Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A Metal-Free $BF_3 \cdot OEt_2$ Mediated Chemoselective Protocol for the Synthesis of Propargylic Cyclic Imines

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Contents

1 .General information:

All the chemicals and reagents were purchased from commercial suppliers and used without further purification. Solvents were dried and stored over molecular sieves under argon atmosphere prior to use. Thin-layer chromatography (TLC) was performed using pre-coated plates purchased from E. Merck (silica gel 60 PF254, 0.25 mm). Column chromatography was performed using E. Merck silica gel 60 (100–200 mesh). ^{1}H, ^{13}C, ^{19}F and DEPT-135 NMR spectra were recorded in $CDCl_3$, on JEOL JNM-ECS spectrometer at operating frequencies of 400 MHz {^{1}H} or 101 MHz {^{13}C} as indicated in the individual spectrum. Chemical shifts (δ) are given in parts per million (ppm) relative to residual solvent (chloroform, δ= 7.26 for ^{1}H & 77.16 for ^{13}C NMR and DMSO-d_6, δ= 2.5 for ^{1}H & 39.58 for ^{13}C NMR, and coupling constants (*J*) in Hz. Multiplicity is tabulated as s for singlet, d for doublet, dd for doublet of doublet, t for triplet, q for quartet, and m for multiplet. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) methods on waters mass spectrometer (XEVO G2-XS QTOF). The data collection for single crystal X-ray was performed at a 298 K on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with INCOATEC micro-focus source with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA.

2. Synthesis of starting materials:

2.1. Synthesis of donor-acceptor cyclopropanes:

Diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**1n**)[1] and Diethyl [1,1'-bi(cyclopropane)]-2,2-dicarboxylate (**1o**)[2] were synthesized according to the reported procedures. All other donor-acceptor cyclopropanes were synthesized according to the GP 1[3].

General procedure for the synthesis of cyclopropane-1,1-diester derivatives (GP 1):

Trimethylsulfoxonium iodide (TMSOI) (1.5 eq.) was added drop-wise into the suspension of sodium hydride (NaH) (60% suspension in mineral oil, 1.5 eq.) and dry dimethyl sulfoxide (DMSO) under nitrogen atmosphere. ***Caution!*** : Reaction of trimethylsulfoxonium iodide with sodium hydride is exothermic (evolution of H_2 and heat). So, the suspension was maintained at 0 ºC before adding trimethylsulfoxonium iodide. After 15-20 min. vigorous stirring, a solution of benzylidenemalonate (1.0 eq.) in DMSO was added, mixture was allowed to warm up to room temperature. Upon completion (as determined by TLC analysis) of the reaction, crushed ice was added in the crude solution and extracted with diethyl ether. The combined organic layers were washed once with brine, dried over sodium sulfate (Na_2SO_4), filtered and concentrated under reduced pressure, which was further purified by silica gel column chromatography using hexane and ethyl actetate as an eluent.

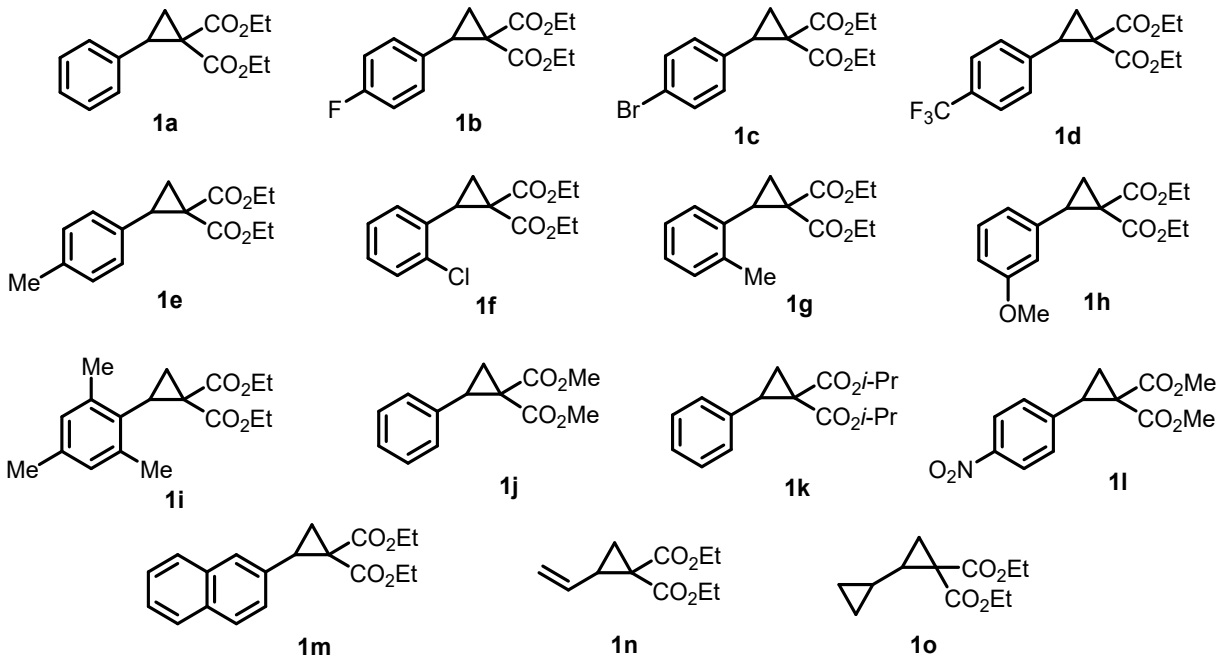


Figure 1. Cyclopropane-1,1-diester derivatives **1**

2.2. Synthesis of alkynyl nitriles :

Synthesis of aromatic alkynyl nitriles (GP2)[4]: Phenylethyne (3 mmol, 1 eq.), benzoyl cyanide (3 mmol, 1 eq.), and $Cu(NO_3)_2 \cdot 3H_2O$ (0.2 mmol, 20 mol%) was dissolved in dimethylformamide (DMF)and heated at 60 °C for 5-6 h under air. After completion of reaction, monitored by TLC, the crude mixture was extracted with ethyl acetate (3×10 mL) and water. The collected organic layer was once washed with brine and water, dried over Na_2SO_4, concentrated in reduced pressure and purified by column chromatography using hexane and ethyl acetate as eluents.

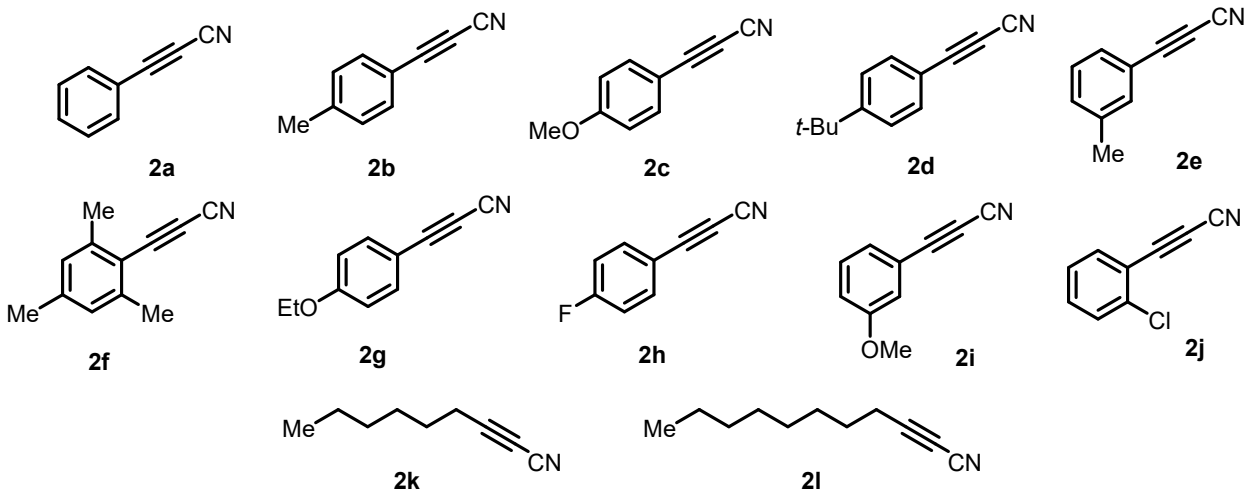


Figure 2. Alkynylnitriles derivatives **2**

Synthesis of aliphatic alkynyl nitriles (GP3)[4c]:

Step-1: N-Bromosuccinimide (NBS) (1.2 eq.) and Silver nitrate (20 mol%) were added sequentially to the stirred solution of the alkyne (1eq.) in acetone at rt and the reaction flask was covered with aluminum foil. The reaction mixture continued stirred for 3hrs. After completing the reaction removed extra acetone under reduced pressure and extracted with dichloromethane three times. Combined organic layers dried over Na_2SO_4 and evaporated under reduced pressure. Collected the residue (1-Bromoalkyne) which was directly used for the next step.

Step-2: Copper(I) cyanide (1eq.) and Potassium iodide (30 mol%) were added sequentially to the stirred solution of 1-Bromoalkyne (1eq.) in DMSO at 60 °C. The reaction mixture continued stirred for 6 – 12 hrs. After full consumption of 1-Bromoalkyne, the reaction mixture was cool to rt and extracted with ethyl acetate and ammonium chloride. The combined organic layers was washed 2 times with water and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and purified through column chromatography over silica gel using hexane/ethyl acetate as eluents to obtain aliphatic alkynyl nitriles.

3. General Procedures:

3.1. Synthesis of propargylic cyclic imines 3:

Donor-acceptor cyclopropanes **1** (0.15 mmol, 1 eq.), alkynylnitriles **2** (0.22 mmol, 1.5 eq.) and $BF_3{\cdot}OEt_2$ (150 mol%) were dissolved in anhydrous 1,2-DCE (1 mL) under N_2 atmosphere. Unlike other cyclic imines **3aa**, **3da** and **3ia** were also synthesized in aerobic conditions. The solution was stirred at 60 °C (oil bath) until TLC analysis (*n*-hexane:Ethyl acetate = 10:1) showed complete consumption of cyclopropanes. After completing the reaction, the mixture was poured into an aqueous $NaHCO_3$ solution (10 mL) and extracted with dichloromethane (3 × 5 mL). The combined organic layer was washed three times with water and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and purified through column chromatography over silica gel using hexane/ethyl acetate as eluents to obtain the desired product.

3.2. Gram scale synthesis of diethyl 5-mesityl-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate 3ia:

In a schlenk tube alkynyl nitrile, **2a** (3.75 mmol, 1.5 eq.) and diethyl 2-mesitylcyclopropane-1,1-dicarboxylate, **1i** (2.5 mmol, 1 eq.) was dissolved in DCE and added $BF_3{\cdot}OEt_2$ (150 mol%). The reaction was stirred at 60 °C for 9 h and after the complete consumption of **1i**, monitored by TLC, the reaction mixture was poured in 10% aq. $NaHCO_3$ (150 mL). The crude was extracted thrice with DCM followed by washing of organic layer with water. The combined organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by column chromatography over silica gel using hexane/ethyl acetate as eluents.
Yield = 862 mg, 80%

3.3. Synthesis of diethyl 5-phenyl-2-(phenylethynyl)pyrrolidine-3,3-dicarboxylate 5:

In the solution of diethyl 5-phenyl-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate **3aa** (0.1 mmol, 1eq.) in MeOH: AcOH (3:1, 2 mL), $NaBH_3CN$ (0.2 mmol, 2eq.) was added and stirred at room temperature. After complete consumption of **3aa** in 3 h, monitored by TLC analysis, the reaction mixture was quenched with 10% aq. $NaHCO_3$ solution, and then extracted with DCM. The combined organic layer was washed thrice with water. The separated organic layer was collected, dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by column chromatography using hexane and ethyl acetate as eluents.
Yield = 33 mg, 85%

3.4. Synthesis of 2-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyrrole 6:

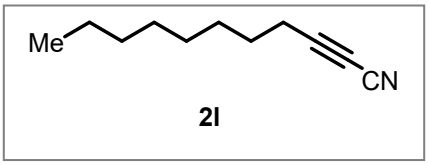
An aqueous solution of NaOH (1 M, 30 eq., 3 mL) was added in the solution of **3aa** (0.1 mmol, 1 eq.) in MeCN: H_2O (1.2:1, 2 mL). The mixture was stirred for 6 h at room temperature. After that crude was acidified with aq. HCl (2 N, 10 mL), then extracted with DCM and water. The combined organic phases were dried over Na_2SO_4, filtered, concentrated, and purified by column chromatography using hexane and ethyl acetate as eluents.
Yield = 18 mg, 73%

3.5. Diethyl (*Z*)-2-(2-hydroxy-2-(*p*-tolyl)vinyl)-5-phenyl-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate 7:

Diethyl 2-(phenylethynyl)-5-(*p*-tolyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate **3ea** (0.1 mmol, 1 eq.) was dissolved in wet DCE (DCE and one drop H_2O) 2 mL, and then cooled to 0 ºC. After that triflic acid (50 mol%) was added to the cooled solution. After 5 minutes, the reaction mixture was warmed up to room temperature and stirred for 12 h. The complete consumption of **3ea** was monitored by TLC. The crude mixture was extracted with EtOAc and water. The combined organic layer was once washed with brine and the organic layer was dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by column chromatography using hexane and ethyl acetate as eluent.
Yield = 26 mg, 55%

4. Characterization of starting material

Undec-2-ynenitrile (2l):



2l

Physical State: Yellow oil.

Overall yield: 381 mg, 78% (reaction performed at 3 mmol scale)

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (t, *J* = 7.1 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.44 – 1.35 (m, 2H), 1.33 – 1.23 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H).

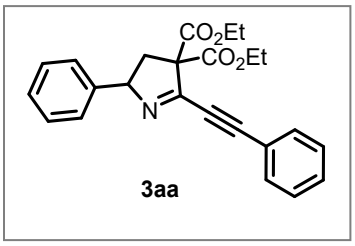
^{13}C NMR (101 MHz, $CDCl_3$): δ 105.4, 87.6, 55.3, 31.8, 29.1, 28.9, 28.8, 27.1, 22.7, 18.9, 14.1.

IR (neat) ($\tilde{\nu}$): 2926, 2856, 2312, 2261, 1462, 1410, 1057, 722, 499cm^{-1}

HRMS: *m/z* calculated for $C_{11}H_{18}N$ $[M+H]^+$ = 164.1439, found 164.1441.

5. Characterization of compounds

Diethyl 5-phenyl-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3aa):



3aa

Physical State: Yellow viscous liquid.

Yield: 48 mg, 82% (under N_2 atm.); 47 mg, 81% (under air atm.).

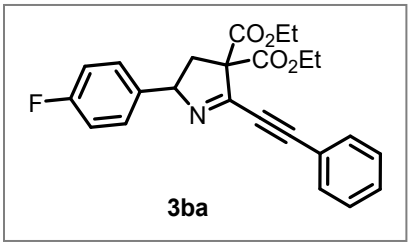
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.54 (m, 2H), 7.41 – 7.28 (m, 7H), 7.17 – 7.11 (m, 1H), 5.32 (t, *J* = 7.8 Hz, 1H), 4.35 – 4.25 (m, 4H), 3.25 (dd, *J* = 13.5, 7.4 Hz, 1H), 2.50 (dd, *J* = 13.4, 8.2 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 167.4, 154.1, 141.8, 132.5, 129.9, 128.8, 128.6, 127.6, 126.8, 121.6, 94.3, 83.4, 75.1, 73.2, 62.6, 62.5, 41.9, 14.2.

IR (neat) ($\tilde{\nu}$): 3030, 2982, 2217, 1730, 1603, 1445, 1304, 1253, 1180, 1100, 1029, 758 cm^{-1}.

HRMS: *m/z* calculated for $C_{24}H_{24}NO_4$ $[M+H]^+$ = 390.1705, found 390.1708.

Diethyl 5-(4-fluorophenyl)-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ba):



3ba

Physical State: Brownish viscous liquid.

Yield: 43 mg, 71%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 2H), 7.41 – 7.36 (m, 3H), 7.30 – 7.26 (m, 2H), 7.07 – 7.01 (m, 2H), 5.29 (t, *J* = 7.8 Hz, 1H), 4.35 – 4.25 (m, 4H), 3.25 – 3.20 (m, 1H), 2.45 (dd, *J* = 13.4, 8.2 Hz, 1H), 1.34 – 1.29 (m, 6H).

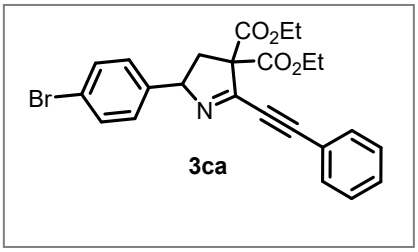
^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9, 167.3, 162.3 (d, $^{1}J_{C\text{-}F}$ = 246.4 Hz), 154.2, 137.6 (d, $^{4}J_{C\text{-}F}$ = 3.79 Hz), 132.5, 130.0, 128.6, 128.5 (d, $^{3}J_{C\text{-}F}$ = 8.52 Hz), 121.4, 115.6 (d, $^{2}J_{C\text{-}F}$ = 21.59 Hz), 94.5, 83.2, 74.3, 73.1, 62.7, 62.5, 41.9, 14.2, 14.1.

^{19}F NMR (377 MHz, $CDCl_3$): δ -115.05.

IR (neat) ($\tilde{\nu}$): 3061, 2982, 2919, 2217, 1730, 1603, 1587, 1490, 1416, 1253, 1158, 860 cm^{-1}.

HRMS: *m/z* calculated for $C_{24}H_{23}FNO_4$ $[M+H]^+$ = 408.1611, found 408.1616.

Diethyl 5-(4-bromophenyl)-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ca):



Physical State: Brownish viscous liquid.

Yield: 60 mg, 85%.

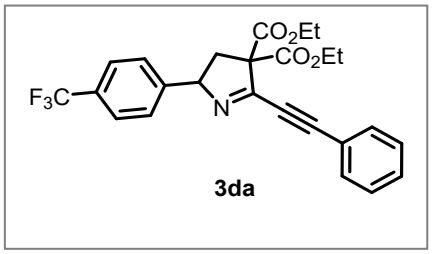
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.54 (m, 2H), 7.50 – 7.46 (m, 2H), 7.42 – 7.35 (m, 3H), 7.21 – 7.18 (m, 2H), 5.27 (t, *J* = 7.8 Hz, 1H), 4.33 – 4.27 (m, 4H), 3.23 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.42 (dd, *J* = 13.4, 8.2 Hz, 1H), 1.32 – 1.28 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9, 167.2, 154.5, 140.9, 132.5, 131.9, 130.0, 128.6, 128.5, 121.5, 121.4, 94.7, 83.2, 74.3, 73.2, 62.7, 62.6, 41.7, 14.2, 14.2.

IR (neat) ($\tilde{\nu}$): 3055, 2982, 2217, 1730, 1589, 1488, 1445, 1367, 1262, 1072, 895 cm^{-1}.

HRMS: *m/z* calculated for $C_{24}H_{22}BrNO_4$ $[M+H]^+$ = 468.0810, found 468.0811.

Diethyl 2-(phenylethynyl)-5-(4-(trifluoromethyl)phenyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3da):



3da

Physical State: Brownish viscous liquid.

Yield: 54 mg, 79% (under N_2 atm.); 51 mg, 75% (under air atm.).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.57 – 7.55 (m, 2H), 7.46 – 7.37 (m, 5H), 5.37 (t, *J* = 7.8 Hz, 1H), 4.34 – 4.27 (m, 4H), 3.28 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.45 (dd, *J* = 13.4, 8.2 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

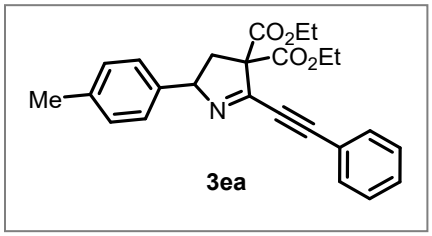
^{13}C NMR (101 MHz, $CDCl_3$): δ 167.8, 167.2, 154.9, 145.8, 132.5, 130.1, 128.6 (q, $^2J_{C\text{-}F}$ = 18.67 Hz) 128.7, 127.0 (q, $^1J_{C\text{-}F}$ = 225.97 Hz), 127.1, 125.7 (q, $^3J_{C\text{-}F}$ = 3.69 Hz), 121.4, 94.9, 83.1, 74.5, 73.2, 62.8, 62.6, 41.6, 14.2.

^{19}F NMR (377 MHz, $CDCl_3$): δ -62.4.

IR (neat) ($\tilde{\nu}$): 3056, 2985, 2217, 1731, 1619, 1446, 1325, 1263, 1167, 732 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{23}F_3NO_4$ $[M+H]^+$ = 458.1579, found 458.1581.

Diethyl 2-(phenylethynyl)-5-(*p*-tolyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ea):



3ea

Physical State: Yellow gum.

Yield: 46 mg, 77%.

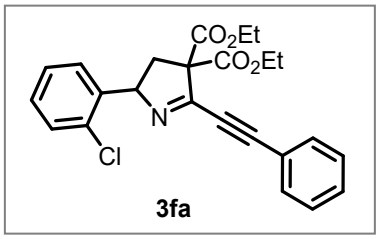
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.53 (m, 2H), 7.38 – 7.35 (m, 2H), 7.21 – 7.15 (m, 3H), 7.05 – 6.93 (m, 1H), 5.29 (t, *J* = 7.8 Hz, 1H), 4.33 – 4.24 (m, 4H), 3.22 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.47 (dd, *J* = 13.5, 8.2 Hz, 1H), 2.34 (s, 3H), 1.34 – 1.28 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 167.4, 153.9, 138.8, 137.2, 132.4, 129.8, 129.4, 128.6, 126.7, 121.6, 94.1, 83.4, 74.9, 73.1, 62.6, 62.4, 41.9, 21.2, 14.2.

IR (neat) ($\tilde{\nu}$): 3057, 2925, 2214, 1731, 1596, 1389, 1069, 759 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{26}NO_4$ $[M+H]^+$ = 404.1862, found 404.1860.

Diethyl 5-(2-chlorophenyl)-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3fa):



3fa

Physical State: Brownish viscous liquid.

Yield: 49 mg, 78%.

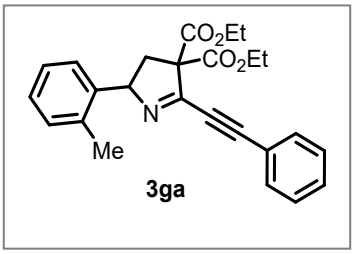
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.55 (m, 2H), 7.44 – 7.34 (m, 4H), 7.29 – 7.19 (m, 3H), 5.70 (t, *J* = 7.6 Hz, 1H), 4.37 – 4.29 (m, 2H), 4.24 (qd, *J* = 7.1, 2.0 Hz, 2H), 3.39 (dd, *J* = 13.5, 7.7 Hz, 1H), 2.37 (dd, *J* = 13.6, 7.5 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9, 167.3, 155.0, 139.9, 132.5, 132.5, 130.0, 129.5, 128.8, 128.6, 127.8, 127.3, 121.5, 94.6, 83. 3, 73.1, 72.2, 62.7, 62.5, 40.7, 14.2, 14.15.

IR (neat) ($\tilde{\nu}$): 2982, 2217, 1731, 1601, 1471, 1367, 1258, 1031, 756 cm^{-1}.

HRMS: *m/z* calculated for $C_{24}H_{23}ClNO_4$ $[M+H]^+$ = 424.1316, found 424.1324.

Diethyl 2-(phenylethynyl)-5-(*o*-tolyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ga):



3ga

Physical State: Yellow viscous liquid.

Yield: 53 mg, 87%.

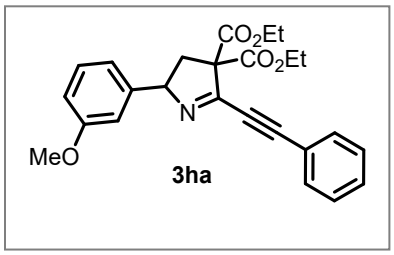
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.55 (m, 2H), 7.41 – 7.34 (m, 3H), 7.20 – 7.13 (m, 4H), 5.51 (t, *J* = 7.6 Hz, 1H), 4.36 – 4.25 (m, 4H), 3.27 (dd, *J* = 13.4, 7.6 Hz, 1H), 2.40 – 2.34 (m, 4H), 1.35 – 1.25 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 167.5, 154.1, 140.3, 134.8, 132.5, 130.4, 129.9, 128.6, 127.5, 126.5, 126.2, 121.6, 94.1, 83.5, 73.1, 72.2, 62.6, 62.4, 40.9, 19.7, 14.2.

IR (neat) ($\tilde{\nu}$): 3054, 2984, 2217, 1729, 1600, 1463, 1367, 1263, 1033, 731 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{26}NO_4$ $[M+H]^+$ = 404.1862, found 404.1865.

Diethyl 5-(3-methoxyphenyl)-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ha):



3ha

Physical State: Pale yellow gum.

Yield: 49 mg, 79%.

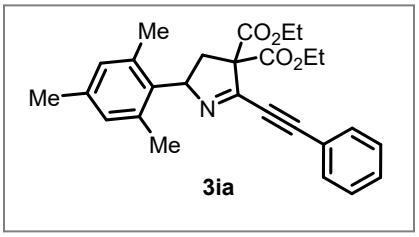
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.60 – 7.46 (m, 5H), 7.29 (t, *J* = 8.1 Hz, 1H), 6.89 – 6.81 (m, 3H), 5.33 (t, *J* = 7.6 Hz, 1H), 4.30 – 4.18 (m, 4H), 3.75 (s, 3H), 3.15 (dd, *J* = 13.5, 7.6 Hz, 1H), 2.36 (dd, *J* = 13.6, 7.8 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 167.5, 167.0, 159.5, 153.0, 143.5, 132.1, 130.5, 129.8, 129.2, 120.4, 118.7, 112.8, 112.4, 93.4, 83.3, 74.2, 72.7, 62.3, 55.2, 40.9, 13.9.

IR (neat) ($\tilde{\nu}$): 2980, 2924, 2216, 1730, 1602, 1443, 1258, 1035, 786 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{26}NO_5$ $[M+H]^+$ = 420.1811, found 420.1812.

Diethyl 5-mesityl-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ia):



3ia

Physical State: Yellow solid.

Melting Point: 87.5 °C – 90 °C.

Yield: 60 mg, 92% (under N_2 atm.); 57 mg, 89% (under air atm.).

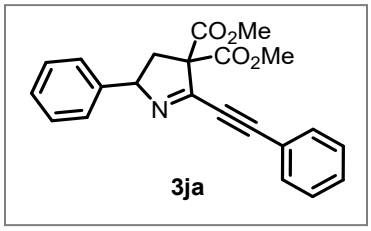
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.54 (m, 2H), 7.42 – 7.34 (m, 3H), 6.83 (s, 2H), 5.56 – 5.51 (m, 1H), 4.38 – 4.23 (m, 4H), 3.12 (dd, *J* = 13.4, 7.3 Hz, 1H), 2.56 (dd, *J* = 13.4, 10.0 Hz, 1H), 2.29 (s, 6H), 2.26 (s, 3H), 1.36 – 1.29 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 167.3, 152.3, 137.0, 136.7, 133.5, 132.5, 130.2, 129.8, 128.6, 121.7, 93.7, 83.6, 72.9, 72.2, 62.5, 62.4, 39.7, 20.9, 20.8, 14.2, 14.2.

IR (neat) ($\tilde{\nu}$): 3029, 2962, 2215, 1731, 1600, 1582, 1485, 1313, 1162, 1076, 1017, 850, 754 cm^{-1}.

HRMS: *m/z* calculated for $C_{27}H_{30}NO_4$ $[M+H]^+$ = 432.2175, found 432.2174.

Dimethyl 5-phenyl-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ja):



3ja

Physical State: Yellow viscous liquid.

Yield: 46 mg, 84%.

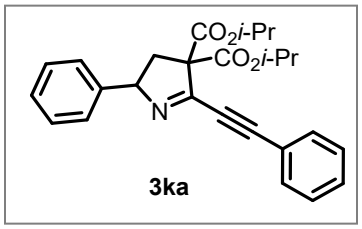
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 2H), 7.41 – 7.24 (m, 8H), 5.31 (t, *J* = 7.8 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.22 (dd, *J* = 13.5, 7.3 Hz, 1H), 2.51 (dd, *J* = 13.4, 8.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4, 167.9, 153.8, 141.6, 132.6, 130.0, 128.8, 128.6, 127.7, 126.8, 121.9, 94.7, 83.1, 75.0, 73.1, 53.6, 53.4, 42.1.

IR (neat) ($\tilde{\nu}$): 3031, 2924, 2216, 1732, 1602, 1491, 1310, 1171, 1029, 787 cm^{-1}.

HRMS: *m/z* calculated for $C_{22}H_{20}NO_4$ $[M+H]^+$ = 362.1392, found 362.1398.

Diisopropyl 5-phenyl-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ka):



Physical State: Yellow viscous liquid.

Yield: 54 mg, 87%.

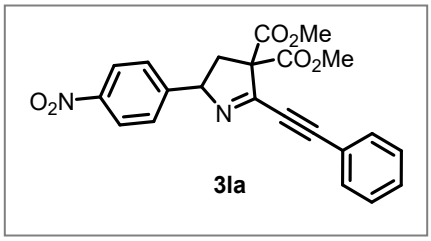
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.28 (m, 8H), 5.32 (t, *J* = 7.7 Hz, 1H), 5.19 – 5.07 (m, 2H), 3.24 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.46 (dd, *J* = 14.0, 8.6 Hz, 1H), 1.33 – 1.27 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.6, 166.9, 154.4, 142.0, 132.4, 129.8, 128.8, 128.6, 127.6, 126.9, 121.7, 93.9, 83.7, 75.1, 73.2, 41.7, 21.8, 21.7, 21.7, 21.6.

IR (neat) ($\tilde{\nu}$): 3055, 2930, 2218, 1725, 1603, 1491, 1376, 1146, 1026, 732 cm^{-1}.

HRMS: *m/z* calculated for $C_{26}H_{28}NO_4$ $[M+H]^+$ = 418.2018, found 418.2021.

Dimethyl 5-(4-nitrophenyl)-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3la):



3la

Physical State: Yellow viscous liquid.

Yield: 44 mg, 72%.

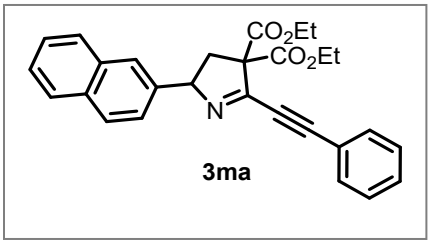
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.58 – 7.56 (m, 2H), 7.50 (d, 2H, *J* = 8.7 Hz, 2H), 7.44 – 7.36 (m, 3H), 5.41 (t, *J* = 7.9 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.29 (dd, *J* = 13.5, 7.4 Hz, 1H), 2.46 (dd, *J* = 13.4, 8.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 167.5, 155.0, 149.0, 147.5, 132.7, 130.3, 128.7, 127.6, 124.1, 121.0, 95.8, 82.7, 74.0, 73.1, 53.8, 53.7, 41.7.

IR (neat) ($\tilde{\nu}$): 3054, 2956, 2217, 1736, 1603, 1491, 1348, 1173, 731 cm^{-1}.

HRMS: *m/z* calculated for $C_{22}H_{19}N_2O_6$ $[M+H]^+$ = 407.1243, found 407.1247.

Diethyl 5-(naphthalen-2-yl)-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ma):



Physical State: Yellow viscous liquid.

Yield: 55 mg, 84%.

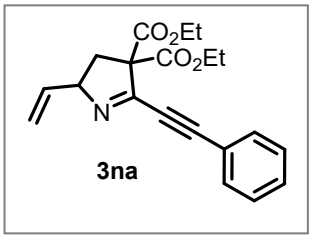
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.79 (m, 5H), 7.59 – 7.54 (m, 2H), 7.48 – 7.37 (m, 5H), 5.50 (t, *J* = 7.8 Hz, 1H), 4.37 – 4.26 (m, 4H), 3.33 (dd, *J* = 13.5, 7.4 Hz, 1H), 2.57 (dd, *J* = 13.4, 8.2 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 167.4, 154.4, 139.2, 133.5, 132.9, 132.5, 129.9, 128.6, 128.1, 127.8, 126.3, 126.0, 125.4, 124.9, 121.5, 94.5, 83.4, 75.1, 73.2, 62.7, 62.5, 41.8, 14.2.

IR (neat) ($\tilde{\nu}$): 3055, 2925, 2217, 1730, 1601, 1489, 1366, 1184, 1073, 756 cm^{-1}.

HRMS: *m/z* calculated for $C_{28}H_{26}NO_4$ $[M+H]^+$ = 440.1862, found 440.1864.

Diethyl 2-(phenylethynyl)-5-vinyl-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3na):



3na

Physical State: White viscous liquid.

Yield: 32 mg, 63%.

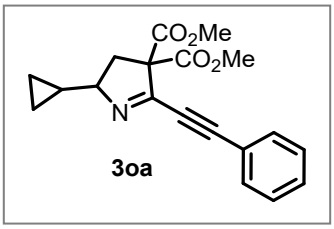
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.51 (m, 2H), 7.42 – 7.33 (m, 3H), 5.98 – 5.90 (m, 1H), 5.31 – 5.17 (m, 2H), 4.78 – 4.73 (m, 1H), 4.34 – 4.23 (m, 4H), 2.93 (dd, *J* = 13.3, 7.4 Hz, 1H), 2.40 (dd, *J* = 13.3, 7.1 Hz, 1H), 1.31 – 1.28 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 167.5, 153.7, 137.7, 132.4, 129.8, 128.6, 121.5, 116.6, 94.0, 83.3, 73.8, 72.6, 62.6, 62.5, 39.1, 14.2, 14.2.

IR (neat) ($\tilde{\nu}$): 2982, 2217, 1731, 1587, 1444, 1367, 1190, 1068, 758 cm^{-1}.

HRMS: *m/z* calculated for $C_{20}H_{22}NO_4$ $[M+H]^+$ = 340.1549, found 340.1548.

Diethyl 5-cyclopropyl-2-(phenylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3oa):



Physical State: Yellow viscous liquid.

Yield: 25 mg, 52%,

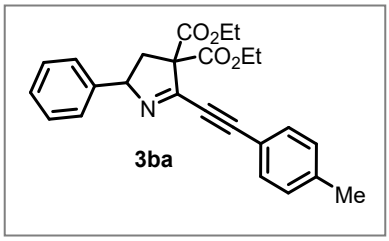
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.51 (m, 2H), 7.41 – 7.32 (m, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.66 – 3.60 (m, 1H), 2.87 (dd, *J* = 13.5, 7.1 Hz, 1H), 2.40 (dd, *J* = 13.5, 7.5 Hz, 1H), 0.97 – 0.87 (m, 1H), 0.68 – 0.53 (m, 2H), 0.50 – 0.45 (m, 1H), 0.41 – 0.35 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.7, 168.2, 152.7, 132.5, 129.9, 128.6, 121.5, 93.9, 83.1, 76.7, 72.5, 53.5, 53.4, 39.2, 16.0, 3.8, 3.1.

IR (neat) ($\tilde{\nu}$): 3004, 2954, 2216, 1734, 1602, 1489, 1311, 1159, 1025, 758 cm^{-1}.

HRMS: *m/z* calculated for $C_{19}H_{20}NO_4$ $[M+H]^+$ = 326.1392, found 326.1391.

Diethyl 5-phenyl-2-(*p*-tolylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ab):



Physical State: Yellow viscous gum.

Yield: 56 mg, 93%.

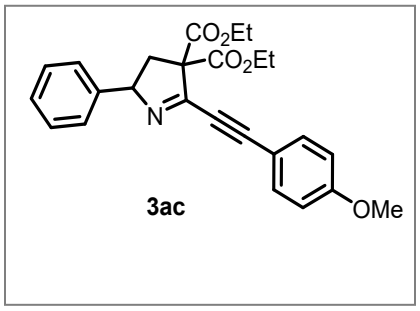
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.28 (m, 5H), 7.17 (d, *J* = 8.2 Hz, 2H), 5.31 (t, *J* = 7.8 Hz, 1H), 4.34 – 4.24 (m, 4H), 3.24 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.49 (dd, *J* = 13.4, 8.2 Hz, 1H), 2.38 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 167.5, 154.2, 141.9, 140.4, 132.4, 129.4, 128.7, 127.6, 126.8, 118.5, 94.8, 83.0, 75.0, 73.2, 62.6, 62.5, 41.9, 21.8, 14.3, 14.2.

IR (neat) ($\tilde{\nu}$): 3010, 2964, 2217, 1730, 1587, 1440, 1263, 1058, 803 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{26}NO_4$ $[M+H]^+$ = 404.1862, found 404.1866.

Diethyl 2-((4-methoxyphenyl)ethynyl)-5-phenyl-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ac):



3ac

Physical State: Yellow viscous liquid.

Yield: 56 mg, 90%.

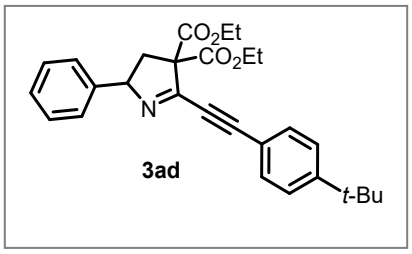
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.27 (m, 5H), 6.88 (d, *J* = 8.9 Hz, 2H), 5.30 (t, *J* = 7.8 Hz, 1H), 4.35 – 4.23 (m, 4H), 3.83 (s, 3H), 3.23 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.49 (dd, *J* = 13.4, 8.2 Hz, 1H), 1.34 – 1.26 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 167.5, 160.9, 154.2, 142.0, 134.2, 128.7, 127.6, 126.8, 114.3, 113.5, 94.9, 82.6, 74.9, 73.1, 62.6, 62.4, 55.5, 41.9, 14.3, 14.2.

IR (neat) ($\tilde{\nu}$): 3055, 2924, 2211, 1730, 1597, 1460, 1259, 1172, 1028, 735 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{26}NO_5$ $[M+H]^+$ = 420.1811, found 420.1815.

Diethyl 2-((4-(tert-butyl)phenyl)ethynyl)-5-phenyl-4,5-dihydro-3*H*-pyrrole 3,3-dicarboxylate (3ad):



Physical State: Yellow viscous liquid.

Yield: 61 mg, 92%.

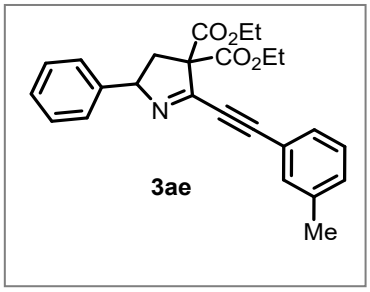
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.46 (m, 2H), 7.40 – 7.26 (m, 7H), 5.31 (t, *J* = 7.8 Hz, 1H), 4.37 – 4.24 (m, 4H), 3.25 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.50 (dd, *J* = 13.4, 8.3 Hz, 1H), 1.35 – 1.27 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 167.4, 154.2, 153.4, 141.9, 132.3, 128.7, 127.6, 126.8, 125.6, 118.5, 94.7, 82.9, 75.0, 73.2, 62.6, 62.4, 41.9, 35.1, 31.2, 14.2.

IR (neat) ($\tilde{\nu}$): 3054, 2931, 2214, 1731, 1596, 1495, 1263, 1181, 1030, 732 cm^{-1}.

HRMS: *m/z* calculated for $C_{28}H_{32}NO_4$ $[M+H]^+$ = 446.2331, found 446.2331.

Diethyl 5-phenyl-2-(*m*-tolylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ae):



Physical State: Yellow viscous gum.

Yield: 51 mg, 85%.

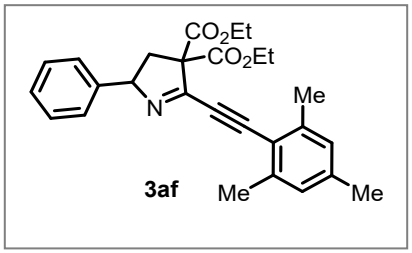
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.15 (m, 9H), 5.32 (t, *J* = 7.8 Hz, 1H), 4.38 – 4.22 (m, 4H), 3.25 (dd, *J* = 13.5, 7.4 Hz, 1H), 2.50 (dd, *J* = 13.4, 8.2 Hz, 1H), 2.35 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): 168.0, 167.4, 154.1, 141.9, 138.3, 133.0, 130.8, 129.6, 128.7, 128.5, 127.6, 126.8, 121.4, 94.6, 83.1, 75.0, 73.2, 62.6, 62.5, 41.9, 21.3, 14.2.

IR (neat) ($\tilde{\nu}$): 3057, 2924, 2212, 1730, 1603, 1449, 1263, 1095, 734 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{26}NO_4$ $[M+H]^+$ = 404.1862, found 404.1863.

Diethyl 2-(mesitylethynyl)-5-phenyl-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3af):



Physical State: Yellow viscous liquid.

Yield: 60 mg, 93%.

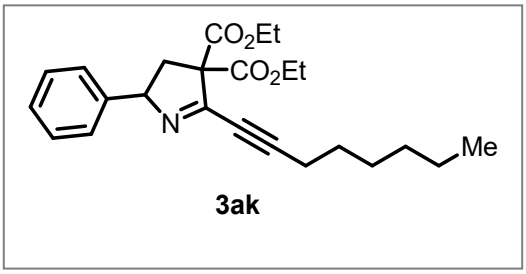
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.28 (m, 5H), 6.94 – 6.84 (s, 2H), 5.32 (t, *J* = 7.7 Hz, 1H), 4.36 – 4.24 (m, 4H), 3.29 (dd, *J* = 13.3, 7.3 Hz, 1H), 2.46 – 2.42 (m, 7H), 2.30 (s, 3H), 1.31 – 1.24 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 167.4, 154.2, 142.0, 141.8, 139.7, 128.7, 127.9, 127.6, 126.9, 118.3, 92.7, 90.8, 75.2, 73.2, 62.6, 62.4, 42.4, 21.6, 21.0, 14.2, 14.1.

IR (neat) ($\tilde{\nu}$): 3053, 2984, 2205, 1730, 1595, 1367, 1292, 1183, 1028, 733 cm^{-1}.

HRMS: *m/z* calculated for $C_{27}H_{30}NO_4$ $[M+H]^+$ = 432.2175, found 432.2179.

Diethyl 2-(oct-1-yn-1-yl)-5-phenyl-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (**3ak**):



3ak

Physical State: Yellow Oil.

Yield: 46 mg, 76%.

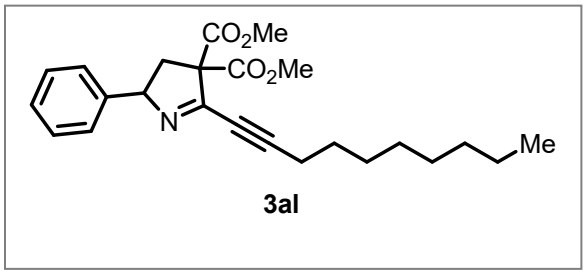
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.29 (m, 2H), 7.28 – 7.21 (m, 3H), 5.21 (t, *J* = 7.8 Hz, 1H), 4.32 – 4.17 (m, 4H), 3.16 (dd, *J* = 13.4, 7.3 Hz, 1H), 2.44 – 2.36 (m, 3H), 1.62 – 1.53 (m, 2H), 1.45 – 1.37 (m, 2H), 1.33 – 1.23 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 167.5, 141.9, 128.7, 127.5, 126.8, 97.1, 75.2, 74.5, 72.9, 62.4, 62.3, 42.0, 31.4, 28.7, 28.1, 22.6, 19.6, 14.2, 14.1.

IR (neat) ($\tilde{\nu}$): 2930, 2230, 1730, 1599, 1450, 1366, 1233, 1178, 1066, 1019, 860, 699 cm^{-1}.

HRMS: *m/z* calculated for $C_{24}H_{31}NO_4$ $[M+H]^+$ = 398.2331, found 398.2339.

Dimethyl 2-(dec-1-yn-1-yl)-5-phenyl-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3al):



3al

Physical State: Yellow Oil.

Yield: 42 mg, 71%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.31 (m, 2H), 7.27 (d, *J* = 8.8 Hz, 3H), 5.22 (t, *J* = 7.8 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.18 (dd, *J* = 13.4, 7.2 Hz, 1H), 2.46 – 2.39 (m, 3H), 1.63 – 1.54 (m, 2H), 1.46 – 1.37 (m, 2H), 1.34 – 1.23 (m, 8H) 0.88 (t, *J* = 6.9 Hz, 3H).

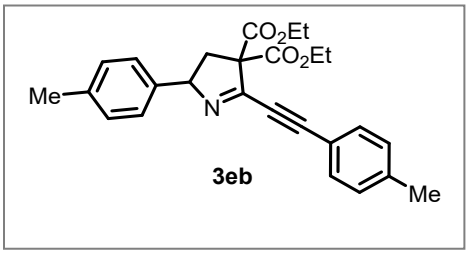
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.57, 167.97, 153.88, 141.77, 128.70, 127.55, 126.74, 97.49, 74.94, 74.54, 72.87, 53.46, 53.31, 42.20, 31.97, 29.31, 29.22, 28.93, 28.16, 22.79, 19.59, 14.24.

IR (neat) (*ṽ*): 2926, 2855, 2230, 1735, 1600, 1434, 1236, 1198, 1169, 1069, 1019, 911, 731, 699cm^{-1}.

HRMS: *m/z* calculated for $C_{24}H_{31}NO_4$ $[M+H]^+$ = 398.2331, found 398.2331.

.

Diethyl 5-(*p*-tolyl)-2-(*p*-tolylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3eb):



3eb

Physical State: Yellow viscous liquid.

Yield: 54 mg, 86%.

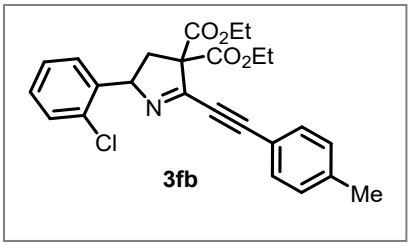
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.39 (m, 2H), 7.21 – 7.12 (m, 6H), 5.27 (t, *J* = 7.7 Hz, 1H), 4.33 – 4.22 (m, 4H), 3.21 (dd, *J* = 13.5, 7.4 Hz, 1H), 2.47 (dd, *J* = 13.4, 8.2 Hz, 1H), 2.37 (s, 3H), 2.34 (s, 3H), 1.35 – 1.28 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 167.5, 154.0, 140.3, 138.9, 137.2, 132.5, 129.4, 129.4, 126.7, 118.5, 94.7, 83.1, 74.8, 73.2, 62.6, 62.4, 41.9, 21.8, 21.3, 14.2.

IR (neat) ($\tilde{\nu}$): 2981, 2923, 2214, 1731, 1606, 1446, 1258, 1179, 1074, 734 cm^{-1}.

HRMS: *m/z* calculated for $C_{26}H_{28}NO_4$ $[M+H]^+$ = 418.2018, found 418.2022.

Diethyl 5-(2-chlorophenyl)-2-(*p*-tolylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3fb):



3fb

Physical State: Brownish viscous liquid.

Yield: 54 mg, 82%.

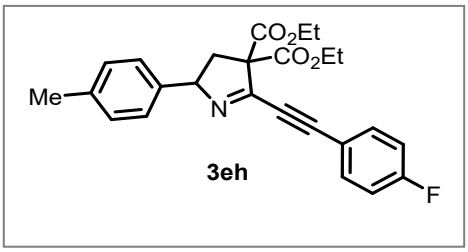
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.26 (m, 4H), 7.25 – 7.13 (m, 4H), 5.68 (t, *J* = 7.6 Hz, 1H), 4.38 – 4.17 (m, 4H), 3.38 (dd, *J* = 13.6, 7.7 Hz, 1H), 2.44 – 2.31 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.6 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9, 167.4, 155.1, 140.5, 140.0, 132.5, 129.5, 129.4, 128.7, 127.4, 127.8, 127.3, 118.4, 95.1, 82.9, 73.1, 72.1, 62.6, 62.5, 40.7, 21.8, 14.2, 14.2.

IR (neat) ($\tilde{\nu}$): 2981, 2818, 2214, 1732, 1594, 1471, 1258, 1180, 1030, 817 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{25}ClNO_4$ $[M+H]^+$ = 438.1472, found 438.1472.

Diethyl 2-((4-fluorophenyl)ethynyl)-5-(*p*-tolyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3eh):



3eh

Physical State: Brownish viscous gum.

Yield: 50 mg, 80%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.50 (m, 2H), 7.21 – 7.14 (m, 4H), 7.06 (t, *J* = 8.7 Hz, 2H), 5.28 (t, *J* = 7.8 Hz, 1H), 4.34 – 4.25 (m, 4H), 3.22 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.46 (dd, *J* = 13.4, 8.2 Hz, 1H), 2.34 (s, 3H), 1.32 (t, *J* = 6.9 Hz, 3H), 1.28 (t, *J* = 7.3 Hz, 3H).

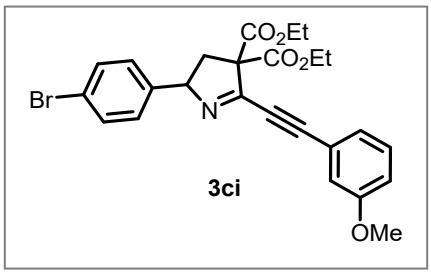
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 167.4, 163.5 (d, $^{1}J_{C\text{-}F}$ = 253.5 Hz), 153.8, 138.8, 137.3, 134.5 (d, $^{3}J_{C\text{-}F}$ = 8.70 Hz), 129.4, 126.7, 117.7 (d, $^{4}J_{C\text{-}F}$ = 2.86 Hz), 116.1 (d, $^{2}J_{C\text{-}F}$ = 22.20 Hz), 93.0, 83.3, 74.9, 73.1, 62.6, 62.5, 41.9, 21.3, 14.2.

^{19}F NMR (377 MHz, $CDCl_3$): δ -108.0.

IR (neat) ($\tilde{\nu}$): 3053, 2985, 2218, 1729, 1591, 1421, 1263, 1155, 1031, 733 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{25}FNO_4$ $[M+H]^+$ = 422.1768, found 422.1775.

Diethyl 5-(4-bromophenyl)-2-((3-methoxyphenyl)ethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3ci):



3ci

Physical State: Brownish viscous liquid.

Yield: 53 mg, 72%.

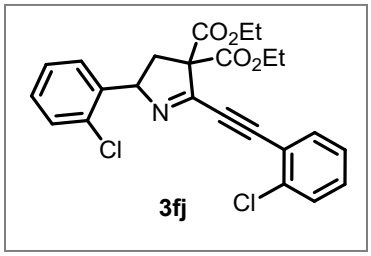
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.26 (t, *J* = 4.0 Hz, 1H), 7.21 (s, 2H), 7.16 – 7.12 (m, 1H), 7.09 – 7.04 (m, 1H), 6.98 – 6.94 (m, 1H), 5.27 (t, *J* = 7.8 Hz, 1H), 4.35 – 4.24 (m, 4H), 3.80 (s, 3H), 3.23 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.42 (dd, *J* = 13.4, 8.2 Hz, 1H), 1.32 (t, *J* = 7.4 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.8, 167.2, 154.5, 140.9, 131.8, 129.7, 128.5, 125.0, 122.3, 121.5, 117.2, 116.6, 94.6, 82.9, 74.3, 73.1, 62.7, 62.6, 55.6, 41.7, 14.19, 14.17.

IR (neat) ($\tilde{\nu}$): 2980, 2935, 2212, 1728, 1599, 1464, 1367, 1227, 1096, 785 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{25}BrNO_5$ $[M+H]^+$ = 498.0916, found 498.0916.

Diethyl 5-(2-chlorophenyl)-2-((2-chlorophenyl)ethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3fj):



3fj

Physical State: Brownish viscous liquid.

Yield: 47 mg, 69%.

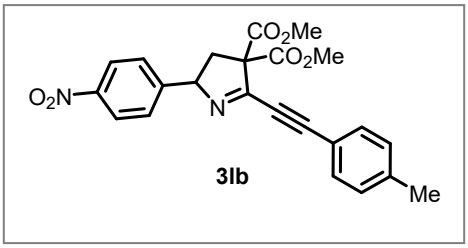
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.60 (m, 1H), 7.45 – 7.27 (m, 5H), 7.27 – 7.20 (m, 2H), 5.72 (t, *J* = 7.6 Hz, 1H), 4.37 – 4.22 (m, 4H), 3.42 (dd, *J* = 13.5, 7.7 Hz, 1H), 2.37 (dd, *J* = 13.5, 7.5 Hz, 1H), 1.34 – 1.25 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9, 167.2, 155.0, 139.8, 136.8, 134.4, 132.5, 131.0, 129.6, 129.5, 128.8, 127.8, 127.3, 126.8, 121.6, 90.7, 87.9, 73.0, 72.4, 62.8, 62.6, 40.9, 14.2, 14.1.

IR (neat) ($\tilde{\nu}$): 3661, 2982, 2852, 2220, 1785, 1730, 1599, 1472, 1390, 1261, 1128, 957, 804 cm^{-1}.

HRMS: *m/z* calculated for $C_{24}H_{22}Cl_2NO_4$ $[M+H]^+$ = 458.0926, found 458.0927.

Diethyl 5-(4-nitrophenyl)-2-(*p*-tolylethynyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3lb):



3lb

Physical State: Yellow viscous liquid.

Yield: 29 mg, 46%.

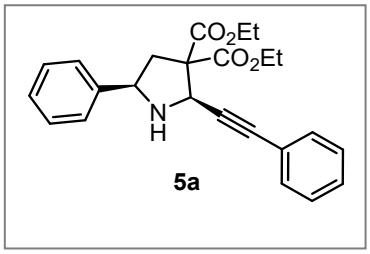
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 – 8.20 (d, *J* = 8.7 Hz, 2H), 7.51 – 7.45 (m, 4H), 7.18 (d, *J* = 8.3 Hz, 2H), 5.39 (t, *J* = 7.9 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.28 (dd, *J* = 13.5, 7.4 Hz, 1H), 2.46 (dd, *J* = 13.4, 8.5 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1, 167.6, 155.1, 149.1, 147.5, 140.9, 132.6, 129.5, 127.7, 124.1, 118.0, 96.3, 82.3, 74.0, 73.1, 53.8, 53.6, 41.8, 21.9.

IR (neat) (ṽ): 3054, 2927, 2213, 1733, 1599, 1522, 1443, 1348, 1263, 1104, 1014, 732 cm^{-1}.

HRMS: *m/z* calculated for $C_{23}H_{21}N_2O_6$ $[M+H]^+$ = 421.1400, found 421.1403.

Diethyl 5-phenyl-2-(phenylethynyl)pyrrolidine-3,3-dicarboxylate (5a):



5a

Physical State: Brown viscous liquid.

Yield: 33 mg, 85%.

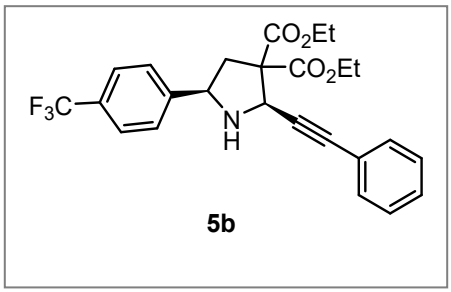
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.27 (m, 9H), 7.24 - 7.22 (m, 1H), 5.12 (s, 1H), 4.72 (t, *J* = 8.0 Hz, 1H), 4.29 – 4.17 (m, 4H), 3.30 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.07 (dd, *J* = 13.8, 8.0 Hz, 1H), 1.26 – 1.23 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 168.9, 142.6, 131.8, 128.6, 128.5, 128.4, 127.4, 126.7, 122.7, 87.1, 85.3, 66.0, 62.0, 61.1, 55.8, 41.5, 14.2, 14.1.

IR (neat) (ῡ): 2954, 2923, 2212, 1735, 1596, 1520, 1435, 1347, 1272, 1173, 1034, 818 cm^{-1}.

HRMS: *m/z* calculated for $C_{24}H_{26}NO_4$ $[M+H]^+$ = 392.1862, found 392.1862.

Diethyl 2-(phenylethynyl)-5-(4-(trifluoromethyl)phenyl)pyrrolidine-3,3-dicarboxylate (5b):



5b

Physical State: yellowish gum.

Yield: 31 mg, 69%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.33 – 7.28 (m, 3H), 5.11 (s, 1H), 4.77 (t, *J* = 8.0 Hz, 1H), 4.28 – 4.16 (m, 4H), 3.32 (dd, *J* = 13.8, 8.2 Hz, 1H), 2.44 (s, 1H), 2.05 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.28 – 1.23 (m, 6H).

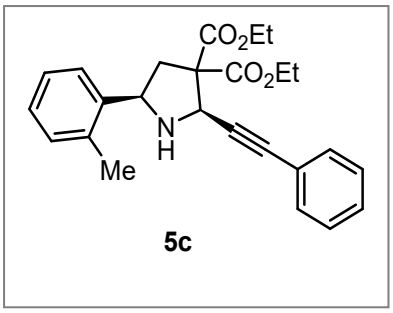
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 168.8, 147.1, 131.8, 130.2, 129.7 (q, $^{2}J_{C\text{-}F}$ = 34.52 Hz), 128.6, 128.5, 127.0, 126.2 (q, $^{1}J_{C\text{-}F}$ = 248.23), 125.6 (q, $^{3}J_{C\text{-}F}$ = 3.36 Hz), 122.6, 86.8, 85.6, 65.7, 62.2, 60.4, 55.7, 41.4, 14.2, 14.1.

^{19}F NMR (377 MHz, $CDCl_3$): δ -62.44.

IR (neat) ($\tilde{\nu}$): 3337, 2982, 2917, 2175, 1734, 1490, 1419, 1325, 1260, 1160, 917, 757 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{25}NO_4F_3$ $[M+H]^+$ = 460.1736, found 460.1737.

Diethyl 2-(phenylethynyl)-5-(*o*-tolyl)pyrrolidine-3,3-dicarboxylate (5c):



5c

Physical State: yellowish gum.

Yield: 31 mg, 77%.

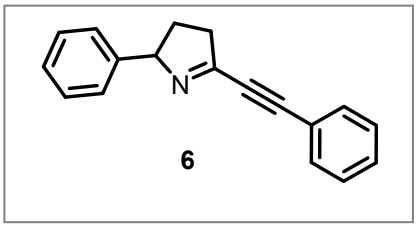
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.2 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.32 – 7.27 (m, 3H), 7.20 – 7.16 (m, 1H), 7.14 (m, 2H), 5.13 (s, 1H), 4.89 (t, *J* = 8.0 Hz, 1H), 4.28 – 4.16 (m, 5H), 3.30 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.39 (s, 3H), 1.94 (dd, *J* = 13.6, 7.9 Hz, 1H), 1.28 – 1.24 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 168.9, 140.9, 135.5, 131.7, 130.3, 128.4, 128.3, 126.9, 126.3, 125.0, 122.7, 87.2, 85.2, 65.7, 70.0, 61.9, 57.4, 55.4, 40.1, 19.5, 14.2, 14.1.

IR (neat) ($\tilde{\nu}$): 3338, 2980, 2915, 2219, 1732, 1489, 1392, 1215, 1177, 756 cm^{-1}.

HRMS: *m/z* calculated for $C_{25}H_{28}NO_4$ $[M+H]^+$ = 406.2018 found 406.2018.

2-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyrrole (6):



6

Physical State: Pale yellow viscous liquid.

Yield: 18 mg, 73%.

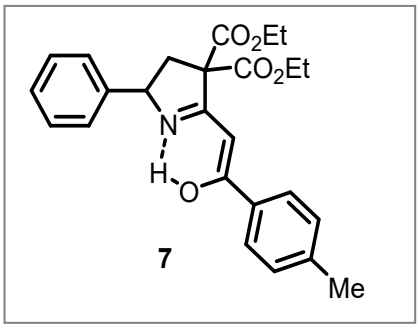
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.55 (m, 2H), 7.42 – 7.27 (m, 8H), 5.27-5.22 (m, 1H), 3.01 – 2.92 (m, 1H), 2.89 – 2.80 (m, 1H), 2.59 – 2.49 (m, 1H), 1.91 – 1.84 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.3, 143.6, 132.4, 129.6, 128.6, 128.5, 127.1, 126.6, 121.6, 93.3, 84.7, 76.5, 40.7, 31.9.

IR (neat) (ṽ): 2922, 2851, 2209, 1600, 1491, 1450, 1330, 1262, 1026, 757 cm^{-1}.

HRMS: *m/z* calculated for $C_{18}H_{16}N$ $[M+H]^+$ = 246.1283, found 246.1285.

Diethyl (*Z*)-2-(2-hydroxy-2-(*p*-tolyl)vinyl)-5-phenyl-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (7):



7

Physical State: Yellow Solid.

Melting Point: 89 ºC – 91 ºC.

Yield: 26 mg, 55%.

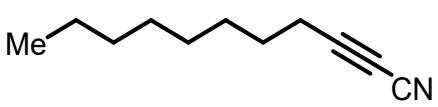
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.51 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.30 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.25 (s, 1H), 5.04 (t, *J* = 7.6 Hz, 1H), 4.34 – 4.21 (m, 4H), 3.11 (dd, *J* = 13.4, 6.8 Hz, 1H), 2.50 (dd, *J* = 13.5, 8.5 Hz, 1H), 2.39 (s, 3H), 1.34 – 1.27 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 189.5, 168.2, 167.9, 161.4, 141.6, 140.5, 137.2, 129.1, 129.0, 128.4, 127.5, 126.4, 89.4, 65.5, 62.8, 62.5, 61.8, 41.1, 21.6, 14.1.

IR (neat) ($\tilde{\nu}$): 3268 (br.), 2976, 2927, 1731, 1607, 1572, 1524, 147, 1367, 1241, 1106, 912, 723 cm^{-1}.

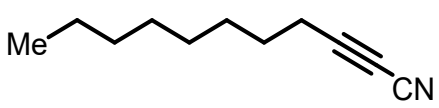
HRMS: *m/z* calculated for $C_{25}H_{28}NO_5$ $[M+H]^+$ = 422.1862, found 422.1848.

6. Copies of ^{1}H, ^{13}C, ^{19}F, DEPT-135 NMR spectra



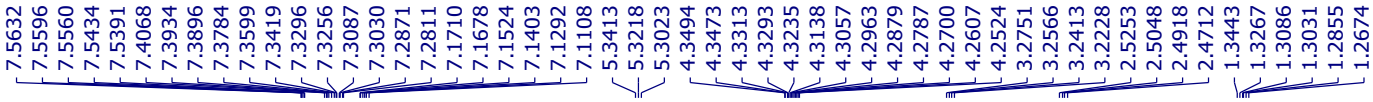
^{1}H NMR (400 MHz, $CDCl_3$)

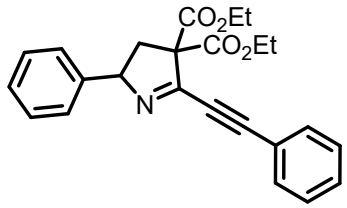
2l



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

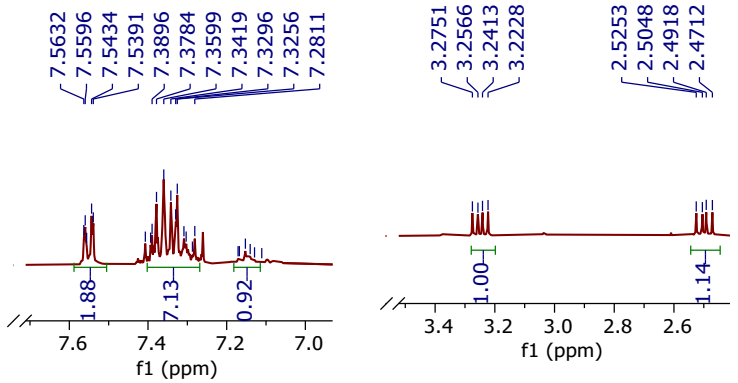
2l

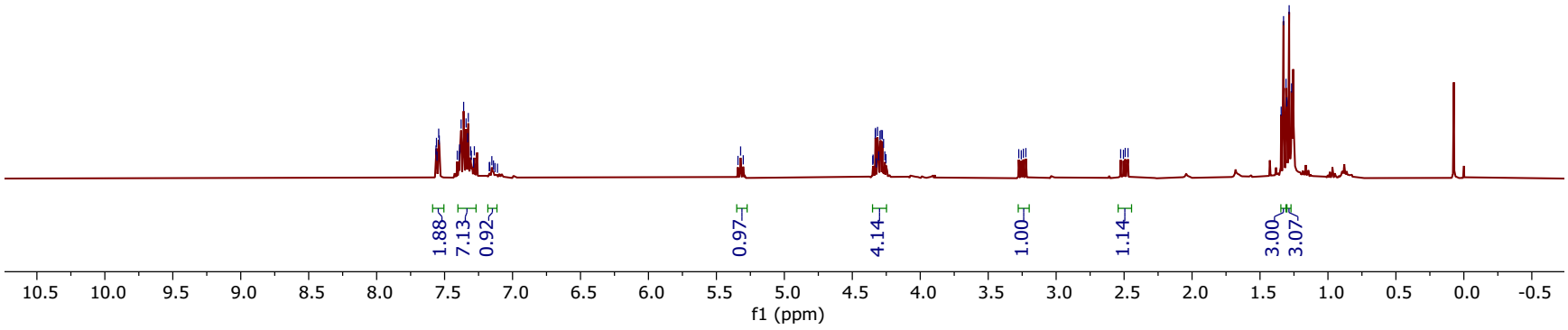


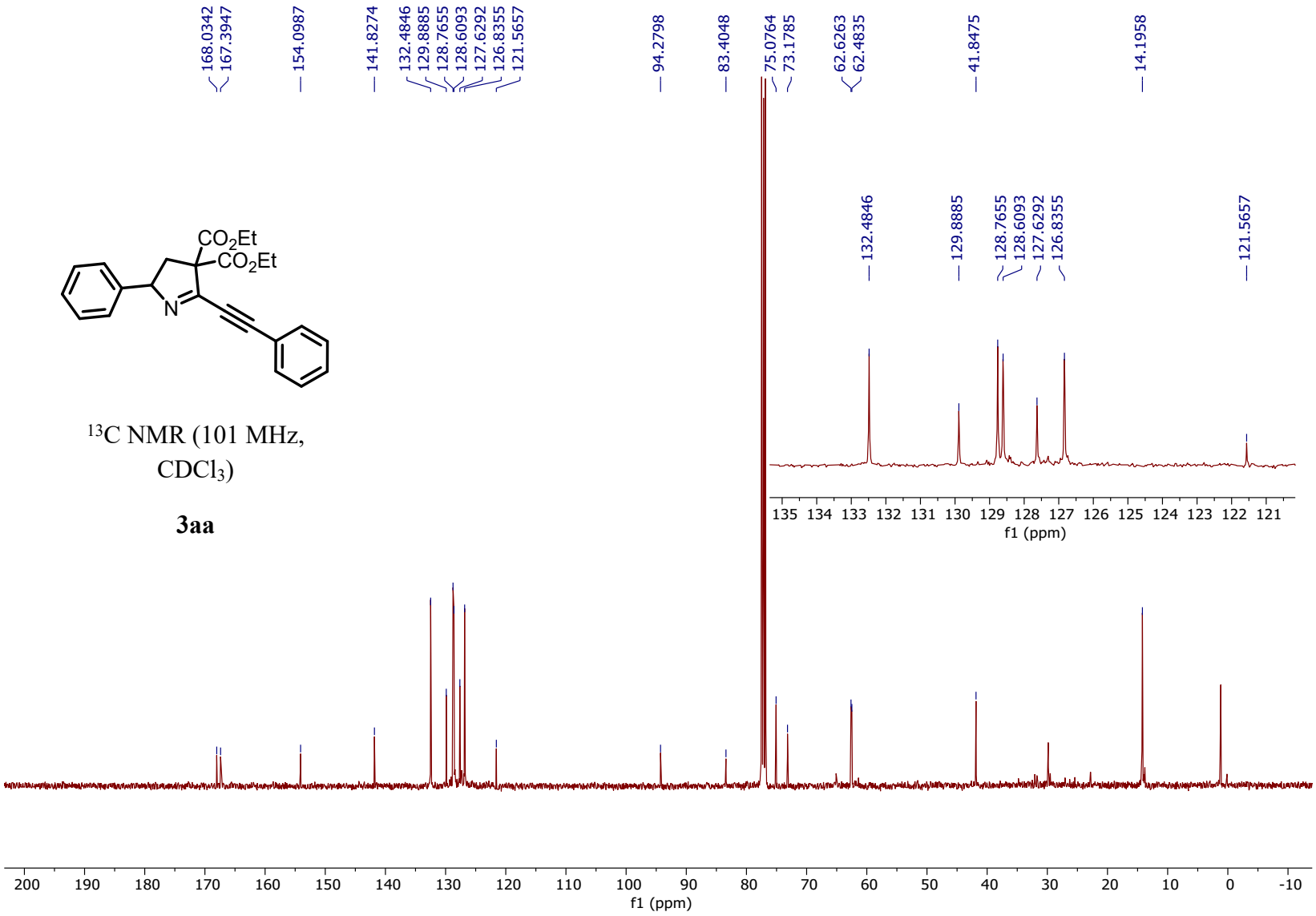


^{1}H NMR (400 MHz, $CDCl_3$)

3aa

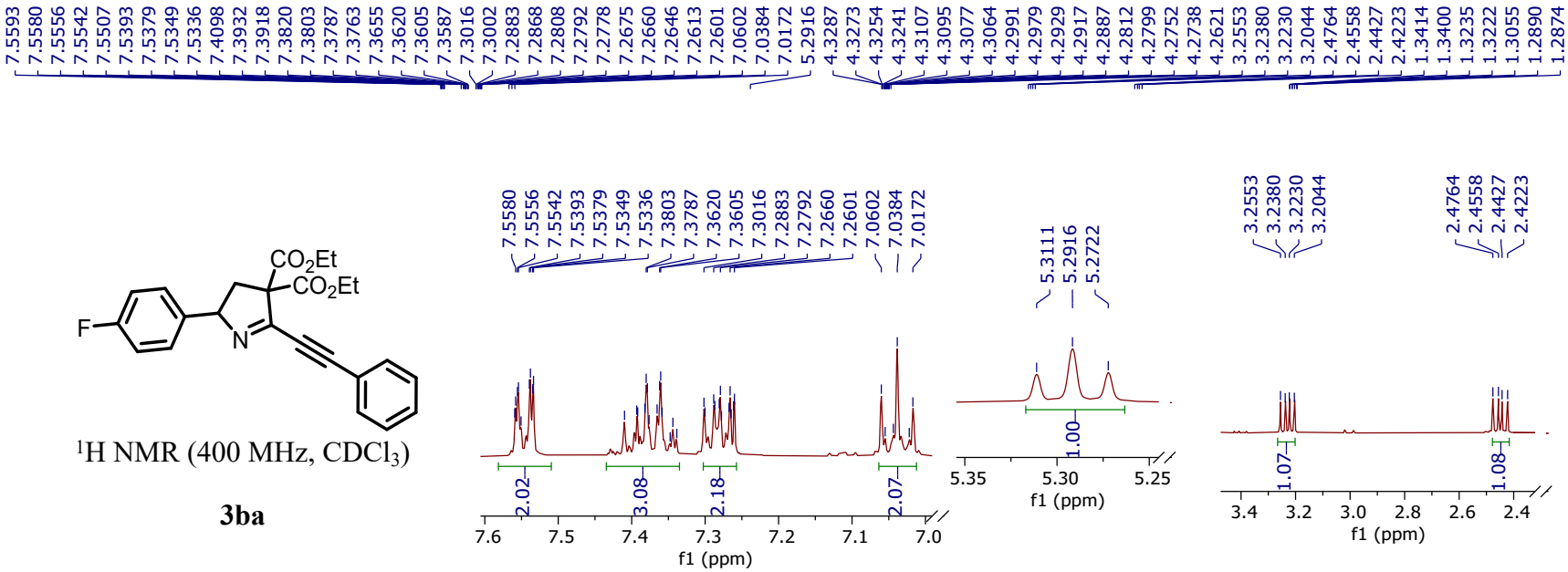






^{13}C NMR (101 MHz, $CDCl_3$)

3aa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7.2660
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4.3241
4.3107
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3.2380
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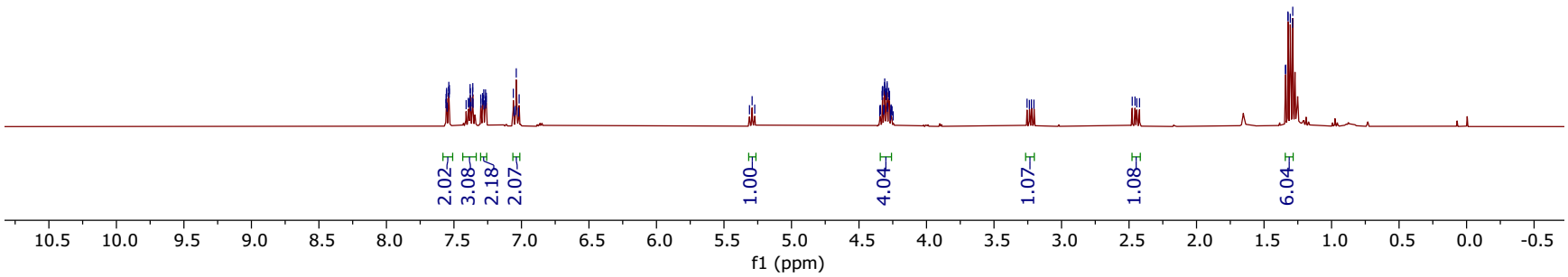
1.2890
1.2874
CO2Et
CO2Et
F
N
1H NMR (400 MHz, CDCl3)
3ba
2.02
3.08
2.18
2.07
1.00
1.07
1.08
f1 (ppm)


2.02
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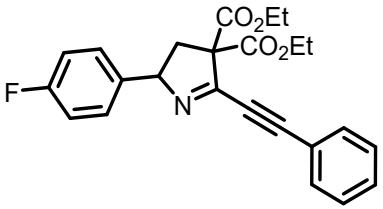
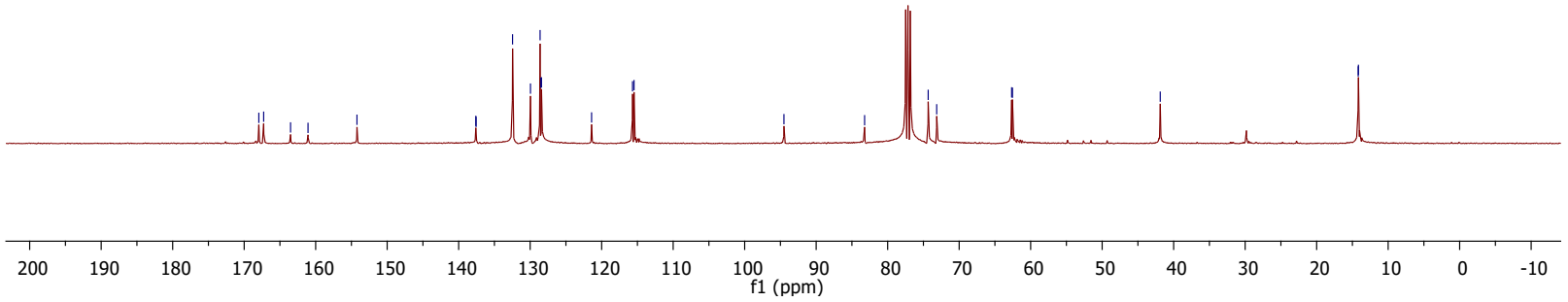
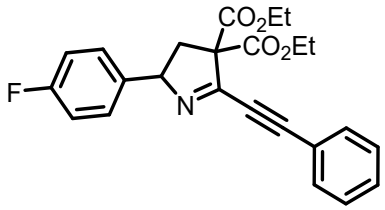
4.04
1.07
1.08
6.04
f1 (ppm)



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

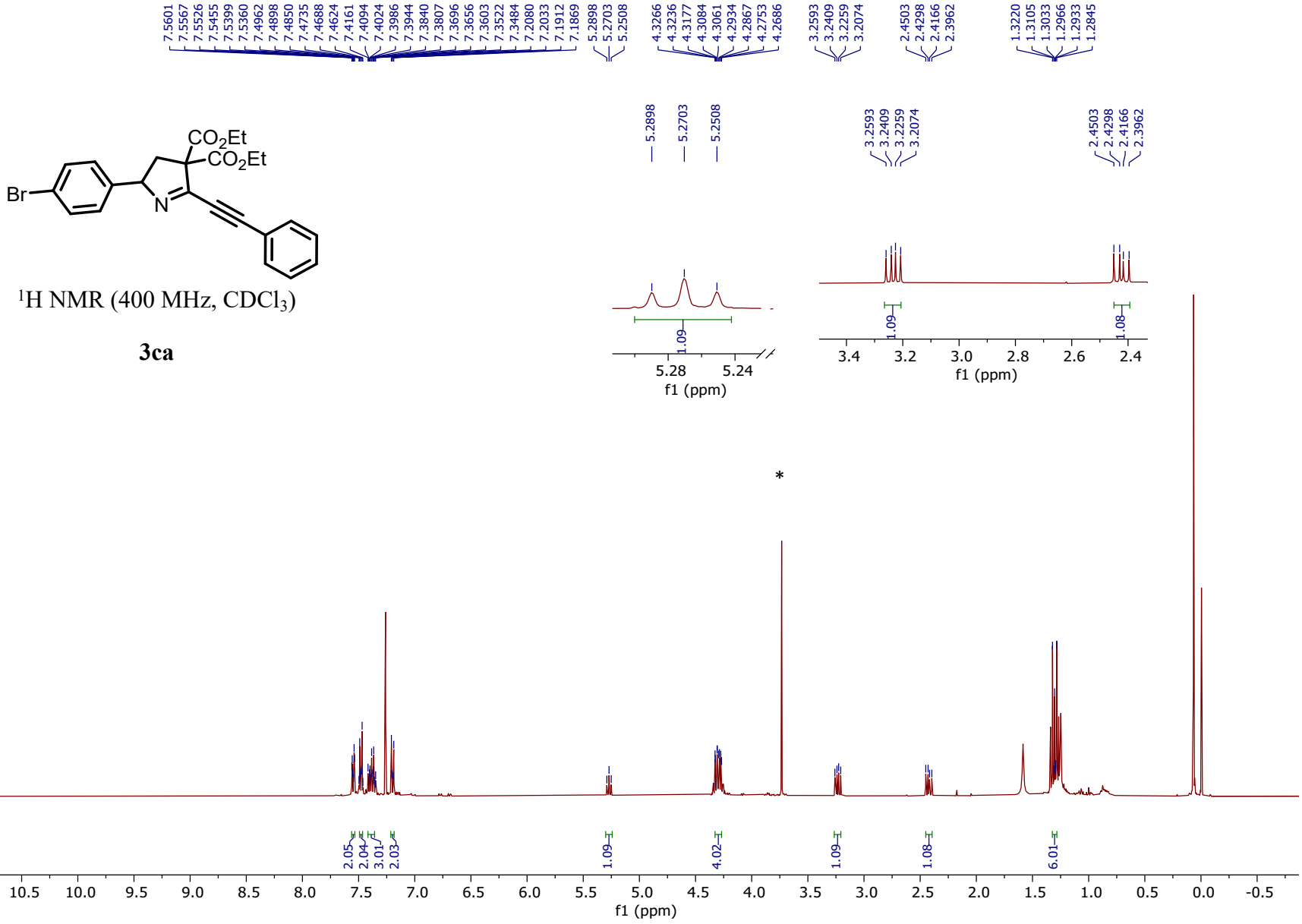
3ba





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

3ba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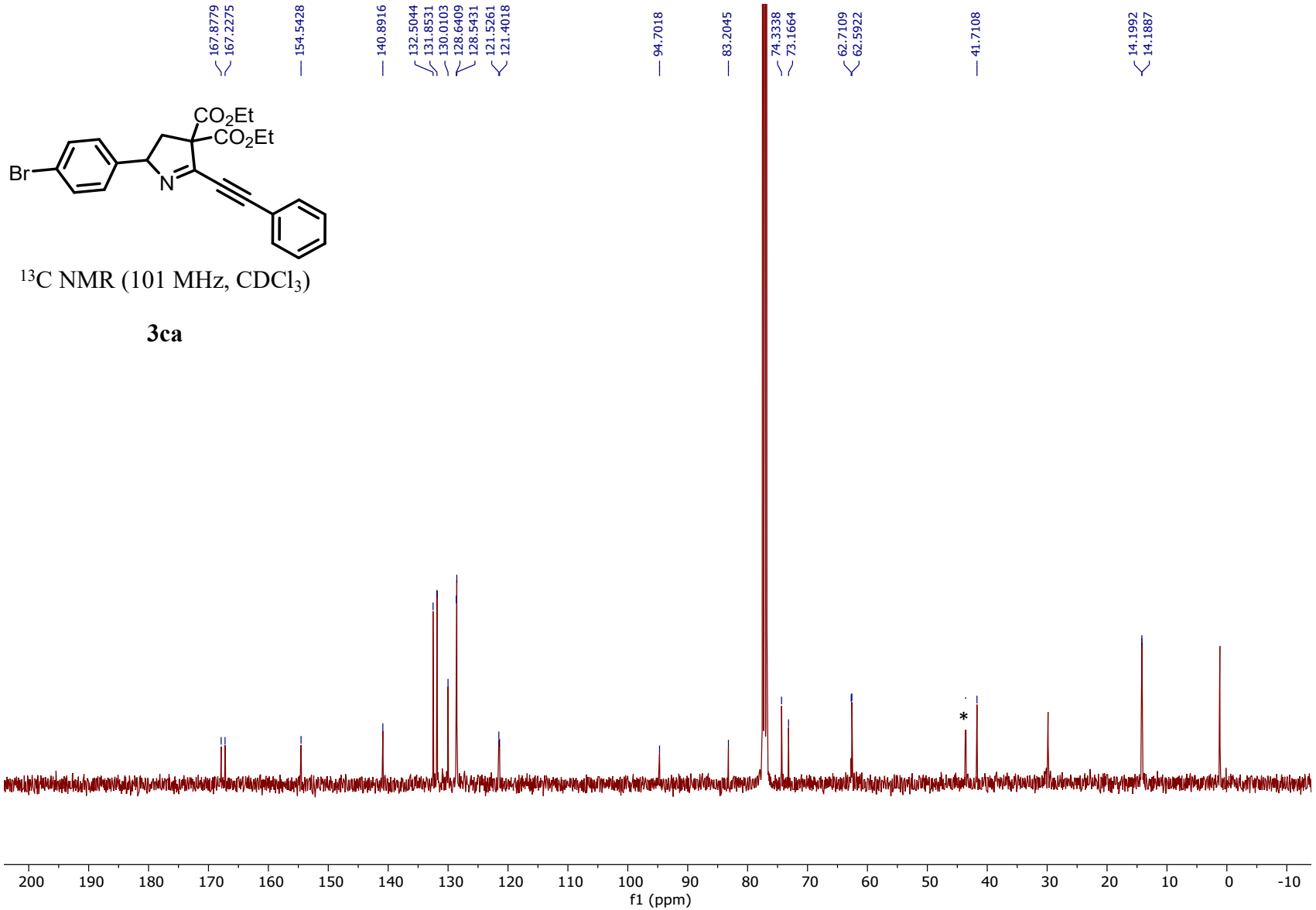
7.5567
7.5526
7.5455
7.5399
7.5360
7.4962
7.4898
7.4850
7.4735
7.4688
7.4624
7.4161
7.4094
7.4024
7.3986
7.3944
7.3840
7.3807
7.3696
7.3656
7.3603
7.3522
7.3484
7.2080
7.2033
7.1912
7.1869
5.2898
5.2703
5.2508
4.3266
4.3236
4.3177
4.3084
4.3061
4.2934
4.2867
4.2753
4.2686
3.2593
3.2409
3.2259
3.2074
2.4503
2.4298
2.4166
2.3962
1.3220
1.3105
1.3033
1.2966
1.2933
1.2845
CO2Et
CO2Et
Br
N
1H NMR (400 MHz, CDCl3)
3ca
1.09
1.09
1.08
f1 (ppm)
*
2.05
2.04
3.01
2.03
1.09
4.02
1.09
1.08
6.01
f1 (ppm)

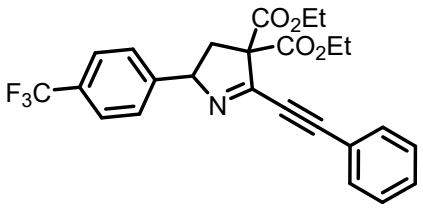
Note: * = 1,2-DCE



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

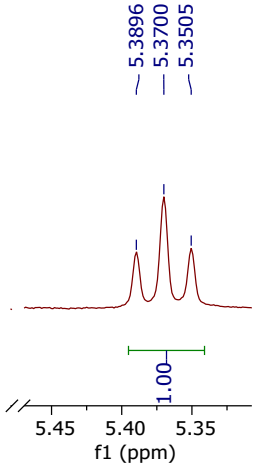
3ca

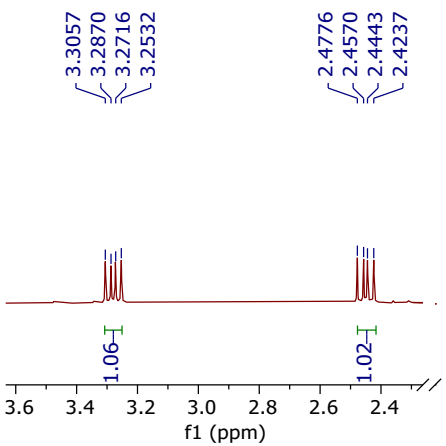
Note: * = 1,2-DCE

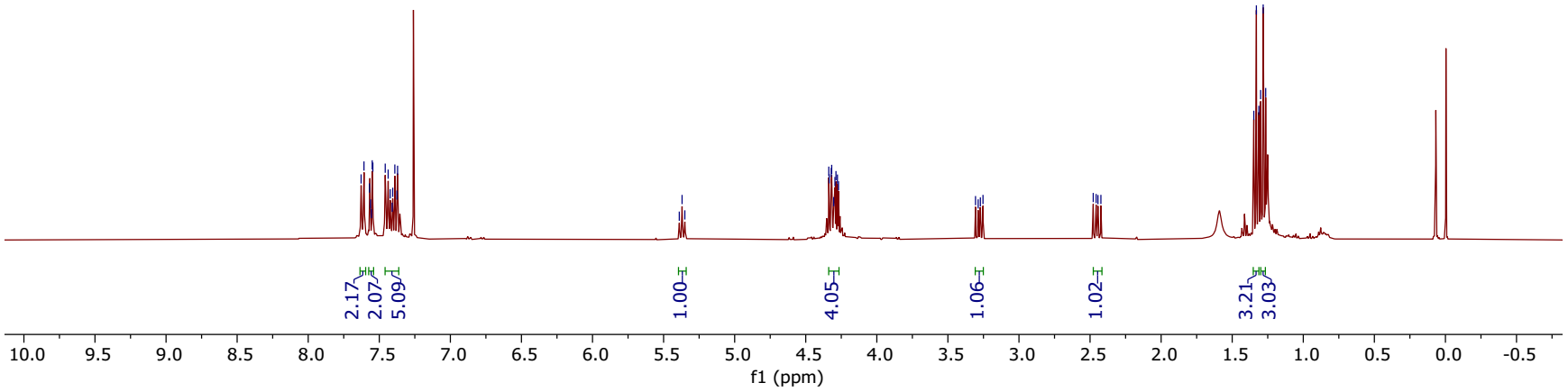


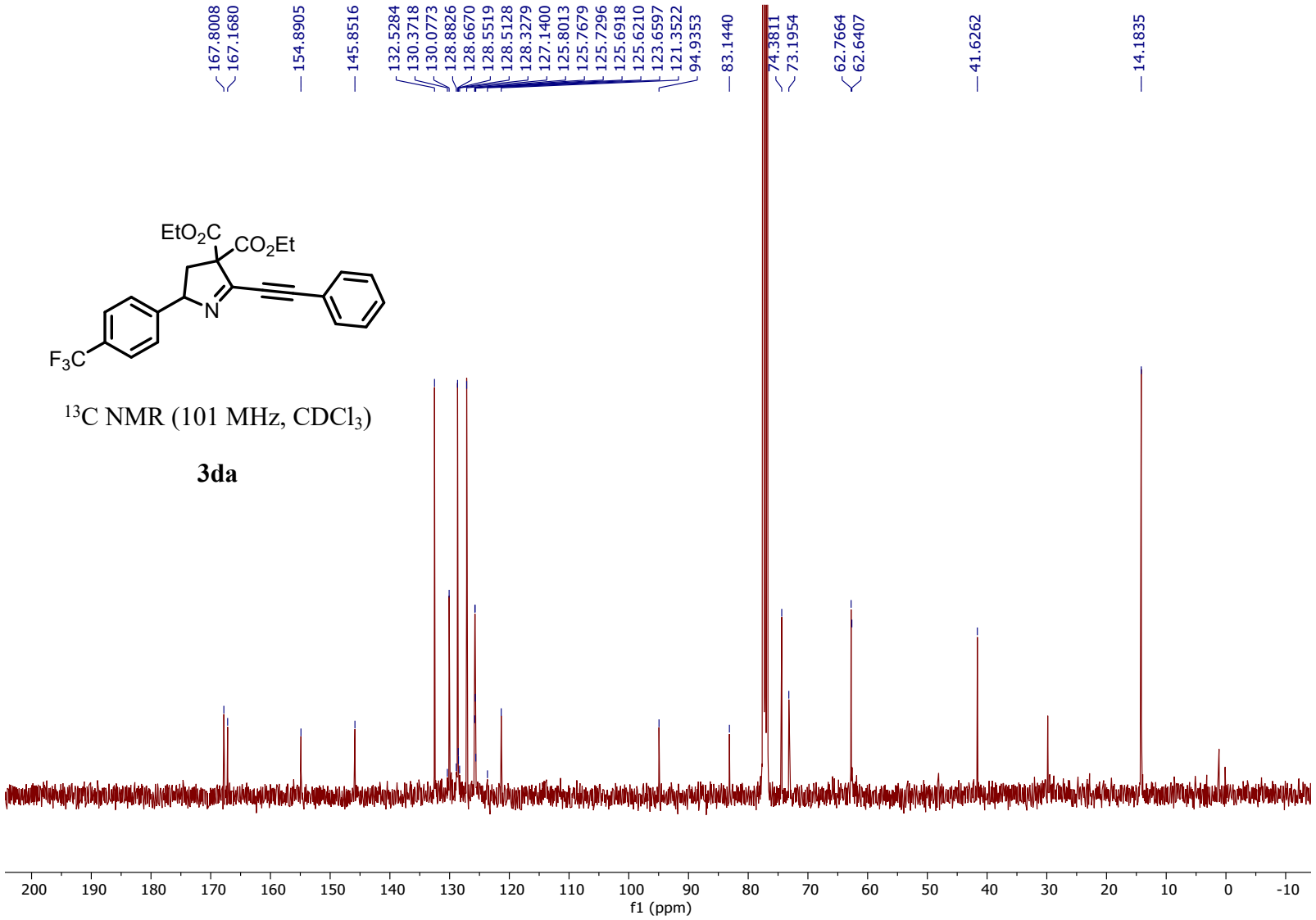
^{1}H NMR (400 MHz, $CDCl_3$)

3da



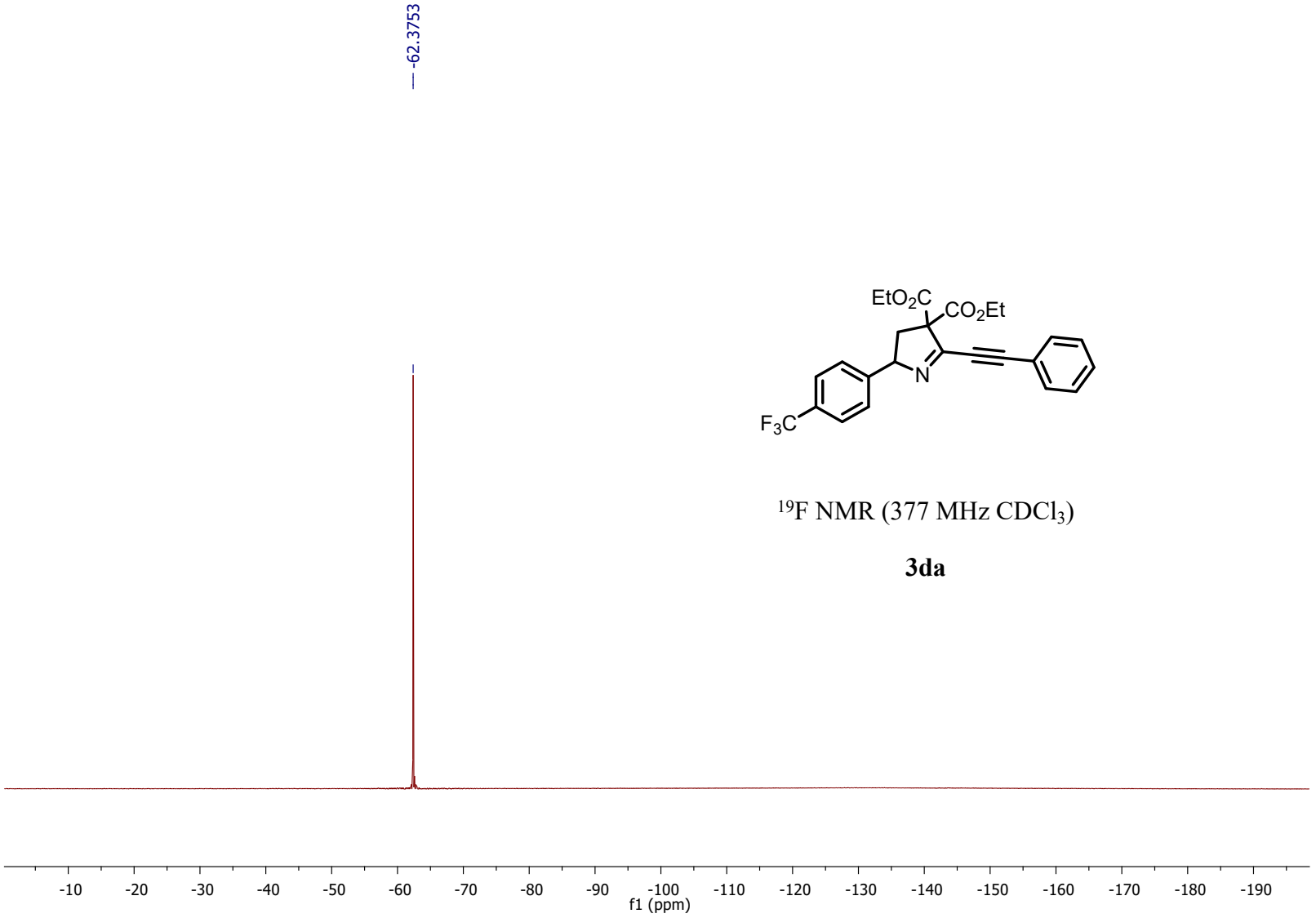






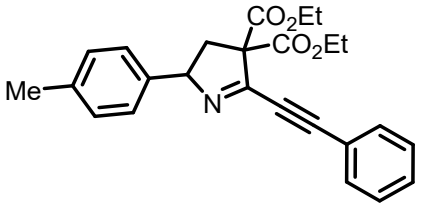
^{13}C NMR (101 MHz, $CDCl_3$)

3da



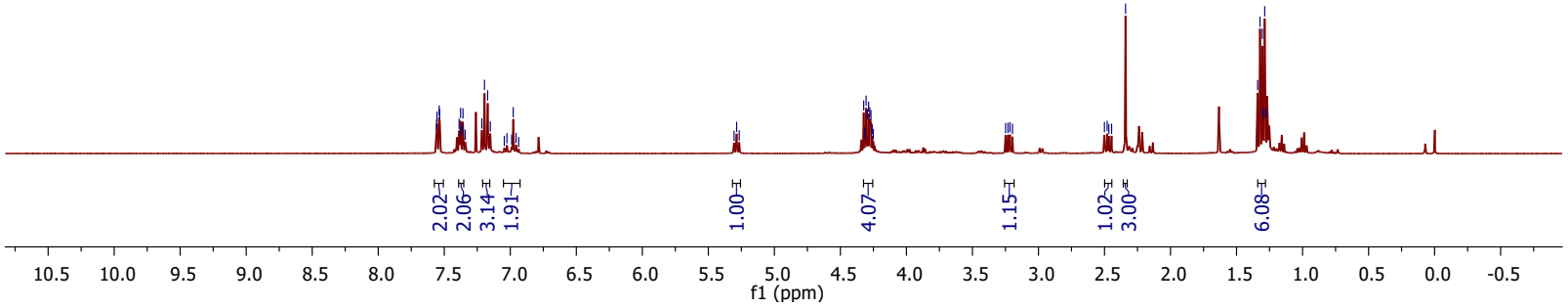
^{19}F NMR (377 MHz $CDCl_3$)

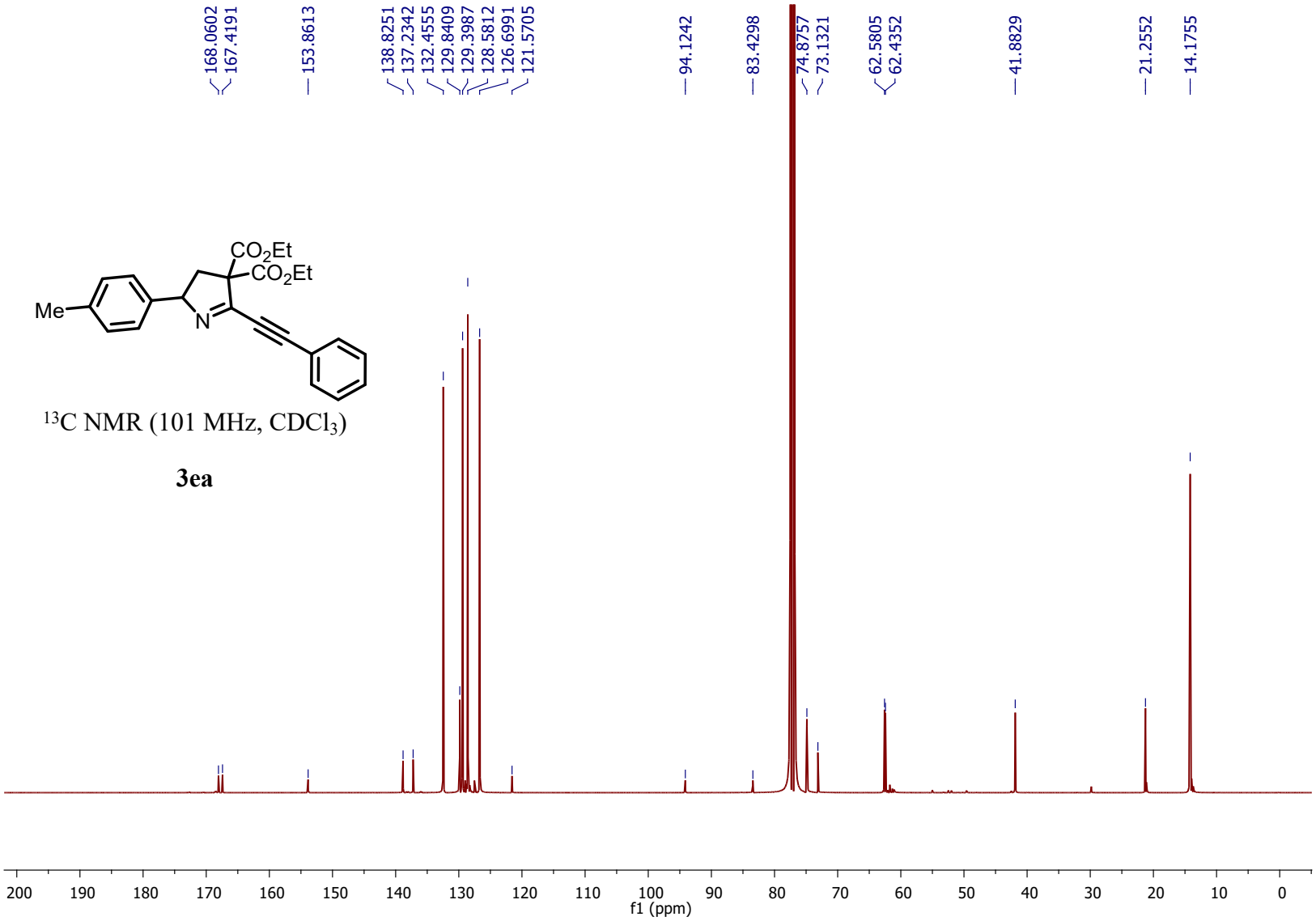
3da



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

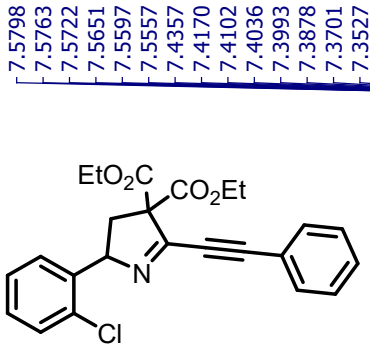
3ea





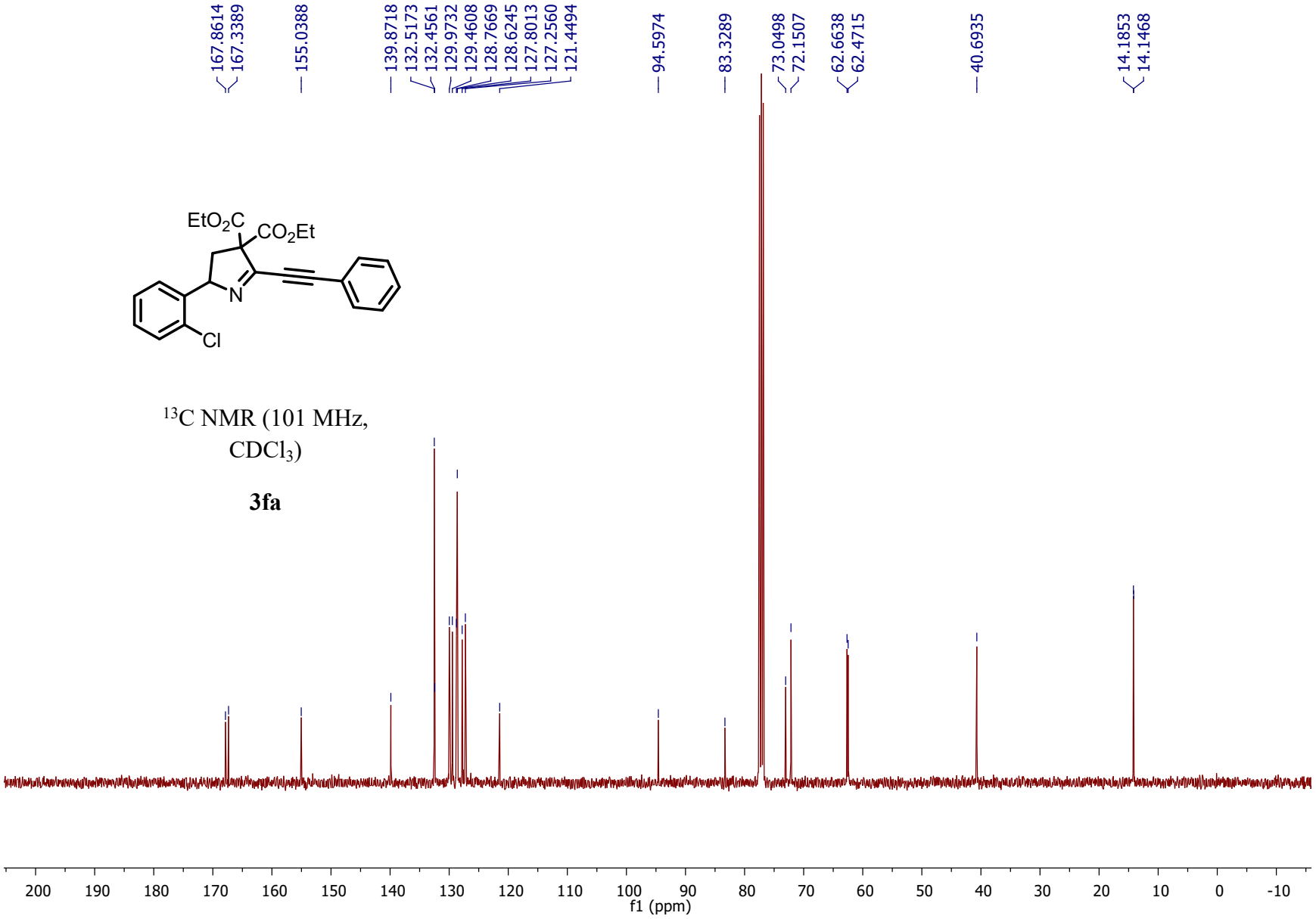
^{13}C NMR (101 MHz, $CDCl_3$)

3ea



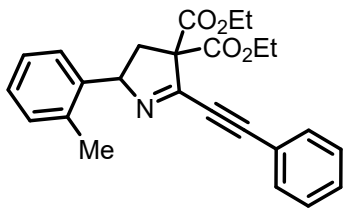
^{1}H NMR (400 MHz, $CDCl_3$)

3fa



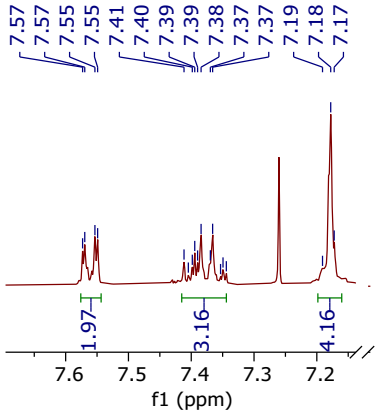
^{13}C NMR (101 MHz, $CDCl_3$)

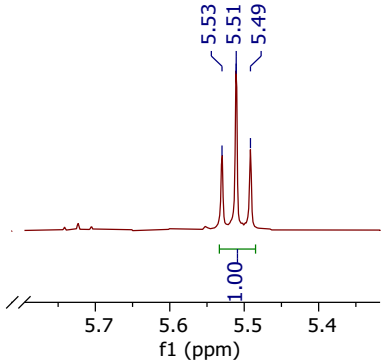
3fa

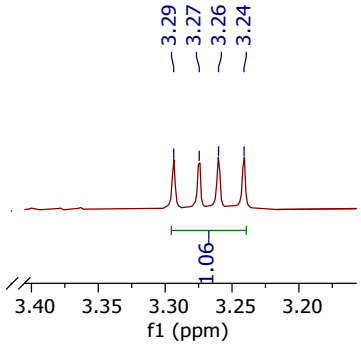


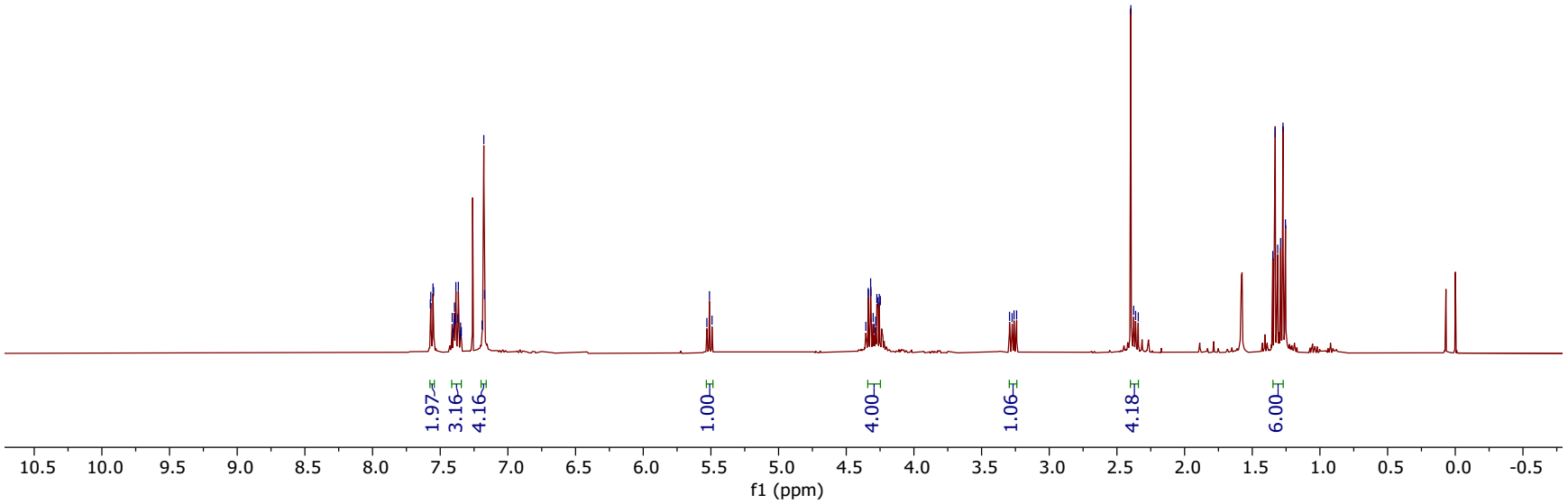
^{1}H NMR (400 MHz, $CDCl_3$)

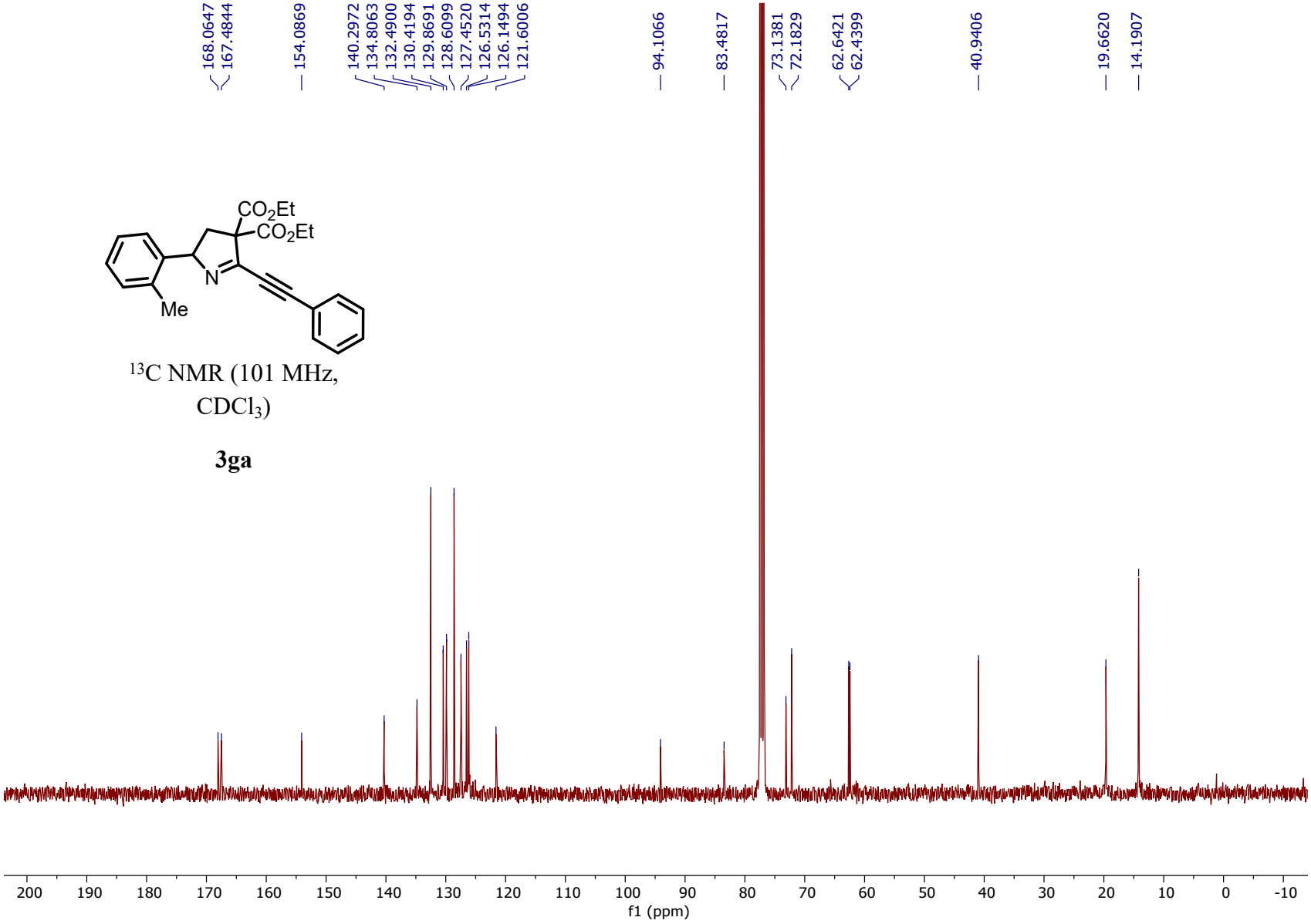
3ga





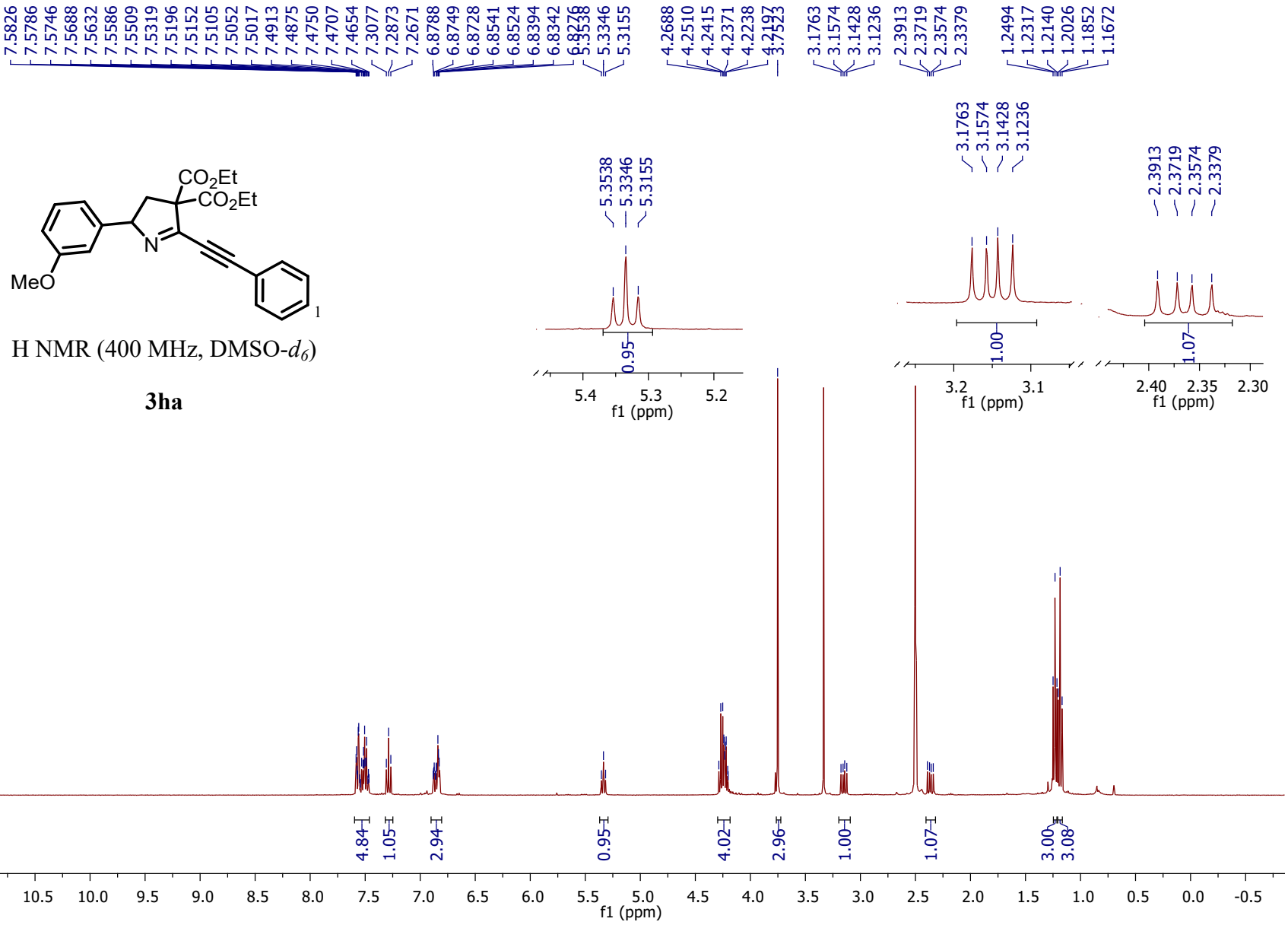






^{13}C NMR (101 MHz, $CDCl_3$)

3ga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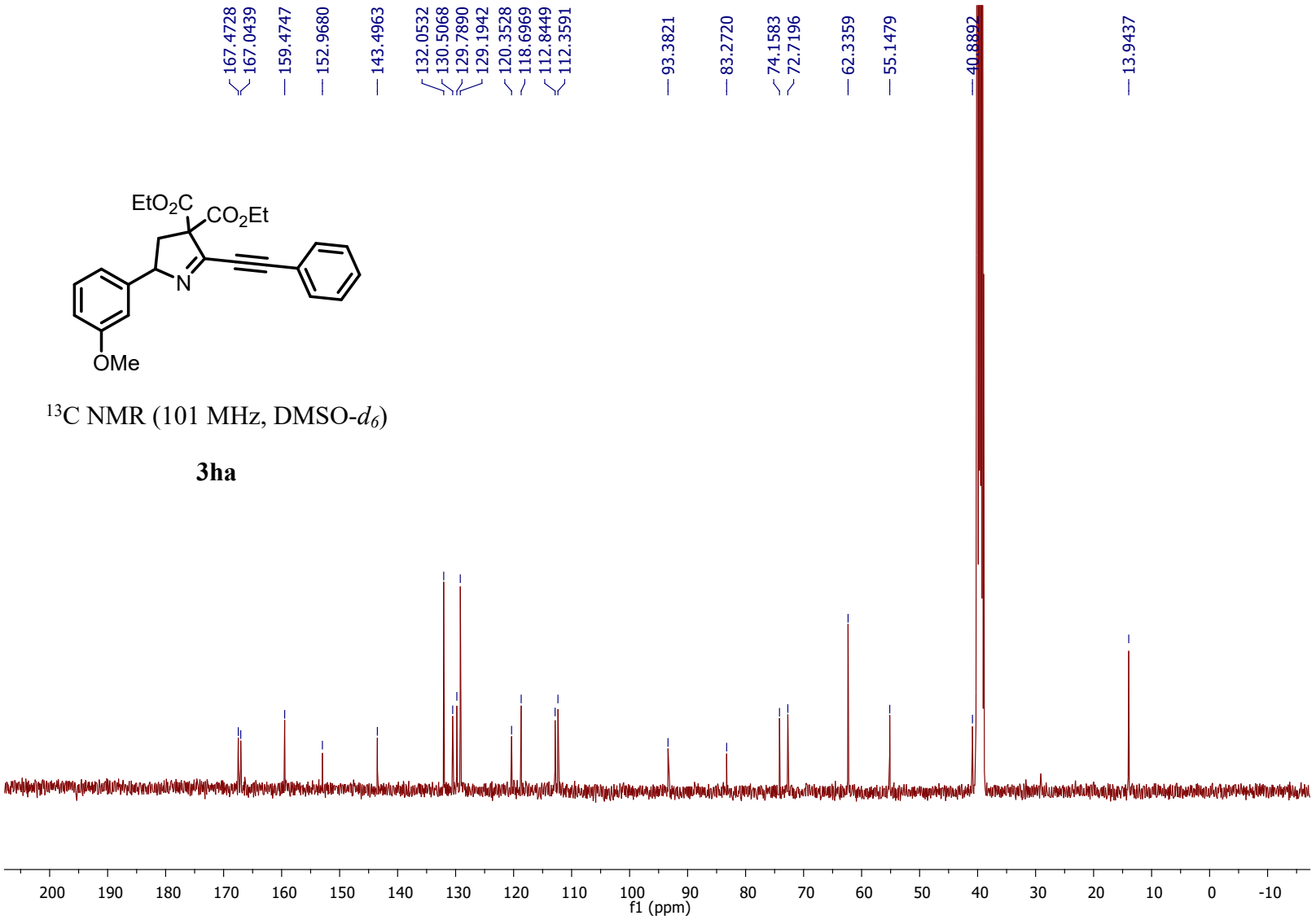
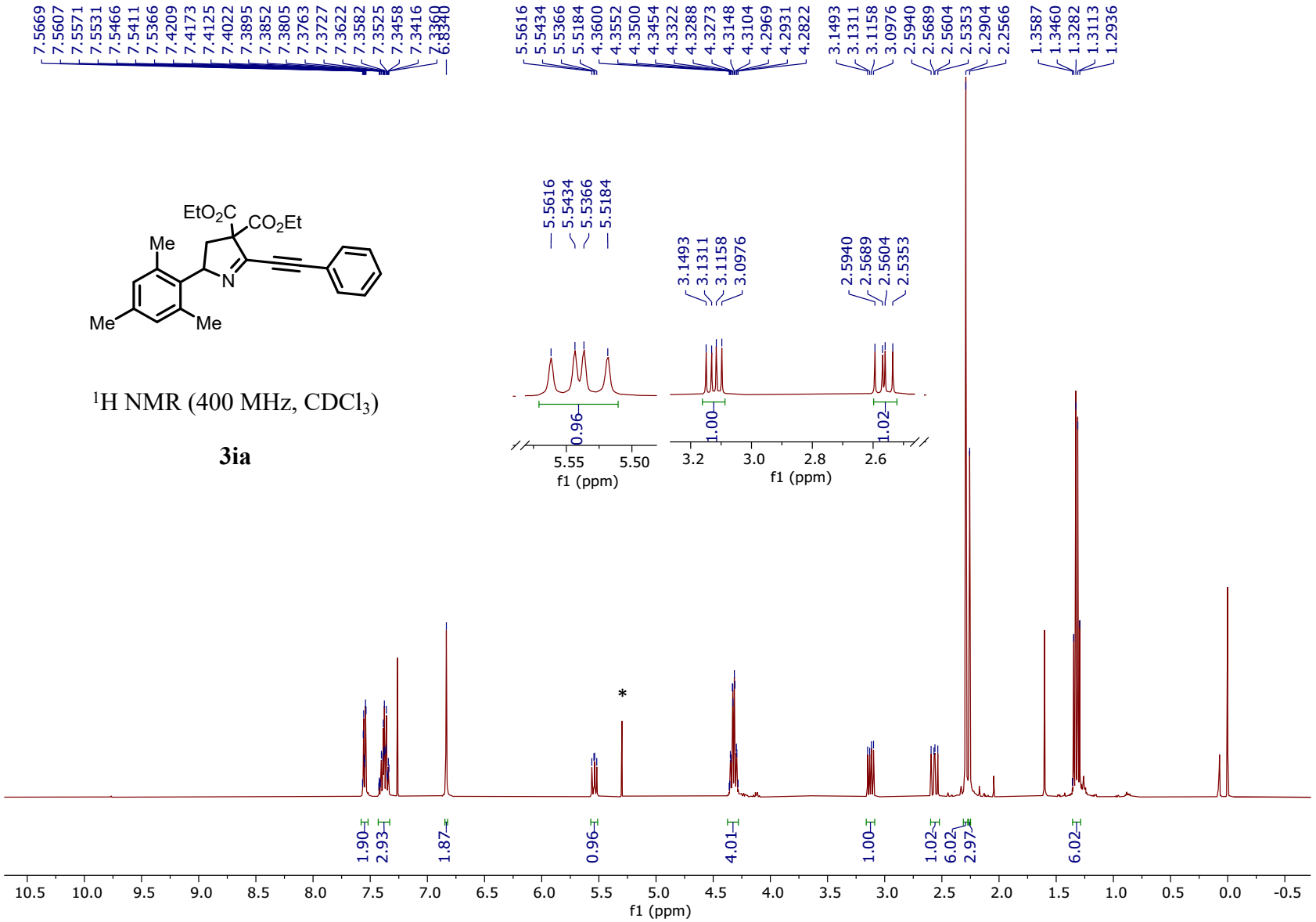
7.5786
7.5746
7.5688
7.5632
7.5586
7.5509
7.5319
7.5196
7.5152
7.5105
7.5052
7.5017
7.4913
7.4875
7.4750
7.4707
7.4654
7.3077
7.2873
7.2671
6.8788
6.8749
6.8728
6.8541
6.8524
6.8394
6.8342
5.3538
5.3346
5.3155
4.2688
4.2510
4.2415
4.2371
4.2238
3.1763
3.1574
3.1428
3.1236
2.3913
2.3719
2.3574
2.3379
1.2494
1.2317
1.2140
1.2026
1.1852
1.1672
CO2Et
CO2Et
N
MeO
1
H NMR (400 MHz, DMSO-d6)
3ha
0.95
1.00
1.07
f1 (ppm)
4.84
1.05
2.94
0.95
4.02
2.96
1.00
1.07
3.00
3.08



^{13}C NMR (101 MHz, DMSO-d_6)

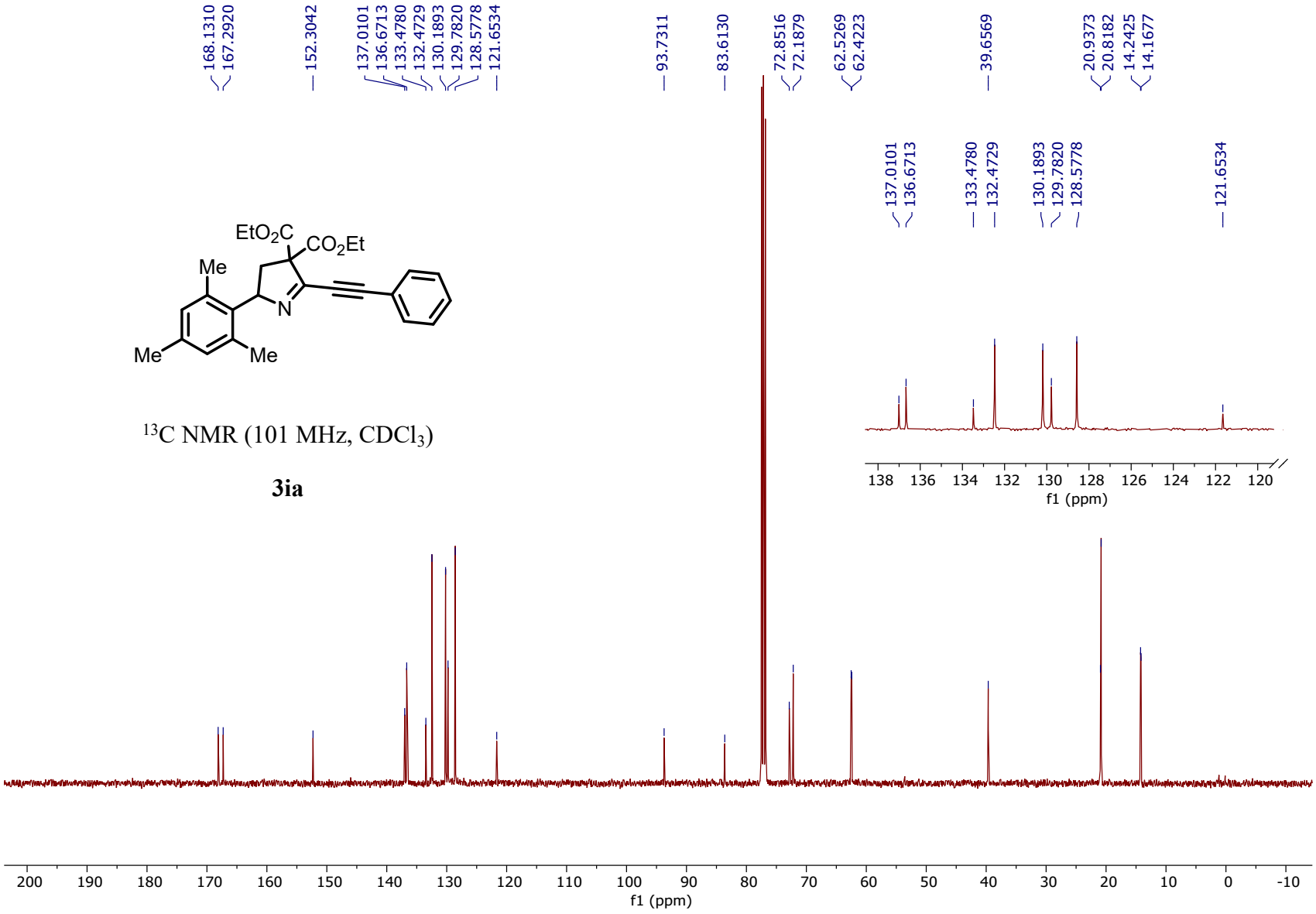
3ha



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

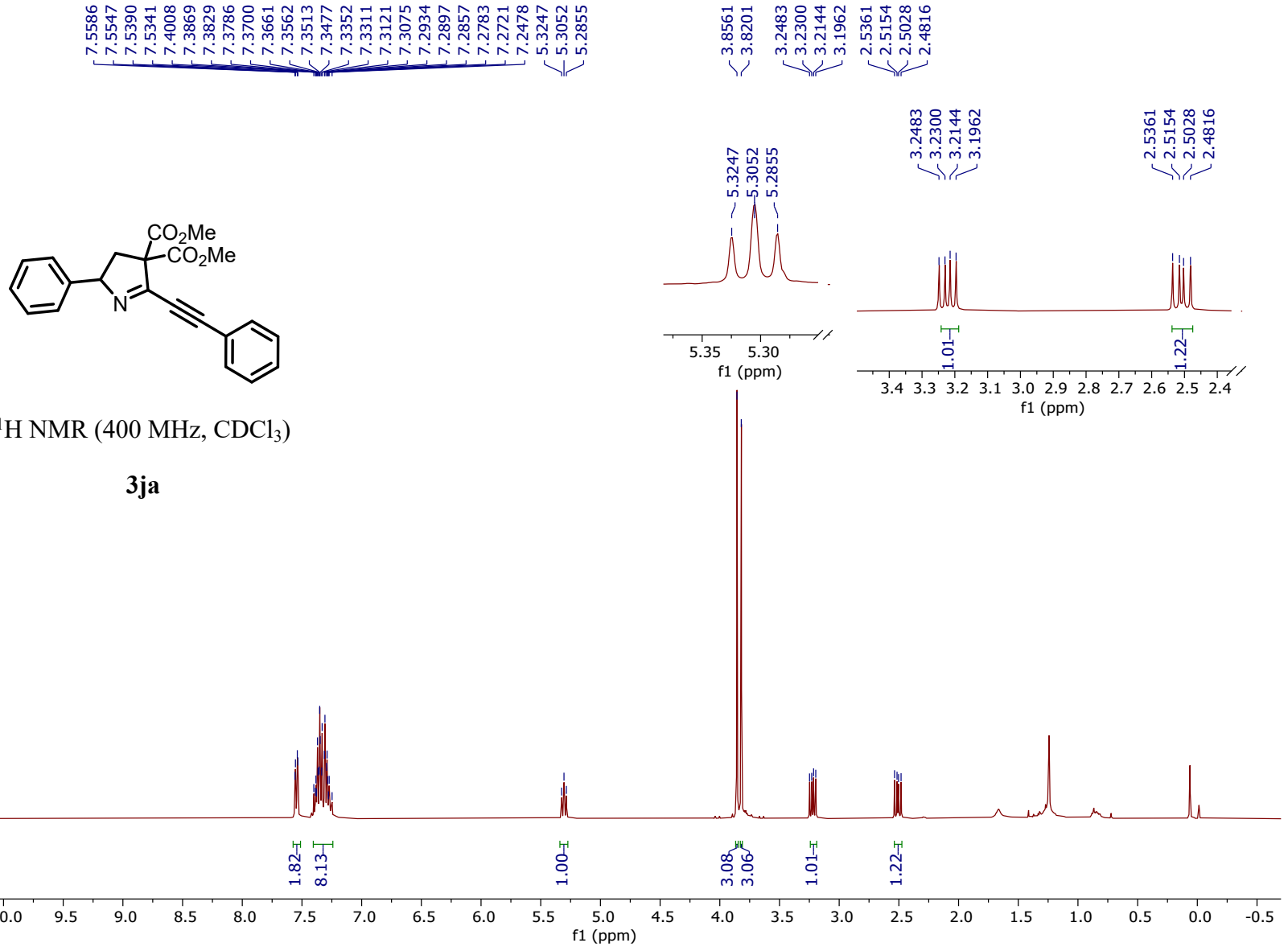
3ia

Note: * = DCM



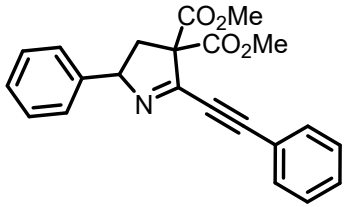
^{13}C NMR (101 MHz, $CDCl_3$)

3ia



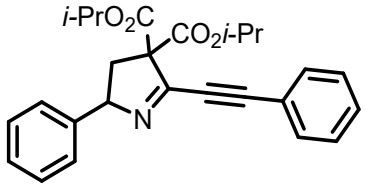
^{1}H NMR (400 MHz, $CDCl_3$)

3ja



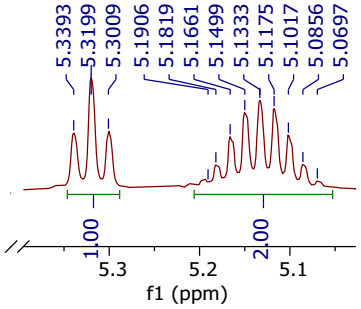
^{13}C NMR (101 MHz, $CDCl_3$)

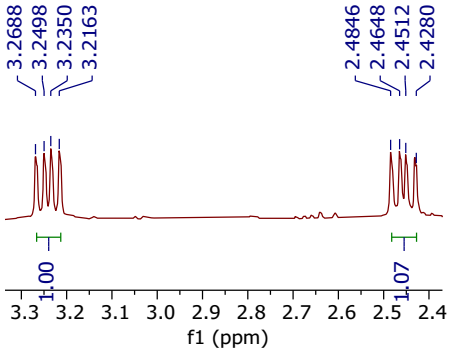
3ja

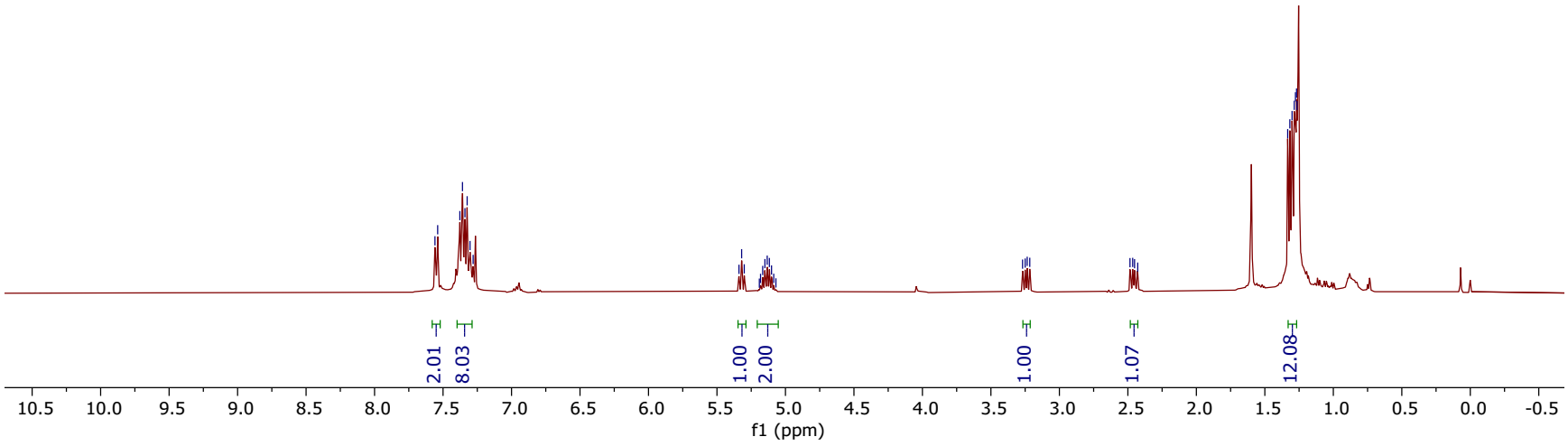


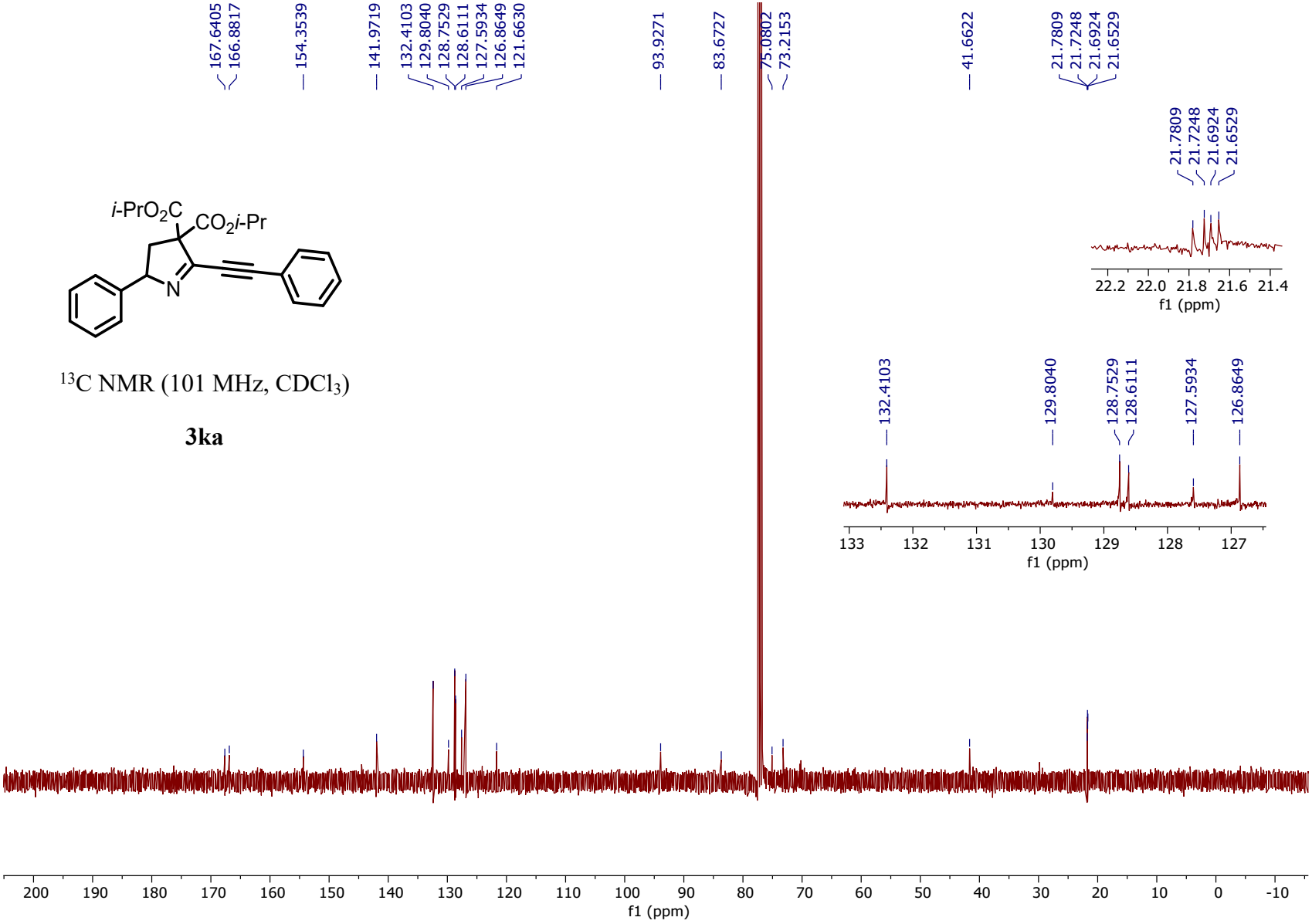
^{1}H NMR (400 MHz, $CDCl_3$)

3ka





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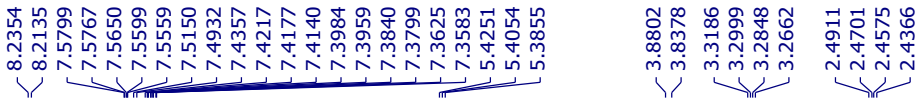
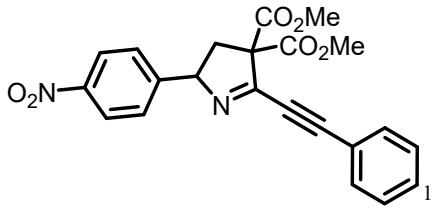
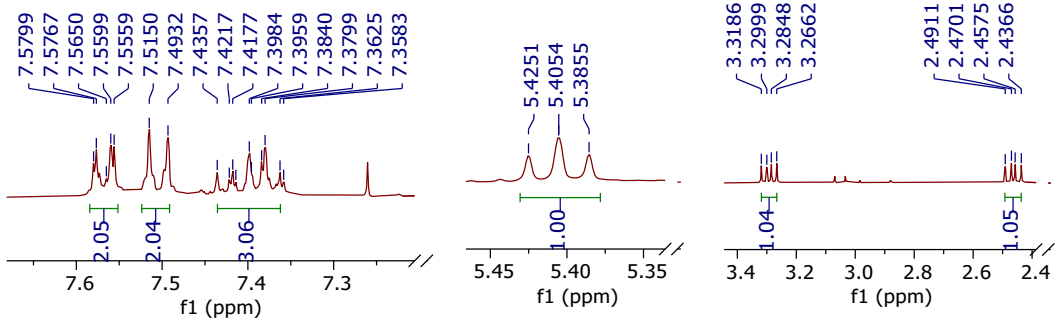
166.8817
154.3539
141.9719
132.4103
129.8040
128.7529
128.6111
127.5934
126.8649
121.6630
93.9271
83.6727
75.0802
73.2153
41.6622
21.7809
21.7248
21.6924
21.6529
i-PrO2C
CO2i-Pr
N
13C NMR (101 MHz, CDCl3)
3ka
f1 (ppm)

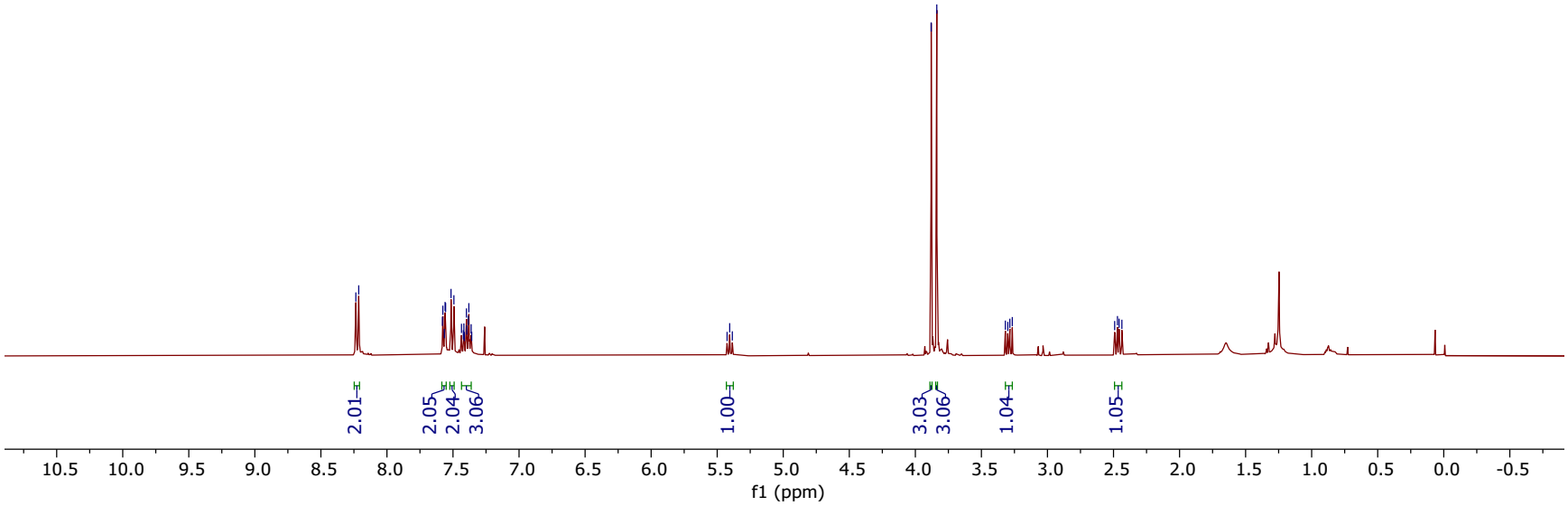


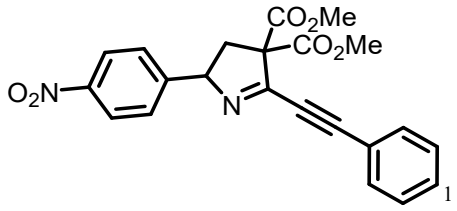


H NMR (400 MHz, $CDCl_3$)

3la

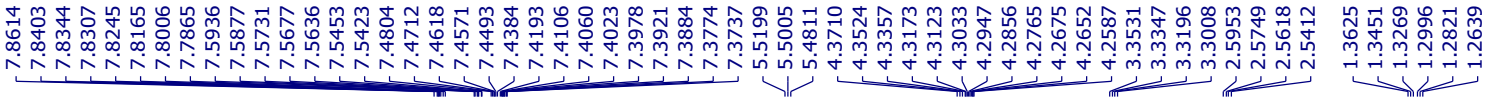


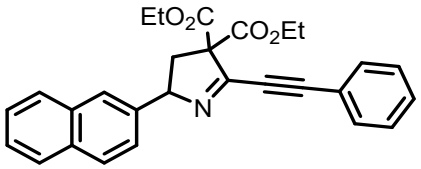




^{3}C NMR (101 MHz, $CDCl_3$)

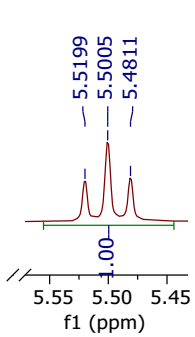
3la

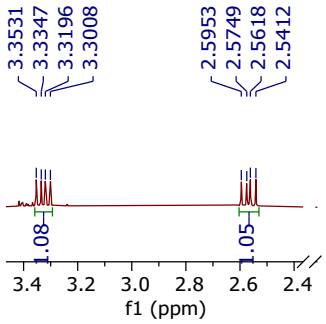


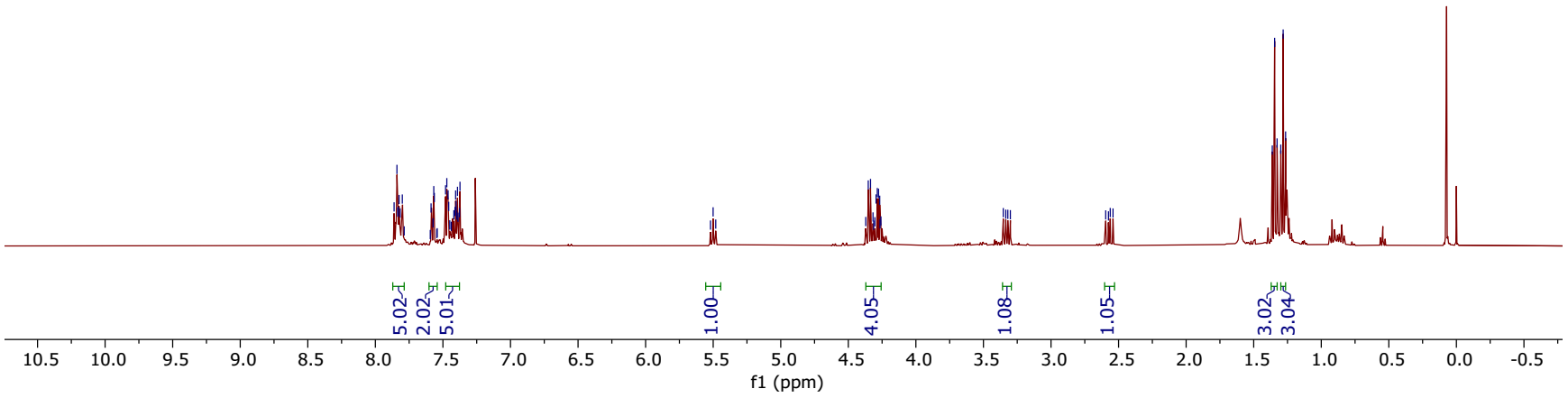


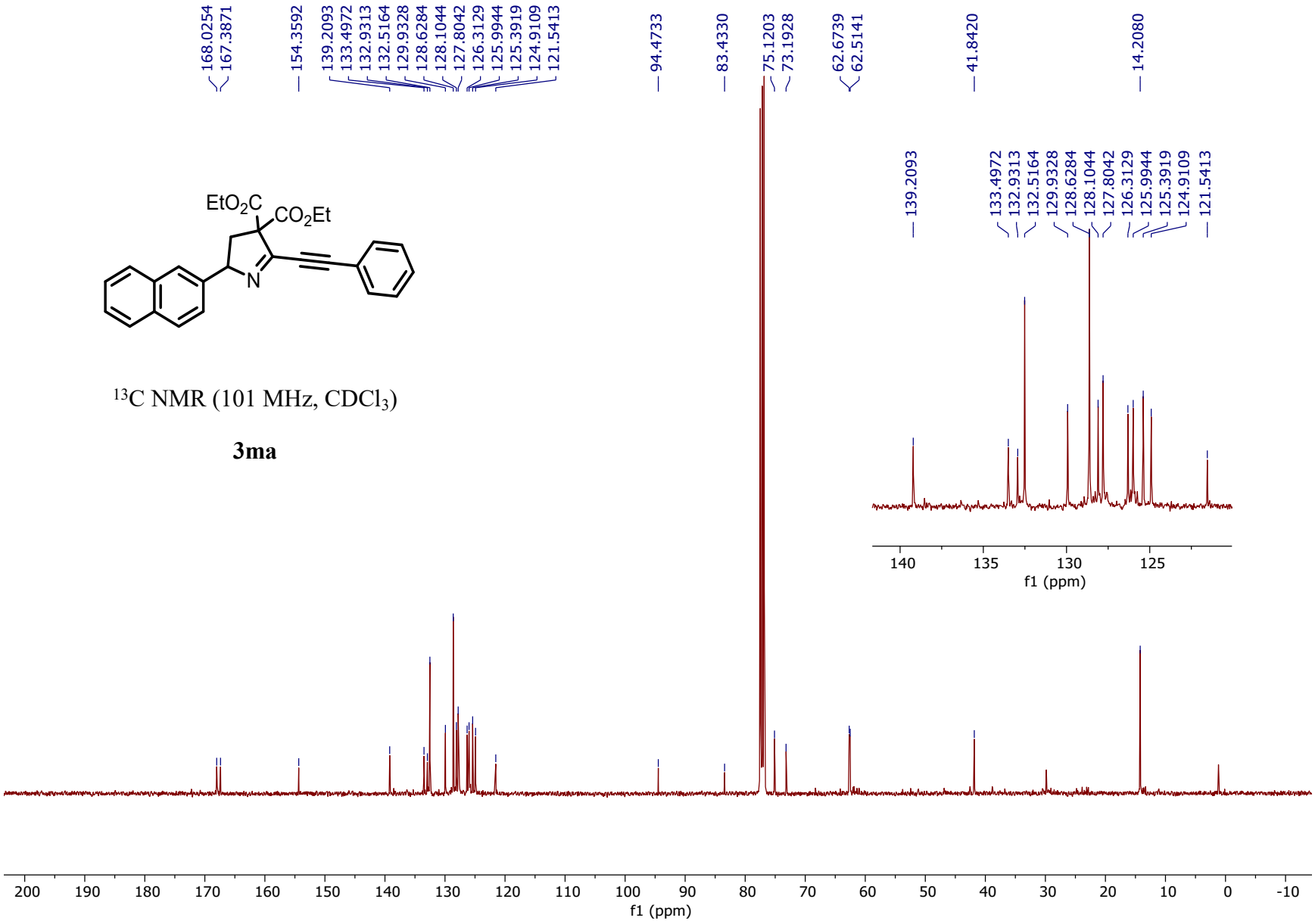
^{1}H NMR (400 MHz, $CDCl_3$)

3ma





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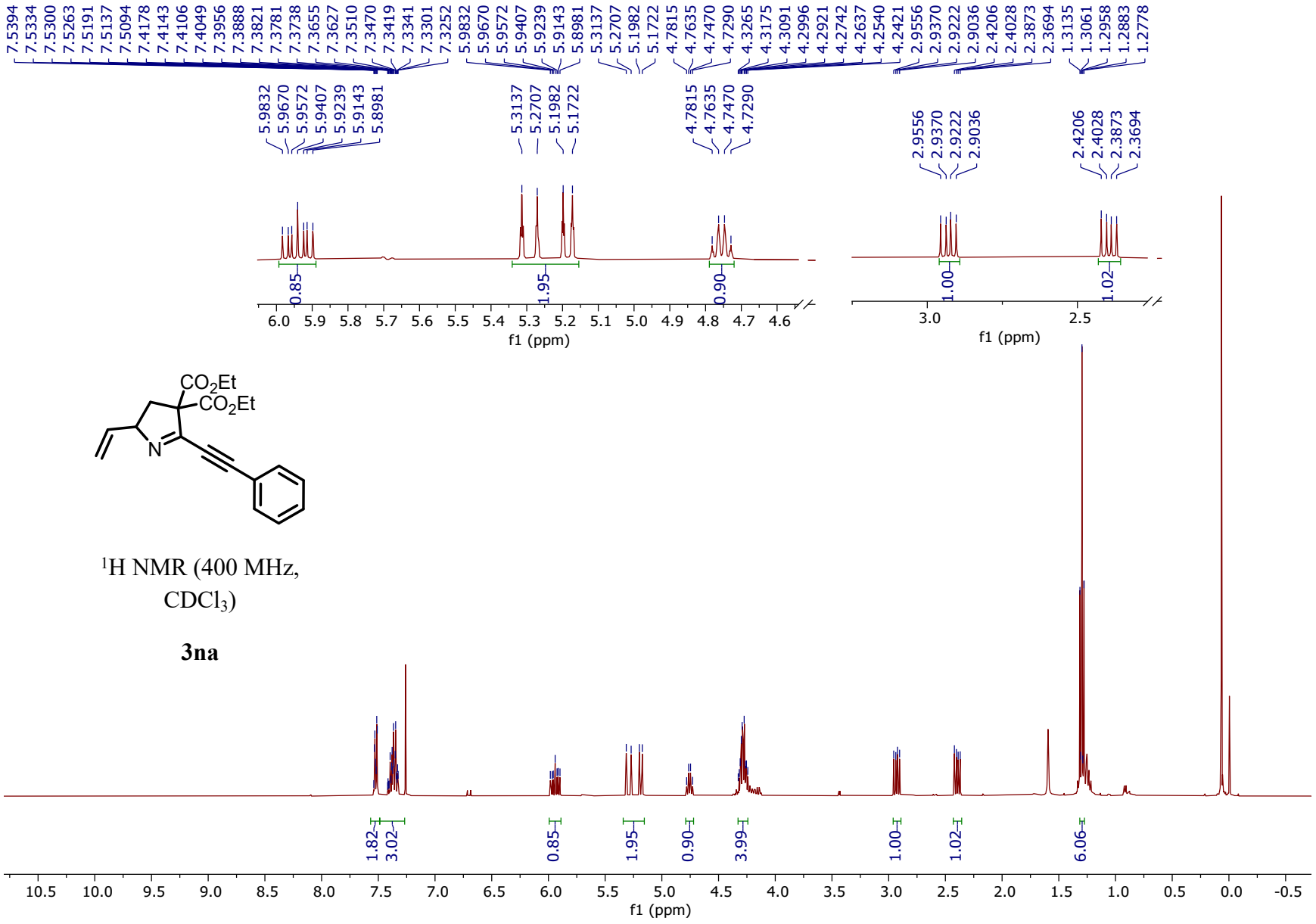
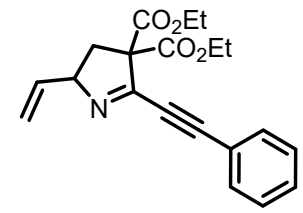
167.3871
154.3592
139.2093
133.4972
132.9313
132.5164
129.9328
128.6284
128.1044
127.8042
126.3129
125.9944
125.3919
124.9109
121.5413
94.4733
83.4330
75.1203
73.1928
62.6739
62.5141
41.8420
14.2080
EtO2C
CO2Et
N
13C NMR (101 MHz, CDCl3)
3ma
f1 (ppm)



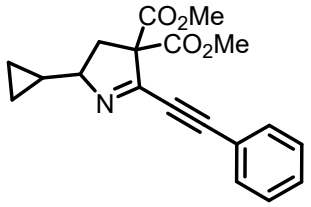
^{1}H NMR (400 MHz, $CDCl_3$)

3na



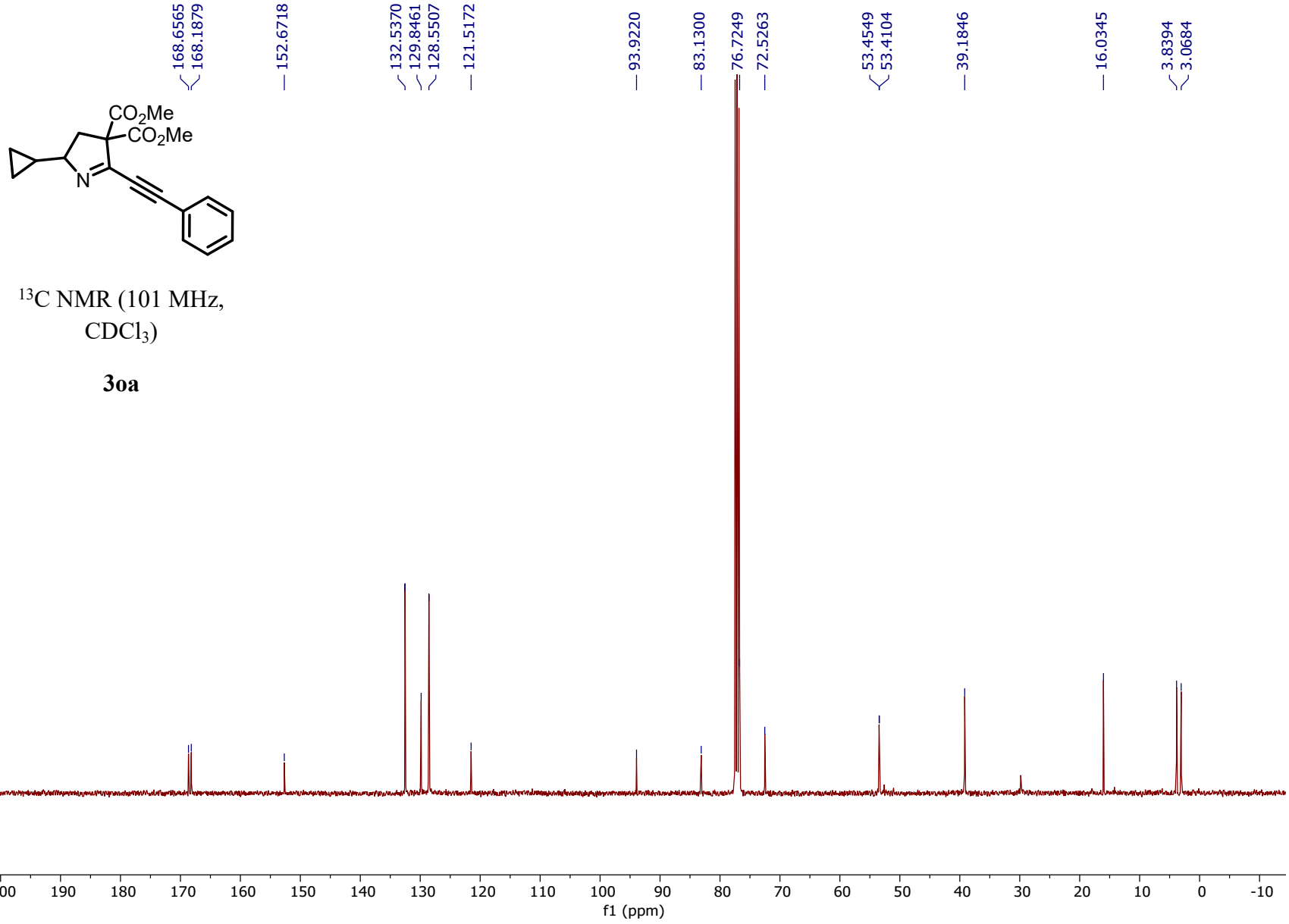
^{13}C NMR (101 MHz, $CDCl_3$)

3na



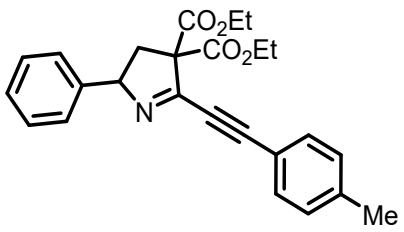
^{1}H NMR (400 MHz, $CDCl_3$)

3oa



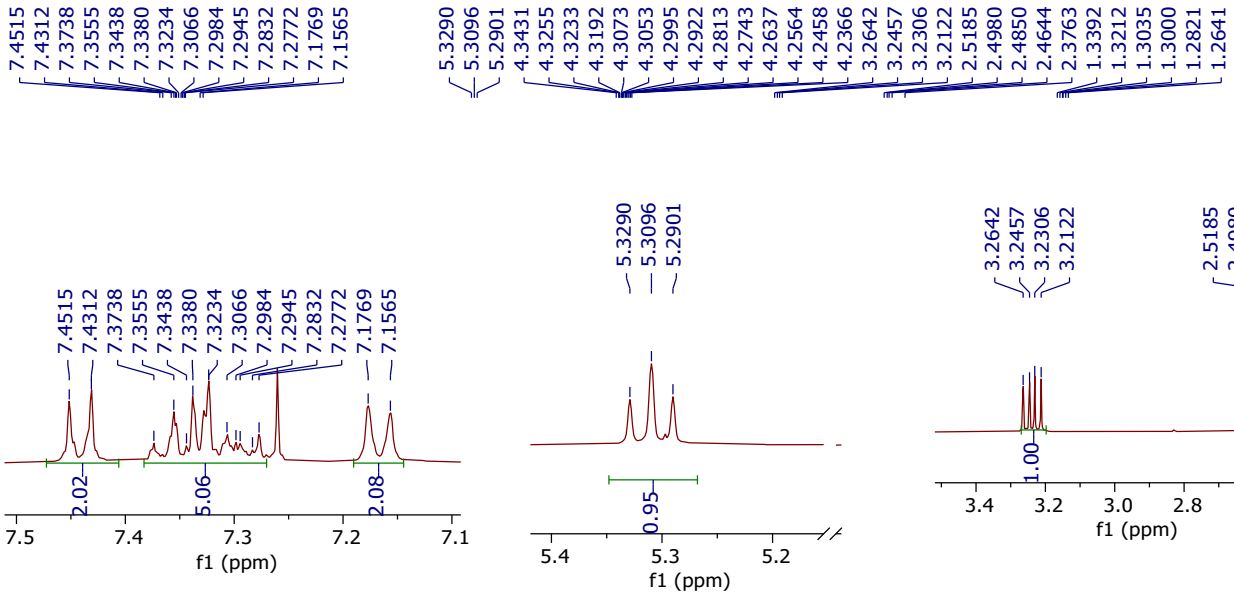
^{13}C NMR (101 MHz, $CDCl_3$)

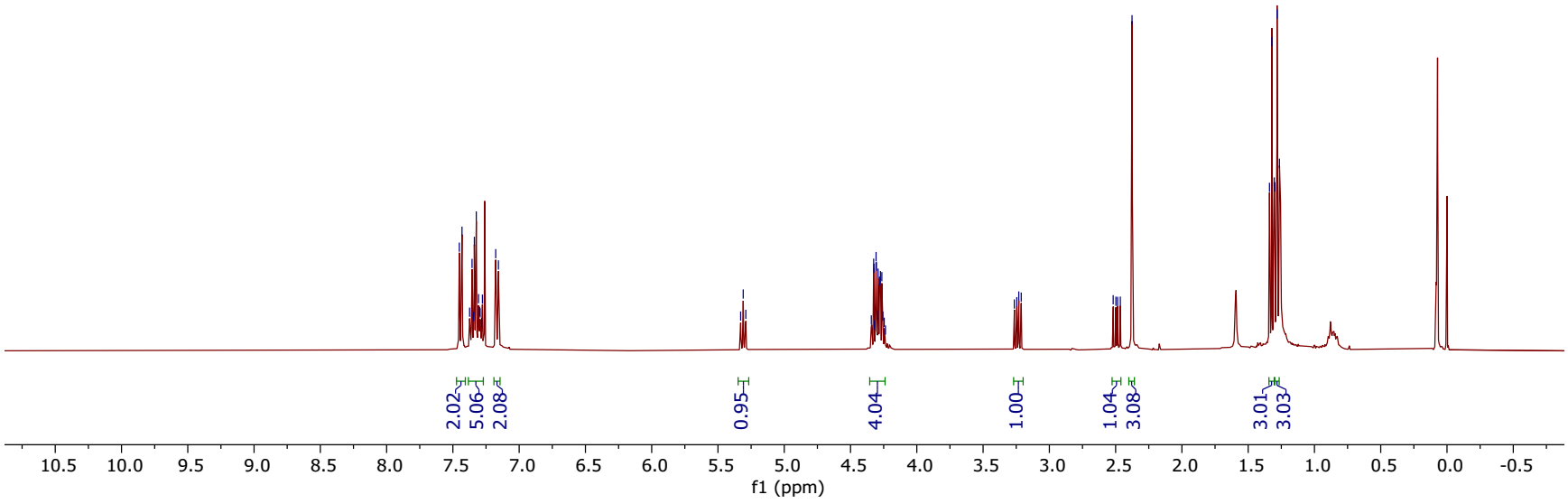
3oa

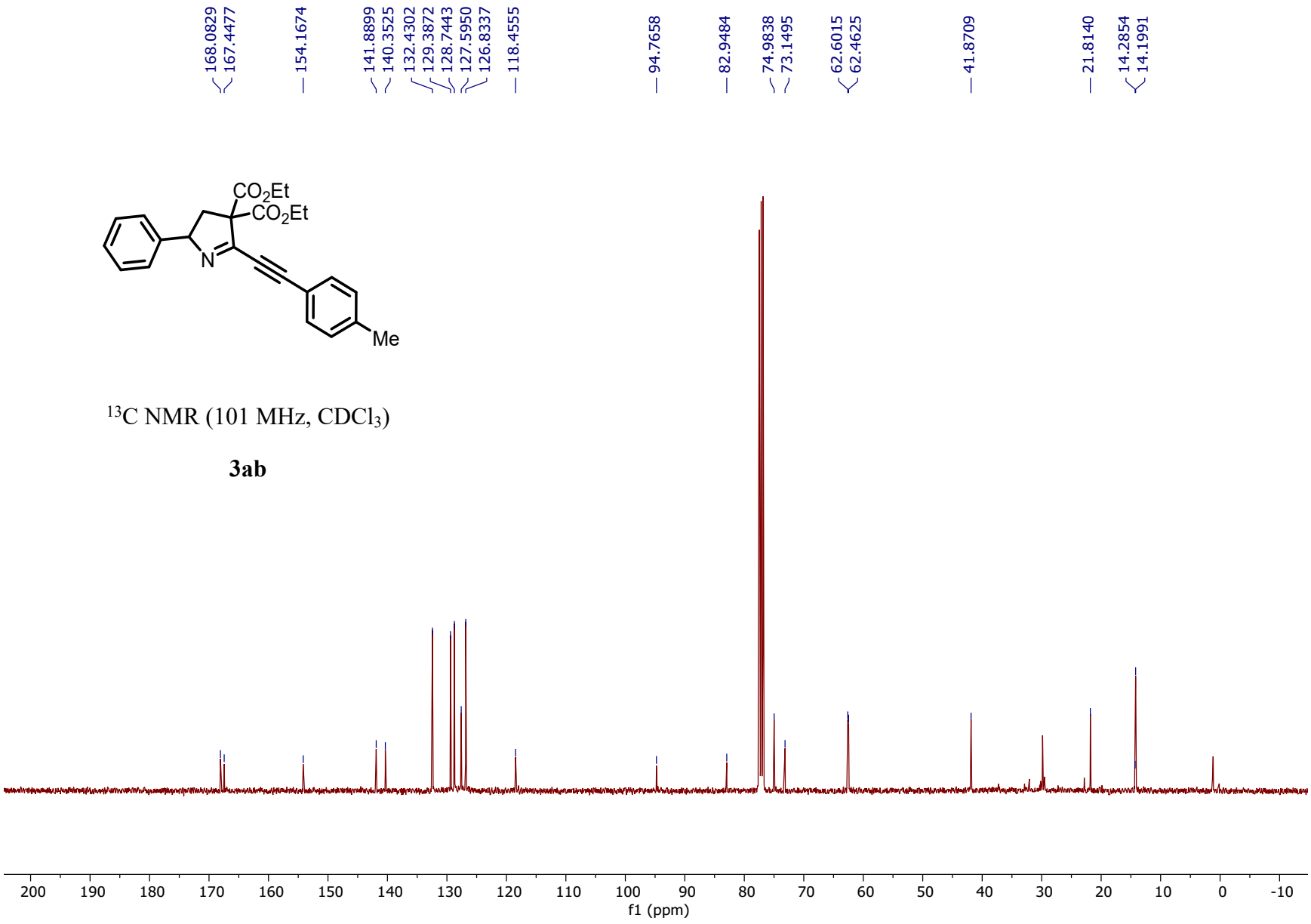


^{1}H NMR (400 MHz, $CDCl_3$)

3ab

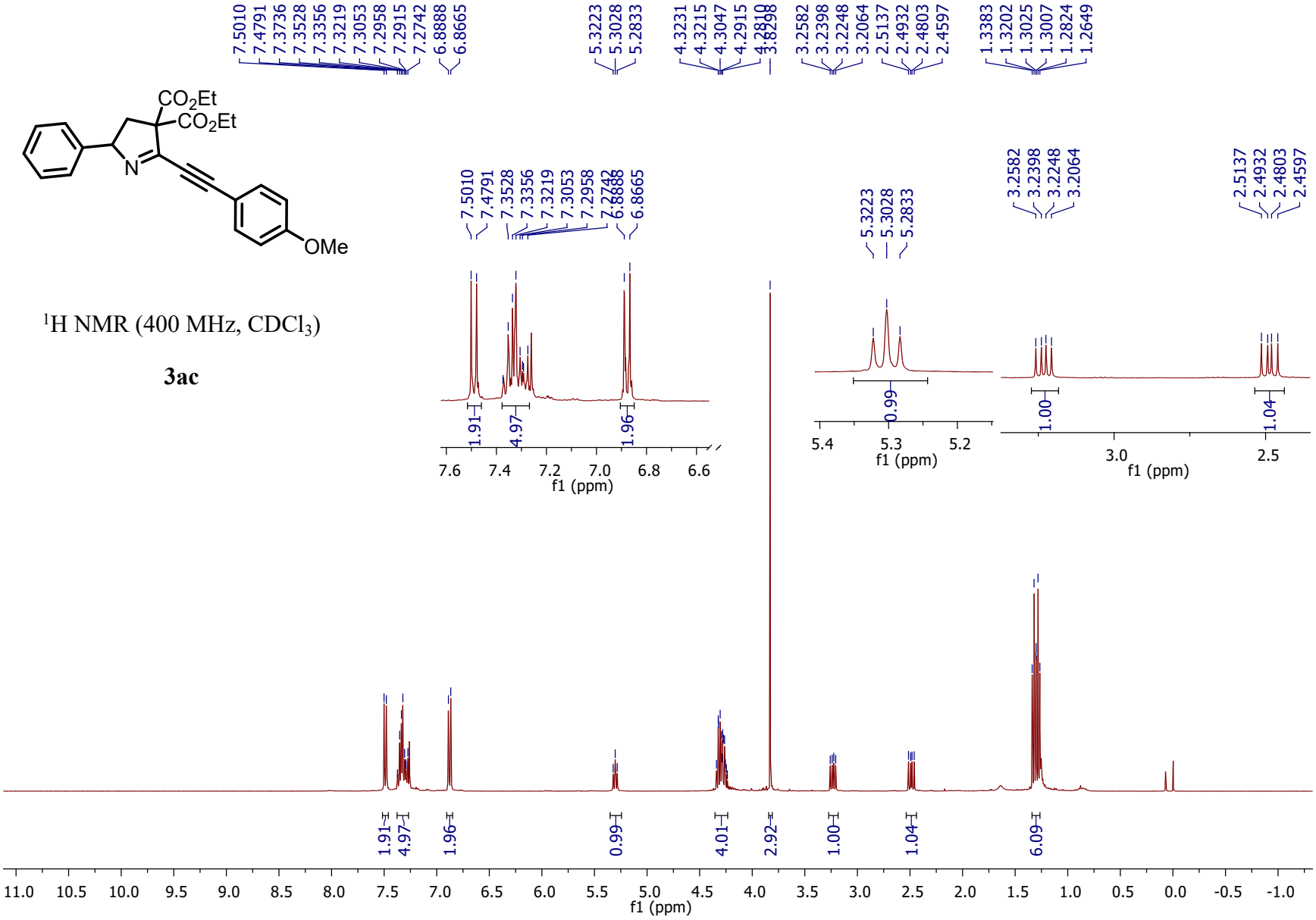






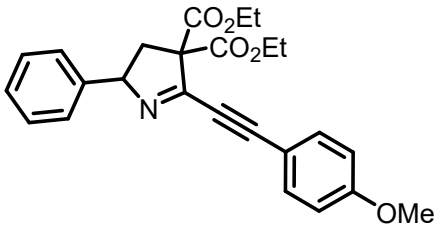
^{13}C NMR (101 MHz, $CDCl_3$)

3ab



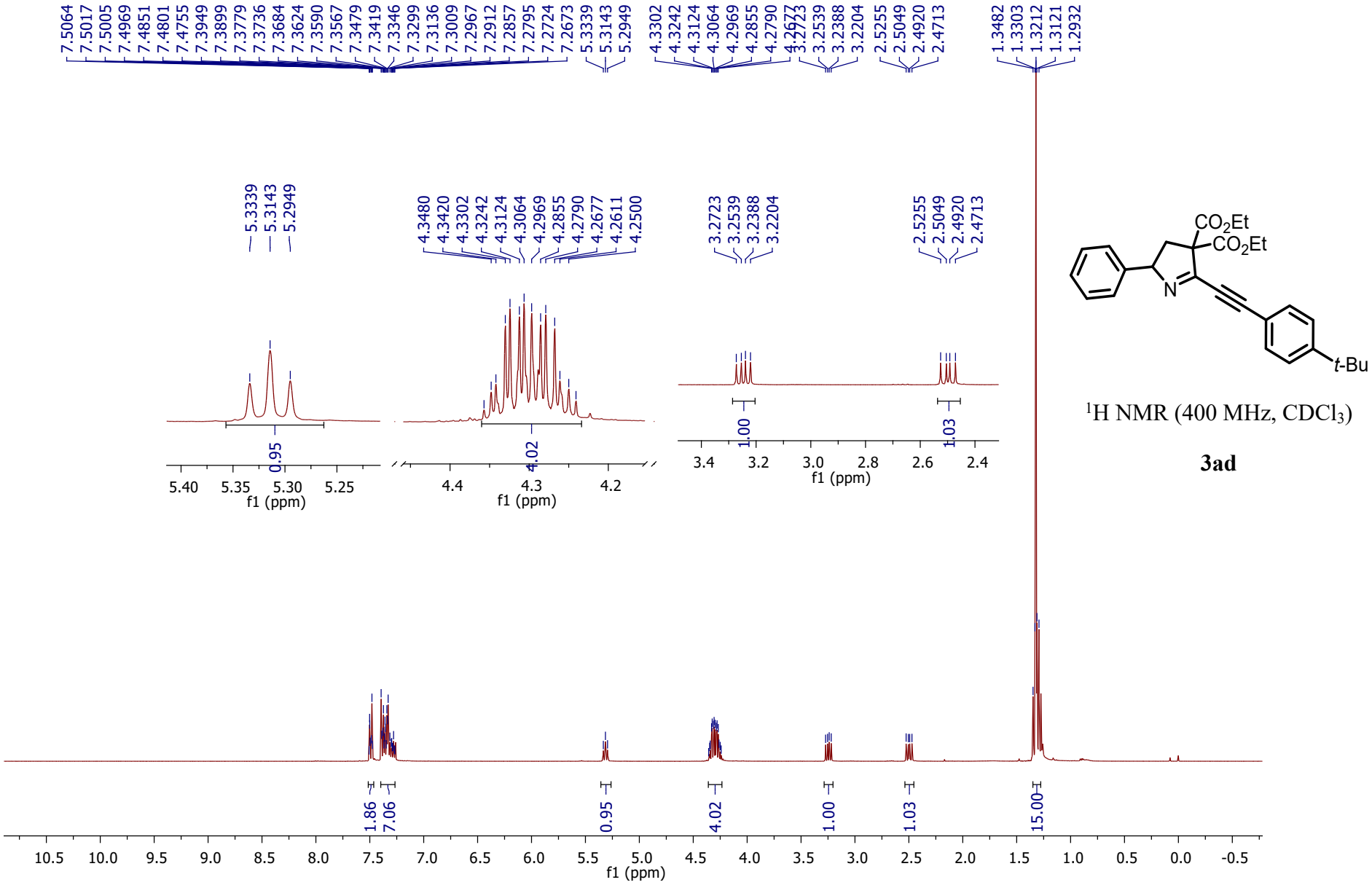
^{1}H NMR (400 MHz, $CDCl_3$)

3ac



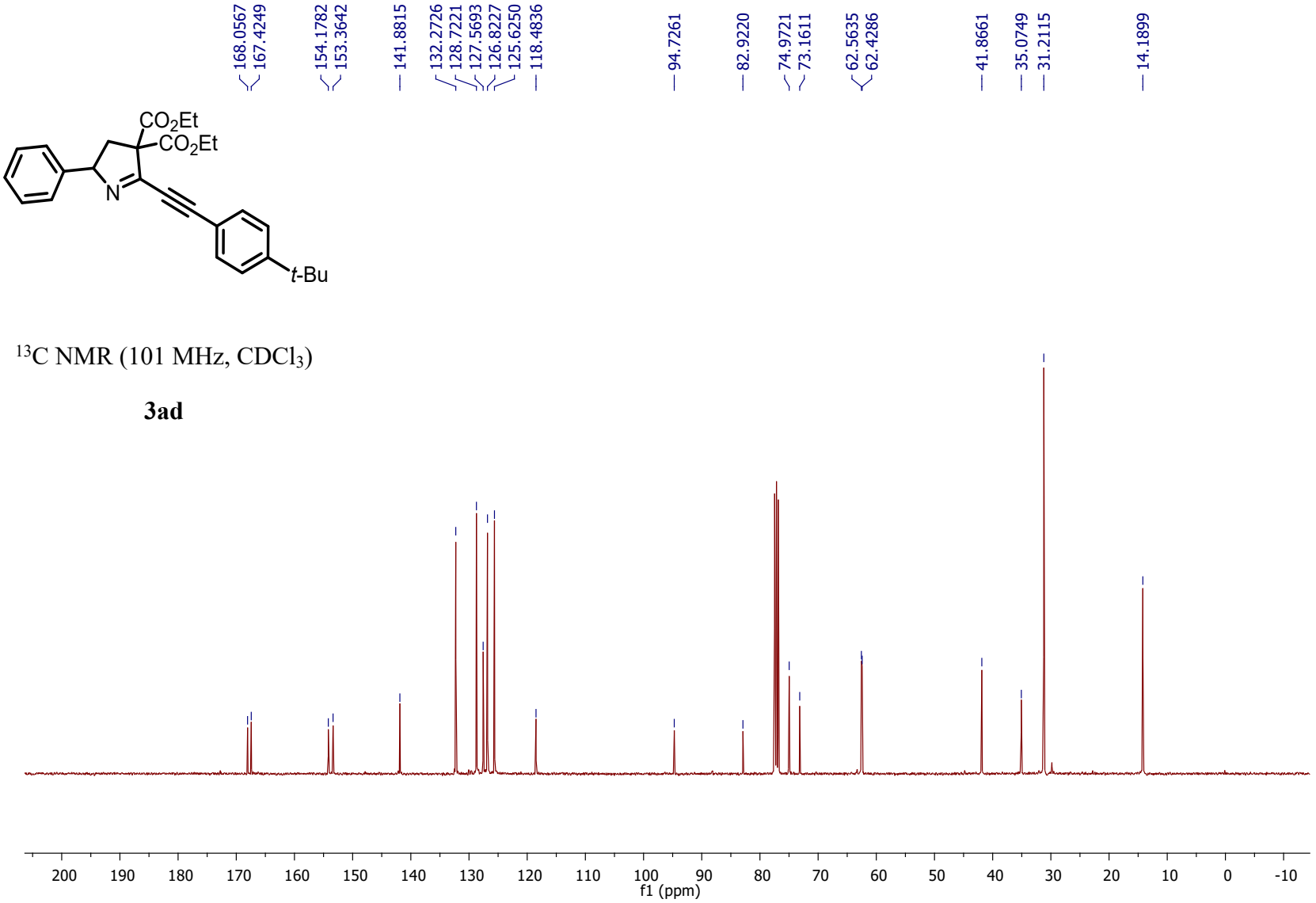
^{13}C NMR (101 MHz, $CDCl_3$)

3ac



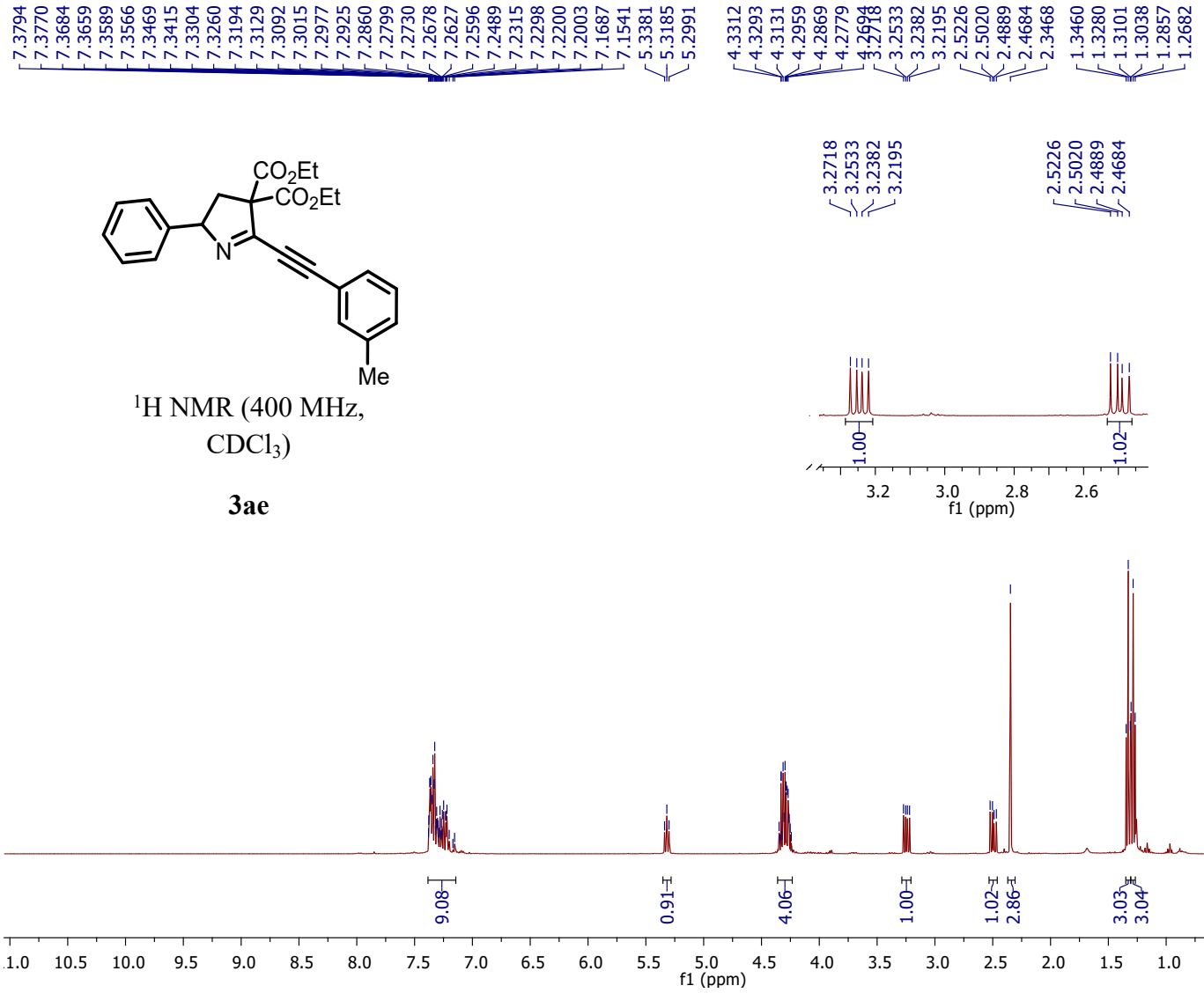
^{1}H NMR (400 MHz, $CDCl_3$)

3ad



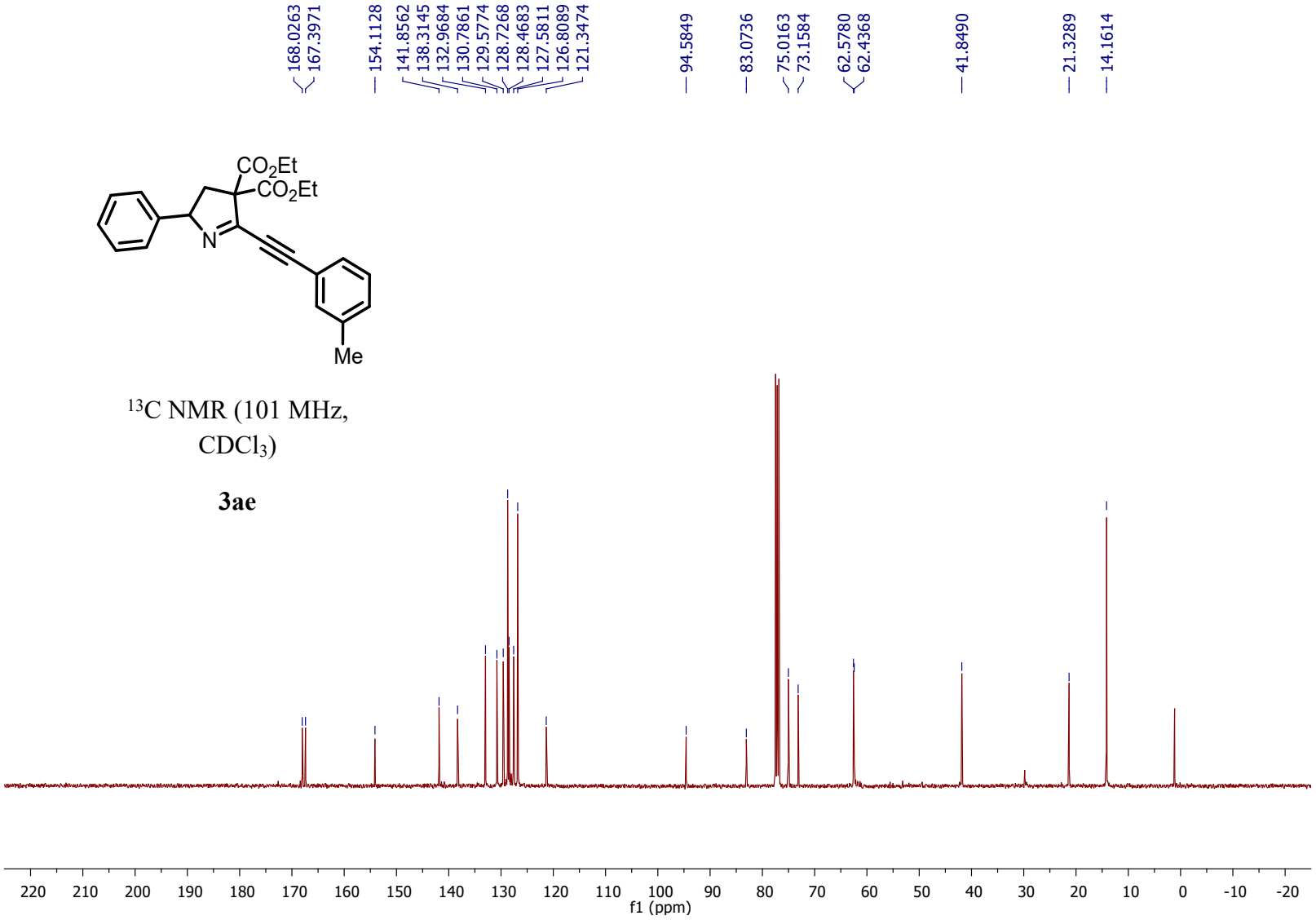
^{13}C NMR (101 MHz, $CDCl_3$)

3ad



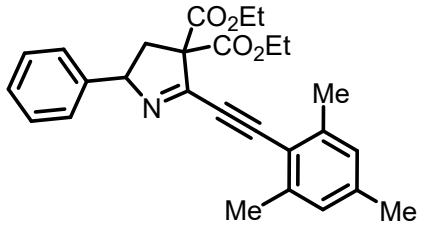
^{1}H NMR (400 MHz, $CDCl_3$)

3ae



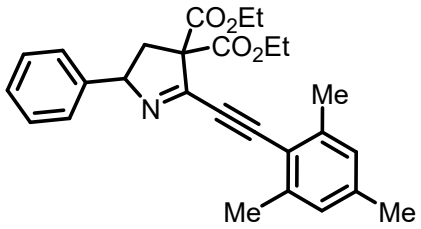
^{13}C NMR (101 MHz, $CDCl_3$)

3ae



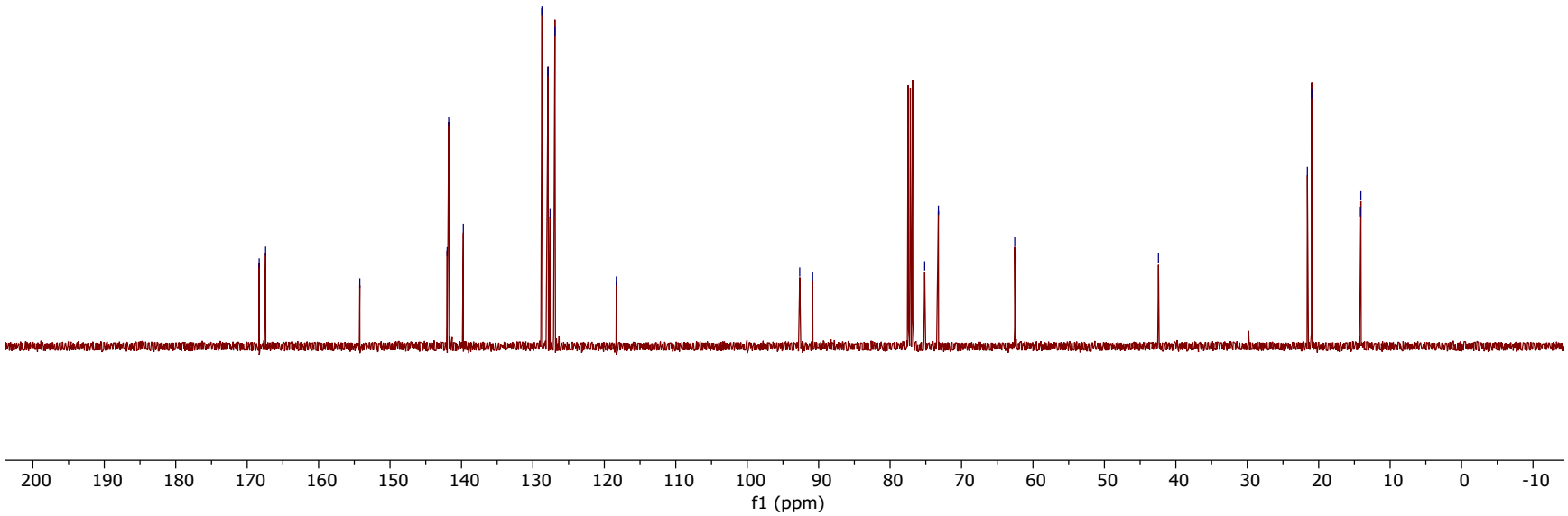
^{1}H NMR (400 MHz, $CDCl_3$)

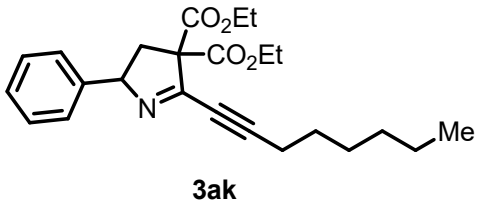
168.3183
167.4177
154.2300
142.0021
141.7889
139.7386
128.7354
127.8746
127.6012
126.9140
118.3202
92.6513
90.8395
75.1549
73.2337
62.5506
62.3866
42.4343
21.5843
20.9750
14.1487
14.0902



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

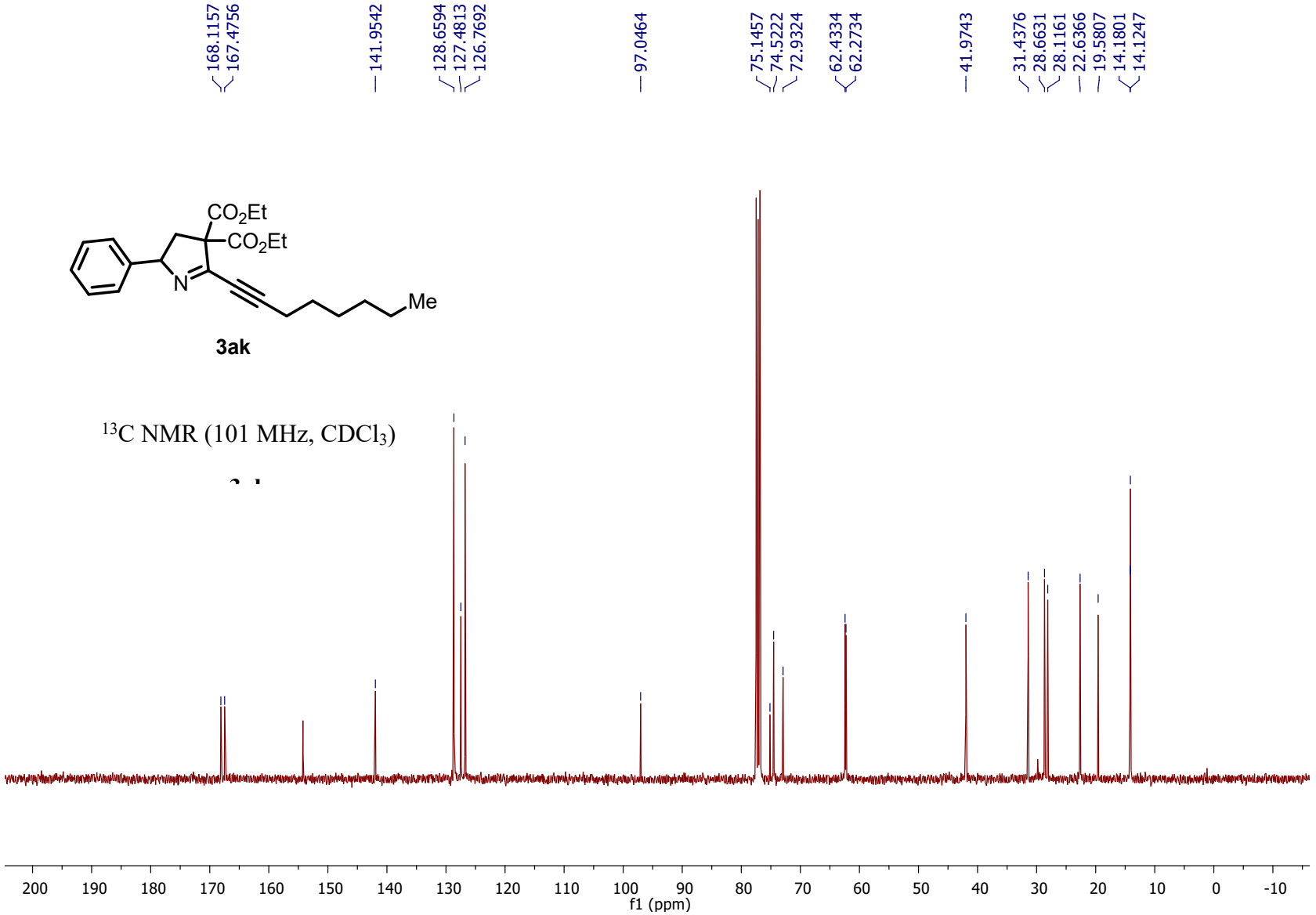
3af

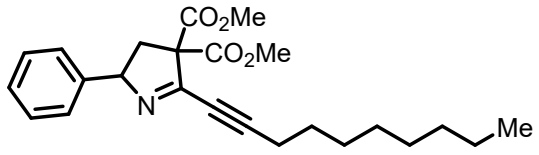




3ak

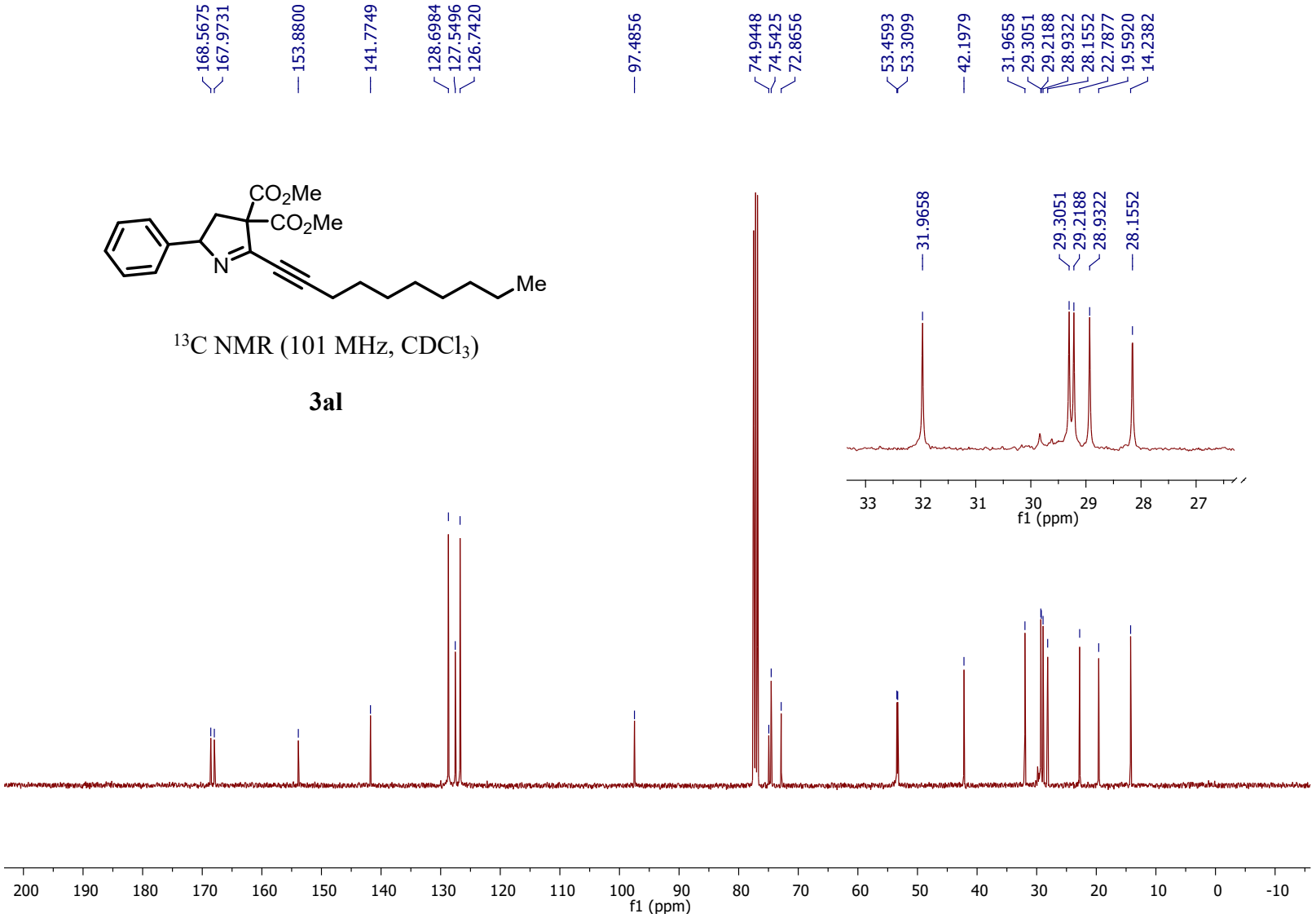
^{1}H NMR (400 MHz, $CDCl_3$)


168.1157
167.4756
141.9542
128.6594
127.4813
126.7692
97.0464
75.1457
74.5222
72.9324
62.4334
62.2734
41.9743
31.4376
28.6631
28.1161
22.6366
19.5807
14.1801
14.1247
CO2Et
CO2Et
N
Me
3ak
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
-10
f1 (ppm)



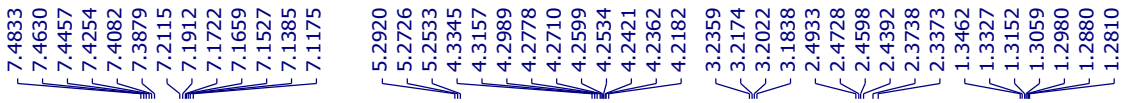
^{1}H NMR (101 MHz, $CDCl_3$)

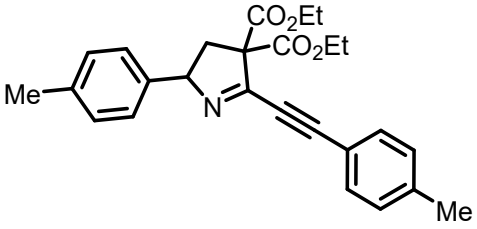
3al

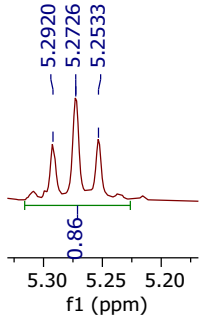


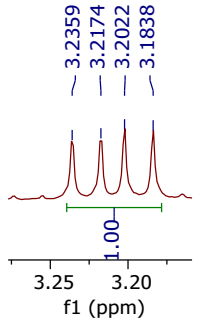
^{13}C NMR (101 MHz, $CDCl_3$)

3al



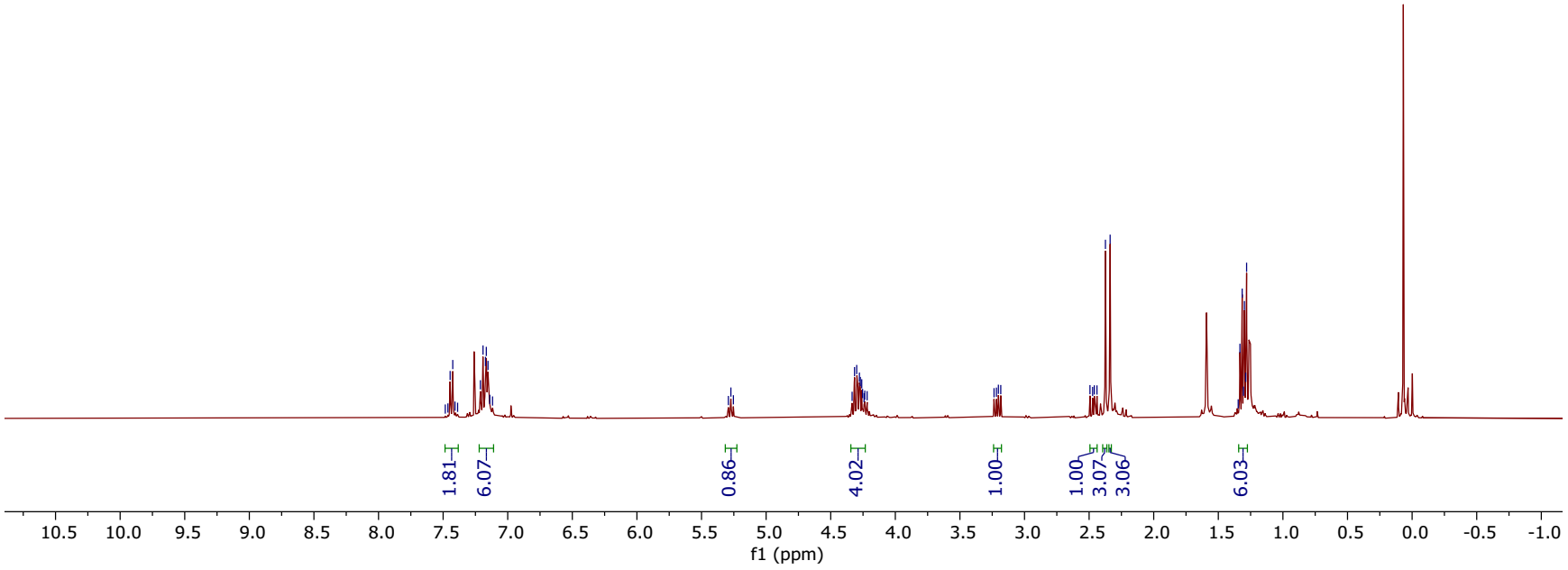


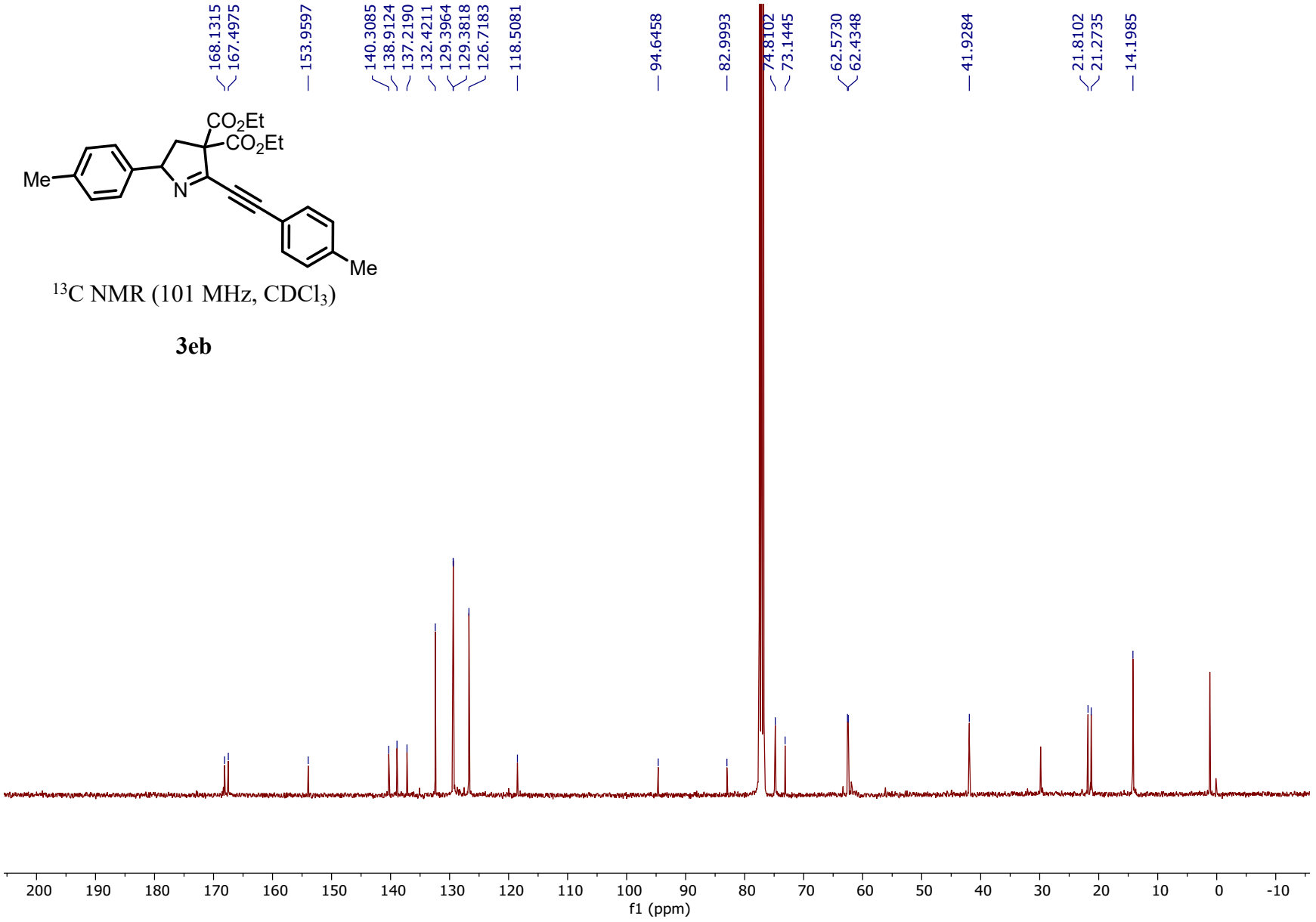




^{1}H NMR (400 MHz, $CDCl_3$)

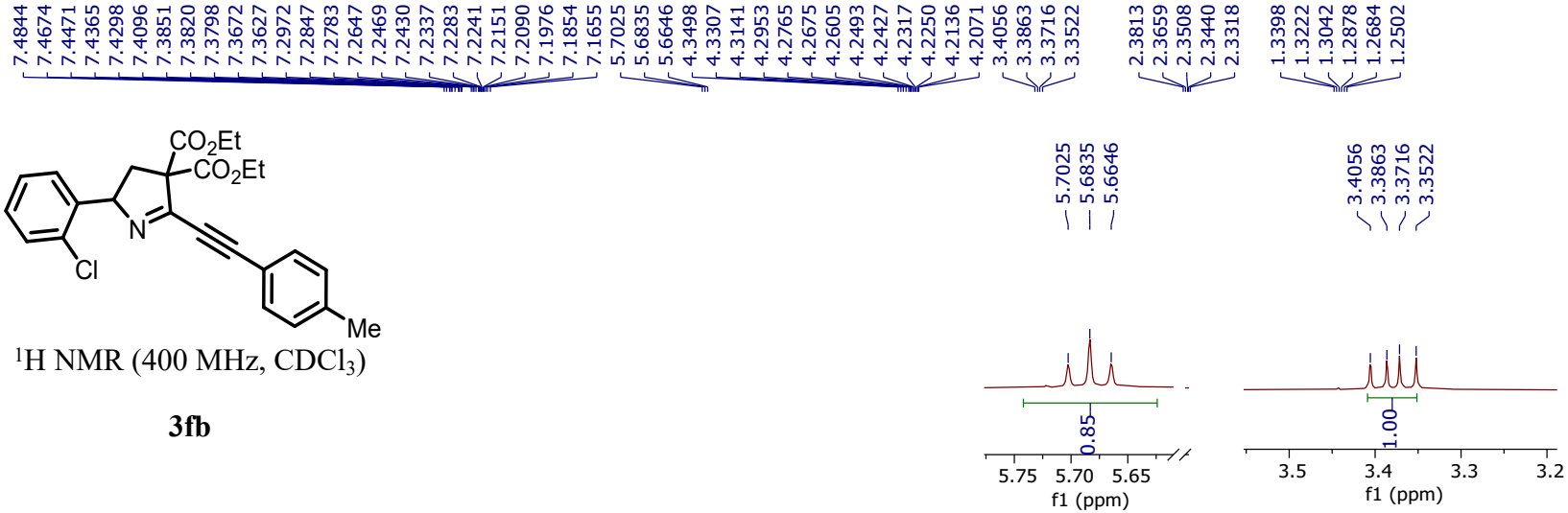
3eb





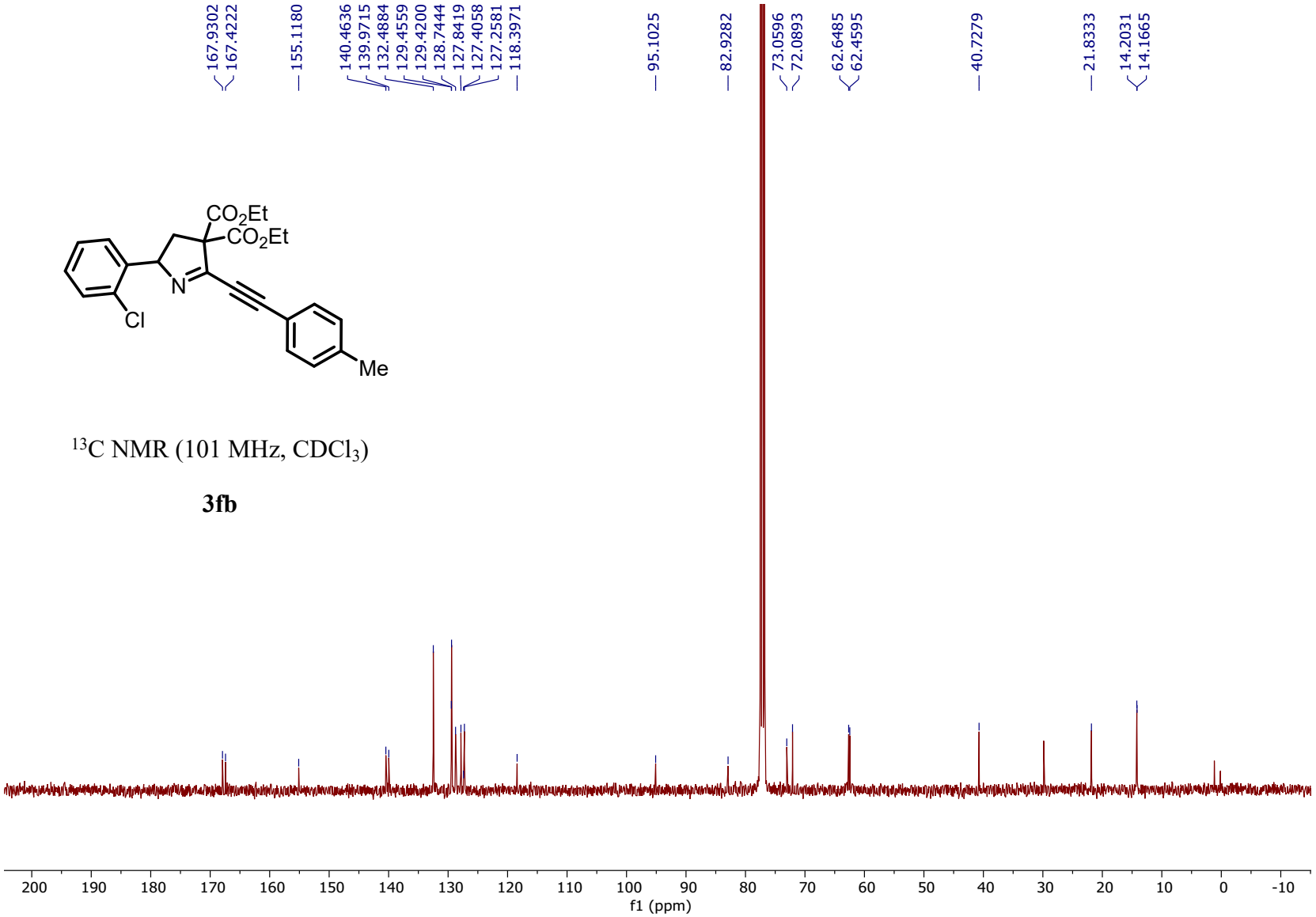
^{13}C NMR (101 MHz, $CDCl_3$)

3eb



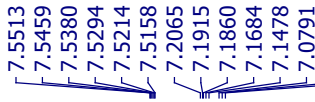
^{1}H NMR (400 MHz, $CDCl_3$)

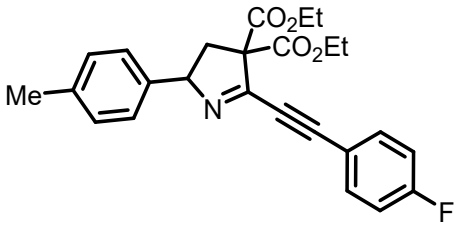
3fb



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

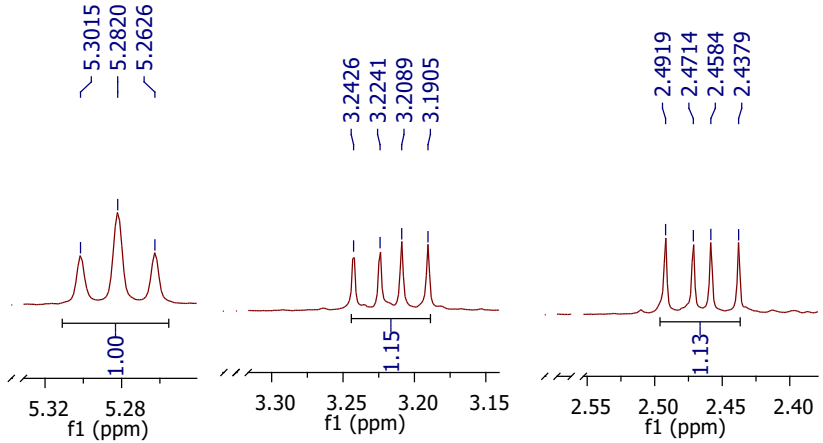
3fb

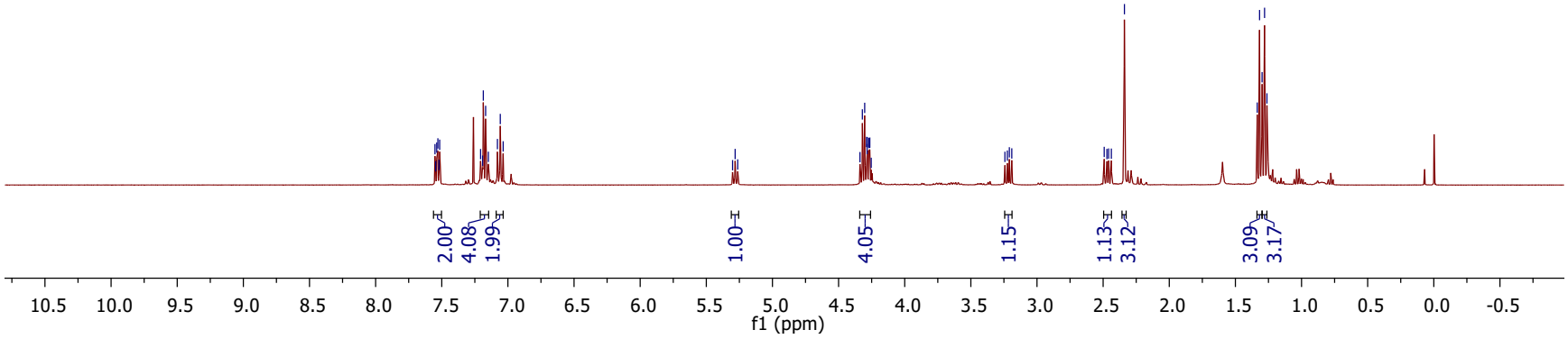


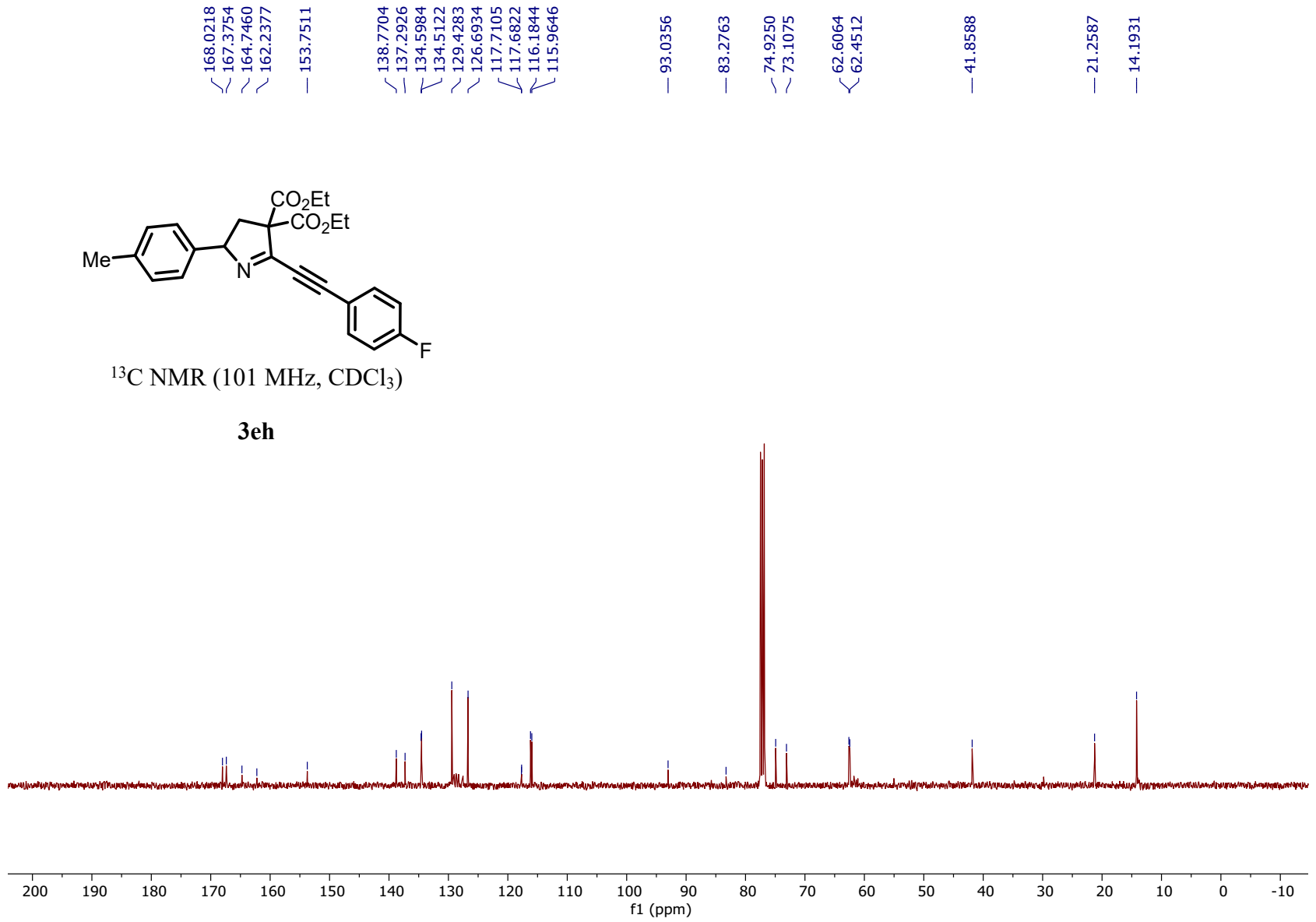


^{1}H NMR (400 MHz, $CDCl_3$)

3eh

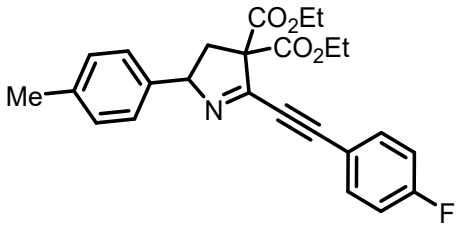






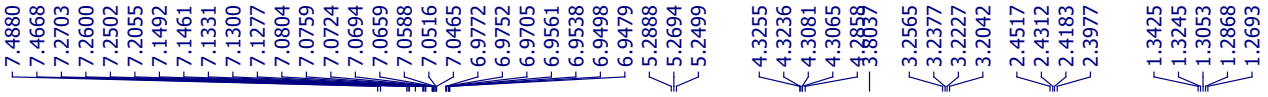
^{13}C NMR (101 MHz, $CDCl_3$)

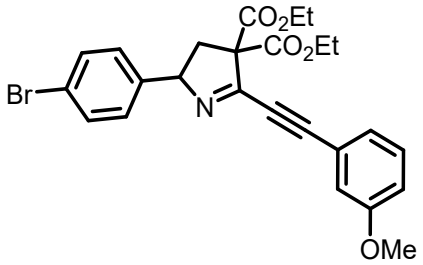
3eh



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

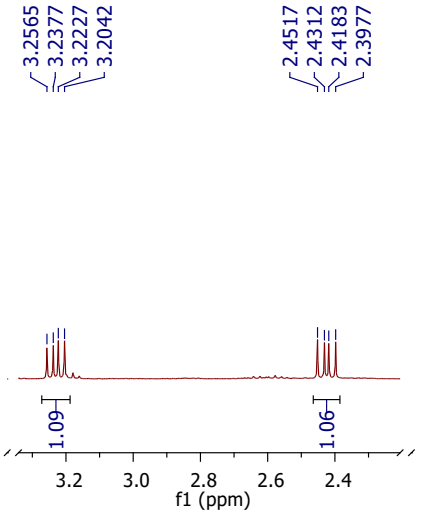
3eh

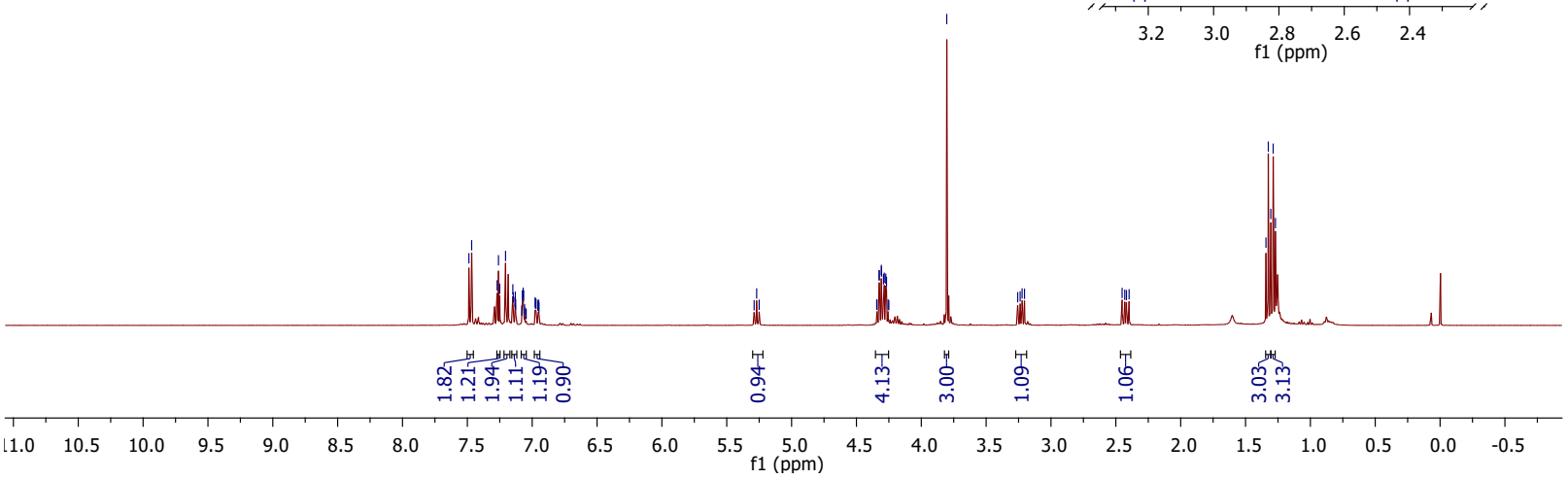


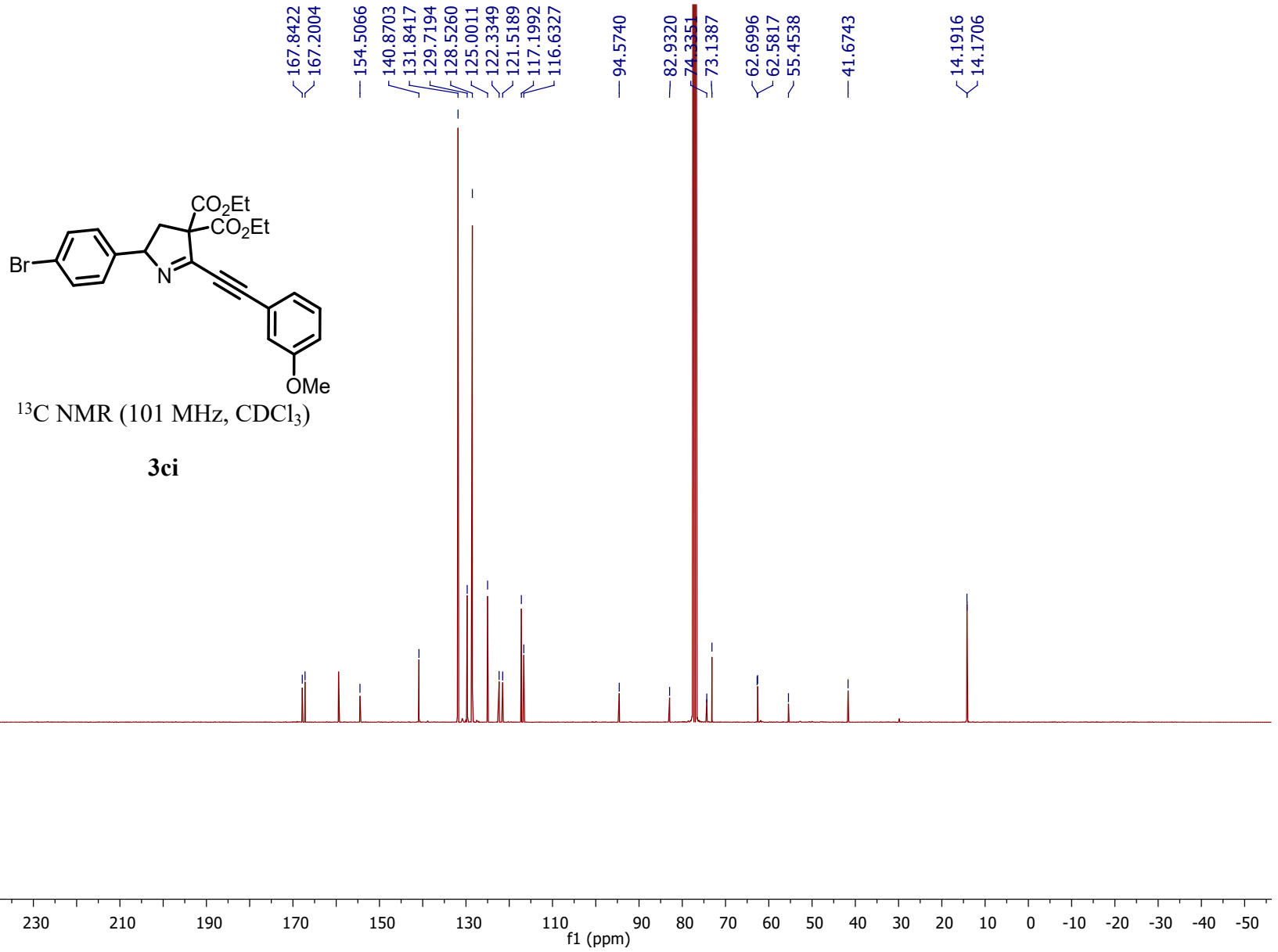


^{1}H NMR (400 MHz, $CDCl_3$)

3ci

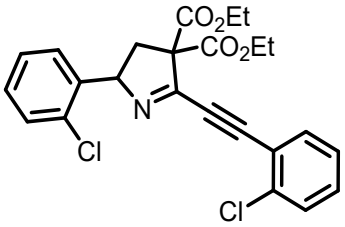


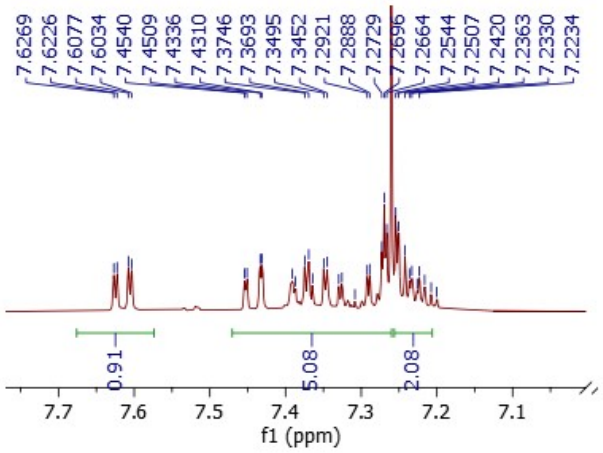




^{13}C NMR (101 MHz, $CDCl_3$)

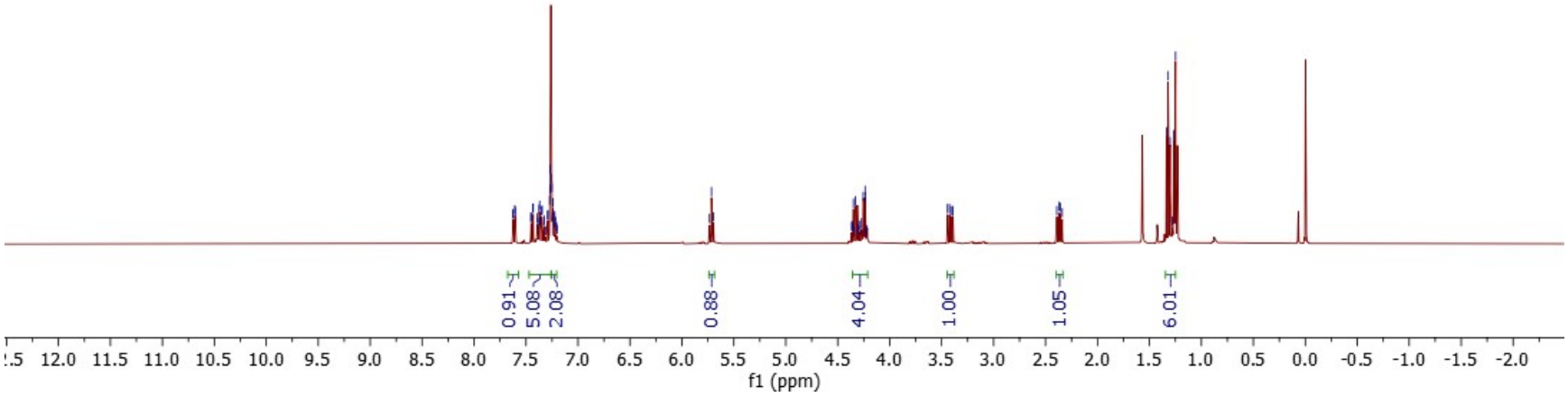
3ci

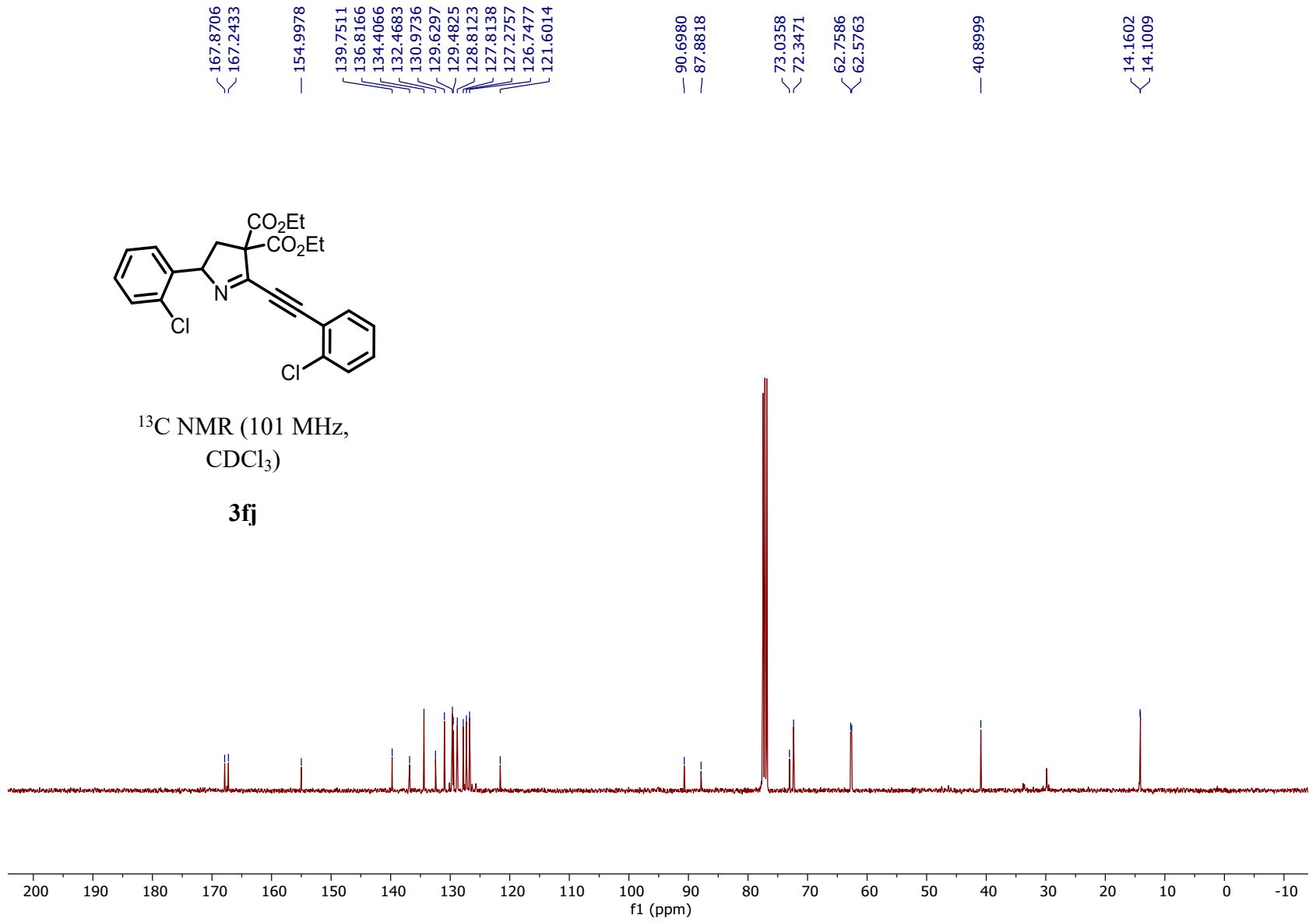




^{1}H NMR (400 MHz, $CDCl_3$)

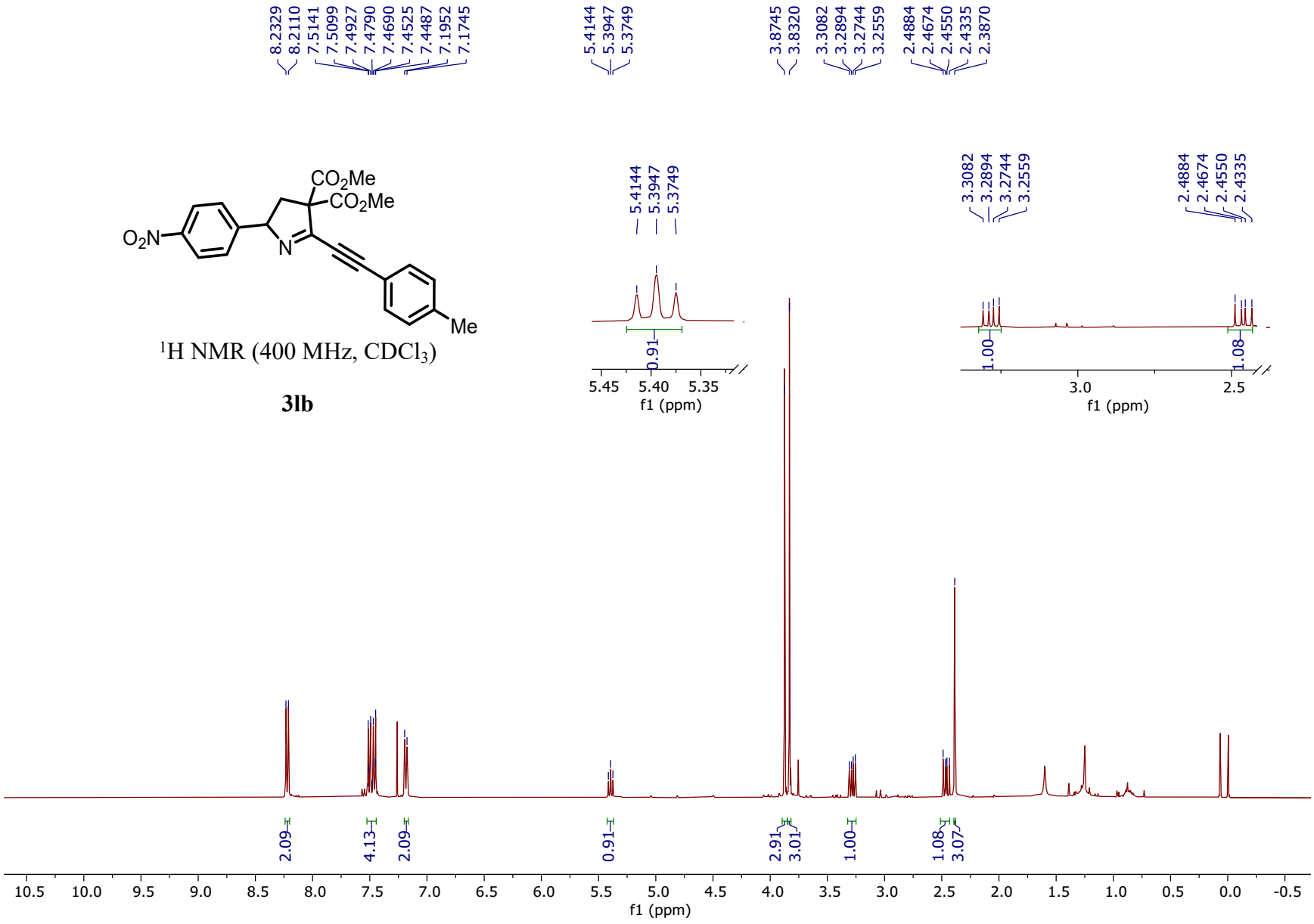
3fj

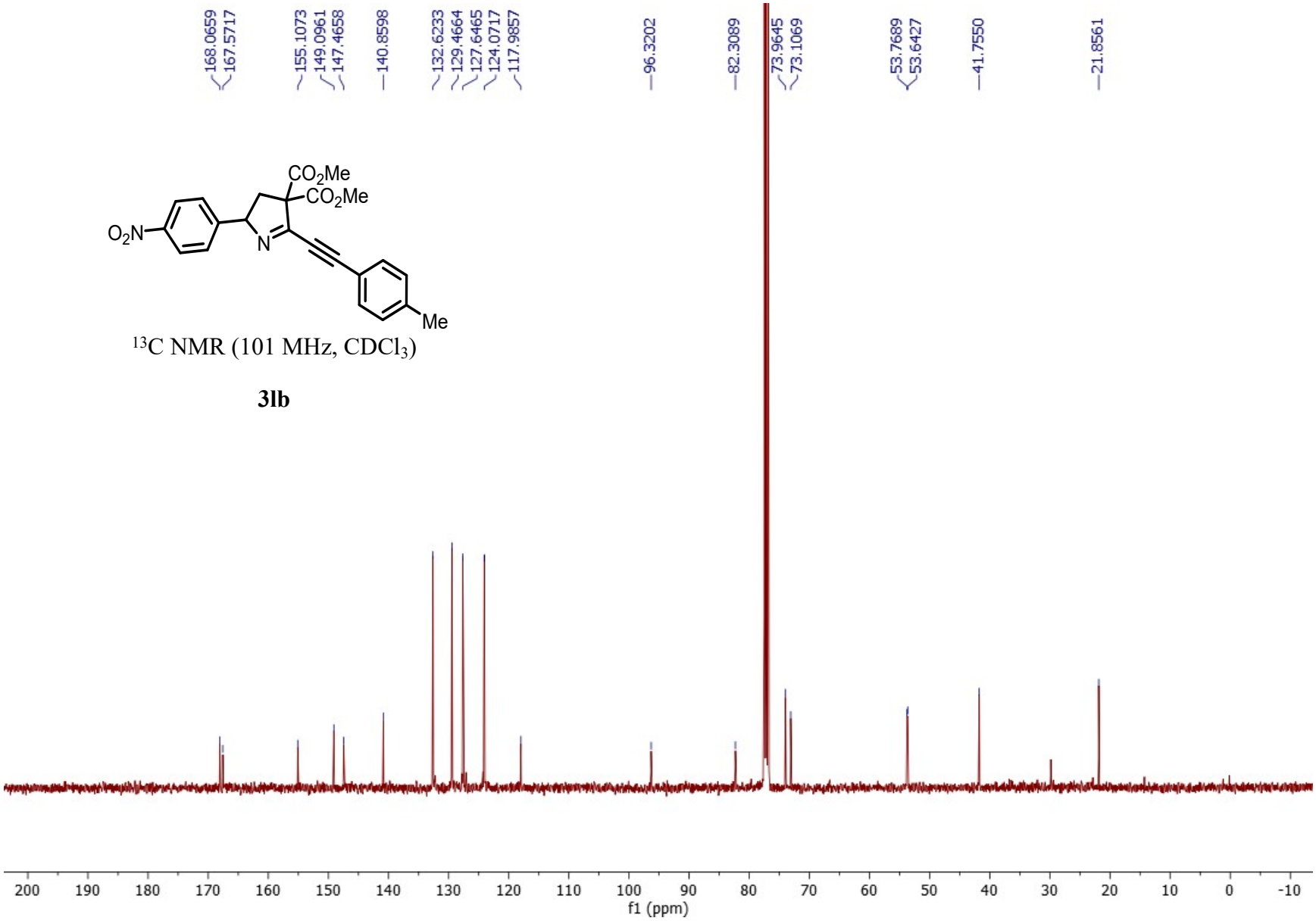




^{13}C NMR (101 MHz, $CDCl_3$)

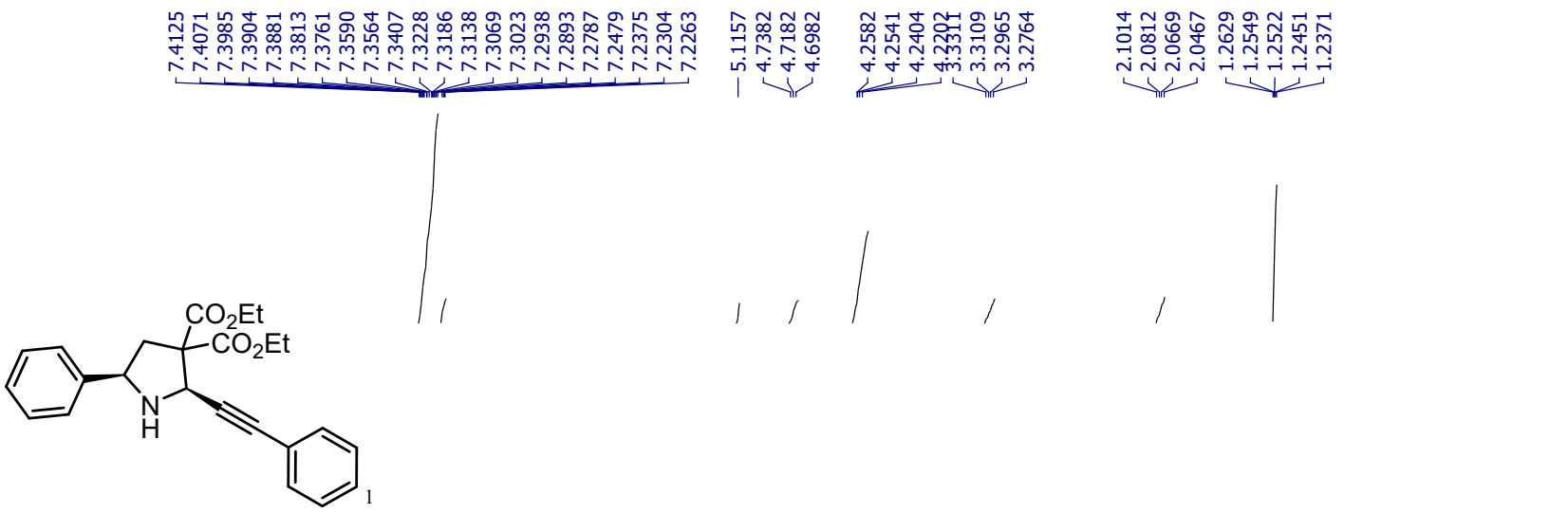
3fj


8.2329
8.2110
7.5141
7.5099
7.4927
7.4790
7.4690
7.4525
7.4487
7.1952
7.1745
5.4144
5.3947
5.3749
3.8745
3.8320
3.3082
3.2894
3.2744
3.2559
2.4884
2.4674
2.4550
2.4335
2.3870
CO2Me
CO2Me
O2N
N
Me
1H NMR (400 MHz, CDCl3)
3lb
0.91
1.00
1.08
f1 (ppm)
2.09
4.13
2.09
0.91
2.91
3.01
1.00
1.08
3.07



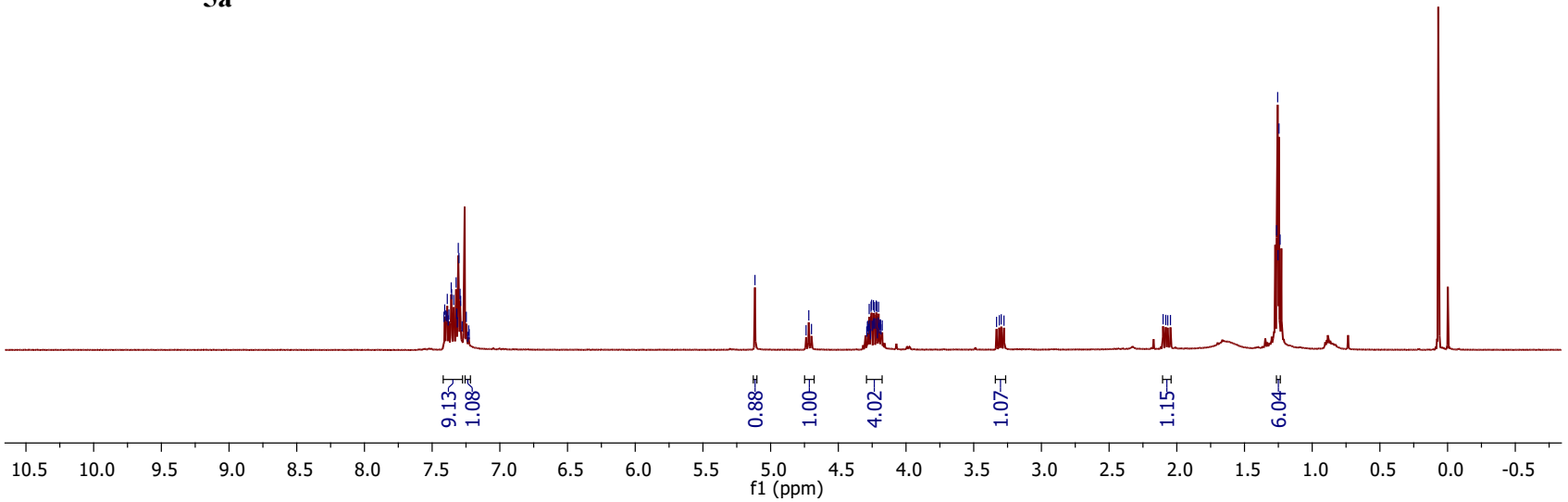
^{13}C NMR (101 MHz, $CDCl_3$)

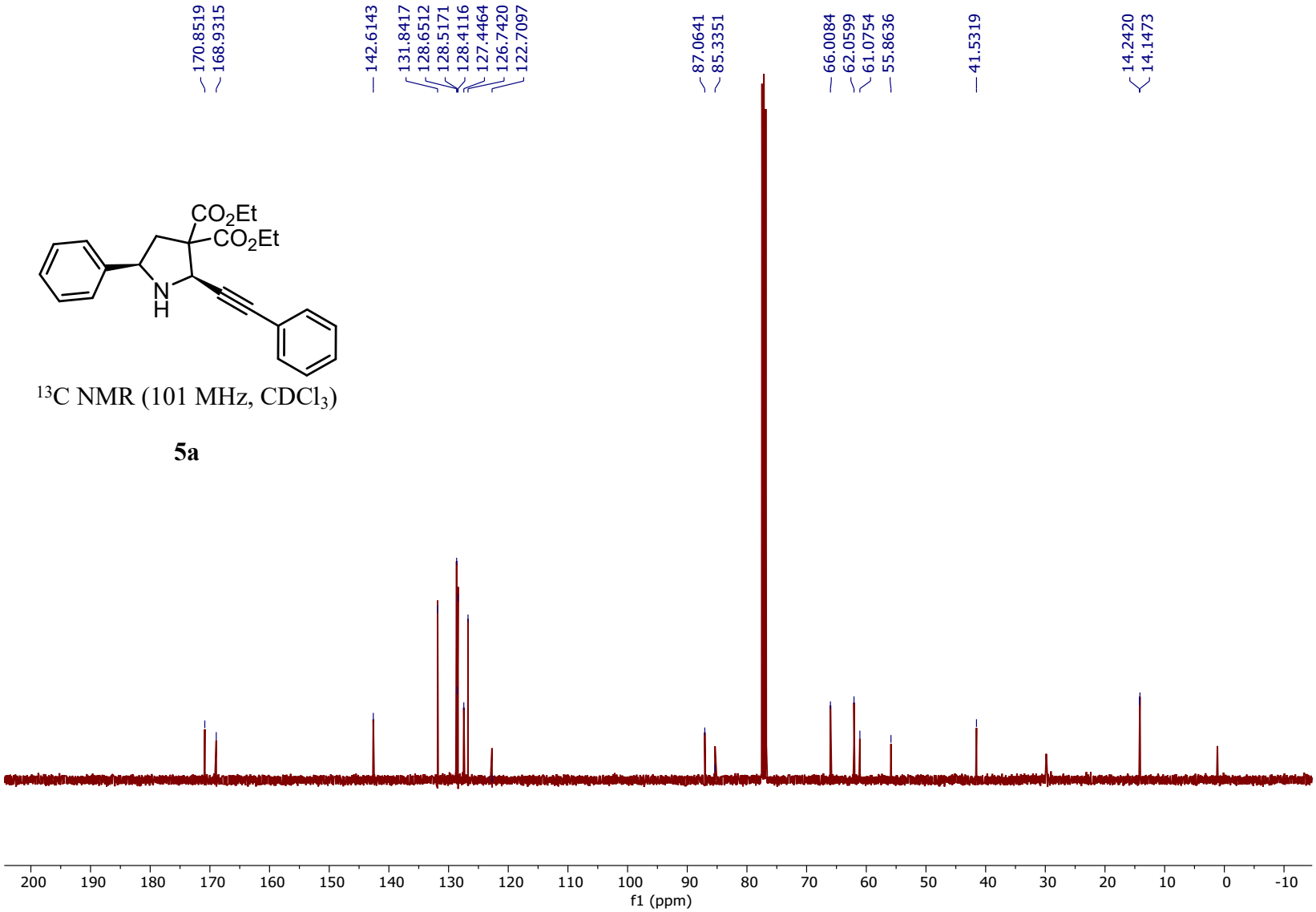
3lb



H NMR (400 MHz, $CDCl_3$)

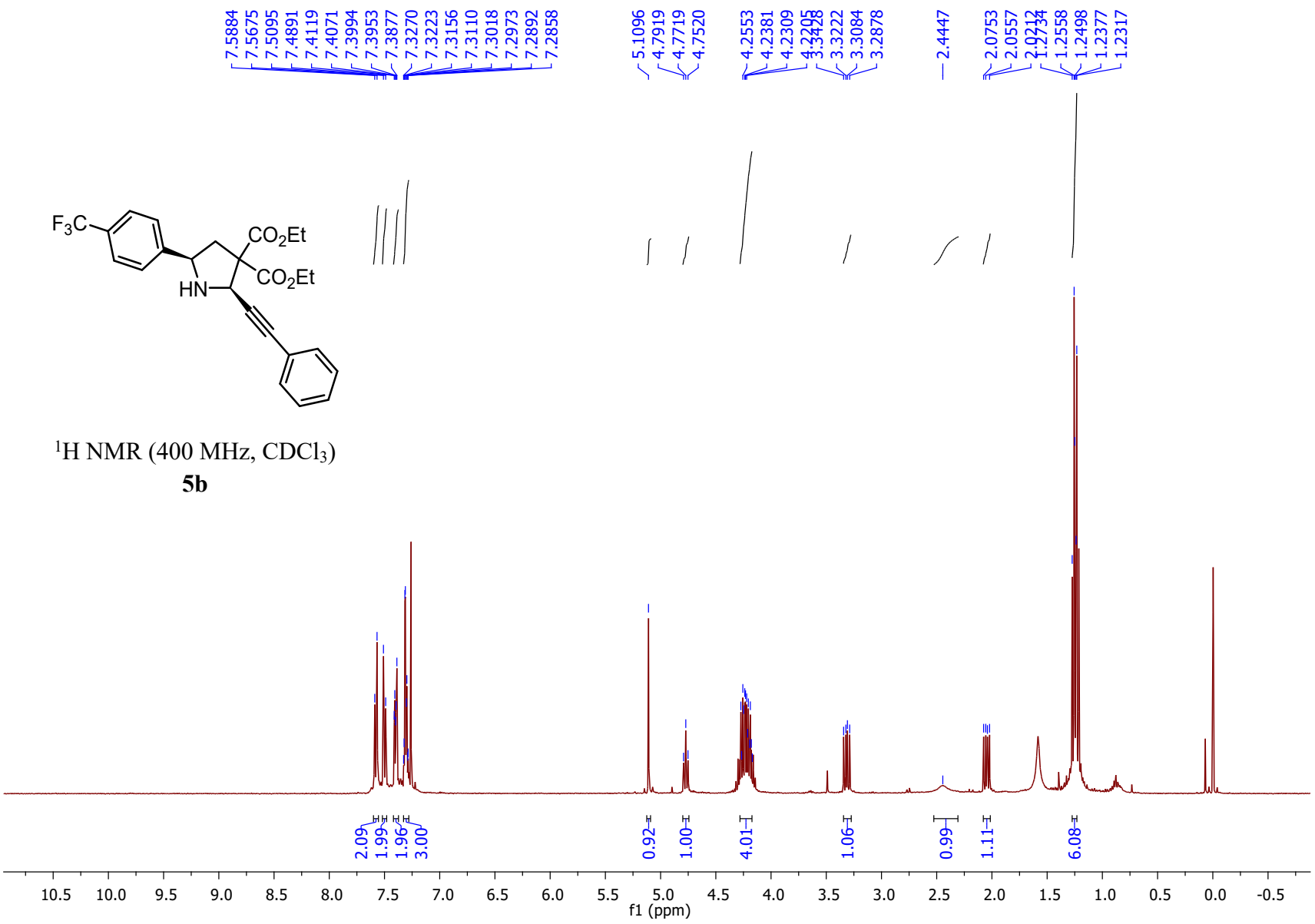
5a





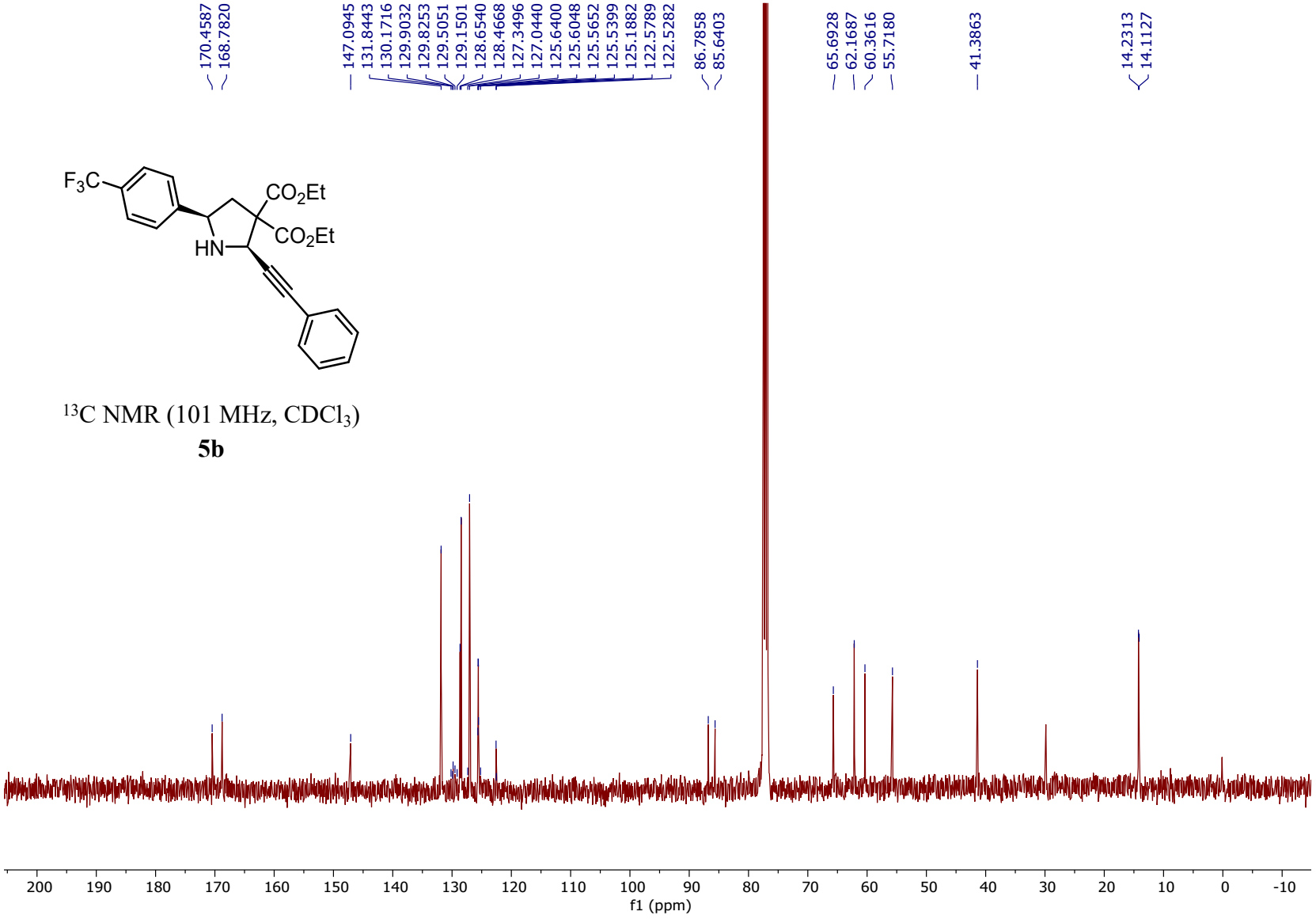
^{13}C NMR (101 MHz, $CDCl_3$)

5a



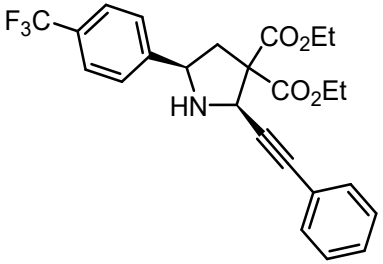
^{1}H NMR (400 MHz, $CDCl_3$)

5b



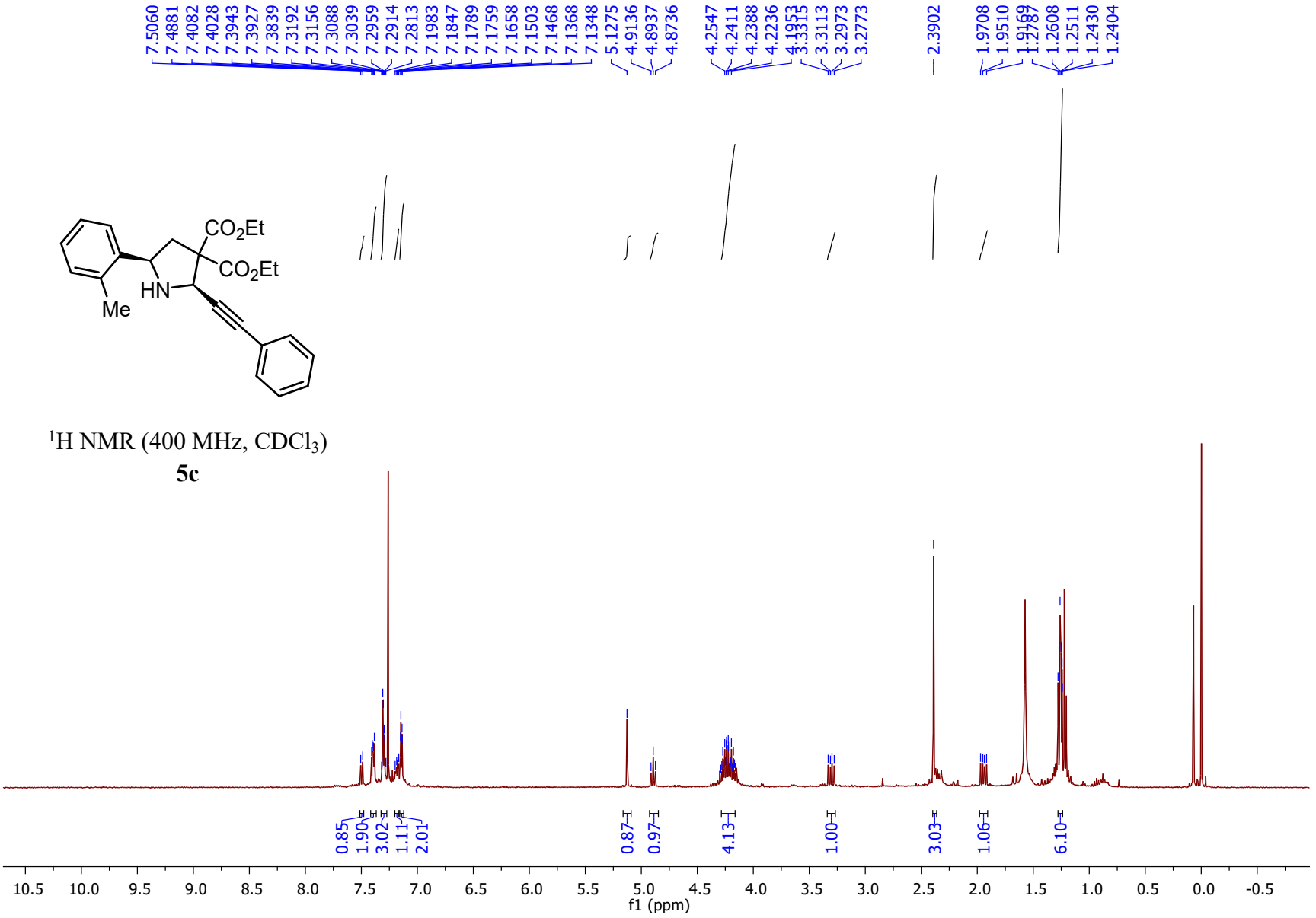
^{13}C NMR (101 MHz, $CDCl_3$)

5b



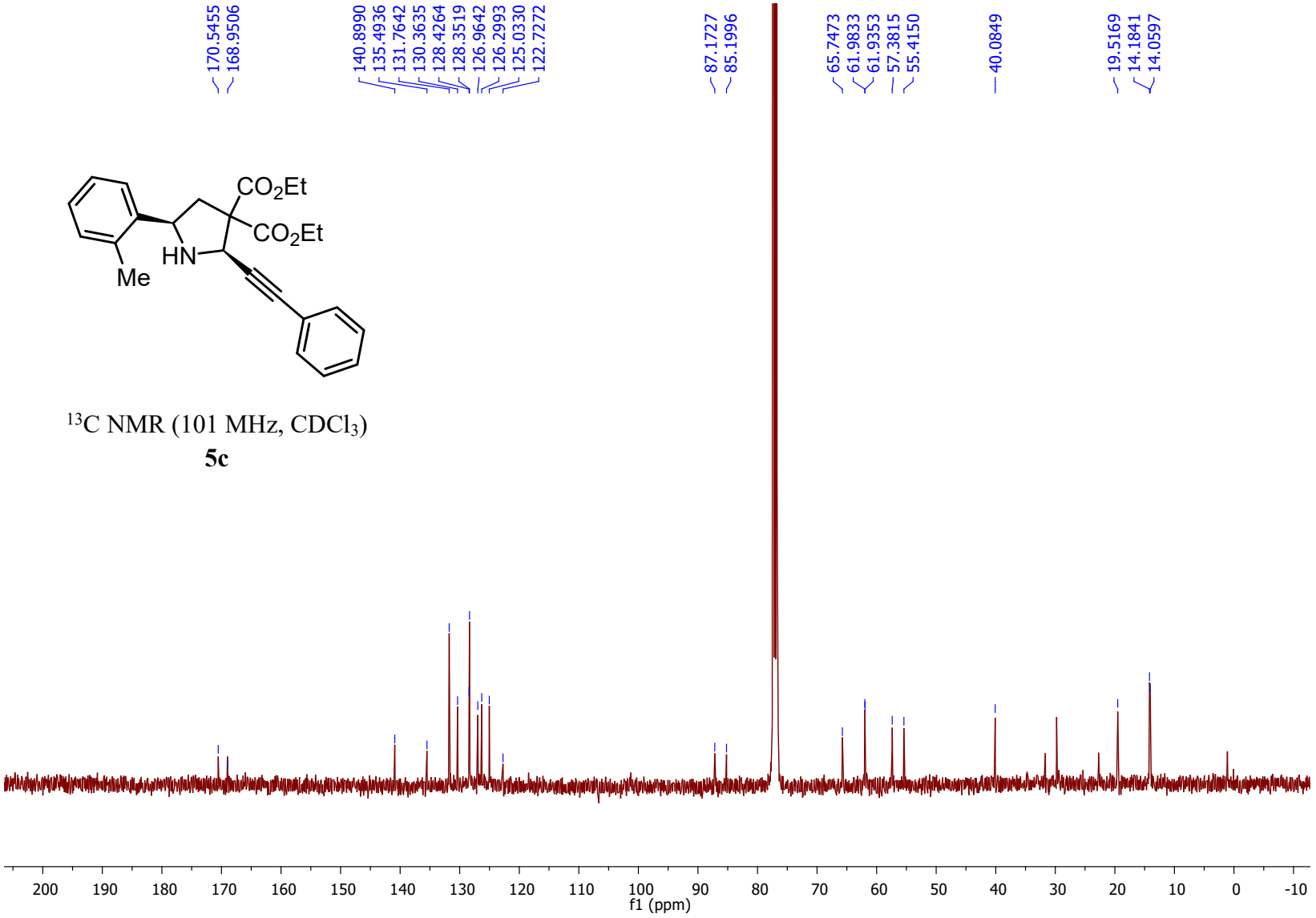
^{19}F NMR (377 MHz, $CDCl_3$)

5b



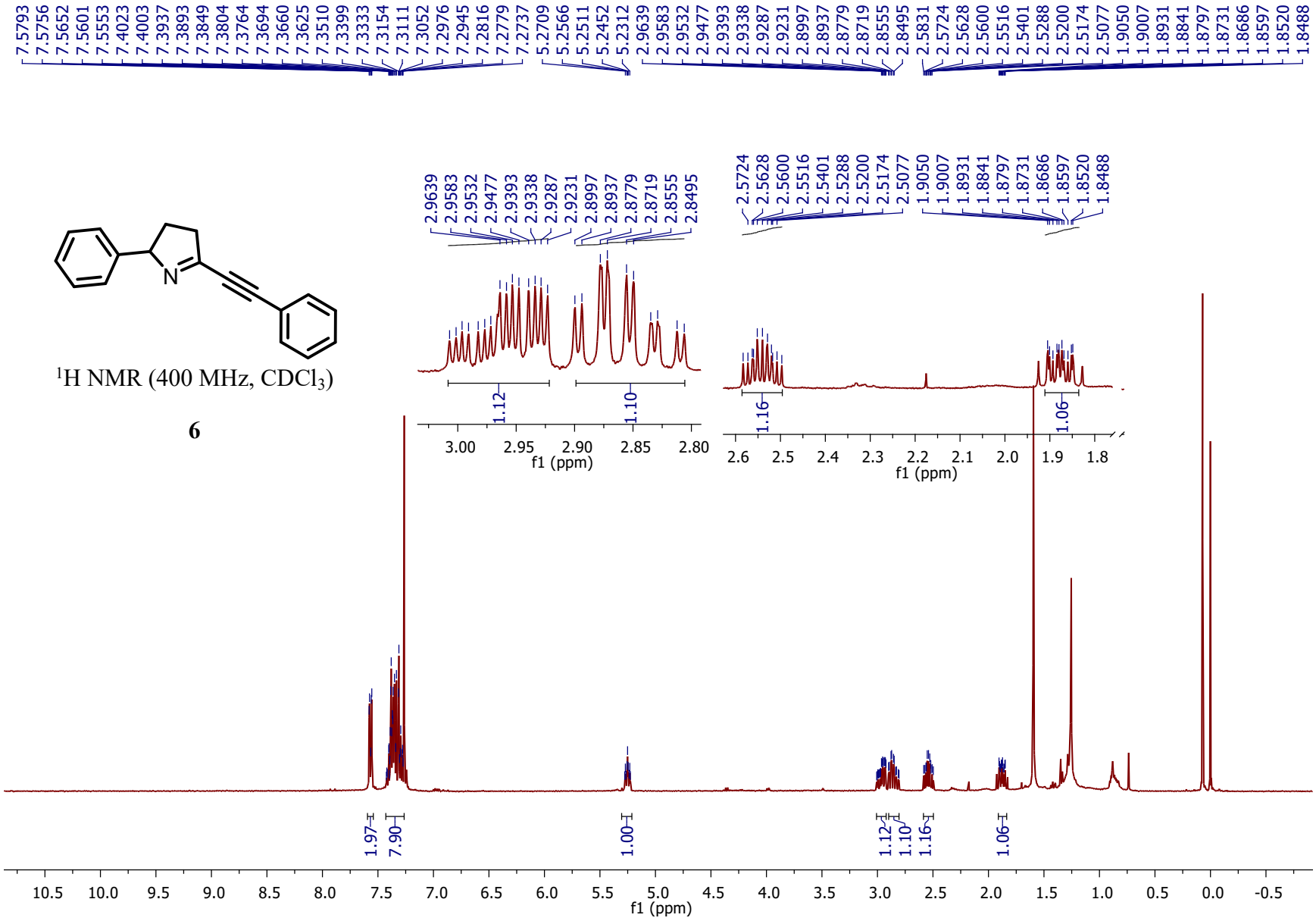
^{1}H NMR (400 MHz, $CDCl_3$)

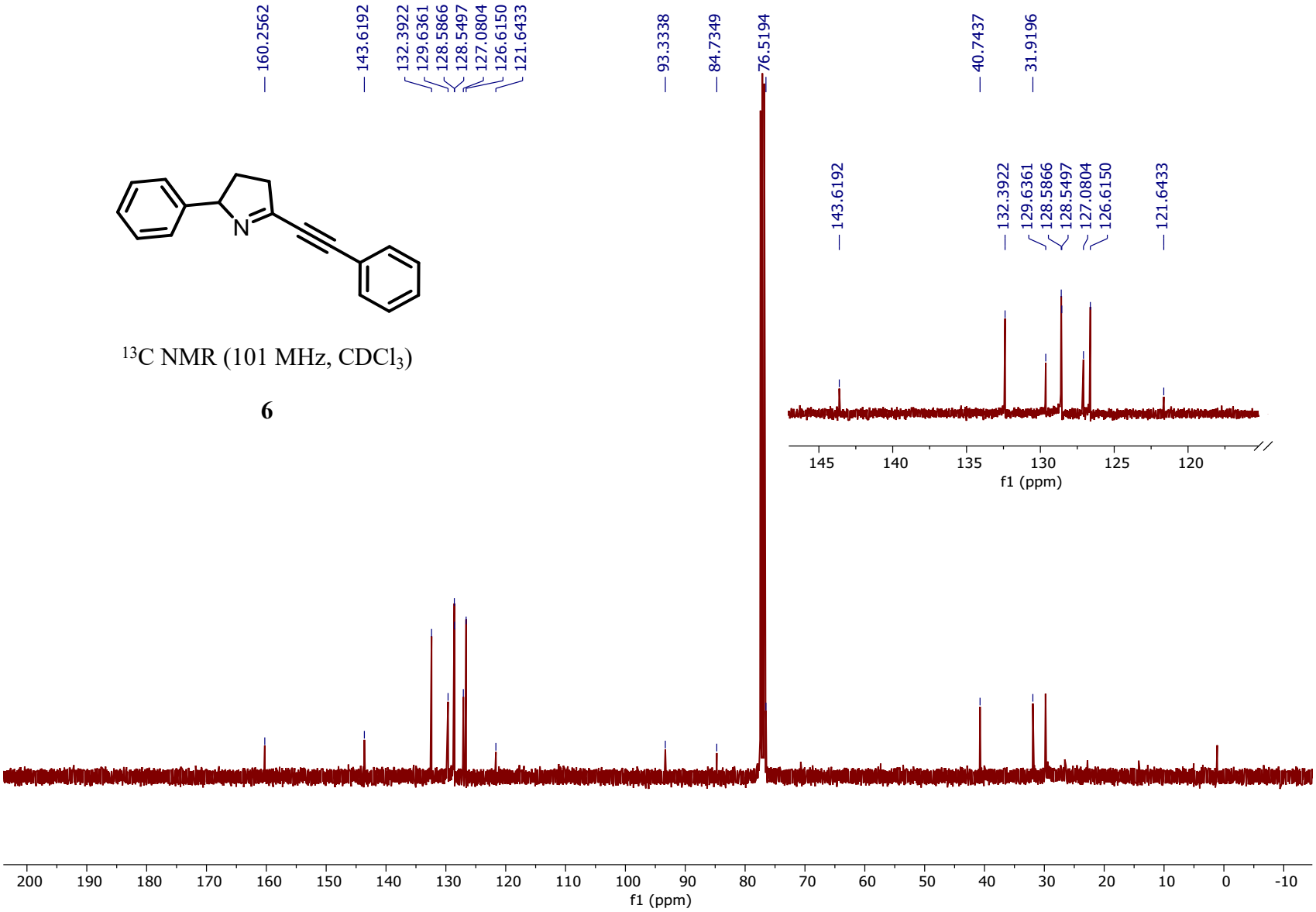
5c



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

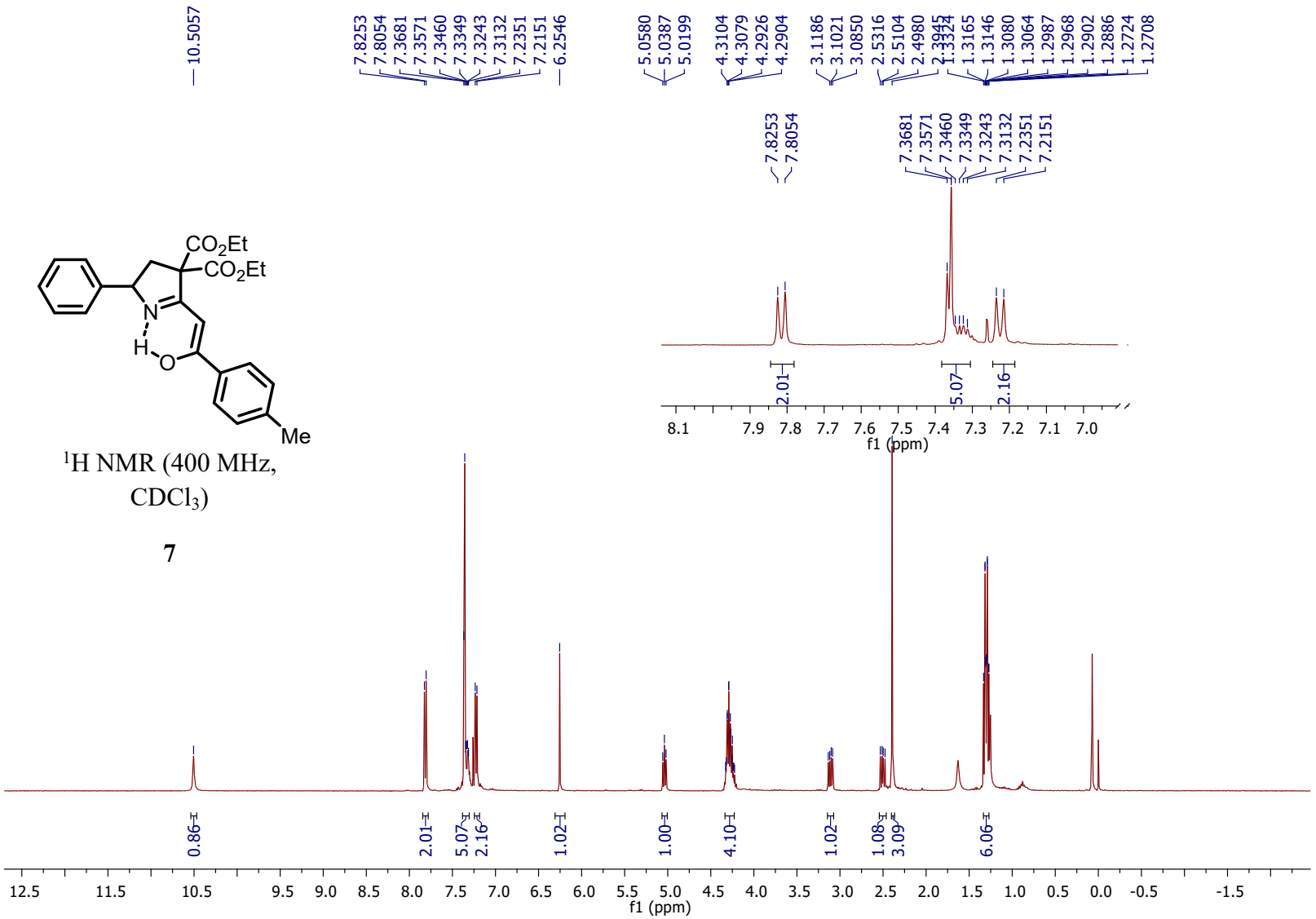
5c


7.5793 7.5756 7.5652 7.5601 7.5553 7.4023 7.4003 7.3937 7.3893 7.3849 7.3804 7.3764 7.3694 7.3660 7.3625 7.3510 7.3399 7.3333 7.3154 7.3111 7.3052 7.2976 7.2945 7.2816 7.2779 7.2737 5.2709 5.2566 5.2511 5.2452 5.2312 2.9639 2.9583 2.9532 2.9477 2.9393 2.9338 2.9287 2.9231 2.8997 2.8937 2.8779 2.8719 2.8555 2.8495 2.5831 2.5724 2.5628 2.5600 2.5516 2.5401 2.5288 2.5200 2.5174 2.5077 1.9050 1.9007 1.8931 1.8841 1.8797 1.8731 1.8686 1.8597 1.8520 1.8488
N
1H NMR (400 MHz, CDCl3)
6
1.12
1.10
1.16
1.06
f1 (ppm)
1.97
7.90
1.00
1.12
1.10
1.16
1.06
f1 (ppm)



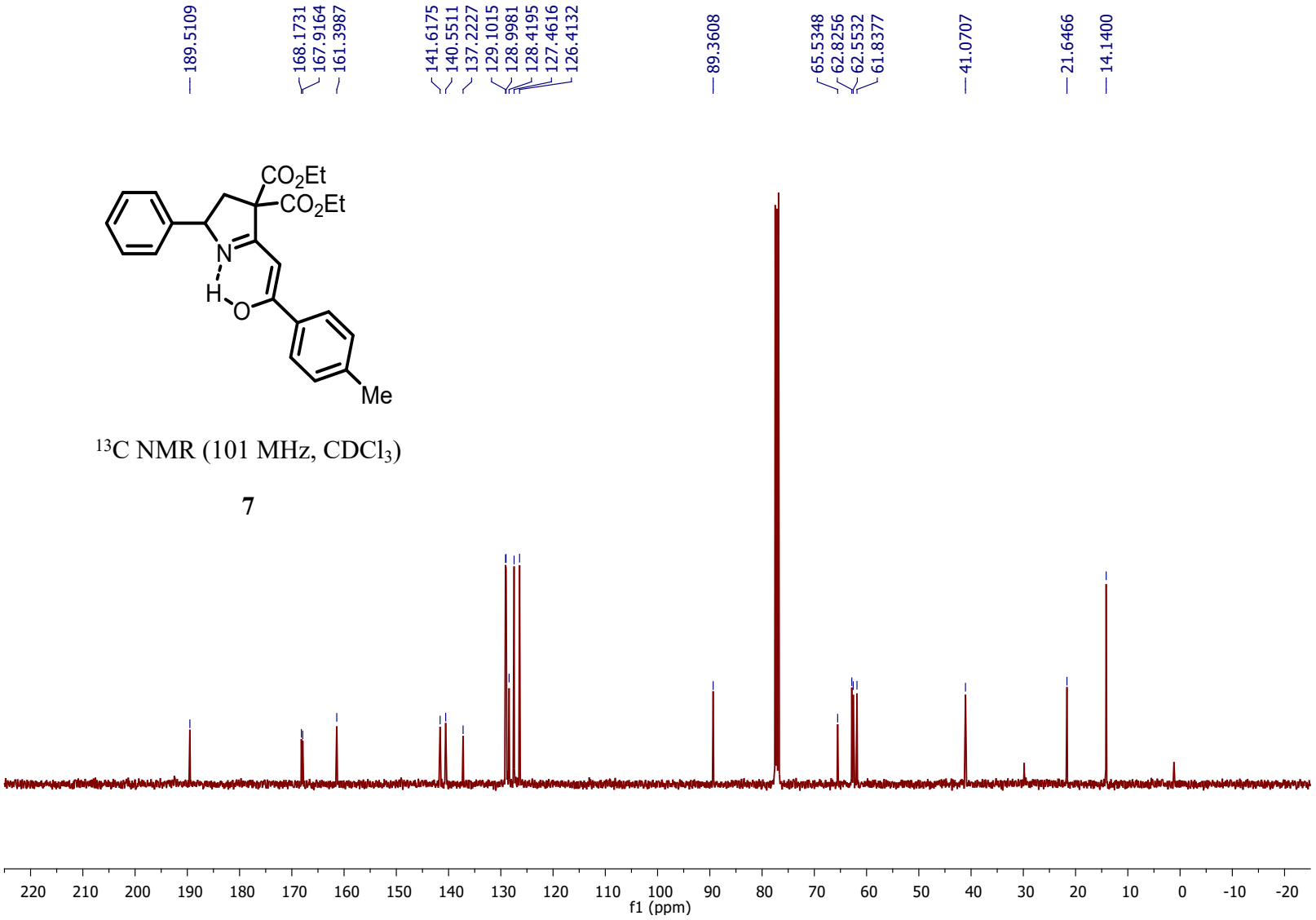
^{13}C NMR (101 MHz, $CDCl_3$)

6



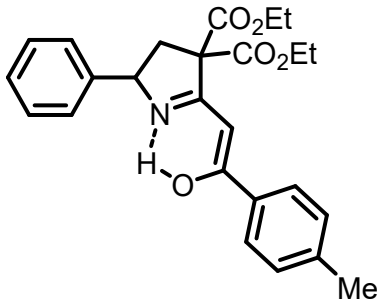
^{1}H NMR (400 MHz, $CDCl_3$)

7



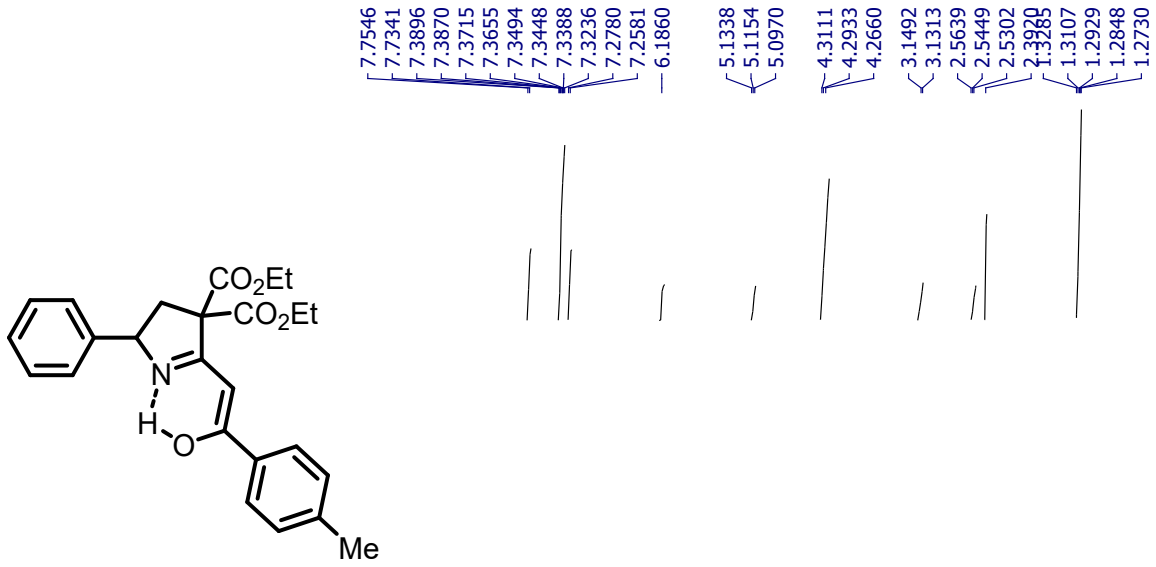
^{13}C NMR (101 MHz, $CDCl_3$)

7



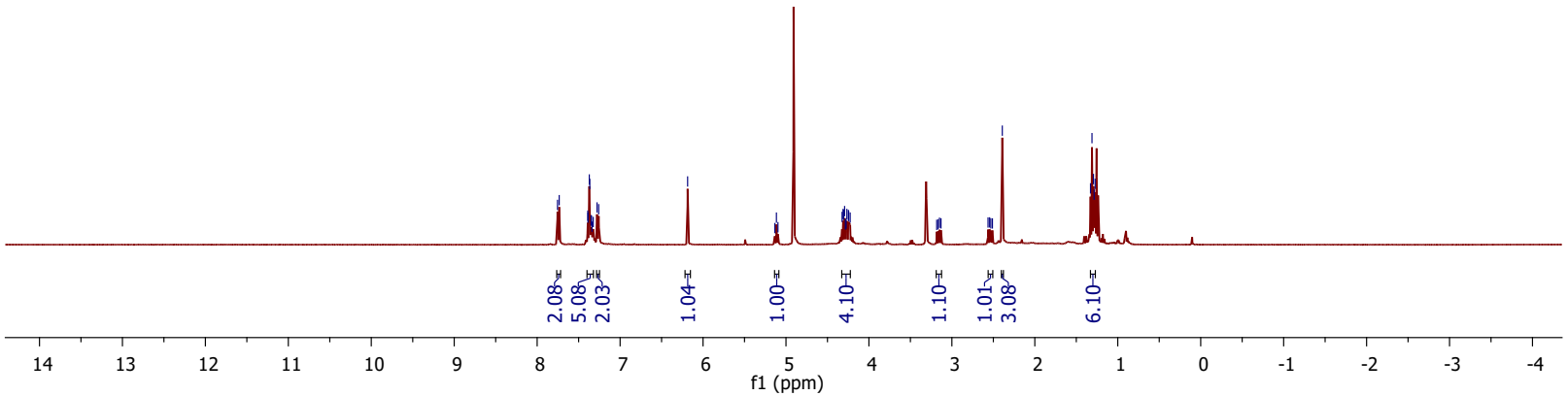
DEPT-135 NMR (101 MHz, $CDCl_3$)

7



^{1}H NMR (400 MHz, CD_3OD)

7



7. X-ray crystallographic data

For the determination of X-ray crystal structure of **3ia** single crystals were selected and mounted with paratone oil on a glass fiber using gum. The data were collected at 293K on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC micro-focus source with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. For the integration of diffraction profiles SAINT program[5] was used. Adsorption correction was done applying SADABS program.[6] The crystal structure was solved by SIR 92[7] and refined by full matrix least square method using SHELXL-97[8] WinGX system, Ver 1.70.01.[9] All the non-hydrogen atoms in the structure were located from the Fourier map and refined anisotropically. The hydrogen atoms were fixed by HFIX in their ideal positions and refined using riding model with isotropic thermal parameters. The crystal structure has been deposited to Cambridge Crystallographic Data Centre and allotted deposition number is ***2063896***.
Suitable single – crystals of **3ia** for X-ray analysis were grown up from slow crystallization in DCM/*n*-hexane (1:3, v/v) at 1 °C.

6.1 Crystal structure of 3ia:

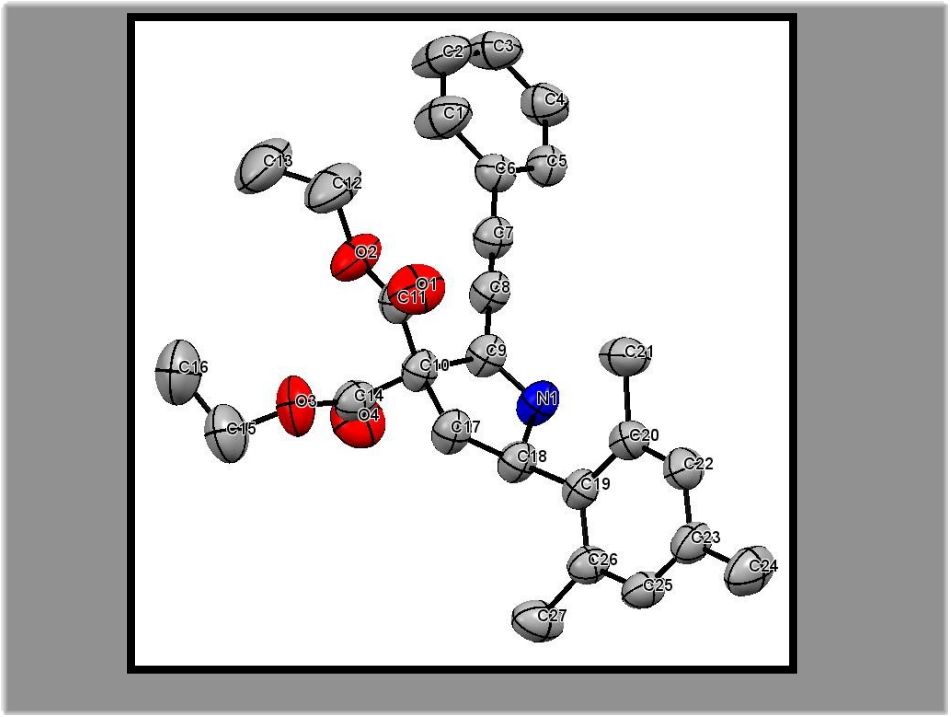


Table S1: Crystal data and structure refinement of 3ia.

CCDC No.	2063896
Formula	C27 H29 N O4
Formula weight	431.51
Crystal system	Triclinic
Space group	P-1
a, b, c (Å)	9.0386 (4), 10.9319 (5), 13.2664 (6)
α, β, γ (°)	75.768 (2), 71.588 (2), 87.843 (2)
V (Å3)	1204.42 (10)
Z	2
Calculated Density (g/cm^3)	1.190
Absorption coefficient (mm^{-1})	0.079
F(000)	460.0
Theta range for data collection:	2.2 to 27.1
Data set	-11: 11 ; -14: 14 ; -16: 17
Reflection	5296
Independent refl.	(R(int) = 0.034)
data [I > 2σ(I)]	3621
R indices (all data)	R = 0.0568, wR2 = 0.1655
S	1.024
Min. and Max. Resd. Dens. (e/Å3)	-0.19 and 0.26

Table S2: Bond lengths and bond angles of 3ia

Selected bond lengths [Å] of 3ia		*Selected bond angles [°] of 3ia*	
Atoms	**Bond lengths [Å]**	**Atoms**	**Bond Angles [°]**
N1-C9	1.276(2)	**N1-C9-C8**	121.96(17)
N1-C18	1.480(2)	**N1-C9-C10**	115.82(16)
O1-C11	1.188(3)	**C9-N1-C18**	108.93(16)
O4-C14	1.186(3)	**N1-C18-C17**	106.20(15)
C6-C7	1.433(3)	**N1-C18-C19**	114.11(15)
C7-C8	1.191(3)	**O1-C11-C10**	124.32(19)
C8-C9	1.433(3)	**O4-C14-C10**	124.91(19)
C10-C11	1.523(3)	**C6-C7-C8**	178.1(2)
C10-C14	1.523(3)	**C7-C8-C9**	177.5(2)
C10-C17	1.540(3)	**C8-C9-C10**	122.22(16)
C17-C18	1.537(3)	**C9-C10-C17**	100.35(14)
C18-C19	1.523(3)	**C11-C10-C14**	111.07(15)
		C11-C10-C17	112.70(15)
		C14-C10-C17	109.86(15)
		C10-C17-C18	103.99(15)
		C17-C18-C19	113.82(15)

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