One-pot ester and thioester formation mediated by pentafluoropyridine (PFP)

Liam N. D. Beardmore,[a] Steven L. Cobb *[a] and William D. G. Brittain *[a]

[a] Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, United Kingdom

*Corresponding Author email: william.d.brittain@durham.ac.uk s.l.cobb@durham.ac.uk

Contents

Experimental

General

All starting materials and reagents were purchased from commercial sources and used as received. MeCN was dried over 4 Å molecular sieves which had been dried under vacuum at 150 °C for 3 h. All reactions were conducted under an atmosphere of air. Column chromatography was carried out on silica purchased from Fluorochem using hexane/ethyl acetate solvent systems or using a Combiflash Nextgen 100 equipped with a 4g redisep column using hexane/ethyl acetate solvent systems.

^{1}H NMR spectra were recorded at 400 or 600 MHz using Bruker Avance III or Varian VNMRS-600 spectrometers respectively. ^{13}C NMR spectra were recorded at 100 or 151 MHz using a Bruker Avance III or Varian VNMRS-600 respectively. ^{19}F NMR spectra were recorded at 376 MHz using a Bruker Avance III spectrometer. All coupling constants are reported in Hertz (Hz). In cases where it was required 2D NMR techniques were used to confirm compound identity. Chemical shifts are reported in ppm and are referenced to residual solvent peaks; $CHCl_3$ (^{1}H 7.26 ppm, ^{13}C 77.0 ppm), CH_3CN (^{1}H 1.94 ppm, ^{13}C ppm) or DMSO (^{1}H 2.50 ppm, ^{13}C 39.5 ppm).

Mass spectra were collected either using ESI-LC or GCMS. ESI-LC in MeCN were collected using a Waters TQD mass spectrometer with a Acquity UPLC BEH C18 1.7 µm (2.1 mm x 50 mm). ESI-LC was collected using water containing formic acid (0.1% v/v) and MeCN mixture in a 95:5 to 5:95 gradient over 5 min. GCMS experiments were carried out on a Shimadzu QP2010-Ultra with a Rxi-5Sil MS (0.15µm x 10m x 0.15 mm). Helium was employed as the carrier gas (0.41 mL/min). EI is carried at 70ev and the working mass range is 35 – 650 u for all GCMS experiments.

ASAP samples were run isothermally at 350 °C vaporising the sample to enable atmospheric pressure chemical ionisation.

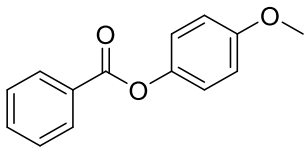
General procedure for the synthesis of esters

To an oven dried glass vial or Radley's carousel tube equipped with a stirrer bar was added carboxylic acid (1.0 equiv.), acetonitrile dried over 4 Å molecular sieves (3 mL), diisopropylethylamine (DIPEA) (2.0 equiv.) and pentafluoropyridine (PFP) (1.1 equiv.). This mixture was allowed to stir at 50 °C for 4 h, at which point the desired alcohol (1.0 equiv.) was added. The mixture was then stirred at 50 °C for 16 h. Following this time, the mixture was concentrated under reduced pressure, the resulting residue was dissolved in a minimum amount of DCM and the recovered crude material was purified directly by flash column chromatography which yielded the desired compounds.

General procedure for the synthesis of thioesters

To an oven dried glass vial or Radley's carousel tube equipped with a stirrer bar was added carboxylic acid (1.0 equiv.), acetonitrile dried over 4 Å molecular sieves (3 mL), diisopropylethylamine (DIPEA) (2.0 equiv.) and pentafluoropyridine (1.1 equiv.). This mixture was allowed to stir for a period of 4 h, after which thiol (1.0 equiv.) was added. The mixture was then allowed to stir at 50 °C for 16 h after this time, the mixture was allowed to cool, was concentrated under reduced pressure, and the resulting residue was dissolved in a minimum amount of dichloromethane (DCM) and purified directly by flash column chromatography which yielded the desired compounds**.**

Synthesis of 4-methoxyphenyl benzoate (5a)



Synthesised according to the general method for esterification from benzoic acid (0.102 g, 0.84 mmol) and 4-methoxyphenol (0.105 g, 0.86 mmol). The crude material was purified by flash column chromatography (100% hexane to 2.5% EtOAc 97.5% hexane) to give the desired product as a white solid in 71% yield (0.135 g).

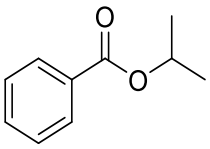
Characterisation data was consistent with previously reported literature values.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.22 (m, 2H), 7.64 (t, *J* = 7.5 , 1H), 7.52 (t, *J* = 7.5 , 2H), 7.17 (d, *J* = 9.1, 2H), 6.97 (d, *J* = 9.1 , 2H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 157.3, 144.4, 133.5, 130.1, 129.6, 128.6, 122.5, 114.5, 55.6.

LCMS (ESI^+) rt = 2.7 mins, *m/z* = 229.2 $[M+H]^+$

Synthesis of isopropyl benzoate (5b)



Synthesised according to the general method for esterification from benzoic acid (0.105 g, 0.86 mmol) and isopropanol (0.057 g, 0.095 mmol). The crude material was purified by automated flash column chromatography combiflash (eluted in 100% hexanes) to give the desired product as a colourless oil in 41% yield (0.055g).

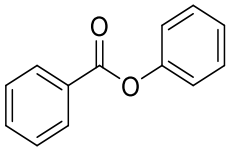
Characterisation data was consistent with previously reported literature values.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.56 – 7.52 (m, 1H), 7.43 (ddt, *J* = 8.1, 6.8, 1.0, 2H), 5.26 (hept, *J* = 6.3 , 1H), 1.37 (d, *J* = 6.3 , 6H).

^{13}C NMR (101 MHz, CDCl3) δ 166.2, 132.8, 131.0, 129.6, 128.4, 68.4, 22.0.

GCMS (EI^+) r.t = 3.3 mins, *m/z* = 164.1 $[M]^+$

Synthesis of phenyl benzoate (5d)



Synthesised according to the general method for esterification from benzoic acid (0.100 g, 0.82 mmol) and phenol (0.082 g, 0.87 mmol). The crude material was purified by flash column chromatography (100% hexane to 5% EtOAc 95% hexane) to give the desired product as a white solid 80% yield (0.130 g)

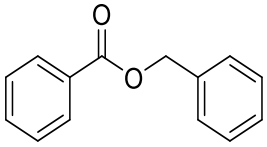
Characterisation data were consistent with previously reported literature values.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.26 (m, 2H), 7.71 – 7.66 (m, 1H), 7.59-7.54 (m, 2H), 7.51 – 7.46 (m, 2H), 7.35 – 7.26 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 151.1, 133.7, 130.3, 130.2, 130.1, 129.7, 129.6, 128.7, 126.0, 121.82.

LCMS (ESI^+) r.t. = 2.8 mins, *m/z* = 199.2 $[M+H]^+$

Synthesis of benzyl benzoate (5e)



Synthesised according to the general method for esterification from benzoic acid (0.101 g, 0.83 mmol) and benzyl alcohol (0.090 g, 0.83 mmol). The crude material was purified by flash column chromatography (100% hexane to 2.5% EtOAc 97.5% hexane) to give the desired product as a colourless oil in 72% yield (0.122 g)

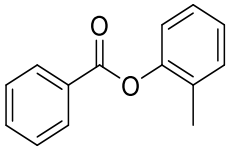
Characterisation data were consistent with previously reported literature values.[3]

^{1}H NMR (599 MHz, $CDCl_3$) δ 8.15-8.12z (m, 2H), 7.60-7.56 (m, 1H), 7.51 – 7.38 (m, 7H), 5.41 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 136.4, 133.3, 130.5, 130.0, 128.9, 128.7, 128.5, 128.5, 67.0.

GCMS (EI^+) – r.t. = 4.8 mins, *m/z*= 212.1 $[M]^+$

Synthesis of o-tolyl benzoate (5f)



Synthesised according to the general method for esterification from benzoic acid (0.101, 0.83 mmol) and *o*-cresol (0.092 g, 0.85 mmol). The crude material was purified using automated flash column chromatography combiflash (100% Hexane for 4 mins to 40% EtOAc 60% Hexane for 10 mins) to give the desired product as a clear oil in 67% yield (0.116 g).

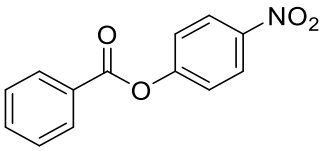
Characterisation data were consistent with previously reported literature values.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.27 (m, 2H), 7.68 – 7.66 (m, 1H), 7.58 – 7.54 (m, 2H), 7.33 – 7.18 (m, 4H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 149.6, 133.7, 131.3, 130.4, 130.2, 129.6, 128.7, 127.1, 126.2, 122.1, 16.3.

LCMS (ESI^+) r.t. = 2.9 mins, *m/z* =213.3 $[M+H]^+$

Synthesis of 4-nitrophenyl benzoate (5g)



Synthesised according to the general method for esterification from benzoic acid (0.101 g, 0.83 mmol) and 4-nitrophenol (0.112 g, 0.81 mmol). The crude material was purified by flash column chromatography (100% hexane to 2.5% EtOAc 97.5% hexane) to give the desired product as a white solid in 58% yield (0.115 g)

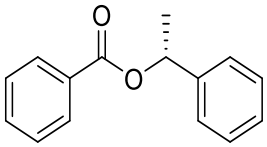
Characterisation data were consistent with previously reported literature values.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.28 (m, 2H), 8.24 – 8.18 (m, 2H), 7.71-7.64 (m, 1H), 7.58 – 7.51 (m, 2H), 7.46 – 7.39 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 155.8, 145.5, 134.4, 130.4, 128.9, 128.6, 125.4, 122.8.

LCMS (ESI^-)- r.t. = 3.8 mins, *m/z* =242.1 $(M)^-$

Synthesis of (5h)



Synthesised according to the general method for esterification from benzoic acid (0.103 g, 0.84 mmol) and (*S*)-(-)-1-phenylethanol (0.102 g, 0.83 mmol). Purified using automated column chromatography combiflash (eluted in 100% hexanes) to give the desired product as a clear oil in 48% yield (0.091 g).

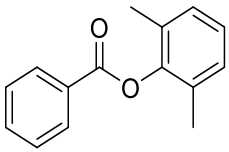
Characterisation data were consistent with previously reported literature values.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.10 (m, 2H), 7.69 – 7.55 (m, 1H), 7.49 – 7.43 (m, 4H), 7.42 – 7.37 (m, 2H), 7.35 – 7.30 (m, 1H), 6.16 (q, *J* = 6.6, 1H), 1.70 (d, *J* = 6.6, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 141.8, 133.0, 130.6, 129.7, 128.6, 128.4, 127.9, 126.1, 73.0, 22.5.

GCMS (EI^+) r.t. = 4.8 mins, *m/z* =226.2 $[M]^+$

Synthesis of 2,6-dimethylphenyl benzoate (5i)



Synthesised according to the general method for esterification from benzoic acid (0.099 g, 0.81 mmol) and 2,6-dimethylphenol (0.103 g, 0.84 mmol). The crude material was purified using automated flash column chromatography combiflash (eluted in 100% hexanes) to give the desired product as a clear oil in 92% yield (0.172 g).

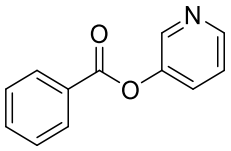
Characterisation data was consistent with previously reported literature values.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.28 (m, 2H), 7.70 – 7.66 (m, 1H), 7.58 – 7.54 (m, 2H), 7.16 – 7.11 (m, 3H), 2.24 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 148.4, 133.7, 130.5, 130.3, 129.4, 128.8, 128.7, 126.0, 16.5.

LCMS (ESI^+) r.t. = 3.1 mins, *m/z* = 227.2 $[M+H]^+$

Synthesis of pyridine-3-yl-benzoate (5j)



Synthesised according to the general method for esterification from benzoic acid (0.100 g, 0.82 mmol) and 3-hydroxypyridine (0.081 g, 0.85 mmol). The crude material was purified by flash column chromatography (100% hexane to 5% EtOAc 95% hexane) to give the desired product as an orange solid in 80% yield (0.130 g).

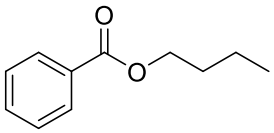
Characterisation data was consistent with previously reported literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56-8.55 (m, 1H), 8.54 (dd, *J* = 4.8, 1.4 , 1H), 8.24 – 8.18 (m, 2H), 7.69 – 7.64 (m, 1H), 7.62 (ddd, *J* = 8.3, 2.7, 1.4 , 1H), 7.53 – 7.48 (m, 2H), 7.36 (ddd, *J* = 8.3, 4.8, 0.7, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 147.6, 147.0, 143.6, 134.0, 130.3, 129.4, 128.8, 128.7, 124.0

LCMS (ESI^+) r.t. = 2.5 mins, *m/z* = 200.1 $[M+H]^+$

Synthesis of butyl benzoate (5k)



Synthesised according to the general method for esterification from benzoic acid (0.100 g, 0.82 mmol) and butan-1-ol (0.067 g, 0.90 mmol). The crude material was purified by flash column chromatography (100% hexane to 5% EtOAc 95% hexane) to give the desired product as a clear oil in 64% yield (0.093 g).

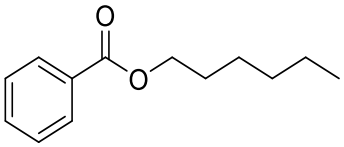
Characterisation data was consistent with previously reported literature values.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 2H), 7.56 – 7.52 (m, 1H), 7.45 – 7.40 (m, 2H), 4.32 (t, *J* = 6.6, 2H), 1.79 – 1.71 (m, 2H), 1.53 – 1.43 (m, 2H), 0.98 (t, *J* = 7.4, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.68, 132.80, 130.54, 129.54, 128.32, 64.83, 30.80, 19.30, 13.79.

LCMS (ESI^+) r.t. = 2.9 mins, *m/z* = 179.2 $[M+H]^+$

Synthesis of hexyl benzoate (5l)



Synthesised according to the general method for esterification from benzoic acid (0.100g, 0.82 mmol) and hexan-1-ol (0.089 g, 0.87 mmol). The crude material was purified by automated flash column chromatography (100% hexane) to give the desired product as a clear oil in 78% yield (0.131 g).

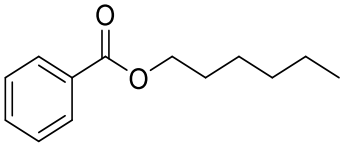
Characterisation data was consistent with reported literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 2H), 7.58 – 7.49 (m, 1H), 7.48 – 7.36 (m, 2H), 4.31 (t, *J* = 6.7 , 2H), 1.76 (dq, *J* = 8.0, 6.7 , 2H), 1.53 – 1.37 (m, 2H), 1.40 – 1.29 (m, 4H), 0.97 – 0.85 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 132.8, 130.6, 129.6, 128.4, 77.5, 77.1, 76.8, 65.2, 31.5, 28.8, 25.8, 22.6, 14.1.

LCMS (ESI^+) r.t. = 3.4 mins, *m/z* = 207.3 $[M+H]^+$

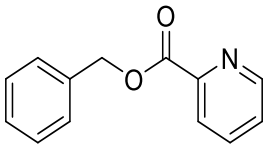
Gram Synthesis of hexyl benzoate (5l)



Following the general method but in a round bottomed flask, using 10 mL of MeCN. Synthesised from benzoic acid (1.001 g, 8.2 mmol) and hexan-1-ol (0.871 g, 8.5 mmol). Purified by automated column chromatography (100% hexane) to yield the desired product as a clear oil in 61% yield (1.030 g)

Characterisation data were consistent with those previously recorded fo **(5k)**

Synthesis of Benzyl picolinate (5m)



Synthesised according to the general method for esterification from picolinic acid (0.105 g, 0.85 mmol) and benzyl alcohol (0.88 g, 0.81 mmol). Purified using automated column chromatography combiflash (100% Hexane to 60% Hexane 40% EtOAc gradient) to give the desired product as a red coloured oil in 68% yield (0.118 g)

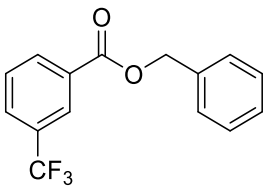
Characterisation data were consistent with previously reported literature values.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (ddd, *J* = 4.8, 1.8, 0.9 , 1H), 8.10 (dt, *J* = 7.9, 1.1 , 1H), 7.78 (td, *J* = 7.8, 1.8 , 1H), 7.50 – 7.26 (m, 6H), 5.44 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 149.9, 147.9, 137.0, 135.6, 128.6, 128.5, 128.4, 126.9, 125.2, 67.4.

GCMS (EI^+) r.t. = 4.9 mins, *m/z* 213.1 $[M]^+$

Synthesis of benzyl 3-(trifluoromethyl)benzoate (5n)



Synthesised according to the general method for esterification from 3-(trifluoromethyl)benzoic acid (0.105 g, 0.55 mmol) and benzyl alcohol (0.064 g, 0.59 mmol). Purified using automated flash column chromatography combiflash (eluted in 100% hexane) to give the desired product as a colourless oil in 55% yield (0.085 g).

Characterisation data were consistent with previously reported literature values.[9]

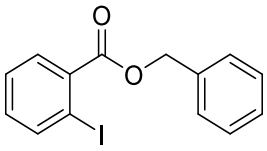
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (app s, 1H), 8.31 – 8.24 (m, 1H), 7.82 (m, 1H), 7.59 (tt, *J* = 7.8, 0.8 , 1H), 7.54 – 7.33 (m, 5H), 5.42 (s, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.75 (s, 3F)

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 135.7, 133.0, 131.2 (q, *J* = 33.0), 129.7 (q, *J* = 3.8), 129.2, 128.8, 128.6, 128.5, 126.7 (q, *J* = 3.8), 125.1, 122.4, 67.4.

GCMS (EI^+) r.t = 4.6 mins, *m/z* = 280.12 $[M]^+$

Synthesis of benzyl 2-iodobenzoate (5o)



Synthesised according to the general method for esterification from 2-iodobenzoic acid (0.100 g, 0.40 mmol) and benzyl alcohol (0.052 g, 0.48 mmol). Purified using automated flash column chromatography combiflash (eluted in 100% hexane) to give the desired product as a colourless oil in 57% yield (0.077 g).

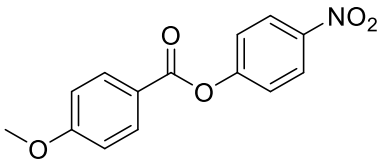
Characterisation data were consistent with previously reported literature values.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.9, 1.2 , 1H), 7.82 (dt, *J* = 7.9, 1.5 , 1H), 7.50 – 7.48 (m, 2H), 7.43 – 7.36 (m, 4H), 7.14 (td, *J* = 7.7, 1.7 , 1H), 5.39 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 141.4, 135.5, 135.0, 132.8, 131.1, 128.7, 128.6, 128.5, 128.0, 94.3, 67.5.

GCMS (EI^+) r.t. = 5.5 mins, *m/z* = 338.1 $[M]^+$

Synthesis of 4-nitrophenyl 4-methoxybenzoate (5p)



Synthesised according to the general method for esterification from 4-methoxybenzoic acid (0.100 g, 0.66 mmol) and 4-nitrophenol (0.096 g, 0.66 mmol). Purified using automated flash

column chromatography combiflash (100% hexane for 6 mins to 50% hexane 50% EtOAc for 12 mins) to give the desired product as a cream solid in 49% yield (0.089 g).

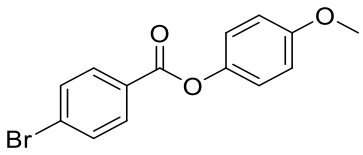
Characterisation data were consistent with previously reported literature values.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (m, 2H), 8.19 – 8.11 (m, 2H), 7.44 – 7.36 (m, 2H), 7.04 – 6.96 (m, 2H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 164.0, 156.1, 145.4, 132.7, 125.3, 122.8, 120.8, 114.2, 55.7.

GCMS (EI^+) r.t. = 6.0 mins, *m/z* = 135.2 $[M]^+$

Synthesis of 4-methoxyphenyl 4-bromobenzoate (5q)



Synthesised according to the general method for esterification from 4-bromobenzoic acid (0.100 g, 0.50 mmol) and 4-methoxyphenol (0.061 g, 0.50 mmol). The crude material was purified by flash column chromatography (eluted in 100% hexane) to give the desired product as a white solid in 50% yield (0.075 g).

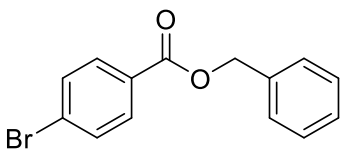
Characterisation data were consistent with previously reported literature values.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.04 (m, 2H), 7.66 – 7.63 (m, 2H), 7.15 – 7.1 (m, 2H), 6.96 – 6.92 (m, 2H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 157.5, 144.3, 132.0, 131.7, 128.8, 128.6, 122.4, 114.6, 55.7.

LCMS (ESI^+) r.t. = 3.1 mins, *m/z* = 307.12 $[M+H]^+$

Synthesis of benzyl 4-bromobenzoate (5r)



Synthesised according to the general method for esterification from 4-bromobenzoic acid (0.104 g, 0.52 mmol) and benzyl alcohol (0.061 g, 0.50 mmol). The crude material was purified by flash column chromatography (100% hexane to 5% EtOAc 95% hexane) to give the desired product as a clear oil in 69% yield (0.100 g).

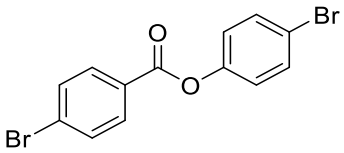
Characterisation data were consistent with previously reported literature values.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.60 – 7.57 (m, 2H), 7.47 – 7.36 (m, 5H), 5.37 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 135.8, 131.8, 131.3, 129.1, 128.7, 128.5, 128.3, 128.3, 67.1.

GCMS (EI^+) r.t. = 5.3 mins, *m/z* = 290.1 $[M]^+$

Synthesis of 4-bromophenyl 4-bromobenzoate (5s)



Synthesised according to the general method for esterification from 4-bromobenzoic acid (0.099 g, 0.49 mmol) and 4-bromophenol (0.087 g. 0.50 mmol). Purified using automated flash column chromatography combiflash (eluted in 100% hexane) to give the product as a white solid in 18% yield (0.031 g).

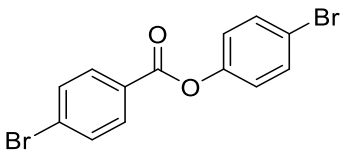
Characterisation data was consistent with previously reported literature values.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.70 – 7.62 (m, 2H), 7.59 – 7.50 (m, 2H), 7.14 – 7.07 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 149.8, 132.6, 132.1, 131.7, 129.1, 128.1, 123.5, 119.2.

GCMS (EI^+) r.t.= 5.7 mins, *m/z* = 353.9, 355.9, 357.9 $[M]^+$

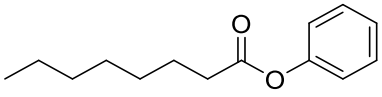
Synthesis of 4-bromophenyl 4-bromobenzoate (5s)



Alternatively synthesised from 4-bromobenzoic acid (0.113 g, 0.56 mmol) and 4-bromophenol (0.094, 0.54 mmol). Following the general method for esterification but heated in a sealed pressure tube at 100°C throughout. Purified using the combiflash equipped with a redisep 12 g column (eluted in 100% hexanes) to yield a white solid in 77% yield (0.148 g).

Characterisation data

Synthesis of Phenyl Octanoate (5t)



Synthesised according to the general method for esterification from octanoic acid (0.099 g, 0.69 mmol) and phenol (0.065 g, 0.69 mmol). The crude material was purified by flash column chromatography (100% hexane to 10% EtOAc 90% hexane) to give the desired product as a clear oil in 79% yield (0.120 g).

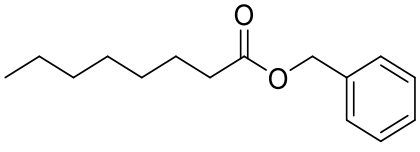
Characterisation data was consistent with previously reported literature values.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.28 – 7.23 (m, 1H), 7.14 – 7.10 (m, 2H), 2.60 (t, *J* = 7.5 , 2H), 1.80 (p, *J* = 7.5, 2H), 1.5 – 1.31 (m, 8H), 0.97 – 0.93 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 150.9, 129.5, 125.8, 121.7, 34.5, 31.8, 29.2, 29.0, 25.0, 22.7, 14.2.

LCMS (ESI^+) r.t. = 3.6 mins, *m/z* = 221.3 $[M+H]^+$

Synthesis of Benzyl Octanoate (5u)



Synthesised according to the general method for esterification from octanoic acid (0.099 g, 0.69 mmol) and benzyl alcohol (0.079 g, 0.73 mmol). The crude material was purified by flash

column chromatography (100% hexane to 10% EtOAc 90% hexane) to give the desired product as a clear oil in 75% yield (0.129 g).

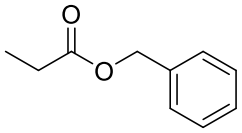
Characterisation data were consistent with previously reported literature values.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 5.13 (s, 2H), 2.37 (t, *J* = 7.5, 2H), 1.72 – 1.62 (m, 2H), 1.37 – 1.23 (m, 8H), 0.91 – 0.87 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 136.2, 128.6, 128.3, 128.2, 66.1, 34.4, 31.8, 29.2, 29.0, 25.1, 22.7, 14.2.

GCMS (EI^+) r.t.= 4.7, *m/z* = 234.2 $[M]^+$

Synthesis of Benzyl Propionate (5v)



Synthesised according to the general method* of esterification from propionic acid (0.100 g, 1.35 mmol) and benzyl alcohol (0.152 g, 1.41 mmol). The crude material was purified using automated flash column chromatography combiflash (eluted in 100% hexane) to give the desired product as a colourless oil in 48% yield (0.107 g)

Characterisation data was consistent with previously reported literature values. [17]

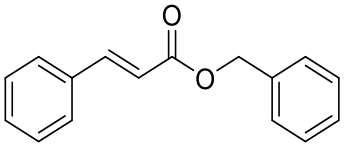
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 5H), 5.13 (s, 2H), 2.40 (q, *J* = 7.6, 2H), 1.18 (t, *J* = 7.6, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 136.2, 128.6, 128.3, 66.2, 27.7, 9.2.

GCMS (EI^+) r.t. = 3.4 mins, *m/z* = 164.1 $[M]^+$

*Performed at 35°C

Synthesis of benzyl cinnamate (5w)



Synthesised according to the general method for esterification from cinnamic acid (0.103 g, 0.070 mmol) and benzyl alcohol (0.084 g, 0.77 mmol). Purified using automated flash column

chromatography combiflash (eluted in step gradient hexane 100% to hexane 99.2% EtOAc 0.8%) to give the desired product as a colourless oil in 80% yield (0.132 g).

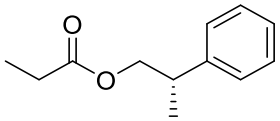
Characterisation data were consistent with previously reported literature values.[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 16.0, 1H), 7.55 – 7.53 (m, 2H), 7.46 – 7.38 (m, 8H), 6.52 (d, *J* = 16.0, 1H), 5.28 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 145.3, 136.2, 134.4, 130.4, 129.0, 128.7, 128.4, 128.3, 128.2, 118.0, 66.4.

LCMS (ESI^+) r.t. = 3.1 mins, *m/z* = 239.2 $[M+H]^+$

Synthesis of (*S*)-2-phenylpropyl propionate (5x)



Synthesised according to the general method* for esterification from propionic acid (0.101 g, 1.36 mmol) and 2-phenylpropanol (0.187 g, 1.37 mmol). The crude material was purified by flash column chromatography (hexane to 10% EtOAc 90% hexane) to give the desired product as a clear oil in 46% yield (0.120 g).

Characterisation data were consistent with previously reported literature values.[19]

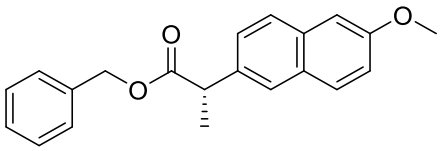
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.9, 6.9, 2H), 7.30 – 7.22 (m, 3H), 4.30 – 4.13 (m, 2H), 3.15 (h, *J* = 7.1, 1H), 2.33 (q, *J* = 7.6, 2H), 1.35 (d, *J* = 7.0, 3H), 1.14 (t, *J* = 7.6, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 143.3, 128.5, 127.4, 126.7, 69.3, 39.0, 27.6, 18.1, 9.2.

GCMS (EI^+) r.t. = 3.8 mins, *m/z* 193.1 $[M]^+$

*Performed at 35°C

Synthesis of benzyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (5y)



Synthesised according to the general method for esterification from naproxen (0.101 g, 0.44 mmol) and benzyl alcohol (0.053 g, 0.49 mmol). Purified using automated flash column chromatography combiflash (step gradient; 100% hexane for 4 mins, 90% hexane to EtOAc for 4 mins) to yield the product as a colourless oil in 69% yield (0.095 g).

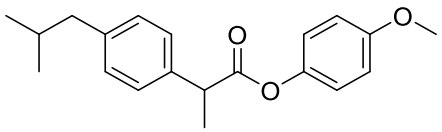
Characterisation data was consistent with previously reported literature values.[20]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 3H), 7.46 (dd, *J* = 8.5, 1.8, 1H), 7.35 – 7.28 (m, 5H), 7.21 – 7.16 (m, 2H), 5.19 (m 2H), 3.95 (m, 4H), 1.65 (d, *J* = 7.1, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 157.7, 136.1, 135.6, 133.8, 129.4, 129.0, 128.6, 128.2, 128.0, 127.2, 126.4, 126.1, 119.1, 105.6, 66.6, 55.4, 45.5, 18.7.

GCMS (EI^+) r.t. = 6.4 mins, *m/z* = 320 $[M+H]^+$

Synthesis of 4-methoxyphenyl 2-(4-isobutylphenyl)propanoate (5z)



Synthesised according to the general method for esterification from ibuprofen (0.100 g, 0.48 mmol) and 4-methoxyphenol (0.061 g, 0.49 mmol). Purified using automated flash column chromatography combiflash (eluted in 100% hexane) to give the desired product as a clear oil in 63% yield (0.094 g).

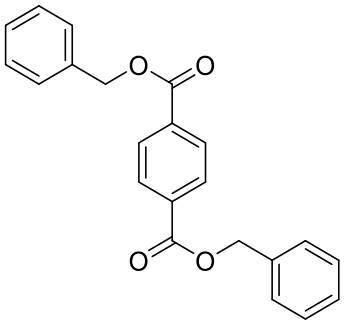
Characterisation data were consistent with previously reported literature values.[21]

^{1}H NMR (400 MHz, CDCl3) δ 7.34 – 7.31 (m, 2H), 7.18 – 7.15 (m, 2H), 6.98 – 6.90 (m, 2H), 6.89 – 6.83 (m, 2H), 3.94 (q, J = 7.1, 1H), 3.78 (s, 3H), 2.50 (d, J = 7.2, 2H), 1.97 – 1.82 (m, 1H), 1.62 (d, J = 7.1, 3H), 0.94 (d, J = 6.6, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 157.2, 144.5, 140.8, 137.5, 129.6, 127.3, 122.2, 114.4, 55.6, 45.3, 45.1, 30.3, 22.5, 18.7.

LCMS (ESI^+) r.t = 3.6 mins, *m/z* = 313.4 $[M+H]^+$

Synthesis of dibenzyl terephthalate (5aa)



Synthesised according to the general method for esterification from terephtalic acid (0.100 g, 0.60 mmol) and benzyl alcohol (0.130 g, 1.20 mmol). The crude material was purified by automated flash column chromatography combiflash (100% hexane 4 mins to 20% EtOAc 80% hexane using a step gradient 9 mins) to give the desired product as a white solid in 40% yield (0.082 g).

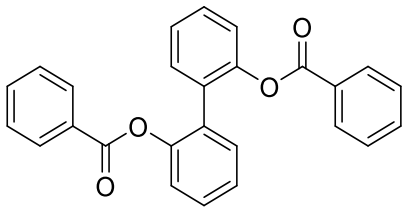
Characterisation data were consistent with previously reported literature value.[22]

^{1}H NMR (400 MHz, CDCl3) δ 8.16 (s, 4H), 7.49 – 7.37 (m, 10H), 5.40 (s, 4H).

^{13}C NMR (101 MHz, CDCl3) δ 165.7, 135.7, 134.1, 129.8, 128.7, 128.5, 128.4, 67.2.

GCMS (EI^+): r.t. = 6.9 mins, *m/z* 346.5 $[M]^+$

Synthesis of [1,1'-biphenyl]-2,2'-diyl dibenzoate (7a)



Synthesised according to the general method for esterification from benzoic acid (0.106 g. 0.87 mmol) and 2,2'-biphenol (0.076 g, 0.41 mmol, 0.82 mmol OH equivalent). The crude material was purified by flash column chromatography (100% hexane to 7.5% EtOAc 92.5% hexane) to give the desired product as a viscous clear oil in 85% yield (0.138 g).

^{1}H NMR (599 MHz, cdcl$_3$) δ 8.00-7.98 (m, 2H), 7.57-7.54 (m, 1H), 7.43 – 7.36 (m, 4H), 7.30– 7.26 (m, 2H).

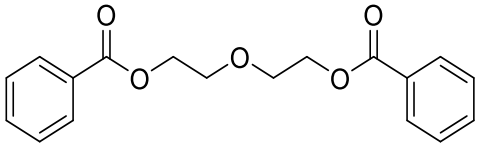
^{13}C NMR (151 MHz, cdcl$_3$) δ 165.0, 148.5, 133.5, 131.3, 130.7, 130.1, 129.5, 129.1, 128.5, 126.0, 122.6.

LCMS (ESI$^+$) r.t. = 3.3 mins, *m/z* = 395.3 $[M+H]^+$

HRMS – Calculated for $[M+H]^+$ $C_{26}H_{19}O_4$ 395.1283, found 395.1281

IR νmax (ATR)/cm^{-1} 3069, 1732, 1601, 1474, 1449, 1248, 1192, 1059, 700

Synthesis of oxybis(ethane-2,1-diyl) dibenzoate (7b)



Synthesised according to the general method for esterification from benzoic acid (0.097 g, 0.79 mmol) and diethylene glycol (0.044 g, 0.41 mmol, 0.82 mmol OH equivalent). The crude material was purified by flash column chromatography (100% hexane to 20% EtOAc 80% hexane) to give the desired product as a viscous clear oil in 64% yield (0.082 g).

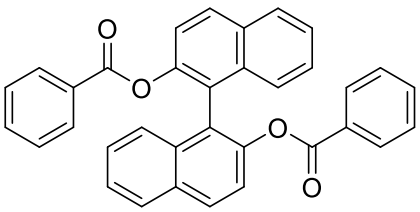
Characterisation data was consistent with previously reported literature values.[23]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.02 (m, 4H), 7.56 – 7.51(m, 2H), 7.42 – 7.37 (m, 4H), 4.51 – 4.49 (m, 4H), 3.89 – 3.87 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 133.1, 130.1, 129.7, 128.4, 69.3, 64.1.

LCMS (ESI$^+$): r.t.= 2.7 mins, *m/z* = 315.2 $[M+H]^+$

Synthesis of [1,1'-binaphthalene]-2,2'-diyl dibenzoate (7c)



Synthesised according to the general method for esterification from benzoic acid (0.106 g, 0.87 mmol) and [1,1′-Binaphthalene]-2,2′-diol (0.120 g, 0.42 mmol, 0.84 OH equivalent). The crude

material was purified by flash column chromatography (100% hexane to 7.5% EtOAc 92.5% hexane) to give the desired product as a white solid in 72% yield (0.149 g).

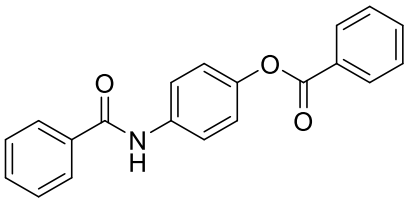
Characterisation data was consistent with previously reported literature values.[24]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.98 (d, *J* = 8.4, 2H), 7.92 (dt, *J* = 8.2, 0.9, 2H), 7.75 – 7.67 (m, 4H), 7.61 (d, *J* = 8.9, 2H), 7.51 – 7.41 (m, 6H), 7.36 (ddd, *J* = 8.7, 6.6, 1.3, 2H), 7.32 – 7.22 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 147.1, 133.5, 133.3, 131.6, 129.9, 129.7, 129.3, 128.3, 128.1, 126.9, 126.2, 125.8, 123.7, 121.9.

LCMS (ESI^+) r.t.= 3.7 mins, *m/z* = 495.3 $[M+H]^+$

Synthesis of 4-benzamidophenyl benzoate (7d)



Synthesised according to the general method for esterification from benzoic acid (0.100 g, 0.82 mmol) and 4-aminophenol (0.048 g, 0.44 mmol (0.88 mol equiv.)). During the course of the reaction a white solid precipitated from the reaction mixture. The solid was filtered and then triturated with MeCN (25 mL), hexane (25 mL), ethyl acetate (50 mL) and DCM (50 mL). The solid was allowed to dry and removed from the filter paper to yield a flaky white solid in 31% yield (0.040 g)

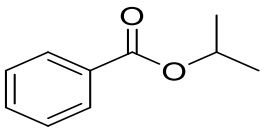
^{1}H NMR (599 MHz, dmso) δ 10.38 (s, 1H), 8.16 – 8.14 (m, 2H), 7.99 – 7.97 (m, 2H), 7.88 – 7.86 (m, 2H), 7.76 – 7.74 (m, 1H), 7.63 – 7.59 (m, 3H), 7.54-7.51 (m, 2H), 7.29 – 7.28 (m, 2H).

^{13}C NMR (101 MHz, DMSO) δ 165.7, 164.8, 146.3, 137.1, 134.9, 134.1, 131.7, 129.8, 129.1, 129.0, 128.5, 127.7, 122.1, 121.4.

ASAP HRMS (ESI^+) Calculated for $[M+H]^+$ $C_{20}H_{16}NO_3$ = 318.1130, Found = 318.1108

IR νmax (ATR)/cm-^{1} 3333, 1726, 1653, 1510, 1410, 1314, 1272, 1194, 1065, 703

Synthesis of S-benzyl benzothioate (9a)



Synthesised according to the general method for thioesterification from benzoic acid (0.103 g, 0.84 mmol) and benzyl mercaptan (0.107 g, 0.86 mmol). The crude material was purified by flash column chromatography (100% hexane to 2.5% EtOAc 97.5% hexane) to give the desired product as a clear oil in 89% yield (0.166 g)

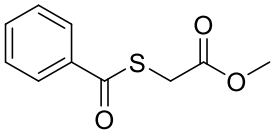
Characterisation data was consistent with previously reported literature values.[25]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.58 (m, 1H), 7.51 – 7.40 (m, 4H), 7.39 – 7.24 (m, app 4H, 3H), 4.37 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 137.6, 136.8, 135.3, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.3, 127.4, 33.4.

LCMS (ESI^+) r.t. = 3.1 mins, *m/z* = 229.2 $[M+H]^+$

Synthesis of methyl 2-(benzoylthio)acetate (9b)



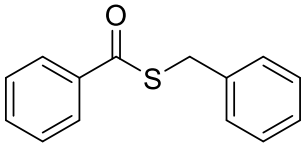
Synthesised according to the general method for thioesterification from benzoic acid (0.107 g, 0.88 mmol) and methyl 2-mercaptoacetate (0.092 g, 0.86 mmol). The crude material was purified by flash column chromatography (100% hexane to 5% EtOAc 95% hexane) to give the desired product as a clear oil in 70% yield (0.126 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96– 7.93 (m, 2H), 7.58-7.54 (m, 1H), 7.45 – 7.41 (m, 2H), 3.87 (s, 2H), 3.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 169.3, 136.1, 133.9, 128.8, 127.4, 52.9, 31.1.

LCMS (ESI^+) r.t. = 2.6 mins, *m/z* = 211.16 $[M+H]^+$
HRMS – Calc $[C_{10}H_{11}O_3S]$ 211.0429, Obtained – $[C_{10}H_{11}O_3S]$ 211.0437 $[M+H]^+$

Synthesis of *S*-(2-acetamidoethyl) benzothioate (9c)



Synthesised according to the general method for esterification from benzoic acid (0.098 g, 0.80 mmol) and *N*-(2-mercaptoethyl)acetamide (0.142 g, 1.20 mmol). The crude material was purified by flash column chromatography (100% hexane to 85% EtOAc 15% hexane) to give the desired product as white solid in 79% yield (0.141 g).

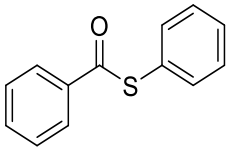
Characterisation data were consistent with previously reported literature values.[26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.58 – 7.52 (m, 1H), 7.45 – 7.40 (m, 2H), 6.36 (s, 1H), 3.49 (q, *J* = 6.3, 2H), 3.19 (t, *J* = 6.5, 2H), 1.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 170.6, 136.7, 133.7, 128.7, 127.3, 39.6, 28.6, 23.2.

LCMS (ESI^+) r.t. = 1.7 mins, *m/z* = 246.2 $[M+Na]^+$

Synthesis of S-Phenyl benzothioate (9d)



Synthesised according to the general method for thioesterification from benzoic acid (0.100 g, 0.082) and thiophenol (0.090 g, 0.082 mmol). The crude material was purified using automated column chromatography combiflash (eluted in 100% hexane) to yield the desired product as cream solid in 52% yield (0.091 g).

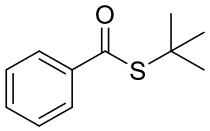
Characterisation data were consistent with previously reported literature.[27]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 2H), 7.64 – 7.60 (m, 1H), 7.57 – 7.45 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 136.7, 135.2, 133.8, 129.6, 129.4, 128.9, 127.6, 127.5.

LCMS (ESI^+) r.t. = 3.2 mins, *m/z* = 215.4 $[M+H]^+$

Synthesis of S-(tert-butyl) benzothioate (9e)



Synthesised according to the general method for thioesterification from benzoic aicd (0.099 g, 0.81 mmol) and 2-methylpropane-2-thiol (0.074 g, 0.82 mmol). The crude material was purified using automated column chromatography (eluted in 100% hexane). The fractions were contaminated with ether side product so the fractions were re-purified using manual column chromatography (100% hexane to 90% hexane and 10% EtOAc) to yield the desired product as a colourless oil in 35% yield (0.052 g).

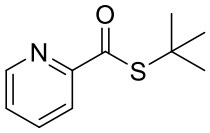
Characterisation data were consistent with previously reported literature values.[28]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.56 – 7.48 (m, 1H), 7.45 – 7.37 (m, 2H), 1.58 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 138.3, 132.9, 128.5, 127.0, 48.2, 30.0.

LCMS (ESI^+) r.t = 3.2 mins, *m/z* 195.2 $[M+H]^+$

Synthesis of S-(tert-butyl) pyridine-2-carbothioate (9f)



Synthesised according to the general method for thioesterification from 2-picolinic acid (0.100 g, 0.81 mmol) and 2-methylpropane-2-thiol (0.074g, 0.82 mmol). The crude material was purified using automated column chromatography (product eluted in 100% hexane) to yield the desired product as a white solid in 59% yield (0.093 g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 7.94 – 7.88 (m, 1H), 7.83 (td, *J* = 7.7, 1.7 Hz, 1H), 7.47 (ddd, *J* = 7.5, 4.8, 1.3 Hz, 1H), 1.57 (s, 9H).

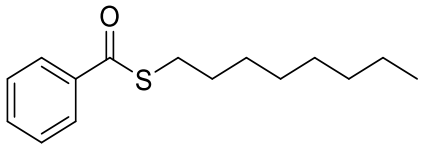
^{13}C NMR (151 MHz, $cdcl_3$) δ 193.8, 153.3, 149.0, 137.4, 127.6, 120.1, 47.1, 47.1, 29.9.

LCMS (ESI^+) r.t = 2.5 mins, *m/z* 196.2 $[M+H]^+$

HRMS – Calculated [$C_{10}H_{14}NOS$] 196.0796, Found [$C_{10}H_{14}NOS$] 196.0794

IR

Synthesis of Octyl Benzothioate (9g)



Synthesised according to the general method for thioesterification from (0.100 g, 0.82 mmol) and octanthiol (0.140g, 0.96 mmol). The crude material was purified by flash column chromatography (100% hexane to 5% EtOAc 95% hexane) to give the desired product as a colourless oil in 40% yield (0.081g).

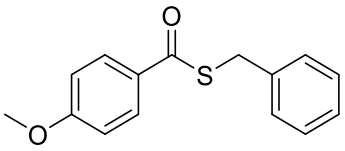
Characterisation data was consistent with previously reported literature.[27]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.96 (m, 2H), 7.55 – 7.53 (m, 1H), 7.45 – 7.41 (m, 2H), 3.09 – 3.05 (m, 2H), 1.69 – 1.63 (m, 2H), 1.44 – 1.27 (m, 9H), 0.90 – 0.87 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 137.4, 133.3, 128.6, 127.3, 31.9, 29.7, 29.3, 29.2, 29.2, 29.1, 22.8, 14.2.

LCMS (ESI^+) r.t. = 4.2 mins, *m/z* = 251.3 $[M+H]^+$

Synthesis of S-benzyl 4-methoxybenzothioate (9h)



Synthesised according to the general method for thioesterification from 4-methoxybenzoic acid (0.099 g, 0.65 mmol) and benzyl mercaptan (0.089 g, 0.72 mmol). The crude material was purified using automated flash column chromatography combiflash (product eluted in 100% hexane) to yield the desired product as a white solid in 49% (0.083 g).

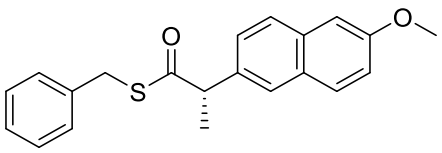
Characterisation data were consistent with previously reported literature values.[29]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H), 7.43 – 7.40 (m, 2H), 7.37 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 6.97 – 6.93 (m, 2H), 4.34 (s, 2H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 163.9, 137.8, 129.7, 129.6, 129.1, 128.7, 127.3, 113.9, 55.6, 33.3.

GCMS (EI^+) r.t = 5.8 mins, *m/z* =258.2 $[M]^+$

Synthesis of S-benzyl 2-(6-methoxynaphthalen-2-yl)propanethioate (9i)



Synthesised according to the general method for thioesterification from Naproxen (0.100 g, 0.43 mmol) and benzyl mercaptan (0.054 g, 0.43 mmol). The crude material was purified using automated column chromatography (100% hexanes 5.5 mins, gradient to 10% EtOAc 90% hexane 0.5 mins, 10% EtOAc 90% hexane 2 mins followed by gradient to 50/50 EtOAc/hexane) to yield the desired product as a colourless oil in 68% yield (0.100 g)

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 3H), 7.46 (dd, *J* = 8.5, 1.9, 1H), 7.32 – 7.25 (m, 5H), 7.21-7.16 (m, 2H), 4.19 – 4.05 (m, 3H), 3.95 (s, 3H), 1.68 (d, *J* = 7.1, 3H).

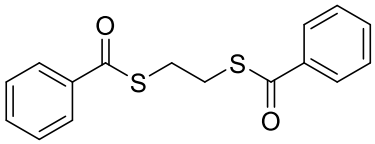
^{13}C NMR (151 MHz, $CDCl_3$) δ 200.8, 157.9, 137.5, 134.9, 134.0, 129.5, 129.0, 128.9, 128.7, 127.3, 127.3, 126.8, 126.5, 119.2, 105.7, 55.4, 54.1, 33.6, 18.5.

LCMS (ESI^+) r.t = 3.5 mins, *m/z* = 337.3 $[M+H]^+$

HRMS – Calculated $[C_{21}H_{21}O_2S]$ 337.1262, Found $[C_{21}H_{21}O_2S]$ 337.1272 $[M+H]^+$

IR νmax (ATR)/cm $^{-1}$ 3029, 2938, 1677, 1601, 1268, 1229, 1029, 944, 854, 818, 750, 698

Synthesis of S,S'-(ethane-1,2-diyl) dibenzothioate (9j)



Synthesised according to the general method for thioesterification from benzoic aicd (0.100 g, 0.82 mmol) and ethandithiol (0.35 mL, 0.41 mmol, 0.82 SH equivalent). The crude material

was purified using automated column chromatography (product eluted in 100% hexane) to give the desired product as a cream solid in 37% yield (0.046 g).

Characterisation data were consistent with previously reported literature values.[30]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 4H), 7.62 – 7.55 (m, 2H), 7.50 – 7.41 (m, 4H), 3.36 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 136.8, 133.7, 128.8, 127.4, 29.0.

LCMS (ESI^+) r.t = 3.6 mins, *m/z* = 303.2 $[M+H]^+$

Acyl Fluoride Reaction Monitoring

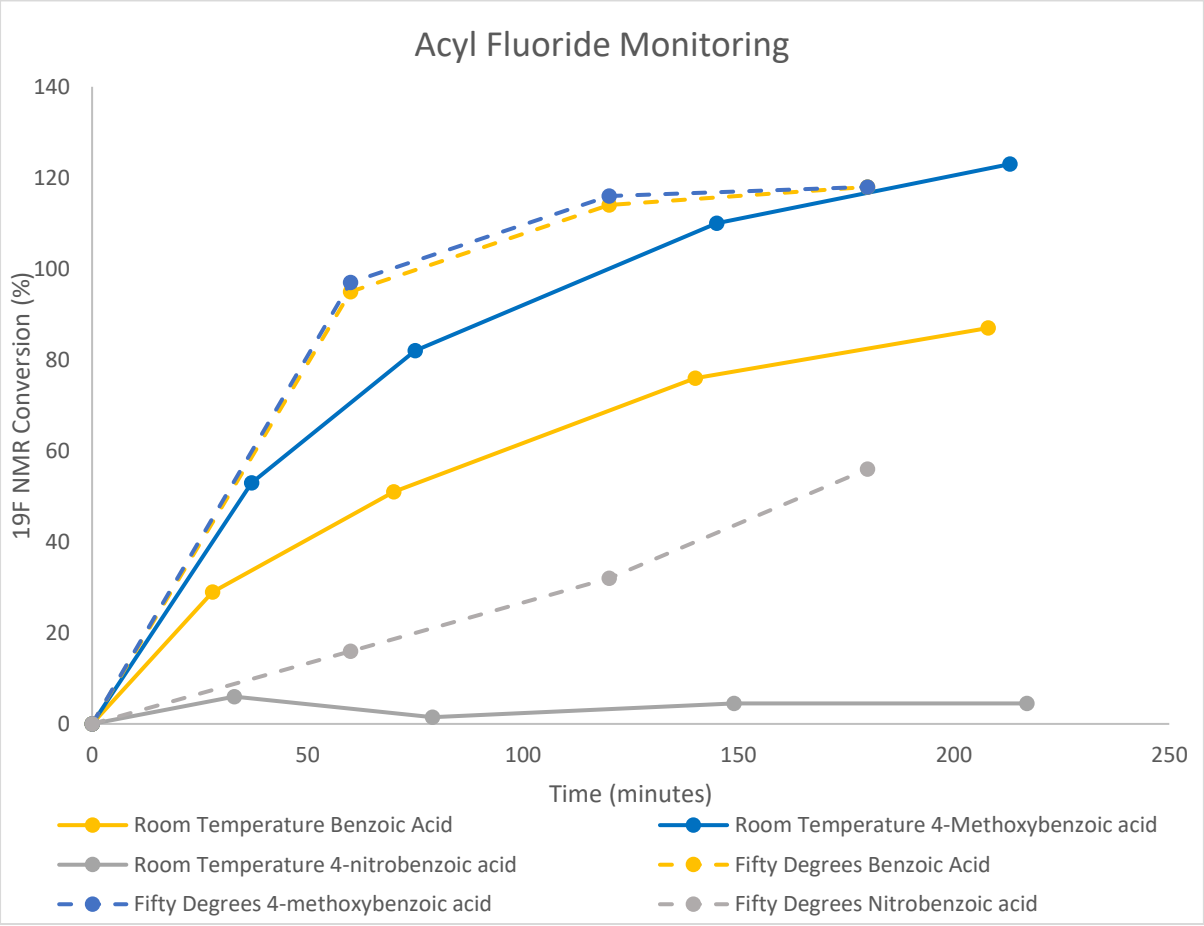
To an oven dried vial was added carboxylic acid (1 equiv.), DIPEA (2 equiv.), PFP (1.1 equiv.), fluorobenzene (1 equiv.) and CD_3CN (0.6 mL). The contents were then transferred from the vial to a clean, dry NMR tube stoppered with a lid.

For rt analysis the NMR tubes were placed into the NMR instrument autosampler and left there for the duration of the experiment.

For reactions conducted above rt the NMR tubes were transferred to a thermostatically controlled water bath set at 50 ˚C, the tubes were removed after 1 h and an NMR spectrum recorded. When the acquisition was complete the tube was retrieved and placed back into the water bath.

The time points recorded equates to the amount of time the sample was held in the water bath.

NMR spectra were analysed by direct integration to the resonance corresponding to the acyl fluoride compared to the integration value of the internal standard.



Raw data for acyl fluoride monitoring at room temperature

Benzoic Acid			4-methoxybenzoic acid			4-nitrobenzoic acid*	
mins	Area AF		mins	Area AF		mins	Area AF
0	0		0	0		0	0
28	0.29		37	0.53		33	0.06
70	0.51		75	0.82		79	0.015
140	0.76		145	1.1		149	0.045
208	0.87		213	1.23		217	0.045

*A 1.5 equiv of fluorobenzene was added, areas of acyl fluorides were multiplied by 1.5 to accommodate.

Raw data for acyl fluoride monitoring 50°C

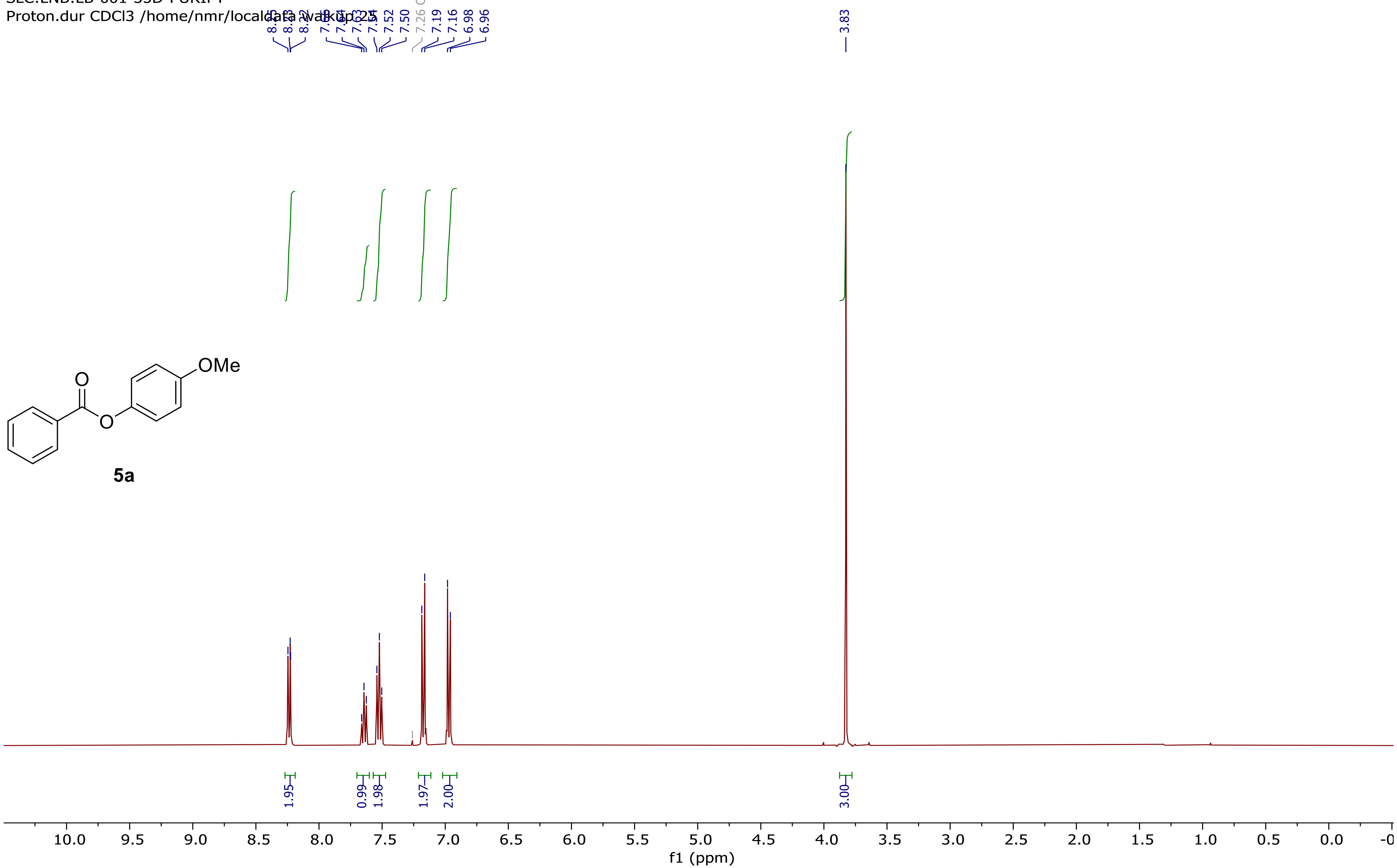
Benzoic Acid			4-methoxybenzoic acid			4-nitrobenzoic acid	
Mins**	Area AF		Mins**	Area AF		Mins**	Area AF
0	0		0	0		0	0
60	0.95		60	0.97		60	0.16
120	1.14		120	1.16		120	0.32
180	1.18		180	1.18		180	0.56

**Minutes spent in the water bath

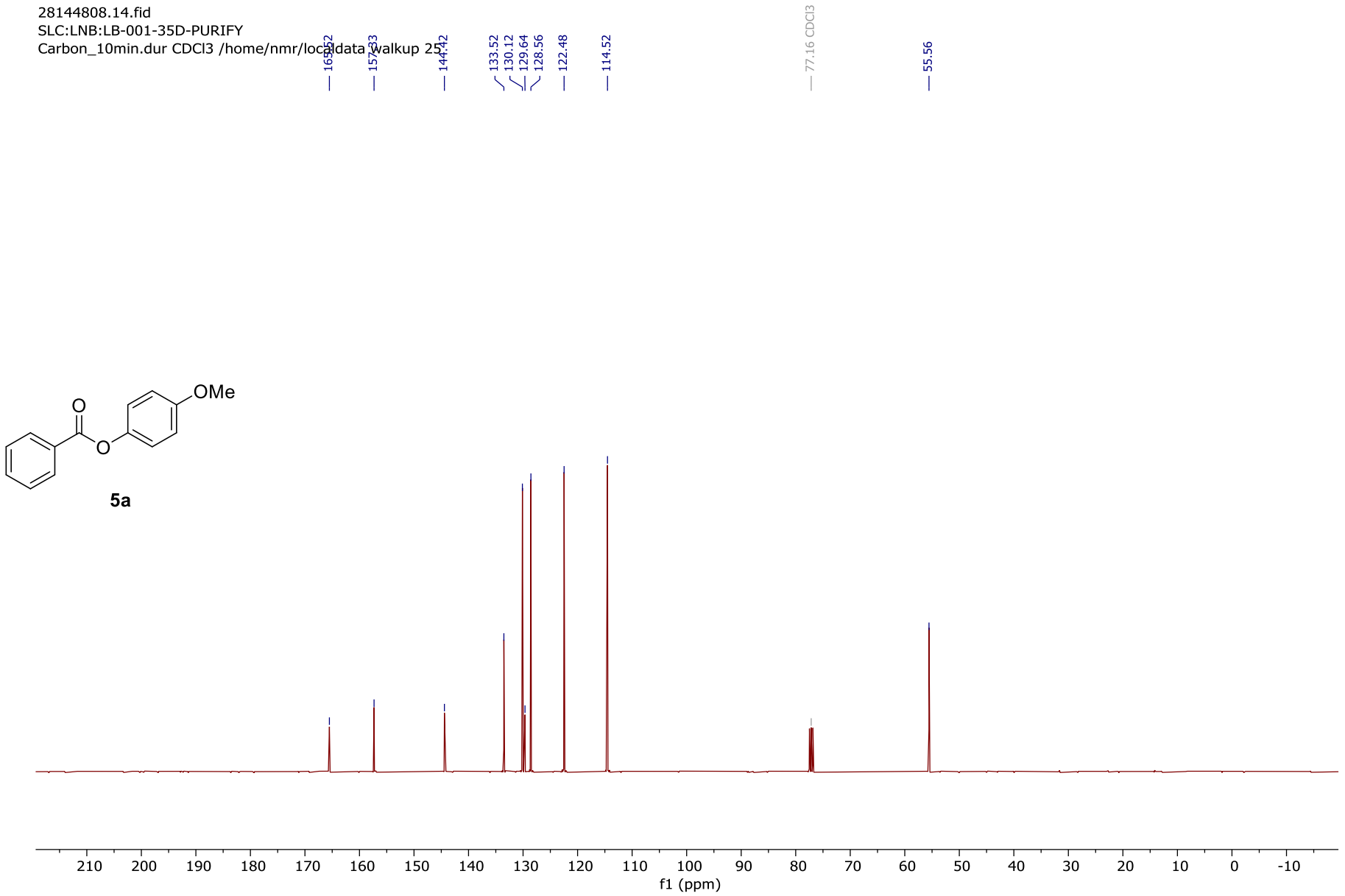
The areas in excess of the expected 1:1 ratio is attributed to different relaxation times. It was not feasible to employ a longer relaxation time on the NMR spectrometers used for this analysis. The relaxation time used was 2.77 seconds.

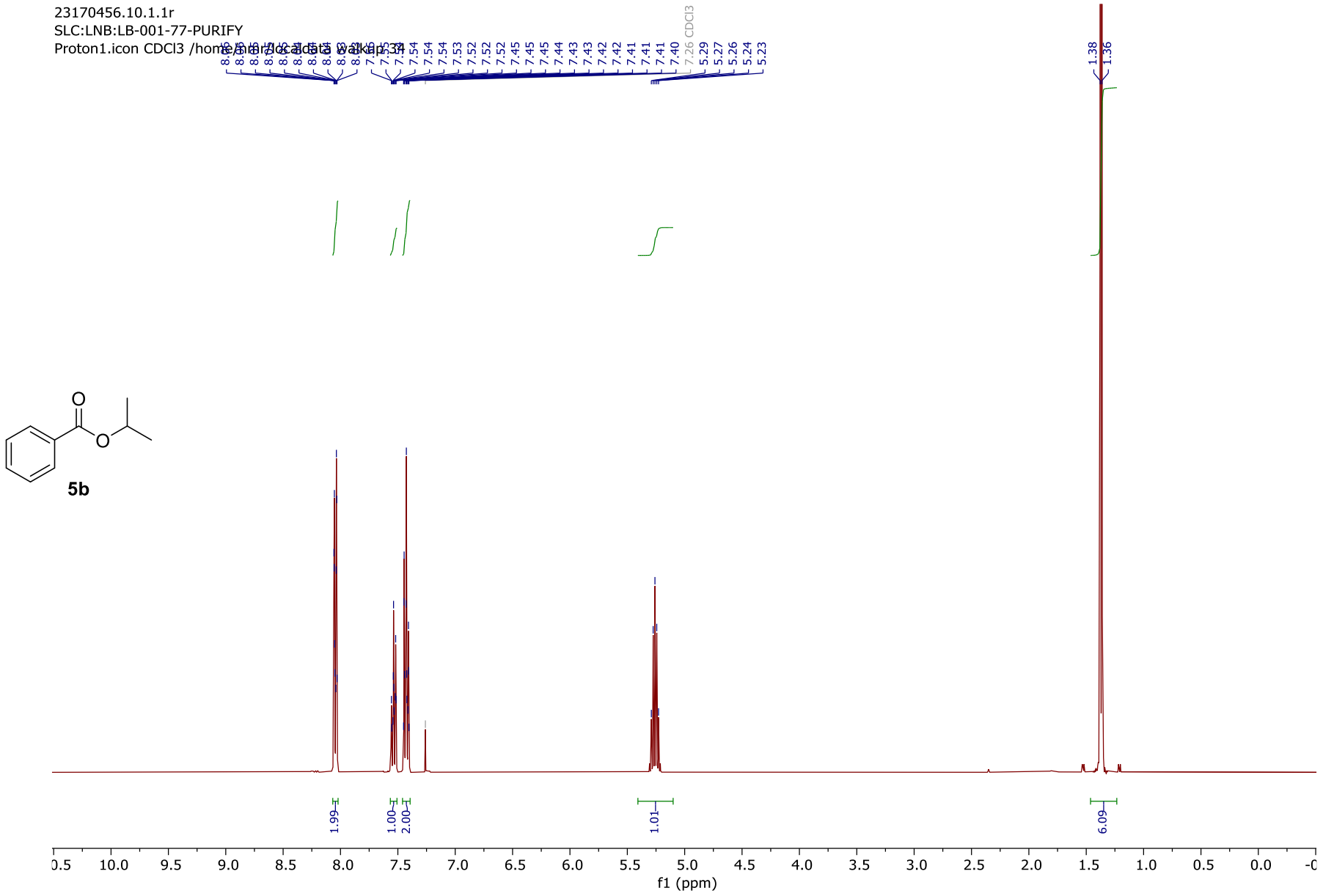
NMR Data for Synthesised Compounds

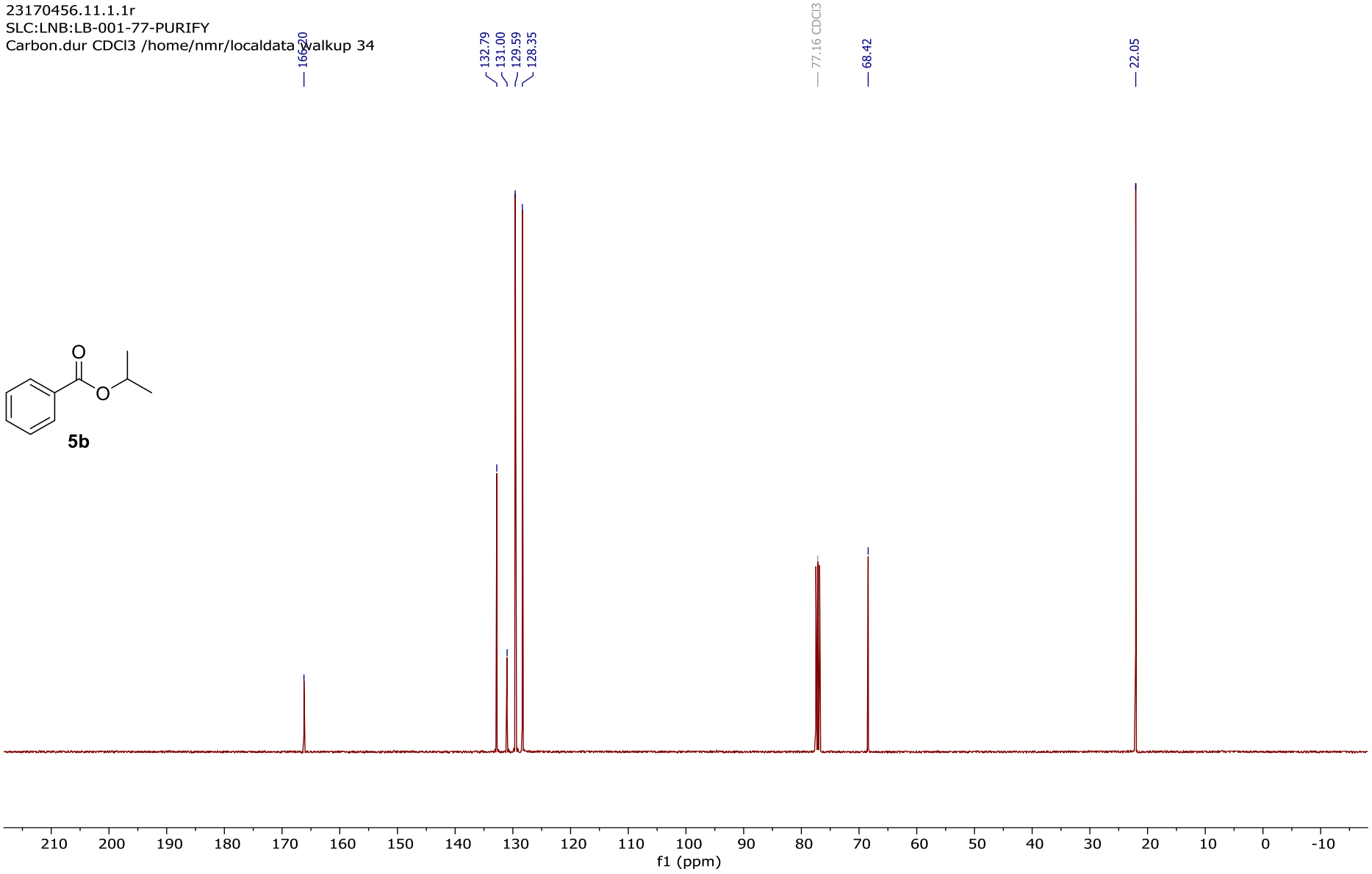
28144808.10.fid
SLC:LNB:LB-001-35D-PURIFY
Proton.dur CDCl3 /home/nmr/localdata walkup 25

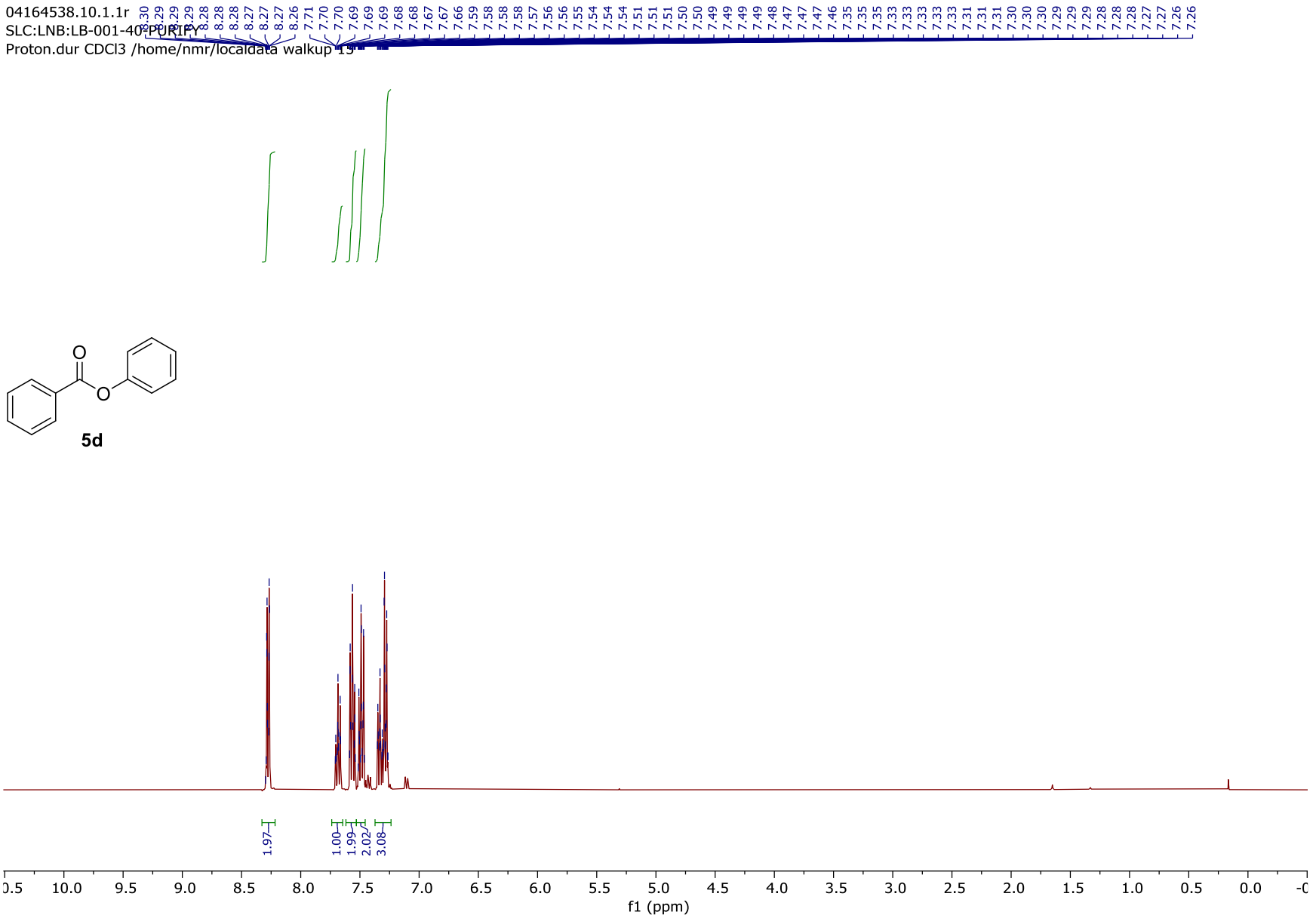


28144808.14.fid
SLC:LNB:LB-001-35D-PURIFY
Carbon_10min.dur CDCl3 /home/nmr/localdata walkup 25

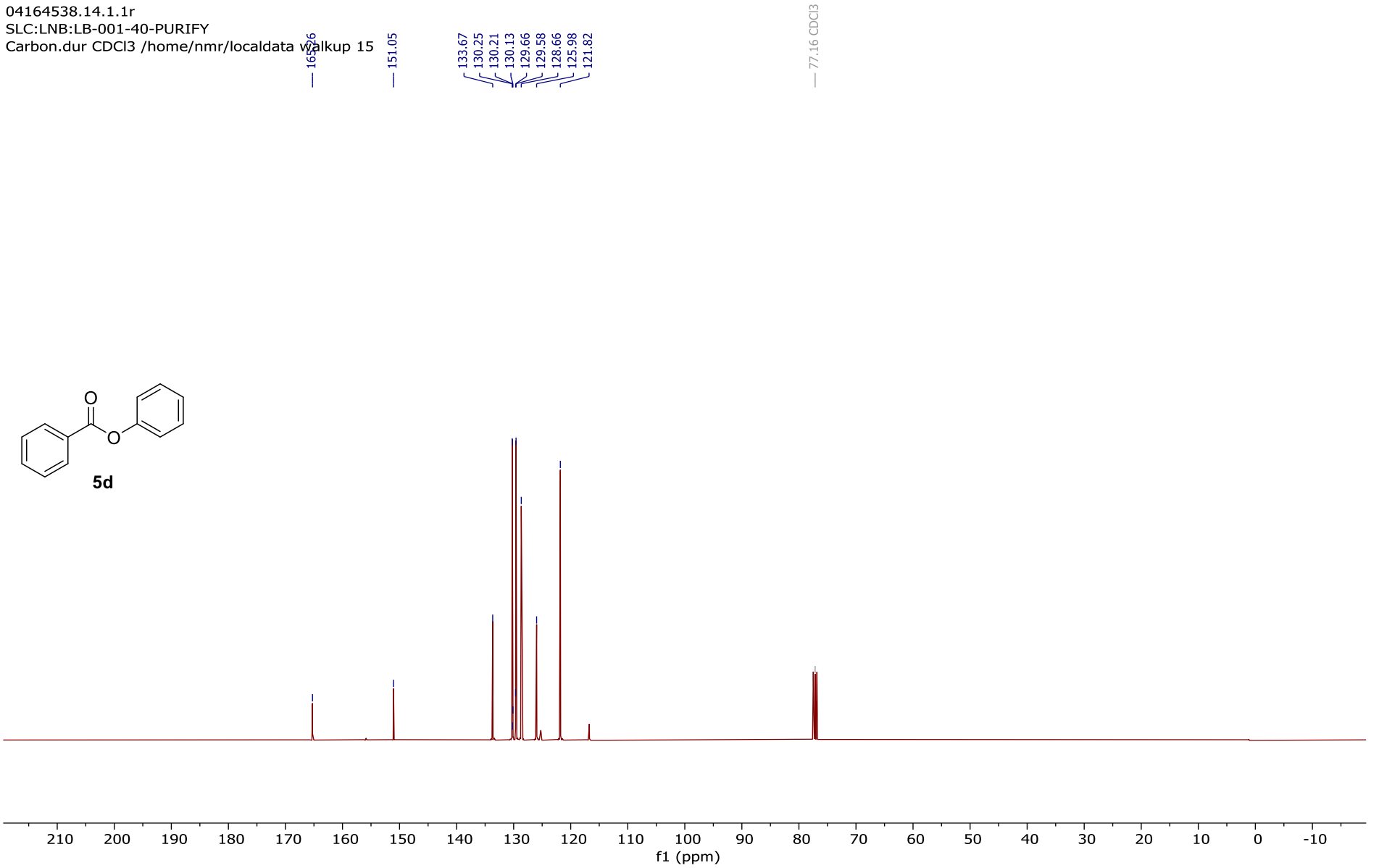


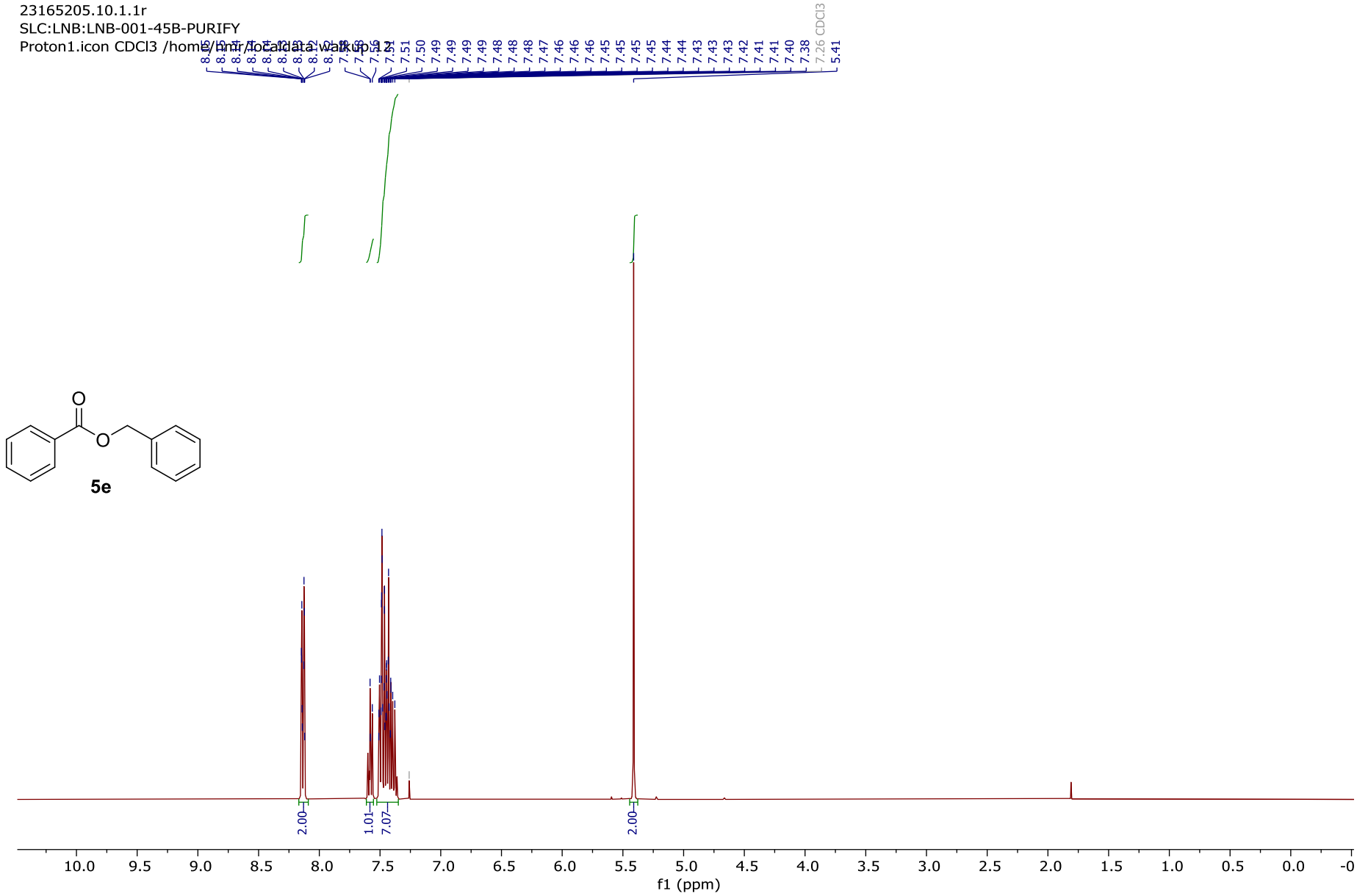

23170456.10.1.1r
SLC:LNB:LB-001-77-PURIFY
Proton1.icon CDCl3 /home/nmrdocadata/walkup 32
7.26 CDCl3
1.38
1.36
5b
1.99
1.00
2.00
1.01
6.09
f1 (ppm)


23170456.11.1.1r
SLC:LNB:LB-001-77-PURIFY
Carbon.dur CDCl3 /home/nmr/localdata/walkup 34
166.20
132.79
131.00
129.59
128.35
77.16 CDCl3
68.42
22.05
O
O
5b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

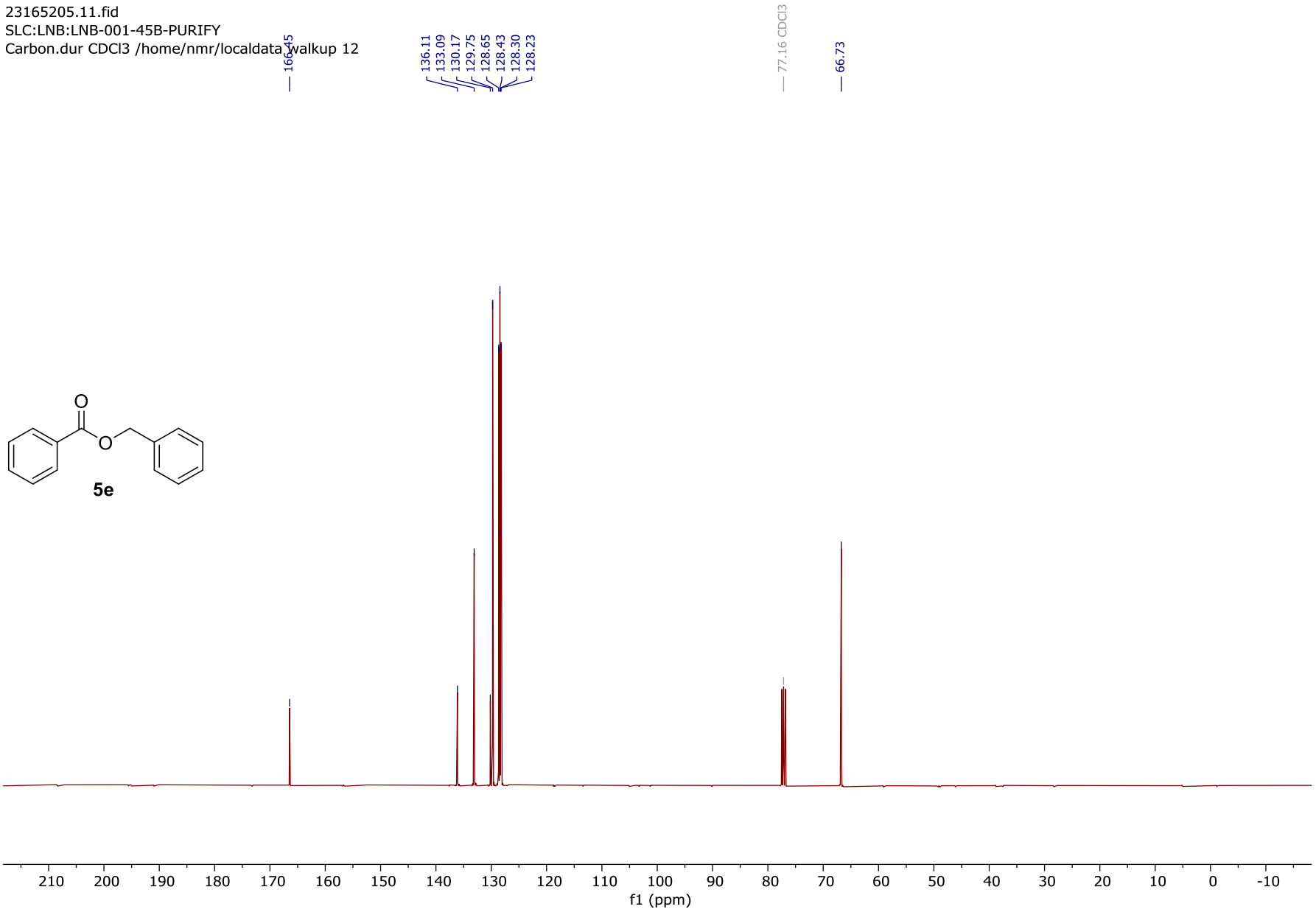

04164538.10.1.1r
SLC:LNB:LB-001-40-PURIFY
Proton.dur CDCl3 /home/nmr/localdata walkup 15
8.30 8.29 8.29 8.29 8.28 8.28 8.28 8.27 8.27 8.27 8.26 7.71 7.70 7.70 7.69 7.69 7.69 7.68 7.68 7.67 7.67 7.66 7.59 7.58 7.58 7.58 7.57 7.56 7.56 7.55 7.54 7.54 7.54 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.49 7.49 7.48 7.47 7.47 7.47 7.46 7.35 7.35 7.35 7.33 7.33 7.33 7.33 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26
O
O
5d
1.97
1.00
1.99
2.02
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

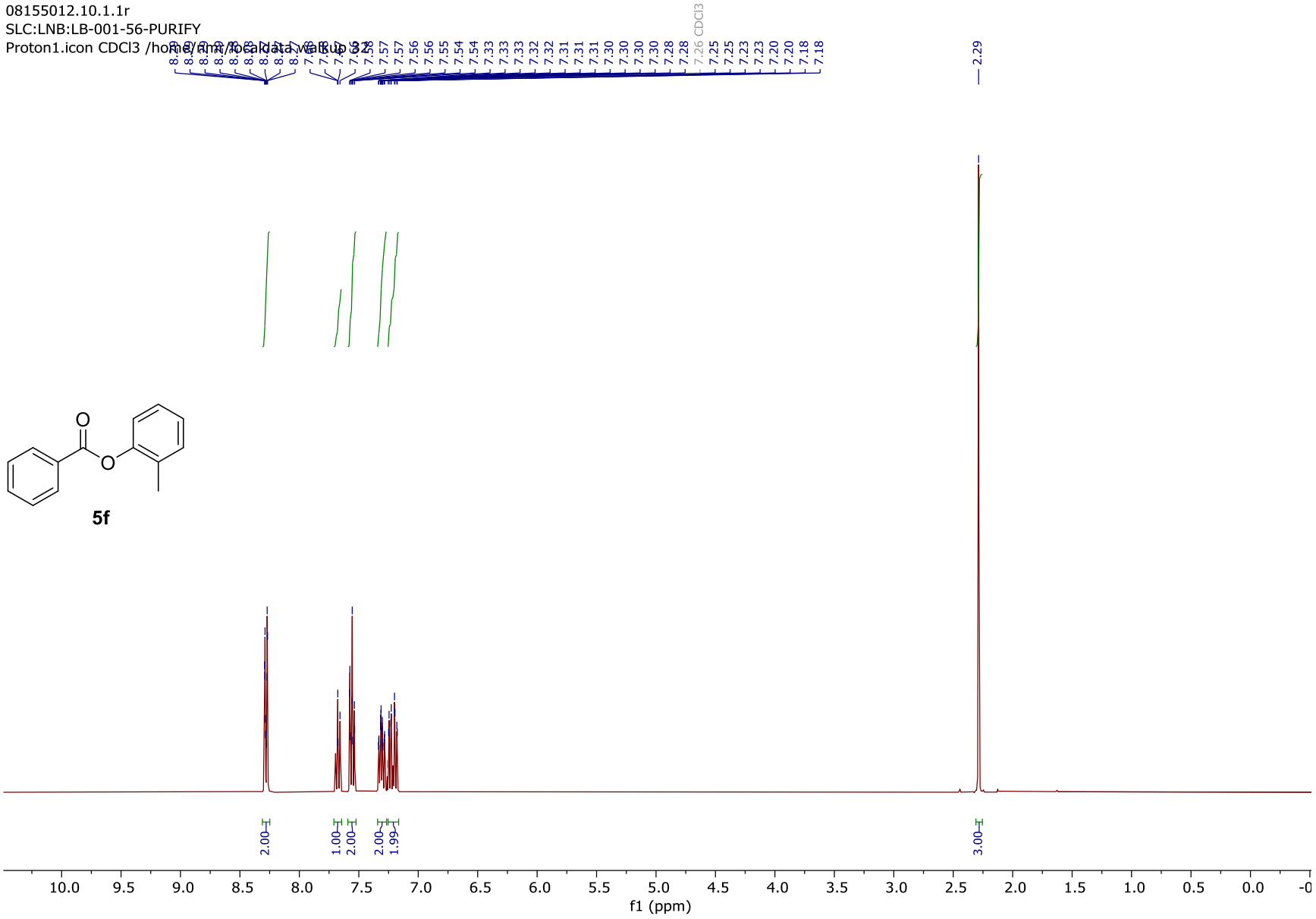
04164538.14.1.1r
SLC:LNB:LB-001-40-PURIFY
Carbon.dur CDCl3 /home/nmr/localdata walkup 15



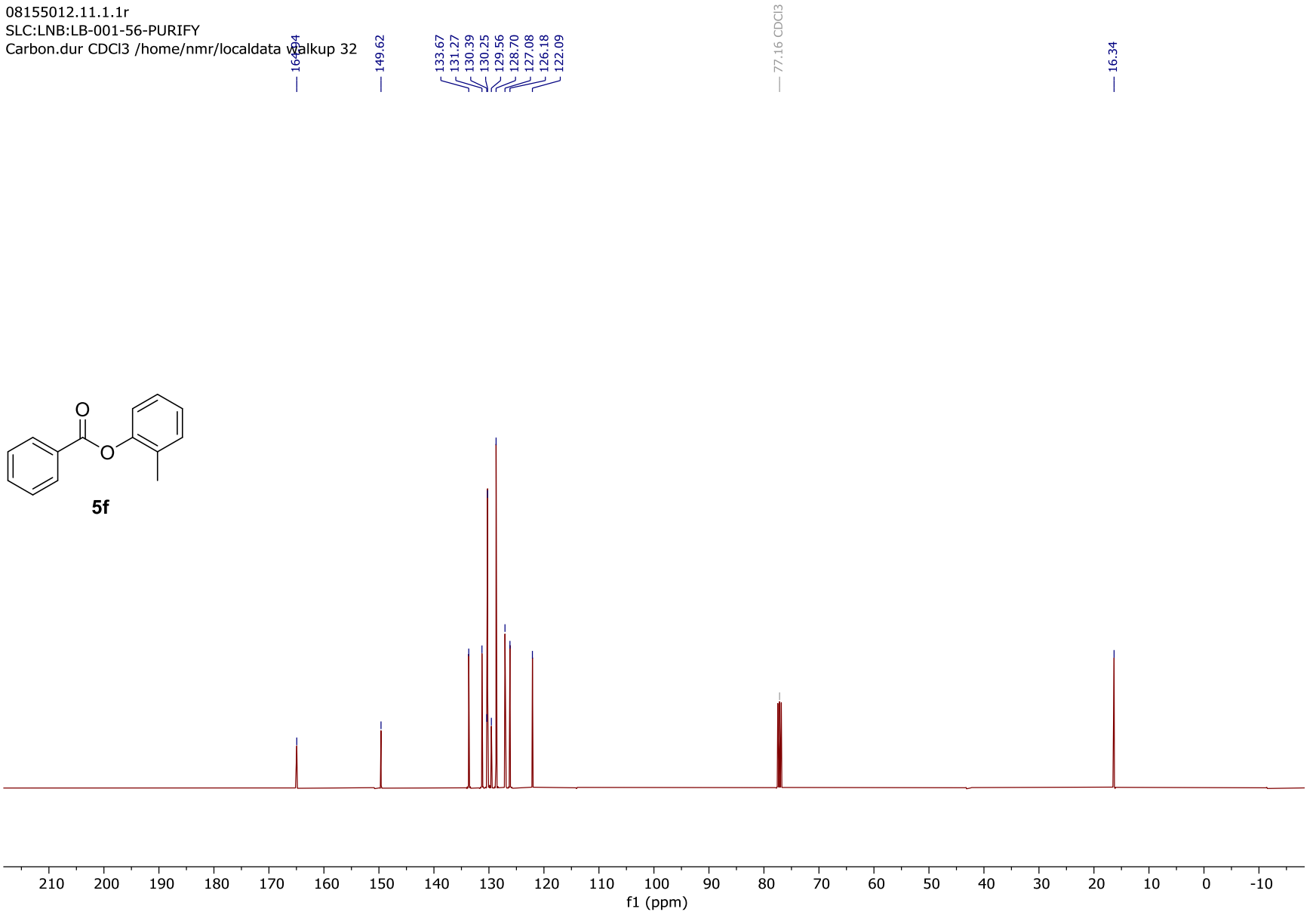

23165205.10.1.1r
SLC:LNB:LNB-001-45B-PURIFY
Proton1.icon CDCl3 /home/nmr/localdata/walkup 1 1r
7.26 CDCl3
5.41
O
O
5e
2.00
1.01
7.07
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

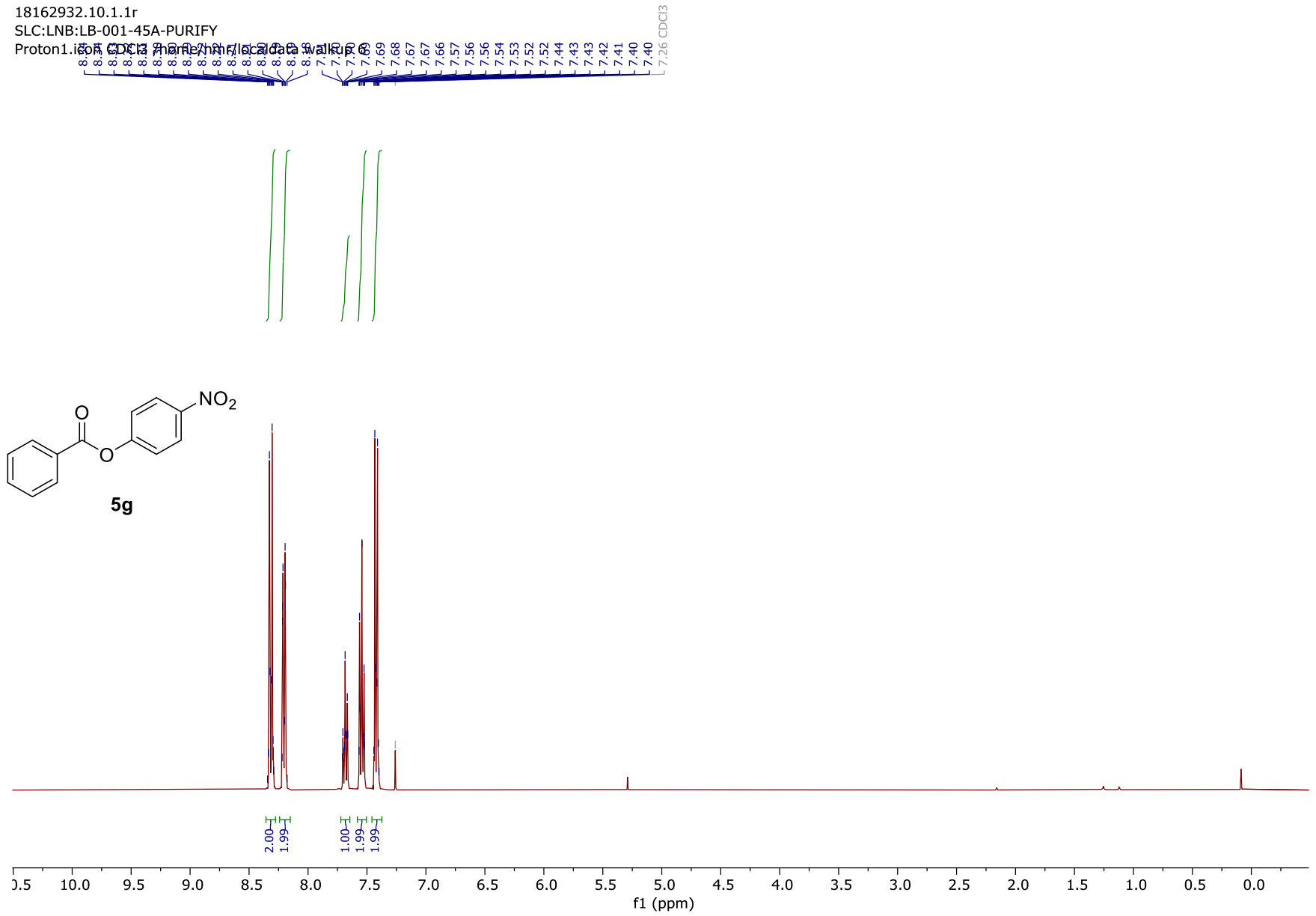
23165205.11.fid
SLC:LNB:LNB-001-45B-PURIFY
Carbon.dur CDCl3 /home/nmr/localdata/walkup 12



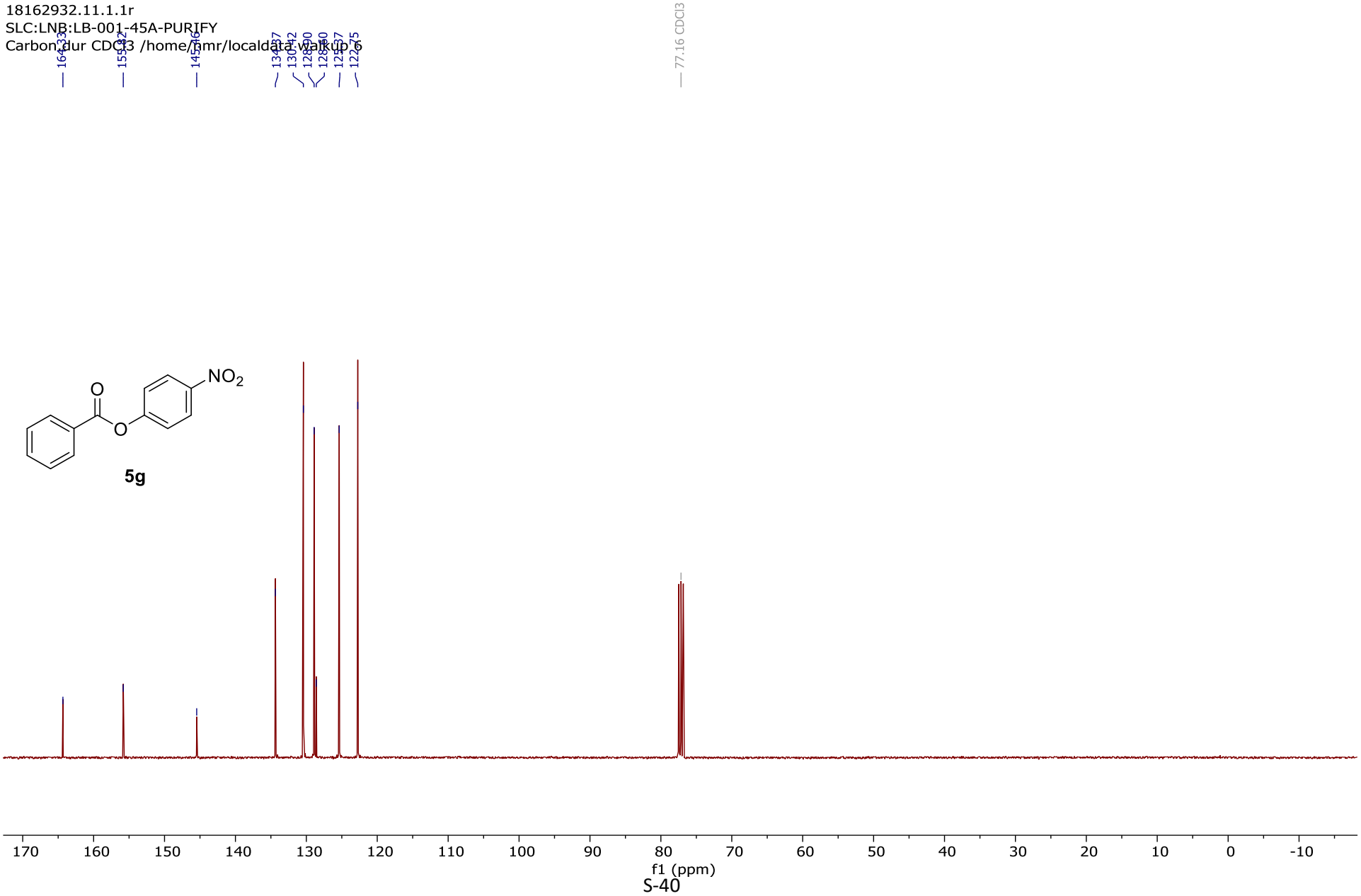

08155012.10.1.1r
SLC:LNB:LB-001-56-PURIFY
Proton1.icon CDCl3 /home/nmr/locadata waltsup 32
7.26 CDCl3
2.29
O
O
5f
2.00
1.00
2.00
2.00
1.99
3.00
f1 (ppm)

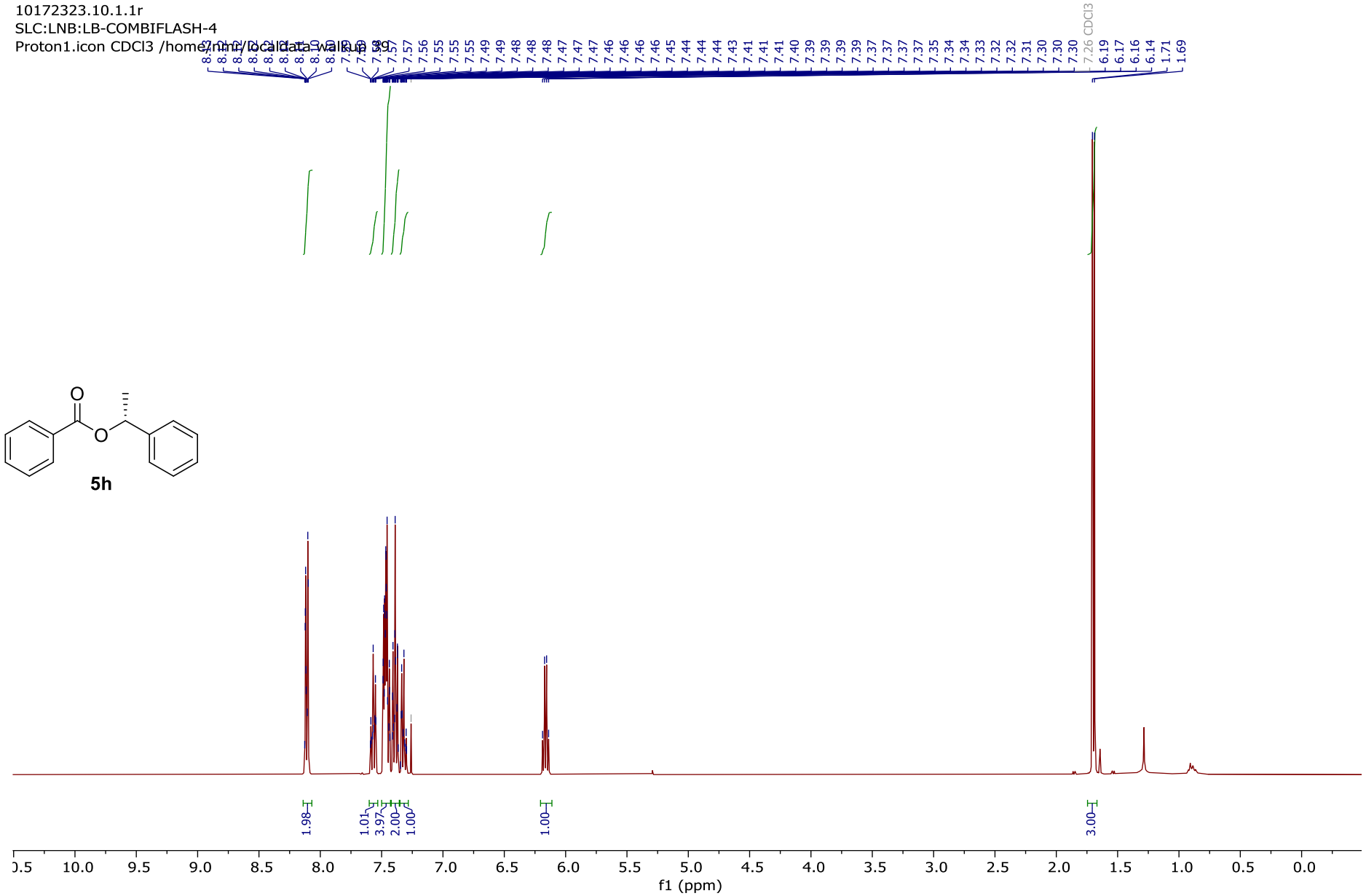
08155012.11.1.1r
SLC:LNB:LB-001-56-PURIFY
Carbon.dur CDCl3 /home/nmr/localdata w alkup 32




18162932.10.1.1r
SLC:LNB:LB-001-45A-PURIFY
Proton1.icon CDCl3 /home/nmr/localdata walkup 6
8.31 8.31 8.30 8.30 8.29 8.29 8.28 8.28 8.27 8.27 8.26 8.26 8.25 8.25 8.24 8.24 8.23 8.23 8.22 8.22 8.21 8.21 8.20 8.20 8.19 8.19 8.18 8.18
7.70 7.69 7.68 7.67 7.67 7.66 7.57 7.56 7.56 7.54 7.53 7.52 7.52 7.44 7.43 7.43 7.42 7.41 7.40 7.40
7.26 CDCl3
O
O
NO2
5g
2.00
1.99
1.00
1.99
1.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

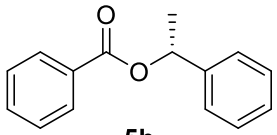
18162932.11.1.1r
SLC:LNB:LB-001-45A-PURIFY
Carbon,dur CDCl3 /home/nmr/localdata/walkup/6



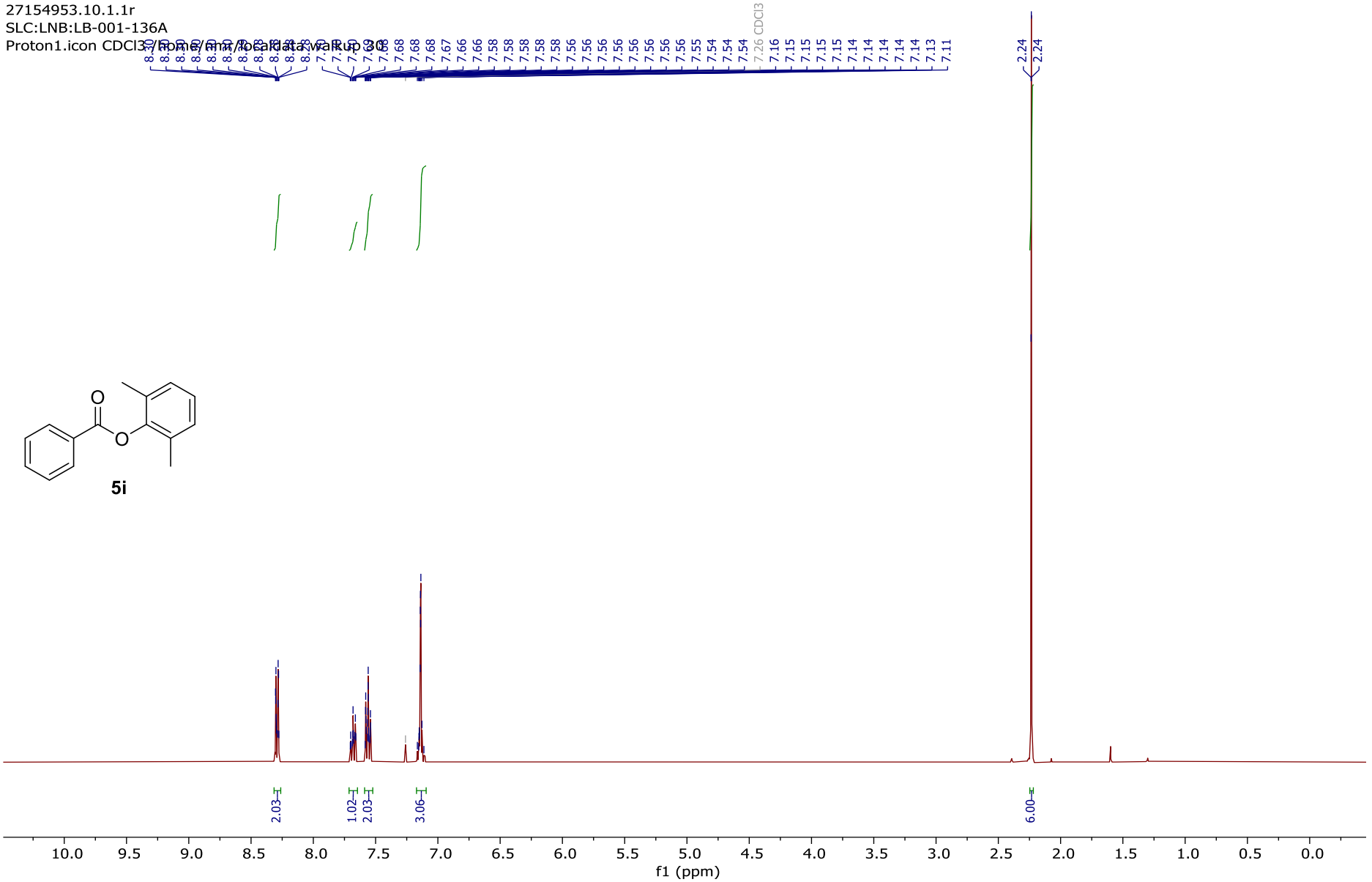

10172323.10.1.1r
SLC:LNB:LB-COMBIFLASH-4
Proton1.icon CDCl3 /home/nmr/localdata-walkup 39
7.26 CDCl3
5h
1.98
1.01
3.97
2.00
1.00
1.00
3.00
f1 (ppm)

10172323.11.1.1r
SLC:LNB:LB-COMBIFLASH-4
Carbon.dur CDCl3 /home/nmr/localdata walkup 39

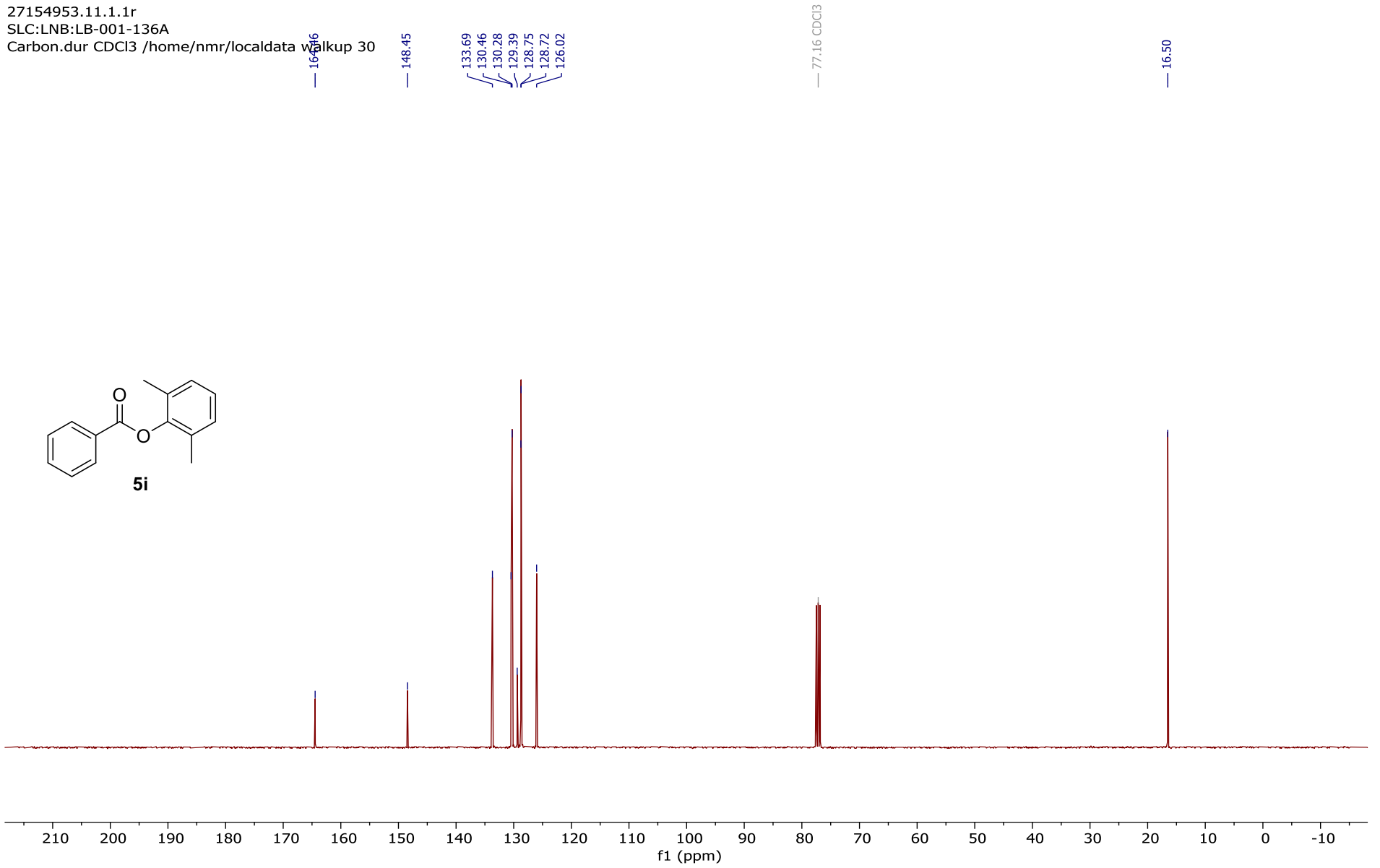
165.85
141.83
132.97
130.55
129.69
128.60
128.38
127.94
126.09
72.96
22.48

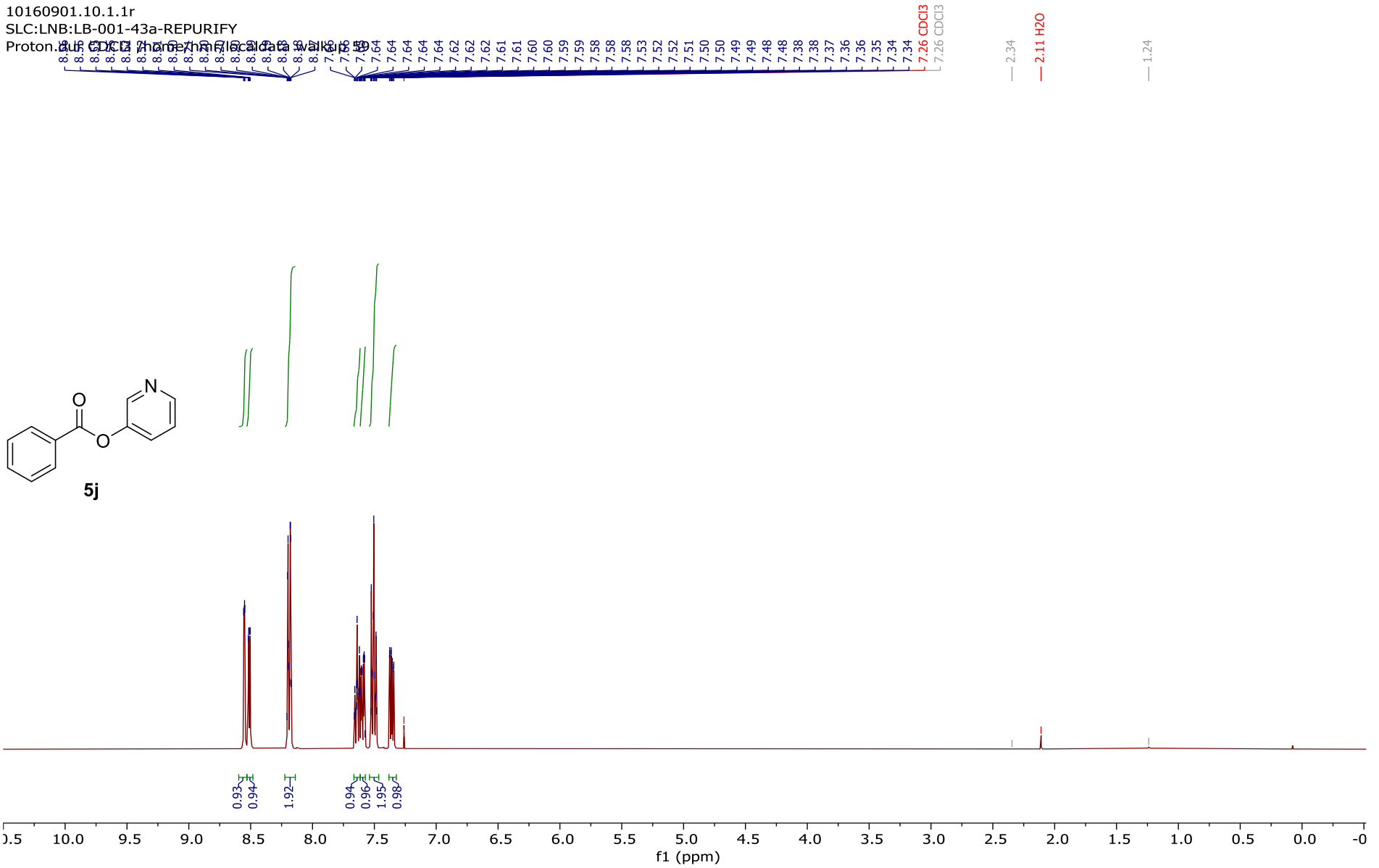


5h


27154953.10.1.1r
SLC:LNB:LB-001-136A
Proton1.icon CDCl3
7.26 CDCl3
2.24
2.24
O
O
5i
2.03
1.02
2.03
3.06
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

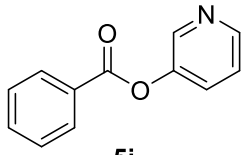
27154953.11.1.1r
SLC:LNB:LB-001-136A
Carbon.dur CDCl3 /home/nmr/localdata walkup 30



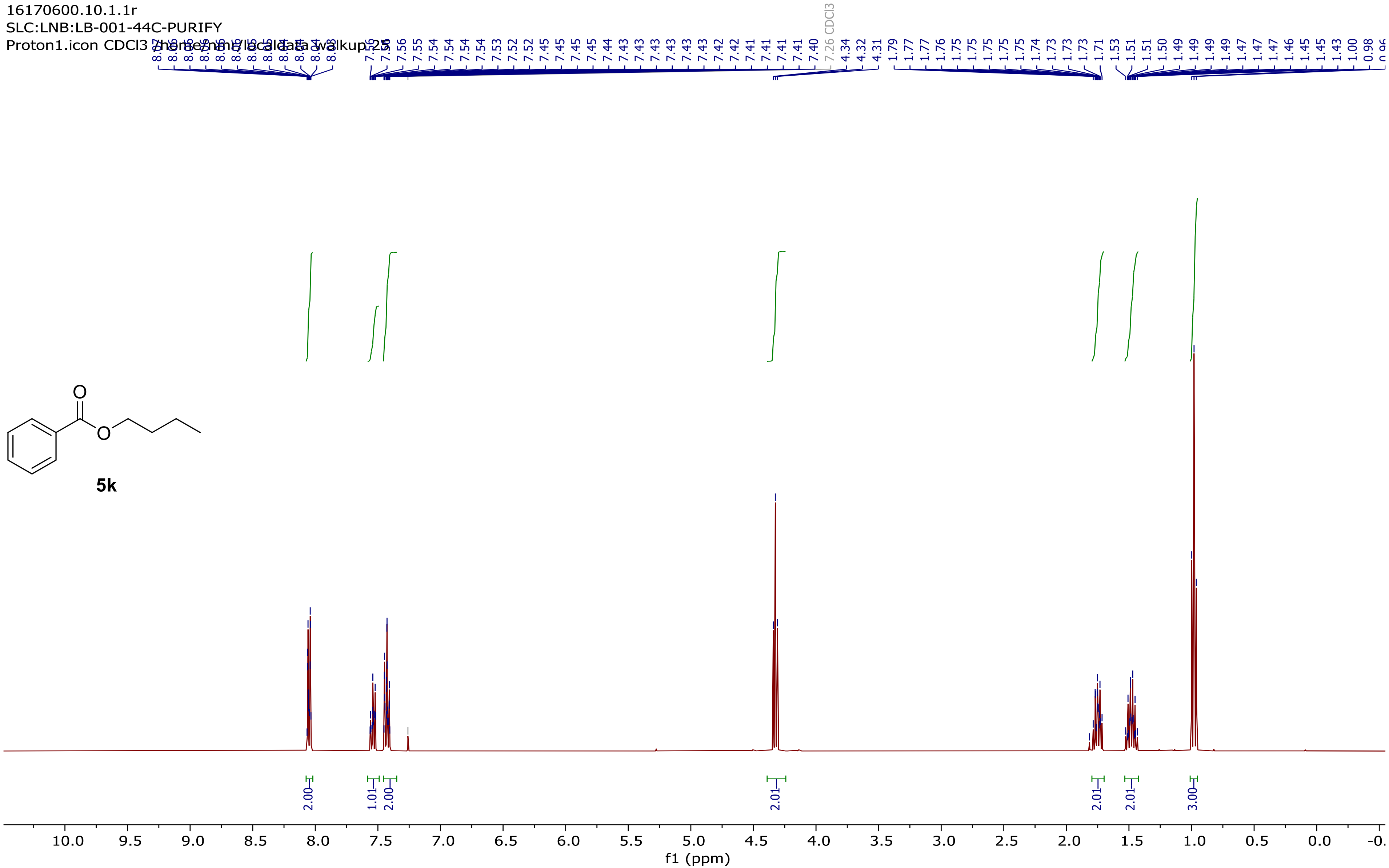

10160901.10.1.1r
SLC:LNB:LB-001-43a-REPURIFY
Proton.aur CDCl3 /home/nmr/localdata walkup 59
7.26 CDCl3
2.34
2.11 H2O
1.24
O
N
O
5j
0.93
0.94
1.92
0.94
0.96
1.95
0.98
f1 (ppm)

10160901.11.1.1r
SLC:LNB:LB-001-43a-REPURIFY
Carbon.dur CDCl3 /home/nmr/localdata wallkup 59

164.69
147.64
147.30
147.04
143.60
134.05
130.29
129.41
128.76
128.73
123.96
77.45 CDCl3
77.34
77.14 CDCl3
76.82 CDCl3



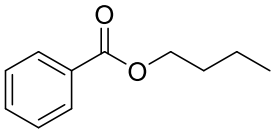
5j



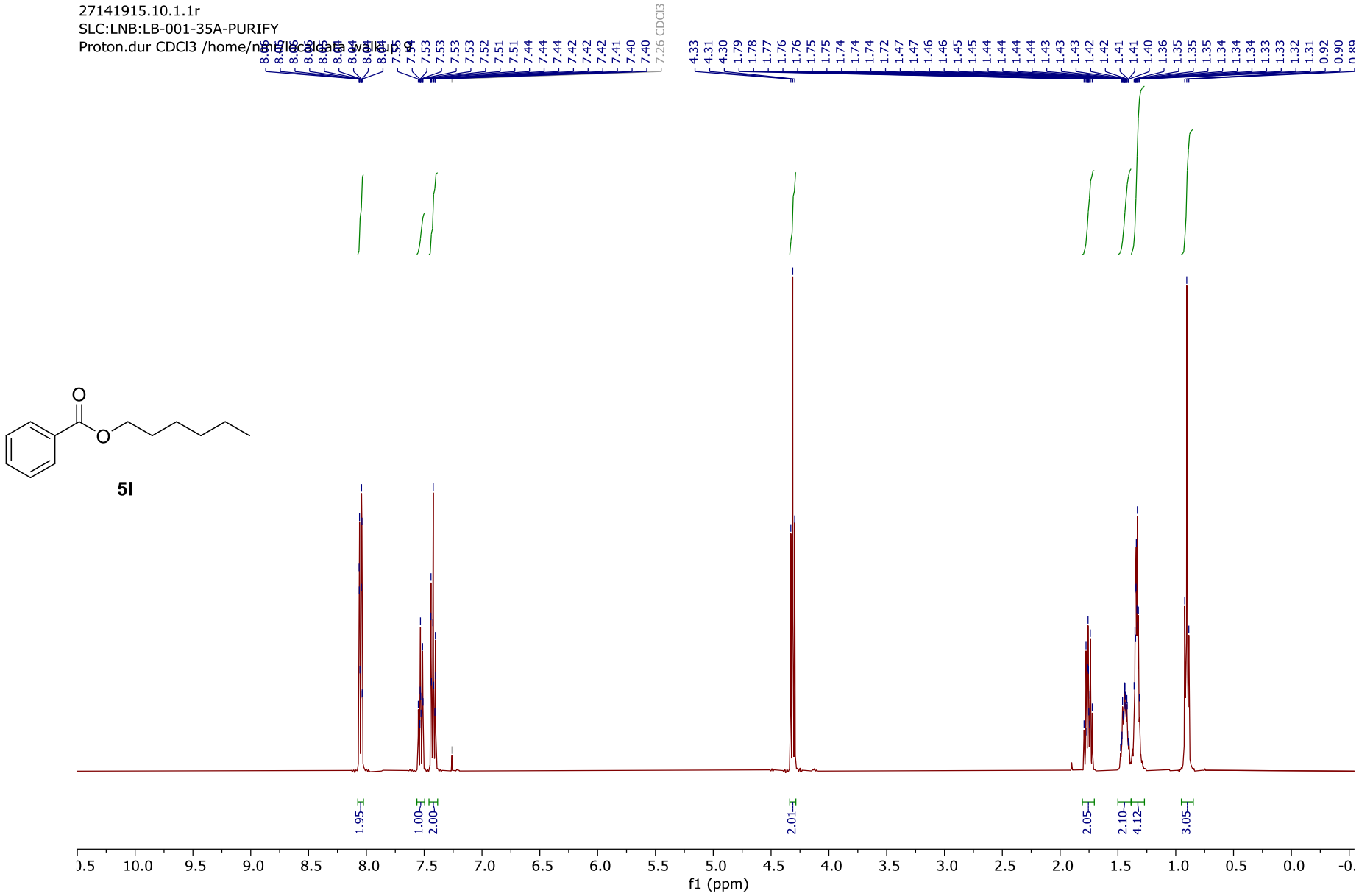
16170600.10.1.1r
SLC:LNB:LB-001-44C-PURIFY
Proton1.icon CDCl3 /home/nmr/localdata walkup 23
7.26 CDCl3
O
O
5k
2.00
1.01
2.00
2.01
2.01
2.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

16170600.11.1.1r
SLC:LNB:LB-001-44C-PURIFY
Carbon.dur CDCl3 /home/nmr/localdata walkup 25

166.68
132.80
130.54
129.54
128.32
64.83
30.80
19.30
13.79

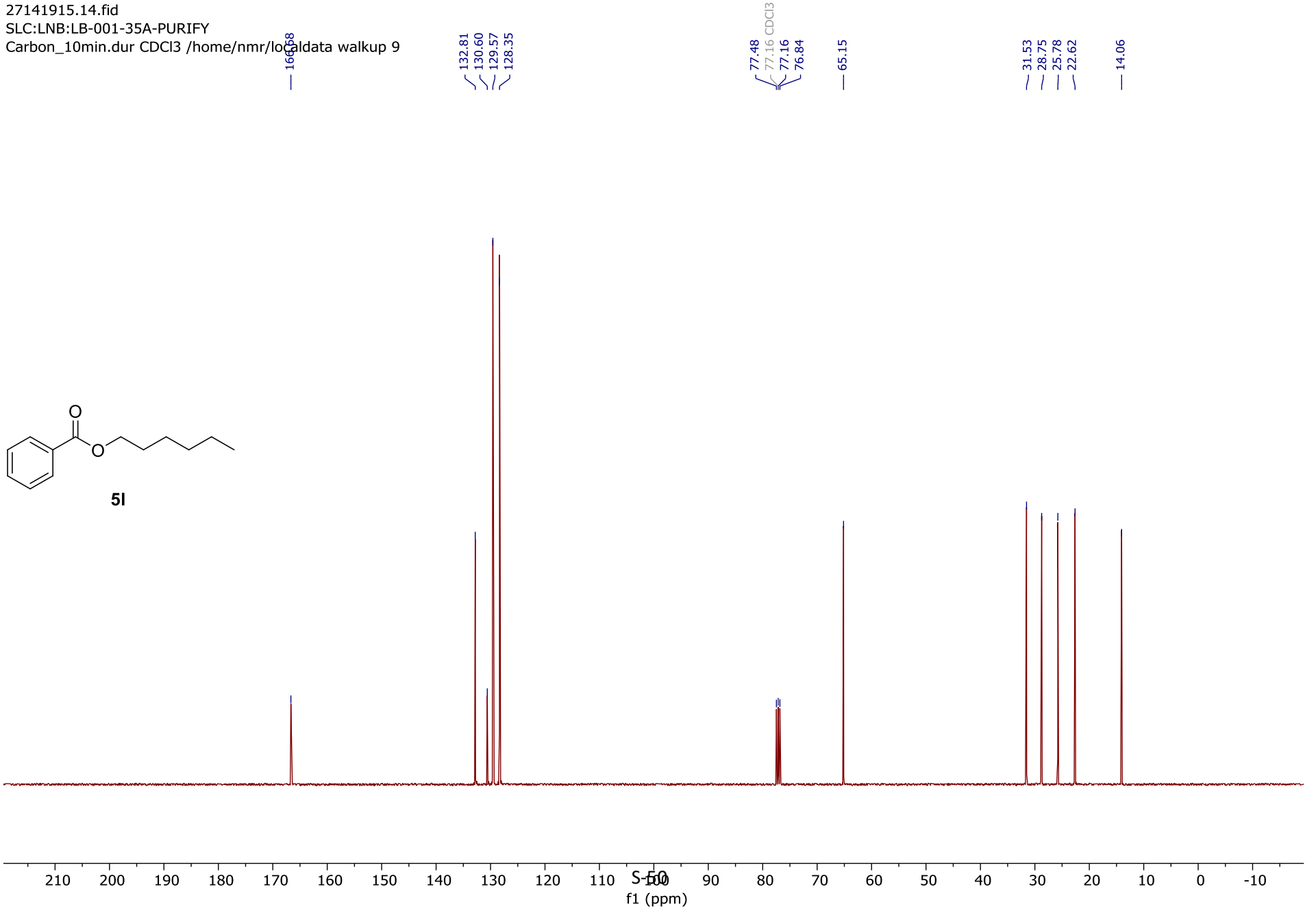


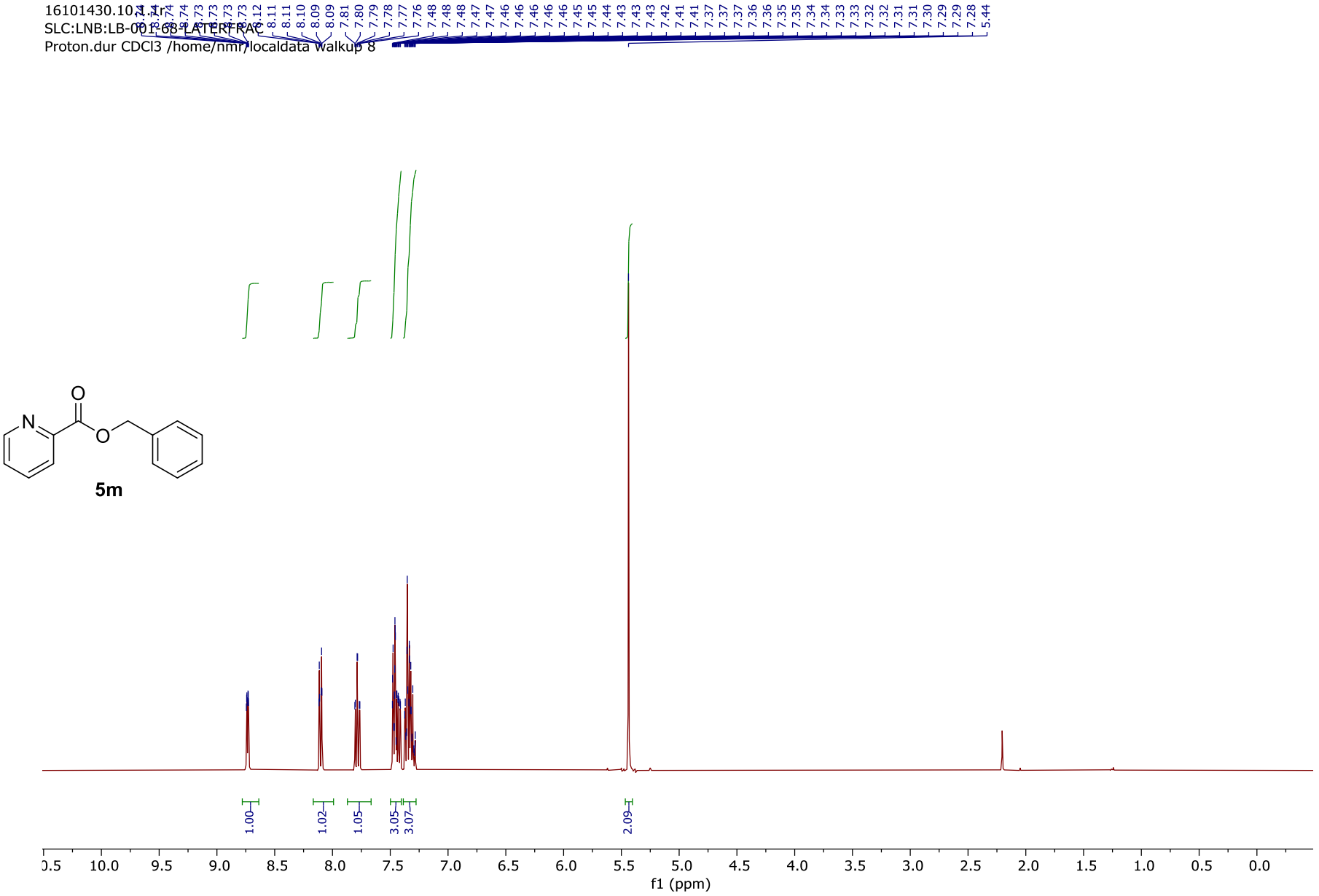
5k


27141915.10.1.1r
SLC:LNB:LB-001-35A-PURIFY
Proton.dur CDCl3 /home/nmrlocaldata/walkup
7.26 CDCl3
1.95
1.00
2.00
2.01
2.05
2.10
4.12
3.05
f1 (ppm)

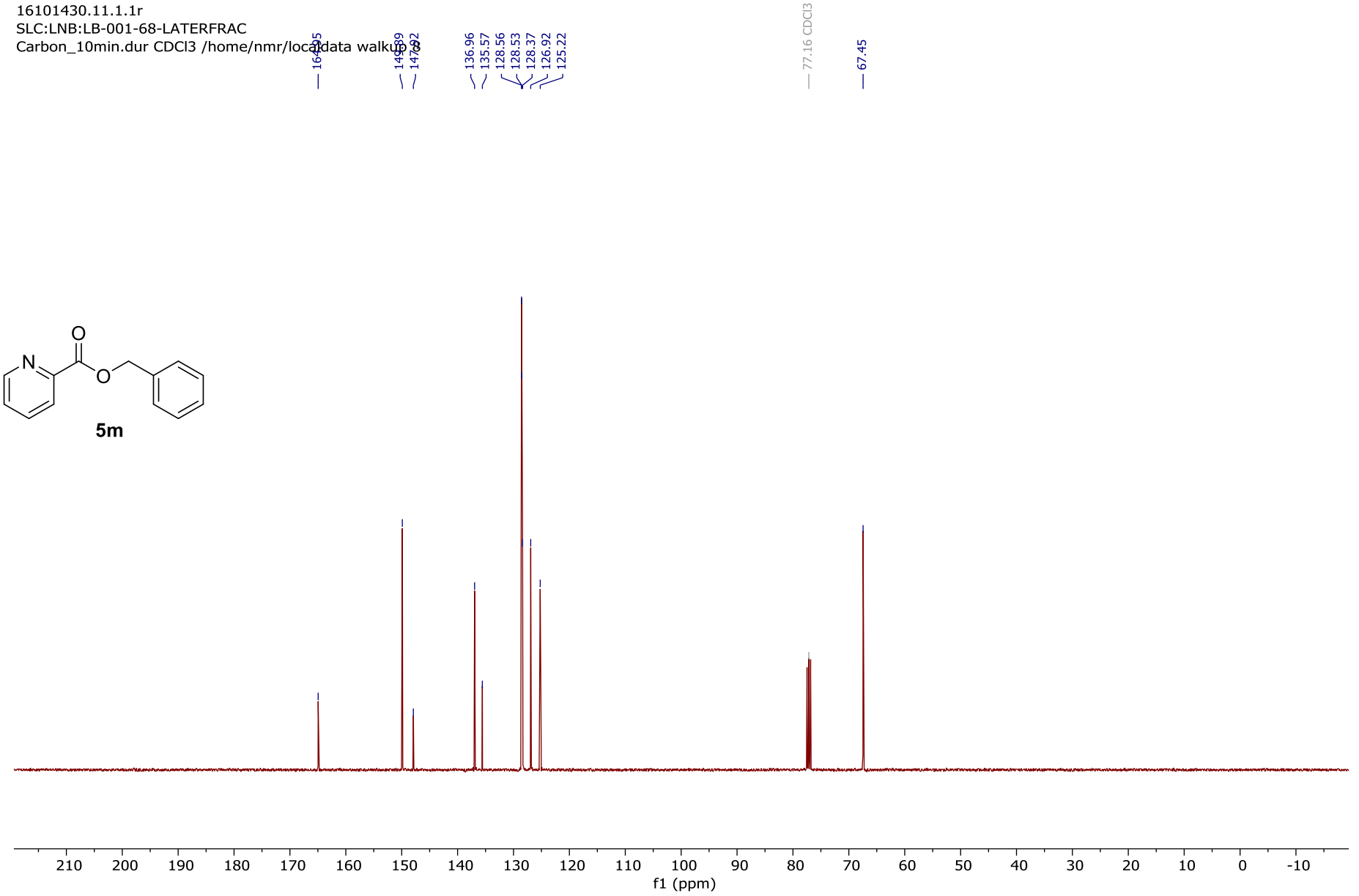
5l

27141915.14.fid
SLC:LNB:LB-001-35A-PURIFY
Carbon_10min.dur CDCl3 /home/nmr/localdata walkup 9

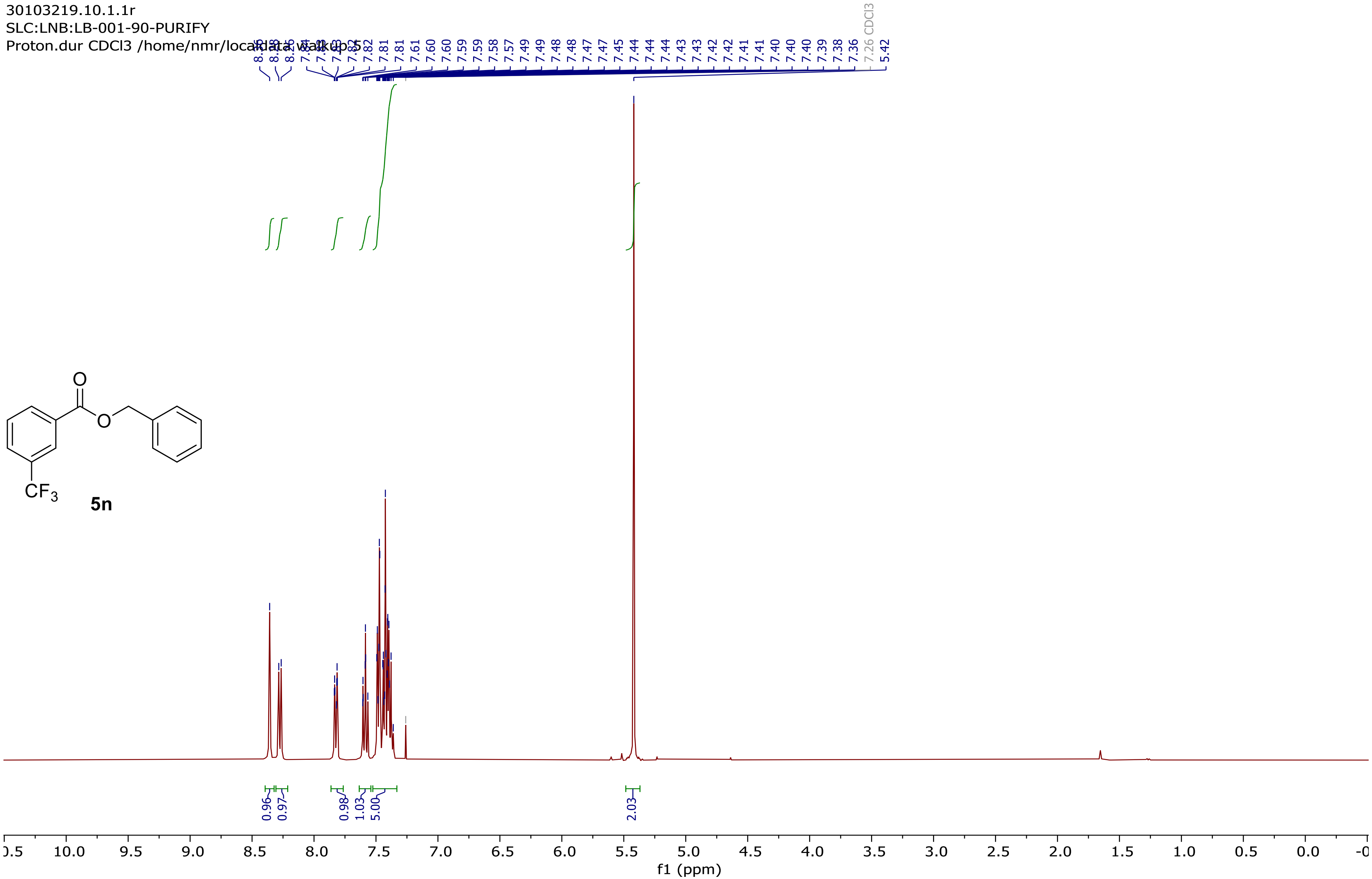



16101430.10.1.1r
SLC:LNB:LB-001-68 LATERFRAC
Proton.dur CDCl3 /home/nmr/localdata walkup 8
8.74 8.74 8.73 8.73 8.73 8.73 8.12 8.11 8.11 8.10 8.09 8.09 7.81 7.80 7.79 7.78 7.77 7.76 7.48 7.48 7.47 7.47 7.46 7.46 7.46 7.46 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.41 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.29 7.28 5.44
O
N
O
5m
1.00
1.02
1.05
3.05
3.07
2.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

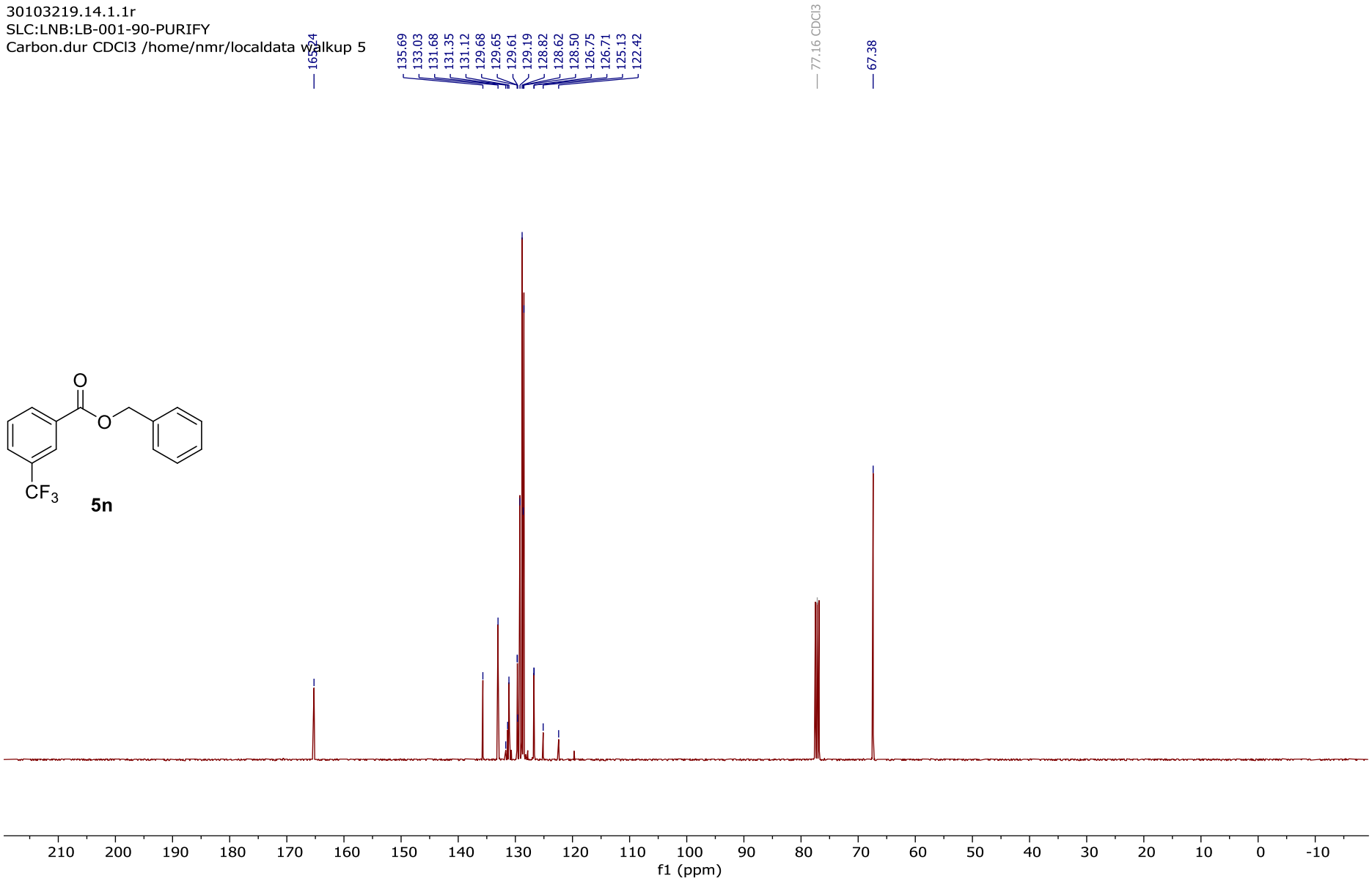
16101430.11.1.1r
SLC:LNB:LB-001-68-LATERFRAC
Carbon_10min.dur CDCl3 /home/nmr/locadata walkup 3



30103219.10.1.1r
SLC:LNB:LB-001-90-PURIFY
Proton.dur CDCl3 /home/nmr/localdata/walkup 5

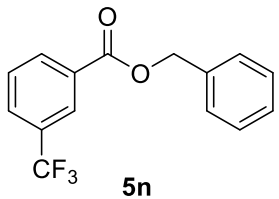


30103219.14.1.1r
SLC:LNB:LB-001-90-PURIFY
Carbon.dur CDCl3 /home/nmr/localdata walkup 5

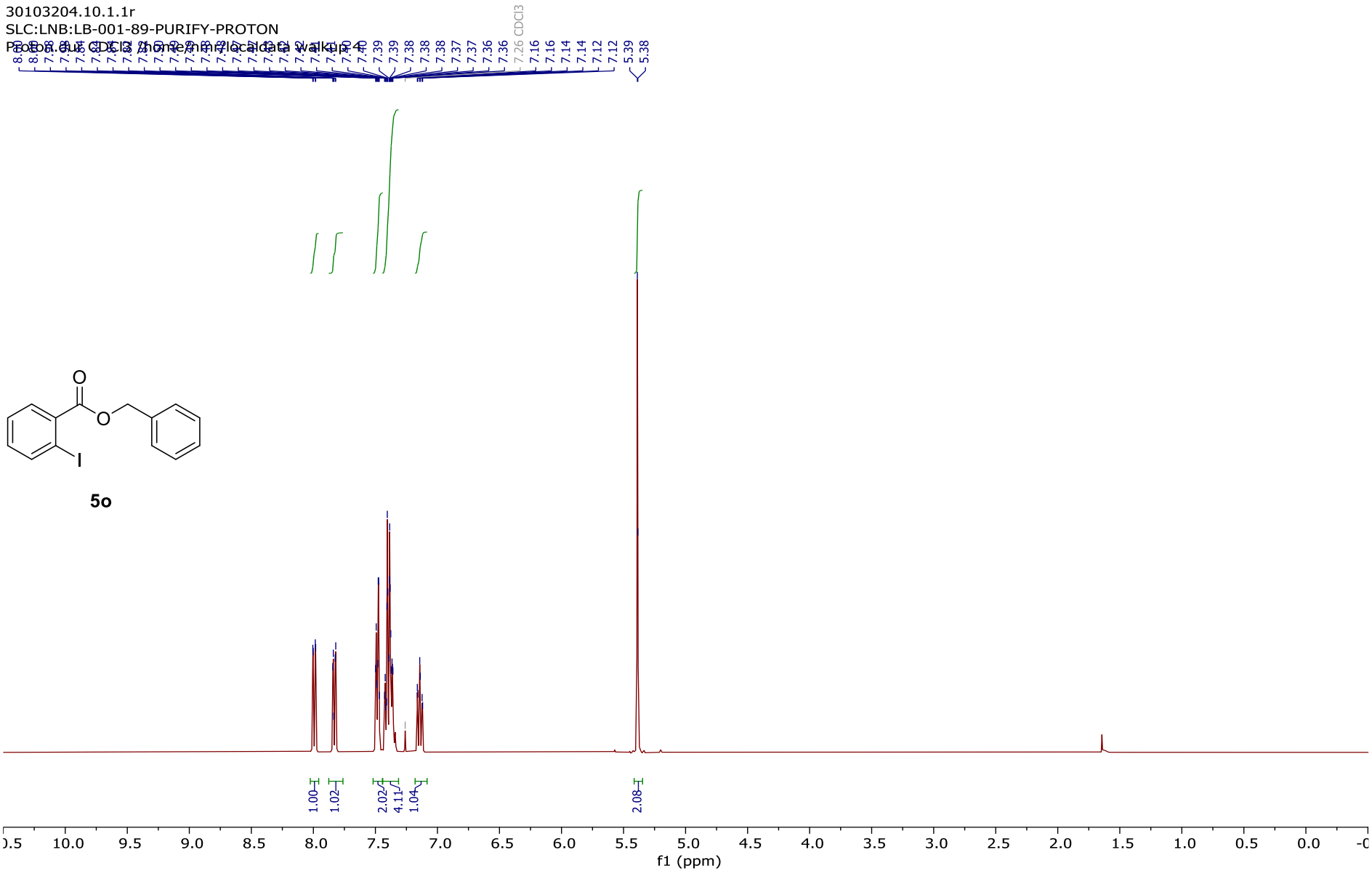


30103219.13.1.1r
SLC:LNB:LB-001-90-PURIFY
F19_limits_dec.dur CDCl3 /home/nmr/localdata walkup 5

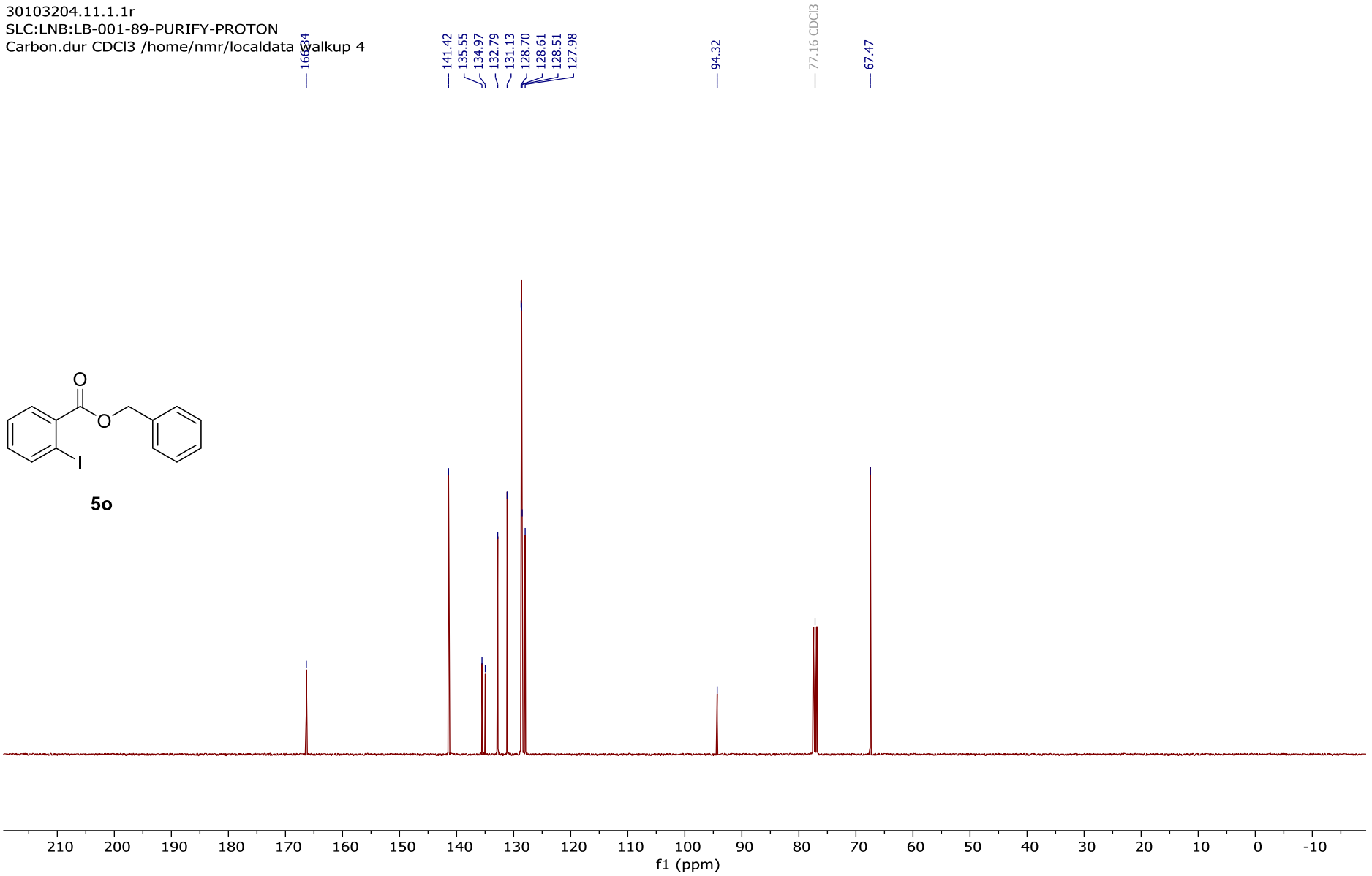
-62.75
-62.75



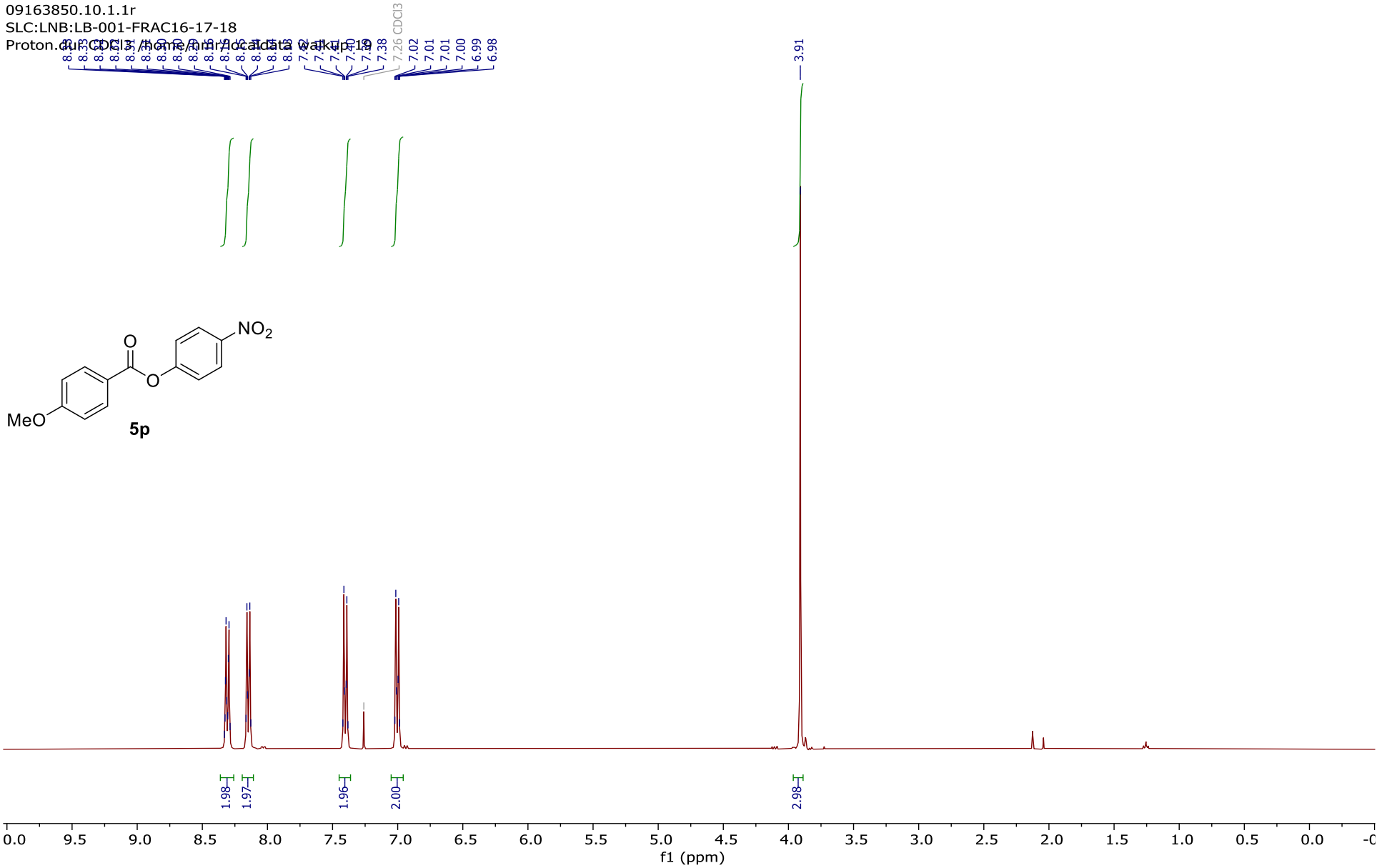
5n

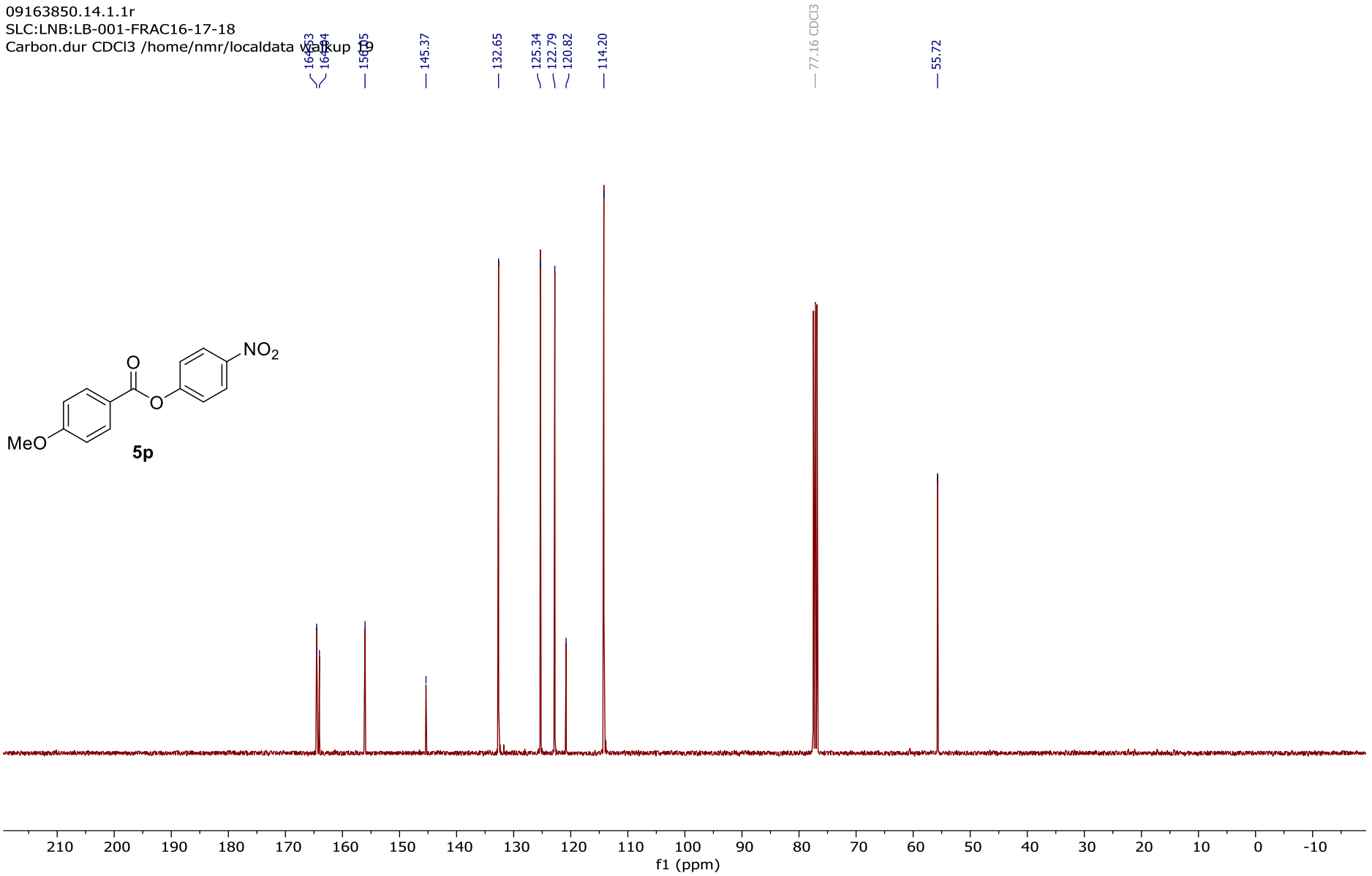

30103204.10.1.1r
SLC:LNB:LB-001-89-PURIFY-PROTON
Proton.dua CDCl3 /home/nmr/lqcaldata walkup 4
7.26 CDCl3
5o
1.00
1.02
2.02
4.11
1.04
2.08
f1 (ppm)

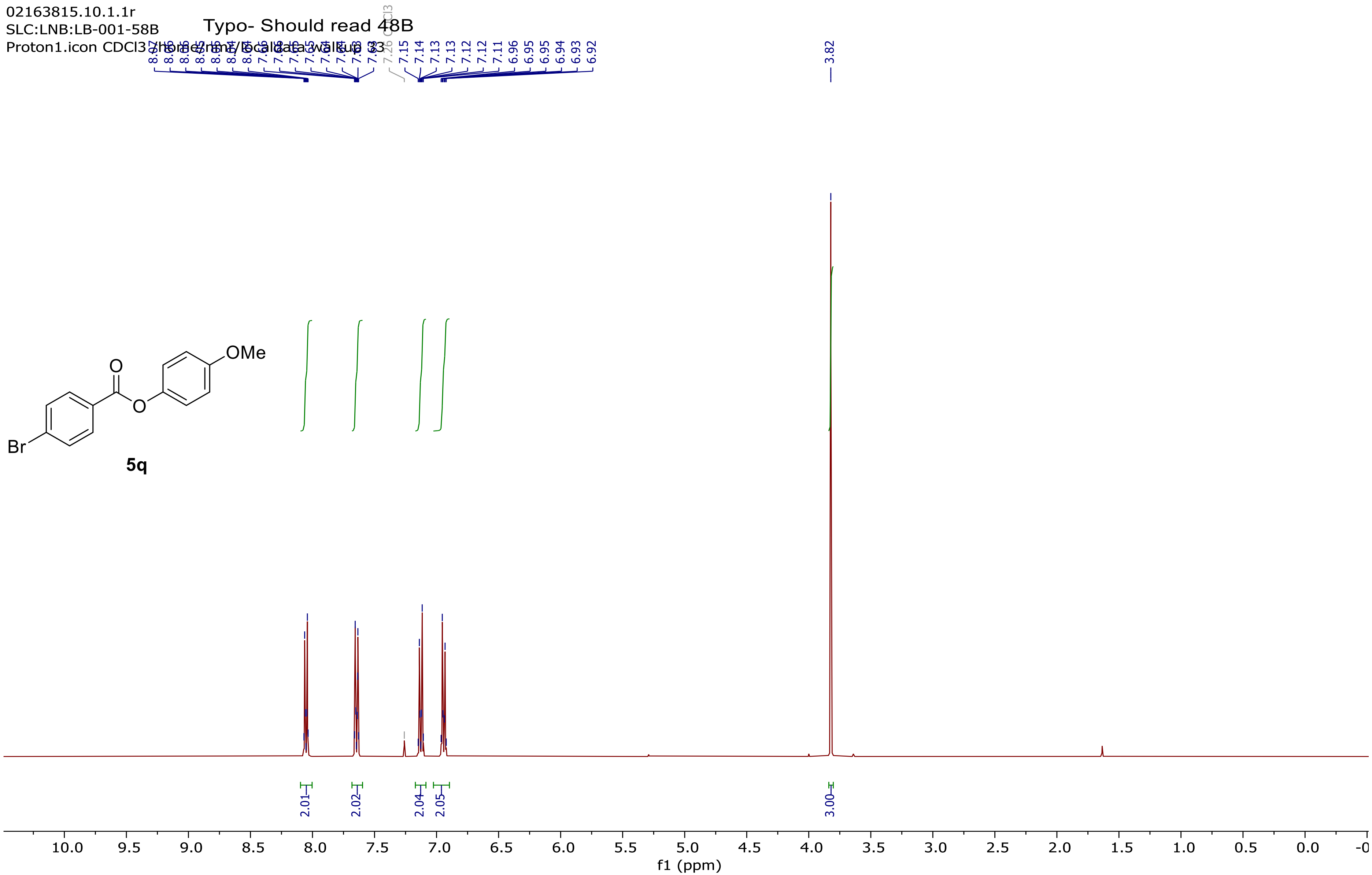
30103204.11.1.1r
SLC:LNB:LB-001-89-PURIFY-PROTON
Carbon.dur CDCl3 /home/nmr/localdata calkup 4



5o

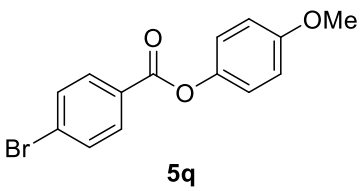

09163850.10.1.1r
SLC:LNB:LB-001-FRAC16-17-18
Proton.dur CDCl3 /home/nmr/locadata walkup 19
7.26 CDCl3
3.91
NO2
O
O
MeO
5p
1.98
1.97
1.96
2.00
2.98
f1 (ppm)


09163850.14.1.1r
SLC:LNB:LB-001-FRAC16-17-18
Carbon.dur CDCl3 /home/nmr/localdata walkup 1p
164.53
164.04
150.15
145.37
132.65
125.34
122.79
120.82
114.20
77.16 CDCl3
55.72
NO2
O
O
MeO
5p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



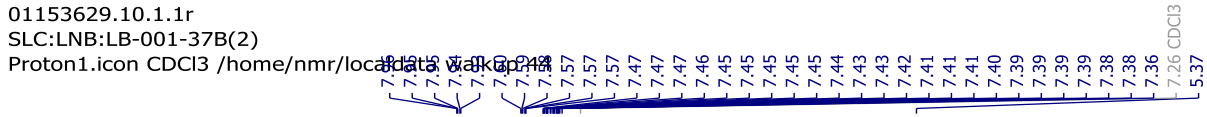
02163815.10.1.1r
SLC:LNB:LB-001-58B
Typo- Should read 48B
7.26 CDCl3
7.15
7.14
7.13
7.13
7.12
7.11
6.96
6.95
6.95
6.94
6.93
6.92
3.82
OMe
O
O
Br
5q
2.01
2.02
2.04
2.05
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

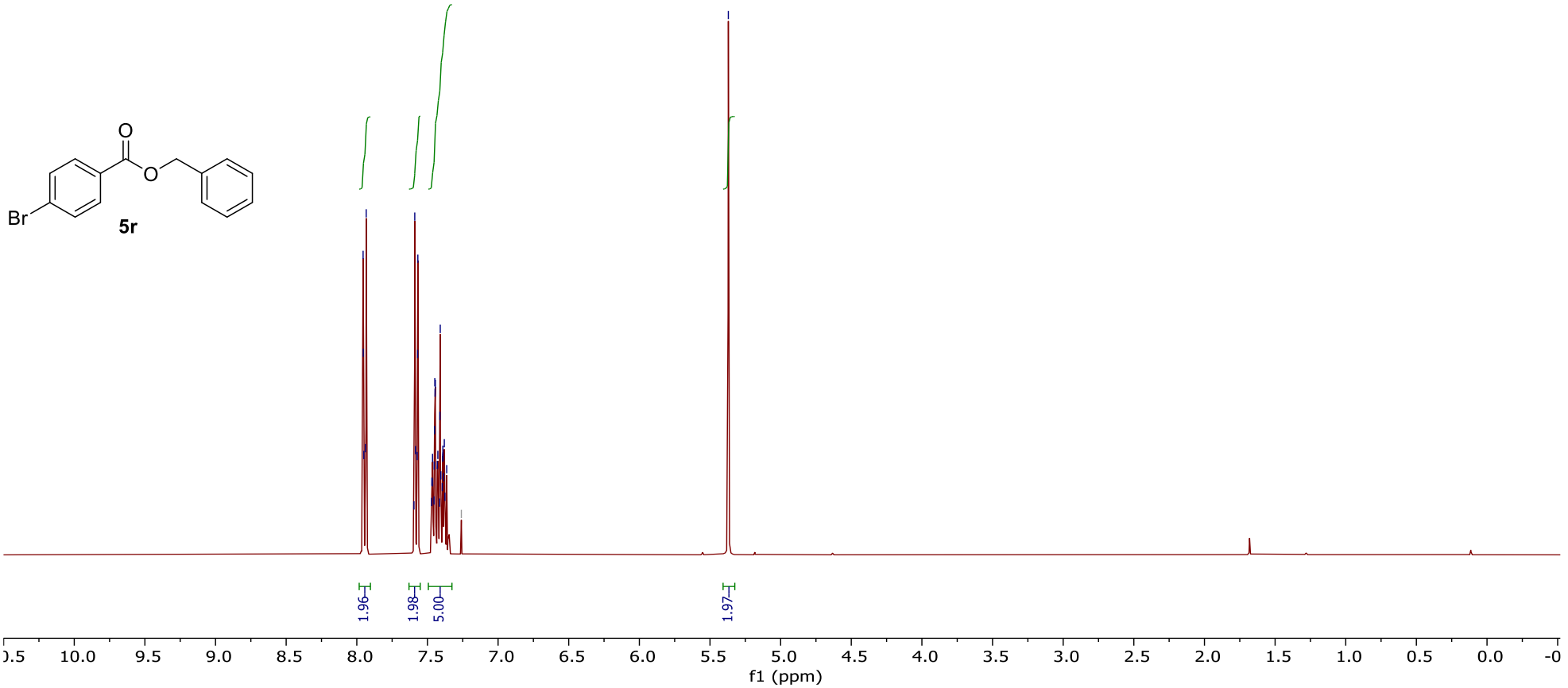
02163815.11.1.1r
SLC:LNB:LB-001-58B
Carbon.dur CDCl3 /home/nmr/localdata walkup 33

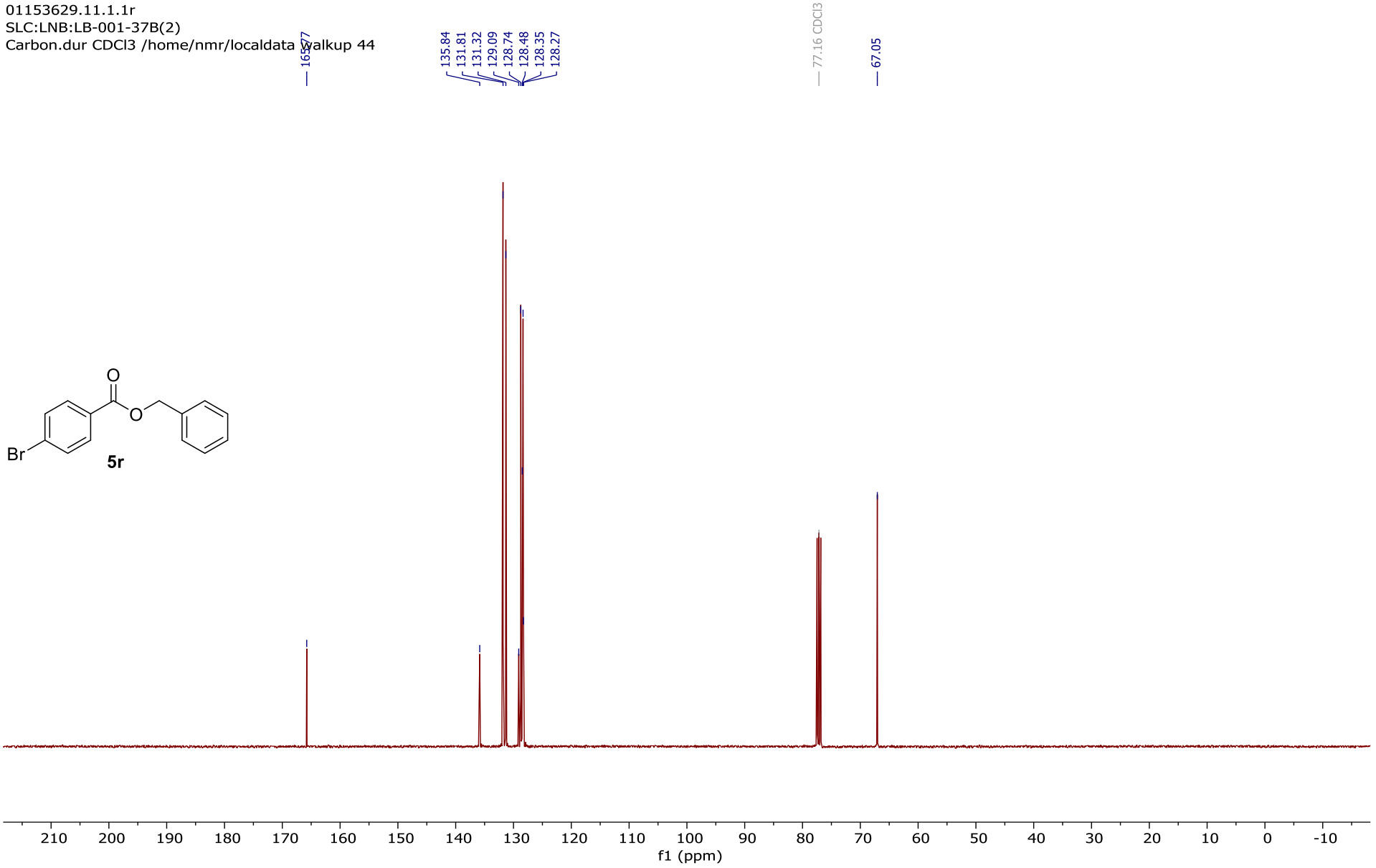


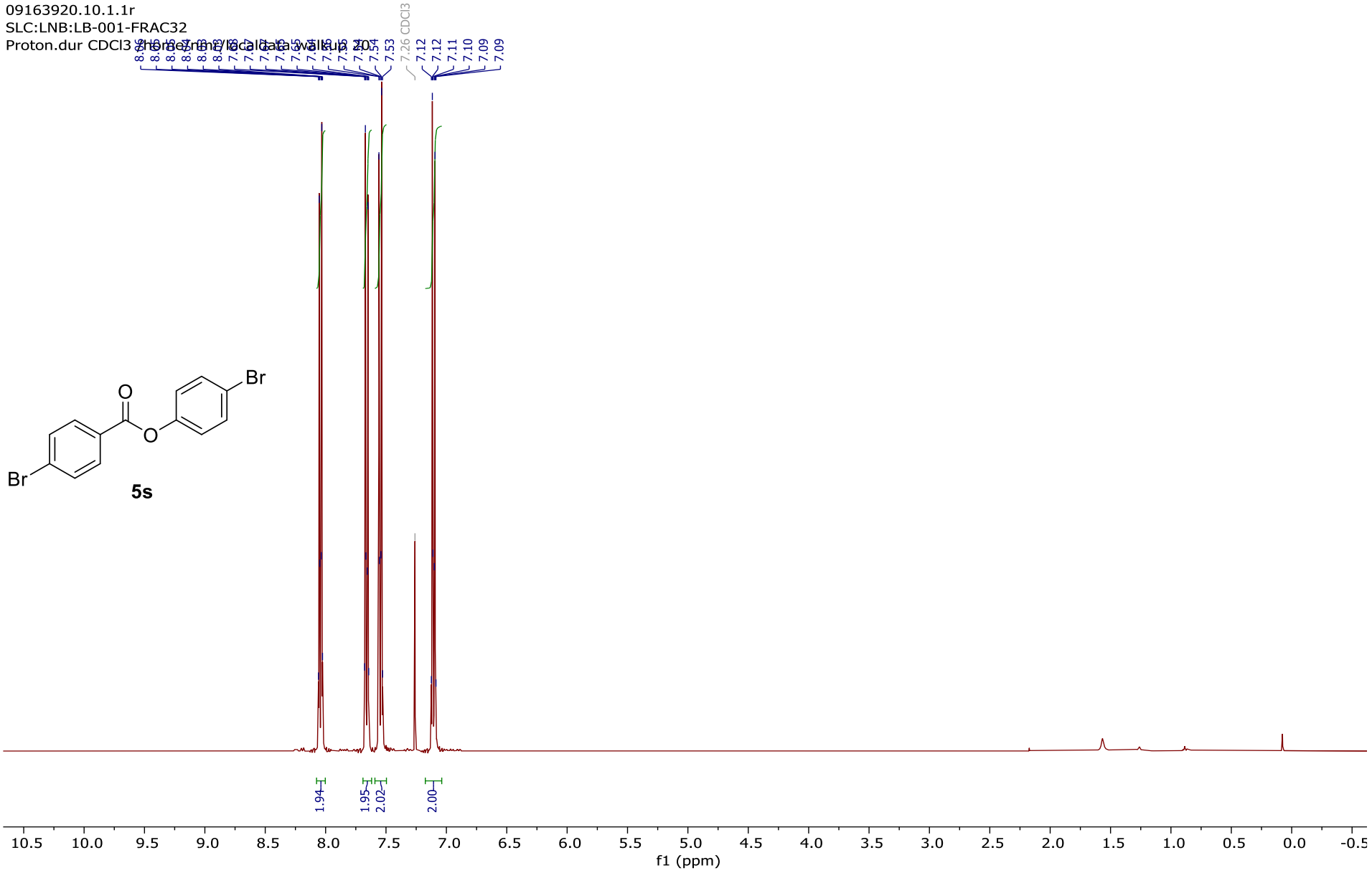
5q

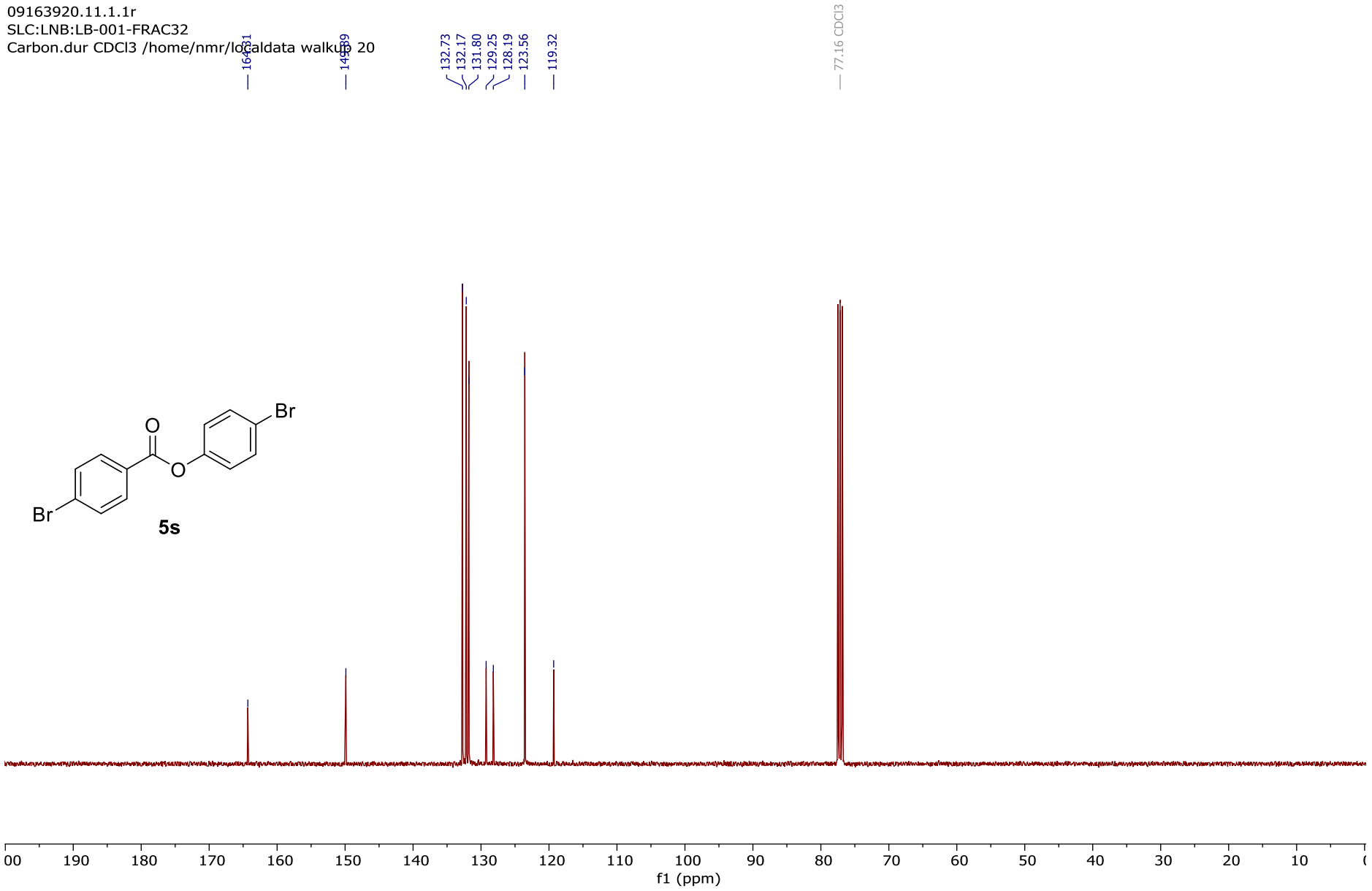
01153629.10.1.1r
SLC:LNB:LB-001-37B(2)
Proton1.icon CDCl3 /home/nmr/locadata wakaki 948

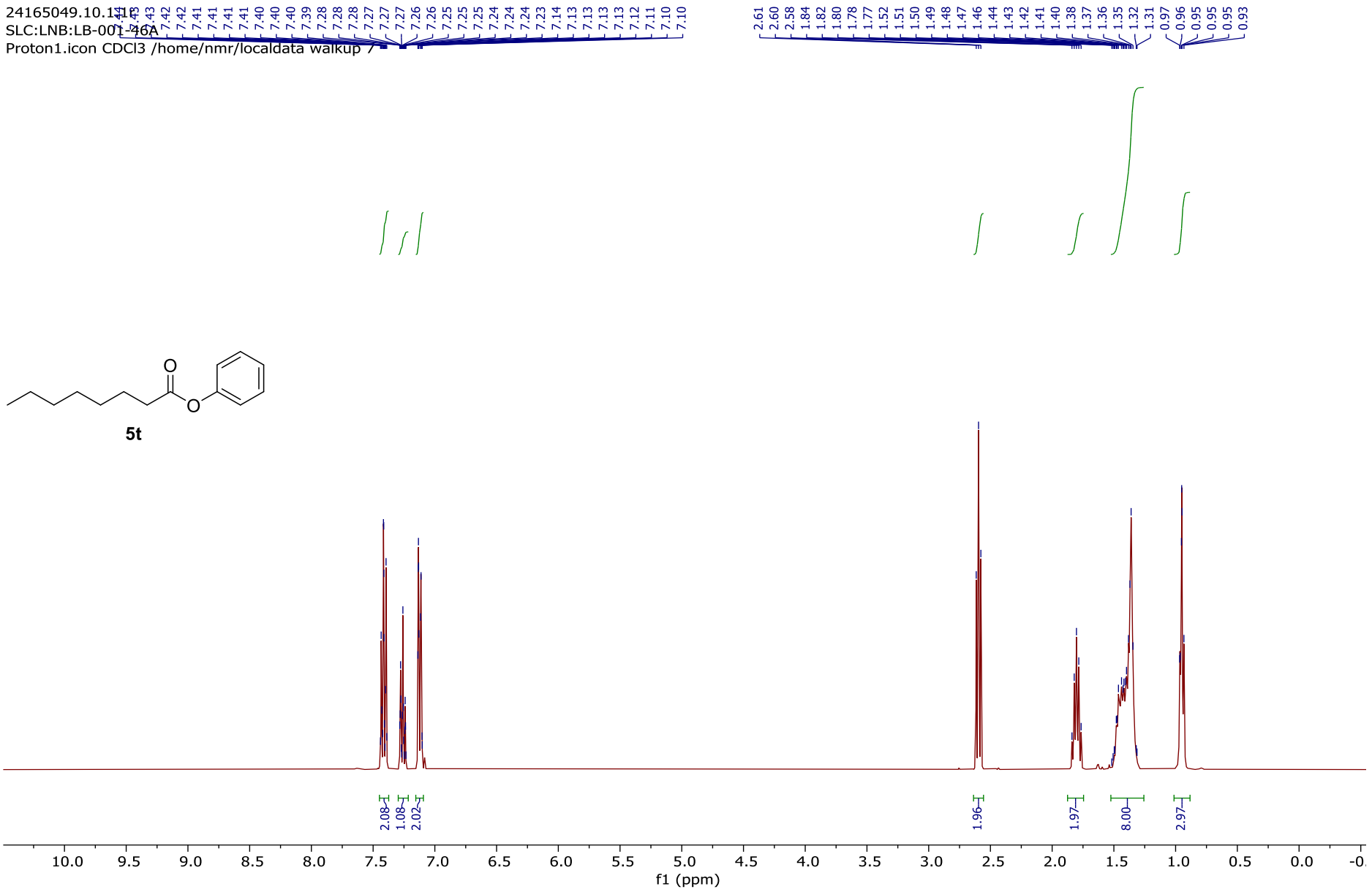




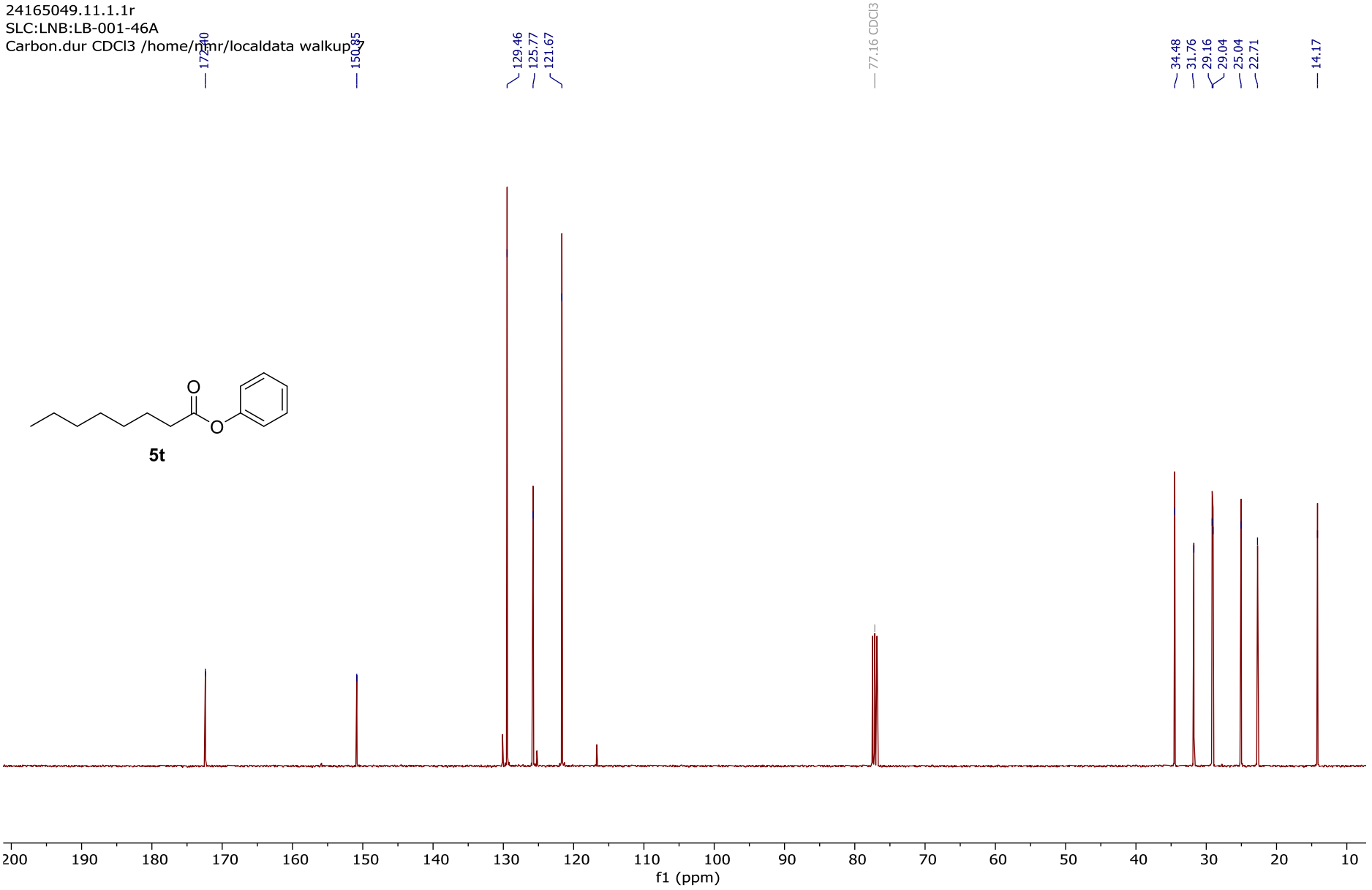

01153629.11.1.1r
SLC:LNB:LB-001-37B(2)
Carbon.dur CDCl3 /home/nmr/localdata walkup 44
165.77
135.84
131.81
131.32
129.09
128.74
128.48
128.35
128.27
77.16 CDCl3
67.05
O
O
Br
5r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


09163920.10.1.1r
SLC:LNB:LB-001-FRAC32
Proton.dur CDCl3
7.26 CDCl3
7.53
7.12
7.12
7.11
7.10
7.09
7.09
O
O
Br
Br
5s
1.94
1.95
2.02
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


09163920.11.1.1r
SLC:LNB:LB-001-FRAC32
Carbon.dur CDCl3 /home/nmr/localdata walku
20
164.31
149.89
132.73
132.17
131.80
129.25
128.19
123.56
119.32
77.16 CDCl3
Br
O
O
Br
5s
f1 (ppm)

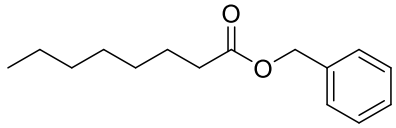

24165049.10.1.1H
SLC:LNB:LB-001-16A
Proton1.icon CDCl3 /home/nmr/localdata walkup 7
O
O
5t
2.08
1.08
2.02
1.96
1.97
8.00
2.97
f1 (ppm)

24165049.11.1.1r
SLC:LNB:LB-001-46A
Carbon.dur CDCl3 /home/nmr/localdata walkup



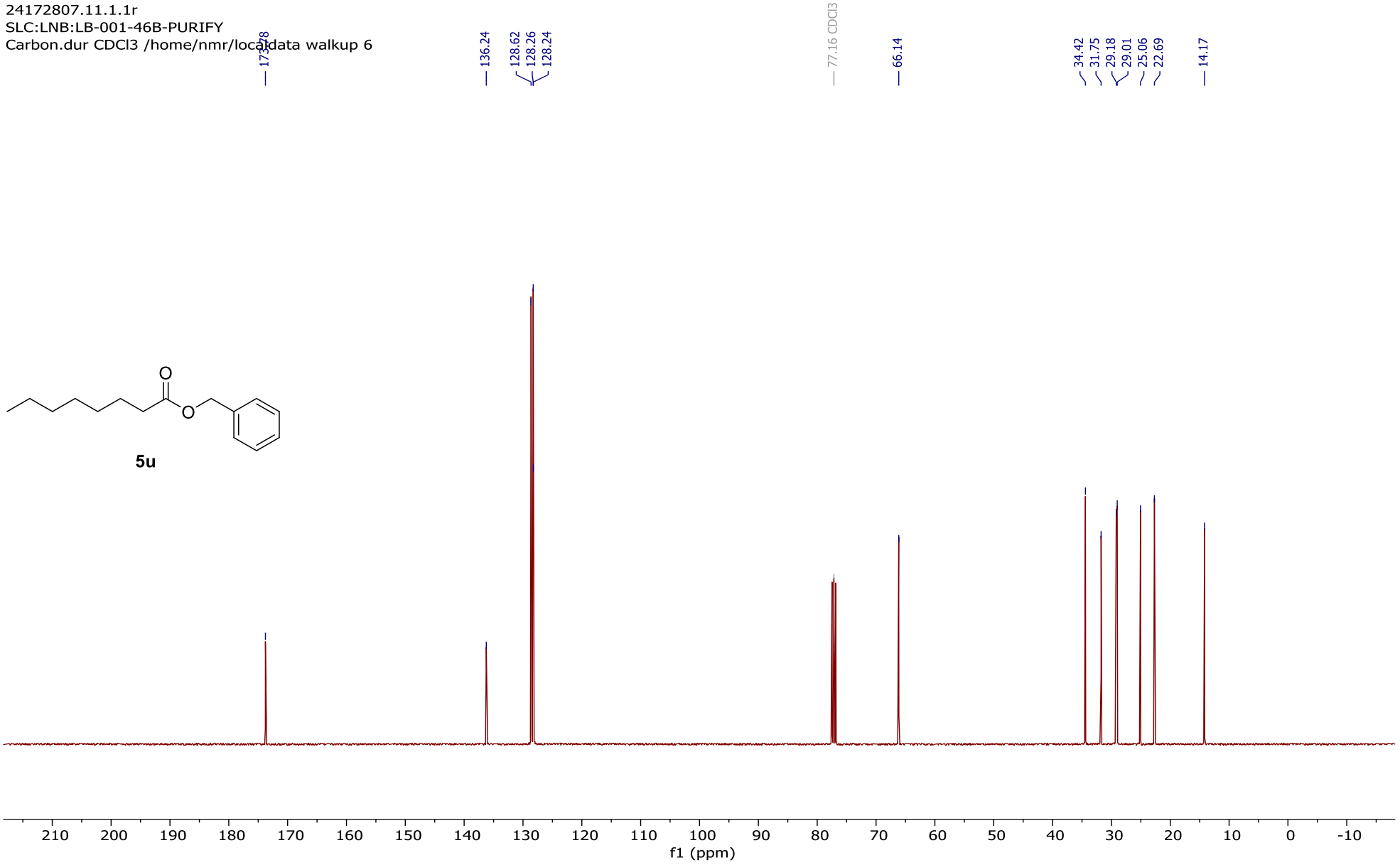
5t

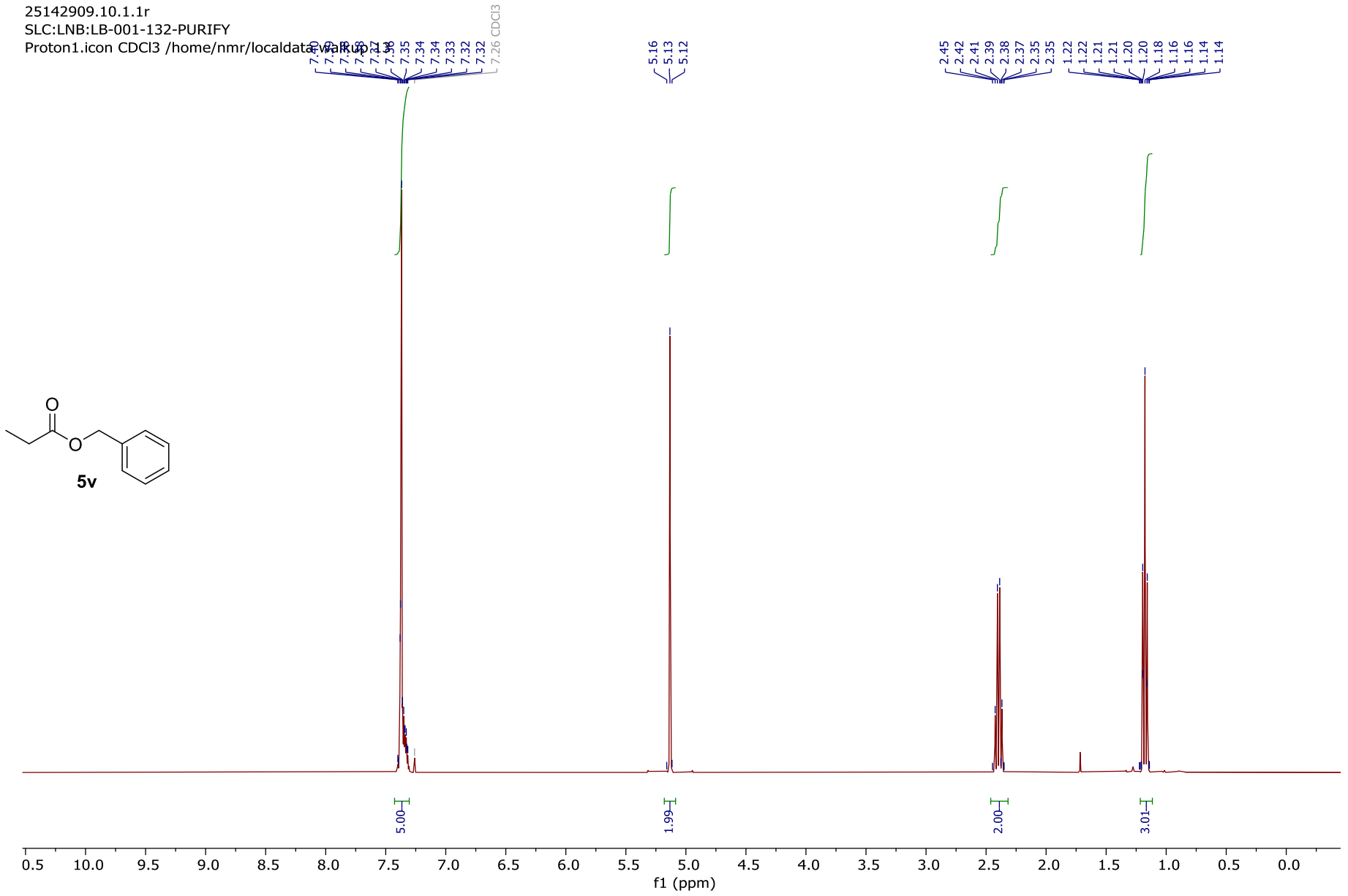
24172807.10.1.1r
SLC:LNB:LB-001-46B-PURIFY
Proton1.icon CDCl3 /home/nmr/localdata-walkup 5



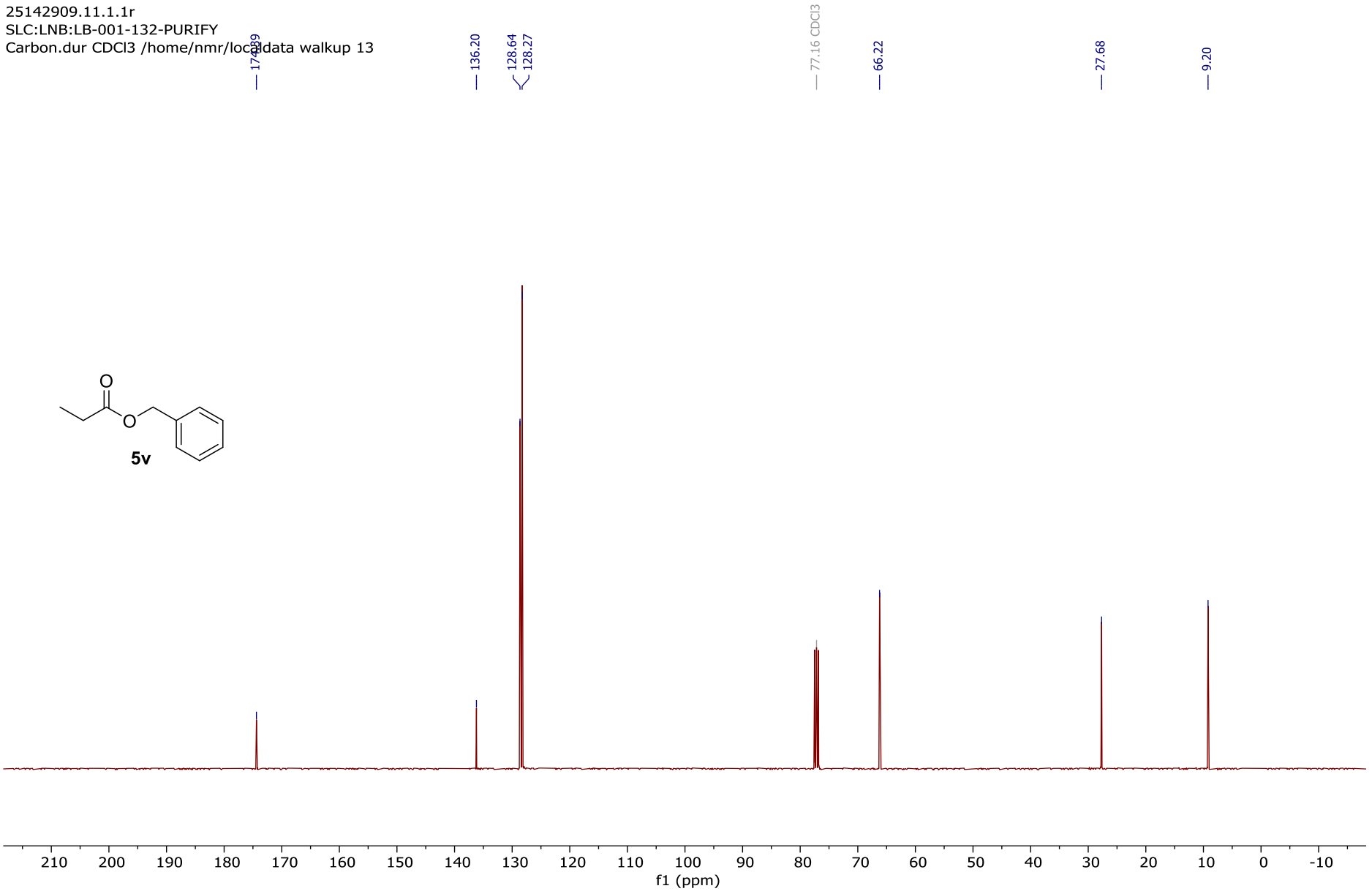
5u

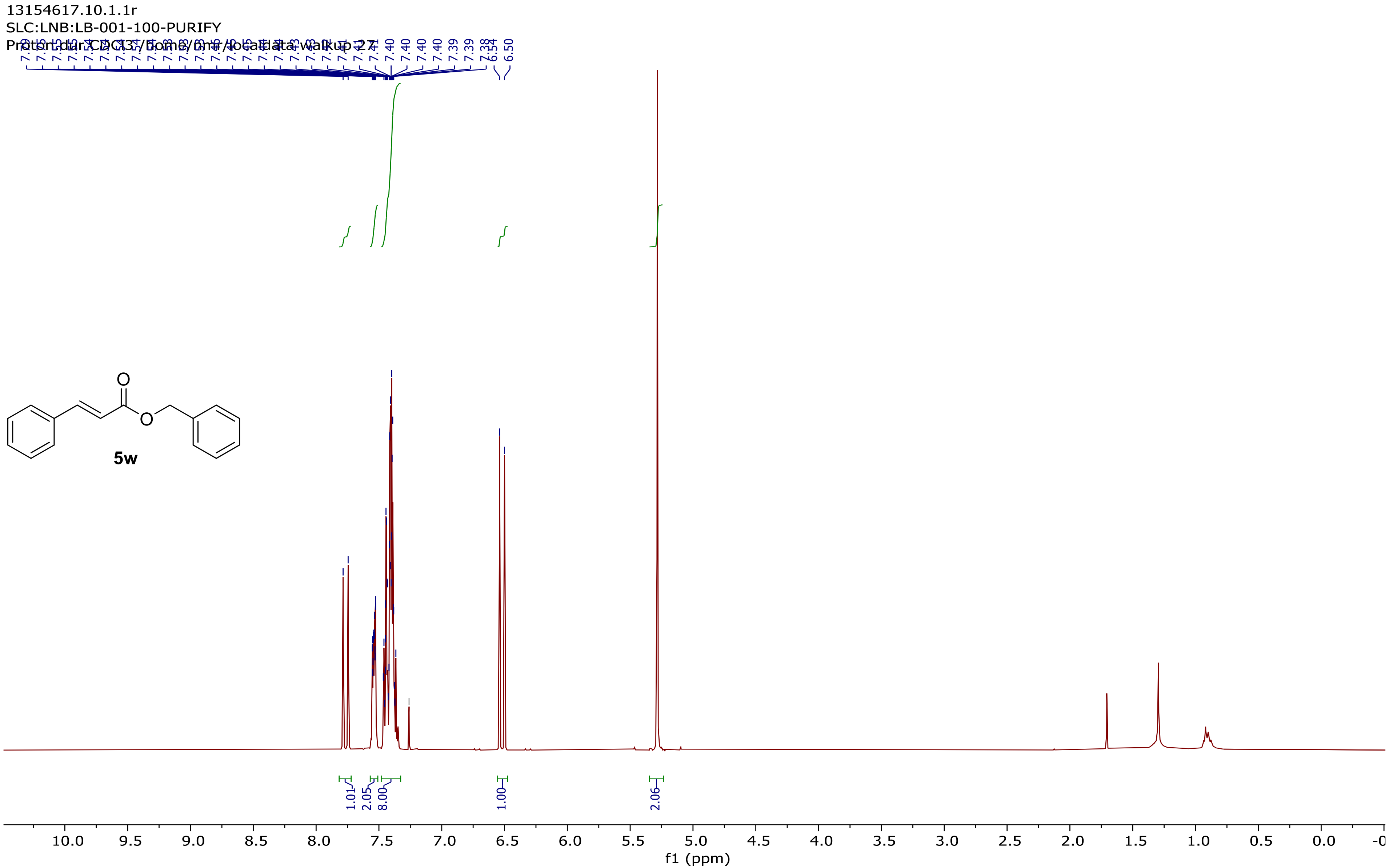
24172807.11.1.1r
SLC:LNB:LB-001-46B-PURIFY
Carbon.dur CDCl3 /home/nmr/local data walkup 6




25142909.10.1.1r
SLC:LNB:LB-001-132-PURIFY
Proton1.icon CDCl3 /home/nmr/localdata/walkup/1
7.40 7.39 7.38 7.37 7.36 7.35 7.34 7.34 7.33 7.32 7.32 7.26 CDCl3
5.16 5.13 5.12
2.45 2.42 2.41 2.39 2.38 2.37 2.35 2.35
1.22 1.22 1.21 1.21 1.20 1.20 1.18 1.16 1.16 1.14 1.14
O
O
5v
5.00
1.99
2.00
3.01
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

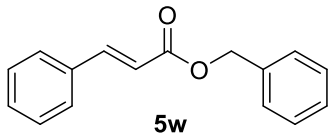
25142909.11.1.1r
SLC:LNB:LB-001-132-PURIFY
Carbon.dur CDCl3 /home/nmr/local/data walkup 13



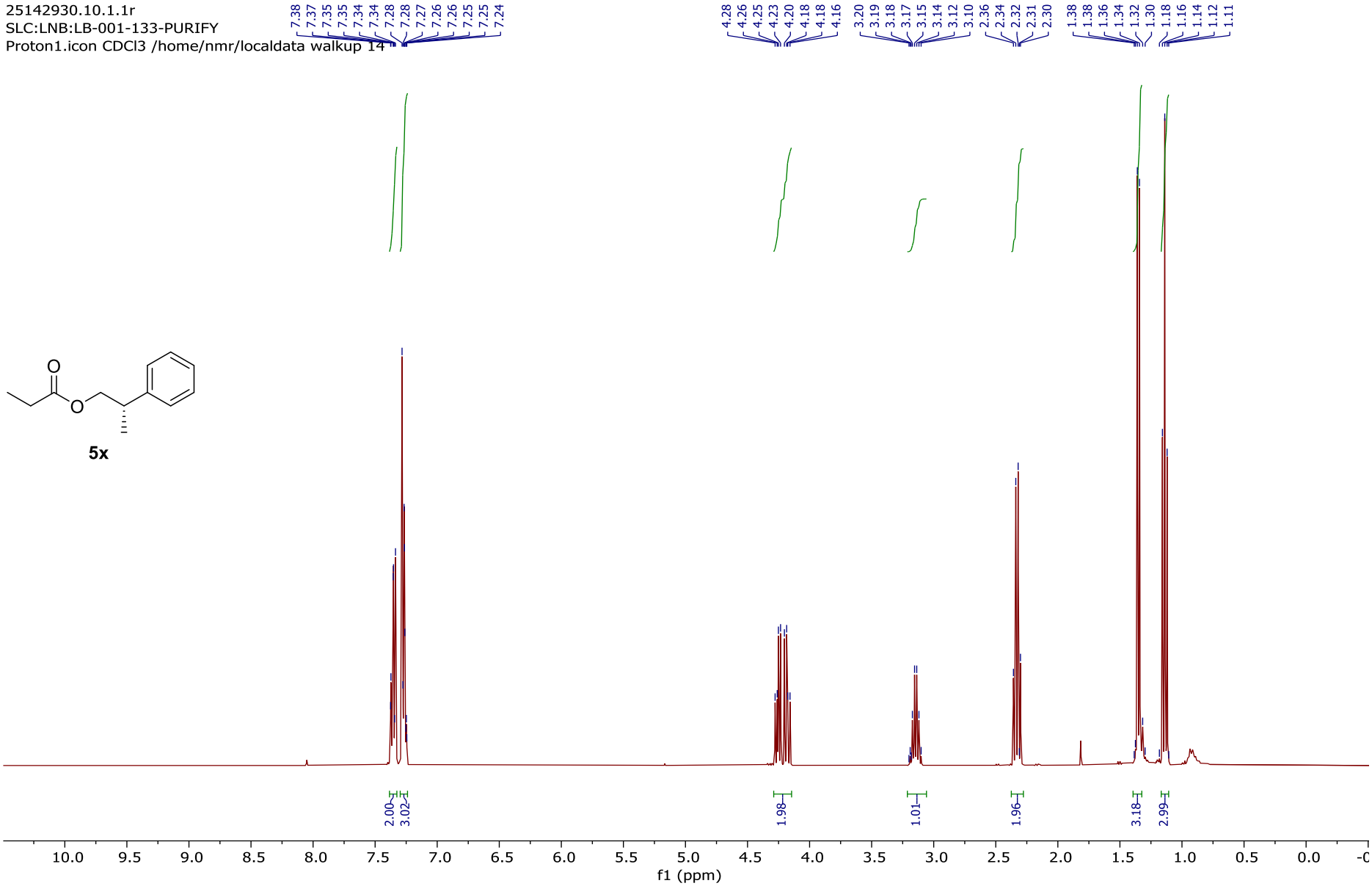

13154617.10.1.1r
SLC:LNB:LB-001-100-PURIFY
O
O
5w
1.01
2.05
8.00
1.00
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

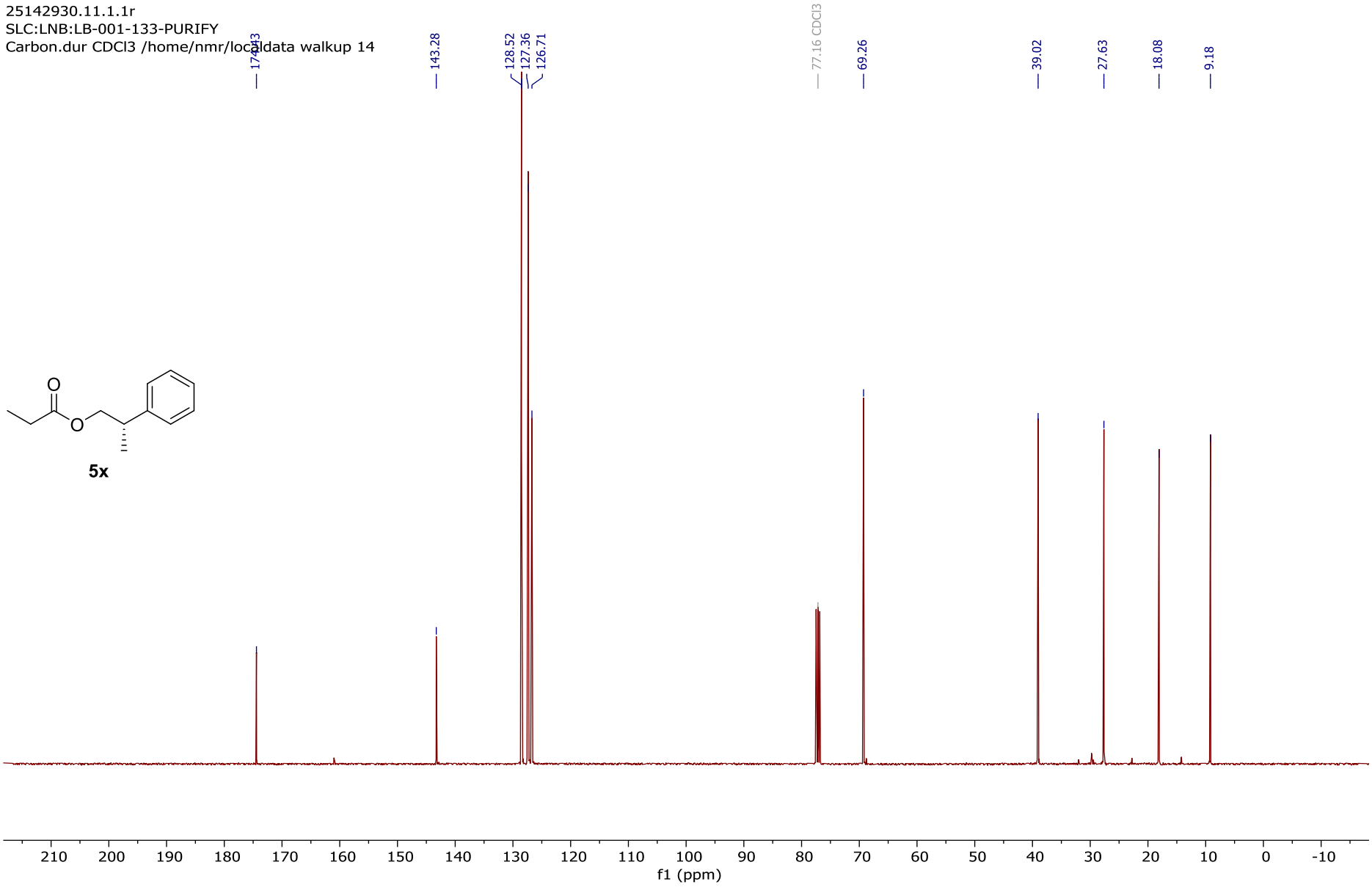
13154617.11.1.1r
SLC:LNB:LB-001-100-PURIFY
Carbon_10min.dur CDCl3 /home/nmr/localdata walkup 27

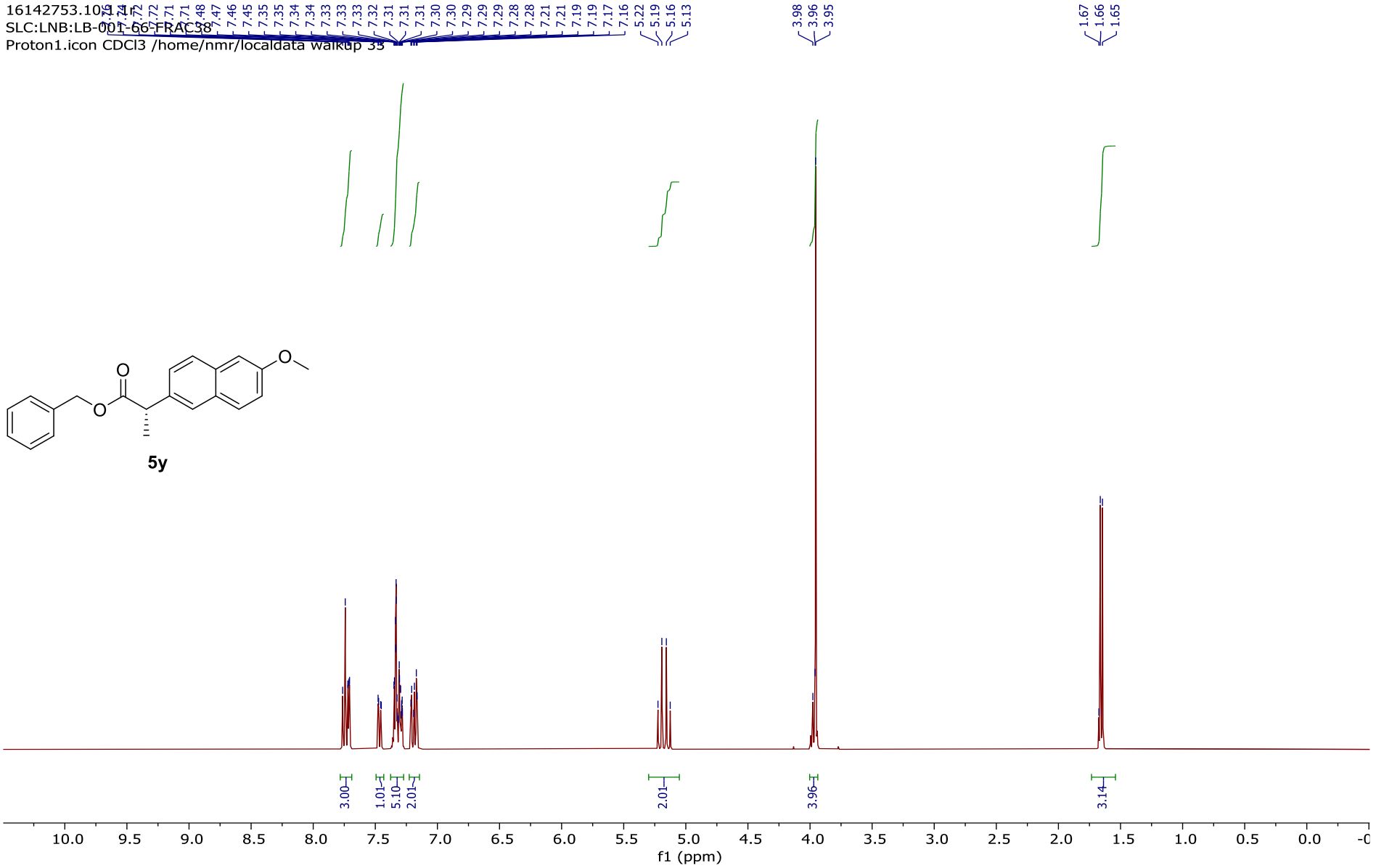
166.36
145.27
136.16
134.43
130.44
128.98
128.69
128.38
128.35
128.20
117.96
77.16 CDCl3
66.44



5w

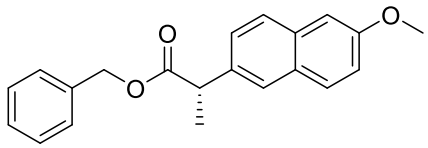

25142930.10.1.1r
SLC:LNB:LB-001-133-PURIFY
Proton1.icon CDCl3 /home/nmr/localdata walkup 14
7.38 7.37 7.35 7.35 7.34 7.34 7.28 7.28 7.27 7.26 7.26 7.25 7.25 7.24
4.28 4.26 4.25 4.23 4.20 4.18 4.18 4.16
3.20 3.19 3.18 3.17 3.15 3.14 3.12 3.10
2.36 2.34 2.32 2.31 2.30
1.38 1.38 1.36 1.34 1.32 1.30 1.18 1.16 1.14 1.12 1.11
O
O
5x
2.00
3.02
1.98
1.01
1.96
3.18
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


25142930.11.1.1r
SLC:LNB:LB-001-133-PURIFY
Carbon.dur CDCl3 /home/nmr/local
data walkup 14
174.43
143.28
128.52
127.36
126.71
77.16 CDCl3
69.26
39.02
27.63
18.08
9.18
O
O
5x
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

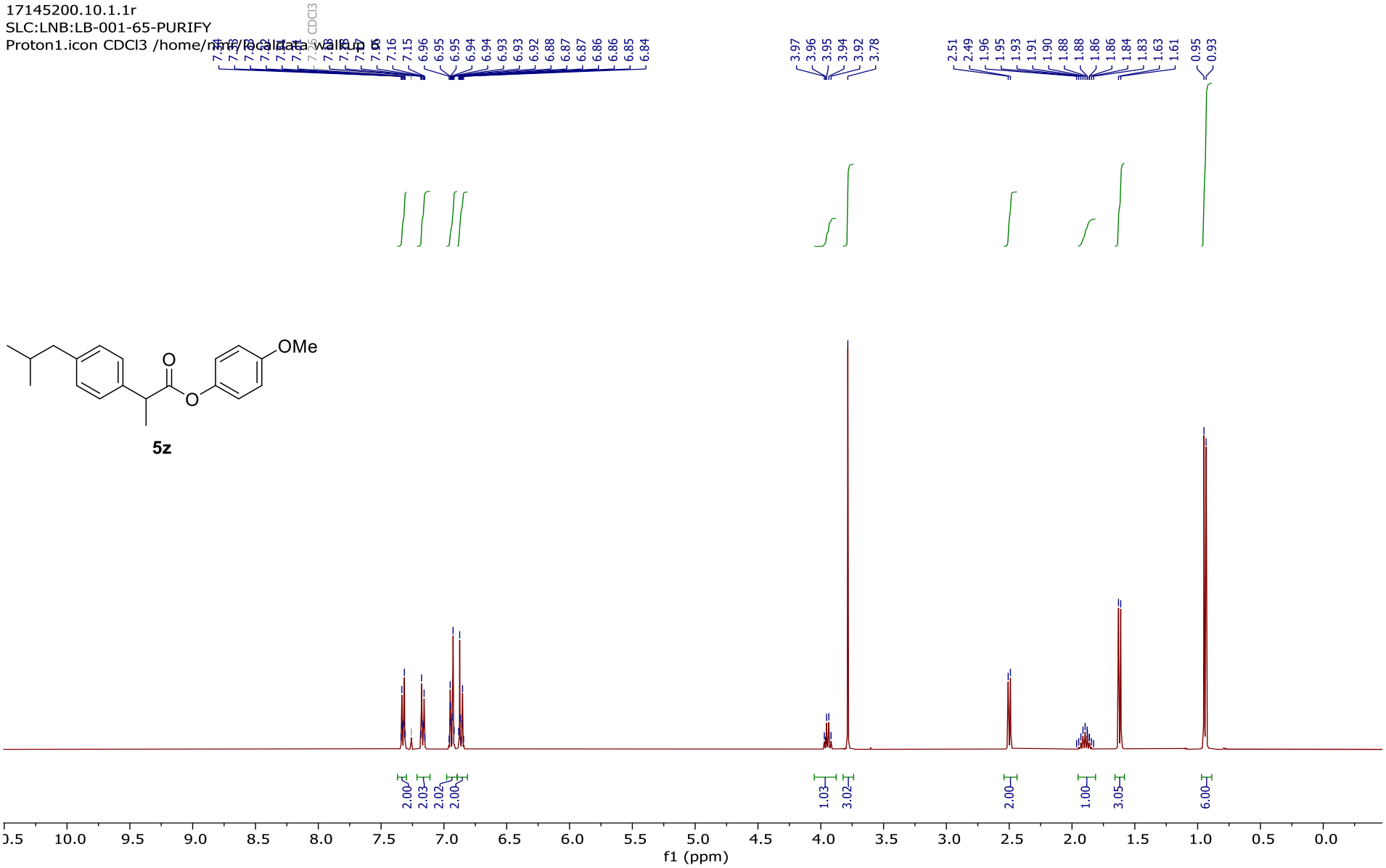

16142753.10117
SLC:LNB:LB-001-66-FRAC38
Proton1.icon CDCl3 /home/nmr/localdata walkup 33
7.76 7.74 7.72 7.72 7.71 7.71 7.48 7.47 7.46 7.45 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.21 7.21 7.19 7.19 7.17 7.16
5.22 5.19 5.16 5.13
3.98 3.96 3.95
1.67 1.66 1.65
O
O
O
5y
3.00 1.01 5.10 2.01 2.01 3.96 3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

16142753.11.1.1r
SLC:LNB:LB-001-66-FRAC38
Carbon.dur CDCl3 /home/nmr/localdata walkup 33

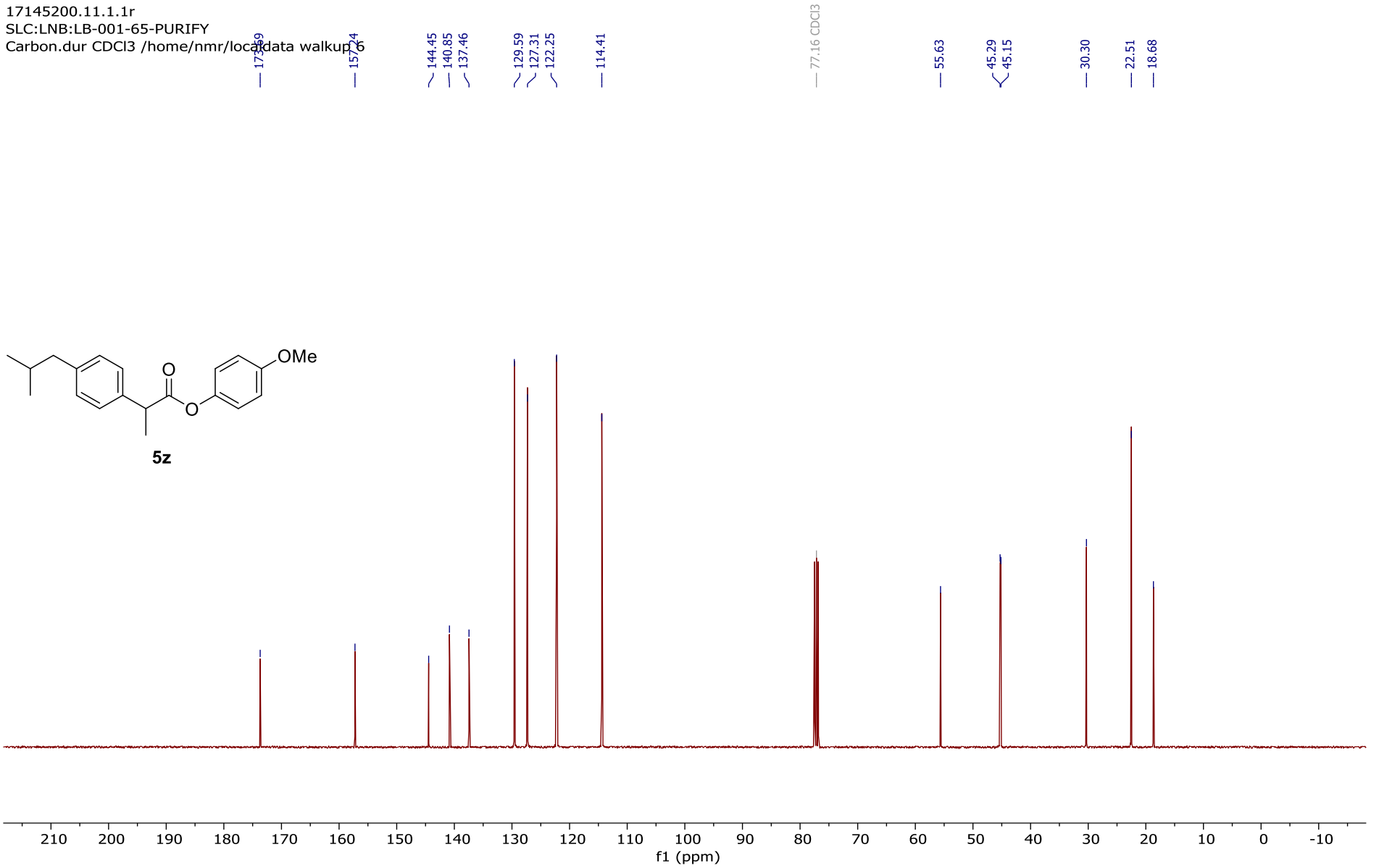
174.56
157.71
136.08
135.64
133.79
129.39
129.00
128.56
128.17
128.03
127.24
126.39
126.09
119.07
105.63
77.16 CDCl3
66.56
55.38
45.54
18.65

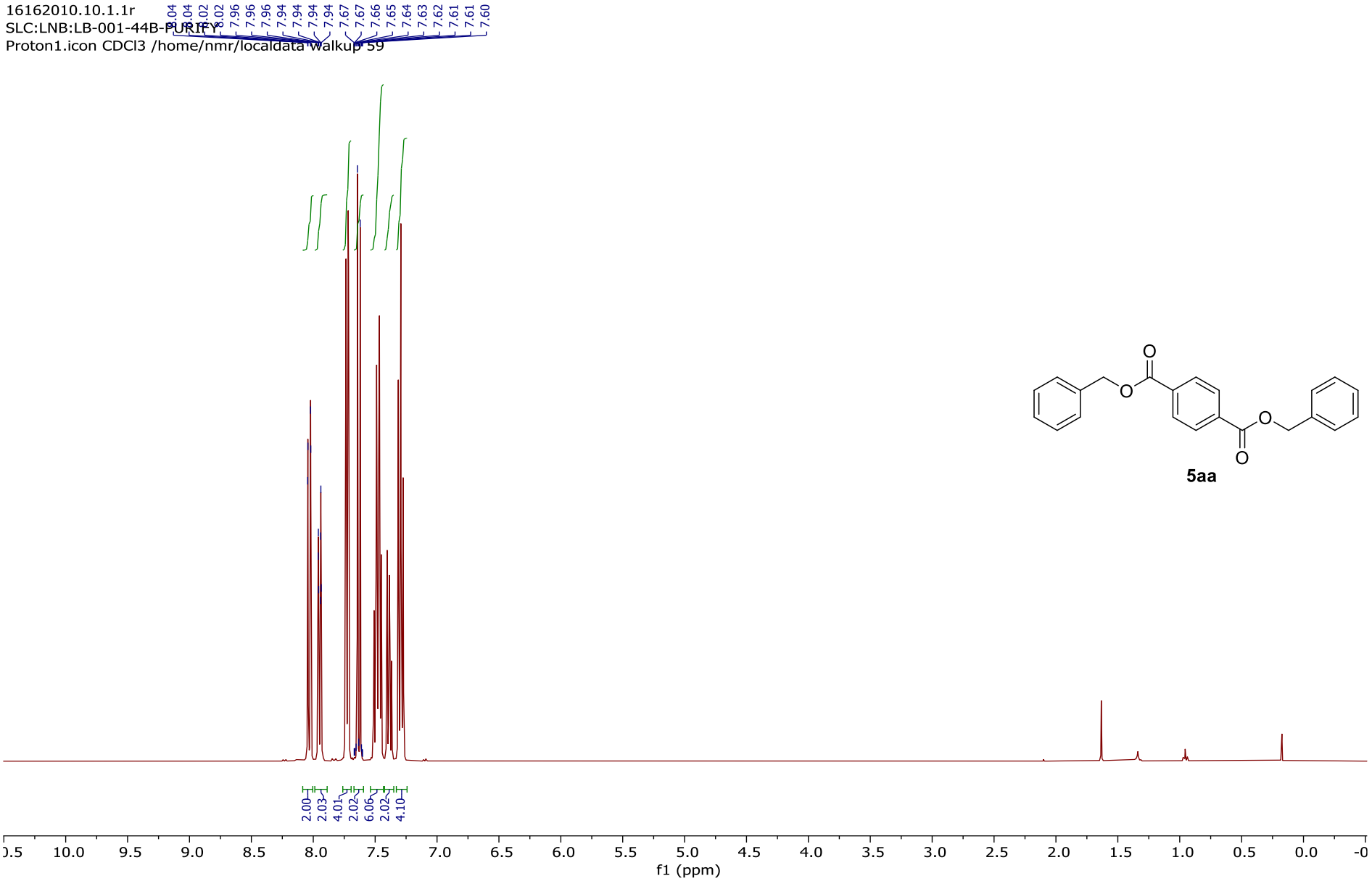


5y

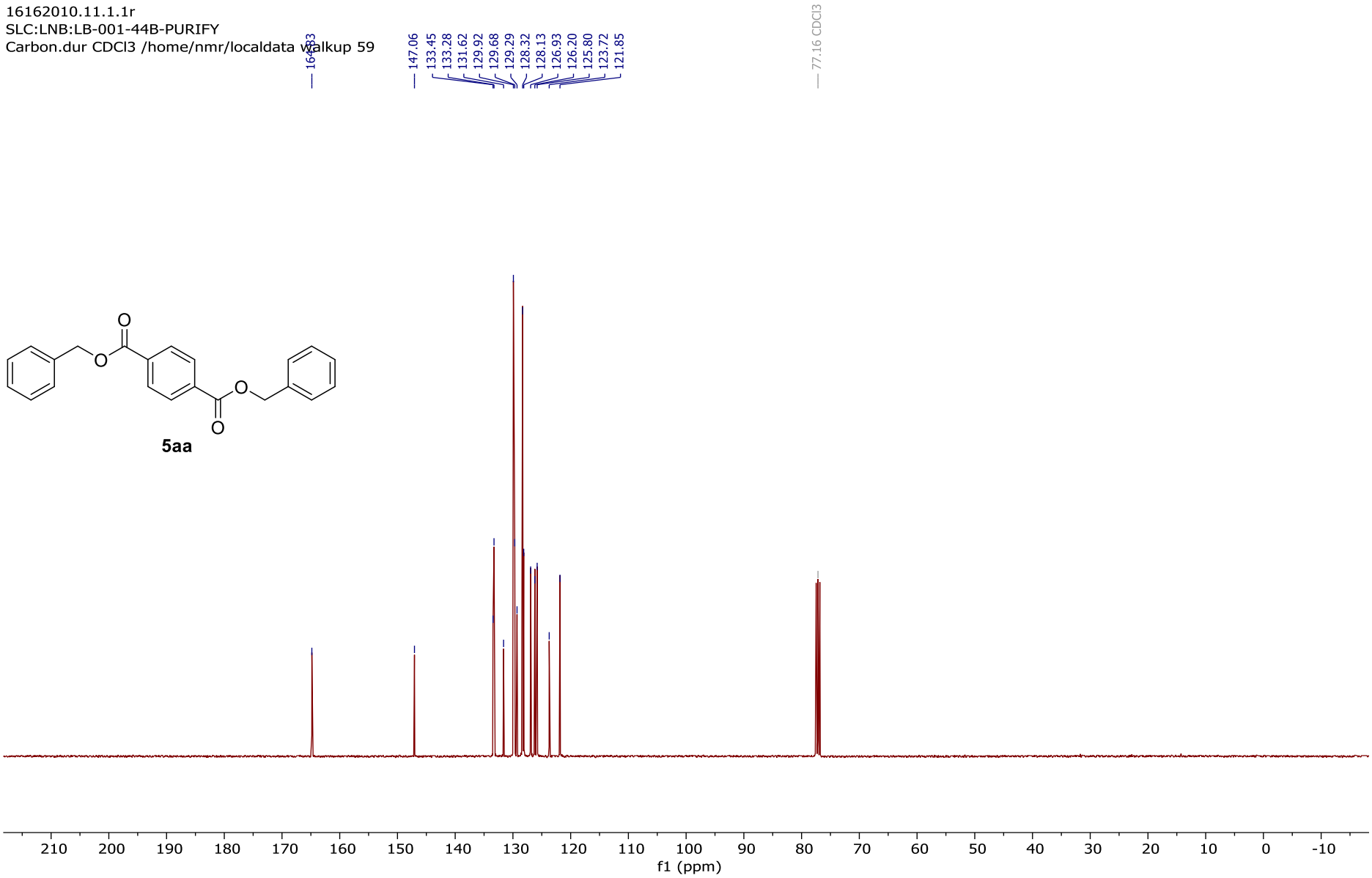

17145200.10.1.1r
SLC:LNB:LB-001-65-PURIFY
Proton1.icon CDCl3 /home/nmr/localdata walkup 5
CDCl3
7.16
7.15
6.96
6.95
6.95
6.94
6.94
6.93
6.93
6.92
6.88
6.87
6.87
6.86
6.86
6.86
6.85
6.84
3.97
3.96
3.95
3.94
3.92
3.78
2.51
2.49
1.96
1.95
1.93
1.91
1.90
1.88
1.88
1.86
1.86
1.84
1.83
1.63
1.61
0.95
0.93
OMe
O
O
5z
2.00
2.03
2.02
2.00
1.03
3.02
2.00
1.00
3.05
6.00
f1 (ppm)

17145200.11.1.1r
SLC:LNB:LB-001-65-PURIFY
Carbon.dur CDCl3 /home/nmr/local/data walkup 6

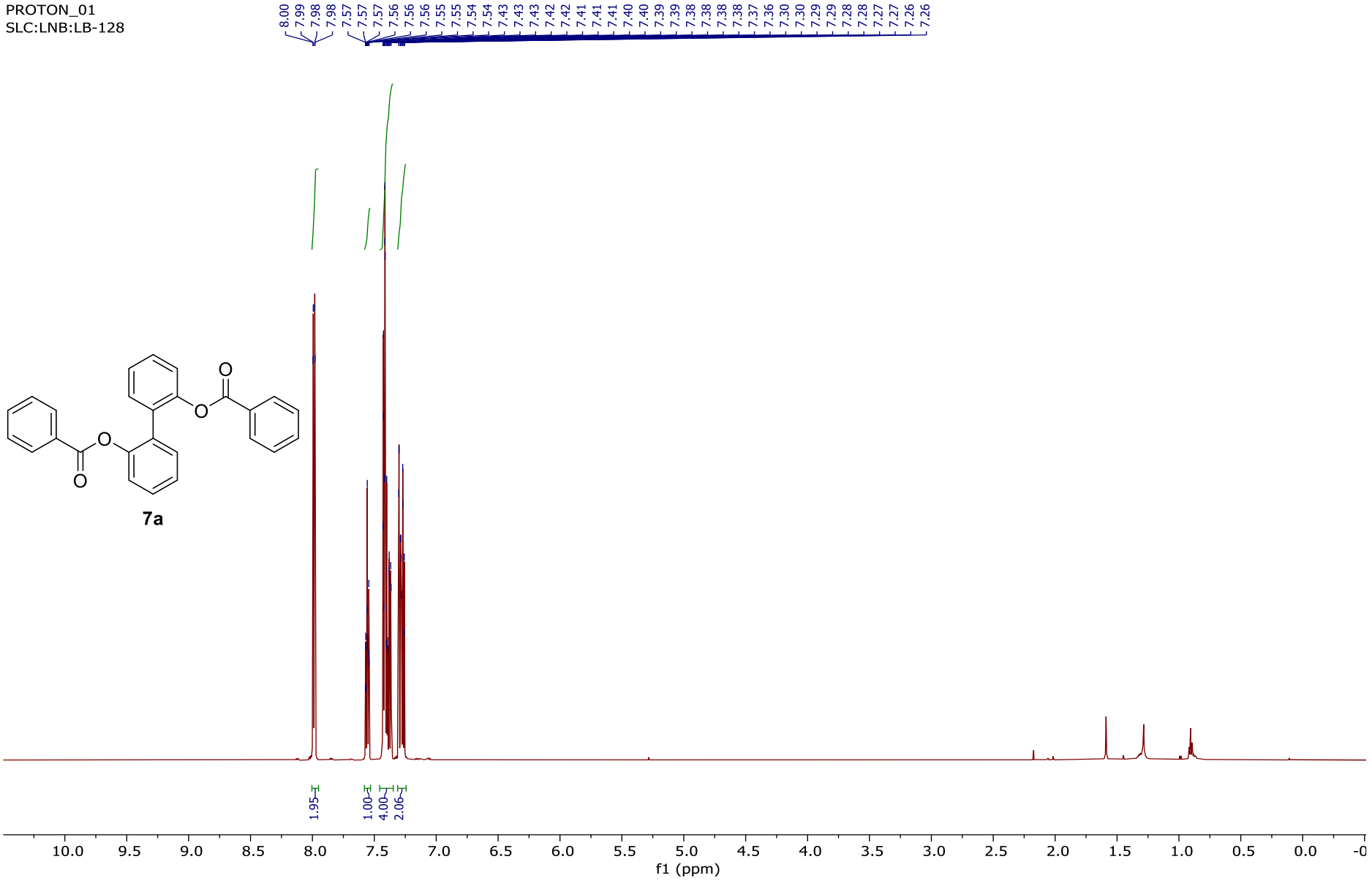



16162010.10.1.1r
SLC:LNB:LB-001-44B-PURIFY
Proton1.icon CDCl3 /home/nmr/localdata/walkup 59
8.04 8.04 8.02 8.02 7.96 7.96 7.96 7.94 7.94 7.94 7.94 7.67 7.67 7.66 7.65 7.64 7.63 7.62 7.61 7.61 7.60
2.00 2.03 4.01 2.02 6.06 2.02 4.10
f1 (ppm)
5aa

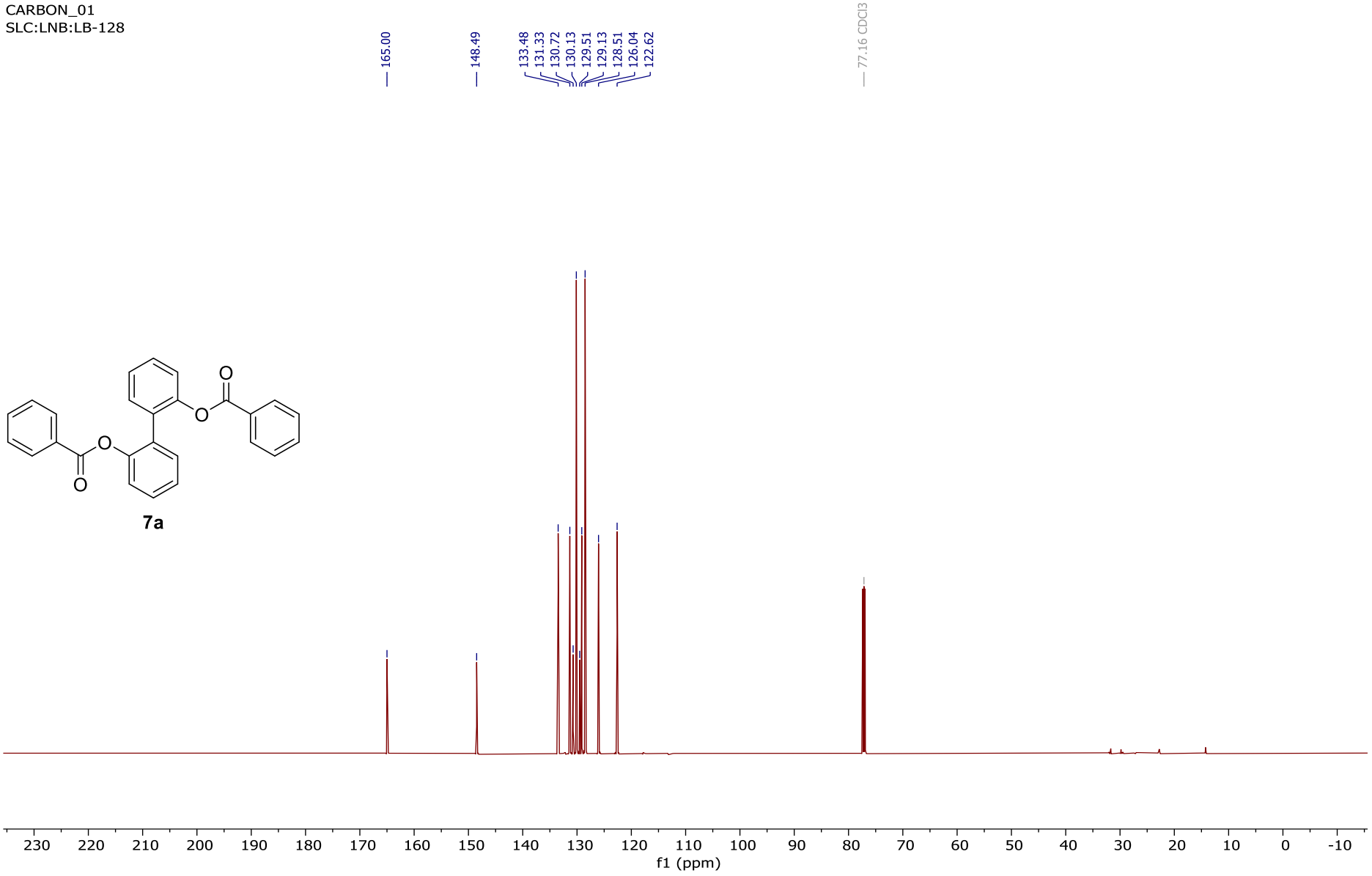
16162010.11.1.1r
SLC:LNB:LB-001-44B-PURIFY
Carbon.dur CDCl3 /home/nmr/localdata walkup 59

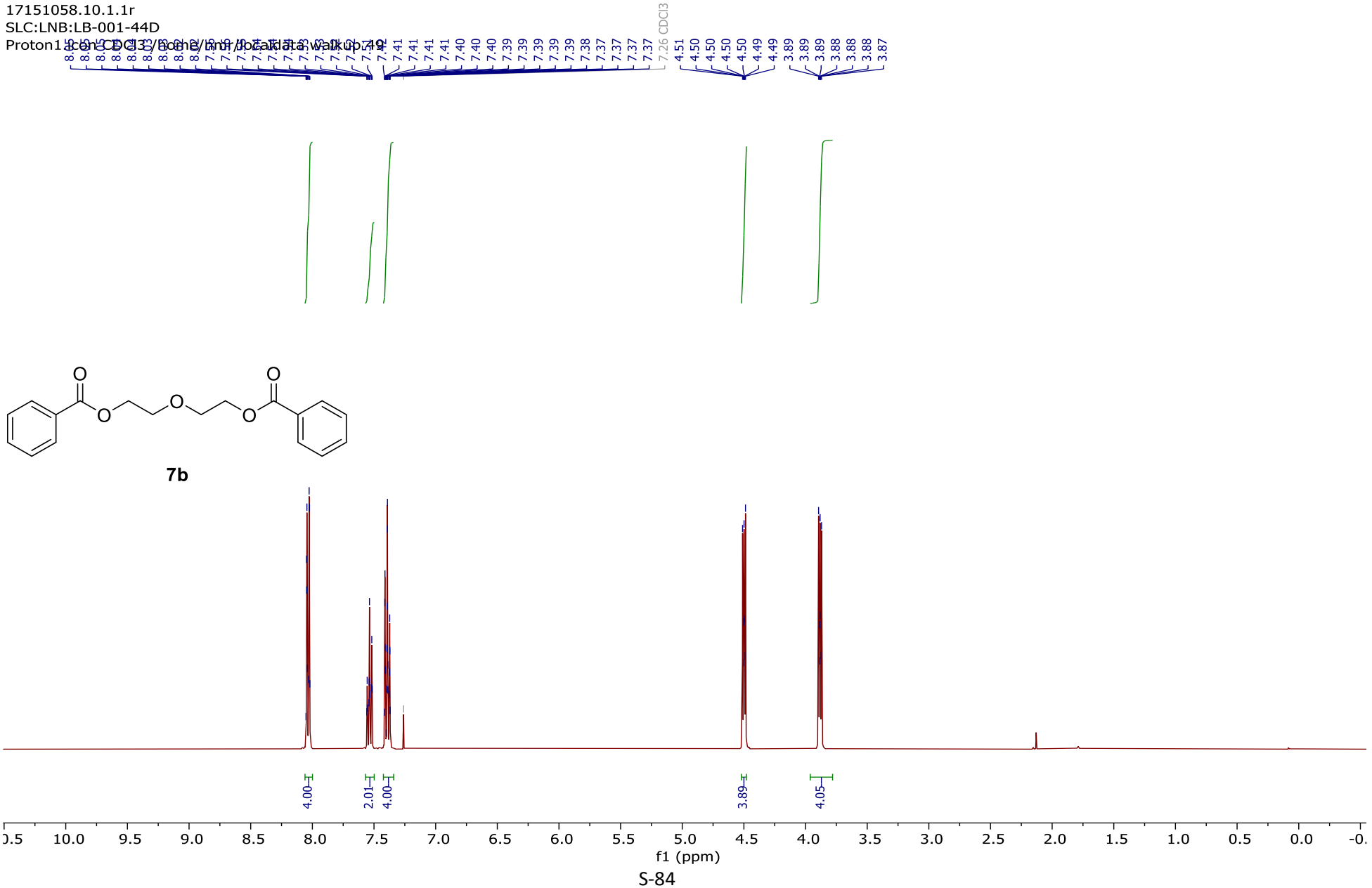


PROTON_01
SLC:LNB:LB-128

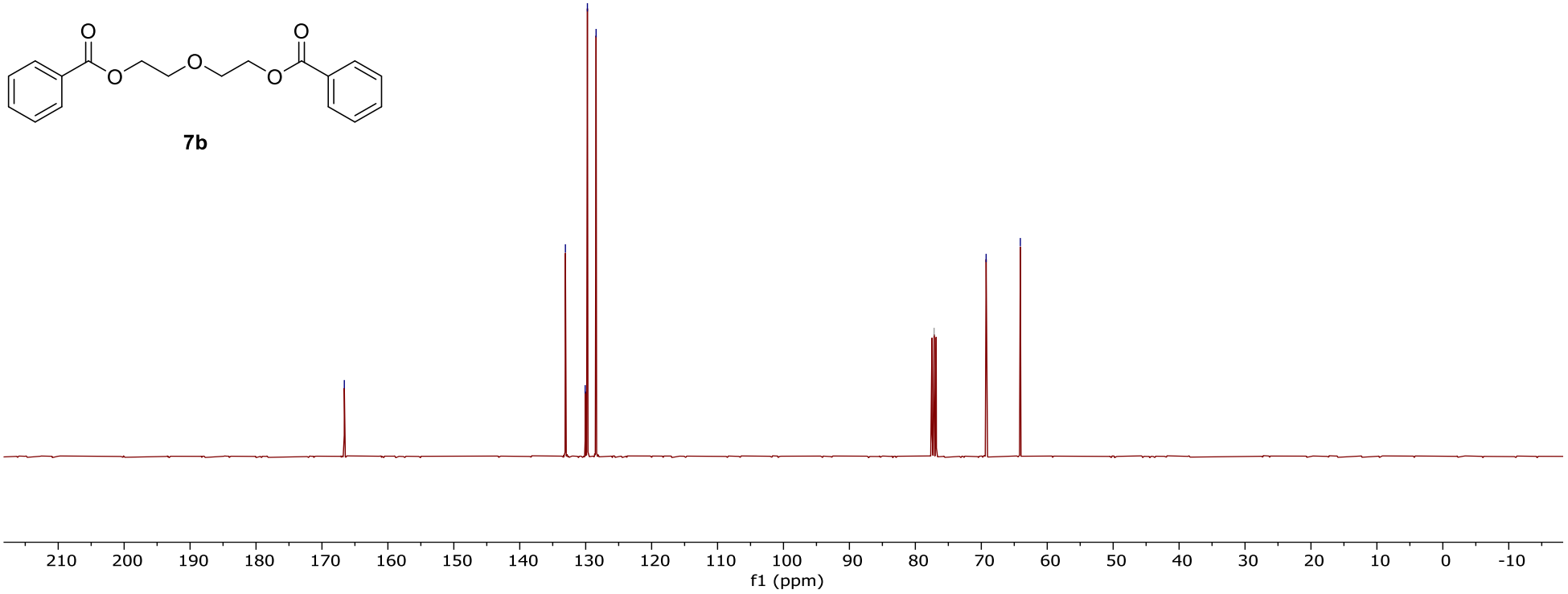


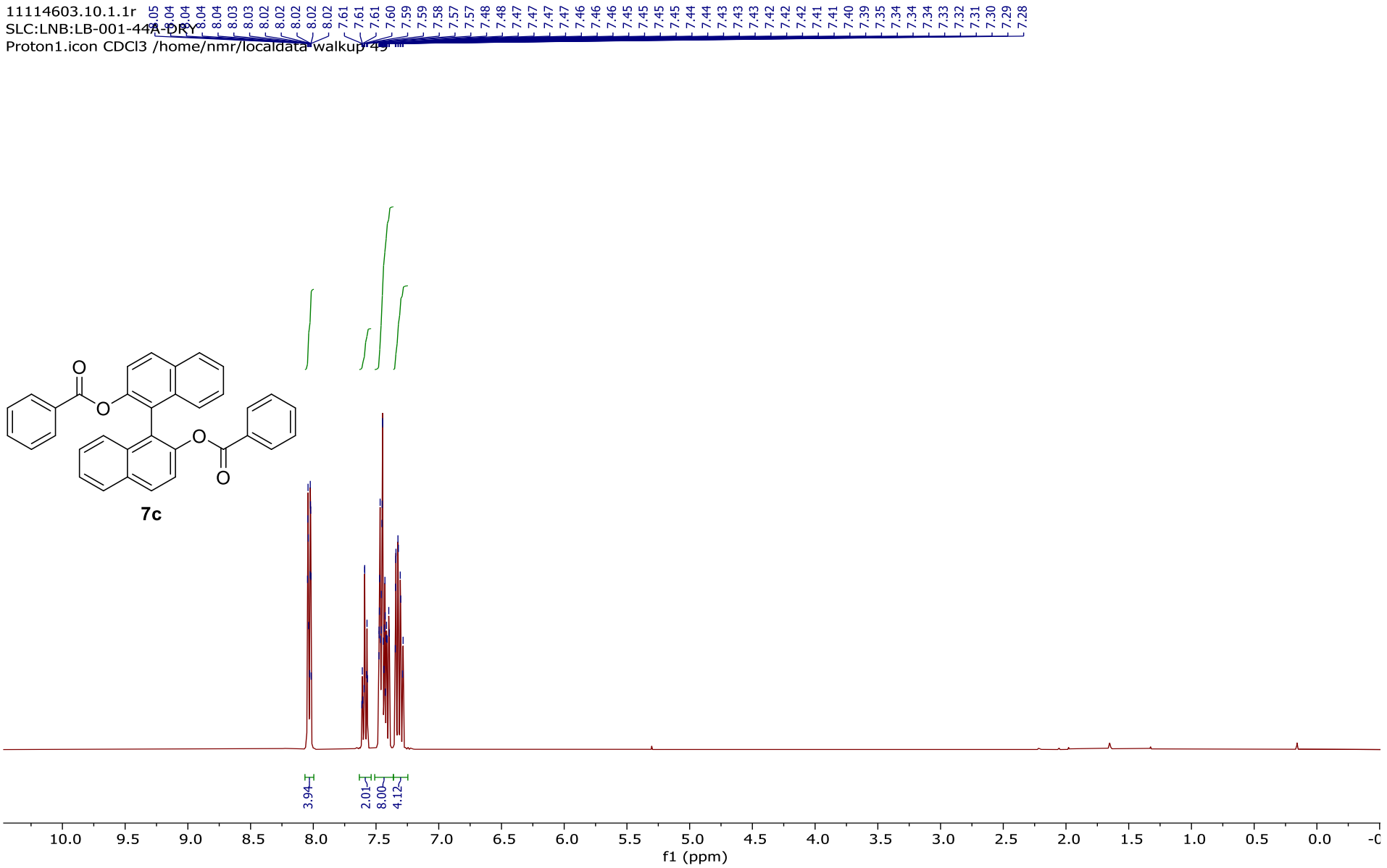
CARBON_01
SLC:LNB:LB-128



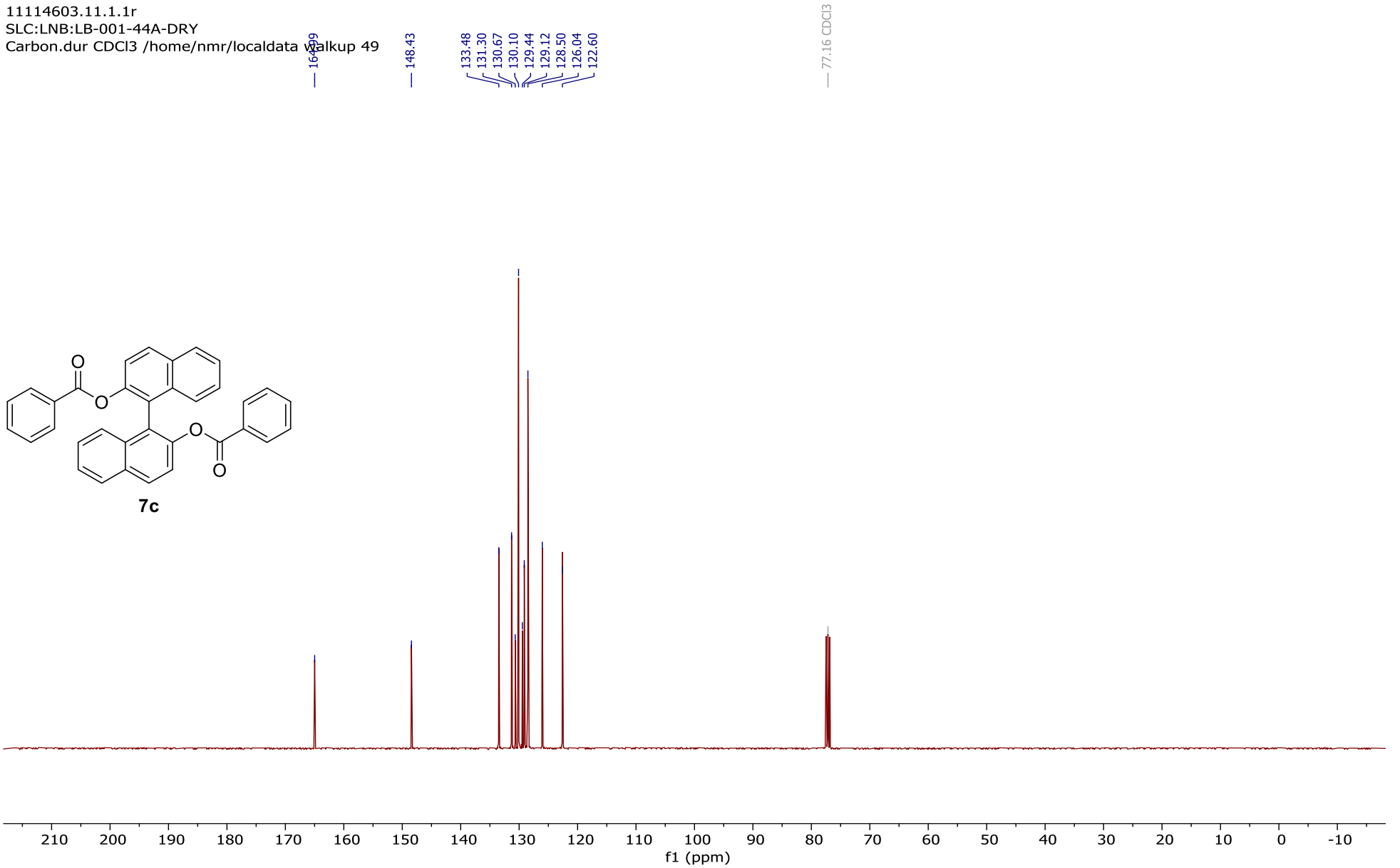

17151058.10.1.1r
SLC:LNB:LB-001-44D
Proton1 acqn CDCl3 /home/nmr/localdata walkup 44
7.26 CDCl3
4.51
4.50
4.49
3.89
3.88
3.87
O
O
O
O
O
7b
4.00
2.01
4.00
3.89
4.05
f1 (ppm)

17151058.11.1.1r
SLC:LNB:LB-001-44D
Carbon.dur CDCl3 /home/nmr/localdata/walkup 49

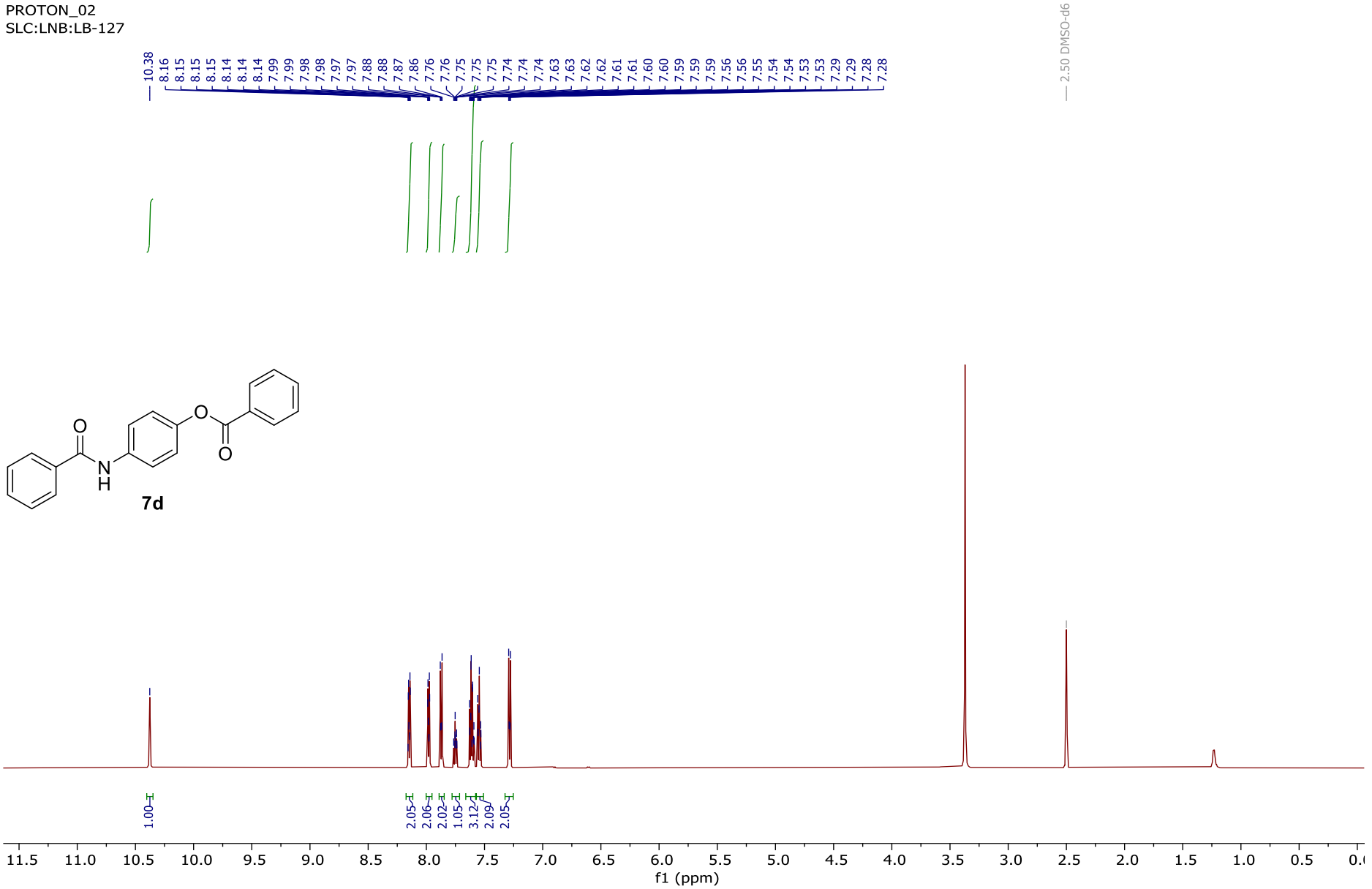



11114603.10.1.1r
SLC:LNB:LB-001-44A-DRY
Proton1.icon CDCl3 /home/nmr/localdata/walkup/49
8.05 8.04 8.04 8.04 8.03 8.03 8.02 8.02 8.02 8.02 8.02 7.61 7.61 7.61 7.60 7.59 7.59 7.58 7.57 7.57 7.48 7.48 7.47 7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.40 7.39 7.35 7.34 7.34 7.34 7.33 7.32 7.31 7.30 7.29 7.28
O
O
O
O
7c
3.94
2.01
8.00
4.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

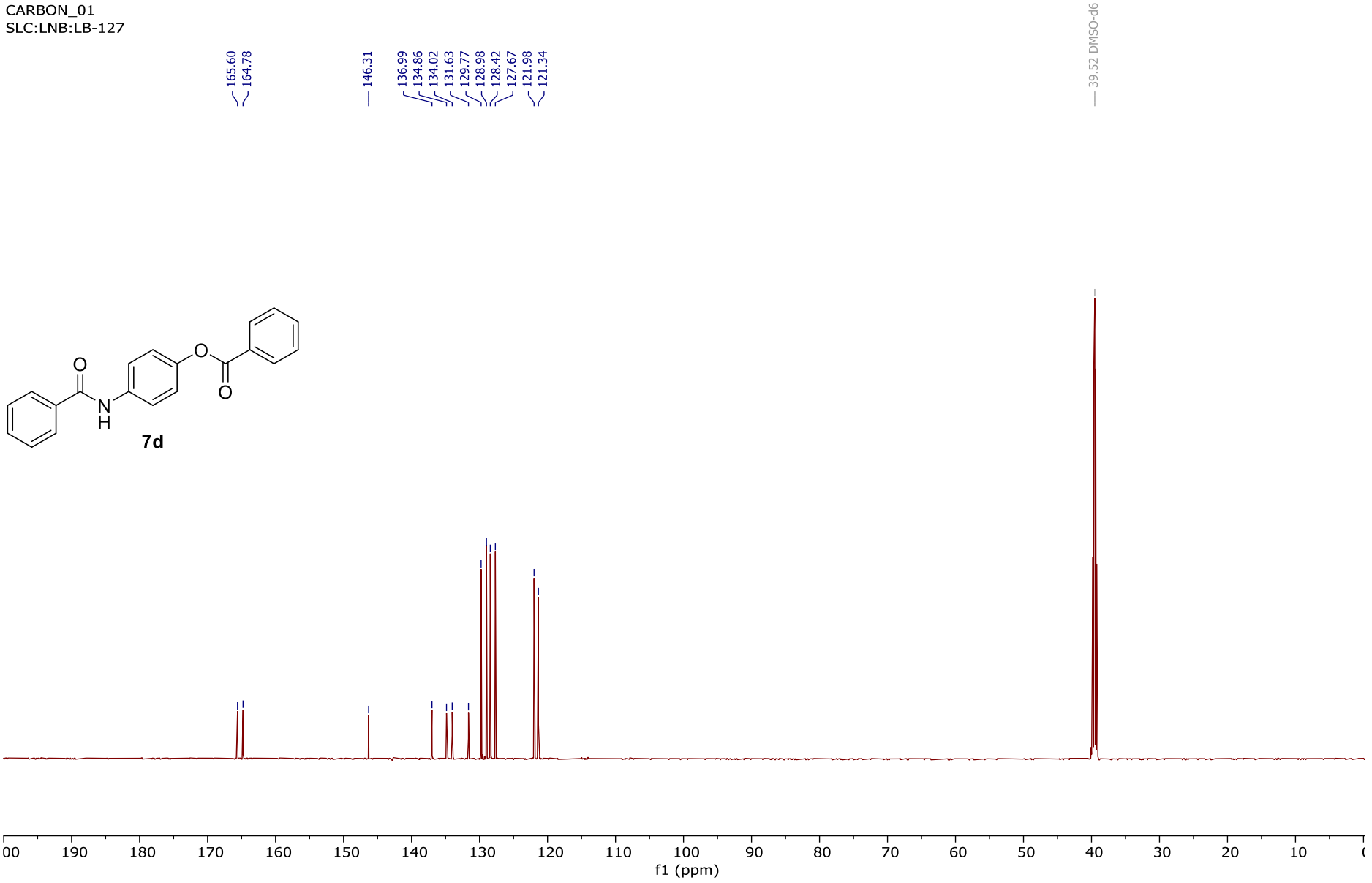
11114603.11.1.1r
SLC:LNB:LB-001-44A-DRY
Carbon.dur CDCl3 /home/nmr/localdata walkup 49



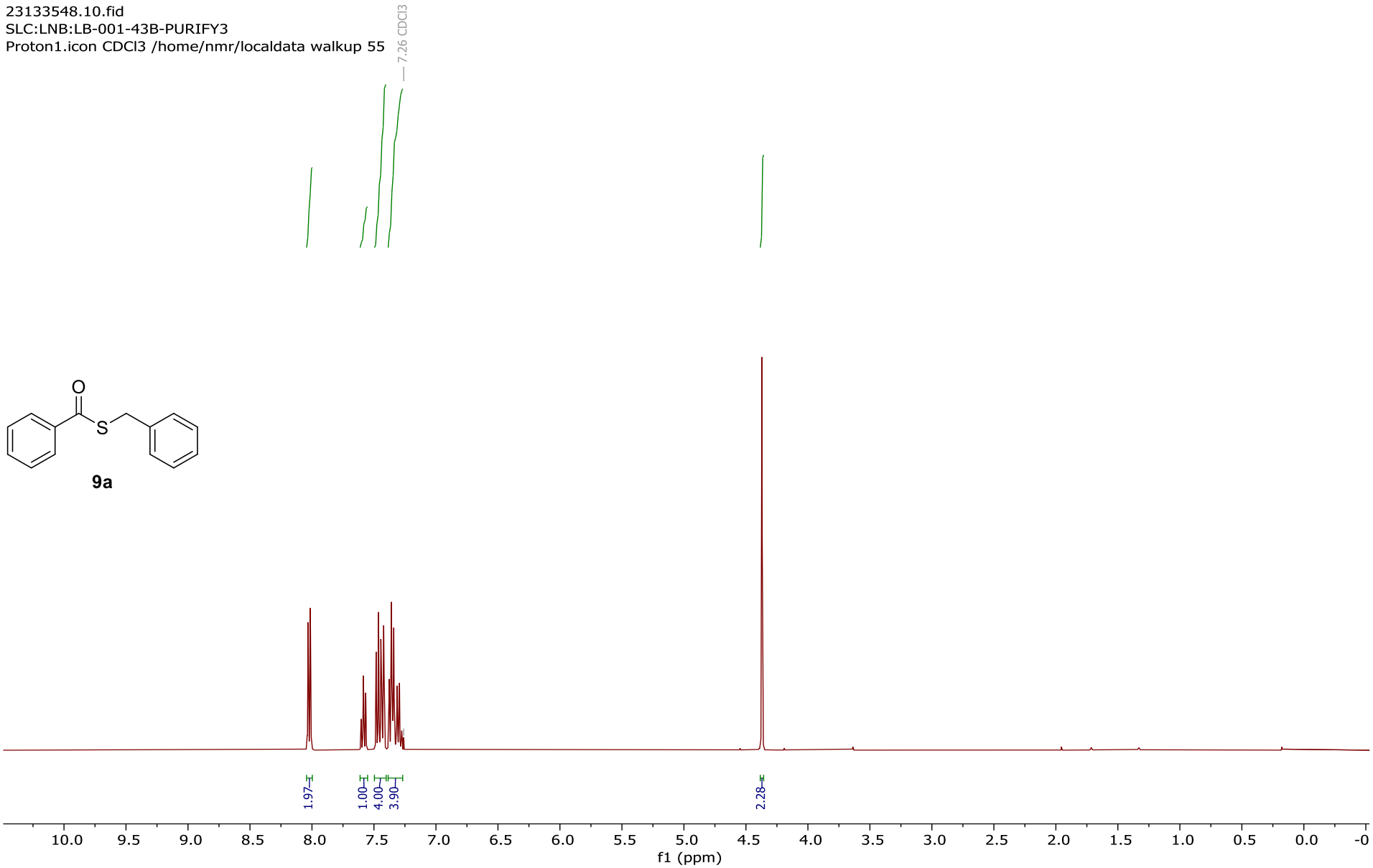
PROTON_02
SLC:LNB:LB-127

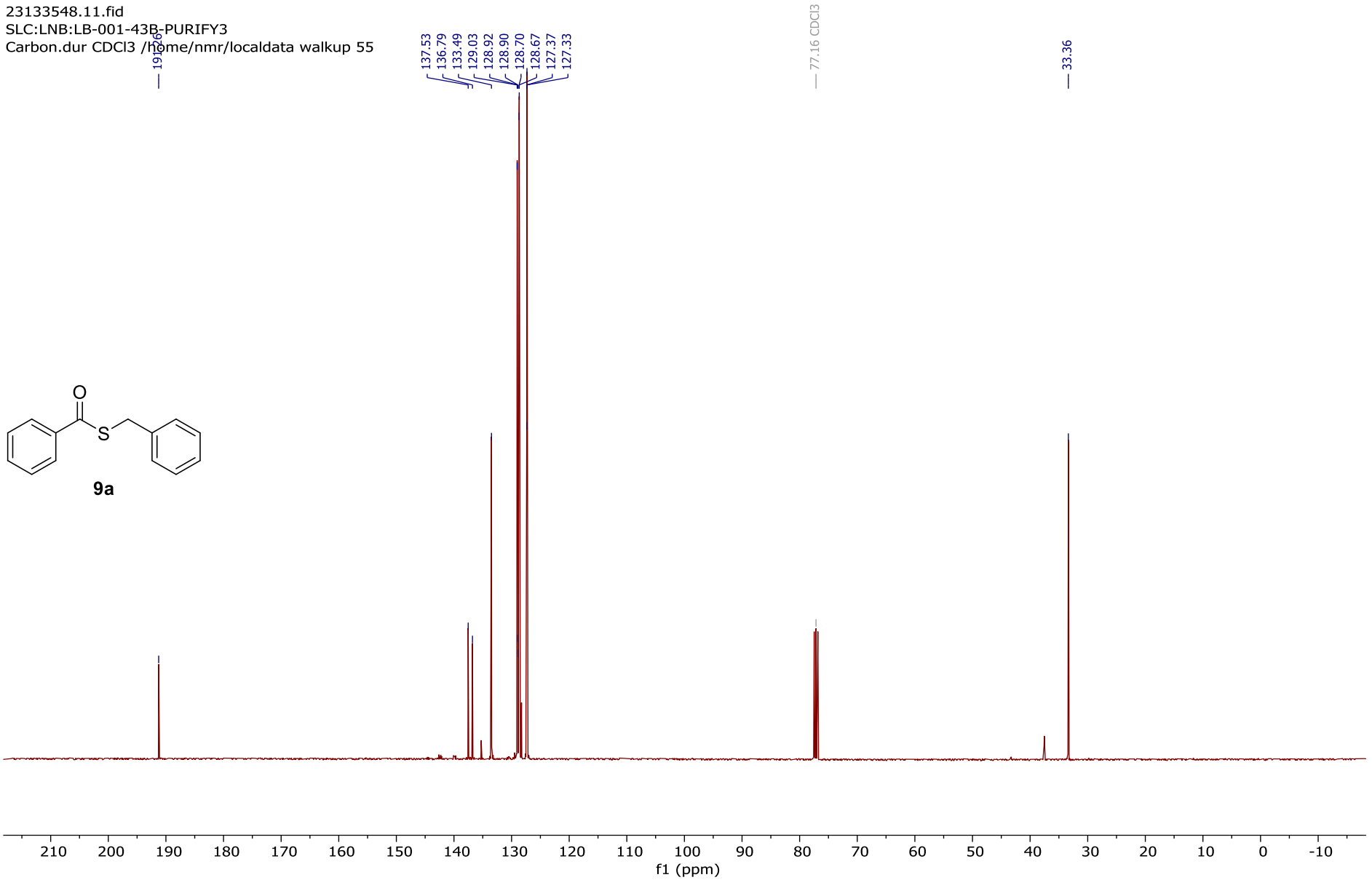


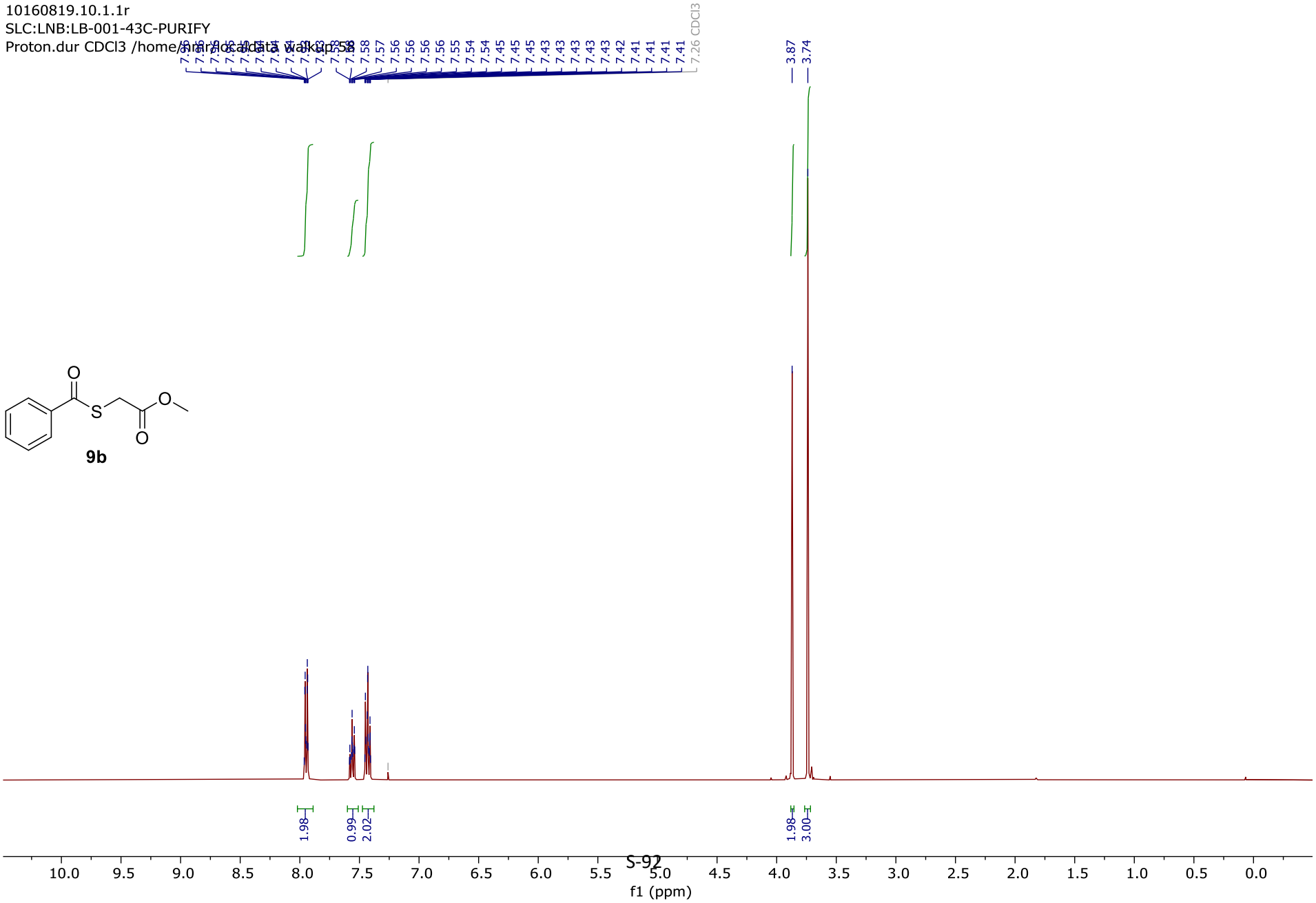
CARBON_01
SLC:LNB:LB-127

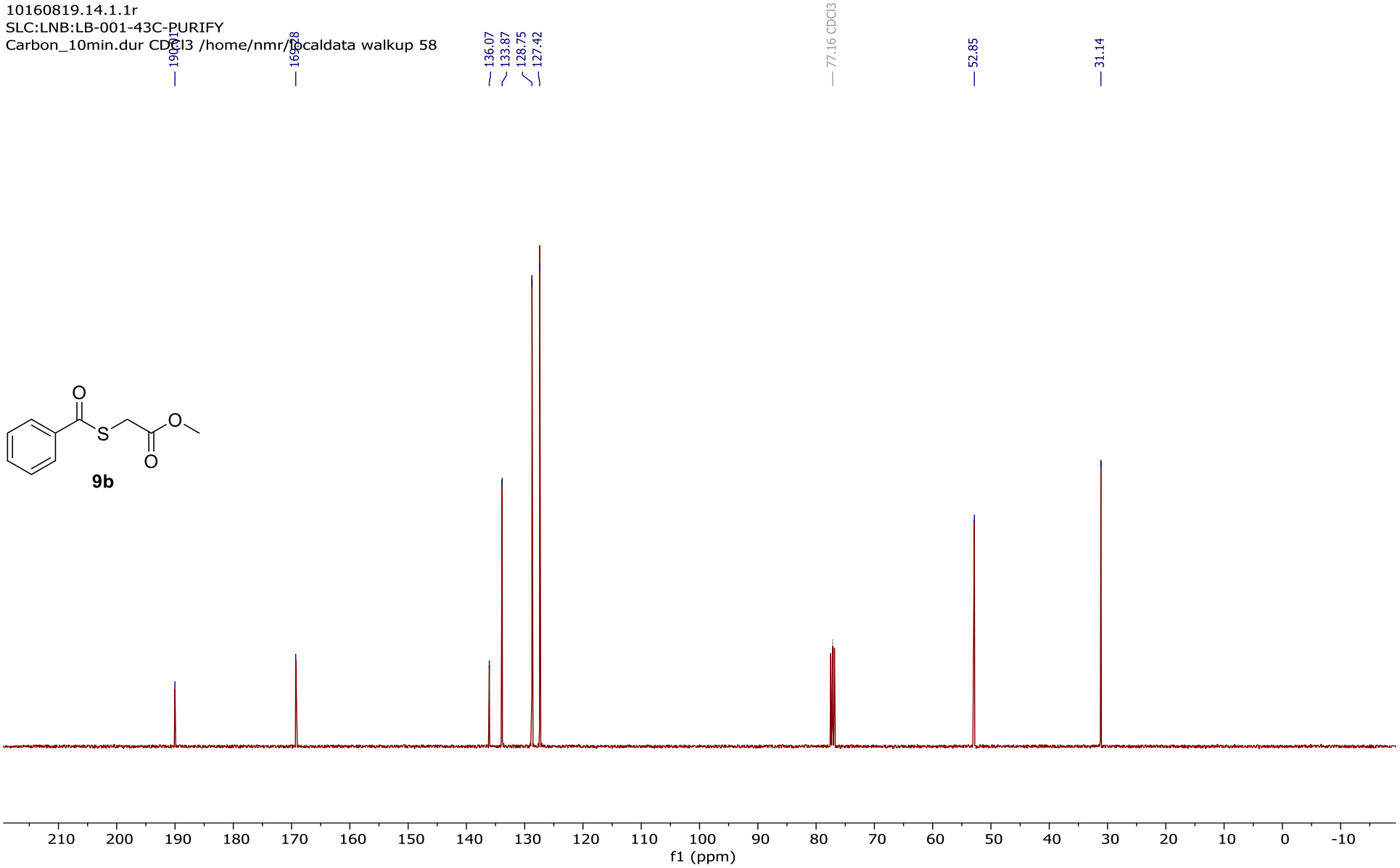


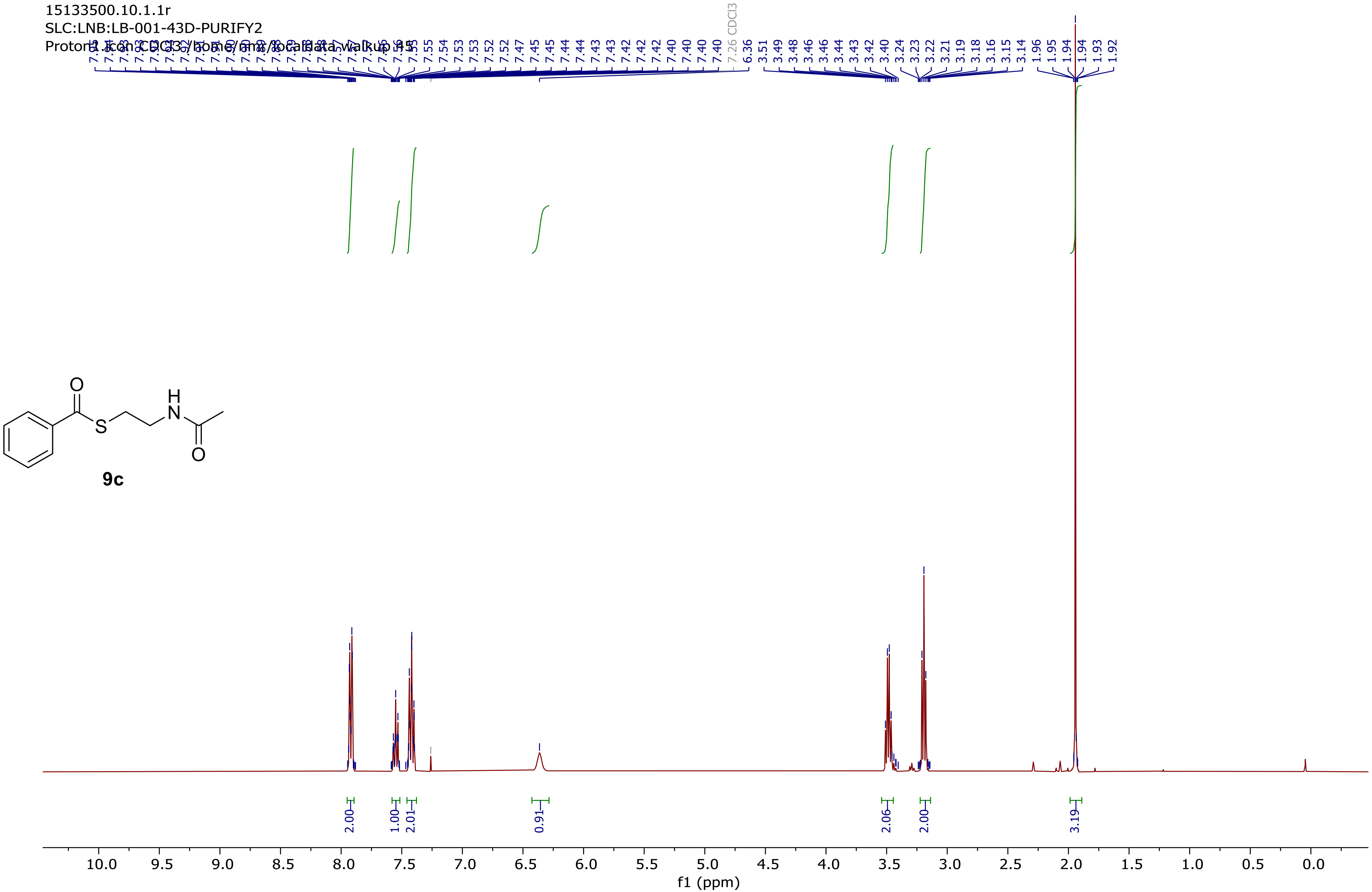
23133548.10.fid
SLC:LNB:LB-001-43B-PURIFY3
Proton1.icon CDCl3 /home/nmr/localdata walkup 55




23133548.11.fid
SLC:LNB:LB-001-43B-PURIFY3
Carbon.dur CDCl3 /home/nmr/localdata walkup 55
191.26
137.53
136.79
133.49
129.03
128.92
128.90
128.70
128.67
127.37
127.33
77.16 CDCl3
33.36
O
S
9a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


10160819.10.1.1r
SLC:LNB:LB-001-43C-PURIFY
Proton.dur CDCl3 /home/nmrlocaldata walkup 58
7.26 CDCl3
3.87
3.74
9b
1.98
0.99
2.02
1.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

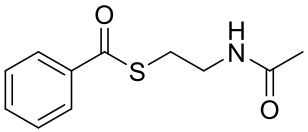

10160819.14.1.1r
SLC:LNB:LB-001-43C-PURIFY
Carbon_10min.dur CDCl3 /home/nmr/localdata walkup 58
190.01
169.28
136.07
133.87
128.75
127.42
77.16 CDCl3
52.85
31.14
O
S
O
O
9b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



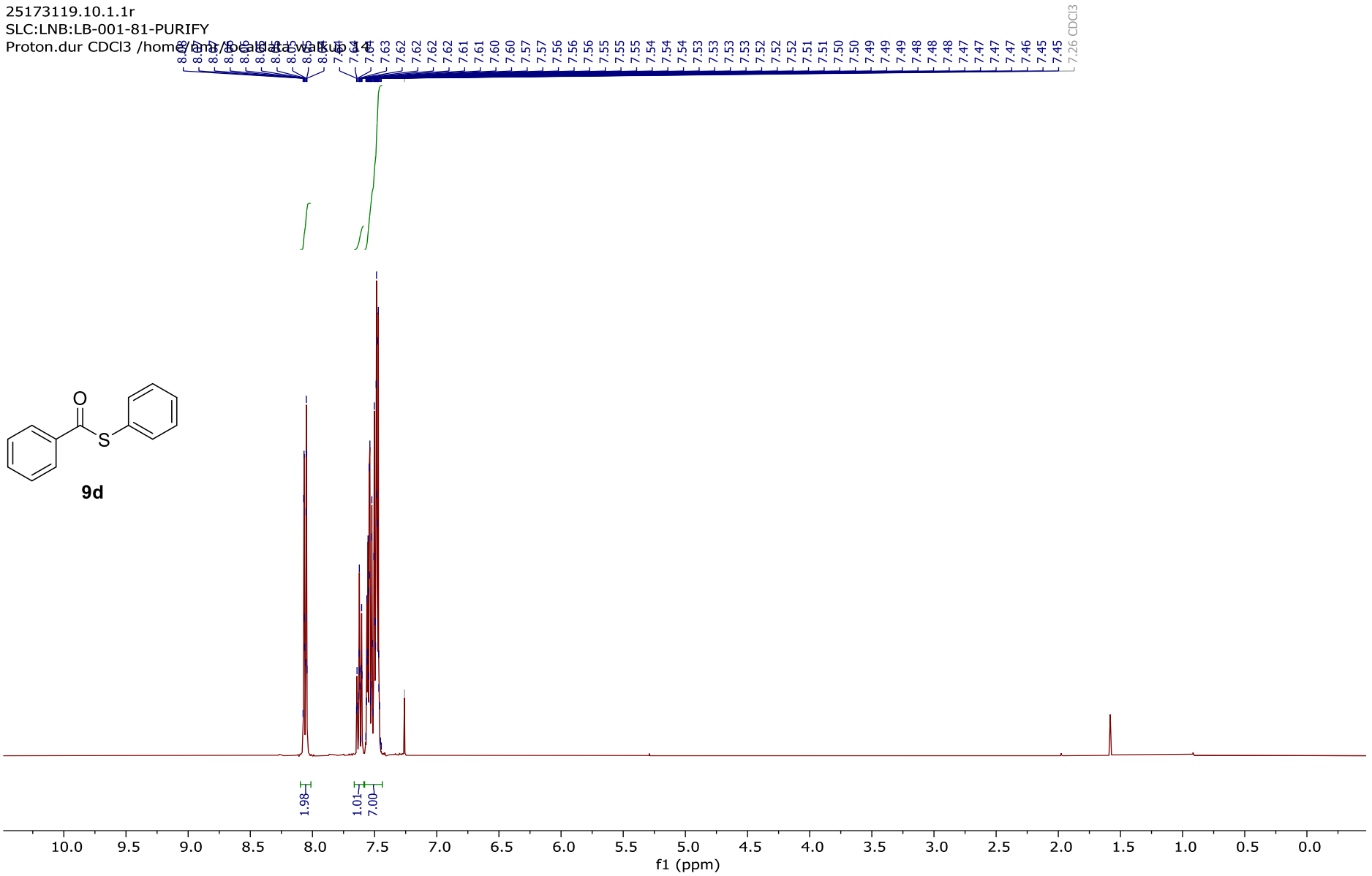
15133500.10.1.1r
SLC:LNB:LB-001-43D-PURIFY2
7.55 7.54 7.53 7.53 7.52 7.52 7.47 7.45 7.45 7.44 7.43 7.43 7.42 7.42 7.42 7.40 7.40 7.40 7.40
7.26 CDCl3
6.36
3.51 3.49 3.48 3.46 3.46 3.44 3.43 3.42 3.40
3.24 3.23 3.22 3.21 3.19 3.18 3.16 3.15 3.14
1.96 1.95 1.94 1.94 1.93 1.92
O
H
N
S
O
2.00
1.00
2.01
0.91
2.06
2.00
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

9c

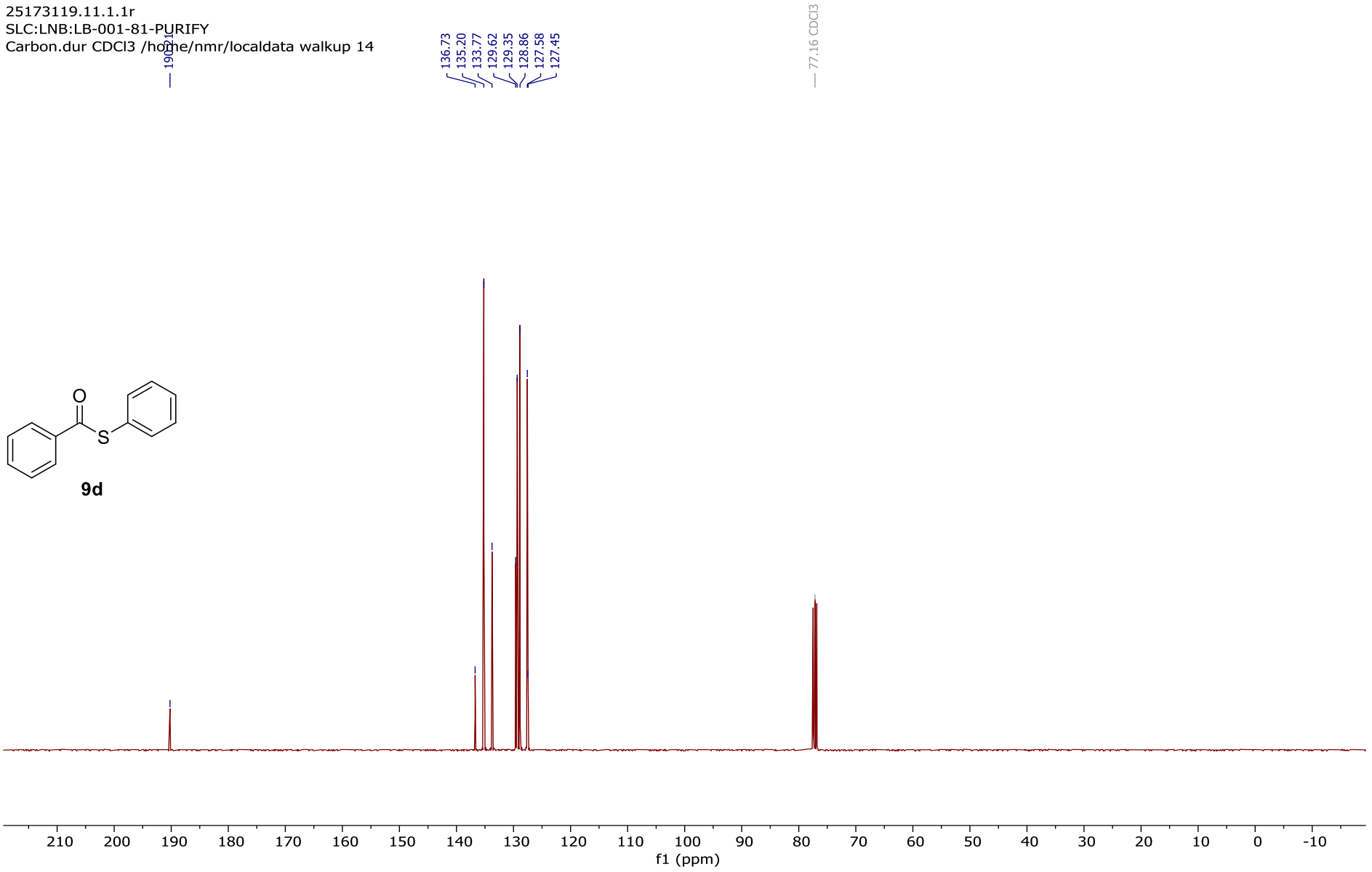
15133500.11.1.1r
SLC:LNB:LB-001-43D-PURIFY2
Carbon.dur CDCl3 /home/nmr/localdata walkup 45



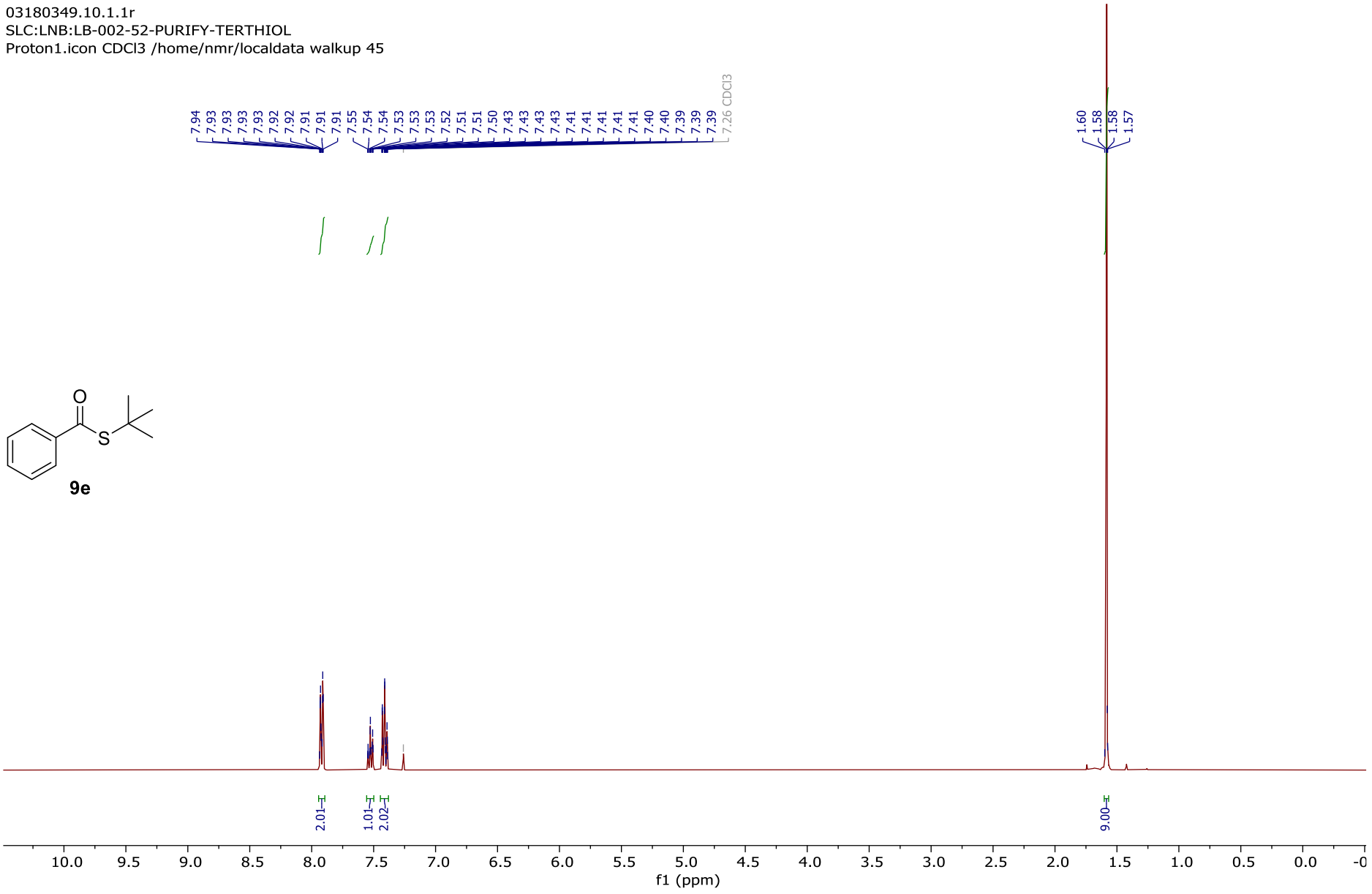
9c


25173119.10.1.1r
SLC:LNB:LB-001-81-PURIFY
Proton.dur CDCl3 /home/ama/boaladata/watkup 1 1
7.26 CDCl3
O
S
9d
1.98
1.01
7.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

25173119.11.1.1r
SLC:LNB:LB-001-81-PURIFY
Carbon.dur CDCl3 /home/nmr/localdata walkup 14

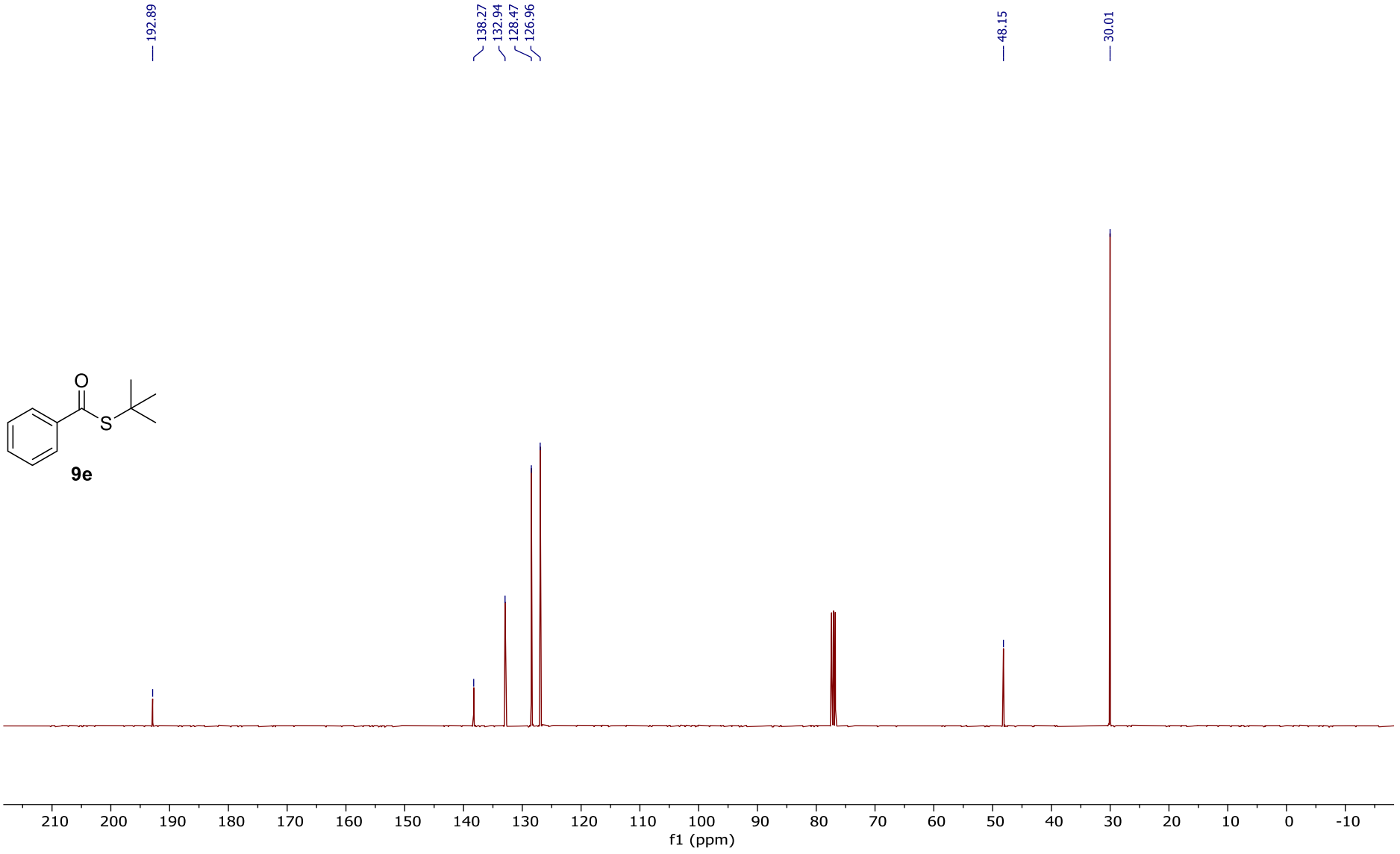


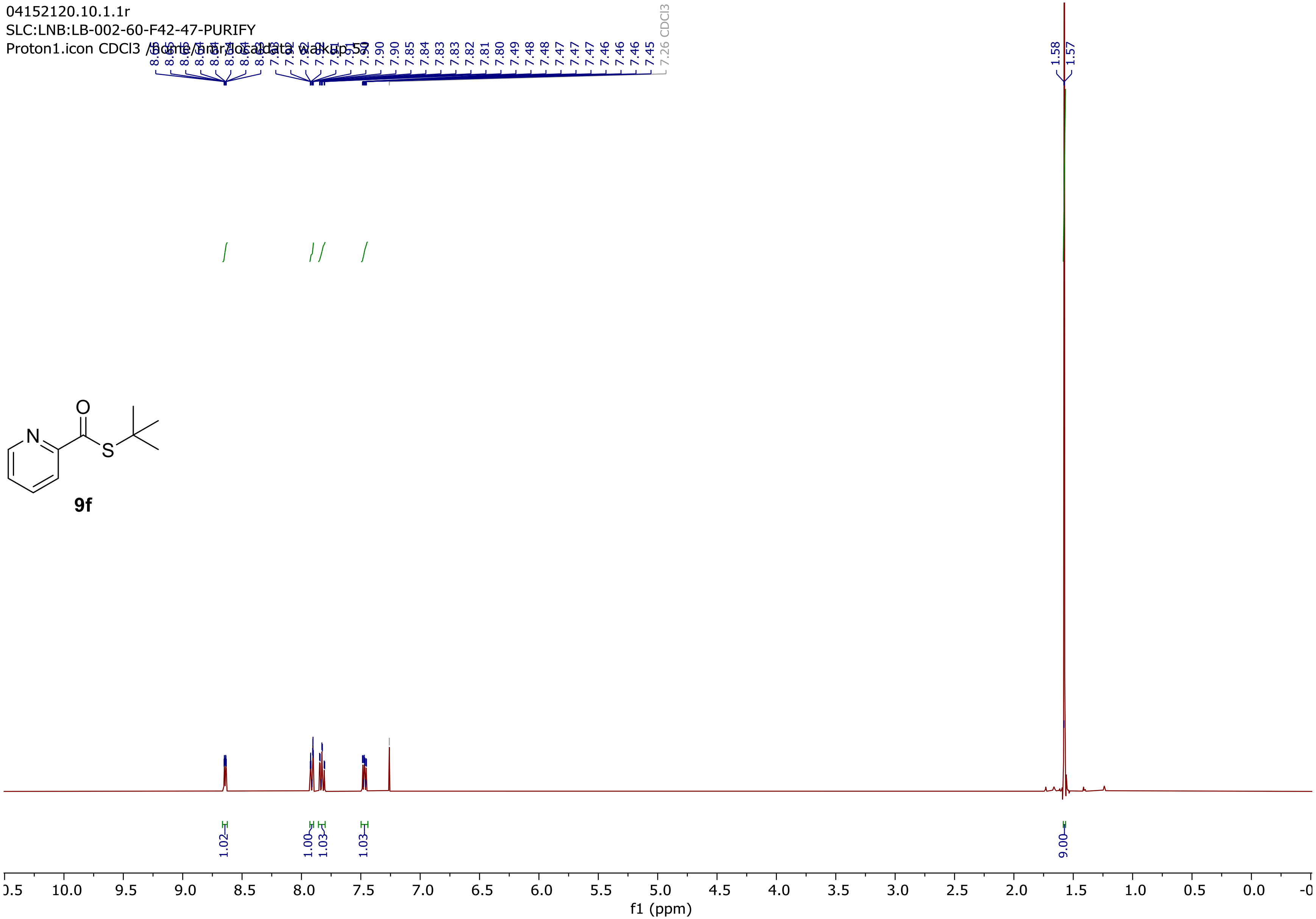
03180349.10.1.1r
SLC:LNB:LB-002-52-PURIFY-TERTHIOL
Proton1.icon CDCl3 /home/nmr/localdata walkup 45



9e

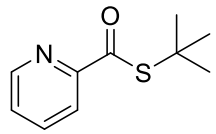
03180349.11.1.1r
SLC:LNB:LB-002-52-PURIFY-TERTHIOL
Carbon.dur CDCl3 /home/nmr/localdata walkup 45



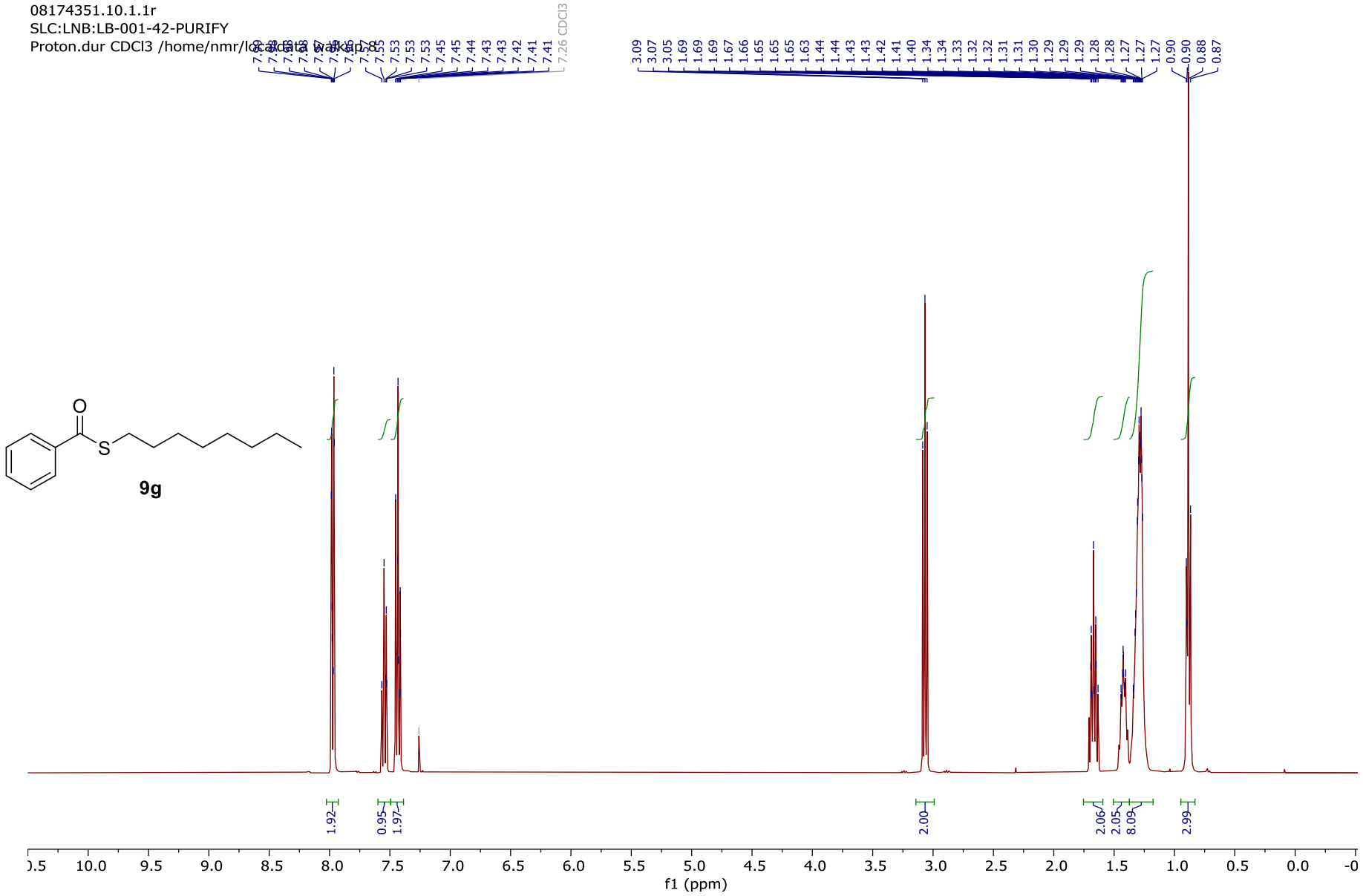

04152120.10.1.1r
SLC:LNB:LB-002-60-F42-47-PURIFY
Proton1.icon CDCl3
7.90
7.90
7.85
7.84
7.83
7.83
7.82
7.81
7.80
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.46
7.45
7.26 CDCl3
1.58
1.57
O
N
S
9f
1.02
1.00
1.03
1.03
9.00
f1 (ppm)

CARBON_01
SLC:LNB:LB-002-60

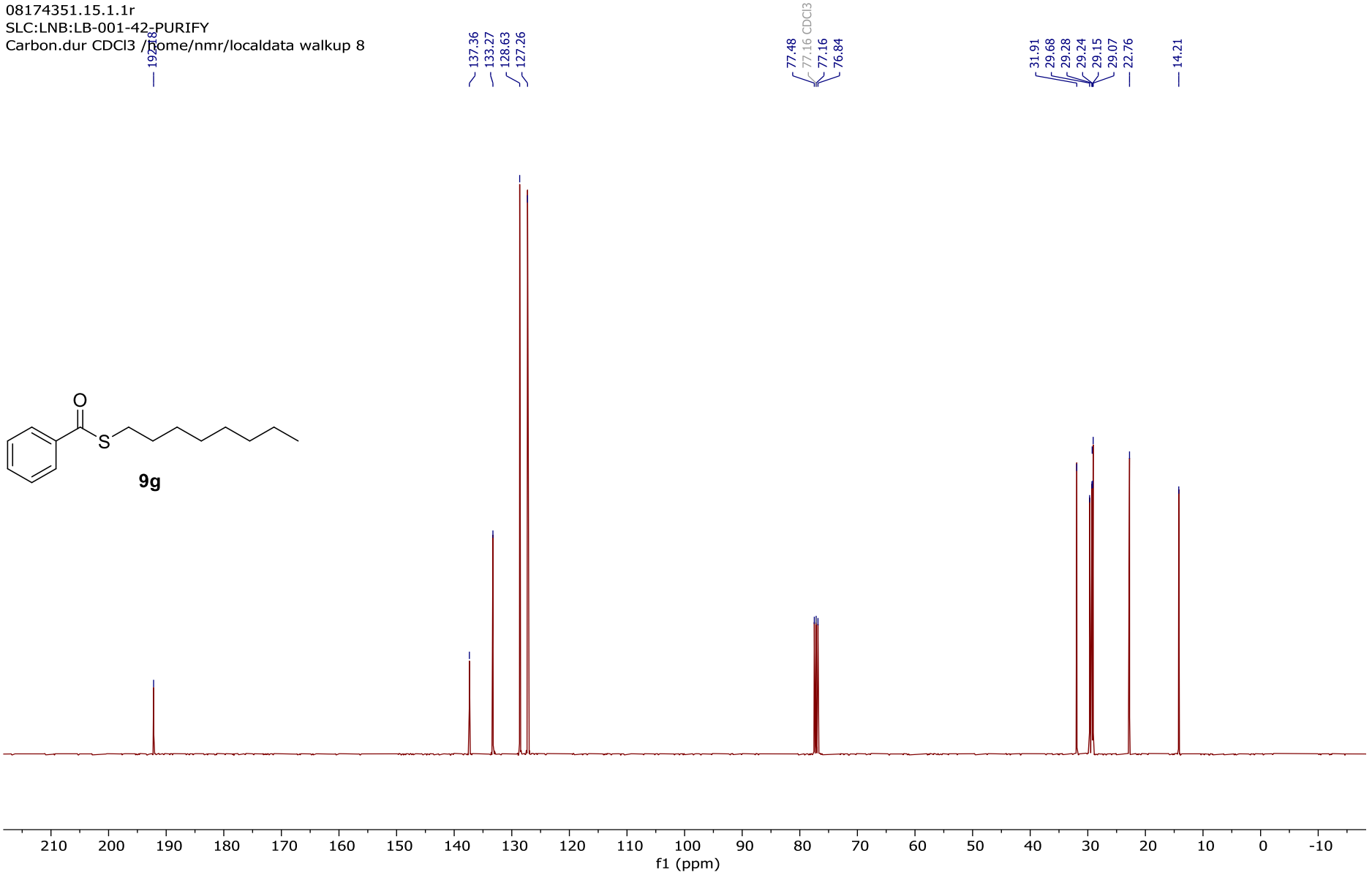
193.79
153.27
148.98
137.35
127.61
120.11
77.16 CDCl3
47.09
47.09
29.89

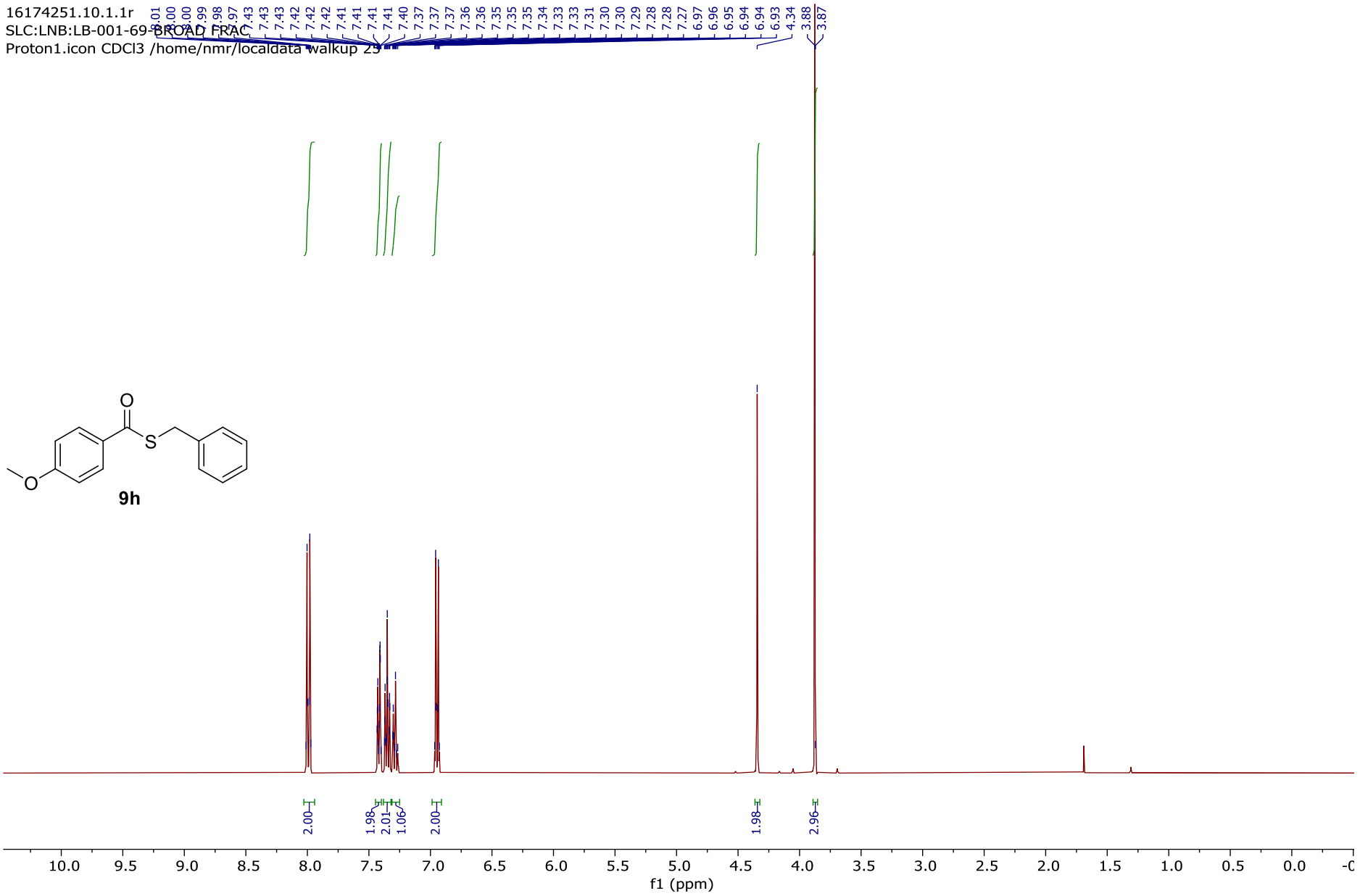


9f

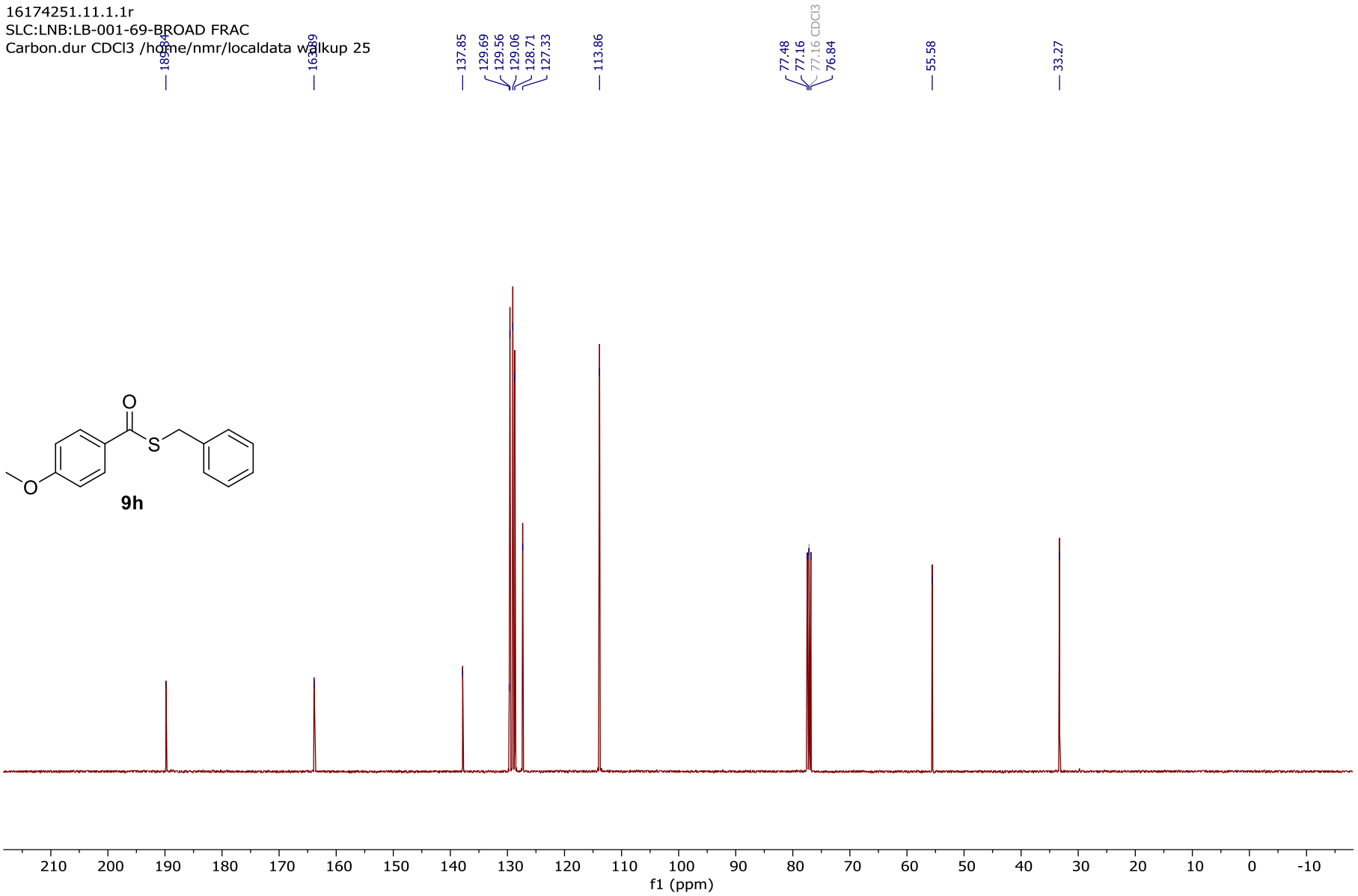

08174351.10.1.1r
SLC:LNB:LB-001-42-PURIFY
Proton.dur CDCl3 /home/nmr/lo
7.26 CDCl3
9g
1.92
0.95
1.97
2.00
2.06
2.05
8.09
2.99
f1 (ppm)

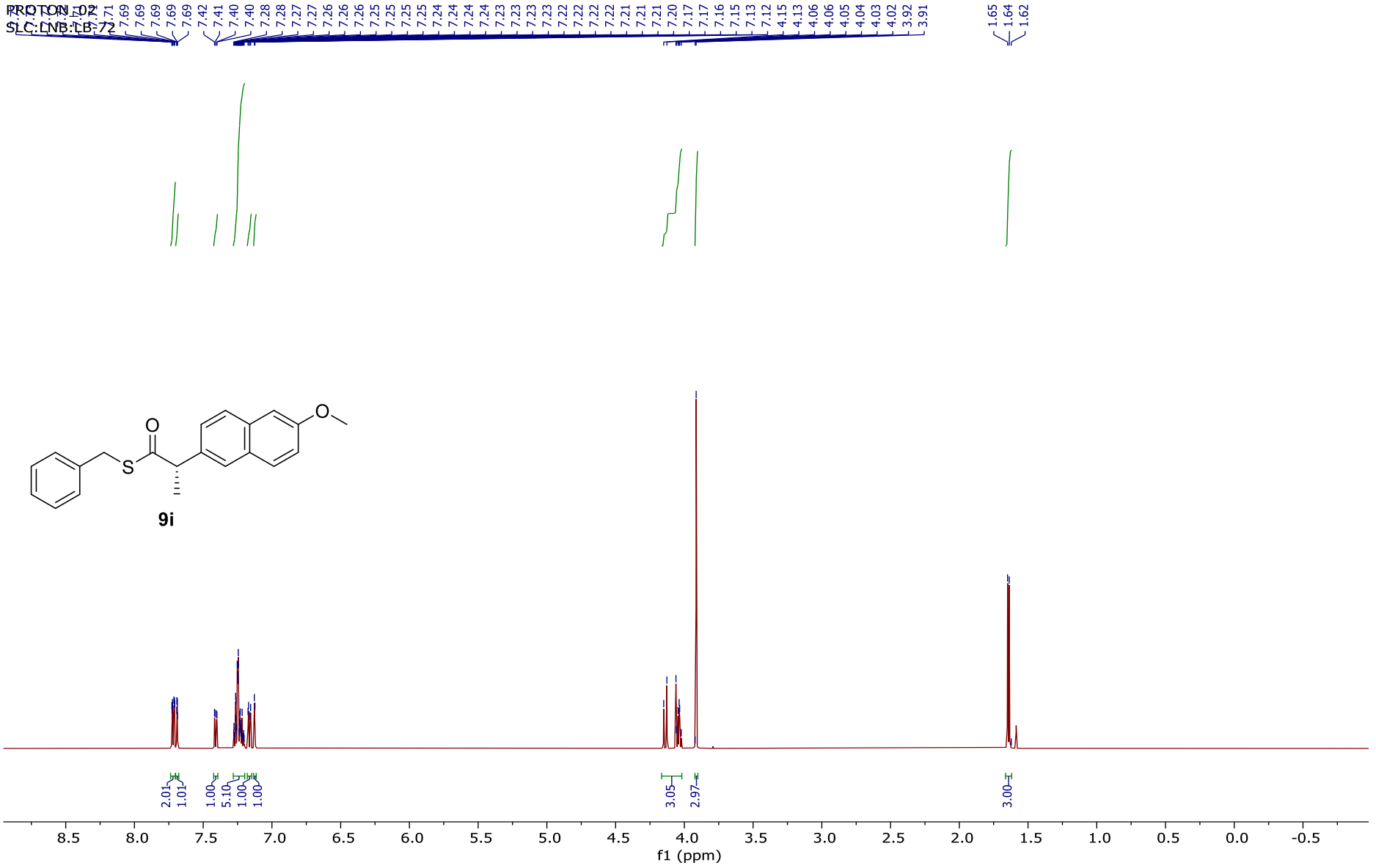
08174351.15.1.1r
SLC:LNB:LB-001-42-PURIFY
Carbon.dur CDCl3 /home/nmr/localdata walkup 8

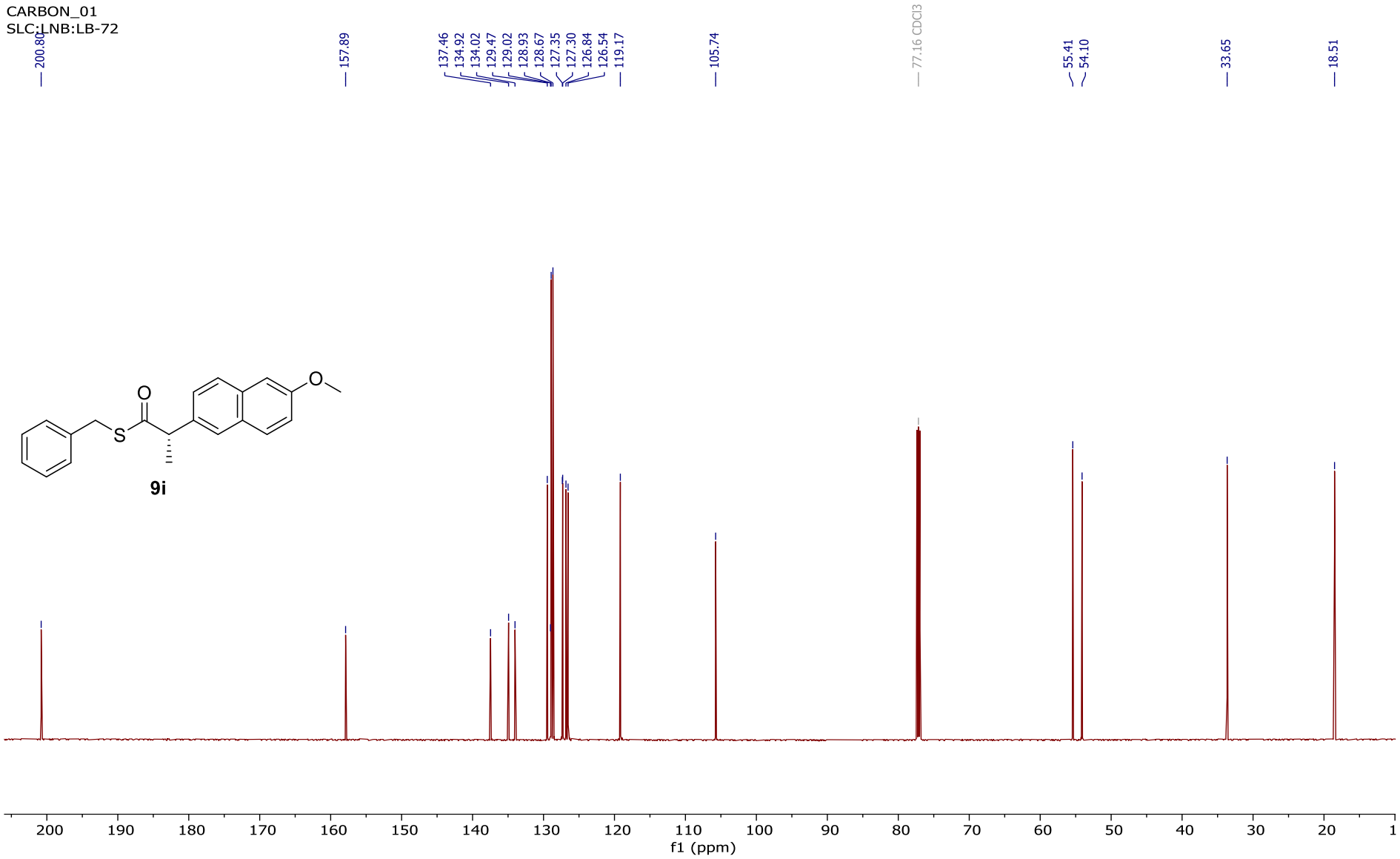


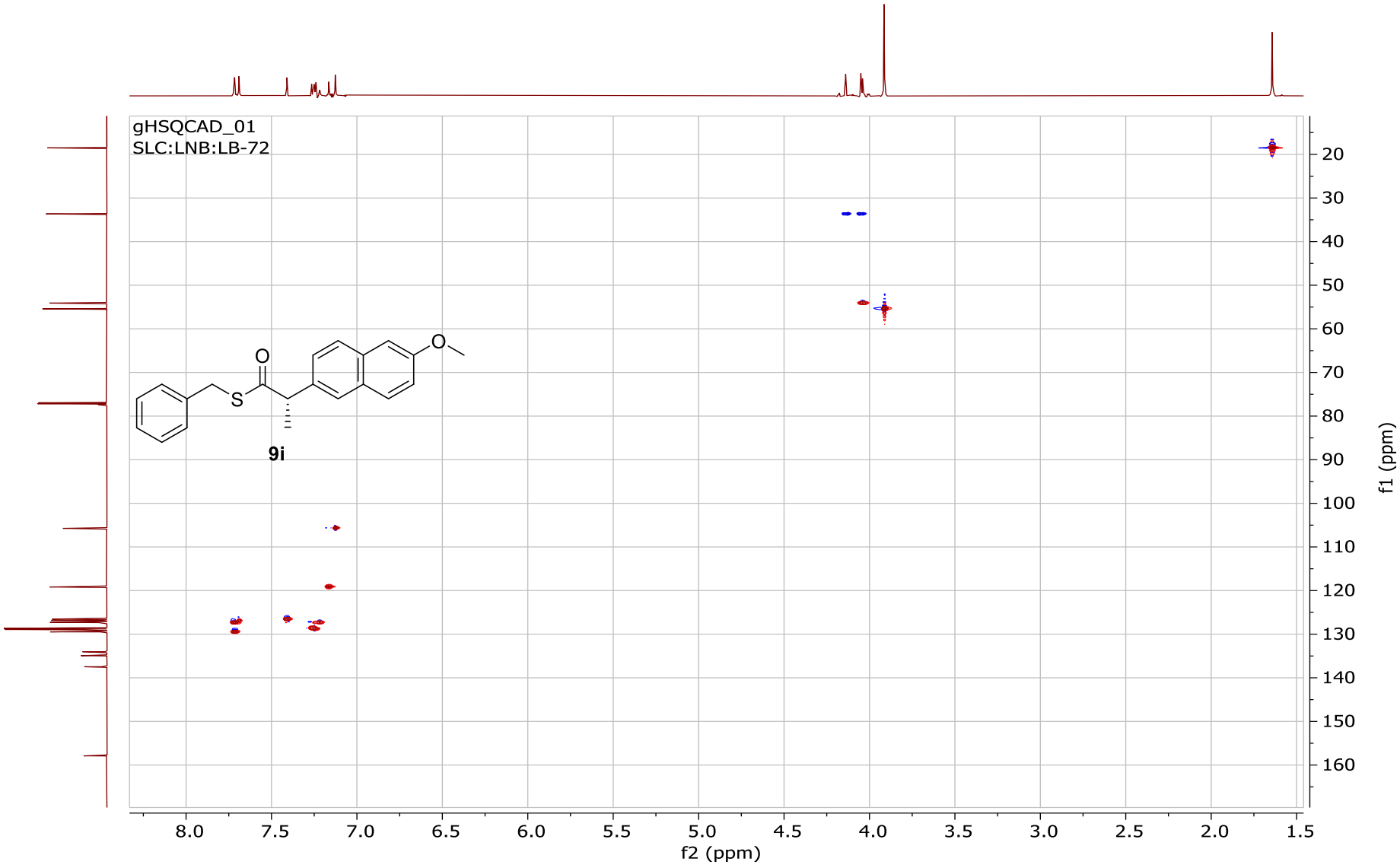

16174251.10.1.1r
SLC:LNB:LB-001-69-BROAD FRAC
Proton1.icon CDCl3 /home/nmr/localdata walkup 29
8.01 8.00 8.00 7.99 7.98 7.97 7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.41 7.41 7.40 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.33 7.33 7.31 7.30 7.30 7.29 7.28 7.28 7.27 6.97 6.96 6.95 6.94 6.94 6.93 4.34 3.88 3.87
O
S
O
9h
2.00
1.98
2.01
1.06
2.00
1.98
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

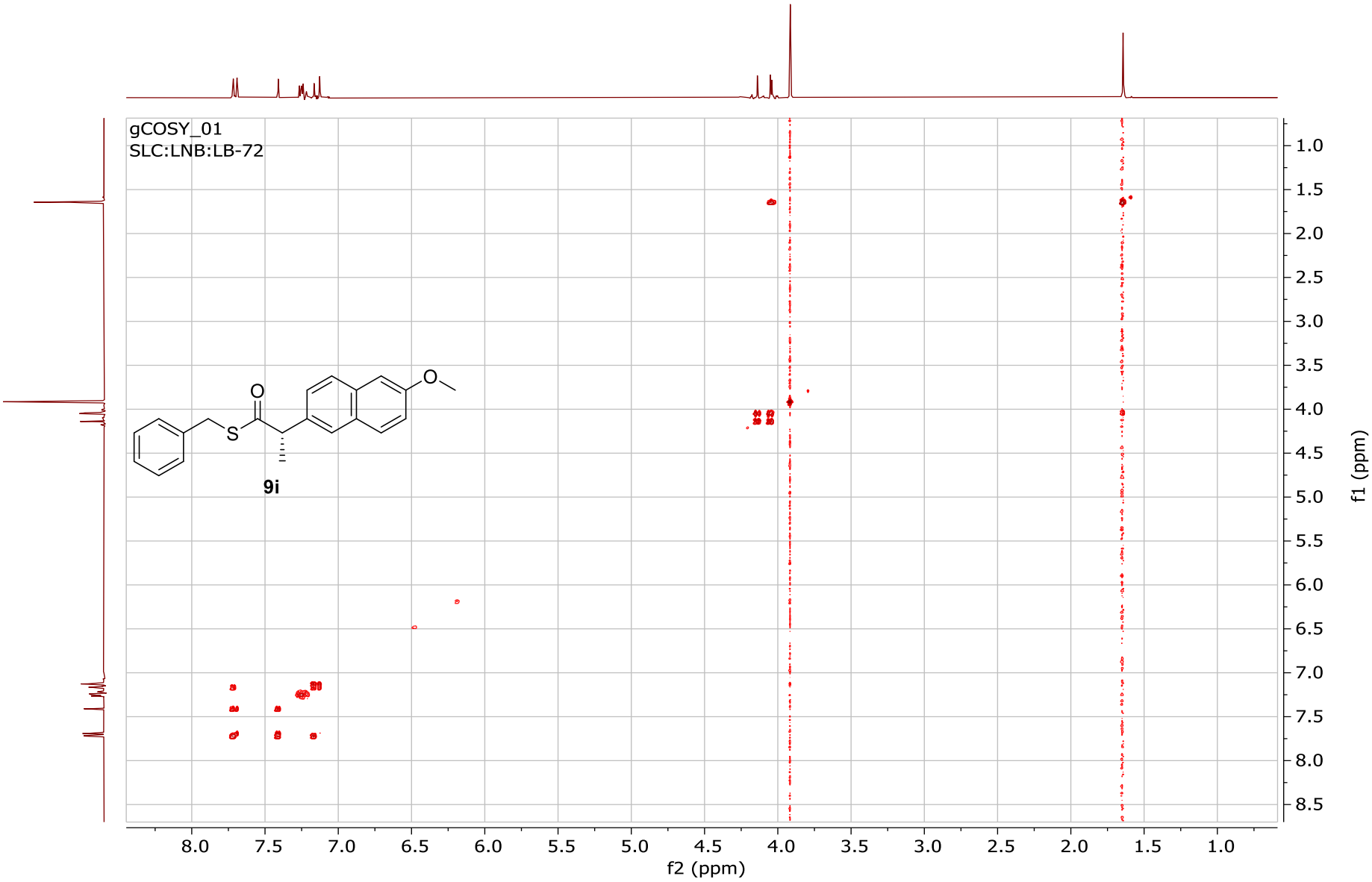
16174251.11.1.1r
SLC:LNB:LB-001-69-BROAD FRAC
Carbon.dur CDCl3 /home/nmr/localdata w/alkup 25

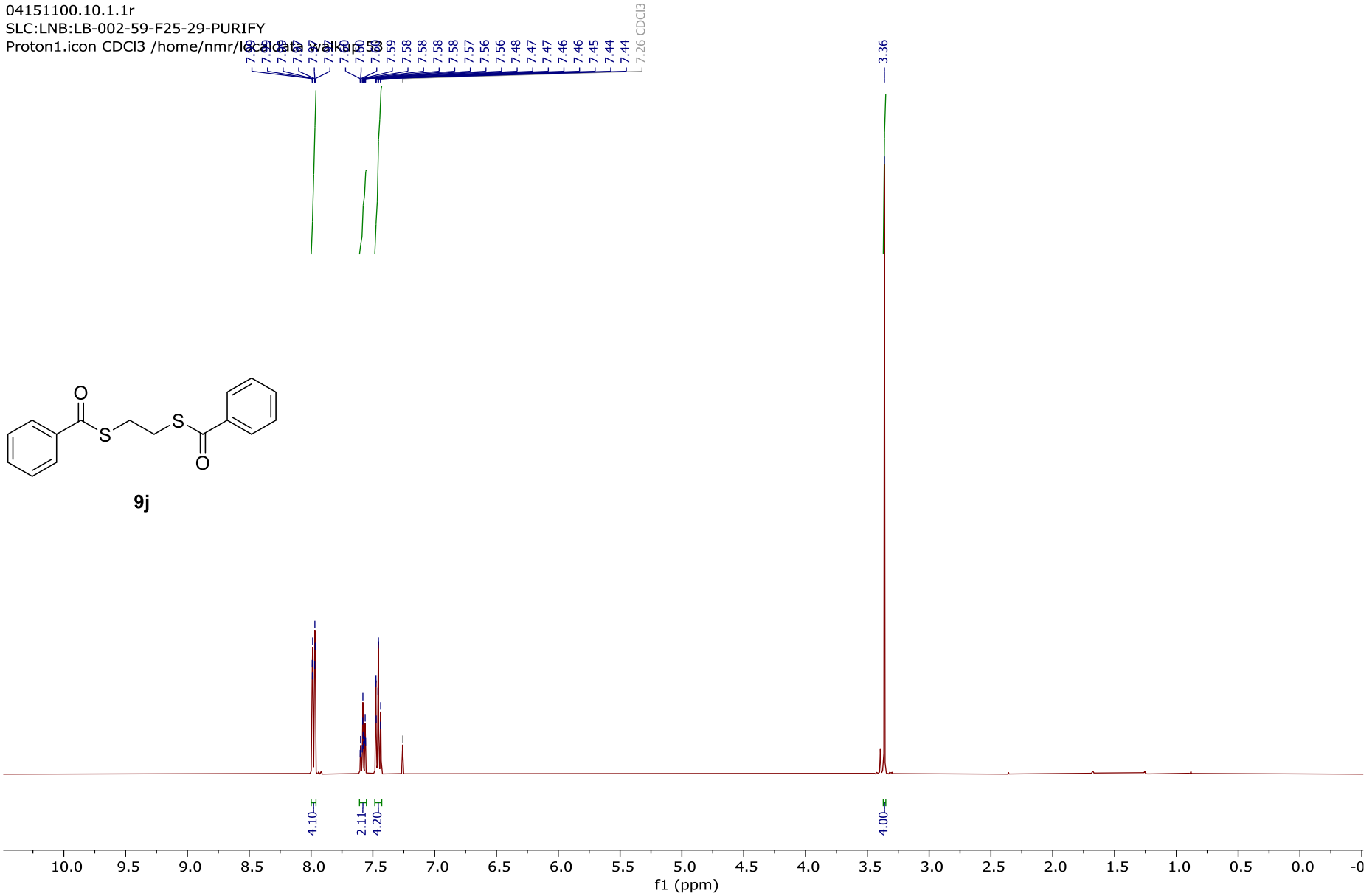



PROTON_02
SLC:LNB:LB-72
7.71 7.69 7.69 7.69 7.69 7.69 7.42 7.41 7.40 7.40 7.28 7.28 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.25 7.24 7.24 7.24 7.24 7.23 7.23 7.23 7.23 7.22 7.22 7.22 7.22 7.21 7.21 7.21 7.20 7.17 7.17 7.16 7.15 7.13 7.12 4.15 4.13 4.06 4.06 4.05 4.04 4.03 4.02 3.92 3.91 1.65 1.64 1.62
O
S
O
9i
2.01 1.01 1.00 5.10 1.00 1.00 3.05 2.97 3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

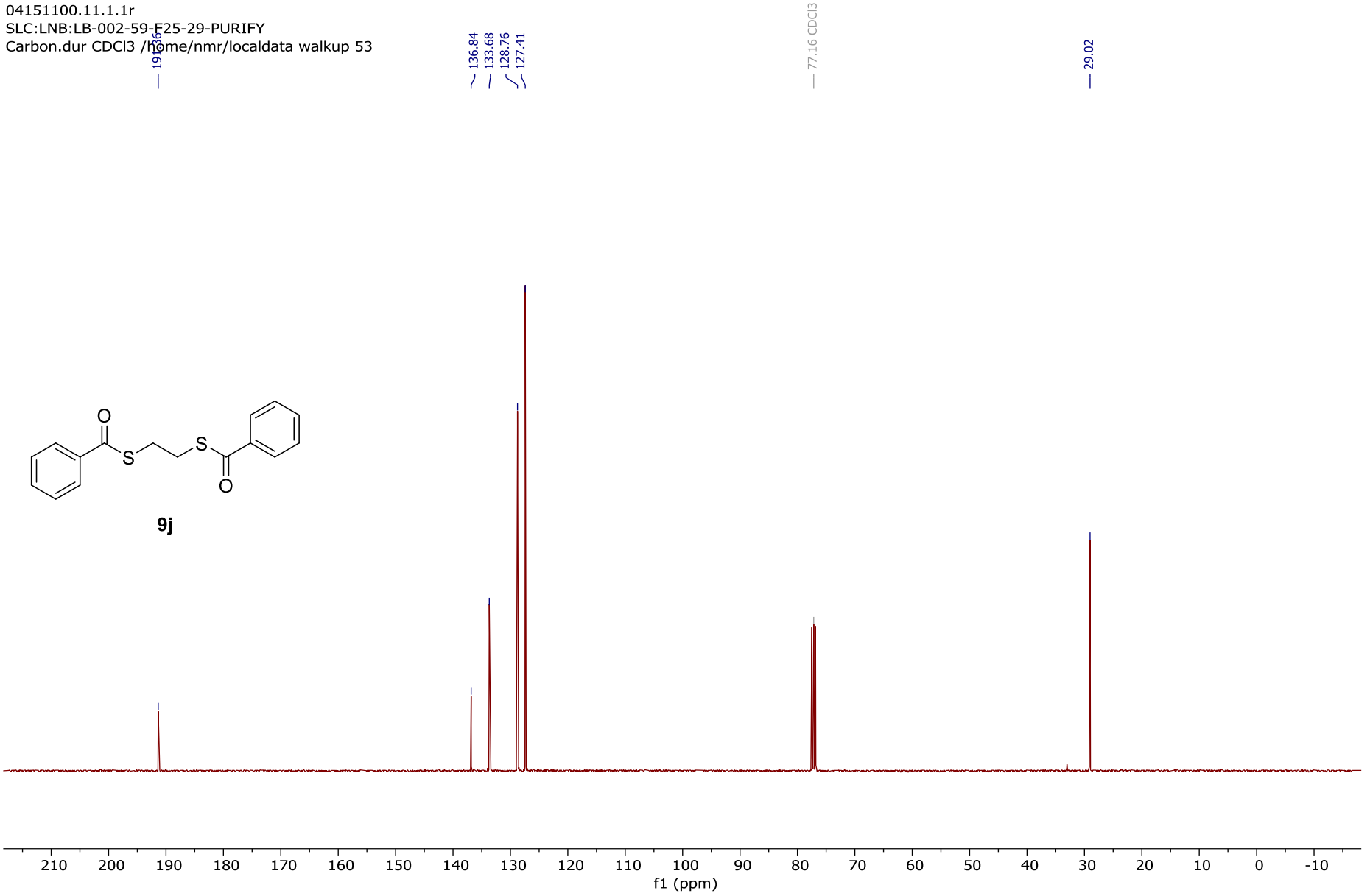

CARBON_01
SLC:LNB:LB-72
200.80
157.89
137.46
134.92
134.02
129.47
129.02
128.93
128.67
127.35
127.30
126.84
126.54
119.17
105.74
77.16 CDCl3
55.41
54.10
33.65
18.51
O
S
O
9i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)


gHSQCAD_01
SLC:LNB:LB-72
O
O
S
9i
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)


gCOSY_01
SLC:LNB:LB-72
O
S
O
9i
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
f1 (ppm)


04151100.10.1.1r
SLC:LNB:LB-002-59-F25-29-PURIFY
Proton1.icon CDCl3 /home/nmr/lacadata walkup 53
7.26 CDCl3
3.36
O
S
S
O
9j
4.10
2.11
4.20
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

04151100.11.1.1r
SLC:LNB:LB-002-59-F25-29-PURIFY
Carbon.dur CDCl3 /home/nmr/localdata walkup 53



References

1. A. M. Pandey, S. G. Agalave, C. P. Vinod and B. Gnanaprakasam, *Chem. Asian J.*, 2019, **14**, 3414-3423.
2. C. Devarajan, V. Vijayakumar, C. Ramalingam and R. Vijayaraghavan, *Res. Chem. Intermed.*, 2016, **42**, 5849-5858.
3. A. Jordan, K. D. Whymark, J. Sydenham and H. F. Sneddon, *Green Chem.*, 2021, **23**, 6405-6413.
4. M. Zhang, S. Zhang, G. Zhang, F. Chen and J. Cheng, *Tetrahedron Lett.*, 2011, **52**, 2480-2483.
5. S. Chun and Y. K. Chung, *Org. Lett.*, 2017, **19**, 3787-3790.
6. B. Lu, F. Zhu, H. M. Sun and Q. Shen, *Org. Lett.*, 2017, **19**, 1132-1135.
7. N. A. Laberge and J. A. Love, *Eur. J. Org. Chem.*, 2015, **2015**, 5546-5553.
8. L. L. Mittapelli and K. R. Gore, *Catal. Commun.*, 2021, **149**.
9. M. März, M. Kohout, T. Neveselý, J. Chudoba, D. Prukała, S. Niziński, M. Sikorski, G. Burdziński and R. Cibulka, *Org. Biomol. Chem.*, 2018, **16**, 6809-6817.
10. L. Liu, L. Yun, Z. Wang, X. Fu and C.-h. Yan, *Tetrahedron Lett.*, 2013, **54**, 5383-5386.
11. T. Wang, Y. Wang, K. Xu, Y. Zhang, J. Guo and L. Liu, *Eur. J. Org. Chem.*, 2021, **2021**, 3274-3277.
12. B. R. Kim, G. H. Sung, S.-G. Lee and Y. J. Yoon, *Tetrahedron*, 2013, **69**, 3234-3237.
13. R. A. Green, D. Pletcher, S. G. Leach and R. C. D. Brown, *Org. Lett.*, 2015, **17**, 3290-3293.
14. E. M. Kwon, C. G. Kim, A. R. Goh, J. Park and J. G. Jun, *Bull. Korean Chem. Soc.*, 2012, **33**, 1939-1944.
15. H. K. Moon, G. H. Sung, B. R. Kim, J. K. Park, Y. J. Yoon and H. J. Yoon, *Adv. Synth. Catal.*, 2016, **358**, 1725-1730.
16. S. A. Yakukhnov and V. P. Ananikov, *Adv. Synth. Catal.*, 2019, **361**, 4781-4789.
17. M. Ficker, S. W. Svenningsen, T. Larribeau and J. B. Christensen, *Tetrahedron Lett.*, 2018, **59**, 1125-1129.
18. L. Y. Jiang, J. J. Ming, L. Y. Wang, Y. Y. Jiang, L. H. Ren, Z. C. Wang and W. C. Cheng, *Green Chem.*, 2020, **22**, 1156-1163.
19. C.-S. Kuai, L.-C. Wang, J.-X. Xu and X.-F. Wu, *Org. Lett.*, 2022, **24**, 451-456.
20. N. S. Mahajani, R. I. L. Meador, T. J. Smith, S. E. Canarelli, A. A. Adhikari, J. P. Shah, C. M. Russo, D. R. Wallach, K. T. Howard, A. M. Millimaci and J. D. Chisholm, *J. Org. Chem.*, 2019, **84**, 7871-7882.
21. F. Legros, T. Martzel, J.-F. Brière, S. Oudeyer and V. Levacher, *Eur. J. Org. Chem.*, 2018, **2018**, 1975-1983.
22. S. Dey, S. K. Gadakh and A. Sudalai, *Org. Biomol. Chem.*, 2015, **13**, 10631-10640.
23. W. Wang, S. Tian and R. E. Stark, *J. Agric. Food. Chem.*, 2010, **58**, 1040-1045.
24. S. Qu, M. D. Greenhalgh and A. D. Smith, *Chemistry - A European Journal*, 2019, **25**, 2816-2823.
25. V. J. Roy, P. P. Sen and S. Raha Roy, *J. Org. Chem.*, 2021, **86**, 16965-16976.
26. M. Sandy, X. Zhu, Z. Rui and W. Zhang, *Org. Lett.*, 2013, **15**, 3396-3399.
27. M. Arisawa, T. Yamada and M. Yamaguchi, *Tetrahedron Lett.*, 2010, **51**, 6090-6092.
28. T. Xu, T. Cao, M. Yang, R. Xu, X. Nie and S. Liao, *Org. Lett.*, 2020, **22**, 3692-3696.
29. Q. Tian, S. Xu, C. Zhang, X. Liu, X. Wu and Y. Li, *J. Org. Chem.*, 2021, **86**, 8797-8804.
30. G.-p. Lu and C. Cai, *Adv. Synth. Catal.*, 2013, **355**, 1271-1276.