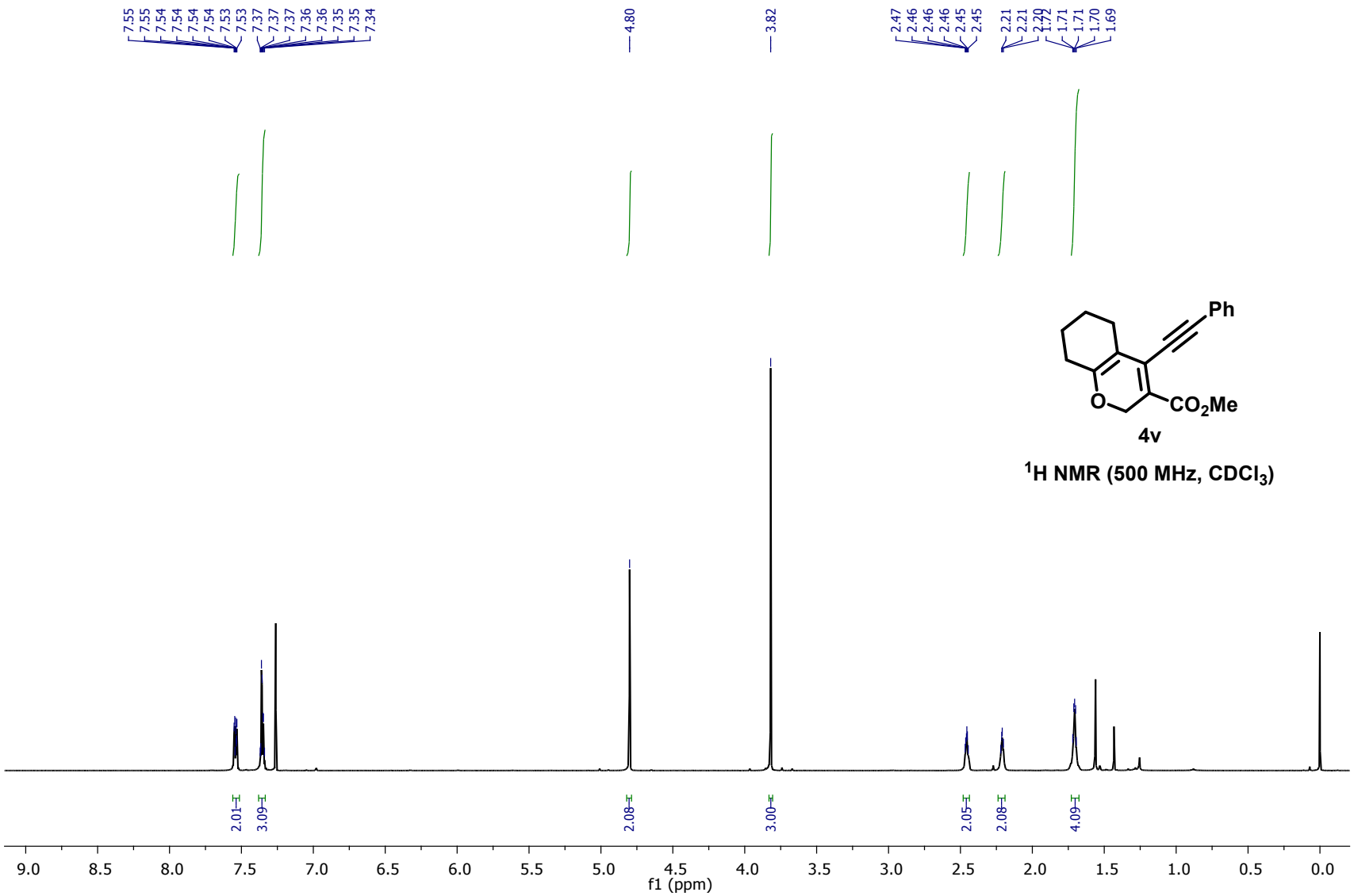

164.40
154.19
136.43
132.10
129.19
128.56
128.05
127.19
122.73
115.15
102.03
98.56
86.93
66.37
51.65
Ph
S
O
CO2Me
4t
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

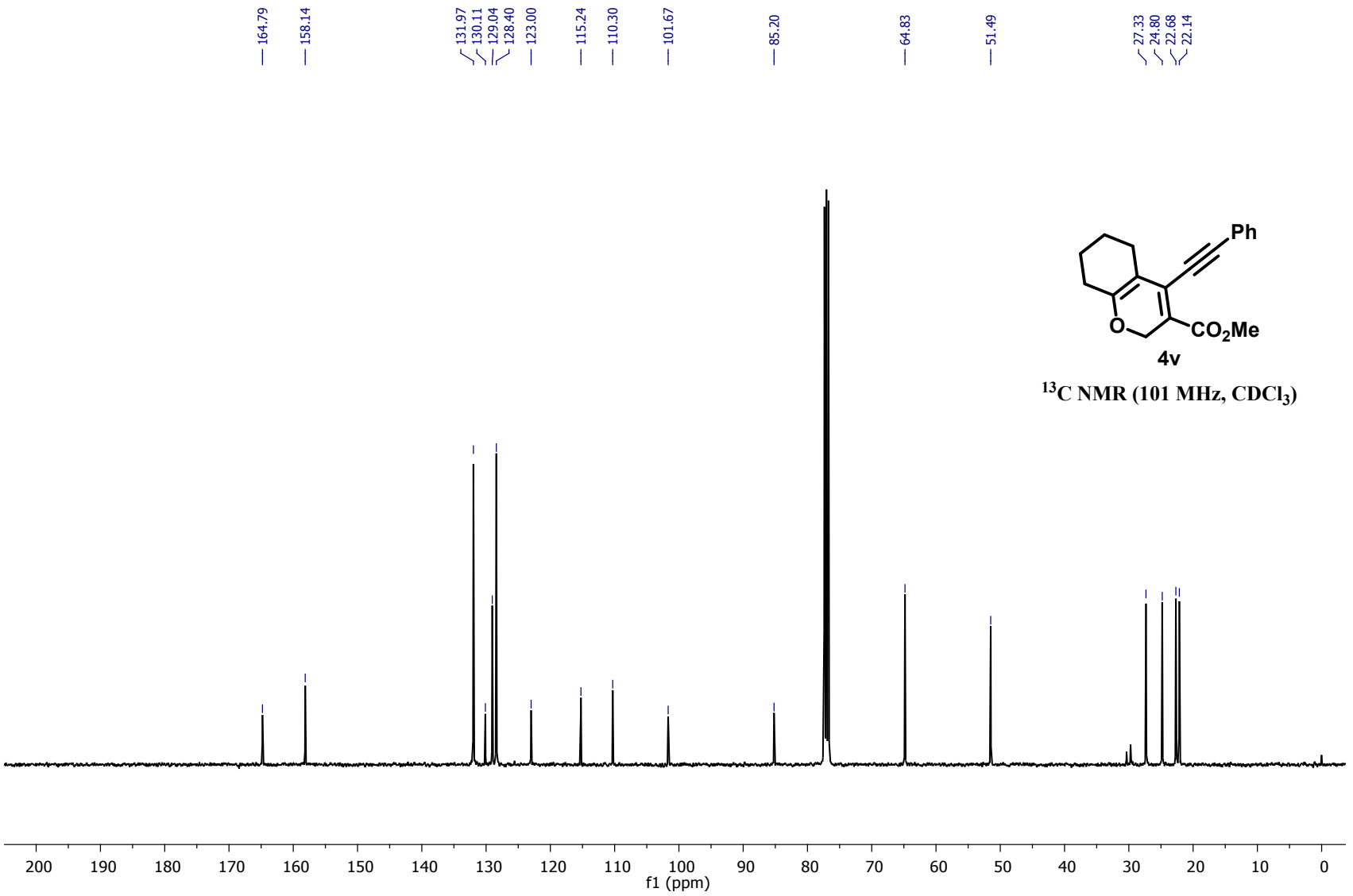


4u

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

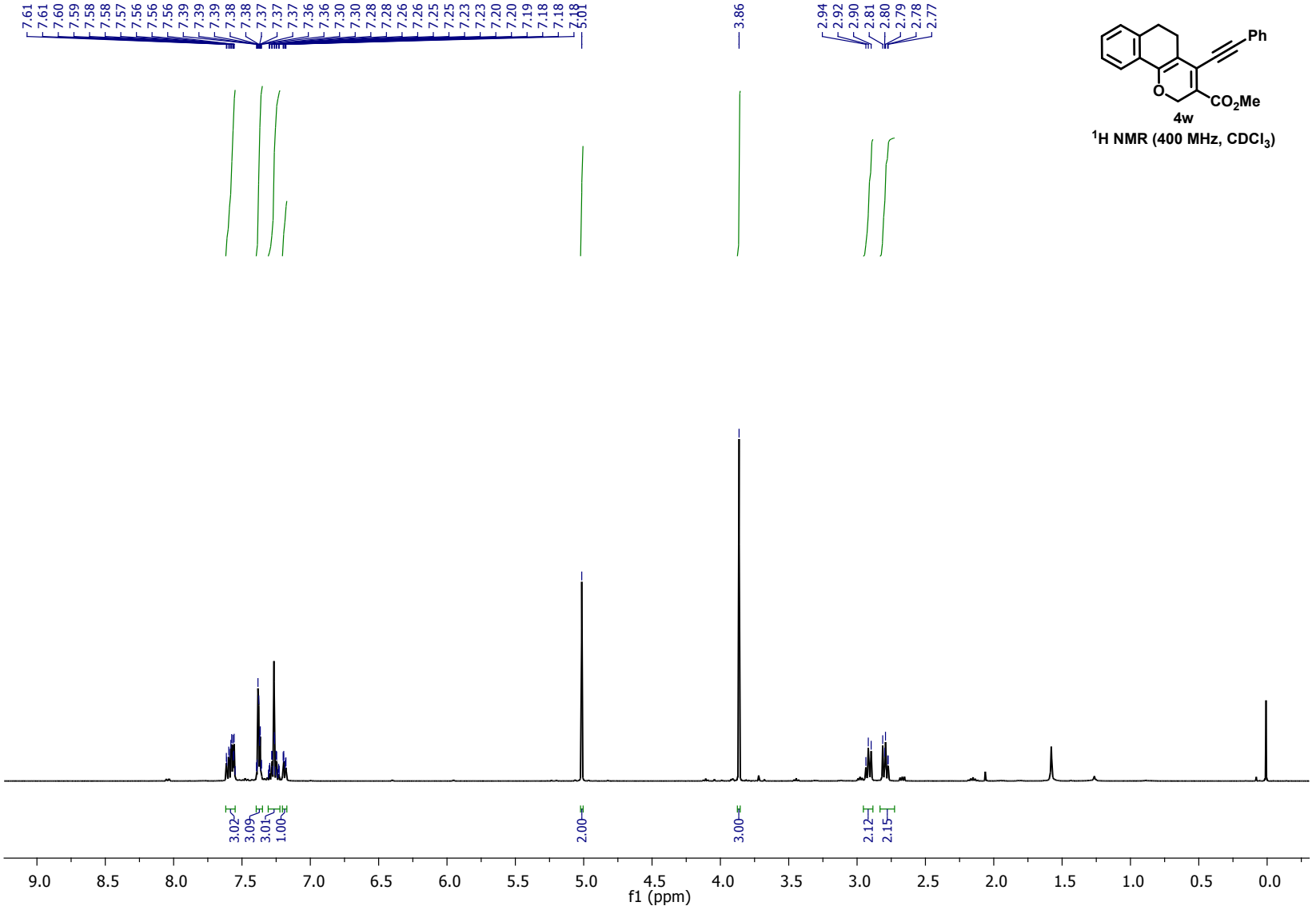

163.36
156.63
131.06
130.73
130.24
128.21
127.43
127.20
126.46
123.73
121.64
114.82
102.03
97.65
85.94
65.17
50.67
Br
Ph
O
CO2Me
4u
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

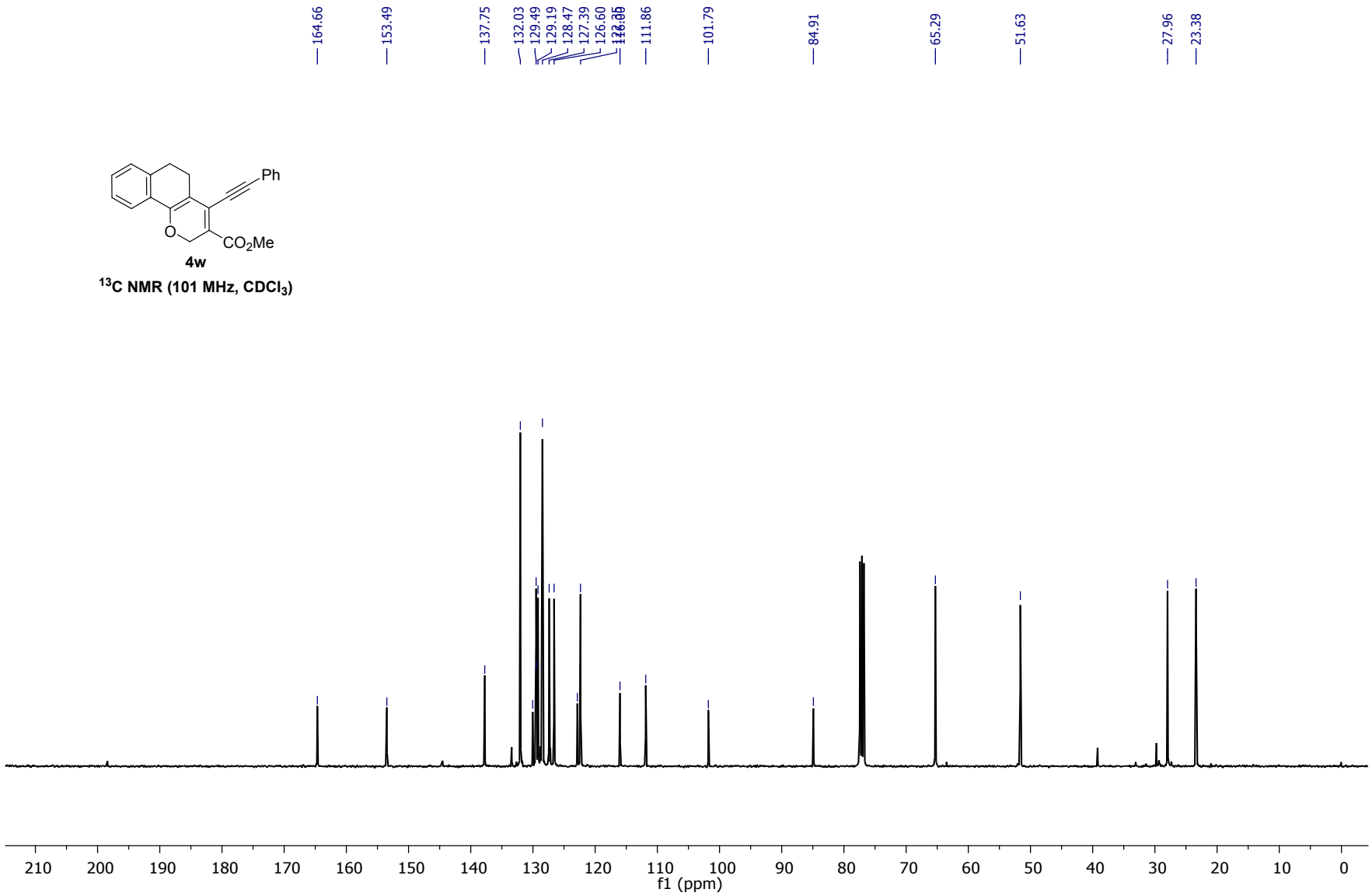

7.55
7.55
7.54
7.54
7.54
7.54
7.53
7.53
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.34
4.80
3.82
2.47
2.46
2.46
2.46
2.45
2.45
2.21
2.21
1.72
1.71
1.71
1.70
1.69
Ph
O
CO2Me
4v
1H NMR (500 MHz, CDCl3)
2.01
3.09
2.08
3.00
2.05
2.08
4.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

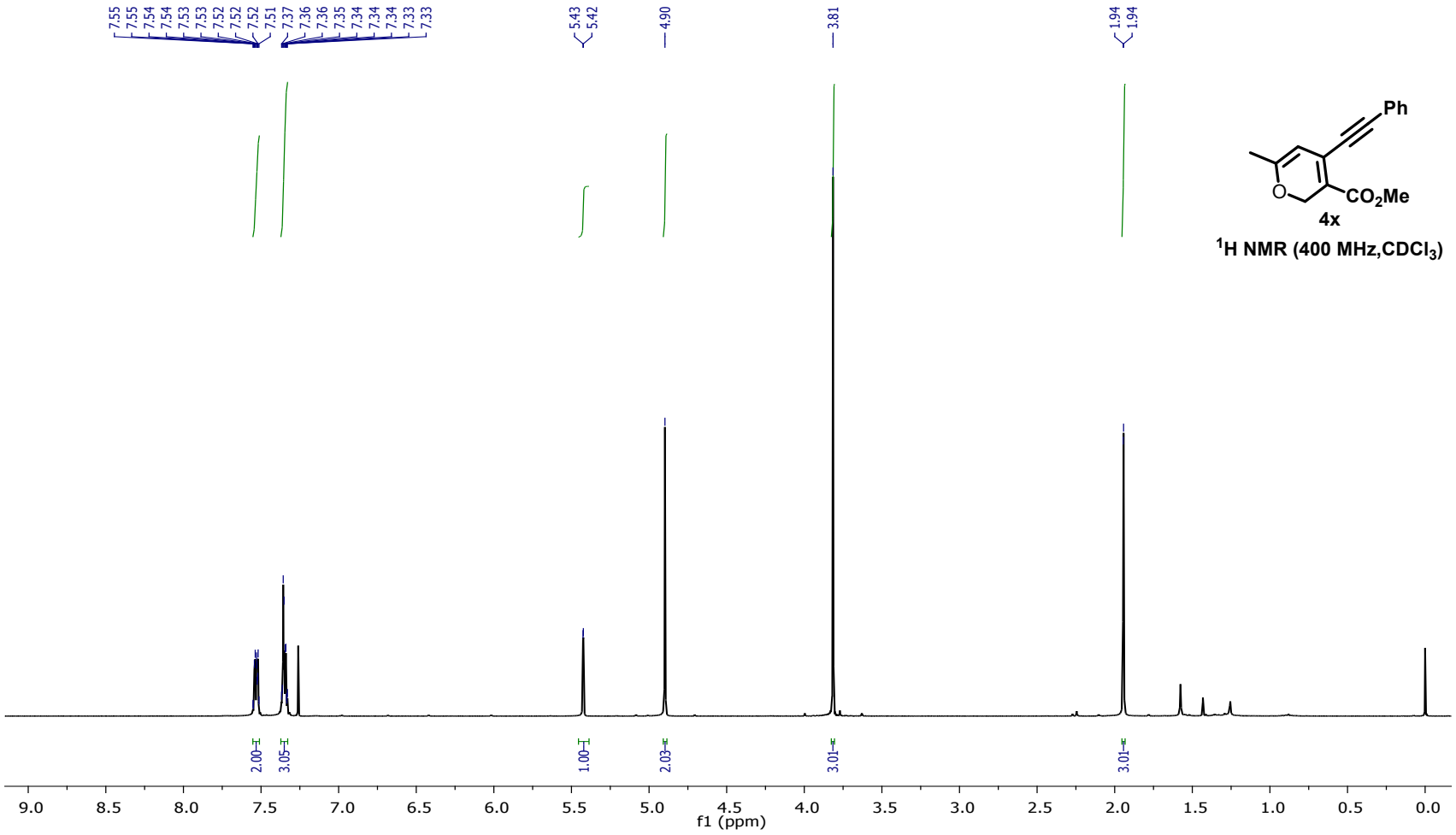


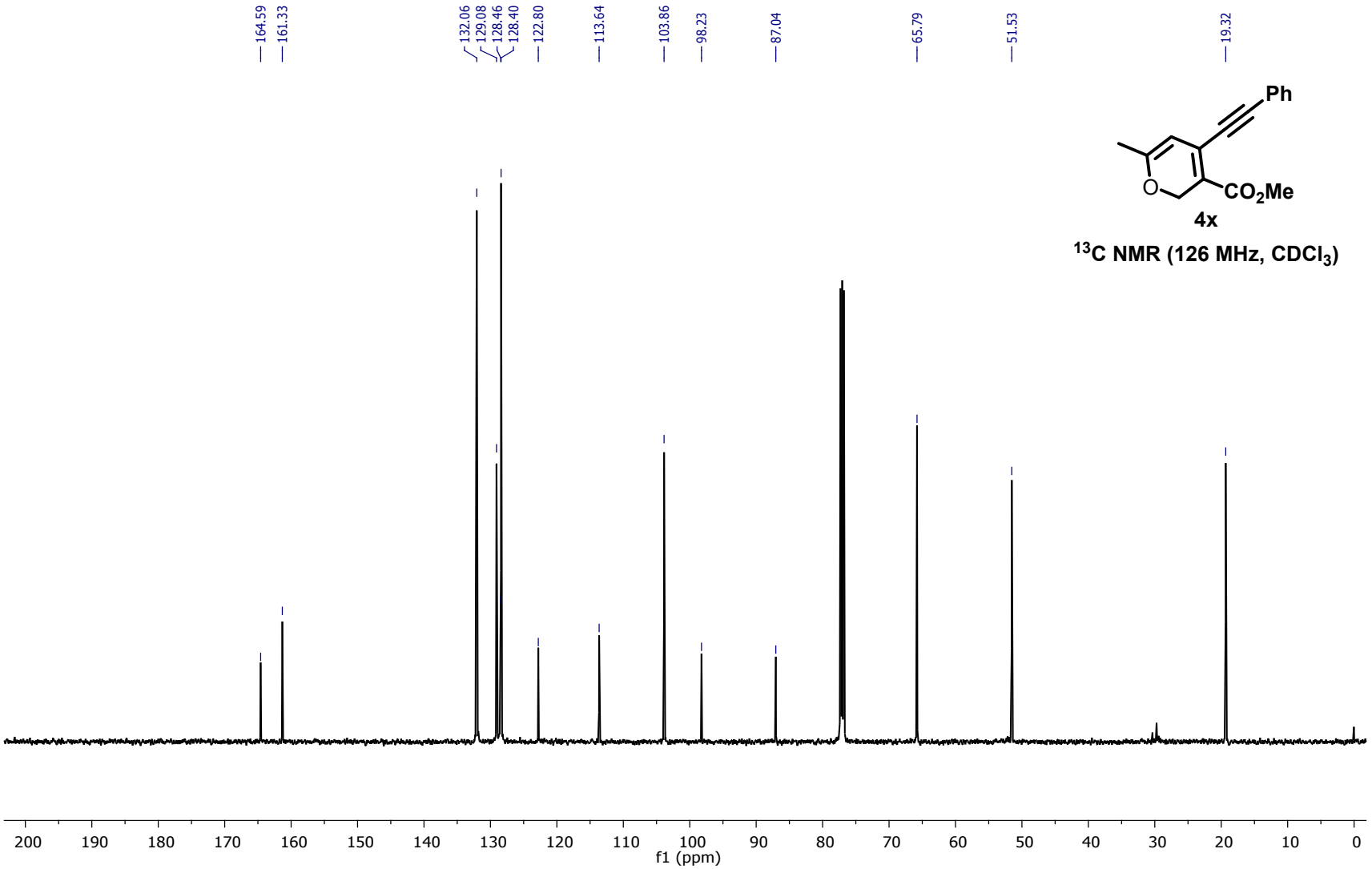
4v

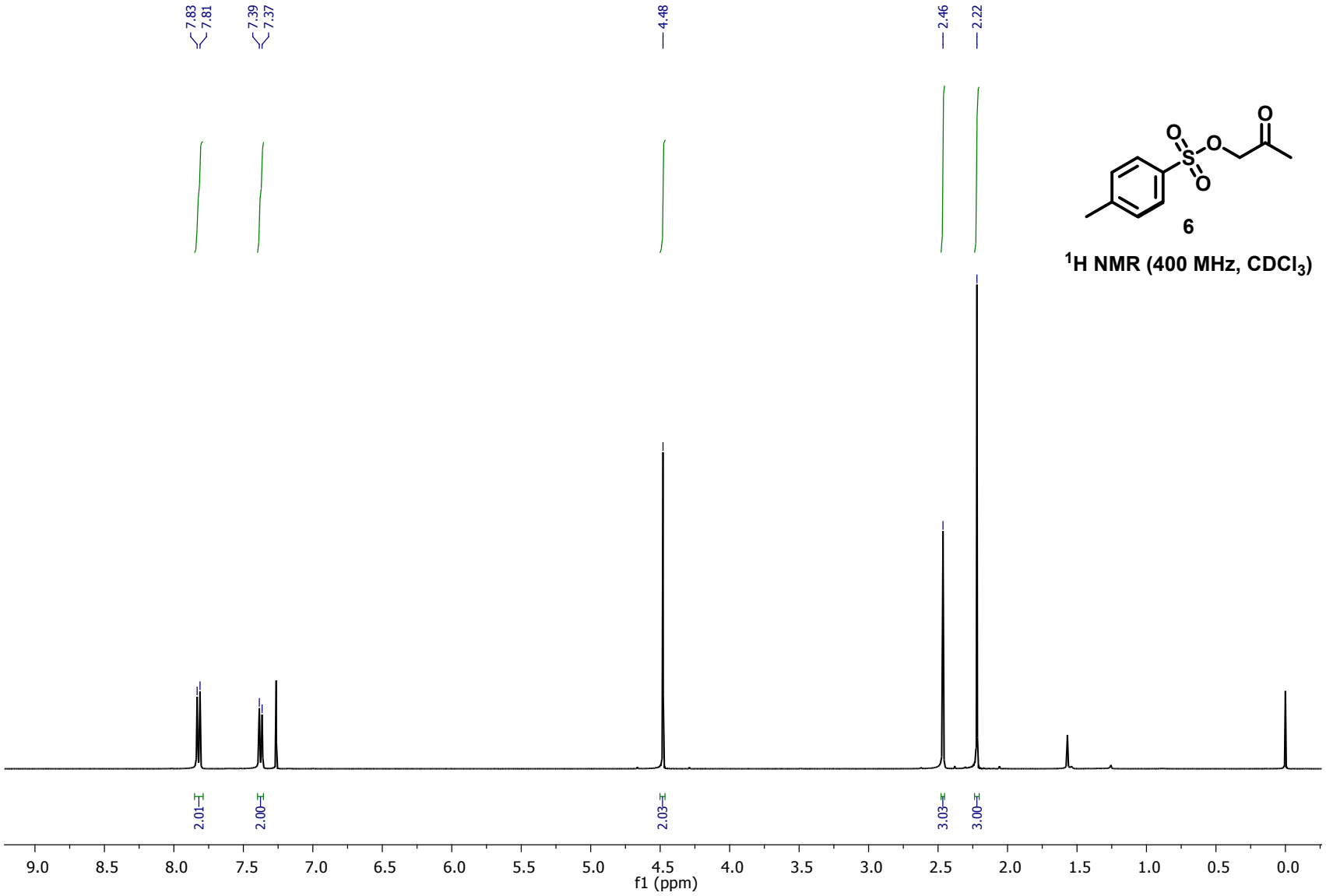
^{13}C NMR (101 MHz, $CDCl_3$)

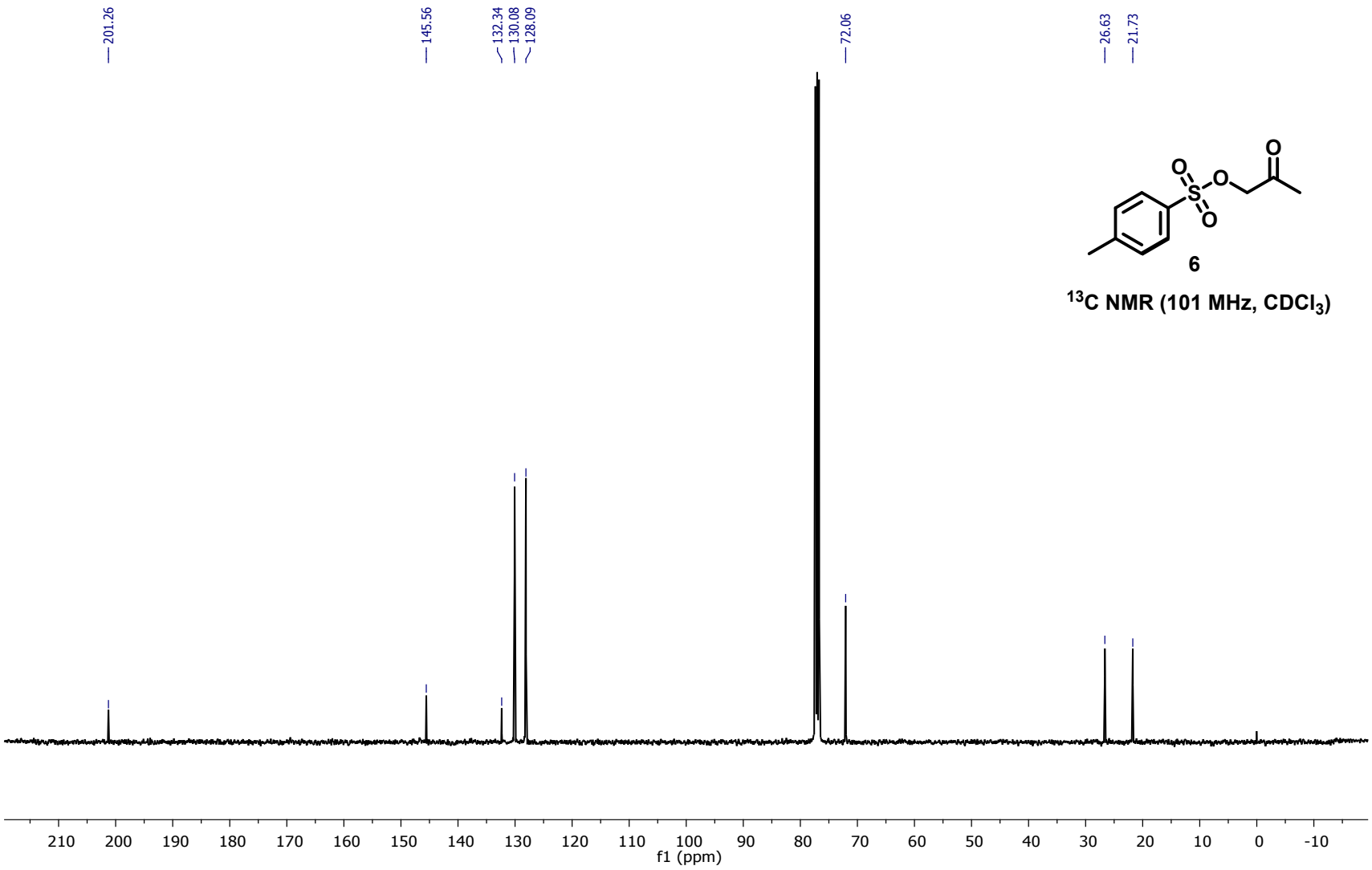

7.61
7.61
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.56
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.30
7.30
7.28
7.28
7.26
7.26
7.25
7.25
7.23
7.23
7.20
7.20
7.19
7.18
7.18
7.18
5.01
3.86
2.94
2.92
2.90
2.81
2.80
2.79
2.78
2.77
Ph
O
CO2Me
4w
1H NMR (400 MHz, CDCl3)
3.02
3.09
3.01
1.00
2.00
3.00
2.12
2.15
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)

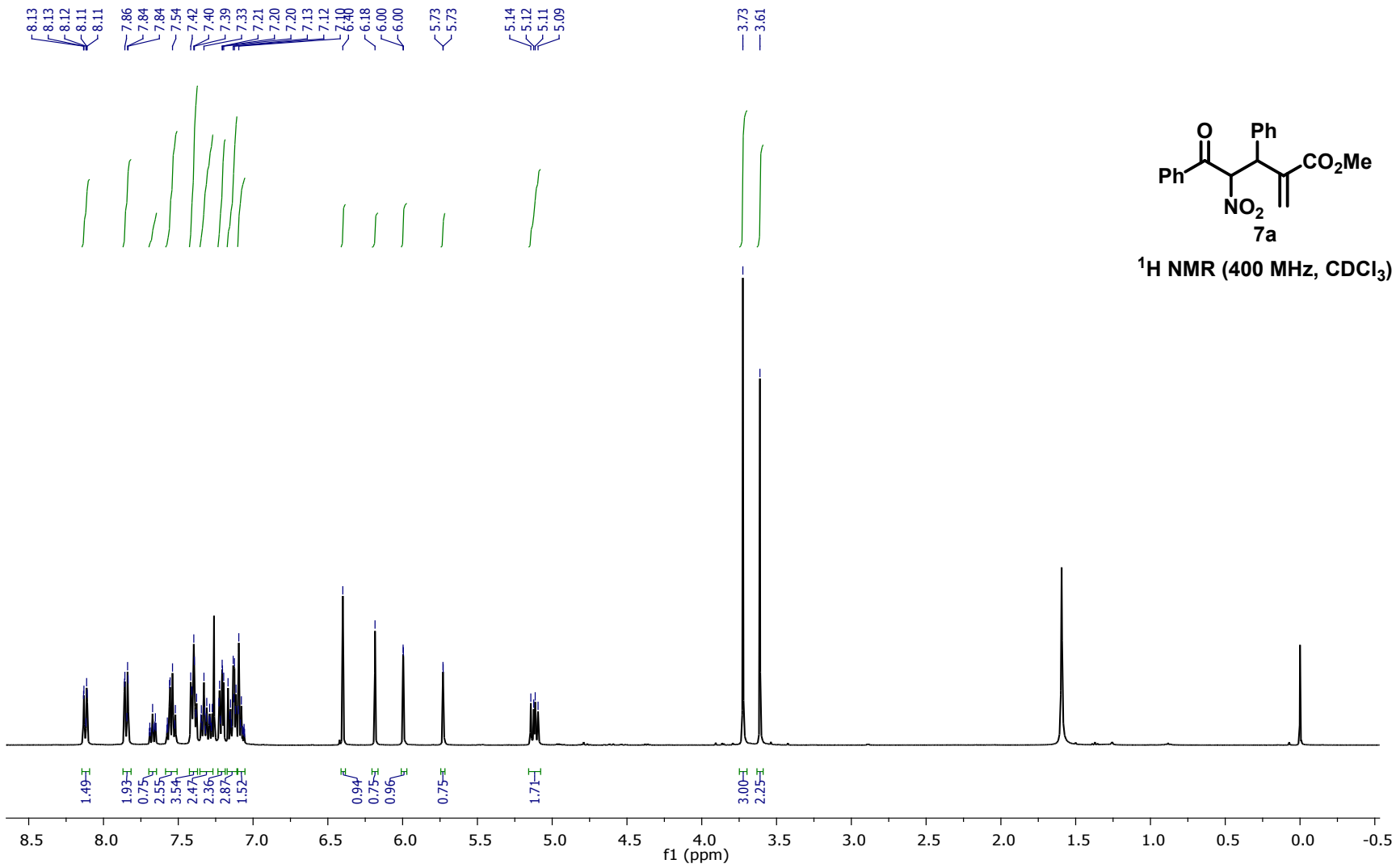

164.66
153.49
137.75
132.03
129.49
129.19
128.47
127.39
126.60
111.86
101.79
84.91
65.29
51.63
27.96
23.38
Ph
O
CO2Me
4w
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.37
7.36
7.36
7.35
7.34
7.34
7.34
7.33
7.33
5.43
5.42
4.90
3.81
1.94
1.94
Ph
CO2Me
4x
1H NMR (400 MHz,CDCl3)
2.00
3.05
1.00
2.03
3.01
3.01
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)


164.59
161.33
132.06
129.08
128.46
128.40
122.80
113.64
103.86
98.23
87.04
65.79
51.53
19.32
Ph
O
CO2Me
4x
13C NMR (126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

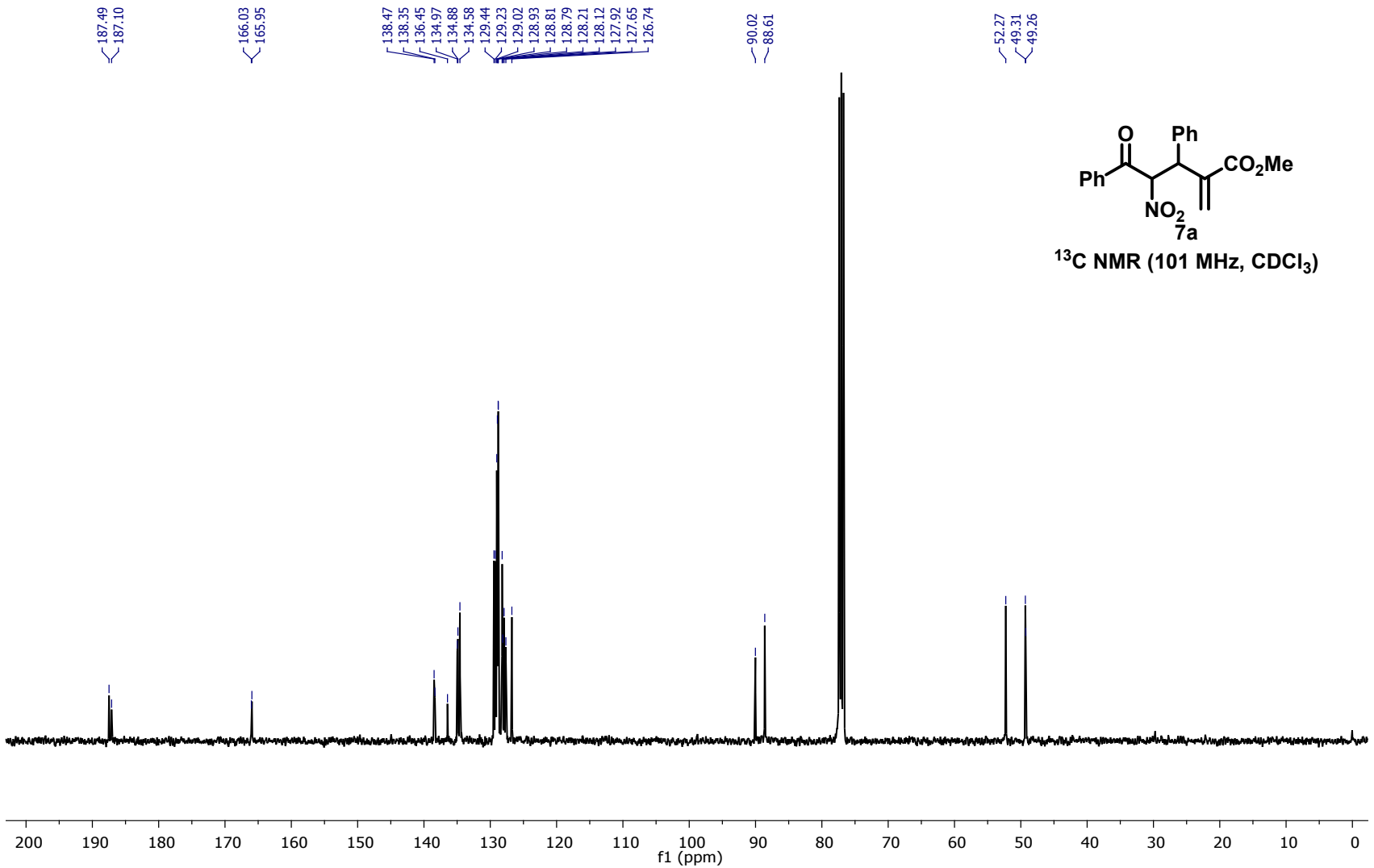

7.83
7.81
7.39
7.37
4.48
2.46
2.22
2.01
2.00
2.03
3.03
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
O
S
O
O
O
6
^{1}H NMR (400 MHz, CDCl$_3$)

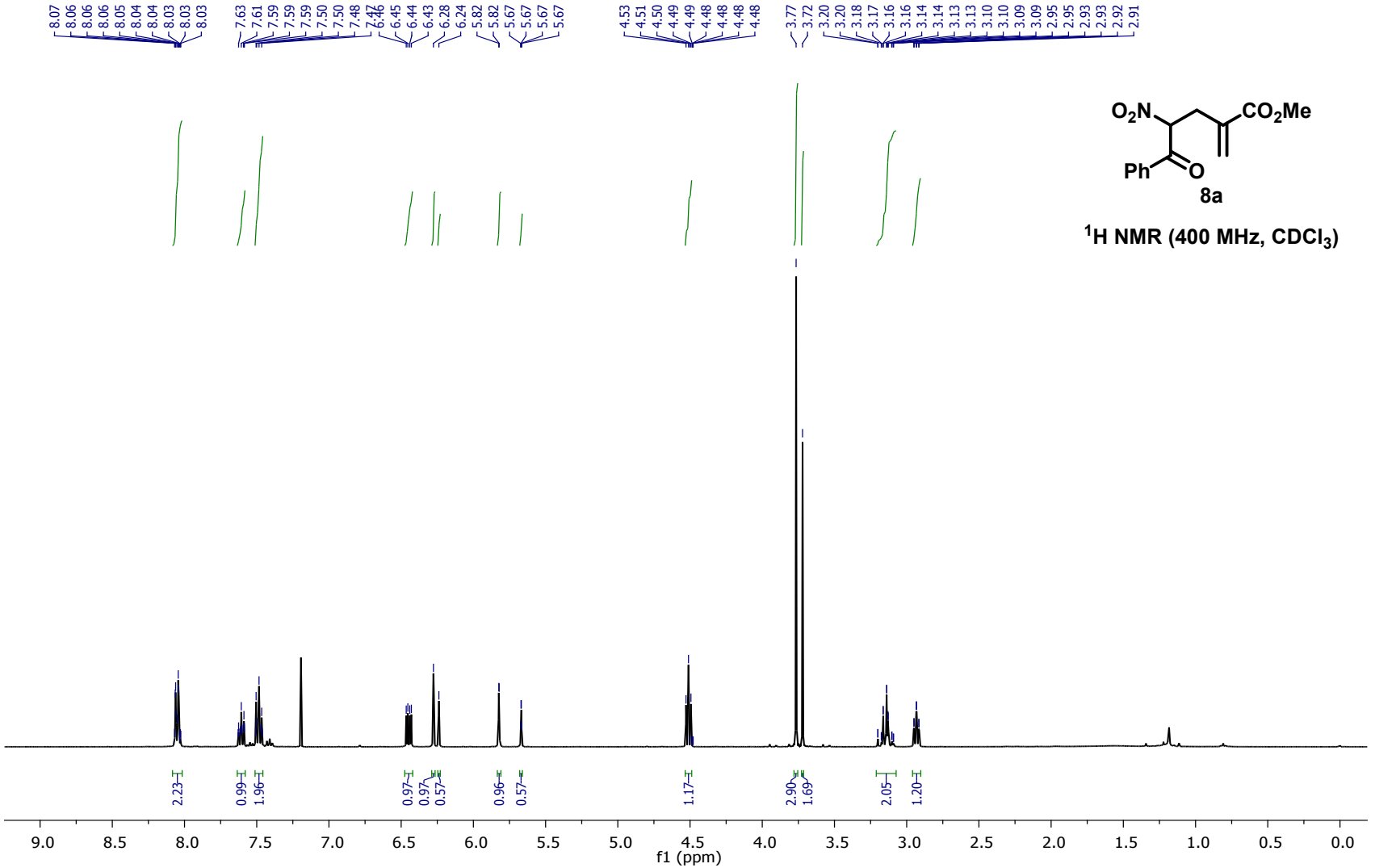

201.26
145.56
132.34
130.08
128.09
72.06
26.63
21.73
O
O
O
S
O
O
6
^{13}C NMR (101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

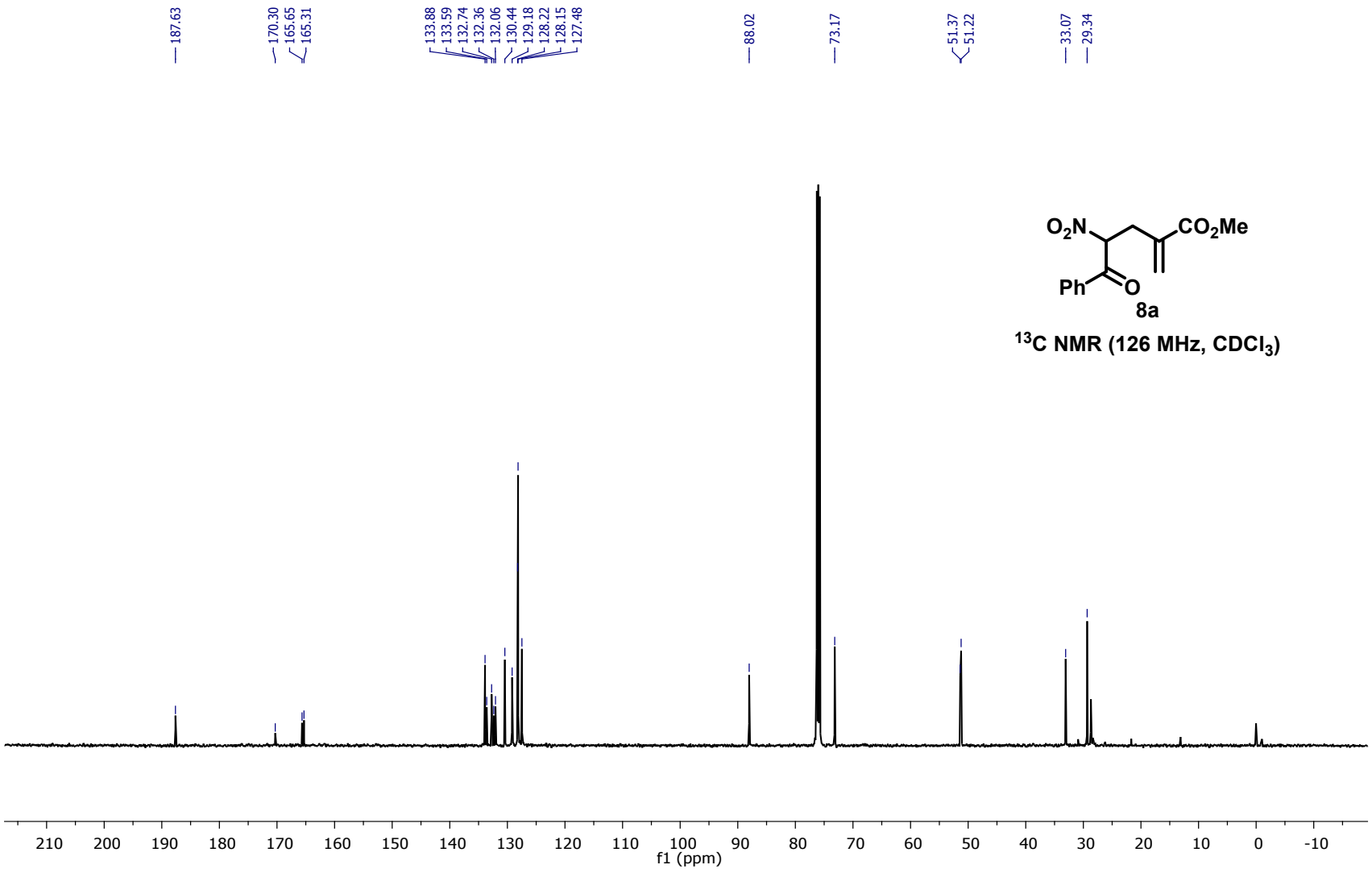


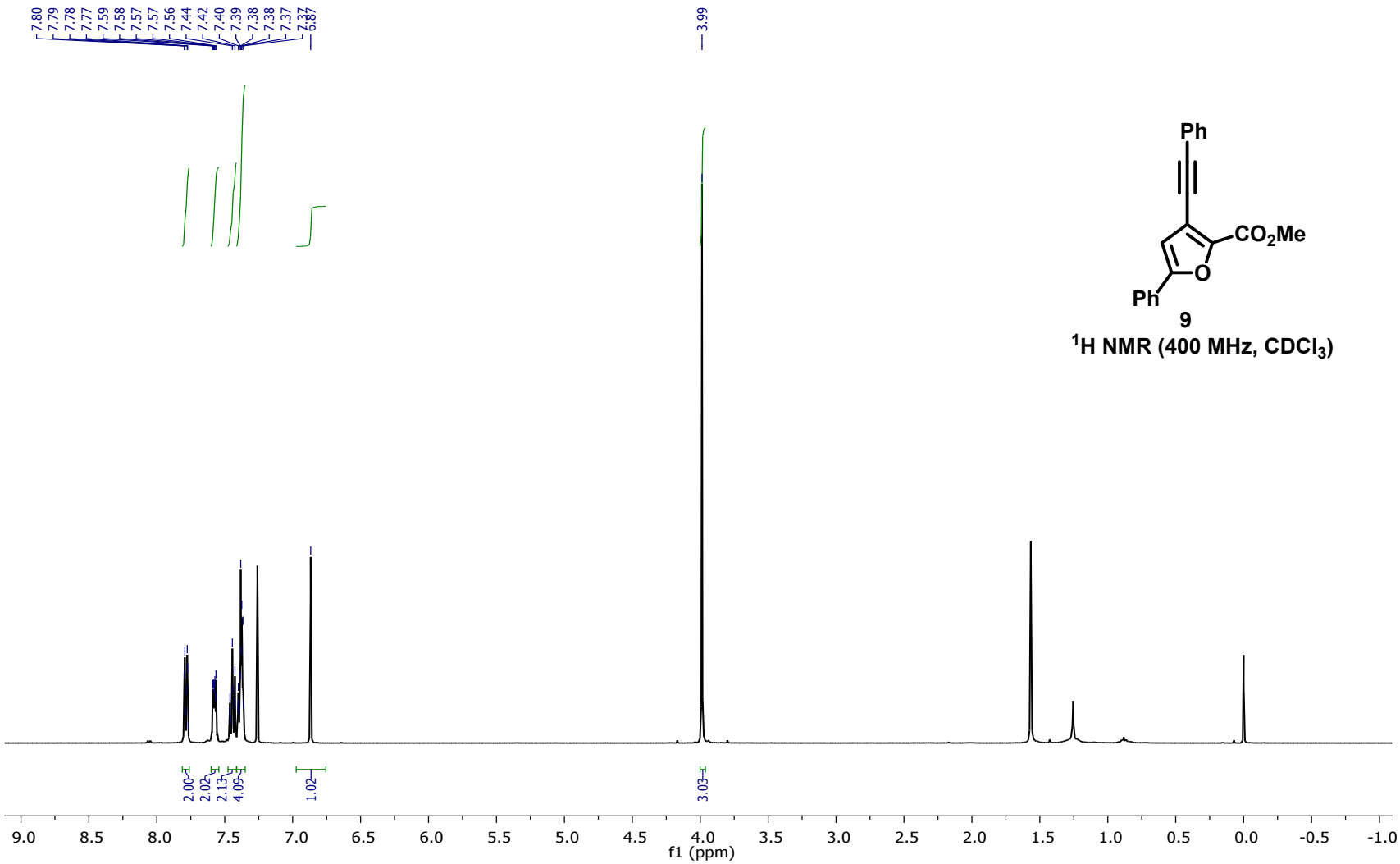
7a

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


187.49
187.10
166.03
165.95
138.47
138.35
136.45
134.97
134.88
134.58
129.44
129.23
129.02
128.93
128.81
128.79
128.21
128.12
127.92
127.65
126.74
90.02
88.61
52.27
49.31
49.26
O
Ph
Ph
CO2Me
NO2
7a
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

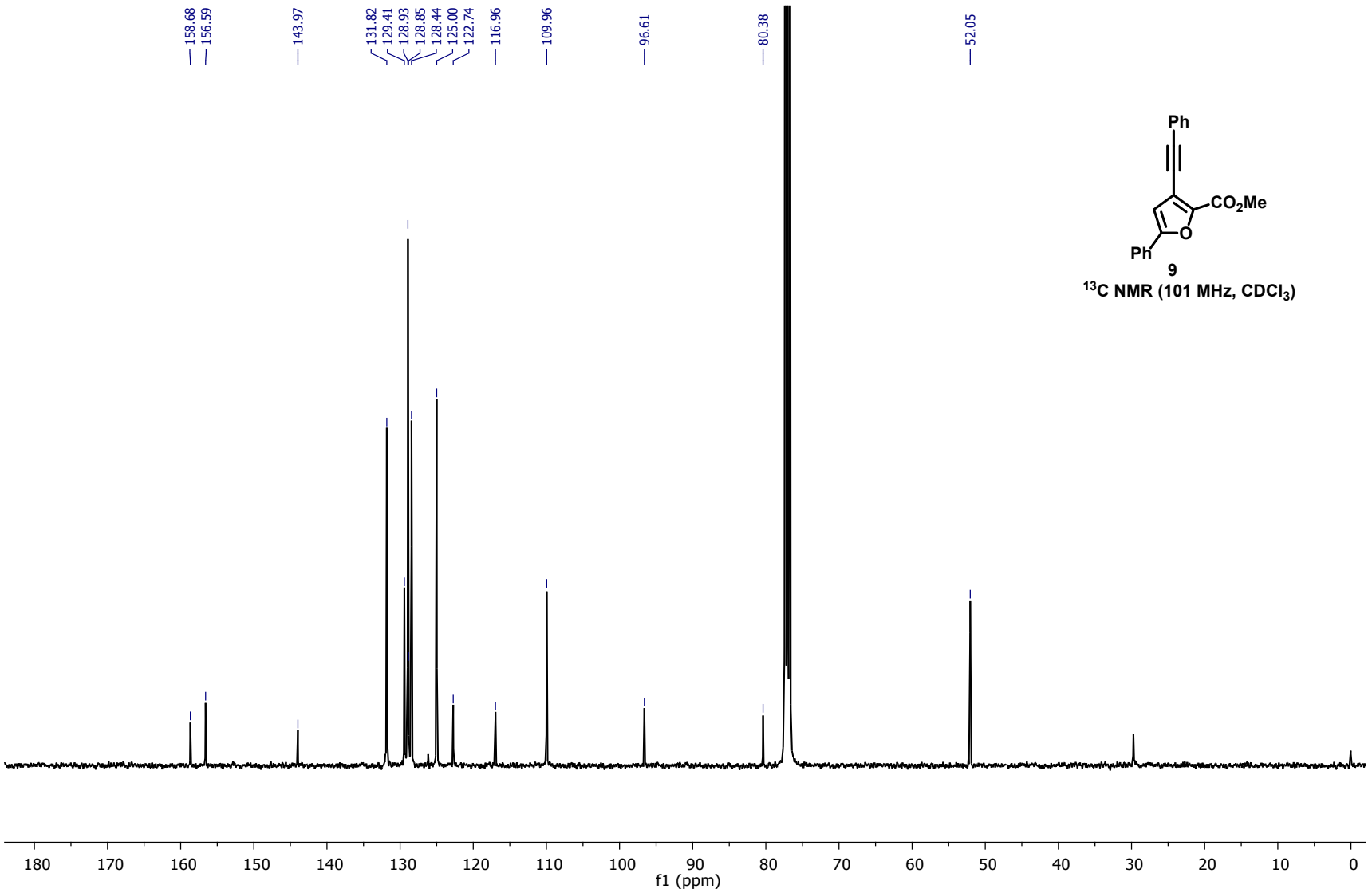

8.07 8.06 8.06 8.06 8.05 8.04 8.04 8.03 8.03 8.03
7.63 7.61 7.59 7.59 7.59 7.50 7.50 7.48 7.47 7.46
6.45 6.44 6.43 6.28 6.24
5.82 5.67 5.67 5.67 5.67
4.53 4.51 4.50 4.49 4.49 4.48 4.48 4.48 4.48
3.77 3.72 3.20 3.20 3.18 3.17 3.16 3.16 3.14 3.14 3.13 3.10 3.10 3.09 3.09 2.95 2.95 2.93 2.93 2.92 2.91
O2N
CO2Me
Ph
O
8a
1H NMR (400 MHz, CDCl3)
2.23 0.99 1.96 0.97 0.97 0.57 0.96 0.57 1.17 2.90 1.69 2.05 1.20
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)


187.63
170.30
165.65
165.31
133.88
133.59
132.74
132.36
132.06
130.44
129.18
128.22
128.15
127.48
88.02
73.17
51.37
51.22
33.07
29.34
O2N
CO2Me
Ph
O
8a
13C 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)



9

^{1}H NMR (400 MHz, $CDCl_3$)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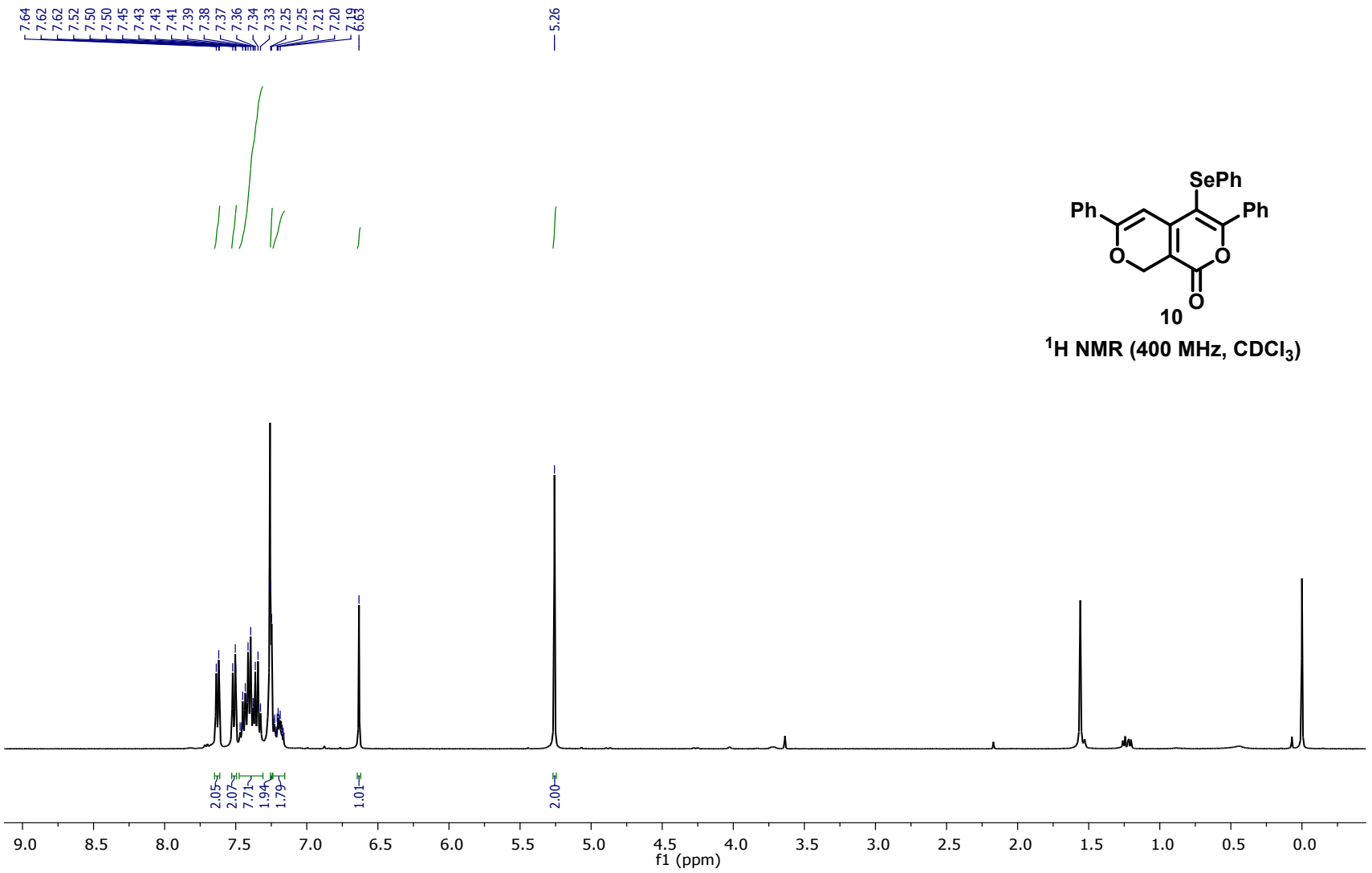
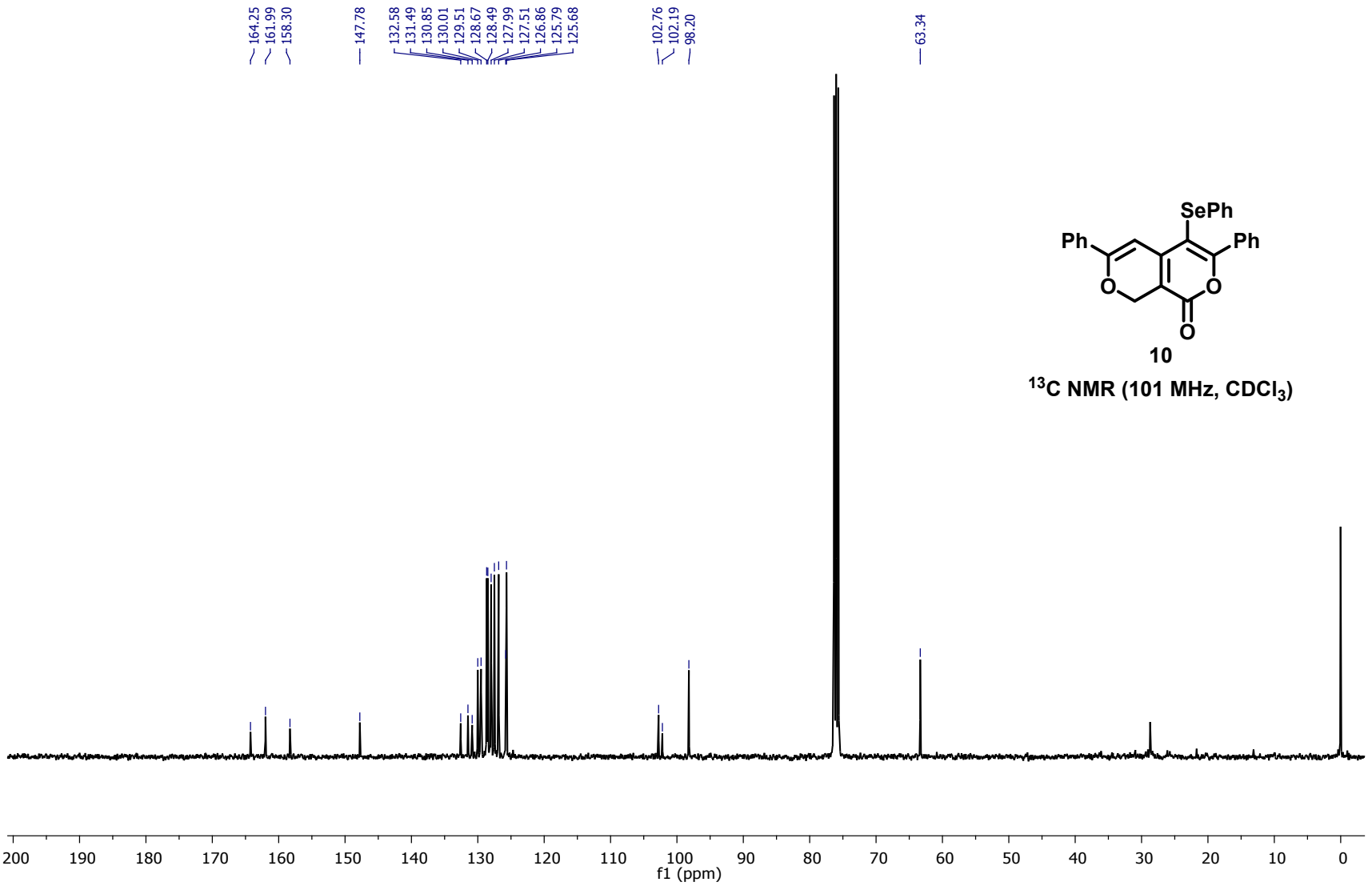
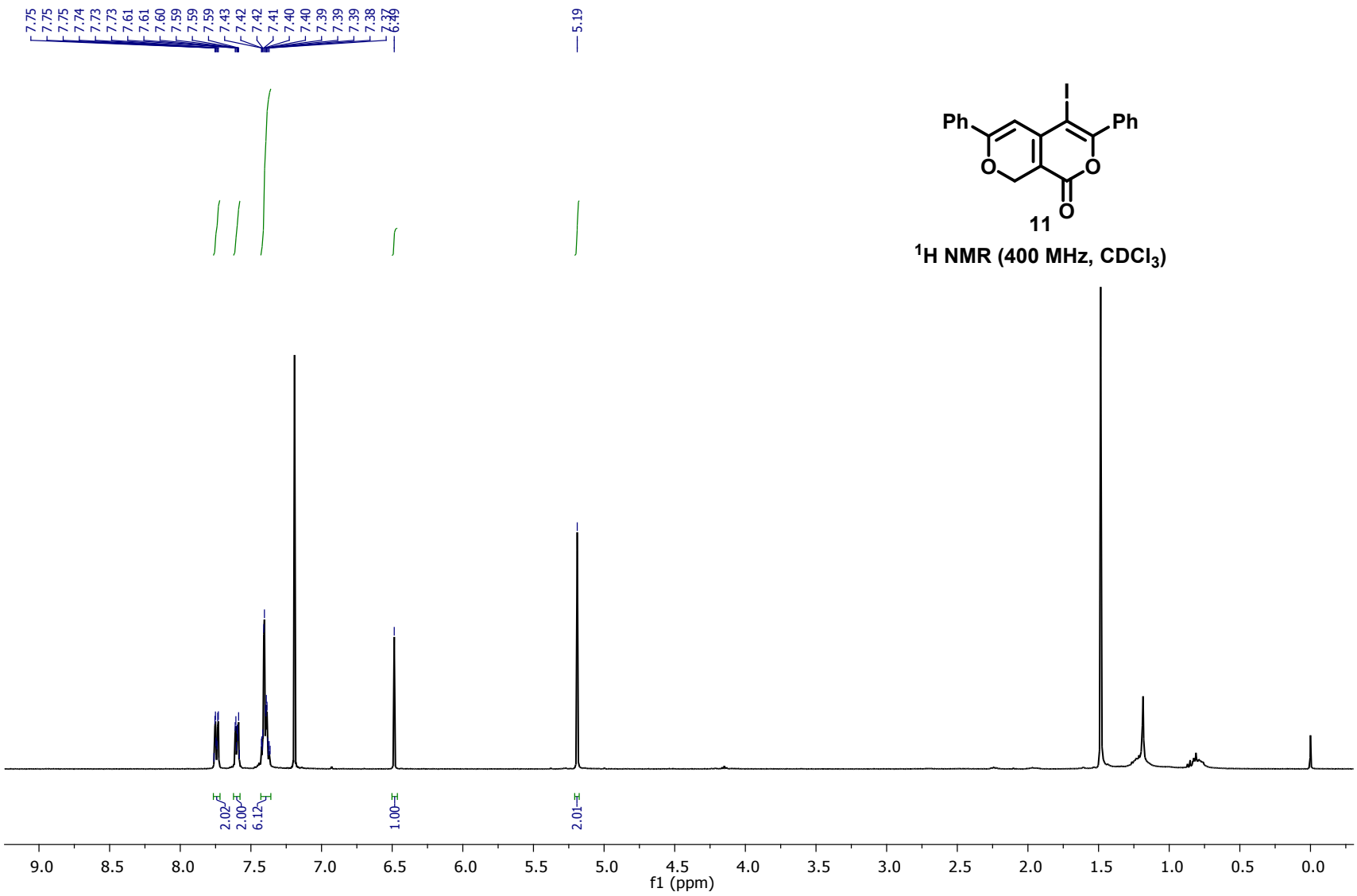
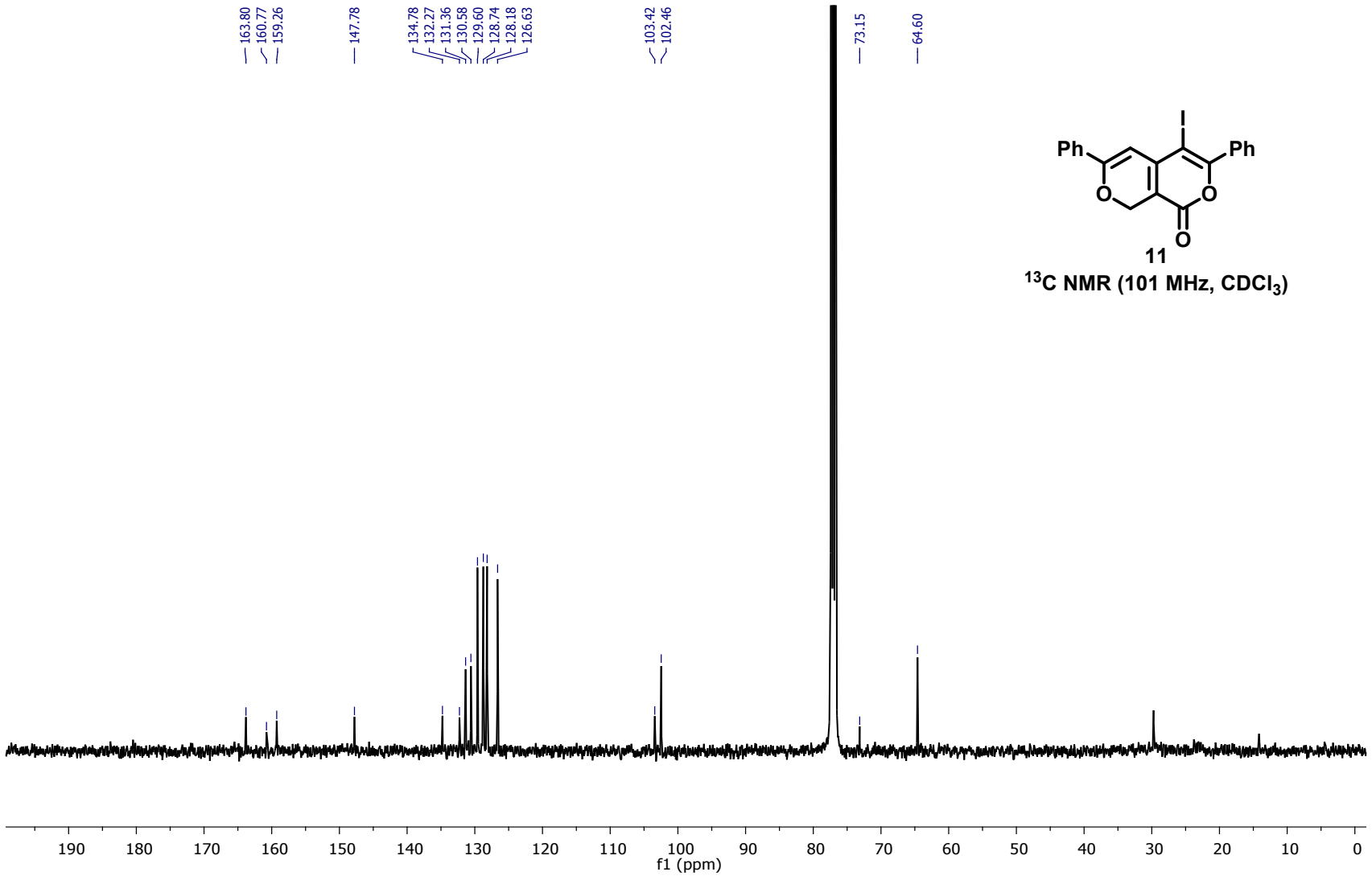
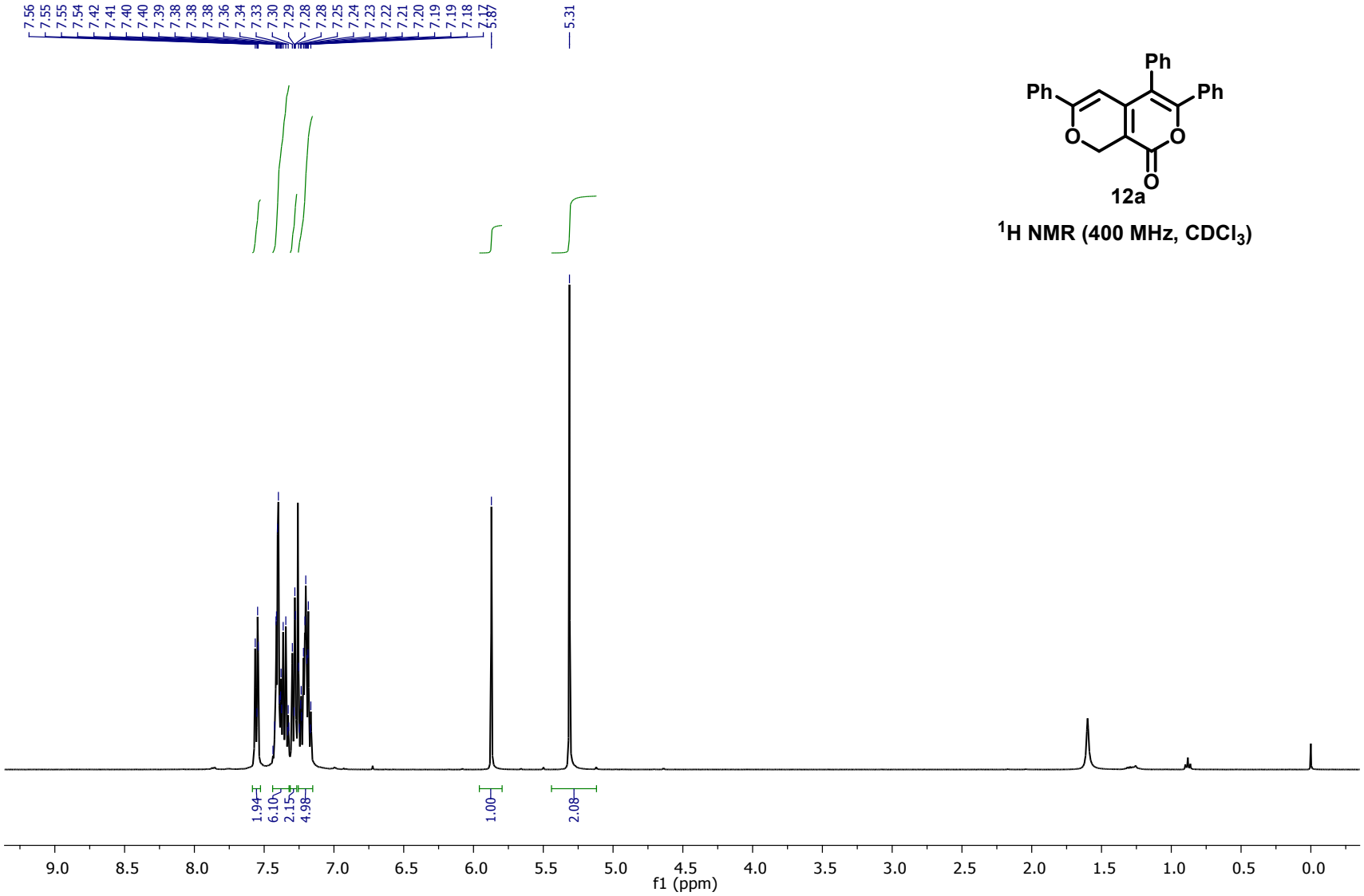
156.59
143.97
131.82
129.41
128.93
128.85
128.44
125.00
122.74
116.96
109.96
96.61
80.38
52.05
Ph
CO2Me
O
Ph
9
13C NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

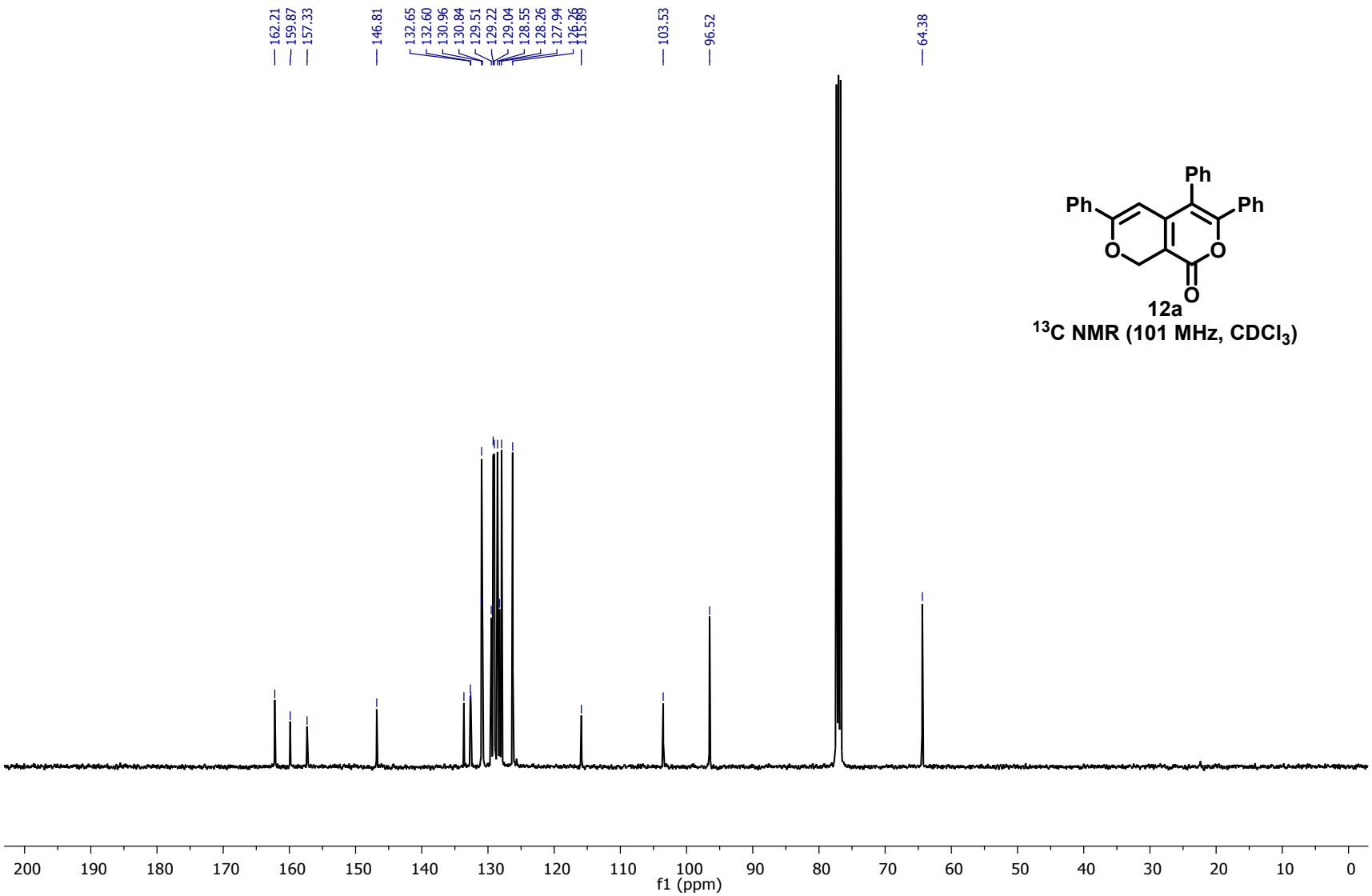

7.64
7.62
7.62
7.52
7.50
7.50
7.45
7.43
7.43
7.41
7.39
7.38
7.37
7.36
7.34
7.33
7.25
7.25
7.21
7.20
7.19
6.63
5.26
SePh
Ph
Ph
O
O
O
10
1H NMR (400 MHz, CDCl3)
2.05
2.07
7.71
1.94
1.79
1.01
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

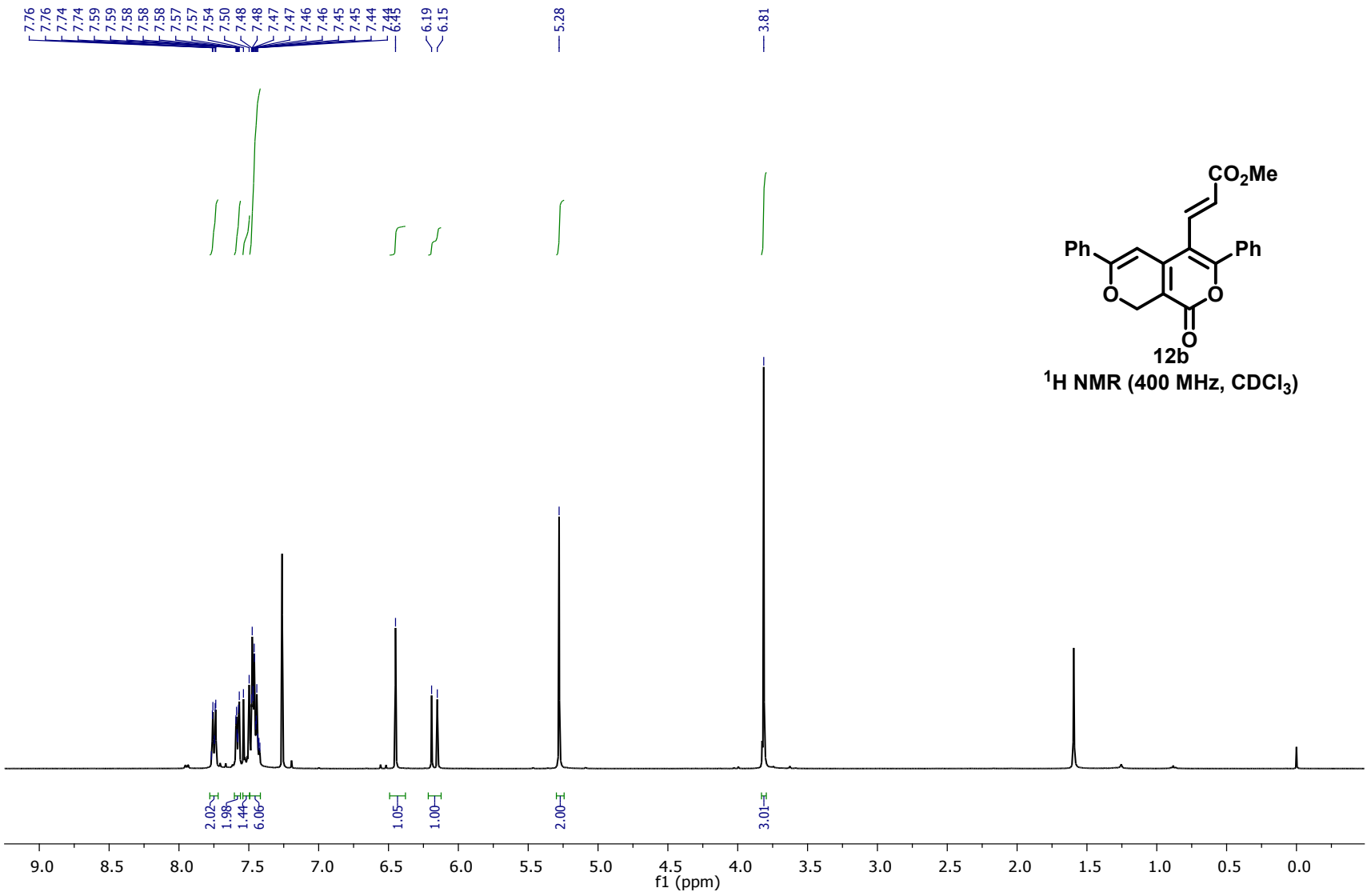

164.25
161.99
158.30
147.78
132.58
131.49
130.85
130.01
129.51
128.67
128.49
127.99
127.51
126.86
125.79
125.68
102.76
102.19
98.20
63.34
SePh
Ph
Ph
O
O
O
10
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

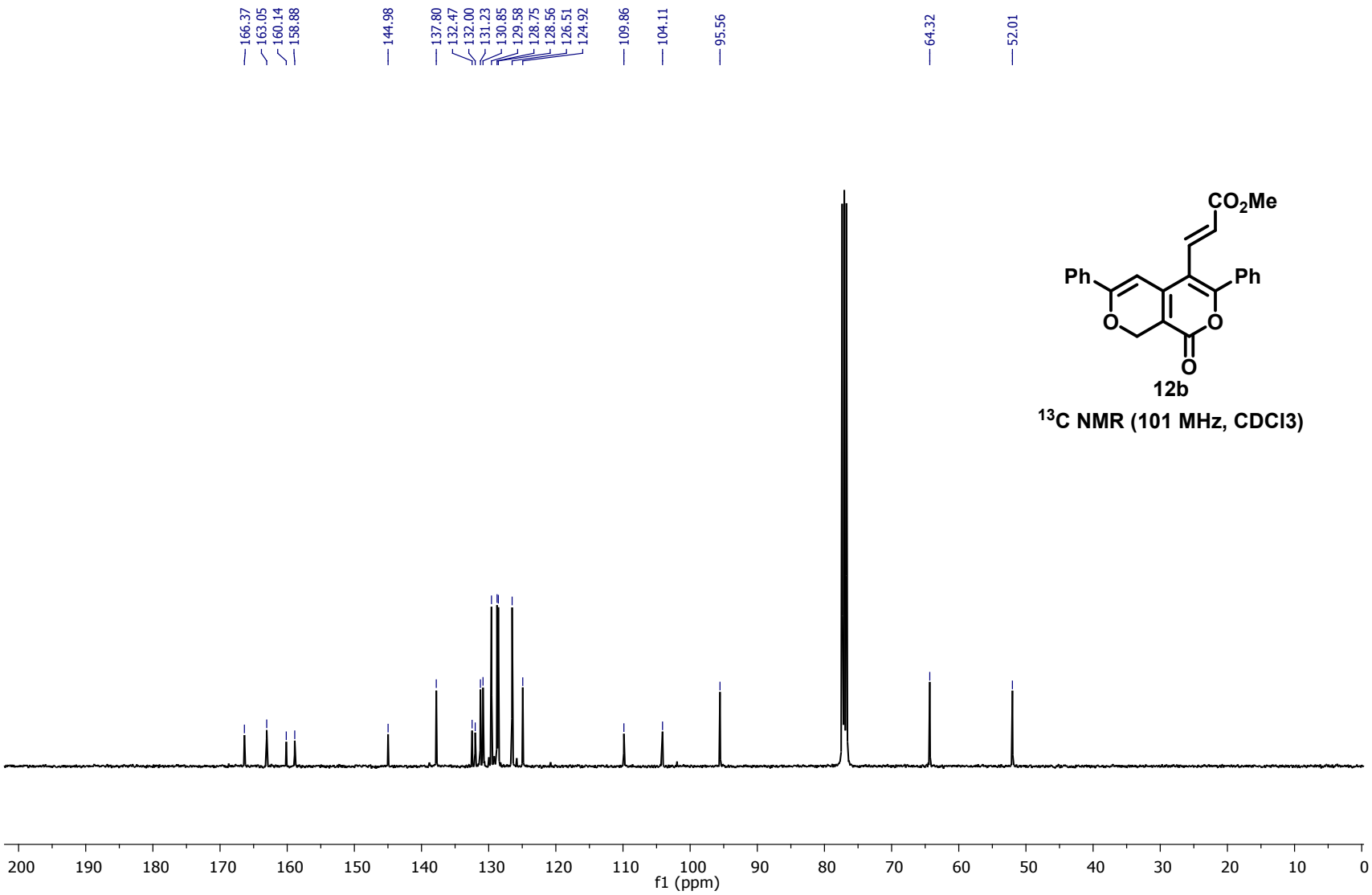

7.75
7.75
7.75
7.74
7.73
7.73
7.61
7.61
7.60
7.59
7.59
7.59
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.39
7.38
6.49
5.19
Ph
Ph
O
O
O
I
11
^{1}H NMR (400 MHz, CDCl$_3$)
2.02
2.00
6.12
1.00
2.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

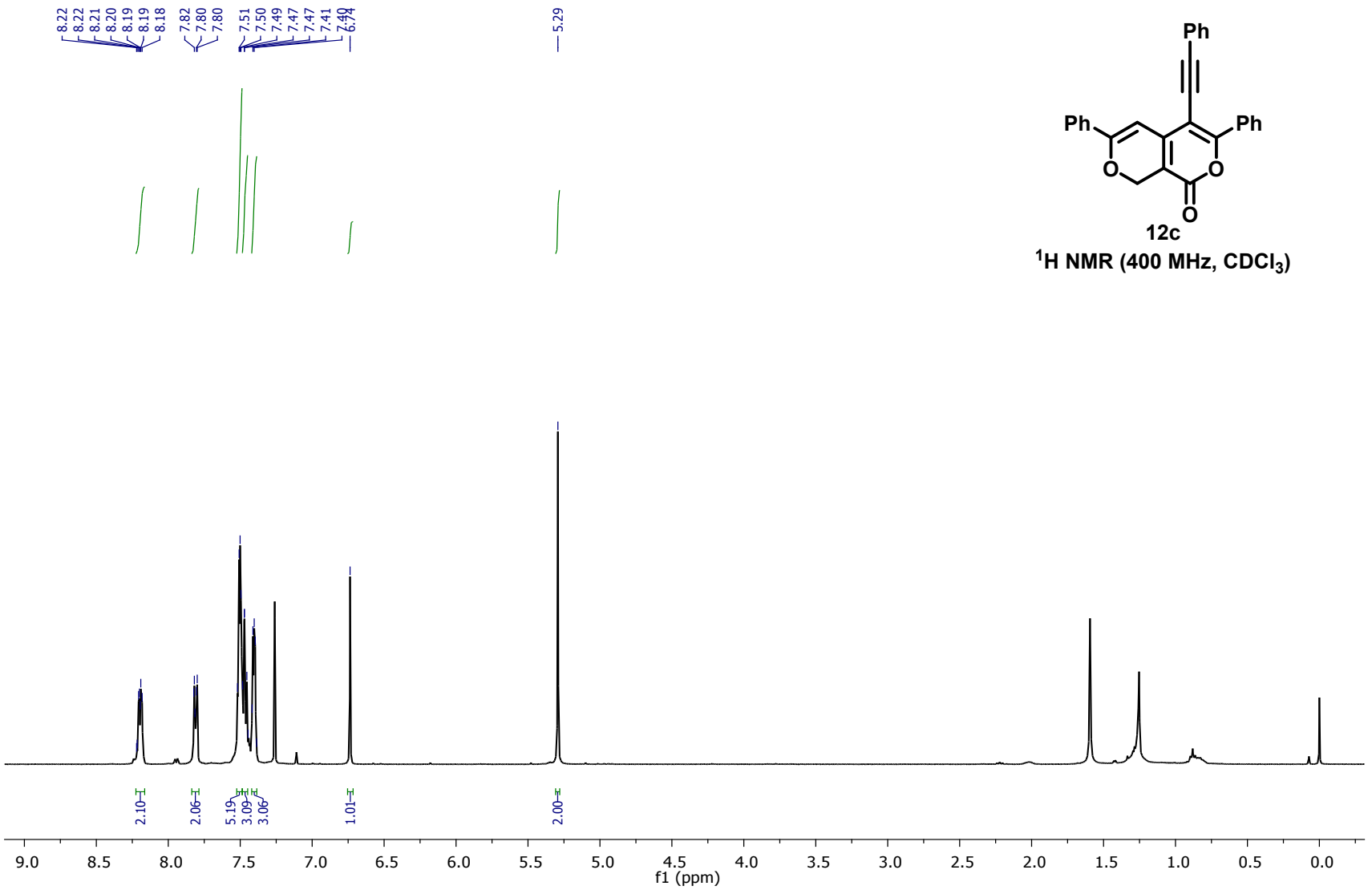

163.80
160.77
159.26
147.78
134.78
132.27
131.36
130.58
129.60
128.74
128.18
126.63
103.42
102.46
73.15
64.60
Ph
Ph
I
O
O
O
11
13C NMR (101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

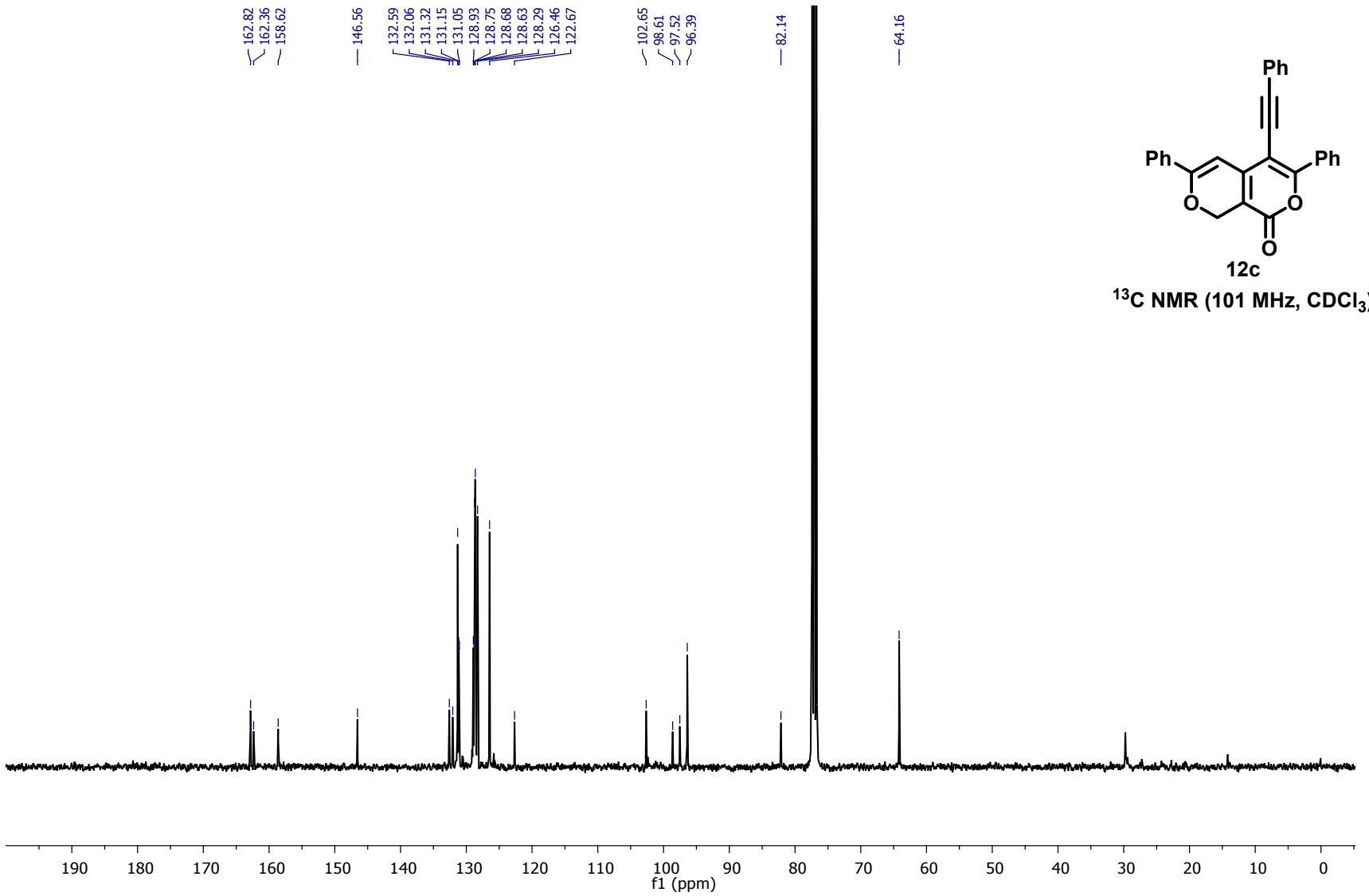

7.56
7.55
7.55
7.54
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.38
7.36
7.34
7.33
7.30
7.29
7.28
7.28
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.19
7.18
7.17
5.87
5.31
Ph
Ph
Ph
O
O
O
12a
^{1}H NMR (400 MHz, $CDCl_3$)
1.94
6.10
2.15
4.98
1.00
2.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.21
159.87
157.33
146.81
132.65
132.60
130.96
130.84
129.51
129.22
129.04
128.55
128.26
127.94
103.53
96.52
64.38
Ph
Ph
Ph
O
O
O
12a
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.76
7.76
7.74
7.74
7.59
7.59
7.58
7.58
7.58
7.57
7.57
7.54
7.50
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
6.45
6.19
6.15
5.28
3.81
CO2Me
Ph
Ph
O
O
O
12b
1H NMR (400 MHz, CDCl3)
2.02
1.98
1.44
6.06
1.05
1.00
2.00
3.01
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)


166.37
163.05
160.14
158.88
144.98
137.80
132.47
132.00
131.23
130.85
129.58
128.75
128.56
126.51
124.92
109.86
104.11
95.56
64.32
52.01
CO2Me
Ph
Ph
O
O
O
12b
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.22
8.22
8.21
8.20
8.19
8.19
8.18
7.82
7.80
7.80
7.51
7.50
7.49
7.47
7.47
7.41
7.40
6.74
5.29
Ph
Ph
Ph
O
O
O
12c
^{1}H NMR (400 MHz, CDCl$_3$)
2.10
2.06
5.19
3.09
3.06
1.01
2.00
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)



12c

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

Investigation of reaction intermediates and mechanism: Density Functional Theory (DFT) calculations

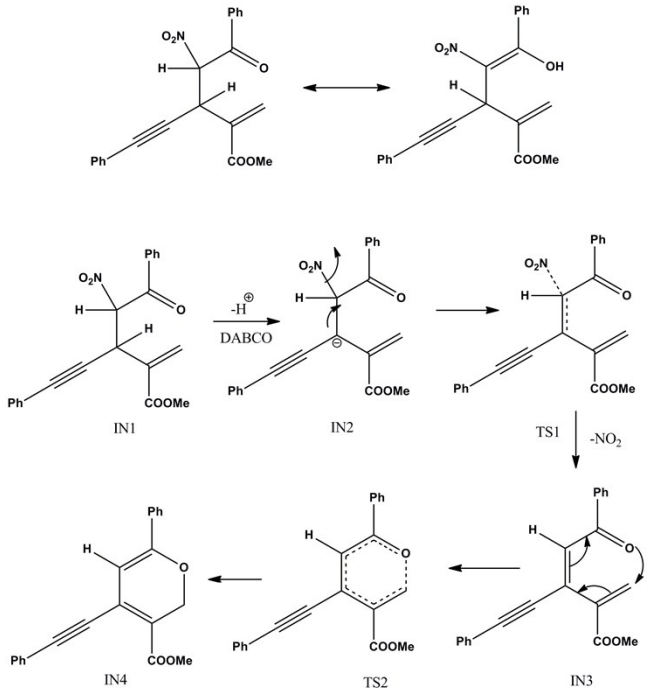
1. Theoretical Methodology

To elucidate the possible reaction mechanism of present method, we have studied reaction profiles using density functional theory (DFT). All geometry optimizations of the intermediates (INs), products and transition states (TSs) were performed using the DFT-B3LYP/6-31+G(d) method. To confirm the INs and TSs, the vibrational frequency analysis calculations were performed with the same method and basis set used for the geometry optimizations. Further, single point calculations carried out using the DFT-B3LYP/6-311++G(d,p) level of theory on the B3LYP/6-31+G(d) optimized geometries. In this study we have reported Gibbs free energies calculated at 298.15K using DFT-B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d) method. The Gaussian 09 package was used for all calculations in the present study.

2. Results and discussion

According to proposed mechanism in scheme S1, **IN1** will form in initial steps from reactants. This first step of the reaction is well known in the literature. The resultant intermediate **IN1** have a possibility of keto and enol tautomeric forms. The energetics of keto/enol products of **IN1** shows that keto form is energetically more stable than the enol form by 11.84 kcal/mol energy. Based on these results we have considered keto form of **IN1** for the next step in the mechanism. Figure S1 depicts the potential energy profile with Gibbs free energies (ΔG) at B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d) level of theory for the reaction mechanism proposed in scheme S1. Further, in presence of DABCO proton abstraction occurs from **IN1**, that results intermediate **IN2**. In the next step NO_2 group leave from the **IN2** and form **IN3** through transition state **TS1**. This reaction step carryout with activation barrier energy of

58.47 kcal/mol. In the final step, product **IN4** formed through cyclisation between carbonyl and alkene groups. This step is carried out by a transition state **TS2** with small activation barrier energy of 12.58 kcal/mol. The removal of NO_2 group and cyclisation steps are facilitated by extended conjugation of the transition states (**TS1** and **TS2**, see Figure S2). In these structures, the acetylene group acts as a bridge between the phenyl group and remaining portion of the transition states. This extended conjugation stabilizes the intermediate **IN3** and **IN4** by eliminating the NO_2 group and after cyclisation. In this mechanism the role of phenyl acetylene group is essential to stabilize the intermediate after removal of NO_2 group as well as the final product.



Scheme S1: The proposed reaction mechanism and keto and enol tautomeric forms of IN1.

Table S1: Gibbs free energies (ΔG in kcal/mol) calculated at B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d) level of theory for the possible reaction mechanism.

Compound	Gibbs free energies (ΔG in kcal/mol)	Gibbs free energies (ΔG in kcal/mol)
IN1	**41.31 (Keto form)**	**53.15 (enol form)**
IN2	**52.51**	
TS1	**110.98**	
IN3	**32.09**	
TS2	**44.67**	
IN4	**27.28**	

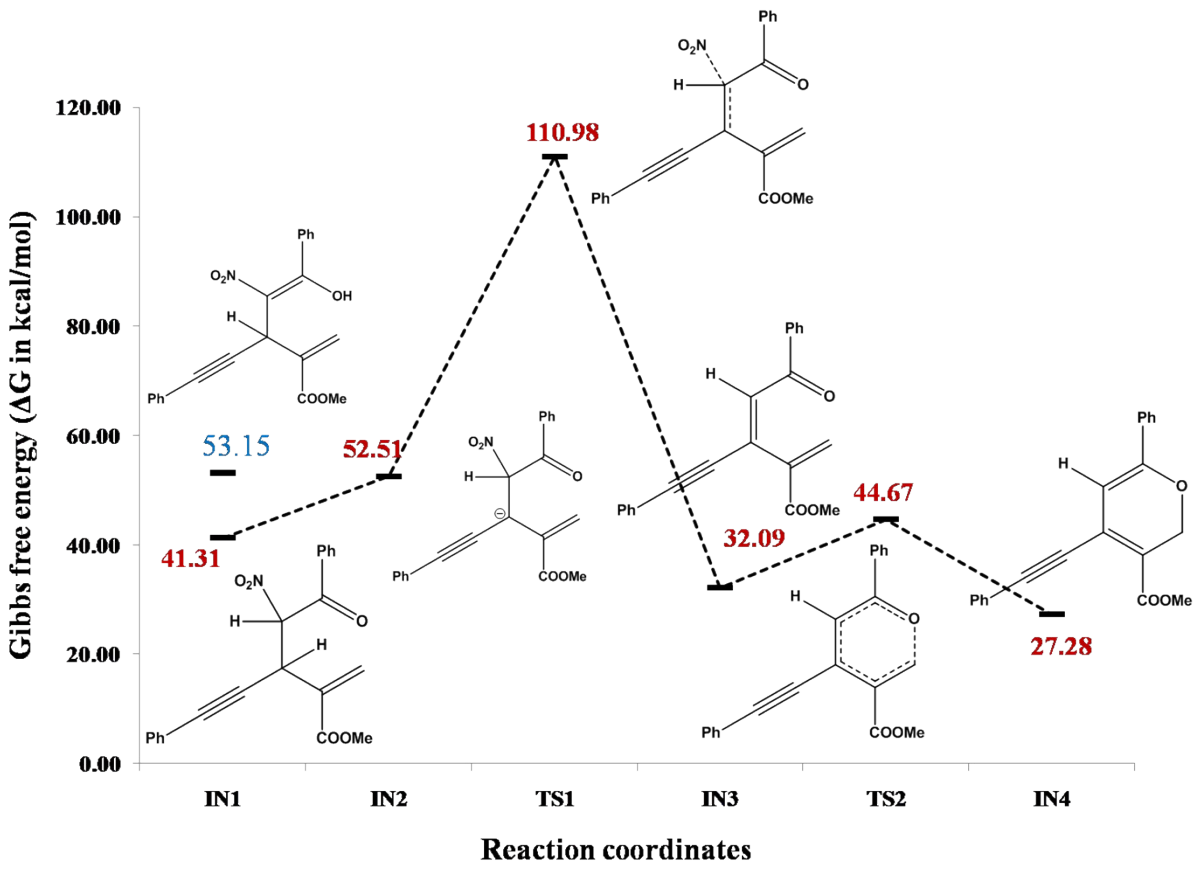
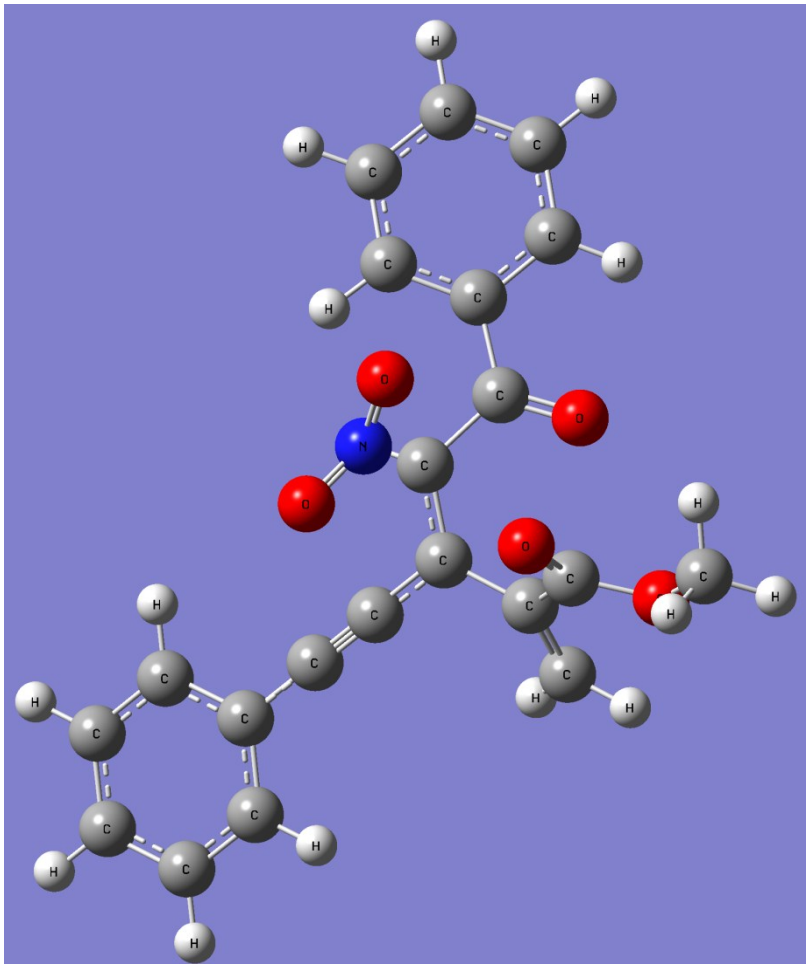
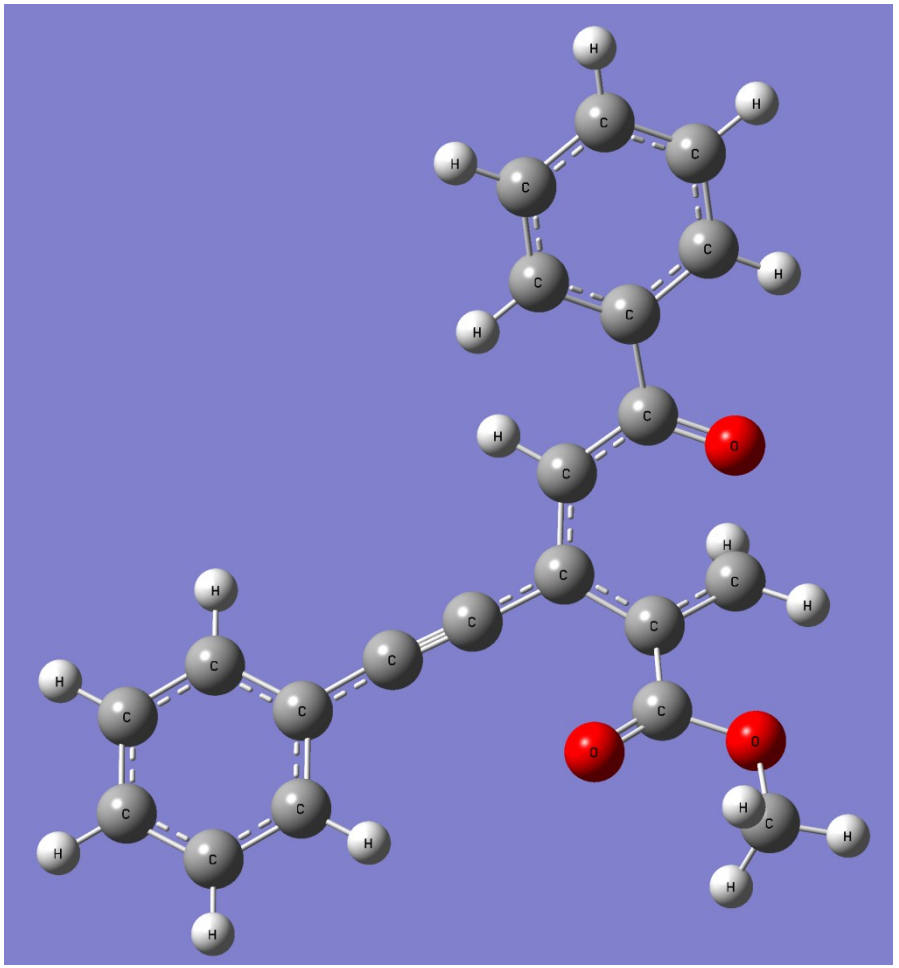


Figure S1: Potential energy profile with Gibbs free energies (ΔG in kcal/mol) at the B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d) level of theory.



TS1



TS2

Figure S2: Optimized transition state structures using B3LYP/6-31+G(d) level theory.