Direct C–C Bond Formation from Alkanes Using Ni-Photoredox Catalysis

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I. General Information

Materials. The Nickel catalyst precursor, bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$), and the photocatalyst (4,4'-di-t-butyl-2,2'-bipyridine)bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-κN]phenyl-κC]iridium(III) hexafluorophosphate ($Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$) were purchased from Strem Chemicals. Nickel precursors used in screening such as Bis[1-(N,N-dimethylamino)-2-propanolato]nickel(II) (Ni(DMAP)), Nickel(II)bromide 2-methoxyethyl ether complex ($NiBr_2$·diglyme), and Nickel(II)chloride ethylene glycol dimethyl ether complex ($NiCl_2$·glyme) were purchased from Strem and Sigma Aldrich. The ligand, 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbbpy), was purchased from Sigma Aldrich. Anhydrous, free-flowing, Redi-Dri™ reagent grade potassium phosphate tribasic (K_3PO_4) was purchased from Sigma Aldrich. *Note: While other grades of K_3PO_4 worked effectively, the free-flowing K_3PO_4 consistently performed in 5-10% higher yields.* Sodium tungstate dihydrate ($Na_2WO_4·2H_2O$) was purchased from Oakwood Chemical and used without drying. Hydrocarbon substrates (ACS grade) as well as alternative metal precursors, ligands, or additives used for screening were purchased from Strem Chemicals, Oakwood Chemical, Alfa Aesar, or Sigma Aldrich and stored in a N_2-filled glovebox. Chloroformates and acid chlorides were purchased from Sigma Aldrich and stored in a 4 °C fridge and used without further purification. OmniSolv® Benzene was purchased from VWR and stored over 4 Å molecular sieves in an N_2-filled glovebox. *Note: Reaction also worked effectively in ACS grade benzene without storage over sieves.*

Methods. Experiments were performed with exclusion of air and moisture. Reactions were set-up in a N_2-filled glovebox, capped, and secured with electrical tape before irradiating in the hood. Solvents and reagents were degassed prior to use. Reactions were monitored by thin-layer chromatography (TLC) on EMD Silica Gel 60 F254 plates, employing either potassium permanganate ($KMnO_4$) or Phosphomolybdic Acid (PMA) stains, and visualizing with UV-light (254 nm) fluorescence quenching. In cases where products were difficult to detect, reaction progress was analyzed using gas chromatography or proton nuclear magnetic resonance (^1H NMR) spectroscopy. Organic solutions were concentrated under reduced pressure using a rotary evaporator (23-30 °C, <50 torr). Automated column chromatography was performed using silica gel cartridges (40-53 µm, 60 Å) on a Biotage SP4.

Instrumentation. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker 500 AVANCE spectrometer (500 MHz), a Bruker NB 300 spectrometer (300 MHz), or a Bruker Avance III HD NanoBay (400 MHz) spectrometer. Deuterium nuclear magnetic resonance (^2H NMR) spectra were recorded on a Bruker 500 AVANCE spectrometer (77 MHz). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker 500 AVANCE spectrometer (126 MHz). Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker NB 300 spectrometer (282 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm). Chemical shifts for fluorine are reported in parts per million referenced to $CFCl_3$ (δ 0 ppm). NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constant in Hertz (Hz), integration. Reversed phase liquid chromatography/mass spectrometry (LC/MS) was performed on an Agilent 1260 Infinity analytical LC and Agilent 6120 Quadrupole LC/MS system, using electrospray ionization/atmospheric-pressure chemical ionization

(ESI/APCI), and UV detection at 254 and 280 nm. High-resolution mass spectra were obtained on an Agilent 6220 LC/MS using electrospray ionization time-of-flight (ESI-TOF) or Agilent 7200 gas chromatography/mass spectrometry using electron impact time-of-flight (EI-TOF). Gas chromatography was performed on an Agilent 7890A series instrument equipped with a split-mode capillary injection system and flame ionization detectors. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum 100 and are reported in terms of frequency of absorption (cm^{-1}).

Light Sources. Reactions were carried out using 12 W blue or violet LED strips (Sapphire Blue Waterproof LED Flex Strips, 12 V DC, Double Density 5050 or Hot Pink Waterproof LED Flex Strips, 12 V DC, Double Density 5050) purchased from Creative Lightings or 34 W blue LED lamps (KSH150B Grow Light Blue) purchased from Kessil. While the convention in photoredox catalysis has been to refer to wattage for describing intensity output by different light sources, we provide the specific photon flux provided by a 34 W Kessil in figure S13 to improve reproducibility in the field. When the Blue LED strips were utilized, they were wrapped three times around a 125 x 65 mm crystallization dish and vials were placed 1 cm away from the lights with a fan directly above the set-up (Westpointe 4-inch personal fan) purchased from Amazon. When Kessil lamps were employed they were placed 8-12 cm away from reaction vials that were stirring in an oil bath without use of a fan. *Note: When Kessil lamps are placed at distances <8 cm away from the oil bath temperatures lower than 36 °C are challenging to maintain.*

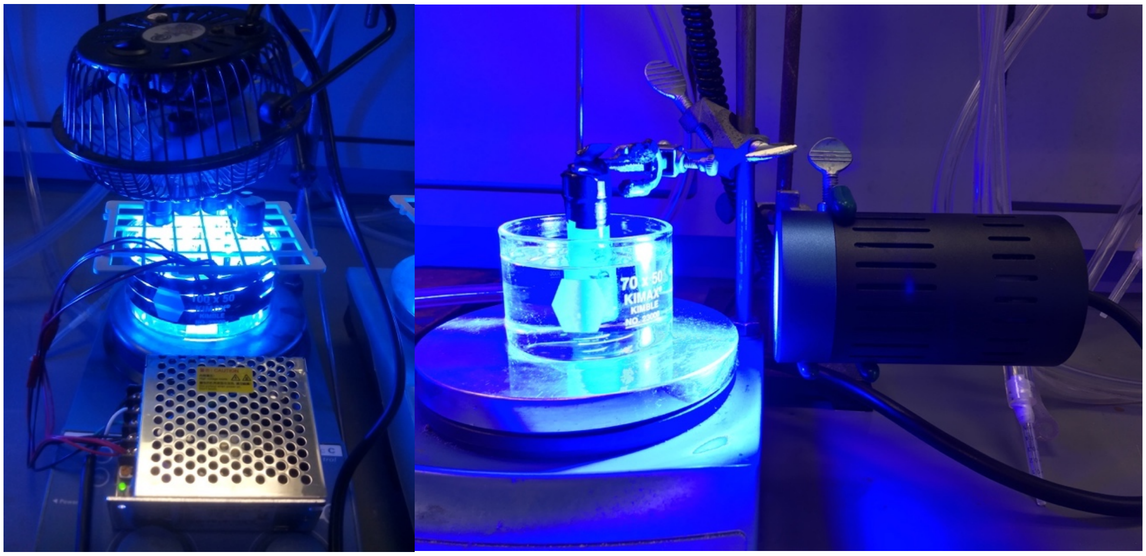
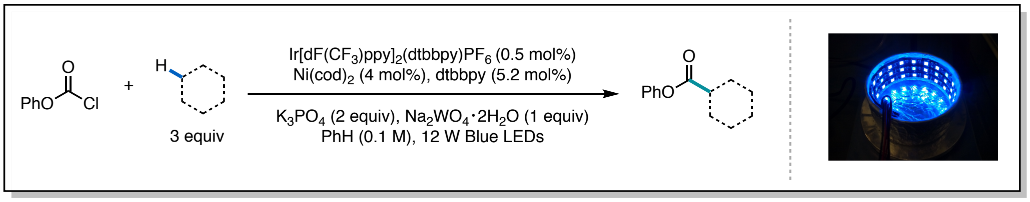


Figure S1. Lighting Set-ups. (Left) LED strip set-up. (Right) Kessil lamp set-up.

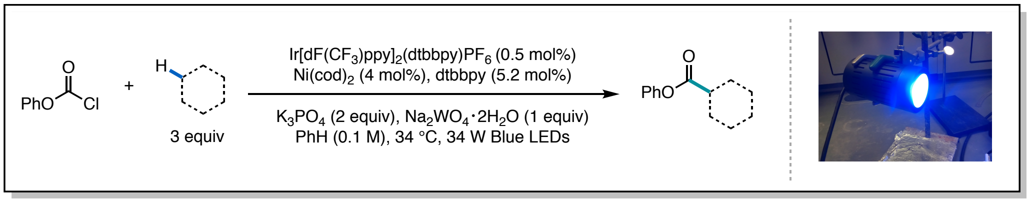
II. Experimental Procedures

A. General Procedure for Reaction Optimization of C(sp^3)–H Esterification (0.08 mmol scale):



An oven-dried 0.5 dram vial (VWR® glass vials, 66011-020) equipped with a PTFE-coated stir bar (VWR® Micro stir bars, 2 x 7 mm, 58948-976) was charged with K_3PO_4 (34 mg, 0.16 mmol, 2 equiv.) and Na_2WO_2•$2H_2O$ (26 mg, 0.08 mmol, 1 equiv.) in a N_2-filled glovebox. To the reaction vial was added 600 µL of benzene and 3 equiv. (0.24 mmol) of hydrocarbon substrate. This was followed successively by 200 µL of a heterogeneous yellow solution of Ir[(dF(CF_3)ppy)]$_2$(dtbbpy)]PF_6 (0.44 mg, 0.4 µmol, 0.005 equiv.) in benzene and 200 µL of a dark purple solution of Ni(cod)$_2$ (0.88 mg, 3.2 µmol, 0.04 equiv.) and 4,4′-di-tert-butyl-2,2′-bipyridine (1.1 mg, 4.1 µmol, 0.052 equiv.) in benzene which had been stirred for 20 minutes prior to use. Lastly, phenyl chloroformate (10 µL, 0.08 mmol, 1 equiv.) was added to the reaction, turning the solution a deep red color. *Note: chloroformate should be added last to the reaction mixture to ensure minimum degradation of chloroformate before irradiation can commence.* The vial was capped with a teflon septum cap and sealed with electrical tape. The reaction vial was removed from the glove box, set to stir (1000 rpm), and irradiated with a 12 W blue LED array for 48-72 hours. An aliquot of the crude product was filtered through a silica plug and analyzed by 1H NMR or GC relative to 4-fluoroanisole as an external standard. *Note: Reactions conducted on 0.24 mmol scale were completed in 2-dram vials using the same procedure at three times the scale.*

B. General Procedure for Control Reactions and Isolations of C(sp^3)–H Esterification (0.6 mmol scale):



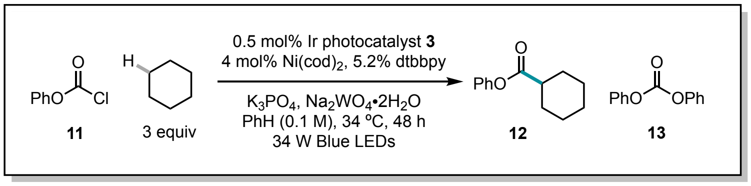
An oven-dried 2 dram vial (VWR glass vials, part no. 66011-085) equipped with a PTFE-coated stir bar (VWR® Micro stir bars, 3 x 10 mm, 76001-878) was charged with K_3PO_4 (0.25 g, 1.2 mmol, 2 equiv.) and Na_2WO_2•$2H_2O$ (0.20 g, 0.6 mmol, 1 equiv.) in a N_2-filled glovebox. To the reaction vial was added 4400 µL of benzene and 3 equiv. (1.8 mmol) of hydrocarbon substrate. This was followed successively by 800 µL of a heterogeneous yellow solution of Ir[(dF(CF_3)ppy)]$_2$(dtbbpy)]PF_6 (20 mg, 3.0 µmol, 0.005 equiv.) in benzene and 800 µL of a dark purple solution of Ni(cod)$_2$ (0.88 mg, 24 µmol, 0.04 equiv.) and 4,4′-di-tert-butyl-2,2′-bipyridine (1.1 mg, 31 µmol, 0.052 equiv.) in benzene, which had been stirred for 20 minutes prior to use. Lastly, phenyl chloroformate (75 µL, 0.6 mmol, 1 equiv.) was added to the reaction, turning the solution a deep red color. *Note 1: as in the reaction optimization procedure, chloroformate should be added last to the reaction mixture to ensure minimum degradation of chloroformate before irradiation can commence. Note 2: When other electrophiles such as acid chlorides were added to the reaction they were also added last to the reaction mixture.* The vial was capped with a closed phenolic cap. The reaction vial was removed from the glove box sealed with electrical tape, and placed in an oil bath set to 34 or 40 °C, set to stir (1000 rpm), and irradiated with a 34 W Kessil lamp for 48 hours. The crude mixture was filtered over a pad of silica and rinsed with dichloromethane or ethyl acetate and concentrated *in vacuo*. The crude product was analyzed by 1H NMR relative to 4-fluoroanisole as an external standard and purified by automated silica gel column chromatography using the indicated solvent system to obtain the desired product.

C. Procedure for Hammett Experiment: An oven-dried 2 dram vial (VWR glass vials, part no. 66011-085) equipped with a PTFE-coated stir bar (VWR® Micro stir bars, 3 x 10 mm, 76001-878) was charged with K_3PO_4 (0.25 g, 1.2 mmol, 2 equiv.) and Na_2WO_2•$2H_2O$ (0.20 g, 0.6 mmol, 1 equiv.) in a N_2-filled glovebox. To the reaction vial was added 4400 µL of benzene and 3 equiv. (1.8 mmol) of each para substituted ethyl benzene. This was followed successively by 800 µL of a heterogeneous yellow solution of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (20 mg, 3.0 µmol, 0.005 equiv.) in benzene and 800 µL of a dark purple solution of Ni(cod)$_2$ (0.88 mg, 24 µmol, 0.04 equiv.) and 4,4′-di-tert-butyl-2,2′-bipyridine (1.1 mg, 31 µmol, 0.052 equiv.) in benzene, which had been stirred for 20 minutes prior to use. Lastly, phenyl chloroformate (75 µL, 0.6 mmol, 1 equiv.) was added to the reaction, turning the solution a deep red color. The vial was capped with a closed phenolic cap and removed from the glove box. Once outside the vial was sealed with electrical tape, placed in an oil bath set to 40 °C, set to stir (1000 rpm), and irradiated with a 34 W Kessil lamp for 48 hours.. The reaction mixture was analyzed by GC using 4-fluoroanisole (67.9 µL, 0.6 mmol, 1 equiv.) as an external standard.

III. Additional Experiments

A. Extended Optimization Tables. Table 1 from the main manuscript is presented below with entries 14 and 15 included to compare yields of desired product and diphenyl carbonate using 2 equiv of K_3PO_4 (entry 14) and 1 equiv of $Na_2WO_4•2H_2O$ (entry 15) versus 3 equiv of K_3PO_4 and 3 equiv of $Na_2WO_4•2H_2O$ (entries 9 and 12). When phenyl isocyanate, a reagent that is known to react with alcohols to generate carbamates (Table 1, entry 16) was added to the standard reaction conditions to prevent the accumulation of PhOH, less diphenyl carbonate was generated, though the overall yield was not improved.

Table S1. Extended Table 1 from main manuscript.



Entry	Deviation from standard conditions	Yield 12 (%)[b]	Yield 13 (%)[c]
1	none	**66**	28
2	1 equiv of cyclohexane	**44**	33
3	no photocatalyst	**0**	48
4	no ligand	**3**	27
5	no nickel	**0**	17
6	no light	**0**	34
7	26 °C	**46**	17
8	40 °C	**55**	32
9	no $Na_2WO_4•2H_2O$[d]	**39**	19
10	no $Na_2WO_4•2H_2O$[d], 72h	**62**	22
11	no $Na_2WO_4•2H_2O$, $Na_2SiO_3•5H_2O$	**57**	25
12	no K_3PO_4[d]	**58**	35
13	no K_3PO_4, no $Na_2WO_4•2H_2O$	**17**	11
14	no $Na_2WO_4•2H_2O$	41	18
15	no K_3PO_4	45	27
16	0.5 equiv of PhNCO[e, f]	49	10

[a] Reactions were carried out on 0.6 mmol scale with K_3PO_4 (2 equiv); $Na_2WO_4•2H_2O$ (1 equiv).
[b] Yields were determined by ^1H NMR spectroscopy using 4-fluoroanisole as an internal standard.
[c] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.
[d] 3 equiv of base used.
[e] Added to the reaction prior to chloroformate addition.
[f] Conducted on 0.3 mmol scale.

When phenyl chloroformate was first reacted with cyclohexane under the previously reported conditions for the arylation of ethers[1] only low yield was obtained (Figure S2). In order to achieve 66% as in Table 1, entry 1, three major changes were made during the optimization process: (1) sodium tungstate was added to the reactions as a base, (2) catalyst loadings were significantly lowered as the concentration was doubled, and (3) mild heating was applied to the reactions.

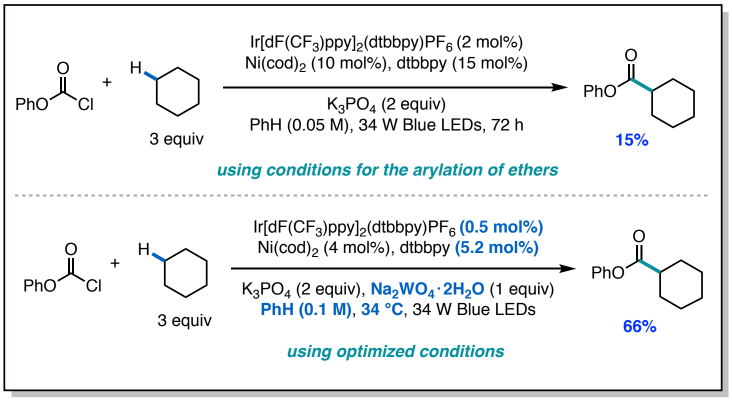
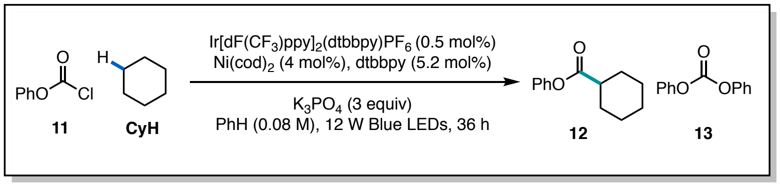


Figure S2. Comparison of the reaction of phenyl chloroformate with cyclohexane using conditions for the arylation of ethers versus optimized conditions. Yield determined by 1H NMR analysis using 4-fluoroanisole as an external standard.

One of the major challenges during optimization is highlighted below in Tables S2 and S3. At the beginning of reaction optimization and when using blue LED strips, lowering the amount of hydrocarbon substrate below 5 equivalents relative to phenyl chloroformate diminished yields (Table S2 and Table S3, entries 1-2). Notably, while the yields of reactions with potassium phosphate as a base remained consistent between 1-4 equivalents and exhibited low conversion after 36 hours, the reactions utilizing sodium tungstate were almost complete at this time point, giving good yields at 3 or 4 equivalents of cyclohexane, and only delivering significantly low yields when the amount of cyclohexane was lowered to 1-2 equivalents.

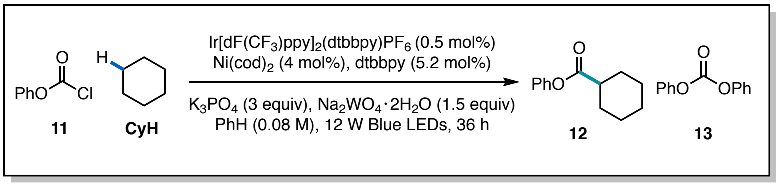
Table S2. Lowering equivalents of cyclohexane using potassium phosphate as a base.



Entry	Equiv of CyH	Conversion of 11 (%)[b]	Yield of 12 (%)[b]	Yield of 13 (%)[b]
1	5	58	33	23
2	4	70	28	21
3	3	72	27	19
4	2	69	27	21
5	1	72	25	22

[a] Reactions were carried out on 0.08 mmol scale.
[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.

Table S3. Lowering equivalents of cyclohexane using potassium phosphate and sodium tungstate dihydrate as bases.



Entry	Equiv of CyH	Conversion of 11 (%)^b	Yield of 12 (%)^b	Yield of 13 (%)^b
1	5	83	64	21
2	4	98	51	20
3	3	100	51	20
4	2	99	47	19
5	1	97	32	23

[a] Reactions were carried out on 0.08 mmol scale.
[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.

B. Reaction Profile. In the esterification of hydrocarbons there are several byproducts observed over the course of the reaction (Figure S4). The major byproduct is diphenylcarbonate (which comprises 10-30% of a reaction's mass balance) and can be caused by the degradation of chloroformate starting material. A less prevalent byproduct formed over the course of the reaction is alkylated benzene, which can be formed via nucleophilic radical substitution of an alkyl radical to the benzene solvent. An example of this byproduct is phenyl cyclohexane which is produced when cyclohexane is the alkane being activated (Figure S3). *Note: alkylated benzene is present whether phenyl chloroformate or another organochloride is used, suggesting that the phenyl group is arising from solvent rather than decomposition of the chloroformate.* Additional trace products include PhOH from the decomposition of chloroformate as well as chlorinated and dichlorinated cyclooctadiene from the nickel catalyst precursor. The amount of each of these products varies depending on the success of the productive photoelimination pathway, however, each individual byproduct never comprises >10% yield when the desired product is obtained in >50% combined (in the case of isomers) yield.

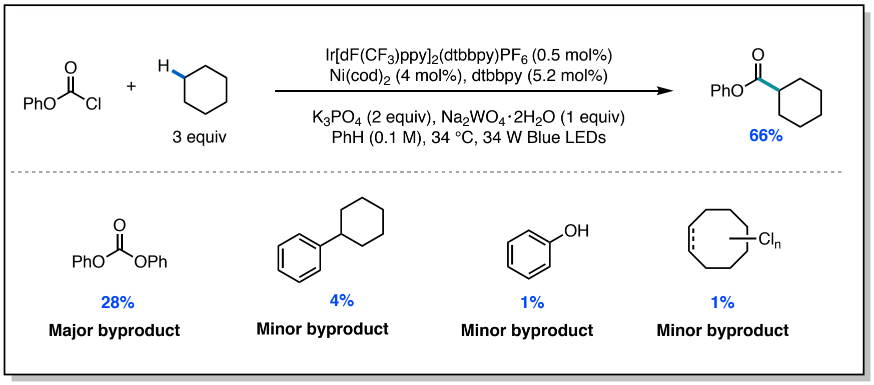
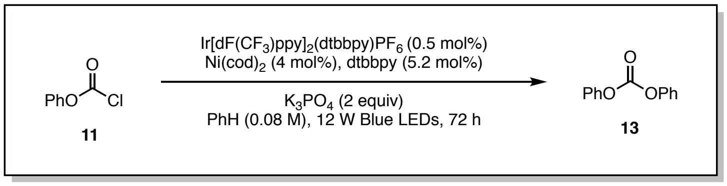


Figure S3. Byproducts formed from the esterification of cyclohexane. Yields determined by ^{1}H NMR and GC analysis using 4-fluoroanisole as an external standard.

To further investigate the formation of the major byproduct in the reaction, chloroformate starting material was monitored under a variety of conditions to determine the origin(s) of decomposition (Table S4). Entries 1-6 in Table S4 demonstrate that diphenyl carbonate can be formed in appreciable yields in the absence of both catalysts and light, however the most byproduct is formed under the full standard reaction conditions with base present, as reported in entries 7-12 in Table S4.

Table S4. Probing the origin of decomposition of phenyl chloroformate.



Entry	Deviation from conditions[a]	Conversion of 11 (%)[b]	Yield of 13 (%)[b]
1	None	24	12
2	No hν	36	16
3	Ambient hν, 45 °C	18	15
4	No K_3PO_4	9	0
5	No K_3PO_4, No hν	1	1
6	No K_3PO_4, Ambient hν, 45 °C	1	1
7	None[c]	47	35
8	No hν[c]	45	26
9	Ambient hν, 45 °C[c]	38	23
10	No K_3PO_4[c]	6	4
11	No K_3PO_4, No hν[c]	7	0
12	No K_3PO_4, Ambient hν, 45 °C[c]	20	0

[a] Reactions were carried out on 0.08 mmol scale.

[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.

[c] Reactions were run without $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, $Ni(cod)_2$, or dtbbpy

By monitoring the reaction progress of a 0.6 mmol reaction and taking aliquots at given time points (Figure S4), it was possible to compare the production of phenyl ester product and diphenyl carbonate, relative to the consumption of starting material. At the first time point it was evident that a significant portion of the chloroformate had decomposed to form byproduct, supporting the hypothesis that the primary mechanism for diphenyl carbonate generation was caused by base rather than via the catalysts.

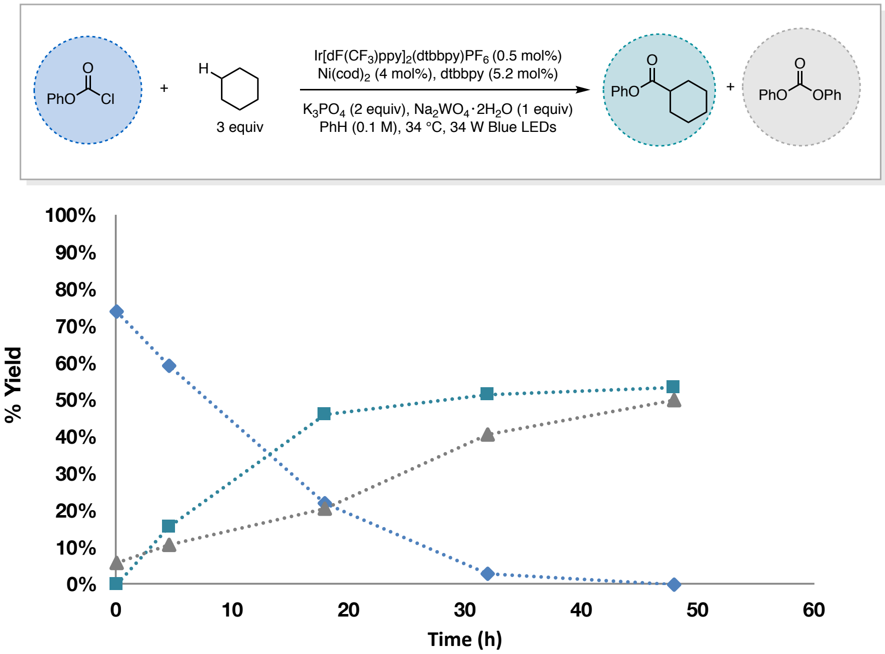


Figure S4. Reaction profile of the esterification of cyclohexane. ^{a}Yield determined by GC analysis using 4-fluoroanisole as an external standard.

Based on the above data a proposal for the base-promoted production of diphenyl carbonate is depicted in Figure S5 via a two-step pathway: first, the generation of phenoxide and second the reaction of phenoxide with phenyl chloroformate. The generation of phenoxide can result via the addition of the base to the chloroformate with the loss of chloride, followed by a second addition of the same base to the same carbonate to extrude phenoxide (path i).[2] Alternatively, phenoxide can result through direct addition of chloride to the chloroformate via direct displacement (path ii). While decomposition of phenyl chloroformate to generate phenoxide without base is possible, due to the acceleration of this byproduct formation in the presence of base and the lack of byproduct formation in entry 20 of Table S5, it is likely that the base participates in a nucleophilic addition to the chloroformate.

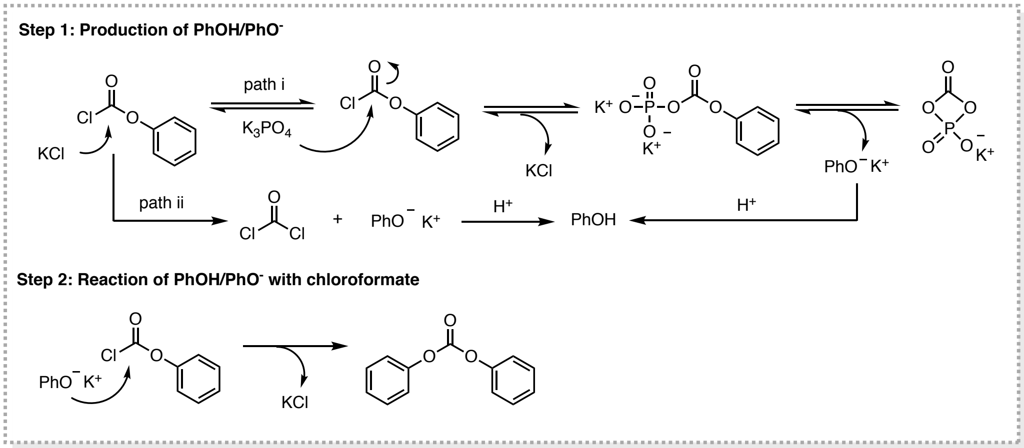


Figure S5. Proposed mechanism for diphenyl carbonate production.

C. Sodium Tungstate Additive. During optimization the combination of sodium tungstate dihydrate and potassium phosphate proved to be optimal for improving reaction yield and the selectivity of desired product over diphenyl carbonate (Table S1, entries 1 vs. 9-13, Tables S3-S4, and Figure S5). Analogous to many other bases used in photoredox catalysis, $Na_2WO_4{\cdot}2H_2O$ is reasonably priced ($0.06/g) and reported to react with HCl (equation S1). While unlikely under our mild conditions, Na_2WO_4 is known to form higher order tungstate derivatives in the presence of acid or base under high temperatures, pressure, or sonication, and of concern to our proposed mechanism is the possibility of tungstate derived polyoxometalates performing a hydrogen atom abstraction of hydrocarbons (equation S2).[3] While the observed selectivities in our products as well as our Evans-Polanyi and Hammett plots are indicative of hydrogen abstraction by chlorine radical, it could be that some minor productive chemistry is occurring via the tungstate additive. To assess if other tungsten derivatives could also lead to improvements in yield and selectivity, a variety of tungstate additives were explored, though no other base performed as effectively, and all additives limited the desired C(sp^3)–H functionalization rather than promoted it. Moreover, the improvement in yield with increasing size of the counterion in entries 2, 5, and 6 in table S5 may be attributed to increasing solubility in benzene, therefore it seems likely that the efficiency of quenching HCl or base-mediated formation of diphenyl carbonate is influenced with different additives.

Use of sodium tungstate as a base

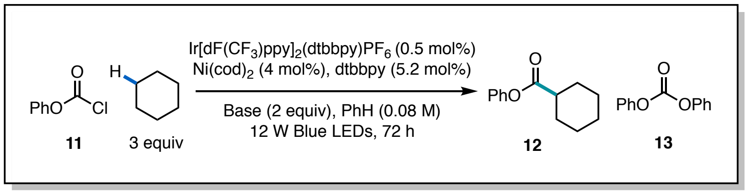
Eq.S1. $Na_2WO_4 + 2HCl \longrightarrow WO_3 + 2NaCl + H_2O$

Use of sodium tungstate to form higher order tungstate derivatives

Eq.S2. $Na_2WO_4{\cdot}2H_2O + H_3PO_4 \xrightarrow{HCl} H_xPW_yO_z$

Figure S6. Potential byproducts from Na_2WO_4.

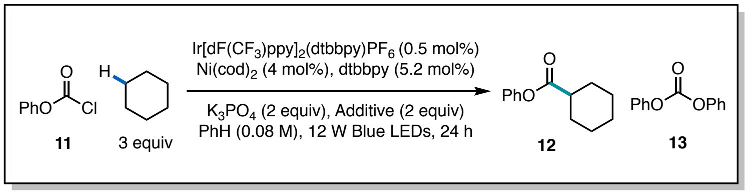
Table S5. Examination of alternative bases/additives.



Entry	Bases[a]	Yield 12 (%)[b]	Yield 13 (%)[b]
1	K_3PO_4 (ACS grade)	56	19
2	K_3PO_4 (redi-dri anhydrous)	68	19
3	K_2HPO_4	3	4
4	KH_2PO_4	0	1
5	Na_3PO_4	21	12
6	Li_3PO_4	0	1
7	K_2CO_3	2	6
8	$KHCO_3$	2	55
9	Na_2CO_3	1	5
10	$NaHCO_3$	4	54
11	Cs_2CO_3	10	23
12	$CsHCO_3$	4	62
13	NaTFA	0	5
14	NaOBz	1	26
15	CsOAc	0	26
16	LiOtBu	8	42
17	KOPiv	0	50
18	KF	17	12
19	LiCl	0	0
20	KCl	0	0

[a] Reactions were carried out on 0.08 mmol scale.
[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.

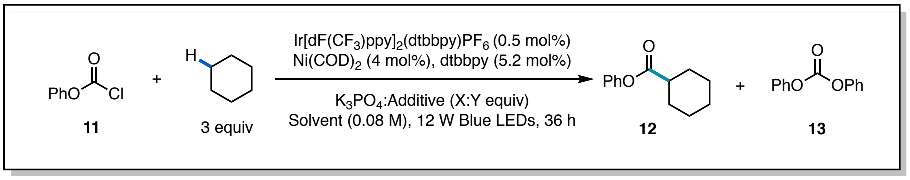
Table S6. Examination of additives in addition to K_3PO_4 at 24 h.



Entry	Additive[a]	Yield 12 (%)[b]	Yield 13 (%)[b]
1	None	28	11
2	NH_4OAc	0	8
3	$NBu_4PO_4H_2$	3	15
4	NH_4BF_4	3	8
5	$NaSnF_6$	1	6
6	$Na_2WO_4 \cdot 2H_2O$	38	14
7	KCO_2H	22	9
8	$CsCO_2H$	5	8
9	$Zn(OTf)_2$	0	5
10	ZnI_2	0	5
11	Ag_2CO_3	0	45
12	$In(OTf)_3$	0	2
13	$La(OTf)_3$	0	8
14	$Ga(OTf)_3$	0	4
15	$Ca(OTf)_3$	0	8
16	$Bi(OTf)_3$	0	3
17	$Cd(OAc)_2$	0	7
18	FeO_2	6	13

[a] Reactions were carried out on 0.08 mmol scale.
[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.

Table S7. Stoichiometry studies of sodium and tungstate additives with potassium phosphate.



Entry	Additive[a]	X:Y	Conversion of 11 (%)[b]	Yield of 12 (%)[b]	Yield of 13 (%)[b]
1	None	2:0	86	40	20
2	Na_2SO_4	2:1	83	39	20
3		2:2	83	37	19
4		1:2	71	28	17
5		0:2	52	17	10
6	Na_2SO_3	2:1	80	39	20
7		2:2	75	38	19
8		1:2	65	29	15
9		0:2	48	17	11
10	NaCl	2:1	74	33	20
11		2:2	72	31	18
12		1:2	64	24	15
13		0:2	43	11	10
14	WCl_6	2:1	80	0	0
15		2:2	75	0	0
16		1:2	65	0	0
17		0:2	48	0	0
18	WO_3	2:1	69	28	22
19		2:2	71	26	25
20		1:2	60	19	18
21		0:2	40	4	10
22	Li_2WO_4	2:1	62	25	35
23		2:2	61	31	26
24		1:2	58	27	30
25		0:2	44	20	24
26	Cs_2WO_4	2:1	70	20	26
27		2:2	92	19	30
28		1:2	91	22	24
29		0:2	91	20	35
30	$CaWO_4$	2:1	60	31	30
31		2:2	77	24	24
32		1:2	61	20	35
33		0:2	30	2	26
34	$(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$	2:1	61	1	24
35		2:2	46	5	35
36		1:2	42	2	26
37		0:2	32	1	30
38	$H_3[P(W_3O_{10})_4] \cdot xH_2O$	2:1	44	0	35
39		2:2	40	0	26
40		1:2	27	0	30
41		0:2	27	0	24
42	$3Na_2WO_4 \cdot 9WO_3 \cdot xH_2O$	2:1	69	41	31
43		2:2	47	17	53
44		1:2	46	17	54
45		0:2	37	5	63

[a] Reactions were carried out on 0.08 mmol scale.
[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.

To examine the possibility of sodium tungstate participating in an electron transfer process during the course of the reaction we performed cyclic voltammetry. Sodium tungstate, which is a white powder, showed no redox activity in acetonitrile (in which it is slightly soluble relative to benzene). While this does not rule out the formation of a redox active species that is formed *in situ,* it does indicate that sodium tungstate independently is not responsible for any electron transfer event.

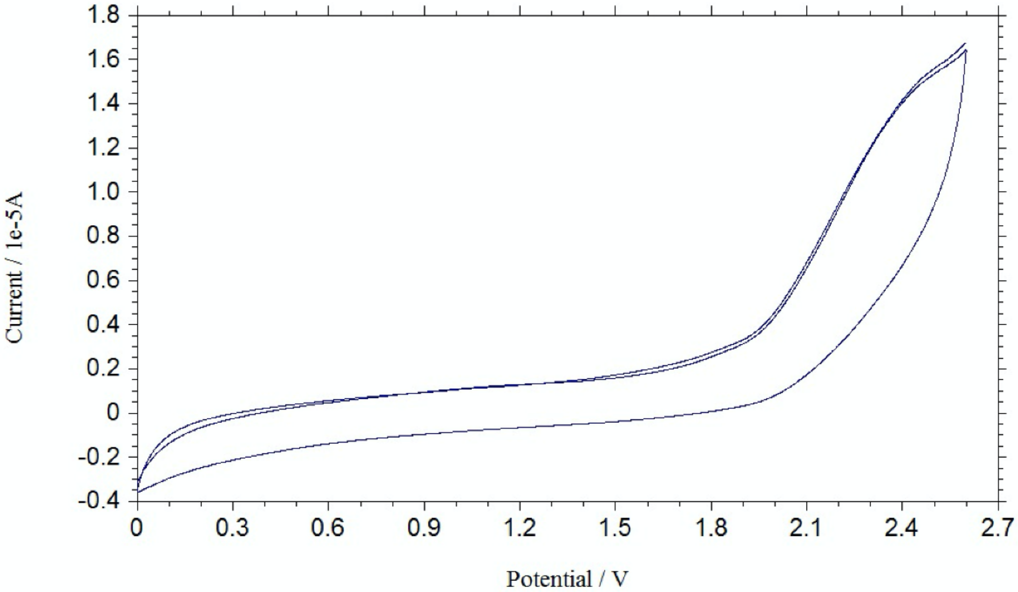


Figure S7. Cyclic Voltammogram of Na_2WO_2•$2H_2O$ in MeCN. [a] 0.1 M TBAPF6 + 0.1 M Na_2WO_2•$2H_2O$ in MeCN.

D. Attempted Arylation, Alkylation, and Acylation Reactions.

After the realization of successful conditions for the esterification of alkanes we applied this strategy to the reaction of other organochlorides with unactivated hydrocarbons (Figure S10), however only poor yield of the desired product, if any, was observed. Both aryl chlorides and alkyl chlorides showed limited conversion after 48 h. The under-performance of these substrates suggests that the efficacy of $C(sp^3)$–H functionalization is related to the electrophile employed, and its role in catalysis (such as the ease of photoelimination of chlorine radical) rather than the employed reaction conditions.

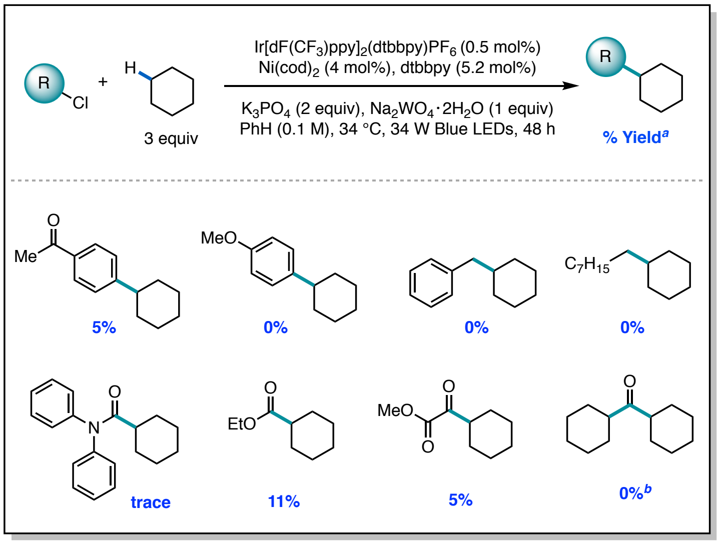
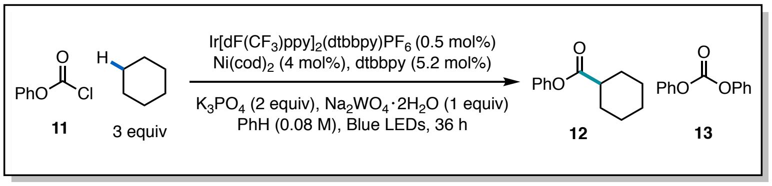


Figure S8. Comparison of the reaction of phenyl chloroformate with cyclohexane using optimized conditions. [a] Yield determined by 1H NMR analysis using 4-fluoroanisole as an external standard. [b]Triphosgene was employed as a source of phosgene to enable a di-functionalization strategy with 6 equiv of cyclohexane.

E. Effect of Lighting, Temperature, and Set-up. Reaction parameters that were most influential in maintaining consistent and reproducible yields over a variety of reaction set-ups and scales were lighting and temperature. As the reaction was scaled (from 0.08 mmol to 0.48 mmol) mild heating was required to maintain good yields, potentially for the effective quenching of HCl by potassium phosphate or sodium tungstate, both of which are insoluble in benzene. Kessil lamps worked most effectively as light sources and the ideal reaction temperature was determined to be 34 °C ± 4 °C for hydrocarbons and 40 °C ± 4 °C for benzylic or heteroatom containing substrates. In cases where temperatures were higher or lower than ideal, a larger amount of diphenyl carbonate and the alkylated benzene product were formed. Notably, as long as a Kessil was employed with sufficient cooling the esterification reaction proceeded when set-up in a round bottom flask or screw cap test tube. The Merck photoreactor was used as reported by MacMillan, D. W. C. *et al.* in *ACS Cent. Sci*. **2017**, *3*, 647–653. The lack of improvement in reactivity with the Merck Photoreactor at full intensity and no significant improvement in yields with the specific wavelength Kessil lamps suggests that the reaction is not photon limited.

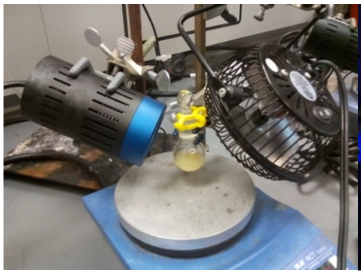
Table S8. Examination of early reaction set-ups for the esterification of cyclohexane.

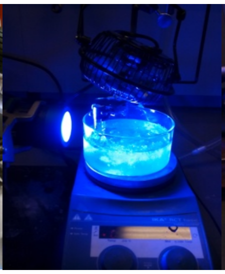


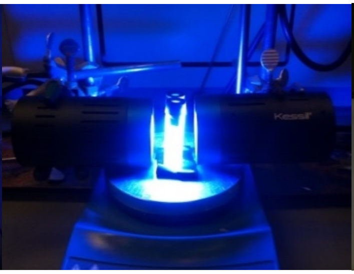
Entry	Reaction Set-up	Conversion of 11 (%)[b]	Yield of 12 (%)[b]	Yield of 13 (%)[b]
1	Round bottom flask[c]	100	51	38
2	Water bath	81	35	55
3	Double Kessil[d]	100	48	42
4	Merck photoreactor[e]	68	19	15
5	Single Kessil	100	55	30

[a] Reactions were carried out on 0.24 mmol scale.
[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.
[c] A 10 mL round bottom flask was used with glass stopper
[d] Fans were not used to reproduce heating effect by an oil bath.
[e] Photoreactor was set to 1000 rpm, cooled to room temperature, with 100% light intensity.

Table S8 Reactions Set-ups:


Round bottom flask


Water bath


Double Kessil


Merck Photoreactor

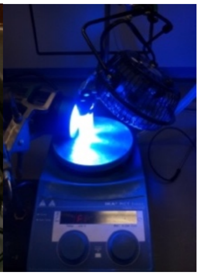
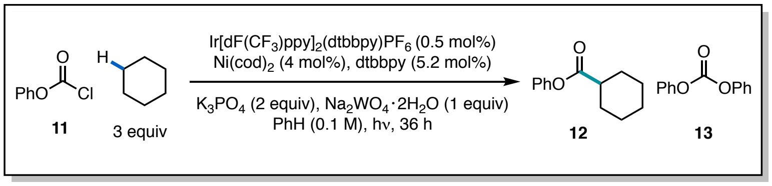

Single Kessil

Table S9. Examination of lighting conditions for the esterification of cyclohexane. Specific wavelength lamps (390 nm, 427 nm, 440 nm, 456 nm, 467 nm) with varied intensities (0, 25, 50, 75, 100%) can be purchased from (see http://kessil.com/photoredox/Products.php).



Entry	Conditions[a,c]	Conversion of 11 (%)[b]	Yield of 12 (%)[b]	Yield of 13 (%)[b]
1	390 nm, 38 °C[e]	53	28	16
2	427 nm, 28 °C	96	44	33
3	427 nm, 33 °C	87	28	20
4	427 nm, 38 °C	77	27	19
5	440 nm, 28 °C	74	18	12
6	440 nm, 33 °C	97	39	21
7	440 nm, 38 °C	89	31	21
8	456 nm, 28 °C	78	18	12
9	456 nm, 33 °C	100	53	23
10	456 nm, 38 °C	94	36	25
11	467 nm, 28 °C	100	32	23
12	467 nm, 33 °C	100	46	24
13	467 nm, 38 °C	95	37	33
14	Kessil, 28 °C[d]	69	25	17
15	Kessil, 33 °C[d]	100	54	24
16	Kessil, 38 °C[d]	87	32	21
17	Kessil, 45 °C[d]	97	34	

[a] Reactions were carried out on 0.6 mmol scale in an oil bath.
[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.
[c] PR150 Kessils employed set at 75% intensity.
[d] HR150 Kessils employed.
[e] Reaction carried out on 0.48 mmol scale in an oil bath.

Table S9 PR160 Kessil Lamps with Reaction Set-up.

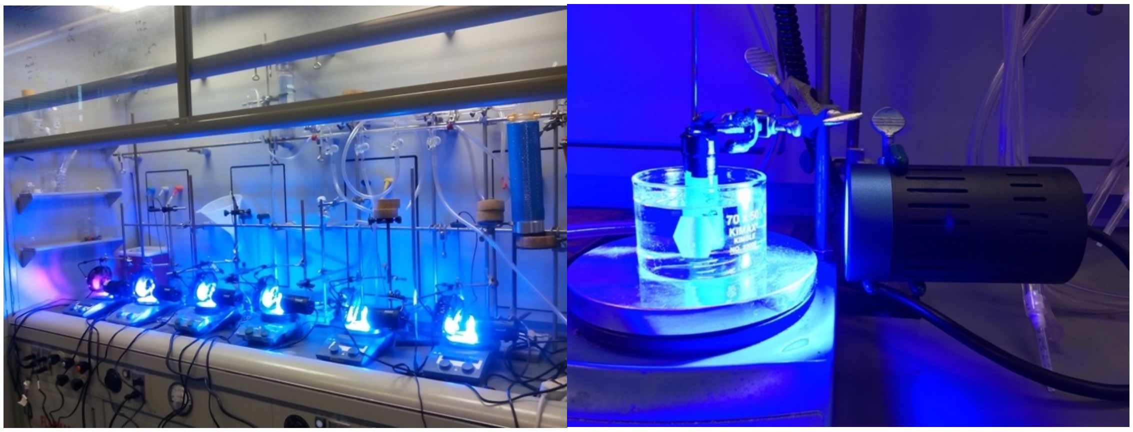
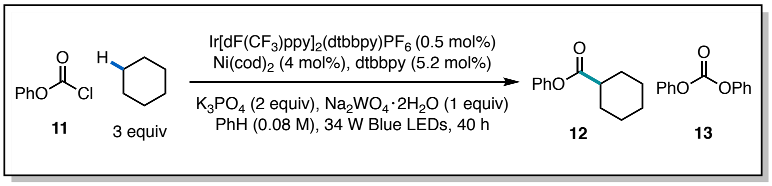


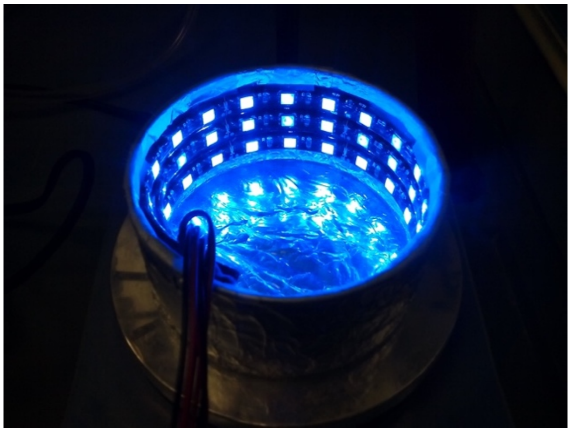
Table S10. Examination of temperature for the esterification of cyclohexane. Used Reaction set-up from Figure S1b.



Entry	Temperature (°C)^{a,c}	Conversion of 11 (%)^{b}	Yield of 12 (%)^{b}	Yield of 13 (%)^{b}
1	30	100	55	32
2	34	100	50	12
3	36	100	54	29
4	38	100	50	25
5	40	100	40	18
6	45	97	34	19

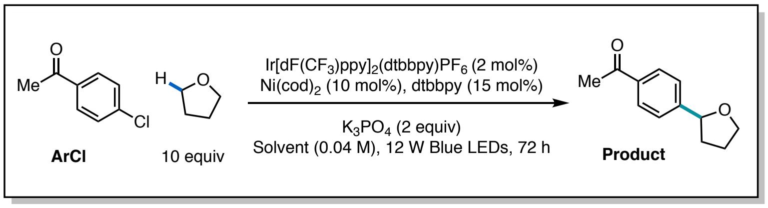
[a] Reactions were carried out on 0.48 mmol scale in an oil bath.
[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.
[c] Average of temperatures taken at the beginning and end of the reaction.

Table S10 Blue LED Array Reaction Set-up:



F. Solvent Optimization. In examining solvent systems two central hypotheses guided our screening: first, the idea that the solvent would have to be inert to chlorine radical relative to the desired hydrocarbon substrate that was to be functionalized, and second that the solvent would have to allow for semi-solubility of the catalysts in solution to afford catalysis. Early studies demonstrated that only poor yields could be achieved with typical polar solvents used in metallaphotoredox catalysis such as acetonitrile, DMF, DMA, and DMSO in the study of the arylation of ethers. Aside from benzene, which had previously been reported to be effective in photoelimination studies, only 4-*tert*-butyl-benzene and 4-trifluorotoluene gave detectable product. From Table S12 it is evident that benzene is the best inert solvent, potentially due to its ability to stabilize chlorine radical. In all cases conversion of the chloroformate was high however only benzene and benzene-*d*6 were able to afford good reactivity. Chlorocyclohexane (ClCy) afforded trace product but most other solvents yielded a larger amount of diphenyl carbonate than was typically observed with benzene. Spiking in a more polar co-solvent (Table S12, entries 7 and 8) to benzene did not lead to improvement in yield.

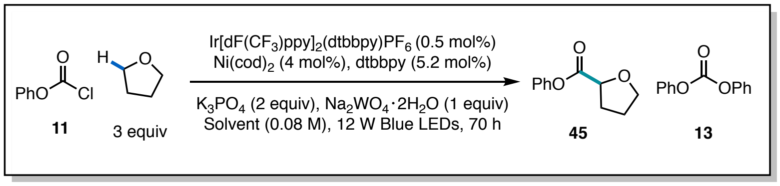
Table S11. Examination of alternative solvents to benzene in the arylation of tetrahydrofuran.



Entry	Solvent[a]	Yield of Product (%)[b]
1	4-*tBu*-benzene	15
2	DMSO	0
3	DMF	0
4	DMA	0
5	MeCN	0
6	PhCN	0
7	DCE	0
8	DCM	0
6	EtOAc	0
7	MeOH	0
8	1-Fluoronaphthalene	0
9	1-Fluorobenzene	0
10	PhCF$_3$	3
11	Ethyl benzene	0
12	Methyl cyclohexane	0

[a] Reactions were carried out on 0.08 mmol scale.
[b] Yields were determined by ^{1}H NMR analysis using 1-fluoronaphthalene as an external standard.

Table S12. Examination of solvents in the esterification of tetrahydrofuran.

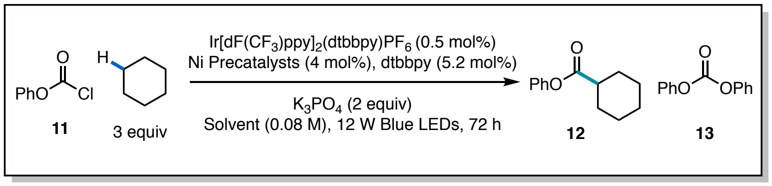


Entry	Solvent[a]	Conversion of 11 (%)[b]	Yield of 45 (%)[b]	Yield of 13 (%)[b]
1	PhH	100	43	23
2	PhH[c]	99	19	72
3	C_6D_6	95	21	21
4	CyH	56	0	39
5	ClCy	60	3	35
6	$PhCF_3$	59	0	29
7	PhH[d]	95	33	46
8	PhH[e]	88	11	75

[a] Reactions were carried out on 0.24 mmol scale.
[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.
[c] Used anhydrous benzene as purchased without storing over sieves.
[d] Added 50 mol% ClCy. [e] Added 50 mol% $PhCF_3$.

G. Catalyst Optimization. Extensive screening confirmed (dtbbpy)Ni(0) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ as uniquely effective catalysts for this C–H transformation. The photocatalyst in particular was challenging to replace with a comparable derivative. While $Ni(cod)_2$ was ultimately employed in these reactions, a variety of Ni(II) precursors were moderately effective for this reaction. Catalyst loadings were kept low in the reaction to eliminate the likelihood of catalyst-promoted deleterious side pathways.

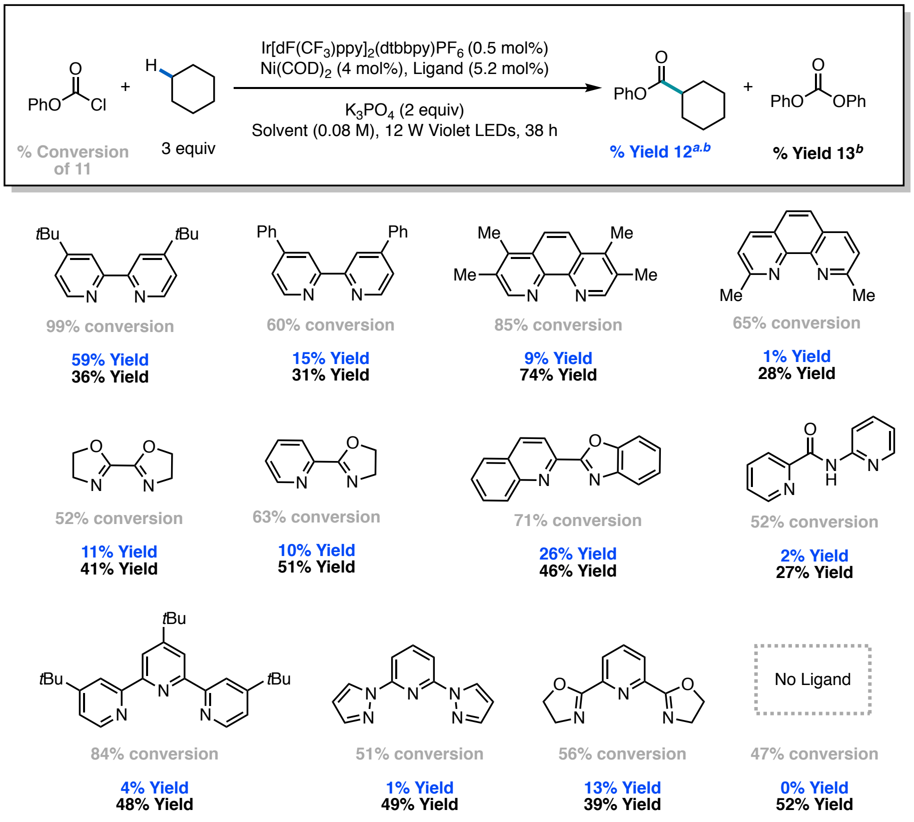
Table S13. Examination of Nickel precursors in the reaction of cyclohexane with phenyl chloroformate.



Entry	Precatalyst[a]	Conversion of 11 (%)[b]	Yield of 12 (%)[b]	Yield of 13 (%)[b]
1	$Ni(COD)_2$	100	60	30
2	$NiCl_2$·glyme	74	22	24
3	$NiBr_2$·diglyme	78	44	35
4	Ni(DMAP)[c]	99	49	26

[a] Reactions were carried out on 0.08 mmol scale prestirring Ni precursors with dtbbpy for 30 min.
[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.
[c] Ni(DMAP) stands for Bis[1-(N,N-dimethylamino)-2-propanolato]Ni(II).

Table S14. Examination of Nickel catalysts in the reaction of cyclohexane with phenyl chloroformate.



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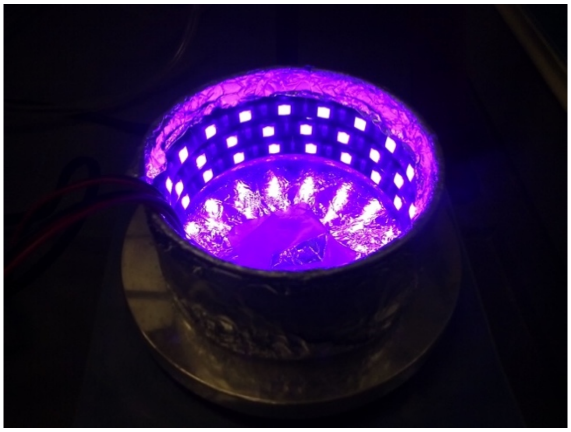
[a] Reactions were carried out on 0.24 mmol scale pre-stirring $Ni(COD)_2$ with the ligands for 30 minutes.

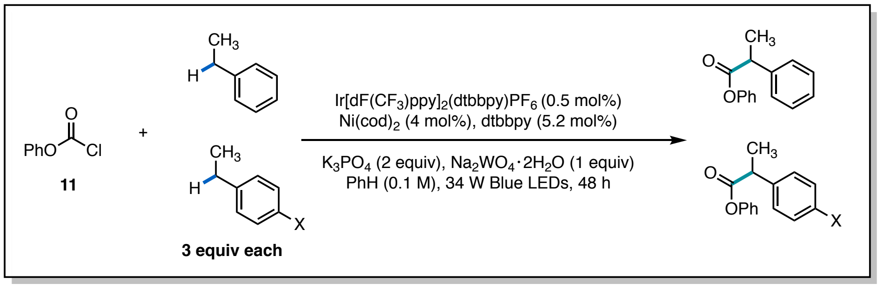
[b] Yields were determined by GC analysis using 4-fluoroanisole as an external standard.

Table S14 Violet LED Array Reaction Set-up:



H. Hammett Studies. Hammett studies were conducted as competition experiments between *para*-substituted ethyl benzene derivatives (R= CN, CF_3, F, Ph, OPh as reported in Table S15) and ethyl benzene (R=H), in which the difference in rates of the reactions were reported as a series of ratios between benzylic ester products. The logarithm of the selectivity was plotted against σ^+ values (Hammett-Brown constants) which have been reported to correlate better than σ values when considering benzylic radicals.[4] As stated in the main manuscript, electron-rich substrates which react much faster with the electron-deficient chlorine radical, have better selectivity over ethyl benzene in the competition experiments. Conversely, electron-deficient substrates which are poorly matched with the chlorine radical and compete poorly with ethyl benzene, giving a poor selectivity. *Note: Ethyl benzene and its derivatives can be functionalized in both the benzylic and primary positions, however the yield of the methyl esterification in all cases was <5% and within error of the reaction. Therefore only the benzylic ester products were used to construct free energy correlations.*

Table S15. Selectivity of ethyl benzene derivatives in competition with ethyl benzene.



X	X/H[a,b]	X/H[a,b]	average X/H[a,b]	log(X/H)
CN	0.52	0.54	0.53	-0.28
CF_3[c]	0.63	0.66	0.64	-0.20
F	1.17	0.86	1.01	0.01
Ph	1.42	1.59	1.50	0.18
OPh	2.16	2.07	2.13	0.33

[a] Reactions were carried out on 0.6 mmol scale.
[b] Ratios of yields were determined by GC analysis using 4-fluoroanisole as an external standard.
[c] Ratios of yields were determined by 19F NMR analysis using 4-fluoroanisole as an external standard.

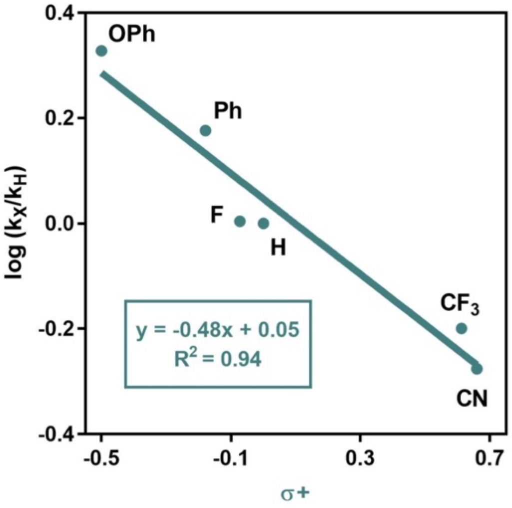


Figure S9. Hammett correlation using Hammett-Brown (σ_p^+) parameters. Hammett-Brown constant for -OPh was taken as the reported calculated value.[5]

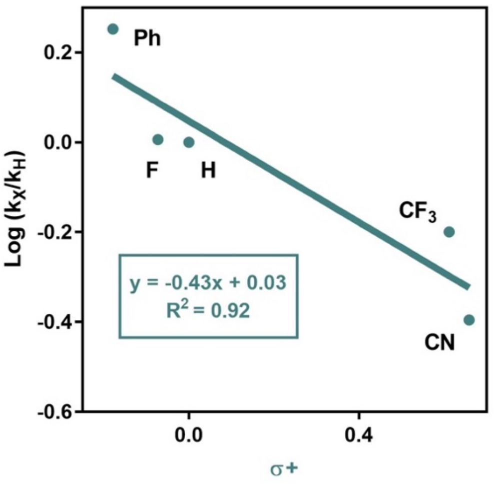


Figure S10 Hammett correlations with omission of -OPh results in a similar linear fit.

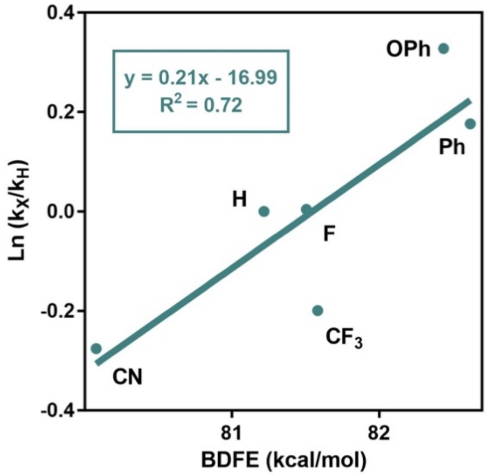
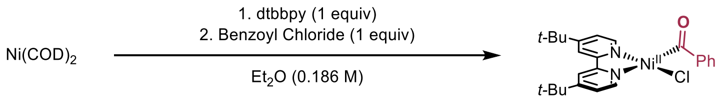


Figure S11. Hammett correlation using calculated bond dissociation free energies (BDFE) rather than σ_p^+.

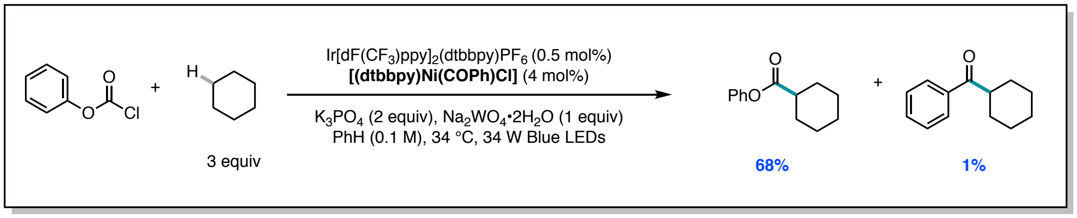
IV. Studies of (dtbbpy)Ni(COPh)Cl

A. Synthesis of (dtbbpy)Ni(COPh)Cl.



[(dtbbpy)Ni(COPh)Cl]. was prepared according to a previously reported literature procedure on a 1.0 mmol scale.[20] After filtration, the red solid was triturated with a 20% ether pentane solution (5 mL). The red powder was collected on a frit, rinsed with pentane, and dried under vacuum overnight in a N_2 filled glovebox (113 mg, 0.242 mmol, 24% yield). The title compound was isolated in an estimated 93% purity with free cyclooctadiene as an impurity.

1H NMR (500 MHz, CD_2Cl_2): δ 8.87 (d, J = 5.7 Hz, 1H), 8.58 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 10.0 Hz, 2H), 7.74 (d, J = 6.0 Hz, 1H), 7.52 (d, J = 5.9 Hz, 1H), 7.49 – 7.40 (m, 3H), 7.21 (d, J = 6.0 Hz, 1H), 1.41 (s, 9H), 1.34 (s, 9H).
13C NMR (126 MHz, CD_2Cl_2): δ 248.85, 164.36, 163.53, 156.06, 152.46, 150.89, 149.30, 131.81, 129.37, 128.51, 124.79, 123.87, 118.49, 117.33, 35.94, 30.63, 30.35.



[(dtbbpy)Ni(COPh)Cl] is catalytically active under our reaction conditions.

B. Spectroscopic and Emission Quenching Experiments.

Absorption and Emission experiments were conducted in line with our previous publication on the arylation of ethereal C–H bonds.[1] An excitation wavelength of 405 nm and an emission wavelength of 472 nm were used for monitoring quenching of the iridium photocatalyst (Excitation: 405 nm, $\varepsilon = 2.21 \times 10^3$ M^{-1} cm^{-1}; Emission: 472 nm, $\varepsilon = 9.23 \times 10^2$ M^{-1} cm^{-1}). Primary and secondary inner filter effects were corrected by linear absorption measurements.[1,19] All reagents were prepared in stock solutions inside a nitrogen filled glove box. Reagents were diluted in benzene (3 mL) and sealed in a screw-top 1.0 cm quartz cuvette. A blank composed of benzene was used in absorbance measurements. Samples for quenching experiment were dispensed from a stock solution of Ir[dF(CF_3)ppy]$_2$ (dtbbpy)PF_6 (3.56 mM in benzene, amount dispensed: 112 μL, 0.40 μmol, 1.34×10^{-4} M after dilution) followed by addition of quencher that was also prepared from a stock solution (6.41 mM in benzene). Absorption spectra were collected on an Agilent Technologies Cary 60 UV-Vis Spectrophotometer. Emission quenching data were collected on an Agilent Cary Eclipse Fluorescence Spectrophotometer with excitation and emissions slit widths of 2.5 nm.

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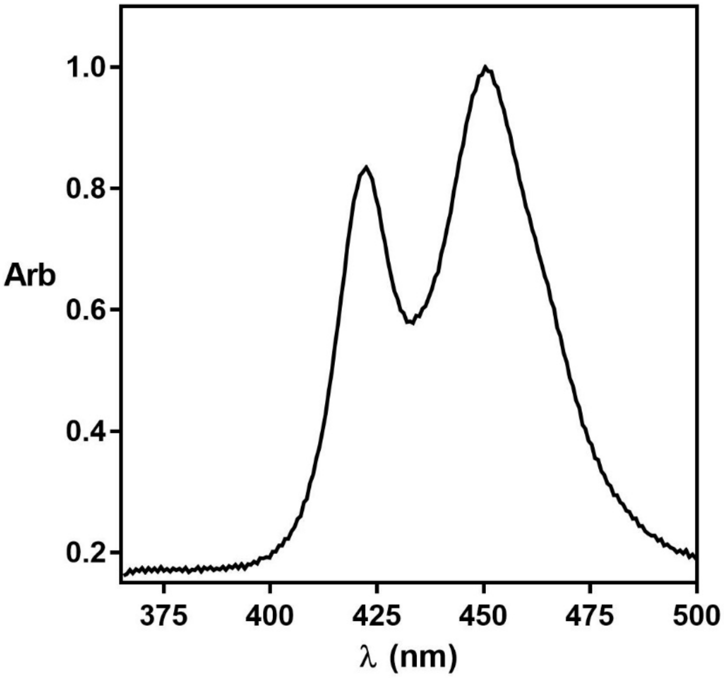


Figure S12. Normalized emission spectrum for 34W Blue LED lamp. Kessil lamp emission maximum at λ_{max} = 450 and 422 nm.

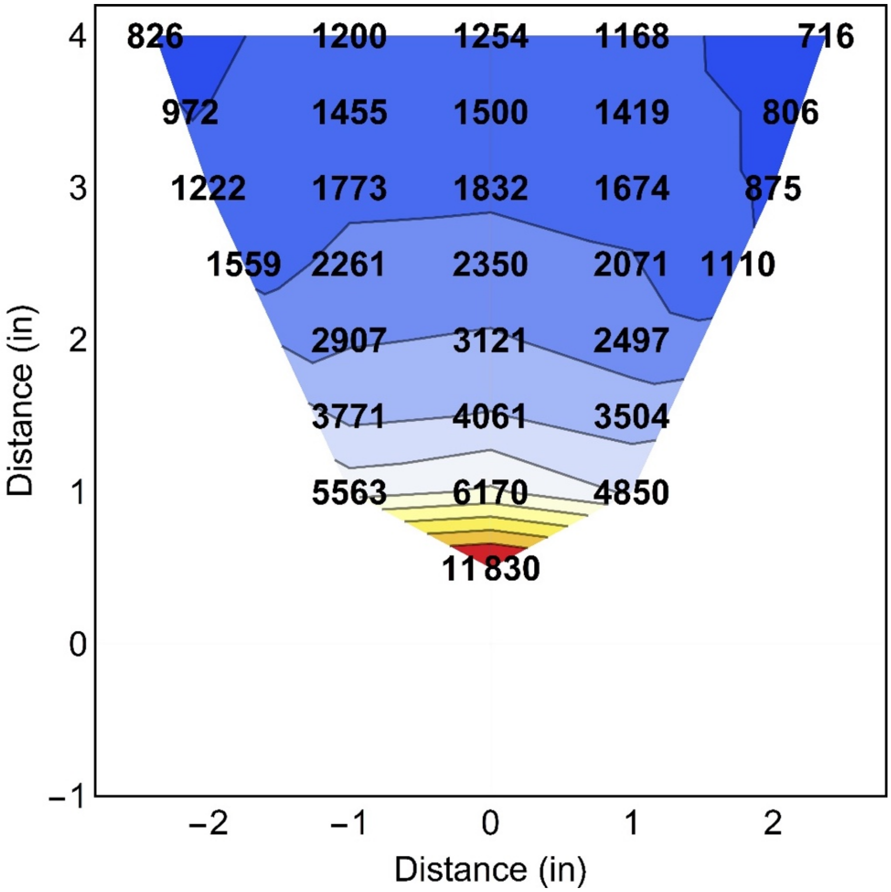


Figure S13. Photon flux at various distances from a kessil lamp. Note units are μEinsteins $s^{-1}m^{-2}$.

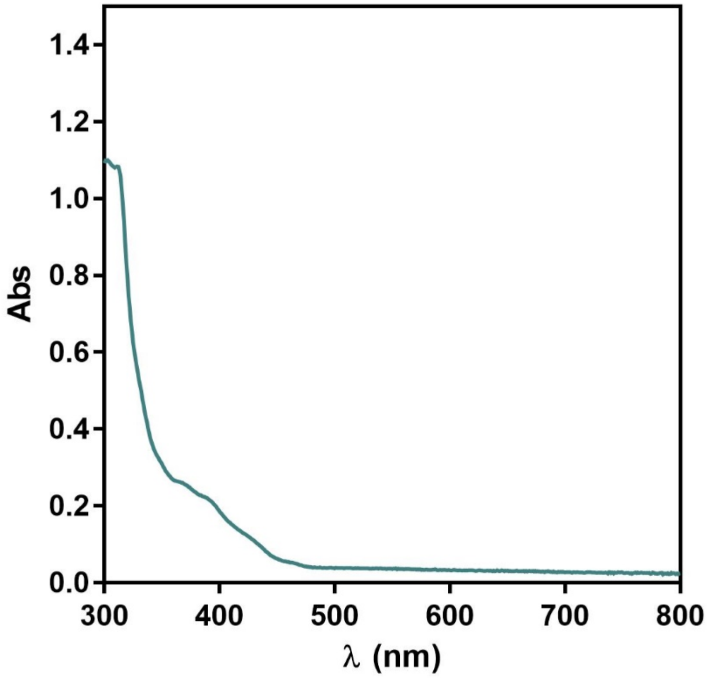


Figure S14. Electronic absorption spectrum of Ir[dF(CF$_3$)ppy]$_2$ (dtbbpy)PF$_6$ (1x10^{-4} M) in benzene.

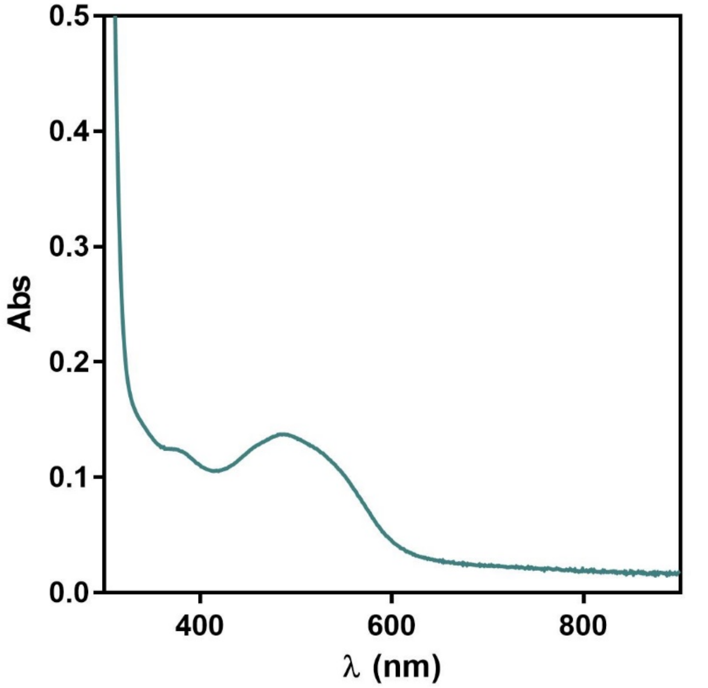


Figure S15. Electronic absorption spectrum of (dtbbpy)Ni(COPh)Cl (3.34x10^{-5} M) in benzene. The visible range shows an absorption band centered at 487 nm. For inner filter effects, optical densities were obtained for quenching experiments (Excitation: 405 nm, ε = 2.07x10^3 M^{-1} cm^{-1}; Emission: 472 nm, ε = 2.65x10^3 M^{-1} cm^{-1}).

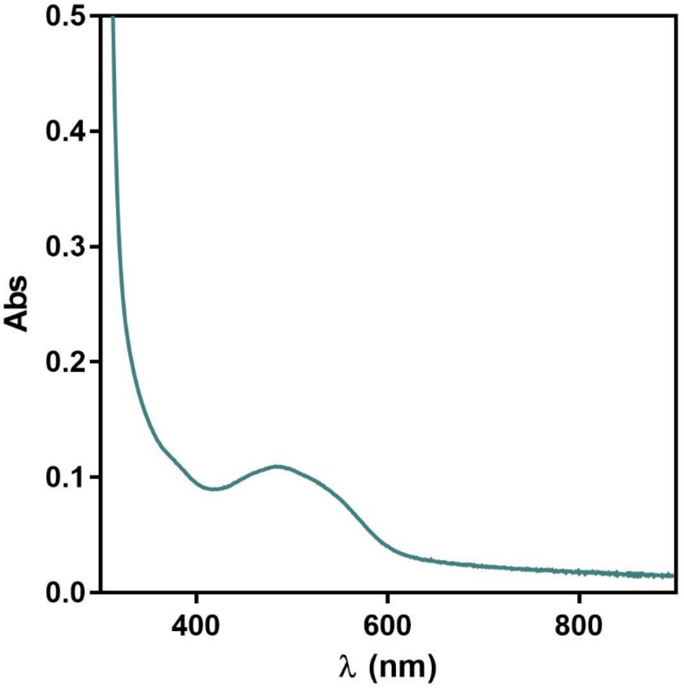


Figure S16. Electronic absorption spectrum of a solution of Ni(dtbbpy)(cod) (3.34×10^{-5} M) and phenyl chloroformate (3.34×10^{-5} M). Note Ni(cod)$_2$ and dtbbpy were allowed to stir for 20 min before addition of phenyl chloroformate in benzene. The visible range shows an absorption band centered at 482 nm.

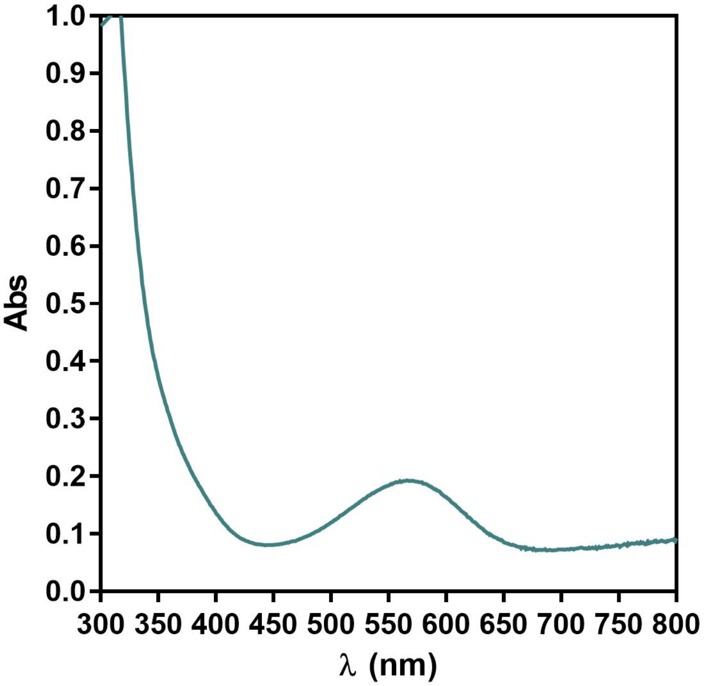


Figure S17. Electronic absorption spectrum of a 20 minute prestirred solution of Ni(cod)$_2$ (3.34×10^{-5} M) and dtbbpy (8.68×10^{-5} M) in benzene. The visible range shows an absorption band centered at 565 nm.

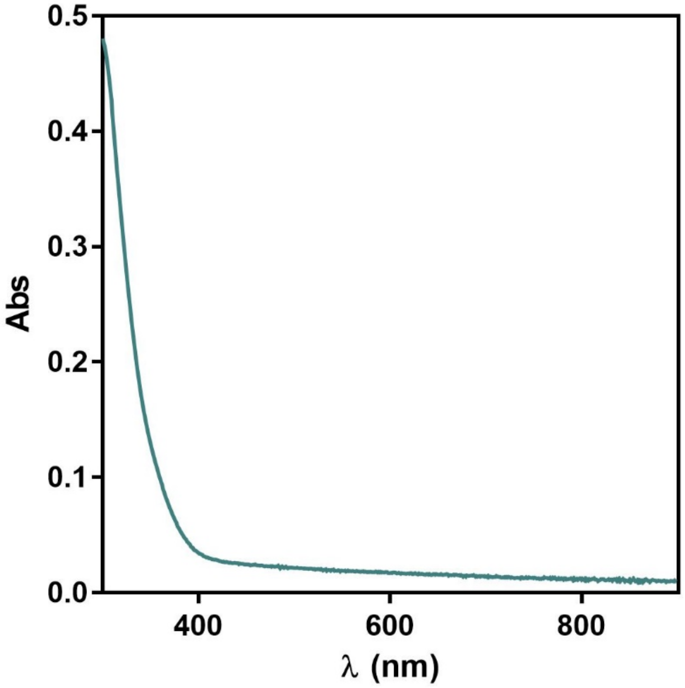


Figure S18. Electronic absorption spectrum of Ni(cod)$_2$ (3.34x10^{-5} M) in benzene.

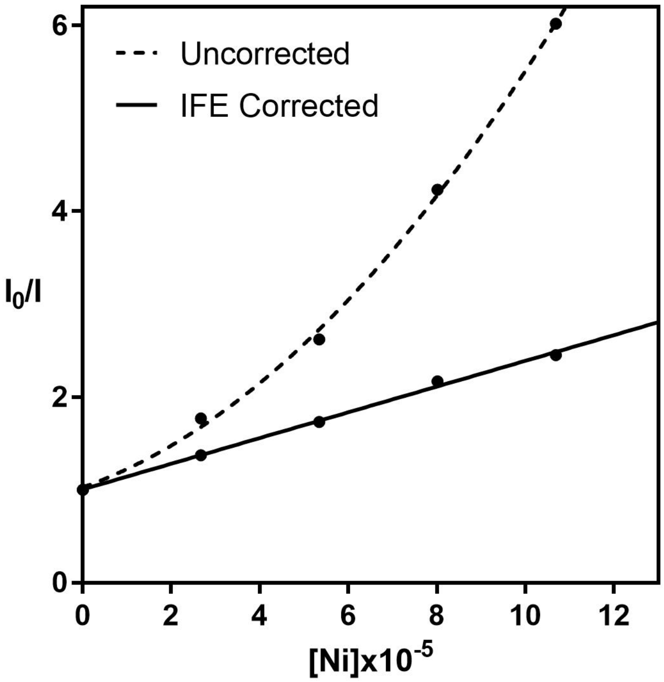
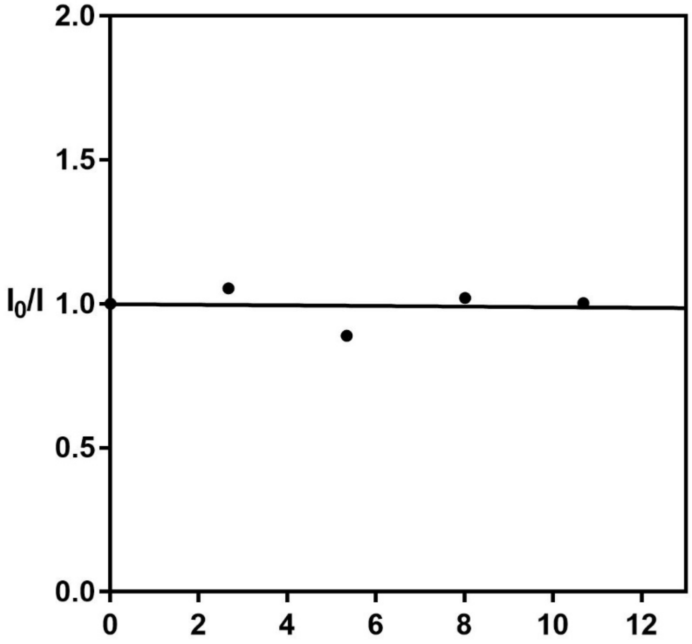


Figure S19. Characteristic plot of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ emission quenching by (dtbbpy)Ni(COPh)Cl complex in benzene for one set of triplicates with and without inner filter effect corrections.

[Ni] x 10^{-5} M	$I_{uncorrected}$	$OD_{405\ nm}$	$OD_{472\ nm}$
0	169.48	0	0
2.67	95.83	0.10	0.12
5.34	64.68	0.15	0.21
8.02	40.06	0.25	0.33
10.69	28.16	0.34	0.44
0	159.17	0	0
2.67	94.00	0.07	0.10
5.34	59.98	0.16	0.22
8.02	29.80	0.24	0.33
10.69	32.20	0.27	0.40
0	159.04	0	0
2.67	96.64	0.13	0.14
5.34	61.35	0.15	0.21
8.02	43.94	0.24	0.32
10.69	25.44	0.42	0.52

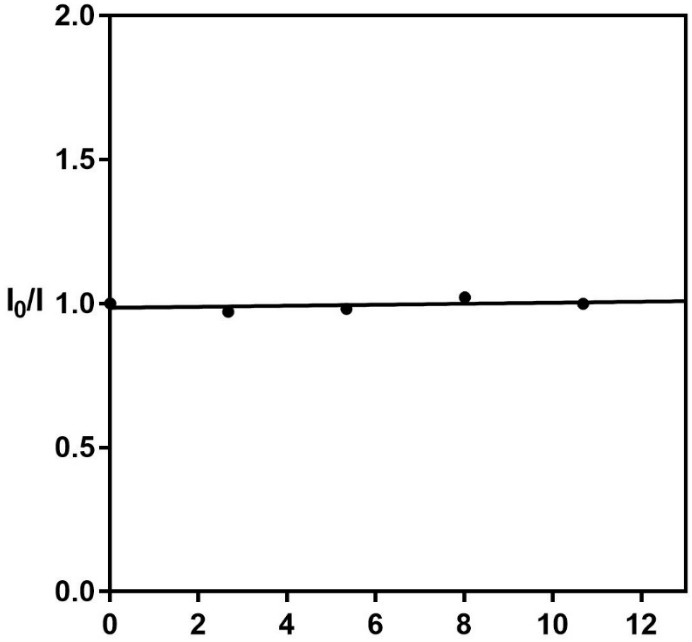
	y-int$_{avg}$	SE$_{y\text{-}int}$	K_{avg} (M^{-1})	SE$_K$ (M^{-1})
Stern-Volmer	1.016	0.013	1.23x10^{4}	8.40x10^{2}

Figure S20. Data of Ir[dF(CF$_3$)ppy]$_2$ (dtbbpy)PF$_6$ emission quenching by (dtbbpy)Ni(COPh)Cl complex in benzene.



[PhCOCl] x 10^{-5} M	I
0	156.64
2.67	165.13
5.34	169.29
8.02	159.84
10.69	157.09

Figure S21. Plot and data of Ir[dF(CF$_3$)ppy]$_2$ (dtbbpy)PF$_6$ emission quenching by benzoyl chloride in benzene.



[PhOCOCl] x 10^{-5} M	I
0	156.99
2.67	161.50
5.34	159.91
8.02	153.71
10.69	157.16

Figure S22. Plot and data of Ir[dF(CF_3)ppy]$_2$ (dtbbpy)PF_6 emission quenching by phenyl chloroformate in benzene.

C. TD-DFT of (dtbbpy)Ni(COPh)Cl and (dtbbpy)Ni(COOPh)Cl. Calculations were performed on Gaussian 16 software suite, revision B.01.[18b] Calculations were carried out using B3LYP TZVP based on gas phase calculations for optimized nickel structures. All frequency calculations gave no imaginary frequencies. Excited states were computed from optimized nickel structures and determined for the first hundred states.

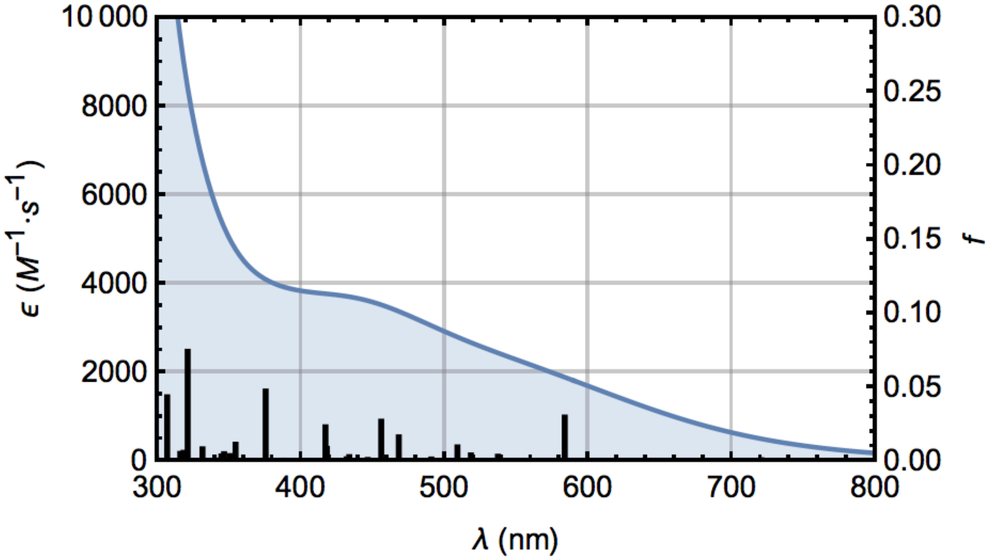


Figure S23. TD-DFT of (dtbbpy)Ni^{II}(COPh)Cl.

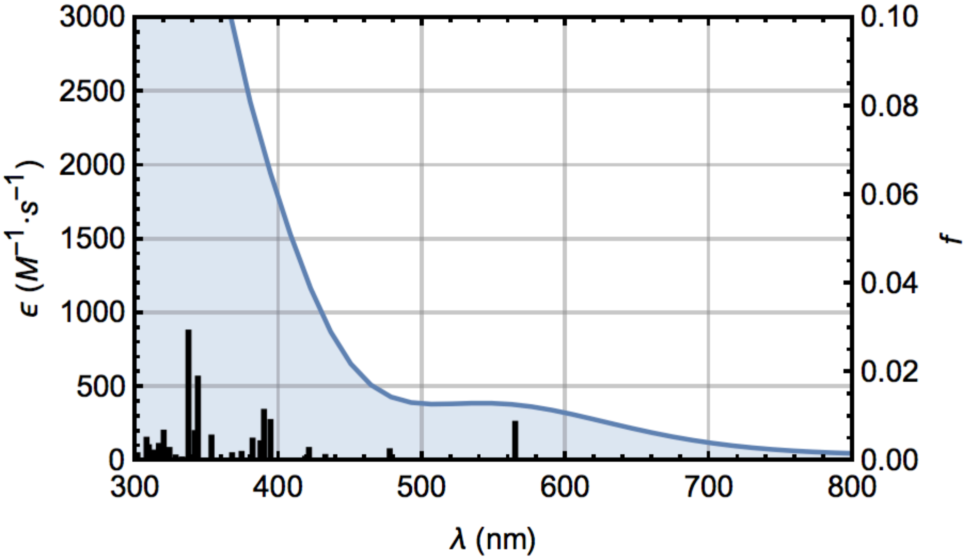


Figure S24. TD-DFT of (dtbbpy)Ni^{III}(COPh)Cl.

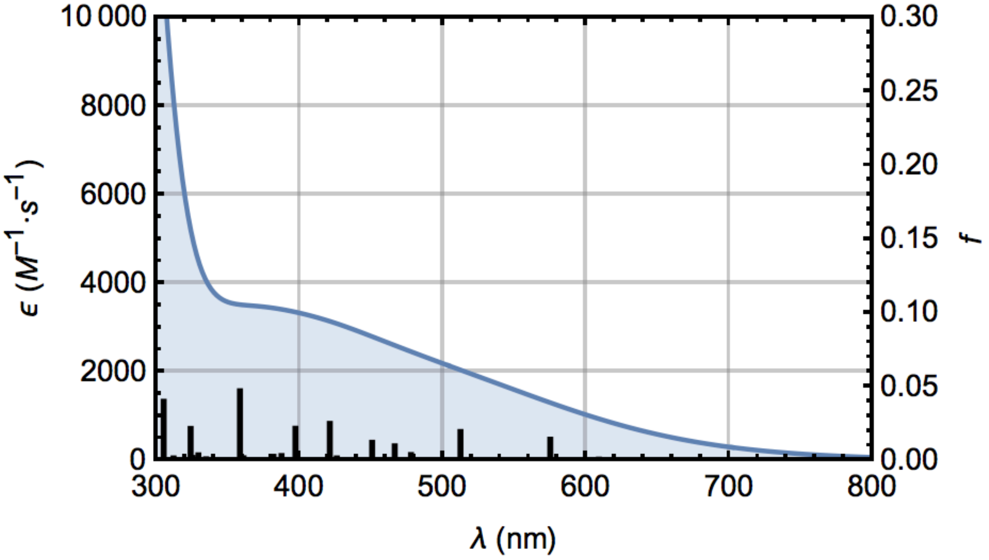


Figure S25. TD-DFT of (dtbbpy)Ni^{II}(COOPh)Cl.

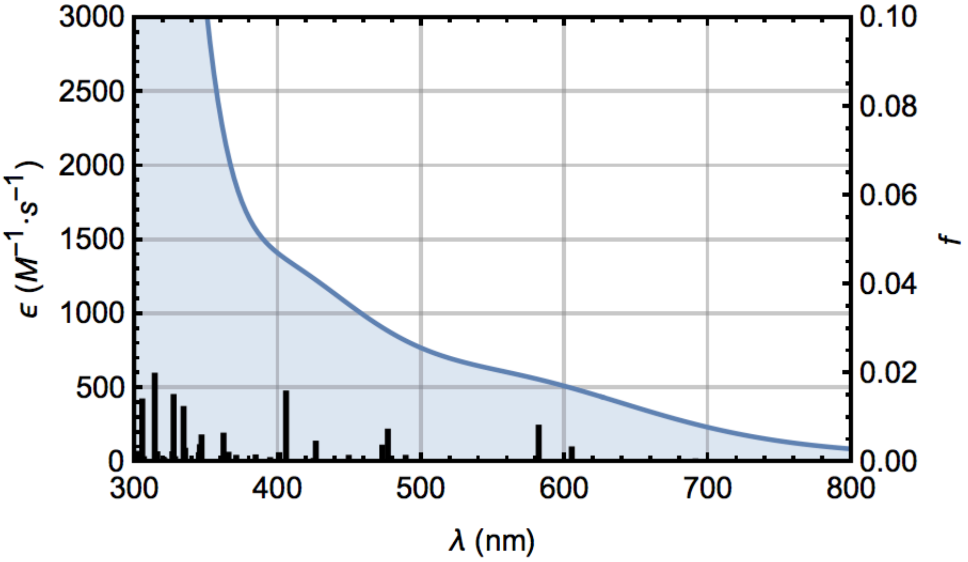


Figure S26. TD-DFT of (dtbbpy)Ni^{III}(COOPh)Cl.

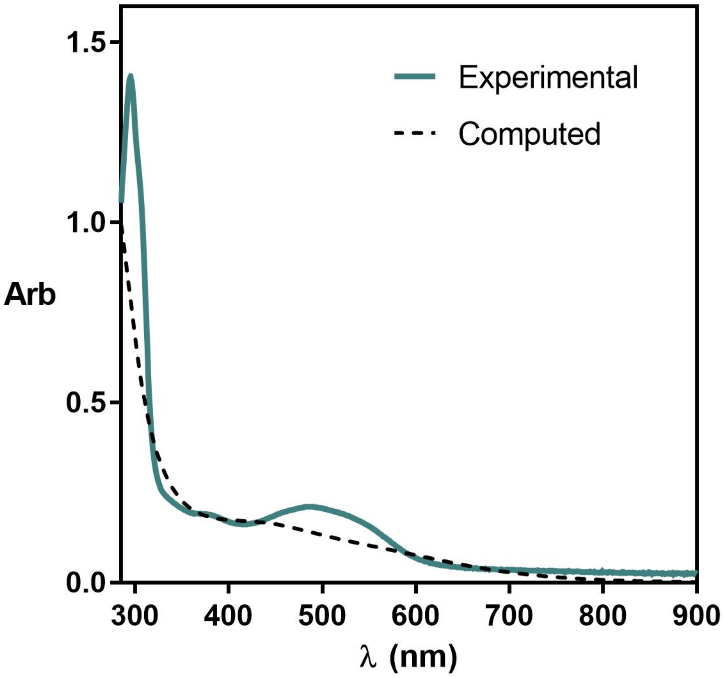


Figure S27. Overlaid computed and experimental absorption spectrum of (dtbbpy)Ni^{II}(COPh)Cl. Both sets of data normalized to 284 nm.

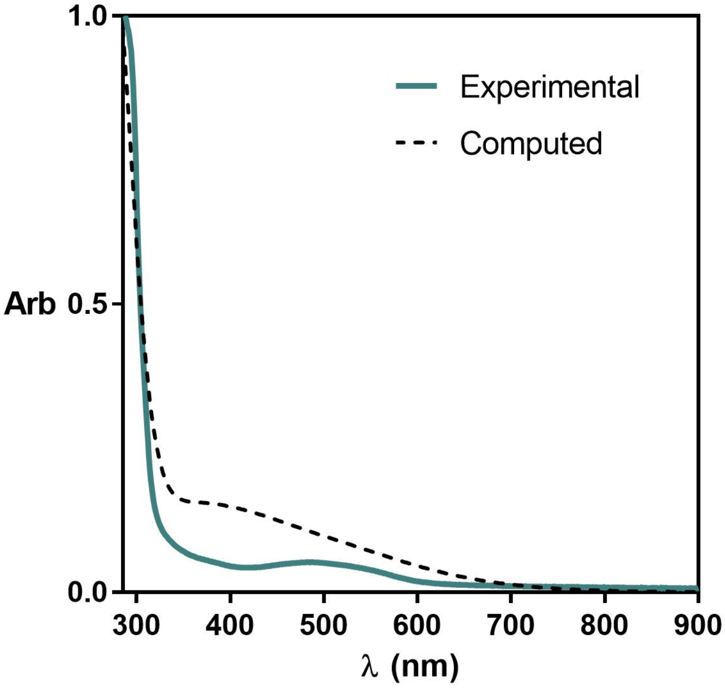


Figure S28. Overlaid computed and experimental absorption spectrum of (dtbbpy)Ni^{II}(COOPh)Cl. Both sets of data normalized to 284 nm.

D. Cyclic Voltammogram of (dtbbpy)Ni(COPh)Cl. Cyclic voltammetry was conducted on a CH Instruments Electrochemical Analyzer (CH1600E). In a nitrogen filled glove box, a 0.5 mM solution of (dtbbpy)Ni(COPh)Cl with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte in MeCN was prepared. The solution was removed from the glove box and a cyclic voltammogram was collected under a nitrogen atmosphere using a glassy carbon working electrode, a platinum mesh counder electrode, and a saturated calomel reference electrode.

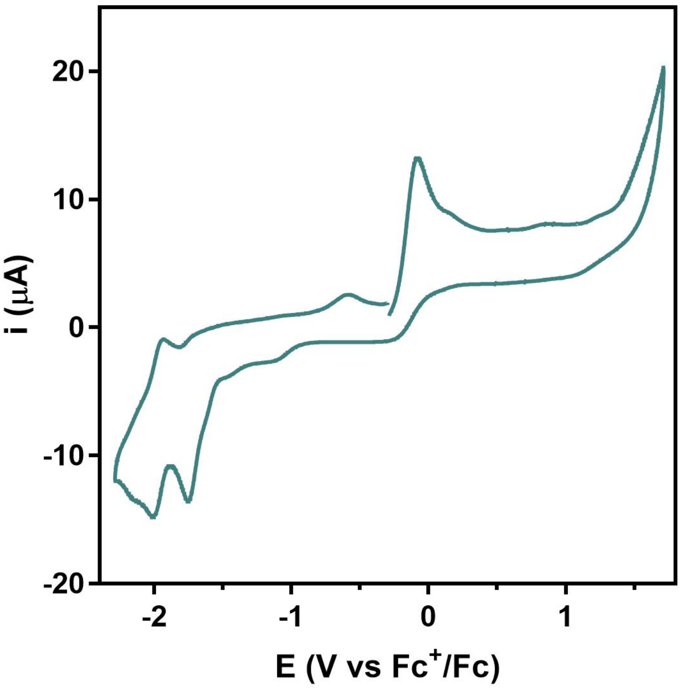


Figure S29. Cyclic Voltammogram of (dtbbpy)Ni(COPh)Cl (Scan rate 0.1 Vs^{-1}).

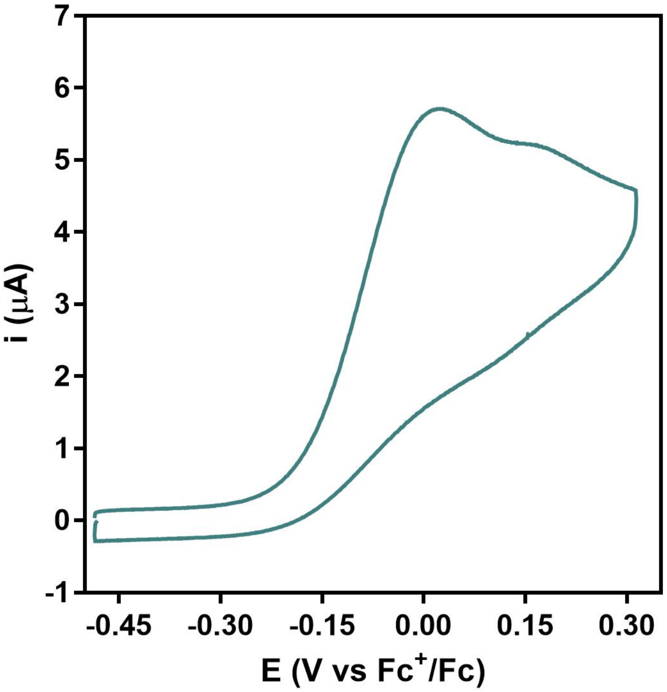
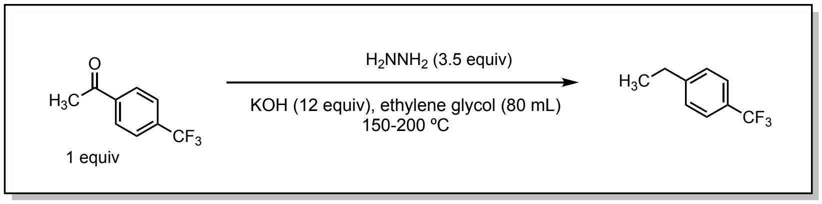


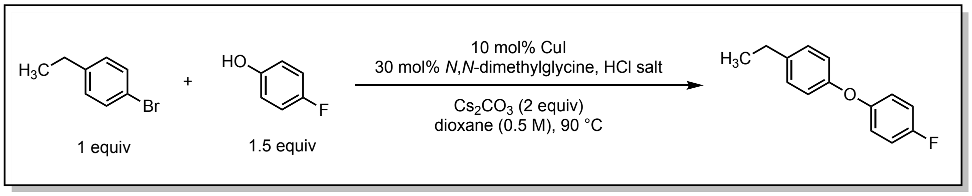
Figure S30. Cyclic Voltammogram of (dtbbpy)Ni(COPh)Cl (Scan rate 0.1 Vs^{-1}) shows an irreversible oxidation at E_p = 0.023 V vs Fc/Fc^+, when ferrocene was used as an external reference (E_p = 0.403 V vs SCE, conversion was conducted according to Pavlishchuk, V. V.; Addison, A. W. *Inorganica Chim. Acta.* **2000**, *298*, 97.).

V. Substrate Preparation

Substrates are characterized as S# where # is the number of the ester product derived from the hydrocarbon structure depicted below. ***S53*** *is presented as an additional substrate that was not presented in the main manuscript that could confirm characterization of* ***49-α and 50-α.***

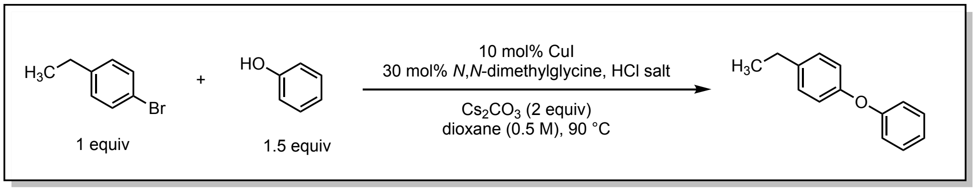


1-Ethyl-4-(trifluoromethyl)benzene (S31) was prepared according to a literature procedure for Wolff-Kishner reduction of a ketone.[6a] In a 3-neck oven-dried round bottom flask was placed 4-trifluoromethylacetophenone (3.4 g, 0.018 mol), anhydrous hydrazine (2 mL, 0.064 mol, 3.5 equiv), and 80 mL of diethylene glycol which was heated to 150 °C with KOH (12 g, 0.22 mol, 12 equiv) that had been ground with a mortar and pestle. After 1 h the reaction was further heated to 200 °C and left for 5 h. Once completed the solution was cooled and 20 mL of water was added. The mixture was washed with dichloromethane (4 x 20 mL). The organic layers were washed with a 10% HCl solution followed by aqueous washes (2 x 20 mL), and dried over MgSO$_4$. Solvent was evaporated *in vacuo* and purified via automated column chromatography (eluting with 100% hexanes) to isolate a clear oil (1.88 g, 60% yield). ^{1}H NMR data were consistent with reported literature values.[6b] This is the first example where^{19}F NMR data is reported.
1H NMR (500 MHz, CDCl$_3$): δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H).
13C NMR (126 MHz, CDCl$_3$): δ 148.41, 128.00, 125.37 (q, *J* = 3.8 Hz), 128.13 – 123.19 (m), 77.41, 28.91, 15.46.
HRMS: (EI-TOF) calculated for $C_9H_9F_3^+$ ([M]$^+$): 174.0651, found: 174.0657.
19F NMR (282 MHz, CDCl$_3$): δ -62.27.

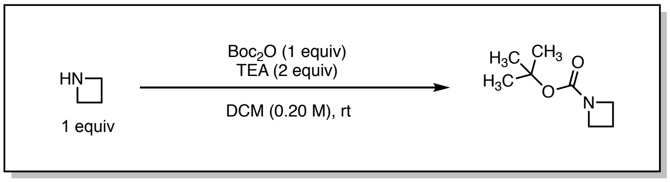


1-Ethyl-4-(4-fluorophenoxy)benzene (S34) was prepared according to literature procedure[7] on 20 mmol scale. To an oven-dried round bottom flask was added 4-bromoethylbenzene (2.7 mL, 20 mmol) and 4-fluorophenol (3.4 g, 30 mmol, 1.5 equiv), using 10 mol% CuI (381 mg, 2.0 mmol), 30 mol% *N*, *N*-dimethylglycine, HCl salt (837 mg, 6 mmol), and cesium carbonate (14 g, 40 mmol, 2 equiv) in dioxane (0.5 M). The reaction was stirred at 90 °C for 72 hours and the mixture was diluted with 20 mL of ethyl acetate and 50 mL of water. The aqueous layer was washed with ethyl acetate (3 x 20 mL). The combined organic layers were washed (2 x 30 mL) with brine and dried over sodium sulfate, filtered, and concentrated *in vacuo* to give an orange liquid. This liquid was evaporated over silica *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: pentane; 0% 6 CV, 0-1% 15 CV) to isolate a clear oil (2.6 g, 62% yield).
1H NMR (500 MHz, CDCl$_3$): δ 7.16 (d, *J* = 6.6 Hz, 2H), 7.04 – 6.87 (m, 6H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H).

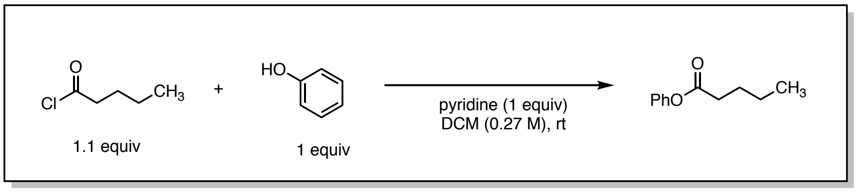
13C NMR (126 MHz, $CDCl_3$): δ 158.73 (d, *J* = 241.1 Hz),155.52, 153.55, 139.36, 129.21, 120.19 *(d, J = 8.2 Hz),* 118.58, 116.31 (d*, J = 23.3* Hz*),* 28.27, 15.90.
19F NMR (282 MHz, $CDCl_3$): δ -120.74.
HRMS: (EI-TOF) calculated for $C_{14}H_{13}FO^+$ ($[M+H]^+$): 216.0945, found: 216.0939.



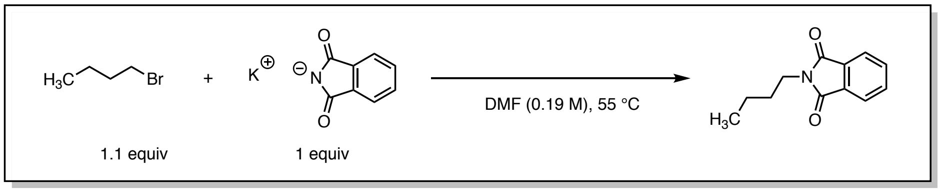
1-Ethyl-4-phenoxybenzene (S35) was prepared according to literature procedure[7] on 20 mmol scale. To an oven-dried round bottom flask was added 4-bromoethylbenzene (2.7 mL, 20 mmol) and phenol (2.8 g, 30 mmol, 1.5 equiv), using 10 mol% CuI (381 mg, 2.0 mmol), 30 mol% *N*, *N*-dimethylglycine, HCl salt (837 mg, 6 mmol), and cesium carbonate (14 g, 40 mmol, 2 equiv) in dioxane (0.5 M). The reaction was stirred at 90 °C for 72 hours and the mixture was diluted with 20 mL of ethyl acetate and 50 mL of water. The aqueous layer was washed with ethyl acetate (3 x 20 mL). The combined organic layers were washed (2 x 30 mL) with brine and dried over sodium sulfate, filtered, and concentrated *in vacuo* to give an orange liquid. This liquid was evaporated over silica *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: pentane; 0% 6 CV, 0-1% 15 CV) to isolate a clear oil (1.9 g, 50% yield). Spectral data were consistent with reported literature values.[7b]
1H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, J = 8.6, 7.4 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 7.01 – 6.89 (m, 4H), 2.64 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H)
13C NMR (101 MHz, $CDCl_3$): δ 157.78, 154.91, 139.32, 129.65, 129.03, 122.83, 119.08, 118.45, 28.17, 15.74.
HRMS: (EI-TOF) calculated for $C_{14}H_{14}O^+$ ($[M+H]^+$): 198.1039, found: 198.1041.



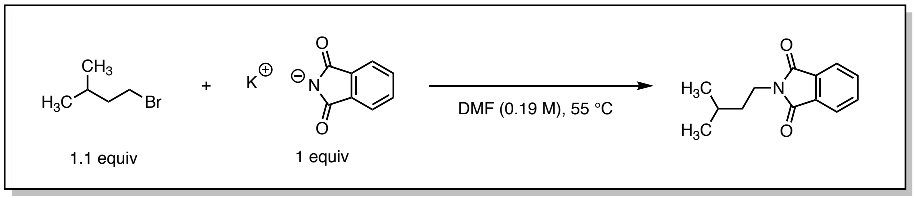
Tert-butyl azetidine-1-carboxylate (S40) was prepared according to a previously reported literature procedure on a 17.0 mmol scale. After workup the mixture was purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-15% 10 CV, 15% 10 CV) to isolate a colorless oil (1.9 g, 69% yield). Spectral data were consistent with reported literature values.[8]
1H NMR (500 MHz, $CDCl_3$): δ 3.94 – 3.87 (m, 4H), 2.14 (p, J = 7.6 Hz, 2H), 1.41 (s, 9H).
13C NMR (126 MHz, $CDCl_3$): δ 156.35, 79.07, 49.20, 28.40, 15.32.
HRMS: (ESI-TOF) calculated for $C_8H_{15}NNaO_2^+$ ($[M+Na]^+$): 180.0995, found: 180.0993



Phenyl pentanoate (S48) To an ice-cooled solution of phenol (1.3 g, 13.6 mmol), pyridine (1.0 mL, 12.4 mmol), and 50 mL of dry dichloromethane was added pentanoyl chloride dropwise (1.47 mL, 12.4 mmol). The mixture was diluted with water (10 mL) and washed with brine (2 x 25 mL). The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-2% 10 CV, 2% 4 CV) to isolate a clear oil (1.8 g, 80% yield). Spectral data were consistent with reported literature values.[9]
1H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.36 (m, 2H), 7.25 – 7.21 (m, 1H), 7.11 – 7.05 (m, 2H), 2.57 (t, J = 7.5 Hz, 2H), 1.76 (p, J = 7.6 Hz, 2H), 1.50 – 1.40 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).
13C NMR (126 MHz, $CDCl_3$): δ 172.35, 150.78, 129.41, 125.72, 121.60, 34.15, 27.03, 22.27, 13.76.



2-Butylisoindoline-1,3-dione (S49) was prepared according to a modified literature procedure.[10a] The reaction temperature and reaction stoichiometry were modified to 55 °C and 0.19 M. Butyl bromide (1.3 mL, 12 mmol) served as the electrophile and 1 equivalent of potassium phthalimide (2.0 g, 11 mmol) was employed. The crude material was purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-10% 10 CV, 10% 10 CV) to isolate a white solid (1.6 g, 75% yield). Spectral data were consistent with reported literature values.[10b]
1H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 5.4, 3.0 Hz, 2H), 7.70 (dd, J = 5.5, 3.0 Hz, 2H), 3.69 (t, J = 7.3 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.43 – 1.31 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H).
13C NMR (126 MHz, $CDCl_3$): δ 168.54, 133.87, 132.21, 123.18, 37.82, 30.67, 20.11, 13.68.
HRMS: (ESI-TOF) calculated for $C_{12}H_{14}NO_2^+$ ($[M+H]^+$): 204.1019, found: 204.1019.
FTIR (ATR cm^{-1}): 2951, 2932, 2871, 1770, 1708, 1692, 1679, 1611, 1463, 1435, 394, 1361, 1332, 1285, 1255, 1186, 1113, 1087, 1046, 967, 933, 863, 804, 792, 746, 713, 618, 603, 541, 528, 459, 437, 406.



2-(3-Methylbutyl)isoindoline-1,3-dione (S50) was prepared according to a modified literature procedure.[10a] The reaction temperature and reaction stoichiometry were modified to 55 °C and 0.19 M. Isopentyl bromide (1.4 mL, 12 mmol) served as the electrophile and 1 equivalent of potassium phthalimide (2.0 g, 11 mmol) was employed. The crude material was purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-10% 10 CV, 10% 10 CV) to isolate a pale yellow oil (3.5 g, 76% yield). Spectral data were consistent with reported literature values.[10c]
1H NMR (500 MHz, $CDCl_3$): δ 7.85 – 7.80 (m, 2H), 7.71 – 7.67 (m, 2H), 3.69 (td, J = 7.3, 1.4 Hz, 2H), 1.68 – 1.52 (m, 3H), 0.96 (dd, J = 6.4, 1.5 Hz, 6H).
13C NMR (126 MHz, $CDCl_3$): δ 168.48, 133.85, 132.23, 123.15, 37.33, 36.51, 25.92, 22.39.
HRMS: (ESI-TOF) calculated for $C_{13}H_{16}NO_2^+$ ($[M+H]^+$): 218.1176, found: 218.1176.
FTIR (ATR cm^{-1}): 2955, 1772, 1704, 1614, 1466, 1435, 1394, 1365, 1333, 1292, 1172, 1061, 973, 937, 906, 865, 792, 715, 616, 542, 528, 471.

2-Propylisoindoline-1,3-dione (S53) was prepared according to a modified literature procedure.[10a] Reaction temperature and reaction stoichiometry were modified to 55 °C and 0.19 M. Propyl bromide (1.0 mL, 12 mmol) served as the electrophile and 1 equivalent of potassium phthalimide (2.0 g, 11 mmol) was employed. The crude material was purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-10% 10 CV, 10% 10 CV) to isolate a white solid (898 mg, 44% yield). Spectral data were consistent with reported literature values.[10c]

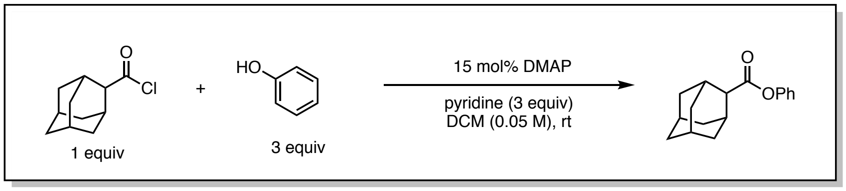
1H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, J = 5.4, 3.1 Hz, 2H), 7.71 (dd, J = 5.5, 3.0 Hz, 2H), 3.65 (t, J = 7.3 Hz, 2H), 1.75 – 1.66 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H).

13C NMR (126 MHz, $CDCl_3$): δ 168.56, 133.88, 132.19, 123.20, 39.64, 21.94, 11.36.

HRMS: (ESI-TOF) calculated for $C_{11}H_{12}NO_2^+$ ($[M+H]^+$): 190.0863, found: 190.0861.

VI. Authentic Product Preparation

Compounds are characterized as #-x where # represents the ester product communicated in the main manuscript and x refers to the classification of the regioisomer when applicable (α, β, γ, δ).



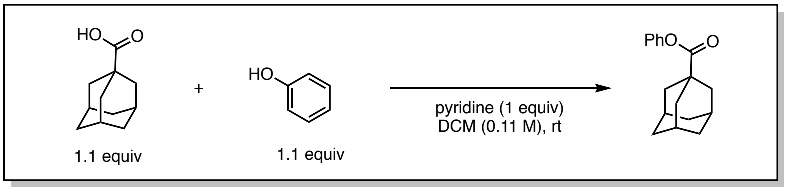
Phenyl (adamantane-2-carboxylate (23-α). To a flame-dried round bottom flask, dry dichloromethane (15 mL) was added, followed by 2-adamantanecarbonyl chloride (100 mg, 0.55 mmol) and two drops of DMF. Under a nitrogen environment a solution of phenol (78 mg, 0.83 mmol) and pyridine (67 μL, 0.83 mmol) in dichloromethane (4 mL) was added dropwise and the reaction was allowed to stir overnight. To ensure full conversion (80% product was observed after 24 h), DMAP (15 mg, 0.123 mmol) and a solution of phenol (78 mg, 0.83 mmol) and pyridine (67 μL, 0.83 mmol) in dichloromethane (2 mL) was added to the flask and stirred for an additional 3 hours. After completion, the reaction was diluted with water (5 mL) and washed with brine (2 x 15 mL). The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-3% 10 CV, 3% 4 CV) and affording a white solid (73 mg, 51% yield).

1H NMR (500 MHz, $CDCl_3$): δ 7.38 (t, J = 8.0 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 2.89 (s, 1H), 2.49 (s, 2H), 2.04 – 1.87 (m, 6H), 1.87 – 1.65 (m, 6H).

13C NMR (126 MHz, $CDCl_3$): δ 173.27, 150.99, 129.40, 125.60, 121.70, 49.67, 38.09, 37.34, 33.57, 29.66, 27.43, 27.42.

HRMS: (ESI-TOF) calculated for $C_{17}H_{21}O_2^+$ ($[M+H]^+$): 257.1536, found: 257.1537.

FTIR (ATR cm^{-1}): 2906, 2849, 1750, 1493, 1196, 1180, 1096, 1039, 1022, 975, 929, 815, 731, 688, 501.

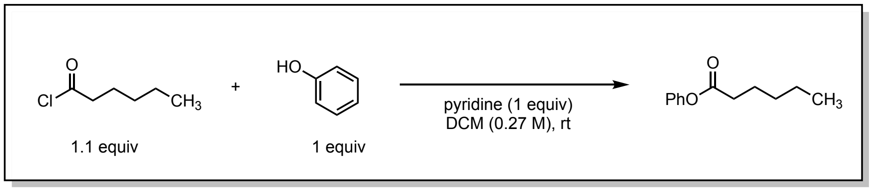


Phenyl adamantane-1-carboxylate (23-β). To a flame-dried round bottom flask 50 mL of dry dichloromethane was added, followed by phenol (573 mg, 6.1 mmol) and pyridine (0.45 mL, 5.5 mmol). The mixture was then cooled to 0 °C under nitrogen, followed by dropwise addition of 1-adamantanecarbonyl chloride (1.1 g, 5.5 mmol). The reaction was allowed to stir overnight. After completion the reaction was diluted with water (10 mL) and washed with brine (2 x 25 mL). The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-2% 10 CV, 2% 4 CV) to isolate the ester as a crystalline white solid (1.2 g, 86% yield). Spectral data were in accordance with the literature values[11]

1H NMR (500 MHz, $CDCl_3$): δ 7.37 (t, J = 7.8 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 7.9 Hz, 2H), 2.13 – 2.05 (m, 9H), 1.82 – 1.70 (m, 6H).

13C NMR (126 MHz, $CDCl_3$): δ 176.23, 151.11, 129.34, 125.53, 121.59, 41.01, 38.77, 36.48, 27.93.

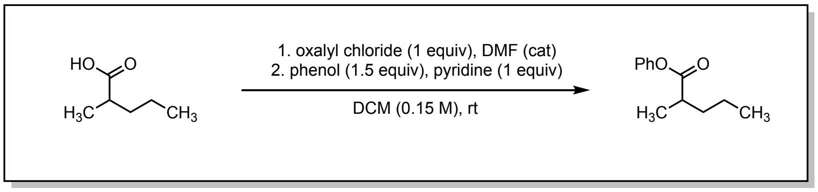
HRMS: (ESI-TOF) calculated for calculated for $C_{17}H_{21}O_2^+$ ($[M+H]^+$): 257.1536, found: 257.1536.



Phenyl hexanoate (25-α). To a solution of phenol (202 mg, 2.14 mmol), pyridine (0.26 mL, 3.2 mmol), and dry dichloromethane (10 mL) at 0 °C under an environment of nitrogen was added hexanoyl chloride dropwise (0.3 mL, 2.1 mmol). After the reaction was allowed to stir overnight, the mixture was diluted with water (5 mL) and washed with brine (2 x 10 mL). The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-10% 10 CV, 10% 4 CV) affording a clear oil (399 mg, 96% yield). Spectral data were consistent with reported literature values.[12]

1H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.34 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.08 (dd, J = 8.6, 1.2 Hz, 2H), 2.56 (t, J = 7.5 Hz, 2H), 1.77 (p, J = 7.5 Hz, 2H), 1.44 – 1.31 (m, 4H), 0.93 (t, J = 7.0 Hz, 3H).

13C NMR (126 MHz, $CDCl_3$): δ 172.40, 150.79, 129.43, 125.74, 121.62, 34.40, 31.30, 24.67, 22.36, 13.96.



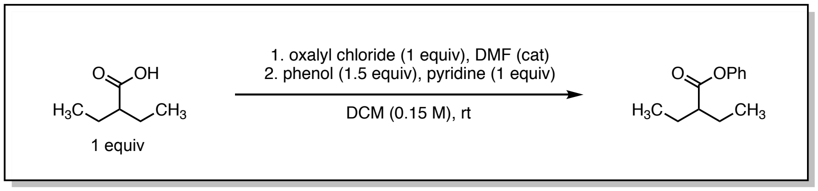
Phenyl 2-methylpentanoate (25-β). To a flame-dried round bottom flask was added 2-methyl pentanoic acid (0.483 mL, 3.87 mmol) and two drops of DMF in dry dichloromethane (21 mL). The mixture was then cooled to 0 °C and oxalyl chloride (0.34 mL, 3.87 mmol) was added drop-wise. The reaction was allowed to stir for 3 hours after which a solution of phenol (547 mg, 5.8 mmol) and pyridine (313 *µ*L, 3.87 mmol) in dichloromethane (4 mL) was added dropwise to the flask. After the reaction was allowed to stir overnight, the reaction mixture was diluted with water (10 mL) and washed with brine (2 x 15 mL). The organic layer was concentrated in vacuo and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-10% 10 CV, 10% 4 CV) to isolate a clear oil (490 mg, 65% yield).

1H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.35 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 7.7 Hz, 2H), 2.74 – 2.65 (m, 1H), 1.85 – 1.74 (m, 1H), 1.59 – 1.50 (m, 1H), 1.49 – 1.40 (m, 2H), 1.30 (d, J = 6.9 Hz, 3H), 0.97 (t, J = 7.3 Hz, 3H).

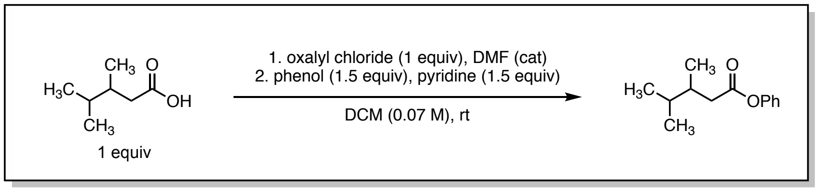
13C NMR (126 MHz, $CDCl_3$): δ 175.40, 150.86, 129.39, 125.67, 121.57, 39.45, 35.94, 20.47, 17.03, 14.02.

HRMS: (ESI-TOF) calculated for $C_{12}H_{16}NaO_2^+$ ($[M+Na]^+$): 215.1043, found: 215.1038.

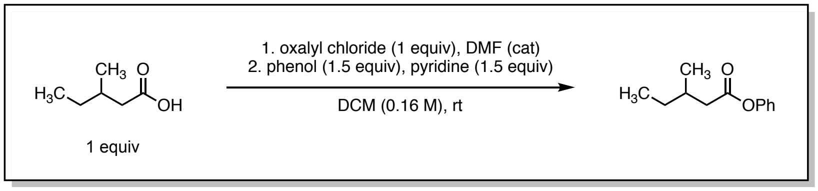
FTIR (ATR cm^{-1}): 2959, 2934, 1754, 1593, 1493, 1456, 1194, 1159, 1112, 1069, 1049, 1024, 996, 912, 742, 688, 500.



Phenyl 2-ethylbutanoate (25-γ). To a flame-dried round bottom flask, 2-ethyl butanoic acid (0.5 mL, 3.96 mmol), and two drops of DMF were added to dry dichloromethane (21 mL). The mixture was then cooled to 0 °C and oxalyl chloride (347 μL, 3.9 mmol) was added dropwise. The reaction was allowed to stir for 3 hours after which a solution of phenol (559 mg, 5.94 mmol) and pyridine (0.32 mL, 3.1 mmol) in dichloromethane (4 mL) was added dropwise to the flask. After the reaction was allowed to stir overnight the reaction mixture was diluted with water (10 mL) and washed with brine (2 x 15 mL). The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-10% 10 CV, 10% 4 CV) to afford a clear oil (761 mg, 100% yield).
1H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.35 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 7.7 Hz, 2H), 2.46 (tt, J = 8.7, 5.5 Hz, 1H), 1.86 – 1.73 (m, 2H), 1.71 – 1.61 (m, 2H), 1.03 (t, J = 7.5 Hz, 6H).
13C NMR (126 MHz, $CDCl_3$): δ174.78, 150.84, 129.42, 125.71, 121.67, 48.99, 25.16, 11.89.
HRMS: (ESI-TOF) calculated for $C_{12}H_{16}NaO_2^+$ ([M+Na]$^+$): 215.1043, found: 215.1048.
FTIR (ATR cm^{-1}): 2964, 1752, 1492, 1458, 1192, 1155, 1109, 1068, 1023, 927, 823, 743, 688, 499.



Phenyl 3,4-dimethylpentanoate (26-α). To a flame-dried round bottom flask, 3,4-dimethylpentanoic acid (0.25 mg, 1.9 mmol) and two drops of DMF were added to dry dichloromethane (25 mL). The mixture was then cooled to 0 °C and oxalyl chloride (170 μL, 1.9 mmol) was added to the flask dropwise. The reaction was allowed to stir for three hours after which a solution of phenol (274 mg, 2.9 mmol) and pyridine (246 μL, 2.9 mmol) in dichloromethane (4 mL) was added dropwise, and the reaction was allowed to stir for an additional period overnight. After completion, the reaction mixture was diluted with water (10 mL) and washed with brine (2 x 15 mL). The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-2% 8 CV, 4% 17 CV) to afford a pale yellow oil (289.6 mg, 72% yield).
1H NMR (500 MHz, $CDCl_3$): δ 7.38 (t, J = 7.9 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.8 Hz, 2H), 2.60 (dd, J = 14.6, 5.4 Hz, 1H), 2.33 (dd, J = 14.7, 9.2 Hz, 1H), 2.10 – 1.98 (m, 1H), 1.73 – 1.64 (m, 1H), 0.99 (dd, J = 7.0, 1.5 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H).
13C NMR (126 MHz, $CDCl_3$): δ 172.25, 150.76, 129.42, 125.73, 121.62, 39.26, 36.10, 32.20, 19.87, 18.38, 15.93.
HRMS: (ESI-TOF) calculated for $C_{13}H_{19}O_2^+$ ([M+H]$^+$): 207.1380, found: 207.1382.
FTIR (ATR cm^{-1}): 2960, 1756, 1492, 1195, 1162, 1142, 1106, 750, 688.



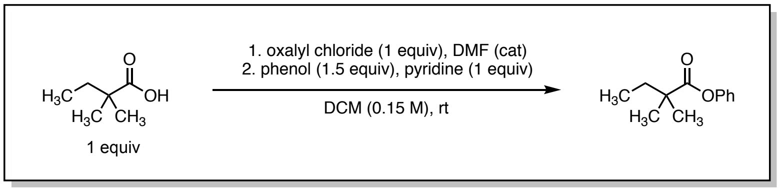
Phenyl 3-methylpentanoate (27-α). To a flame-dried round bottom, 3-methyl pentanoic acid (0.5 mL, 4.00 mmol) and two drops of DMF were added to dry dichloromethane (21 mL). The mixture was then cooled to 0 °C and oxalyl chloride (0.35 mL, 4.00 mmol) was added dropwise. The reaction was allowed to stir for 3 hours after which a solution of phenol (565 mg, 6.0 mmol) and pyridine (486 μL, 6.0 mmol) in dichloromethane (4 mL) was added dropwise and allowed to stir overnight. After completion, the reaction mixture was diluted with water (10 mL) and washed with brine (2 x 15 mL). The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-10% 10 CV, 10% 4 CV) to isolate phenyl ester as a clear oil (678 mg, 88% yield).

1H NMR (500 MHz, CDCl3): δ 7.38 (t, J = 7.9 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.6 Hz, 2H), 2.57 (dd, J = 14.7, 6.1 Hz, 1H), 2.36 (dd, J = 14.7, 8.1 Hz, 1H), 2.10 – 1.98 (m, J = 6.6 Hz, 1H), 1.53 – 1.41 (m, 1H), 1.39 – 1.29 (m, 1H), 1.05 (d, J = 6.7 Hz, 3H), 0.96 (t, J = 7.5 Hz, 3H).

13C NMR (126 MHz, CDCl3): δ 171.87, 150.78, 129.43, 125.74, 121.64, 41.48, 32.13, 29.40, 19.33, 11.35.

HRMS: (ESI-TOF) calculated for $C_{12}H_{17}O_2^+$ ([M+H]$^+$): 193.1223, found: 193.1222.

FTIR (ATR cm^{-1}): 2961, 1753, 1593, 1492, 1456, 1234, 1194, 1161, 1144, 1103, 1070, 1023, 937, 887, 759, 713, 687, 498.



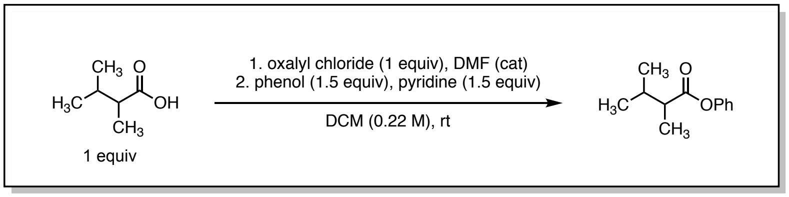
Phenyl 2,2-dimethylbutanoate (27-β). To a flame-dried round bottom flask, dry dichloromethane (8 mL) was added, followed by 2,2-dimethylbutanoic acid (0.3 mL, 2.4 mmol) and two drops of DMF. The mixture was then cooled to 0 °C and oxalyl chloride (210 μL, 2.4 mmol) was added dropwise. The reaction was allowed to stir for 3 hours at which point a solution of phenol (338 mg, 3.60 mmol) and pyridine (0.291 mL, 3.60 mmol) in dichloromethane (3 mL) was added dropwise and the reaction was allowed to stir overnight. The reaction mixture was diluted with water (5 mL) and washed with brine (2 x 5 mL). The crude material was purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-4% 10 CV, 4% 6 CV) to isolate phenyl 2,2-dimethylbutanoate as a clear oil (104 mg, 22% yield).

1H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.34 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.05 (dd, J = 8.6, 1.2 Hz, 2H), 1.73 (q, J = 7.5 Hz, 2H), 1.31 (s, 6H), 0.98 (t, J = 7.5 Hz, 3H).

13C NMR (126 MHz, $CDCl_3$): δ 176.59, 151.11, 129.38, 125.61, 121.60, 42.99, 33.41, 24.71, 9.38.

HRMS: (ESI-TOF) calculated for $C_{12}H_{17}O_2^+$ ([M+H]$^+$): 193.1223, found: 193.1228.

FTIR (ATR cm^{-1}): 2964, 1751, 1593, 1493, 1474, 1457, 1234, 1192, 1161, 1108, 1070, 1022, 931, 913, 738, 714, 687, 499.



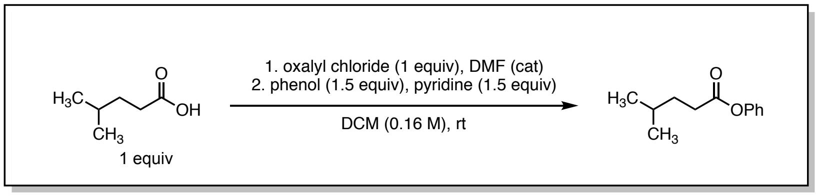
Phenyl 2,3-dimethylbutanoate (27-γ). To a flame-dried round bottom flask, 2,3-dimethylbutanoic acid (0.3 mL, 2.4 mmol) and two drops of DMF were added to dry dichloromethane (8 mL). The mixture was then cooled to 0 °C and oxalyl chloride (210 μL, 2.4 mmol) was added dropwise. The reaction was allowed to stir for 3 hours after which, a solution of phenol (338 mg, 3.60 mmol) and pyridine (291 μL, 3.60 mmol) in dichloromethane (3 mL) was added dropwise to the flask and the reaction was allowed to stir overnight. The reaction mixture was diluted with water (5 mL) and washed with brine (2 x 5 mL). The crude material was purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-4% 10 CV, 4% 4 CV) to isolate phenyl 2,3-dimethylbutanoate as a clear oil (223 mg, 48% yield).

<u>1H NMR (500 MHz, CDCl$_3$):</u> δ7.40 – 7.35 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.07 (dd, J = 8.5, 1.0 Hz, 2H), 2.49 (p, J = 7.0 Hz, 1H), 2.15 – 2.03 (m, 1H), 1.25 (d, J = 7.0 Hz, 3H), 1.06 (d, J = 6.8 Hz, 3H), 1.02 (d, J = 6.8 Hz, 3H).

<u>13C NMR (126 MHz, CDCl$_3$):</u> δ 174.92, 150.84, 129.41, 125.69, 121.62, 46.22, 31.18, 20.75, 19.25, 13.75.

<u>HRMS:</u> (ESI-TOF) calculated for $C_{12}H_{17}O_2^+$ ([M+H]$^+$): 193.1223, found: 193.1225.

<u>FTIR (ATR cm^{-1}):</u> 2952, 1754, 1492, 1195, 1160, 1110, 1084, 1069, 688.



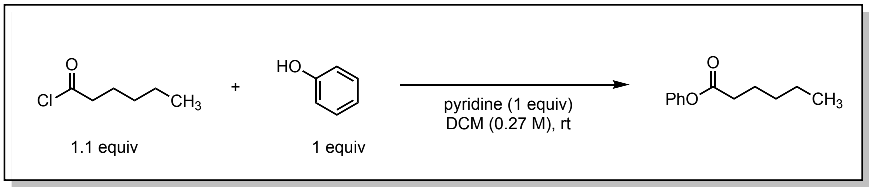
Phenyl 4-methylpentanoate (27-δ). To a flame-dried round bottom flask, 4-methyl pentanoic acid (0.5 mL, 3.97 mmol) and two drops of DMF were added to dry dichloromethane (21 mL). The mixture was cooled to 0 °C and oxalyl chloride (0.35 mL, 3.97 mmol) was added dropwise to the flask. The reaction was allowed to stir for 3 hours after which a solution of phenol (561 mg, 5.9 mmol) and pyridine (314 μL, 3.97 mmol) in dichloromethane (4 mL) was added dropwise and the reaction was allowed to stir overnight. The reaction mixture was diluted with water (10 mL) and washed with brine (2 x 15 mL). The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-10% 10 CV, 10% 4 CV) to afford a clear oil (644 mg, 84% yield).

<u>1H NMR (500 MHz, CDCl$_3$):</u> δ 7.38 (tt, J = 7.6, 2.1 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.09 (dd, J = 8.6, 1.0 Hz, 2H), 2.60 – 2.54 (m, 2H), 1.73 – 1.62 (m, 3H), 0.98 (d, J = 6.3 Hz, 6H).

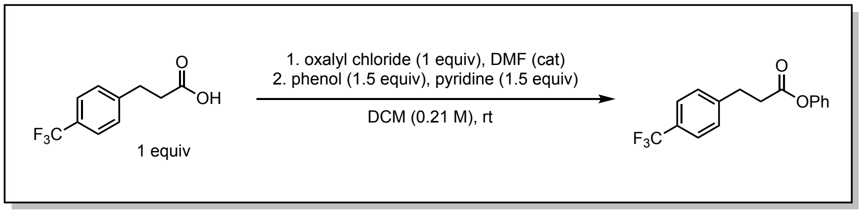
<u>13C NMR (126 MHz, CDCl$_3$):</u> δ 172.56, 150.81, 129.44, 125.75, 121.62, 33.75, 32.54, 27.77, 22.29.

<u>HRMS:</u> (ESI-TOF) calculated for $C_{12}H_{17}O_2^+$ ([M+H]$^+$): 193.1223, found: 193.1227.

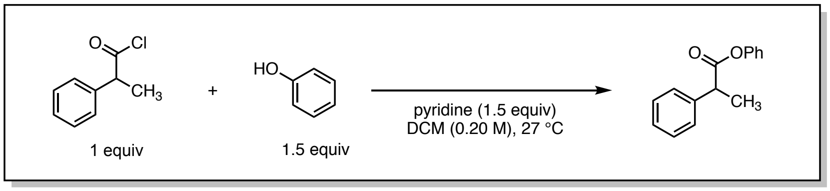
<u>FTIR (ATR cm^{-1}):</u> 2956, 1754, 1593, 1492, 1468, 1232, 1194, 1161, 1140, 1094, 1070, 1023, 927, 813, 748, 687, 498.



Phenyl 2-phenylacetate (28). To a solution of phenol (107 mg, 1.13 mmol), pyridine (0.092 mL, 1.13 mmol), and dry dichloromethane (5 mL) was added 2-phenylacetyl chloride (0.10 mL, 0.76 mmol). The reaction was allowed to stir for 15 minutes then concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-5% 8 CV, 5% 4 CV) affording a clear oil (119 mg, 74% yield).
<u>1H NMR (500 MHz, CDCl$_3$):</u> δ 7.44 – 7.28 (m, 7H), 7.21 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 3.86 (s, 2H).
<u>13C NMR (126 MHz, CDCl$_3$):</u> δ170.08, 150.81, 133.56, 129.47, 129.40, 128.81, 127.43, 125.94, 121.54, 41.50.
<u>HRMS:</u> (ESI-TOF) calculated for $C_{14}H_{13}O_2^+$ ([M+H]$^+$): 213.0910, found: 213.0907.
<u>FTIR (ATR cm^{-1}):</u> 3040, 1748, 1491, 1233, 1189, 1116, 1070, 926, 741, 719, 687, 518, 495.



Phenyl 3-(4-(trifluoromethyl)phenyl)propanoate (31-β). To a flame-dried round bottom flask, 3-(4-(trifluoromethyl)phenyl)propanoic acid (654 mg, 3.00 mmol) and two drops of DMF was added in dry dichloromethane (13 mL). The mixture was then cooled to 0 °C and oxalyl chloride (0.262 mL, 3.00 mmol) was added dropwise. The reaction was allowed to stir for 3 hours after which a solution of phenol (423 mg, 4.50 mmol) and pyridine (0.363 mL, 4.45 mmol) in dichloromethane (2 mL) was added dropwise and the reaction was allowed to stir overnight. The reaction was diluted with water (5 mL) and washed with brine (2 x 10 mL).The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-7% 10 CV, 7% 8 CV) to isolate product as a white solid (471 mg, 53% yield). Spectral data were consistent with reported literature values.[13]
<u>1H NMR (500 MHz, CDCl$_3$):</u> δ 7.58 (d, J = 8.0 Hz, 2H), 7.42 – 7.33 (m, 4H), 7.26 – 7.19 (m, 1H), 7.02 – 6.98 (m, 2H), 3.13 (t, J = 7.6 Hz, 2H), 2.92 (t, J = 7.6 Hz, 2H).
<u>13C NMR (126 MHz, CDCl$_3$):</u> δ 170.99, 150.52, 144.22, 129.48, 128.81, 125.96, 125.56 (q, J = 3.8 Hz), 121.45, 35.51, 30.66.
<u>19F NMR (376 MHz, CDCl$_3$):</u> δ -62.44.

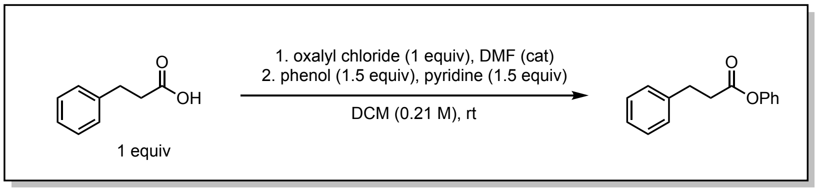


1-Ethyl-4-phenoxybenzene (32-α). To a flame-dried round bottom flask was added phenol (251 mg, 2.67 mmol) and pyridine (0.216 *μ*L, 2.67 mmol) in dry dichloromethane (9 mL). The mixture was cooled to 0 °C, after which 2-phenylpropanoyl chloride (300 mg, 1.78 mmol) was added dropwise and the reaction was allowed to stir overnight. The reaction was diluted with water (4 mL) and washed with brine (2 x 5 mL). The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-10% 10 CV, 10% 4 CV) to isolate a crystalline solid (403 mg, 45% yield). Spectral data were consistent with reported literature values.[13]

1H NMR (300 MHz, $CDCl_3$): δ 7.47 – 7.28 (m, 7H), 7.20 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 8.1 Hz, 2H), 3.98 (q, J = 7.1 Hz, 1H), 1.63 (d, J = 7.1 Hz, 3H).

13C NMR (75 MHz, $CDCl_3$): δ 173.06, 150.86, 140.12, 129.36, 128.84, 127.58, 127.40, 125.79, 121.41, 45.68, 18.56.

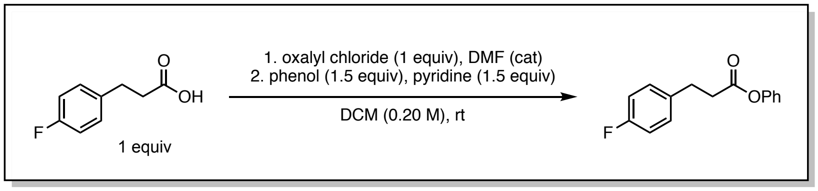
HRMS: (ESI-TOF) calculated for $C_{15}H_{15}O_2^+$ ($[M+H]^+$): 227.1067, found: 227.1070.



Phenyl 3-phenylpropanoate (32-β). To a flame-dried round bottom flask was added 3-(4-fluorophenyl)propanoic acid (311 mg, 2.07 mmol) and two drops of DMF in dry dichloromethane (8 mL). The mixture was cooled to 0 °C and oxalyl chloride (0.181 *μ*L, 2.07 mmol) was added. The reaction was allowed to stir for 3 hours after which a solution of phenol (246 mg, 3.11 mmol) and pyridine (0.25 mL, 3.11 mmol) in dichloromethane (2 mL) was added dropwise. After the reaction was allowed to stir overnight, it was diluted with water (4 mL) and washed with brine (2 x 5 mL). The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-5% 10 CV, 5% 6 CV, 5-10% 5 CV, 10% 2 CV) to afford a crystalline solid (469 mg, 97% yield). Spectral data were consistent with reported literature values.[13]

1H NMR (500 MHz, $CDCl_3$): δ 7.49 (t, J = 8.0 Hz, 1H), 7.42 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 7.27 – 7.21 (m, 2H), 7.04 (d, J = 7.6 Hz, 2H), 3.11 (t, J = 7.7 Hz, 2H), 2.92 (t, J = 7.7 Hz, 2H).

13C NMR (126 MHz, $CDCl_3$): δ 171.45, 150.71, 140.19, 129.45, 128.65, 128.47, 126.50, 125.85, 121.59, 36.04, 31.01.

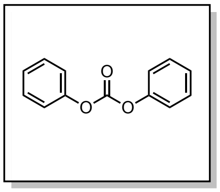


Phenyl 3-(4-fluorophenyl)propanoate (33-β). To a flame-dried round bottom flask, 3-(4-fluorophenyl)propanoic acid (200 mg, 1.19 mmol) and two drops of DMF was added in dry dichloromethane (4 mL). The mixture was then cooled to 0 °C and oxalyl chloride (0.104 mL, 1.19 mmol) was added dropwise. The reaction was allowed to stir for 3 hours after which a solution of phenol (168 mg, 1.78 mmol) and pyridine (0.144 mL, 1.78 mmol) in dichloromethane (2 mL) was added dropwise and the reaction was allowed to stir overnight. The reaction was diluted with water (4 mL) and washed with brine (2 x 5 mL).The organic layer was concentrated *in vacuo* and purified by automated column chromatography (eluting with ethyl acetate: hexanes; 0% 4 CV, 0-10% 5 CV, 10% 5 CV) to isolate product as a crystalline solid (176 mg, 61% yield). Spectral data were consistent with reported literature values.[13]

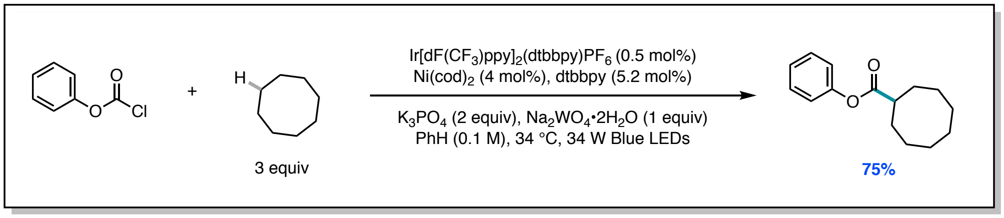
1H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.33 (m, 2H), 7.25 – 7.19 (m, 3H), 7.05 – 6.97 (m, 4H), 3.05 (t, J = 7.5 Hz, 2H), 2.87 (t, J = 7.5 Hz, 2H).
13C NMR (126 MHz, $CDCl_3$): δ 171.27, 161.61 (d, J = 244.3 Hz), 150.58, 135.79, 129.90 (d, J = 7.9 Hz), 129.46, 125.89, 121.51, 115.39 (d, J = 21.2 Hz), 36.10, 30.16.
19F NMR (376 MHz, $CDCl_3$): δ -117.01 to -117.15 (m).

VII. Compound Characterization

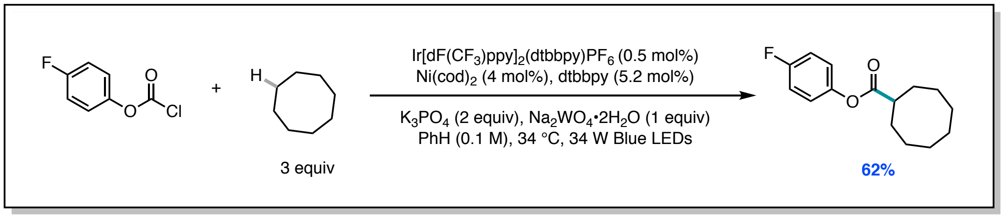
*Compounds are characterized as #-x where # represents the ester product communicated in the main manuscript and x refers to the classification of the regioisomer when applicable (α, β, γ, δ). Compounds **53**-α, **53**-β, and **53**-γ were additional compounds characterized for use in determining the regioisomers of **49** and **50**. Compound **54** was an additional ethylbenzene derivative evaluated for use in the Hammett-Brown plot. When NMR yields are reported and isomers were not independently synthesized, the spectra of the crude sample are included. Characterization for diphenyl carbonate is included below for ease of analysis of crude NMR samples.*



Diphenyl carbonate (13) was purchased from Sigma Aldrich and the spectra were taken without further purification and found to be consistent with literature precedent.[14]
<u>1H NMR (500 MHz, $CDCl_3$):</u> δ 7.43 – 7.36 (m, 5H), 7.25 – 7.21 (m, 5H).
<u>13C NMR (126 MHz, $CDCl_3$):</u> δ 152.24, 151.11, 129.72, 126.46, 121.06.

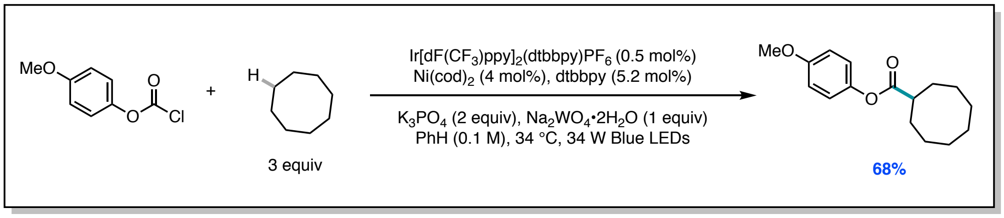


Phenyl cyclooctanecarboxylate (14) was prepared according to the general procedure for isolations from cyclooctane and phenyl chloroformate. The title compound was isolated via flash chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification (eluting with a 0%-0.5% THF: hexanes gradient) to produce a yellow oil (Run 1= 111.5 mg, 80% yield; Run 2= 97.6 mg, 70% yield, 75% average yield).
<u>1H NMR (500 MHz, $CDCl_3$):</u> δ 7.29 (m, 2H), 7.14 (m, 1H), 6.98 (m, 2H), 2.70 (tt, *J* = 9.3, 3.9 Hz, 1H), 2.04 – 1.93 (m, 2H), 1.83 – 1.66 (m, 4H), 1.60 – 1.36 (m, 8H).
<u>13C NMR (126 MHz, $CDCl_3$):</u> δ 175.79, 150.97, 129.38, 125.63, 121.57, 43.63, 28.71, 26.79, 26.14, 25.24.
<u>HRMS:</u> (ESI-TOF) calculated for $C_{15}H_{21}O_2^+$ ($[M+H]^+$): 233.1536, found: 233.1535.

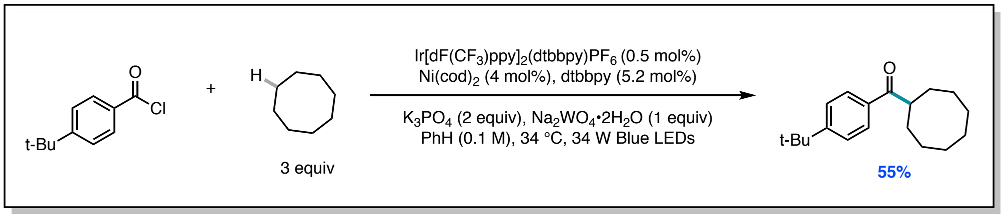


4-Fluorophenyl cyclooctanecarboxylate (15) was prepared according to the general procedure for isolations, resulting in 62% average NMR yield (Run 1= 64% yield; Run 2= 60% yield). Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with EtOAc: hexanes; 0% 4 CV, 0-5% 6 CV, 5-7% 3 CV) enabling characterization.

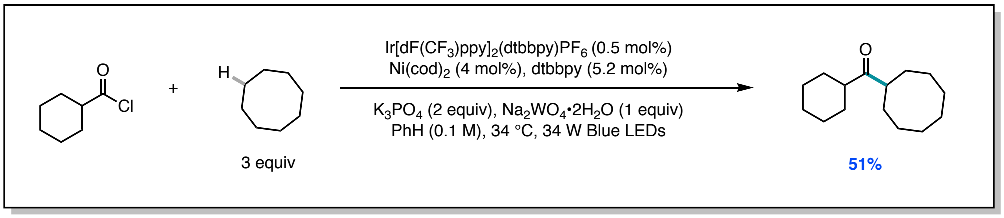
1H NMR (500 MHz, $CDCl_3$): δ 7.07 – 6.99 (m, 4H), 2.76 (tt, J = 9.3, 3.9 Hz, 1H), 2.04 (ddt, J = 15.5, 8.8, 3.5 Hz, 2H), 1.88 – 1.73 (m, 4H), 1.67 – 1.47 (m, 8H).
13C NMR (126 MHz, $CDCl_3$): δ 175.81, δ 160.12 (d, J = 243.8 Hz), 146.76 (d, J = 2.9 Hz), 122.92 (d, J = 8.5 Hz), 116.01 (d, J = 23.4 Hz), 43.53, 28.67, 26.76, 26.11, 25.20.
19F NMR (470 MHz, $CDCl_3$) δ -117.55.
HRMS: (ESI-TOF) calculated for $C_{15}H_{20}FO_2^+$ ($[M+H]^+$): 251.1442, found: 251.1444.
FTIR (ATR cm^{-1}): 2919, 1751, 1501, 1223, 1183, 1170, 1141, 1111, 1088, 1044, 846, 828, 515.



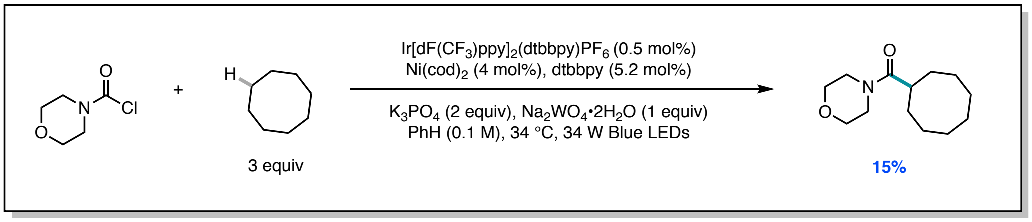
4-Methoxyphenyl cyclooctanecarboxylate (16) was prepared according to the general procedure for isolations, resulting in 68% average NMR yield (Run 1= 67% yield; Run 2= 68% yield). Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with Ethyl Acetate: hexanes; 0% 3 CV, 0-2% 2 CV, 2-4% 2 CV, 4-10% 8 CV, 10% 9 CV) enabling characterization.
1H NMR (500 MHz, $CDCl_3$): δ 6.98 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 3.79 (s, 3H), 2.76 (tt, J = 9.3, 3.9 Hz, 1H), 2.11 – 1.98 (m, 2H), 1.89 – 1.74 (m, 4H), 1.67 – 1.39 (m, 8H).
13C NMR (126 MHz, $CDCl_3$): δ 176.16, 157.11, 144.44, 122.29, 114.40, 55.58, 43.57, 28.74, 26.79, 26.14, 25.25.
HRMS: (ESI-TOF) calculated for $C_{15}H_{23}O_3^+$ ($[M+H]^+$): 263.1642, found: 263.1643.
FTIR (ATR cm^{-1}): 2918, 1748, 1503, 1246, 1190, 1161, 1142, 1113, 1031, 1008, 843, 821, 519.



(4-(*tert*-butyl)phenyl)(cyclooctyl)methanone (17) was prepared according to the general procedure for isolations, resulting in 55% average NMR yield (Run 1= 51% yield; Run 2= 58% yield). Isolation of fractions of authentic product alongside a byproduct, dicyclooctane, were obtained using automated column chromatography (eluting with EtOAc: hexanes; 0% 5 CV, 0-20% 10 CV, 20% 1 CV) enabling characterization.
1H NMR (500 MHz, $CDCl_3$): δ 7.90 – 7.87 (m, 2H), 7.47 (d, J = 8.5 Hz, 2H), 3.51 – 3.43 (m, 1H), 1.90 – 1.51 (m, 14H), 1.34 (s, 9H).
13C NMR (126 MHz, $CDCl_3$): δ 204.07, 156.27, 133.80, 128.29, 125.53, 49.26, 35.05, 31.13, 29.14, 26.65, 25.66, 25.57.
HRMS: (ESI-TOF) calculated for $C_{19}H_{29}O^+$ ($[M+H]^+$): 273.2213, found: 273.2209.
FTIR (ATR cm^{-1}): 2918, 2854, 1676, 1604, 1464, 1446, 1407, 1363, 1268, 1223, 1187, 1108, 985, 850.

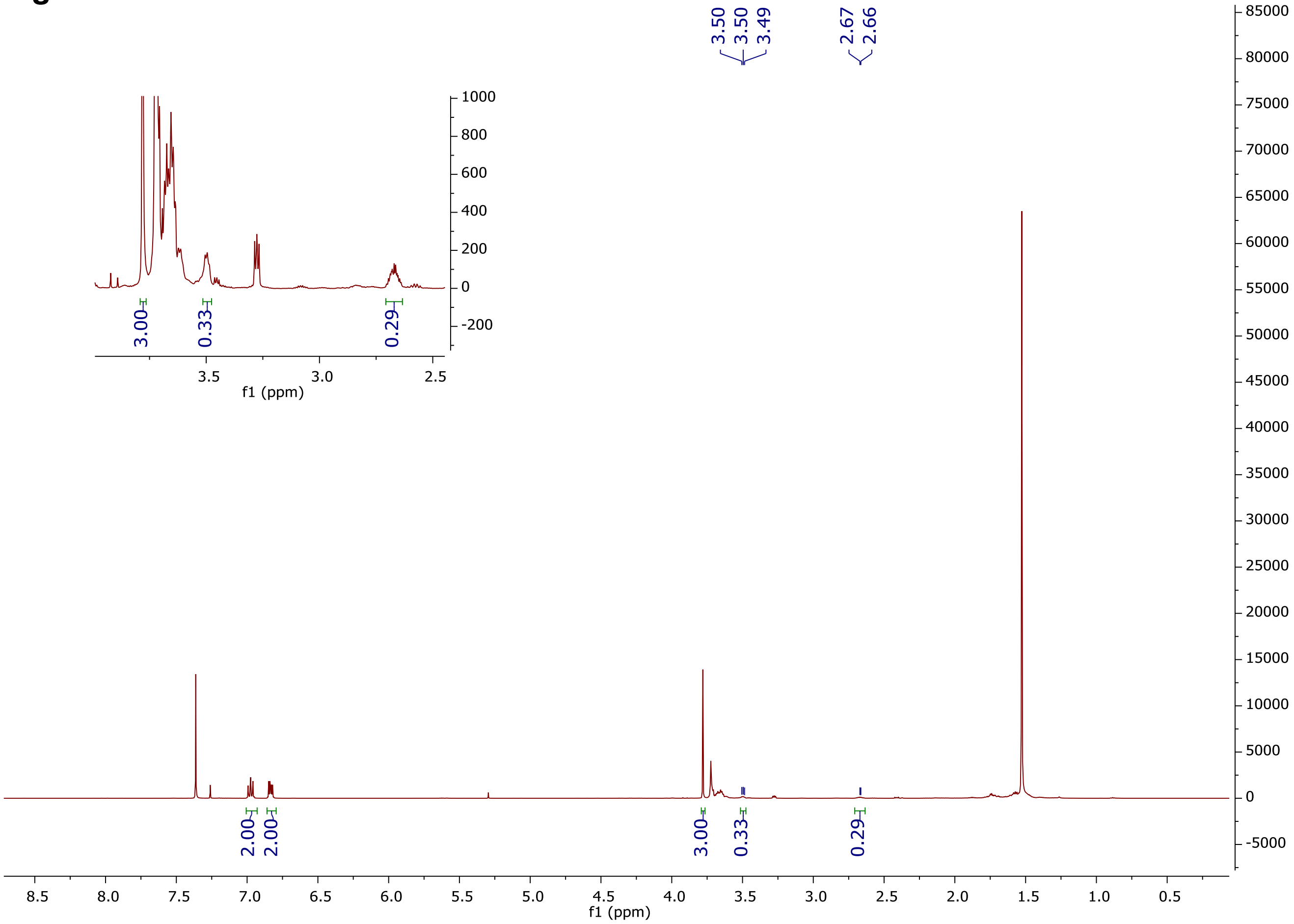


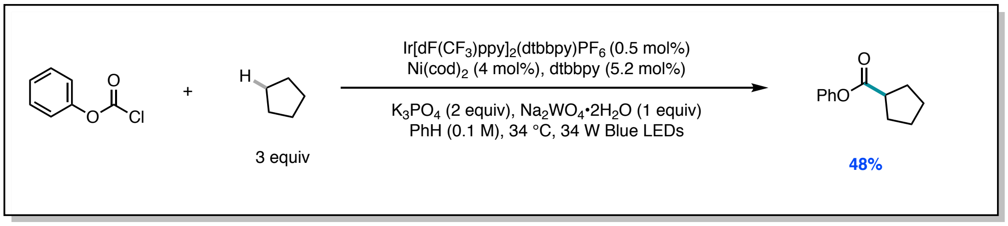
Cyclohexyl(cyclooctyl)methanone (18) was prepared according to the general procedure for isolations, resulting in 51% average NMR yield (Run 1= 49% yield, Run 2= 53% yield). Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with EtOAc: hexanes; 0% 5 CV, 0-20% 10 CV, 20% 6 CV) enabling characterization.
1H NMR (500 MHz, CDCl$_3$): δ 2.68 (tt, J = 9.2, 3.2 Hz, 1H), 2.45 (tt, J = 11.2, 3.1 Hz, 1H), 1.81 – 1.65 (m, 10H), 1.63 – 1.44 (m, 10H), 1.38 – 1.13 (m, 4H).
13C NMR (126 MHz, CDCl$_3$): δ 217.60, 49.69, 48.87, 28.83, 28.27, 26.58, 26.39, 25.88, 25.78, 25.62.
HRMS: (ESI-TOF) calculated for $C_{15}H_{27}O^+$ ($[M+H]^+$): 223.2056, found: 223.2067.
FTIR (ATR cm^{-1}): 2920, 2851, 1702, 1466, 1447, 1377, 1316, 1239, 1145, 1063, 998.



Cyclooctyl(morpholino)methanone (19) was prepared acccording to the general procedure for isolations from cyclooctane and morpholine-4-carbonyl chloride. Isolation of fractions of authentic product were obtained by automated column chromatography (eluting with Ether:Pentane 0% 4 CV, 0-18% 10 CV, 18% 10 CV, 40% 16 CV, 80% 16 CV) enabling characterization. Comparison of the crude reaction mixture to clean product resulted in 15% average NMR yield (Run 1= 14% yield; Run 2= 16% yield).
1H NMR (500 MHz, CDCl$_3$): δ 3.69 – 3.64 (m, 4H), 3.61 – 3.58 (m, 2H), 3.51 – 3.46 (m, 2H), 2.71 – 2.62 (m, 1H), 1.79 – 1.68 (m, 7H), 1.65 – 1.53 (m, 4H), 1.52 – 1.44 (m, 3H).
13C NMR (126 MHz, CDCl$_3$): δ 176.30, 67.05, 66.78, 46.10, 42.04, 39.54, 29.57, 26.63, 26.44, 25.45.
HRMS: (ESI-TOF) calculated for $C_{13}H_{24}NO_2^+$ ($[M+H]^+$): 226.1802, found: 226.1803.
FTIR (ATR cm^{-1}): 2921, 2855, 1642, 1427, 1266,1229, 1116, 735, 700.

Figure S31 Crude 1H NMR of 19.



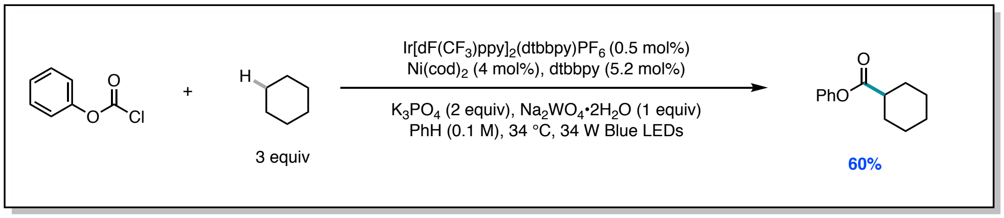


Phenyl cyclopentanecarboxylate (20) was prepared according to the general procedure for isolations from cyclopentane and phenyl chloroformate. The title compound was isolated via flash chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification, (eluting with a 0%-0.5% THF: hexanes gradient) to produce a yellow oil (Run 1= 46.8 mg, 41% yield; Run 2= 62.8 mg, 55% yield; 48% average yield). Spectral data were consistent with reported literature values.[15]

1H NMR (500 MHz, $CDCl_3$): δ 7.37 (m, 2H), 7.22 (m, 1H), 7.10 – 7.03 (m, 2H), 2.99 (p, *J* = 8.0 Hz, 1H), 2.12 – 1.87 (m, 4H), 1.83 – 1.73 (m, 2H), 1.72 – 1.59 (m, 2H).

13C NMR (126 MHz, $CDCl_3$): δ 175.33, 150.93, 129.38, 125.63, 121.56, 43.88, 30.10, 25.91.

HRMS: (ESI-TOF) calculated for $C_{12}H_{15}O_2^+$ ($[M+H]^+$): 191.1067, found: 191.1067.

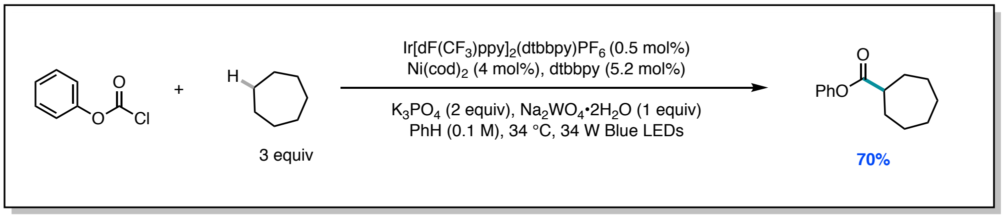


Phenyl cyclohexanecarboxylate (12) was prepared according to the general procedure for isolations from cyclohexane and phenyl chloroformate. The title compound was isolated via flash chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification (eluting with a 0%-0.5% THF: hexanes gradient) to produce a yellow oil (Run 1= 73.5 mg, 60% yield; Run 2= 72.3 mg, 59% yield; 60% average yield). Spectral data were consistent with reported literature values.[16]

1H NMR (500 MHz, $CDCl_3$): δ 7.37 (m, 2H), 7.23 (m, 1H), 7.08 – 7.01 (m, 2H), 2.56 (tt, *J* = 11.2, 3.7 Hz, 1H), 2.07 (dd, *J* = 13.0, 3.7 Hz, 2H), 1.83 (dt, *J* = 12.8, 3.7 Hz, 2H), 1.74 – 1.68 (m, 1H), 1.60 (qd, *J* = 11.7, 3.6 Hz, 2H), 1.43 – 1.14 (m, 3H).

13C NMR (126 MHz, $CDCl_3$): δ 174.60, 150.91, 129.38, 125.63, 121.59, 43.22, 28.98, 25.75, 25.40.

HRMS: (ESI-TOF) calculated $C_{13}H_{17}O_2^+$ ([M+H]$^+$): 205.1223, found: 205.1222.

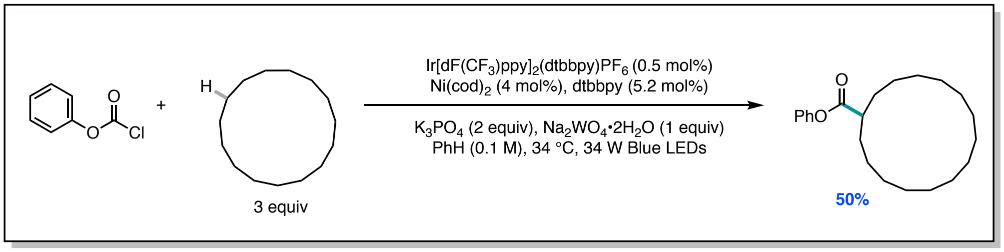


Phenyl cycloheptanecarboxylate (21) was prepared according to the general procedure for isolations from cycloheptane and phenyl chloroformate. The title compound was isolated via flash chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification, (eluting with a 0%-0.5% THF: hexanes gradient) to produce a yellow oil (Run 1= 94.3 mg, 72% yield; Run 2= 97.6 mg, 68% yield; 70% average yield).

1H NMR (500 MHz, $CDCl_3$): δ 7.29 (m, 2H), 7.13 (m, 1H), 6.98 (m, 2H), 2.66 (tt, *J* = 9.3, 4.3 Hz, 1H), 2.01 (ddt, *J* = 14.7, 7.5, 3.7 Hz, 2H), 1.82 – 1.65 (m, 4H), 1.59 – 1.34 (m, 6H).

13C NMR (126 MHz, $CDCl_3$): δ 175.49, 150.94, 129.37, 125.61, 121.55, 44.99, 30.78, 28.31, 26.36.

HRMS: (ESI-TOF) calculated for $C_{14}H_{19}O_2^+$ ([M+H]$^+$): 219.1380, found: 219.1379.

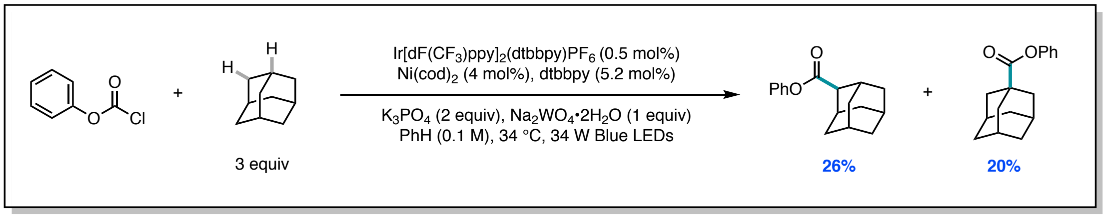


Phenyl cyclopentadecanecarboxylate (22) was prepared according to the general procedure for isolations from cyclopentadecane and phenyl chloroformate. The title compound was isolated via flash chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification (eluting with a 0%-0.5% THF: hexanes gradient) to produce a yellow oil (Run 1= 99.2 mg, 50% yield; Run 2= 97.2 mg, 49% yield; 50% average yield).

1H NMR (500 MHz, CDCl$_3$): δ 7.30 (m, 2H), 7.14 (m, 1H), 6.99 (m, 2H), 2.59 (p, *J* = 6.7 Hz, 1H), 1.67 (ddt, *J* = 31.4, 13.7, 6.8 Hz, 4H), 1.47 – 1.36 (m, 6H), 1.35 – 1.20 (m, 18H).

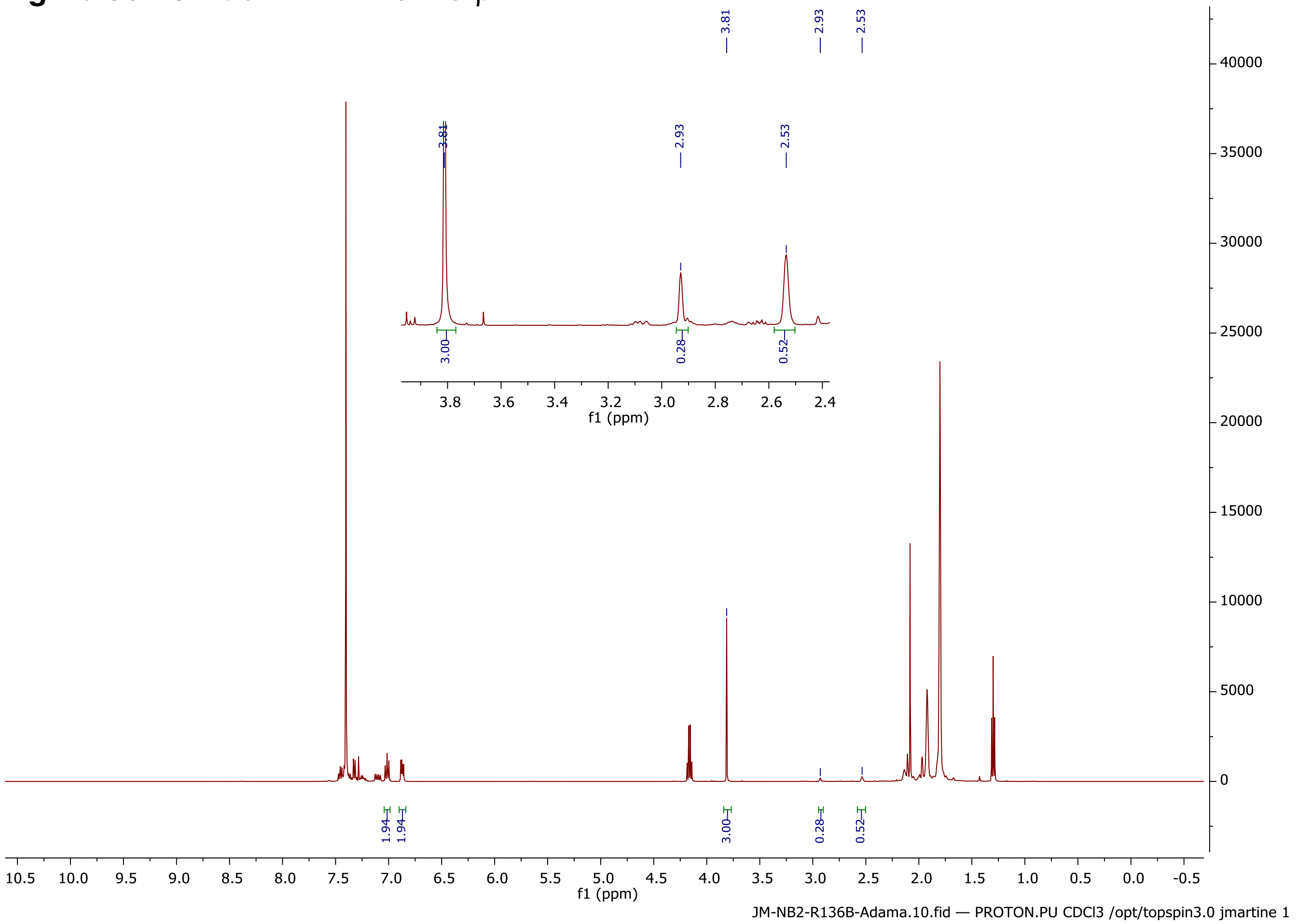
13C NMR (126 MHz, CDCl$_3$): δ 175.15, 150.89, 129.36, 125.62, 121.60, 43.15, 29.64, 26.90, 26.81, 26.78, 26.75, 26.74, 25.07.

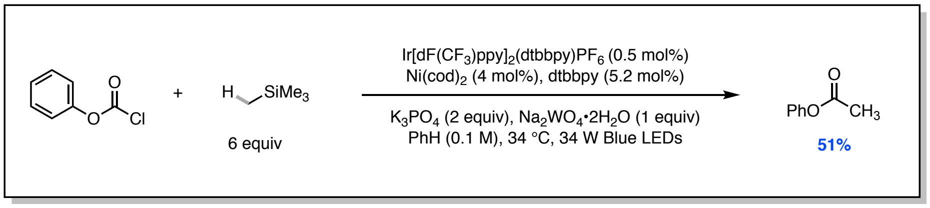
HRMS: (ESI-TOF) calculated for $C_{22}H_{35}O_2^+$ ([M+H]$^+$): 331.2632, found: 331.2632.



Phenyl adamantane-2-carboxylate (23-α) and phenyl adamantane-1-carboxylate (23-β) were prepared according to the general procedure for isolations from adamantane and phenyl chloroformate. Comparison of the crude reaction mixture to independently synthesized products (reported in section V - A GC assay was made for **23-**α, and the crude NMR yield was used for **23-**β). resulted in 46% combined average yield (Run 1= 43% yield, with 25% yield of **23-**α and 18% yield of **23-**β; Run 2= 47% yield, with 26% yield of **23-**α and 21% yield of **23-**β).

Figure S32 Crude 1H NMR of 23-β.





Phenyl 2-(trimethylsilyl)acetate (24) was prepared according to the general procedure for isolations from tetramethylsilane (6 equiv) and phenyl chloroformate, resulting in 51% average NMR yield of the desilylated product (Run 1= 47% yield; Run 2= 55% yield). Product was analyzed by comparison to authentic desilylated product.

Figure S33. Crude 1H NMR of 24.

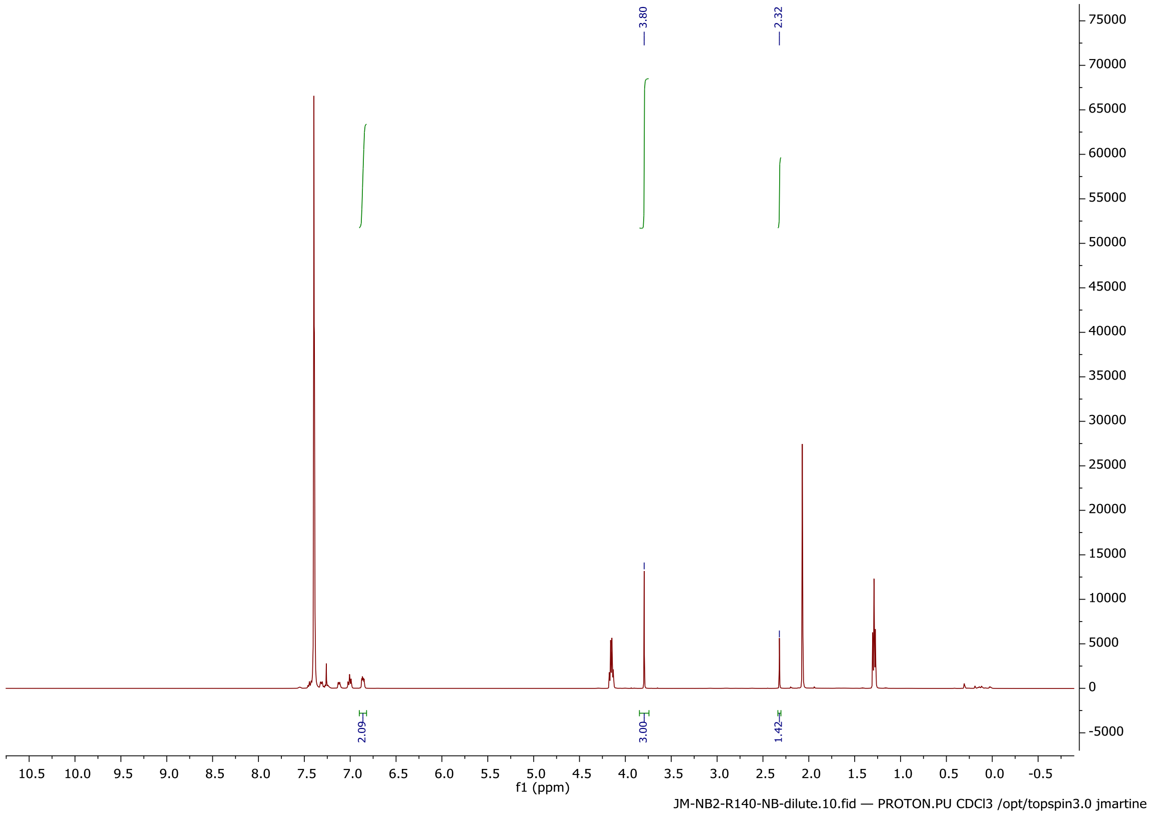
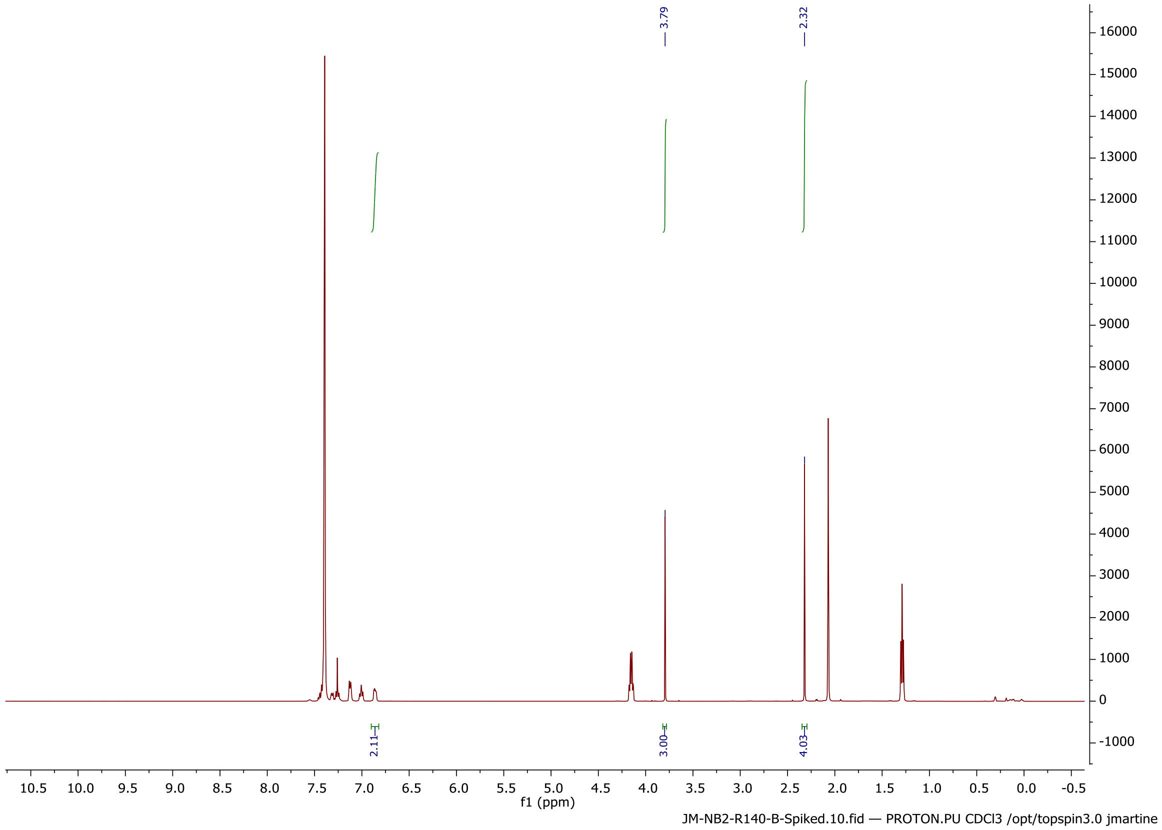
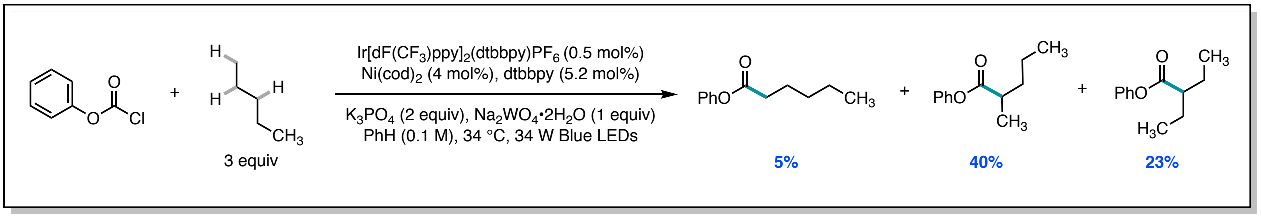


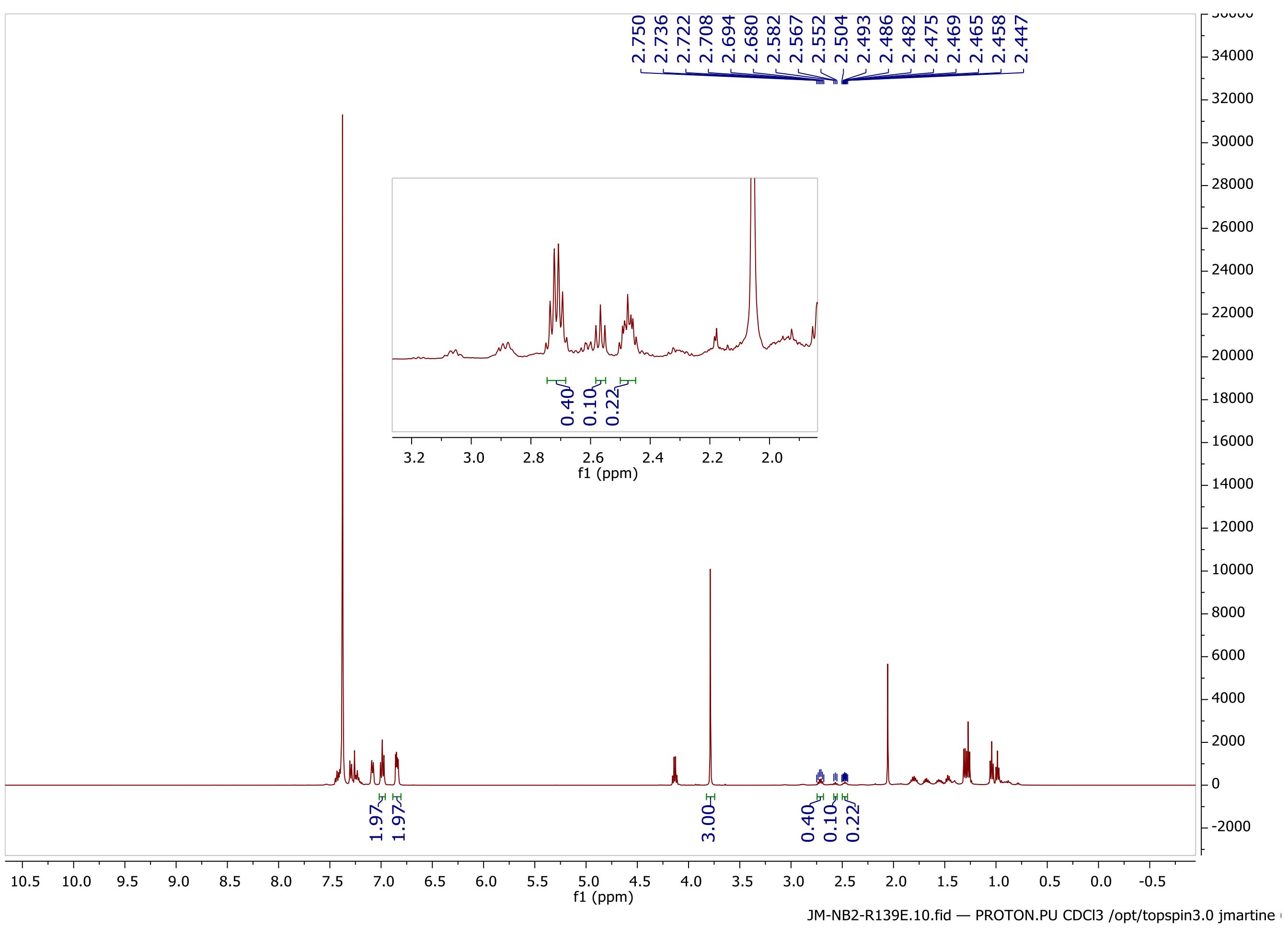
Figure S34. Crude 1H NMR of 24 with addition of phenylacetate.

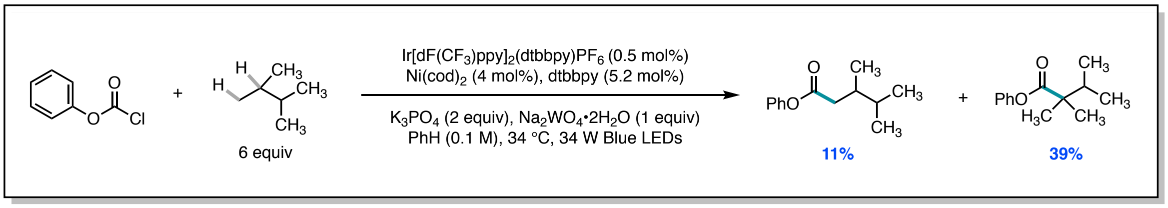




Phenyl hexanoate (25-α) and phenyl 2-methylpentanoate (25-β) and phenyl 2-ethylbutanoate (25-γ) were prepared according to the general procedure for isolations from pentane and phenyl chloroformate. Comparison of the crude reaction mixture to independently synthesized products (reported in section V) resulted in 68% combined average NMR yield (Run 1= 67% yield, with 5% yield of **25-**α, 40% yield of **25-**β, and 22% yield of **25-**γ; Run 2= 70% yield, with 5% yield of **25-**α, 41% yield of **25-**β, and 24% yield of **25-**γ).

Figure S35. Crude 1H NMR of 25-α, 25-β, and 25-γ.





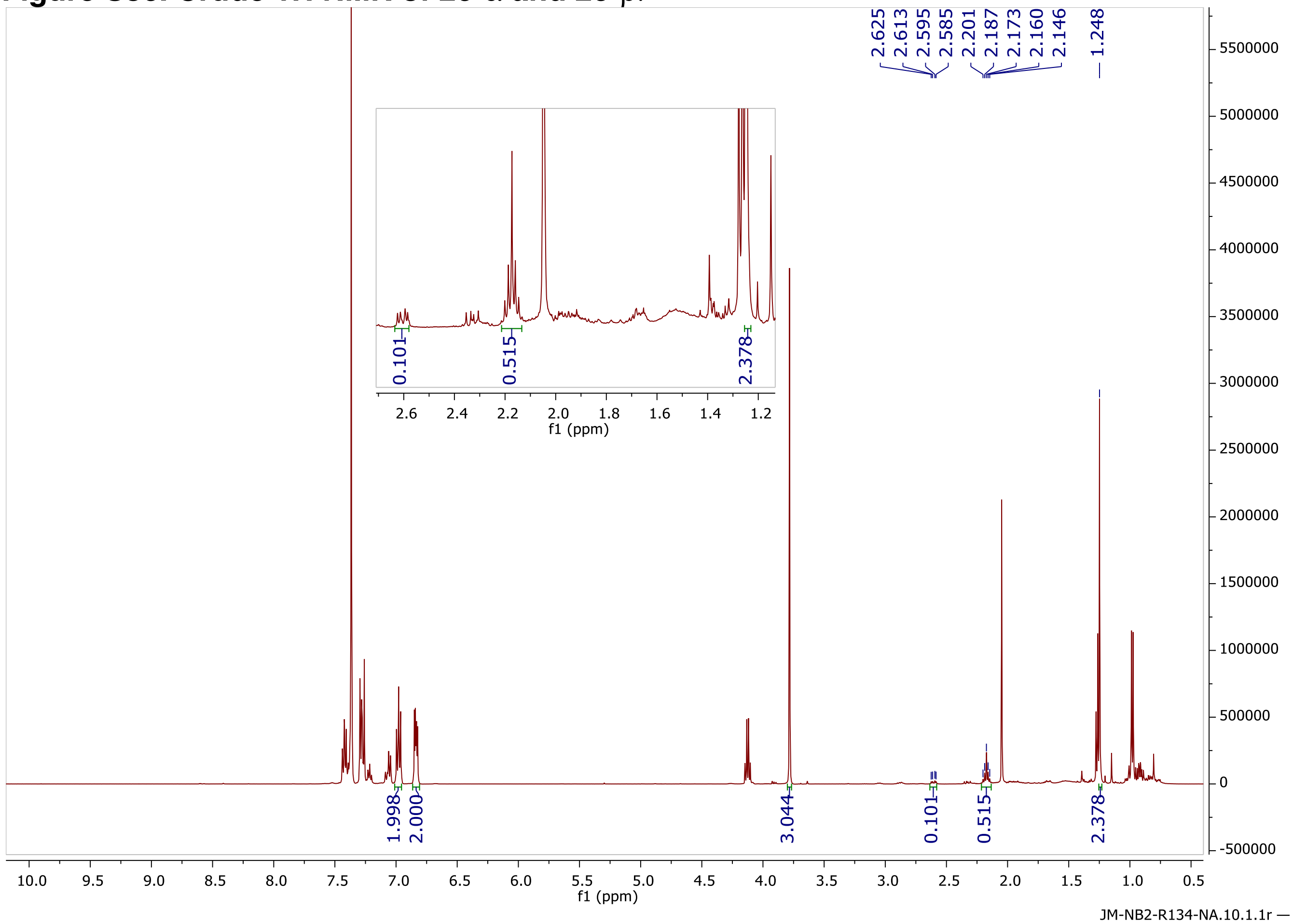
Phenyl 3,4-dimethylpentanoate (26-α) was prepared according to the general procedure for isolations from 2,3-dimethylbutane (6 equiv) and phenyl chloroformate. Comparison of the crude reaction mixture to independently synthesized product (reported in section V) resulted in 11% average NMR yield (Run 1= 12% yield; Run 2= 10% yield).

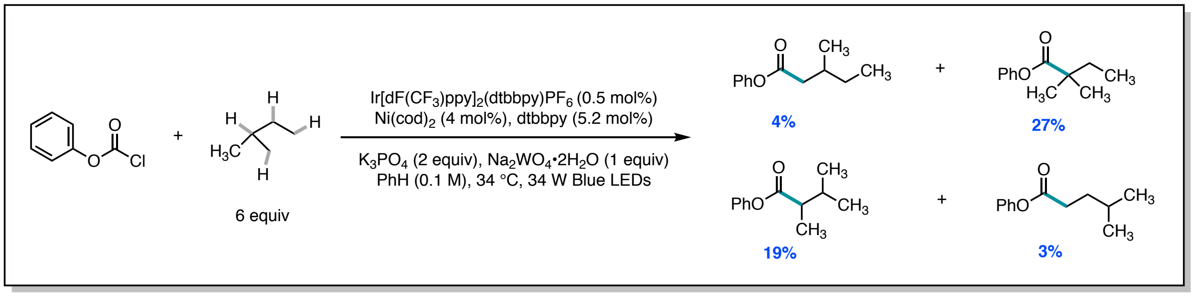
Phenyl 2,2,3-trimethylbutanoate (26-β) was prepared according to the general procedure for isolations from 2,3-dimethylbutane (6 equiv) and phenyl chloroformate. Isolation of fractions of authentic product were obtained by flash column chromatography (eluting with THF: hexanes; 0% 4 CV, 0-1% 10 CV, 5% 10 CV) enabling characterization. Comparison of the crude reaction mixture to clean product resulted in 39% average NMR yield (Run 1= 38% yield; Run 2= 40% yield).

1H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.35 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.05 (dd, J = 8.6, 1.2 Hz, 2H), 2.18 (heptet, J = 6.9 Hz, 1H), 1.25 (s, 6H), 0.98 (d, J = 6.9 Hz, 6H).

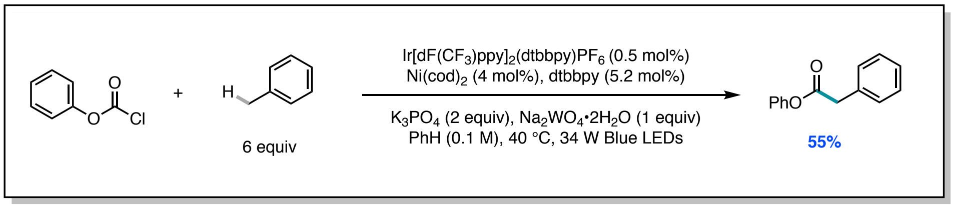
13C NMR (126 MHz, CDCl$_3$): δ 176.86, 151.10, 129.38, 125.59, 121.59, 46.02, 34.97, 21.52, 17.69.
HRMS: (ESI-TOF) calculated for $C_{13}H_{19}O_2^+$ ([M+H]$^+$): 207.1380, found: 207.1375.
FTIR (ATR cm^{-1}): 2965, 1748, 1492, 1466, 1253, 1193, 1161, 1097, 1062, 1023, 1001, 915, 727, 687.

Figure S36. Crude 1H NMR of 26-α and 26-β.



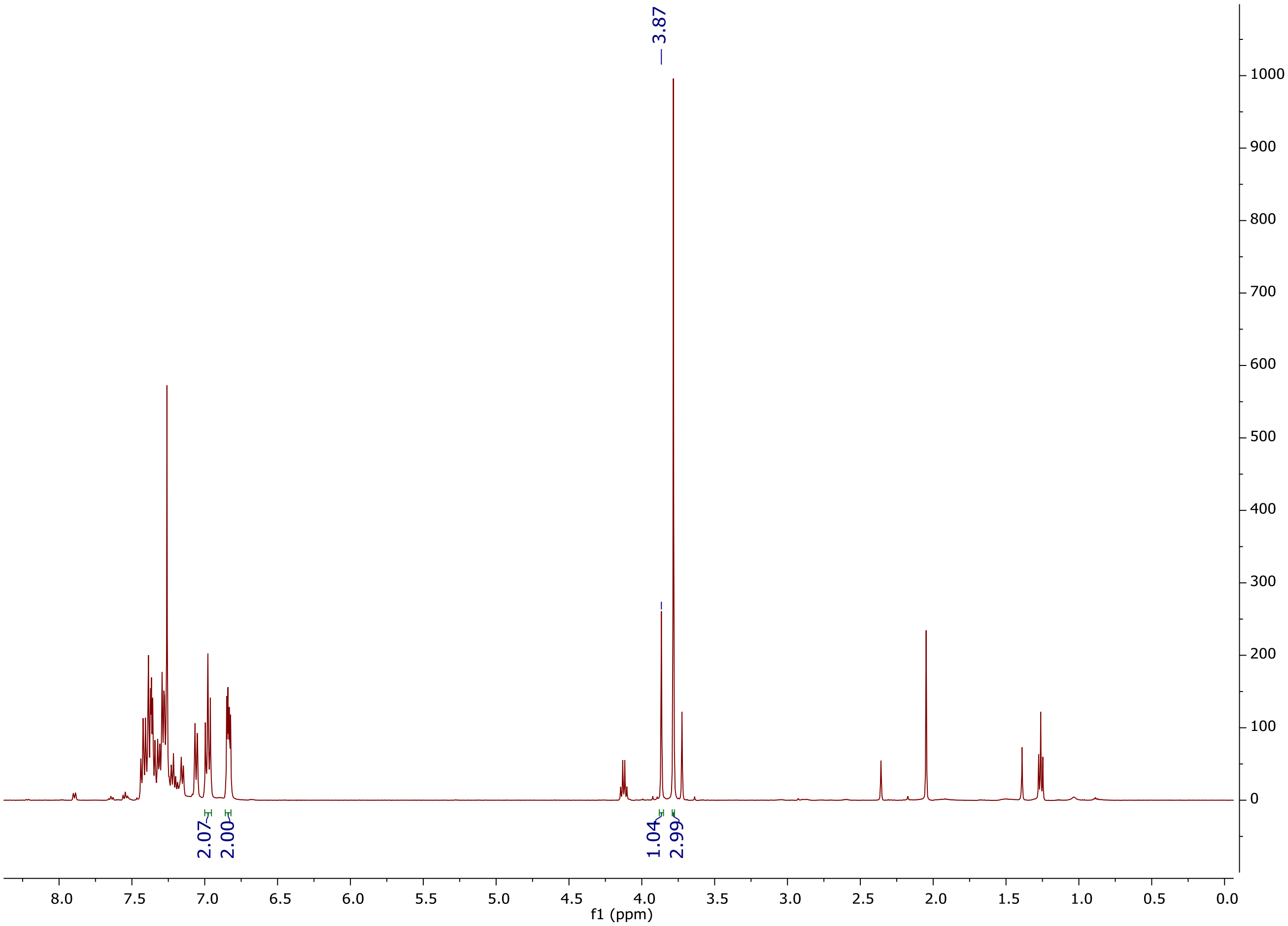


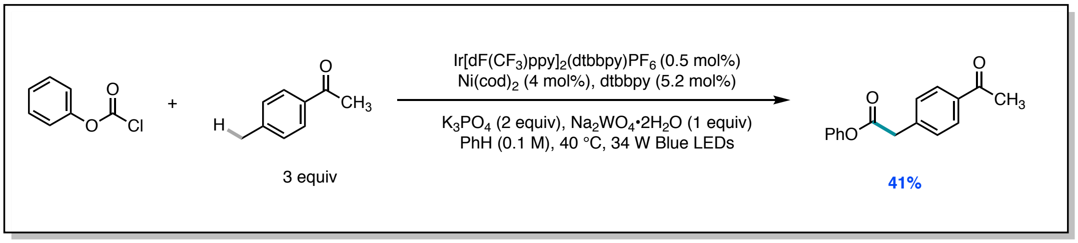
Phenyl 3-methylpentanoate (27-α) and phenyl 2,2-dimethylbutanoate (27-β) and phenyl 2,3-dimethylbutanoate (27-γ) and phenyl 4-methylpentanoate (27-δ) were prepared according to the general procedure for isolations from 2-methylbutane (6 equiv) and phenyl chloroformate. Comparison of the crude reaction mixture to independently synthesized products (reported in section V) resulted in 53% combined average GC yield (Run 1= 52% yield, with 3% yield of **27-**α, 27% yield of **27-**β, 20% yield of **27-**γ, and 2% yield of **27-**δ; Run 2= 54% yield, with 4% yield of **27-**α, 28% yield of **27-**β, 19% yield of **27-**γ, and 3% yield of **27-**δ).



Phenyl 2-phenylacetate (28) was prepared according to the general procedure for isolations from toluene (6 equiv) and phenyl chloroformate at 40 °C. Comparison of the crude reaction mixture to independently synthesized product (reported in section V) resulted in 55% average NMR yield (Run 1= 52% yield; Run 2= 58% yield).

Figure S37. Crude 1H NMR of 28.





Phenyl 2-(4-acetylphenyl)acetate (29) was prepared according to the general procedure for isolations from 4'-methylacetophenone and phenyl chloroformate at 40 °C. Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with

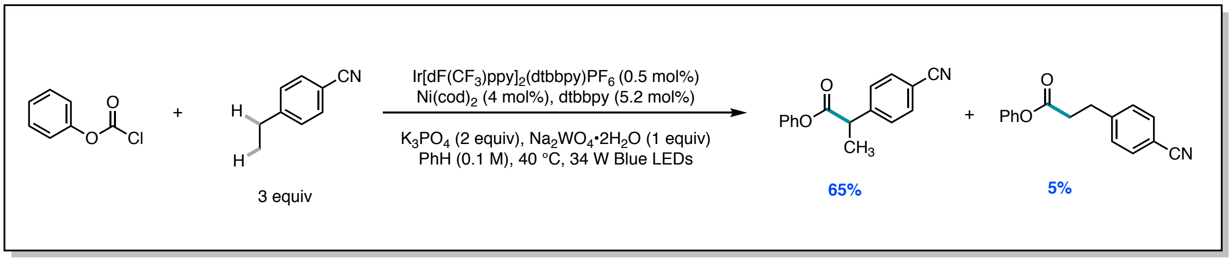
EtOAc: hexanes; 0-2%, 10 CV, 2% 3 CV, 4% 8 CV, 5% 8 CV, 6% 5 CV, 7% 29 CV, 9% 12 CV) enabling characterization. Comparison of the crude reaction mixture to clean product resulted in 41% average NMR yield (Run 1= 41% yield; Run 2= 41% yield). Note: *α-esterification of the ketone or malonate-derived products were not generated in sufficient yield to be observed.*

<u>1H NMR (500 MHz, $CDCl_3$):</u> δ 7.97 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.37 (t, J = 8.0 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.08 – 7.03 (m, 2H), 3.93 (s, 2H), 2.61 (s, 3H).

<u>13C NMR (126 MHz, $CDCl_3$):</u> 197.69, 169.27, 150.59, 138.76, 136.28, 129.65, 129.48, 128.80, 126.06, 121.36, 41.33, 26.67.

<u>HRMS:</u> (ESI-TOF) calculated for $C_{16}H_{15}O_3^+$ ($[M+H]^+$): 255.1016, found: 255.1021.

<u>FTIR (ATR cm^{-1}):</u> 1750, 1673, 1606, 1590, 1493, 1482, 1360, 1270, 1215, 1201, 1188, 1164, 1138, 1068, 1017, 1005, 955, 941, 928, 797, 772, 734, 699, 687, 600, 589, 562, 495.



Phenyl 2-(4-cyanophenyl)propanoate (30-α) was prepared according to the general procedure for isolations from 4-ethylbenzonitrile and phenyl chloroformate at 40 °C. Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with Ethyl Acetate: Hexanes; 0% 4 CV, 0-13% 10 CV, 13% 19 CV) enabling characterization. Comparison of the crude reaction mixture to clean product resulted in 65% average NMR yield (Run 1= 67% yield; Run 2= 62% yield).

<u>1H NMR (500 MHz, $CDCl_3$):</u> δ 7.68 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 6.98 (dd, J = 8.6, 1.0 Hz, 2H), 4.03 (q, J = 7.2 Hz, 1H), 1.64 (d, J = 7.2 Hz, 3H).

<u>13C NMR (126 MHz, $CDCl_3$):</u> δ 171.92, 150.52, 145.23, 132.67, 129.49, 128.53, 126.10, 121.19, 118.65, 111.50, 45.74, 18.35.

<u>HRMS:</u> (ESI-TOF) calculated for $C_{16}H_{14}NO_2^+$ ($[M+H]^+$): 252.1019, found: 252.1017.

<u>FTIR (ATR cm^{-1}):</u> 2929, 2228, 1750, 1607, 1591, 1503, 1491, 1455, 1415, 1377, 1314, 1190, 1160, 1135, 1068, 1044, 1020, 1003, 918, 880, 842, 809, 752, 687, 559, 501, 451.

Phenyl 3-(4-cyanophenyl)propanoate (30-β) was prepared alongside **31-α** according to the general procedure for isolations from 4-ethylbenzonitrile and phenyl chloroformate at 40 °C. Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with EtOAc: hexanes; 0% 4 CV, 0-13% 10 CV, 13% 19 CV) enabling characterization. Comparison of the crude reaction mixture to clean product resulted in 5% average NMR yield (Run 1= 5% yield; Run 2= 5% yield).

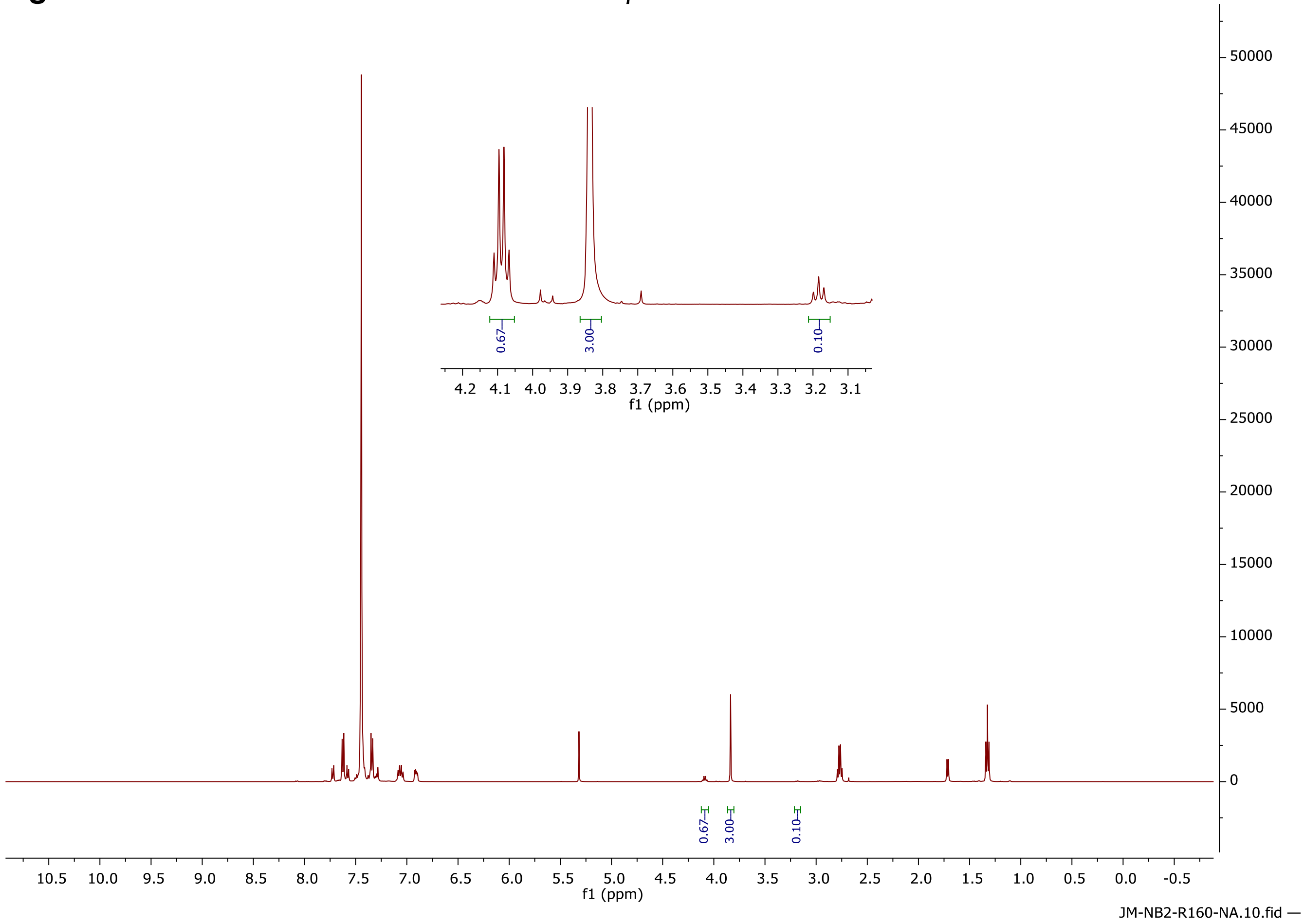
<u>1H NMR (500 MHz, $CDCl_3$):</u> δ 7.62 (d, J = 8 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.23 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 7.9 Hz, 2H), 3.13 (t, J = 7.5 Hz, 2H), 2.92 (t, J = 7.5 Hz, 2H).

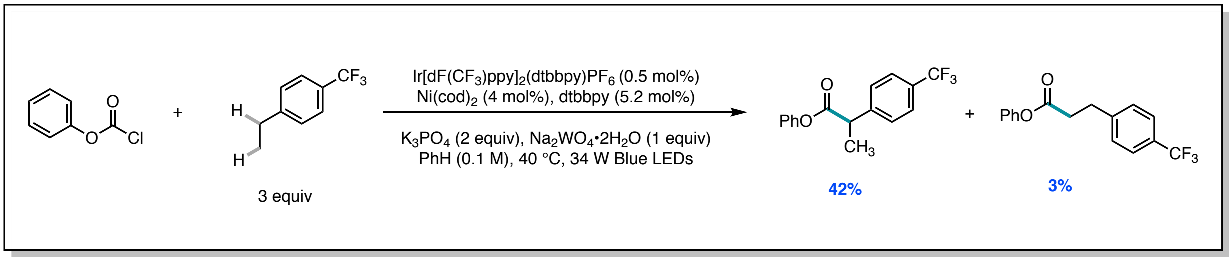
<u>13C NMR (126 MHz, $CDCl_3$):</u> δ 170.80, 150.46, 145.73, 132.47, 129.53, 129.35, 126.05, 121.41, 118.91, 110.53, 35.19, 30.89.

<u>HRMS:</u> (ESI-TOF) calculated for $C_{16}H_{14}NO_2^+$ ($[M+H]^+$): 252.1019, found: 252.1013.

<u>FTIR (ATR cm^{-1}):</u> 2981, 2226, 1758, 1509, 1374, 1246, 1195, 1160,1130, 1049.

Figure S38. Crude 1H NMR of 30-α and 30-β.





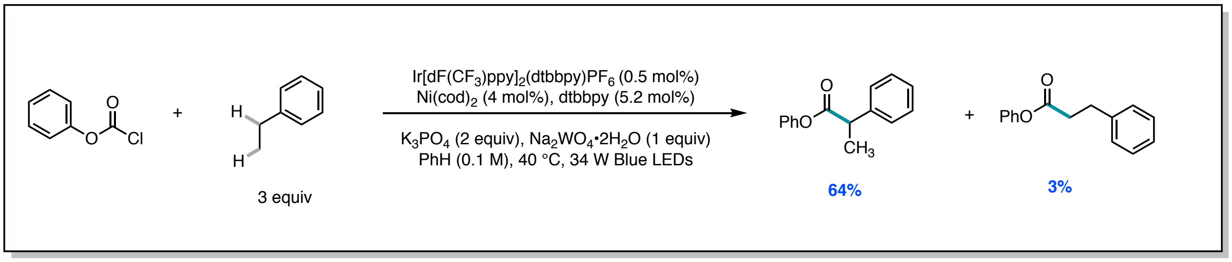
Phenyl 2-(4-(trifluoromethyl)phenyl)propanoate (31-α) was prepared according to the general procedure for isolations from 4-ethylbenzotrifluoride and phenyl chloroformate at 40 °C. Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with Ether: Pentane; 0% 15 CV, 0-5% 10 CV, 5% 10 CV) enabling characterization. Comparison of the crude reaction mixture to clean product resulted in 42% average NMR yield (Run 1= 44%; Run 2= 42%).

1H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.23 – 7.18 (m, 1H), 6.99 (dd, J = 8.7, 1.2 Hz, 2H), 4.03 (q, J = 7.2 Hz, 1H), 1.64 (d, J = 7.2 Hz, 3H).

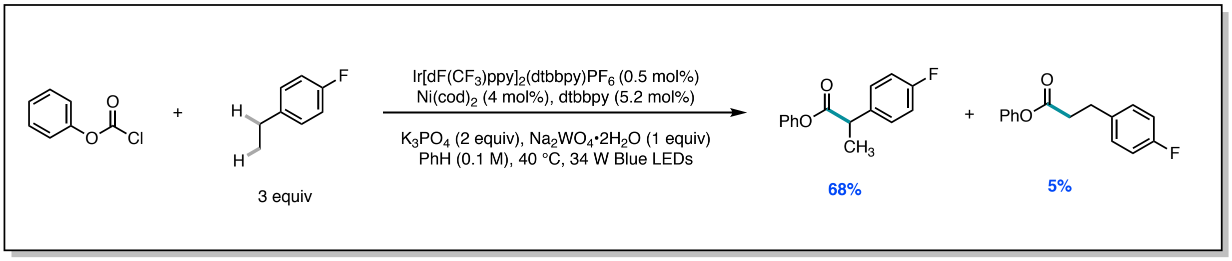
13C NMR (126 MHz, $CDCl_3$): δ 172.33, 150.61, 143.96, 129.45, 128.03, 126.00, 125.81 (q, J = 3.8 Hz), 121.26, 45.53, 18.49.

19F NMR (376 MHz, $CDCl_3$): δ -62.57.

Phenyl 3-(4-(trifluoromethyl)phenyl)propanoate (31-β) Comparison of the crude reaction mixture to independently synthesized product (reported in section V) resulted in 3% average GC yield (Run 1= 3% yield, Run 2= 2% yield).



Phenyl 2-phenylpropanoate (32-α) and phenyl 3-phenylpropanoate (32-β) were prepared according to the general procedure for isolations from ethylbenzene and phenyl chloroformate at 40 °C. Comparison of the crude reaction mixture to independently synthesized products (reported in section V) resulted in 67% average GC yield of **32-**α and **32-**β (Run 1= 66% yield, with 63% yield of **32-**α and 3% yield of **32-**β; Run 2= 67% yield, with 64% yield of **32-**α and 3% yield of **32-**β.



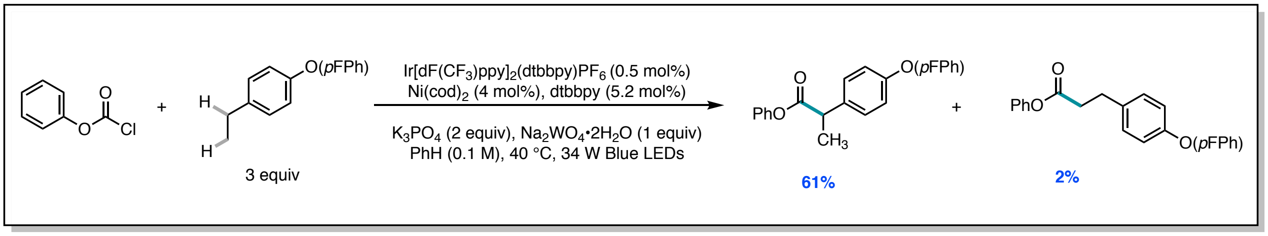
Phenyl 2-(4-fluorophenyl)propanoate (33-α) was prepared according to the general procedure for isolations from 4-fluoroethylbenzene and phenyl chloroformate at 40 °C. Isolation of fractions of authentic product for characterization were obtained using supercritical fluid chromatography with a ChiralPak AD-H (2 x 25 cm) column and the following conditions: 10% EtOH (0.1% DEA)/CO2, 100 bar, 70 mL/min, 220 nm. Spectral data were consistent with reported literature values.[13] Comparison of the crude reaction mixture to clean product resulted in 68% average NMR yield (Run 1= 67%; Run 2= 69%).

1H NMR (500 MHz, $CDCl_3$): δ 7.43 – 7.34 (m, 4H), 7.26 – 7.20 (m, 1H), 7.11 – 7.06 (m, 1H), 7.02 (dd, J = 8.6, 1.2 Hz, 2H), 3.98 (q, J = 7.2 Hz, 1H), 1.64 (d, J = 7.2 Hz, 3H).

13C NMR (126 MHz, $CDCl_3$): δ 172.94, 162.15 (d, J = 245.7 Hz), 150.78, 135.82, 135.79, 129.44,129.20 (d, J = 8.1 Hz), 125.92, 121.37, 115.70 (d, J = 21.4 Hz), 44.93, 18.63.

19F NMR (376 MHz, $CDCl_3$): δ -115.19.

Phenyl 3-(4-fluorophenyl)propanoate (33-β) was prepared according to the general procedure for isolations from 4-fluoroethylbenzene and phenyl chloroformate at 40 °C. Comparison of the crude reaction mixture to independently synthesized product (reported in section V) resulted in 5% average NMR yield (Run 1= 4%; Run 2= 5%).



Phenyl 2-(4-(4-fluorophenoxy)phenyl)propanoate (34-α) was prepared according to the general procedure for isolations from 1-ethyl-4-(4-fluorophenoxy)benzene and phenyl chloroformate at 40 °C. Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with EtOAc: hexanes; 0% 4 CV, 0-12% 12 CV) enabling characterization. Comparison of the crude reaction mixture to clean product resulted in 61% average GC yield (Run 1= 60%; Run 2= 61%).

1H NMR (500 MHz, $CDCl_3$): δ 7.35 (m, 4H), 7.21 (m, 1H), 7.07 – 6.92 (m, 8H), 3.95 (q, J = 7.2 Hz, 1H), 1.61 (d, J = 7.2 Hz, 3H).

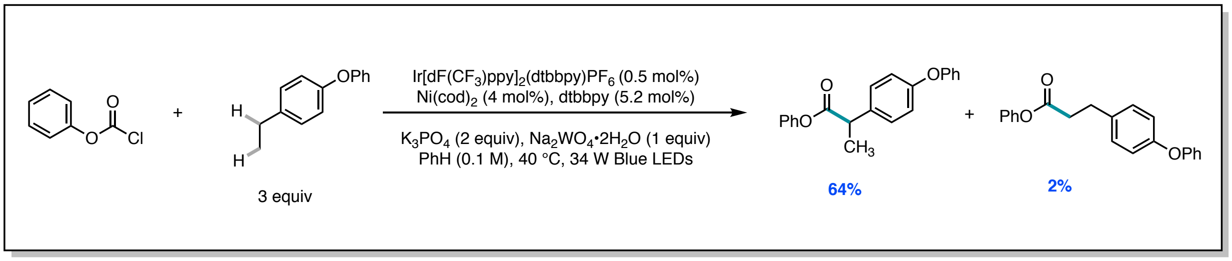
13C NMR (126 MHz, $CDCl_3$): δ 173.06, 158.92 (d, J = 242.0 Hz), 152.67 (d, J = 2.5 Hz), 150.79, 134.67, 129.38, 128.94, 125.84, 121.36, 120.72 (d, J = 8.3 Hz), 118.36, 116.36 (d, J = 23.3 Hz), 44.92, 18.62.

19F NMR (376 MHz, $CDCl_3$): δ -119.89.

HRMS: (ESI-TOF) calculated for $C_{21}H_{18}FO_3^+$ ($[M+H]^+$): 337.1235, found: 337.1241.

Phenyl 3-(4-(4-fluorophenoxy)phenyl)propanoate (34-β) was prepared alongside **34-α** according to the general procedure for isolations from 1-ethyl-4-(4-fluorophenoxy)benzene and phenyl chloroformate at 40 °C. Isolation of fractions containing authentic product and the major isomer were obtained using automated column chromatography (eluting with EtOAc: hexanes; 0% 4 CV, 0-12% 12 CV). Comparison of the crude reaction mixture to the product resulted in 2% average GC yield (Run 1= 2% yield; Run 2= 2% yield). Insufficient product was made for full characterization. Provided are NMR peaks used for identification

1H NMR (500 MHz, $CDCl_3$): δ 3.09 (t, J = 7.5 Hz, 1H), 2.91 (t, J = 7.5 Hz, 1H).



Phenyl 2-(4-phenoxyphenyl)propanoate (35-α) was prepared according to the general procedure for isolations from 1-ethyl-4-phenoxybenzene and phenyl chloroformate at 40 °C. Isolation of fractions of authentic product for characterization were obtained using supercritical fluid chromatography with a ChiralCel OJ-H (2 x 25 cm) column and the following conditions: 15% iPrOH/CO2, 100 bar, 70 mL/min, 220 nm. Comparison of the crude reaction mixture to clean product resulted in 64% average GC yield (Run 1= 68% yield; Run 2= 60% yield).

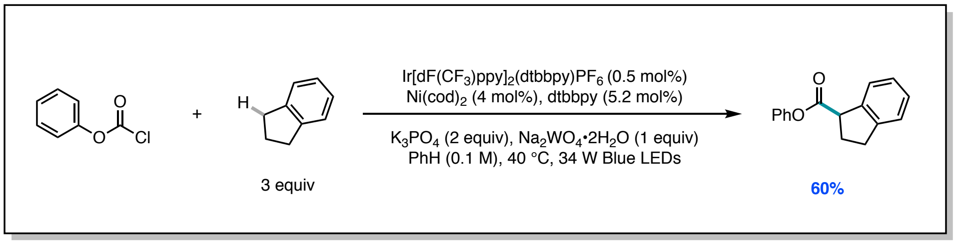
1H NMR (500 MHz, $CDCl_3$): δ 7.45 – 7.28 (m, 6H), 7.21 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 7.07 – 6.98 (m, 6H), 3.96 (q, J = 7.2 Hz, 1H), 1.63 (d, J = 7.2 Hz, 3H).

13C NMR (126 MHz, $CDCl_3$): δ 173.10, 157.05, 156.63, 150.83, 134.75, 129.81, 129.39, 128.91, 125.83, 123.42, 121.39, 119.06, 118.98, 44.97, 18.62.

HRMS: (ESI-TOF) calculated for $C_{21}H_{19}O_3^+$ ($[M+H]^+$): 319.1329, found: 319.1325.

Phenyl 3-(4-phenoxyphenyl)propanoate (35-β) was prepared alongside **35-α** according to the general procedure for isolations from 1-ethyl-4-phenoxybenzene and phenyl chloroformate at 40 °C. Isolation of fractions containing authentic product and the major isomer were obtained using automated column chromatography (eluting with EtOAc: hexanes; 0% 4 CV, 0-12% 12 CV). Comparison of the crude reaction mixture to the product resulted in 2% average GC yield (Run 1= 2% yield; Run 2= 2% yield). Insufficient product was made for full characterization. Provided are NMR peaks used for identification

1H NMR (500 MHz, $CDCl_3$): δ 3.08 (t, J = 7.7 Hz, 1H), 2.94 – 2.86 (m, 1H).

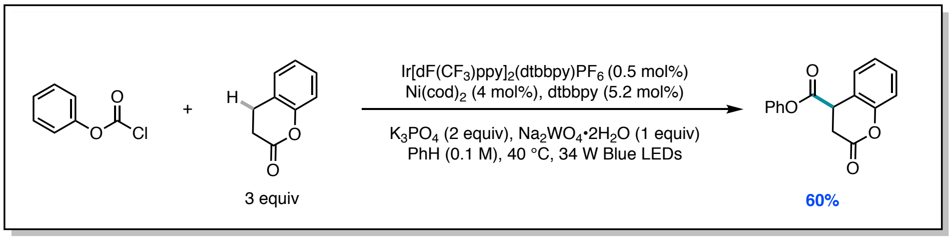


Phenyl 2,3-dihydro-1*H*-indene-1-carboxylate (36) was prepared according to the general procedure for isolations from indane and phenyl chloroformate at 40 °C. The title compound was isolated using flash column chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification, (eluting with a 0%-0.5% THF: hexanes gradient) to produce a colorless oil (Run 1= 85 mg, 59% yield; Run 2= 88 mg, 61% yield; 60% average yield).

1H NMR (500 MHz, $CDCl_3$): δ 7.63 – 7.55 (m, 1H), 7.49 – 7.39 (m, 2H), 7.37 – 7.24 (m, 5H), 7.16 – 7.11 (m, 2H), 4.36 (dd, J = 8.5, 6.1 Hz, 1H), 3.23 (ddd, J = 15.1, 8.8, 5.8 Hz, 1H), 3.04 (ddd, J = 15.6, 8.8, 6.3 Hz, 1H), 2.73 – 2.59 (m, 1H), 2.56 – 2.42 (m, 1H).

13C NMR (126 MHz, $CDCl_3$): δ 172.41, 150.95, 144.29, 140.30, 129.63, 129.46, 127.86, 126.68, 126.35, 125.86, 124.93, 124.90, 121.56, 120.97, 50.33, 31.84, 28.66.

HRMS: (ESI-TOF) calculated for $C_{16}H_{15}O_2^+$ ($[M+H]^+$): 239.1067, found: 239.1068.



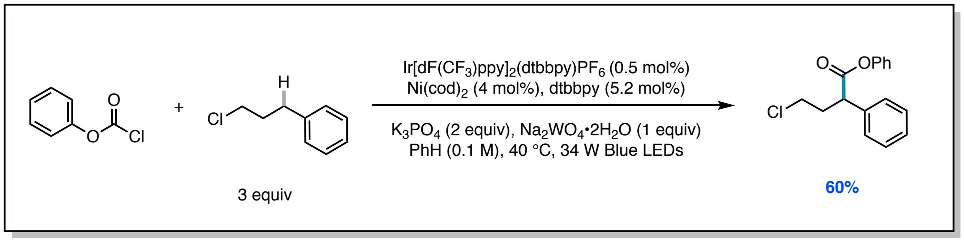
Phenyl 2-oxochromane-4-carboxylate (37) was prepared according to the general procedure for isolations from chroman-2-one and phenyl chloroformate at 40 °C. The title compound was isolated using automated column chromatography, (eluting with EtOAc: hexanes; 0% 4 CV, 0-9% 9.2 CV, 9% 6.8 CV, 9-10% 1.4 CV, 10% 13.6 CV) as a white solid (two runs were combined for isolation to give 194 mg of product, or 60% yield per run).

1H NMR (500 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.21 (qd, *J* = 7.6, 1.2 Hz, 2H), 7.14 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.02 (d, J = 7.6 Hz, 2H), 4.21 (dd, *J* = 6.3, 3.4 Hz, 1H), 3.29 (dd, *J* = 16.3, 3.4 Hz, 1H), 2.98 (dd, *J* = 16.4, 6.3 Hz, 1H).

13C NMR (126 MHz, $CDCl_3$): δ 169.28, 165.83, 151.72, 150.25, 130.13, 129.51, 128.69, 126.34, 124.92, 121.06, 118.81, 117.78, 41.52, 31.34.

HRMS: (ESI-TOF) calculated for $C_{16}H_{12}NaO_4^+$ ($[M+Na]^+$): 291.0628, found: 291.0628.

FTIR (ATR cm^{-1}): 1740, 1486, 1454, 1242, 1217, 1198, 1164, 1143, 1107, 1072, 1041, 991, 919, 895, 874, 759, 743, 727, 689, 479.

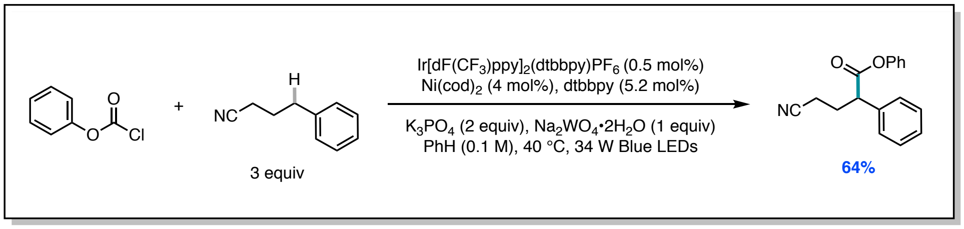


Phenyl 4-chloro-2-phenylbutanoate (38) was prepared according to the general procedure for isolations from 1-chloro-3-phenylpropane and phenyl chloroformate at 40 °C, resulting in 60% average NMR yield (Run 1= 62% yield; Run 2= 58% yield). Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with THF: hexanes; 0% 4 CV, 0-20% 20 CV) enabling characterization.

<u>1H NMR (500 MHz, $CDCl_3$):</u> δ 7.44 – 7.38 (m, 4H), 7.37 – 7.33 (m, 3H), 7.21 (t, J = 7.4 Hz, 1H), 7.01 – 6.97 (m, 2H), 4.16 (t, J = 7.6 Hz, 1H), 3.64 (dt, J = 11.4, 5.8 Hz, 1H), 3.45 (ddd, J = 11.1, 8.3, 5.1 Hz, 1H), 2.72 – 2.55 (m, 1H), 2.43 – 2.24 (m, 1H).

<u>13C NMR (126 MHz, $CDCl_3$):</u> δ 171.87, 150.66, 137.24, 129.41, 129.11, 128.10, 127.92, 125.96, 121.33, 48.37, 42.44, 35.64.

<u>HRMS:</u> (ESI-TOF) calculated for $C_{16}H_{16}ClO_2^+$ ($[M+H]^+$): 275.0833, found: 275.0833.

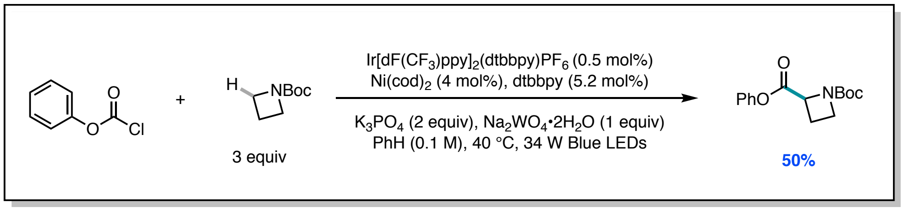


Phenyl 4-cyano-2-phenylbutanoate (39) was prepared according to the general procedure for isolations from 4-phenylbutyronitrile and phenyl chloroformate at 40 °C. The title compound was isolated using automated column chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification, (eluting with EtOAc: hexanes; 0-3% 20 CV, 3-15% 22 CV) to produce a yellow oil (Run 1= 101 mg, 63% yield; Run 2= 105 mg, 66% yield; 64% average yield).

<u>1H NMR (500 MHz, $CDCl_3$):</u> δ 7.45 – 7.31 (m, 7H), 7.24 – 7.19 (m, 1H), 7.00 – 6.94 (m, 2H), 3.99 (dd, *J* = 8.4, 6.8 Hz, 1H), 2.58 – 2.39 (m, 2H), 2.36 – 2.15 (m, 2H).

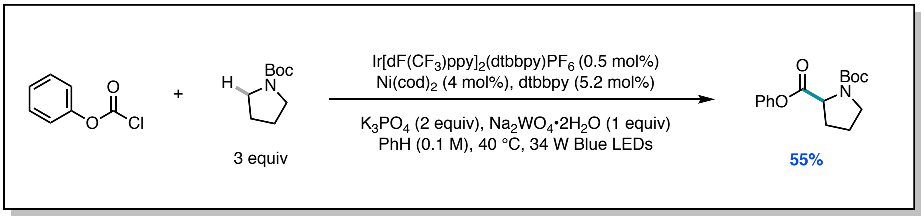
<u>13C NMR (126 MHz, $CDCl_3$):</u> δ 171.29, 150.49, 136.50, 129.47, 129.35, 128.31, 127.93, 126.11, 121.24, 118.85, 49.92, 28.63, 15.16.

<u>HRMS:</u> (ESI-TOF) calculated for $C_{17}H_{16}NO_2^+$ ($[M+H]^+$): 266.1176, found: 266.1178.

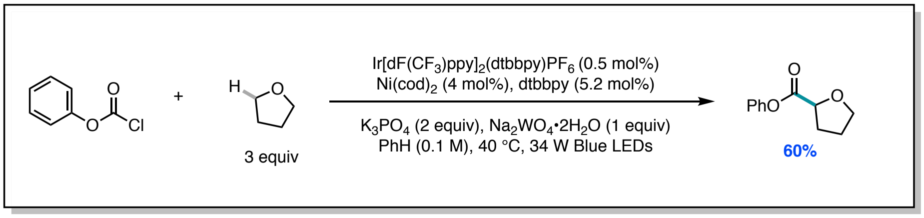


1-(*tert*-butyl) 2-phenyl azetidine-1,2-dicarboxylate (40) was prepared according to the general procedure for isolations from *tert*-butyl azetidine-1-carboxylate and phenyl chloroformate at 40 °C. The title compound was isolated using automated column chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification, (eluting with EtOAc: hexanes; 1-5% 6 CV, 5-30% 20 CV) to produce a yellow oil (Run 1= 73 mg, 44% yield; Run 2= 93 mg, 56% yield; 50% average yield).

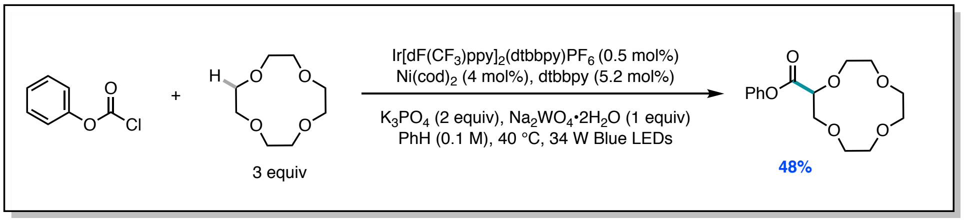
1H NMR (500 MHz, CDCl₃): δ 7.40 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 1H), 4.83 (dd, *J* = 9.2, 5.2 Hz, 1H), 4.12 (td, *J* = 8.5, 6.0 Hz, 1H), 3.97 (td, *J* = 8.5, 5.5 Hz, 1H), 2.64 (dtd, *J* = 11.4, 9.1, 6.2 Hz, 1H), 2.45 – 2.25 (m, 1H), 1.45 (s, 9H).
13C NMR (126 MHz, CDCl₃): δ 170.03, 150.61, 129.64, 129.48, 129.11, 128.06, 126.18, 121.40, 80.43, 28.48, 20.49.
HRMS: (ESI-TOF) calculated for $C_{15}H_{20}NO_4^+$ ($[M+H]^+$): 278.1387, found: 278.1385.



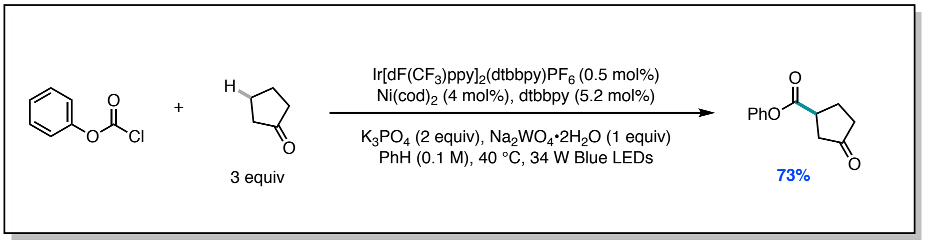
1-(*tert*-butyl) 2-phenyl pyrrolidine-1,2-dicarboxylate (41) was prepared according to the general procedure for isolations from *tert*-butyl pyrrolidine-1-carboxylate and phenyl chloroformate at 40 °C. The title compound was isolated using automated column chromatography, (eluting with EtOAc: hexanes; 0% 4 CV, 0-12% 10 CV, 12% 4 CV) to produce a white solid (Run 1= 91 mg, 52% yield; Run 2= 100 mg, 57% yield; 55% average yield).
1H NMR (500 MHz, CDCl₃): δ 7.44 – 7.33 (m, 2H), 7.25 – 7.19 (m, 1H), 7.13 – 7.06 (m, 2H), 4.56 – 4.40 (m, 1H), 3.66 – 3.41 (m, 2H), 2.45 – 2.26 (m, 1H), 2.22 – 2.13 (m, 1H), 2.08 – 1.99 (m, 1H), 1.95 (ddt, J = 10.6, 7.3, 5.3 Hz, 1H), 1.54 – 1.43 (m, 9H).
13C NMR (126 MHz, CDCl₃): δ 171.64, 154.47, 153.78, 150.79, 150.59, 129.52, 129.37, 125.95, 125.80, 121.48, 121.15, 80.23, 79.98, 59.20, 59.08, 46.64, 46.46, 31.08, 30.04, 28.44, 24.51, 23.72.
HRMS: (ESI-TOF) calculated for $C_{16}H_{21}NNaO_4^+$ ($[M+Na]^+$): 314.1363, found: 314.1366.
FTIR (ATR cm⁻¹): 2974, 1764, 1701, 1590, 1484, 1456, 1391, 1367, 1346, 1240, 1189, 1162, 1139, 1118, 1089, 1023, 1005, 975, 934, 919, 893, 858, 809, 789, 773, 750, 728, 688, 597, 538.



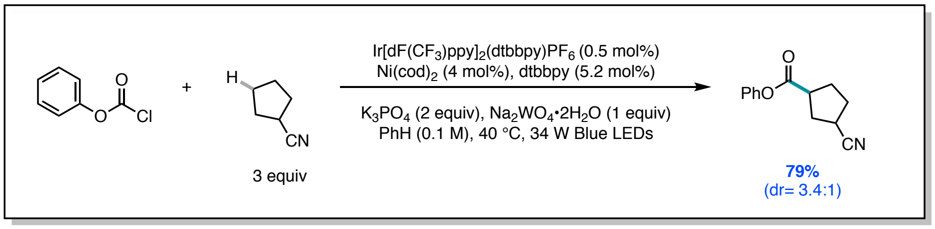
Phenyl tetrahydrofuran-2-carboxylate (42) was prepared according to the general procedure for isolations from tetrahydrofuran and phenyl chloroformate at 40 °C. The title compound was isolated using automated column chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification, (eluting with EtOAc:hexanes; 0% 4 CV, 0-12% 10 CV, 12% 10 CV) to produce a colorless oil (Run 1= 67 mg, 58% yield; Run 2= 72 mg, 62% yield; 60% average yield).
1H NMR (500 MHz, CDCl₃): δ 7.43 – 7.32 (m, 2H), 7.27 – 7.20 (m, 1H), 7.13 – 7.06 (m, 2H), 4.71 (dd, *J* = 8.5, 5.4 Hz, 1H), 4.10 (dt, *J* = 8.2, 6.8 Hz, 1H), 4.00 (td, *J* = 7.8, 6.0 Hz, 1H), 2.40 (dtd, *J* = 12.8, 8.4, 6.6 Hz, 1H), 2.27 – 2.16 (m, 1H), 2.12 – 1.92 (m, 2H).
13C NMR (126 MHz, CDCl₃): δ 171.94, 150.41, 129.49, 126.00, 121.35, 69.63, 30.45, 25.30.
HRMS: (ESI-TOF) calculated for $C_{11}H_{12}NaO_3^+$ ($[M+Na]^+$): 215.0679, found: 215.0682.



Phenyl 1,4,7,10-tetraoxacyclododecane-2-carboxylate (43) was prepared according to the general procedure for isolations from 1, 4, 7,10-tetraoxacyclododecane(12-crown-4) and phenyl chloroformate at 40 °C, resulting in 48% average NMR yield (Run 1= 48% yield; Run 2= 48% yield). Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with EtOAc: hexanes; 0% 4 CV, 0-25% 15 CV, 25% 30 CV). The compound was then placed on high vacuum with heat (55 °C) to isolate the title compound as a viscous yellow oil, enabling characterization.
1H NMR (500 MHz, $CDCl_3$): δ 7.38 (t, J = 7.9 Hz, 2H), 7.24 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 7.7 Hz, 2H), 4.69 (dd, *J* = 8.6, 2.4 Hz, 1H), 4.09 (dd, *J* = 11.9, 2.3 Hz, 1H), 4.05 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.91 – 3.84 (m, 2H), 3.81 – 3.71 (m, 9H), 3.70 – 3.64 (m, 1H).
13C NMR (126 MHz, $CDCl_3$): δ 169.53, 150.32, 129.52, 126.11, 121.37, 79.79, 71.69, 71.01, 70.94, 70.45, 70.38, 70.34.
HRMS: (ESI-TOF) calculated for $C_{15}H_{21}O_6^+$ ($[M+H]^+$): 297.1333, found: 297.1329.
FTIR (ATR cm^{-1}): 2904, 2854, 1766, 1360, 1293, 1245, 1192, 1122, 1095, 1068, 1020, 909, 843, 738, 690, 524, 501.



Phenyl 3-oxocyclopentane-1-carboxylate (44) was prepared according to the general procedure for isolations from cyclopentanone and phenyl chloroformate at 40 °C, resulting in 73% average NMR yield (Run 1= 70% yield; Run 2= 75% yield). Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with EtOAc:hexanes; 0% 4 CV, 0-5% 12 CV, 5-12% 20 CV) enabling characterization.
1H NMR (500 MHz, $CDCl_3$): δ 7.44 – 7.35 (m, 2H), 7.14 – 7.03 (m, 3H), 3.49 – 3.28 (m, 1H), 2.63 (qd, *J* = 18.5, 8.3 Hz, 2H), 2.55 – 2.42 (m, 2H), 2.31 (m, 2H).
13C NMR (126 MHz, $CDCl_3$): δ 216.13, 172.97, 150.60, 129.68, 126.24, 121.44, 41.21, 37.62, 29.85, 26.77.
HRMS: (EI-TOF) calculated for $C_{12}H_{12}O_3^+$ ($[M]^+$): 204.0781, found: 204.0782.



Phenyl 3-cyanocyclopentane-1-carboxylate (45) was prepared according to the general procedure for isolations from cyclopentylcarbonitrile and phenyl chloroformate at 40 °C, resulting in 79% average NMR yield, average dr= 3.4:1 (Run 1= 84% yield, dr= 3.2:1; Run 2= 74% yield, dr= 3.6:1). Isolation of fractions of authentic product were obtained using automated column chromatography, (eluting with Ether:hexanes; 0% 4 CV, 0-15% 10 CV, 15% 30 CV, 25% 20 CV) enabling characterization.

1H NMR of major diastereomer (400 MHz, $CDCl_3$): δ 7.51 – 7.34 (m, 2H), 7.27 – 7.10 (m, 1H), 7.07 – 6.99 (m, 2H), 3.29 (tt, J = 8.7, 6.3 Hz, 1H), 3.12 – 2.95 (m, 1H), 2.47 (ddd, J = 14.1, 8.3, 6.1 Hz, 1H), 2.39 – 2.15 (m, 3H), 2.15 – 1.88 (m, 2H).

13C NMR of major diastereomer (126 MHz, $CDCl_3$): δ 173.46, 150.51, 129.53, 126.07, 122.24, 121.31, 42.70, 34.14, 30.97, 29.30, 28.11.

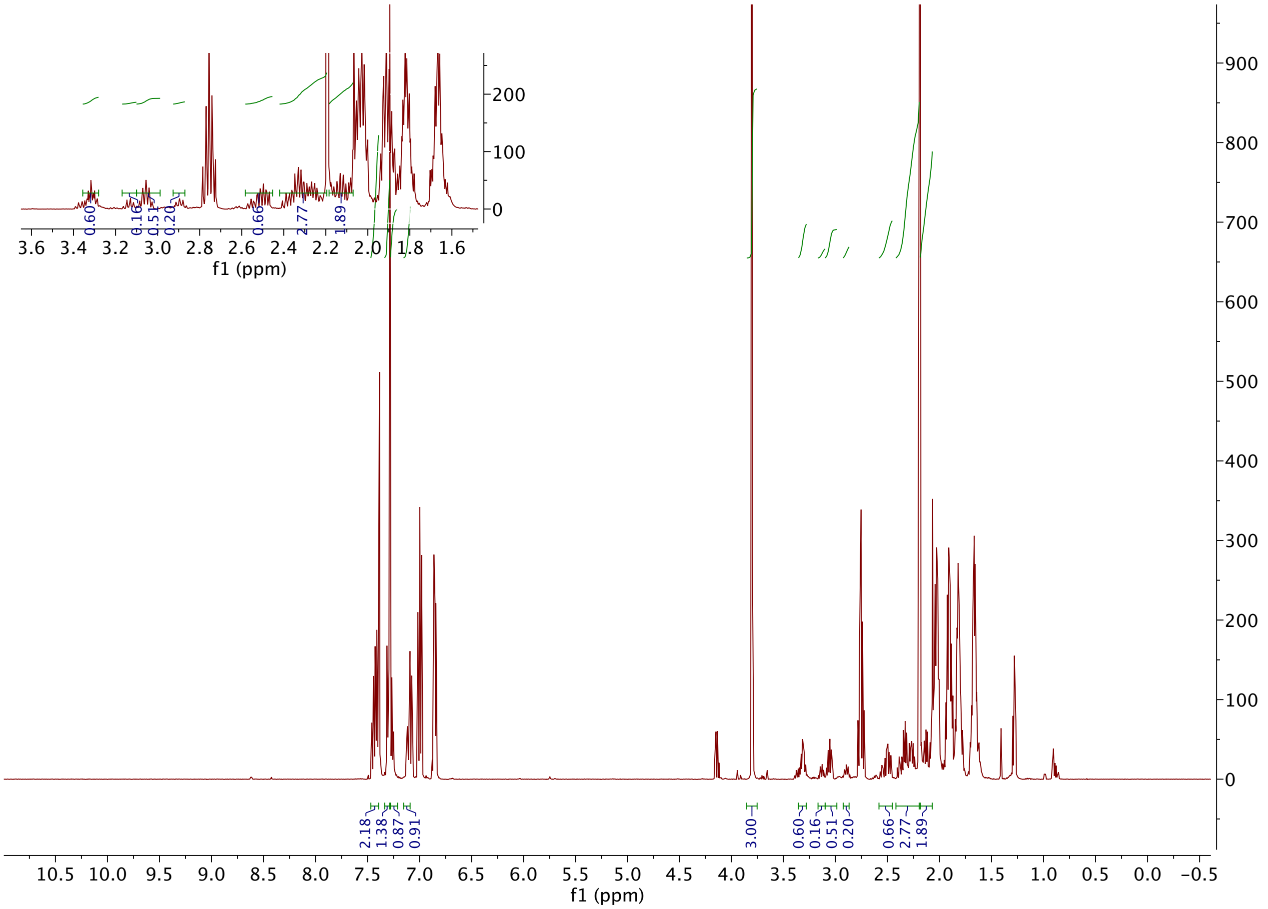
HRMS: (EI-TOF) calculated for $C_{13}H_{13}NO_2^+$ ($[M]^+$): 215.0941, found: 215.0940.

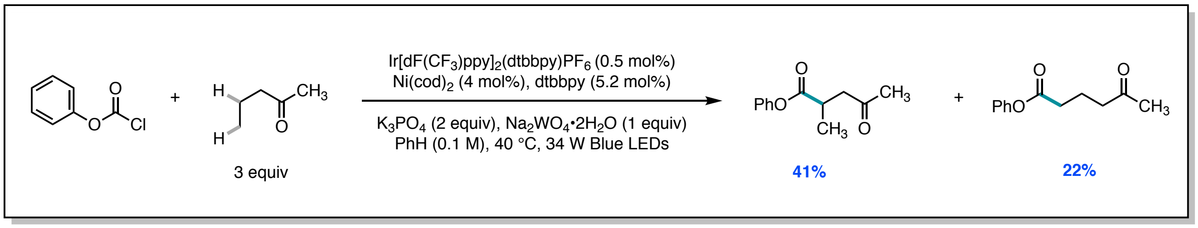
1H NMR of minor diastereomer (500 MHz, $CDCl_3$): δ 7.45 – 7.37 (m, 2H), 7.32 – 7.24 (m, 1H), 7.11 (dd, J = 8.6, 1.2 Hz, 2H), 3.18 – 3.09 (m, 1H), 2.90 (p, J = 8.3 Hz, 1H), 2.54 (dt, J = 13.4, 8.1 Hz, 1H), 2.38 (dt, J = 13.4, 8.6 Hz, 1H), 2.33 – 2.09 (m, 4H).

13C NMR of minor diastereomer (126 MHz, $CDCl_3$): δ 172.74, 150.57, 129.52, 126.03, 121.88, 121.35, 43.34, 34.14, 30.75, 29.03, 28.06.

Note: *α-esterification and β-esterification were not detected.*

Figure S39. Crude 1H NMR of 45.





Phenyl 5-oxohexanoate (46-β) was prepared according to the general procedure for isolations from pentan-2-one and phenyl chloroformate at 40 °C, resulting in 41% average NMR yield (Run 1= 37% yield; Run 2= 44% yield). Isolation of fractions of authentic product were obtained using automated column chromatography, (eluting with Ether:hexanes; 0% 4 CV, 0-15% 10 CV, 15% 30 CV, 25% 20 CV) enabling characterization.

1H NMR (500 MHz, $CDCl_3$): 7.37 (t, J = 7.9 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.6 Hz, 2H), 3.20 – 3.11 (m, 1H), 3.02 (dd, J = 18.0, 8.6 Hz, 1H), 2.63 (dd, J = 18.0, 5.1 Hz, 1H), 2.19 (s, 3H), 1.34 (d, J = 7.2 Hz, 3H).

13C NMR (126 MHz, $CDCl_3$): δ 206.49, 174.52, 150.81, 129.40, 125.79, 121.52, 46.68, 34.92, 30.06, 17.02.

HRMS: (ESI-TOF) calculated for $C_{12}H_{14}O_3^+$ ($[M+Na]^+$): 229.0835, found: 229.0833.

FTIR (ATR cm^{-1}): 2986, 1754, 1713, 1493, 1359, 1267, 1194, 1148, 1117, 1070, 736, 692.

Phenyl 2-methyl-4-oxopentanoate (46-γ) was prepared alongside **46-β** according to the general procedure for isolations from pentan-2-one and phenyl chloroformate at 40 °C, resulting in 22% average NMR yield (Run 1= 21% yield; Run 2= 23% yield). Isolation of fractions of authentic product were obtained using automated column chromatography, (eluting with Ether:hexanes; 0% 4 CV, 0-15% 10 CV, 15% 30 CV, 25% 20 CV) enabling characterization.

1H NMR (500 MHz, $CDCl_3$): δ 7.35 (m, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.10 – 7.06 (m, 2H), 2.61 (t, J = 7.2 Hz, 4H), 2.17 (s, 3H), 2.02 (p, J = 7.2 Hz, 2H).

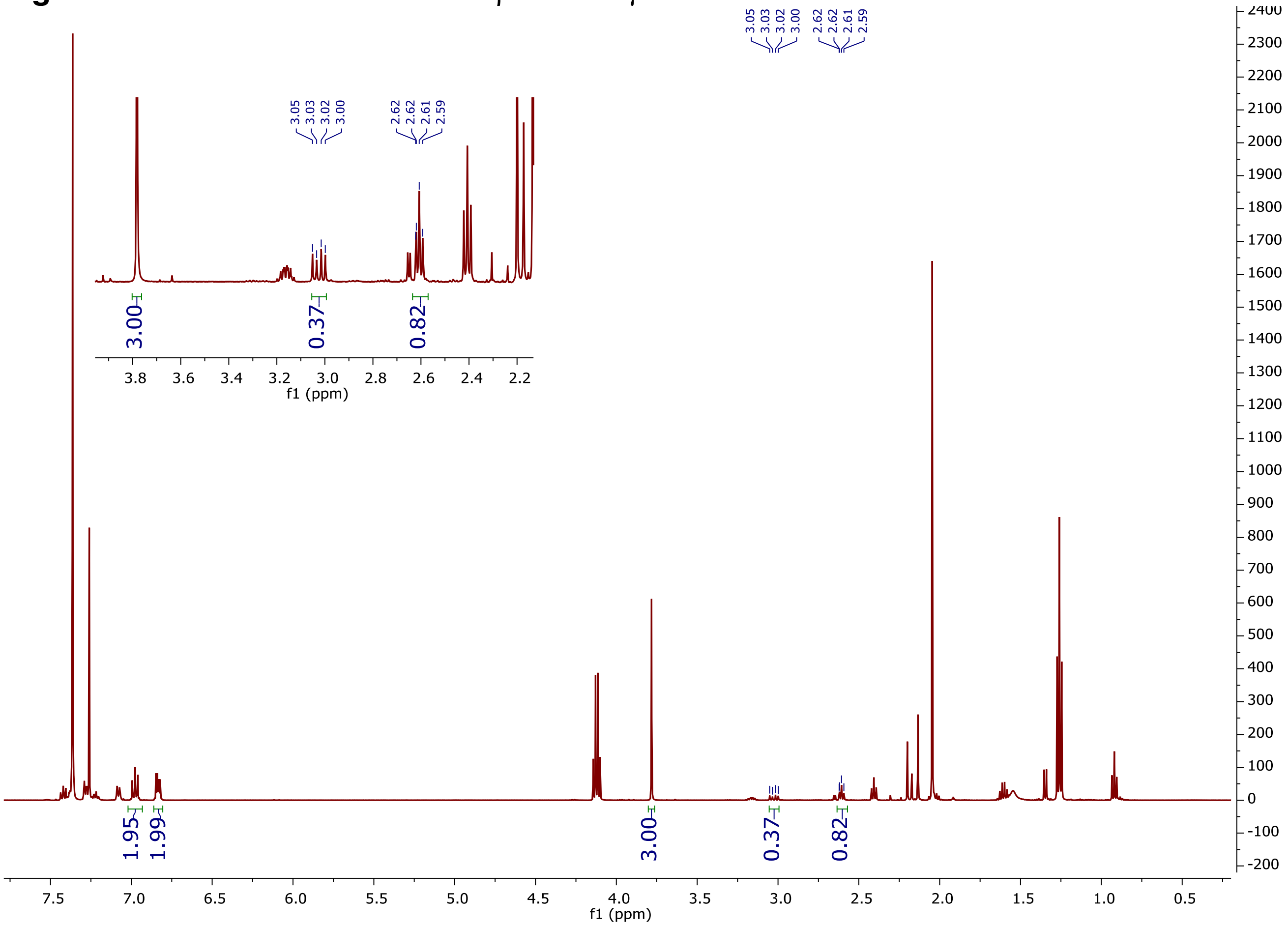
13C NMR (126 MHz, $CDCl_3$): δ 207.94, 171.74, 150.60, 129.45, 125.85, 121.54, 42.31, 33.28, 30.04, 18.78.

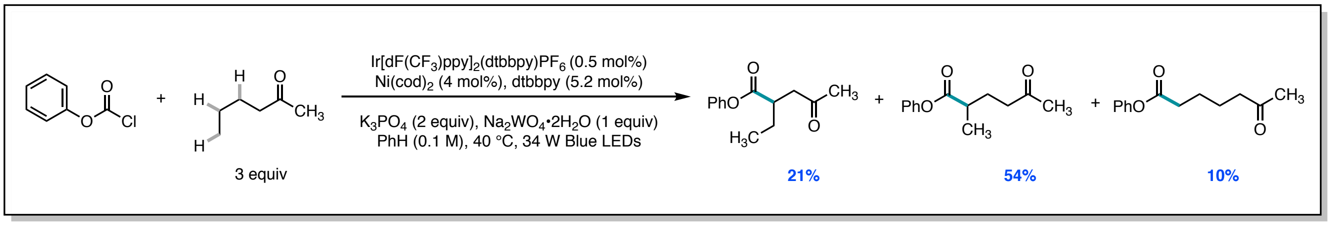
HRMS: (ESI-TOF) calculated for $C_{12}H_{14}O_3^+$ ($[M+Na]^+$): 229.0835, found: 229.0833.

FTIR (ATR cm^{-1}): 1756, 1712, 1593, 1493, 1365, 1266, 1194, 1162, 1131, 763, 736, 700.

Note: α*-esterification was not detected.*

Figure S40. Crude 1H NMR of 46-β and **46-**γ.





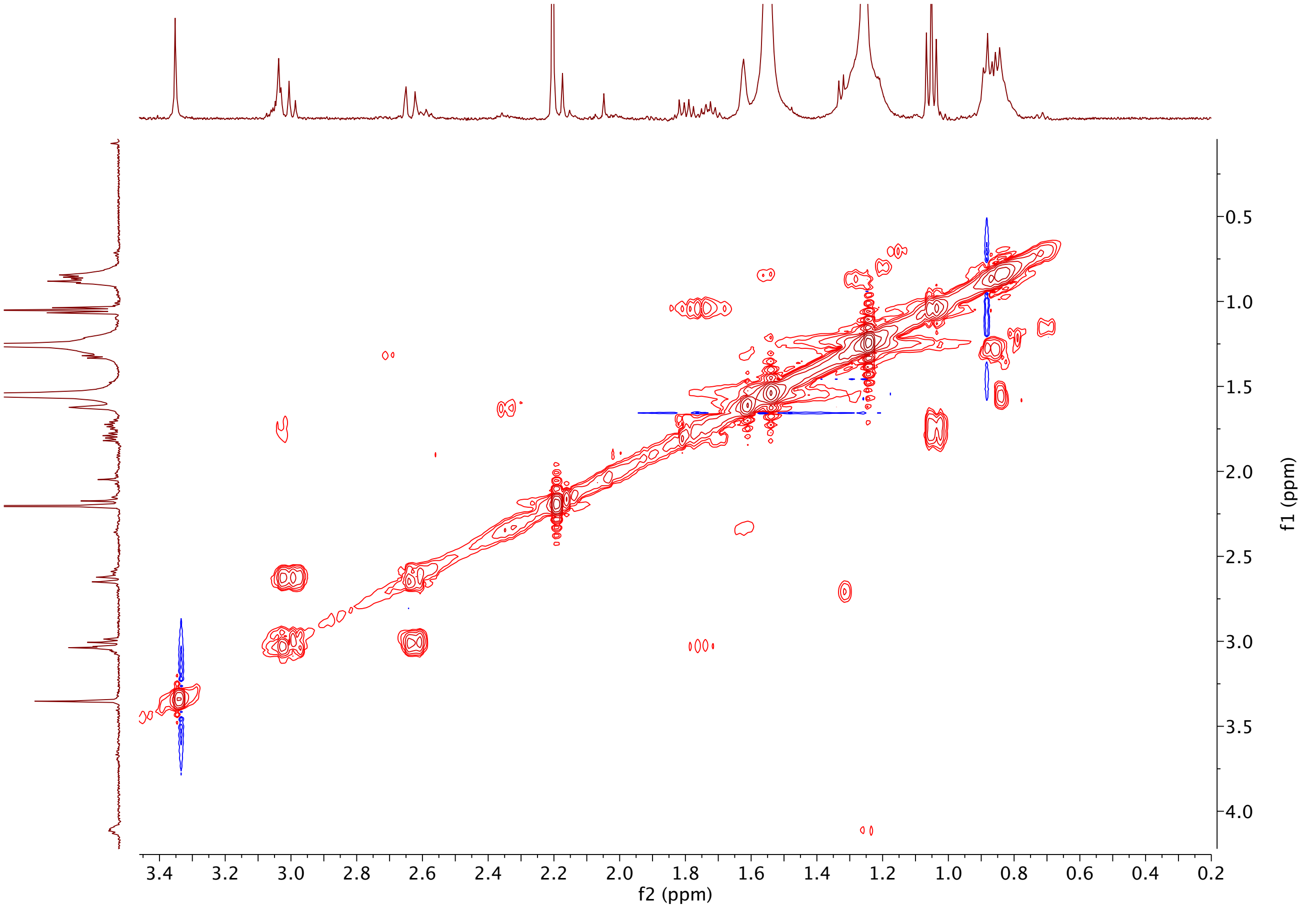
Phenyl 2-ethyl-4-oxopentanoate (47-β**)** was prepared according to the general procedure for isolations from hexan-2-one and phenyl chloroformate at 40 °C, resulting in 21% average NMR yield (Run 1= 20% yield; Run 2= 22% yield). Isolation of fractions of authentic product with amounts of **47-**γ were obtained using automated column chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification (eluting with Ether:hexanes; 0% 4 CV, 0-15% 10 CV, 15% 30 CV, 25% 20 CV) enabling characterization.

1H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.34 (m, 2H), 7.25 – 7.19 (m, 1H), 7.12 – 7.03 (m, 2H), 3.08 – 2.96 (m, 2H), 2.66 – 2.61 (m, 1H), 2.19 (s, 3H), 1.83 – 1.68 (m, 2H), 1.05 (t, J = 7.5 Hz, 3H).

13C NMR (126 MHz, $CDCl_3$): δ 206.75, 174.07, 150.81, 129.40, 125.77, 121.59, 44.76, 41.59, 30.03, 25.04, 11.50.

HRMS: (ESI-TOF) calculated for $C_{13}H_{16}NaO_3^+$ ([M+Na]$^+$): 243.0992, found: 243.0995.

Figure S41. COSY of 47-β.



Phenyl 2-methyl-5-oxohexanoate (47-γ) was prepared alongside **47-β** according to the general procedure for isolations from hexan-2-one and phenyl chloroformate at 40 °C, resulting in 54% average NMR yield (Run 1= 52% yield; Run 2= 56% yield). Isolation of fractions of authentic product with amounts of **47-β** were obtained using automated column chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification (eluting with Ether:hexanes; 0% 4 CV, 0-15% 10 CV, 15% 30 CV, 25% 20 CV) enabling characterization.

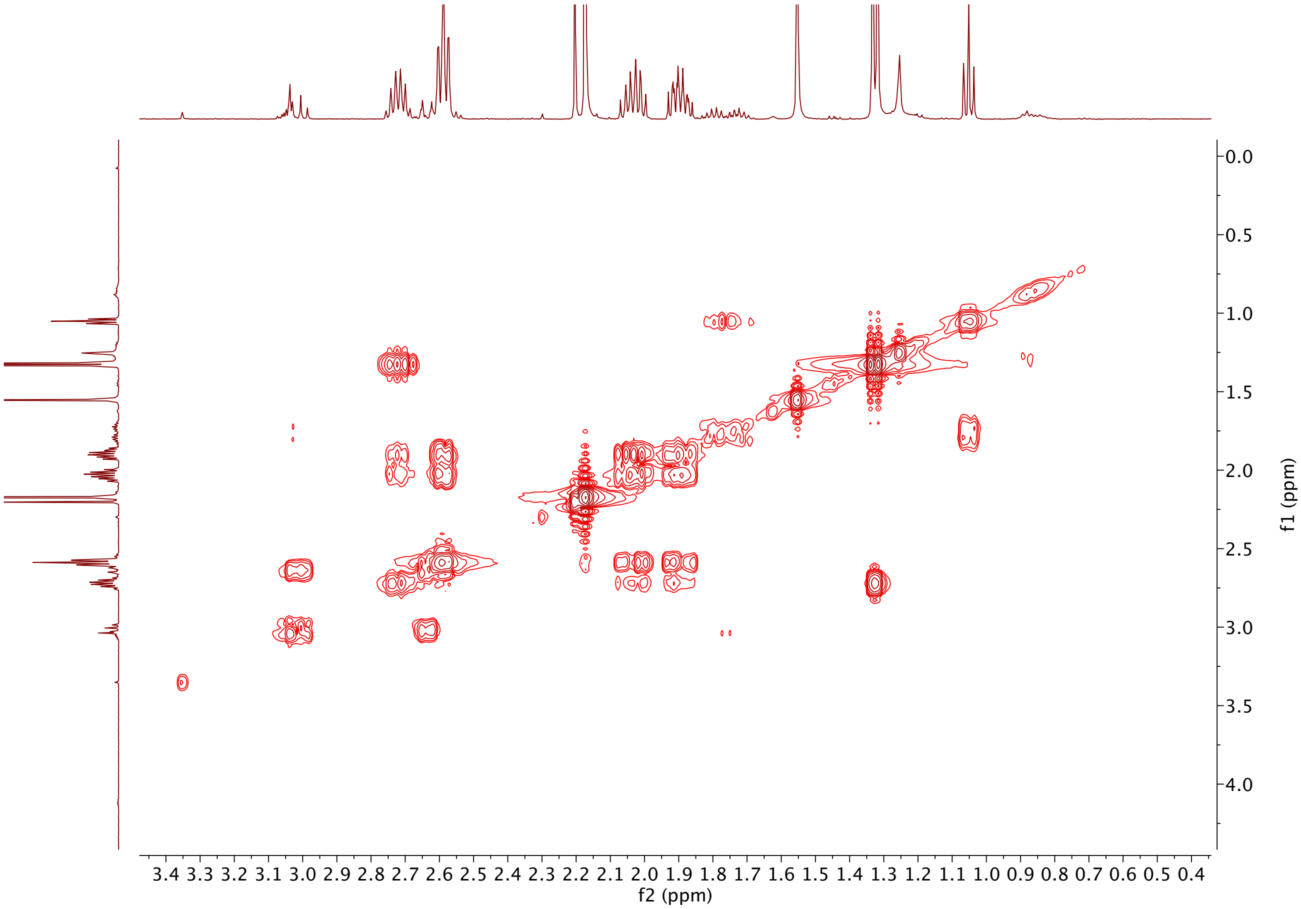
1H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.35 (m, 2H), 7.25 – 7.20 (m, 1H), 7.09 – 7.03 (m, 2H), 2.78 – 2.68 (m, 1H), 2.59 (td, J = 7.8, 7.3, 1.8 Hz, 2H), 2.17 (s, 3H), 2.09 – 1.98 (m, 1H), 1.93 – 1.85 (m, 1H), 1.32 (d, J = 7.0 Hz, 3H).

13C NMR (126 MHz, $CDCl_3$): δ 207.94, 174.66, 150.67, 129.45, 125.83, 121.48, 40.95, 38.84, 30.07, 27.26, 17.22.

HRMS: (ESI-TOF) calculated for $C_{13}H_{16}NaO_3^+$ ([M+Na]$^+$): 243.0992, found: 243.0993.

FTIR (ATR cm^{-1}): 2975, 1745, 1681, 1593, 1467, 1436, 1396, 1371, 1301, 1235, 1191, 1162, 1117, 1043, 973, 937, 917, 867, 846, 790, 719, 689, 633, 607, 529, 501, 461, 407.

Figure S42. COSY of 47-γ.



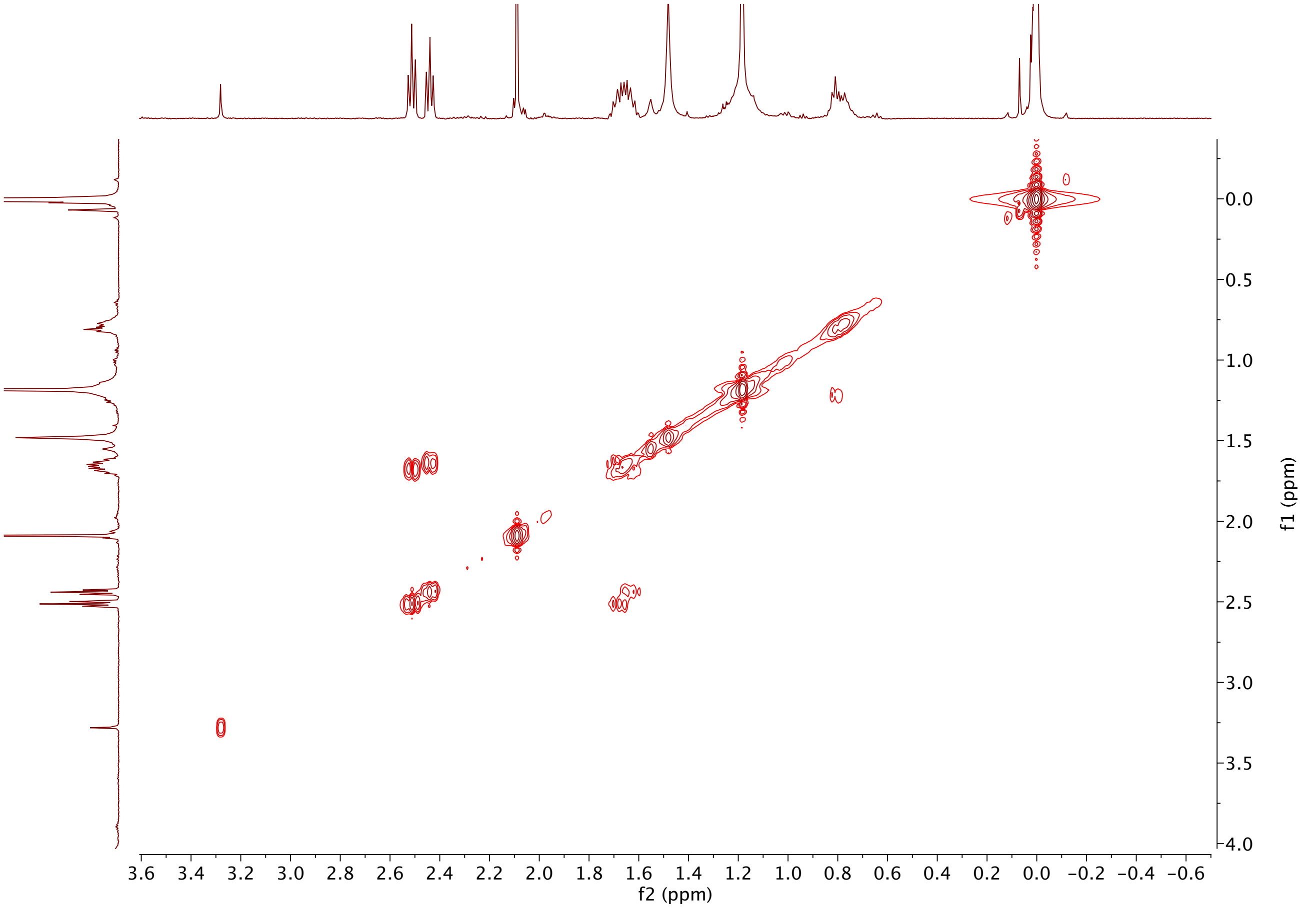
Phenyl 6-oxoheptanoate (47-δ) was prepared alongside **47-β** and **47-γ** according to the general procedure for isolations from hexan-2-one and phenyl chloroformate at 40 °C, resulting in 10% average NMR yield (Run 1= 10% yield; Run 2= 10% yield). Isolation of fractions of authentic product were obtained using automated column chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification (eluting with Ether:hexanes; 0% 4 CV, 0-15% 10 CV, 15% 30 CV, 25% 20 CV) enabling characterization.

1H NMR (500 MHz, $CDCl_3$): δ 7.38 (t, J = 7.9 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 7.6 Hz, 2H), 2.58 (t, J = 7.0 Hz, 2H), 2.51 (t, J = 6.9 Hz, 2H), 2.16 (s, 3H), 1.80 – 1.66 (m, 4H).

13C NMR (126 MHz, $CDCl_3$): δ 208.48, 171.92, 150.67, 129.44, 125.81, 121.56, 43.24, 34.15, 29.98, 24.36, 23.10.

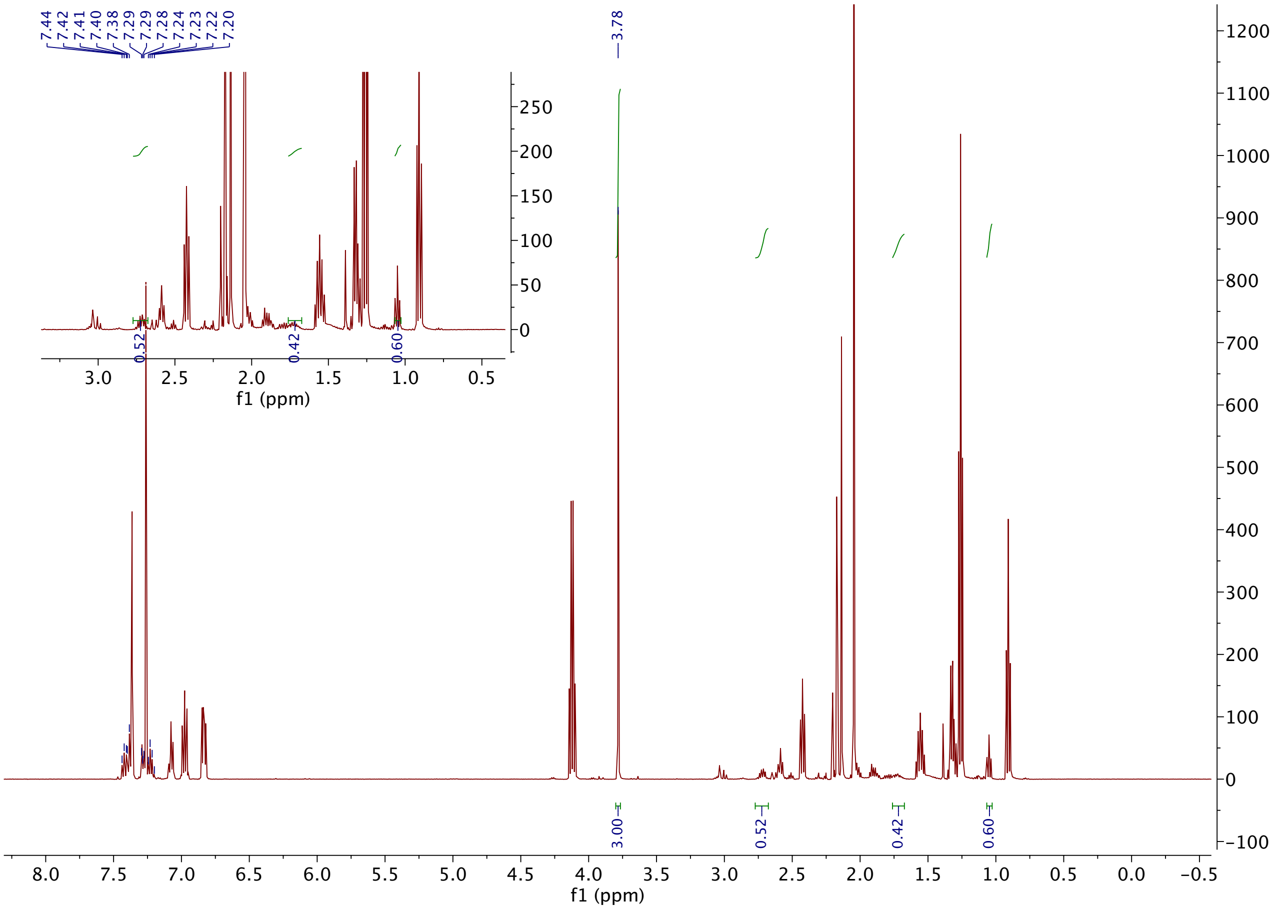
HRMS: (ESI-TOF) calculated for $C_{13}H_{16}NaO_3^+$ ([M+Na]$^+$): 243.0992, found: 243.0988.

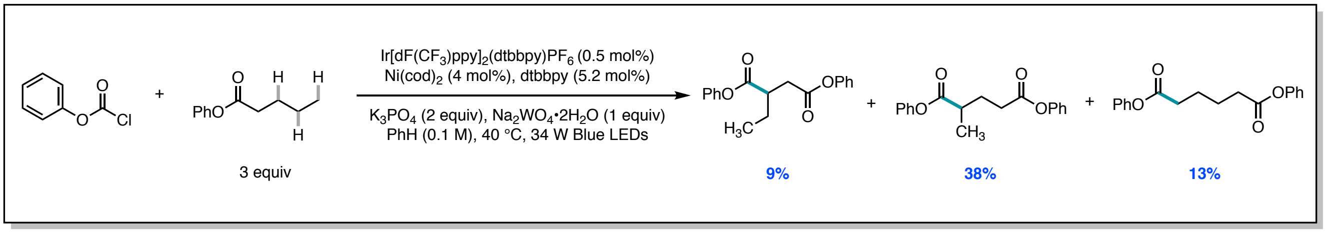
Figure S43. COSY of 47-δ.



Note: α*-esterification was not detected.*

Figure S44. Crude 1H NMR of 47.





Diphenyl 2-ethylsuccinate (48-β) was prepared according to the general procedure for isolations from phenyl pentanoate and phenyl chloroformate at 40 °C, resulting in 9% average NMR yield (Run 1= 9% yield; Run 2= 9% yield). Isolation of fractions of authentic product were obtained using automated column chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification (eluting with EtOAc:hexanes; 0% 4 CV, 0-9% 5 CV, 12% 7 CV, 15% 5 CV) enabling characterization.

1H NMR (500 MHz, CDCl$_3$): δ 7.37 (m, 4H), 7.24 – 7.20 (m, 2H), 7.08 (m, 4H), 3.20 – 3.06 (m, 2H), 2.82 (dd, *J* = 16.2, 4.2 Hz, 1H), 1.99 – 1.89 (m, 1H), 1.89 – 1.80 (m, 1H), 1.12 (t, *J* = 7.5 Hz, 3H).

13C NMR (126 MHz, CDCl$_3$): δ 173.33, 170.55, 150.70, 150.54, 129.48, 129.45, 125.97, 125.90, 121.56, 121.53, 42.76, 35.77, 25.12, 11.44.

Phenyl 2-methyl-5-oxohexanoate (48-γ) was prepared alongside **48-β** according to the general procedure for isolations from phenyl pentanoate and phenyl chloroformate at 40 °C, resulting in 38% average NMR yield (Run 1= 36% yield; Run 2= 39% yield). Isolation of fractions of authentic product were obtained using automated column chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification (eluting with EtOAc:hexanes; 0% 4 CV, 0-9% 5 CV, 12% 7 CV, 15% 5 CV) enabling characterization.

<u>1H NMR (500 MHz, $CDCl_3$):</u> δ 7.38 (dt, *J* = 7.6, 3.8 Hz, 4H), 7.27 – 7.20 (m, 2H), 7.09 (dd, *J* = 8.0, 4.5 Hz, 4H), 2.90 – 2.82 (m, 1H), 2.76 – 2.70 (m, 2H), 2.30 – 2.16 (m, 1H), 2.10 – 1.98 (m, 1H), 1.39 (d, *J* = 6.9 Hz, 3H).

<u>13C NMR (126 MHz, $CDCl_3$):</u> δ 174.44, 171.54, 150.67, 150.62, 129.47, 125.89, 121.56, 121.52, 38.84, 31.97, 28.47, 17.18.

<u>HRMS:</u> (ESI-TOF) calculated for $C_{18}H_{18}NaO_4^+$ ([M+H]$^+$): 321.1097, found: 321.1098.

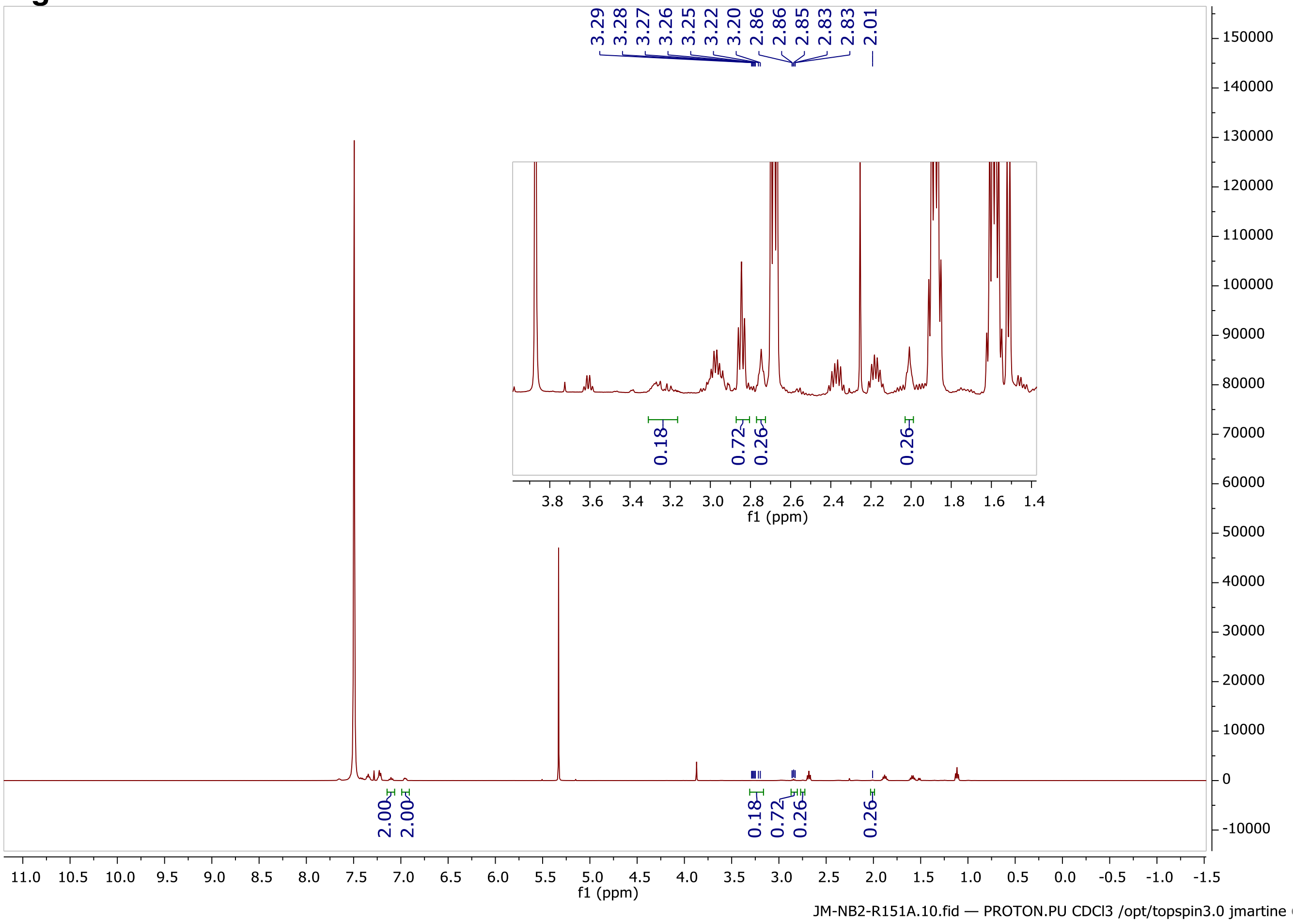
Diphenyl adipate (48-δ) was prepared alongside **48-β** and **48-γ** according to the general procedure for isolations from phenyl pentanoate and phenyl chloroformate at 40 °C, resulting in 13% average NMR yield (Run 1= 13% yield; Run 2= 13% yield). Isolation of fractions of authentic product were obtained using automated column chromatography, concentrating the reaction mixture *in vacuo* onto silica prior to purification (eluting with EtOAc:hexanes; 0% 4 CV, 0-9% 5 CV, 12% 7 CV, 15% 5 CV) enabling characterization.

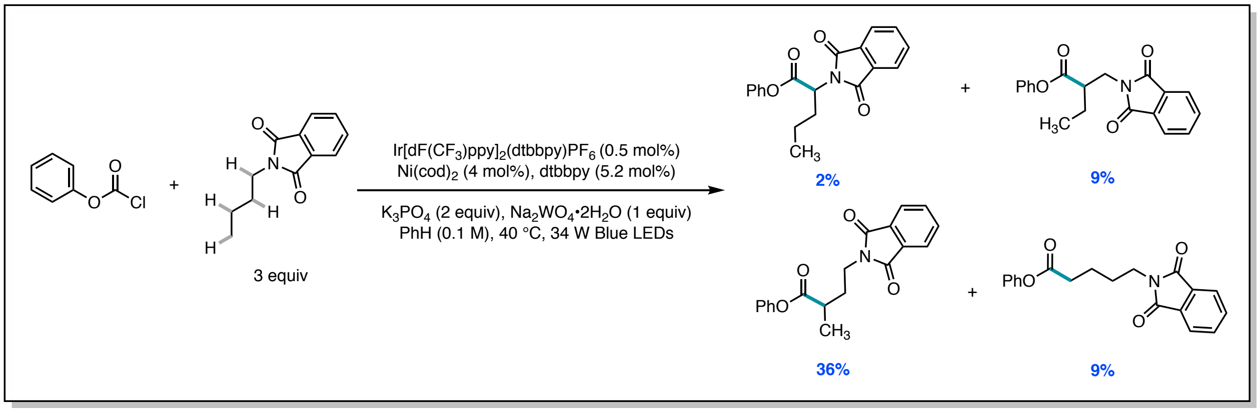
<u>1H NMR (500 MHz, $CDCl_3$):</u> δ 7.40 – 7.34 (m, 2H), 7.25 – 7.21 (m, 1H), 7.11 – 7.04 (m, 2H), 2.68 – 2.54 (m, 2H), 1.90 (q, J = 3.4 Hz, 2H).

<u>13C NMR (126 MHz, $CDCl_3$):</u> δ 171.79, 150.65, 129.45, 125.84, 121.57, 34.01, 24.32.

Note: α*-esterification was not observed.*

Figure S45. Crude 1H NMR of 48.





Phenyl 2-(1,3-dioxoisoindolin-2-yl)pentanoate (49-α) was prepared according to the general procedure for isolations from 2-butylisoindoline-1,3-dione and phenyl chloroformate at 40 °C, resulting in 2% average NMR yield (Run 1= 2% yield; Run 2= 2% yield). Yield was assigned based on **55-**α chemical shift for the methine proton of the esterification of propyl phthalimide: δ 5.01 (dd, J = 10.5, 5.1 Hz). δ 5.10 (dd, J = 10.5, 5.1 Hz).

Phenyl 2-((1,3-dioxoisoindolin-2-yl)methyl)butanoate (49-β) was prepared alongside **49-**α according to the general procedure for isolations from 2-butylisoindoline-1,3-dione and phenyl chloroformate at 40 °C, resulting in 9% average NMR yield (Run 1= 8% yield; Run 2= 9% yield). Isolation of fractions of authentic product were obtained using automated column chromatography, (eluting with EtOAc:hexanes; 0% 4 CV, 0-8% 10 CV, 8% 32 CV, 10% 29 CV, 11% 3 CV, 15% 7 CV) enabling characterization.
1H NMR (500 MHz, $CDCl_3$): Isolated material contains 28% of phenyl 4-(1,3-dioxoisoindolin-2-yl)-2-methylbutanoate (50-γ) δ 7.88 – 7.83 (m, 2H), 7.72 (dt, J = 4.9, 2.4 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.23 – 7.18 (m, 1H), 7.10 (dd, J = 8.6, 1.2 Hz, 2H), 4.14 (dd, J = 13.9, 8.3 Hz, 1H), 3.94 (dd, J = 13.9, 5.7 Hz, 1H), 3.05 (tt, J = 8.6, 5.4 Hz, 1H), 1.95 – 1.84 (m, 1H), 1.82 – 1.73 (m, 1H), 1.10 (t, J = 7.4 Hz, 3H).
13C NMR (126 MHz, $CDCl_3$): Isolated material contains 28% of phenyl 4-(1,3-dioxoisoindolin-2-yl)-2-methylbutanoate (50-γ). HSQC used to assign carbon peaks. δ 171.97, 168.17, 150.58, 134.13, 131.94, 129.42, 125.88, 123.46, 121.59, 46.42, 39.17, 23.10, 11.42.

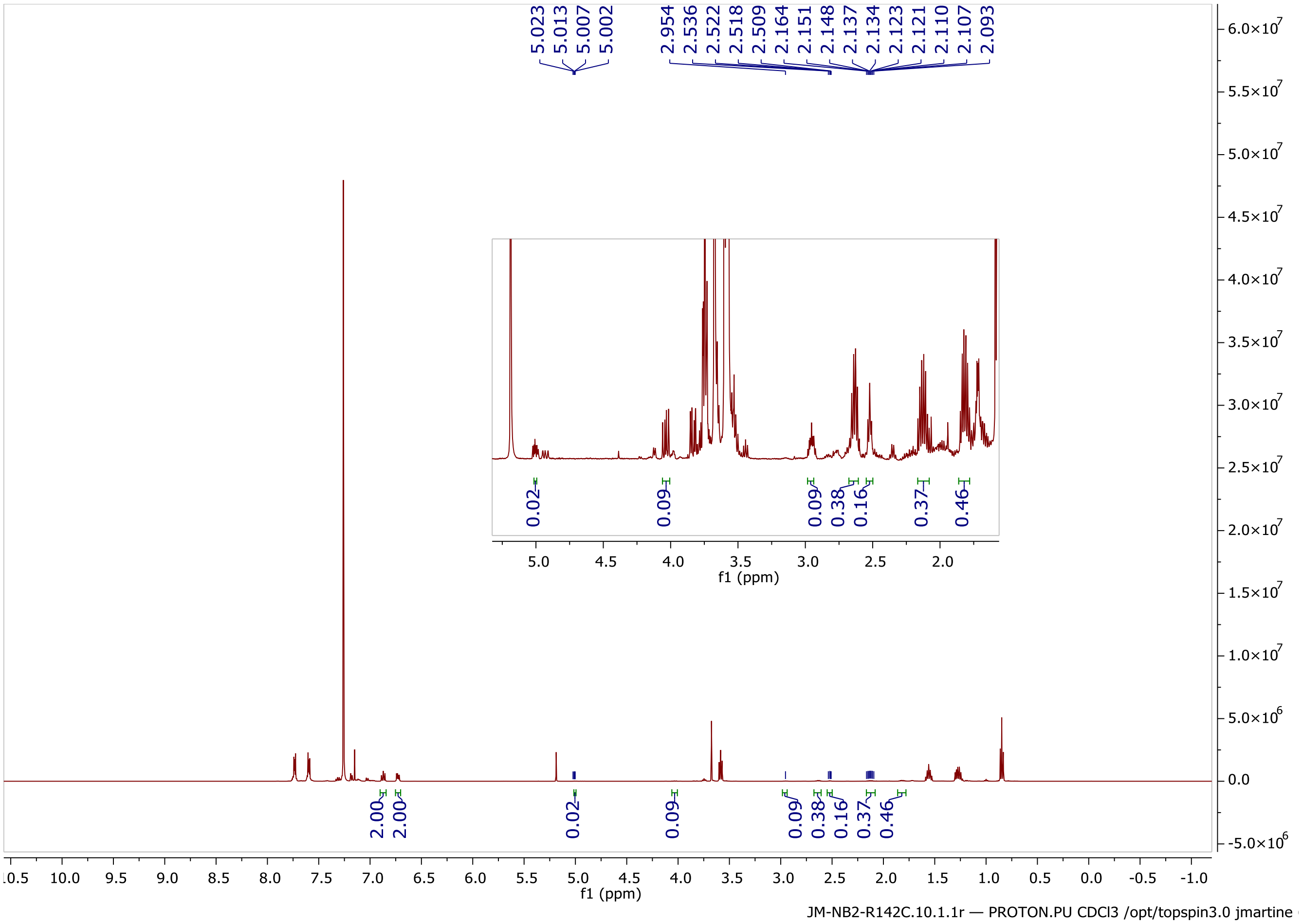
Phenyl 4-(1,3-dioxoisoindolin-2-yl)-2-methylbutanoate (49-γ) was prepared alongside **49-**α and **49-**β according to the general procedure for isolations from 2-butylisoindoline-1,3-dione and phenyl chloroformate at 40 °C, resulting in 36% average NMR yield (Run 1= 35% yield; Run 2= 37% yield). Isolation of fractions of authentic product were obtained using automated column chromatography, (eluting with EtOAc:hexanes, 0% 4 CV, 0-8% 10 CV, 8% 32 CV, 10% 29 CV, 11% 3 CV, 15% 7 CV) enabling characterization.
1H NMR (500 MHz, $CDCl_3$): δ 7.85 (m, 2H), 7.71 (m, 2H), 7.40 – 7.34 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.13 (dd, J = 8.6, 1.0 Hz, 2H), 3.84 (td, J = 6.8, 2.0 Hz, 2H), 2.78 – 2.68 (m, 1H), 2.27 – 2.17 (m, 1H), 1.97 – 1.86 (m, 1H), 1.39 (d, J = 7.1 Hz, 3H).
13C NMR (126 MHz, $CDCl_3$): δ 174.31, 168.39, 150.76, 134.04, 132.10, 129.44, 125.82, 123.33, 121.61, 37.26, 35.86, 32.01, 17.32.
HRMS: (ESI-TOF) calculated for $C_{19}H_{17}NNaO_4^+$ ($[M+Na]^+$): 345.0972, found: 346.1055.
FTIR (ATR cm^{-1}): 2980, 1735, 1708, 1593, 1493, 1466, 1437, 1395, 1371, 1238, 1193, 1161, 1127, 1071, 1044, 976, 918, 870, 791, 719, 690, 633, 607, 529, 500, 462, 411.

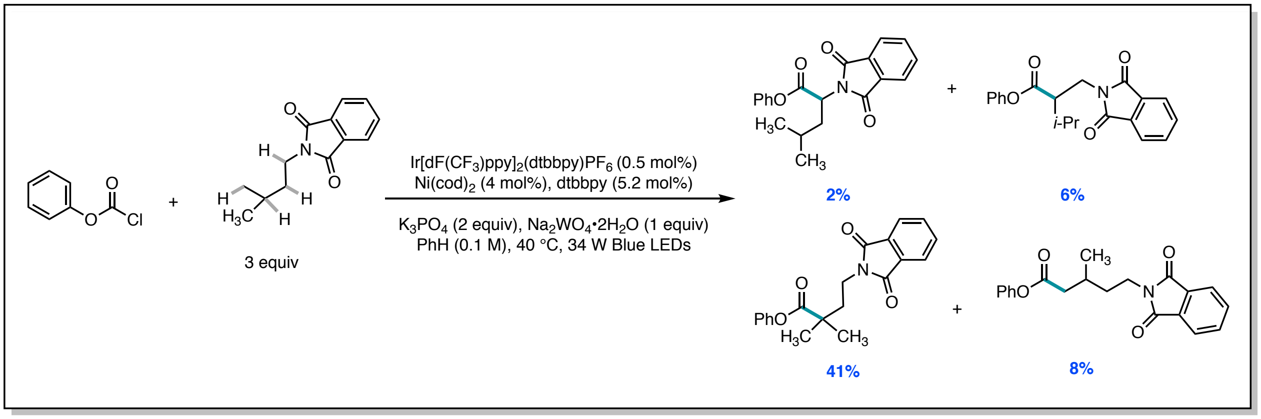
Phenyl 5-(1,3-dioxoisoindolin-2-yl)pentanoate (49-δ) was prepared alongside **49-α** and **49-β** and **49-δ** according to the general procedure for isolations from 2-butylisoindoline-1,3-dione and phenyl chloroformate at 40 °C, resulting in 9% average NMR yield (Run 1= 8% yield; Run 2= 9% yield). Isolation of fractions of authentic product were obtained using automated column chromatography, (eluting with EtOAc:hexanes; 0% 4 CV, 0-8% 10 CV, 8% 32 CV, 10% 29 CV, 11% 3 CV, 15% 7 CV) enabling characterization.

<u>1H NMR (500 MHz, CDCl₃):</u> Isolated with 30% of Phenyl 4-(1,3-dioxoisoindolin-2-yl)-2-methylbutanoate (50-γ). δ 7.85 (dd, J = 5.5, 3.1 Hz, 2H), 7.72 (dd, J = 5.5, 3.0 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.24 – 7.16 (m, 1H), 7.06 (d, J = 7.9 Hz, 2H), 3.79 – 3.71 (m, 2H), 2.68 – 2.57 (m, 2H), 1.84 – 1.79 (m, 4H).

<u>13C NMR (126 MHz, CDCl₃):</u> Isolated with 30% of Phenyl 4-(1,3-dioxoisoindolin-2-yl)-2-methylbutanoate (50-γ). δ 171.72, 168.43, 150.65, 134.02, 133.98, 132.10, 129.42, 125.79, 123.28, 121.59, 121.57, 37.46, 33.76, 27.98, 22.13.

Figure S46. Crude NMR of 49.





Phenyl 2-(1,3-dioxoisoindolin-2-yl)-4-methylpentanoate (50-α) was prepared according to the general procedure for isolations from 2-isopentylisoindoline-1,3-dione and phenyl chloroformate at 40 °C, resulting in 2% average NMR yield (Run 1= 1% yield; Run 2= 2% yield). Yield was assigned based on **55-α** chemical shift for the methine proton of the esterification of propyl phthalimide: δ 5.01 (dd, J = 10.5, 5.1 Hz). δ 5.10 (dd, J = 10.5, 5.1 Hz).

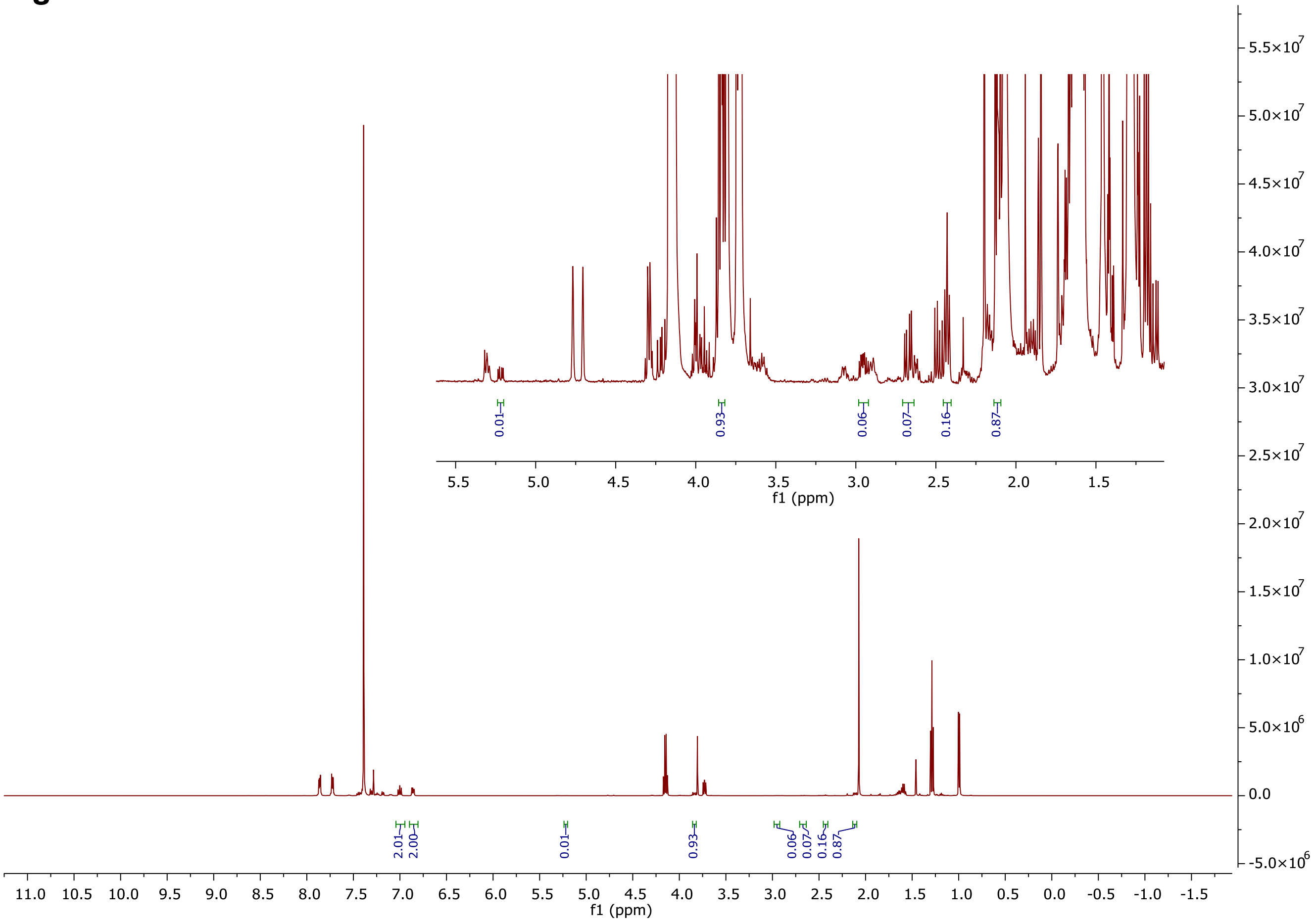
Phenyl 2-((1,3-dioxoisoindolin-2-yl)methyl)-3-methylbutanoate (50-β) was prepared alongside **51-α** according to the general procedure for isolations from 2-isopentylisoindoline-1,3-dione and phenyl chloroformate at 40 °C, resulting in 6% average NMR yield (Run 1= 6% yield; Run 2= 5% yield). Isolation of fractions of authentic product with **52-γ** were obtained using automated column chromatography, (eluting with EtOAc:hexanes; 0% 4 CV, 0-10% 12 CV, 10% 50 CV, 15% 16 CV, 25% 9 CV, 50% 3 CV) enabling characterization.
1H NMR (500 MHz, CDCl$_3$): Isolated material contains 88% of Phenyl 4-(1,3-dioxoisoindolin-2-yl)-2,2-dimethylbutanoate (51-γ), which overlap in the aryl region. 4.18 (dd, J = 13.9, 9.2 Hz, 1H), 3.95 (dd, J = 14.0, 4.9 Hz, 1H), 2.93 (ddd, J = 9.2, 7.2, 5.0 Hz, 1H), 2.19 – 2.11 (m, 1H), 1.20 (d, J = 6.8 Hz, 3H), 1.15 (d, J = 6.8 Hz, 3H).
13C NMR (126 MHz, CDCl$_3$): Isolated material contains 88% of Phenyl 4-(1,3-dioxoisoindolin-2-yl)-2,2-dimethylbutanoate (51-γ), HMBC and relative intensities used to assign carbon peaks. δ 171.67, 168.12, 150.55, 134.11, 131.99, 129.42, 125.86, 123.43, 121.60, 51.59, 38.02, 29.10, 20.47, 19.96.

Phenyl 4-(1,3-dioxoisoindolin-2-yl)-2,2-dimethylbutanoate (50-γ) was prepared alongside **51-α** and **51-β** according to the general procedure for isolations from 2-isopentylisoindoline-1,3-dione and phenyl chloroformate at 40 °C, resulting in 41% average NMR yield (Run 1= 40% yield; Run 2= 42% yield). Isolation of fractions of authentic product with **51-β** were obtained using automated column chromatography, (eluting with EtOAc:hexanes; 0% 4 CV, 0-10% 12 CV, 10% 50 CV, 15% 16 CV, 25% 9 CV, 50% 3 CV) enabling characterization.
^{1}H NMR (500 MHz, CDCl$_3$): Isolated material contains 12% of Phenyl 2-((1,3-dioxoisoindolin-2-yl)methyl)-3-methylbutanoate (51-β) δ 7.84 (dd, J = 5.5, 3.1 Hz, 2H), 7.70 (dd, J = 5.5, 3.0 Hz, 2H), 7.38 (t, J = 7.9 Hz, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.15 (d, J = 7.7 Hz, 2H), 3.85 – 3.76 (m, 2H), 2.12 – 2.05 (m, 2H), 1.43 (s, 6H).
13C NMR (126 MHz, CDCl$_3$): Isolated material contains 12% of Phenyl 2-((1,3-dioxoisoindolin-2-yl)methyl)-3-methylbutanoate (51-β), HMBC and relative intensities used to assign carbon peaks. δ 175.63, 168.15, 150.97, 133.96, 132.19, 129.42, 125.75, 123.25, 121.60, 41.56, 38.40, 34.50, 25.09.
HRMS: (ESI-TOF) calculated for $C_{20}H_{19}NNaO_4^+$ ([M+Na]$^+$): 360.1201, found: 360.1204.

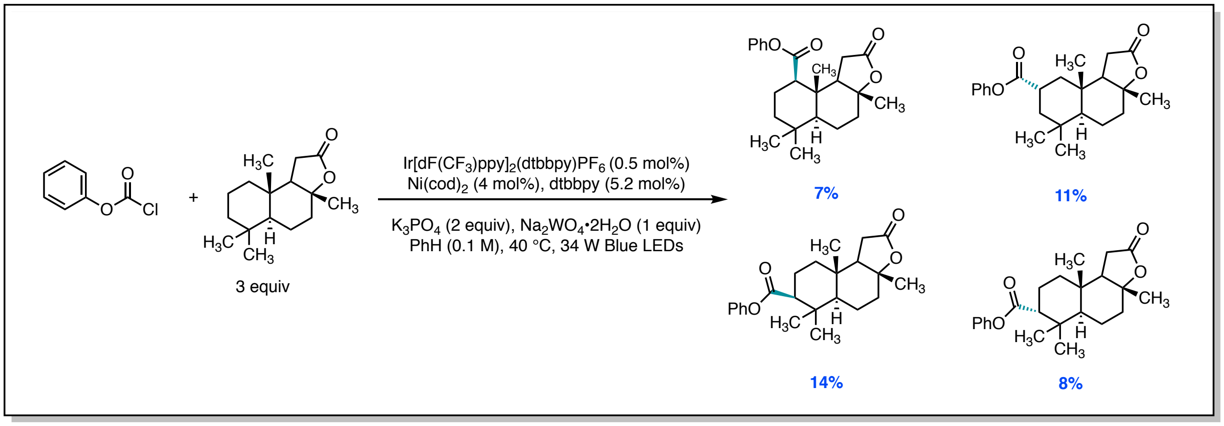
FTIR (ATR cm^{-1}): 2980, 1735, 1708, 1593, 1493, 1466, 1437, 1395, 1371, 1238, 1193, 1161, 1127, 1071, 1044, 976, 918, 870, 791, 719, 690, 633, 607, 529, 500, 462, 411.

Phenyl 5-(1,3-dioxoisoindolin-2-yl)-3-methylpentanoate (50-δ) was prepared alongside **50-**α and **50-**β and **50-**γ according to the general procedure for isolations from 2-isopentylisoindoline-1,3-dione and phenyl chloroformate at 40 °C, resulting in 8% average NMR yield (Run 1= 7% yield; Run 2= 8% yield). Isolation of fractions of authentic product were obtained with other isomers using automated column chromatography, (eluting with EtOAc:hexanes; 0% 4 CV, 0-10% 12 CV, 10% 50 CV, 15% 16 CV, 25% 9 CV, 50% 3 CV) enabling characterization.
1H NMR (500 MHz, CDCl$_3$): *Note: Aryl protons overlap with other isomers.* δ 7.85 – 7.78 (m, 2H), 7.73 – 7.68 (m, 2H), 7.41 – 7.33 (m, 2H), 7.24 – 7.20 (m, 1H), 7.10 – 7.03 (m, 2H). 3.78 (m, 1H, overlap with other products), 2.64 (dd, J = 15.1, 5.9 Hz, 1H), 2.45 (dd, J = 15.1, 8.1 Hz, 1H), 2.19 – 2.11 (m, 1H), 2.11 – 2.05 (m, 1H), 1.90 – 1.82 (m, 1H), 1.71-1.62 (m, 1H), 1.16 (d, J = 6.6 Hz, 3H).
13C NMR (126 MHz, CDCl$_3$): *Note: All Carbon peaks found reported.* δ 175.63, 171.15, 168.40, 168.16, 150.97, 133.96, 133.95, 132.19, 132.14, 129.50, 129.43, 129.40, 125.80, 125.76, 123.26, 121.63, 121.60, 121.56, 41.56, 41.39, 38.40, 35.88, 35.09, 34.50, 29.73, 28.18, 25.09, 19.46.

Figure S47. Crude NMR of 50.



JM-NB2-R134-ND.10.1.1r — PROTON.PU CDCl3 /opt/topspin3.0 jmartine



Phenyl (3a*R*,5a*S*,9*R*,9a*S*)-3a,6,6,9a-tetramethyl-2-oxododecahydronaphtho[2,1-*b*]furan-9-carboxylate (51-α) was prepared according to the general procedure for isolations from (3aR)-(+)-Sclareolide and phenyl chloroformate. Comparison of the crude reaction mixture to clean product resulted in 7% GC yield (Run 1= 7% yield; Run 2= 6% yield). Isolation of fractions of authentic product were obtained with other isomers using automated column chromatography, (eluting with EtOAc:hexanes; 2% 4 CV, 2-13% 10 CV, 13% 4 CV, 13-15% 1 CV, 15% 6 CV, 15-20% 3 CV, 20% 3 CV, 35% 10 CV; Second column 4% 4 CV, 4-15% 21 CV, 15-20% 17 CV, 50% 3CV) enabling characterization for GC assay.

Note: NMRs used for characterization required at least one or two more columns for complete characterization.

1H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.34 (m, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 8.4 Hz, 2H), 2.56 (dd, J = 16.3, 14.3 Hz, 1H), 2.46 – 2.38 (m, 2H), 2.18 – 2.08 (m, 2H), 2.06 – 1.85 (m, 3H), 1.78 – 1.69 (m, 1H), 1.62 – 1.57 (m, 1H), 1.53 – 1.47 (m, 1H), 1.42 – 1.37 (m, 4H) (Two Nuclei overlapping), 1.20 (s, 3H), 1.12 (dd, J = 12.5, 2.8 Hz, 1H), 0.94 (s, 3H), 0.91 (s, 3H).

13C NMR (126 MHz, $CDCl_3$): δ 176.21, 173.22, 150.29, 129.56, 126.01, 121.28, 86.19, 58.16, 57.19, 54.46, 41.54, 39.21, 38.41, 33.15, 33.11, 30.45, 23.62, 21.82, 21.09, 19.94, 13.52.

Figure S48. HSQC of 51-α.

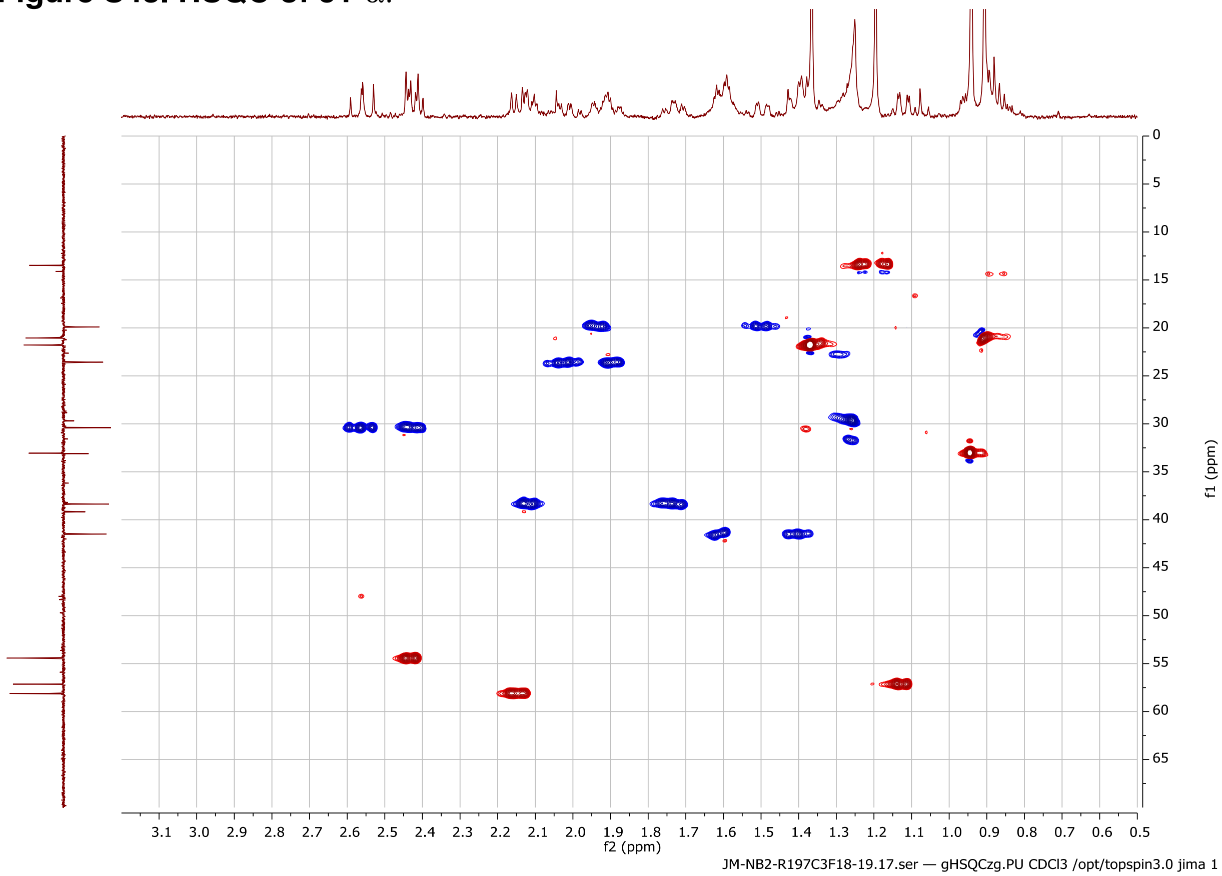
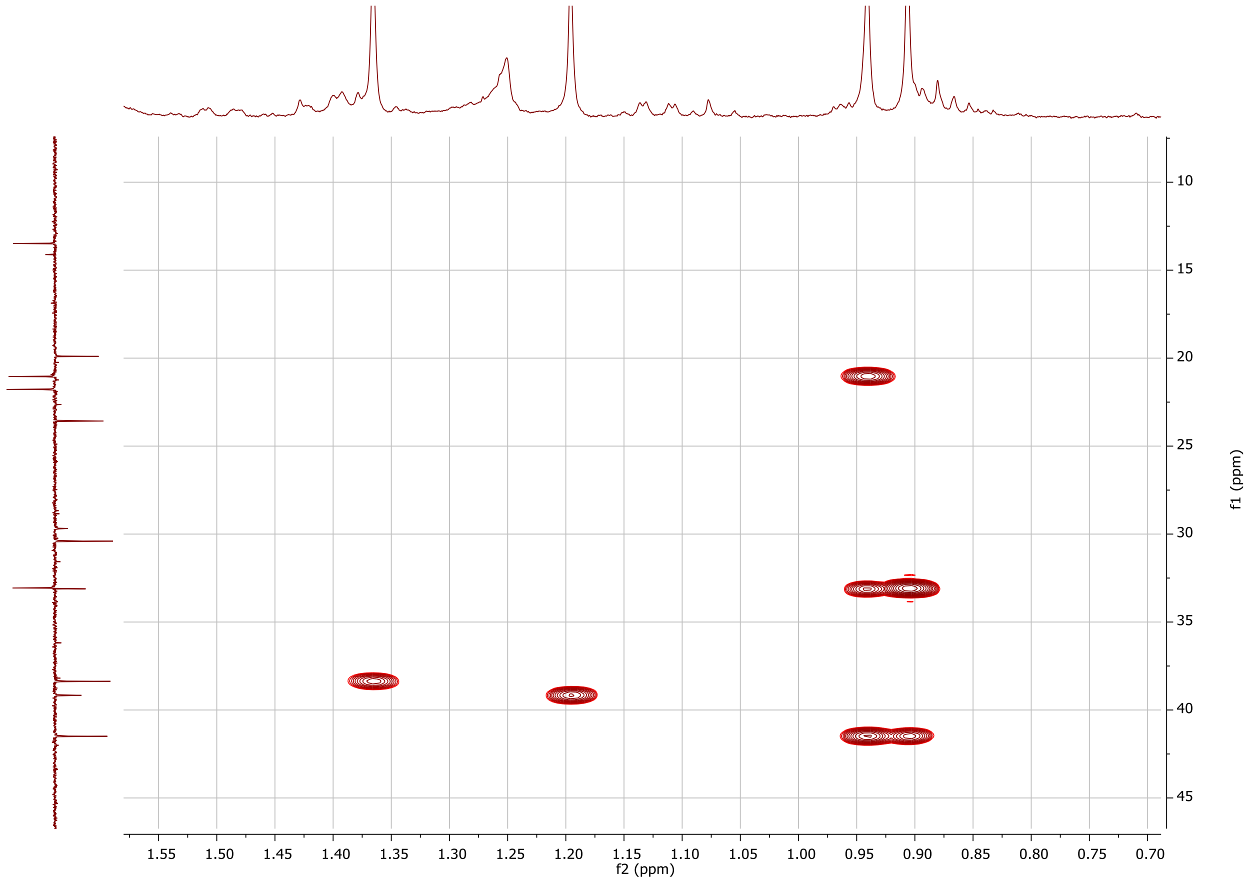
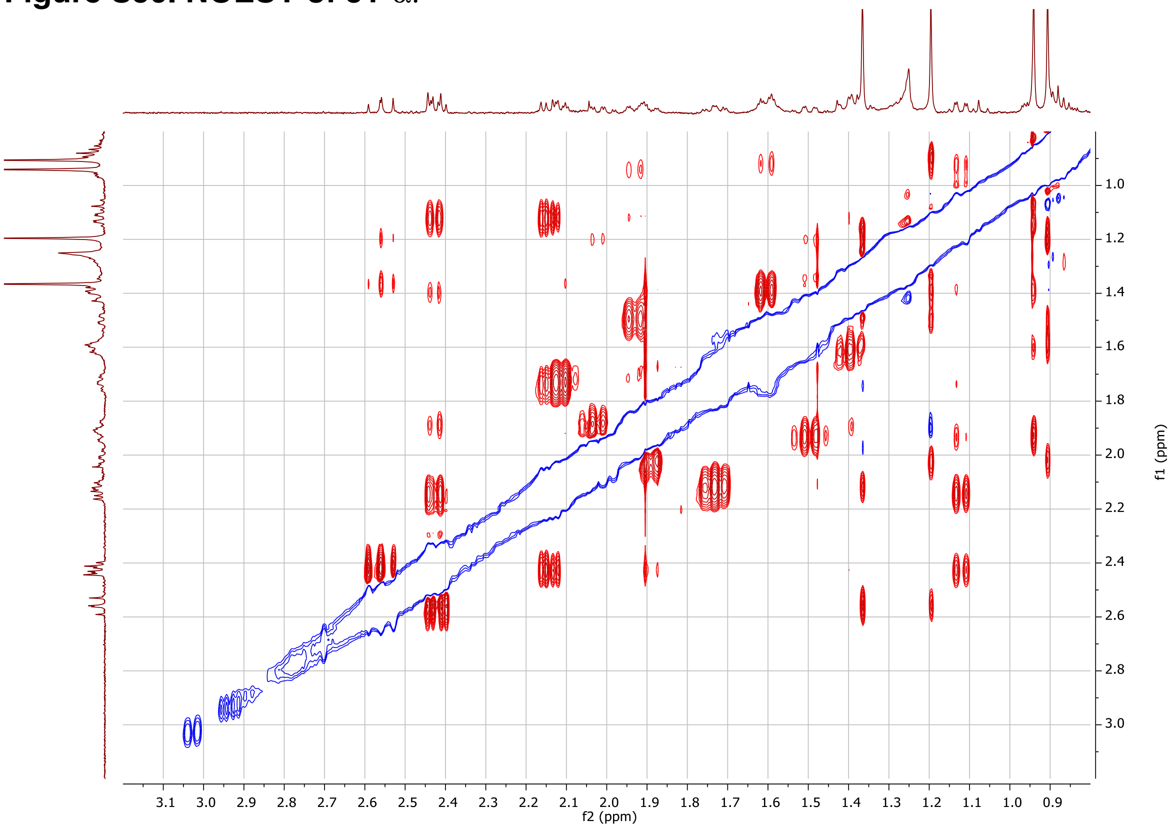


Figure S49. HMBC of 51-α.



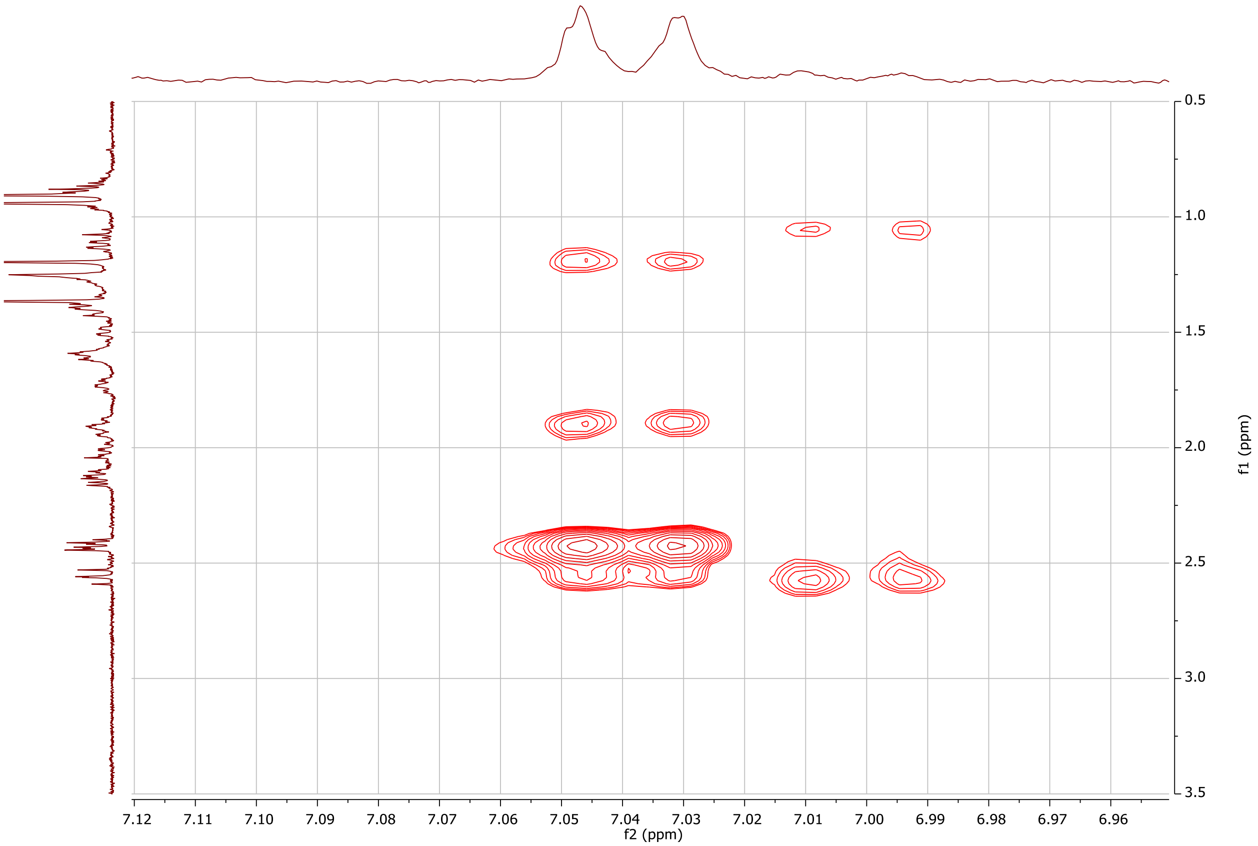
JM-NB2-R197C3F18-19.14.ser — gHMBCzg.PU CDCl3 /opt/topspin3.0 jima 1

Figure S50. NOESY of 51-α.



JM-NB2-R197C3F18-19.15.ser — shNOESYzg.PU CDCl3 /opt/topspin3.0 jima 1

Figure S51. NOESY of 51-α.



JM-NB2-R197C3F18-19.15.ser — shNOESYzg.PU CDCl3 /opt/topspin3.0 jima 1

Phenyl (3aR,5aS,8S,9aS)-3a,6,6,9a-tetramethyl-2-oxododecahydronaphtho[2,1-b]furan-8-carboxylate (51-β) was prepared according to the general procedure for isolations from (3aR)-(+)-Sclareolide and phenyl chloroformate. Comparison of the crude reaction mixture to clean product resulted in 11% GC yield (Run 1= 11% yield; Run 2= 12% yield). Isolation of fractions of authentic product were obtained with other isomers using automated column chromatography, (eluting with EtOAc:hexanes; 2% 4 CV, 2-13% 10 CV, 13% 4 CV, 13-15% 1 CV, 15% 6 CV, 15-20% 3 CV, 20% 3 CV, 35% 10 CV) enabling characterization for GC assay.
Note: NMRs used for characterization required at least one or two more columns for complete characterization.
1H NMR (500 MHz, $CDCl_3$): Characterized with 23% of Phenyl (3aR,5aS,7R,9aS)-3a,6,6,9a-tetramethyl-2-oxododecahydronaphtho[2,1-b]furan-7-carboxylate (53-γ-trans) in NMR. δ 7.09 – 7.03 (m, 2H), 7.25 – 7.21 (m, 1H), 7.07 – 7.03 (m, 2H), 2.96 (tt, J = 12.7, 3.6 Hz, 1H), 2.50 – 2.41 (m, 1H), 2.32 (dd, J = 16.2, 6.5 Hz, 1H), 2.12 (dt, J = 11.7, 3.2 Hz, 1H), 2.09 – 2.01 (m, 2H), 1.97 – 1.93 (m, 1H), 1.92 – 1.88 (m, 1H), 1.87 – 1.80 (m, 1H), 1.73 (td, J = 12.7, 4.2 Hz, 1H), 1.51 (t, J = 13.1 Hz, 1H), 1.48 – 1.38 (m, 1H), 1.36 (s, 3H), 1.20 – 1.13 (m, 1H), 1.01 (s, 3H), 1.00 (s, 3H), 0.95 (s, 3H).
13C NMR (126 MHz, $CDCl_3$): δ 176.49, 172.74, 150.60, 129.46, 125.83, 121.57, 85.93, 58.97, 57.13, 55.03, 38.57, 38.45, 36.48, 35.99, 30.26, 28.70, 21.53, 21.38, 20.21, 18.07, 15.15.

Figure S52. HSQC of 51-β.

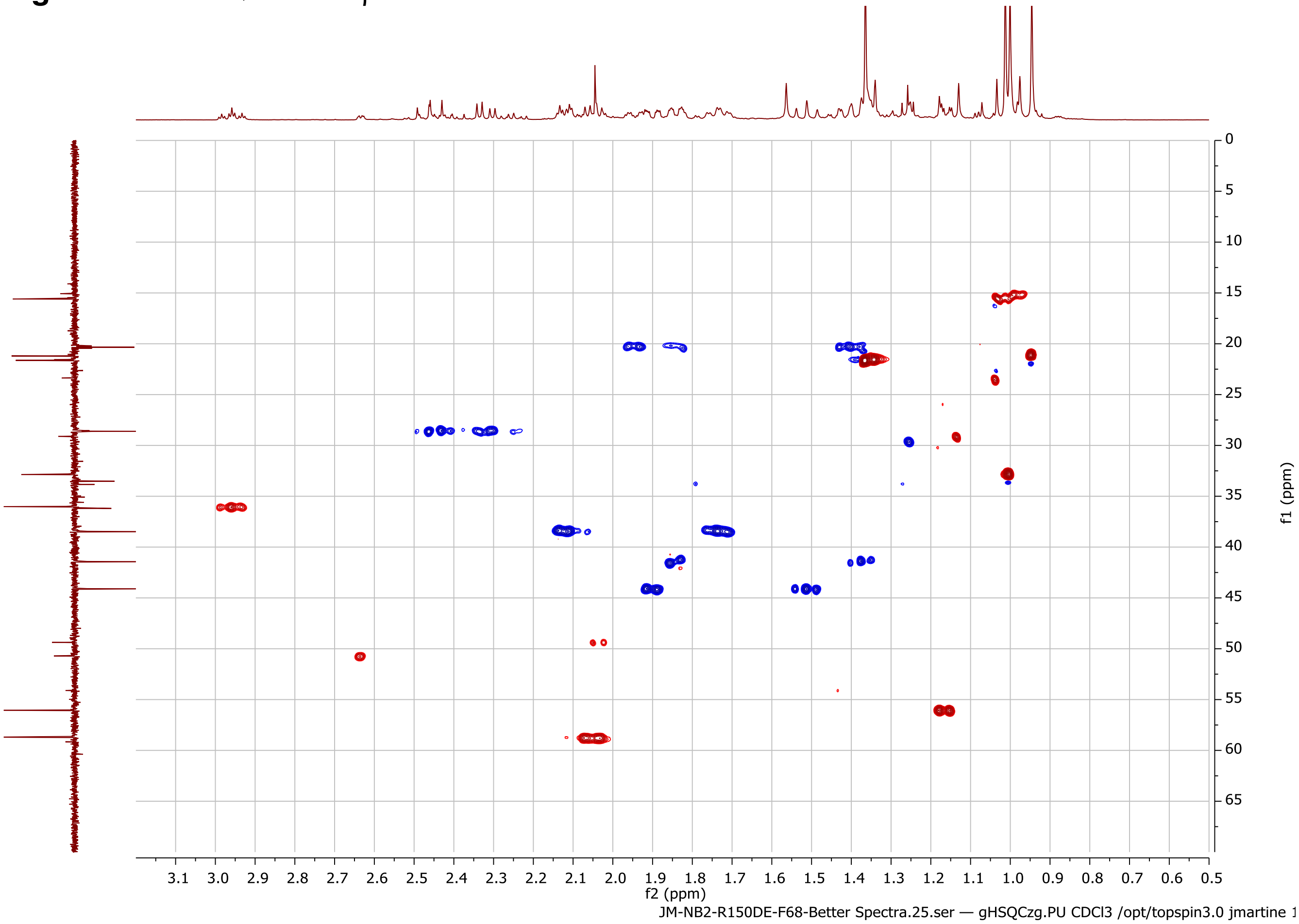
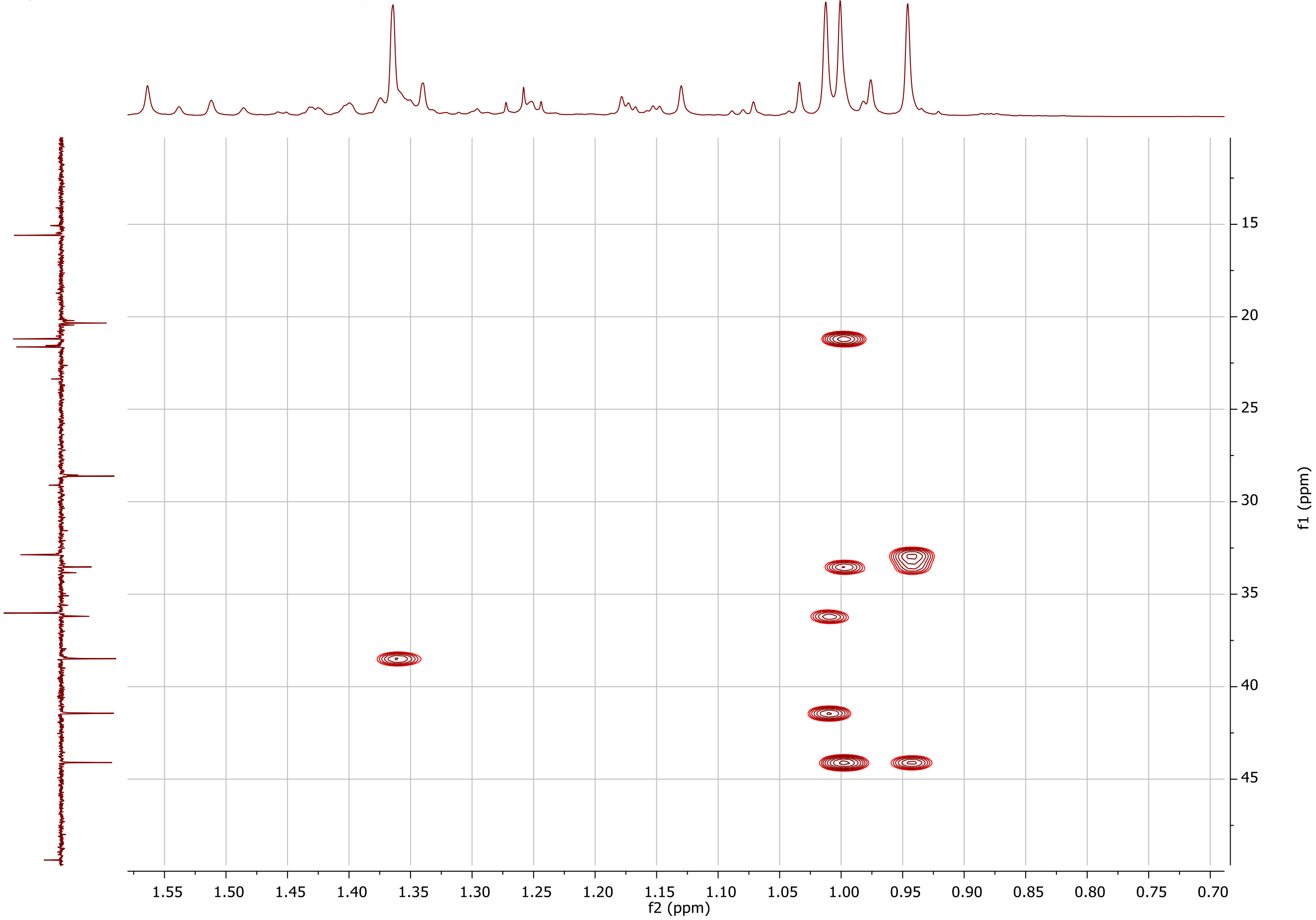


Figure S53. HMBC of 51-β.



JM-NB2-R150DE-F68-Better Spectra.21.ser — gHMBCzg.PU CDCl3 /opt/topspin3.0 jmartine 1

Figure S54. NOESY of 51-β.

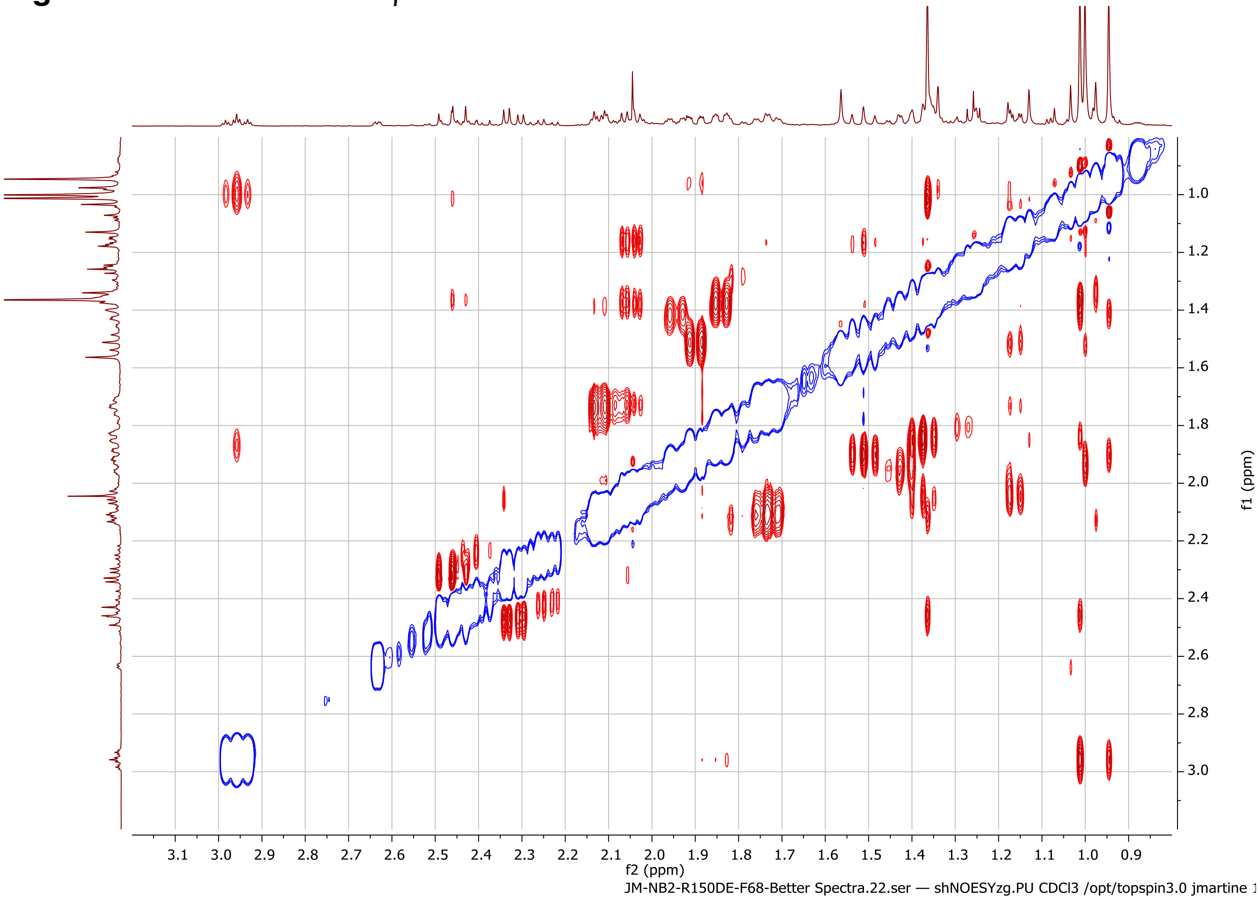
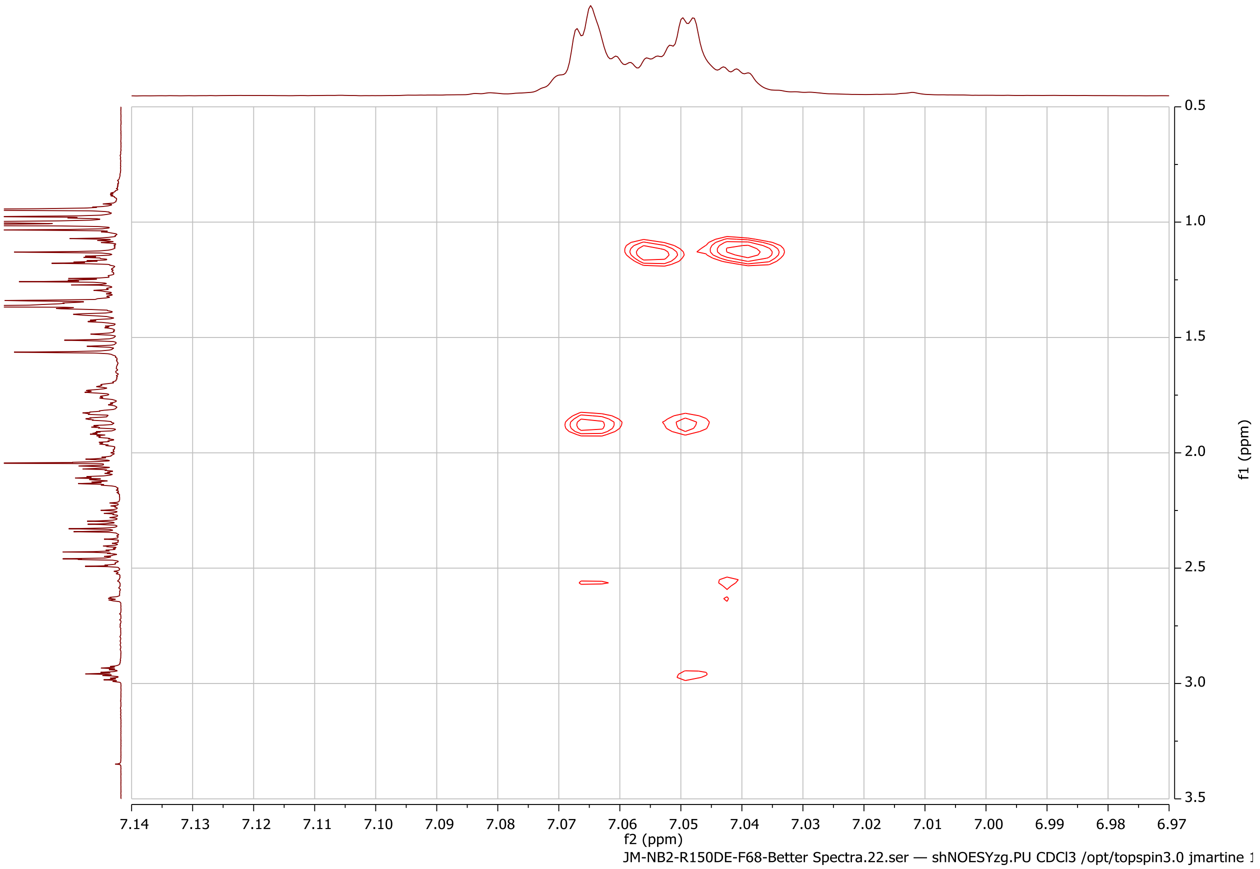


Figure S55. NOESY of 51-β.



Phenyl (3a*R*,5a*S*,7*S*,9a*S*)-3a,6,6,9a-tetramethyl-2-oxododecahydronaphtho[2,1-*b*]furan-7-carboxylate (51-γ-*cis*) was prepared according to the general procedure for isolations from (3aR)-(+)-Sclareolide and phenyl chloroformate. Comparison of the crude reaction mixture to clean product resulted in 8% GC yield (Run 1= 8% yield; Run 2= 7% yield). Isolation of fractions of authentic product were obtained with other isomers using automated column chromatography, (eluting with EtOAc:hexanes; 2% 4 CV, 2-13% 10 CV, 13% 4 CV, 13-15% 1 CV, 15% 6 CV, 15-20% 3 CV, 20% 3 CV, 35% 10 CV) enabling characterization for GC assay.

Note: NMRs used for characterization required at least one or two more columns for complete characterization.

1H NMR (500 MHz, CDCl$_3$): δ 7.41 – 7.35 (m, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.09 – 7.03 (m, 2H), 2.50 – 2.40 (m, 2H), 2.27 (dd, J = 16.2, 6.5 Hz, 1H), 2.18 – 2.05 (m, 2H), 1.99 (dd, J = 14.7, 6.4 Hz, 2H), 1.81 (dq, J = 14.4, 3.5 Hz, 1H), 1.74 (td, J = 12.5, 4.1 Hz, 1H), 1.60 – 1.52 (m, 1H), 1.46 (dtd, J = 14.3, 12.9, 3.5 Hz, 1H), 1.36 (s, 3H), 1.26 – 1.20 (m, 1H), 1.19 – 1.14 (m, 4H, two nuclei overlapping), 1.01 (s, 3H), 1.00 (s, 3H).

13C NMR (126 MHz, CDCl$_3$): δ 176.32, 174.29, 150.67, 129.48, 125.88, 121.45, 86.03, 58.75, 56.10, 44.15, 41.48, 38.53, 36.24, 36.07, 33.57, 32.91, 28.66, 21.68, 21.25, 20.39, 15.64.

Figure S56. HSQC of 51-γ-*cis*.

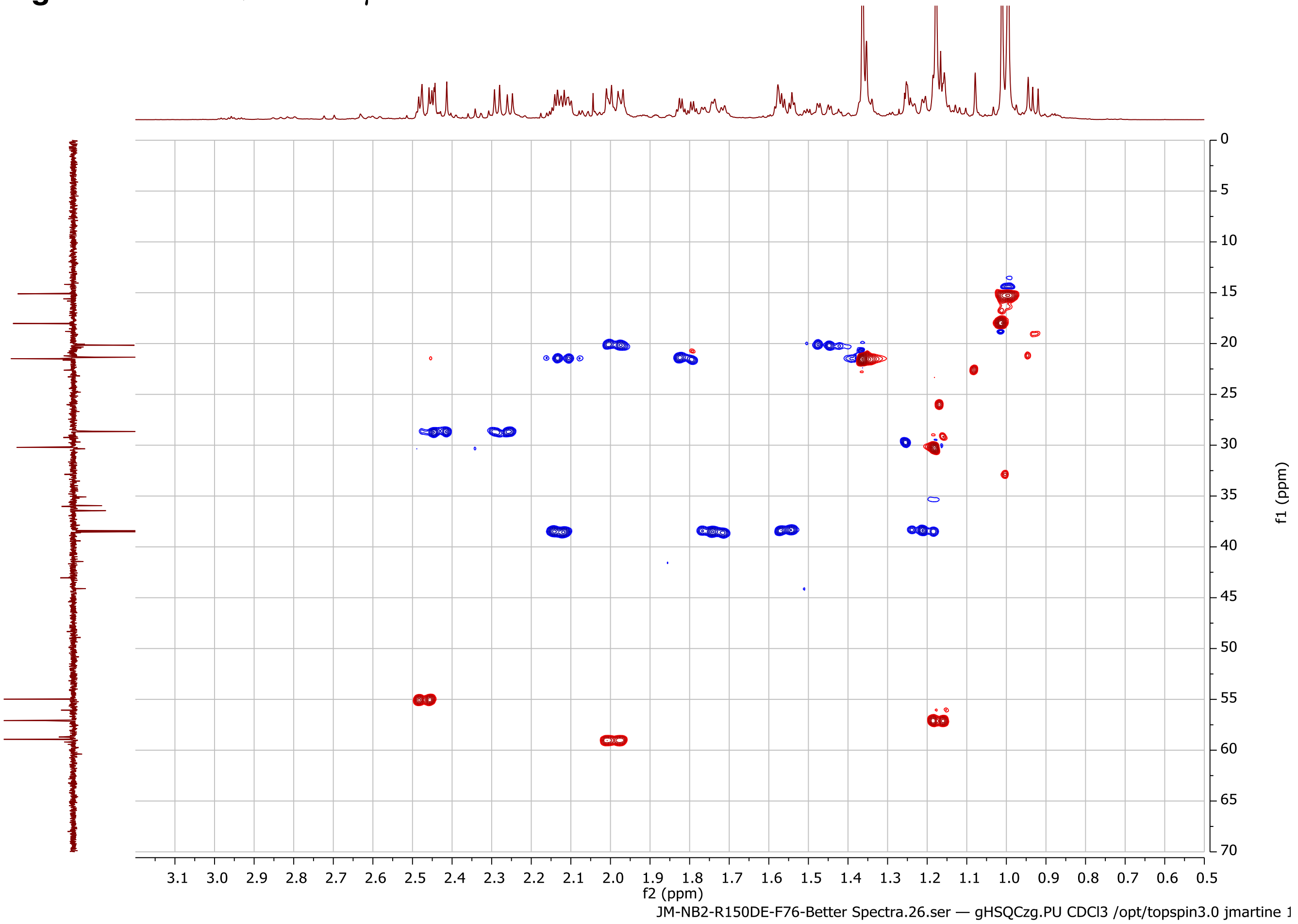
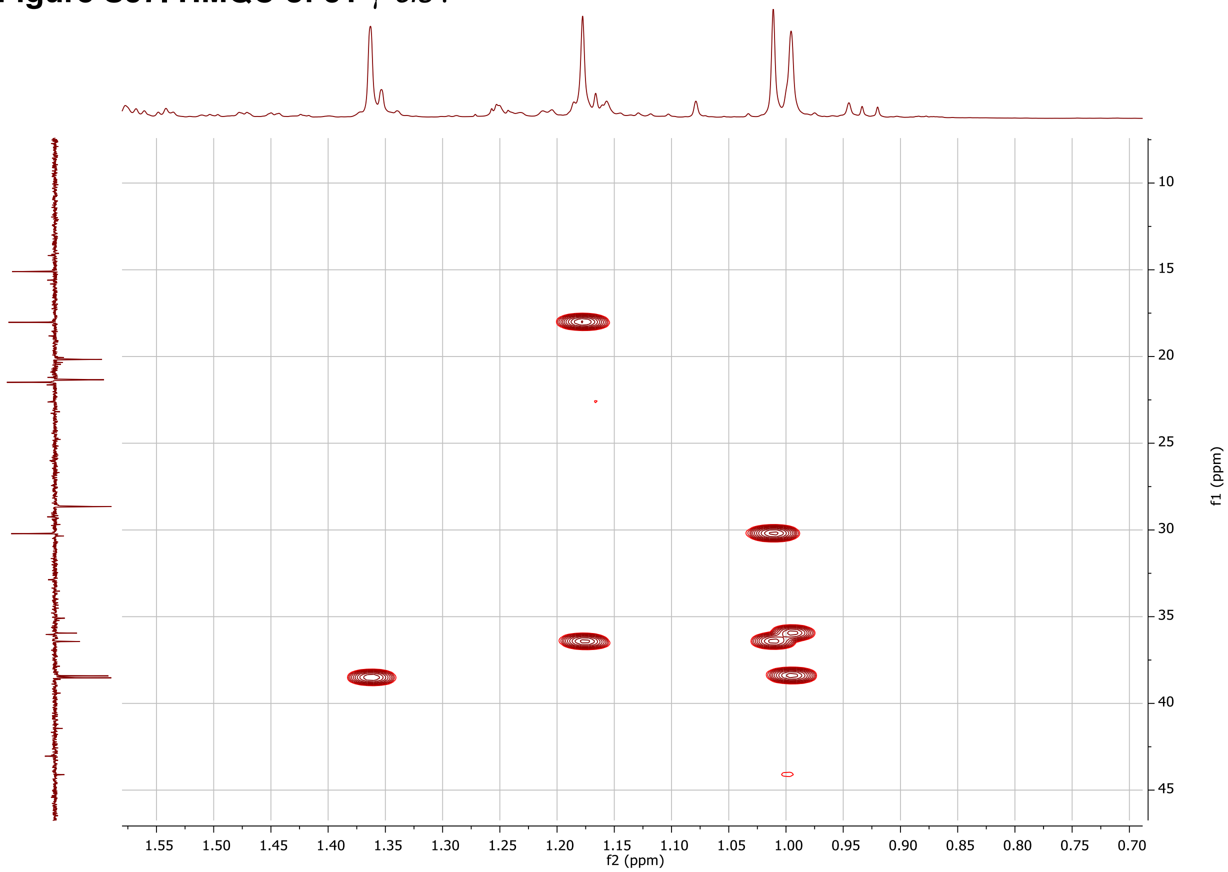


Figure S57. HMQC of 51-γ-*cis* .



JM-NB2-R150DE-F76-Better Spectra.21.ser — gHMBCzg.PU CDCl3 /opt/topspin3.0 jmartine 1

Figure S58. NOESY of 51-γ-*cis.*

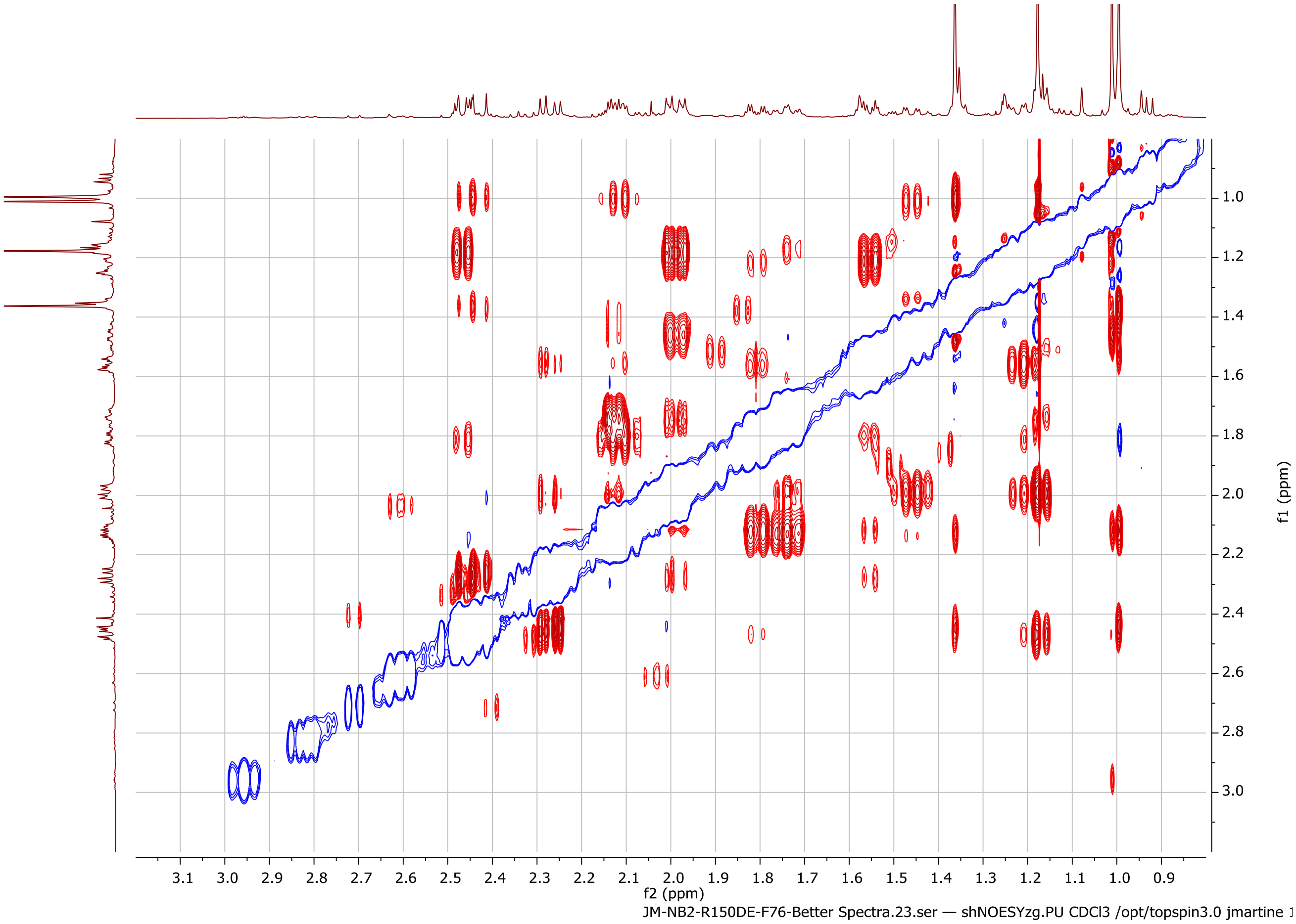
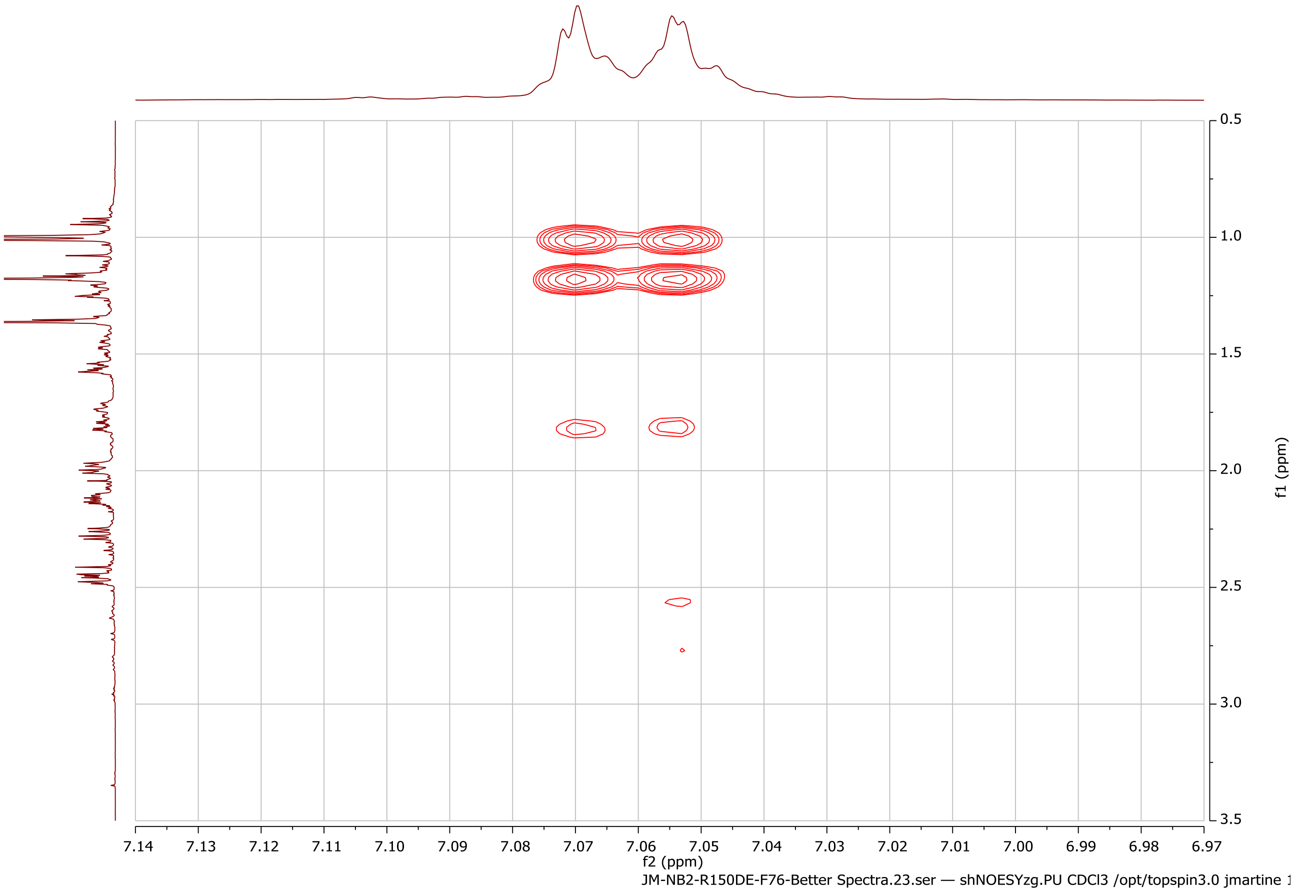


Figure S59. NOESY of 51-γ-*cis.*



Phenyl (3a*R*,5a*S*,7*R*,9a*S*)-3a,6,6,9a-tetramethyl-2-oxododecahydronaphtho[2,1-*b*]furan-7-carboxylate (51-γ-*trans*) was prepared according to the general procedure for isolations from (3aR)-(+)-Sclareolide and phenyl chloroformate. Comparison of the crude reaction mixture to clean product resulted in 14% GC yield (Run 1= 14% yield; Run 2= 13% yield). Isolation of fractions of authentic product were obtained with other isomers using automated column chromatography, (eluting with EtOAc:hexanes; 2% 4 CV, 2-13% 10 CV, 13% 4 CV, 13-15% 1 CV, 15% 6 CV, 15-20% 3 CV, 20% 3 CV, 35% 10 CV; Second column 5% 4 CV, 5-18% 21 CV, 19-20% 1 CV, 20% 12CV) enabling characterization for GC assay.

Note: NMRs used for characterization required at least one or two more columns for complete characterization.

1H NMR (500 MHz, CDCl$_3$): 7.41 – 7.35 (m, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.05 (dd, J = 8.6, 1.2 Hz, 2H), 2.63 (dd, J = 5.8, 2.1 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.24 (dd, J = 16.2, 6.5 Hz, 1H), 2.17 – 2.01 (m, 4H), 1.88 – 1.81 (m, 2H), 1.80 – 1.68 (m, 2H), 1.45 – 1.37 (m, 1H), 1.34 (s, 3H), 1.30 – 1.24 (m, 1H), 1.13 (s, 3H), 1.03 (s, 3H), 0.98 (s, 3H).

13C NMR (126 MHz, CDCl$_3$): 176.64, 173.51, 150.47, 129.46, 125.89, 121.62, 86.14, 58.69, 50.76, 49.42, 38.54, 35.65, 35.13, 33.89, 29.16, 28.61, 23.41, 21.60, 20.49, 20.26, 15.12.

HRMS: (ESI-TOF) calculated for $C_{23}H_{31}O_4^+$ ([M+H]$^+$): 371.2217, found: 371.2225.

FTIR (ATR cm^{-1}): 2943, 1775, 1753, 1492, 1226, 1193, 1176, 1162, 1111, 1047, 1013, 956, 925, 913.

Figure S60. HSQC of 51-γ-*trans* .

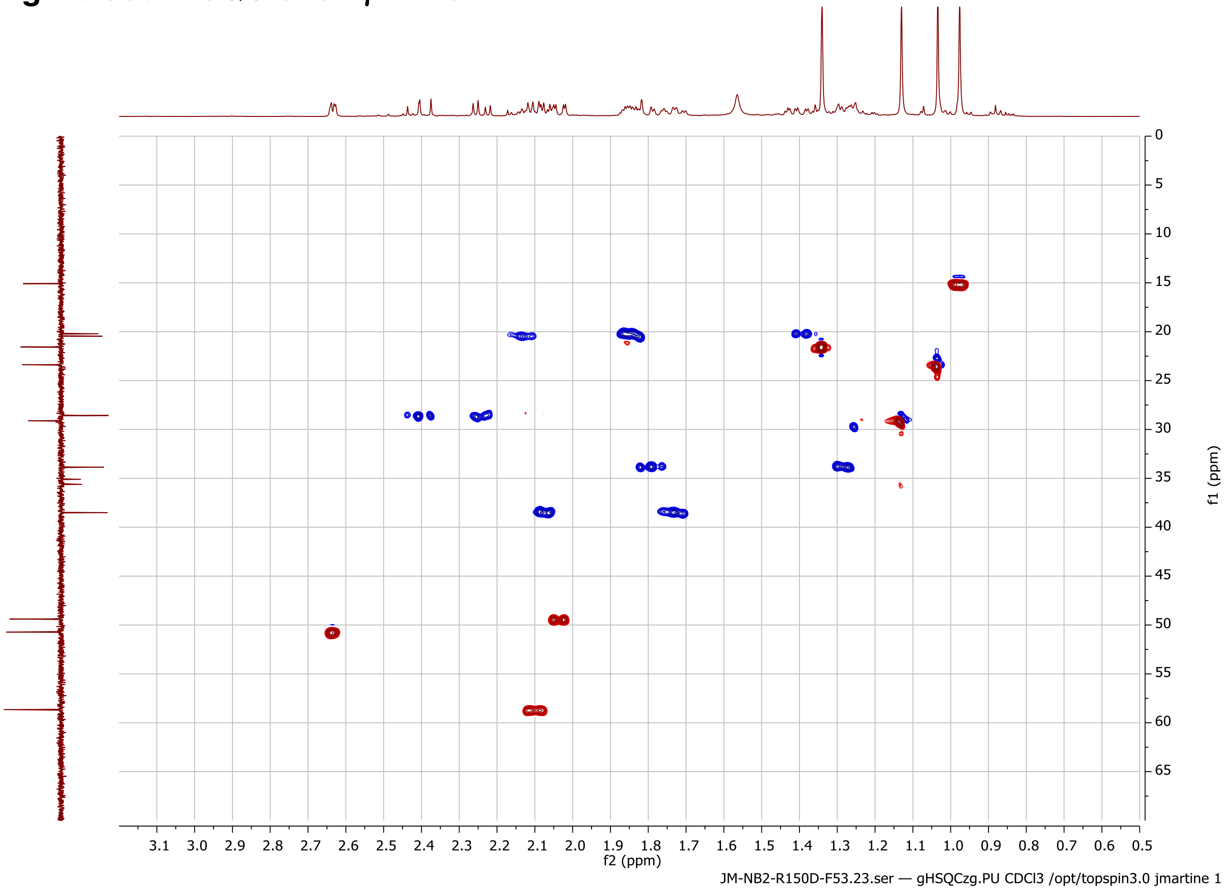


Figure S61. HMBC of 51-γ-*trans* .

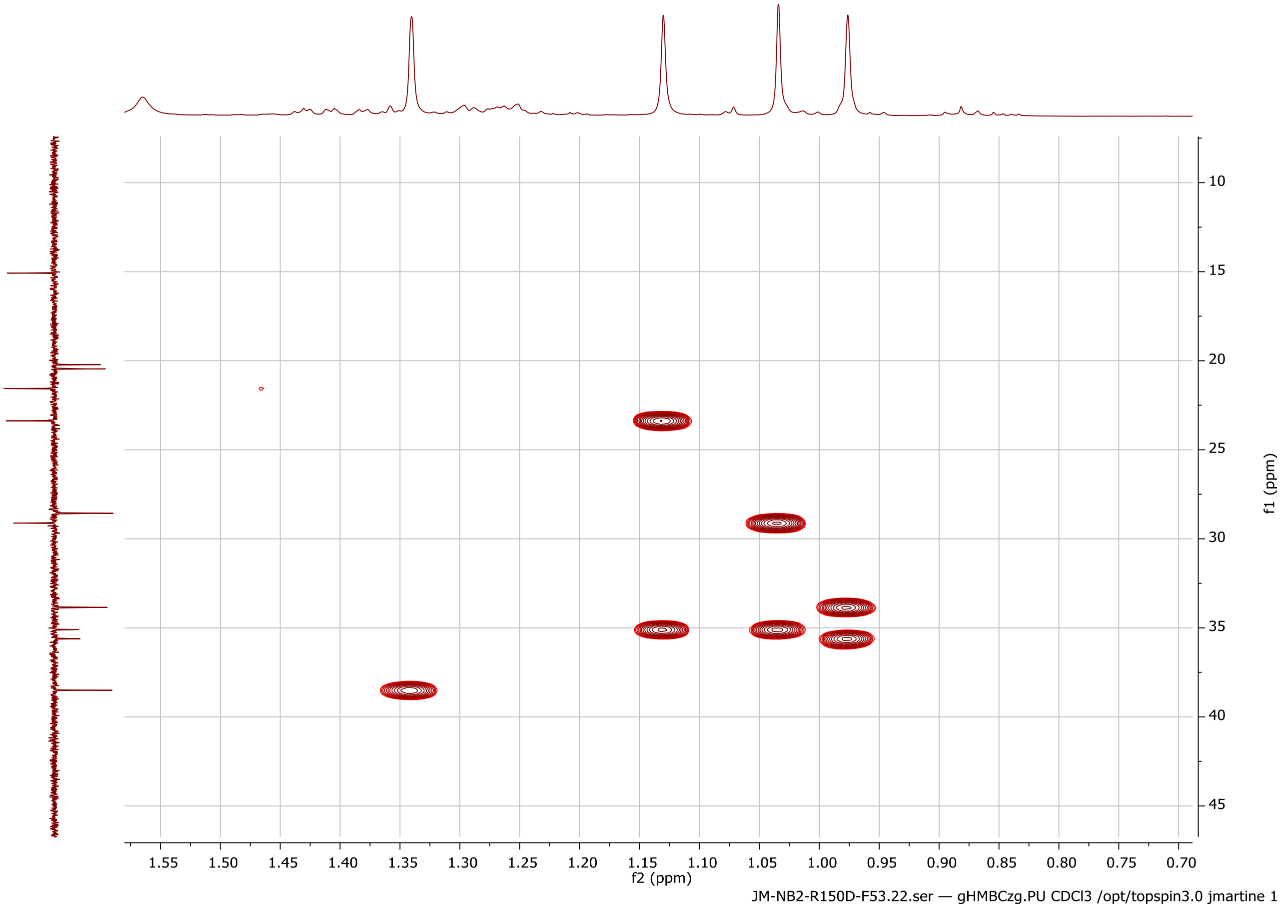


Figure S62. NOESY of 52-γ-*trans*.

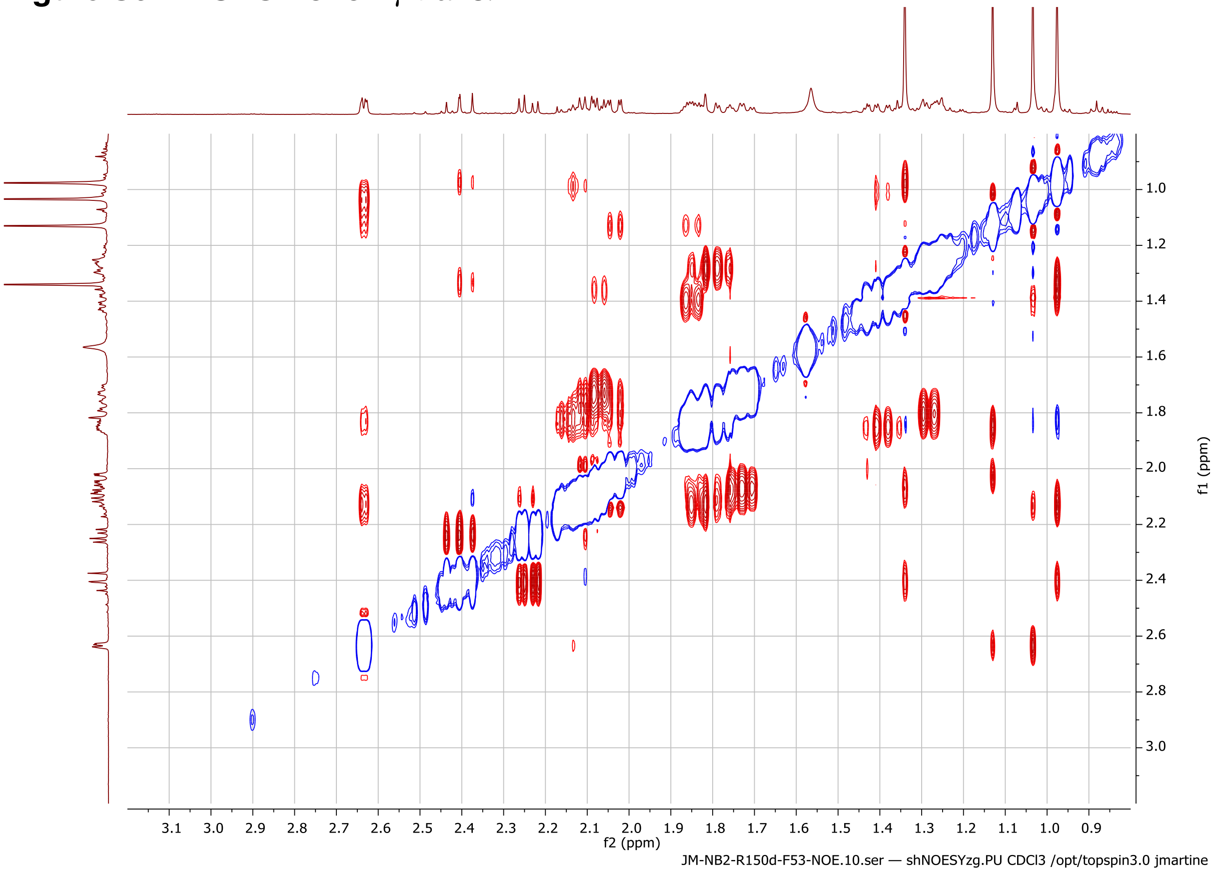
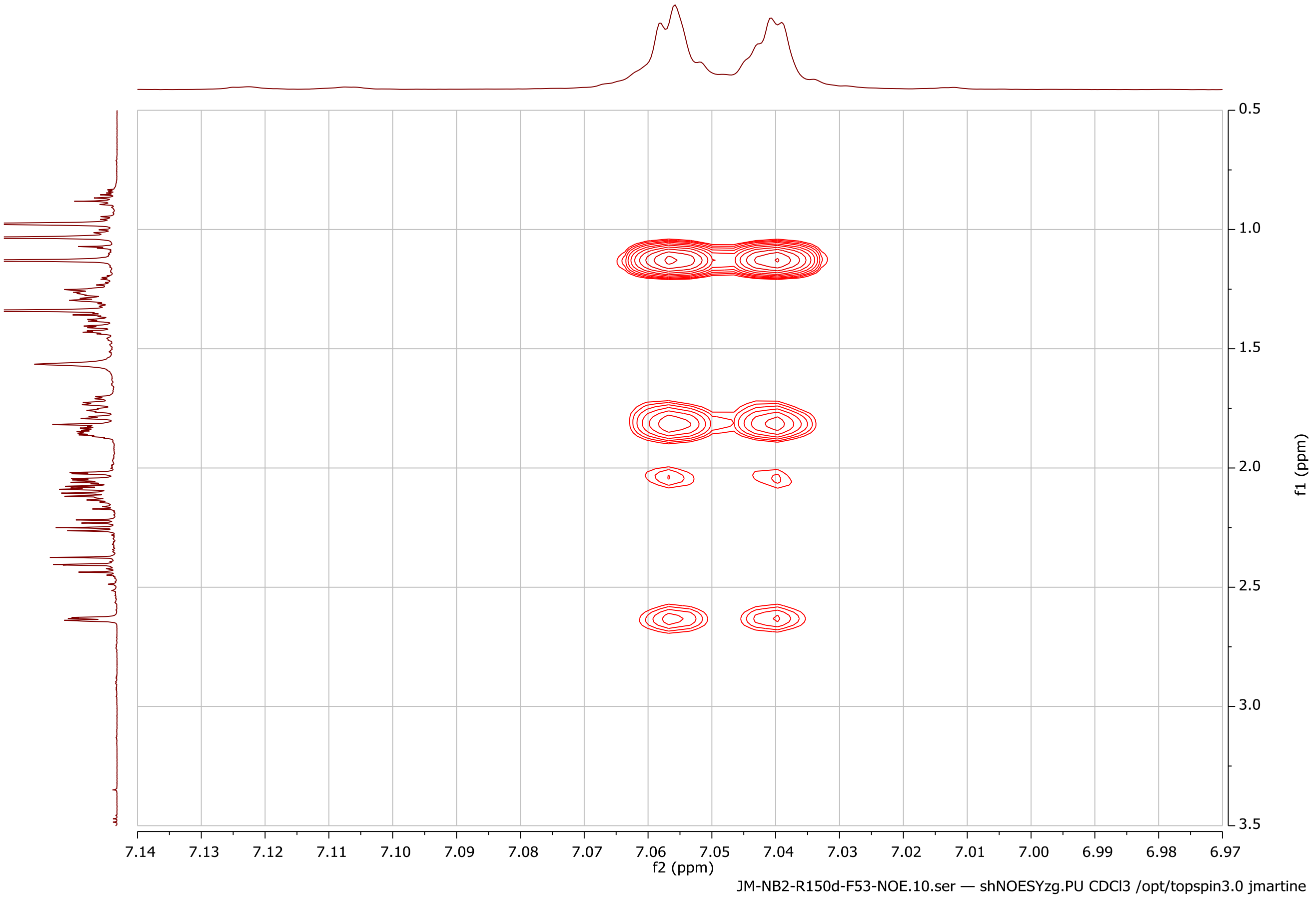


Figure S63. NOESY of 51-γ-*trans* .

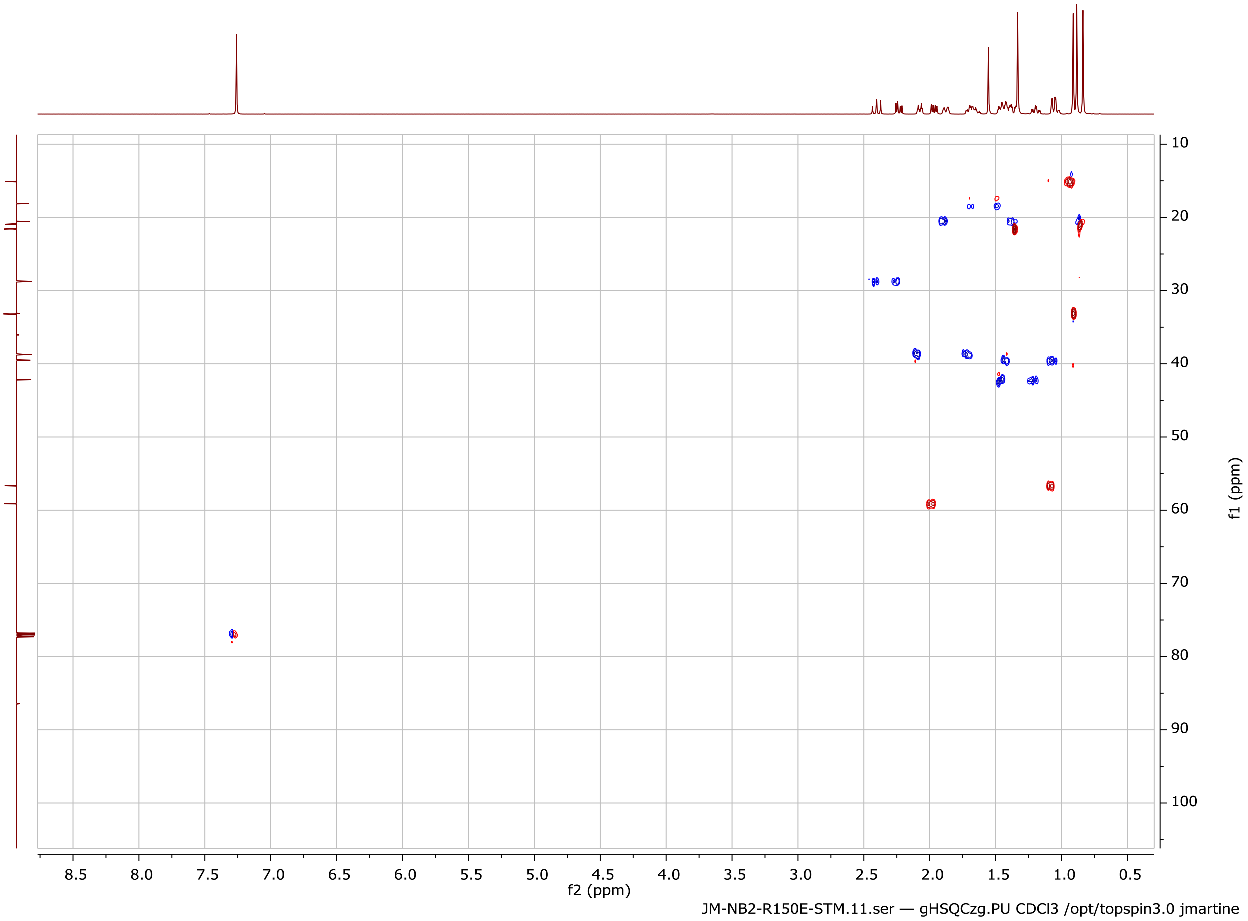


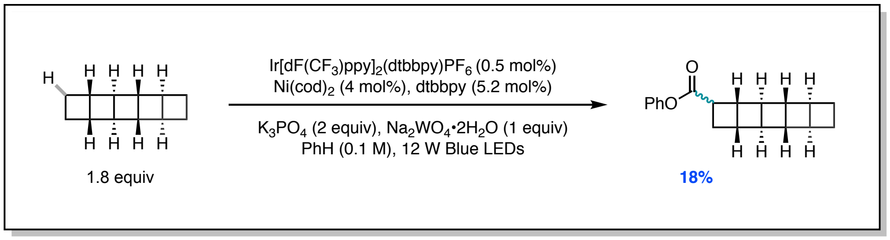
(3aR,5aS,9aS)-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-b]furan-2(1H)-one (S51) for reference

<u>1H NMR (500 MHz, $CDCl_3$):</u> δ 2.40 (dd, J = 16.2, 14.8 Hz, 1H), 2.23 (dd, J = 16.2, 6.5 Hz, 1H), 2.08 (dt, J = 11.9, 3.4 Hz, 1H), 1.97 (dd, J = 14.8, 6.5 Hz, 1H), 1.88 (dq, J = 14.2, 3.3 Hz, 1H), 1.74 – 1.61 (m, 2H), 1.50 – 1.37 (m, 2H), 1.19 (td, J = 13.6, 4.5 Hz, 1H), 1.05 (td, J = 13.0, 3.4 Hz, 2H), 0.91 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H).

<u>13C NMR (126 MHz, $CDCl_3$):</u> δ 176.94, 86.43, 59.12, 56.65, 42.17, 39.51, 38.71, 36.06, 33.19, 33.14, 28.74, 21.59, 20.94, 20.57, 18.10, 15.09.

Figure S64. HSQC of S51.





Phenyl (1*R*,2*R*,3*S*,6*S*,7*R*,8*S*,9*R*,12*S*)-pentacyclo[6.4.0.02,7.03,6.09,12]dodecane-4-carboxylate (52) was prepared according to the general procedure for reaction optimization from [5]-ladderane (1.8 equiv) and phenyl chloroformate to afford 18% NMR yield. The title compound was analyzed as a crude mixture to ensure effective concentration for characterization via 2D NMR. Three carbonyls, indicative of three ester-containing products are reported at 174.27 ppm, 173.46 ppm, and 172.87 ppm. Several multiplets featured at 4.17, 4.12, and 3.87 ppm exhibit coupling that is indicative of adjacent methylene protons. HSQC-13-APT analysis reveals correlations with a methine carbon, rather than a quaternary carbon. While the peak at 4.12 correlates to olefinic protons, 4.17 does not and is consistent with esterification at the reported C-H site.

HRMS: (ESI-TOF) calculated for $C_{19}H_{21}O_2^+$ ($[M+H]^+$): 281.1536, found: 281.1536.

Figure S65. Crude 1H NMR of 52.

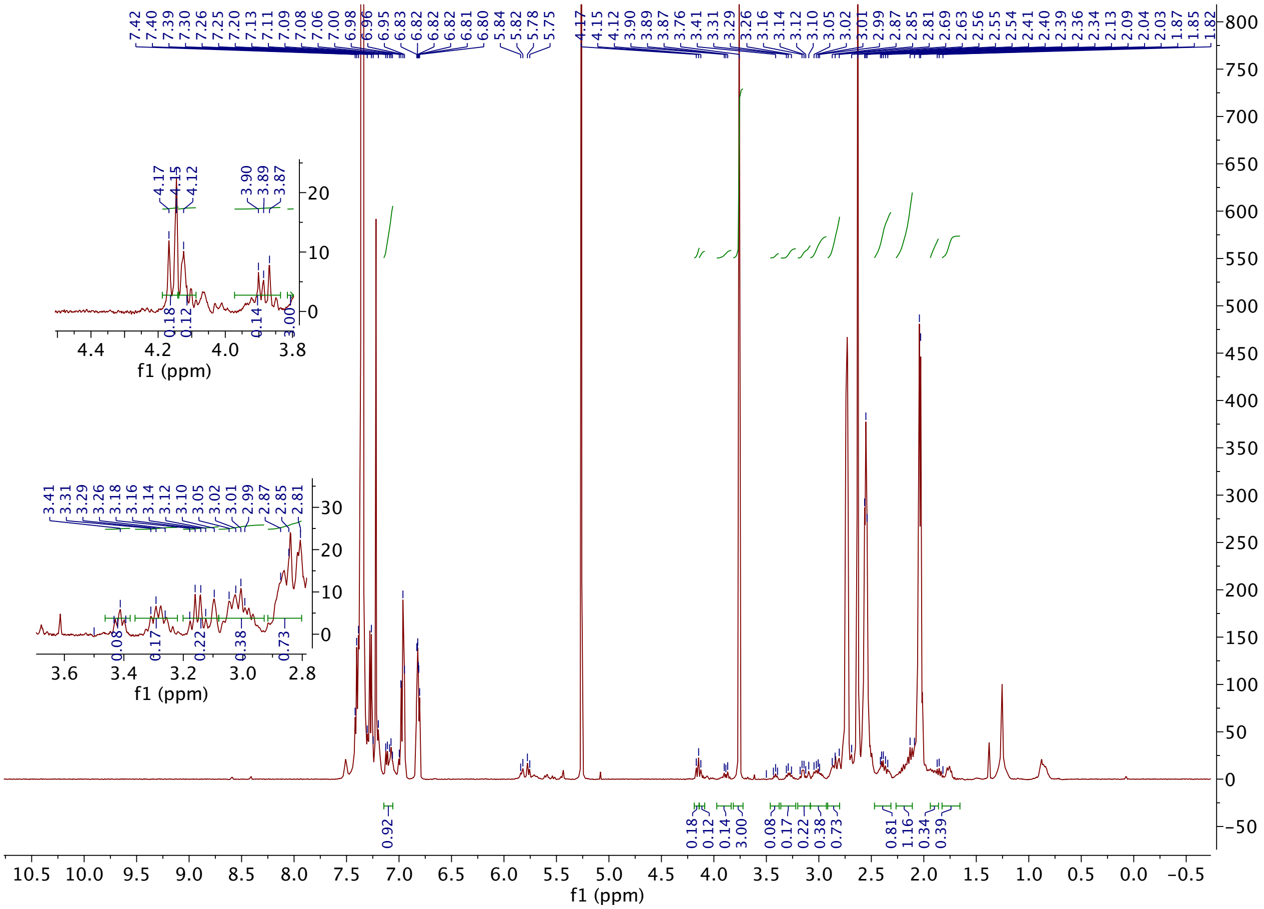


Figure S66. Crude 13C-APT of 52.

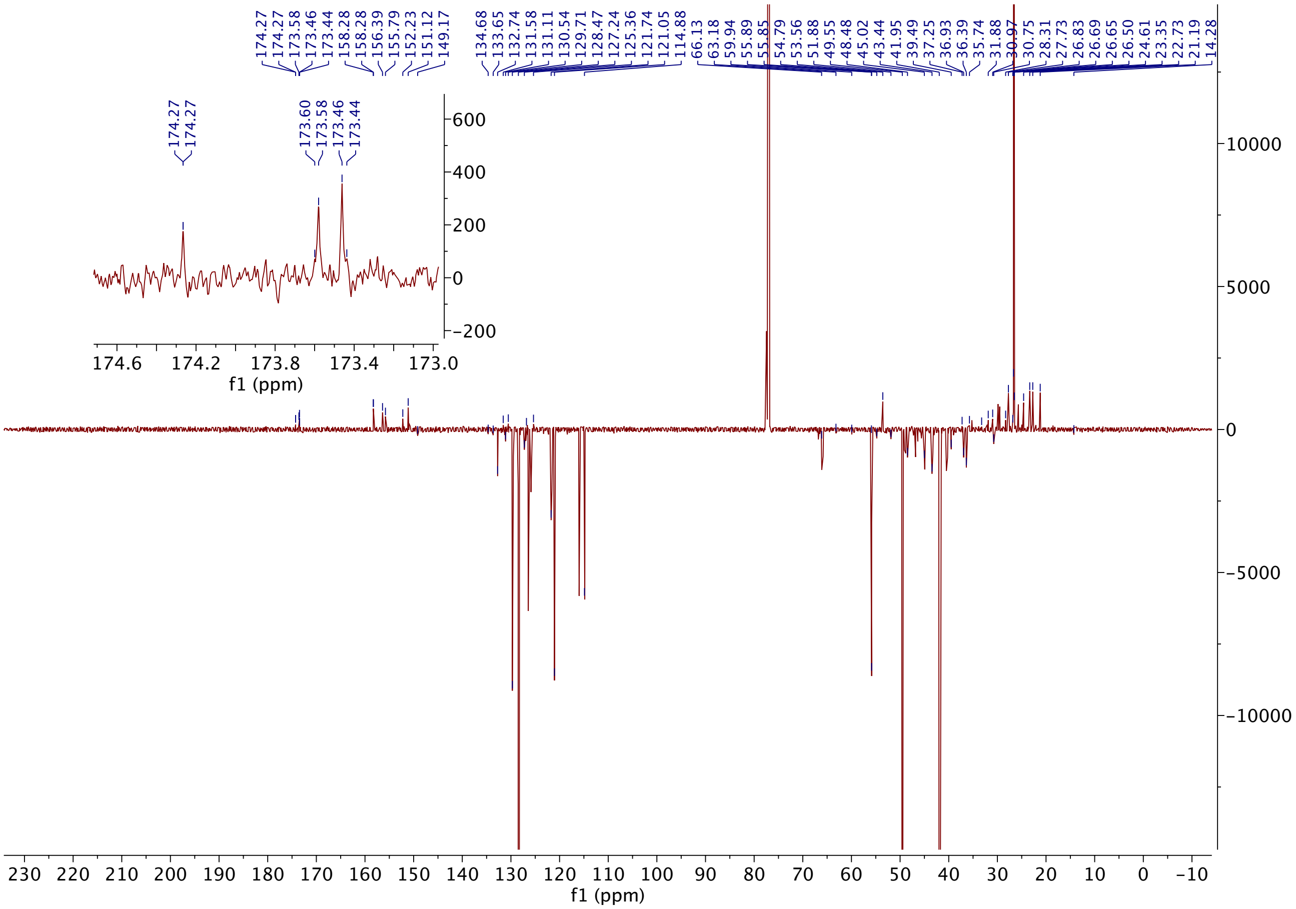


Figure S67. Crude HSQC-13C-APT of 52.

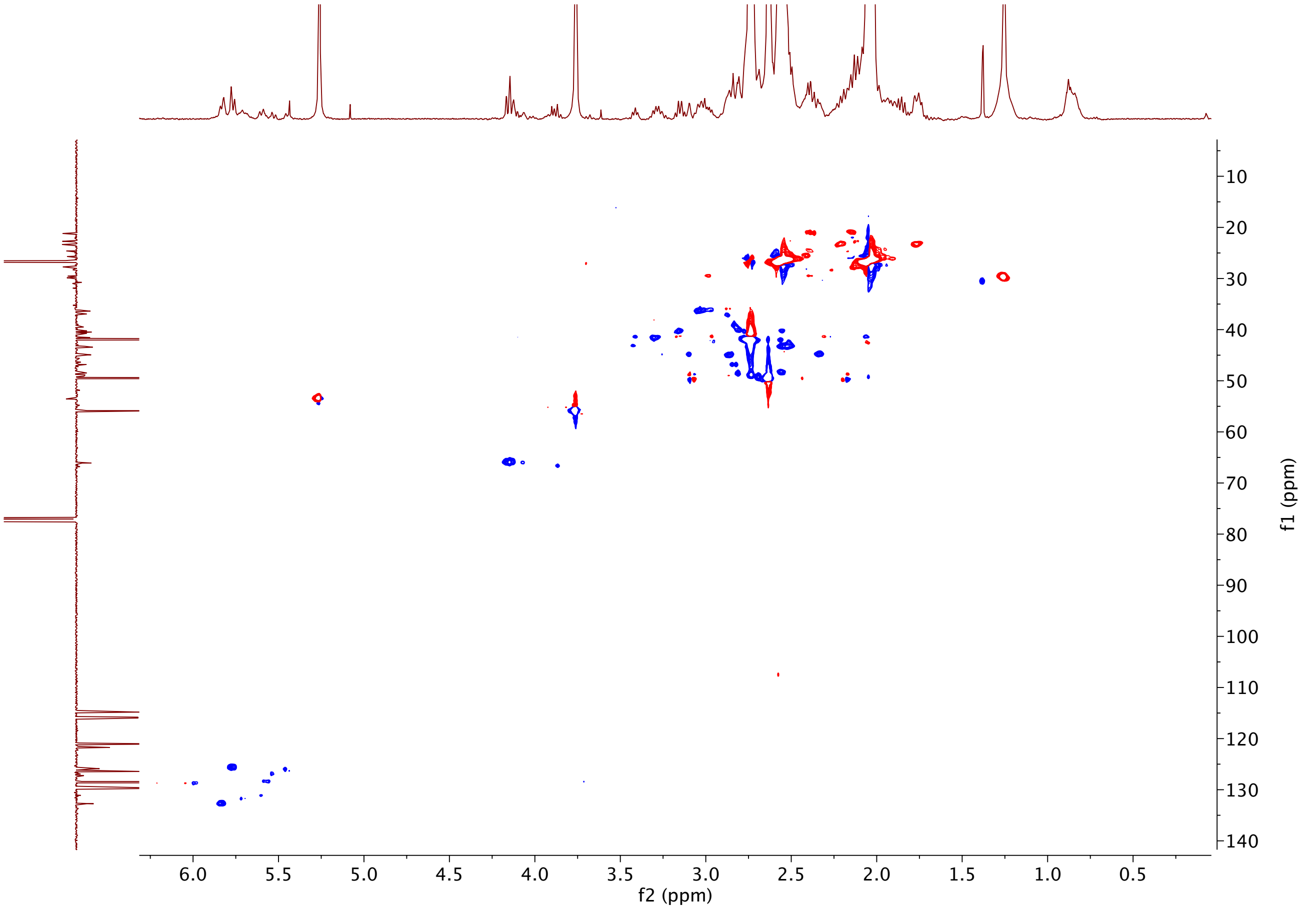


Figure S68. Crude HSQC-13C-APT of 52 from 1.5 ppm to 4.5 ppm.

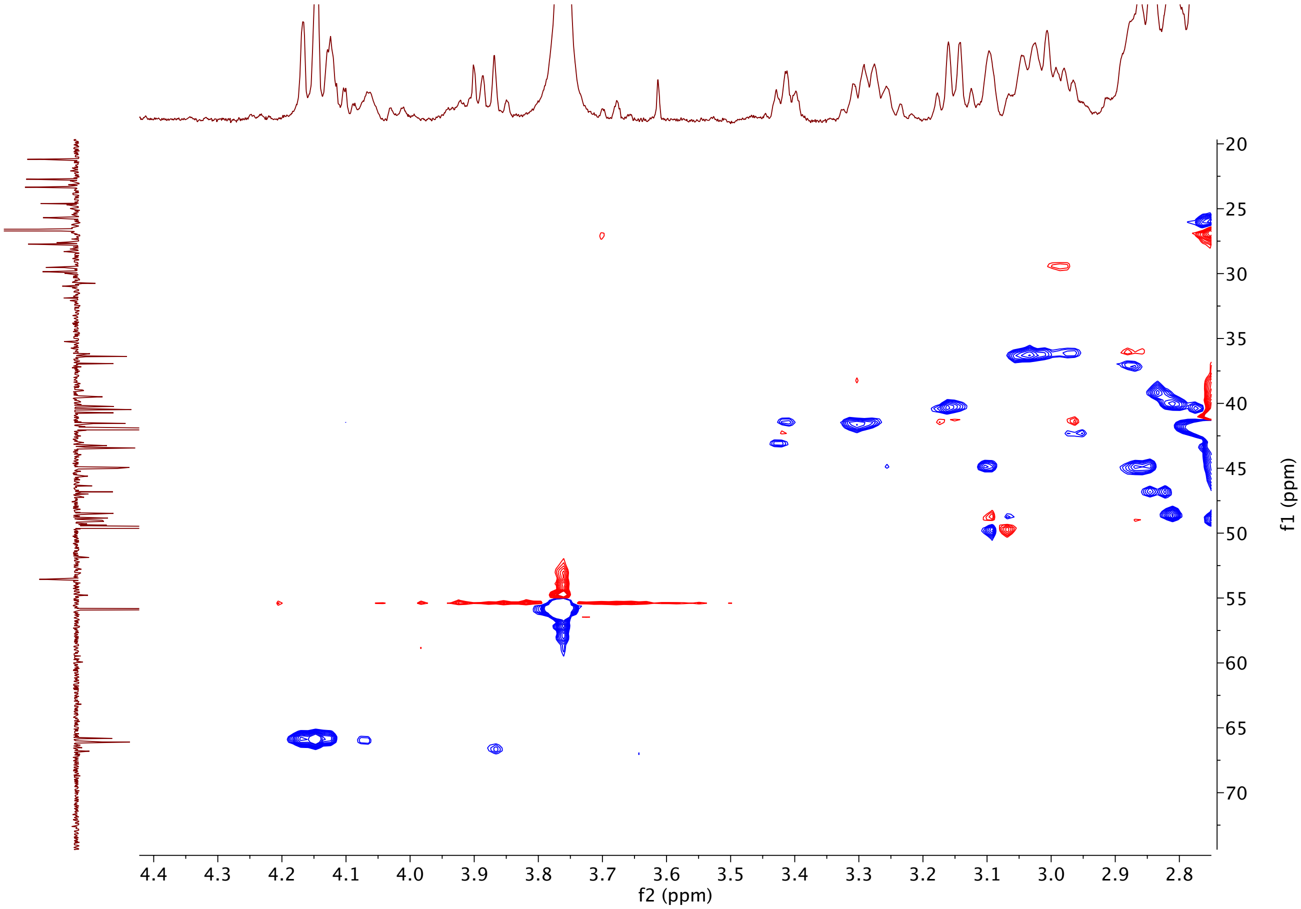


Figure S69. Crude TOCSY of 52.

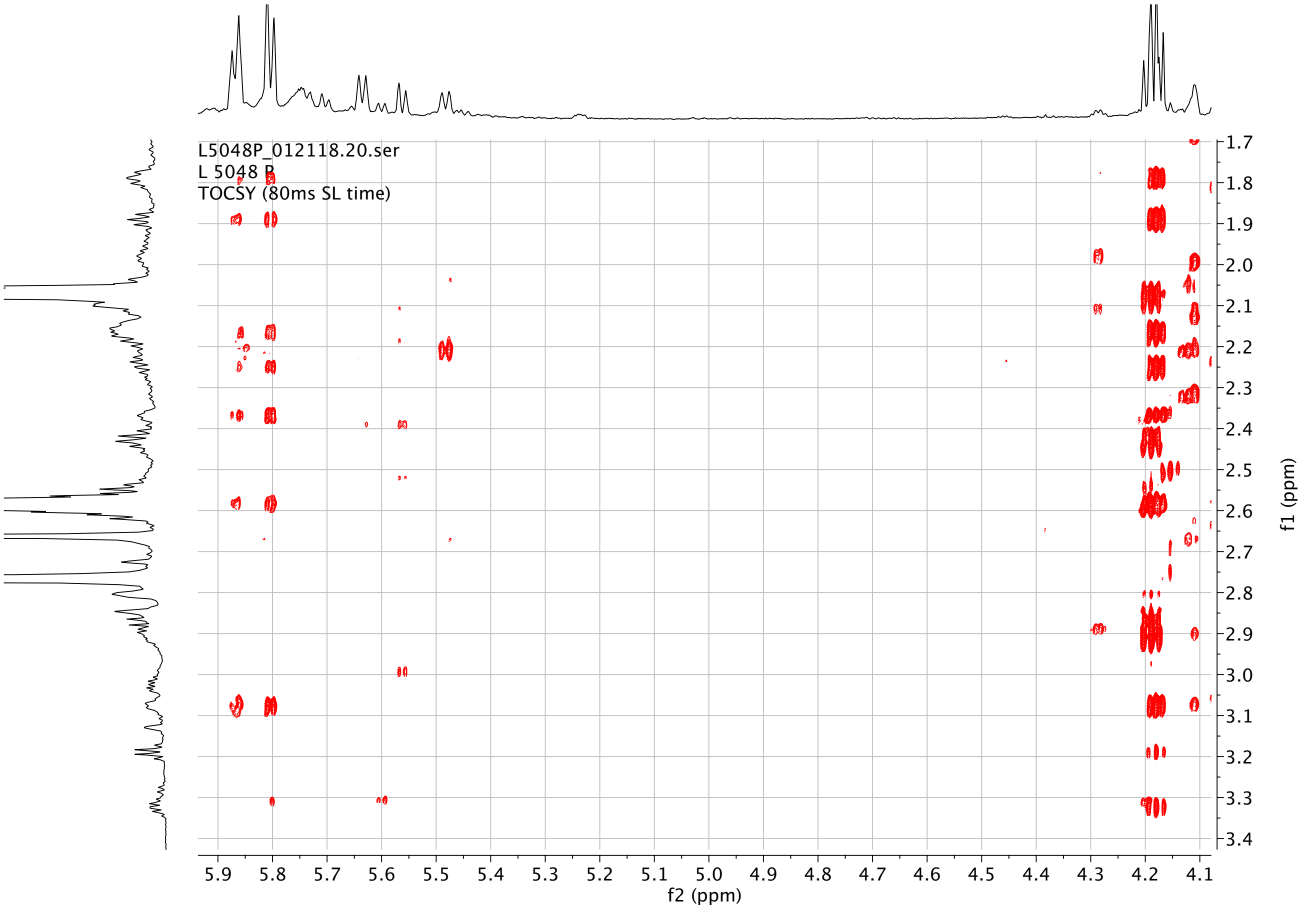


Figure S70. 1H NMR of [5]-Ladderane for Comparison to 52.

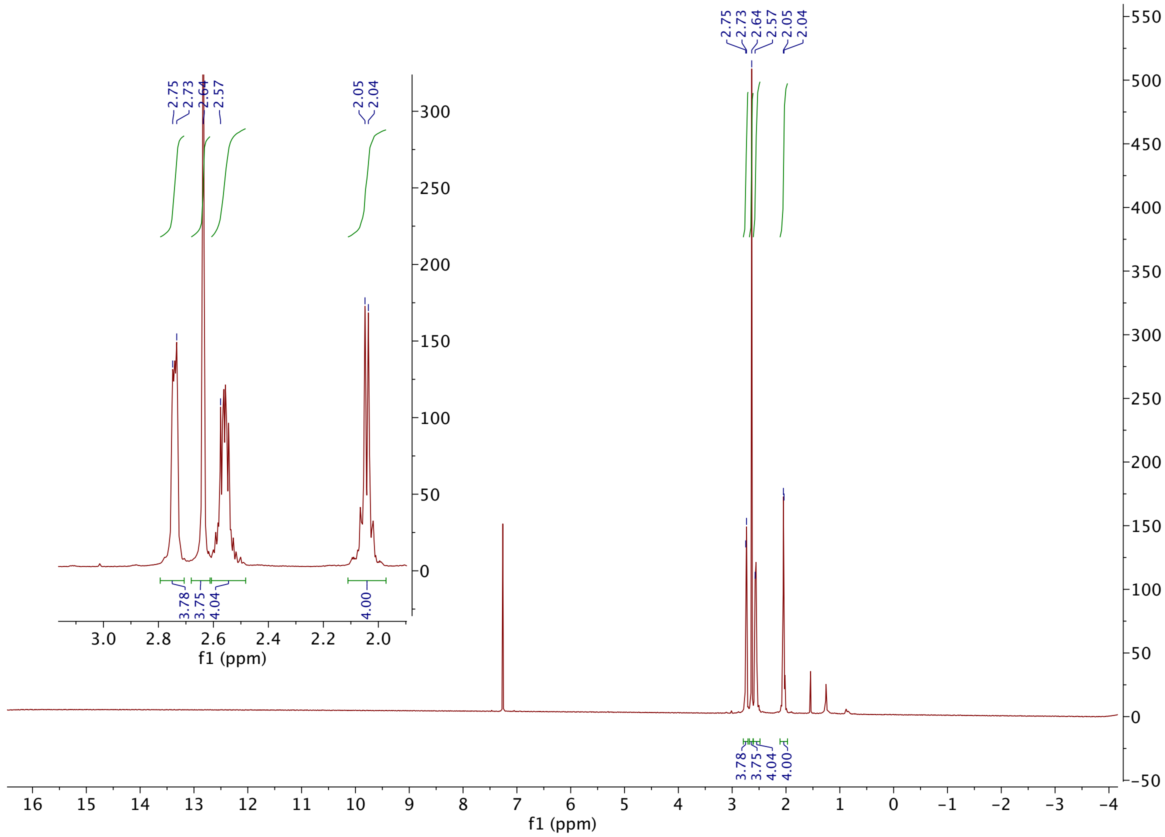


Figure S71. 13C NMR of [5]-Ladderane for Comparison to 52.

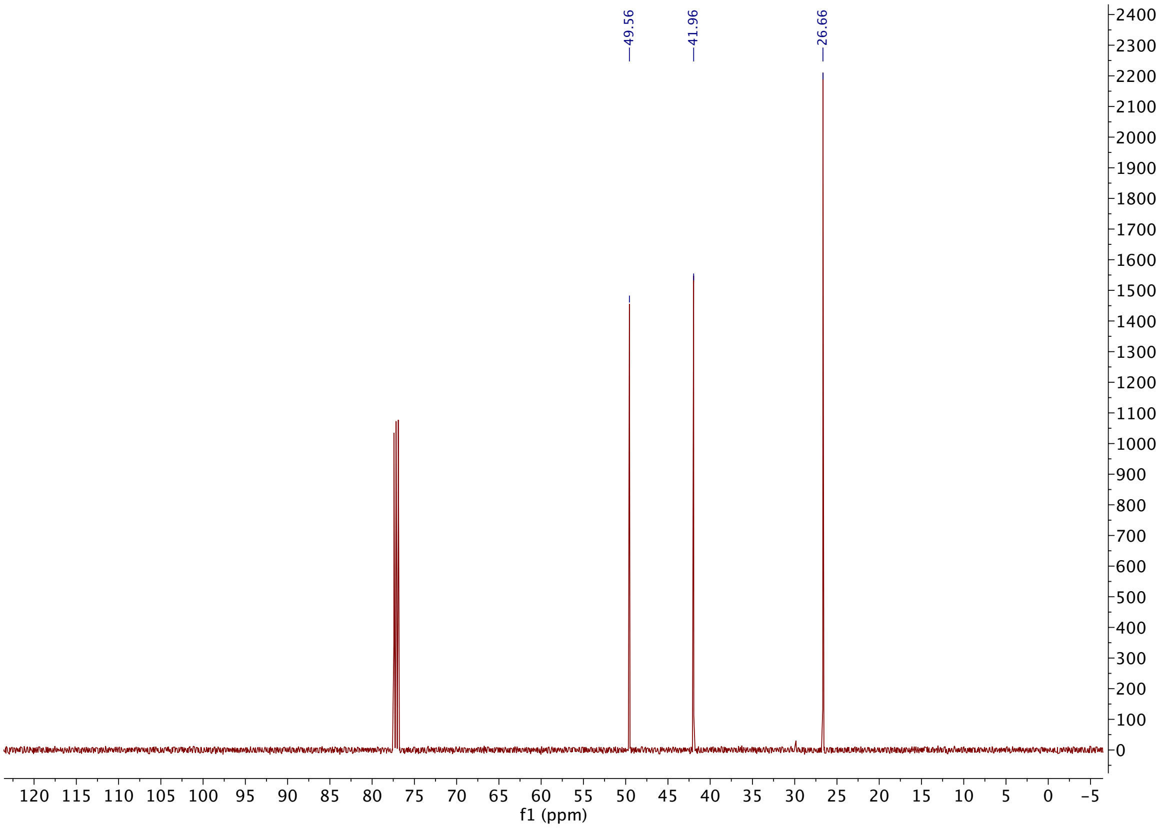


Figure S72. COSY of [5]-Ladderane for Comparison to 52.

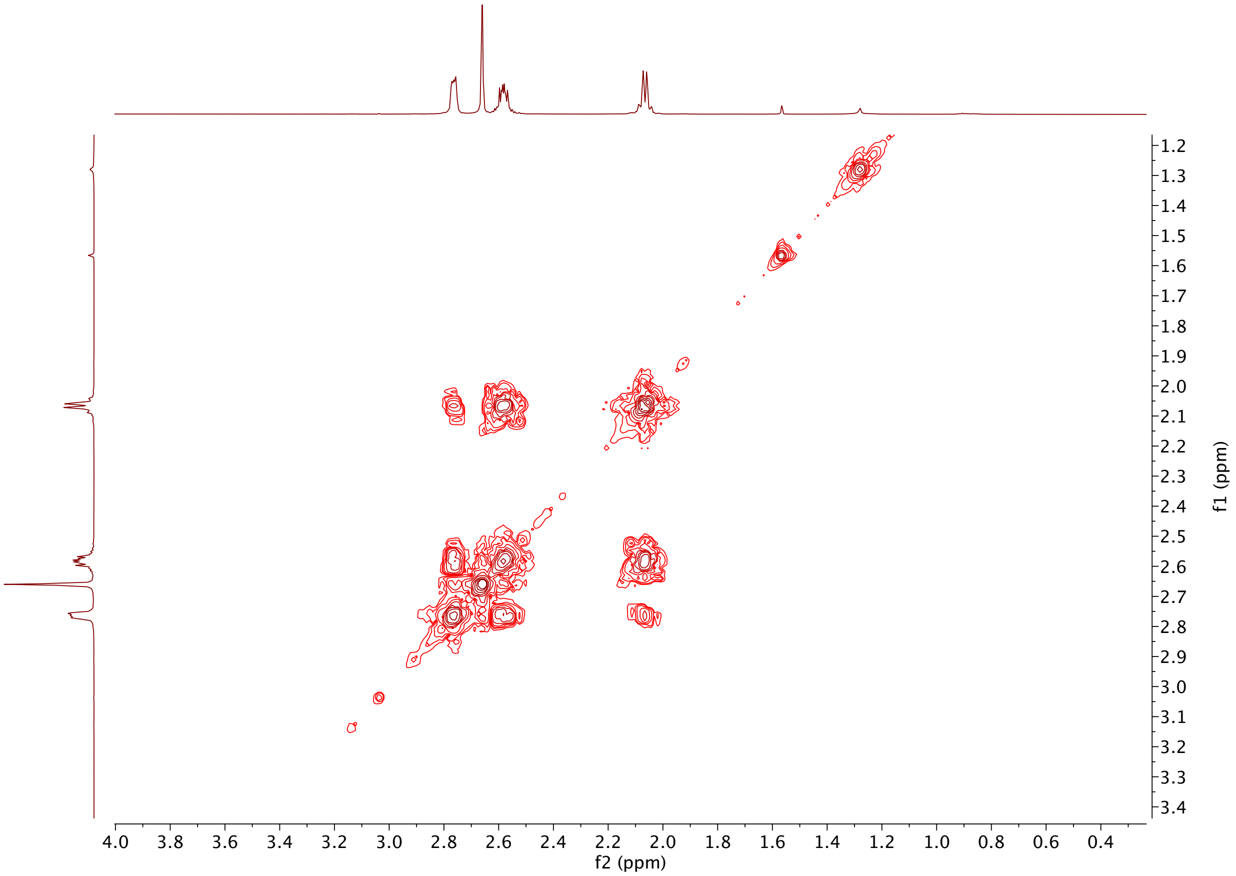
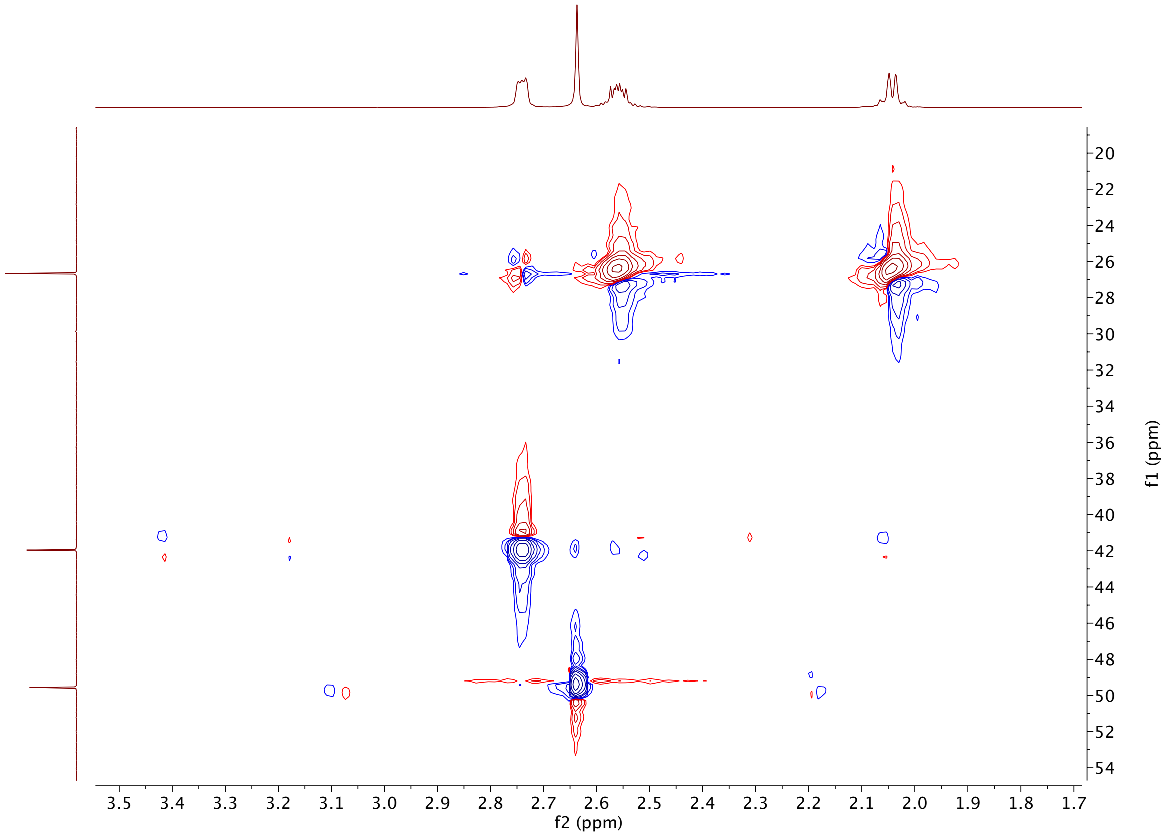
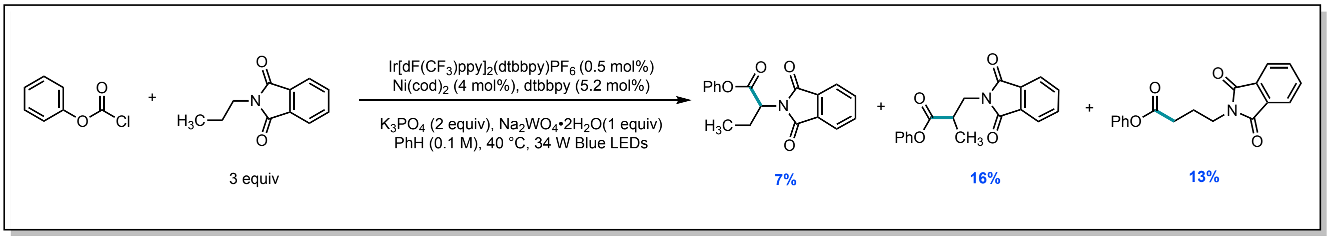


Figure S73. HSQC of [5]-Ladderane for Comparison to 52.



Additional Compound Prepared for Identification of α−Phthalimide Isomers:



Phenyl 2-(1,3-dioxoisoindolin-2-yl)butanoate (53-α) was prepared according to the general procedure for isolations from propyl phthalimide **S53** and phenyl chloroformate. The title compound was isolated via automated column chromatography, (eluting with EtOAc: hexanes, 0% 4 CV, 12-20% 20 CV) enabling characterization. Comparison of the crude reaction mixture to clean product resulted in 7% average NMR yield (Run 1= 7%; Run 2= 7%).
1H NMR (500 MHz, $CDCl_3$): δ 7.90 (dd, J = 5.4, 3.1 Hz, 2H), 7.76 (dd, J = 5.5, 3.0 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.10 – 7.04 (m, 2H), 5.01 (dd, J = 10.5, 5.1 Hz, 1H), 2.44 – 2.28 (m, 2H), 1.01 (t, J = 7.5 Hz, 3H).
13C NMR (126 MHz, $CDCl_3$): δ 168.20, 167.71, 150.56, 134.34, 131.80, 129.48, 126.15, 123.68, 121.47, 53.52, 22.51, 10.85.

Phenyl 3-(1,3-dioxoisoindolin-2-yl)-2-methylpropanoate (**53-**β) was prepared alongside **53-**α according to the general procedure for isolations from propyl phthalimide **S53** and phenyl chloroformate. The title compound was isolated via automated column chromatography, (eluting with EtOAc: hexanes; 0% 4 CV, 0-9% 10 CV, 9% 32 CV, 11% 15 CV, 15% 16 CV) enabling characterization. Comparison of the crude reaction mixture to clean product resulted in 16% average NMR yield (Run 1= 15% yield; Run 2= 17% yield).

1H NMR (500 MHz, $CDCl_3$): δ 7.86 (dd, J = 5.3, 3.1 Hz, 2H), 7.72 (dd, J = 5.4, 3.0 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 7.7 Hz, 2H), 4.17 – 4.1 (m, 1H), 3.91 (dd, J = 13.9, 6.4 Hz, 1H), 3.28 – 3.19 (m, 1H), 1.37 (d, J = 7.1 Hz, 3H).

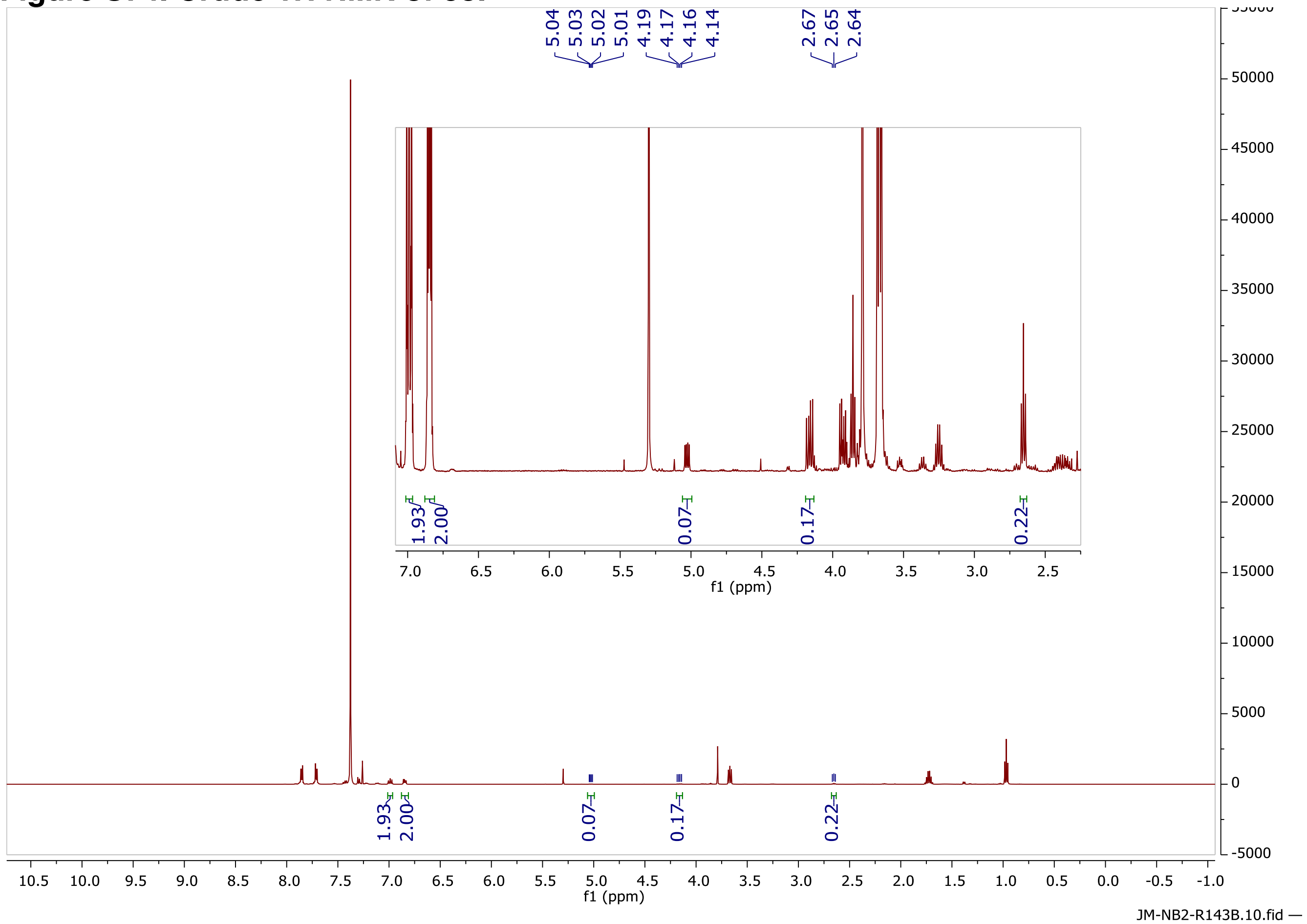
13C NMR (126 MHz, $CDCl_3$): δ 172.48, 168.24, 150.61, 134.17, 131.94, 129.44, 125.91, 123.49, 121.54, 40.44, 38.90, 14.78.

Phenyl 4-(1,3-dioxoisoindolin-2-yl)butanoate (**53-**γ) was prepared alongside **53-**α and **53-**β according to the general procedure for isolations from propyl phthalimide **S53** and phenyl chloroformate. The title compound was isolated via automated column chromatography, (eluting with EtOAc:hexanes; 0% 4 CV, 0-9% 10 CV, 9% 32 CV, 11% 15 CV, 15% 16 CV) enabling characterization. Comparison of the crude reaction mixture to clean product resulted in 13% average NMR yield (Run 1= 14%; Run 2= 11% yield).

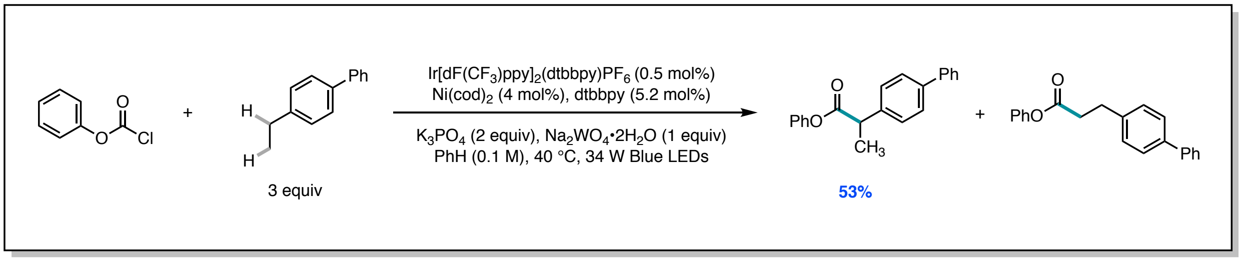
1H NMR (500 MHz, $CDCl_3$): δ 7.86 (dd, J = 5.4, 3.1 Hz, 2H), 7.72 (dd, J = 5.5, 3.0 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.09 (d, J = 7.7 Hz, 2H), 3.84 (t, J = 6.8 Hz, 2H), 2.64 (t, J = 7.3 Hz, 2H), 2.14 (p, J = 6.9 Hz, 2H).

13C NMR (126 MHz, $CDCl_3$): δ 171.20, 168.43, 150.65, 134.05, 132.07, 129.42, 125.83, 123.34, 121.58, 37.04, 31.58, 23.84.

Figure S74. Crude 1H NMR of 53.



Additional Compound Prepared for Hammett Analysis:



Phenyl 2-phenylpropanoate (54-α) was prepared according to the general procedure for isolations from 4-ethylbiphenyl and phenyl chloroformate at 40 °C. Isolation of fractions of authentic product were obtained using automated column chromatography (eluting with EtOAc:hexanes; 0% 4 CV, 0-1% 20 CV) enabling characterization. Comparison of the crude reaction mixture to clean product resulted in 53% average GC yield (Run 1= 49%, Run 2= 56%).

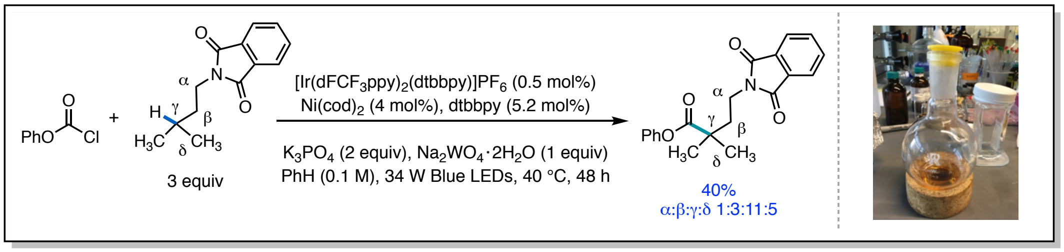
<u>1H NMR (500 MHz, CDCl$_3$):</u> δ 7.64 – 7.58 (m, 4H), 7.51 – 7.42 (m, 4H), 7.38 – 7.31 (m, 3H), 7.20 (m, 1.2 Hz, 1H), 7.04 – 7.00 (m, 2H), 4.02 (q, J = 7.2 Hz, 1H), 1.66 (d, J = 7.3 Hz, 3H).

<u>13C NMR (126 MHz, CDCl$_3$):</u> δ 173.03, 150.84, 140.70, 140.34, 139.09, 129.37, 128.81, 127.99, 127.55, 127.36, 127.10, 125.81, 121.41, 45.35, 18.58.

<u>HRMS:</u> (ESI-TOF) calculated for $C_{21}H_{19}O_2^+$ ([M+H]$^+$): 303.1380, found: 303.1379.

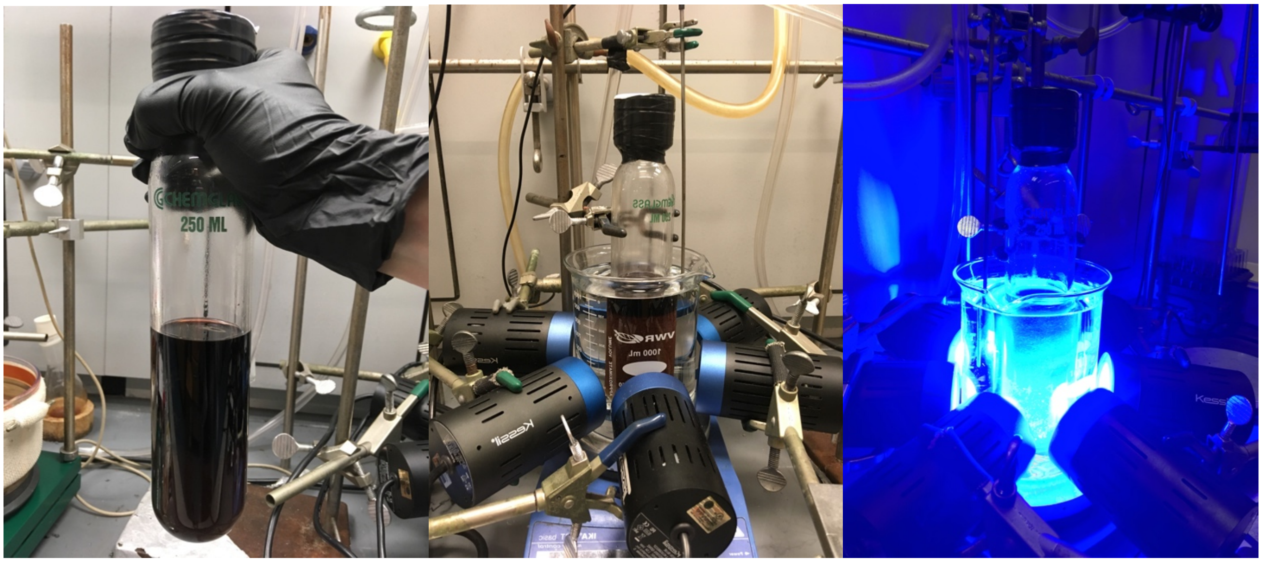
<u>FTIR (ATR cm^{-1}):</u> 2988, 1748.3, 1588, 1483, 1451, 1375, 1333, 1321, 1246, 1185, 1164, 1138, 1071, 1020, 1006, 923, 881, 843, 805, 779, 763, 749, 731, 709, 695, 687, 635, 614, 596, 564, 508, 497, 445, 410.

VIII. Large Scale C(sp^3)–H Functionalization (12 mmol scale):



An oven-dried 250 mL microwave reactor tube equipped with a teflon stir bar (VWR® egg-shaped magnetic stir bar, 58949-196) was charged with K_3PO_4 (5.1 g, 24 mmol, 2 equiv.) and Na_2WO_2•$2H_2O$ (4.0 g, 12 mmol, 1 equiv.) in a N_2-filled glovebox. To the reaction tube was added 80 mL of benzene and 3 equiv (7.8 g, 1.8 mmol) of isopentyl phthalimide (oil weighed into tube in glovebox). This was followed successively by 20 mL of a heterogeneous yellow solution of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (67 mg, 0.06 mmol, 0.005 equiv.) in benzene and 20 mL of a dark purple solution of Ni(cod)$_2$ (132 mg, 0.48 mmol, 0.04 equiv.) and 4,4′-di-tert-butyl-2,2′-bipyridine (167 mg, 0.62 mmol, 0.052 equiv.) in benzene, which had been stirred for 20 minutes prior to use. Lastly, phenyl chloroformate (1.5 mL, 12 mmol, 1 equiv.) was added to the reaction, turning the solution a deep red color. The tube was sealed with a teflon cap and reinforced with electrical tape. The reaction vessel was removed from the glove box, placed in an oil bath set to 40 °C, set to stir (780 rpm), and irradiated with five 34 W Kessil lamps for 48 hours. The crude mixture was filtered over a pad of silica and rinsed with dichloromethane and concentrated *in vacuo*. The crude product was analyzed by 1H NMR relative to 4-fluoroanisole as an external standard (40% combined yield with a ratio of isomers α:β:γ:δ 1:3:11:5) and purified by automated silica gel column chromatography. Two columns were used for separation to yield (1 g, 25% total) of the four isomers.

Figure S75. Large-scale reaction set-up.



IX. Calculation of Bond Dissociation Enthalpies and Free Energies

A. C(sp^3)–H Bond Strength Calculations. Calculations were performed on Gaussian 09 D.01 software suite.[18a] For all BDE and BDFE calculations the Complete Basis Set extrapolation method was used. Solution-phase composite calculations were carried out using CBS-QB3 and SMD (benzene) solvation model. All frequency calculations gave no imaginary frequencies. Absolute BDFEs were corrected by 1.894 kcal/mol to account for the conversion from 298.15 K and 1 atm to 298.15 K and 1 M.

Figure S76. Template for closed shell submissions

```
%chk=alpha.chk
# cbs-qb3 scrf=(smd,Solvent=Benzene)

Title Card Required

0 1
C   -3.34646   -0.41212    0.00228
C   -3.19107   -1.79945   -0.00082
C   -2.21550    0.40785    0.00046
C   -0.93464   -0.15574   -0.00430
C   -0.76461   -1.54639   -0.00684
C   -1.91059   -2.35950   -0.00552
C    0.58747   -2.22551   -0.01332
C    1.81410   -1.32225    0.00222
H    0.64433   -2.86106   -0.90600
H    0.64088   -2.88511    0.86200
H    1.84257   -0.67295   -0.87907
H    2.72597   -1.92842   -0.00039
H    1.83422   -0.69229    0.89768
C   -4.65747    0.16714    0.00705
N   -5.71922    0.63625    0.01090
H   -2.31986    1.49140    0.00258
H   -0.07955    0.51579   -0.00597
H   -4.06043   -2.45406    0.00028
H   -1.80881   -3.44376   -0.00819
```

Figure S77. Template for open shell submissions

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%chk=alpha1.chk
# cbs-qb3 scrf=(smd,Solvent=Benzene)

Title Card Required

0 2
C        1.66767709   0.10142794  -1.23951631
C        2.99142095   0.31994919  -0.83470449
C        3.27994887   1.31225705   0.11186759
C        2.24473258   2.08604166   0.65363006
C        0.92098867   1.86752014   0.24881855
C        0.63246103   0.87521388  -0.69775530
H        1.44737982  -0.65621997  -1.96224639
H        3.78183138  -0.27085359  -1.24835100
H        2.46502986   2.84368959   1.37636011
H        0.13057818   2.45832257   0.66246543
C        5.05316531   0.66248128   1.77251854
H        4.56103568  -0.28047065   1.88892338
H        5.76662685   0.98711828   2.50086149
C       -0.82220290   0.63507865  -1.14260126
N       -1.90526784   0.45629066  -1.47380626
C        4.73461284   1.55239250   0.55671332
H        4.86054701   2.58063944   0.82457298
H        5.39805483   1.30930784  -0.24681302
```

Table S16. C(sp^3)–H bond strengths of 2-methyl butane in kcal/mol.

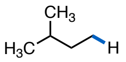
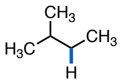
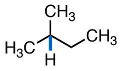
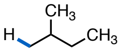
Bond	BDEs	BDFEs
	102.0	94.8
	99.4	91.7
	97.6	89.7
	102.7	95.6

Table S17. Enthalpies and energies of 2-methyl butane derivatives reported in Hartrees.

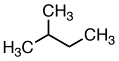
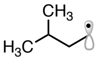
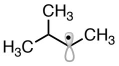
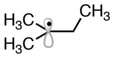
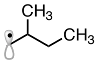
Entry	Bond	CBS-QB3 Enthalpies	CBS-QB3 Free Energies
1	$H^\bullet$	-0.497103	-0.510118
2		-197.306486	-197.344458
3		-196.646853	-196.686226
4		-196.650957	-196.691253
5		-196.653811	-196.694393
6		-196.645759	-196.685062

Table S18. C(sp^3)–H bond strengths of substituted ethyl benzene derivatives in kcal/mol.

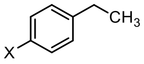
	BDEs		BDFEs	
	Benzylic	**Primary**	**Benzylic**	**Primary**
CN	86.9	102.3	80.1	95.2
CF_3	88.0	102.2	81.5	95.0
H	87.9	101.4	81.2	94.7
F	88.1	102.1	81.5	94.6
Ph	88.7	102.2	82.6	95.6
OPh	88.4	103.8	82.4	97.1

Table S19. Enthalpies and energies of substituted ethyl benzenes reported in Hartrees.

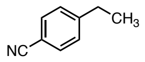
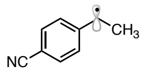
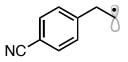
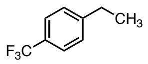
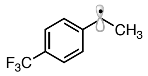
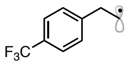
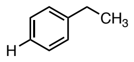
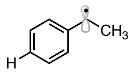
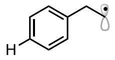
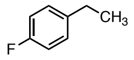
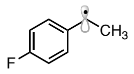
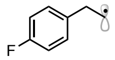
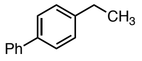
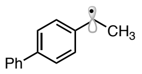
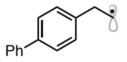
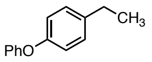
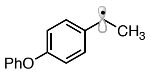
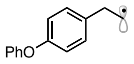
Entry	Bond	CBS-QB3 Enthalpies	CBS-QB3 Free Energies
1	$H^{\bullet}$	-0.497103	-0.510118
2		-402.371245	-402.416072
3		-401.735700	-401.780776
4		-401.711121	-401.757242
5		-646.999238	-647.049478
6		-646.361966	-646.412368
7		-636.361966	-646.412368
8		-310.245893	-310.285798
9		-309.608812	-309.64927
10		-309.587224	-309.627756
11		-409.413061	-409.45519
12		-408.775606	-408.818200
13		-408.753253	-408.797253
14		-540.872214	-540.924652
15		-540.233719	-540.285887
16		-540.21229	-540.265129
17		-616.003377	-616.059497
18		-615.365385	-615.421024
19		-615.340842	-615.397655

Table S20. C(sp^3)–H bond strengths of tetramethylsilane in kcal/mol.

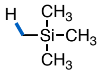
Bond	BDE	BDFE
	103.1	96.0

Table S21. Enthalpies and energies of tetramethylsilane reported in Hartrees.

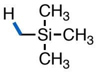
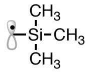
Entry	Bond	CBS-QB3 Enthalpies	CBS-QB3 Free Energies
1	H•	-0.497103	-0.510118
2		-448.373967	-448.416843
3		-447.712554	-447.756691

Figure S78. Cartesian Coordinates for Solution Phase Optimized Geometries.

Table S17; Entry 2

	X	Y	Z
C	-1.7421450	-0.8192110	-0.0088150
C	-0.4835040	-0.0027070	-0.3299140
H	-1.6510280	-1.8509760	-0.3627770
H	-2.6302260	-0.3838840	-0.4775960
H	-1.9225940	-0.8538670	1.0717450
H	-0.3524340	-0.0035060	-1.4210490
C	0.7636410	-0.6659600	0.2861600
C	-0.6567320	1.4539140	0.1213910
H	0.7729640	-1.7223880	-0.0074700
H	0.6653800	-0.6559110	1.3798540
C	2.0999790	-0.0328530	-0.1116840
H	-1.5525320	1.8979090	-0.3239680
H	0.1933670	2.0785890	-0.1648590
H	-0.7644250	1.5152020	1.2106940
H	2.2213680	-0.0138890	-1.2001560
H	2.9386750	-0.6008250	0.3021320
H	2.1940580	0.9944460	0.2506210

Table S17; Entry 3

	X	Y	Z
C	-1.6904410	-0.8079030	-0.0173720
C	-0.4304110	0.0075230	-0.3292580
H	-1.6086140	-1.8325370	-0.3935470
H	-2.5775850	-0.3563060	-0.4719840
H	-1.8653110	-0.8631230	1.0631410
H	-0.2945930	0.0178340	-1.4191890
C	0.8230950	-0.6588490	0.2825490
C	-0.5816660	1.4585400	0.1436260
H	0.8107020	-1.7257330	-0.0047210
H	0.7391040	-0.6536450	1.3771130
C	2.1157190	-0.0497300	-0.1337690
H	-1.4402340	1.9427910	-0.3319520
H	0.3088820	2.0497640	-0.0878520
H	-0.7353230	1.5006690	1.2281620
H	2.2717340	0.2599270	-1.1623170
H	2.9734630	-0.0371220	0.5284920

Table S17; Entry 4

	X	Y	Z
C	-1.6508810	-0.9420830	-0.0305430
C	-0.4561920	-0.0195000	-0.3130390
H	-1.4568010	-1.9600320	-0.3803900
H	-2.5567460	-0.5809980	-0.5270940
H	-1.8587010	-0.9919680	1.0440180
H	-0.2949060	0.0098010	-1.4007070
C	0.8002720	-0.5300680	0.3259600
C	-0.7730760	1.4299200	0.1297930
H	0.7119030	-1.0447040	1.2802620
C	2.1538850	-0.0921720	-0.1179280
H	-1.6674030	1.8057060	-0.3788950
H	0.0526150	2.1085570	-0.1015300
H	-0.9539420	1.4754790	1.2087910
H	2.2014830	0.0381900	-1.2054060
H	2.9272160	-0.8110070	0.1713750
H	2.4512320	0.8743930	0.3241160

Table S17; Entry 5

	X	Y	Z
C	1.7696130	-0.8071400	-0.1170180
C	0.5080940	-0.0027290	-0.1076460
H	2.1762470	-0.9442710	0.9019640
H	2.5589240	-0.3215210	-0.7006410
H	1.6120280	-1.8107510	-0.5256140
C	0.6250670	1.4792710	0.0645850
C	-0.7648340	-0.7031740	0.2777180
H	0.7132320	1.7601100	1.1304350
H	-0.2422250	2.0199590	-0.3254380
H	1.5159310	1.8712080	-0.4357860
H	-0.8038100	-0.8094230	1.3790580
H	-0.7324540	-1.7300730	-0.1053370
C	-2.0675080	-0.0367890	-0.1853640
H	-2.2108240	0.9453270	0.2728100
H	-2.9301600	-0.6519700	0.0866270
H	-2.0794810	0.0947710	-1.2717300

Table S17; Entry 6

	X	Y	Z
C	-1.7794090	-0.7428960	0.0006500
C	-0.4908390	0.0551830	0.3202380
H	-1.9469460	-0.7949960	-1.0798140
H	-2.6575500	-0.2740720	0.4530790
H	-1.7065240	-1.7665320	0.3836970
C	-0.6245700	1.4727610	-0.1324600
C	0.7422730	-0.6386980	-0.2930960
H	-0.3746010	0.0498840	1.4130210
H	-0.3868650	1.7487740	-1.1555150
H	-1.1283030	2.2113930	0.4814400
H	0.6536730	-0.6083090	-1.3867680
H	0.7250200	-1.6984500	-0.0139020
C	2.0775860	-0.0244150	0.1327940
H	2.1428750	1.0296930	-0.1525160
H	2.9193360	-0.5482860	-0.3300050
H	2.2096440	-0.0807040	1.2185140

Table S19; Entry 2

	X	Y	Z
C	1.5918500	-0.0317840	-0.0007530
C	1.0324700	1.2560170	0.0146360
C	0.7493690	-1.1493290	-0.0269280
C	-0.6310950	-0.9789870	-0.0379760
C	-1.2038400	0.2969810	-0.0239610
C	-0.3443630	1.4065720	0.0037390
C	-2.7024830	0.5314730	-0.0457390
C	-3.5936600	-0.7044360	0.0699600
H	-2.9463750	1.0655930	-0.9724780
H	-2.9464890	1.2288630	0.7636770
H	-3.4459970	-1.3955060	-0.7645060
H	-4.6454810	-0.4073310	0.0645450
H	-3.4110240	-1.2515280	0.9994520
C	3.0109920	-0.1987940	0.0122560
N	4.1586500	-0.3332110	0.0225680
H	1.1773530	-2.1442630	-0.0378140
H	-1.2620980	-1.8586000	-0.0571360
H	1.6812120	2.1231380	0.0370720
H	-0.7670760	2.4058290	0.0178020

Table S19; Entry 3

	X	Y	Z
C	-0.7046340	-1.1570080	-0.0032320
C	0.6643330	-0.9999470	-0.0052430
C	1.2621140	0.2959140	-0.0043160
C	0.3814900	1.4195180	-0.0020310
C	-0.9858350	1.2641400	-0.0006440
C	-1.5515760	-0.0291710	-0.0008590
H	-1.1409530	-2.1485450	-0.0027610
H	1.2957530	-1.8797370	-0.0053400
H	0.8072660	2.4168310	-0.0013490
H	-1.6370970	2.1297220	0.0012400
C	2.6556700	0.4902890	-0.0026760
H	3.0095400	1.5162510	0.0130150
C	3.6772450	-0.5974650	0.0043200
H	3.4927630	-1.3456260	-0.7752650
H	4.6794720	-0.1944480	-0.1503660
H	3.6882880	-1.1392110	0.9605370
C	-2.9648330	-0.1942830	0.0022510
N	-4.1141250	-0.3295940	0.0049820

Table S19; Entry 4

	X	Y	Z
C	-0.9050920	-1.2397270	0.0662370
C	0.4769540	-1.3337360	-0.0445470
C	1.2676370	-0.1945590	-0.2235090
C	0.6357800	1.0551990	-0.2860420
C	-0.7423000	1.1674370	-0.1802010
C	-1.5241350	0.0153300	-0.0014810
H	-1.5061590	-2.1296600	0.2074920
H	0.9481080	-2.3090660	0.0103960
H	1.2352960	1.9491780	-0.4193700
H	-1.2204630	2.1377910	-0.2347170
C	3.5253050	0.4986430	0.6674490
H	3.1510770	0.5939770	1.6800220
H	4.5286630	0.8488800	0.4566240
C	-2.9451800	0.1225980	0.1096040
N	-4.0938500	0.2102230	0.1985780
C	2.7751180	-0.2956990	-0.3487830
H	3.0754060	0.0226300	-1.3554580
H	3.0605030	-1.3582130	-0.2873990

Table S19; Entry 5

	X	Y	Z
C	-1.9683100	0.3120240	0.0029580
C	-1.1264340	1.4350520	-0.0093120
C	0.2537120	1.3036850	-0.0259530
C	-1.3738620	-0.9521230	-0.0052680
C	0.0126960	-1.0966410	-0.0216630
C	0.8293170	0.0296570	-0.0329910
C	2.3219490	-0.1074370	-0.0010060
C	-3.4716270	0.5210340	0.0257060
C	-4.3372970	-0.7379060	-0.0047570
H	-3.7385190	1.1614480	-0.8232350
H	-3.7187400	1.1051560	0.9205060
H	-4.1622090	-1.3292440	-0.9080550
H	-5.3956060	-0.4649690	0.0090490
H	-4.1528060	-1.3793890	0.8615230
F	2.7415560	-1.3261270	-0.4084300
F	2.8249810	0.0733140	1.2477420
F	2.9380950	0.8061750	-0.7887670
H	0.8849640	2.1841870	-0.0409490
H	-1.5645630	2.4279460	-0.0078990
H	-1.9882360	-1.8437540	-0.0007030
H	0.4531590	-2.0857160	-0.0314200

Table S19; Entry 6

	X Y	Z	
C	-2.0244990	0.3085040	0.0008460
C	-1.1631330	1.4445640	-0.0063460
C	0.2088540	1.3080740	-0.0229140
C	-1.4059430	-0.9740440	-0.0114490
C	-0.0295090	-1.1056290	-0.0276390
C	0.7892300	0.0298550	-0.0357840
C	2.2792100	-0.1047520	-0.0005860
C	-3.4254110	0.4804830	0.0151580
C	-4.4256480	-0.6272650	0.0128650
H	-3.7969990	1.5001550	0.0105720
H	-4.4189780	-1.1822750	-0.9358410
H	-5.4370110	-0.2428600	0.1558930
F	2.7024360	-1.3168270	-0.4253610
F	2.7809710	0.0567610	1.2528490
F	2.8977140	0.8225450	-0.7711690
H	0.8422570	2.1870980	-0.0334700
H	-1.6039480	2.4354200	-0.0006090
H	-2.0210070	-1.8655180	-0.0109610
H	0.4190450	-2.0911580	-0.0410730
H	-4.2323590	-1.3619100	0.8037120

Table S19; Entry 7

	X	Y	Z
C	-2.0233580	0.2006660	-0.2329920
C	-1.2485890	1.3490670	-0.0534570
C	0.1370380	1.2713540	0.0580930
C	-1.3732940	-1.0390780	-0.2926430
C	0.0081630	-1.1282120	-0.1845740
C	0.7674330	0.0305160	-0.0059240
C	2.2629880	-0.0624860	0.0601720
C	-3.5328080	0.2807950	-0.3574430
C	-4.2720040	-0.5143410	0.6660180
H	-3.8317490	-0.0485670	-1.3610070
H	-3.8315500	1.3402030	-0.3036550
H	-5.2740260	-0.8730920	0.4625500
H	-3.8914460	-0.6033600	1.6768490
F	2.6807130	-1.1995680	0.6635160
F	2.8167160	0.9697100	0.7358180
F	2.8302200	-0.0587130	-1.1739950
H	0.7219240	2.1710020	0.2039020
H	-1.7325800	2.3181920	0.0033630
H	-1.9590480	-1.9427760	-0.4226110
H	0.4962190	-2.0941390	-0.2309330

Table S19; Entry 8

	X	Y	Z
C	-0.4089010	-0.2869790	0.0428560
C	0.5680080	-1.2921570	-0.0094280
C	1.9233150	-0.9816300	-0.0436900
C	0.0216150	1.0428040	0.0555770
C	1.3809980	1.3595650	0.0203760
C	2.3371960	0.3507050	-0.0298910
C	-1.8758390	-0.6821970	0.0914530
C	-2.8934330	0.4419880	-0.1055050
H	-2.0457810	-1.4538670	-0.6679240
H	-2.8359190	1.1925270	0.6879590
H	-3.9087180	0.0363620	-0.0941400
H	2.6584940	-1.7784150	-0.0843190
H	0.2580780	-2.3331690	-0.0232780
H	-0.7026250	1.8477130	0.0902310
H	1.6882470	2.4000420	0.0293970
H	-2.7522490	0.9523720	-1.0628690
H	3.3930180	0.5964350	-0.0592470
H	-2.0702940	-1.1726050	1.0536990

Table S19; Entry 9

	X	Y	Z
C	0.4616650	-0.2927460	-0.0037080
C	-0.5389460	-1.3073390	-0.0006700
C	-1.8854160	-0.9911540	0.0020830
C	0.0124560	1.0585940	-0.0029100
C	-1.3394290	1.3627460	-0.0004850
C	-2.3001060	0.3463560	0.0019870
C	1.8314260	-0.6429280	-0.0056400
C	2.9639610	0.3307770	0.0032200
H	2.0718080	-1.7014190	0.0045450
H	3.9222390	-0.1806760	-0.1056710
H	-2.6246950	-1.7851860	0.0046720
H	-0.2261310	-2.3466620	-0.0003650
H	0.7390340	1.8624430	-0.0029660
H	-1.6541660	2.4011120	0.0000800
H	3.0063560	0.9058230	0.9392310
H	-3.3559650	0.5917080	0.0041060
H	2.8878610	1.0670110	-0.8068960

Table S19; Entry 10

	X	Y	Z
C	0.4782570	-0.1930690	-0.2089340
C	-0.3891530	-1.2711480	-0.0126540
C	-1.7577210	-1.0679390	0.1637780
C	-0.0605830	1.0998660	-0.2223160
C	-1.4258530	1.3071420	-0.0473240
C	-2.2809630	0.2222560	0.1463980
C	1.9671790	-0.4069510	-0.4138250
C	2.8334160	0.3269000	0.5540130
H	2.1749150	-1.4887890	-0.3617700
H	3.8565840	0.5756700	0.2966360
H	-2.4128610	-1.9187830	0.3168190
H	0.0104810	-2.2802400	0.0040400
H	0.5996430	1.9485530	-0.3706870
H	-1.8242640	2.3159200	-0.0633820
H	2.5119650	0.4796600	1.5776840
H	-3.3445910	0.3828790	0.2832650
H	2.2406560	-0.1172110	-1.4374160

Table S19; Entry 11

	X	Y	Z
C	-0.0278240	1.3764210	0.0061850
C	-1.4030470	1.1727890	0.0262690
C	-1.8790480	-0.1296720	0.0072600
C	-1.0277590	-1.2184510	-0.0298010
C	0.3496800	-0.9915340	-0.0502270
C	0.8746930	0.3035260	-0.0346560
C	2.3660780	0.5946590	-0.0710960
C	3.3005140	-0.6040550	0.0931490
H	2.5897480	1.3293950	0.7104760
H	3.1868170	-1.3284820	-0.7184580
H	4.3418500	-0.2709500	0.0864770
H	0.3535470	2.3924950	0.0230230
H	-2.1014340	2.0003130	0.0589370
H	-1.4369690	-2.2214870	-0.0409360
H	1.0127440	-1.8472450	-0.0771150
H	3.1277150	-1.1268000	1.0386400
H	2.5965990	1.0971940	-1.0187360
F	-3.2211480	-0.3385040	0.0283540

Table S19; Entry 12

	X	Y	Z
C	0.3849910	-1.0079890	-0.0024810
C	-0.9835820	-1.2236250	-0.0011820
C	-1.8380430	-0.1276770	0.0003100
C	-1.3622630	1.1802740	0.0009940
C	0.0039950	1.3920680	-0.0005300
C	0.9297450	0.3082650	-0.0029160
C	2.3213600	0.5575210	-0.0047090
C	3.3769900	-0.4987550	0.0027950
H	3.2446400	-1.2268650	-0.8075560
H	3.3787950	-1.0747540	0.9392820
H	1.0508260	-1.8621520	-0.0020320
H	-1.3997090	-2.2240760	-0.0008290
H	-2.0657420	2.0042290	0.0029420
H	0.3861290	2.4070850	0.0001130
H	2.6400620	1.5947930	0.0059330
F	-3.1783230	-0.3375520	0.0018610
H	4.3707510	-0.0607860	-0.1082870

Table S19; Entry 13

	X	Y	Z
C	-0.1338710	1.3074910	-0.0573040
C	1.2480810	1.1931170	0.0925870
C	1.8136250	-0.0694420	0.0544050
C	1.0506010	-1.2129730	-0.1276170
C	-0.3264620	-1.0771380	-0.2733590
C	-0.9404690	0.1818230	-0.2430360
C	-2.4448130	0.3052690	-0.4016450
C	-3.2266410	-0.3938950	0.6595830
H	-2.7452340	-0.0763250	-1.3862430
H	-2.8555690	-0.4415880	1.6767820
H	-4.2427000	-0.7198120	0.4689690
H	-0.5875200	2.2924660	-0.0274550
H	1.8782670	2.0620040	0.2390130
H	1.5333600	-2.1824030	-0.1529940
H	-0.9349910	-1.9645480	-0.4121260
H	-2.7069340	1.3760340	-0.4205860
F	3.1578900	-0.1945930	0.1992170

Table S19; Entry 14

	X	Y	Z
C	-1.8473830	1.3760660	-0.4080900
C	-0.4621020	1.2915870	-0.3847470
C	0.1856860	0.0958300	-0.0335100
C	-0.6199860	-1.0014520	0.2923420
C	-2.0109120	-0.9120630	0.2675510
C	-2.6548680	0.2770220	-0.0825790
C	1.6681840	0.0006850	-0.0048910
C	-4.1660680	0.4254040	-0.1282080
C	-4.9852300	-0.8024270	0.2694910
H	-4.4507490	0.7291950	-1.1429210
H	-4.7748500	-1.1162460	1.2959820
H	-6.0534410	-0.5779230	0.2076000
C	2.3256480	-1.1682930	-0.4192460
C	3.7141680	-1.2592440	-0.3908480
C	4.4803930	-0.1821380	0.0505450
C	3.8430860	0.9860630	0.4643440
C	2.4543070	1.0761000	0.4376160
H	1.7439140	-2.0046500	-0.7897940
H	4.1986390	-2.1706460	-0.7241390
H	5.5622290	-0.2521540	0.0715370
H	4.4284660	1.8279860	0.8178700
H	1.9720680	1.9821690	0.7868320
H	-2.3157740	2.3136550	-0.6931950
H	0.1274250	2.1572490	-0.6655220
H	-0.1575230	-1.9346700	0.5940660
H	-2.5919800	-1.7861300	0.5363830
H	-4.7902270	-1.6532110	-0.3898640
H	-4.4477390	1.2665390	0.5165470

Table S19; Entry 15

	X	Y	Z
C	-1.8861070	1.3987180	-0.3563370
C	-0.5108740	1.3067350	-0.3367170
C	0.1436640	0.0946090	-0.0263260
C	-0.6683600	-1.0206540	0.2663120
C	-2.0470520	-0.9405610	0.2521890
C	-2.7167080	0.2777560	-0.0614830
C	1.6199760	-0.0002900	-0.0045790
C	-4.1194300	0.3986020	-0.0903210
C	-5.0818580	-0.7099890	0.1870690
H	-4.5274710	1.3693670	-0.3536470
H	-4.8777870	-1.2105350	1.1416360
H	-6.1081670	-0.3393650	0.2220010
C	2.2783960	-1.1895900	-0.3640200
C	3.6663180	-1.2786630	-0.3417720
C	4.4366480	-0.1811550	0.0391610
C	3.8012860	1.0064970	0.3978110
C	2.4133020	1.0961010	0.3768910
H	1.6977230	-2.0446530	-0.6900890
H	4.1480720	-2.2059530	-0.6324390
H	5.5185430	-0.2502920	0.0556790
H	4.3886570	1.8652510	0.7044520
H	1.9374210	2.0193860	0.6863440
H	-2.3570410	2.3429470	-0.6106890
H	0.0791020	2.1796800	-0.5917640
H	-0.2014370	-1.9614440	0.5351170
H	-2.6283940	-1.8229890	0.4927530
H	-5.0444330	-1.4900980	-0.5866220

Table S19; Entry 16

	X	Y	Z
C	1.9545740	-1.1970860	-0.5898180
C	0.5645500	-1.1782170	-0.5102660
C	-0.1219730	-0.0238080	-0.1107220
C	0.6424270	1.1100820	0.2079850
C	2.0294500	1.0864830	0.1293140
C	2.7124560	-0.0676950	-0.2725410
C	-1.6049810	-0.0009180	-0.0186790
C	4.2270690	-0.0796460	-0.3544060
C	4.9091860	0.2120840	0.9402280
H	4.5609620	0.6423650	-1.1112920
H	4.5484140	-1.0622670	-0.7377370
H	5.9166900	0.6117790	0.9528710
H	4.4785110	-0.1196720	1.8778460
C	-2.3353090	1.1376790	-0.3934050

C	-3.7240790	1.1604740	-0.3028940
C	-4.4167380	0.0446200	0.1631840
C	-3.7061210	-1.0941500	0.5377900
C	-2.3172620	-1.1163360	0.4487320
H	-1.8115650	2.0043200	-0.7807980
H	-4.2667060	2.0497150	-0.6049840
H	-5.4985880	0.0622770	0.2334880
H	-4.2332950	-1.9658200	0.9102400
H	-1.7768070	-2.0001080	0.7683380
H	2.4564320	-2.1047760	-0.9103870
H	0.0059390	-2.0662910	-0.7838430
H	0.1453650	2.0130110	0.5445370
H	2.5951480	1.9740750	0.3947090

Table S19; Entry 17

	X	Y	Z
C	1.9502200	-0.8977900	-0.6601970
C	0.6490840	-0.4101310	-0.7447860
C	0.2760080	0.6809610	0.0386280
C	2.8990660	-0.3139610	0.1871130
C	2.4985010	0.7837180	0.9567100
C	1.1991560	1.2797480	0.8911520
H	-0.0687400	-0.8705470	-1.4130670
O	-0.9762360	1.2620510	-0.0560660
H	2.2322580	-1.7497000	-1.2709850
C	4.3228030	-0.8255550	0.2361180
H	3.2096690	1.2556140	1.6274400
H	0.8902550	2.1280050	1.4905460
C	-2.1161640	0.4861600	-0.0220860
C	-2.2316730	-0.6560610	0.7717260
C	-3.2009890	0.9388510	-0.7727430
C	-4.4067610	0.2451390	-0.7279120
C	-4.5330090	-0.9017000	0.0549640
C	-3.4427190	-1.3443870	0.8017660
H	-5.4718310	-1.4422920	0.0858860
H	-3.5323000	-2.2305220	1.4204880
H	-1.3896670	-0.9975020	1.3609910
H	-3.0842330	1.8312530	-1.3760020
H	-5.2478950	0.6008450	-1.3125500
H	4.3300820	-1.8984640	0.0191310
H	4.7151960	-0.7108530	1.2516800
C	5.2586690	-0.1060520	-0.7491050
H	4.9166050	-0.2296890	-1.7807170
H	6.2761170	-0.5030950	-0.6813710
H	5.3012260	0.9668910	-0.5410370

Table S19; Entry 18

	X	Y	Z
C	2.0157400	-0.7772560	-0.4481760
C	0.6834400	-0.4039040	-0.5023320
C	0.2950070	0.8611410	-0.0471040
C	3.0203990	0.0987190	0.0540560
C	2.5827410	1.3808370	0.4985500
C	1.2548570	1.7521910	0.4508490
H	-0.0560740	-1.0867970	-0.9023270
O	-0.9965090	1.3333580	-0.1321120
H	2.2958330	-1.7599070	-0.8083850
C	4.3849400	-0.2566100	0.1170700
H	3.3176300	2.0782890	0.8867760
H	0.9323320	2.7296710	0.7900750
C	-2.0754030	0.4751550	-0.0295750
C	-2.1877460	-0.4509610	1.0079930
C	-3.1001800	0.6285990	-0.9604270
C	-4.2465900	-0.1553920	-0.8543790
C	-4.3672600	-1.0918990	0.1705660
C	-3.3357100	-1.2341750	1.0982980
H	-5.2590460	-1.7028540	0.2492020
H	-3.4259580	-1.9538410	1.9044330
H	-1.3900100	-0.5506220	1.7341350
H	-2.9875490	1.3621840	-1.7497150
H	-5.0439180	-0.0347660	-1.5792420
H	5.0727110	0.4824470	0.5152800
C	4.9460830	-1.5682980	-0.3276970
H	4.7660220	-1.7562650	-1.3951180
H	6.0252300	-1.6079380	-0.1677960
H	4.5029550	-2.4153400	0.2134300

Table S19; Entry 19

	X	Y	Z
C	1.9915950	-0.9153070	-0.6862640
C	0.6916380	-0.4212780	-0.7547790
C	0.3337340	0.6727810	0.0315710
C	2.9495000	-0.3336760	0.1503590
C	2.5684290	0.7699170	0.9208160
C	1.2708940	1.2701100	0.8709590
H	-0.0366200	-0.8795390	-1.4131540
O	-0.9159300	1.2600800	-0.0457680
H	2.2637180	-1.7685910	-1.2992990
C	4.3844710	-0.8555090	0.1862230
H	3.2925110	1.2414930	1.5774560
H	0.9730030	2.1212840	1.4717670
C	-2.0598850	0.4893240	-0.0134550
C	-2.1794140	-0.6541120	0.7778650
C	-3.1434380	0.9494880	-0.7610470
C	-4.3526300	0.2616420	-0.7156900
C	-4.4830220	-0.8865280	0.0644520
C	-3.3936970	-1.3366340	0.8082950
H	-5.4244980	-1.4224600	0.0957650
H	-3.4867190	-2.2237820	1.4250240
H	-1.3380770	-1.0007930	1.3650770
H	-3.0233730	1.8429500	-1.3620620
H	-5.1931400	0.6230930	-1.2976660
H	4.3788030	-1.9138110	-0.0955040
H	4.7597790	-0.7961410	1.2126610
C	5.2760910	-0.0836290	-0.7330010
H	5.2608280	-0.2800220	-1.7993170
H	5.7756350	0.8161390	-0.3924170

Table S21; Entry 2

	X	Y	Z
C	-0.4902220	0.8578530	1.6036810
Si	-0.0002910	-0.0005930	-0.0006590
H	-1.1348530	1.7231040	1.4138370
H	0.3886730	1.2169500	2.1498900
H	-1.0367060	0.1819430	2.2704200
C	-1.5497860	-0.5992810	-0.8893850
H	-2.1135130	-1.3089460	-0.2743280
H	-1.3041870	-1.1035770	-1.8301690
H	-2.2210370	0.2325610	-1.1289570
C	0.9289540	1.2137740	-1.1018490
H	0.3116430	2.0843660	-1.3489820
H	1.2315450	0.7482150	-2.0460610
H	1.8366410	1.5833900	-0.6125940
C	1.1113490	-1.4718150	0.3881220
H	0.6045840	-2.1985190	1.0323110
H	2.0248340	-1.1570900	0.9042420
H	1.4146820	-1.9972900	-0.5238040

Table S21; Entry 3

	X	Y	Z
C	1.5151280	-0.8300720	-0.7183680
Si	-0.0019280	-0.0135810	0.0434740
H	1.5901850	-0.6032280	-1.7874670
H	1.4835370	-1.9192180	-0.6127670
H	2.4374000	-0.4786040	-0.2435230
C	0.1064480	1.8515190	-0.2357630
H	1.0194970	2.2695300	0.2003720
H	-0.7437380	2.3759490	0.2120340
H	0.1132400	2.0836600	-1.3068090
C	-1.5729470	-0.6661900	-0.7640550
H	-1.5827010	-0.4577070	-1.8394040
H	-2.4660840	-0.2015910	-0.3324320
H	-1.6697480	-1.7490480	-0.6356890
C	-0.0518000	-0.3822160	1.8595110
H	0.8434330	-0.5169920	2.4635760
H	-0.9790070	-0.4508610	2.4255200

B. Ni–Cl Bond Strength Calculations. Calculations were performed on Gaussian 16 software suite, revision B.01.[18b] Gas-phase composite calculations were carried out using B3LYP. All frequency calculations gave no imaginary frequencies. Absolute BDFEs were corrected by 1.894 kcal/mol to account for the conversion from 298.15 K and 1 atm to 298.15 K and 1 M.

Table S22. Ni–Cl bond strengths of (dtbbpy)Ni^{II}(COOPh)(Cl) in kcal/mol.

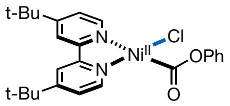
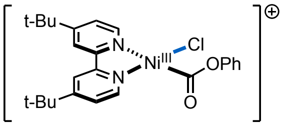
Bond	BDE	BDFE
	74.1	65.1
	41.8	37.3

Table S23. Enthalpies and energies of (dtbbpy)Ni^{III}(COOPh)(Cl) reported in Hartrees.

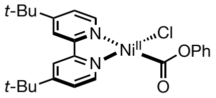
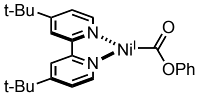
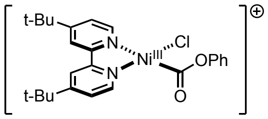
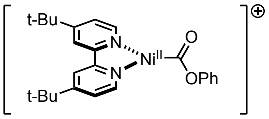
Entry	Bond	B3LYP TZVP Enthalpies	B3LYP TZVP Free Energies
1	Cl$^{\bullet}$	-460.162051	-460.180089
2		-3198.691156	-3198.789991
3		-2738.410967	-2738.509221
4		-3198.453797	-3198.555573
5		-2738.225127	-2738.319027

Table S24. Ni–Cl bond strengths of (dtbbpy)Ni^{II}(COPh)(Cl) in kcal/mol.

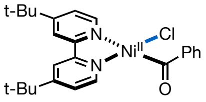
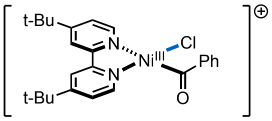
Bond	BDE	BDFE
	80.4	72.0
	46.1	40.4

Table S25. Enthalpies and energies of (dtbbpy)Ni^{III}(COPh)(Cl) reported in Hartrees.

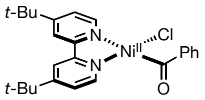
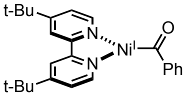
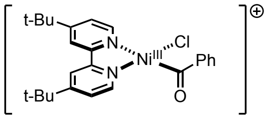
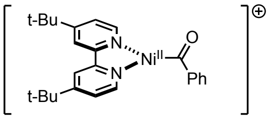
Entry	Bond	B3LYP TZVP Enthalpies	B3LYP TZVP Free Energies
1		-3123.438121	-3123.534427
2		-2663.147912	-2663.242610
3		-3123.222403	-3123.319792
4		-2662.986812	-2663.078378

Figure S79. Cartesian Coordinates for Gas Phase Optimized Geometries.

Table 23; entry 1

0.00000	0.00000	0.00000

Table 23; entry 2

Ni	0.88686	-1.02942	-0.59423
C	-1.18796	0.82010	-0.17491
C	0.79766	1.91596	-0.61085
C	-1.85026	2.03322	-0.05310
C	0.18542	3.15494	-0.49506
H	1.84454	1.83683	-0.86393
C	-1.17343	3.24687	-0.20086
H	-2.91075	2.03021	0.15130
H	0.79331	4.03435	-0.64464
C	-1.85248	-0.49407	-0.08088
C	-3.18888	-0.68365	0.24436
C	-3.73969	-1.96893	0.27929
H	-3.80554	0.17270	0.47477
C	-1.54491	-2.76730	-0.32951
C	-2.87526	-3.02048	-0.02304
H	-0.83903	-3.55723	-0.55632
H	-3.21256	-4.04598	-0.02244
C	2.68060	-0.45895	-0.66759
Cl	1.61588	-3.07230	-0.92738
N	0.14266	0.76038	-0.44101
N	-1.03994	-1.53445	-0.36079
C	-1.91884	4.57768	-0.05482
C	-5.21623	-2.16939	0.64056

C	-3.04275	4.64954	-1.11194
H	-2.63580	4.58557	-2.12304
H	-3.77030	3.84527	-0.99119
H	-3.57859	5.59692	-1.02156
C	-2.53462	4.66134	1.35918
H	-3.24780	3.85611	1.54292
H	-1.76162	4.60763	2.12840
H	-3.06613	5.60796	1.47844
C	-0.98801	5.78453	-0.25202
H	-0.18162	5.80193	0.48391
H	-0.54448	5.79884	-1.24959
H	-1.55912	6.70702	-0.13449
C	-6.09636	-1.40695	-0.37408
H	-5.89437	-0.33461	-0.36633
H	-5.93182	-1.77261	-1.38965
H	-7.15185	-1.54655	-0.13054
C	-5.47023	-1.61771	2.06068
H	-4.85476	-2.13550	2.79902
H	-5.25163	-0.55089	2.13029
H	-6.51825	-1.75966	2.33351
C	-5.62107	-3.65178	0.61606
H	-5.48786	-4.09454	-0.37306
H	-5.05196	-4.24180	1.33714
H	-6.67667	-3.74439	0.87728
O	3.22617	0.11194	-1.57778
O	3.33389	-0.71218	0.53194
C	4.70144	-0.47413	0.65308
C	5.12304	0.31933	1.71259
C	5.62260	-1.07791	-0.19600
C	6.48440	0.51535	1.92480
H	4.38234	0.76567	2.36389
C	6.97975	-0.87125	0.02195
H	5.27563	-1.70080	-1.00856
C	7.41677	-0.07595	1.07863
H	6.81403	1.13032	2.75372
H	7.70054	-1.33920	-0.63771
H	8.47626	0.07714	1.24286

Table 23; entry 3

Ni	1.18271	-0.59015	-0.02958
C	-1.37349	0.71802	0.00578
C	0.31214	2.29822	-0.00042
C	-2.34232	1.71292	0.03914
C	-0.60919	3.33850	0.03058
H	1.38387	2.46835	-0.01783
C	-1.97670	3.06394	0.05186
H	-3.38768	1.44012	0.05662
H	-0.23720	4.35204	0.03863
C	-1.66105	-0.73706	-0.01150

C	-2.94032	-1.27761	-0.02015
C	-3.14384	-2.66076	-0.03579
H	-3.79072	-0.61141	-0.01565
C	-0.74272	-2.85516	-0.03516
C	-1.99404	-3.45171	-0.04330
H	0.15743	-3.45704	-0.04114
H	-2.04900	-4.52988	-0.05568
C	2.99812	0.10090	-0.05178
N	-0.05910	1.01766	-0.01351
N	-0.56064	-1.53005	-0.01946
C	-3.05363	4.15574	0.08853
C	-4.56418	-3.23795	-0.04504
C	-3.95726	4.02228	-1.15686
H	-3.37763	4.13249	-2.07560
H	-4.46286	3.05591	-1.19326
H	-4.72603	4.79824	-1.14576
C	-3.90731	3.98645	1.36445
H	-4.41134	3.01902	1.39357
H	-3.29168	4.07114	2.26223
H	-4.67567	4.76182	1.40574
C	-2.44628	5.56754	0.09650
H	-1.81579	5.73493	0.97198
H	-1.85058	5.75986	-0.79805
H	-3.24770	6.30811	0.12269
C	-5.30860	-2.73799	-1.30261
H	-5.38900	-1.65003	-1.32414
H	-4.79693	-3.05471	-2.21370
H	-6.32177	-3.14562	-1.32352
C	-5.31435	-2.76462	1.21939
H	-4.80687	-3.10051	2.12595
H	-5.39491	-1.67735	1.26348
H	-6.32760	-3.17250	1.22707
C	-4.56292	-4.77472	-0.06124
H	-4.06930	-5.17256	-0.95027
H	-4.07254	-5.19124	0.82101
H	-5.59152	-5.13946	-0.06699
O	3.38046	1.24820	-0.09408
O	3.99572	-0.94905	0.01180
C	5.34723	-0.66554	0.00664
C	6.12643	-1.20627	1.02749
C	5.95150	0.07186	-1.01137
C	7.50462	-1.01953	1.02759
H	5.63762	-1.77519	1.80834
C	7.32913	0.25980	-0.99953
H	5.34306	0.49393	-1.79824
C	8.11282	-0.28274	0.01564
H	8.10313	-1.44885	1.82270
H	7.79355	0.83514	-1.79205
H	9.18579	-0.13423	0.01623

Table 23; entry 4

Ni	0.76461	-1.30898	0.14170
C	-1.11299	0.80526	0.03788
C	1.03786	1.66349	0.20487
C	-1.62911	2.09030	-0.00200
C	0.57013	2.96508	0.17023
H	2.09593	1.46494	0.29828
C	-0.79815	3.21592	0.05862
H	-2.69765	2.22133	-0.07900
H	1.28834	3.76826	0.23085
C	-1.94474	-0.41996	0.01156
C	-3.32742	-0.43204	-0.07238
C	-4.03701	-1.64220	-0.07368
H	-3.86674	0.50091	-0.13587
C	-1.89408	-2.73451	0.10064
C	-3.27666	-2.80843	0.01864
H	-1.28065	-3.62259	0.18474
H	-3.74025	-3.78292	0.02950
C	2.56143	-1.03519	-0.43433
Cl	1.44797	-3.20502	0.90827
N	0.22802	0.59907	0.13520
N	-1.24236	-1.57137	0.09153
C	-1.39272	4.62408	0.00878
C	-5.56457	-1.64236	-0.16931
C	-2.17619	4.79055	-1.31343
H	-1.52576	4.65656	-2.17985
H	-3.00255	4.08271	-1.39631
H	-2.59918	5.79511	-1.36257
C	-2.35181	4.80491	1.20772
H	-3.18171	4.09678	1.18327
H	-1.82777	4.68152	2.15740
H	-2.77704	5.80951	1.18626
C	-0.30831	5.71048	0.07783
H	0.26022	5.66465	1.00903
H	0.38862	5.64868	-0.76058
H	-0.77933	6.69292	0.03517
C	-5.98450	-0.95295	-1.48746
H	-5.65303	0.08580	-1.53436
H	-5.58068	-1.47764	-2.35545
H	-7.07254	-0.95383	-1.57020
C	-6.14329	-0.86171	1.03265
H	-5.85322	-1.32034	1.97988
H	-5.81623	0.17944	1.04535
H	-7.23312	-0.86206	0.97853
C	-6.14326	-3.06574	-0.15421
H	-5.79113	-3.66077	-0.99930
H	-5.90390	-3.59626	0.76962
H	-7.23015	-3.01378	-0.22534

O	2.56164	-1.08477	-1.62854
O	3.48162	-0.75614	0.44553
C	4.85339	-0.51586	0.09120
C	5.53831	0.27549	0.99725
C	5.45407	-1.08466	-1.01800
C	6.88690	0.52512	0.76934
H	5.02847	0.67111	1.86556
C	6.80644	-0.82187	-1.22690
H	4.90486	-1.71237	-1.70346
C	7.52053	-0.02061	-0.34299
H	7.44033	1.14029	1.46688
H	7.29889	-1.25618	-2.08717
H	8.57092	0.17295	-0.51694

Table 23; entry 5

Ni	-1.16087	-0.38326	-0.01588
C	1.35333	0.74301	-0.01295
C	-0.29678	2.37559	-0.04582
C	2.33818	1.71567	-0.02239
C	0.65081	3.38684	-0.05569
H	-1.35423	2.59831	-0.05541
C	2.01159	3.07833	-0.04411
H	3.37459	1.41265	-0.01307
H	0.30546	4.40916	-0.07288
C	1.59996	-0.71430	0.00972
C	2.84735	-1.31483	0.03137
C	2.97251	-2.71128	0.05307
H	3.73327	-0.69726	0.03184
C	0.56144	-2.78494	0.03020
C	1.78297	-3.44139	0.05208
H	-0.37194	-3.33345	0.02983
H	1.78559	-4.52046	0.06852
C	-2.94108	-0.08587	-0.02622
N	0.03726	1.08068	-0.02476
N	0.46597	-1.45413	0.00913
C	3.11368	4.14003	-0.05480
C	4.35709	-3.36385	0.07699
C	3.98030	3.97710	1.21459
H	3.38407	4.10320	2.12037
H	4.46499	3.00045	1.26091
H	4.76636	4.73396	1.22107
C	3.99107	3.94005	-1.31145
H	4.47565	2.96236	-1.32511
H	3.40265	4.03980	-2.22558
H	4.77748	4.69626	-1.33329
C	2.54107	5.56574	-0.07814
H	1.93996	5.75190	-0.97056
H	1.93203	5.77771	0.80308
H	3.36156	6.28398	-0.08493

C	5.11134	-2.89496	1.34190
H	5.25665	-1.81350	1.35849
H	4.57663	-3.17930	2.25023
H	6.09846	-3.35911	1.37324
C	5.13869	-2.93022	-1.18385
H	4.62386	-3.24018	-2.09529
H	5.28451	-1.84960	-1.22761
H	6.12621	-3.39455	-1.18069
C	4.27198	-4.89796	0.09743
H	3.75359	-5.26835	0.98424
H	3.77172	-5.29289	-0.78920
H	5.27945	-5.31501	0.11354
O	-2.86469	-1.32507	-0.02125
O	-3.98686	0.67787	-0.02334
C	-5.31609	0.13298	-0.01000
C	-6.17021	0.65274	0.94444
C	-5.71748	-0.78951	-0.95952
C	-7.48838	0.20735	0.96073
H	-5.81080	1.38544	1.65450
C	-7.03999	-1.22253	-0.92872
H	-5.02830	-1.16315	-1.70390
C	-7.92234	-0.72849	0.02707
H	-8.17389	0.59728	1.70186
H	-7.37859	-1.94449	-1.66047
H	-8.94909	-1.07016	0.04135

Table 24; entry 1

Ni	1.28615	-0.91623	-0.73818
C	-0.86028	0.83963	-0.19249
C	1.07444	2.03144	-0.58529
C	-1.56538	2.01983	0.00126
C	0.42032	3.23904	-0.39569
H	2.11973	2.01064	-0.85118
C	-0.93793	3.26460	-0.08606
H	-2.62229	1.96552	0.21641
H	0.99516	4.14689	-0.49958
C	-1.48191	-0.49882	-0.14463
C	-2.80907	-0.74123	0.18836
C	-3.32144	-2.04222	0.17666
H	-3.44887	0.08542	0.46036
C	-1.11153	-2.74839	-0.48622
C	-2.43004	-3.05492	-0.17713
H	-0.38514	-3.50755	-0.75099
H	-2.73745	-4.08915	-0.21582
C	3.05101	-0.26738	-0.94545
Cl	2.07760	-2.94466	-1.07232
N	0.46851	0.84150	-0.47797
N	-0.64308	-1.50097	-0.47353
C	-1.73123	4.55633	0.13822

C	-4.78784	-2.30083	0.54379
C	-2.86568	4.64416	-0.90626
H	-2.46475	4.65204	-1.92176
H	-3.56060	3.80664	-0.82636
H	-3.43674	5.56368	-0.75994
C	-2.33832	4.53956	1.55828
H	-3.01931	3.69904	1.70152
H	-1.55752	4.47259	2.31858
H	-2.90380	5.45754	1.73303
C	-0.84765	5.80643	0.00240
H	-0.03661	5.81346	0.73343
H	-0.41280	5.89176	-0.99545
H	-1.45165	6.69913	0.17386
C	-5.70108	-1.52615	-0.43149
H	-5.53045	-0.44943	-0.38335
H	-5.53606	-1.84650	-1.46217
H	-6.74954	-1.70665	-0.18411
C	-5.04364	-1.81331	1.98678
H	-4.40618	-2.34191	2.69839
H	-4.85436	-0.74428	2.09667
H	-6.08444	-1.99578	2.26343
C	-5.14914	-3.79253	0.46461
H	-5.01365	-4.19177	-0.54253
H	-4.55456	-4.39314	1.15583
H	-6.19862	-3.92713	0.73244
O	3.33319	0.33708	-1.96187
C	4.07258	-0.41172	0.15565
C	5.33676	0.16637	-0.00509
C	3.77155	-1.07031	1.34818
C	6.28056	0.08537	1.00930
H	5.55914	0.67093	-0.93698
C	4.71565	-1.15044	2.36552
H	2.80380	-1.54175	1.45953
C	5.97065	-0.57259	2.19843
H	7.25959	0.53045	0.87564
H	4.47668	-1.67062	3.28537
H	6.70801	-0.63821	2.98992

Table 24; entry 2

Ni	-1.63707	0.11645	-0.12294
C	1.12879	-0.70069	-0.01336
C	-0.24227	-2.55978	-0.02321
C	2.26216	-1.50302	0.03305
C	0.85296	-3.41506	0.01986
H	-1.26816	-2.91400	-0.06344
C	2.14773	-2.89759	0.05290
H	3.24050	-1.04458	0.04998
H	0.67068	-4.47928	0.02785
C	1.15054	0.78136	-0.04442

C	2.31135	1.54348	0.00249
C	2.26551	2.93948	-0.05074
H	3.26485	1.04187	0.08286
C	-0.12654	2.69617	-0.19238
C	0.99548	3.50930	-0.15361
H	-1.11751	3.12605	-0.27068
H	0.85748	4.57894	-0.20463
C	-3.30855	-0.90661	-0.14712
N	-0.10972	-1.23264	-0.03761
N	-0.07159	1.36120	-0.13591
C	3.40476	-3.77569	0.10235
C	3.55747	3.76342	0.00338
C	4.27595	-3.48937	-1.14031
H	3.73068	-3.70963	-2.06029
H	4.59722	-2.44735	-1.18247
H	5.17303	-4.11250	-1.12011
C	4.20701	-3.44609	1.38022
H	4.52698	-2.40308	1.40394
H	3.61197	-3.63477	2.27608
H	5.10303	-4.06901	1.43062
C	3.06358	-5.27421	0.11894
H	2.46815	-5.54659	0.99262
H	2.51798	-5.57759	-0.77675
H	3.98585	-5.85704	0.15504
C	4.46193	3.37200	-1.18579
H	4.73666	2.31638	-1.15948
H	3.96384	3.56532	-2.13803
H	5.38507	3.95547	-1.16121
C	4.29384	3.46889	1.32871
H	3.67506	3.73333	2.18861
H	4.56268	2.41543	1.42068
H	5.21576	4.05241	1.38186
C	3.28303	5.27367	-0.07348
H	2.78608	5.55057	-1.00554
H	2.66877	5.61921	0.76056
H	4.22806	5.81809	-0.03182
O	-3.30517	-2.13196	-0.31492
C	-4.67294	-0.24909	0.00826
C	-5.85095	-0.93600	-0.30061
C	-4.76169	1.07022	0.44814
C	-7.08527	-0.31296	-0.17418
H	-5.76872	-1.96352	-0.63491
C	-5.99551	1.69682	0.59398
H	-3.84286	1.59345	0.70080
C	-7.16083	1.00586	0.27536
H	-7.99399	-0.84965	-0.42309
H	-6.05083	2.71944	0.94971
H	-8.12496	1.49067	0.37673

Table 24; entry 3

Ni	1.13684	-1.23048	-0.02593
C	-0.84363	0.81900	0.01658
C	1.26508	1.77430	0.09994
C	-1.42333	2.07863	0.04201
C	0.73786	3.05390	0.12797
H	2.33604	1.62370	0.12652
C	-0.64486	3.24058	0.09560
H	-2.49940	2.15988	0.02134
H	1.41945	3.88933	0.17498
C	-1.61724	-0.44495	-0.01082
C	-3.00134	-0.51791	-0.03317
C	-3.65612	-1.75758	-0.04149
H	-3.58365	0.39103	-0.04222
C	-1.46112	-2.75433	0.00573
C	-2.84154	-2.88980	-0.01832
H	-0.80624	-3.61574	0.03920
H	-3.26012	-3.88455	-0.01673
C	2.83624	-0.93606	-0.82561
Cl	1.89821	-3.06366	0.88242
N	0.50589	0.67481	0.04228
N	-0.86167	-1.56394	0.00180
C	-1.30734	4.61976	0.12055
C	-5.18551	-1.82424	-0.07024
C	-2.16683	4.78747	-1.15300
H	-1.55768	4.70989	-2.05564
H	-2.96205	4.04289	-1.21565
H	-2.63859	5.77140	-1.14898
C	-2.20852	4.72009	1.37232
H	-3.00303	3.97213	1.36937
H	-1.62905	4.59576	2.28916
H	-2.68242	5.70250	1.40433
C	-0.27318	5.75532	0.16751
H	0.34606	5.70973	1.06582
H	0.38018	5.75144	-0.70749
H	-0.79121	6.71476	0.18048
C	-5.69542	-1.11347	-1.34430
H	-5.41149	-0.06002	-1.37095
H	-5.30859	-1.59171	-2.24623
H	-6.78511	-1.16049	-1.37940
C	-5.74368	-1.11003	1.18145
H	-5.39103	-1.58537	2.09878
H	-5.46145	-0.05632	1.21556
H	-6.83390	-1.15750	1.17534
C	-5.69977	-3.27226	-0.07821
H	-5.35899	-3.82349	-0.95700
H	-5.39609	-3.82033	0.81599
H	-6.79007	-3.26785	-0.10093
O	2.32978	-0.96095	-1.91072

C	4.18211	-0.67423	-0.36883
C	4.51901	-0.75935	0.98871
C	5.14723	-0.31078	-1.32797
C	5.81835	-0.48470	1.38432
H	3.77460	-1.07080	1.70821
C	6.43977	-0.03951	-0.91668
H	4.87218	-0.25543	-2.37320
C	6.77393	-0.12571	0.43572
H	6.09145	-0.55870	2.42863
H	7.19167	0.23326	-1.64573
H	7.78897	0.08307	0.74994

Table 24; entry 4

Ni	-1.33708	-0.91405	-0.02325
C	0.86913	0.75843	-0.00600
C	-1.08334	1.99973	-0.03087
C	1.62428	1.91965	-0.00153
C	-0.37692	3.19182	-0.02729
H	-2.16261	1.99674	-0.04722
C	1.01785	3.18177	-0.01062
H	2.70130	1.84372	0.00827
H	-0.93342	4.11652	-0.03791
C	1.43512	-0.60754	-0.00519
C	2.78676	-0.91134	0.01146
C	3.22429	-2.24293	0.00648
H	3.51087	-0.11046	0.02860
C	0.89222	-2.85727	-0.02988
C	2.23014	-3.22225	-0.01508
H	0.10689	-3.60211	-0.04581
H	2.47587	-4.27313	-0.02046
C	-3.15747	-1.15177	-0.00994
N	-0.48967	0.80185	-0.01843
N	0.49796	-1.58238	-0.02549
C	1.86896	4.45373	-0.00396
C	4.72077	-2.56639	0.02463
C	2.74431	4.46559	1.26968
H	2.13053	4.45284	2.17244
H	3.42436	3.61312	1.31032
H	3.35225	5.37165	1.28861
C	2.77498	4.45916	-1.25602
H	3.45636	3.60702	-1.27556
H	2.18329	4.44115	-2.17331
H	3.38273	5.36550	-1.26510
C	1.00601	5.72505	-0.01775
H	0.38318	5.78819	-0.91251
H	0.36163	5.79274	0.86129
H	1.65447	6.60178	-0.01211
C	5.34965	-1.96520	1.30189
H	5.24667	-0.87946	1.34053

H	4.89252	-2.38119	2.20180
H	6.41617	-2.19487	1.32908
C	5.38526	-1.94305	-1.22366
H	4.95352	-2.34276	-2.14327
H	5.28355	-0.85672	-1.24591
H	6.45210	-2.17281	-1.22501
C	4.98428	-4.08024	0.01504
H	4.56196	-4.57551	0.89179
H	4.58642	-4.56006	-0.88153
H	6.05990	-4.25948	0.02833
O	-2.63482	-2.27730	-0.03173
C	-4.57195	-0.86126	0.00753
C	-5.51026	-1.90864	-0.04027
C	-5.01158	0.46782	0.07407
C	-6.86304	-1.61845	-0.02356
H	-5.16337	-2.93246	-0.09096
C	-6.36836	0.75055	0.09290
H	-4.28666	1.26936	0.11603
C	-7.29123	-0.29176	0.04304
H	-7.58933	-2.42000	-0.06141
H	-6.71033	1.77584	0.14598
H	-8.35125	-0.07083	0.05651

Table S26. C(sp^3)–H bond strengths of substituted cyclohexanes reported in kcal/mol. Gaussian 16 was used for the following calculations.

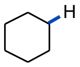
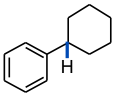
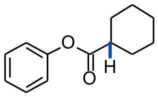
Bond	BDEs	BDFEs
	100	91
	89	80
	91	84

Table S27. Enthalpies and energies of substituted cyclohexanes reported in Hartrees. Gaussian 16 was used for the following calculations.

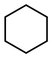
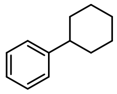
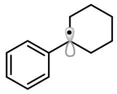
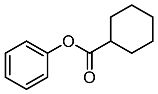
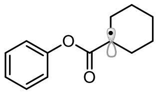
Entry	Bond	CBS-QB3 Enthalpies	CBS-QB3 Free Energies
1	H•	-0.497103	-0.510118
2		-235.775196	-235.809039
3		-235.122774	-235.159525
4		-465.974010	-466.021737
5		-465.334701	-465.383461
6		-654.321045	-654.377393
7		-653.677928	-653.734936

Figure S80. Cartesian Coordinates for Solution Phase Optimized Geometries

Table 27 entry 2

	X	Y	Z
C	-1.2705000	0.7335230	0.2277470
C	0.0000000	1.4670470	-0.2277470
C	1.2705000	0.7335230	0.2277470
C	1.2705000	-0.7335230	-0.2277470
C	0.0000000	-1.4670470	0.2277470
C	-1.2705000	-0.7335230	-0.2277470
H	2.1600600	1.2471110	-0.1524590
H	0.0000000	1.5392440	-1.3230940
H	0.0000000	2.4942230	0.1524590
H	-1.3330240	0.7696220	1.3230940
H	-2.1600600	1.2471110	-0.1524590
H	1.3330240	-0.7696220	-1.3230940
H	2.1600600	-1.2471110	0.1524590
H	0.0000000	-2.4942230	-0.1524590
H	0.0000000	-1.5392440	1.3230940
H	-1.3330240	-0.7696220	-1.3230940
H	-2.1600600	-1.2471110	0.1524590

H	1.3330240	0.7696220	1.3230940

Table 27 entry 3

	X	Y	Z
C	0.0487790	0.7500640	1.2685100
C	-0.6210730	1.2960470	0.0000000
C	0.0487790	0.7500640	-1.2685100
C	0.0487790	-0.7927420	-1.2882210
C	0.5381550	-1.3710300	0.0000000
C	0.0487790	-0.7927420	1.2882210
H	-0.4542920	1.1342730	-2.1619570
H	-1.6829670	1.0150030	0.0000000
H	-0.5890780	2.3907960	0.0000000
H	1.0847810	1.1071920	1.3090840
H	-0.4542920	1.1342730	2.1619570
H	-0.9879830	-1.1303170	-1.4767300
H	0.6394150	-1.1651310	-2.1313130
H	1.0350240	-2.3357990	0.0000000
H	-0.9879830	-1.1303170	1.4767300
H	0.6394150	-1.1651310	2.1313130
H	1.0847810	1.1071920	-1.3090840

Table 27 entry 4

	X	Y	Z
C	2.8264710	1.3207690	-0.0196710
C	1.4505490	1.1060260	-0.0163400
C	0.9206580	-0.1917260	0.0030110
C	1.8186350	-1.2650450	0.0188900
C	3.1970910	-1.0557220	0.0156330
C	3.7070120	0.2398390	-0.0037040
H	3.2123140	2.3346210	-0.0347890
H	0.7828770	1.9609340	-0.0290040
H	1.4318340	-2.2794750	0.0339760
H	3.8710600	-1.9057550	0.0281910
H	4.7784730	0.4071080	-0.0063240
C	-0.5783010	-0.4387490	0.0067860
C	-1.2692450	0.1309070	1.2663730
C	-1.2691870	0.0917440	-1.2698160
H	-0.7241160	-1.5266410	0.0235670
C	-2.7777840	-0.1550690	1.2696680
H	-1.1061920	1.2148800	1.3090590
H	-0.8015850	-0.2895490	2.1626370
C	-2.7777190	-0.1942260	-1.2643630
H	-1.1061600	1.1738880	-1.3459250
H	-0.8014650	-0.3561480	-2.1526540
C	-3.4569450	0.3615620	-0.0056490
H	-3.2394520	0.2952690	2.1548080
H	-2.9396470	-1.2378520	1.3516440

H	-3.2393460	0.2285610	-2.1630100
H	-2.9395760	-1.2790240	-1.3128670
H	-4.5201460	0.0990780	-0.0016140
H	-3.4062880	1.4582420	-0.0226010

Table 27 entry 5

	X	Y	Z
C	-2.9681470	1.2025400	-0.1519050
C	-1.6007510	1.2088130	0.0644430
C	-0.8477980	-0.0000150	0.1805250
C	-1.6008590	-1.2088050	0.0647440
C	-2.9682530	-1.2024590	-0.1516140
C	-3.6720370	0.0000580	-0.2643240
H	-3.4961780	2.1469570	-0.2339070
H	-1.1006590	2.1642410	0.1468590
H	-1.1008710	-2.1642620	0.1474440
H	-3.4963730	-2.1468470	-0.2333770
H	-4.7425110	0.0000850	-0.4340990
C	0.5623800	-0.0000570	0.4002890
C	1.3858060	1.2542830	0.5383840
C	1.3857740	-1.2544490	0.5380530
C	2.5895010	1.2640820	-0.4312980
H	1.7788600	1.3032740	1.5665830
H	0.7992290	2.1605380	0.3936360
C	2.5894150	-1.2639890	-0.4317080
H	1.7788910	-1.3037270	1.5662110
H	0.7991740	-2.1606520	0.3930750
C	3.4425100	-0.0000050	-0.2843120
H	3.1954990	2.1579650	-0.2497100
H	2.2161540	1.3366700	-1.4597890
H	3.1953690	-2.1579770	-0.2504950
H	2.2159970	-1.3361730	-1.4602030
H	4.2504810	0.0000900	-1.0235040
H	3.9216970	-0.0001850	0.7036270

Table 27 entry 6

	X	Y	Z
C	-3.5361800	1.2711140	0.8238850
C	-2.0990170	1.1738330	0.2945940
C	-1.6328870	-0.3019130	0.2076670
C	-2.6067290	-1.1412160	-0.6337120
C	-4.0417050	-1.0352320	-0.0997990
C	-4.5083070	0.4239160	-0.0077670
H	-2.0454410	1.6206250	-0.7059890
H	-1.4181920	1.7393430	0.9368570
H	-3.5591010	0.9325720	1.8675890

H	-3.8529570	2.3190020	0.8291610
H	-2.5670660	-0.7935340	-1.6711550
H	-2.2811600	-2.1859810	-0.6447710
H	-4.7163200	-1.6081940	-0.7438070
H	-4.0957700	-1.4966630	0.8949890
H	-4.5791490	0.8442460	-1.0190450
H	-5.5137410	0.4733080	0.4225950
H	-1.5913420	-0.6977880	1.2281930
C	-0.2270550	-0.3545800	-0.3510270
C	2.0450680	-0.0048020	0.3276030
C	2.5311130	0.9975870	-0.5052560
C	2.9015660	-0.9101100	0.9422060
C	3.9033180	1.0868590	-0.7248550
H	1.8466760	1.6932490	-0.9739060
C	4.2733940	-0.8086200	0.7192440
H	2.4910990	-1.6758690	1.5894310
C	4.7767210	0.1869720	-0.1153720
H	4.2890800	1.8640060	-1.3748990
H	4.9464180	-1.5107500	1.1981710
H	5.8438280	0.2628780	-0.2896460
O	0.6848230	-0.0870930	0.6401440
O	0.0810940	-0.5733200	-1.4911750

Table 27 entry 7 (SCF=xqc was used for convergence for this calculation)

	X	Y	Z
C	3.2918300	1.5866340	0.1527330
C	2.0906990	0.9583180	0.8976610
C	1.6617360	-0.3257310	0.2623900
C	2.7261360	-1.3255930	-0.0569390
C	3.9183750	-0.6759690	-0.7943550
C	4.4217710	0.5736300	-0.0628190
H	2.4055160	0.7416720	1.9314040
H	1.2618130	1.6615540	0.9625910
H	2.9492680	1.9626070	-0.8184100
H	3.6512970	2.4516710	0.7180820
H	3.0985290	-1.7489800	0.8899460
H	2.3072220	-2.1527270	-0.6304070
H	4.7213700	-1.4117120	-0.8989090
H	3.6040370	-0.4037260	-1.8086750
H	4.8410110	0.2828910	0.9092620
H	5.2363400	1.0370770	-0.6286620
C	0.2840210	-0.6606000	-0.0343280
C	-1.9547190	0.2197660	0.1257000
C	-2.6696040	-0.8619540	0.6351100
C	-2.6046670	1.2651010	-0.5238740
C	-4.0535900	-0.8890030	0.4815390
H	-2.1529080	-1.6693130	1.1353890
C	-3.9895950	1.2286120	-0.6668820

H	-2.0207890	2.0942940	-0.9052600
C	-4.7178540	0.1508710	-0.1673280
H	-4.6139150	-1.7302360	0.8739750
H	-4.4967090	2.0433810	-1.1713480
H	-5.7953810	0.1213010	-0.2813340
O	-0.5837940	0.3596270	0.3128580
O	-0.0941960	-1.7026570	-0.5340200

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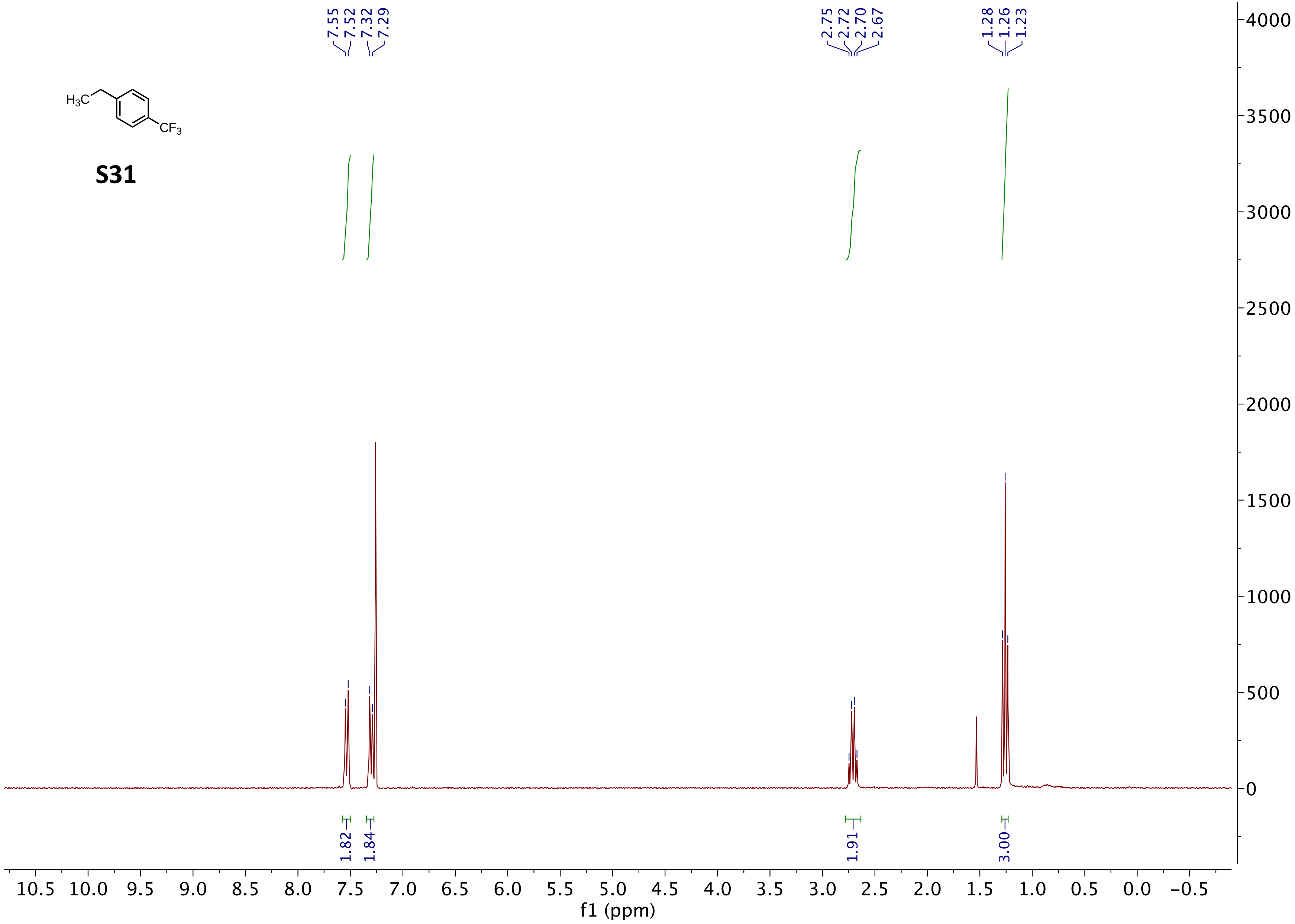
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7.29
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2.72
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2.67
1.28
1.26
1.23
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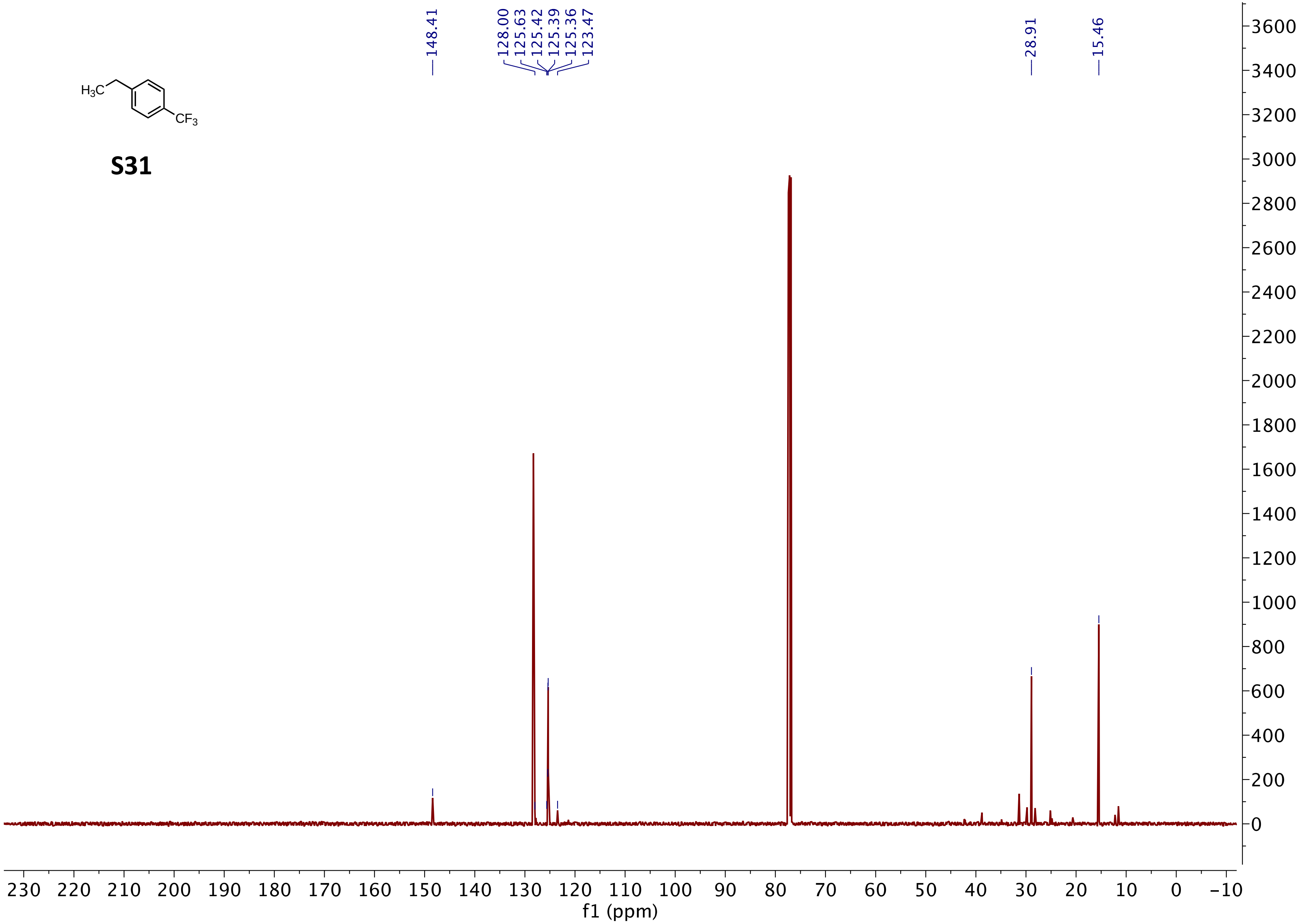
CF_3
1.82
1.84
1.91
3.00
4000
3500
3000
2500
2000
1500
1000
500
0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

S31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CF3
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28.91
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3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
230
220
210
200
190
180
170
160
150
140
130
120
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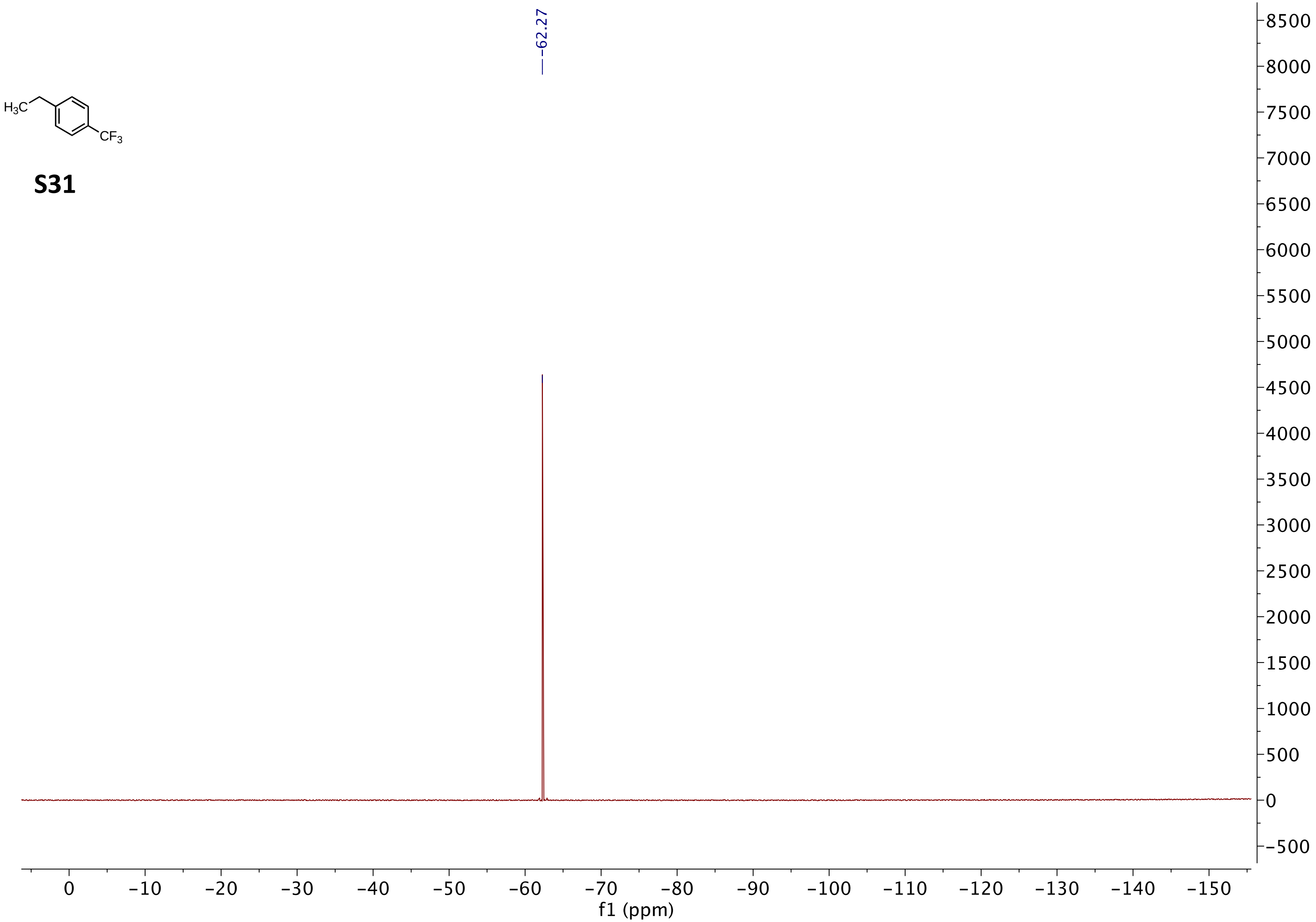
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

S31


H3C
CF3

S31

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7500
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6000
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5000
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4000
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3000
2500
2000
1500
1000
500
0
−500
0
−10
−20
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−40
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−90
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−120
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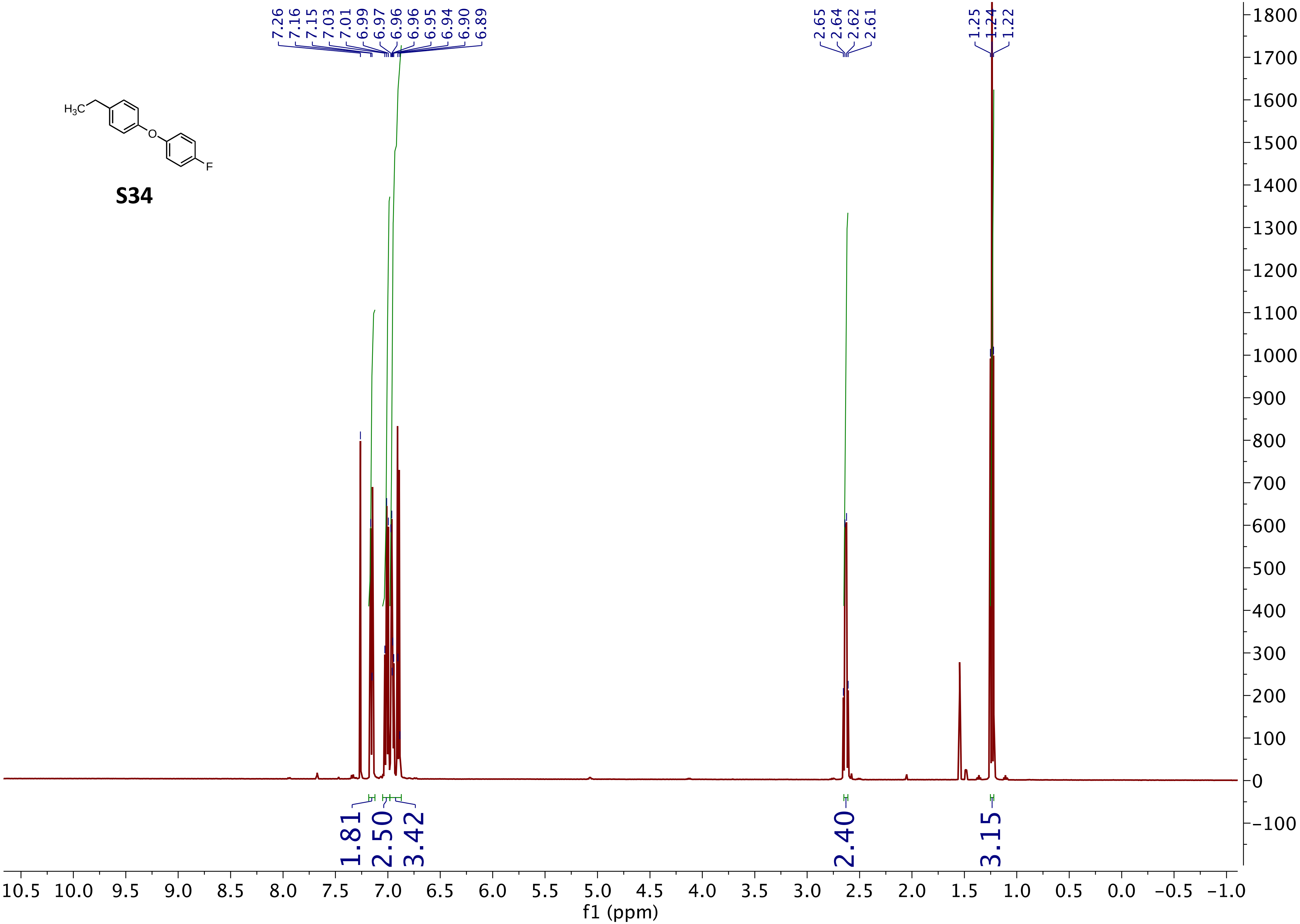
−150
f1 (ppm)



S34

H3C
O
F
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7.03
7.01
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6.97
6.96
6.96
6.95
6.94
6.90
6.89
2.65
2.64
2.62
2.61
1.25
1.24
1.22
1.81
2.50
3.42
2.40
3.15
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 −1.0
f1 (ppm)
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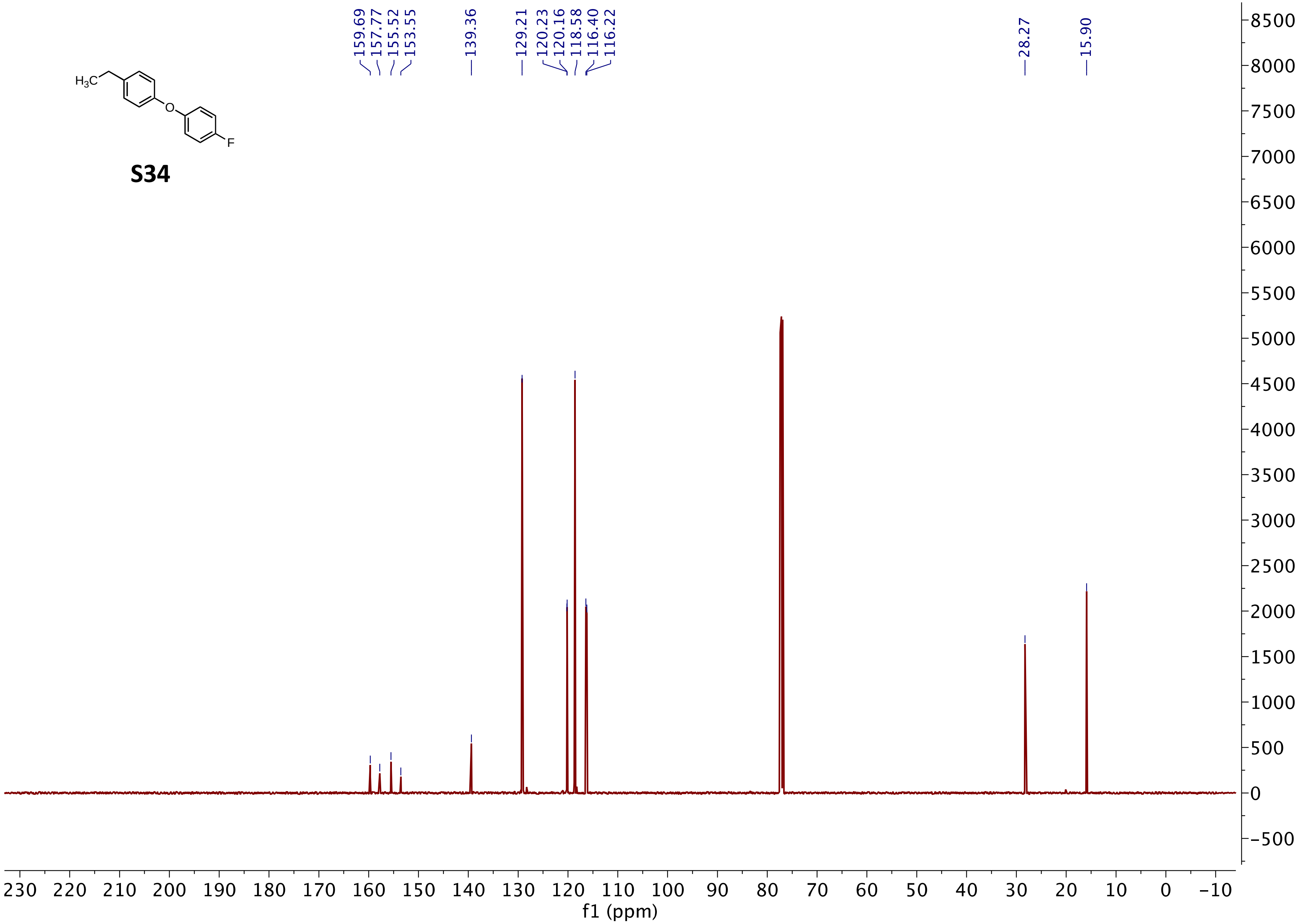
H3C
O
F

S34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8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
230
220
210
200
190
180
170
160
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100
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60
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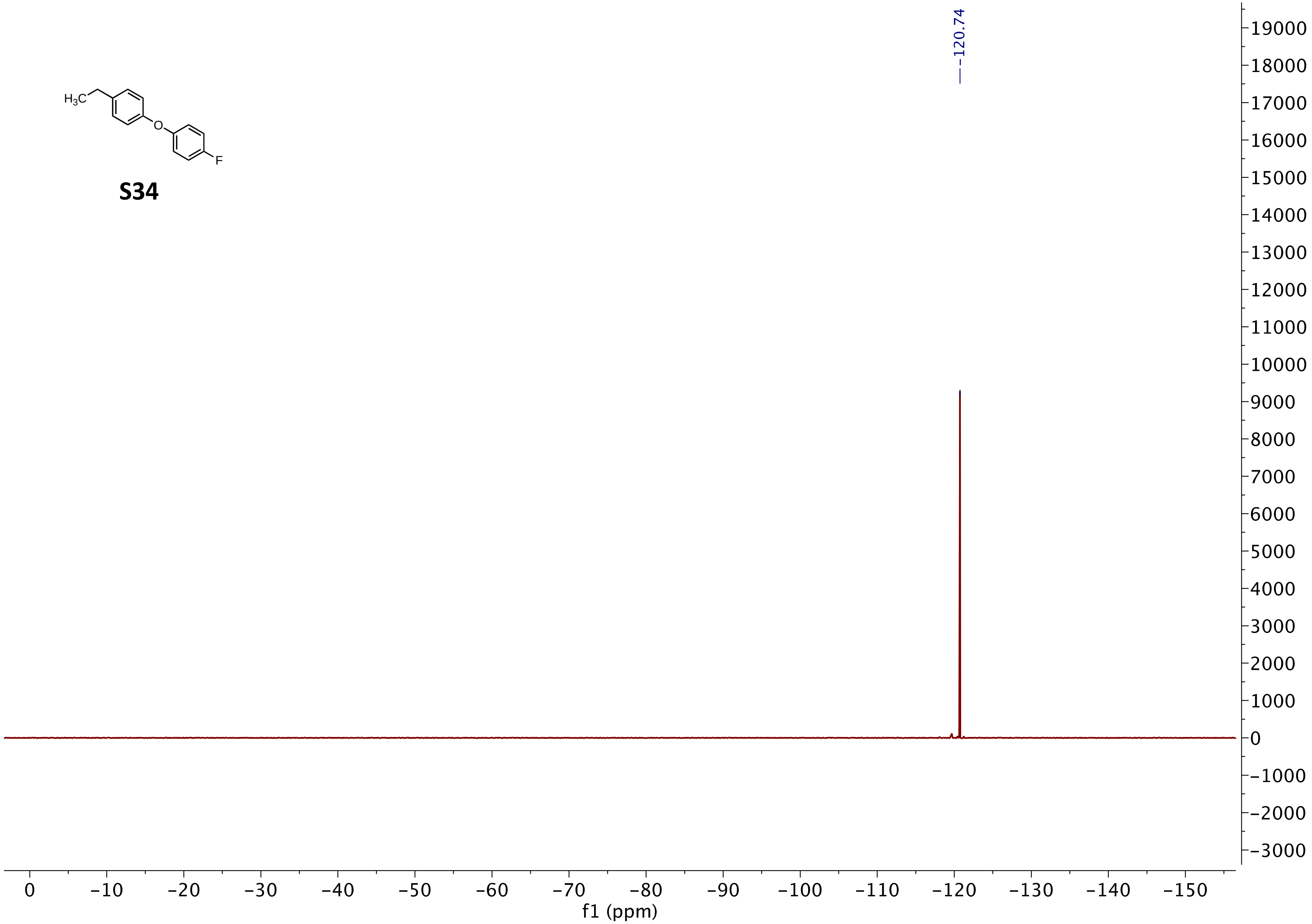
40
30
20
10
0
−10
f1 (ppm)


H3C
O
F

S34

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17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
0
-10
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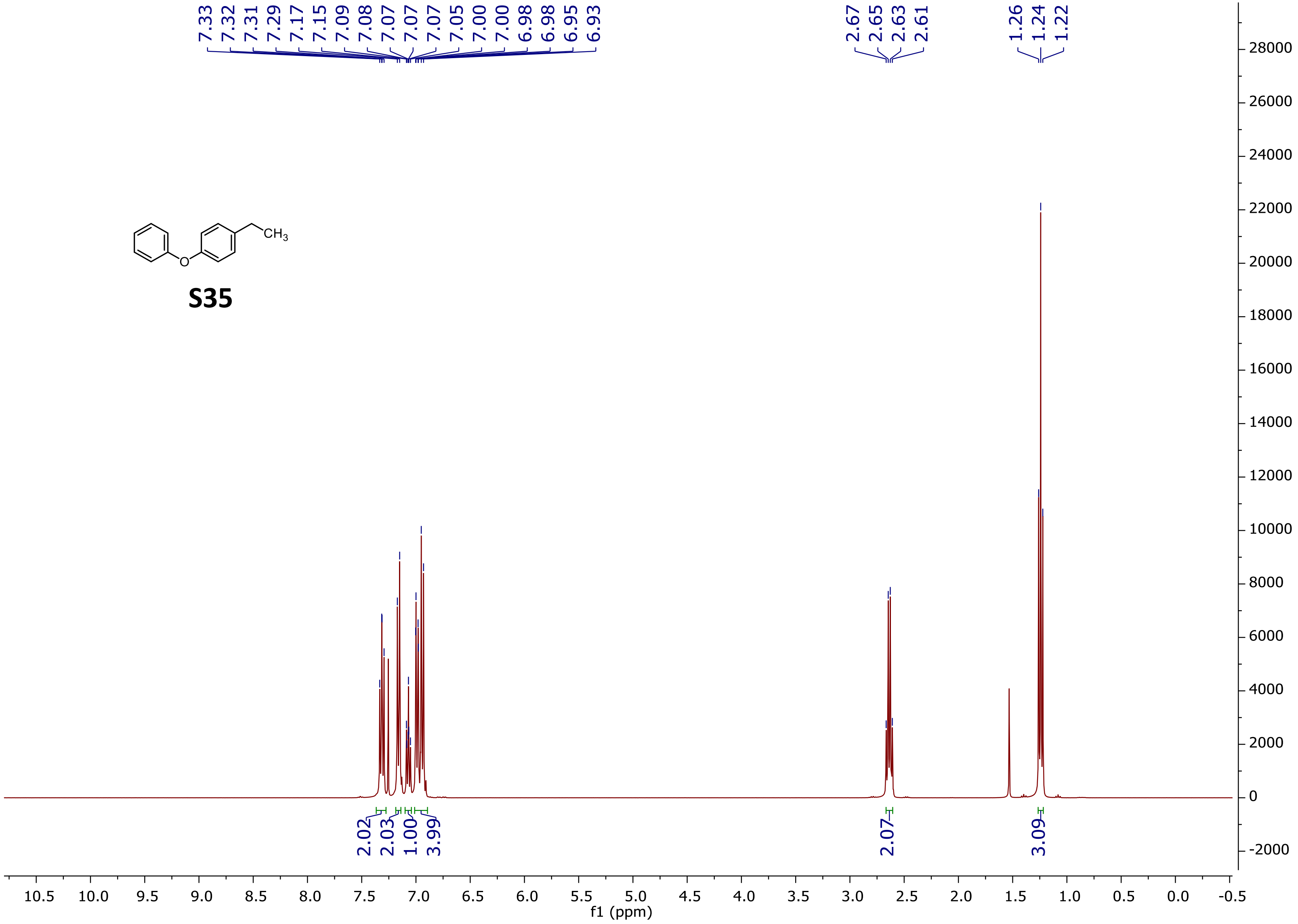
-140
-150
f1 (ppm)



S35

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7.05
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6.95
6.93
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2.63
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3.99
2.07
3.09
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24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
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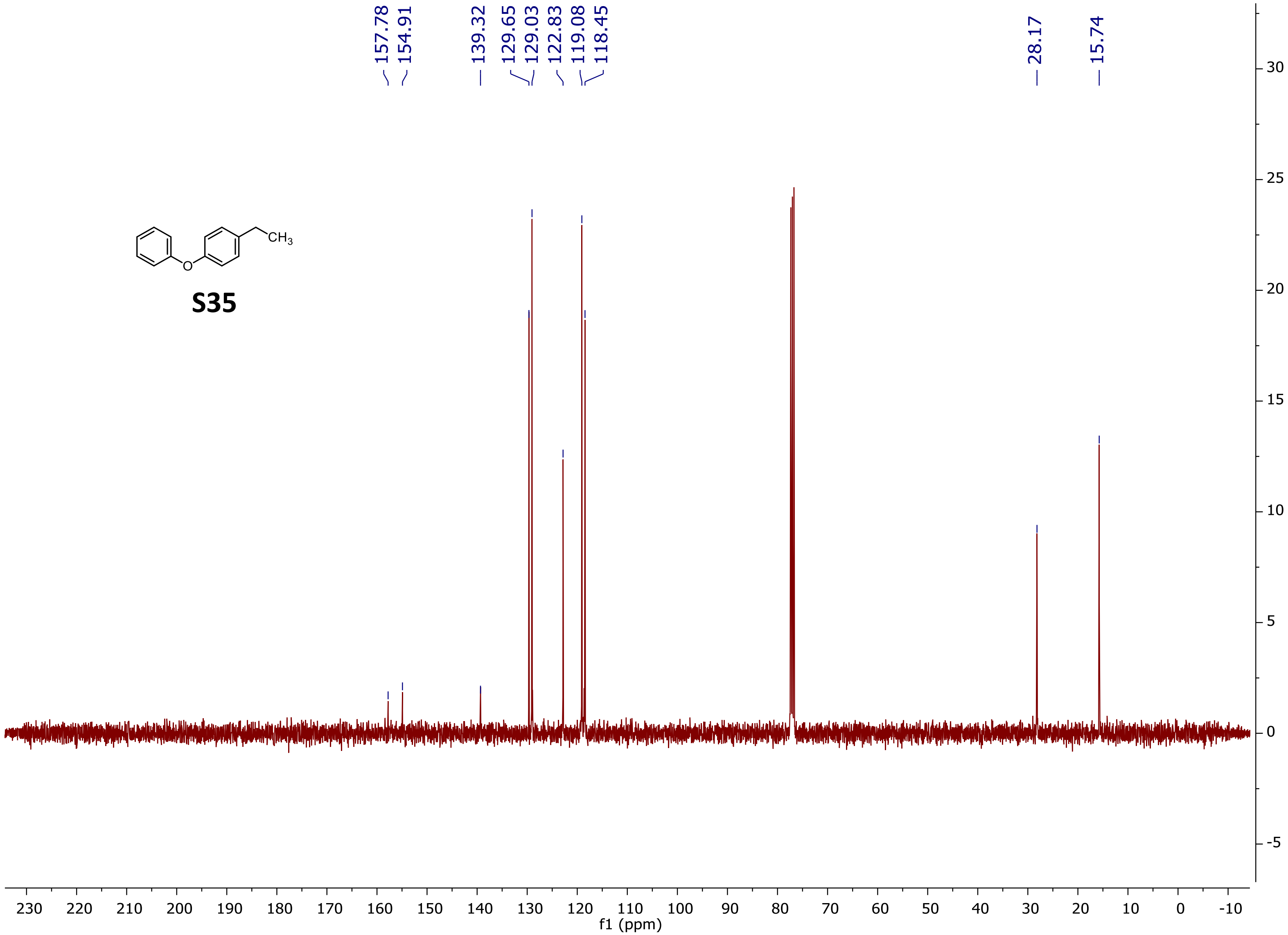
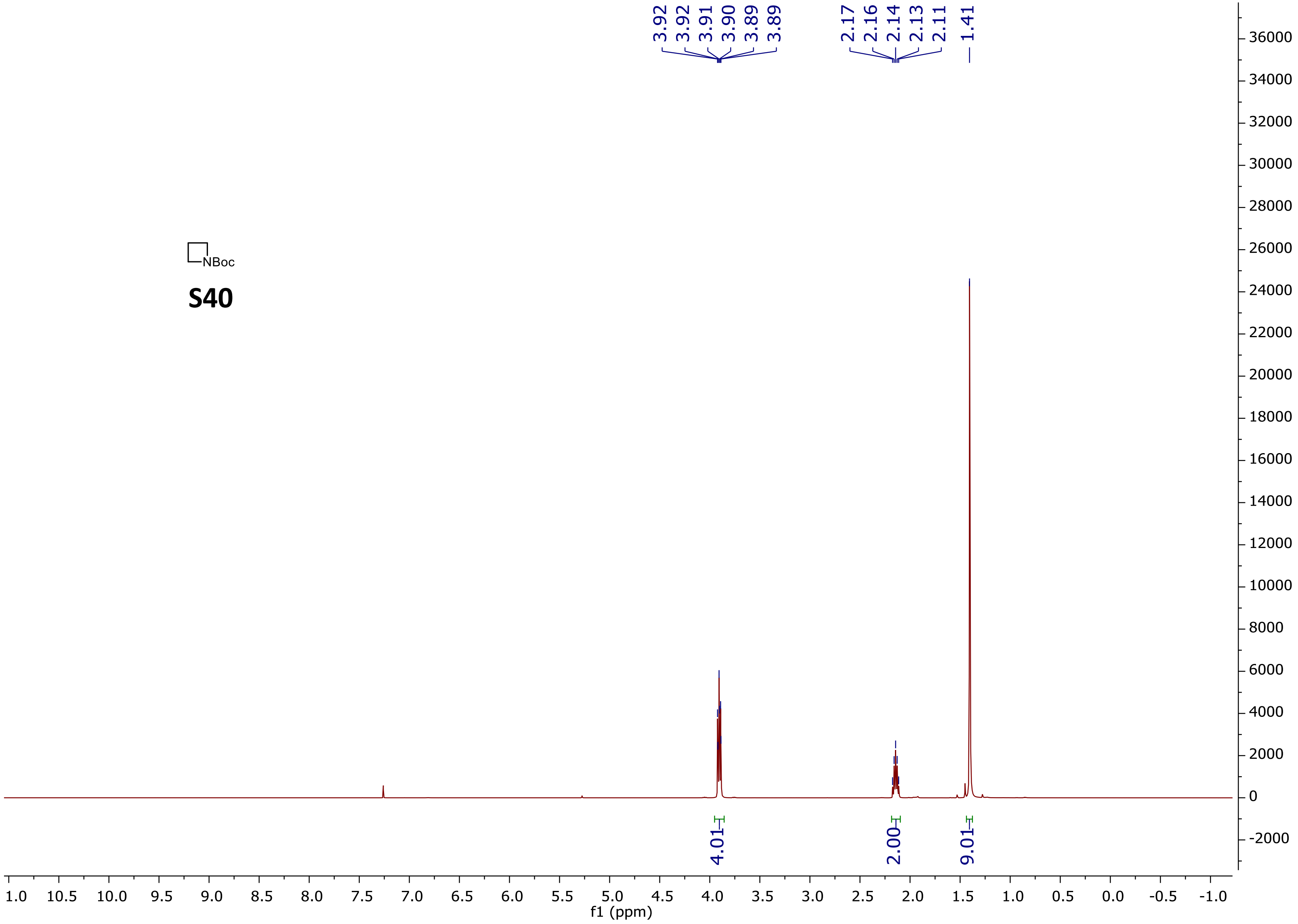
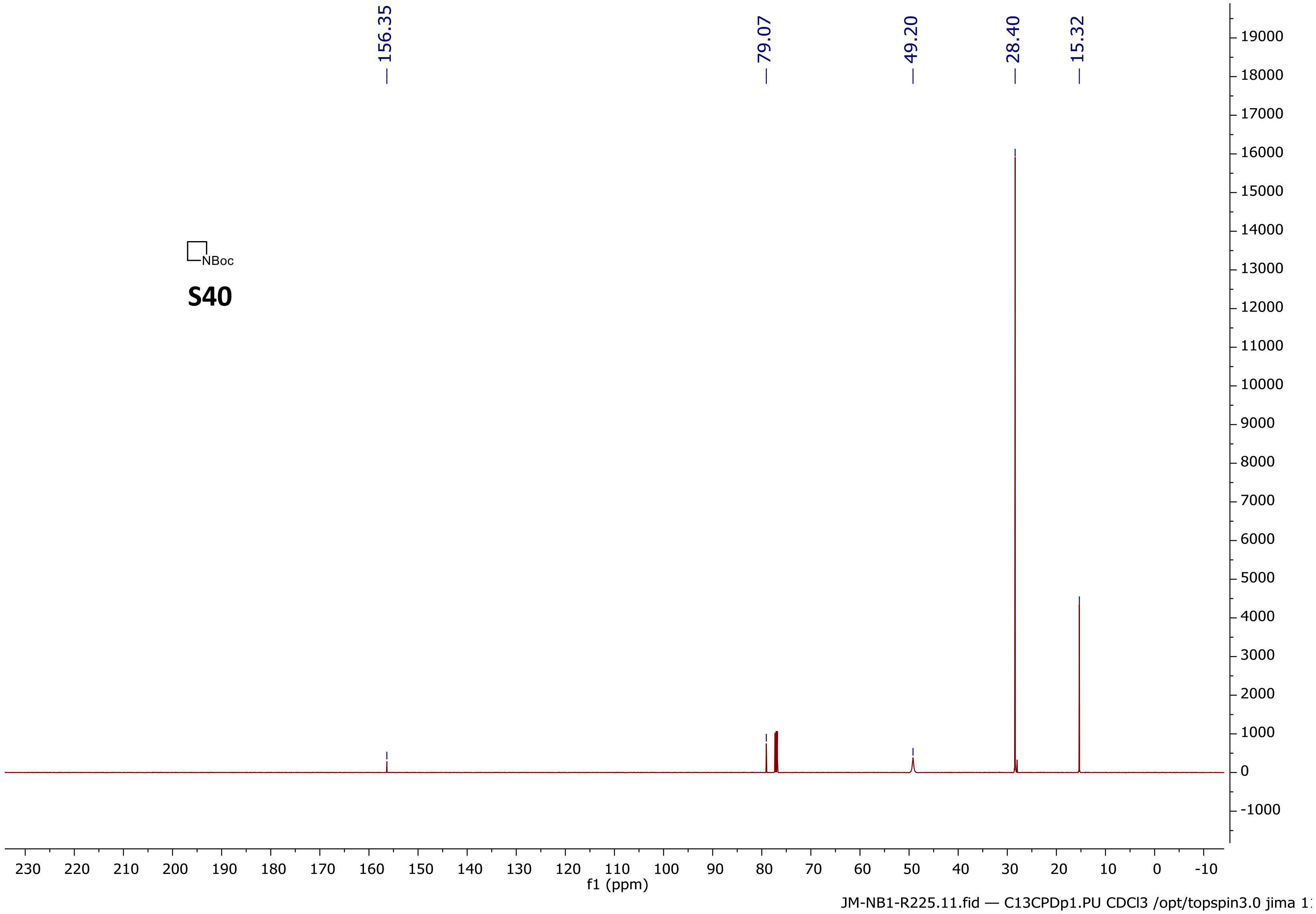
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

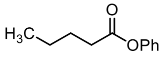

157.78
154.91
139.32
129.65
129.03
122.83
119.08
118.45
28.17
15.74
O
CH3
S35
30
25
20
15
10
5
0
-5
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


NBoc
3.92
3.92
3.91
3.90
3.89
3.89
2.17
2.16
2.14
2.13
2.11
1.41
4.01
2.00
9.01
1.0
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
-1.0
f1 (ppm)
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

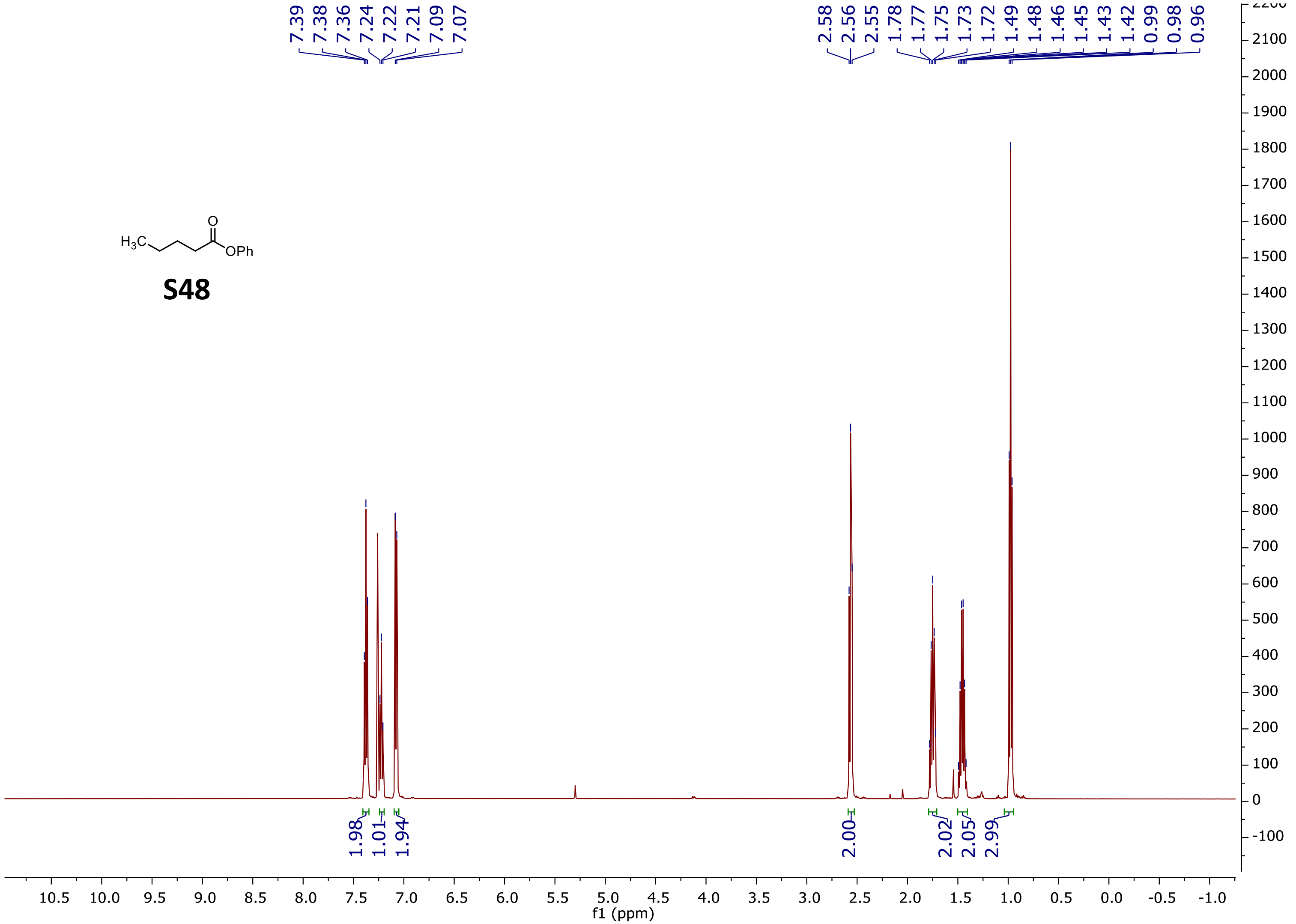
S40

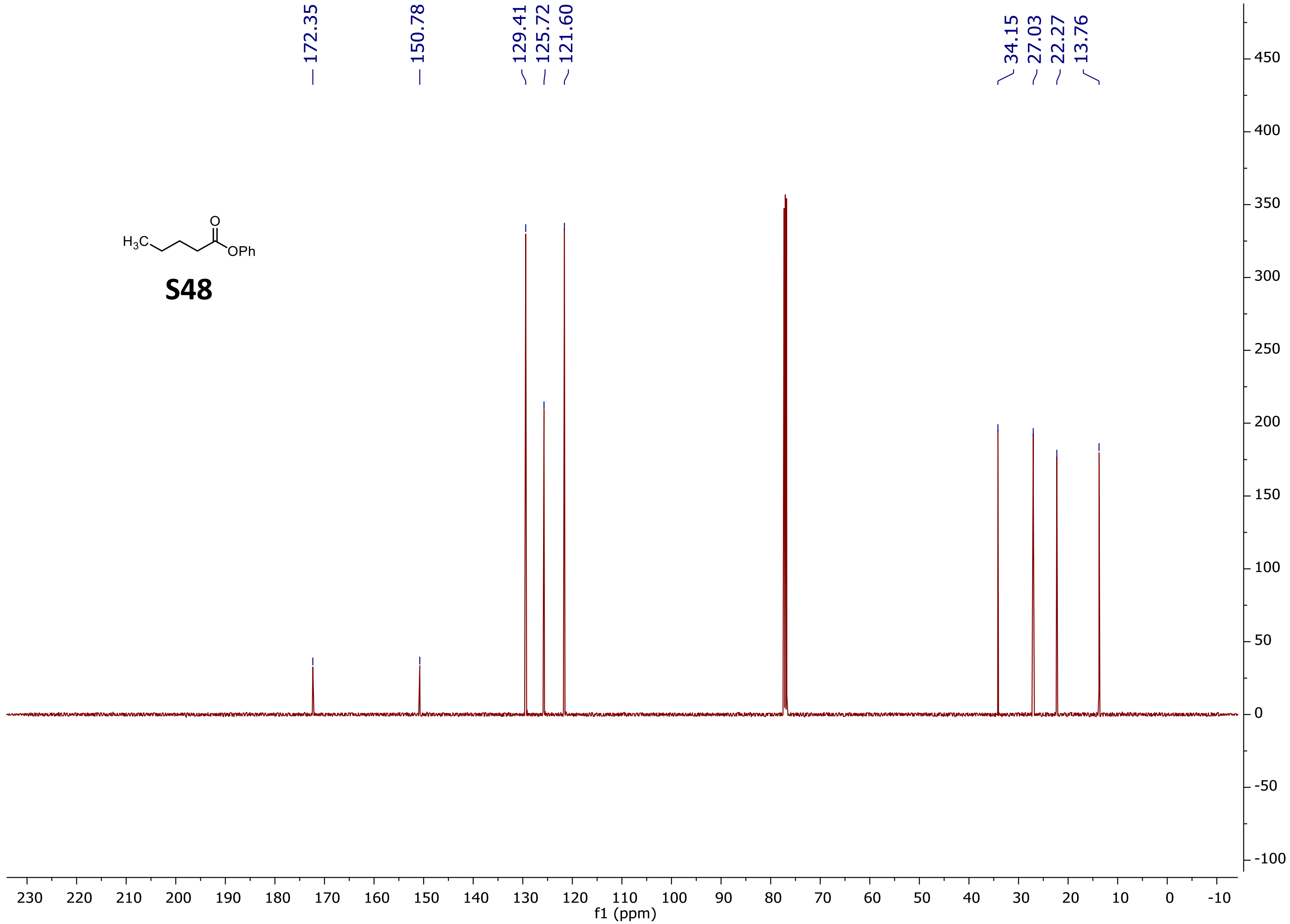

156.35
79.07
49.20
28.40
15.32
NBoc
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
JM-NB1-R225.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima 1

S40


O
H$_3$C
OPh

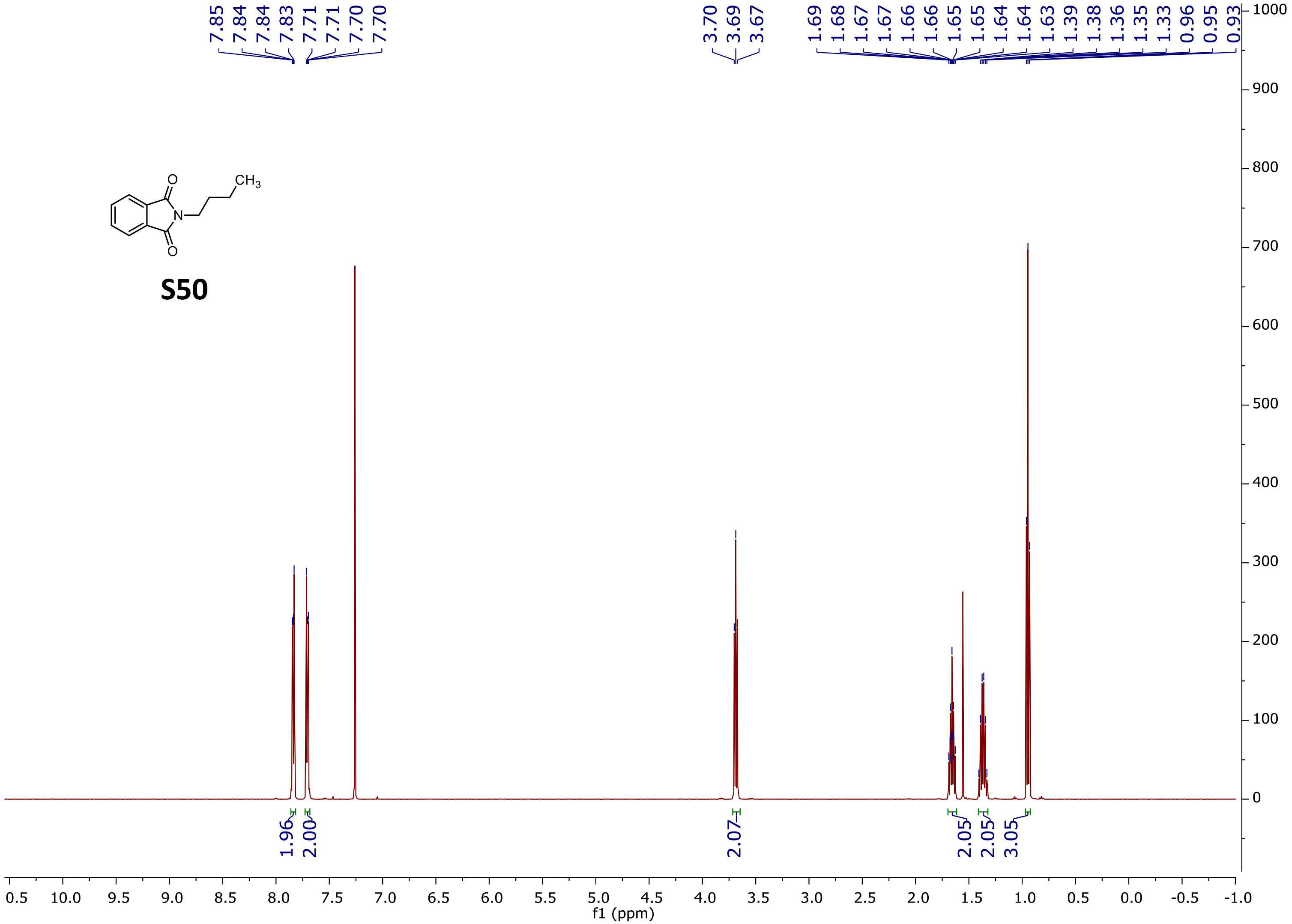
S48


7.39
7.38
7.36
7.24
7.22
7.21
7.09
7.07
2.58
2.56
2.55
1.78
1.77
1.75
1.73
1.72
1.49
1.48
1.46
1.45
1.43
1.42
0.99
0.98
0.96
1.98
1.01
1.94
2.00
2.02
2.05
2.99
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
-0.5
-1.0
f1 (ppm)
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

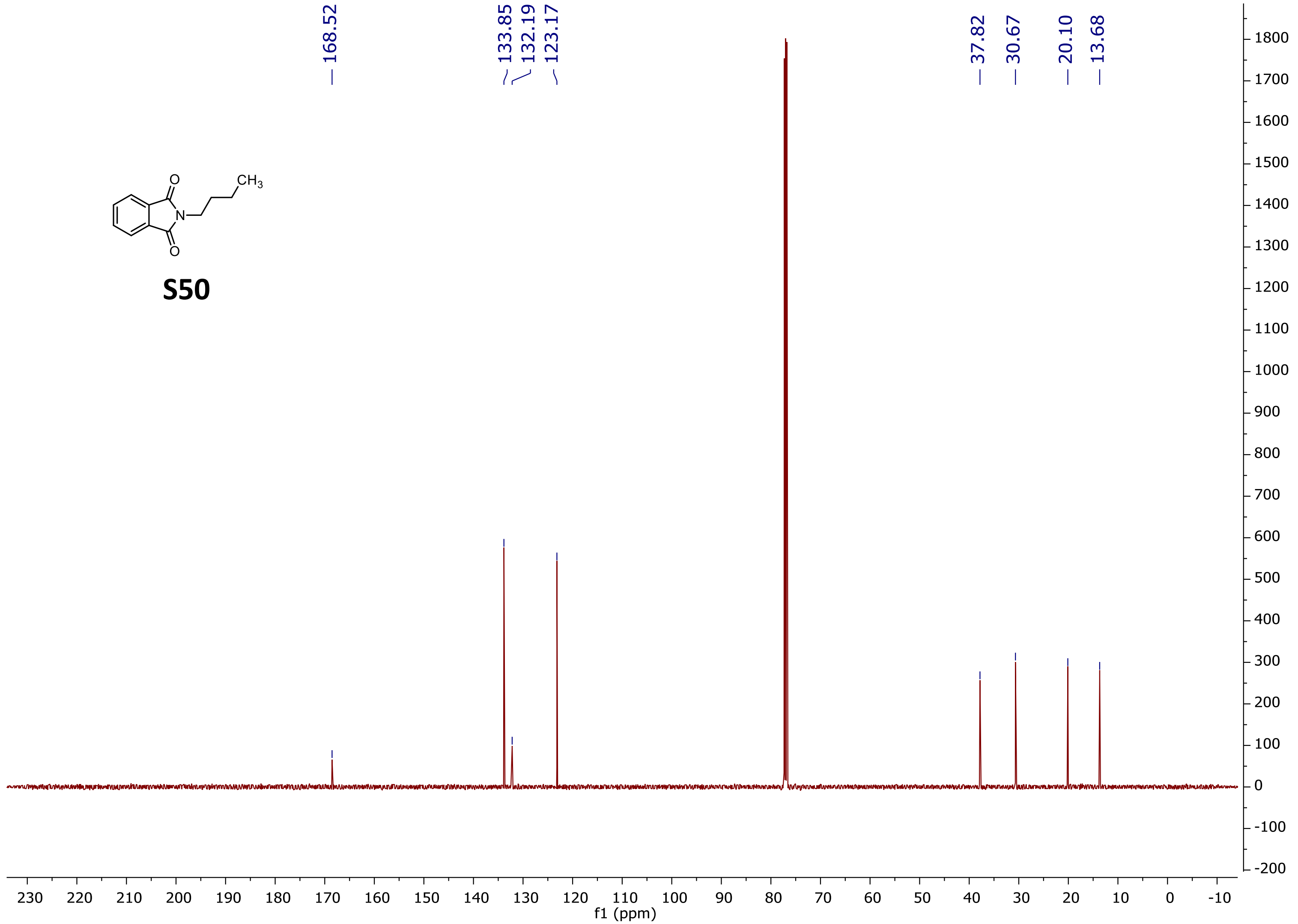


S48

172.35
150.78
129.41
125.72
121.60
34.15
27.03
22.27
13.76
H_3C
O
OPh
450
400
350
300
250
200
150
100
50
0
-50
-100
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

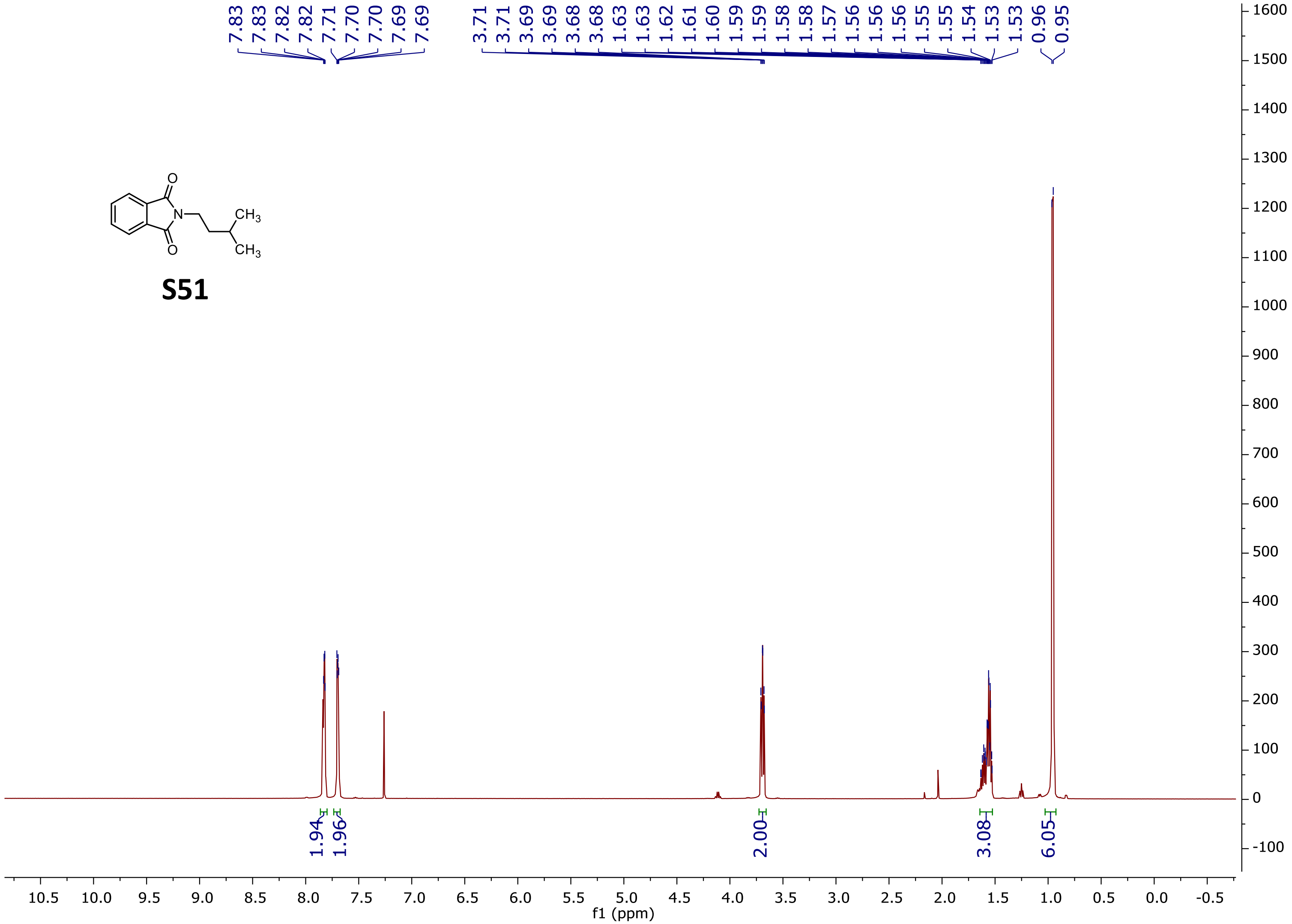

7.85
7.84
7.84
7.83
7.71
7.71
7.70
7.70
3.70
3.69
3.67
1.69
1.68
1.67
1.67
1.66
1.66
1.65
1.65
1.64
1.64
1.63
1.39
1.38
1.36
1.35
1.33
0.96
0.95
0.93
O
N
O
CH3
1.96
2.00
2.07
2.05
2.05
3.05
1000
900
800
700
600
500
400
300
200
100
0
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

S50



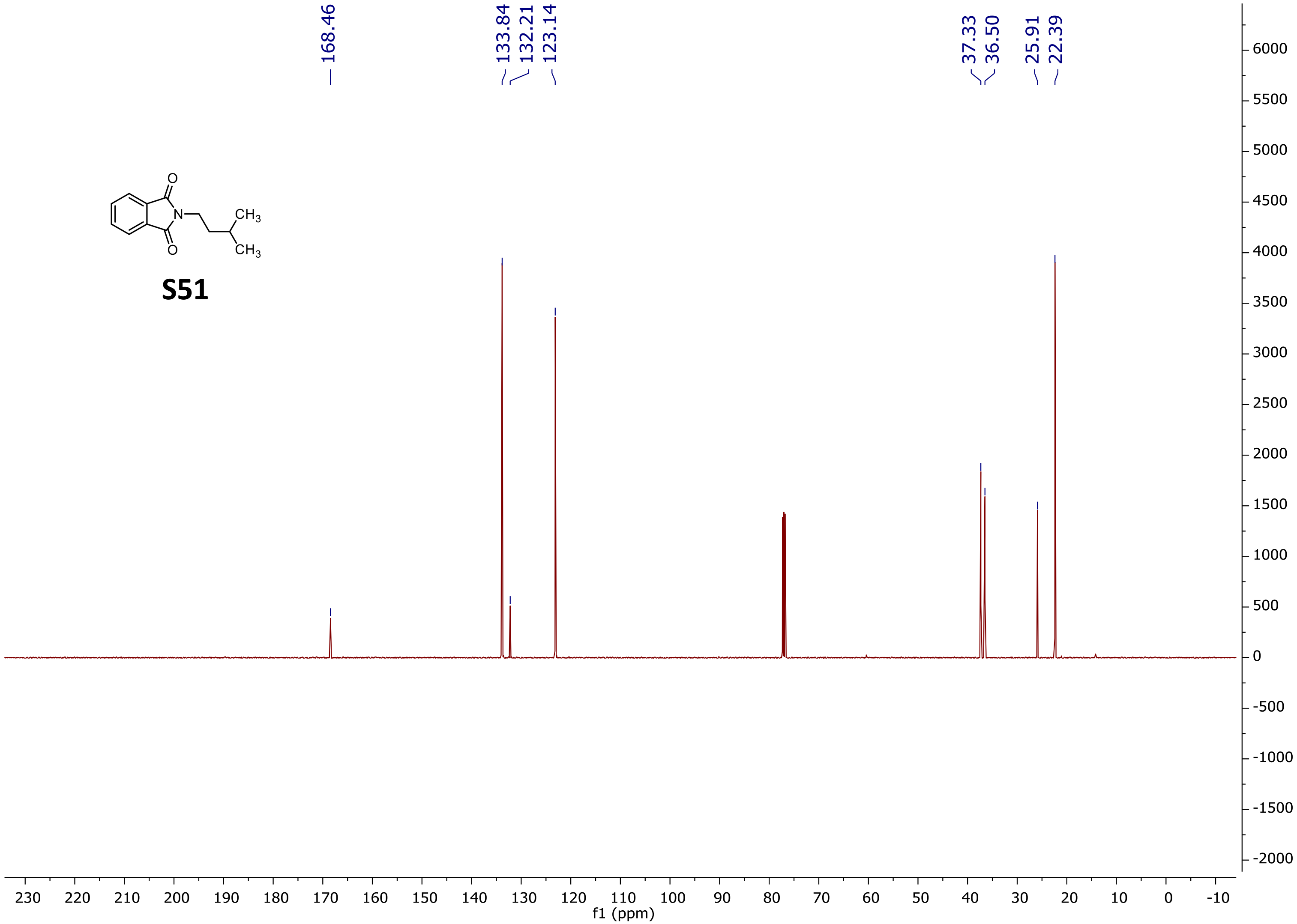
S50

168.52
133.85
132.19
123.17
37.82
30.67
20.10
13.68
O
N
O
CH3
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

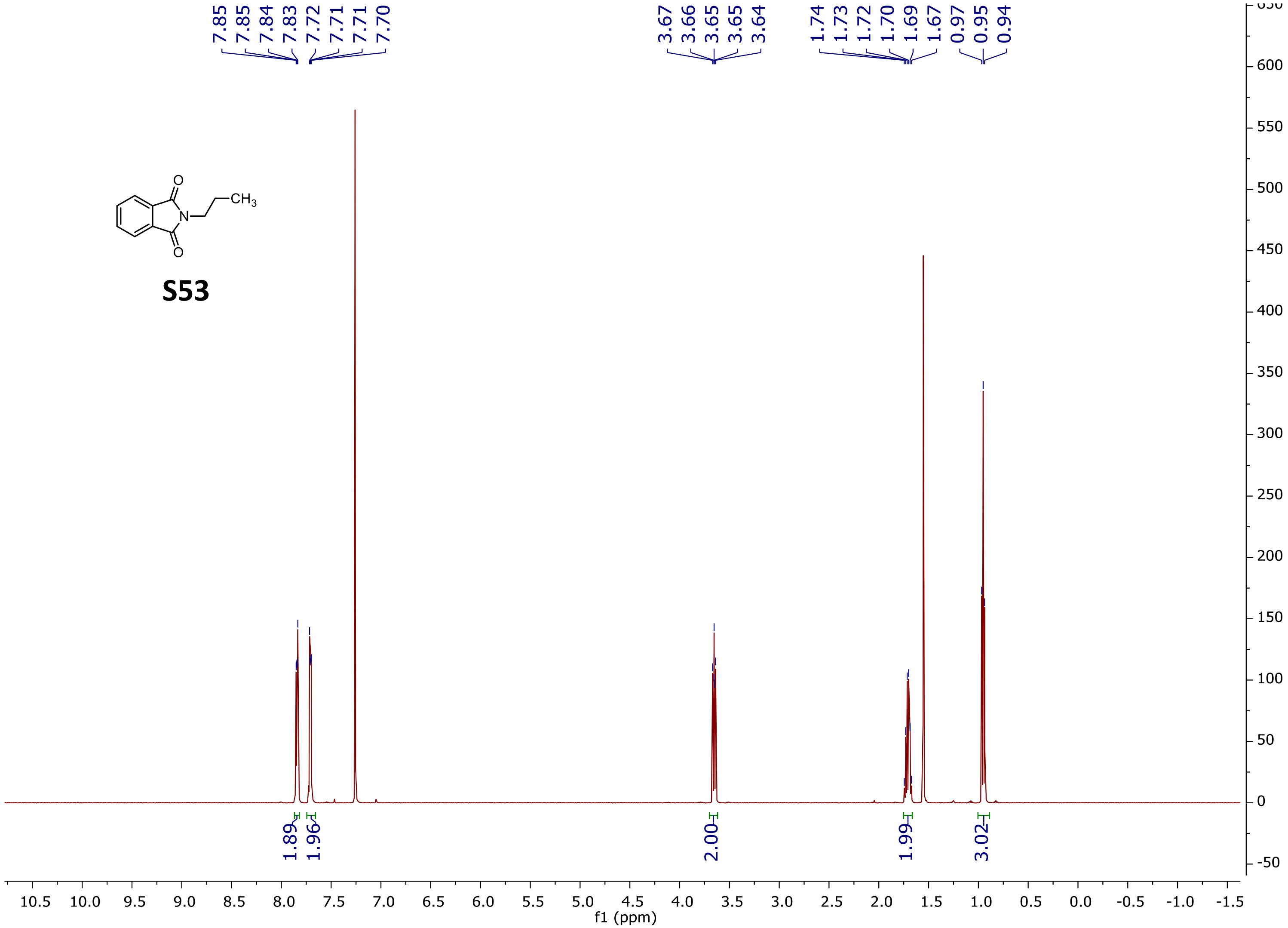


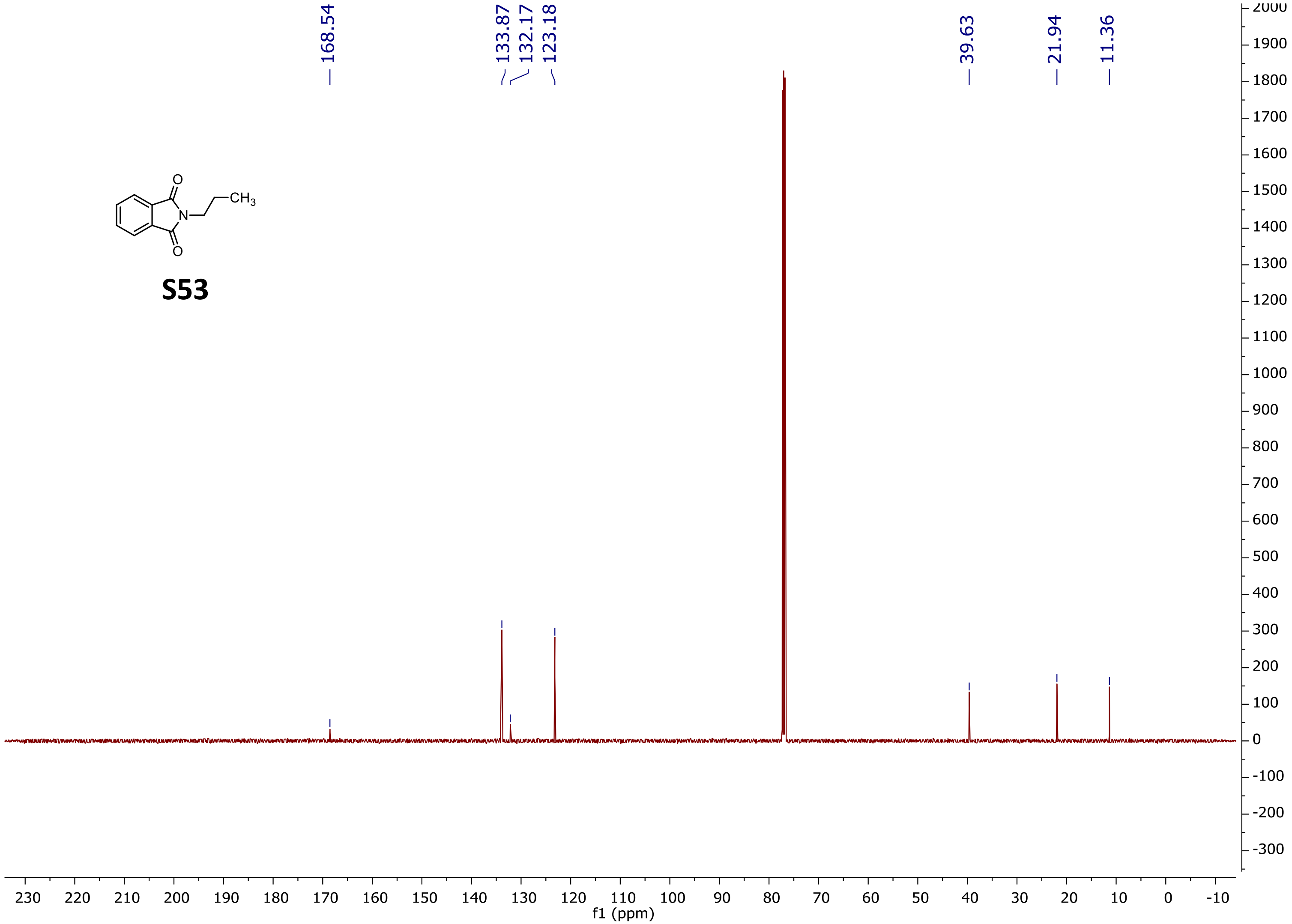
S51

7.83
7.83
7.82
7.82
7.71
7.70
7.70
7.69
7.69
3.71
3.71
3.69
3.69
3.68
3.68
1.63
1.63
1.62
1.61
1.60
1.59
1.59
1.58
1.58
1.57
1.56
1.56
1.55
1.55
1.54
1.53
1.53
0.96
0.95
O
N
O
CH3
CH3
1.94
1.96
2.00
3.08
6.05
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)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

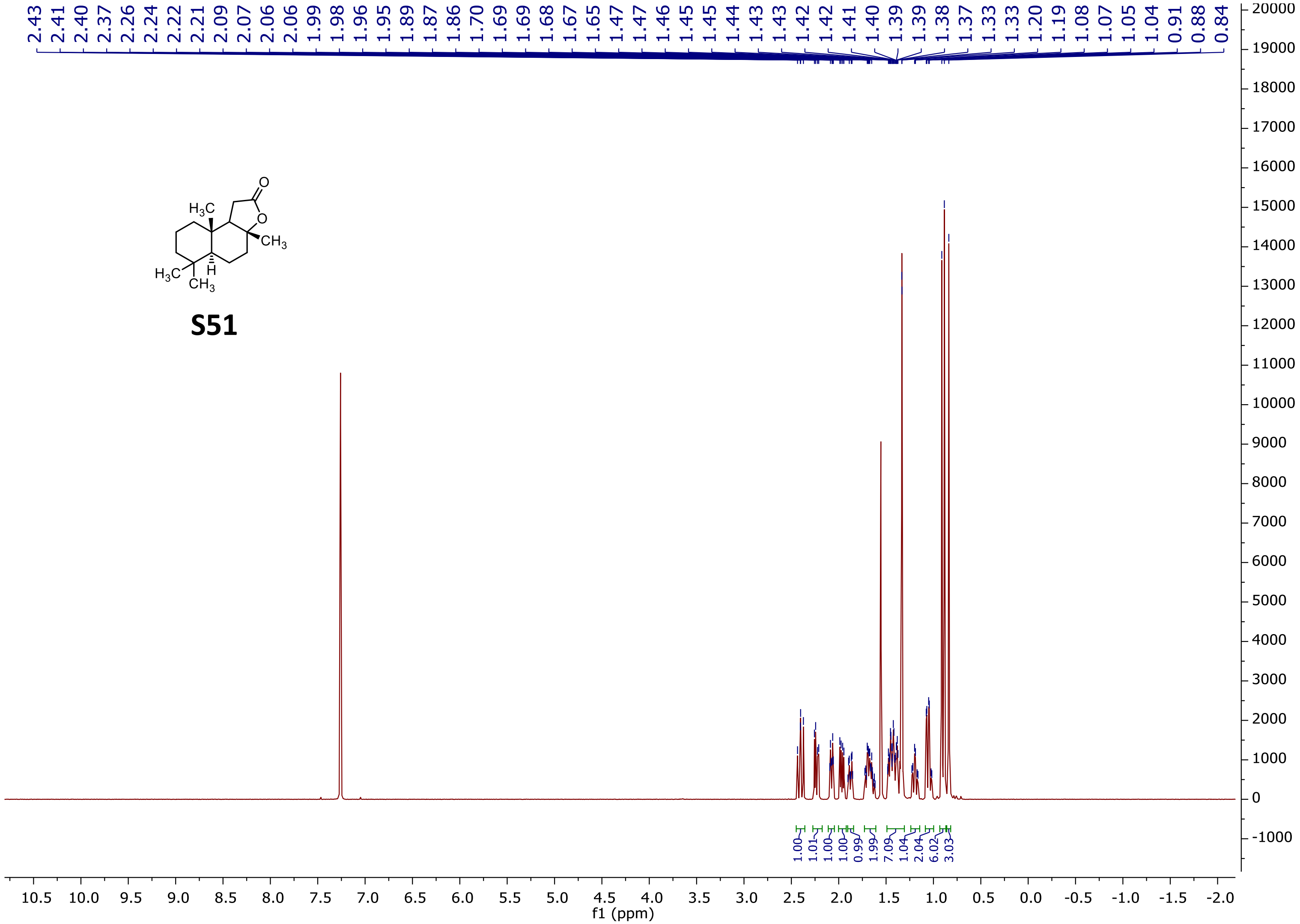

168.46
133.84
132.21
123.14
37.33
36.50
25.91
22.39
O
N
O
CH3
CH3
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

S51

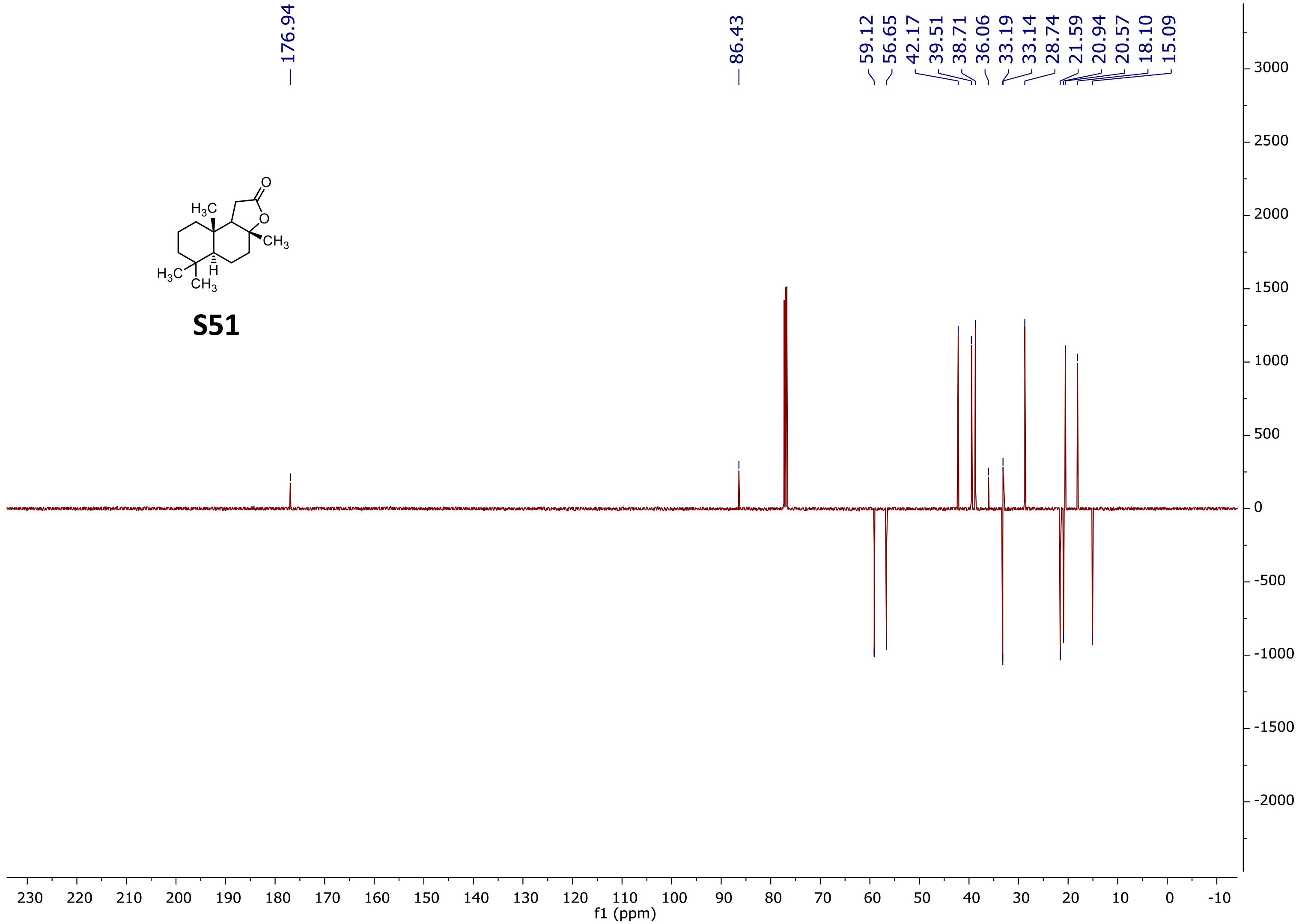

7.85
7.85
7.84
7.83
7.72
7.71
7.71
7.70
3.67
3.66
3.65
3.65
3.64
1.74
1.73
1.72
1.70
1.69
1.67
0.97
0.95
0.94
O
N
CH3
O
S53
1.89
1.96
2.00
1.99
3.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50


S53

O
N
CH3
O
168.54
133.87
132.17
123.18
39.63
21.94
11.36
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
230
220
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)

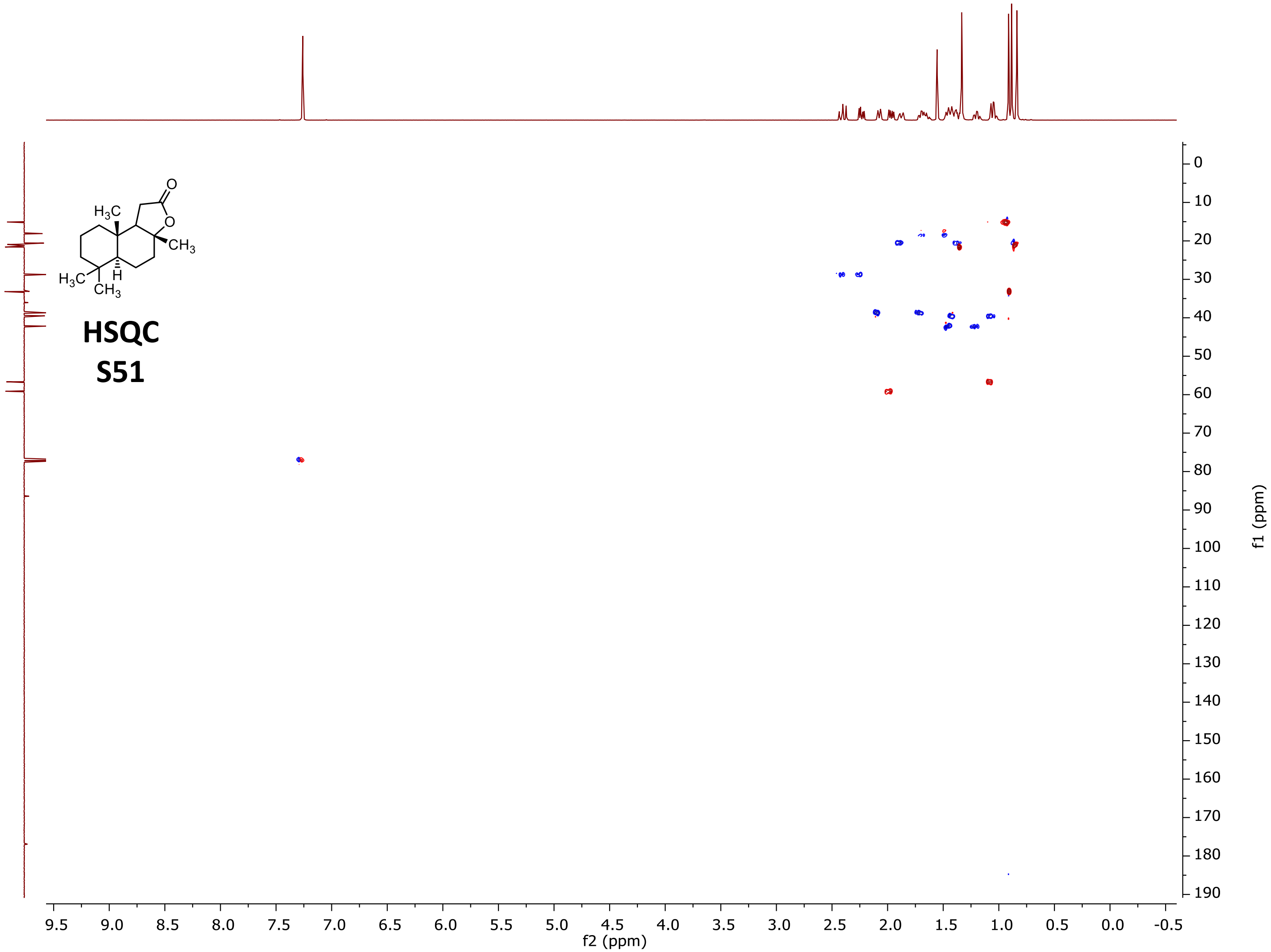

2.43
2.41
2.40
2.37
2.26
2.24
2.22
2.21
2.09
2.07
2.06
2.06
1.99
1.98
1.96
1.95
1.89
1.87
1.86
1.70
1.69
1.69
1.68
1.67
1.65
1.47
1.47
1.46
1.45
1.45
1.44
1.43
1.43
1.42
1.42
1.41
1.40
1.39
1.39
1.38
1.37
1.33
1.33
1.20
1.19
1.08
1.07
1.05
1.04
0.91
0.88
0.84
O
H_3C
O
CH_3
H
H_3C
CH_3
1.00
1.01
1.00
1.00
0.99
1.99
7.09
1.04
2.04
6.02
3.03
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
-1.0
-1.5
-2.0
f1 (ppm)
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

S51



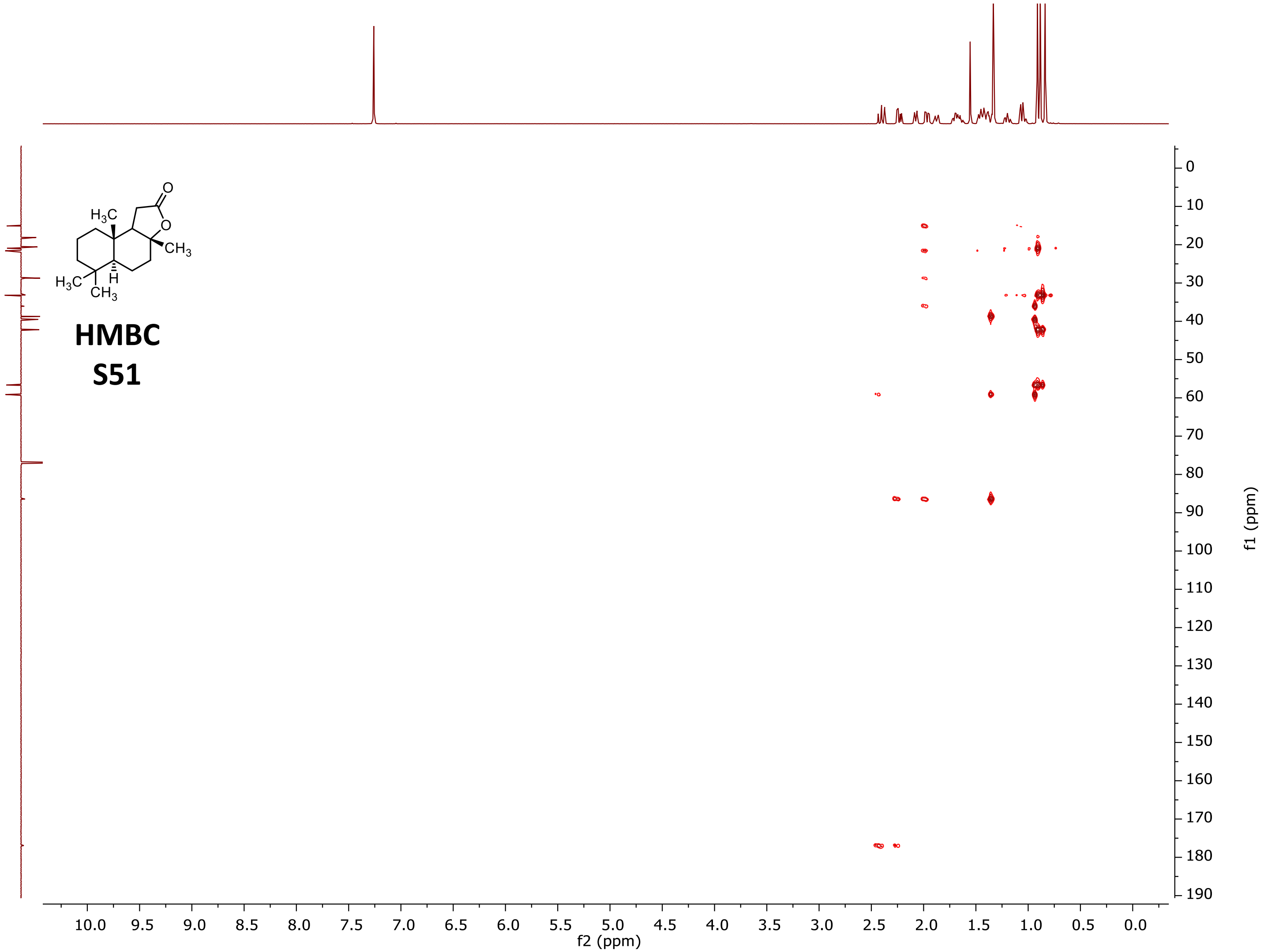
S51

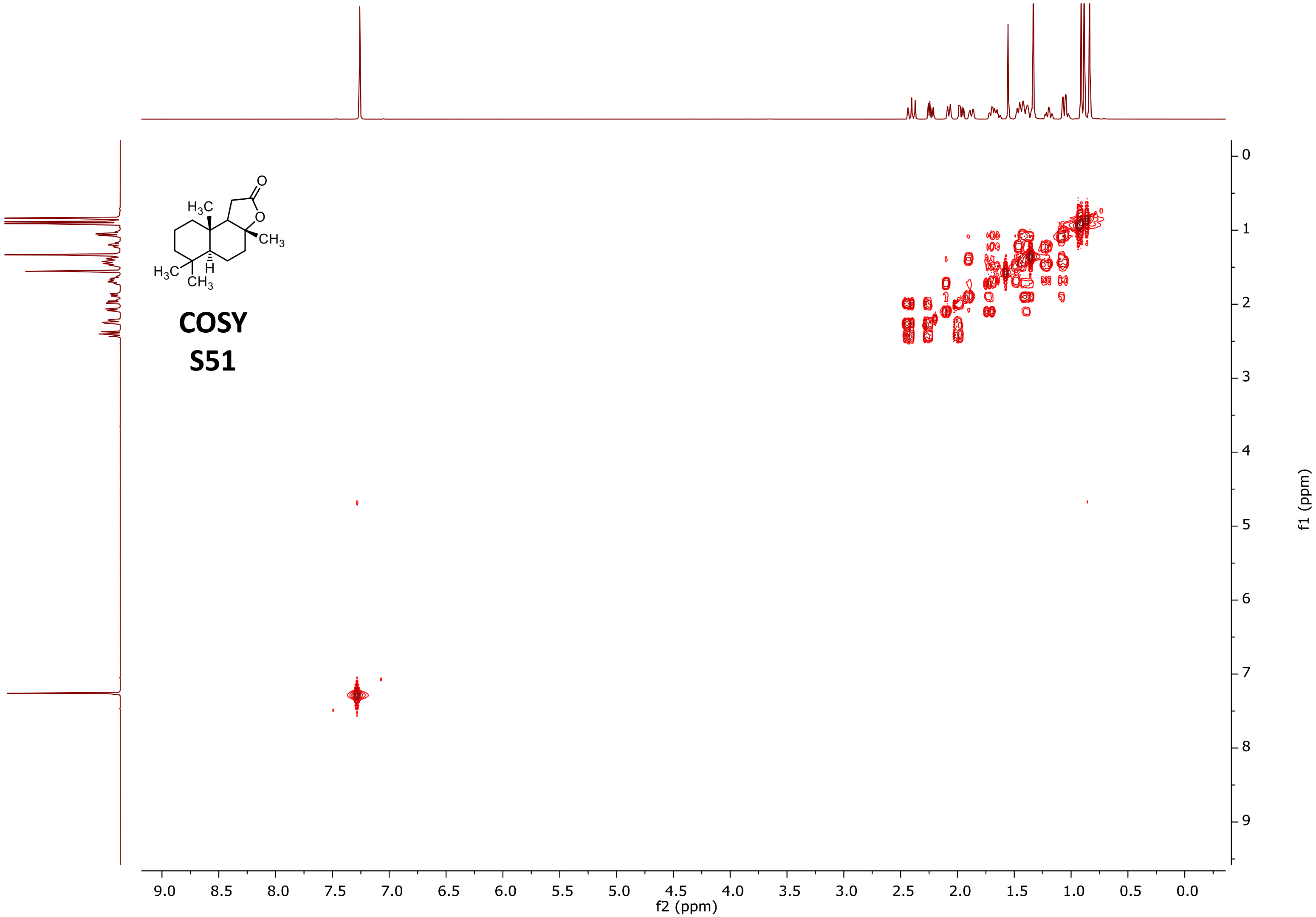
176.94
86.43
59.12
56.65
42.17
39.51
38.71
36.06
33.19
33.14
28.74
21.59
20.94
20.57
18.10
15.09
H_3C
O
O
CH_3
H
H_3C
CH_3
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
H3C
CH3
H3C
CH3
H
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
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)

HSQC

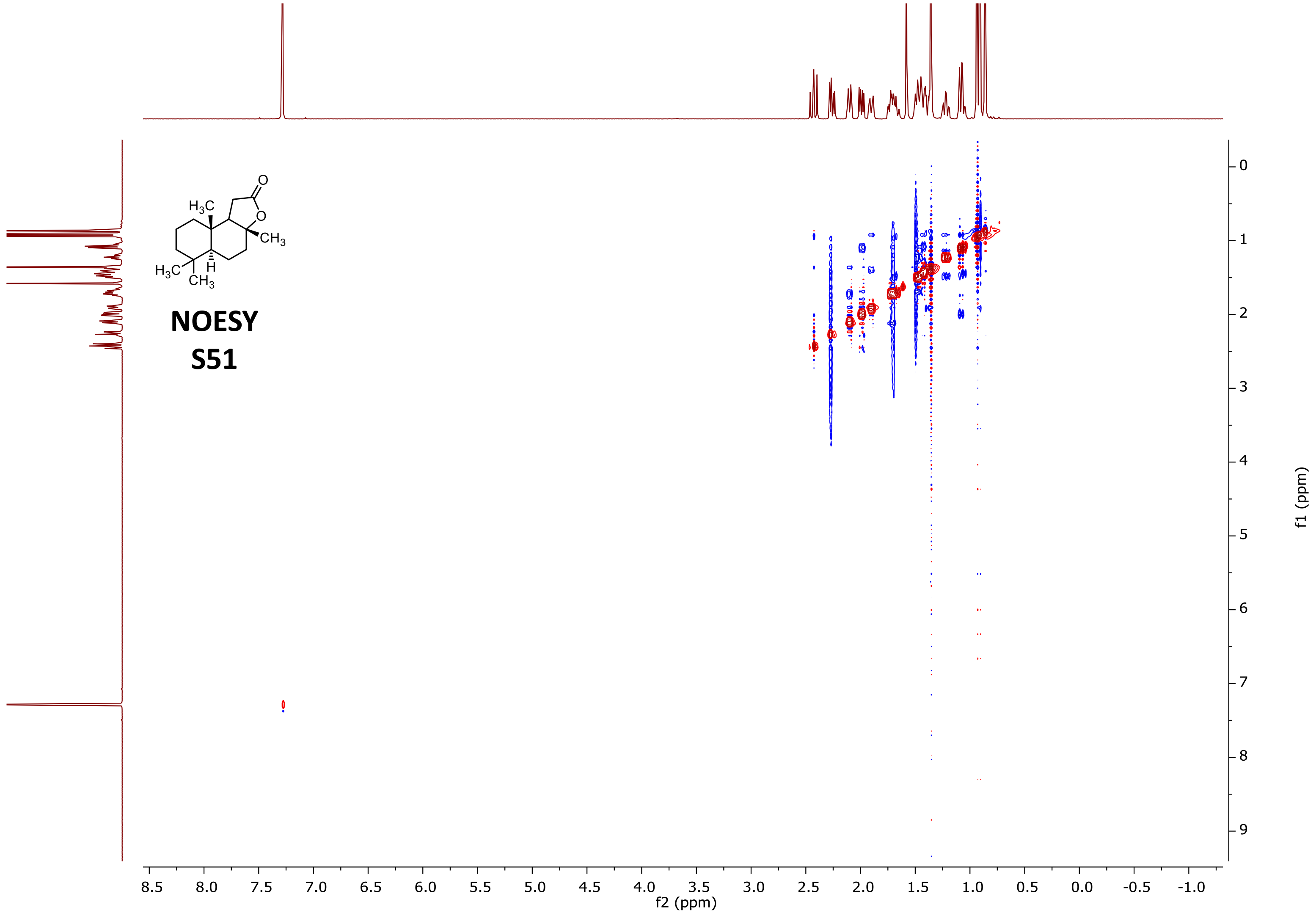
S51


HMBC
S51
H3C
O
O
CH3
H3C
CH3
H
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
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)


H3C
O
O
CH3
H3C
H
CH3
f2 (ppm)
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)
0
1
2
3
4
5
6
7
8
9

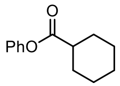
COSY

S51

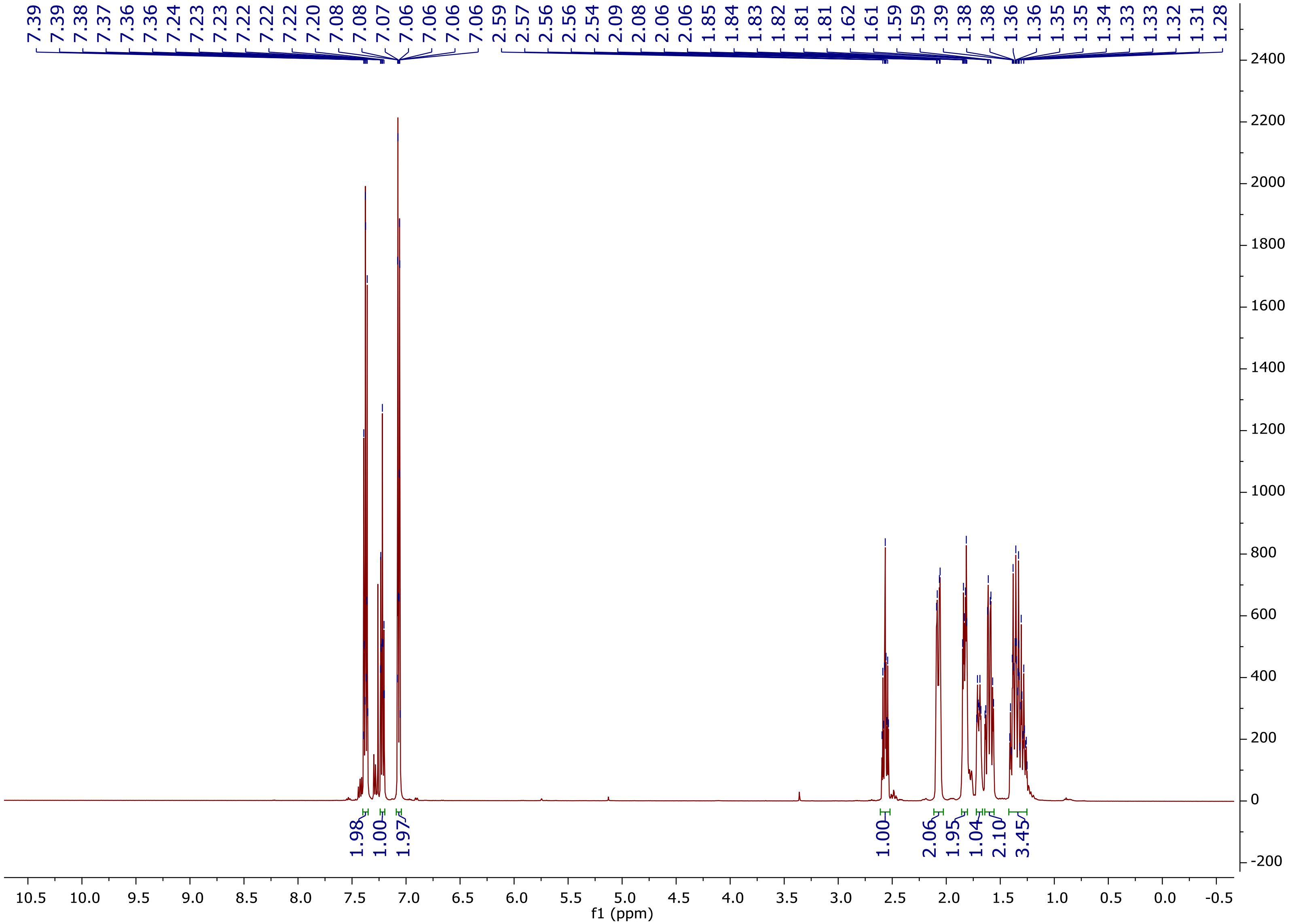


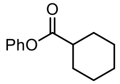
NOESY
S51

O
H3C
O
CH3
H3C
H
CH3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)

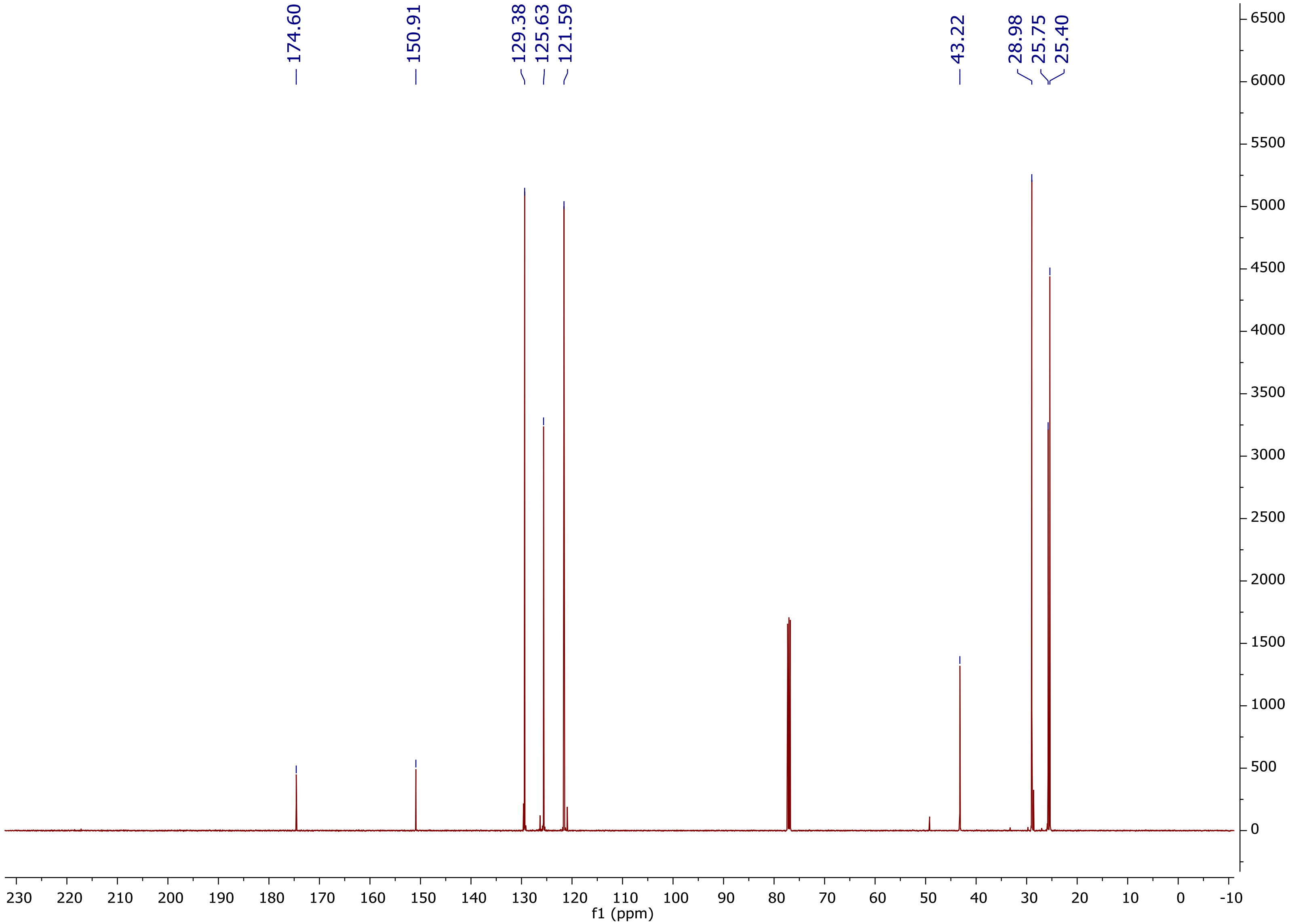

PhO
O

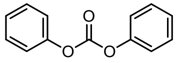
12


7.39
7.39
7.38
7.37
7.36
7.36
7.24
7.23
7.23
7.22
7.22
7.22
7.20
7.08
7.08
7.07
7.06
7.06
7.06
7.06
2.59
2.57
2.56
2.56
2.54
2.09
2.08
2.06
2.06
1.85
1.84
1.83
1.82
1.81
1.81
1.62
1.61
1.59
1.59
1.39
1.38
1.38
1.36
1.36
1.35
1.35
1.34
1.33
1.33
1.32
1.31
1.28
1.98
1.00
1.97
1.00
2.06
1.95
1.04
2.10
3.45
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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)

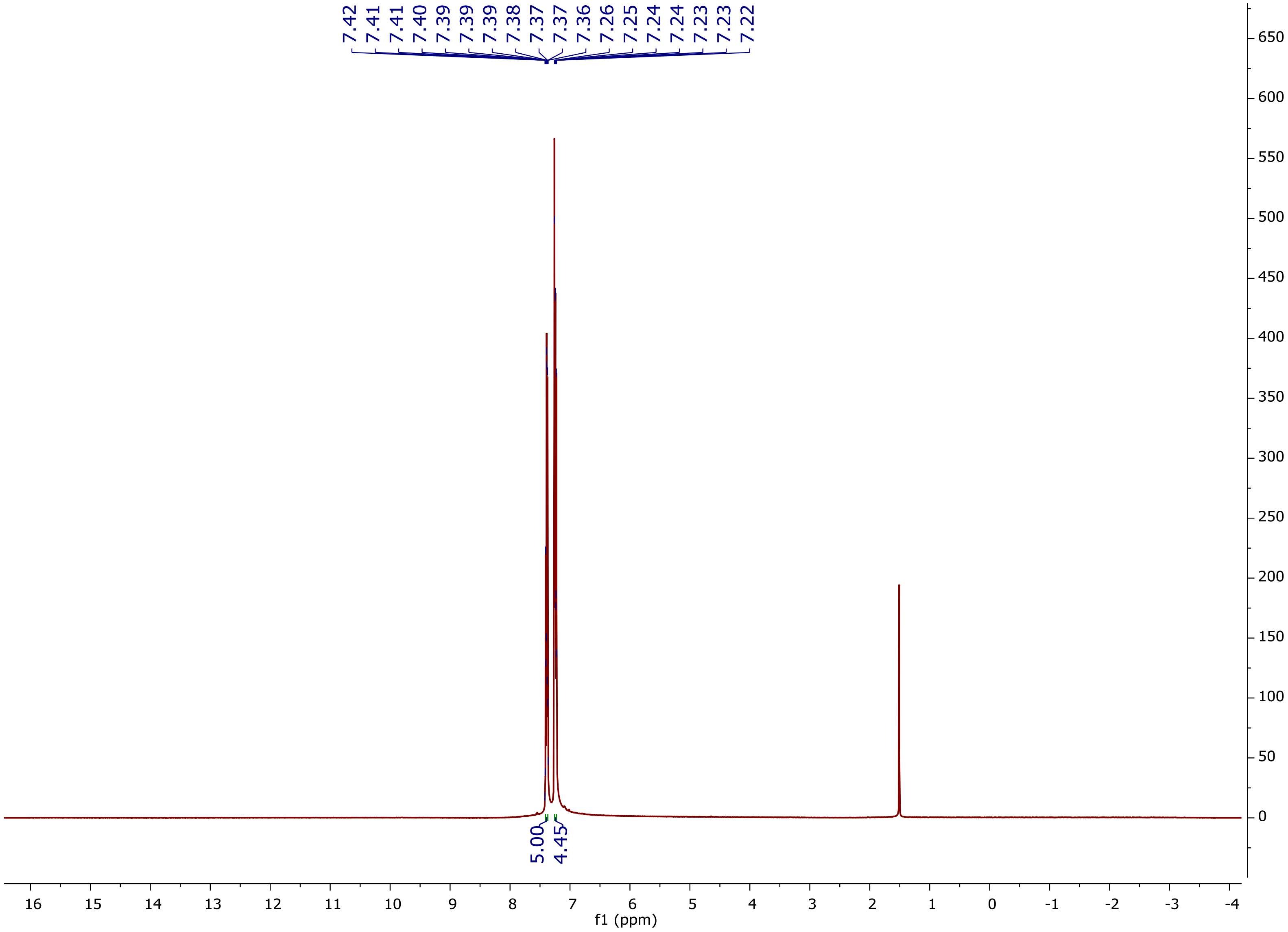

O
PhO

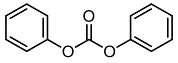
12


174.60
150.91
129.38
125.63
121.59
43.22
28.98
25.75
25.40
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
230
220
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)

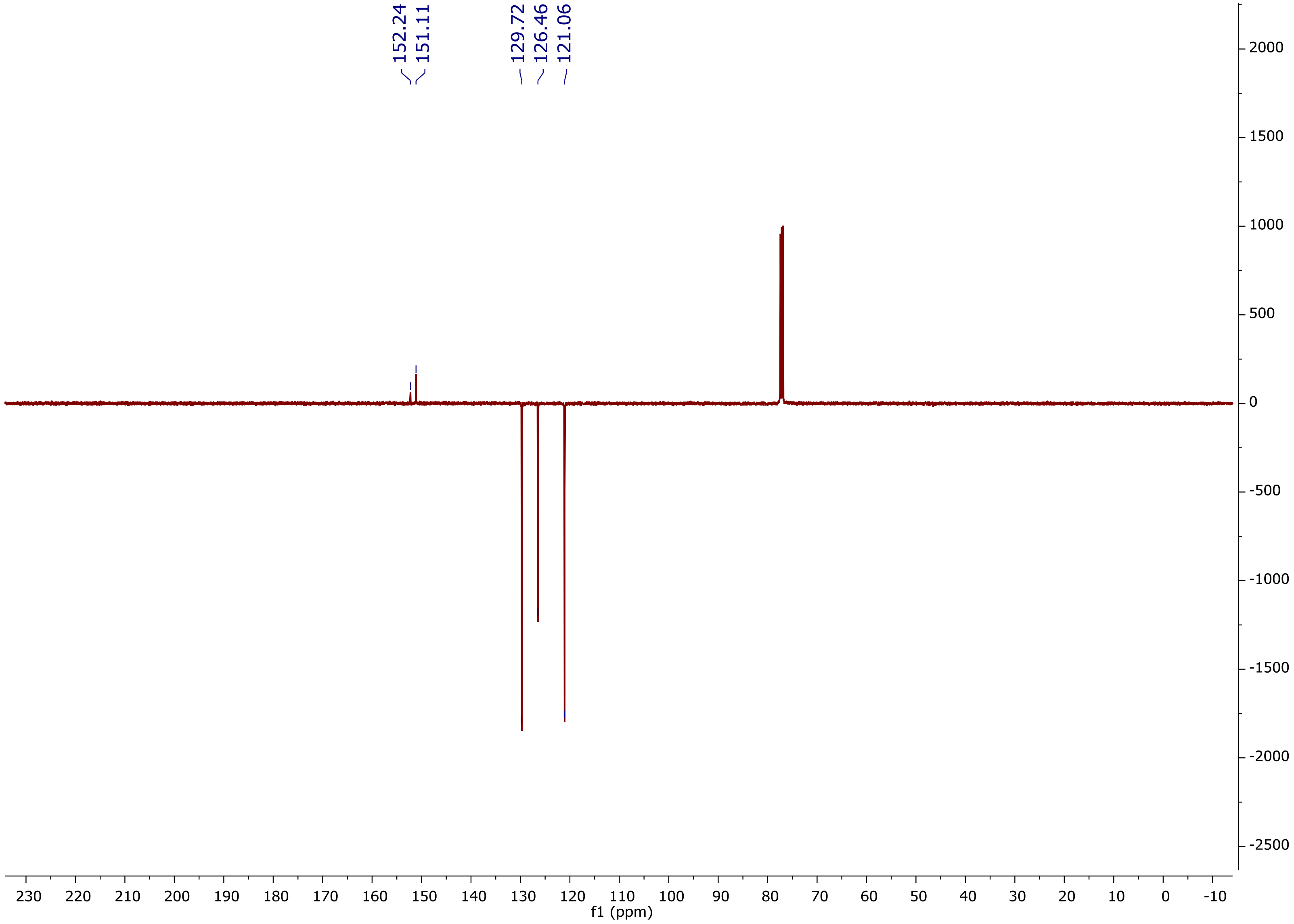


13

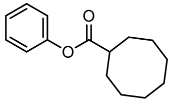

7.42
7.41
7.41
7.40
7.39
7.39
7.39
7.38
7.37
7.37
7.36
7.26
7.25
7.24
7.24
7.23
7.23
7.22
5.00
4.45
650
600
550
500
450
400
350
300
250
200
150
100
50
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)



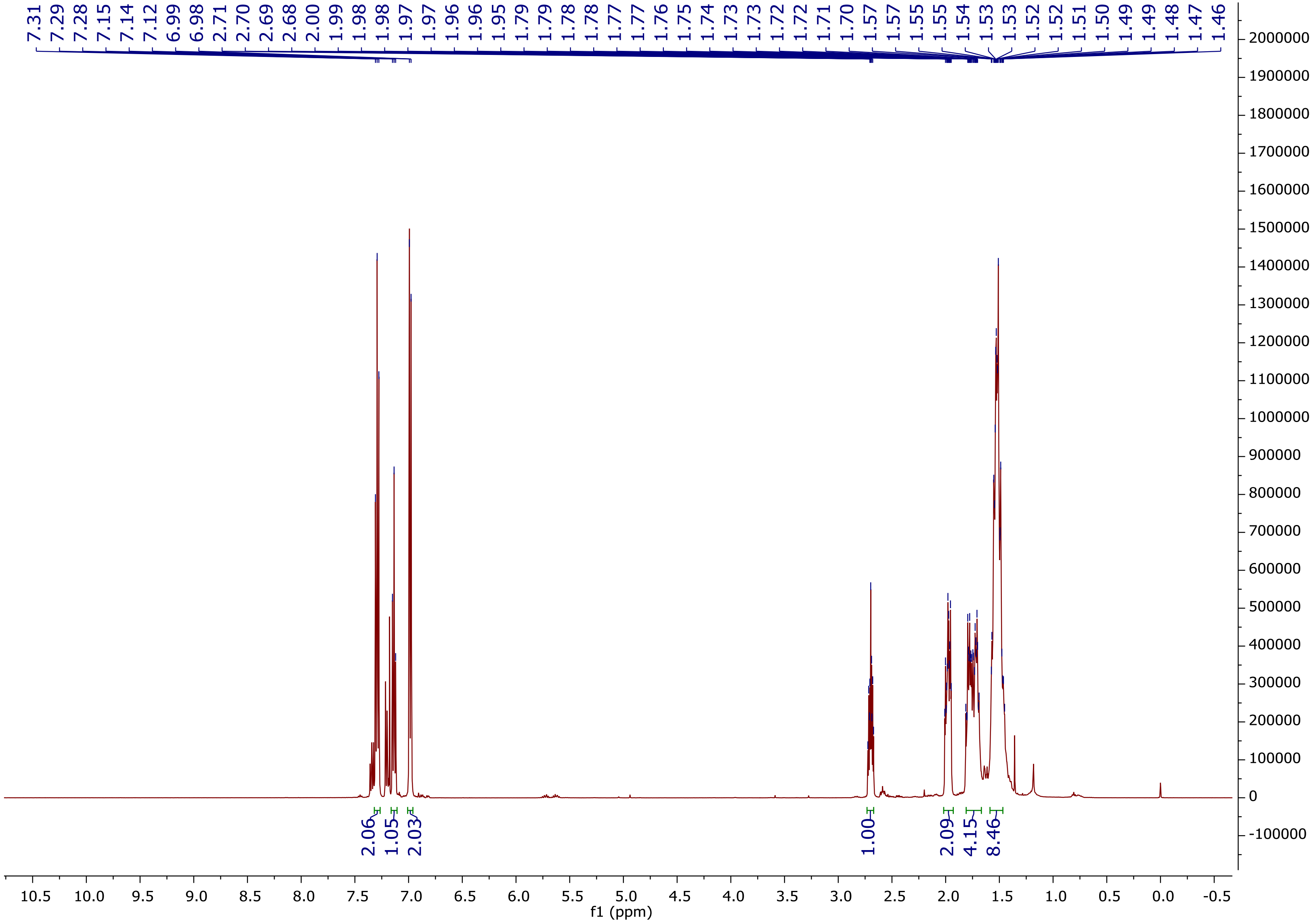
13

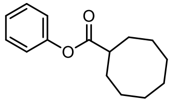


152.24
151.11
129.72
126.46
121.06
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

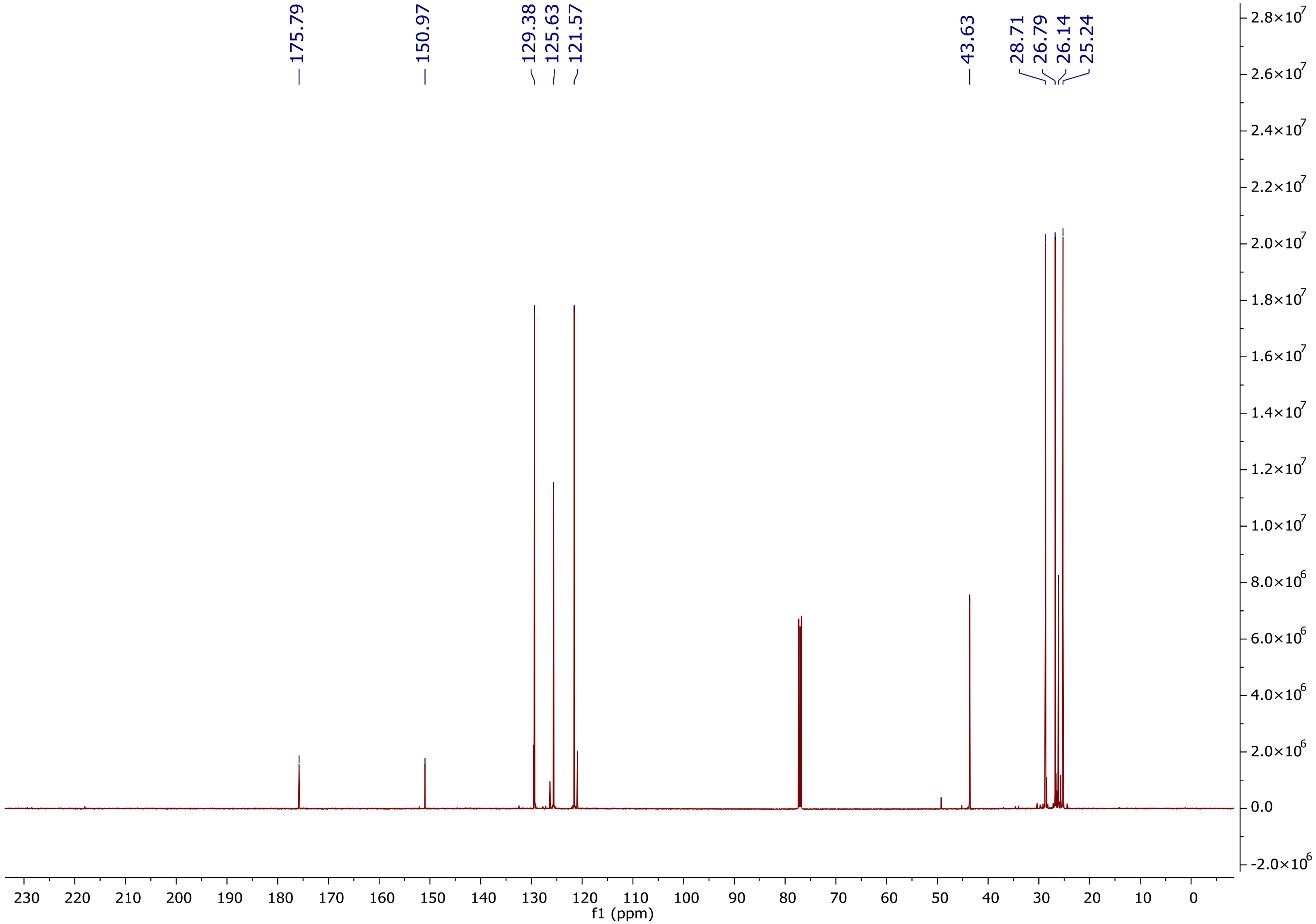

O
O

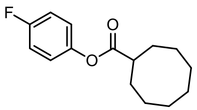
14


7.31
7.29
7.28
7.15
7.14
7.12
6.99
6.98
2.71
2.70
2.69
2.68
2.00
1.99
1.98
1.98
1.97
1.97
1.96
1.96
1.95
1.79
1.79
1.78
1.78
1.77
1.77
1.76
1.75
1.74
1.73
1.73
1.72
1.72
1.71
1.70
1.57
1.57
1.55
1.55
1.54
1.53
1.53
1.52
1.52
1.51
1.50
1.49
1.49
1.48
1.47
1.46
2.06
1.05
2.03
1.00
2.09
4.15
8.46
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
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)

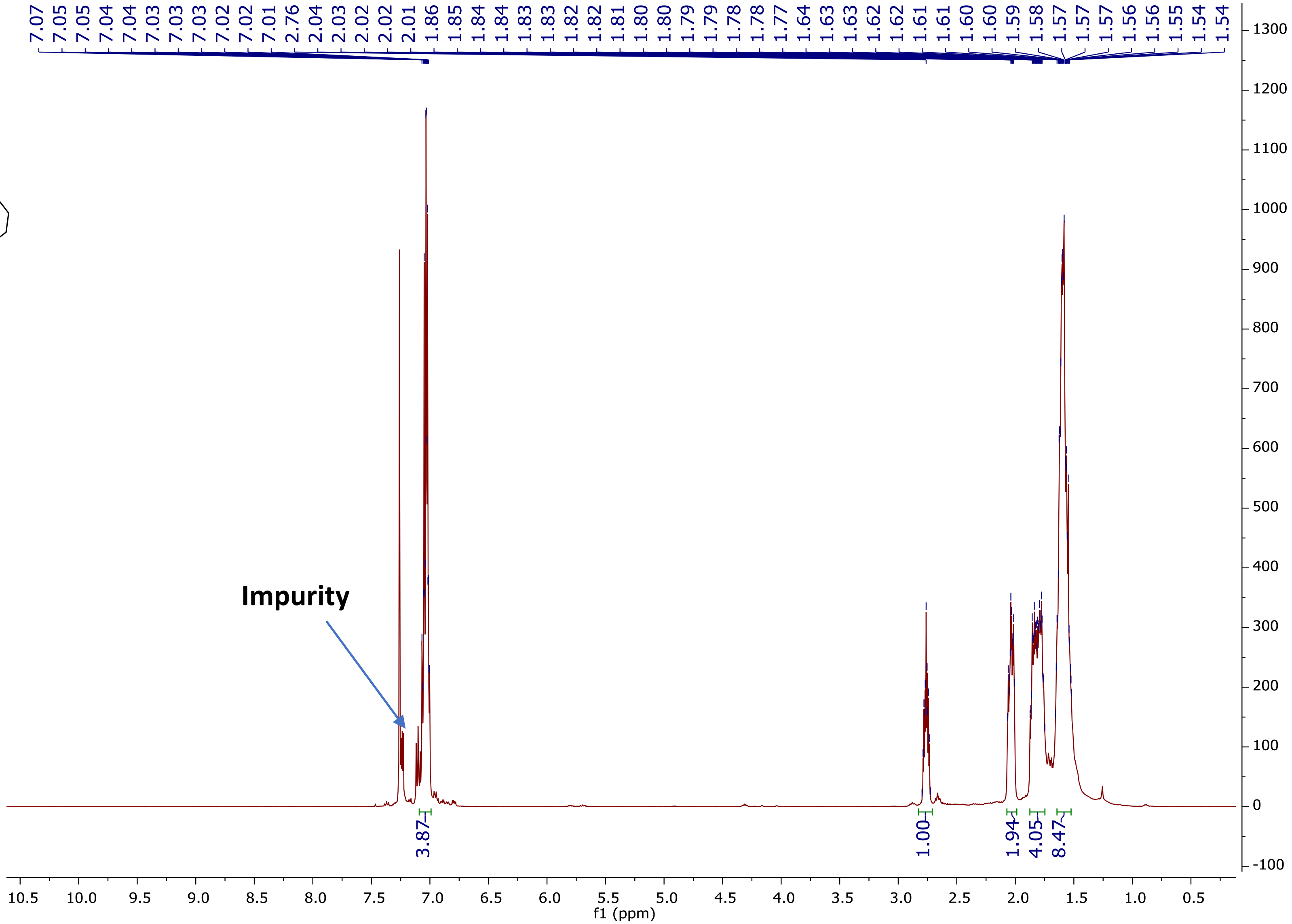


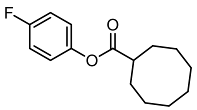
14


175.79
150.97
129.38
125.63
121.57
43.63
28.71
26.79
26.14
25.24
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

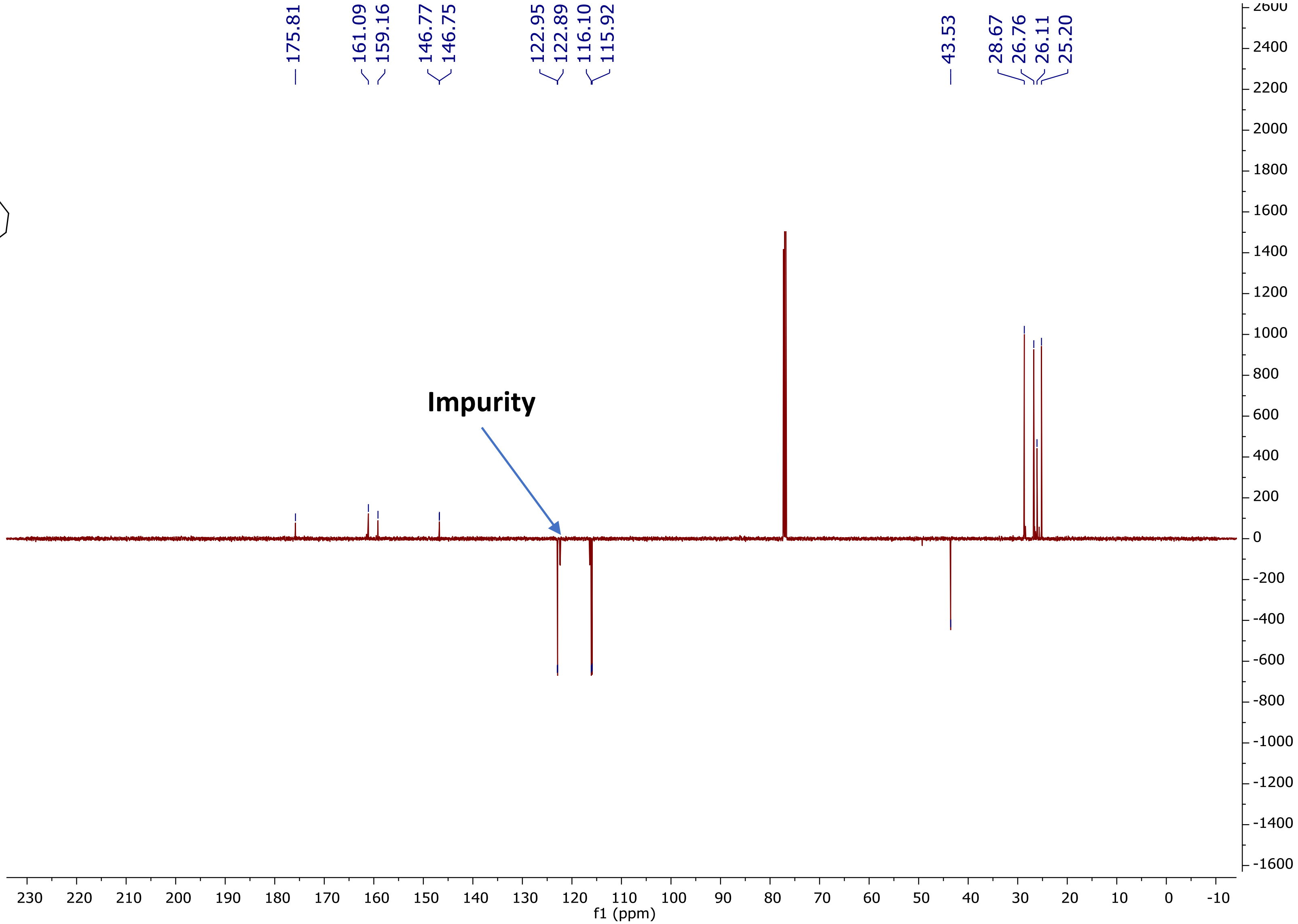

F
O
O

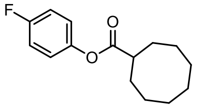
15


7.07
7.05
7.05
7.04
7.04
7.03
7.03
7.03
7.02
7.02
7.01
2.76
2.04
2.03
2.02
2.02
2.01
1.86
1.85
1.84
1.84
1.83
1.83
1.82
1.82
1.81
1.80
1.80
1.79
1.79
1.78
1.78
1.77
1.64
1.63
1.63
1.62
1.62
1.61
1.61
1.60
1.60
1.59
1.58
1.57
1.57
1.57
1.56
1.56
1.55
1.54
1.54
Impurity
3.87
1.00
1.94
4.05
8.47
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
f1 (ppm)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

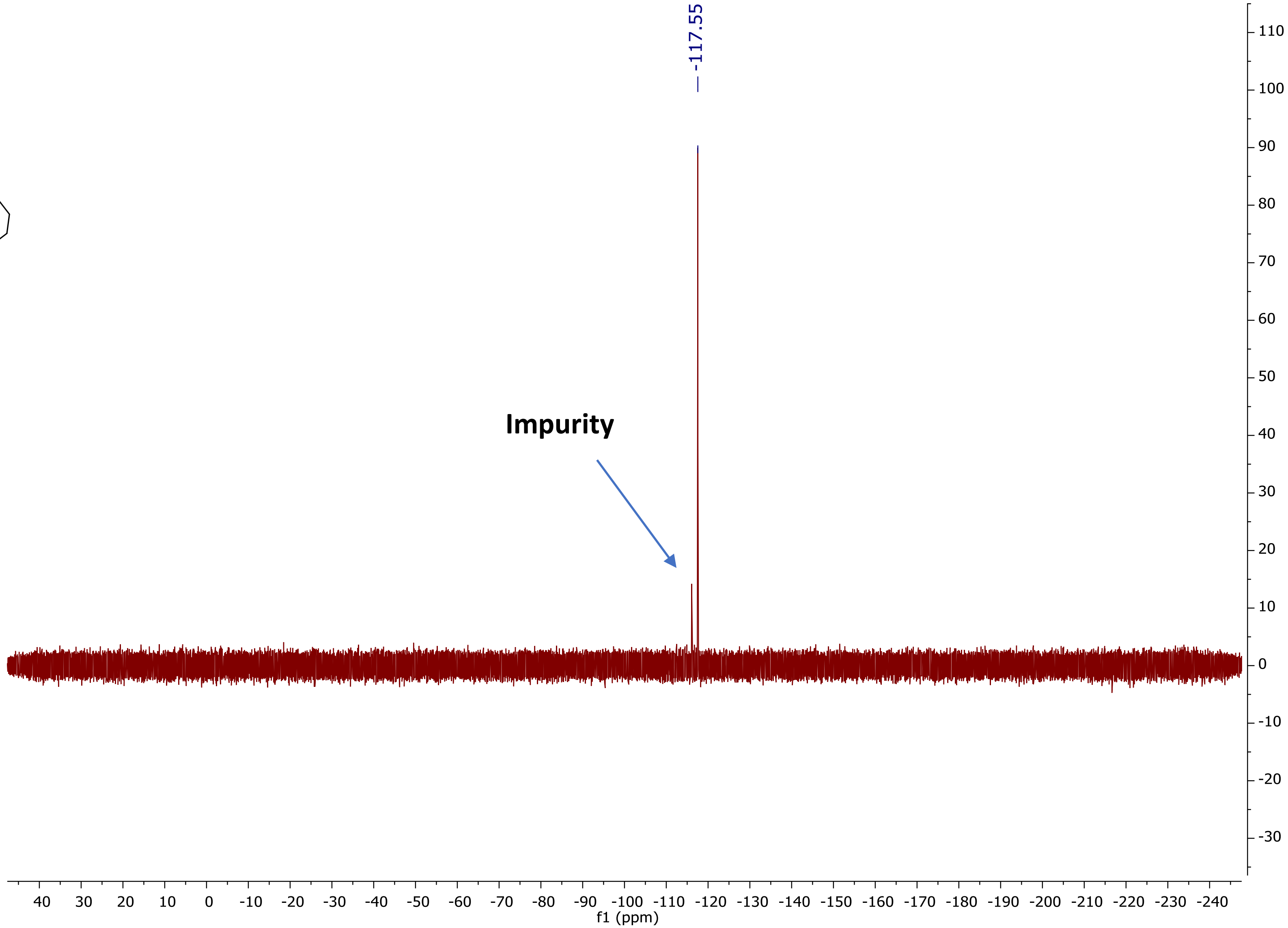

F
O
O

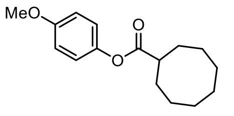
15


175.81
161.09
159.16
146.77
146.75
122.95
122.89
116.10
115.92
43.53
28.67
26.76
26.11
25.20
Impurity
230
220
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)
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-1000
-1200
-1400
-1600

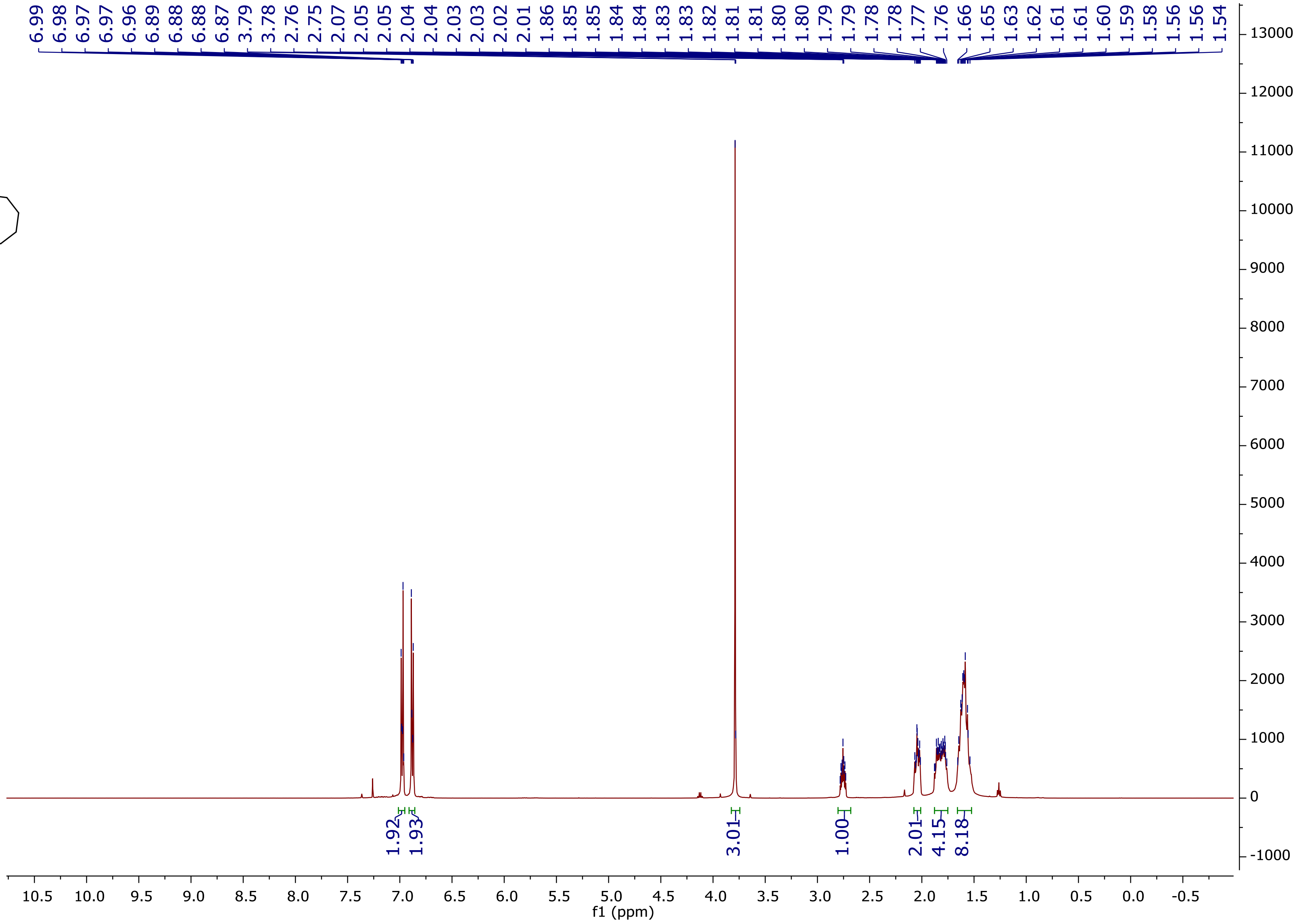

F
O
O

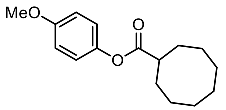
15


-117.55
Impurity
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

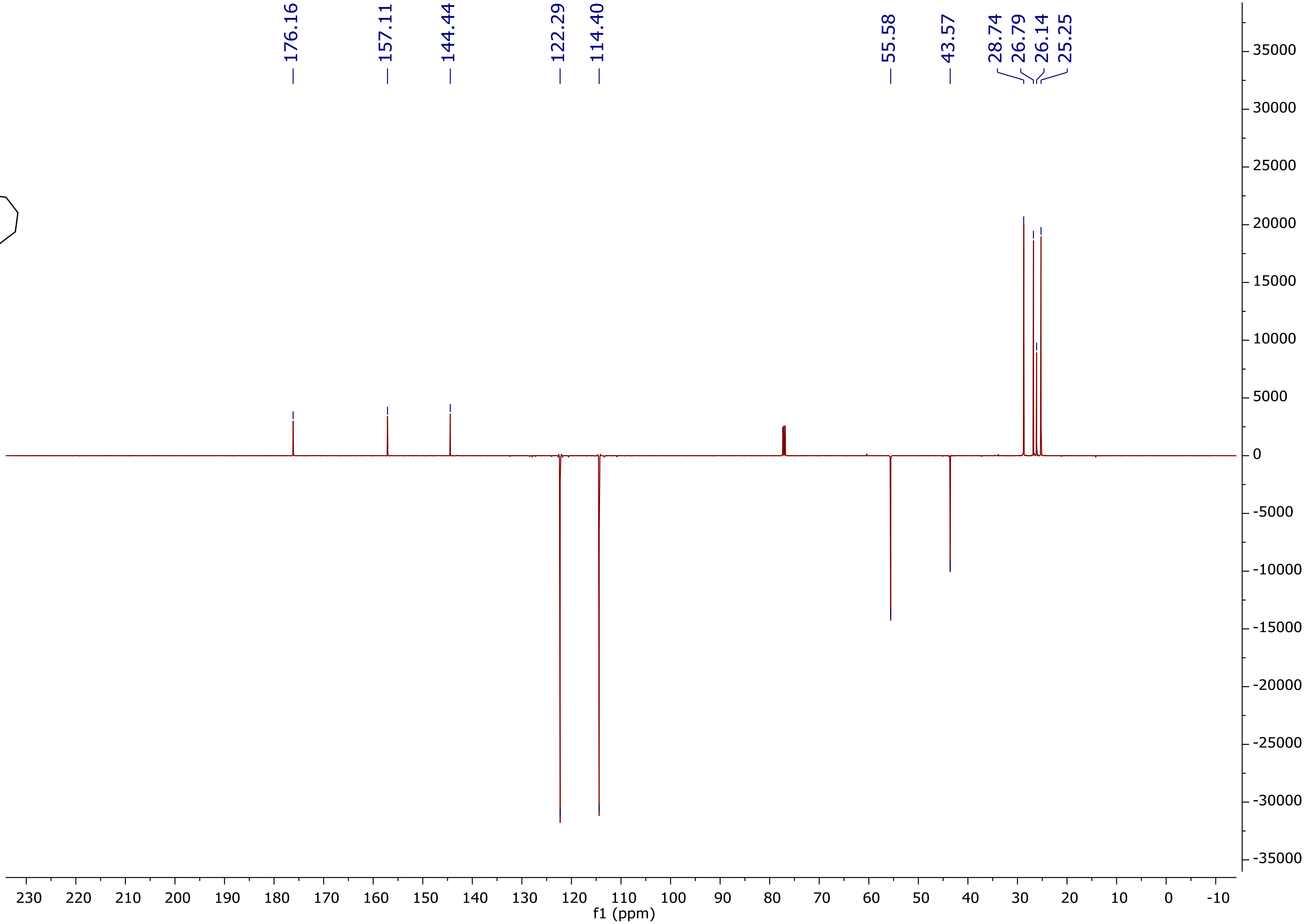

MeO
O
O

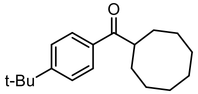
16


6.99
6.98
6.97
6.97
6.96
6.89
6.88
6.88
6.87
3.79
3.78
2.76
2.75
2.07
2.05
2.05
2.04
2.04
2.03
2.03
2.02
2.01
1.86
1.85
1.85
1.84
1.84
1.83
1.83
1.82
1.81
1.81
1.80
1.80
1.79
1.79
1.78
1.78
1.77
1.76
1.66
1.65
1.63
1.62
1.61
1.61
1.60
1.59
1.58
1.56
1.56
1.54
1.92
1.93
3.01
1.00
2.01
4.15
8.18
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)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

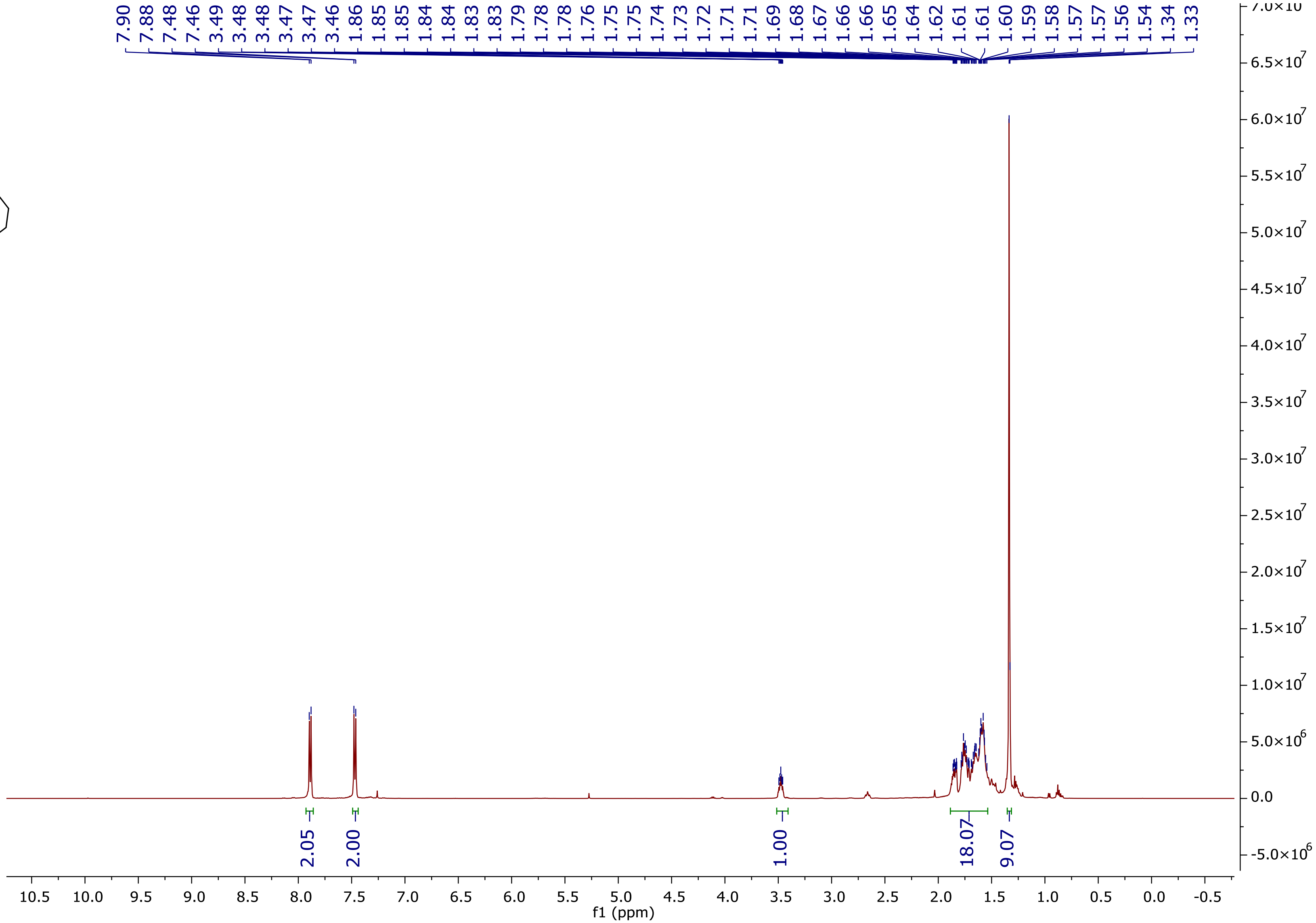

MeO
O
O

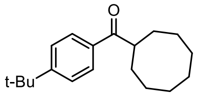
16


176.16
157.11
144.44
122.29
114.40
55.58
43.57
28.74
26.79
26.14
25.25
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
-30000
-35000
230
220
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)

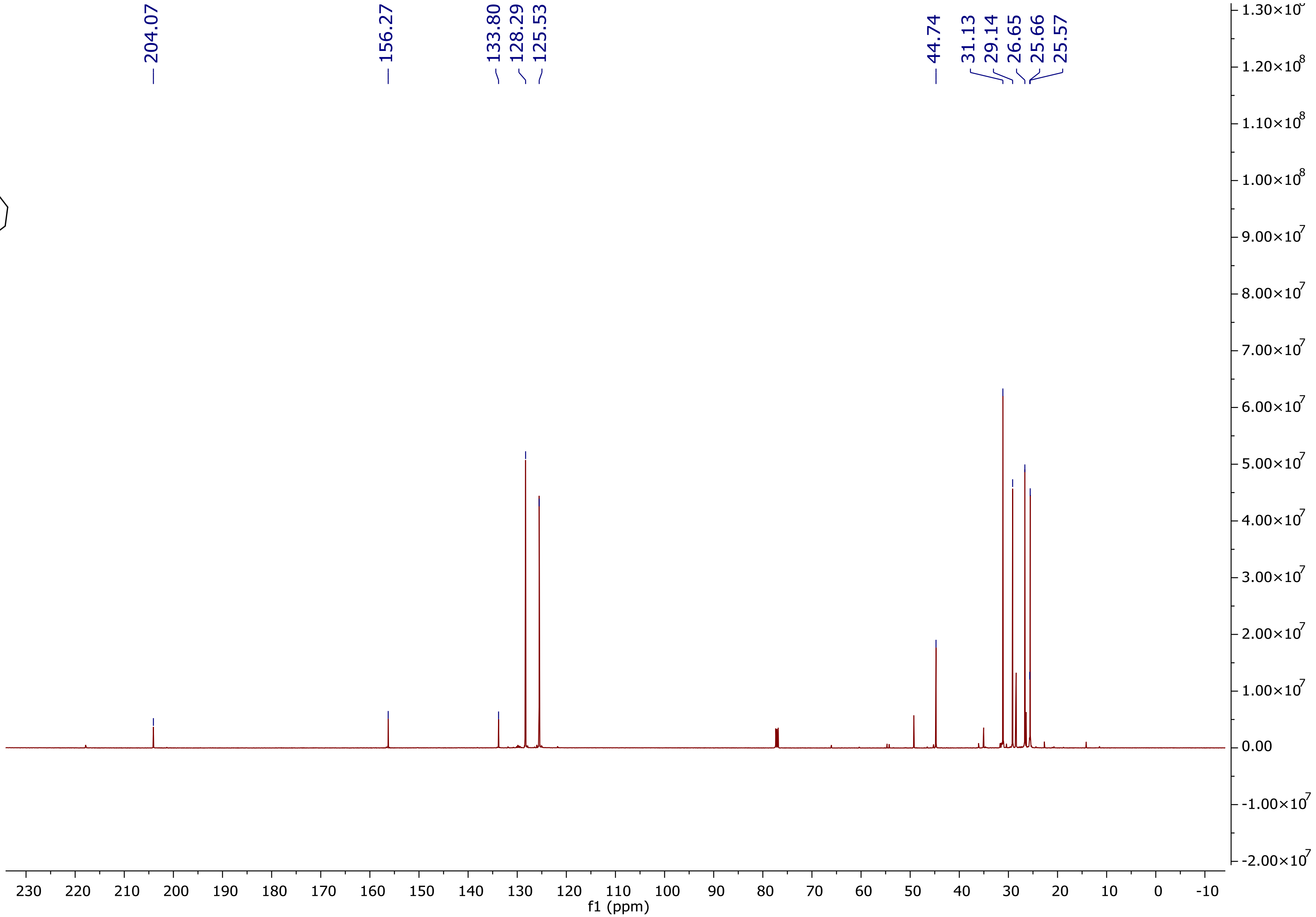

O
t-Bu

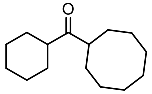
17


7.90
7.88
7.48
7.46
3.49
3.48
3.48
3.47
3.47
3.46
1.86
1.85
1.85
1.84
1.84
1.83
1.83
1.79
1.78
1.78
1.76
1.75
1.75
1.74
1.73
1.72
1.71
1.71
1.69
1.68
1.67
1.66
1.66
1.65
1.64
1.62
1.61
1.61
1.60
1.59
1.58
1.57
1.57
1.56
1.54
1.34
1.33
2.05
2.00
1.00
18.07
9.07
7.0×10
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
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)

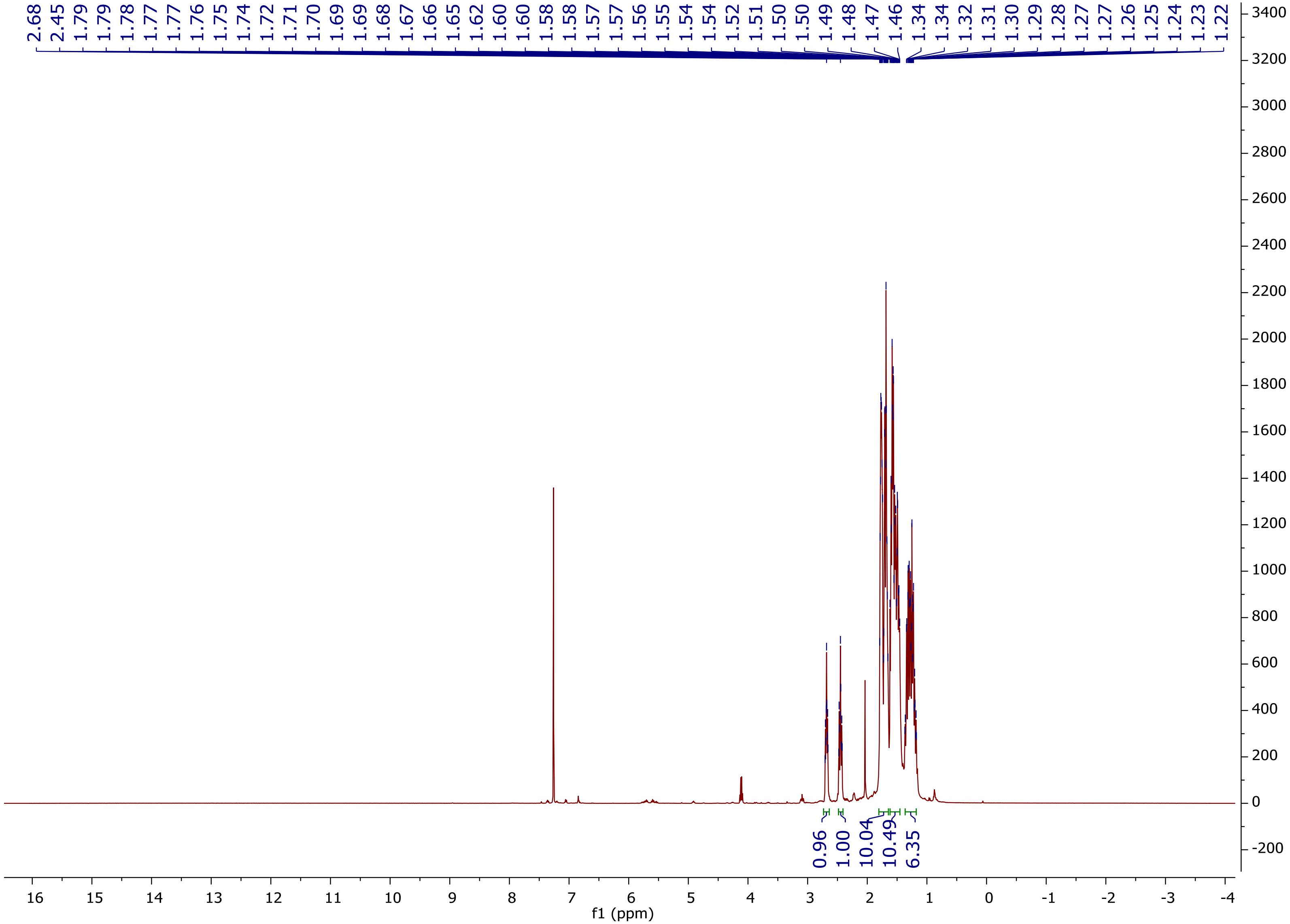

O
t-Bu

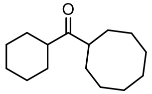
17


204.07
156.27
133.80
128.29
125.53
44.74
31.13
29.14
26.65
25.66
25.57
1.30×10⁸
1.20×10⁸
1.10×10⁸
1.00×10⁸
9.00×10⁷
8.00×10⁷
7.00×10⁷
6.00×10⁷
5.00×10⁷
4.00×10⁷
3.00×10⁷
2.00×10⁷
1.00×10⁷
0.00
-1.00×10⁷
-2.00×10⁷
230
220
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)

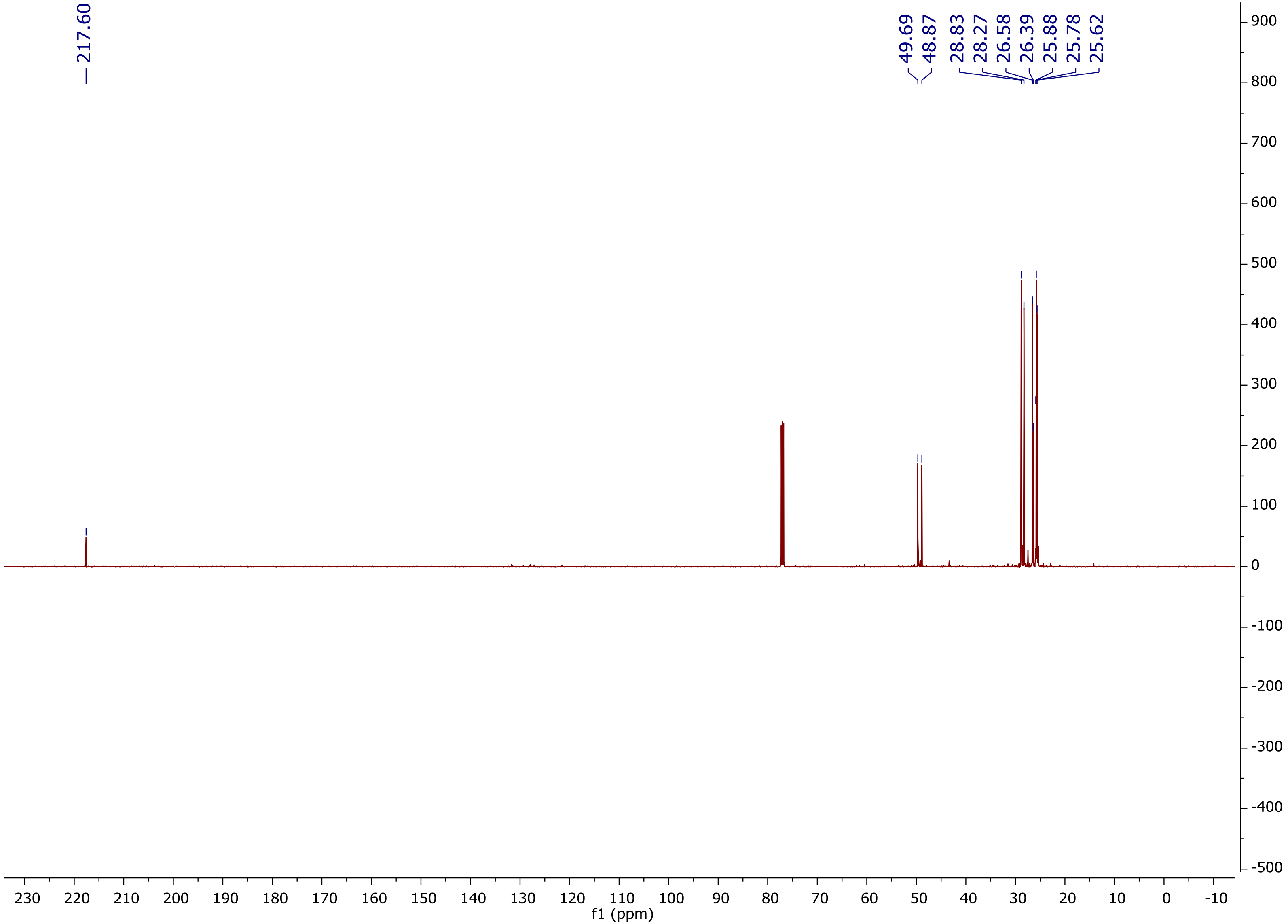

O

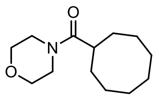
18


2.68
2.45
1.79
1.79
1.78
1.77
1.77
1.76
1.75
1.74
1.72
1.71
1.70
1.69
1.69
1.68
1.67
1.66
1.65
1.62
1.60
1.60
1.58
1.58
1.57
1.57
1.56
1.55
1.54
1.54
1.52
1.51
1.50
1.50
1.49
1.48
1.47
1.46
1.34
1.34
1.32
1.31
1.30
1.29
1.28
1.27
1.27
1.26
1.25
1.24
1.23
1.22
0.96
1.00
10.04
10.49
6.35
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

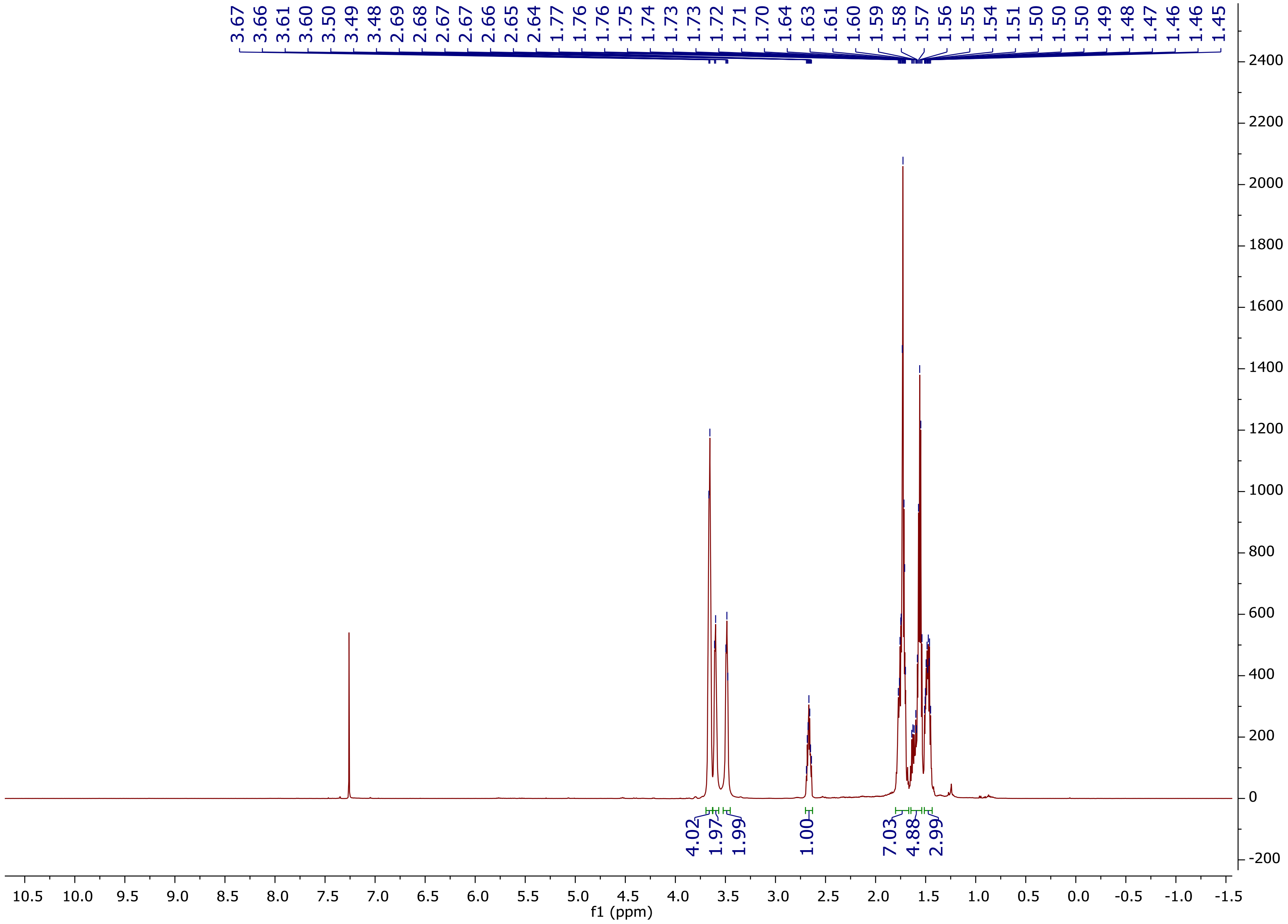

O

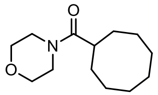
18


217.60
49.69
48.87
28.83
28.27
26.58
26.39
25.88
25.78
25.62
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
230
220
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)

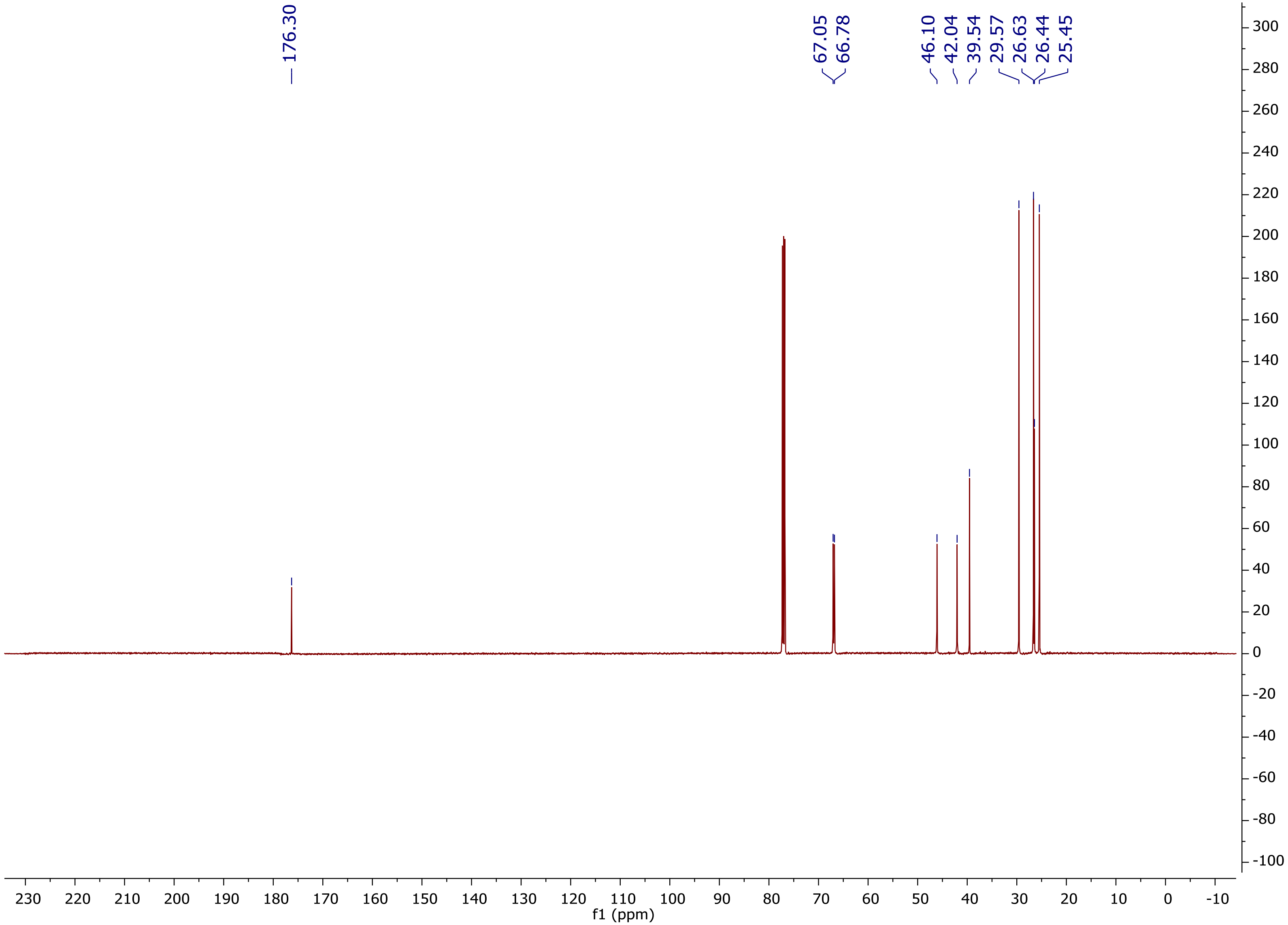

O
N
O

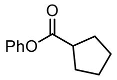
19


3.67
3.66
3.61
3.60
3.50
3.49
3.48
2.69
2.68
2.67
2.67
2.66
2.65
2.64
1.77
1.76
1.76
1.75
1.74
1.73
1.73
1.72
1.71
1.70
1.64
1.63
1.61
1.60
1.59
1.58
1.57
1.56
1.55
1.54
1.51
1.50
1.50
1.50
1.49
1.48
1.47
1.46
1.46
1.45
4.02
1.97
1.99
1.00
7.03
4.88
2.99
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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
-1.0
-1.5
f1 (ppm)

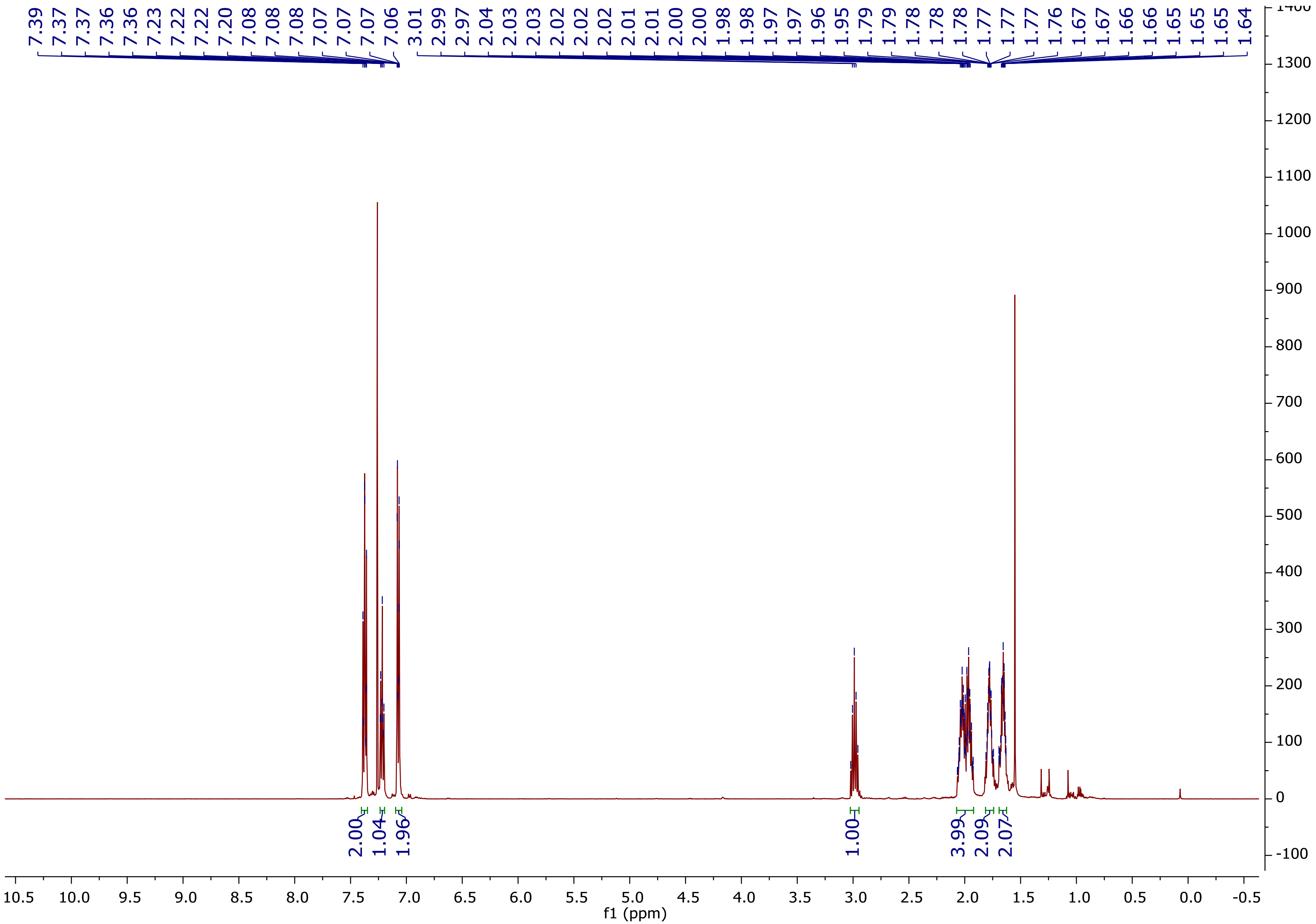

O
N
O

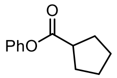
19


176.30
67.05
66.78
46.10
42.04
39.54
29.57
26.63
26.44
25.45
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
230
220
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)

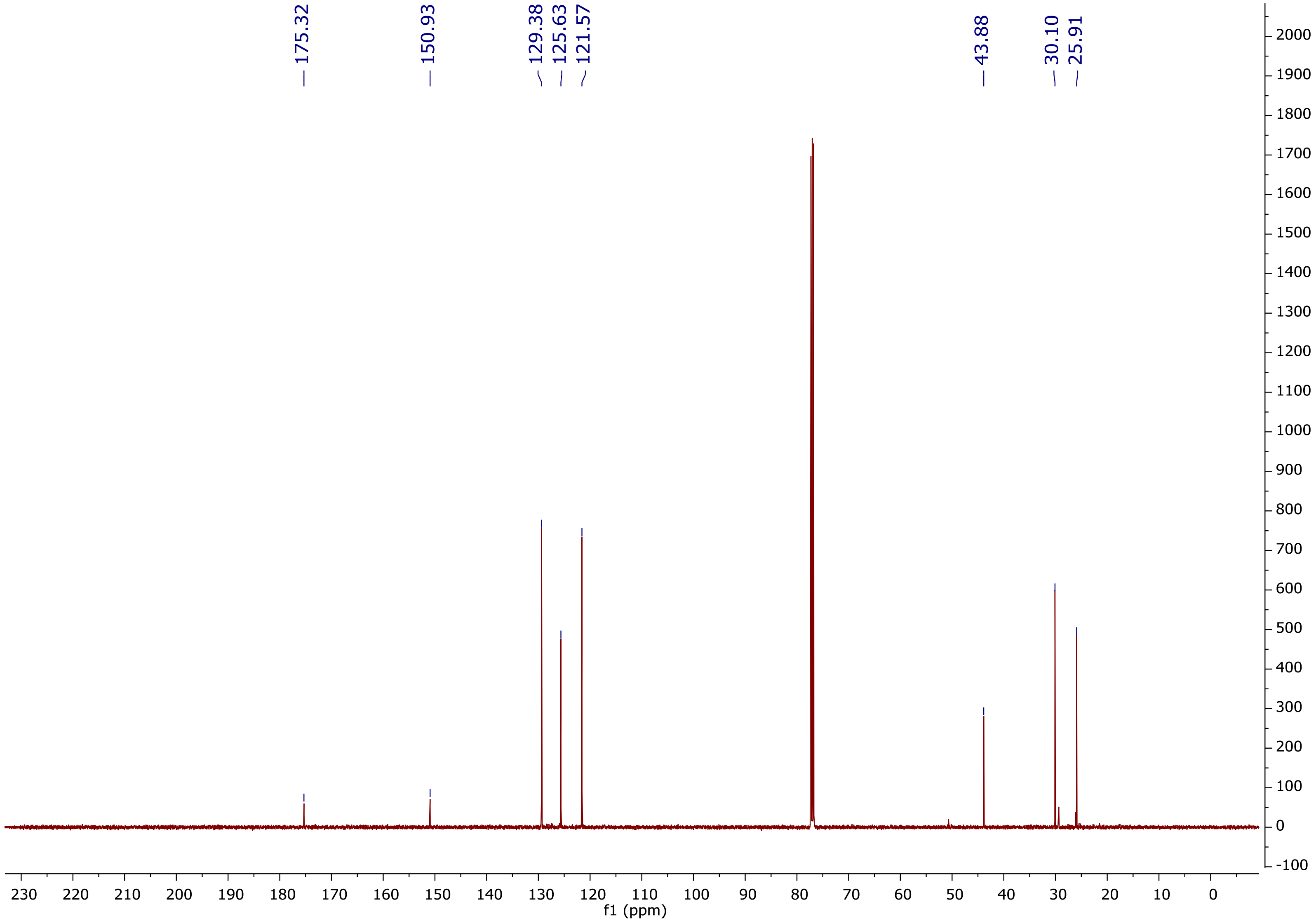

O
PhO

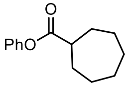
20


7.39
7.37
7.37
7.36
7.36
7.23
7.22
7.22
7.20
7.08
7.08
7.08
7.07
7.07
7.06
3.01
2.99
2.97
2.04
2.03
2.03
2.02
2.02
2.02
2.01
2.01
2.00
2.00
1.98
1.98
1.97
1.97
1.96
1.95
1.79
1.79
1.78
1.78
1.78
1.77
1.77
1.77
1.76
1.67
1.67
1.66
1.66
1.65
1.65
1.65
1.64
2.00
1.04
1.96
1.00
3.99
2.09
2.07
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)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

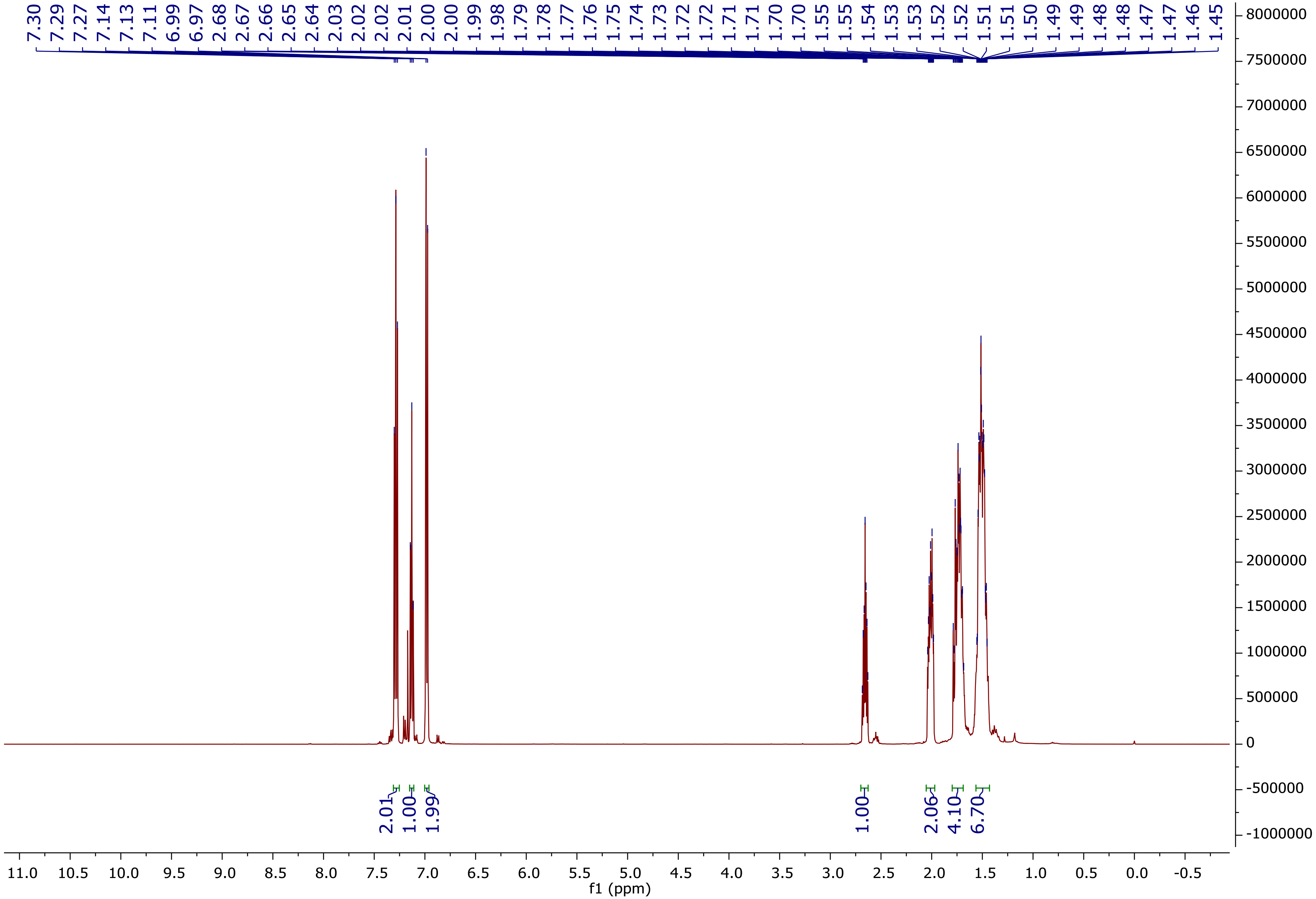

O
PhO

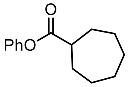
20


175.32
150.93
129.38
125.63
121.57
43.88
30.10
25.91
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

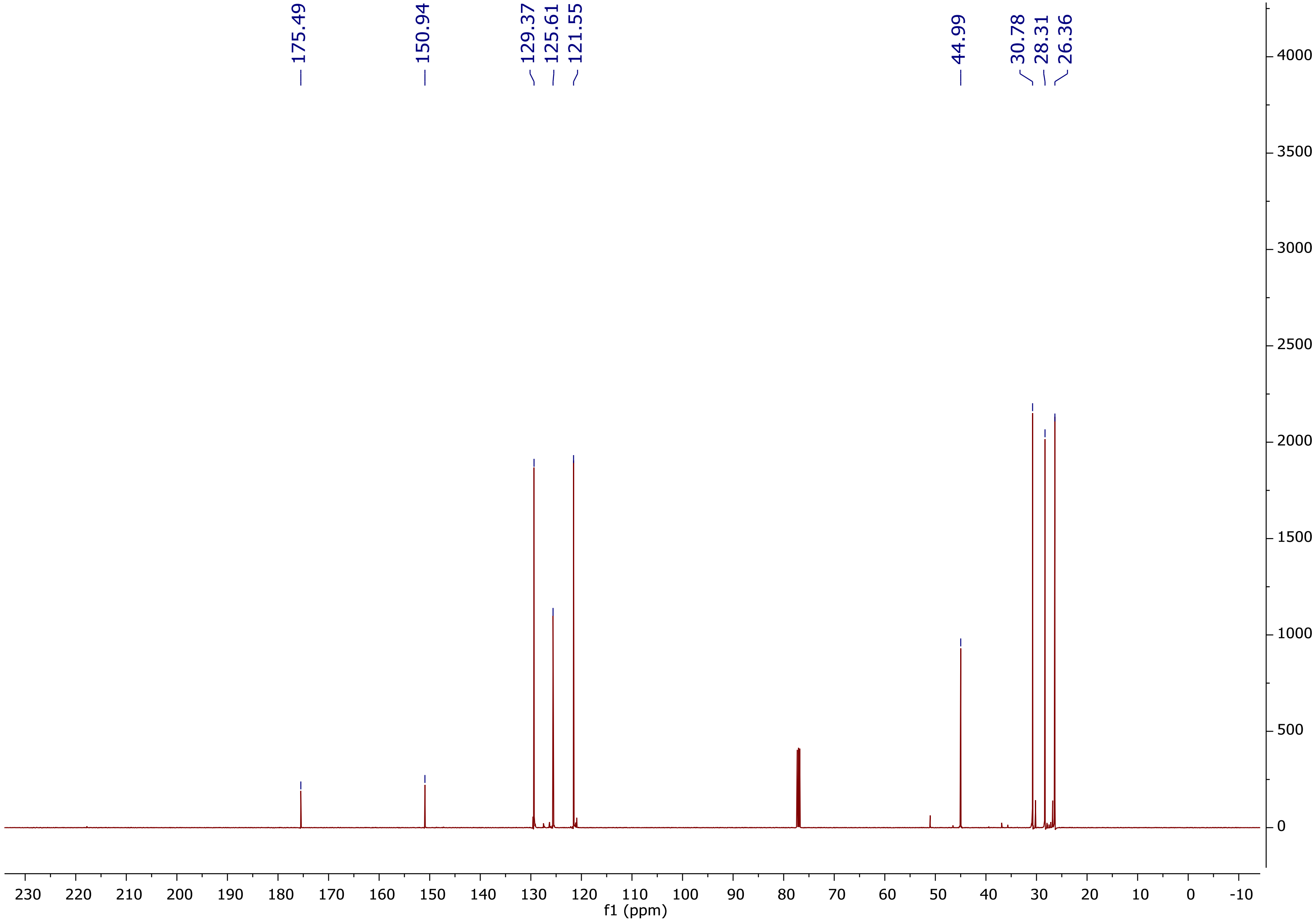

O
PhO

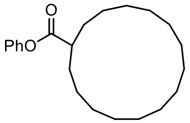
21


7.30
7.29
7.27
7.14
7.13
7.11
6.99
6.97
2.68
2.67
2.66
2.65
2.64
2.03
2.02
2.02
2.01
2.00
2.00
1.99
1.98
1.79
1.78
1.77
1.76
1.75
1.74
1.73
1.72
1.72
1.71
1.71
1.70
1.70
1.55
1.55
1.54
1.53
1.53
1.52
1.52
1.51
1.51
1.50
1.49
1.49
1.48
1.48
1.47
1.47
1.46
1.45
2.01
1.00
1.99
1.00
2.06
4.10
6.70
11.0
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)
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
-1000000

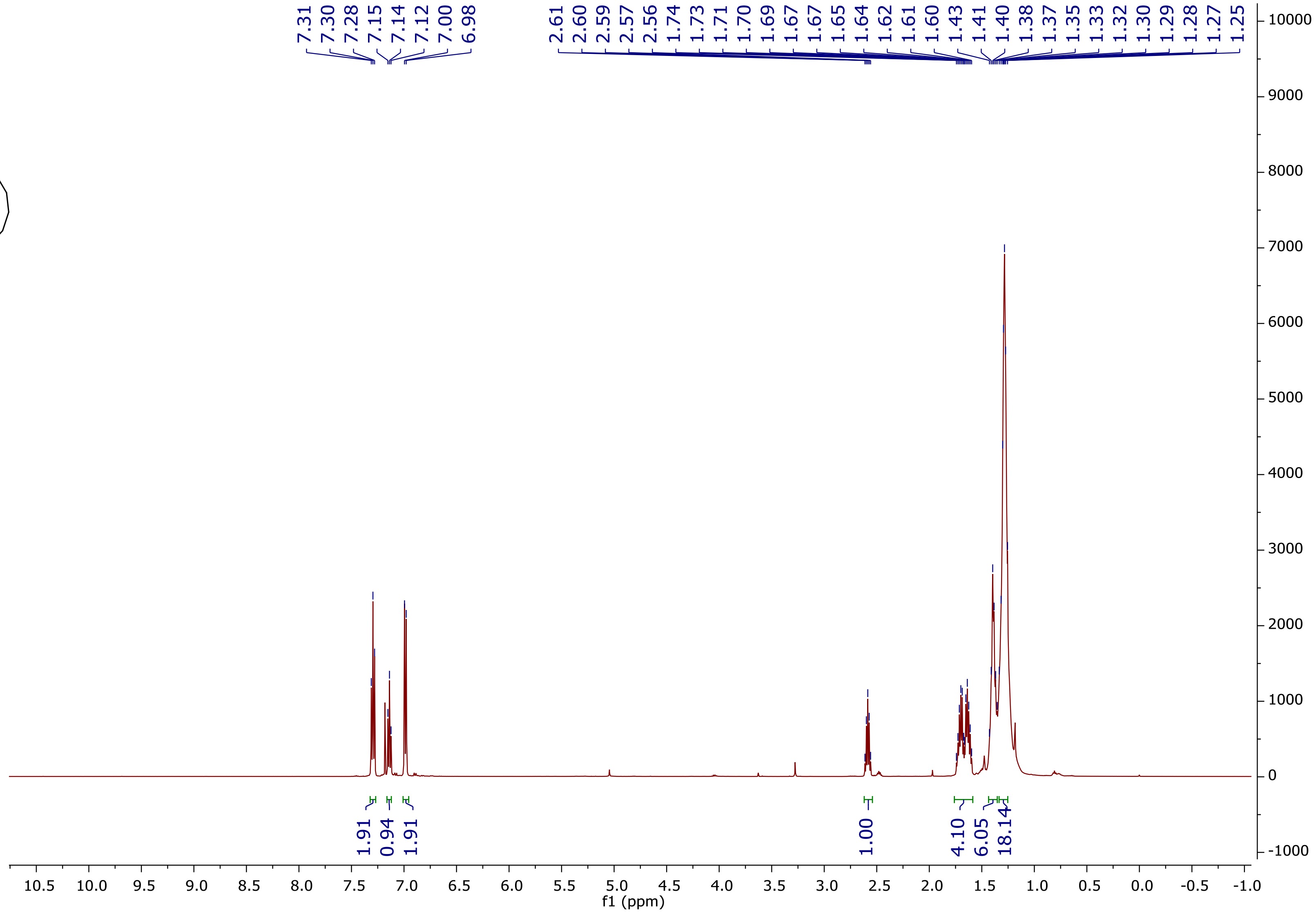

O
PhO

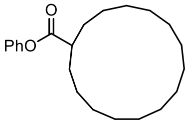
21


175.49
150.94
129.37
125.61
121.55
44.99
30.78
28.31
26.36
4000
3500
3000
2500
2000
1500
1000
500
0
230
220
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)

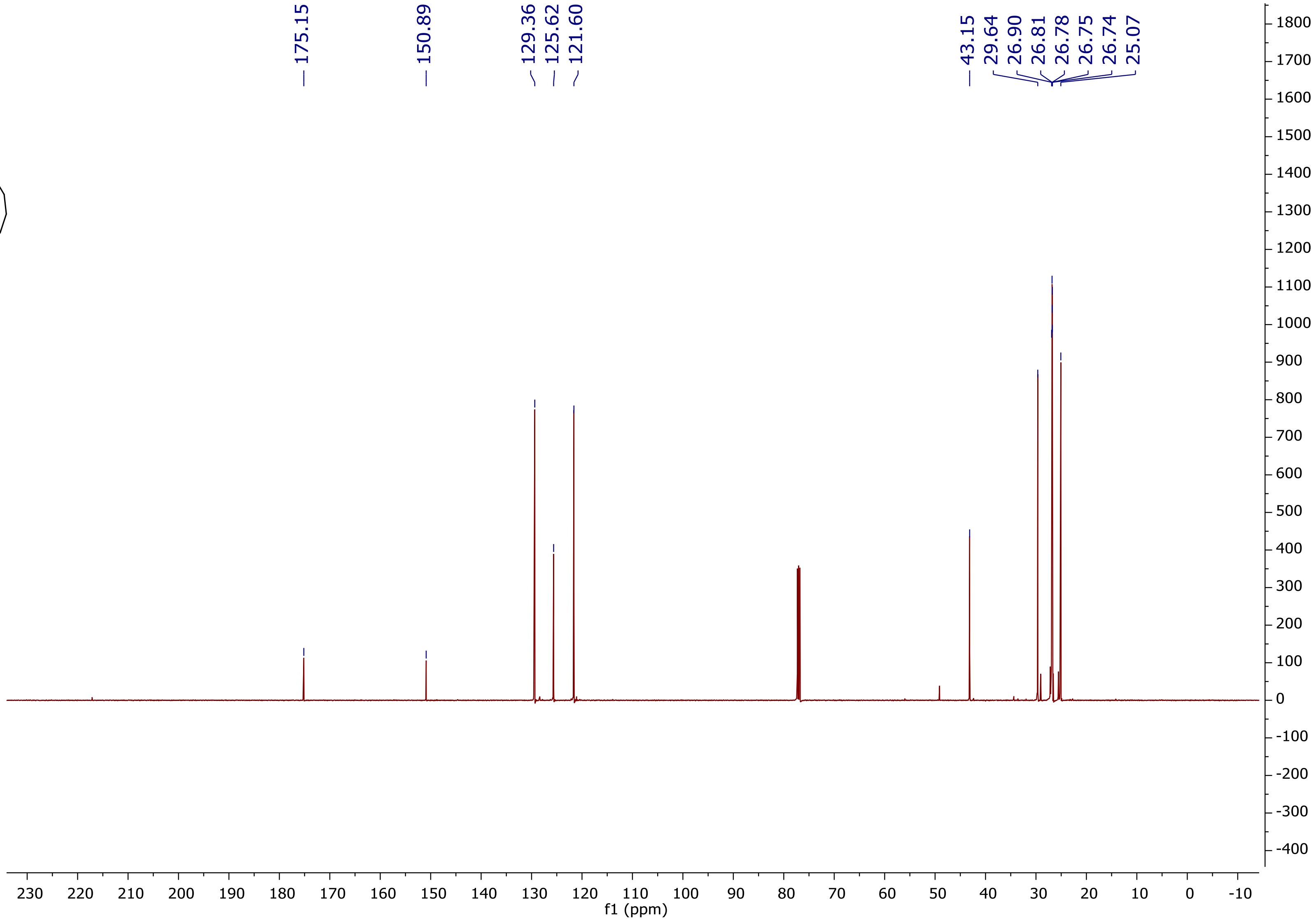


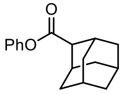
22


7.31
7.30
7.28
7.15
7.14
7.12
7.00
6.98
2.61
2.60
2.59
2.57
2.56
1.74
1.73
1.71
1.70
1.69
1.67
1.67
1.65
1.64
1.62
1.61
1.60
1.43
1.41
1.40
1.38
1.37
1.35
1.33
1.32
1.30
1.29
1.28
1.27
1.25
1.91
0.94
1.91
1.00
4.10
6.05
18.14
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
-1.0
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

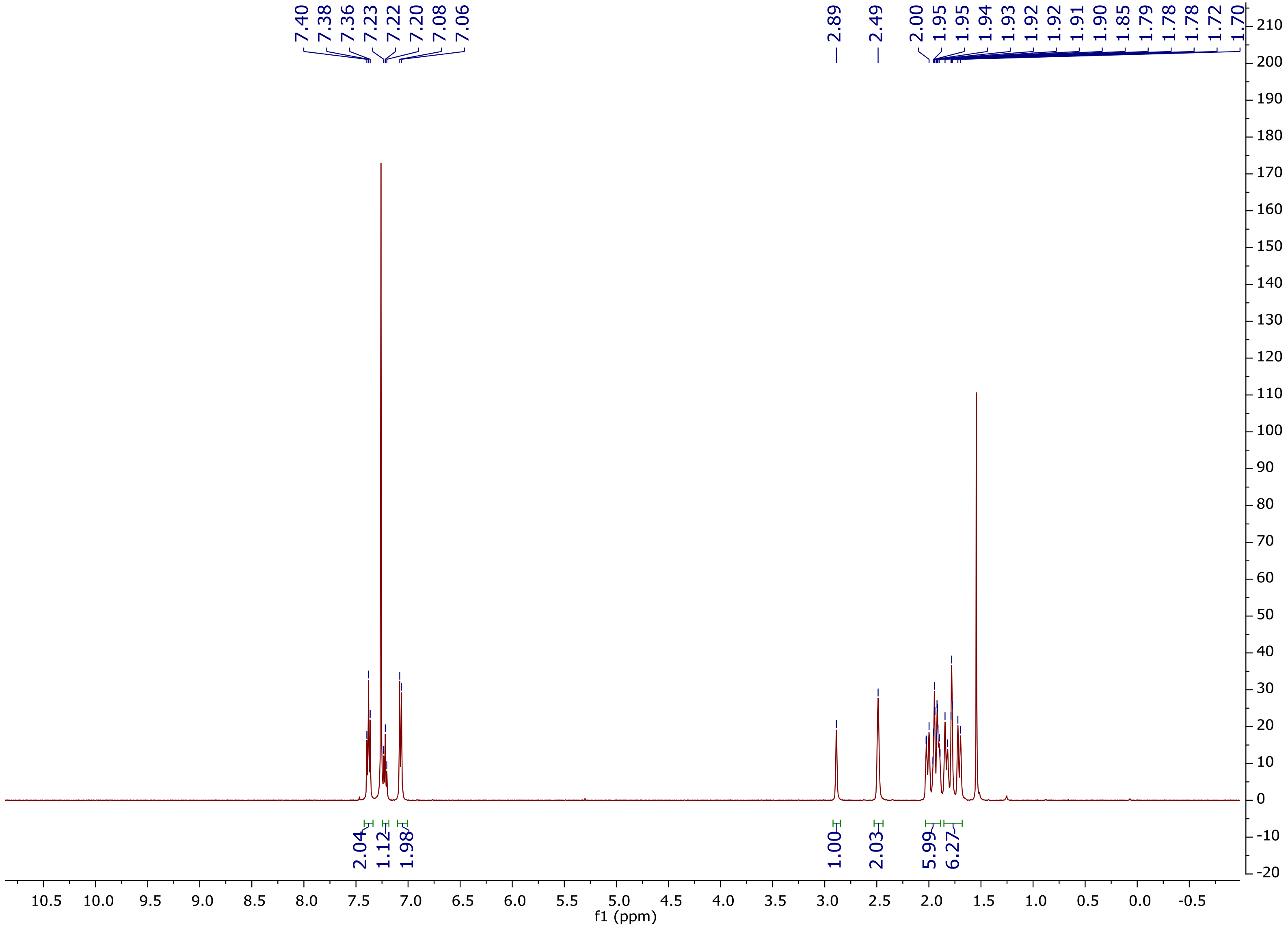

O
PhO

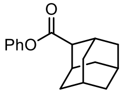
22


175.15
150.89
129.36
125.62
121.60
43.15
29.64
26.90
26.81
26.78
26.75
26.74
25.07
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
-400
230
220
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)

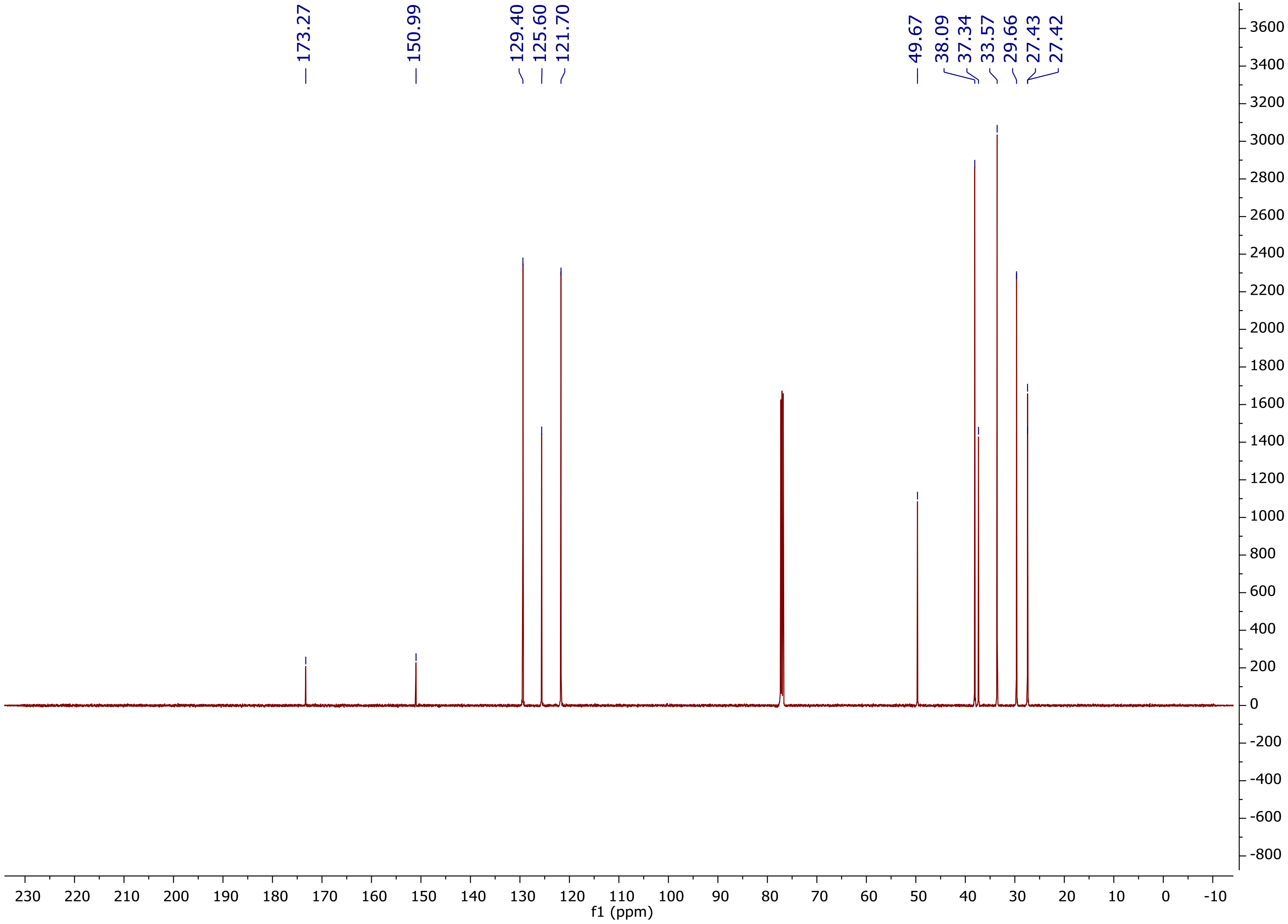

O
PhO

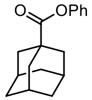
23-α


7.40
7.38
7.36
7.23
7.22
7.20
7.08
7.06
2.89
2.49
2.00
1.95
1.95
1.94
1.93
1.92
1.92
1.91
1.90
1.85
1.79
1.78
1.78
1.72
1.70
2.04
1.12
1.98
1.00
2.03
5.99
6.27
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)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

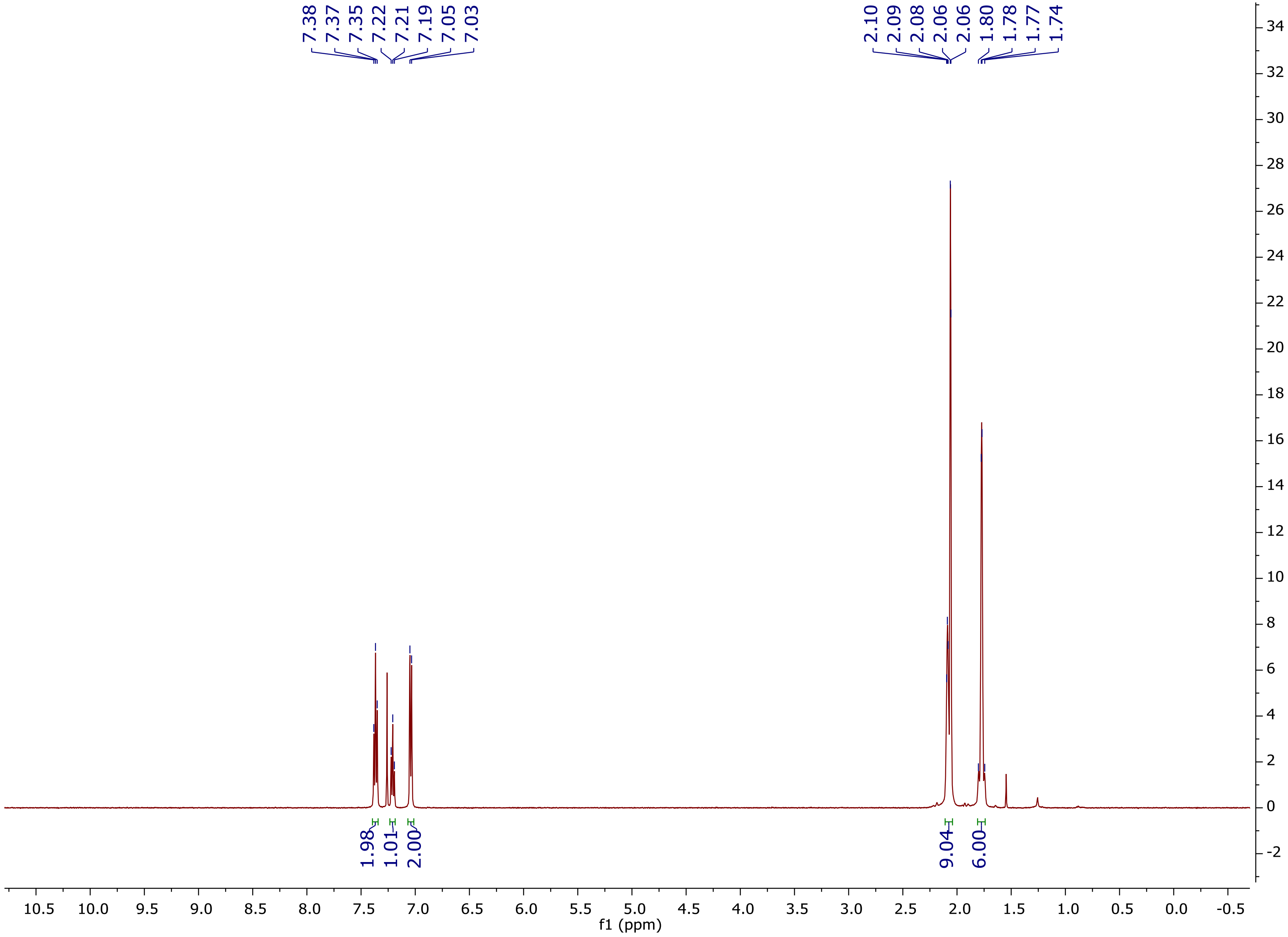

PhO
O

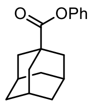
23-α


173.27
150.99
129.40
125.60
121.70
49.67
38.09
37.34
33.57
29.66
27.43
27.42
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
230
220
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)

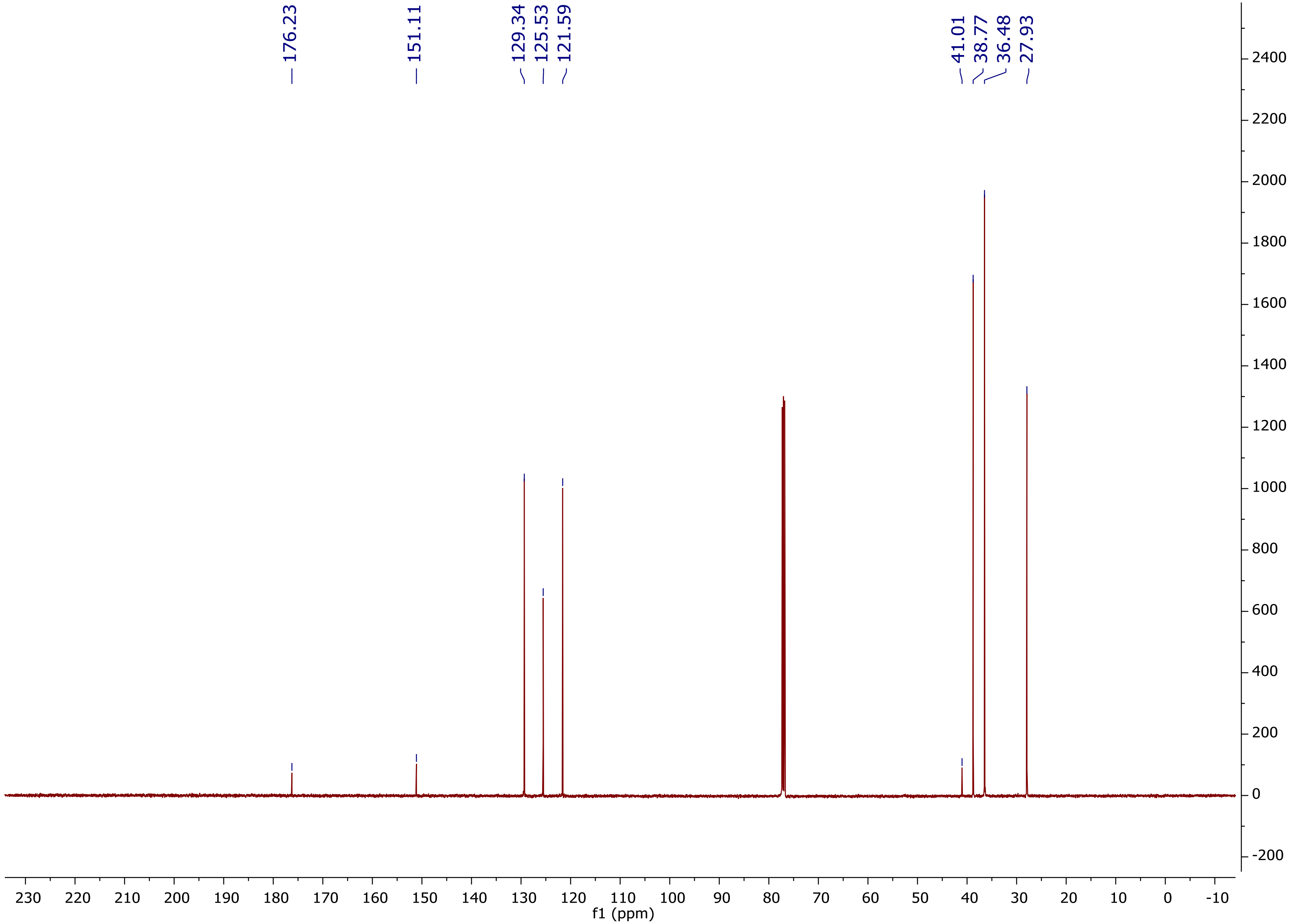

O
OPh

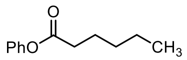
23-β


7.38
7.37
7.35
7.22
7.21
7.19
7.05
7.03
2.10
2.09
2.08
2.06
2.06
1.80
1.78
1.77
1.74
1.98
1.01
2.00
9.04
6.00
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
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)

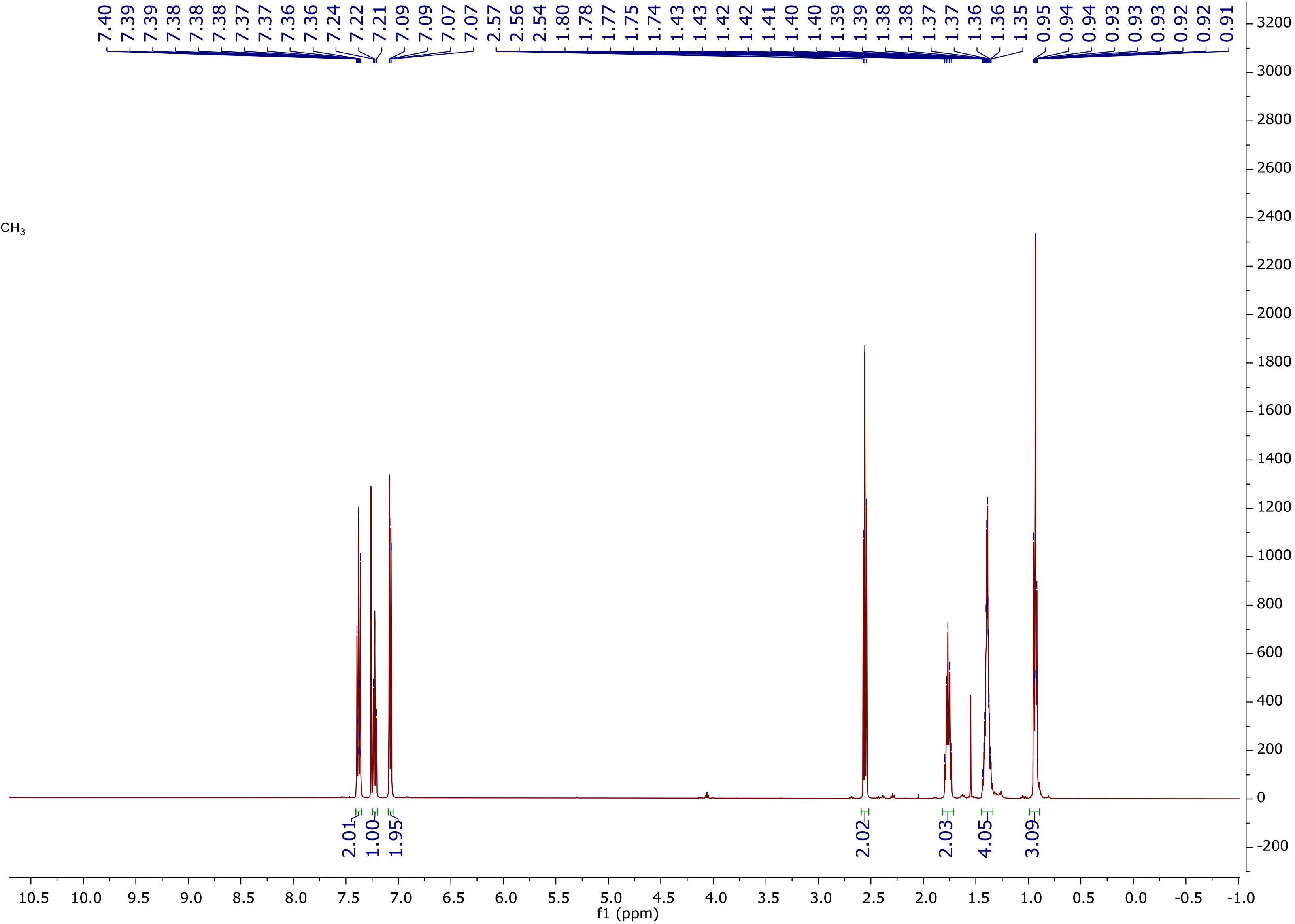

O
OPh

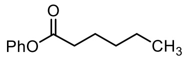
23-β


176.23
151.11
129.34
125.53
121.59
41.01
38.77
36.48
27.93
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
230
220
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)

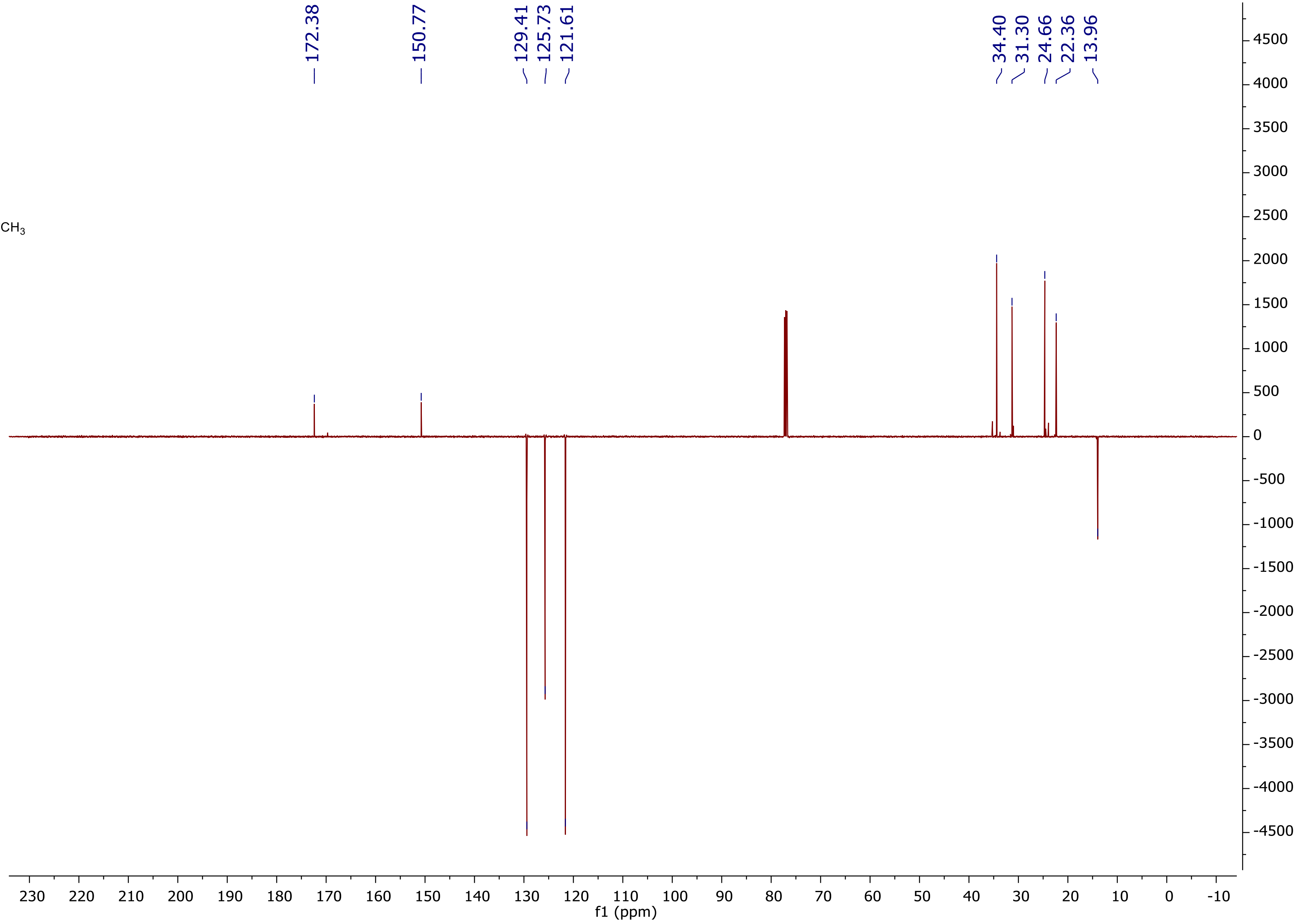

O
PhO
CH3

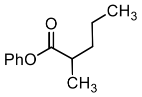
25-α


7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.24
7.22
7.21
7.09
7.09
7.07
7.07
2.57
2.56
2.54
1.80
1.78
1.77
1.75
1.74
1.43
1.43
1.42
1.42
1.41
1.40
1.40
1.39
1.39
1.38
1.38
1.37
1.37
1.36
1.36
1.35
0.95
0.94
0.94
0.93
0.93
0.93
0.92
0.92
0.91
2.01
1.00
1.95
2.02
2.03
4.05
3.09
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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
-1.0
f1 (ppm)

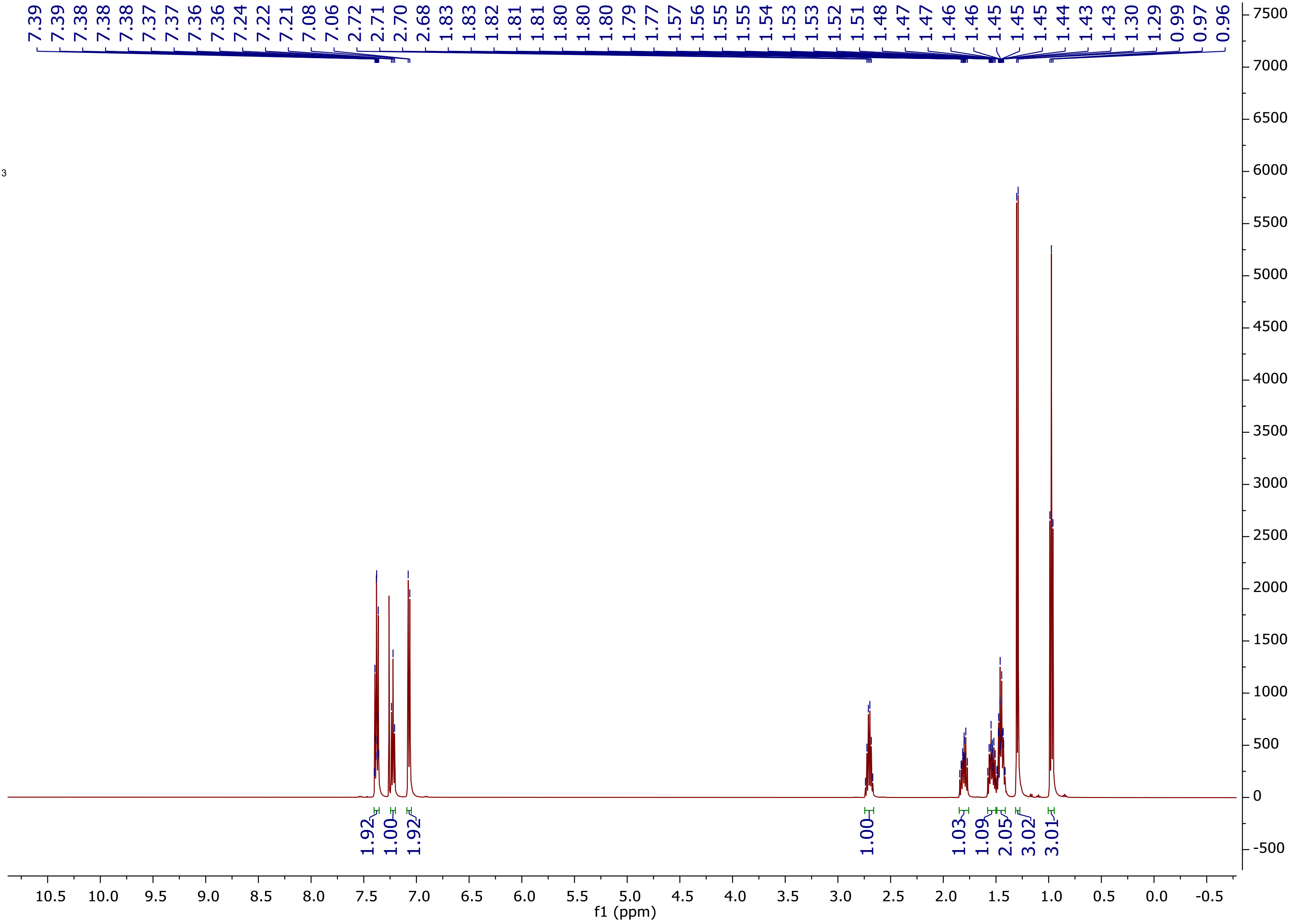

O
PhO
CH3

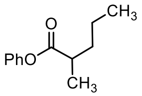
25-α


172.38
150.77
129.41
125.73
121.61
34.40
31.30
24.66
22.36
13.96
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000
-3500
-4000
-4500
230
220
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)

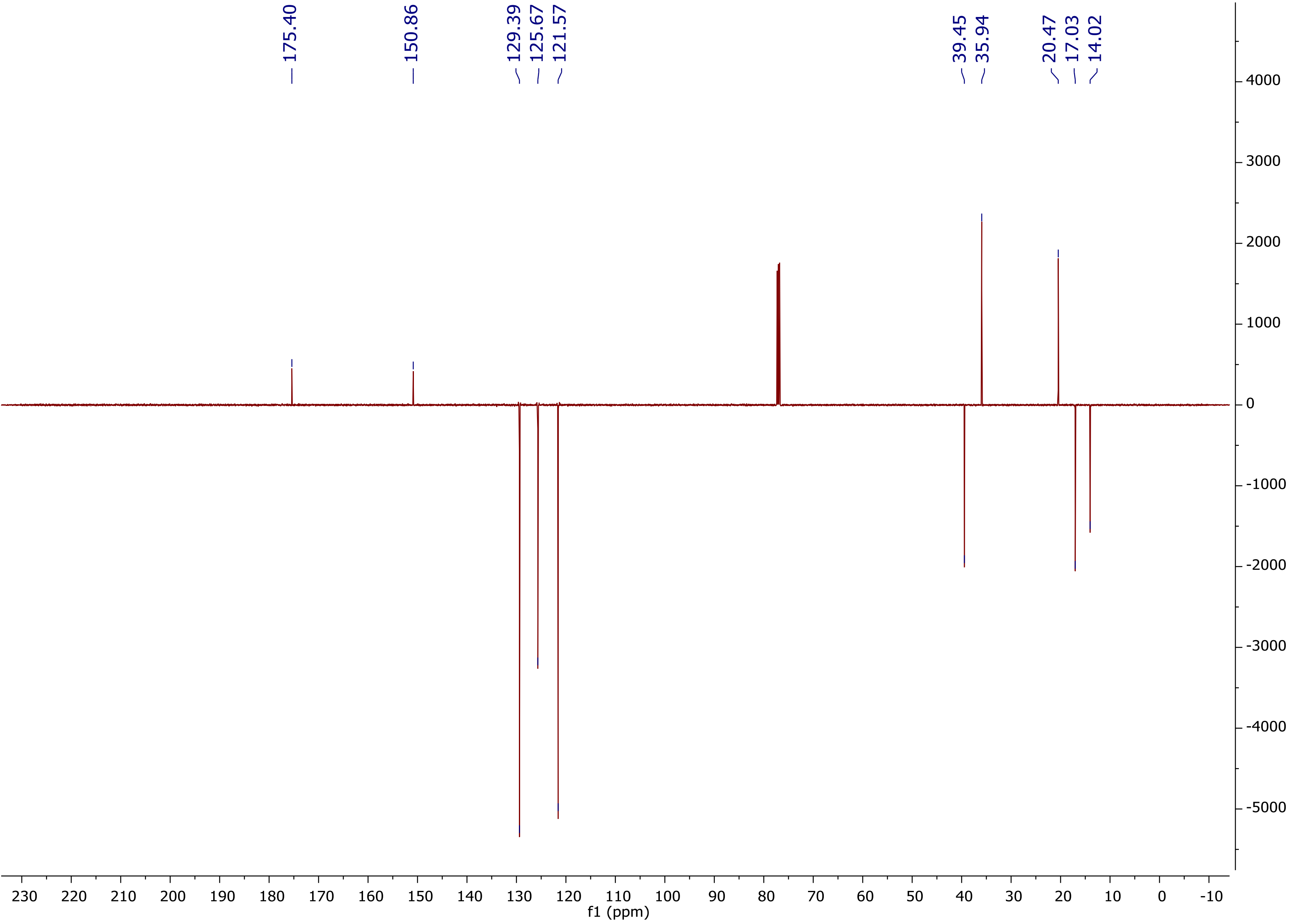

CH3
O
PhO
CH3

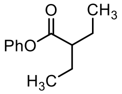
25-β


7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.24
7.22
7.21
7.08
7.06
2.72
2.71
2.70
2.68
1.83
1.83
1.82
1.81
1.81
1.80
1.80
1.80
1.79
1.77
1.57
1.56
1.55
1.55
1.54
1.53
1.53
1.52
1.51
1.48
1.47
1.47
1.46
1.46
1.45
1.45
1.45
1.44
1.43
1.43
1.30
1.29
0.99
0.97
0.96
1.92
1.00
1.92
1.00
1.03
1.09
2.05
3.02
3.01
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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)

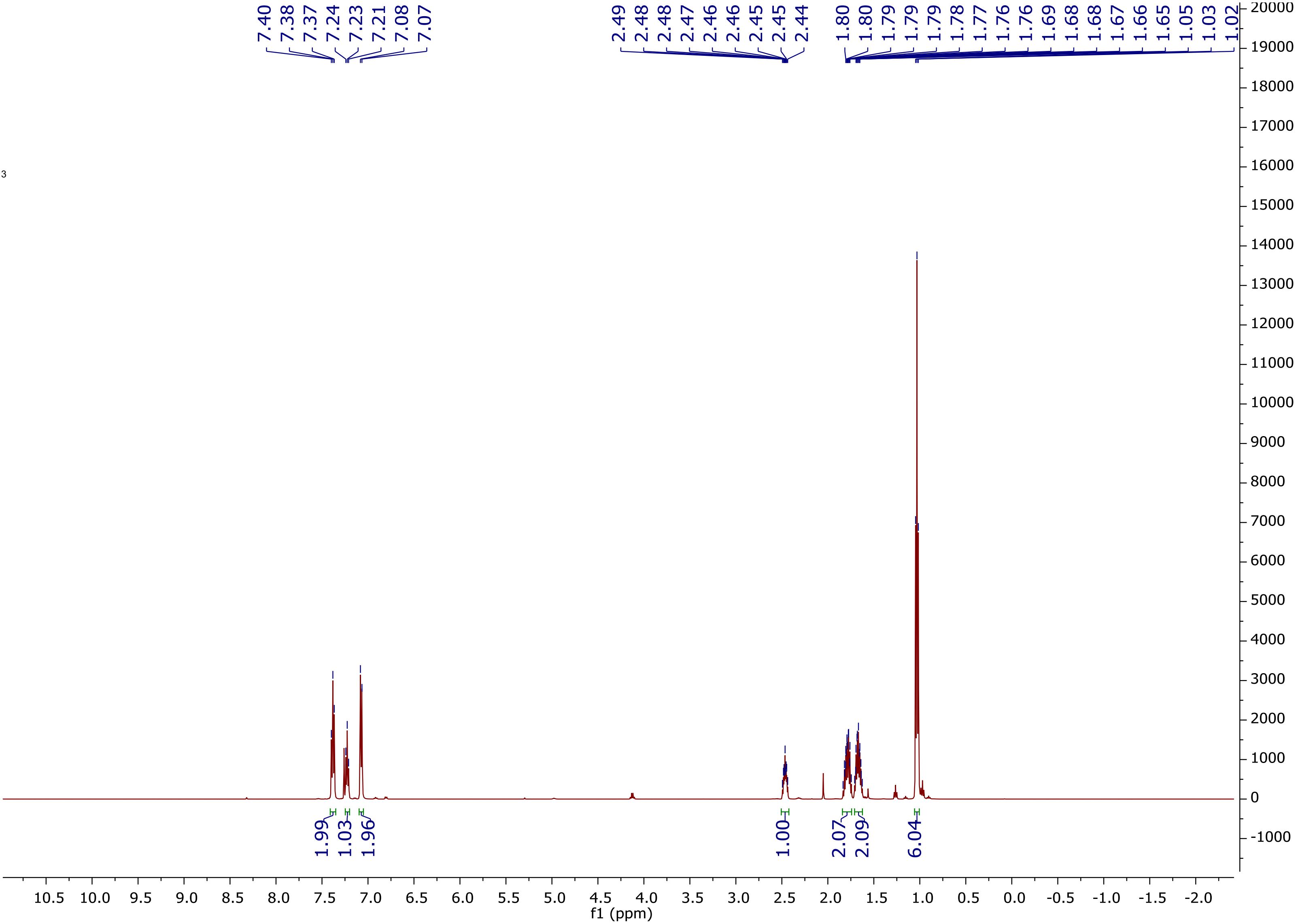

CH3
O
PhO
CH3

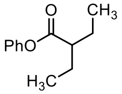
25-β


175.40
150.86
129.39
125.67
121.57
39.45
35.94
20.47
17.03
14.02
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
230
220
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)

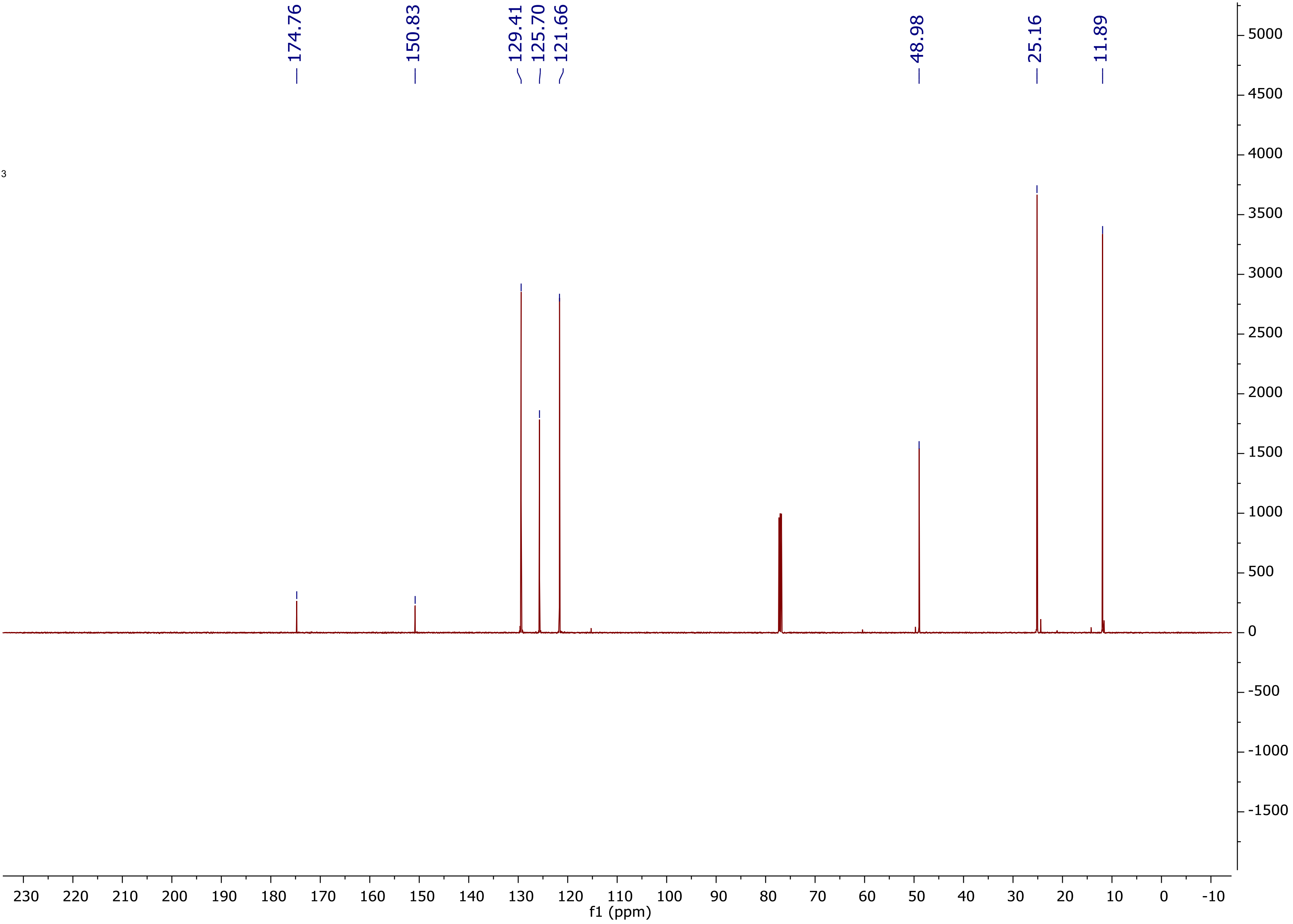

O
CH3
PhO
H3C

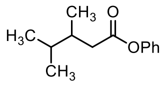
25-γ


7.40
7.38
7.37
7.24
7.23
7.21
7.08
7.07
2.49
2.48
2.48
2.47
2.46
2.46
2.45
2.45
2.44
1.80
1.80
1.79
1.79
1.79
1.78
1.77
1.76
1.76
1.69
1.68
1.68
1.67
1.66
1.65
1.05
1.03
1.02
1.99
1.03
1.96
1.00
2.07
2.09
6.04
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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
-1.0
-1.5
-2.0
f1 (ppm)

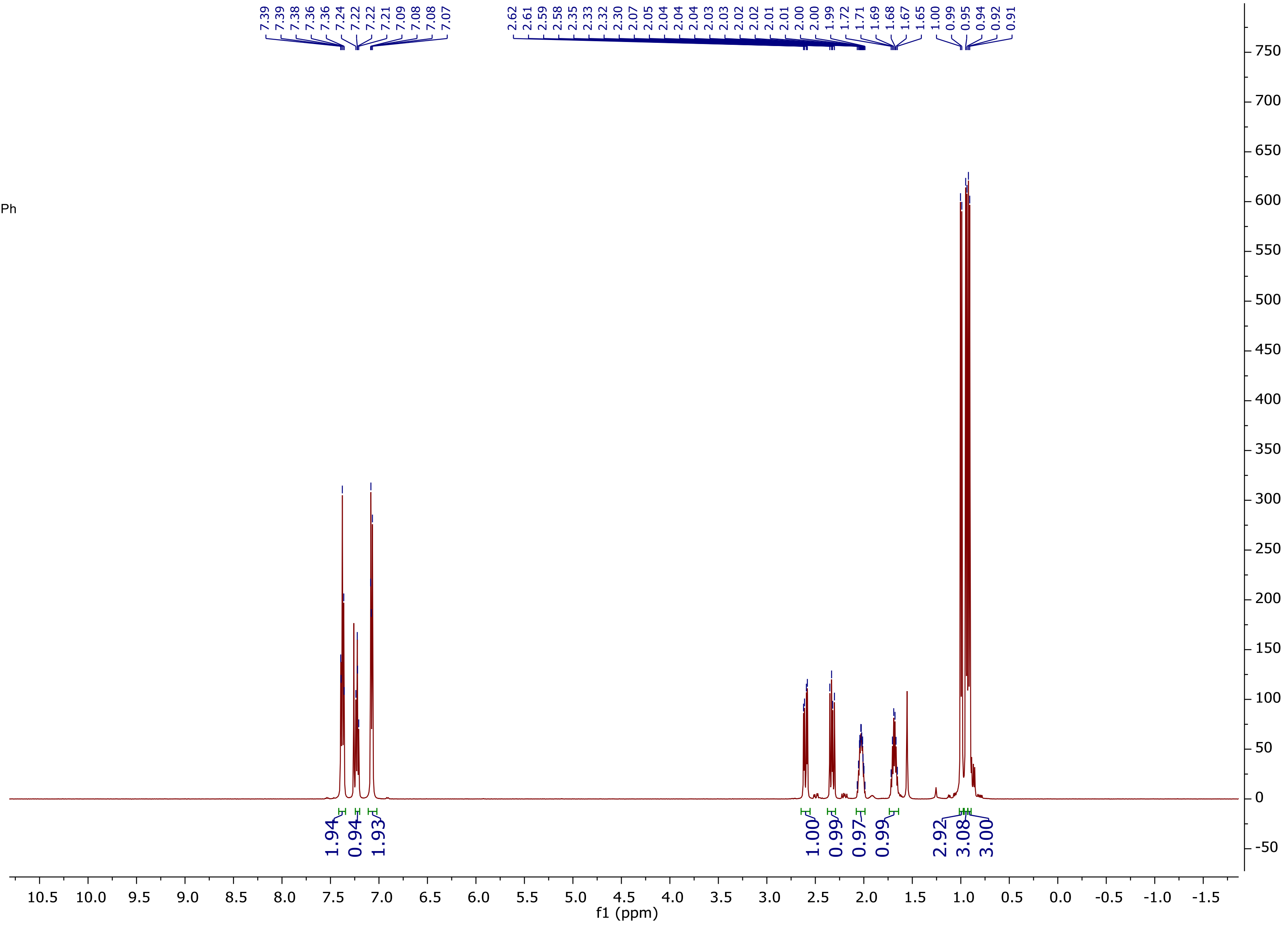

O
CH$_3$
PhO
H$_3$C

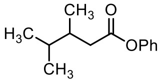
25-γ


174.76
150.83
129.41
125.70
121.66
48.98
25.16
11.89
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
230
220
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)

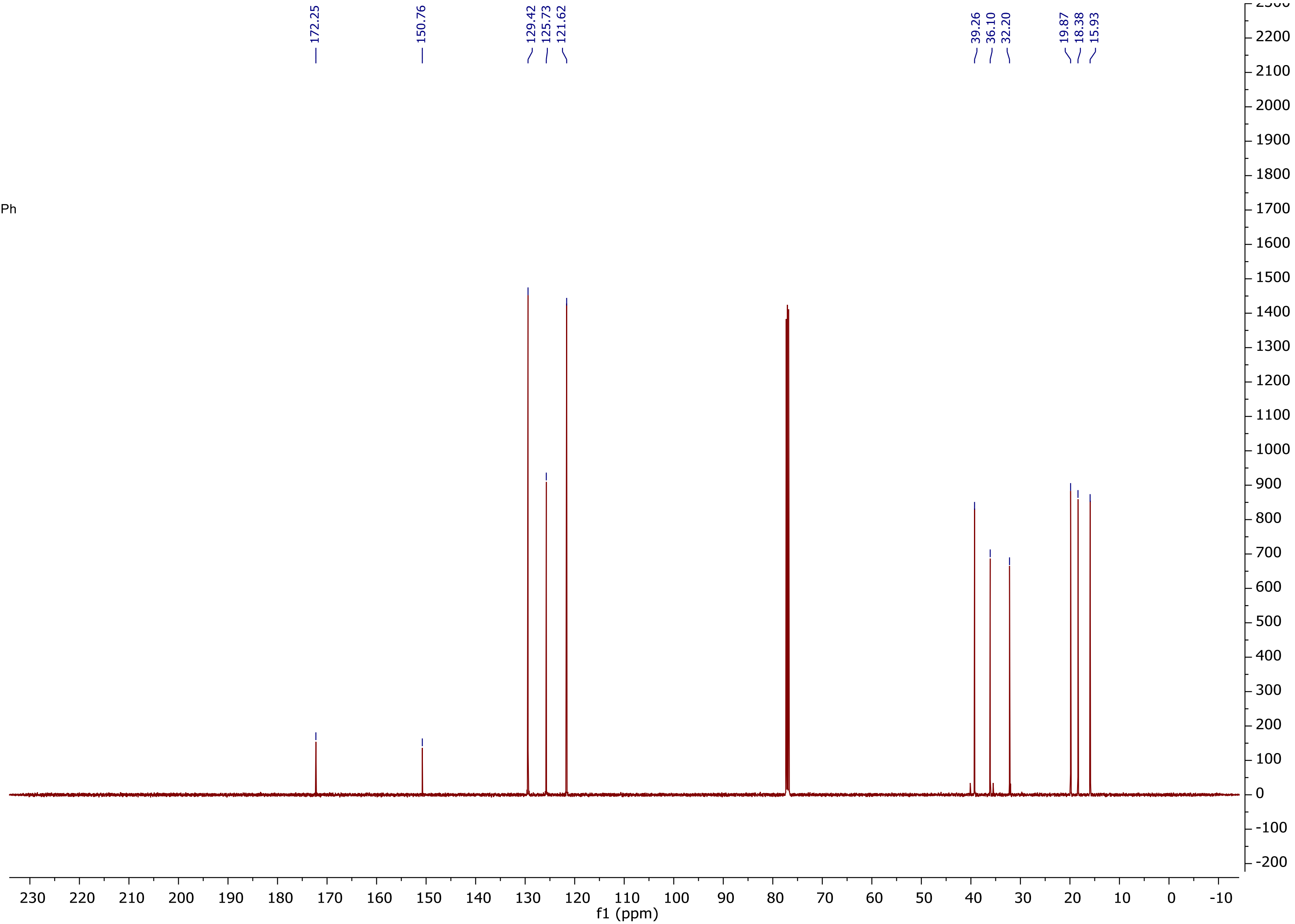

CH3
O
H3C
OPh
CH3

26-α

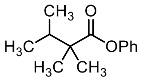

7.39
7.39
7.38
7.36
7.36
7.24
7.22
7.22
7.21
7.09
7.08
7.08
7.07
2.62
2.61
2.59
2.58
2.35
2.33
2.32
2.30
2.07
2.05
2.04
2.04
2.04
2.03
2.03
2.02
2.02
2.01
2.01
2.00
2.00
1.99
1.72
1.71
1.69
1.68
1.67
1.65
1.00
0.99
0.95
0.94
0.92
0.91
1.94
0.94
1.93
1.00
0.99
0.97
0.99
2.92
3.08
3.00
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
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
-1.0
-1.5
f1 (ppm)



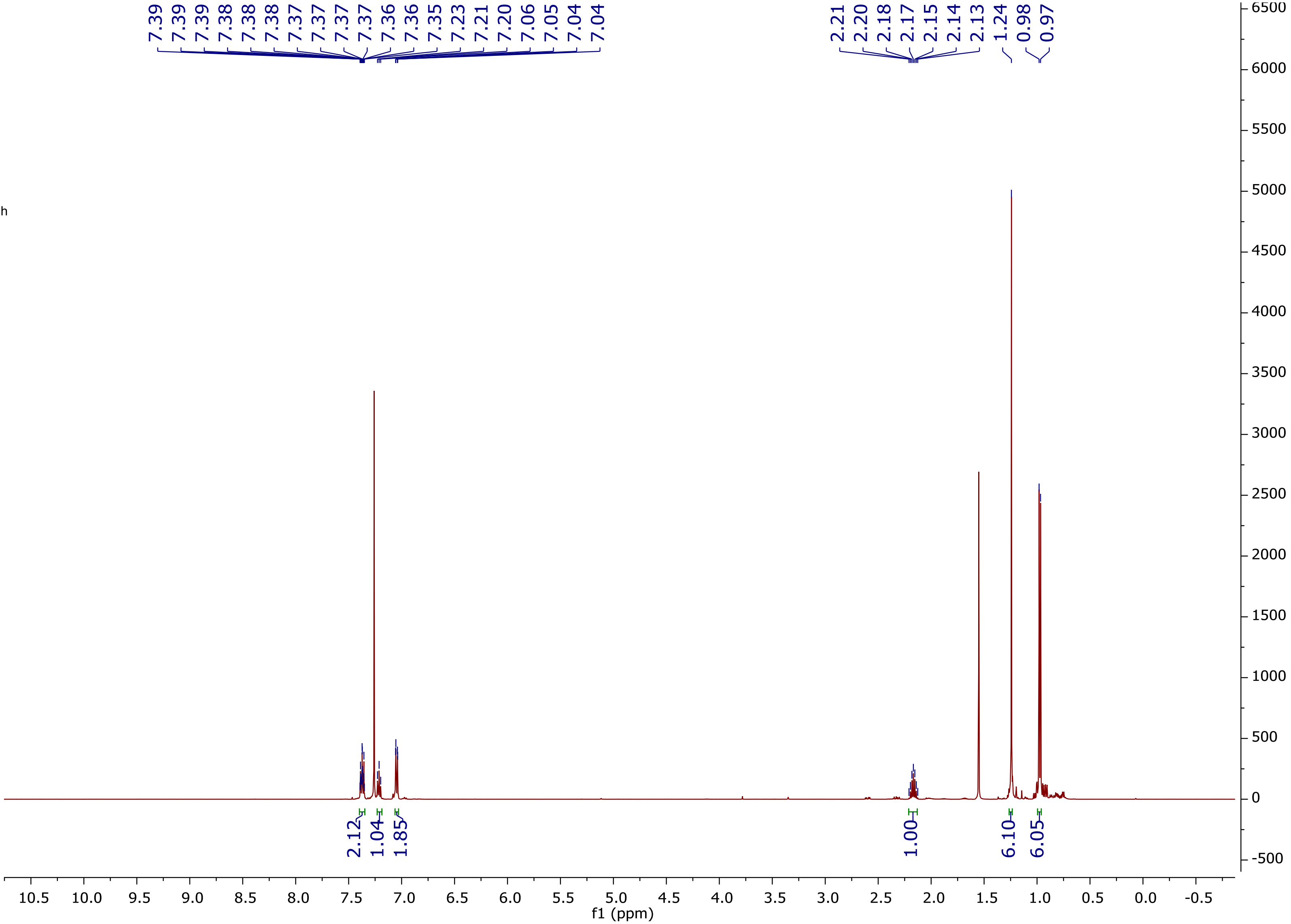
26-α

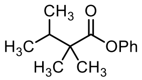


172.25
150.76
129.42
125.73
121.62
39.26
36.10
32.20
19.87
18.38
15.93
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

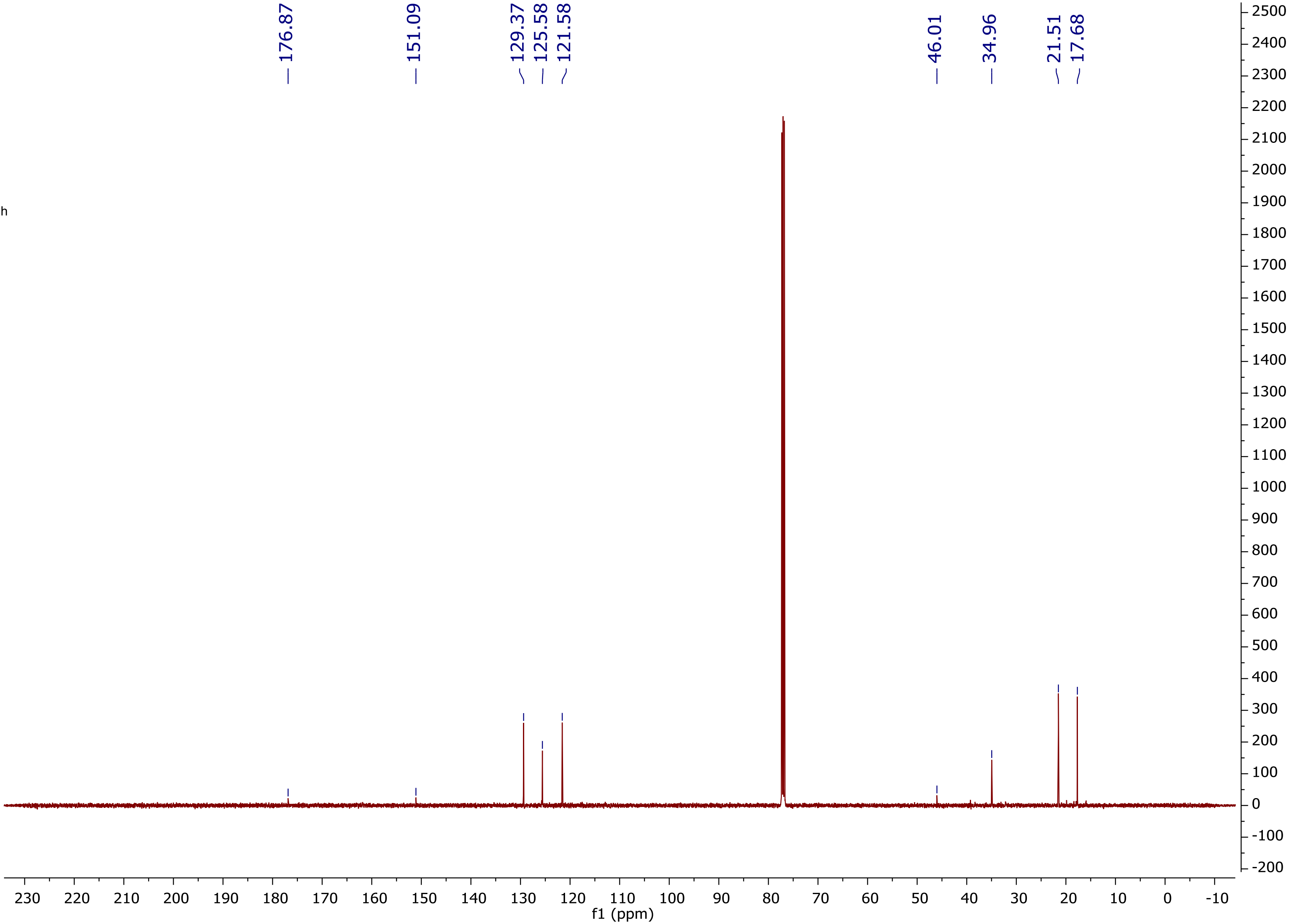

CH3
O
H3C
OPh
H3C
CH3

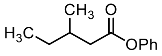
26-β


7.39
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.37
7.36
7.36
7.35
7.23
7.21
7.20
7.06
7.05
7.04
7.04
2.21
2.20
2.18
2.17
2.15
2.14
2.13
1.24
0.98
0.97
2.12
1.04
1.85
1.00
6.10
6.05
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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)

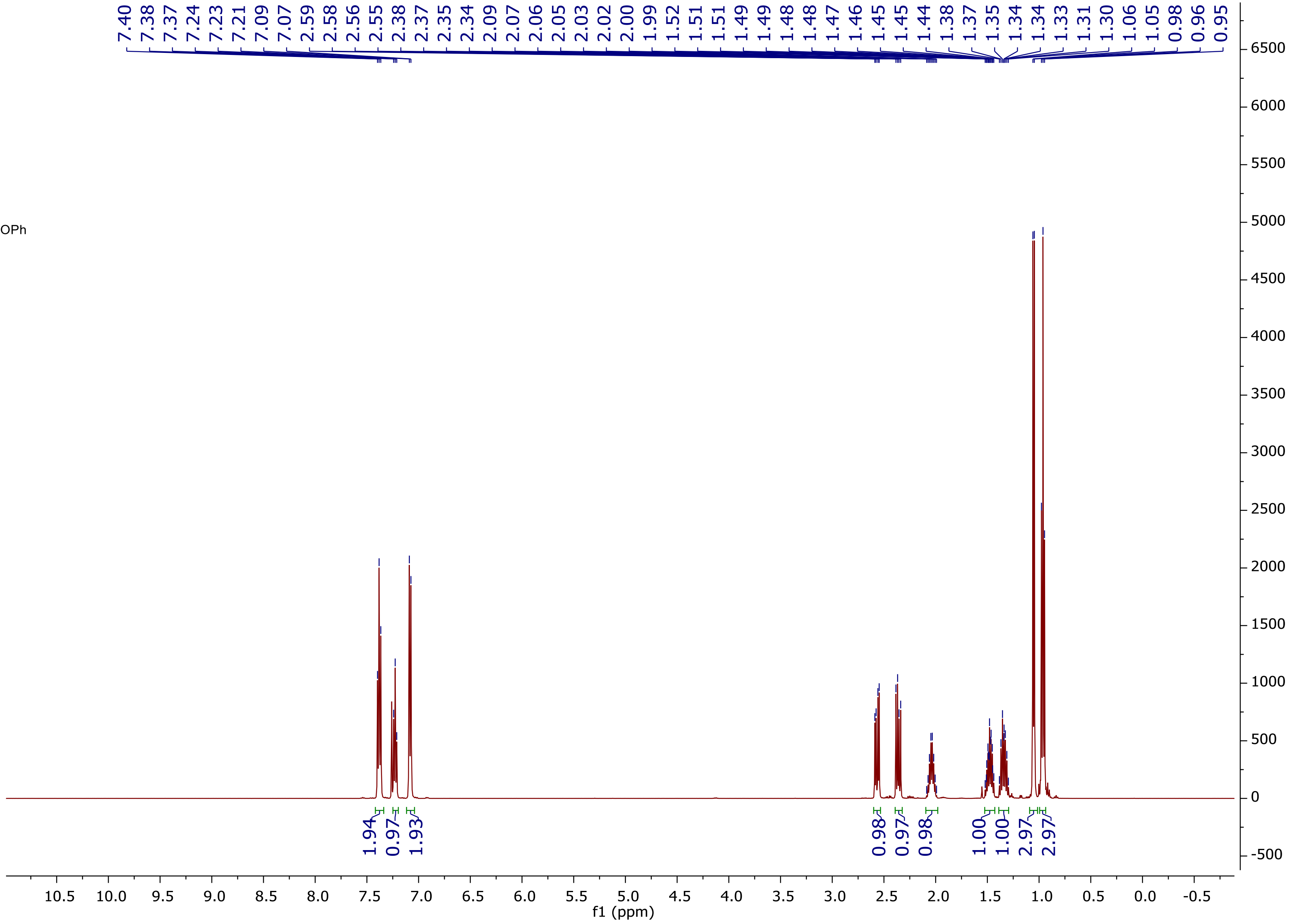

CH3
O
H3C
OPh
H3C
CH3

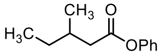
26-β


176.87
151.09
129.37
125.58
121.58
46.01
34.96
21.51
17.68
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
230
220
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)


CH3
O
H3C
OPh

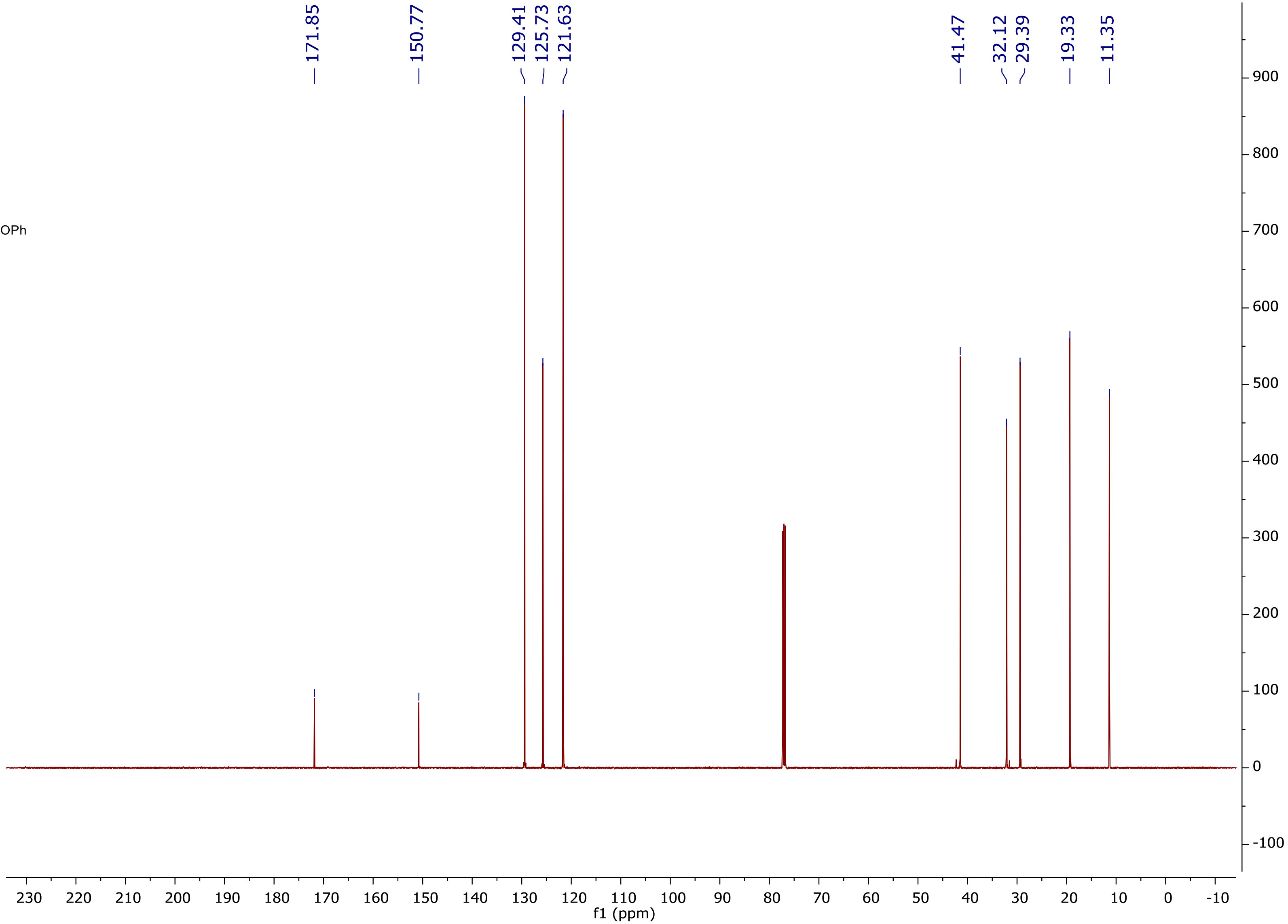
27-α


7.40
7.38
7.37
7.24
7.23
7.21
7.09
7.07
2.59
2.58
2.56
2.55
2.38
2.37
2.35
2.34
2.09
2.07
2.06
2.05
2.03
2.02
2.00
1.99
1.52
1.51
1.51
1.49
1.49
1.48
1.48
1.47
1.46
1.45
1.45
1.44
1.38
1.37
1.35
1.34
1.34
1.33
1.31
1.30
1.06
1.05
0.98
0.96
0.95
1.94
0.97
1.93
0.98
0.97
0.98
1.00
1.00
2.97
2.97
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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)

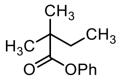


CH3
O
H3C
OPh

27-α

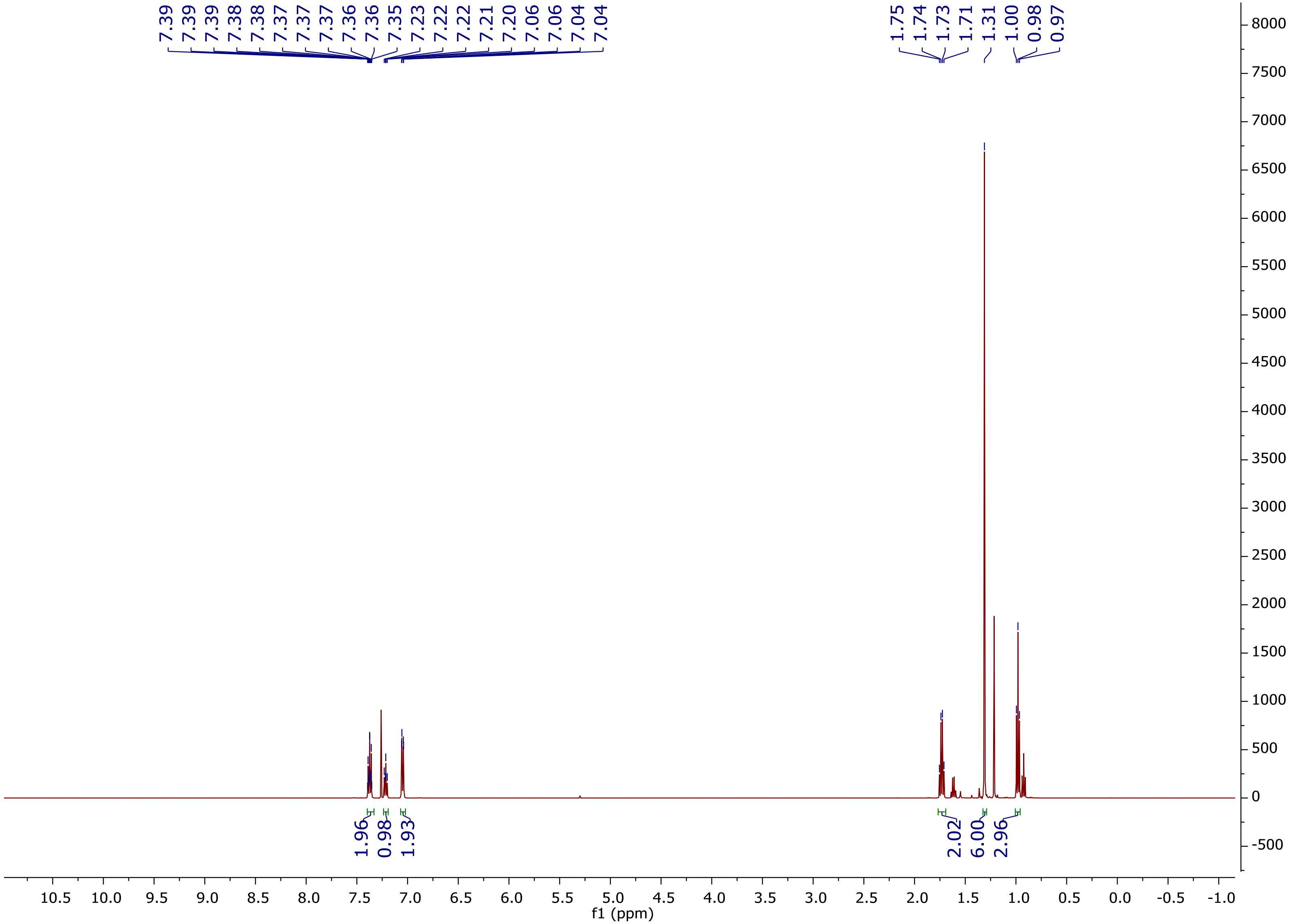


171.85
150.77
129.41
125.73
121.63
41.47
32.12
29.39
19.33
11.35
900
800
700
600
500
400
300
200
100
0
-100
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

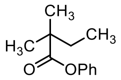


CH3
H3C
CH3
O
OPh

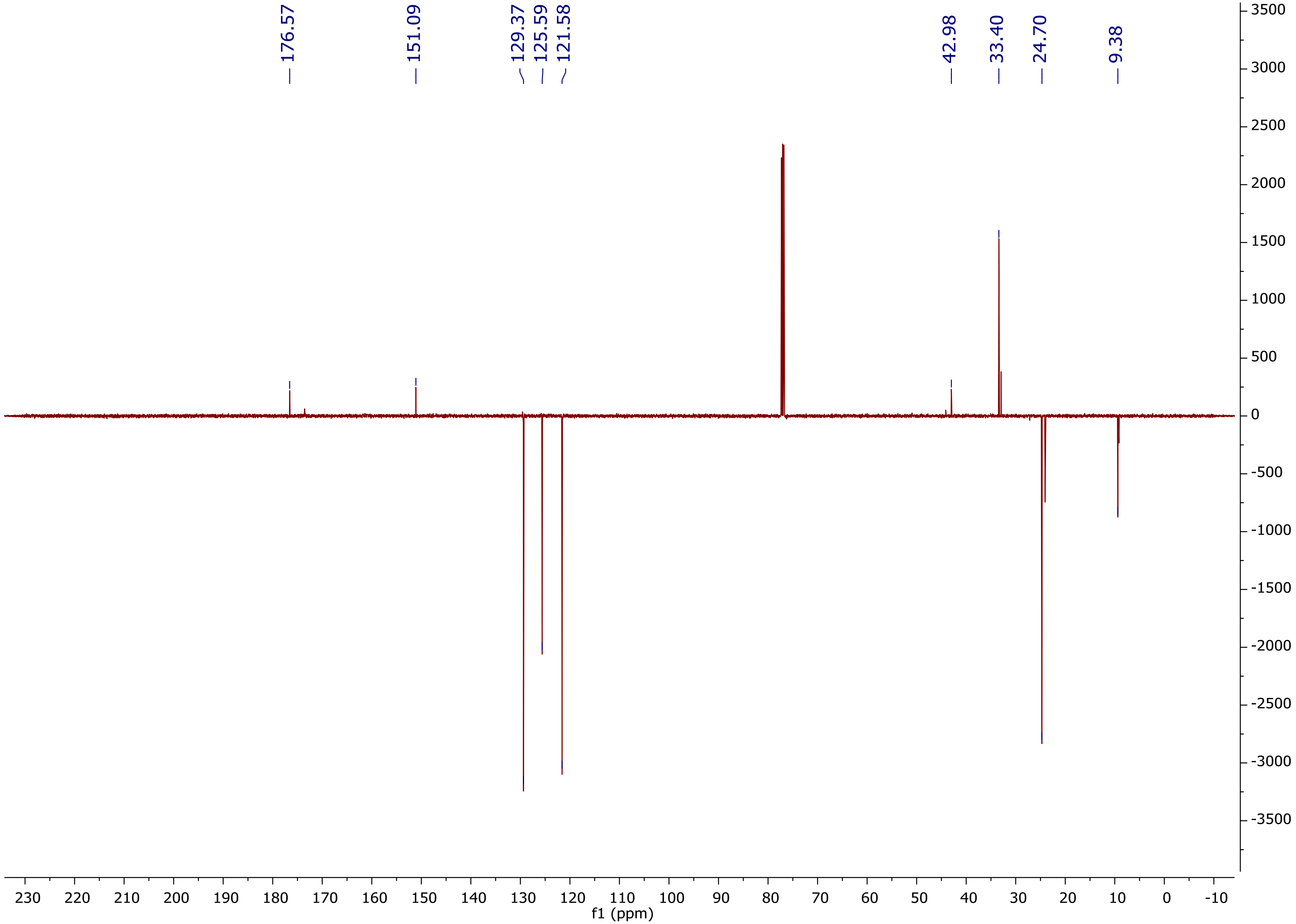
27-β

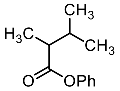


7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.23
7.22
7.22
7.21
7.20
7.06
7.06
7.04
7.04
1.75
1.74
1.73
1.71
1.31
1.00
0.98
0.97
1.96
0.98
1.93
2.02
6.00
2.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

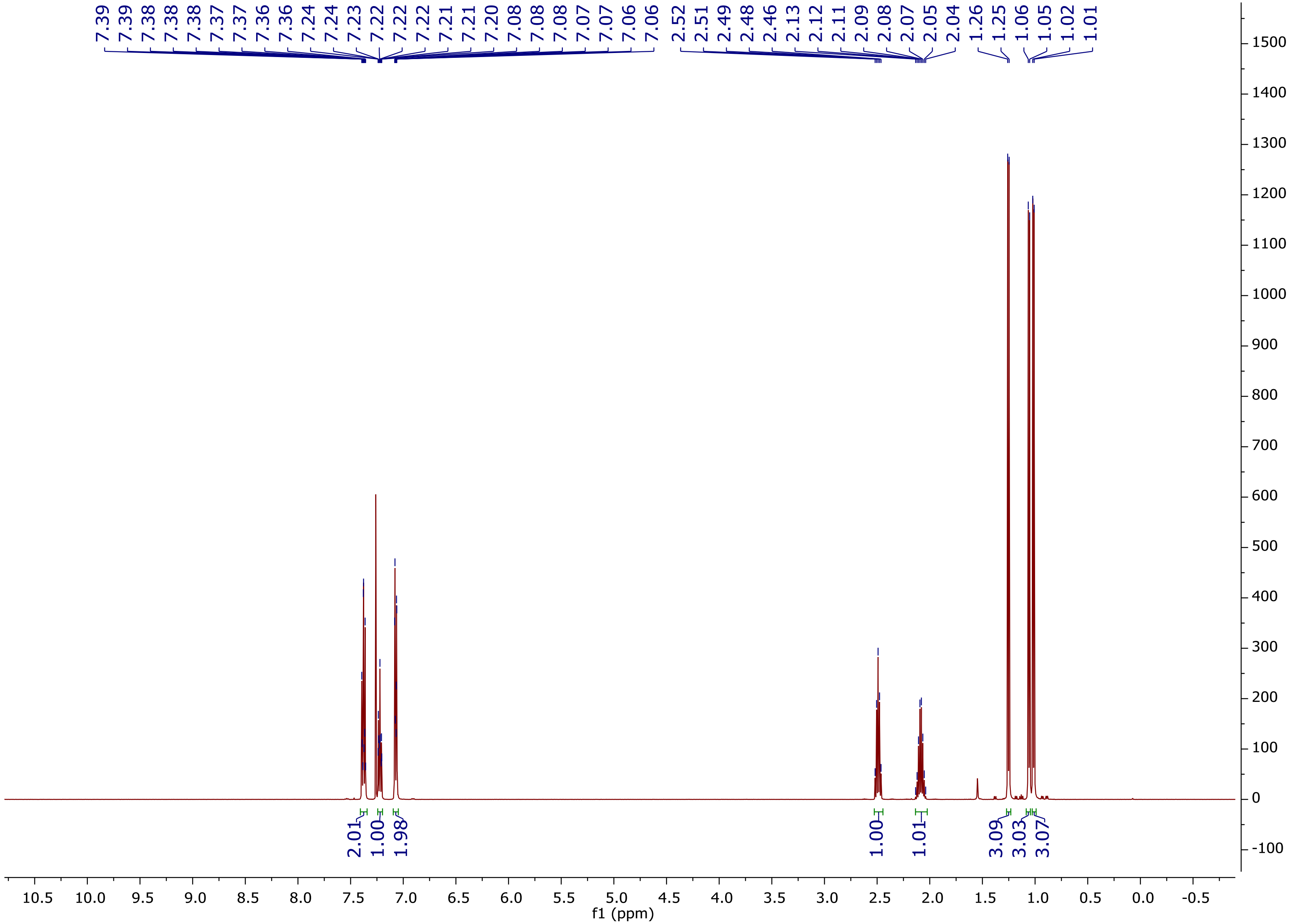

CH3
H3C
CH3
O
OPh

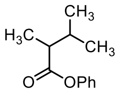
27-β


176.57
151.09
129.37
125.59
121.58
42.98
33.40
24.70
9.38
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000
-3500
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

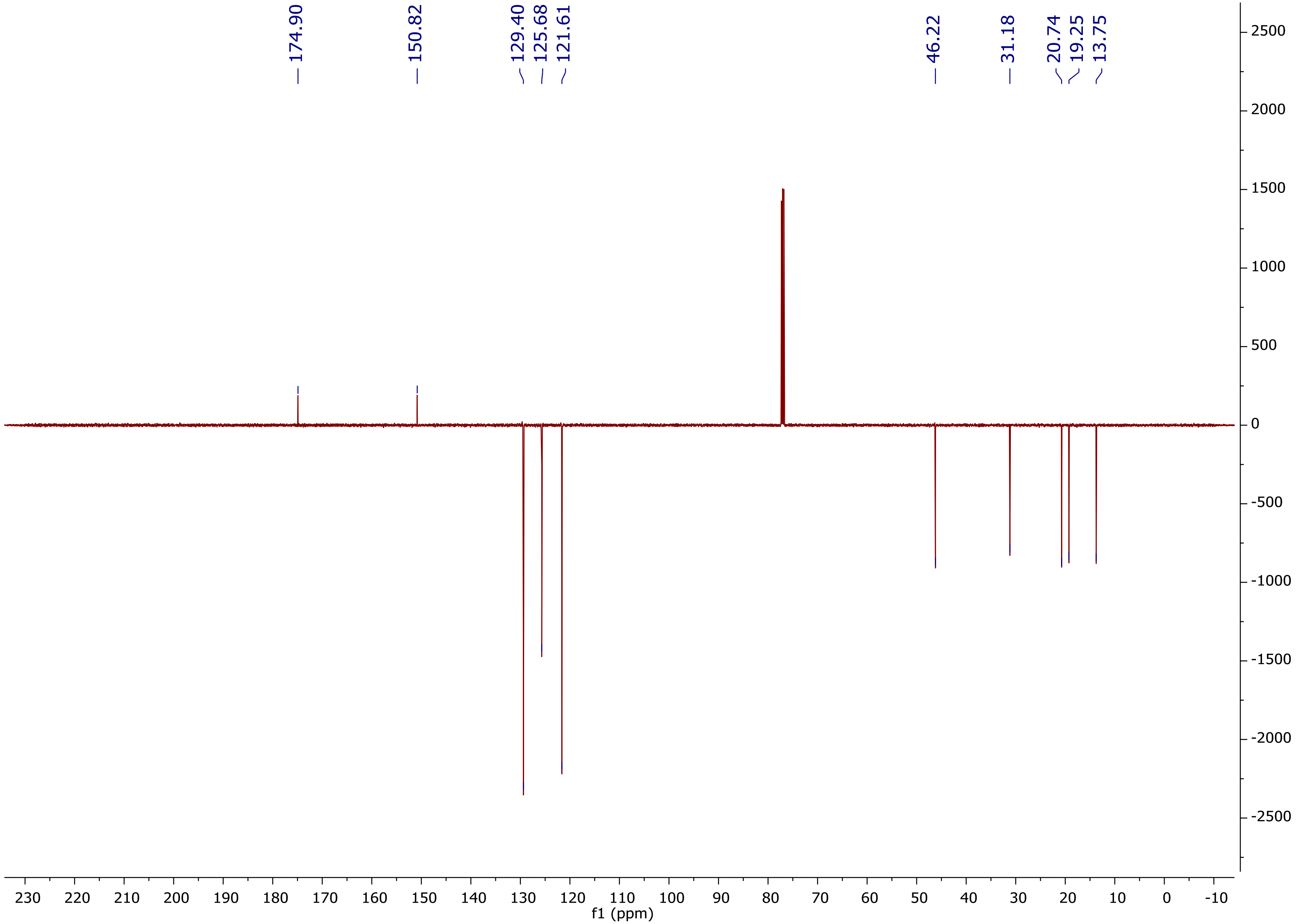

CH3
H3C
CH3
O
OPh

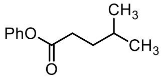
27-γ


7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.24
7.24
7.23
7.22
7.22
7.22
7.21
7.21
7.20
7.08
7.08
7.08
7.07
7.07
7.06
7.06
2.52
2.51
2.49
2.48
2.46
2.13
2.12
2.11
2.09
2.08
2.07
2.05
2.04
1.26
1.25
1.06
1.05
1.02
1.01
2.01
1.00
1.98
1.00
1.01
3.09
3.03
3.07
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)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

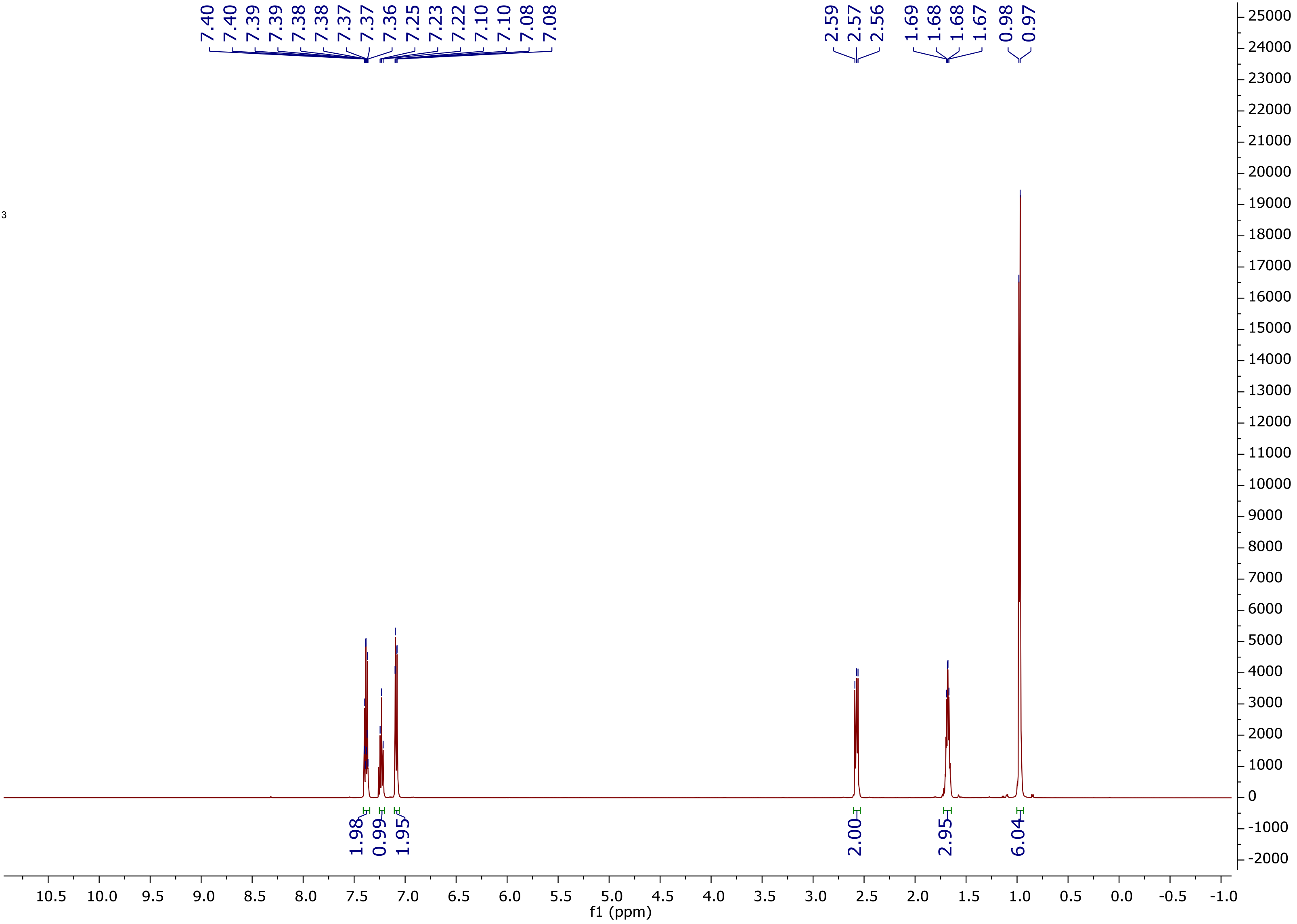

CH3
H3C
CH3
O
OPh

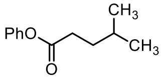
27-γ


174.90
150.82
129.40
125.68
121.61
46.22
31.18
20.74
19.25
13.75
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
230
220
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)

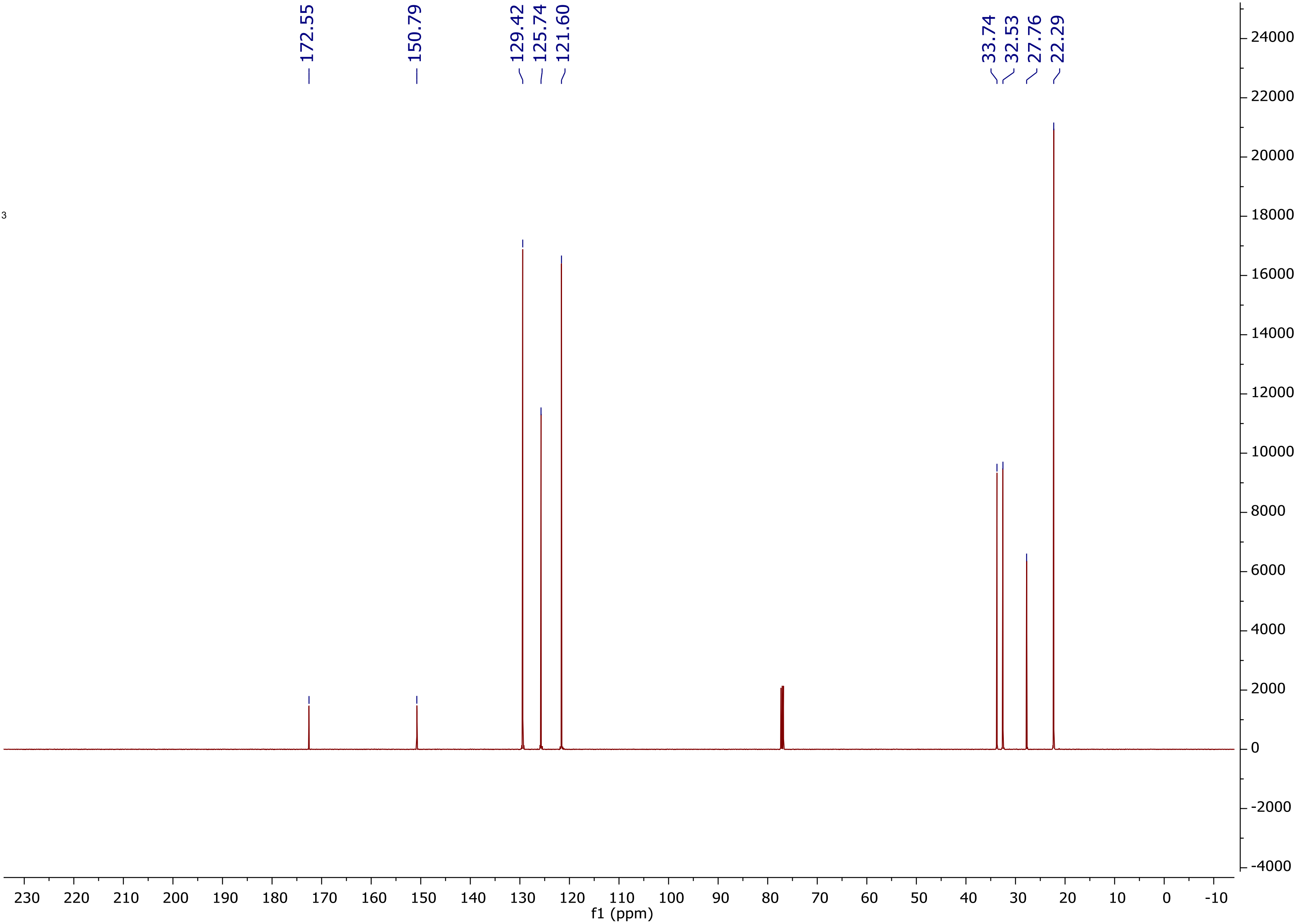

PhO
O
CH3
CH3

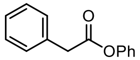
27-δ


7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.25
7.23
7.22
7.10
7.10
7.08
7.08
2.59
2.57
2.56
1.69
1.68
1.68
1.67
0.98
0.97
1.98
0.99
1.95
2.00
2.95
6.04
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
-1.0
f1 (ppm)
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

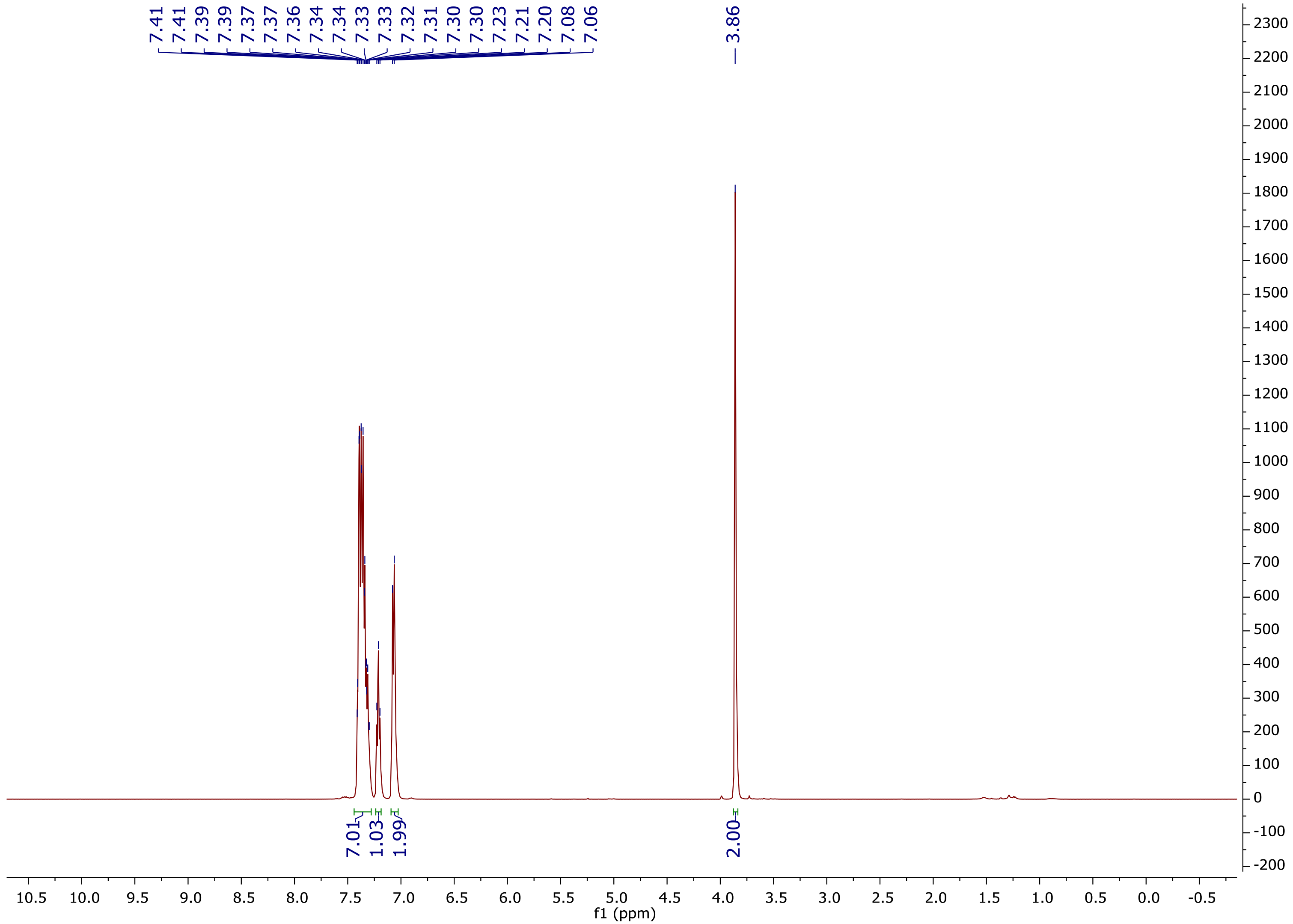

PhO
CH3
CH3
O

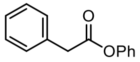
27-δ


172.55
150.79
129.42
125.74
121.60
33.74
32.53
27.76
22.29
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
230
220
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)

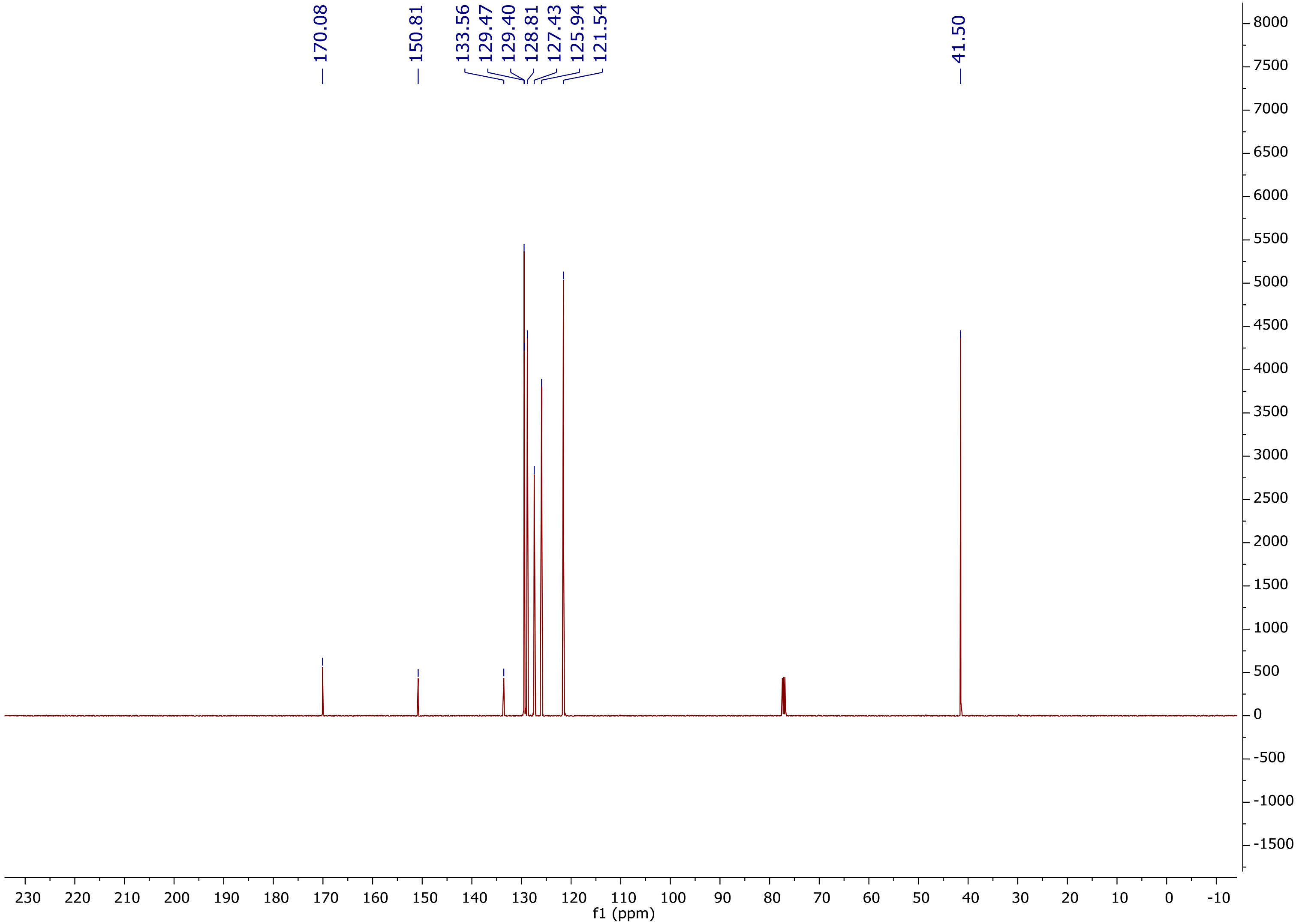

O
OPh

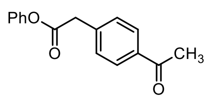
28


7.41
7.41
7.39
7.39
7.37
7.37
7.36
7.34
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.23
7.21
7.20
7.08
7.06
3.86
7.01
1.03
1.99
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)
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

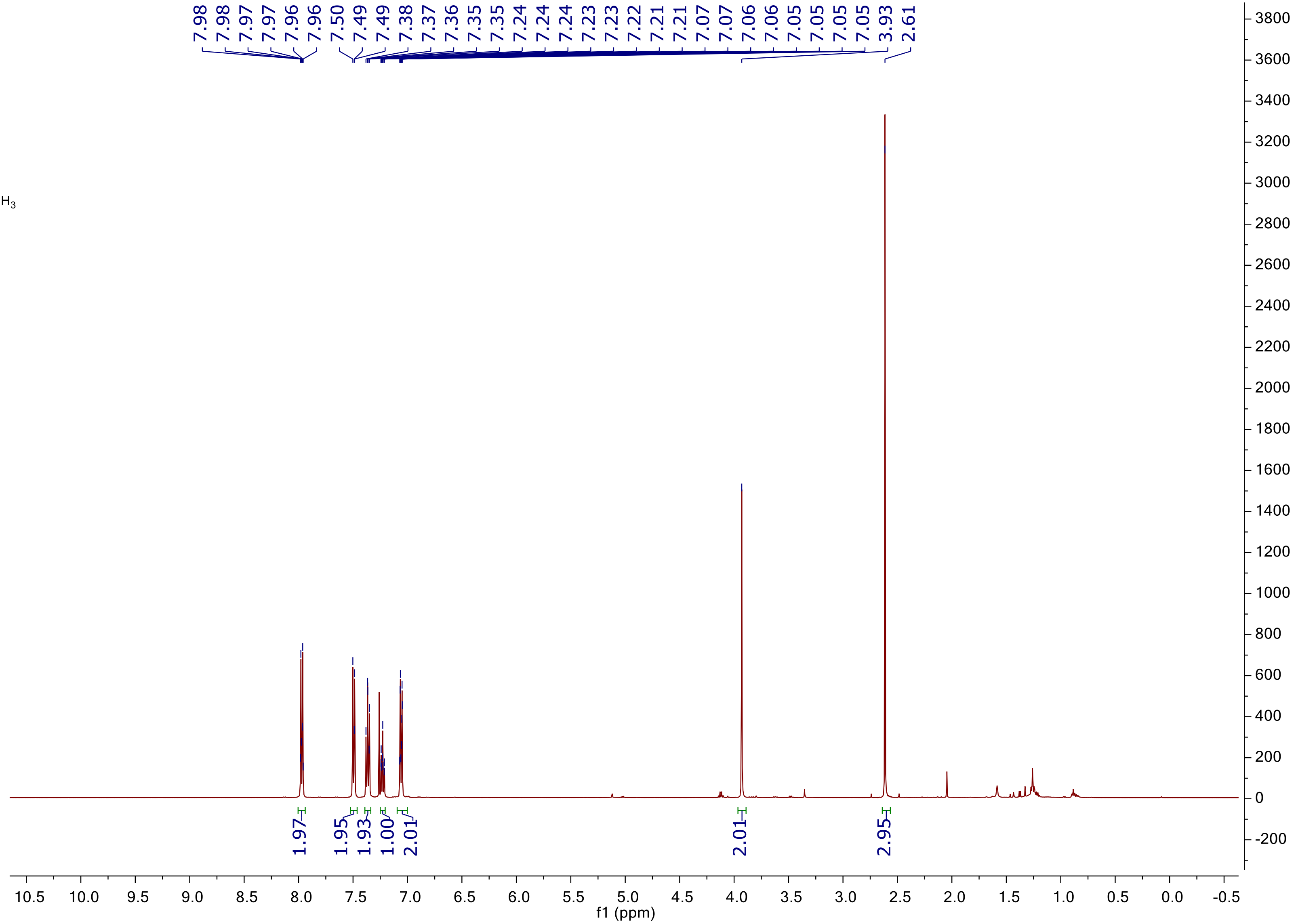

O
OPh

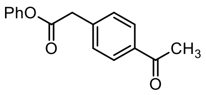
28


170.08
150.81
133.56
129.47
129.40
128.81
127.43
125.94
121.54
41.50
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
230
220
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)

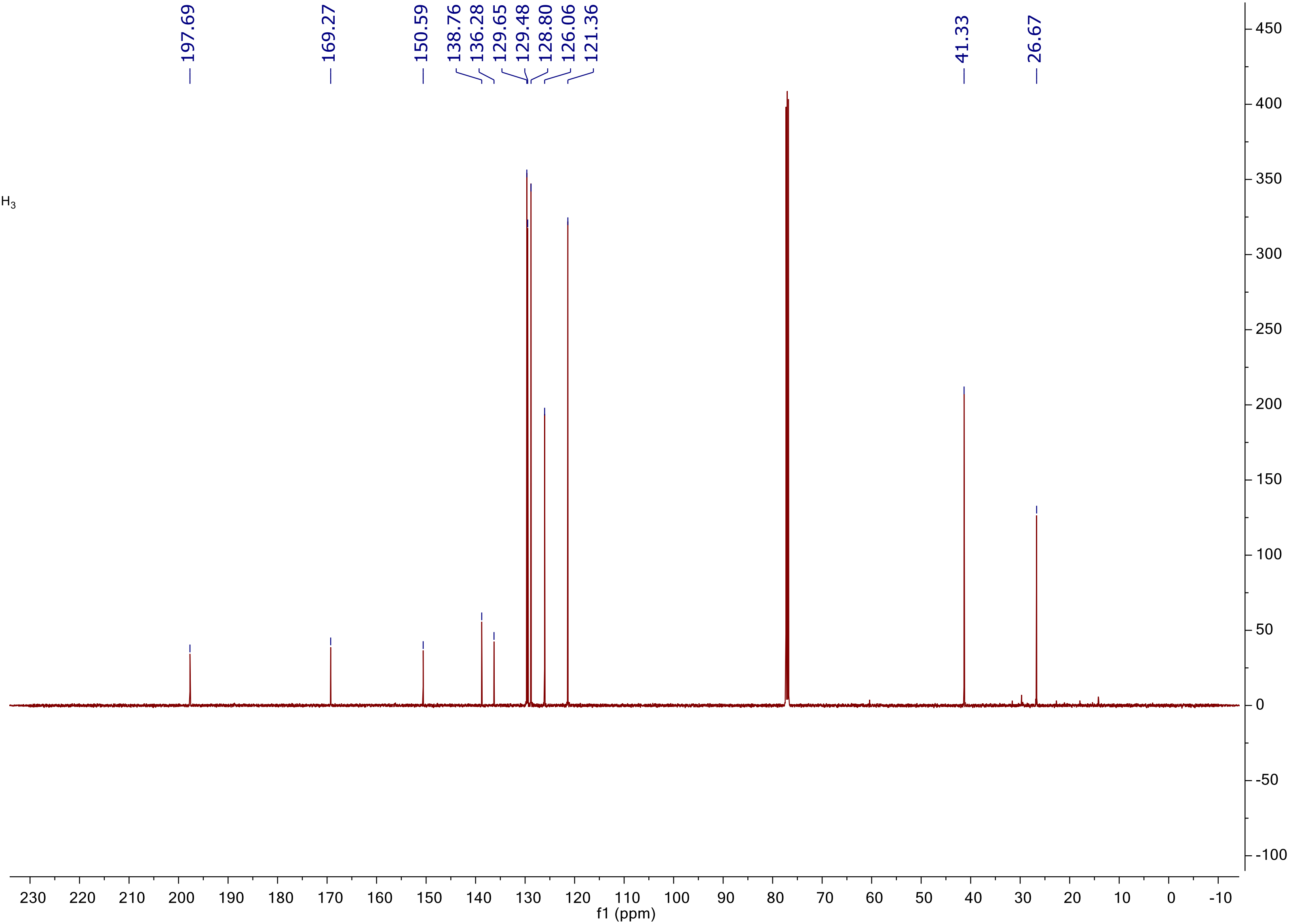

PhO
O
CH3
O

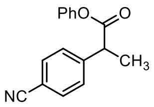
29


7.98
7.98
7.97
7.97
7.96
7.96
7.50
7.49
7.49
7.38
7.37
7.36
7.35
7.35
7.24
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.07
7.07
7.06
7.06
7.05
7.05
7.05
7.05
3.93
2.61
1.97
1.95
1.93
1.00
2.01
2.01
2.95
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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)

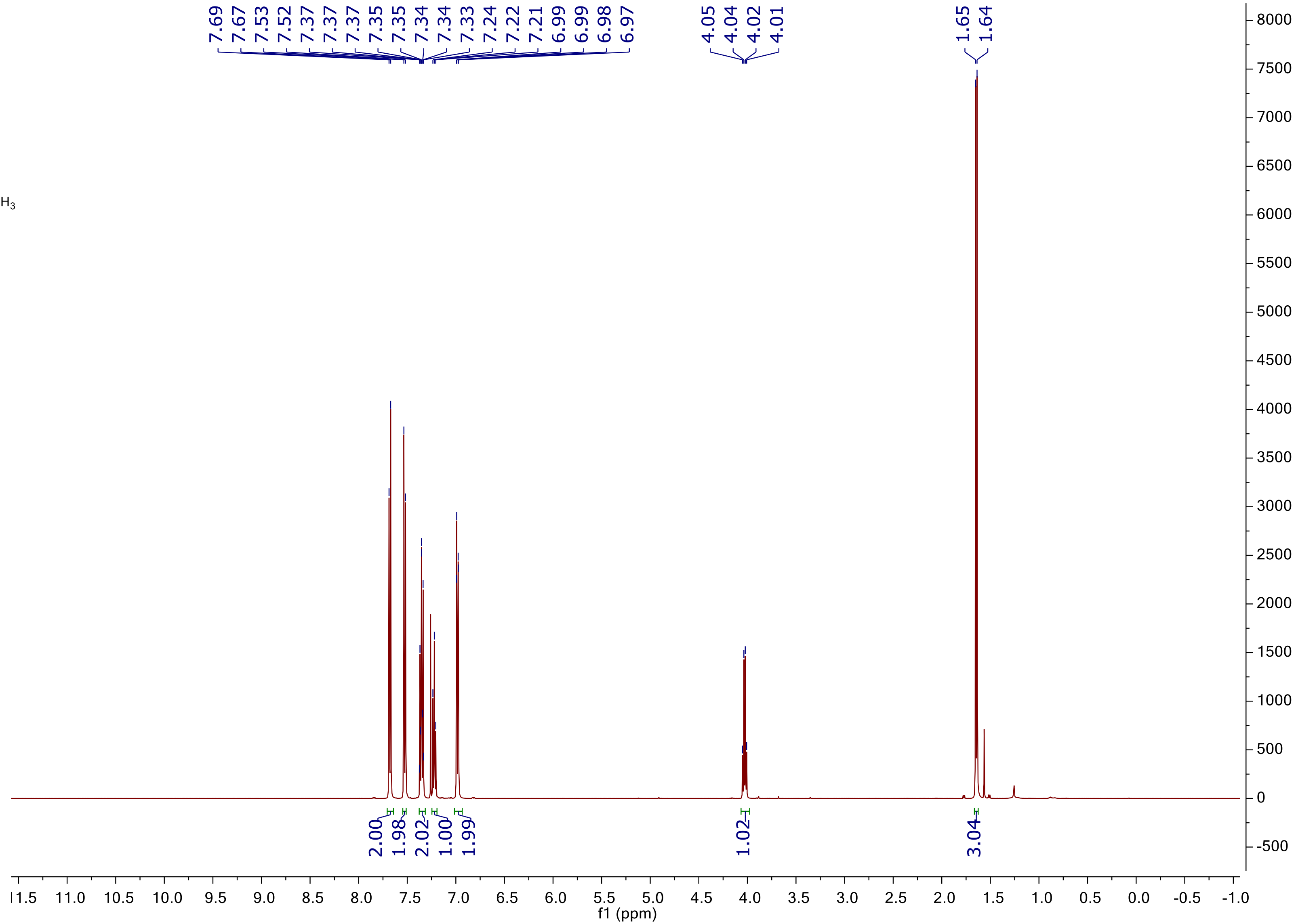

PhO
O
CH3
O

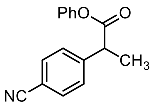
29


197.69
169.27
150.59
138.76
136.28
129.65
129.48
128.80
126.06
121.36
41.33
26.67
450
400
350
300
250
200
150
100
50
0
-50
-100
230
220
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)

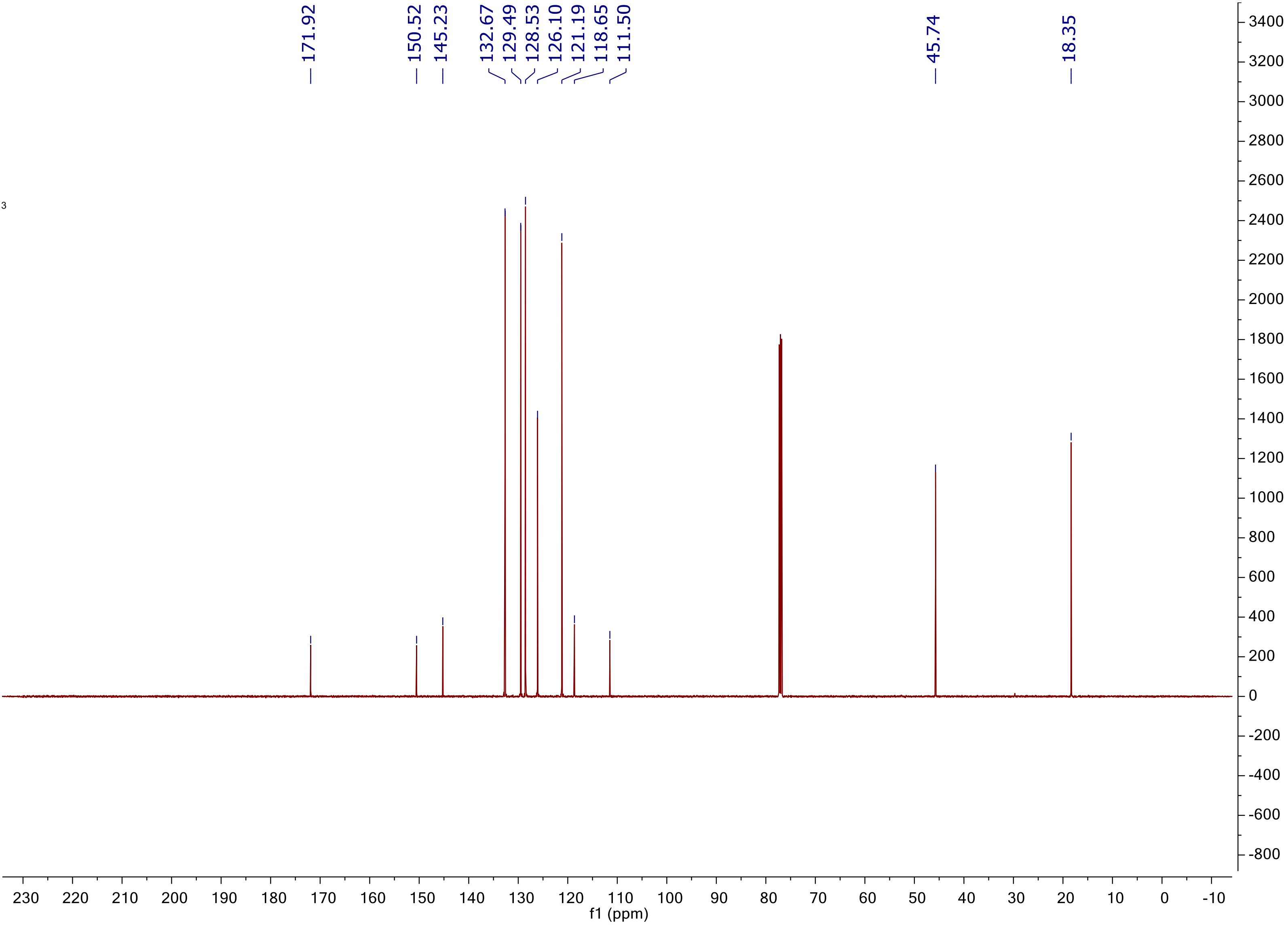

PhO
O
CH3
NC

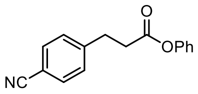
30-α


7.69
7.67
7.53
7.52
7.37
7.37
7.37
7.35
7.35
7.34
7.34
7.33
7.24
7.22
7.21
6.99
6.99
6.98
6.97
4.05
4.04
4.02
4.01
1.65
1.64
2.00
1.98
2.02
1.00
1.99
1.02
3.04
11.5
11.0
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
-1.0
f1 (ppm)
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

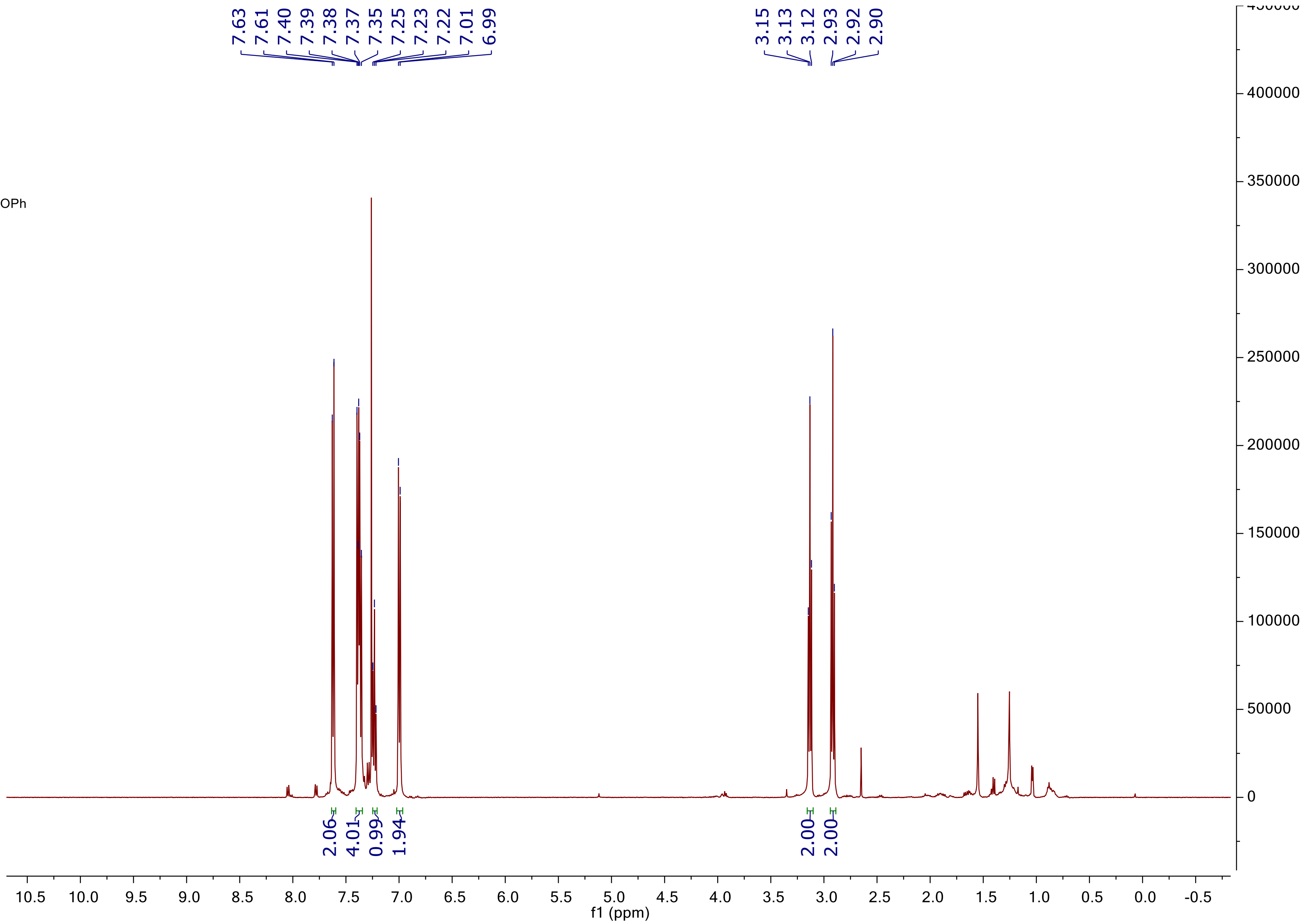

PhO
O
CH3
NC

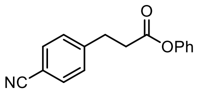
30-α


171.92
150.52
145.23
132.67
129.49
128.53
126.10
121.19
118.65
111.50
45.74
18.35
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
230
220
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)

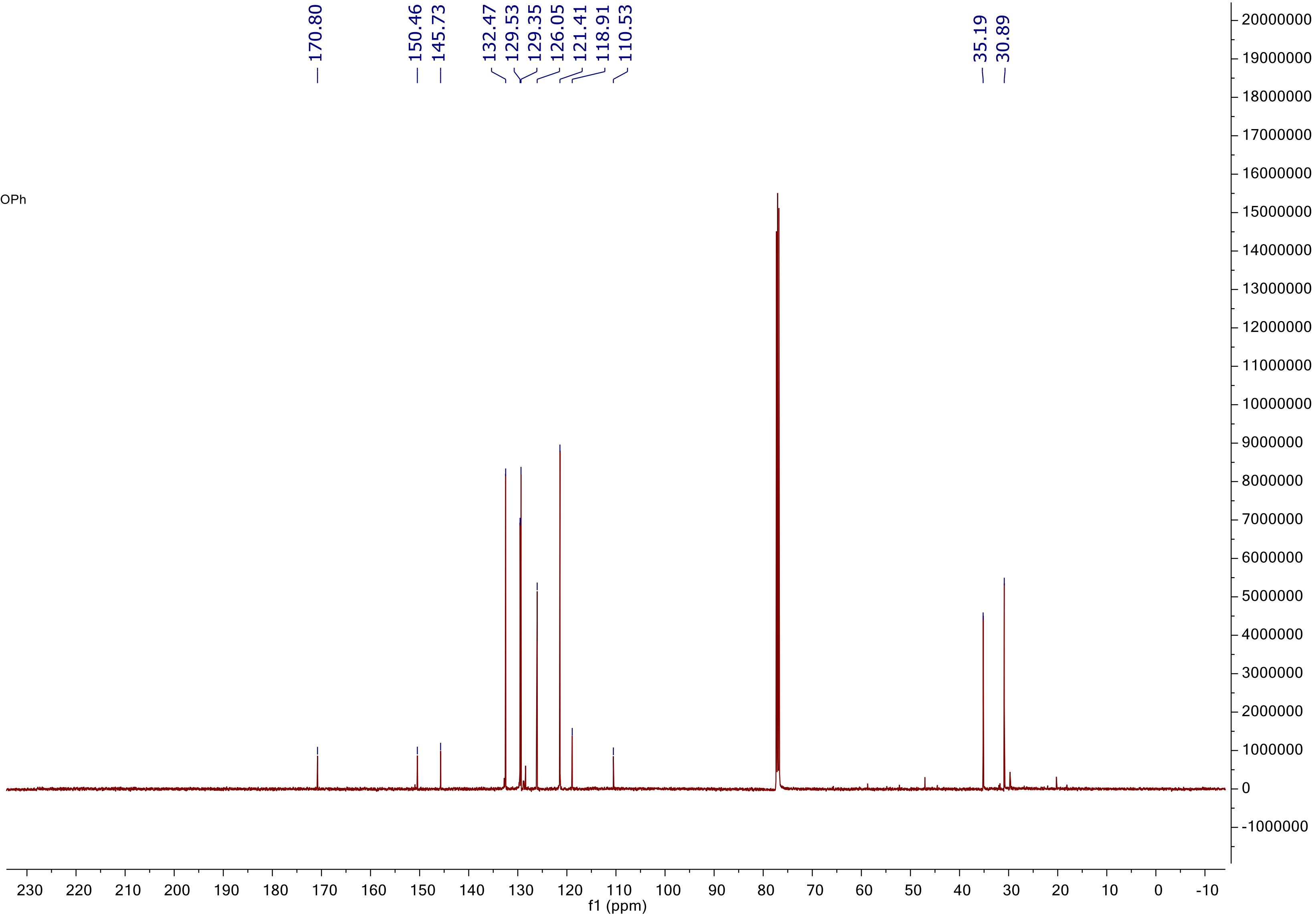

O
OPh
NC

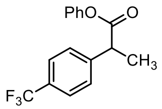
30-β


7.63
7.61
7.40
7.39
7.38
7.37
7.35
7.25
7.23
7.22
7.01
6.99
3.15
3.13
3.12
2.93
2.92
2.90
2.06
4.01
0.99
1.94
2.00
2.00
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
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)

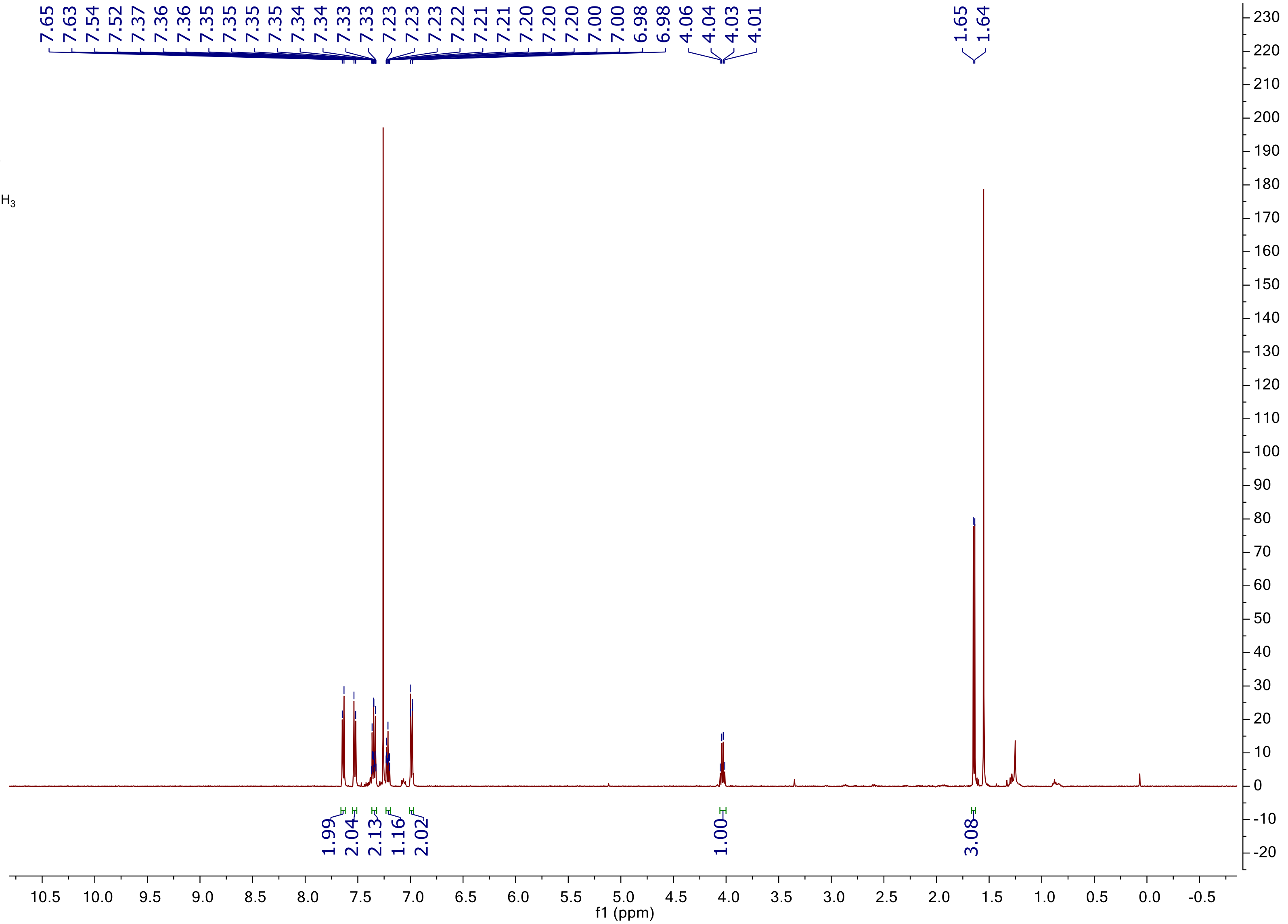

O
OPh
NC

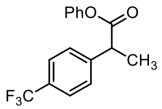
30-β


170.80
150.46
145.73
132.47
129.53
129.35
126.05
121.41
118.91
110.53
35.19
30.89
20000000
19000000
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
230
220
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)

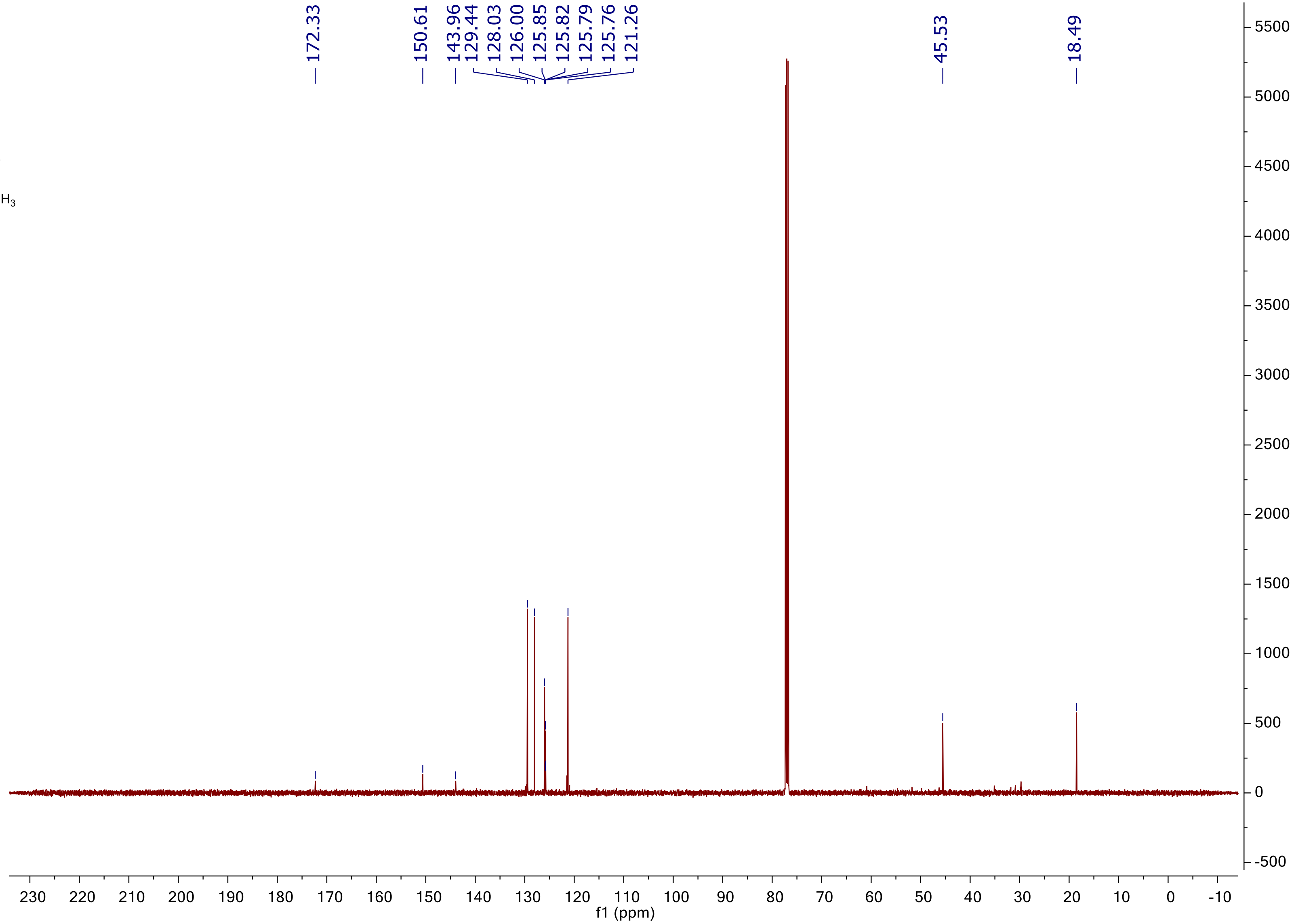

PhO
O
CH3
F3C

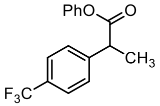
31-α


7.65
7.63
7.54
7.52
7.37
7.36
7.36
7.35
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.23
7.23
7.23
7.22
7.21
7.21
7.20
7.20
7.20
7.00
7.00
6.98
6.98
4.06
4.04
4.03
4.01
1.65
1.64
1.99
2.04
2.13
1.16
2.02
1.00
3.08
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)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

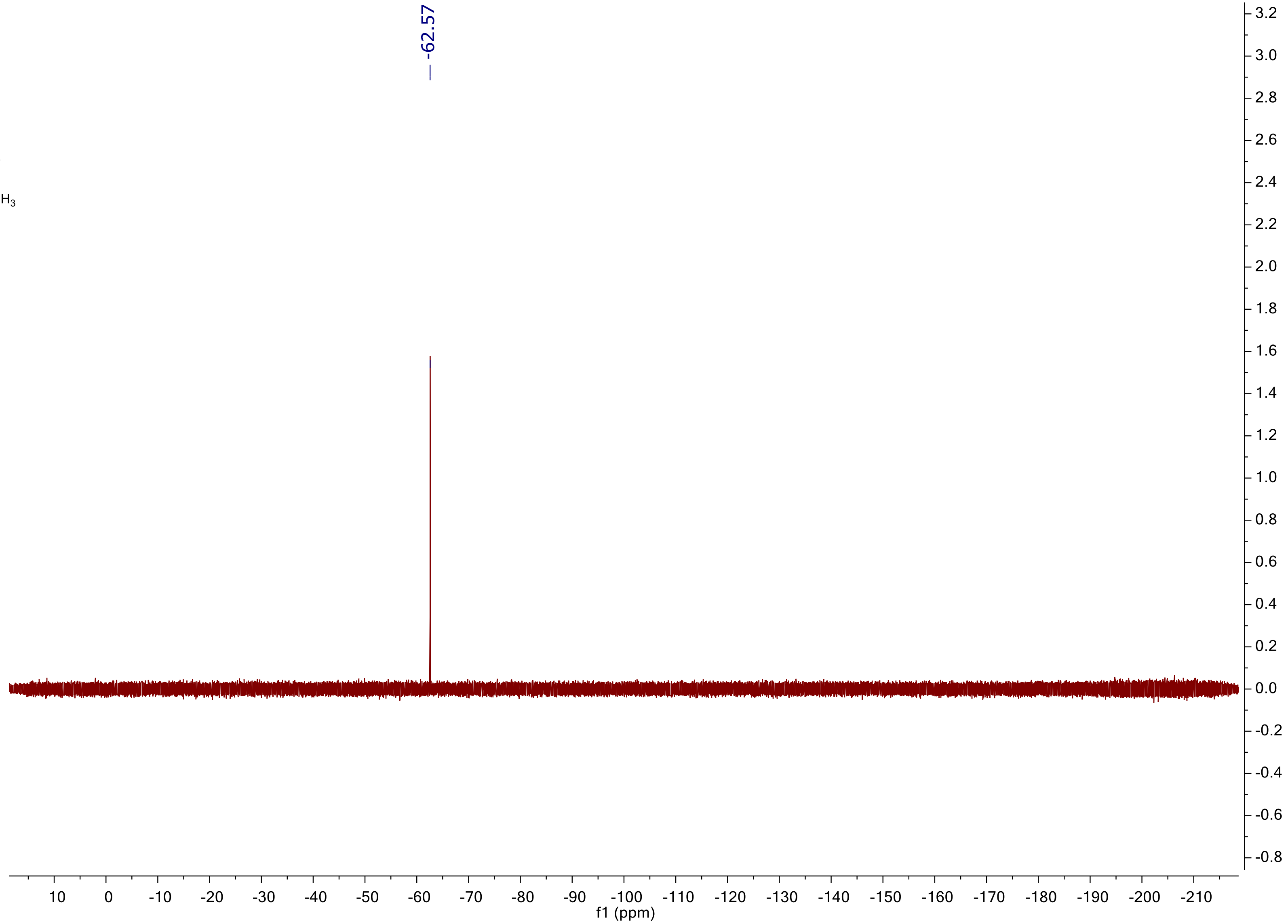

PhO
O
CH3
F3C

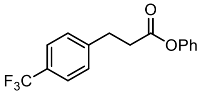
31-α


172.33
150.61
143.96
129.44
128.03
126.00
125.85
125.82
125.79
125.76
121.26
45.53
18.49
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
230
220
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)

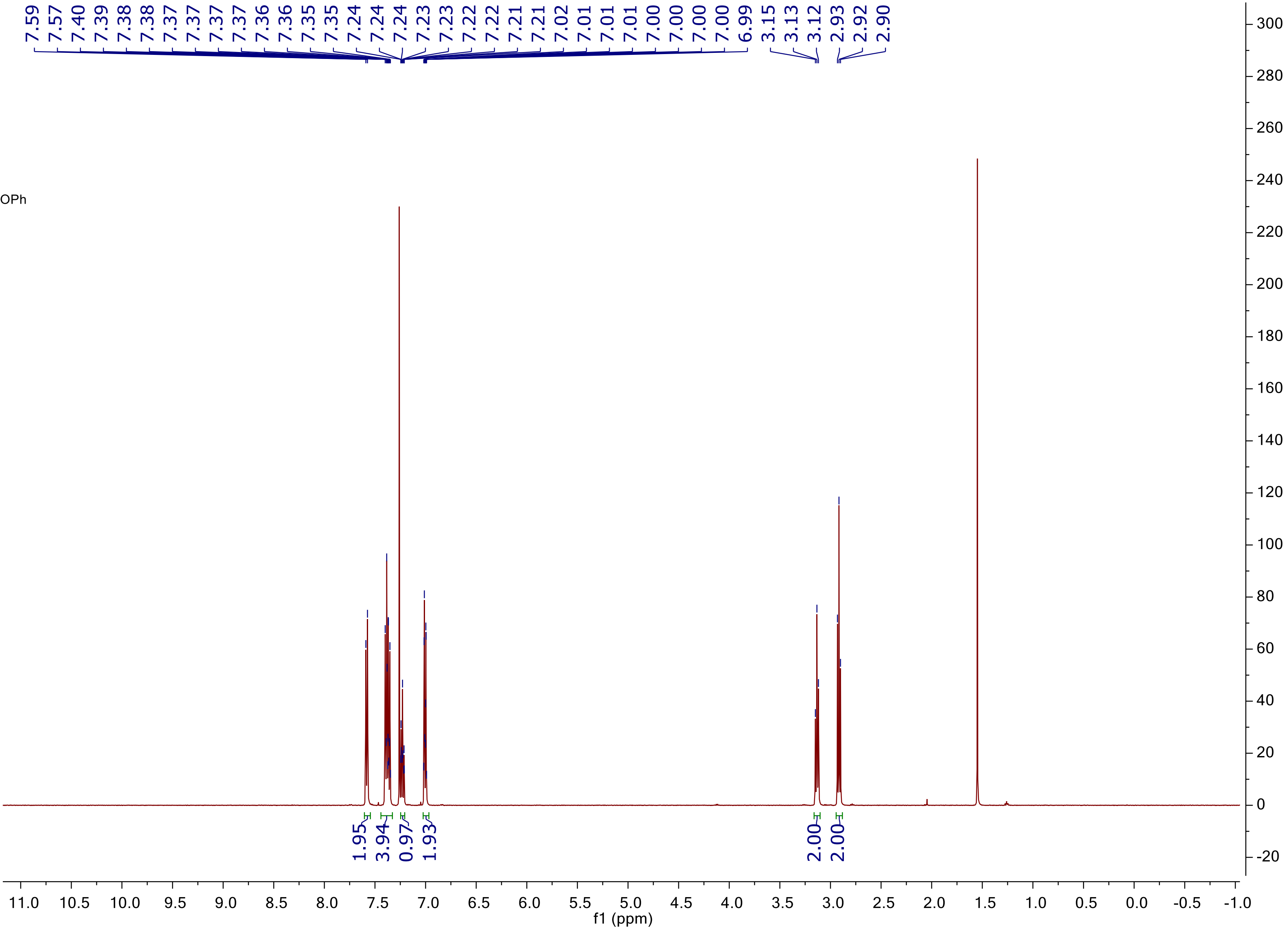

PhO
O
CH3
F3C

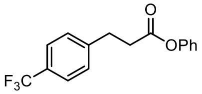
31-α


-62.57
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


O
OPh
F$_3$C

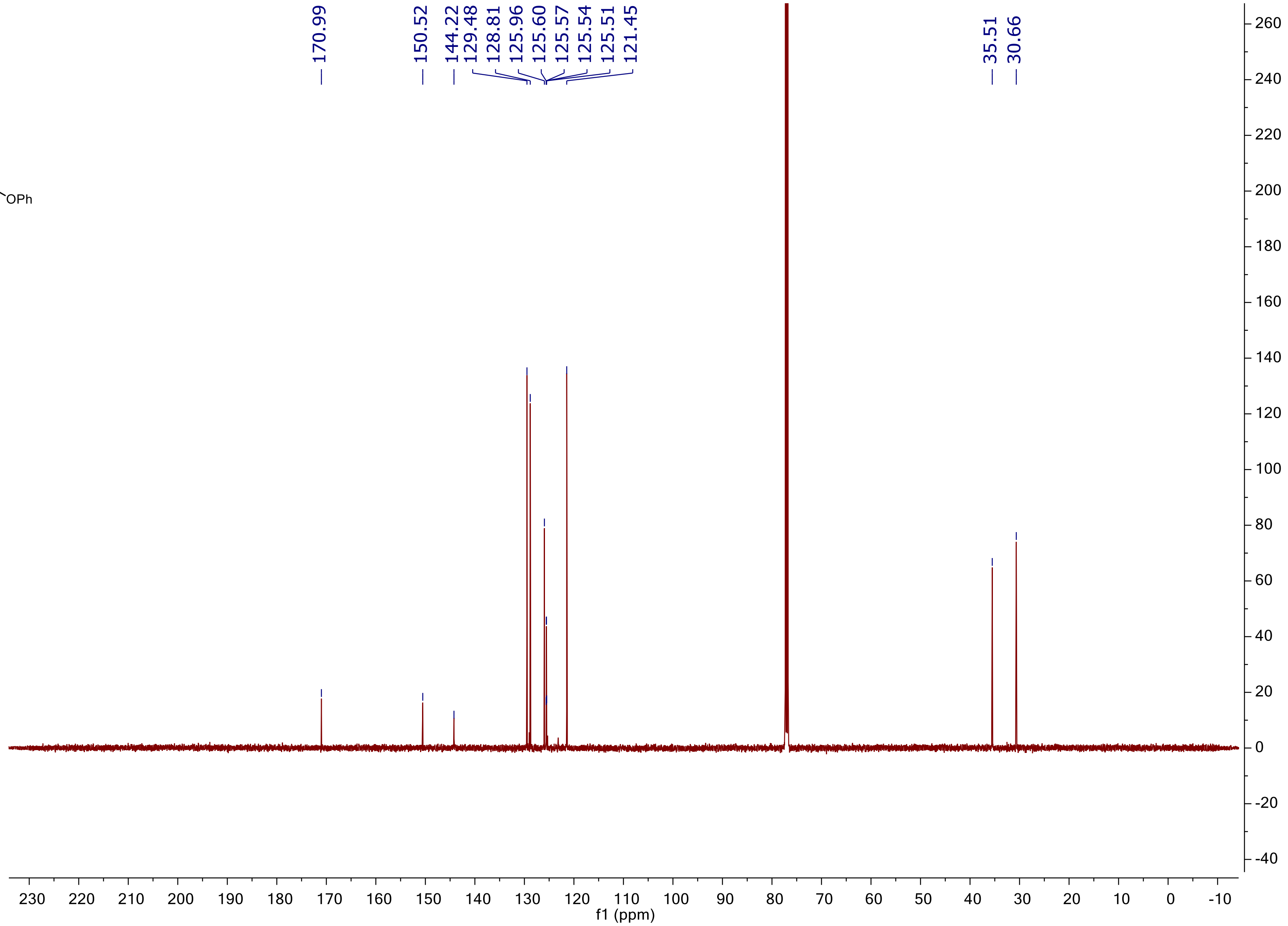
31-β


7.59
7.57
7.40
7.39
7.38
7.38
7.37
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.24
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.02
7.01
7.01
7.01
7.00
7.00
7.00
7.00
6.99
3.15
3.13
3.12
2.93
2.92
2.90
1.95
3.94
0.97
1.93
2.00
2.00
11.0
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
-1.0
f1 (ppm)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

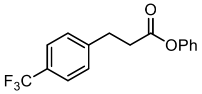


O
OPh
F$_3$C

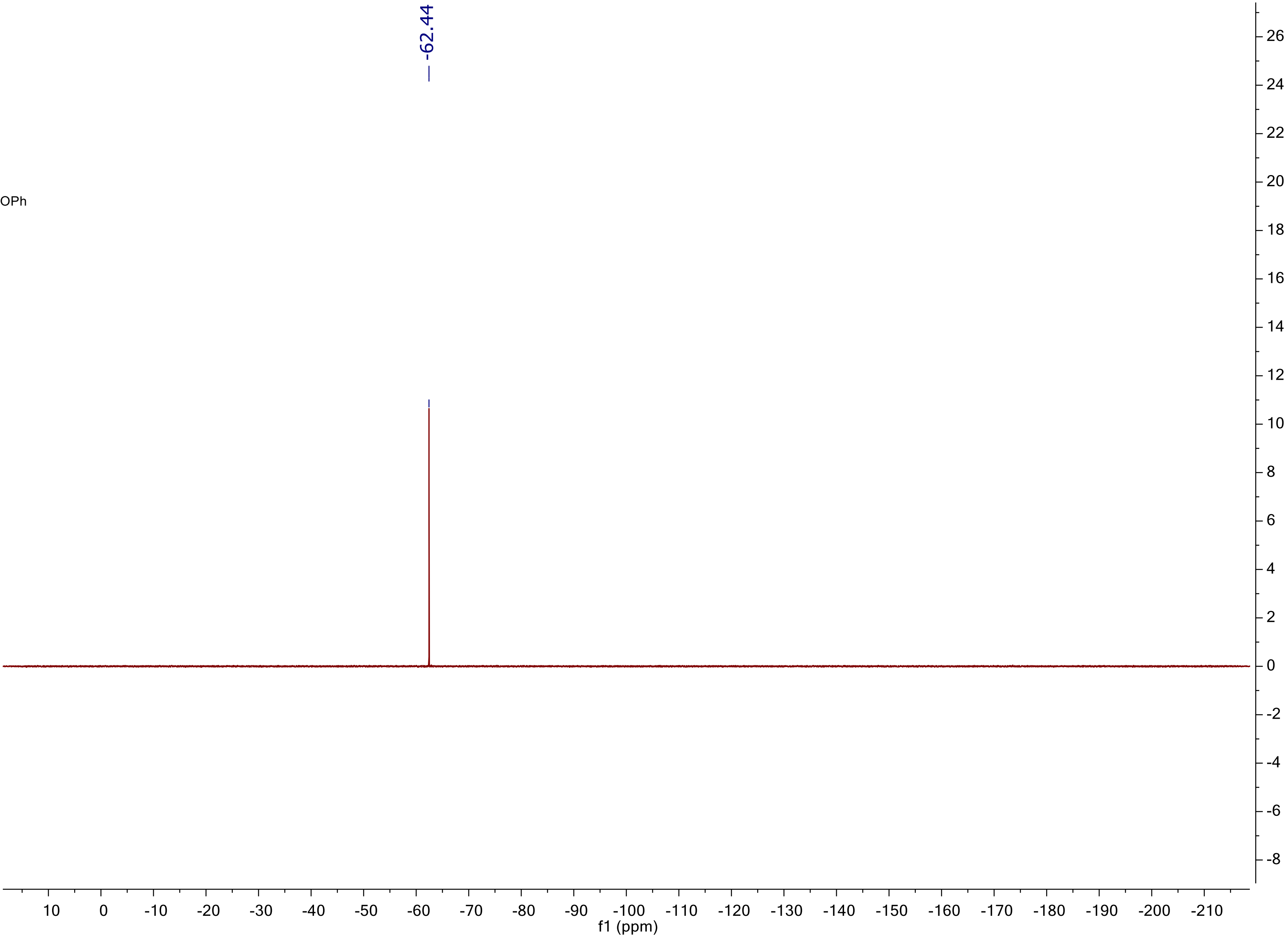
31-β

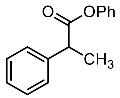


170.99
150.52
144.22
129.48
128.81
125.96
125.60
125.57
125.54
125.51
121.45
35.51
30.66
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40

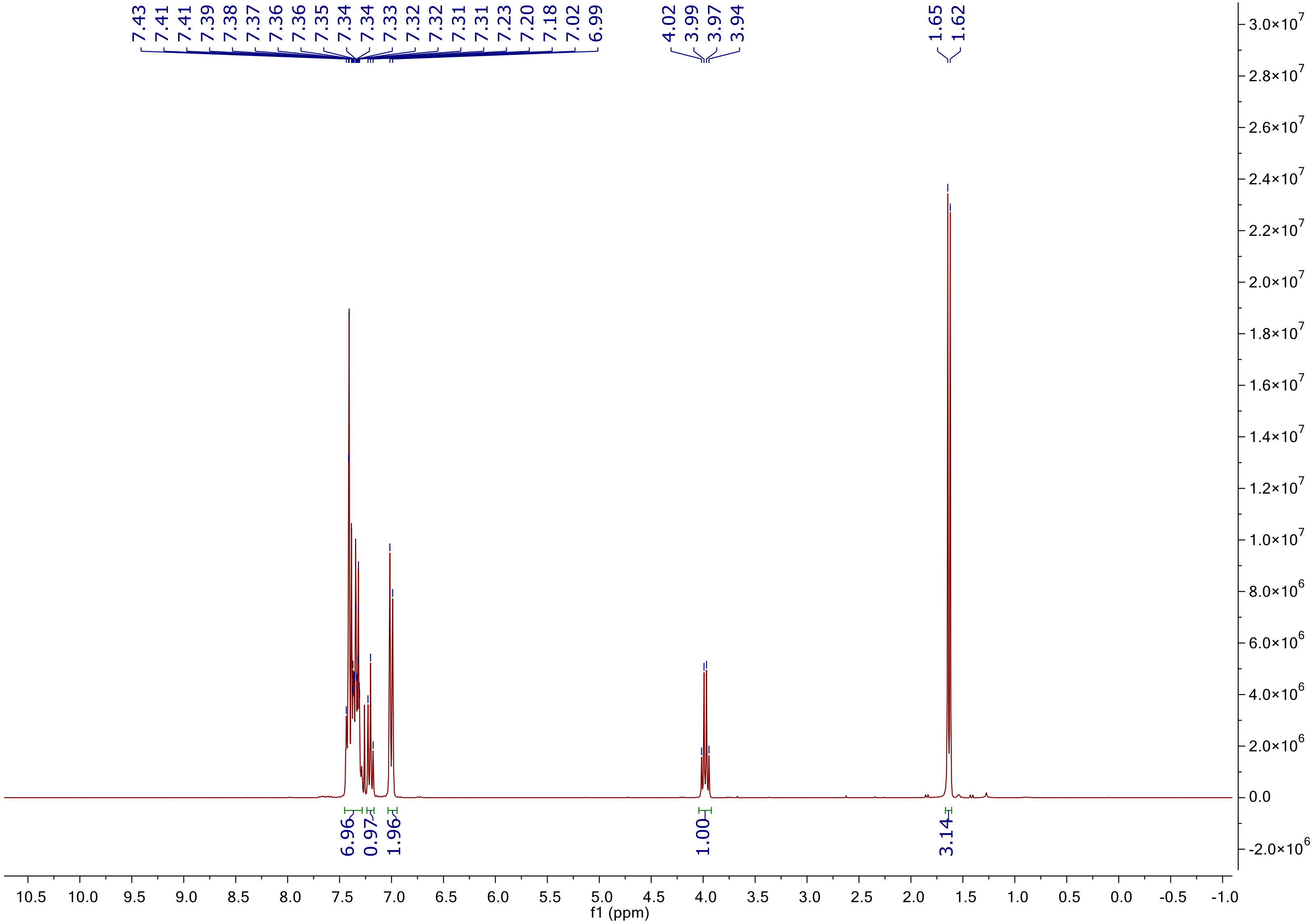

O
OPh
F3C

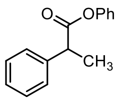
31-β


-62.44
26
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

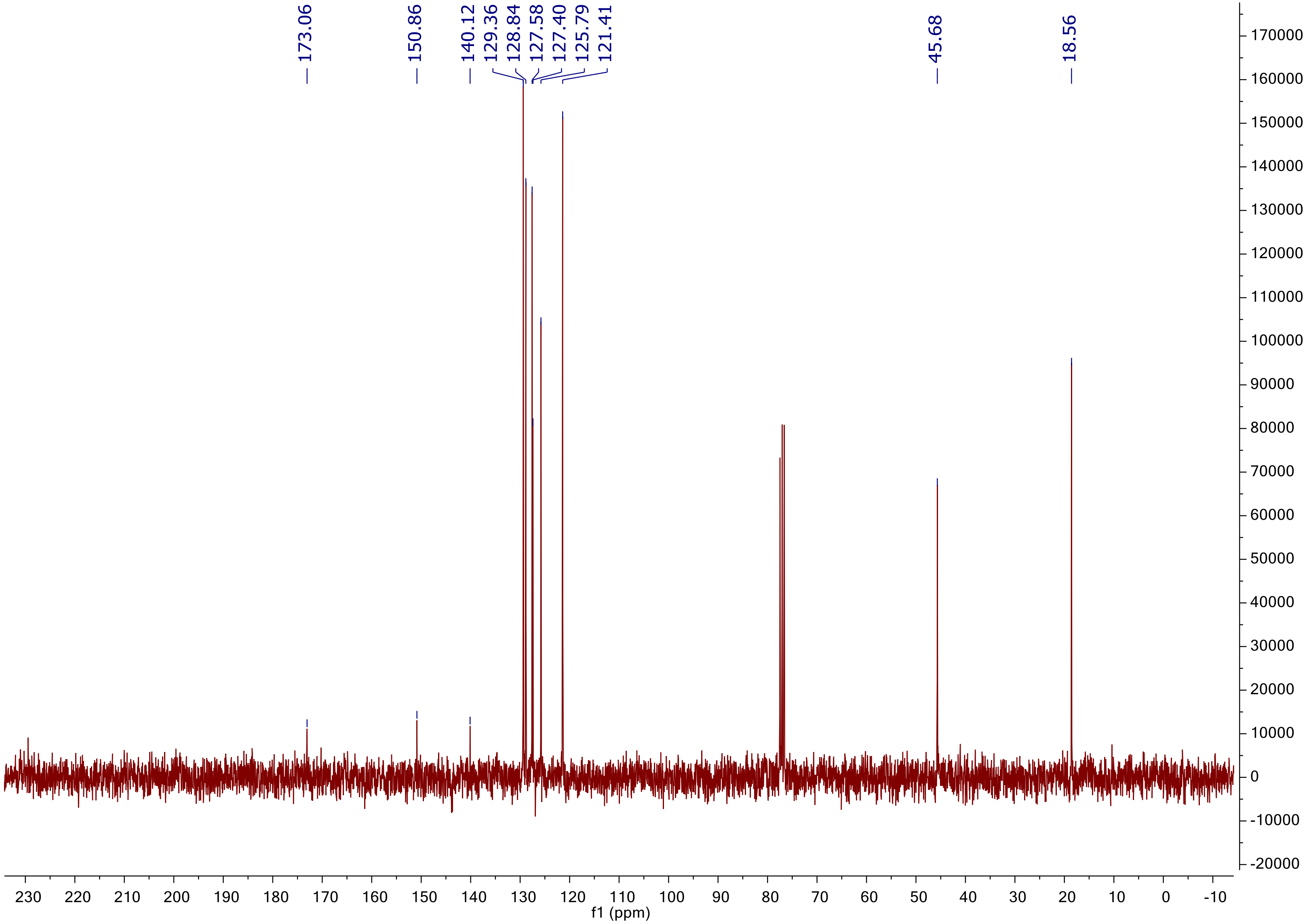

O
OPh
CH3

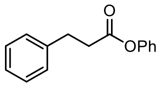
32-α


7.43
7.41
7.41
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.23
7.20
7.18
7.02
6.99
4.02
3.99
3.97
3.94
1.65
1.62
6.96
0.97
1.96
1.00
3.14
3.0×10^7
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
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
-1.0
f1 (ppm)

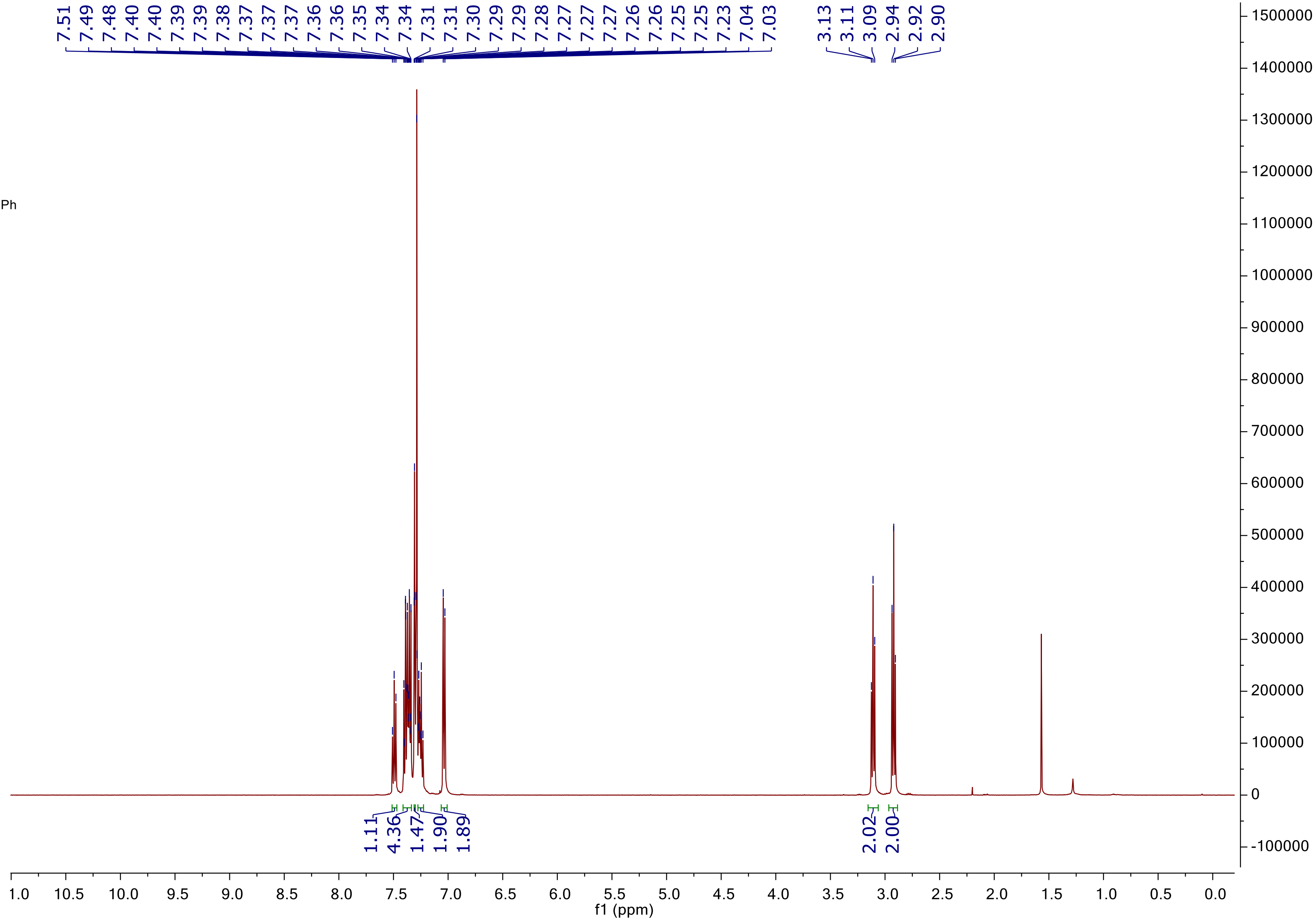

O
OPh
CH3

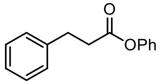
32-α


173.06
150.86
140.12
129.36
128.84
127.58
127.40
125.79
121.41
45.68
18.56
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
230
220
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)

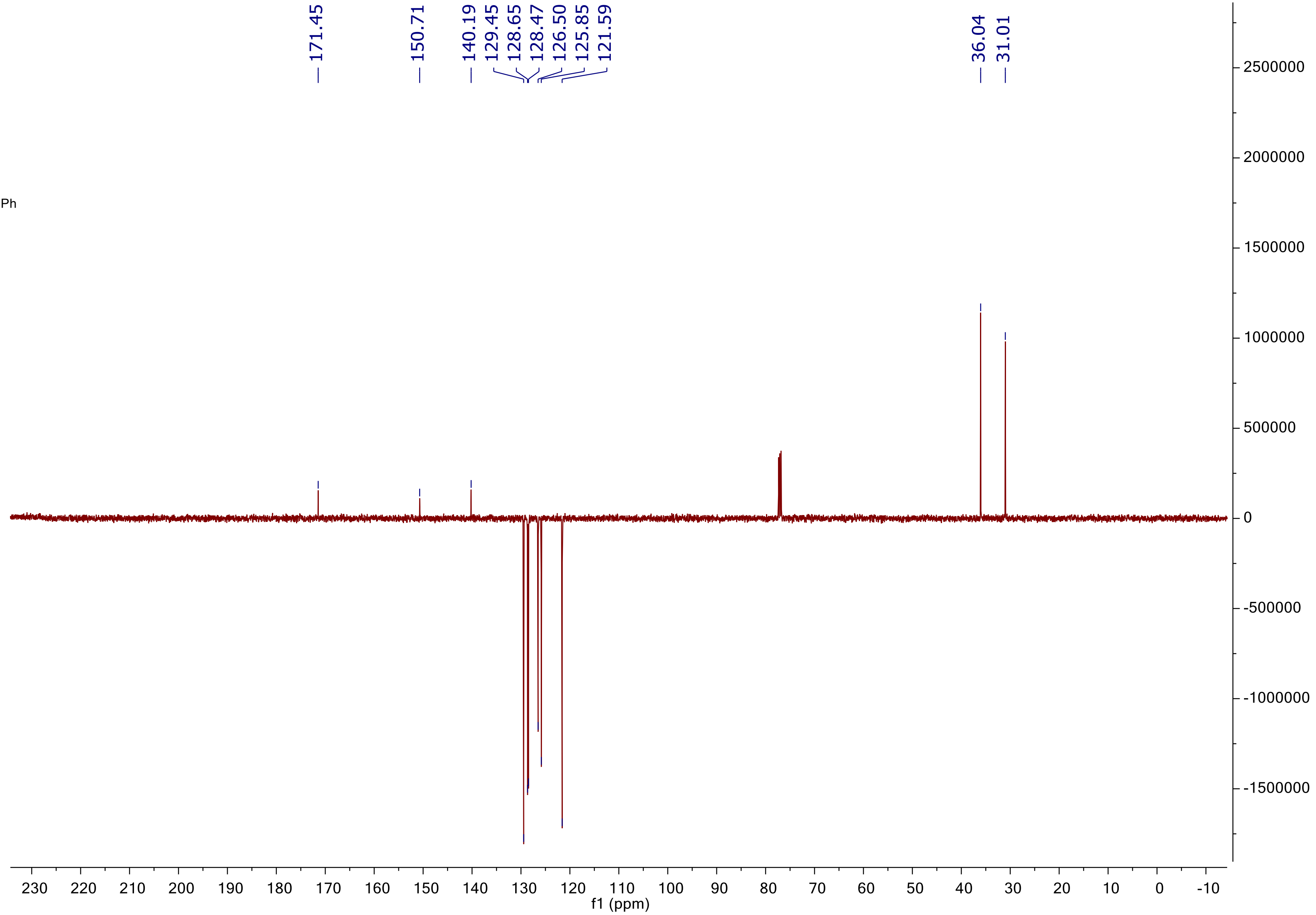

O
OPh

32-β

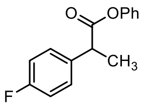

7.51
7.49
7.48
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.23
7.04
7.03
3.13
3.11
3.09
2.94
2.92
2.90
1.11
4.36
1.47
1.90
1.89
2.02
2.00
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
1.0
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)



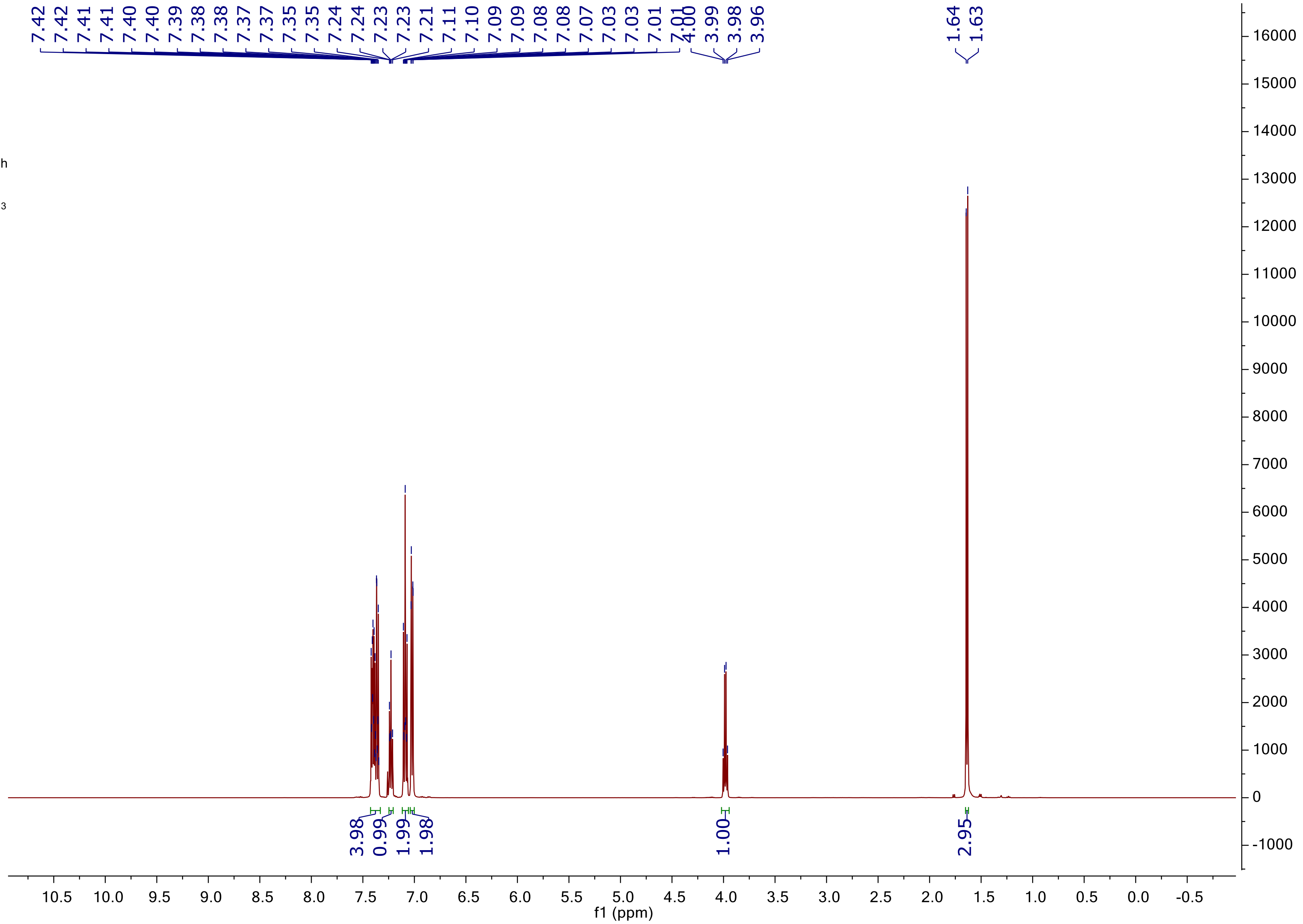
32-β

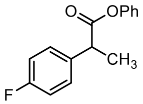


171.45
150.71
140.19
129.45
128.65
128.47
126.50
125.85
121.59
36.04
31.01
2500000
2000000
1500000
1000000
500000
0
-500000
-1000000
-1500000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

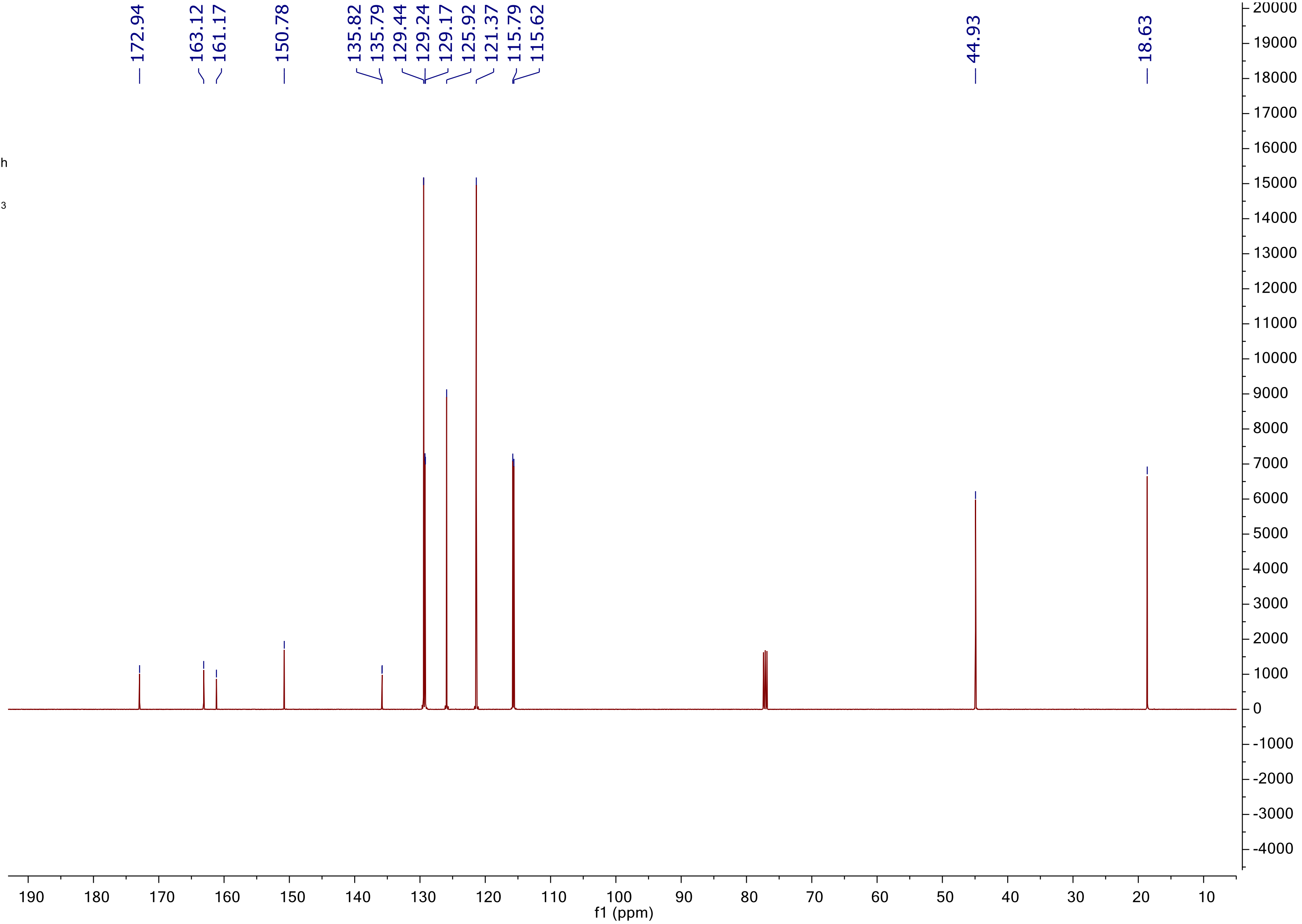

O
OPh
CH3
F

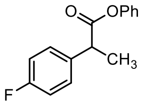
33-α


7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.35
7.35
7.24
7.24
7.23
7.23
7.21
7.11
7.10
7.09
7.09
7.08
7.08
7.07
7.03
7.03
7.01
7.01
4.00
3.99
3.98
3.96
1.64
1.63
3.98
0.99
1.99
1.98
1.00
2.95
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)
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

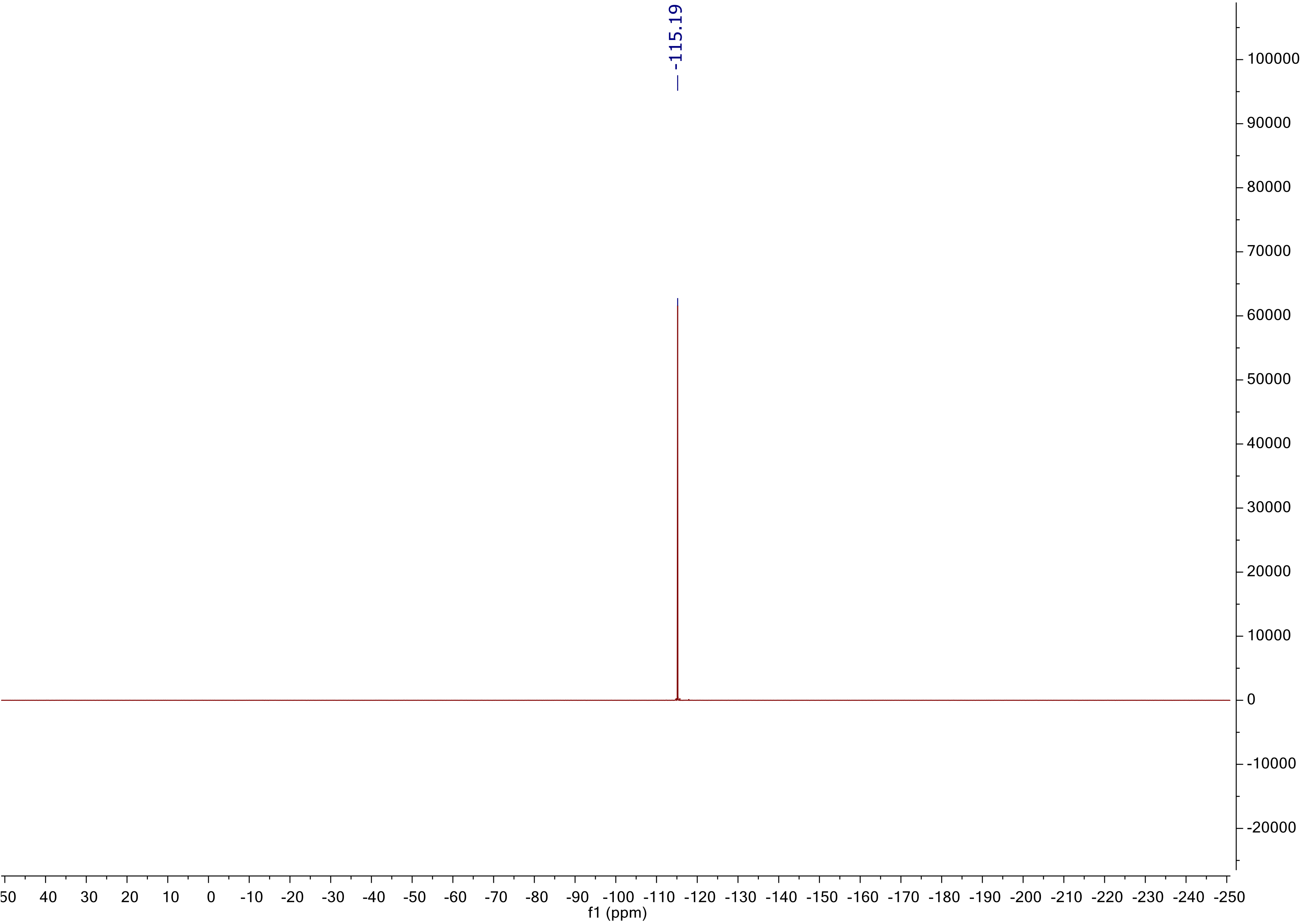

O
OPh
CH$_3$
F

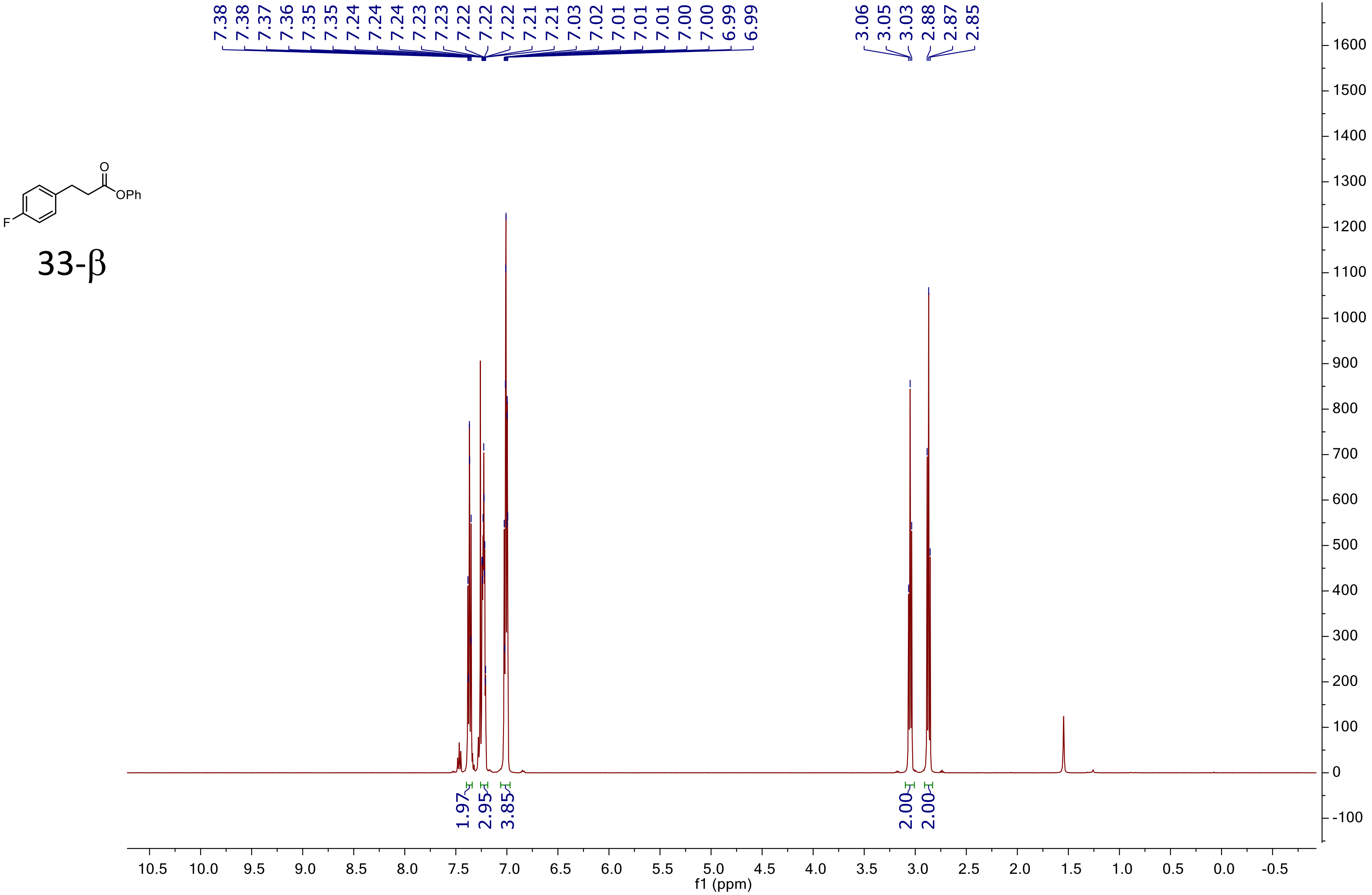
33-α


172.94
163.12
161.17
150.78
135.82
135.79
129.44
129.24
129.17
125.92
121.37
115.79
115.62
44.93
18.63
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

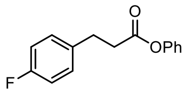

O
OPh
CH3
F

33-α

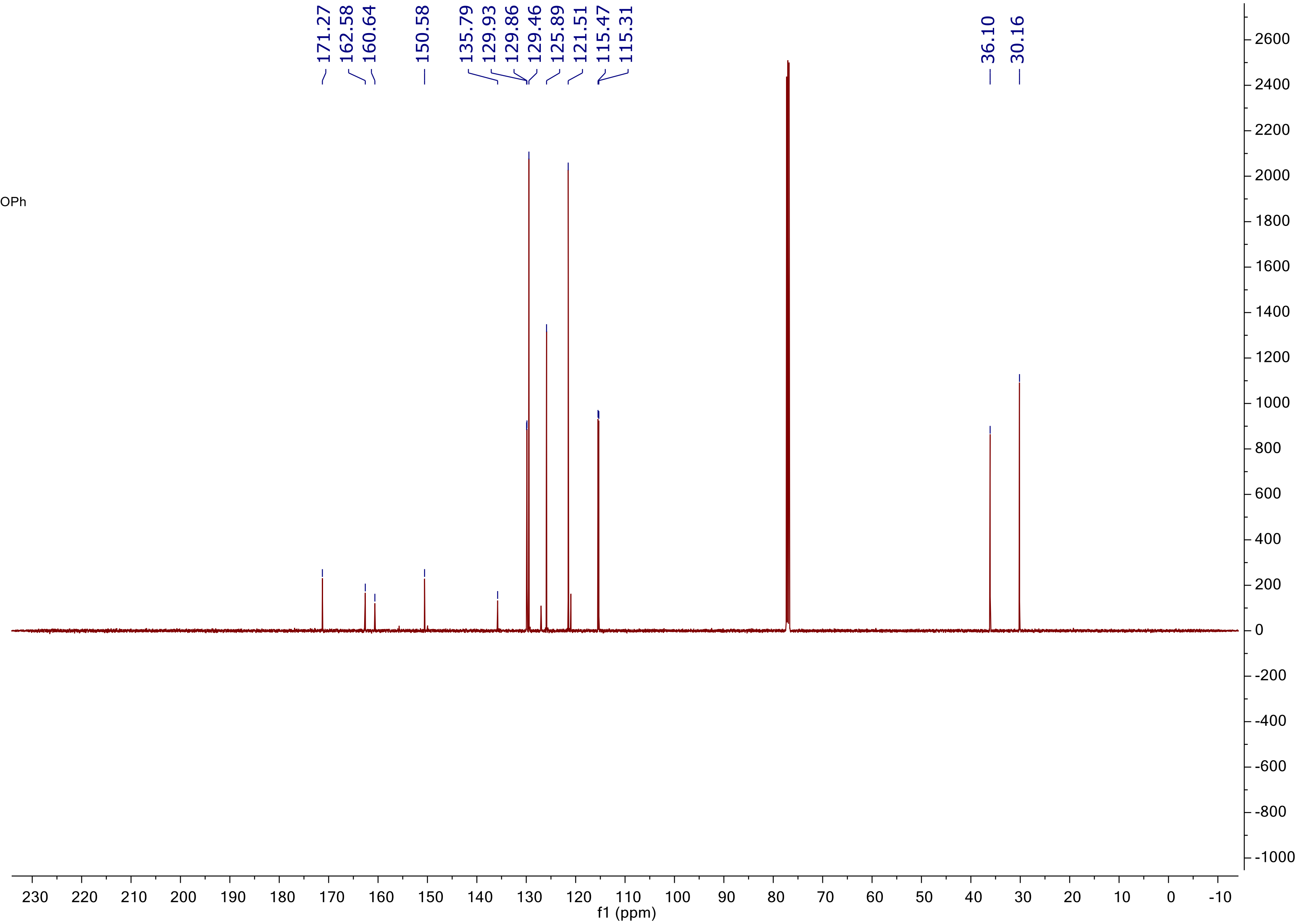

-115.19
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

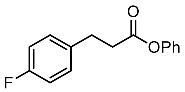

7.38
7.38
7.37
7.36
7.35
7.35
7.24
7.24
7.24
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.03
7.02
7.01
7.01
7.01
7.00
7.00
6.99
6.99
3.06
3.05
3.03
2.88
2.87
2.85
O
OPh
F
1.97
2.95
3.85
2.00
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

33-β

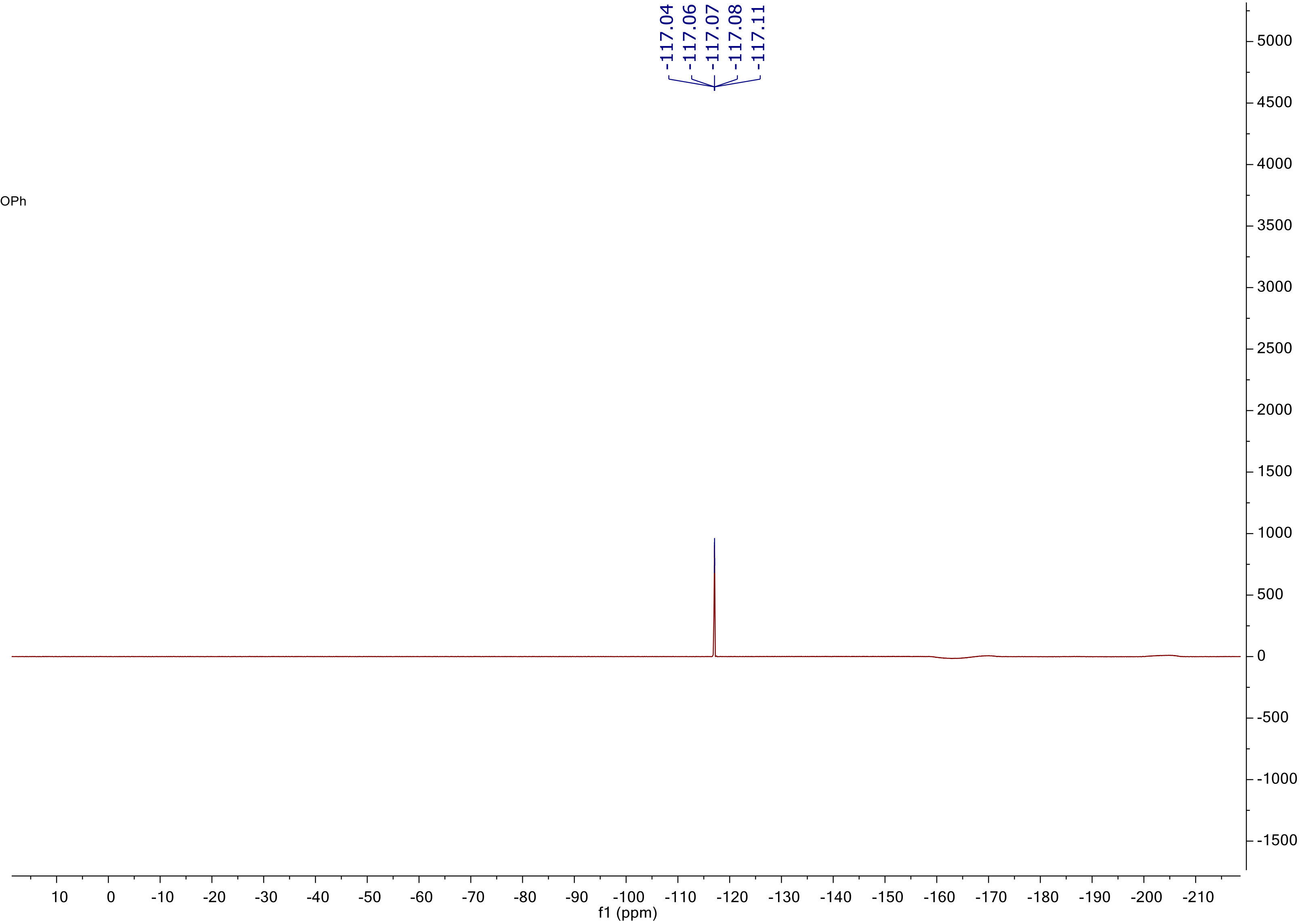

O
OPh
F

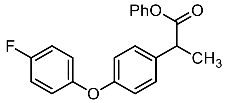
33-β


171.27
162.58
160.64
150.58
135.79
129.93
129.86
129.46
125.89
121.51
115.47
115.31
36.10
30.16
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-1000
230
220
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)

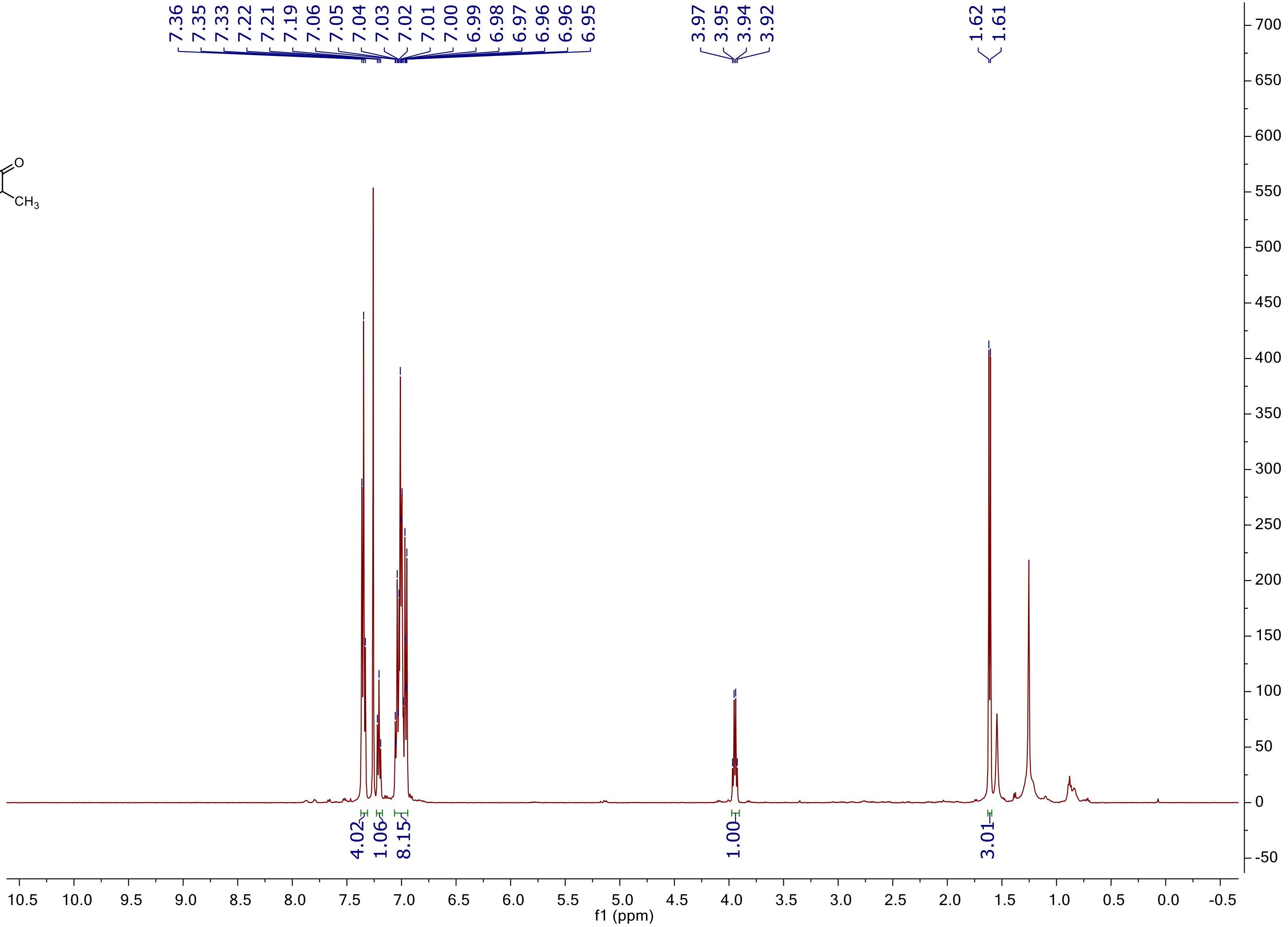

O
OPh
F

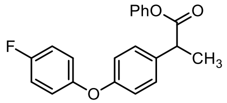
33-β


-117.04
-117.06
-117.07
-117.08
-117.11
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

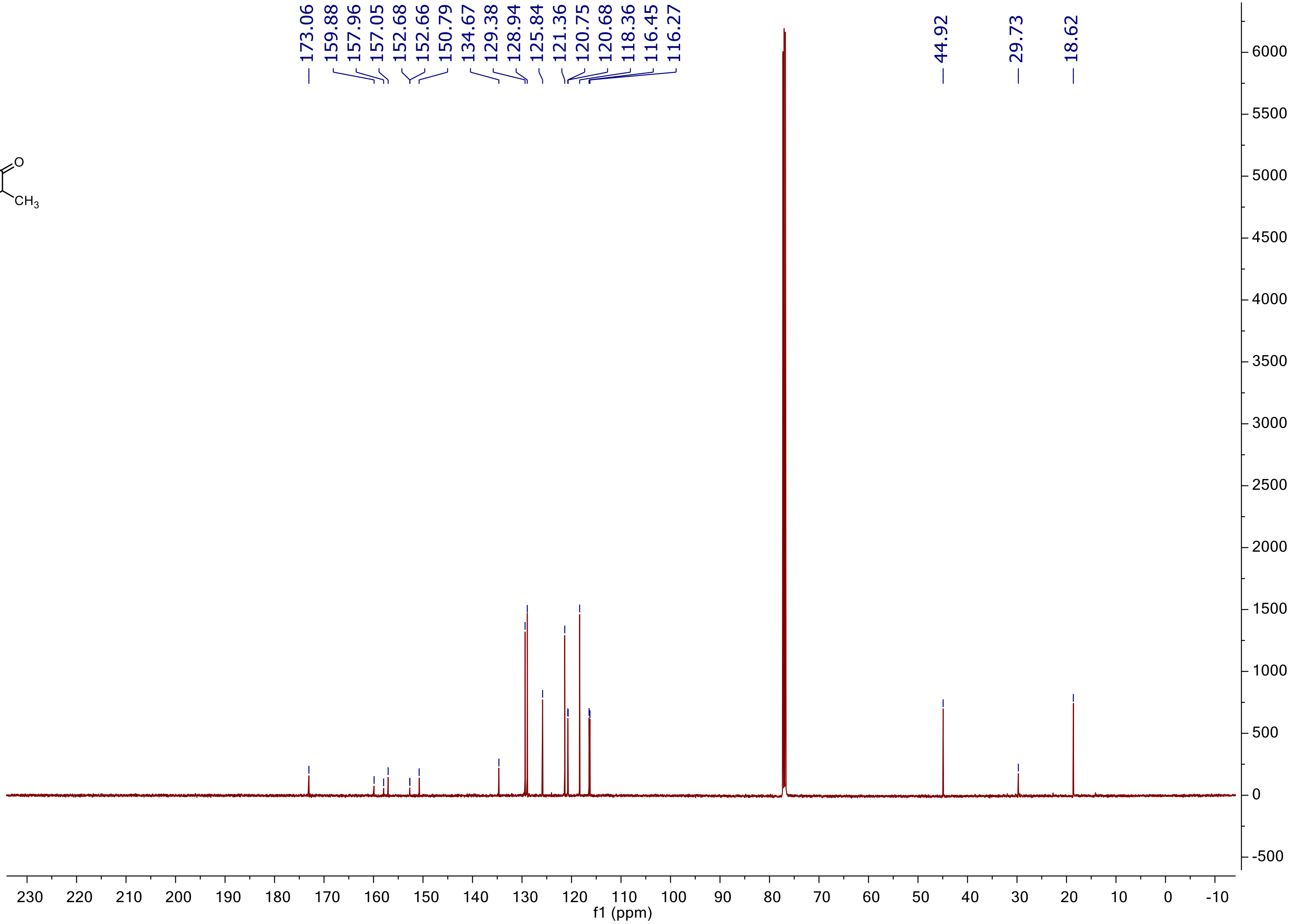

PhO
O
F
O
CH3

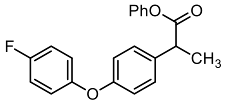
34-α


7.36
7.35
7.33
7.22
7.21
7.19
7.06
7.05
7.04
7.03
7.02
7.01
7.00
6.99
6.98
6.97
6.96
6.96
6.95
3.97
3.95
3.94
3.92
1.62
1.61
4.02
1.06
8.15
1.00
3.01
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
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)

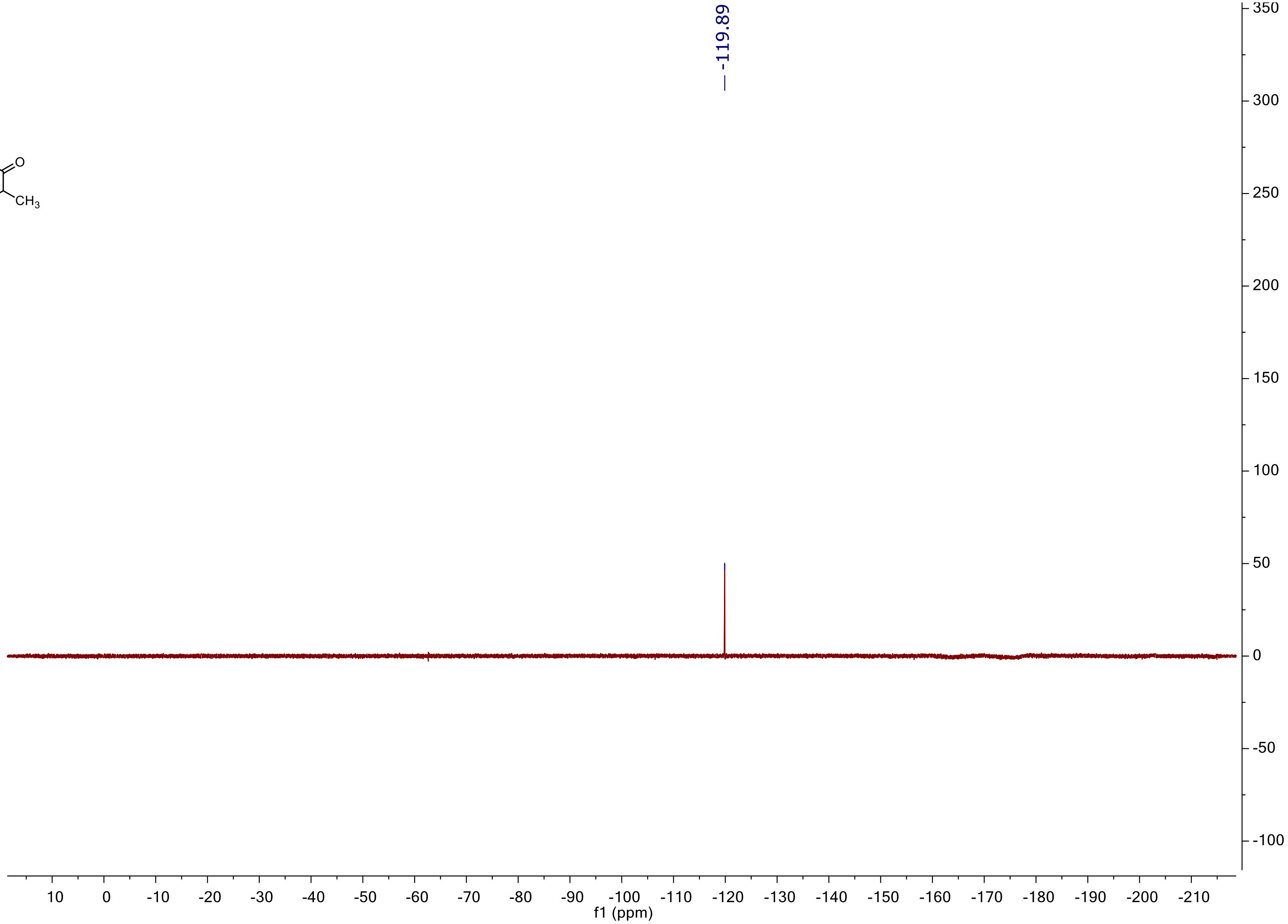

F
O
PhO
O
CH3

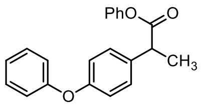
34-α


173.06
159.88
157.96
157.05
152.68
152.66
150.79
134.67
129.38
128.94
125.84
121.36
120.75
120.68
118.36
116.45
116.27
44.92
29.73
18.62
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
230
220
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)

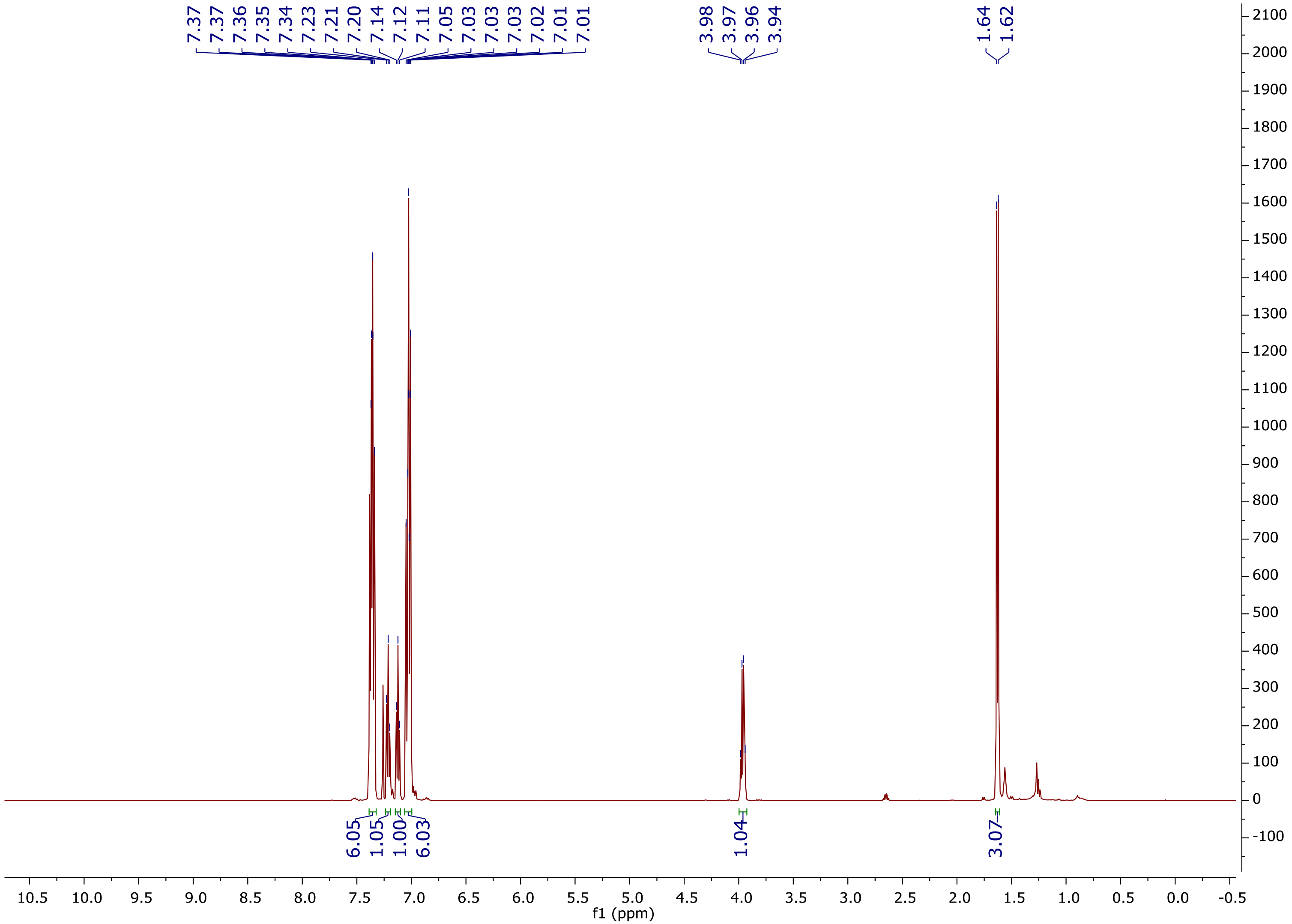

PhO
O
F
O
CH3

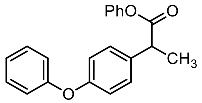
34-α


-119.89
350
300
250
200
150
100
50
0
-50
-100
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


PhO
O
CH3
O

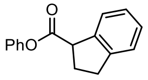
35-α


7.37
7.37
7.36
7.35
7.34
7.23
7.21
7.20
7.14
7.12
7.11
7.05
7.03
7.03
7.03
7.02
7.01
7.01
3.98
3.97
3.96
3.94
1.64
1.62
6.05
1.05
1.00
6.03
1.04
3.07
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)
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

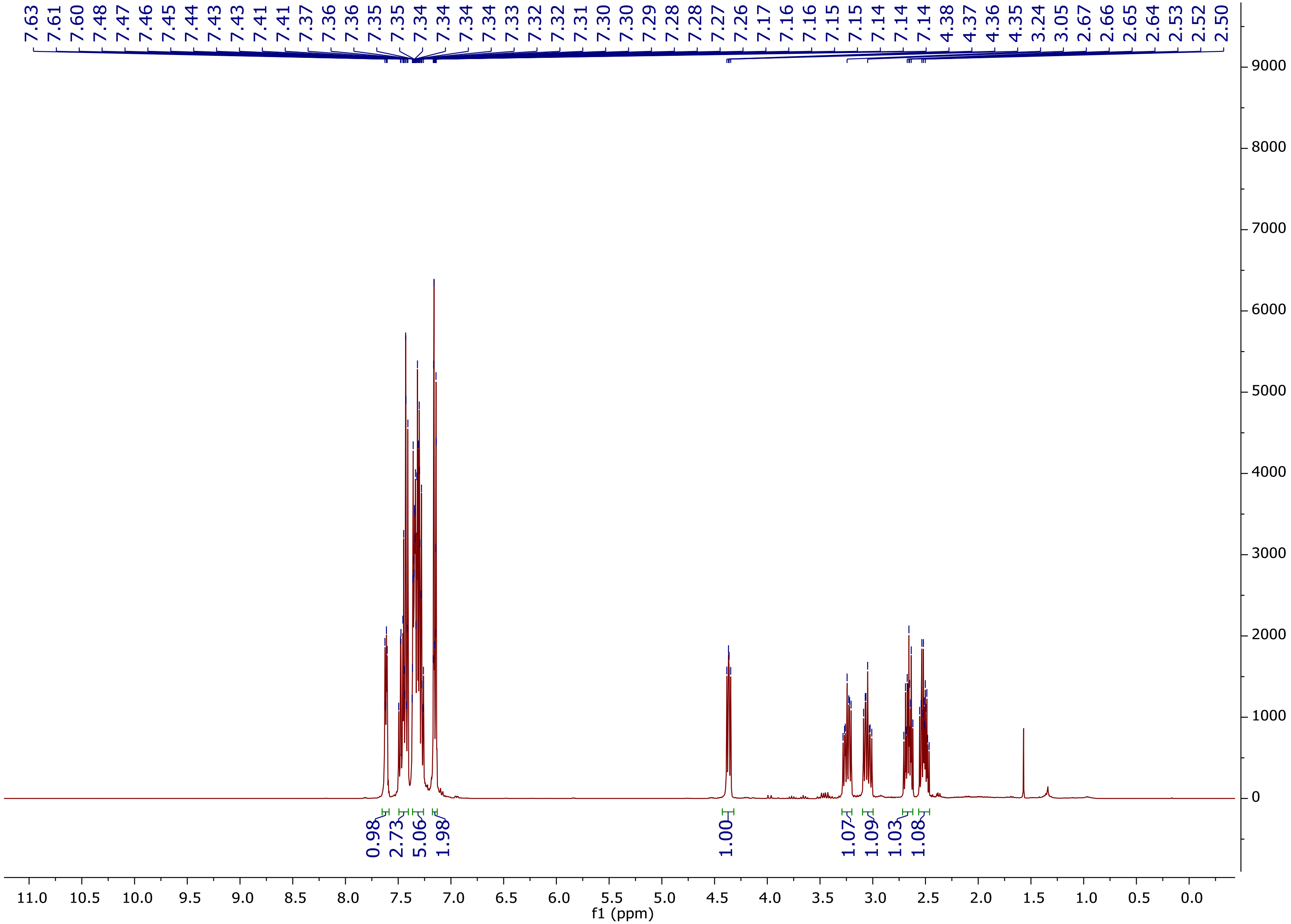

PhO
O
CH$_3$
O

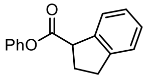
35-α


173.10
157.05
156.63
150.83
134.75
129.81
129.39
128.91
125.83
123.42
121.39
119.06
118.98
44.97
18.62
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
230
220
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)

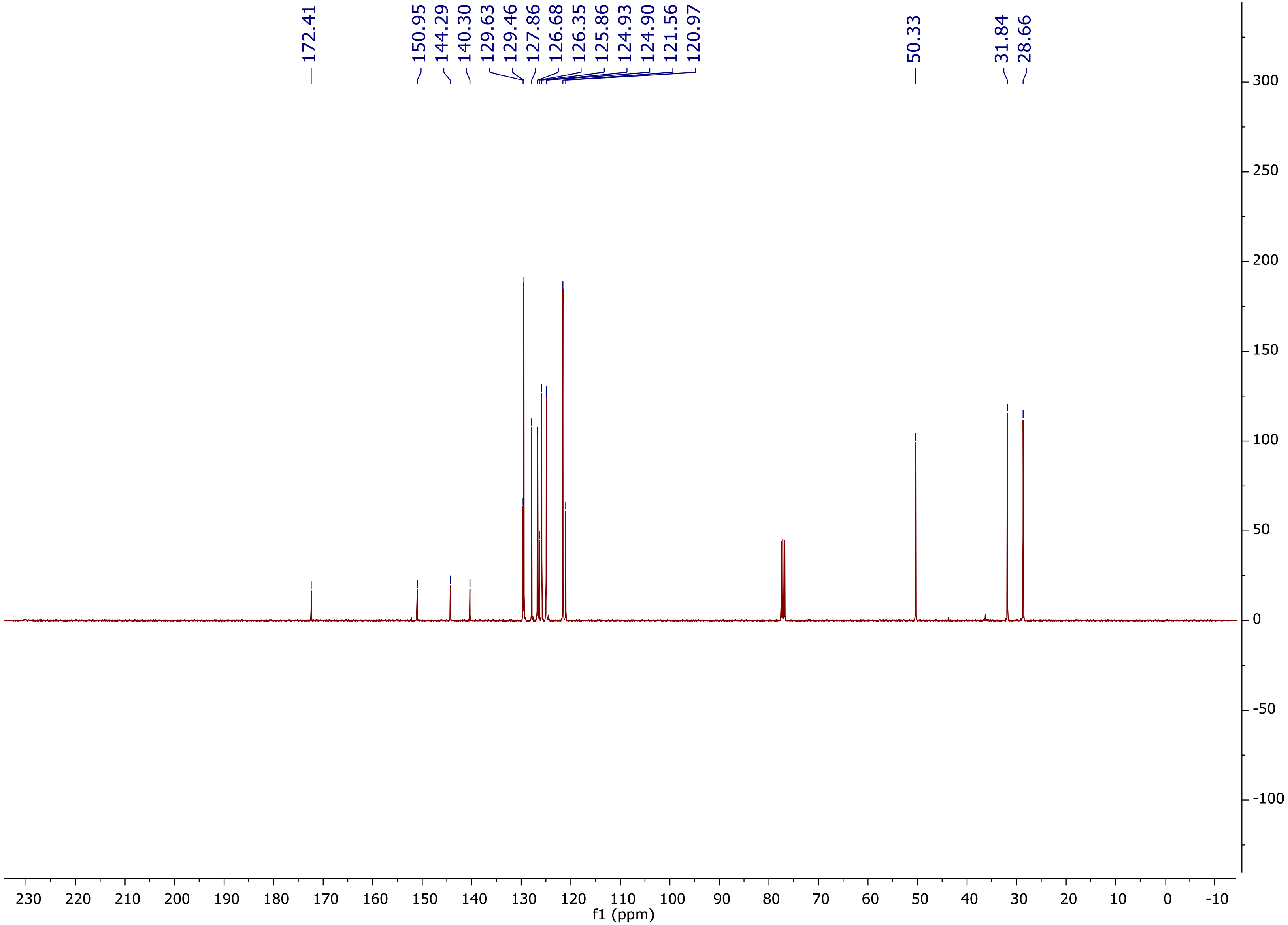

O
PhO

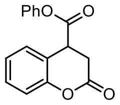
36


7.63
7.61
7.60
7.48
7.47
7.46
7.45
7.44
7.43
7.43
7.41
7.41
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.17
7.16
7.16
7.15
7.15
7.14
7.14
7.14
4.38
4.37
4.36
4.35
3.24
3.05
2.67
2.66
2.65
2.64
2.53
2.52
2.50
0.98
2.73
5.06
1.98
1.00
1.07
1.09
1.03
1.08
11.0
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)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

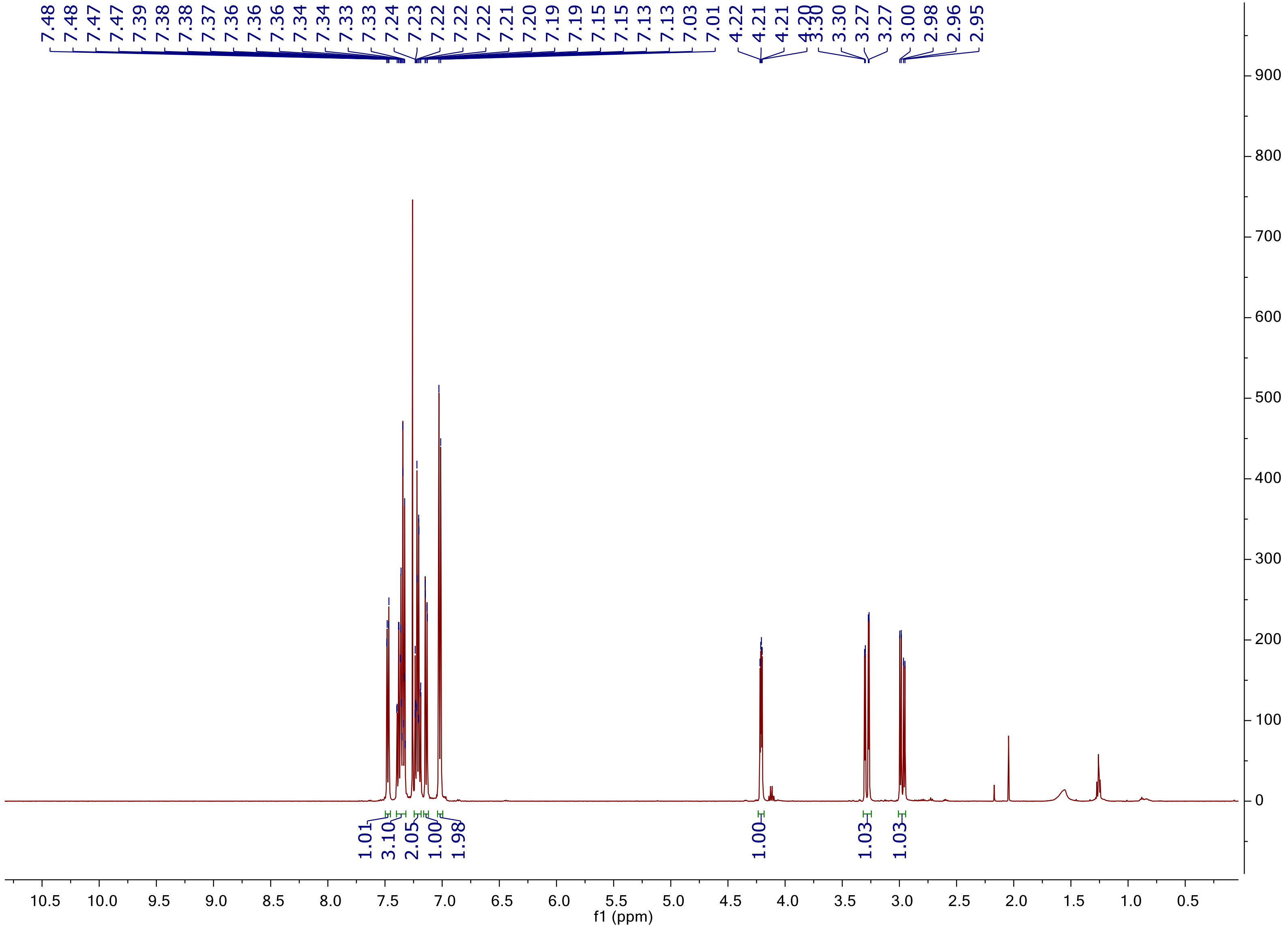

PhO
O

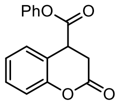
36


172.41
150.95
144.29
140.30
129.63
129.46
127.86
126.68
126.35
125.86
124.93
124.90
121.56
120.97
50.33
31.84
28.66
300
250
200
150
100
50
0
-50
-100
230
220
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)

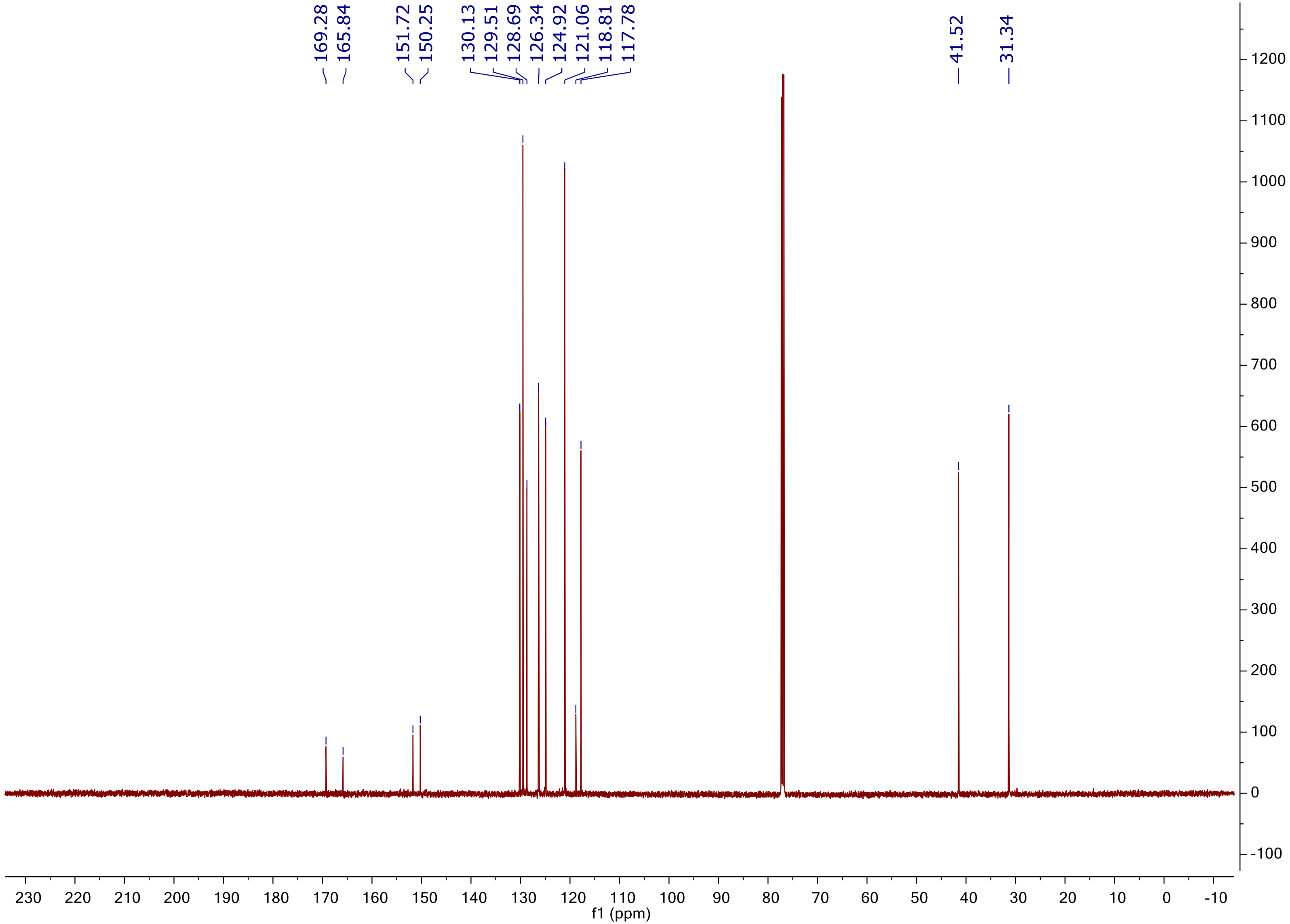

PhO
O
O
O

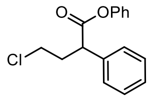
37


7.48
7.48
7.47
7.47
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.34
7.34
7.33
7.33
7.24
7.23
7.22
7.22
7.22
7.21
7.20
7.19
7.19
7.15
7.15
7.13
7.13
7.03
7.01
4.22
4.21
4.21
4.20
3.30
3.30
3.27
3.27
3.00
2.98
2.96
2.95
1.01
3.10
2.05
1.00
1.98
1.00
1.03
1.03
900
800
700
600
500
400
300
200
100
0
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
f1 (ppm)

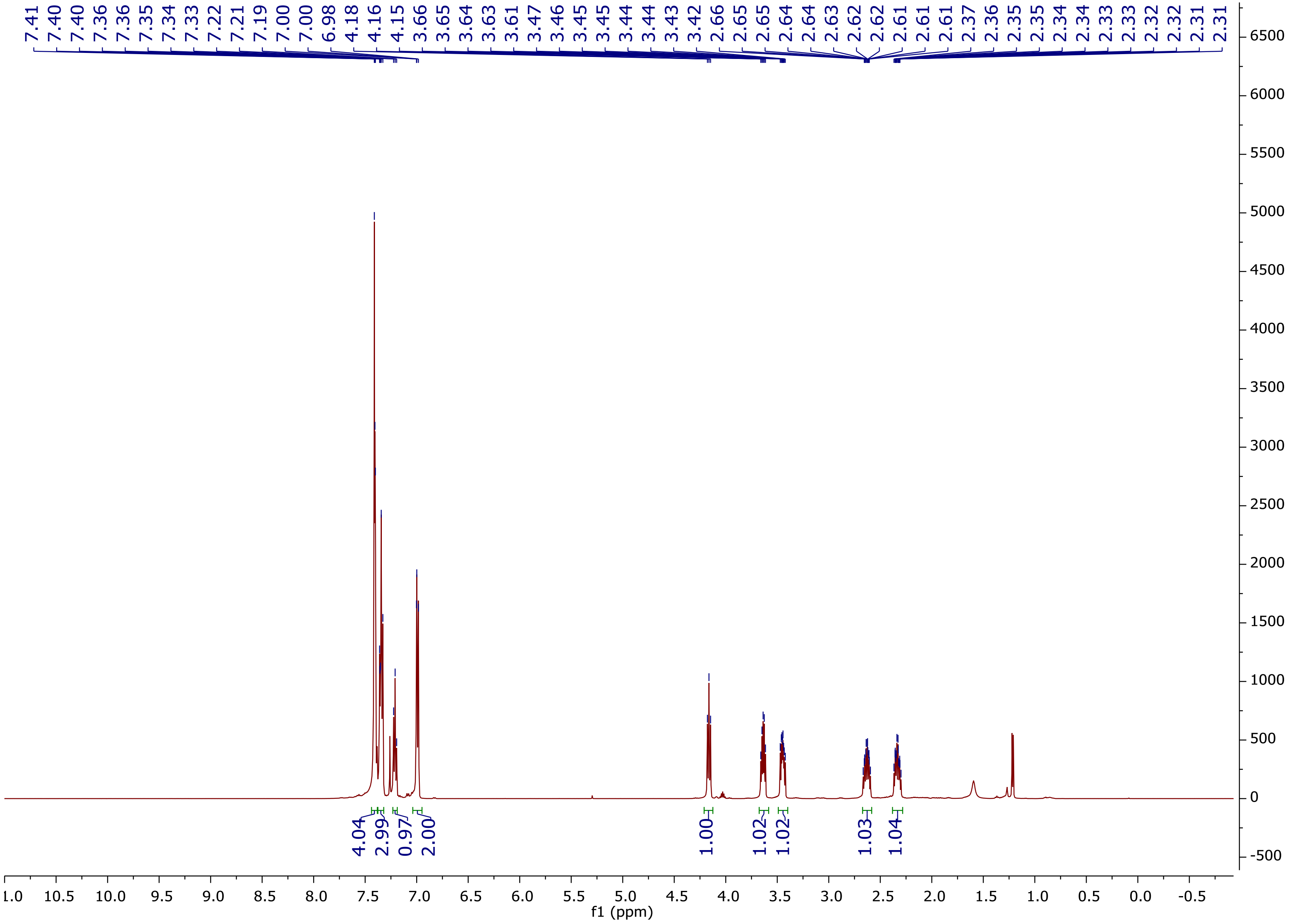

PhO
O
O
O

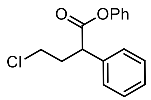
37


169.28
165.84
151.72
150.25
130.13
129.51
128.69
126.34
124.92
121.06
118.81
117.78
41.52
31.34
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
230
220
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)

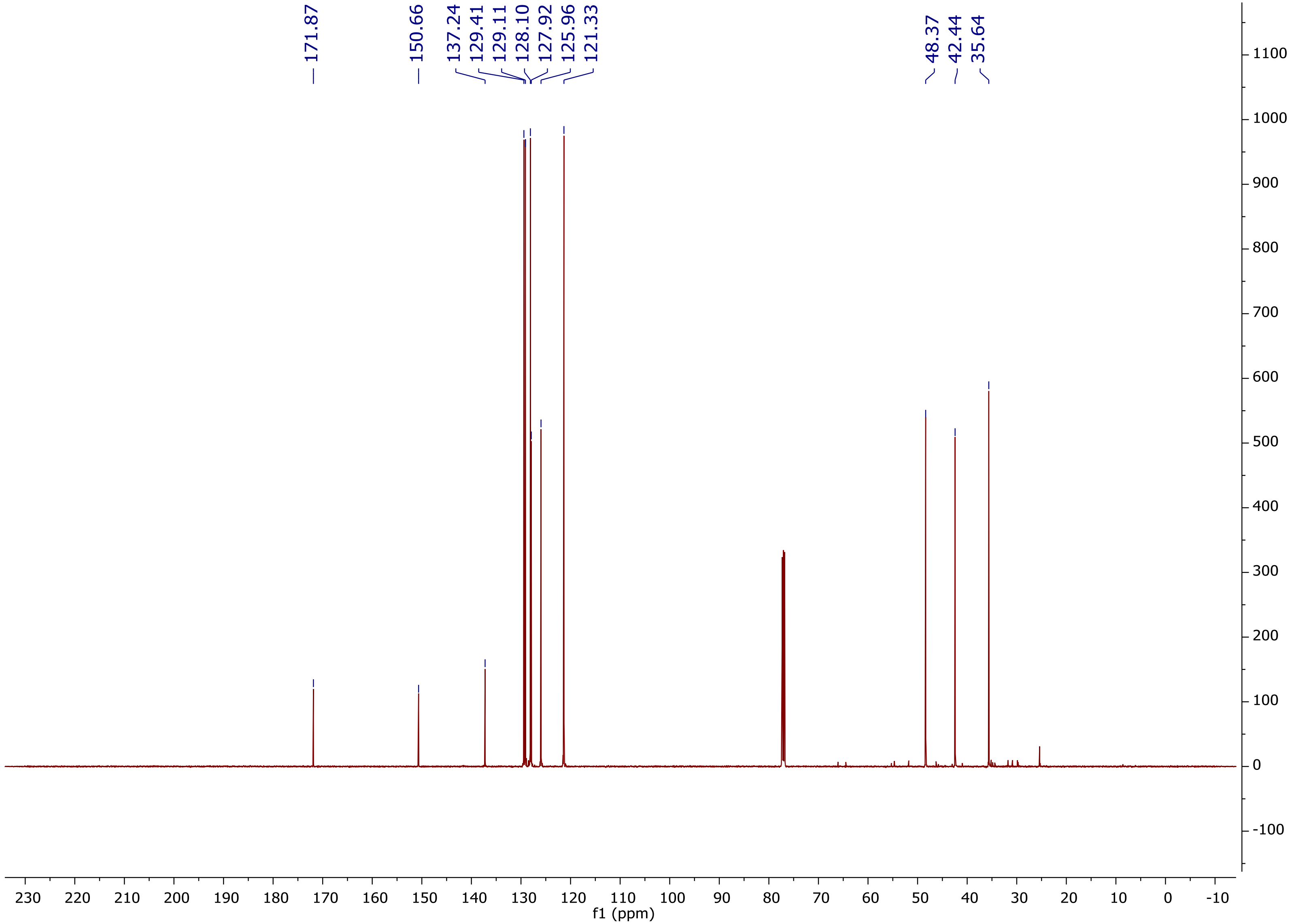

O
OPh
Cl

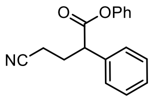
38


7.41
7.40
7.40
7.36
7.36
7.35
7.34
7.33
7.22
7.21
7.19
7.00
7.00
6.98
4.18
4.16
4.15
3.66
3.65
3.64
3.63
3.61
3.47
3.46
3.45
3.45
3.44
3.44
3.43
3.42
2.66
2.65
2.65
2.64
2.64
2.63
2.62
2.62
2.61
2.61
2.61
2.37
2.36
2.35
2.35
2.34
2.34
2.33
2.33
2.32
2.32
2.31
2.31
4.04
2.99
0.97
2.00
1.00
1.02
1.02
1.03
1.04
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
1.0
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)

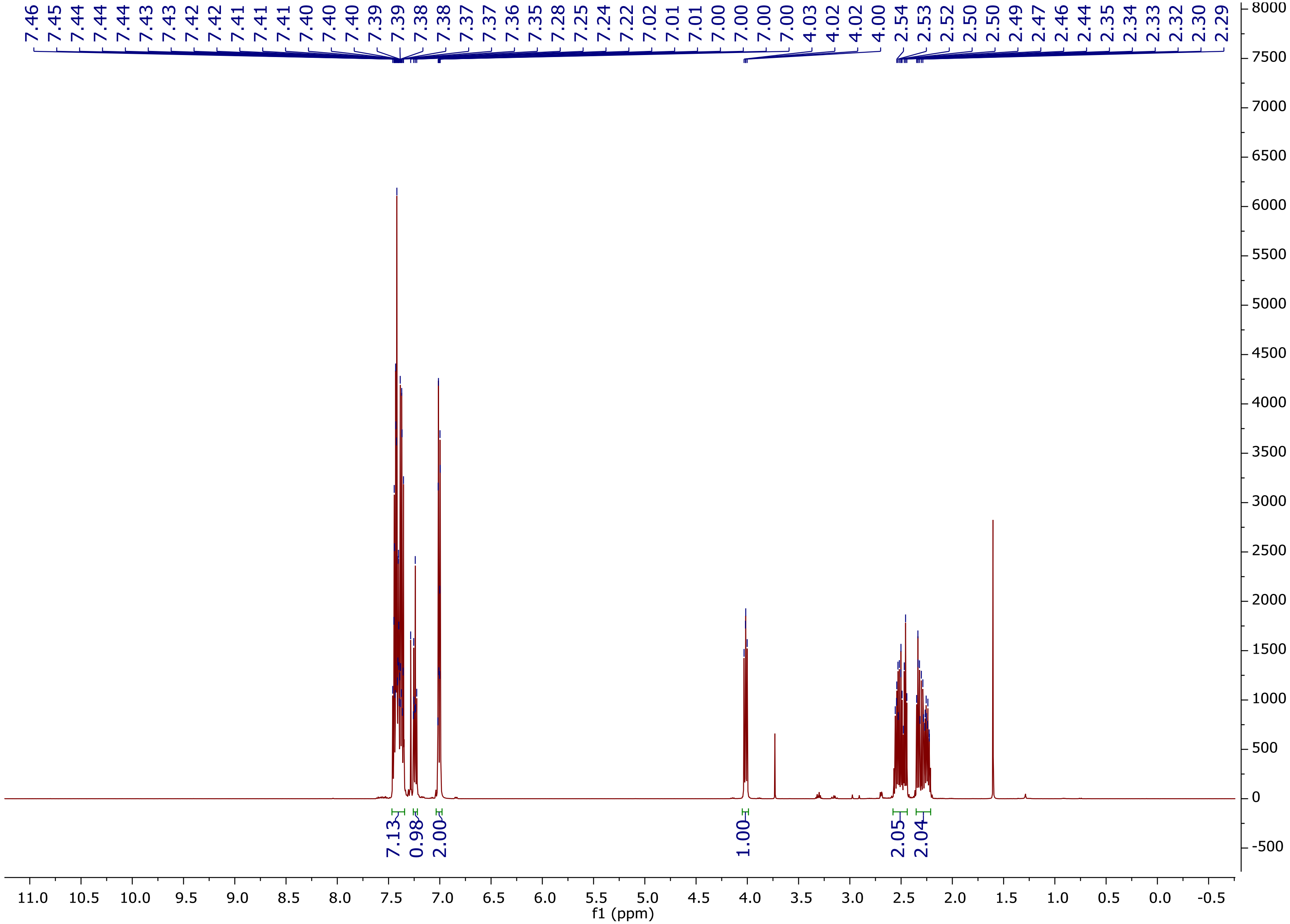

O
OPh
Cl

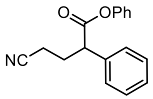
38


171.87
150.66
137.24
129.41
129.11
128.10
127.92
125.96
121.33
48.37
42.44
35.64
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
230
220
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)

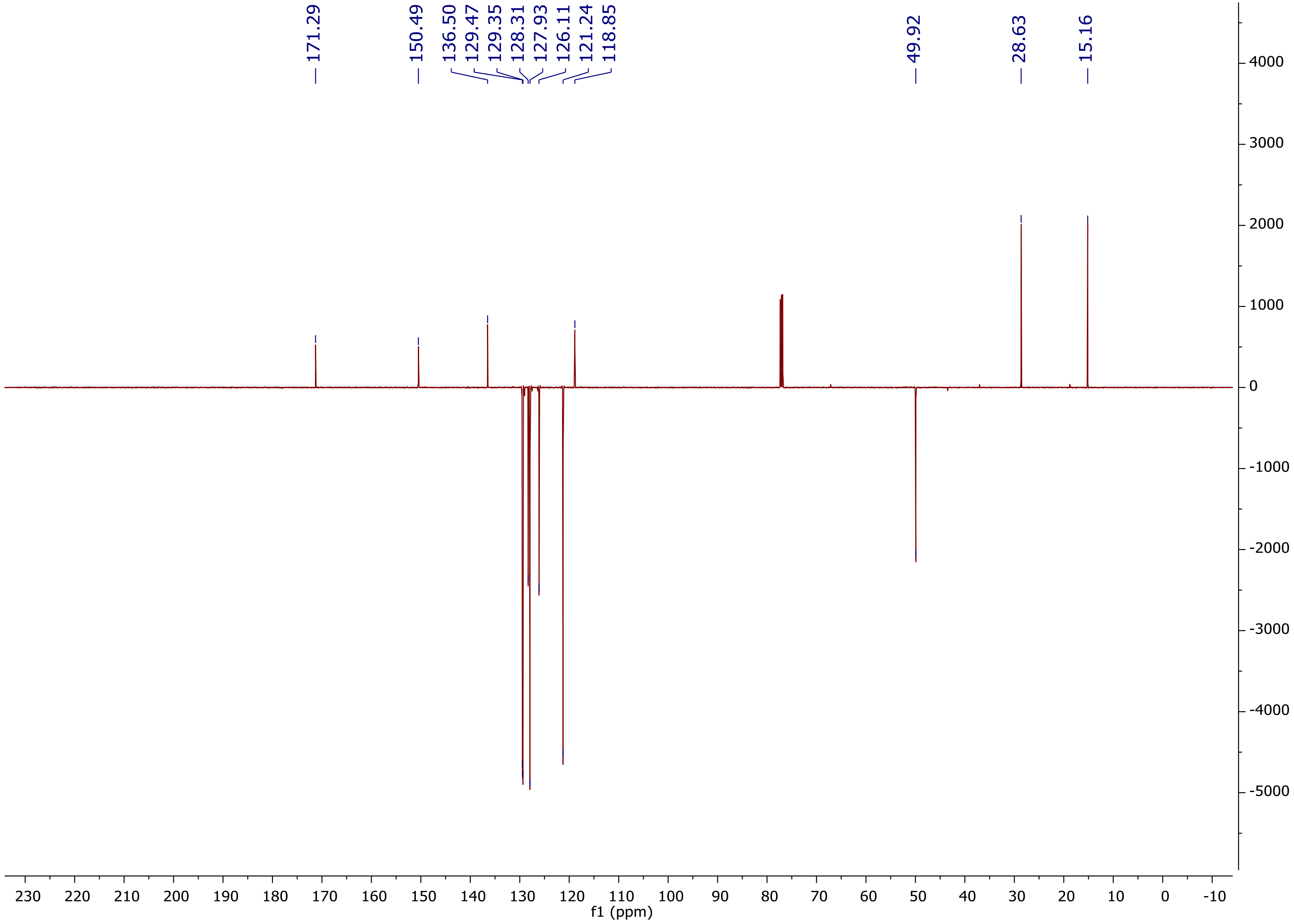

O
OPh
NC

39

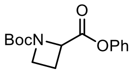

7.46
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.28
7.25
7.24
7.22
7.02
7.01
7.01
7.00
7.00
7.00
7.00
4.03
4.02
4.02
4.00
2.54
2.53
2.52
2.50
2.50
2.49
2.47
2.46
2.44
2.35
2.34
2.33
2.32
2.30
2.29
7.13
0.98
2.00
1.00
2.05
2.04
11.0
10.5
10.0
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)
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500



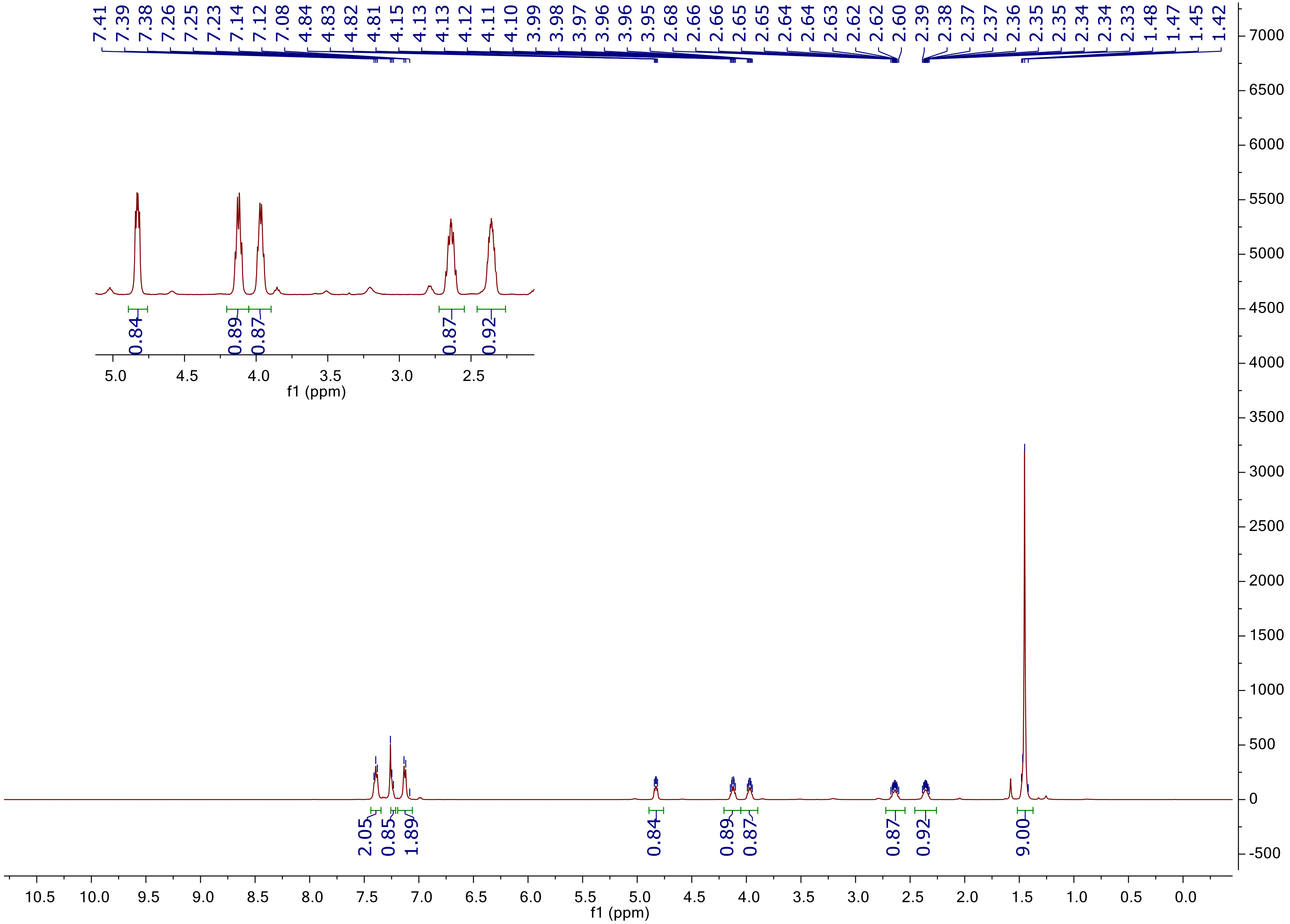
39

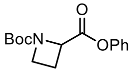


171.29
150.49
136.50
129.47
129.35
128.31
127.93
126.11
121.24
118.85
49.92
28.63
15.16
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

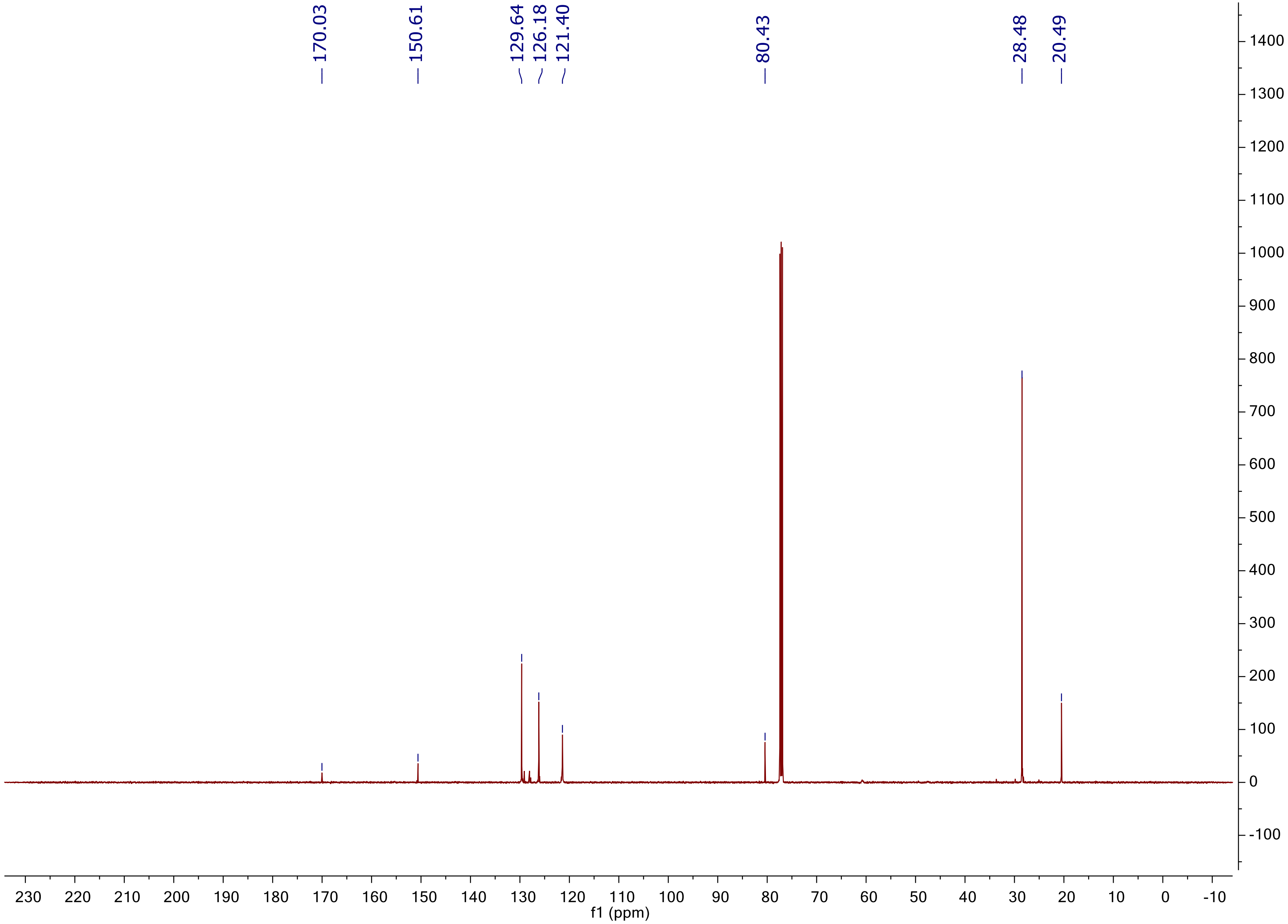

BocN
O
OPh

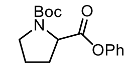
40


7.41
7.39
7.38
7.26
7.25
7.23
7.14
7.12
7.08
4.84
4.83
4.82
4.81
4.15
4.13
4.13
4.12
4.11
4.10
3.99
3.98
3.97
3.96
3.96
3.95
2.68
2.66
2.66
2.65
2.65
2.64
2.64
2.63
2.62
2.62
2.60
2.39
2.38
2.37
2.37
2.36
2.35
2.35
2.34
2.34
2.33
1.48
1.47
1.45
1.42
0.84
0.89
0.87
0.87
0.92
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)
2.05
0.85
1.89
0.84
0.89
0.87
0.87
0.92
9.00
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
f1 (ppm)
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

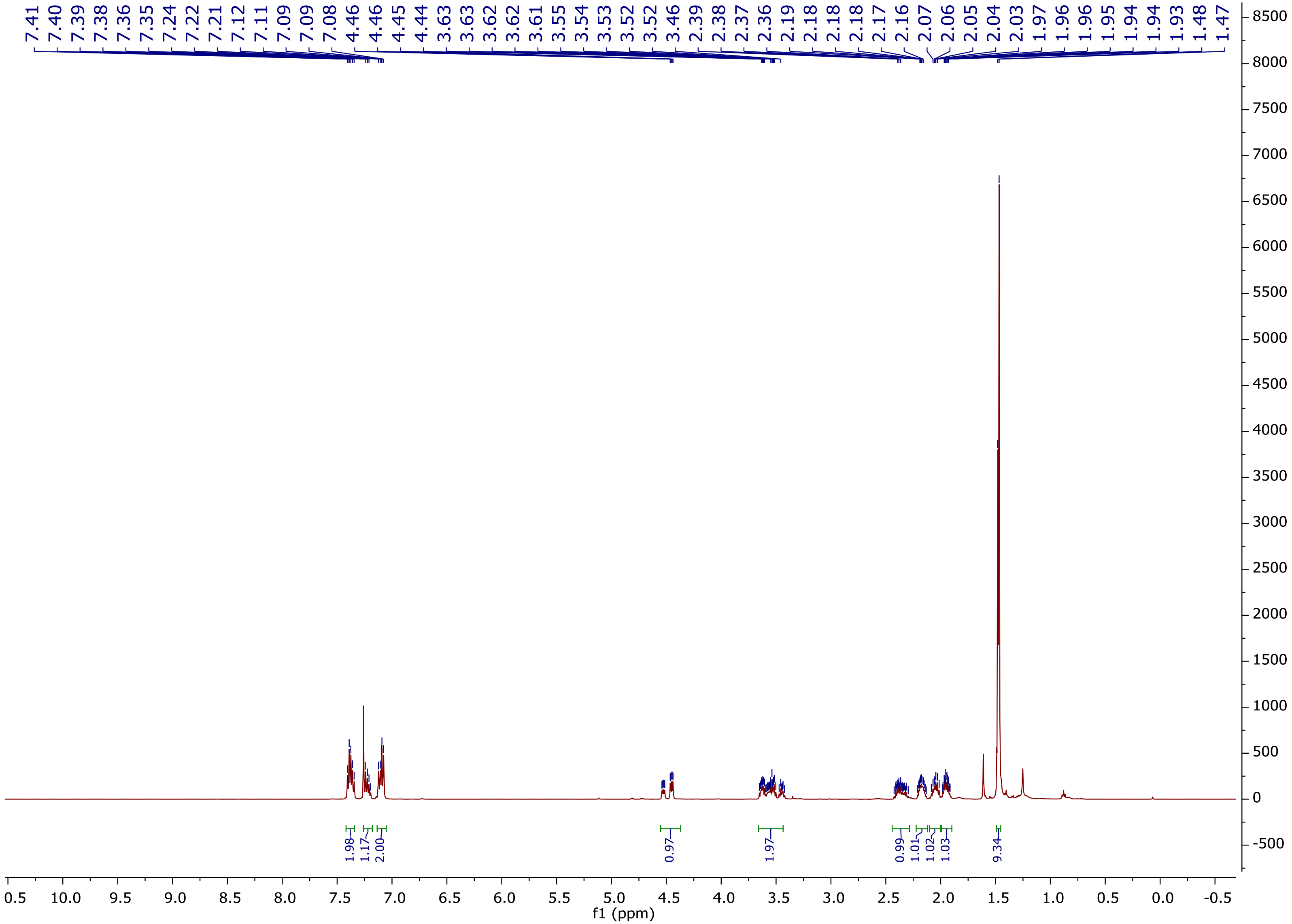

O
BocN
OPh

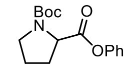
40


170.03
150.61
129.64
126.18
121.40
80.43
28.48
20.49
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
230
220
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)

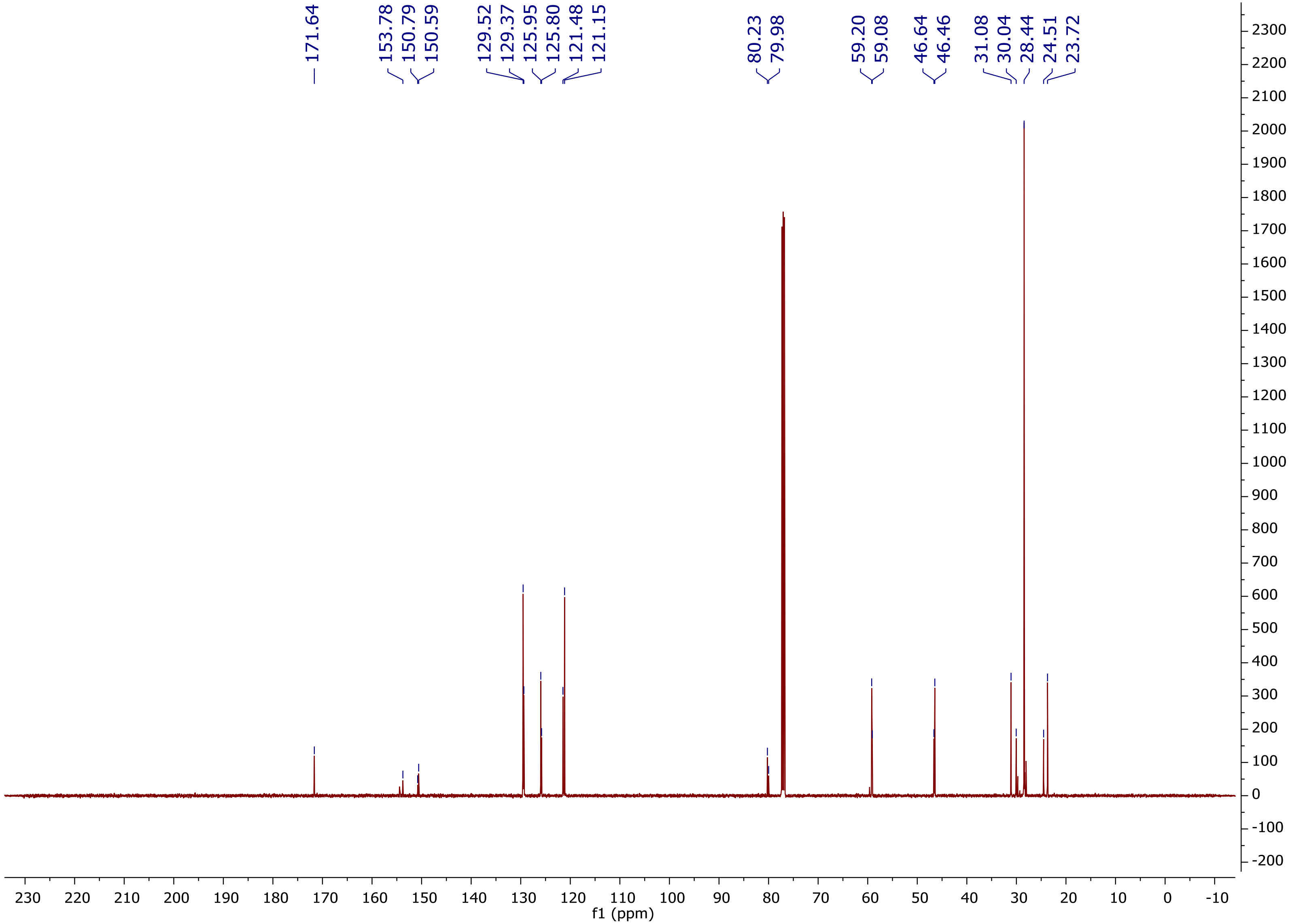

Boc
N
O
OPh

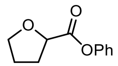
41


7.41
7.40
7.39
7.38
7.36
7.35
7.24
7.22
7.21
7.12
7.11
7.09
7.09
7.08
4.46
4.46
4.45
4.44
3.63
3.63
3.62
3.62
3.61
3.55
3.54
3.53
3.52
3.52
3.46
2.39
2.38
2.37
2.36
2.19
2.18
2.18
2.18
2.17
2.16
2.07
2.06
2.05
2.04
2.03
1.97
1.96
1.96
1.95
1.94
1.94
1.93
1.48
1.47
1.98
1.17
2.00
0.97
1.97
0.99
1.01
1.02
1.03
9.34
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
-0.5
f1 (ppm)
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

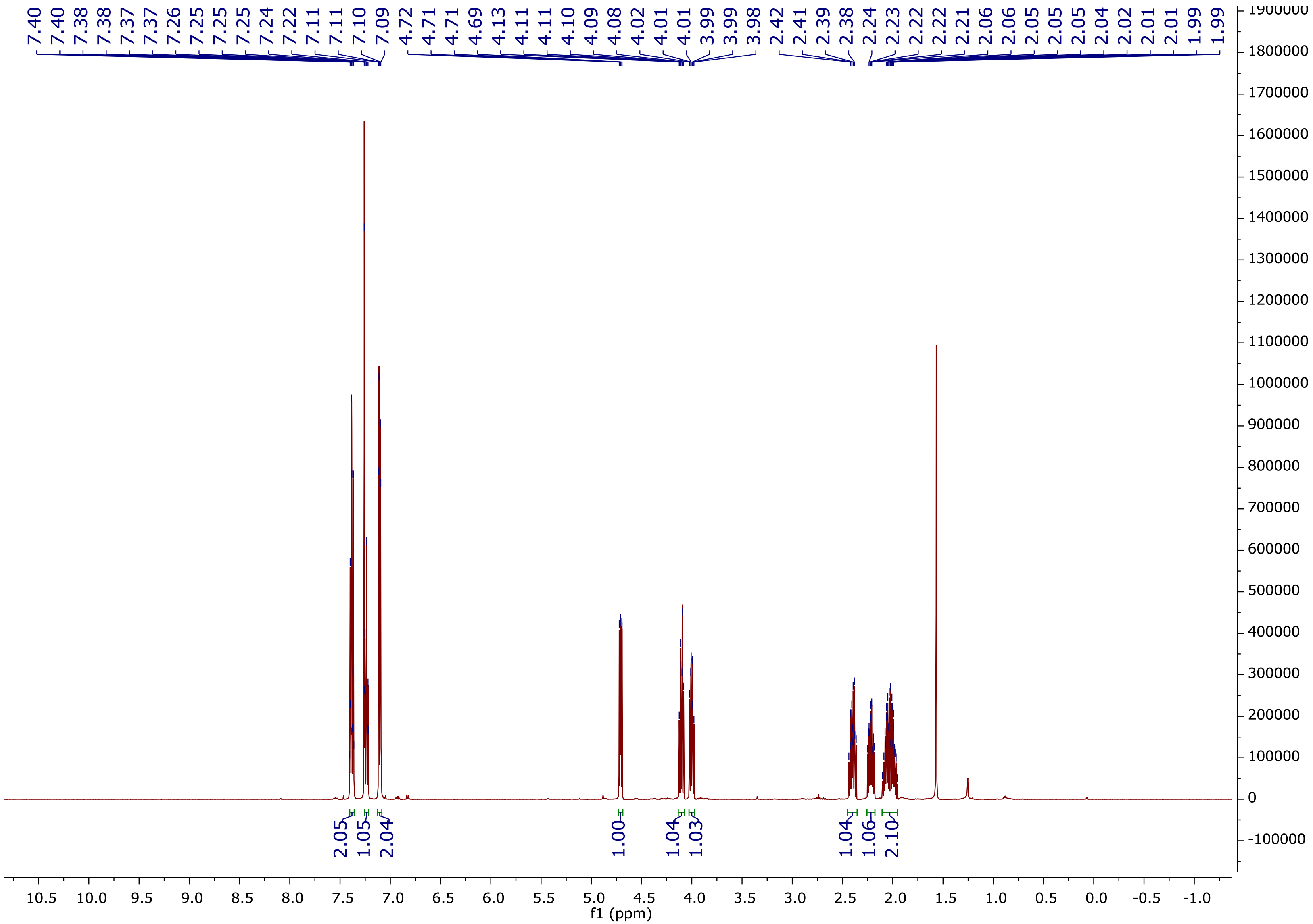

Boc
N
O
OPh

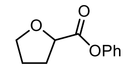
41


171.64
153.78
150.79
150.59
129.52
129.37
125.95
125.80
121.48
121.15
80.23
79.98
59.20
59.08
46.64
46.46
31.08
30.04
28.44
24.51
23.72
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
230
220
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)

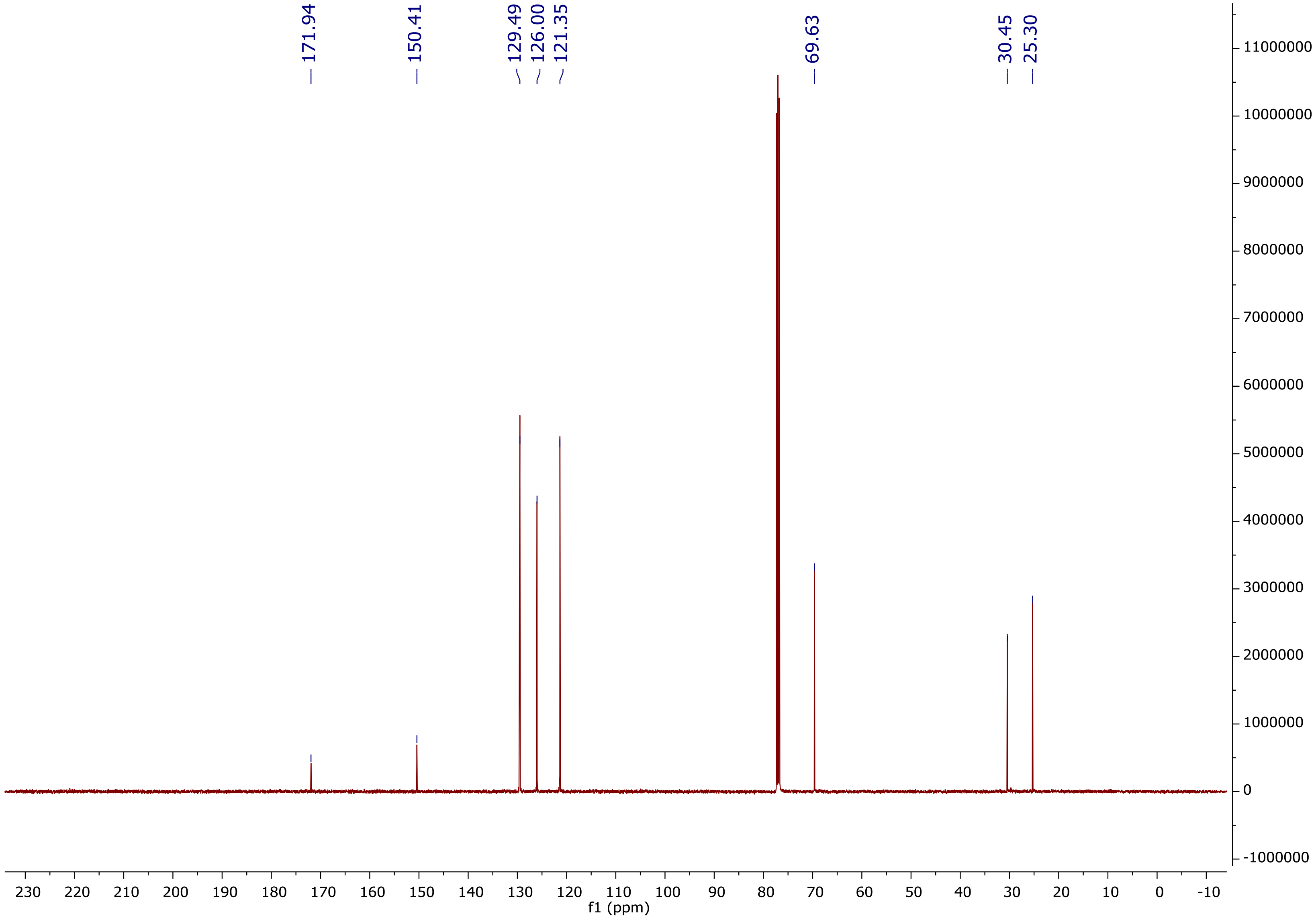

O
O
OPh

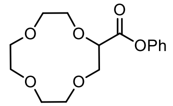
42


7.40
7.40
7.38
7.38
7.37
7.37
7.26
7.25
7.25
7.25
7.24
7.22
7.11
7.11
7.10
7.09
4.72
4.71
4.71
4.69
4.13
4.11
4.11
4.10
4.09
4.08
4.02
4.01
4.01
3.99
3.99
3.98
2.42
2.41
2.39
2.38
2.24
2.23
2.22
2.22
2.21
2.06
2.06
2.05
2.05
2.05
2.04
2.02
2.01
2.01
1.99
1.99
2.05
1.05
2.04
1.00
1.04
1.03
1.04
1.06
2.10
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
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
-1.0
f1 (ppm)

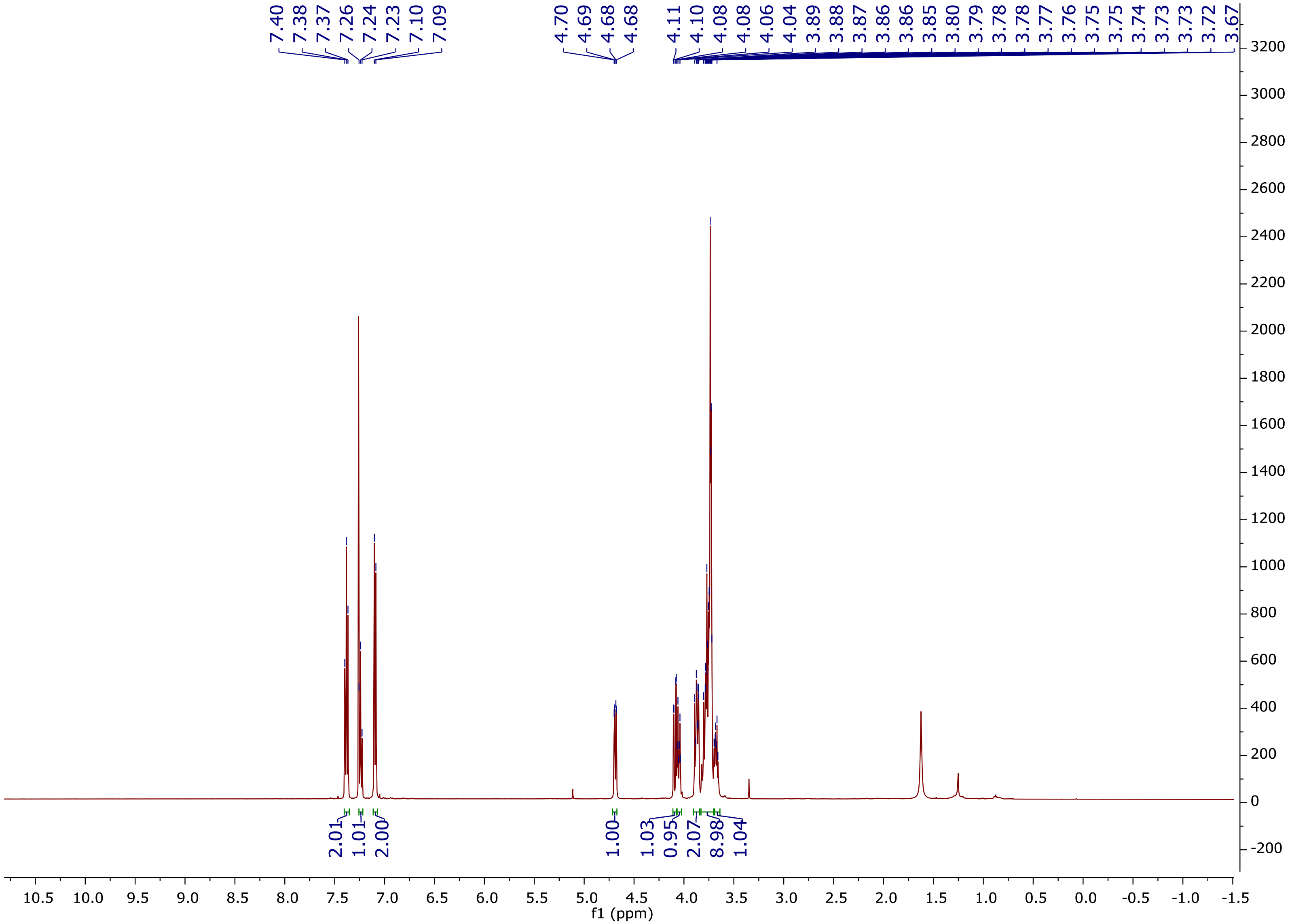

O
O
OPh

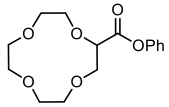
42


171.94
150.41
129.49
126.00
121.35
69.63
30.45
25.30
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
230
220
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)

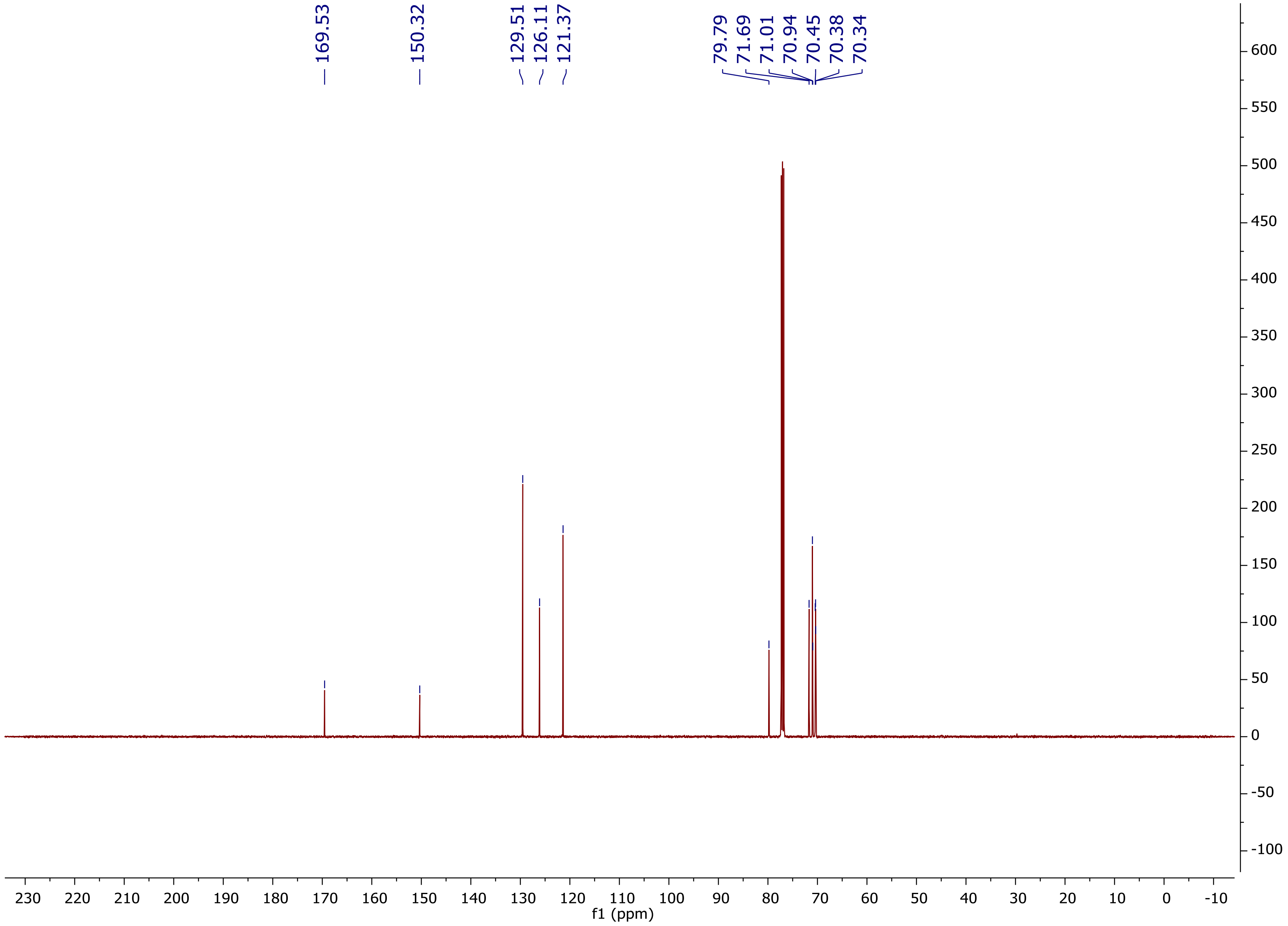

O
OPh
O
O
O
O

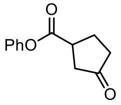
43


7.40
7.38
7.37
7.26
7.24
7.23
7.10
7.09
4.70
4.69
4.68
4.68
4.11
4.10
4.08
4.08
4.06
4.04
3.89
3.88
3.87
3.86
3.86
3.85
3.80
3.79
3.78
3.78
3.77
3.76
3.75
3.75
3.74
3.73
3.73
3.72
3.67
2.01
1.01
2.00
1.00
1.03
0.95
2.07
8.98
1.04
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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
-1.0
-1.5
f1 (ppm)

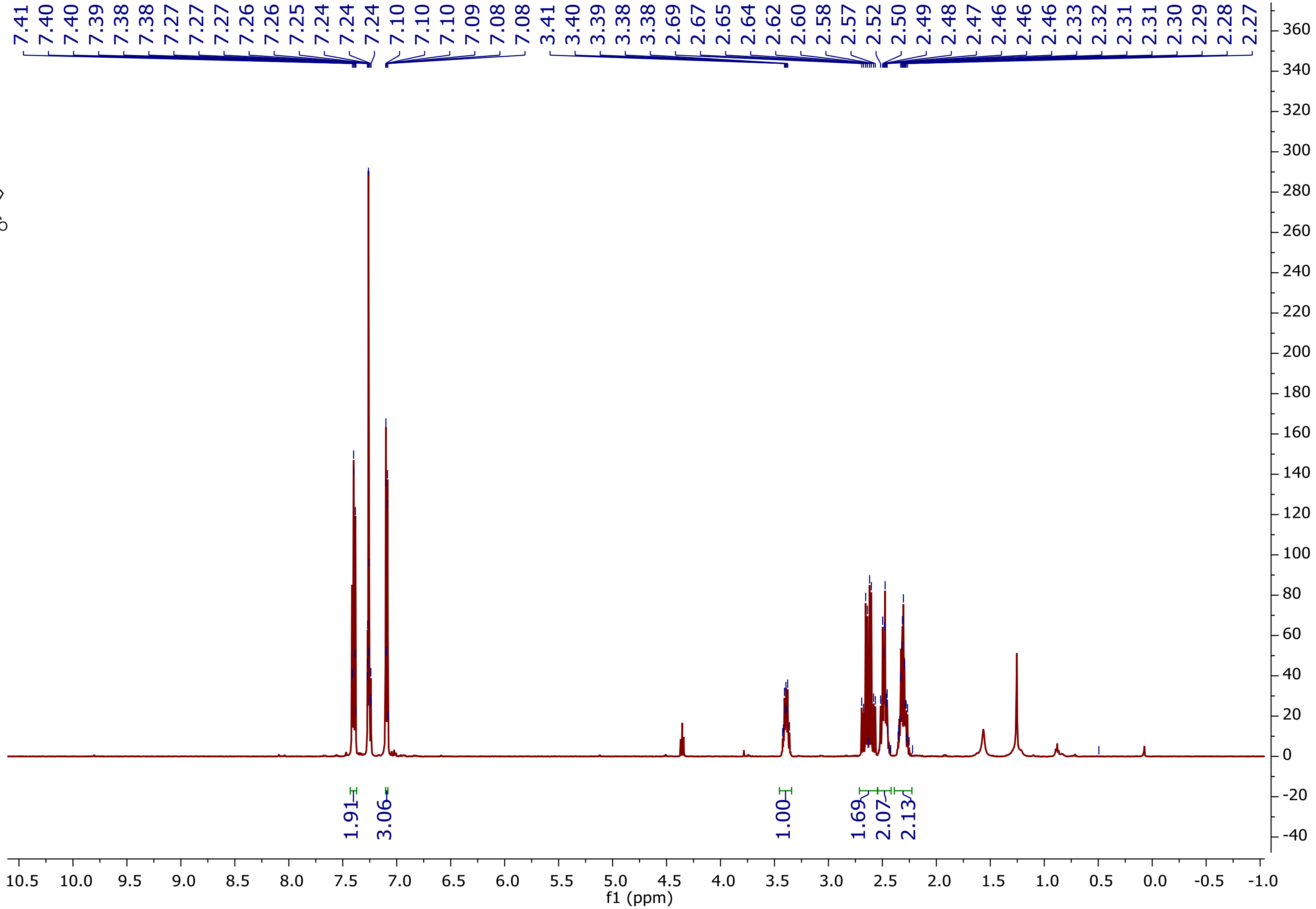

O
OPh
O
O
O
O

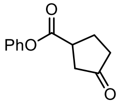
43


169.53
150.32
129.51
126.11
121.37
79.79
71.69
71.01
70.94
70.45
70.38
70.34
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
230
220
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)

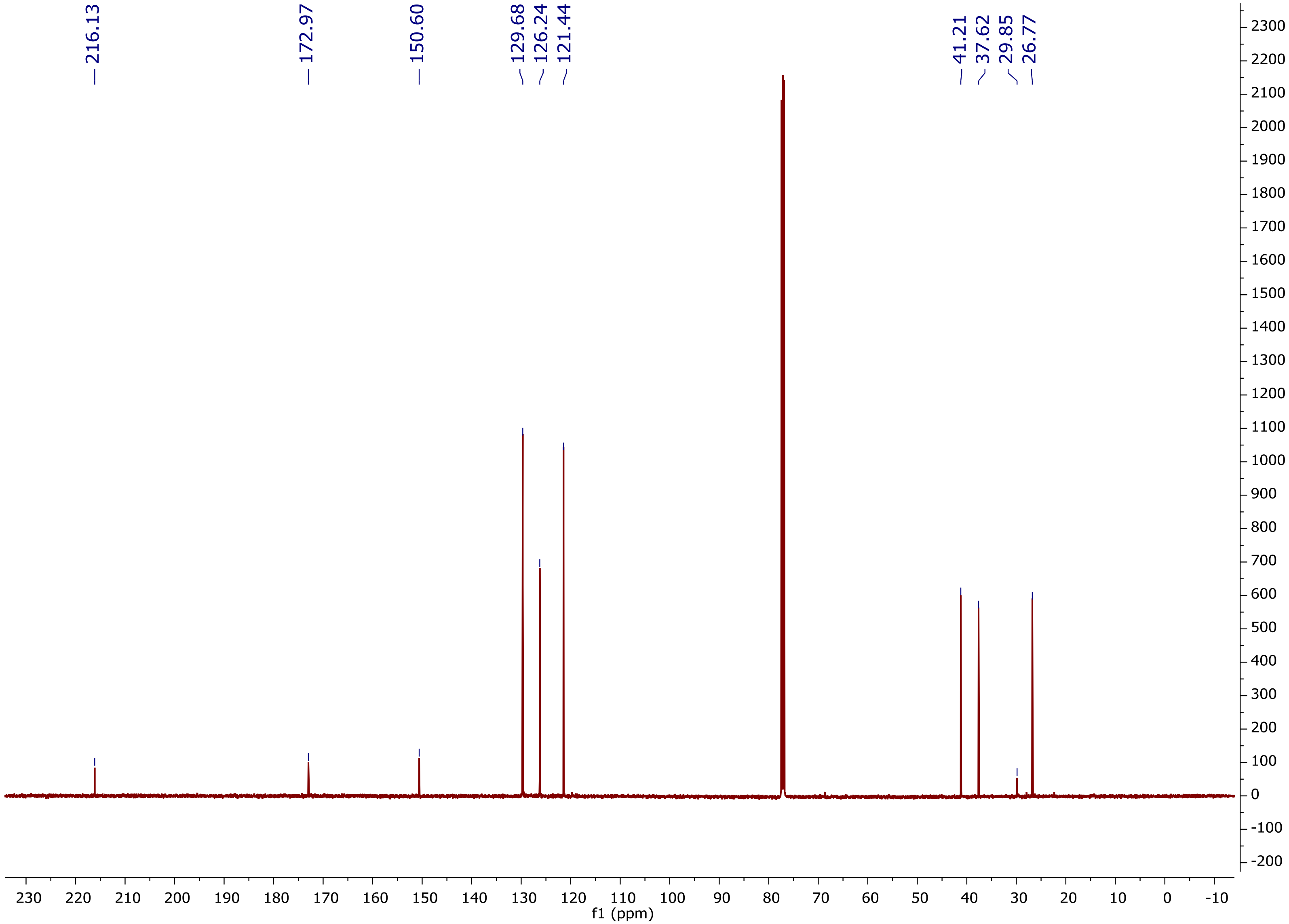

O
PhO
O

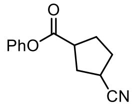
44


7.41
7.40
7.40
7.39
7.38
7.38
7.27
7.27
7.27
7.26
7.26
7.25
7.24
7.24
7.24
7.10
7.10
7.10
7.09
7.08
7.08
3.41
3.40
3.39
3.38
3.38
2.69
2.67
2.65
2.64
2.62
2.60
2.58
2.57
2.52
2.50
2.49
2.48
2.47
2.46
2.46
2.46
2.33
2.32
2.31
2.31
2.30
2.29
2.28
2.27
1.91
3.06
1.00
1.69
2.07
2.13
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
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
-1.0
f1 (ppm)

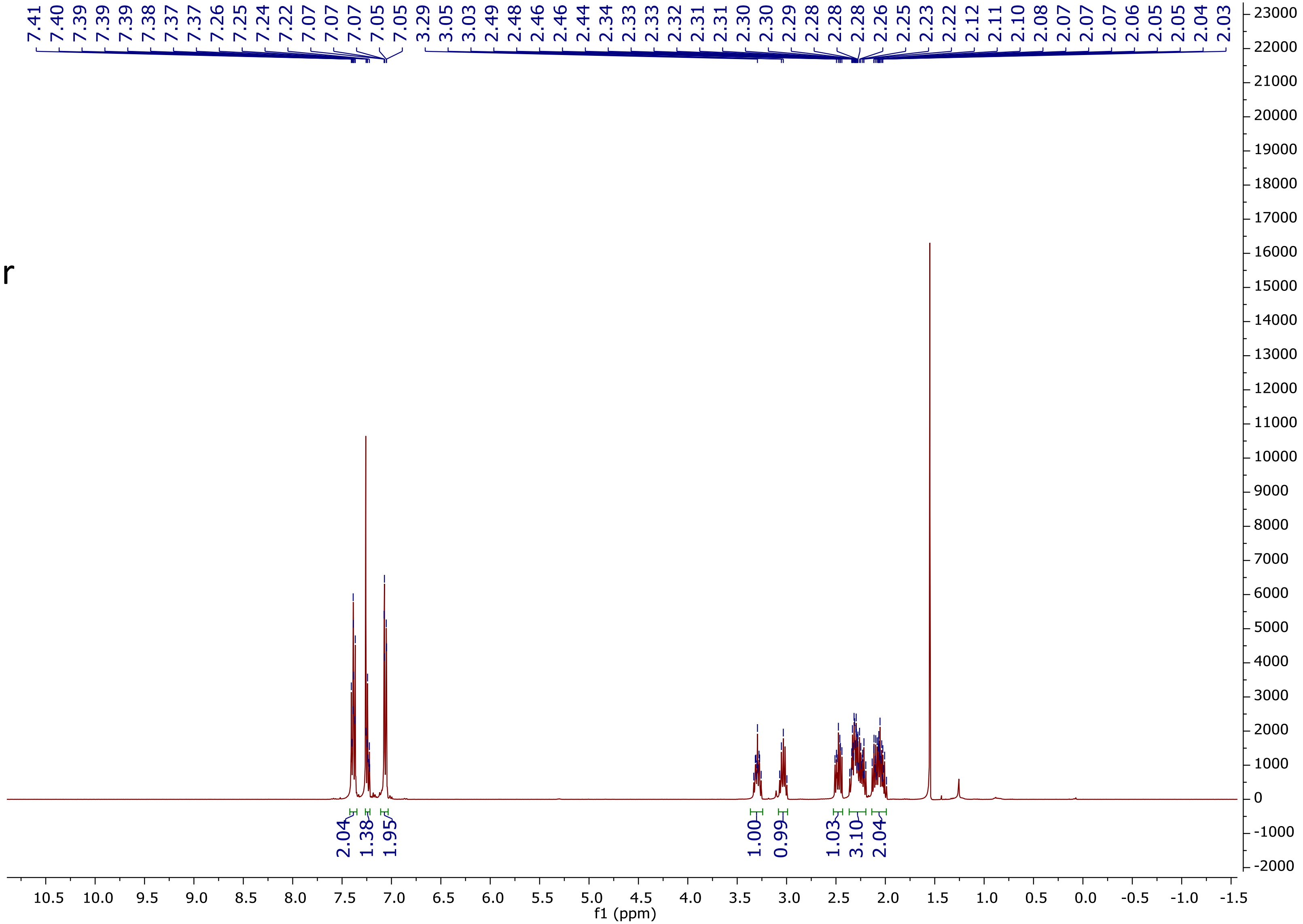

PhO
O
O

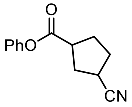
44


216.13
172.97
150.60
129.68
126.24
121.44
41.21
37.62
29.85
26.77
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
230
220
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)

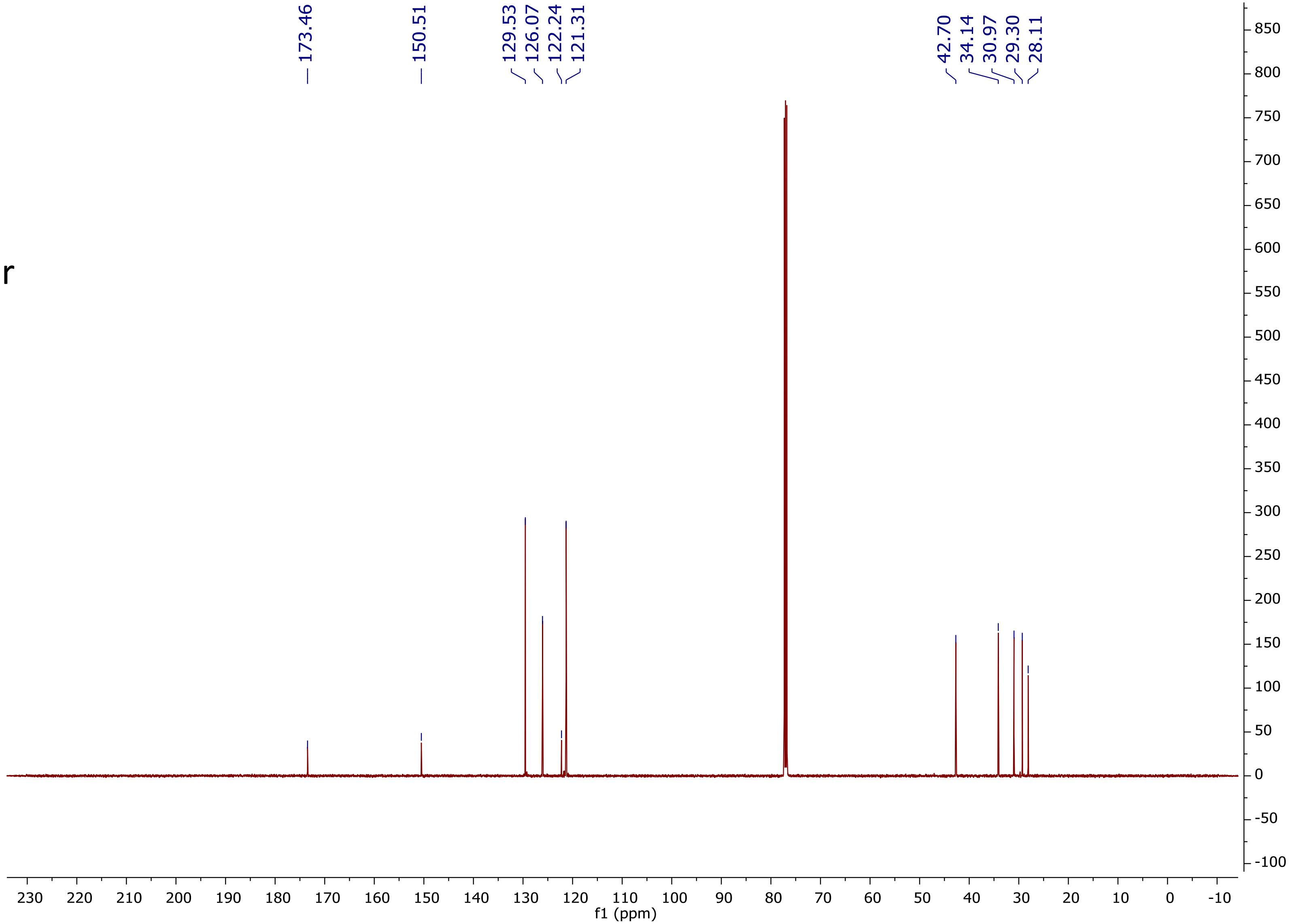

O
PhO
CN

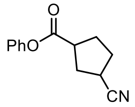
45 - Major


7.41
7.40
7.39
7.39
7.39
7.38
7.37
7.37
7.26
7.25
7.24
7.22
7.07
7.07
7.07
7.05
7.05
3.29
3.05
3.03
2.49
2.48
2.46
2.46
2.44
2.34
2.33
2.33
2.32
2.31
2.31
2.30
2.30
2.29
2.28
2.28
2.28
2.26
2.25
2.23
2.22
2.12
2.11
2.10
2.08
2.07
2.07
2.07
2.06
2.05
2.05
2.04
2.03
2.04
1.38
1.95
1.00
0.99
1.03
3.10
2.04
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
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
-1.0
-1.5
f1 (ppm)

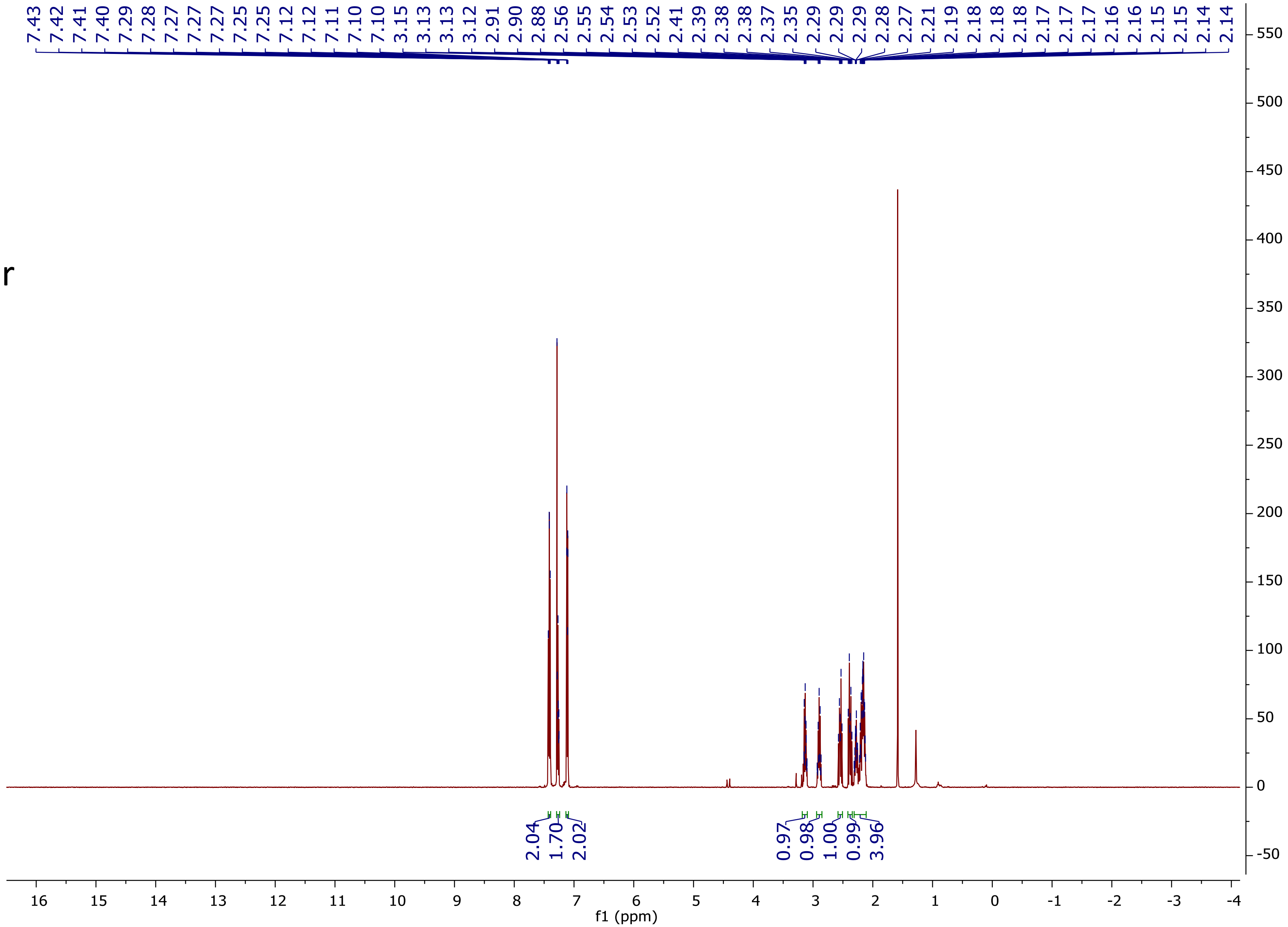

O
PhO
CN

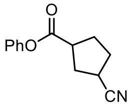
45 - Major


173.46
150.51
129.53
126.07
122.24
121.31
42.70
34.14
30.97
29.30
28.11
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
230
220
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)

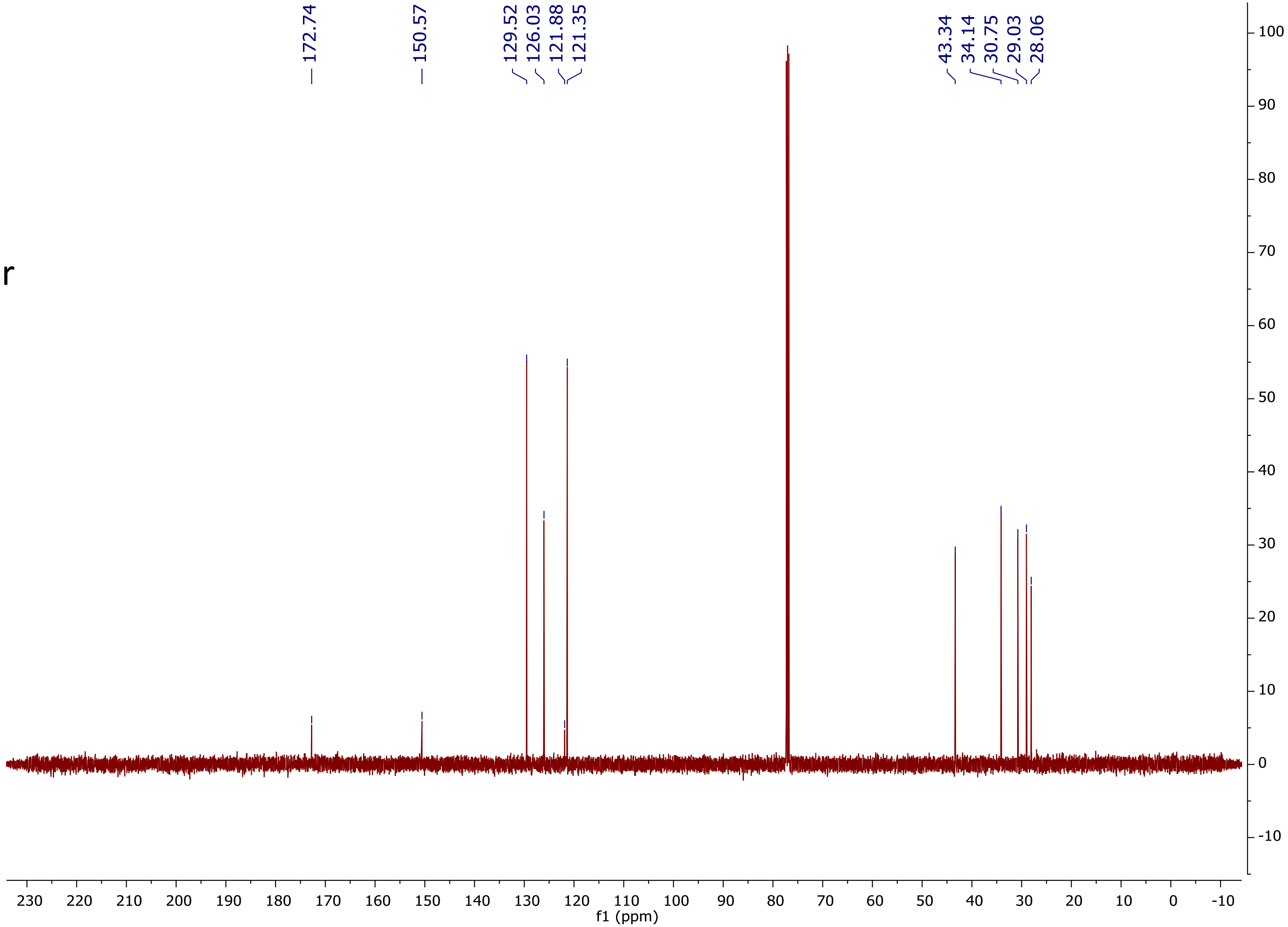

O
PhO
CN

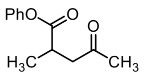
45 - Minor


7.43
7.42
7.41
7.40
7.29
7.28
7.27
7.27
7.27
7.25
7.25
7.12
7.12
7.11
7.10
7.10
3.15
3.13
3.13
3.12
2.91
2.90
2.88
2.56
2.55
2.54
2.53
2.52
2.41
2.39
2.38
2.38
2.37
2.35
2.29
2.29
2.29
2.28
2.27
2.21
2.19
2.18
2.18
2.18
2.17
2.17
2.17
2.16
2.16
2.15
2.15
2.14
2.14
2.04
1.70
2.02
0.97
0.98
1.00
0.99
3.96
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)
550
500
450
400
350
300
250
200
150
100
50
0
-50

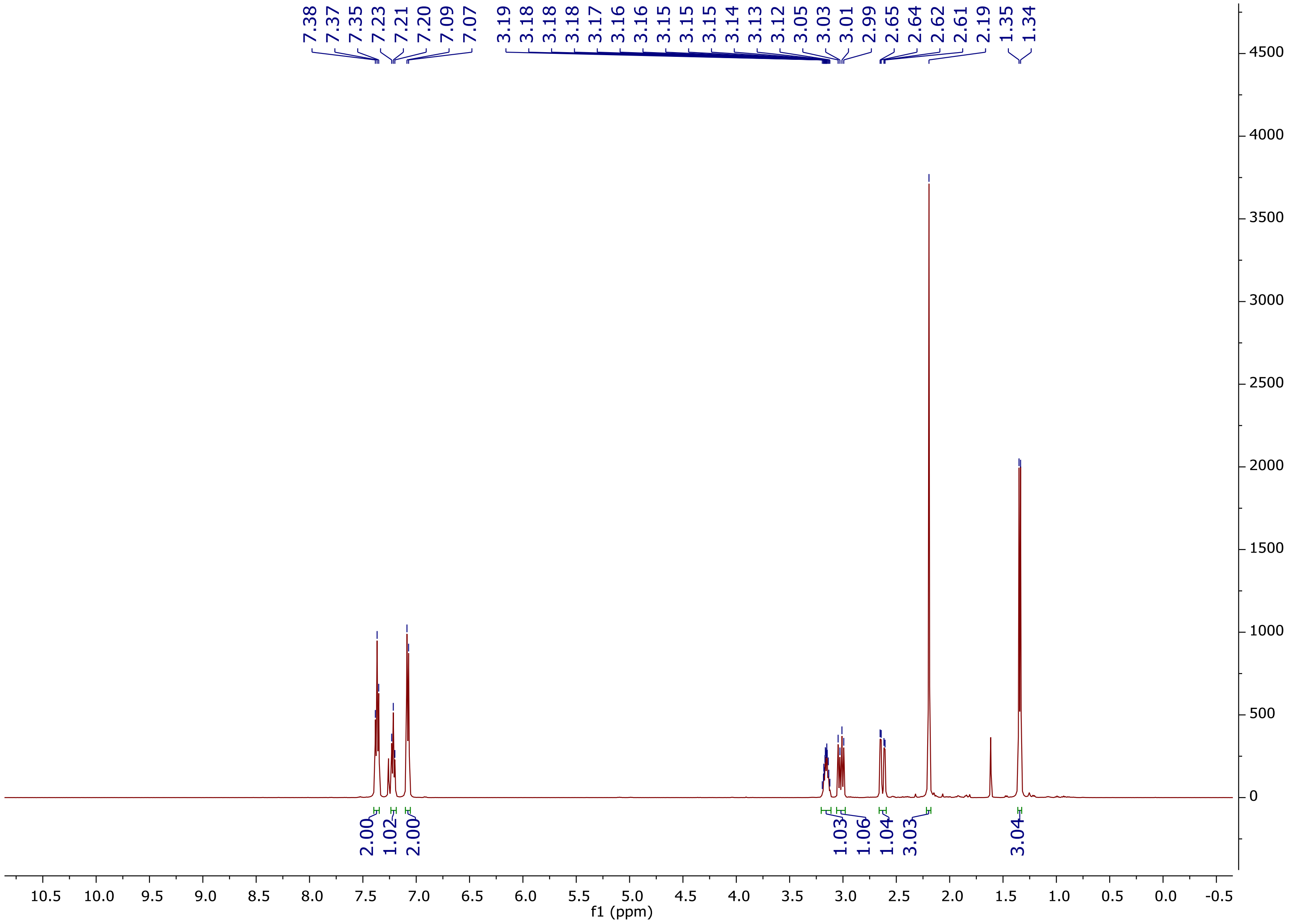

O
PhO
CN

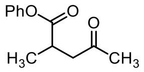
45 - Minor


172.74
150.57
129.52
126.03
121.88
121.35
43.34
34.14
30.75
29.03
28.06
100
90
80
70
60
50
40
30
20
10
0
-10
230
220
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)

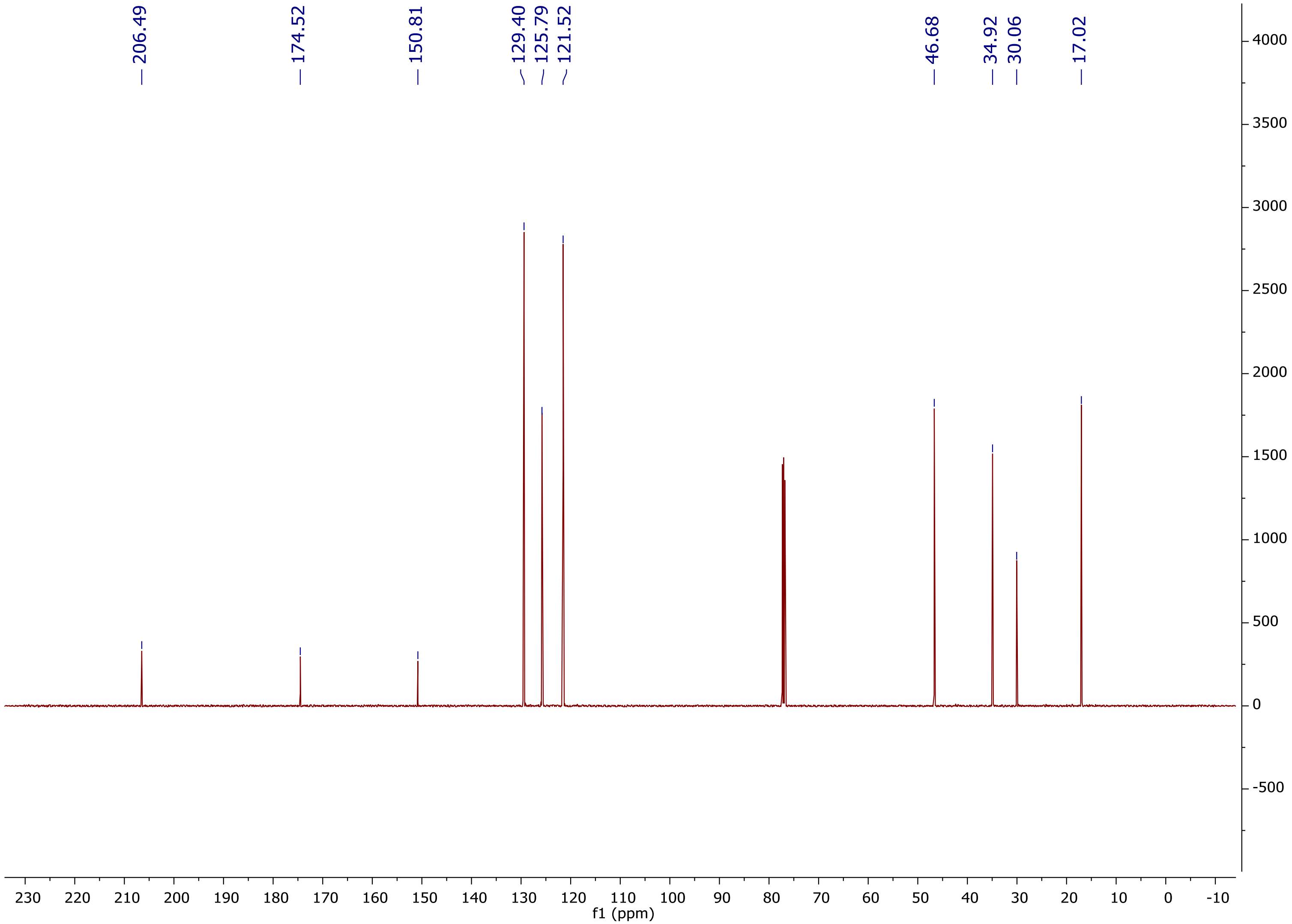

PhO
O
O
H3C
CH3

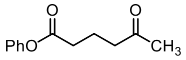
46-β


7.38
7.37
7.35
7.23
7.21
7.20
7.09
7.07
3.19
3.18
3.18
3.18
3.17
3.16
3.16
3.15
3.15
3.15
3.14
3.13
3.12
3.05
3.03
3.01
2.99
2.65
2.64
2.62
2.61
2.19
1.35
1.34
4500
4000
3500
3000
2500
2000
1500
1000
500
0
2.00
1.02
2.00
1.03
1.06
1.04
3.03
3.04
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)

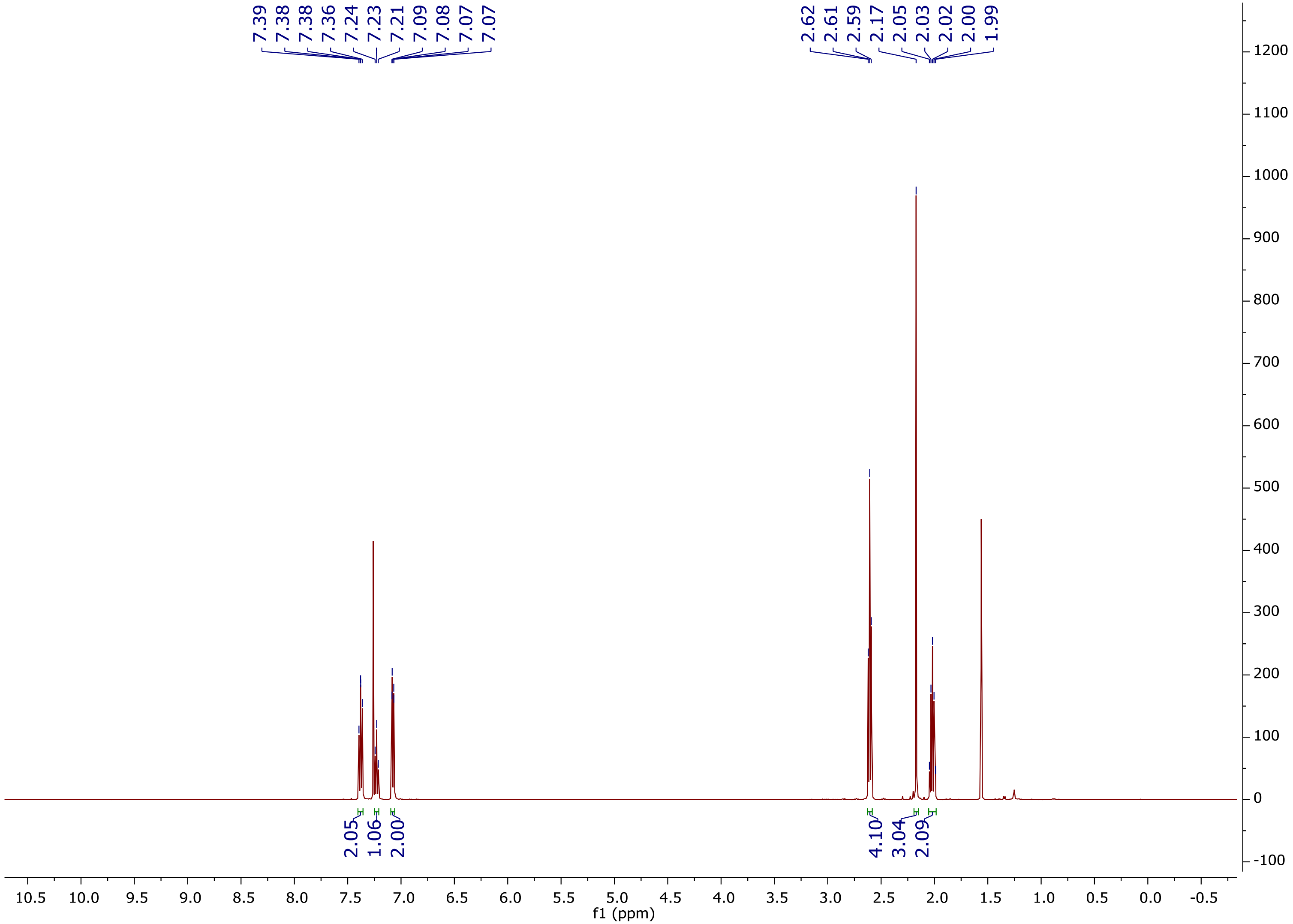

PhO
O
O
H3C
CH3

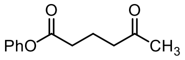
46-β


206.49
174.52
150.81
129.40
125.79
121.52
46.68
34.92
30.06
17.02
4000
3500
3000
2500
2000
1500
1000
500
0
-500
230
220
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)

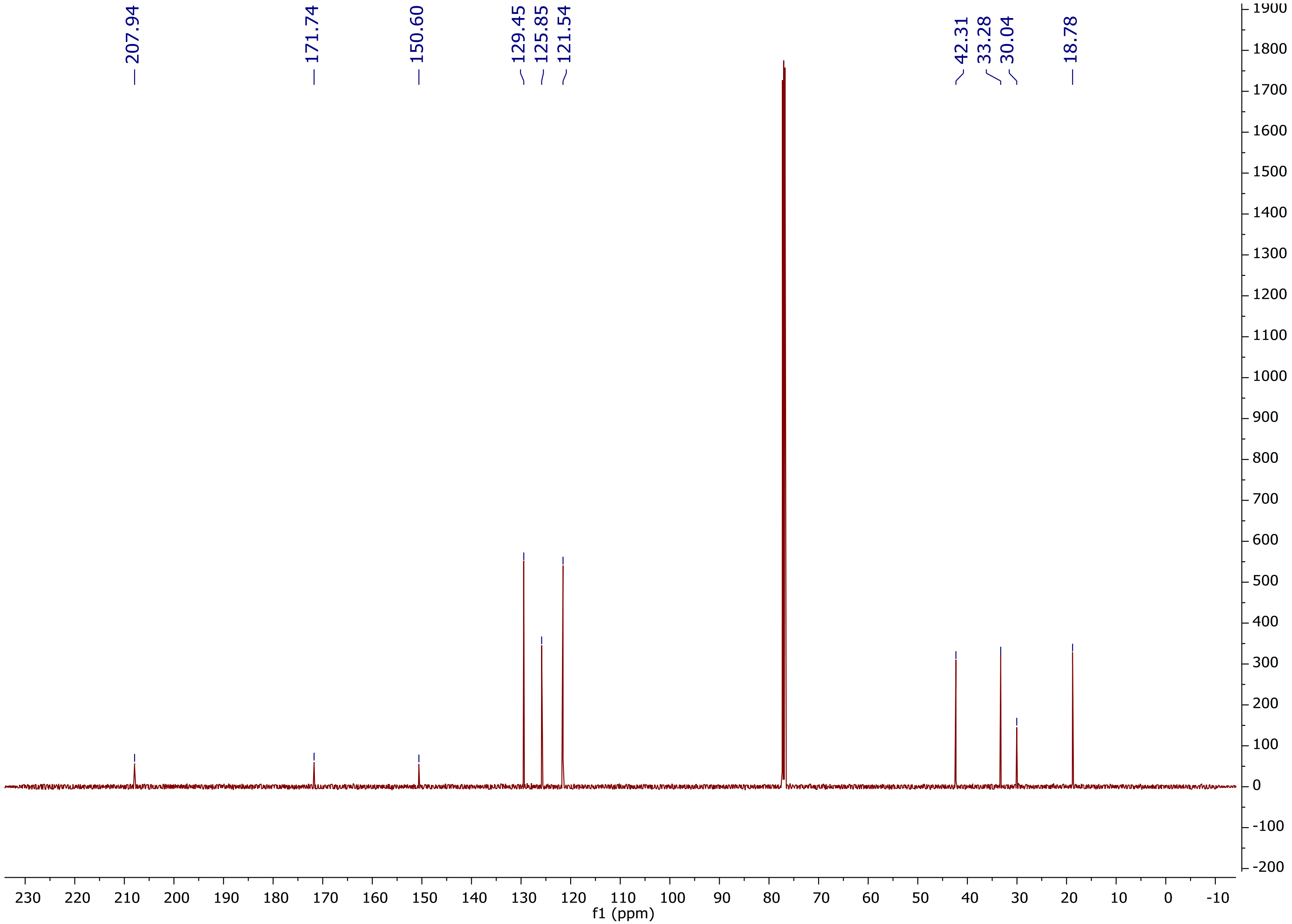

O
O
PhO
CH3

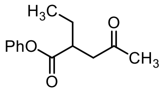
46-γ


7.39
7.38
7.38
7.36
7.24
7.23
7.21
7.09
7.08
7.07
7.07
2.62
2.61
2.59
2.17
2.05
2.03
2.02
2.00
1.99
2.05
1.06
2.00
4.10
3.04
2.09
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
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)

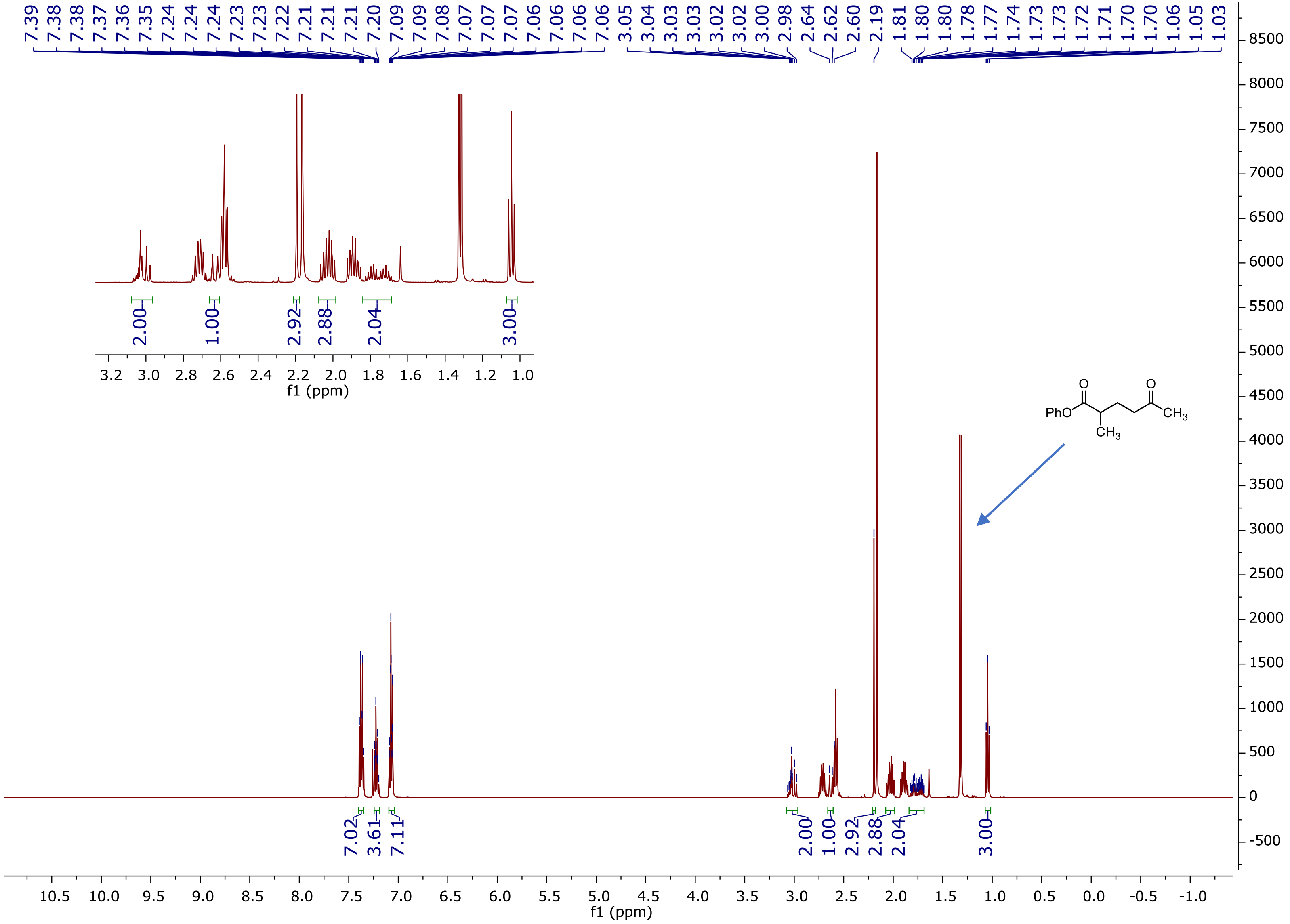

O
O
PhO
CH$_3$

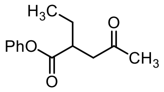
46-γ


207.94
171.74
150.60
129.45
125.85
121.54
42.31
33.28
30.04
18.78
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
230
220
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)

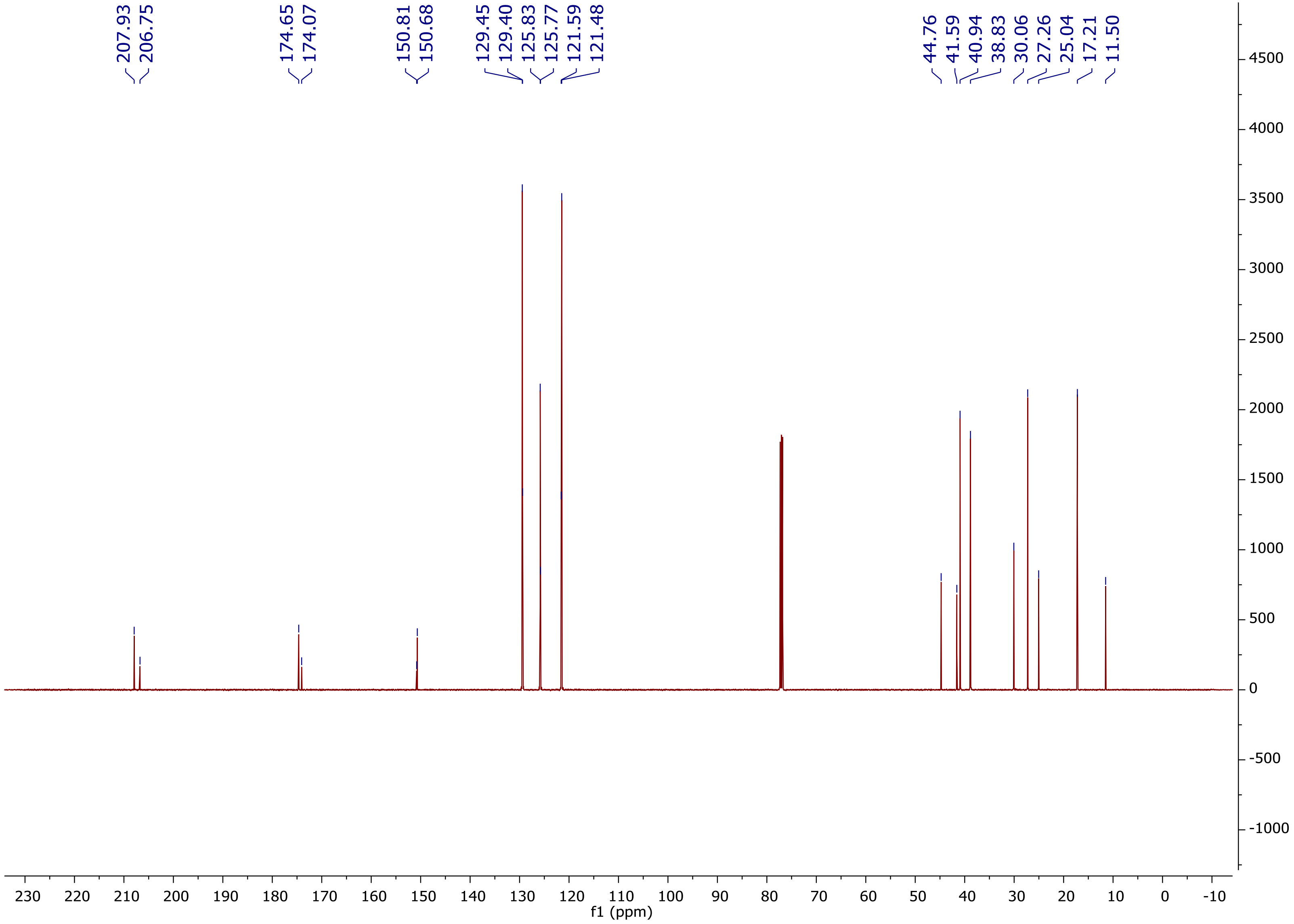

H$_3$C
PhO
O
O
CH$_3$

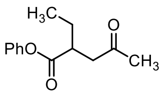
47-β


7.39
7.38
7.38
7.37
7.36
7.35
7.24
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.21
7.20
7.09
7.09
7.08
7.07
7.07
7.07
7.06
7.06
7.06
7.06
3.05
3.04
3.03
3.03
3.02
3.02
3.00
2.98
2.64
2.62
2.60
2.19
1.81
1.80
1.80
1.78
1.77
1.74
1.73
1.73
1.72
1.71
1.70
1.70
1.06
1.05
1.03
2.00
1.00
2.92
2.88
2.04
3.00
3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f1 (ppm)
PhO
O
O
CH$_3$
CH$_3$
7.02
3.61
7.11
2.00
1.00
2.92
2.88
2.04
3.00
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 -1.0
f1 (ppm)
8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500


H3C
PhO
O
O
CH3

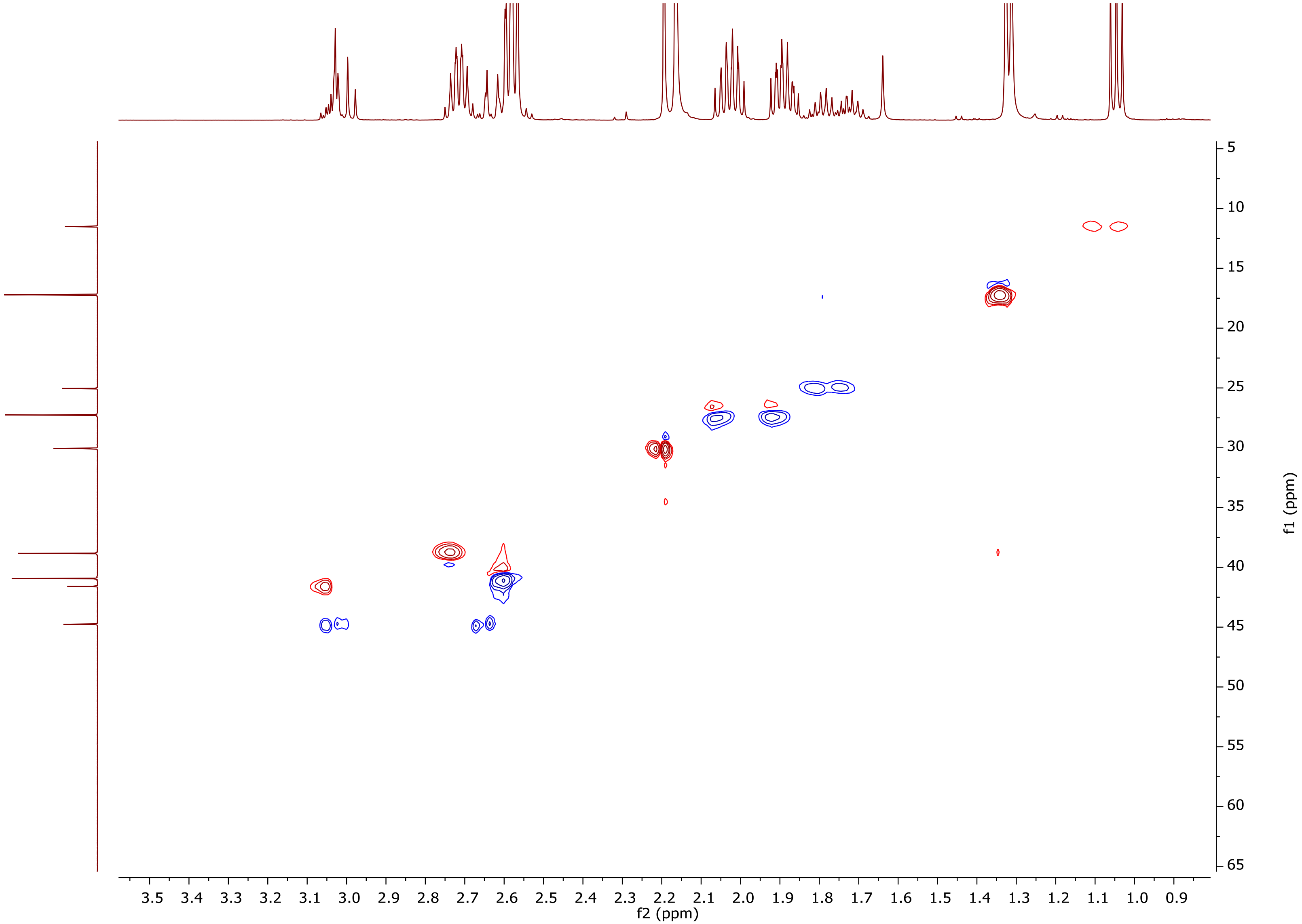
47-β


207.93
206.75
174.65
174.07
150.81
150.68
129.45
129.40
125.83
125.77
121.59
121.48
44.76
41.59
40.94
38.83
30.06
27.26
25.04
17.21
11.50
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
230
220
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)

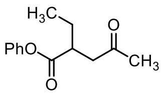


47-β

HSQC



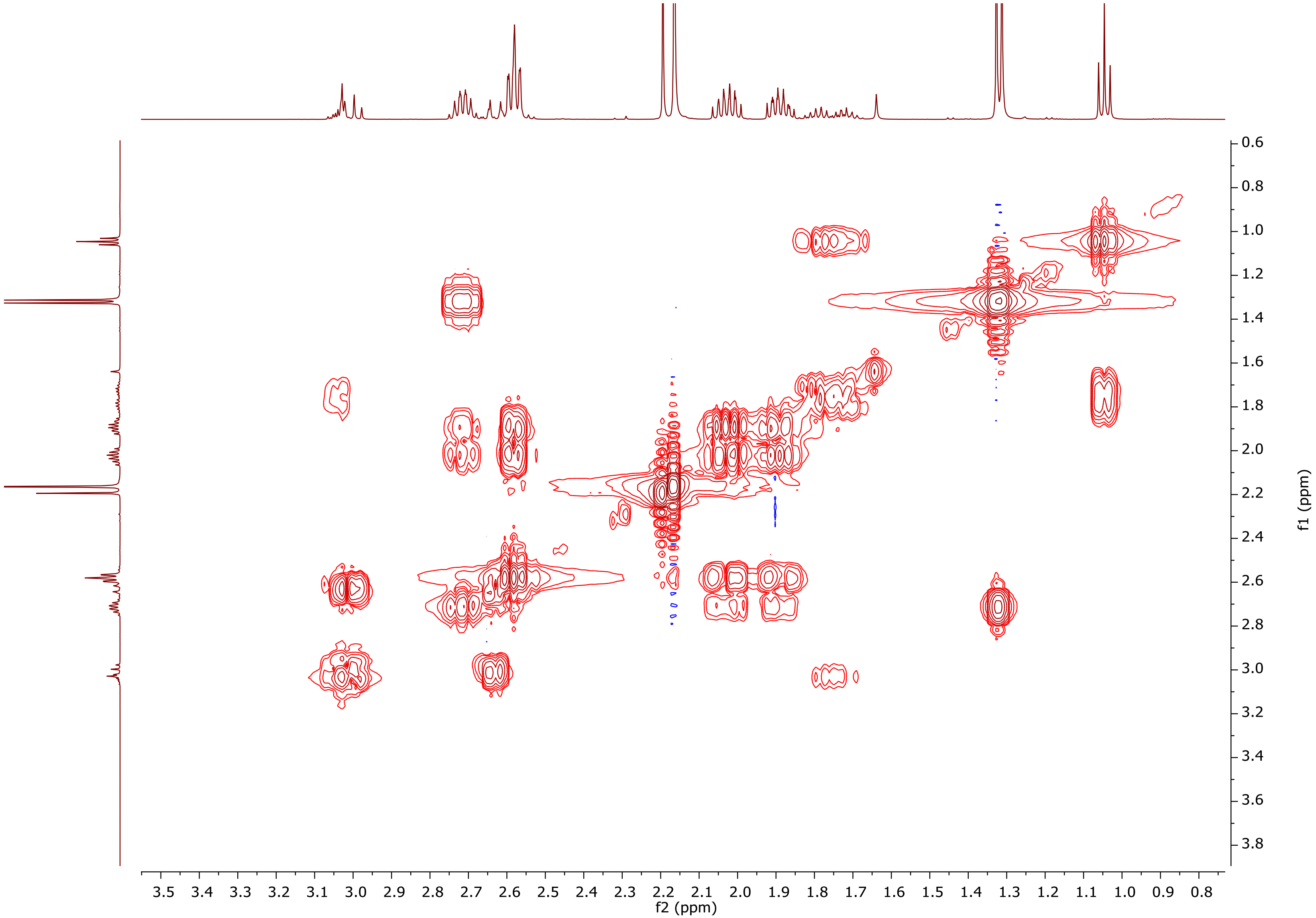
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
f2 (ppm)
5
10
15
20
25
30
35
40
45
50
55
60
65
f1 (ppm)



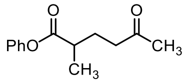
H_3C
PhO
O
O
CH_3

47-β

COSY

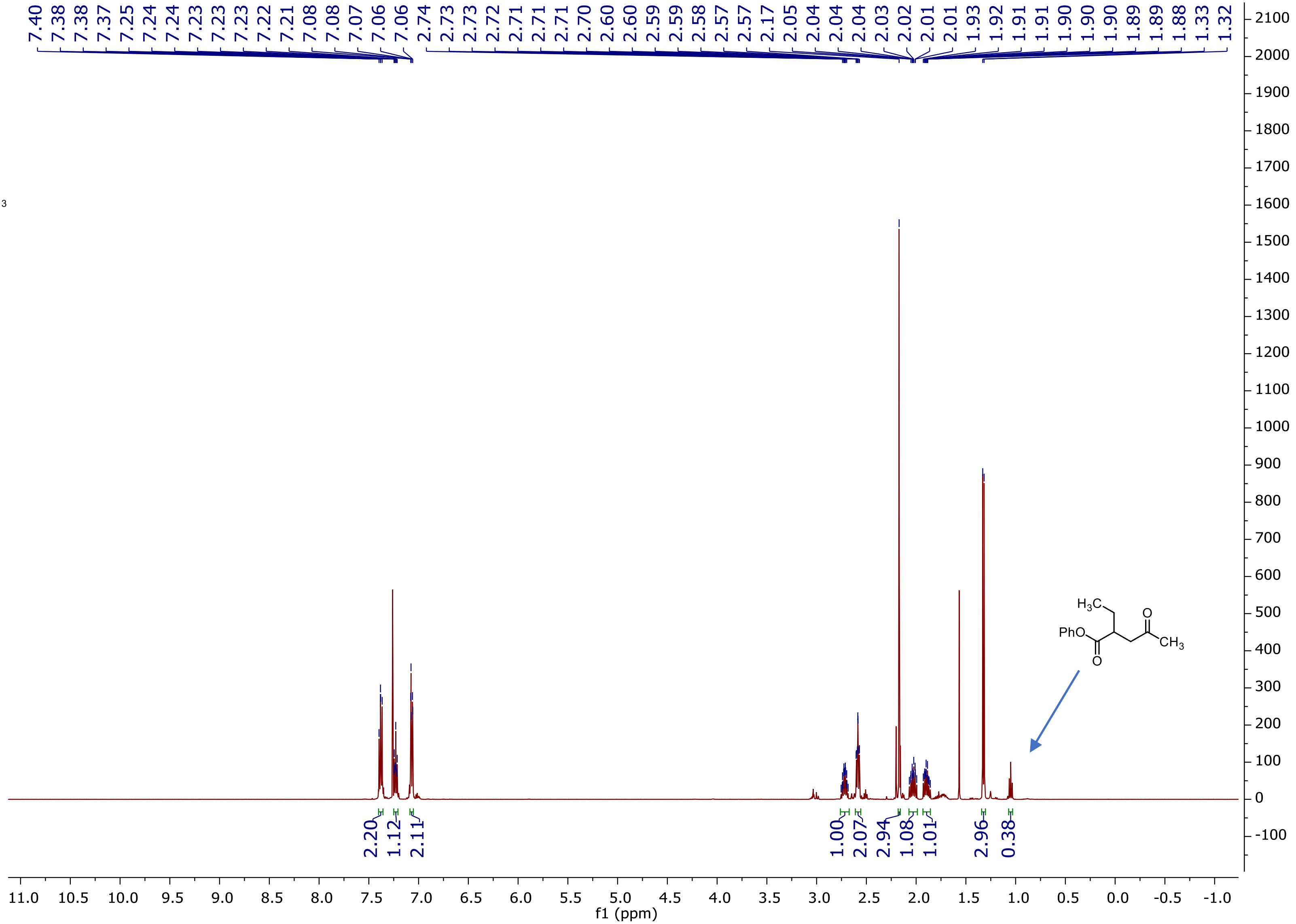


0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
f1 (ppm)
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
f2 (ppm)

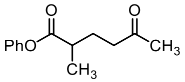


PhO
O
O
CH3
CH3

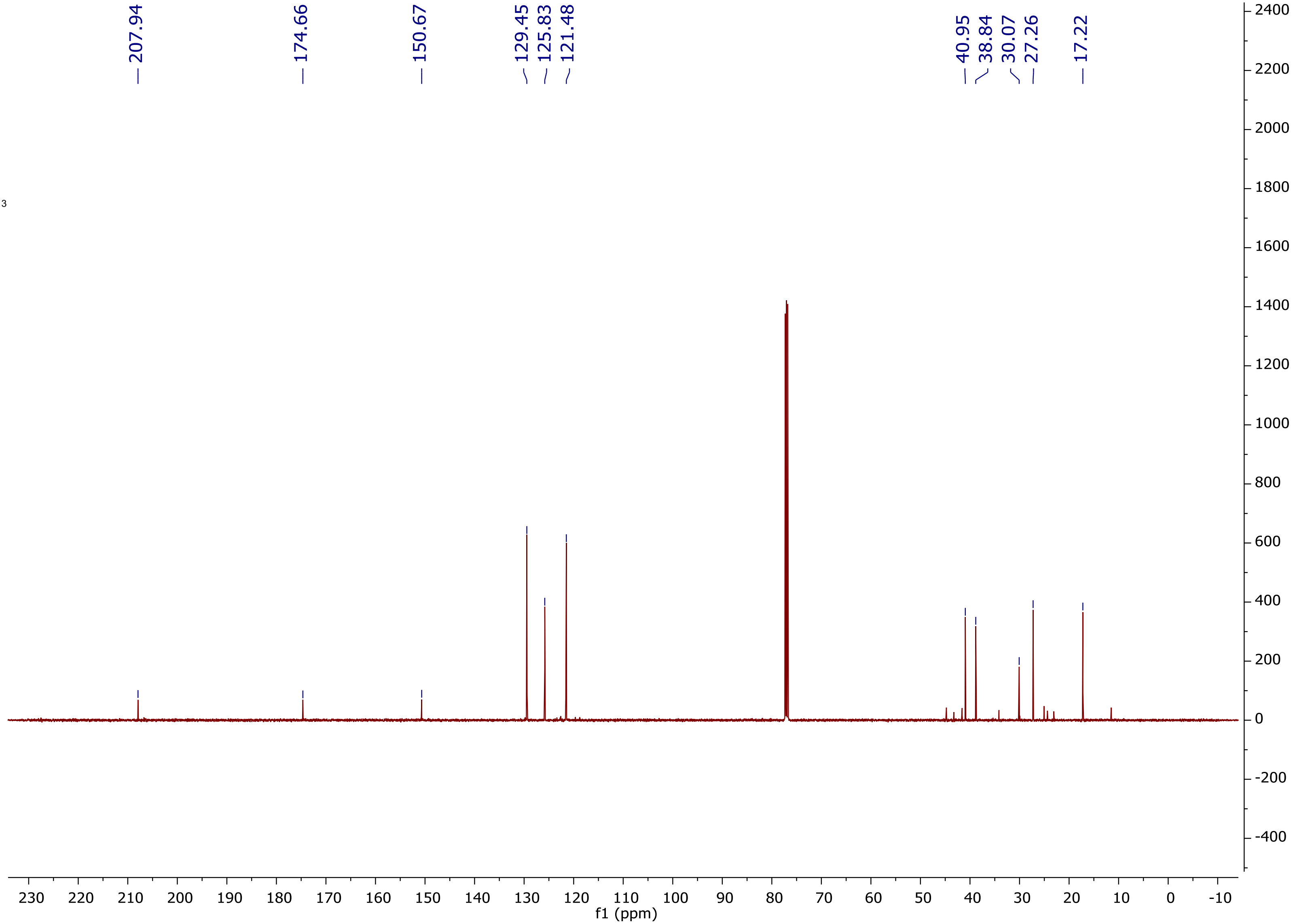
47-γ

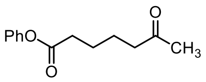


7.40 7.38 7.38 7.37 7.25 7.24 7.24 7.23 7.23 7.23 7.22 7.21 7.08 7.08 7.07 7.06 7.06 2.74 2.73 2.73 2.72 2.71 2.71 2.71 2.70 2.60 2.60 2.59 2.59 2.58 2.57 2.57 2.17 2.05 2.04 2.04 2.04 2.03 2.02 2.01 2.01 1.93 1.92 1.91 1.91 1.90 1.90 1.90 1.89 1.89 1.88 1.33 1.32
2.20
1.12
2.11
1.00
2.07
2.94
1.08
1.01
2.96
0.38
H3C
PhO
O
O
CH3
11.0 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 -1.0
f1 (ppm)
2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

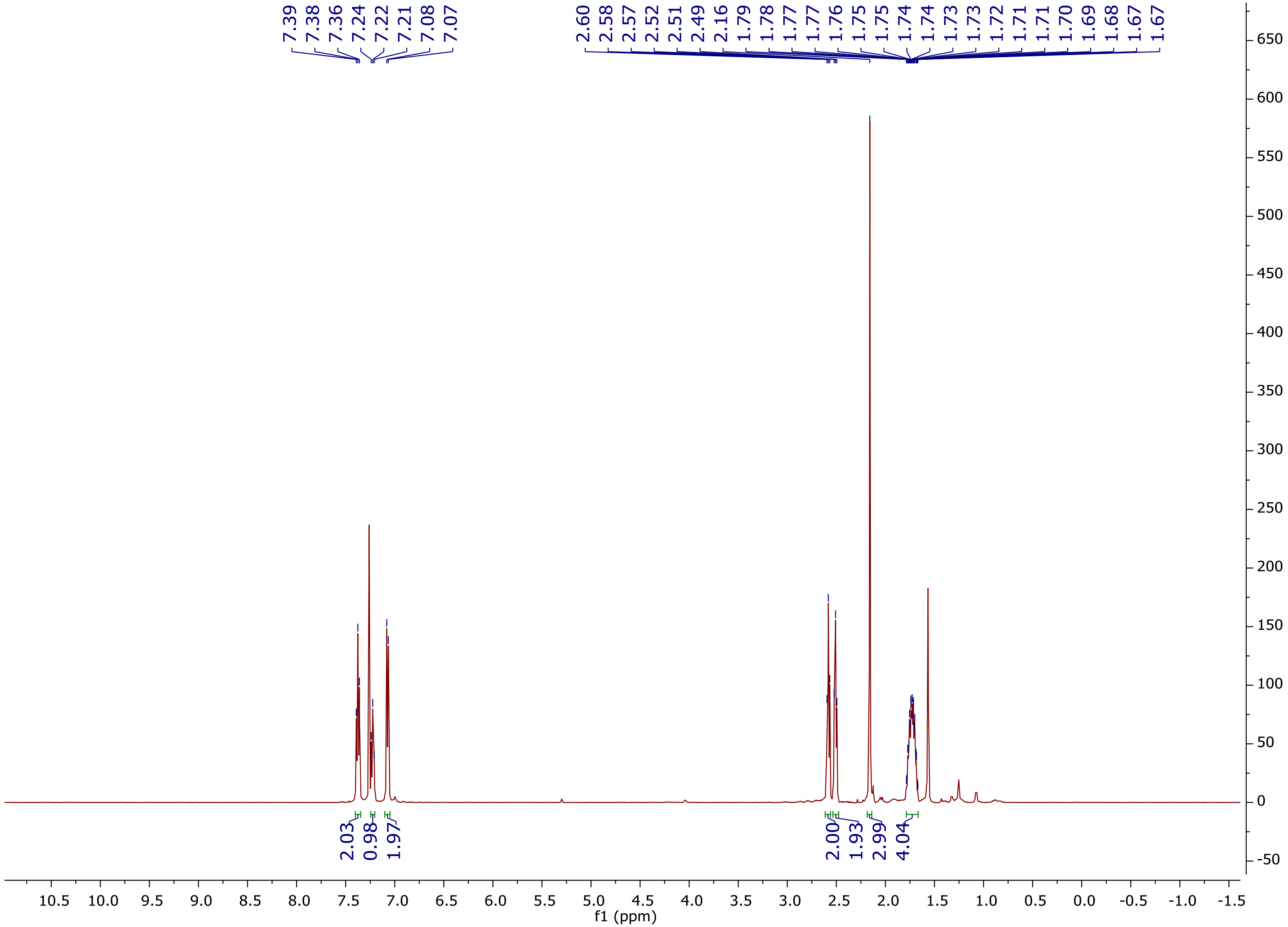

PhO
O
O
CH3
CH3

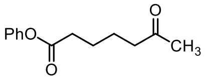
47-γ


207.94
174.66
150.67
129.45
125.83
121.48
40.95
38.84
30.07
27.26
17.22
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
230
220
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)

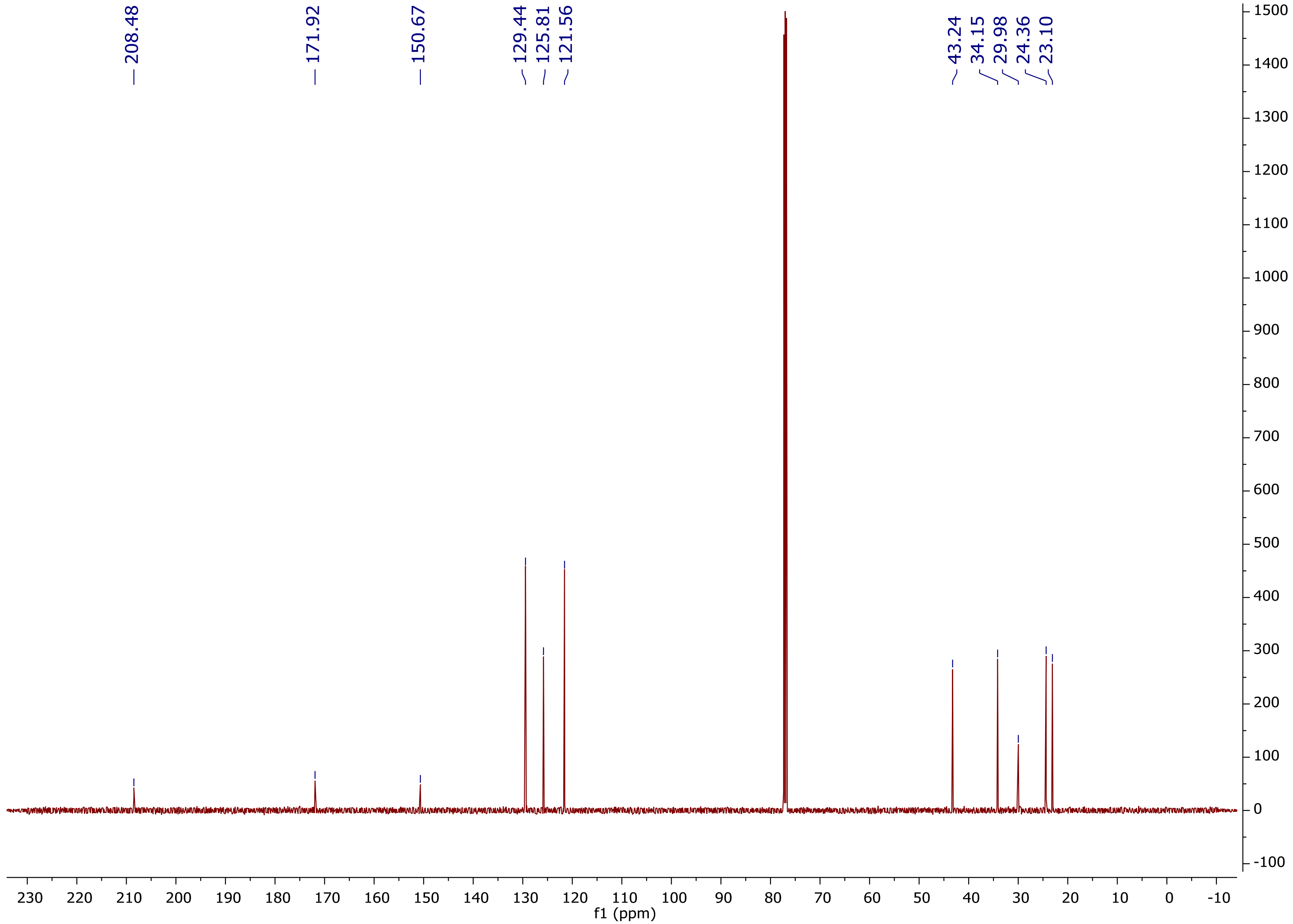

PhO
O
O
CH3

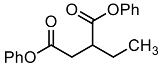
47-δ


7.39
7.38
7.36
7.24
7.22
7.21
7.08
7.07
2.60
2.58
2.57
2.52
2.51
2.49
2.16
1.79
1.78
1.77
1.77
1.76
1.75
1.75
1.74
1.74
1.73
1.73
1.72
1.71
1.71
1.70
1.69
1.68
1.67
1.67
2.03
0.98
1.97
2.00
1.93
2.99
4.04
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
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
-1.0
-1.5
f1 (ppm)

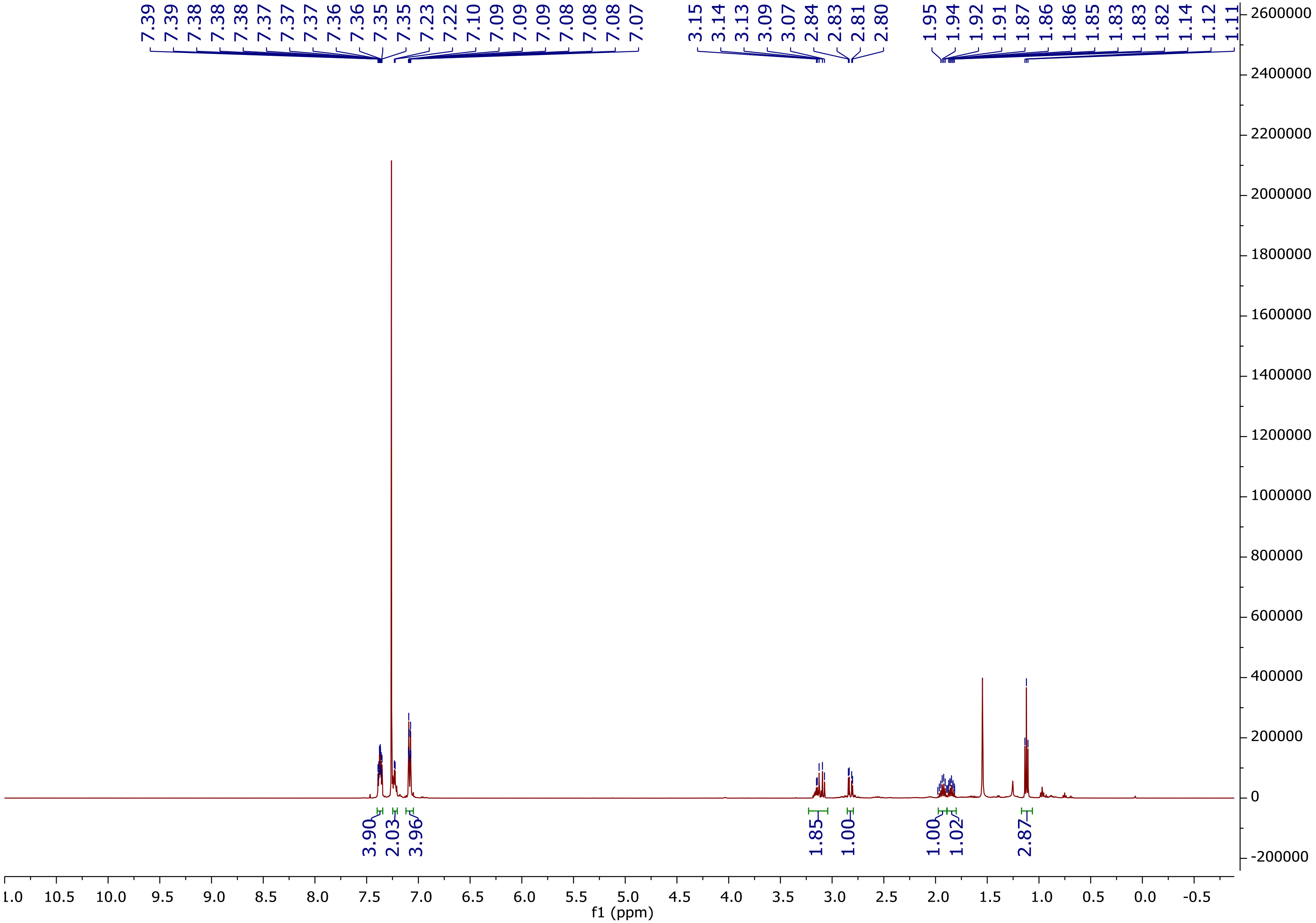

PhO
O
O
CH3

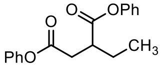
47-δ


208.48
171.92
150.67
129.44
125.81
121.56
43.24
34.15
29.98
24.36
23.10
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
230
220
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)

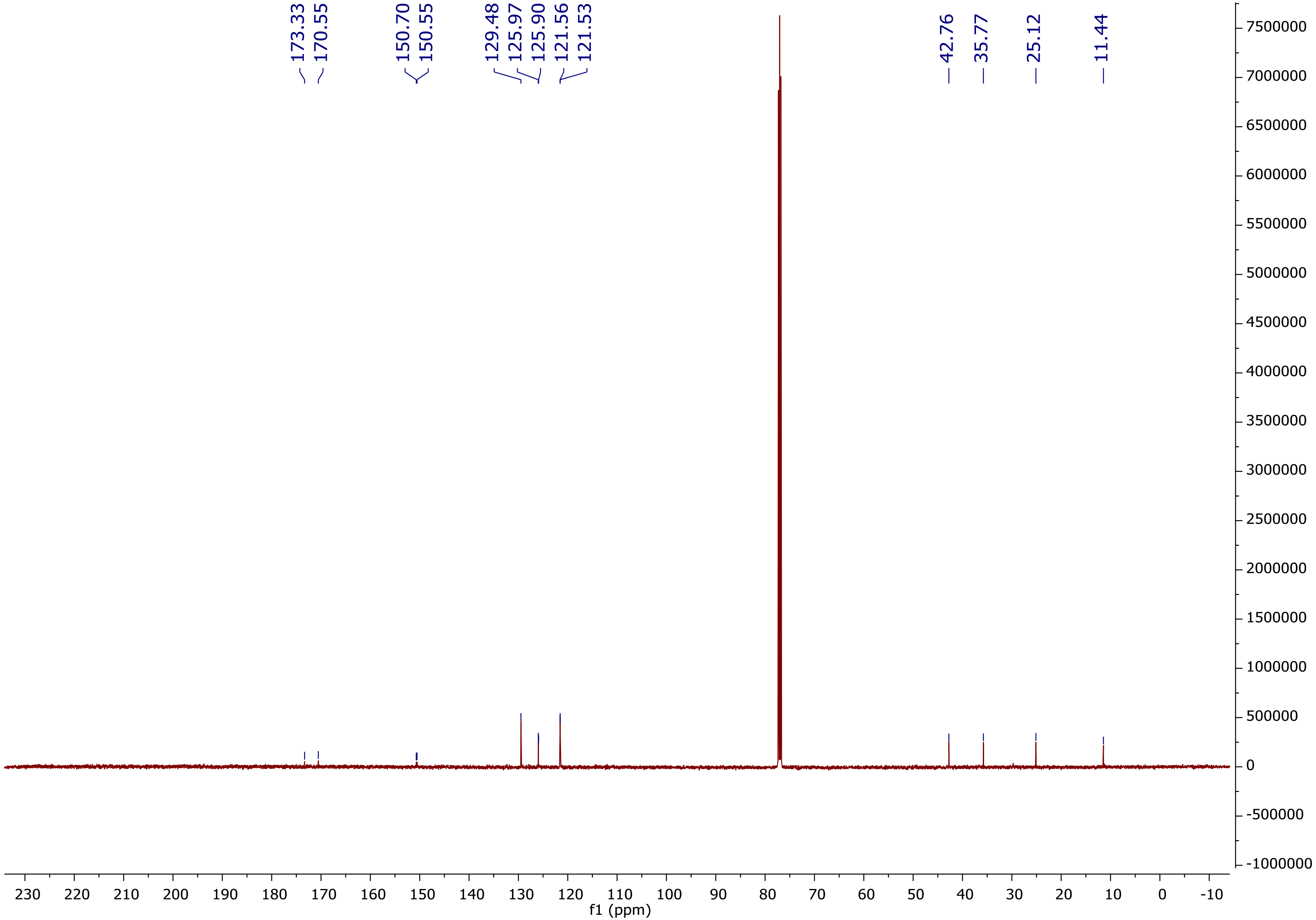

O
OPh
O
PhO
CH3

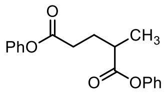
48-β


7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.23
7.22
7.10
7.09
7.09
7.09
7.08
7.08
7.08
7.07
3.15
3.14
3.13
3.09
3.07
2.84
2.83
2.81
2.80
1.95
1.94
1.92
1.91
1.87
1.86
1.86
1.85
1.83
1.83
1.82
1.14
1.12
1.11
3.90
2.03
3.96
1.85
1.00
1.00
1.02
2.87
1.0
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)
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000

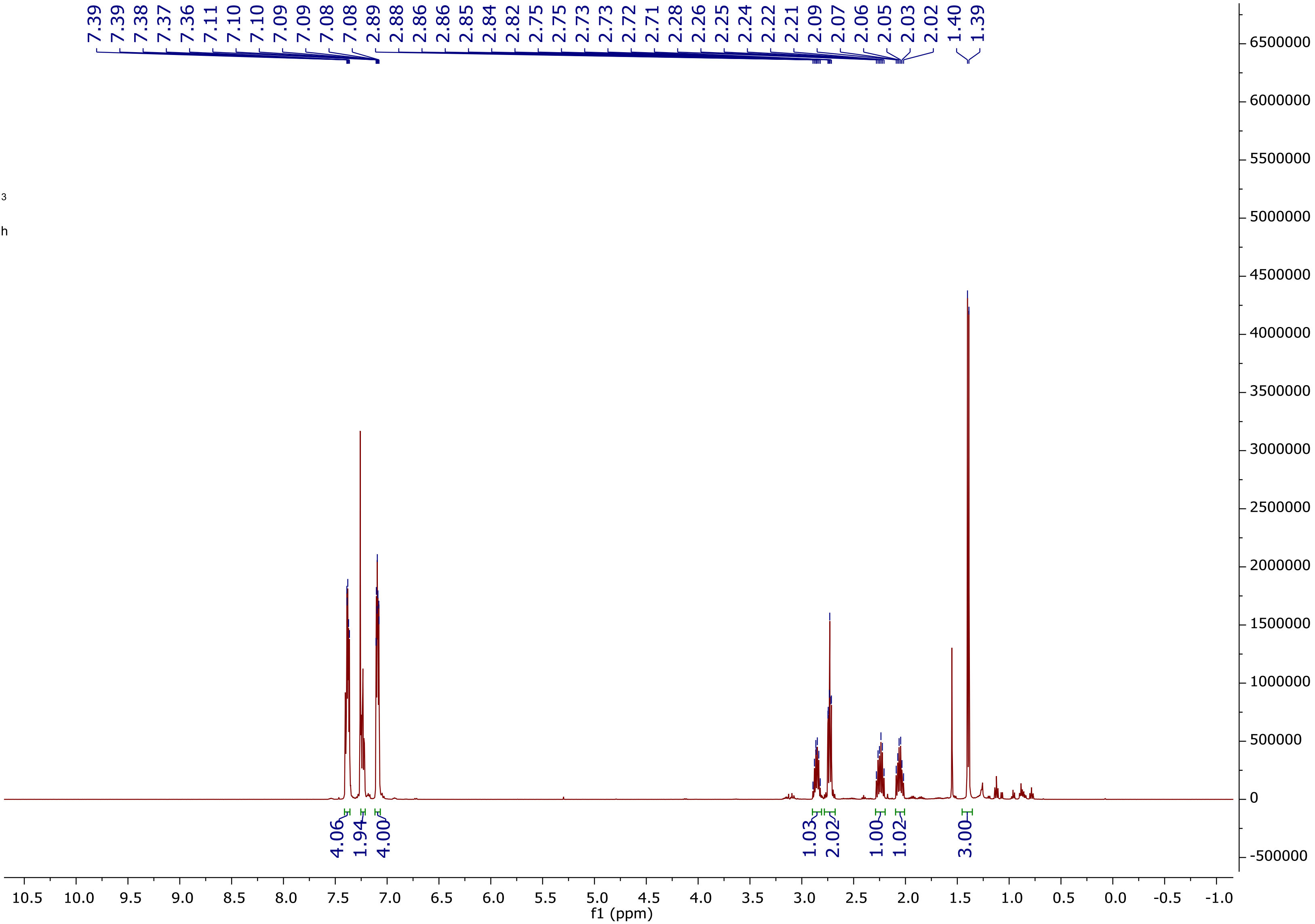

O
OPh
O
PhO
CH3

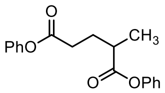
48-β


173.33
170.55
150.70
150.55
129.48
125.97
125.90
121.56
121.53
42.76
35.77
25.12
11.44
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
-1000000
230
220
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)

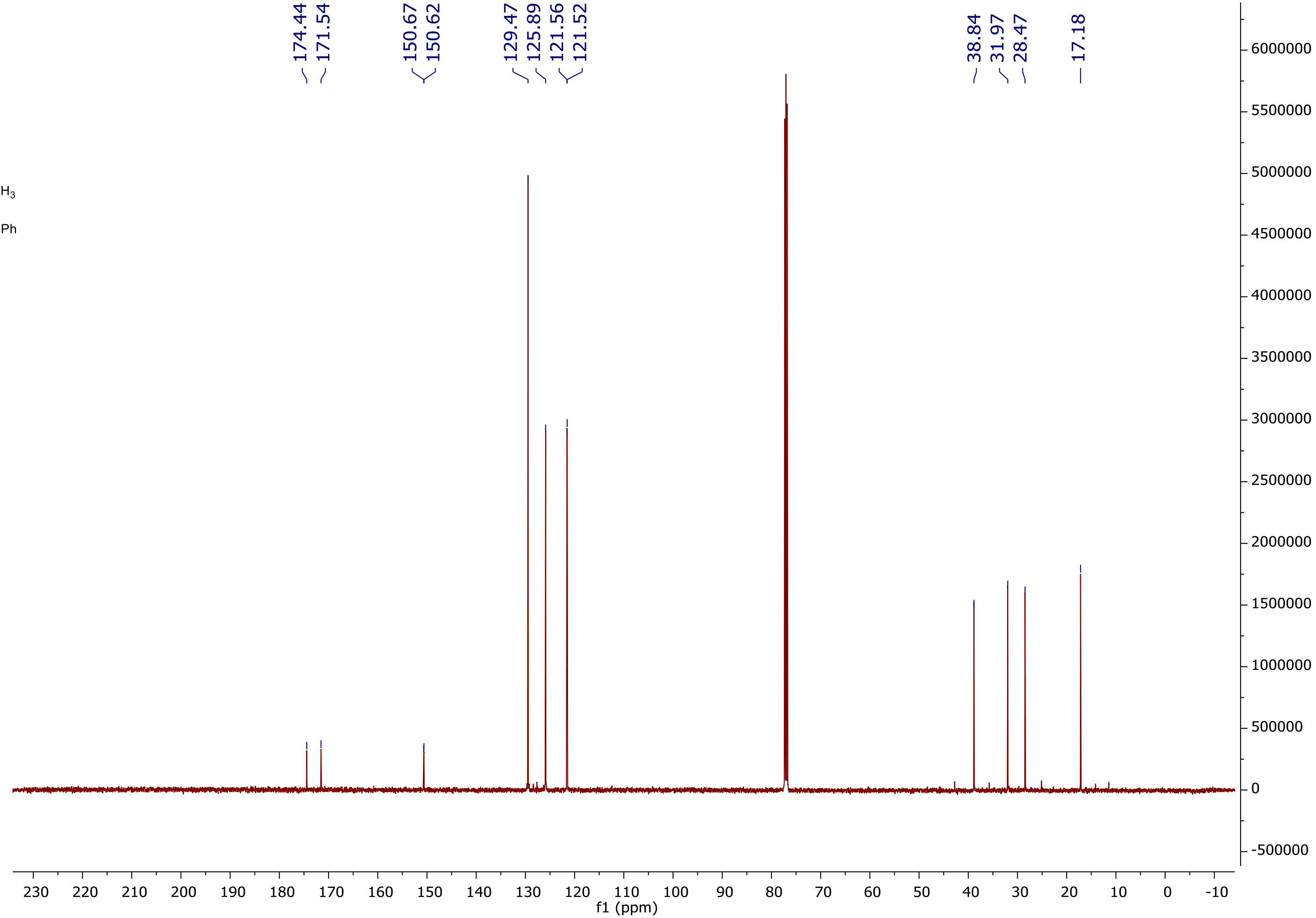

O
PhO
CH3
O
OPh

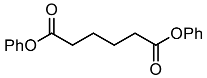
48-γ


7.39
7.39
7.38
7.37
7.36
7.11
7.10
7.10
7.09
7.09
7.08
7.08
2.89
2.88
2.86
2.86
2.85
2.84
2.82
2.75
2.75
2.73
2.73
2.72
2.71
2.28
2.26
2.25
2.24
2.22
2.21
2.09
2.07
2.06
2.05
2.03
2.02
1.40
1.39
4.06
1.94
4.00
1.03
2.02
1.00
1.02
3.00
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
-1.0
f1 (ppm)
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000

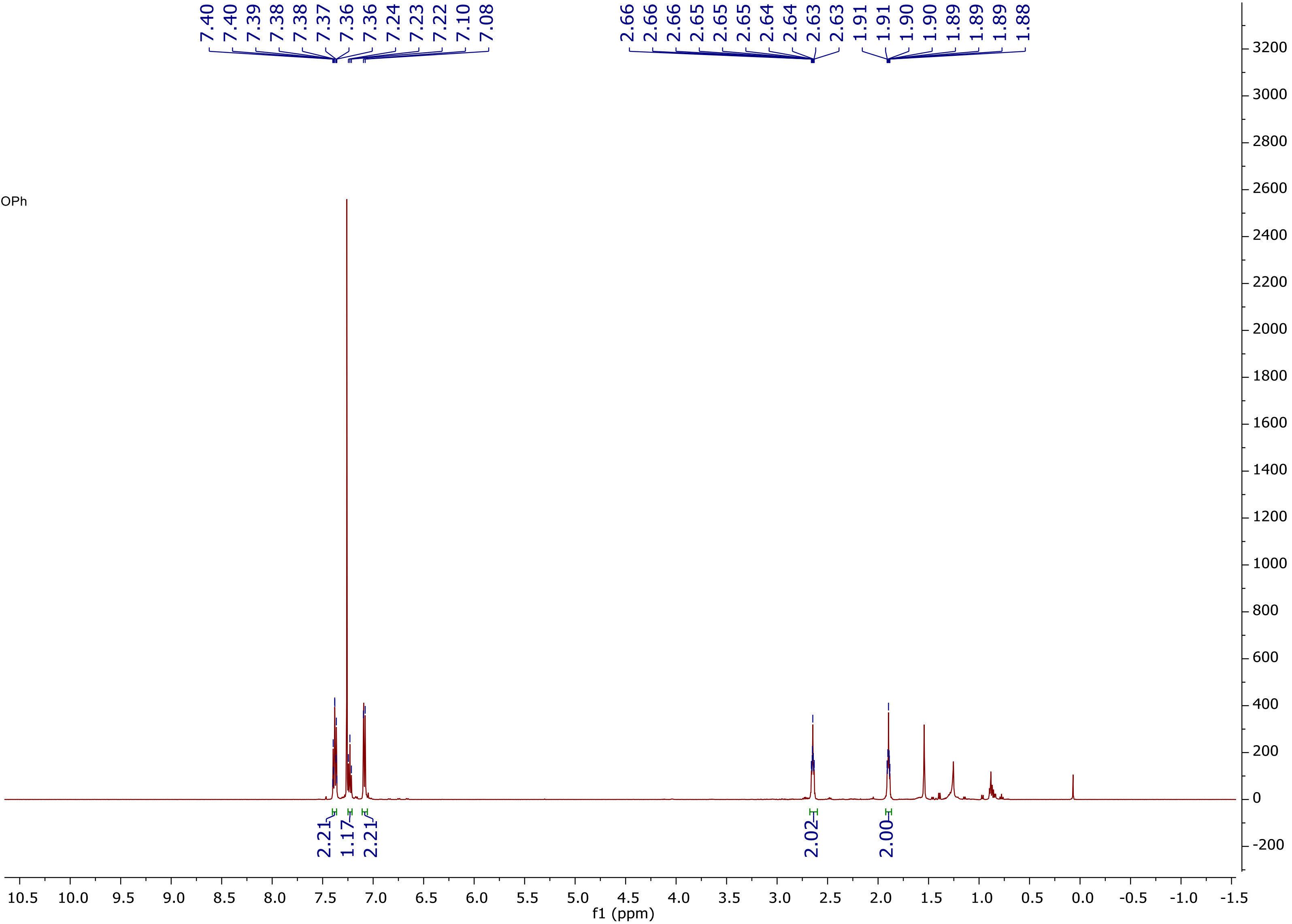

O
CH3
PhO
O
OPh

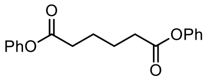
48-γ


174.44
171.54
150.67
150.62
129.47
125.89
121.56
121.52
38.84
31.97
28.47
17.18
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
230
220
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)

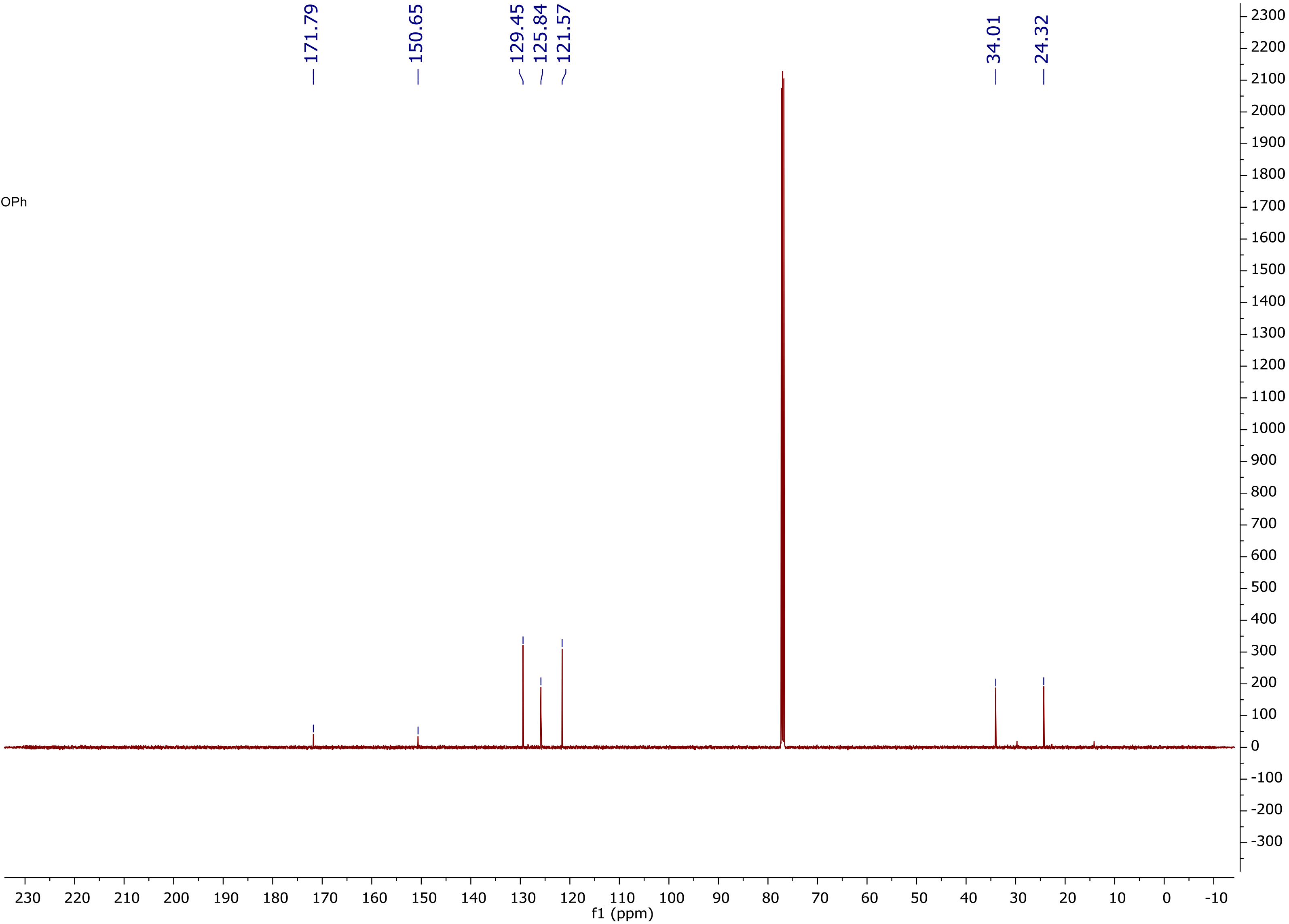

O
PhO
OPh
O

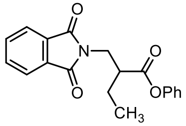
48-δ


7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.24
7.23
7.22
7.10
7.08
2.66
2.66
2.66
2.65
2.65
2.65
2.64
2.64
2.63
2.63
1.91
1.91
1.90
1.90
1.89
1.89
1.89
1.88
2.21
1.17
2.21
2.02
2.00
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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
-1.0
-1.5
f1 (ppm)

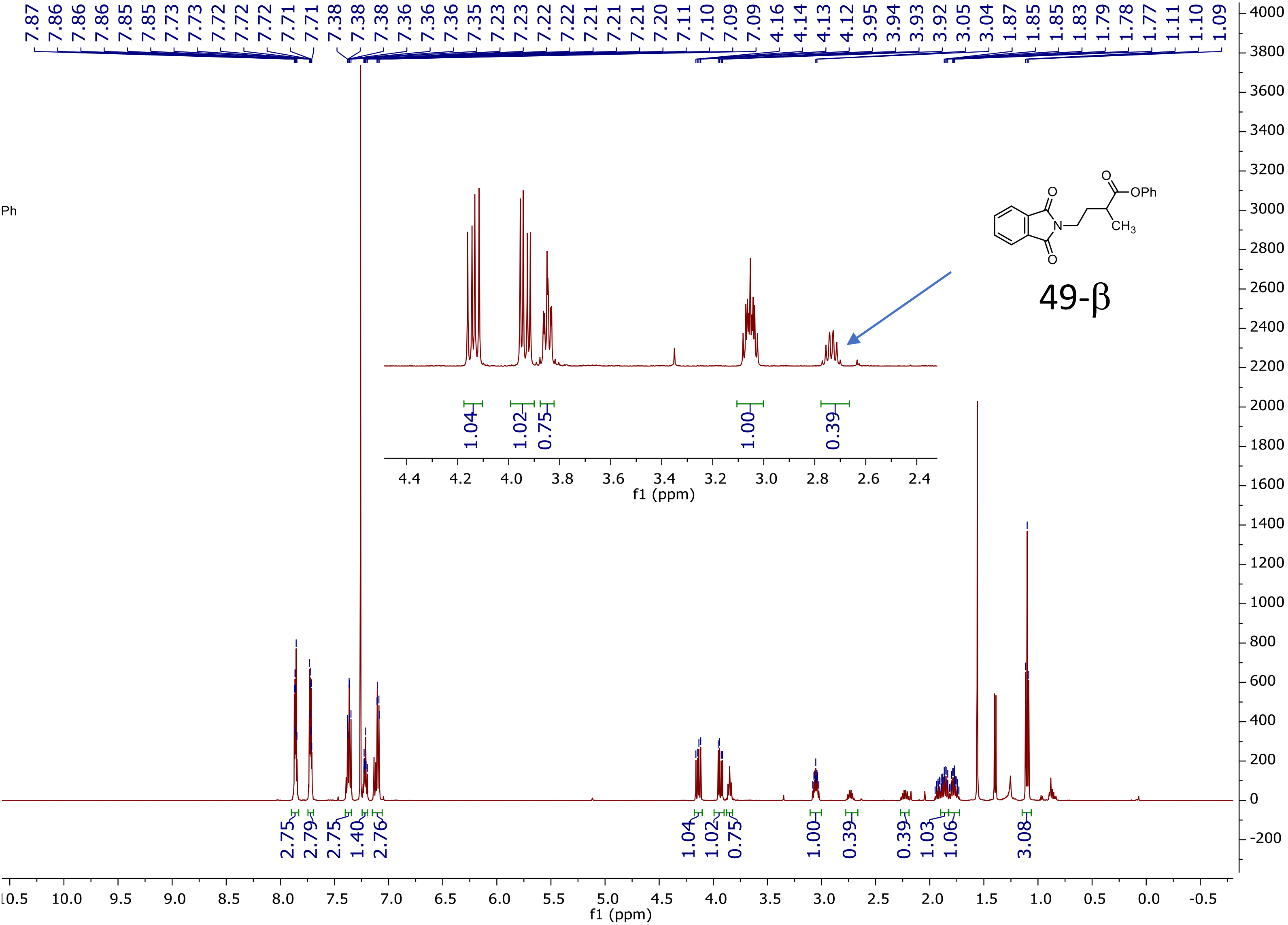

PhO
O
OPh
O

48-δ

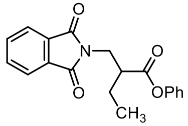

171.79
150.65
129.45
125.84
121.57
34.01
24.32
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300



49-β



7.87 7.86 7.86 7.86 7.85 7.85 7.73 7.73 7.72 7.72 7.72 7.71 7.71 7.38 7.38 7.38 7.36 7.36 7.36 7.35 7.23 7.23 7.22 7.22 7.21 7.21 7.21 7.20 7.11 7.10 7.09 7.09 4.16 4.14 4.13 4.12 3.95 3.94 3.93 3.92 3.05 3.04 1.87 1.85 1.85 1.83 1.79 1.78 1.77 1.11 1.10 1.09
OPh
CH3
N
O
49-β
1.04
1.02
0.75
1.00
0.39
4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
f1 (ppm)
2.75
2.79
2.75
1.40
2.76
1.04
1.02
0.75
1.00
0.39
0.39
1.03
1.06
3.08
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)
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200



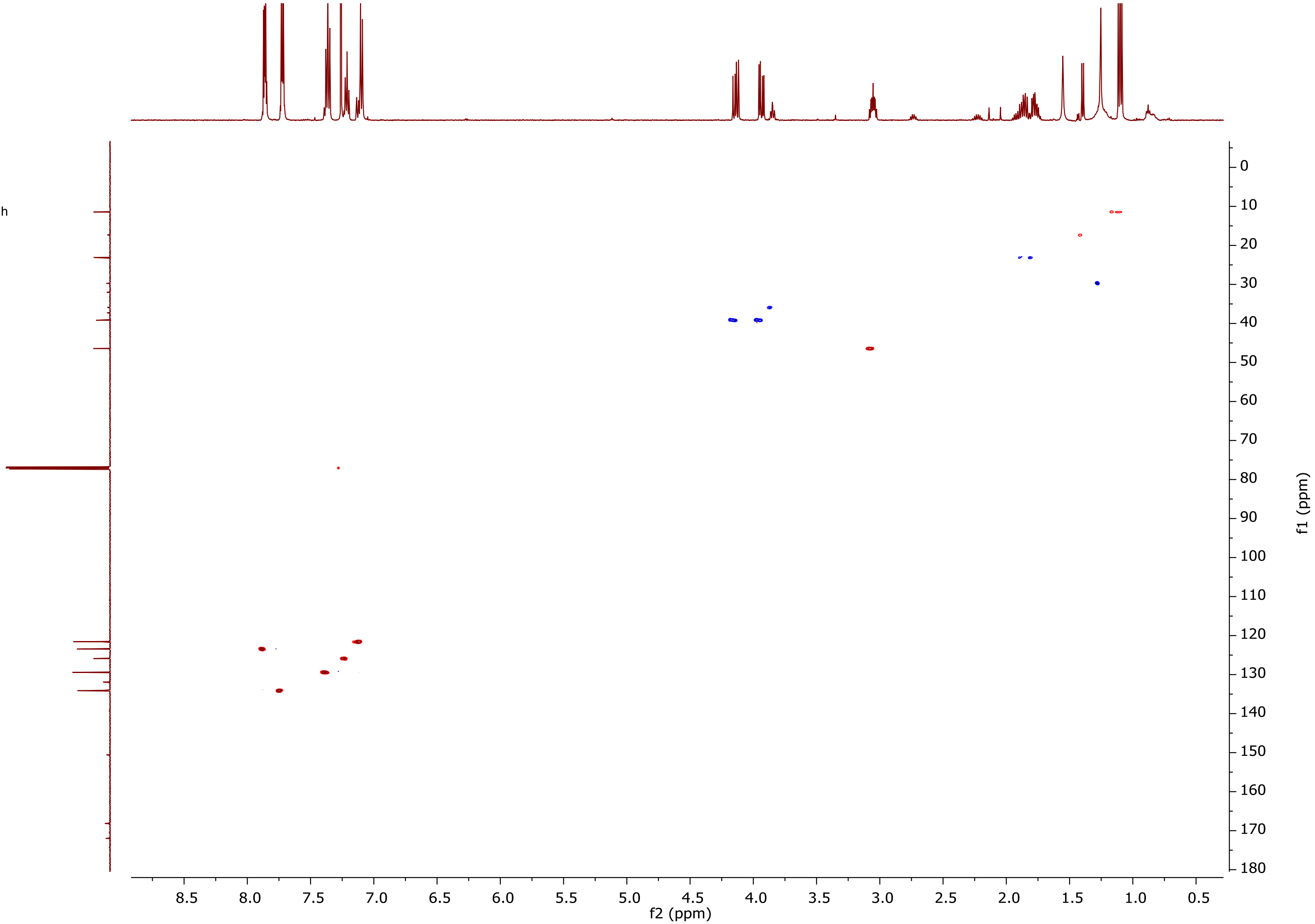
49-β

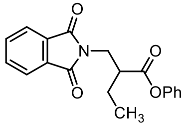
HSQC

Mix of

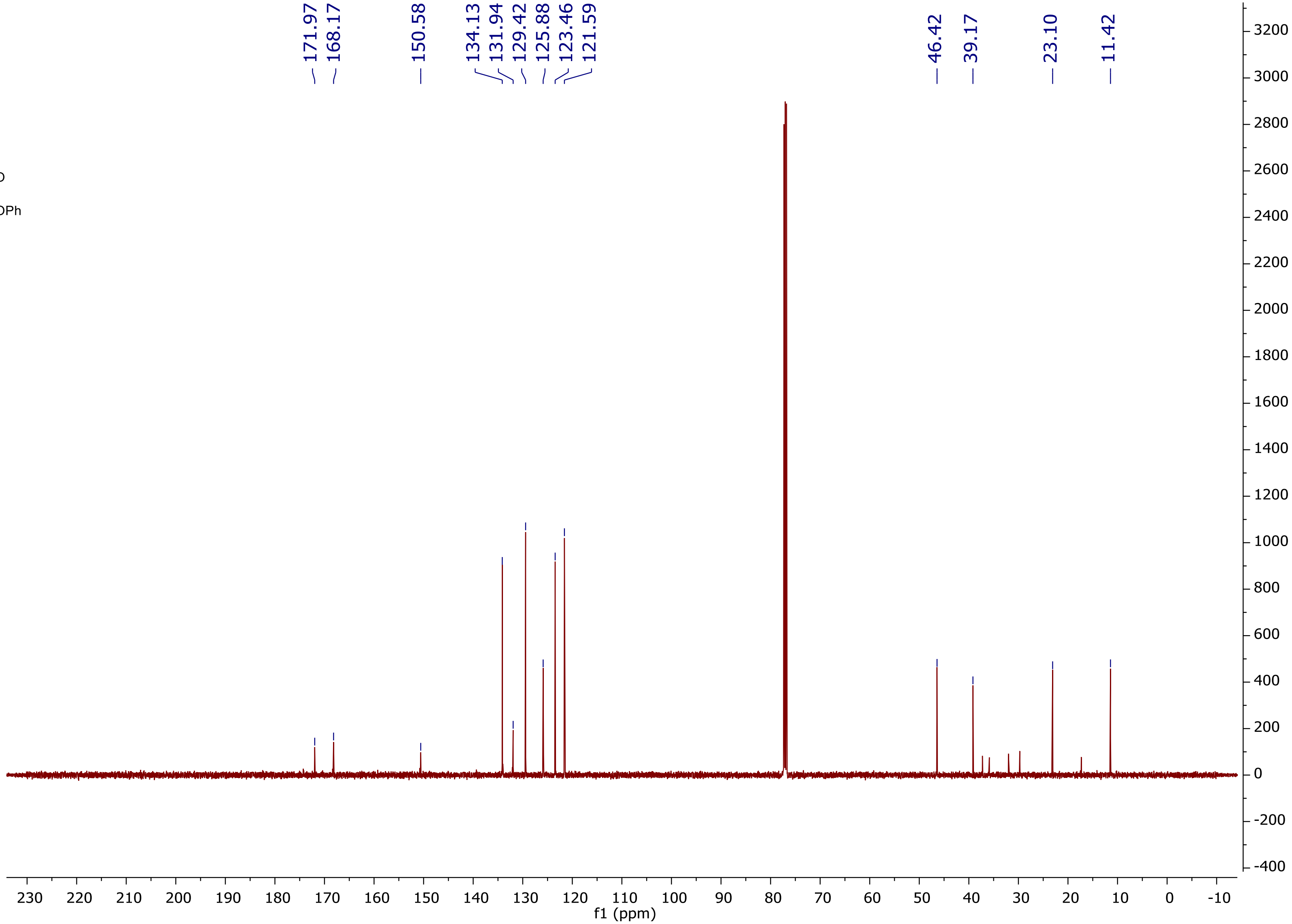
49-β

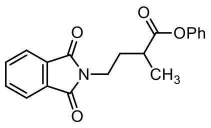
49-γ




O
N
O
O
OPh
CH3

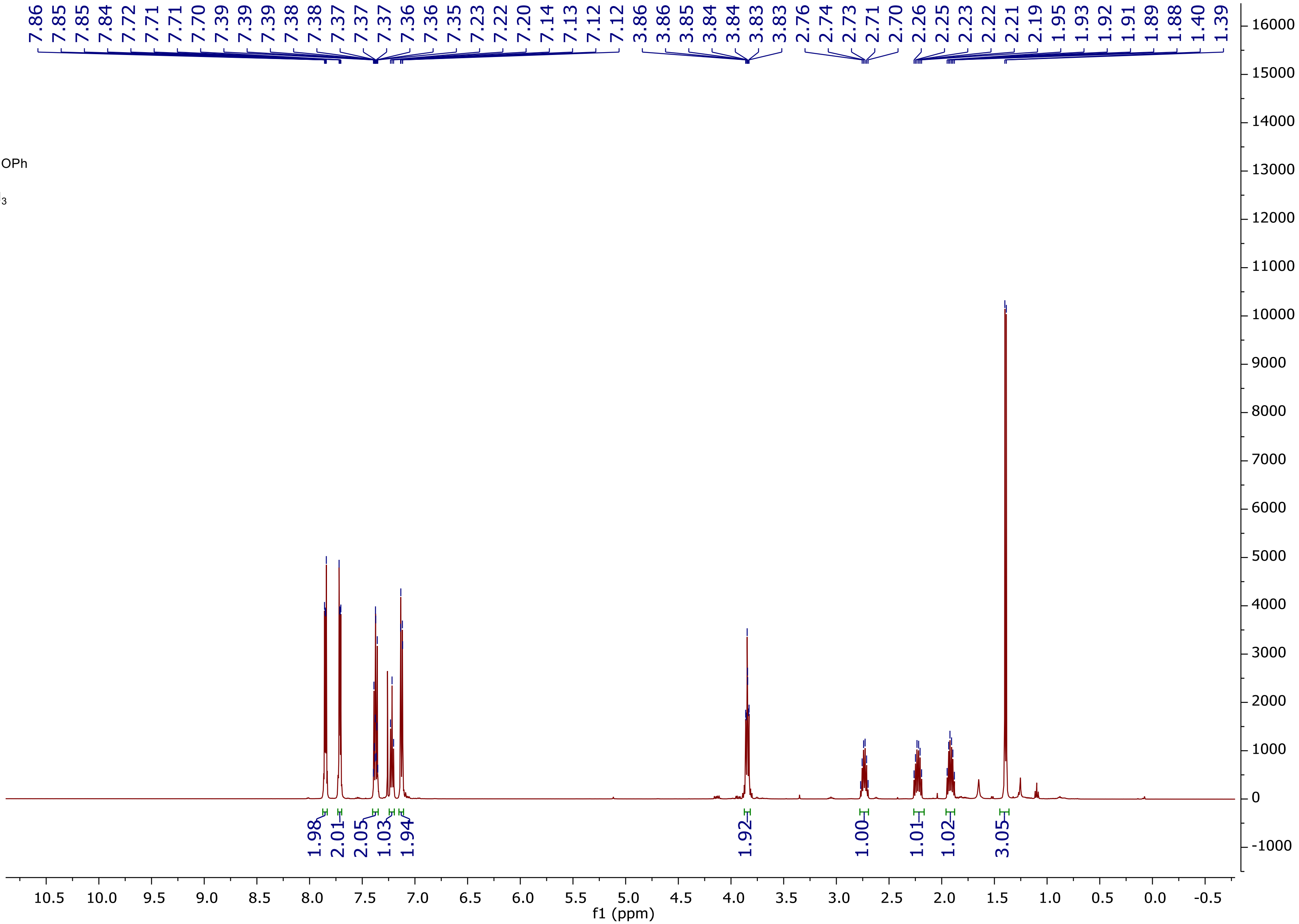
49-β


171.97
168.17
150.58
134.13
131.94
129.42
125.88
123.46
121.59
46.42
39.17
23.10
11.42
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
230
220
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)

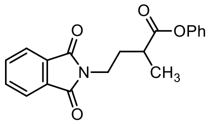


O
OPh
O
N
CH$_3$
O

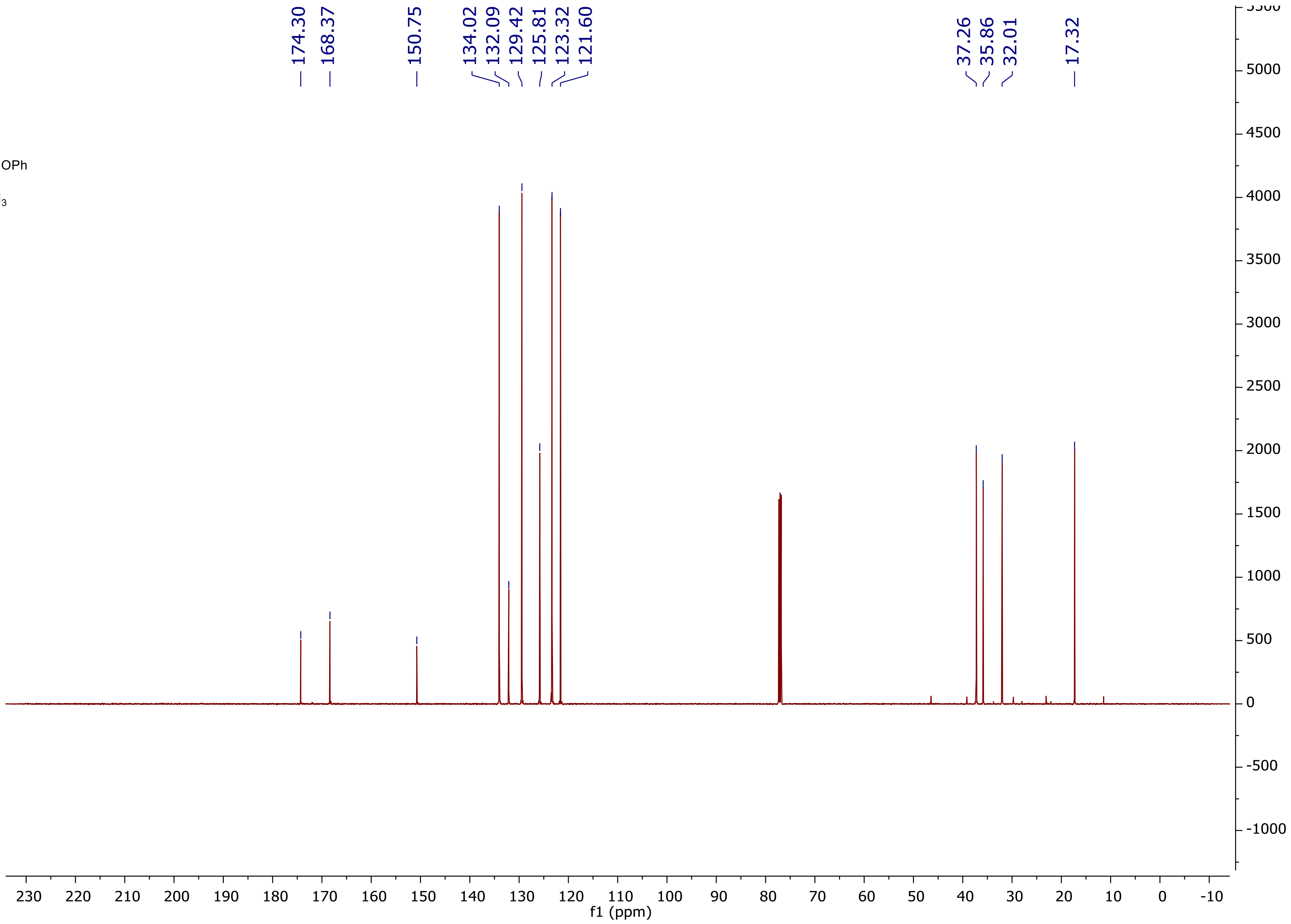
49-γ

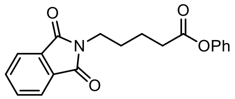


7.86
7.85
7.85
7.84
7.72
7.71
7.71
7.70
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.23
7.22
7.20
7.14
7.13
7.12
7.12
3.86
3.86
3.85
3.84
3.84
3.83
3.83
2.76
2.74
2.73
2.71
2.70
2.26
2.25
2.23
2.22
2.21
2.19
1.95
1.93
1.92
1.91
1.89
1.88
1.40
1.39
1.98
2.01
2.05
1.03
1.94
1.92
1.00
1.01
1.02
3.05
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)
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

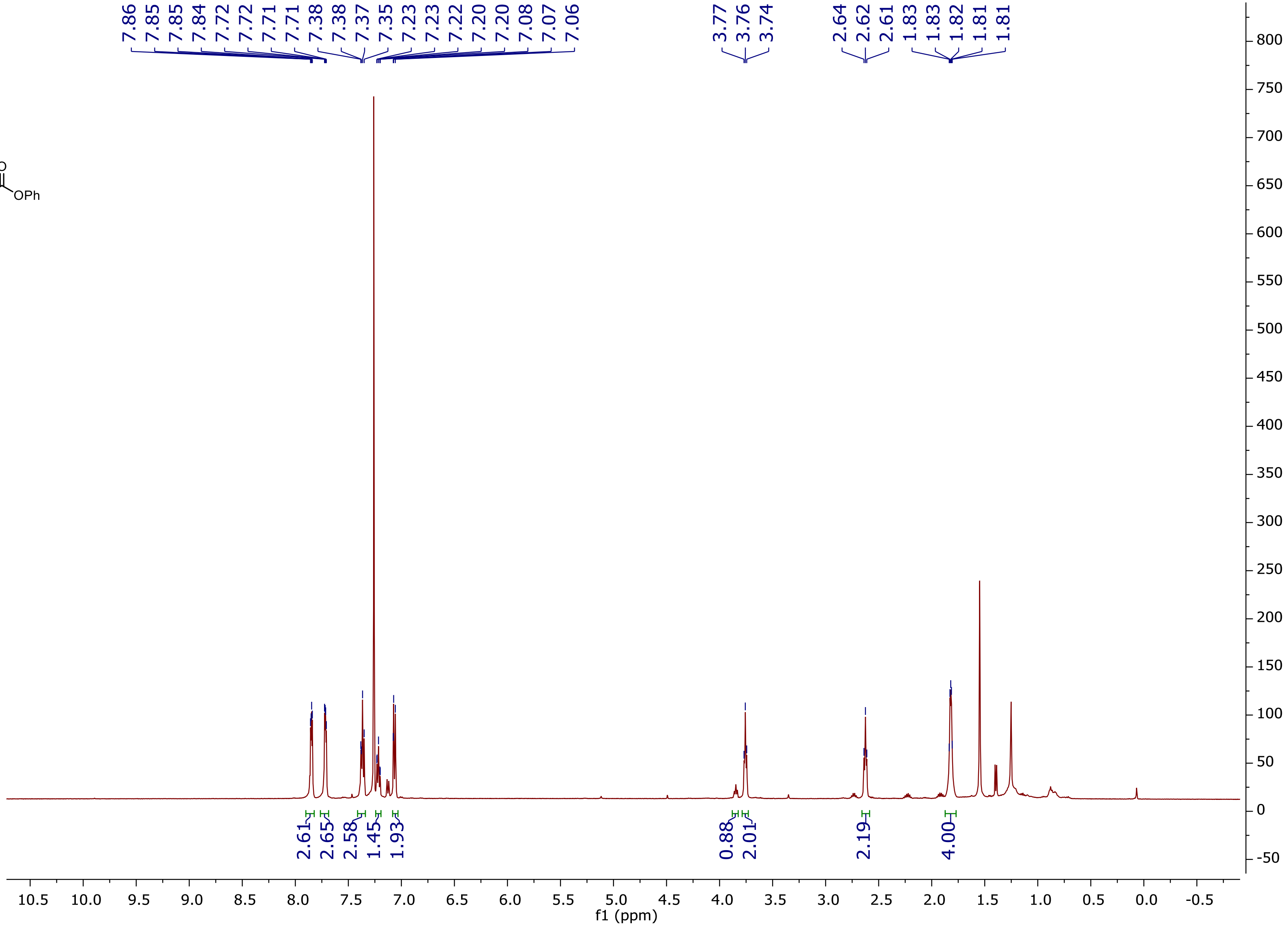

O
OPh
O
N
CH3
O

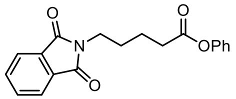
49-γ


174.30
168.37
150.75
134.02
132.09
129.42
125.81
123.32
121.60
37.26
35.86
32.01
17.32
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
230
220
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)

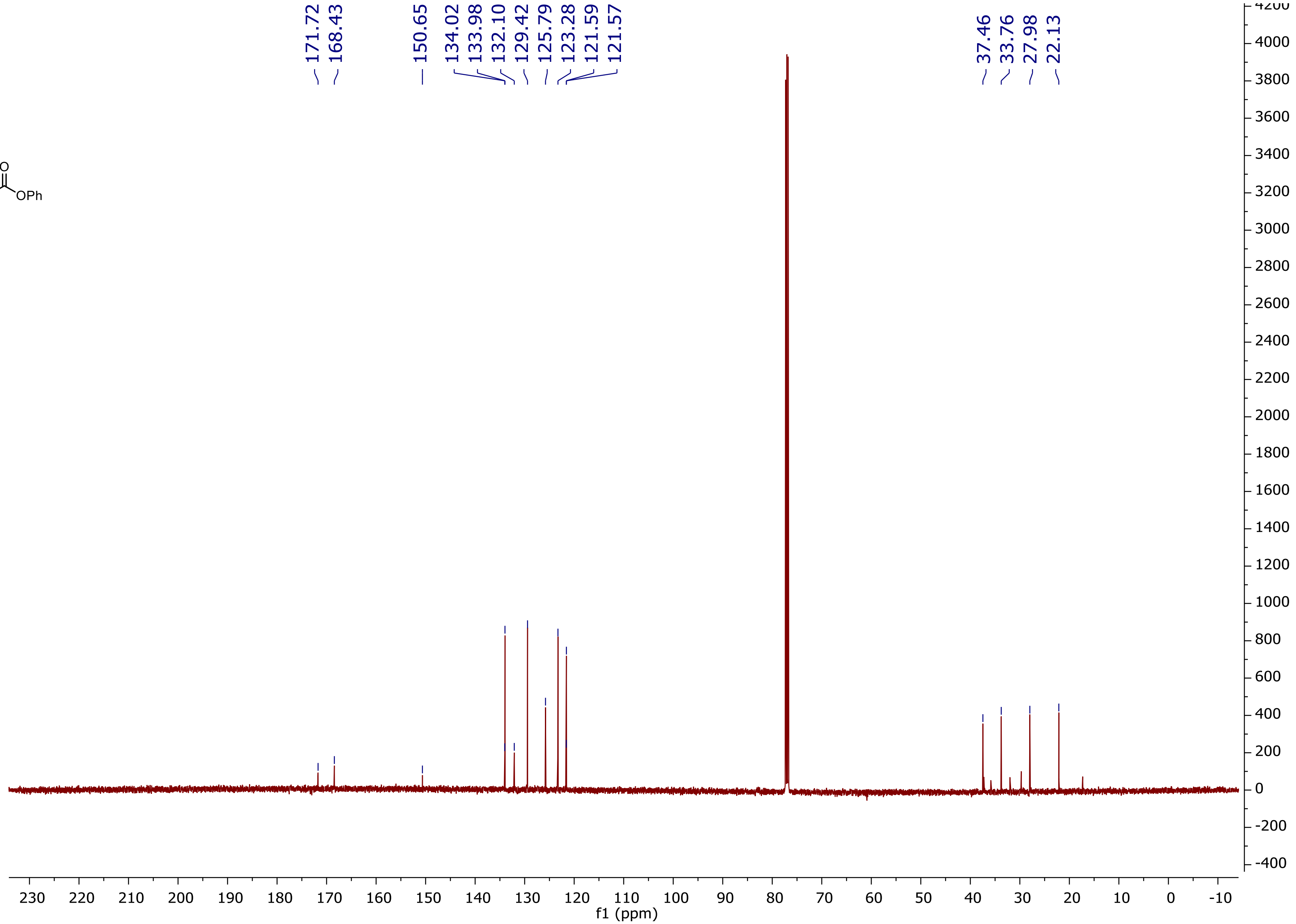

O
N
O
O
OPh

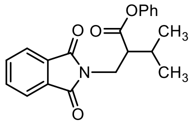
49-δ


7.86
7.85
7.85
7.84
7.72
7.72
7.71
7.71
7.38
7.38
7.37
7.35
7.23
7.23
7.22
7.20
7.20
7.08
7.07
7.06
3.77
3.76
3.74
2.64
2.62
2.61
1.83
1.83
1.82
1.81
1.81
2.61
2.65
2.58
1.45
1.93
0.88
2.01
2.19
4.00
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
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)

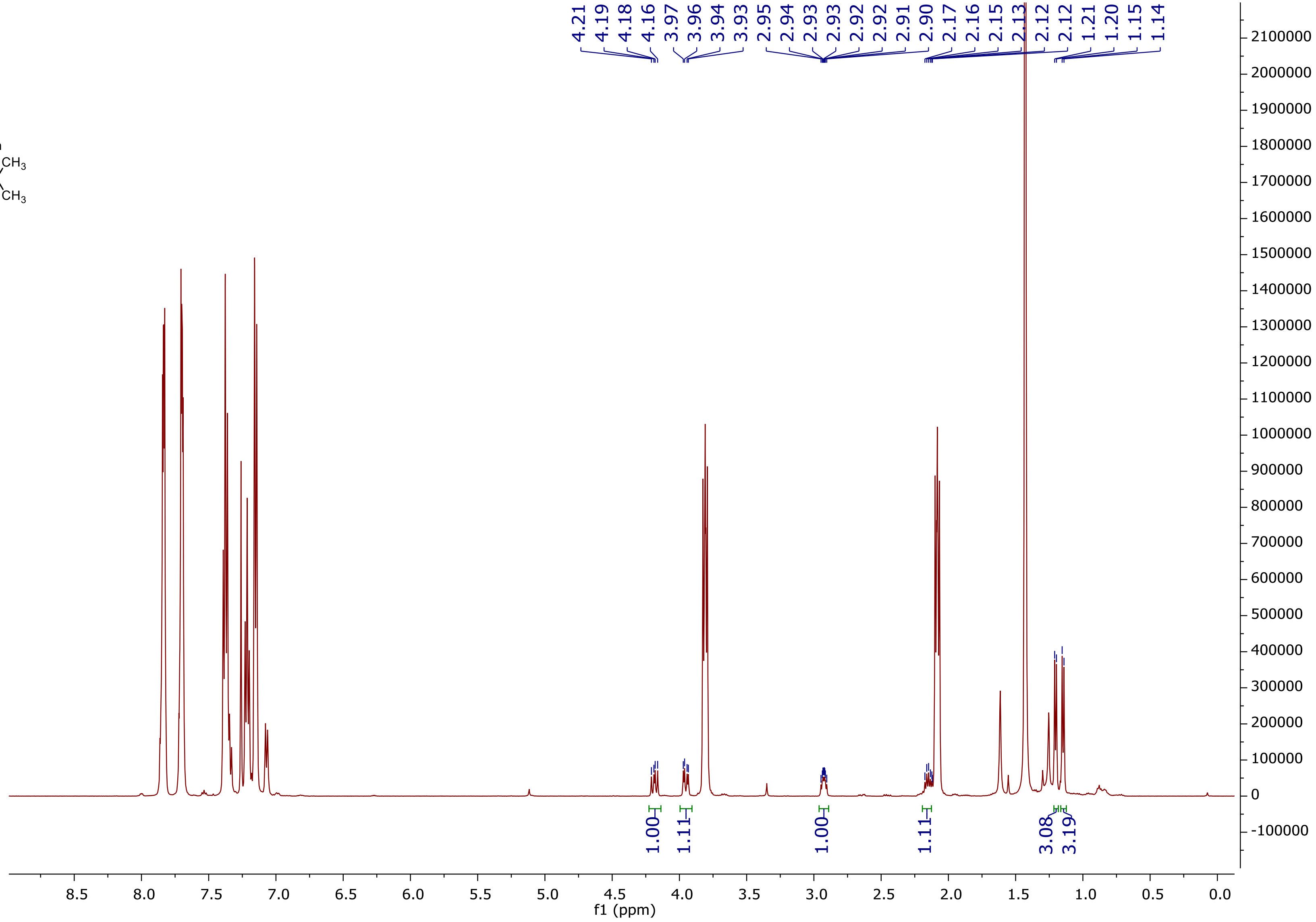

O
N
O
OPh
O

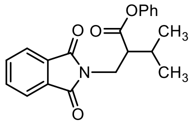
49-δ


171.72
168.43
150.65
134.02
133.98
132.10
129.42
125.79
123.28
121.59
121.57
37.46
33.76
27.98
22.13
4200
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
230
220
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)


OPh
O
CH3
O
N
CH3
O

50-β


4.21
4.19
4.18
4.16
3.97
3.96
3.94
3.93
2.95
2.94
2.93
2.93
2.92
2.92
2.91
2.90
2.17
2.16
2.15
2.13
2.12
2.12
1.21
1.20
1.15
1.14
1.00
1.11
1.00
1.11
3.08
3.19
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
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)



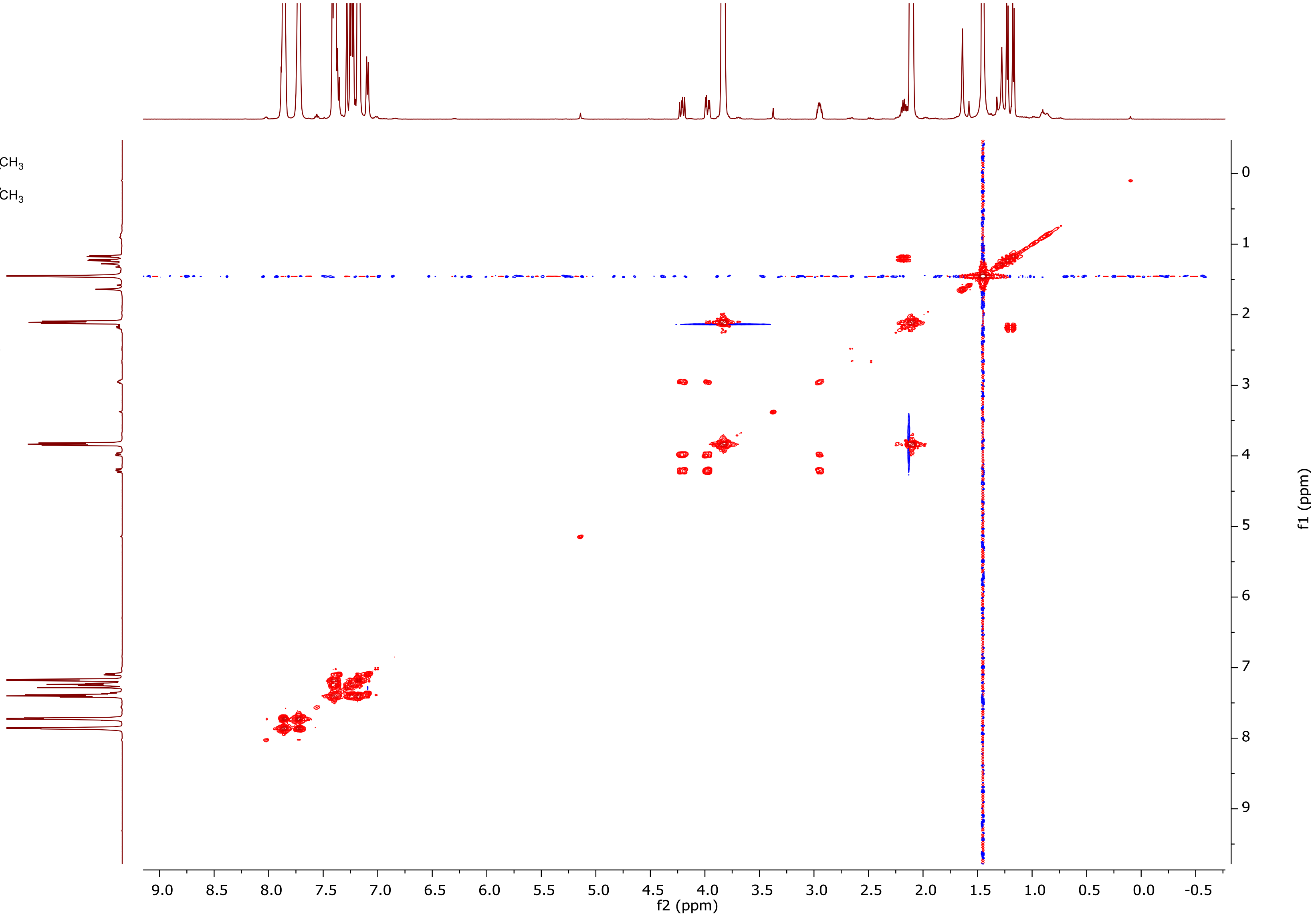
50-β

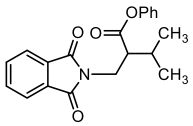
COSY

Mix of

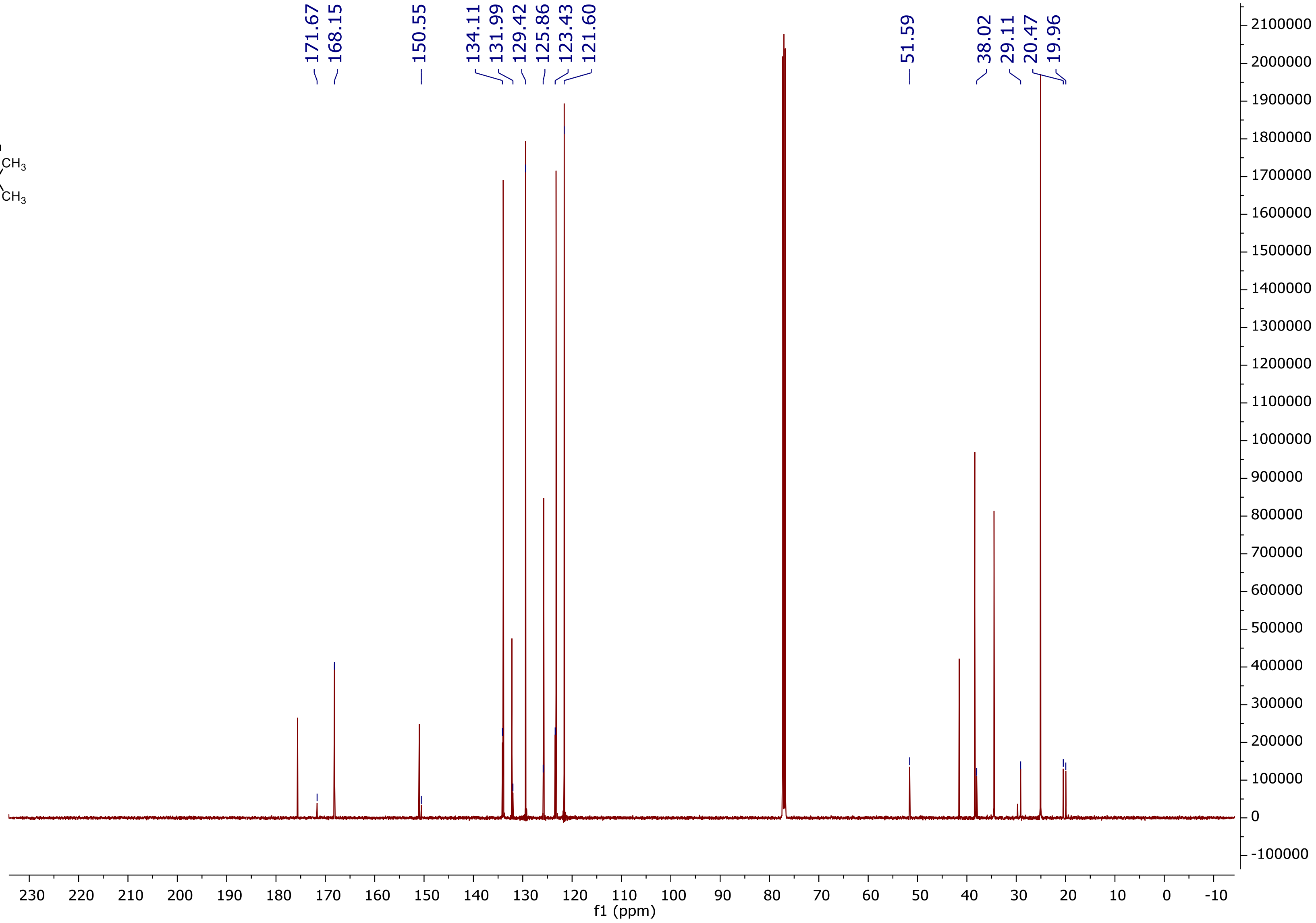
50-β

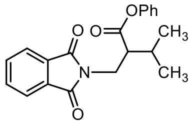
50-γ




OPh
O
CH$_3$
CH$_3$
N
O
O

50-β


171.67
168.15
150.55
134.11
131.99
129.42
125.86
123.43
121.60
51.59
38.02
29.11
20.47
19.96
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
230
220
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)



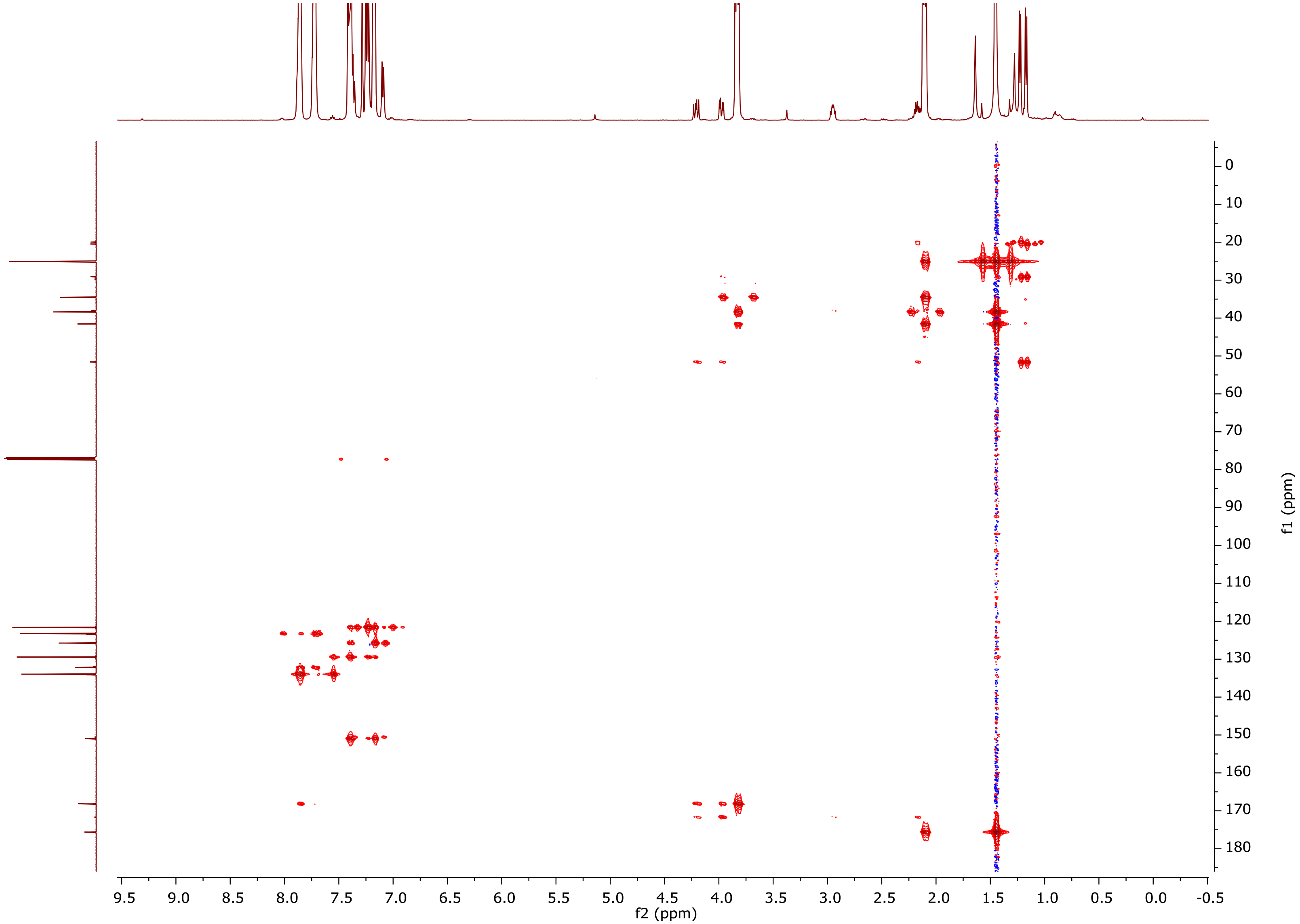
50-β

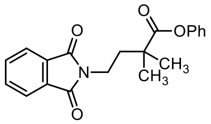
HMBC

Mix of

50-β

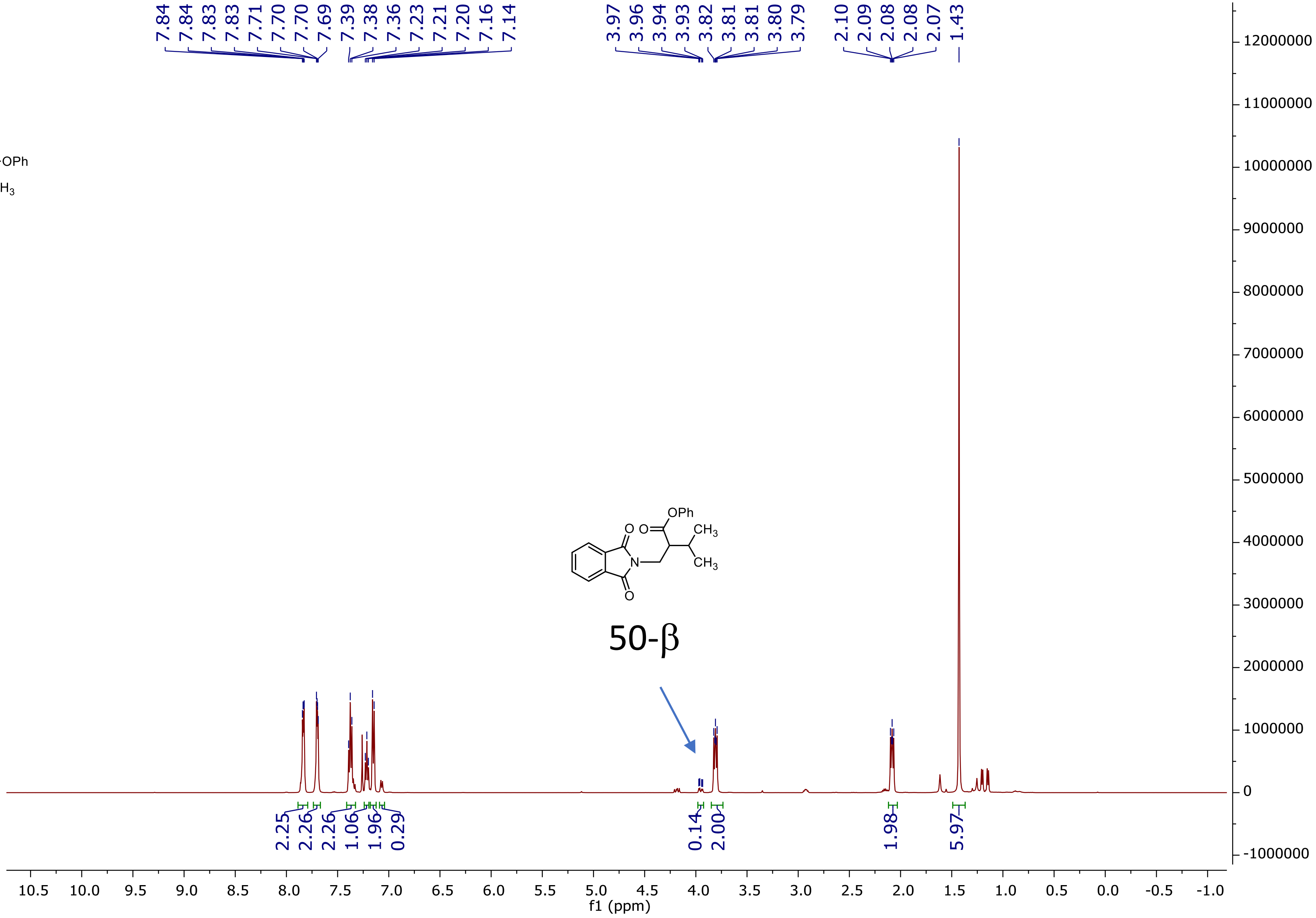
50-γ





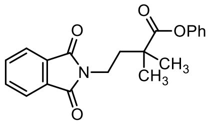
O
OPh
O
N
CH3
CH3
O

50-γ

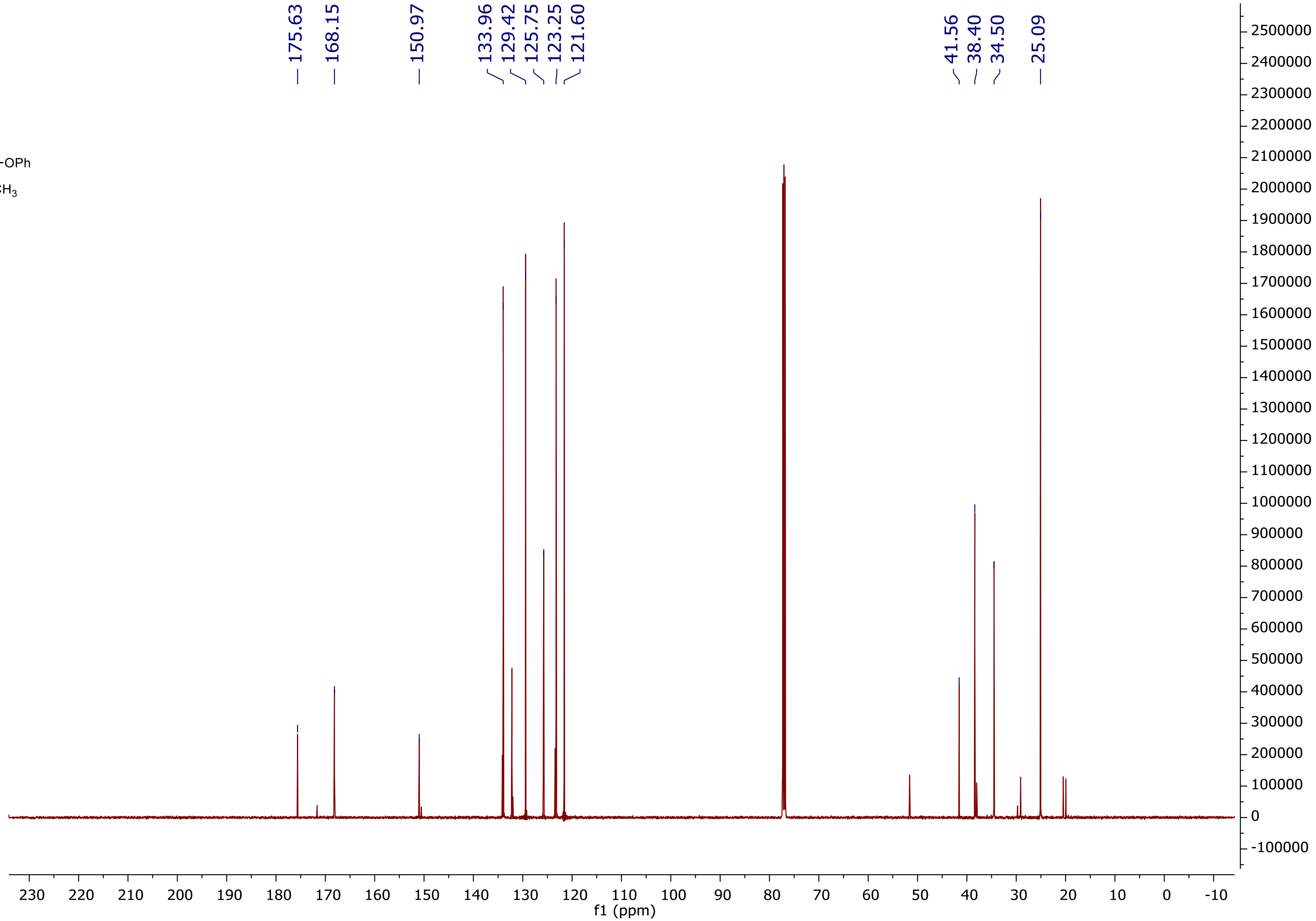


7.84
7.84
7.83
7.83
7.71
7.70
7.70
7.69
7.39
7.38
7.36
7.23
7.21
7.20
7.16
7.14
3.97
3.96
3.94
3.93
3.82
3.81
3.81
3.80
3.79
2.10
2.09
2.08
2.08
2.07
1.43
OPh
O
CH3
O
N
CH3
O
2.25
2.26
2.26
1.06
1.96
0.29
0.14
2.00
1.98
5.97
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
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
-1.0
f1 (ppm)

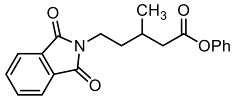
50-β



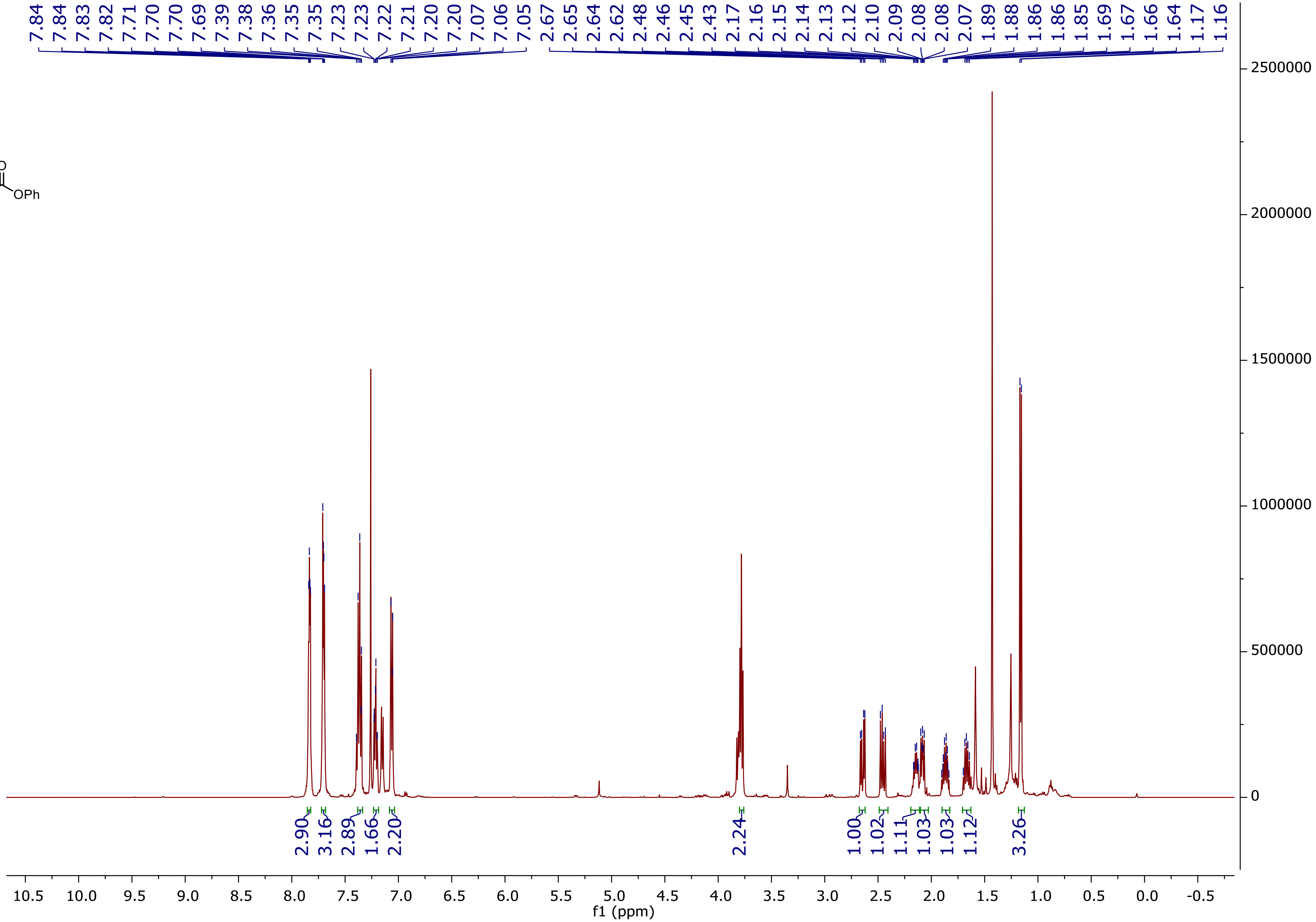
50-γ

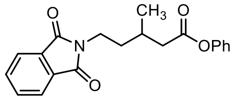


175.63
168.15
150.97
133.96
129.42
125.75
123.25
121.60
41.56
38.40
34.50
25.09
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2500000
2400000
2300000
2200000
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000


CH3
O
O
N
O
OPh

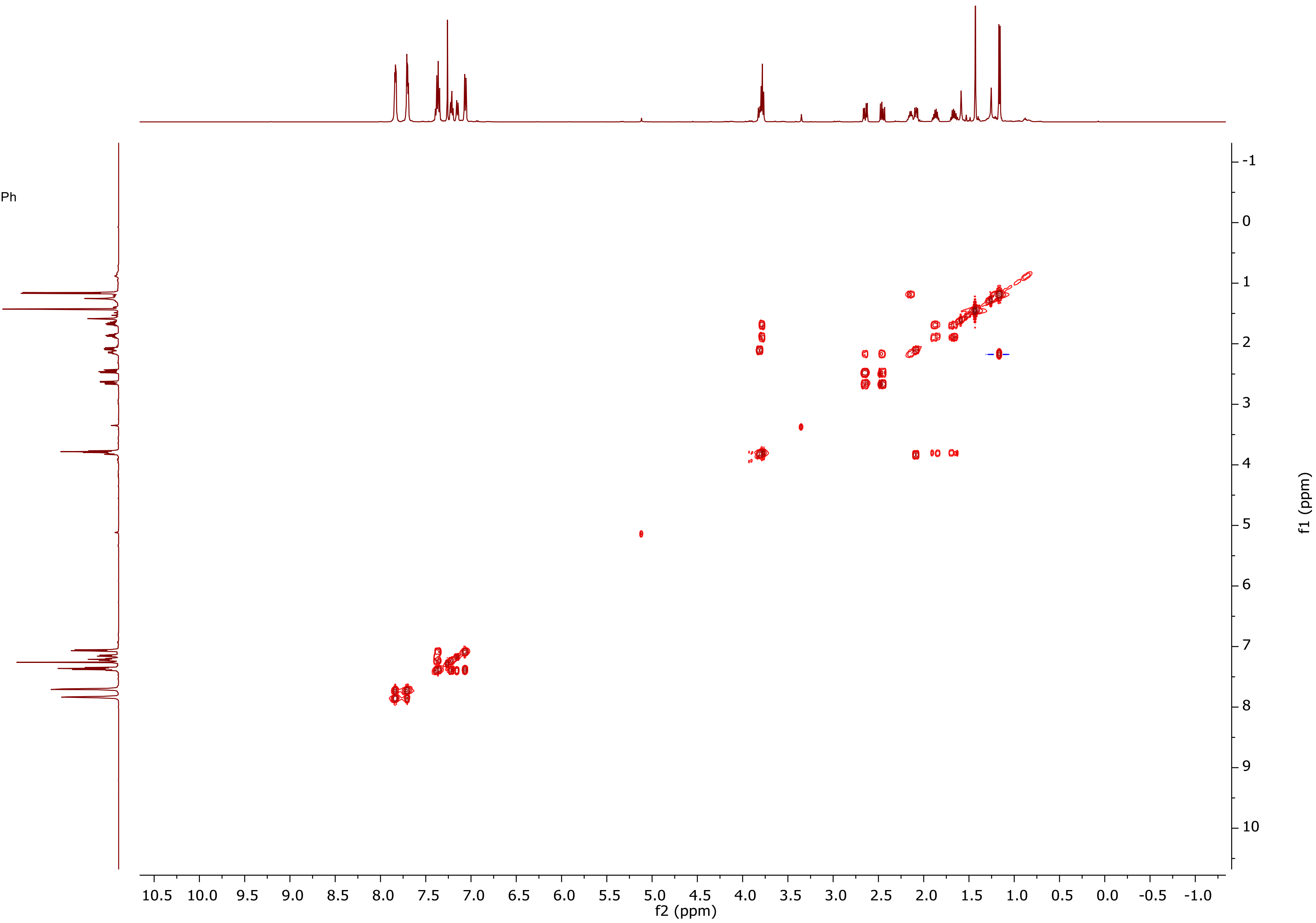
50-δ

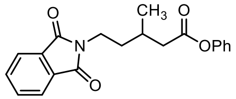

7.84
7.84
7.83
7.82
7.71
7.70
7.70
7.69
7.39
7.38
7.36
7.35
7.35
7.23
7.23
7.22
7.21
7.20
7.20
7.07
7.06
7.05
2.67
2.65
2.64
2.62
2.48
2.46
2.45
2.43
2.17
2.16
2.15
2.14
2.13
2.12
2.10
2.09
2.08
2.08
2.07
1.89
1.88
1.86
1.86
1.85
1.69
1.67
1.66
1.64
1.17
1.16
2.90
3.16
2.89
1.66
2.20
2.24
1.00
1.02
1.11
1.03
1.03
1.12
3.26
2500000
2000000
1500000
1000000
500000
0
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)


O
CH$_3$
O
N
OPh
O

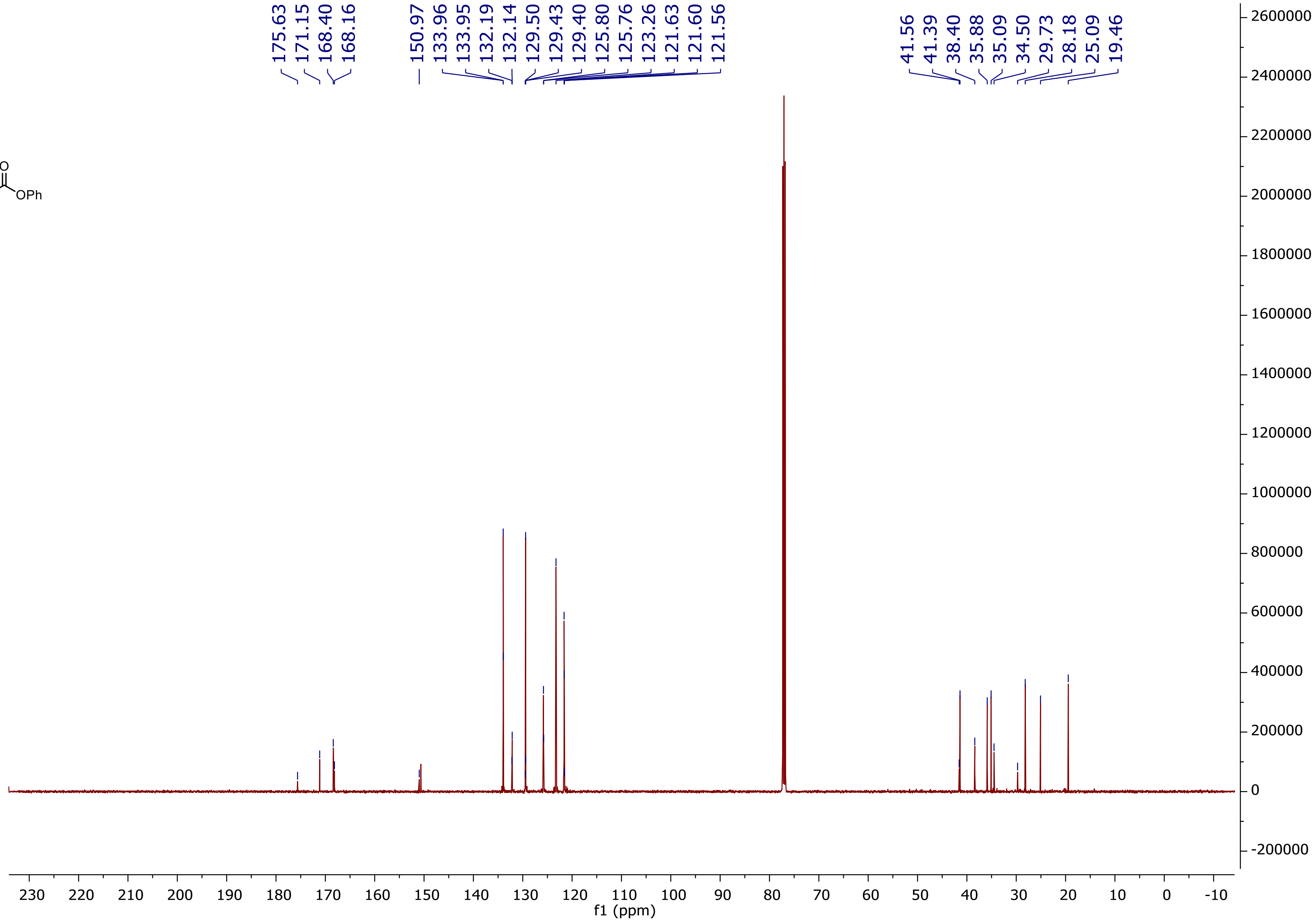
50-δ

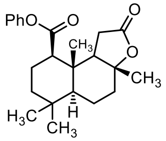
COSY


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
-1.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
9
10
f1 (ppm)

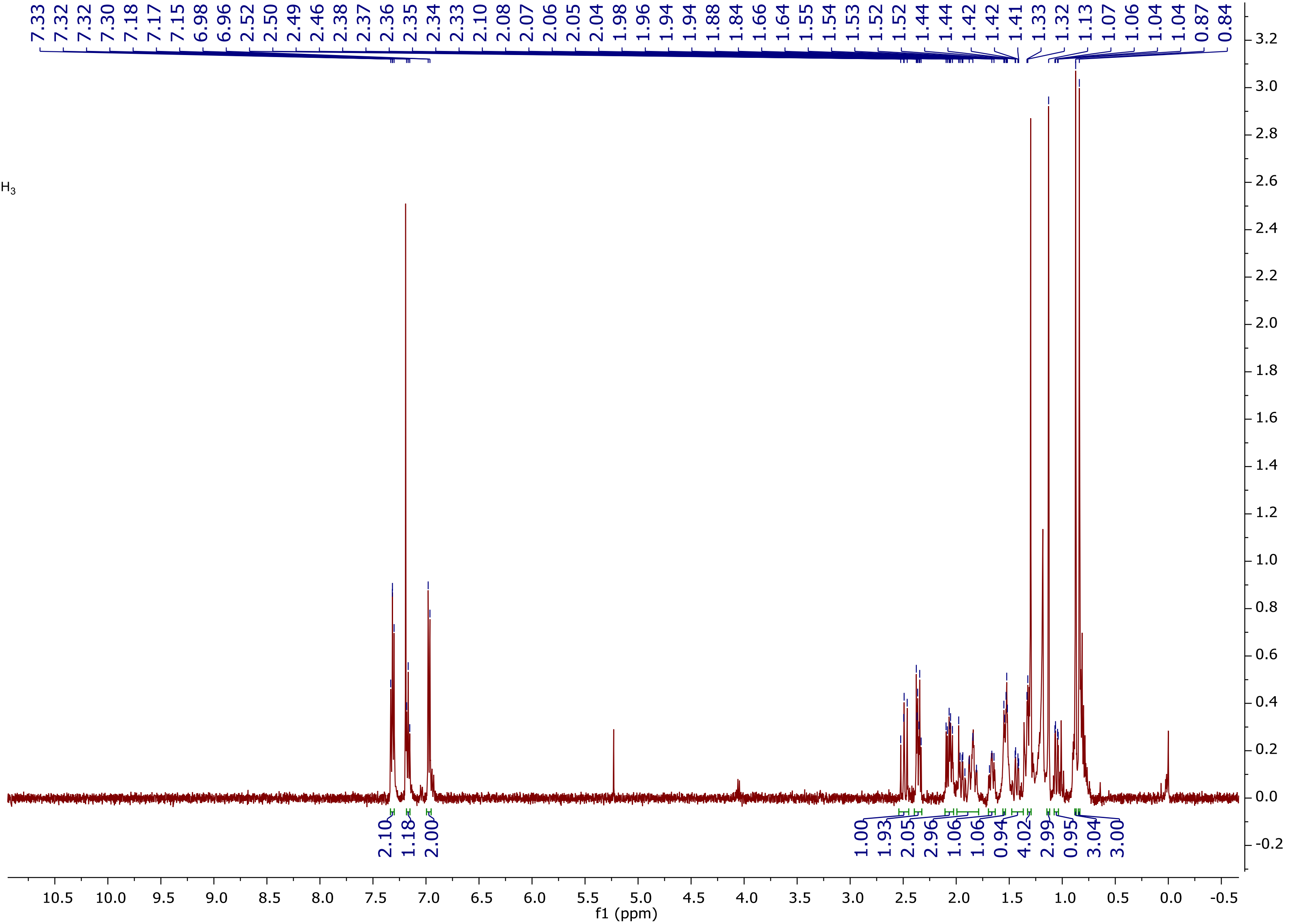

O
CH3
O
N
OPh
O

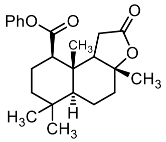
50-δ


175.63
171.15
168.40
168.16
150.97
133.96
133.95
132.19
132.14
129.50
129.43
129.40
125.80
125.76
123.26
121.63
121.60
121.56
41.56
41.39
38.40
35.88
35.09
34.50
29.73
28.18
25.09
19.46
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
230
220
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)

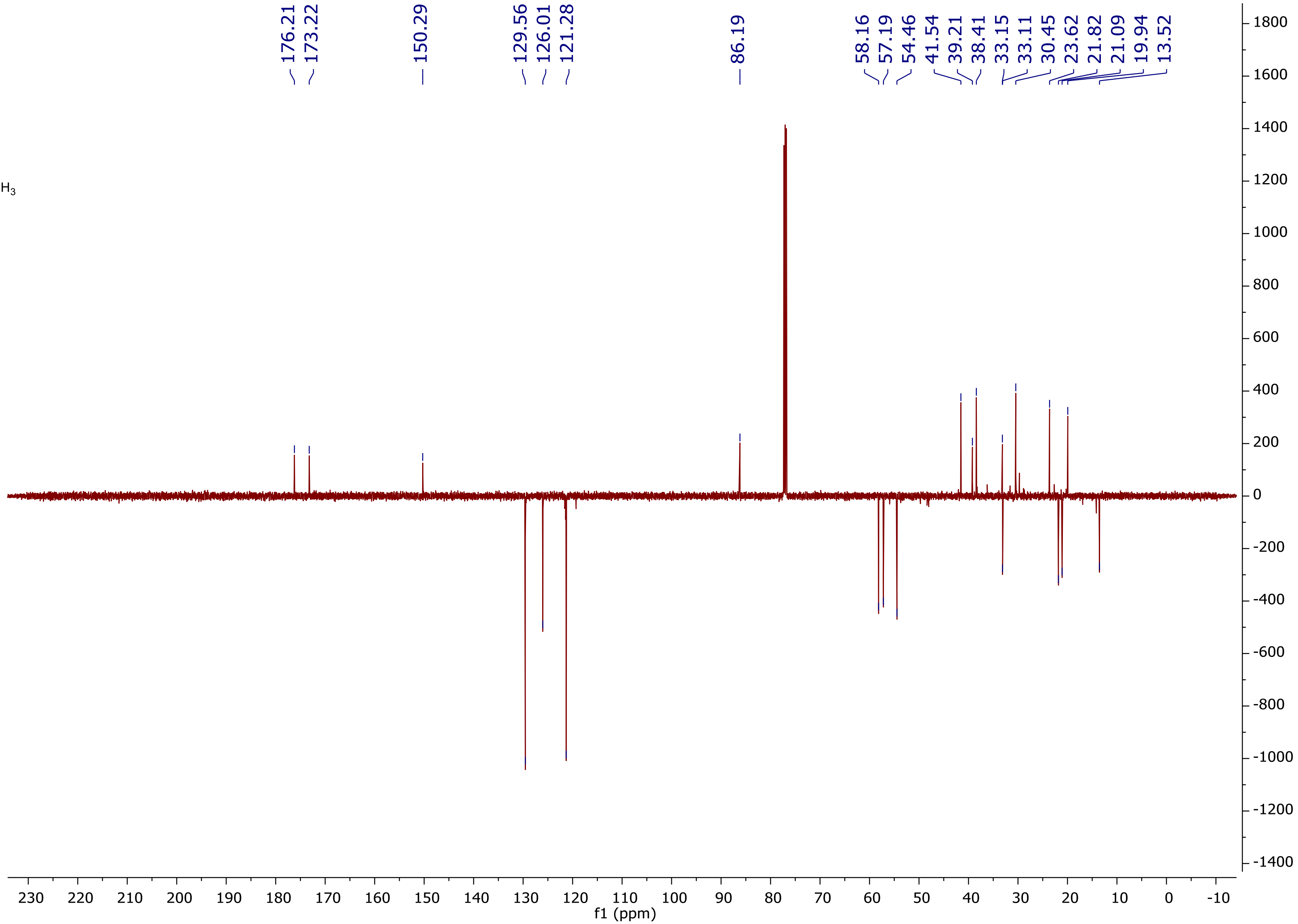

PhO
O
O
O
CH3
CH3
H
H3C
CH3

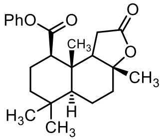
51-α


7.33
7.32
7.32
7.30
7.18
7.17
7.15
6.98
6.96
2.52
2.50
2.49
2.46
2.38
2.37
2.36
2.35
2.34
2.33
2.10
2.08
2.07
2.06
2.05
2.04
1.98
1.96
1.94
1.94
1.88
1.84
1.66
1.64
1.55
1.54
1.53
1.52
1.52
1.44
1.44
1.42
1.42
1.41
1.33
1.32
1.13
1.07
1.06
1.04
1.04
0.87
0.84
2.10
1.18
2.00
1.00
1.93
2.05
2.96
1.06
1.06
0.94
4.02
2.99
0.95
3.04
3.00
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)
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2

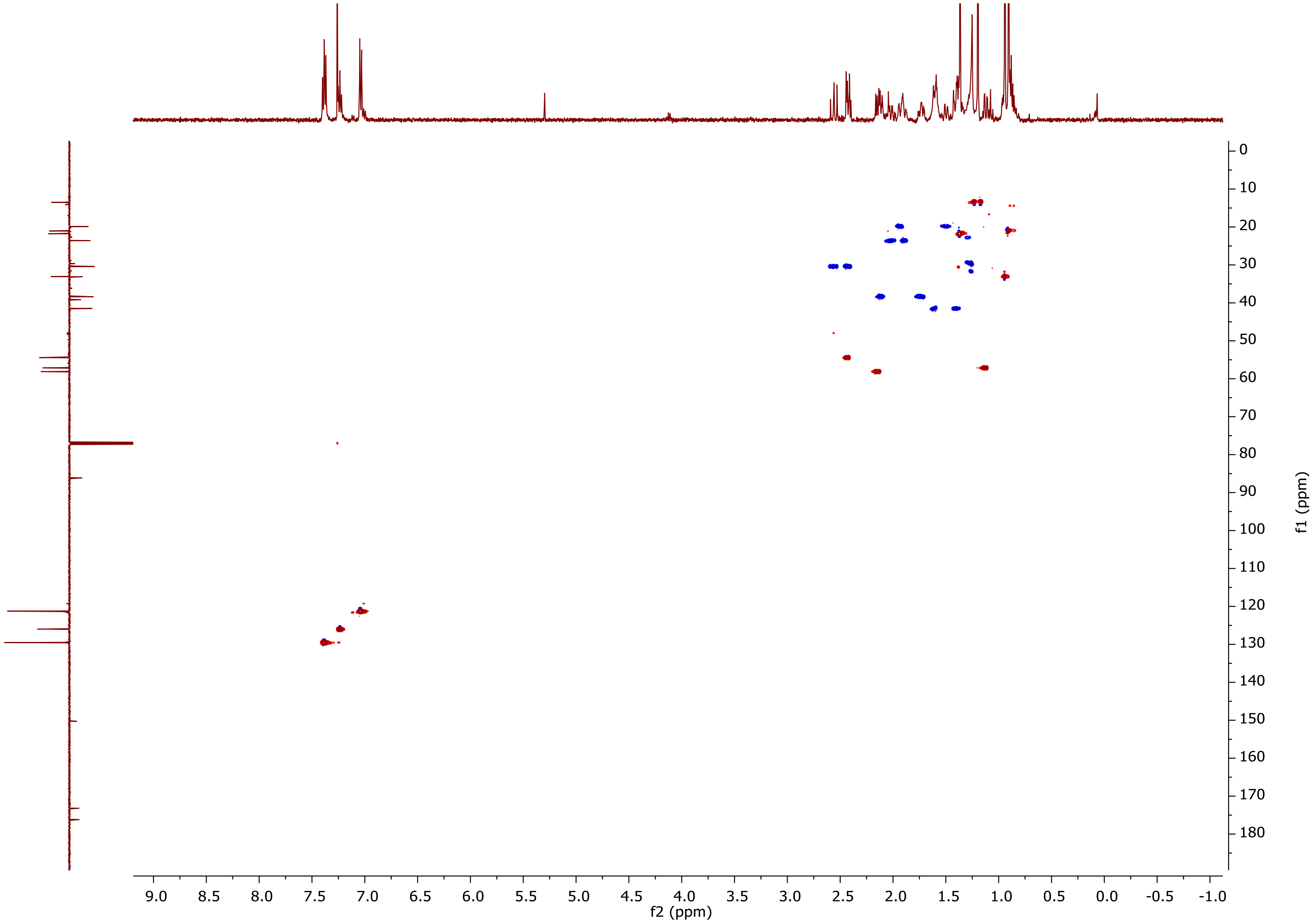

PhO
O
O
O
CH3
CH3
H3C
CH3
CH3
H

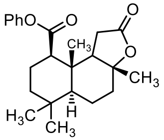
51-α


176.21
173.22
150.29
129.56
126.01
121.28
86.19
58.16
57.19
54.46
41.54
39.21
38.41
33.15
33.11
30.45
23.62
21.82
21.09
19.94
13.52
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-1000
-1200
-1400
230
220
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)

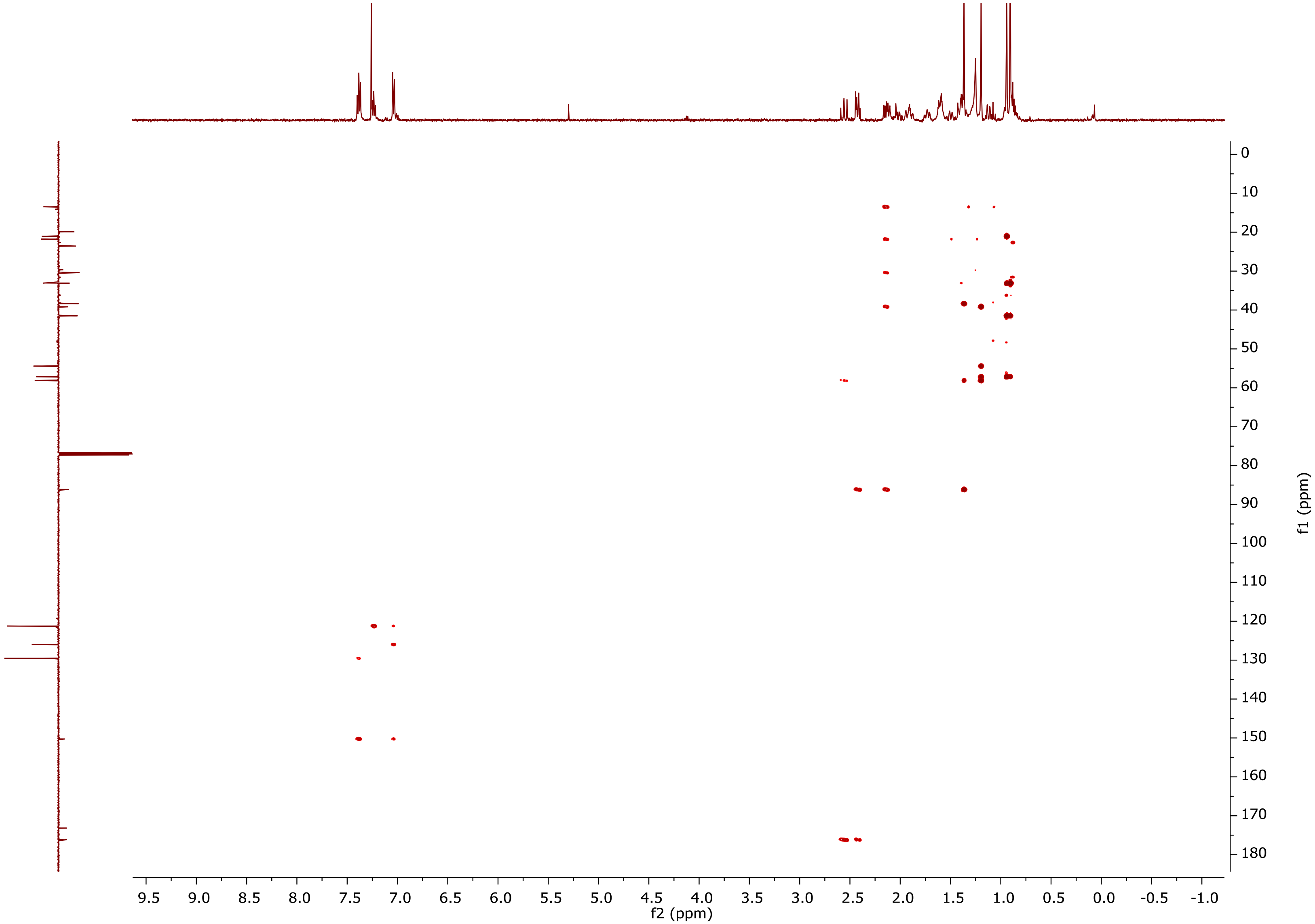

PhO
O
O
O
CH3
CH3
H3C
CH3
H

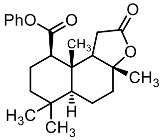
51-α
HSQC


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)


PhO
O
O
O
CH3
CH3
H3C
CH3
H

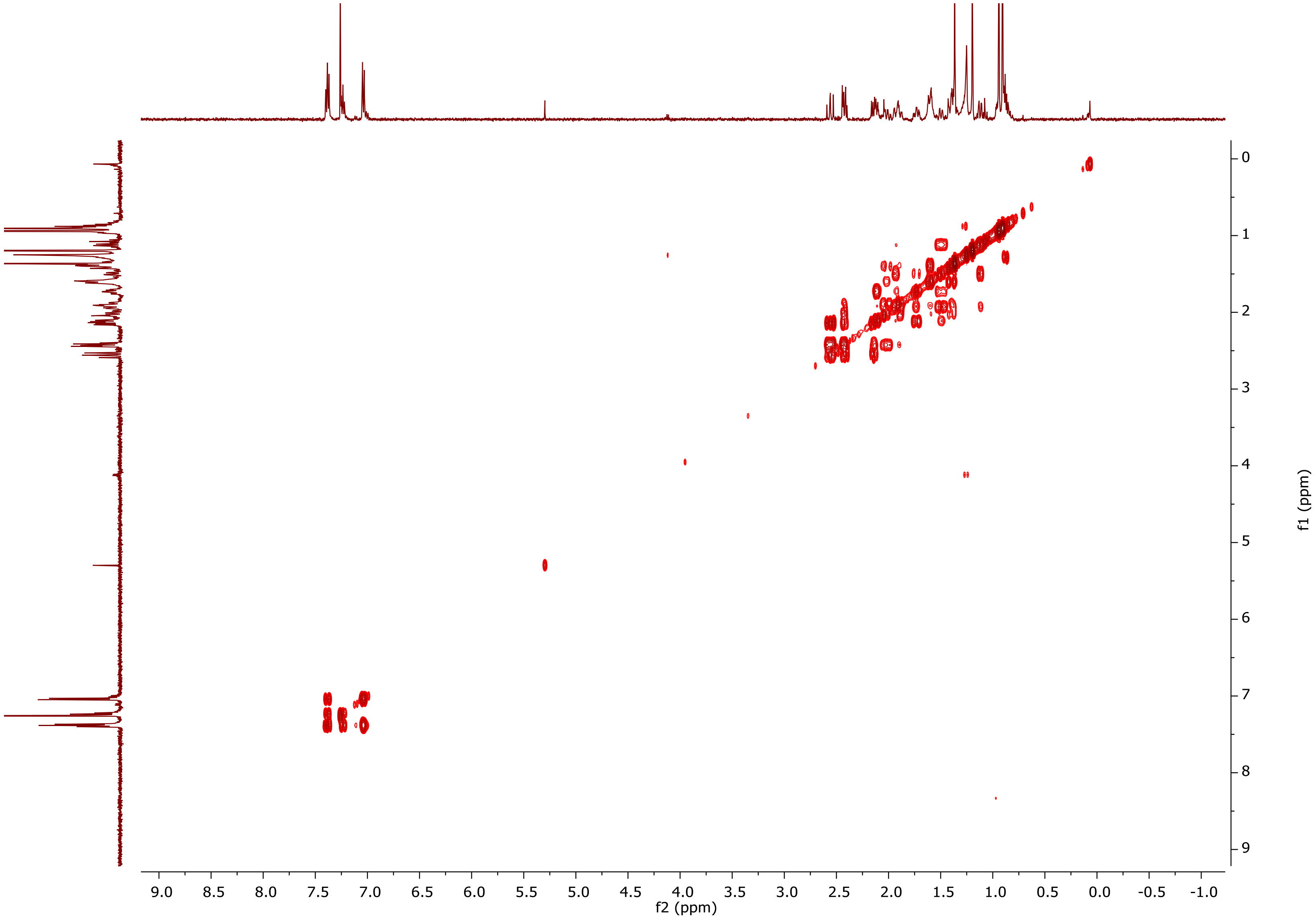
51-α
HMBC

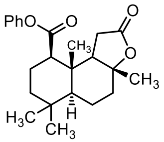

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)


PhO
O
O
O
CH3
CH3
H3C
CH3
H

51-α

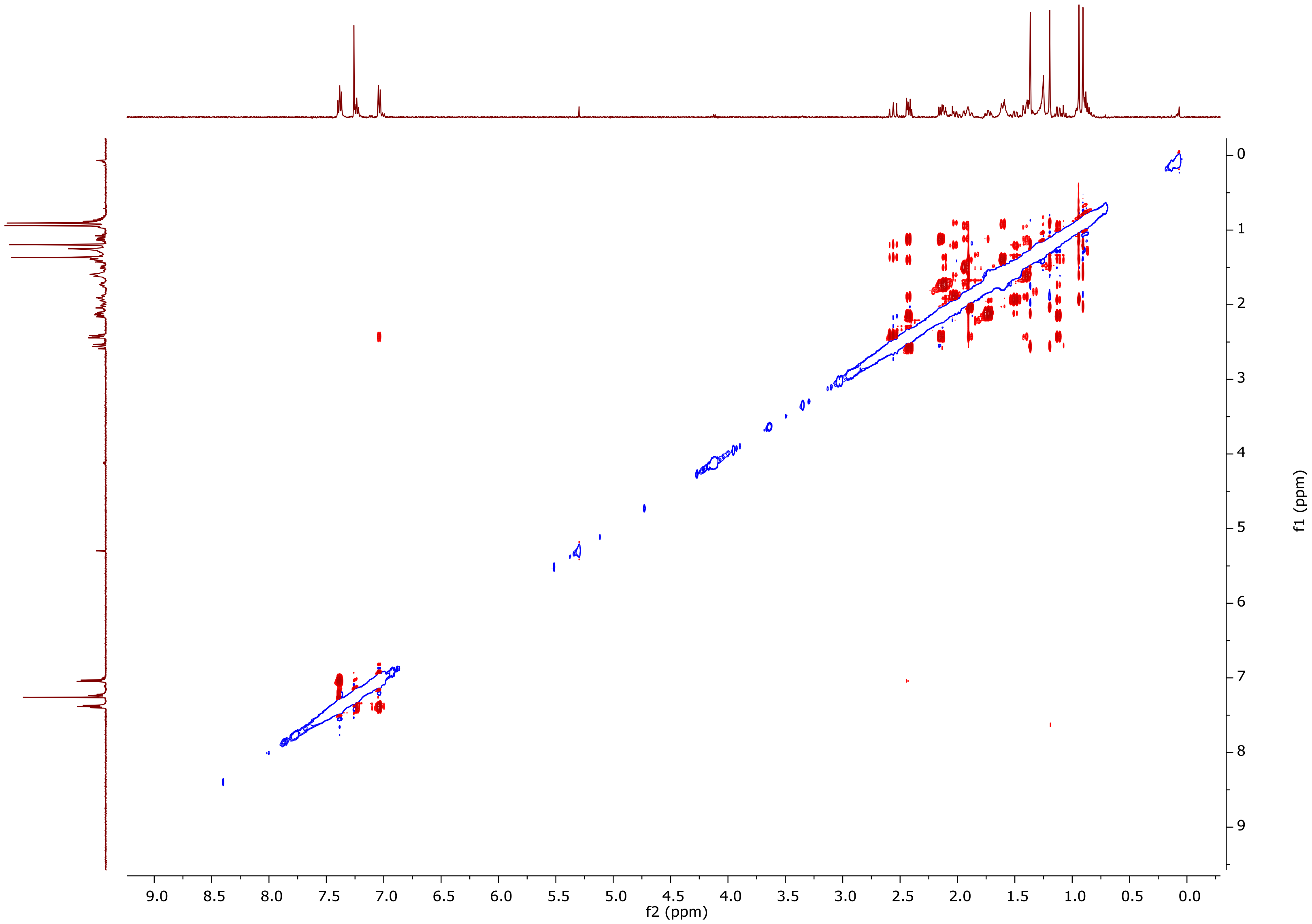
COSY

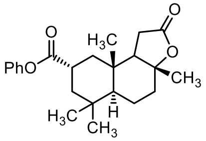

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)


PhO
O
O
CH$_3$
O
CH$_3$
H$_3$C
H
CH$_3$

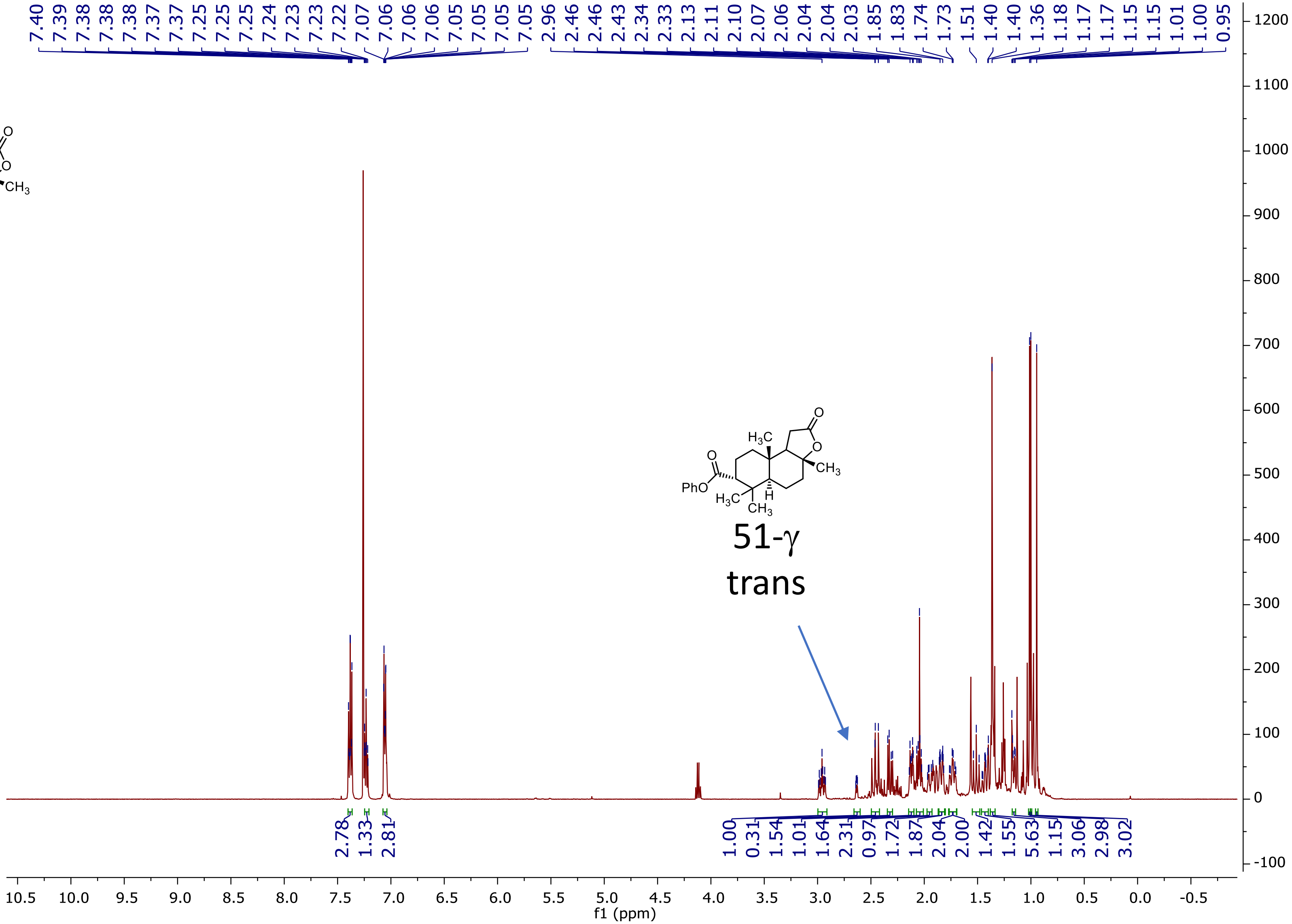
51-α

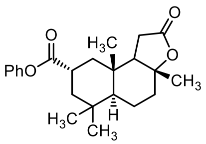
NOESY


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
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)

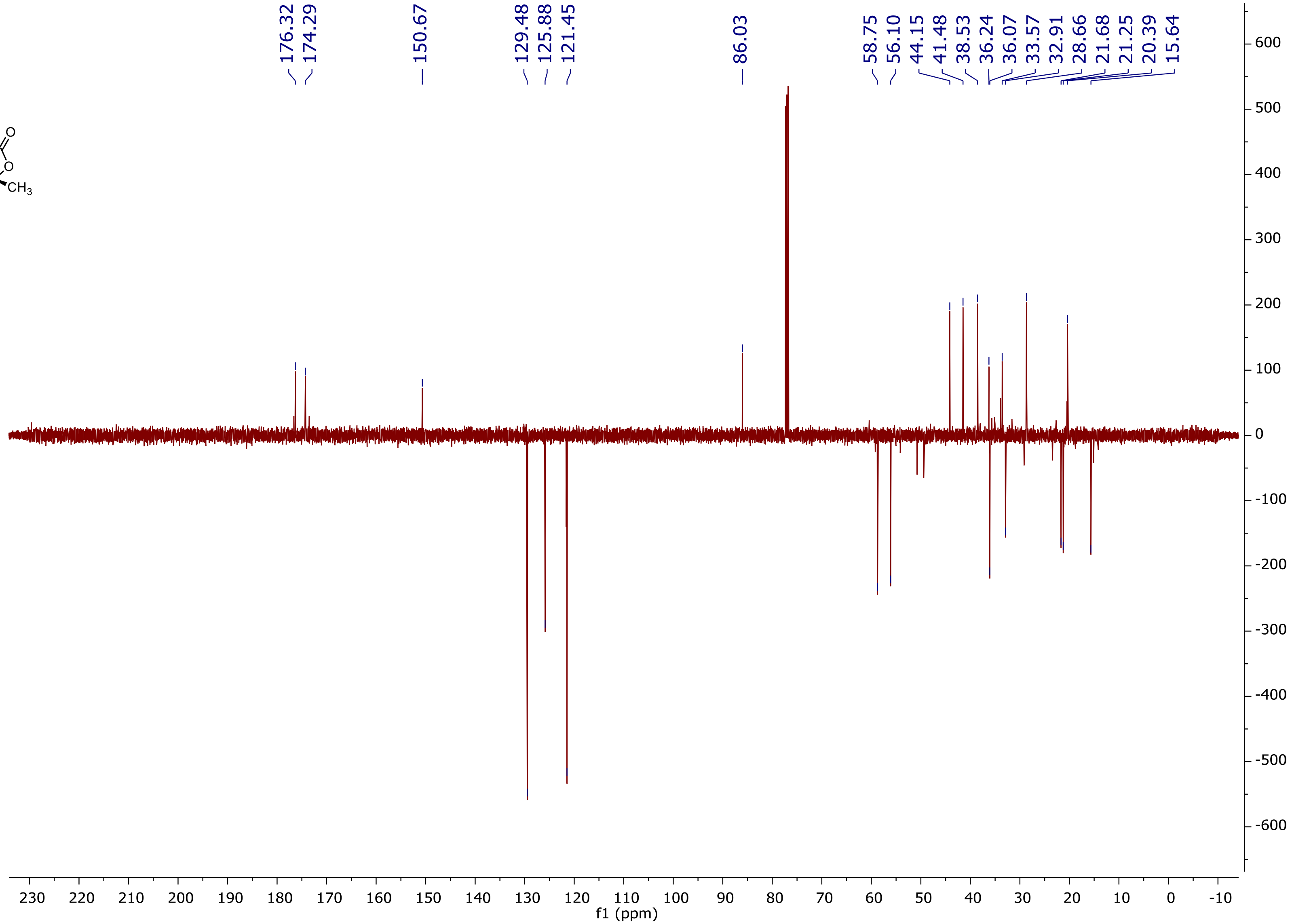


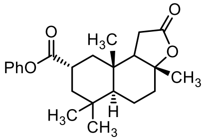
51-β


7.40
7.39
7.38
7.38
7.38
7.37
7.37
7.25
7.25
7.25
7.24
7.23
7.23
7.22
7.07
7.06
7.06
7.06
7.05
7.05
7.05
7.05
2.96
2.46
2.46
2.43
2.34
2.33
2.13
2.11
2.10
2.07
2.06
2.04
2.04
2.03
1.85
1.83
1.74
1.73
1.51
1.40
1.40
1.36
1.18
1.17
1.17
1.15
1.15
1.01
1.00
0.95
51-γ
trans
2.78
1.33
2.81
1.00
0.31
1.54
1.01
1.64
2.31
0.97
1.72
1.87
2.04
2.00
1.42
1.55
5.63
1.15
3.06
2.98
3.02
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)
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

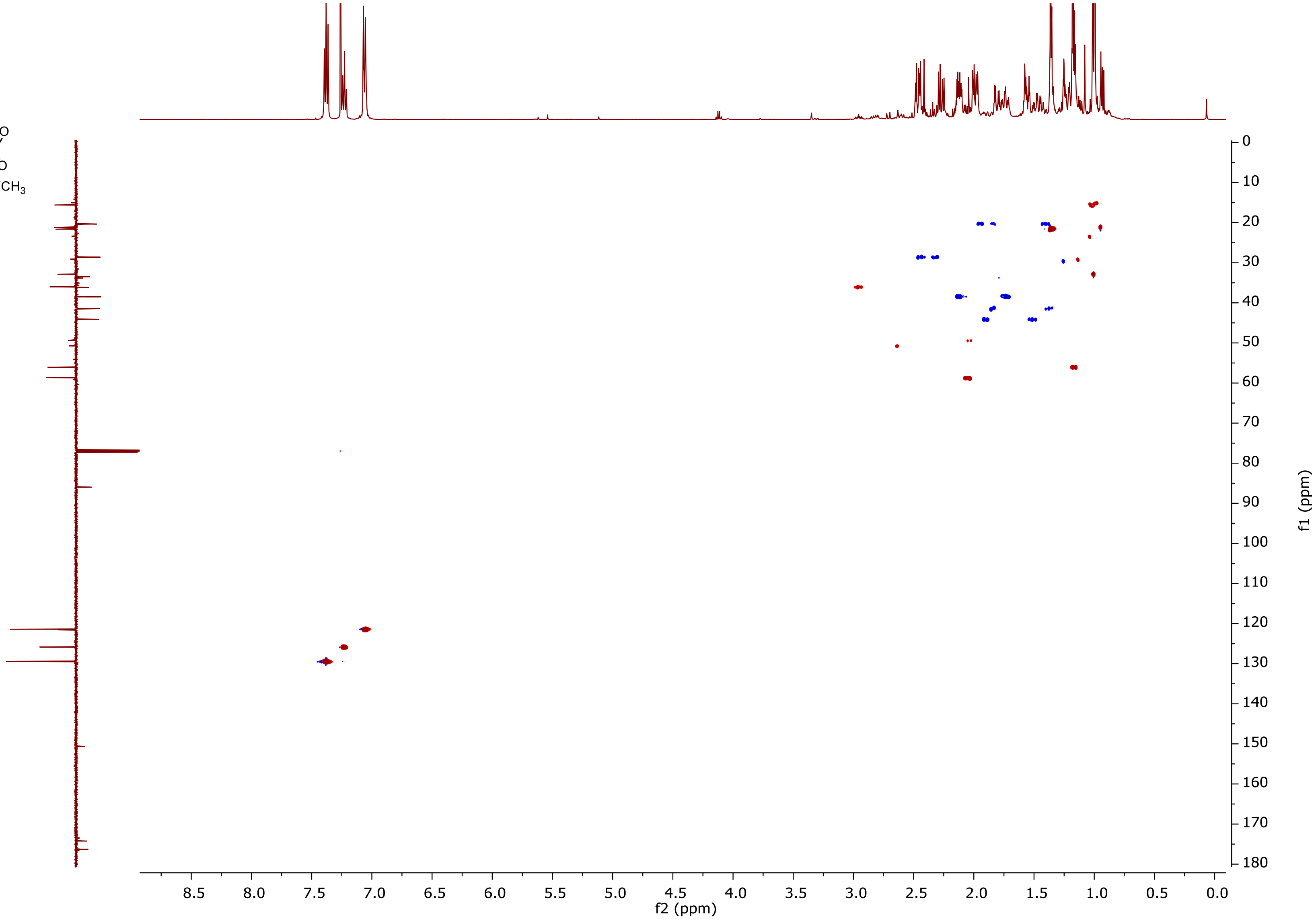

O
PhO
H3C
O
O
CH3
H3C
CH3
H

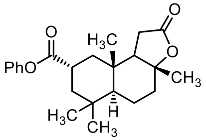
51-β


176.32
174.29
150.67
129.48
125.88
121.45
86.03
58.75
56.10
44.15
41.48
38.53
36.24
36.07
33.57
32.91
28.66
21.68
21.25
20.39
15.64
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
230
220
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)


O
PhO
H_3C
O
O
CH_3
H_3C
H
CH_3

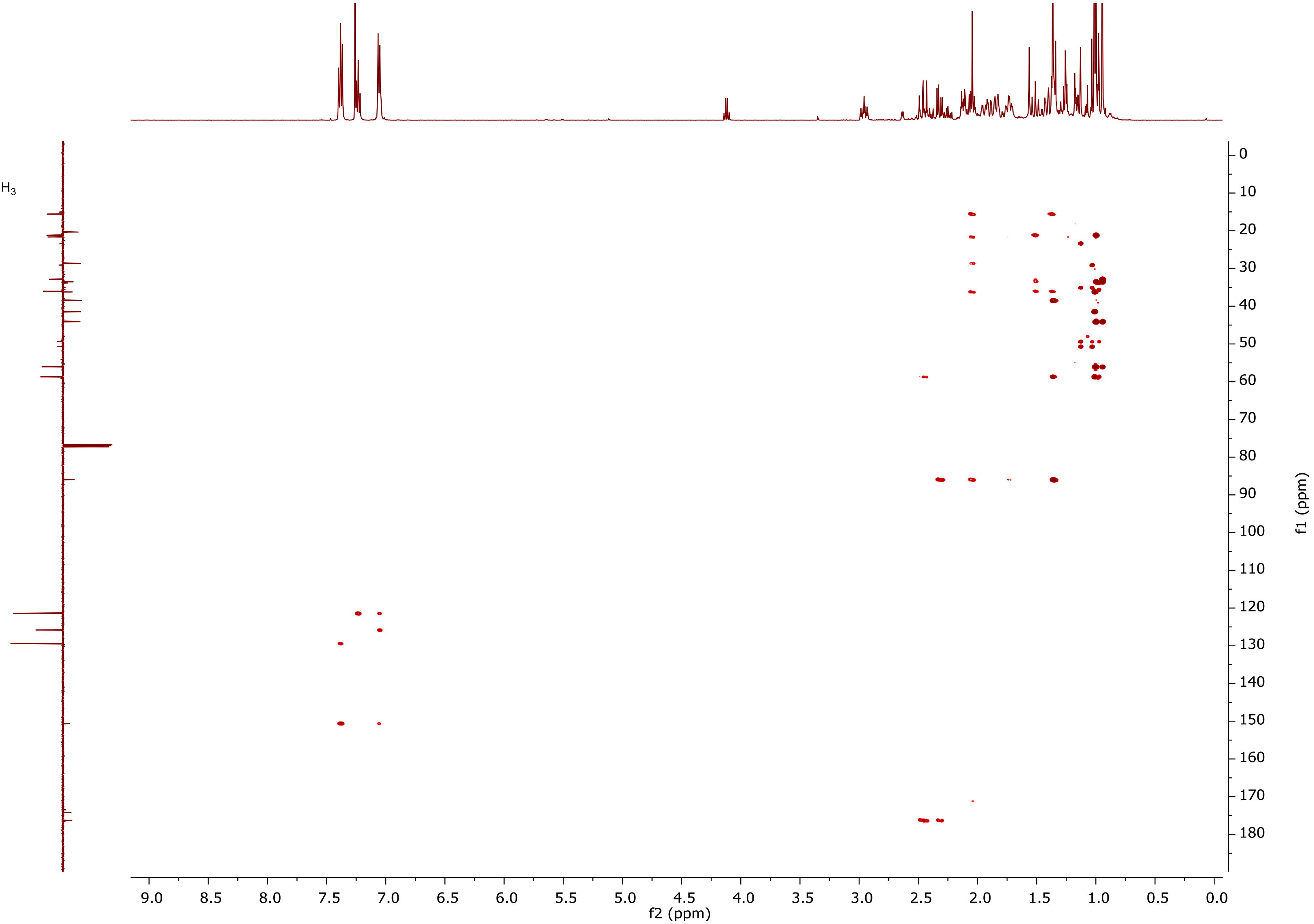
51-β
HSQC

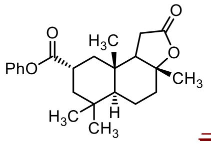

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)


O
PhO
H_3C
O
O
CH_3
H_3C
H
CH_3

51-β

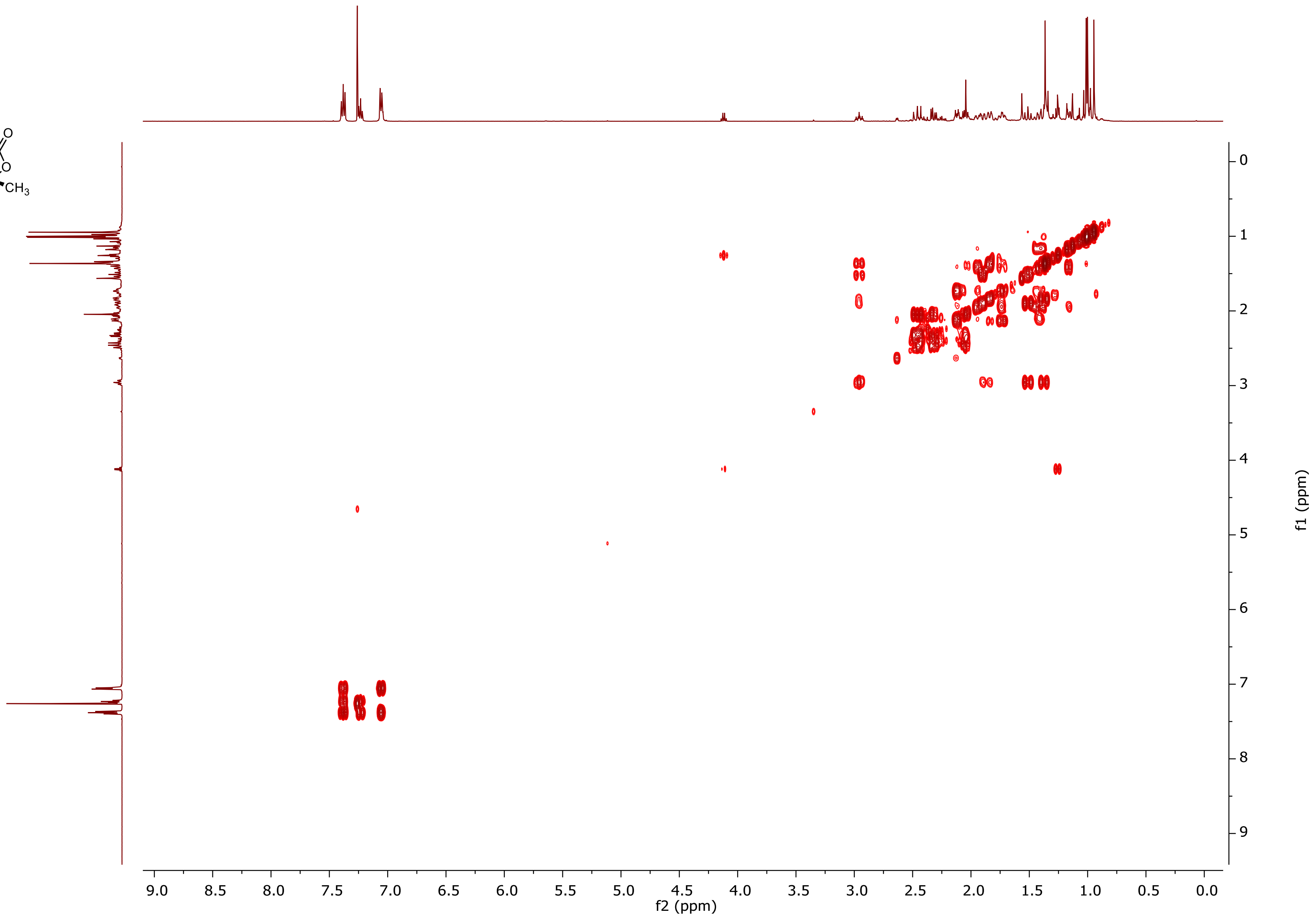
HMBC

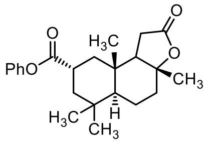

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)


O
PhO
H$_3$C
O
O
CH$_3$
H$_3$C
H
CH$_3$

51-β

COSY

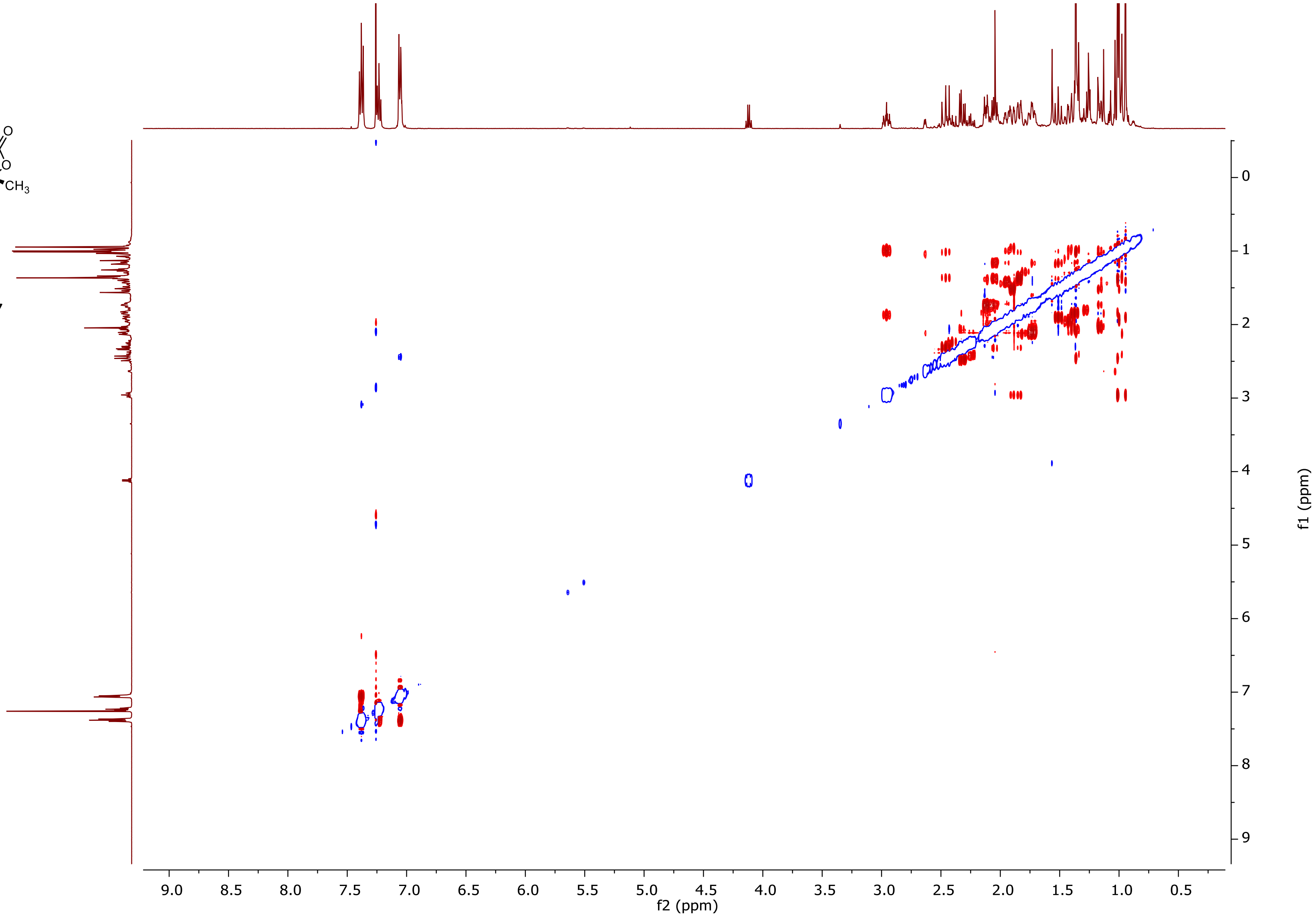

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)



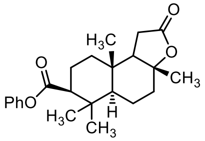
PhO
O
H$_3$C
O
O
CH$_3$
H$_3$C
H
CH$_3$

51-β

NOESY

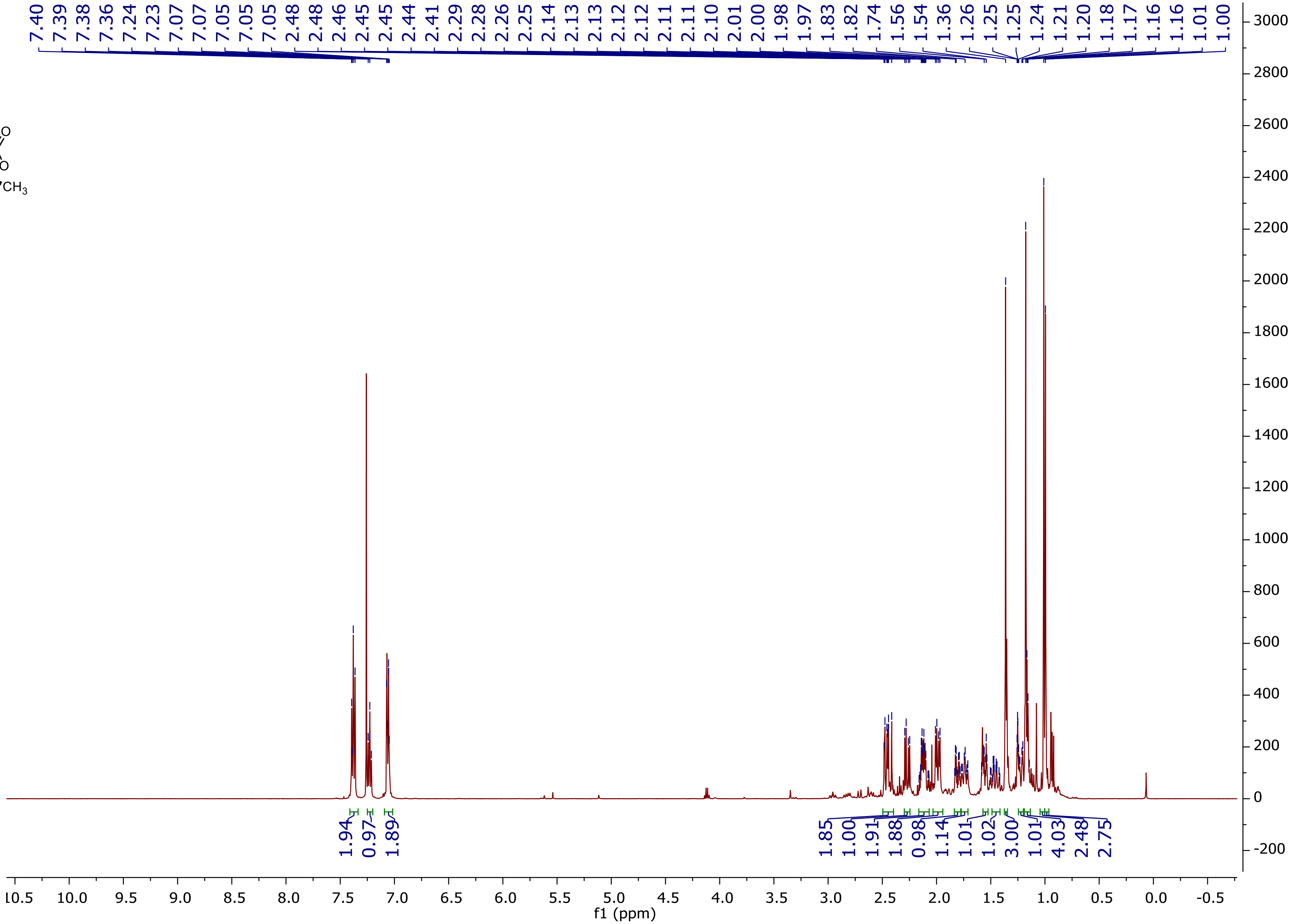


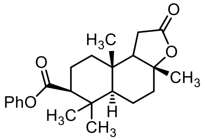
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)


O
H$_3$C
O
O
CH$_3$
PhO
H$_3$C
H
CH$_3$

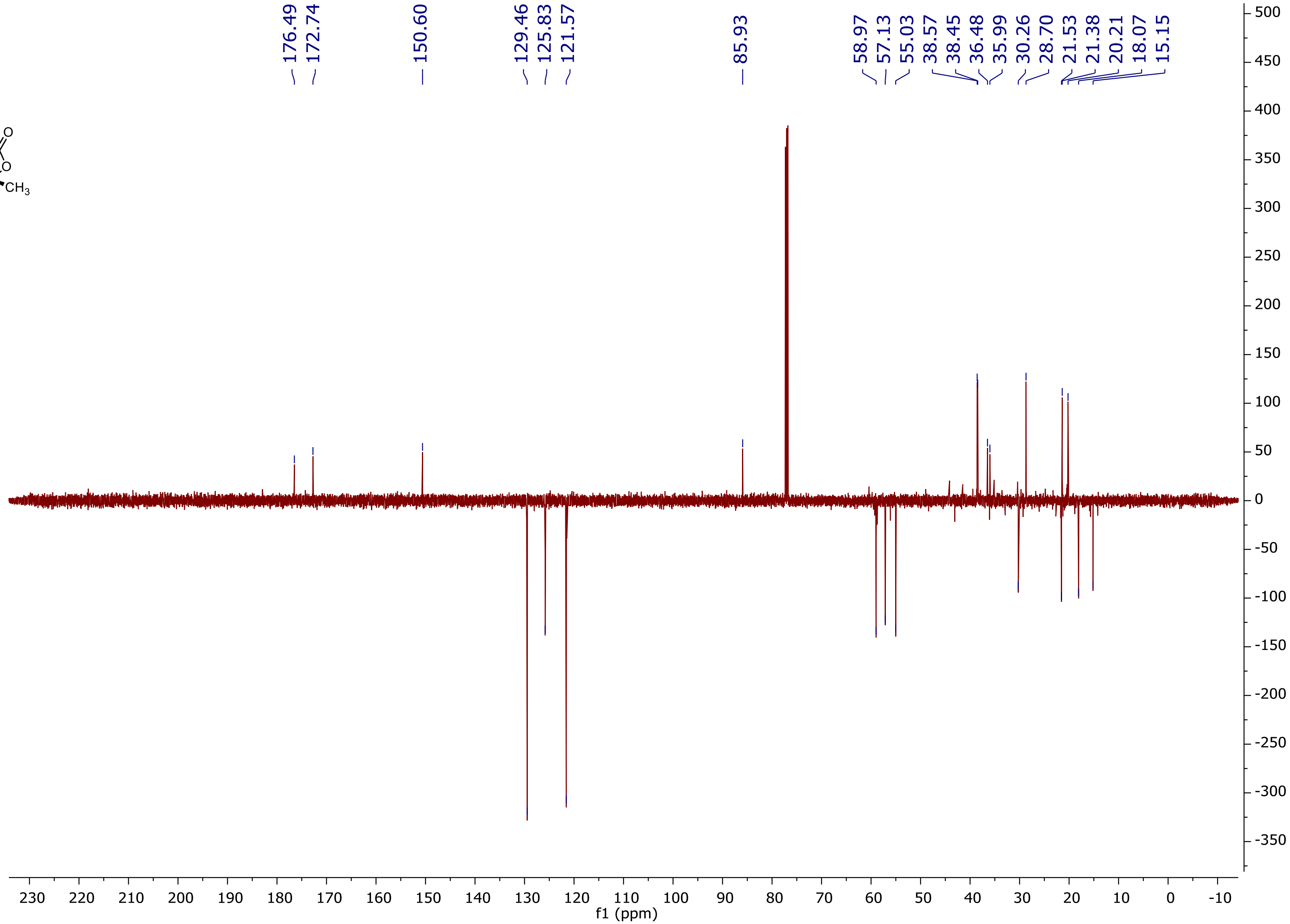
51-γ

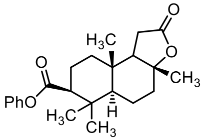
cis


7.40
7.39
7.38
7.36
7.24
7.23
7.07
7.07
7.05
7.05
7.05
2.48
2.48
2.46
2.45
2.45
2.44
2.41
2.29
2.28
2.26
2.25
2.14
2.13
2.13
2.12
2.12
2.11
2.11
2.10
2.01
2.00
1.98
1.97
1.83
1.82
1.74
1.56
1.54
1.36
1.26
1.25
1.25
1.24
1.21
1.20
1.18
1.17
1.16
1.16
1.01
1.00
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
1.94
0.97
1.89
1.85
1.00
1.91
1.88
0.98
1.14
1.01
1.02
3.00
1.01
4.03
2.48
2.75
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)

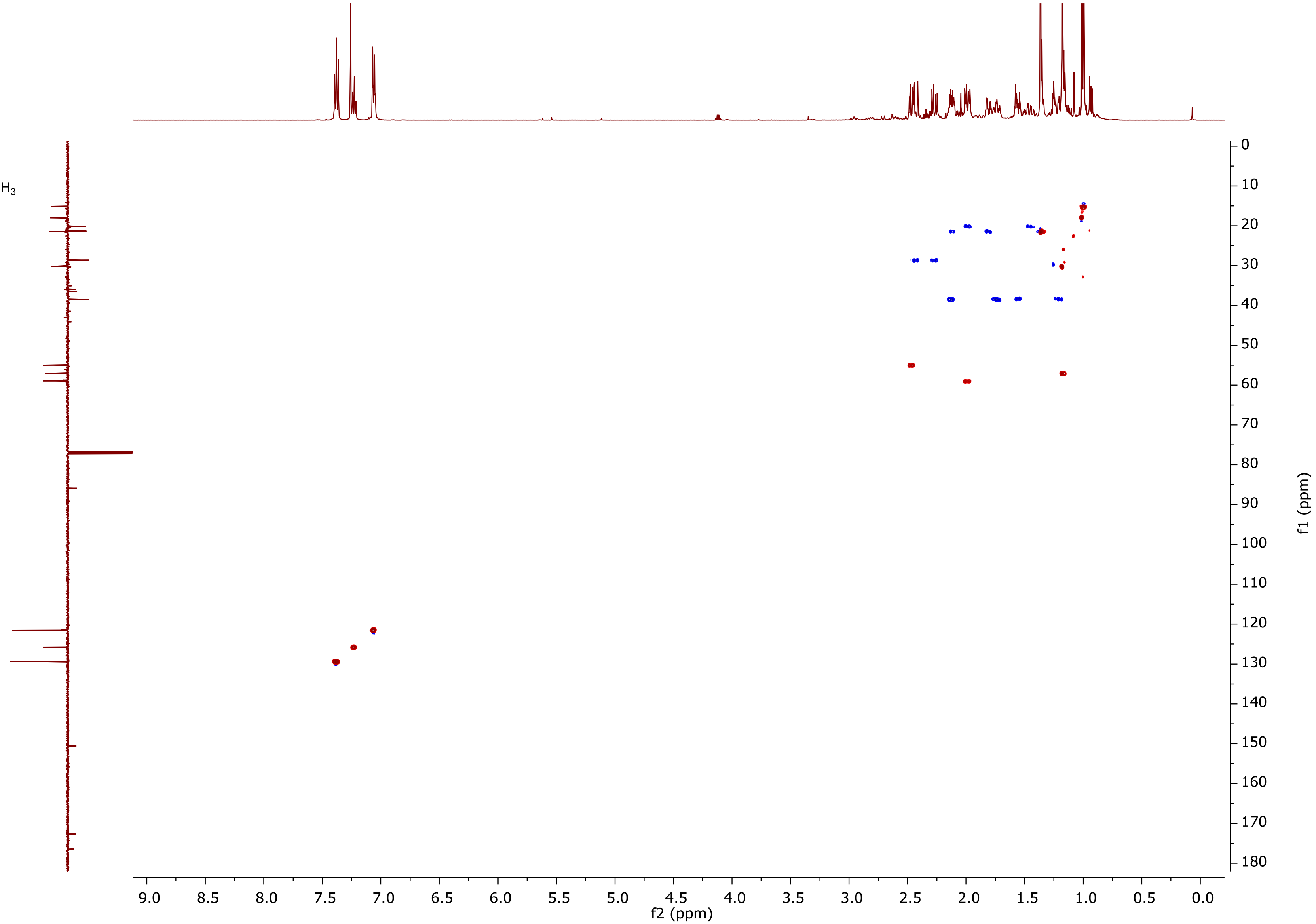

O
O
O
H3C
CH3
PhO
H3C
CH3
H
CH3

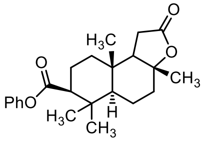
51-γ
cis


176.49
172.74
150.60
129.46
125.83
121.57
85.93
58.97
57.13
55.03
38.57
38.45
36.48
35.99
30.26
28.70
21.53
21.38
20.21
18.07
15.15
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
230
220
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)


O
H$_3$C
O
O
PhO
CH$_3$
H$_3$C
H
CH$_3$

51-γ
Cis
HSQC


0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)
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
f2 (ppm)

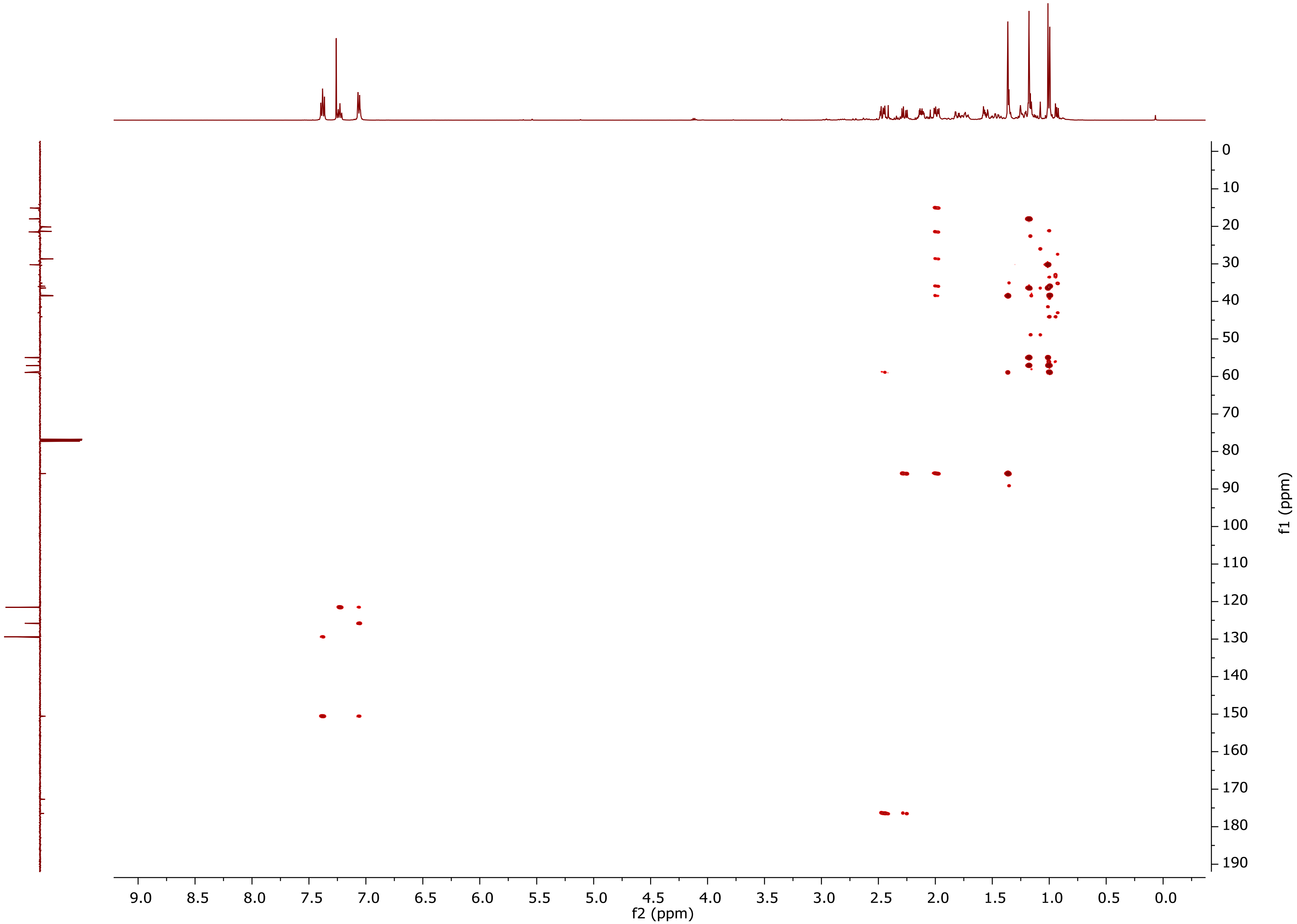


O
H$_3$C
O
O
CH$_3$
PhO
H$_3$C
H
CH$_3$

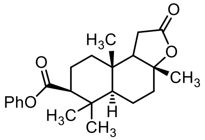
51-γ

Cis

HMBC



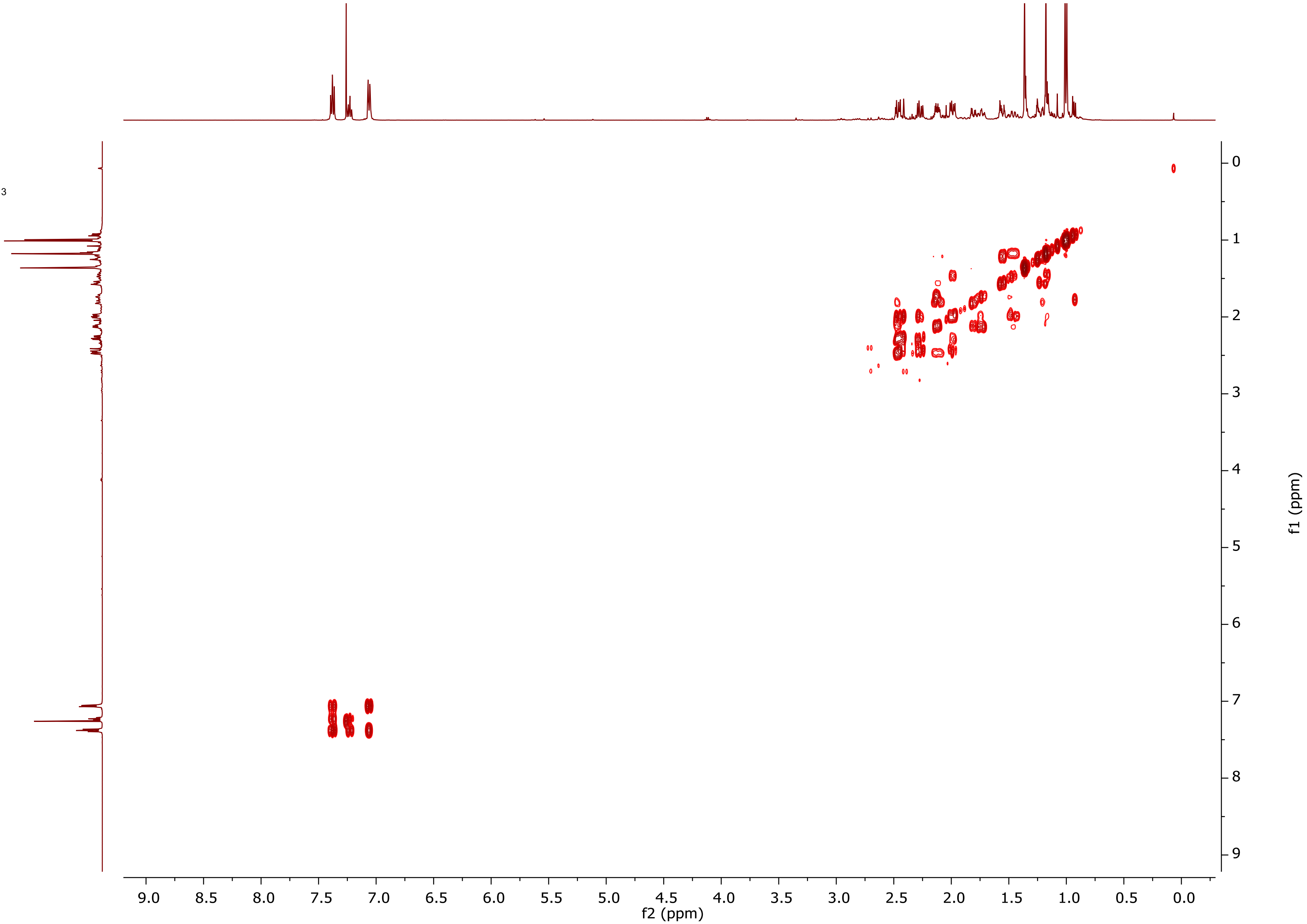
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)

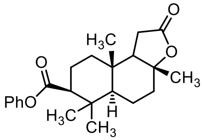

O
H$_3$C
O
CH$_3$
PhO
H$_3$C
H
CH$_3$
O

51-γ

Cis

COSY

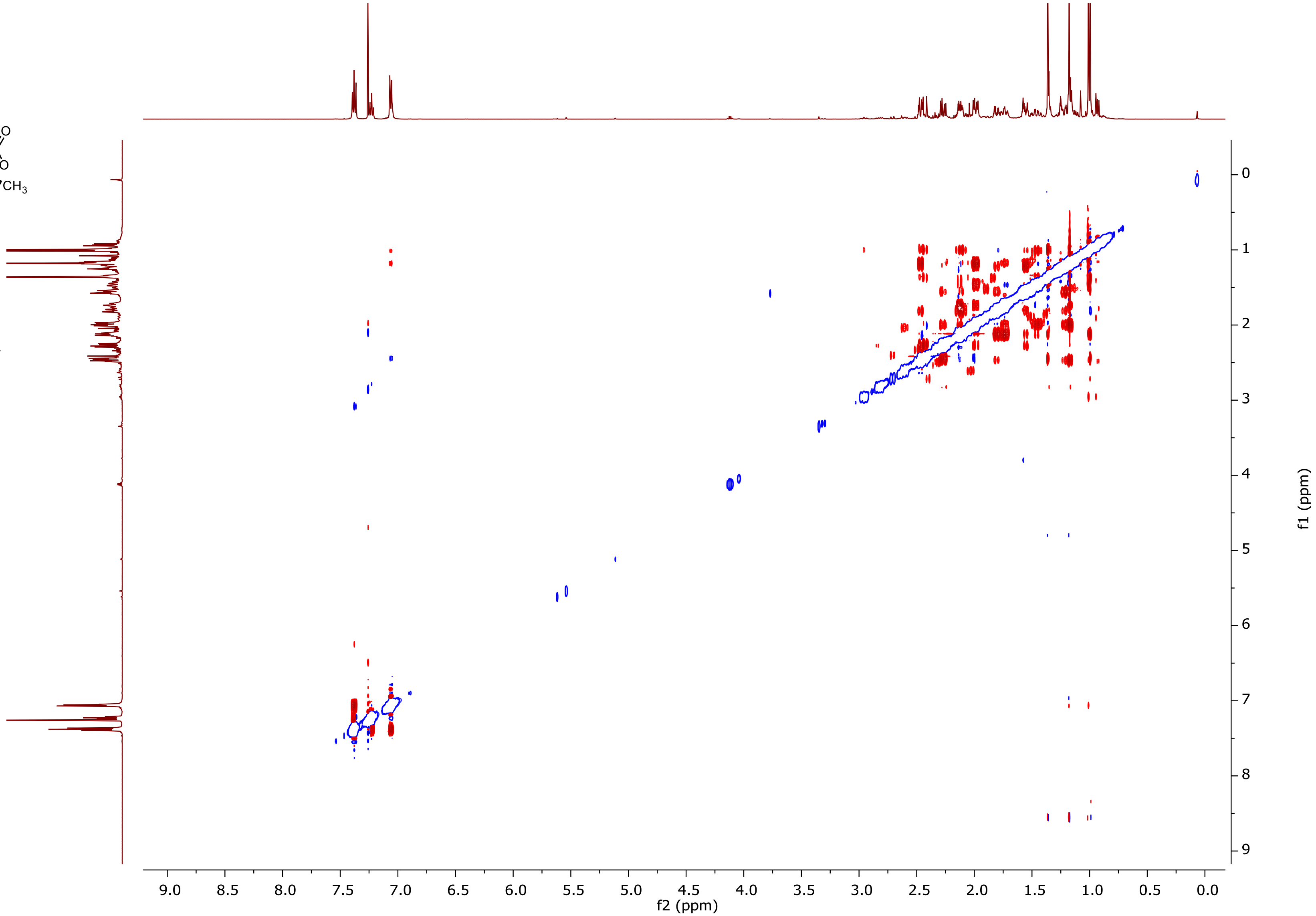

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)

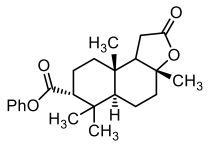


51-γ

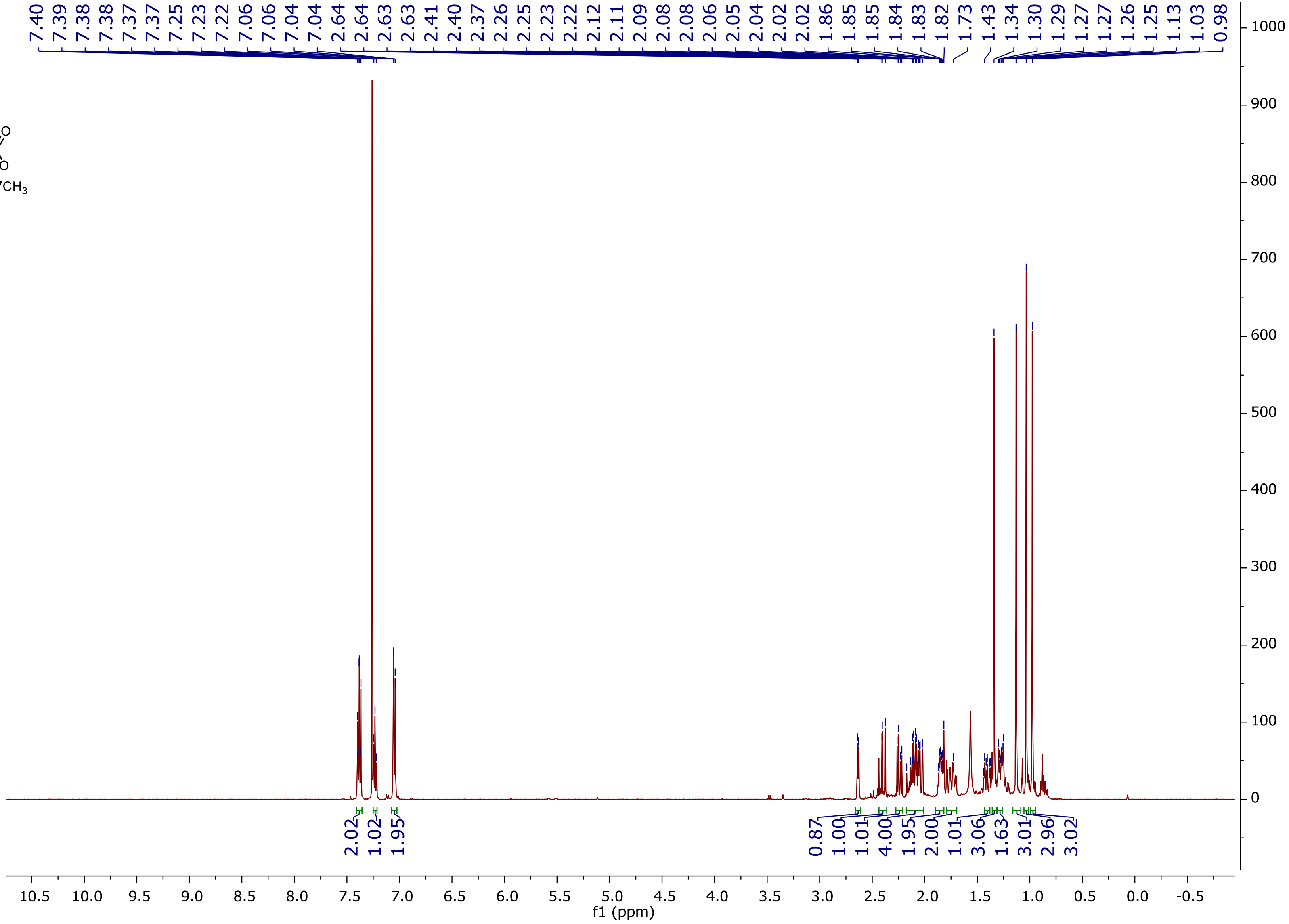
Cis

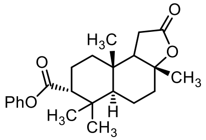
NOESY



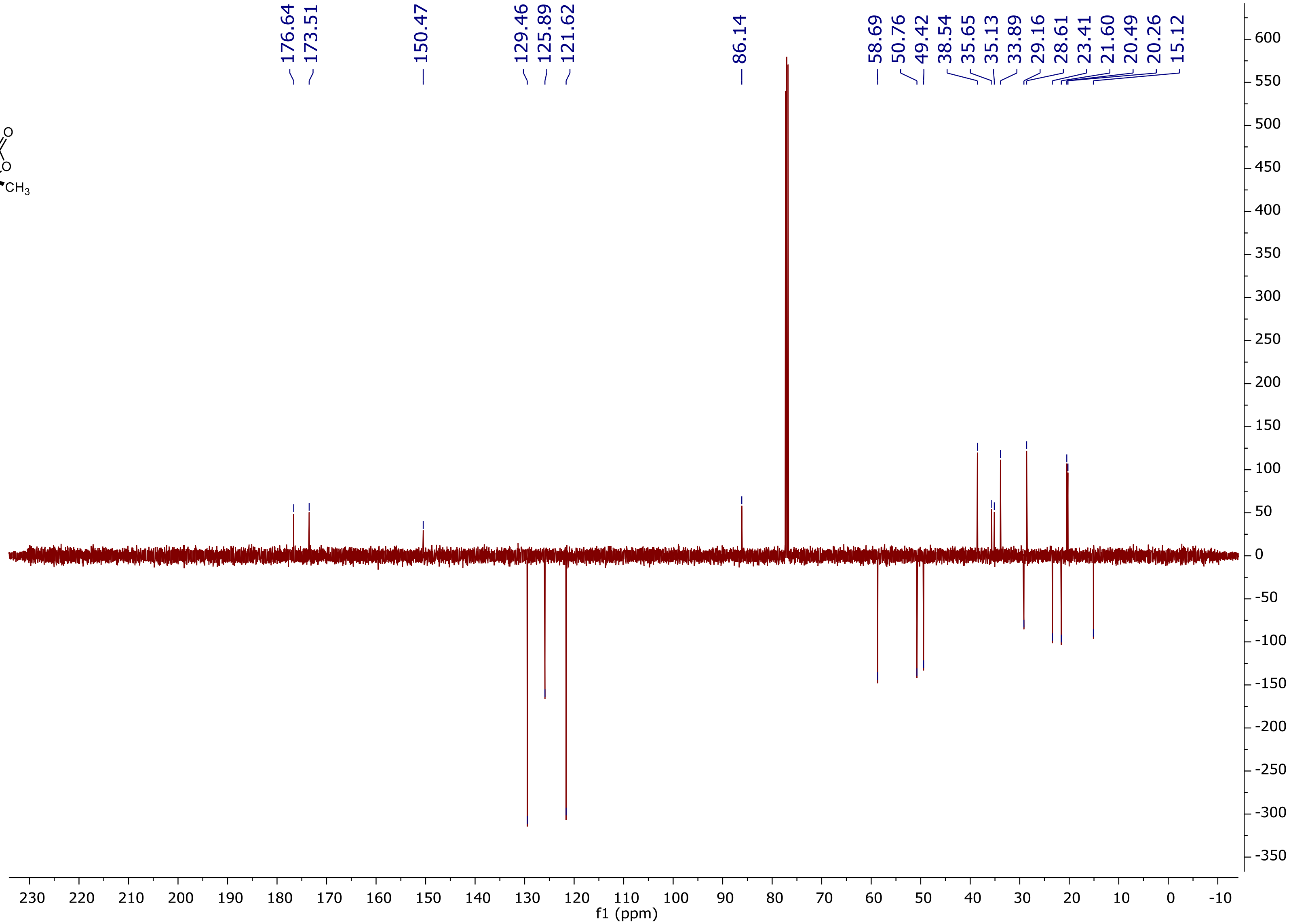

O
H3C
O
O
CH3
PhO
H3C
H
CH3

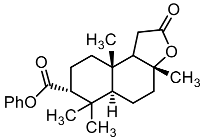
51-γ
trans


7.40
7.39
7.38
7.38
7.37
7.37
7.25
7.23
7.22
7.06
7.06
7.04
7.04
2.64
2.64
2.63
2.63
2.41
2.40
2.37
2.26
2.25
2.23
2.22
2.12
2.11
2.09
2.08
2.08
2.06
2.05
2.04
2.02
2.02
1.86
1.85
1.85
1.84
1.83
1.82
1.73
1.43
1.34
1.30
1.29
1.27
1.27
1.26
1.25
1.13
1.03
0.98
2.02
1.02
1.95
0.87
1.00
1.01
4.00
1.95
2.00
1.01
3.06
1.63
3.01
2.96
3.02
1000
900
800
700
600
500
400
300
200
100
0
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)


O
H$_3$C
O
O
CH$_3$
PhO
H$_3$C
H
CH$_3$

51-γ
trans

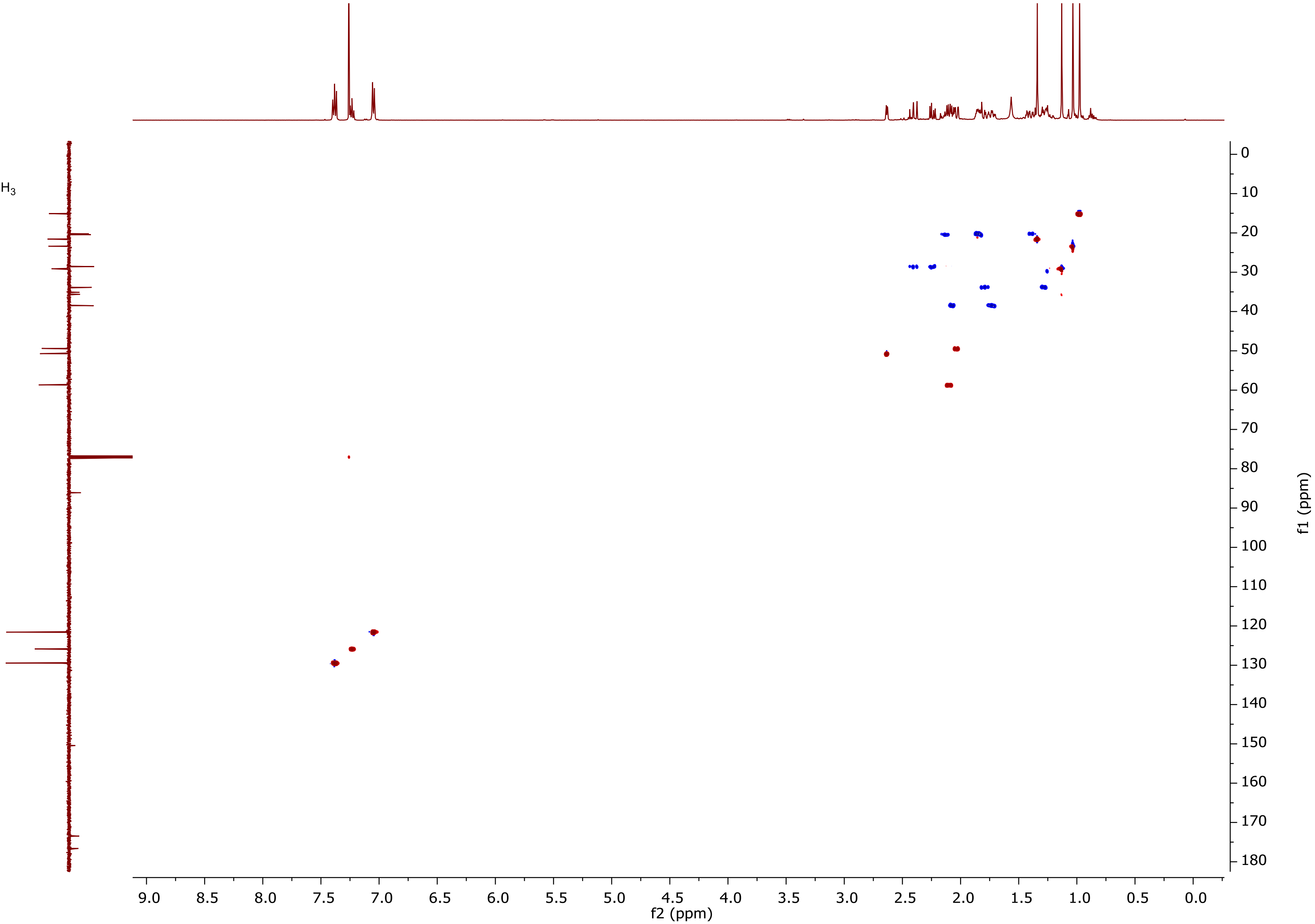

176.64
173.51
150.47
129.46
125.89
121.62
86.14
58.69
50.76
49.42
38.54
35.65
35.13
33.89
29.16
28.61
23.41
21.60
20.49
20.26
15.12
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
600 550 500 450 400 350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350

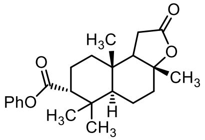


51-γ

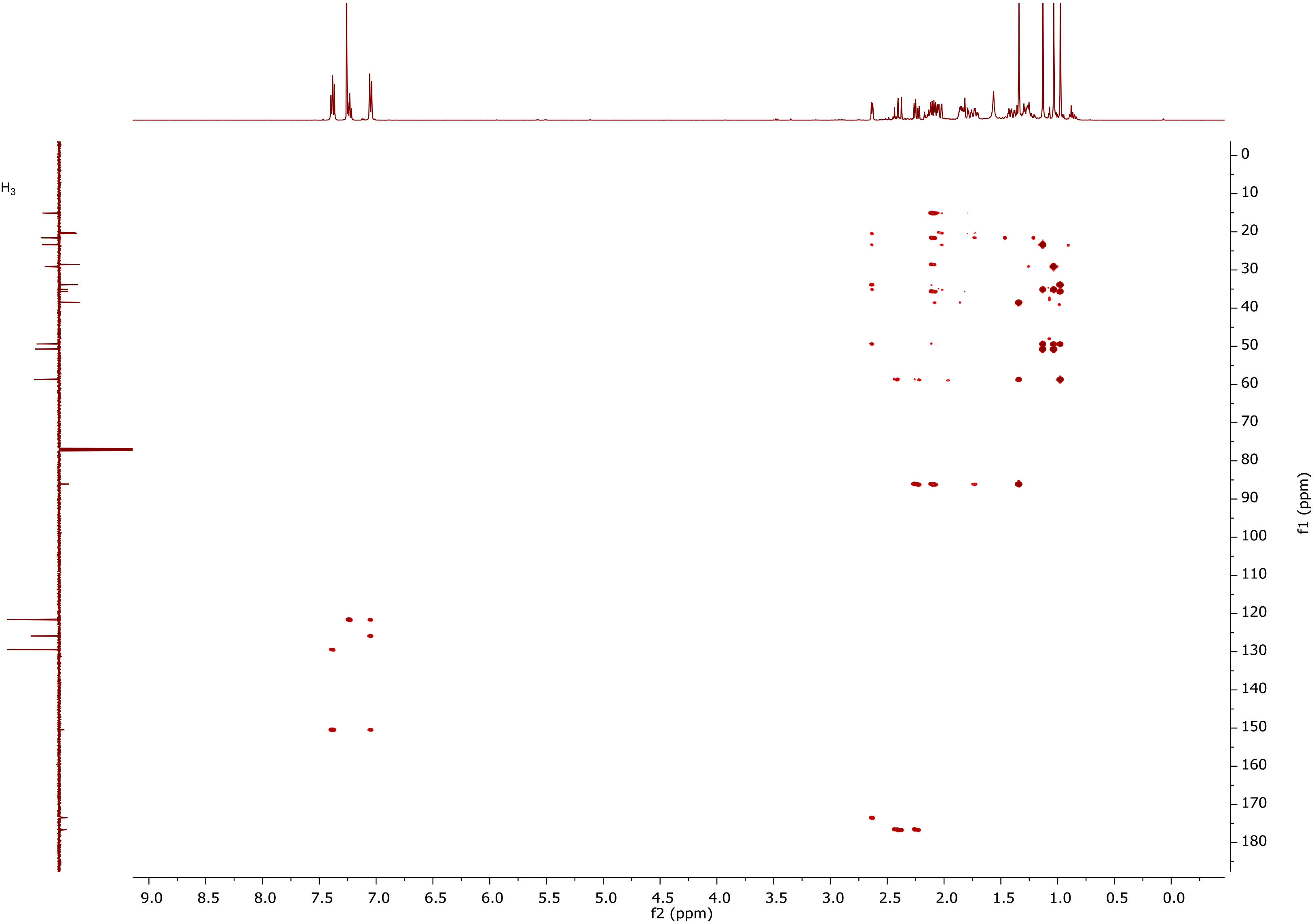
Trans

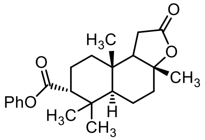
HSQC



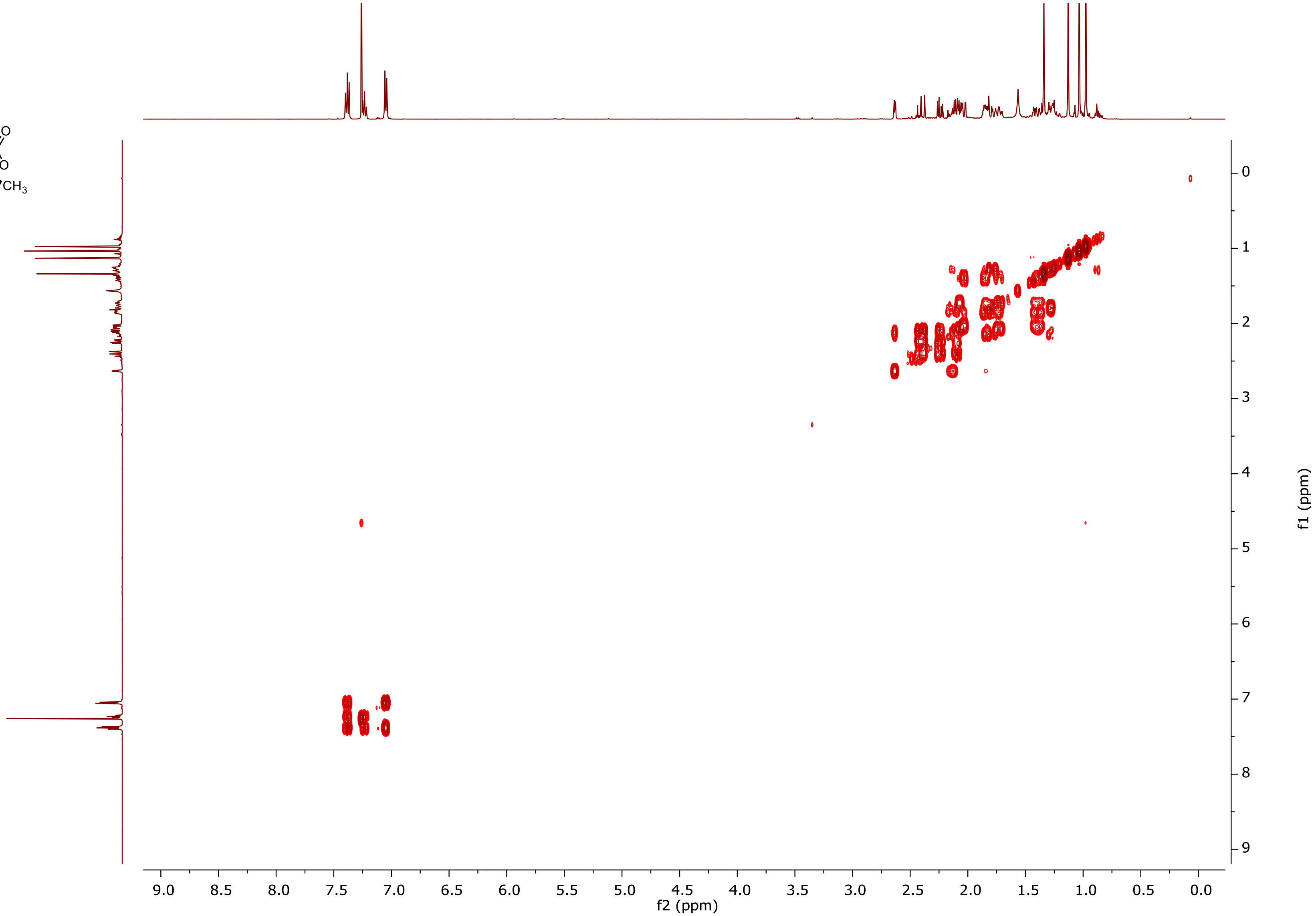


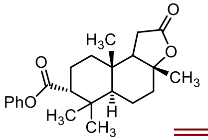
51-γ
Trans
HMBC



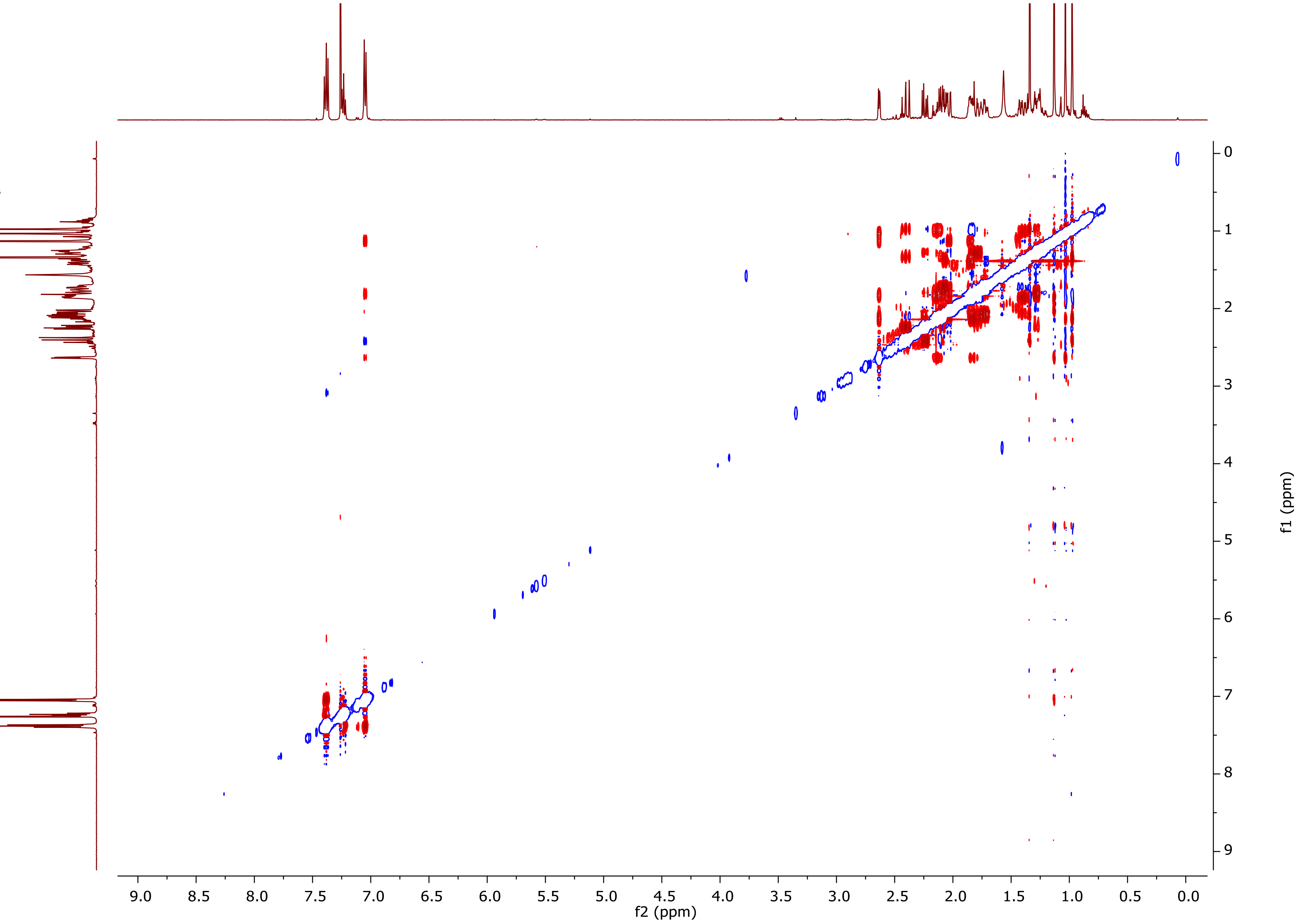


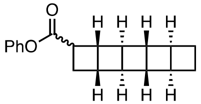
51-γ
Trans
COSY





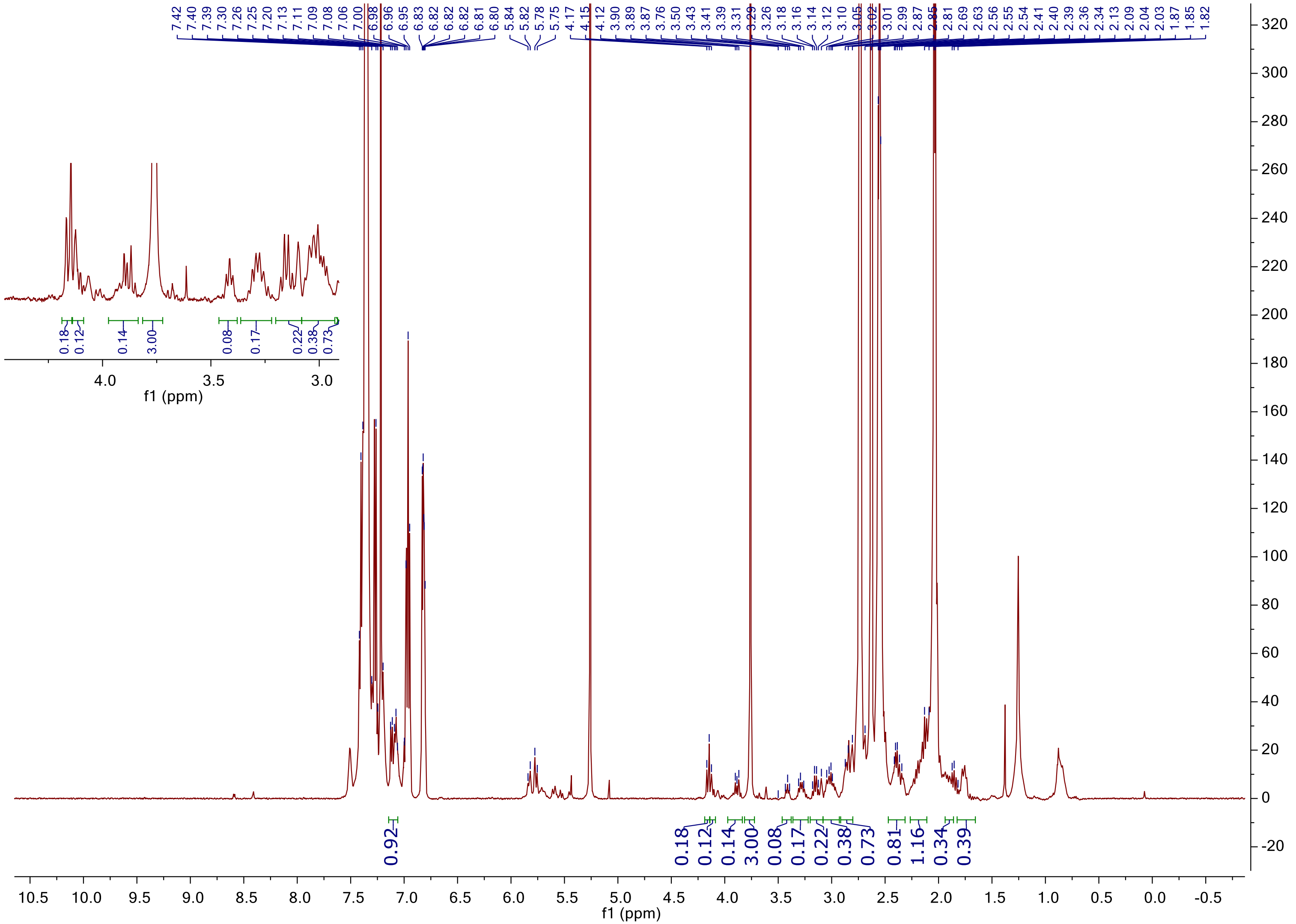
51-γ
Trans
NOESY

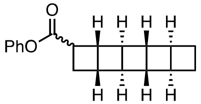




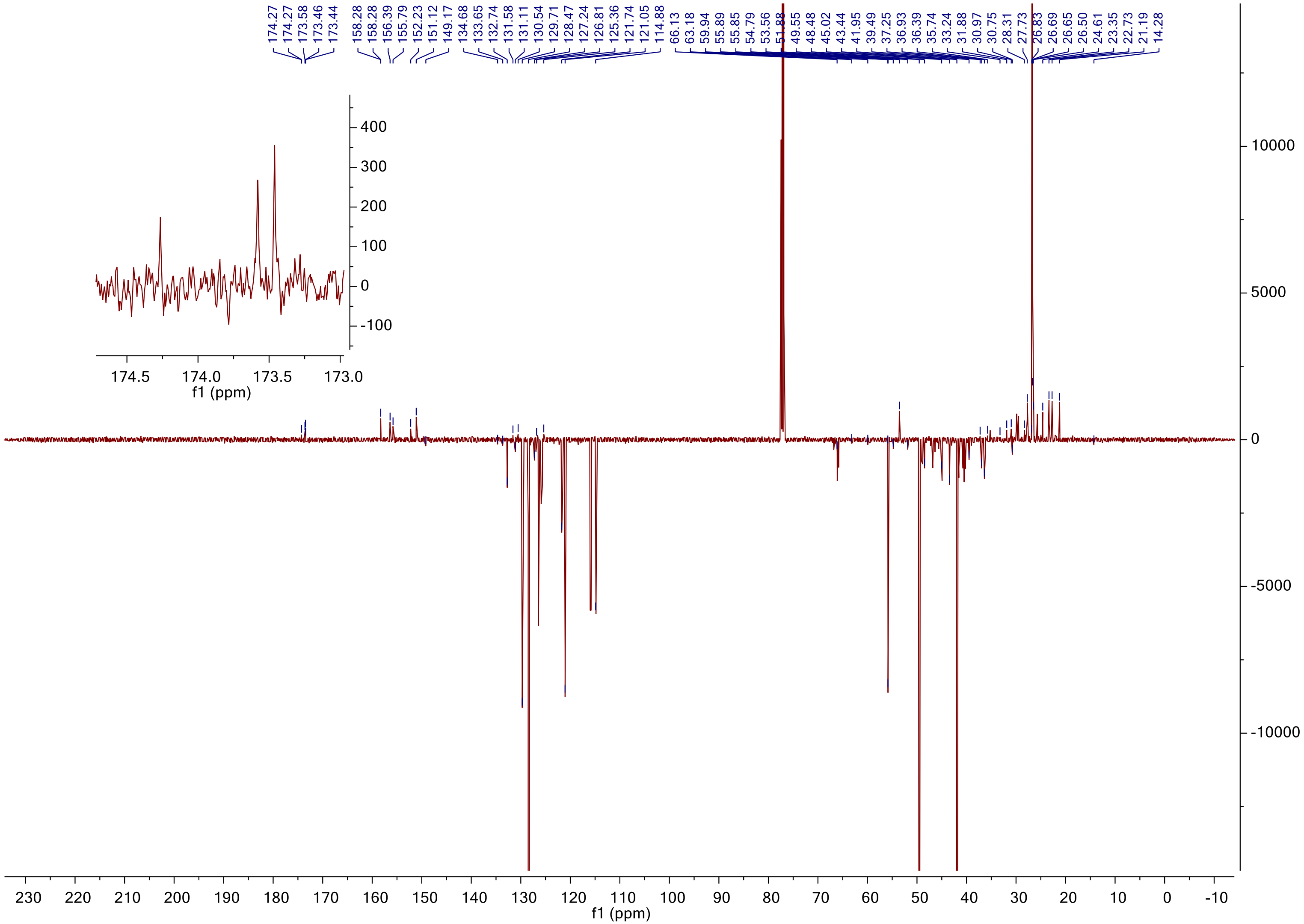
52

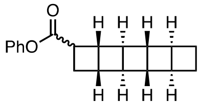
Crude Reaction



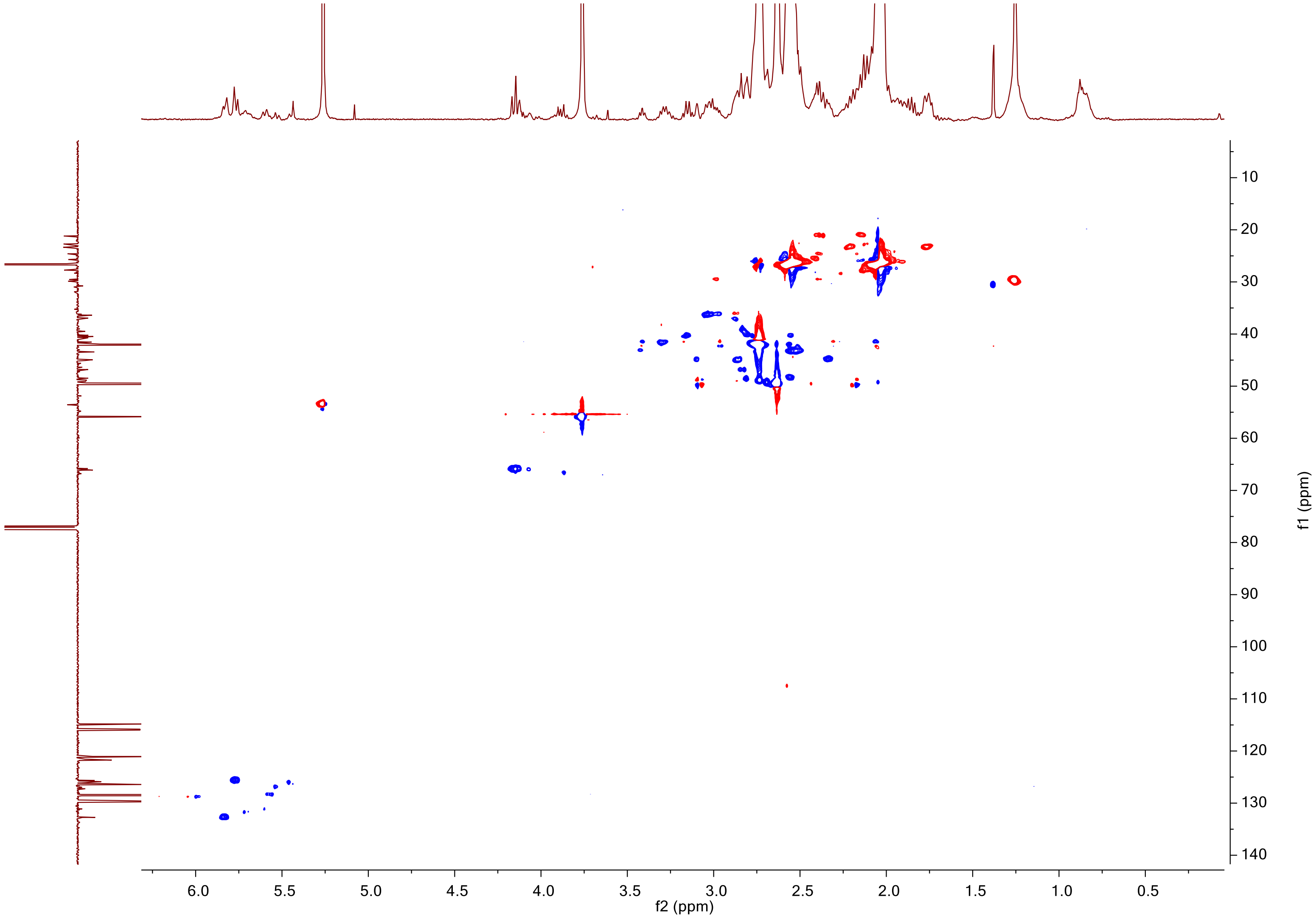

O
PhO
H H H H
H H H H

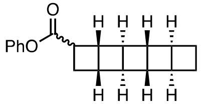
52


174.27
174.27
173.58
173.46
173.44
158.28
158.28
156.39
155.79
152.23
151.12
149.17
134.68
133.65
132.74
131.58
131.11
130.54
129.71
128.47
127.24
126.81
125.36
121.74
121.05
114.88
66.13
63.18
59.94
55.89
55.85
54.79
53.56
51.88
49.55
48.48
45.02
43.44
41.95
39.49
37.25
36.93
36.39
35.74
33.24
31.88
30.97
30.75
28.31
27.73
26.83
26.69
26.65
26.50
24.61
23.35
22.73
21.19
14.28
400
300
200
100
0
-100
174.5
174.0
173.5
173.0
f1 (ppm)
10000
5000
0
-5000
-10000
230
220
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)

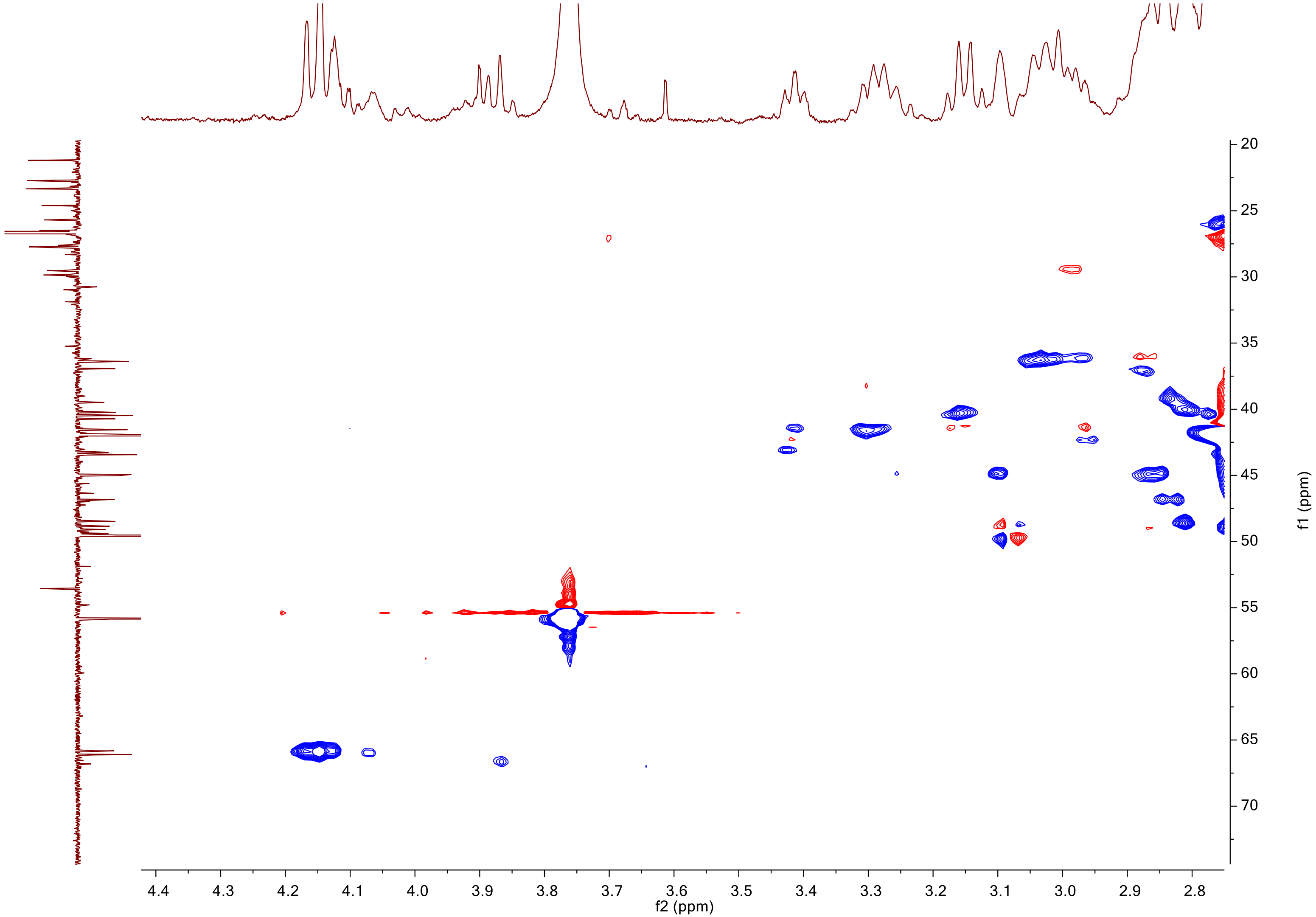


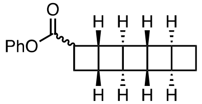
Reaction of 52
HSQC-13C-APT



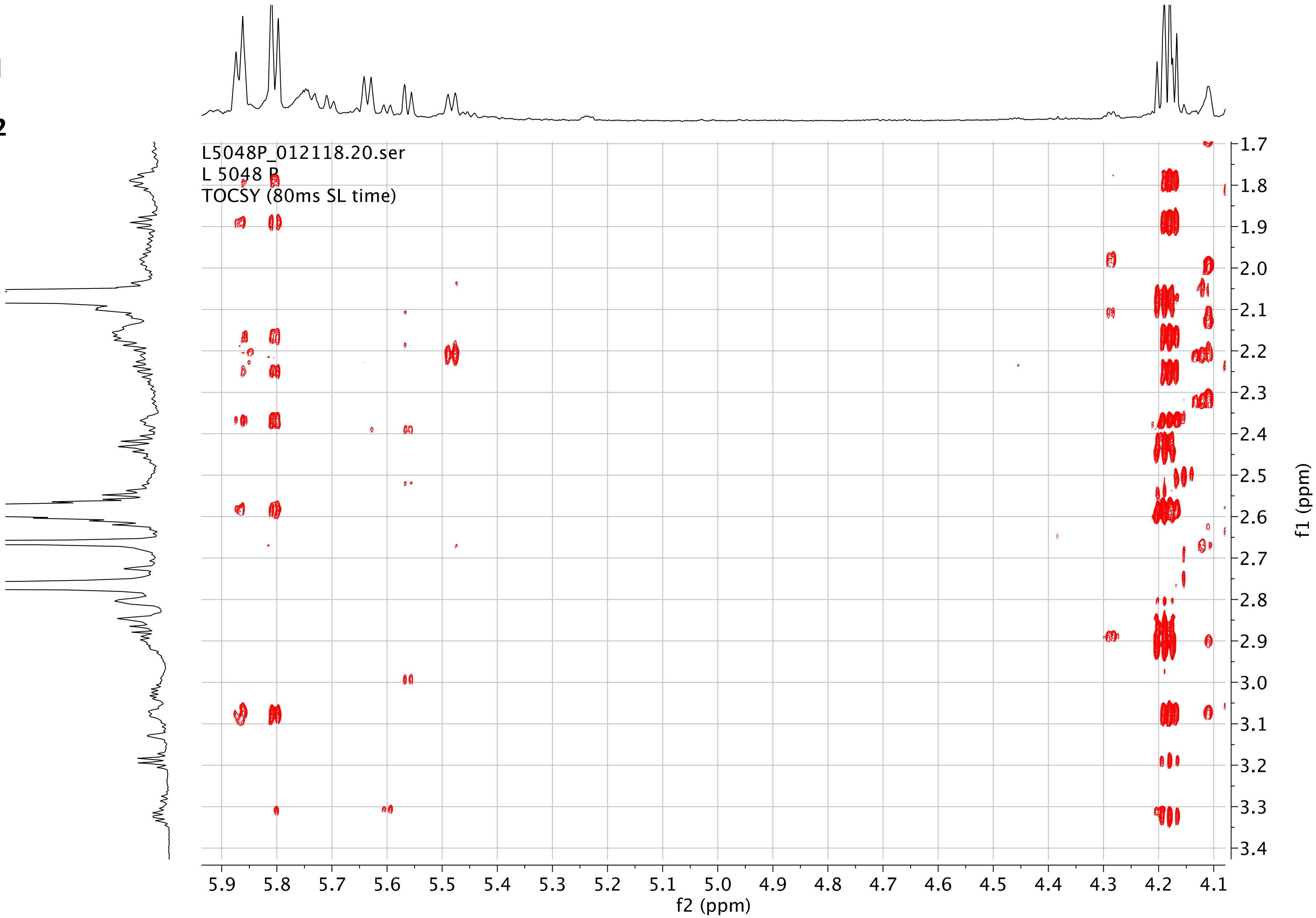


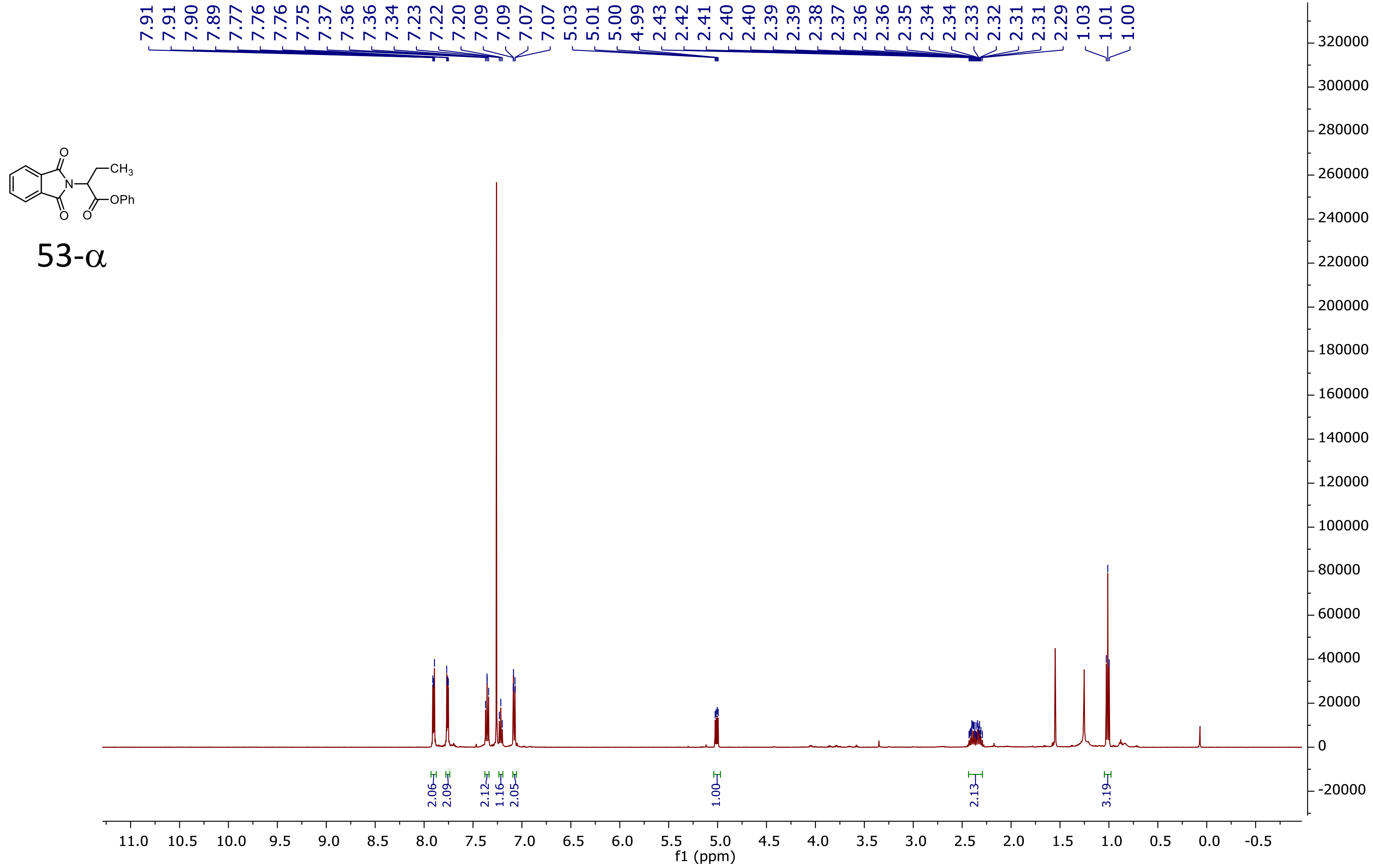
Reaction of 52
HSQC-13C-APT
0.5 ppm-4.5 ppm

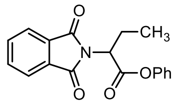




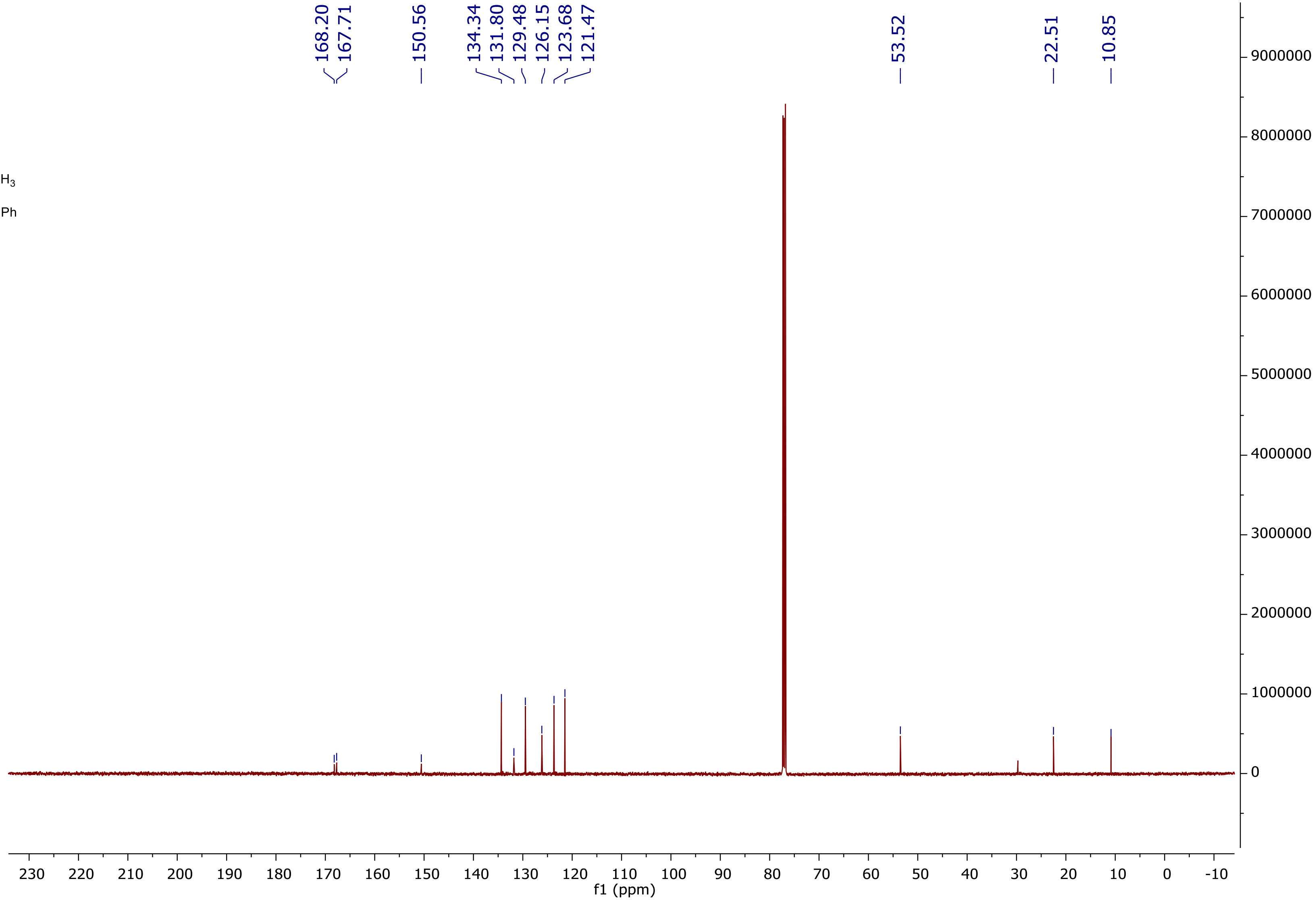
Reaction of 52
TOCSY



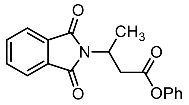

53-α
CH3
O
N
OPh
O
O
7.91
7.91
7.90
7.89
7.77
7.76
7.76
7.75
7.37
7.36
7.36
7.34
7.23
7.22
7.20
7.09
7.09
7.07
7.07
5.03
5.01
5.00
4.99
2.43
2.42
2.41
2.40
2.40
2.39
2.39
2.38
2.37
2.36
2.36
2.35
2.34
2.34
2.33
2.32
2.31
2.31
2.29
1.03
1.01
1.00
2.06
2.09
2.12
1.16
2.05
1.00
2.13
3.19
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
11.0
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)



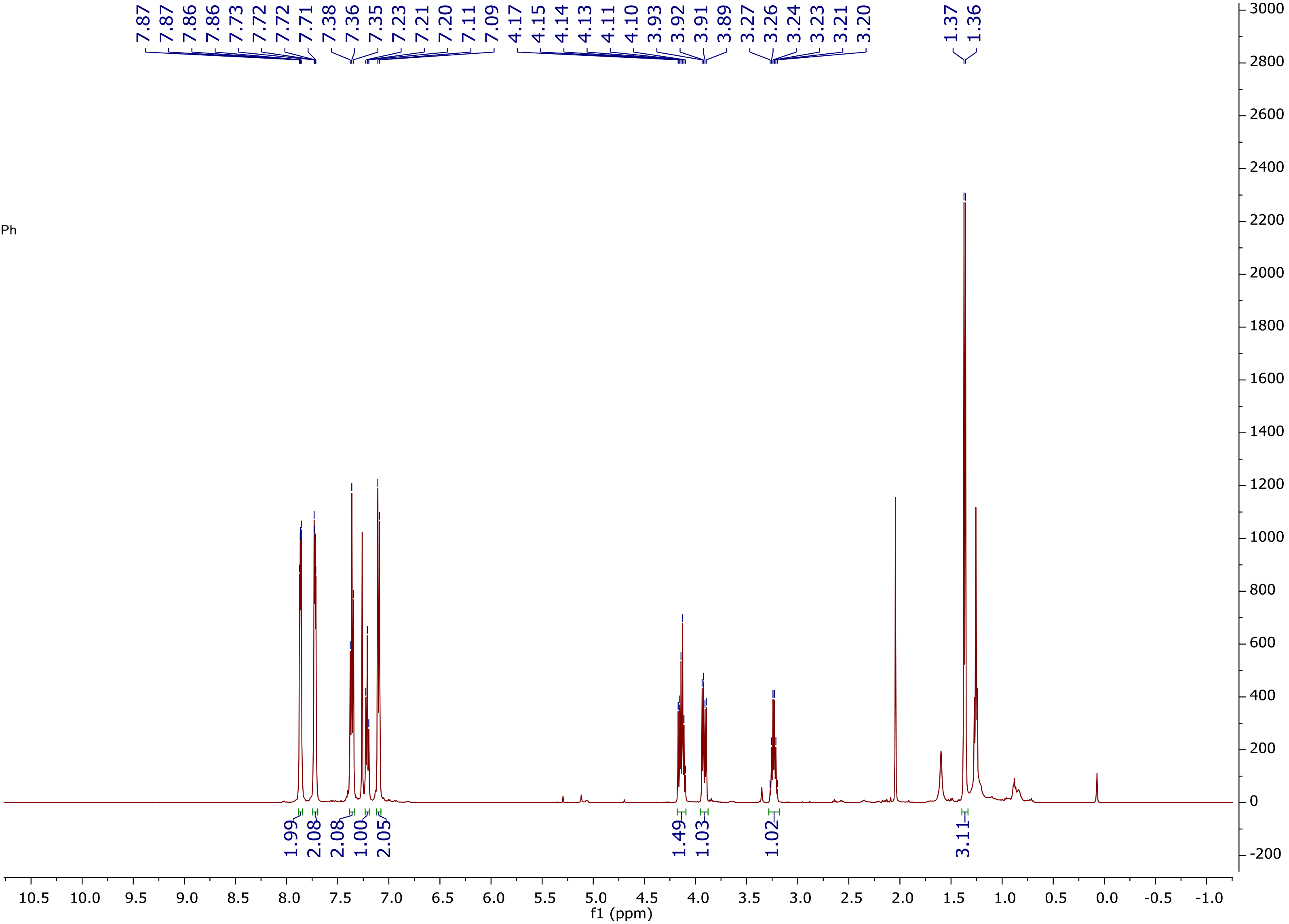
53-α

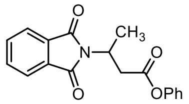


JM-NB2-R143A-F39.11.1.1r — C13CPDp1.PU CDCl3 /opt/topspin3.0 jmartine 1

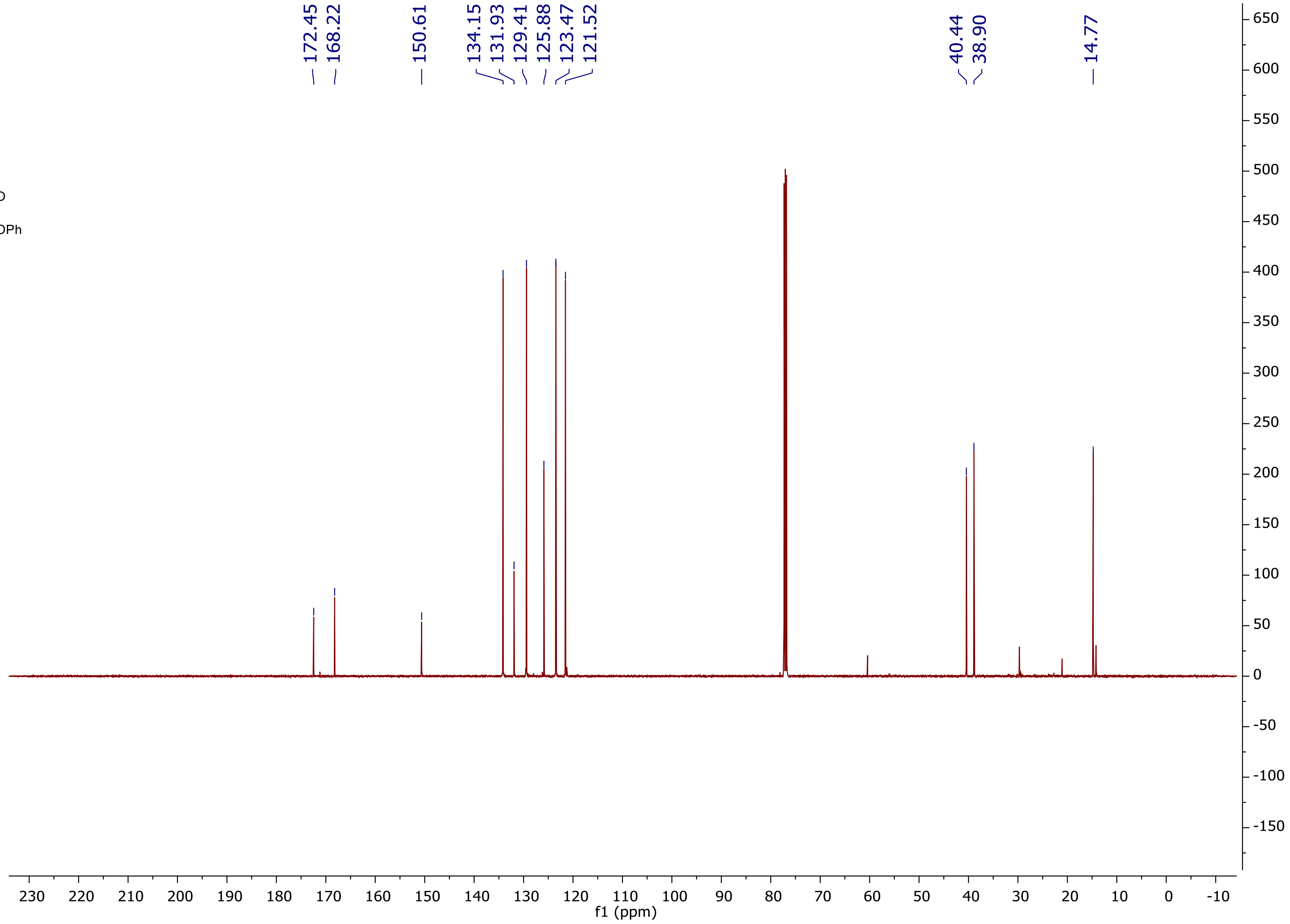

O
CH3
N
O
OPh
O

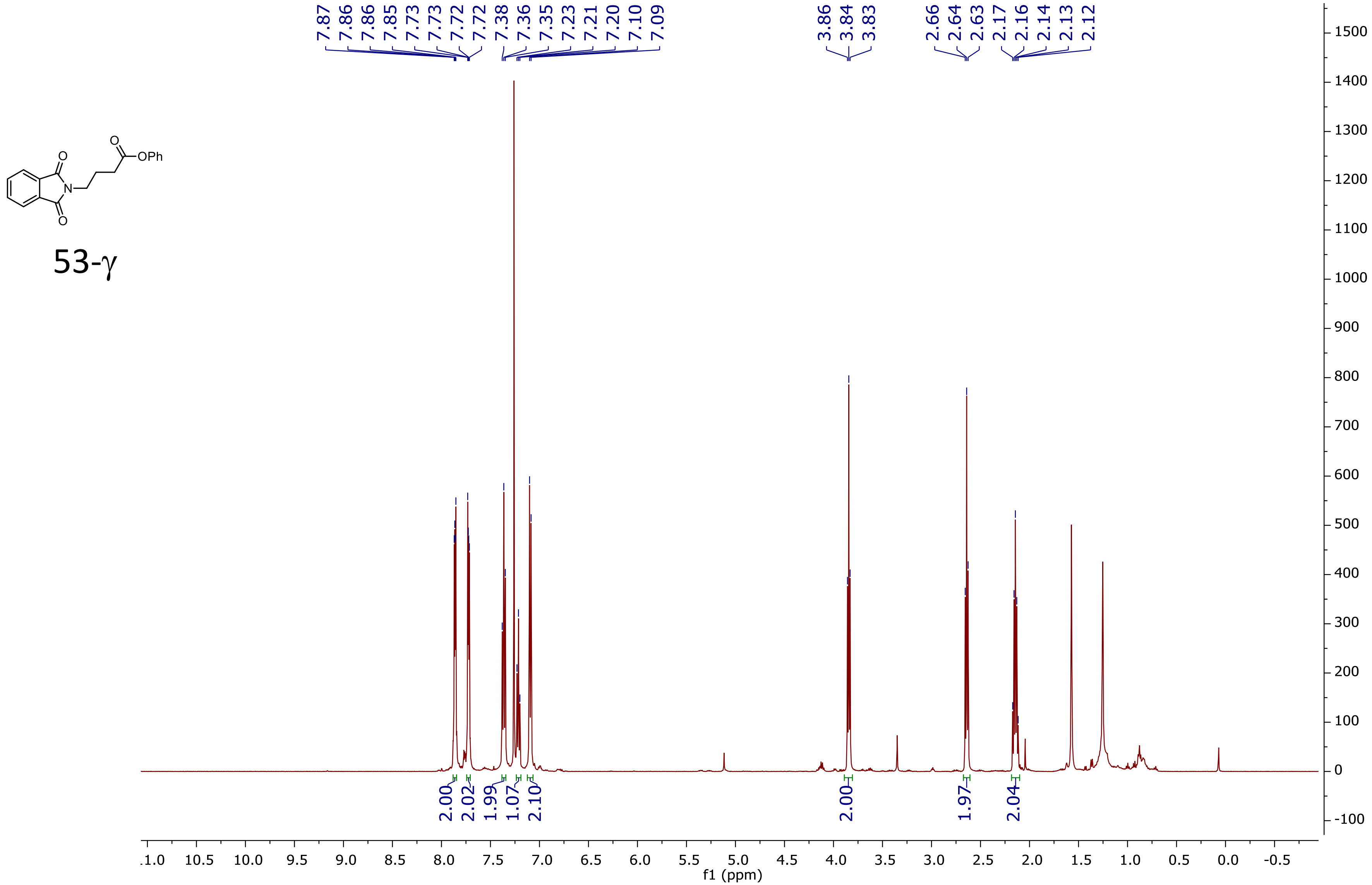
53-β


7.87
7.87
7.86
7.86
7.73
7.72
7.72
7.71
7.38
7.36
7.35
7.23
7.21
7.20
7.11
7.09
4.17
4.15
4.14
4.13
4.11
4.10
3.93
3.92
3.91
3.89
3.27
3.26
3.26
3.24
3.23
3.21
3.20
1.37
1.36
1.99
2.08
2.08
1.00
2.05
1.49
1.03
1.02
3.11
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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
-1.0
f1 (ppm)


O
CH3
N
O
OPh
O

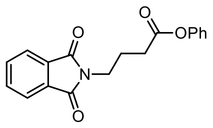
53-β


172.45
168.22
150.61
134.15
131.93
129.41
125.88
123.47
121.52
40.44
38.90
14.77
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
230
220
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)

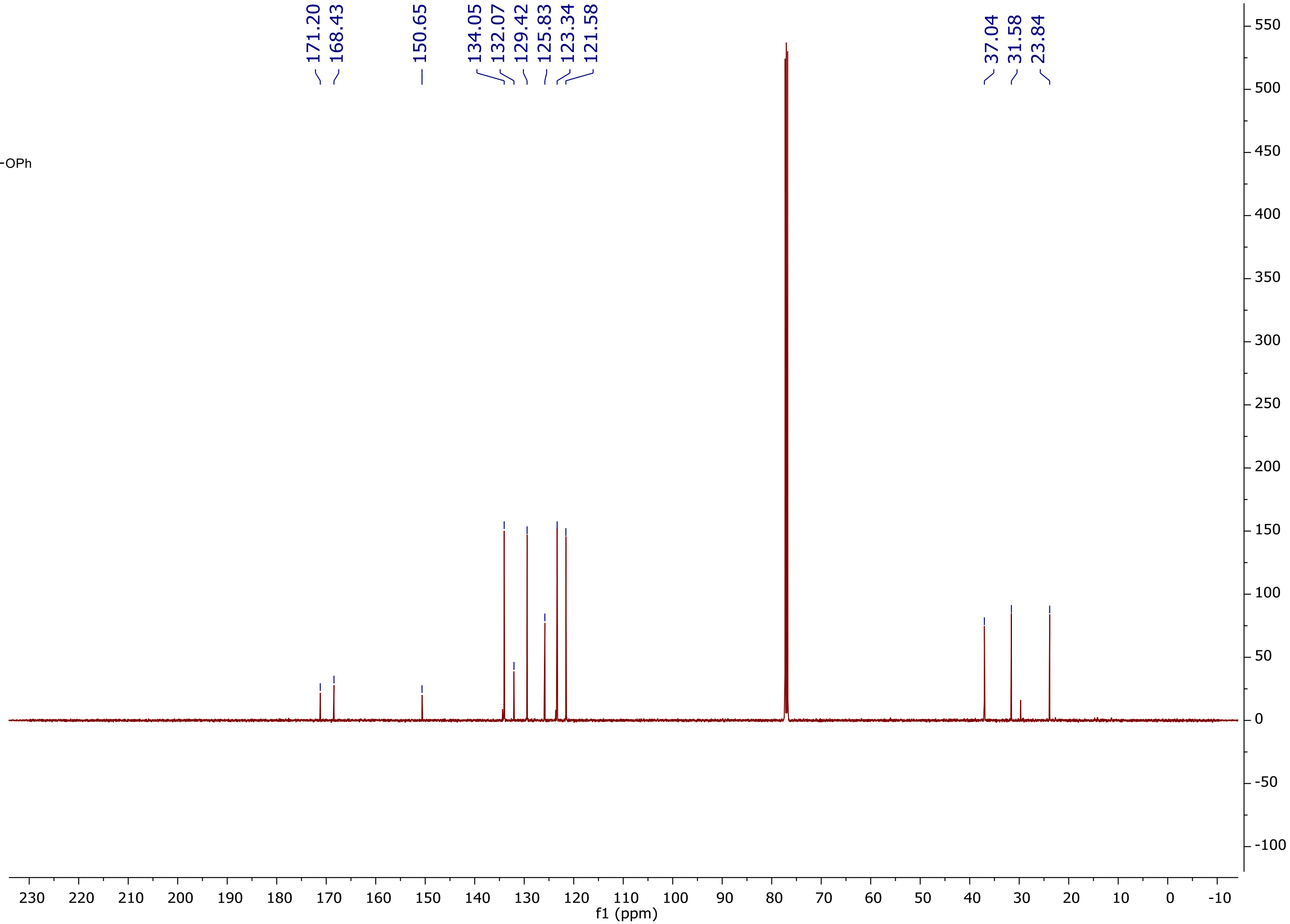


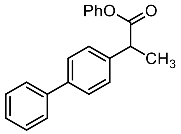
53-γ

O
OPh
O
N
O
7.87
7.86
7.86
7.85
7.73
7.73
7.72
7.72
7.38
7.36
7.35
7.23
7.21
7.20
7.10
7.09
3.86
3.84
3.83
2.66
2.64
2.63
2.17
2.16
2.14
2.13
2.12
2.00
2.02
1.99
1.07
2.10
2.00
1.97
2.04
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
.1.0
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)

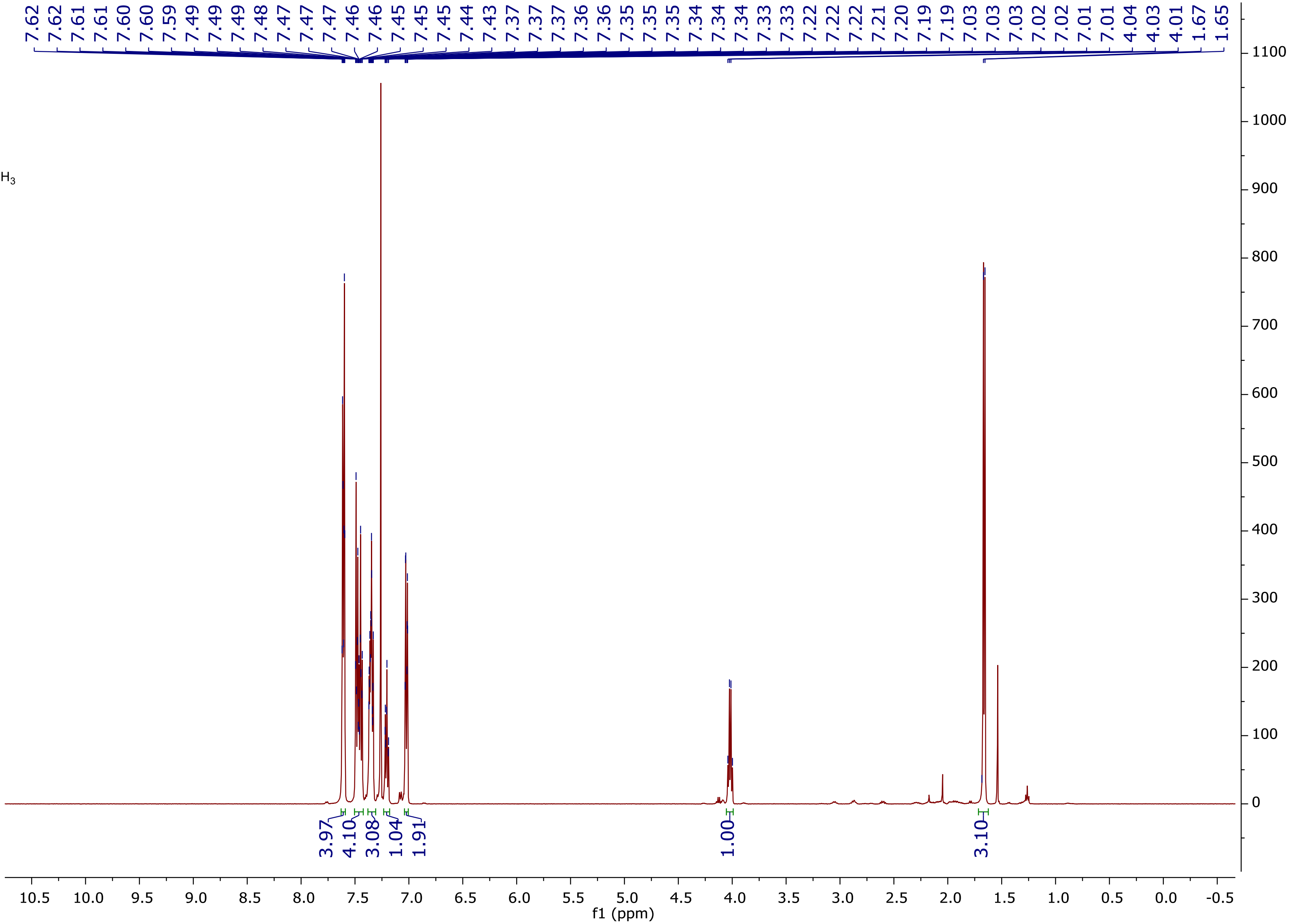

O
OPh
O
N
O

53-γ


171.20
168.43
150.65
134.05
132.07
129.42
125.83
123.34
121.58
37.04
31.58
23.84
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
230
220
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)


PhO
O
CH3

54


7.62
7.62
7.61
7.61
7.60
7.60
7.59
7.49
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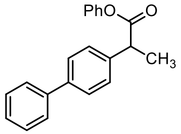
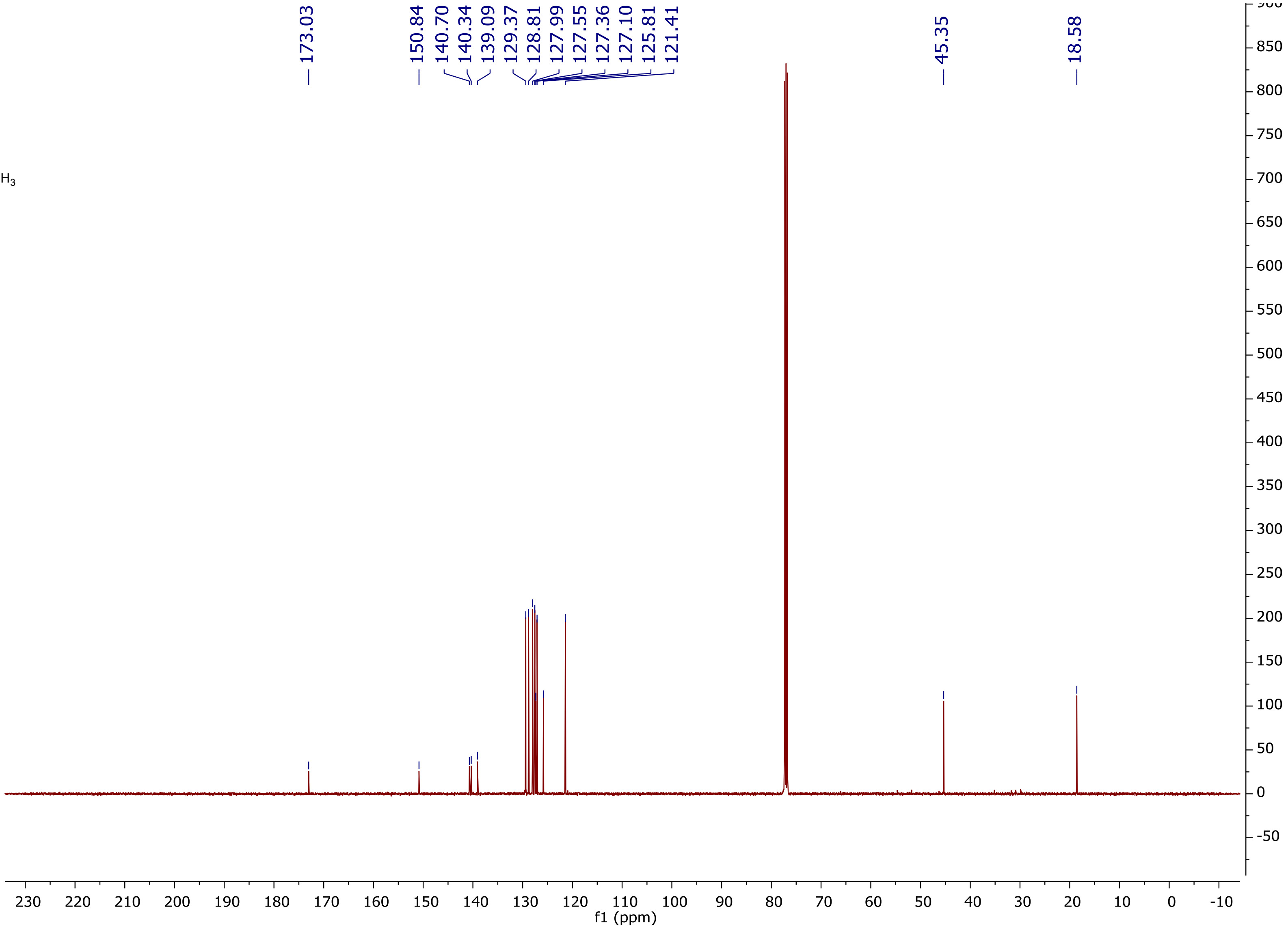
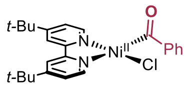
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.44
7.43
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.22
7.22
7.22
7.21
7.20
7.19
7.19
7.03
7.03
7.03
7.02
7.02
7.01
7.01
4.04
4.03
4.01
1.67
1.65
3.97
4.10
3.08
1.04
1.91
1.00
3.10
1100
1000
900
800
700
600
500
400
300
200
100
0
10.5
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)

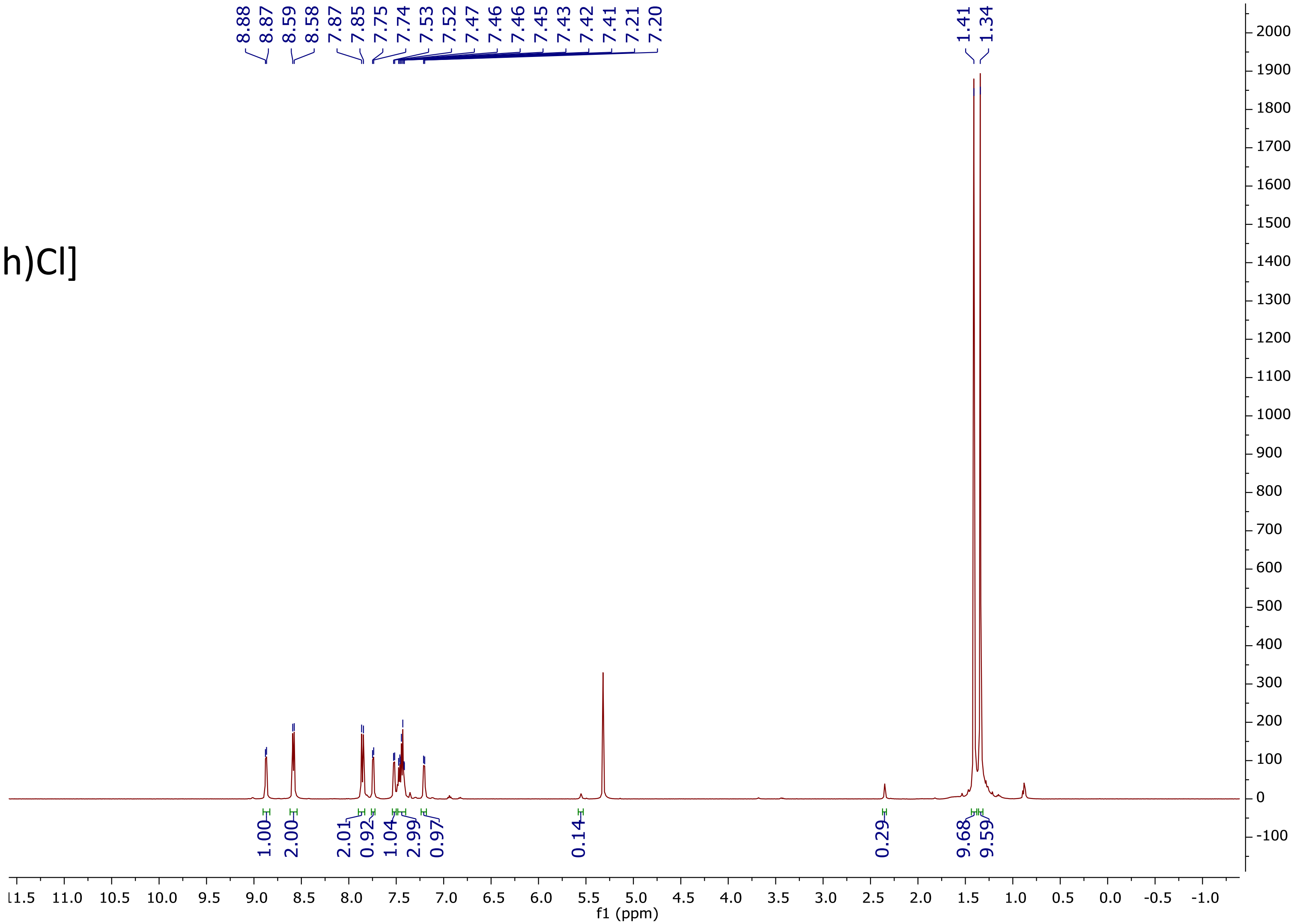

PhO
O
CH$_3$

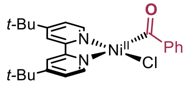
54


173.03
150.84
140.70
140.34
139.09
129.37
128.81
127.99
127.55
127.36
127.10
125.81
121.41
45.35
18.58
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
230
220
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)



[(dtbbpy)Ni(COPh)Cl]





[(dtbbpy)Ni(COPh)Cl]