Direct Use of Carboxylic Acids in the Photocatalytic Hydroacylation of Styrenes To Generate Dialkyl Ketones

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Supporting Information

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I. General Information

Materials. Commercial reagents were acquired from Sigma-Aldrich, Alfa Aesar, Acros, Strem, TCI, or Oakwood and used as received. Diethyl ether (Et_2O), tetrahydrofuran (THF), and toluene (PhMe) were dried by passing through activated alumina columns and stored over molecular sieves in a N_2-filled glovebox; *N,N*-dimethylformamide (DMF) was dried by passing through a column of activated molecular sieves. Acetonitrile (MeCN) was purchased from Millipore Sigma ***without sieves*** and subsequently sparged with nitrogen before bringing it into the glovebox. Sieves were detrimental for reactivity.

Instrumentation. Proton nuclear magnetic resonance (^{1}H 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 (^{2}H 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 (ppm) 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, bs = broad singlet, d = doublet, appd = apparent doublet, t = triplet, q = quartet, p = pentet, sx = sextet 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}). High-performance liquid chromatography (HPLC) was performed on an Agilent 1200 series instrument with a binary pump and a diode array detector, using Chiralcel OD-H (25 cm x 0.46 cm), Chiralcel OJ-H (25 cm x 0.46 cm), Chiralpak AS-H (25 cm x 0.46 cm), Chiralpak AD-H (25 cm x 0.46 cm), Chiralpak IC (25 cm x 0.46 cm) and Chiralpack ID (25 cm x 0.46 cm).

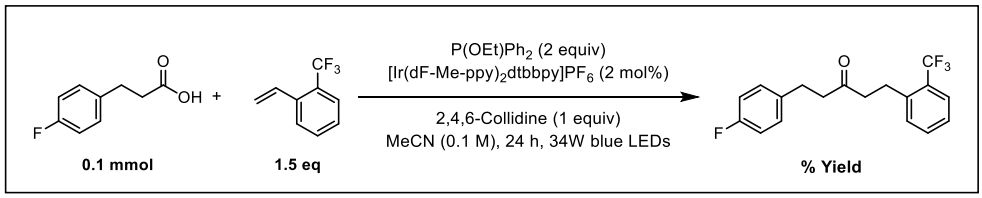
Light Sources. Reactions were initially optimized on 34 W blue LED lamps (KSH150B Grow Light Blue) purchased from Kessil. When Kessil lamps were used, they were placed 2 cm away from 1-dram reaction vials without the use of fans. Isolations yields were obtained using a Photoreactor (PR). Photoreactors were generously obtained from the MacMillan lab. A Penn OC Photoreactor M1 series was used with a 450 nm light source.[1]

II. Control and Optimization Studies

Procedure for reaction optimization: An oven-dried 1-dram reaction vial (VWR® glass vials, 66011-041) was charged with carboxylic acid (0.1 mmol, 1.0 equiv) and equipped with a PTFE-coated stir bar (VWR® Micro stir bars, 2 x 7 mm, 58948-976). The vial was Teflon taped on the threads, and then taken into a N_2-filled glovebox. To the vial was added MeCN (0.1 M), alkene (0.3 mmol, 3.0 equiv) and base (0.1 mmol, 1.0 equiv). From a stock solution was added $[Ir(dF\text{-}Me\text{-}ppy)_2dtbbpy]PF_6$ (2 mg, 0.002 mmol, 0.02 equiv) and Ph_2S_2 (1.0 mg, 0.005 mmol, 0.05 equiv). Finally, phosphine (0.1 mmol, 1.0 equiv) was added. The vial was then capped and sealed with electrical tape. The vial was irradiated for 24 h with 34 W blue LEDs. An aliquot of the crude reaction mixture was analzed by ^{1}H-NMR with 1-fluoronaphthalene (0.1 mmol, 1.0 equiv) as an external standard.

Our initial efforts began employing 3-(4-fluorophenyl)propanoic acid with 1-(trifluoromethyl)-2-vinylbenzene as alkene acceptor and ethyl diphenyl phosphinite as mediator.

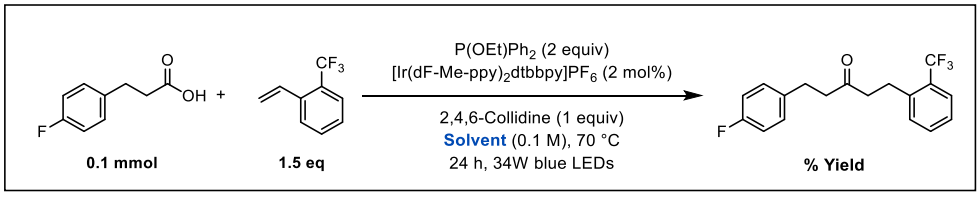
Table S1. Control and optimization of the coupling reaction between 3-(4-fluorophenyl)propanoic acid and 1-(trifluoromethyl)-2-vinylbenzene



Entry	Deviation	% Yield[a]
a	none	12
b	PPh_3 instead of $P(OEt)Ph_2$	2
c	70 °C	21
d	no light	0
e	no [Ir]	0
f	no $P(OEt)Ph_2$	0

[a]Yield was determined by ^{19}F NMR spectroscopy using 1-fluoronaphthalene as an external standard

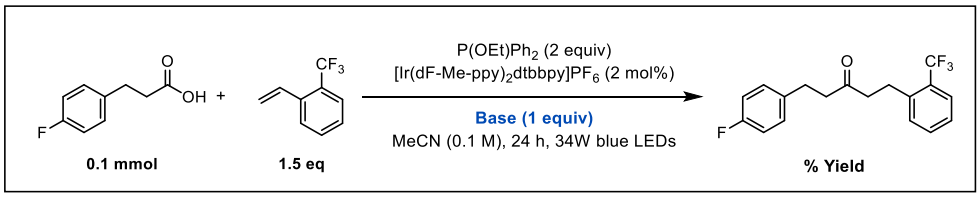
Table S2. Optimization of solvent using ethyl diphenyl phosphinite as phosphine mediator.



Entry	Solvent	% Yield[a]
a	TFT	5
b	MTBE	0
c	DME	3
d	NMP	4
e	Et_2O	0
f	THF	0
g	DMF	6
h	DMA	12
i	PhOMe	8
j	MeCN	19

[a]Yield was determined by ^{19}F NMR spectroscopy using 1-fluoronaphthalene as an external standard

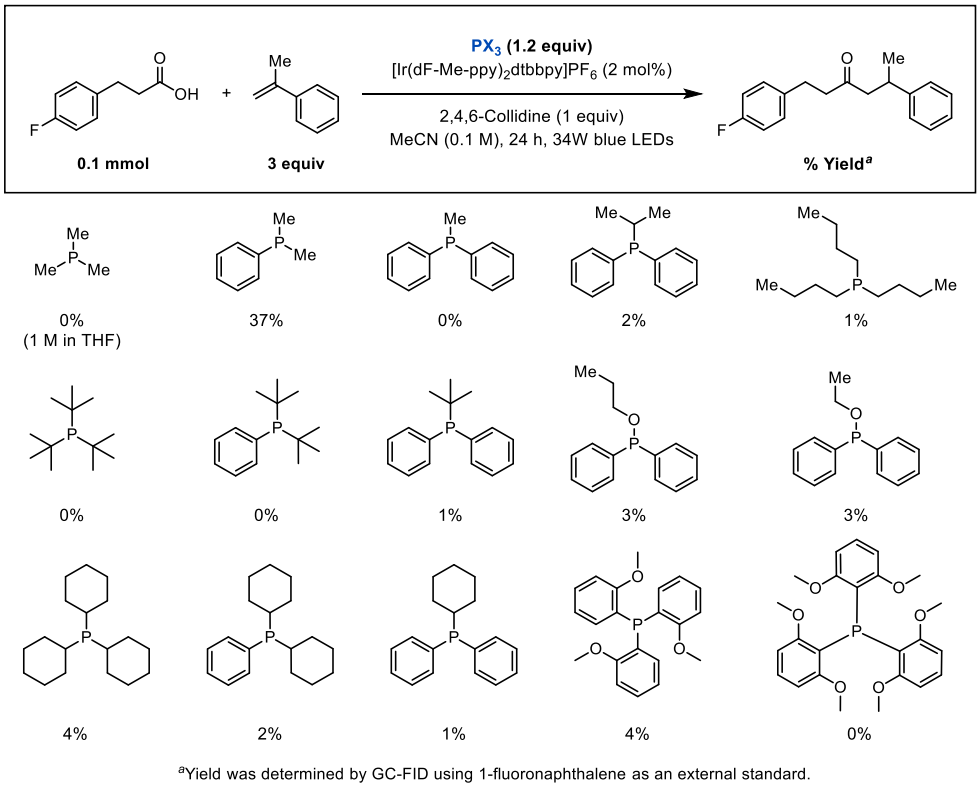
Table S3. Optimization of bases using ethyl diphenyl phosphinite as phosphine mediator.



Entry	Base	% Yield[a]
a	KOEt	0
b c	DBU	9
d	LiO*t*-Bu	0
e	Li_2CO_3	20
f	Na_2CO_3	2
g	K_2CO_3	3
h	Cs_2CO_3	4
i j	KH_2PO_4	22

[a]Yield was determined by ^{19}F NMR spectroscopy using 1-fluoronaphthalene as an external standard

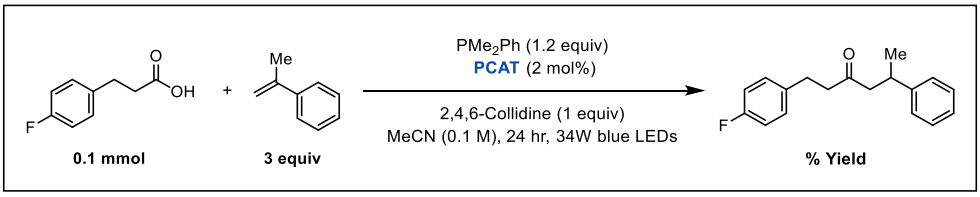
Given the poor success of ethyl diphenyl phosphinite in this reaction, emission quenching experiments were undertaken (See Section V). More importantly, other phosphines were explored for this reaction. The alkene acceptor was substituted for α-methyl styrene in order to bias the reaction toward radical addition.



[a]Yield was determined by GC-FID using 1-fluoronaphthalene as an external standard.

Figure S1. Optimization of phosphines using 3-(4-fluorophenyl)propanoic acid and alpha methyl styrene.

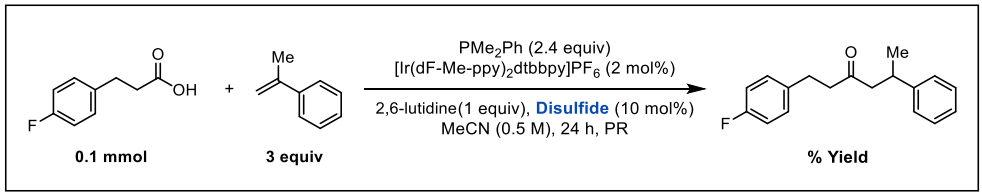
Table S4. Examination of photocatalysts.



Entry	Disulfide	% Yield
a	$Ir(dF\text{-}ppy)_3$	0
b	$[Ir(ppy)_2(dtbbpy)]PF_6$	2
c	$[Ir(F\text{-}ppy)_3$	2
d	$[Ru(dtbbpy)_3](PF_6)_2$	0
e	$[Ru(bpy)_3](PF_6)_2$	0
f	$[Ir(dF\text{-}CF_3ppy)_2(dtbbpy)]PF_6$	22
g	$[Ir(dF\text{-}Bn\text{-}triazole)_2(dtbbpy)]PF_6$	7
h	4-CzIPN	0

[a]Yield was determined by GC-FID using 1-fluoronaphthalene as an external standard

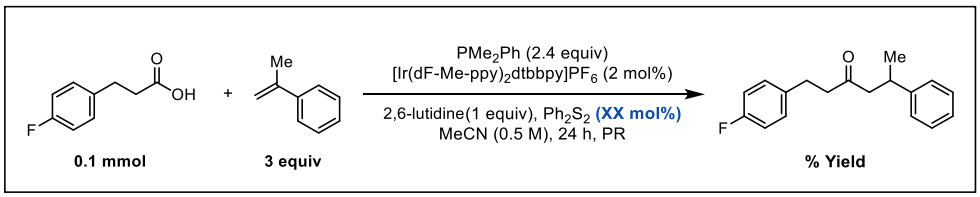
Table S5. Examination of hydrogen atom donors.



Entry	Disulfide	% Yield
a	none	44
b	tBu_2S_2	41
c	iPr_2S_2	41
d	Ph_2S_2	56
e	$TRIP_2S_2$	38
f	$(4\text{-Cl-Ph})_2S_2$	57
g	$(4\text{-MeO-Ph})_2S_2$	57
h	Ph_2CHCN	37

[a]Yield was determined by GC-FID using 1-fluoronaphthalene as an external standard

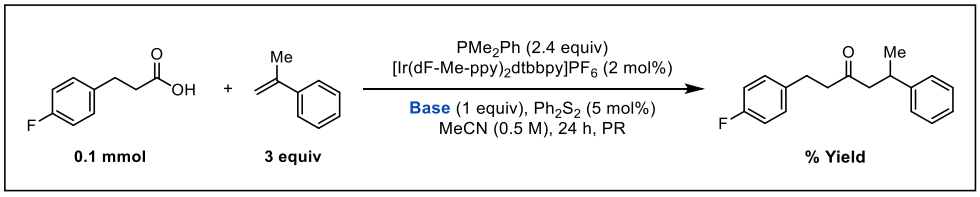
Table S6. Examination of phenyl disulfide loading. Yield was determined by GC-FID using 1-fluoronaphthalene as an external standard.



Entry	XX mol%	% Yield[a]
a	5	47
b	10	38
c	20	15

[a]Yield was determined by GC-FID using 1-fluoronaphthalene as an external standard

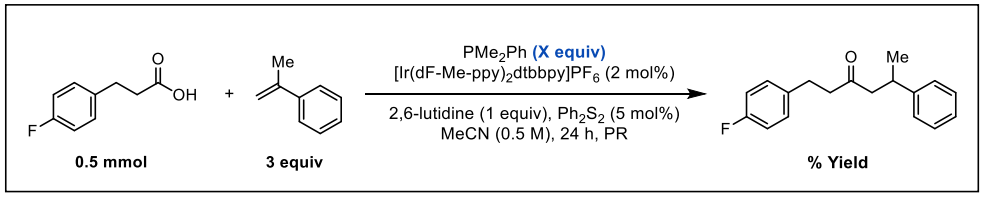
Table S7. Examination of base additives. Yield was determined by GC-FID using 1-fluoronaphthalene as an external standard.



Entry	Base	% Yield[a]
a	**none**	41
b	**2,6-lutidine**	46

[a]Yield was determined by ^{19}F NMR spectroscopy using 1-fluoronaphthalene as an external standard

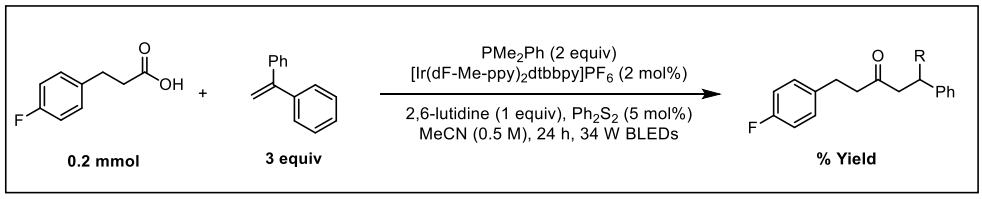
Table S8. Optimization of Phosphine loading using methyl diphenyl phosphinite, 3-(4-fluorophenyl)propanoic acid, and alpha methyl styrene.



Entry	Phosphine Equiv	% Yield	% Acid conversion
a	1.0	41	64
b	1.5	63	93
c	2.0	72	100

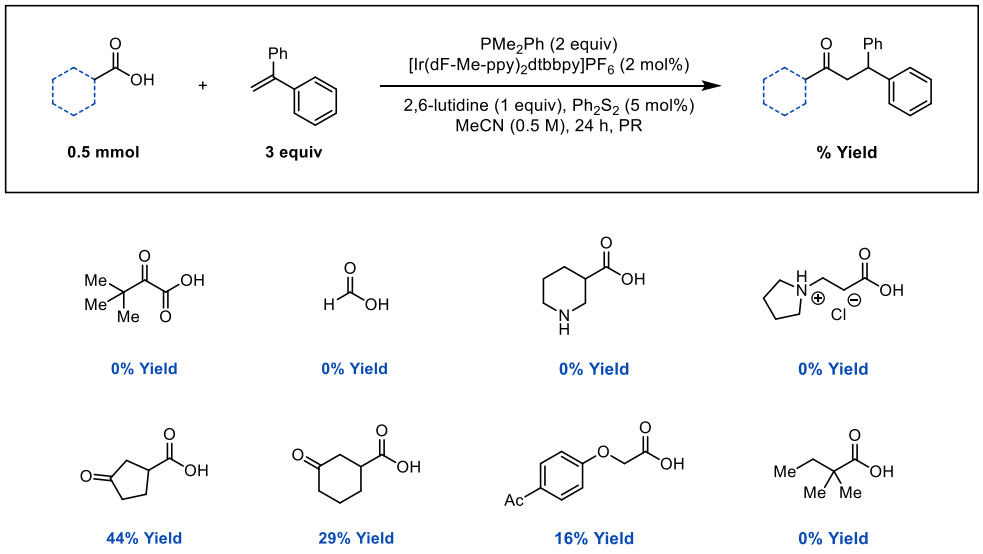
[a]Yield was determined by GC-FID using 1-fluoronaphthalene as an external standard

Table S9. Deoptimization table highlights the need for Iridium and phosphine for reactivity. While kessils provide moderate yield, Photoreactors were used because they provide a standardized light and temperature set up. Use of 5-cyclohexylpentanoic acid on 0.5 mmol scale without diphenyl disulfide results in lower yield. The yield was restored by using 2.4 equivalents of phosphine. Diphenyl disulfide was removed from non-polar carboxylic acids to provide an easier isolation.



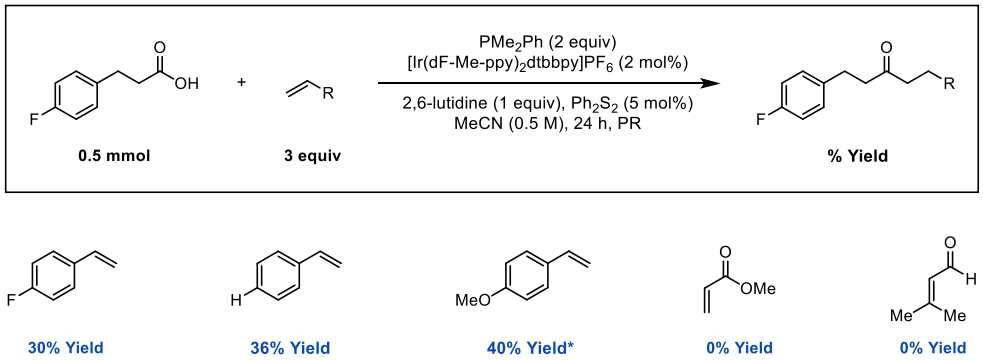
Entry	Deviation	% Yield
a	Merck Photoreactor	81[b]
b	none	64
c	no photocatalyst	0
d	no phosphine	0
e	no disulfide	62
f	no base	60
g	5-cyclohexylpentanoic acid	92[b]
h	5-cyclohexylpentanoic acid and no Ph_2S_2	80[b]
i	5-cyclohexylpentanoic acid, no Ph_2S_2, and 2.4 equiv PMe_2Ph	90[b]

[a]Yield was determined by ^{1}H NMR spectroscopy using 1-fluoronaphthalene as an external standard.
[b]0.5 mmol scale in a Photoreactor



[a]Yield was determined by ^{1}H NMR spectroscopy using 1-fluoronaphthalene as an external standard

Figure S2. Poorly performing carboxylic acids when coupling with 1,1 diphenyl ethylene.



[a]Yield was determined by ^{1}H NMR spectroscopy using 1-fluoronaphthalene as an external standard
[b]1 equivalent of alkene, 15 mol% of $(TripS)_2$

Figure S3. Poorly performing alkenes when coupling with 4-fluoro hydrocinnamic acid. Morita-Baylis Hillman reactivity was observed by GC-MS for the acrylate derivatives.

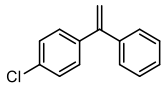
II. General Procedures

General procedure A. An oven-dried 1-dram reaction vial (VWR® glass vials, 66011-041) was charged with carboxylic acid (0.5 mmol, 1.0 equiv) and equipped with a PTFE-coated stir bar (VWR® Micro stir bars, 2 x 7 mm, 58948-976). The vial was Teflon taped on the threads, and then taken into a N_2-filled glovebox. To the vial was added MeCN (0.5 M), alkene (265 μL, 1.5 mmol, 3.0 equiv) and 2,6-lutidine (58 μL, 0.5 mmol, 1.0 equiv). From a stock solution was added [Ir] (8.7 mg, 0.01 mmol, 0.017 equiv) and Ph_2S_2 (5.46 mg, 0.025 mmol, 0.05 equiv). Finally, phosphine (142 μL, 1.0 mmol, 2.0 equiv) was added. The vial was then capped and sealed with electrical tape. The vial was irradiated for 24 h in a Photoreactor (800 rpm, 1500 fan speed, 100% light intensity). An aliquot of the crude reaction mixture was analzed by ^{1}H-NMR with 1-fluoronaphthalene (65 μL, 0.5 mmol, 1.0 equiv) as an external standard.

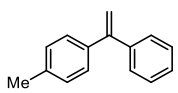
General procedure B. An oven-dried 1-dram reaction vial (VWR® glass vials, 66011-041) was charged with carboxylic acid (0.5 mmol, 1.0 equiv) and equipped with a PTFE-coated stir bar (VWR® Micro stir bars, 2 x 7 mm, 58948-976). The vial was Teflon taped on the threads, and then taken into a N_2-filled glovebox. To the vial was added MeCN (0.5 M), alkene (265 μL, 1.5 mmol, 3.0 equiv) and 2,6-lutidine (58 μL, 0.5 mmol, 1.0 equiv). From a stock solution was added [Ir] (8.7 mg, 0.01 mmol, 0.017 equiv). Finally, phosphine (171 μL, 1.2 mmol, 2.4 equiv) was added. The vial was then capped and sealed with electrical tape. The vial was irradiated for 24 h in a Photoreactor (800 rpm, 1500 fan speed, 100% light intensity). An aliquot of the crude reaction mixture was analzed by ^{1}H-NMR with 1-fluoronaphthalene (65 μL, 0.5 mmol, 1.0 equiv) as an external standard.

IV. Compound Characterization

A. Starting Material Synthesis

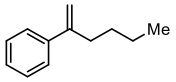


1-chloro-4-(1-phenylvinyl)benzene (S33) was prepared on a 23.08 mmol scale according to a published literature procedure.[2] The title compound was isolated using automated column chromatography eluting with Hexanes (10 CV). The title compound was concentrated to produce a colorless oil (4.05 g, 82% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.17 (m, 8H), 5.44 (d, *J* = 9.1 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 149.11, 141.15, 140.08, 133.72, 129.70, 128.49, 128.41, 128.33, 128.07, 114.85.

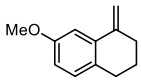


1-methyl-4-(1-phenylvinyl)benzene (S34) was prepared on a 12.33 mmol scale according to a published literature procedure.[2] The title compound was isolated using automated column

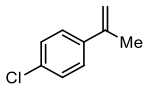
chromatography eluting with Hexanes (10 CV). The title compound was concentrated to produce a colorless oil (2.24 g, 94% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (dt, *J* = 7.1, 3.1 Hz, 5H), 7.30 – 7.25 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 5.45 (d, *J* = 13.3 Hz, 2H), 2.40 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.03, 141.83, 138.74, 137.66, 129.00, 128.43, 128.29, 128.26, 127.77, 113.79, 21.32.



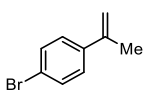
hex-1-en-2-ylbenzene (S35) was prepared on a 5.28 mmol scale according to a published literature procedure.[2] The title compound was isolated using automated column chromatography eluting with Hexanes (10 CV). The title compound was concentrated to produce a colorless oil (428 mg, 50% yield). Spectral data were consistent with reported literature values.[4]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 5.27 (d, *J* = 1.6 Hz, 1H), 5.06 (d, *J* = 1.5 Hz, 1H), 2.51 (t, *J* = 7.5 Hz, 2H), 1.49 – 1.29 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 148.93, 141.67, 128.36, 127.37, 126.27, 112.14, 35.22, 30.61, 22.56, 14.07.



7-methoxy-1-methylene-1,2,3,4-tetrahydronaphthalene (S36) was prepared on a 11.35 mmol scale according to a published literature procedure.[2] The title compound was isolated using automated column chromatography eluting with Hexanes (10 CV). The title compound was concentrated to produce a colorless oil (1.17 g, 59% yield). Spectral data were consistent with reported literature values.[5]
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (d, *J* = 2.7 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.7 Hz, 1H), 5.46 (d, *J* = 1.3 Hz, 1H), 4.96 (d, *J* = 1.4 Hz, 1H), 3.82 (s, 3H), 2.79 (t, *J* = 6.3 Hz, 2H), 2.53 (ddt, *J* = 7.7, 4.2, 1.4 Hz, 2H), 1.87 (p, *J* = 6.3 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 157.86, 143.71, 135.68, 130.26, 130.00, 114.47, 108.67, 108.16, 55.46, 33.31, 29.77, 24.19.

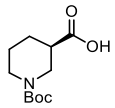


1-chloro-4-(prop-1-en-2-yl)benzene (S38) was prepared on a 32.3 mmol scale according to a published literature procedure.[2] The title compound was isolated using automated column chromatography eluting with Hexanes (10 CV). The title compound was concentrated to produce a colorless oil (4.94 g, 100% yield). Spectral data were consistent with reported literature values.[3]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.36 (m, 2H), 7.34 – 7.25 (m, 2H), 5.36 (s, 1H), 5.10 (h, *J* = 1.4 Hz, 1H), 2.14 (d, *J* = 1.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 142.33, 139.83, 133.33, 128.47, 126.96, 113.10, 21.88.

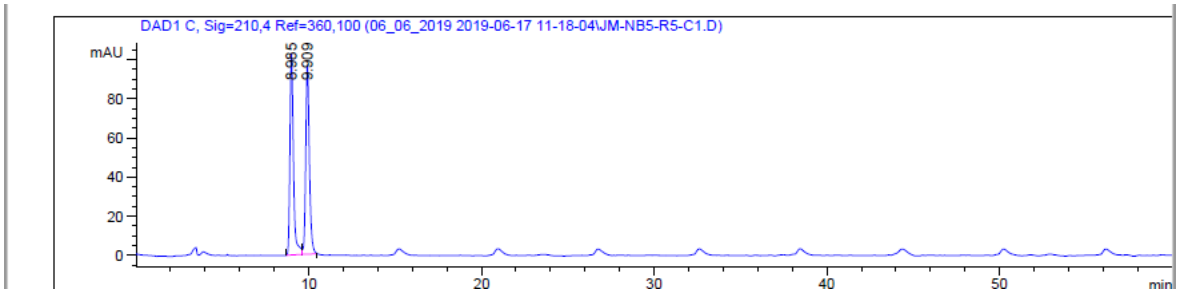


1-bromo-4-(prop-1-en-2-yl)benzene (S39) was prepared on a 11.35 mmol scale according to a published literature procedure.[2] The title compound was isolated using automated column chromatography eluting with Hexanes (10 CV). The title compound was concentrated to produce a colorless oil (1.63 g, 72% yield). Spectral data were consistent with reported literature values.[3]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.42 (m, 2H), 7.35 – 7.31 (m, 2H), 5.36 (bs, 1H), 5.10 (p, *J* = 1.5 Hz, 1H), 2.20 – 2.01 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.38, 140.28, 131.43, 127.31, 121.48, 113.20, 21.83.



(*R*)-1-(*tert*-butoxycarbonyl)piperidine-3-carboxylic acid (S41) was prepared on a 4.03 mmol scale according to a published literature procedure.[6] The title compound was isolated using automated column chromatography eluting with MeOH:DCM (0% 4 CV, 0-10% 10 CV, 10% 6 CV). The title compound was concentrated to produce a white solid (655 mg, 72% yield).
^{1}H NMR (500 MHz, (CD_3)$_2$SO): δ 12.37 (s, 1H), 4.17 – 3.81 (m, 1H), 3.69 (s, 1H), 3.17 – 2.76 (m, 2H), 2.31 (d, *J* = 9.1 Hz, 1H), 1.90 (d, *J* = 12.5 Hz, 1H), 1.65 – 1.59 (m, 1H), 1.54 – 1.49 (m, 1H), 1.39 (s, 9H), 1.38 – 1.28 (m, 1H).



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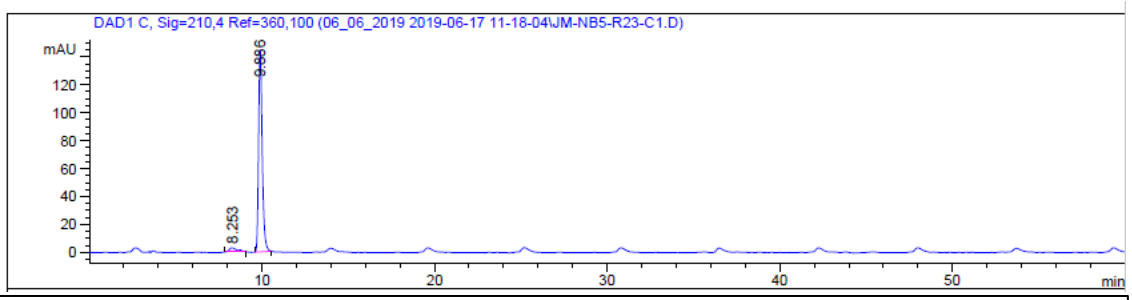
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.985	BV	0.2165	1471.61523	103.12862	50.6539
2	9.909	VB	0.2225	1433.61816	96.93424	49.3461
Totals :				2905.23340	200.06287	

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.985	BB	0.1947	64.44628	5.12428	49.6135
2	9.907	BB	0.2078	65.45048	4.77829	50.3865
Totals :				129.89676	9.90257	

Figure S4. Racemic standard of (**S41**).
ChiralPak® IC, 10% IPA in Hexanes, 60 min run, 1 mL/min.

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Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.253 BB    0.4575   95.93243    2.88862   4.2877
   2   9.886 BB    0.2245 2141.44922  144.82851  95.7123

Totals :                  2237.38165  147.71713


Signal 4: DAD1 D, Sig=230,4 Ref=360,100


Signal 5: DAD1 E, Sig=280,4 Ref=360,100

================================================================================
                           *** End of Report ***
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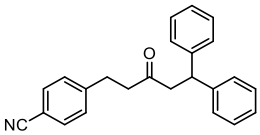
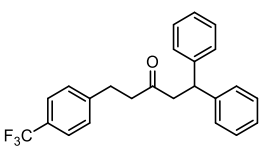
Figure S5. Enantioenriched carboxylic acid (**S41**; >99% e.e.).
ChiralPak® IC, 10% IPA in Hexanes, 60 min run, 1 mL/min.

B. Product Characterization



4-(3-oxo-5,5-diphenylpentyl)benzonitrileone (4) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-5% 12 CV, 10% 3 CV, 15% 2 CV, 20% 2 CV. 25% 5 CV) to produce a white solid (116 mg, 68% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.22 (m, 4H), 7.21 – 7.16 (m, 6H), 7.12 (d, *J* = 8.2 Hz, 2H), 4.57 (t, *J* = 7.7 Hz, 1H), 3.14 (d, *J* = 7.7 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 207.35, 146.75, 143.68, 132.35, 129.26, 128.77, 127.78, 126.70, 119.13, 110.04, 49.10, 46.29, 44.27, 29.38.
HRMS: (ESI-TOF) calculated for $C_{24}H_{21}NaO^+$ ([M+Na]$^+$): 362.1515, found: 362.1512.
FTIR (ATR cm^{-1}): 2923, 2225, 1712, 1605, 1579, 1493, 1450, 1412, 1369, 1241, 1177, 1155, 1091, 1074, 1030, 822, 748, 696, 625, 607, 550, 474, 425.

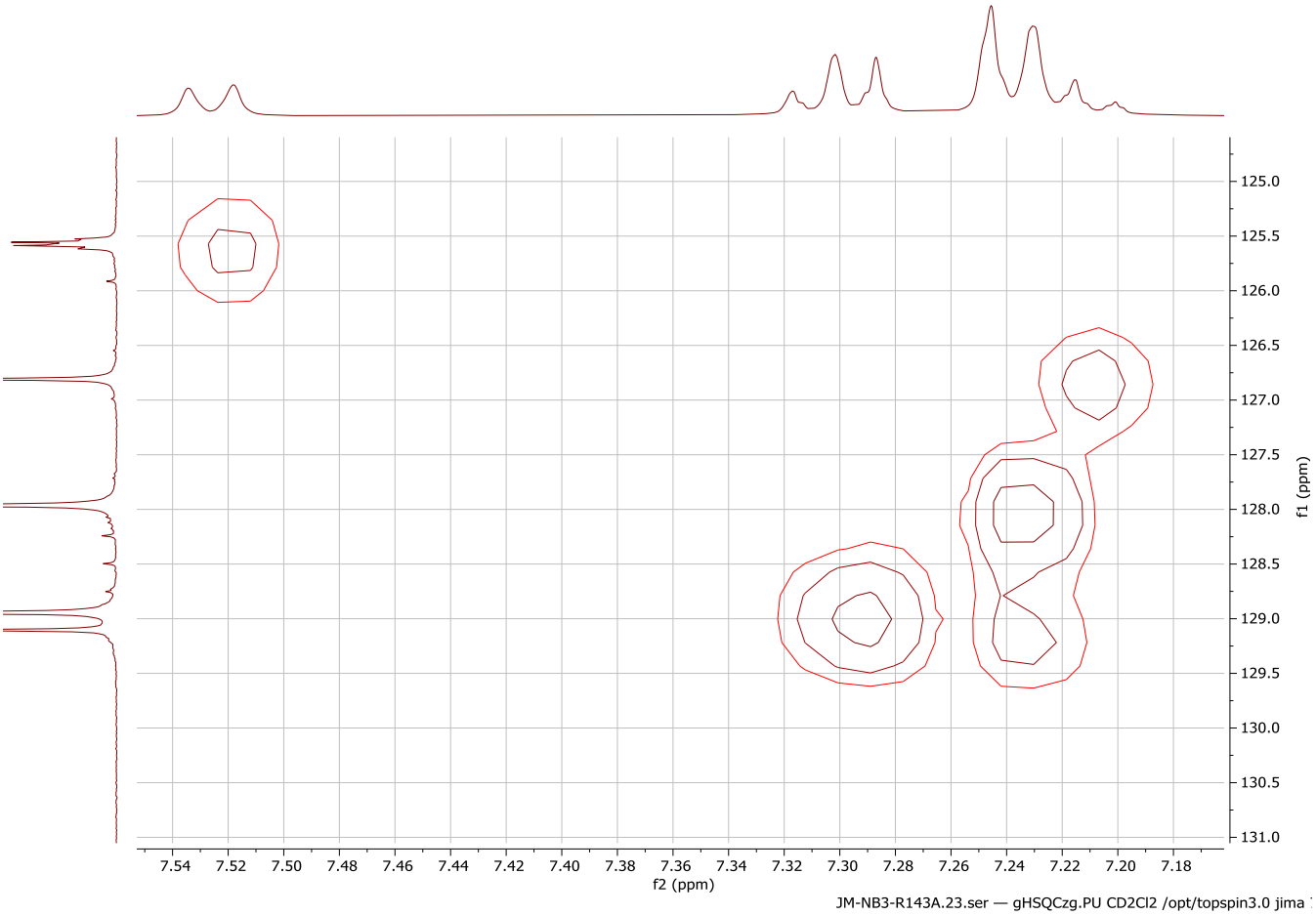


1,1-diphenyl-5-(4-(trifluoromethyl)phenyl)pentan-3-one (5) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-10% 10 CV, 10% 10 CV) to produce a white solid (121 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.35 – 7.29 (m, 4H), 7.28 – 7.17 (m, 8H), 4.65 (t, *J* = 7.6 Hz, 1H), 3.20 (d, *J* = 7.7 Hz, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.70 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 207.50, 145.95 (d, J = 1.5 Hz), 129.10, 128.95, 128.37 (appd, J = 32.2 Hz), 127.96, 126.81, 125.57 (q, J = 3.8 Hz), 124.83 (q, J = 271.7 Hz), 48.96, 46.39, 44.54, 29.41. *Note: Carbon peaks for this compound are overlaping, so assignment is missing one carbon peak.*

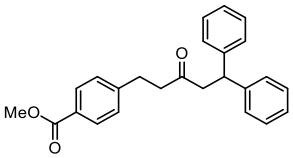
Note: HSQC NMR of **(5)** in CD_2Cl_2.



^{19}F NMR (282 MHz, $CDCl_3$): δ -62.39.

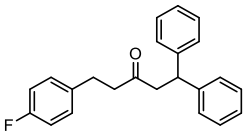
HRMS: (ESI-TOF) calculated for $C_{24}H_{21}F_3NaO^+$ ([M+Na]$^+$): 405.1437, found: 405.1435.

FTIR (ATR cm^{-1}): 3027, 1713, 1617, 1599, 1494, 1450, 1417, 1322, 1161, 1109, 1065, 1030, 1017, 907, 825, 791, 729, 697, 648, 617, 603, 573, 554, 516, 471, 413.

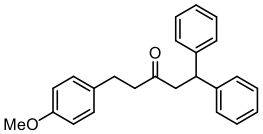


methyl 4-(3-oxo-5,5-diphenylpentyl)benzoate (6) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 7 CV, 0-5% 12 CV, 5% 2 CV, 5-10% 4 CV, 10% 2 CV, 15% 8 CV) to produce a white solid (121 mg, 65% yield).

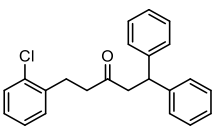
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.30 – 7.21 (m, 6H), 7.20 – 7.15 (m, 2H), 4.65 (t, *J* = 7.6 Hz, 1H), 3.96 (s, 3H), 3.21 (d, *J* = 7.6 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 207.68, 167.14, 146.56, 143.79, 129.89, 128.73, 128.43, 128.12, 127.78, 126.62, 52.15, 49.12, 46.19, 44.59, 29.40.
HRMS: (ESI-TOF) calculated for $C_{25}H_{25}O_3^+$ ([M+H]$^+$): 373.1798, found: 373.1794.
FTIR (ATR cm^{-1}): 1703, 1607, 1435, 1277, 1255, 1179, 1104, 1093, 1076, 1030, 1019, 986, 757, 749, 727, 699, 628, 606, 571, 551, 511, 486, 471.



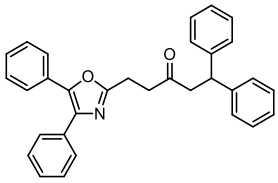
5-(4-fluorophenyl)-1,1-diphenylpentan-3-one (7) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-10% 10 CV, 10% 12 CV) to produce a yellow white solid (123 mg, 74% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.29 (m, 5H), 7.28 – 7.21 (m, 5H), 7.10 – 7.03 (m, 2H), 7.01 – 6.93 (m, 2H), 4.65 (t, J = 7.6 Hz, 1H), 3.20 (d, J = 7.6 Hz, 2H), 2.82 (t, J = 7.4 Hz, 2H), 2.68 (t, J = 7.4 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 207.99, 161.44 (d, *J* = 243.7 Hz), 143.88, 136.67 (d, *J* = 3.2 Hz), 129.79 (d, *J* = 7.8 Hz), 128.74, 127.83, 126.62, 115.30 (d, *J* = 21.1 Hz), 49.21, 46.17, 45.21 (d, *J* = 1.1 Hz), 28.67.
^{19}F NMR (282 MHz, $CDCl_3$): δ -117.39.
HRMS: (ESI-TOF) calculated for $C_{23}H_{22}FO^+$ ([M+H]$^+$): 333.1649, found: 333.1643.
FTIR (ATR cm^{-1}): 1701, 1660, 1593, 1509, 1355, 1344, 1253, 1220, 836, 812, 749, 701.



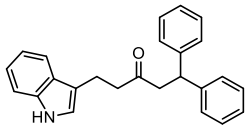
5-(4-methoxyphenyl)-1,1-diphenylpentan-3-one (8) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-10% 10 CV, 10% 7 CV) to produce a white solid (140 mg, 81% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.30 (m, 4H), 7.27 – 7.20 (m, 6H), 7.06 – 7.03 (m, 2H), 6.86 – 6.82 (m, 2H), 4.66 (t, *J* = 7.6 Hz, 1H), 3.83 (s, 3H), 3.19 (d, *J* = 7.5 Hz, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.69 – 2.62 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 208.30, 158.00, 143.96, 133.07, 129.31, 128.70, 127.83, 126.55, 113.96, 55.36, 49.20, 46.10, 45.43, 28.70.
HRMS: (ESI-TOF) calculated for $C_{24}H_{24}NaO_2^+$ ([M+Na]$^+$): 367.1668, found: 367.1660.
FTIR (ATR cm^{-1}): 2915, 1702, 1607, 1580, 1511, 1492, 1464, 1448, 1401, 1366, 1317, 1298, 1240, 1176, 1091, 1076, 1028, 854, 828, 806, 788, 768, 742, 700, 625, 607, 571, 557, 543, 528, 518, 468, 436, 408, 401.



5-(2-chlorophenyl)-1,1-diphenylpentan-3-one (9) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 7 CV, 0-5% 10 CV, 5% 6 CV) to produce a yellow tinted solid (110 mg, 63% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.24 (m, 5H), 7.23 – 7.15 (m, 6H), 7.11 (ddd, *J* = 12.4, 6.0, 2.6 Hz, 3H), 4.60 (t, *J* = 7.6 Hz, 1H), 3.15 (d, *J* = 7.6 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 207.99, 143.89, 138.61, 133.95, 130.75, 129.62, 128.74, 127.84, 127.77, 127.01, 126.61, 49.06, 46.28, 43.21, 27.67.
HRMS: (ESI-TOF) calculated for $C_{23}H_{22}ClO^+$ ($[M+H]^+$): 349.1354, found: 349.1351.
FTIR (ATR cm^{-1}): 3025, 2931, 2892, 1703, 1599, 1492, 1473, 1445, 1414, 1367, 1305, 1268, 1232, 1196, 1077, 1050, 1034, 1000, 991, 753, 742, 727, 719, 697, 665, 624, 610, 582, 557, 523, 483, 457, 436.

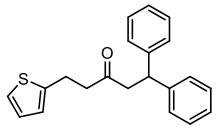


5-(4,5-diphenyloxazol-2-yl)-1,1-diphenylpentan-3-one (10) was prepared according to the general Procedure A using 2.4 equivalents of phosphine and at a concentration of 0.33 M. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 5 CV, 5-20% 18 CV, 20% 5 CV) to produce a white solid (228 mg, 34% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 6.8 Hz, 2H), 7.57 (d, *J* = 6.9 Hz, 2H), 7.42 – 7.31 (m, 6H), 7.31 – 7.24 (m, 8H), 7.22 – 7.16 (m, 2H), 4.69 (t, *J* = 7.5 Hz, 1H), 3.32 (d, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 7.2 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 206.76, 162.31, 145.43, 143.88, 135.12, 132.59, 129.07, 128.72, 128.66, 128.51, 128.14, 128.00, 127.80, 126.58, 126.55, 49.06, 45.98, 39.76, 22.10.
Note: Carbon peaks for this compound are overlaping, so assignment is missing one carbon peak.
HRMS: (ESI-TOF) calculated for $C_{32}H_{27}NNaO_2^+$ ($[M+Na]^+$): 480.1935, found: 480.1934.
FTIR (ATR cm^{-1}): 3026, 2921, 1716, 1569, 1493, 1447, 1365, 1264, 1218, 1156, 1094, 1072, 1057, 1024, 1000, 961, 913, 762, 733, 692, 673, 625, 606, 572, 555, 522, 470.

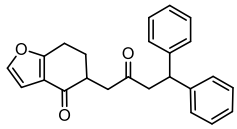


5-(1*H*-indol-3-yl)-1,1-diphenylpentan-3-one (11) was prepared according to the general procedure A using 2.4 equivalents of phosphine and at a concentration of 0.33 M. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (10% 4 CV, 10-20% 6.8 CV, 20% 10 CV) to produce a yellow white solid (106.2 mg, 60% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (bs, 1H), 7.50 (d, J = 7.4 Hz, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.29 – 7.24 (m, 4H), 7.21 – 7.16 (m, 7H), 7.14 – 7.02 (m, 1H), 6.78 (d, J = 2.3 Hz, 1H), 4.61 (t, J = 7.6 Hz, 1H), 3.15 (d, J = 7.6 Hz, 2H), 2.96 (t, J = 7.6 Hz, 2H), 2.74 (t, J = 7.4 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 208.98, 143.98, 136.31, 128.68, 127.84, 127.18, 126.52, 122.10, 121.61, 119.36, 118.76, 115.09, 111.25, 49.10, 46.12, 44.05, 19.17.
HRMS: (ESI-TOF) calculated for $C_{25}H_{23}NNaO^+$ ($[M+Na]^+$): 376.1672, found: 376.1678.

FTIR (ATR cm^{-1}): 2360, 1707, 1493, 1455, 1418, 1338, 1264, 1092, 1030, 1010, 731, 697, 608, 580, 552, 470, 423.



1,1-diphenyl-5-(thiophen-2-yl)pentan-3-one (12) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with EtOAc:Hexanes (0% 4 CV, 1% 4 CV, 1-7% 9 CV, 7% 13 CV) to produce a yellow oil (109 mg, 68% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 4H), 7.23 – 7.15 (m, 6H), 7.09 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.87 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.68 (d, *J* = 3.4 Hz, 1H), 4.61 (td, *J* = 7.6, 2.4 Hz, 1H), 3.17 (dd, *J* = 7.6, 1.6 Hz, 2H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 207.53, 143.89, 143.66, 128.74, 127.83, 126.94, 126.61, 124.69, 123.44, 49.18, 46.08, 45.27, 23.75.
HRMS: (ESI-TOF) calculated for $C_{21}H_{20}NaOS^+$ ([M+Na]$^+$): 343.1127, found: 343.1122.
FTIR (ATR cm^{-1}): 3025, 2921, 1711, 1598, 1492, 1449, 1406, 1368, 1235, 1091, 1073, 1030, 1003, 847, 821, 744, 692, 626, 609, 548, 502, 470.



5-(2-oxo-4,4-diphenylbutyl)-6,7-dihydrobenzofuran-4(5H)-one (13) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-15% 8 CV, 15% 15 CV) to produce a white solid (68 mg, 38% yield). Crude NMR analysis shows a 52% Yield.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.21 (m, 9H), 7.20 – 7.15 (m, 2H), 6.62 (d, *J* = 2.0 Hz, 1H), 4.62 (t, *J* = 7.7 Hz, 1H), 3.28 (qd, *J* = 16.4, 7.7 Hz, 2H), 3.13 (dd, *J* = 17.6, 4.7 Hz, 1H), 2.96 – 2.75 (m, 3H), 2.26 (dd, *J* = 17.6, 7.5 Hz, 1H), 2.04 – 1.96 (m, 1H), 1.71 (tdd, *J* = 12.9, 11.4, 5.7 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 207.64, 194.82, 166.67, 144.02, 143.85, 142.95, 128.73, 127.93, 127.86, 126.61, 120.68, 106.83, 49.28, 46.28, 43.15, 42.58, 28.79, 23.49.
HRMS: (ESI-TOF) calculated for $C_{24}H_{22}NaO_3^+$ ([M+Na]$^+$): 381.1461, found: 381.1457.
FTIR (ATR cm^{-1}): 2922, 2853, 1772, 1713, 1671, 1594, 1579, 1493, 1451, 1372, 1288, 1261, 1196, 1155, 1117, 1031, 947, 883, 773, 735, 696, 607, 558, 535, 474, 447, 403.

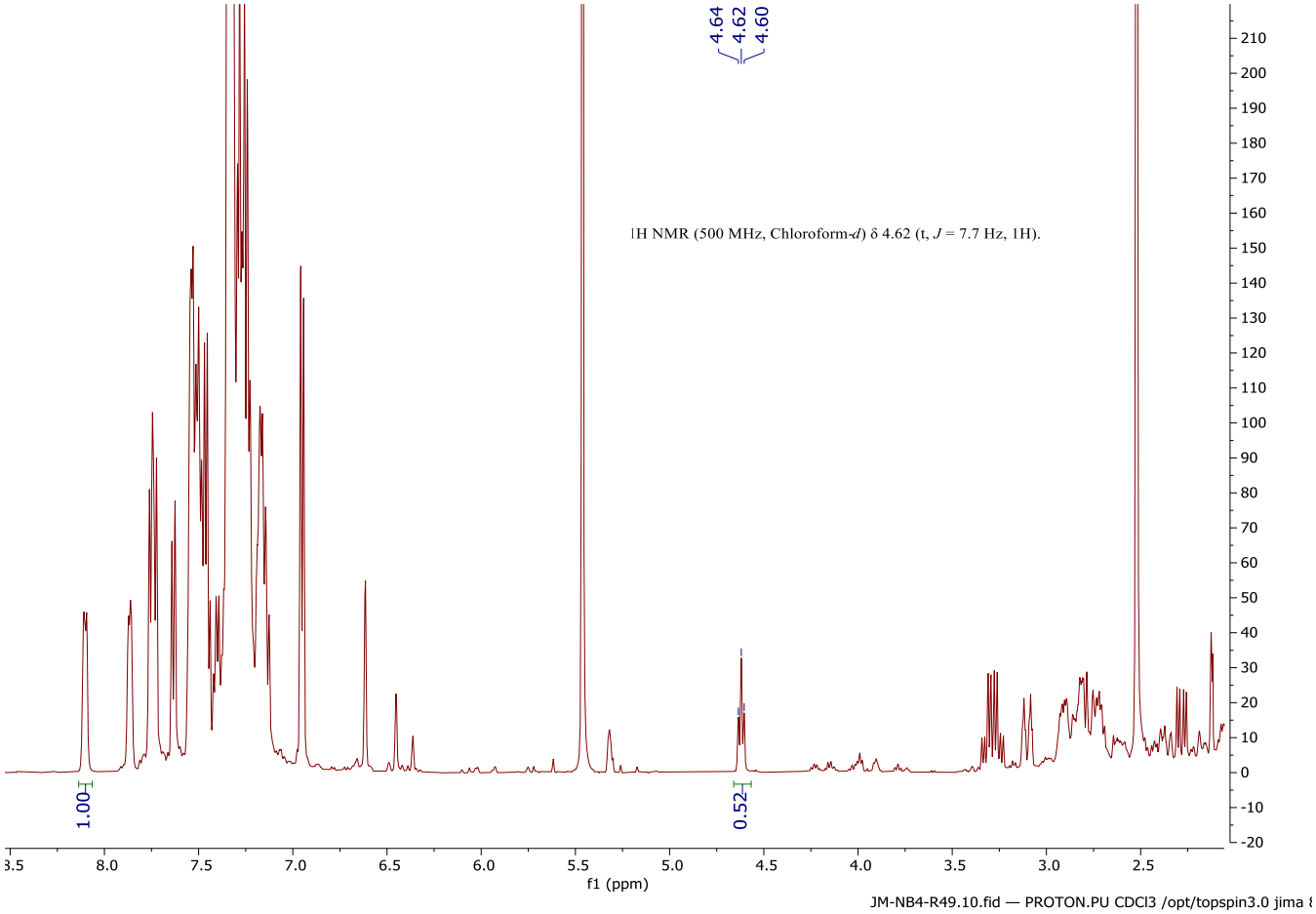
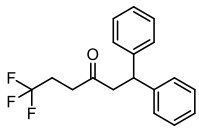
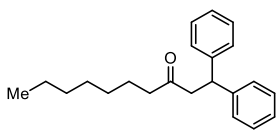


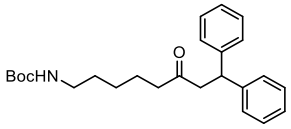
Figure S6. Crude NMR Yield for **(13)**. Referenced to one equivalent of 1-fluoronaphthalene.



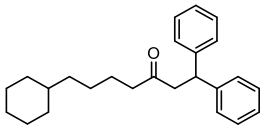
6,6,6-trifluoro-1,1-diphenylhexan-3-one (14) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-4% 9 CV, 6% 7 CV) to produce a yellow oil (93 mg, 61% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 4H), 7.24 – 7.16 (m, 6H), 4.59 (t, *J* = 7.6 Hz, 1H), 3.21 (d, *J* = 7.6 Hz, 2H), 2.59 – 2.53 (m, 2H), 2.29 (qt, J = 10.8, 7.7 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 205.37, 143.55, 128.82, 127.73, 126.95 (q, J = 275.8 Hz), 126.77, 48.90, 46.20, 35.91 (q, J = 2.6 Hz), 27.81 (q, J = 29.9 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ -66.68 (t, *J* = 10.7 Hz).
HRMS: (ESI-TOF) calculated for $C_{18}H_{17}F_3NaO^+$ ([M+Na]$^+$): 329.1124, found: 329.1126.
FTIR (ATR cm^{-1}): 3028, 1720, 1597, 1494, 1452, 1439, 1423, 1379, 1314, 1255, 1233, 1195, 1175, 1134, 1101, 1089, 1001, 983, 927, 850, 823, 794, 746, 726, 696, 627, 602, 565, 538, 469, 458, 403.



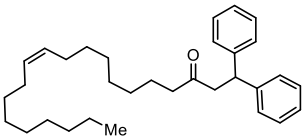
1,1-diphenyldecan-3-one (15) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-5% 8 CV, 5% 6 CV) to produce a yellow oil (107 mg, 69% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.23 (m, 8H), 7.22 – 7.18 (m, 2H), 4.65 (t, *J* = 7.5 Hz, 1H), 3.18 (d, *J* = 7.5 Hz, 2H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.50 (p, *J* = 7.3 Hz, 2H), 1.34 – 1.13 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 209.30, 144.09, 128.63, 127.84, 126.48, 48.86, 46.08, 43.72, 31.73, 29.11, 23.62, 22.69, 14.18.
Note: 13 carbon signals observed due to overlap.
HRMS: (ESI-TOF) calculated for $C_{22}H_{28}NaO^+$ ([M+Na]$^+$): 331.2032, found: 331.2029.
FTIR (ATR cm^{-1}): 2924, 2853, 1711, 1493, 1450, 1368, 1068, 1030, 744, 696, 608, 575, 555.



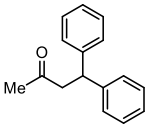
***tert*-butyl (6-oxo-8,8-diphenyloctyl)carbamate (16)** was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with EtOAc:Hexanes (5% 6 CV, 5-20% 10 CV, 20% 7 CV) to produce a white solid (198 mg, 82% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (t, *J* = 3.7 Hz, 4H), 7.24 – 7.19 (m, 4H), 7.17 (td, *J* = 6.9, 1.5 Hz, 2H), 4.59 (t, *J* = 7.6 Hz, 1H), 4.46 (bs, 1H), 3.14 (d, *J* = 7.6 Hz, 2H), 3.04 (q, *J* = 6.8 Hz, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 1.54 – 1.45 (m, 2H), 1.44 (s, 9H) 1.37 (p, *J* = 7.3 Hz, 2H), 1.14 (p, *J* = 7.7 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 209.11, 156.07, 144.03, 128.71, 127.87, 126.58, 79.20, 48.94, 46.21, 43.54, 40.48, 29.92, 28.57, 26.32, 23.17.
HRMS: (ESI-TOF) calculated for $C_{25}H_{33}NNaO_3^+$ ([M+Na]$^+$): 418.2353, found: 418.2360.
FTIR (ATR cm^{-1}): 3356, 3026, 2929, 2860, 1697, 1599, 1494, 1450, 1390, 1364, 1246, 1165, 1064, 1031, 987, 866, 780, 746, 697, 626, 608, 575, 555, 468.



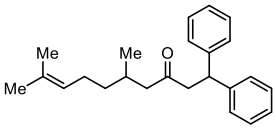
7-cyclohexyl-1,1-diphenylheptan-3-one (17) was prepared according to the general procedure B. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-10% 10 CV, 10% 10 CV) to produce a slightly yellow tinted white solid (149.8 mg, 86% yield)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 4H), 7.24 – 7.20 (m, 4H), 7.17 (t, J = 7.2 Hz, 2H), 4.61 (t, J = 7.6 Hz, 1H), 3.15 (d, J = 7.5 Hz, 2H), 2.30 (t, J = 7.4 Hz, 2H), 1.75 – 1.59 (m, 5H), 1.44 (p, J = 7.4 Hz, 2H), 1.27 – 1.03 (m, 8H), 0.80 (q, J = 13.9, 12.1 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 209.42, 144.13, 128.68, 127.88, 126.53, 48.93, 46.11, 43.81, 37.57, 37.30, 33.49, 26.85, 26.54, 26.45, 23.96.
HRMS: (ESI-TOF) calculated for $C_{25}H_{33}O^+$ ([M+H]$^+$): 349.2526, found: 349.2531.
FTIR (ATR cm^{-1}): 3027, 1713, 1617, 1599, 1494, 1450, 1417, 1322, 1161, 1109, 1065, 1030, 1017, 907, 825, 791, 729, 697, 648, 617, 603, 573, 554, 516, 471, 413.



(*Z*)-1,1-diphenylicos-11-en-3-one (18) was prepared according to the general procedure B. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 7 CV, 0-2% 4 CV, 2-7% 5 CV, 7% 7 CV) to produce a yellow oil (223 mg, 78% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 4H), 7.24 – 7.20 (m, 4H), 7.19 – 7.14 (m, 2H), 5.34 (dq, J = 5.6, 5.0 Hz, 2H), 4.61 (t, *J* = 7.5 Hz, 1H), 3.15 (d, *J* = 7.6 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 2.00 (p, *J* = 6.9 Hz, 4H), 1.46 (p, *J* = 7.4 Hz, 2H), 1.38 – 1.09 (m, 20H), 0.88 (t, J = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 209.35, 144.12, 130.12, 129.91, 128.68, 127.88, 126.53, 48.91, 46.13, 43.77, 32.05, 29.91, 29.82, 29.67, 29.47, 29.39, 29.22, 29.17, 27.36, 27.31, 23.65, 22.83, 14.27.
Note: 23 carbon signals observed due to overlap.
HRMS: (ESI-TOF) calculated for $C_{32}H_{47}O^+$ ($[M+H]^+$): 447.3621, found: 447.3617.
FTIR (ATR cm^{-1}): 2921, 2851, 1713, 1493, 1451, 1366, 1064, 1031, 742, 696, 608, 575, 555.

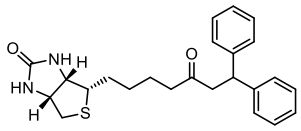


4,4-diphenylbutan-2-one (19) was prepared according to the general procedure B. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-8% 12 CV, 15% 3 CV) to produce a yellow oil (86.1 mg, 76% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 4H), 7.25 – 7.22 (m, 4H), 7.20 – 7.15 (m, 2H), 4.60 (t, J = 7.6 Hz, 1H), 3.19 (d, J = 7.5 Hz, 2H), 2.09 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 207.02, 143.96, 128.72, 127.83, 126.58, 49.80, 46.15, 30.81.
HRMS: (ESI-TOF) calculated for $C_{16}H_{16}NaO^+$ ($[M+Na]^+$): 247.1093, found: 247.1089.
FTIR (ATR cm^{-1}): 3024, 2926, 1706, 1595, 1583, 1491, 1450, 1407, 1368, 1332, 1249, 1201, 1162, 1086, 1050, 1031, 1017, 966, 776, 745, 694, 633, 617, 596, 565, 543, 469.



5,9-dimethyl-1,1-diphenyldec-8-en-3-one (20) was prepared according to the general procedure B. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-7% 10 CV, 7% 3 CV) to produce a pale yellow oil (69 mg, 41% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.23 (m, 8H), 7.20 (t, *J* = 7.0 Hz, 2H), 5.06 (t, *J* = 6.5 Hz, 1H), 4.64 (t, *J* = 7.6 Hz, 1H), 3.17 (dd, *J* = 7.5, 1.6 Hz, 2H), 2.34 (dd, *J* = 16.0, 5.6 Hz, 1H), 2.16 (dd, *J* = 16.0, 8.2 Hz, 1H), 2.07 – 1.80 (m, 3H), 1.70 (s, 3H), 1.60 (s, 3H), 1.27 – 1.18 (m, 1H), 1.18 – 1.08 (m, 1H), 0.79 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 208.96, 144.10, 131.56, 128.66, 127.88, 127.87, 126.51, 124.43, 51.17, 49.39, 46.04, 36.97, 28.78, 25.84, 25.52, 19.73, 17.78.

HRMS: (ESI-TOF) calculated for $C_{24}H_{30}NaO^+$ ([M+Na]$^+$): 357.2189, found: 357.2184.
FTIR (ATR cm^{-1}): 2959, 2913, 1709, 1493, 1449, 1407, 1374, 1060, 1031, 747, 696, 627, 609, 547, 470.



(3aS,4S,6aR)-4-(5-oxo-7,7-diphenylheptyl)tetrahydro-1H-thieno[3,4-d]imidazol-2(3H)-one (21) was prepared according to the general procedure B in DMA and at 0.25 mmol scale and 0.25 M concentration and six equivalents of alkene. The title compound was isolated using automated column chromatography eluting with EtOAc:Hexanes (60% 4CV, 60-100% 10 CV, 100% 5 CV) followed by (35% MeOH:EtOAc):EtOAc 0-10% 6 CV, 10% 2 CV, 15%% 2 CV, 15-25% 5 CV, 25% 12 CV) to produce a pale yellow oil with 80% purity. Isolation of authentic product was obtained using supercritical fluid chromatography with a ChiralCel AD-H (2 x 25 cm) column and the following conditions: 30% EtOH (0.1 DEA)/CO_2, 100 bar, 60 mL/min, 220 nm to produce a white/yellow semisolid (28 mg, 27% Yield). Comparison of the crude reaction mixture to clean product resulted in 62% crude NMR yield. When using three equivalents of alkene a 44% crude NMR yield is obtained.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 – 7.24 (m, 4H), 7.23 – 7.20 (m, 4H), 7.17 (t, *J* = 7.2 Hz, 2H), 5.66 (s, 1H), 5.26 (s, 1H), 4.59 (t, *J* = 7.6 Hz, 1H), 4.45 (dd, *J* = 7.8, 4.9 Hz, 1H), 4.22 (dd, *J* = 8.4, 4.6 Hz, 1H), 3.15 (d, *J* = 7.6 Hz, 2H), 3.06 (td, *J* = 7.3, 4.5 Hz, 1H), 2.86 (dd, *J* = 12.8, 4.9 Hz, 1H), 2.65 (d, *J* = 12.8 Hz, 1H), 2.34 (t, *J* = 7.3 Hz, 2H), 1.63 – 1.42 (m, 4H), 1.25 (q, *J* = 7.8, 7.3 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 209.22, 163.59, 144.02, 128.71, 127.86, 127.85, 126.56, 61.96, 60.18, 55.39, 48.89, 46.11, 43.22, 40.65, 28.38, 28.32, 23.38.
HRMS: (ESI-TOF) calculated for $C_{24}H_{28}N_2NaO_2S^+$ ([M+Na]$^+$): 431.1764, found: 431.1770.
FTIR (ATR cm^{-1}): 3234, 2925, 1701, 1493, 1451, 1371, 1330, 1265, 748, 701, 608.

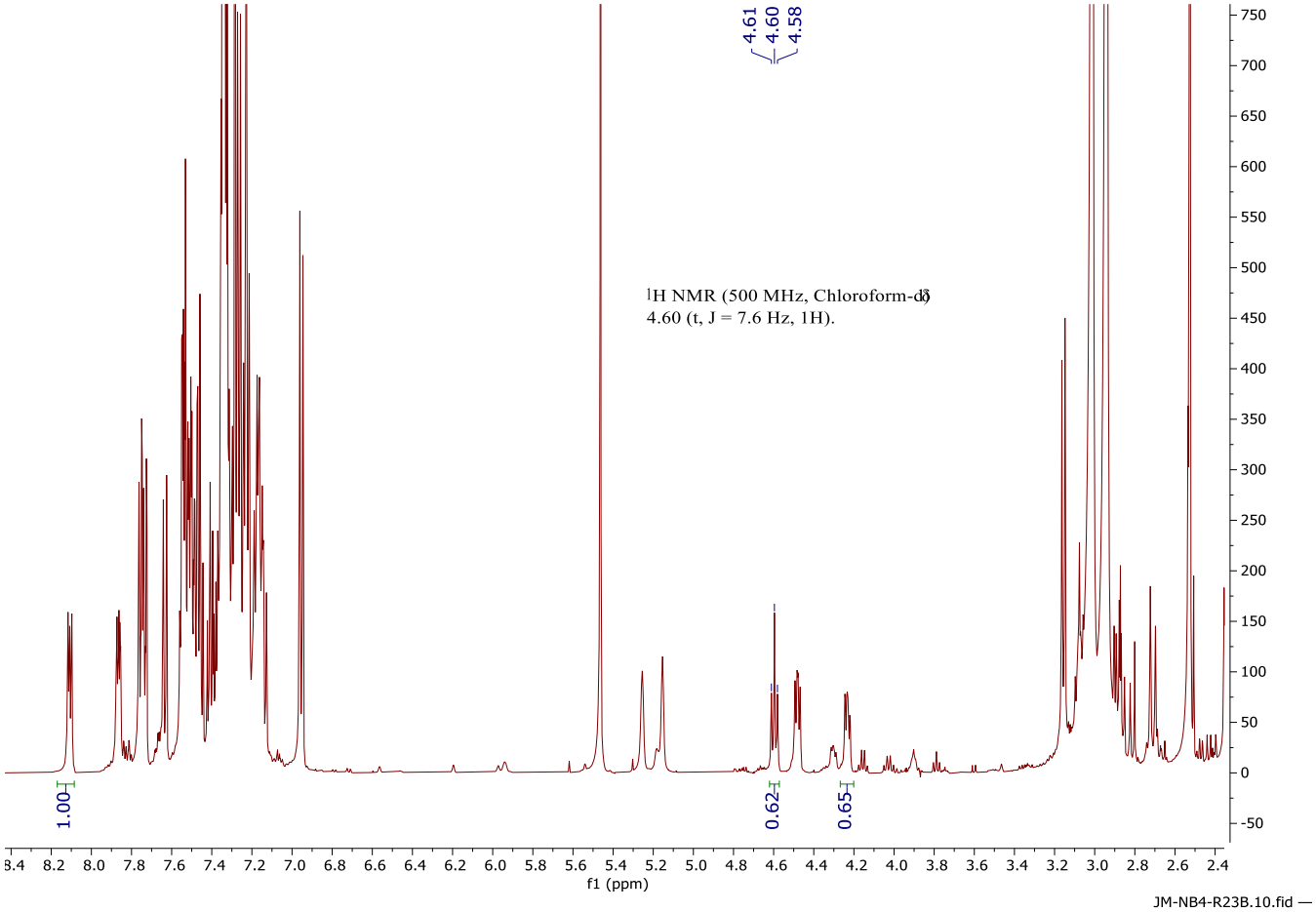
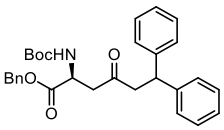


Figure S7. Crude NMR Yield for **(21)**. Referenced to one equivalent of 1-fluoronaphthalene.



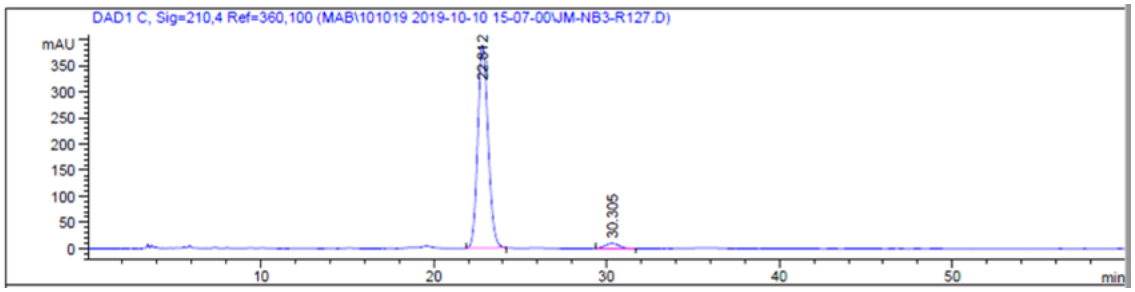
Benzyl (S)-2-((tert-butoxycarbonyl)amino)-4-oxo-6,6-diphenylhexanoate (22) was prepared according to the general procedure A and at a 0.25 M concentration. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-10% 4 CV, 10% 6 CV, 10-25% 6 CV, 25% 10 CV) to produce a slightly yellow tinted white solid (79 mg, 32% Yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.31 (m, 3H), 7.27 – 7.22 (m, 6H), 7.20 – 7.14 (m, 6H), 5.38 (d, *J* = 8.8 Hz, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 5.00 (d, *J* = 12.3 Hz, 1H), 4.54 (t, *J* = 7.5 Hz, 1H), 4.46 (dt, *J* = 8.7, 4.4 Hz, 1H), 3.28 – 3.04 (m, 3H), 2.86 (dd, *J* = 18.1, 4.2 Hz, 1H), 1.40 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 207.07, 171.27, 155.62, 143.65, 143.61, 135.48, 128.78, 128.74, 128.65, 128.44, 128.29, 127.77, 126.70, 126.67, 80.08, 67.38, 49.62, 48.88, 45.89, 45.20, 28.41.

HRMS: (ESI-TOF) calculated for $C_{30}H_{34}NO_5^+$ ([M+H]$^+$): 488.2432, found: 488.2424.

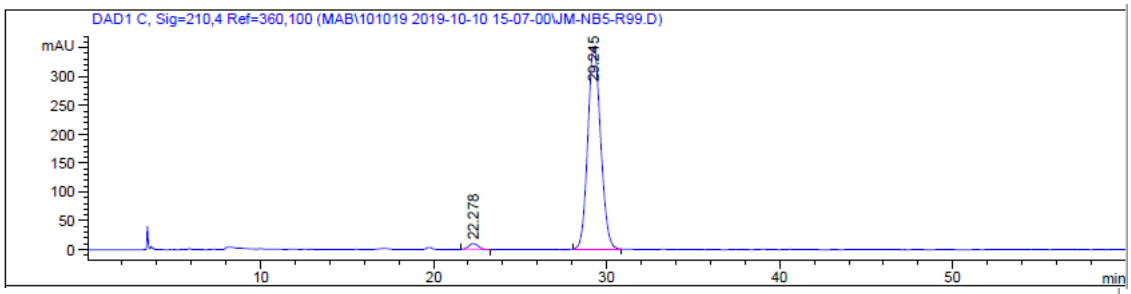
FTIR (ATR cm^{-1}): 1712, 1495, 1453, 1367, 1336, 1264, 1160, 1074, 1025, 731, 697, 607, 493.



Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.812	BB	0.6448	1.62293e4	388.96356	96.8081
2	30.305	BB	0.7581	535.09869	9.66287	3.1919
Totals :				1.67644e4	398.62643	

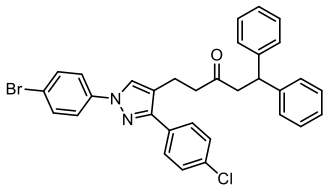
Figure S8. HPLC trace of benzyl (S)-2-((tert-butoxycarbonyl)amino)-4-oxo-6,6-diphenylhexanoate (93% e.e.)**.**
ChiralPak® IC, 10% IPA in Hexanes, 60 min run, 1 mL/min.



Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.278	BB	0.5893	394.00177	10.18627	2.1199
2	29.245	BB	0.8019	1.81922e4	351.44846	97.8801
Totals :				1.85862e4	361.63472	

Figure S9. HPLC trace of benzyl (R)-2-((tert-butoxycarbonyl)amino)-4-oxo-6,6-diphenylhexanoate (95% e.e.).
ChiralPak® IC, 10% IPA in Hexanes, 60 min run, 1 mL/min.



5-(1-(4-bromophenyl)-3-(4-chlorophenyl)-1H-pyrazol-4-yl)-1,1-diphenylpentan-3-one (23) was prepared according to the general Procedure A using 2.4 equivalents of phosphine and at

a concentration of 0.33 M. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 5 CV, 0-10% 6 CV, 10-13% 2 CV, 13-25% 4 CV, 25% 5 CV) to produce a white solid (142.8 mg, 50% yield in 91% purity which corresponds to an isolated yield of 45%). Crude NMR analysis shows a 50% Yield.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 – 7.42 (m, 6H), 7.42 – 7.34 (m, 2H), 7.29 – 7.10 (m, 11H), 4.58 (t, *J* = 7.7 Hz, 1H), 3.13 (d, *J* = 7.6 Hz, 2H), 2.85 (t, *J* = 7.0 Hz, 2H), 2.63 (t, *J* = 7.0 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 207.93, 150.58, 143.72, 138.98, 134.06, 132.50, 131.91, 129.14, 128.96, 128.74, 127.76, 126.83, 126.68, 120.52, 120.29, 119.50, 48.97, 46.26, 43.81, 18.25.
HRMS: (ESI-TOF) calculated for $C_{32}H_{27}BrClN_2O^+$ ([M+H]$^+$): 569.0989, found: 569.0983.
FTIR (ATR cm^{-1}): 1738, 1492, 1450, 1353, 1269, 1155, 1092, 1077, 1009, 984, 955, 902, 874, 831, 790, 765, 694, 603, 552, 503.

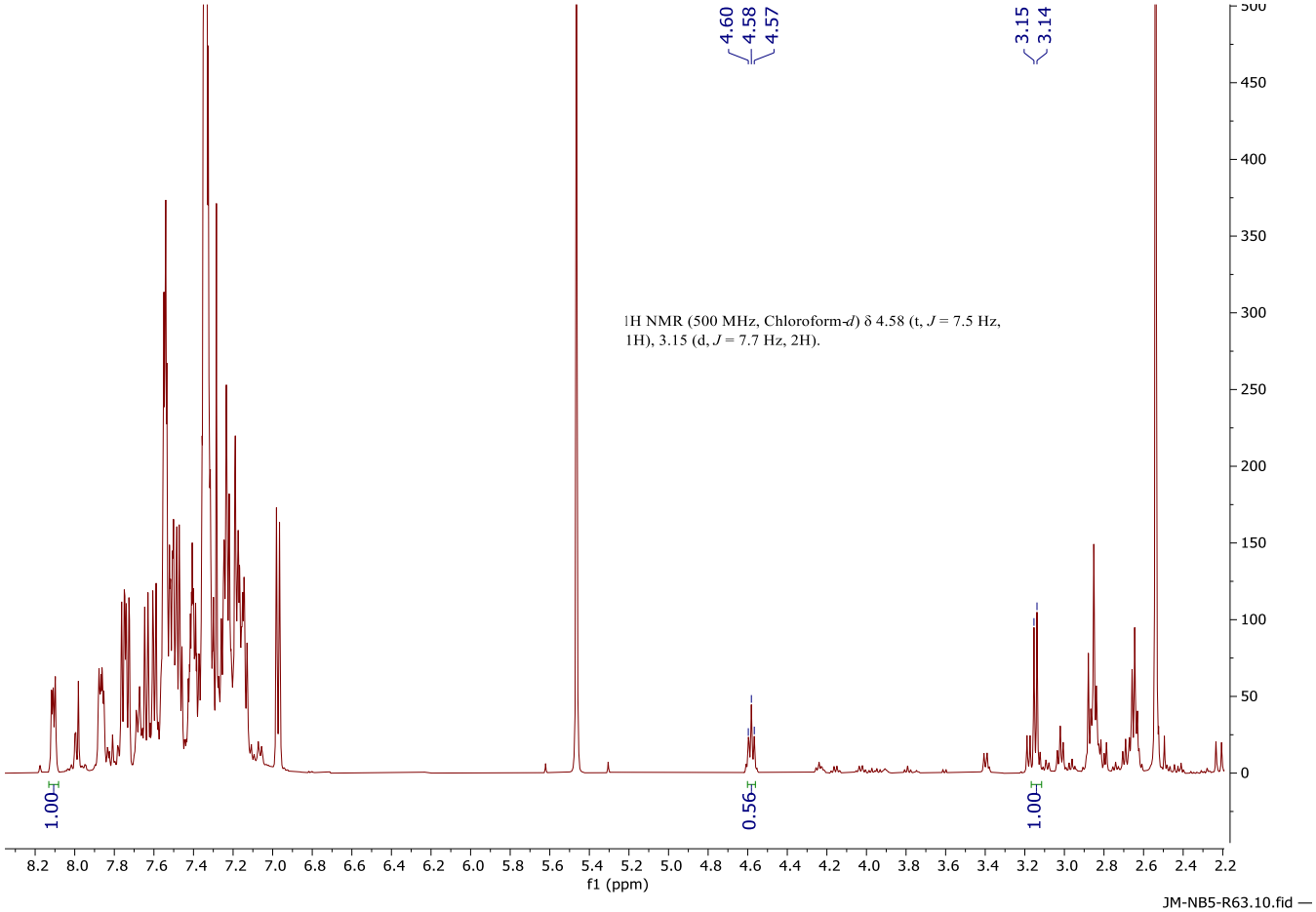
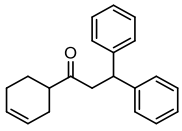
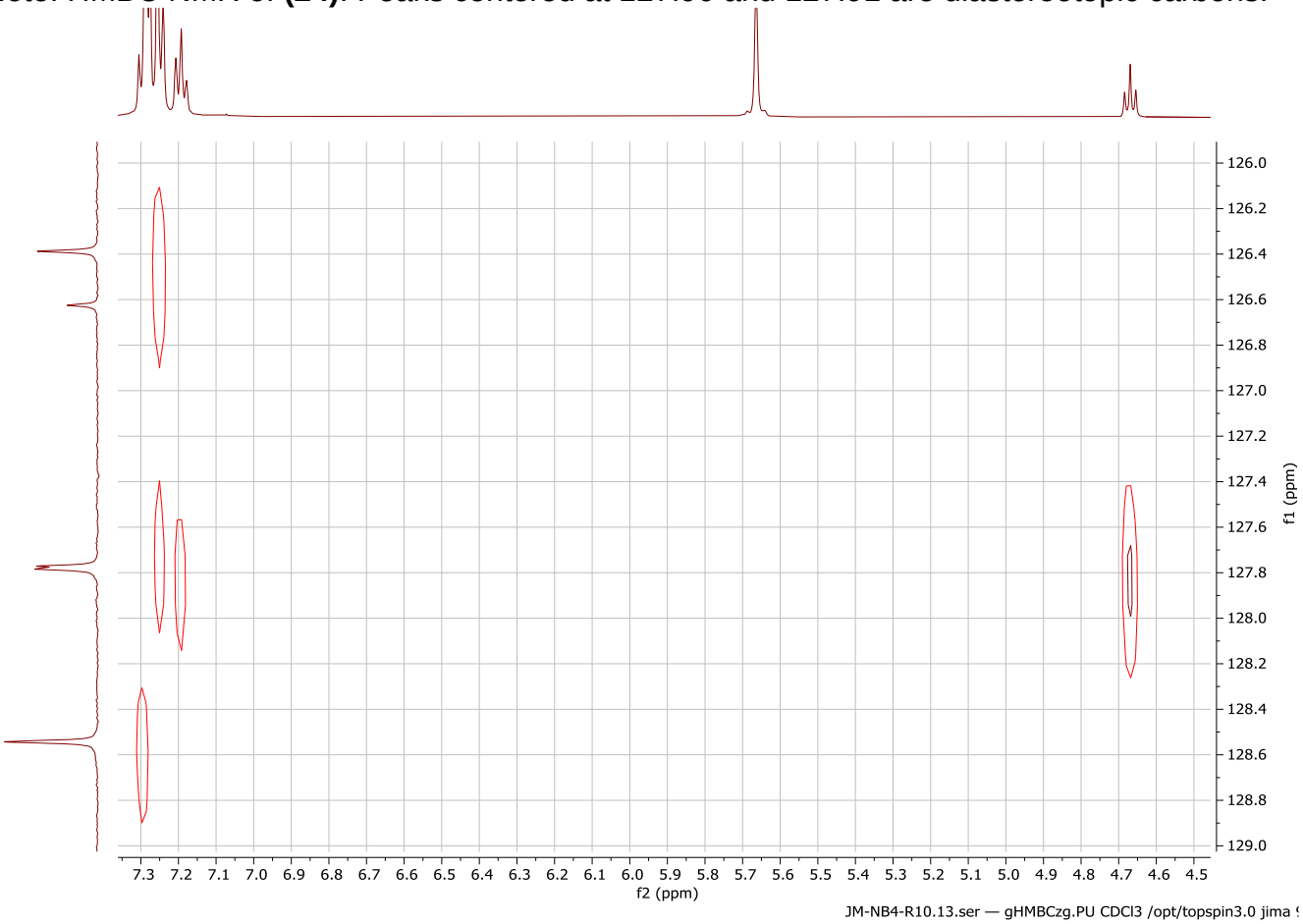


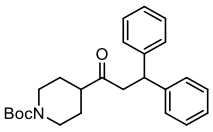
Figure S10. Crude NMR Yield for **(23)**. Referenced to one equivalent of 1-fluoronaphthalene.



1-(cyclohex-3-en-1-yl)-3,3-diphenylpropan-1-one (24) was prepared according to the general procedure B. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-5% 12 CV, 5% 10 CV) to produce a pale yellow oil (75 mg, 51% yield in 94% purity which corresponds to an isolated yield of 48%).

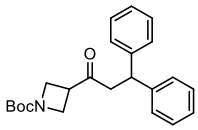
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.23 (m, 8H), 7.22 – 7.17 (m, 2H), 5.67 (s, 2H), 4.68 (t, *J* = 7.5 Hz, 1H), 3.26 (p, *J* = 9.3 Hz, 2H), 2.54 (dddd, *J* = 11.7, 9.1, 5.9, 2.8 Hz, 1H), 2.10 – 1.98 (m, 4H), 1.89 – 1.76 (m, 1H), 1.55 – 1.44 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 211.43, 144.25, 144.22, 128.66, 127.91, 127.90, 126.75, 126.51, 125.41, 47.22, 47.10, 45.86, 26.66, 24.76, 24.39.
HRMS: (ESI-TOF) calculated for $C_{21}H_{22}NaO^+$ ([M+Na]$^+$): 313.1563, found: 313.1563.
FTIR (ATR cm^{-1}): 3024, 2921, 1707, 1493, 1450, 1436, 1373, 1103, 1031, 747, 732, 698, 648, 611.
Note: HMBC NMR of **(24)**. Peaks centered at 127.90 and 127.91 are diastereotopic carbons.



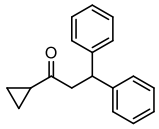


***tert*-butyl 4-(3,3-diphenylpropanoyl)piperidine-1-carboxylate (25)** was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-8% 8 CV, 8% 2 CV, 8-12% 2 CV, 15% 15 CV) to produce a white solid (157 mg, 80% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.23 (m, 4H), 7.23 – 7.14 (m, 6H), 4.62 (t, J = 7.4 Hz, 1H), 4.01 (bs, 2H), 3.20 (d, J = 7.5 Hz, 2H), 2.70 (t, J = 12.2 Hz, 2H), 2.35 (tt, J = 11.2, 3.7 Hz, 1H), 1.65 (bs, 2H), 1.43 (s, 9H), 1.42 – 1.32 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 210.16, 154.75, 144.03, 128.71, 127.85, 126.61, 79.74, 49.25, 46.96, 45.82, 29.85, 28.55, 27.23.
HRMS: (ESI-TOF) calculated for $C_{25}H_{31}NNaO_3^+$ ([M+Na]$^+$): 416.2196, found: 416.2200.

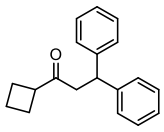
FTIR (ATR cm^{-1}): 2925, 2848, 1706, 1688, 1494, 1450, 1420, 1383, 1365, 1335, 1308, 1276, 1248, 1232, 1159, 1129, 1079, 1064, 1028, 1014, 980, 950, 921, 906, 869, 791, 770, 747, 702, 694, 650, 629, 594, 555, 540, 471.



***tert*-butyl 3-(3,3-diphenylpropanoyl)azetidine-1-carboxylate (26)** was prepared according to the general Procedure A using 2.4 equivalents of phosphine and at a concentration of 0.33 M. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-25% 10 CV, 25% 20 CV) to produce a slightly yellow tinted white solid (92 mg, 50% Yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 4H), 7.24 – 7.12 (m, 6H), 4.61 (t, *J* = 7.5 Hz, 1H), 4.00 – 3.75 (m, 4H), 3.30 (p, *J* = 7.7 Hz, 1H), 3.17 (d, *J* = 7.5 Hz, 2H), 1.40 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 206.32, 156.25, 143.61, 128.84, 127.74, 126.81, 79.91, 50.30, 47.31, 45.95, 39.15, 28.46.
HRMS: (ESI-TOF) calculated for $C_{23}H_{27}NNaO_3^+$ ([M+Na]$^+$): 388.1883, found: 388.1876.
FTIR (ATR cm^{-1}): 2972, 2929, 2887, 1714, 1697, 1598, 1492, 1474, 1448, 1404, 1368, 1342, 1296, 1251, 1163, 1129, 1102, 1083, 1070, 1031, 983, 958, 904, 862, 792, 770, 751, 730, 697, 628, 614, 587, 568, 543, 494, 470, 414.

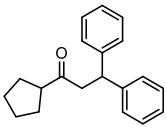


1-cyclopropyl-3,3-diphenylpropan-1-one (27) was prepared according to the general procedure B. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-5% 12 CV, 5% 5 CV) to produce a white solid (88.7 mg, 70% yield in 92% purity which corresponds to an isolated yield of 65%).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.25 (m, 8H), 7.21 (qd, *J* = 7.0, 6.6, 1.7 Hz, 2H), 4.67 (t, *J* = 7.4 Hz, 1H), 3.34 (dd, *J* = 7.5, 1.7 Hz, 2H), 1.93 (tt, *J* = 8.2, 4.7 Hz, 1H), 0.96 – 0.83 (m, 2H), 0.81 (dd, *J* = 7.7, 3.6 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 208.99, 144.17, 128.64, 127.92, 126.48, 49.72, 46.23, 21.24, 10.90.
HRMS: (ESI-TOF) calculated for $C_{18}H_{19}O^+$ ([M+H]$^+$): 251.1430, found: 251.1426.
FTIR (ATR cm^{-1}): 3025, 3003, 2892, 1694, 1596, 1492, 1449, 1412, 1386, 1362, 1244, 1193, 1095, 1070, 1044, 1019, 999, 982, 958, 904, 866, 789, 780, 751, 736, 702, 692, 626, 612, 592, 575, 564, 548, 504, 465.

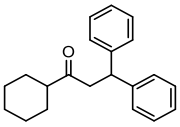


1-cyclobutyl-3,3-diphenylpropan-1-one (28) was prepared according to the general procedure B. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-5% 12 CV, 5% 2.5 CV) to produce a white solid (99 mg, 74% yield).

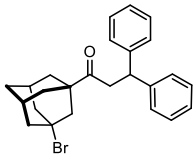
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.24 (m, 4H), 7.23 – 7.20 (m, 4H), 7.17 (td, *J* = 7.0, 1.5 Hz, 2H), 4.62 (t, *J* = 7.5 Hz, 1H), 3.15 (p, *J* = 8.5 Hz, 1H), 3.09 (d, *J* = 7.5 Hz, 2H), 2.10 – 1.99 (m, 4H), 1.94 – 1.83 (m, 1H), 1.75 – 1.66 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 209.77, 144.24, 128.67, 127.88, 126.51, 46.39, 46.02, 45.87, 24.11, 17.72.
HRMS: (ESI-TOF) calculated for $C_{19}H_{21}O^+$ ([M+H]$^+$): 265.1587, found: 265.1593.
FTIR (ATR cm^{-1}): 2987, 2941, 2860, 1705, 1596, 1493, 1451, 1415, 1376, 1341, 1248, 1120, 1029, 985, 920, 907, 794, 747, 738, 696, 628, 612, 570, 546, 471.



1-cyclopentyl-3,3-diphenylpropan-1-one (29) was prepared according to the general procedure B. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 10 CV, 0-1% 3 CV, 1-5% 8 CV, 5% 2 CV) to produce a white solid (62 mg, 52% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.16 (m, 8H), 7.20 – 7.13 (m, 2H), 4.64 (t, J = 7.5 Hz, 1H), 3.20 (d, J = 7.5 Hz, 2H), 2.82 – 2.73 (m, 1H), 1.70 (dtd, J = 12.1, 8.8, 5.3 Hz, 2H), 1.63 – 1.46 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 211.09, 144.31, 128.64, 127.92, 126.47, 52.10, 48.14, 45.92, 28.62, 26.02.
HRMS: (ESI-TOF) calculated for $C_{20}H_{23}O^+$ ([M+H]$^+$): 279.1743, found: 279.1750.
FTIR (ATR cm^{-1}): 2960, 1704, 1493, 1450, 1421, 1375, 1089, 1058, 1032, 743, 702, 611, 568, 547, 471.

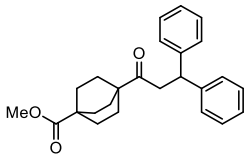


1-cyclohexyl-3,3-diphenylpropan-1-one (30) was prepared according to the general procedure B. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-5% 12 CV, 5% 5 CV) to produce a white solid (87 mg, 59% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 4H), 7.24 – 7.20 (m, 4H), 7.19 – 7.14 (m, 2H), 4.62 (t, *J* = 7.4 Hz, 1H), 3.19 (d, *J* = 7.4 Hz, 2H), 2.28 – 2.20 (m, 1H), 1.78 – 1.67 (m, 4H), 1.62 (d, *J* = 11.3 Hz, 1H), 1.27 – 1.12 (m, 5H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 211.92, 144.35, 128.63, 127.92, 126.45, 51.45, 46.97, 45.76, 28.27, 25.94, 25.73.
HRMS: (ESI-TOF) calculated for $C_{21}H_{24}NaO^+$ ([M+Na]$^+$): 315.1719, found: 315.1715.
FTIR (ATR cm^{-1}): 2928, 2849, 1704, 1494, 1450, 994, 748, 697, 628, 613, 587, 554.

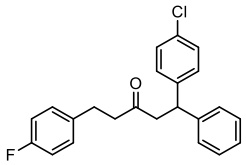


1-((1r,3s,5R,7S)-3-bromoadamantan-1-yl)-3,3-diphenylpropan-1-one (31) was prepared according to the general procedure B. The title compound was isolated using automated column chromatography eluting with a 10% Ether Hexanes stock solution:Hexanes (0% 8 CV, 0-10%

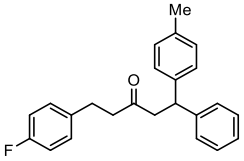
10 CV, 12% 8 CV, 15% 9 CV, 18% 2 CV, 20% 5 CV) to produce a white solid (100 mg, 47% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.25 (m, 4H), 7.24 – 7.20 (m, 4H), 7.20 – 7.15 (m, 2H), 4.65 (t, *J* = 7.3 Hz, 1H), 3.20 (d, *J* = 7.3 Hz, 2H), 2.34 – 2.28 (m, 4H), 2.28 – 2.22 (m, 2H), 2.21 – 2.17 (m, 2H), 1.76 – 1.60 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 210.38, 144.18, 128.65, 127.89, 126.51, 64.23, 50.95, 48.95, 48.23, 45.40, 42.84, 36.32, 34.60, 31.78.
HRMS: (ESI-TOF) calculated for $C_{25}H_{28}BrO^+$ ($[M+H]^+$): 423.1318, found: 423.1314.
FTIR (ATR cm^{-1}): 2908, 2855, 1697, 1493, 1449, 1306, 1173, 1153, 1132, 1029, 956, 906, 820, 727, 697, 647, 630, 612, 591, 561, 477.



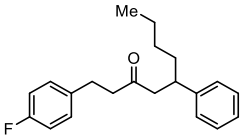
Methyl 4-(3,3-diphenylpropanoyl)bicyclo[2.2.2]octane-1-carboxylate (32) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-5% 10 CV, 5% 5 CV, 10% 12 CV) to produce a white fluffy solid (50.8 mg, 54% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 4H), 7.22 – 7.13 (m, 6H), 4.63 (t, *J* = 7.3 Hz, 1H), 3.63 (s, 3H), 3.18 (d, *J* = 7.3 Hz, 2H), 1.81 – 1.72 (m, 6H), 1.66 – 1.60 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 212.40, 177.93, 144.34, 128.63, 127.91, 126.46, 51.92, 45.42, 44.79, 43.78, 39.03, 27.85, 26.93.
HRMS: (ESI-TOF) calculated for $C_{25}H_{29}O_3^+$ ($[M+H]^+$): 377.2111, found: 377.2117.
FTIR (ATR cm^{-1}): 2947, 2919, 2870, 1720, 1695, 1494,1453, 1432, 1373, 1255, 1237, 1191, 1077, 1061, 1031, 1004, 905, 841, 795, 761, 751, 727, 704, 696, 628, 611, 570, 549, 470.



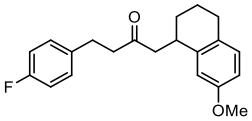
1-(4-chlorophenyl)-5-(4-fluorophenyl)-1-phenylpentan-3-one (33) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-5% 10 CV, 5% 10 CV) to produce a white powdery solid (128 mg, 69% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.20 (m, 5H), 7.19 – 7.10 (m, 4H), 7.06 – 7.00 (m, 2H), 6.96 – 6.89 (m, 2H), 4.58 (t, *J* = 7.5 Hz, 1H), 3.12 (d, *J* = 7.5 Hz, 2H), 2.79 (t, *J* = 7.3 Hz, 2H), 2.68 – 2.60 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 207.60, 161.47 (d, J = 243.9 Hz), 143.40, 142.43, 136.56 (d, J = 2.9 Hz), 132.37, 129.81 (d, J = 7.8 Hz), 129.20, 129.19, 128.84, 127.72, 126.82, 115.33 (d, J = 21.2 Hz), 49.04, 45.41, 45.19, 28.66.
^{19}F NMR (376 MHz, $CDCl_3$): δ -117.20 – -117.28 (m).
HRMS: (ESI-TOF) calculated for $C_{23}H_{20}ClFNaO^+$ ($[M+Na]^+$): 389.1079, found: 389.1078.
FTIR (ATR cm^{-1}): 2925, 1712, 1600, 1508, 1488, 1451, 1407, 1365, 1305, 218, 1156, 1088, 1030, 1013, 858, 821, 750, 717, 697, 594, 556, 533, 478, 420.



5-(4-fluorophenyl)-1-phfenyl-1-(p-tolyl)pentan-3-one (34) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 7 CV, 0-5% 11 CV, 5% 16 CV) to produce a slightly yellow tinted solid (126 mg, 73% yield).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 7.10 – 7.05 (m, 4H), 7.02 – 6.96 (m, 2H), 6.93 – 6.85 (m, 2H), 4.54 (t, J = 7.6 Hz, 1H), 3.11 (d, J = 7.6 Hz, 2H), 2.75 (t, J = 7.4 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 2.29 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 208.11, 161.45 (d, J = 243.6 Hz), 144.13, 140.87, 136.71 (d, J = 3.0 Hz), 136.15, 129.80 (d, J = 7.8 Hz), 129.42, 128.71, 127.76, 127.67, 126.54, 115.28 (d, J = 21.2 Hz), 49.28, 45.84, 45.20, 28.67, 21.11.
^{19}F NMR (376 MHz, $CDCl_3$): δ -117.31 – -117.51 (m).
HRMS: (ESI-TOF) calculated for $C_{24}H_{23}FNaO^+$ ([M+Na]$^+$): 369.1625, found: 369.1631.
FTIR (ATR cm^{-1}): 1701, 1598, 1508, 1492, 1452, 1417, 1371, 1319, 1258, 1218, 1194, 1157, 1109, 1078, 1015, 855, 825, 786, 772, 752, 733, 701, 608, 565, 544, 529, 516, 483, 450, 420.

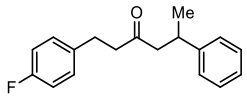


1-(4-fluorophenyl)-5-phenylnonan-3-one (35) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-5% 12 CV, 5% 5 CV) to produce a white oil (76 mg, 48% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 2H), 7.24 – 7.17 (m, 1H), 7.16 – 7.10 (m, 2H), 7.01 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.91 (t, *J* = 8.7 Hz, 2H), 3.10 (dt, *J* = 14.7, 7.1 Hz, 1H), 2.80 – 2.55 (m, 5H), 2.47 (ddd, *J* = 17.4, 8.4, 6.7 Hz, 1H), 1.62 – 1.48 (m, 2H), 1.35 – 1.00 (m, 4H), 0.81 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 209.10, 161.42 (d, J = 243.7 Hz), 144.65, 136.80 (d, J = 3.3 Hz), 129.79 (d, J = 7.8 Hz), 128.60, 127.60, 126.46, 115.26 (d, J = 21.1 Hz), 50.47, 45.24 (d, J = 1.1 Hz), 41.50, 36.26, 29.70, 28.72, 22.72, 14.09.
^{19}F NMR (376 MHz, $CDCl_3$): δ-118.33 (tt, J = 9.0, 4.6 Hz).
HRMS: (ESI-TOF) calculated for $C_{21}H_{25}FNaO^+$ ([M+Na]$^+$): 335.1782, found: 335.1786.
FTIR (ATR cm^{-1}): 2954, 2926, 2856, 1711, 1601, 1508, 1494, 1452, 1406, 1367, 1219, 1157, 1095, 1073, 823, 757, 727, 699, 533, 479, 420.

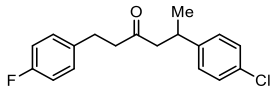


4-(4-fluorophenyl)-1-(7-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)butan-2-one (36) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-5% 10 CV, 5% 18 CV, 8% 2 CV) to produce a yellow tinted white solid (110 mg, 66% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (dd, *J* = 8.3, 5.5 Hz, 2H), 6.96 (td, *J* = 8.5, 1.8 Hz, 3H), 6.68 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.60 – 6.57 (m, 1H), 3.74 (s, 3H), 3.38 (dq, *J* = 10.5, 5.6 Hz, 1H), 2.89

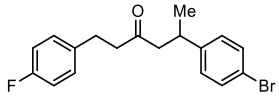
(t, *J* = 7.4 Hz, 2H), 2.78 – 2.60 (m, 6H), 1.87 – 1.79 (m, 1H), 1.75 – 1.68 (m, 2H), 1.56 – 1.46 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 209.16, 161.52 (d, *J* = 243.9 Hz), 157.76, 140.97, 136.74 (d, *J* = 3.3 Hz), 130.25, 129.90 (d, *J* = 7.8 Hz), 129.35, 115.38 (d, *J* = 21.1 Hz), 113.22, 112.21, 55.39, 50.89, 45.21, 33.52, 29.09, 28.81, 28.43, 19.91.
^{19}F NMR (376 MHz, $CDCl_3$): δ -117.23 (tt, *J* = 9.0, 4.9 Hz).
HRMS: (ESI-TOF) calculated for $C_{21}H_{23}FNaO_2^+$ ([M+Na]$^+$): 349.1574, found: 349.1573.
FTIR (ATR cm^{-1}): 2927, 1709, 1607, 1507, 1463, 1450, 1359, 1278, 1247, 1217, 1156, 1125, 1096, 1038, 1015, 809, 701, 533, 477.



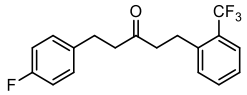
1-(4-fluorophenyl)-5-phenylhexan-3-one (37) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-10% 10 CV, 10% 12 CV) to produce a yellow white solid (97 mg, 71% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, J = 7.4 Hz, 2H), 7.24 – 7.17 (m, 3H), 7.06 (dd, J = 8.3, 5.5 Hz, 2H), 6.94 (t, J = 8.5 Hz, 2H), 3.32 (sx, J = 7.1 Hz, 1H), 2.85 – 2.70 (m, 3H), 2.69 – 2.51 (m, 3H), 1.26 (d, J = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 208.83, 161.42 (d, *J* = 243.7 Hz), 146.15, 136.76 (d, *J* = 3.2 Hz), 129.79 (d, *J* = 7.8 Hz), 128.66, 126.87, 126.45, 115.27 (d, *J* = 21.1 Hz), 51.48, 45.11 (d, *J* = 1.1 Hz), 35.62, 28.77, 22.09.
^{19}F NMR (376 MHz, $CDCl_3$): δ -117.33 – -117.46 (m).
HRMS: (ESI-TOF) calculated for $C_{18}H_{20}FO^+$ ([M+H]$^+$): 271.1493, found: 271.1491.
FTIR (ATR cm^{-1}): 1601, 1508, 1493, 1451, 1407, 1365, 1218, 1157, 1113, 1095, 1074, 1015, 822, 760, 698, 532, 478, 422.



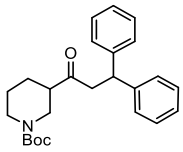
5-(4-chlorophenyl)-1-(4-fluorophenyl)hexan-3-one (38) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-5% 12 CV, 5-10% 2 CV, 10% 5 CV) to produce a white solid (Run 1= 93.9 mg, 61% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.25 (m, 2H), 7.16 – 7.11 (m, 2H), 7.10 – 7.04 (m, 2H), 7.00 – 6.90 (m, 2H), 3.32 (h, *J* = 7.1 Hz, 1H), 2.82 (t, *J* = 7.8 Hz, 2H), 2.74 – 2.52 (m, 4H), 1.24 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 208.45, 161.47 (d, *J* = 243.8 Hz), 144.64, 136.66 (d, *J* = 3.3 Hz), 132.06, 129.81 (d, *J* = 7.9 Hz), 128.76, 128.30, 115.32 (d, *J* = 21.2 Hz), 51.33, 45.15, 34.94, 28.76, 22.08.
^{19}F NMR (376 MHz, $CDCl_3$): δ -117.17 – -117.30 (m).
HRMS: (ESI-TOF) calculated for $C_{18}H_{18}ClFNaO^+$ ([M+Na]$^+$): 327.0923, found: 327.0926.
FTIR (ATR cm^{-1}): 2925, 1712, 1600, 1508, 1488, 1451, 1407, 1365, 1305, 1218, 1156, 1088, 1030, 1013, 858, 821, 750, 717, 697, 594, 556, 533, 478, 420.



5-(4-bromophenyl)-1-(4-fluorophenyl)hexan-3-one (39) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 8 CV, 0-5% 10 CV, 5% 5 CV, 10% 7 CV) to produce a white solid (Run 1= 97.9 mg, 56% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.35 (m, 2H), 7.05 (dt, *J* = 8.4, 2.7 Hz, 4H), 6.93 (t, *J* = 8.7 Hz, 2H), 3.27 (h, *J* = 7.0 Hz, 1H), 2.79 (t, *J* = 7.8 Hz, 2H), 2.70 – 2.50 (m, 4H), 1.21 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 208.42, 161.48 (d, *J* = 243.9 Hz), 145.17, 136.66 (d, *J* = 3.2 Hz), 131.72, 129.82 (d, *J* = 7.8 Hz), 128.72, 120.12, 115.34 (d, *J* = 21.1 Hz), 51.27, 45.16 (d, *J* = 1.1 Hz), 35.01, 28.78, 22.03.
^{19}F NMR (376 MHz, $CDCl_3$): δ -117.23 (tt, J = 8.4, 5.3 Hz).
HRMS: (ESI-TOF) calculated for $C_{18}H_{18}BrFNaO^+$ ([M+Na]$^+$): 371.0417, found: 371.0420.
FTIR (ATR cm^{-1}): 3027, 2925, 1712, 1600, 1508, 1488, 1451, 1407, 1365, 1305, 1218, 1156, 1088, 1030, 1013, 858, 821, 750, 717, 697, 594, 556, 533, 478, 420.



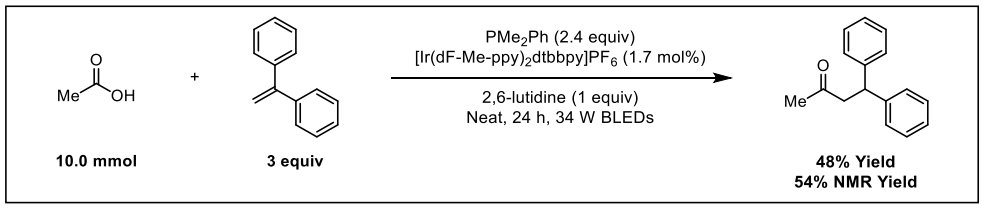
1-(4-fluorophenyl)-5-(2-(trifluoromethyl)phenyl)pentan-3-one (40) was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 4 CV, 0-10% 10 CV, 10% 10 CV) to produce a yellow white solid (Run 1= 87 mg, 53% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.13 – 7.06 (m, 2H), 6.93 (t, *J* = 8.6 Hz, 2H), 3.03 (t, *J* = 7.8 Hz, 2H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.70 – 2.64 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 208.41, 161.52 (d, J = 243.9 Hz), 139.91 (d, J = 1.9 Hz), 136.65 (d, J = 3.2 Hz), 132.07, 131.30, 129.86 (d, J = 7.8 Hz), 128.58 (q, J = 29.8 Hz), 126.46, 126.23 (q, J = 5.7 Hz), 124.68 (q, J = 273.7 Hz), 115.38 (d, J = 21.1 Hz), 44.76, 44.44, 29.05, 26.68 (d, J = 1.9 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ -59.76 (s, 3F), -117.22 (tt, J = 9.2, 5.2 Hz, 1F).
HRMS: (ESI-TOF) calculated for $C_{18}H_{17}F_4O^+$ ([M+H]$^+$): 325.1210, found: 325.1213.
FTIR (ATR cm^{-1}): 2931, 1714, 1607, 1583, 1509, 1453, 1415, 1372, 1311, 1220, 1158, 1113, 1059, 1037, 1016, 979, 956, 909, 823, 767, 731, 651, 598, 533, 478, 425



***tert*-butyl 3-(3,3-diphenylpropanoyl)piperidine-1-carboxylate (41)** was prepared according to the general procedure A. The title compound was isolated using automated column chromatography eluting with Ether:Hexanes (0% 6 CV, 0-20% 12 CV, 20% 8 CV) to produce a white solid (140 mg, 71% yield).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.24 (m, 5H), 7.24 – 7.20 (m, 3H), 7.17 (t, J = 7.3 Hz, 2H), 4.61 (t, J = 7.4 Hz, 1H), 3.90 (bs, 2H), 3.31 – 3.17 (m, 2H), 2.79 (bs, 1H), 2.70 (bs, 1H), 2.41 (bs, 1H), 1.81 (bs, 1H), 1.63 (bs, 1H), 1.44 (s, 9H), 1.42 – 1.34 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 209.45, 154.80, 143.98, 128.72, 128.70, 127.87, 127.81, 126.58, 79.87, 49.15, 47.56, 45.68, 28.56, 26.67, 24.51.
HRMS: (ESI-TOF) calculated for $C_{25}H_{31}NNaO_3^+$ ([M+Na]$^+$): 416.2196, found: 416.2192.

FTIR (ATR cm^{-1}): 2932, 2861,1697, 1653,1495, 1473, 1463, 1451, 1417, 1364, 1348, 1301, 1290, 1266, 1237, 1106, 1090, 1079, 1060, 1043, 1033, 1015, 996, 960, 940, 918, 889, 866, 854, 791, 762, 742.

V. Scale Up

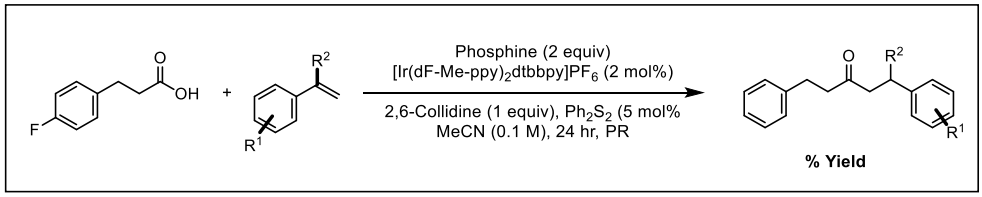


An oven-dried 20 mL reaction vial (Fisher® glass vials, 03-337-15) was charged with Iridium (172 mg, 0.017 mmol, 0.017 equiv) and equipped with a PTFE-coated stir bar. The vial was Teflon taped on the threads, and then taken into a N_2-filled glovebox. To the vial was added diphenyl ethylene (5.30 mL, 30 mmol, 3.0 equiv), 2,6-lutidine (1.16 mL, 10 mmol, 1.0 equiv), and acetic acid (571 μL, 10.0 mmol, 1.0 equiv). Finally, phosphine (3.41 mL, 24 mmol, 2.4 equiv) was added. The vial was then capped and sealed with electrical tape. The vial was irradiated for 24 h in a Photoreactor (800 rpm, 1500 fan speed, 100% light intensity). An aliquot of the crude reaction mixture was analzed by ^{1}H-NMR with 1-fluoronaphthalene (647 μL, 5.0 mmol, 0.5 equiv) as an external standard. Comparison of the crude reaction mixture to clean product resulted in a 54% crude NMR Yield. The title compound, 4,4-diphenylbutan-2-one (**19**) was isolated using automated column chromatography eluting with Ether:Hexanes (0% 15 CV, 0-8% 12 CV, 15% 3 CV) to produce a yellow oil that solidified into a white solid inside the freezer (1.09 g, 48% yield).

VI. Mechanistic Studies

In the course of optimization, differential reactivity was observed between electron neutral and electron deficient alkenes in the presence of different phosphines. To probe the origin of this reactivity, emission quenching experiments were undertaken to rule out the possibility of competitive electron transfer to the alkenes.

Table S10. Reactivity observed with diphenyl ethylene, alpha methyl styrene, and 1-(trifluoromethyl)-2-vinylbenzene in the coupling of 3-(4-fluorophenyl)propanoic acid with triphenyl phosphine, ethyl diphenyl phosphinite, and dimethyl phenyl phosphine



Entry	Alkene	% Yield ($POEtPh_2$)	% Yield (PPh_3)	% Yield (PMe_2Ph)
A		26	6	81
B		25	2	74
C		34	10	54

[a]Yield was determined by ^1H NMR spectroscopy using 1-fluoronaphthalene as an external standard.

A. Emission Quenching Experiments

Absorption and Emission experiments were conducted in line with our previous publication on the arylation of ethereal C–H bonds.[7] An excitation wavelength of 415 nm and an emission wavelength of 515 nm were used for monitoring quenching of the iridium photocatalyst. All reagents were prepared in stock solutions inside a nitrogen filled glove box. Reagents were diluted in acetonitrile (3 mL) and sealed in a screw-top 1.0 cm quartz cuvette. A blank composed of acetonitrile was used in absorbance measurements. Samples for quenching experiment were dispensed from a stock solution of $Ir[dF(Me)ppy]_2(dtbbpy)PF_6$ (1.314 mM in MeCN, amount dispensed: 456 μL, 0.6 μmol, $2.0x10^{-4}$ M after dilution) followed by addition of quenchers that were also prepared from stock solutions in MeCN. 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 and 5 nm were used, respectively.

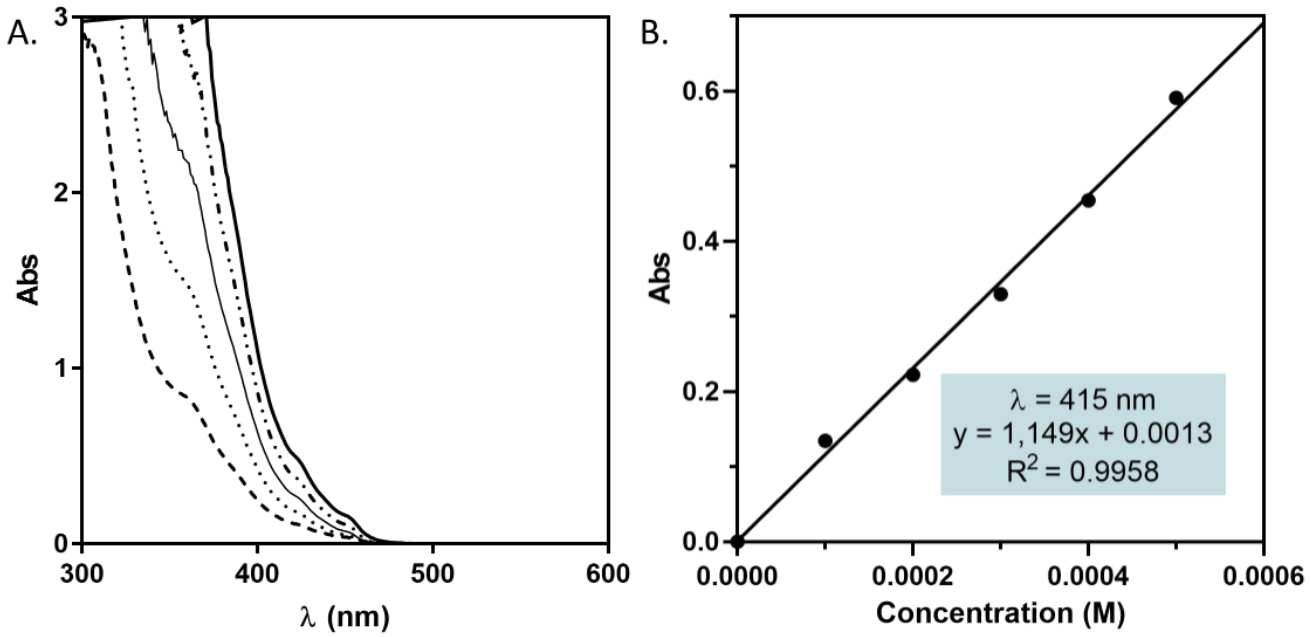
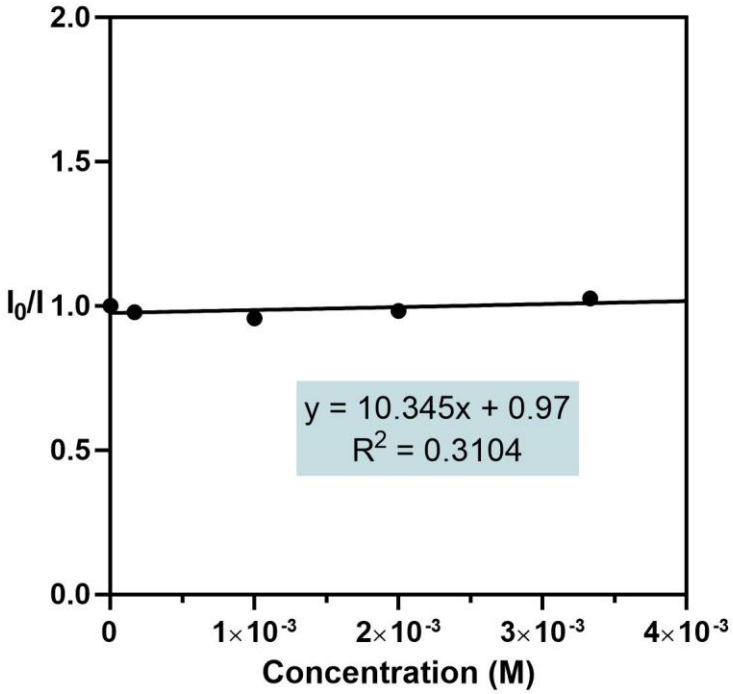
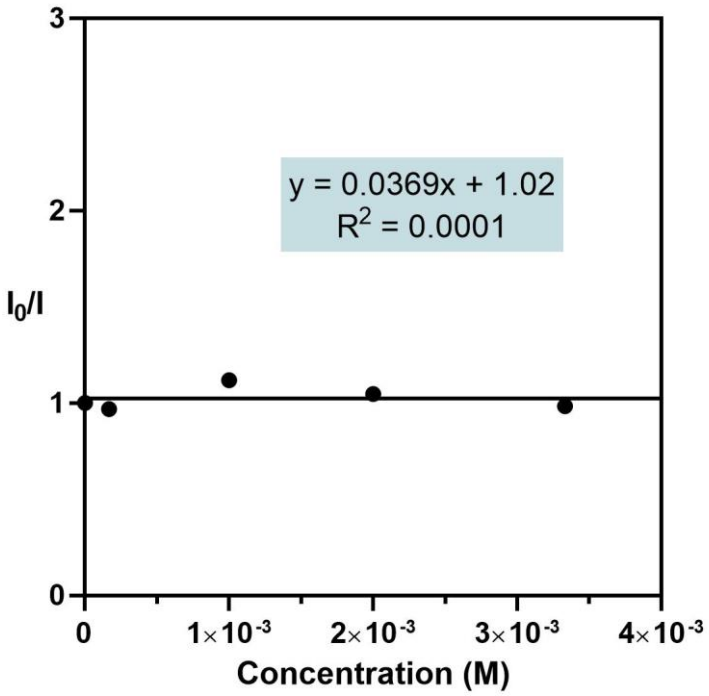


Figure S11. A. The electronic absorption spectra of $Ir[dF(Me)ppy]_2(dtbbpy)PF_6$ at concentrations ranging from $1.0x10^{-4}$ to $5.0x10^{-4}$ M in MeCN. On the right is the calibration curve for $Ir[dF(Me)ppy]_2(dtbbpy)PF_6$ at a wavelength of 415 nm ($\varepsilon = 1.149x10^3$ M^{-1} cm^{-1}).



Acid and Base x10^4 M	Intensity
0	699.59
1.6	715.46
10	730.43
20	711.63
33	681.63

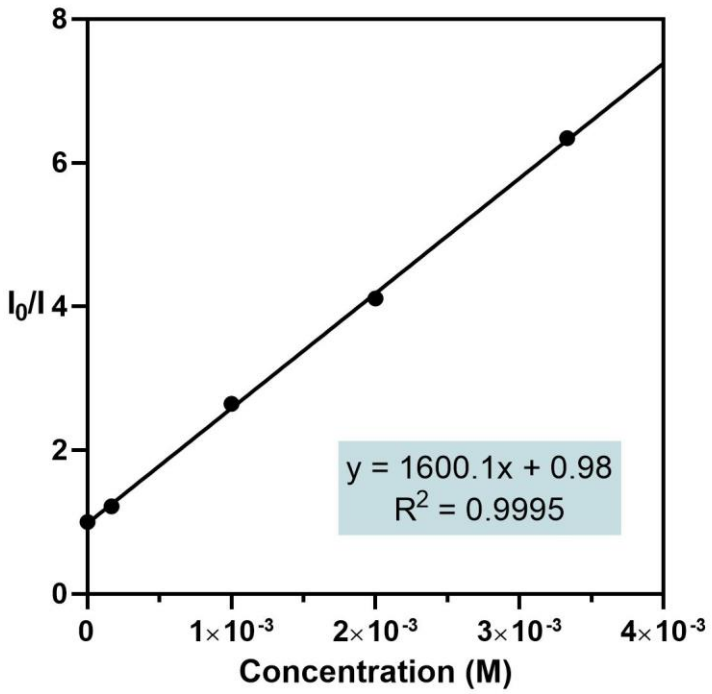
Figure S12. Characteristic plot of Ir[dF(Me)ppy]$_2$(dtbbpy)PF_6 (2.0×10^{-4} M) emission quenching by 3-(4-fluorophenyl)propanoic acid and 2,6-lutidine. Base and acid were used in a one to one stoichiometry.



Diphenyl Disulfide x10^4 M	Intensity
0	579.84
1.6	598.76
10	518.24
20	553.33
33	588.77

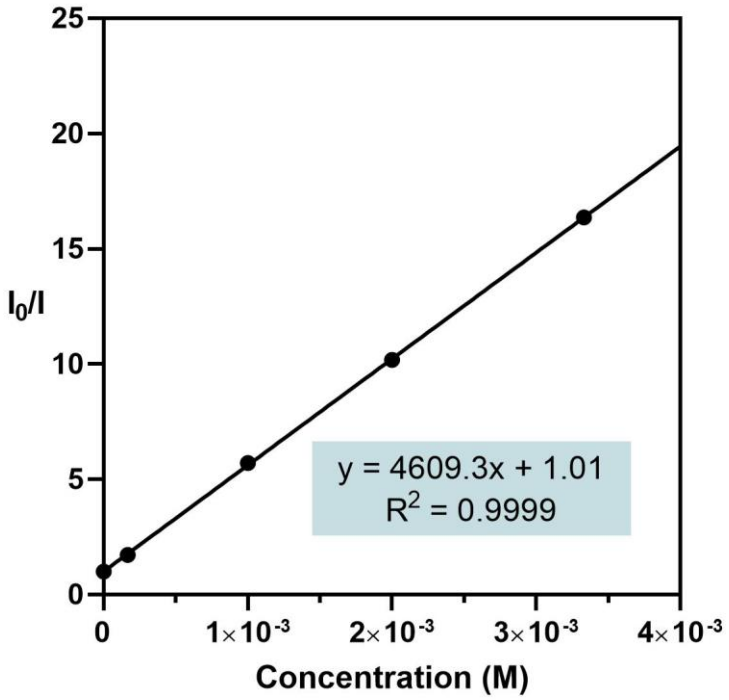
Figure S13. Characteristic plot of Ir[dF(Me)ppy]$_2$(dtbbpy)PF_6 (2.0x10^{-4} M) emission quenching by diphenyl disulfide.

Our current rationale for the modest boost in yield with diphenyl disulfide is that it is capable of oxidizing Ir(II) to regenerate the ground-state Ir(III) photocatalyst.[8] This likely increases the concentration of phosphine radical cation present in solution. It is possible that disulfide bond homolysis *via* blue-light irradiation could generate aryl thiyl radicals that are also capable of oxidizing Ir(II).[9]



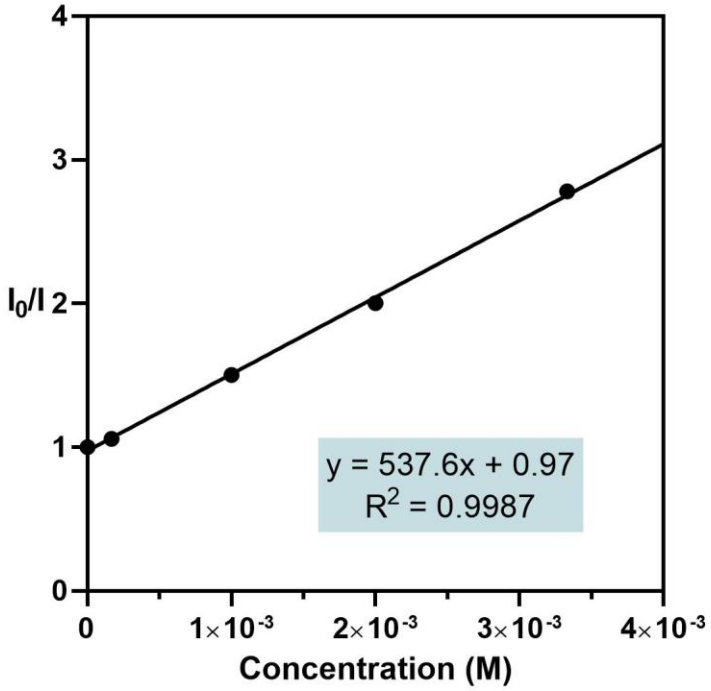
Dimethyl Phenyl Phosphine x10^4 M	Intensity	Intensity
0	567.34	578.92
1.6	470.11	460.31
10	227.22	203.00
20	139.24	136.65
33	87.64	91.27

Figure S14. Characteristic plot of Ir[dF(Me)ppy]$_2$(dtbbpy)PF_6 (2.0×10^{-4} M) emission quenching by dimethyl phenyl phosphine.



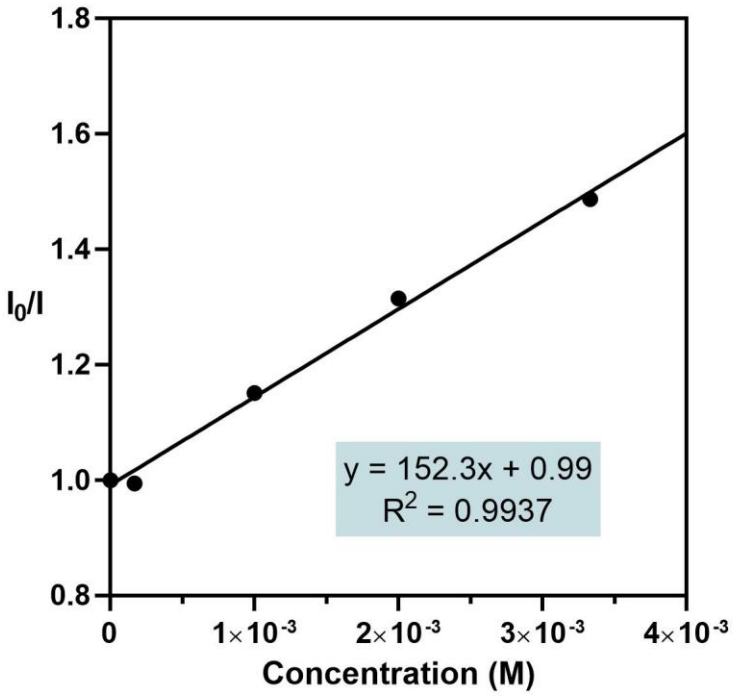
Tris(4-methoxyphenyl) phosphine x10^4 M	Intensity	Intensity
0	559.85	592.30
1.6	341.76	326.78
10	107.98	95.01
20	60.60	53.03
33	39.31	32.03

Figure S15. Characteristic plot of Ir[dF(Me)ppy]$_2$(dtbbpy)PF_6 (2.0x10^{-4} M) emission quenching by tris(4-methoxyphenyl)phosphine.



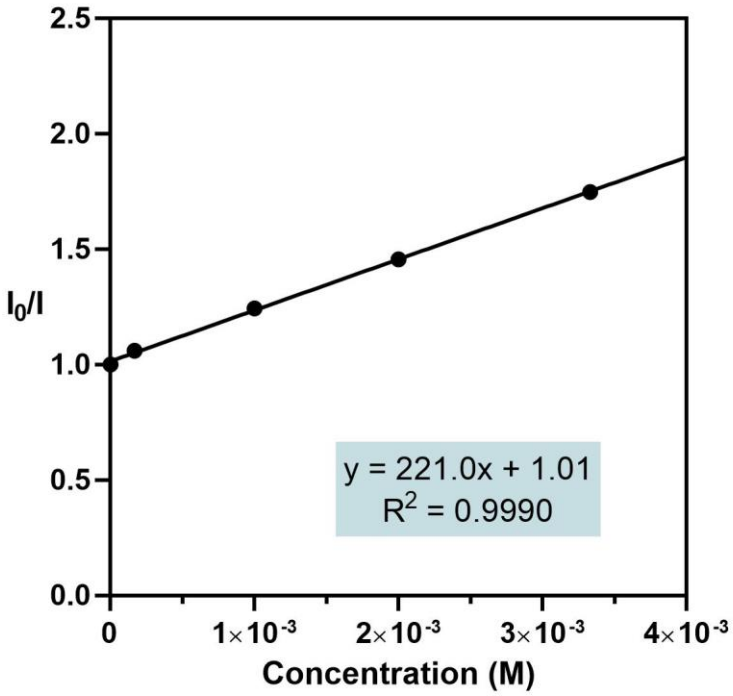
Diphenyl Ethylene x10^4 M	Intensity	Intensity
0	582.32	616.73
1.6	564.06	567.05
10	425.51	376.46
20	312.27	288.12
33	212.61	218.53

Figure S16. Characteristic plot of Ir[dF(Me)ppy]$_2$(dtbbpy)PF_6 (2.0x10^{-4} M) emission quenching by diphenyl ethylene.



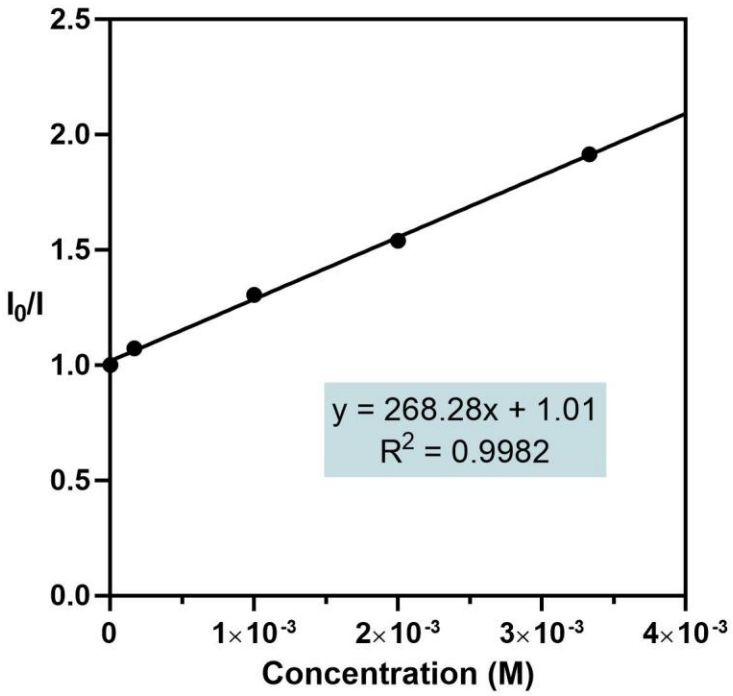
Ethyl Diphenyl Phosphine x10^4 M	Intensity	Intensity
0	600.61	596.31
1.6	595.94	575.22
10	501.65	455.90
20	429.33	428.34
33	358.68	428.34

Figure S17. Characteristic plot of Ir[dF(Me)ppy]$_2$(dtbbpy)PF$_6$ (2.0x10^{-4} M) emission quenching by ethyl diphenyl phosphinite.



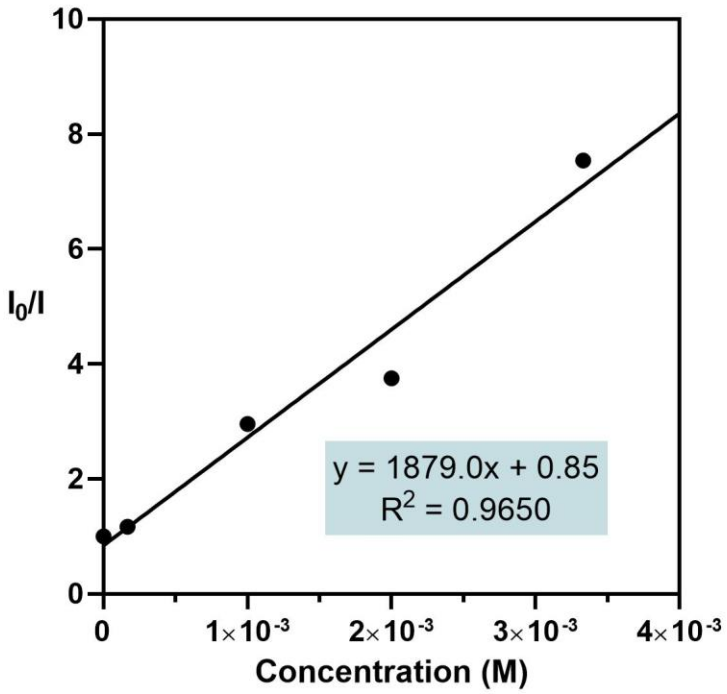
Triphenyl Phosphine x10^4 M	Intensity	Intensity
0	650.75	589.15
1.6	606.73	562.54
10	498.64	498.31
20	422.51	429.43
33	340.01	372.26

Figure S18. Characteristic plot of Ir[dF(Me)ppy]$_2$(dtbbpy)PF_6 (2.0x10^{-4} M) emission quenching by triphenyl phosphine.



1-(trifluoromethyl)-2-vinylbenzene x10^4 M	Intensity
0	650.75
1.6	606.73
10	498.64
20	422.51
33	340.01

Figure S19. Characteristic plot of Ir[dF(Me)ppy]$_2$(dtbbpy)PF_6 (2.0x10^{-4} M) emission quenching by 1-(trifluoromethyl)-2-vinylbenzene.



Reaction Mixture x10^4 M	Intensity
0	587.01
1.6	503.09
10	198.46
20	156.36
33	77.86

Figure S20. Characteristic plot of Ir[dF(Me)ppy]$_2$(dtbbpy)PF_6 (2.0x10^{-4} M) emission quenching by the reaction mixture. Aliquots of the reaction mixture were added relative to phosphine. The mixture contained dimethyl phenyl phosphine (2 equiv), 2,6-lutidine (1.0 equiv), 3-(4-fluoro-phenyl)propanoic acid (1.0 equiv), dipheny disulfide (5 mol%), and diphenyl ethylene (3 equiv).

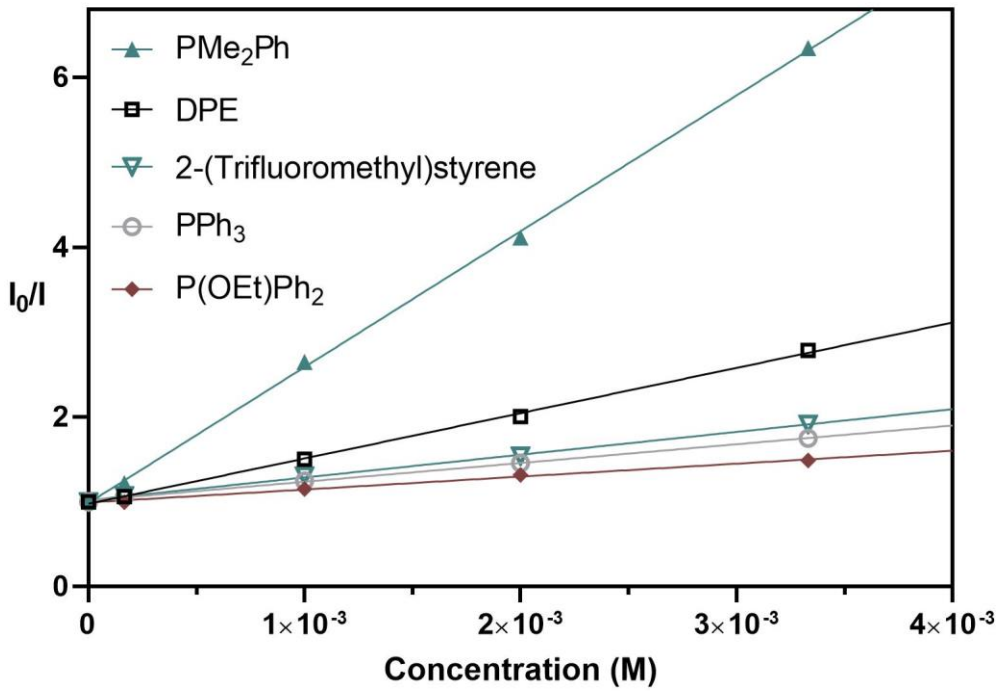


Figure S21. Overlay plot of Ir[dF(Me)ppy]$_2$(dtbbpy)PF$_6$ emission quenching by dimethyl phenyl phosphine, diphenyl ethylene, 1-(trifluoromethyl)-2-vinylbenzene, triphenyl phosphine, and ethyl diphenyl phosphinite.

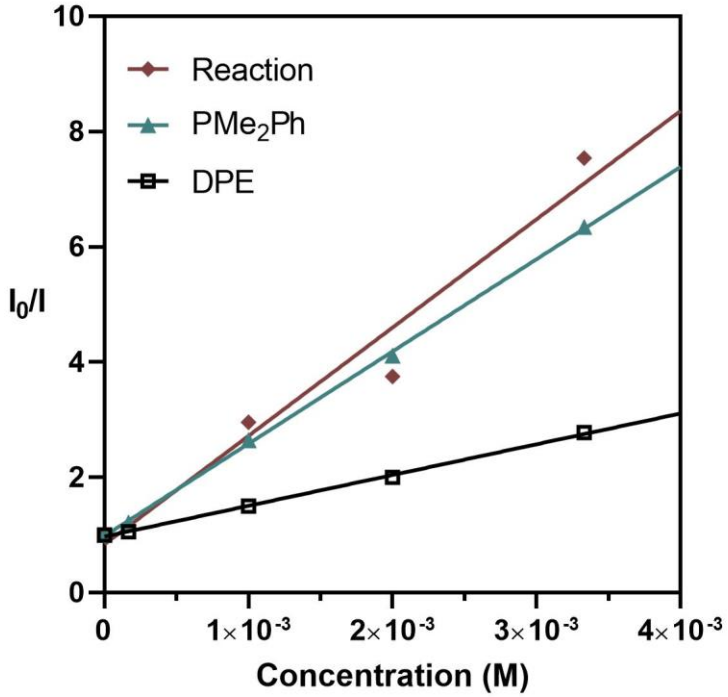


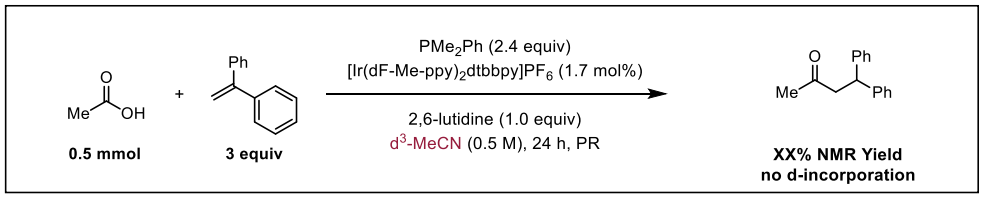
Figure S22. Overlay plot of Ir[dF(Me)ppy]$_2$(dtbbpy)PF$_6$ emission quenching by the reaction, dimethyl phenyl phosphine, and diphenyl ethylene.

Based on the Stern-Volmer quenching constants, it is likely that competitive electron transfer between dimethyl phenyl phosphine and an alkene takes place during the course of the reaction. Moreover, we propose that the higher quenching rate of dimethyl phenyl phosphine to quench

the excited state of iridium relative to diphenyl ethylene is crucial for productive chemistry to occur. Likewise, the closer proximity of the Stern-Volmer quenching constant of ethyl diphenyl phosphinite to 1-(trifluoromethyl)-2-vinylbenzene than diphenyl ethylene leads to an increased efficiency in the coupling with 3-(4-fluorophenyl)propanoic acid with 1-(trifluoromethyl)-2-vinylbenzene (Table S10).

B. Deuterium Studies

General procedure for deuterium experiments. An oven-dried 1-dram reaction vial (VWR® glass vials, 66011-041) was charged with carboxylic acid (0.5 mmol, 1.0 equiv) and equipped with a PTFE-coated stir bar (VWR® Micro stir bars, 2 x 7 mm, 58948-976). The vial was Teflon taped on the threads, and then taken into a N_2-filled glovebox. To the vial was added MeCN (0.5 M), 1,1-diphenyl ethylene (265 μL, 1.5 mmol, 3.0 equiv) and pyridine (40 μL, 0.5 mmol, 1.0 equiv). Pyridine was used instead of 2,6-lutidine to prevent other hydrogen atom transfer reagents from interfering with the reaction. From a stock solution was added $Ir[dF(Me)ppy]_2(dtbbpy)PF_6$ (8.7 mg, 0.01 mmol, 0.017 equiv). Finally, dimethyl phenyl phosphine (171 μL, 1.2 mmol, 2.4 equiv) was added. The vial was then capped and sealed with electrical tape. The vial was irradiated for 24 h in a Photoreactor (800 rpm, 1500 fan speed, 100% light intensity). An aliquot of the crude reaction mixture was analzed by ^{1}H-NMR with 1-fluoronaphthalene (65 μL, 0.5 mmol, 1.0 equiv) as an external standard. Quantitative carbon was used for calculating deuterium incorporation.



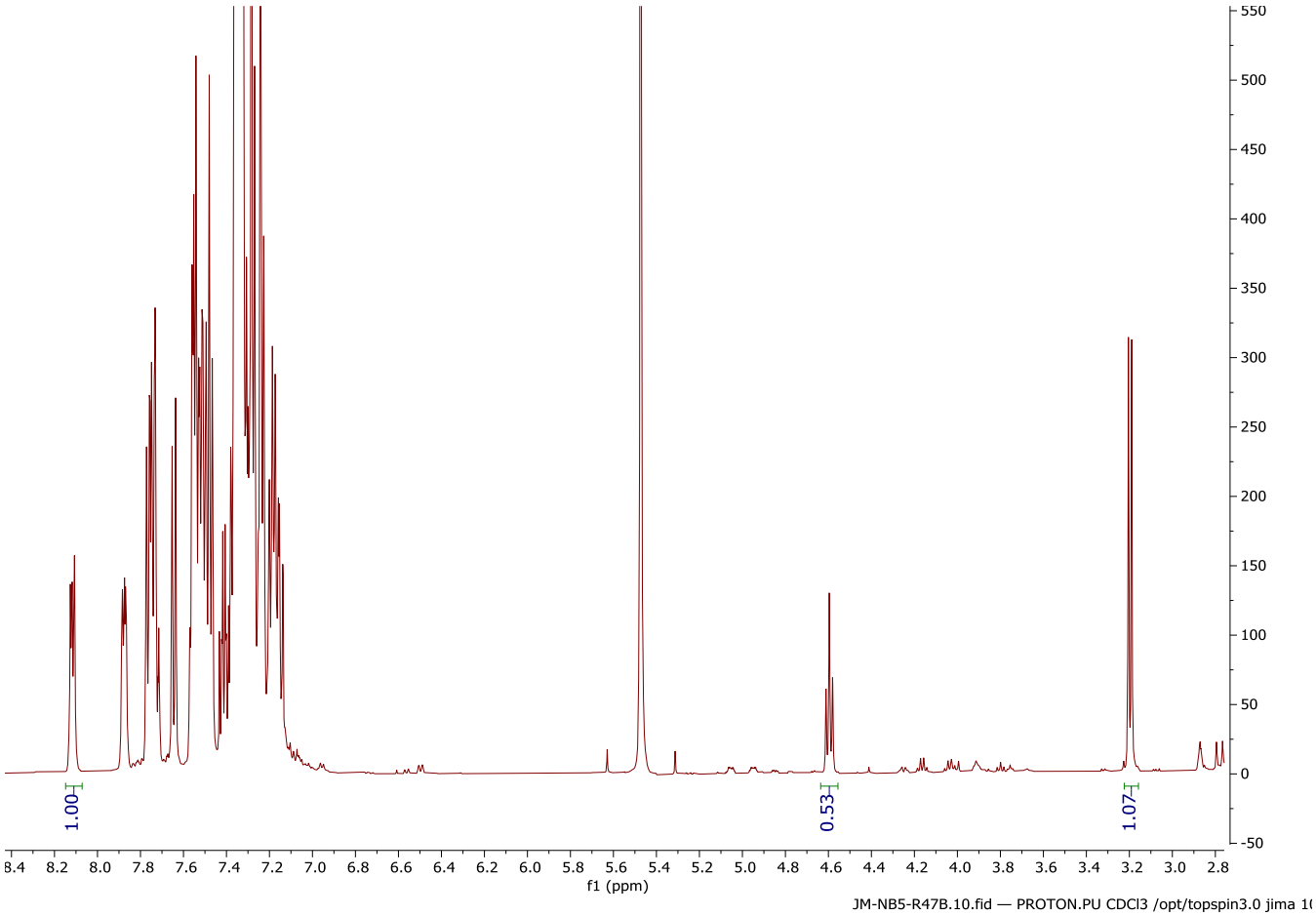


Figure S23. Crude reaction mixture of acetic acid and diphenyl ethylene in d_3-MeCN after 24 hours.

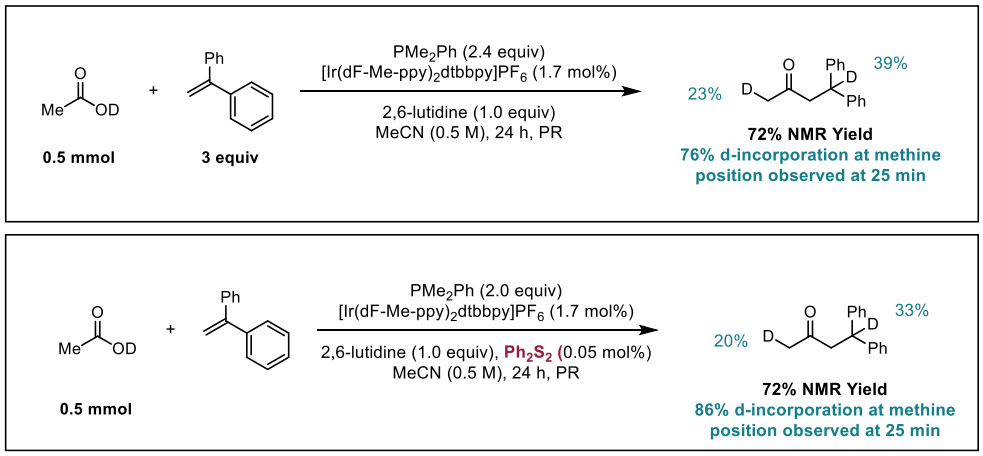


Figure S24. A. The reaction of monodeuteroacetic acid with diphenyl ethylene in MeCN. B. The reaction of monodeuteroacetic acid with diphenyl ethylene in MeCN with diphenyl disulfide.

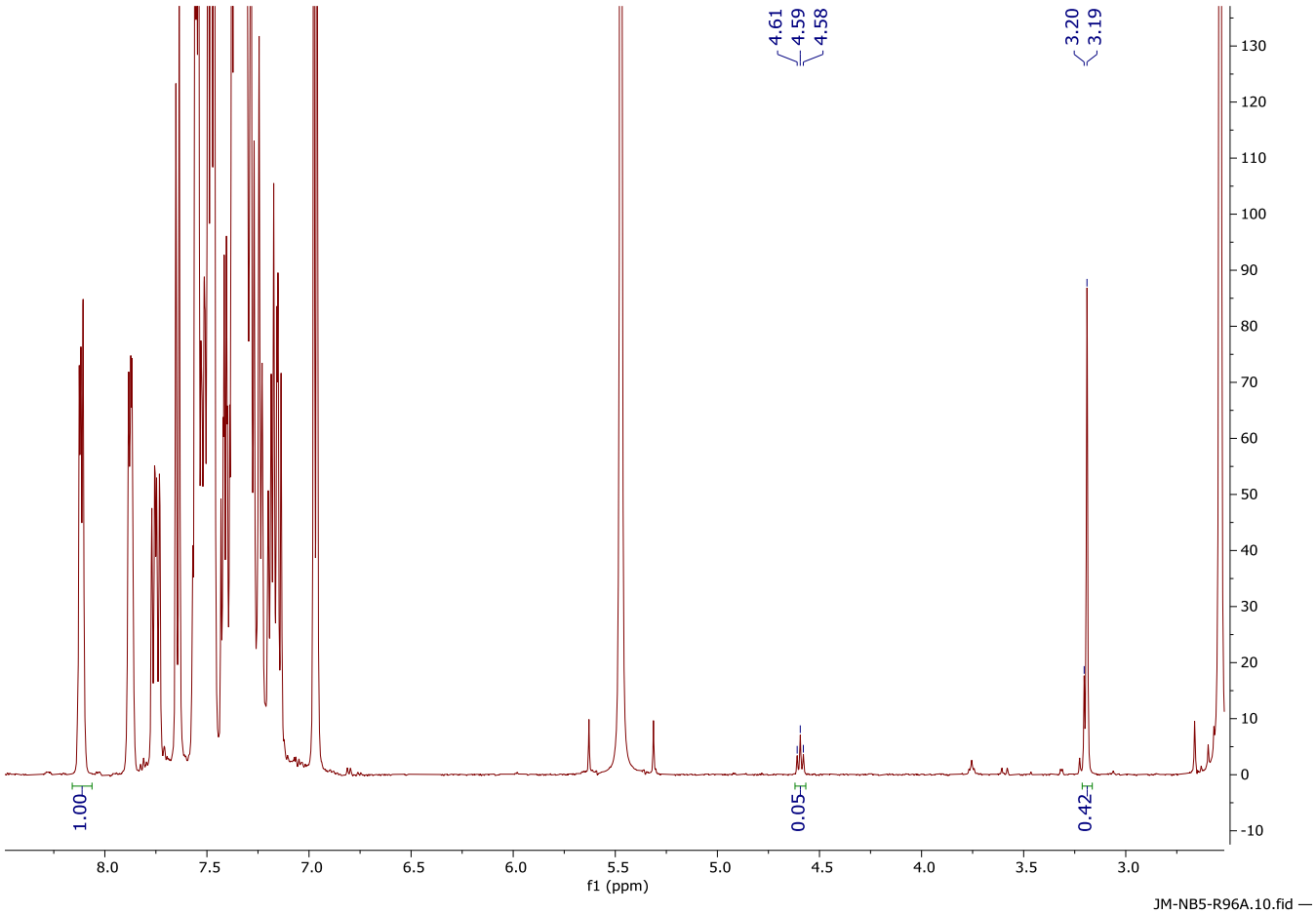


Figure S25. Crude reaction mixture of monodeuteroacetic acid and diphenyl ethylene after 25 minutes when diphenyl disulfide is excluded. The crude ^{1}H-NMR using 1-fluoronaphthalene as standard reveals 76% deuterium incorporation.

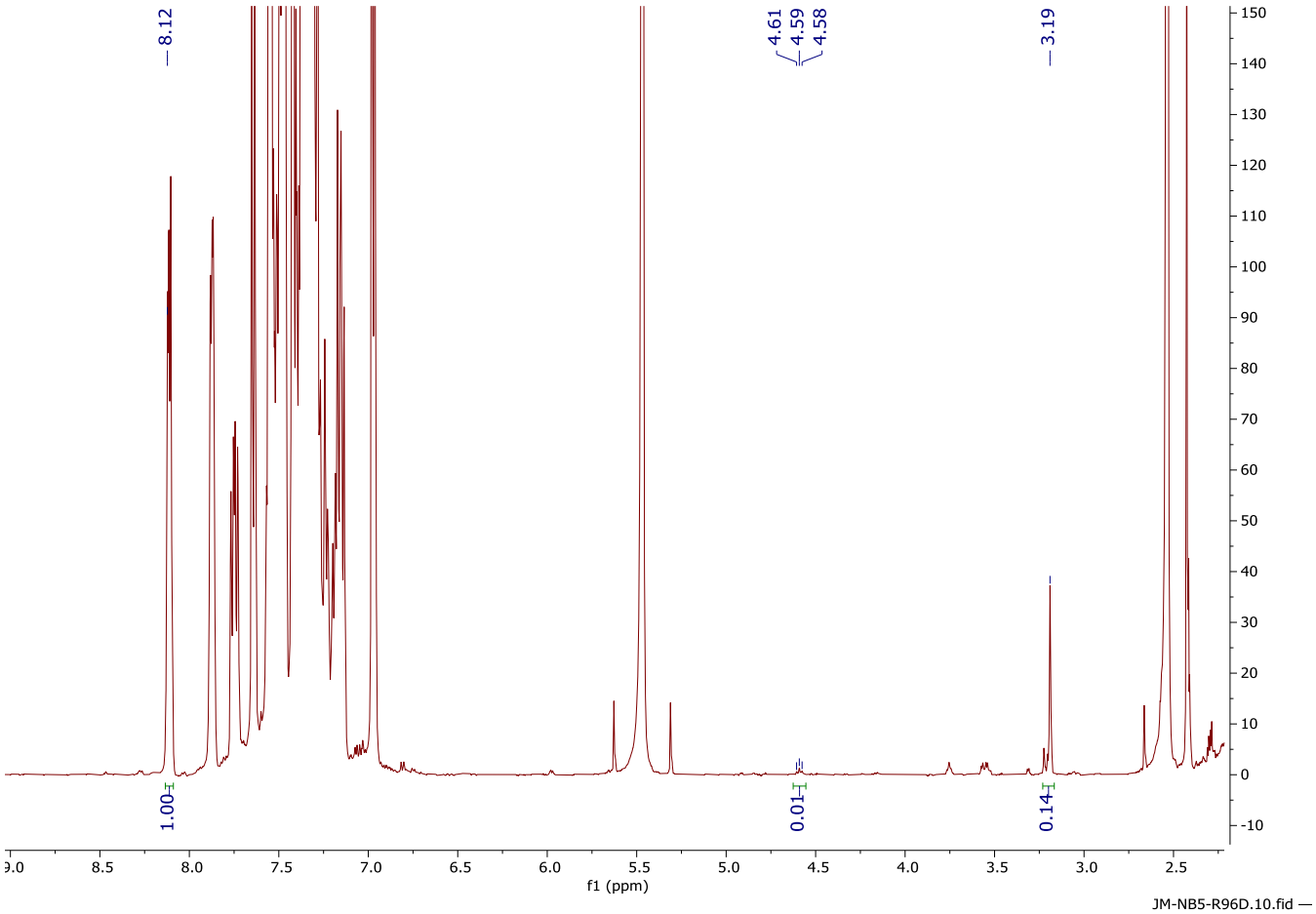
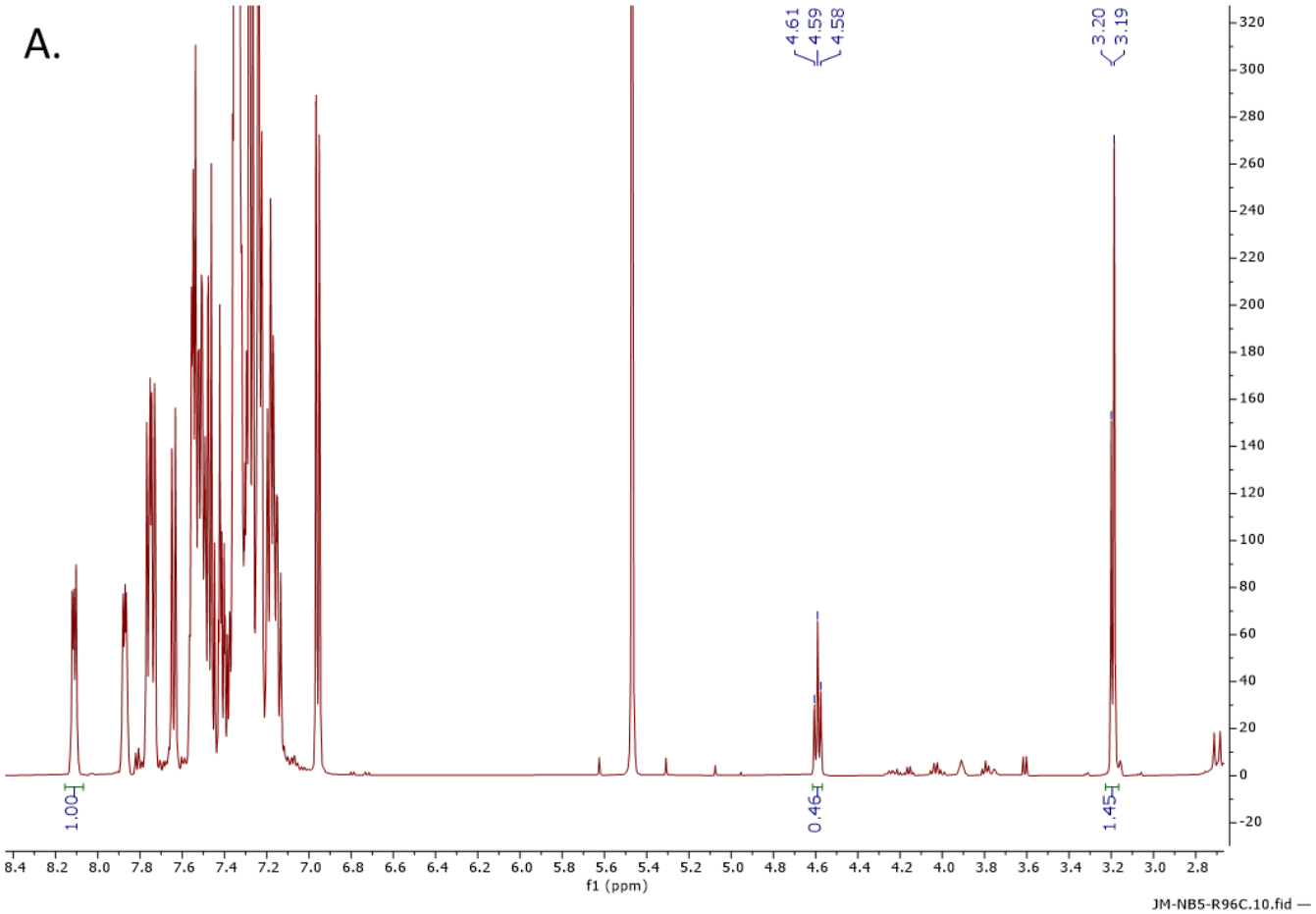
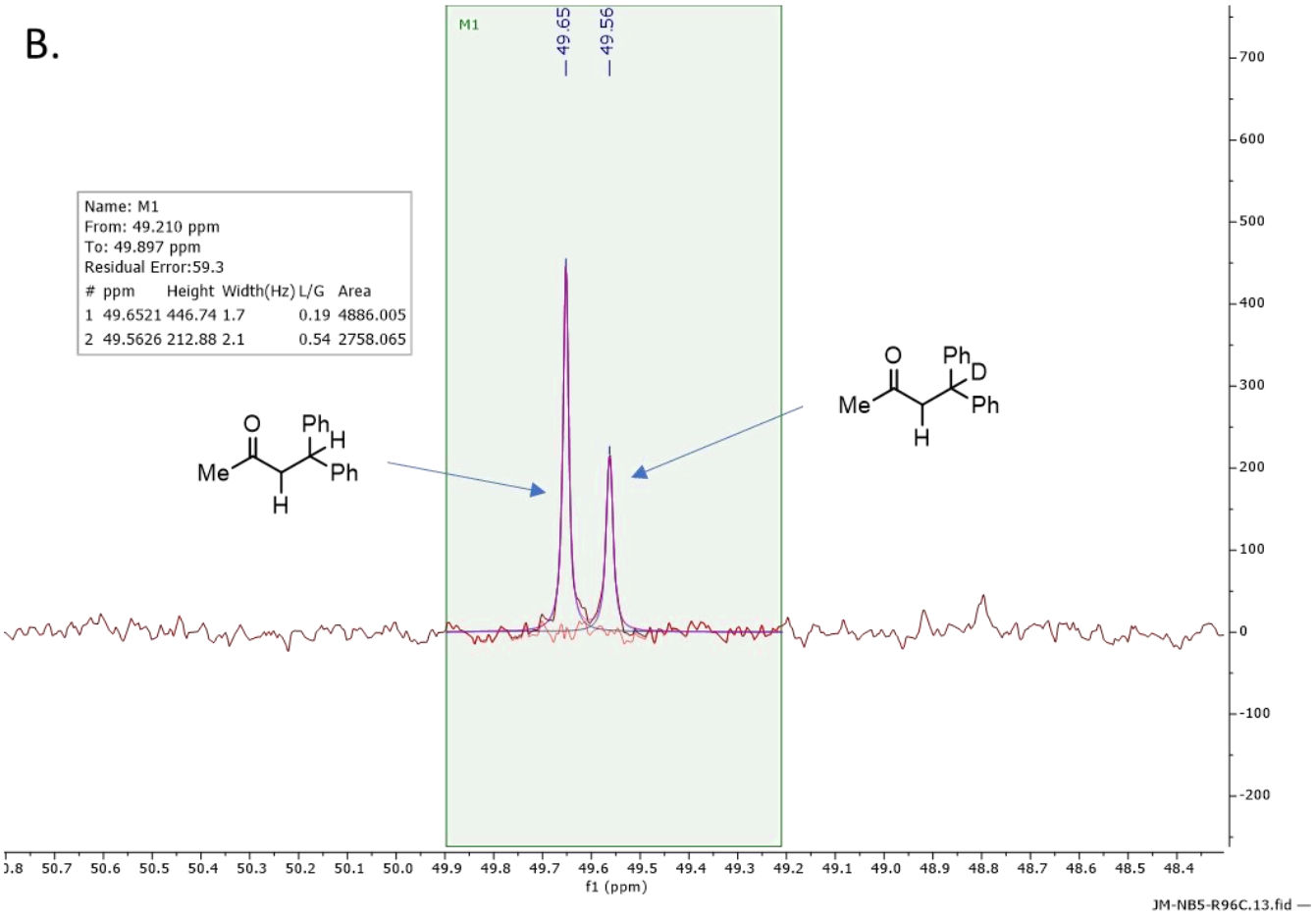
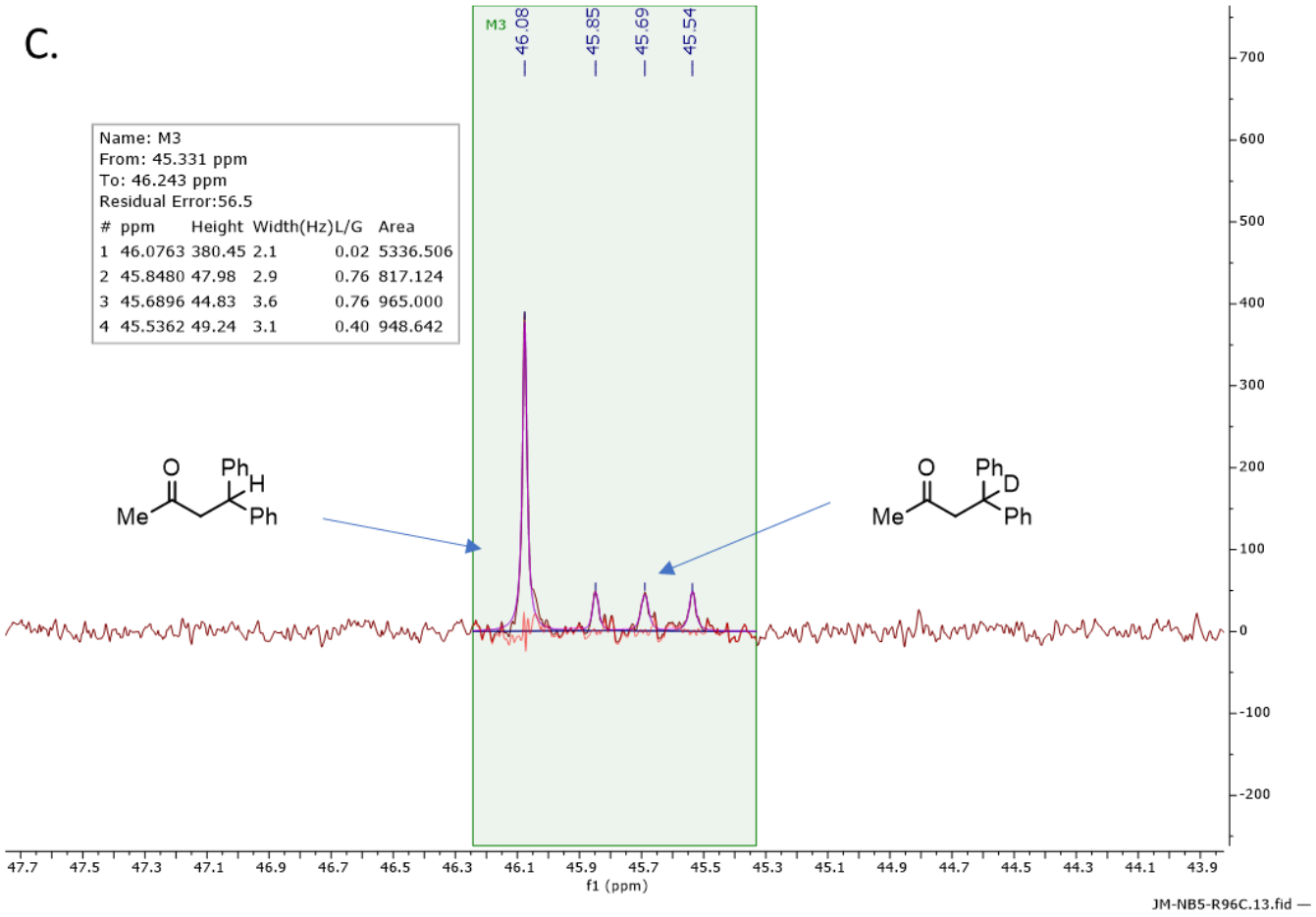


Figure S26. Crude reaction mixture of monodeuteroacetic acid and diphenyl ethylene after 25 minutes when diphenyl disulfide is included. The crude ^{1}H-NMR using 1-fluoronaphthalene as standard reveals 86% deuterium incorporation.


A.
4.61
4.59
4.58
3.20
3.19
1.00
0.46
1.45
f1 (ppm)
JM-NB5-R96C.10.fid


B.
M1
49.65
49.56
Name: M1
From: 49.210 ppm
To: 49.897 ppm
Residual Error:59.3
ppm Height Width(Hz) L/G Area
1 49.6521 446.74 1.7 0.19 4886.005
2 49.5626 212.88 2.1 0.54 2758.065
f1 (ppm)
JM-NB5-R96C.13.fid

C.


M3
46.08
45.85
45.69
45.54
Name: M3
From: 45.331 ppm
To: 46.243 ppm
Residual Error:56.5
ppm Height Width(Hz) L/G Area
1 46.0763 380.45 2.1 0.02 5336.506
2 45.8480 47.98 2.9 0.76 817.124
3 45.6896 44.83 3.6 0.76 965.000
4 45.5362 49.24 3.1 0.40 948.642
O
Ph
H
Me
Ph
O
Ph
D
Me
Ph
700
600
500
400
300
200
100
0
-100
-200
47.7
47.5
47.3
47.1
46.9
46.7
46.5
46.3
46.1
45.9
45.7
45.5
45.3
45.1
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44.3
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43.9
f1 (ppm)
JM-NB5-R96C.13.fid

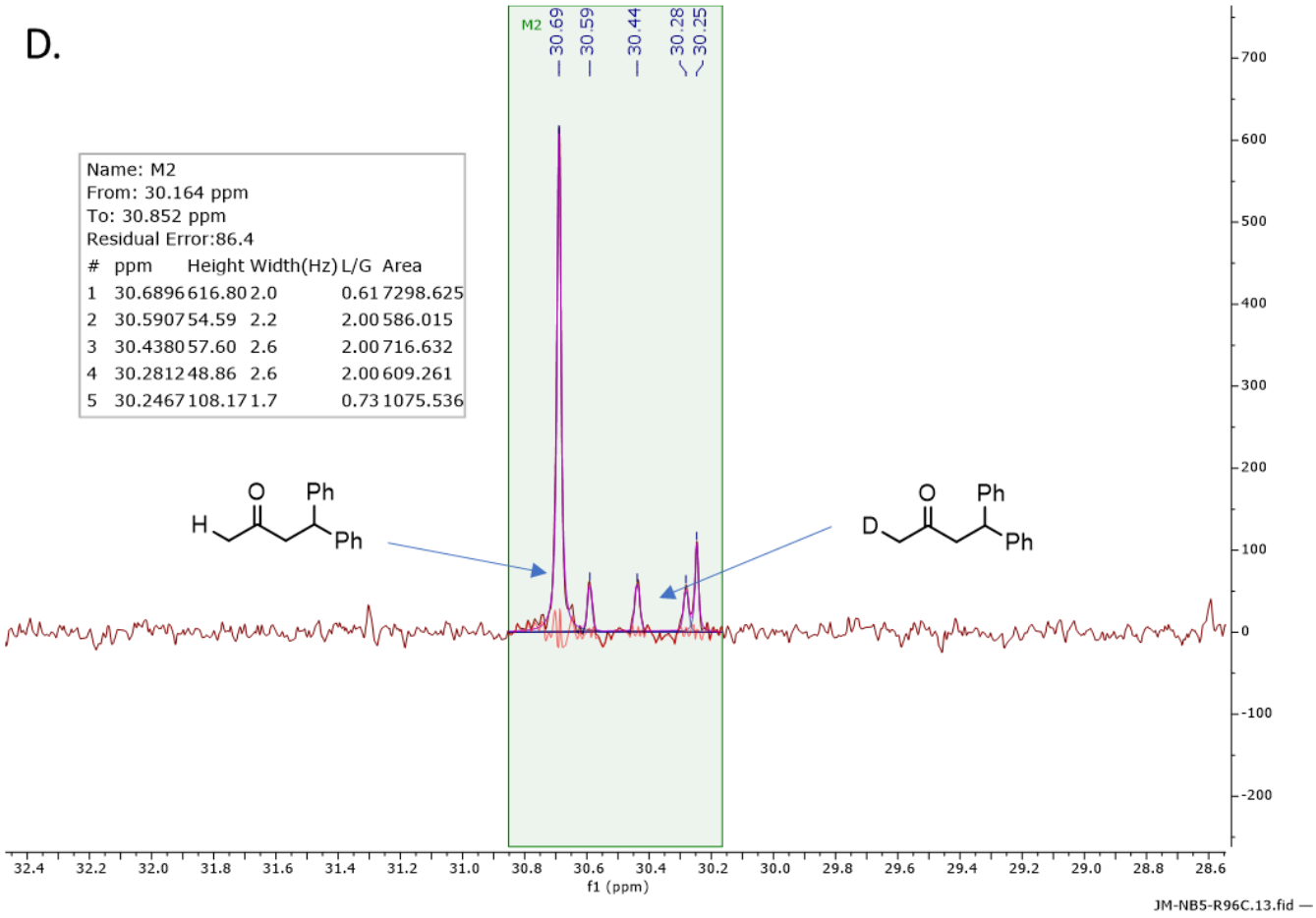
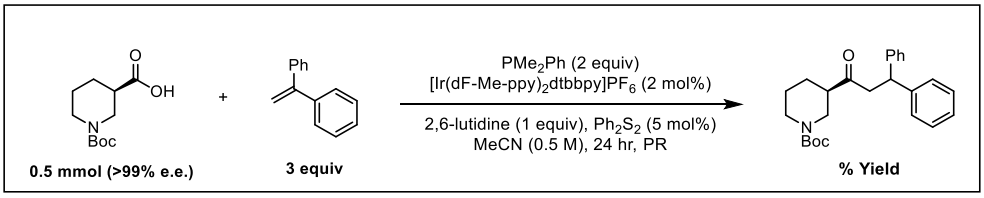


Figure S27. Crude reaction mixture of monodeuteroacetic acid and diphenyl ethylene after 24 hours. Phenyl disulfide was included in this reaction. A. The crude ^{1}H-NMR using 1-fluoronaphthalene as standard. B. The quantitative ^{13}C-NMR of the secondary alpha C–H bond. C. The quantitative ^{13}C-NMR centered about the methine carbon of the product. D. The quantitative ^{13}C-NMR centered about the primary alpha carbon of the carbonyl. All quantitative carbon signals show an isotropic shift associated with deuteration.

In order to further probe the configurational stability of enolizable C–H bonds in the product, an enantioenriched derivative of nipecotic acid was subjected to the reaction conditions (Table S11). An erosion of e.e. was measured in the product during the reaction conditions. Notably, the enantioenriched ketone maintains the same level of e.e. when cyclohexane carboxylic acid is coupled with diphenyl ethylene (Figure S28).



Time (min)	% Yield	% e.e.
300	65	81
1440	80	61

Table S11. Reaction of an enantioenriched derivative of nipecotic acid with diphenyl ethylene.

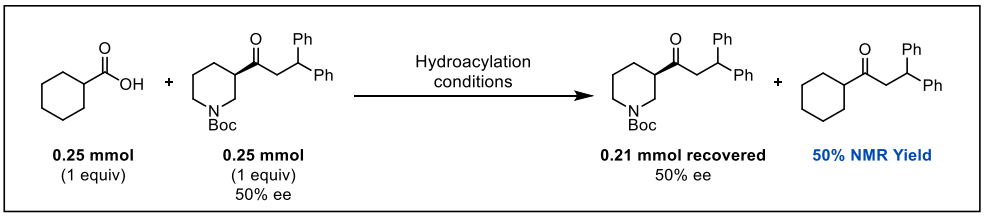
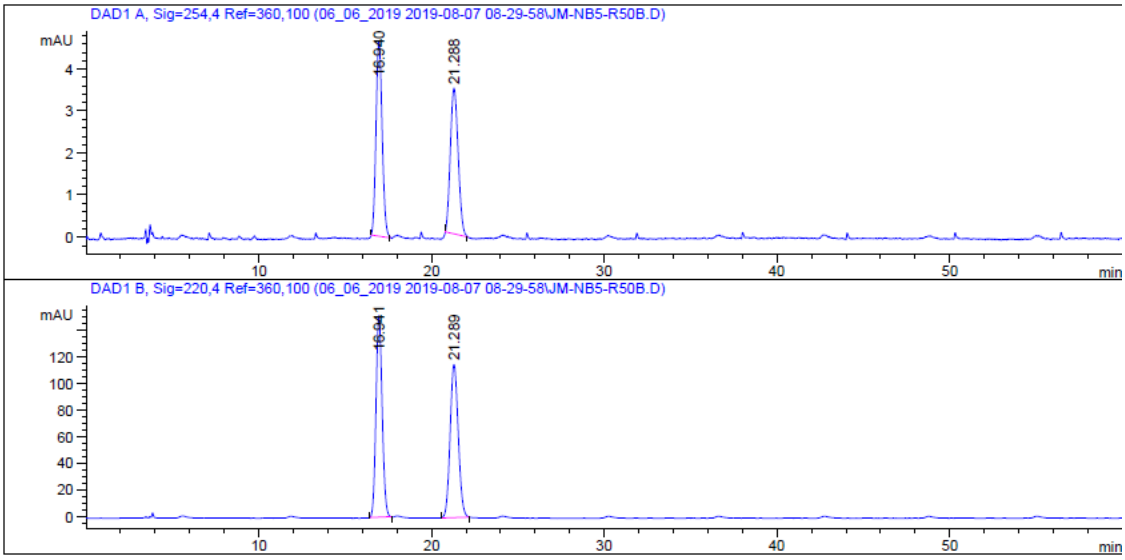


Figure S28. Reaction between cyclohexane carboxylic acid and diphenyl ethylene with the product of nipecotic acid added as an additive.

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================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.940 BB    0.3803  114.87151    4.64775  51.2303
   2  21.288 BB    0.4751  109.35429    3.47574  48.7697

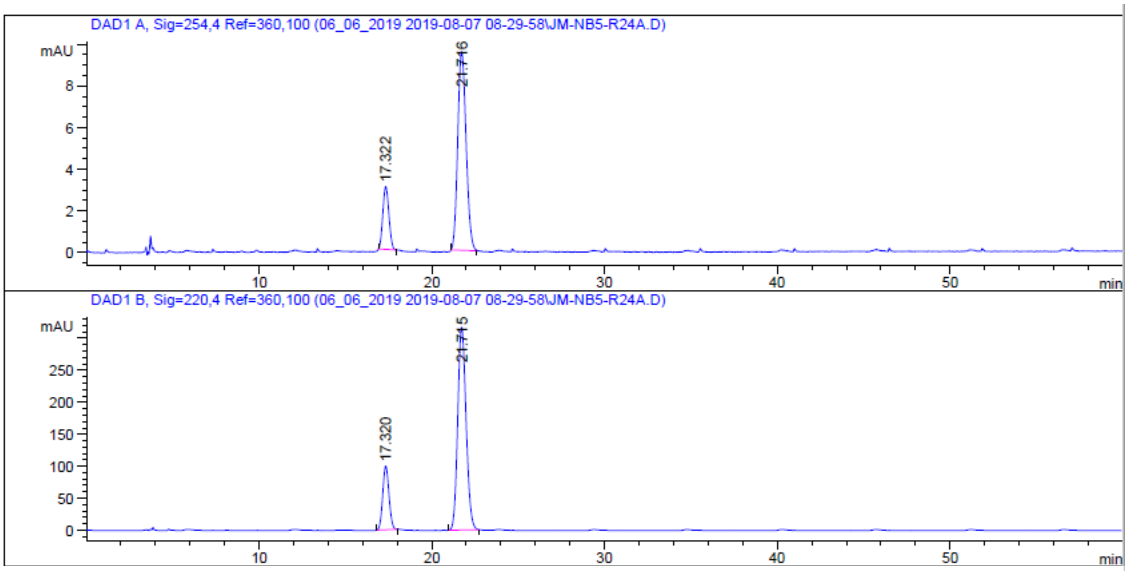
Totals :                   224.22579    8.12349


Signal 2: DAD1 B, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.941 BB    0.3866 3780.63452  151.78204  50.0242
   2  21.289 BB    0.5102 3776.96997  115.29298  49.9758

strument 1 8/8/2019 2:57:30 PM MAB                          Page   3 of 4
```

Figure S29. Racemic standard of product. ChiralPak® IC, 5% IPA in Hexanes, 60 min run, 1 mL/min.

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=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.322 BB    0.3762   74.38911    3.03192  18.7797
   2  21.716 BB    0.5247  321.72604    9.55714  81.2203

Totals :                   396.11516   12.58906



Signal 2: DAD1 B, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.320 BB    0.3948 2521.13037   99.77121  19.1191
   2  21.715 BB    0.5225 1.06653e4   317.04135  80.8809

Instrument 1 8/8/2019 2:58:18 PM MAB                    Page   3 of 4
```

Figure S30. Product of enantioenriched acid after 24 h. ChiralPak® IC, 5% IPA in Hexanes, 60 min run, 1 mL/min.

Given the lack of deuterium incorporation when d_3-MeCN was used as solvent, and the observed reactivity at enolizable C–H bonds, a reduction/protonation sequence is proposed to close the catalytic cycle of this reaction.

C. CV of PMe_2Ph

Cyclic voltammetry was conducted on a CH Instruments Electrochemical Analyzer (CH1600E). In a nitrogen filled glove box, a 1.3 mM solution of PMe_2Ph with 0.2 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.

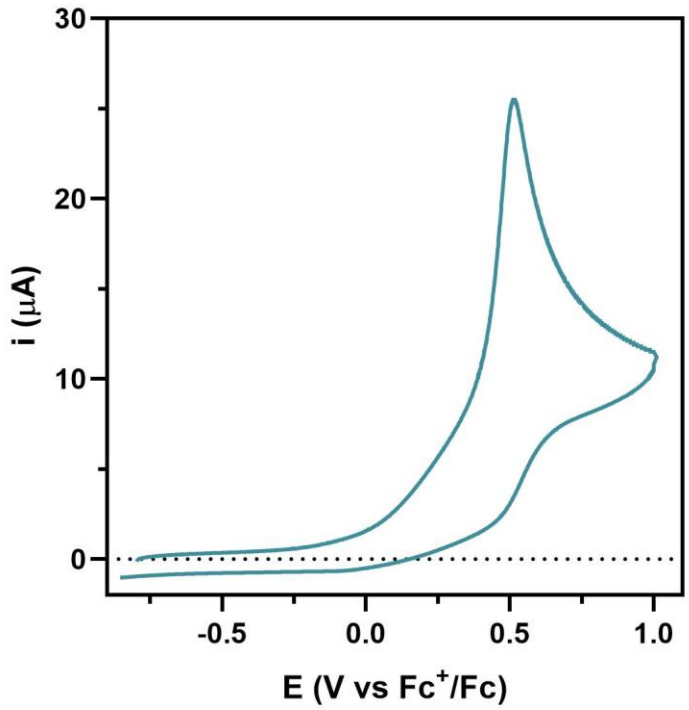

Figure S31. Cyclic Voltammogram of PMe_2Ph (Scan rate 0.1 Vs^{-1}) shows an irreversible oxidation at Ep = 0.51 V vs Fc/Fc^+, when ferrocene was used as an external reference (Ep = 0.89 V vs SCE).[10]

VII. References

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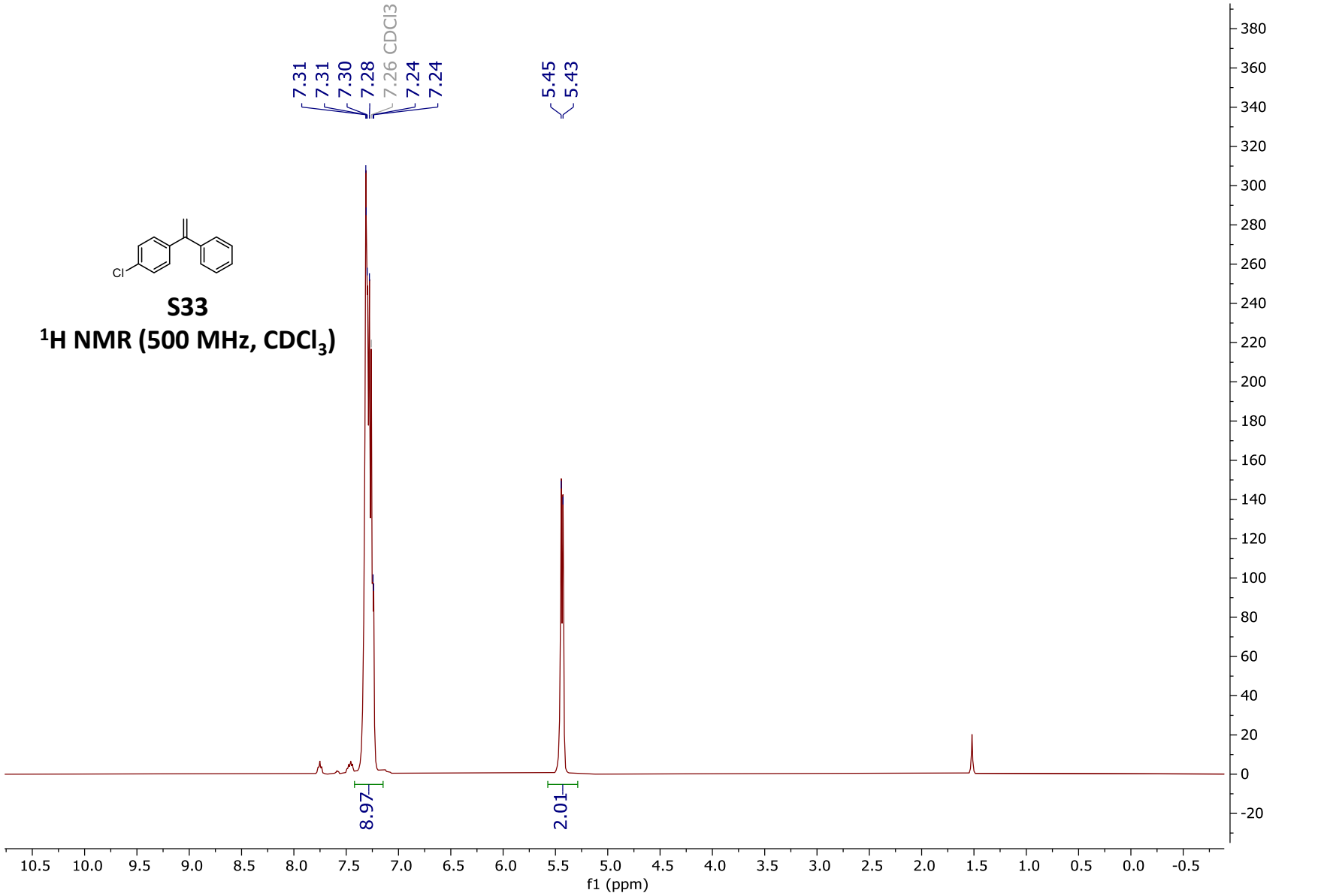
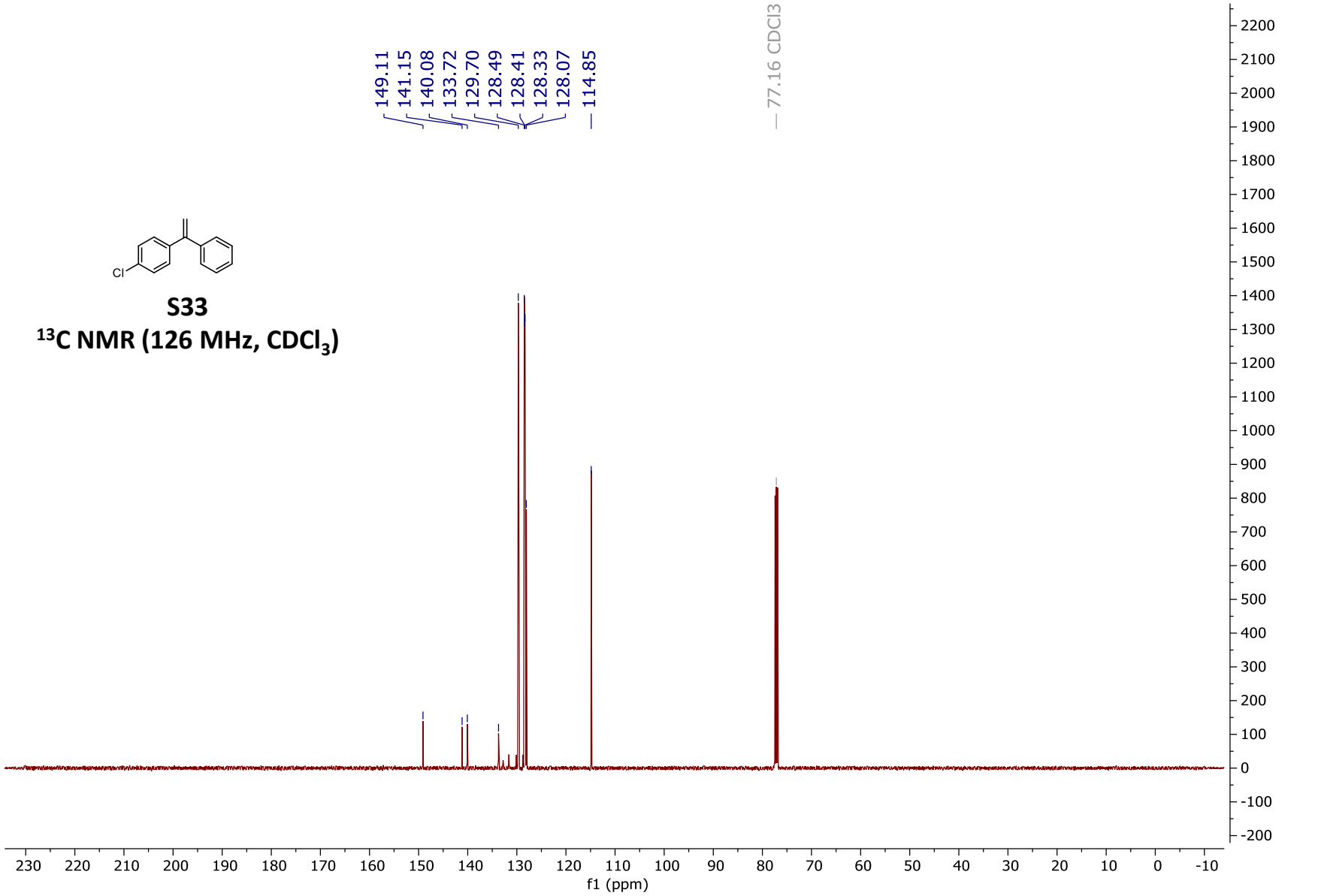
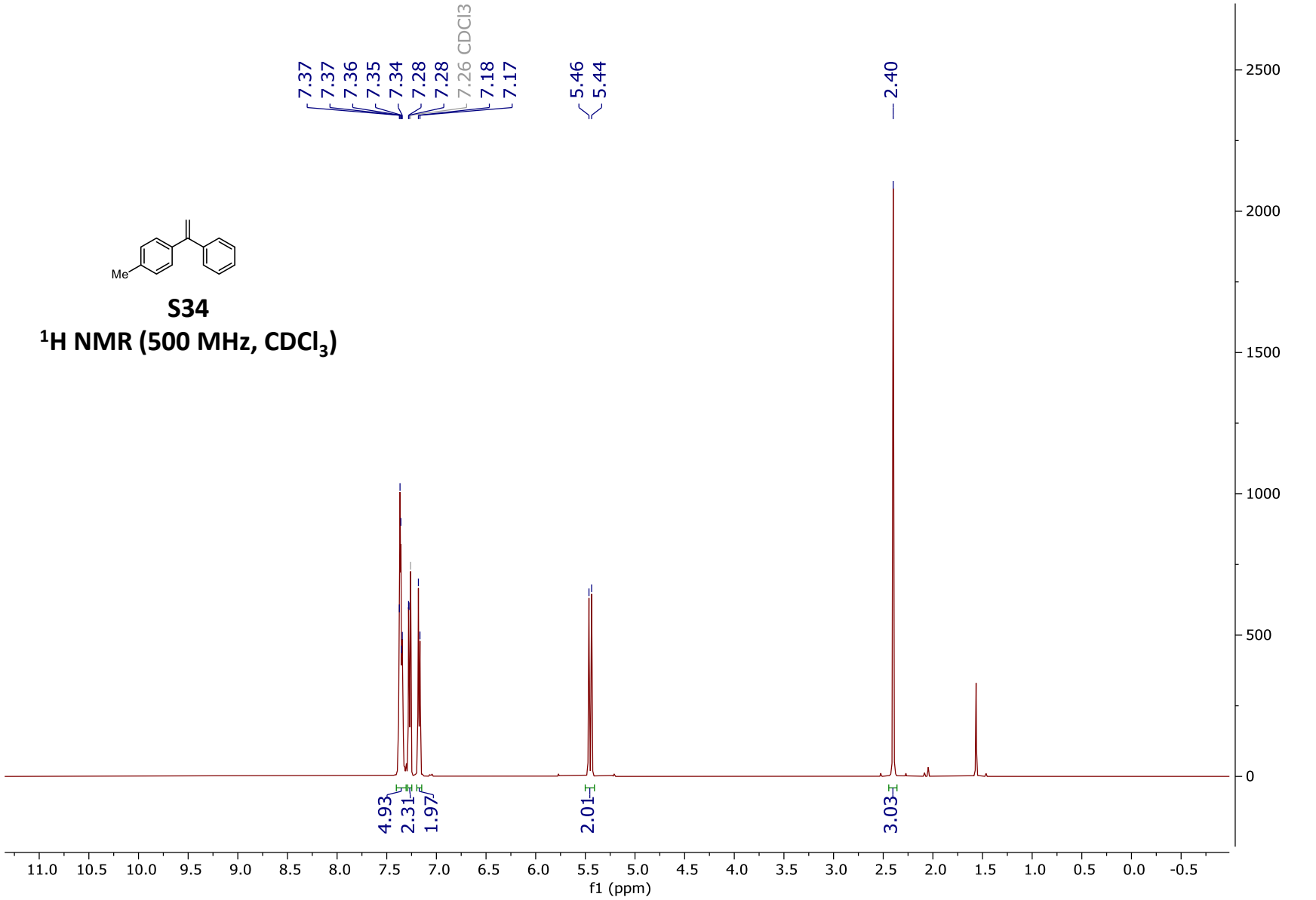
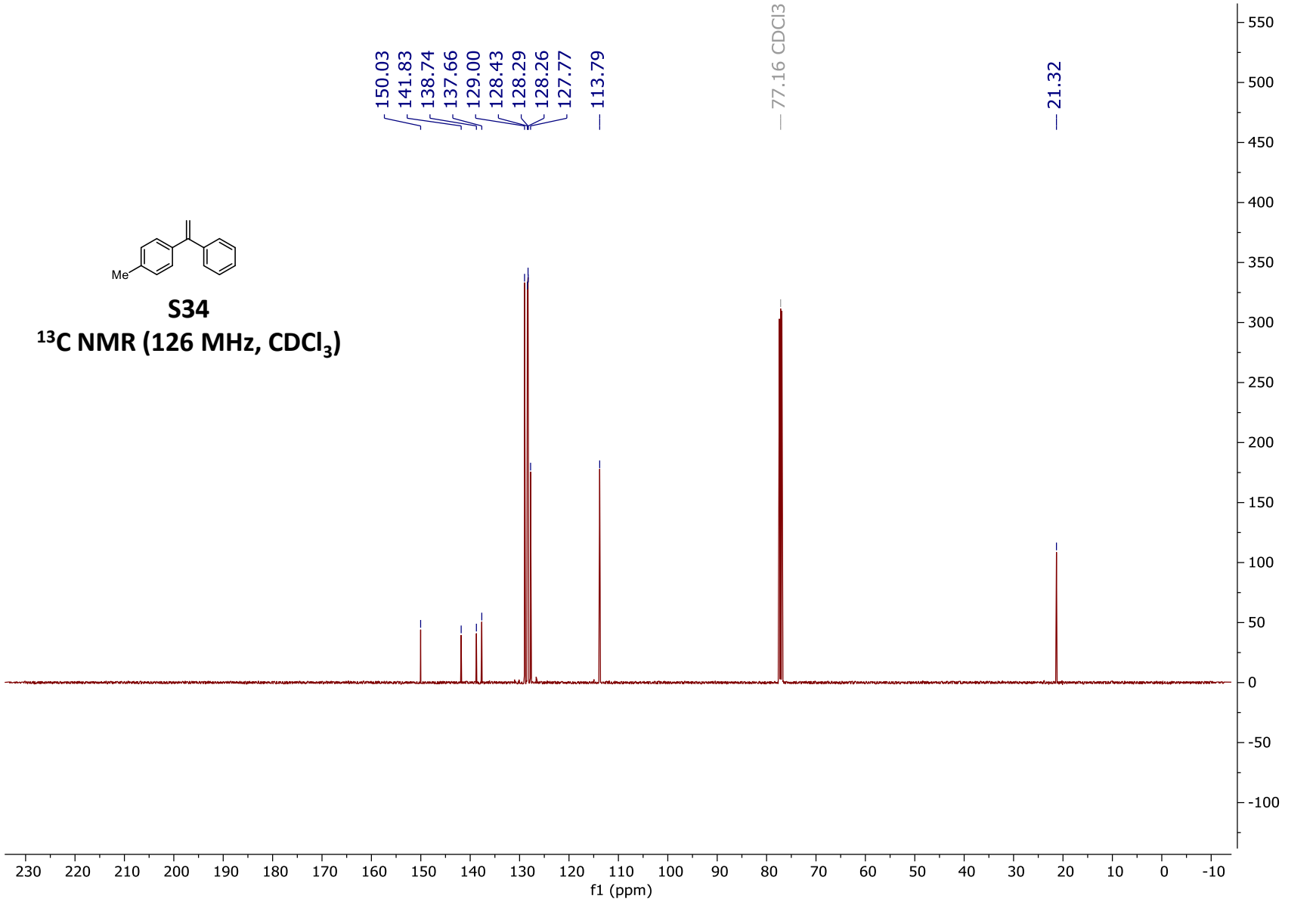

7.31
7.31
7.30
7.28
7.26 CDCl3
7.24
7.24
5.45
5.43
Cl
S33
1H NMR (500 MHz, CDCl3)
8.97
2.01
f1 (ppm)
JM-NB3-R178R2.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima 1

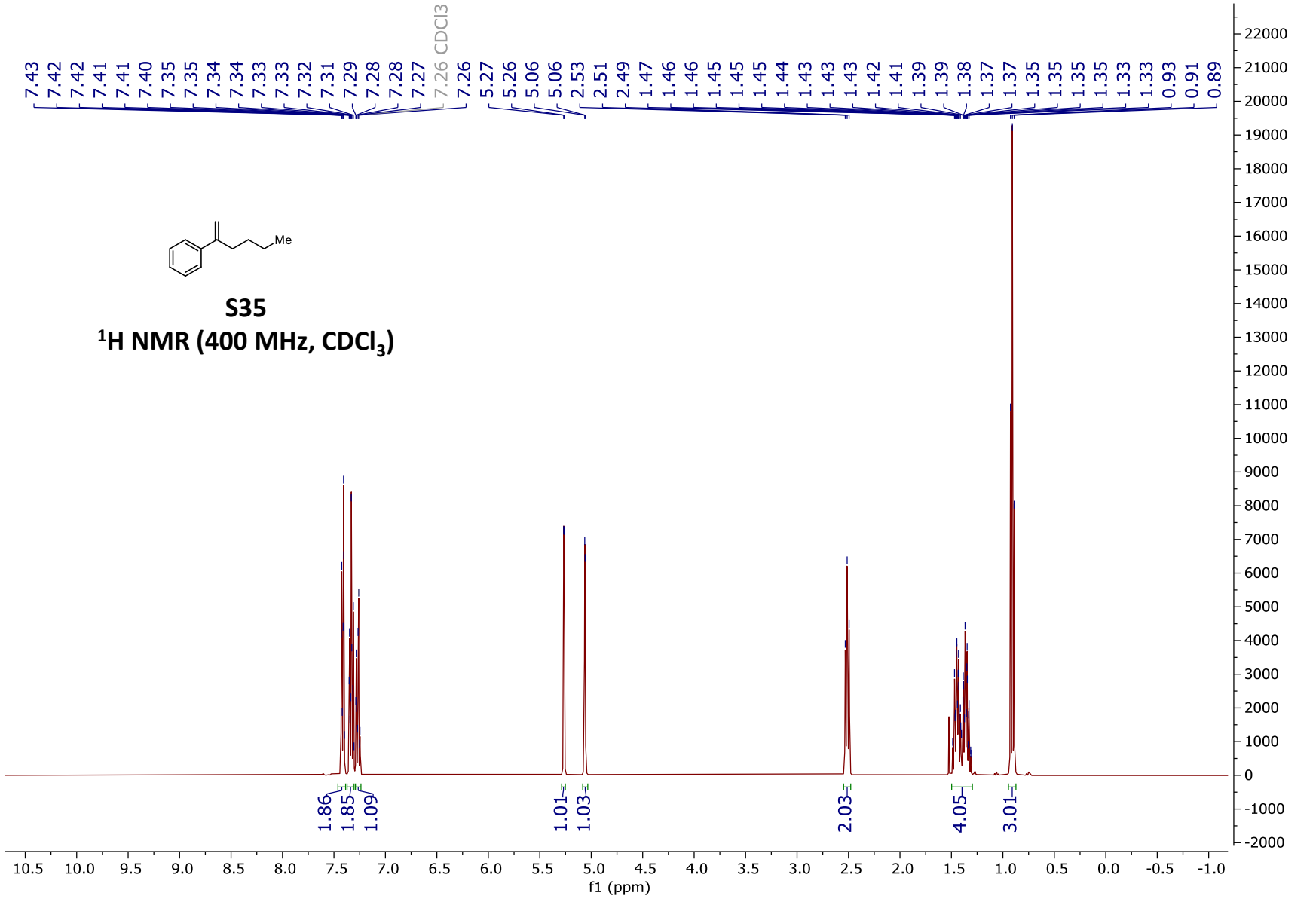

149.11
141.15
140.08
133.72
129.70
128.49
128.41
128.33
128.07
114.85
77.16 CDCl3
Cl
S33
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB3-R178R2.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima 1



S34

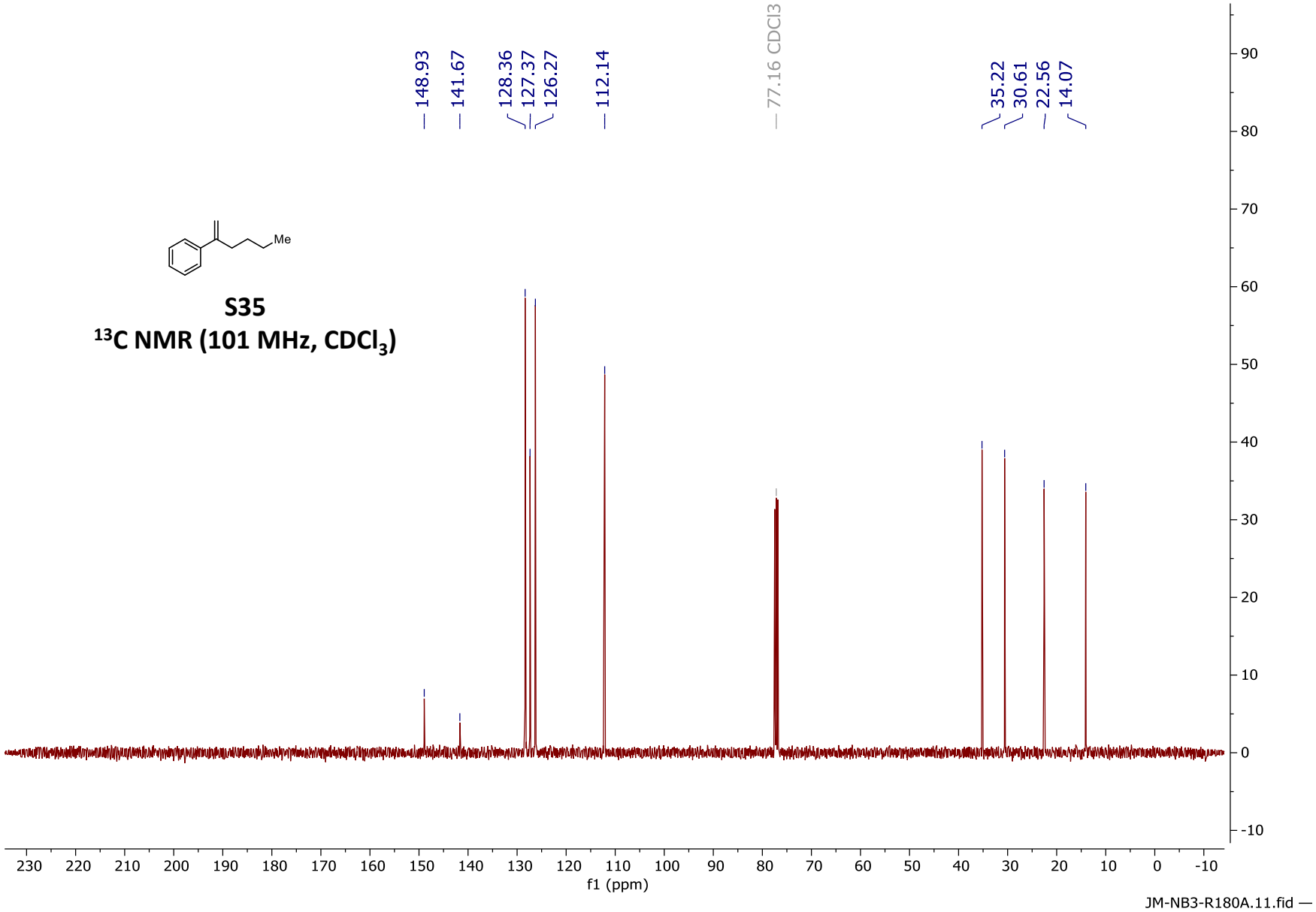
^{1}H NMR (500 MHz, $CDCl_3$)

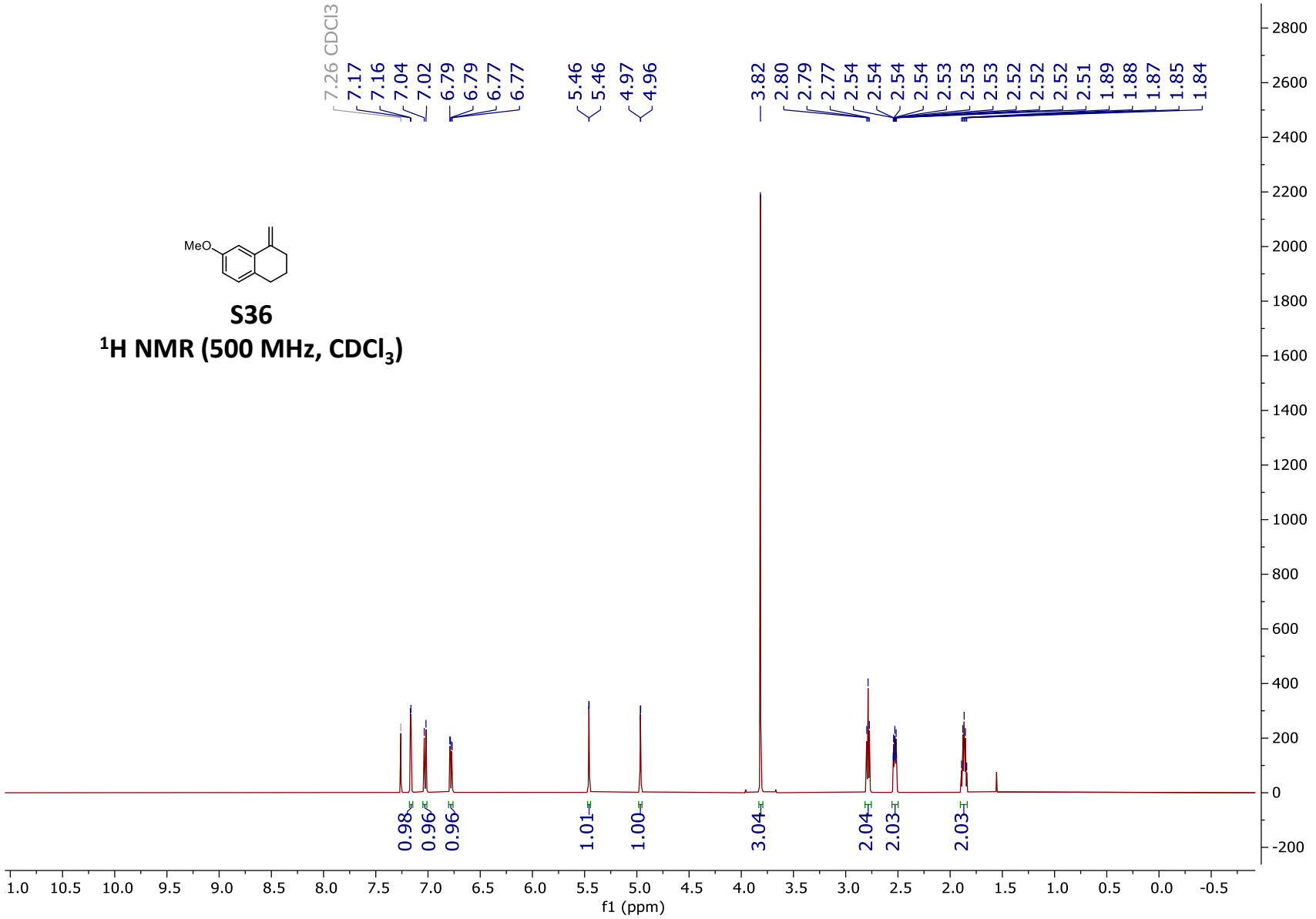

150.03
141.83
138.74
137.66
129.00
128.43
128.29
128.26
127.77
113.79
77.16 CDCl3
21.32
Me
S34
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB3-R188.11.fid



S35

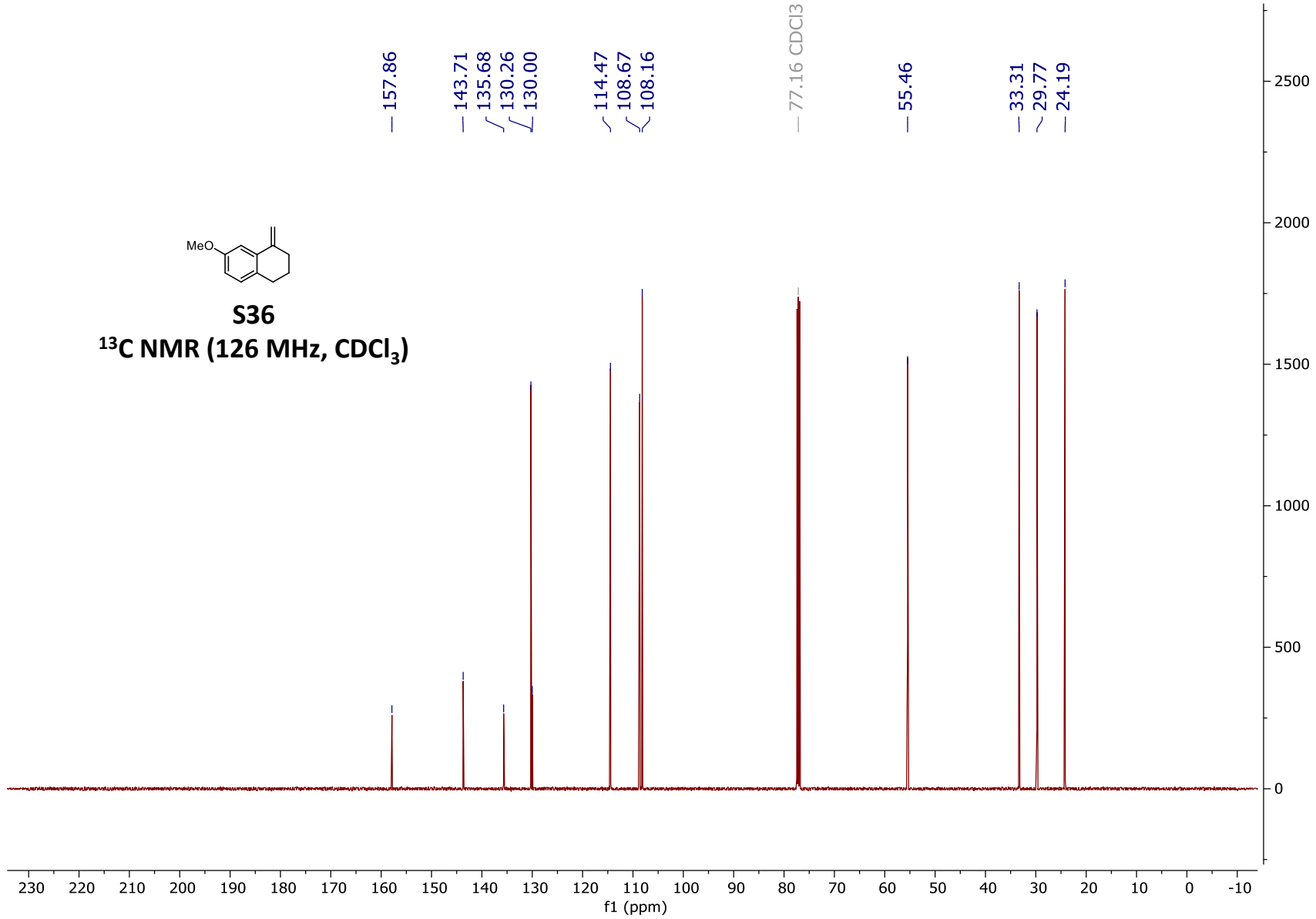
^{1}H NMR (400 MHz, $CDCl_3$)


148.93
141.67
128.36
127.37
126.27
112.14
77.16 CDCl3
35.22
30.61
22.56
14.07
Me
S35
13C NMR (101 MHz, CDCl3)
f1 (ppm)
JM-NB3-R180A.11.fid



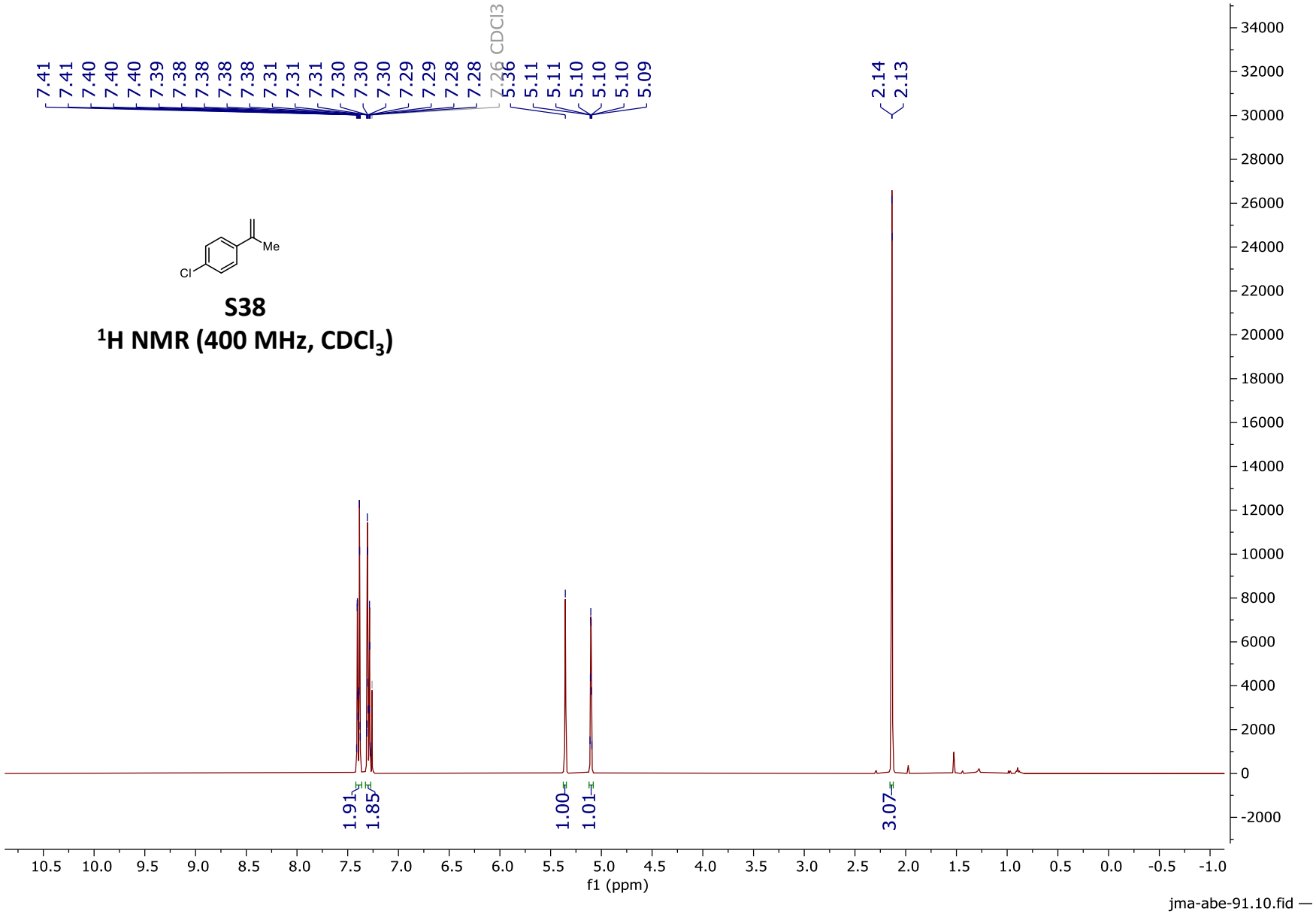
S36

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



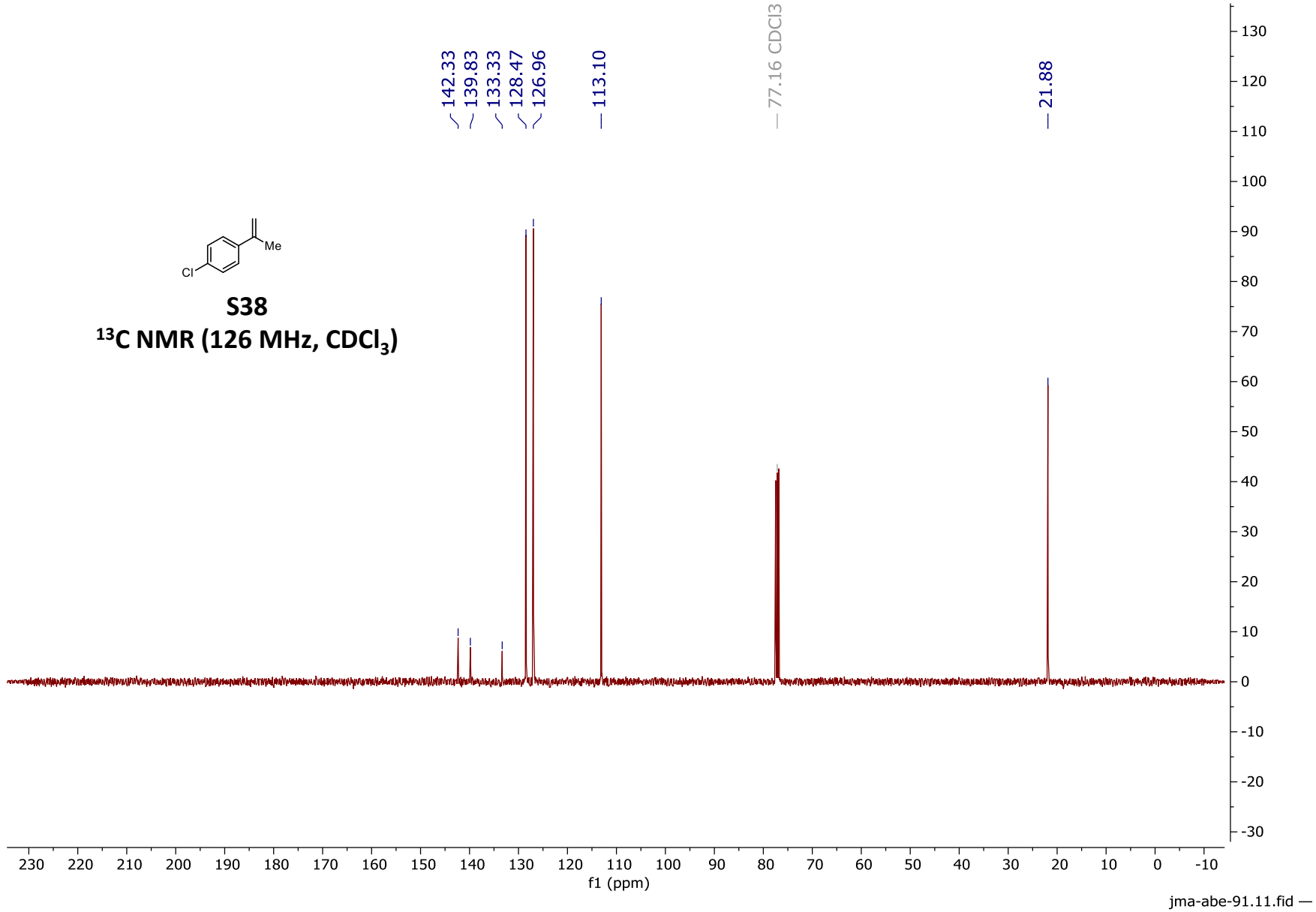
S36

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



S38

^{1}H NMR (400 MHz, $CDCl_3$)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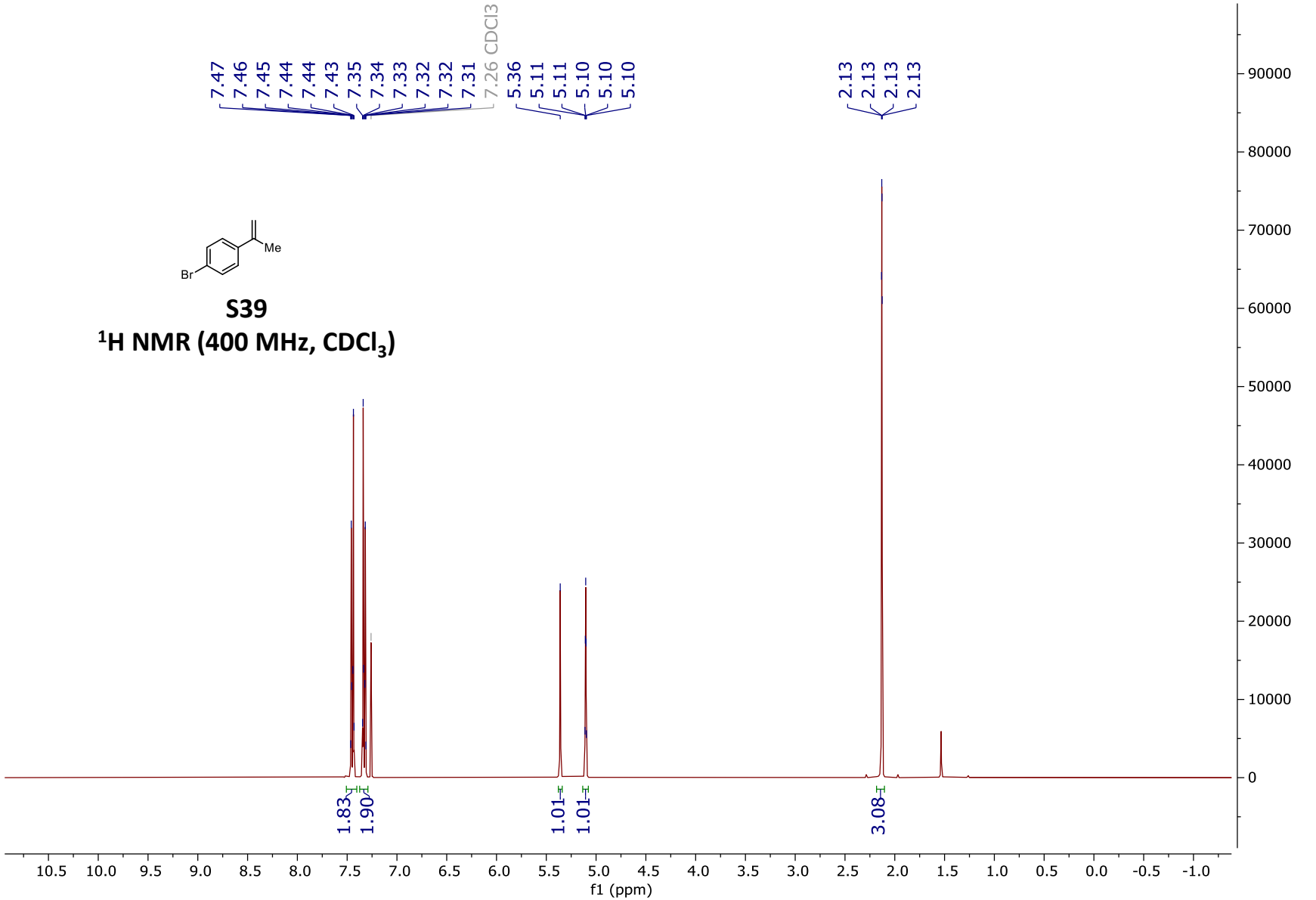
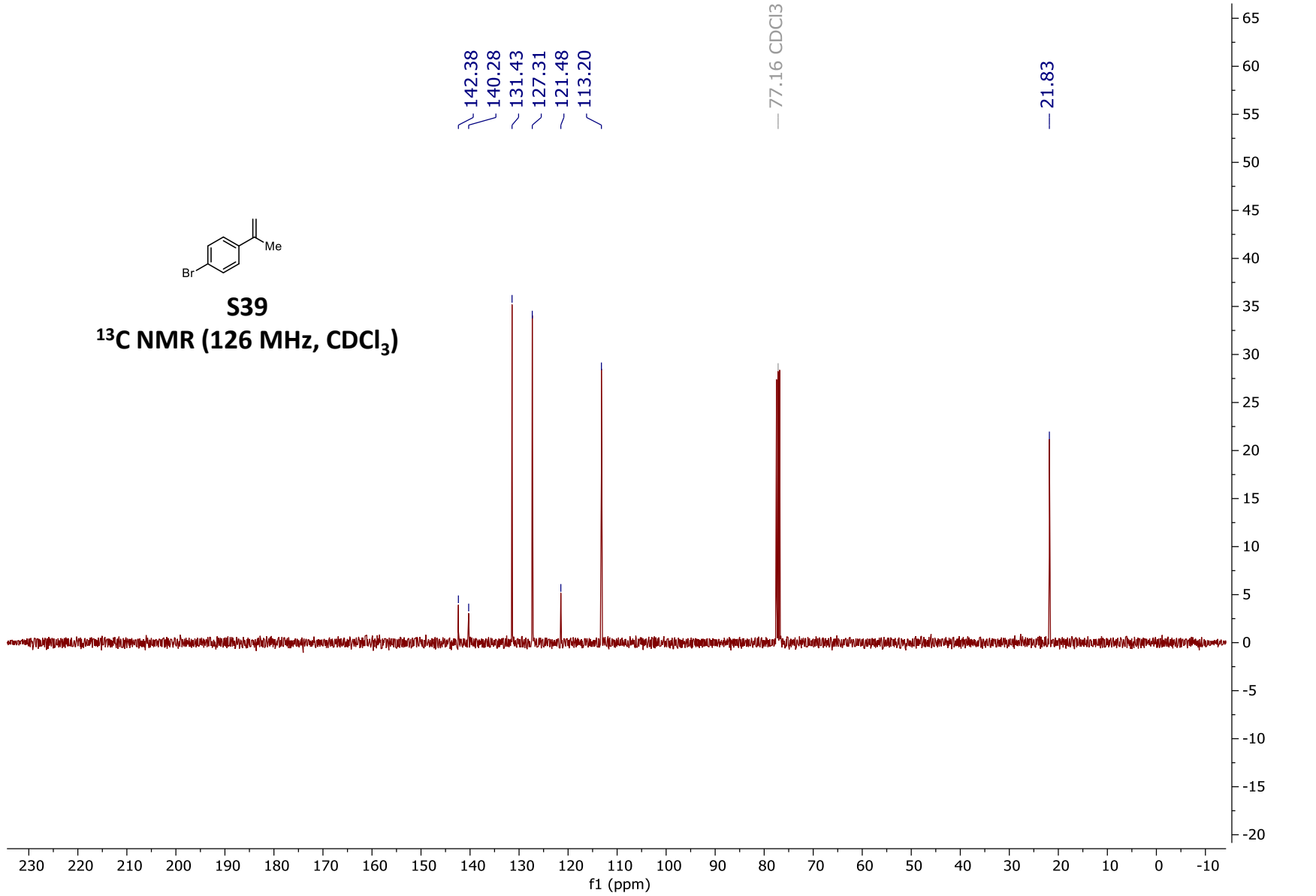
139.83
133.33
128.47
126.96
113.10
77.16 CDCl3
21.88
Me
Cl
S38
13C NMR (126 MHz, CDCl3)
f1 (ppm)
jma-abe-91.11.fid



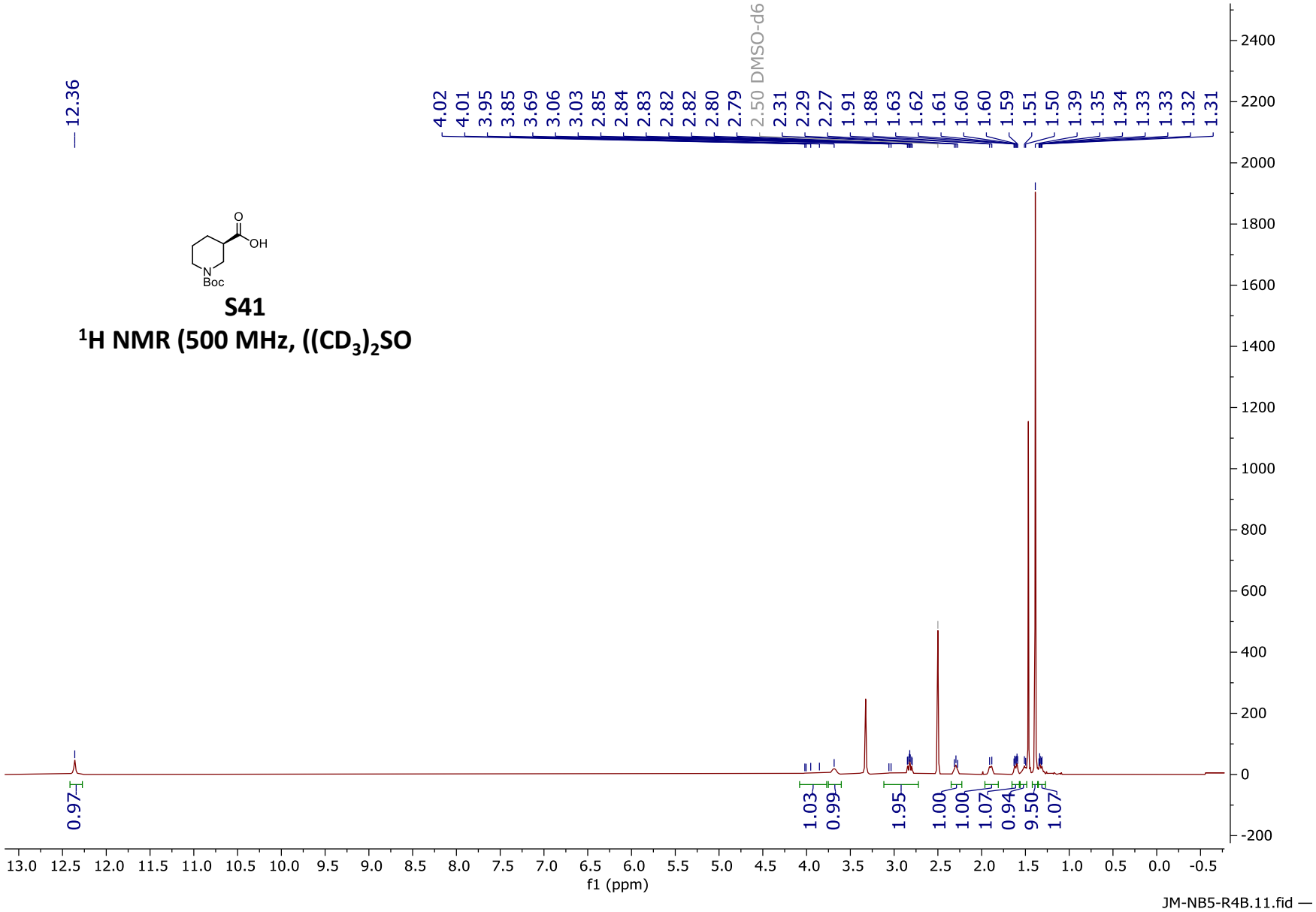
S39

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



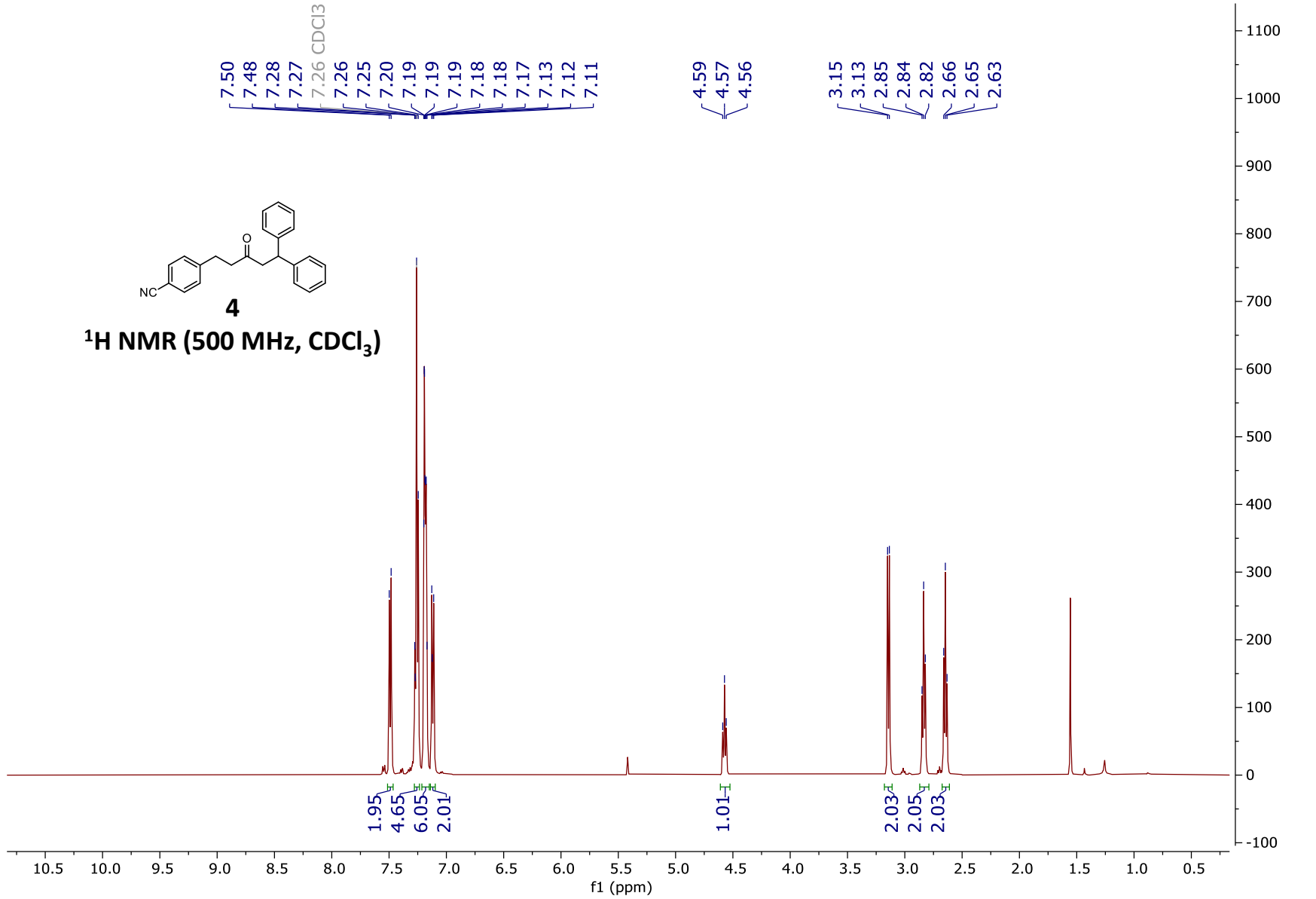
S39

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



S41

^{1}H NMR (500 MHz, $((CD_3)_2SO$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7.27
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7.26
7.25
7.20
7.19
7.19
7.19
7.18
7.18
7.17
7.13
7.12
7.11
4.59
4.57
4.56
3.15
3.13
2.85
2.84
2.82
2.66
2.65
2.63
O
NC
4
1H NMR (500 MHz, CDCl3)
1.95
4.65
6.05
2.01
1.01
2.03
2.05
2.03
f1 (ppm)
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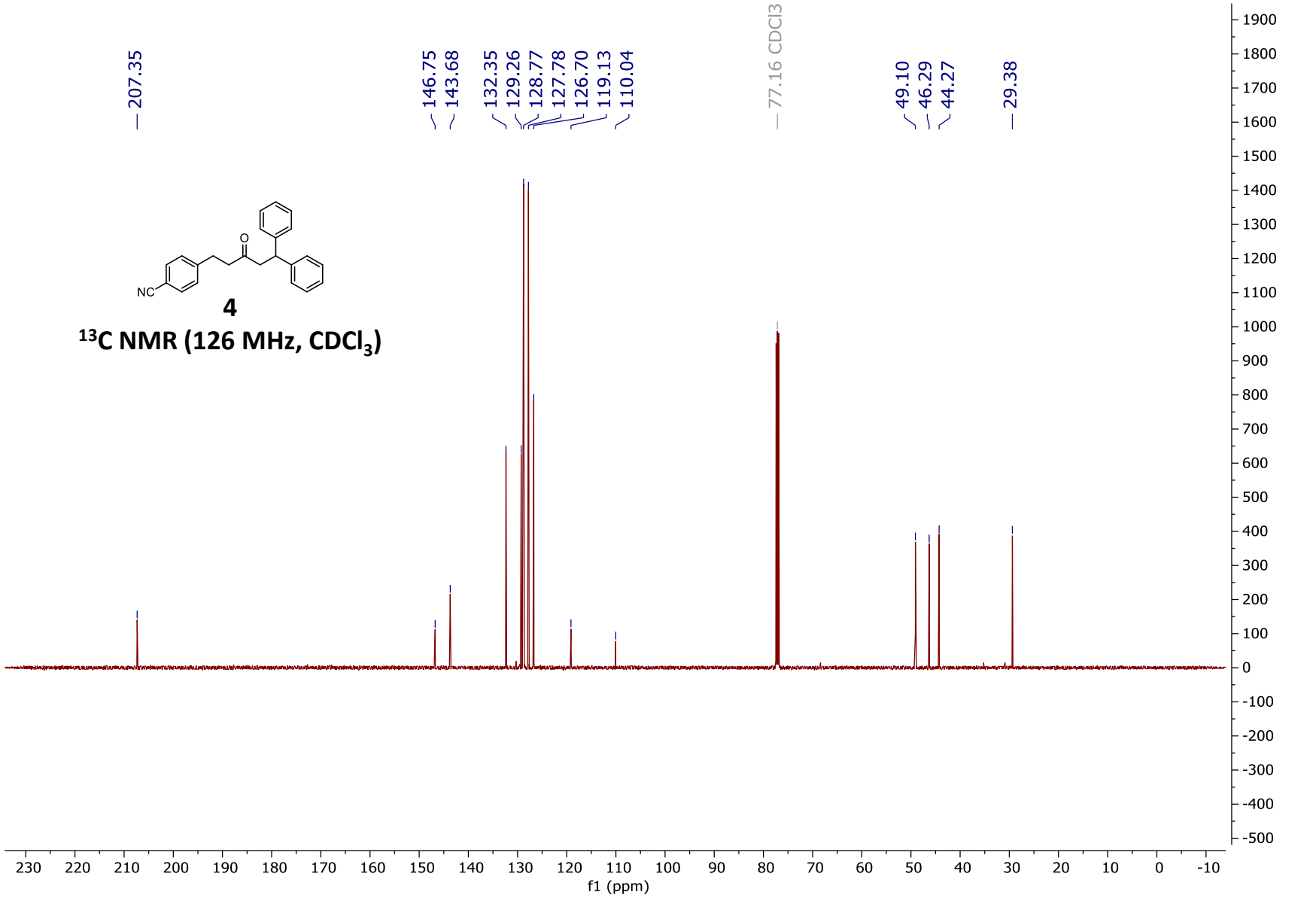
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143.68
132.35
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128.77
127.78
126.70
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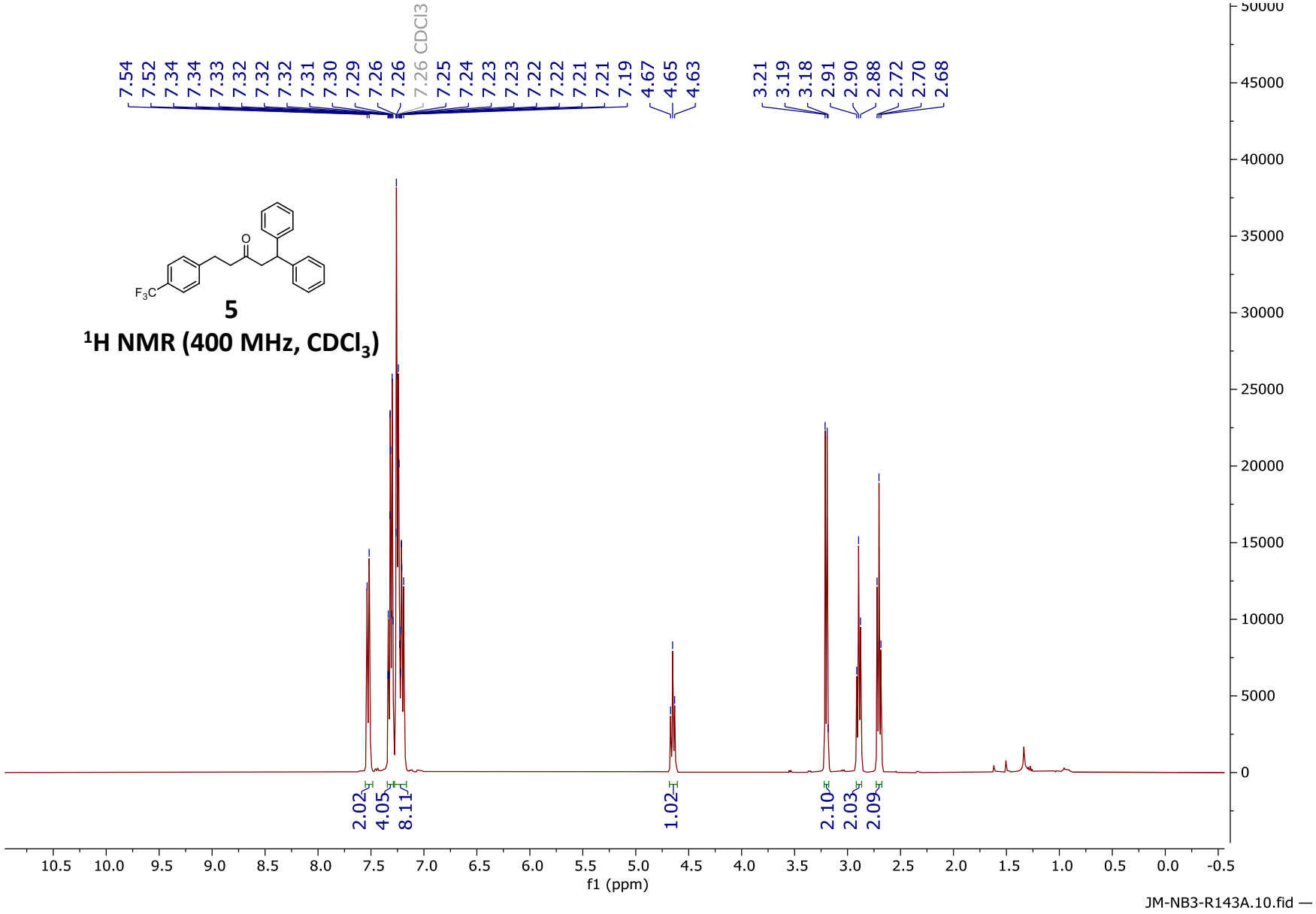
110.04
77.16 CDCl3
49.10
46.29
44.27
29.38
O
NC
4
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB4-R42BCARBON.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima 1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7.52
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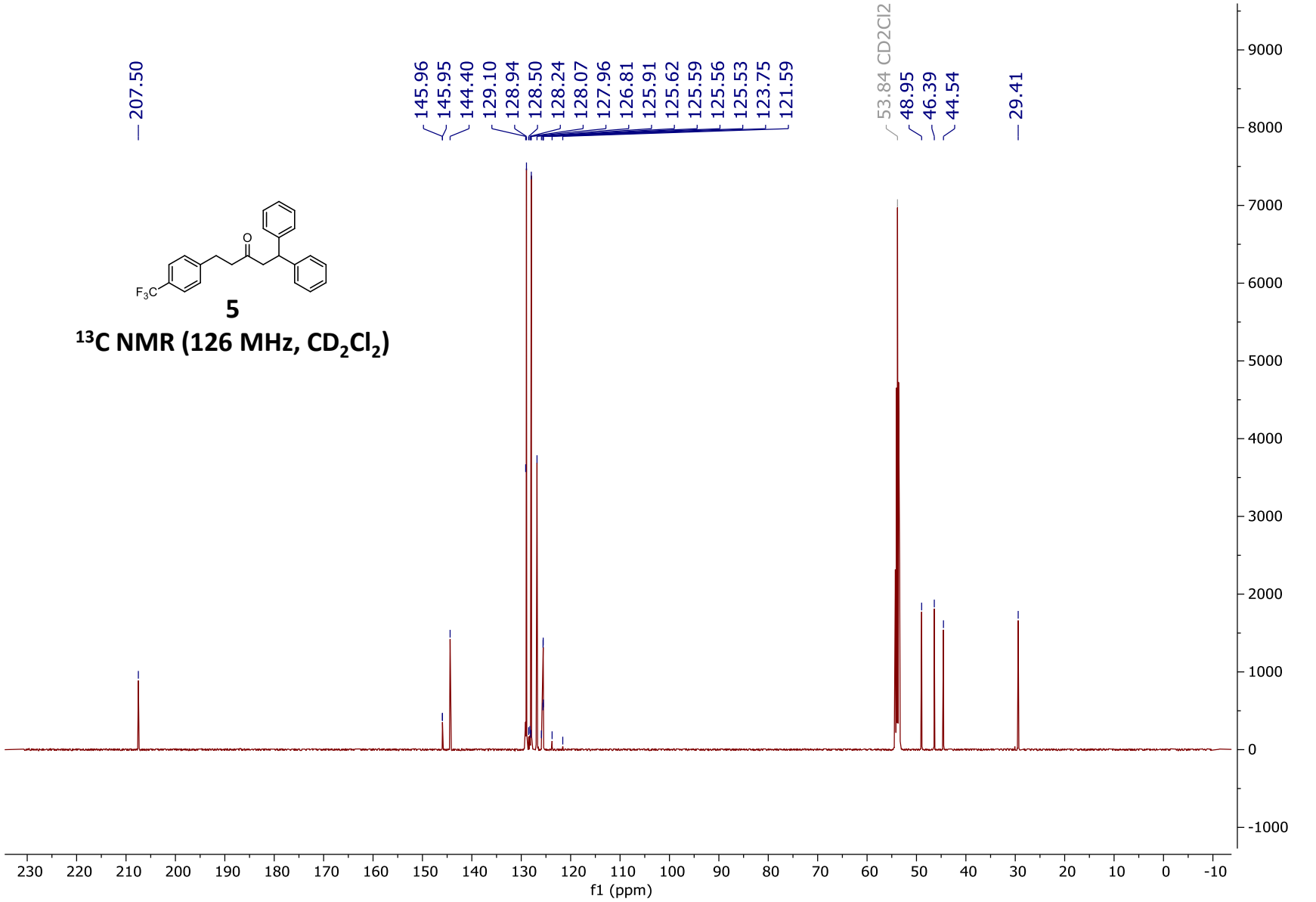
7.34
7.33
7.32
7.32
7.32
7.31
7.30
7.29
7.26
7.26
CDCl3
7.25
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.19
4.67
4.65
4.63
3.21
3.19
3.18
2.91
2.90
2.88
2.72
2.70
2.68
O
F3C
5
1H NMR (400 MHz, CDCl3)
2.02
4.05
8.11
1.02
2.10
2.03
2.09
f1 (ppm)
JM-NB3-R143A.10.fid


207.50
145.96
145.95
144.40
129.10
128.94
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128.24
128.07
127.96
126.81
125.91
125.62
125.59
125.56
125.53
123.75
121.59
53.84 CD2Cl2
48.95
46.39
44.54
29.41
O
F3C
5
13C NMR (126 MHz, CD2Cl2)
f1 (ppm)
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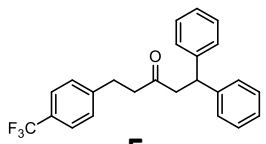
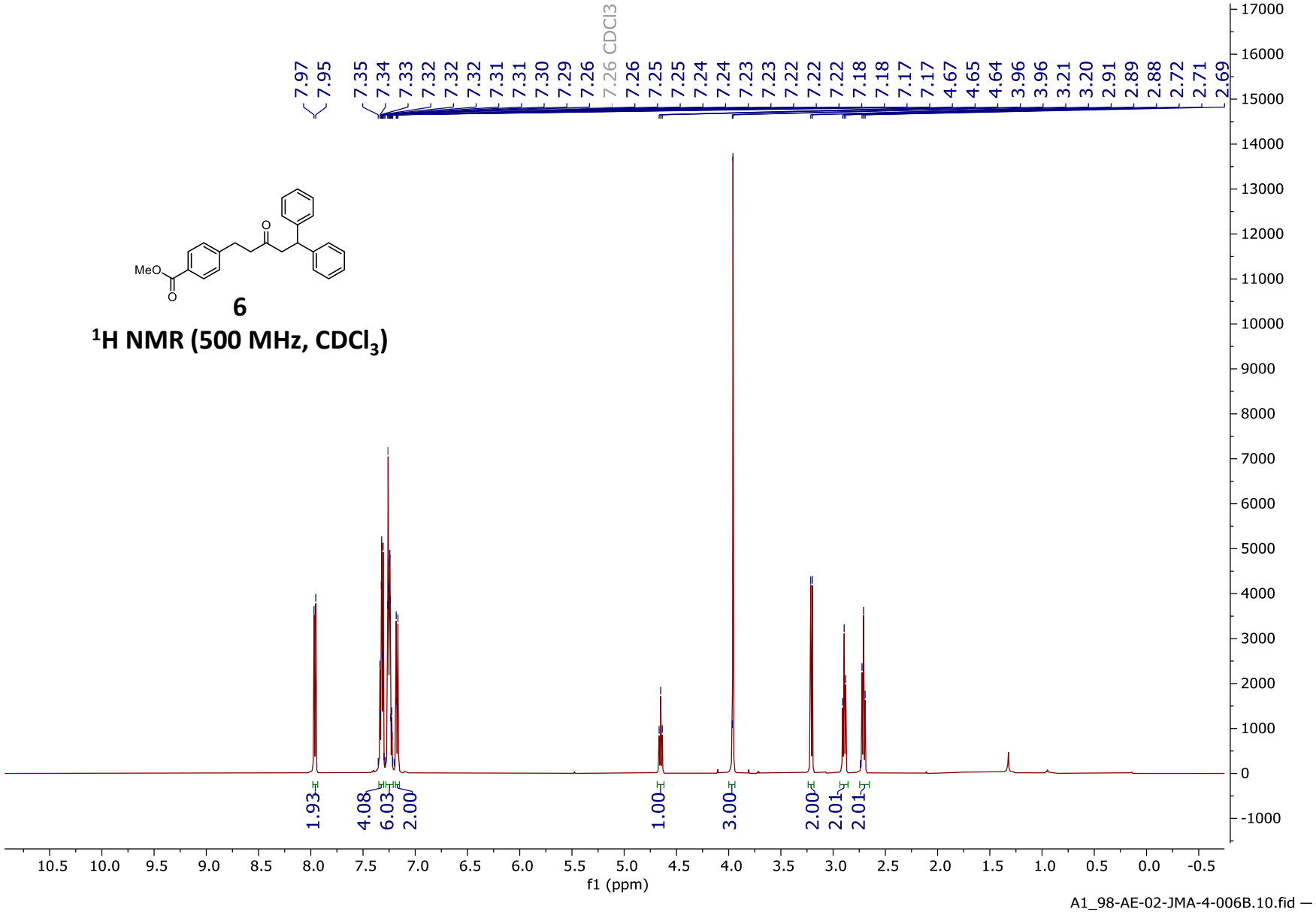
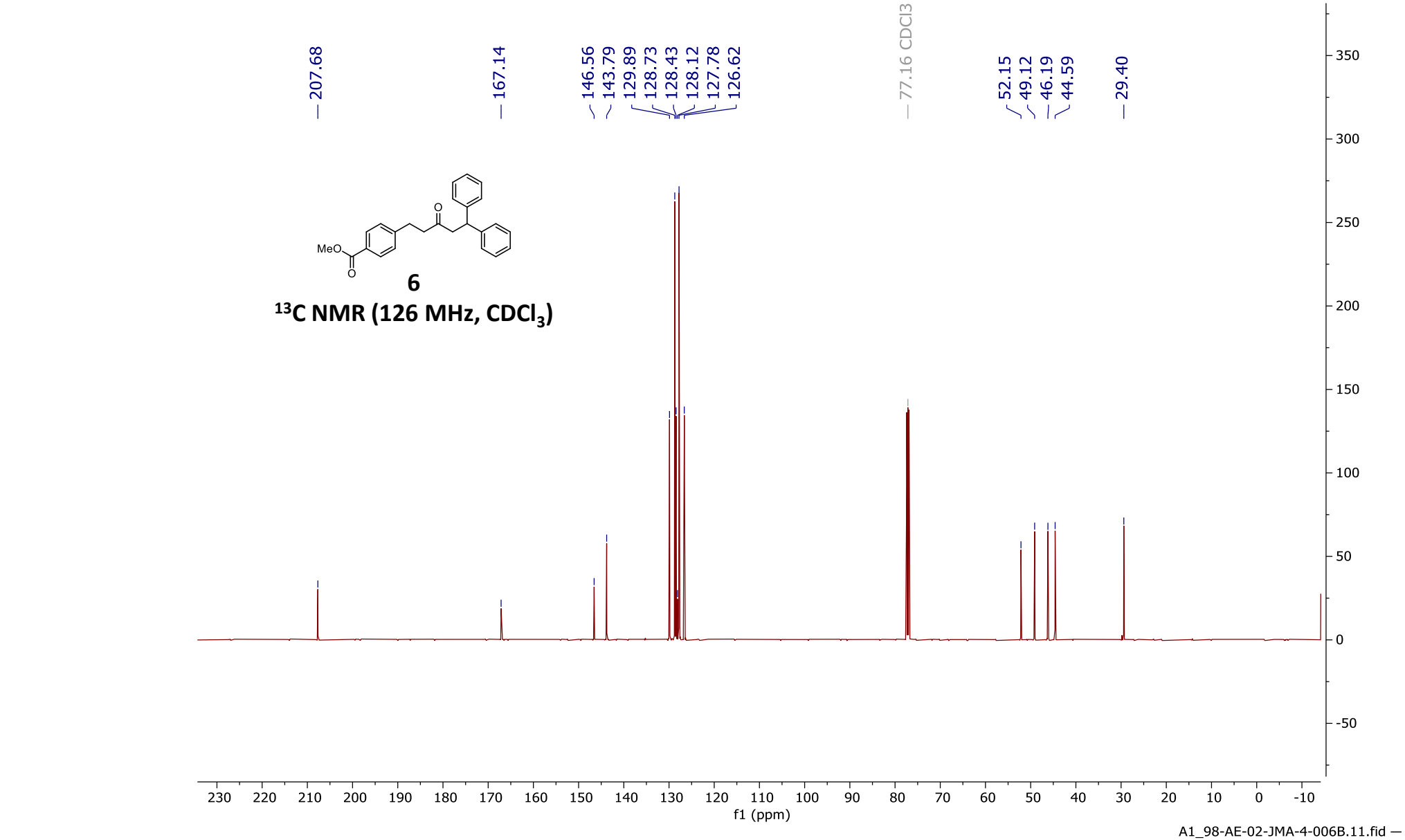
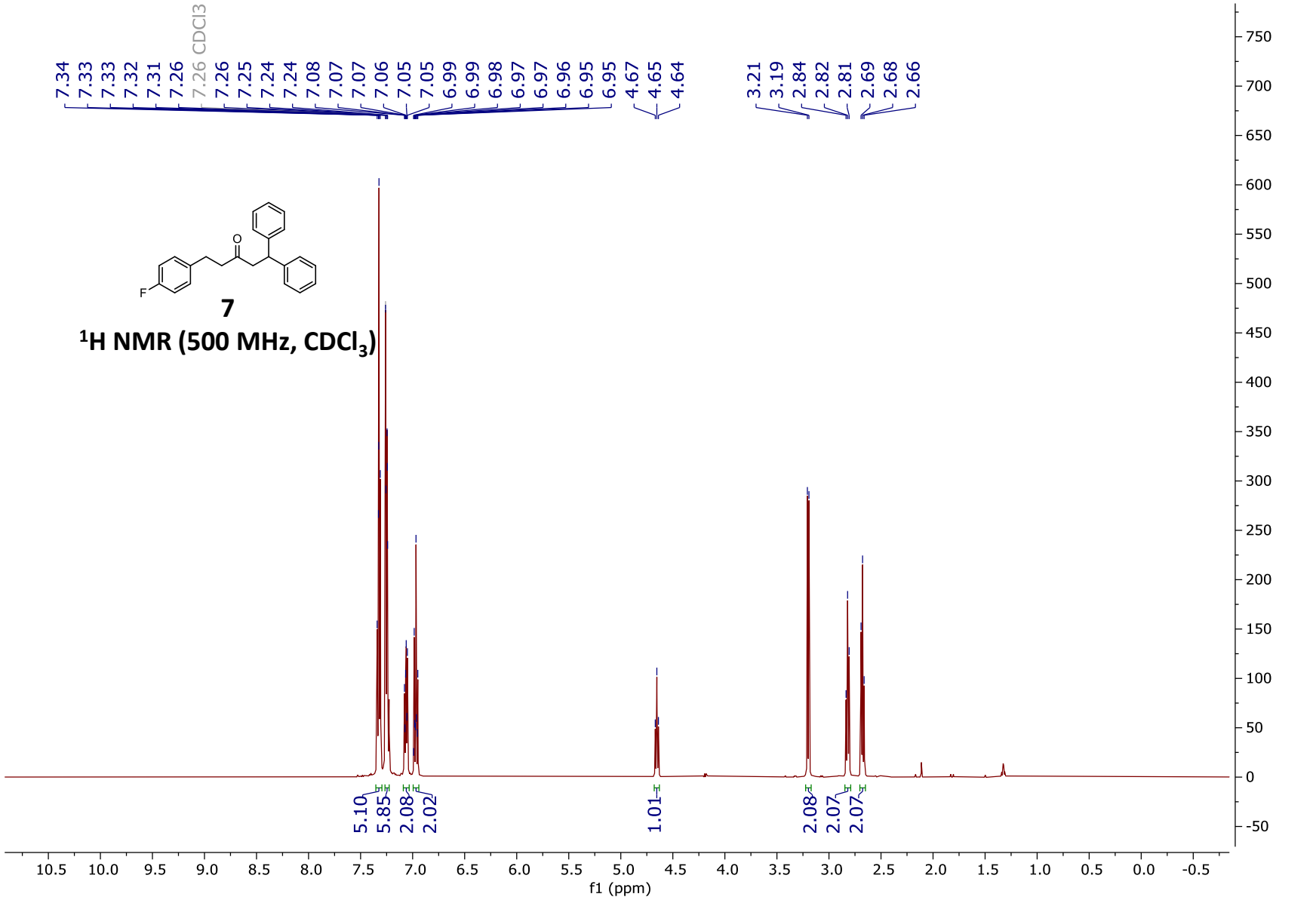


5

^{19}F NMR (282 MHz, $CDCl_3$)


7.97
7.95
7.35
7.34
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.29
7.26
7.26 CDCl3
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.22
7.18
7.18
7.17
7.17
4.67
4.65
4.64
3.96
3.96
3.21
3.20
2.91
2.89
2.88
2.72
2.71
2.69
MeO
O
O
6
1H NMR (500 MHz, CDCl3)
1.93
4.08
6.03
2.00
1.00
3.00
2.00
2.01
2.01
f1 (ppm)
A1_98-AE-02-JMA-4-006B.10.fid


207.68
167.14
146.56
143.79
129.89
128.73
128.43
128.12
127.78
126.62
77.16 CDCl3
52.15
49.12
46.19
44.59
29.40
MeO
O
O
6
13C NMR (126 MHz, CDCl3)
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)
A1_98-AE-02-JMA-4-006B.11.fid


7.34
7.33
7.33
7.32
7.31
7.26
7.26 CDCl3
7.26
7.25
7.24
7.24
7.08
7.07
7.07
7.06
7.05
7.05
6.99
6.99
6.98
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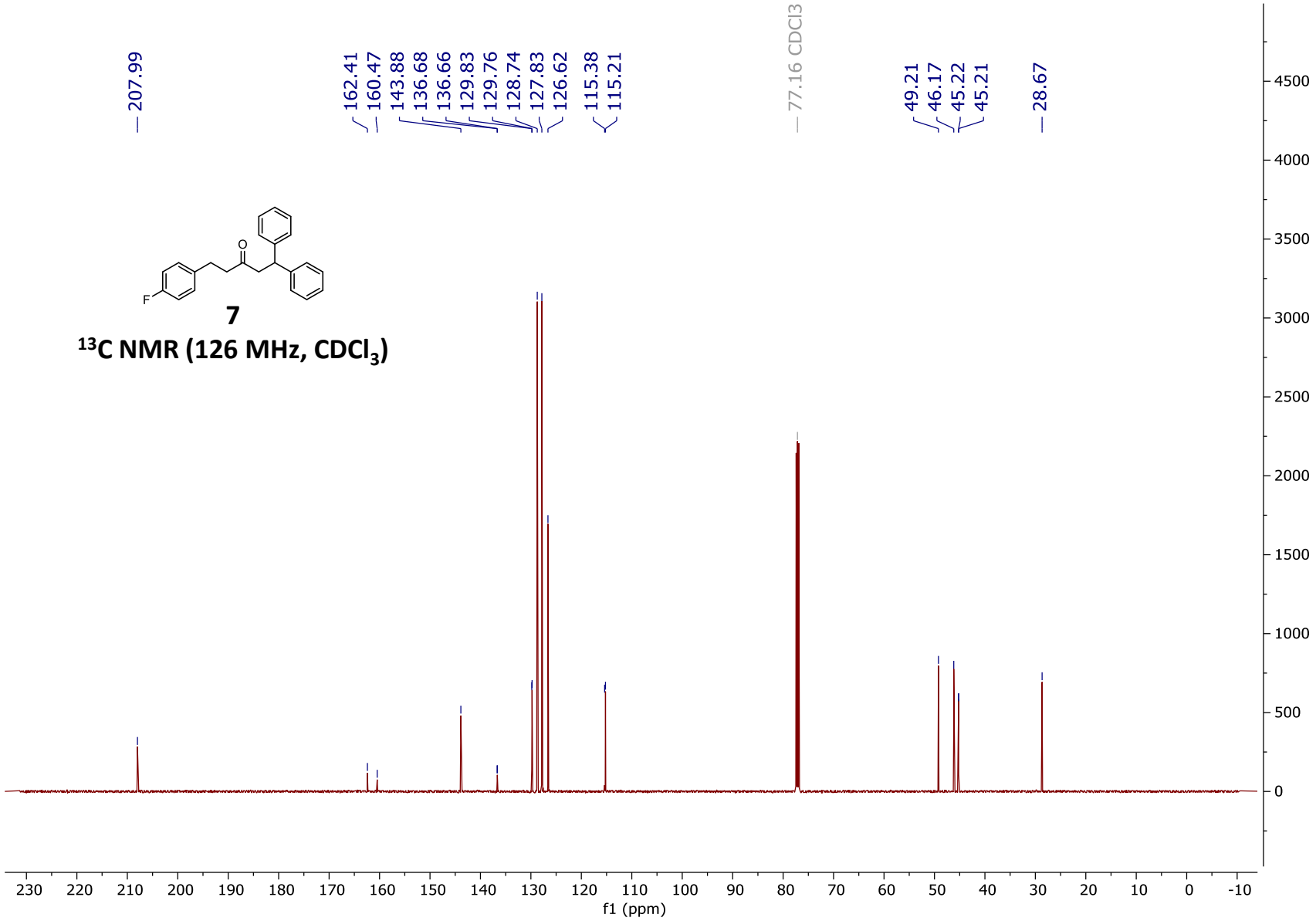
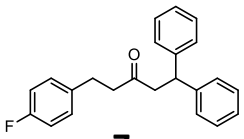
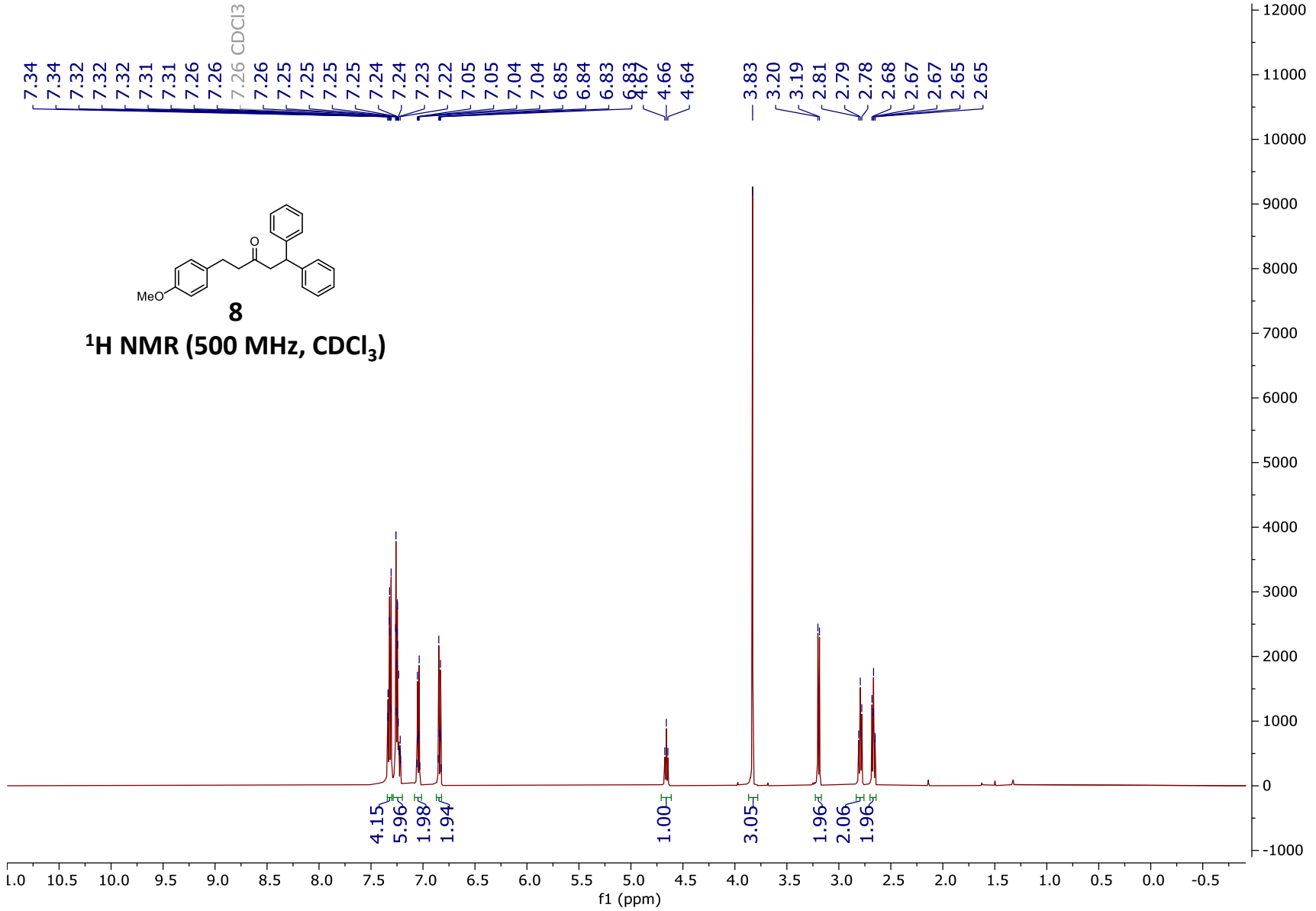
6.97
6.96
6.95
6.95
4.67
4.65
4.64
3.21
3.19
2.84
2.82
2.81
2.69
2.68
2.66
O
F
7
1H NMR (500 MHz, CDCl3)
5.10
5.85
2.08
2.02
1.01
2.08
2.07
2.07
f1 (ppm)
JM-NB3-ABE54B.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima

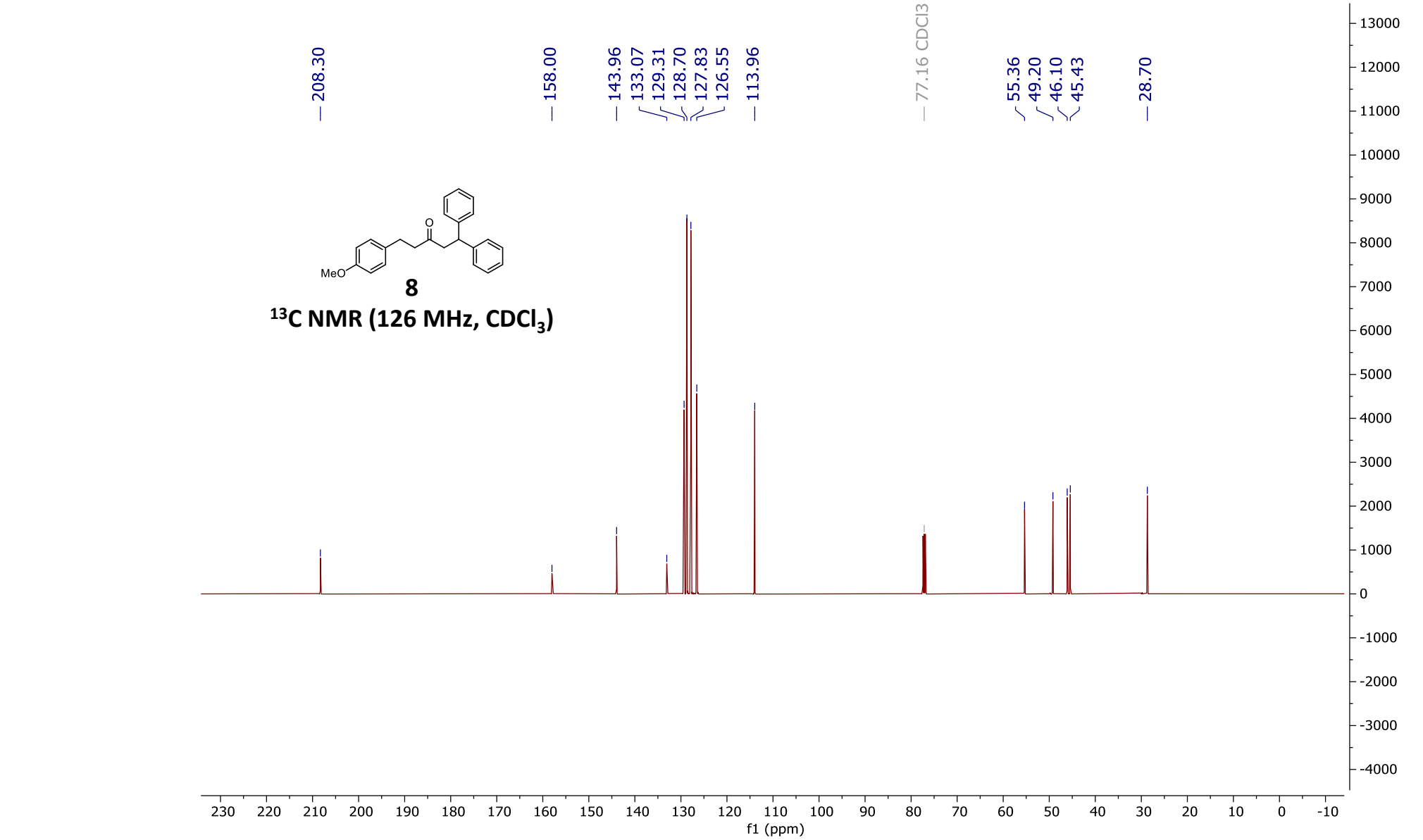

207.99
162.41
160.47
143.88
136.68
136.66
129.83
129.76
128.74
127.83
126.62
115.38
115.21
77.16 CDCl3
49.21
46.17
45.22
45.21
28.67
O
F
7
13C NMR (126 MHz, CDCl3)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
JM-NB3-ABE54B.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima

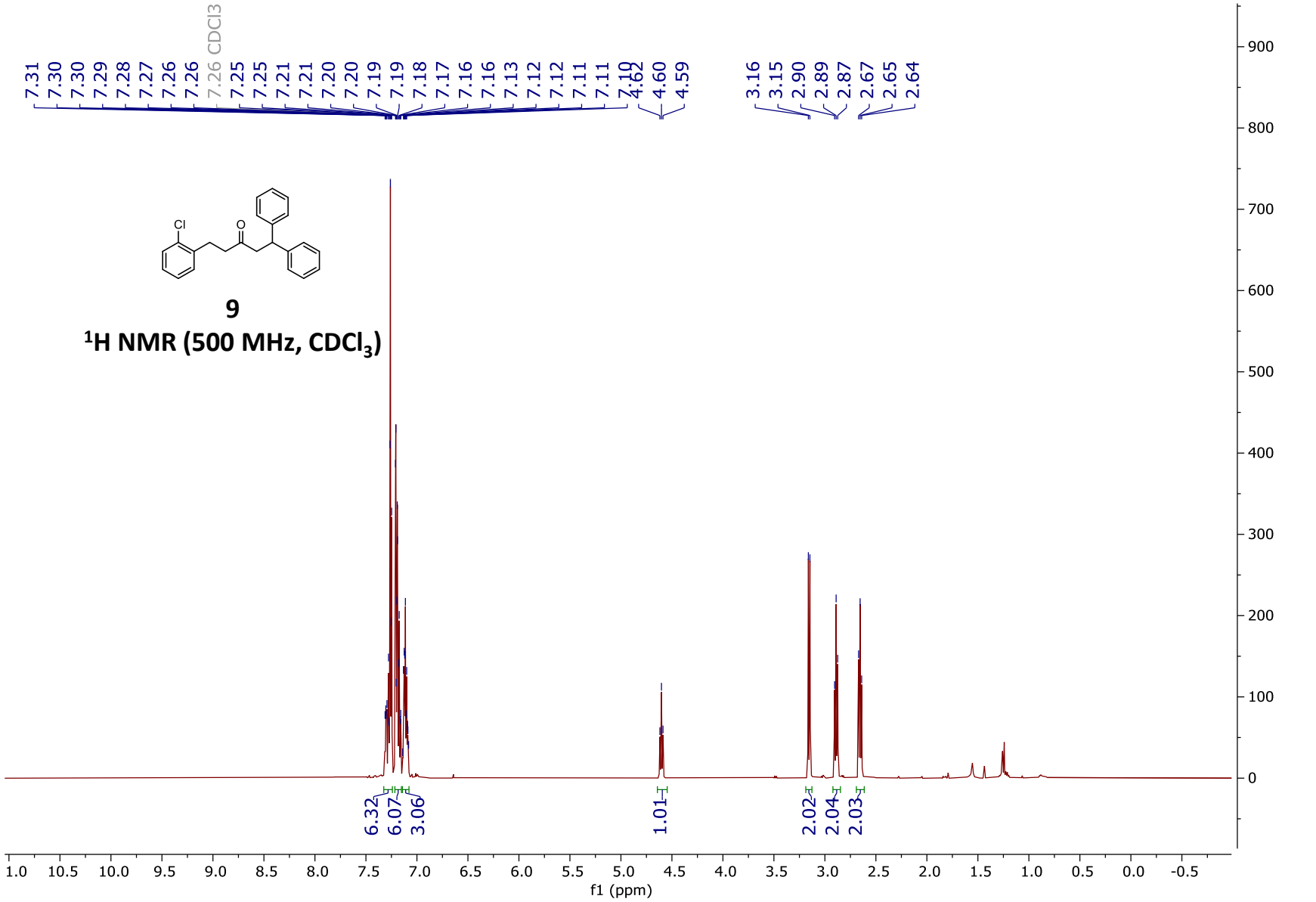


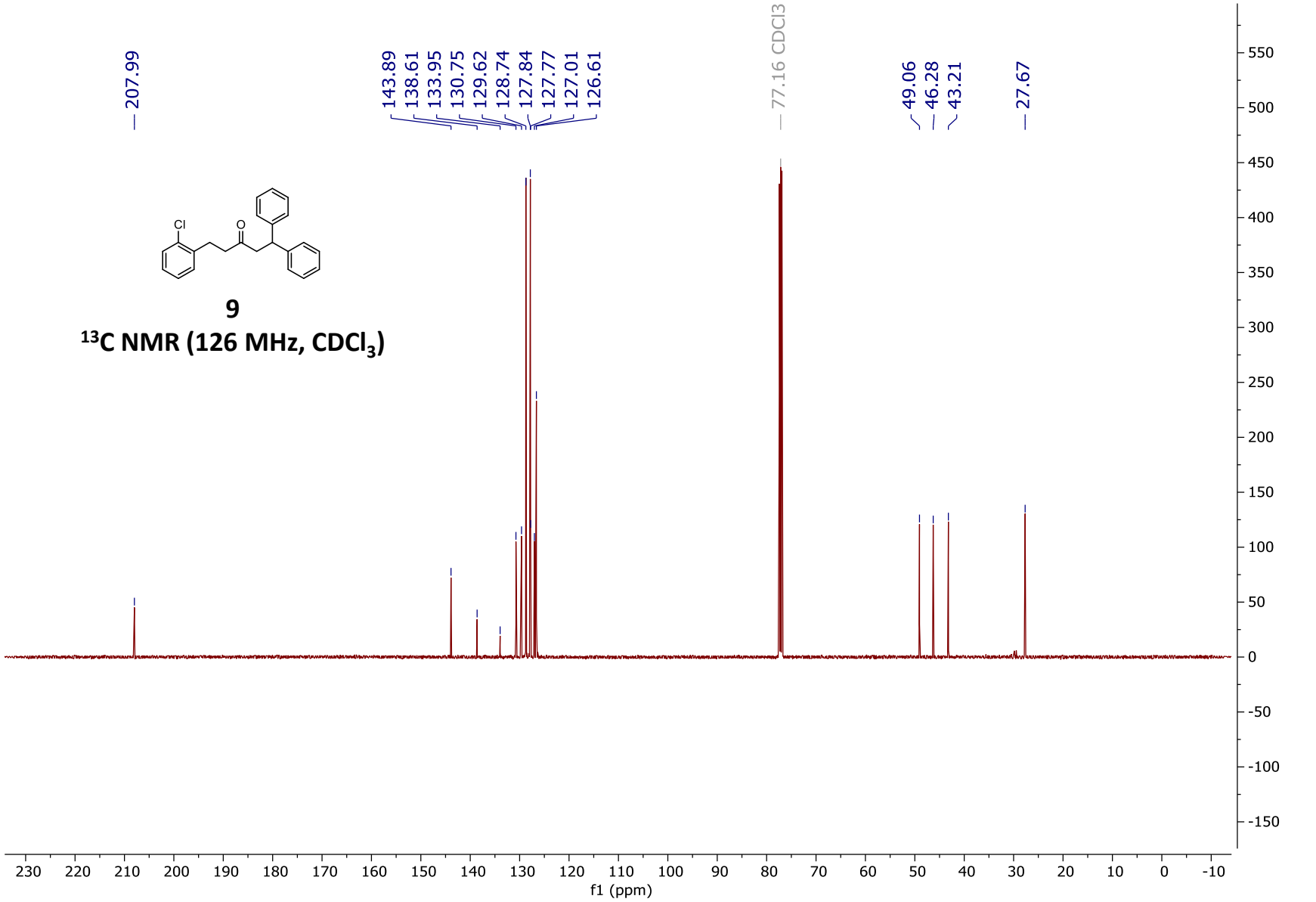
7

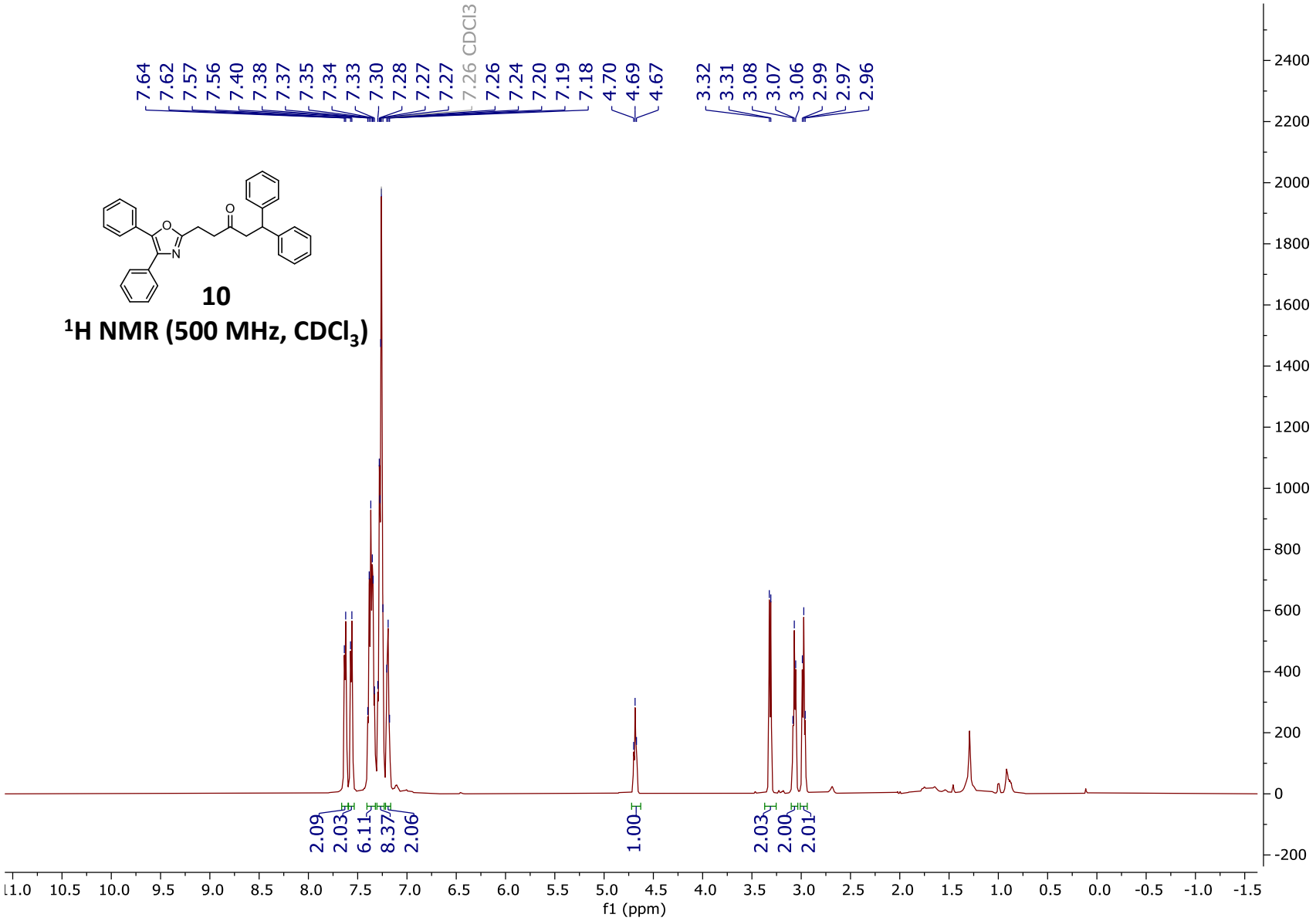
^{19}F NMR (282 MHz, $CDCl_3$)

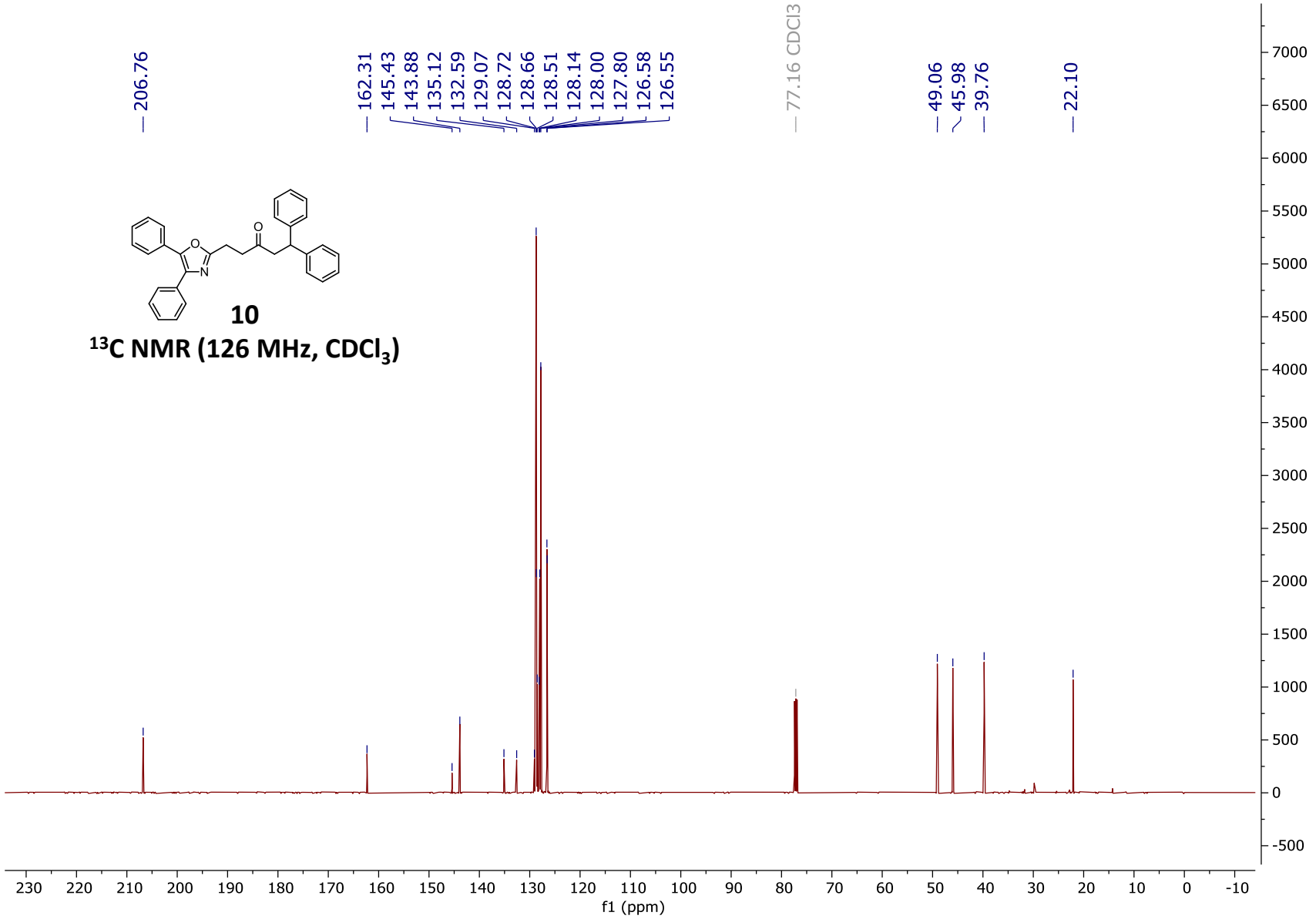

7.34 7.34 7.32 7.32 7.32 7.31 7.31 7.26 7.26 7.26 CDCl3 7.26 7.25 7.25 7.25 7.25 7.24 7.24 7.23 7.22 7.05 7.05 7.04 7.04 6.85 6.84 6.83 6.83 4.67 4.66 4.64
3.83 3.20 3.19 2.81 2.79 2.78 2.68 2.67 2.67 2.65 2.65
MeO
O
8
1H NMR (500 MHz, CDCl3)
4.15 5.96 1.98 1.94 1.00 3.05 1.96 2.06 1.96
f1 (ppm)
JM-NB3-R134BISOL-24HVAC.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima 1

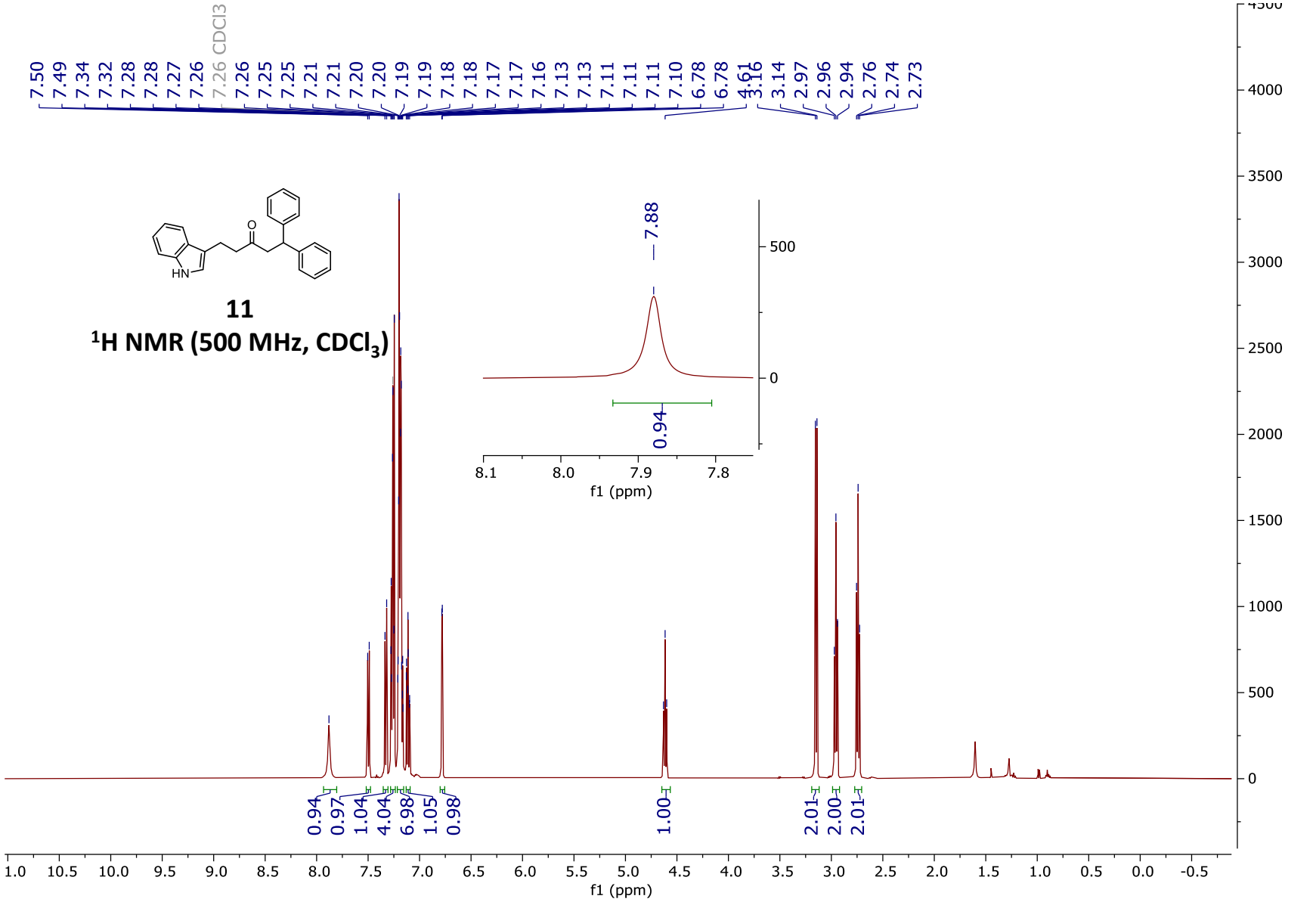

208.30
158.00
143.96
133.07
129.31
128.70
127.83
126.55
113.96
77.16 CDCl3
55.36
49.20
46.10
45.43
28.70
MeO
O
8
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB3-R134BISOL-24HVAC.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima 1

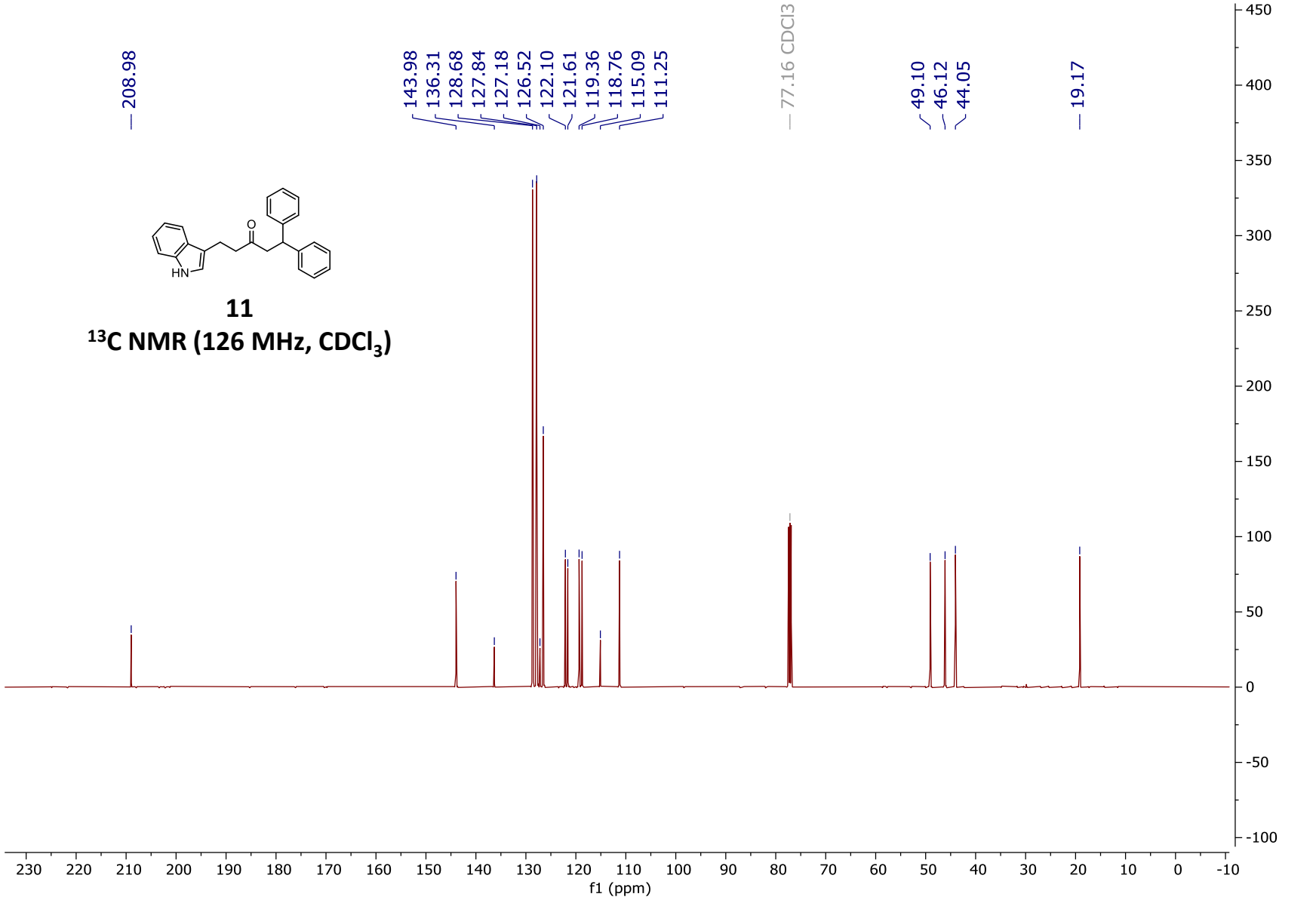

7.31
7.30
7.30
7.29
7.28
7.27
7.26
7.26
7.26 CDCl3
7.25
7.25
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.16
7.16
7.13
7.12
7.12
7.11
7.11
7.10
4.62
4.60
4.59
3.16
3.15
2.90
2.89
2.87
2.67
2.65
2.64
Cl
O
9
1H NMR (500 MHz, CDCl3)
6.32
6.07
3.06
1.01
2.02
2.04
2.03
f1 (ppm)
JM-NB4-R25B.10.fid

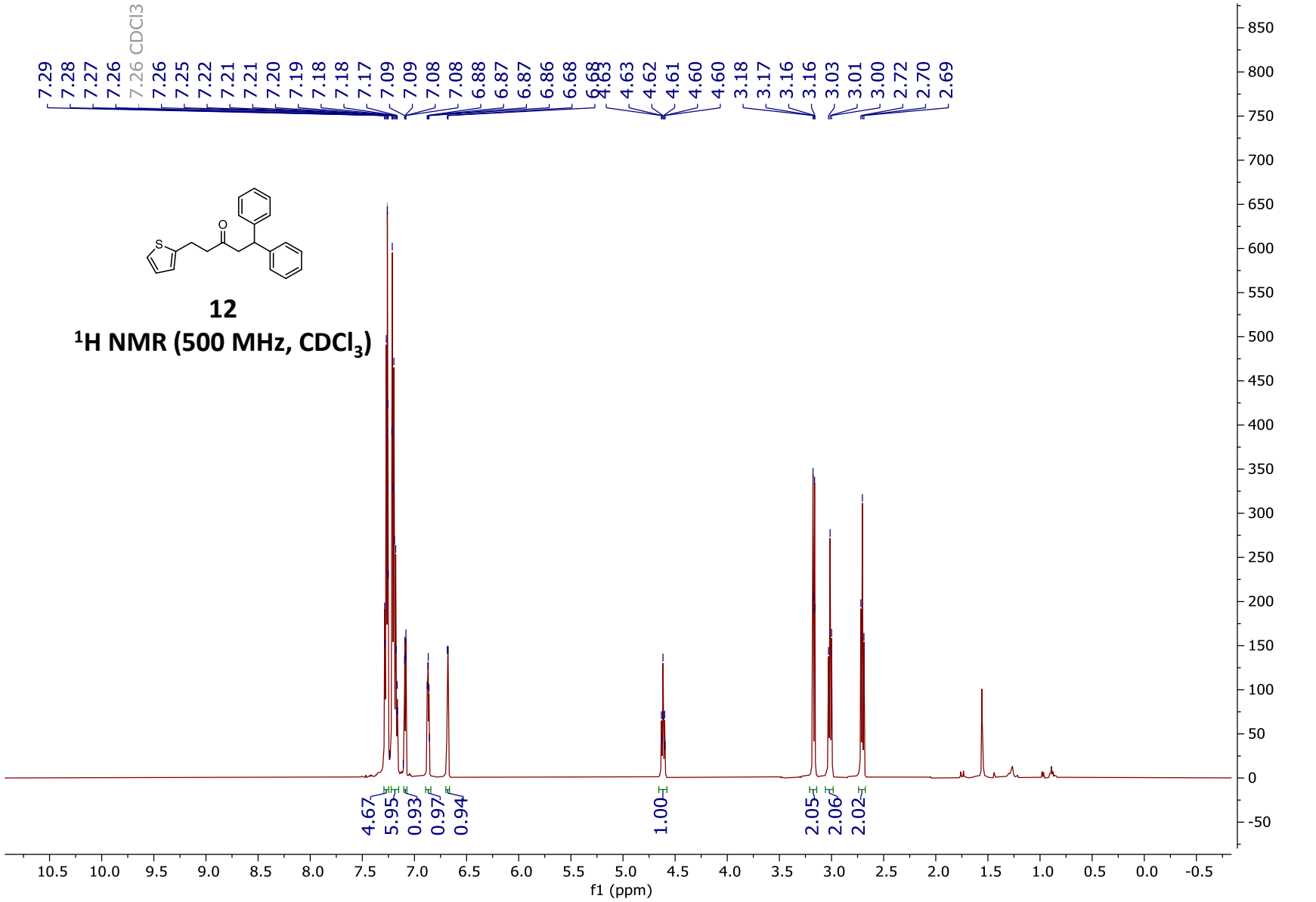

207.99
143.89
138.61
133.95
130.75
129.62
128.74
127.84
127.77
127.01
126.61
77.16 CDCl3
49.06
46.28
43.21
27.67
Cl
O
9
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB4-R25B.11.fid

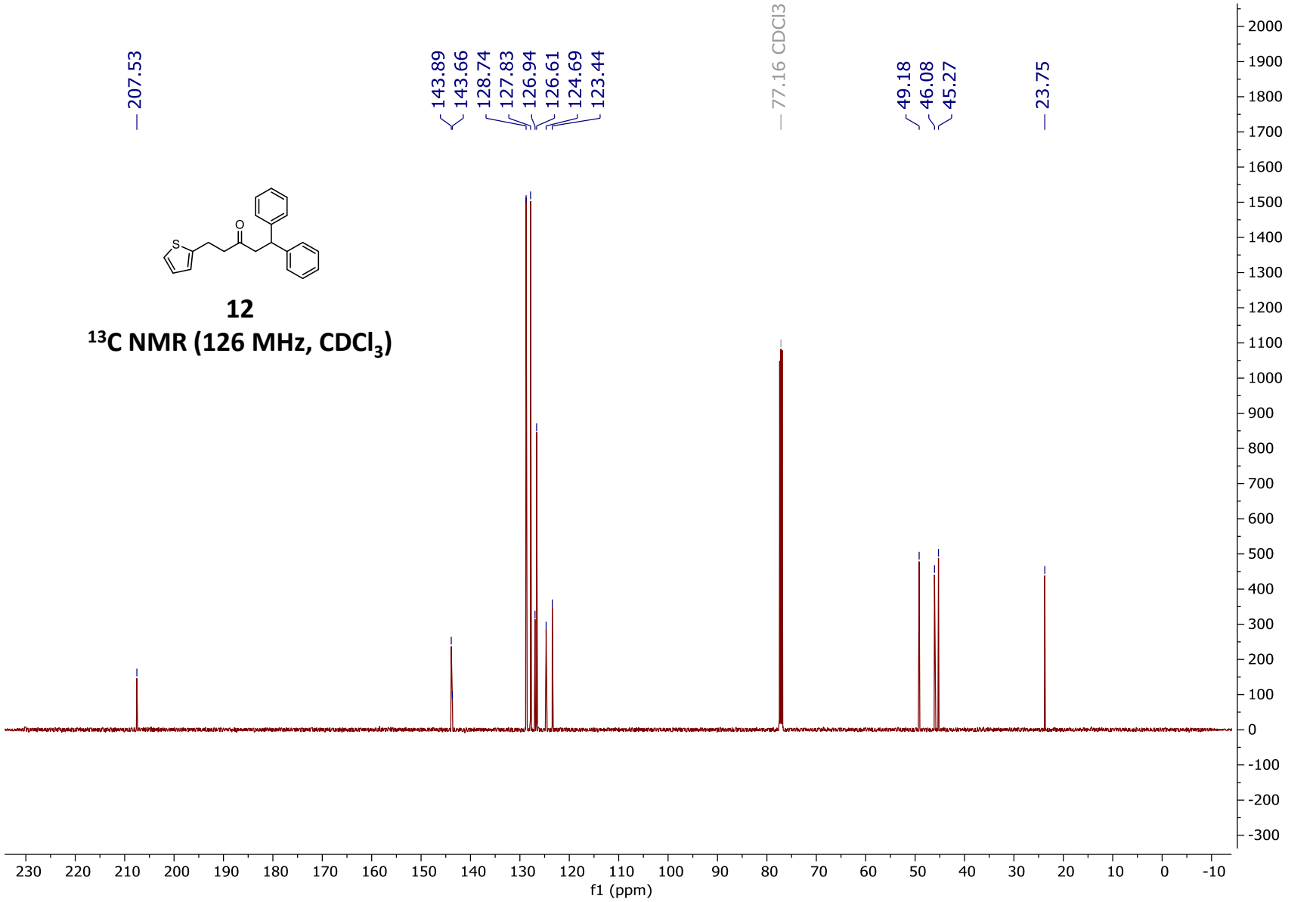

7.64
7.62
7.57
7.56
7.40
7.38
7.37
7.35
7.34
7.33
7.30
7.28
7.27
7.27
7.26 CDCl3
7.26
7.24
7.20
7.19
7.18
4.70
4.69
4.67
3.32
3.31
3.08
3.07
3.06
2.99
2.97
2.96
O
O
N
10
1H NMR (500 MHz, CDCl3)
2.09
2.03
6.11
8.37
2.06
1.00
2.03
2.00
2.01
f1 (ppm)
JM-NB5-R34B-isol.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima 1


206.76
162.31
145.43
143.88
135.12
132.59
129.07
128.72
128.66
128.51
128.14
128.00
127.80
126.58
126.55
77.16 CDCl3
49.06
45.98
39.76
22.10
O
N
O
10
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB5-R34B-isol.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima 1


7.50 7.49 7.34 7.32 7.28 7.28 7.27 7.26 7.26 CDCl3 7.26 7.25 7.25 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.13 7.13 7.11 7.11 7.11 7.10 6.78 6.78 4.61 3.16 3.14 2.97 2.96 2.94 2.76 2.74 2.73
HN
O
11
1H NMR (500 MHz, CDCl3)
7.88
0.94
f1 (ppm)
0.94 0.97 1.04 4.04 6.98 1.05 0.98 1.00 2.01 2.00 2.01
f1 (ppm)
JM-NB3-R153A.10.fid

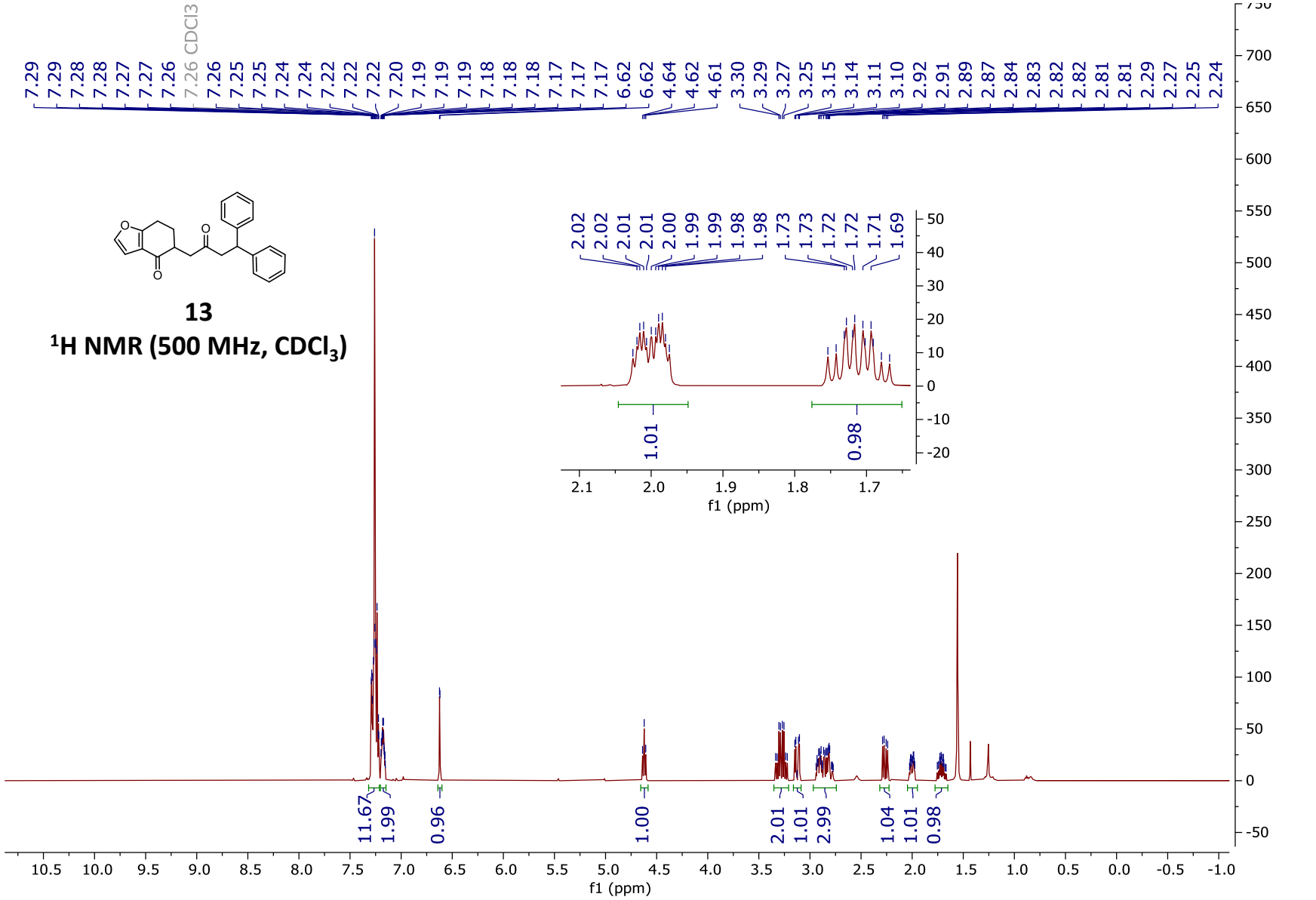

208.98
143.98
136.31
128.68
127.84
127.18
126.52
122.10
121.61
119.36
118.76
115.09
111.25
77.16 CDCl3
49.10
46.12
44.05
19.17
O
HN
11
13C NMR (126 MHz, CDCl3)
450
400
350
300
250
200
150
100
50
0
-50
-100
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
JM-NB3-R153A.11.fid

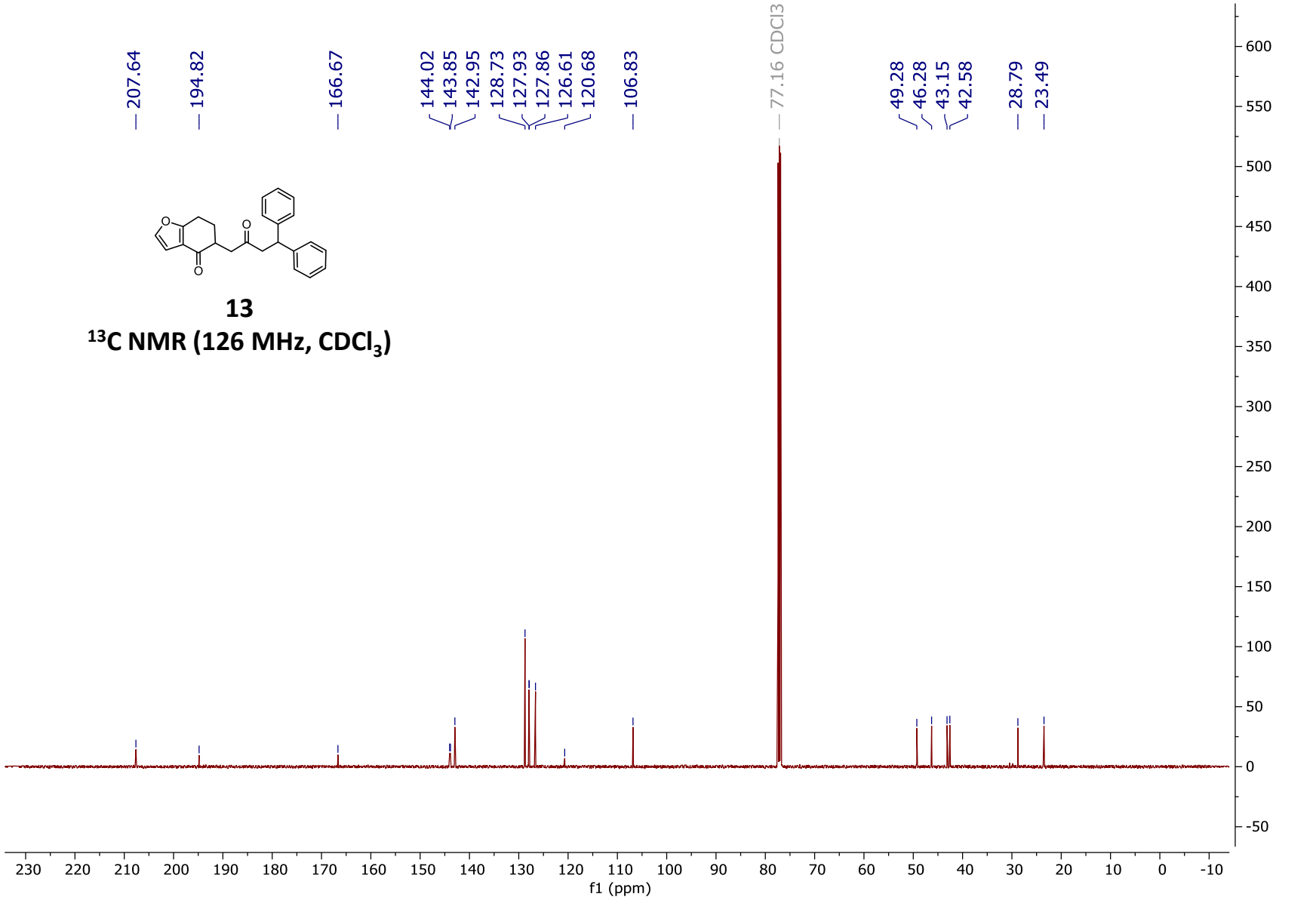

7.29 7.28 7.27 7.26 7.26 CDCl3 7.26 7.25 7.22 7.21 7.21 7.20 7.19 7.18 7.18 7.17 7.09 7.09 7.08 7.08 6.88 6.87 6.87 6.86 6.68 6.68 4.63 4.63 4.62 4.61 4.60 4.60 3.18 3.17 3.16 3.16 3.03 3.01 3.00 2.72 2.70 2.69
12
1H NMR (500 MHz, CDCl3)
4.67 5.95 0.93 0.97 0.94 1.00 2.05 2.06 2.02
f1 (ppm)
JM-NB4-R48C-ISOL.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima



12

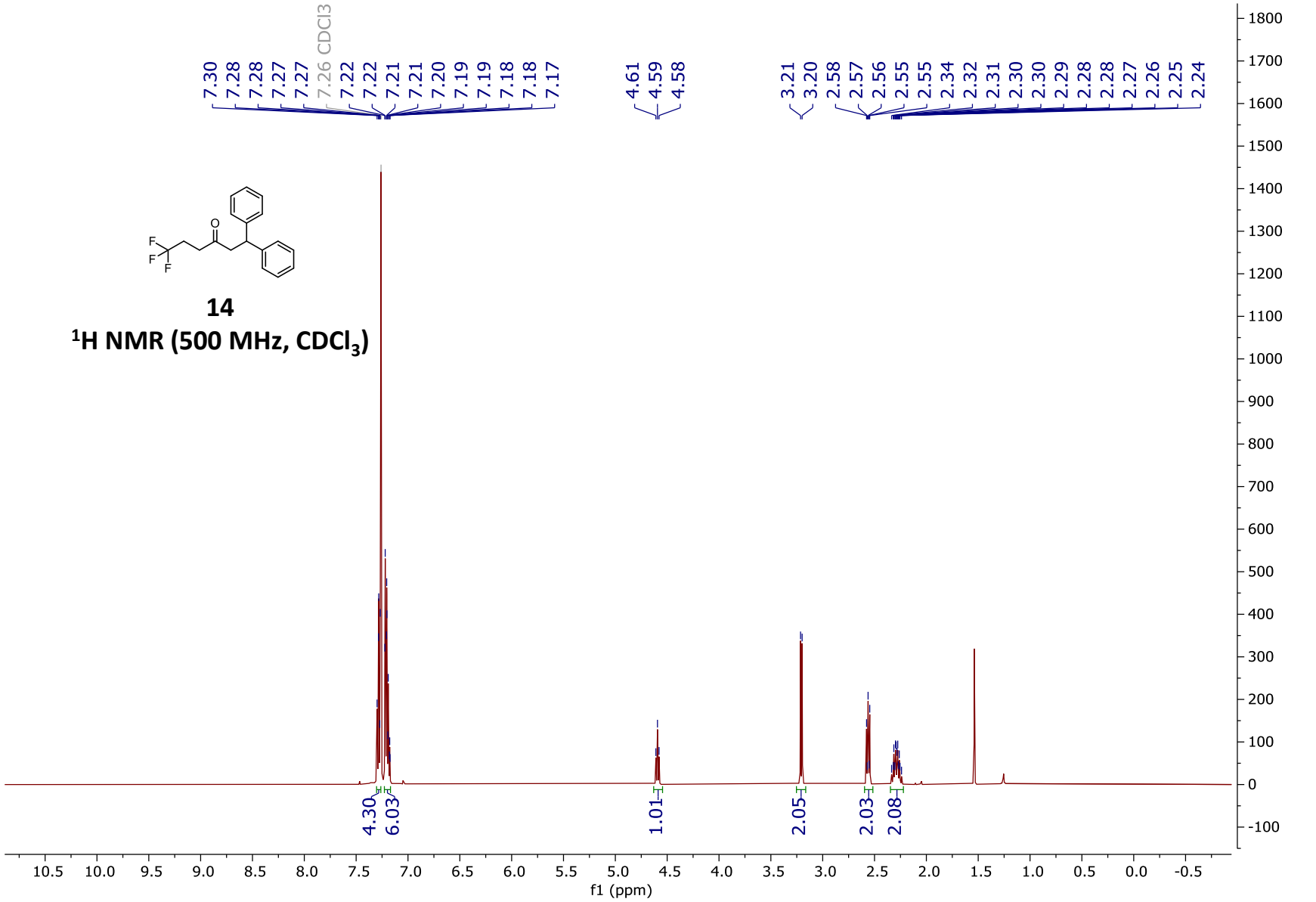
^{13}C NMR (126 MHz, $CDCl_3$)

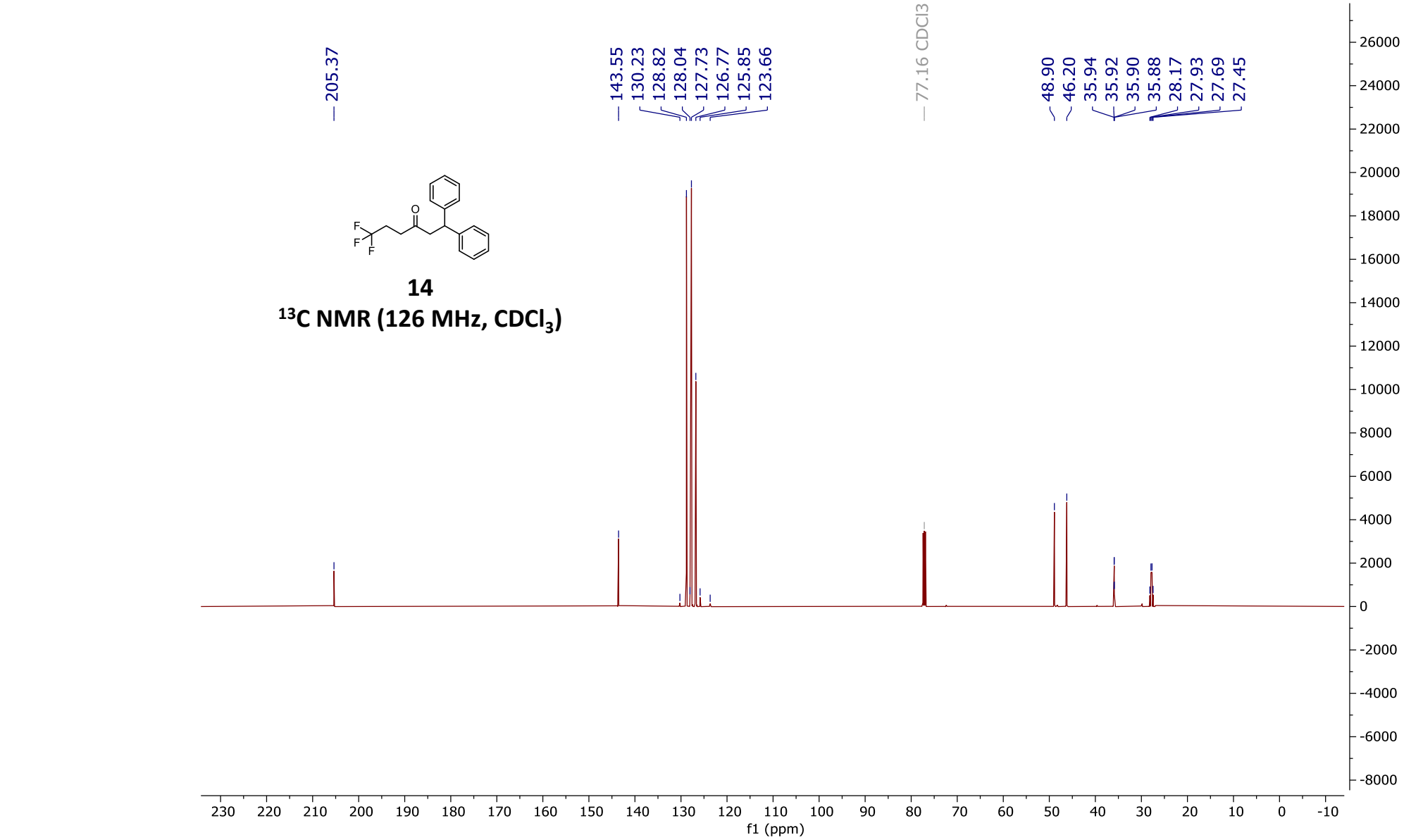

7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 CDCl3 7.26 7.25 7.25 7.24 7.24 7.22 7.22 7.22 7.20 7.19 7.19 7.19 7.18 7.18 7.18 7.17 7.17 7.17 6.62 6.62 4.64 4.62 4.61 3.30 3.29 3.27 3.25 3.15 3.14 3.11 3.10 2.92 2.91 2.89 2.87 2.84 2.83 2.82 2.82 2.81 2.81 2.29 2.27 2.25 2.24
13
1H NMR (500 MHz, CDCl3)
2.02 2.02 2.01 2.01 2.00 1.99 1.99 1.98 1.98 1.73 1.73 1.72 1.72 1.71 1.69
1.01
0.98
f1 (ppm)
11.67
1.99
0.96
1.00
2.01
1.01
2.99
1.04
1.01
0.98
f1 (ppm)
JM-NB4-R49B.10.fid

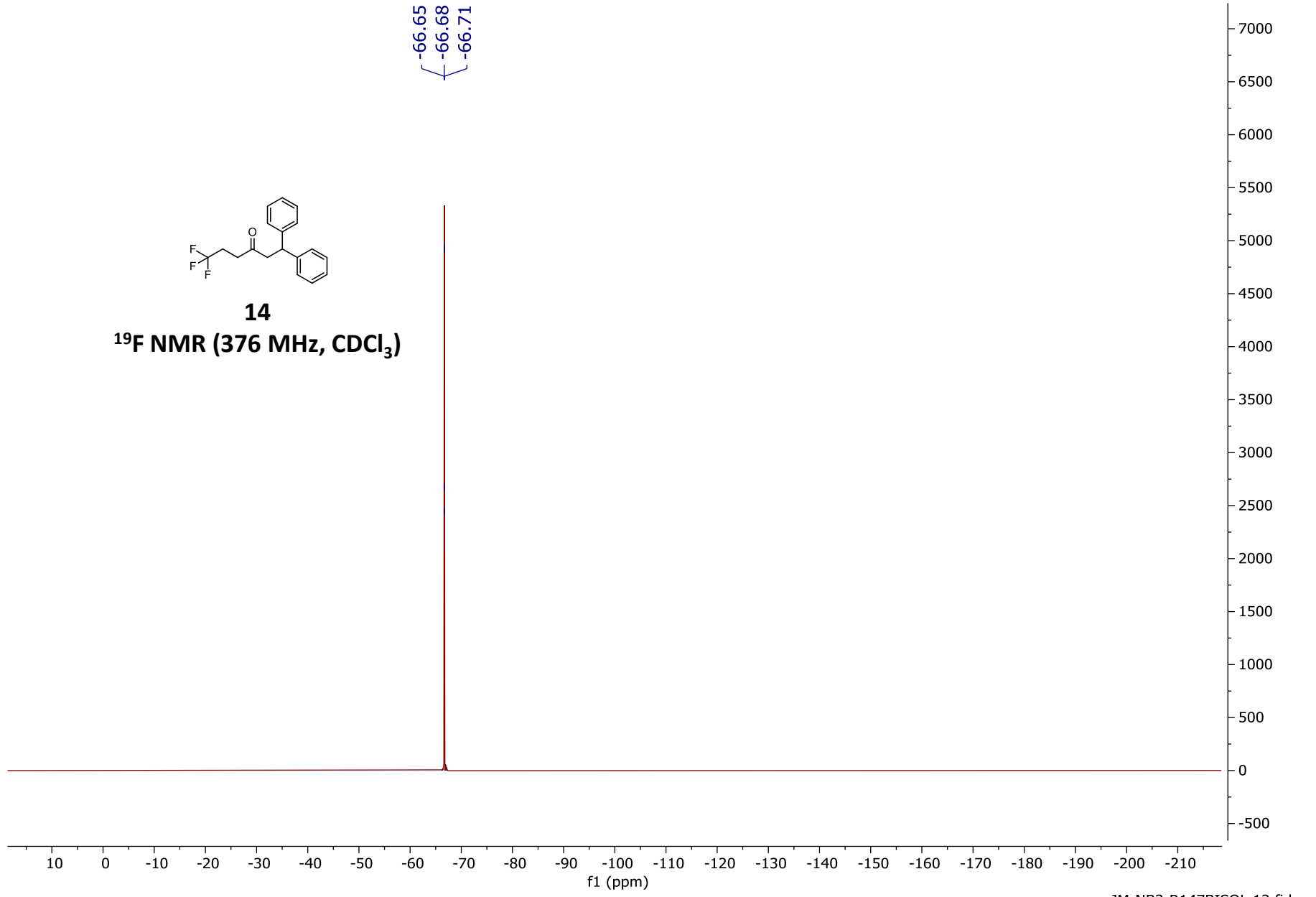


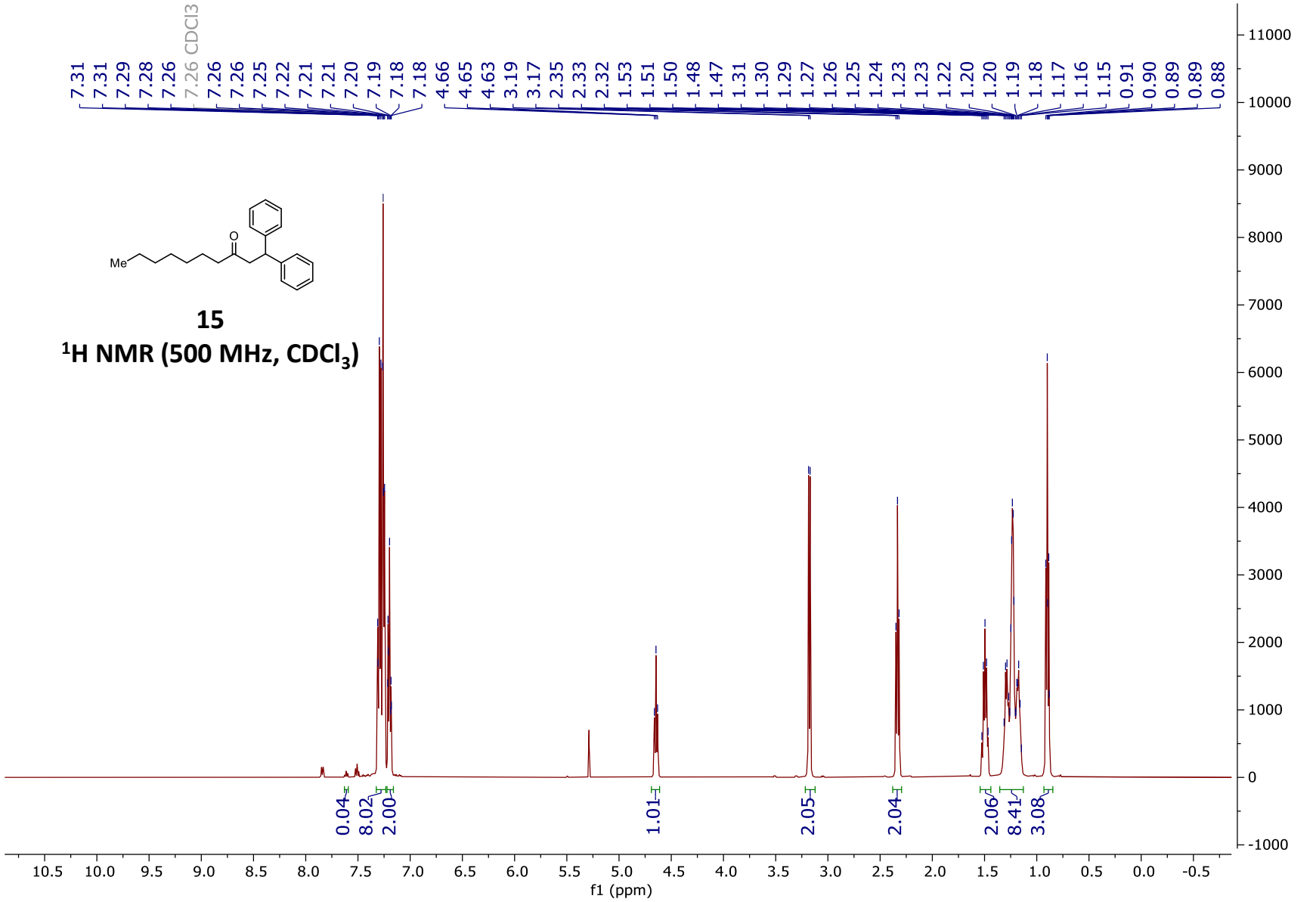
13

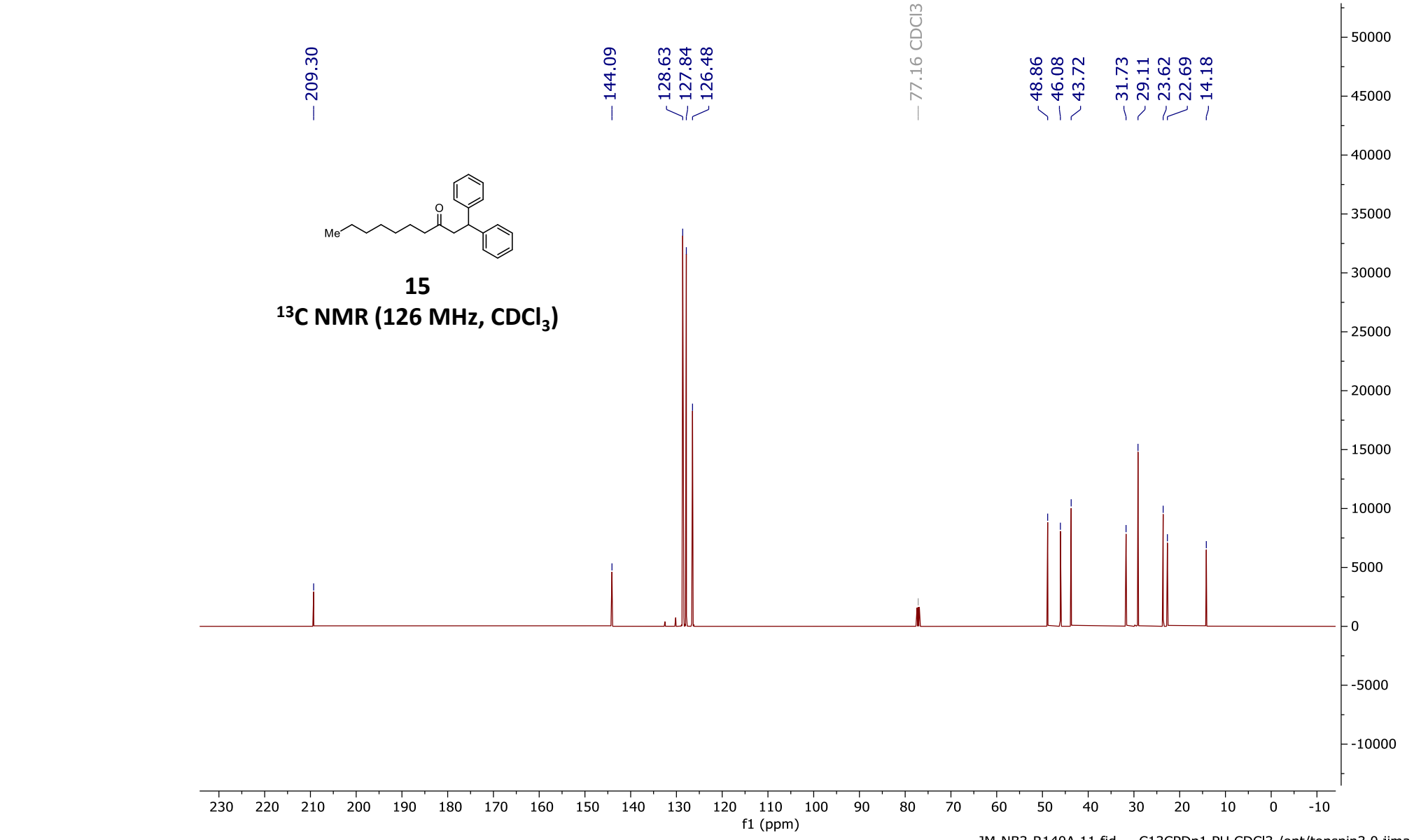
^{13}C NMR (126 MHz, $CDCl_3$)

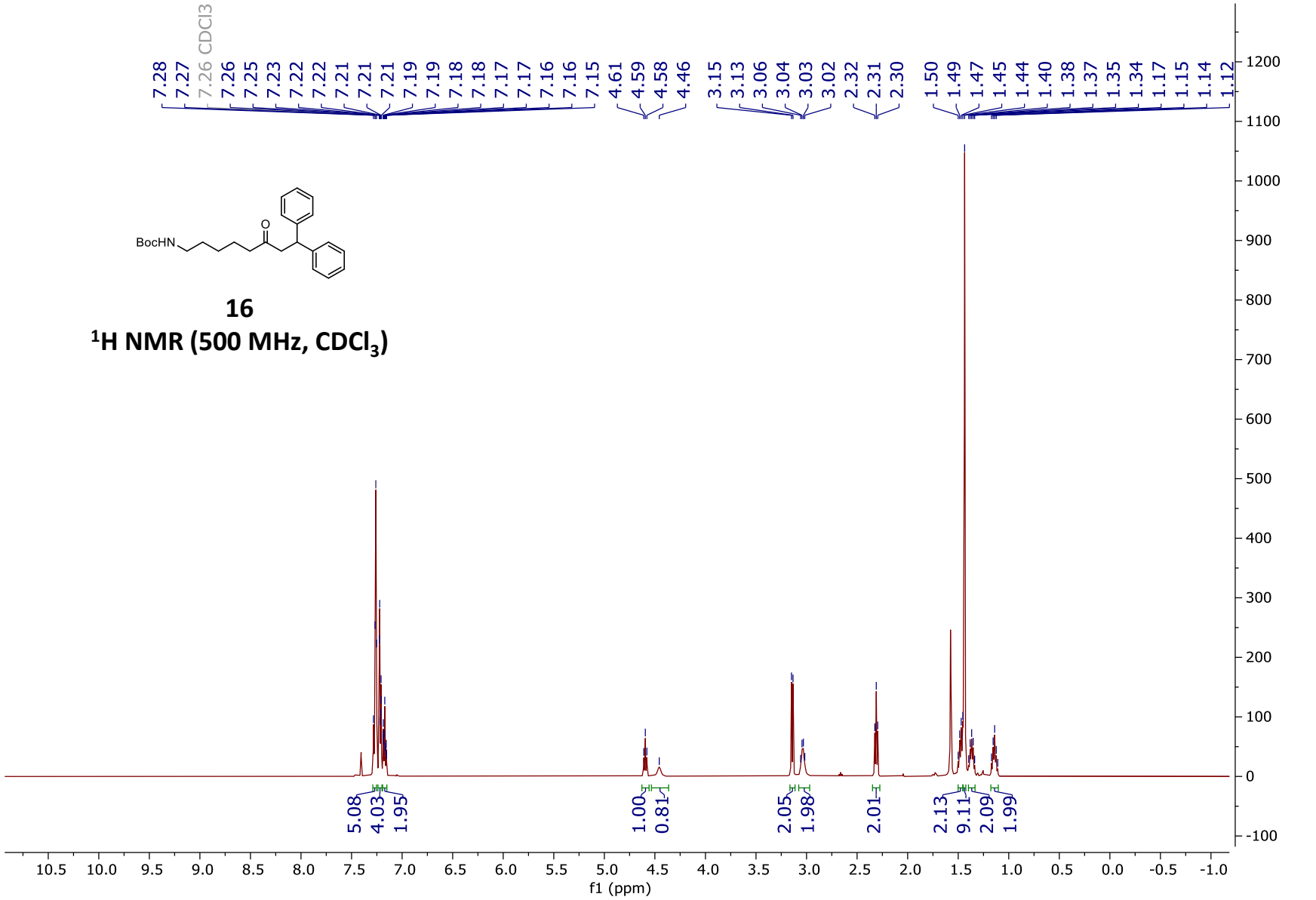

7.30
7.28
7.28
7.27
7.27
7.26 CDCl3
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.18
7.17
4.61
4.59
4.58
3.21
3.20
2.58
2.57
2.56
2.55
2.55
2.34
2.32
2.31
2.30
2.30
2.29
2.28
2.28
2.27
2.26
2.25
2.24
F
F
F
O
14
1H NMR (500 MHz, CDCl3)
4.30
6.03
1.01
2.05
2.03
2.08
f1 (ppm)
JM-NB3-R147BISOL.20.fid


205.37
143.55
130.23
128.82
128.04
127.73
126.77
125.85
123.66
77.16 CDCl3
48.90
46.20
35.94
35.92
35.90
35.88
28.17
27.93
27.69
27.45
O
F
F
F
14
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB3-R147CARBON.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima


-66.65
-66.68
-66.71
O
F
F
F
14
19F NMR (376 MHz, CDCl3)
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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)
JM-NB3-R147BISOL.12.fid —

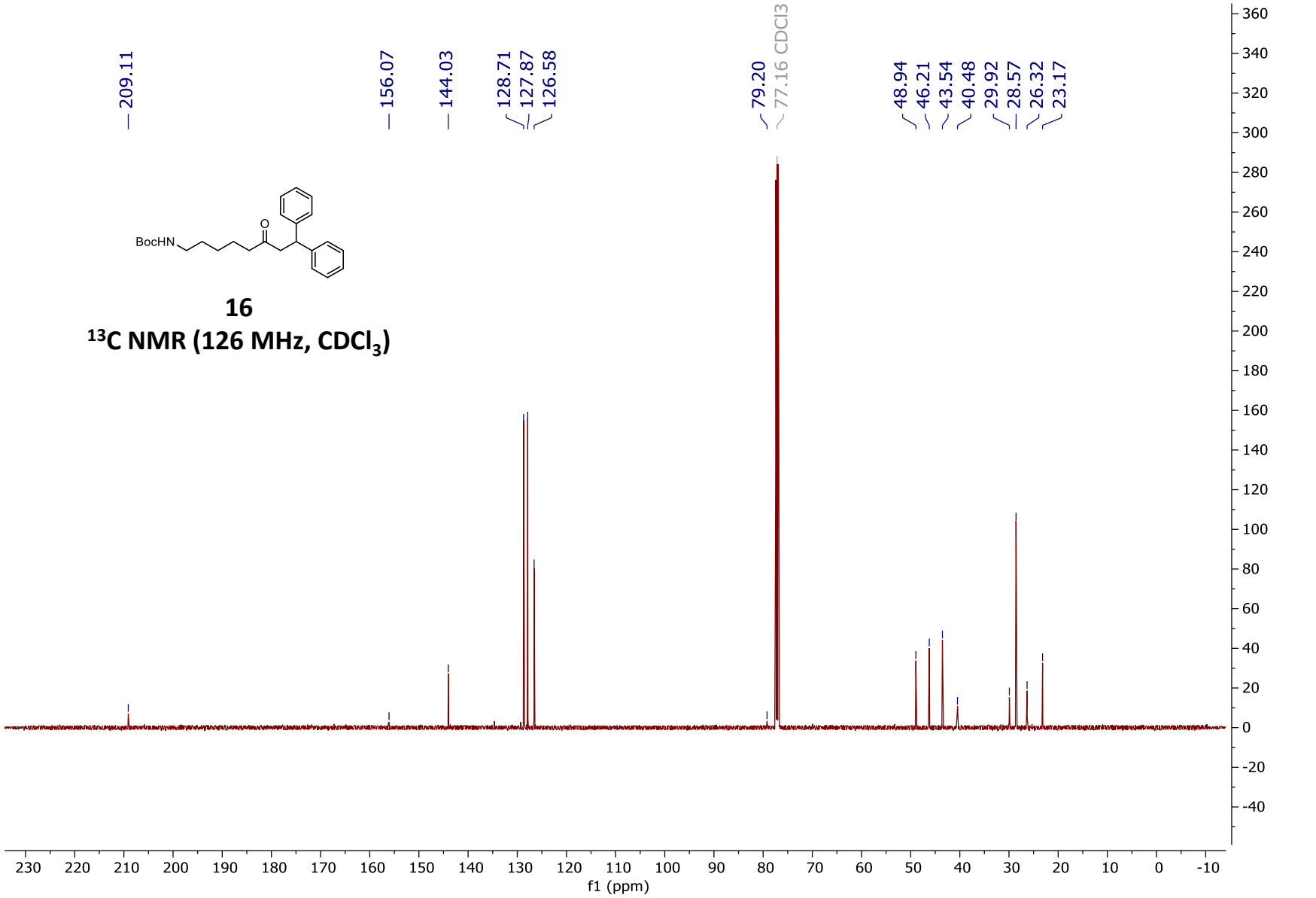

7.31 7.31 7.29 7.28 7.26 7.26 CDCl3 7.26 7.26 7.25 7.22 7.21 7.21 7.20 7.19 7.18 7.18 4.66 4.65 4.63 3.19 3.17 2.35 2.33 2.32 1.53 1.51 1.50 1.48 1.47 1.31 1.30 1.29 1.27 1.26 1.25 1.24 1.23 1.23 1.22 1.20 1.20 1.19 1.18 1.17 1.16 1.15 0.91 0.90 0.89 0.89 0.88
Me
O
15
1H NMR (500 MHz, CDCl3)
0.04 8.02 2.00 1.01 2.05 2.04 2.06 8.41 3.08
f1 (ppm)
JM-NB3-R140A.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima


209.30
144.09
128.63
127.84
126.48
77.16 CDCl3
48.86
46.08
43.72
31.73
29.11
23.62
22.69
14.18
O
Me
15
13C NMR (126 MHz, CDCl3)
50000
45000
40000
35000
30000
25000
20000
15000
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)
JM-NB3-R140A.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima



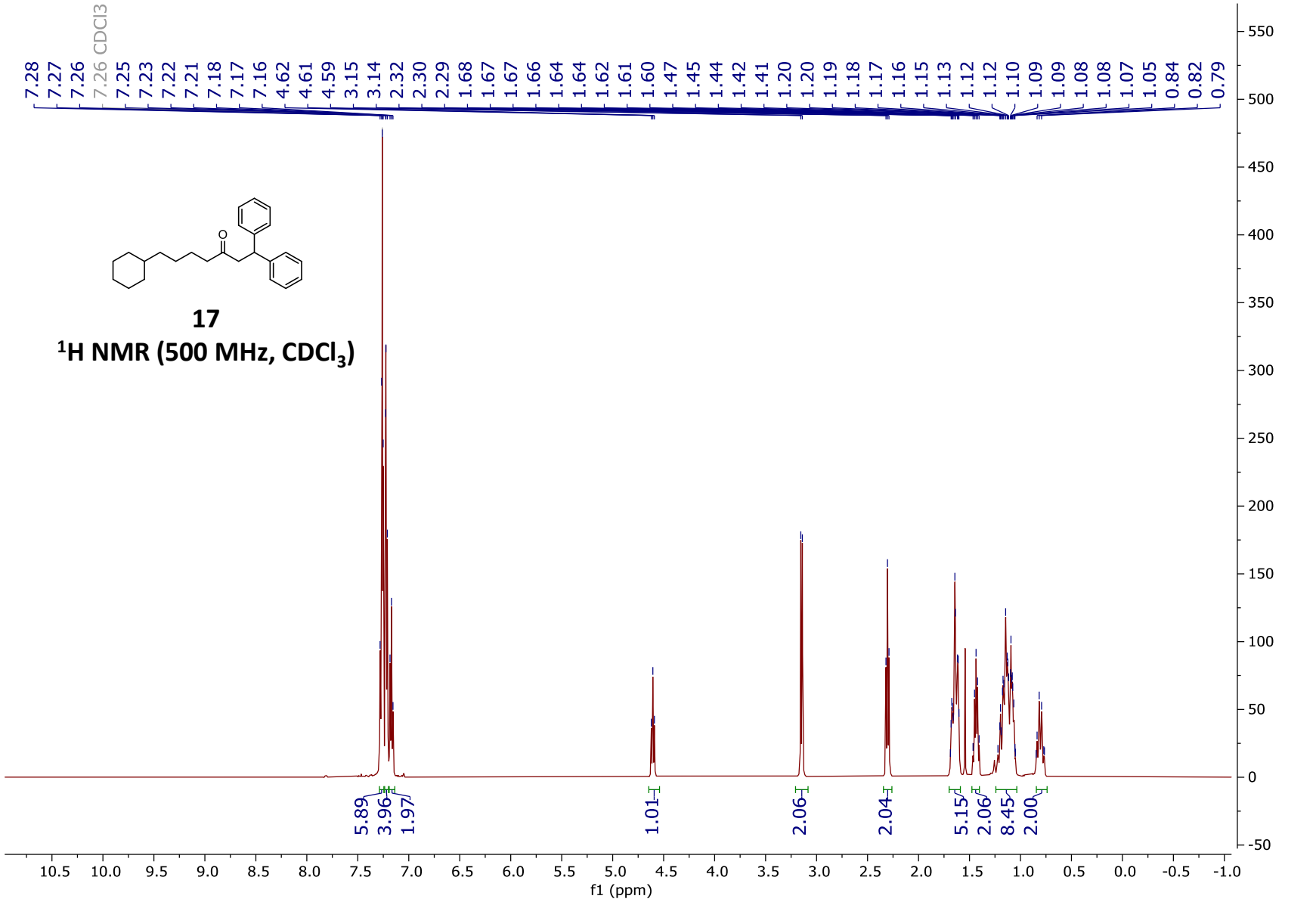
16

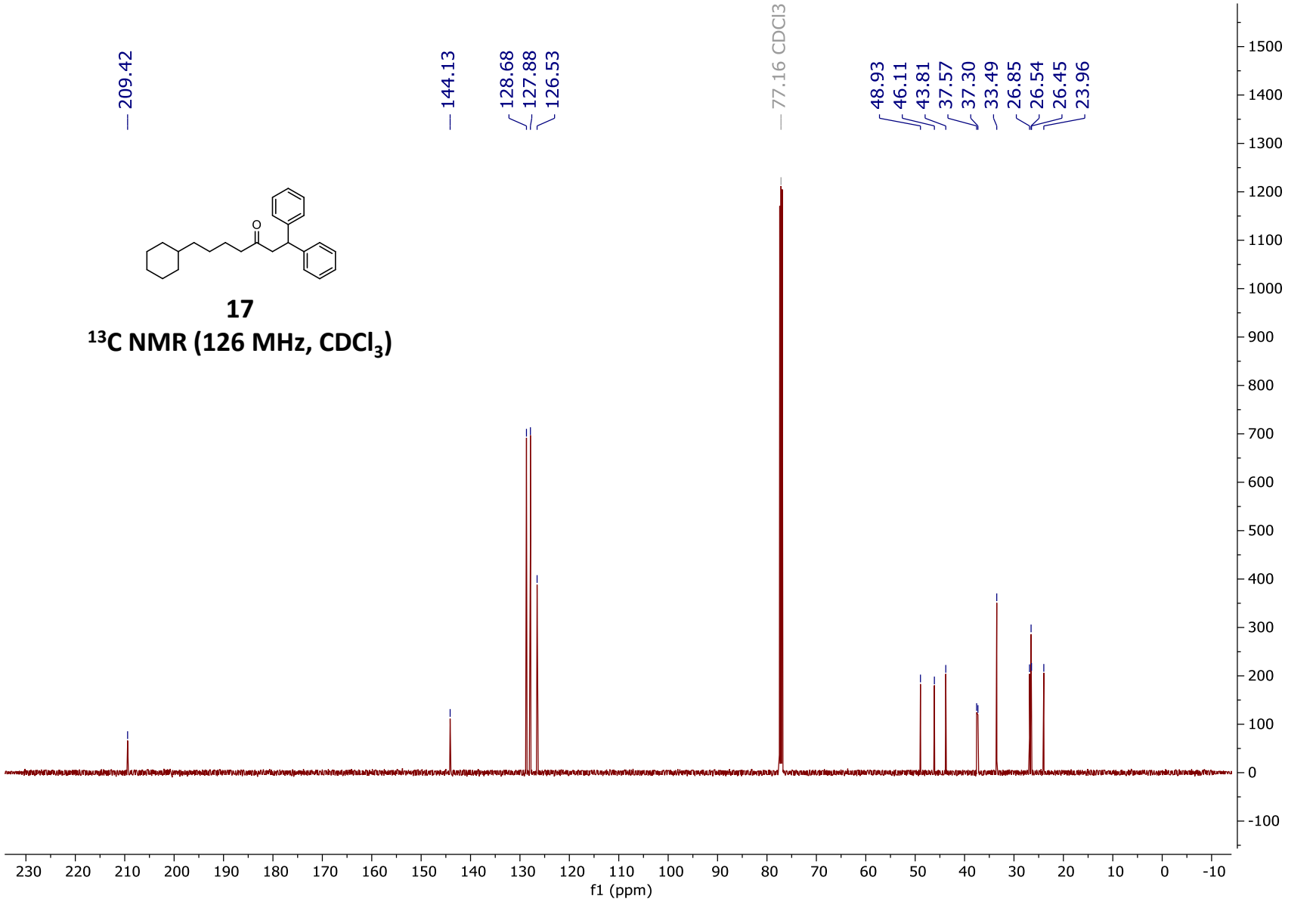
^{1}H NMR (500 MHz, $CDCl_3$)

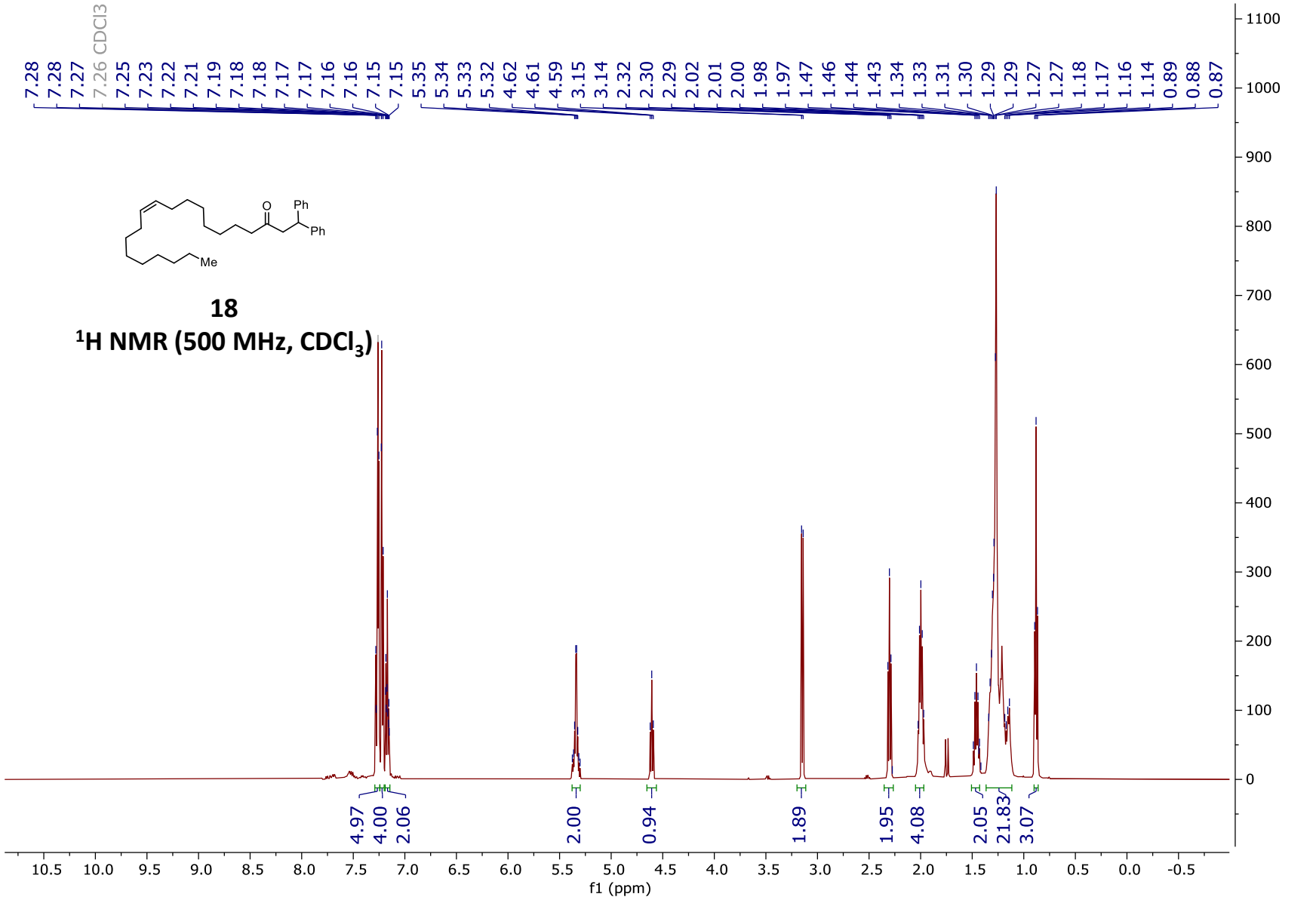


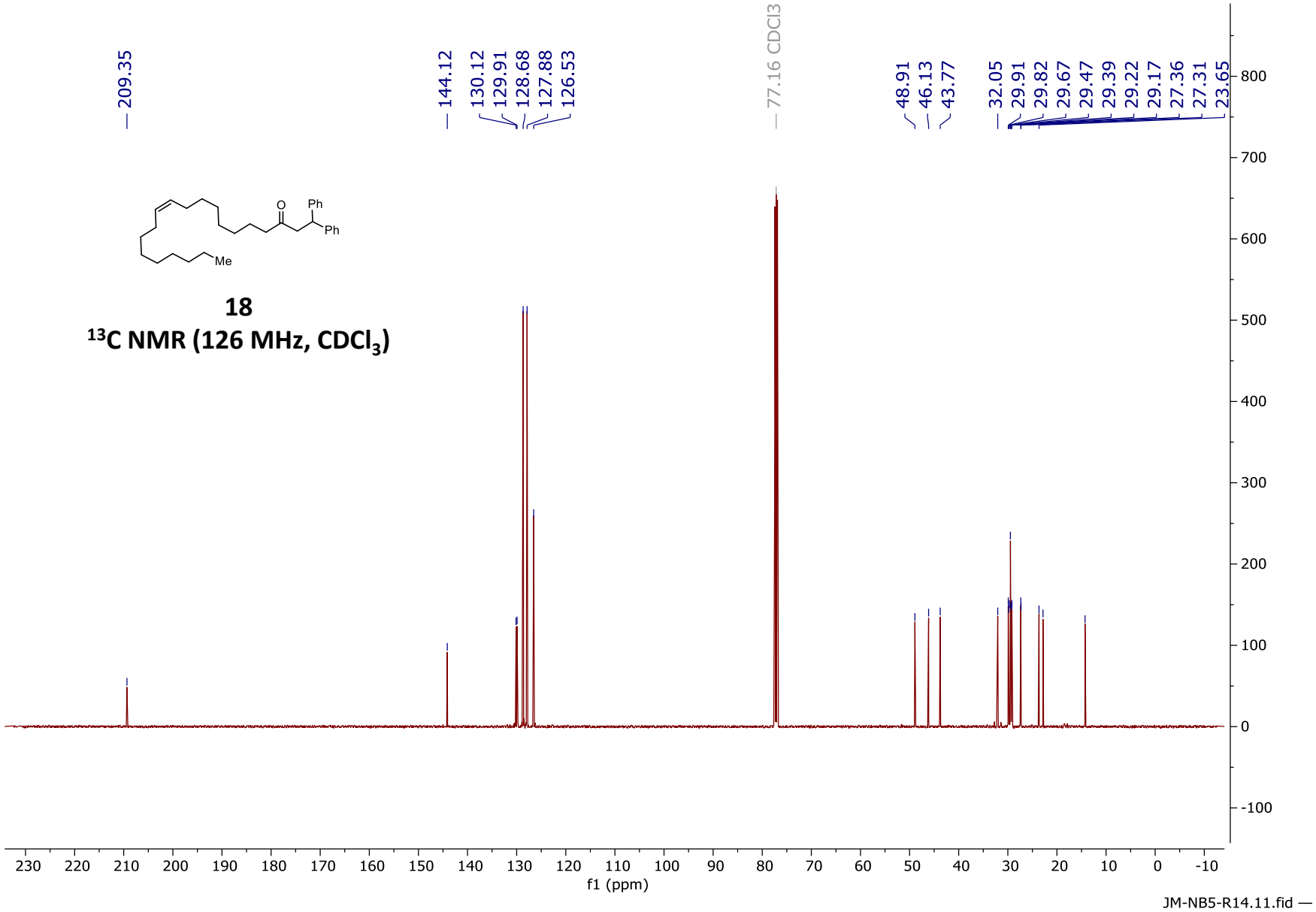
16

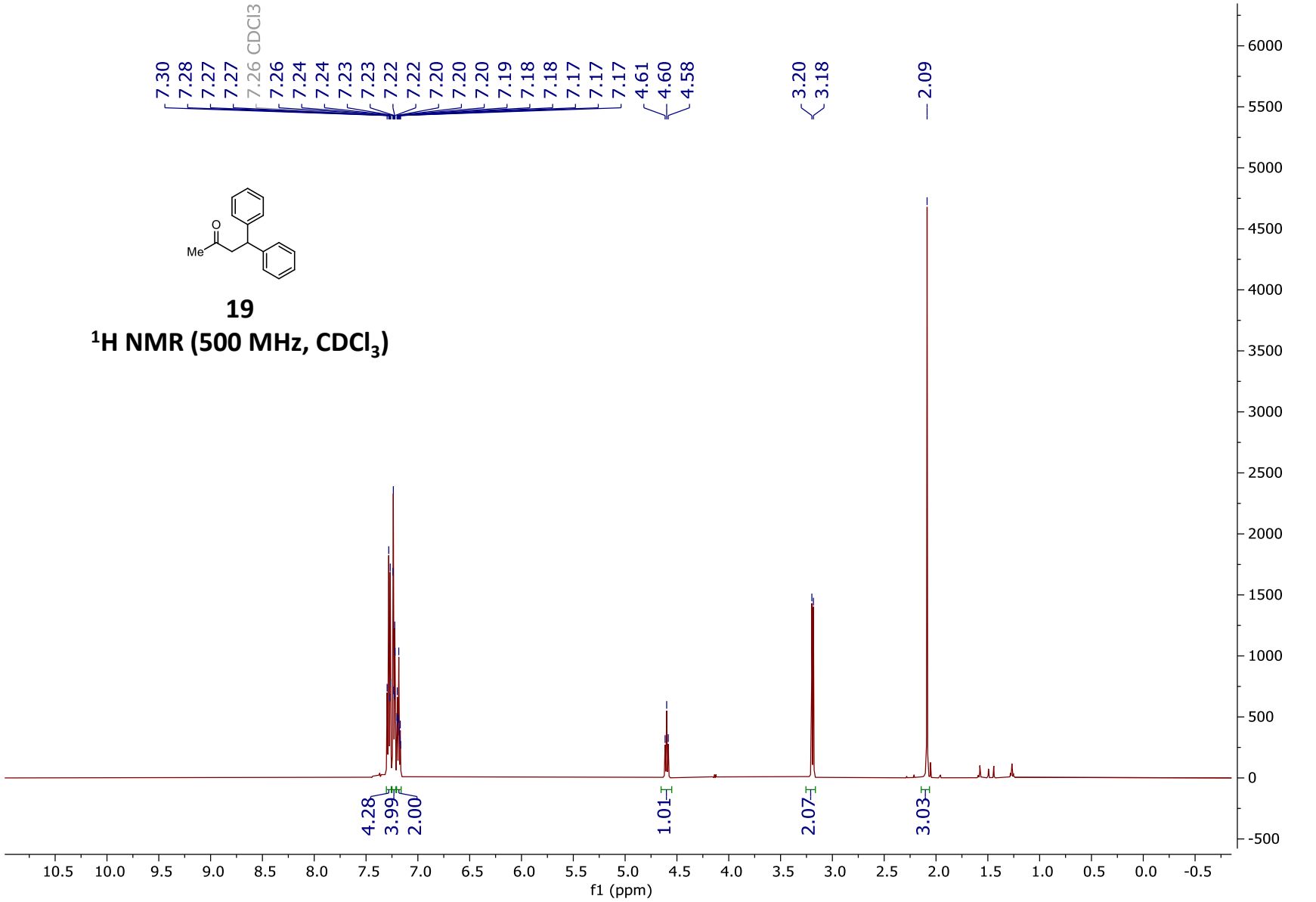
^{13}C NMR (126 MHz, $CDCl_3$)


7.28 7.27 7.26 7.26 CDCl3 7.25 7.23 7.22 7.21 7.18 7.17 7.16 4.62 4.61 4.59 3.15 3.14 2.32 2.30 2.29 1.68 1.67 1.67 1.66 1.64 1.64 1.62 1.61 1.60 1.47 1.45 1.44 1.42 1.41 1.20 1.20 1.19 1.18 1.17 1.16 1.15 1.13 1.12 1.12 1.10 1.09 1.09 1.08 1.08 1.07 1.05 0.84 0.82 0.79
O
17
1H NMR (500 MHz, CDCl3)
5.89 3.96 1.97 1.01 2.06 2.04 5.15 2.06 8.45 2.00
f1 (ppm)
JM-NB3-R145BISOL.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima


209.42
144.13
128.68
127.88
126.53
77.16 CDCl3
48.93
46.11
43.81
37.57
37.30
33.49
26.85
26.54
26.45
23.96
O
17
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB3-R145BISOL.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima

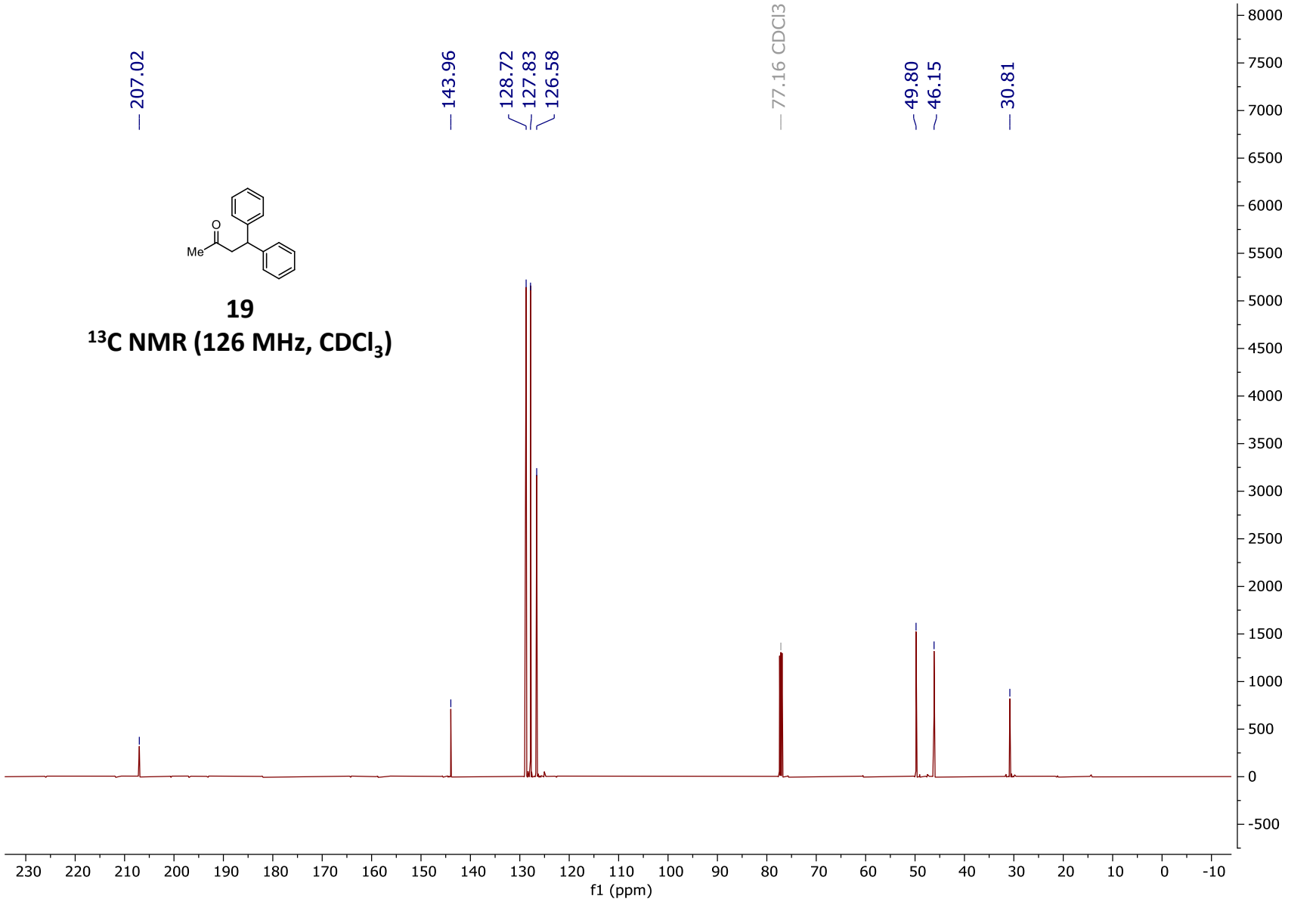

7.28 7.28 7.27 7.26 CDCl3 7.25 7.23 7.22 7.21 7.19 7.18 7.18 7.17 7.17 7.16 7.16 7.15 7.15
5.35 5.34 5.33 5.32 4.62 4.61 4.59 3.15 3.14 2.32 2.30 2.29 2.02 2.01 2.00 1.98 1.97 1.47 1.46 1.44 1.43 1.34 1.33 1.31 1.30 1.29 1.29 1.27 1.27 1.18 1.17 1.16 1.14 0.89 0.88 0.87
O
Ph
Ph
Me
18
1H NMR (500 MHz, CDCl3)
4.97 4.00 2.06 2.00 0.94 1.89 1.95 4.08 2.05 21.83 3.07
f1 (ppm)
JM-NB5-R14.10.fid


209.35
144.12
130.12
129.91
128.68
127.88
126.53
77.16 CDCl3
48.91
46.13
43.77
32.05
29.91
29.82
29.67
29.47
29.39
29.22
29.17
27.36
27.31
23.65
O
Ph
Ph
Me
18
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB5-R14.11.fid



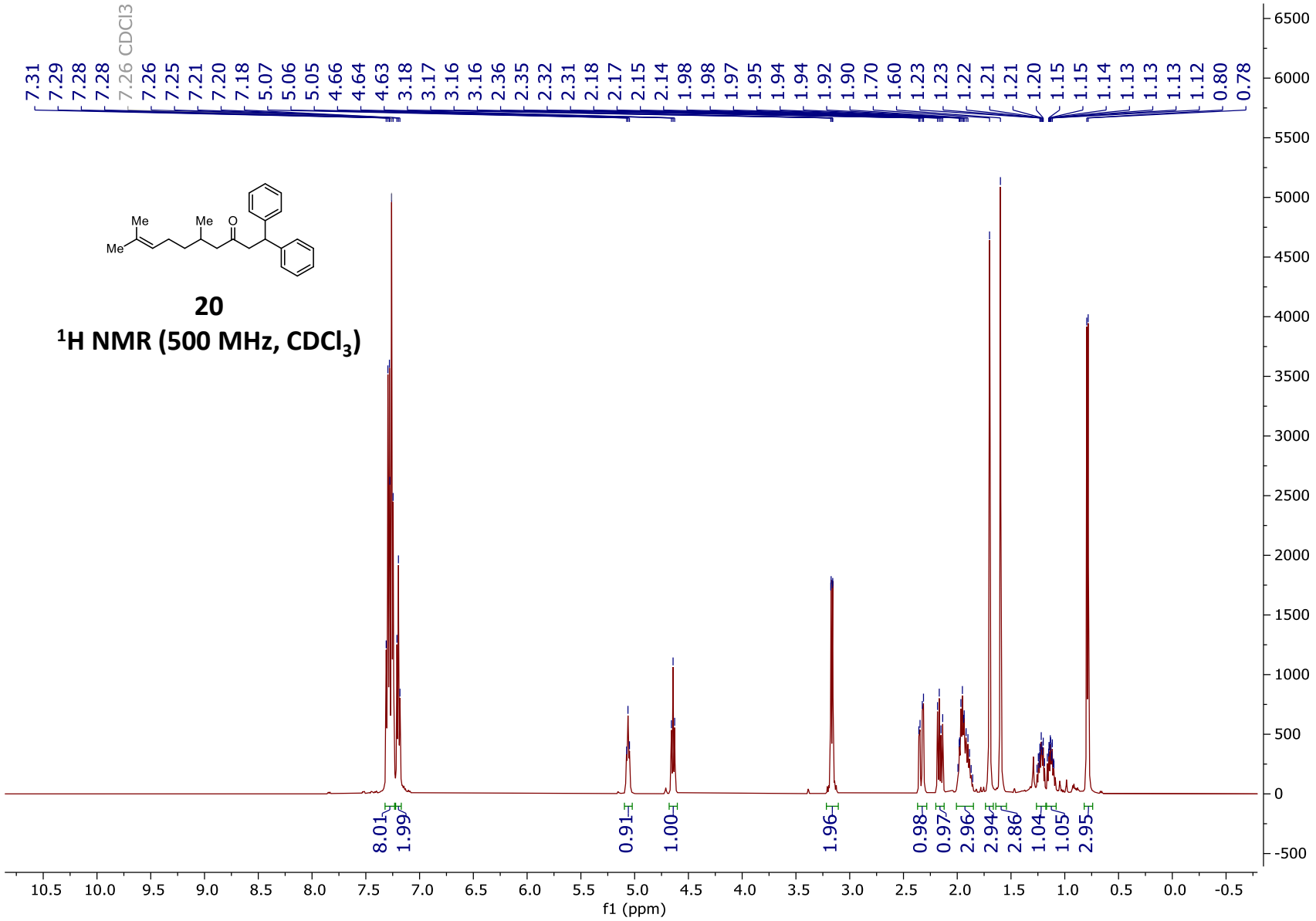
19

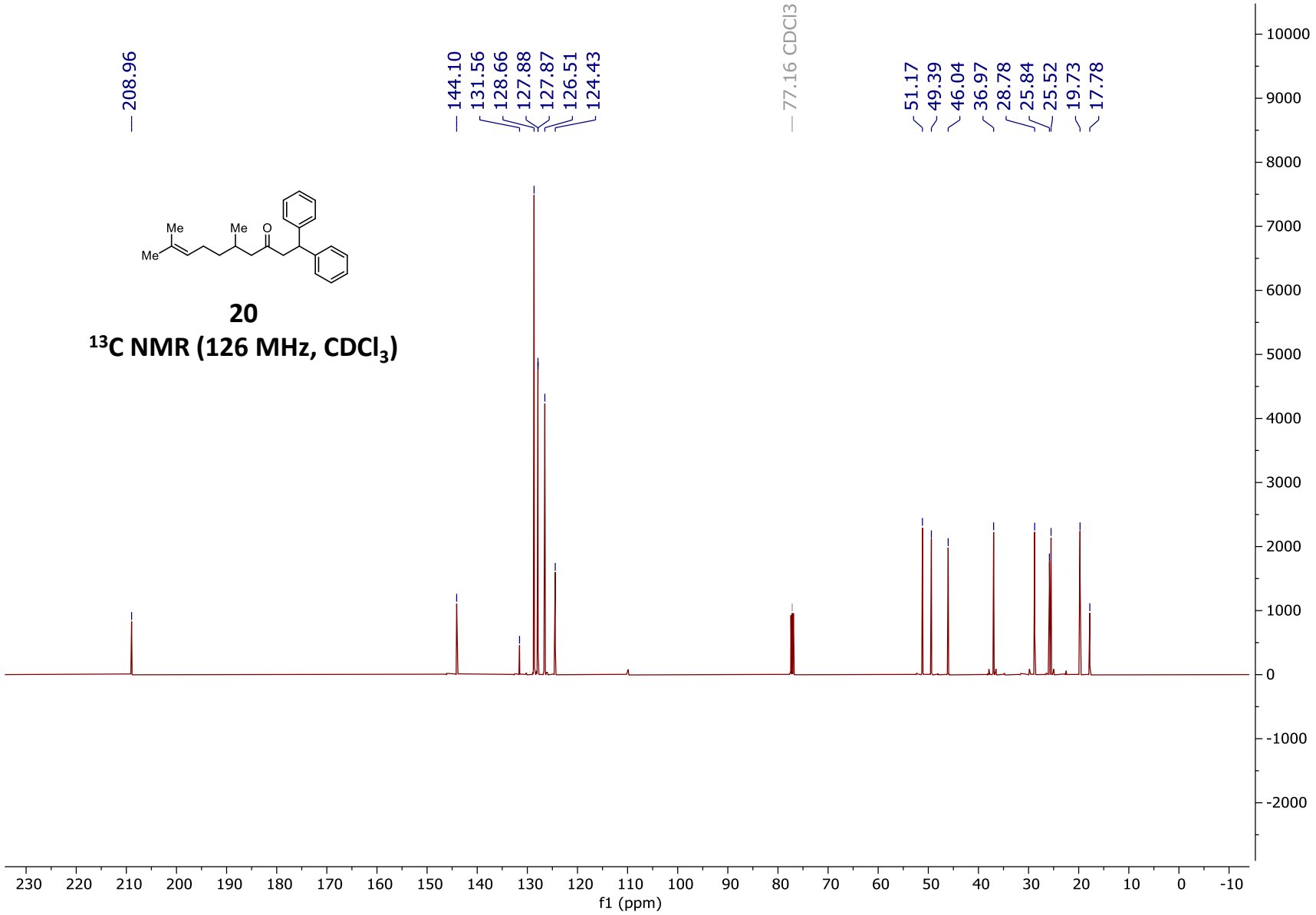
^{1}H NMR (500 MHz, $CDCl_3$)



19

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

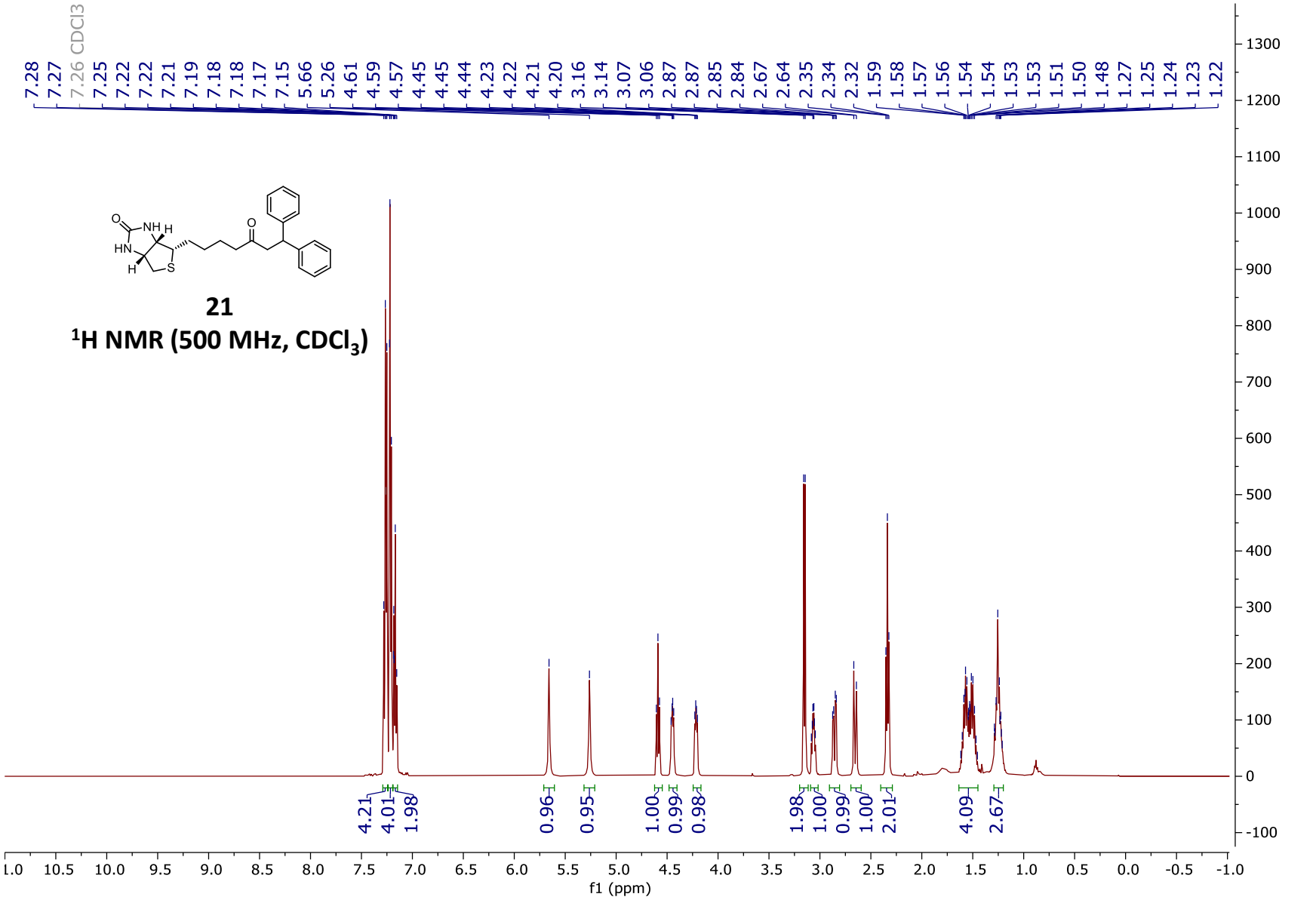

7.31 7.29 7.28 7.28 7.26 CDCl3 7.26 7.25 7.21 7.20 7.18 5.07 5.06 5.05 4.66 4.64 4.63 3.18 3.17 3.16 3.16 2.36 2.35 2.32 2.31 2.18 2.17 2.15 2.14 1.98 1.98 1.97 1.95 1.94 1.94 1.92 1.90 1.70 1.60 1.23 1.23 1.22 1.21 1.21 1.20 1.15 1.15 1.14 1.13 1.13 1.13 1.12 0.80 0.78
Me
Me
O
Me
20
1H NMR (500 MHz, CDCl3)
8.01 1.99 0.91 1.00 1.96 0.98 0.97 2.96 2.94 2.86 1.04 1.05 2.95
f1 (ppm)
JM-NB3-R177A.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima 1

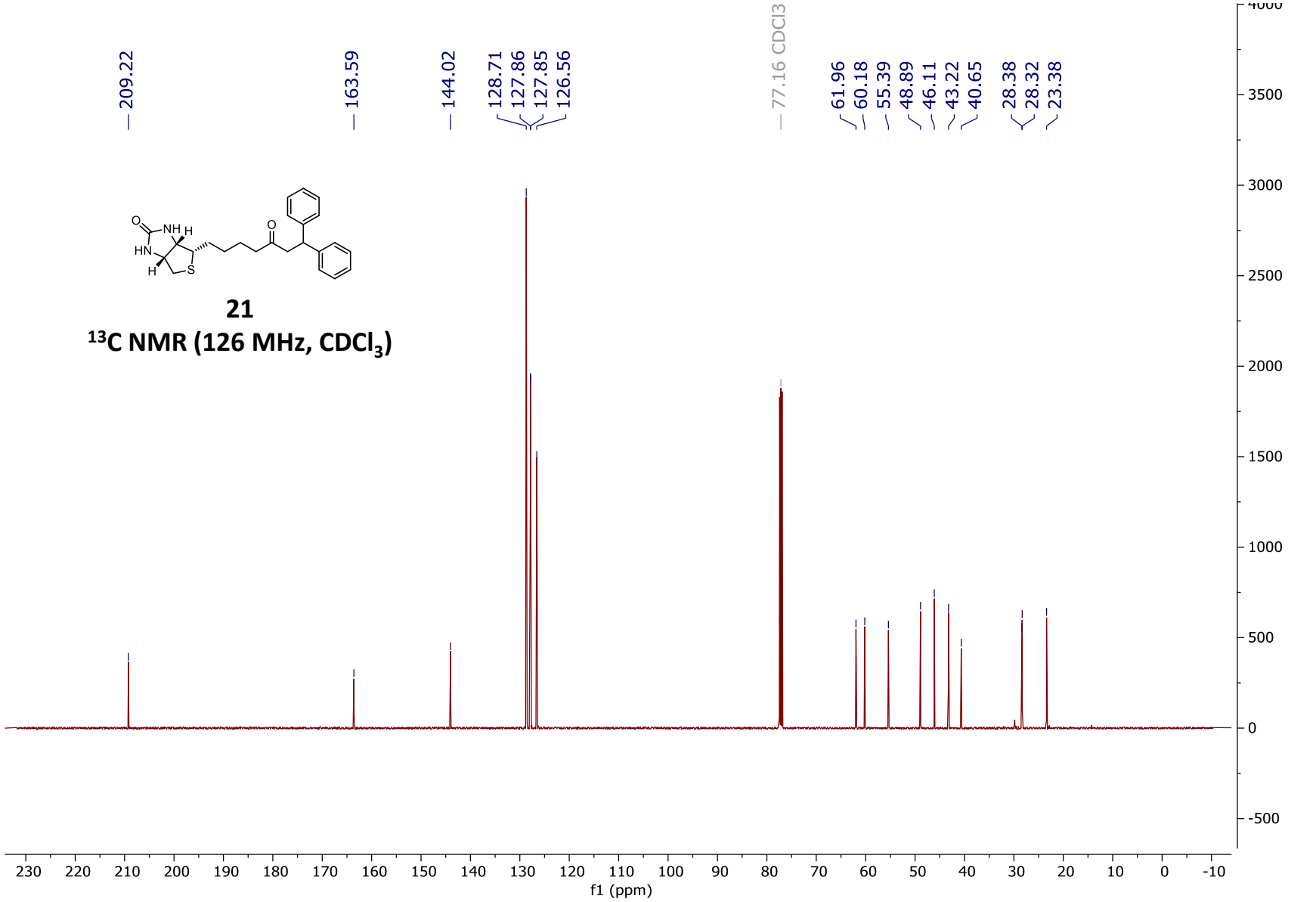


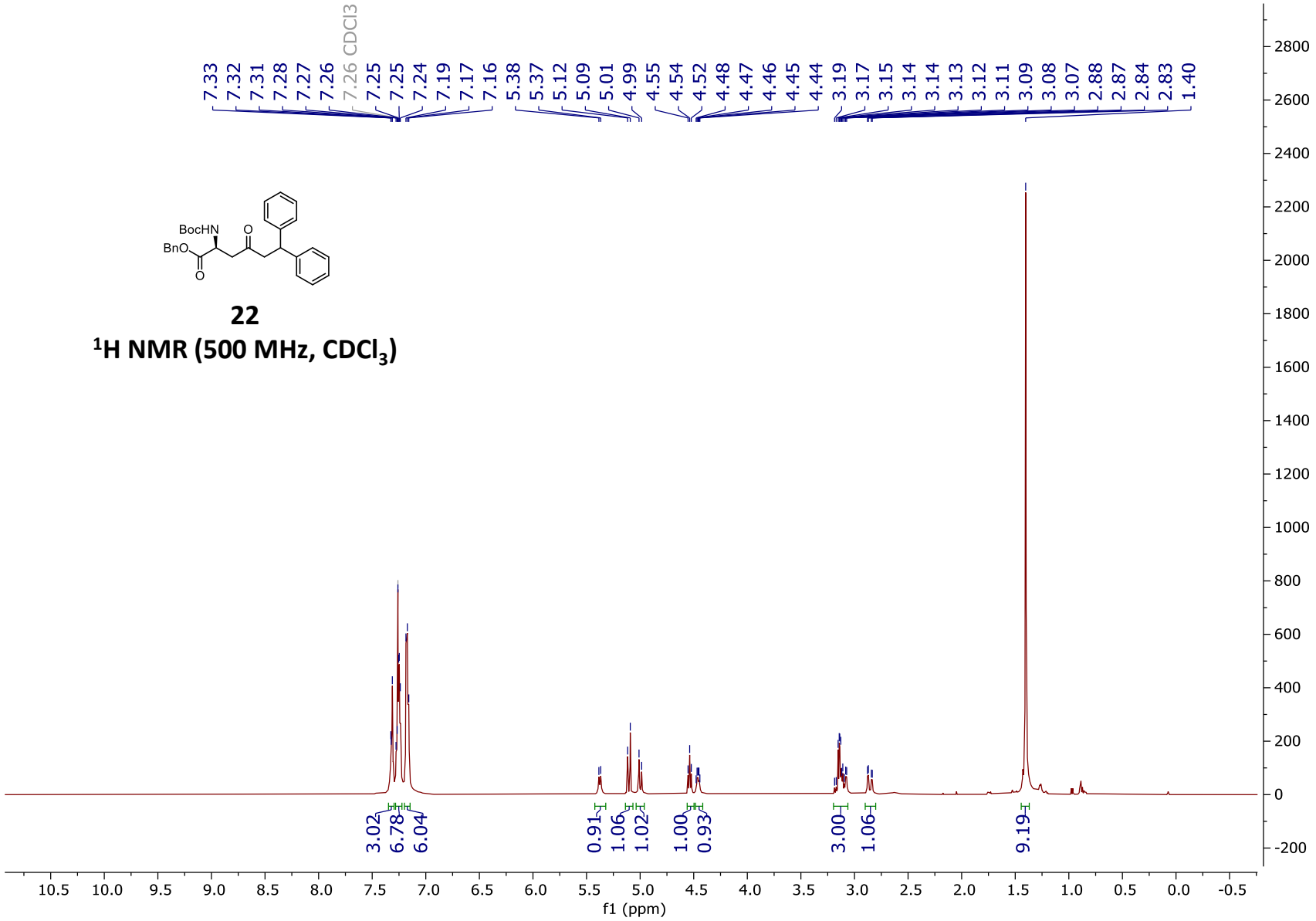
20

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

JM-NB3-R177A.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima 1

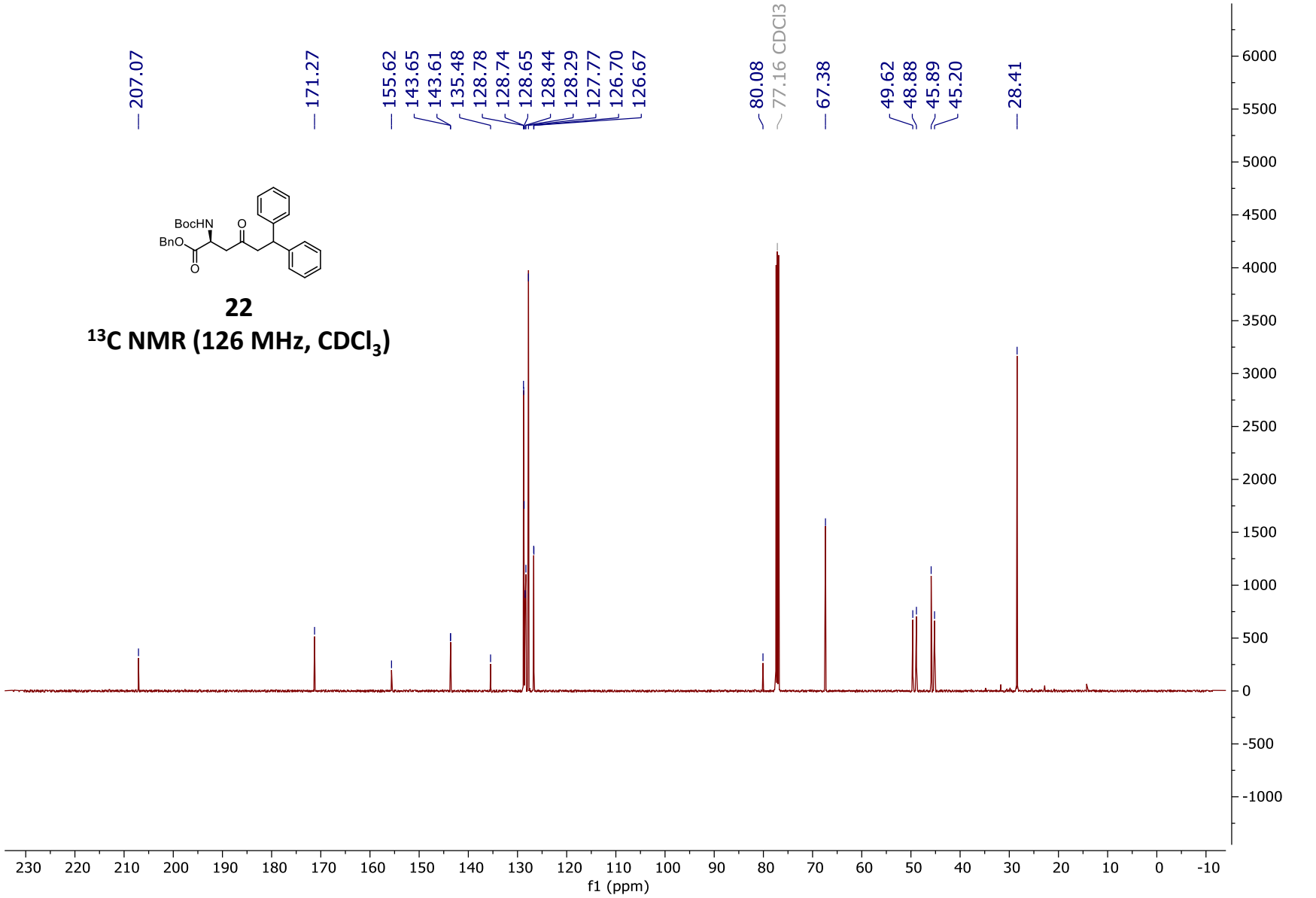

7.28 7.27 7.26 CDCl3 7.25 7.22 7.22 7.21 7.19 7.18 7.18 7.17 7.15 5.66 5.26 4.61 4.59 4.57 4.45 4.45 4.44 4.23 4.22 4.21 4.20 3.16 3.14 3.07 3.06 2.87 2.87 2.85 2.84 2.67 2.64 2.35 2.34 2.32 1.59 1.58 1.57 1.56 1.54 1.54 1.53 1.53 1.51 1.50 1.48 1.27 1.25 1.24 1.23 1.22
21
1H NMR (500 MHz, CDCl3)
4.21 4.01 1.98 0.96 0.95 1.00 0.99 0.98 1.98 1.00 0.99 1.00 2.01 4.09 2.67
f1 (ppm)
JM-NB4-R30LOTUS-bb.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima


209.22
163.59
144.02
128.71
127.86
127.85
126.56
77.16 CDCl3
61.96
60.18
55.39
48.89
46.11
43.22
40.65
28.38
28.32
23.38
21
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB4-R30LOTUS-bb.12.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima



22

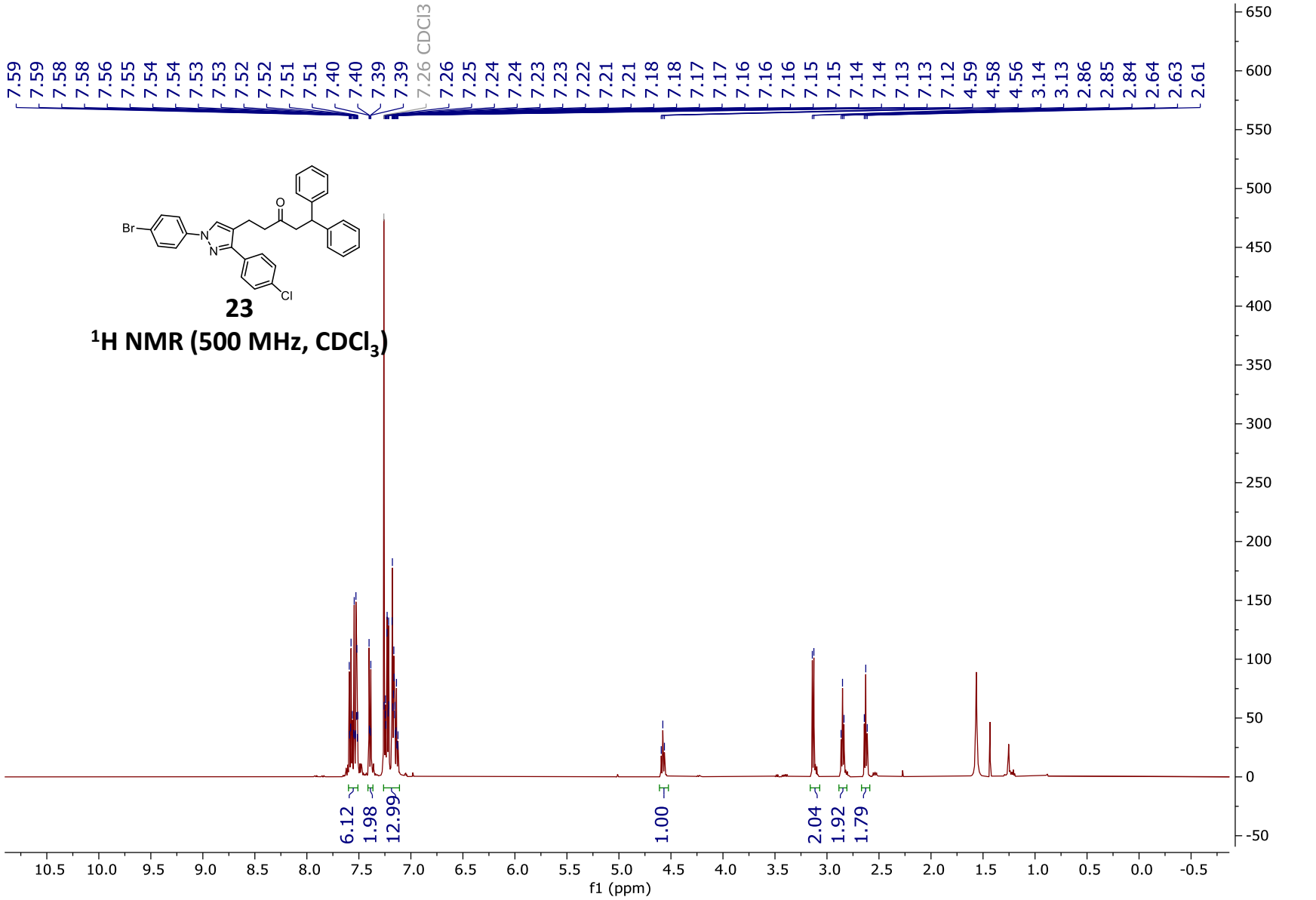
^{1}H NMR (500 MHz, $CDCl_3$)

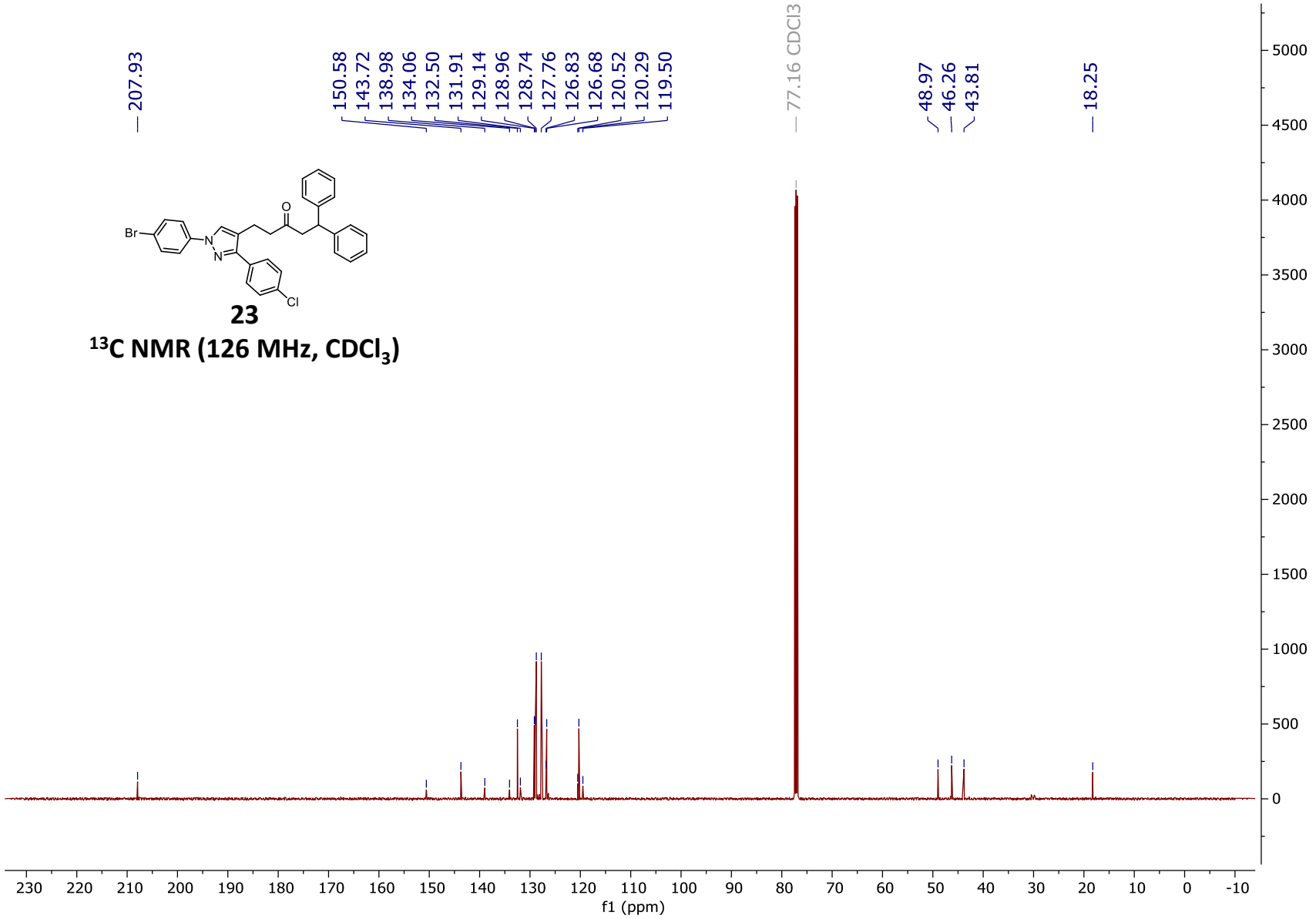


22

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

JM-NB3-R227AF63.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima 1

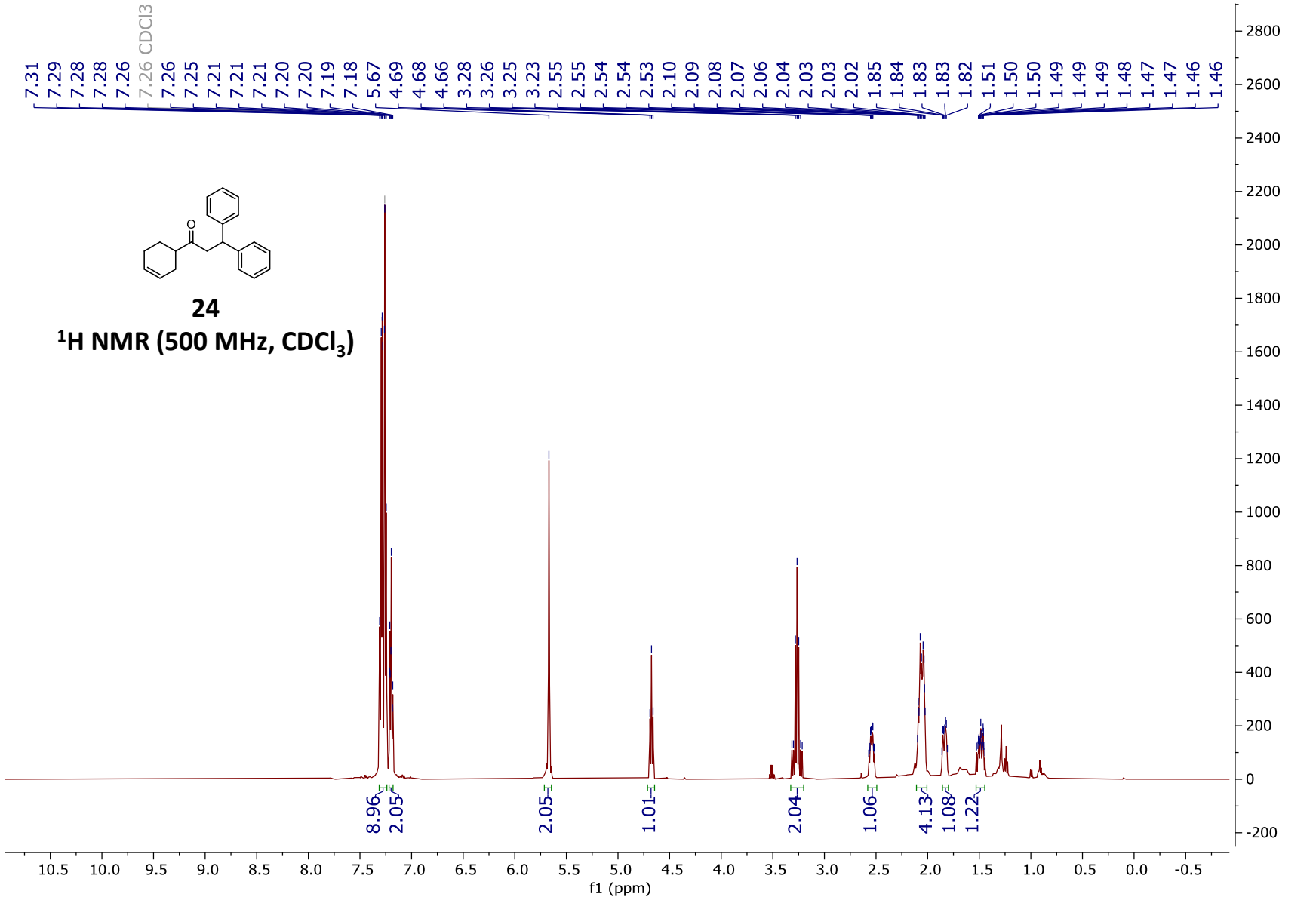

7.59 7.59 7.58 7.58 7.56 7.55 7.54 7.54 7.53 7.53 7.52 7.52 7.51 7.51 7.40 7.40 7.39 7.39 7.26 CDCl3 7.26 7.25 7.24 7.24 7.23 7.23 7.22 7.21 7.21 7.18 7.18 7.17 7.17 7.16 7.16 7.16 7.15 7.15 7.14 7.14 7.13 7.13 7.12 4.59 4.58 4.56 3.14 3.13 2.86 2.85 2.84 2.64 2.63 2.61
Br
N
N
O
Cl
23
1H NMR (500 MHz, CDCl3)
6.12
1.98
12.99
1.00
2.04
1.92
1.79
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)
JM-NB5-R63-F46.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima

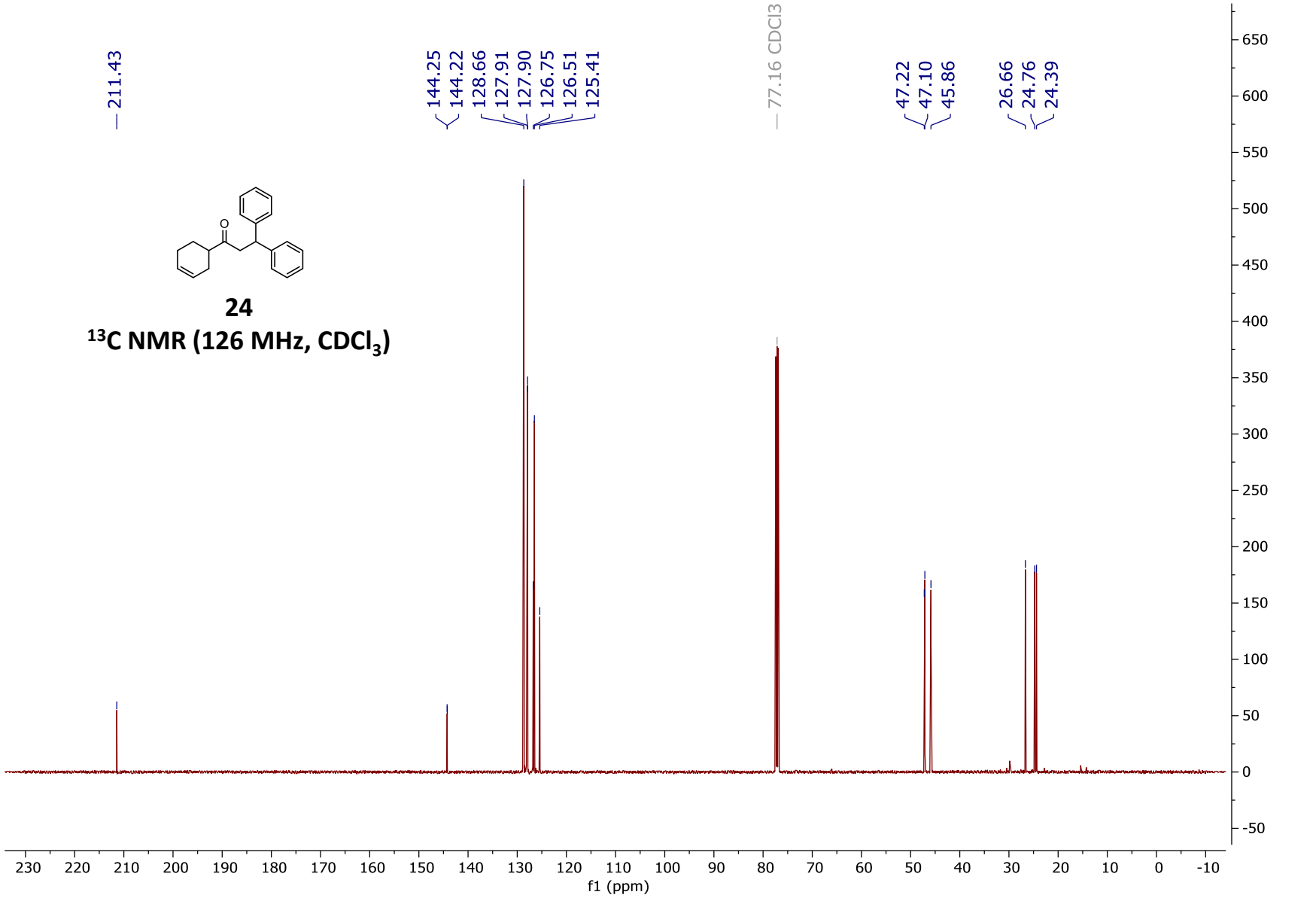


23

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

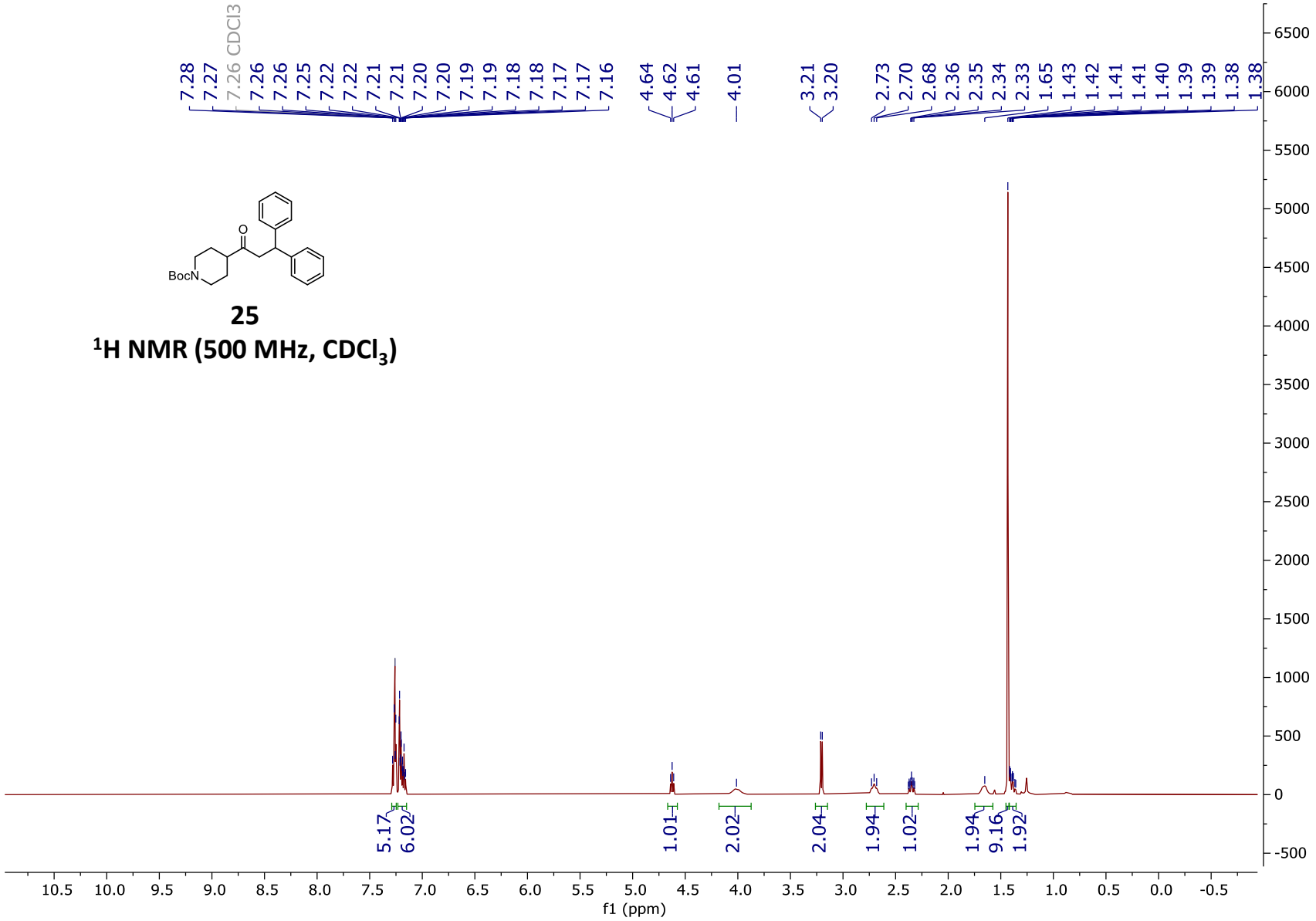
JM-NB5-R63-F46.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima


7.31 7.29 7.28 7.28 7.26 7.26 CDCl3 7.26 7.25 7.21 7.21 7.21 7.20 7.20 7.19 7.18 5.67 4.69 4.68 4.66 3.28 3.26 3.25 3.23 2.55 2.55 2.54 2.54 2.53 2.10 2.09 2.08 2.07 2.06 2.04 2.03 2.03 2.02 1.85 1.84 1.83 1.83 1.82 1.51 1.50 1.50 1.49 1.49 1.49 1.48 1.47 1.47 1.46 1.46
O
24
1H NMR (500 MHz, CDCl3)
8.96 2.05 2.05 1.01 2.04 1.06 4.13 1.08 1.22
f1 (ppm)
JM-NB4-R10BISOL.10.fid



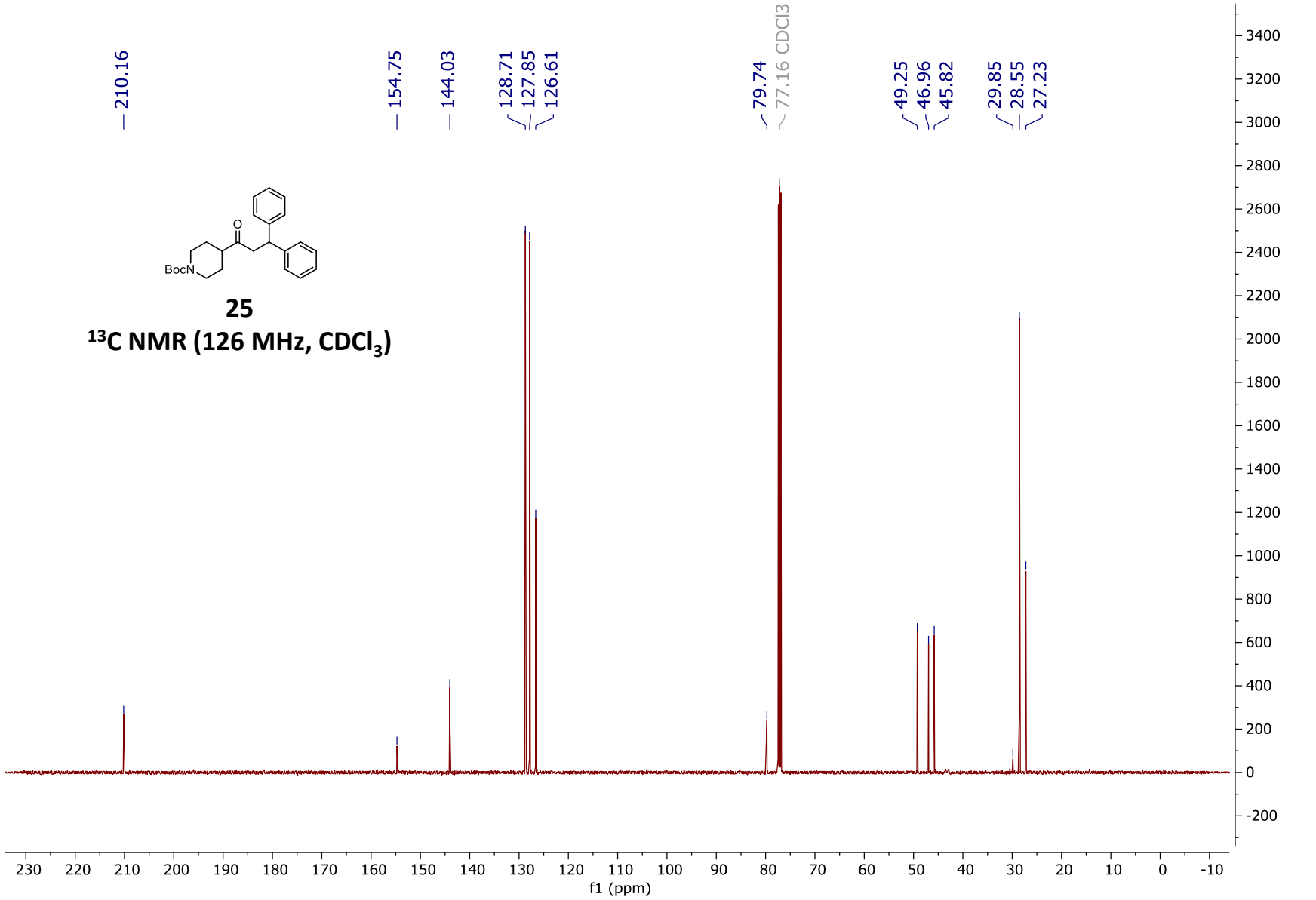
24

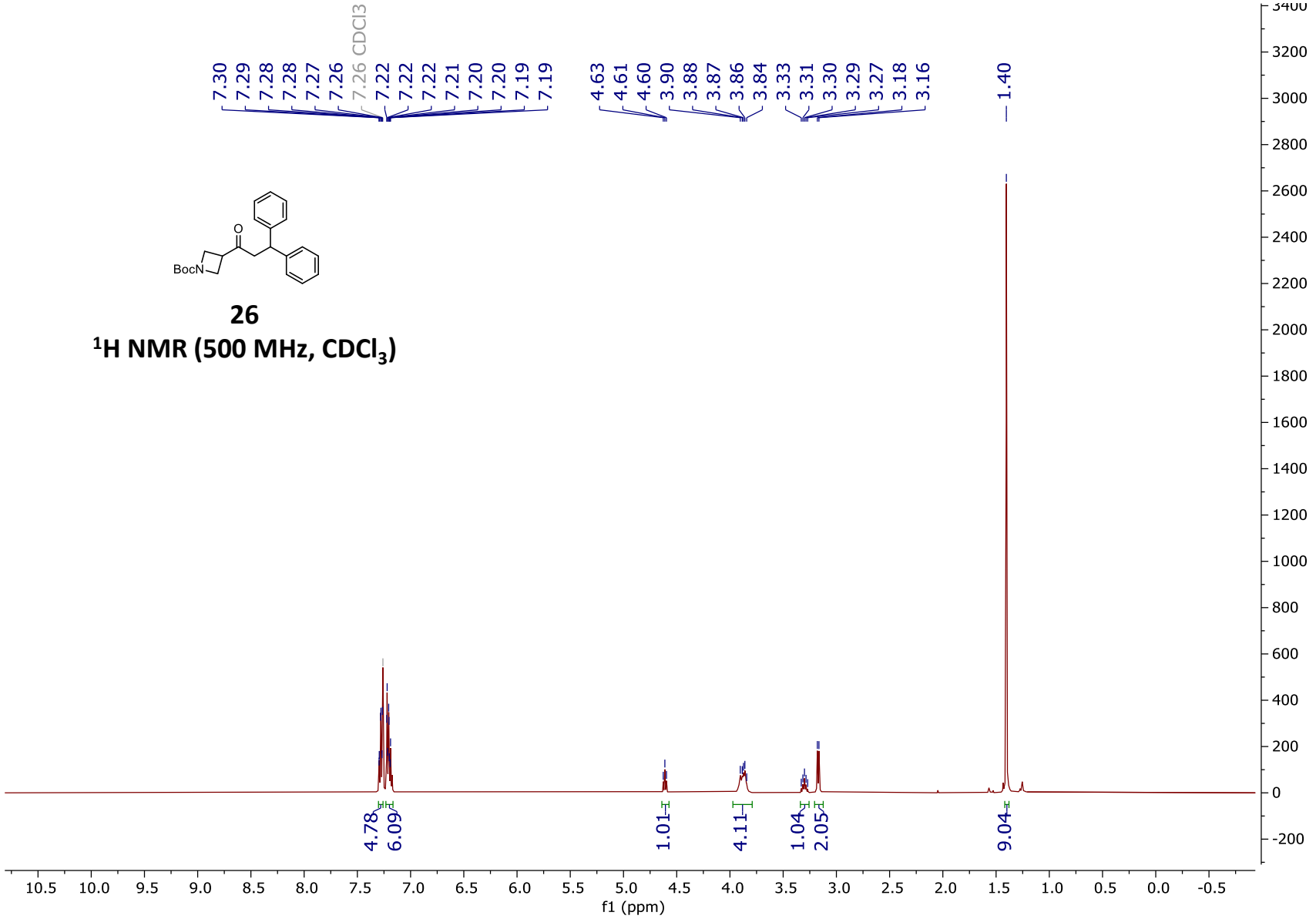
^{13}C NMR (126 MHz, $CDCl_3$)



25

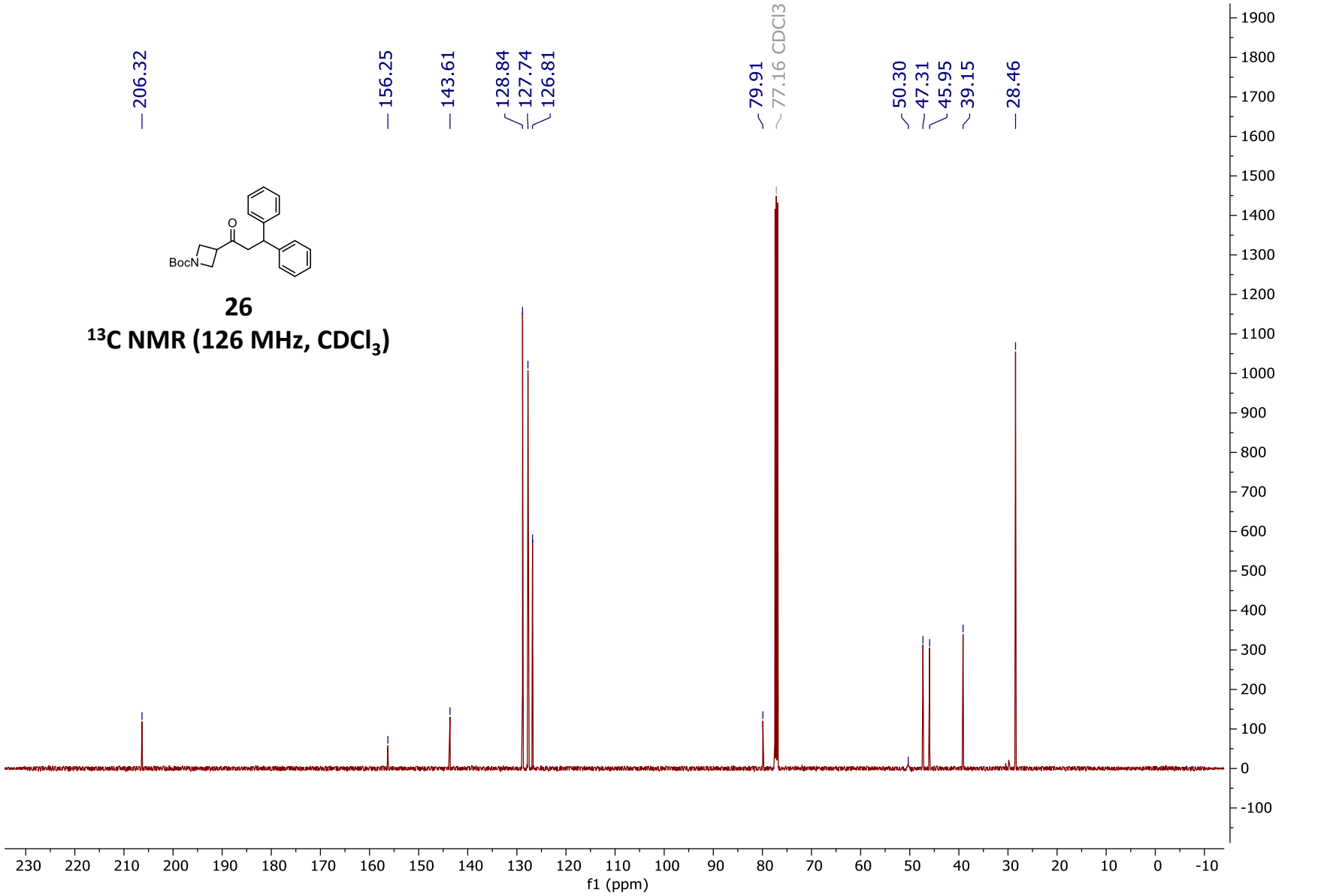
^{1}H NMR (500 MHz, $CDCl_3$)

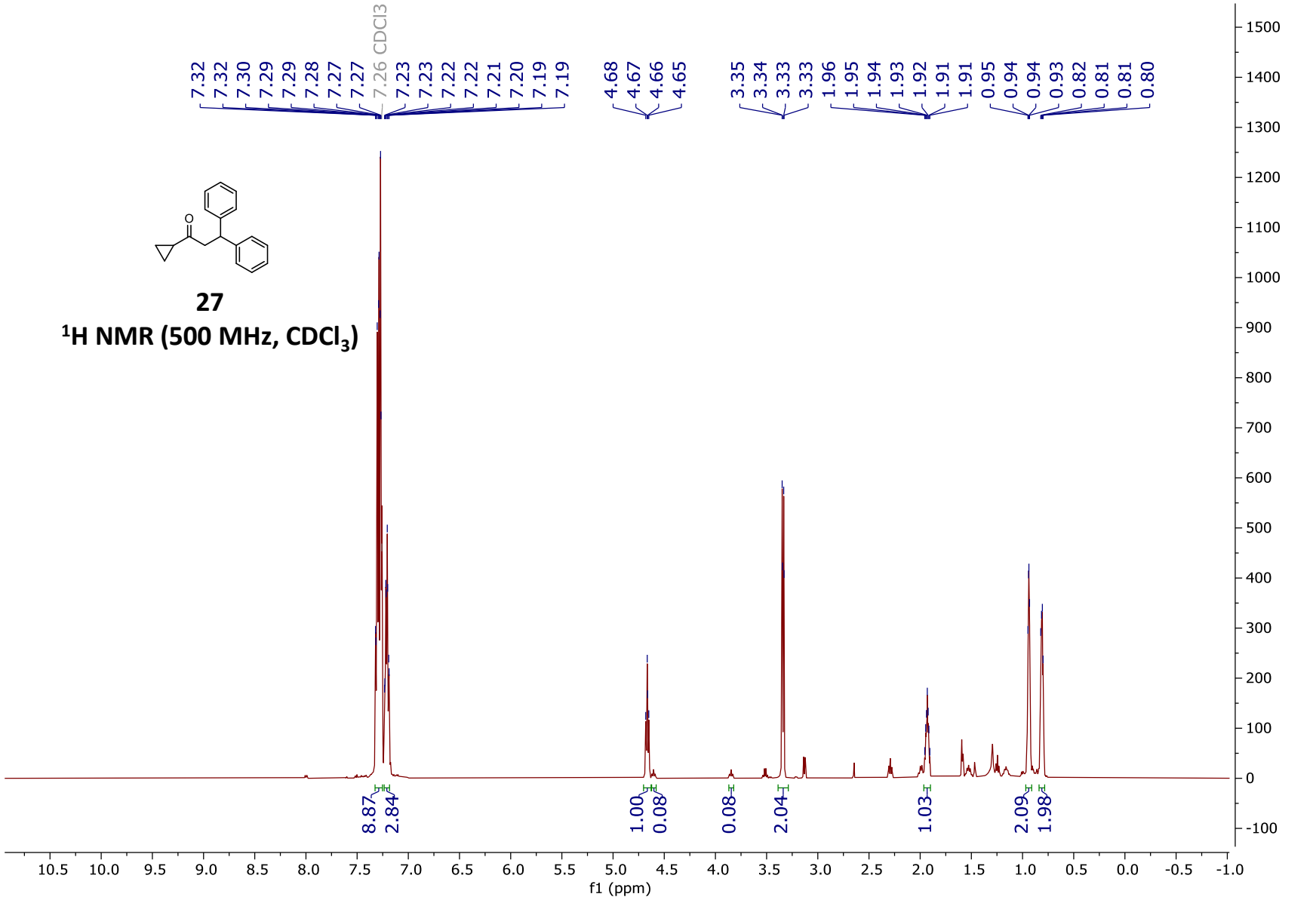

210.16
154.75
144.03
128.71
127.85
126.61
79.74
77.16 CDCl3
49.25
46.96
45.82
29.85
28.55
27.23
BocN
O
25
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB3-R138AISOL.21.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima 1

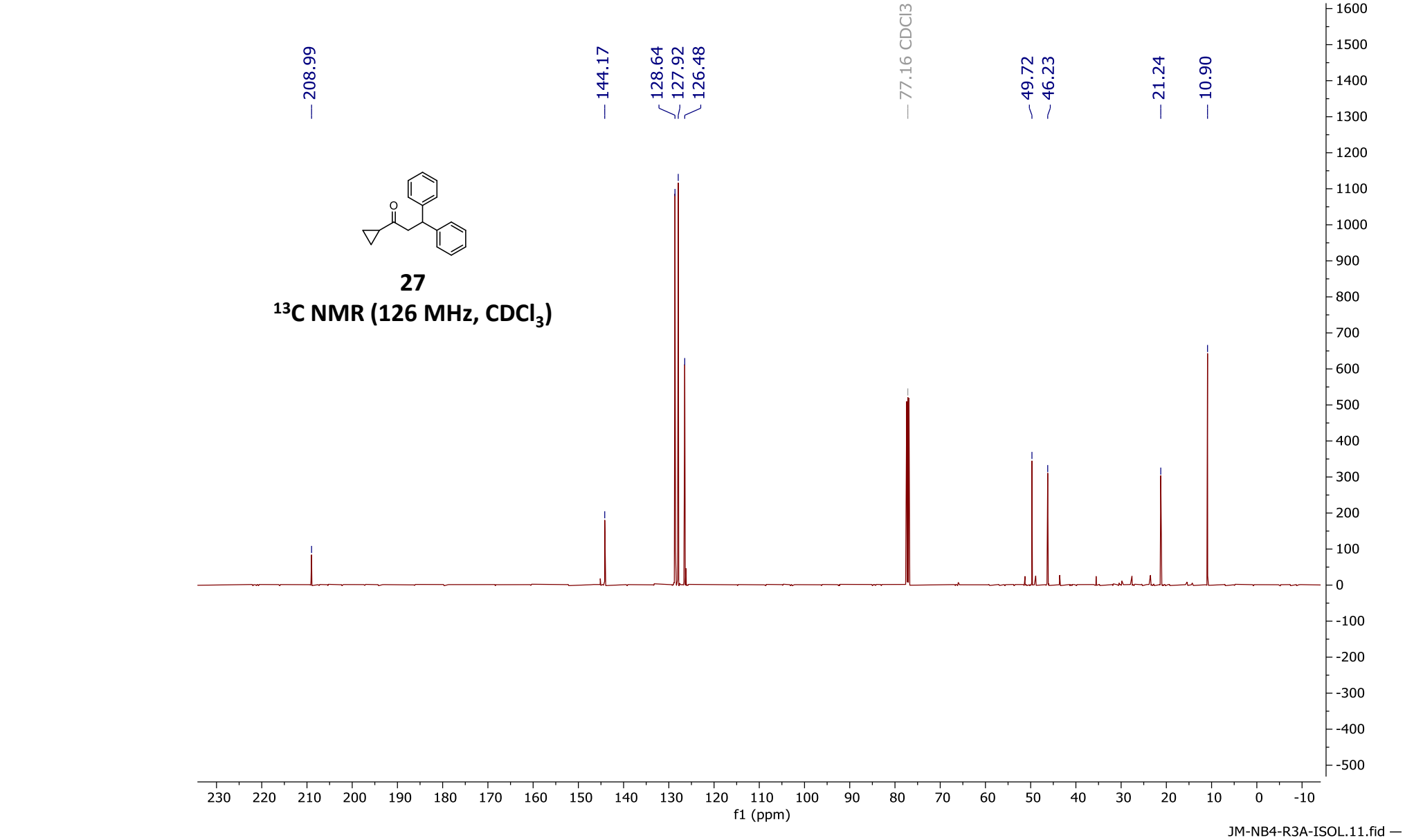


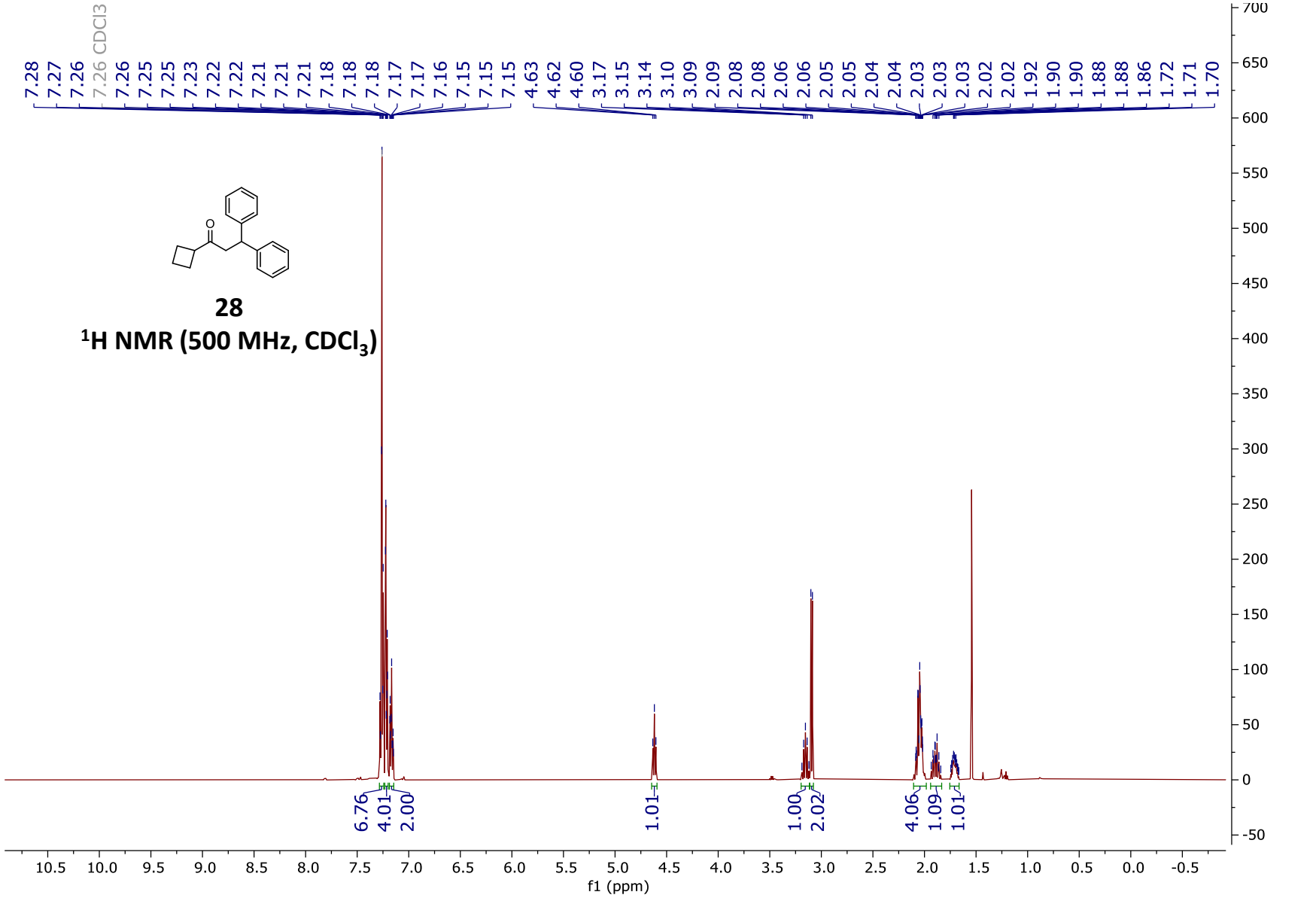
26

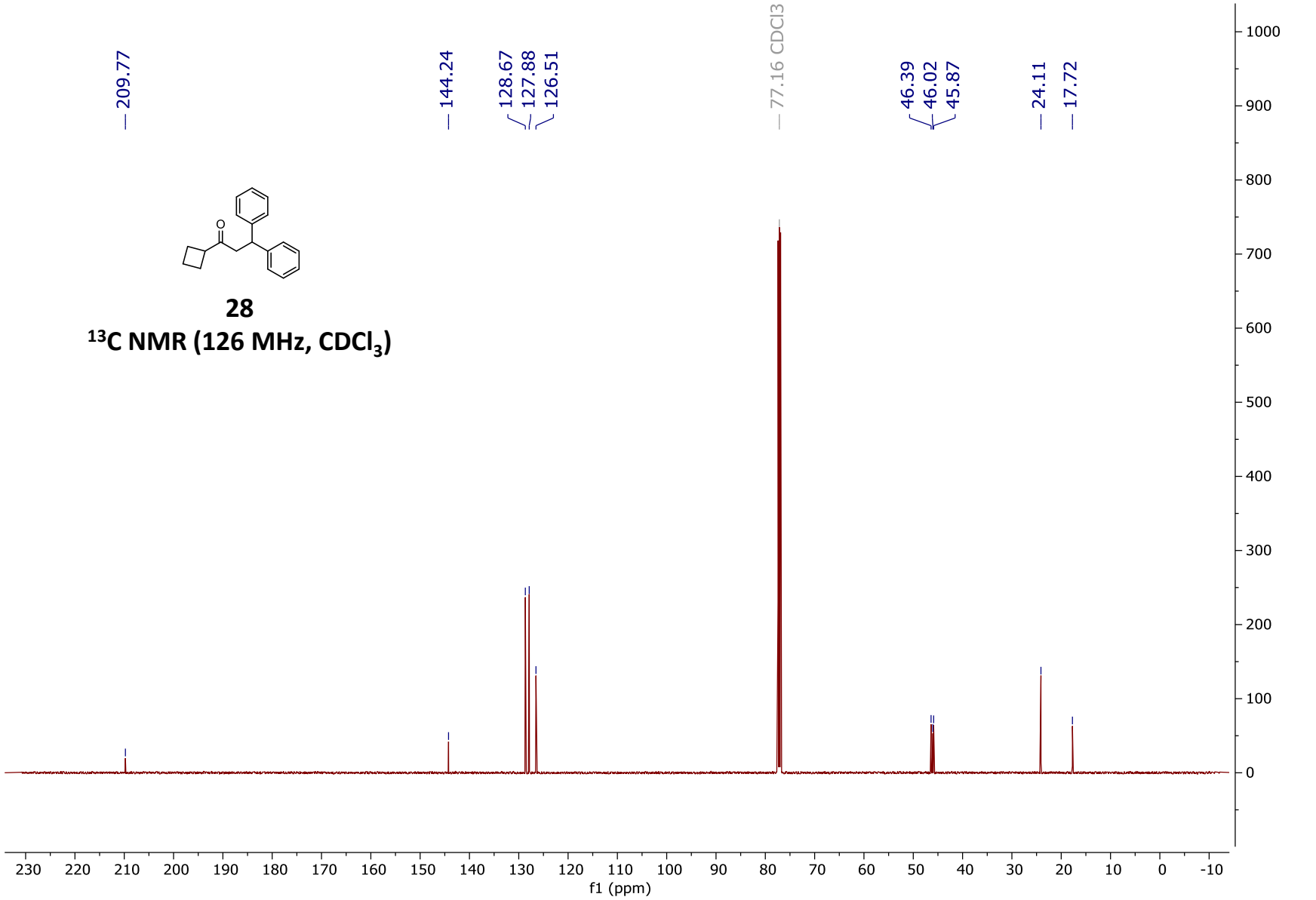
^{1}H NMR (500 MHz, $CDCl_3$)


206.32
156.25
143.61
128.84
127.74
126.81
79.91
77.16 CDCl3
50.30
47.31
45.95
39.15
28.46
O
BocN
26
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB3-R165AC2ISOL.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima 1


7.32
7.32
7.30
7.29
7.29
7.28
7.27
7.27
7.26 CDCl3
7.23
7.23
7.22
7.22
7.21
7.20
7.19
7.19
4.68
4.67
4.66
4.65
3.35
3.34
3.33
3.33
1.96
1.95
1.94
1.93
1.92
1.91
1.91
0.95
0.94
0.94
0.93
0.82
0.81
0.81
0.80
O
27
1H NMR (500 MHz, CDCl3)
8.87
2.84
1.00
0.08
0.08
2.04
1.03
2.09
1.98
f1 (ppm)
JM-NB4-R3A-ISOL.10.fid

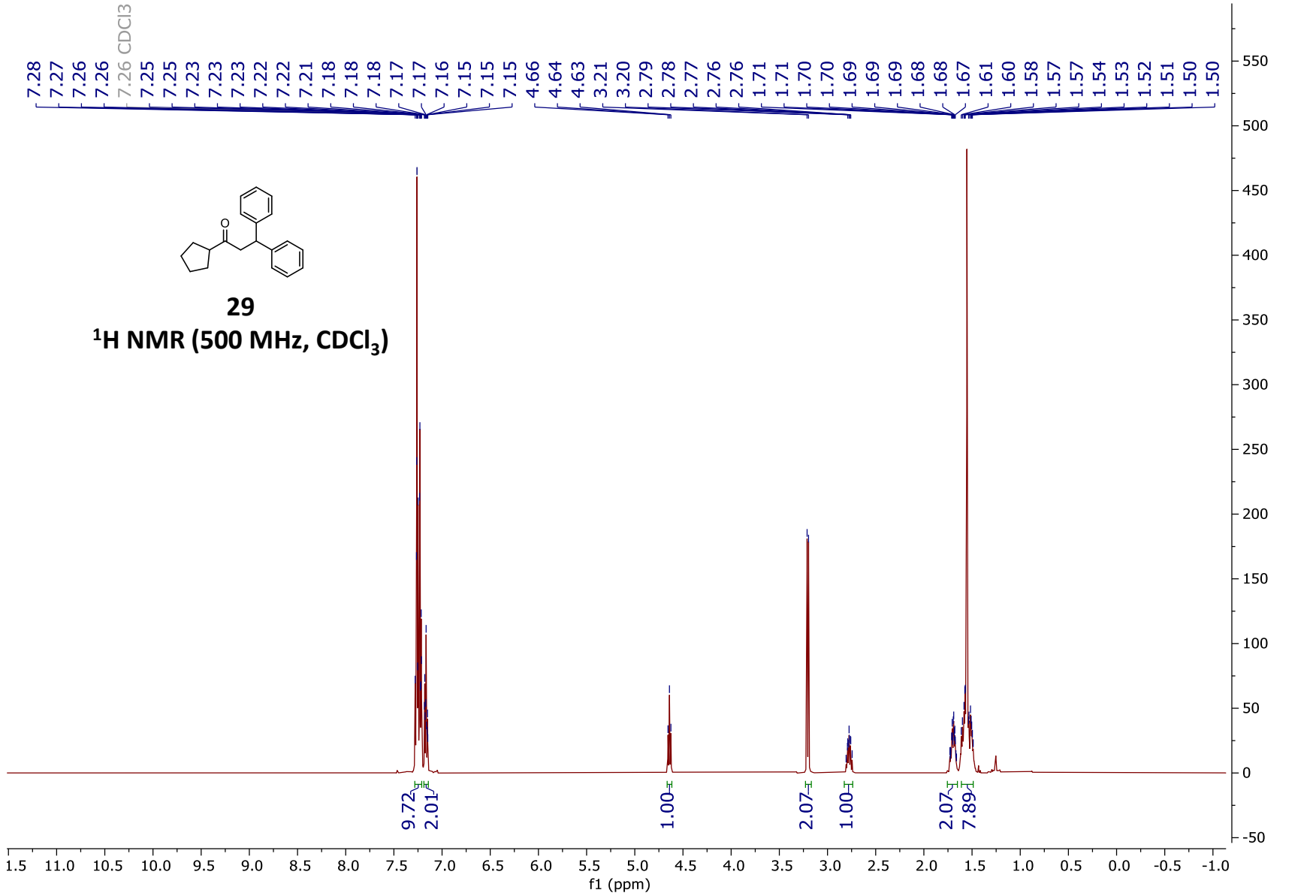

208.99
144.17
128.64
127.92
126.48
77.16 CDCl3
49.72
46.23
21.24
10.90
O
27
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB4-R3A-ISOL.11.fid

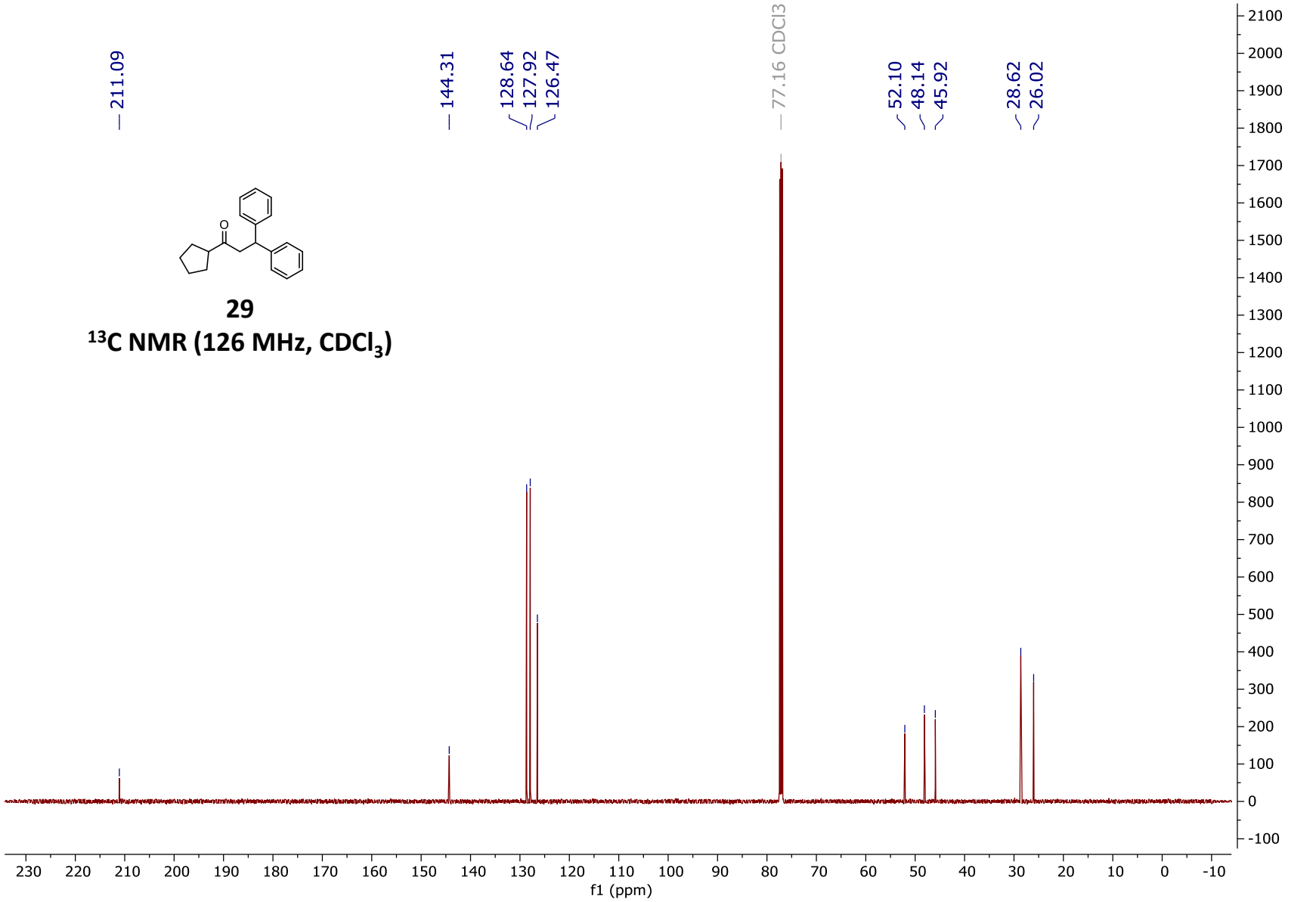

7.28 7.27 7.26 7.26 CDCl3 7.26 7.25 7.25 7.23 7.22 7.22 7.21 7.21 7.21 7.18 7.18 7.18 7.17 7.17 7.16 7.15 7.15 7.15
4.63 4.62 4.60 3.17 3.15 3.14 3.10 3.09 2.09 2.08 2.08 2.06 2.06 2.05 2.05 2.04 2.04 2.03 2.03 2.03 2.02 2.02 1.92 1.90 1.90 1.88 1.88 1.86 1.72 1.71 1.70
O
28
1H NMR (500 MHz, CDCl3)
6.76
4.01
2.00
1.01
1.00
2.02
4.06
1.09
1.01
f1 (ppm)
JM-NB4-R3B-ISOL.10.fid



28

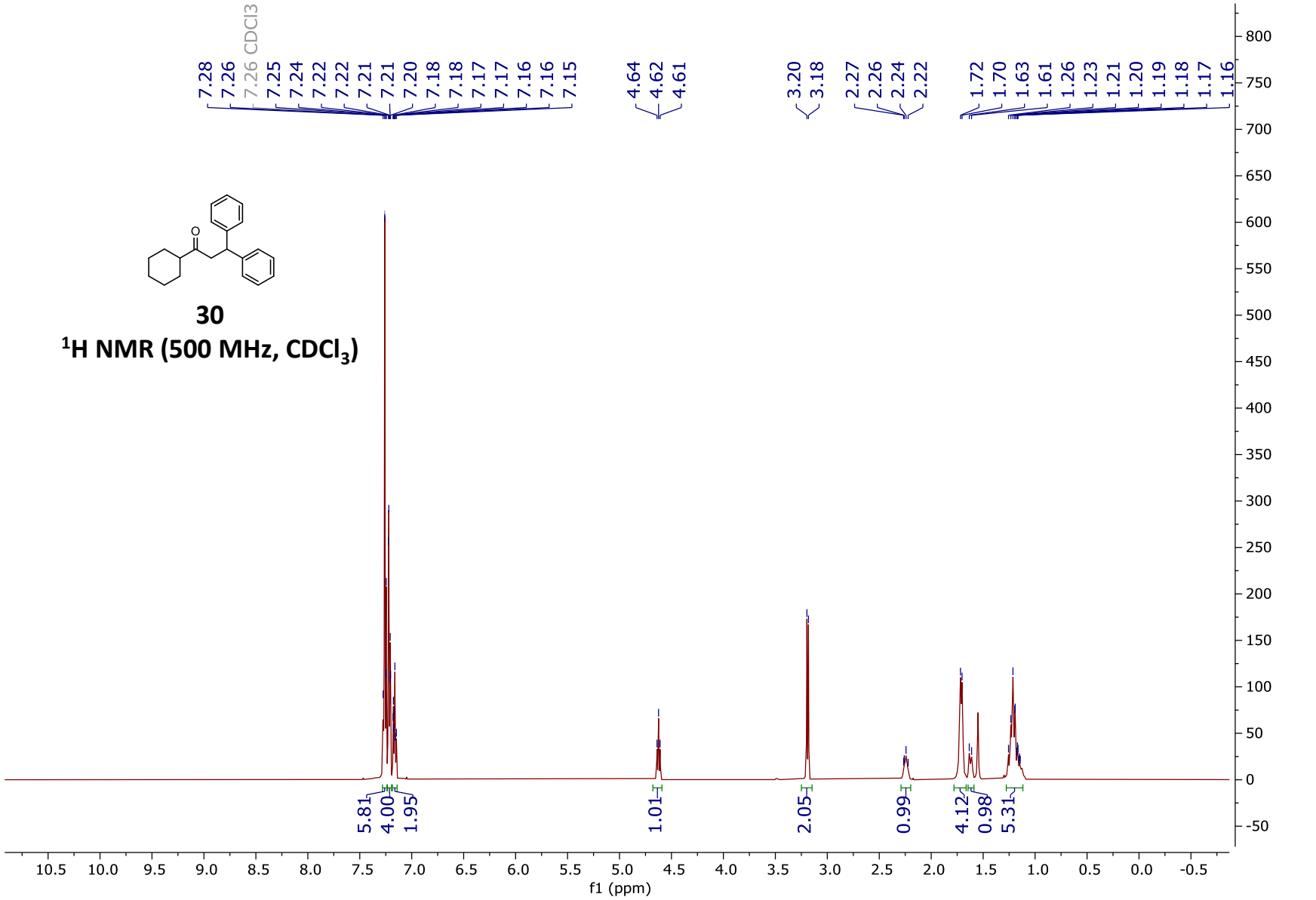
^{13}C NMR (126 MHz, $CDCl_3$)

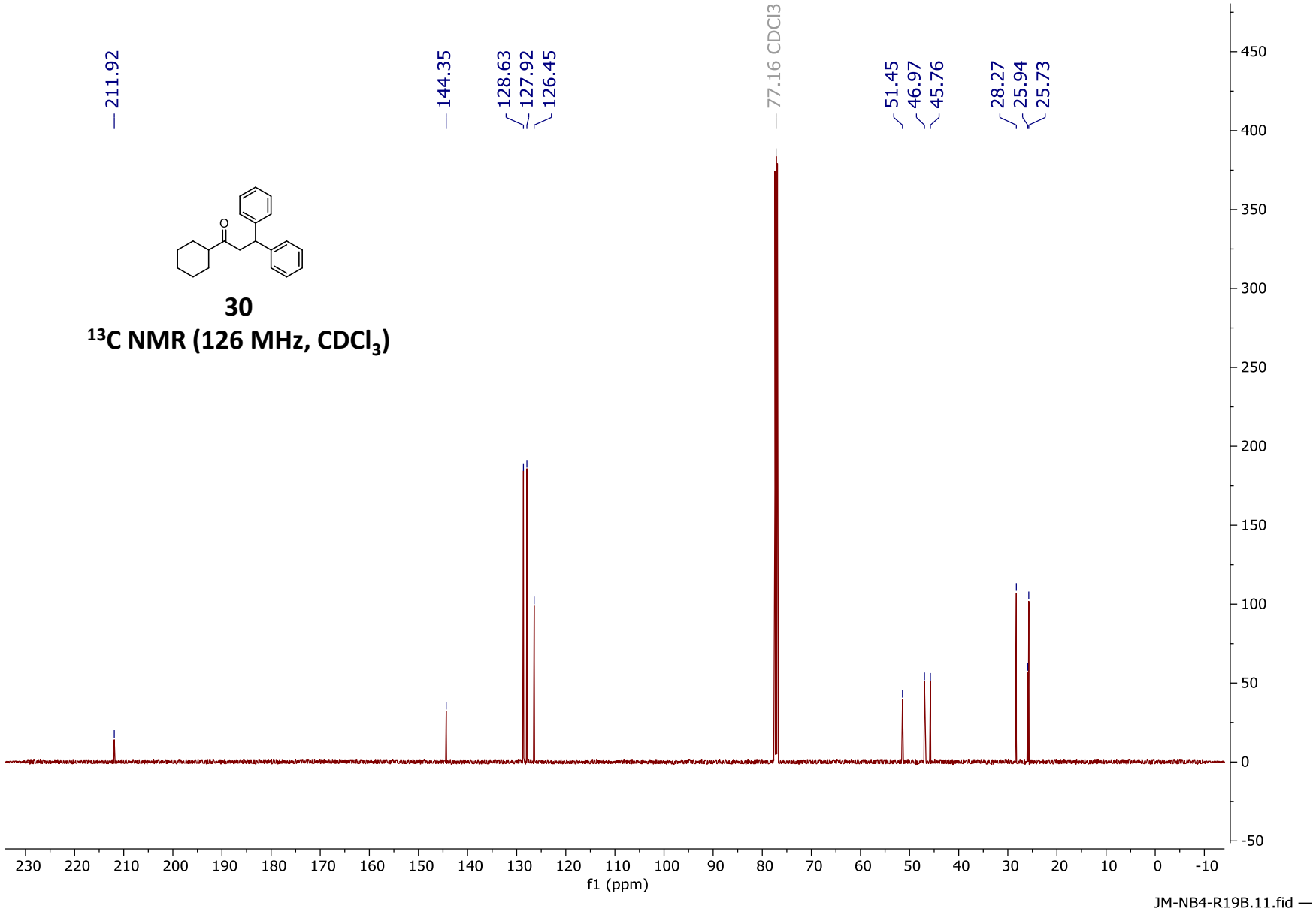

7.28 7.27 7.26 7.26 7.26 CDCl3 7.25 7.25 7.23 7.23 7.23 7.22 7.22 7.21 7.18 7.18 7.18 7.17 7.17 7.16 7.15 7.15 7.15
4.66 4.64 4.63 3.21 3.20 2.79 2.78 2.77 2.76 2.76 1.71 1.71 1.70 1.70 1.69 1.69 1.69 1.68 1.68 1.67 1.61 1.60 1.58 1.57 1.57 1.54 1.53 1.52 1.51 1.50 1.50
O
29
1H NMR (500 MHz, CDCl3)
9.72
2.01
1.00
2.07
1.00
2.07
7.89
f1 (ppm)
JM-NB5-R93A.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima 1



29

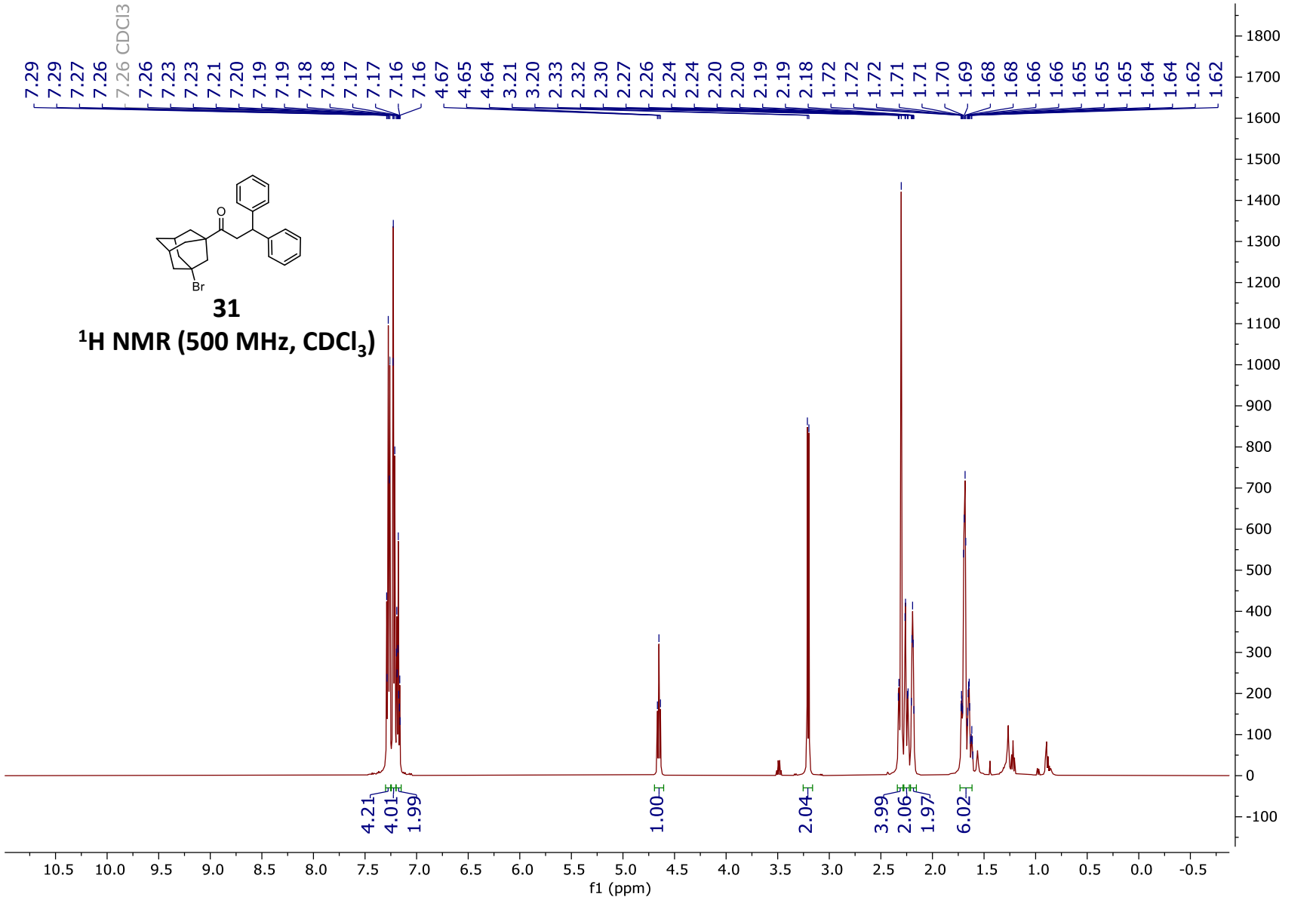
^{13}C NMR (126 MHz, $CDCl_3$)

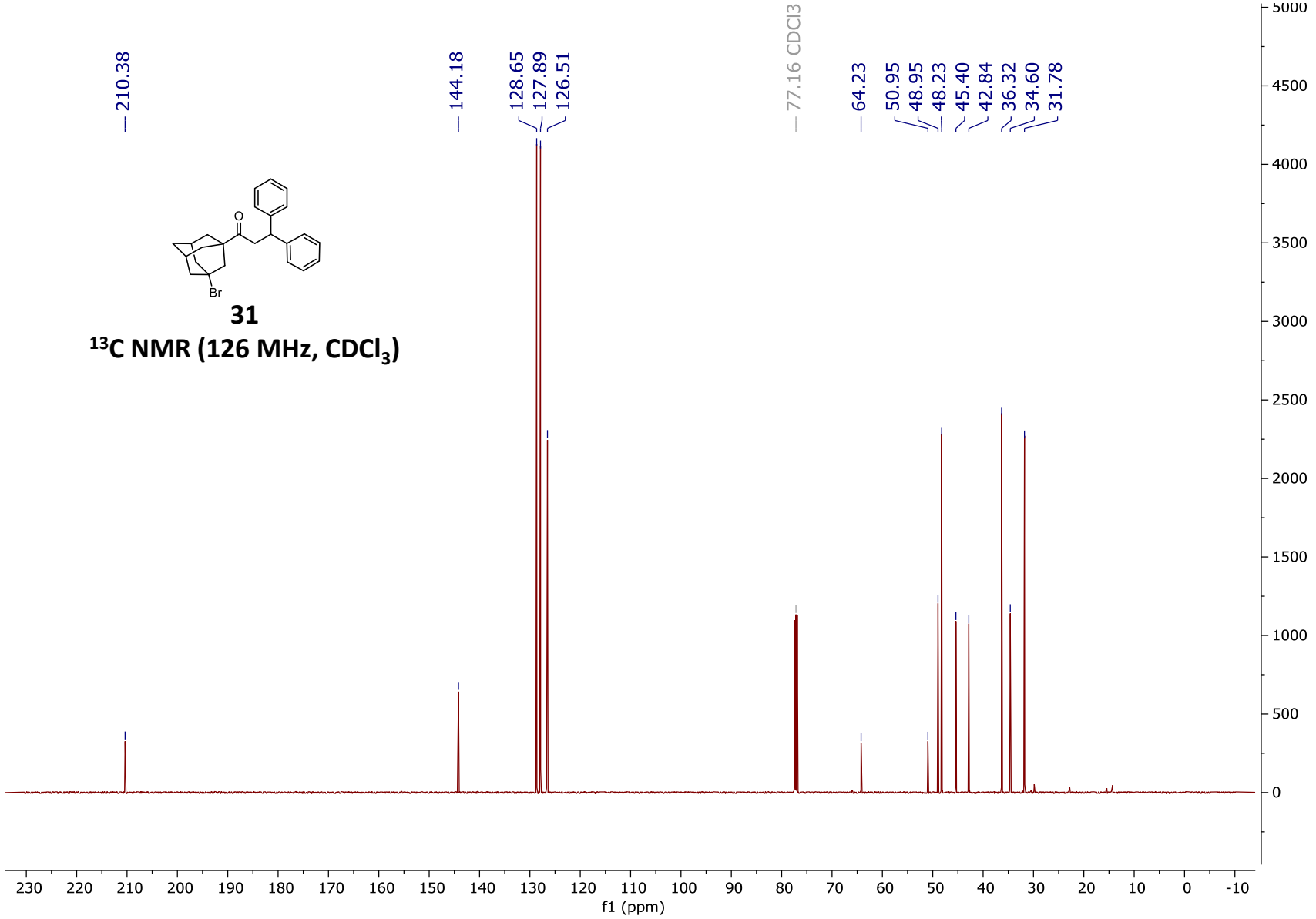

7.28
7.26
7.26 CDCl3
7.25
7.24
7.22
7.22
7.21
7.21
7.20
7.18
7.18
7.17
7.17
7.16
7.16
7.15
4.64
4.62
4.61
3.20
3.18
2.27
2.26
2.24
2.22
1.72
1.70
1.63
1.61
1.26
1.23
1.21
1.20
1.19
1.18
1.17
1.16
O
30
1H NMR (500 MHz, CDCl3)
5.81
4.00
1.95
1.01
2.05
0.99
4.12
0.98
5.31
f1 (ppm)
JM-NB4-R19B.10.fid



30

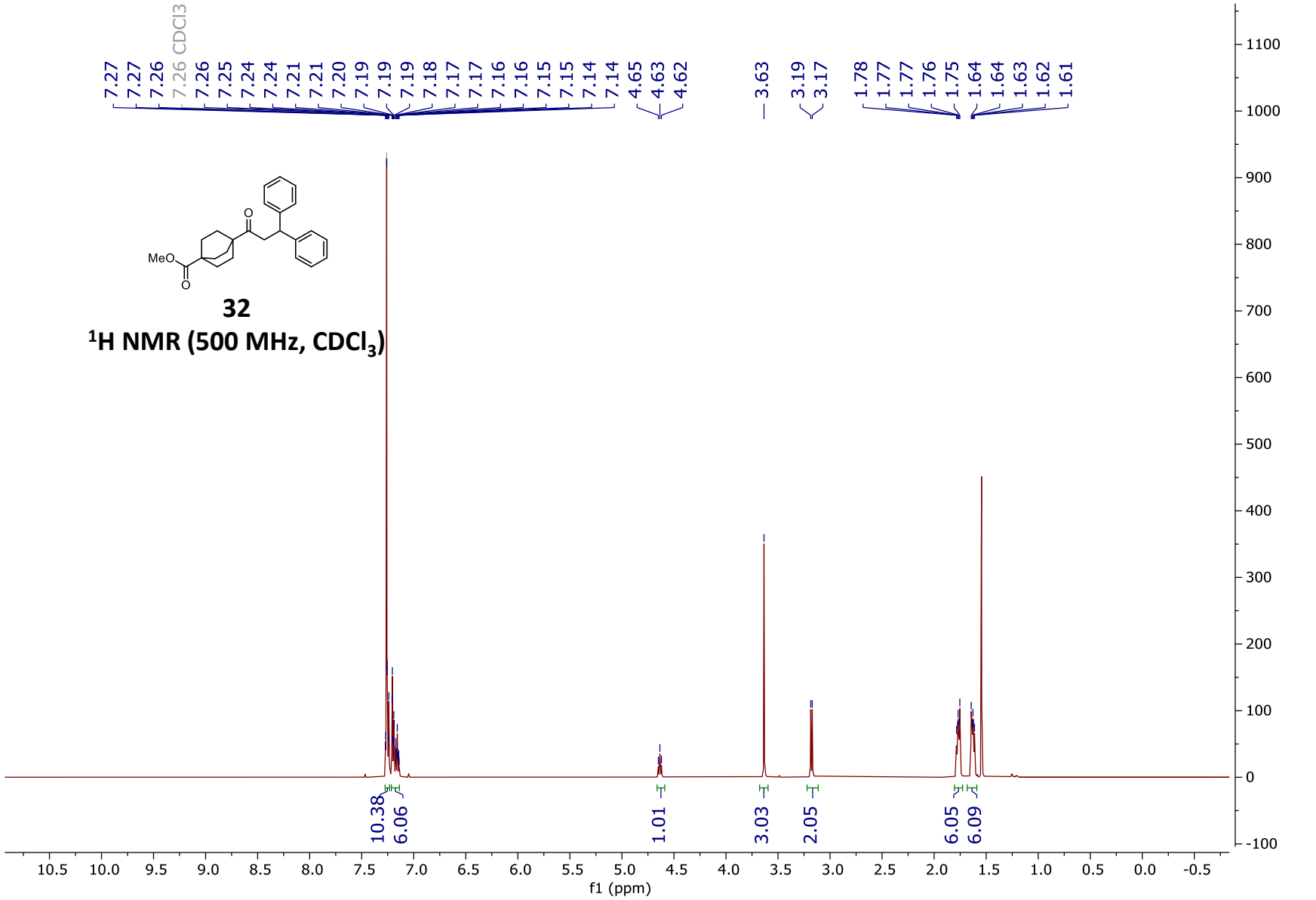
^{13}C NMR (126 MHz, $CDCl_3$)

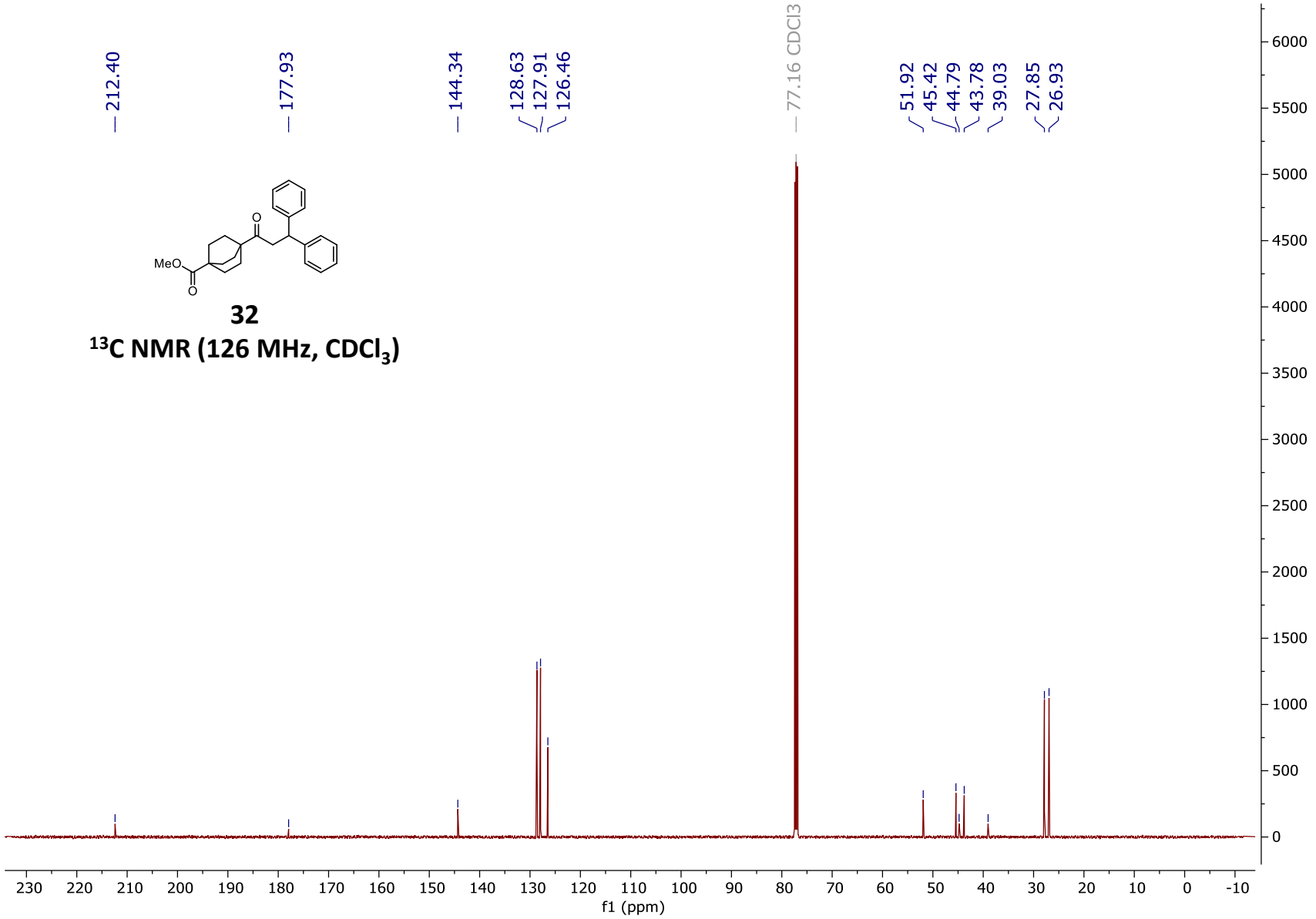

7.29 7.29 7.27 7.26 7.26 CDCl3 7.26 7.23 7.23 7.21 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.16
4.67 4.65 4.64 4.21 3.20 2.33 2.32 2.30 2.27 2.26 2.24 2.24 2.20 2.20 2.19 2.19 2.18 1.72 1.72 1.72 1.71 1.71 1.70 1.69 1.68 1.68 1.66 1.66 1.65 1.65 1.65 1.64 1.64 1.62 1.62
O
Br
31
1H NMR (500 MHz, CDCl3)
4.21 4.01 1.99 1.00 2.04 3.99 2.06 1.97 6.02
f1 (ppm)
JM-NB4-R48A-ISOL.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima



31

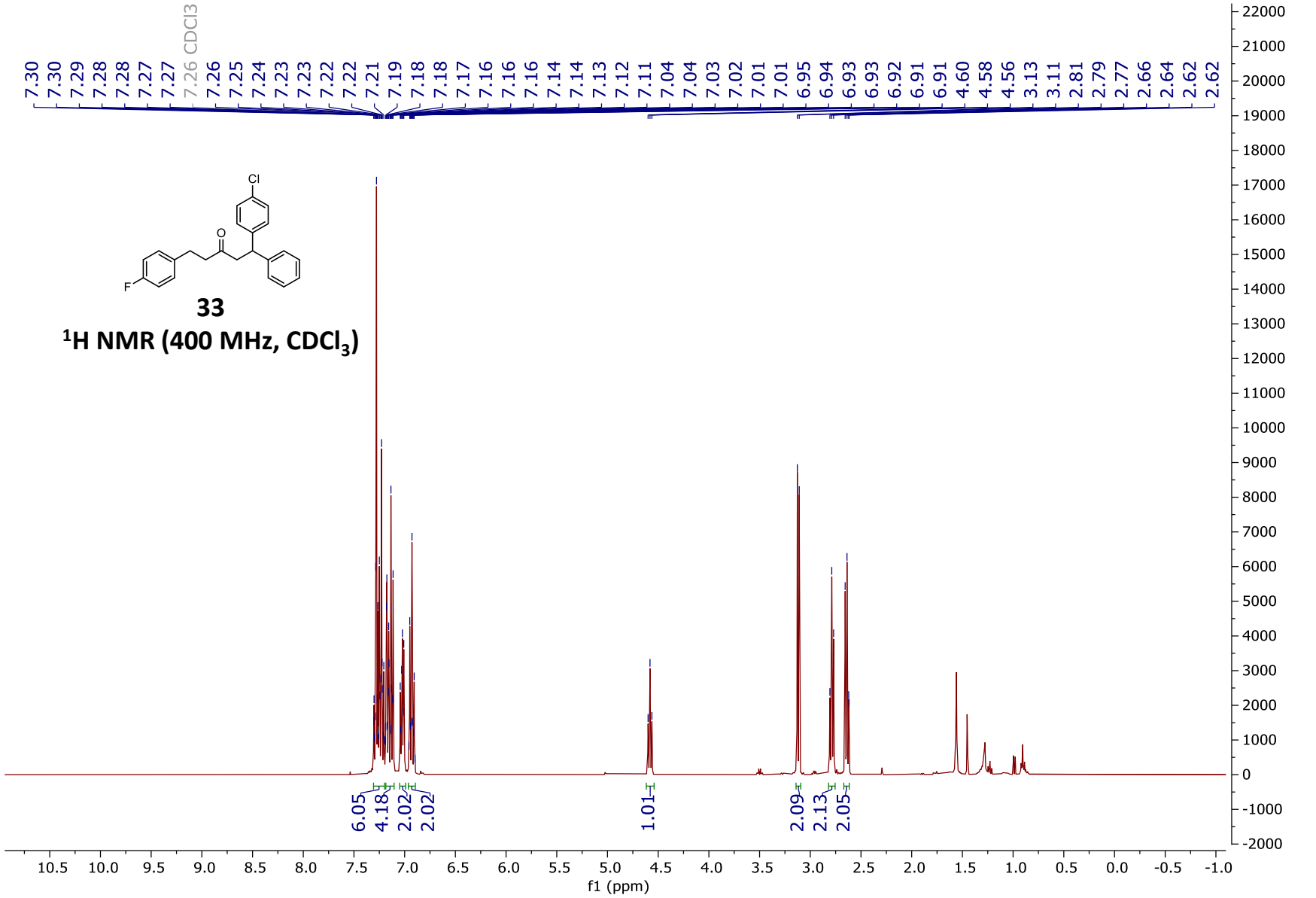
^{13}C NMR (126 MHz, $CDCl_3$)

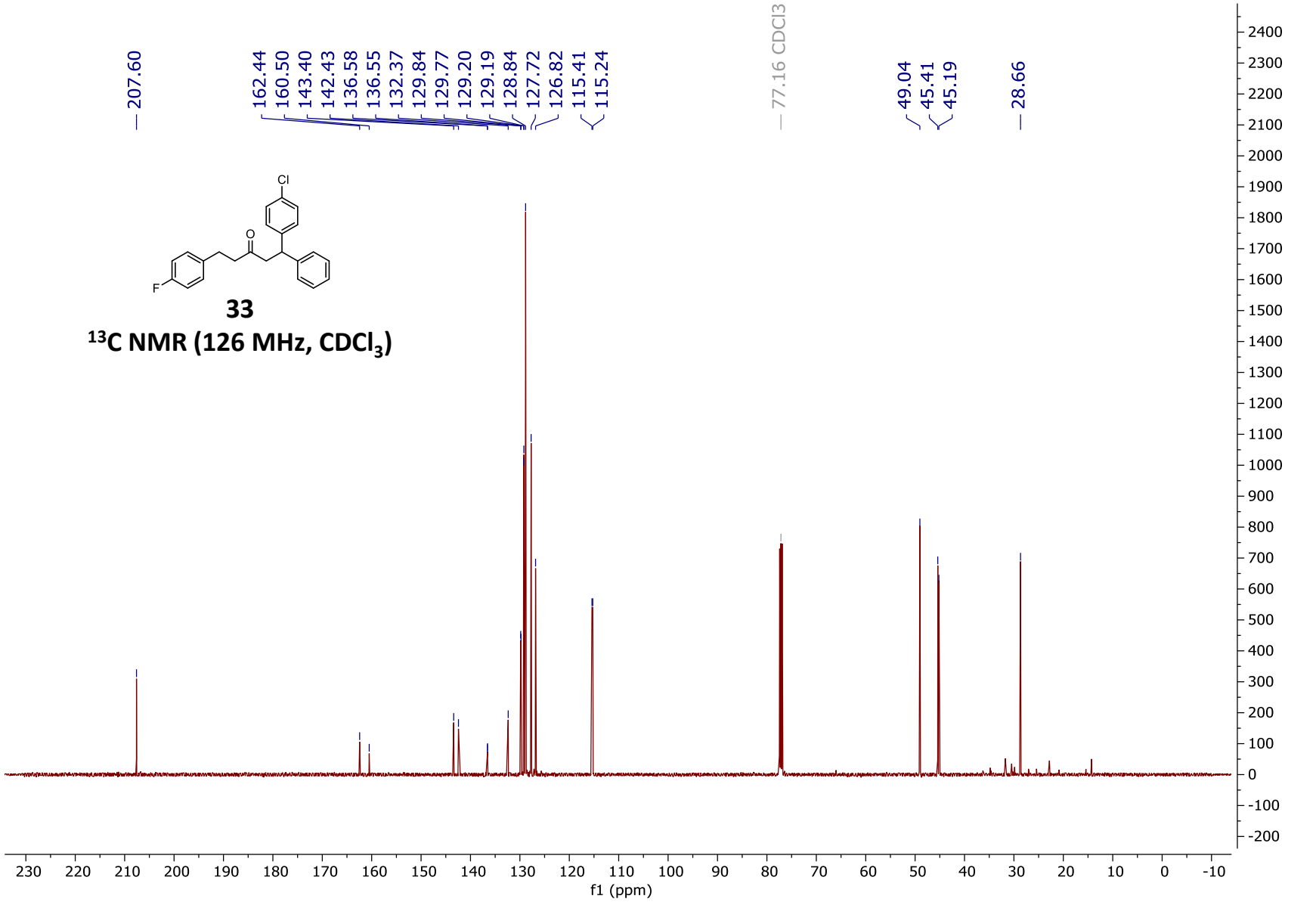

7.27 7.27 7.26 7.26 CDCl3 7.26 7.25 7.24 7.24 7.21 7.21 7.20 7.19 7.19 7.19 7.18 7.17 7.17 7.16 7.16 7.15 7.15 7.14 7.14 4.65 4.63 4.62 3.63 3.19 3.17 1.78 1.77 1.77 1.76 1.75 1.64 1.64 1.63 1.62 1.61
MeO
O
O
32
1H NMR (500 MHz, CDCl3)
10.38 6.06 1.01 3.03 2.05 6.05 6.09
f1 (ppm)
JM-NB4-R18A.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima



32

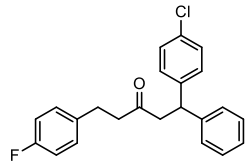
^{13}C NMR (126 MHz, $CDCl_3$)


7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.26 CDCl3 7.26 7.25 7.24 7.23 7.23 7.22 7.22 7.21 7.19 7.18 7.18 7.17 7.16 7.16 7.16 7.14 7.14 7.13 7.12 7.11 7.04 7.04 7.03 7.02 7.01 7.01 6.95 6.94 6.93 6.93 6.92 6.91 6.91 4.60 4.58 4.56 3.13 3.11 2.81 2.79 2.77 2.66 2.64 2.62 2.62
Cl
O
F
33
1H NMR (400 MHz, CDCl3)
6.05 4.18 2.02 2.02 1.01 2.09 2.13 2.05
f1 (ppm)
JM-NB4-R14B-H.10.fid



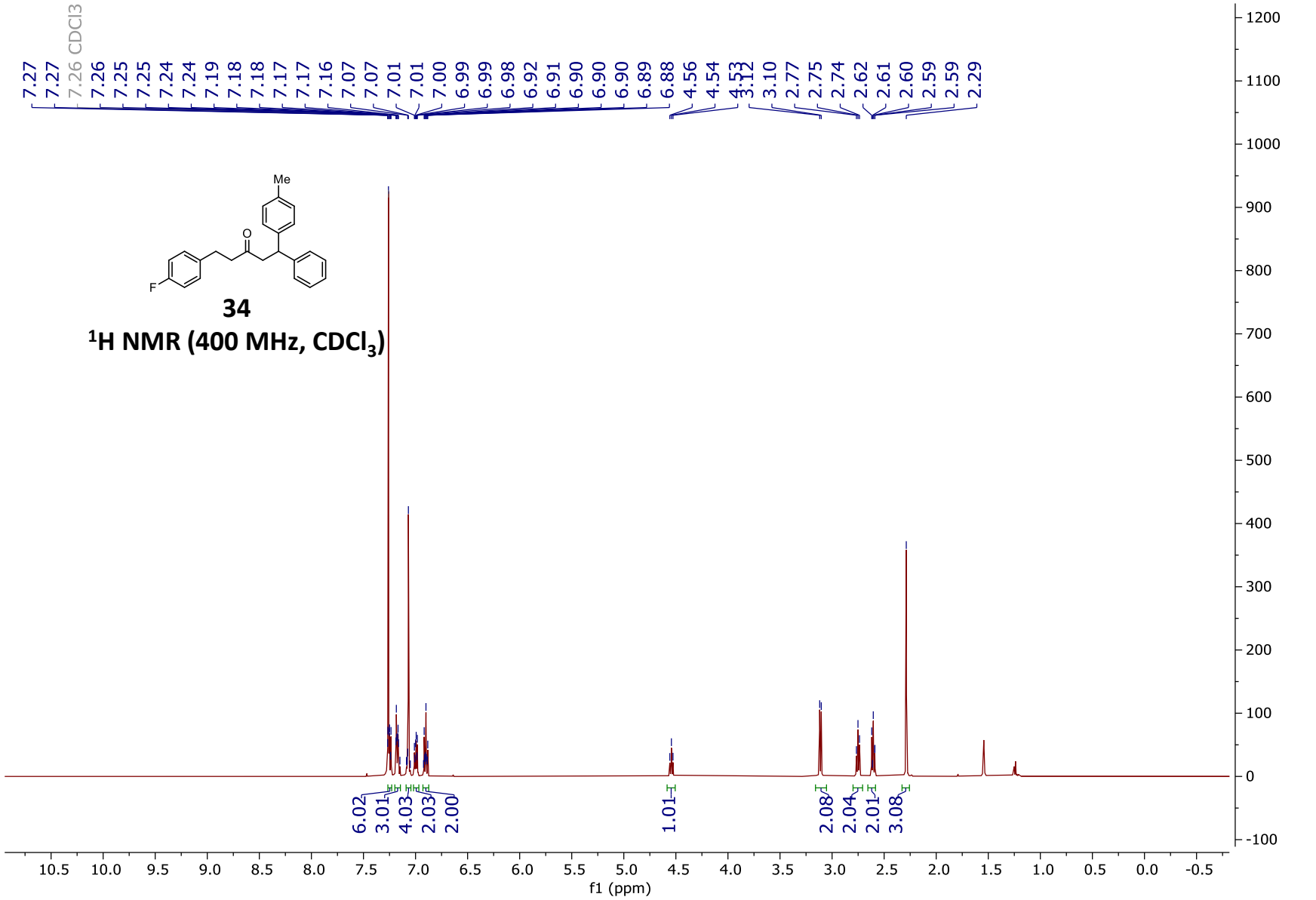
33

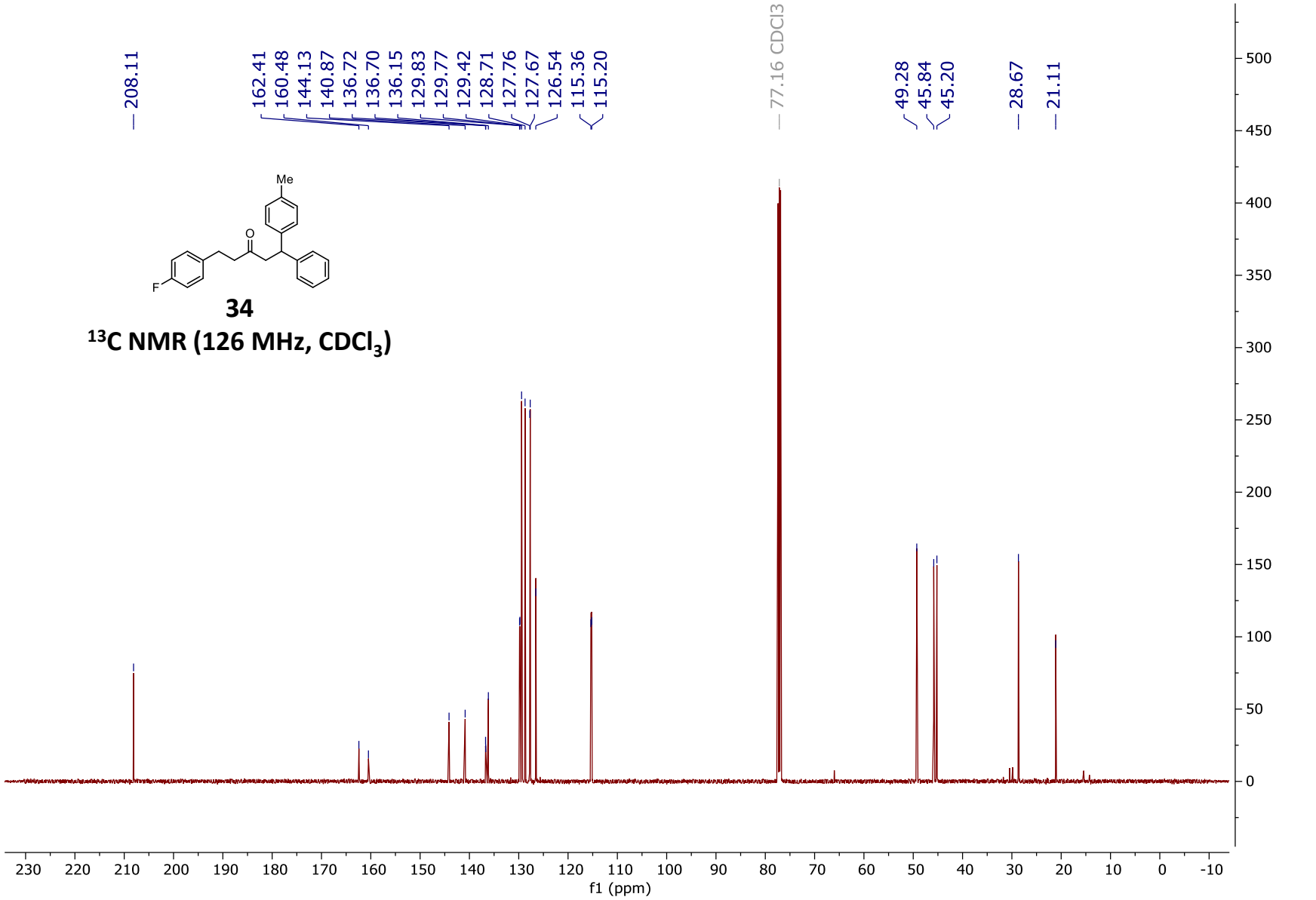
^{13}C NMR (126 MHz, $CDCl_3$)

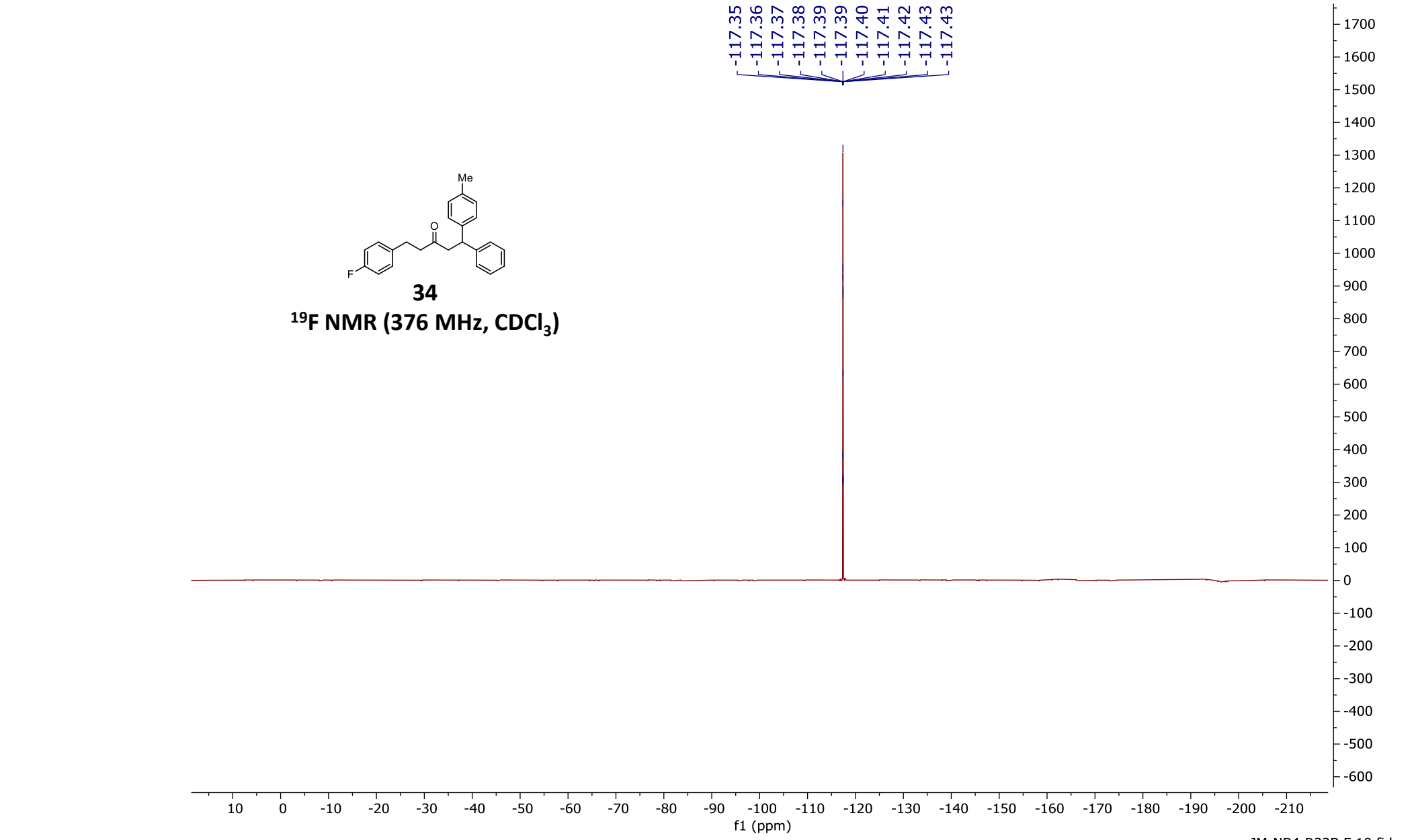


33

^{19}F NMR (376 MHz, $CDCl_3$)

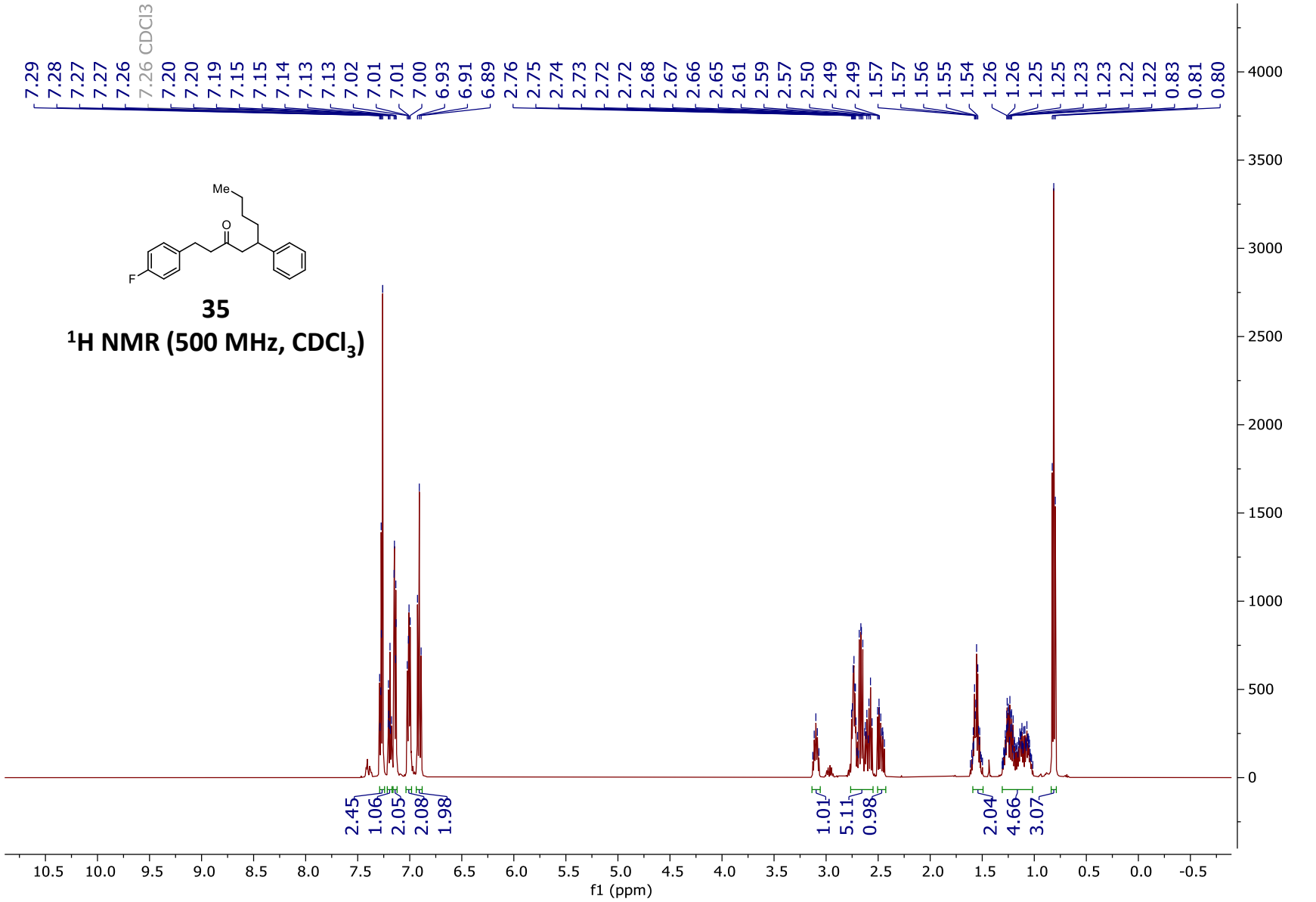

7.27 7.27 7.26 CDCl3 7.26 7.25 7.25 7.24 7.24 7.19 7.18 7.18 7.17 7.17 7.16 7.07 7.07 7.01 7.01 7.00 6.99 6.99 6.98 6.92 6.91 6.90 6.90 6.90 6.89 6.88 4.56 4.54 4.53 3.12 3.10 2.77 2.75 2.74 2.62 2.61 2.60 2.59 2.59 2.29
Me
O
F
34
1H NMR (400 MHz, CDCl3)
6.02 3.01 4.03 2.03 2.00 1.01 2.08 2.04 2.01 3.08
f1 (ppm)
JM-NB4-R22B.10.fid

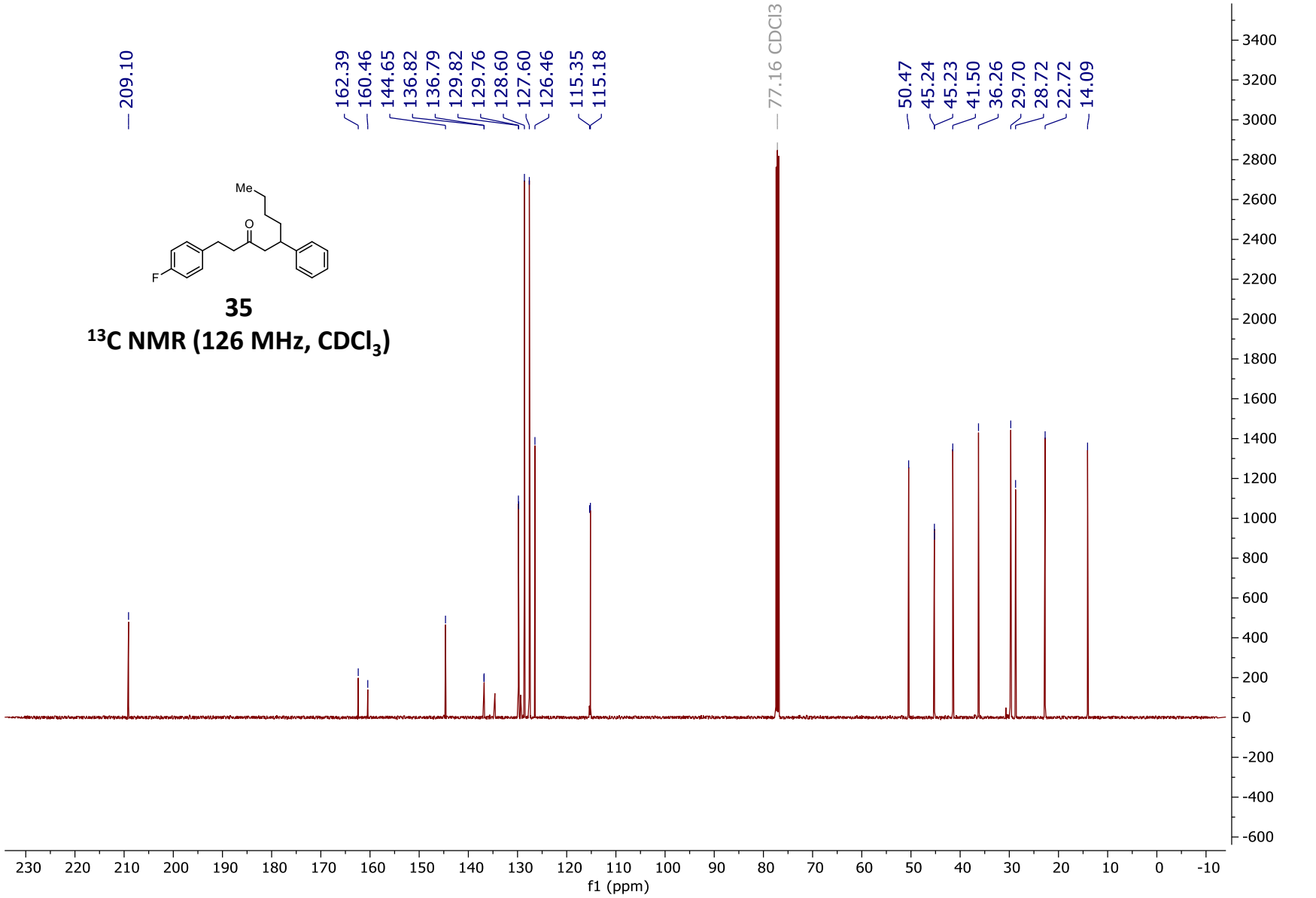

208.11
162.41
160.48
144.13
140.87
136.72
136.70
136.15
129.83
129.77
129.42
128.71
127.76
127.67
126.54
115.36
115.20
77.16 CDCl3
49.28
45.84
45.20
28.67
21.11
Me
O
F
34
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB4-R22B.11.fid

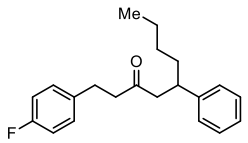


34

^{19}F NMR (376 MHz, $CDCl_3$)

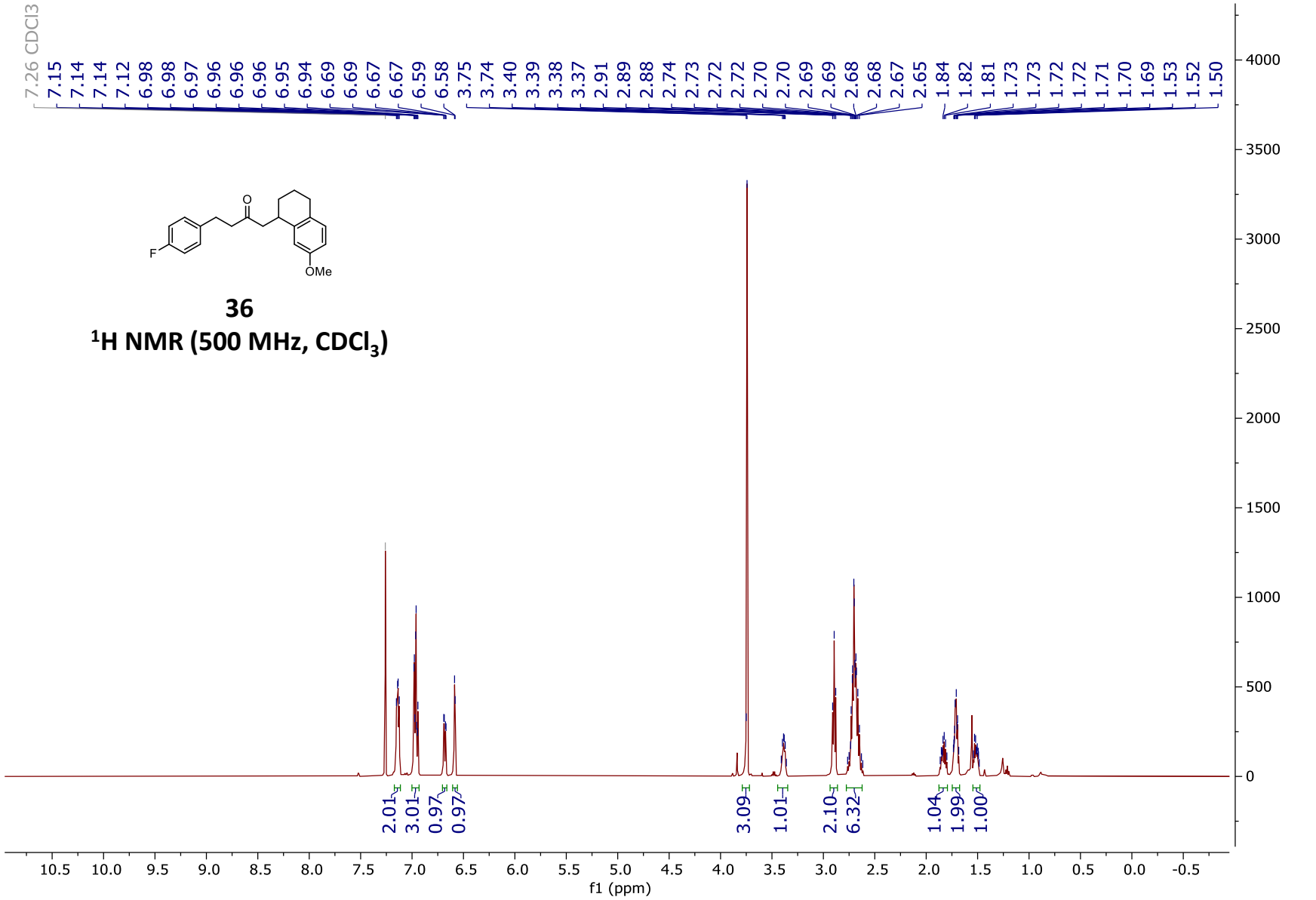

7.29 7.28 7.27 7.27 7.26 7.26 CDCl3 7.20 7.20 7.19 7.15 7.15 7.14 7.13 7.13 7.02 7.01 7.01 7.00 6.93 6.91 6.89 2.76 2.75 2.74 2.73 2.72 2.72 2.68 2.67 2.66 2.65 2.61 2.59 2.57 2.50 2.49 2.49 1.57 1.57 1.56 1.55 1.54 1.26 1.26 1.25 1.25 1.23 1.23 1.22 1.22 0.83 0.81 0.80
Me
O
F
35
1H NMR (500 MHz, CDCl3)
2.45 1.06 2.05 2.08 1.98 1.01 5.11 0.98 2.04 4.66 3.07
f1 (ppm)
JM-NB4-R8.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima

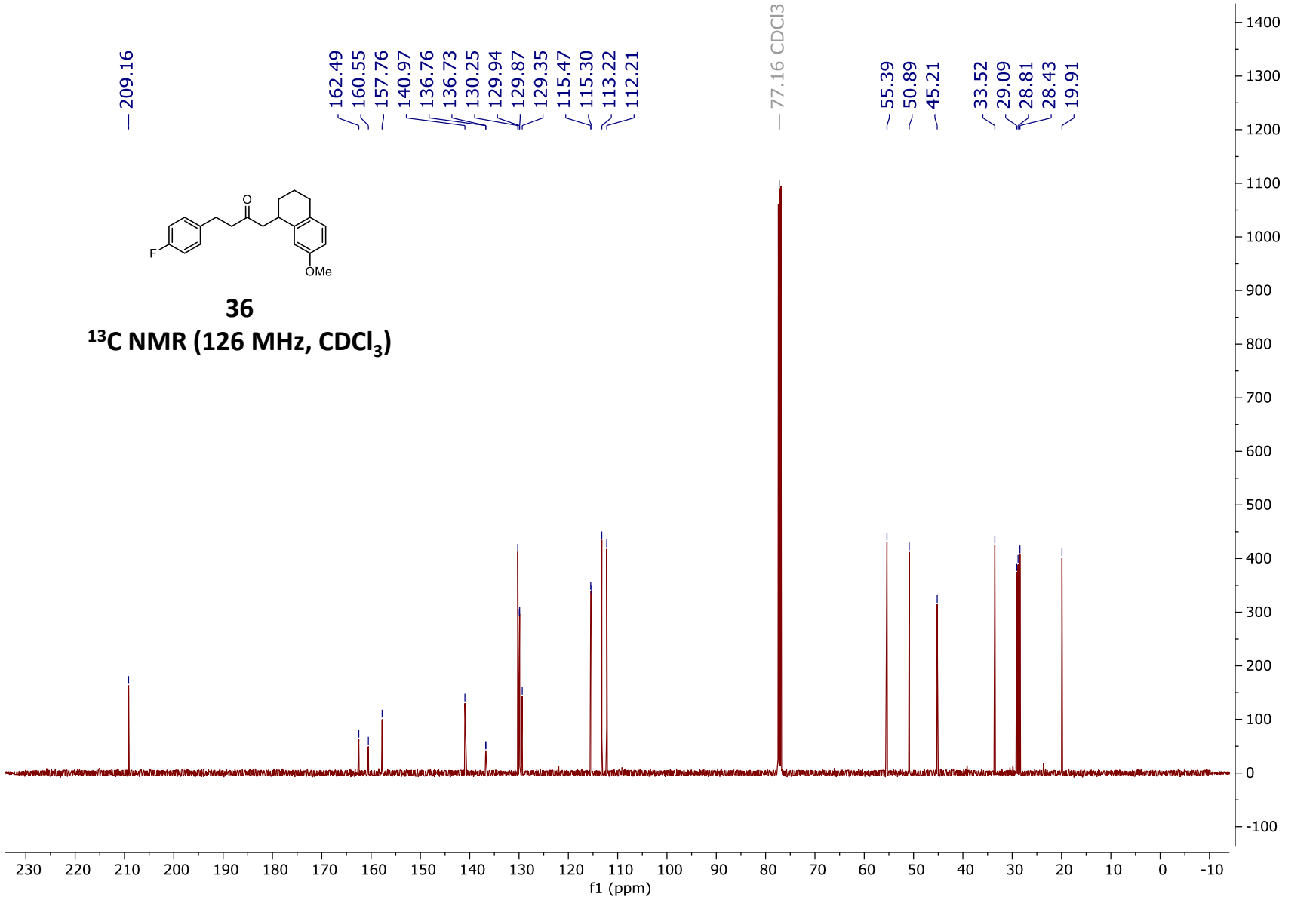

209.10
162.39
160.46
144.65
136.82
136.79
129.82
129.76
128.60
127.60
126.46
115.35
115.18
77.16 CDCl3
50.47
45.24
45.23
41.50
36.26
29.70
28.72
22.72
14.09
Me
O
F
35
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB4-R8.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima



35

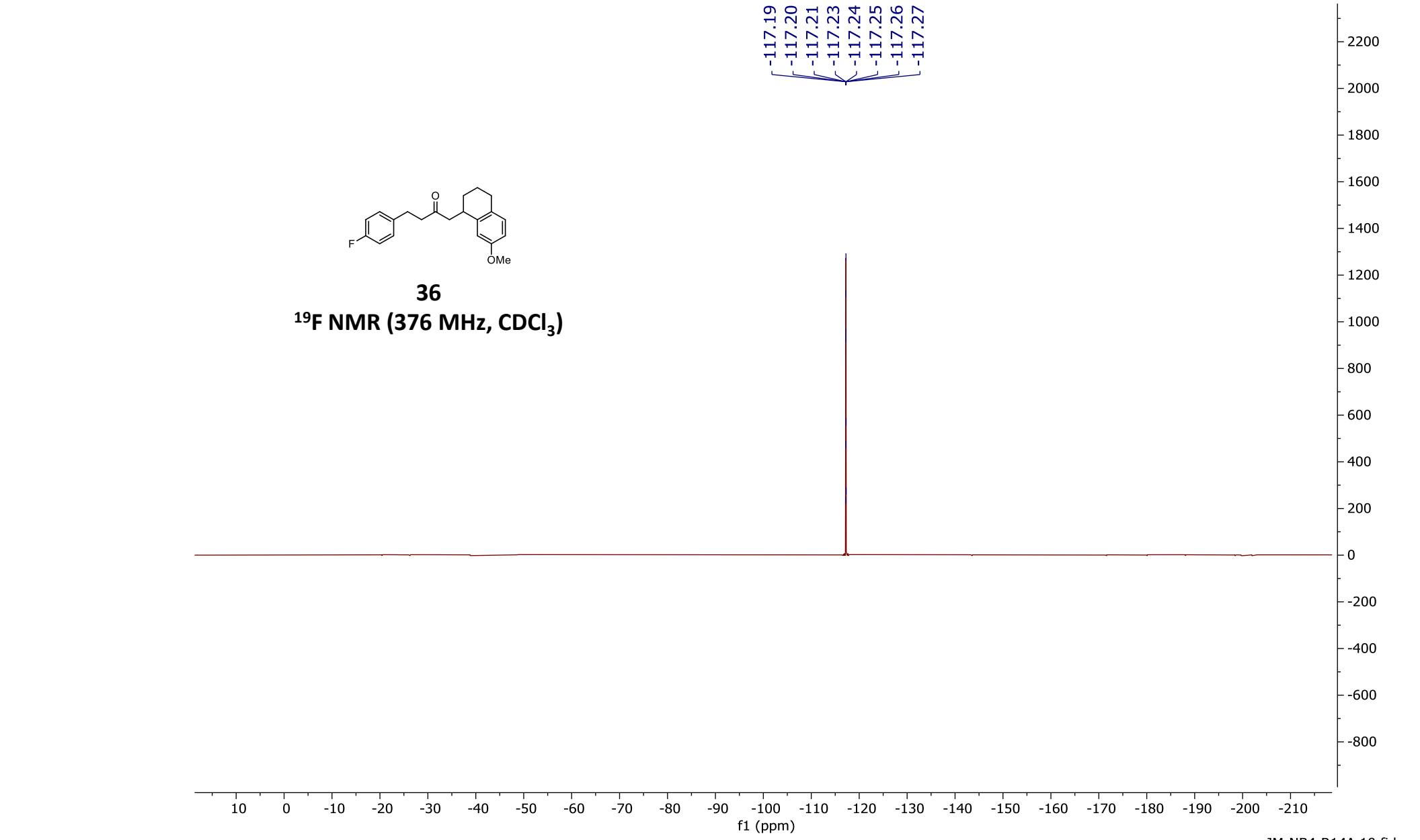
^{19}F NMR (376 MHz, $CDCl_3$)


7.26 CDCl3
7.15 7.14 7.14 7.12 6.98 6.98 6.97 6.96 6.96 6.96 6.95 6.94 6.69 6.69 6.67 6.67 6.59 6.58
3.75 3.74 3.40 3.39 3.38 3.37 2.91 2.89 2.88 2.74 2.73 2.72 2.72 2.70 2.70 2.69 2.69 2.68 2.68 2.67 2.65
1.84 1.82 1.81 1.73 1.73 1.72 1.72 1.71 1.70 1.69 1.53 1.52 1.50
O
F
OMe
36
1H NMR (500 MHz, CDCl3)
2.01 3.01 0.97 0.97 3.09 1.01 2.10 6.32 1.04 1.99 1.00
f1 (ppm)
JM-NB4-R14A.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima



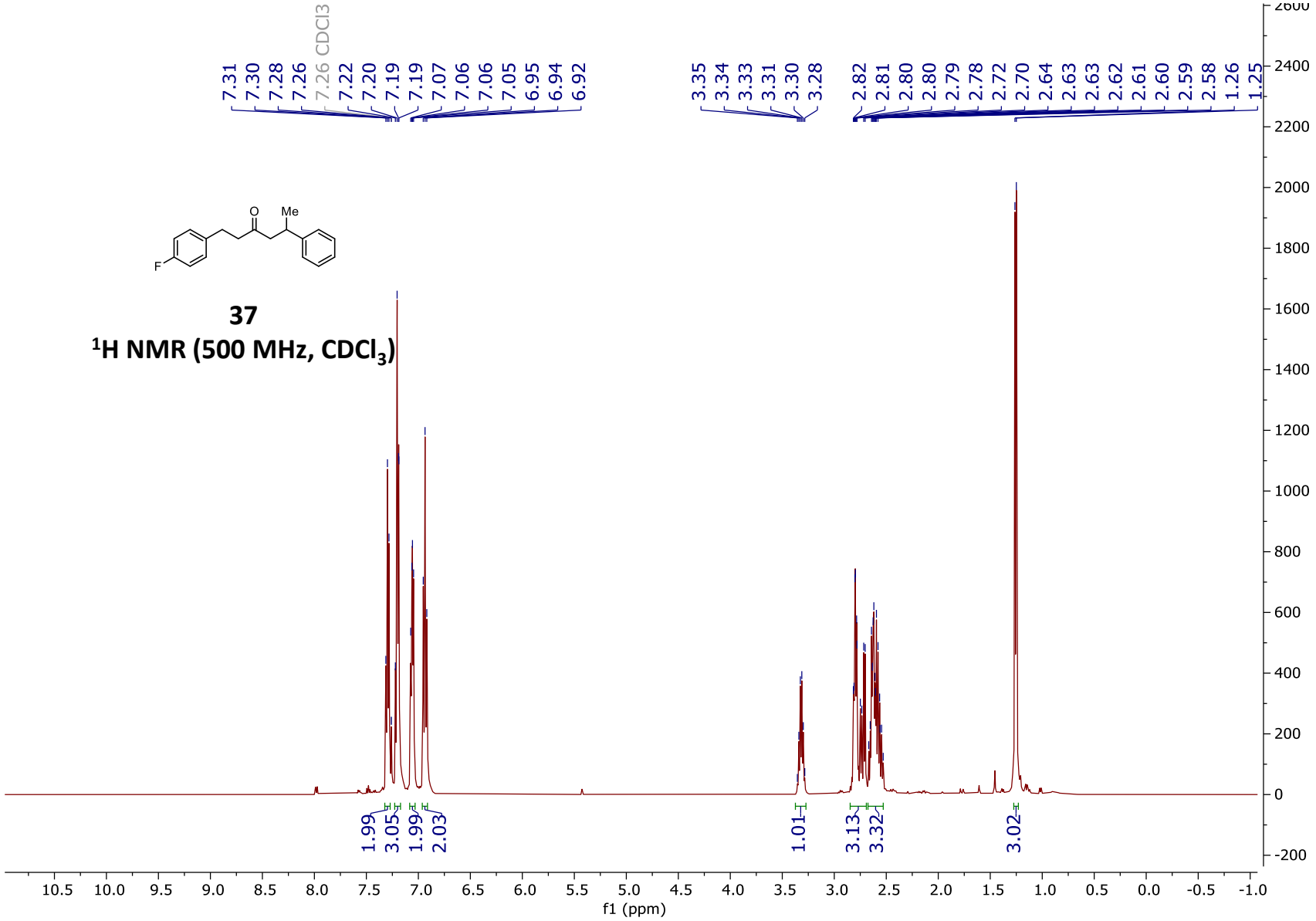
36

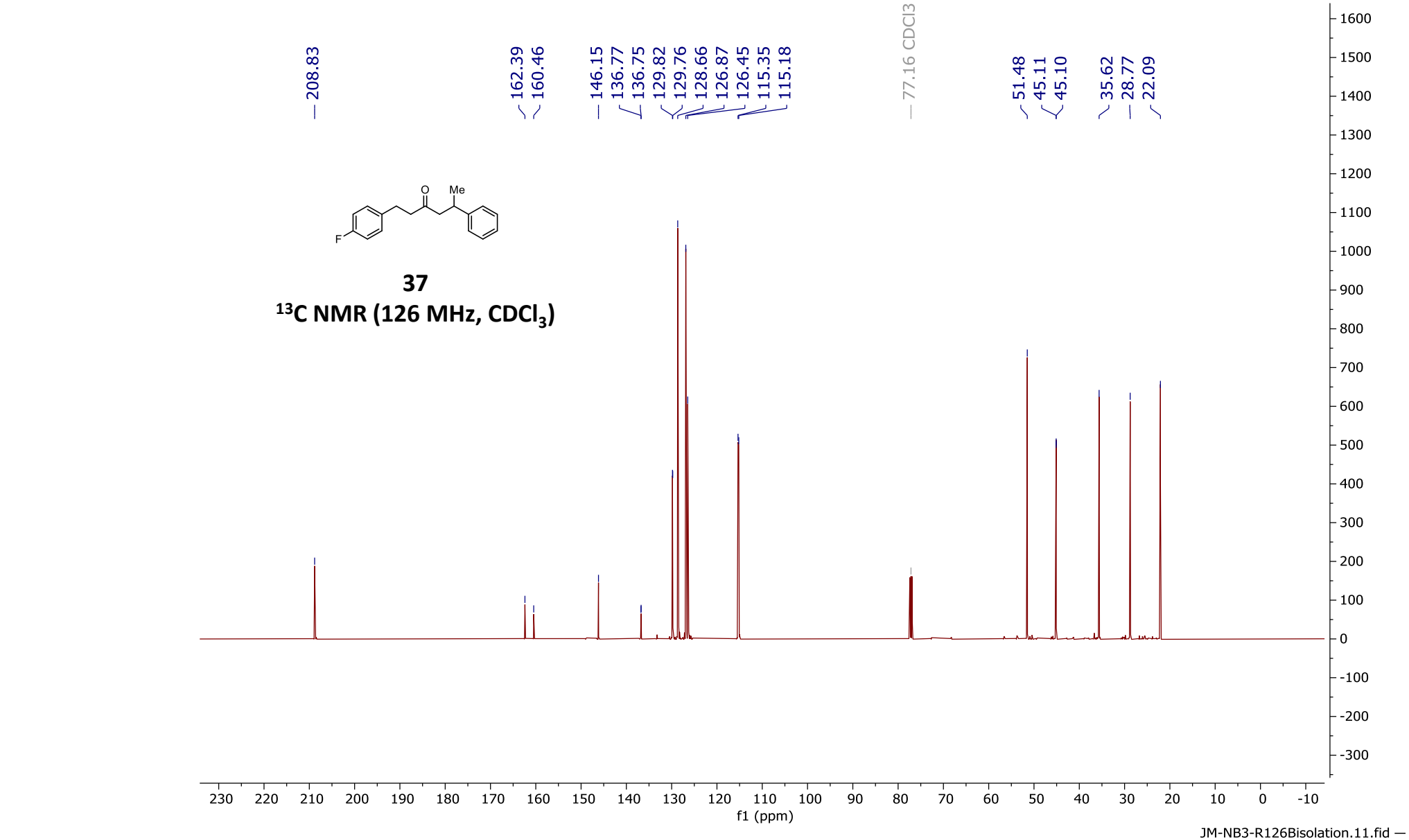
^{13}C NMR (126 MHz, $CDCl_3$)

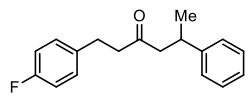


36

^{19}F NMR (376 MHz, $CDCl_3$)

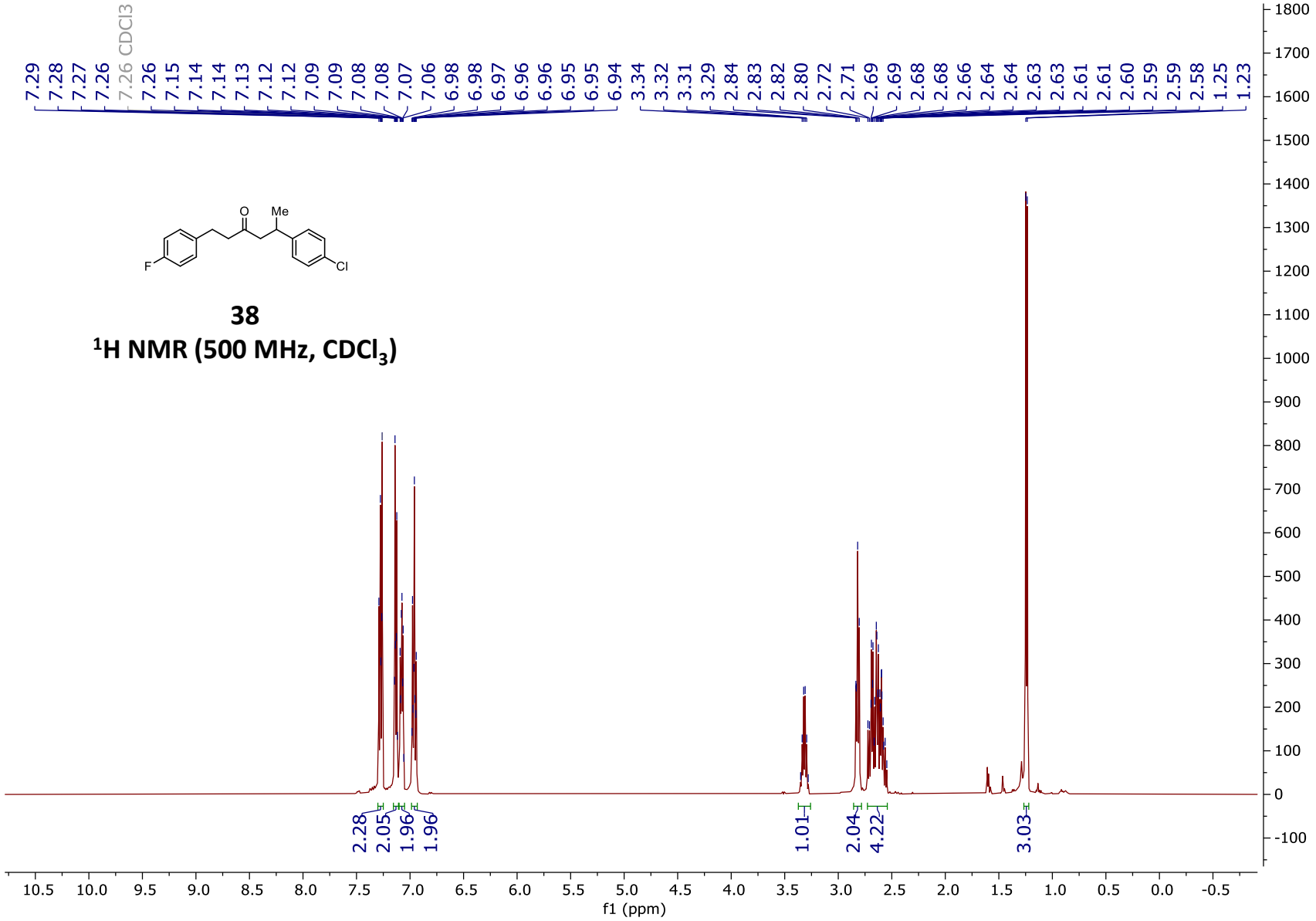

7.31
7.30
7.28
7.26
7.26 CDCl3
7.22
7.20
7.19
7.19
7.07
7.06
7.06
7.05
6.95
6.94
6.92
3.35
3.34
3.33
3.31
3.30
3.28
2.82
2.81
2.80
2.80
2.79
2.78
2.72
2.70
2.64
2.63
2.63
2.62
2.61
2.60
2.59
2.58
1.26
1.25
O
Me
F
37
1H NMR (500 MHz, CDCl3)
1.99
3.05
1.99
2.03
1.01
3.13
3.32
3.02
f1 (ppm)
JM-NB3-R126Bisolation.10.fid

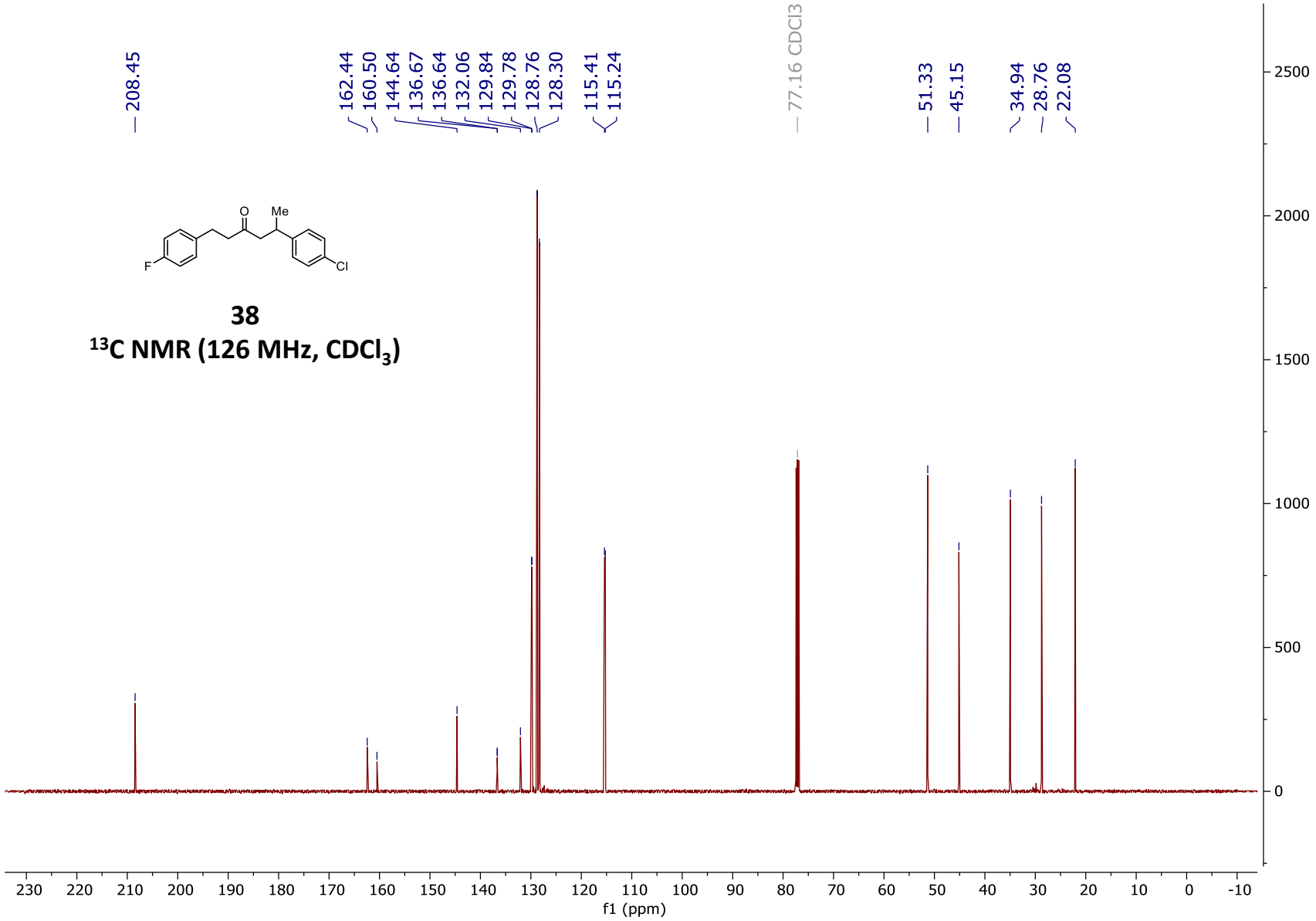

208.83
162.39
160.46
146.15
136.77
136.75
129.82
129.76
128.66
126.87
126.45
115.35
115.18
77.16 CDCl3
51.48
45.11
45.10
35.62
28.77
22.09
O
Me
F
37
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB3-R126Bisolation.11.fid



37

^{19}F NMR (376 MHz, $CDCl_3$)

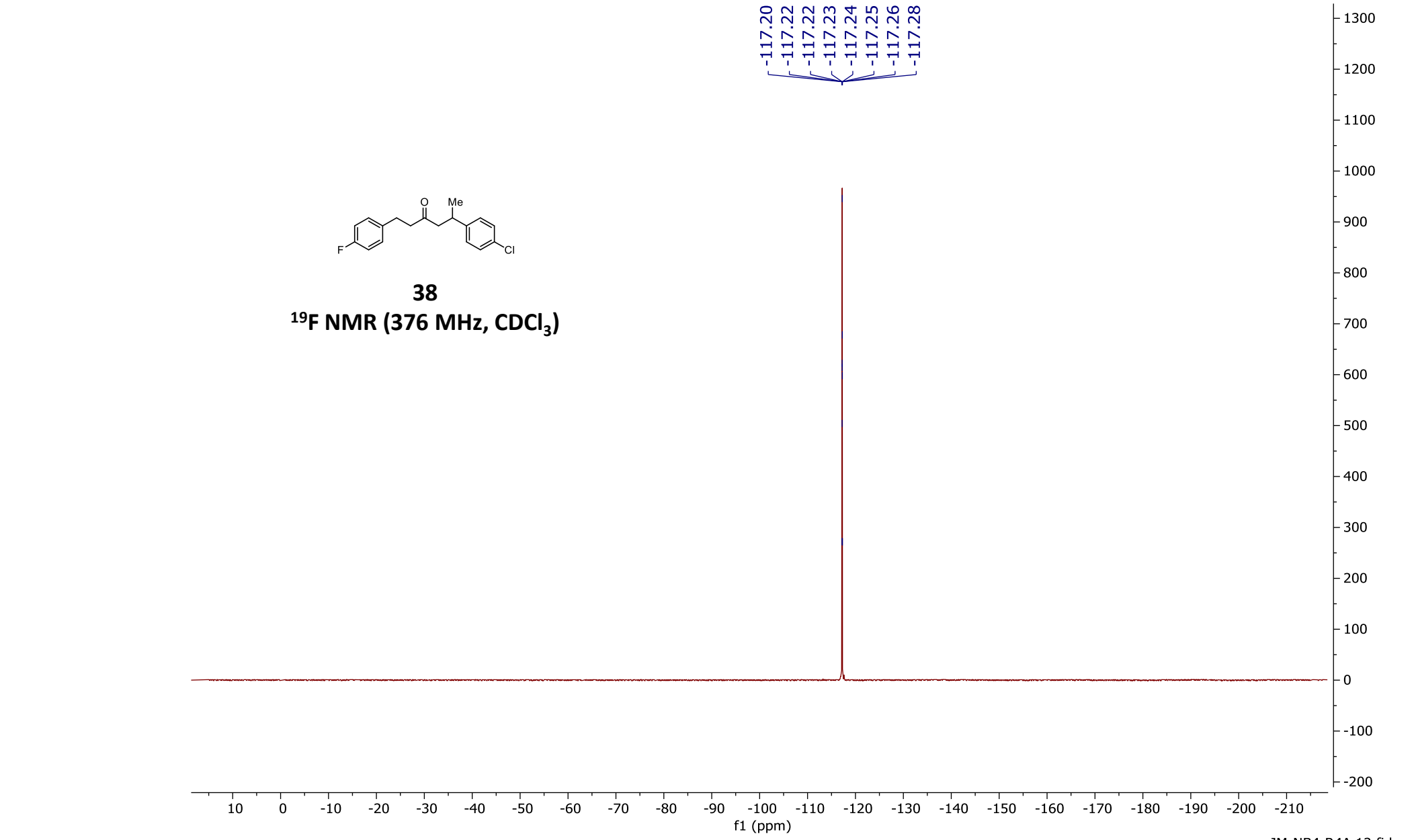

7.29 7.28 7.27 7.26 7.26 CDCl3 7.26 7.15 7.14 7.14 7.13 7.12 7.12 7.09 7.09 7.08 7.08 7.07 7.06 6.98 6.98 6.97 6.96 6.96 6.95 6.95 6.94 3.34 3.32 3.31 3.29 2.84 2.83 2.82 2.80 2.72 2.71 2.69 2.69 2.68 2.68 2.66 2.64 2.64 2.63 2.63 2.61 2.61 2.60 2.59 2.59 2.58 1.25 1.23
O
Me
F
Cl
38
1H NMR (500 MHz, CDCl3)
2.28 2.05 1.96 1.96 1.01 2.04 4.22 3.03
f1 (ppm)
JM-NB4-R5A-ISOL.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima 1



38

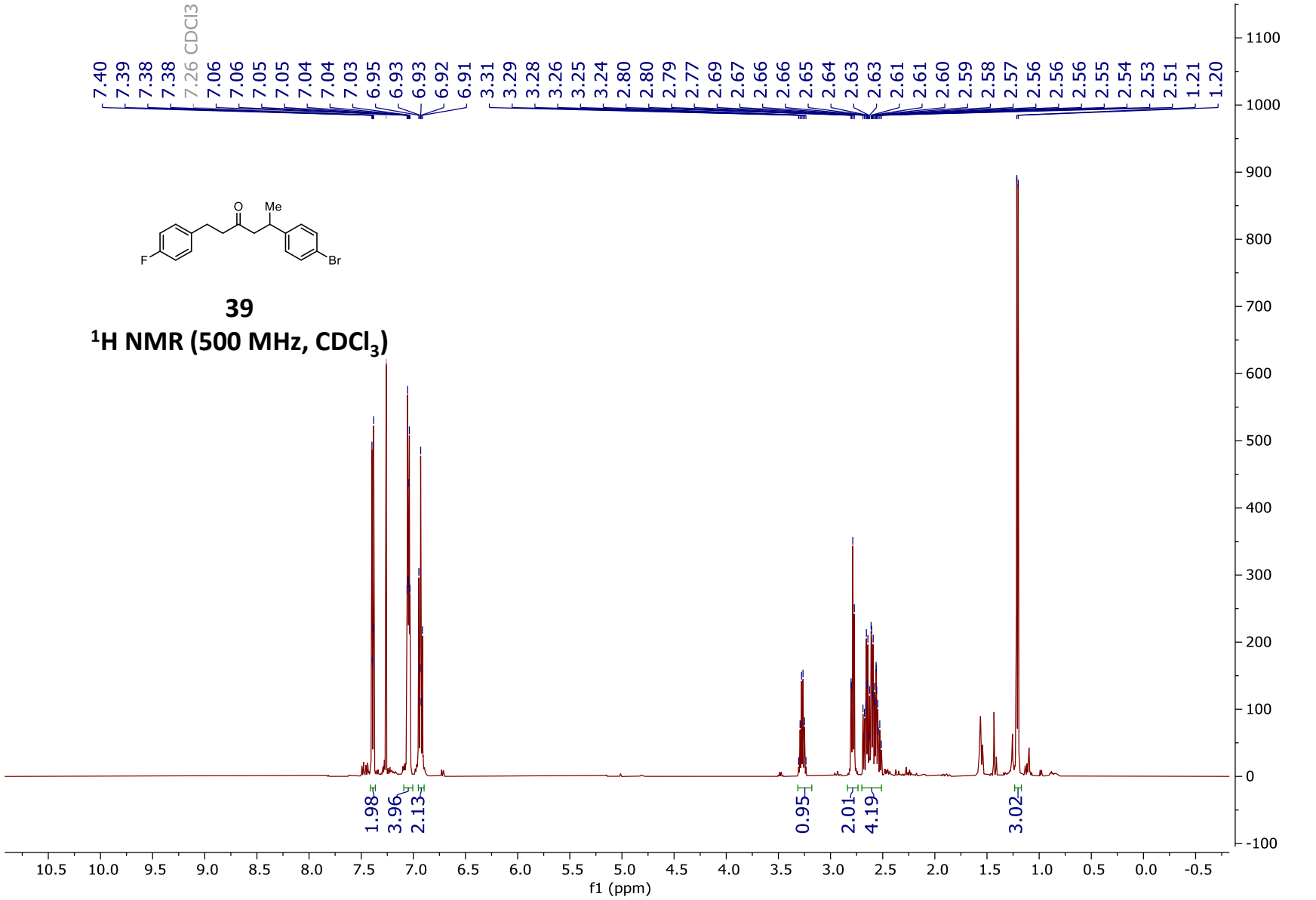
^{13}C NMR (126 MHz, $CDCl_3$)

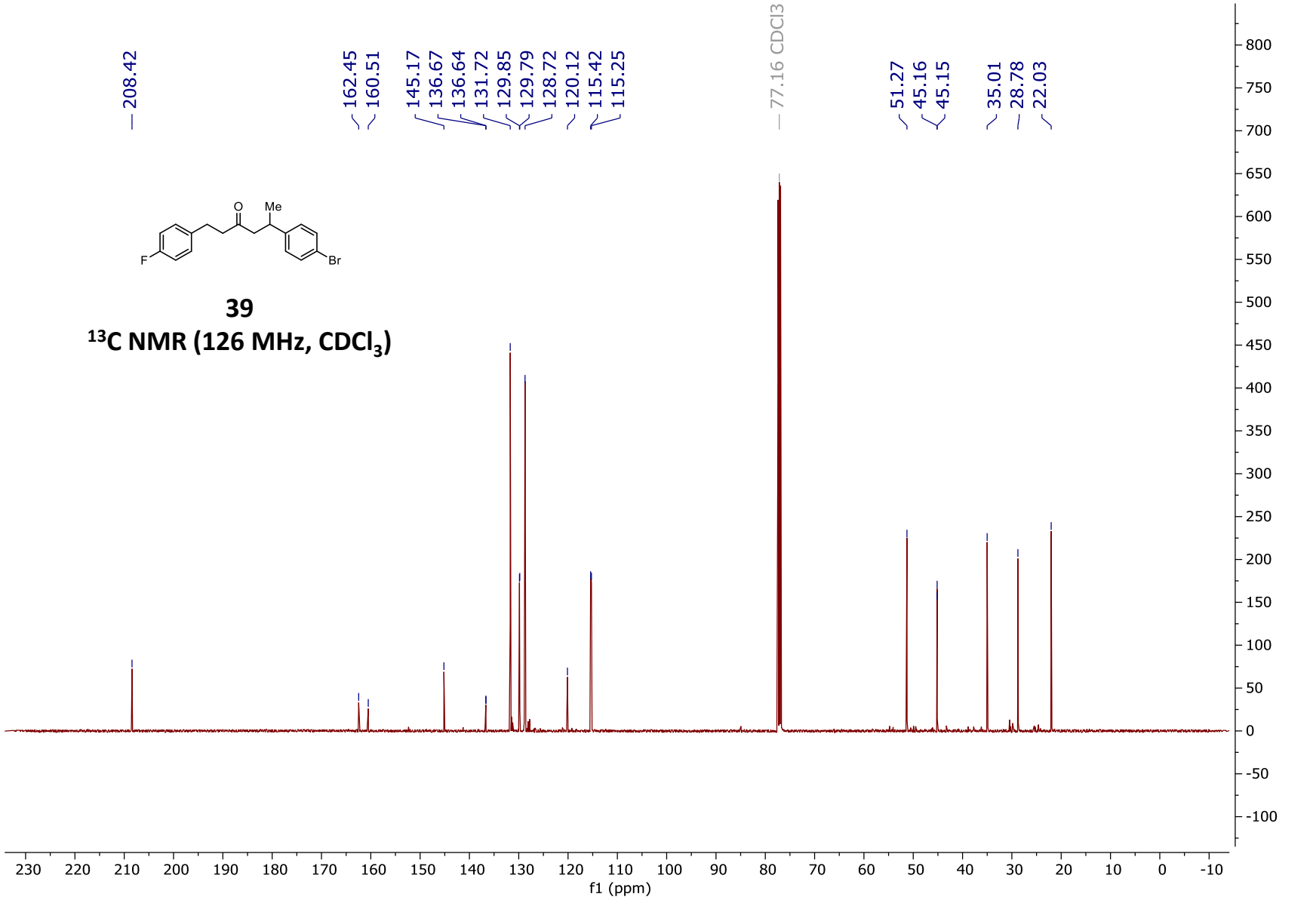
JM-NB4-R5A-ISOL.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima 1



38

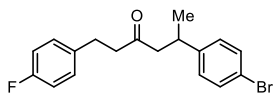
^{19}F NMR (376 MHz, $CDCl_3$)


7.40 7.39 7.38 7.38 7.26 CDCl3 7.06 7.06 7.05 7.05 7.04 7.04 7.03 6.95 6.93 6.93 6.92 6.91
3.31 3.29 3.28 3.26 3.25 3.24 2.80 2.80 2.79 2.77 2.69 2.67 2.66 2.66 2.65 2.64 2.63 2.63 2.61 2.61 2.60 2.59 2.58 2.57 2.56 2.56 2.56 2.55 2.54 2.53 2.51 1.21 1.20
O
Me
F
Br
39
1H NMR (500 MHz, CDCl3)
1.98
3.96
2.13
0.95
2.01
4.19
3.02
f1 (ppm)
JM-NB4-R16A.10.fid



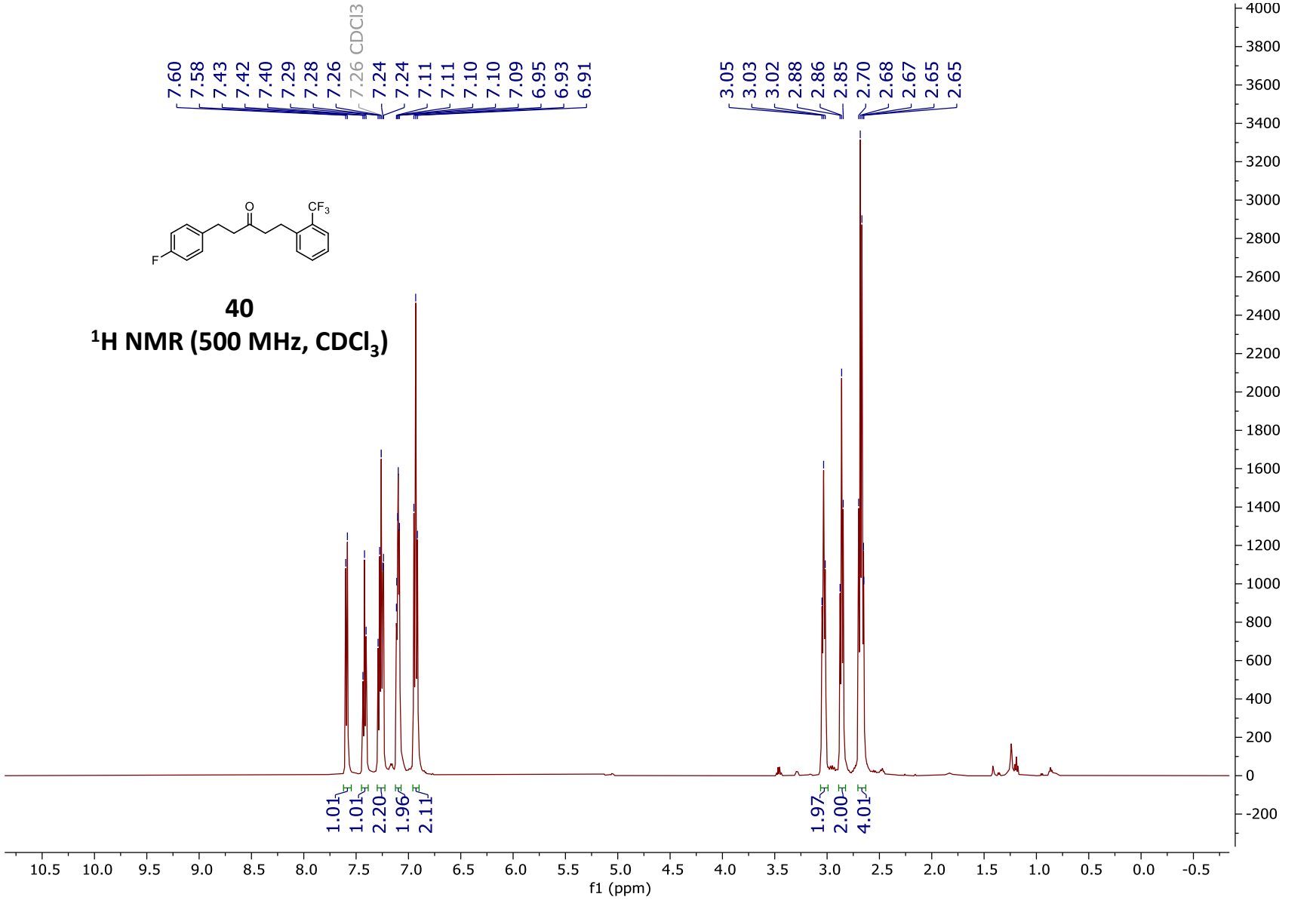
39

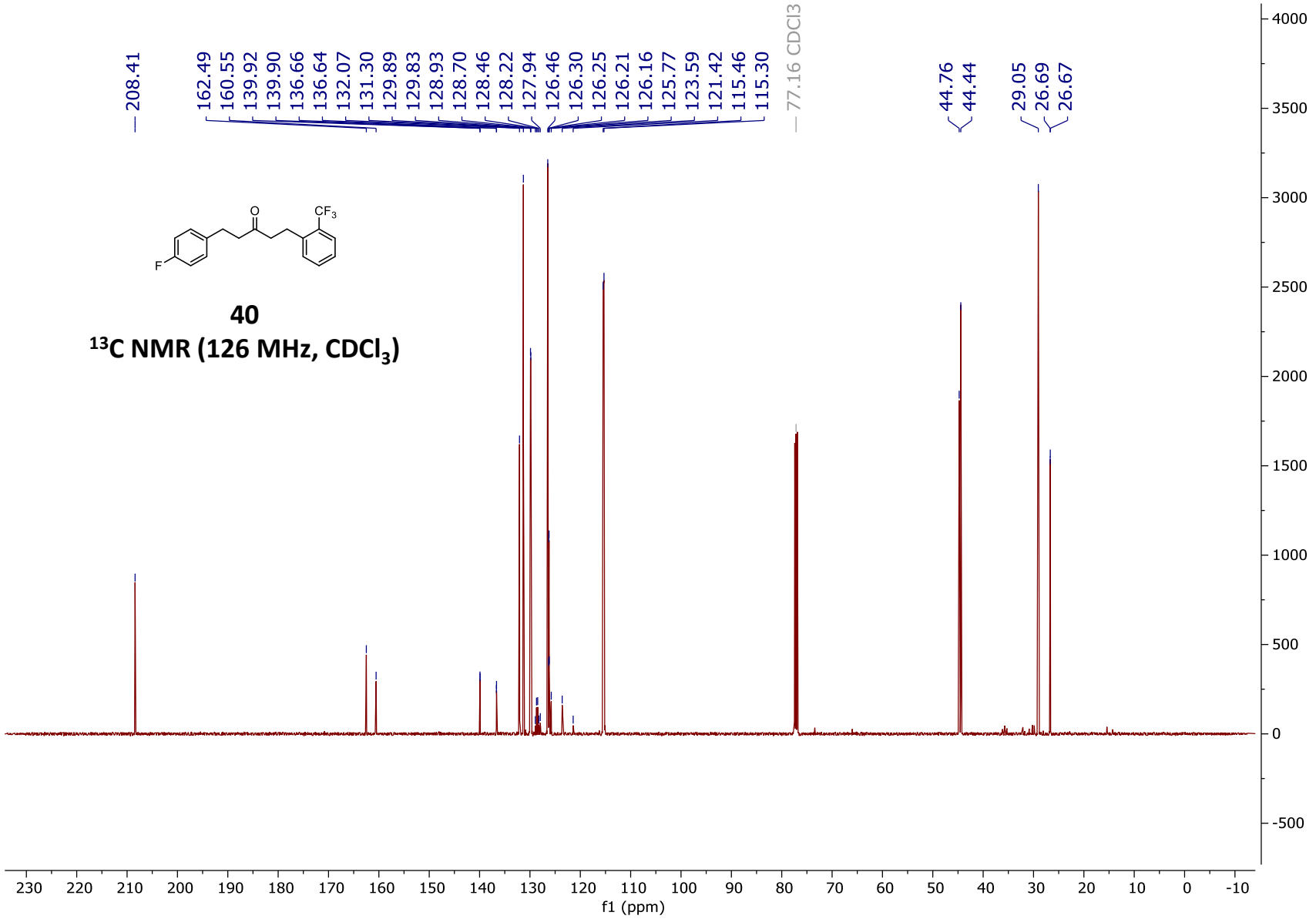
^{13}C NMR (126 MHz, $CDCl_3$)

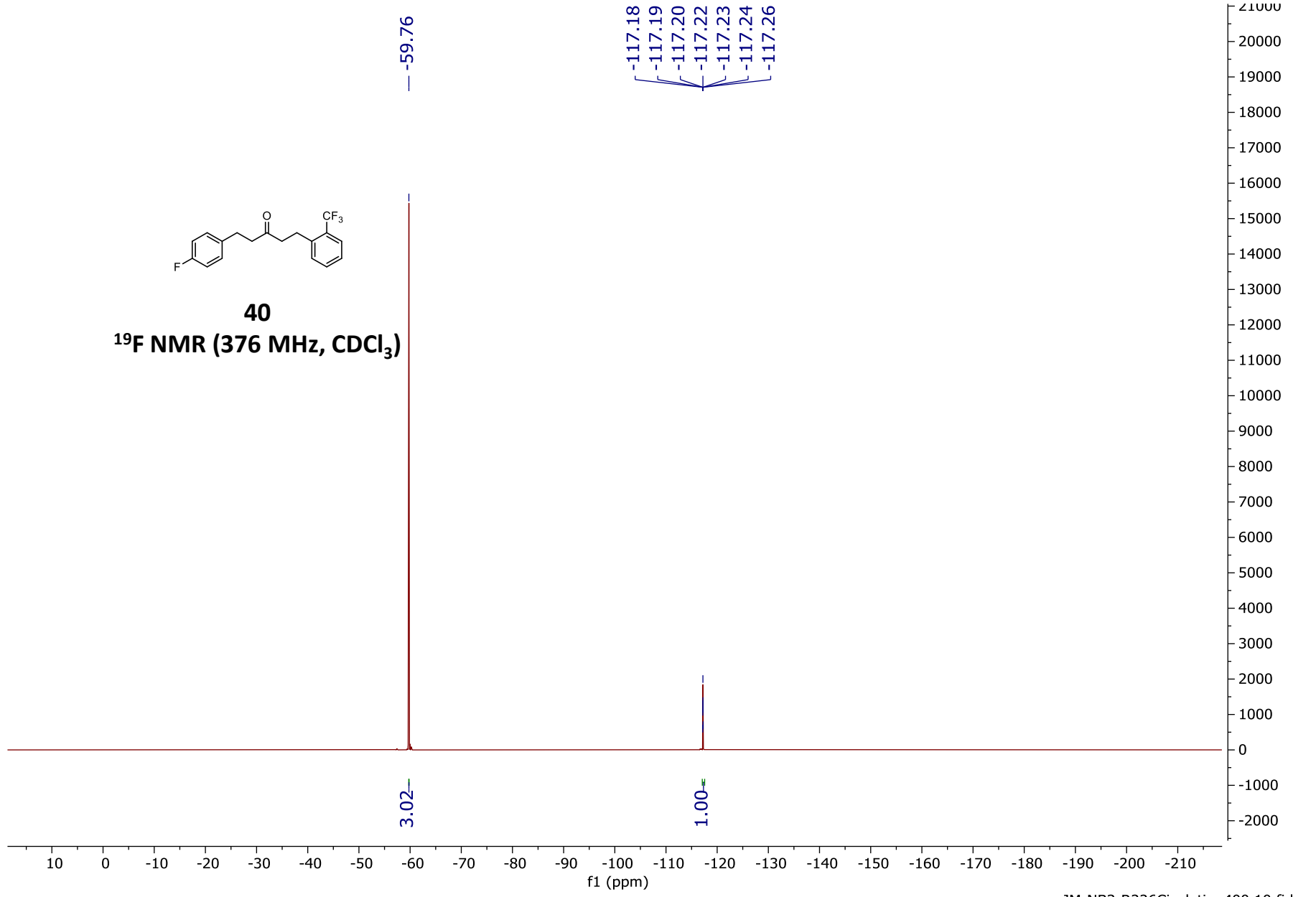


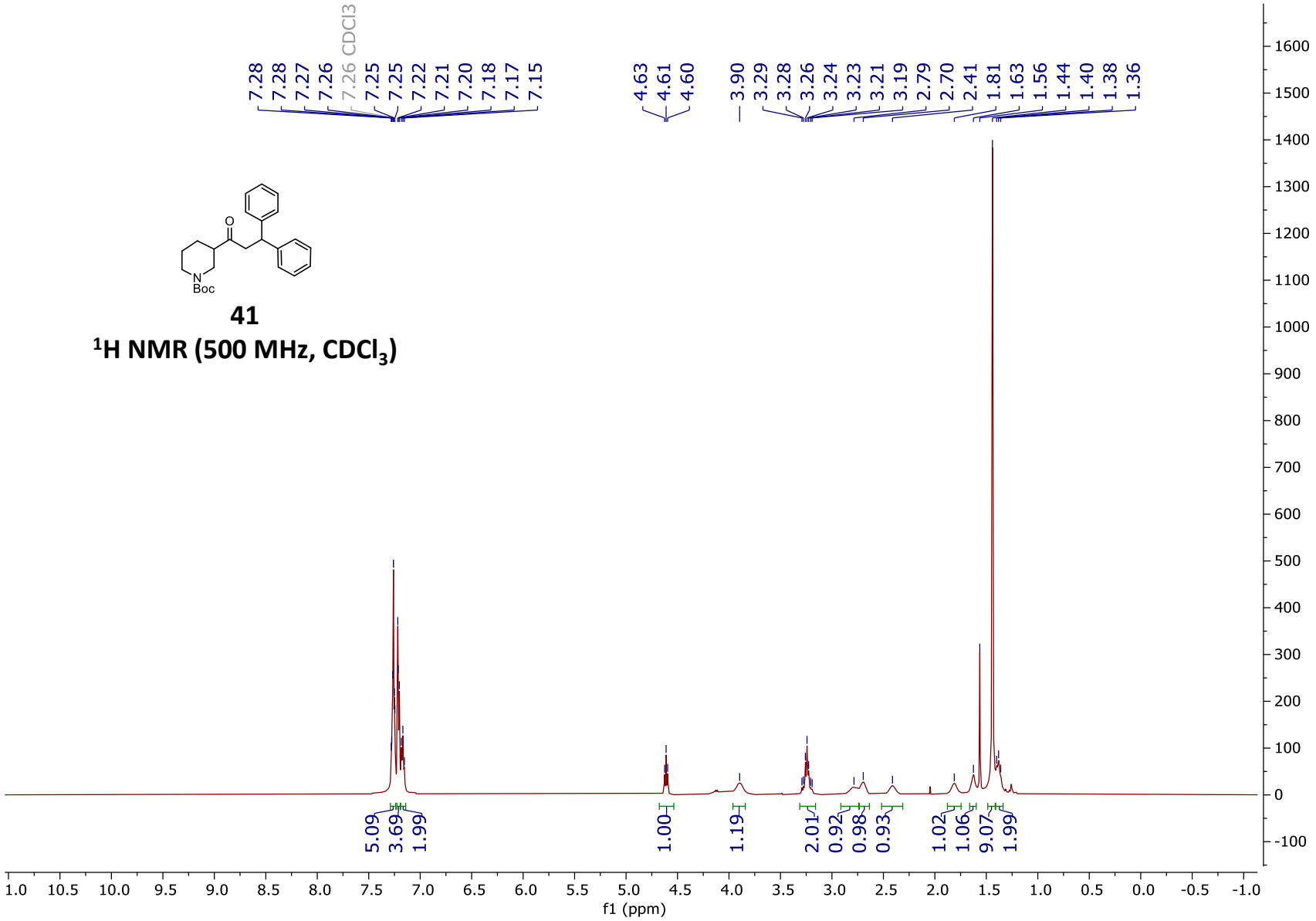
39

^{19}F NMR (376 MHz, $CDCl_3$)


7.60
7.58
7.43
7.42
7.40
7.29
7.28
7.26
7.26 CDCl3
7.24
7.24
7.11
7.11
7.10
7.10
7.09
6.95
6.93
6.91
3.05
3.03
3.02
2.88
2.86
2.85
2.70
2.68
2.67
2.65
2.65
O
CF3
F
40
1H NMR (500 MHz, CDCl3)
1.01
1.01
2.20
1.96
2.11
1.97
2.00
4.01
f1 (ppm)
JM-NB3-R226Cisolation.10.fid — PROTON.PU CDCl3 /opt/topspin3.0 jima 1

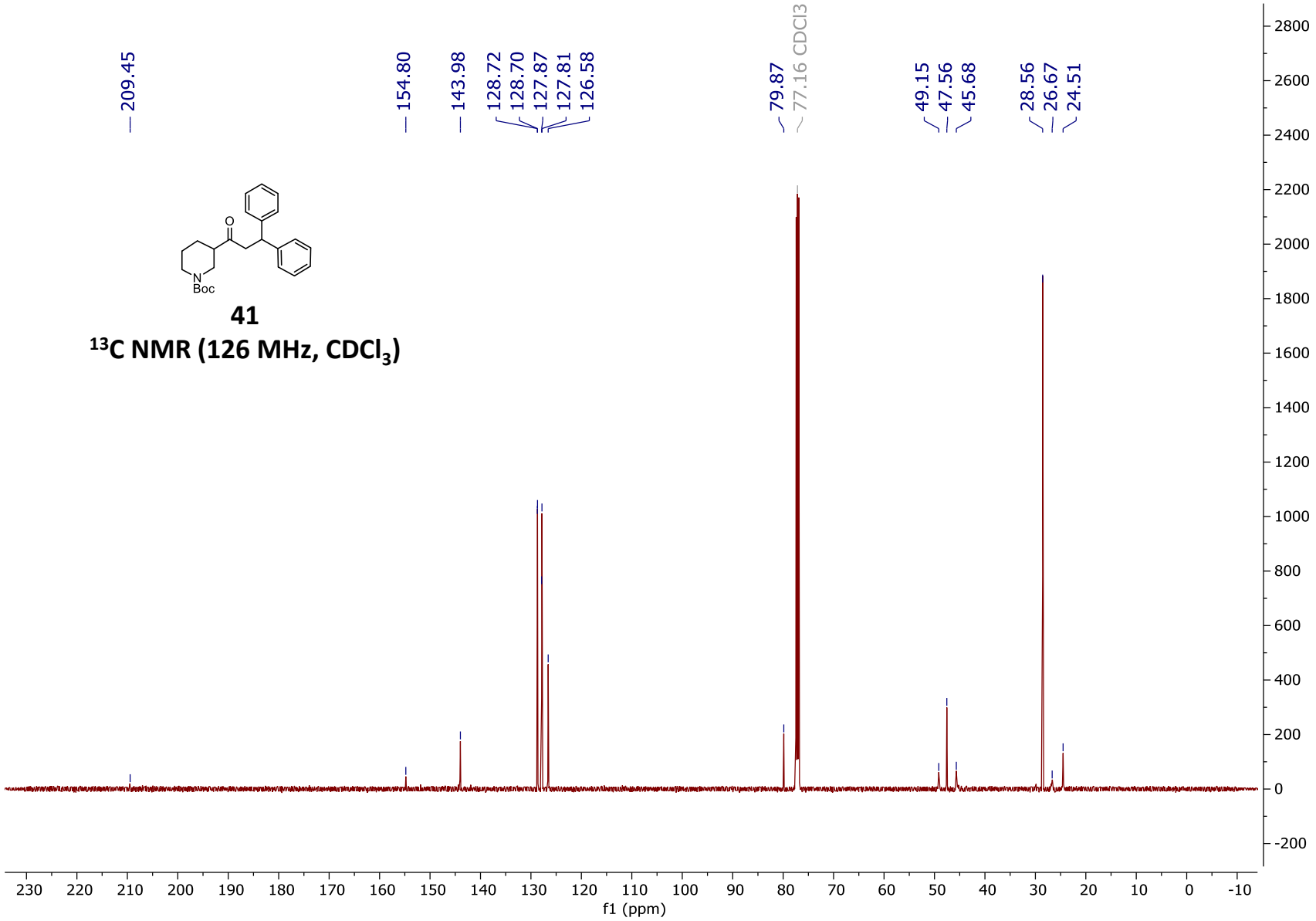

208.41
162.49
160.55
139.92
139.90
136.66
136.64
132.07
131.30
129.89
129.83
128.93
128.70
128.46
128.22
127.94
126.46
126.30
126.25
126.21
126.16
125.77
123.59
121.42
115.46
115.30
77.16 CDCl3
44.76
44.44
29.05
26.69
26.67
O
CF3
F
40
13C NMR (126 MHz, CDCl3)
4000
3500
3000
2500
2000
1500
1000
500
0
-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)
JM-NB3-R226Cisolation.11.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima 1


-59.76
-117.18
-117.19
-117.20
-117.22
-117.23
-117.24
-117.26
O
CF3
F
40
19F NMR (376 MHz, CDCl3)
3.02
1.00
f1 (ppm)
JM-NB3-R226Cisolation400.10.fid



41

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


209.45
154.80
143.98
128.72
128.70
127.87
127.81
126.58
79.87
77.16 CDCl3
49.15
47.56
45.68
28.56
26.67
24.51
O
N
Boc
41
13C NMR (126 MHz, CDCl3)
f1 (ppm)
JM-NB4-R50B.31.fid — C13CPDp1.PU CDCl3 /opt/topspin3.0 jima