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Blue Light Promoted Photolysis of Aryldiazoacetates

Supplementary Information

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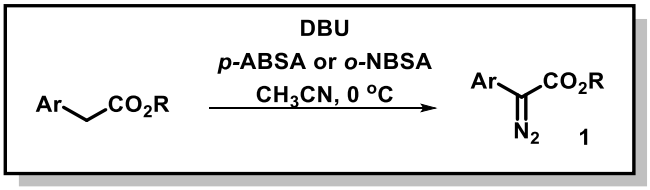
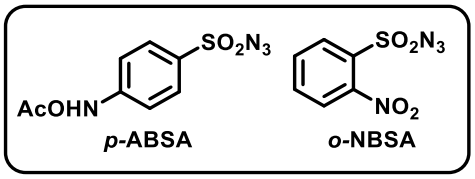
1. General Considerations

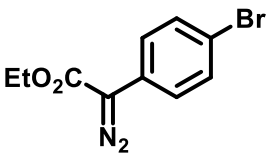
All reactions were conducted in oven-dried glassware under an inert atmosphere of dry argon. All reagents were used as received from commercial suppliers, unless otherwise stated. All solvents were purchased from Sigma Aldrich, dried over calcium hydride, and freshly distilled prior to use in synthesis. Proton (^{1}H) NMR spectra were recorded at 400 or 500 MHz on a Varian- 400 or an Inova-500 spectrometer, respectively. Carbon-13 (^{13}C) NMR spectra were recorded at 100 or 125 MHz on a Varian-400 or an Inova-500 spectrometer, respectively. NMR spectra were recorded in deuterated chloroform ($CDCl_3$) solutions, with residual chloroform (δ 7.26 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR) as the internal standard, and were reported in parts per million (ppm). Abbreviations for signal couplings are as follows: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sex, sextet; sep, septet; and m, multiplet. Coupling constants were taken from the spectra directly and are uncorrected. Infrared (IR) Spectra were collected on a Nicolet Impact Series 10 FT-IR. Mass spectrometric determinations were carried out on a Thermo Finnigan LTQ-FTMS spectrometer with nano-spray ionization (NSI). Analytical thin layer chromatography (TLC) was performed on silica gel plates using ultraviolet (UV) light or stained with either $KMnO_4$ or phosphomolybdic acid (PMA). Flash column chromatography was performed with silica gel 60 Å (230 – 400 mesh) according to the literature procedure.

2. Preparation of Aryldiazoacetates





ethyl 2-(4-bromophenyl)-2-diazoacetate (**1a**)

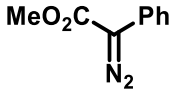


Prepared according to the literature.[1]

^{1}H (CDCl$_3$, 400MHz) δ: 7.47 (d, *J* = 8.8Hz, 2H), 7.35 (d, *J* = 8.8Hz, 2H), 4.31 (q, *J* = 7.0Hz, 2H), 1.32 (t, *J* = 7.0Hz, 3H).

^{13}C (CDCl$_3$, 100MHz) δ: 164.8, 132.0, 125.3, 124.8, 119.2, 61.1, 14.4.

methyl 2-diazo-2-phenylacetate (**1b**)

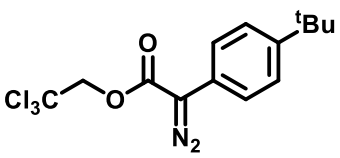


Prepared according to the literature.[2]

^{1}H (CDCl$_3$, 400MHz) δ: 7.50-7.40 (m, 2H), 7.41-7.38 (m, 2H), 7.21-7.18 (m, 1H), 3.87 (s, 3H).

^{13}C (CDCl$_3$, 100MHz) δ: 165.6, 128.9, 125.8, 125.5, 124.0, 52.0.

2,2,2-trichloroethyl 2-(4-(tert-butyl)phenyl)-2-diazoacetate (**1c**)



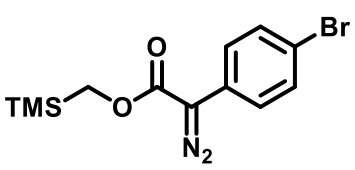
Prepared according to the literature.[1]

^{1}H (CDCl$_3$, 500MHz) δ: 7.46-7.42 (m, 4H), 4.92 (s, 2H), 1.33 (s, 9H).

^{13}C (CDCl$_3$, 125MHz) δ: 163.6, 149.6, 126.1, 124.0, 121.3, 95.1, 73.8, 34.5, 31.2.

[1] E. N. Bess, D. M. Guptill, H. M. L. Davies, M. S. Sigman, *Chem. Sci.* 2015, **6**, 3057.
[2] Z. Song, Y. Wu, T. Xin, C. Jin, X. Wen, H. Sun, Q.-L. Xu, *Chem. Commun.* 2016, **52**, 6079.

(trimethylsilyl)methyl 2-(4-bromophenyl)-2-diazoacetate (**1d**)

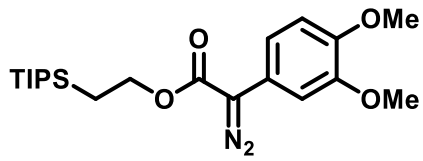


Prepared according to the literature.[3]

^{1}H (CDCl$_3$, 500 MHz) δ: 7.5 (d, *J* = 7.5Hz, 2H), 7.37 (d, *J* = 7.5Hz, 2H), 3.94 (s, 2H), 0.11 (s, 9H).

^{13}C (CDCl$_3$, 125 MHz) δ: 165.6, 132.0, 125.2, 124.9, 119.2, 58.3, 3.2.

2-(triisopropylsilyl)ethyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (**1e**)

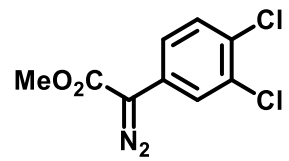


Prepared according to the literature.[3]

^{1}H (CDCl$_3$, 500 MHz) δ: 7.20 (s, 1H), 6.89 (d, *J* = 2.0Hz, 2H), 4.43-4.39 (m, 2H), 3.91 (s, 3H), 3.88 (s, 3H), 1.18-1.14 (m, 2H), 1.07 (s, 21H).

^{13}C (CDCl$_3$, 125 MHz) δ: 165.9, 149.4, 147.3, 117.6, 116.5, 111.6, 108.4, 63.4, 56.0, 55.9, 18.7, 11.1, 11.0.

methyl 2-diazo-2-(3,4-dichlorophenyl)acetate (**1f**)

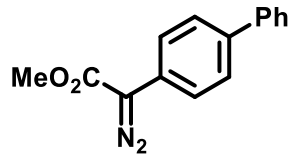


Prepared according to the literature.[1]

^{1}H (CDCl$_3$, 500 MHz) δ: 7.64 (d, *J* = 2.5Hz, 1H), 7.43 (d, *J* = 8.5Hz, 1H), 7.29 (dd, *J* = 2.5Hz, *J* = 8.5Hz, 1H), 3.88 (s, 3H).

^{13}C (CDCl$_3$, 125 MHz) δ: 164.8, 133.2, 130.7, 129.4, 126.0, 125.3, 122.6, 52.2.

methyl 2-([1,1'-biphenyl]-4-yl)-2-diazoacetate (**1g**)



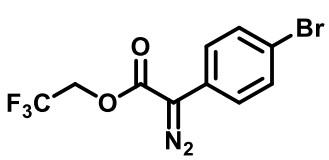
Prepared according to the literature.[4]

^{1}H (CDCl$_3$, 500 MHz) δ: 7.64 (d, *J* = 8.5Hz, 2H), 7.61-7.59 (m, 2H), 7.56 (d, *J* = 8.5Hz, 2H), 7.45 (t, *J* = 7.5Hz, 2H), 7.37-7.33 (m, 1H), 3.90 (s, 3H).

^{13}C (CDCl$_3$, 125MHz) δ: 165.6, 140.3, 138.6, 128.8, 127.6, 127.4, 126.9, 124.3 (2x), 52.1.

[3] D. M. Guptill, C. M. Cohen, H. M. L. Davies, *Org. Lett.* 2013, **15**, 6120.
[4] Z. Qu, W. Shi, J. Wang, *J. Org. Chem.* 2001, **66**, 8139.

2,2,2-trifluoroethyl 2-(4-bromophenyl)-2-diazoacetate (**1h**)

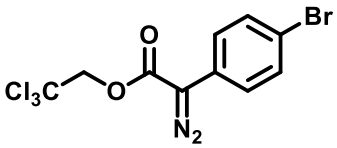


Prepared according to the literature.[1]

^{1}H (CDCl$_3$, 500MHz) δ: 7.53 (d, *J* = 8.5Hz, 2H), 7.34 (d, *J* = 8.5Hz, 2H), 4.65 (q, *J* = 8.5Hz, 2H).

^{13}C (CDCl$_3$, 125MHz) δ: 162.8, 132.2, 125.4, 123.7, 122.8 (q, *J* = 275.8Hz), 120.0, 60.4 (q, *J* = 36.8Hz).

2,2,2-trichloroethyl 2-(4-bromophenyl)-2-diazoacetate (**1i**)

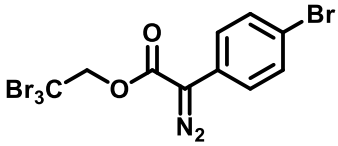


Prepared according to the literature.[1]

^{1}H (CDCl$_3$, 500MHz) δ: 7.52 (d, *J* = 9.0Hz, 2H), 7.37 (d, *J* = 9.0Hz, 2H), 4.91 (s, 2H).

^{13}C (CDCl$_3$, 125MHz) δ: 162.9, 132.2, 125.4, 123.8, 119.9, 94.9, 73.9.

2,2,2-tribromoethyl 2-(4-bromophenyl)-2-diazoacetate (**1j**)

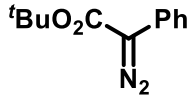


Prepared according to the literature.[1]

^{1}H (CDCl$_3$, 500MHz) δ: 7.52 (d, *J* = 8.5Hz, 2H), 7.39 (d, *J* = 8.5Hz, 2H), 5.09 (s, 2H).

^{13}C (CDCl$_3$, 125MHz) δ: 162.8, 132.2, 125.4, 123.9, 119.9, 76.7, 35.7.

tert-butyl 2-diazo-2-phenylacetate (**1k**)



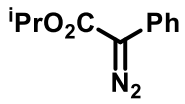
Prepared according to the literature.[5]

^{1}H (CDCl$_3$, 500 MHz) δ: 7.47 (d, *J* = 7.5Hz, 2H), 7.37 (t, *J* = 7.5Hz, 2H), 7.16 (t, *J* = 7.5Hz, 1H), 1.56 (s, 9H).

^{13}C (CDCl$_3$, 125 MHz) δ: 164.6, 128.8, 126.1, 125.5, 124.0, 82.0, 28.4.

[5] S. I. Lee, G.-S. Hwang, D. H. Ryu, *J. Am. Chem. Soc.* 2013, **135**, 7126.

isopropyl 2-diazo-2-phenylacetate (**1l**)

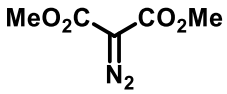


Prepared according to the literature.[6]

^{1}H ($CDCl_3$, 500MHz) δ: 7.50-7.48 (m, 2H), 7.40-7.37 (m, 2H), 7.20-7.17 (m, 1H), 5.22 (hept, *J* = 6.3Hz, 1H), 1.33 (d, *J* = 6.3Hz, 6H).

^{13}C ($CDCl_3$, 125 MHz) δ: 164.8, 128.9, 125.8, 125.7, 123.9, 68.7, 22.1.

dimethyl 2-diazomalonate **(2b)**



Prepared according to the literature.[7]

^{1}H ($CDCl_3$, 500MHz) δ: 3.82 (s, 6H).

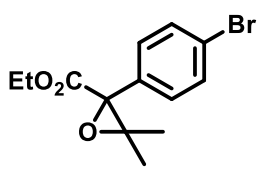
^{13}C ($CDCl_3$, 125MHz) δ: 161.4, 52.5.

3. Trapping Reactions: General Procedure

General Procedure: Under air, a 4 mL-vial is charged with a diazocompound (0.1 mmol, 1 eq), and DCM (1 mL, 0.1M) as solvent or neat, and the trapping agent (0.2 – 0.5 mmol, 2 - 5 eq; or 10 mmol, 100 eq, if neat reaction). The vial is closed and allowed to stir overnight, at rt, under blue light irradiation (using two lamps, blue LED, 15W each). Then, the reaction mixture is concentrated under reduced pressure and the crude material is purified by flash column chromatography to afford the corresponding target compounds in the stated yields.

3.1 Preliminary Experiments: Products Derived from the Reaction of Aryldiazoacetates with Solvents

ethyl 2-(4-bromophenyl)-3,3-dimethyloxirane-2-carboxylate (**3a**)



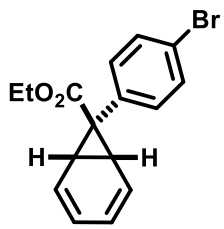
The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol) in acetone (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as

[6] O. A. Davis, R. A. Croft, J. A. Bull, *Chem. Commun.* 2015, **51**, 15446.
[7] S. Racine, B. Hegedüs, R. Scopelliti, J. Waser, *Chem. Eur. J.* 2016, **22**, 11997.

an yellowish oil (10 mg, 33%).

^{1}H ($CDCl_3$, 600MHz) δ: 7.49 (d, *J* = 8.4Hz, 2H), 7.45 (d, *J* = 8.4Hz, 2H), 4.23 (q, *J* = 7.2Hz, 2H), 1.45 (s, 3H), 1.28 (t, *J* = 7.2Hz, 3H), 1.03 (s, 3H).
^{13}C ($CDCl_3$, 150MHz) δ: 168.7, 133.4, 131.3, 129.2, 122.5, 68.0, 64.7, 61.7, 21.1, 20.3, 14.1.
IR (neat, ATR): 2980 (w), 2928 (w), 1748 (s), 1728 (s), 1489 (m), 1455 (w), 1396 (w), 1378 (w), 1294 (m), 1267 (m), 1219 (s), 1122 (m), 1082 (s), 1071 (s), 1011 (s).
HRMS (NSI+): Calcd. for $[C_{13}H_{15}BrO_3+H]^+$: 299.0277 Found: 299.0278.

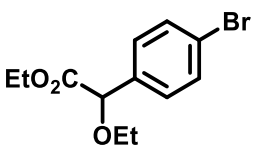
ethyl 7-(4-bromophenyl)bicyclo[4.1.0]hepta-2,4-diene-7-carboxylate (**3b**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol) in benzene (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a singe diastereoisomer, a transparent oil (10 mg, 31%). The relative stereochemistry is inferred in analogy to **5g**.

^{1}H ($CDCl_3$, 500MHz) δ: 7.27 (d, *J* = 8.5Hz, 2H), 7.03 (d, *J* = 8.5Hz, 2H), 6.27-6.24 (m, 2H), 6.02 (dd, *J* = 6.0Hz, *J* = 3.0Hz, 2H), 4.35 (d, *J* = 6.0Hz, 2H), 4.11 (q, *J* = 7.0Hz, 2H), 1.15 (t, *J* = 7.0Hz, 3H).
^{13}C ($CDCl_3$, 125MHz) δ: 174.8, 134.8, 132.8, 130.2, 127.6, 125.0, 120.7, 74.4, 61.7, 37.7, 14.1.
IR (neat, ATR): 3045 (w), 2997 (w), 2975 (w), 2957 (w), 2921 (w), 2161 (w), 2035 (w), 1692 (s), 1589 (w), 1492 (w), 1481 (w), 1445 (w), 1423 (w), 1396 (w), 1366 (w), 1295 (w), 1238 (s), 1171 (w), 1141 (w).
HRMS (NSI+): Calcd. for $[C_{16}H_{15}BrO_2+H]^+$: 319.0328 Found: 319.0329.

ethyl 2-(4-bromophenyl)-2-ethoxyacetate (**4a**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol) in EtOH (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (26 mg, 90%).

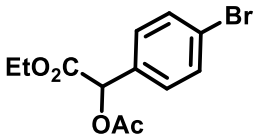
^{1}H ($CDCl_3$, 500MHz) δ: 7.49 (d, *J* = 8.5Hz, 2H), 7.34 (d, *J* = 8.5Hz, 2H), 4.82 (s, 1H), 4.22-4.17 (m, 1H), 4.16-4.11 (m, 1H), 3.63-3.57 (m, 1H), 3.53-3.47 (m, 1H), 1.27 (t, *J* = 7.0Hz, 3H), 1.21 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 170.6, 135.9, 131.7, 128.7, 122.6, 80.3, 65.4, 61.3, 15.1, 14.1.

IR (neat, ATR): 2978 (w), 2935 (w), 2875 (w), 1745 (s), 1732 (s), 1591 (w), 1487 (m), 1487 (m), 1399 (m), 1368 (w), 1334 (w), 1254 (w), 1204 (m), 1175 (s), 1109 (s).

HRMS (NSI+): Calcd. for: $[C_{12}H_{15}BrO_2+H]^+$: 282.0277 Found: 282.0288.

ethyl 2-acetoxy-2-(4-bromophenyl)acetate (**4b**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol) in AcOH (1 mL, 0.1M). The reaction mixture is concentrated under reduced pressure to afford the pure compound as a transparent oil (29 mg, 98%).

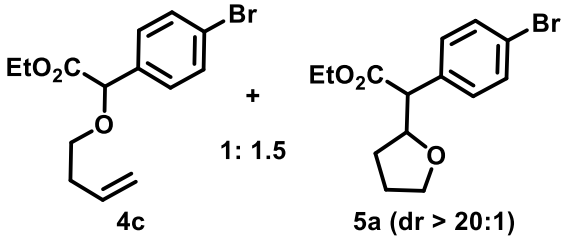
^{1}H ($CDCl_3$, 500MHz) δ: 7.52 (d, *J* = 8.5Hz, 2H), 7.35 (d, *J* = 8.5Hz, 2H), 5.86 (s, 1H), 4.25-4.18 (m, 1H), 4.17-4.11 (m, 1H), 2.19 (s, 3H), 1.22 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 170.1, 168.4, 132.9, 131.9, 129.2, 123.4, 73.8, 61.9, 20.7, 14.0.

IR (neat, ATR): 2982 (w), 2938 (w), 1741 (s), 1489 (m), 1489 (m), 1445 (w), 1371 (m), 1292 (w), 1227 (s), 1207 (s), 1178 (s), 1069 (s), 1054 (s), 1178 (s), 1069 (s), 1012 (s).

HRMS (NSI+): Calcd. for: $[C_{12}H_{13}BrO_4+Na]^+$: 322.9889 Found: 322.9895

ethyl 2-(4-bromophenyl)-2-(but-3-en-1-yloxy)acetate (**4c**) and ethyl 2-(4-bromophenyl)-2-(tetrahydrofuran-2-yl)acetate (**5a**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol) in THF (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords an inseparable 1:1.5 mixture of isomers **4c**:**5a**, as a pale yellow oil (18 mg, 57%).

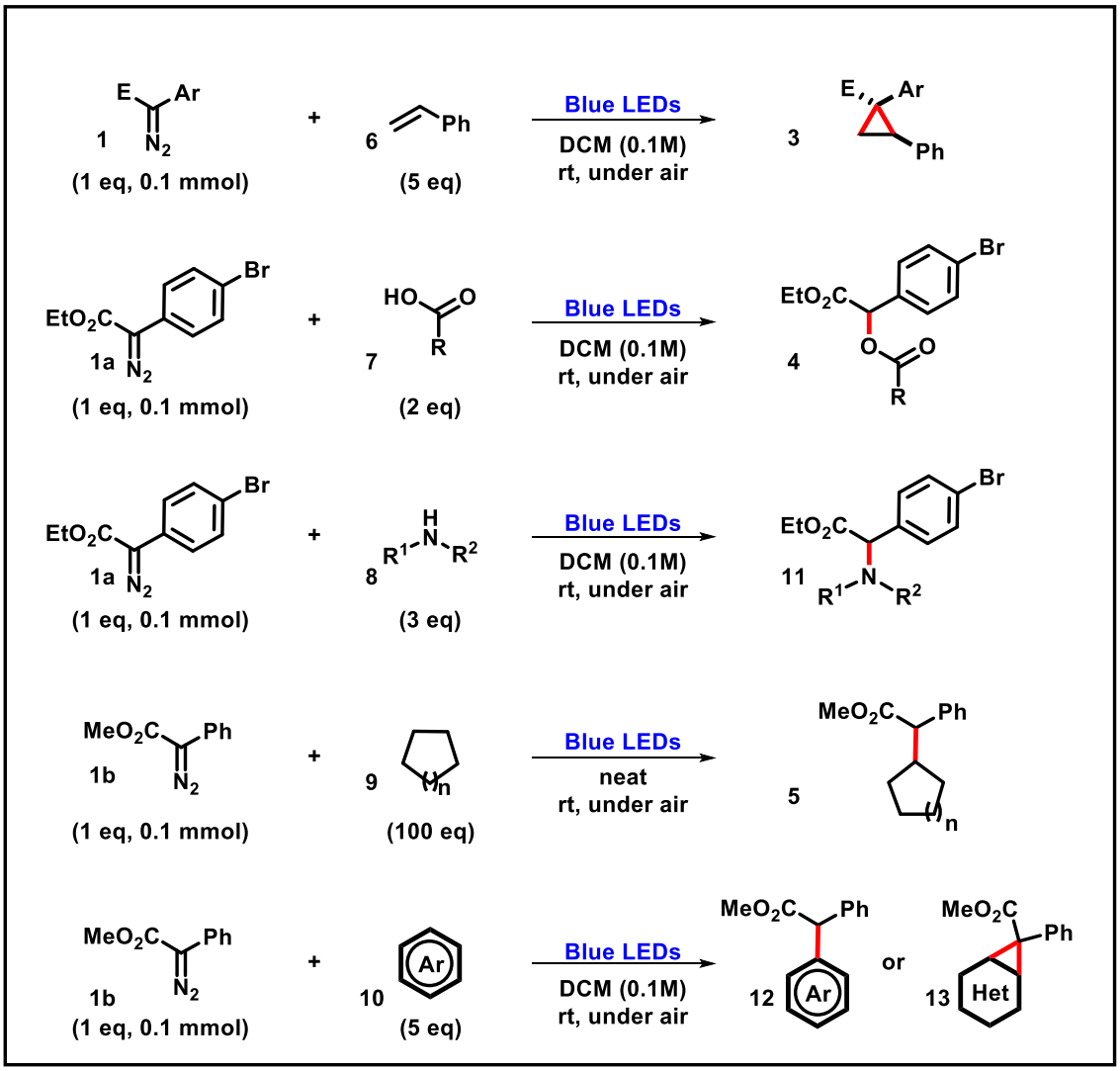
^{1}H ($CDCl_3$, 500MHz) δ: 7.48 (d, *J* = 8.5Hz, 0.8H), 7.46 (d, *J* = 8.5Hz, 1.2H), 7.40 (d, *J* = 8.5Hz, 1.2H), 7.34 (d, *J* = 8.5Hz, 0.8H), 5.86-5.78 (m, 0.4H), 5.10 (dq, *J* = 17.0Hz, *J* = 1.7Hz, 0.4H), 5.04 (dq, *J* = 10.0Hz, *J* = 1.7Hz, 0.4Hz), 4.82 (s, 0.4H), 4.21-4.13 (m, 2.0H), 3.98-3.94 (m, 0.6H), 3.78-3.74 (m, 0.6H), 3.62-3.59 (m, 0.4H), 3.50-3.46 (m, 0.4H), 2.55-2.51 (m, 0.6H), 2.44-2.39 (m, 0.8H), 1.81-1.75 (m, 1.2H), 1.66-1.58 (m, 1.8H), 1.21 (t, *J* = 7.5Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 172.1, 170.4, 140.5, 135.7, 134.6, 131.7, 131.4, 128.7, 127.0, 122.6, 121.8, 116.7, 80.4, 80.3, 69.3, 65.0, 61.5, 61.3, 34.0, 33.7, 25.0, 20.7, 14.1, 14.0.

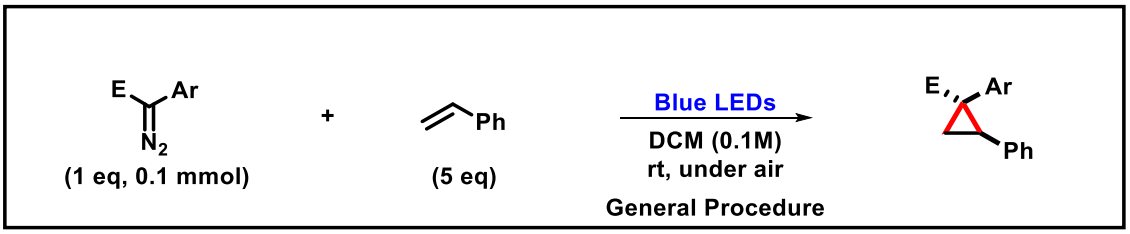
IR (neat, ATR): 3075 (w), 2977 (w), 2939 (w), 2866 (w), 1728 (s), 1641 (w), 1588 (w), 1488 (m), 1443 (w), 1396 (w), 1367 (w), 1289 (w), 1239 (s), 1218 (m), 1175 (s), 1099 (s), 1072 (s), 1053 (s), 1031 (s), 1009 (s).

HRMS (NSI+): Calcd. for $[C_{14}H_{17}O_3Br+H]^+$: 313.0434 Found: 313.0435.

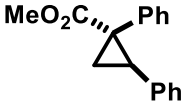
3.2 Trapping Reactions



3.3 Cyclopropanation Reactions of Styrene



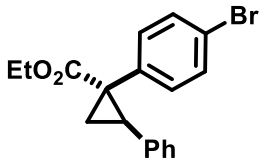
methyl 1,2-diphenylcyclopropane-1-carboxylate (**3c**)



The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq), styrene (58 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Analysis of the crude reaction mixture by ^{1}H NMR reveals 9:1 dr. Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (20 mg, 80%, 10:1 dr).

^{1}H ($CDCl_3$, 500MHz) δ: major diastereoisomer: 7.14-7.13 (m, 3H), 7.07-7.03 (m, 5H), 6.78-6.77 (m, 2H), 3.67 (s, 3H), 3.12 (dd, *J* = 7.5Hz, *J* = 6.0Hz, 1H), 2.14 (dd, *J* = 7.5Hz, *J* = 4.0Hz, 1H), 1.88 (dd, *J* = 6.0Hz, *J* = 4.0Hz, 1H).
minor diastereoisomer: 7.52 (d, *J* = 6.0Hz, 2H), 7.39-7.36 (m, 4H), 7.34-7.30 (m, 3H), 7.26-7.23 (m, 1H), 3.31 (s, 3H), 2.88 (t, *J* = 7.0Hz, 1H), 2.35 (dd, *J* = 7.0Hz, *J* = 4.5Hz, 1H), 1.63 (dd, *J* = 7.0, *J* = 4.0Hz, 1H).
^{13}C ($CDCl_3$, 125MHz) δ: major diastereoisomer: 174.4, 136.4, 134.7, 132.0, 128.1, 127.7 (x2), 127.1, 126.3, 52.7, 37.4, 33.2, 20.5. minor diastereoisomer: 171.1, 140.3, 136.6, 130.3, 129.0, 128.4, 128.1, 127.4, 126.8, 52.0, 38.2, 33.2, 18.3.
IR (neat, ATR): 3028 (w), 2950 (w), 1714 (s), 1603 (w), 1498 (w), 1433 (w), 1376 (w), 1313 (w), 1254 (s), 1211 (w), 1191 (w), 1161 (m), 1093 (w), 1076 (w), 1055 (w), 1029 (w), 992 (w).
HRMS (APCI+): Calcd. for $[C_{17}H_{16}O_2+H]^+$: 253.1223 Found: 253.1223.

ethyl 1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (**3d**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), styrene (58 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Analysis of the crude reaction mixture by ^{1}H NMR reveals 11:1 dr. Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a pale yellow oil (26 mg, 75%, > 20:1 dr).

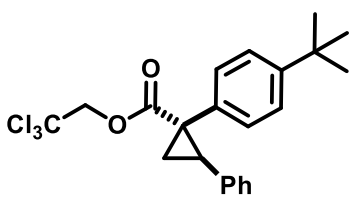
^{1}H ($CDCl_3$, 500MHz) δ**:** 7.25 (d, *J* = 8.5Hz, 2H), 7.10-7.08 (m, 3H), 6.90 (d, *J* = 8.5Hz, 2H), 6.79-6.77 (m, 2H), 4.20-4.07 (m, 2H), 3.10 (dd, *J* = 9.0Hz, *J* = 7.0Hz, 1H), 2.13 (dd, *J* = 9.0Hz, *J* = 5.0Hz, 1H), 1.83 (dd, *J* = 7.0Hz, *J* = 5.0Hz, 1H), 1.18 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ**:** 173.2, 136.0, 134.1, 133.5, 130.8, 128.0, 127.9, 126.5, 121.0, 61.4, 36.9, 32.9, 20.0, 14.1.

IR (neat, ATR): 2980 (w), 1712 (s), 1604 (w), 1488 (m), 1456 (w), 1395 (w), 1375 (w), 1300 (w), 1251 (s), 1210 (m), 1159 (s), 1089 (m), 1071 (m), 1054 (w), 1023 (w), 1011 (m), 975 (m).

HRMS (APCI+): Calcd. for $[C_{18}H_{17}BrNO_2+H]^+$: 345.0485 Found: 345.0484.

2,2,2-trichloroethyl 1-(4-(tert-butyl)phenyl)-2-phenylcyclopropane-1-carboxylate (**3e**)



The general procedure is employed with diazocompound **1c** (35 mg, 0.1 mmol, 1 eq), styrene (58 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Analysis of the crude reaction mixture by ^{1}H NMR reveals > 20:1 dr. Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a white solid (42 mg, 99%, > 20:1 dr).

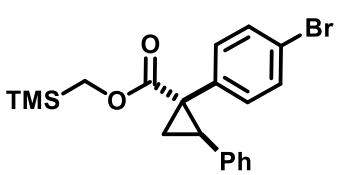
^{1}H ($CDCl_3$, 500MHz) δ**:** 7.14 (d, *J* = 8.5Hz, 2H), 7.08-7.06 (m, 3H), 6.98 (d, *J* = 8.5Hz, 2H), 4.84 (d, *J* = 12.0Hz, 2H), 4.66 (d, *J* = 12.0Hz, 2H), 3.19 (dd, *J* = 9.0Hz, *J* = 7.5Hz, 1H), 2.28 (dd, *J* = 9.0Hz, *J* = 5.0Hz, 1H), 1.98 (dd, *J* = 7.5Hz, *J* = 5.0Hz, 1H), 1.23 (s, 9H).

^{13}C ($CDCl_3$, 125MHz) δ**:** 172.2, 150.1, 135.9, 131.5, 130.5, 128.1, 127.7, 126.4, 124.5, 95.1, 74.3, 36.9, 34.4, 33.7, 31.2, 20.3.

IR (neat, ATR): 3030 (w), 2964 (w), 2160 (w), 2033 (w), 1977 (w), 1728 (s), 1605 (w), 1511 (w), 1498 (w), 1457 (w), 1383 (w), 1328 (w), 1312 (w), 1250 (s), 1212 (s), 1164 (s), 1110 (m), 1096 (w), 1050 (m), 1015 (w).

HRMS (NSI+): Calcd. for $[C_{22}H_{23}Cl_3O_2+H]^+$: 425.0836 Found: 425.0840.

(trimethylsilyl)methyl 1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (**3f**)



The general procedure is employed with diazocompound **1d** (33 mg, 0.1 mmol, 1 eq), styrene (58 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Analysis of the crude reaction mixture by ^{1}H NMR reveals 16:1 dr. Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as an yellowish solid (37 mg, 92%, 16:1 dr).

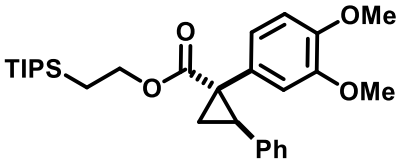
^{1}H ($CDCl_3$, 500MHz) δ**:** 7.24 (d, *J* = 8.5Hz, 2H), 7.11-7.09 (m, 3H), 6.87 (d, *J* = 8.5Hz, 2H), 6.79-6.77 (m, 2H), 3.78 (d, *J* = 14.0Hz, 1H), 3.69 (d, *J* = 14Hz, 1H), 3.08 (dd, *J* = 9.0Hz, *J* = 7.0Hz, 1H), 2.12 (dd, *J* = 9.0Hz, *J* = 5.0Hz, 1H), 1.81 (dd, *J* = 7.0Hz, *J* = 5.0Hz, 1H), -0.05 (s, 9H).

^{13}C ($CDCl_3$, 125MHz) δ**:** 174.0, 136.0, 134.3, 133.5, 130.7, 128.0, 127.9, 126.5, 120.9, 58.7, 37.0, 32.9, 20.1, -3.3.

IR (neat, ATR): 3102 (w), 2955 (w), 2361 (w), 2159 (w), 2030 (w), 1816 (w), 1708 (s), 1605 (w), 1500 (w), 1487 (m), 1457 (w), 1432 (w), 1395 (w), 1379 (w), 1331 (w), 1290 (s), 1238 (s), 1209 (s), 1166 (s), 1100 (m), 1071 (m), 1033 (w), 1011 (s).

HRMS(NSI+): Calcd. for $[C_{20}H_{23}BrO_2Si+H]^+$: 403.0724 Found: 403.0726.

2-(triisopropylsilyl)ethyl 1-(3,4-dimethoxyphenyl)-2-phenylcyclopropane-1-carboxylate (**3g**)



The general procedure is employed with diazocompound **1e** (41 mg, 0.1 mmol, 1 eq), styrene (58 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Analysis of the crude reaction mixture by ^{1}H NMR reveals > 20:1 dr. Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a transparent oil (18 mg, 37%, > 20:1 dr).

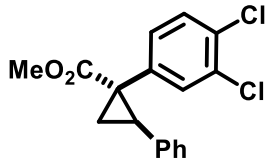
^{1}H ($CDCl_3$, 500MHz) δ: 7.08-7.06 (m, 3H), 6.81-6.79 (m, 2H), 6.70-6.66 (m, 2H), 6.37 (d, *J* = 1.0Hz, 1H), 4.28-4.18 (m, 2H), 3.81 (s, 3H), 3.56 (s, 3H), 3.07 (dd, *J* = 9.0Hz, *J* = 7.0Hz, 1H), 2.12 (dd, *J* = 9.0Hz, *J* = 4.5Hz, 1H), 1.81 (dd, *J* = 7.0Hz, *J* = 4.5Hz, 1H),1.04-1.00 (m, 23H).

^{13}C ($CDCl_3$, 125MHz) 2C cannot be unambiguouly assigned, δ: 174.0, 147.8, 136.7, 128.0, 127.7, 127.5, 126.2, 124.1, 115.5, 110.2, 63.8, 55.6 (x2), 37.3, 20.6, 18.7, 10.9, 10.7.

IR (neat, ATR): 2941 (m), 2865 (m), 1708 (s), 1590 (w), 1518 (s), 1463 (s), 1413 (s), 1413 (m), 1383 (w), 1341 (w), 1251 (s), 1229 (m), 1177 (s), 1154 (s), 1140 (s), 1090 (m), 1030 (s), 916 (m).

HRMS(APCI-): Calcd. for $[C_{29}H_{42}O_4Si\text{-}H]^-$: 481.2780 Found: 481.2782.

methyl 1-(3,4-dichlorophenyl)-2-phenylcyclopropane-1-carboxylate (**3h**)



The general procedure is employed with diazocompound **1f** (24 mg, 0.1 mmol, 1 eq), styrene (58 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Analysis of the crude reaction mixture by ^{1}H NMR reveals 6:1 dr. Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a transparent oil (24 mg, 76%, 13:1 dr).

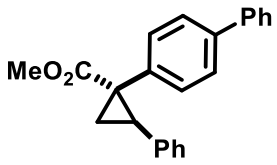
^{1}H ($CDCl_3$, 500MHz) δ: 7.17-7.16 (m, 2H), 7.13-7.10 (m, 3H), 6.82-6.79 (m, 3H), 3.68 (s, 3H), 3.13 (dd, *J* = 9.0Hz, *J* = 7.5Hz, 1H), 2.15 (dd, *J* = 9.0Hz, *J* = 5.0Hz, 1H), 1.85 (dd, *J* = 7.5Hz, *J* = 5.0Hz, 1H).

^{13}C ($CDCl_3$, 125MHz) δ: 173.3, 135.4, 135.3, 133.7, 131.4, 131.2, 129.6, 128.1, 128.0 (x2), 126.8, 52.7, 36.3, 33.3, 20.1.

IR (neat, ATR): 3030 (w), 2951 (w), 1719 (s), 1603 (w), 1557 (w), 1499 (w), 1474 (m), 1456 (m), 1433 (m), 1379 (m), 1332 (w), 1312 (w), 1257 (s), 1201 (s), 1192 (m), 1163 (s), 1134 (s), 1092 (s), 1057 (w), 1031 (m), 994 (w).

HRMS (NSI+): Calcd. for $[C_{17}H_{14}Cl_2O_2+H]^+$: 321.0444 Found: 321.0445.

methyl 1-([1,1'-biphenyl]-4-yl)-2-phenylcyclopropane-1-carboxylate (**3i**)



The general procedure is employed with diazocompound **1g** (25 mg, 0.1 mmol, 1 eq), styrene (58 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Analysis of the crude reaction mixture by ^{1}H NMR reveals 13:1 dr. Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a white solid (25 mg, 77%, > 20:1 dr).

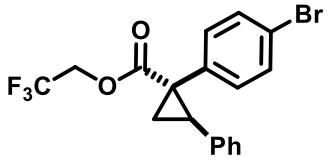
^{1}H ($CDCl_3$, 500MHz) δ: 7.54 (d, *J* = 6.0Hz, 2H), 7.41 -7.38 (m, 4H), 7.22 (tt, *J* = 6.0Hz, *J* = 1.0Hz, 1H), 7.10 (d, *J* = 7.0Hz, 2H), 7.09-7.07 (m, 3H), 6.83-6.81 (m, 2H), 3.70 (s, 3H), 3.15 (dd, *J* = 7.5Hz, *J* = 6.0Hz, 1H), 2.19 (dd, *J* = 7.5Hz, *J* = 4.0Hz, 1H), 1.92 (dd, *J* = 6.0Hz, *J* = 4.0Hz, 1H).

^{13}C ($CDCl_3$, 125MHz) δ: 174.4, 140.7, 139.6, 136.3, 133.9, 132.3, 128.7, 128.1, 127.8, 127.2, 127.0, 126.4 (x2), 52.7, 37.1, 33.3, 20.6.

IR (neat, ATR): 3034 (w), 2957 (w), 2160 (w), 2029 (w), 1976 (w), 1713 (s), 1685 (m), 1601 (w), 1561 (w), 1498 (w), 1488 (m), 1458 (w), 1430 (w), 1404 (w), 1343 (w), 1295 (w), 1253 (s), 1207 (m), 1189 (m), 1164 (s), 1109 (w), 1089 (s), 1071 (w).

HRMS (APCI+): Calcd. for $[C_{23}H_{20}O_2+H]^+$: 329.1536 Found: 329.1538.

2,2,2-trifluoroethyl 1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (**3j**)



The general procedure is employed with diazocompound **1h** (32 mg, 0.1 mmol, 1 eq), styrene (58 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Analysis of the crude reaction mixture by ^{1}H NMR reveals 15:1 dr. Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (36 mg, 90%, 17:1 dr).

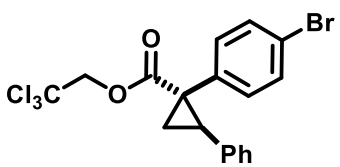
^{1}H (CDCl$_3$, 600MHz) δ: 7.18 (d, *J* = 8.4Hz, 2H), 7.03-7.02 (m, 3H), 6.82 (d, *J* = 8.4Hz, 2H), 6.72-6.71 (m, 2H), 4.50-4.43 (m, 1H), 4.35-4.29 (m, 1H), 3.09 (dd, *J* = 9.6Hz, *J* = 7.8Hz, 1H), 2.14 (dd, *J* = 9.6Hz, *J* = 5.4Hz, 1H), 1.88 (dd, *J* = 7.8Hz, *J* = 5.4Hz, 1H).

^{13}C (CDCl$_3$, 150MHz) δ: 171.7, 135.1, 133.5, 132.8, 131.0, 128.1, 128.0, 126.9, 122.7 (q, *J* = 276.0Hz), 121.6, 60.9 (q, *J* = 36.0Hz), 36.4, 33.9, 20.4.

IR (neat, ATR): 3033 (w), 1735 (s), 1594 (w), 1490 (m), 1456 (w), 1396 (m), 1283 (s), 1234 (s), 1210 (w), 1149 (s), 1110 (m), 1090 (s), 1072 (s), 1028 (w), 1011 (s), 971 (s).

HRMS (NSI+): Calcd. for $[C_{18}H_{14}BrF_3O_2+H]^+$: 399.0202 Found: 399.0205.

2,2,2-trichloroethyl 1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (**3k**)



The general procedure is employed with diazocompound **1i** (37 mg, 0.1 mmol, 1 eq), styrene (58 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Analysis of the crude reaction mixture by ^{1}H NMR reveals 19:1 dr. Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (42 mg, 94%, 19:1 dr).

^{1}H (CDCl$_3$, 500MHz) δ: 7.26 (d, *J* = 8.5Hz, 2H), 7.13-7.10 (m, 3H), 6.94 (d *J* = 8.5Hz, 2H), 6.82-6.80 (m, 2H), 4.84 (d, *J* = 12.0Hz, 1H), 4.65 (d, *J* = 12.0Hz, 1H),

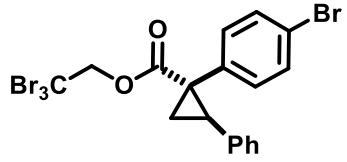
3.22 (dd, *J* = 9.5Hz, *J* = 7.5Hz, 1H), 2.29 (dd, *J* = 9.5Hz, *J* = 5.0Hz, 1H), 1.98 (dd, *J* = 7.5Hz, *J* = 5.0Hz, 1H).

^{13}C ($CDCl_3$, 125MHz) δ: 171.6, 135.2, 133.6, 132.9, 130.9, 128.1, 128.0, 126.9, 121.5, 94.9, 74.4, 36.6, 33.9, 20.2.

IR (neat, ATR): 3031 (w), 1732 (s), 1593 (w), 1489 (m), 1455 (w), 1432 (w), 1396 (w), 1377 (w), 1239 (s), 1209 (s), 1151 (s), 1093 (s), 1071 (s), 1051 (s), 1011 (s), 970 (w).

HRMS(NSI-): Calcd. for $[C_{18}H_{14}BrCl_3O_2+Cl]^-$: 480.8937 Found: 480.8941.

2,2,2-tribromoethyl 1-(4-bromophenyl)-2-phenylcyclopropane-1-carboxylate (**3l**)



The general procedure is employed with diazocompound **1j** (50 mg, 0.1 mmol, 1 eq), styrene (58 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Analysis of the crude reaction mixture by ^{1}H NMR reveals 7:1 dr. Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (43 mg, 75%, 14:1 dr).

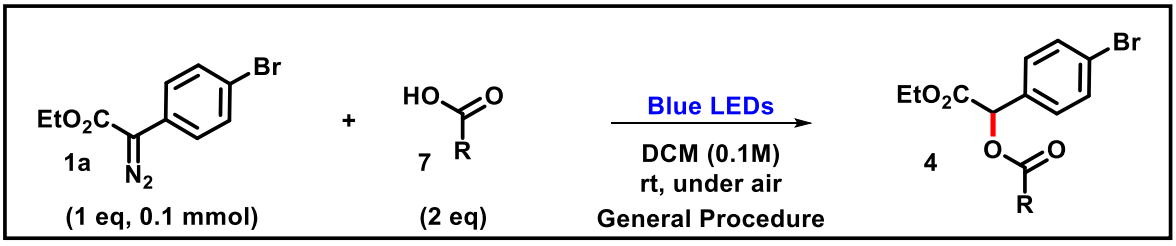
^{1}H ($CDCl_3$, 600MHz) δ: 7.19 (d, *J* = 8.4Hz, 2H), 7.05-7.02 (m, 3H), 6.89 (d, *J* = 8.4Hz, 2H), 6.75-6.73 (m, 2H), 4.92 (d, *J* = 12.0Hz, 1H), 4.75 (d, *J* = 12.0Hz, 1H), 3.18 (dd, *J* = 9.6Hz, *J* = 7.2Hz, 1H), 2.24 (dd, *J* = 9.6Hz, *J* = 5.4Hz, 1H), 1.91 (dd, *J* = 7.2Hz, *J* = 5.4Hz, 1H).

^{13}C ($CDCl_3$, 150MHz) δ (1C cannot be unambigously assigned): 171.4, 135.3, 133.8, 133.0, 130.9, 128.1 (x2), 126.9, 121.5, 36.7, 35.8, 34.0, 20.2.

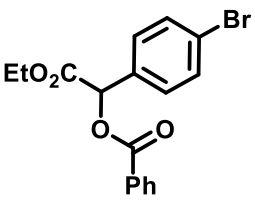
IR (neat, ATR): 2940 (w), 2109 (w), 1730 (s), 1593 (w), 1488 (m), 1455 (w), 1395 (w), 1362 (w), 1239 (s), 1208 (m), 1149 (s), 1110 (w), 1089 (s), 1071 (s), 1046 (m), 1010 (s), 969 (m).

HRMS (NSI+): Calcd. for $[C_{18}H_{14}Br_4O_2+H]^+$: 578.7800 Found: 578.7803.

3.4 O-H Insertion of Carboxylic Acids



1-(4-bromophenyl)-2-ethoxy-2-oxoethyl benzoate (**4d**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), $PhCO_2H$ **7a** (24 mg, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a pale yellow oil (33 mg, 91%).

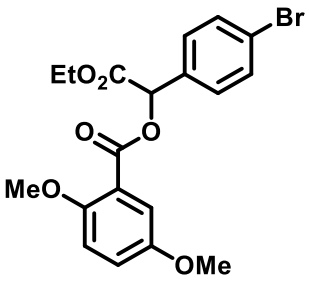
^{1}H (CDCl$_3$, 500MHz) δ: 8.12 (d, *J* = 7.0Hz, 2H), 7.62-7.55 (m, 3H), 7.48-7.45 (m, 4H), 6.10 (s, 1H), 4.29-4.22 (m, 1H), 4.22-4.15 (m, 1H), 1.24 (t, *J* = 7.0Hz, 3H).

^{13}C (CDCl$_3$, 125MHz) δ: 168.3, 165.7, 133.5, 133.2, 132.0, 129.9, 129.2, 129.1, 128.5, 123.4, 74.3, 61.9, 14.0.

IR (neat, ATR): 3063 (w), 2981 (w), 2928 (w), 2851 (w), 1752 (m), 1722 (s), 1601 (w), 1489 (m), 1465 (w), 1315 (w), 1296 (w), 1274 (s), 1296 (s), 1210 (s), 1175 (s), 1106 (s), 1069 (s).

HRMS (NSI+): Calcd. for $[C_{17}H_{15}O_4Br+H]^+$:363.0227 Found: 363.0228.

1-(4-bromophenyl)-2-ethoxy-2-oxoethyl 2,5-dimethoxybenzoate (**4e**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), 2,5-dimethoxybenzoic acid (36 mg, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2

Hex:AcOEt) affords the title compound as a pale yellow oil (32 mg, 75%).

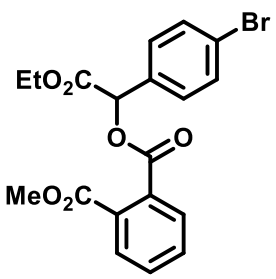
^{1}H ($CDCl_3$, 500MHz) δ: 7,54 (d, *J* = 8.5Hz, 2H), 7.48 (d, *J* = 3.5Hz, 1H), 7.47 (d, *J* = 8.5Hz, 2H), 7.07 (dd, *J* = 9.2Hz, *J* = 3.5Hz, 1H), 6.94 (d, *J* = 9.2Hz, 1H), 6.08 (s, 1H), 4.29-4.15 (m, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 1.24 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 168.4, 164.8, 154.2, 153.0, 133.2, 131.9, 129.1, 123.2, 120.3, 119.0, 116.6, 114.0, 74.2, 61.9, 56.8, 55.9, 14.0.

IR (neat, ATR): 2959 (w), 2915 (w), 2849 (w), 2846 (w), 1734 (s), 1707 (m), 1498 (s), 1464 (m), 1417 (w), 1370 (w), 1342 (w), 1319 (w), 1282 (w), 1239 (m), 1203 (s), 1176 (s), 1070 (s), 1040 (s), 1012 (s).

HRMS (APCI+): Calcd for $[C_{19}H_{19}BrO_6]^+$: 422.0359 Found: 422.0360.

1-(4-bromophenyl)-2-ethoxy-2-oxoethyl methyl phthalate (**4f**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), 2-(methoxycarbonyl)benzoic acid (36 mg, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as an yellow oil (35 mg, 83%).

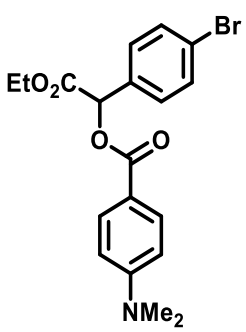
^{1}H ($CDCl_3$, 500MHz) δ: 7.87-7.84 (m, 1H), 7.76-7.72 (m, 1H), 7.59-7.56 (m, 2H), 7.54 (d, *J* = 8.3Hz, 2H), 7.40 (d, *J* = 8.3Hz, 2H), 6.10 (s, 1H), 4.28-4.22 (m, 1H), 4.22-4.16 (m, 1H), 3.75 (s, 3H), 1.25 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 168.0, 167.7, 166.6, 132.7, 132.1, 132.0, 131.6, 131.2, 130.9, 129.4, 129.3, 129.0, 123.5, 74.7, 62.0, 52.6, 14.0.

IR (neat, ATR): 2952 (w), 1725 (s), 1596 (w), 1579 (w), 1489 (w), 1433 (w), 1370 (w), 1341 (w), 1279 (s), 1255 (s), 1210 (s), 1180 (m), 1117 (s), 1070 (s), 1032 (m), 1012 (s).

HRMS (NSI+): Calcd. for: $[C_{19}H_{17}O_6Br+H]^+$: 421.0281 Found: 421.0289.

1-(4-bromophenyl)-2-ethoxy-2-oxoethyl 4-(dimethylamino)benzoate (**4g**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), 4-(dimethylamino)benzoic acid (33 mg, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a white solid (25 mg, 61%).

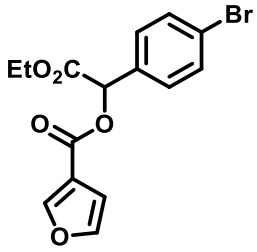
^{1}H ($CDCl_3$, 500MHz) δ: 7.97 (d, *J* = 9.0Hz, 2H), 7.54 (d, *J* = 8.5Hz, 2H), 7.47 (d, *J* = 8.5Hz, 2H), 6.65 (d, *J* = 9.0Hz, 2H), 6.06 (s, 1H), 4.27-4.20 (m, 1H), 4.20-4.14 (m, 1H), 3.05 (s, 6H), 1.23 (t, *J* = 7.5Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 168.8, 165.9, 153.7, 133.8, 131.9, 131.7, 129.2, 123.1, 115.6, 110.7, 73.7, 61.7, 40.0, 14.0.

IR (neat, ATR): 2908 (w), 2159 (w), 2027 (w), 1818 (w), 1749 (s), 1696 (s), 1603 (s), 1532 (m), 1486 (m), 1446 (w), 1371 (m), 1349 (w), 1310 (w), 1296 (w), 1276 (s), 1257 (s), 1211 (m), 1171 (s), 1091 (s), 1069 (s).

HRMS (NSI+): Calcd. for $[C_{19}H_{20}O_4NBr+H]^+$: 406.0649 Found: 406.0647.

1-(4-bromophenyl)-2-ethoxy-2-oxoethyl furan-3-carboxylate (**4h**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), furan-3-carboxylic acid (22 mg, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a pale yellow oil (28 mg, 80%).

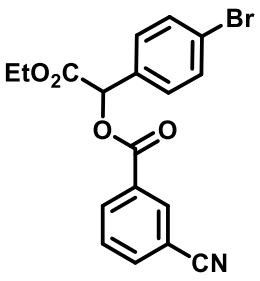
^{1}H ($CDCl_3$, 500MHz) δ: 8.11 (dd, *J* = 1.7Hz, *J* = 1.0Hz, 1H), 7.55 (d, *J* = 8.2Hz, 2H), 7.45 (t, *J* = 1.7Hz, 1H), 7.41 (d, *J* = 8.2Hz, 2H), 6,80 (d, *J* = 1.7Hz, *J* =1.0Hz, 1H), 6.03 (s, 1H), 4.28-4.21 (m, 1H), 4.20-4.14 (m, 1H), 1.23 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 168.3, 162.0, 148.5, 143.9, 133.0, 132.0, 129.2, 123.5, 118.3, 109.8, 73.8, 61.9, 14.0.

IR (neat, ATR): 3152 (w), 2981 (w), 2937 (w), 1726 (s), 1593 (w), 1576 (w), 1508 (w), 1489 (w), 1398 (w), 1370 (w), 1342 (w), 1300 (w), 1288 (w), 1262 (w), 1212 (w), 1158 (s), 1133 (s), 1073 (s), 1040 (m).

HRMS (NSI+): Calcd. for $[C_{15}H_{13}BrO_5+Na]^+$: 374.9839. Found: 374.9841.

1-(4-bromophenyl)-2-ethoxy-2-oxoethyl 3-cyanobenzoate (**4i**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), 3-cyanobenzoic acid (29 mg, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a white solid (25 mg, 64%).

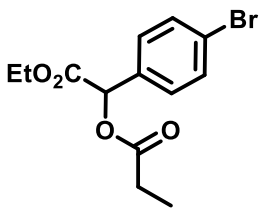
^{1}H ($CDCl_3$, 500MHz) δ: 8.39 (t, *J* = 1.5Hz, 1H), 8.33 (dt, *J* = 8.0Hz, *J* = 1.5Hz, 1H), 7.88 (dt, *J* = 8.0Hz, *J* = 1.5Hz, 1H), 7.62 (t, *J* = 8.0Hz, 1H), 7.58 (d, *J* = 8.0Hz, 2H), 7.44 (d, *J* = 8.0Hz, 2H), 6.11 (s, 1H), 4.30-4.23 (m, 1H), 4.22-4.15 (m, 1H), 1.24 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 167.9, 163.8, 136.5, 133.9, 133.5, 132.5, 132.2, 130.5, 129.6, 129.3, 123.8, 117.7, 113.2, 74.8, 62.2, 14.0.

IR (neat, ATR): 2992 (w), 2916 (w), 2850 (w), 2232 (m), 2160 (w), 2029 (w), 1977 (w), 1745 (s), 1720 (s), 1488 (m), 1369 (w), 1348 (w), 1300 (m), 1389 (s), 1213 (s), 1176 (s), 1099 (s), 1083 (s), 1071 (m).1039 (s).

HRMS(NSI+): Calcd. for $[C_{18}H_{14}O_4NBr+H]^+$: 388.0179 Found: 388.0181.

1-(4-bromophenyl)-2-ethoxy-2-oxoethyl butyrate (**4j**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), propionic acid (15 μL, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a pale yellow oil (27 mg, 85%).

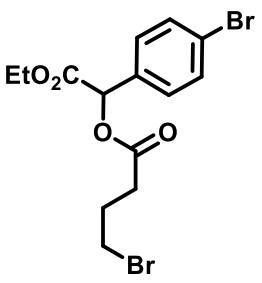
^{1}H ($CDCl_3$, 500MHz) δ: 7.52 (d, *J* = 8.5Hz, 2H), 7.35 (d, *J* = 8.5Hz, 2H), 5.87 (s, 1H), 4.24-4.18 (m, 1H), 4.18-4.11 (m, 1H), 2.56-2.41 (m, 2H), 1.22 (t, *J* = 7.0Hz, 3H), 1.20 (t, *J* = 7.5Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 173.6, 168.4, 133.1, 131.9, 129.2, 123.3, 73.7, 61.8, 27.3, 14.0, 8.9.

IR (neat, ATR): 2982 (w), 2942 (w), 1742 (s), 1489 (m), 1463 (w), 1369 (w), 1339 (w), 1262 (w), 1211 (m), 1159 (s), 1084 (m), 1071 (m), 1043 (m), 1012 (s).

HRMS(NSI+): Calcd. for $[C_{13}H_{15}BrO_4+Na]^+$: 337.0046 Found: 337.0049.

1-(4-bromophenyl)-2-ethoxy-2-oxoethyl 4-bromobutanoate (**4k**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), 4-bromobutanoic acid (33 mg, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (35 mg, 86%).

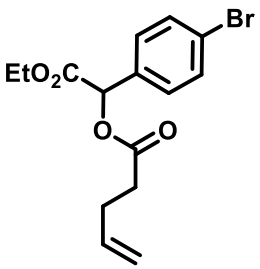
^{1}H ($CDCl_3$, 500MHz) δ: 7.53 (d, *J* = 8.5Hz, 2H), 7.34 (d, *J* = 8.5Hz, 2H), 5.87 (s, 1H), 4.25-4.18 (m, 1H), 4.18-4.11 (m, 1H), 3.50 (dt, *J* = 6.5Hz, *J* = 1.5Hz, 2H), 2.73-2.60 (m, 2H), 2.23 (quint., *J* = 7.0Hz, 2H), 1.22 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 171.2, 168.2, 132.7, 132.0, 129.2, 123.5, 73.9, 62.0, 32.3, 32.2, 27.7, 14.0.

IR (neat, ATR): 2918 (w), 1739 (s), 1489 (w), 1442 (w), 1407 (w), 1370 (w), 1259 (m), 1210 (s), 1159 (s), 1126 (s), 1070 (s).

HRMS(NSI+): Calcd. for $[C_{14}H_{16}O_4Br_2+H]^+$: 406.9488 Found: 406.9491.

1-(4-bromophenyl)-2-ethoxy-2-oxoethyl pent-4-enoate (**4l**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), pent-4-enoic acid (20 μL, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (30 mg, 88%).

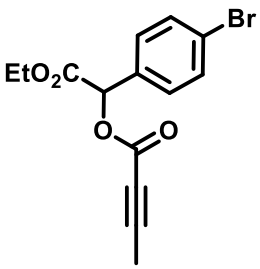
^{1}H ($CDCl_3$, 500MHz) δ: 7.52 (d, *J* = 8.5Hz, 2H), 7.35 (d, *J* = 8.5Hz, 2H), 5.88-5.80 (m, 1H), 5.87 (s, 1H), 5.07 (dq, *J* = 17.0Hz, *J* = 1.5Hz, 1H), 5.02 (dq, *J* = 10.5Hz, *J* = 1.5Hz, 1H), 4.24-4.18 (m, 1H), 4.18-4.11 (m, 1H), 2.63-2.51 (m, 2H), 2.46-2.41 (m, 2H), 1.22 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 172.2, 168.3, 136.3, 133.0, 131.9, 129.2, 123.4, 115.7, 73.8, 61.9, 33.2, 28.6, 14.0.

IR (neat, ATR): 2980 (w), 1741 (s), 1642 (w), 1489 (w), 1370 (w), 1339 (w), 1210 (m), 1152 (s), 1071 (m), 1029 (m), 1011 (s).

HRMS (NSI+): Calcd. for $[C_{15}H_{17}O_4Br+H]^+$: 341.0383 Found: 341.0387

1-(4-bromophenyl)-2-ethoxy-2-oxoethyl but-2-ynoate (**4m**)

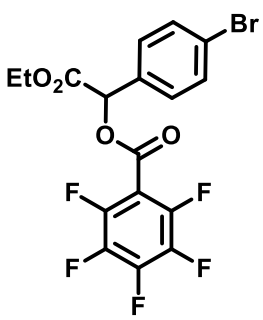


The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), but-2-ynoic acid (17 mg, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a transparent oil (32

mg, 98%). This same substrate (**4m**) has been prepared in the dark and isolated in 90% yield.

^{1}H (CDCl$_3$, 500MHz) δ: 7.52 (d, *J* = 8.5Hz, 2H), 7.35 (d, *J* = 8.5Hz, 2H), 5.90 (s, 1H), 4.26-4.19 (m, 1H), 4.18-4.13 (m, 1H), 2.02 (s, 3H), 1.22 (t, *J* = 7.0Hz, 3H).
^{13}C (CDCl$_3$, 125MHz) δ: 167.2, 152.5, 132.3, 132.0, 129.2, 123.6, 87.8, 74.6, 71.7, 62.1, 14.0, 3.9.
IR (neat, ATR): 2981 (w), 2923 (w), 2238 (m), 1752 (m), 1713 (s), 1489 (w), 1445 (w), 1370 (w), 1340 (w), 1294 (w), 1268 (m), 1242 (s), 1209 (s), 1178 (s), 1067 (s), 1028 (s), 1012 (s).
HRMS(NSI+): Calcd. for $[C_{14}H_{13}O_4Br+NH_4]^+$: 342.0336 Found: 342.0338.

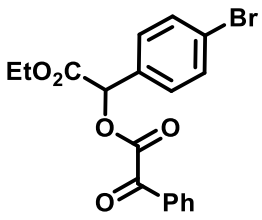
1-(4-bromophenyl)-2-ethoxy-2-oxoethyl 2,3,4,5,6-pentafluorobenzoate (**4n**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), 2,3,4,5,6-pentafluorobenzoic acid (42 mg, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a white solid (45 mg, 99%). This same substrate (**4n**) has been prepared in the dark and also isolated in 99% yield.

^{1}H (CDCl$_3$, 500MHz) δ: 7.55 (d, *J* = 8.5Hz, 2H), 7.40 (d, *J* = 8.5Hz, 2H), 6.12 (s, 1H), 4.29-4.17 (m, 2H), 1.25 (t, *J* = 7.0Hz, 3H).
^{13}C (CDCl$_3$, 125MHz) (4C cannot be unambiguously assigned) δ: 167.2, 158.2, 132.1, 131.8, 129.1, 123.8, 75.6, 62.4, 13.9.
IR (neat, ATR): 2995 (w), 2973 (w), 2947 (w), 2162 (w), 2035 (w), 1759 (m), 1727 (s), 1705 (w), 1651 (m), 1529 (m), 1494 (s), 1412 (m), 1351 (m), 1329 (m), 1290 (w), 1238 (s), 1218 (s), 1188 (s), 1148 (w), 1118 (w), 1070 (w), 1051 (m).
HRMS (NSI+): Calcd for $[C_{17}H_{10}O_4BrF_5 + Na]^+$: 474.9575 Found: 474.9576.

1-(4-bromophenyl)-2-ethoxy-2-oxoethyl 2-oxo-2-phenylacetate (**4o**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), 2-oxo-2-phenylacetic acid (30 mg, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a transparent oil (27 mg, 70%). This same substrate (**4o**) has been prepared in the dark and isolated in 80% yield.

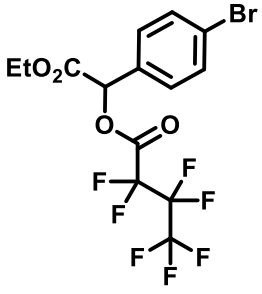
^{1}H ($CDCl_3$, 500MHz) δ: 8.14 (d, *J* = 7.0Hz, 2H), 7.70 (t, *J* = 7.5Hz, 1H), 7.56-7.53 (m, 4H), 7.38 (d, *J* = 8.5Hz, 2H), 6.01 (s, 1H), 4.35-4.28 (m, 1H), 4.27-4.21 (m, 1H), 1.28 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 185.4, 167.5, 163.1, 135.2, 132.3, 132.1, 131.6, 130.3, 129.3, 129.0, 123.9, 75.1, 62.5, 14.0.

IR (neat, ATR): 2980 (w), 1741 (s), 1687 (s), 1596 (w), 1581 (w), 1489 (w), 1451 (w), 1407 (w), 1370 (w), 1263 (w), 1214 (w), 1193 (s), 1170 (s), 1072 (w), 1029 (m), 1001 (m), 1002 (m), 980 (m).

HRMS (NSI+): Calcd. for $[C_{18}H_{15}O_5Br+H]^+$: 391.0176 Found: 391.0174.

1-(4-bromophenyl)-2-ethoxy-2-oxoethyl 2,2,3,3,4,4,4-heptafluorobutanoate (**4p**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), 2,2,3,3,4,4,4-heptafluorobutanoic acid (26 μL, 0.2 mmol, 2 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (45 mg, 99%). This same substrate (**4p**) has been prepared in the dark and isolated in 99% yield.

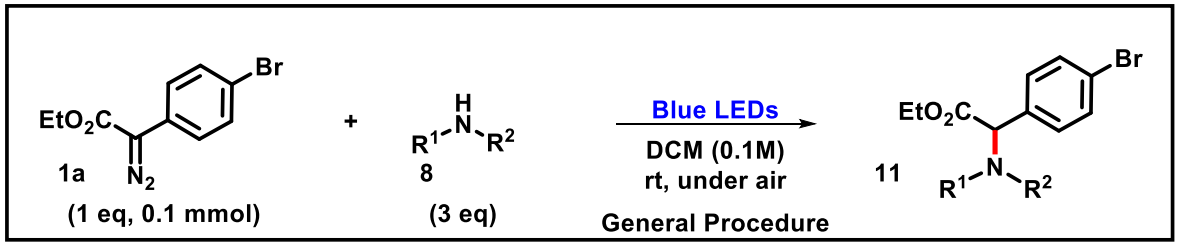
^{1}H ($CDCl_3$, 500MHz) δ: 7.57 (d, *J* = 8.5Hz, 2H), 7.35 (d, *J* = 8.5Hz, 2H), 6.03 (s, 1H), 4.29-4.17 (m, 2H), 1.24 (t, *J* = 7.0Hz, 3H).

^{13}C (CDCl$_3$, 125MHz) δ (3C cannot be unambigously assigned): 166.0, 157.5, 132.3, 130.7, 129.0, 124.4, 76.7, 62.7, 13.8.

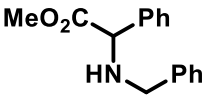
IR (neat, ATR): 2897 (w), 2159 (w), 2031 (w), 1786 (s), 1755 (s), 1491 (w), 1302 (w), 1211 (s), 1182 (s), 1143 (s), 1123 (m), 1084 (m), 1073 (m), 1027 (m), 1014 (m), 971 (m).

HRMS (NSI+): Calcd. for $[C_{14}H_{10}BrF_7O_4+Na]^+$: 476.9543 Found: 476.9540.

3.5 N-H Insertion of Amines



methyl 2-(benzylamino)-2-phenylacetate (**11a**)



The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq), benzylamine (33 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a pale yellow oil (22 mg, 86%).

This protocol has been performed also in a preparative scale employing diazocompound **1b** (180 mg, 1 mmol, 1 eq) and benzylamine (330 μL, 3 mmol, 3 eq). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a pale yellow oil (214 mg, 84%).

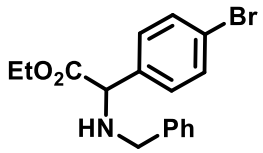
^{1}H (CDCl$_3$, 500MHz) δ: 7.40-7.25 (m, 10H), 4.40 (s, 1H), 3.74 (d, *J* = 13.5 Hz, 1H), 3.71 (d, *J* = 13.5Hz, 1H), 3.69 (s, 3H).

^{13}C (CDCl$_3$, 125MHz) δ**:** 173.4, 139.4, 138.0, 128.7, 128.4, 128.3, 128.1, 127.6, 127.1, 64.3, 52.2, 51.3.

IR (neat, ATR): 3028 (w), 2951 (w), 1735 (s), 1602 (w), 1495 (w), 1454 (m), 1434 (m), 1200 (m), 1168 (s), 1127 (w), 1074 (w), 1028 (w), 1010 (w), 909 (m).

HRMS (APCI+): Calcd. for $[C_{16}H_{17}NO_2+H]^+$: 256.1332 Found: 256.1330.

ethyl 2-(benzylamino)-2-(4-bromophenyl)acetate (**11b**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), benzylamine (33 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a transparent oil (31 mg, 90%).

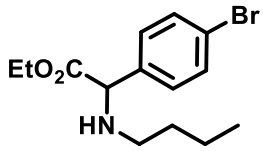
^{1}H (CDCl$_3$, 500MHz) δ**:** 7.48 (d, *J* = 8.5Hz, 2H), 7.35-7.25 (m, 7H), 4.33 (s, 1H), 4.22-4.15 (m, 1H), 4.15-4.09 (m, 1H), 3.74 (d, *J* = 13.0Hz, 1H), 3.70 (d, *J* = 13.0Hz, 1H), 1.20 (t, *J* = 7.0Hz, 3H).

^{13}C (CDCl$_3$, 125MHz) δ**:** 172.5, 139.3, 137.2, 131.7, 129.3, 128.5, 128.3, 127.2, 122.0, 63.8, 61.3, 51.3, 14.1.

IR (neat, ATR): 3337 (w), 3085 (w), 3062 (w), 3027 (w), 2978 (w), 2930 (w), 2847 (w), 1731 (s), 1589 (w), 1486 (m), 1454 (m), 1404 (w), 1369 (w), 1322 (w), 1299 (w), 1192 (m), 1174 (s), 1128 (m), 1096 (w), 1071 (m), 1026 (m), 1011 (s).

HRMS (APCI+): Calcd for $[C_{17}H_{18}BrNO_2+H]^+$: 348.0594 Found: 348.0595.

ethyl 2-(4-bromophenyl)-2-(butylamino)acetate (**11c**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), *n*-butylamine (30 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a transparent oil (26 mg, 82%).

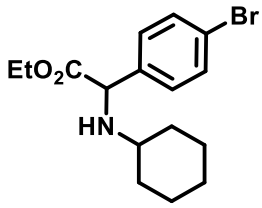
^{1}H ($CDCl_3$, 500MHz) δ: 7.46 (d, *J* = 8.5Hz, 2H), 7.26 (d, *J* = 8.5Hz, 2H), 4.30 (s, 1H), 4.22-4.15 (m, 1H), 4.15-4.09 (m, 1H), 2.58-2.53 (m, 1H), 2.49-2.44 (m, 1H), 1.51-1.45 (m, 2H), 1.37-1.30 (m, 2H), 1.21 (t, *J* = 7.0Hz, 3H), 0.89 (t, *J* = 7.5Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 172.7, 137.5, 131.7, 129.1, 121.9, 65.1, 61.3, 47.5, 32.1, 20.3, 14.1, 13.9.

IR (neat, ATR): 2957 (m), 2929 (m), 2871 (w), 1732 (s), 1486 (m), 1465 (m), 1404 (w), 1367 (w), 1300 (w), 1174 (s), 1124 (m), 1071 (m), 1011 (s).

HRMS (APCI+): Calcd. for $[C_{14}H_{20}BrNO_2+H]^+$: 314.0750 Found: 314.0749.

ethyl 2-(4-bromophenyl)-2-(cyclohexylamino)acetate (**11d**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), cyclohexylamine (34 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a transparent oil (24 mg, 70%).

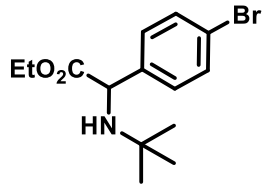
^{1}H ($CDCl_3$, 500MHz) δ: 7.46 (d, *J* = 8.5Hz, 2H), 7.26 (d, *J* = 8.5Hz, 2H), 4.46 (s, 1H), 4.21-4.14 (m, 1H), 4.14-4.08 (m, 1H), 2.36-2.31 (m, 1H), 1.85-1.78 (m, 2H), 1.72-1.69 (m, 2H), 1.59-1.57 (m, 1H), 1.20 (t, *J* = 7.5Hz, 3H), 1.20-1.10 (m, 5H).

^{13}C ($CDCl_3$, 125MHz) δ: 173.1, 138.0, 131.7, 129.1, 121.8, 61.9, 61.3, 54.5, 33.5, 33.2, 26.0, 24.8, 24.7, 14.1.

IR (neat, ATR): 2925 (m), 2852 (m), 1824 (w), 1732 (s), 1589 (w), 1486 (m), 1448 (m), 1404 (w), 1368 (w), 1299 (w), 1234 (w), 1174 (s), 1127 (m), 1071 (m), 1022 (m), 1011 (s).

HRMS (APCI+): Calcd. for $[C_{16}H_{22}BrNO_2+H]^+$: 340.0907 Found: 340.0907.

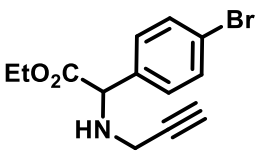
ethyl 2-(4-bromophenyl)-2-(tert-butylamino)acetate (**11e**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), *tert*-butylamine (32 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a pale yellow oil (20 mg, 63%).

^{1}H ($CDCl_3$, 500MHz) δ: 7.43 (d, *J* = 8.5Hz, 2H), 7.30 (d, *J* = 8.5Hz, 2H), 4.40 (s, 1H), 4.21-4.15 (m, 1H), 4.13-4.07 (m, 1H), 1.21 (t, *J* = 7.0Hz, 3H), 1.08 (s, 9H).
^{13}C ($CDCl_3$, 125MHz) δ: 174.5, 139.9, 131.5, 129.0, 121.4, 61.4, 59.1, 51.2, 29.5, 14.0.
IR (neat, ATR): 2962 (m), 1732 (s), 1589 (w), 1485 (m), 1462 (w), 1389 (w), 1364 (m), 1301 (w), 1232 (s), 1208 (s), 1159 (s), 1124 (w), 1071 (w), 1011 (s).
HRMS (APCI+): Calcd. for $[C_{14}H_{20}BrNO_2+H]^+$: 314.0750 Found: 314.0750.

ethyl 2-(4-bromophenyl)-2-(prop-2-yn-1-ylamino)acetate (**11f**)

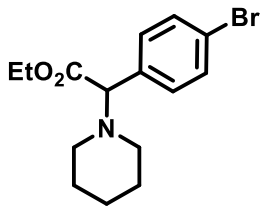


The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), propargylamine (19 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a yellowish oil (22 mg, 74%).

^{1}H ($CDCl_3$, 500MHz) δ: 7.48 (d, *J* = 8.5Hz, 2H), 7.29 (d, *J* = 8.5Hz, 2H), 4.58 (s, 1H), 4.19-4.16 (m, 1H), 4.16-4.09 (m, 1H), 3.47 (dd, *J* = 17.5Hz, *J* = 2.5Hz, 1H), 3.24 (dd, *J* = 17.5Hz, *J* = 2.5Hz, 1H), 2.25 (t, *J* = 2.5Hz, 1H), 1.20 (t, *J* = 7.0Hz, 3H).
^{13}C ($CDCl_3$, 125MHz) δ: 171.9, 136.5, 131.8, 129.6, 122.2, 80.9, 72.2, 62.9, 61.5, 35.8, 14.0.

IR (neat, ATR): 3294 (w), 2981 (w), 1731 (s), 1590 (w), 1487 (m), 1405 (w), 1369 (w), 1307 (w), 1234 (m), 1177 (s), 1128 (m), 1097 (m), 1024 (s), 1011 (s).
HRMS (APCI+): Calcd. for $[C_{13}H_{14}BrNO_2+H]^+$: 296.0281 Found: 296.0281.

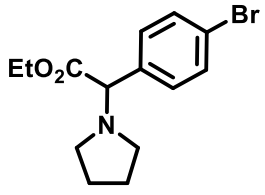
ethyl 2-(4-bromophenyl)-2-(piperidin-1-yl)acetate (**11g**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), piperidine (31 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as an yellowish oil (24 mg, 74%).

^{1}H ($CDCl_3$, 500MHz) δ: 7.46 (d, *J* = 8.5Hz, 2H), 7.33 (d, *J* = 8.5Hz, 2H), 4.21-4.15 (m, 1H), 4.14-4.08 (m, 1H), 3.91 (s, 1H), 2.40-2.37 (m, 4H), 1.60-1.56 (m, 4H), 1.46-1.41 (m, 2H), 1.21 (t, *J* = 7.0Hz, 3H).
^{13}C ($CDCl_3$, 125MHz) δ: 171.3, 135.6, 131.5, 130.4, 122.1, 74.3, 60.9, 52.3, 25.8, 24.3, 14.1.
IR (neat, ATR): 2933 (w), 2851 (w), 2804 (w), 2758 (w), 2709 (w), 1732 (s), 1589 (w), 1486 (m), 1443 (w), 1392 (w), 1368 (w), 1332 (w), 1298 (w), 1254 (w), 1223 (w), 1195 (w), 1151 (s), 1115 (m), 1096 (m), 1070 (m), 1027 (s), 1011 (s).
HRMS (APCI+): Calcd. for $[C_{15}H_{20}BrNO_2+H]^+$: 326.0750 Found: 326.0750.

ethyl 2-(4-bromophenyl)-2-(pyrrolidin-1-yl)acetate (**11h**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), pyrrolidine (25 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a transparent oil (19 mg, 60%).

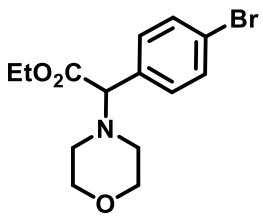
^{1}H ($CDCl_3$, 500MHz) δ: 7.46 (d, *J* = 8.5Hz, 2H), 7.36 (d, *J* = 8.5Hz, 2H), 4.21-4.15 (m, 1H), 4.14-4.08 (m, 1H), 3.85 (s, 1H), 2.57-2.51 (m, 2H), 2.45-2.40 (m, 2H), 1.83-1.77 (m, 4H), 1.20 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 171.3, 136.6, 131.6, 130.0, 122.2, 73.3, 61.0, 52.4, 23.3, 14.1.

IR (neat, ATR): 2970 (w), 2796 (w), 1741 (s), 1694 (w), 1587 (w), 1486 (m), 1461 (w), 1404 (w), 1370 (w), 1325 (w), 1287 (w), 1255 (w), 1197 (m), 1158 (s), 1096 (w), 1070 (m), 1025 (m), 1011 (s).

HRMS (APCI+): Calcd. for $[C_{14}H_{18}BrNO_2+H]^+$: 312.0594 Found: 312.0593.

ethyl 2-(4-bromophenyl)-2-morpholinoacetate (**11i**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), morpholine (26 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt – 7:3 Hex:AcOEt) affords the title compound as a transparent oil (28 mg, 85%).

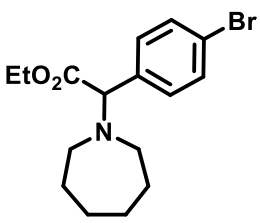
^{1}H ($CDCl_3$, 500MHz) δ: 7.47 (d, *J* = 8.5Hz, 2H), 7.33 (d, *J* = 8.5Hz, 2H), 4.21-4.14 (m, 1H), 4.14-4.08 (m, 1H), 3.91 (s, 1H), 3.71 (t, *J* = 5.0Hz, 4H), 2.47-2.40 (m, 4H), 1.20 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 170.7, 134.6, 131.8, 130.5, 122.5, 73.8, 66.8, 61.1, 51.5, 14.1.

IR (neat, ATR): 2958 (w), 2854 (w), 1732 (s), 1589 (w), 1486 (m), 1451 (w), 1397 (w), 1368 (w), 1331 (w), 1272 (w), 1240 (w), 1174 (m), 1152 (m), 1116 (s), 1070 (m), 1029 (s), 1010 (s).

HRMS (APCI+): Calcd. for $[C_{14}H_{18}BrNO_3+H]^+$: 328.0543 Found: 328.0541.

ethyl 2-(azepan-1-yl)-2-(4-bromophenyl)acetate (**11j**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), hexamethyleneimine (34 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a transparent oil (26 mg, 76%).

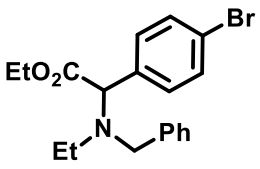
^{1}H ($CDCl_3$, 500MHz) δ: 7.45 (d, *J* = 8.5Hz, 2H), 7.31 (d, *J* = 8.5Hz, 2H), 4.34 (s, 1H), 4.23-4.12 (m, 2H), 2.70-2.62 (m, 4H), 1.60-1.56 (m, 8H), 1.24 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 172.0, 136.8, 131.4, 130.3, 121.7, 72.4, 60.6, 52.6, 28.9, 26.9, 14.2.

IR (neat, ATR): 2925 (m), 2852 (w), 1732 (s), 1694 (w), 1587 (w), 1486 (m), 1447 (w), 1397 (w), 1367 (w), 1295 (w), 1241 (w), 1197 (s), 1172 (s), 1149 (s), 1071 (s), 1025 (m), 1011 (s).

HRMS (APCI+): Calcd. for $[C_{16}H_{22}BrNO_2+H]^+$: 340.0907 Found: 340.0907.

ethyl 2-(benzyl(ethyl)amino)-2-(4-bromophenyl)acetate (**11k**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), N-ethylbenzylamine (45 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a transparent oil (22 mg, 58%).

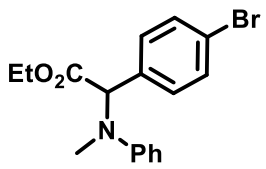
^{1}H ($CDCl_3$, 500MHz) δ: 7.46 (d, *J* = 8.5Hz, 2H), 7.35-7.28 (m, 6H), 7.25-7.22 (m, 1H), 4.54 (s, 1H), 4.32-4.16 (m, 2H), 3.77 (d, *J* = 14.5Hz, 1H), 3.66 (d, *J* = 14.5Hz, 1H), 2.66-2.59 (m, 2H), 1.28 (t, *J* = 7.0Hz, 3H), 1.00 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 171.7, 139.7, 136.4, 131.4, 130.3, 128.5, 128.2, 126.9, 121.7, 66.9, 60.6, 54.2, 44.1, 14.3, 12.3.

IR (neat, ATR): 2972 (w), 2847 (w), 1732 (s), 1587 (w), 1487 (w), 1453 (w), 1368 (w), 1298 (w), 1243 (w), 1200 (s), 1171 (s), 1132 (m), 1096 (w), 1072 (s), 1027 (m), 1011 (s).

HRMS (APCI+): Calcd. for $[C_{19}H_{22}BrNO_2+H]^+$: 376.0907 Found: 376.0906.

ethyl 2-(4-bromophenyl)-2-(methyl(phenyl)amino)acetate (**11l**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), *N*-methylaniline (33 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as an yellowish oil (24 mg, 69%).

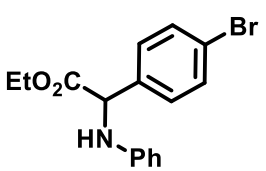
^{1}H ($CDCl_3$, 500MHz) δ: 7.50 (d, *J* = 8.5Hz, 2H), 7.27 (dd, *J* = 8.5Hz, *J* = 7.0Hz, 2H), 7.18 (d, *J* = 8.5Hz, 2H), 6.87 (d, *J* = 8.5Hz, 2H), 6.83 (t, J = 7.0Hz, 1H), 5.56 (s, 1H), 4.31-4.21 (m, 2H), 2.80 (s, 3H), 1.26 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 171.2, 149.7, 135.0, 131.8, 130.1, 129.3, 122.1, 118.4, 113.7, 65.5, 61.2, 34.8, 14.2.

IR (neat, ATR): 2976 (w), 2878 (w), 2813 (w), 1733 (s), 1692 (w), 1596 (s), 1496 (s), 1451 (w), 1424 (w), 1408 (w), 1368 (w), 1349 (w), 1286 (m), 1225 (w), 1189 (s), 1107 (s), 1072 (m), 1020 (s), 1012 (s), 992 (m).

HRMS (APCI+): Calcd. for $[C_{17}H_{18}BrNO_2]^+$: 348.0594 Found: 348.0594.

ethyl 2-(4-bromophenyl)-2-(phenylamino)acetate (**11m**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), aniline (27 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (27 mg, 81%).

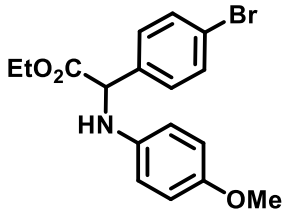
^{1}H ($CDCl_3$, 500MHz) δ: 7.47 (d, *J* = 8.5Hz, 2H), 7.39 (d, *J* = 8.5Hz, 2H), 7.12 (dd, *J* = 8.5Hz , *J* = 7.5Hz, 2H), 6.71 (tt, *J* = 7.0Hz, *J* = 0.5Hz, 1H), 6.52 (dd, *J* = 8.5Hz, *J* = 1.0Hz, 2H), 5.02-5.00 (m, 2H), 4.27-4.21 (m, 1H), 4.18-4.12 (m, 1H), 1.23 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 171.2, 145.6, 136.9, 131.9, 129.2, 128.9, 122.2, 118.2, 113.4, 62.1, 60.2, 14.0.

IR (neat, ATR): 3400 (br), 3051 (w), 2980 (w), 2935 (w), 1731 (s), 1603 (s), 1505 (w), 1485 (s), 1433 (w), 1368 (w), 1305 (m), 1249 (m), 1175 (s), 1070 (m), 1010 (s).

HRMS (APCI+): Calcd. for $[C_{16}H_{16}BrNO_2+H]^+$: 334.0437 Found: 334.0437.

ethyl 2-(4-bromophenyl)-2-((4-methoxyphenyl)amino)acetate (**11n**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), *p*-anisidine (37 mg, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as an yellow oil (30 mg, 82%).

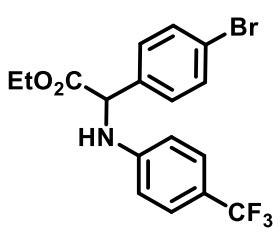
^{1}H ($CDCl_3$, 500MHz) δ: 7.47 (d, *J* = 8.5Hz, 2H), 7.38 (d, *J* = 8.5Hz, 2H), 6.72 (d, *J* = 8.5Hz, 2H), 6.50 (d, *J* = 8.5Hz, 2H), 4.96 (s, 1H), 4.26-4.19 (m, 1H), 4.17-4.11 (m, 1H), 3.71 (s, 3H), 1.22 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 171.4, 152.6, 139.8, 137.1, 131.9, 128.9, 122.1, 114.9, 114.8, 61.9, 61.1, 55.7, 14.0.

IR (neat, ATR): 3395 (br), 2981 (w), 2832 (w), 1731 (s), 1587 (w), 1511 (s), 1485 (m), 1464 (m), 1442 (w), 1402 (w), 1368 (w), 1303 (m), 1236 (s), 1176 (s), 1135 (w), 1071 (w).

HRMS (APCI+): Calcd. for $[C_{17}H_{18}BrNO_3+H]^+$: 364.0543 Found: 464.0545.

ethyl 2-(4-bromophenyl)-2-((4-(trifluoromethyl)phenyl)amino)acetate (**11o**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq), 4-(trifluoromethyl)aniline (37 μL, 0.3 mmol, 3 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as an yellow oil (29 mg, 72%).

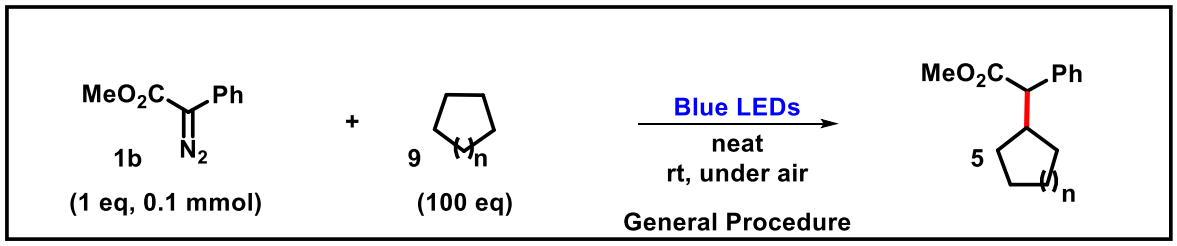
^{1}H ($CDCl_3$, 500MHz) δ: 7.49 (d, *J* = 8.5Hz, 2H), 7.36 (t, *J* = 8.5Hz, 4H), 6.52 (d, *J* = 8.5Hz, 2H), 5.38 (d, *J* = 5.0Hz, 1H), 5.03 (d, *J* = 5.0Hz, 1H), 4.29-4.23 (m, 1H), 4.19-4.13 (m, 1H), 1.23 (t, *J* = 7.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 170.6, 147.9, 132.1, 128.7, 126.6 (q, *J* = 4.0Hz), 124.7 (q, *J* = 268.4Hz), 122.5, 120.0, 119.7, 112.7, 62.4, 59.6, 14.0.

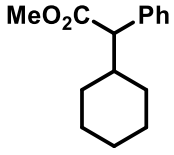
IR (neat, ATR): 3400 (br), 2984 (w), 1732 (s), 1616 (s), 1588 (w), 1532 (m), 1486 (m), 1417 (w), 1370 (w), 1317 (s), 1285 (m), 1251 (m), 1207 (w), 1183 (m), 1160 (m), 1106 (s), 1064 (s), 1010 (s).

HRMS (APCI+): Calcd. for $[C_{17}H_{15}BrF_3NO_2+H]^+$: 402.0311 Found: 402.0310.

3.6 C-H Insertion of Cycloalkanes (and Other Molecules)



methyl 2-cyclohexyl-2-phenylacetate (**5b**)



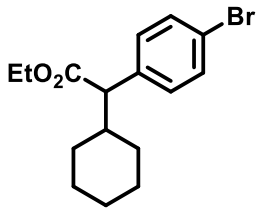
The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq) and cyclohexane (1.1 mL, 10 mmol, 100 eq). Purification by flash column chromatography (SiO_2, gradient: Hex –

98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (13 mg, 55%).

This protocol has been performed also in a preparative scale employing diazocompound **1b** (180 mg, 1 mmol, 1 eq) and cyclohexane (11 mL, 100 mmol, 100 eq). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (122 mg, 53%).

^{1}H ($CDCl_3$, 500MHz) δ: 7.34-7.28 (m, 4H), 7.26-7.23 (m, 1H), 3.64 (s, 3H), 3.22 (d, *J* = 10.5Hz, 1H), 2.05-1.97 (m, 1H), 1.81-1.72 (m, 2H), 1.65-1.59 (m, 2H), 1.36-1.26 (m, 2H), 1.19-1.12 (m, 2H), 1.09-1.01 (m, 1H), 0.78-0.71 (m, 1H).
^{13}C ($CDCl_3$, 125MHz) δ: 174.4, 137.9, 128.6, 128.4, 127.1, 58.8, 51.7, 41.0, 32.0, 30.4, 26.3, 26.0, 25.9.
IR (neat, ATR): 2924 (m), 2851 (w), 1734 (s), 1601 (w), 1497 (w), 1449 (m), 1433 (m), 1334 (w), 1286 (m), 1241 (m), 1221 (m), 1194 (m), 1153 (s), 1128 (m), 1071 (w), 1006 (w).
HRMS (NSI+): Calcd. for $[C_{15}H_{20}O_2+H]^+$: 233.1536 Found: 233.1536.

ethyl 2-(4-bromophenyl)-2-cyclohexylacetate (**5c**)



The general procedure is employed with diazocompound **1a** (27 mg, 0.1 mmol, 1 eq) and cyclohexane (1.1 mL, 10 mmol, 100 eq). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (21 mg, 64%).

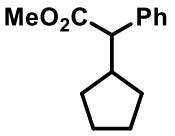
^{1}H ($CDCl_3$, 500MHz) δ: 7.42 (d, *J* = 8.5H, 2H), 7.21 (d, *J* = 8.5Hz, 2H), 4.18-4.11 (m, 1H), 4.09-4.02 (m, 1H), 3.16 (d, *J* = 10.5Hz, 1H), 2.00-1.92 (m, 1H), 1.80-1.72 (m, 2H), 1.65-1.60 (m, 2H), 1.34-1.24 (m, 2H), 1.21 (t, *J* = 7.0Hz, 3H), 1.18-1.11 (m, 2H), 1.08-1.00 (m, 1H), 0.77-0.69 (m, 1H).

^{13}C ($CDCl_3$, 125MHz) δ: 173.5, 137.0, 131.5, 130.3, 121.1, 60.6, 58.3, 41.1, 31.8, 30.4, 26.2, 25.9 (x2), 14.1.

IR (neat, ATR): 2979 (w), 2926 (m), 2851 (w), 1729 (s), 1590 (w), 1487 (m), 1447 (m), 1407 (w), 1368 (w), 1330 (w), 1391 (w), 1294 (w), 1283 (w), 1269 (w), 1257 (w), 1237 (w), 1219 (w), 1191 (w), 1154 (s), 1127 (m), 1098 (w), 1072 (m), 1027 (m), 1011 (s).

HRMS (NSI+): Calcd. For $[C_{16}H_{21}O_2Br+H]^+$: 325.0798 Found: 325.0798.

methyl 2-cyclopentyl-2-phenylacetate (**5d**)



The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq) and cyclopentane (932 μL, 10 mmol, 100 eq). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a pale yellow oil (12 mg, 54%).

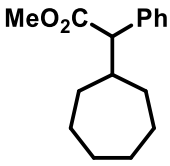
^{1}H ($CDCl_3$, 500MHz) δ: 7.35-7.29 (m, 4H), 7.26-7.22 (m, 1H), 3.65 (s, 3H), 3.28 (d, *J* = 11.0Hz, 1H), 2.60-2.52 (m, 1H), 1.93-1.87 (m, 1H), 1.70-1.55 (m, 3H), 1.52-1.38 (m, 2H), 1.29-1.21 (m, 1H), 1.04-0.96 (m, 1H).

^{13}C ($CDCl_3$, 125MHz) δ: 174.4, 139.0, 128.4, 128.2, 127.1, 57.7, 51.8, 43.5, 31.5, 30.7, 25.1, 24.8.

IR (neat, ATR): 2951 (m), 2868 (w), 1734 (s), 1602 (w), 1497 (w), 1453 (w), 1433 (w), 1347 (w), 1321 (w), 1268 (w), 1233 (w), 1202 (m), 1166 (m), 1144 (s), 1074 (w), 1024 (w).

HRMS (NSI+): Calcd. for $[C_{14}H_{18}O_2+H]^+$: 219.1380 Found: 219.1382.

methyl 2-cycloheptyl-2-phenylacetate (**5e**)



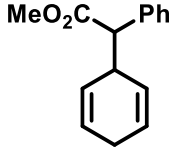
The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq) and cycloheptane (1.2 mL, 10 mmol, 100 eq). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (20 mg, 79%).

^{1}H ($CDCl_3$, 500MHz) δ: 7.34-7.29 (m, 4H), 7.26-7.23 (m, 1H), 3.64 (s, 3H), 3.31 (d, *J* = 11.0Hz, 1H), 2.30-2.23 (m, 1H), 1.79-1.74 (m, 1H), 1.72-1.64 (m, 1H), 1.63-1.58 (m, 1H), 1.56-1.42 (m, 5H), 1.39-1.26 (m, 3H), 1.02-0.95 (m, 1H).
^{13}C ($CDCl_3$, 125MHz) δ: 174.6, 138.4, 128.6, 128.4, 127.1, 58.9, 51.7, 42.2, 33.2, 31.3, 28.4, 28.3, 26.3, 26.2.
IR (neat, ATR): 2923 (m), 2853 (w), 1733 (s), 1601 (w), 1496 (w), 1454 (m), 1433 (m), 1337 (w), 1271 (w), 1227 (w), 1199 (m), 1145 (s), 1076 (w), 1017 (w), 988 (w).
HRMS (NSI+): Calcd. for $[C_{16}H_{22}O_2+H]^+$: 247.1693 Found: 247.1695.

methyl 2-(cyclohexa-2,5-dien-1-yl)-2-phenylacetate (**5f**) and methyl 7-phenylbicyclo[4.1.0]hept-3-ene-7-carboxylate (**5g**)

The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq) and 1,4-cyclohexadiene (945 μL, 10 mmol, 100 eq). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords methyl 2-(cyclohexa-2,5-dien-1-yl)-2-phenylacetate **5f** as a transparent oil (11 mg, 47%) and methyl 7-phenylbicyclo[4.1.0]hept-3-ene-7-carboxylate **5g** as a white solid (12 mg, 50%).

methyl 2-(cyclohexa-2,5-dien-1-yl)-2-phenylacetate (**5f**)



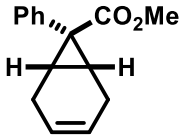
^{1}H ($CDCl_3$, 500MHz) δ: 7.35-7.31 (m, 4H), 7.29-7.26 (m, 1H), 5.83-5.79 (m, 1H), 5.74-5.67 (m, 2H), 5.28-5.25 (m, 1H), 3.68 (s, 3H), 3.50-3.46 (m, 1H), 3.42 (d, *J* = 10.5Hz, 1H), 2.64-2.60 (m, 2H).

^{13}C ($CDCl_3$, 125MHz) δ**:** 173.4, 136.7, 128.6, 128.5, 127.4, 126.6, 126.3, 125.8 (x2), 58.3, 51.9, 38.5, 26.4.

IR (neat, ATR): 3029 (w), 2951 (w), 1732 (s), 1600 (w), 1495 (w), 1454 (w), 1434 (w), 1329 (w), 1271 (w), 1192 (m), 1154 (s), 1078 (w), 1005 (w).

HRMS (APCI+): Calcd. for $[C_{15}H_{16}O_2+H]^+$: 229.1223 Found: 229.1223.

methyl 7-phenylbicyclo[4.1.0]hept-3-ene-7-carboxylate (**5g**)



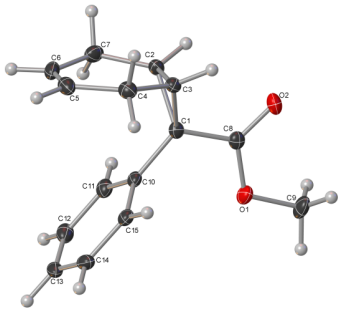
^{1}H ($CDCl_3$, 500MHz) δ**:** 7.29-2.21 (m, 5H), 5.01 (s, 2H), 3.56 (s, 3H), 2.52 (d, *J* = 18.0Hz, 2H), 2.42 (d, *J* = 18.0Hz, 2H), 2.15 (s, 2H).

^{13}C ($CDCl_3$, 125MHz) δ**:** 175.3, 134.4, 130.0, 127.9, 126.8, 123.3, 52.4, 33.3, 25.1, 21.0.

IR (neat, ATR): 3031 (w), 2997 (w), 2947 (w), 2910 (w), 1850 (w), 2160 (w), 2032 (w), 1977 (w), 1702 (s), 1603 (w), 1496 (w), 1445 (w), 1428 (m), 1394 (w), 1338 (w), 1246 (s), 1211 (s), 1175 (m), 1153 (w), 1117 (w).

HRMS (NSI+): Calcd. for $[C_{15}H_{16}O_2+H]^+$: 229.1223 Found: 229.1223.

X-ray determination of 5g (CCDC 1824108), Crystal Data and Experimental:



Experimental. Single colourless block-shaped crystals of **5g** were crystallised from $CHCl_3$ by slow evaporation. A suitable crystal 0.54×0.41×0.23 mm^3 was selected and mounted on a loop with paratone oil on an XtaLAB Synergy-S diffractometer. The crystal was cooled to T = 100.00(10) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2014/7 of **ShelXL** (Sheldrick, 2015) using Least Squares minimisation.

Crystal Data. $C_{15}H_{16}O_2$, M_r = 228.28, monoclinic, $P2_1$ (No. 4), a = 8.6189(2) Å, b = 8.0477(2) Å, c = 8.68530(10) Å, β = 101.240(2)°, α = γ = 90°, V = 590.88(2) $Å^3$, T = 100.00(10) K, Z = 2, Z' = 1, $\mu(CuK_\alpha)$ = 0.666 mm^{-1}, 6438 reflections measured, 2010 unique (R_{int} = 0.0212) which were used in all calculations. The final wR_2 was 0.0719 (all data) and R_1 was 0.0283 (I > 2σ(I)).

Compound	**5g**
Formula	$C_{15}H_{16}O_2$
$D_{calc.}$/ g cm^{-3}	1.283
μ/mm^{-1}	0.666
Formula Weight	228.28
Colour	colourless
Shape	block
Size/mm^3	0.54×0.41×0.23
T/K	100.00(10)
Crystal System	monoclinic
Flack Parameter	0.06(8)
Hooft Parameter	0.08(5)
Space Group	$P2_1$
a/Å	8.6189(2)
b/Å	8.0477(2)
c/Å	8.68530(10)
α/°	90
β/°	101.240(2)
γ/°	90
V/$Å^3$	590.88(2)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	CuK_α
Θ_{min}/°	5.232
Θ_{max}/°	67.120
Measured Refl.	6438
Independent Refl.	2010
Reflections with I > 2σ(I)	1986
R_{int}	0.0212
Parameters	205
Restraints	28
Largest Peak	0.198
Deepest Hole	-0.268
GooF	1.106
wR_2 (all data)	0.0719
wR_2	0.0716
R_1 (all data)	0.0290
R_1	0.0283

Structure Quality Indicators

Reflections:	d min (Cu)	0.84	I/σ	49.1	Rint	2.12%	complete at 2θ=135°	95%
Refinement:	Shift	0.000	Max Peak	0.2	Min Peak	-0.3	GooF	1.106	0.06(8)

A colourless block-shaped crystal with dimensions 0.54×0.41×0.23 mm^3 was mounted on a loop with paratone oil. Data were collected using an XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 100.00(10) K.

Data were measured using ω scans of 0.5° per frame for s using CuK_α radiation (micro-focus sealed X-ray tube, 50 kV, 1.0 mA).The total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.39.35c, 2017). The maximum resolution that was achieved was Θ = 67.120°.

The diffraction patterns were indexed using **CrysAlisPro** (Rigaku, V1.171.39.35c, 2017) and the unit cells were refined using **CrysAlisPro** (Rigaku, V1.171.39.35c, 2017) on 6379 reflections, 99 % of the observed reflections. Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.39.35c, 2017) and CrysAlisPro 1.171.39.35c (Rigaku Oxford Diffraction, 2017). A numerical absorption correction based on Gaussian integration over a multifaceted crystal model was applied. An empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was also applied. The final completeness is 99.2 % out to 67.120° in Θ. The absorption coefficient □ of this material is 0.666 mm^{-1} at this wavelength (λ = 1.54184 Å) and the minimum and maximum transmissions are 0.253 and 1.000.

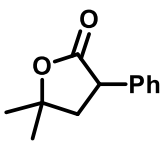
The structure was solved and the space group $P2_1$ (# 4) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2014/7 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located from the electron density maps and refined using restraints.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

Interestingly, the crystal collected was enantiomerically enriched, albeit it

has been synthesized via a racemic reaction. Indeed, the Flack parameter was refined to 0.06(8). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.08(5). (Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.)

5,5-dimethyl-3-phenyldihydrofuran-2(3H)-one (**5h**)



The general procedure is employed with diazocompound **1b** (44 mg, 0.2 mmol, 1 eq) and DCM (2 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a transparent oil (35 mg, 91%).

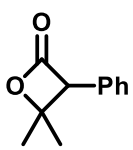
^{1}H ($CDCl_3$, 500MHz) δ: 7.38-7.35 (m, 2H), 7.31-7.28 (m, 3H), 4.04 (dd, *J* = 12.5Hz, *J* = 9.0Hz, 1H), 2.58 (dd, *J* = 12.5Hz, *J* = 9.0Hz, 1H), 2.24 (t, *J* = 12.5Hz, 1H), 1.54 (s, 3H), 1.49 (s, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 176.5, 137.0, 128.8, 128.0, 127.5, 82.1, 46.9, 44.1, 28.9, 27.0.

IR (neat, ATR): 2967 (w), 2160 (w), 1977 (w), 1770 (s), 1603 (w), 1499 (w), 1457 (w), 1375 (w), 1389 (w), 1303 (m), 1275 (s), 1259 (s), 1187 (m), 1139 (s), 1113 (s), 1075 (w).

HRMS (APCI+): Calcd. for $[C_{12}H_{14}O_2+H]^+$: 191.1067 Found: 191.1068.

4,4-dimethyl-3-phenyloxetan-2-one (**5i**)



The general procedure is employed with diazocompound **1b** (41 mg, 0.2 mmol, 1 eq) and DCM (2 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a pale yellow oil (20 mg, 57%).

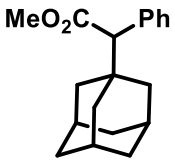
^{1}H ($CDCl_3$, 500MHz) δ: 7.40-7.32 (m, 3H), 7.22-7.21 (m, 2H), 4.63 (s, 1H), 1.78 (s, 3H), 1.22 (s, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 169.0, 131.6, 128.9, 128.1, 128.0, 81.6, 63.9, 27.9, 23.2.

IR (neat, ATR): 2977 (w), 2921 (w), 2850 (w), 1807 (s), 1719 (w), 1498 (w), 1453 (w), 1379 (w), 1268 (w), 1244 (s), 1220 (s), 1207 (s), 1134 (w), 1067 (s), 1034 (w), 1005 (w), 969 (m).

HRMS (APCI+): Calcd. for $[C_{11}H_{12}O_2+H]^+$: 177.0910 Found: 177.0911.

methyl 2-((3r,5r,7r)-adamantan-1-yl)-2-phenylacetate (**5j**)



The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq), adamantane (68 mg, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a transparent oil (14 mg, 48%).

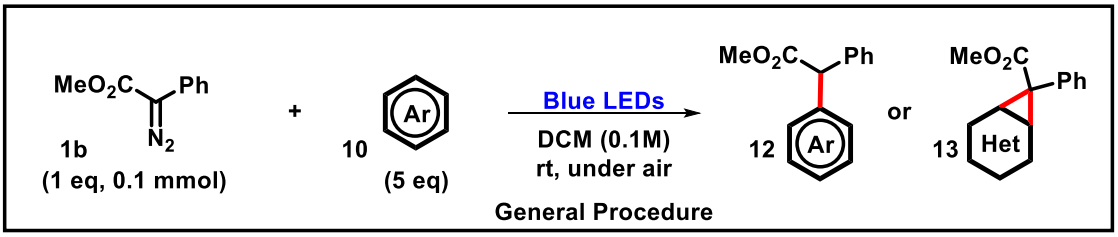
^{1}H ($CDCl_3$, 500MHz) δ: 7.39-7.37 (m, 2H), 7.33-7.25 (m, 3H), 3.64 (s, 3H), 3.28 (s, 1H), 1.98-1.93 (m, 2H), 1.71 (ddd, *J* = 12.0Hz, *J* = 5.0Hz, *J* = 3.0Hz, 3H), 1.64 (d, *J* = 12.0Hz, 3H), 1.59-1.57 (m, 2H), 1.57-1.55 (m, 2H), 1.52 (ddd, *J* = 12.0Hz, *J* = 5.0Hz, *J* = 3.0Hz, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 173.1, 134.8, 130.2, 128.5 (x2), 127.6, 127.0, 63.0, 51.2, 39.9, 36.7, 36.3, 28.6.

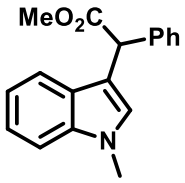
IR (neat, ATR): 2904 (s), 2847 (m), 1732 (s), 1601 (w), 1497 (w), 1453 (m), 1432 (m), 1362 (m), 1344 (w), 1329 (w), 1312 (w), 1263 (w), 1227 (w), 1197 (m), 1147 (s), 1080 (w), 1016 (m).

HRMS (APCI+): Calcd. for $[C_{19}H_{24}O_2+H]^+$: 285.1849 Found: 285.1849.

3.7 C-H Insertion or Cyclopropanation of Arenes



methyl 2-(1-methyl-1H-indol-3-yl)-2-phenylacetate (**12a**)



The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq), 1-methylindole (62 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a pale yellow oil (18 mg, 63%).

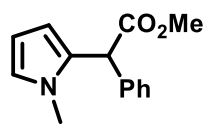
^{1}H ($CDCl_3$, 500MHz) δ: 7.47-7.43 (m, 3H), 7.34-7.26 (m, 5H), 7.10-7.07 (m, 1H), 7.06 (s, 1H), 5.28 (s, 1H), 3.76 (s, 6H).

^{13}C ($CDCl_3$, 125MHz) δ: 173.5, 138.7, 137.0, 128.5, 128.4, 127.9, 127.2, 127.0, 121.8, 119.2, 119.0, 112.1, 109.3, 52.3, 48.8, 32.8.

IR (neat, ATR): 3027 (w), 2949 (w), 1732 (s), 1614 (w), 1546 (w), 1495 (w), 1474 (m), 1453 (m), 1432 (m), 1373 (w), 1331 (m), 1307 (m), 1230 (w), 1193 (m), 1149 (s), 1119 (m), 1062 (w), 1013 (m).

HRMS (APCI+): Calcd. for $[C_{18}H_{17}NO_2+H]^+$: 280.1332 Found: 280.1333.

methyl 2-(1-methyl-1H-pyrrol-2-yl)-2-phenylacetate (**12b**)



The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq), 1-methylpyrrole (45 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a pale yellow oil (15 mg, 64%).

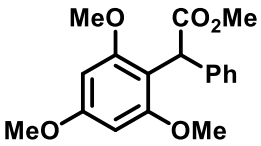
^{1}H ($CDCl_3$, 500MHz) δ: 7.35-7.32 (m, 2H), 7.29-7.26 (m, 3H), 6.60 (t, *J* = 2.0Hz, 1H), 6.11-6.08 (m, 2H), 5.01 (s, 1H), 3.75 (s, 3H), 3.41 (s, 3H).

^{13}C (CDCl$_3$, 125MHz) δ: 172.0, 137.1, 128.9, 128.6, 128.5, 127.5, 122.8, 108.7, 106.8, 52.4, 49.8, 34.0.

IR (neat, ATR): 2950 (w), 1736 (s), 1601 (w), 1491 (m), 1453 (m), 1433 (m), 1300 (m), 1245 (m), 1196 (s), 1163 (s), 1138 (s), 1089 (m), 1057 (w), 1004 (m)**.**

HRMS (APCI+): Calcd. for $[C_{14}H_{15}NO_2+H]^+$: 230.1176 Found: 230.1176.

methyl 2-phenyl-2-(2,4,6-trimethoxyphenyl)acetate (**12c**)



The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq), 1,3,5-trimethoxybenzene (84 mg, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a white solid (18 mg, 56%).

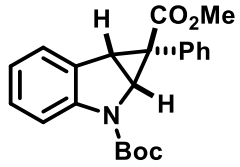
^{1}H (CDCl$_3$, 500MHz) δ: 7.32 (d, *J* = 7.5Hz, 2H), 7.26 (t, *J* = 7.5Hz, 2H), 7.20 (t, *J* = 7.5Hz, 1H), 6.16 (s, 2H), 5.32 (s, 1H), 3.81 (s, 3H), 3.79 (s, 6H), 3.69 (s, 3H).

^{13}C (CDCl$_3$, 125MHz) δ: 174.1, 160.4, 158.2, 138.9, 129.3, 127.9, 126.5, 109.6, 91.0, 55.8, 55.3, 51.9, 45.7.

IR (neat, ATR): 2993 (w), 2947 (w), 2843 (w), 2545 (w), 2160 (w), 2031 (w), 1977 (w), 1735 (s), 1592 (s), 1497 (m), 1456 (s), 1470 (s), 1442 (s), 1420 (s), 1342 (w), 1319 (w), 1278 (w), 1231 (m), 1196 (s), 1173 (s), 1147 (s), 1113 (s).

HRMS (APCI+): Calcd. for $[C_{18}H_{20}O_5+H]^+$: 317.1384 Found: 317.1385.

2-(tert-butyl) 1-methyl 1-phenyl-1a,6b-dihydrocyclopropa[b]indole-1,2(1H)-dicarboxylate (**13a**)

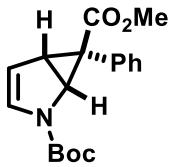


The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq), *tert*-butyl 1-indolecarboxylate (101 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5

Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a single diastereoisomer, but a mixture of rotamers (as demonstrated by ^{1}H NMR experiments at high temperatures), white foam (36 mg, 98%).

^{1}H (CDCl$_3$, 500MHz) 2 rotamers, δ: 7.42 (d, *J* = 7.5Hz, 1H), 7.38 (d, *J* = 7.5Hz, 1H), 7.05-7.02 (m, 2H), 7.00-6.96 (m, 4H), 6.92-6.89 (m, 1H), 4.97 (d, *J* = 7.0Hz, 0.5H), 4.86 (d, *J* = 7.0Hz, 0.5H), 3.73 (dd, *J* = 9.5Hz, *J* = 7.0Hz, 1H), 3.68 (s, 1.5Hz), 3.65 (s, 1.5H), 1.65 (s, 4.5H), 1.59 (s, 4.5H).
^{13}C (CDCl$_3$, 125MHz) 2 rotamers, δ: 173.6, 173.3, 152.8, 151.6, 142.4, 141.3, 132.3, 132.0, 130.4, 130.3, 129.2, 128.4, 127.8, 127.6, 127.5, 127.3, 127.1, 125.5, 125.1, 122.3, 122.2, 116.6, 114.6, 114.4, 82.6, 81.8, 52.7, 52.6, 50.7, 50.5, 35.5, 34.6, 32.1, 31.8, 28.4, 28.3.
IR (neat, ATR): 2980 (w), 2160 (w), 1977 (w), 1708 (s), 1607 (w), 1477 (m), 1467 (m), 1435 (w), 1386 (s), 1368 (s), 1321 (s), 1304 (m), 1277 (m), 1230 (s), 1190 (m), 1150 (s), 1123 (s), 1106 (m), 1078 (m), 1056 (m), 1041 (m), 1030 (m), 1018 (m).
HRMS (NSI+): Calcd. for $[C_{22}H_{23}NO_4+Na]^+$: 388.1519 Found: 388.1519.

2-(tert-butyl) 6-methyl 6-phenyl-2-azabicyclo[3.1.0]hex-3-ene-2,6-dicarboxylate (**13b**)



The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq), *tert*-butyl 1-pyrrolecarboxylate (84 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a single diastereoisomer, but a mixture of rotamers (as demonstrated by ^{1}H NMR experiments at high temperatures), pale orange solid (30 mg, 94%).

^{1}H (CDCl$_3$, 500MHz) 2 rotamers, δ: 7.28-7.23 (m, 3H), 7.14-7.13 (m, 1H), 7.11-7.09 (m, 1H), 6.14 (d, *J* = 4.0Hz, 0.4H), 5.98 (d, *J* = 4.0Hz, 0.6H), 5.19 (dd, *J* = 3.5Hz, *J* = 3.0Hz, 0.4H), 5.12 (dd, *J* = 4.0Hz, *J* = 2.5Hz, 0.6H), 4.70 (d, *J* =

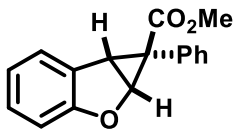
6.5Hz, 0.6H), 4.60 (d, *J* = 7.0Hz, 0.4H), 3.63 (s, 1.2H), 3.60 (s, 1.8H), 3.33-3.30 (m, 1H), 1.59 (s, 3.6H), 1.45 (s, 5.4H).

^{13}C ($CDCl_3$, 125MHz) 2 rotamers, δ: 174.1, 173.8, 151.3, 151.2, 132.7, 132.4, 131.2, 131.0, 130.8, 130.5, 127.9, 127.8, 127.4, 127.2, 107.3 (x2), 81.9, 81.6, 52.6, 52.5, 49.4, 49.3, 39.6, 38.3, 29.7, 29.3, 28.4, 28.2.

IR (neat, ATR): 3117 (w), 2980 (w), 2159 (w), 2030 (w), 1699 (s), 1592 (m), 1493 (w), 1475 (w), 1445 (w), 1431 (w), 1399 (s), 1367 (s), 1322 (m), 1255 (s), 1241 (s), 1175 (m), 1136 (s), 1075 (m), 1055 (m), 1023 (w), 1003 (m), 955 (s).

HRMS (APCI+): Calcd. for $[C_{18}H_{21}NO_4+H]^+$: 316.1543 Found: 316.1544.

methyl 1-phenyl-1a,6b-dihydro-1H-cyclopropa[b]benzofuran-1-carboxylate (**13c**)



The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq), 2,3-benzofuran (55 μL, 0.5 mmol, 5 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a single diastereoisomer, white solid (21 mg, 78%).

^{1}H ($CDCl_3$, 500MHz), δ: 7.35 (dd, *J* = 7.7Hz, *J* = 1.2Hz, 1H), 7.08 (s, 5H), 6.90 (td, *J* = 7.7Hz, *J* = 1.2Hz, 1H), 6.81 (td, *J* = 7.7Hz, *J* = 1.2Hz, 1H), 6.46 (d, J = 7.7Hz, 1H), 5.36 (d, *J* = 5.5Hz, 1H), 3.79 (d, *J* = 5.5Hz, 1H), 3.67 (s, 3H).

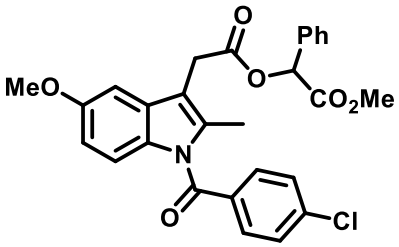
^{13}C ($CDCl_3$, 125MHz), δ: 173.3, 159.5, 132.5, 129.6, 128.0, 127.5, 127.1, 126.4, 125.0, 121.1, 109.7, 70.4, 52.7, 37.4, 30.9.

IR (neat, ATR): 3052 (w), 2950 (w), 2923 (w), 2849 (w), 2360 (w), 2160 (w), 1976 (w), 1703 (s), 1613 (w), 1594 (w), 1497 (w), 1475 (w), 1465 (m), 1447 (w), 1436 (m), 1323 (m), 1301 (w), 1258 (s), 1240 (s), 1182 (w), 1157 (s), 1102 (w), 1086 (m), 1073 (m), 1054 (m), 1030 (s).

HRMS(APCI-): Calcd. for $[C_{17}H_{14}NO_3-H]^-$: 265.0870 Found: 265.0870.

3.8 Functionalization of Complex Molecules

methyl 2-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetoxy)-2-phenylacetate (**16**)



The general procedure is employed with diazocompound **1b** (18 mg, 0.1 mmol, 1 eq), Indometacin **14** (36 mg, 0.1 mmol, 1 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as an yellowish foam (39 mg, 77%).

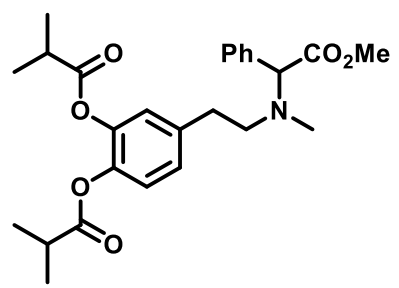
^{1}H ($CDCl_3$, 500MHz) δ: 7.65 (d, *J* = 8.5Hz, 2H), 7.45 (d, *J* = 8.5Hz, 2H), 7.43-7.42 (m, 2H), 7.39-7.36 (m, 3H), 6.98 (d, *J* = 2.5Hz, 1H), 6.90 (d, *J* = 9.0Hz, 1H), 6.67 (dd, *J* = 9.0Hz, *J* = 2.5Hz, 1H), 5.95 (s, 1H), 3.84 (s, 2H), 3.79 (s, 3H), 3.69 (s, 3H), 2.38 (s, 3H).

^{13}C ($CDCl_3$, 125MHz) δ: 170.1, 169.0, 168.3, 156.1, 139.2, 136.0, 133.9, 133.6, 131.2, 130.8, 130.5, 129.3, 129.1, 128.8, 127.6, 114.9, 112.0 (x2), 101.1, 74.8, 55.6, 52.6, 30.0, 13.4.

IR (neat, ATR): 2953 (w), 1744 (s), 1682 (s), 1590 (m), 1477 (s), 1456 (s), 1436 (m), 1400 (w), 1356 (s), 1314 (s), 1257 (m), 1217 (s), 1141 (s), 1088 (s), 1067 (s), 1036 (s), 1014 (s), 978 (w).

HRMS (NSI+): Calcd. for $[C_{28}H_{24}ClNO_6+NH_4]^+$:523.1630 Found: 523.1639.

4-(2-((2-methoxy-2-oxo-1-phenylethyl)(methyl)amino)ethyl)-1,2-phenylene bis(2-methylpropanoate) (**17**)



The general procedure is employed with diazocompound **1b** (53 mg, 0.3 mmol, 3 eq), Ibopamine **15** (31 mg, 0.1 mmol, 1 eq), in DCM (1 mL, 0.1M). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt – 7:3 Hex:AcOEt) affords the title compound as a transparent oil (26 mg, 57%).

^{1}H ($CDCl_3$, 500MHz) δ: 7.37-7.30 (m, 5H), 7.01 (d, *J* = 8.5Hz, 1H), 6.93 (dd, *J* = 8.5Hz, *J* = 2.0Hz, 1H), 6.88 (d, J = 2.0Hz, 1H), 4.27 (s, 1H), 3.70 (s, 3H), 2.79-2.69 (m, 5H), 2.67-2.63 (m, 1H), 2.36 (s, 3H), 1.29 (d, *J* = 7.0Hz, 6H), 1.28 (d, *J* = 7.0Hz, 6H).

^{13}C ($CDCl_3$, 125MHz) δ (2C cannot be unambigously assigned): 174.5, 174.3, 172.3, 141.9, 140.4, 138.8, 136.3, 128.7, 128.5, 128.2, 126.7, 123.5, 123.0, 72.7, 55.9, 51.8, 39.3, 34.0, 32.9, 18.9.

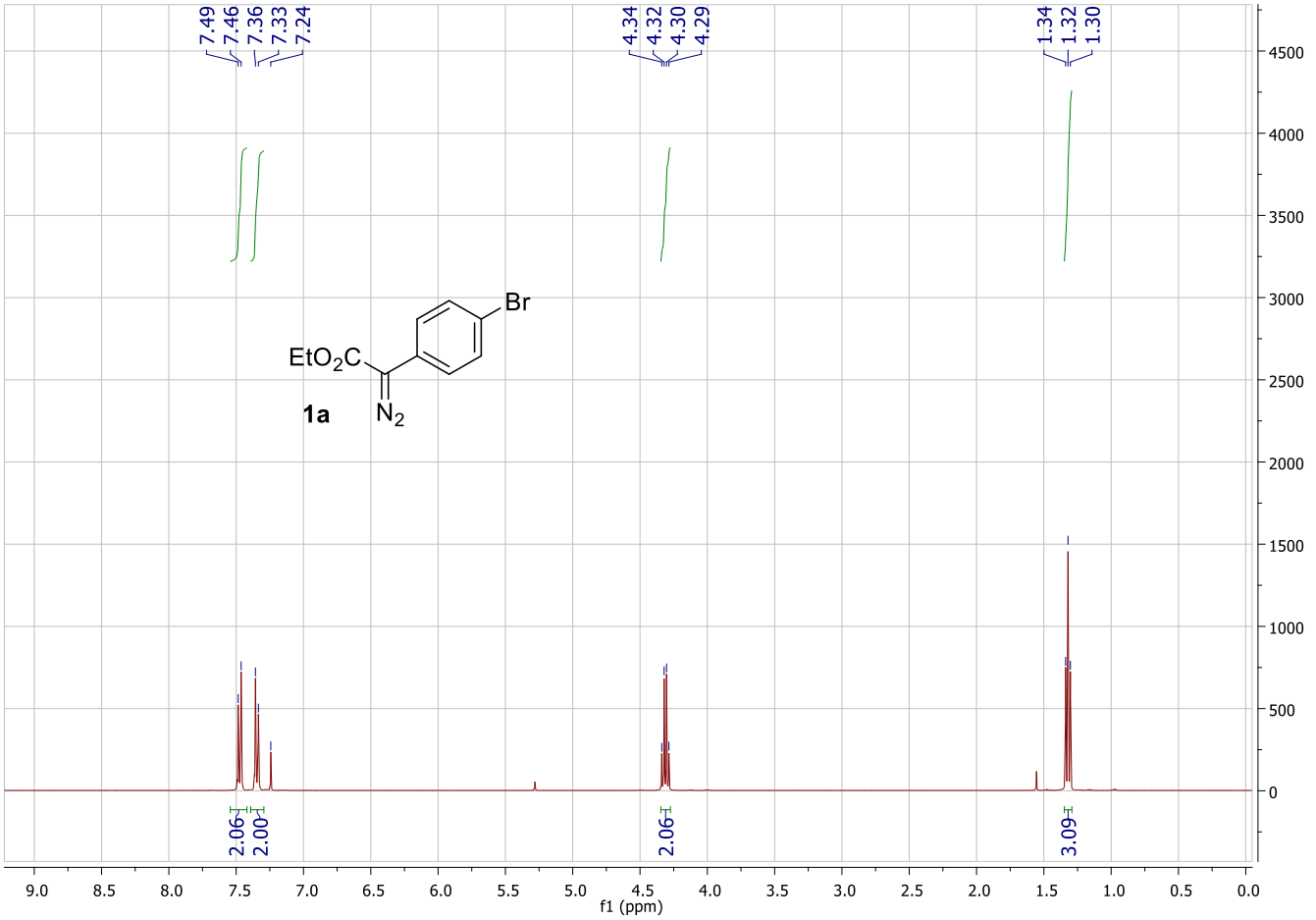
IR (neat, ATR): 2974 (w), 1763 (s), 1595 (w), 1505 (m), 1469 (m), 1387 (w), 1346 (w), 1256 (s), 1233 (m), 1202 (s), 1181 (s), 1110 (s), 1089 (s), 1043 (s), 910 (w).

HRMS (APCI+): Calcd. for $[C_{26}H_{33}NO_6+H]^+$: 456.2381 Found: 456.2379.

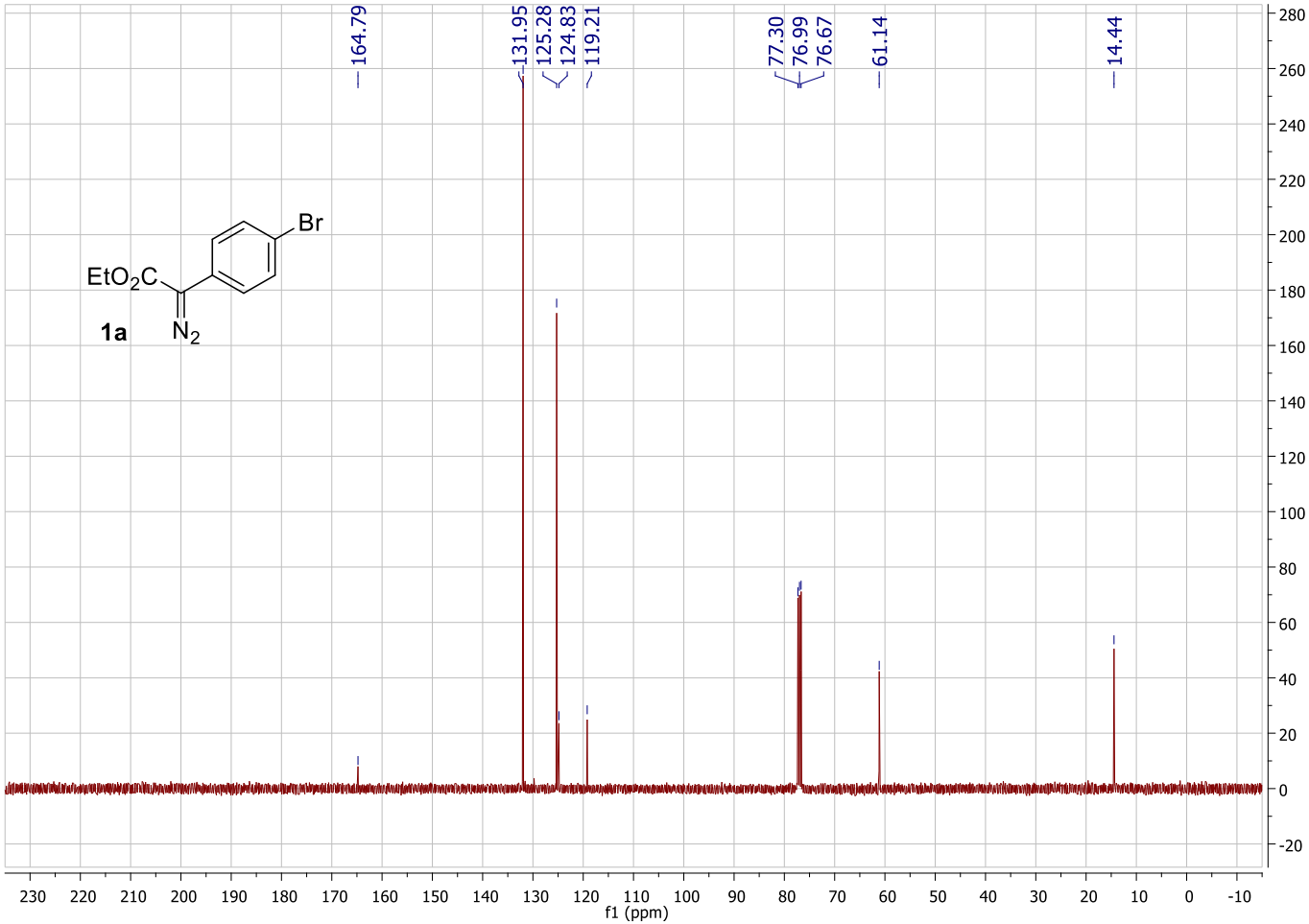
4. NMR spectra:

4.1 Aryldiazoacetates

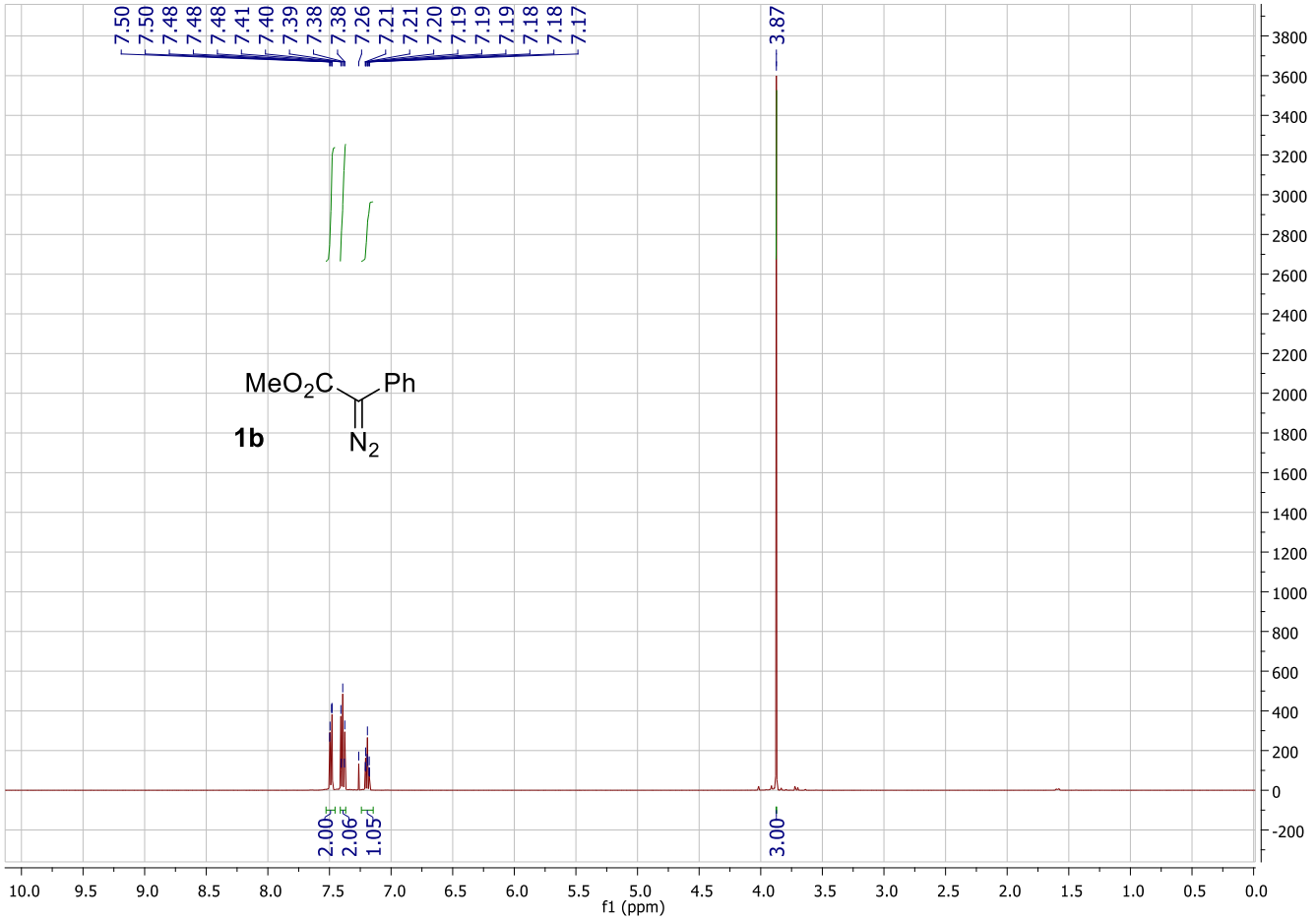
500MHz, $CDCl_3$



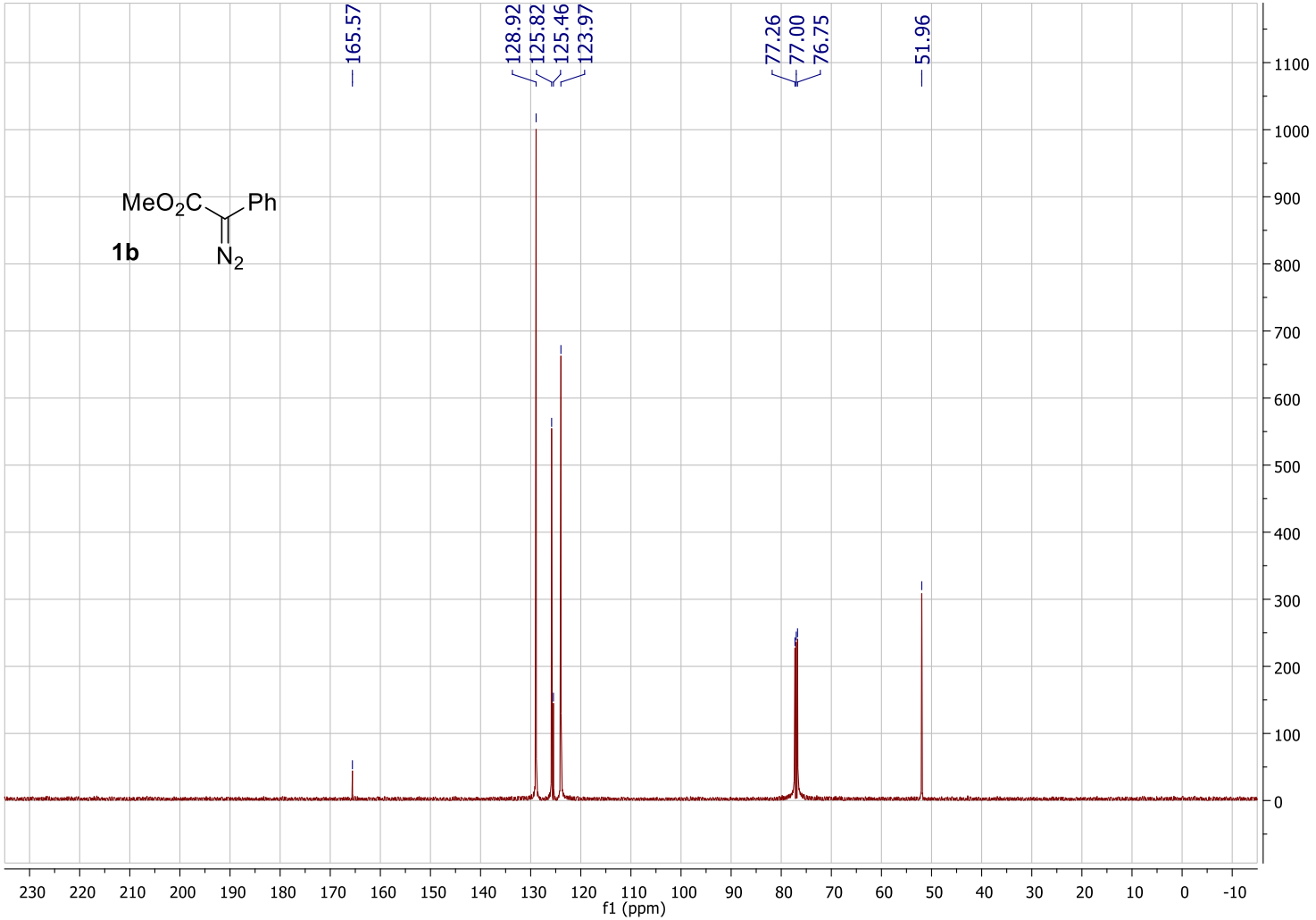
125MHz, $CDCl_3$



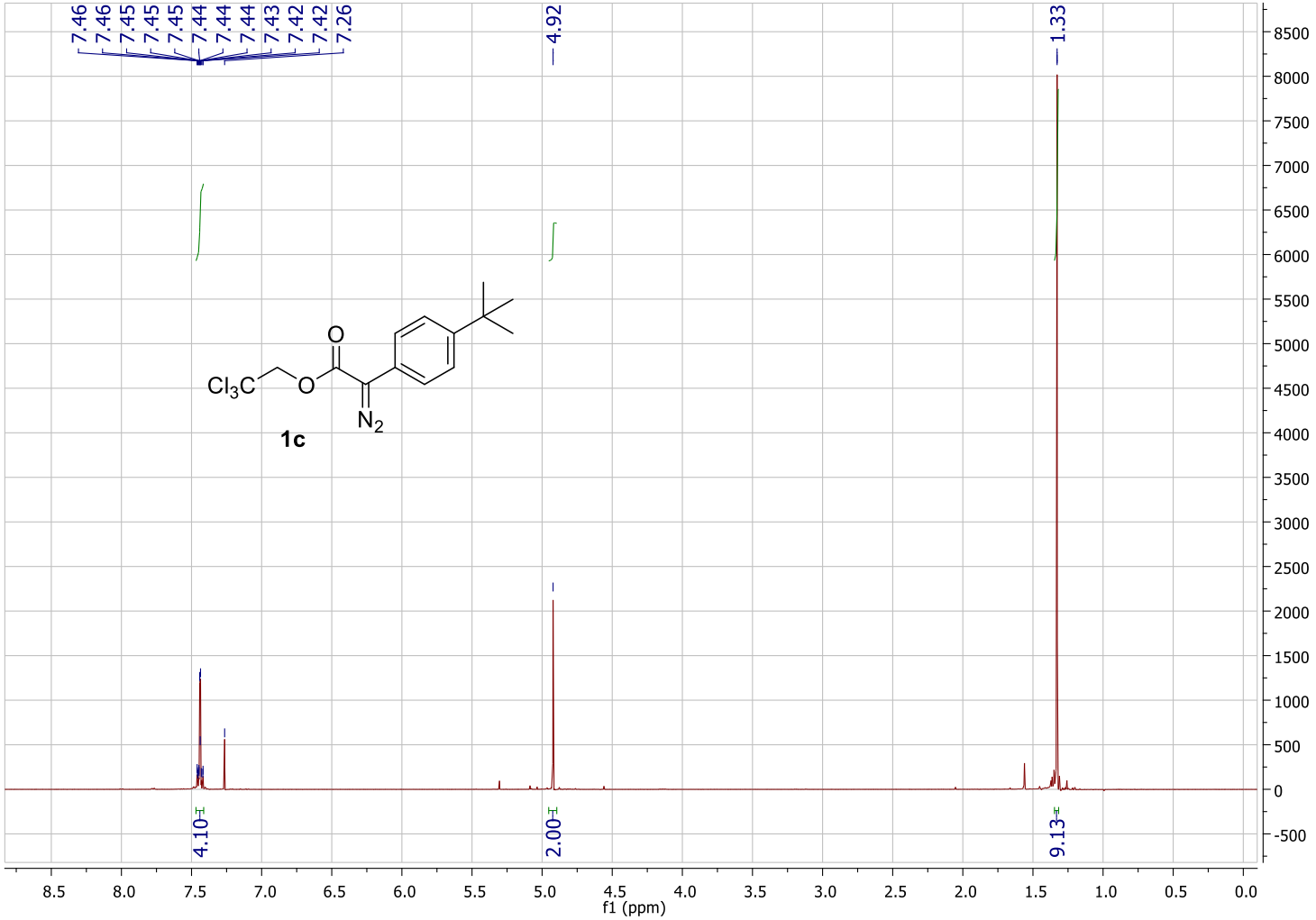
500MHz, $CDCl_3$



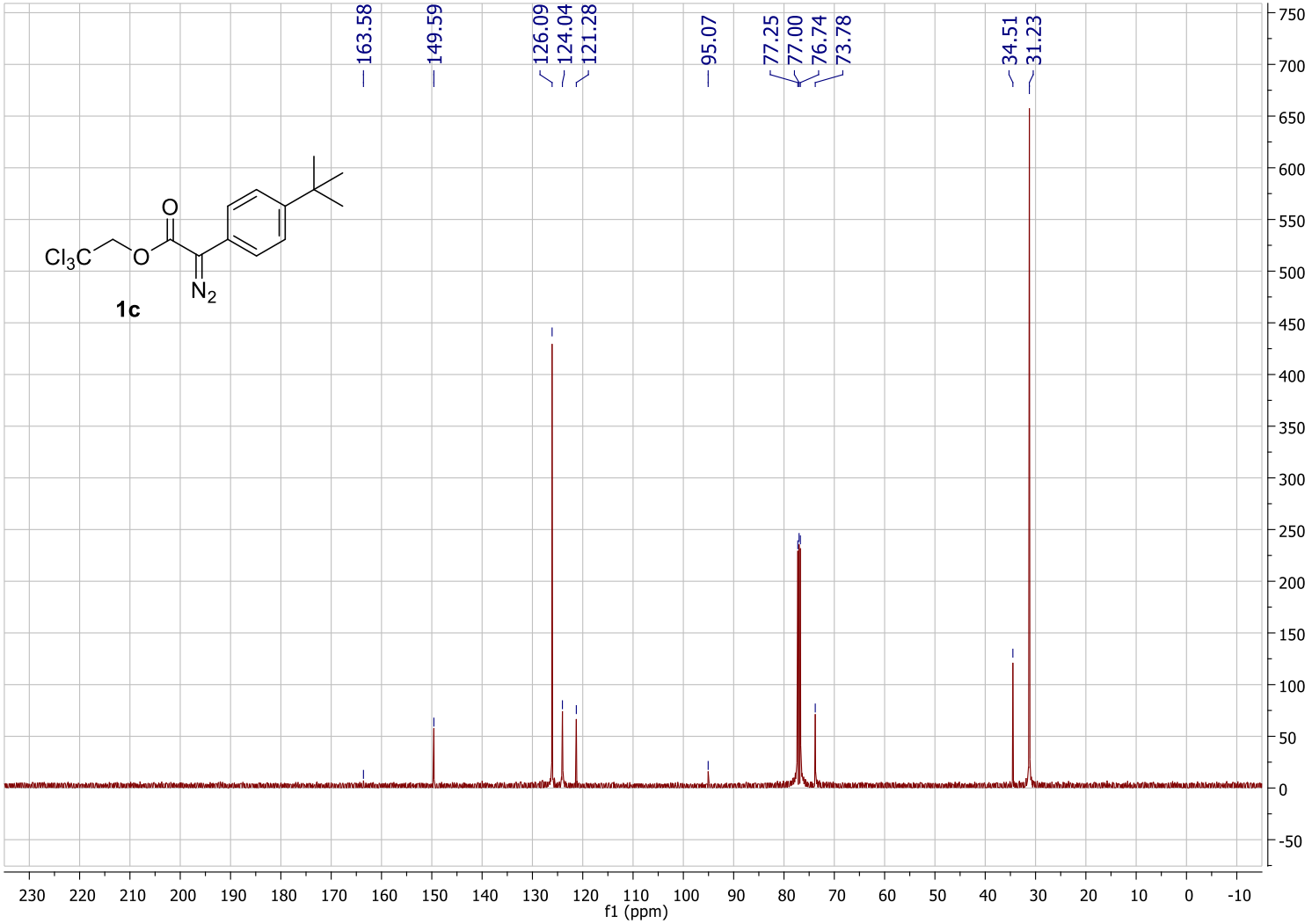
125MHz, $CDCl_3$



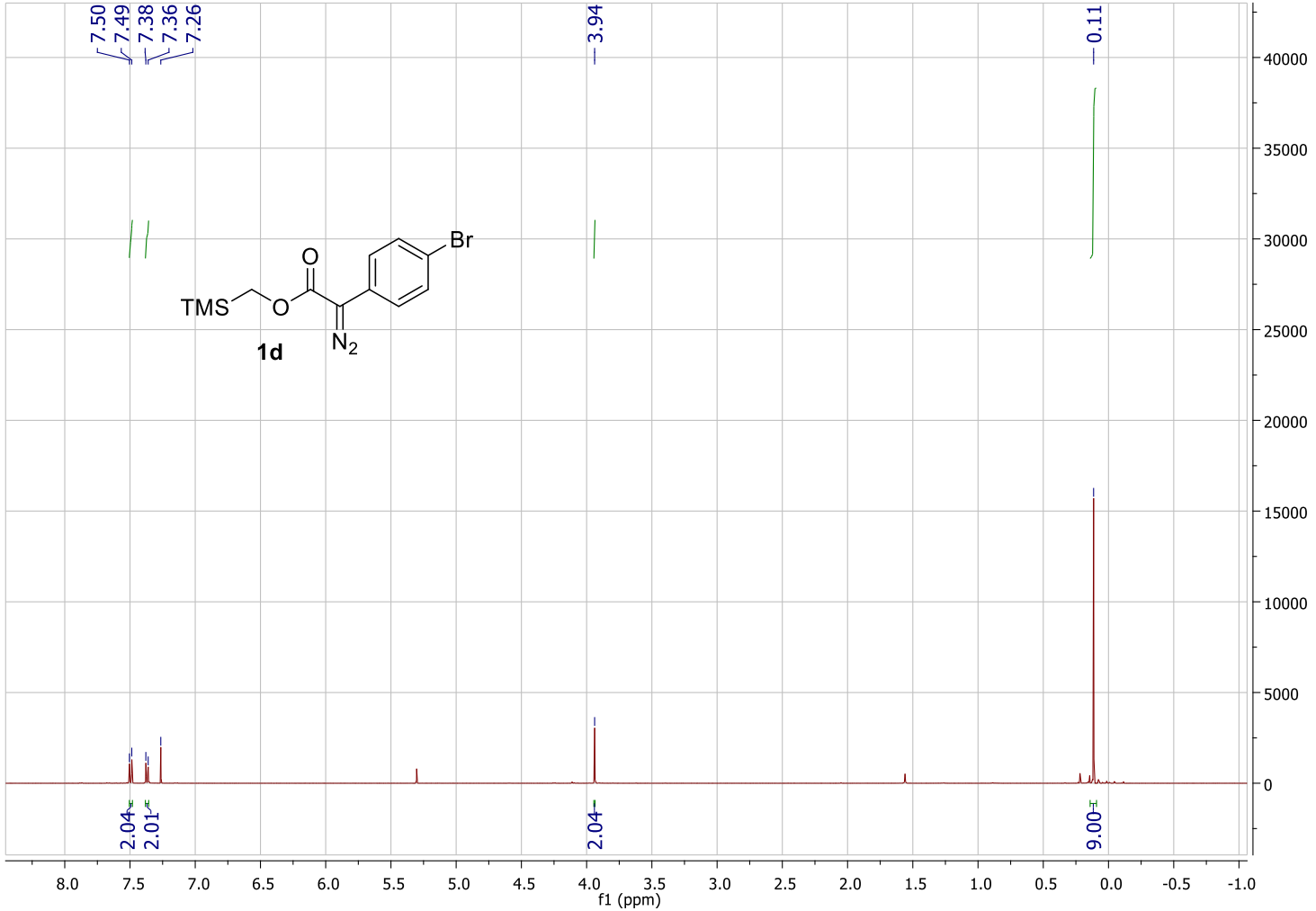
500MHz, $CDCl_3$



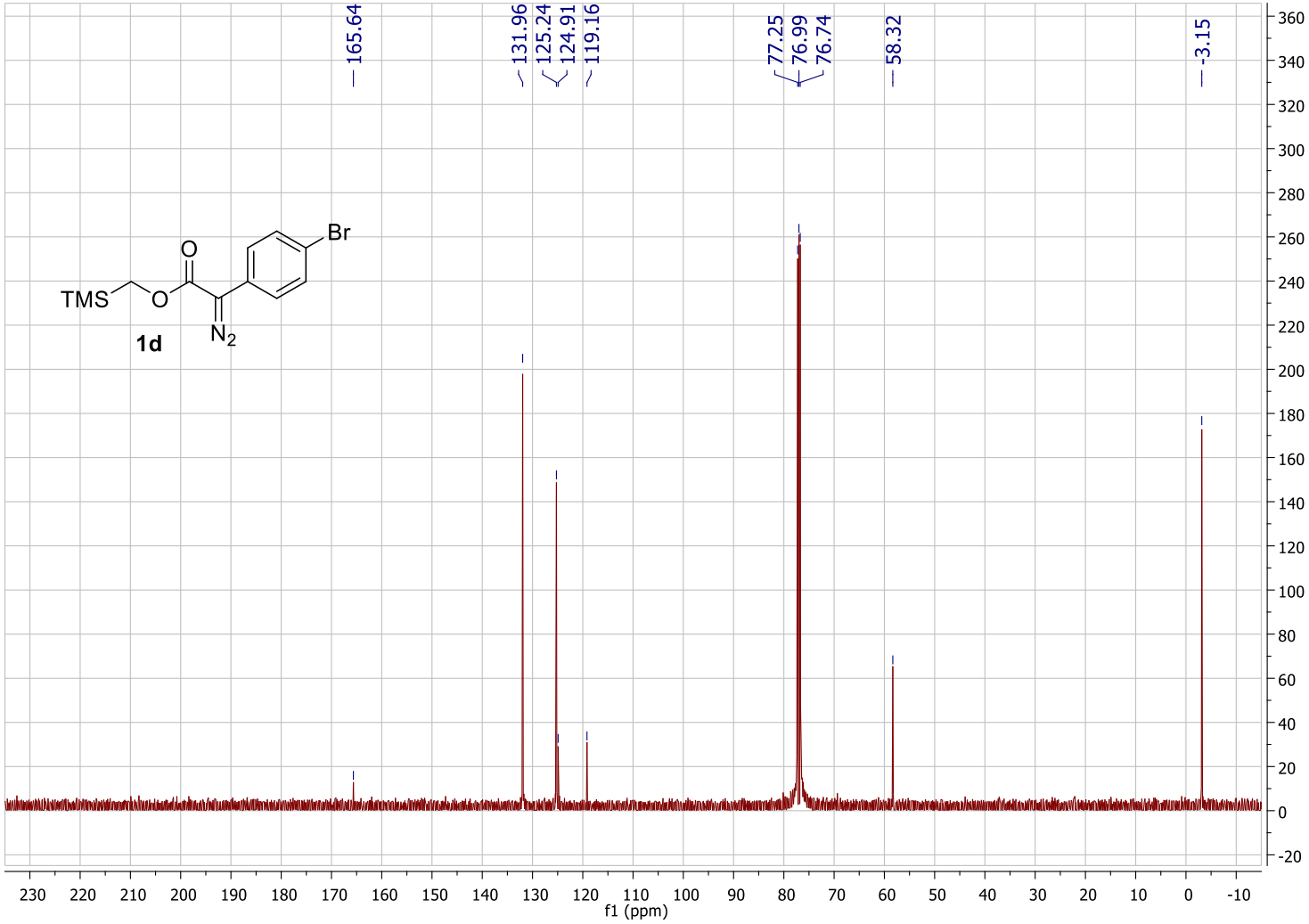
125MHz, $CDCl_3$



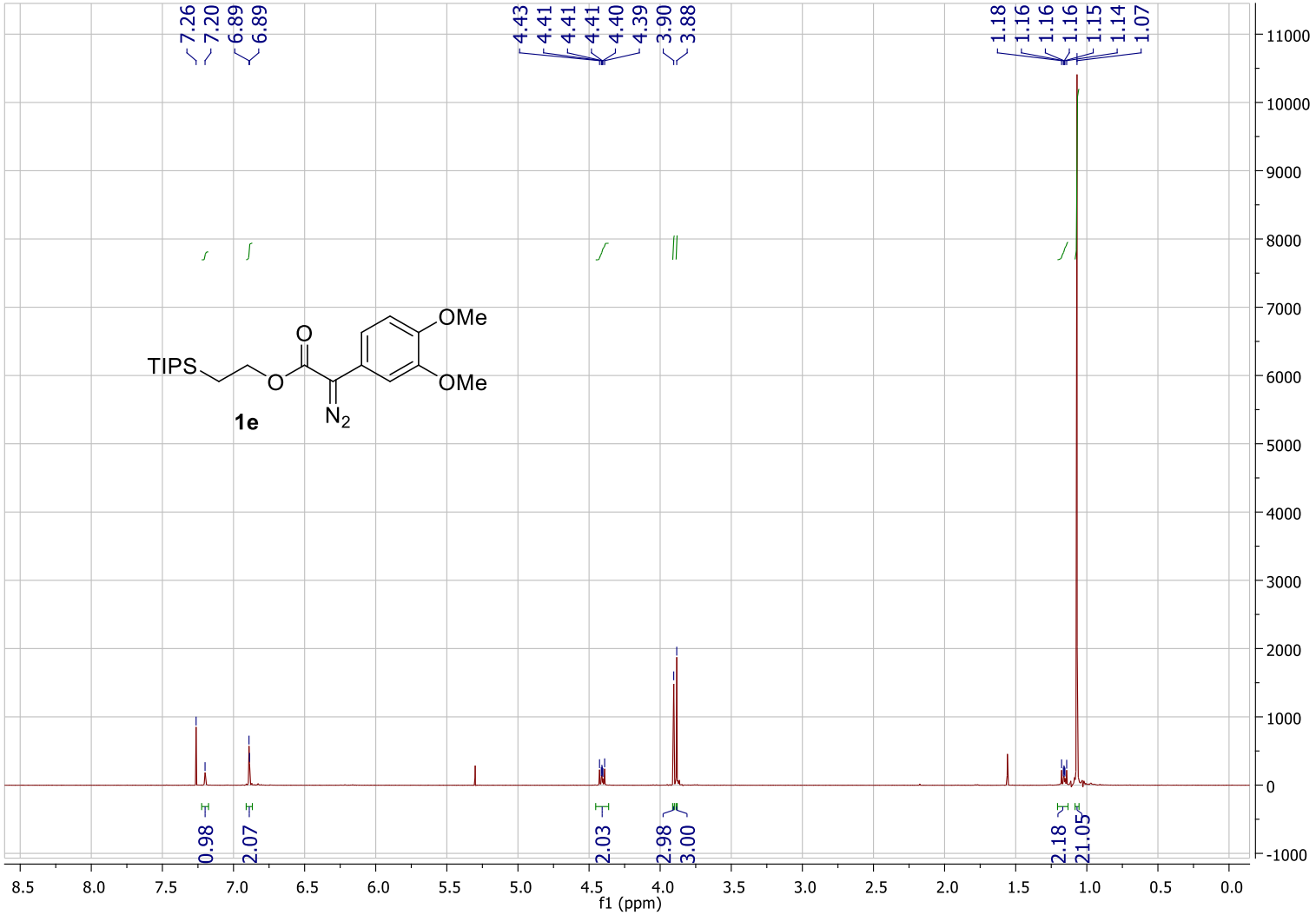
500MHz, $CDCl_3$



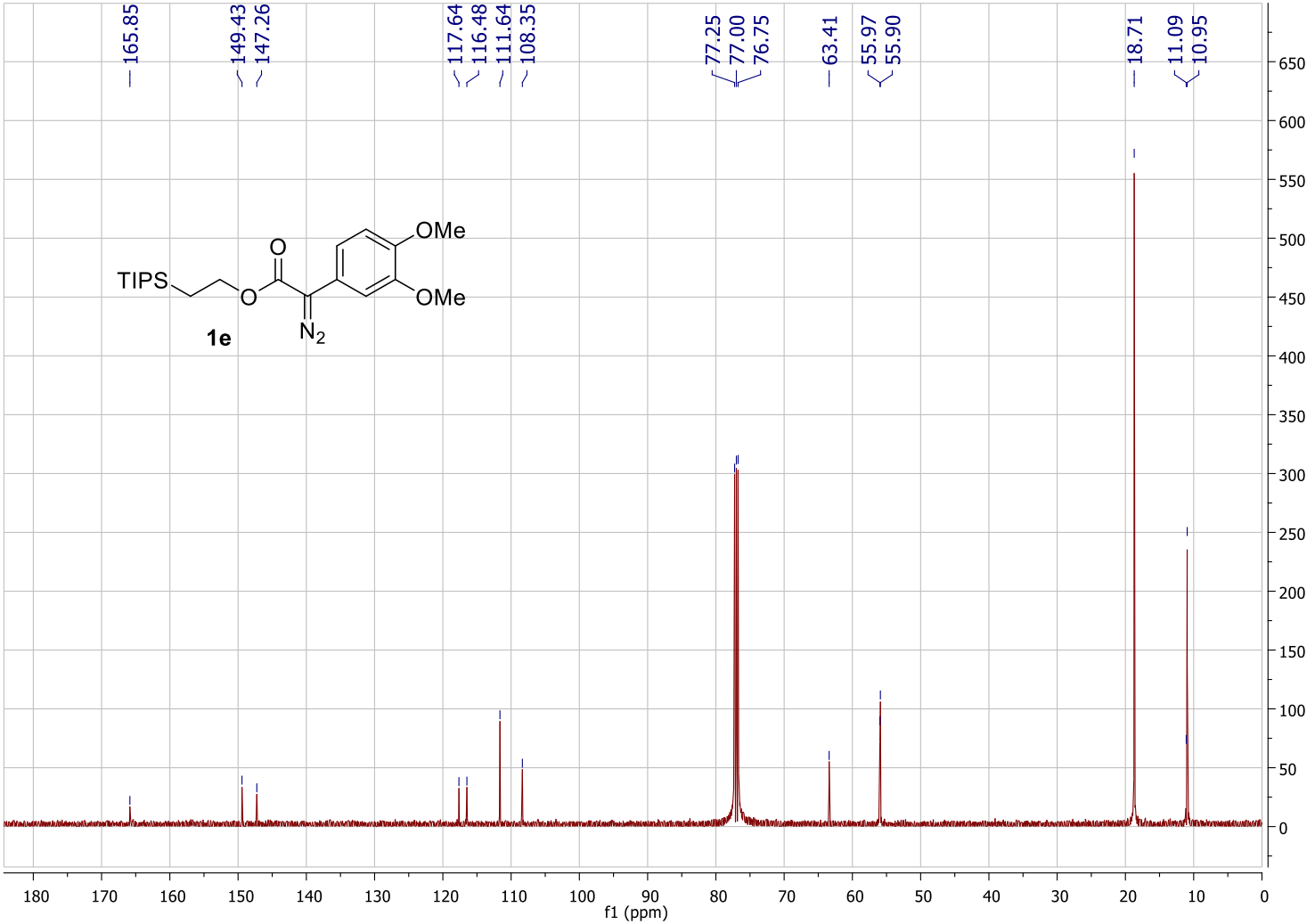
125MHz, $CDCl_3$



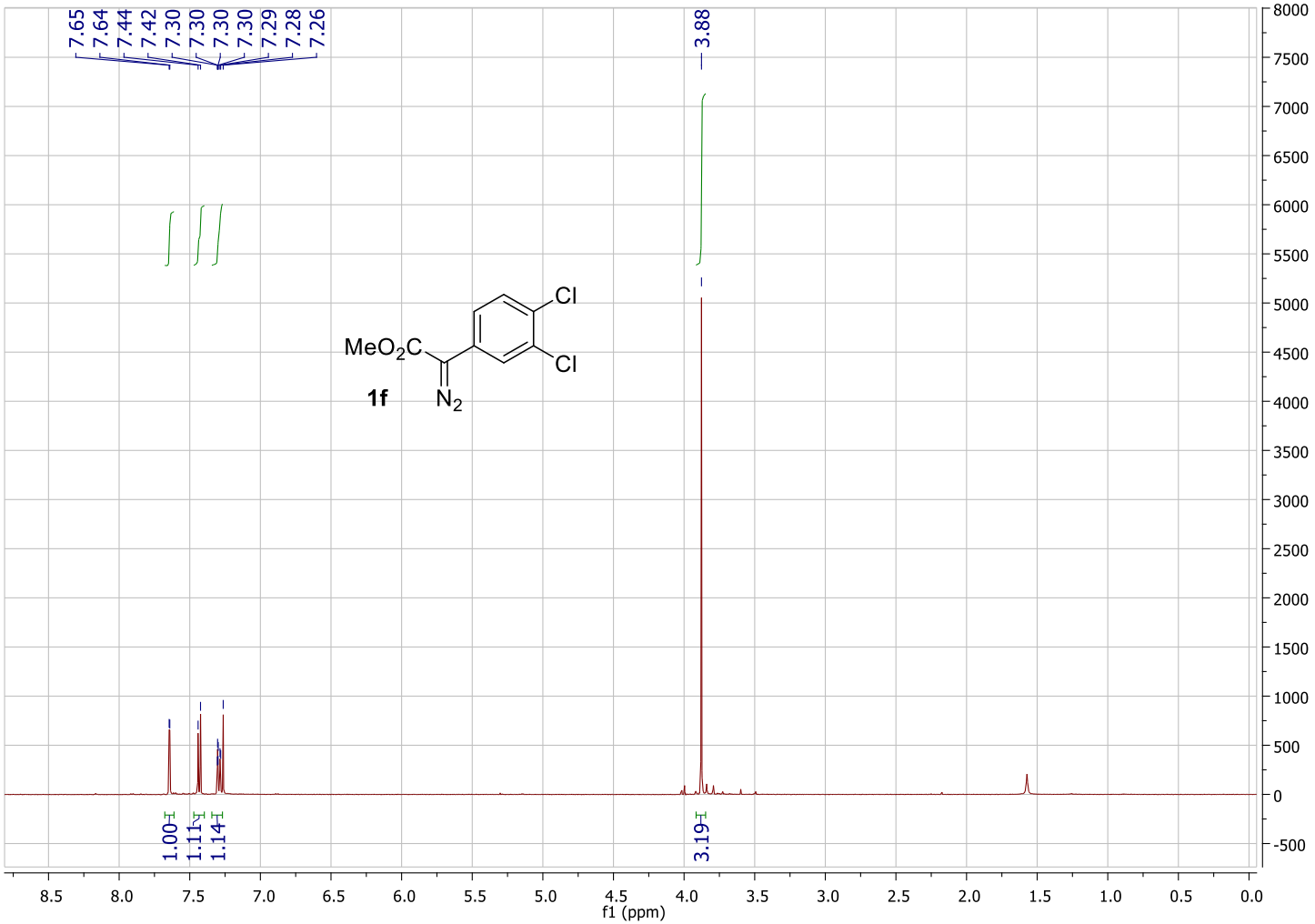
500MHz, $CDCl_3$



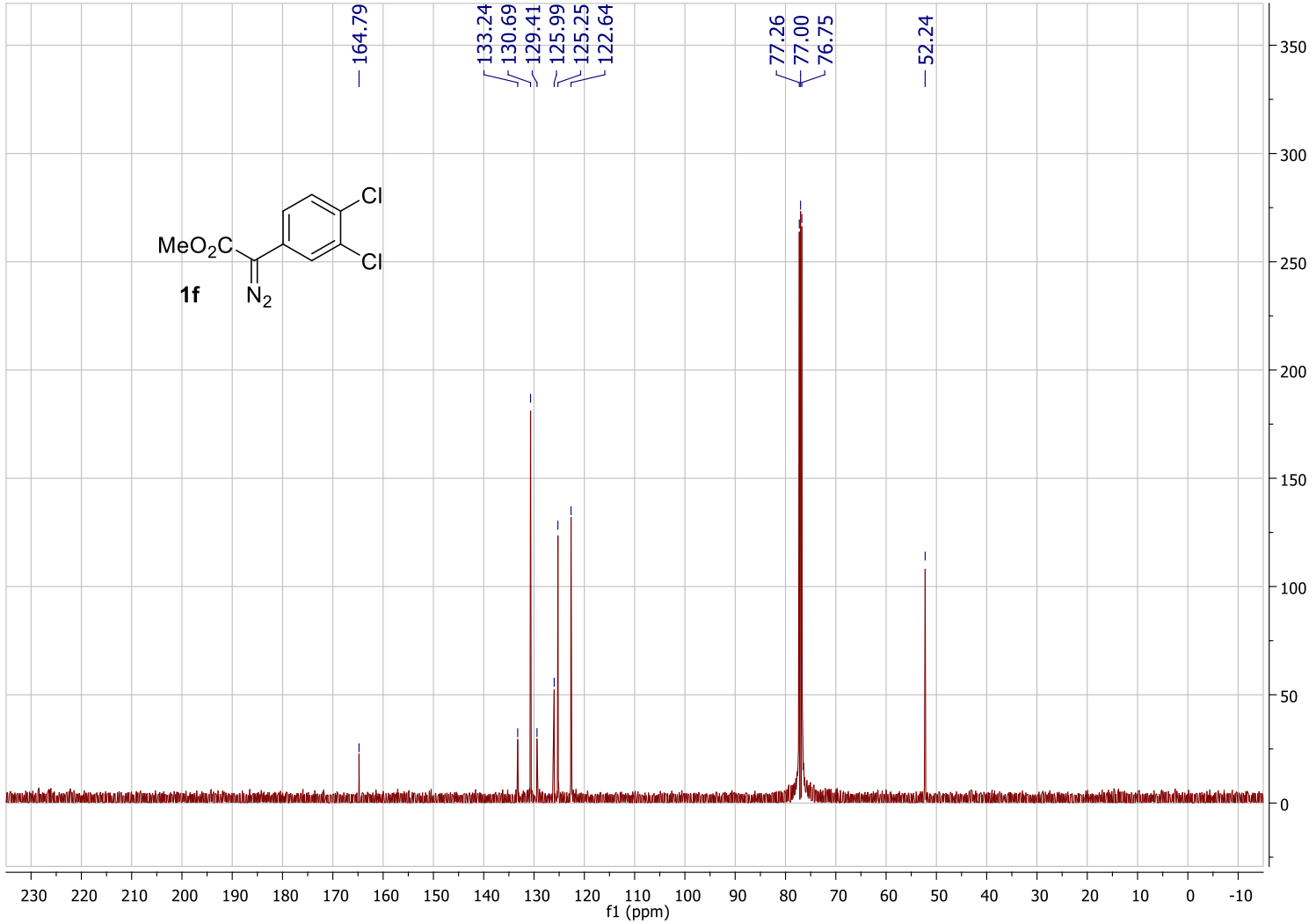
125MHz, $CDCl_3$



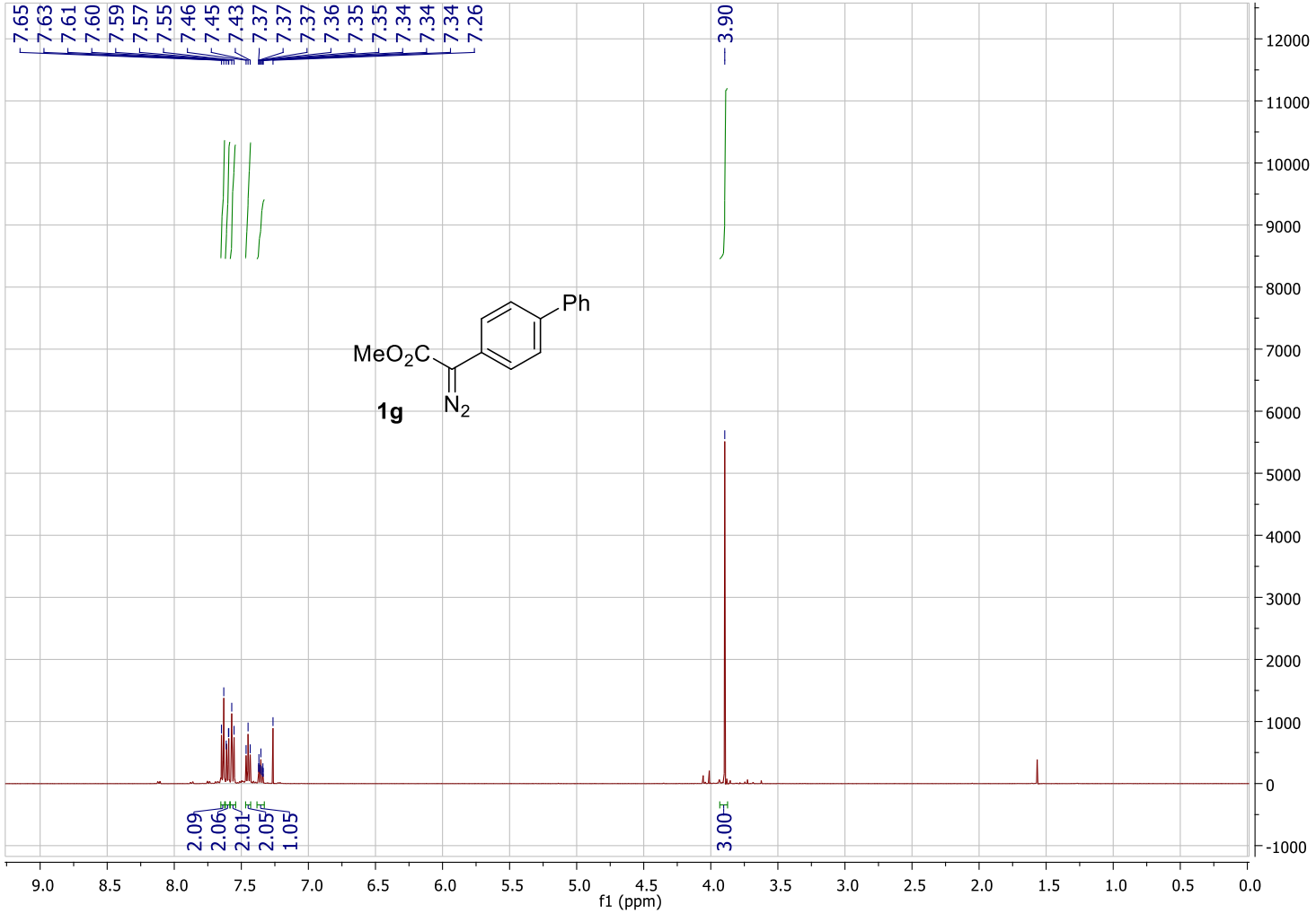
500MHz, $CDCl_3$



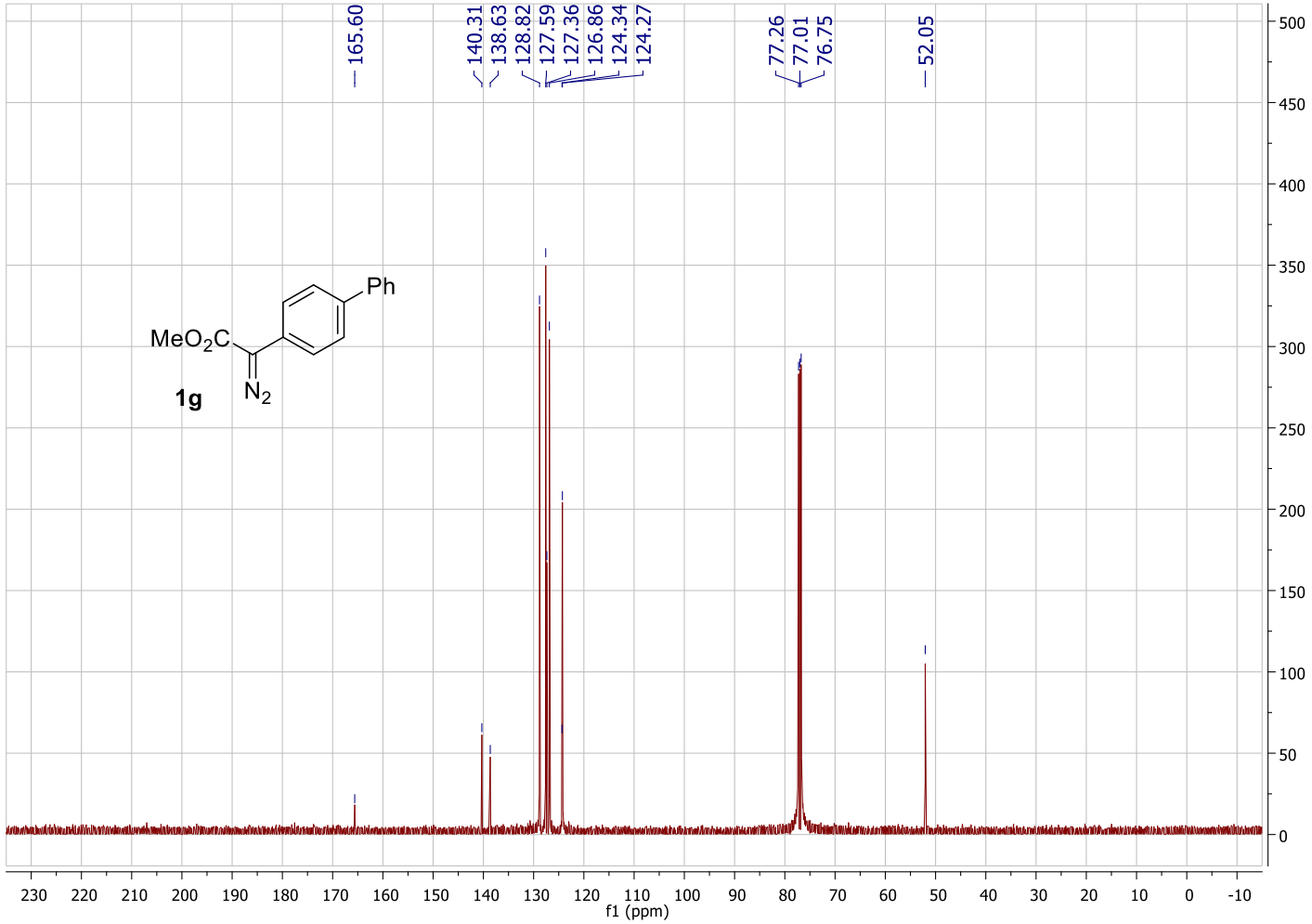
125MHz, $CDCl_3$



500MHz, $CDCl_3$



125MHz, $CDCl_3$



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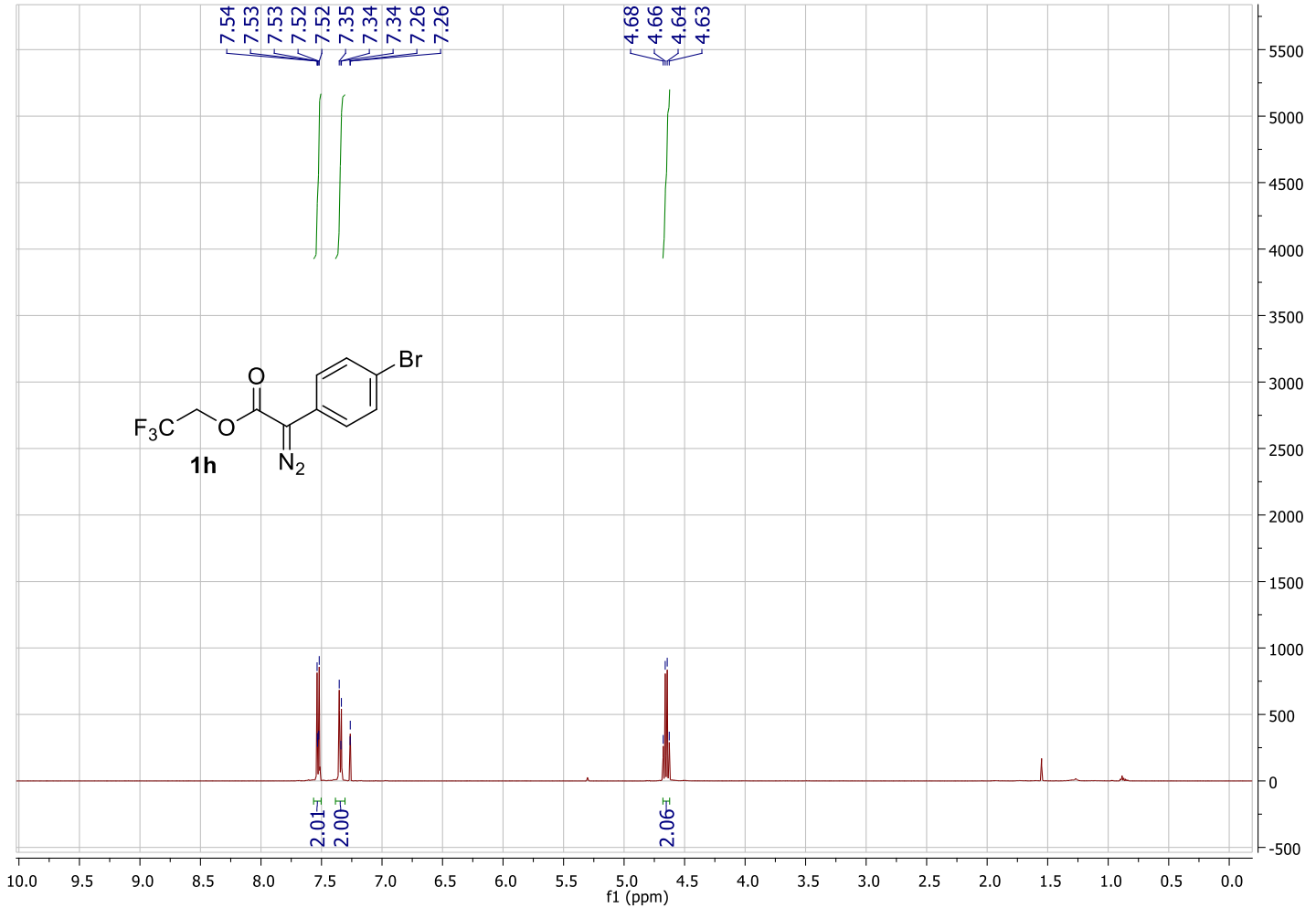
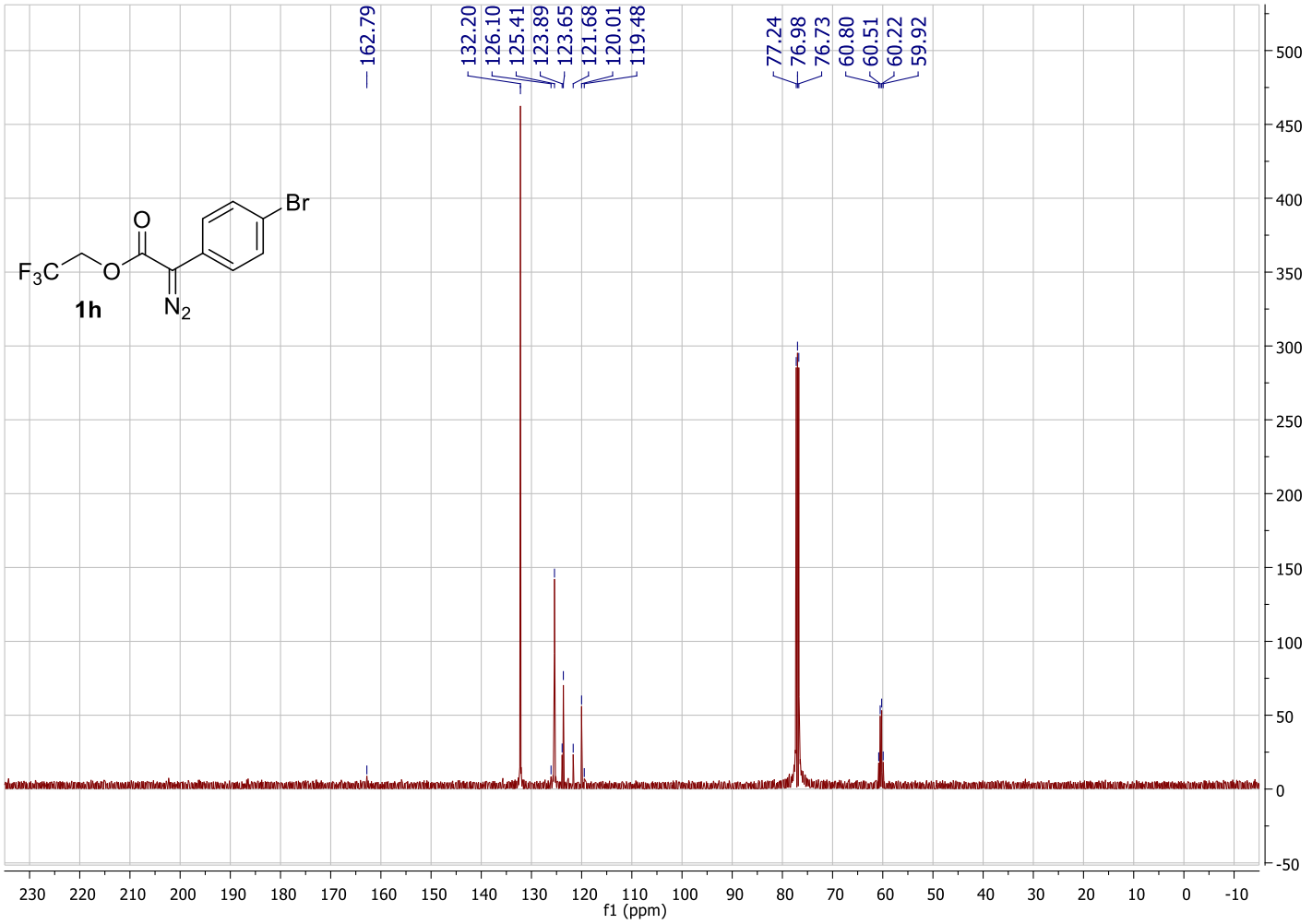
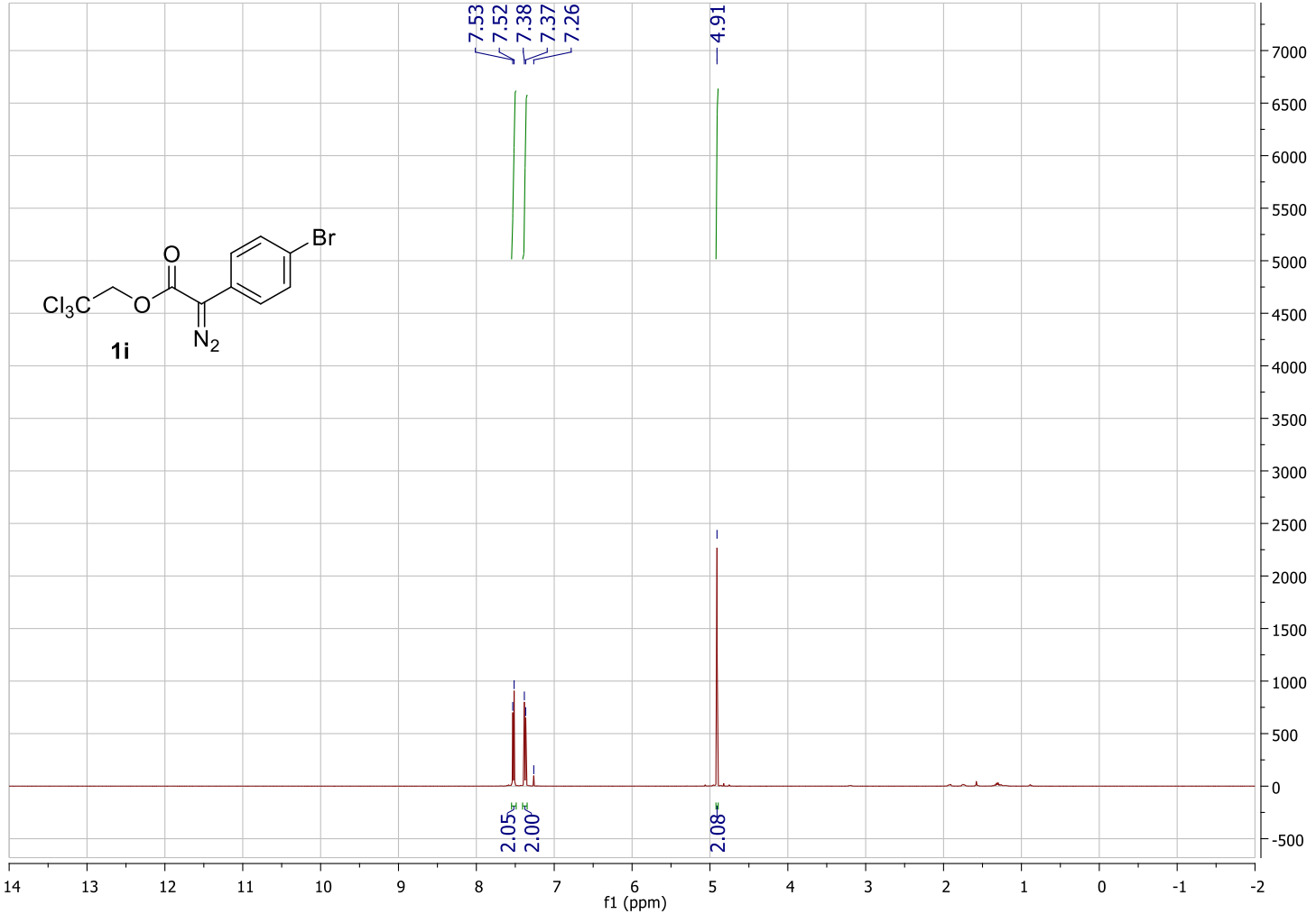


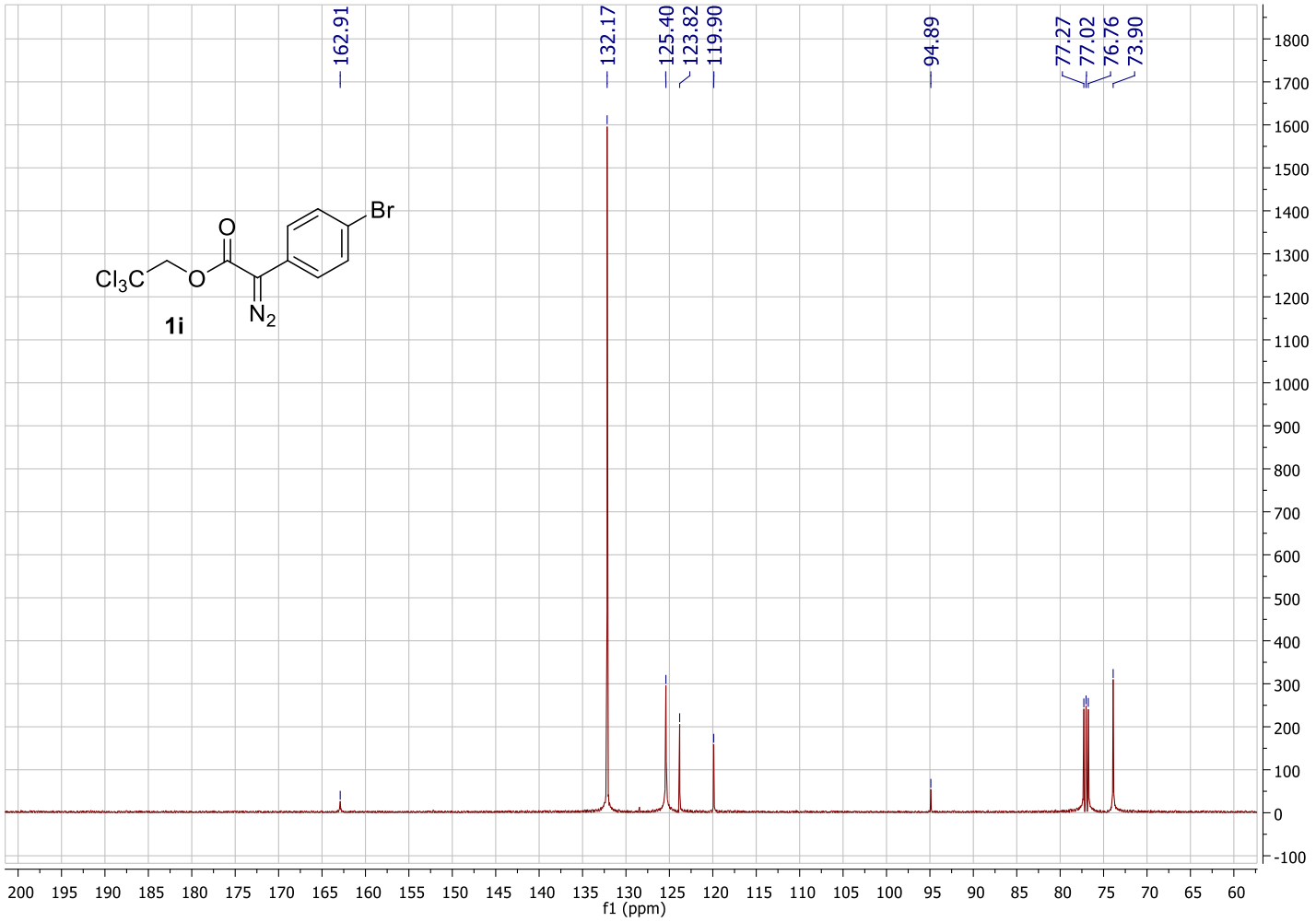
125MHz, $CDCl_3$



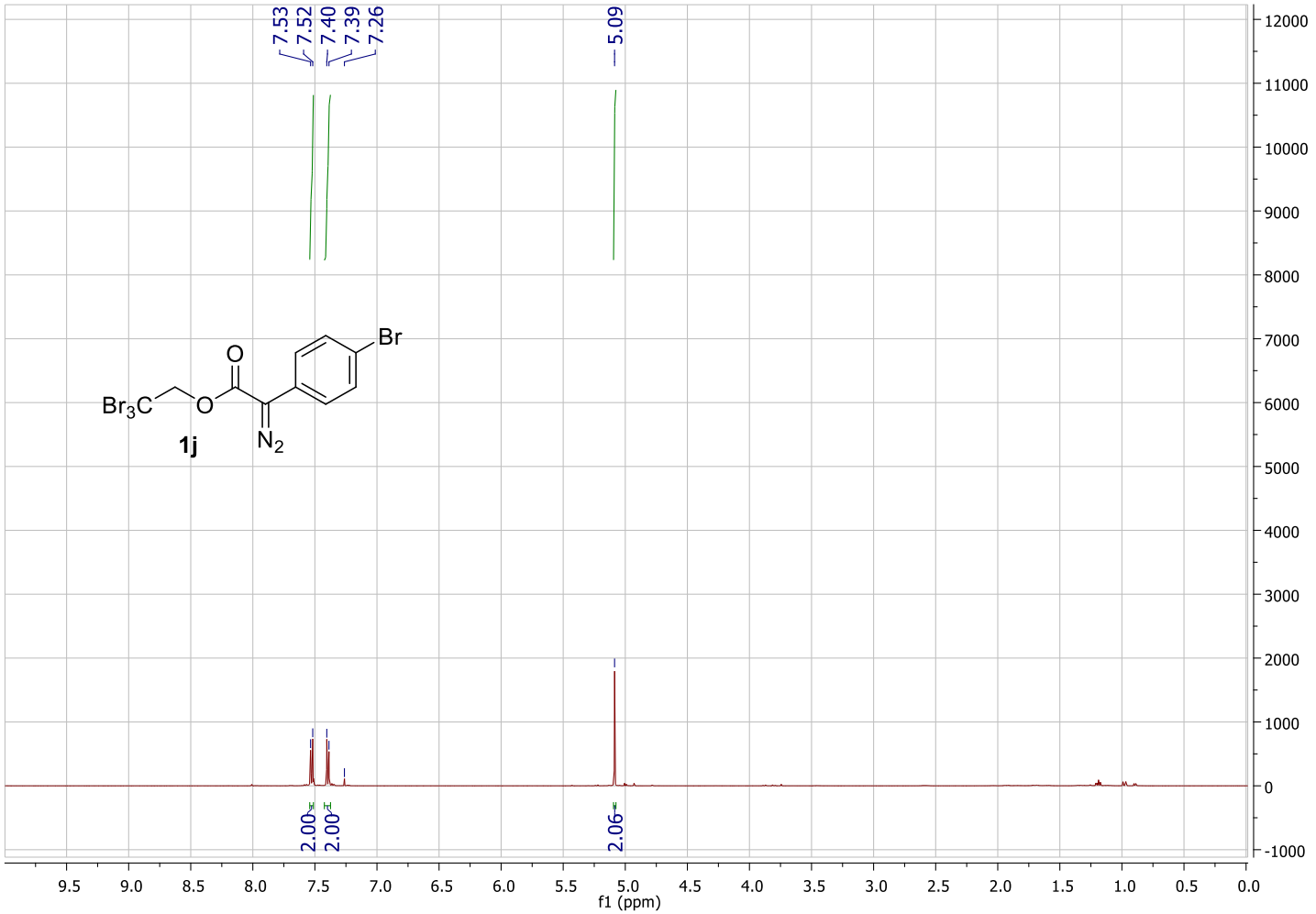
500MHz, $CDCl_3$



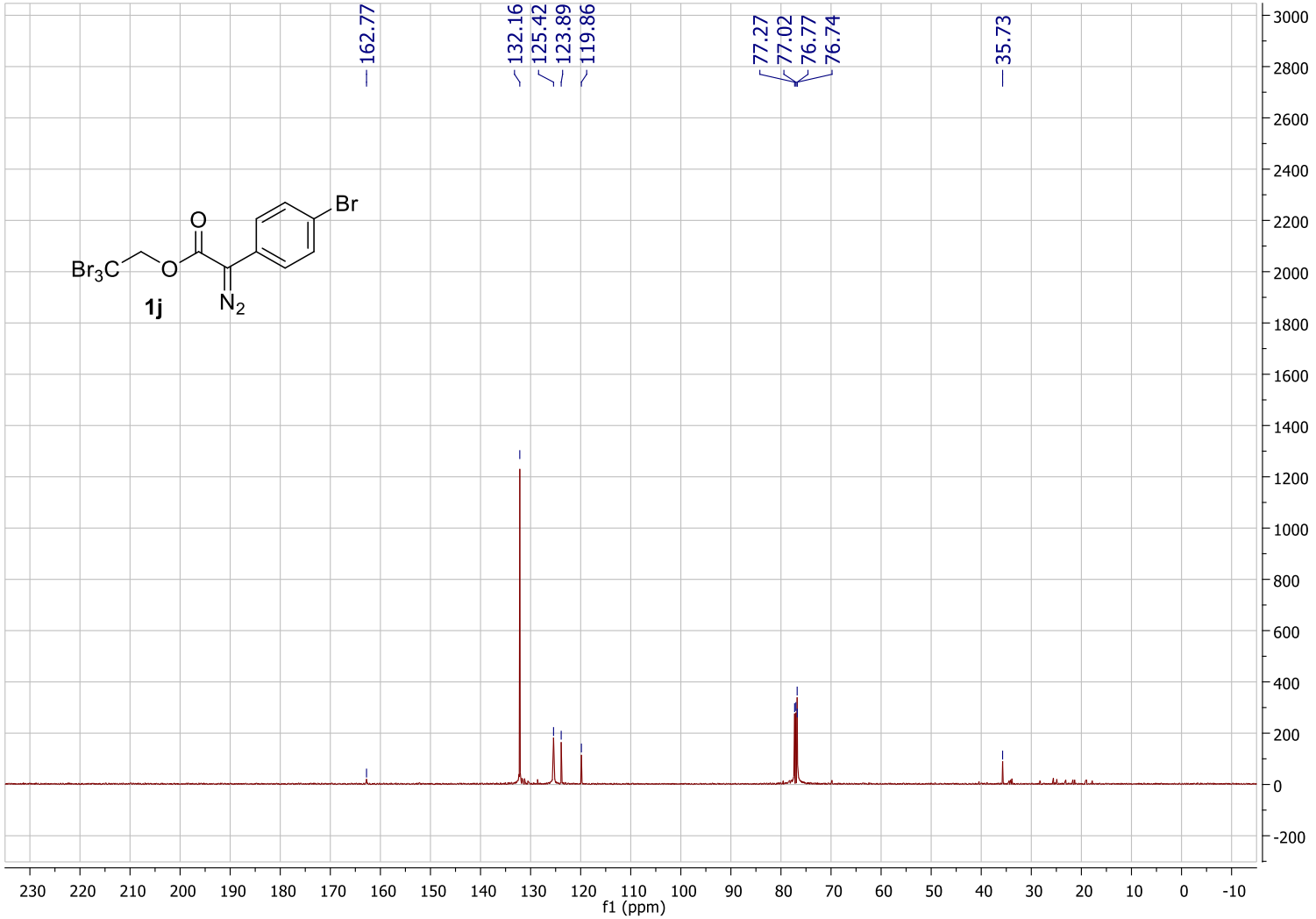
125MHZ, $CDCl_3$



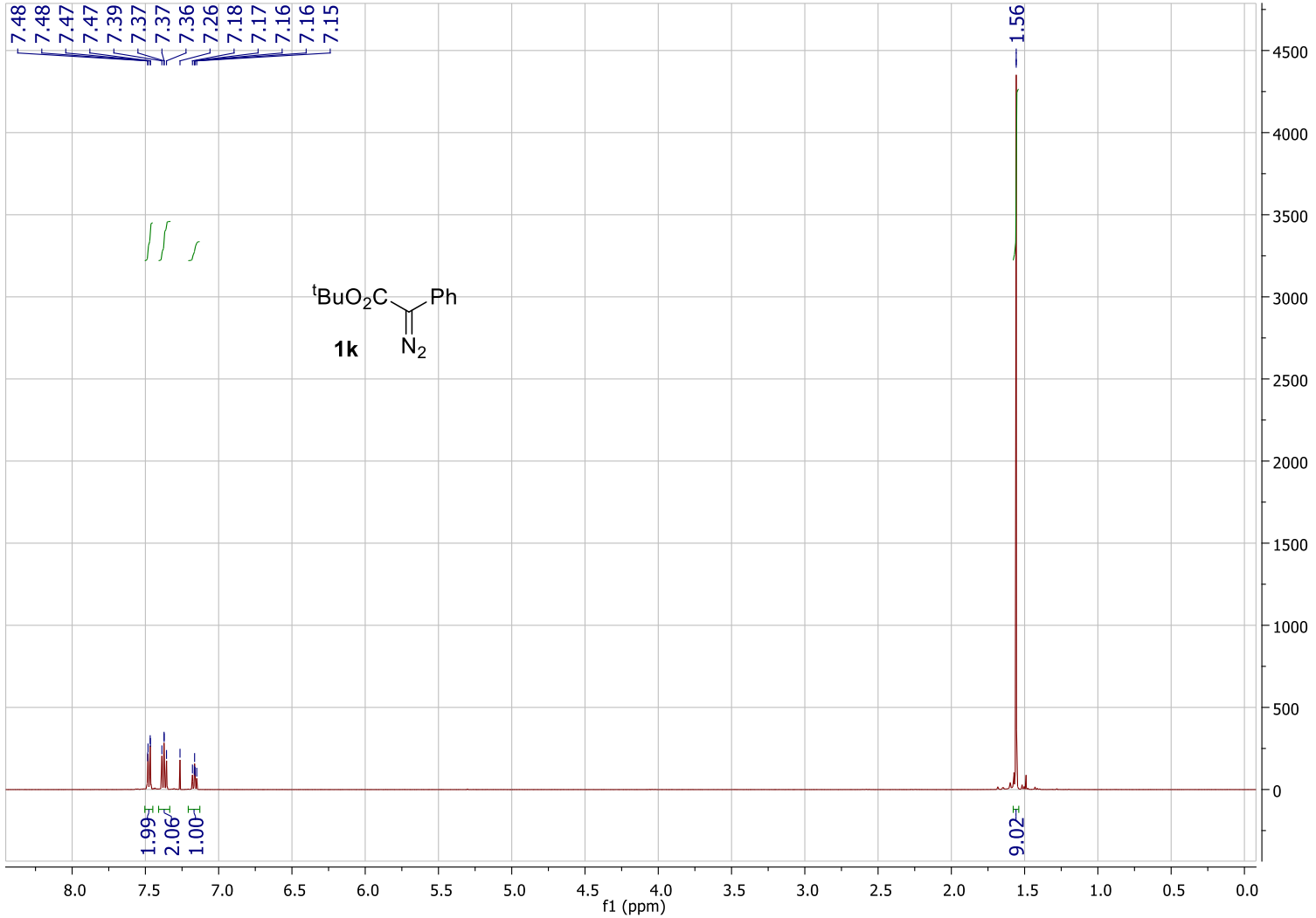
500MHz, $CDCl_3$



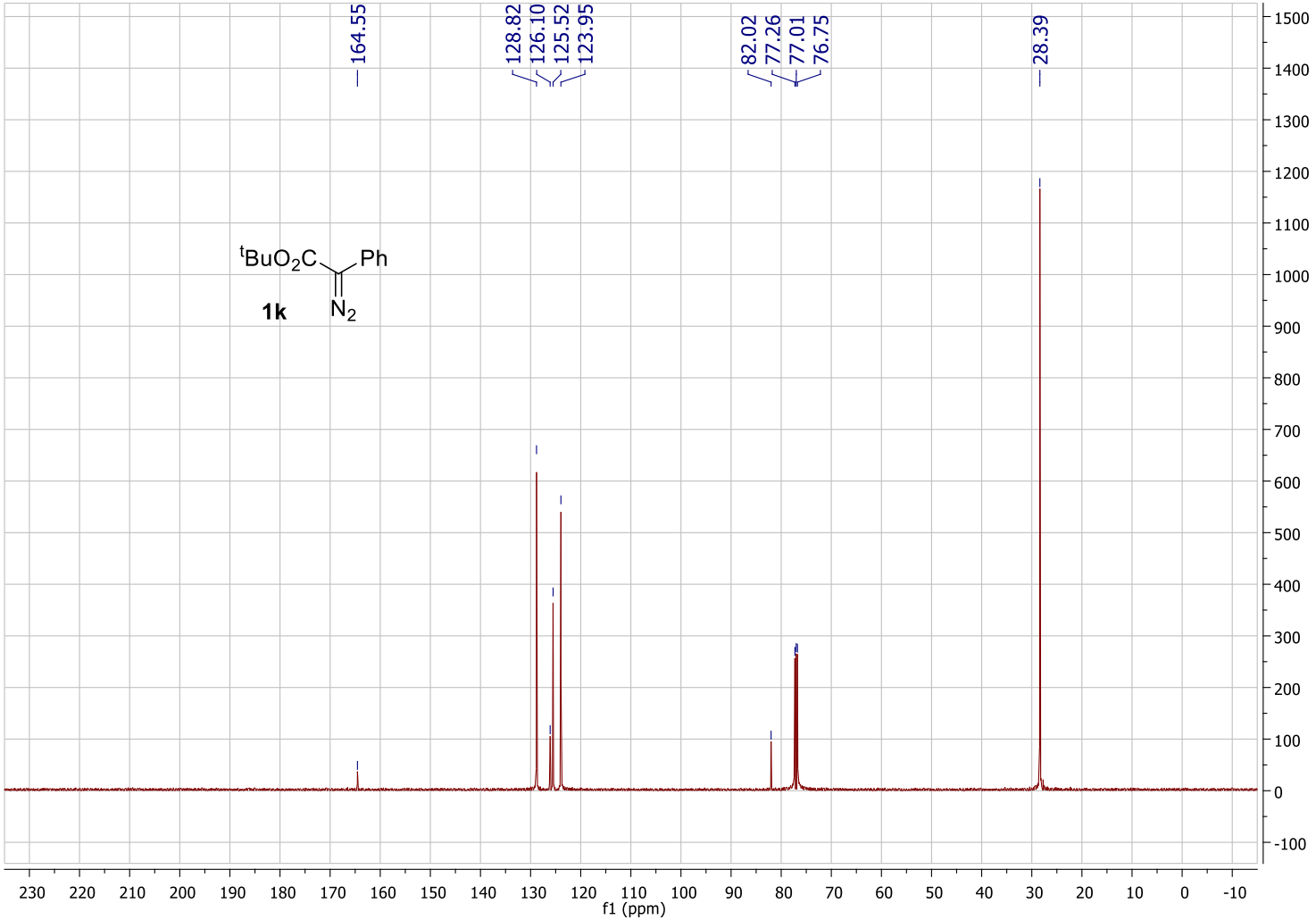
125MHz, $CDCl_3$



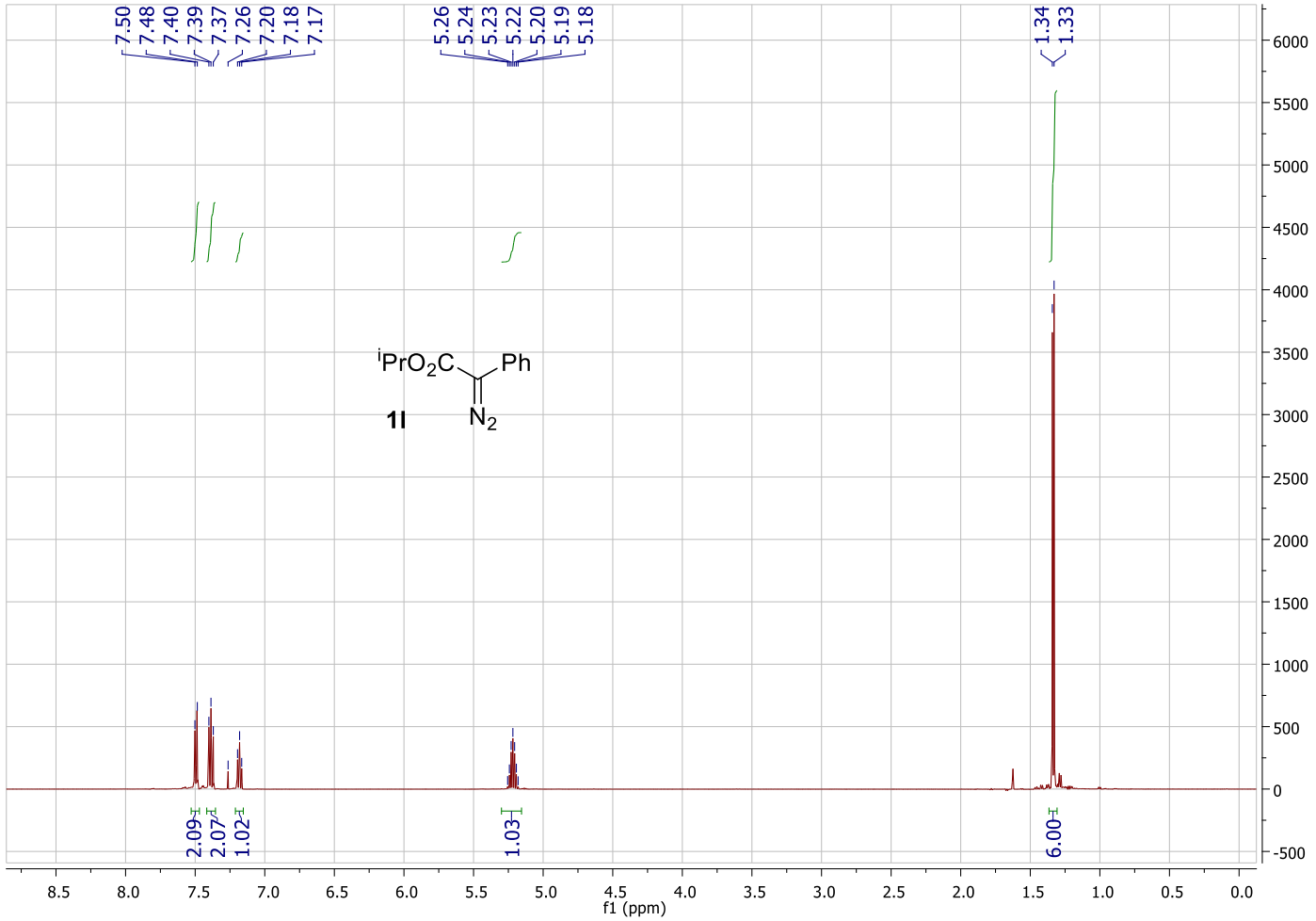
500MHz, $CDCl_3$



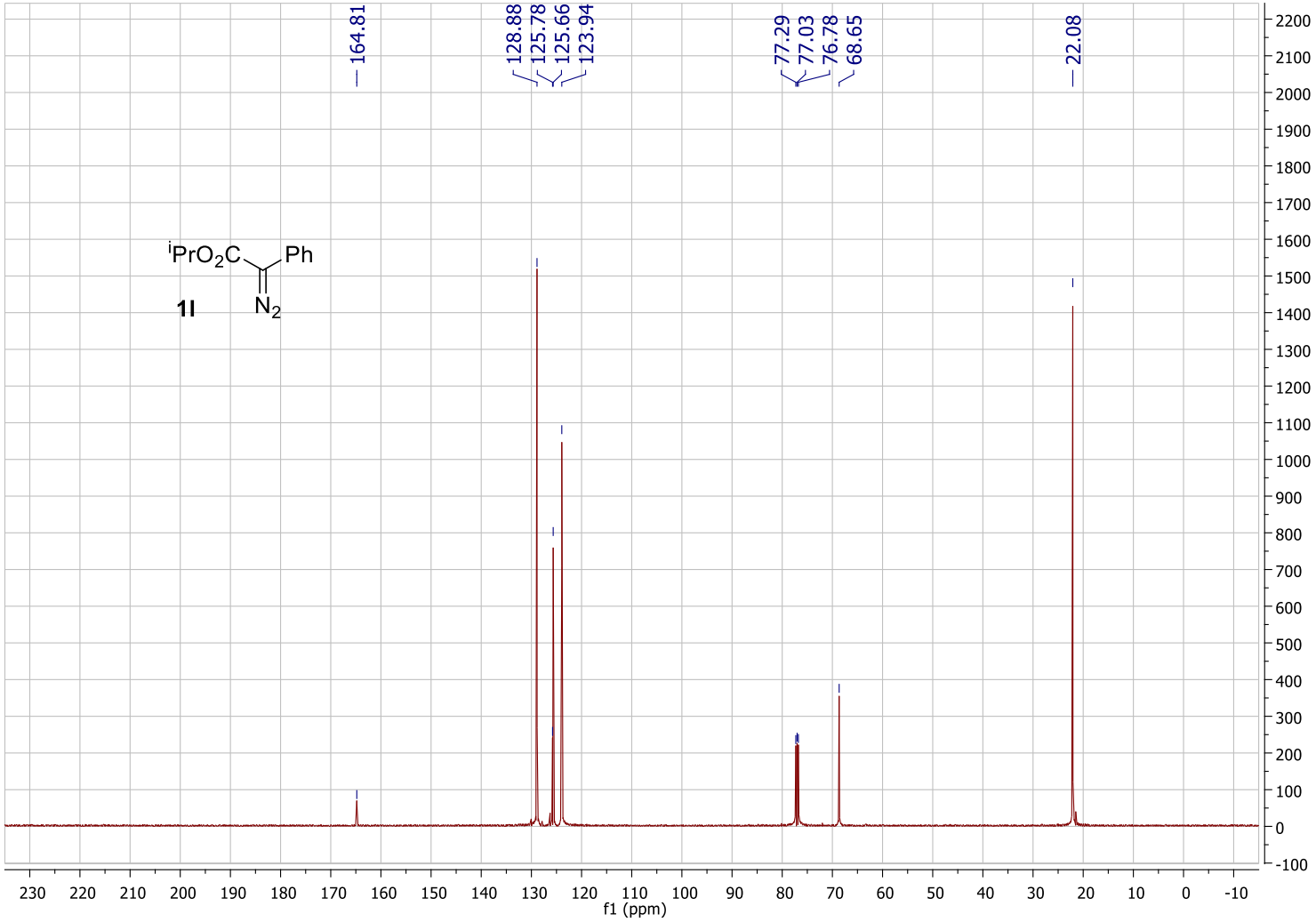
125MHz, $CDCl_3$



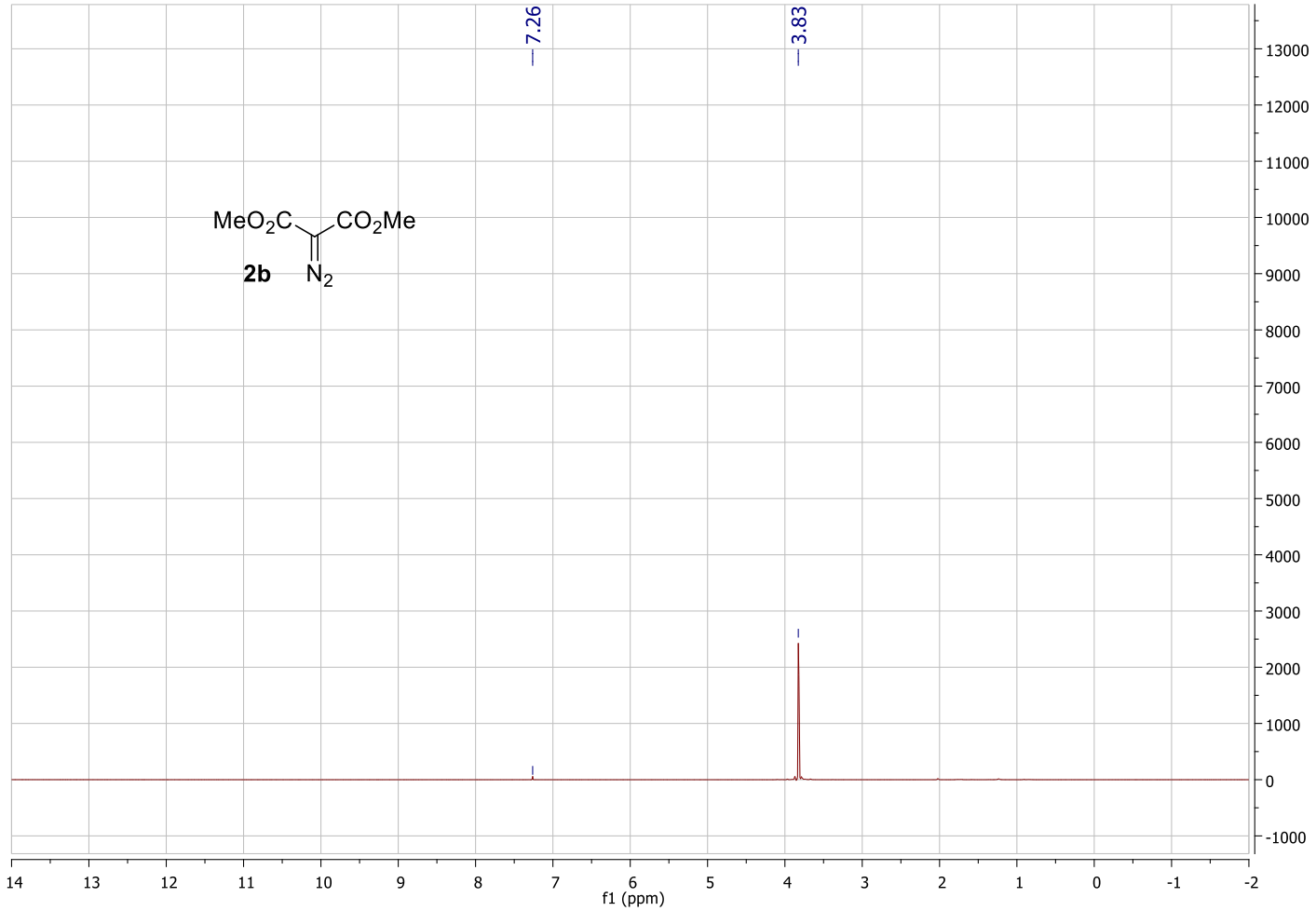
500MHz, $CDCl_3$



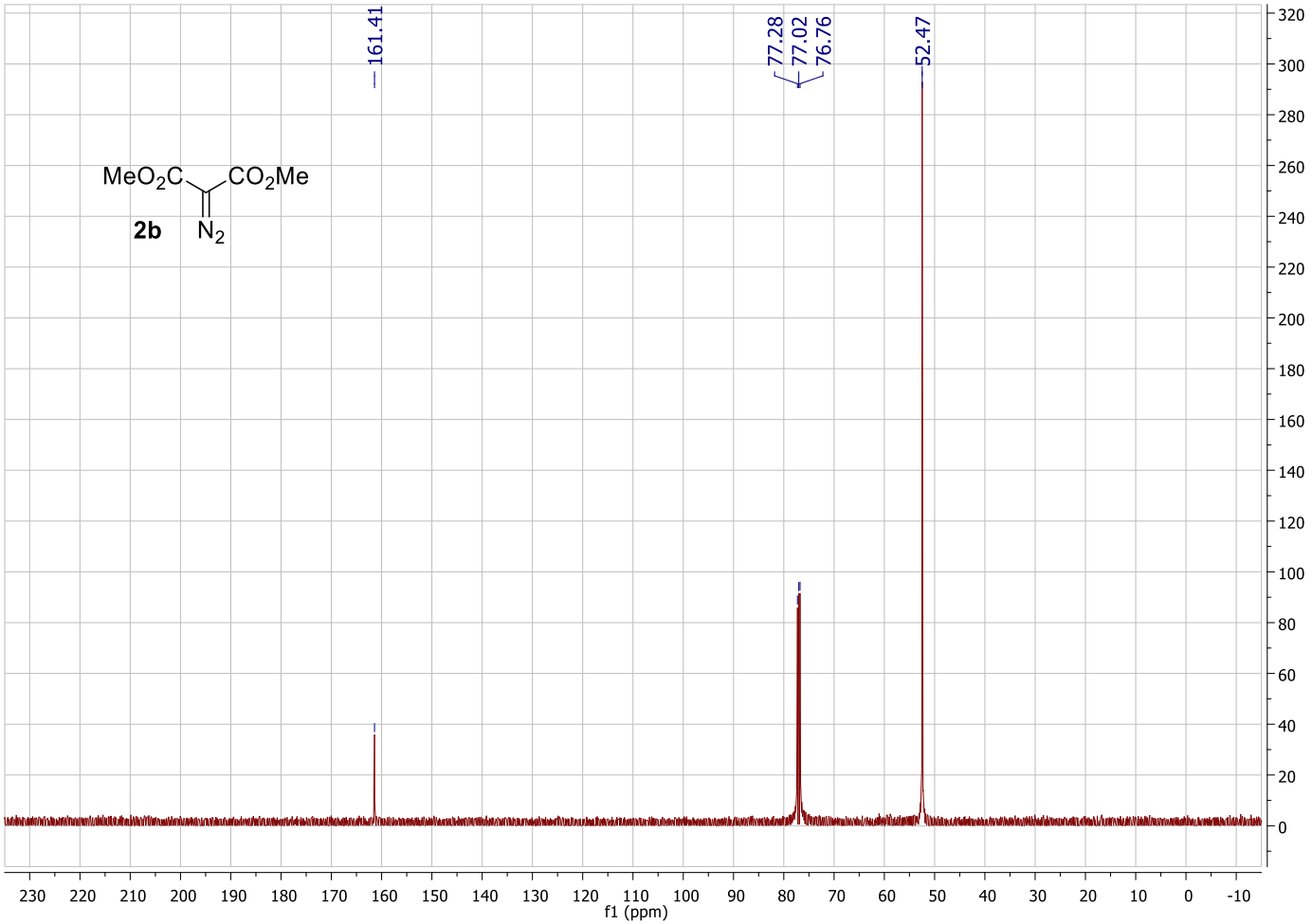
125MHz, $CDCl_3$



500MHz, $CDCl_3$

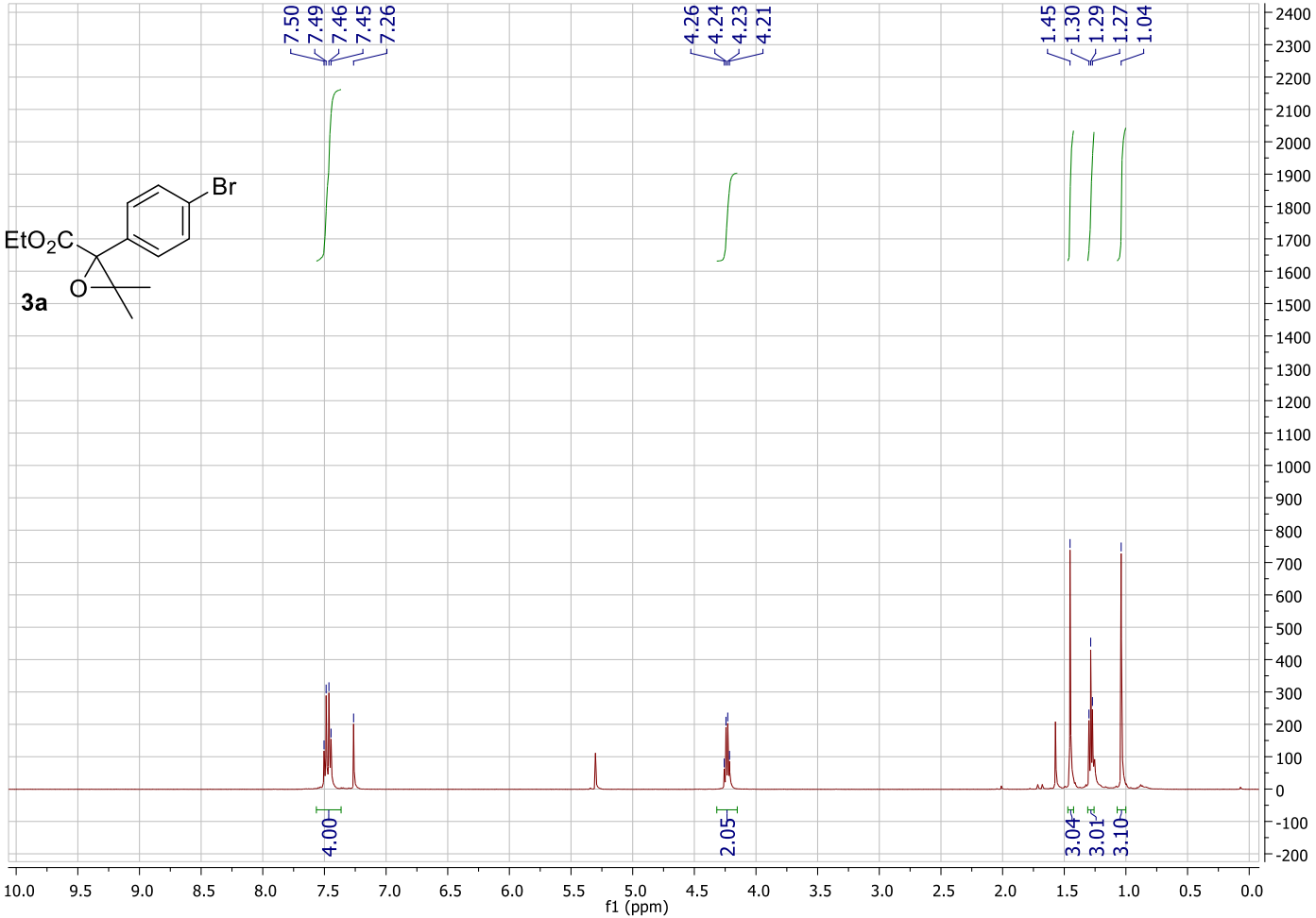


125MHz, $CDCl_3$

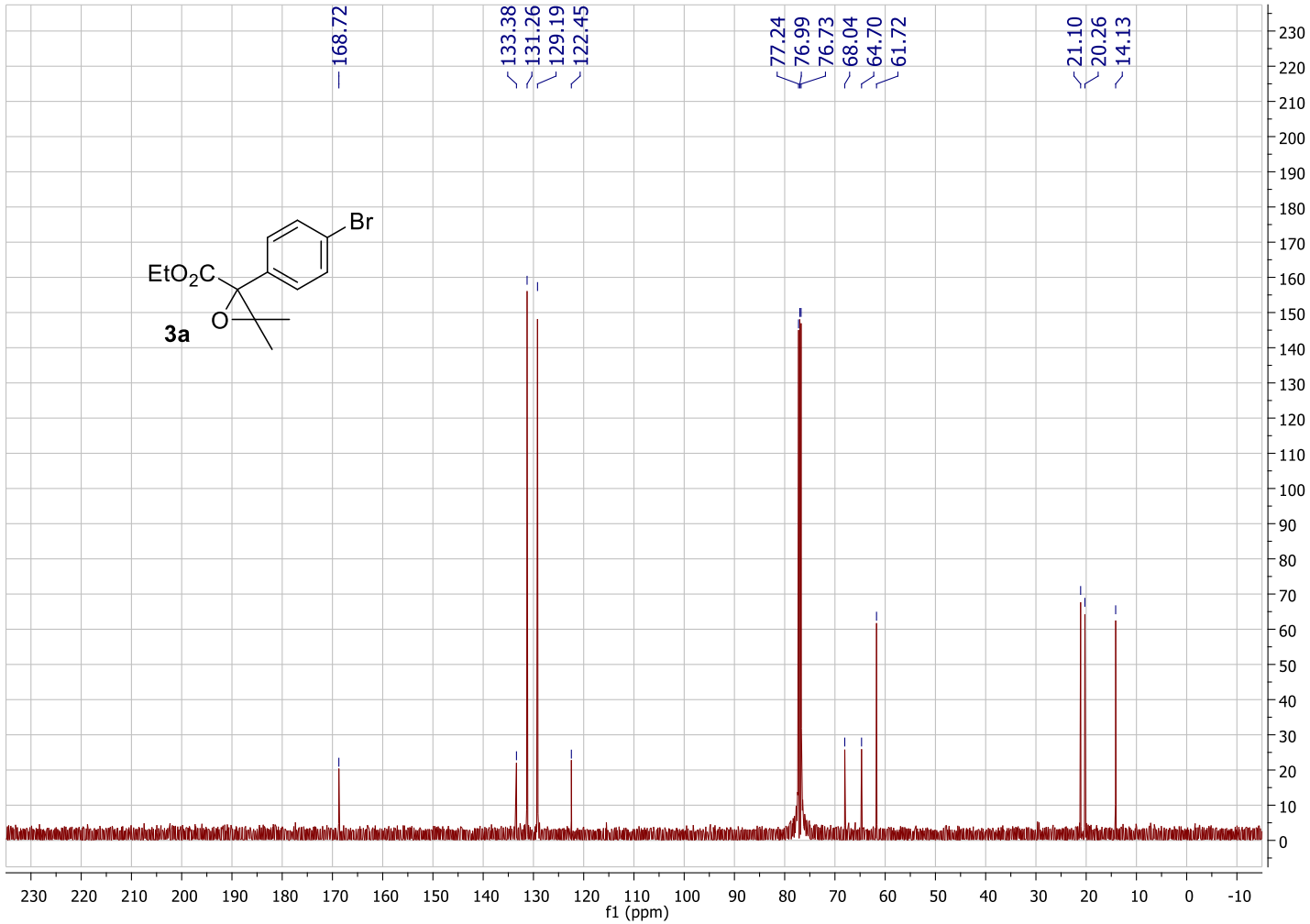


4.2 Products Derived from the Reaction of Aryldiazoacetates with Solvents

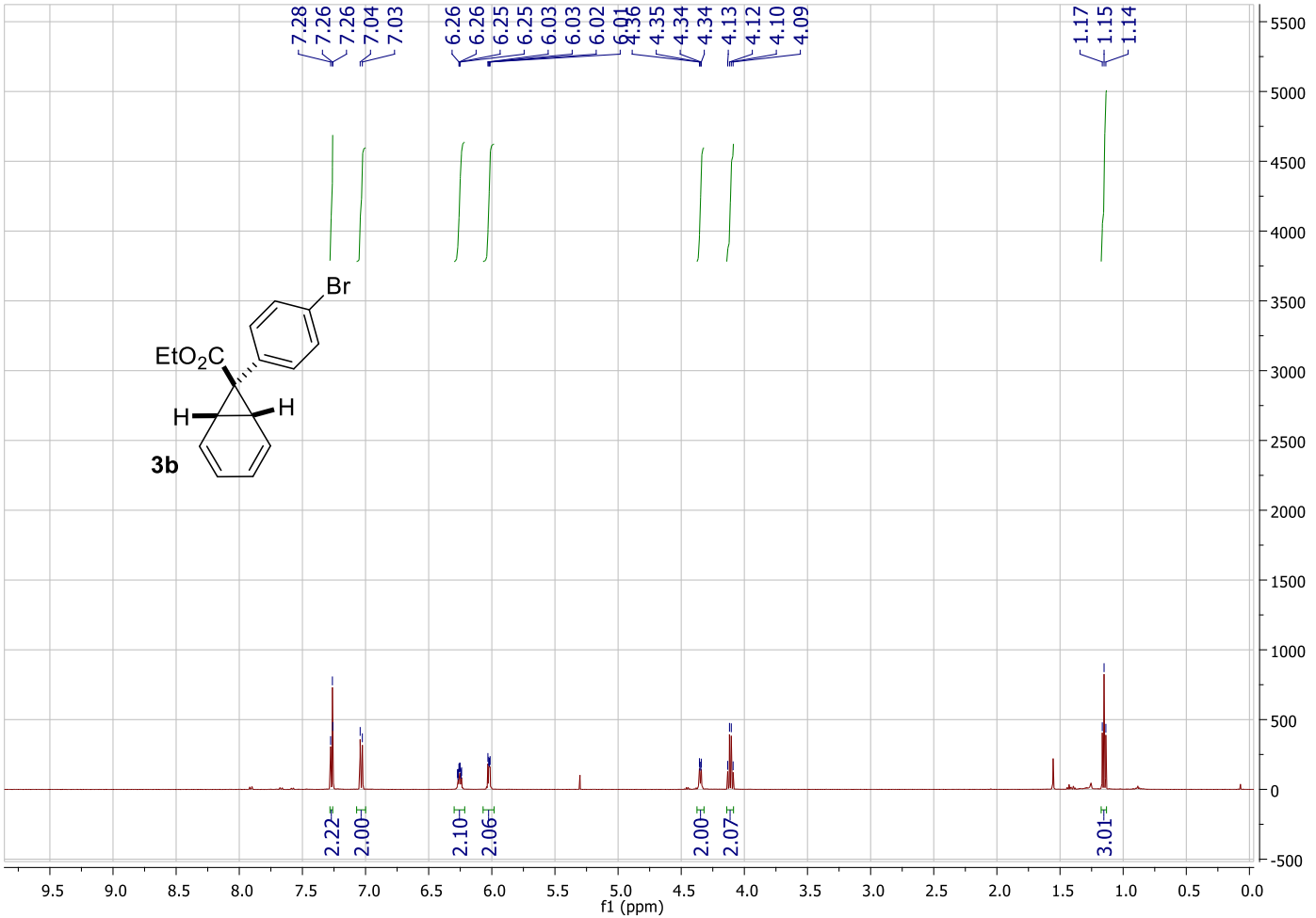
500MHz, $CDCl_3$



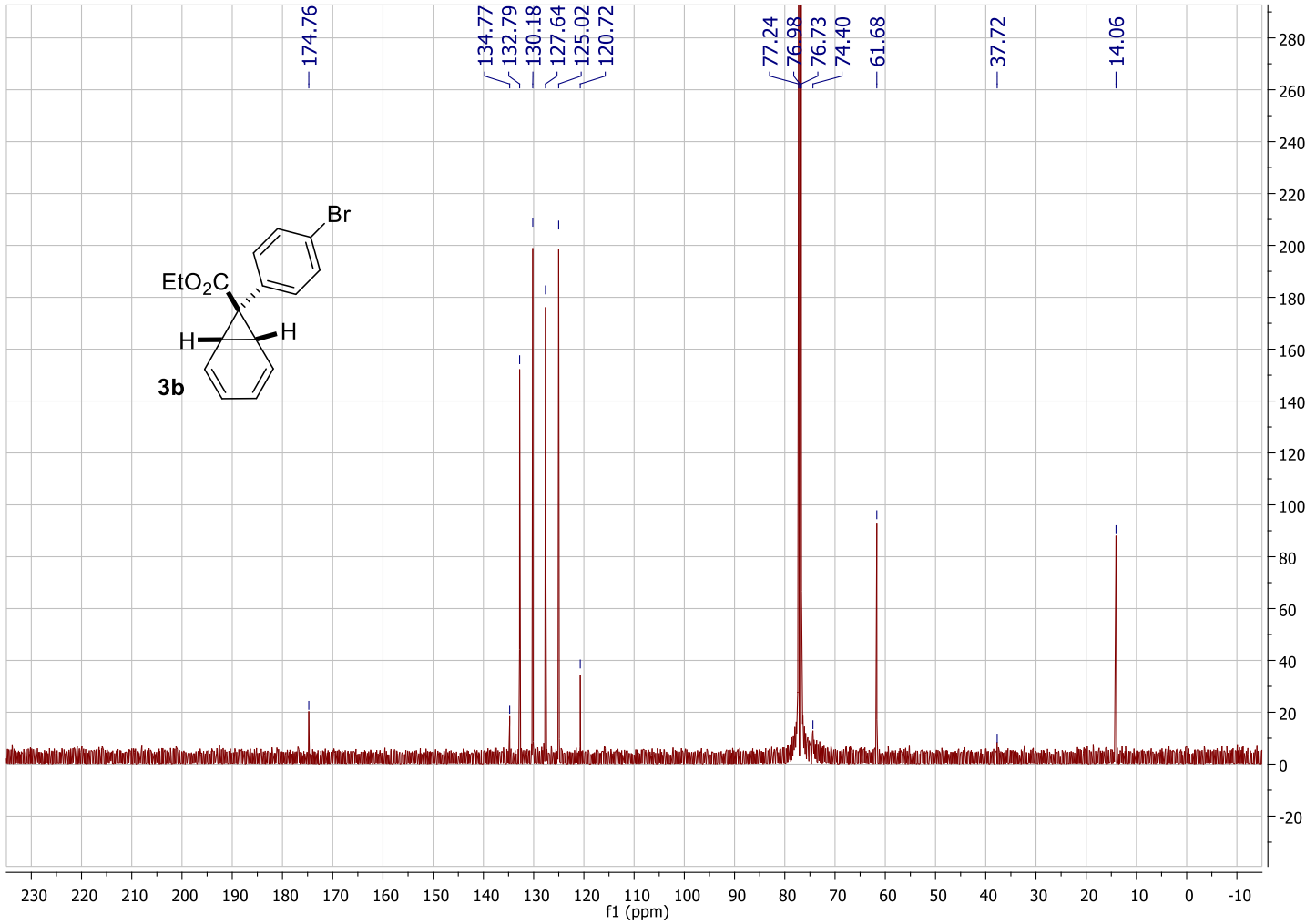
125MHz, $CDCl_3$



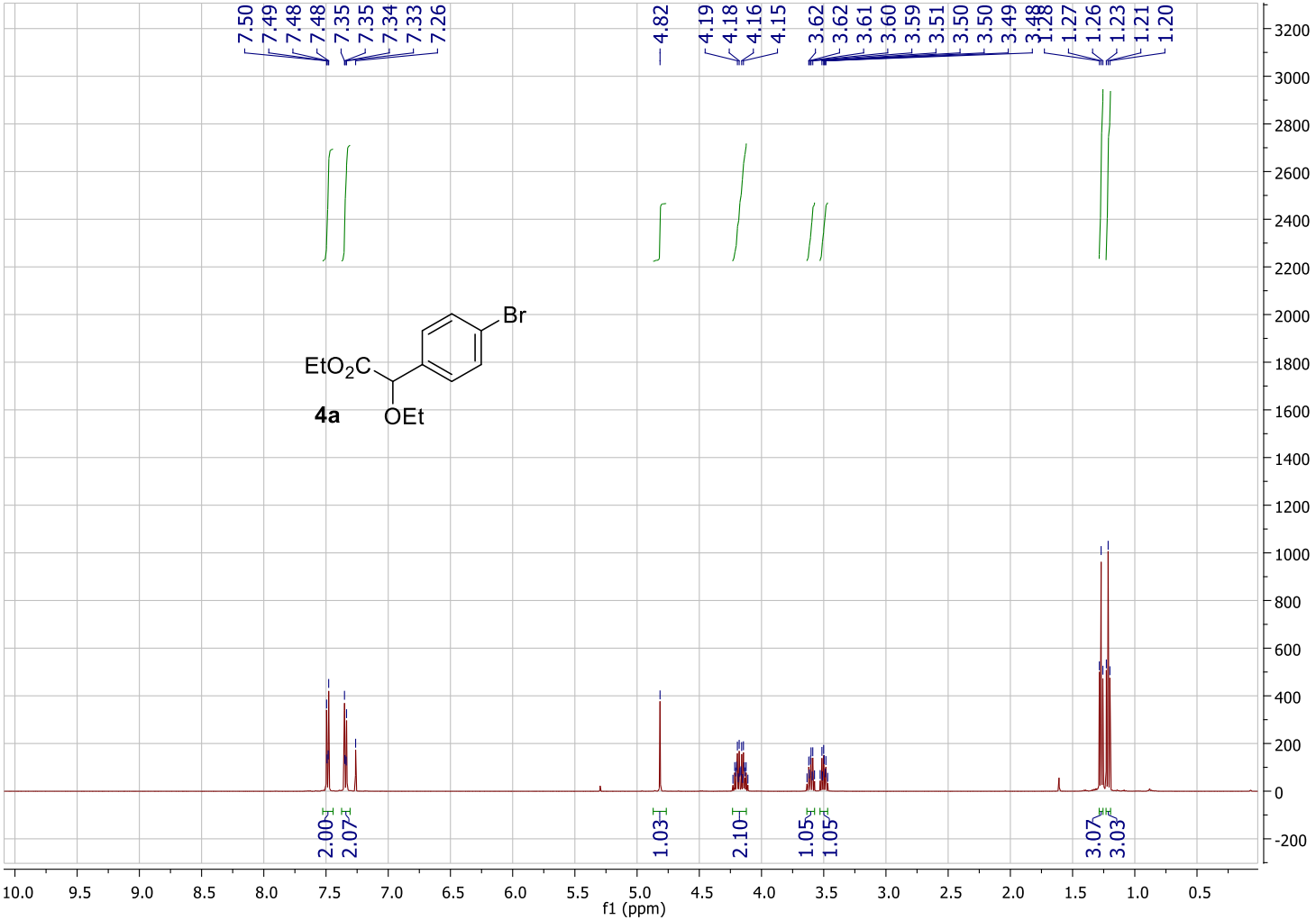
500MHz, $CDCl_3$



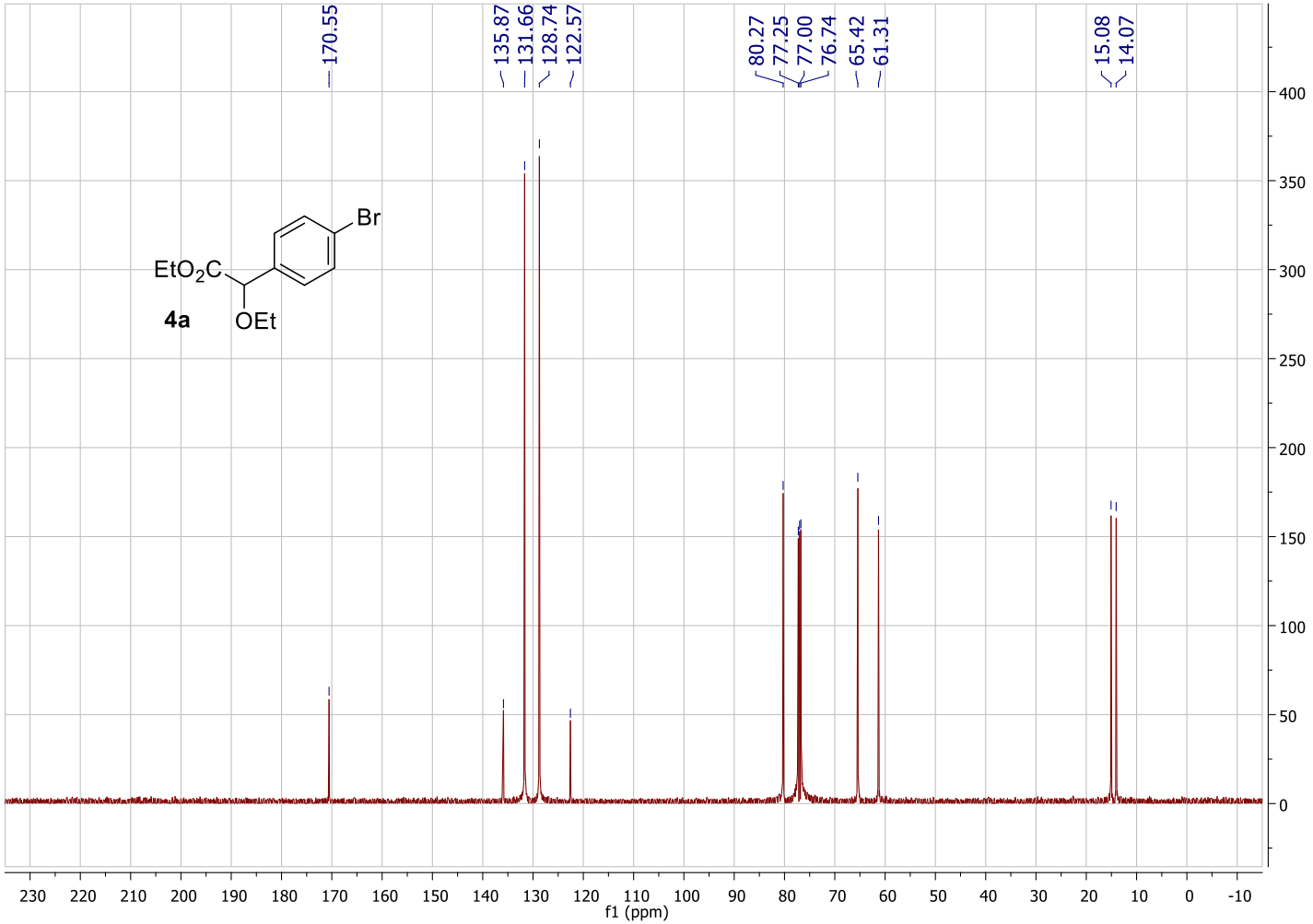
125MHz, $CDCl_3$



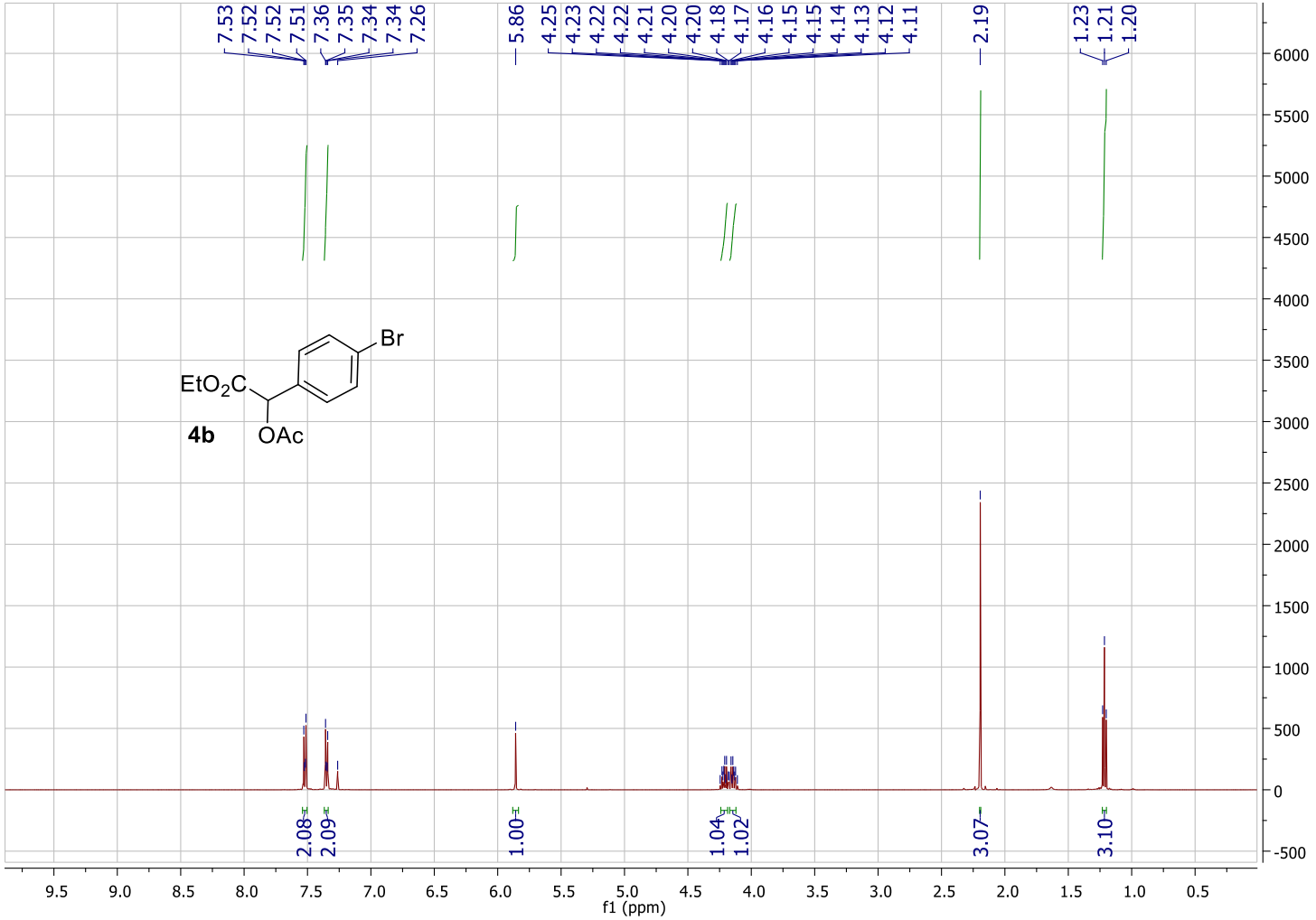
500MHz, $CDCl_3$



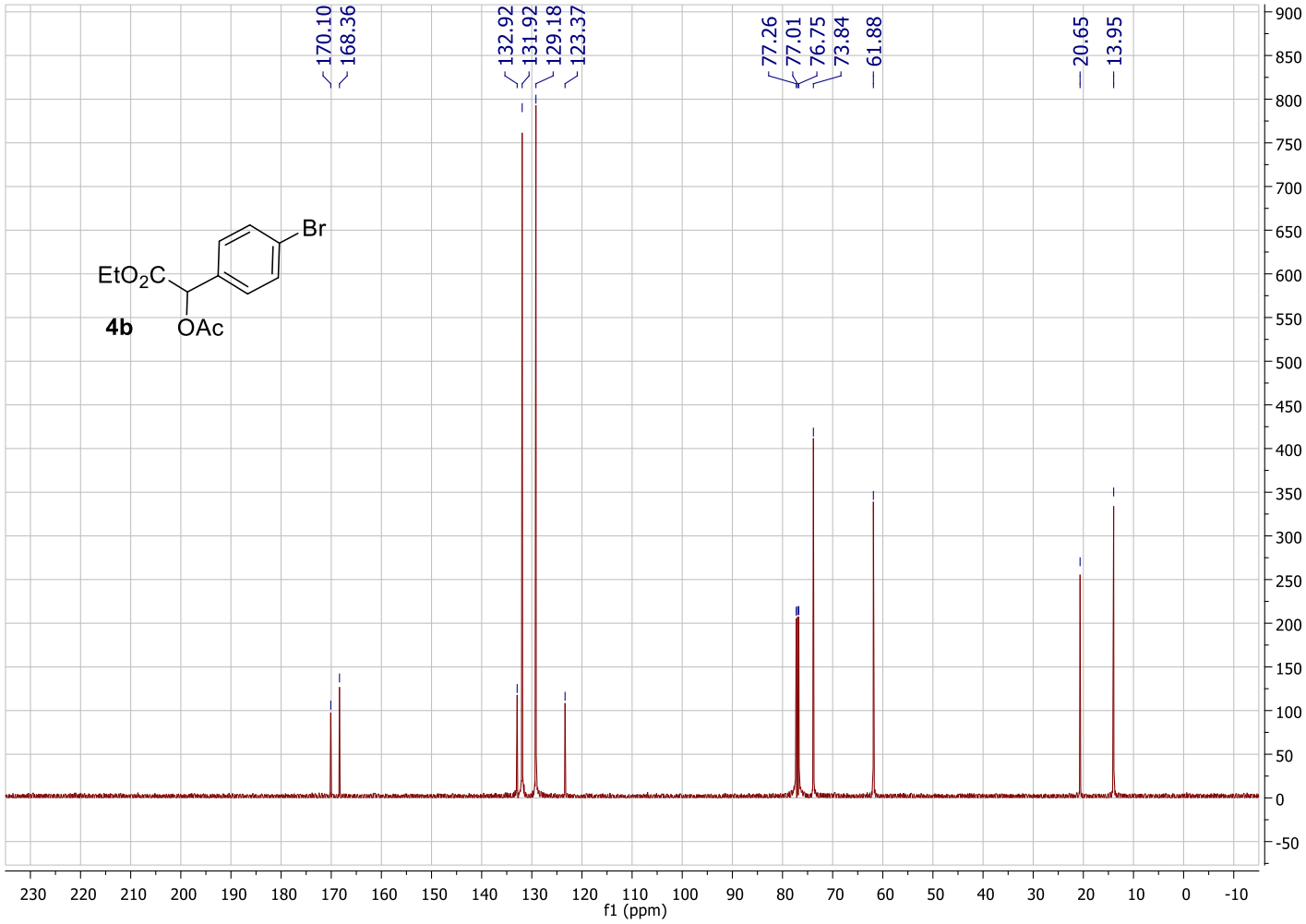
125MHz, $CDCl_3$



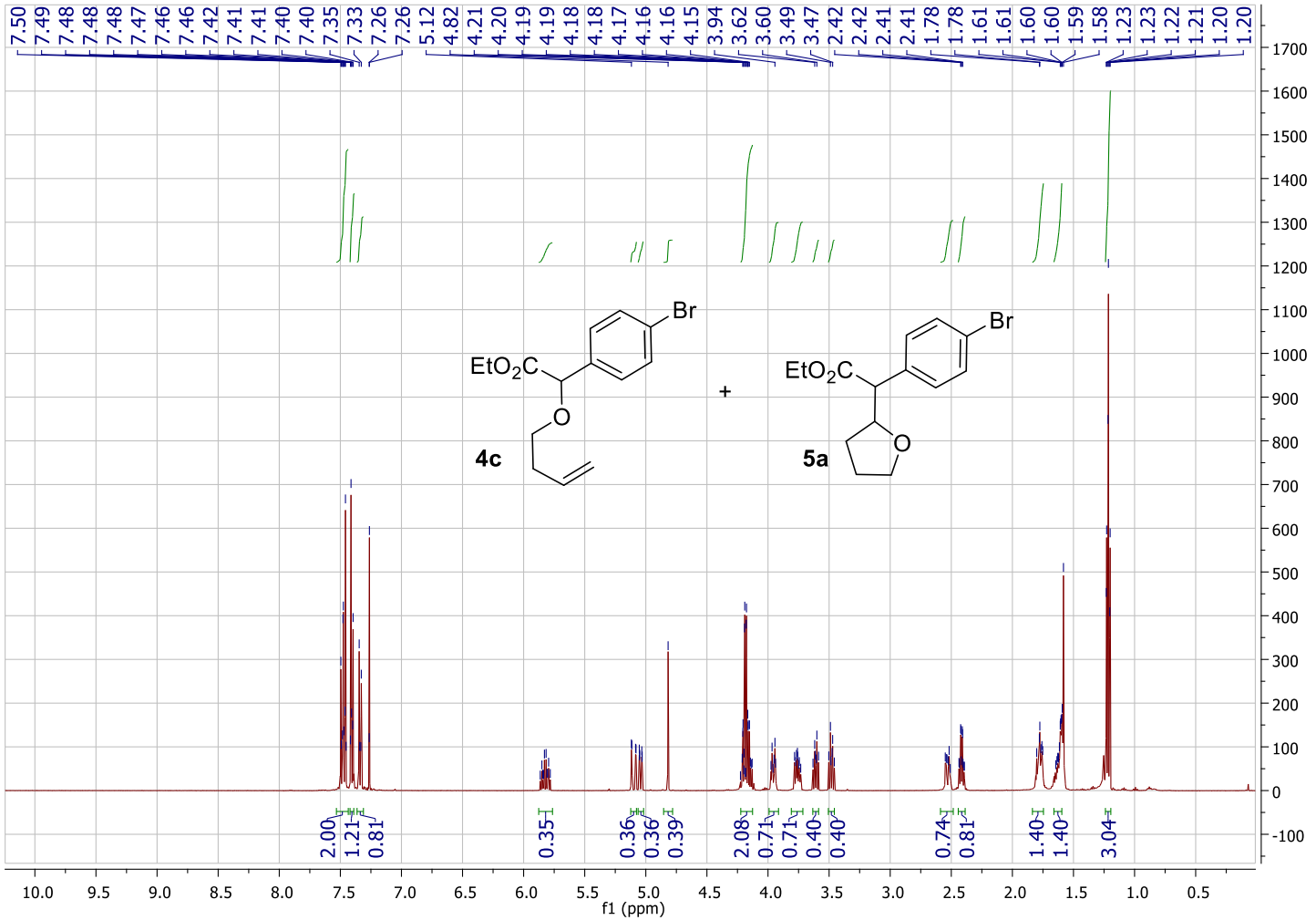
500MHz, $CDCl_3$



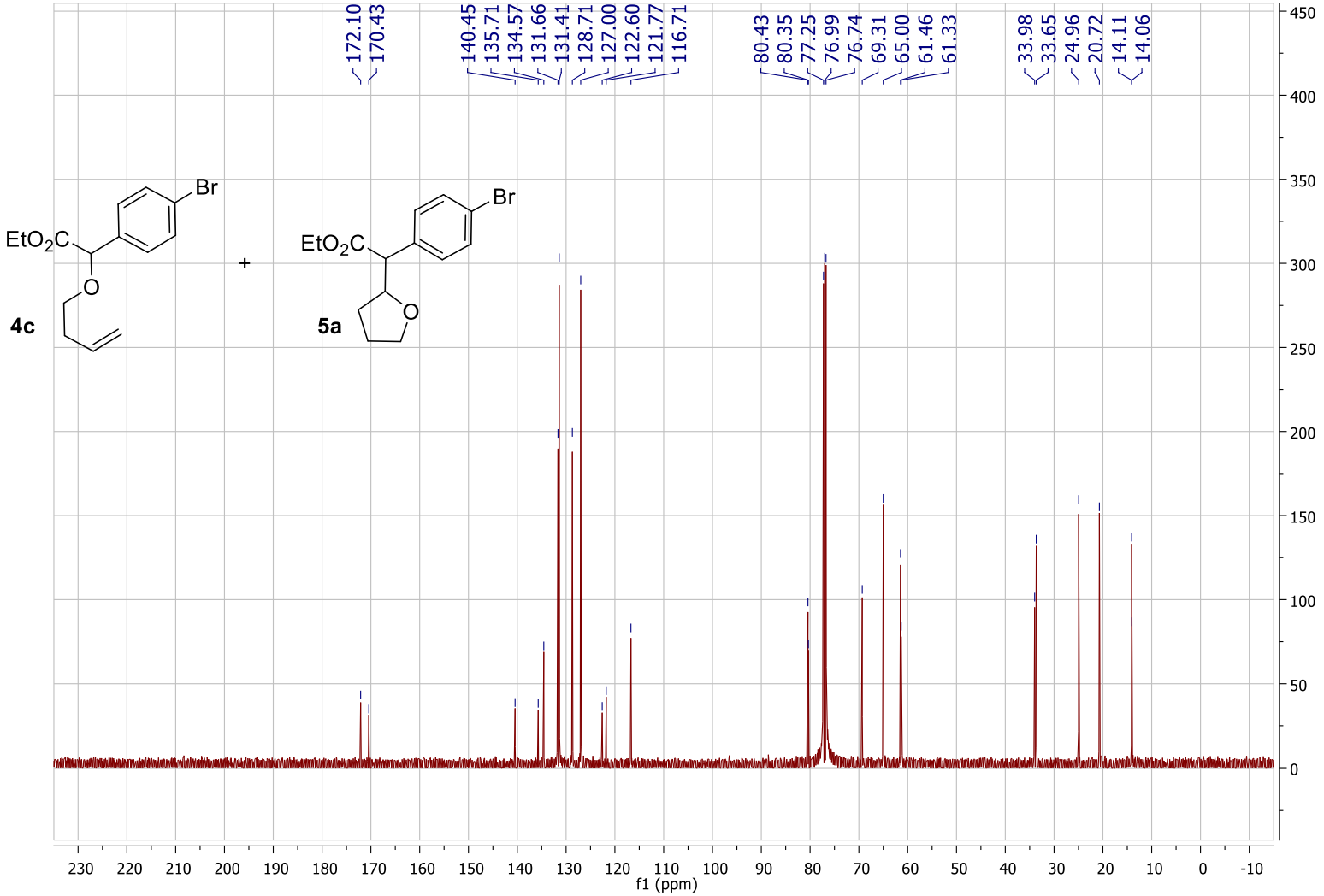
125MHz, $CDCl_3$



500MHz, $CDCl_3$

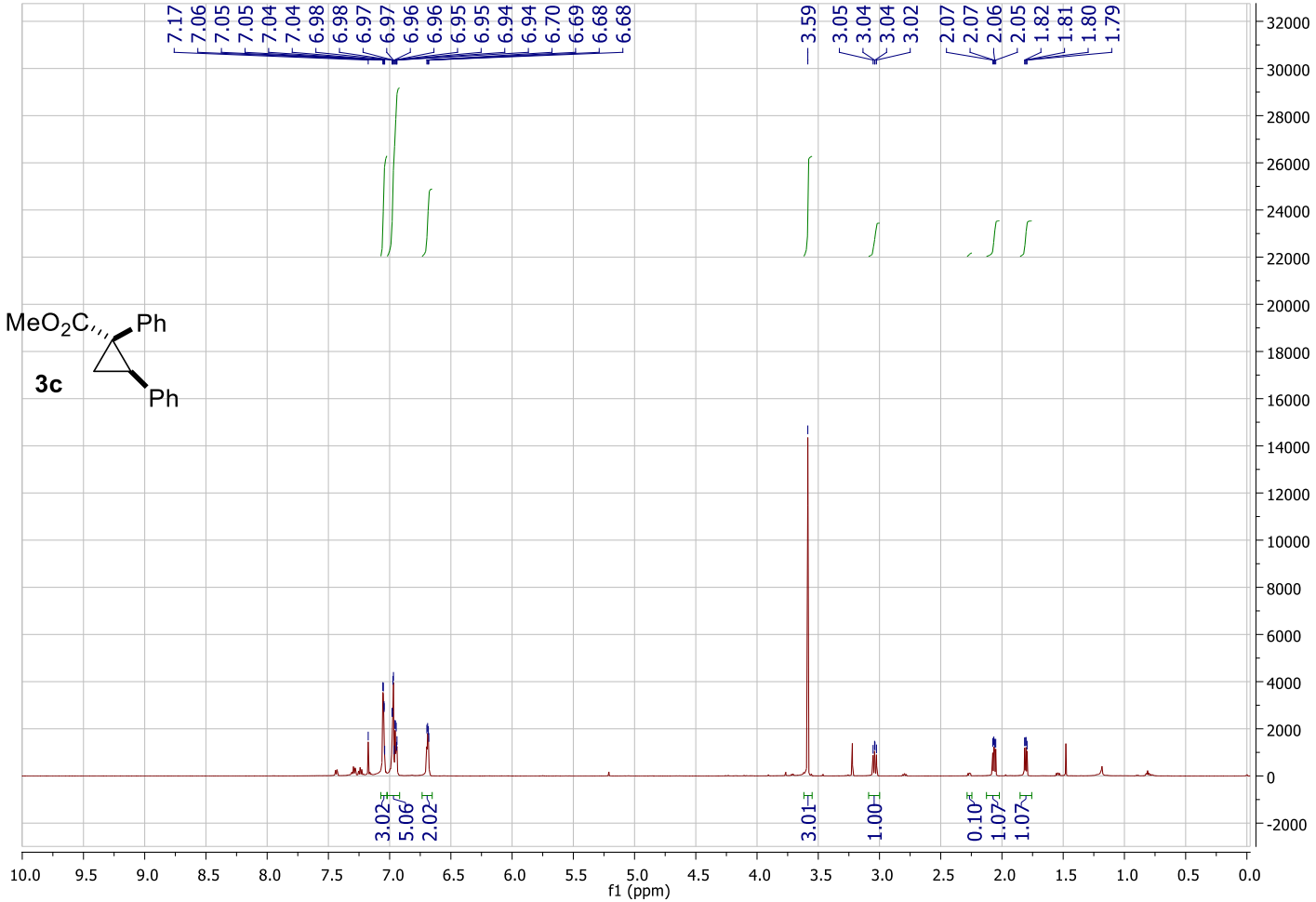


125MHz, $CDCl_3$

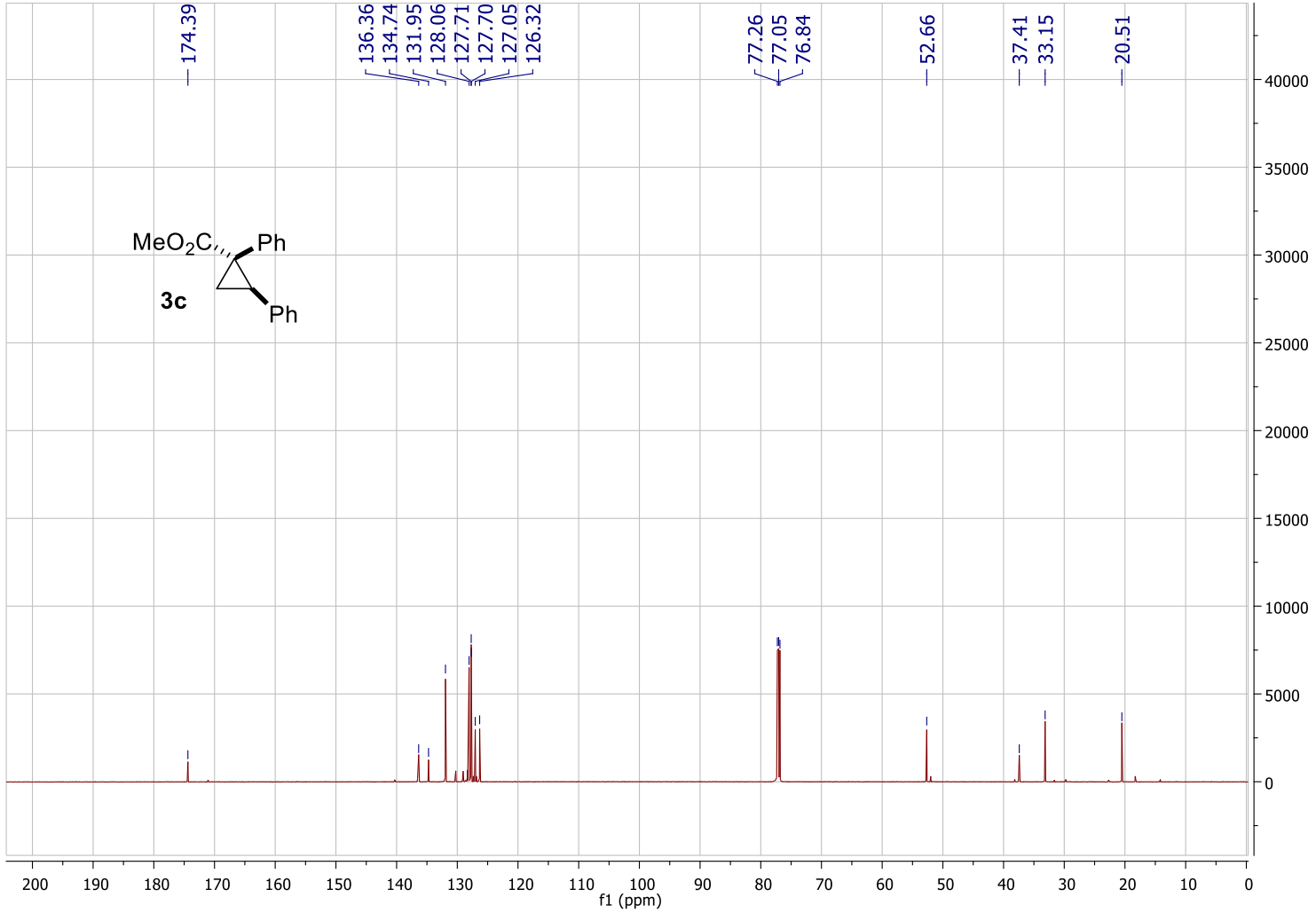


4.3 Products Derived from Cyclopropanation Reactions of Styrene

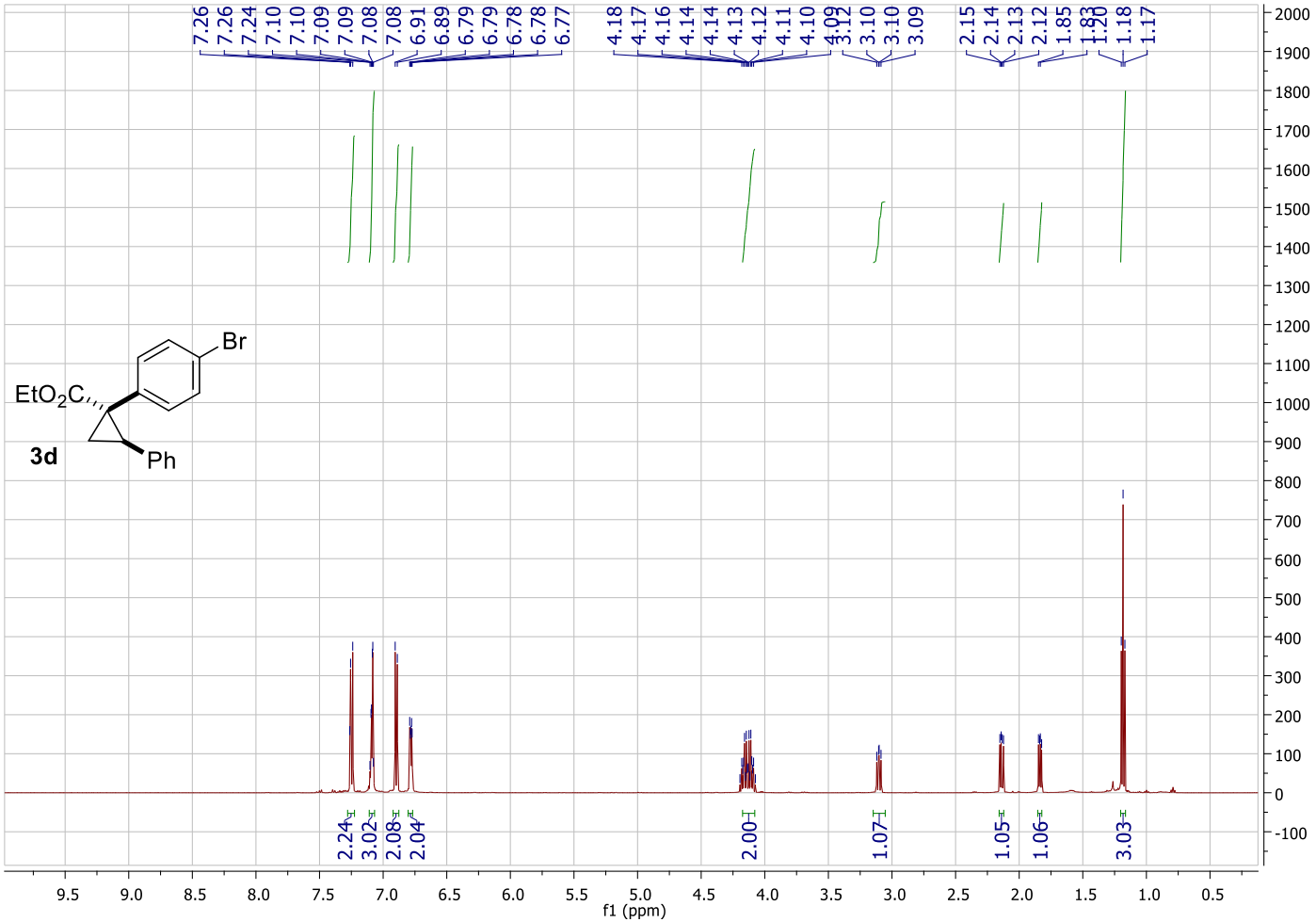
600MHz, $CDCl_3$



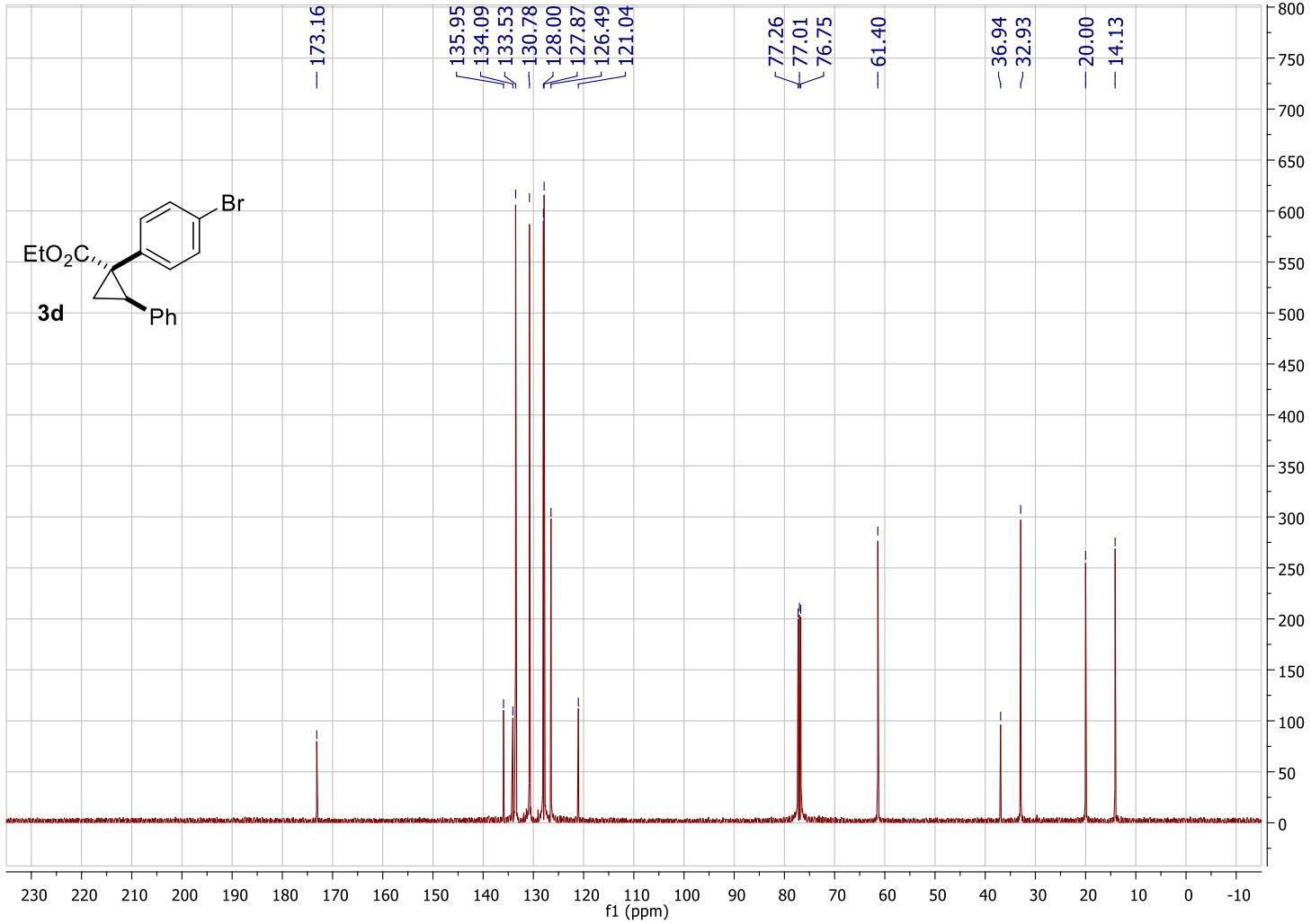
150MHz, $CDCl_3$



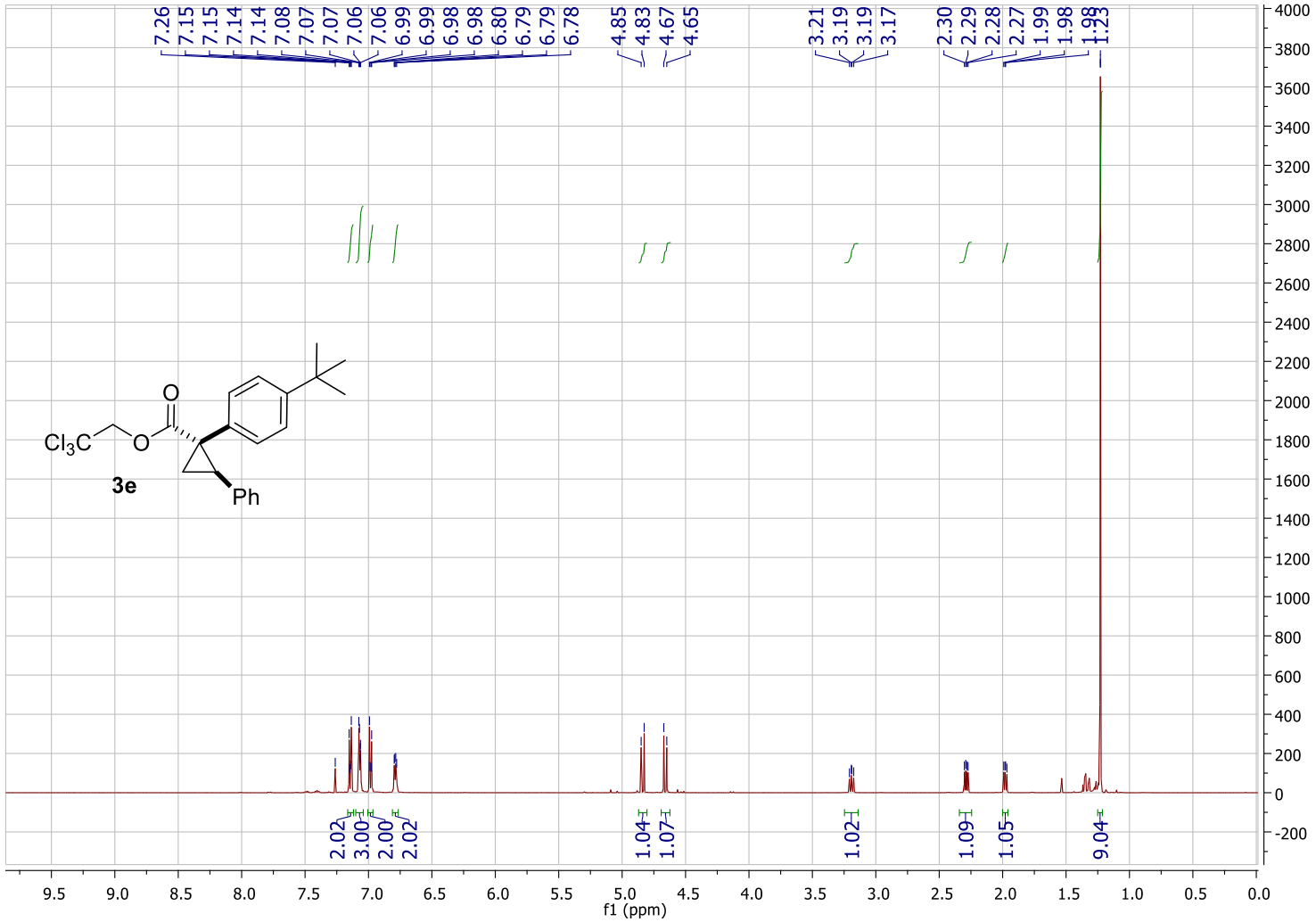
500MHz, $CDCl_3$



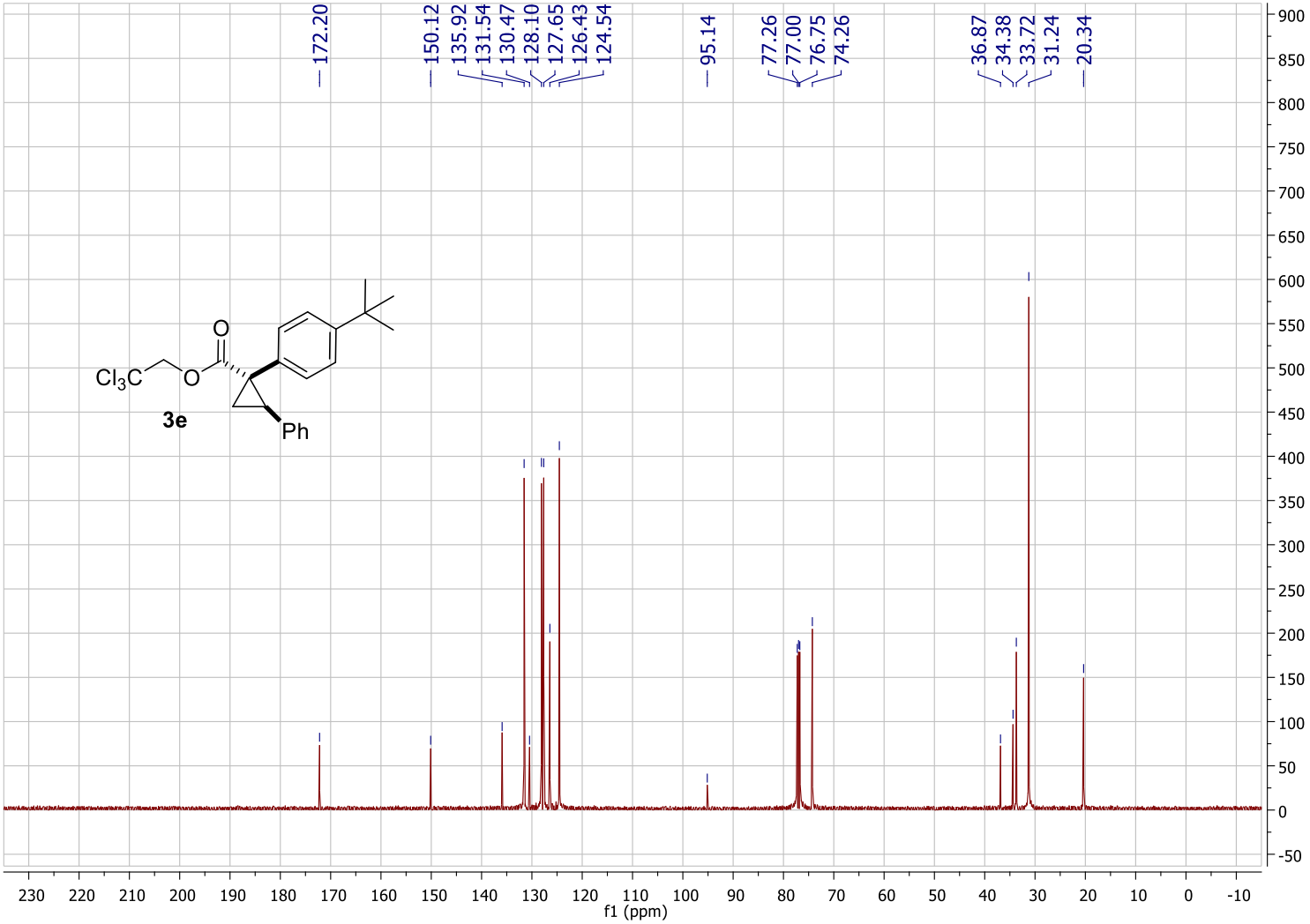
125MHz, $CDCl_3$



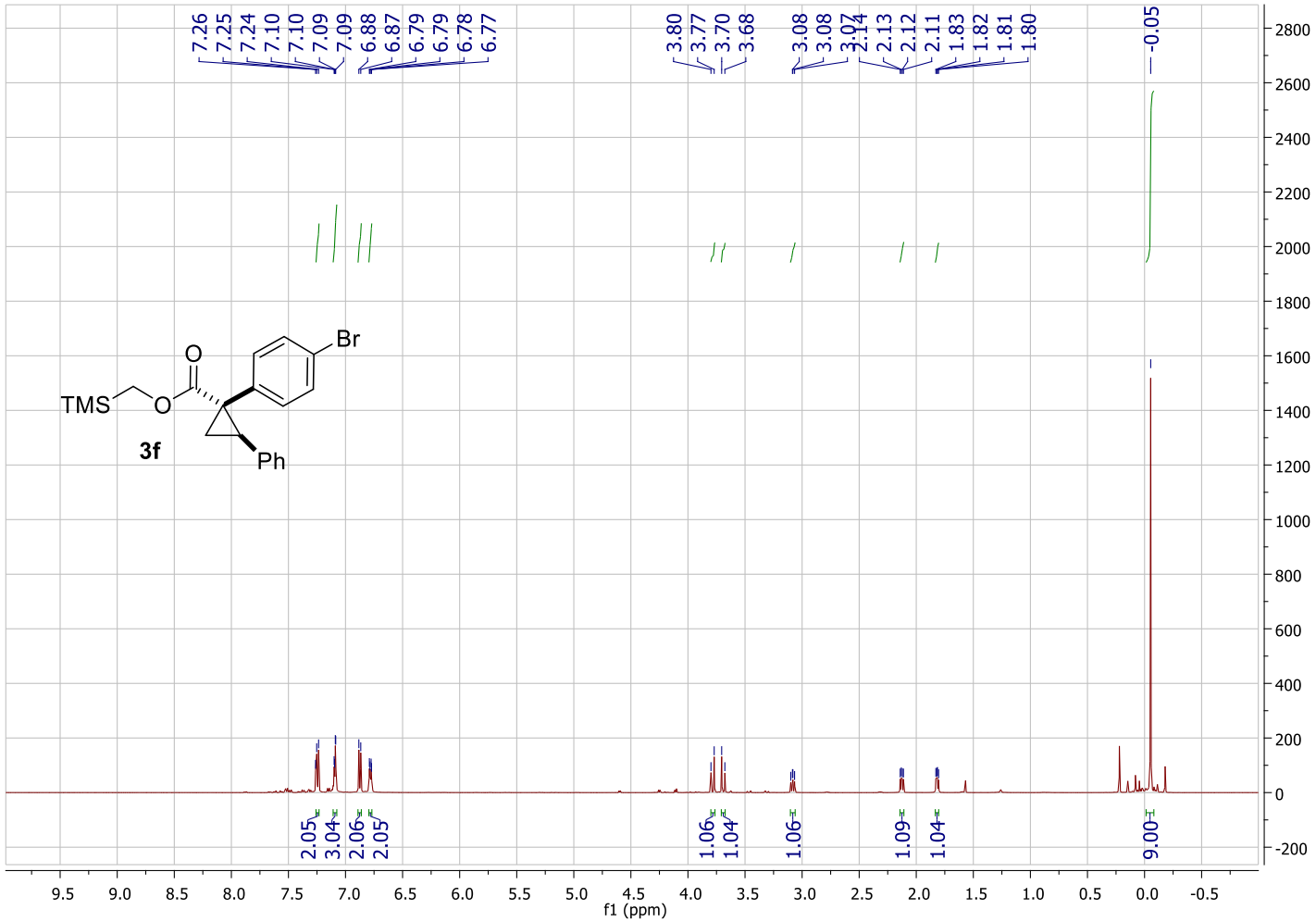
500MHz, $CDCl_3$



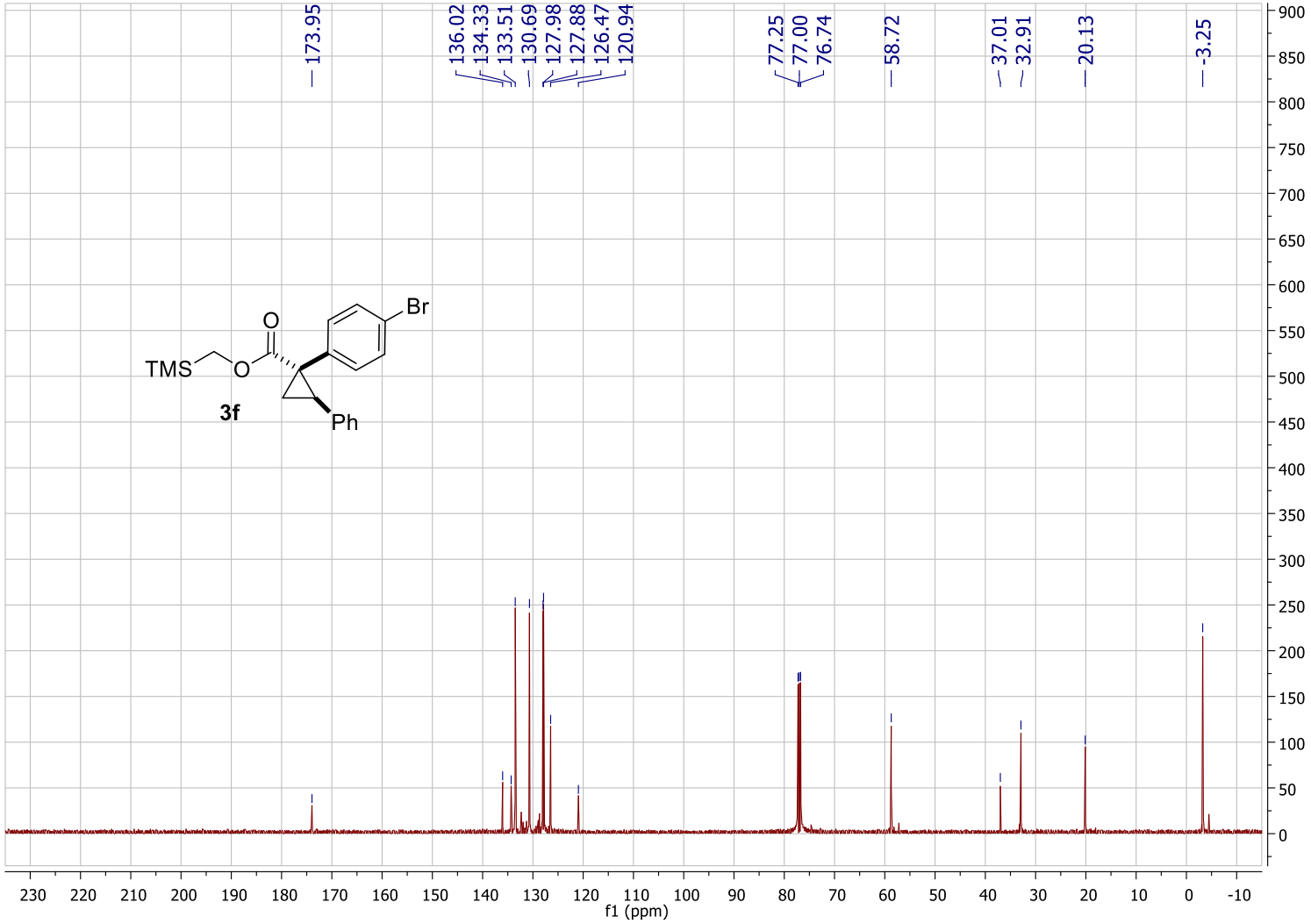
125MHz, $CDCl_3$



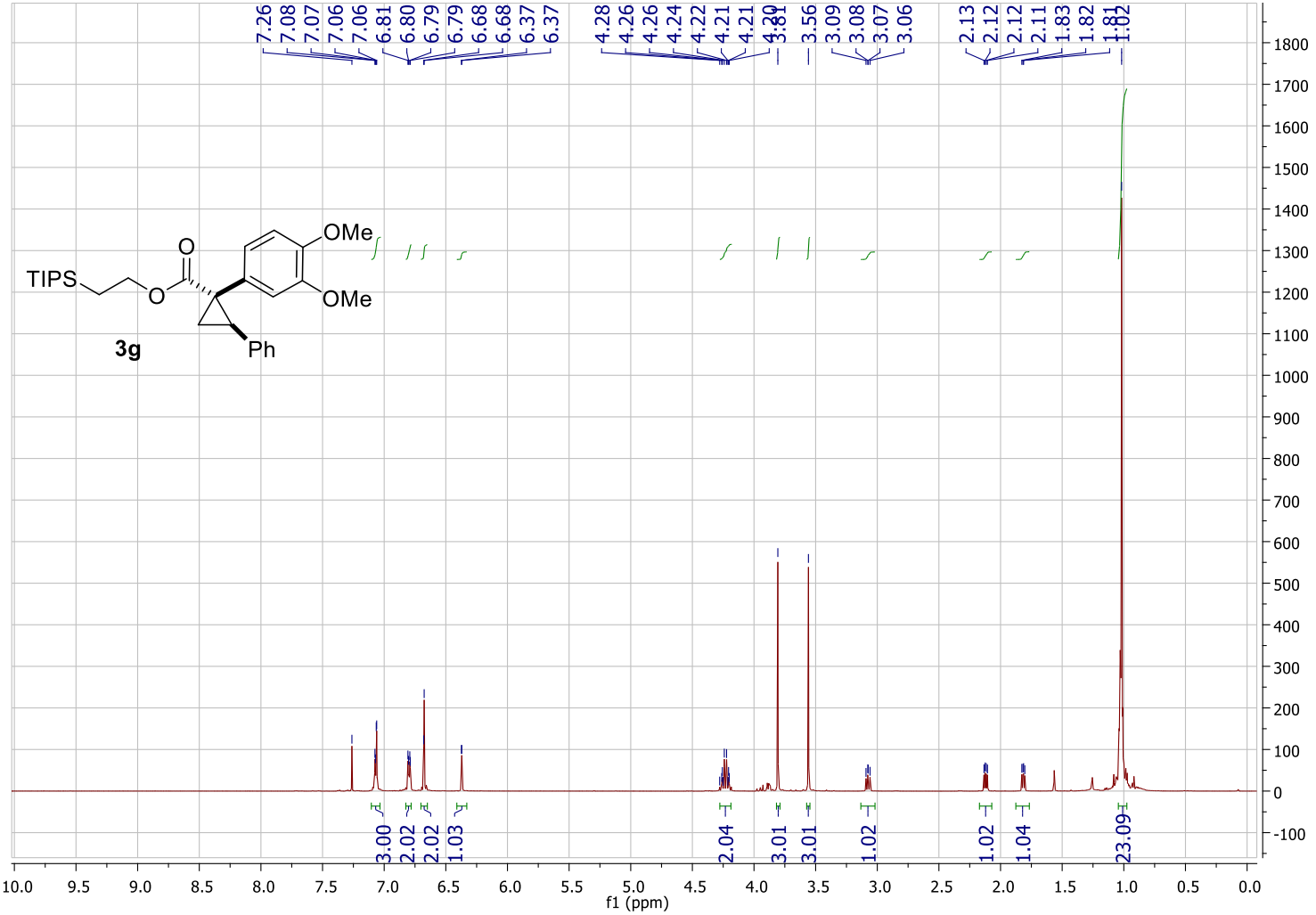
500MHz, $CDCl_3$



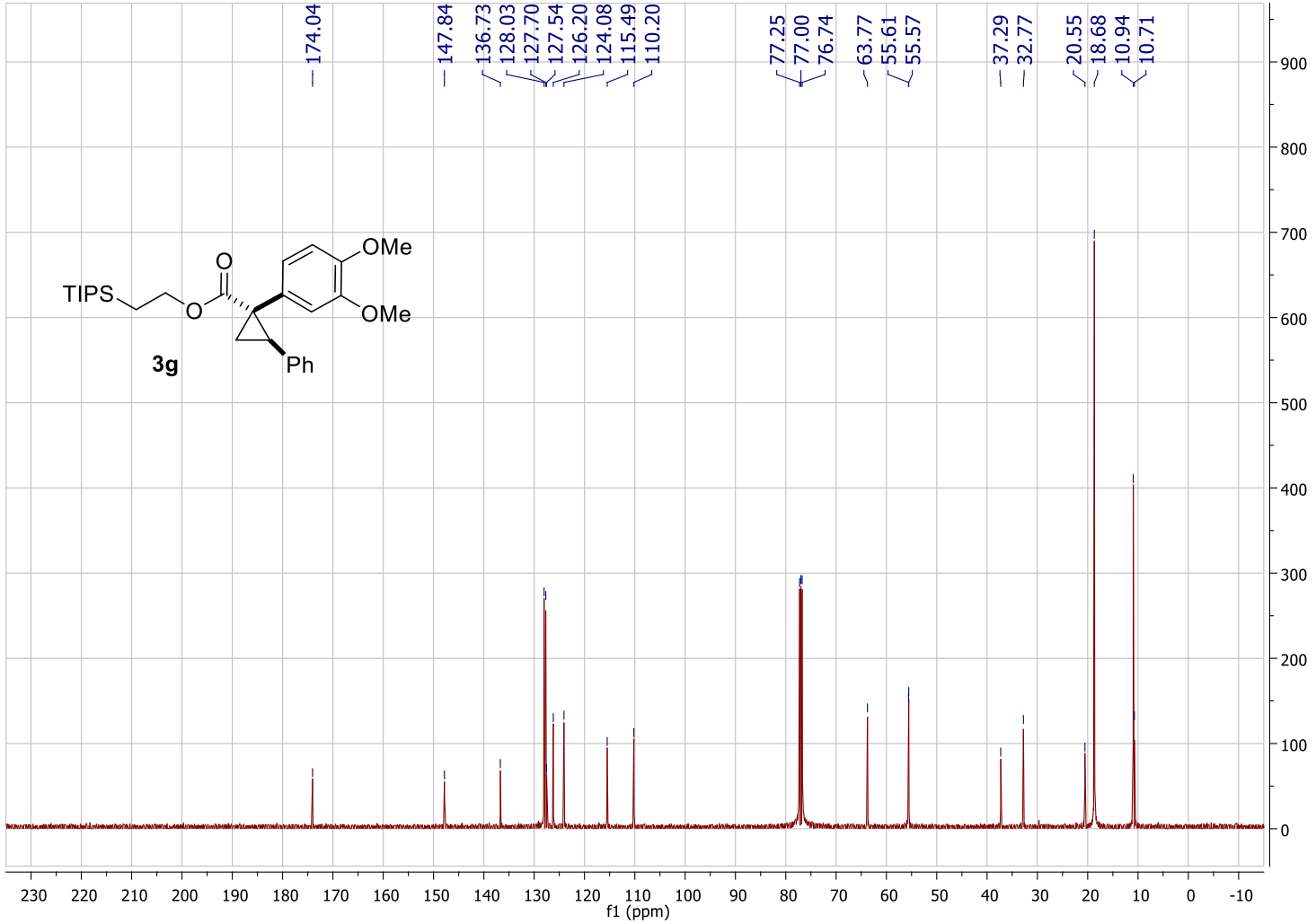
125MHz, $CDCl_3$



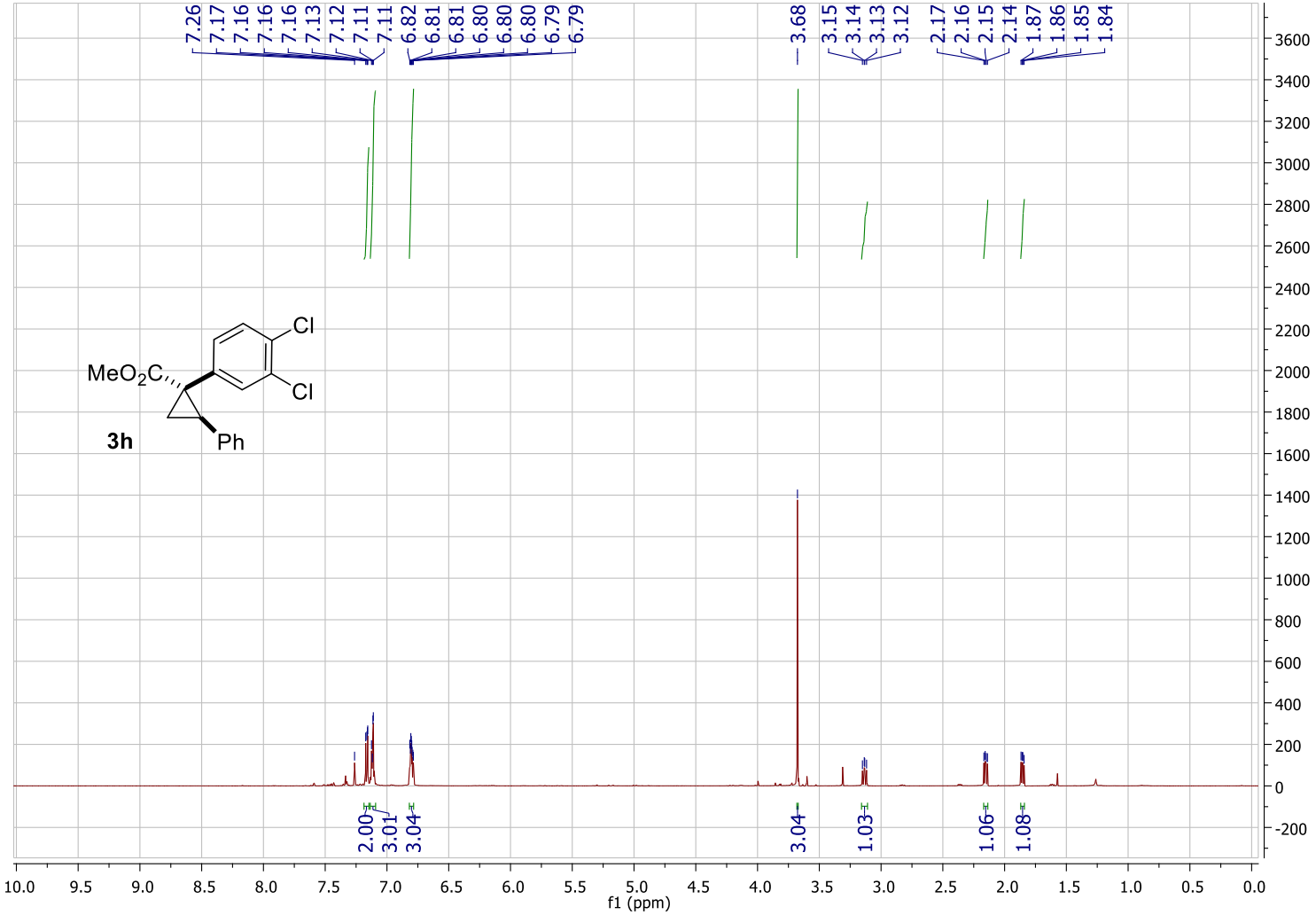
500MHz, $CDCl_3$



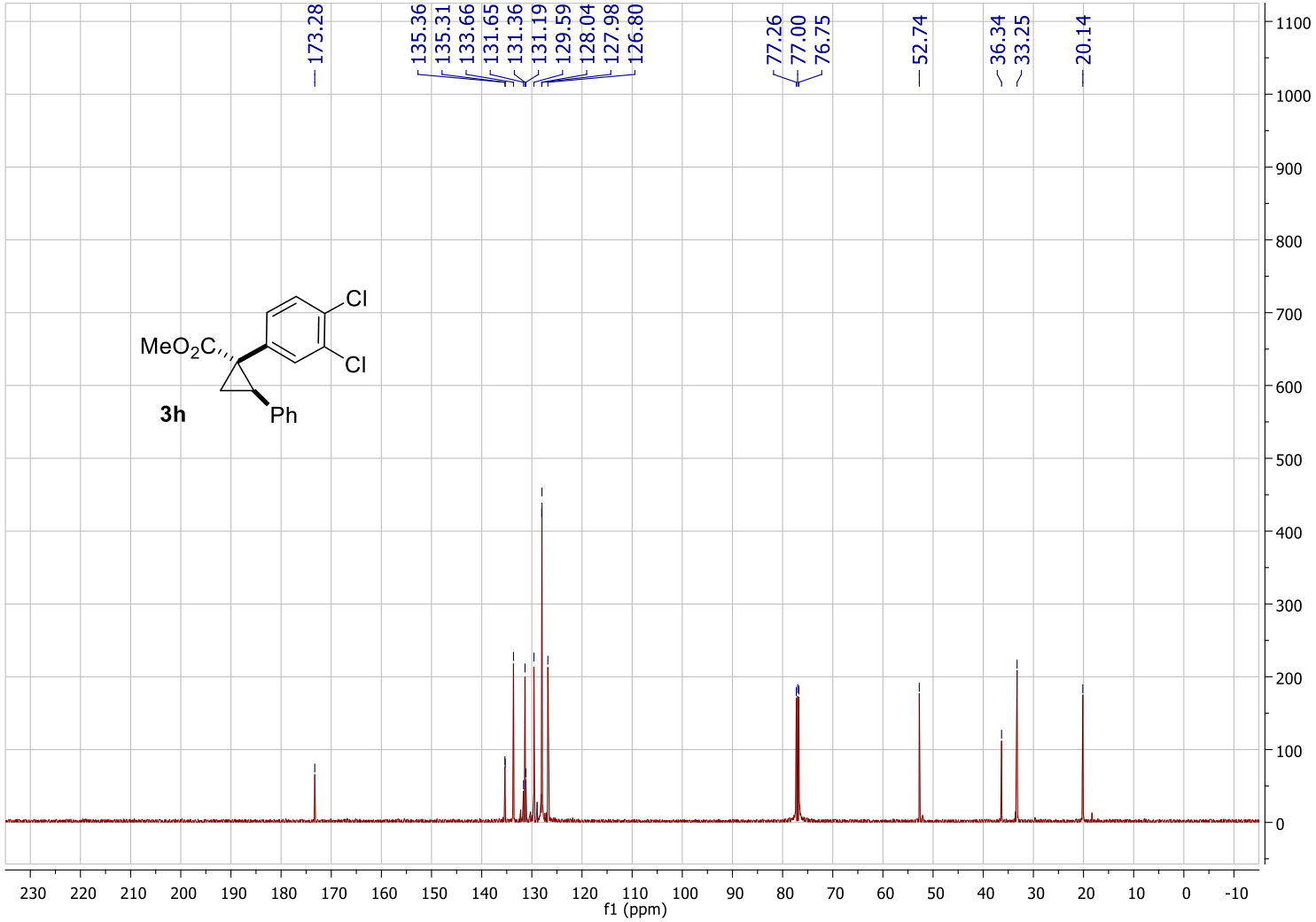
125MHz, $CDCl_3$



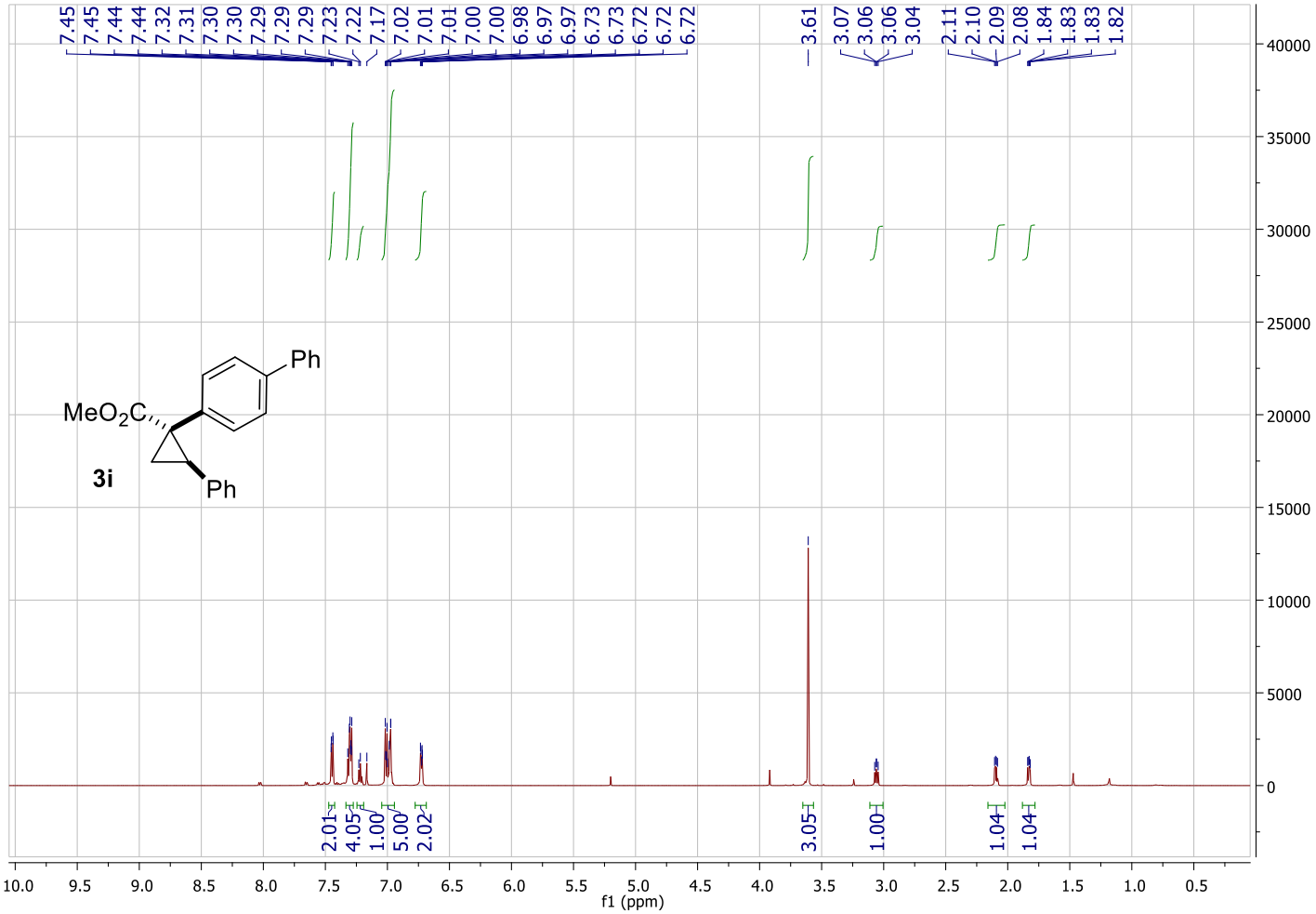
500MHz, $CDCl_3$



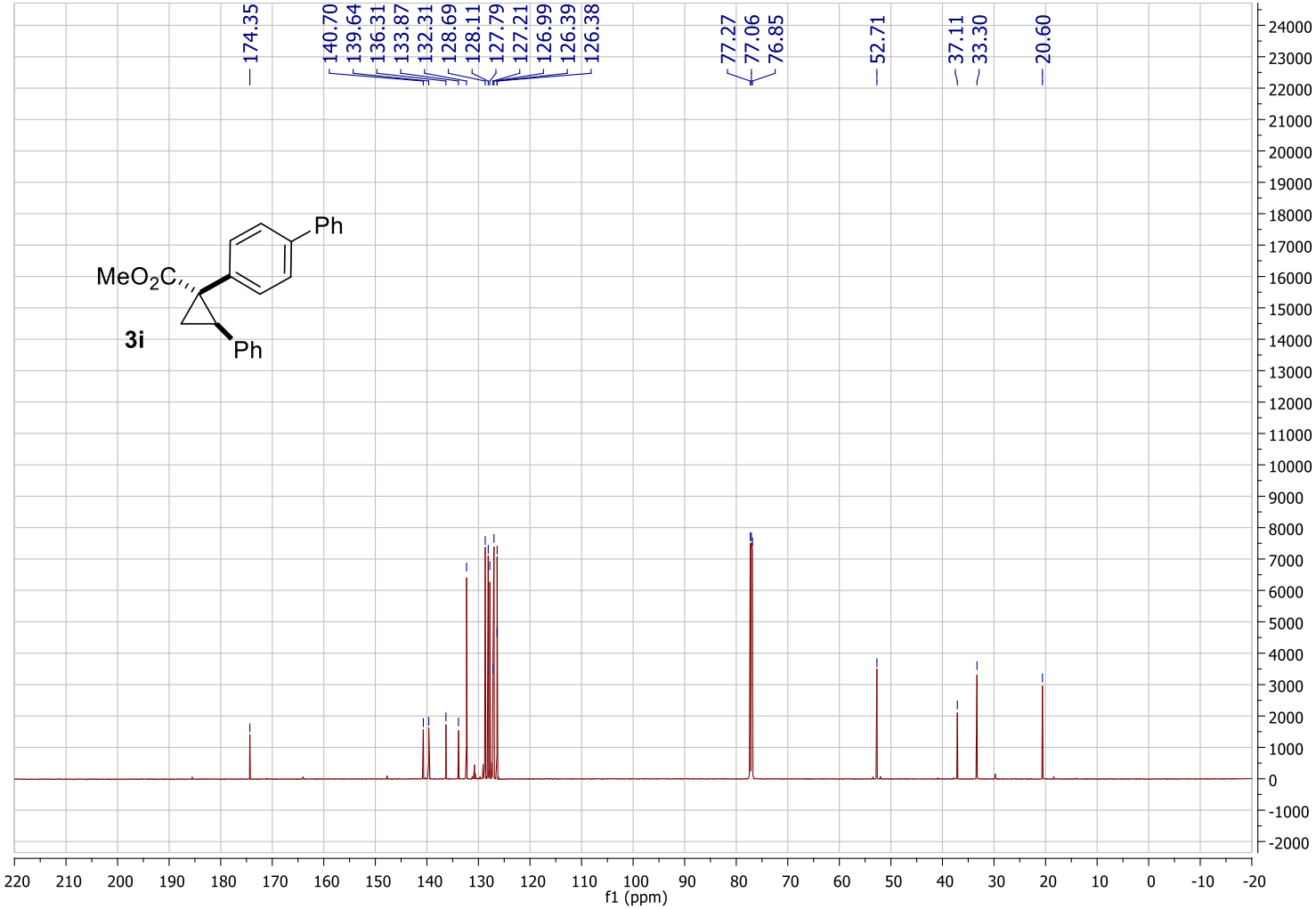
125MHz, $CDCl_3$



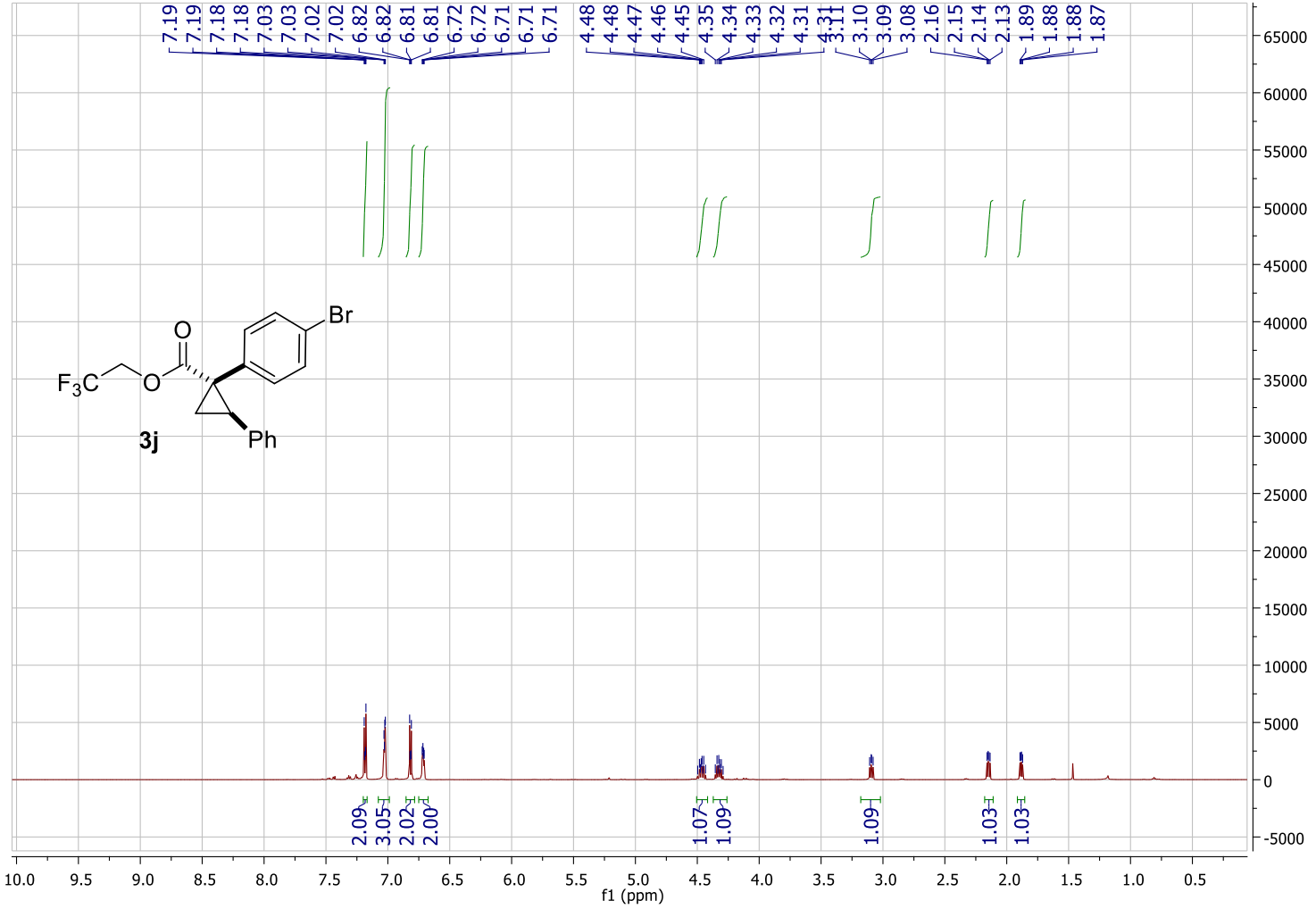
600MHz, $CDCl_3$



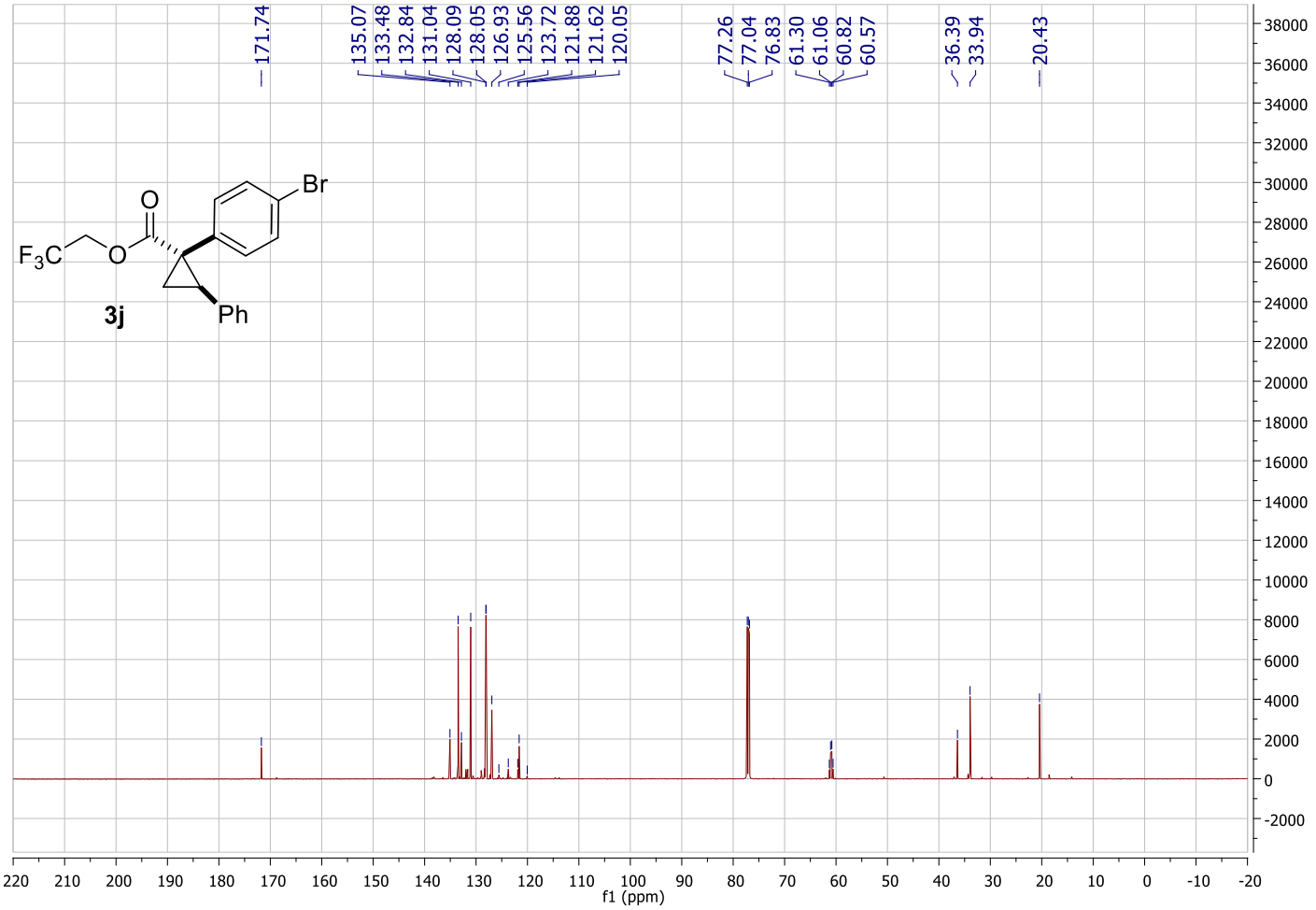
150MHz, $CDCl_3$



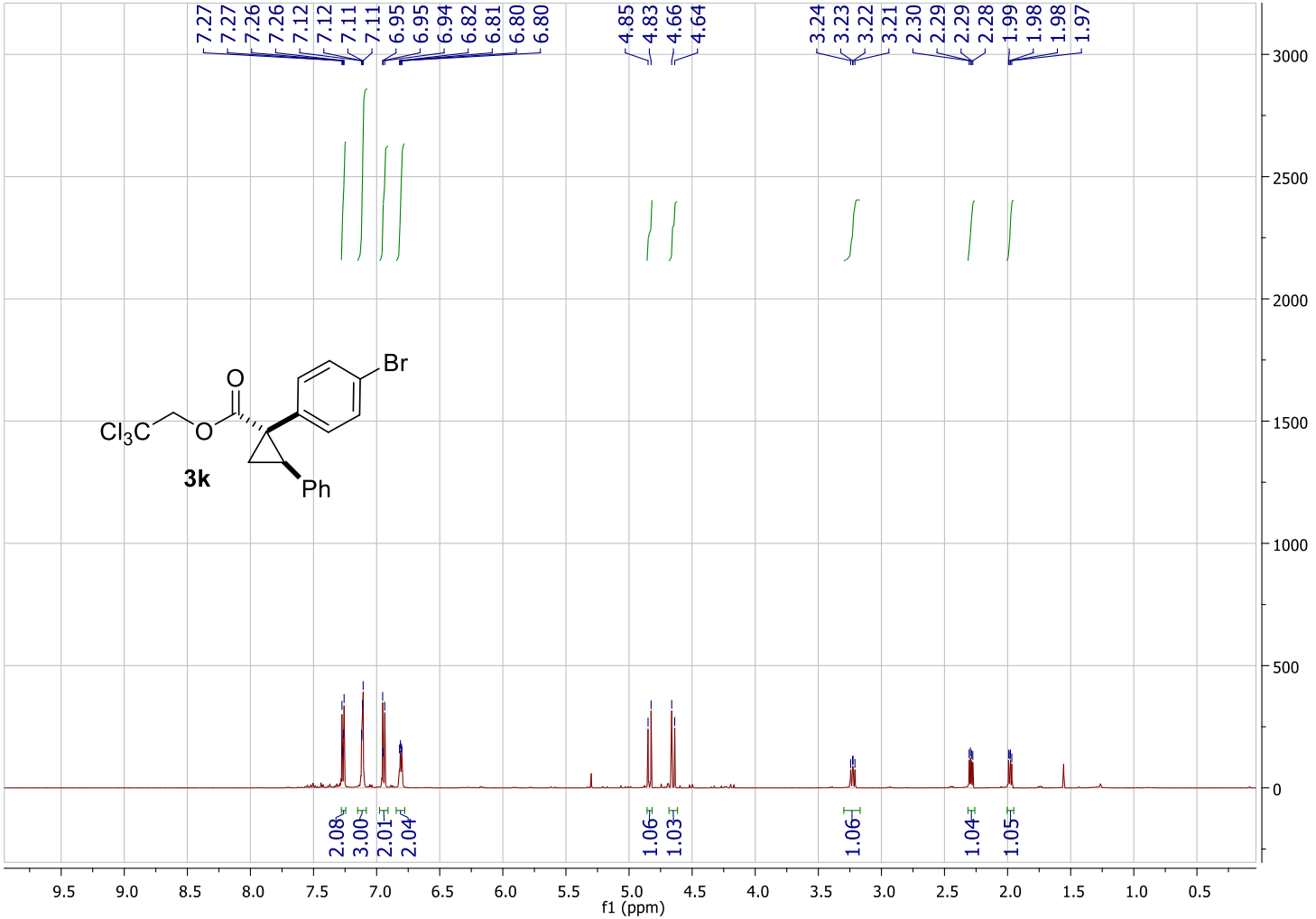
600MHz, $CDCl_3$



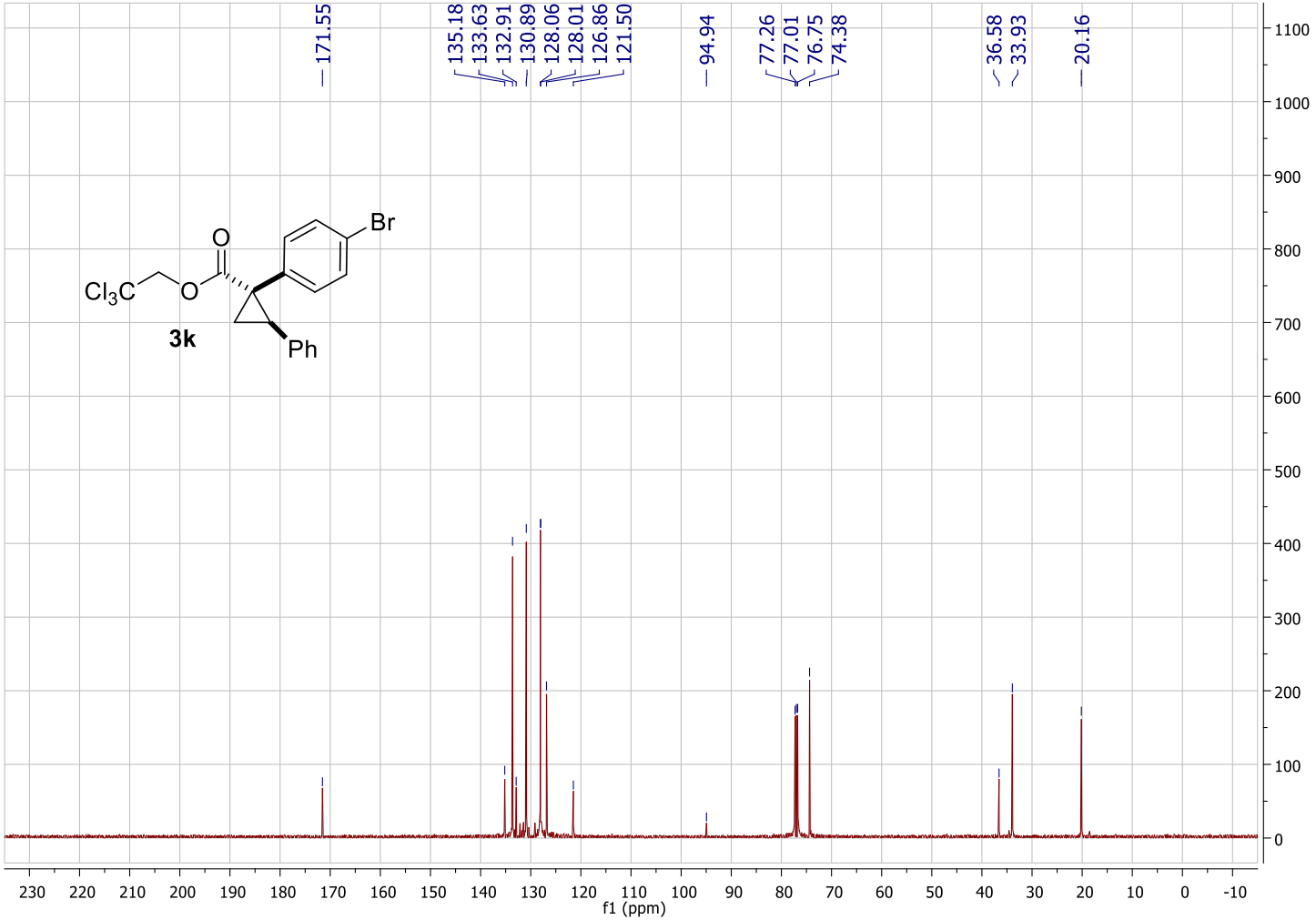
150MHz, $CDCl_3$



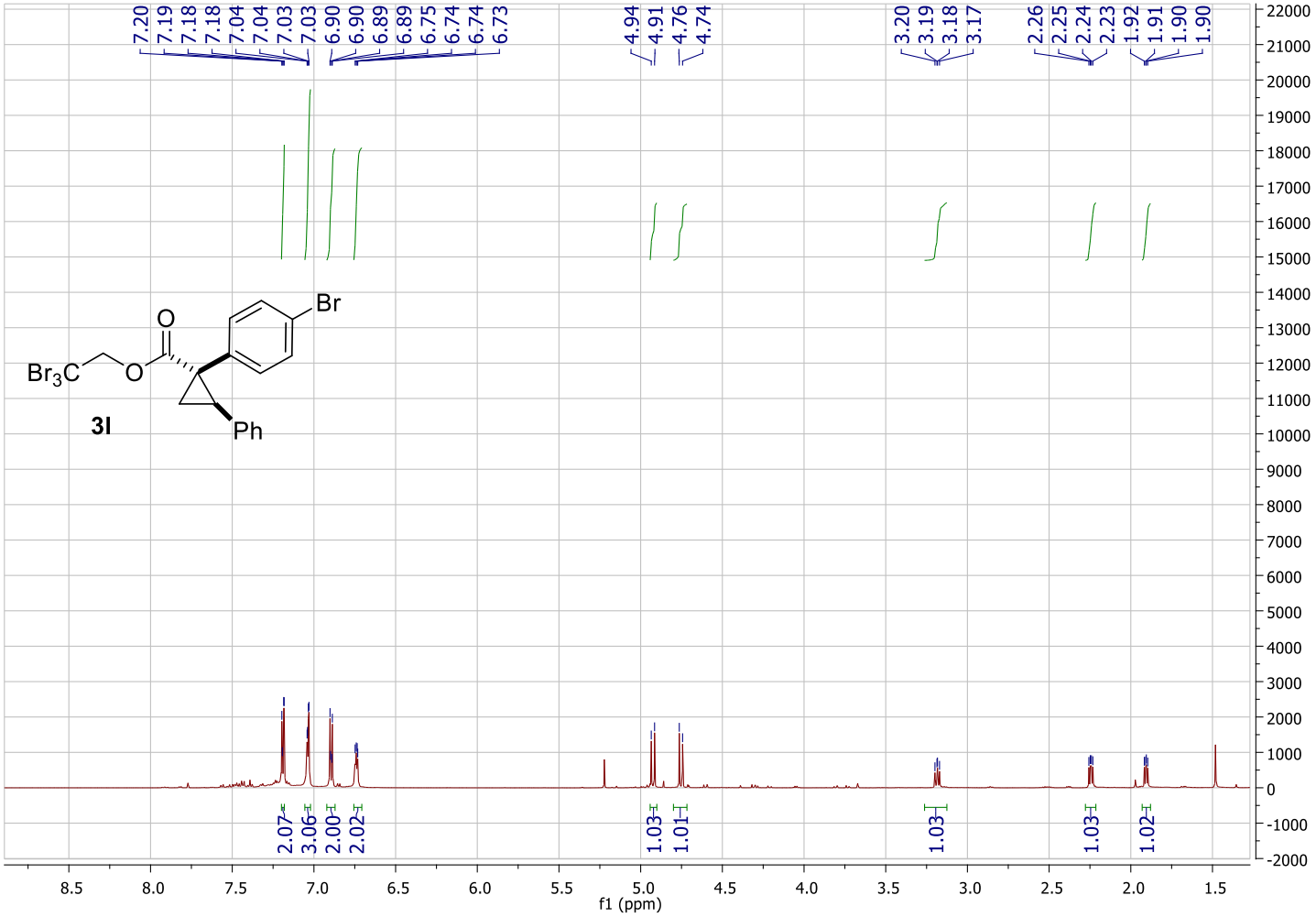
500MHz, $CDCl_3$



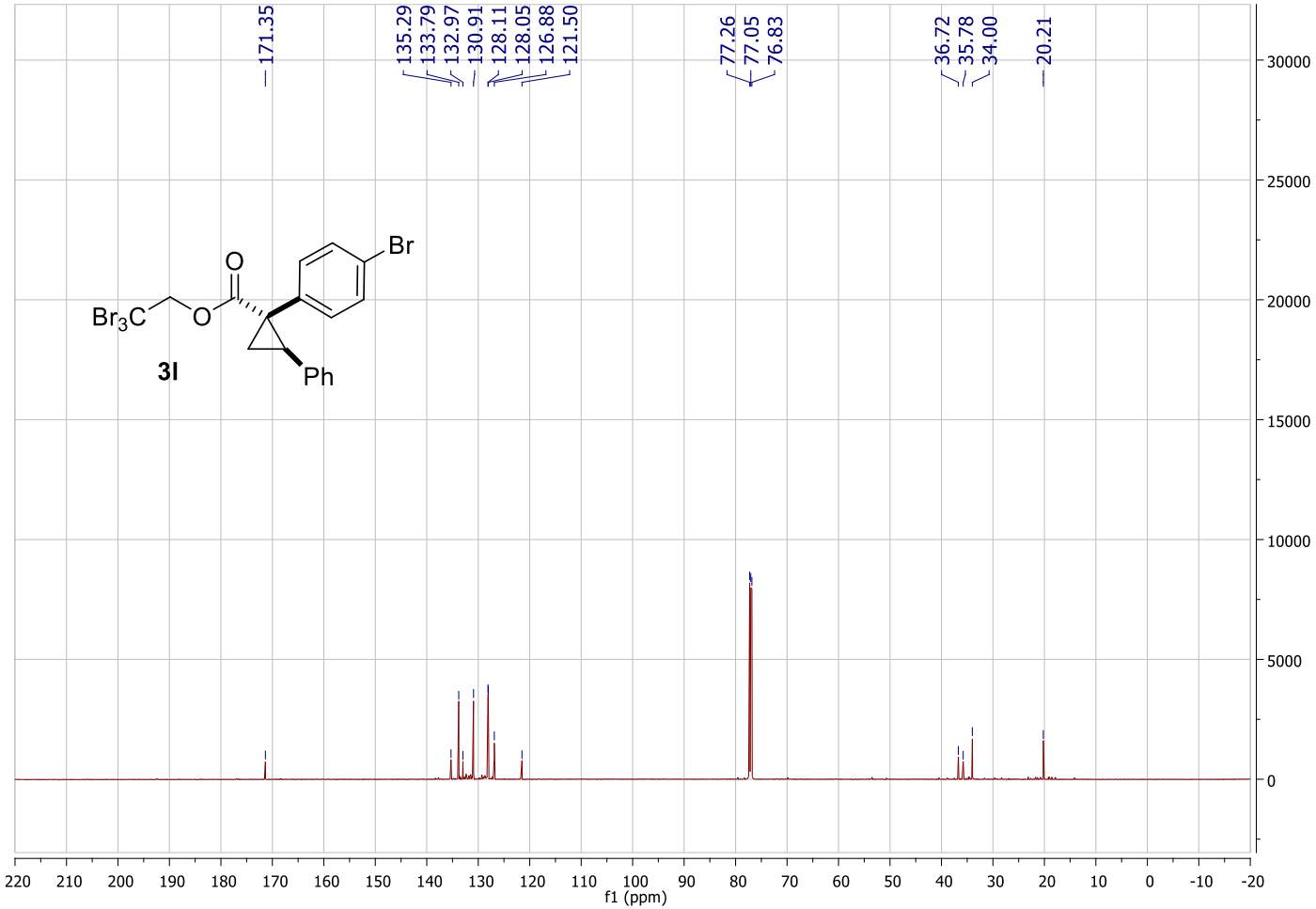
125MHz, $CDCl_3$



600MHz, $CDCl_3$

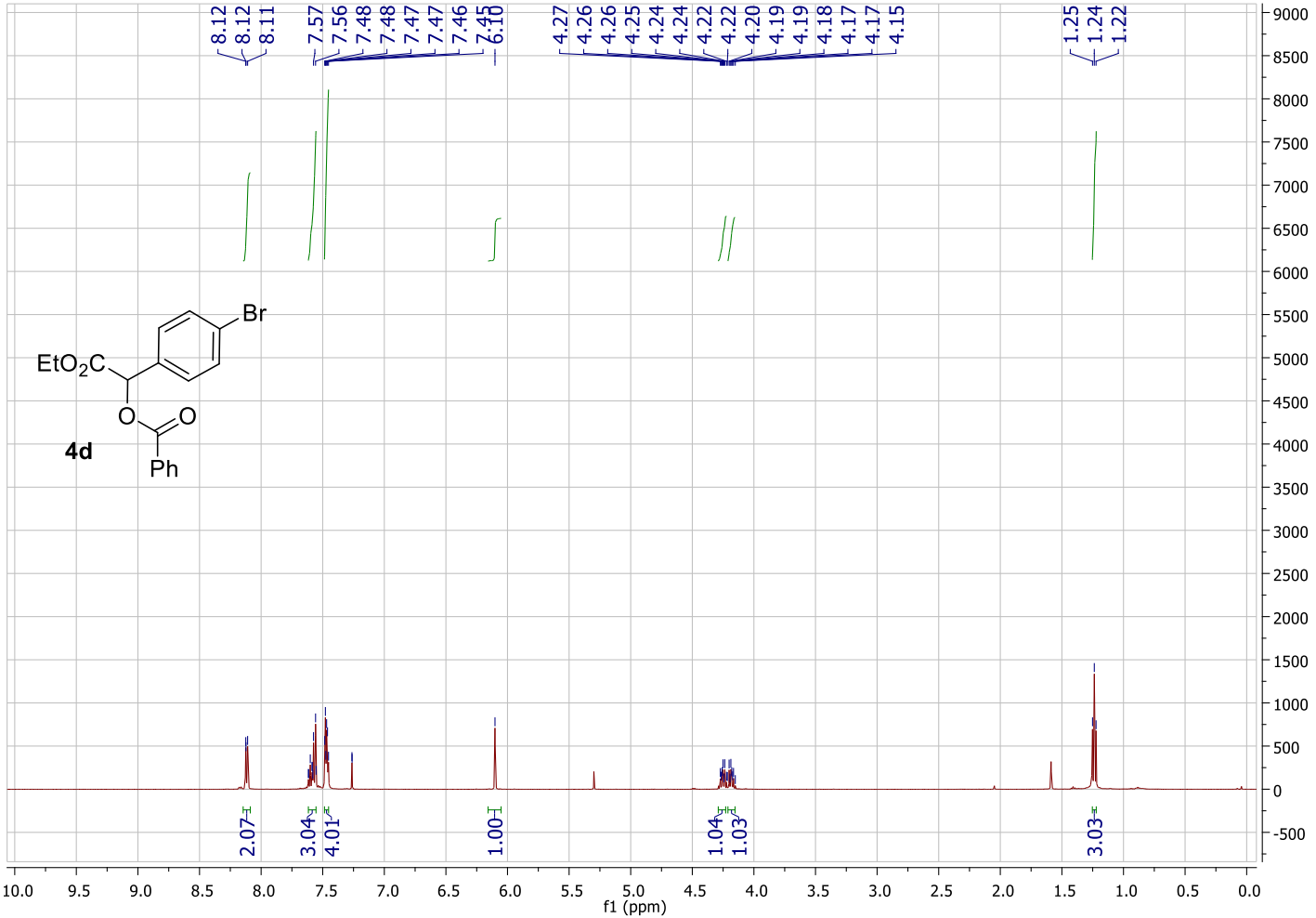


150MHz, $CDCl_3$

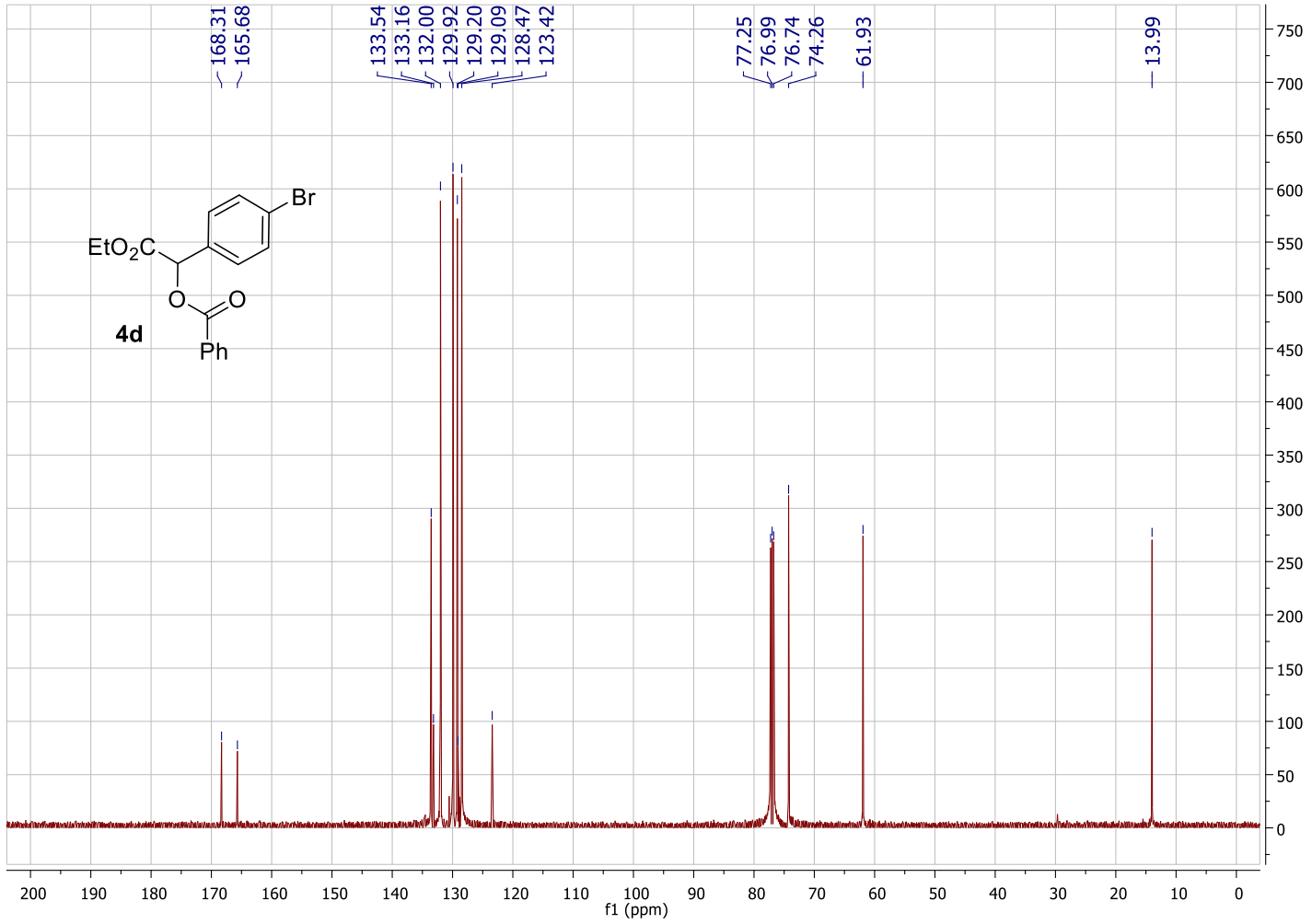


4.4 Products Derived from O-H Insertion of Carboxylic Acids

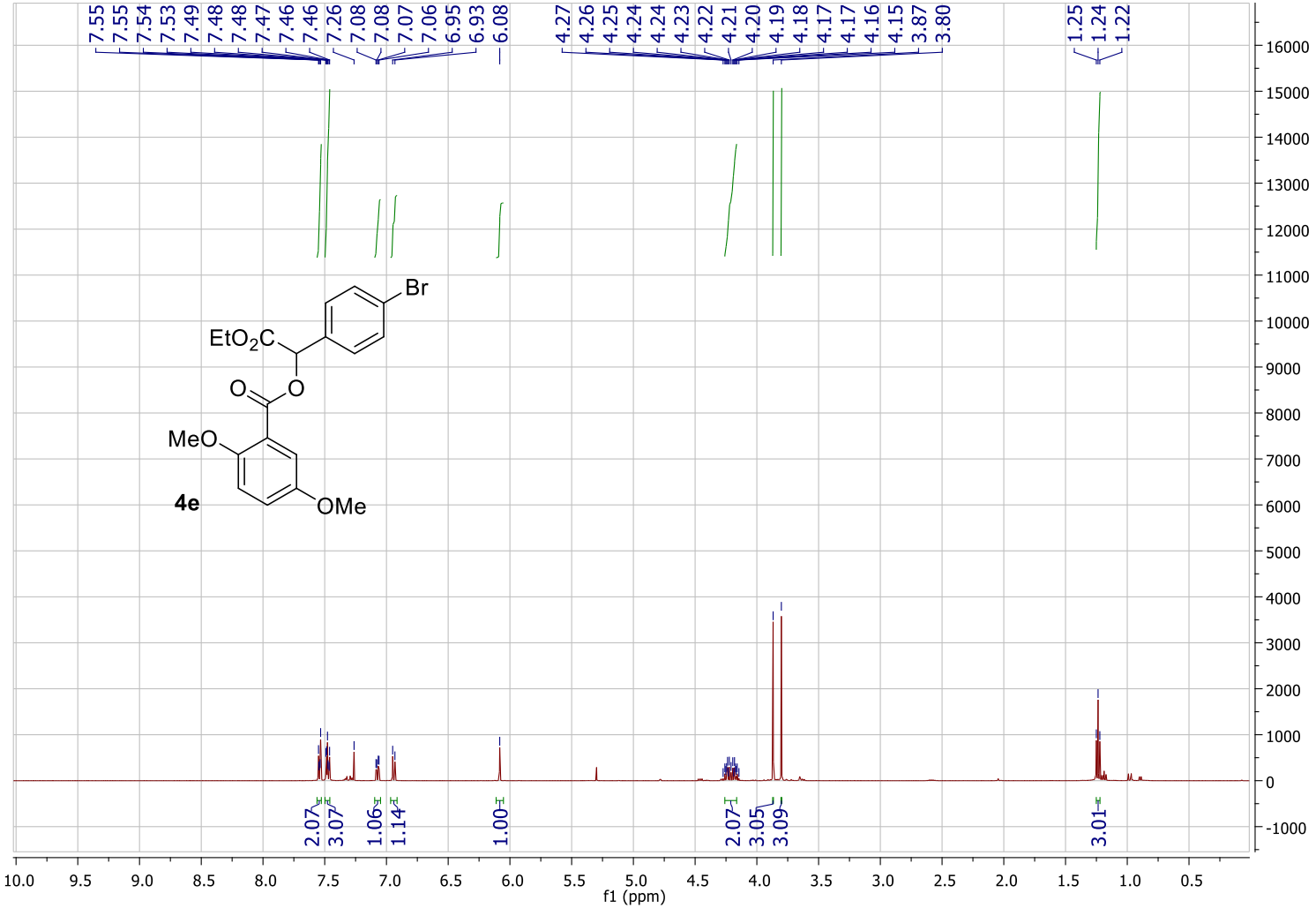
500MHz, $CDCl_3$



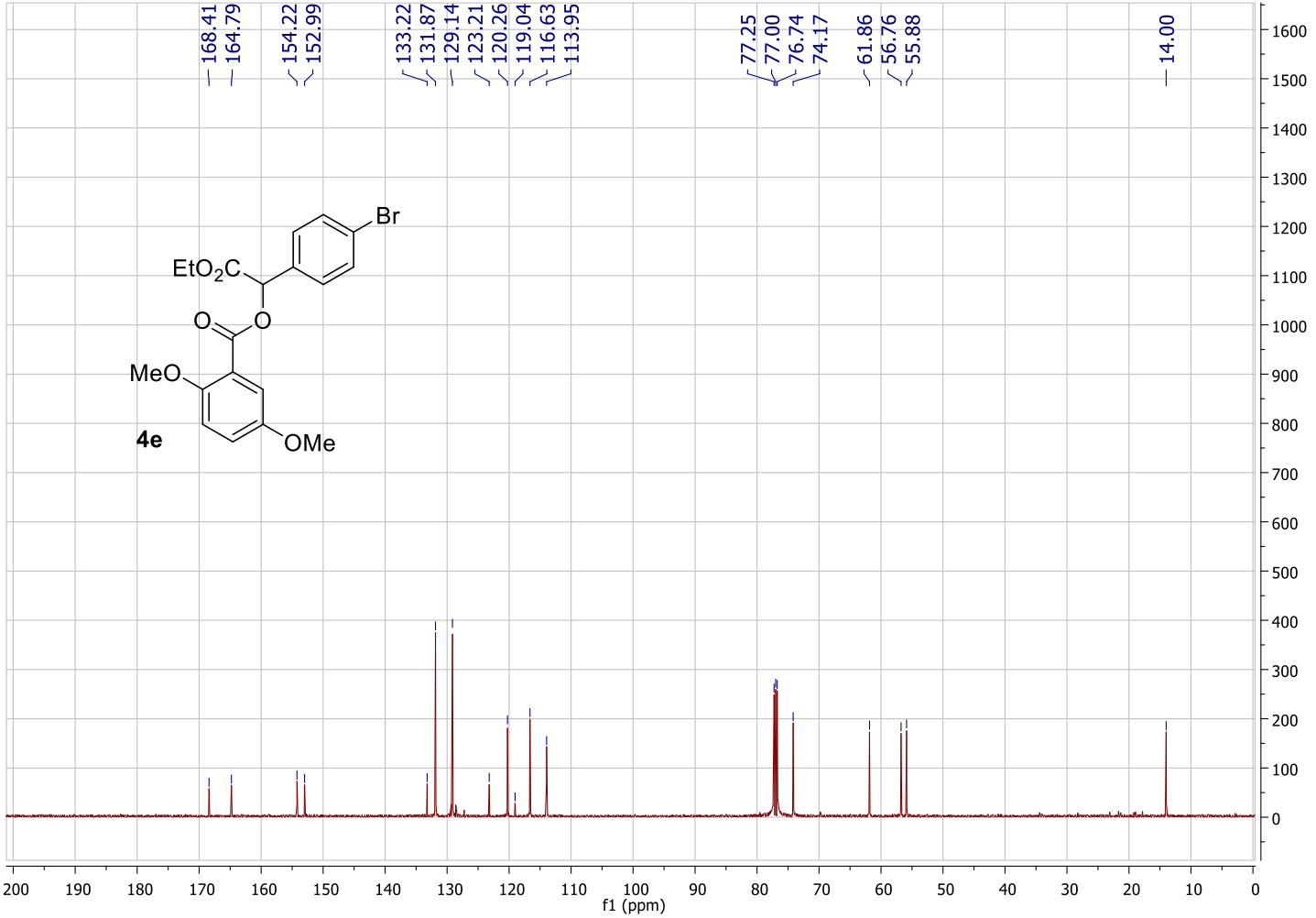
125MHz, $CDCl_3$



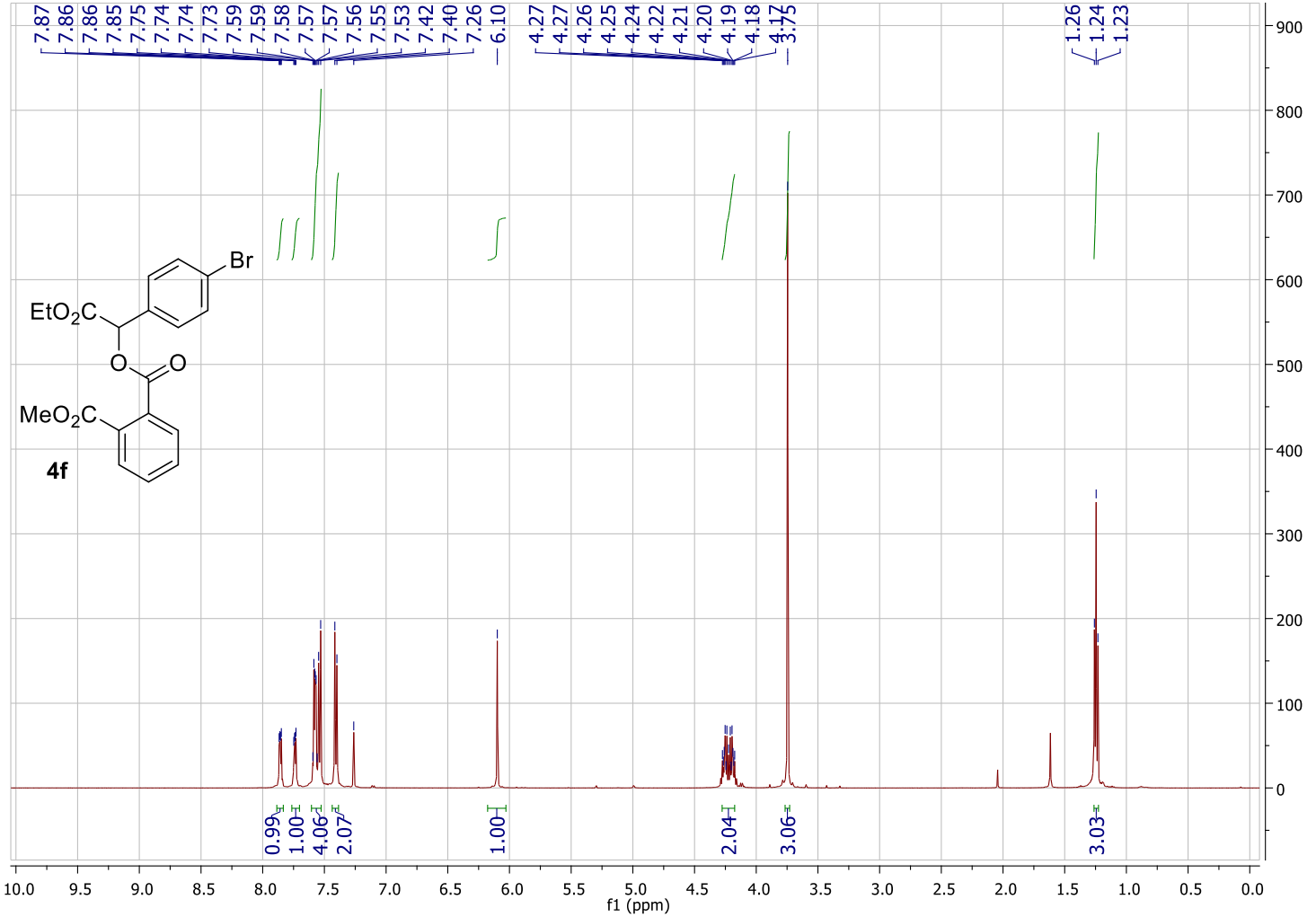
500MHz, $CDCl_3$



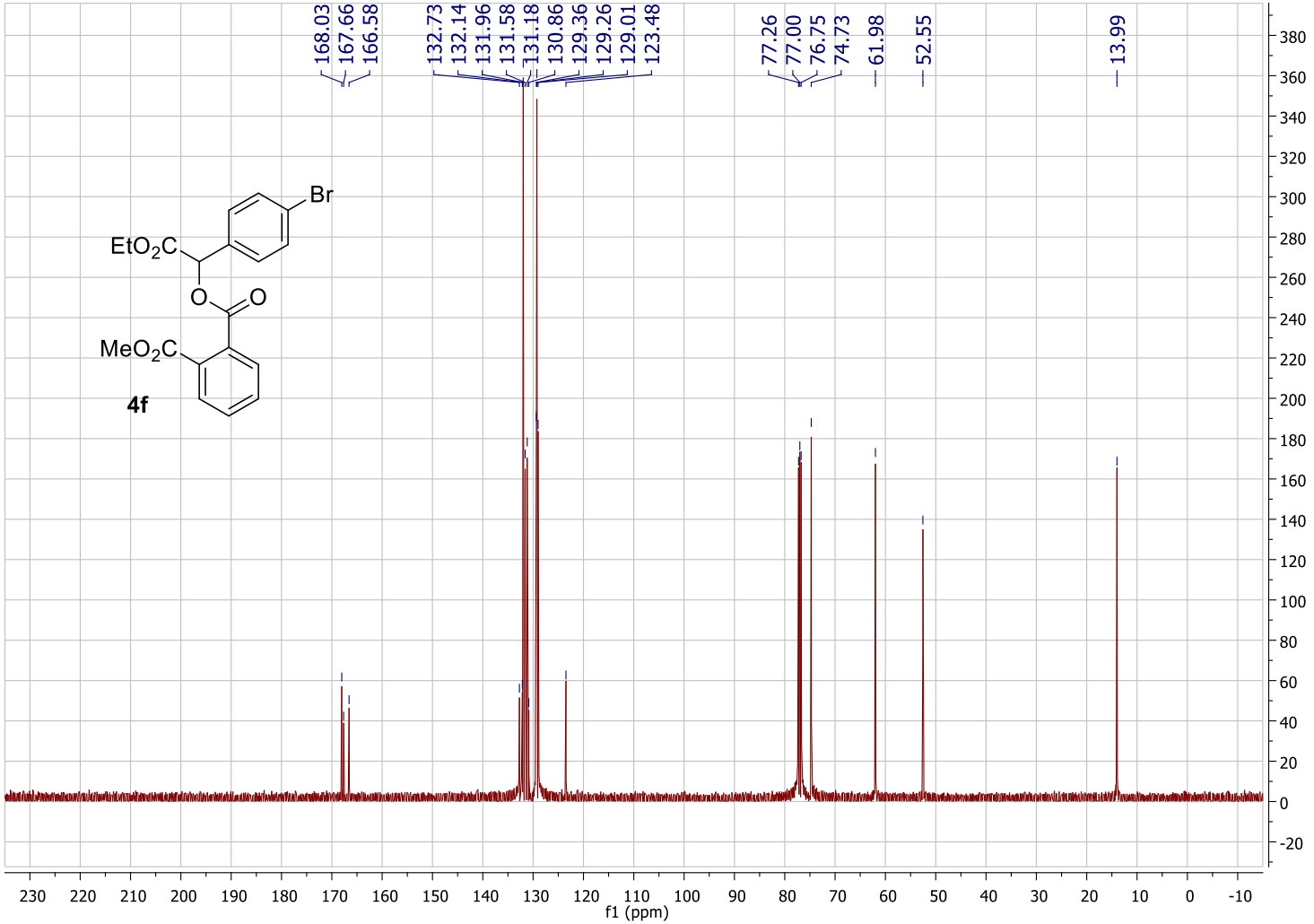
125MHz, $CDCl_3$



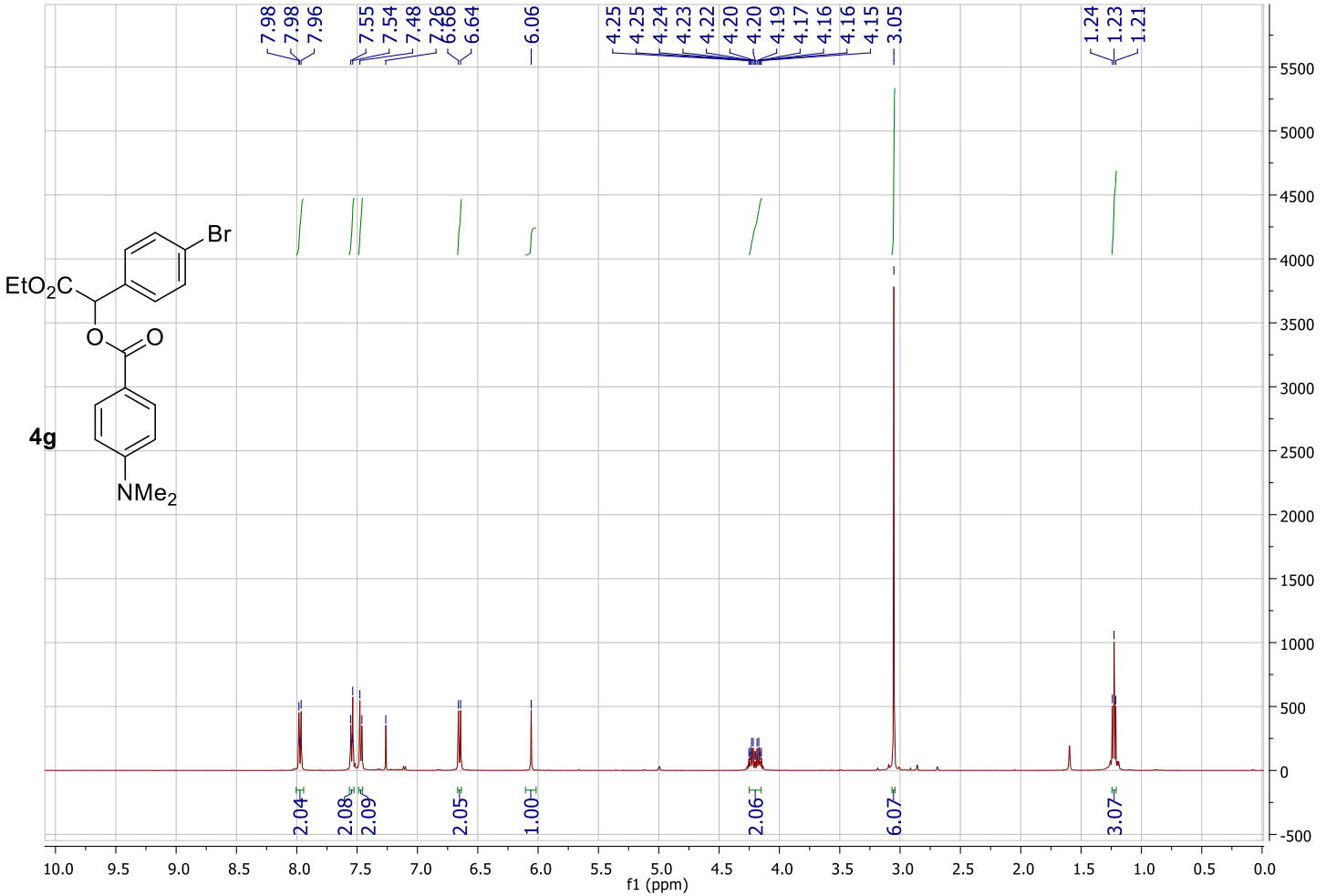
500MHz, $CDCl_3$



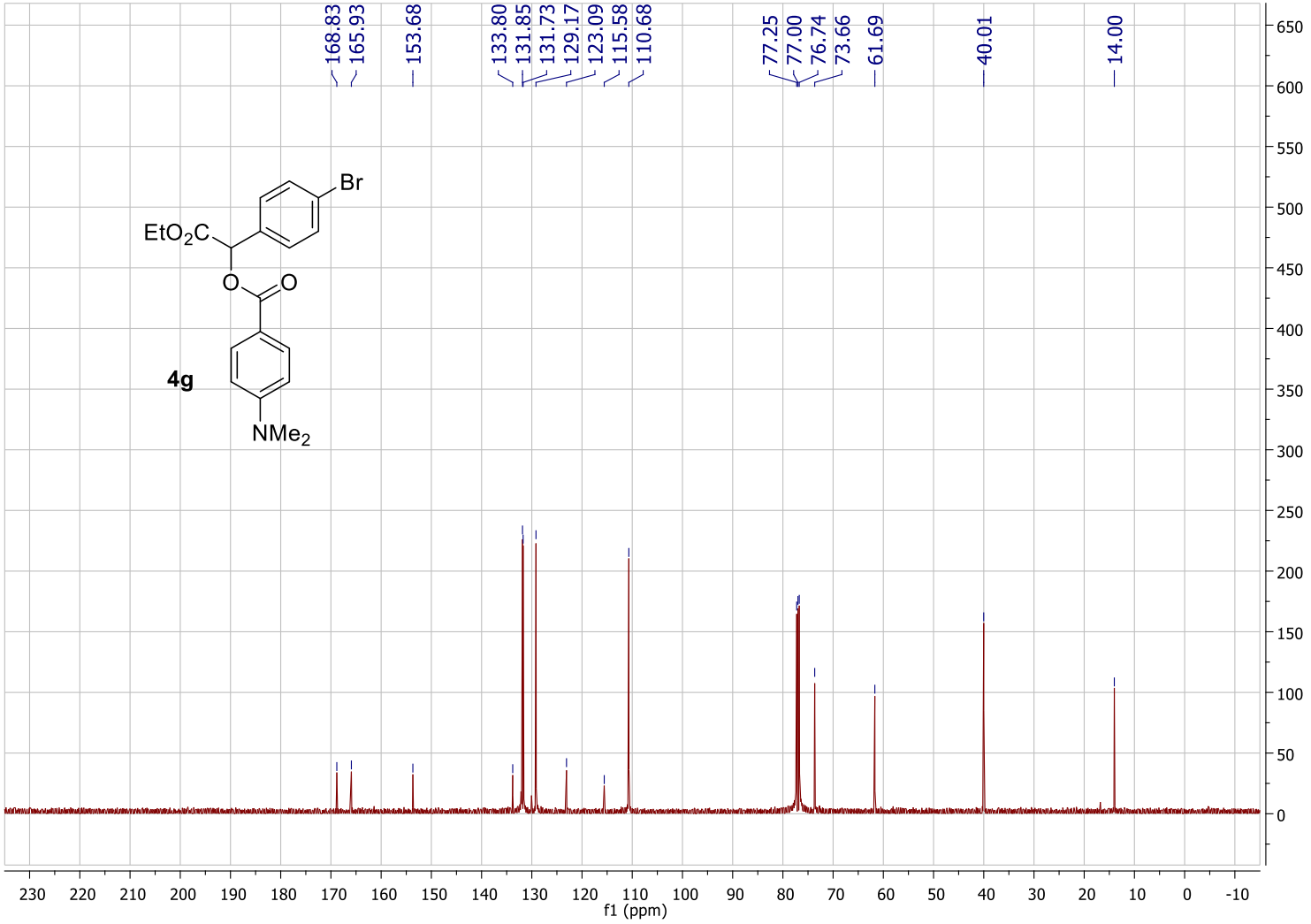
125MHz, $CDCl_3$



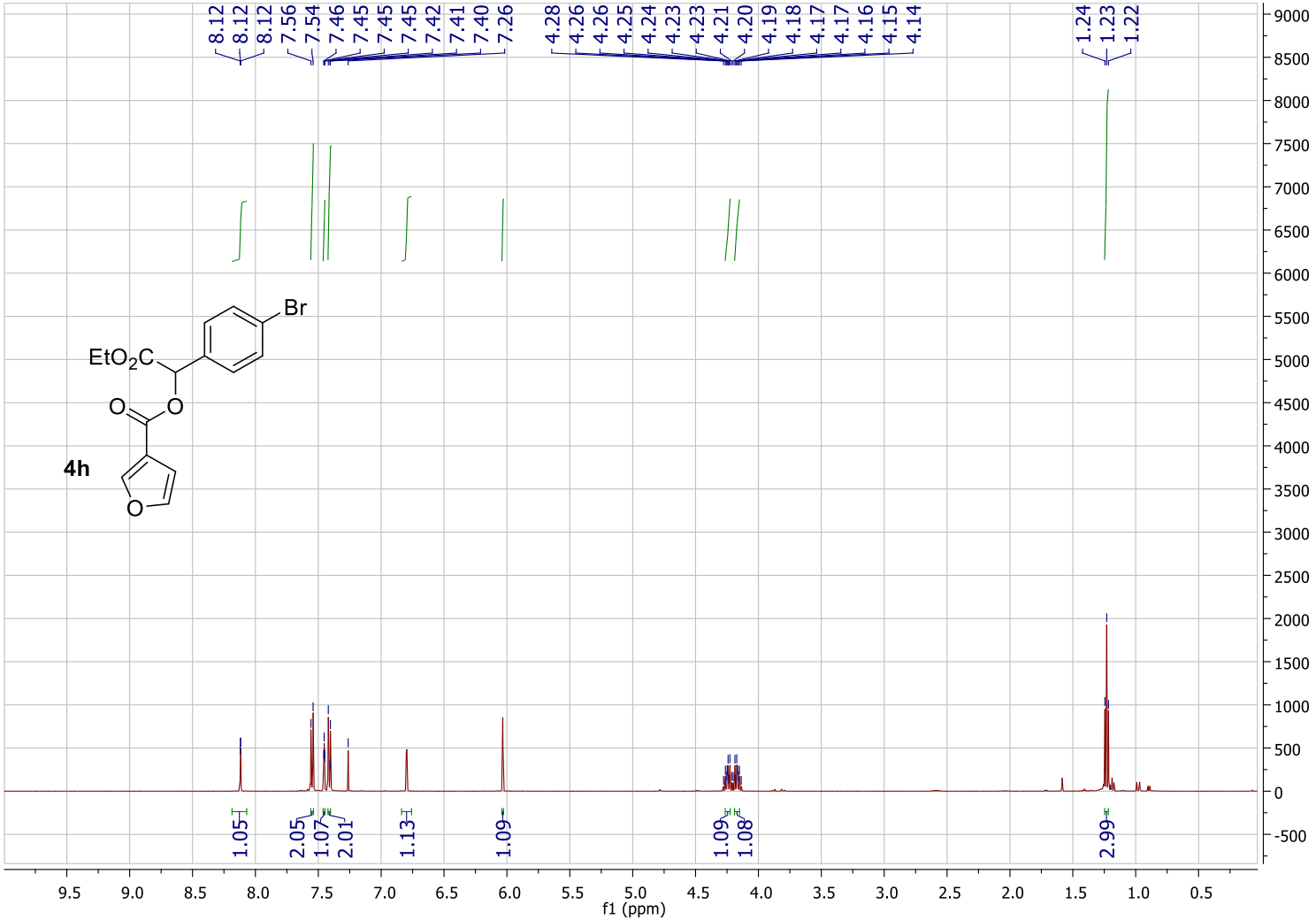
500MHz, $CDCl_3$



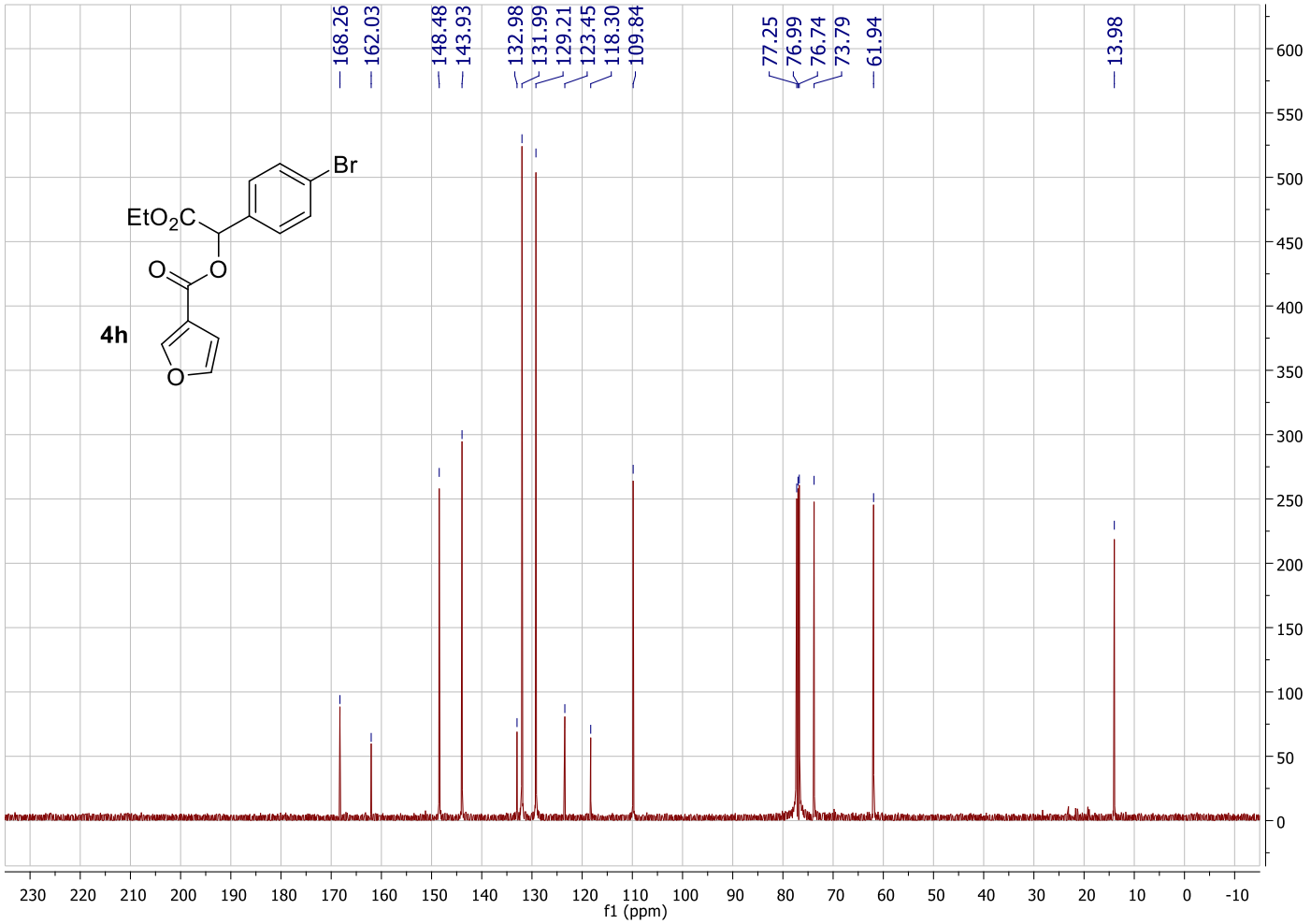
125MHz, $CDCl_3$



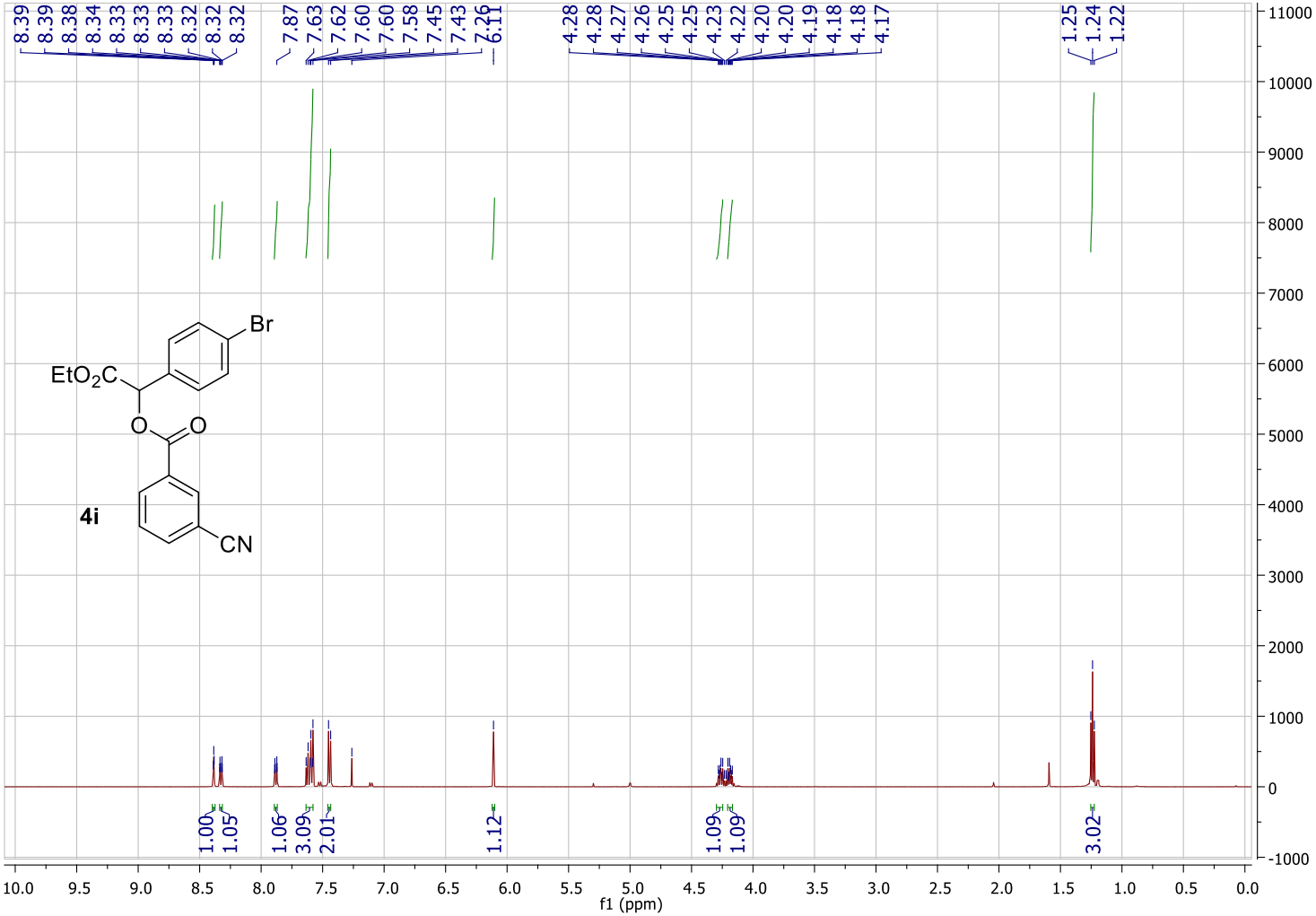
500MHz, $CDCl_3$



125MHz, $CDCl_3$



500MHz, $CDCl_3$



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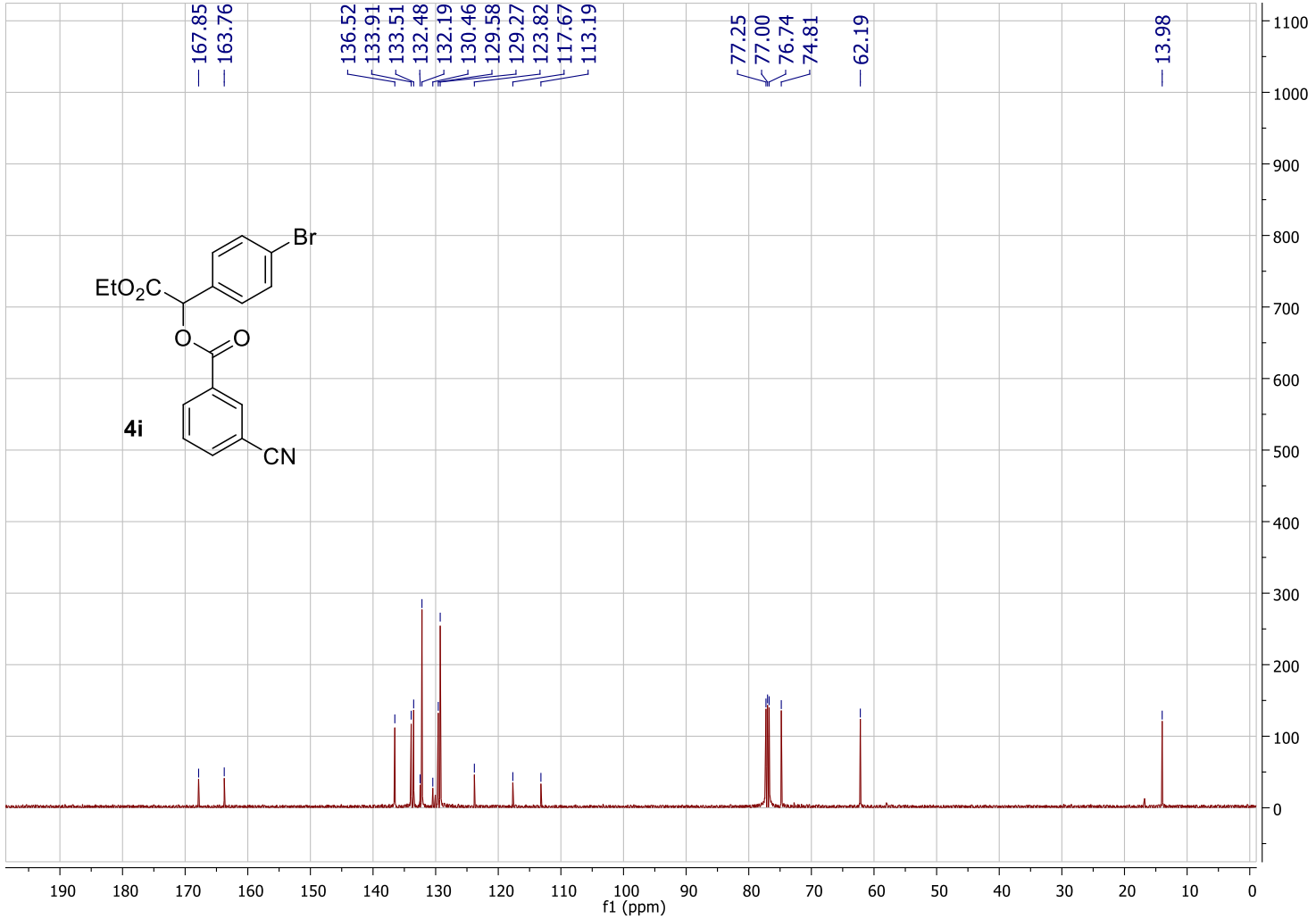
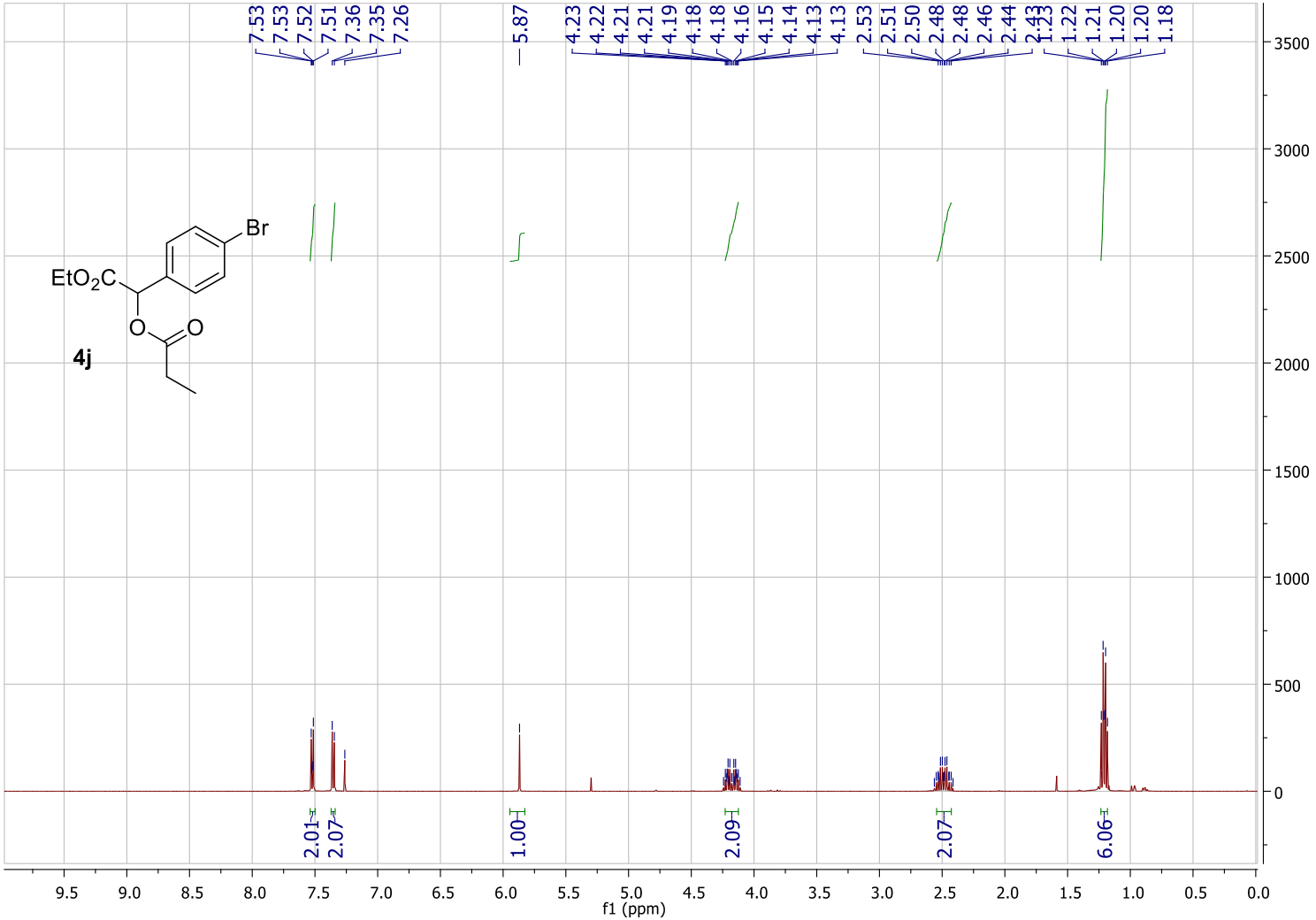
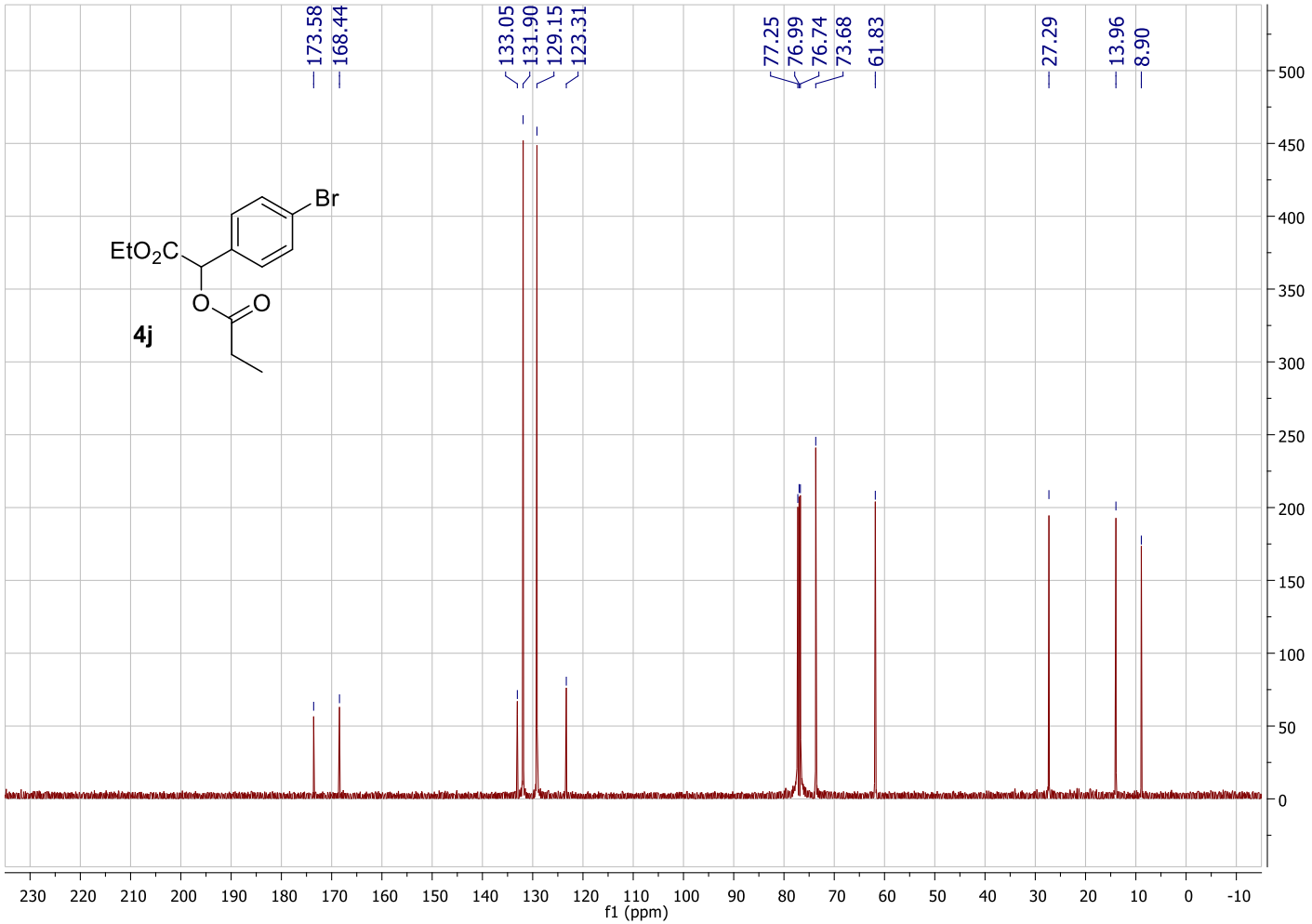


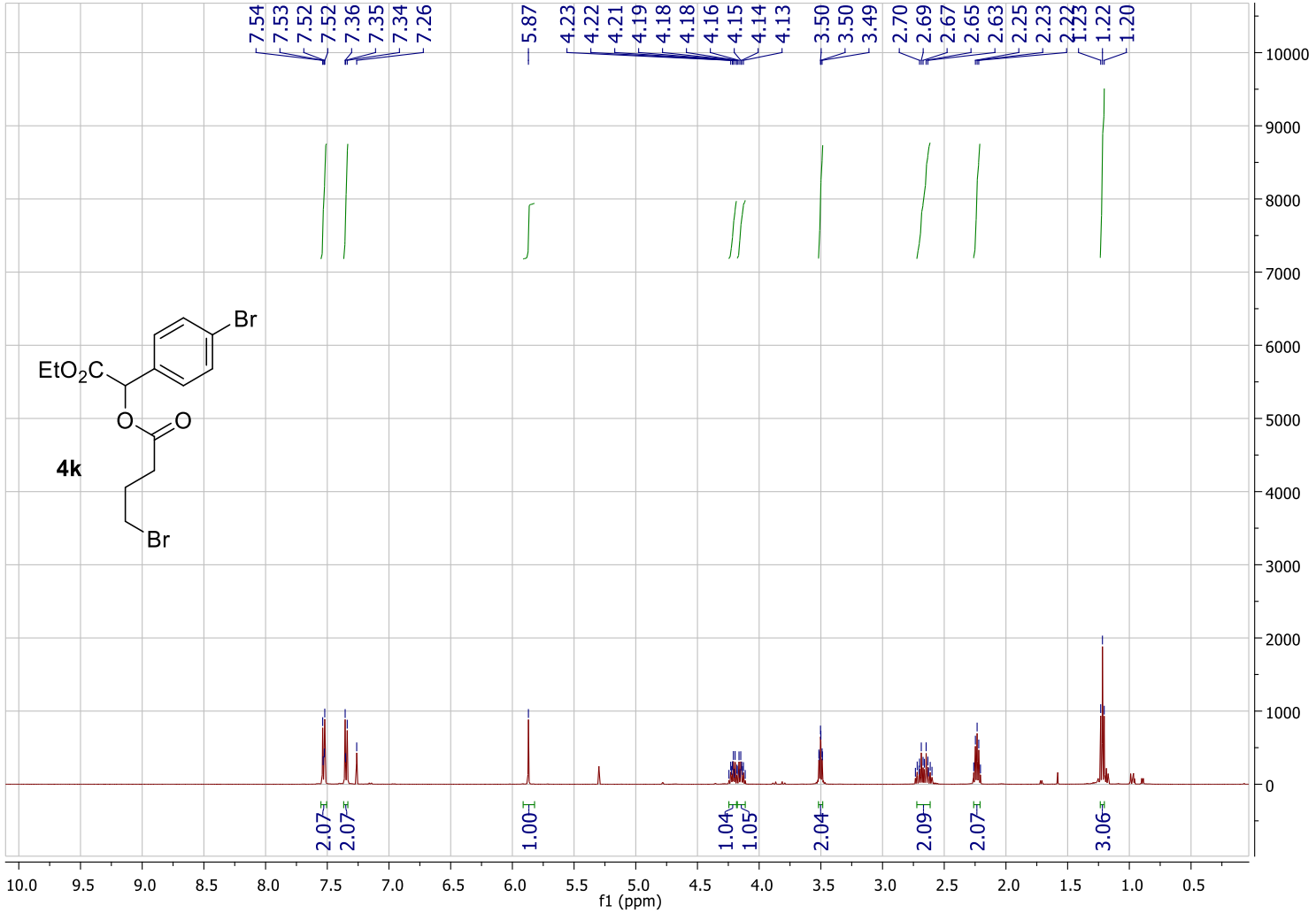
500MHz, $CDCl_3$



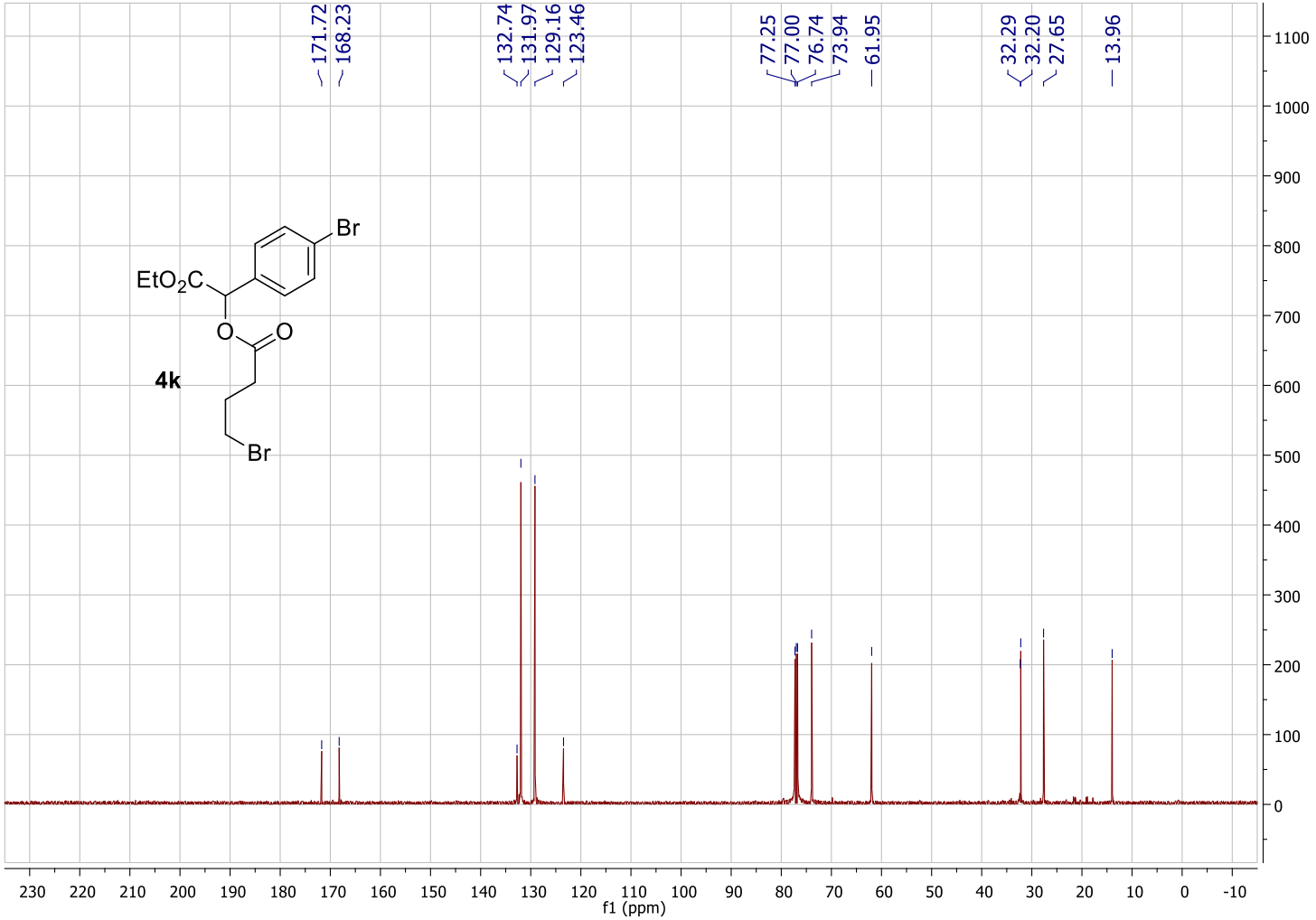
125 MHz, $CDCl_3$



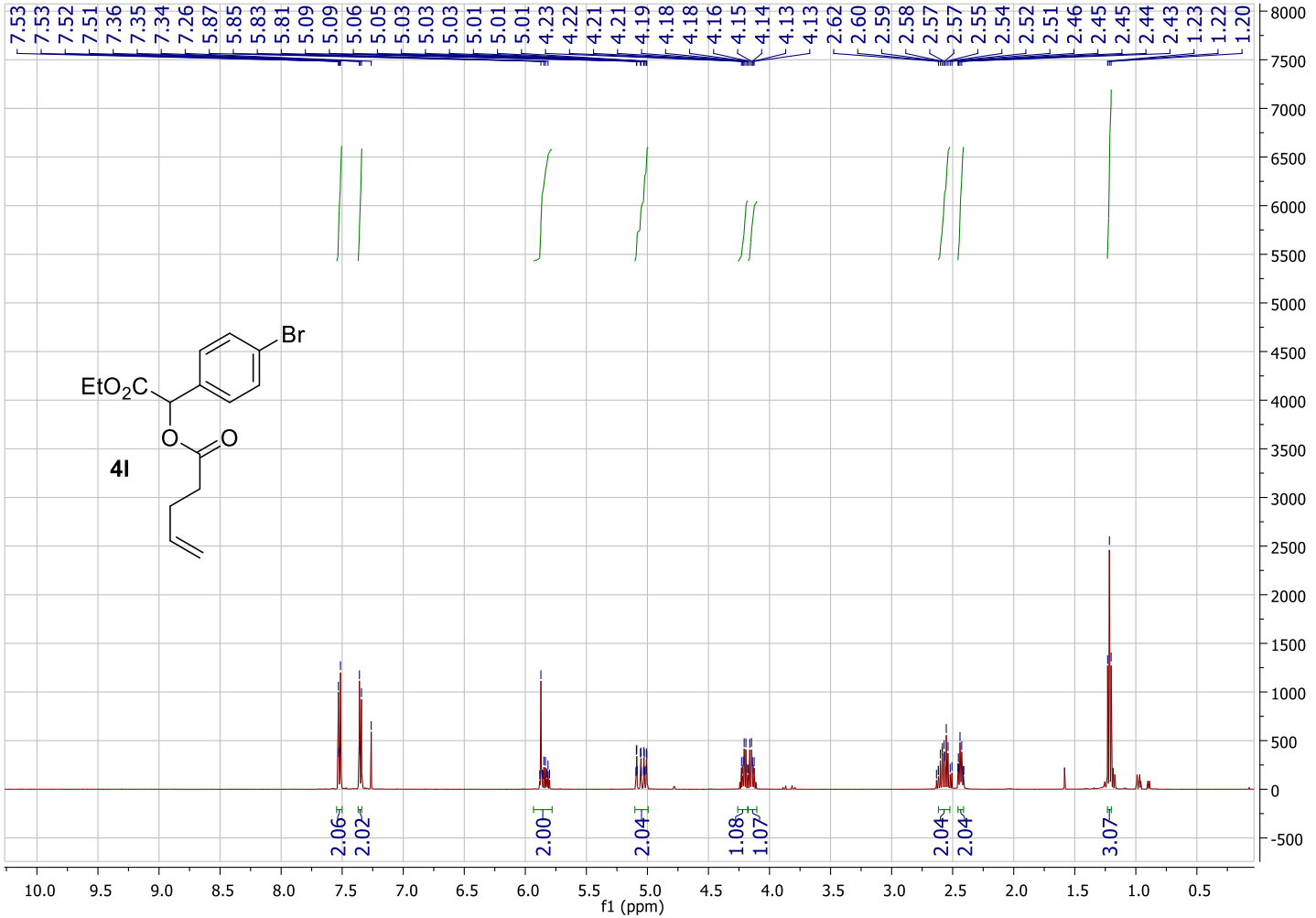
500MHz, $CDCl_3$



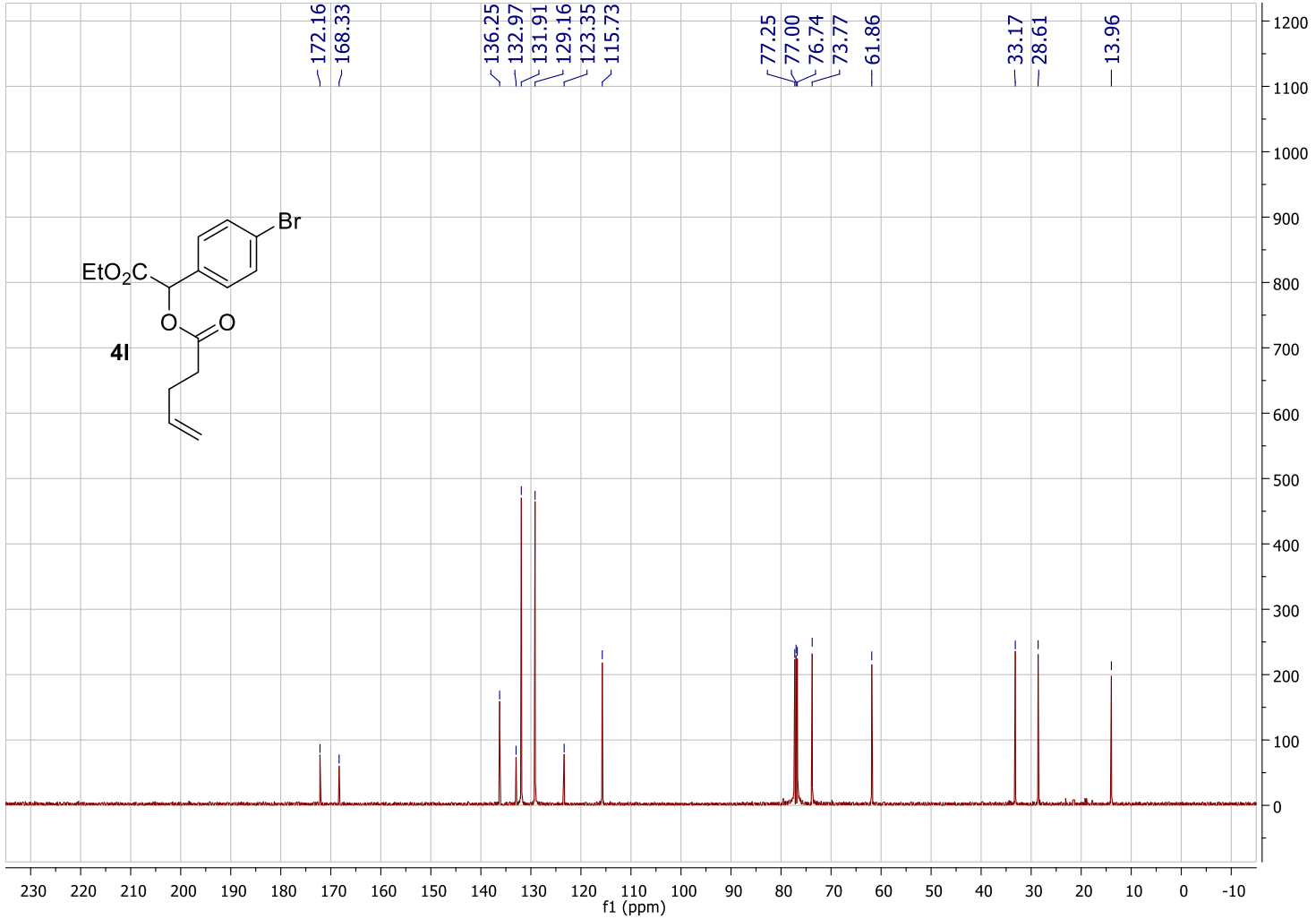
125MHz, $CDCl_3$



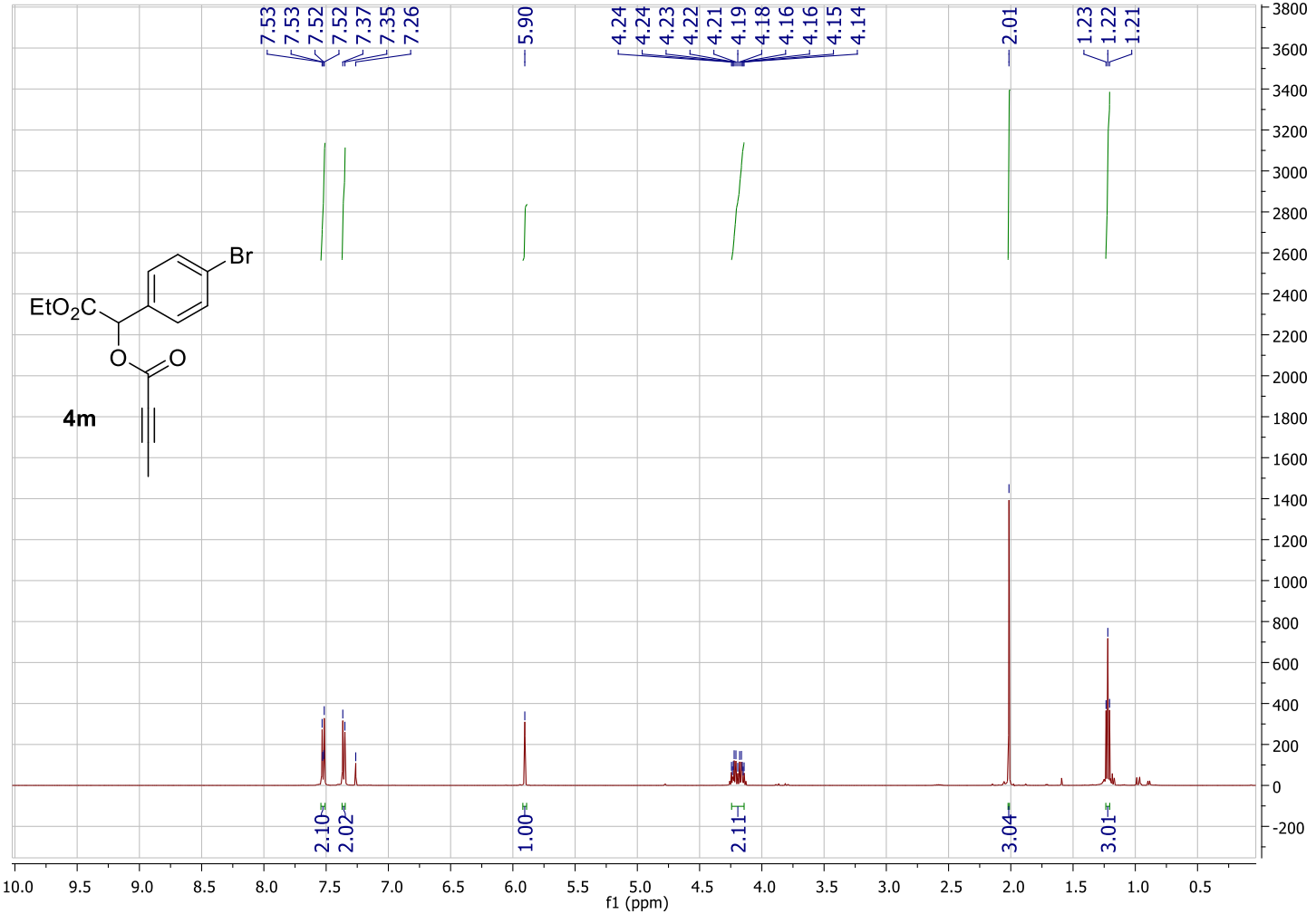
500MHz, $CDCl_3$



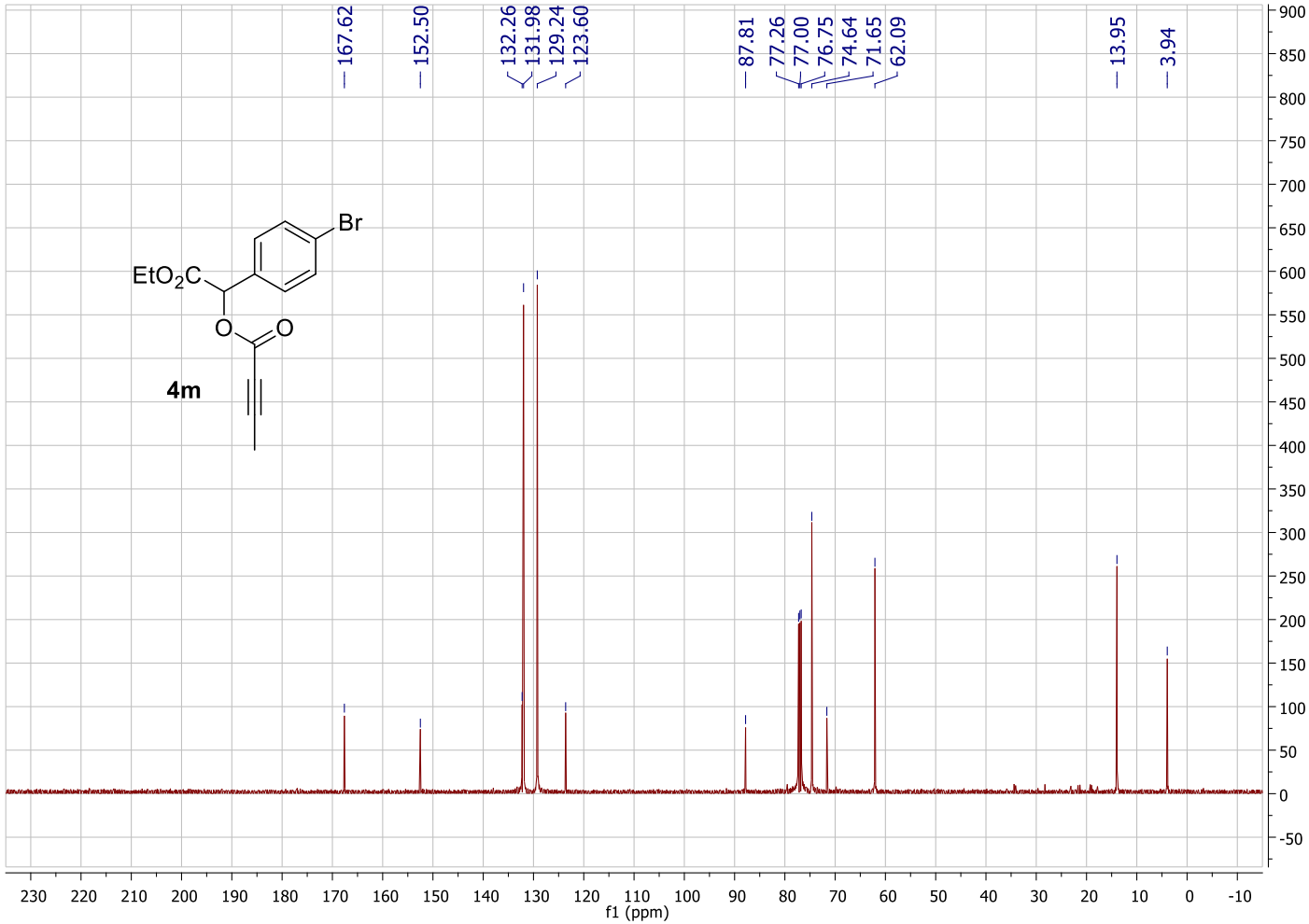
125MHz, $CDCl_3$



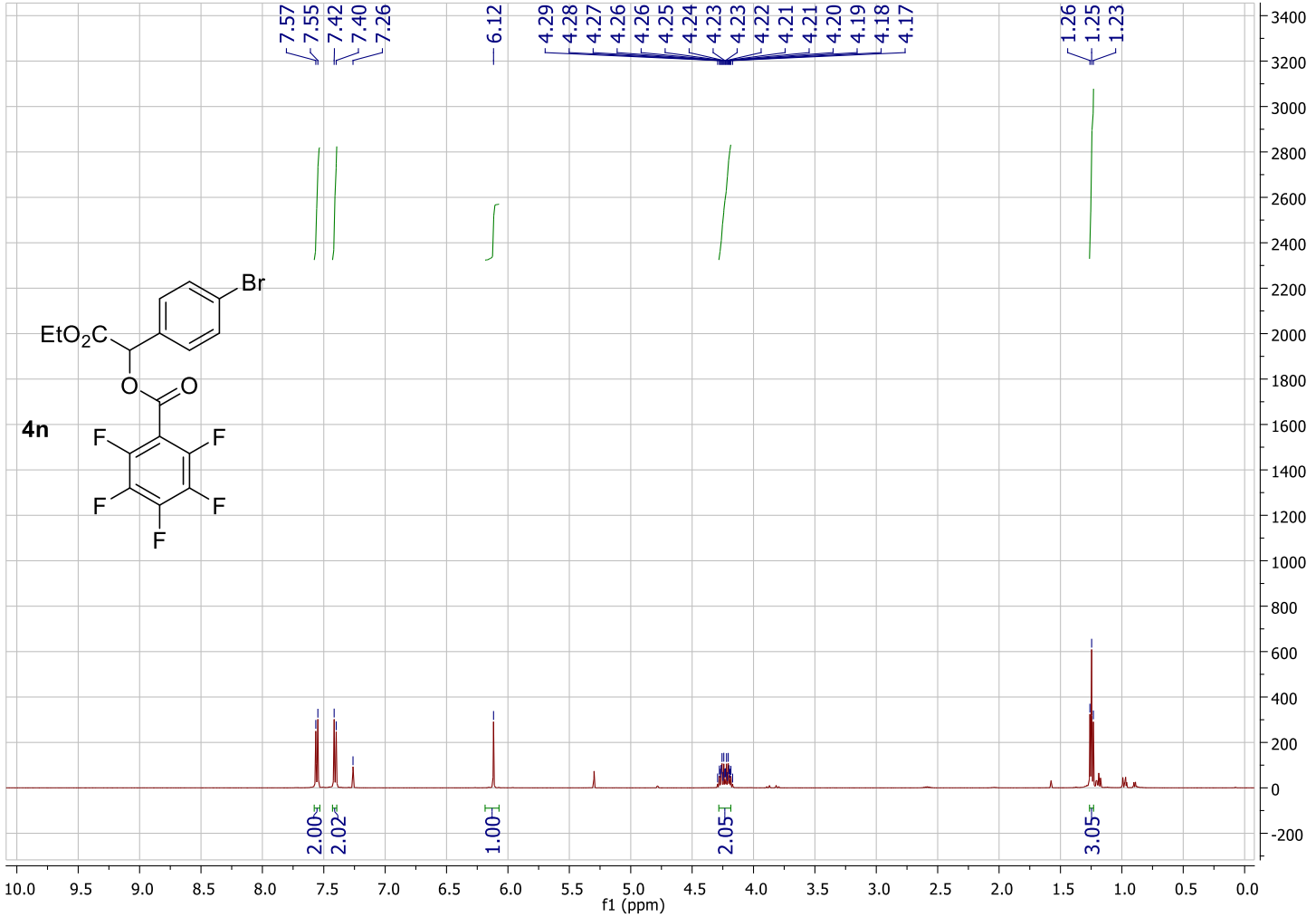
500MHz, $CDCl_3$



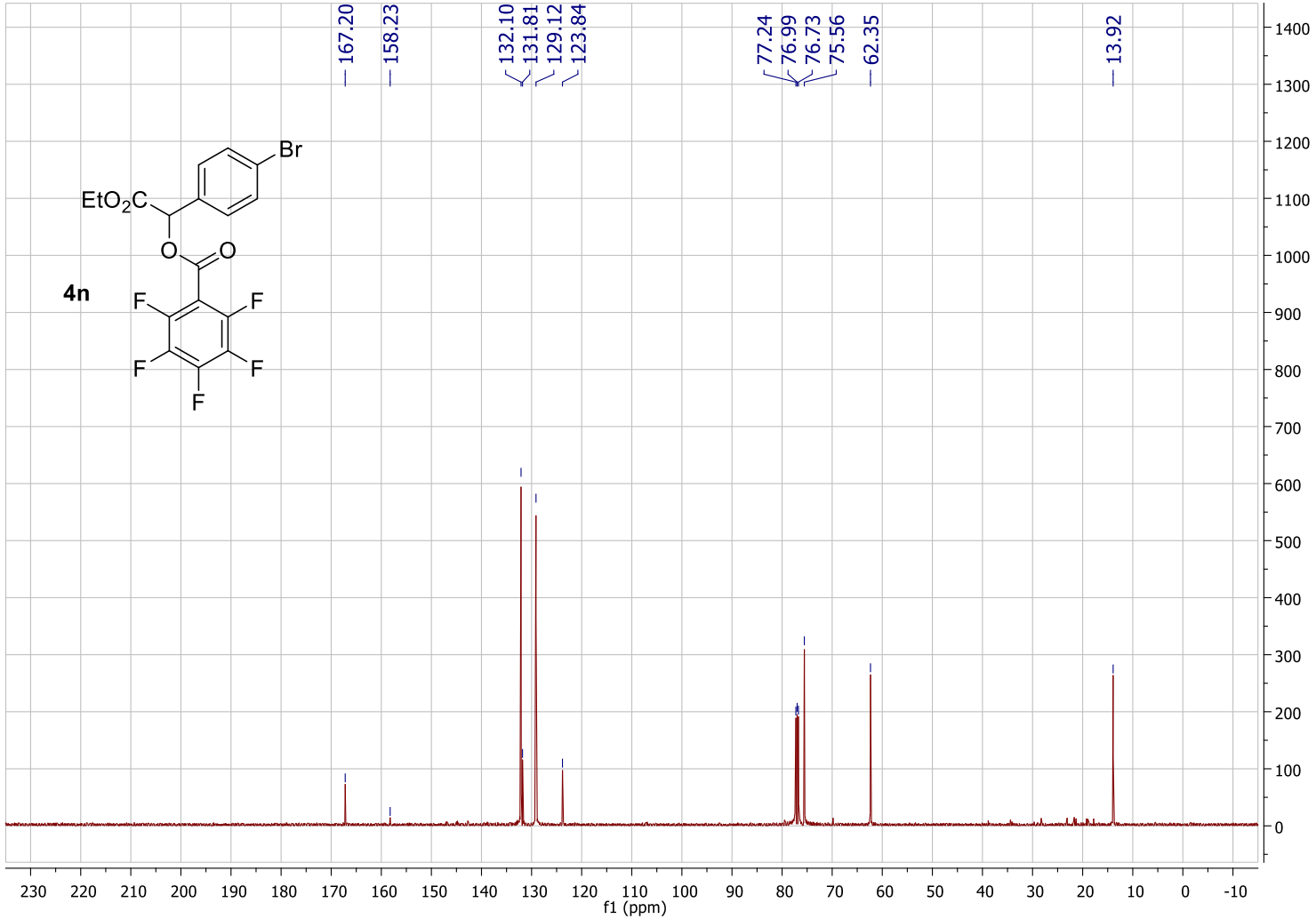
125MHz, $CDCl_3$



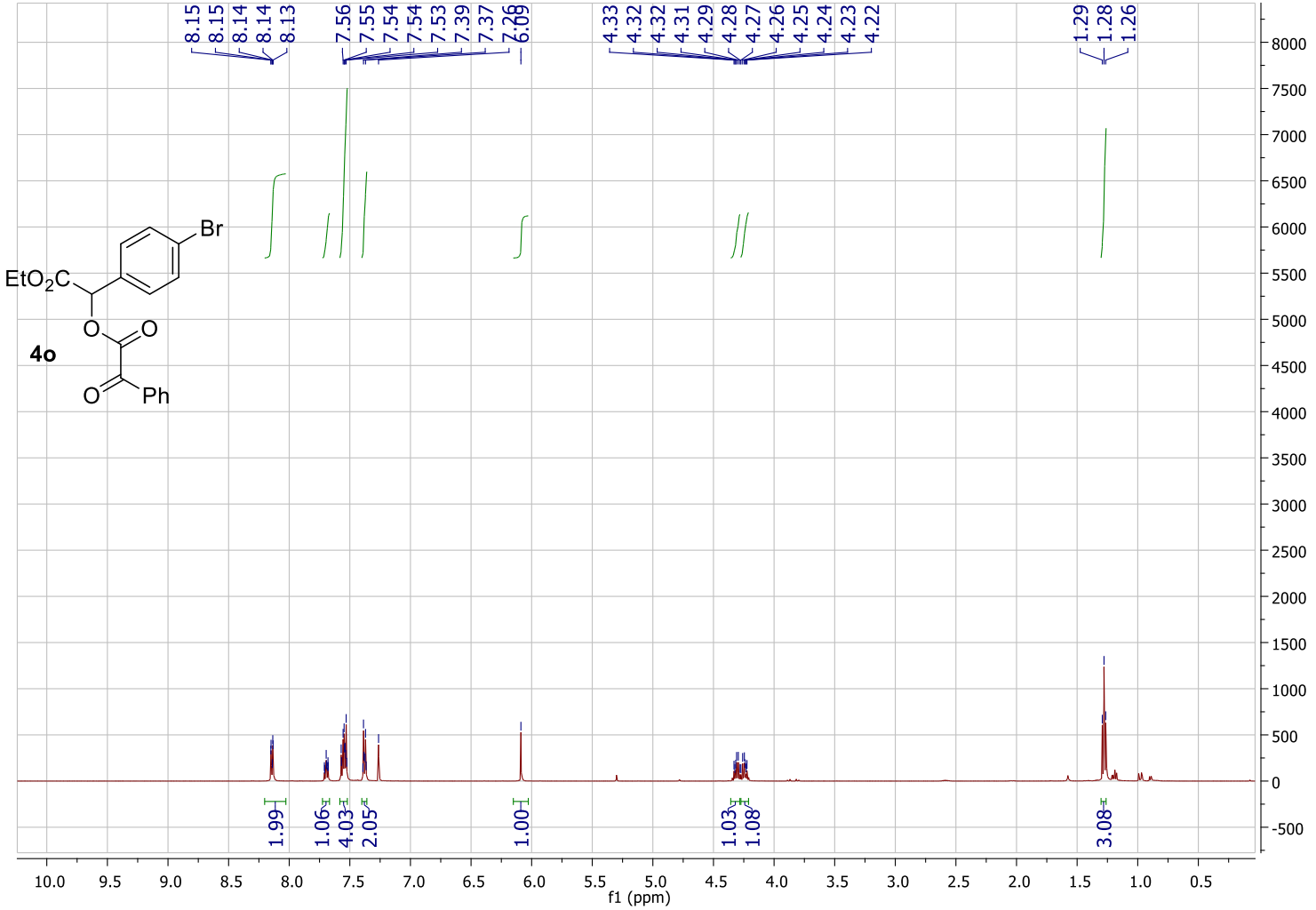
500MHz, $CDCl_3$



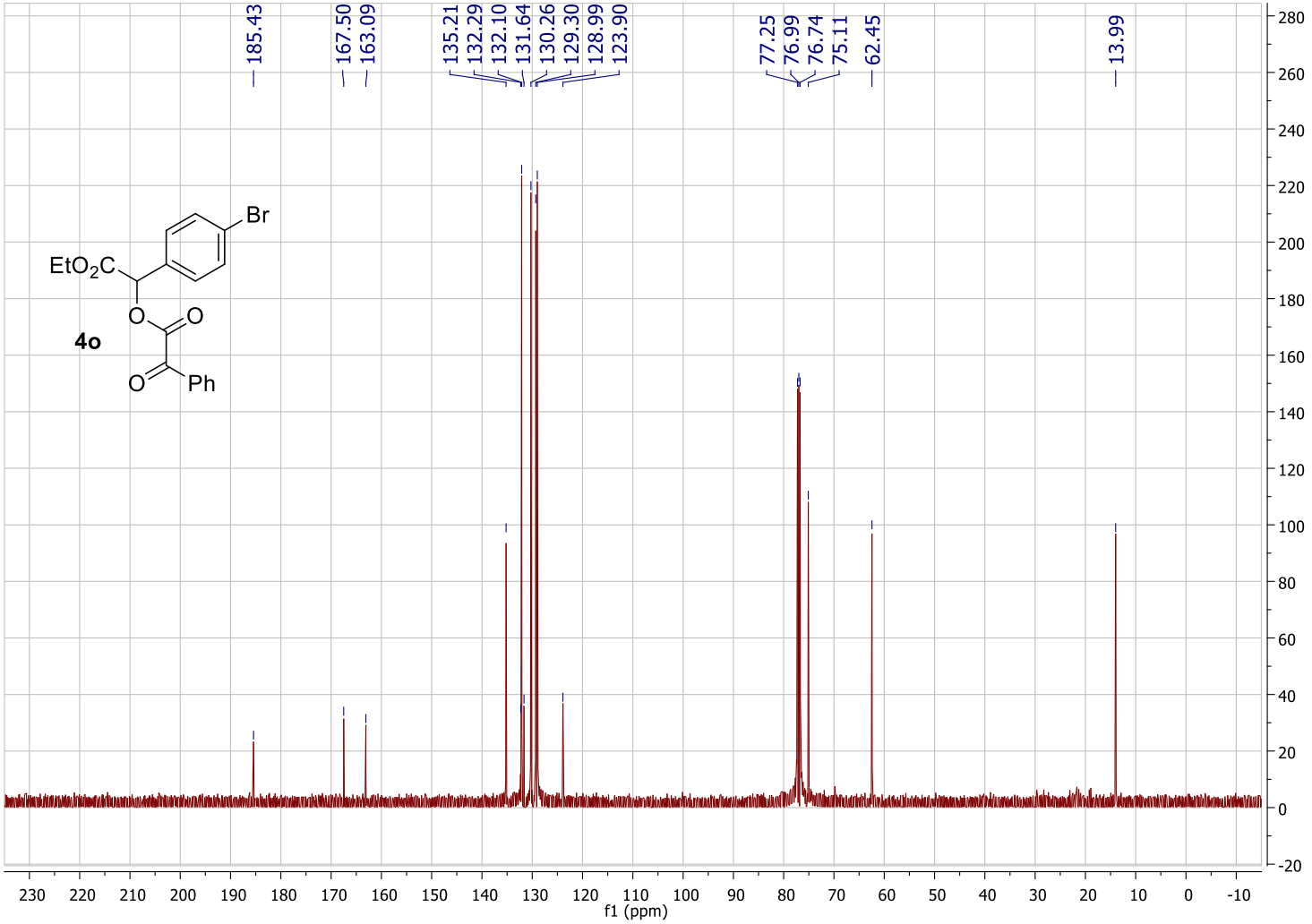
125MHz, $CDCl_3$



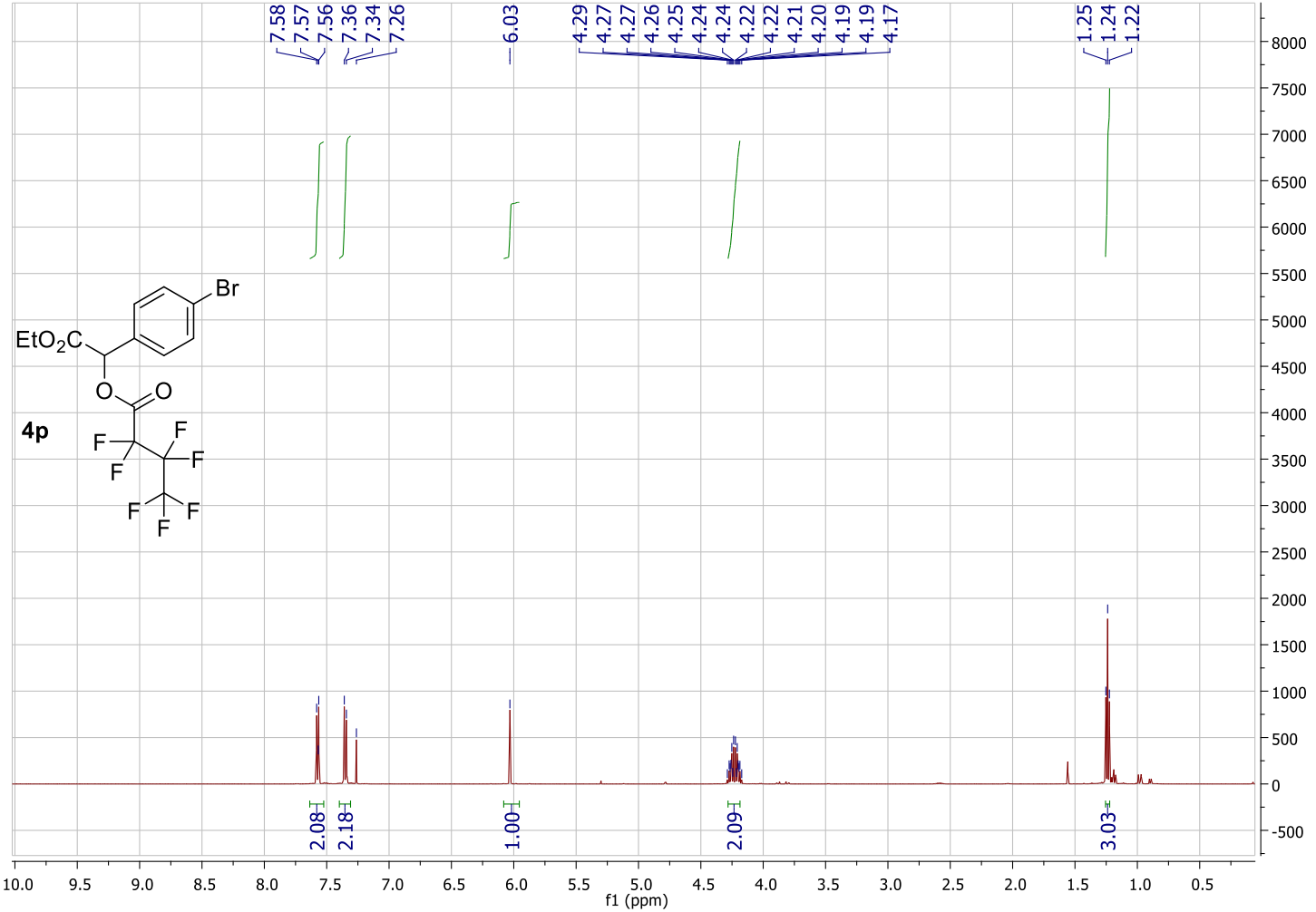
500MHz, $CDCl_3$



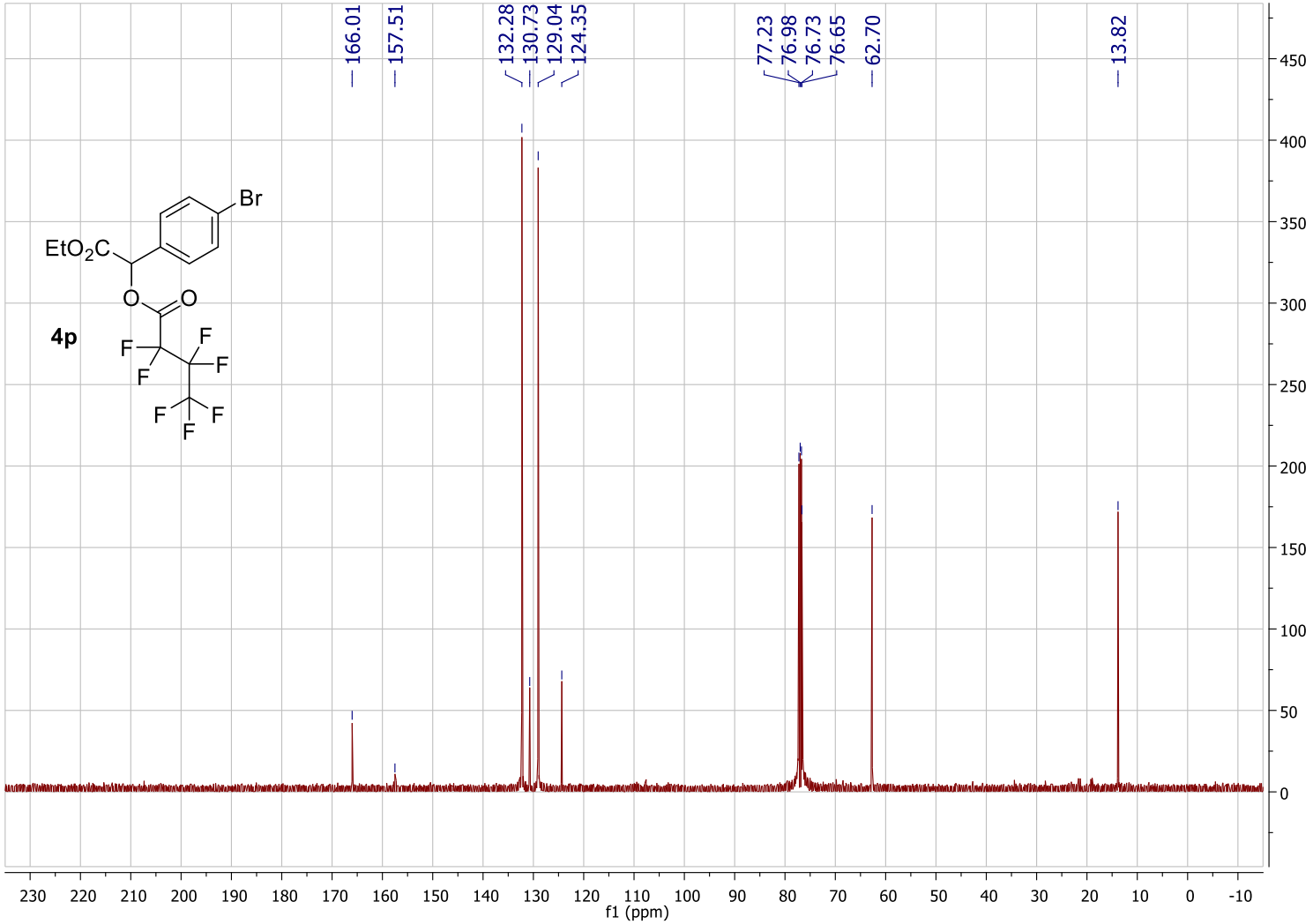
125MHz, $CDCl_3$



500MHz, $CDCl_3$

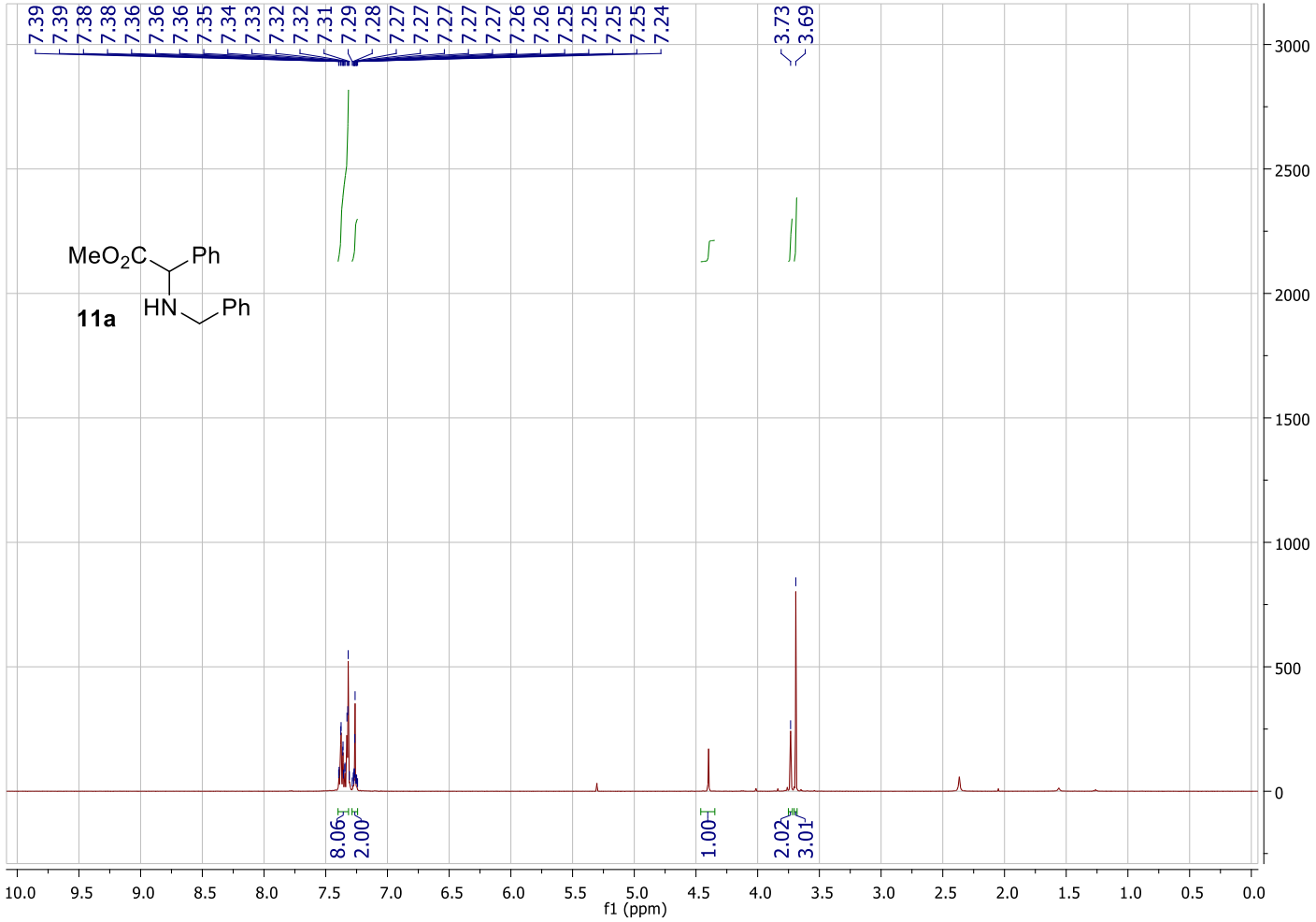


125MHz, $CDCl_3$

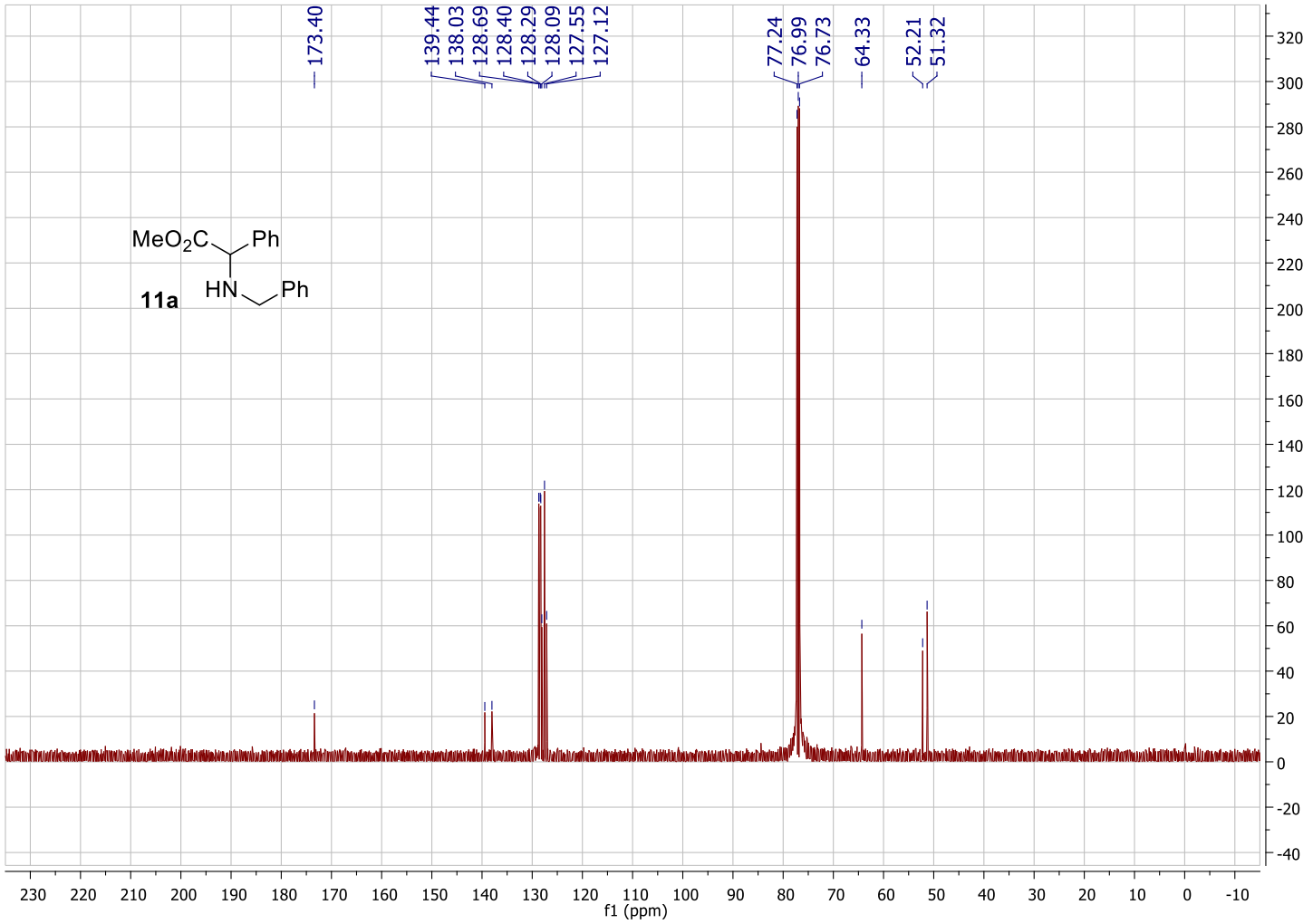


4.5 Products Derived from N-H Insertion of Amines

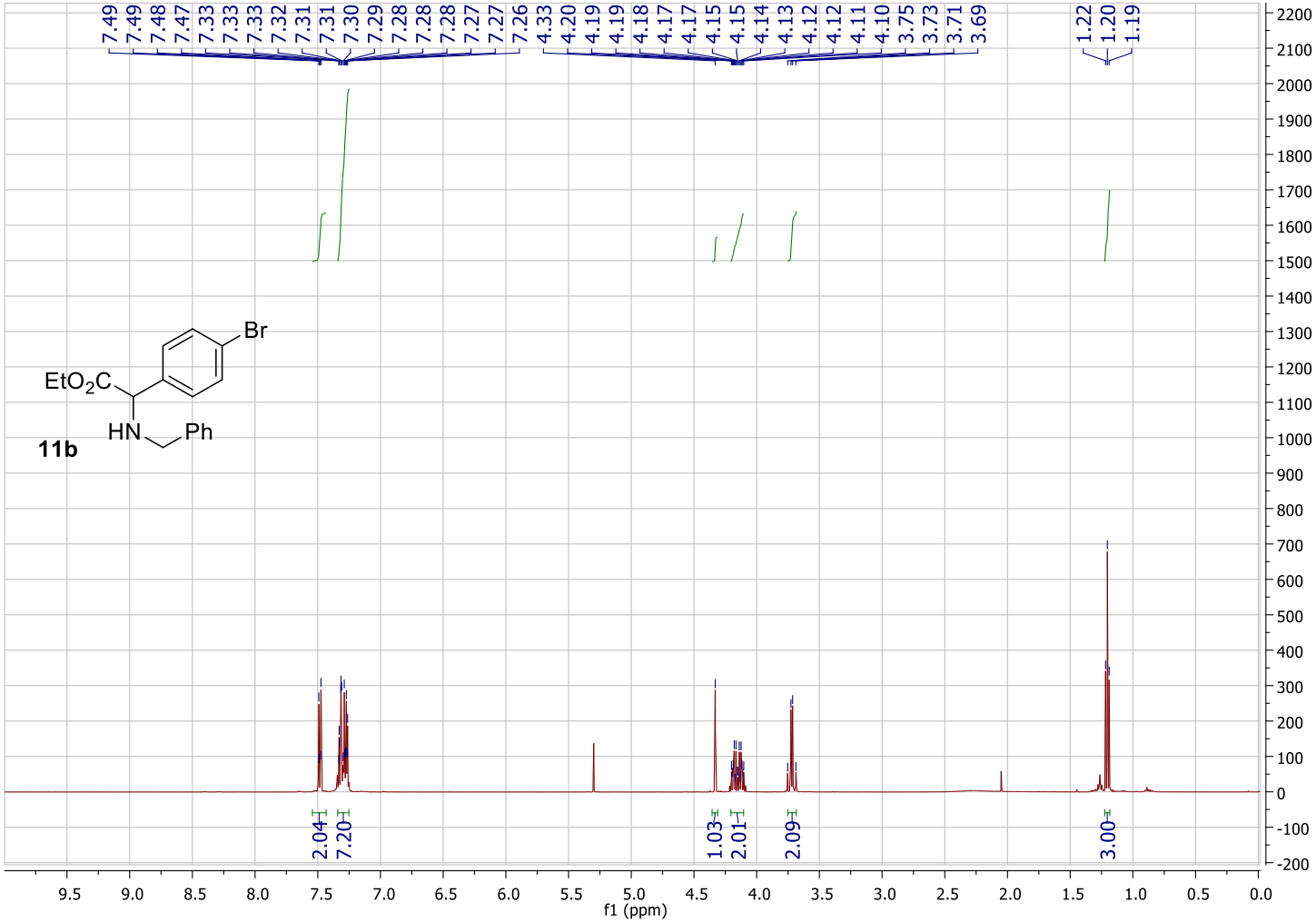
500MHz, $CDCl_3$



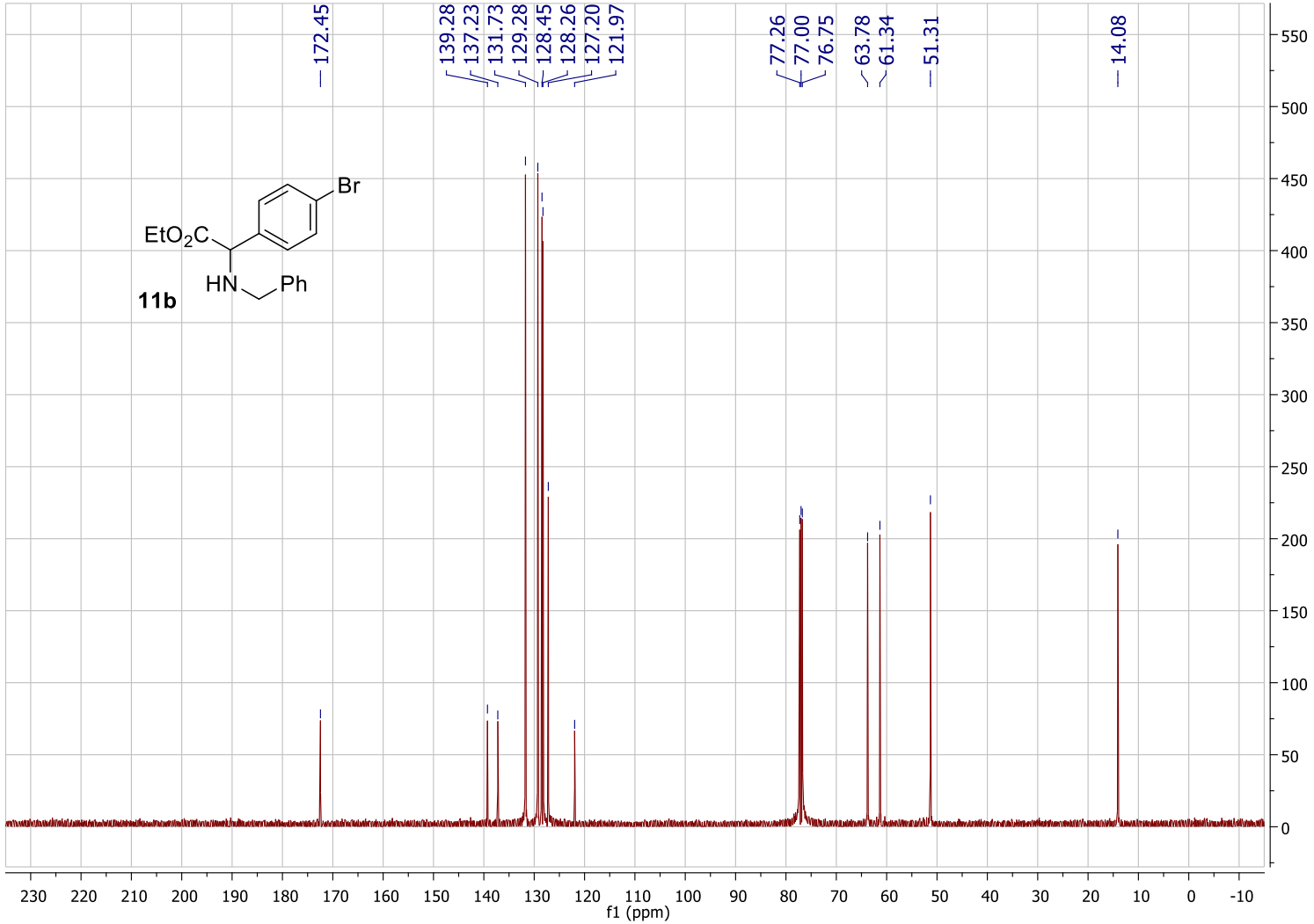
125MHz, $CDCl_3$



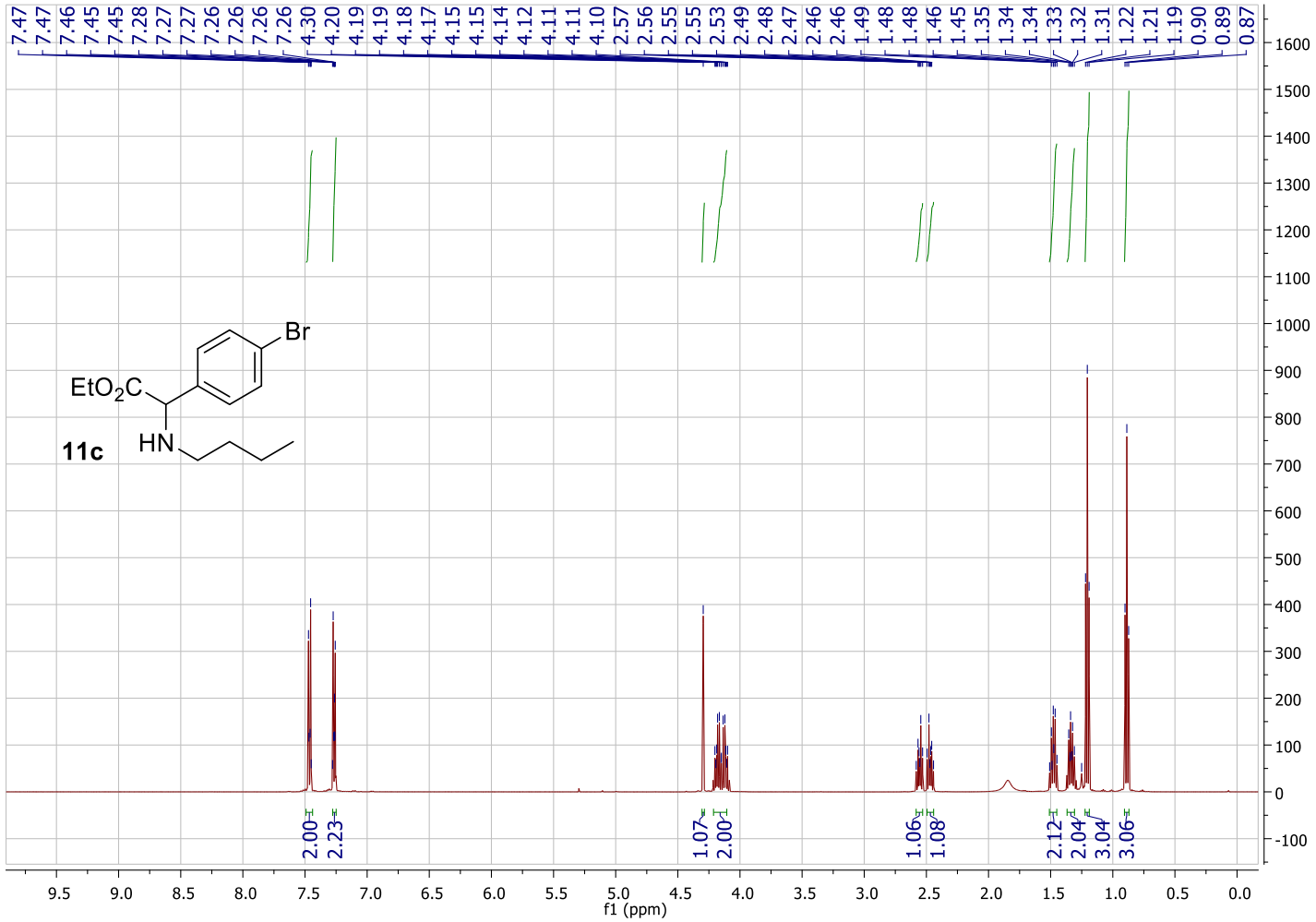
500MHz, $CDCl_3$



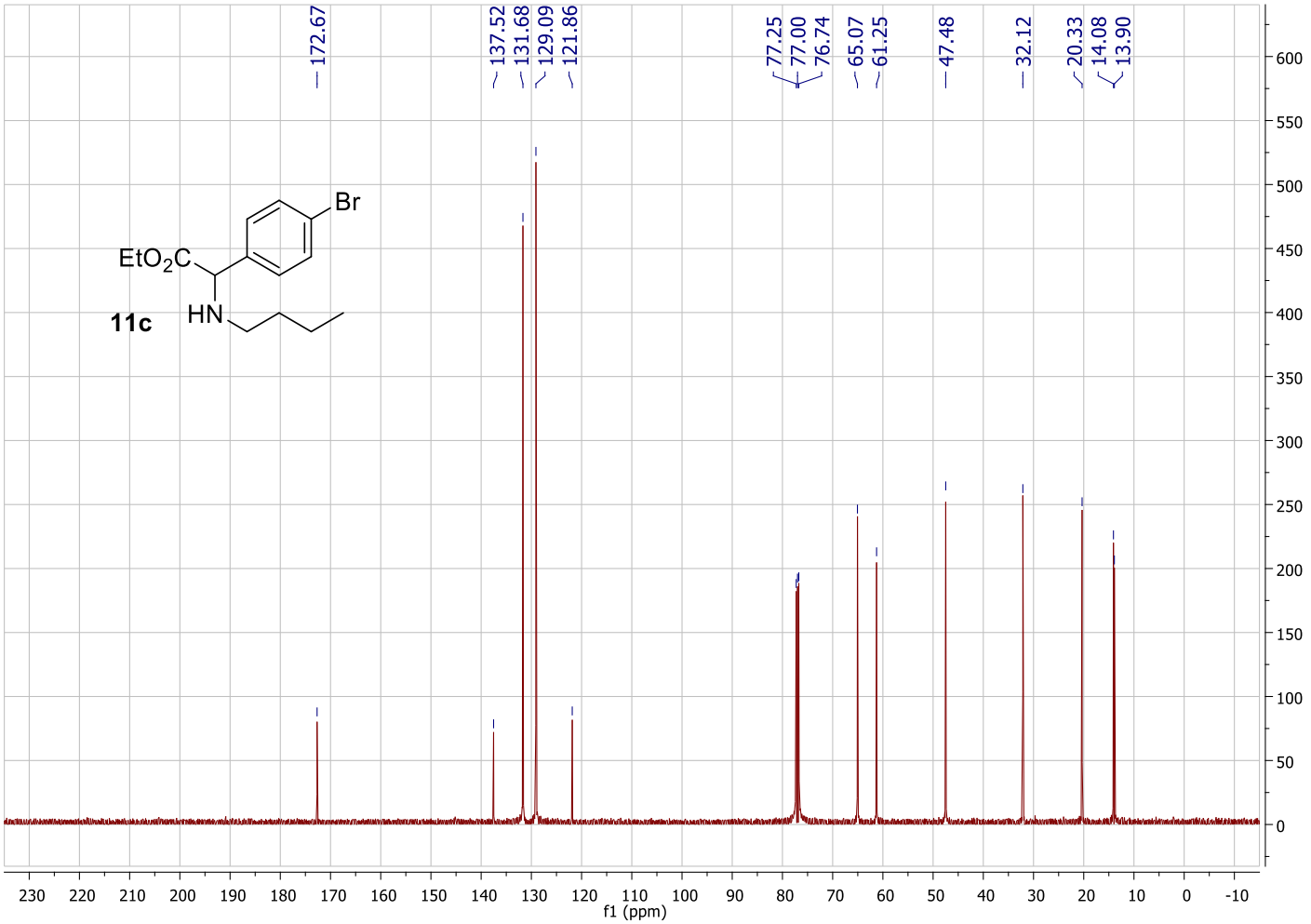
125MHz, $CDCl_3$



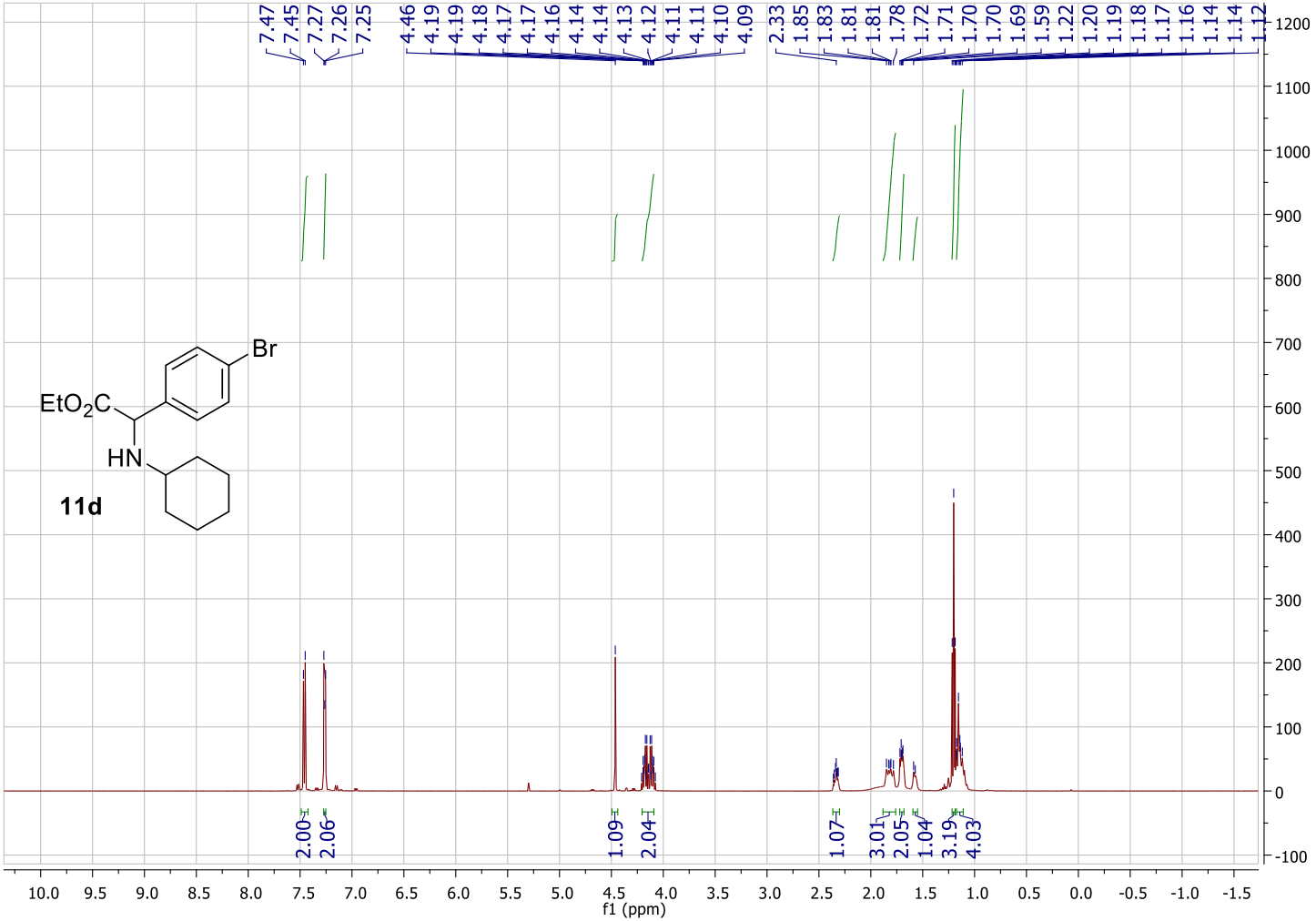
500MHz, $CDCl_3$



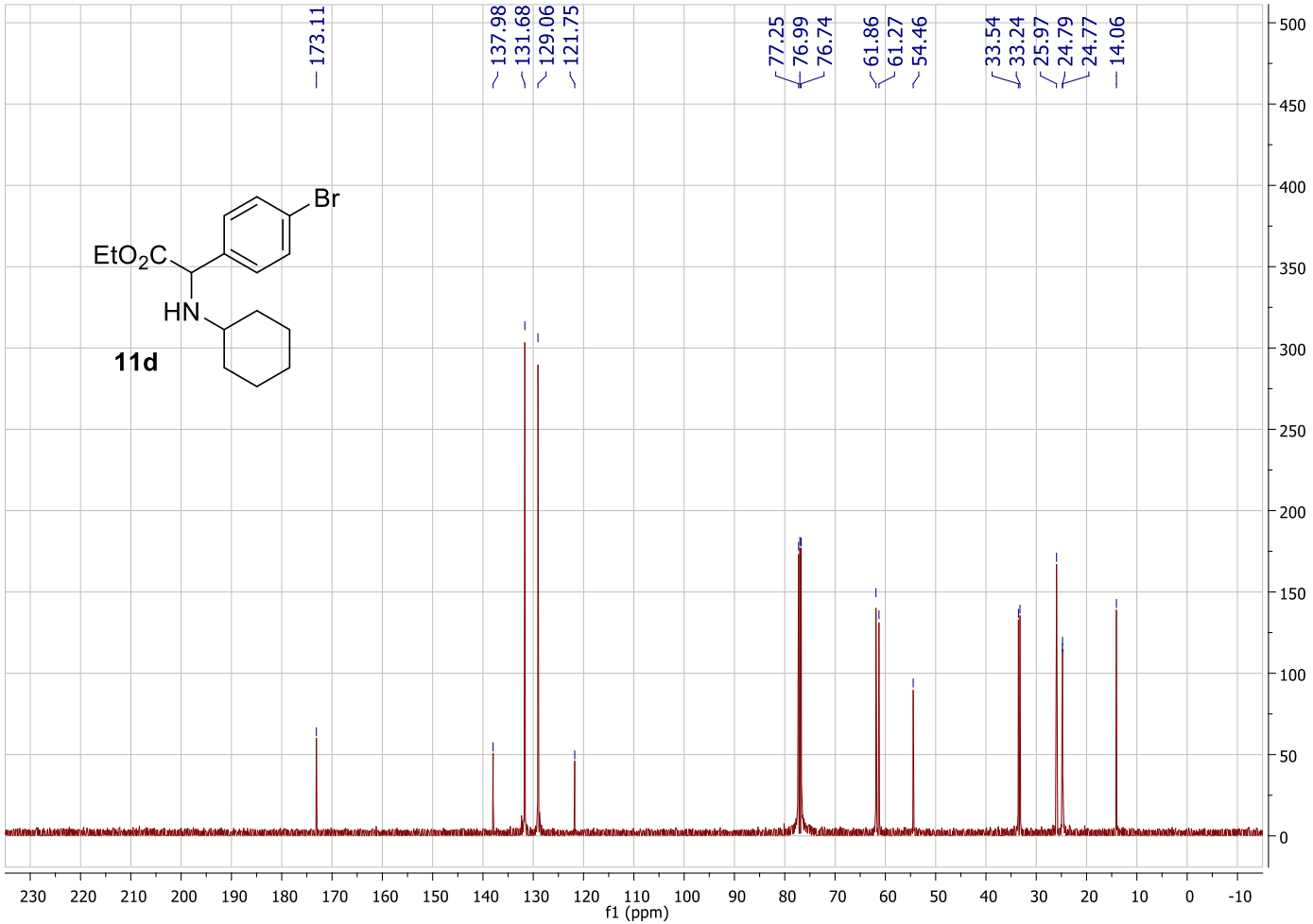
125MHz, $CDCl_3$



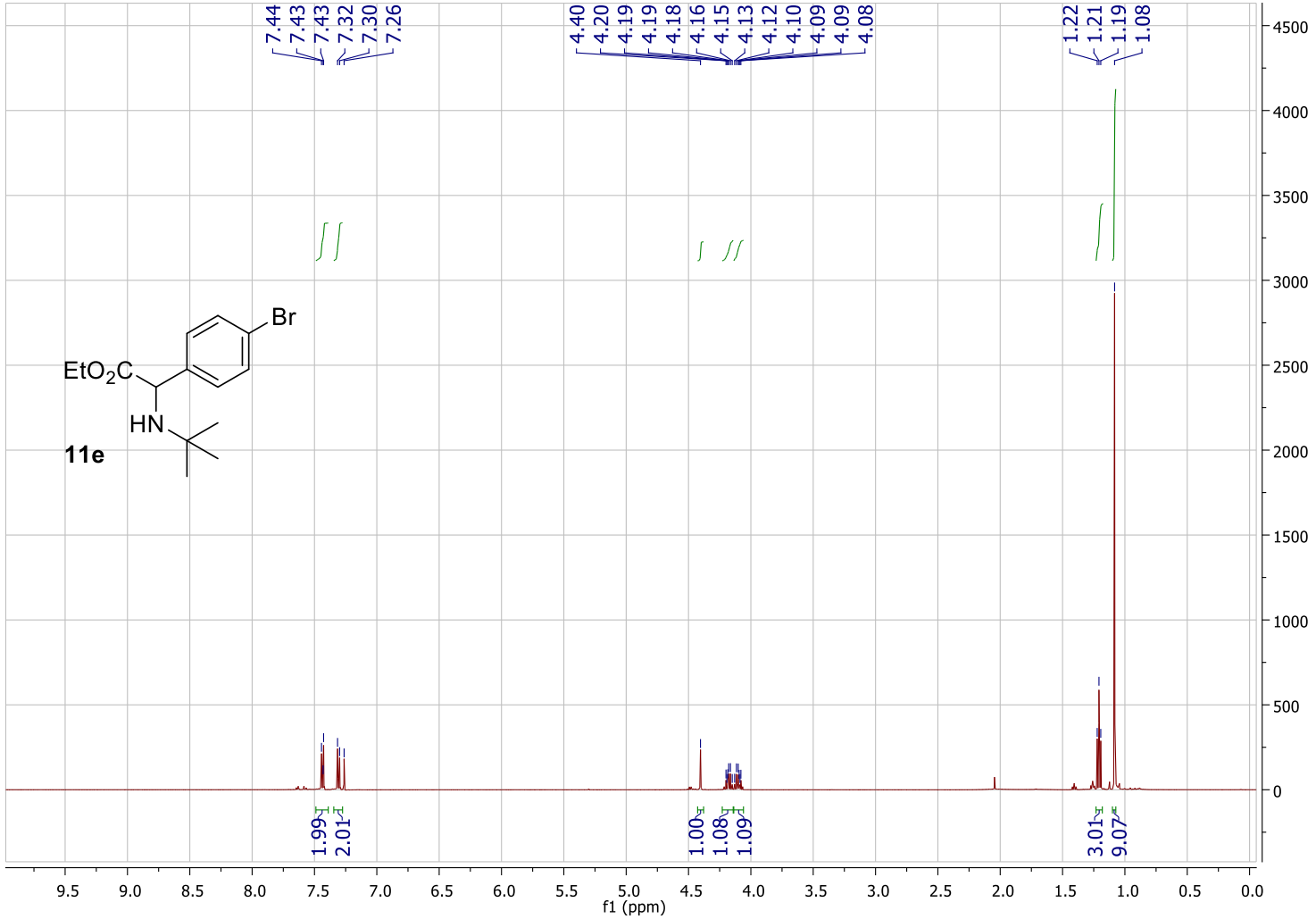
500MHz, $CDCl_3$



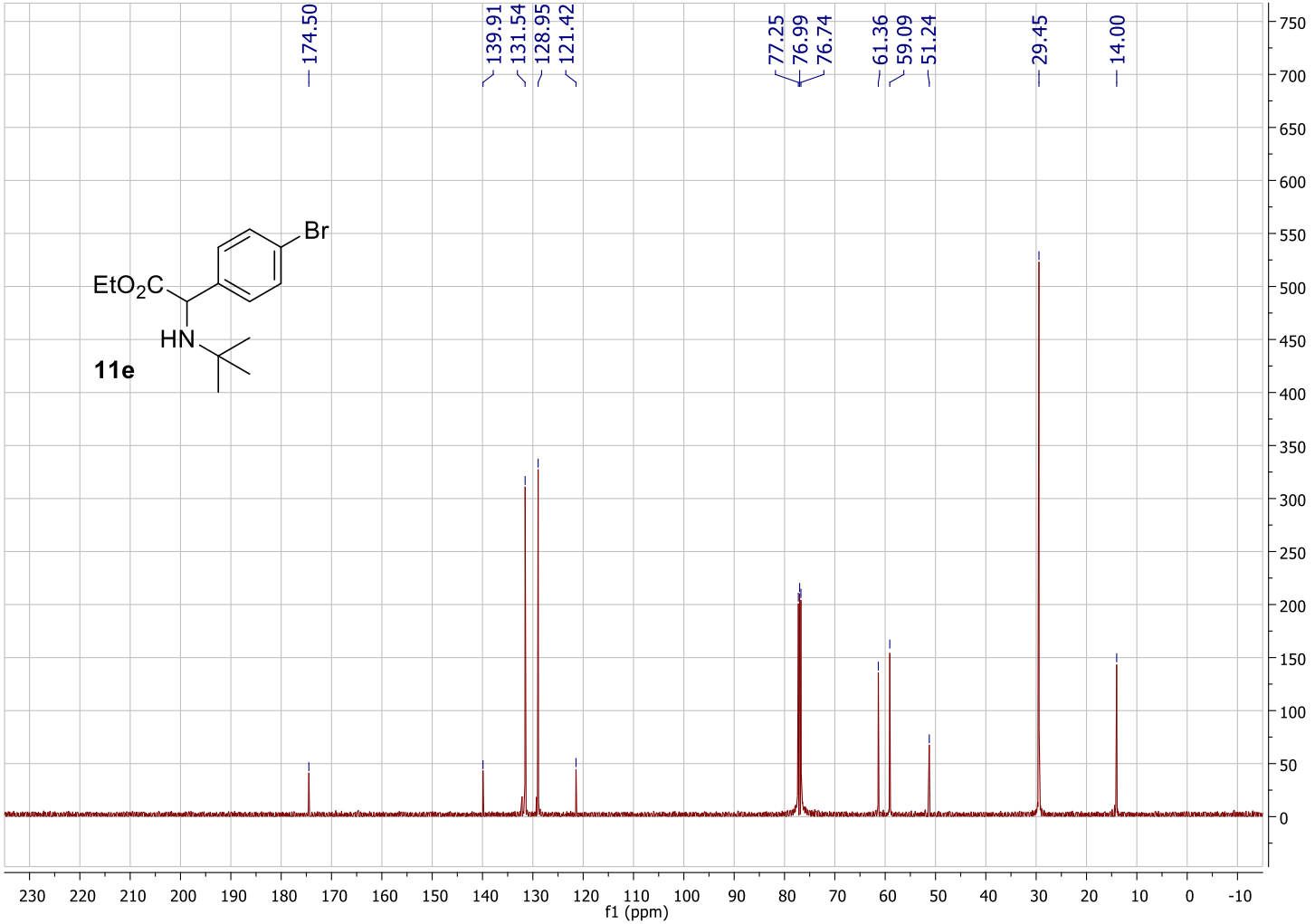
125MHz, $CDCl_3$



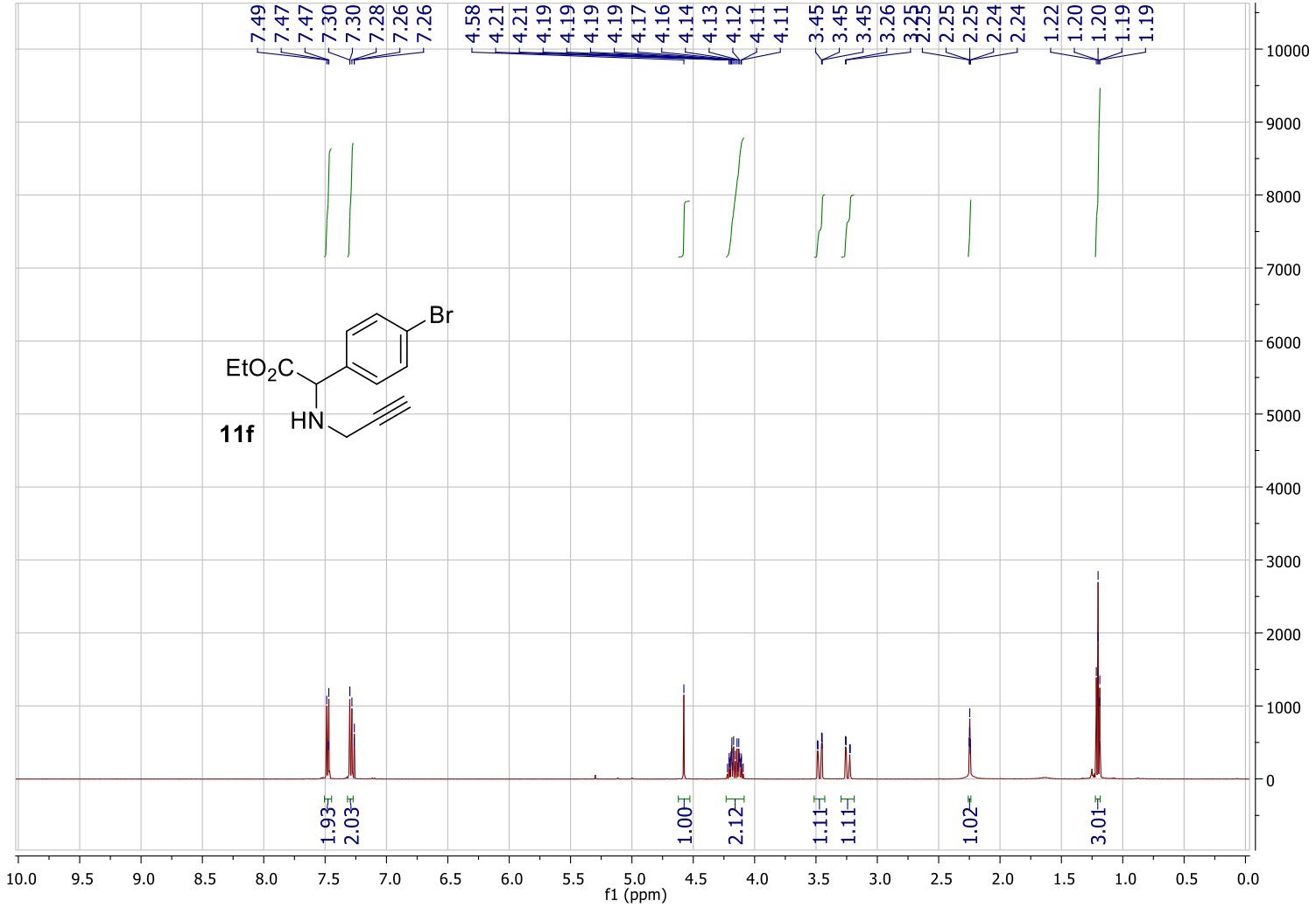
500MHz, $CDCl_3$



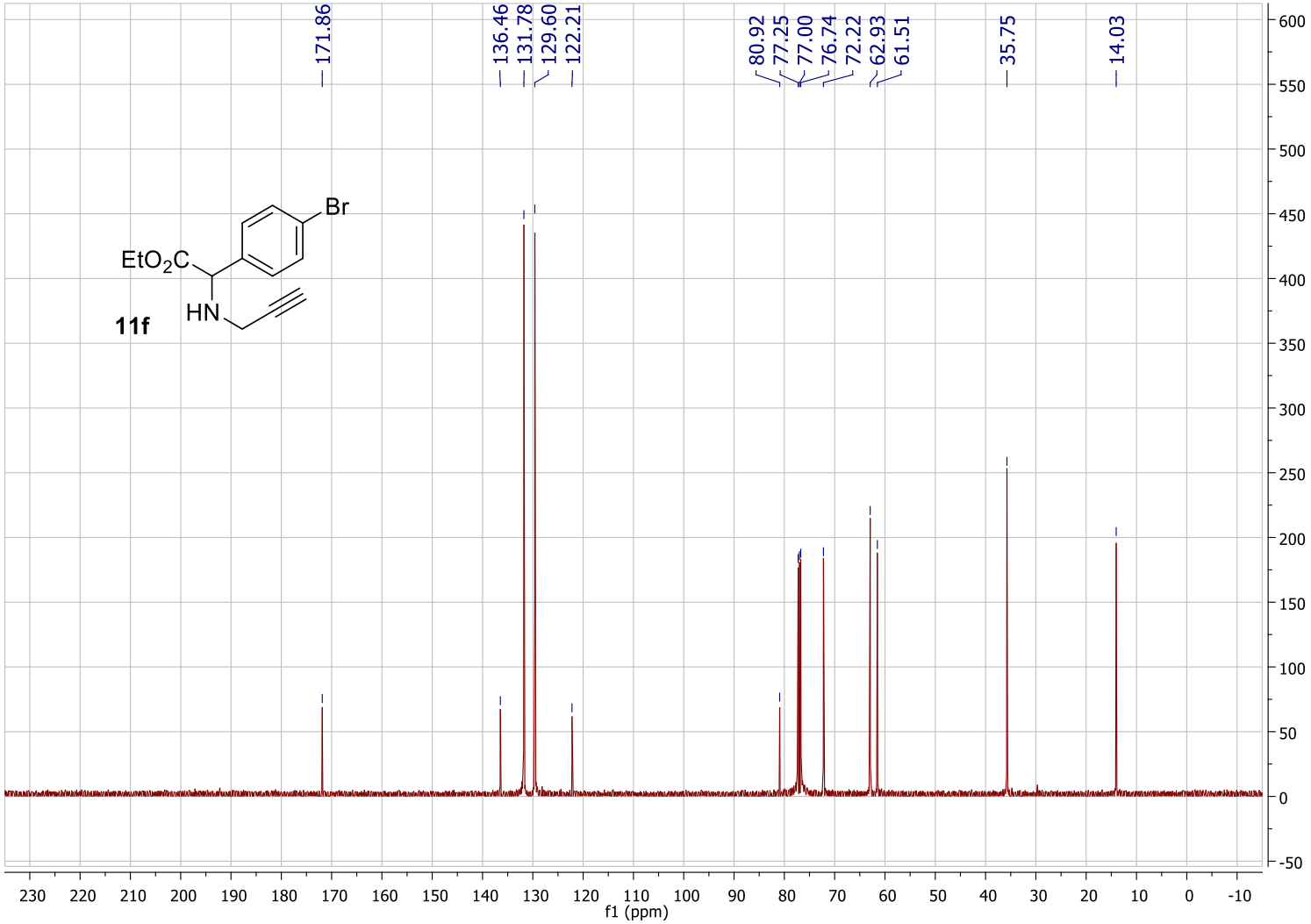
125MHz, $CDCl_3$



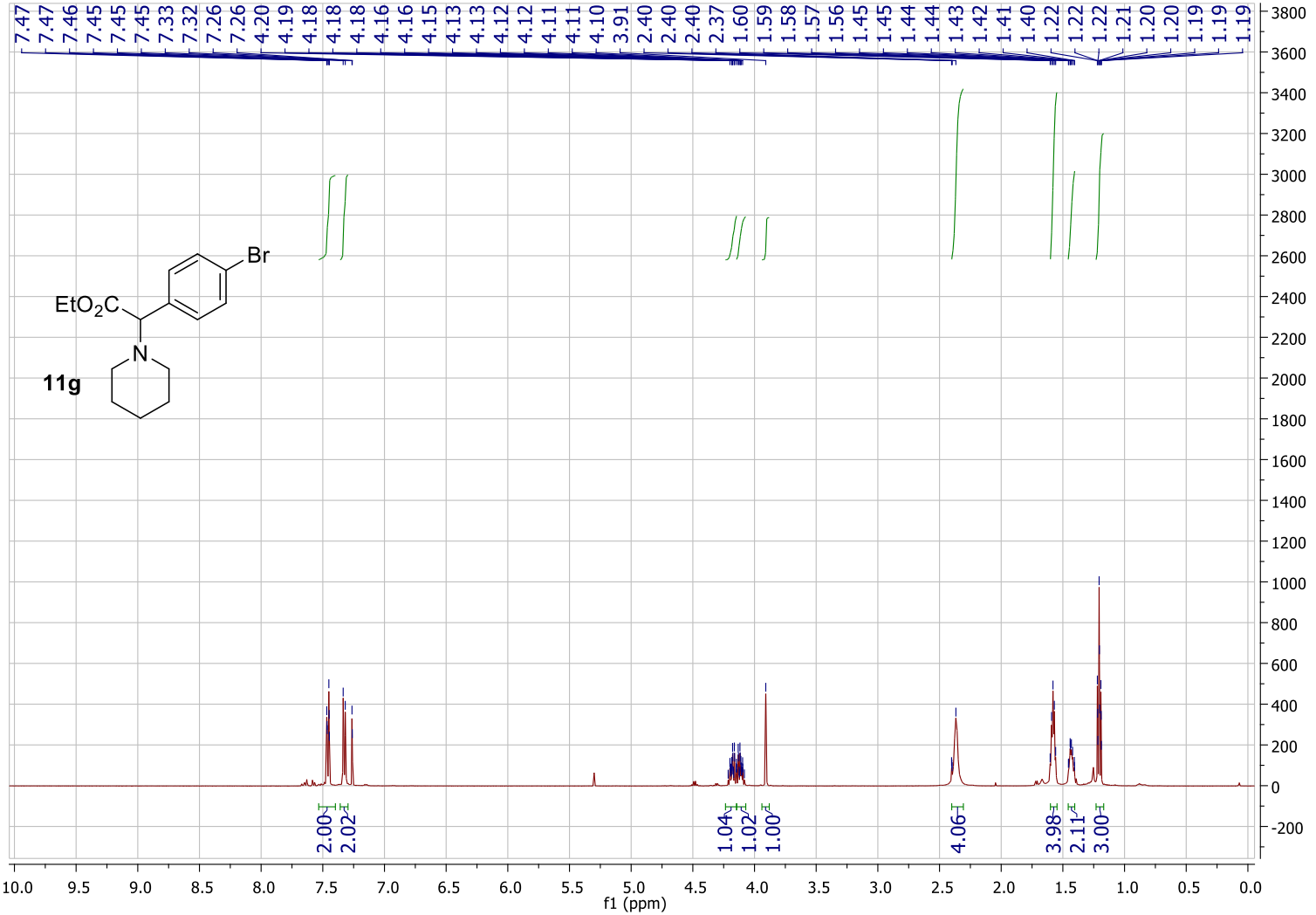
500MHz, $CDCl_3$



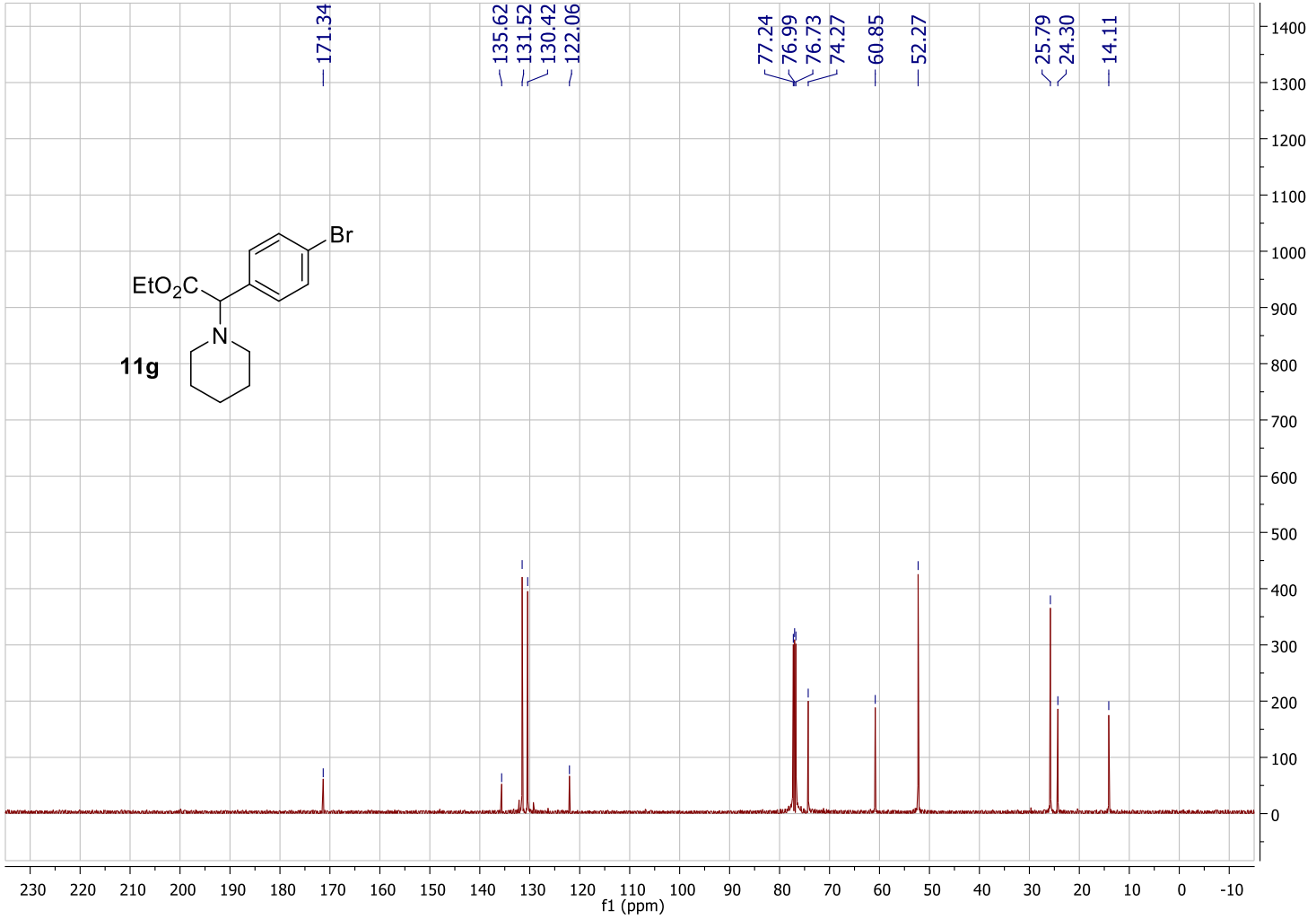
125MHz, $CDCl_3$



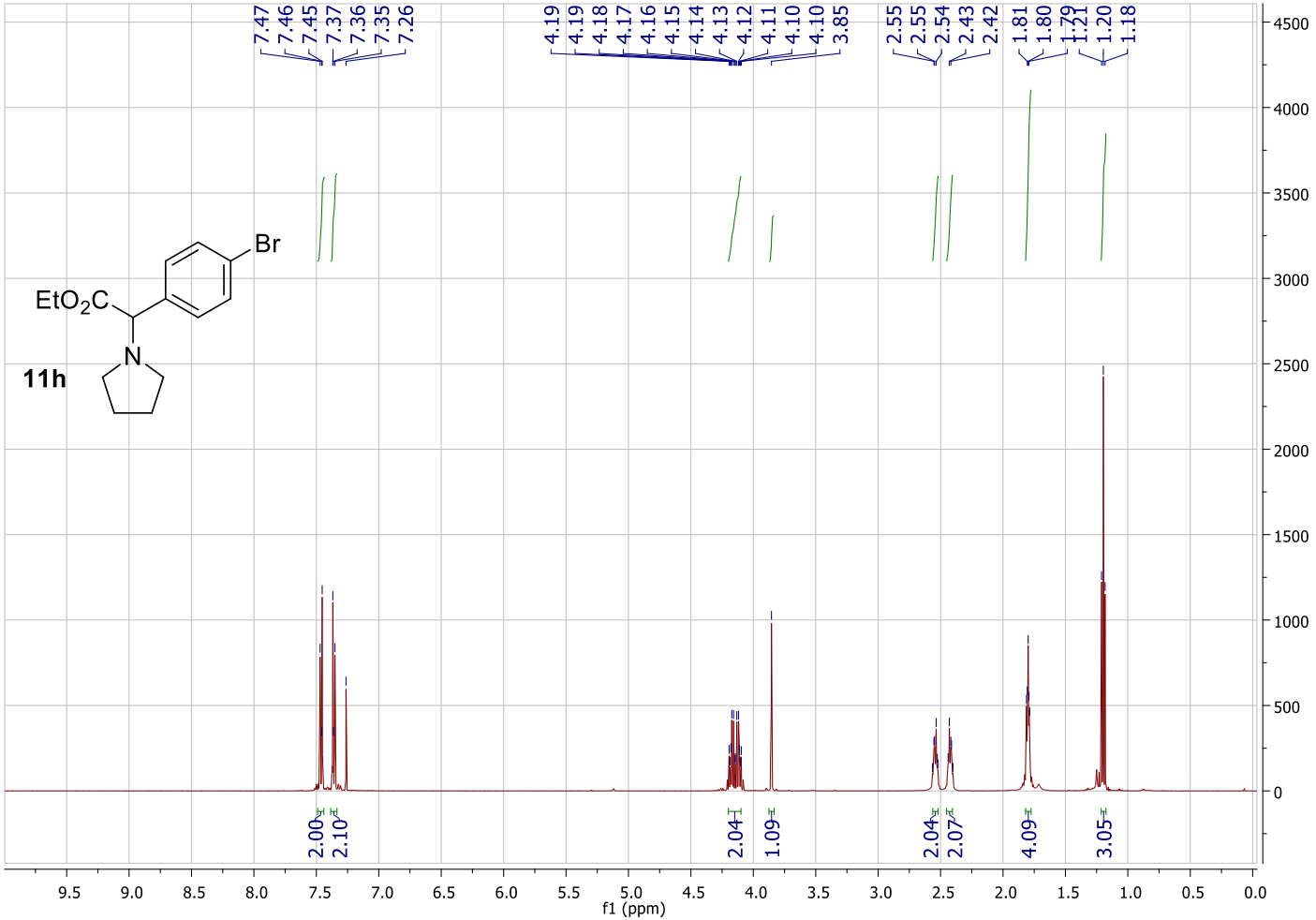
500MHz, $CDCl_3$



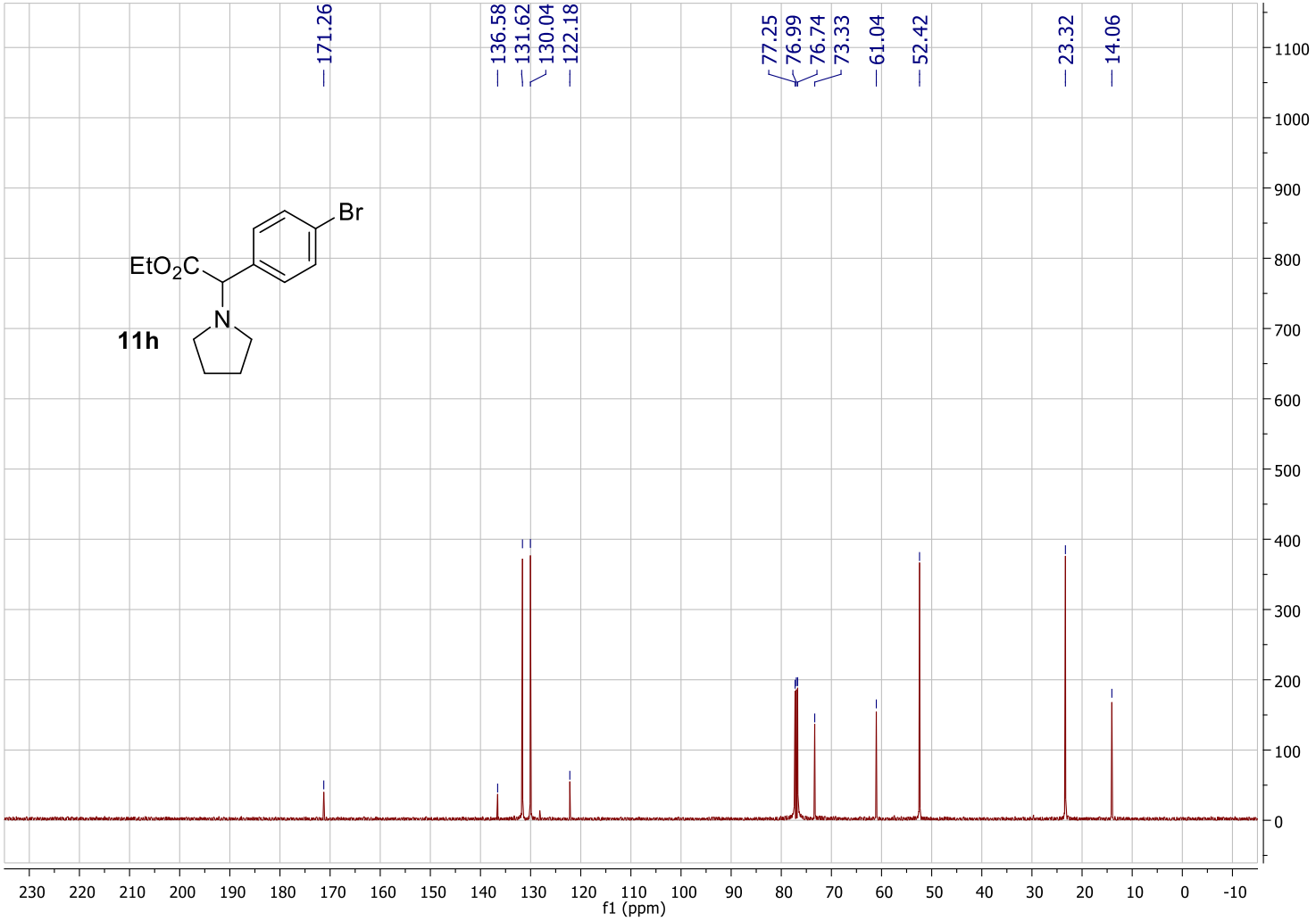
125MHz, $CDCl_3$



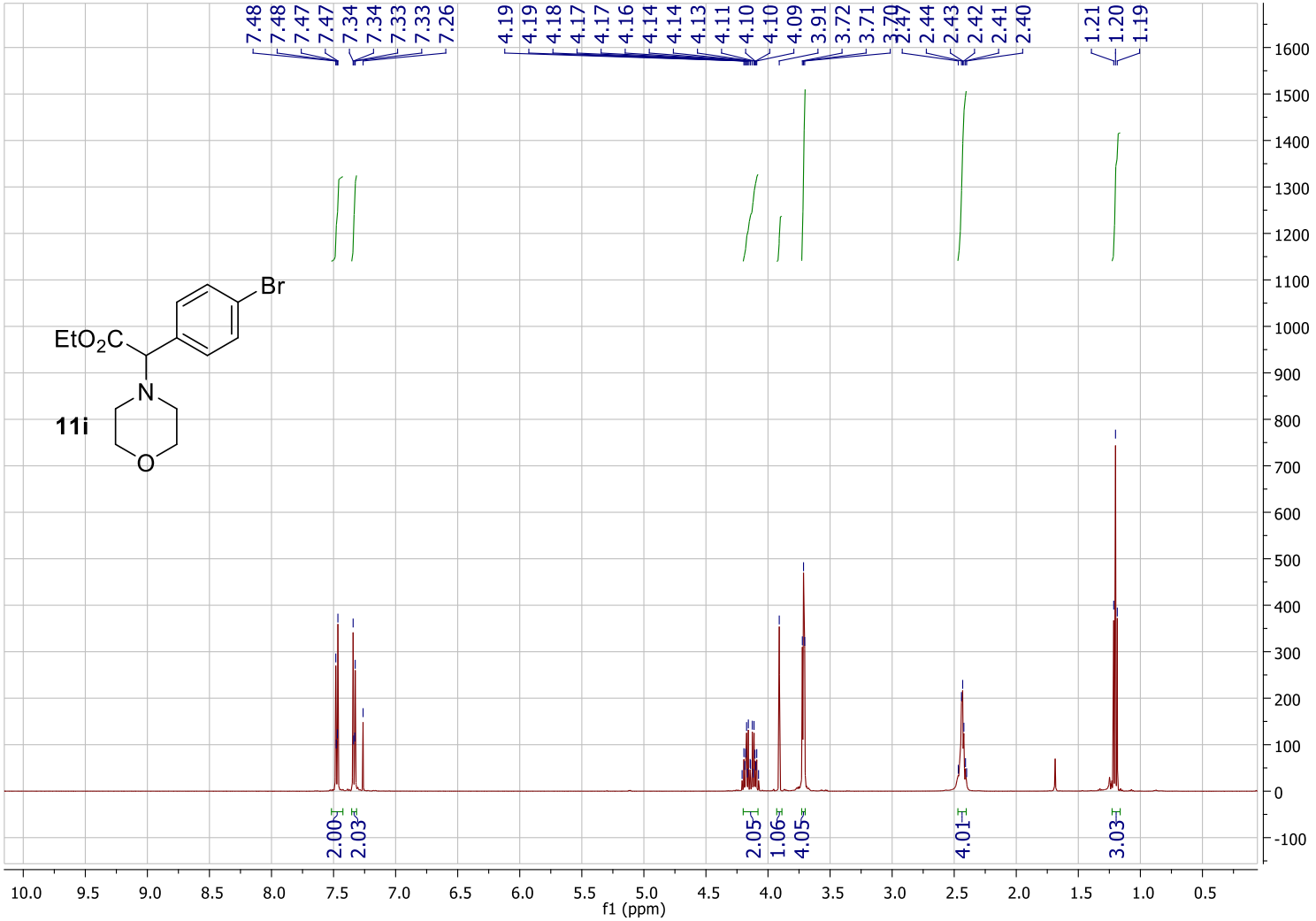
500MHz, $CDCl_3$



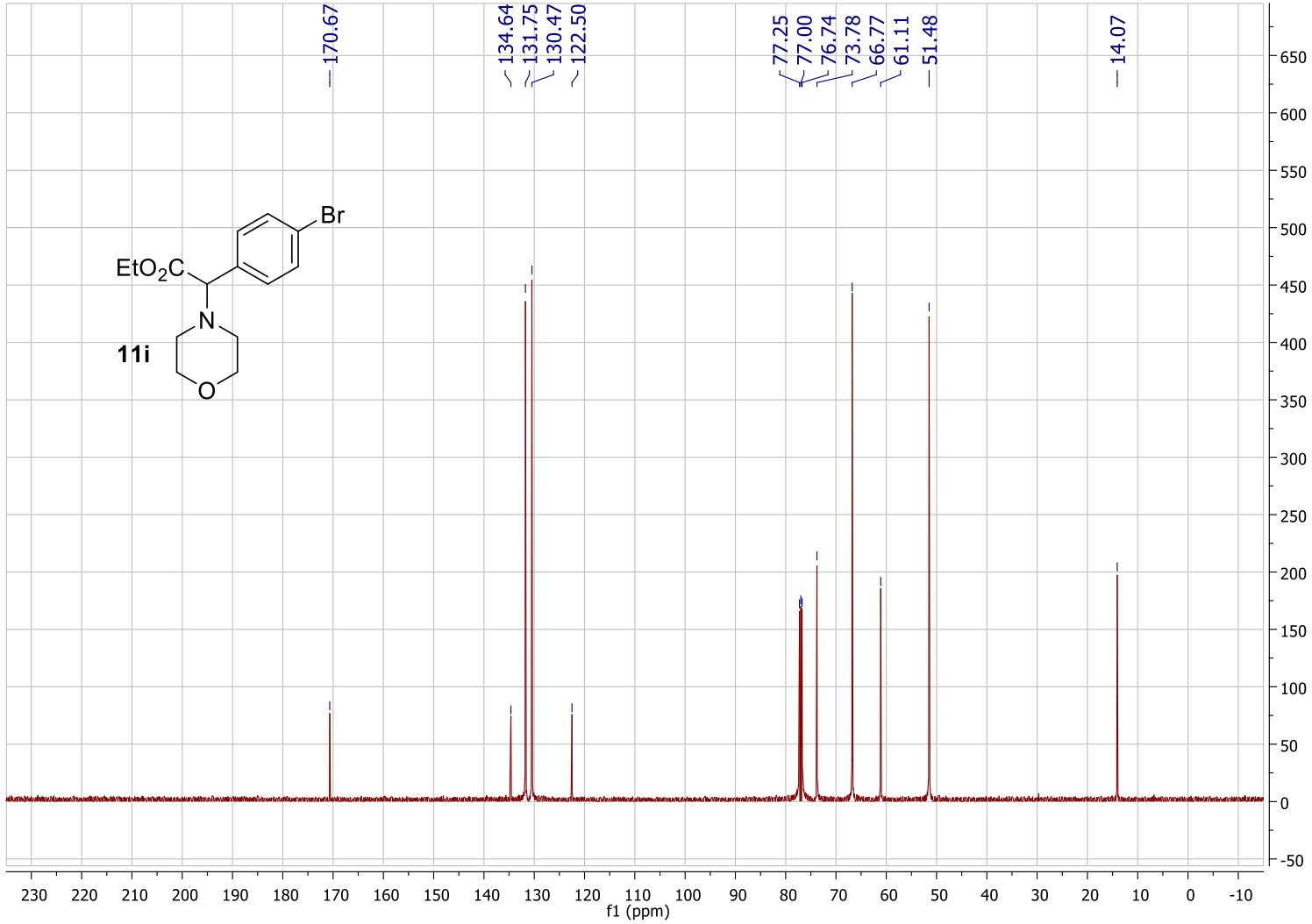
125MHz, $CDCl_3$



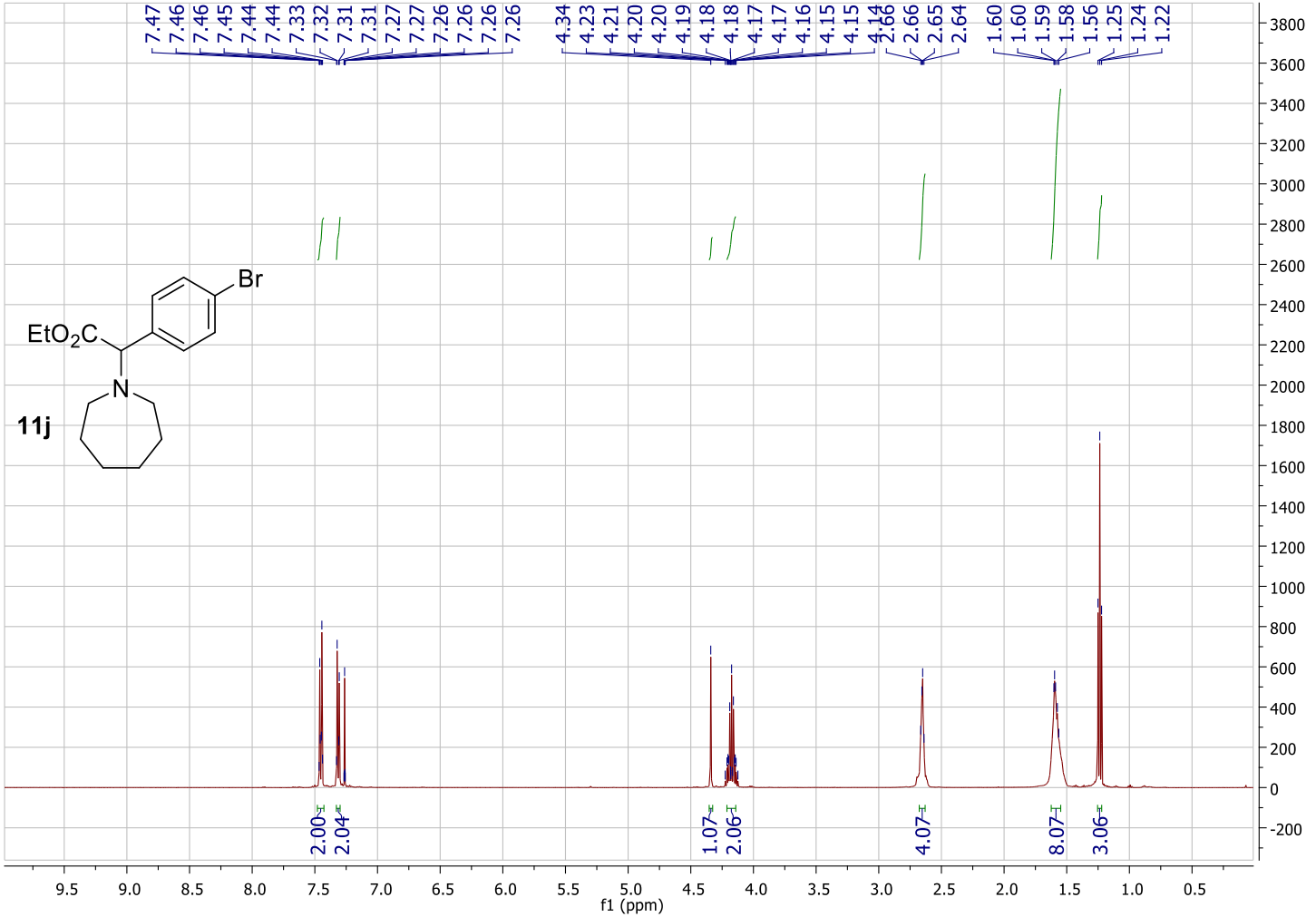
500MHz, $CDCl_3$



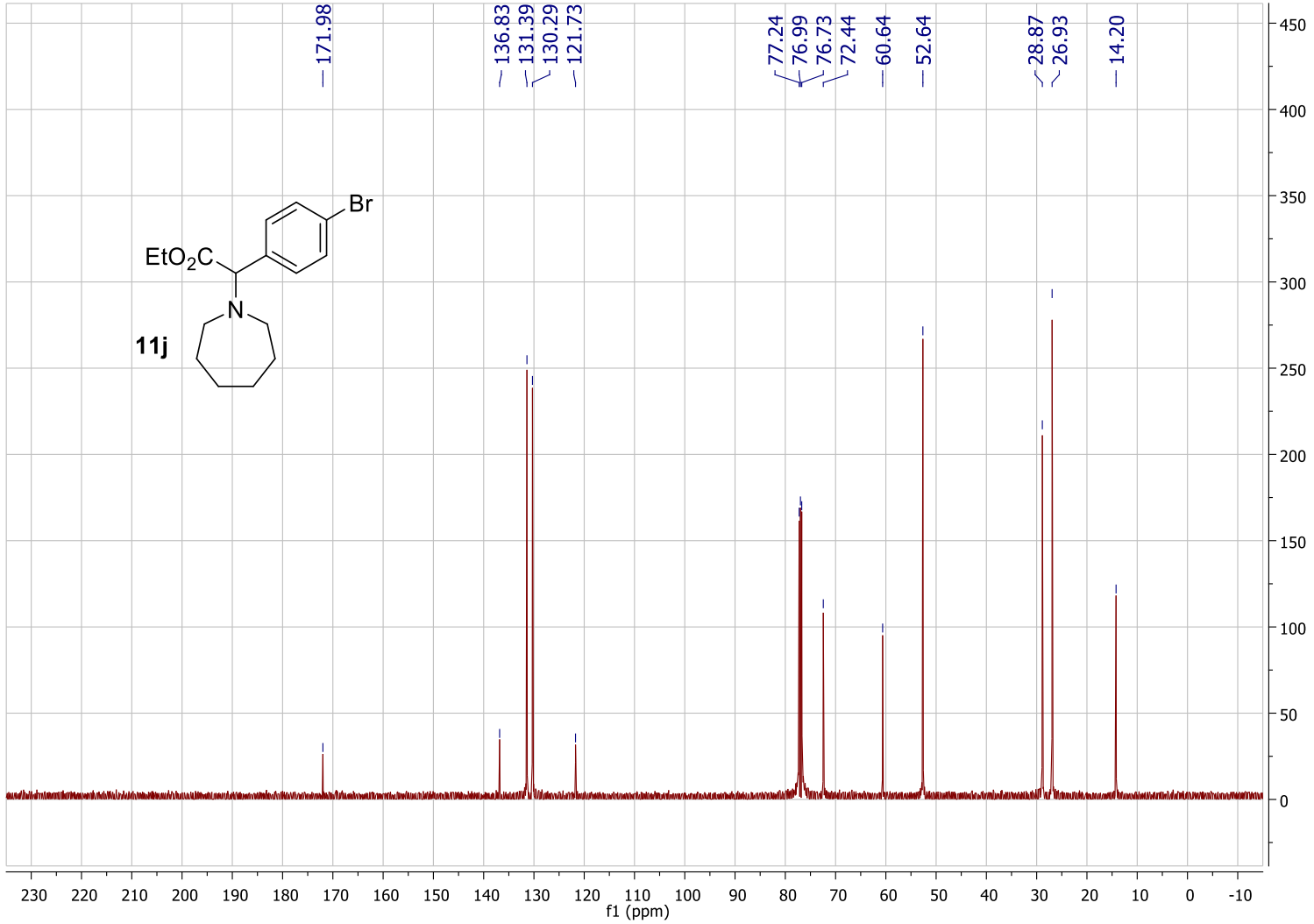
125MHz, $CDCl_3$



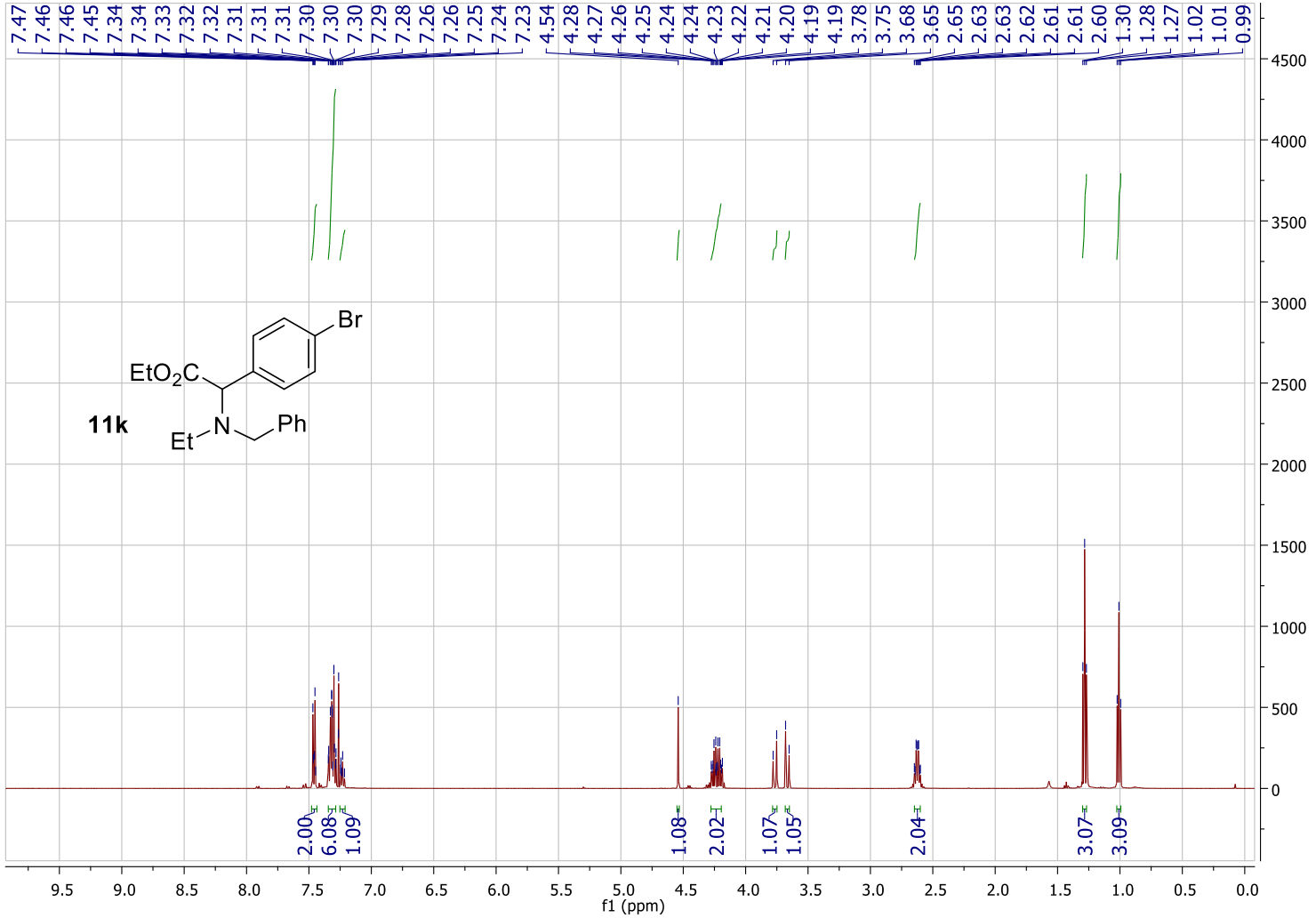
500MHz, $CDCl_3$



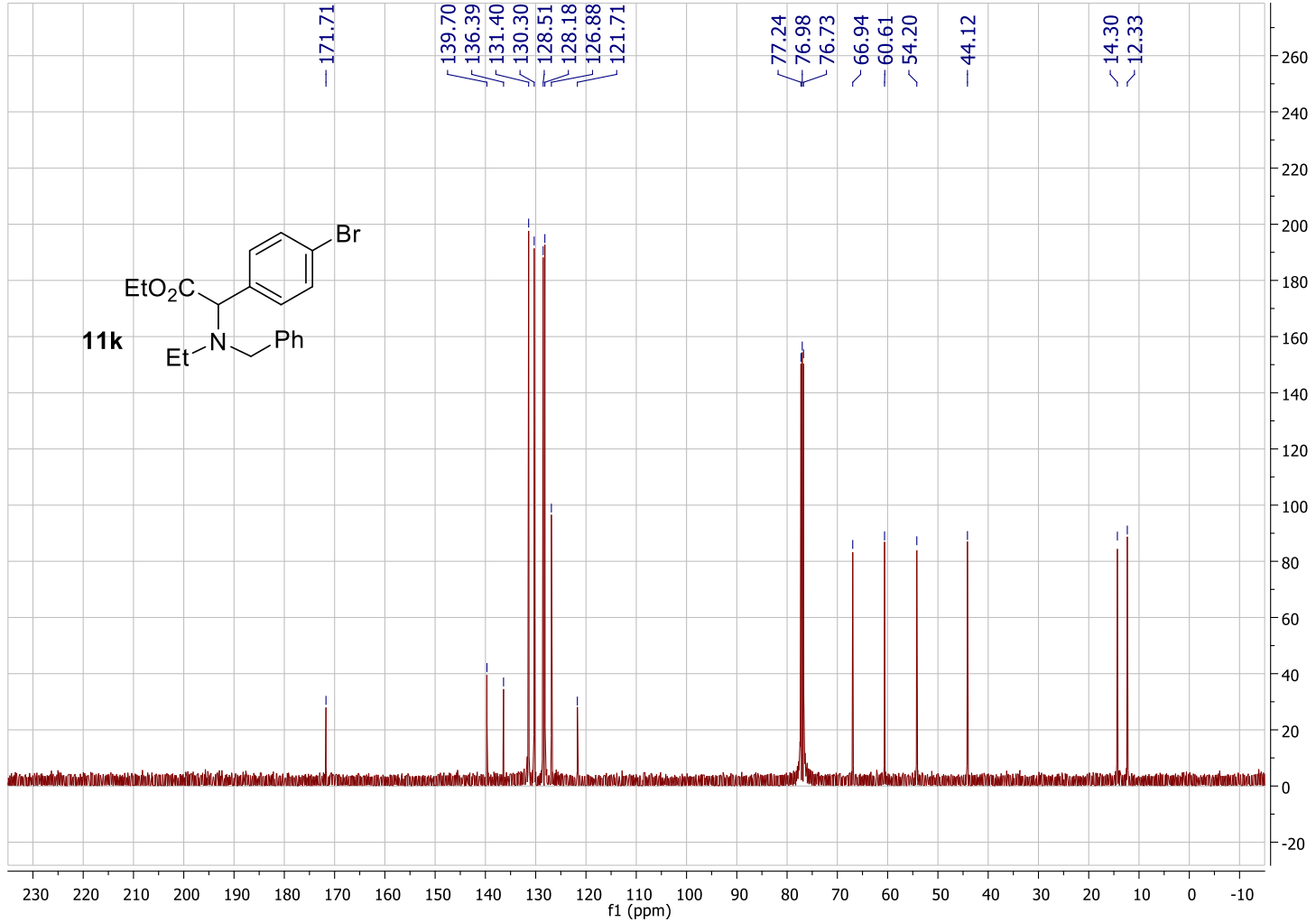
125 MHz, $CDCl_3$



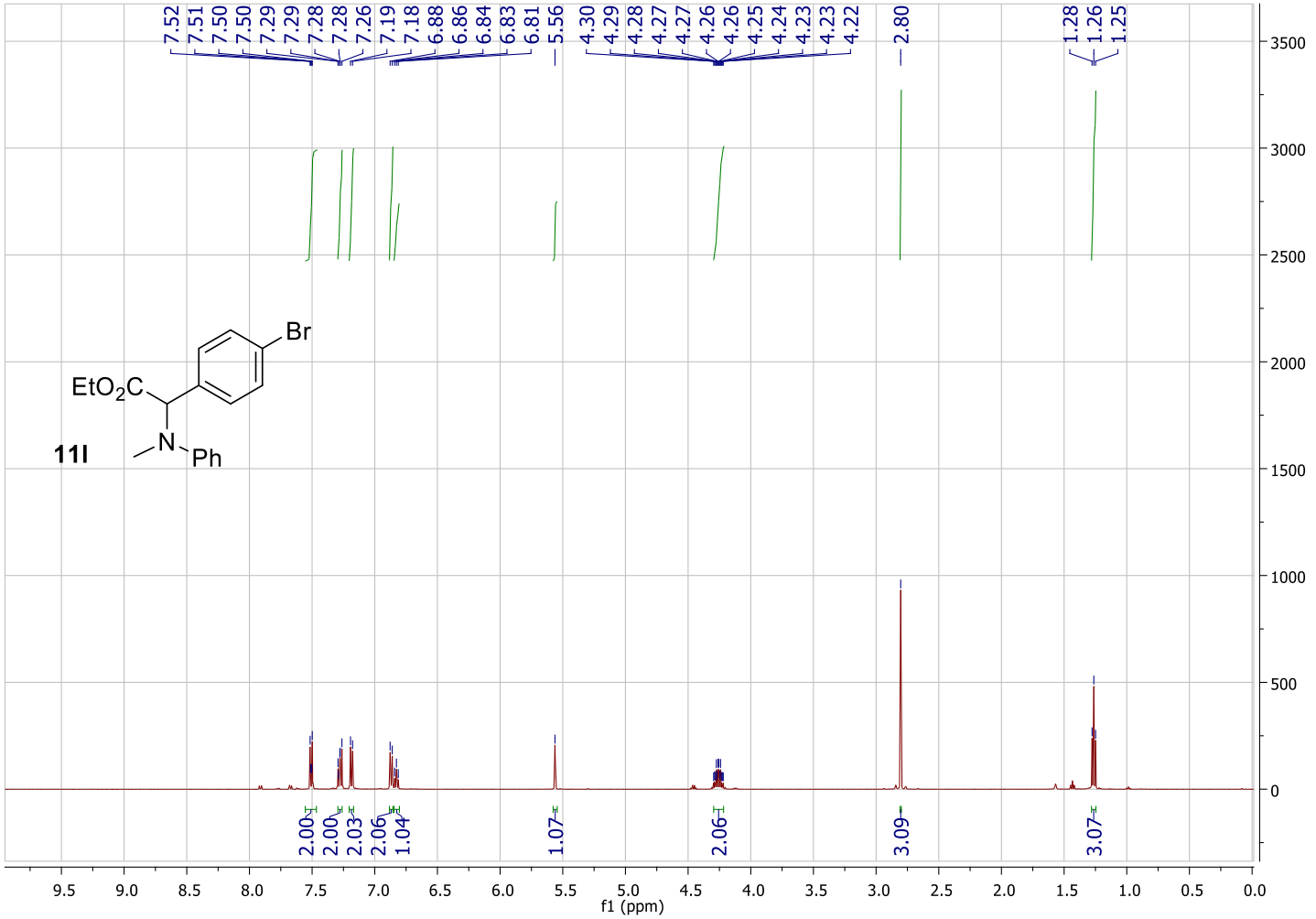
500MHz, $CDCl_3$



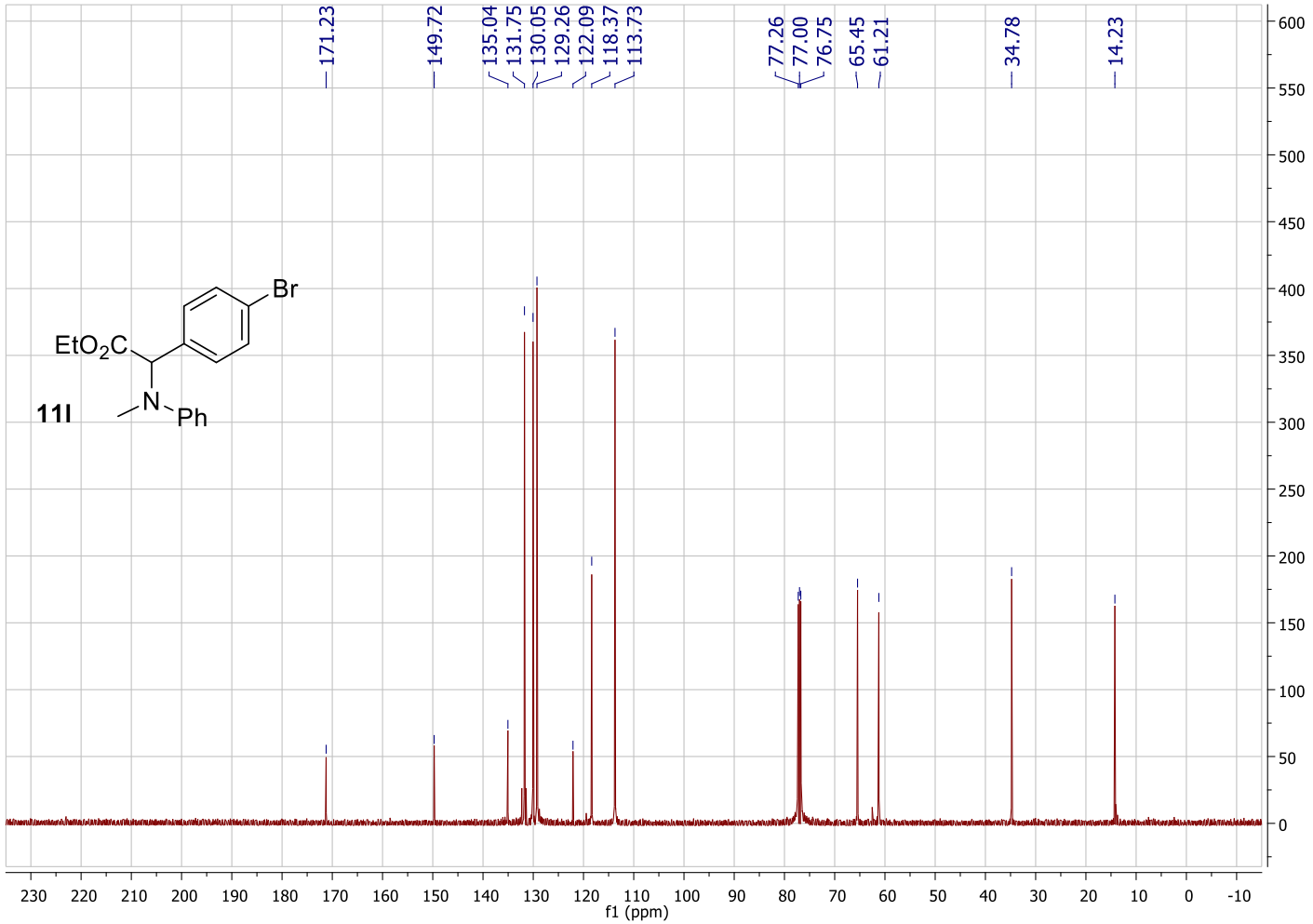
125MHz, $CDCl_3$



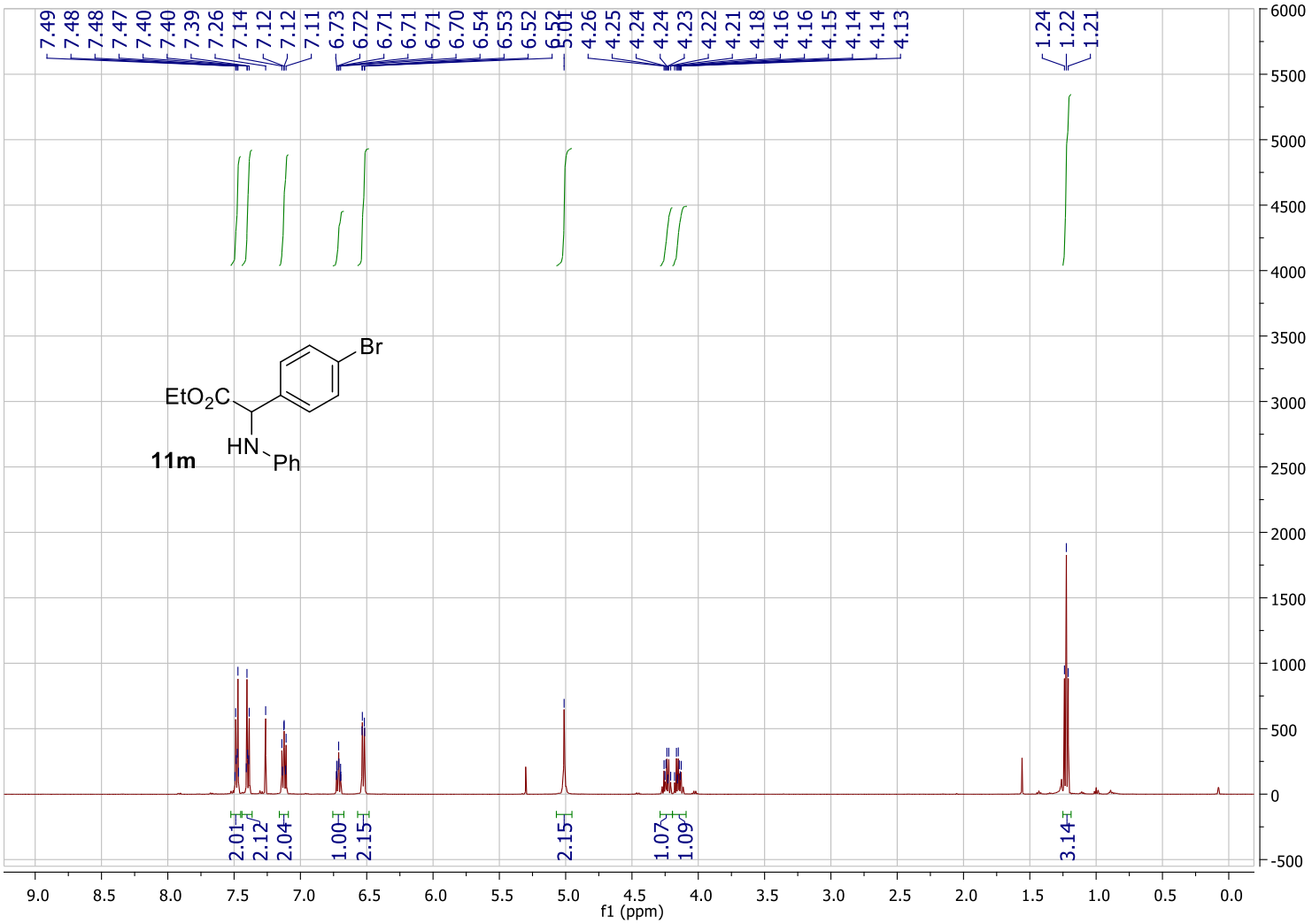
500MHz, $CDCl_3$



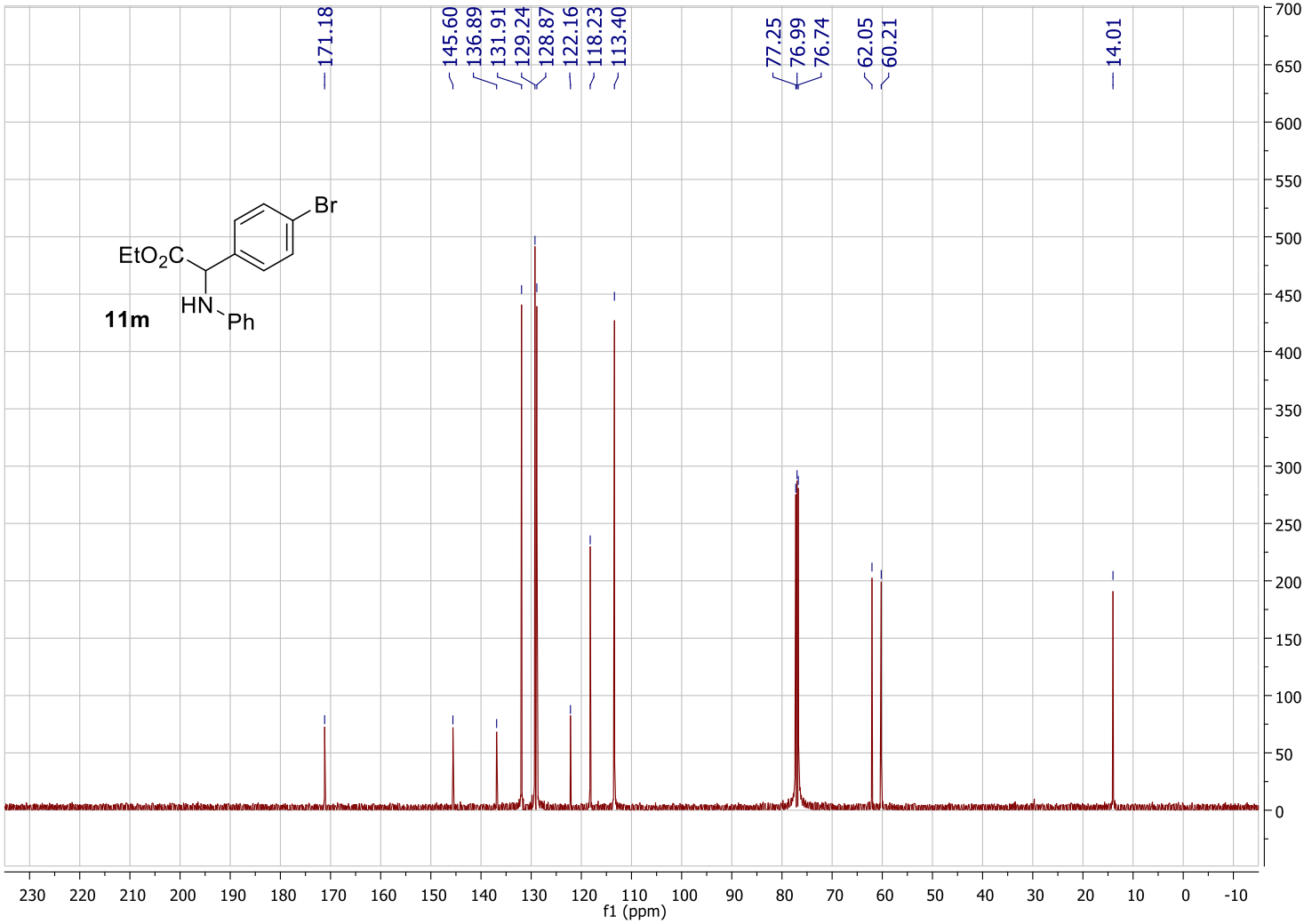
125MHz, $CDCl_3$



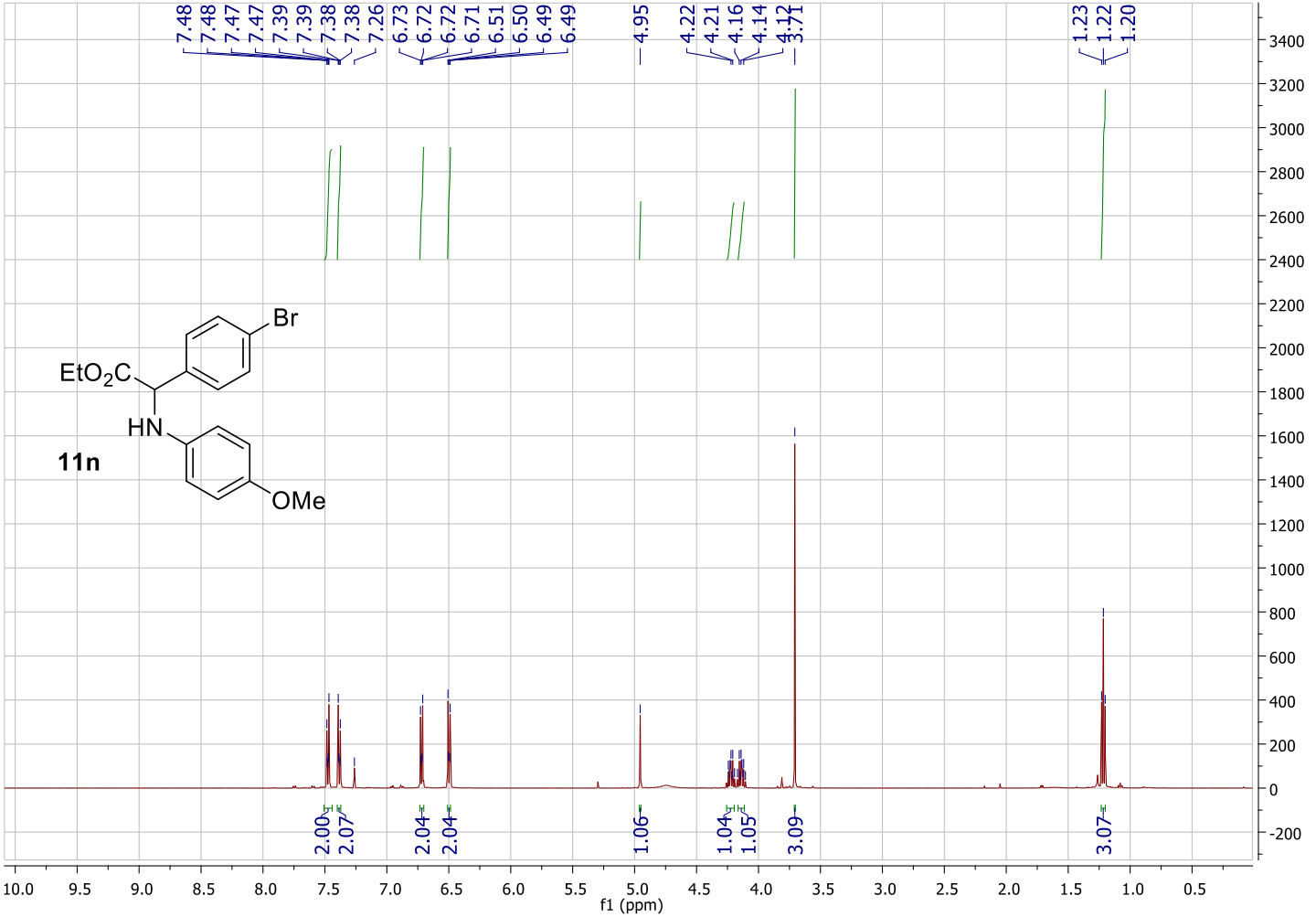
500MHz, $CDCl_3$



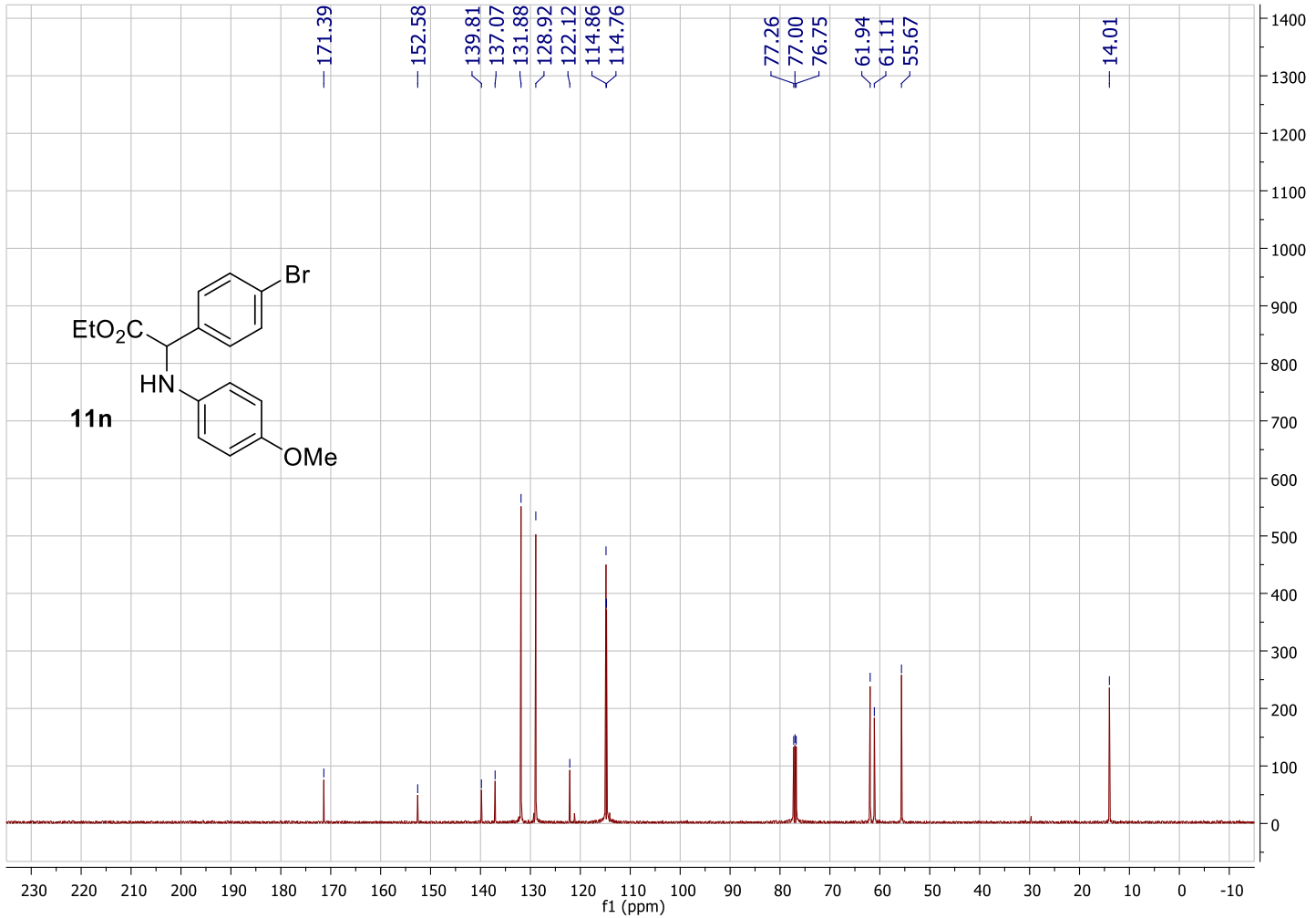
125MHz, $CDCl_3$



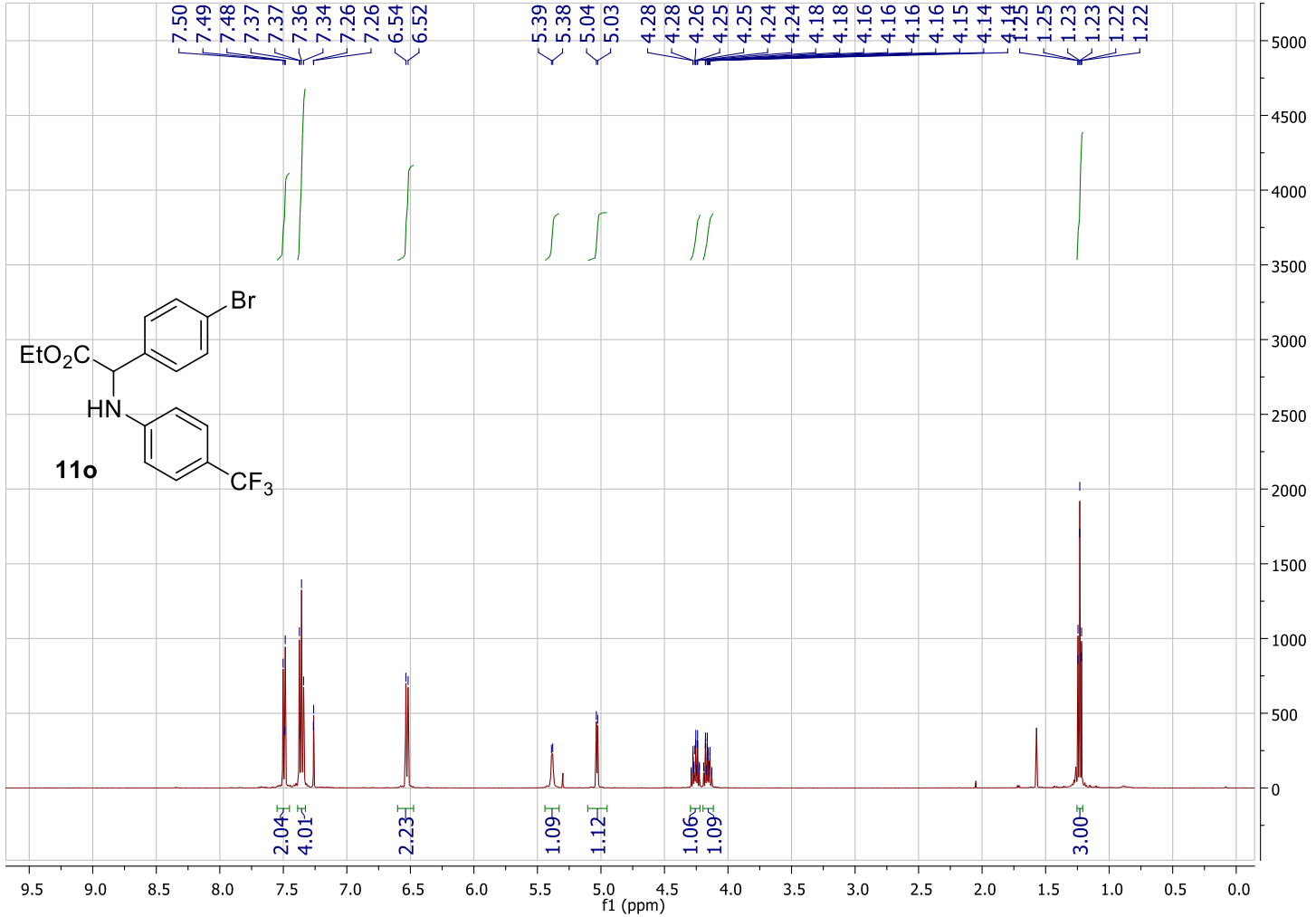
500MHz, $CDCl_3$



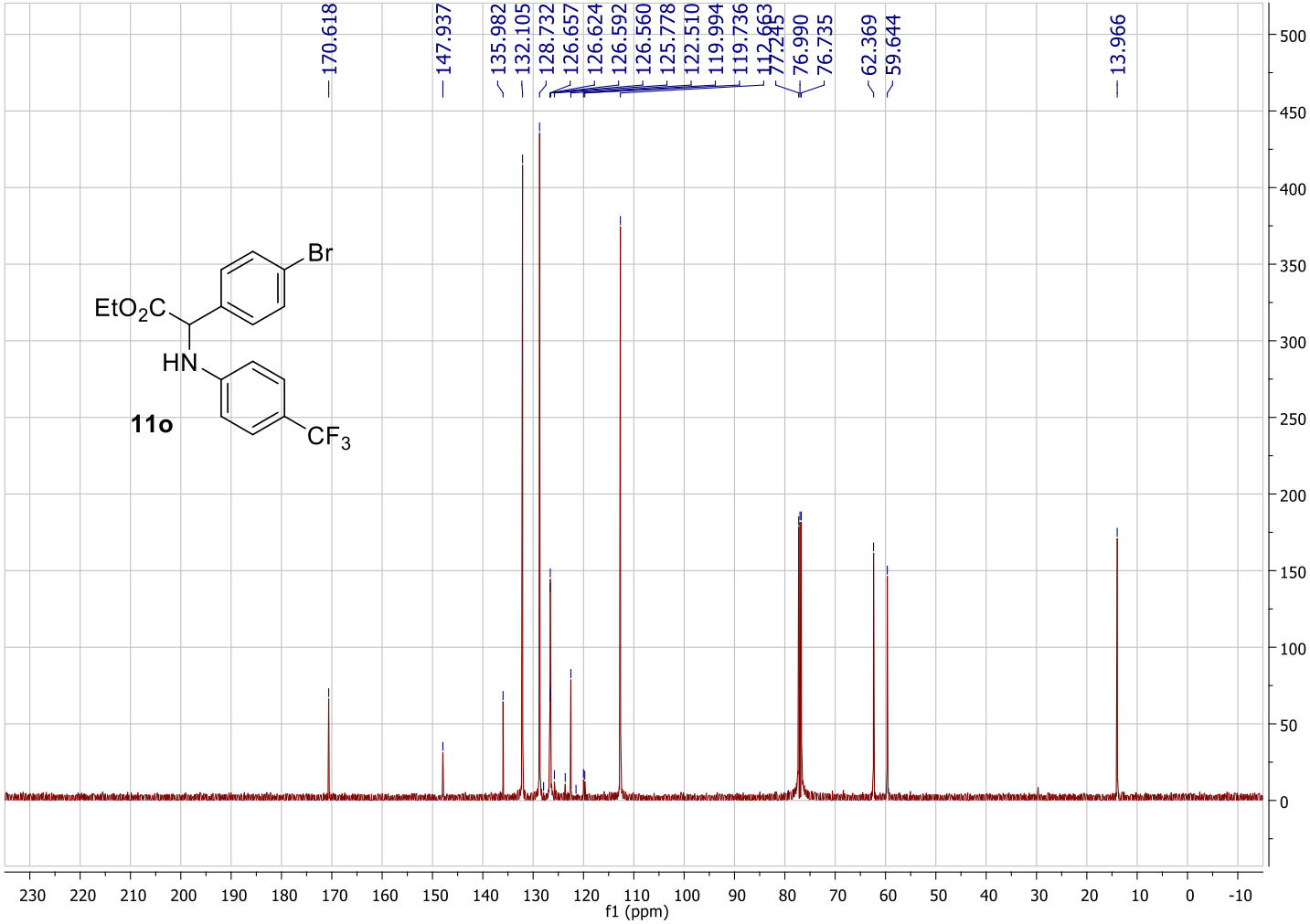
125MHz, $CDCl_3$



500MHz, $CDCl_3$

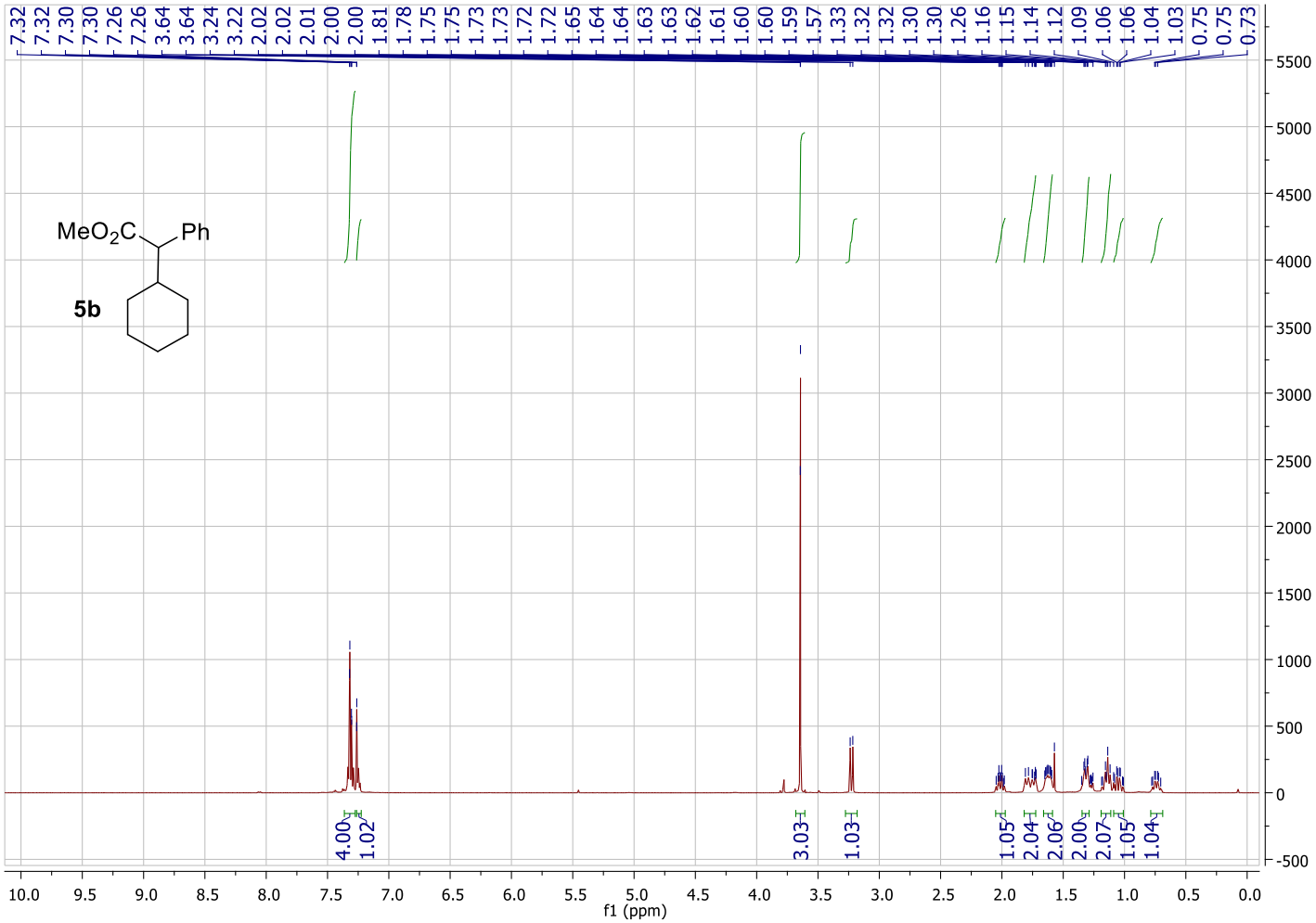


125MHz, $CDCl_3$

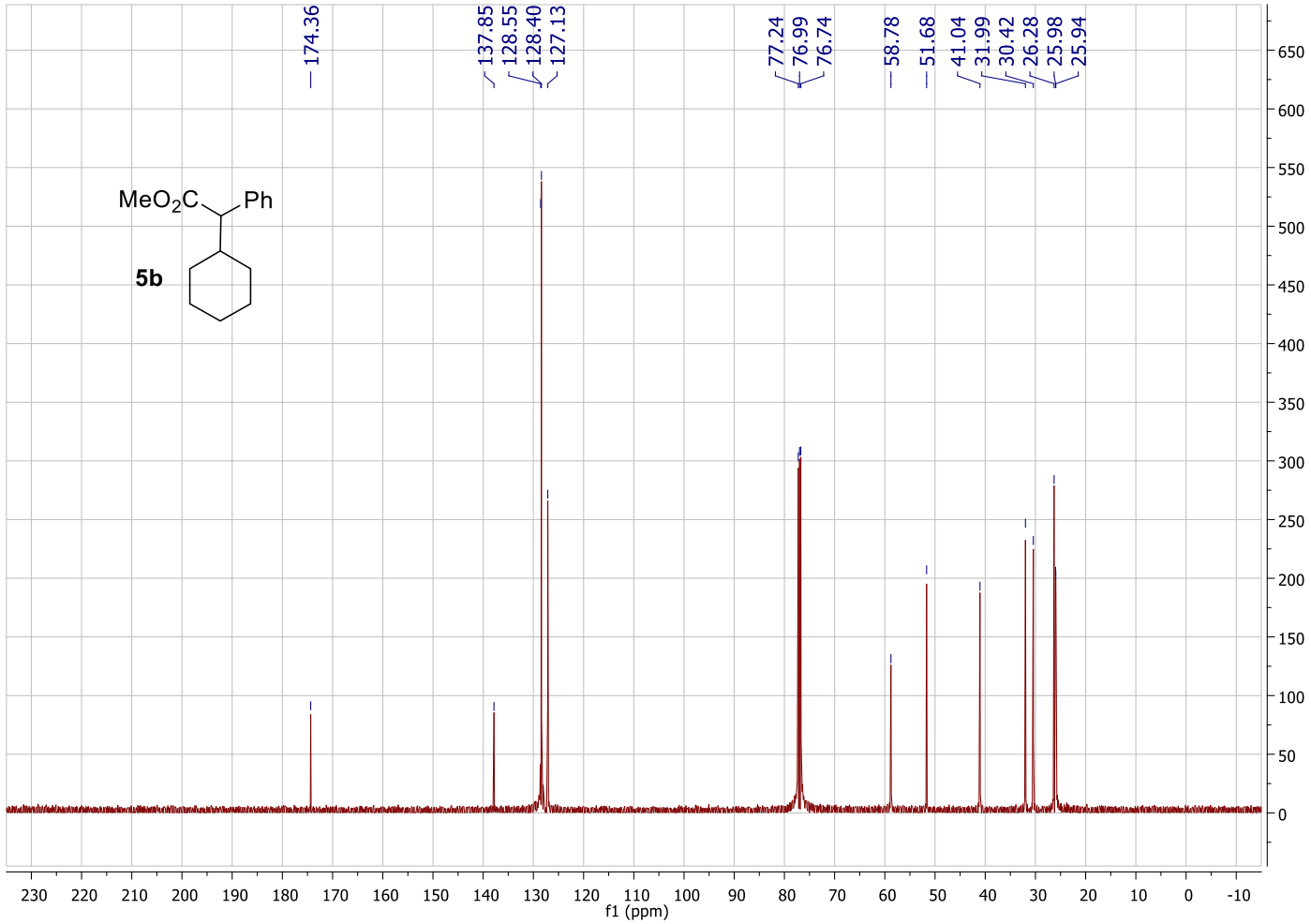


4.6 Products Derived from C-H Insertion of Cycloalkanes (and Other Molecules)

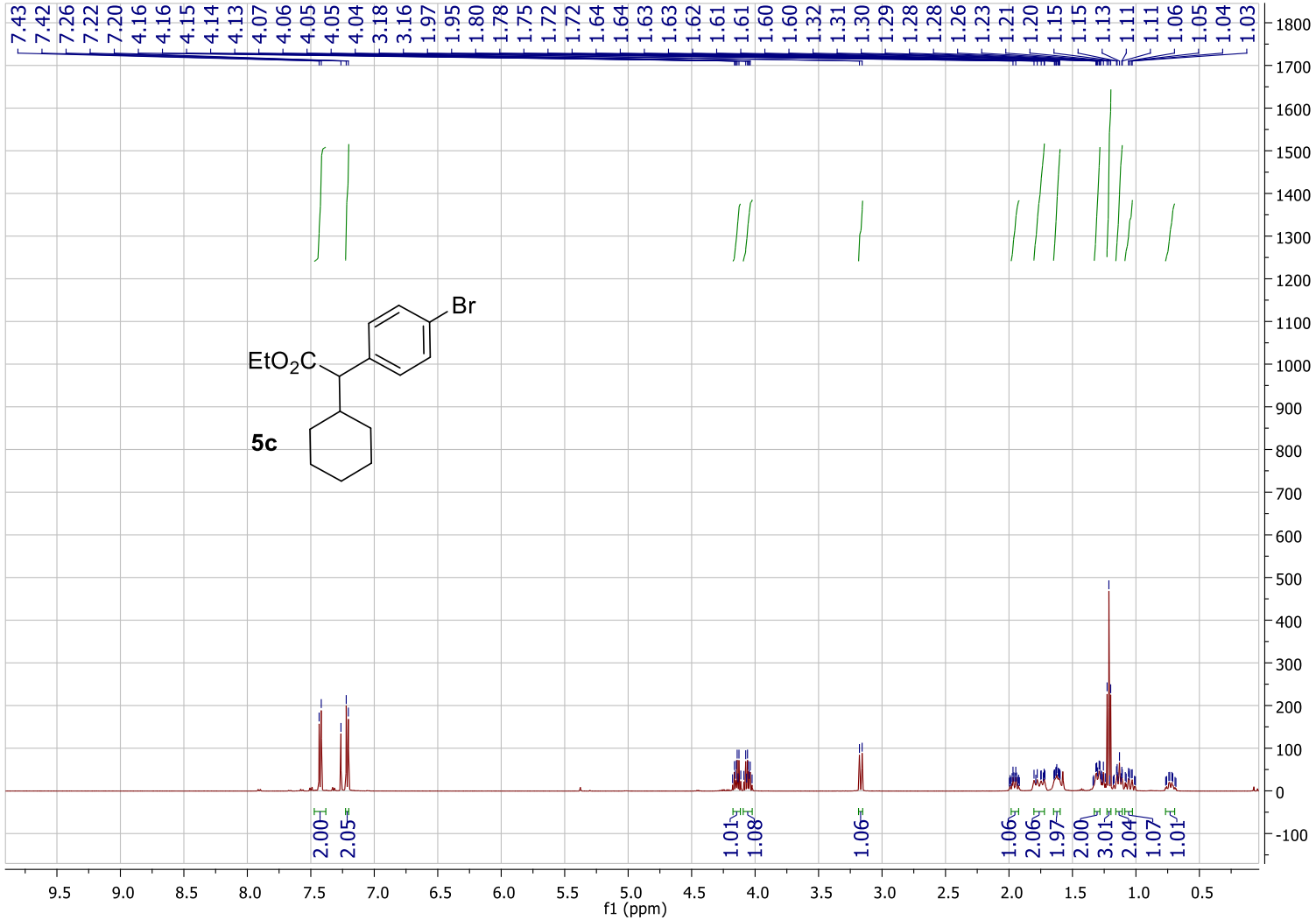
500MHz, $CDCl_3$



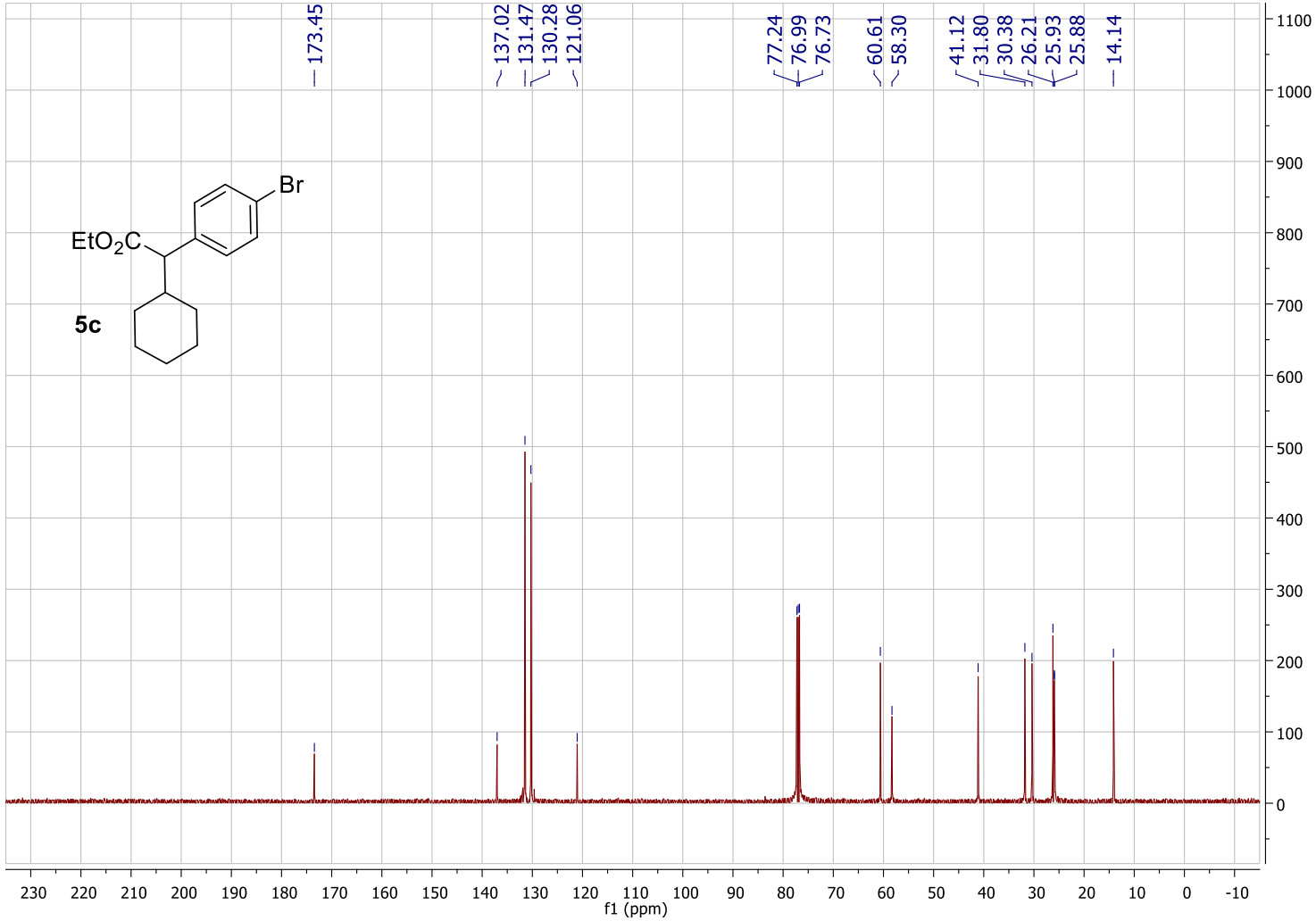
125MHz, $CDCl_3$



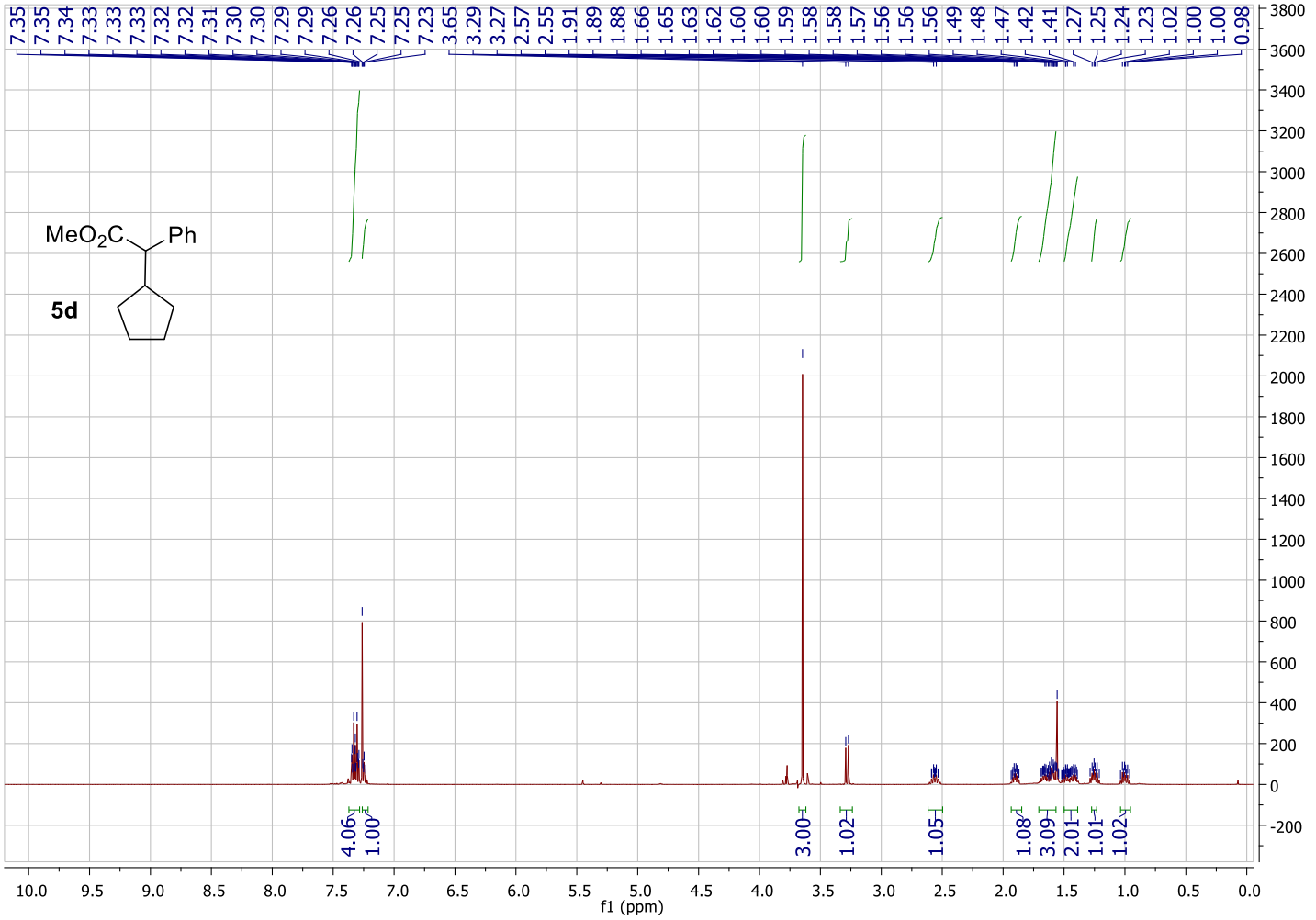
500MHz, $CDCl_3$



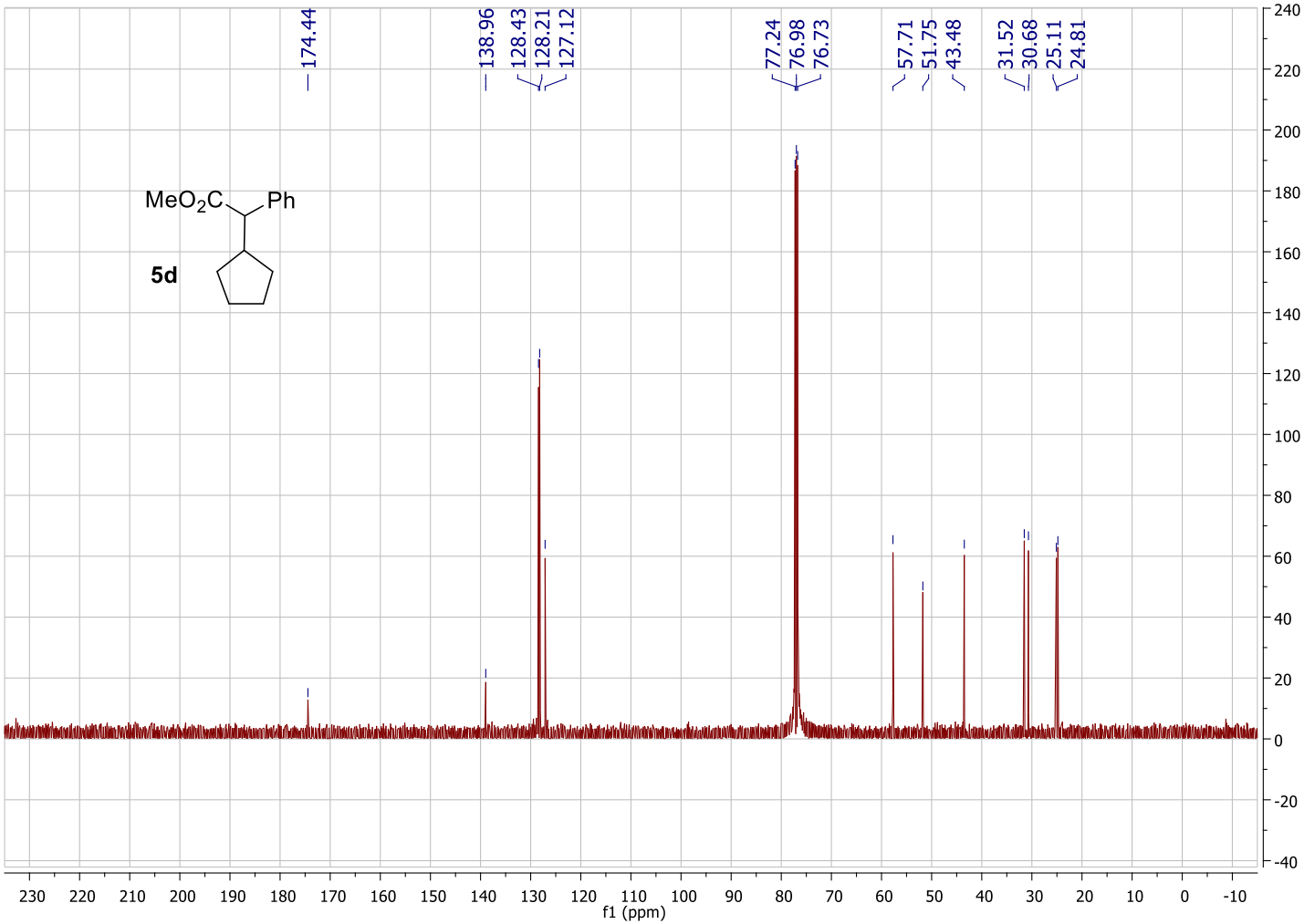
125MHz, $CDCl_3$



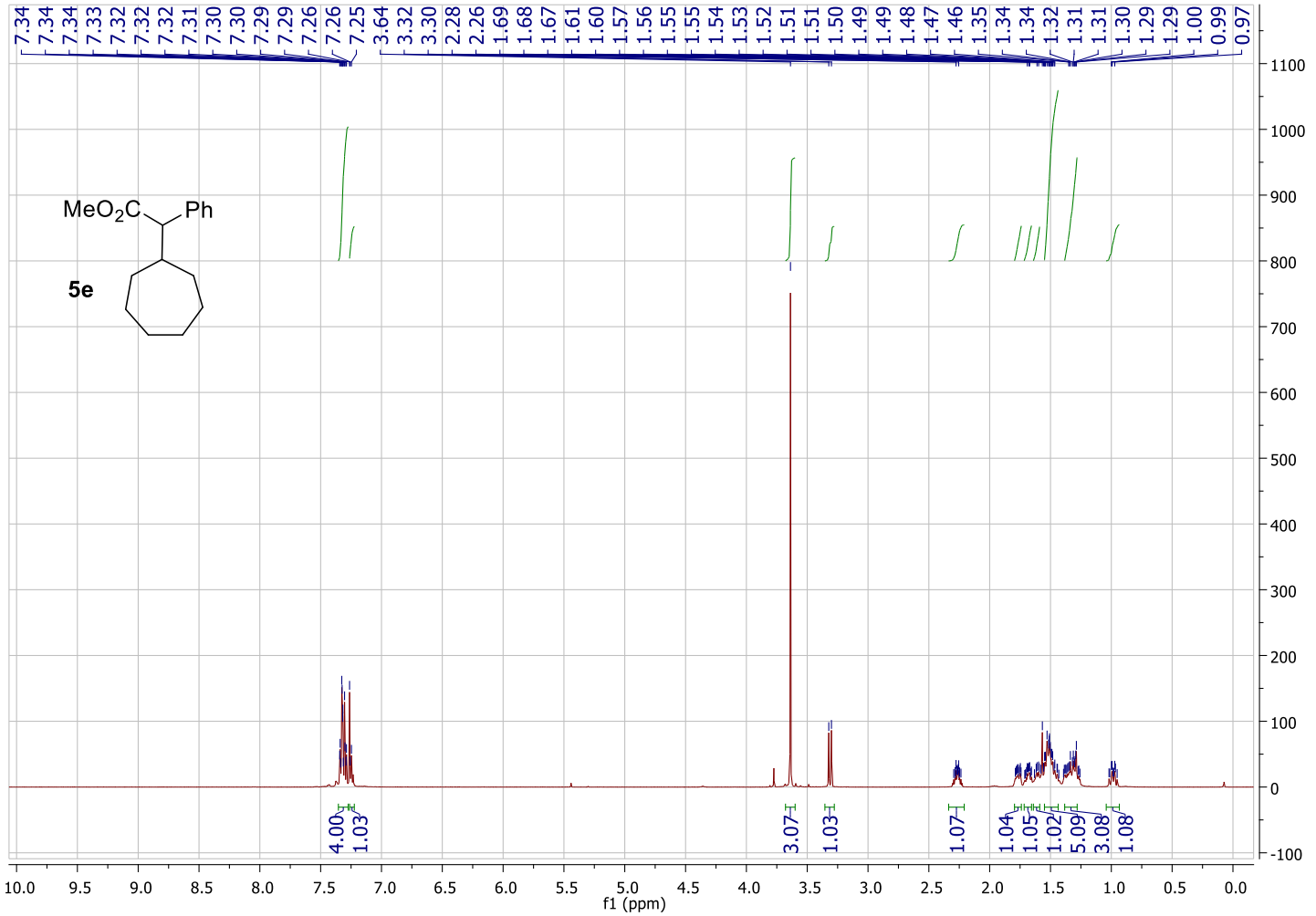
500MHz, $CDCl_3$



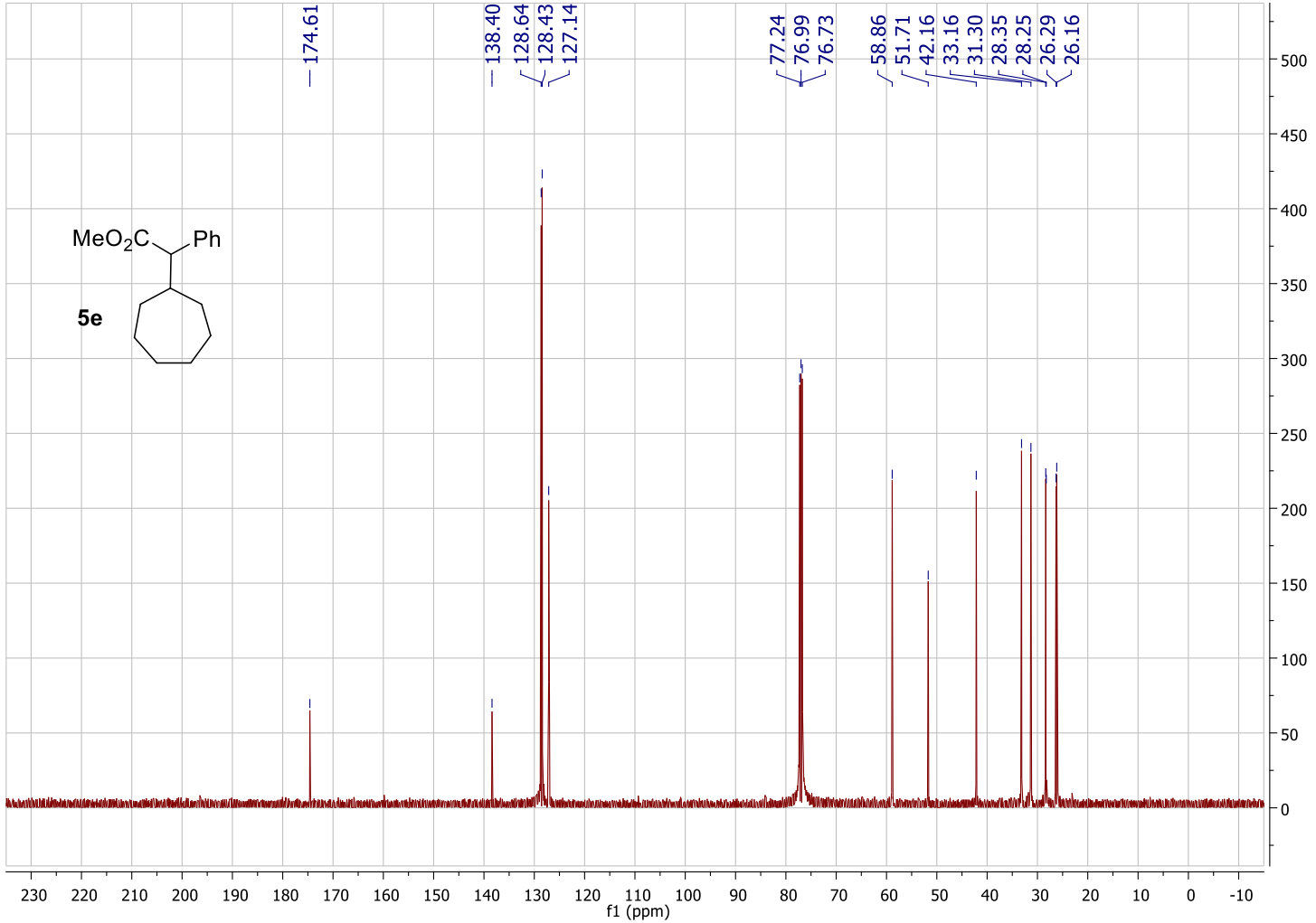
500MHz, $CDCl_3$



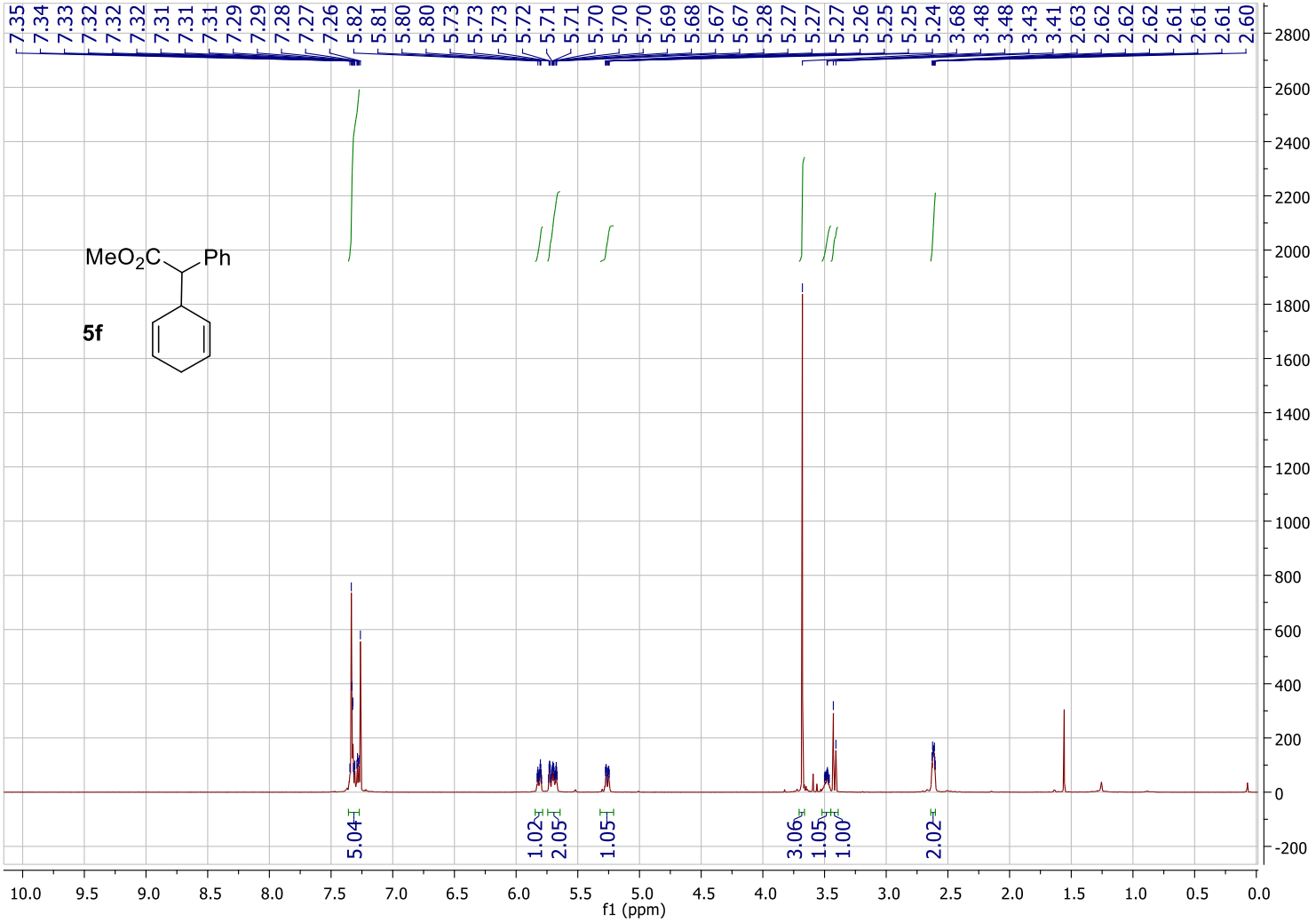
500MHz, $CDCl_3$



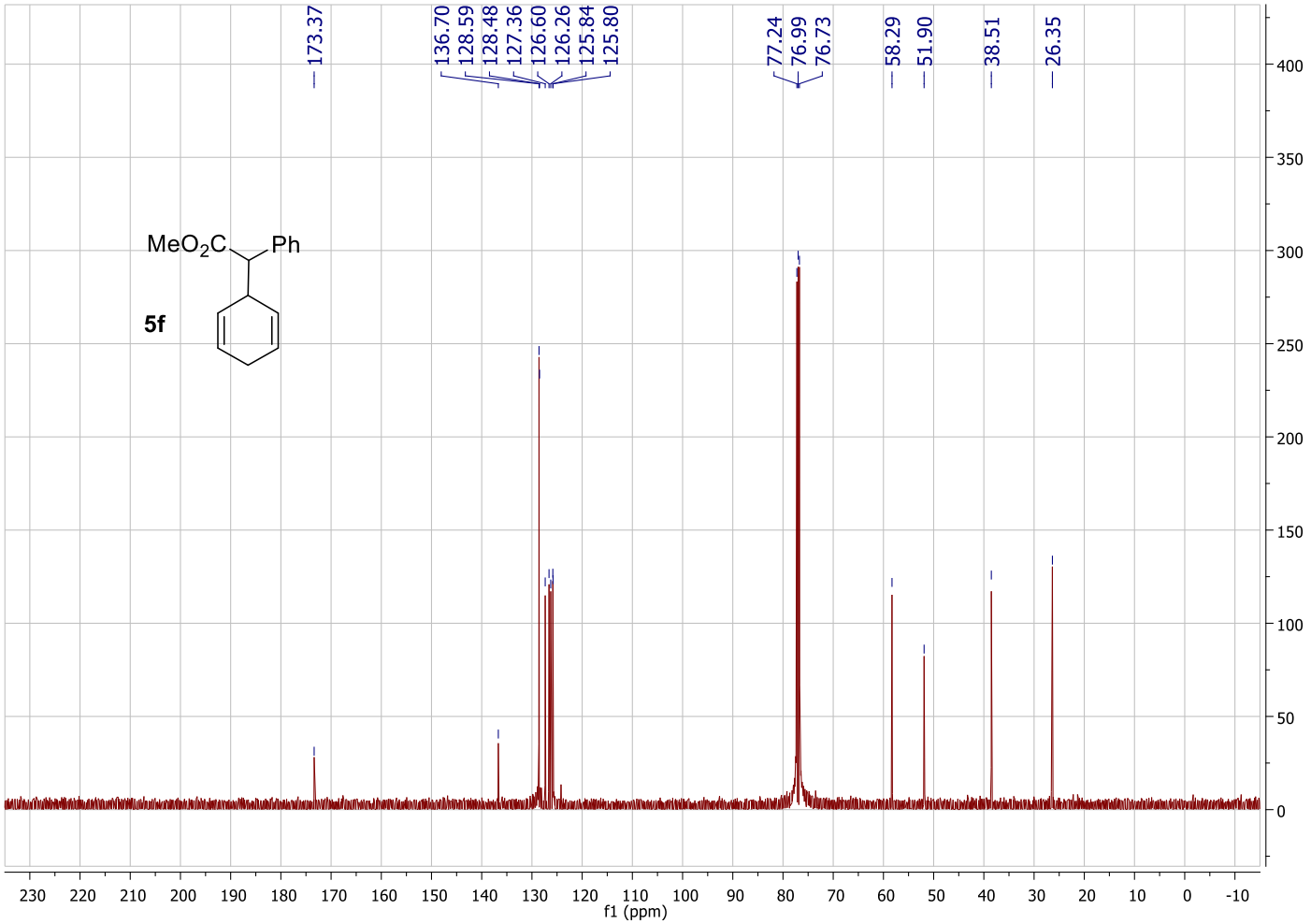
125MHz, $CDCl_3$



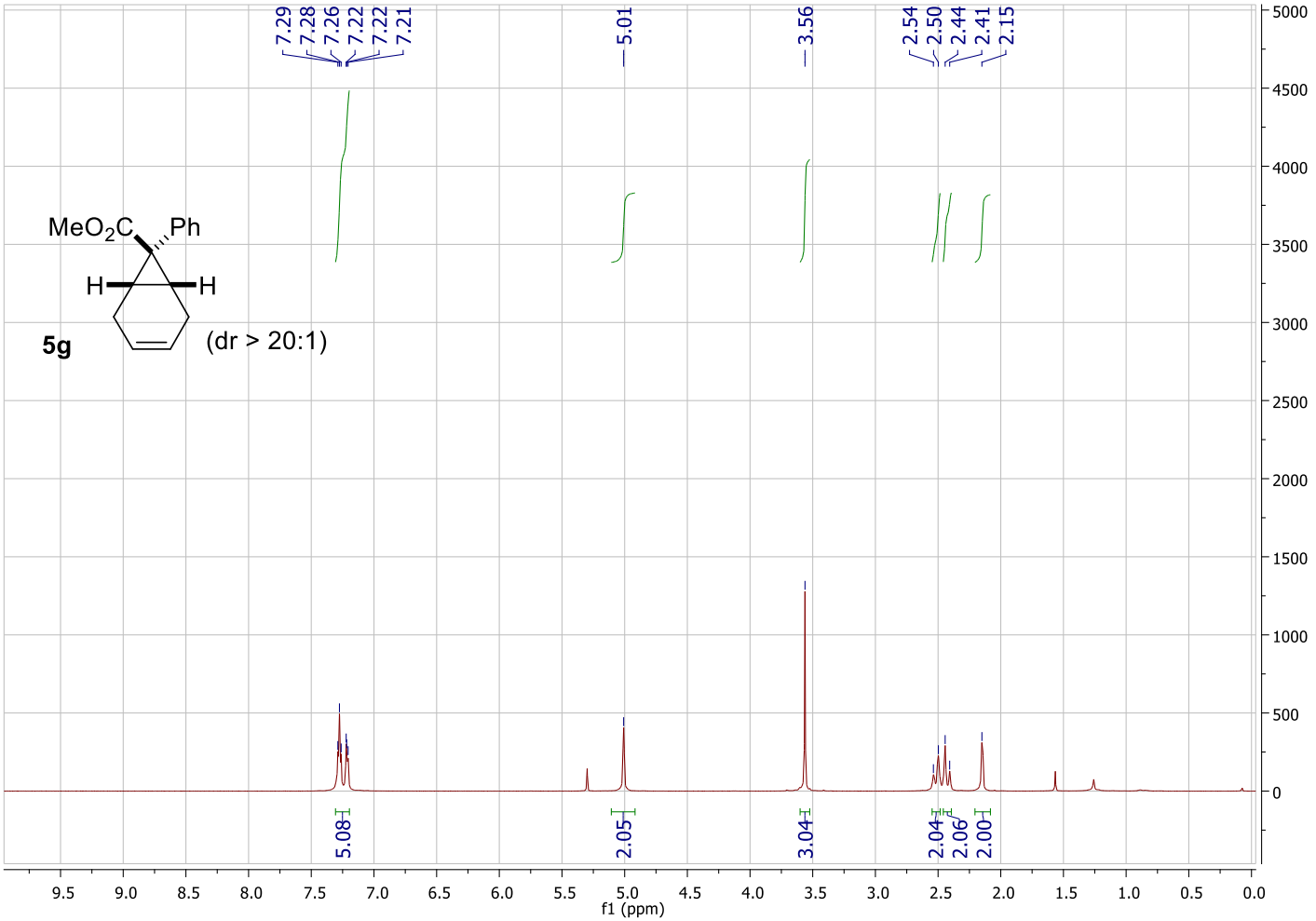
500MHz, $CDCl_3$



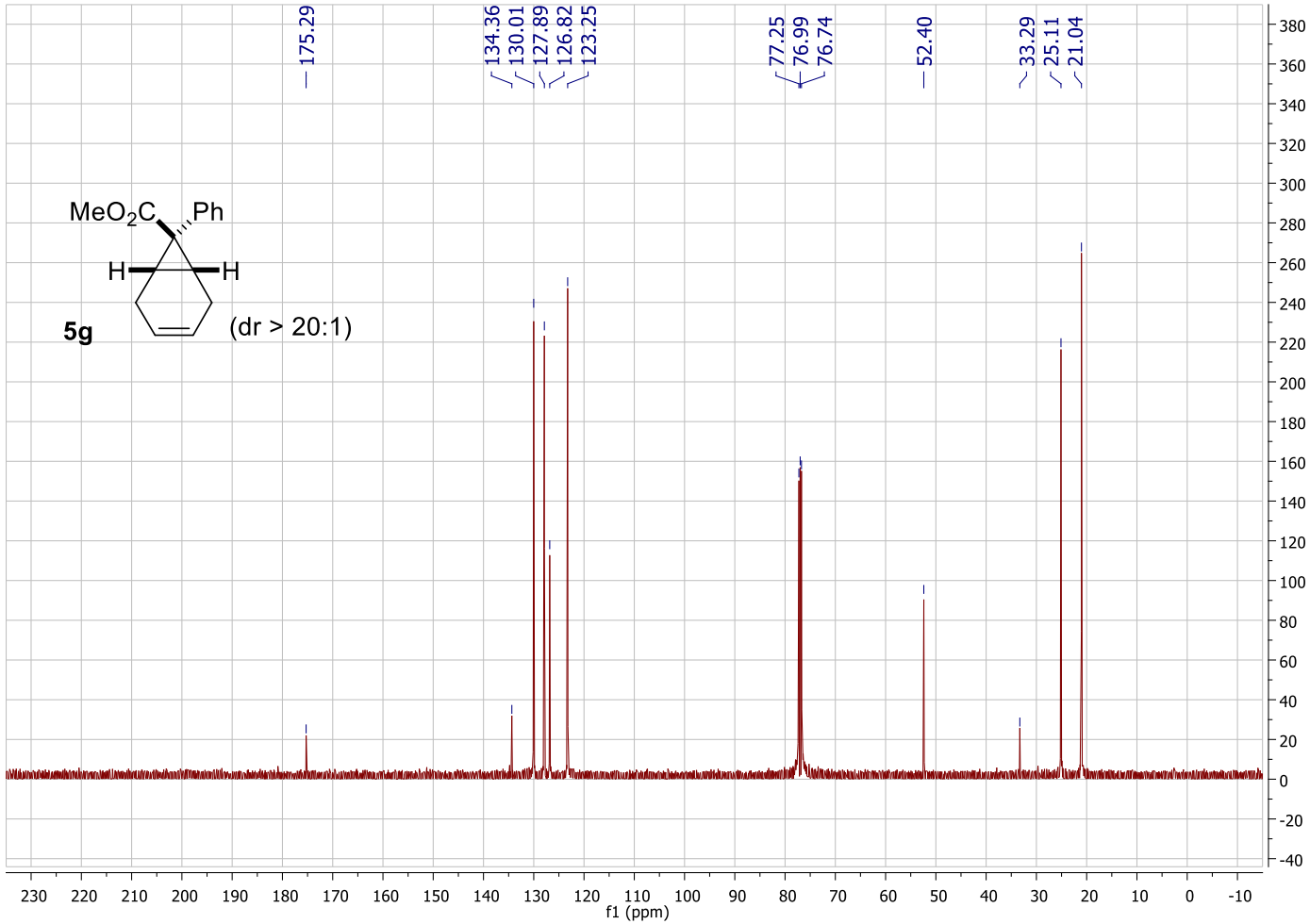
125MHz, $CDCl_3$



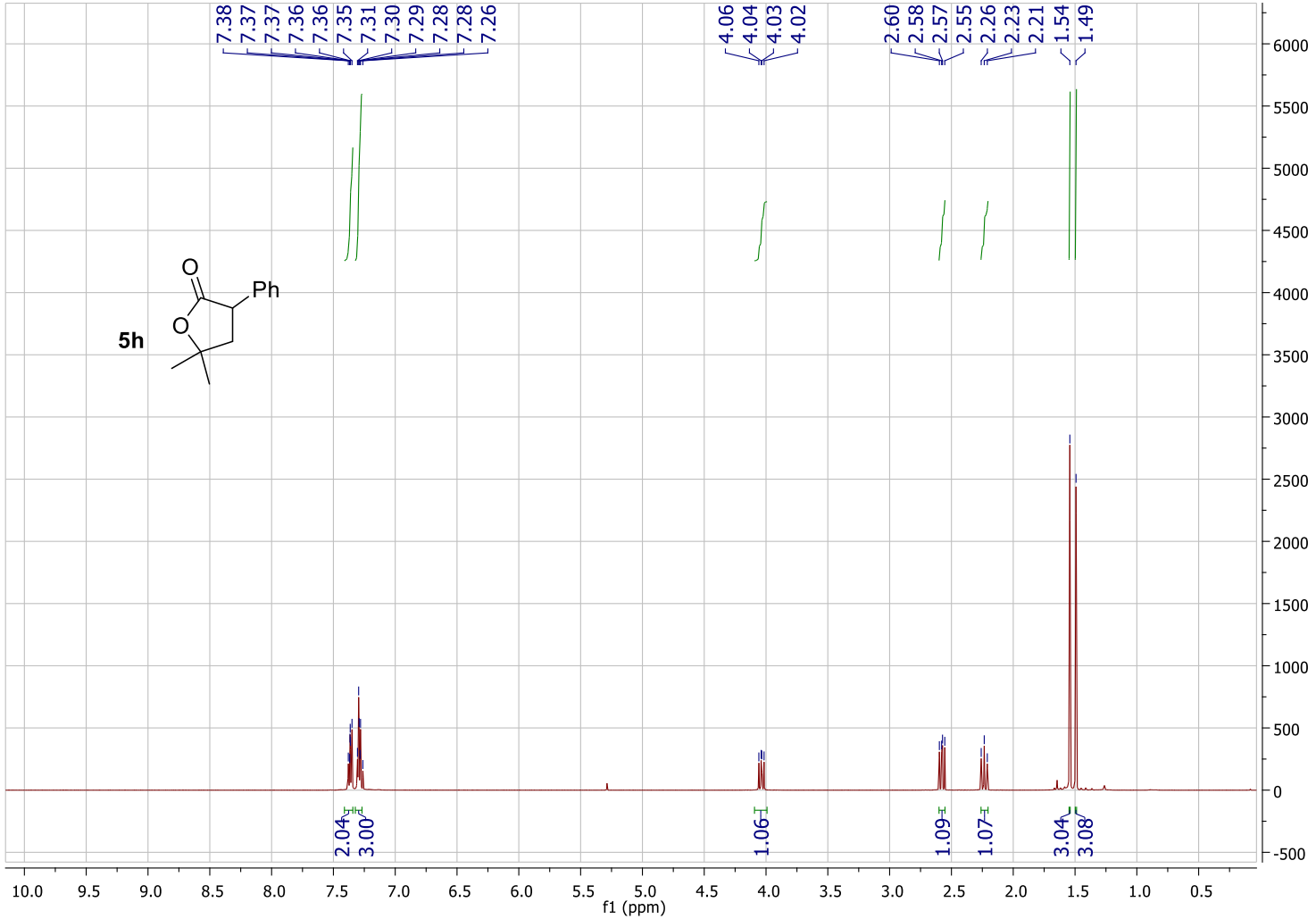
500MHz, $CDCl_3$



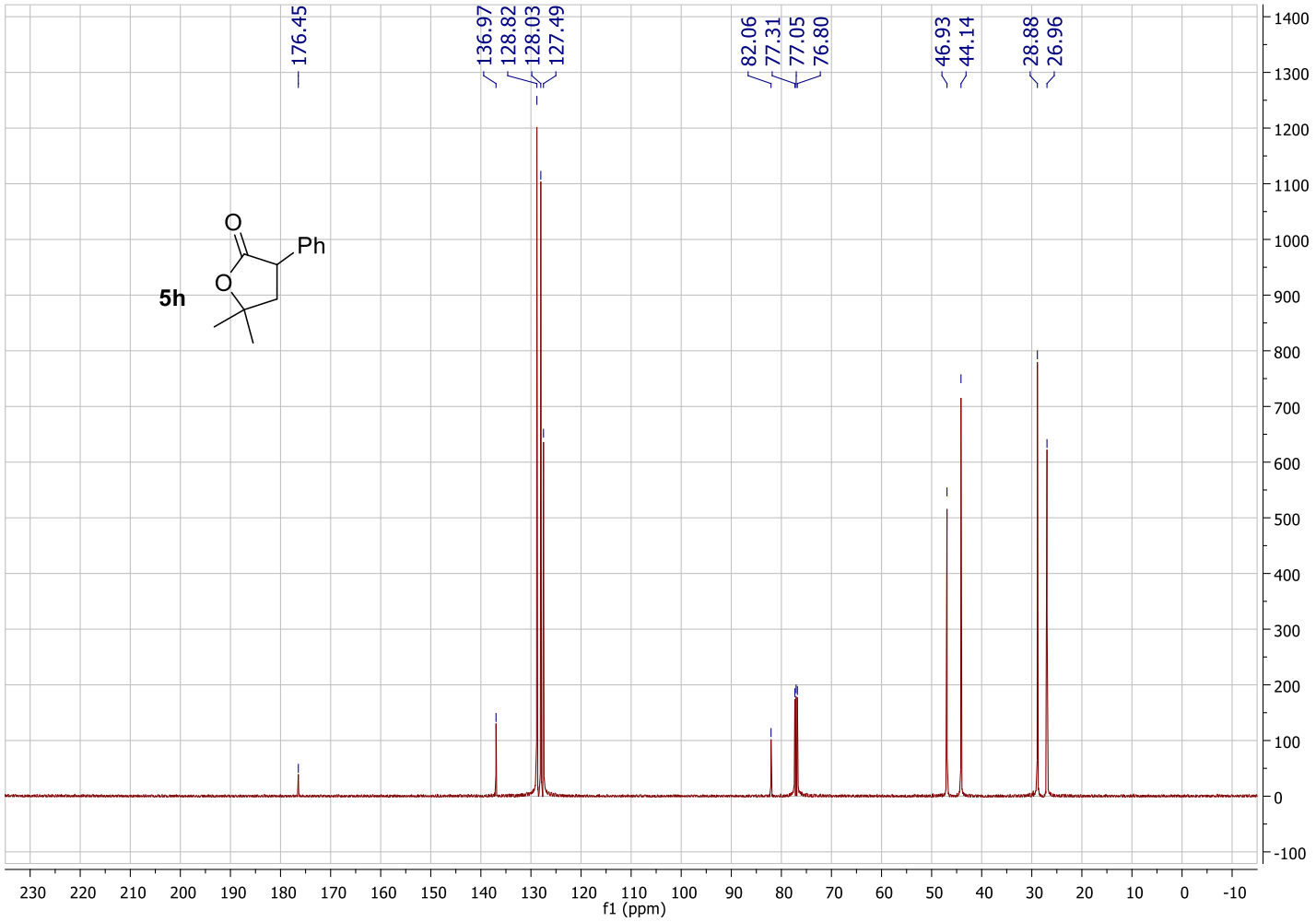
500MHz, $CDCl_3$



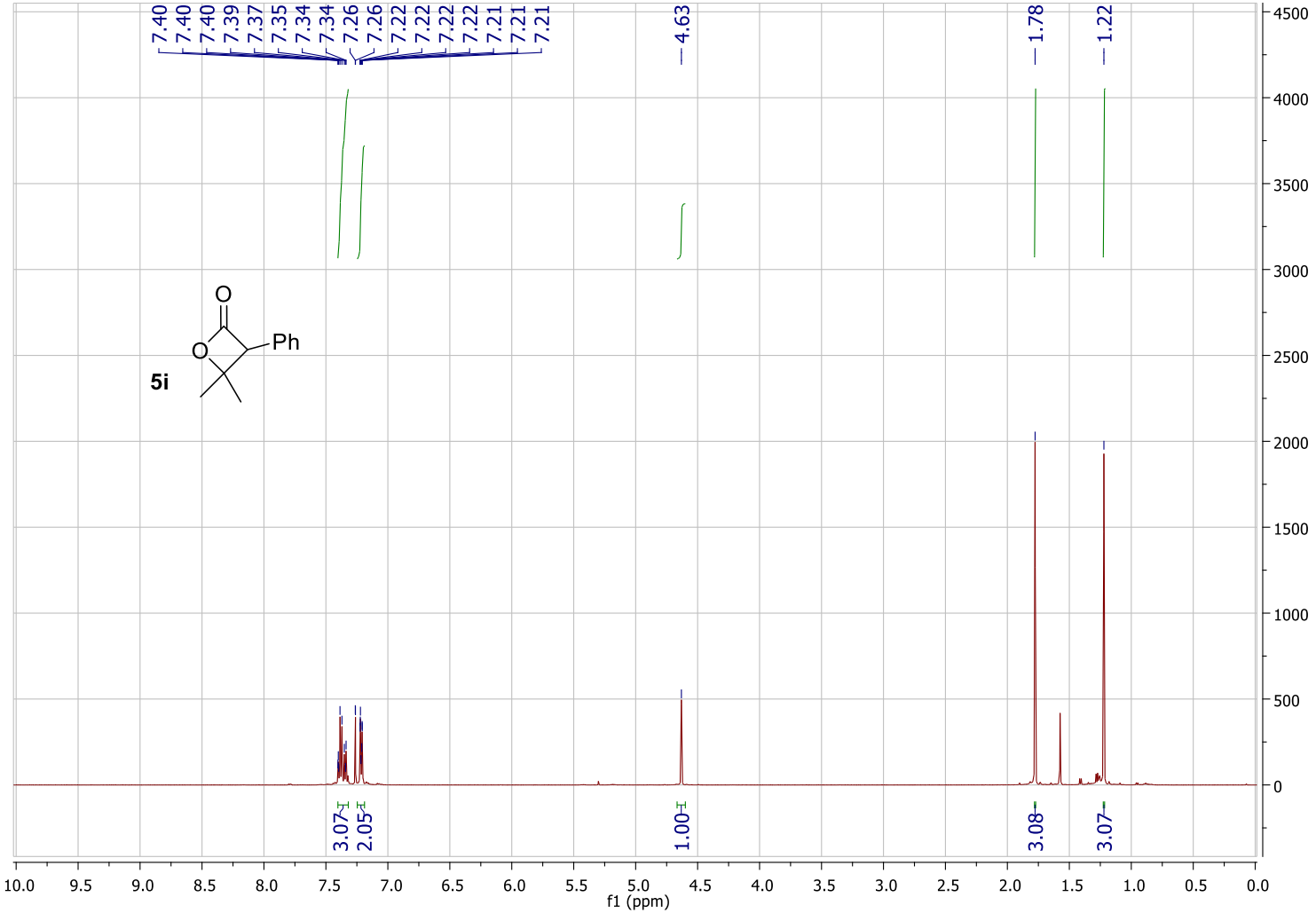
500MHz, $CDCl_3$



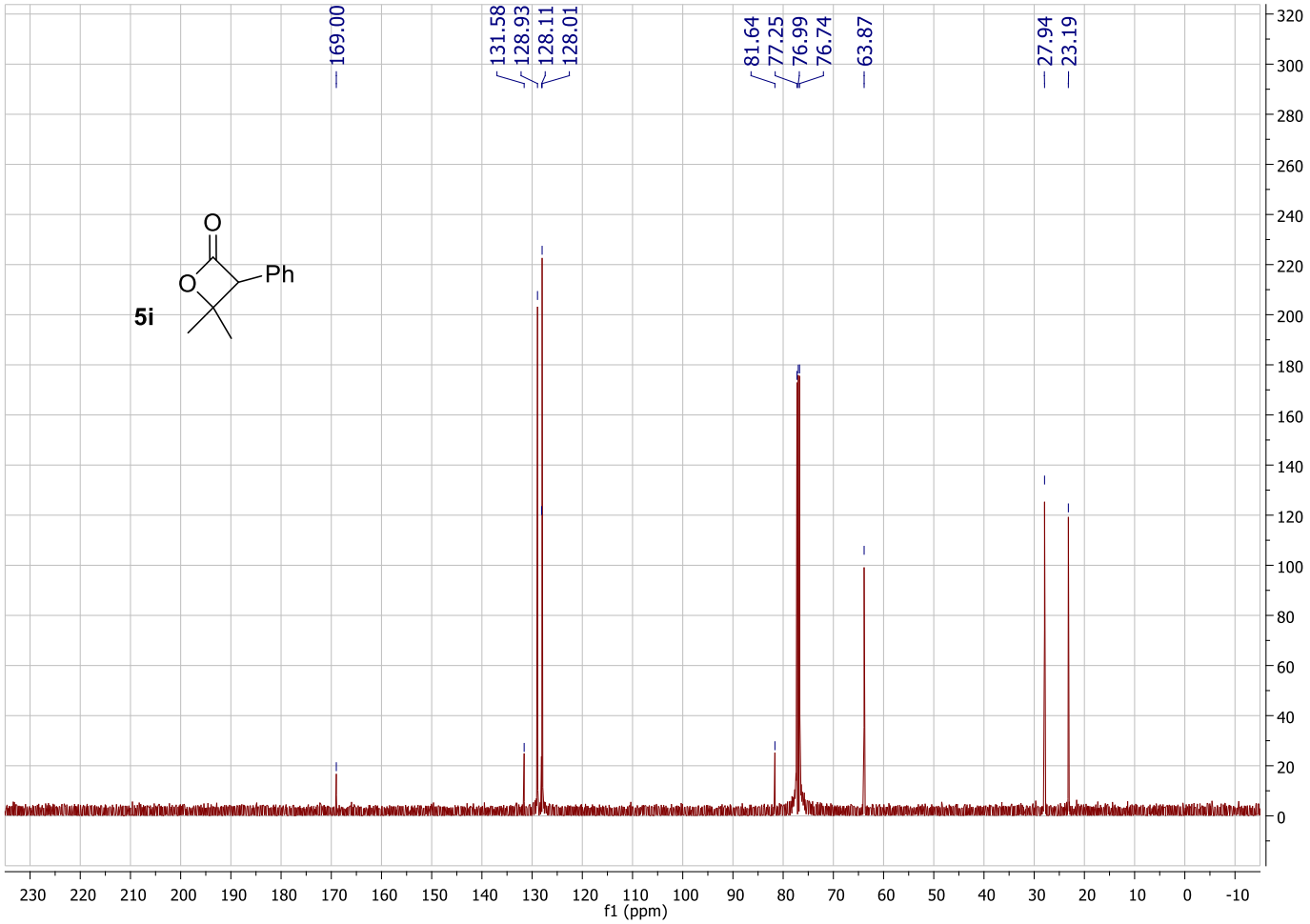
125MHz, $CDCl_3$



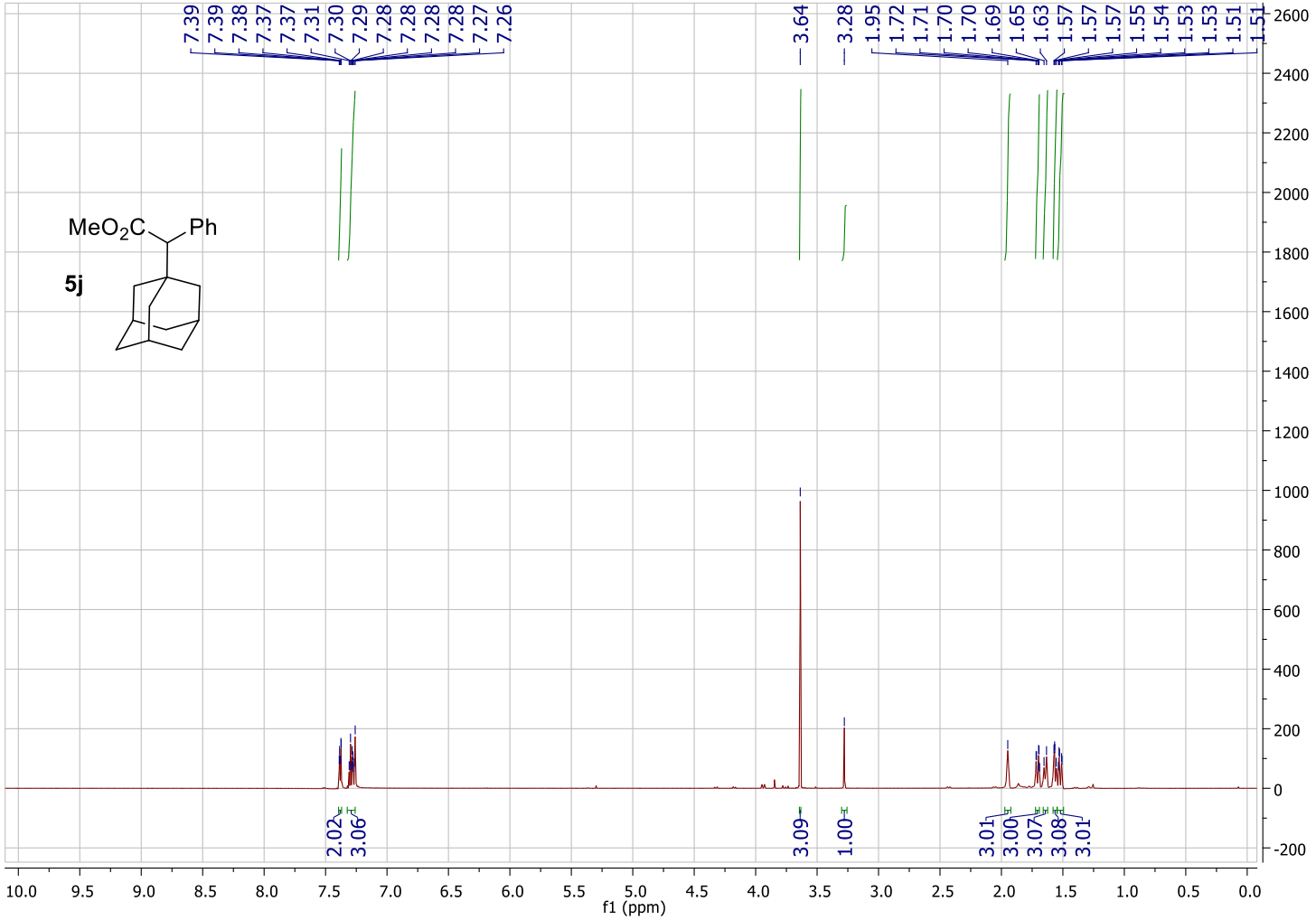
500MHz, $CDCl_3$



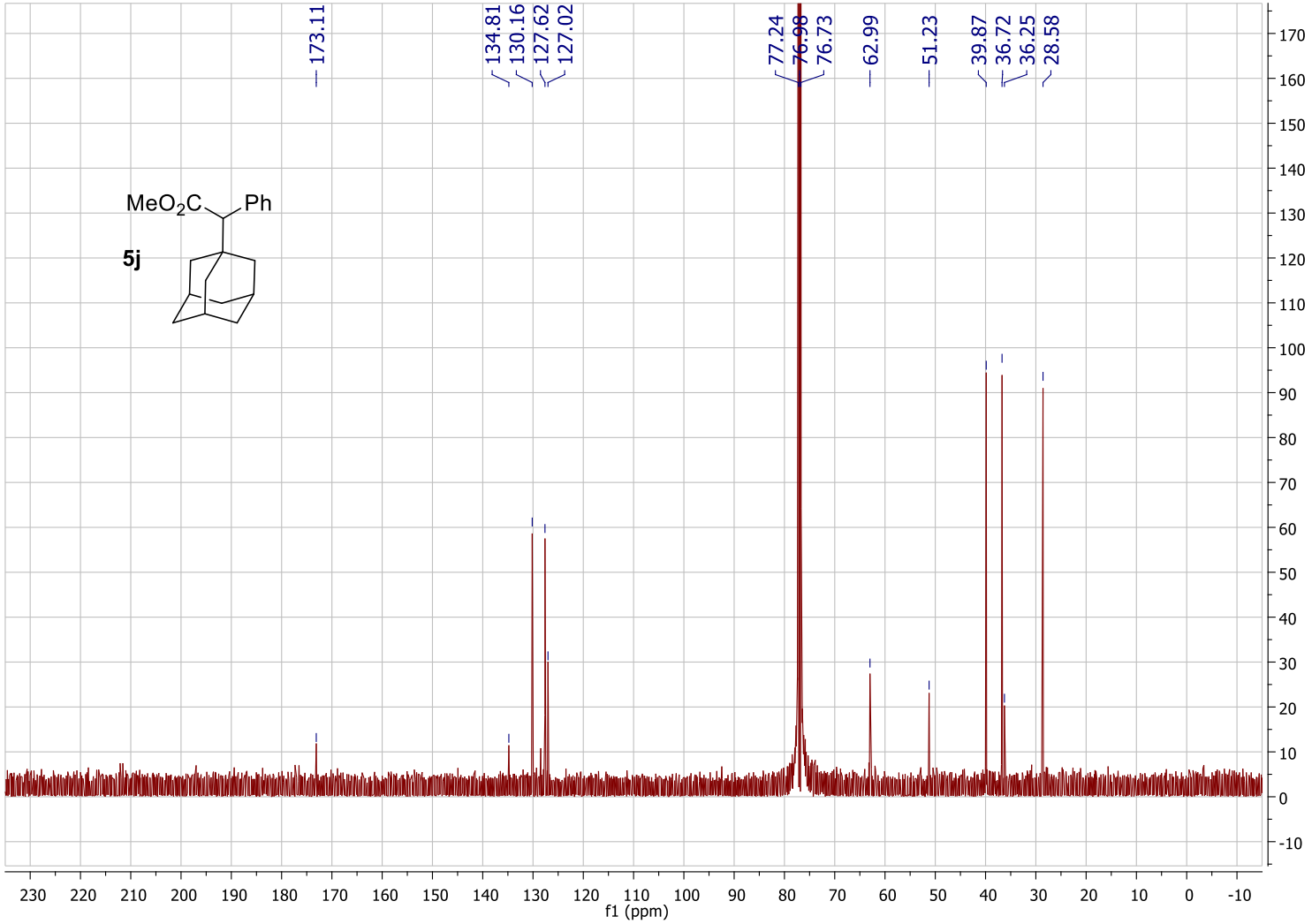
125MHz, $CDCl_3$



600MHz, $CDCl_3$

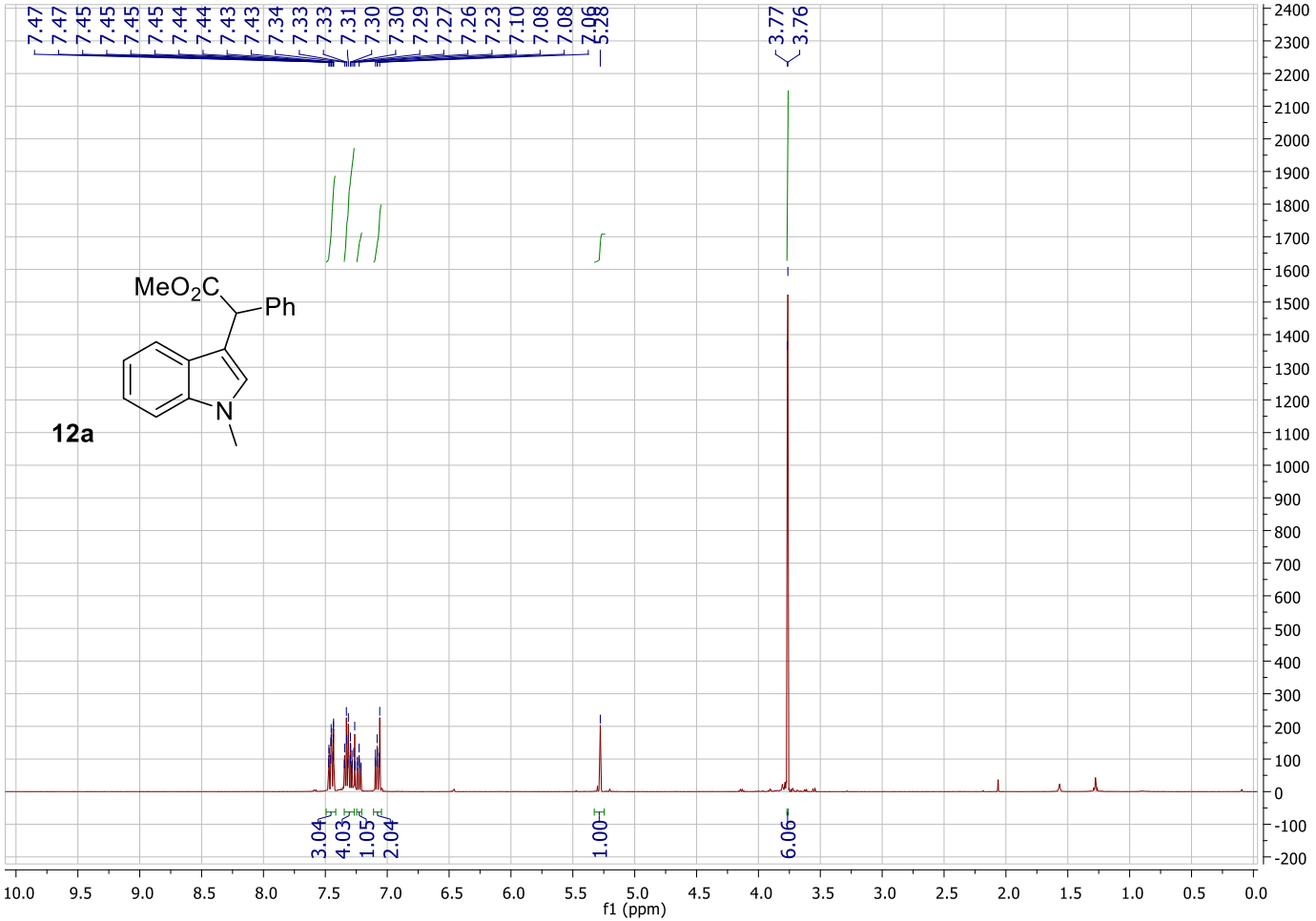


125MHz, $CDCl_3$

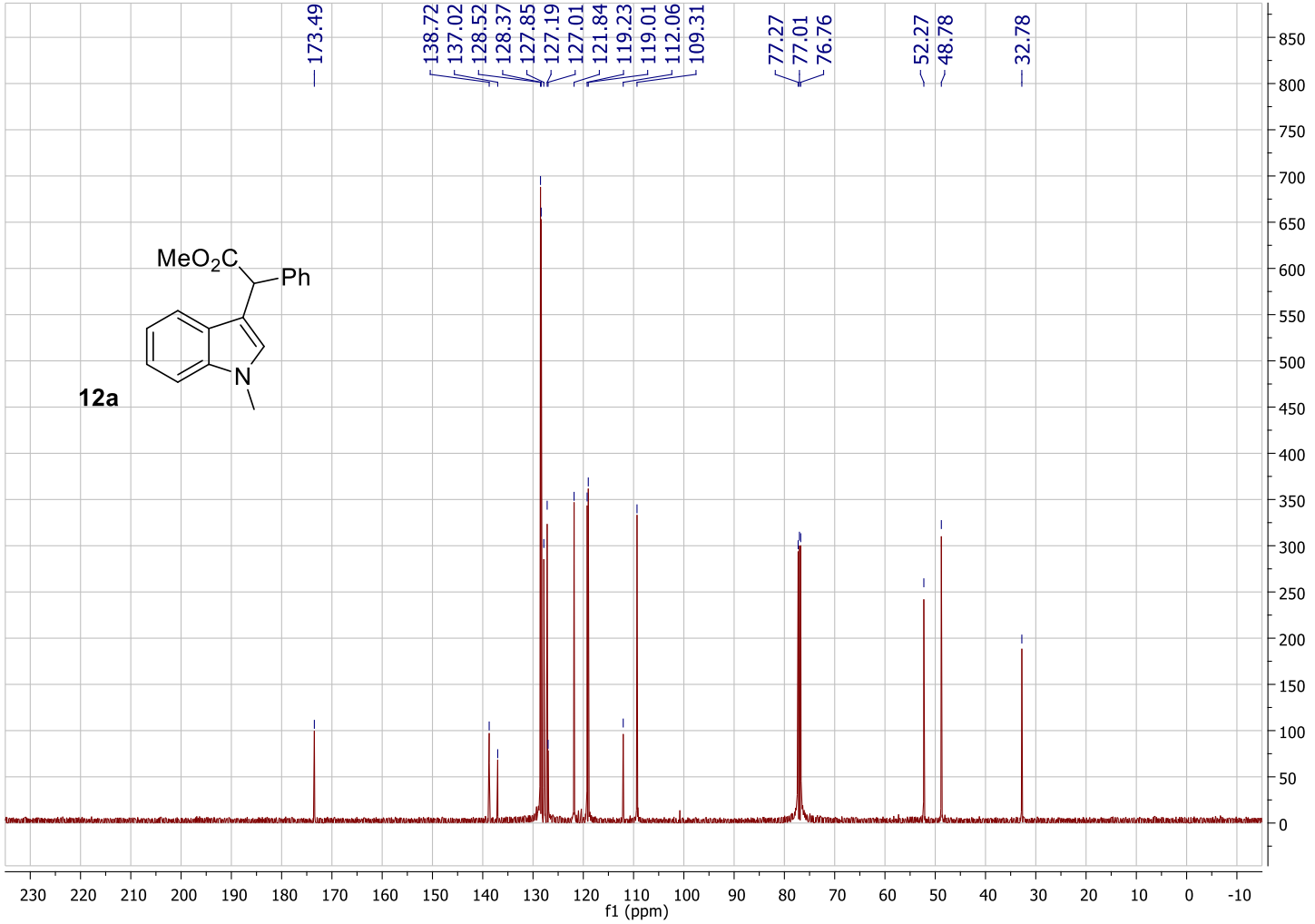


4.7 Products Derived from C-H Insertion or Cyclopropanation of Arenes

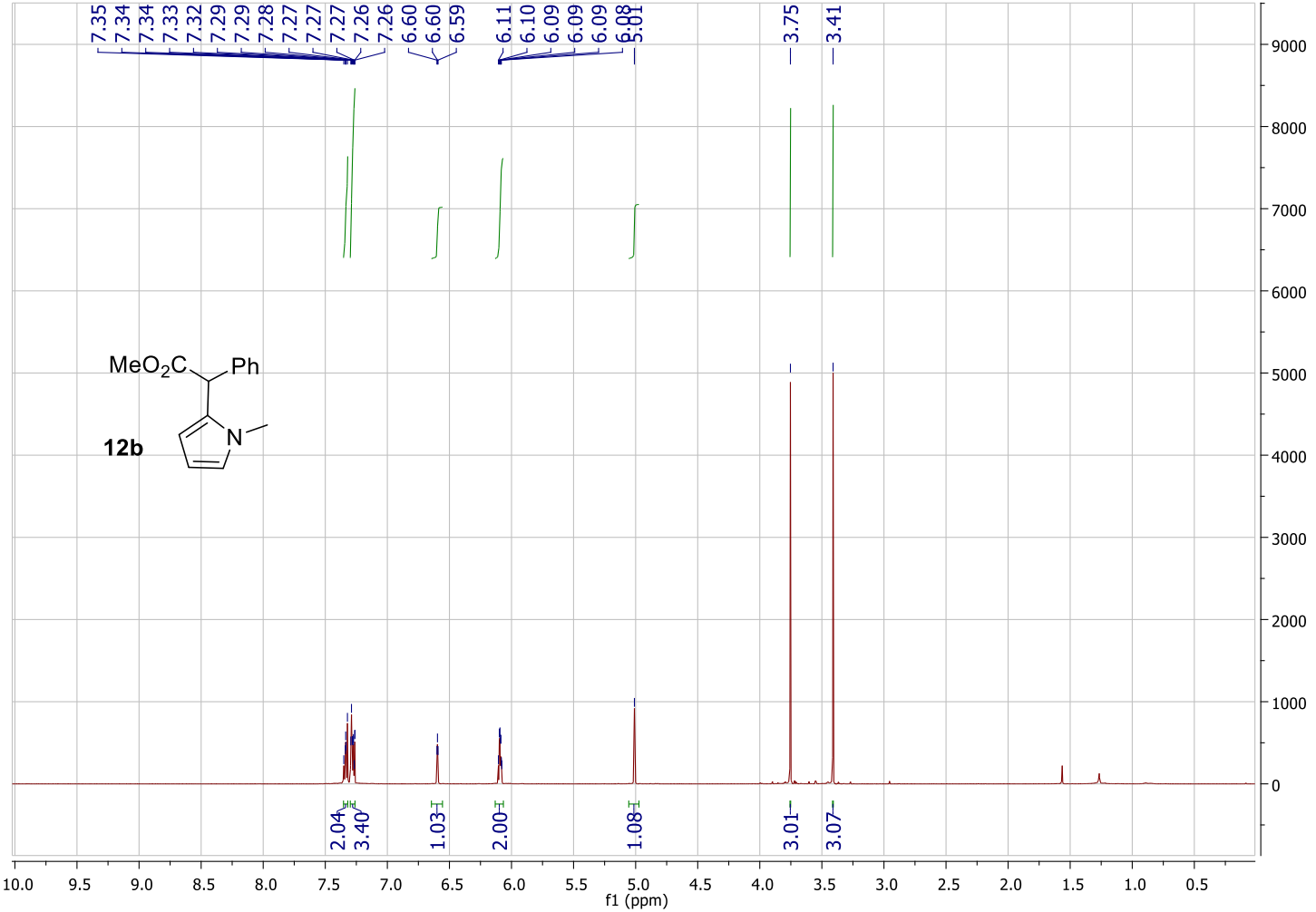
500MHz, $CDCl_3$



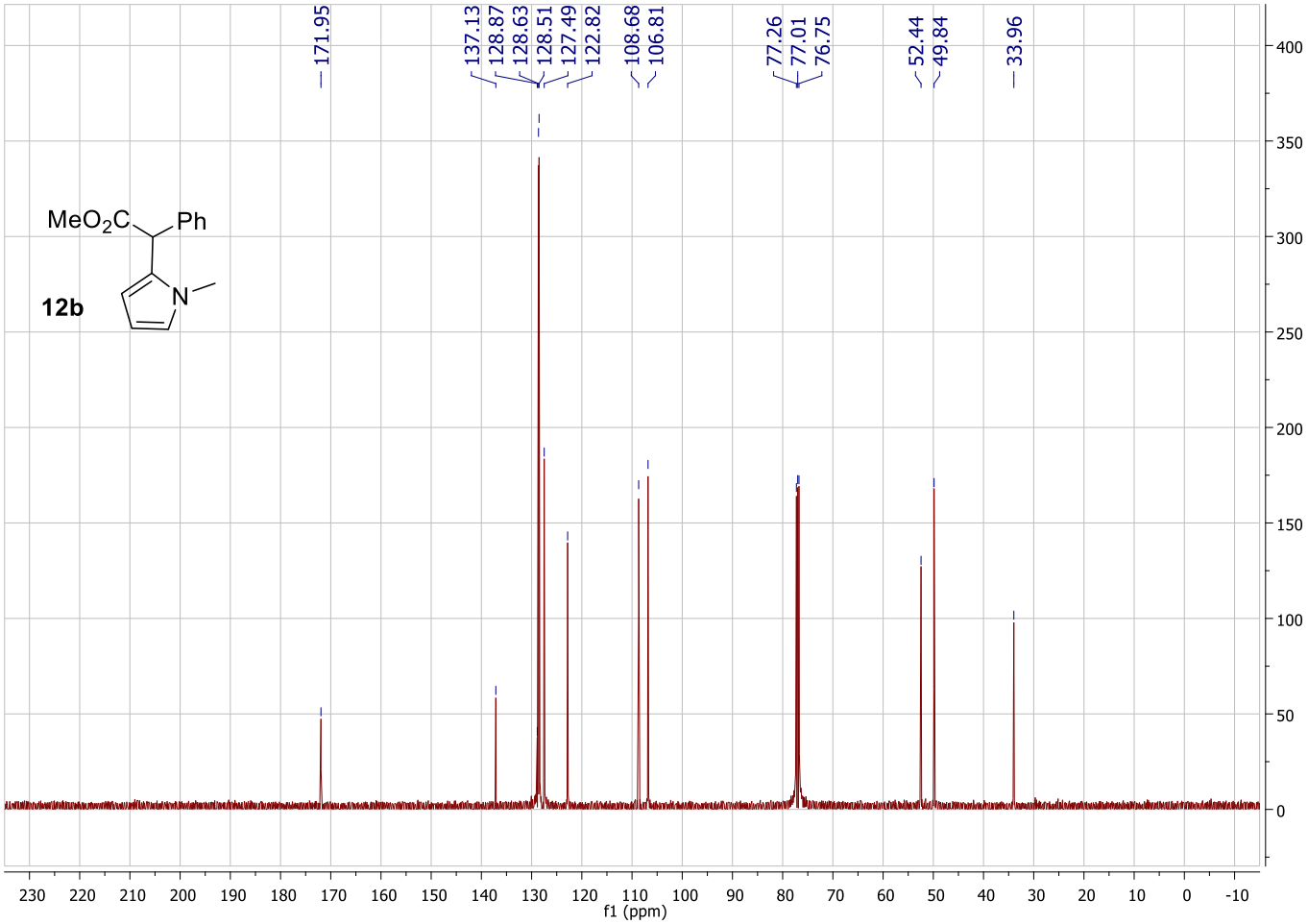
500MHz, $CDCl_3$



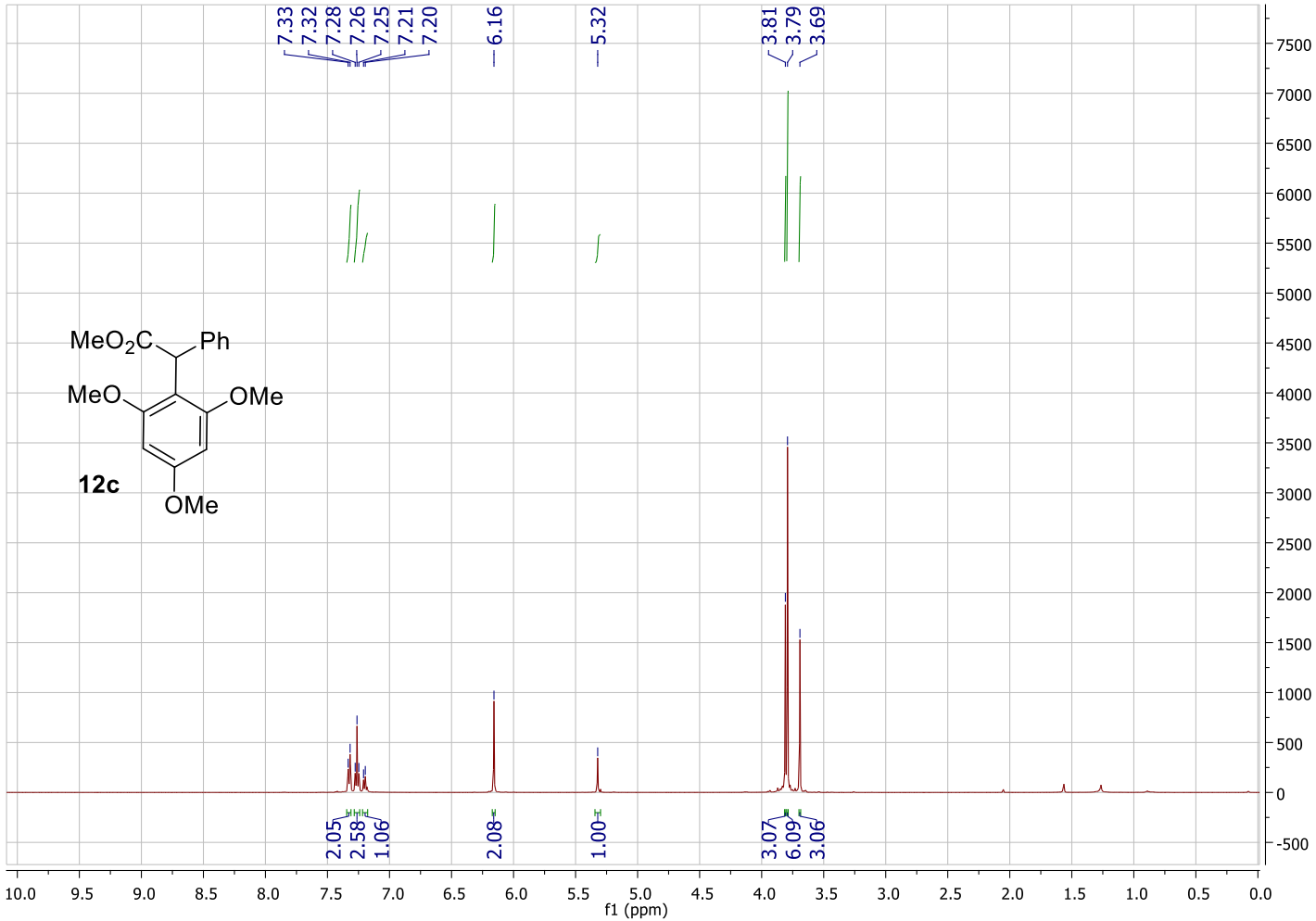
500MHz, $CDCl_3$



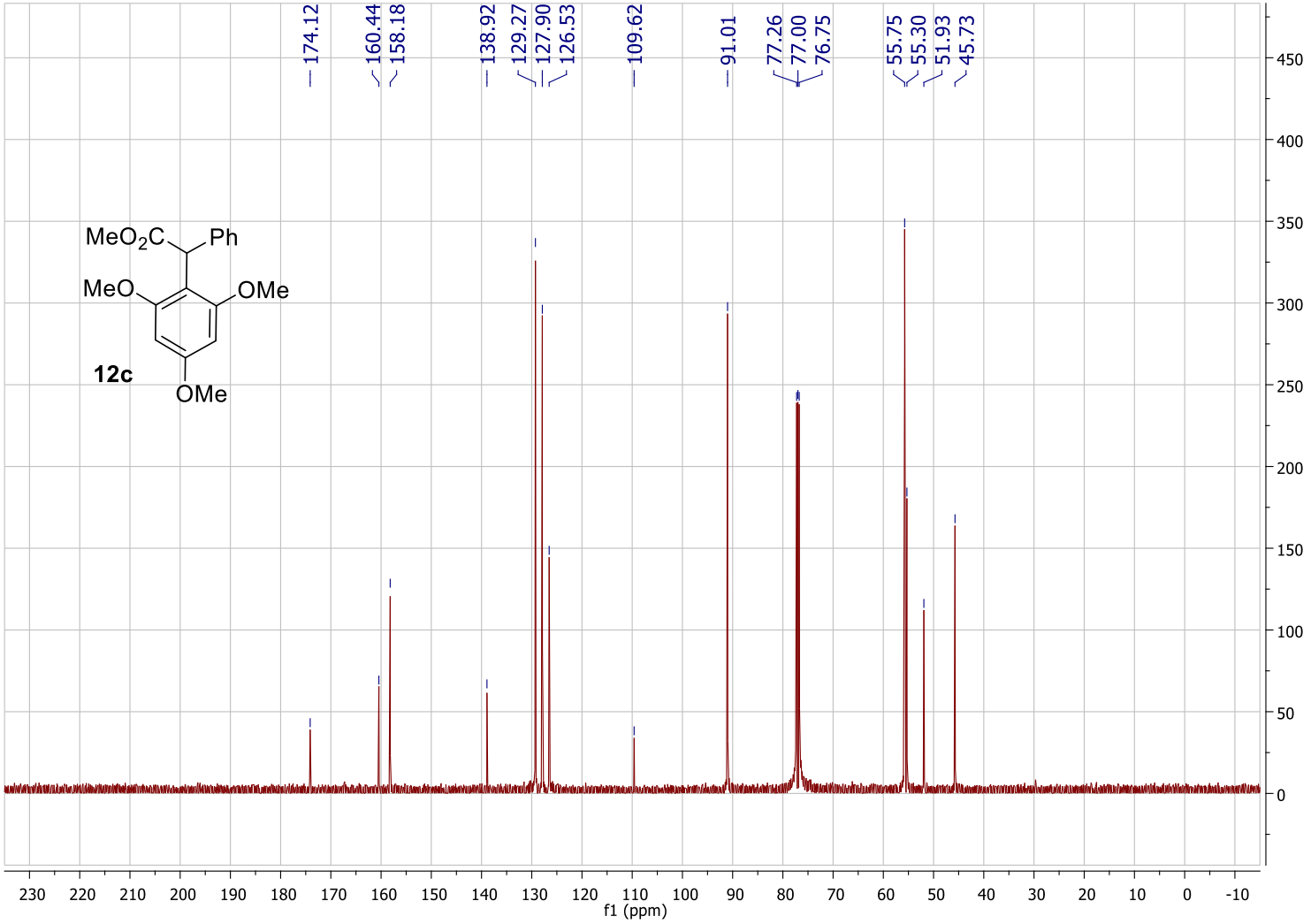
125MHz, $CDCl_3$



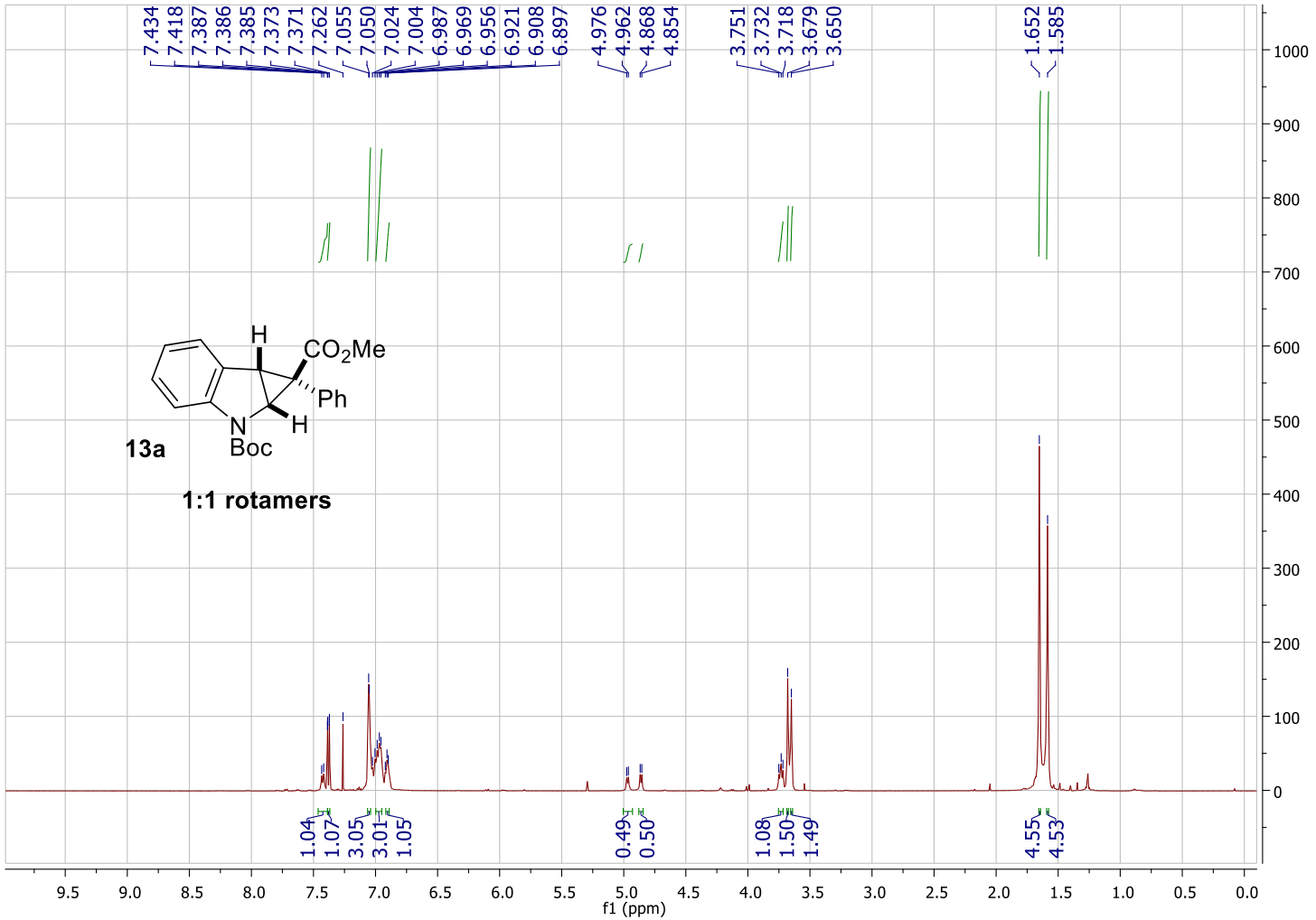
500MHz, $CDCl_3$



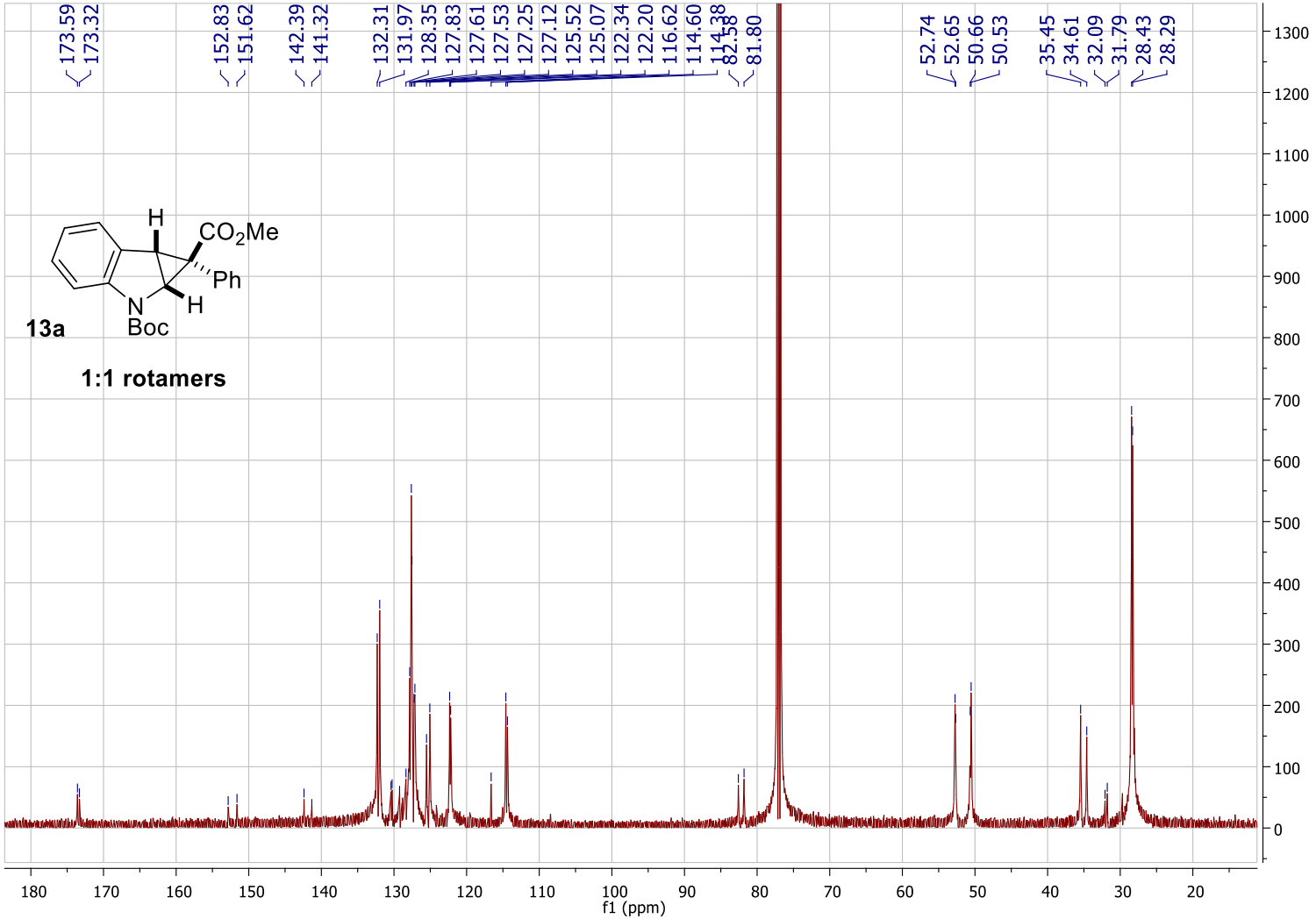
125MHz, $CDCl_3$



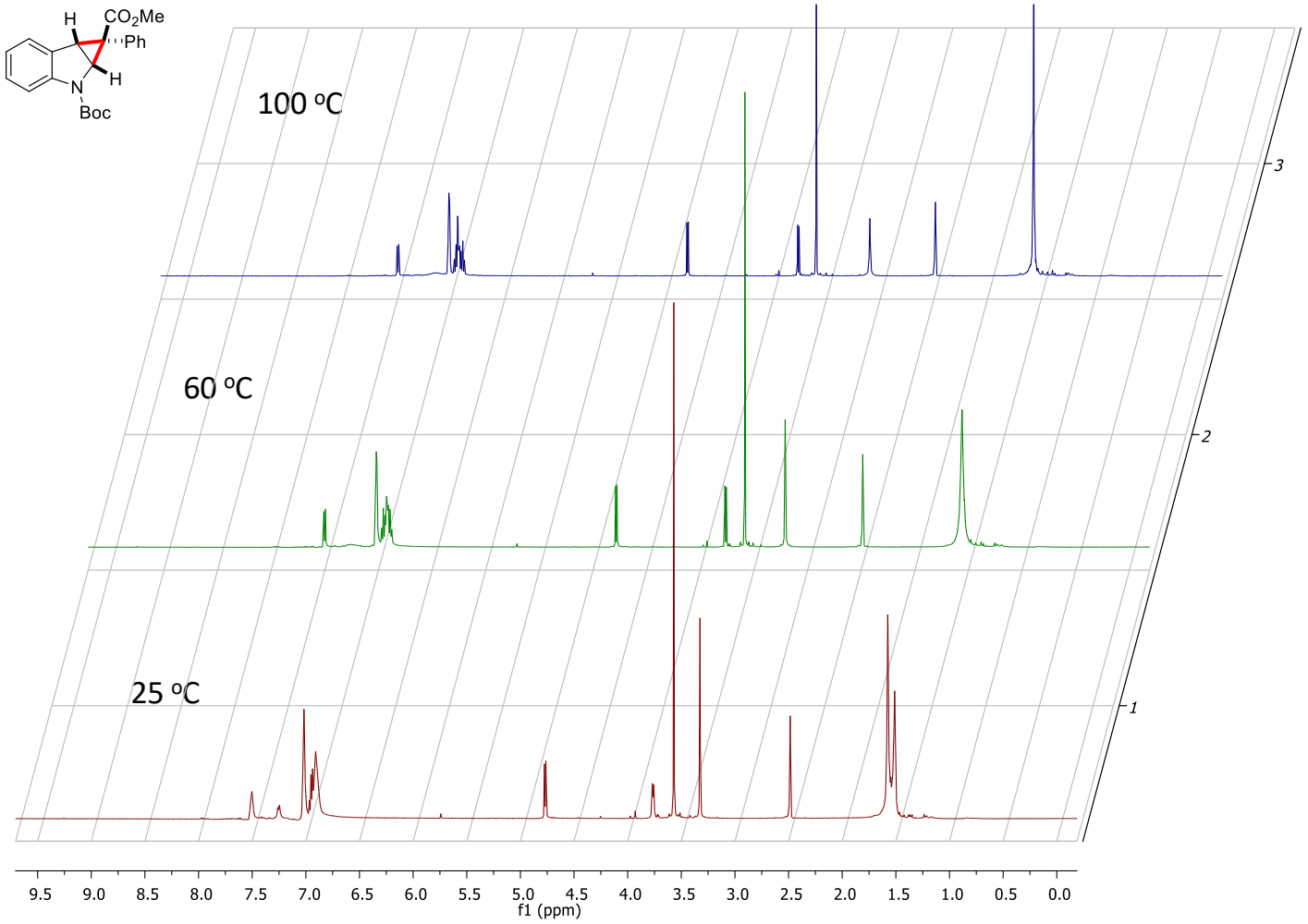
500MHz, $CDCl_3$



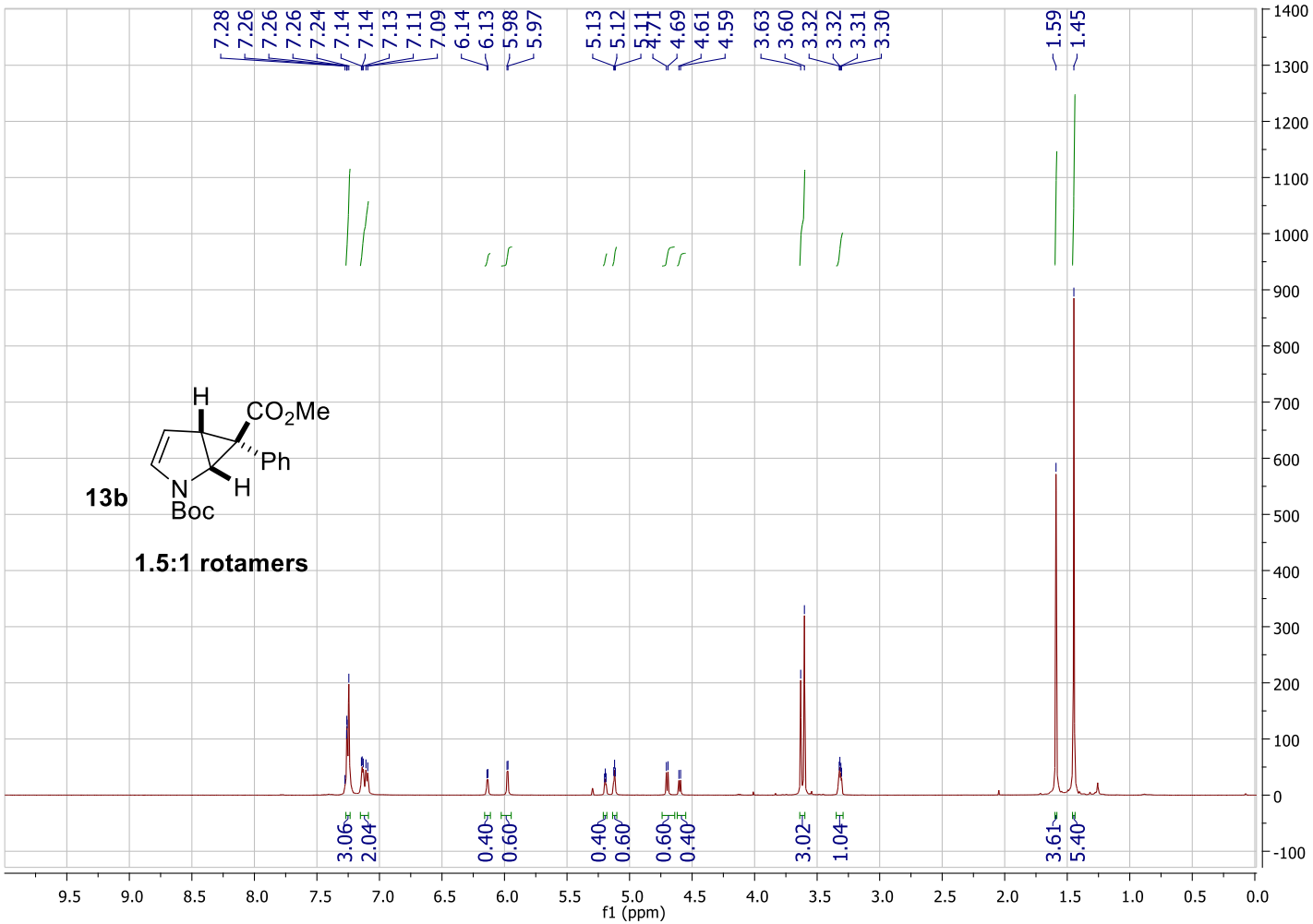
125MHz, $CDCl_3$



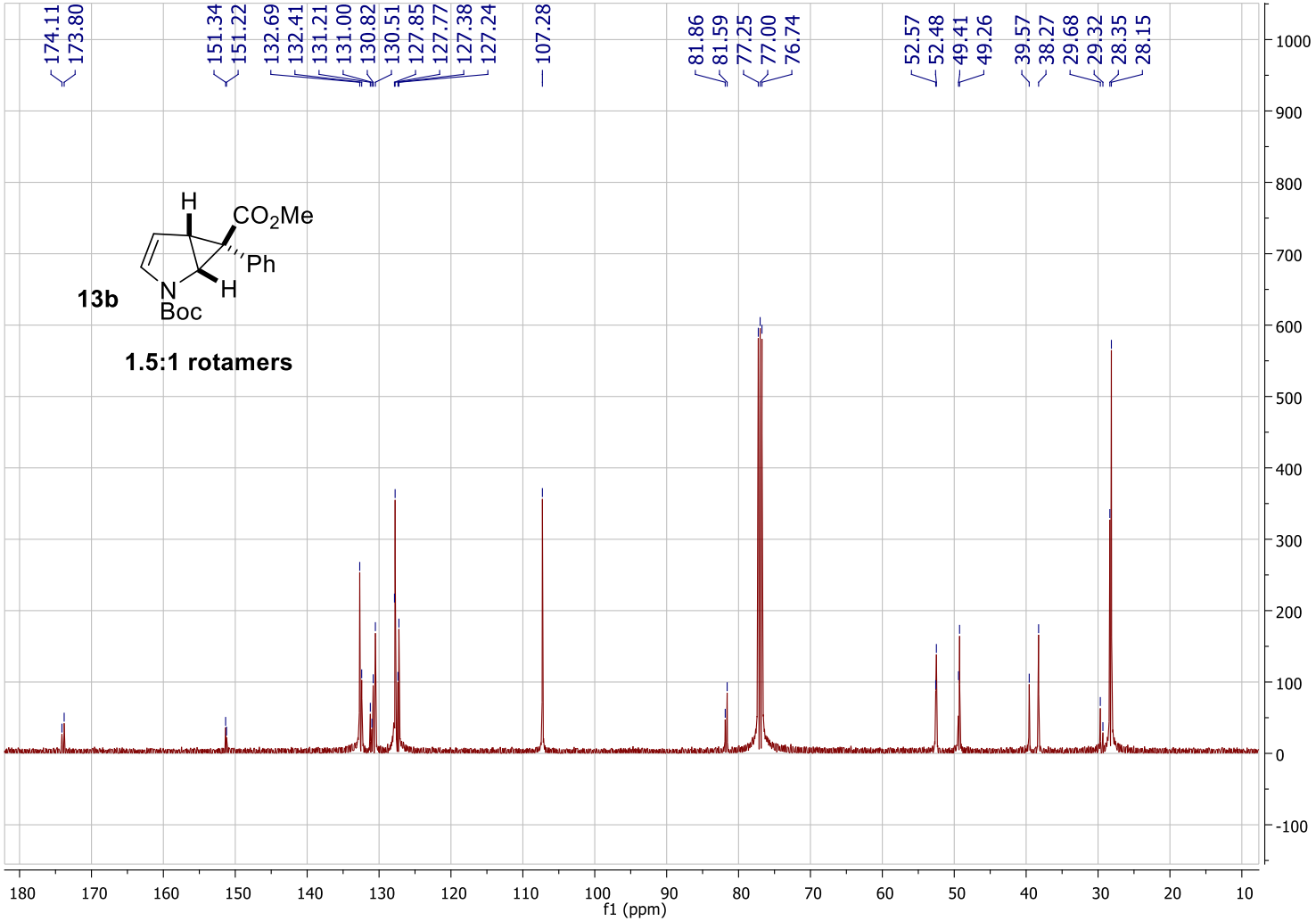
^{1}H NMR of 13a in d^{6}-DMSO, 500MHz, at high temperatures:



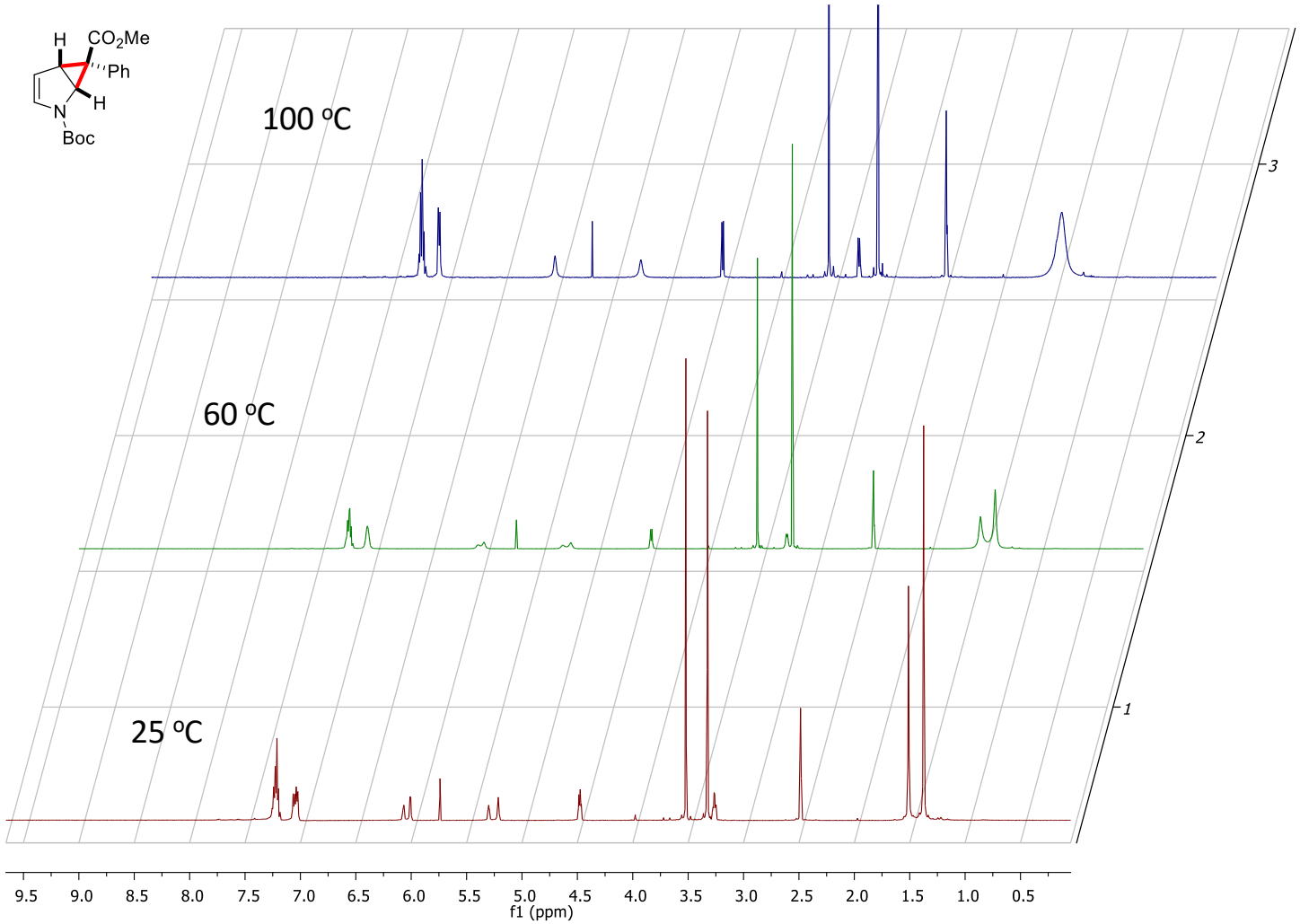
500MHz, $CDCl_3$



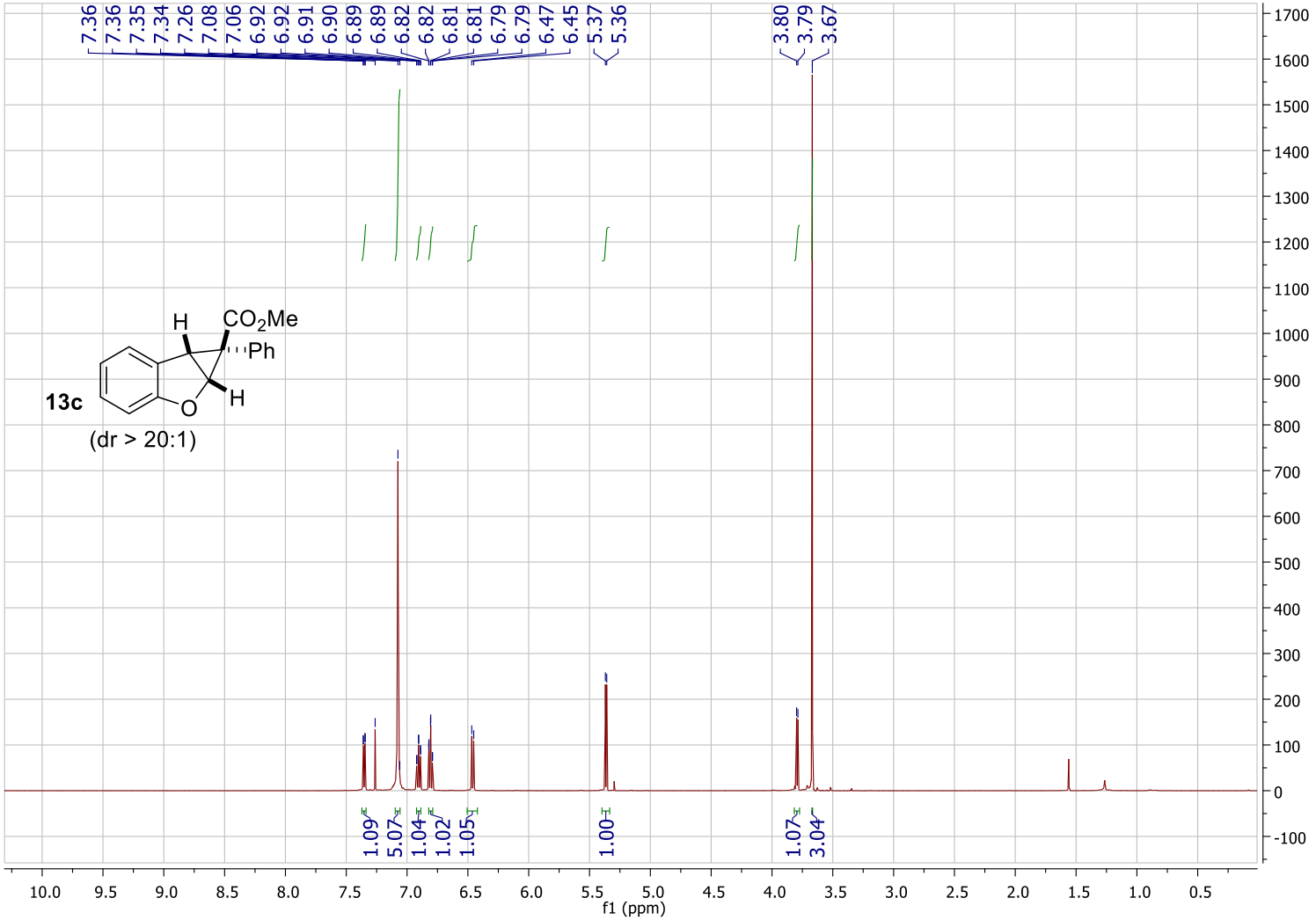
125MHz, $CDCl_3$



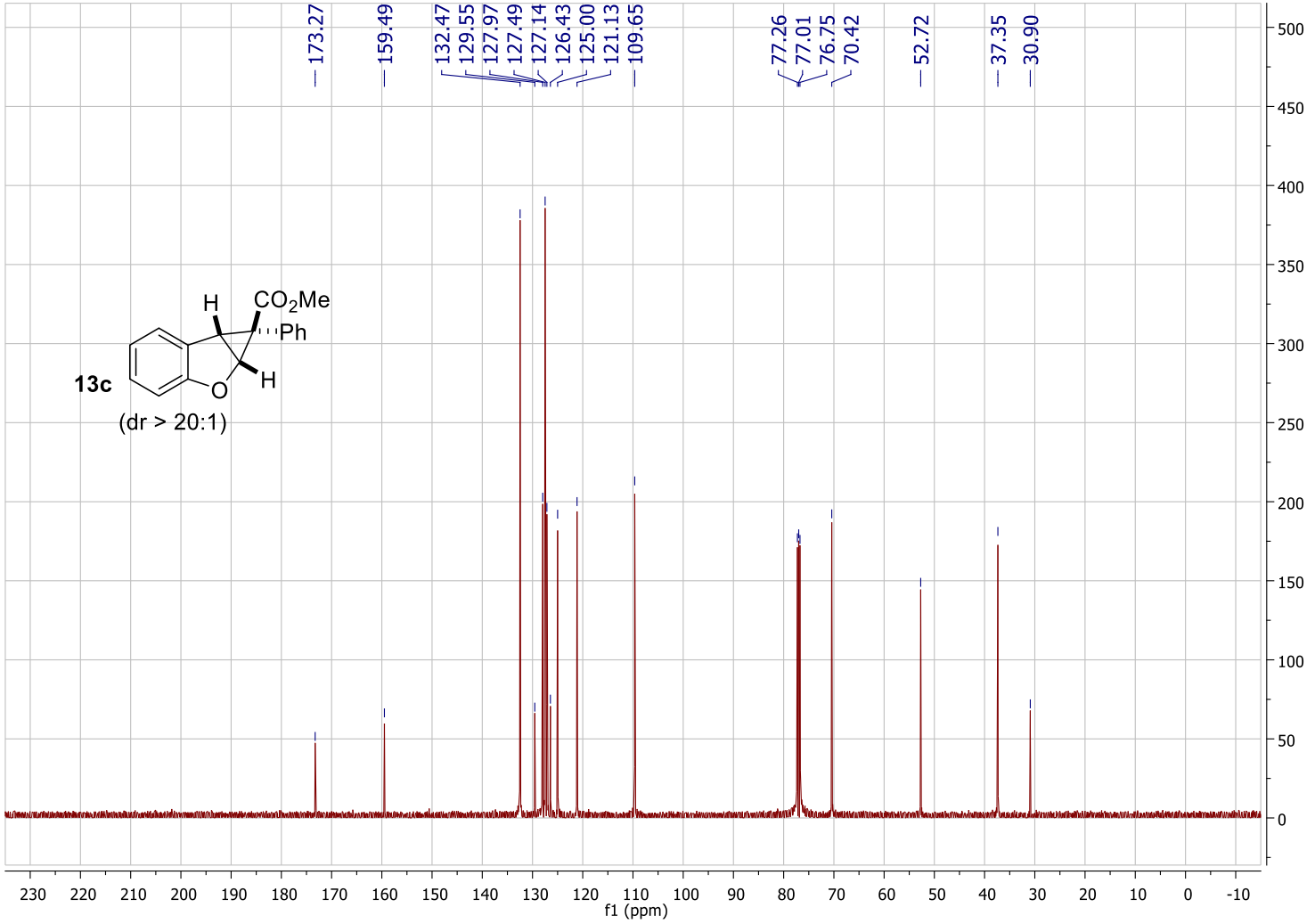
^{1}H NMR of 13b in d^{6}-DMSO, 500MHz, at high temperatures:



500MHz, $CDCl_3$

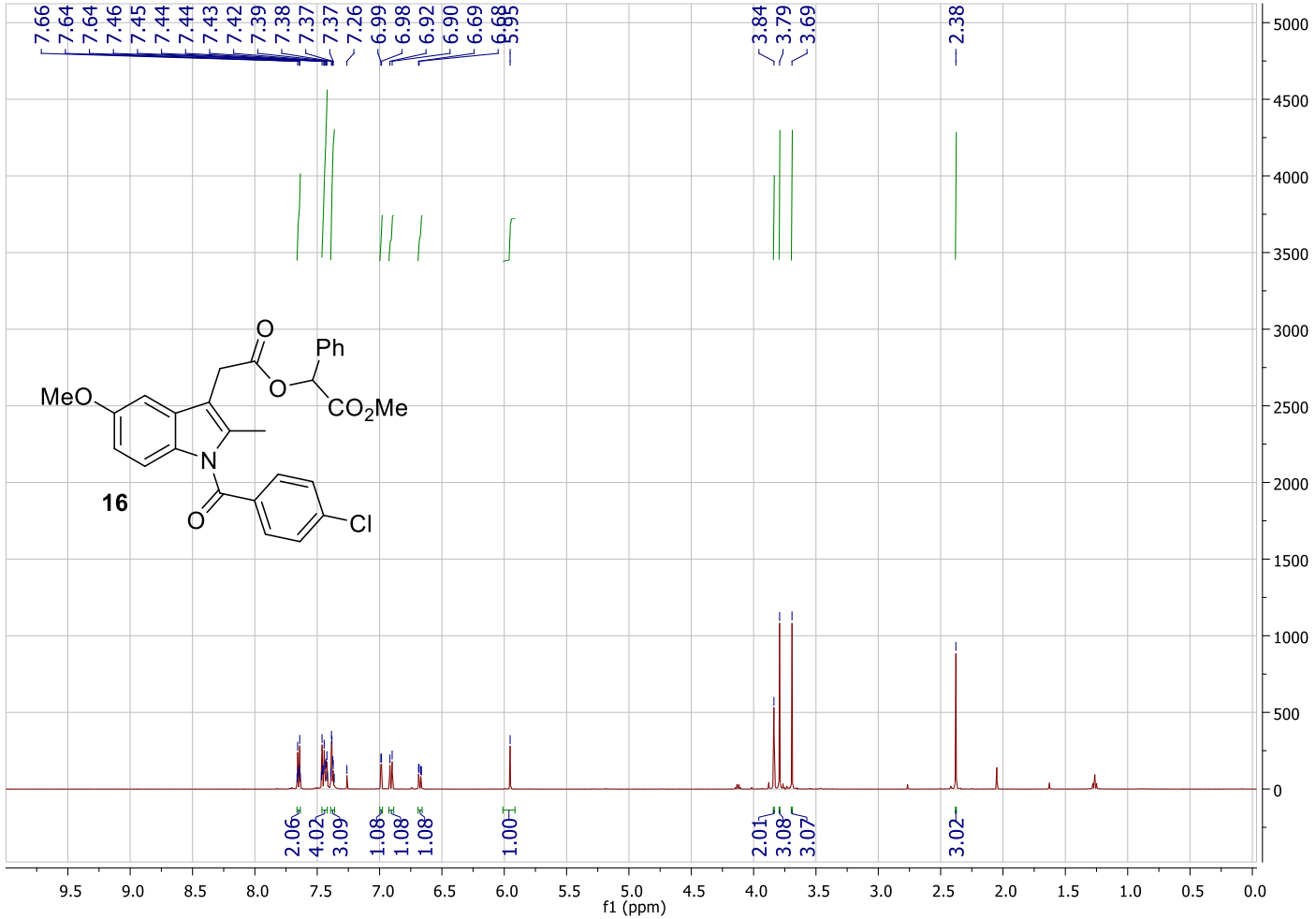


125MHz, $CDCl_3$

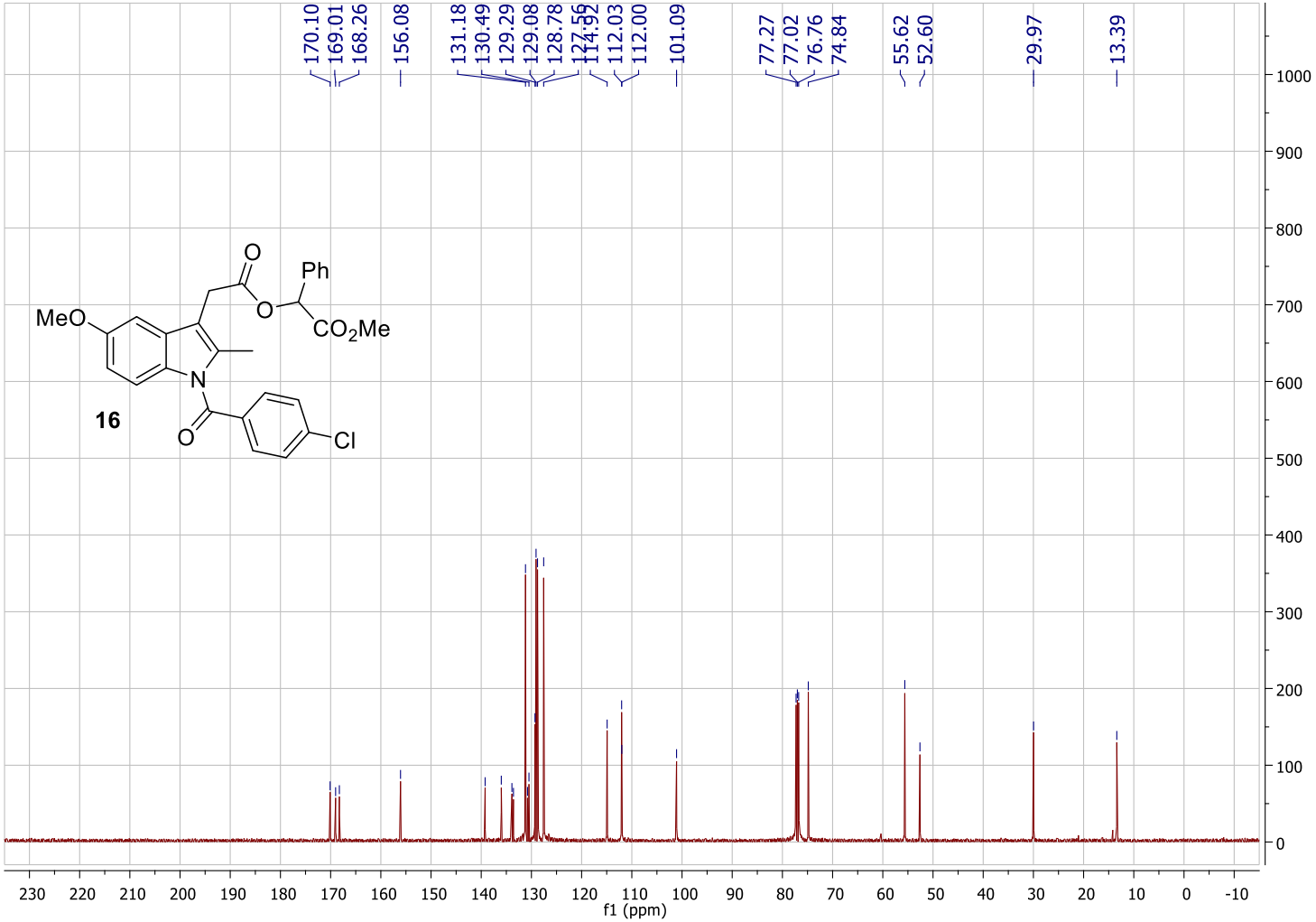


4.8 Products derived form the Functionalization of Complex Molecules

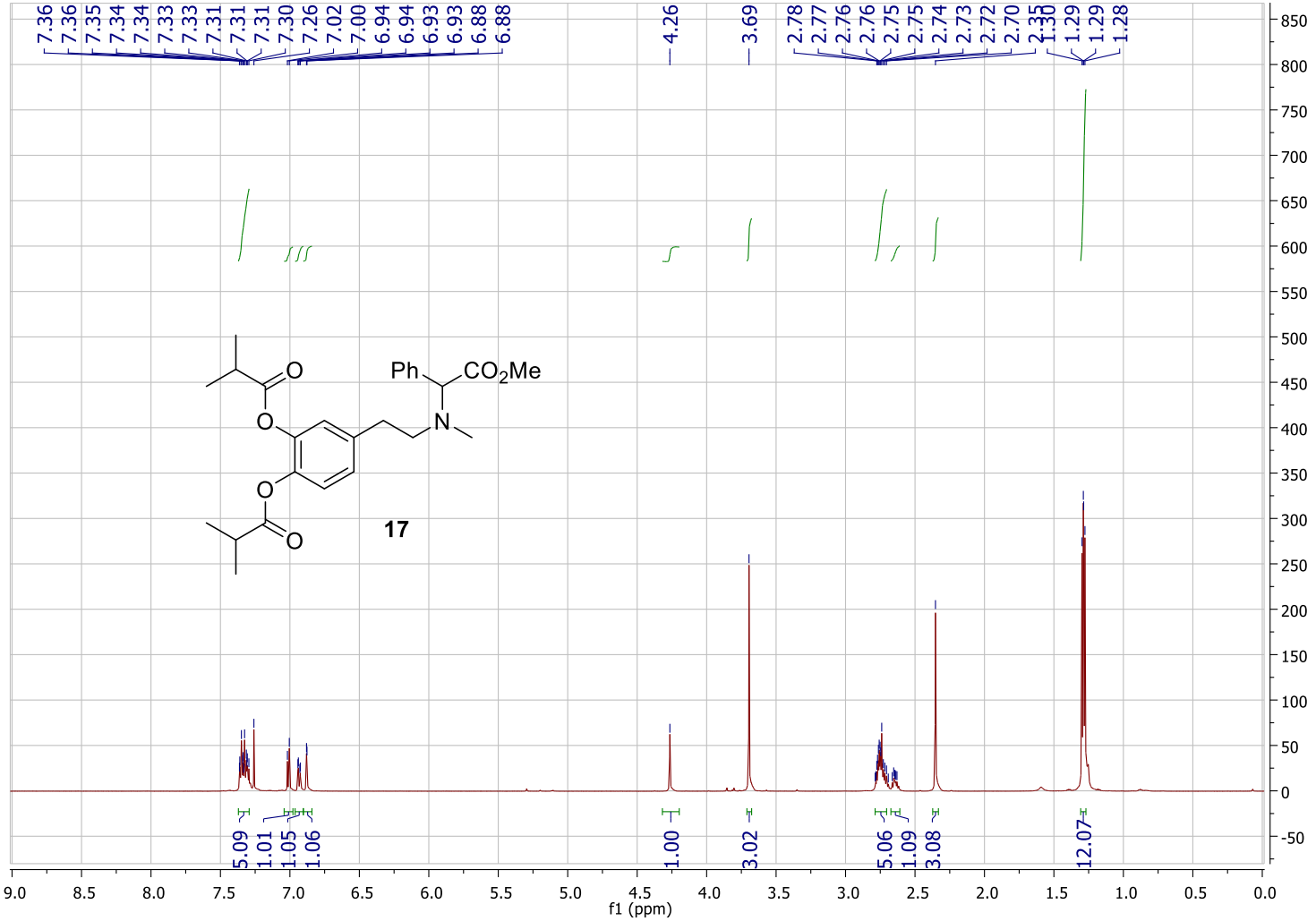
500MHz, $CDCl_3$



125MHz, $CDCl_3$



500MHz, $CDCl_3$



150MHz, $CDCl_3$