Synthesis
Reviews and Full Papers in Chemical Synthesis

Supporting Information
for DOI: 10.1055/s-0037-1610437

Thieme

Short Enantioselective Formal Synthesis of (–)-Platencin

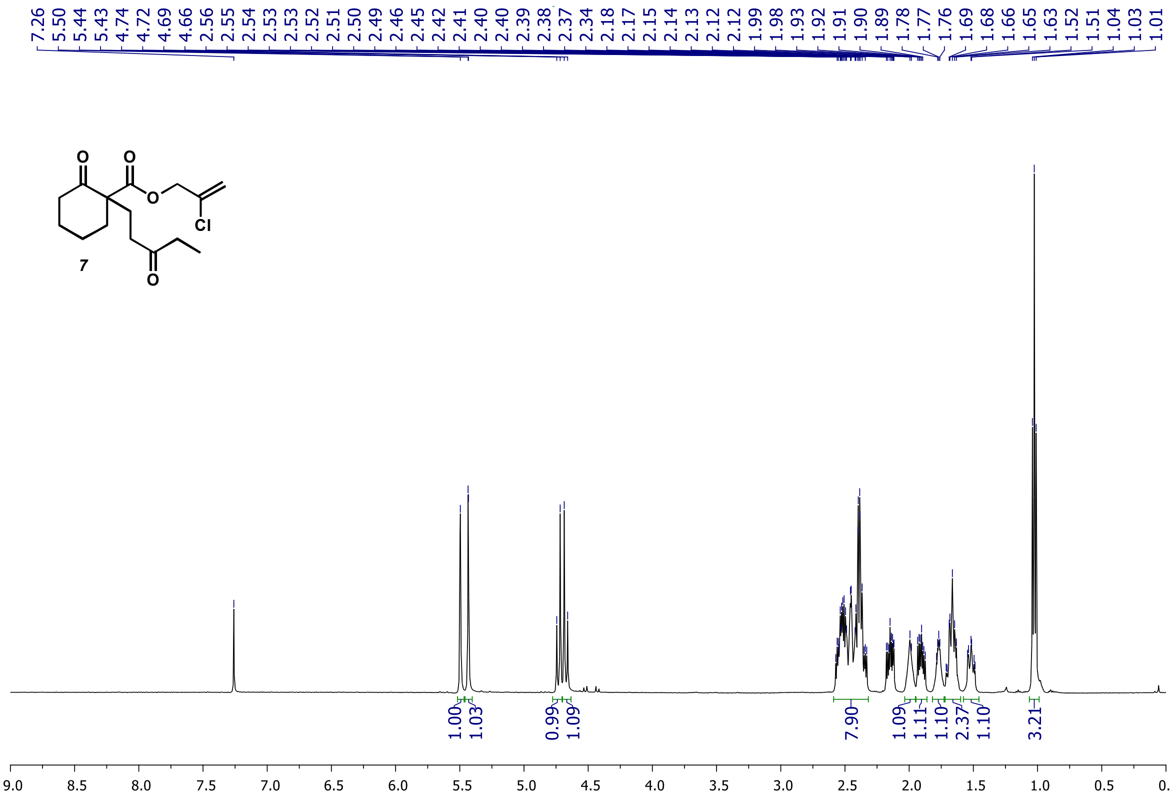
*Christian Defieber, Justin T. Mohr, Gennadii A. Grabovyi, Brian M. Stoltz**

Supporting Information

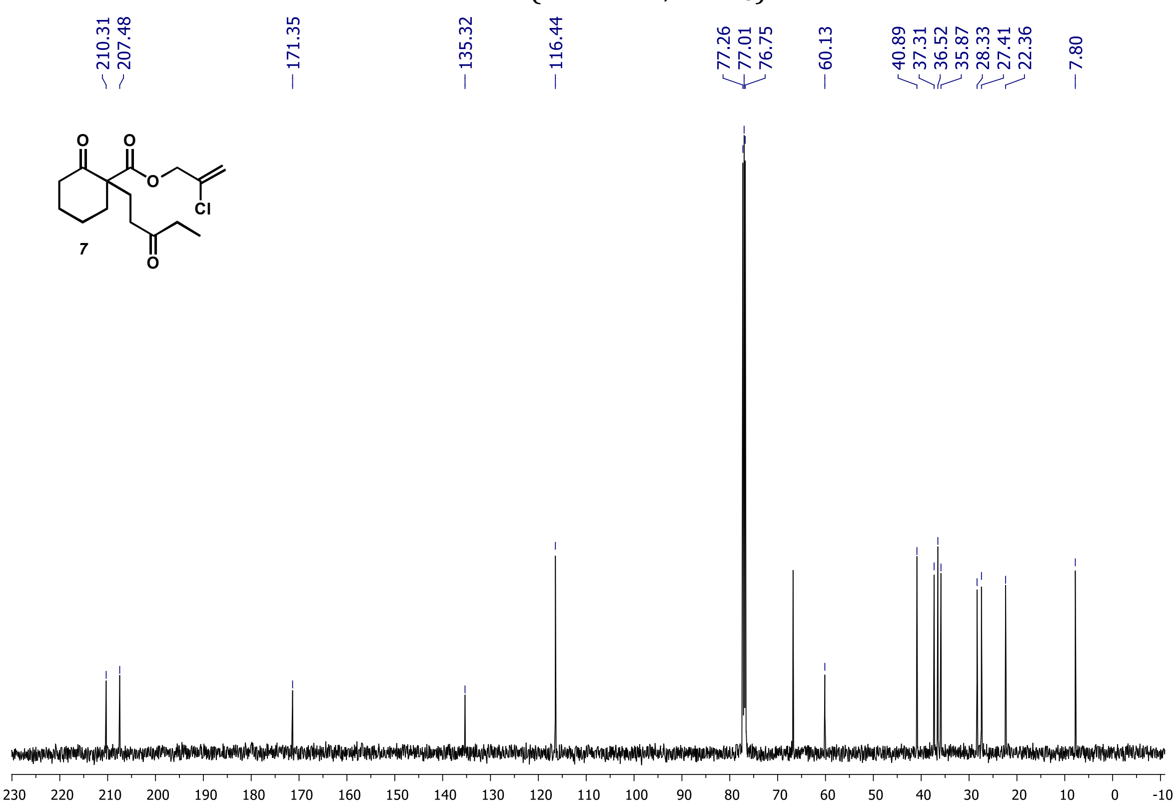
NMR Spectra

and

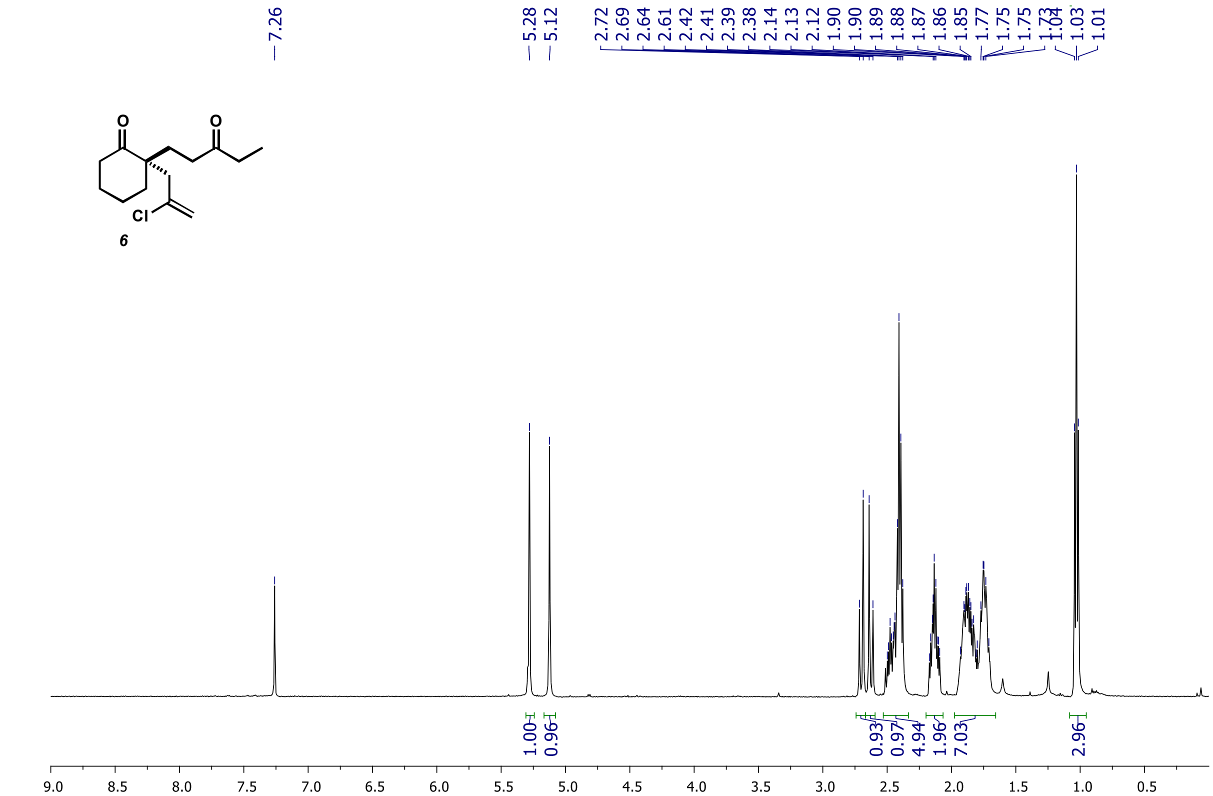
Crystallographic Data for Compound 21



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



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



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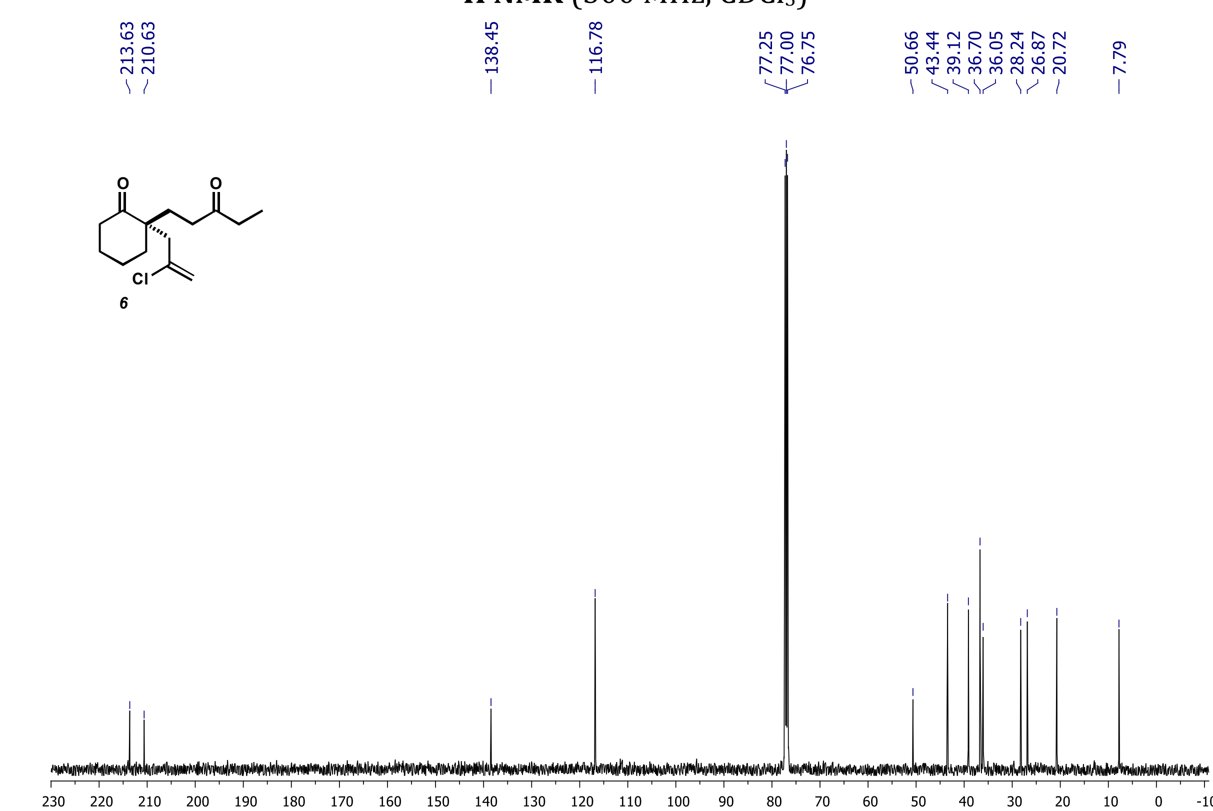

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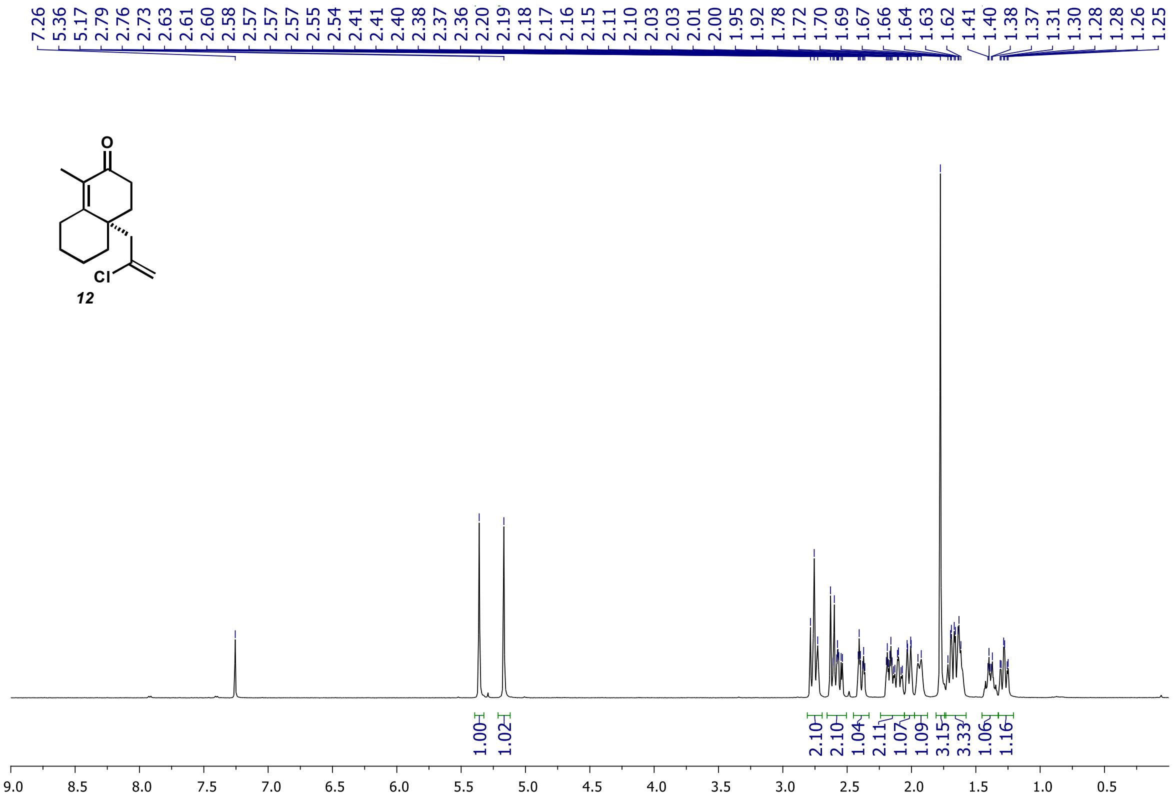

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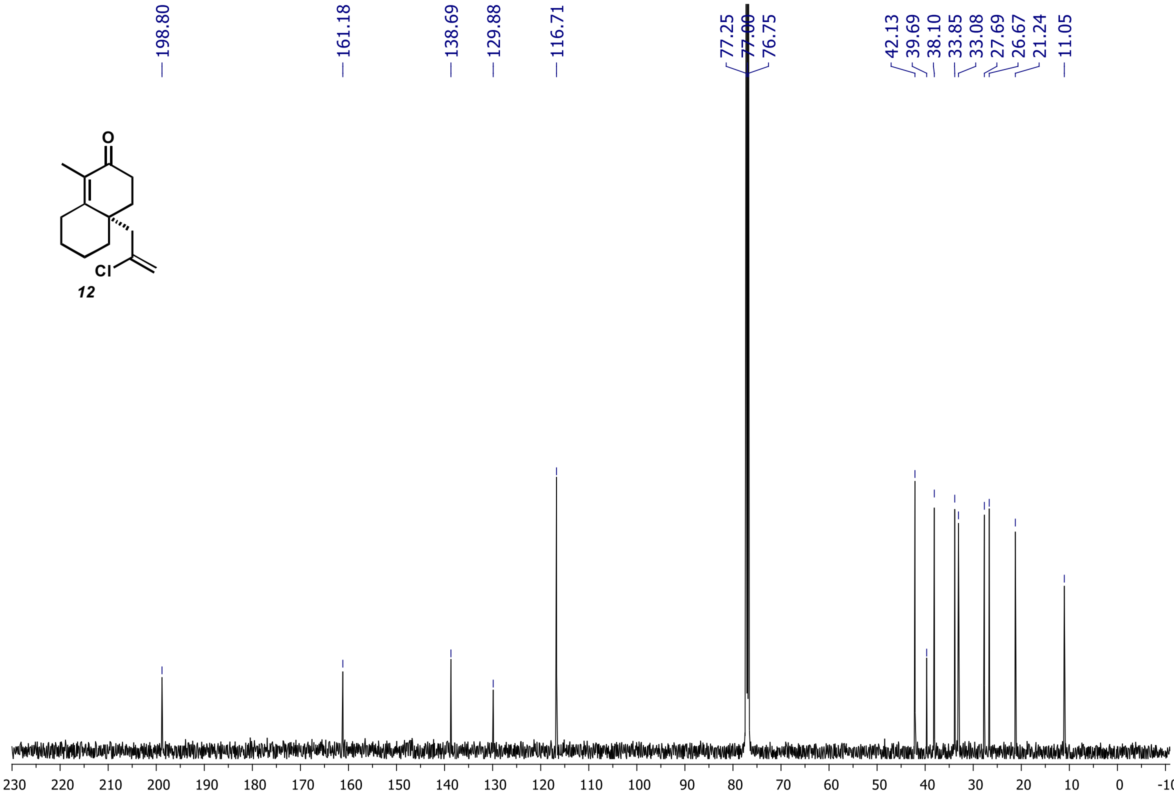

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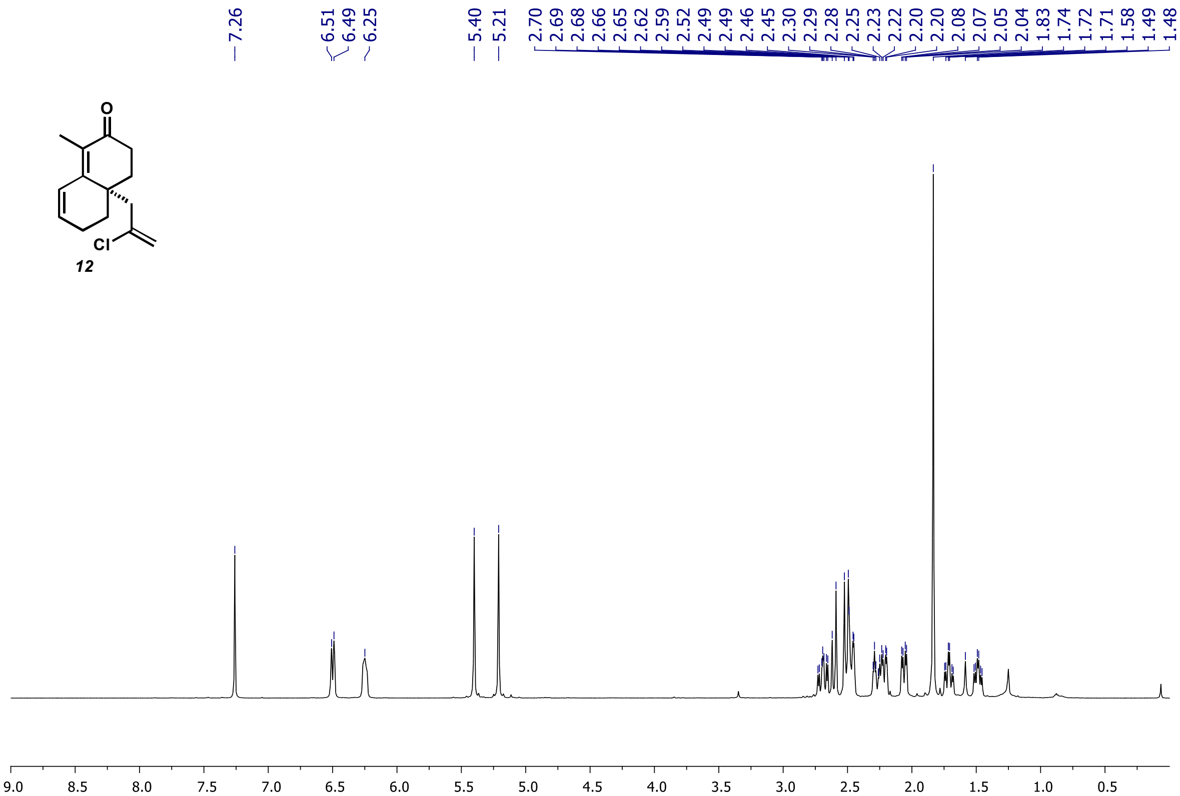

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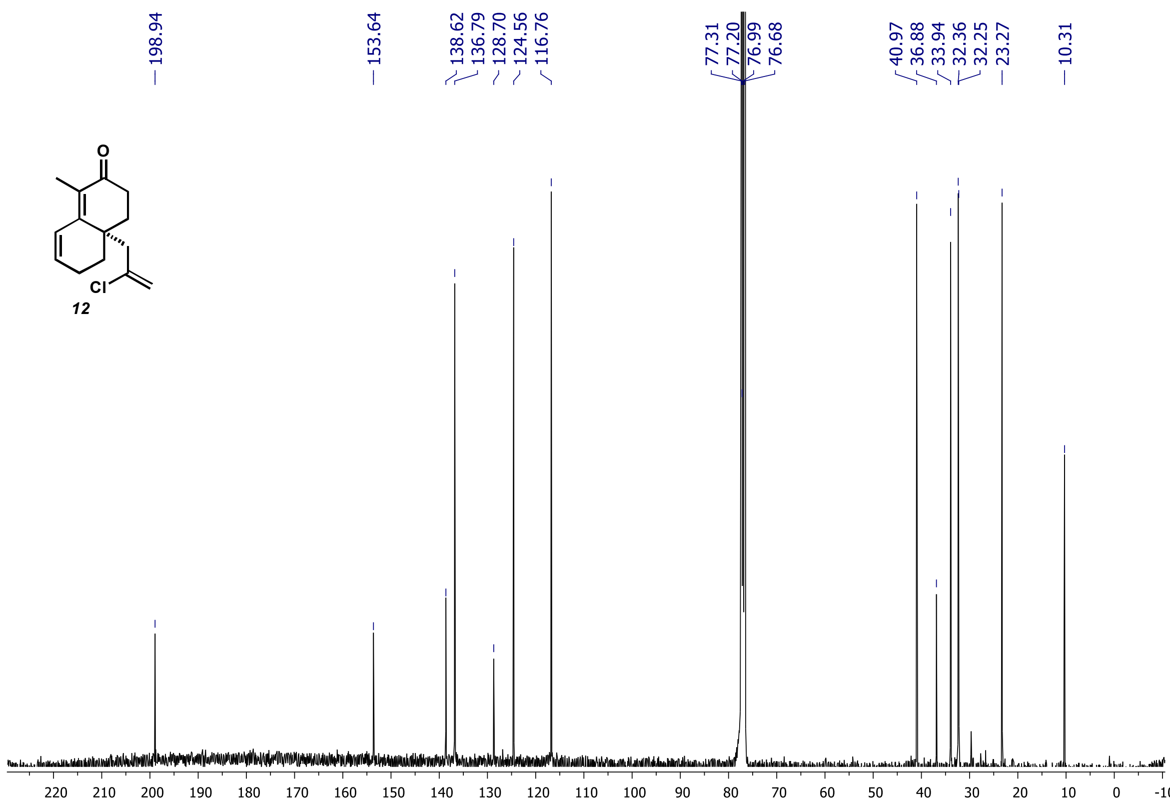
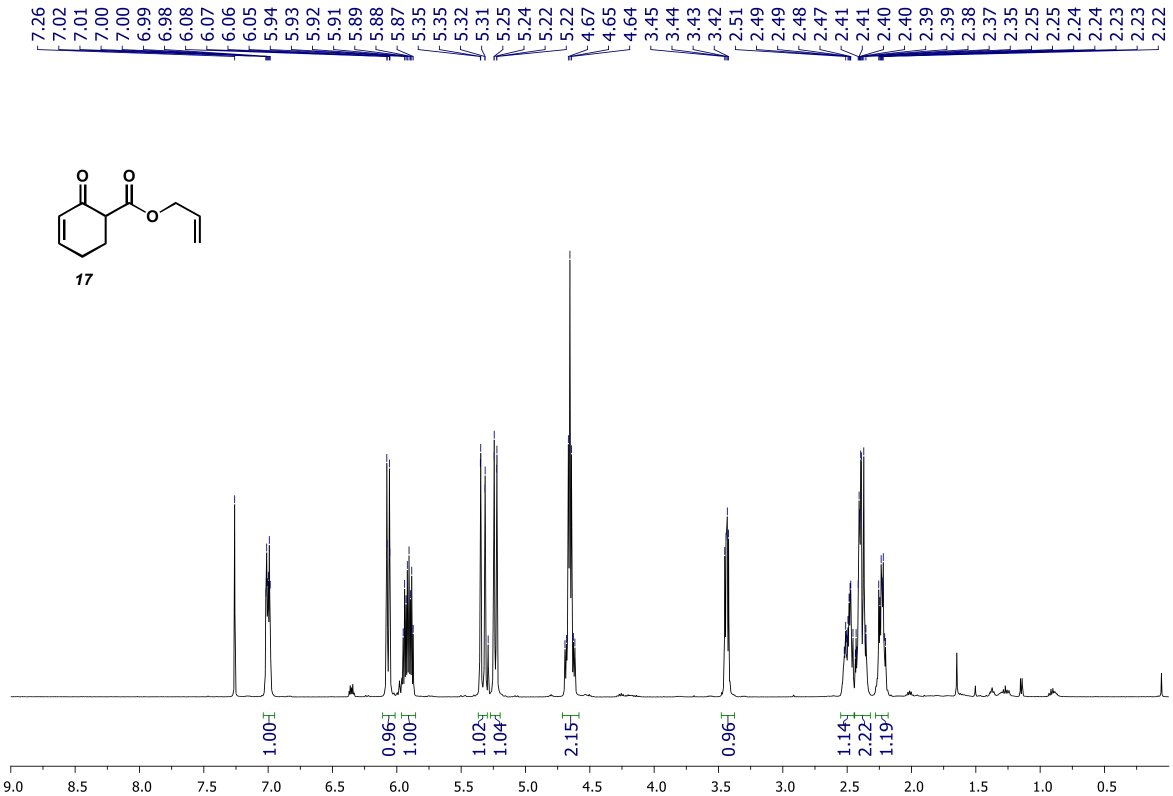


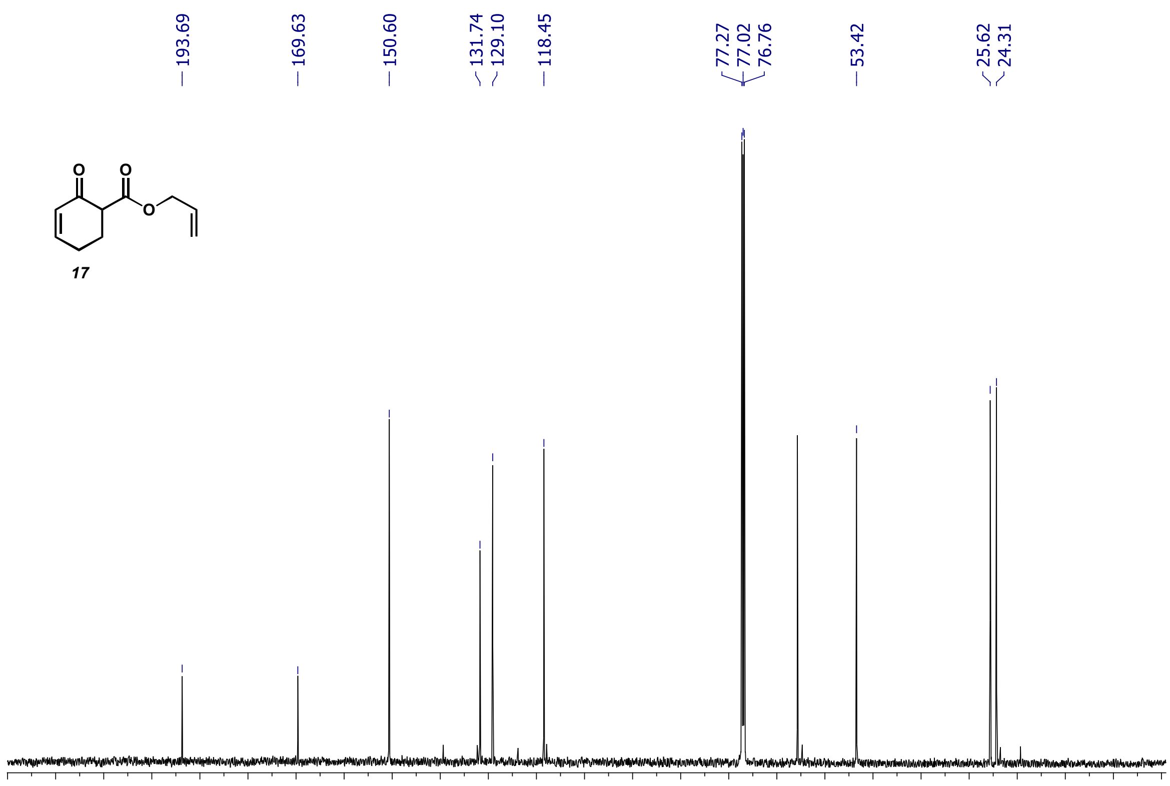
^{13}C NMR (126 MHz, $CDCl_3$)

17

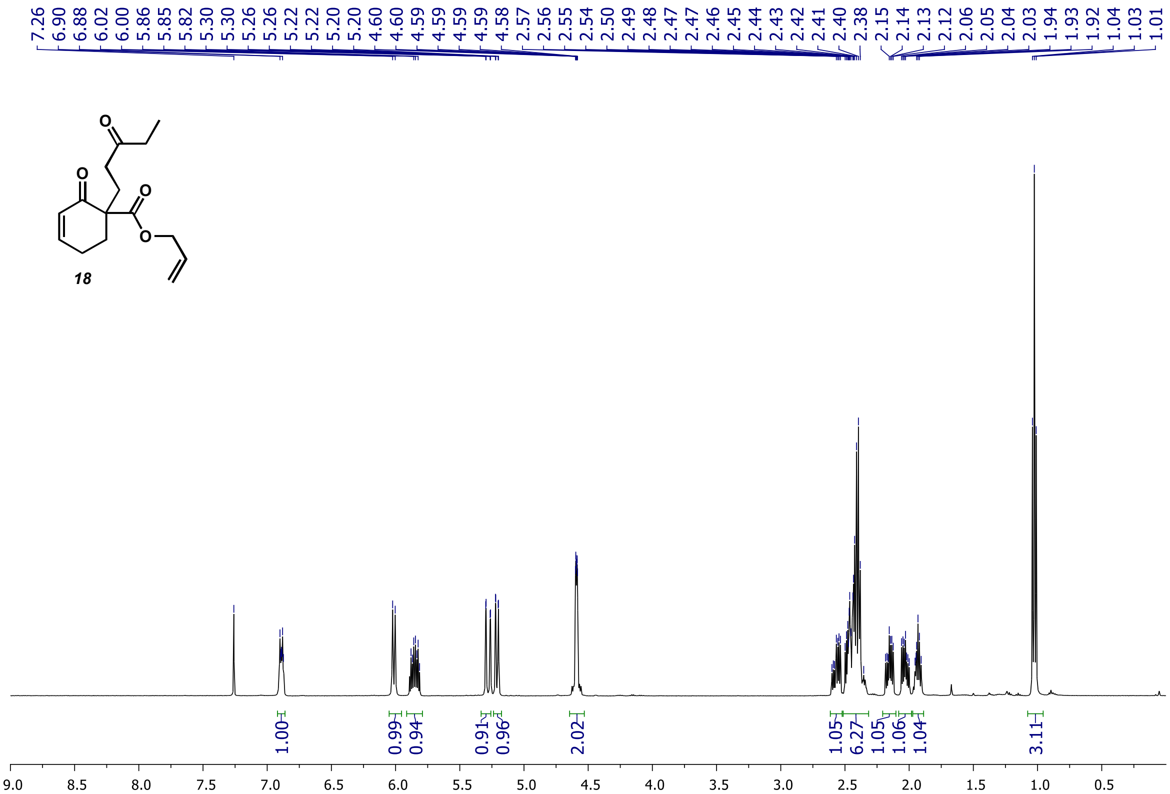


^{1}H NMR (500 MHz, $CDCl_3$)

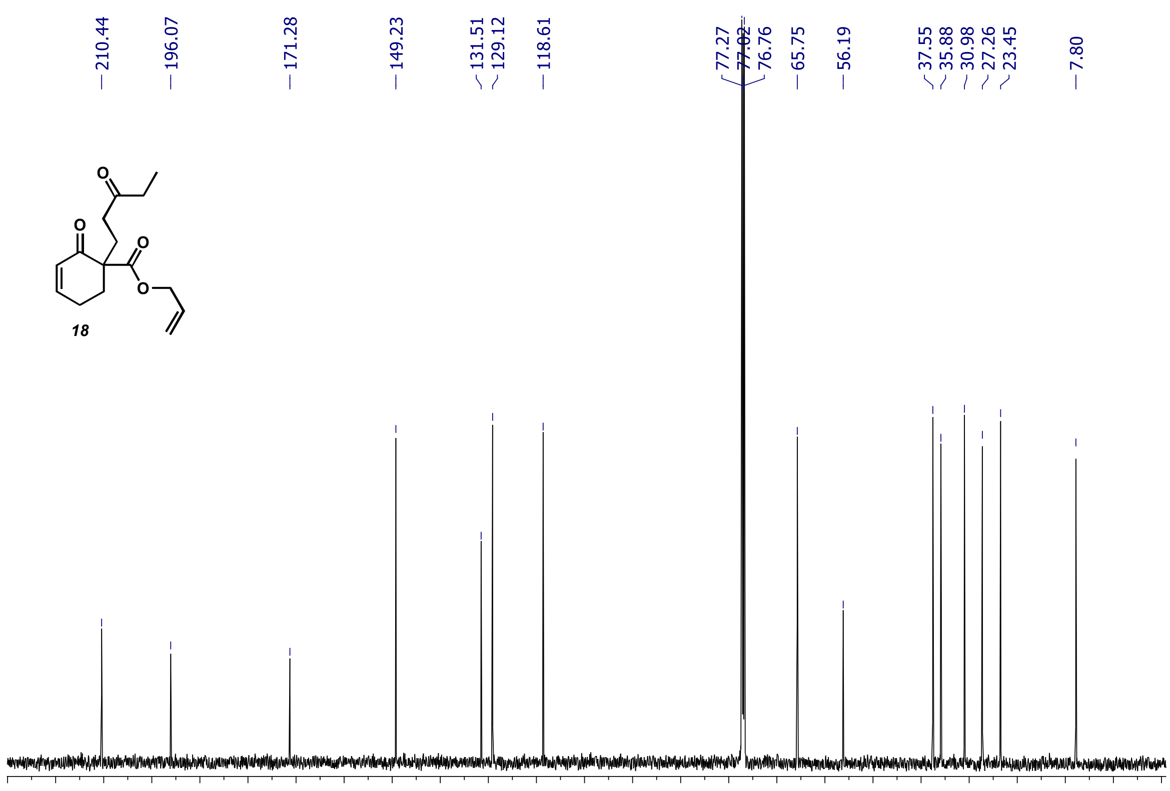
17



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



¹H NMR (500 MHz, $CDCl_3$)



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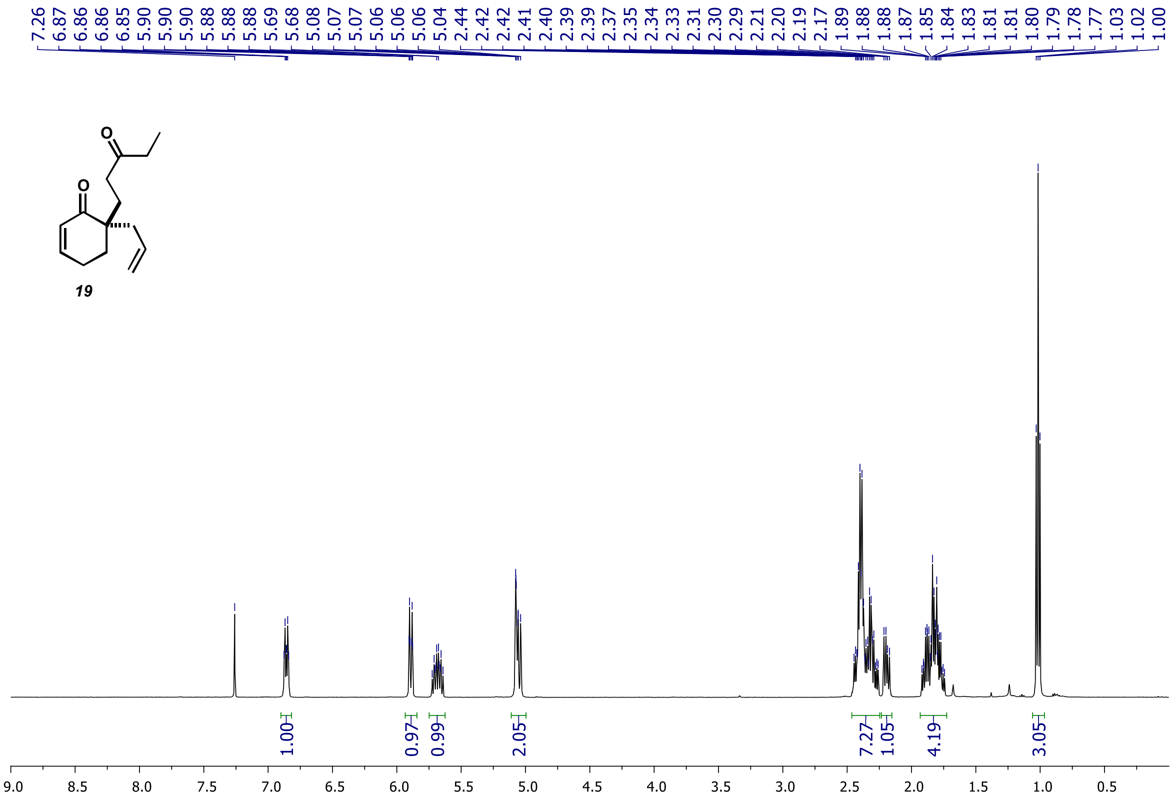

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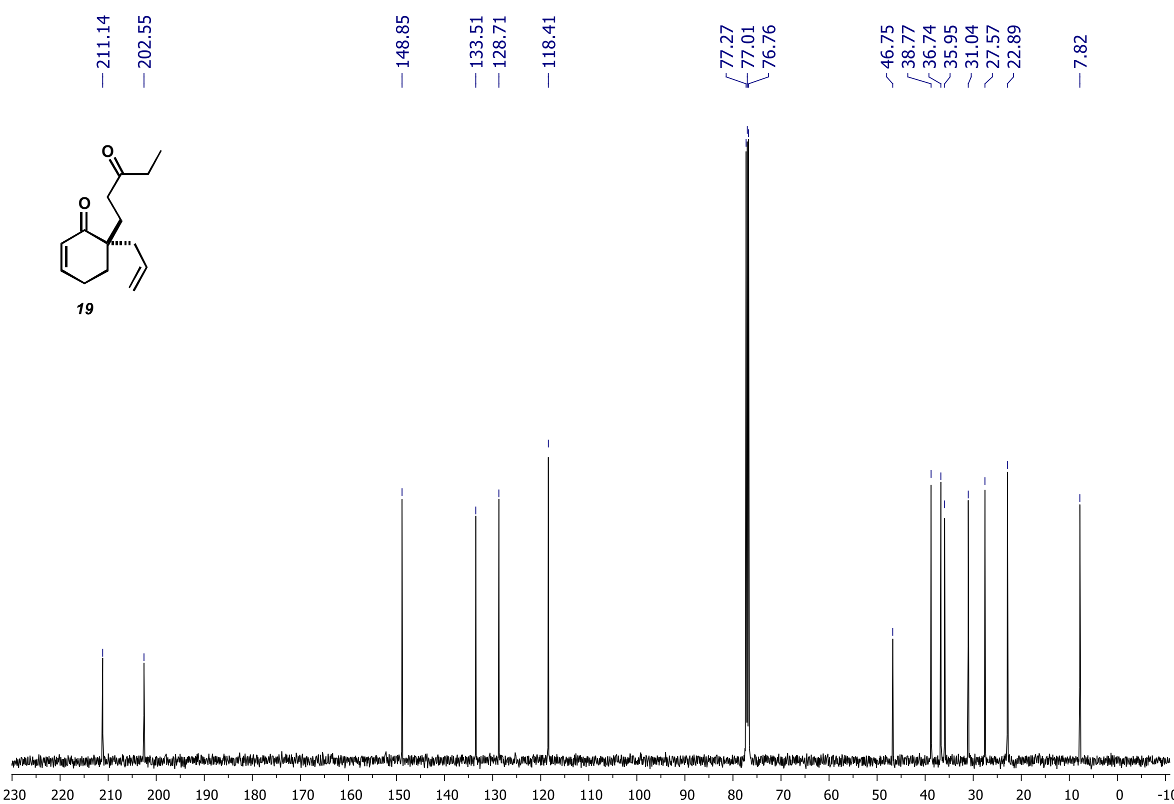

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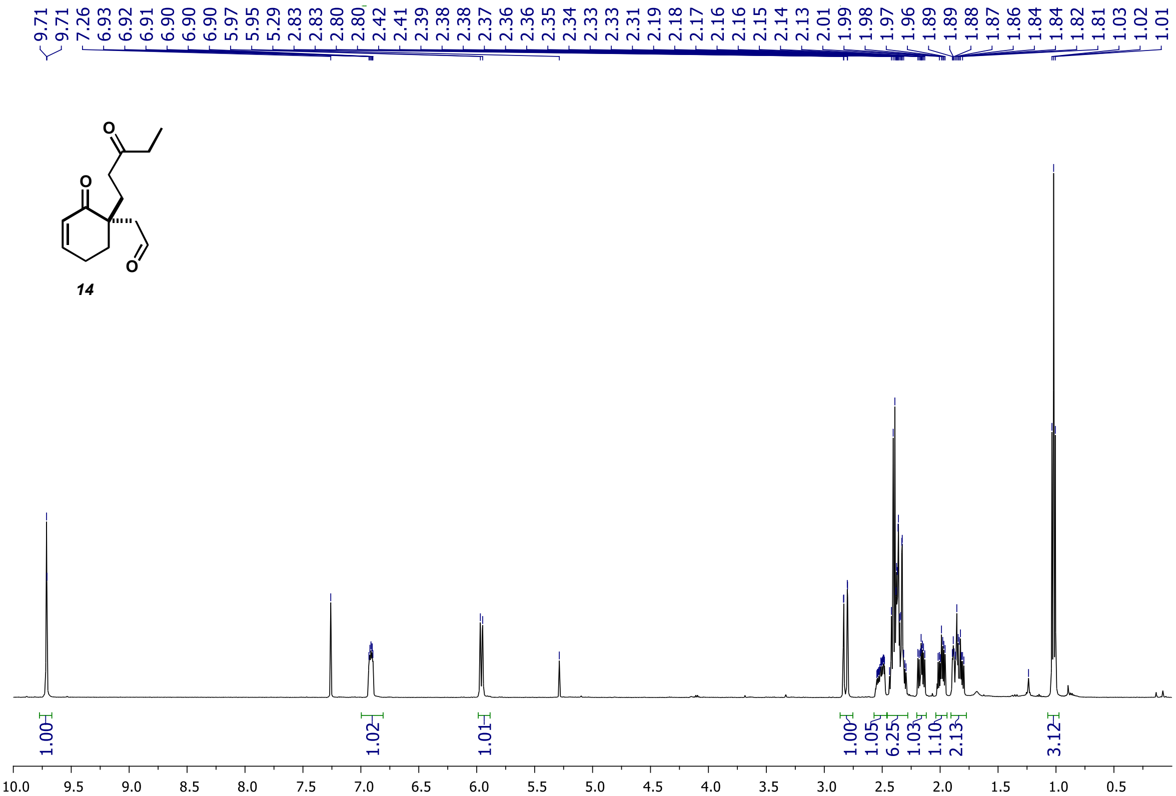

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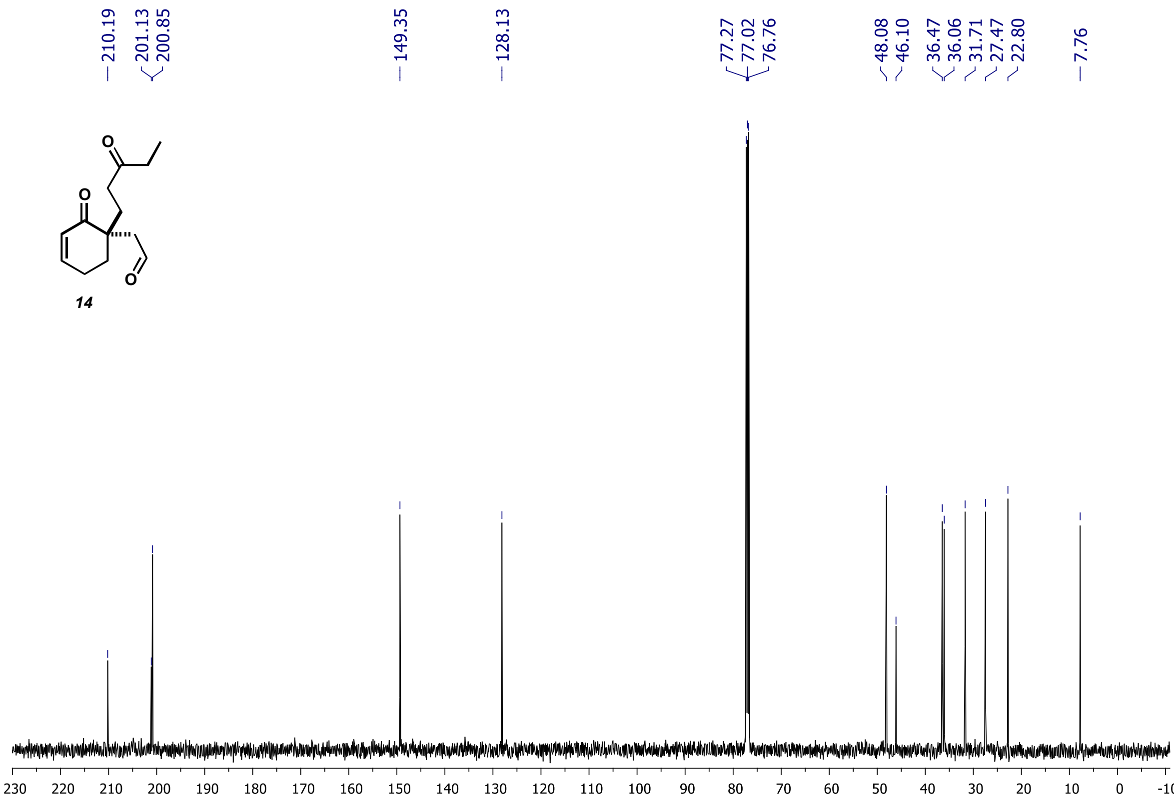

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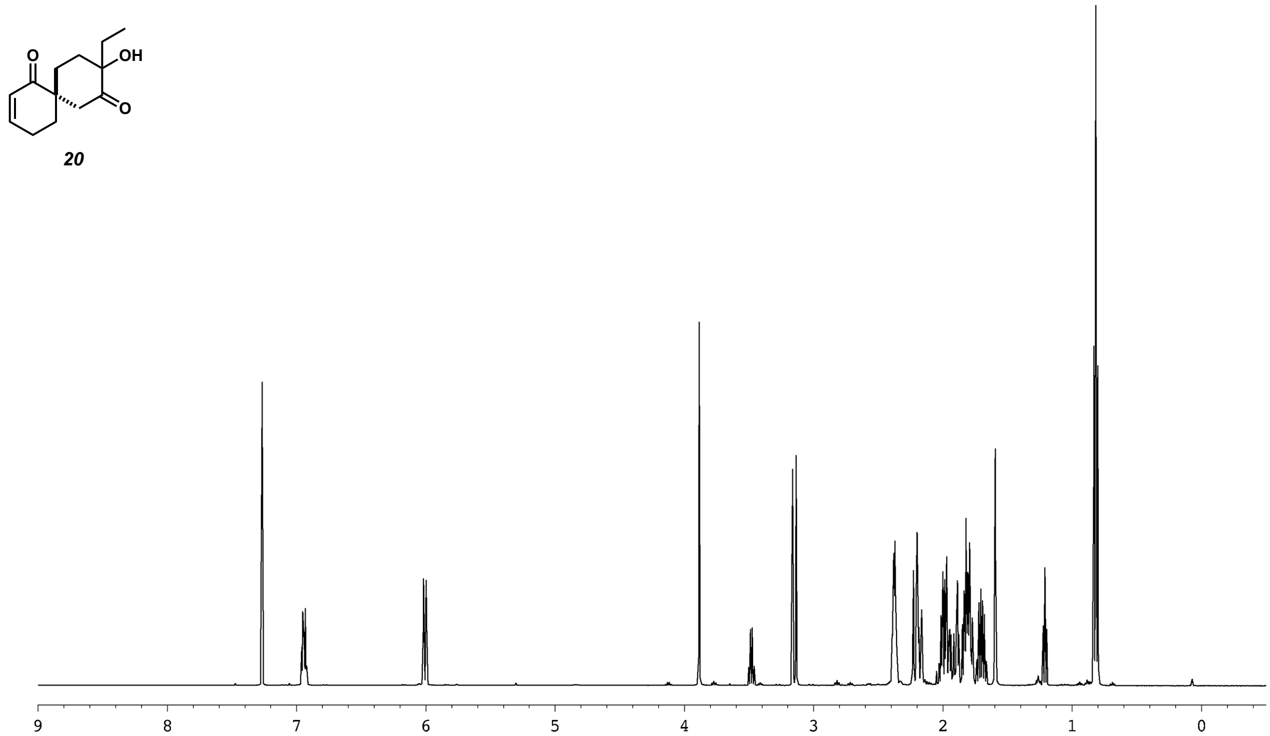

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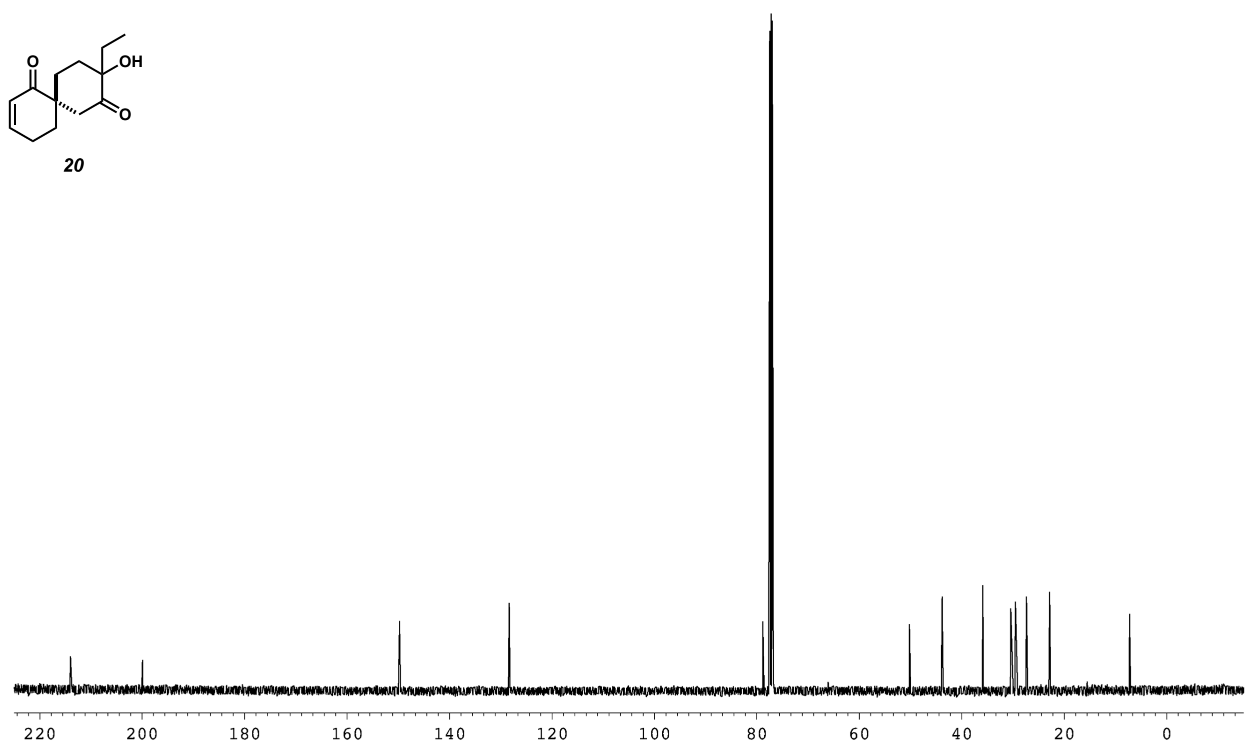

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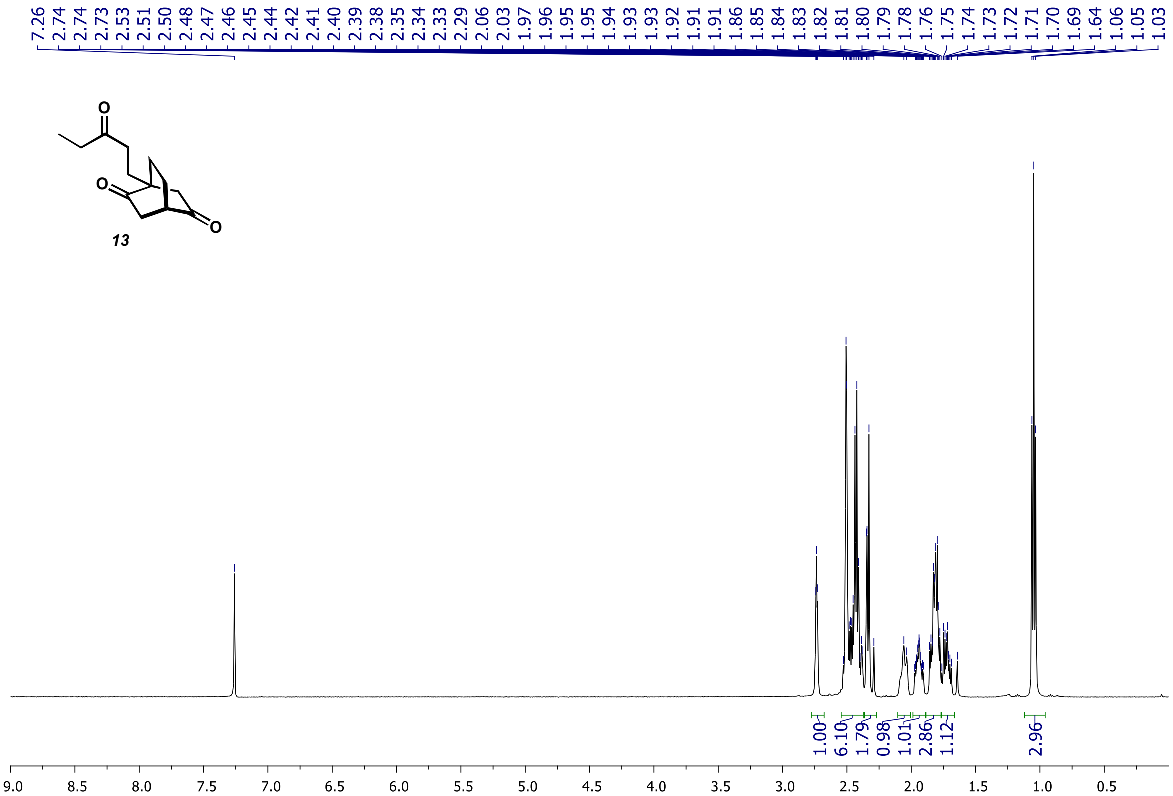

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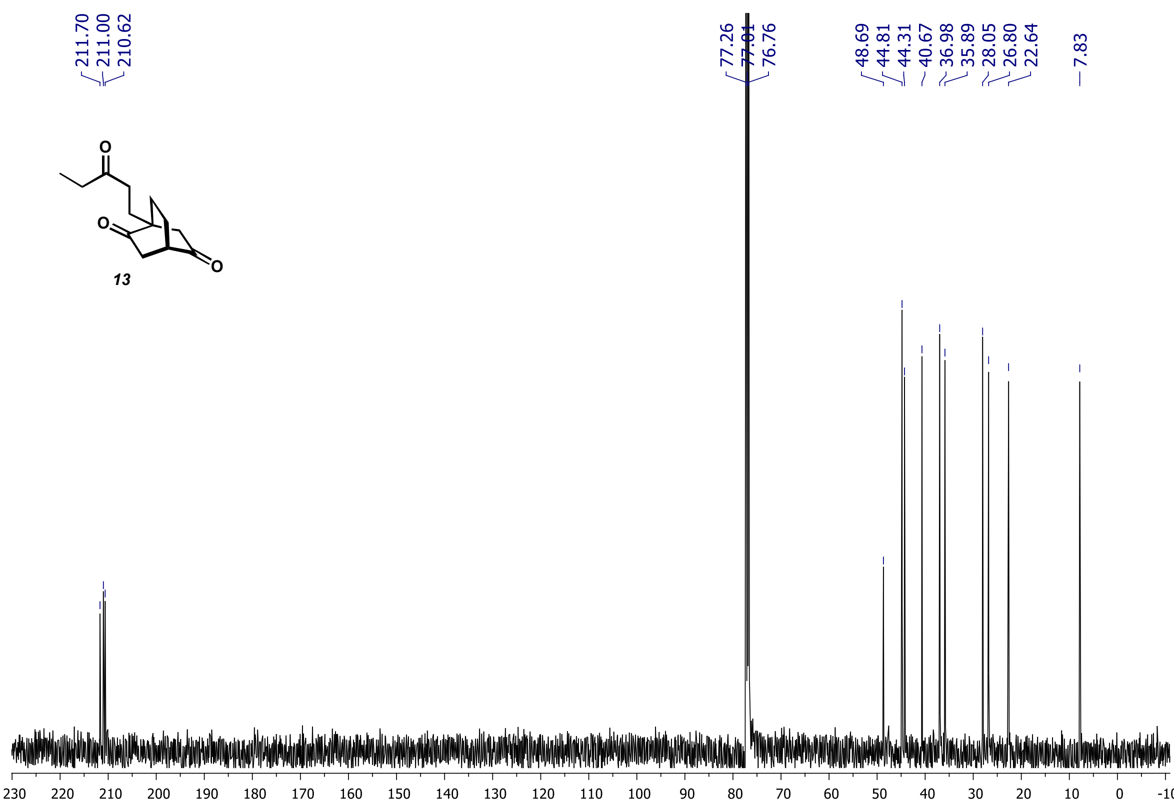

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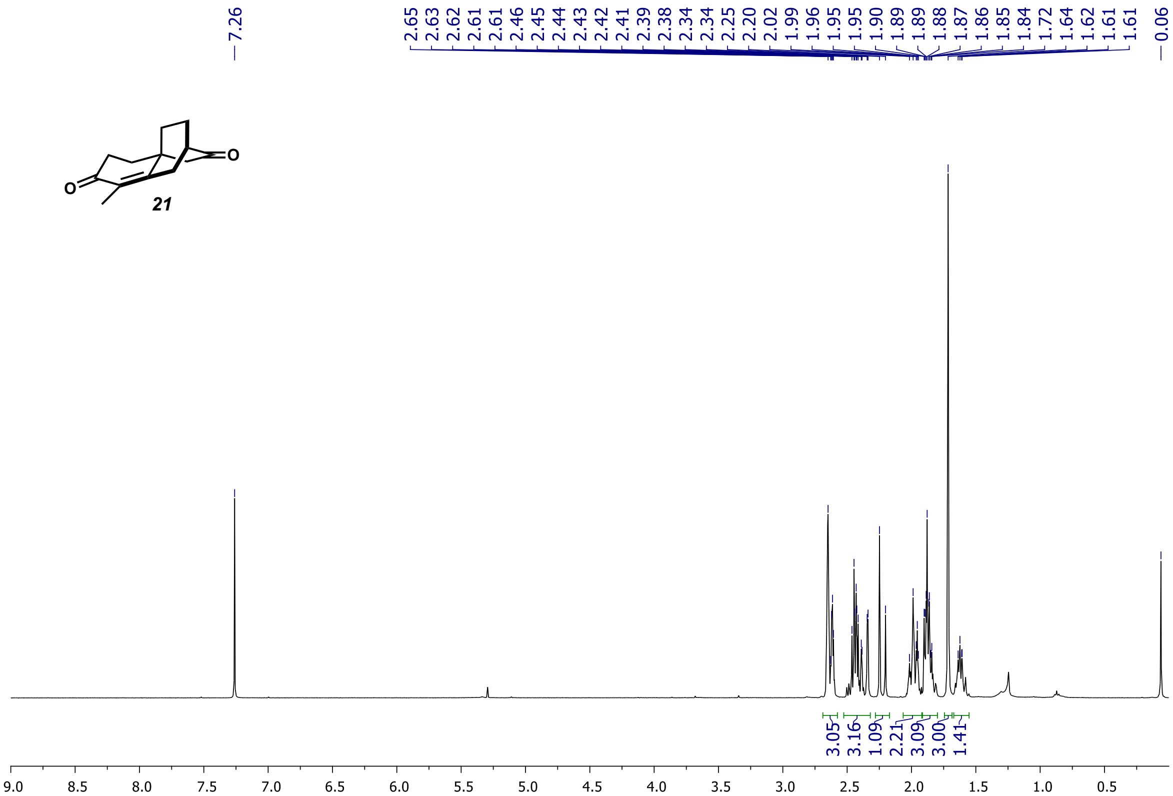

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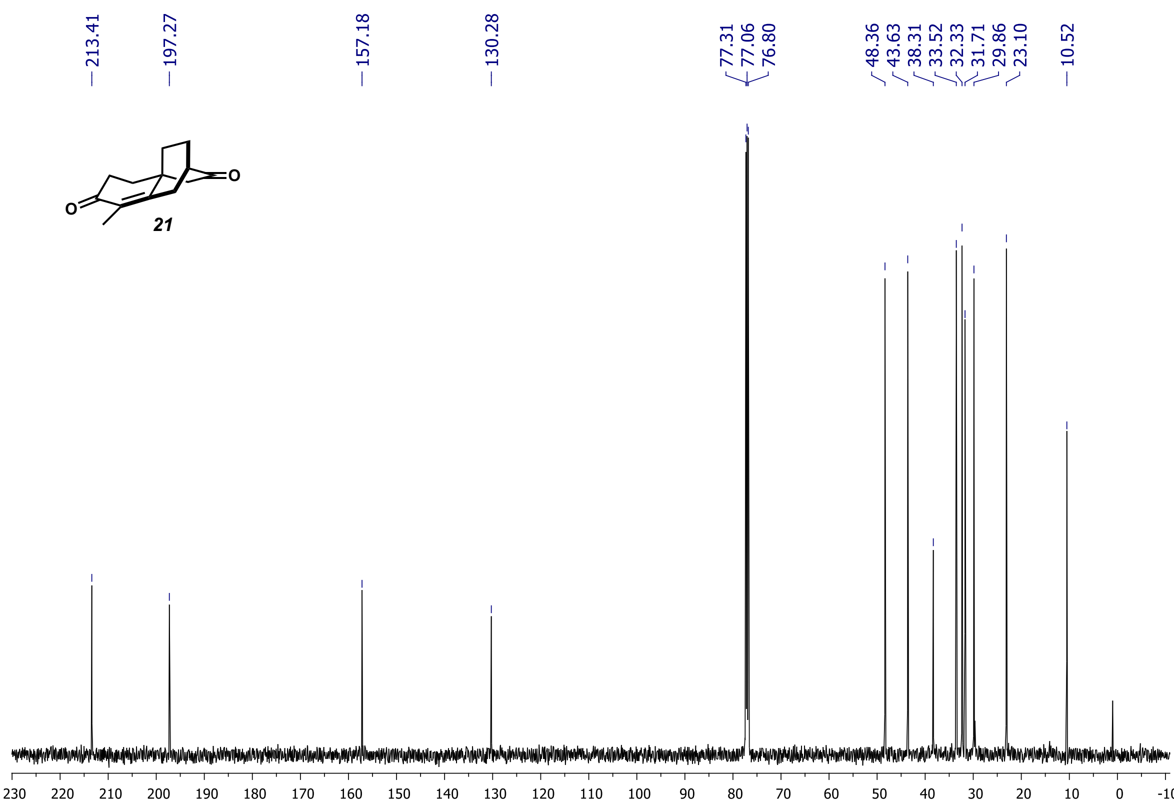

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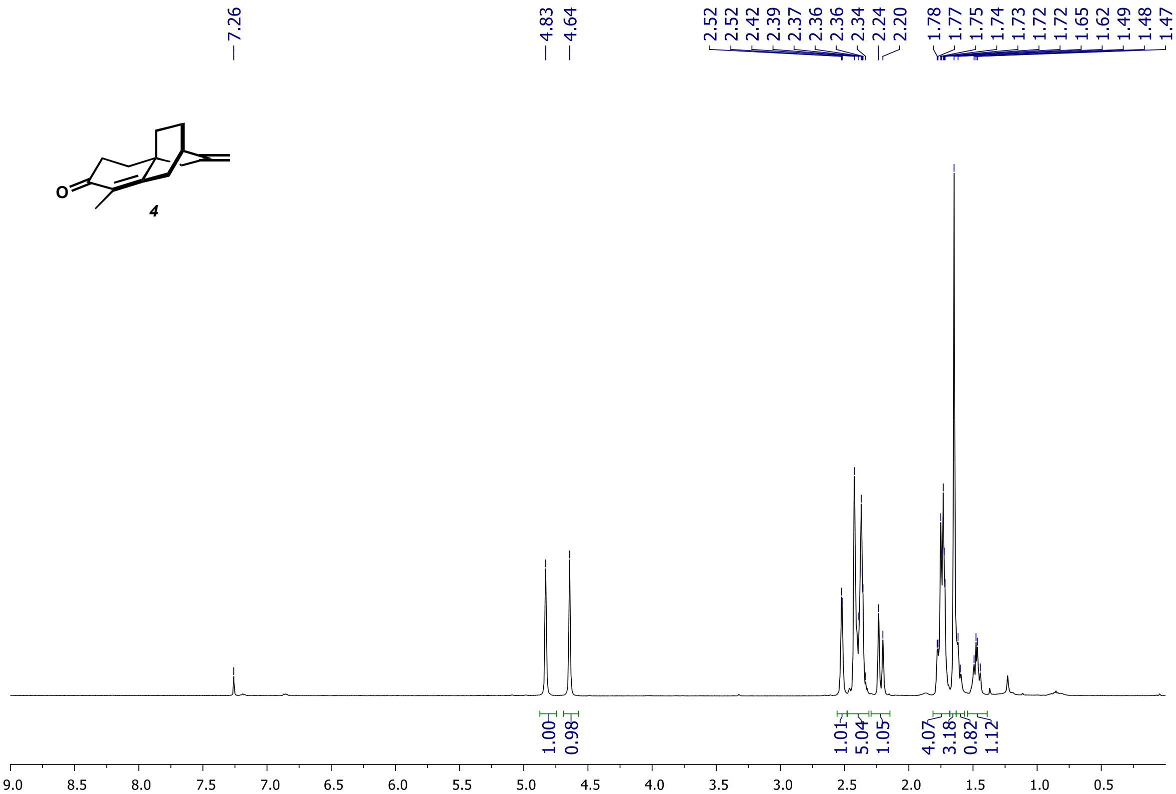

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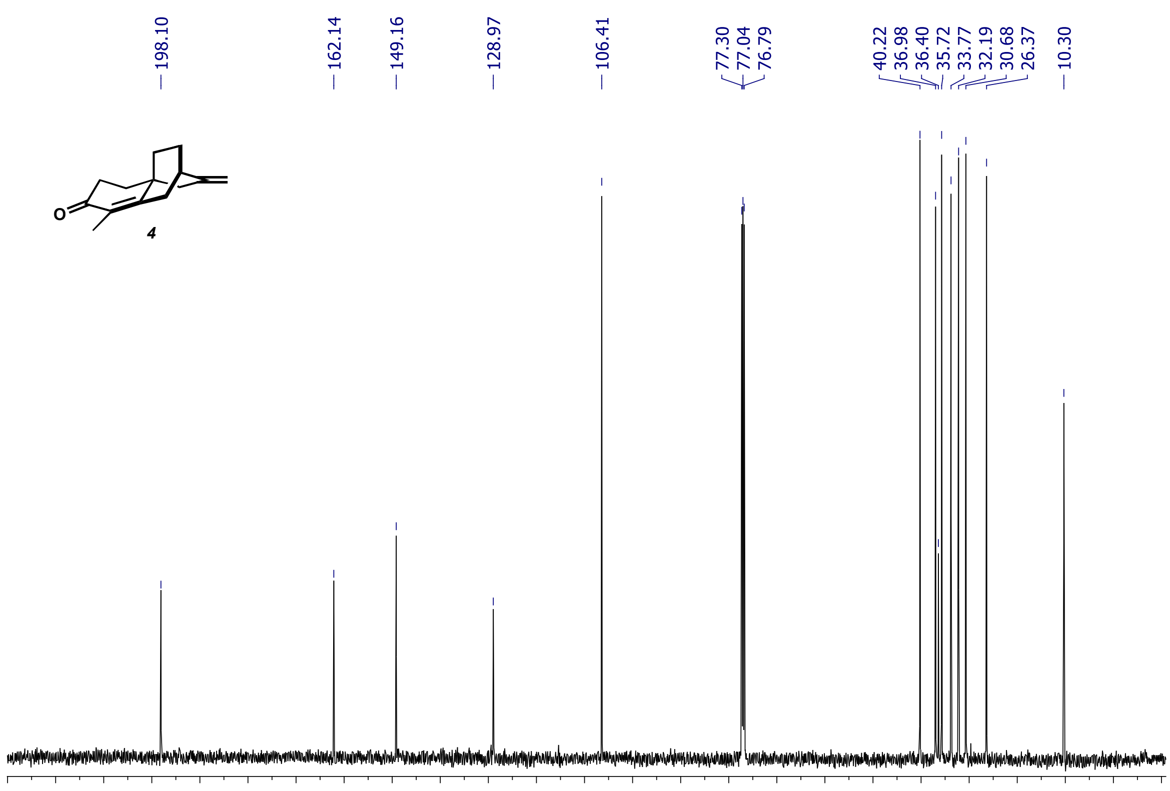

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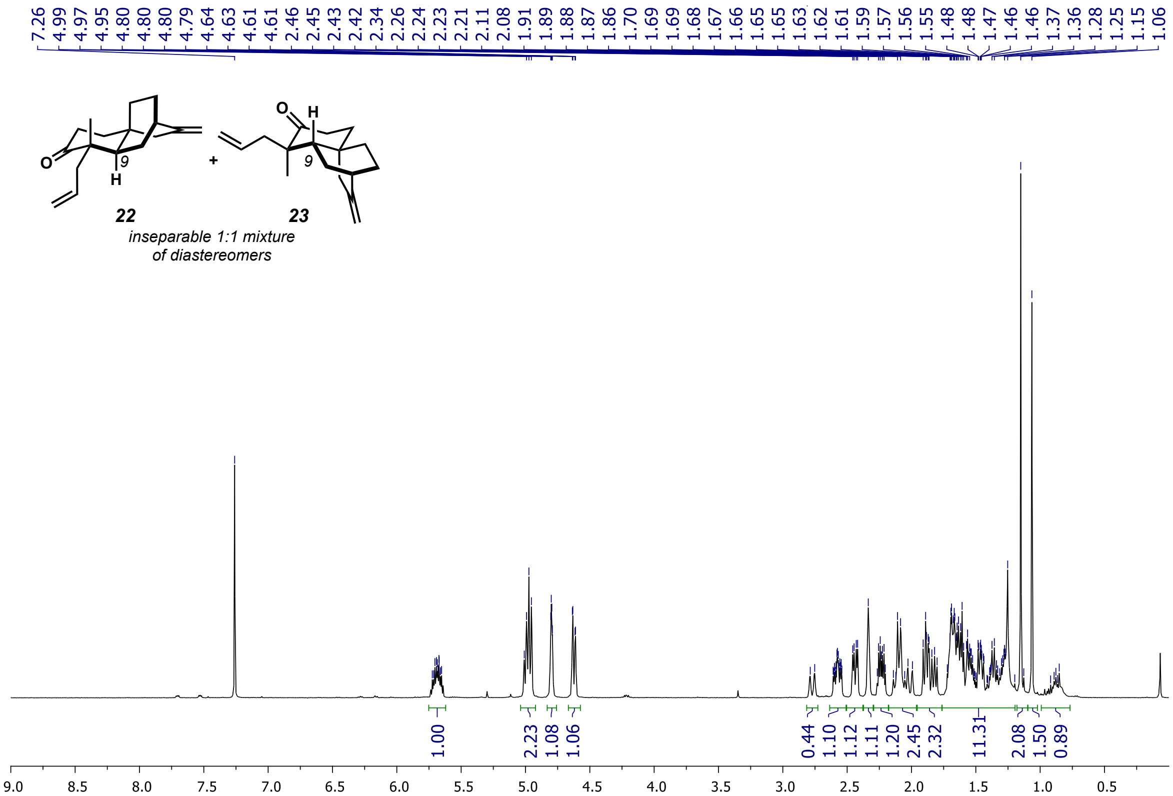

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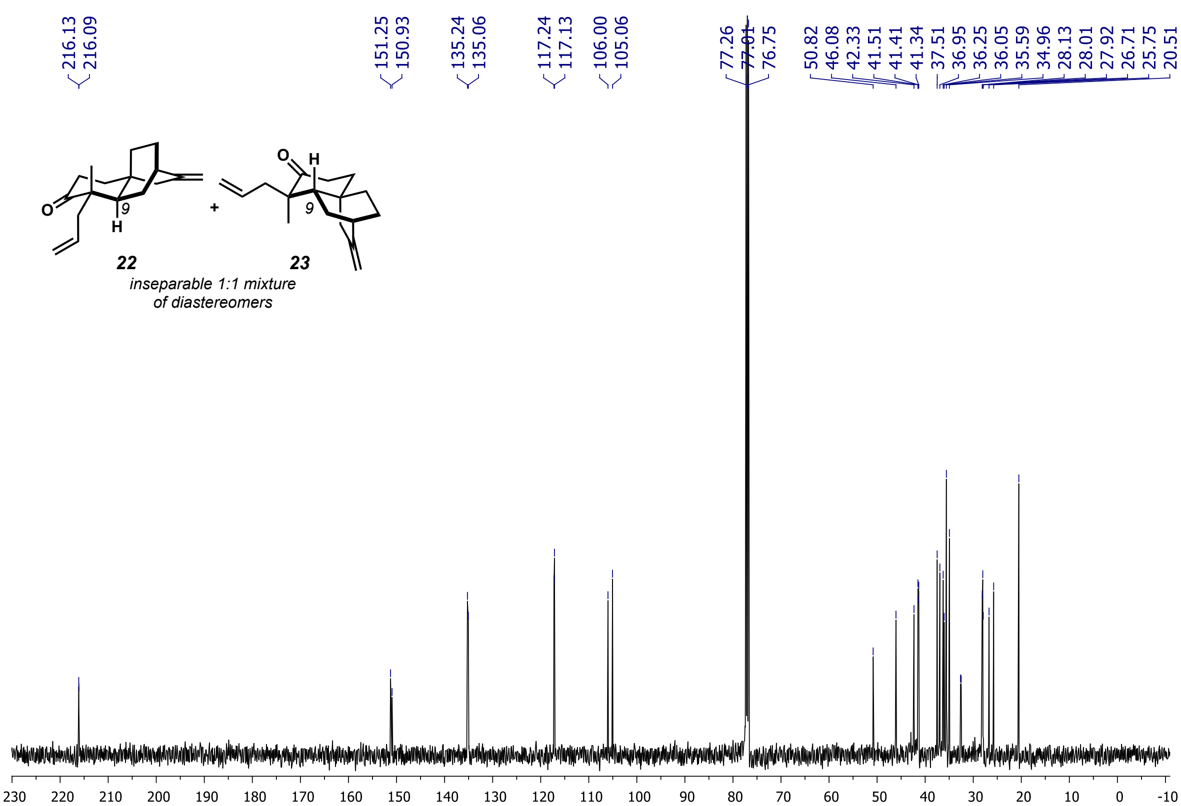

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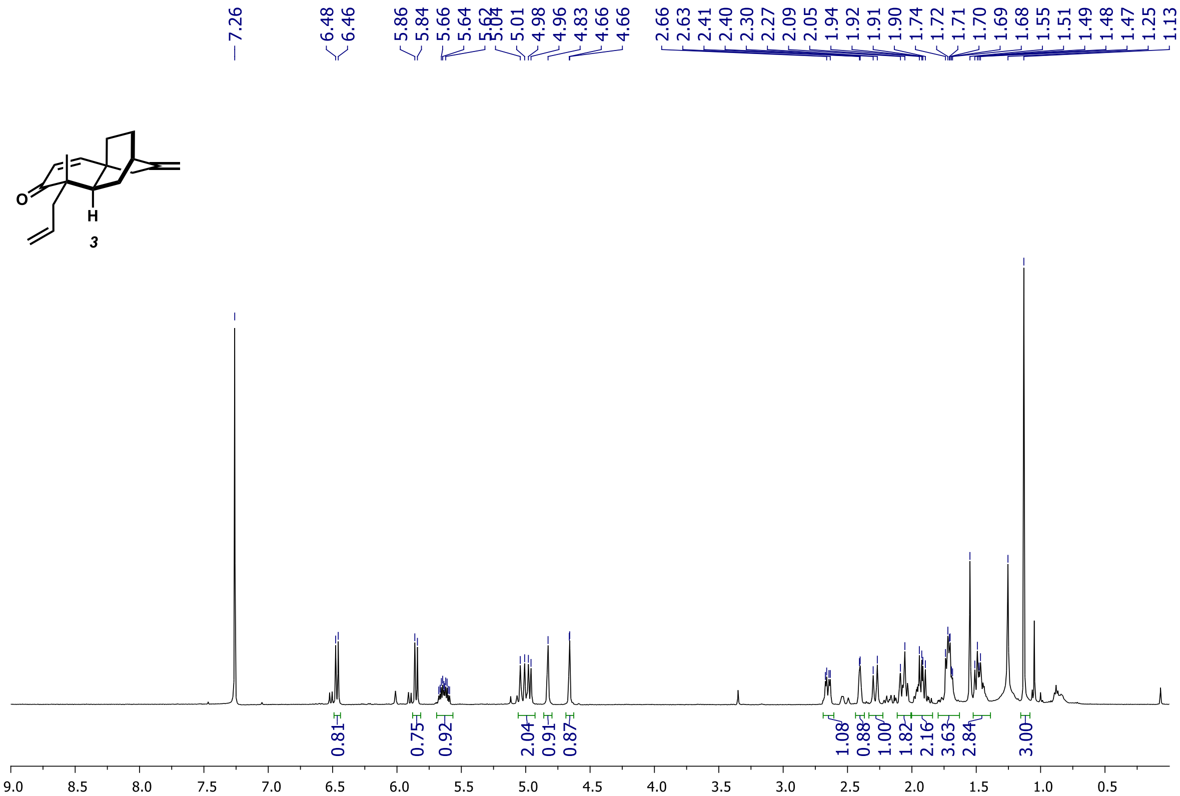

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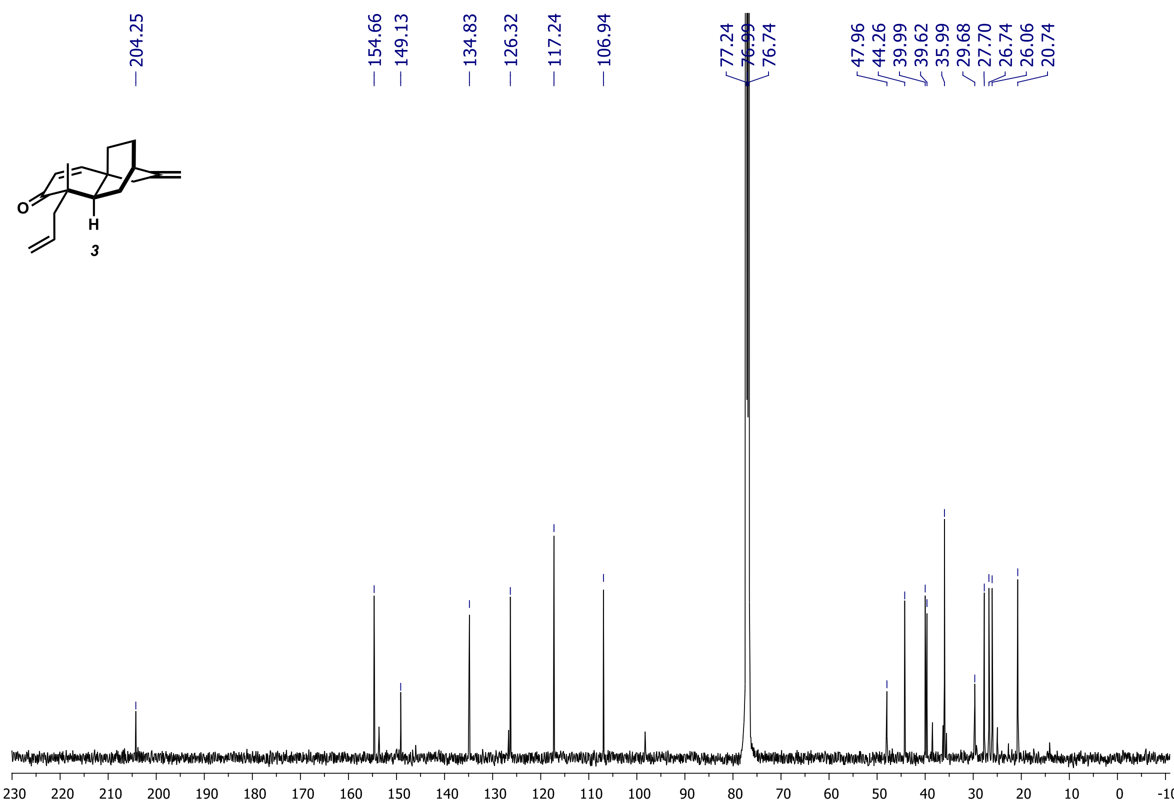

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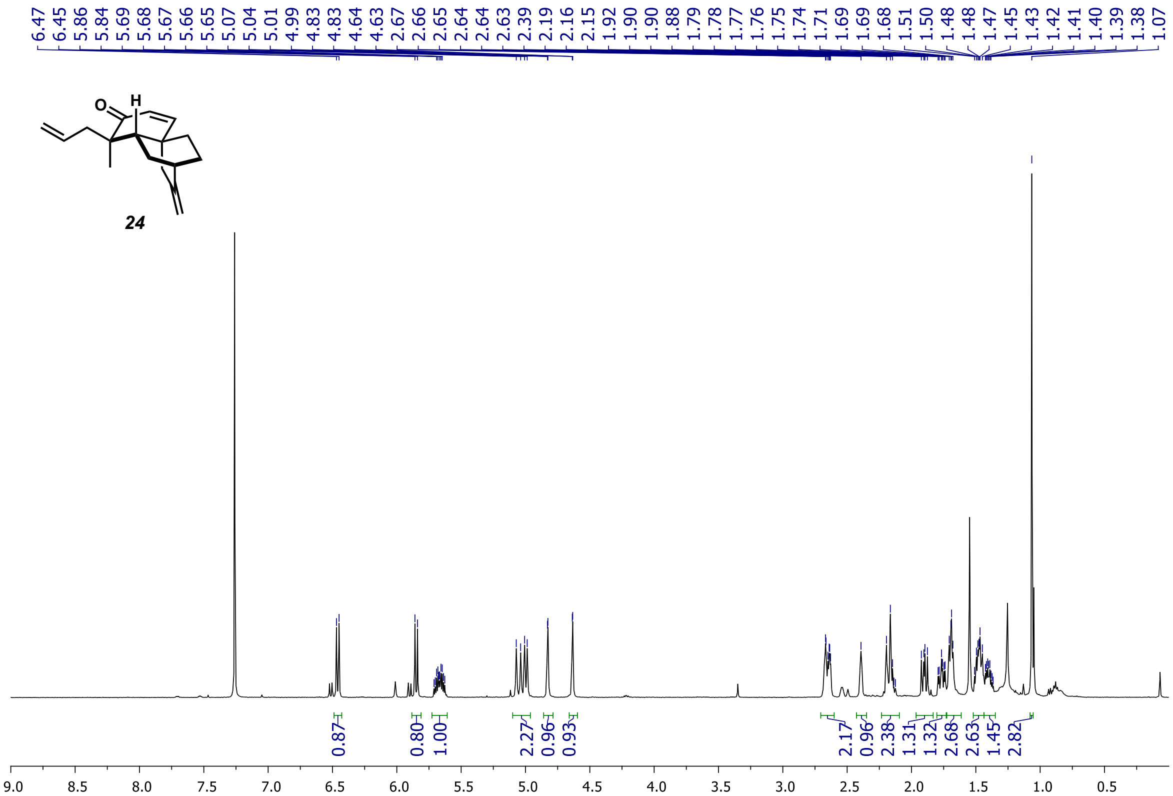

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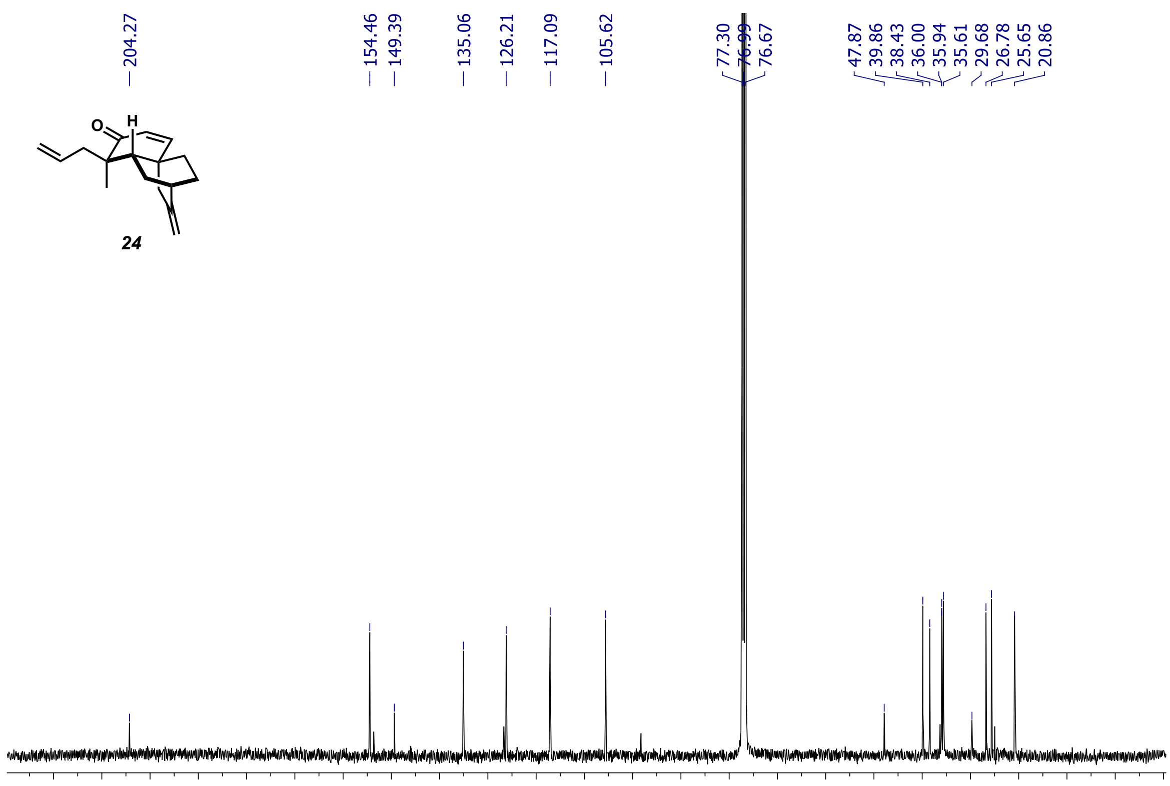

¹³C NMR (126 MHz, $CDCl_3$)

CALIFORNIA INSTITUTE OF TECHNOLOGY

BECKMAN INSTITUTE

X-RAY CRYSTALLOGRAPHY LABORATORY

Date 30 April 2008

Crystal Structure Analysis of 21

(shown below)

For

Investigator: Christian Defieber

Advisor: B. M. Stoltz

By
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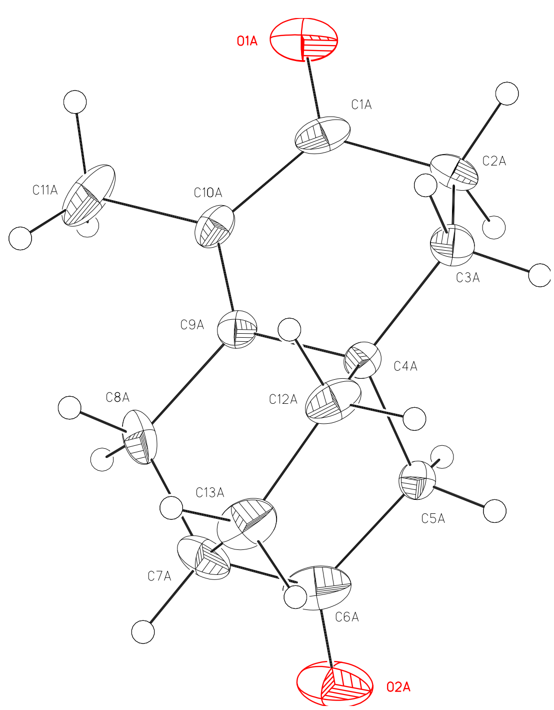
e-mail: mikeday@caltech.edu

Contents



Compound **21**

Table 1. Crystal data and structure refinement for 21 (CCDC 686706).

Empirical formula	$C_{13}H_{16}O_2$
Formula weight	204.26
Crystallization Solvent	Hexanes
Crystal Habit	Prism
Crystal size	0.42 x 0.15 x 0.11 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker KAPPA APEX II
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 2641 reflections used in lattice determination	2.33 to 34.42°
Unit cell dimensions	a = 12.0658(7) Å
b = 7.1991(4) Å	β= 92.724(5)°
c = 12.0987(10) Å	
Volume	1049.74(12) Å^3
Z	4
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.292 Mg/m^3
F(000)	440
Data collection program	Bruker APEX2 v2.1-0
θ range for data collection	2.44 to 34.55°
Completeness to θ = 34.55°	78.3 %
Index ranges	$-17 \leq h \leq 17$, $0 \leq k \leq 11$, $0 \leq l \leq 17$
Data collection scan type	ω scans; 12 settings
Data reduction program	Bruker SAINT-Plus v7.34A
Reflections collected	3732
Independent reflections	3732 [R_{int}= 0.0000]
Absorption coefficient	0.086 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7468 and 0.6368

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	3732 / 1 / 274
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.574
Final R indices [$I>2\sigma(I)$, 3246 reflections]	R1 = 0.0659, *w*R2 = 0.0929
R indices (all data)	R1 = 0.0805, *w*R2 = 0.0943
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Absolute structure determination	Unable to determine reliably
Absolute structure parameter	-1.8(16)
Largest diff. peak and hole	0.387 and -0.359 e.Å^{-3}

Special Refinement Details

The structure was refined as a twin with two orientations, BASF=0.452, using an HKLF 5 format reflection file prepared with TWINABS (see below). The two orientations were separated using CELL_NOW as follows.
Rotated from first domain by 179.7 degrees about reciprocal axis 0.000 0.000 1.000 and real axis 0.042 0.003 1.000. Twin law to convert hkl from first to this domain (SHELXL TWIN matrix):

```
 -1.000   0.007  -0.001
 -0.003  -1.000   0.000
  0.085   0.005   1.000
```

Saint refined twin law; Twin Law, Sample 1 of 1 transforms h1.1(1)->h1.2(2)

```
-1.00019  0.00027 -0.00402
-0.00010 -1.00014 -0.00007
 0.09148 -0.00022  1.00008
```

Twinabs;

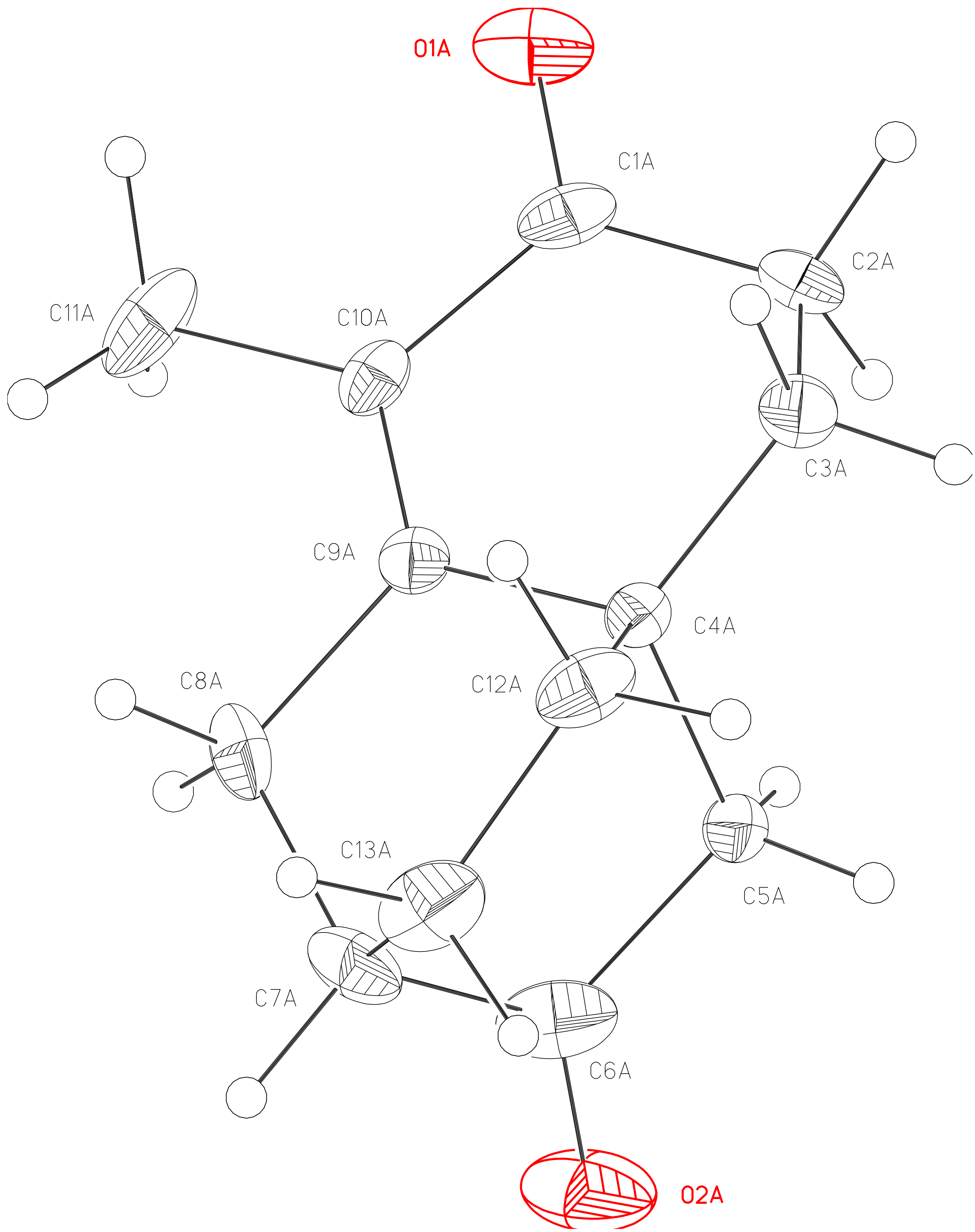
PART 1 - Refinement of parameters to model systematic errors

```
   2121 data (    819 unique ) involve domain  1 only,  mean I/sigma  18.8
   2180 data (    823 unique ) involve domain  2 only,  mean I/sigma  16.4
  12491 data (   3743 unique ) involve   2 domains,  mean I/sigma  13.2
```

HKLF 5 dataset constructed from all observations involving domain 1
7697 Corrected reflections written to file twin5.hkl
Reflections merged according to point-group 2/m
Single reflections that also occur in composites omitted
Minimum and maximum apparent transmission: 0.636799 0.746793

Additional spherical absorption correction applied with mu*r = 0.2000

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.
Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.
All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.


O1A
C1A
C2A
C11A
C10A
C3A
C9A
C4A
C8A
C12A
C13A
C5A
C7A
C6A
O2A

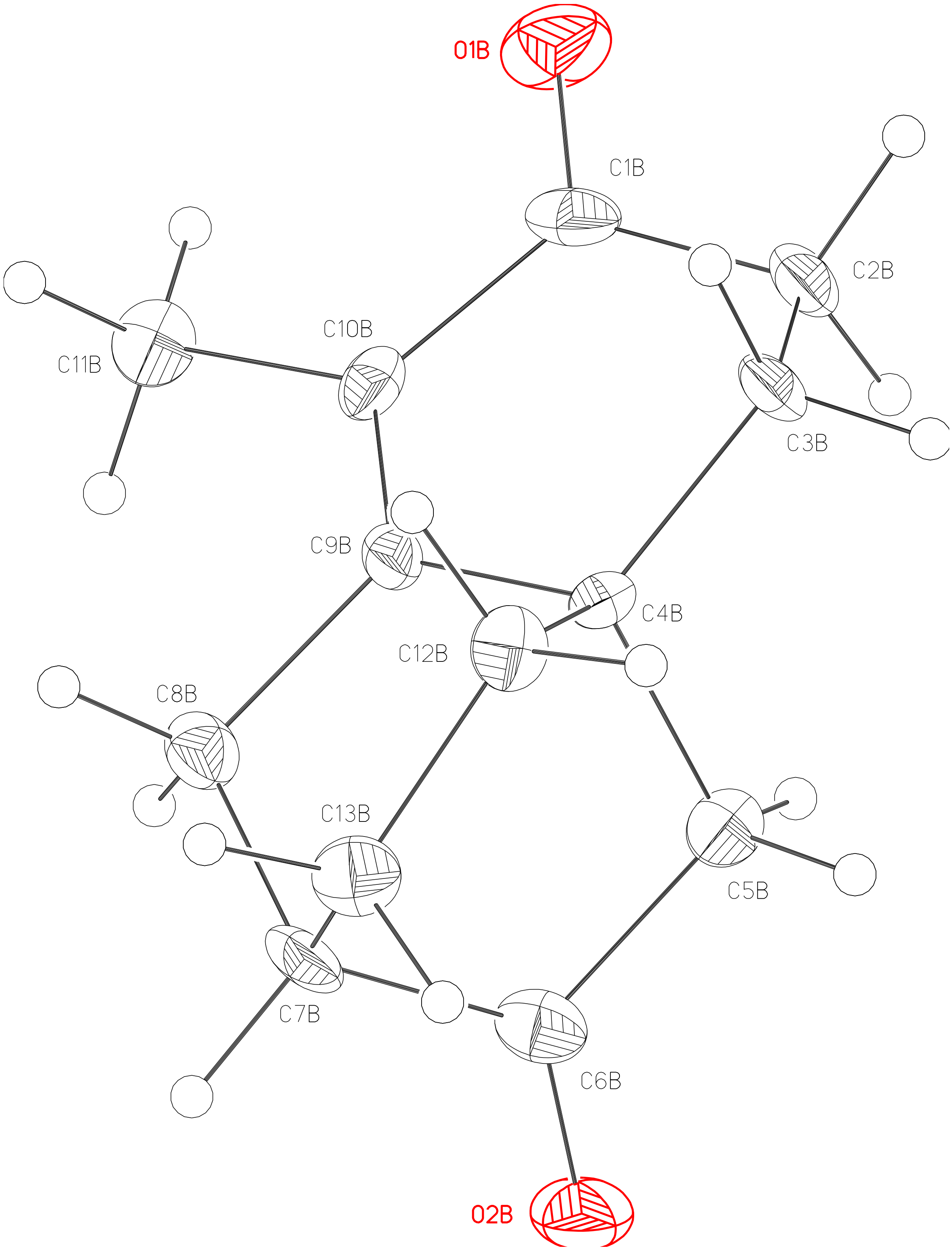

O1B
C1B
C2B
C11B
C10B
C3B
C9B
C4B
C12B
C8B
C13B
C5B
C7B
C6B
O2B

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for CTD01 (CCDC 686706). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

x	y	z	U_{eq}	
O(1A)	8680(2)	193(3)	8344(2)	34(1)
O(2A)	6770(3)	4232(3)	3573(3)	44(1)
C(1A)	8512(3)	250(4)	7345(3)	24(1)
C(2A)	9440(3)	503(5)	6585(3)	27(1)
C(3A)	9187(3)	-422(4)	5456(3)	24(1)
C(4A)	8084(3)	196(4)	4923(3)	17(1)
C(5A)	8115(3)	2139(4)	4372(3)	18(1)
C(6A)	6953(4)	2683(4)	3920(3)	32(1)
C(7A)	6156(3)	1123(4)	3966(3)	27(1)
C(8A)	6042(3)	637(4)	5198(3)	24(1)
C(9A)	7182(3)	315(4)	5760(3)	16(1)
C(10A)	7346(3)	262(4)	6850(3)	18(1)
C(11A)	6440(3)	272(5)	7646(3)	32(1)
C(12A)	7718(3)	-1199(4)	4011(3)	26(1)
C(13A)	6617(3)	-572(4)	3390(3)	32(1)
O(1B)	779(2)	360(3)	3326(2)	34(1)
O(2B)	3569(2)	-3383(3)	-872(2)	32(1)
C(1B)	1121(3)	274(4)	2398(3)	21(1)
C(2B)	358(3)	-75(4)	1415(3)	22(1)
C(3B)	714(3)	901(4)	388(3)	20(1)
C(4B)	1919(3)	450(4)	129(3)	16(1)
C(5B)	2022(3)	-1471(4)	-433(3)	20(1)
C(6B)	3247(3)	-1894(4)	-580(3)	23(1)
C(7B)	3990(3)	-237(4)	-312(3)	20(1)
C(8B)	3889(3)	213(4)	922(3)	20(1)
C(9B)	2657(3)	388(4)	1167(3)	16(1)
C(10B)	2324(2)	336(4)	2205(3)	17(1)
C(11B)	3100(3)	345(5)	3213(3)	22(1)
C(12B)	2369(3)	1934(4)	-650(3)	20(1)
C(13B)	3541(3)	1410(4)	-1012(3)	23(1)

Table 3. Bond lengths [Å] and angles [°] for 21 (CCDC 686706).

O(1A)-C(1A)	1.217(4)	C(12A)-C(4A)-C(5A)	107.0(3)
O(2A)-C(6A)	1.208(4)	C(6A)-C(5A)-C(4A)	110.1(3)
C(1A)-C(2A)	1.493(5)	O(2A)-C(6A)-C(7A)	127.2(4)
C(1A)-C(10A)	1.502(4)	O(2A)-C(6A)-C(5A)	120.6(4)
C(2A)-C(3A)	1.537(5)	C(7A)-C(6A)-C(5A)	112.2(3)
C(3A)-C(4A)	1.518(5)	C(6A)-C(7A)-C(13A)	109.7(3)
C(4A)-C(9A)	1.523(4)	C(6A)-C(7A)-C(8A)	107.2(3)
C(4A)-C(12A)	1.541(5)	C(13A)-C(7A)-C(8A)	108.1(3)
C(4A)-C(5A)	1.550(4)	C(9A)-C(8A)-C(7A)	110.3(3)
C(5A)-C(6A)	1.531(5)	C(10A)-C(9A)-C(8A)	122.5(3)
C(6A)-C(7A)	1.482(5)	C(10A)-C(9A)-C(4A)	125.7(3)
C(7A)-C(13A)	1.524(5)	C(8A)-C(9A)-C(4A)	111.7(3)
C(7A)-C(8A)	1.543(6)	C(9A)-C(10A)-C(11A)	124.3(3)
C(8A)-C(9A)	1.523(4)	C(9A)-C(10A)-C(1A)	119.3(3)
C(9A)-C(10A)	1.325(4)	C(11A)-C(10A)-C(1A)	116.4(3)
C(10A)-C(11A)	1.491(4)	C(4A)-C(12A)-C(13A)	111.3(3)
C(12A)-C(13A)	1.561(5)	C(7A)-C(13A)-C(12A)	109.4(3)
O(1B)-C(1B)	1.215(4)	O(1B)-C(1B)-C(10B)	121.4(3)
O(2B)-C(6B)	1.199(4)	O(1B)-C(1B)-C(2B)	121.5(3)
C(1B)-C(10B)	1.482(4)	C(10B)-C(1B)-C(2B)	116.8(3)
C(1B)-C(2B)	1.491(5)	C(1B)-C(2B)-C(3B)	112.9(3)
C(2B)-C(3B)	1.508(5)	C(2B)-C(3B)-C(4B)	112.3(3)
C(3B)-C(4B)	1.537(4)	C(9B)-C(4B)-C(3B)	111.3(3)
C(4B)-C(9B)	1.505(4)	C(9B)-C(4B)-C(12B)	108.7(3)
C(4B)-C(12B)	1.540(4)	C(3B)-C(4B)-C(12B)	110.0(3)
C(4B)-C(5B)	1.548(4)	C(9B)-C(4B)-C(5B)	106.4(2)
C(5B)-C(6B)	1.527(4)	C(3B)-C(4B)-C(5B)	112.0(2)
C(6B)-C(7B)	1.518(4)	C(12B)-C(4B)-C(5B)	108.2(3)
C(7B)-C(8B)	1.539(5)	C(6B)-C(5B)-C(4B)	109.1(3)
C(7B)-C(13B)	1.540(4)	O(2B)-C(6B)-C(7B)	124.6(3)
C(8B)-C(9B)	1.535(4)	O(2B)-C(6B)-C(5B)	122.8(3)
C(9B)-C(10B)	1.337(5)	C(7B)-C(6B)-C(5B)	112.5(3)
C(10B)-C(11B)	1.502(4)	C(6B)-C(7B)-C(8B)	107.4(3)
C(12B)-C(13B)	1.546(5)	C(6B)-C(7B)-C(13B)	107.4(3)
		C(8B)-C(7B)-C(13B)	109.2(3)
O(1A)-C(1A)-C(2A)	121.4(3)	C(9B)-C(8B)-C(7B)	109.0(3)
O(1A)-C(1A)-C(10A)	120.3(3)	C(10B)-C(9B)-C(4B)	126.4(3)
C(2A)-C(1A)-C(10A)	118.0(3)	C(10B)-C(9B)-C(8B)	121.0(3)
C(1A)-C(2A)-C(3A)	111.8(3)	C(4B)-C(9B)-C(8B)	112.4(3)
C(4A)-C(3A)-C(2A)	112.6(3)	C(9B)-C(10B)-C(1B)	119.3(3)
C(3A)-C(4A)-C(9A)	111.9(3)	C(9B)-C(10B)-C(11B)	124.0(3)
C(3A)-C(4A)-C(12A)	109.2(3)	C(1B)-C(10B)-C(11B)	116.7(3)
C(9A)-C(4A)-C(12A)	108.9(3)	C(4B)-C(12B)-C(13B)	110.9(3)
C(3A)-C(4A)-C(5A)	114.1(3)	C(7B)-C(13B)-C(12B)	109.6(3)
C(9A)-C(4A)-C(5A)	105.5(2)		

Table 4. Anisotropic displacement parameters ($Å^2$x 10^4) for 21 (CCDC 686706). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1A)	469(17)	284(11)	261(15)	12(13)	-90(14)	47(14)
O(2A)	573(19)	210(11)	500(19)	80(11)	-201(18)	-1(13)
C(1A)	380(20)	126(11)	227(19)	59(15)	17(18)	38(16)
C(2A)	200(18)	295(16)	310(20)	100(16)	-34(18)	90(16)
C(3A)	210(20)	208(14)	300(20)	64(13)	16(19)	34(13)
C(4A)	169(17)	169(12)	169(16)	25(13)	6(14)	-13(15)
C(5A)	163(19)	185(13)	188(19)	24(12)	-3(16)	-28(12)
C(6A)	520(30)	213(14)	210(20)	-26(13)	-60(20)	27(16)
C(7A)	230(20)	294(16)	280(20)	-21(15)	-131(19)	0(16)
C(8A)	130(17)	251(16)	340(20)	-42(14)	14(17)	-39(13)
C(9A)	183(16)	110(11)	200(17)	10(13)	16(15)	13(15)
C(10A)	230(18)	103(12)	204(18)	5(13)	61(16)	-15(15)
C(11A)	500(20)	240(14)	250(20)	-25(17)	230(20)	-40(20)
C(12A)	410(20)	225(14)	157(18)	-5(12)	63(19)	22(16)
C(13A)	450(30)	304(16)	200(20)	-25(14)	-60(20)	-135(18)
O(1B)	416(16)	360(12)	255(15)	-63(12)	157(14)	-73(15)
O(2B)	294(14)	213(10)	450(18)	-94(11)	112(14)	24(11)
C(1B)	248(19)	130(12)	250(20)	-12(15)	108(17)	33(16)
C(2B)	99(16)	167(14)	410(20)	-48(13)	28(17)	11(12)
C(3B)	91(17)	216(14)	300(20)	-37(13)	24(17)	26(12)
C(4B)	165(16)	154(12)	161(16)	-60(12)	22(15)	-5(13)
C(5B)	220(18)	172(13)	190(20)	2(12)	-19(17)	14(13)
C(6B)	230(20)	235(14)	230(20)	18(13)	72(18)	20(14)
C(7B)	108(16)	236(14)	270(20)	3(13)	87(17)	4(12)
C(8B)	161(16)	177(12)	264(19)	5(14)	-4(15)	20(14)
C(9B)	119(15)	115(12)	255(19)	-33(13)	14(15)	-14(13)
C(10B)	203(17)	118(11)	177(17)	-24(13)	-35(15)	-9(14)
C(11B)	252(18)	184(12)	227(18)	30(14)	-21(16)	12(17)
C(12B)	216(19)	204(14)	160(20)	46(12)	-35(17)	11(14)
C(13B)	255(19)	228(15)	210(20)	13(13)	37(18)	3(15)