Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2019

Supporting Information

Formation of Allylated Quaternary Carbon Centers via C–O/C–O Bond Fragmentation of Oxalates and Allyl Carbonates

Haifeng Chen, Yang Ye, Jianhui Fang and Hegui Gong*

School of Materials Science and Engineering, The Center for Supramolecular Chemistry and Catalysis and *Department of Chemistry, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China*

hegui_gong@shu.edu.cn

Table of Contents

I. Experimental Section ……..…….…..……..S1-S60

Part 1. General Information…….…….....S1

Part 2. Details of Optimization and Control Experiments……..…S2-S7

Part 3. Mechanistic Studies…..……...……S8-S12

Part 4. Preparation of Allylic Carbonate ……..…..……..….S13-S16

Part 5. Preparation of Tertiary Alkyl Oxalates……..……..S16-S31

Part 6. Allylation of Tertiary Alkyl Oxalates with Allylic Electrophiles....S31-S53

Part 7. Three Component Reactions……...……S53-S58

Part 8. Cyclization/allylation Reactions.…….....S59-S60

II. Spectral Data for New Compounds…….…….…….....S61-S184

III. References…….....…S185-186

I. Experimental Section

Part 1. General Information.

1. Chemicals and Reagents.

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk or glove box techniques. DMA (*N*, *N*-dimethylacetamide, 99.5%, extra dry, Acros) was purchased and used directly. Deuterated solvents were used as received ($CDCl_3$ from Maclin Co., China). Fe $(acac)_3$ (Sigma-Aldrich), FePc (TCI), $FeCl_3$ (Alfa Aesar), $FeBr_3$ (Alfa Aesar), $Fe_2(SO_4)_3$ (Adamas), Ni $(COD)_2$ (Strem), $Fe_2(OTf)_3$ (Alfa Aesar), $Ni(acac)_2$ (Maclin Co., China), $Co(acac)_2$ (Alfa Aesar), CuI (Alfa Aesar) were used as received. Zinc powder (Aladdin) was activated with hydrochloric acid before use. Anhydrous $MgCl_2$ (Alfa Aesar) and anhydrous LiCl (TCI) were purchased and used directly. DMAP (4-(dimethylamine) pyridine (>99%, Adamas), Dtbbipy (98%, Alfa Aesar) were purchased and used directly. Procedures for the ligand synthesis have been reported.[1] Tertiary alcohols and allylic carbonates were prepared according to literature procedures [2,3] or purchased and used directly. Methyl magnesium bromide (3M in THF, Adamas) was purchased and used directly.

2. Physical Method.

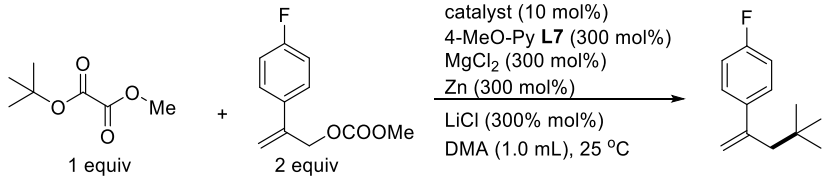
Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer, a Bruker Avance 500 MHz spectrometer, or a JEOL 400 MHz at STP, unless otherwise indicated. ^1H NMR and ^{13}C NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^1H NMR and ^{13}C NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker APEXIII 7.0 or IonSpec 4.7 TESLA FTMS instruments. Melting points were recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China). In situ IR spectra were recorded on a Thermo Scientific Nicolet iS10 Fourier transform infrared (FT-IR) spectrometer. GC chromatograms were recorded on a GCMS-QP2010 SE (SHIMADZU) using an Agilent column CP7502 and Rxi-5 ms (Restek).

Part 2. Details of Optimization and Control Experiments

Method A: To a flame-dried Schlenk tube equipped with a stir bar was loaded zinc power (29.4 mg, 0.45 mmol, 300 mol %), followed by addition of $MgCl_2$ (42.9 mg, 0.45 mmol, 300 mol %), ligand (0.03 mmol, 20 mol %) and Fe $(acac)_3$ (0.015 mmol, 10 mol%). The tube was evacuated and refilled nitrogen (N_2) three time. A solvent (1.0 mL) was added via a syringe, followed by addition of *tertiary* alkyl oxalate (0.15 mmol, 100 mol %), and allylic carbonate (0.3 mmol, 200 mol %). After the reaction mixture was stirred for 12 h under a N_2 atmosphere at 45 °C, the reaction mixture was loaded onto a silica column. Flash column chromatography provided the product as an oil or a solid.

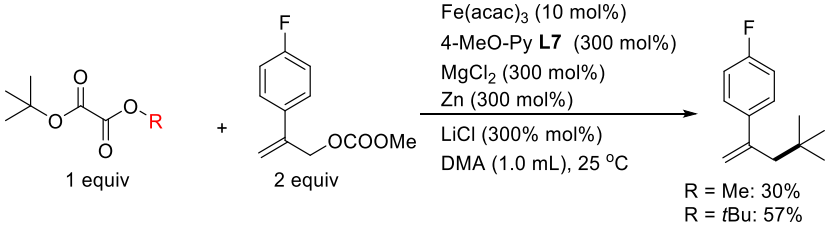
1. Reaction of methyl (2-arylallyl) carbonate with different oxalates.

Table S1. Screening of the catalyst for the coupling of *tert*-butyl methyl oxalate with methyl 2-(4-fluorophenyl) allyl carbonate.



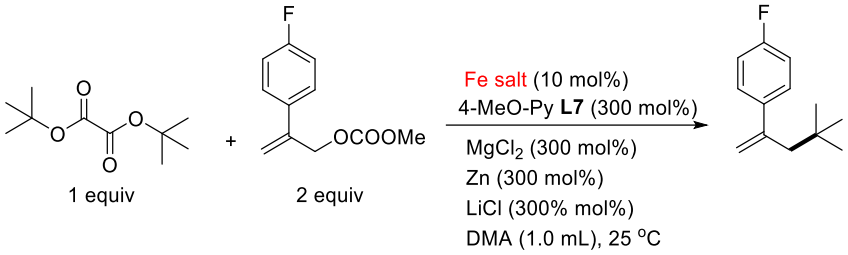
entry	catalyst	yield [a]	entry	catalyst	yield [a]
1	Ni $(TMHD)_2$	21%	12	$NiCl_2 \cdot (PPh_3)_2$	18%
2	Ni $(COD)_2$	13%	13	Ni $(CF_3SO_3)_2$	31%
3	$NiBr_2$·glyme	14%	14	Ni $(OAc)_2 \cdot 4H_2O$	17%
4	$NiBr_2$·diglyme	13%	15	$NiCl_2 \cdot$ (dppp)	17%
5	Ni $(acac)_2$	11%	16	$NiCl_2 \cdot$ (dppe)	ND
6	NiI_2	trace	17	$NiCl_2 \cdot$ (dppf)	27%
7	$NiBr_2$	6%	18	$CoBr_2$	24%
8	$NiCl_2$	11%	19	$CoCl_2$	16%
9	$NiCl_2$ $(Py)_4$	15%	20	Co $(acac)_2$	29%
10	Ni $(ClO_4)_2 \cdot 6H_2O$	11%	21	Fe $(acac)_3$	30%
11	$NiCl_2$·DME	16%			

[a] NMR yield using 2,5-dimethyl-furan as internal reference.



Scheme S1. Use of methyl and *t*-butyl oxalates (NMR yield using 2,5-dimethylfuran as internal reference). .

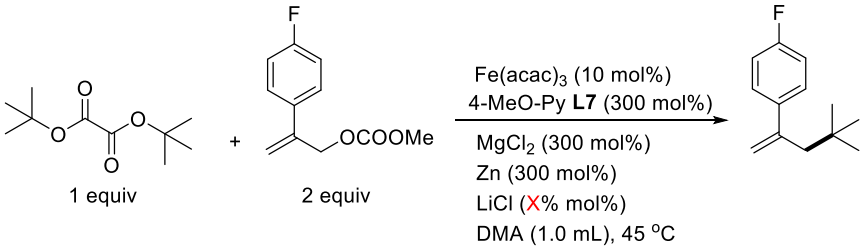
Table S2. Screening of the iron salts for the coupling of di-*tert*-butyl oxalate with methyl 2-(4-fluorophenyl) allyl carbonate.



entry	iron salt	yield [a]
1	$Fe(acac)_3$	57%
2	$FeCl_3$	56%
3	$FeBr_3$	36%
4	FeF_3	52%
5	$FeBr_2$	36%
6	Dppf	56%
7	$FeCp_2$	55%
8	$FeSO_4{\cdot}7H_2O$	45%
9	$Fe_2(SO_4)_3$	48%

[a]NMR yield using 2,5-dimethyl-furan as internal reference.

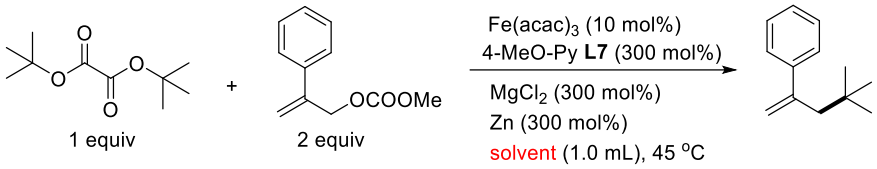
Table S3. Screening of the loading of LiCl



Entry.	X%	yield [a]
1	0	68%
2	100	55%
3	200	57%
4	300	58%

[a]NMR yield using 2,5-dimethyl-furon as internal reference.

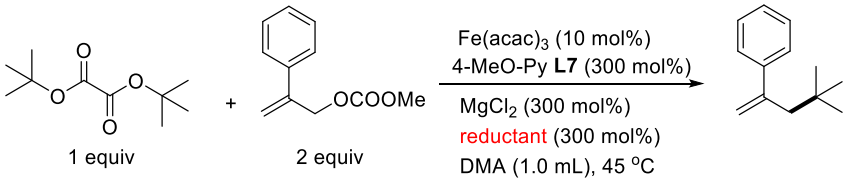
Table S4. Screening of solvent for the coupling of di-*tert*-butyl oxalate with methyl (2-phenyl allyl) carbonate.



entry	solvent	yield [a]
1 [a]	DMA	69%
2 [b]	THF	ND
3 [a]	DMF	30%
4 [b]	NMP	ND
5 [b]	1,4-Dioxane	ND
6 [b]	DMSO	ND
7 [b]	DME	ND
8 [b]	MeCN	ND

[a]NMR yield using 2,5-dimethyl-furon as internal reference. [b] Detected by TLC.

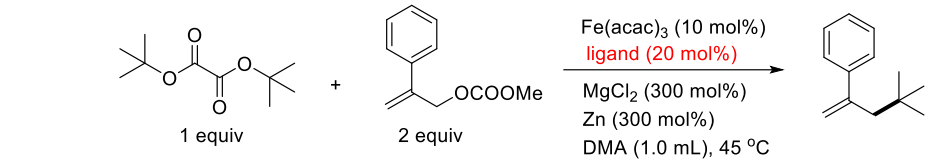
Table S5. Screening of reductant for the coupling of di-*tert*-butyl oxalate with methyl (2-phenyl allyl) carbonate.

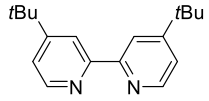


entry	reductant	yield [a]
1	Zn	61%
2	Mn	31%
3	$(BPin)_2$	ND
4	TDAE	trace

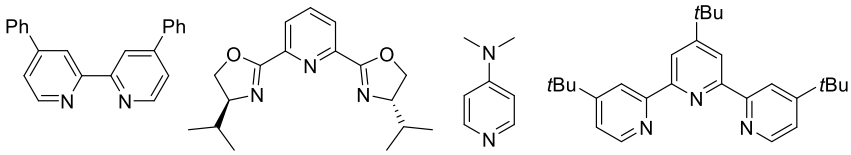
[a]NMR yield using 2,5-dimethyl-furan as internal reference.

Table S6. Screening of ligands for the coupling of di-*tert*-butyl oxalate with methyl (2-phenyl allyl) carbonate.

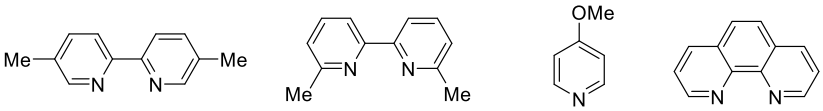




	L1a	L1b	L1c	L1d
yield:	84%	61%	74%	74%
recovered oxalate:	7%	6%	5%	trace
recovered carbonate:	106%	88%	94%	84%



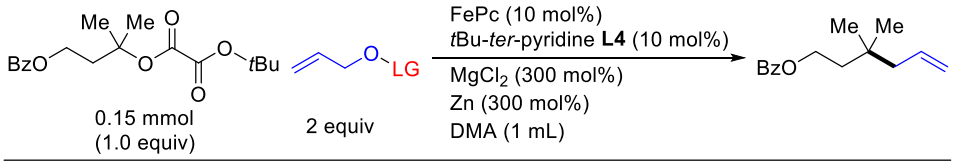
	L1e	L2	L3	L4
yield:	64%	58%	53%	60%
recovered oxalate:	33%	33%	not detected	15%
recovered carbonate:	98%	132%	112%	70%

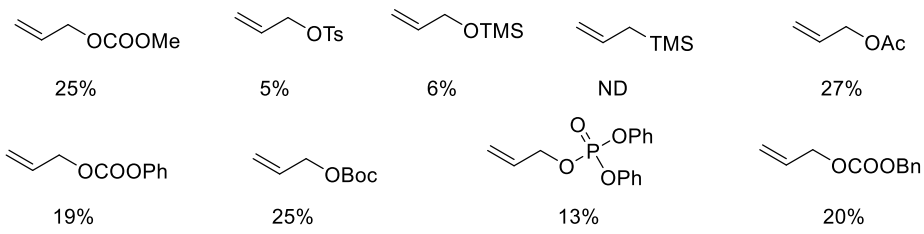


	L5	L6	L7	L8
yield:	60%	47%	69%	44%
recovered oxalate:	24%	10%	10%	23%
recovered carbonate:	74%	118%	118%	120%

2. Optimization for unsubstituted allyl electrophiles.

Table S7. Screening of the allylic substrates.

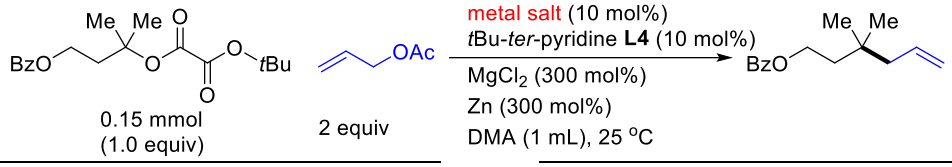




OCOOMe	OTs	OTMS	TMS	OAc
25%	5%	6%	ND	27%

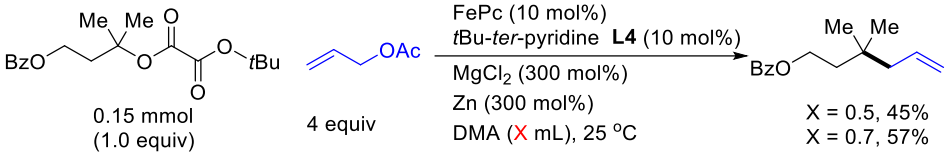
OCOOPh	OBoc	OPh / OPh	OCOOBn
19%	25%	13%	20%

Table S8. Screening of metal salts.

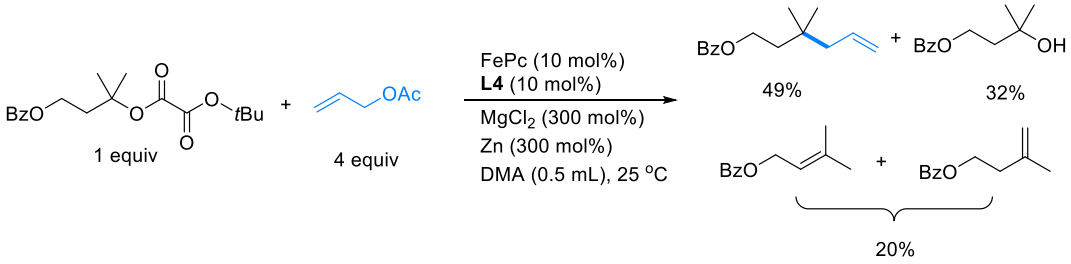


entry	metal salt	yield[a]	entry	metal salt	yield [a]
1	$FeCl_3{\cdot}6H_2O$	8%	15	$Fe(OAc)_2$	Trace
2	$FeBr_2$	8%	16	$FeBr_3$	Trace
3	FeF_3	Trace	17	$Fe(ClO_4)_3{\cdot}6H_2O$	Trace
4	FeS	ND	18	$Ni(COD)_2$	Trace
5	$Fe_2(SO_4)_3$	Trace	19	$NiBr_2{\cdot}$glyme	ND
6	$Fe_2(C_2O_4)_3{\cdot}6H_2O$	33%	20	$NiBr_2{\cdot}$diglyme	ND
7	$Fe(dibm)_3$	11%	21	NiI_2	ND
8	$Fe(dmp)_3$	Trace	22	$Ni(CF_3SO_3)_2$	12%
9	$Fe(acac)_3$	Trace	23	$Ni(acac)_2$	Trace
10	$Fe(acac)_2$	11%	24	$NiBr_2$	ND
11	$FeCl_3$	Trace	25	$Ni(TMHD)_2$	trace
12	$FeCp_2$	Trace	26	$Co(acac)_2$	12%
13	$Fe(OTf)_3$	Trace	27	CoPc	Trace
14	**FePc**	**33%**	28	without Fe salt	no reaction

[a] Detected by NMR using 2,5-dimethylfuran as internal reference.



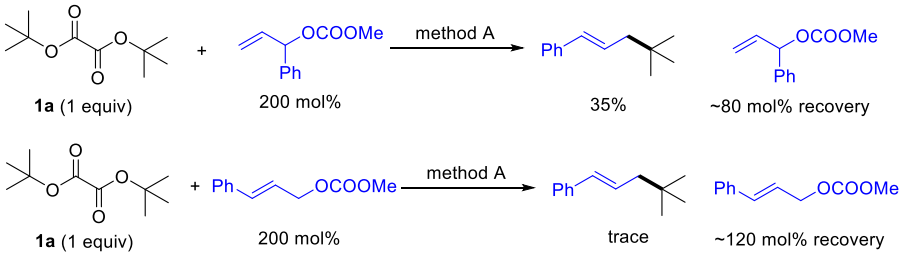
Scheme S2. Screening of the concentrations of reaction (NMR yield using 2,5-dimethyl-furan as internal reference).



Scheme S3. Mass balance for **1b** for the coupling with allyl acetate.

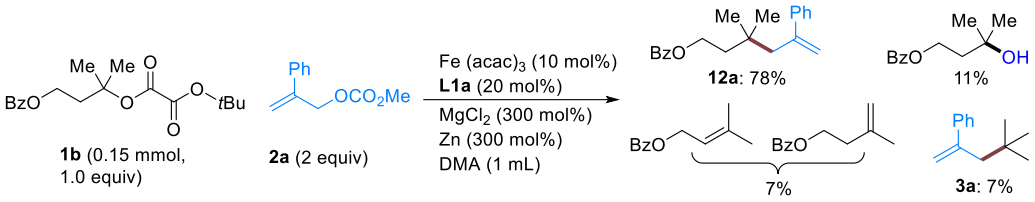
3. Examination of 1- and 3-phenyl substituted allylic carbonates

The reaction of **1a** with 1-phenyl and 3-phenyl allyl carbonates indicated that all the starting **1a** was consumed. However, substantial amounts of allylic carbonates were recovered, indicating the low reactivities of the 1-phenyl and 3-phenyl allyl carbonates as compared to the 2-phenyl analog (**2a**).

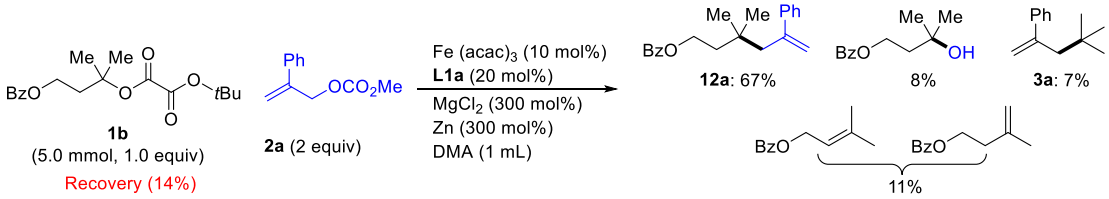


Scheme S4. Reaction of **1a** with 1-phenyl and 3-phenyl allyl carbonates.

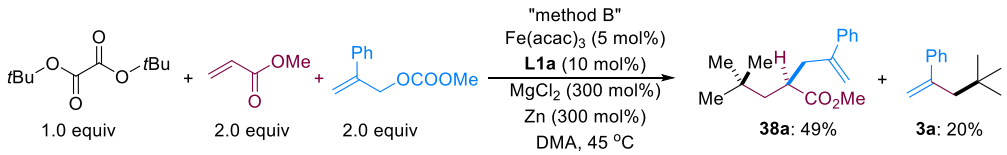
4. Product distribution



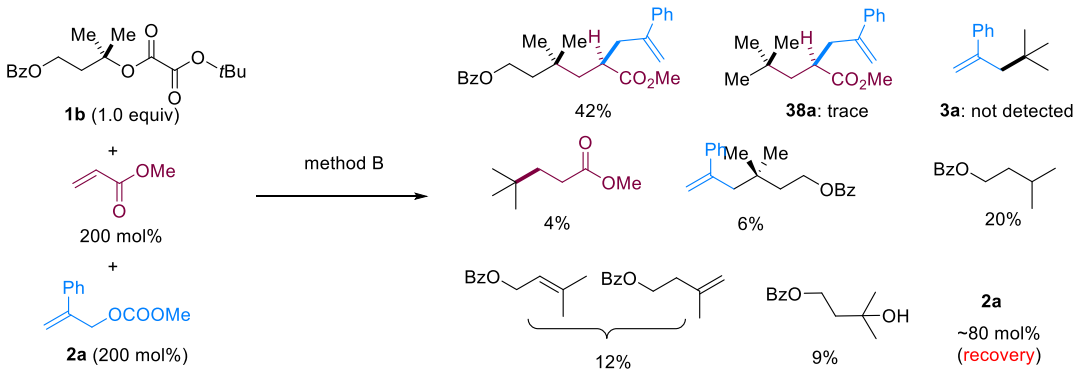
Scheme S5. The product distribution of the reaction of **1b** with **2a** using method A.



Scheme S6. The product distribution of the scale-up reaction **1b** with **2a** using method A.



Scheme S7. The product distribution of the three-component reaction of di-tert-butyl oxalate **1a**, methyl acrylate and **2a** using method B.

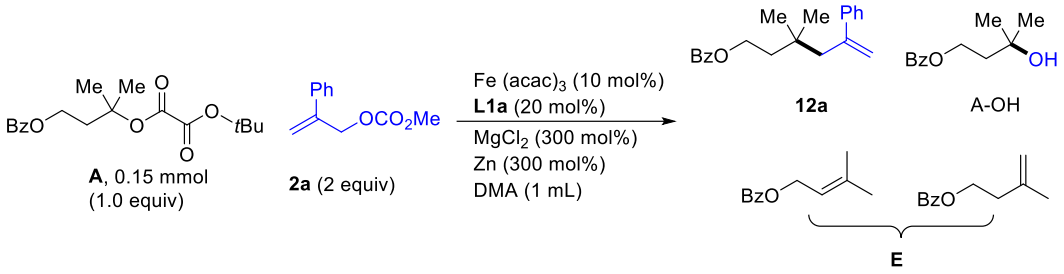


Scheme S8. The product distribution of the three-component reaction of oxalate **1b**, methyl acrylate and **2b** using method B.

Part 3. Mechanistic Studies.

1. Monitoring the reaction progress.

Table S9. Tracking the reaction progress.



Entry.	Time/h	Recovered **A**[a]	Recovered **2a**[a]	**12a**[a]	**A-OH**[a]	**E**[a]
1	0.5h	29%	132%	30%	41%	0%
2	1h	19%	120%	53%	29%	Trace
3	2h	5%	108%	72%	22%	Trace
4	3h	Trace	91%	78%	16%	Trace
5	4h	Trace	80%	78%	11%	7%
6	5h	Trace	80%	79%	9%	7%
7	8h	Trace	55%	82%	4%	8%

[a] Detected by NMR using 2,5-dimethyl-furan as internal reference.

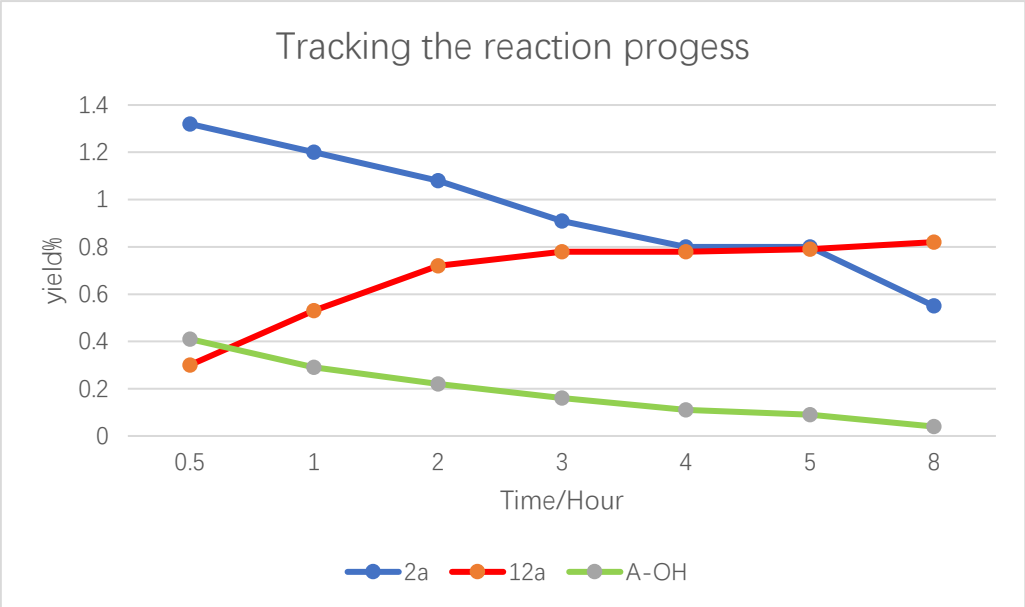
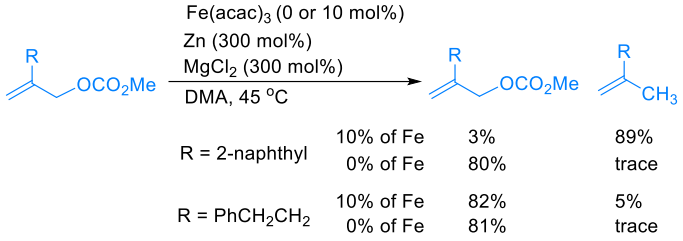
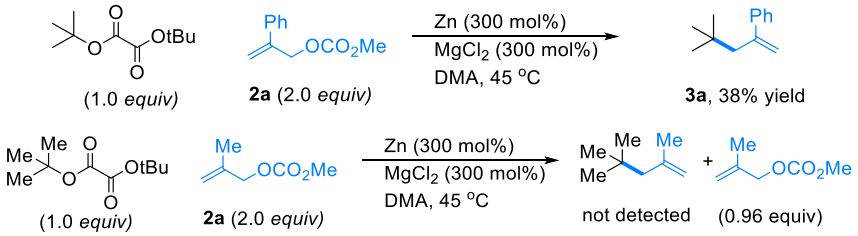


Figure S1. Monitoring the reaction progress

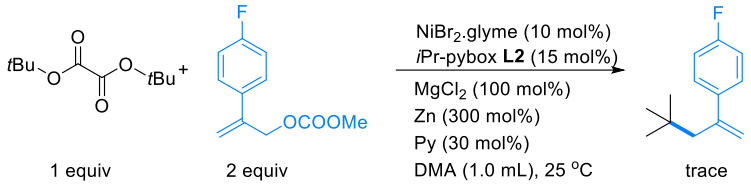
2. Control experiments



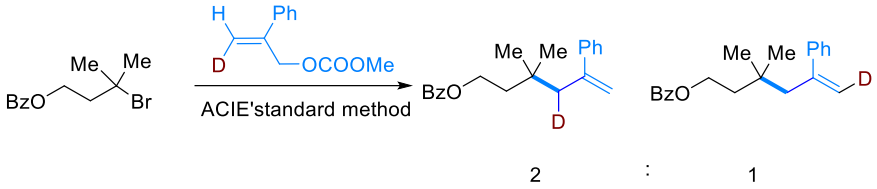
Scheme S9. Control experiment in the absence of oxalate **1a**.



Scheme S10. Control experiment in the absence of Fe salts.



Scheme S11. Control experiments using previously reported Ni-catalyzed reaction conditions.[2a]



Scheme S12. Nickel catalyzed allylation of 3-bromo-3-methylbutyl benzoate with (Z)-methyl (2-phenylallyl-3-*d*) carbonate (**2a**-*d*).[2a]

3. ^{1}H NMR spectroscopic analysis

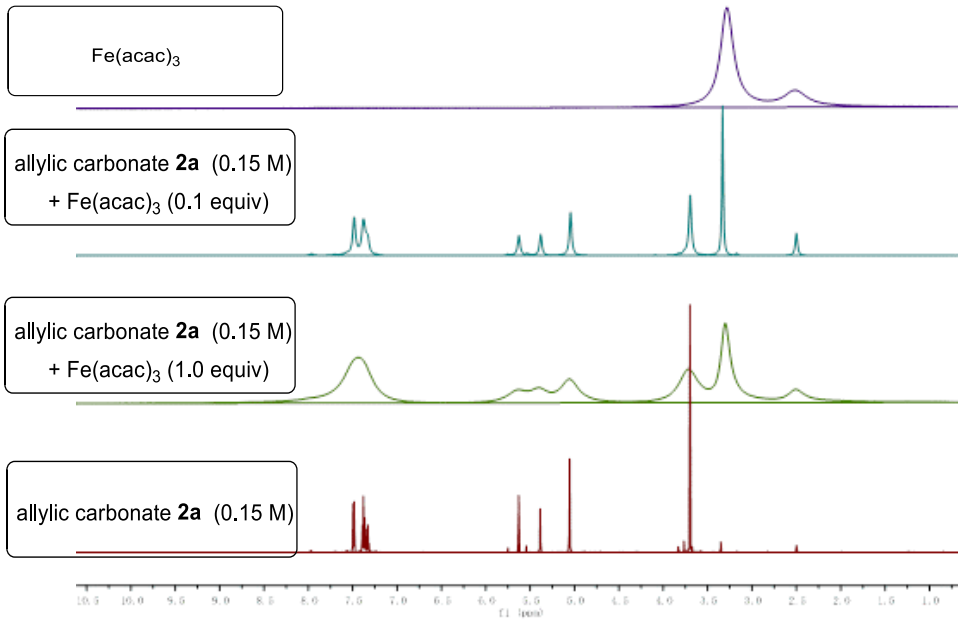


Figure S2. ^{1}H NMR spectra of Fe(acac)$_3$, **2a**, and an equimolar mixture of Fe(acac)$_3$ and **2a** in DMSO-d_6. The ^{1}H NMR spectra was recorded after stirring overnight. No obvious changes of the chemical shifts were detected.

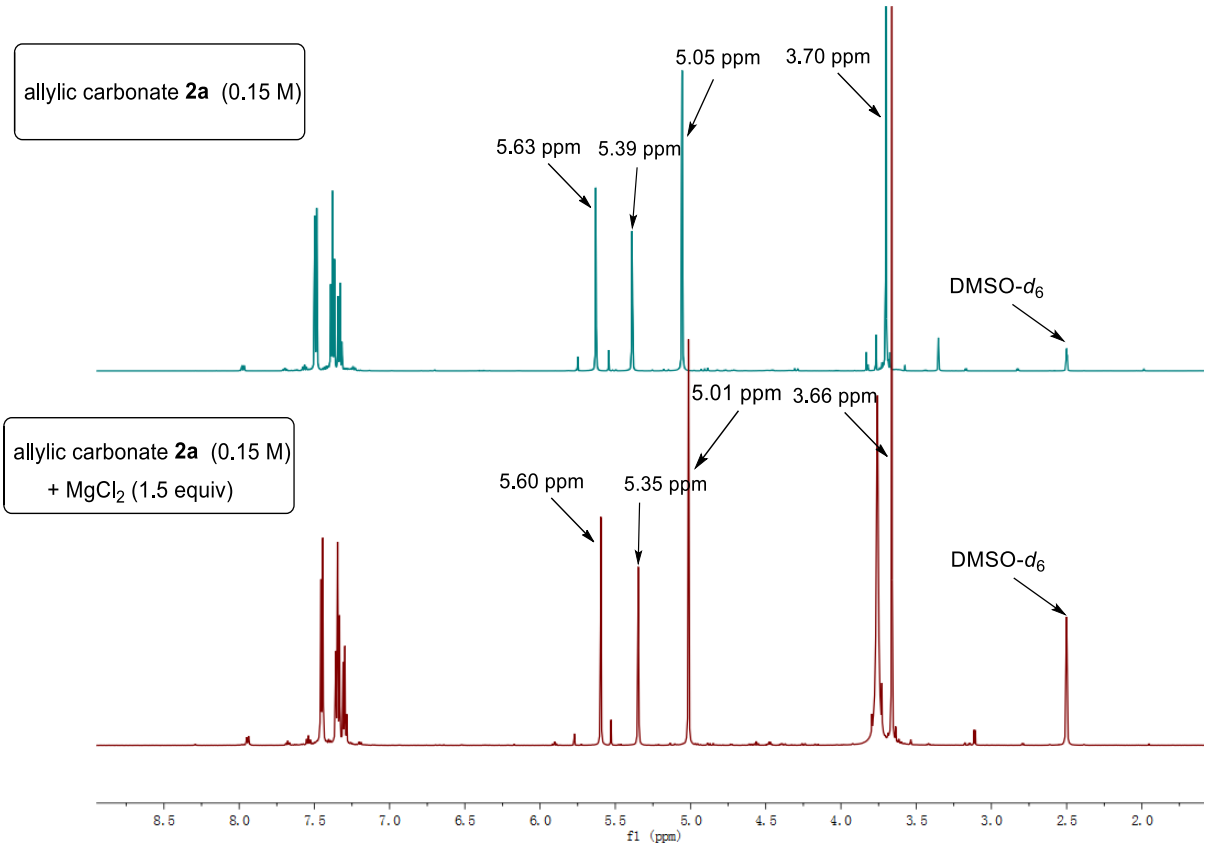


Figure S3. ^{1}H NMR spectra of allyl carbonate **2a** (0.15 M) without (above) and with (bottom) $MgCl_2$ (1.5 equiv) in DMSO-d_6 (bottom). The spectra were recorded about 10 minutes after the sample was prepared.

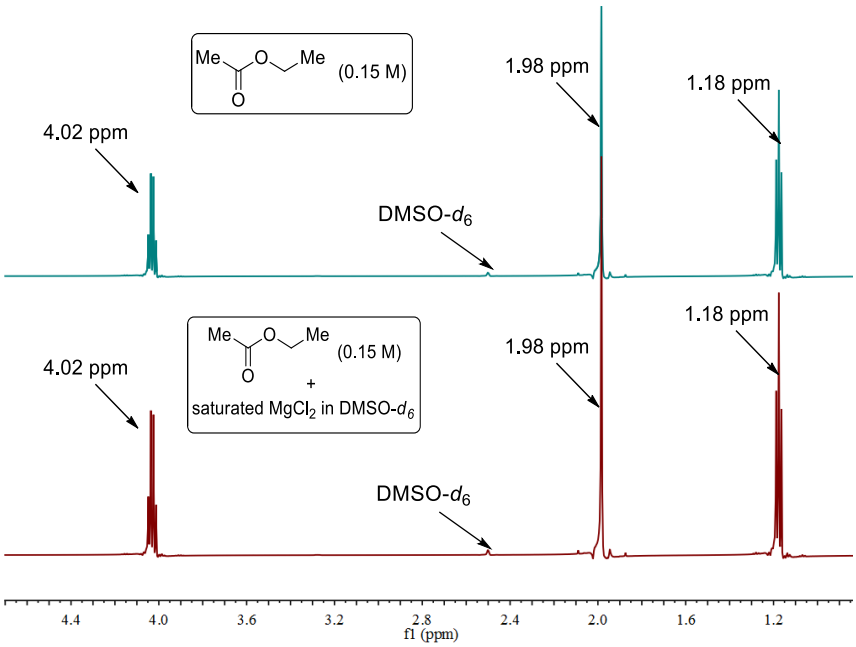


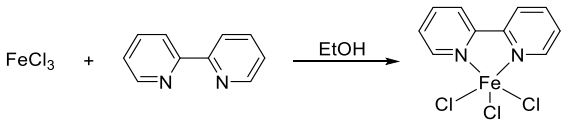
Figure S4. The ^{1}H NMR spectra for ethyl acetate (top) and its mixture with $MgCl_2$ (saturated, bottom) in DMSO-d_6.

4. Roles of Fe

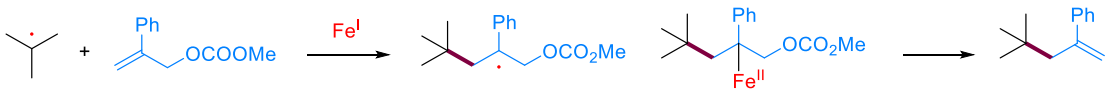
In this time, we are still far from fully understanding the role of iron complex in the radical addition process. However, there are key points that we would like to highlight.

First, without an iron salt, the radical addition/allyl C-O bond fragmentation product **3a** was obtained in ~40% yield, indicating that the reaction was governed by Zn and $MgCl_2$. Thus, iron complex only acts to promote the reaction.

Second, we speculate Fe^{3+} or Fe^{2+} may serve as a Lewis acid to coordinate with allyl carbonate similar to Mg^{2+} (Figure S3). However, no appreciable interaction of Fe^{3+} nor Fe^{2+} with allylic carbonate was detected for a mixture of these two species in DMSO-*d6* (Figure S2). In addition, such an interaction was not seen for a pre-formed bipy-$FeCl_3$ (see below) with allyl carbonate from ^1H NMR studies, although a control experiment showed that bipy-$FeCl_3$ gave **3a** in 65% yield. Thus, coordination of Fe^{3+} or Fe^{2+} with allyl carbonate so as to promote allyl C-O bond cleavage or activation of alkenes within the allyl groups is not clear.



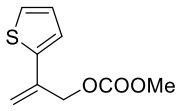
Third, since Hu has reported Fe^{+} is likely to mediate the addiction of unactivated tertiary alkyl radical with alkynes by formation of vinyl-Fe after addition of tertiary alkyl radical to alkyne. The formation of tertiary benzyl-Fe^{II} intermediate may operate in our work, which may facilitate the allyl C-O bond scission by elimination of a Fe-O product.



Part 4. Preparation of Allylic Carbonates.

General procedure for the preparation of allylic carbonates. Methyl chloroformate (200 mol%) was added to a solution of allylic alcohol (100 mol %) and pyridine (300 mol %) in DCM (0.4 M) at 0 °C. The reaction mixture was warmed to room temperature, and stirred overnight, at which point it was washed with brine and extracted with DCM. The combined organic layer was washed with HCl (1N), dried over $MgSO_4$. Silica gel was added, and the solvent was removed under reduced pressure. The residue was loaded to a silica column. Flash chromatography provided the desired allylic carbonate.

Methyl (2-(thiophen-2-yl) allyl) carbonate



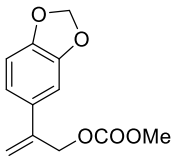
The title compound was prepared according the general procedure using 2-(thiophen-2-yl) prop-2-en-1-ol [4] (1.40 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 3% ethyl acetate in petroleum ether), the title compound was isolated in 92% yield (1.82 g, 9.2 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.21 (d, *J* = 5.4 Hz, 1H), 7.08 (d, *J* = 3.6 Hz, 1H), 6.99 (dd, *J* = 7.2, 3.6 Hz, 1H), 5.60 (s, 1H), 5.30 (s, 1H), 4.99 (s, 2H), 3.81 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 155.51, 141.42, 135.78, 127.51, 124.86, 124.13, 114.28, 68.84, 54.92.

HRMS (ESI) exact mass calculated for [M+Na^+] ($C_9H_{10}NaO_3S^+$): m/z 221.0243; found: 221.0249.

2-(Benzo[d] [1,3] dioxol-5-yl) allyl methyl carbonate



The title compound was prepared according the general procedure using 2-(benzo[d] [1,3] dioxol-5-yl) prop-2-en-1-ol [5] (1.78 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 3% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (2.15 g, 9.1 mmol) as a colorless liquid.

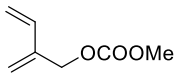
^{1}H NMR (600 MHz, Chloroform-*d*): δ 6.93 (d, *J* = 1.8 Hz, 1H), 6.91 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 5.96 (s, 2H), 5.46 (s, 1H), 5.32 (s, 1H), 4.97 (s, 2H), 3.79 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 155.56, 147.87, 147.55, 141.49, 131.96, 119.64, 114.83,

108.19, 106.57, 101.13, 69.22, 54.84.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{12}H_{13}O_5^+$): m/z 237.0757; found: 237.0764.

Methyl (2-methylenebut-3-en-1-yl) carbonate



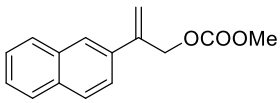
The title compound was prepared according the general procedure using 2-methylenebut-3-en-1-ol [6] (0.84 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 96% yield (1.36 g, 9.6 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 6.34 (dd, *J* = 18.0, 10.8 Hz, 1H), 5.28 (s, 1H), 5.24 (d, *J* = 18.0 Hz, 1H), 5.21 (s, 1H), 5.12 (d, *J* = 10.8 Hz, 1H), 4.79 (s, 2H), 3.76 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 155.47, 139.98, 135.67, 118.18, 114.63, 66.76, 54.68.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_7H_{10}NaO_3^+$): m/z 165.0522; found: 165.0517.

Methyl (2-(naphthalen-2-yl) allyl) carbonate



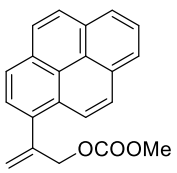
The title compound was prepared according the general procedure using 2-(naphthalen-2-yl) prop-2-en-1-ol [6] (1.84 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (2.20 g, 9.1 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.87 - 7.82 (m, 4H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.51 - 7.47 (m, 2H), 5.74 (s, 1H), 5.53 (s, 1H), 5.18 (s, 2H), 3.81 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 155.62, 141.82, 134.92, 133.24, 133.02, 128.25, 128.13, 127.51, 126.27, 126.17, 124.86, 124.03, 116.14, 69.07, 54.83.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{15}H_{14}NaO_3^+$): m/z 265.0835; found: 265.0841.

Methyl (2-(pyren-1-yl) allyl) carbonate



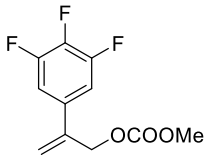
The title compound was prepared according the general procedure using 2-(pyren-1-yl) prop-2-en-1-ol (2.58 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 86% yield (2.72 g, 8.6 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.31 (d, *J* = 9.0 Hz, 1H), 8.19 (dd, *J* = 7.8, 1.8 Hz, 2H), 8.16 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 9.0 Hz, 1H), 8.07 (d, *J* = 6.0 Hz, 2H), 8.02 (t, *J* = 7.2 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 5.86 (s, 1H), 5.46 (s, 1H), 5.11 (s, 2H), 3.80 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 155.61, 142.76, 134.32, 131.30, 130.88, 128.83, 127.75, 127.57, 127.27, 126.14, 126.03, 125.19, 125.04, 124.83, 124.73, 124.55, 124.45, 118.04, 70.60, 54.91.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{21}H_{27}O_3^+$): m/z 317.1172; found: 317.1184.

Methyl (2-(3,4,5-trifluorophenyl) allyl) carbonate



The title compound was prepared according the general procedure using 2-(3,4,5-trifluorophenyl) prop-2-en-1-ol (1.88 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 88% yield (2.17 g, 8.8 mmol) as a colorless liquid.

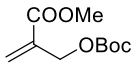
^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.05 (dd, *J* = 9.0, 6.6 Hz, 2H), 5.56 (s, 1H), 5.49, (s, 1H), 4.94 (s, 2H), 3.80 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 155.39, 152.03, 1511.99, 151.97, 150.41, 150.38, 150.31, 140.37, 139.65, 138.69, 133.90, 133.86, 118.37, 110.42, 110.39, 110.31, 110.28, 68.53, 55.01.

^{19}F NMR (565 MHz, Chloroform-*d*): -134.06, -134.09, -160.76.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{11}H_{10}F_3O_3^+$): m/z 247.0577; found: 247.0585.

Methyl 2- (((*tert*-butoxy carbonyl) oxy) methyl) acrylate [7]



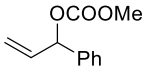
The title compound was prepared according the general procedure using methyl 2-(hydroxymethyl) acrylate (1.16 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 60% yield (1.30g, 6.0 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 6.34 (s, 1H), 5.85 (s, 1H), 4.76 (s, 2H), 3.75 (s, 3H), 1.45 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 165.46, 152.96, 135.00, 127.56, 82.38, 64.63, 51.93, 27.65.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{10}H_{16}NaO_5^+$): m/z 239.0890; found: 239.0896.

Methyl (1-phenylallyl) carbonate [8]

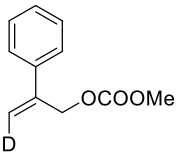


The title compound was prepared according the general procedure using 1-phenylprop-2-en-1-ol (1.34 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (1.75 g, 9.1 mmol) as a light-yellow liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.37 - 7.33 (m, 4H), 7.31 - 7.28 (m, 1H), 6.08 (d, *J* = 6.0 Hz, 1H), 6.05 - 6.00 (m, 1H), 5.34 (d, *J* = 17.4 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 154.91, 138.20, 135.69, 128.49, 128.30, 126.95, 117.32, 80.05, 54.65.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{11}H_{12}NaO_3^+$): m/z 215.0679; found: 215.0678.



(Z)-methyl (2-phenylallyl-3-d) carbonate

The title compound was prepared according the general procedure using (Z)-2-phenylprop-2-en-3-d-1-ol-d [9] (1.36 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (1.76 g, 9.1 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 5.56 (s, 1H), 5.42 (d, *J* = 0.6 Hz, 0.13H), 5.05 (s, 2H), 3.80 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 155.56, 141.90, 137.70, 128.48, 128.09, 125.95, 116.64, 115.48, 115.32, 115.16, 69.00, 54.80.

^{2}D NMR (61 MHz, $CHCl_3$) δ 5.47.

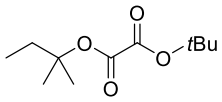
HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{11}H_{11}DNaO_3^+$): m/z 216.0741; found: 216.0746.

Part 5. Preparation of Tertiary Alkyl Oxalates.

General procedure for the preparation of tertiary alkyl oxalates. The *tertiary* alkyl oxalates were prepared according to a literature procedure from the corresponding *tertiary* alcohols. [10] To a solution of alcohol (10.0 mmol, 100 mol%) in CH_2Cl_2 (50 mL) was added pyridine (20.0 mmol, 200 mol%), DMAP (1.0 mmol, 10 mol%) at 0 ºC. Following this, *tert*-butyl 2-chloro-2-oxoacetate

[11] (12.0 mmol, 120 mol%) was added dropwise. The reaction mixture was allowed to warm to r.t. and stirred overnight. The reaction mixture was diluted with Et_2O, washed with water, saturated $NaHCO_3$, and brine. The organic phase was collected, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatograph to afford the product as a solid or oil.

***tert*-Butyl *tert*-pentyl oxalate**



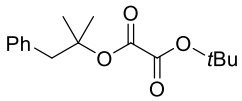
The title compound was prepared according the general procedure using 2-methylbutan-2-ol (0.88 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 95% yield (2.05 g, 9.5 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 1.85 (q, *J* = 15.0 Hz, 2H), 1.54 (s, 9H), 1.51 (s, 6H), 0.93 (t, *J* = 15.0 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 157.80, 157.76, 86.78, 84.16, 33.31, 27.74, 25.13, 8.14.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{11}H_{20}NaO_4^+$): m/z 239.1254; found: 239.1259.

***tert*-Butyl (2-methyl-1-phenylpropan-2-yl) oxalate**



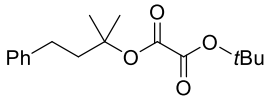
The title compound was prepared according the general procedure using 2-methyl-1-phenylpropan-2-ol (1.50 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 88% yield (2.45 g, 8.8 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.33 - 7.19 (m, 5H), 3.09 (d, *J* = 10.3 Hz, 2H), 1.56 (s, 6H), 1.53 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*): δ 157.65, 157.47, 136.44, 130.68, 127.97, 126.65, 85.85, 84.22, 46.96, 27.72, 25.23.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{16}H_{22}NaO_4^+$): m/z 301.1410; found: 301.1419.

***tert*-Butyl (2-methyl-4-phenylbutan-2-yl) oxalate**



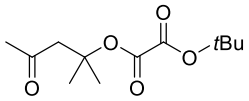
The title compound was prepared according the general procedure using 2-methyl-4-phenylbutan-2-ol (1.64 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (2.63 g, 9.0 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.31 - 7.25 (m, 2H), 7.20 (dd, *J* = 7.2, 3.9 Hz, 3H), 2.76 - 2.65 (m, 2H), 2.20 - 2.09 (m, 2H), 1.60 (s, 6H), 1.56 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*): δ 157.67, 157.59, 141.63, 128.39, 128.30, 125.88, 85.89, 84.25, 42.62, 30.15, 27.71, 25.61.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{17}H_{24}NaO_4^+$): m/z 315.1567; found: 315.1573.

***tert*-Butyl (2-methyl-4-oxopentan-2-yl) oxalate**



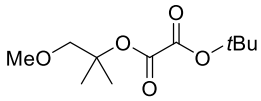
The title compound was prepared according the general procedure using 4-hydroxy-4-methylpentan-2-one (1.16 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (2.20 g, 9.0 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 2.99 (s, 2H), 2.19 (s, 3H), 1.60 (s, 6H), 1.52 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*): δ 205.50, 157.44, 157.16, 84.58, 84.15, 52.57, 31.84, 27.67, 25.67.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{12}H_{20}NaO_5^+$): m/z 267.1203; found: 267.1211.

***tert*-Butyl (1-methoxy-2-methylpropan-2-yl) oxalate**



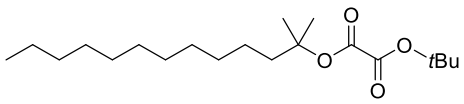
The title compound was prepared according the general procedure using 1-methoxy-2-methylpropan-2-ol (1.04 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (2.09 g, 9.0 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 3.52 (s, 2H), 3.38 (s, 3H), 1.51 (s, 15H).

^{13}C NMR (100 MHz, Chloroform-*d*): δ 157.48, 157.26, 84.88, 84.25, 77.62, 59.44, 27.63, 22.80.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{11}H_{20}NaO_5^+$): m/z 255.1203; found: 255.1213.

***tert*-Butyl (2-methyltridecan-2-yl) oxalate**



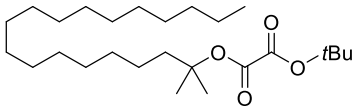
The title compound was prepared according the general procedure using 2-methyltridecan -2-ol (2.14 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 93% yield (3.19 g, 9.3 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-d): δ 1.80 - 1.77 (m, 2H), 1.53 (s, 9H), 1.50 (s, 6H), 1.34 - 1.31 (m, 2H), 1.27 (d, *J* = 3.6 Hz, 6H), 1.25 (s, 10H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-d): δ 157.77, 157.72, 86.60, 84.06, 40.57, 31.87, 29.77, 29.61, 29.58, 29.55, 29.49, 29.30, 27.71, 25.59, 23.74, 22.64, 14.07.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{20}H_{38}NaO_4^+$): m/z 365.2662; found: 365.2675.

***tert*-Butyl (2-methylnonadecan-2-yl) oxalate**



The title compound was prepared according the general procedure using 2-methylnonadecan-2-ol (2.99 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (3.84 g, 9.0 mmol) as a white solid.

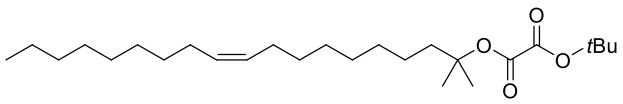
^{1}H NMR (600 MHz, Chloroform-d): δ 1.79 - 1.77 (m, 2H), 1.53 (s, 9H), 1.50 (s, 6H), 1.25 (s, 30H), 0.87 - 0.86 (m, 3H).

^{13}C NMR (150 MHz, Chloroform-d): δ 157.77, 157.73, 86.59, 84.04, 40.58, 31.90, 29.79, 29.67, 29.63, 29.56, 29.50, 29.33, 27.71, 25.59, 23.75, 22.66, 14.08.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{26}H_{50}NaO_4^+$): m/z 449.3601; found: 449.3618.

M.P.: 40.8 - 41.5 °C.

(Z)- *tert*-Butyl (2-methylnonadec-10-en-2-yl) oxalate



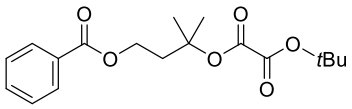
The title compound was prepared according the general procedure using (Z)-2-methylnonadec-10-en-2-ol (2.97 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (3.82 g, 9.0 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-d): δ 5.33 (t, *J* = 6.0 Hz, 2H), 2.00 (q, *J* = 6.6 Hz, 4H), 1.80 - 1.77 (m, 2H), 1.53 (s, 9H), 1.50 (s, 6H), 1.33 - 1.26 (m, 22H), 0.87 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-d): δ 157.75, 157.71, 129.90, 129.74, 86.55, 84.04, 40.57, 31.86, 29.75, 29.73, 29.70, 29.48, 29.39, 29.28, 29.20, 27.70, 27.17, 27.15, 25.58, 23.74, 22.64, 14.06.

HRMS (ESI) exact mass calculated for [M+Na^{+}] ($C_{26}H_{48}NaO_4^{+}$): m/z 447.3445; found: 447.3457.

4-(Benzoyloxy)-2-methylbutan-2-yl tert-butyl oxalate



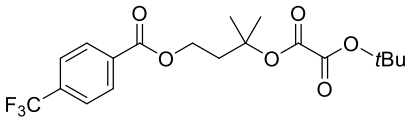
The title compound was prepared according the general procedure using 3-hydroxy-3-methylbutyl benzoate (2.08 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 97% yield (3.26 g, 9.7 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 4.46 (t, *J* = 6.8 Hz, 2H), 2.34 (t, *J* = 6.8 Hz, 2H), 1.63 (s, 6H), 1.51 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 166.43, 157.59, 157.32, 132.94, 130.07, 129.52, 128.36, 84.60, 84.40, 60.83, 39.11, 27.67, 26.01.

HRMS (ESI) exact mass calculated for [M+Na^{+}] ($C_{18}H_{24}NaO_6^{+}$): m/z 359.1465; found: 359.1474.

***tert*-Butyl (2-methyl-4-((4-(trifluoromethyl) benzoyl) oxy) butan-2-yl) oxalate**



The title compound was prepared according the general procedure using 3-hydroxy-3-methylbutyl 4-(trifluoromethyl) benzoate (2.76 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 92% yield (3.72 g, 9.2 mmol) as a colorless liquid.

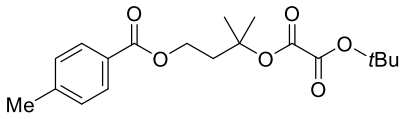
^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 4.50 (t, *J* = 6.7 Hz, 2H), 2.35 (t, *J* = 6.7 Hz, 2H), 1.63 (s, 6H), 1.49 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 165.21, 157.58, 157.27, 133.29, 129.96, 125.43, 125.41, 84.40, 61.39, 38.98, 27.65, 26.02.

^{19}F NMR (376 MHz, Chloroform-d): δ -63.04.

HRMS (ESI) exact mass calculated for [M+Na^{+}] ($C_{19}H_{23}FNaO_6^{+}$): m/z 427.1339; found: 427.1345.

***tert*-Butyl (2-methyl-4-((4-methylbenzoyl) oxy) butan-2-yl) oxalate**



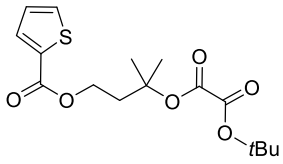
The title compound was prepared according the general procedure using 3-hydroxy-3-methylbutyl 4-methylbenzoate (2.22 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 95% yield (3.33 g, 9.5 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 4.44 (t, *J* = 6.7 Hz, 2H), 2.40 (s, 3H), 2.33 (t, *J* = 6.7 Hz, 2H), 1.63 (s, 6H), 1.51 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*): δ 166.51, 157.57, 157.30, 143.62, 129.54, 129.07, 127.30, 84.67, 84.40, 60.63, 39.08, 27.64, 25.98, 21.60.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{19}H_{26}NaO_6^+$): m/z 373.1622; found: 373.1631.

***tert*-Butyl (2-methyl-4-((thiophene-2-carbonyl) oxy) butan-2-yl) oxalate**



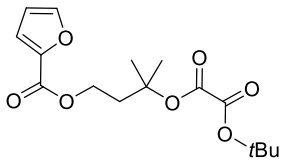
The title compound was prepared according the general procedure using 3-hydroxy-3-methylbutyl thiophene-2-carboxylate (2.14 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 4% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (3.08 g, 9.0 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.78 (s, 1H), 7.54 (s, 1H), 7.08 (s, 1H), 4.43 (t, *J* = 6.0 Hz, 2H), 2.30 (t, *J* = 6.0 Hz, 2H), 1.62 (s, 6H), 1.51 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 161.20, 157.55, 157.31, 133.44, 132.41, 127.75, 84.56, 84.40, 60.95, 39.10, 27.67, 25.99.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{16}H_{22}NaO_6S^+$): m/z 365.1029; found: 365.1035.

***tert*-Butyl (4-((furan-2-carbonyl) oxy)-2-methylbutan-2-yl) oxalate**



The title compound was prepared according the general procedure using 3-hydroxy-3-methylbutyl furan-2-carboxylate (1.98 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 4% ethyl

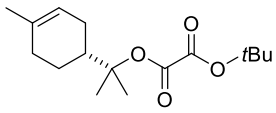
acetate in petroleum ether), the title compound was isolated in 90% yield (2.94 g, 9.0 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.56 (s, 1H), 7.15 (s, 1H), 6.49 (s, 1H), 4.43 (t, *J* = 6.0 Hz, 2H), 2.29 (t, *J* = 6.0 Hz, 2H), 1.60 (s, 6H), 1.51 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 158.49, 157.54, 157.29, 146.36, 144.53, 117.94, 111.79, 84.45, 60.72, 39.06, 27.67, 25.95.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{16}H_{22}NaO_7^+$): m/z 349.1258; found: 349.1265.

(R)- *tert*-Butyl (2-(4-methylcyclohex-3-en-1-yl) propan-2-yl) oxalate



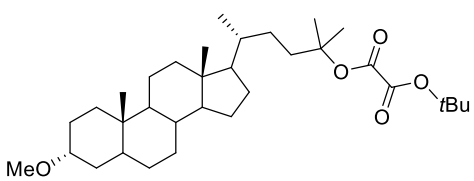
The title compound was prepared according the general procedure using (R)-2-(4-methylcyclohex-3-en-1-yl) propan-2-ol (1.54 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 91% yield (2.57 g, 9.1 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-d): δ 5.36 (s, 1H), 2.10 - 1.94 (m, 4H), 1.88 - 1.82 (m, 2H), 1.64 (s, 3H), 1.53 (s, 9H), 1.50 (d, *J* = 11.8 Hz, 6H), 1.36 - 1.29 (m, 1H).

^{13}C NMR (150 MHz, Chloroform-d): δ 157.79, 157.73, 133.93, 120.03, 88.99, 84.08, 42.69, 30.73, 27.74, 26.27, 23.75, 23.25, 22.96, 22.75.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{16}H_{26}NaO_4^+$): m/z 305.1723; found: 305.1727.

***tert*-Butyl ((5R)-5-((3R,10S,13R)-3-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-methylhexan-2-yl) oxalate**



The title compound was prepared according the general procedure using (5R)-5-((3R,10S,13R)-3-methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren -17-yl)-2-methylhexan-2-ol (4.04 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 82% yield (4.37 g, 8.2 mmol) as a white

solid.

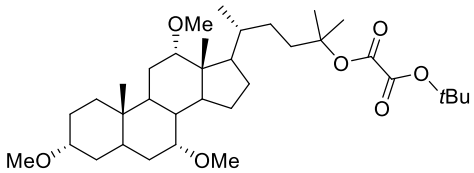
^{1}H NMR (600 MHz, Chloroform-d): δ 3.34 (s, 3H), 3.17 - 3.12 (m, 1H), 1.93 (d, *J* = 12.6 Hz, 1H), 1.84 - 1.78 (m, 4H), 1.75 - 1.65 (m, 3H), 1.59 - 1.54 (m, 2H), 1.52 (s, 9H), 1.49 (d, *J* = 7.8 Hz, 6H), 1.41 - 1.32 (m, 8H), 1.25 - 1.20 (m, 4H), 1.12 - 1.08 (m, 4H), 1.02 (d, *J* = 7.2 Hz, 2H), 0.89 (d, *J* = 8.4 Hz, 6H), 0.62 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-d): δ 157.81, 157.75, 86.81, 84.02, 80.37, 56.42, 55.69, 55.50, 42.63, 42.01, 40.29, 40.09, 36.79, 35.81, 35.68, 35.27, 34.85, 32.74, 29.47, 28.14, 27.72, 27.29, 26.74, 26.37, 25.67, 25.53, 24.16, 23.38, 20.75, 18.66, 11.98.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{33}H_{56}NaO_5^+$): m/z 555.4020; found: 555.4009.

M.P.: 91.2 - 91.6 ^{o}C.

***tert*-Butyl ((5R)-2-methyl-5-((3R,7R,10S,12S,13R)-3,7,12-trimethoxy-10,13-dimethyl hexadecahydro-1H-cyclopenta[a]phenanthren-17-yl) hexan-2-yl) oxalate**



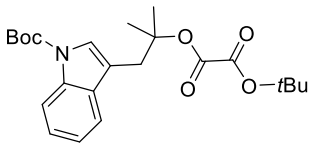
The title compound was prepared according the general procedure using (5R)-2-methyl 5-((3R,7R,10S,12S,13R)-3,7,12-tri methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl) hexan-2-ol (4.65 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 69% yield (4.09 g, 6.9 mmol) as a white foam solid.

^{1}H NMR (600 MHz, Chloroform-d): δ 3.35 (s, 1H), 3.32 (s, 3H), 3.25 (s, 3H), 3.20 (s, 3H), 3.13 (d, *J* = 2.4 Hz, 1H), 3.01 - 2.96 (m, 1H), 2.19 (q, *J* = 12.0 Hz, 1H), 2.11 - 2.03 (m, 2H), 1.94 (q, *J* = 9.6 Hz, 1H), 1.84 - 1.79 (m, 4H), 1.78 - 1.71 (m, 3H), 1.67 (d, *J* = 13.2 Hz, 1H), 1.63 - 1.57 (m, 2H), 1.53 (s, 9H), 1.49 (d, *J* = 10.8 Hz, 6H), 1.46 - 1.25 (m, 5H), 1.20 - 1.14 (m, 3H), 1.04 - 0.99 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.89 (s, 3H), 0.64 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-d): δ 157.86, 157.79, 86.91, 84.02, 81.96, 80.73, 55.82, 55.66, 55.37, 46.11, 46.02, 42.64, 41.96, 39.63, 36.74, 35.43, 35.26, 34.90, 34.43, 29.47, 27.98, 27.75, 27.35, 26.71, 25.76, 25.52, 23.12, 22.84, 21.93, 17.80, 12.43.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{35}H_{60}NaO_7^+$): m/z 615.4231; found: 615.4216.

1-(1-(*tert*-Butoxy carbonyl)-1H-indol-3-yl)-2-methylpropan-2-yl tert-butyl oxalate



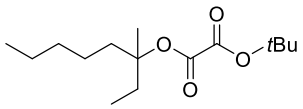
The title compound was prepared according the general procedure using *tert*-butyl 3-(2-hydroxy-2-methylpropyl)-1H-indole-1-carboxylate (2.89 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 88% yield (3.67 g, 8.8 mmol) as a colorless semi-solid.

^{1}H NMR (600 MHz, Chloroform-d): δ 8.13 (bs, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.54 (s, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 3.19 (s, 2H), 1.68 (s, 9H), 1.61 (s, 6H), 1.55 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-d): δ 157.84, 157.55, 149.66, 131.30, 125.15, 124.11, 122.39, 119.43, 115.34, 115.06, 85.98, 84.25, 83.48, 36.00, 28.15, 27.68, 25.49.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{23}H_{31}NNaO_6^+$): m/z 440.2044; found: 440.2042.

***tert*-Butyl (3-methyloctan-3-yl) oxalate**



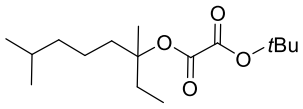
The title compound was prepared according the general procedure using 3-methyloctan-3-ol (1.44 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 96% yield (2.59 g, 9.6 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 1.90 - 1.72 (m, 4H), 1.51 (s, 9H), 1.49 (d, *J* = 3.6 Hz, 9H), 1.43 (d, *J* = 3.6 Hz, 3H), 1.26 - 1.24 (m, 6H), 0.85 - 0.84 (m, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 157.75, 157.63, 89.22, 83.87, 37.37, 31.90, 30.56, 27.62, 23.03, 22.85, 22.39, 13.84, 7.79.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{15}H_{28}NaO_4^+$): m/z 295.1880; found: 295.1884.

***tert*-Butyl (3,7-dimethyloctan-3-yl) oxalate**



The title compound was prepared according the general procedure using 3,7-dimethyloctan-3-ol (1.58 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 94% yield (2.69 g, 9.4 mmol) as a colorless liquid.

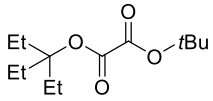
^{1}H NMR (400 MHz, Chloroform-d): δ 2.00 - 1.67 (m, 4H), 1.51 (m, 10H), 1.45 (s, 3H), 1.35 -

1.22 (m, 2H), 1.19 - 1.10 (m, 2H), 0.90 - 0.81 (m, 9H).

^{13}C NMR (100 MHz, Chloroform-d): δ 157.60, 89.91, 84.10, 32.76, 27.72, 26.05, 26.00, 23.83, 22.27, 21.85, 19.27.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{16}H_{30}NaO_4^+$): m/z 309.2036; found: 309.2046.

***tert*-Butyl (3-ethylpentan-3-yl) oxalate**



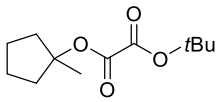
The title compound was prepared according the general procedure using 3-ethylpentan-3-ol (1.16 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 95% yield (2.32 g, 9.5 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 1.88 (q, *J* = 7.5 Hz, 6H), 1.51 (s, 9H), 0.84 (t, *J* = 7.5 Hz, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 157.90, 157.65, 92.47, 83.97, 27.72, 26.66, 7.51.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{13}H_{24}NaO_4^+$): m/z 267.1567; found: 267.1574.

***tert*-Butyl (1-methylcyclopentyl) oxalate**



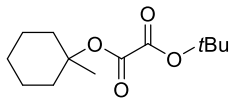
The title compound was prepared according the general procedure using 1-methylcyclopentan-1-ol (1.00 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 93% yield (2.12 g, 9.3 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-d): δ 2.24 - 2.12 (m, 2H), 1.78 - 1.70 (m, 4H), 1.67 - 1.61 (m, 2H), 1.60 (s, 3H), 1.53 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-d): δ 158.00, 157.74, 93.49, 84.21, 38.79, 27.69, 23.66.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{12}H_{20}NaO_4^+$): m/z 251.1254; found: 251.1256.

***tert*-Butyl (1-methylcyclopentyl) oxalate**



The title compound was prepared according the general procedure using 1-methylcyclohexan-1-ol (1.14 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was

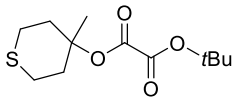
isolated in 90% yield (2.18 g, 9.0 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-d): δ 2.20 (dt, *J* = 15.3, 3.5 Hz, 2H), 1.62 - 1.56 (m, 2H), 1.54 (s, 13H), 1.51 (m, 3H), 1.47 (m, 1H), 1.29 (m, 1H).

^{13}C NMR (100 MHz, Chloroform-d): δ 157.80, 157.67, 85.88, 84.11, 36.27, 27.74, 25.17, 21.92.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{13}H_{22}NaO_4^+$): m/z 265.1410; found: 265.1415.

***tert*-Butyl (4-methyltetrahydro-2H-thiopyran-4-yl) oxalate**



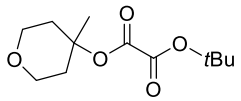
The title compound was prepared according the general procedure using 4-methyltetrahydro-2H-thiopyran-4-ol (1.32 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (2.34 g, 9.0 mmol) as a white solid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 2.89 (t, *J* = 12.0 Hz, 2H), 2.58 (d, *J* = 14.4 Hz, 2H), 2.44 (d, *J* = 14.4 Hz, 2H), 1.78 - 1.73 (m, 2H), 1.56(s, 3H), 1.55 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 157.37, 157.29, 84.54, 83.52, 37.15, 27.75, 25.96, 23.88.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{12}H_{20}NaO_4S^+$): m/z 283.0975; found: 283.0986.

M.P.: 72.3 - 73.4 °C.



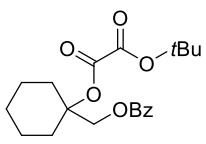
***tert*-Butyl (4-methyltetrahydro-2H-pyran-4-yl) oxalate**

The title compound was prepared according the general procedure using 4-methyltetrahydro-2H-pyran-4-ol (1.16 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 87% yield (2.13 g, 8.7 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 3.74 - 3.67 (m, 4H), 2.19 - 2.18 (m, 2H), 1.77 - 1.75 (m, 2H), 1.62(s, 3H), 1.56 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 157.58, 157.36, 84.51, 84.44, 82.38, 63.55, 36.43, 27.71, 24.82.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{12}H_{20}NaO_5^+$): m/z 267.1203; found: 267.1211.



1-((Benzoyloxy)methyl) cyclohexyl tert-butyl oxalate

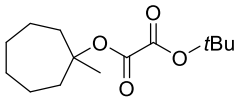
The title compound was prepared according the general procedure using (1-hydroxycyclohexyl) methyl benzoate (2.34 g, 10.0 mmol). After purification

by a flash column chromatography (SiO_2: 3% ethyl acetate in petroleum ether), the title compound was isolated in 73% yield (2.65 g, 7.3 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 4.70 (s, 2H), 2.42 - 2.29 (m, 2H), 1.62 - 1.58 (m, 6H), 1.55 (d, *J* = 1.2 Hz, 2H), 1.54 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 165.99, 157.61, 133.08, 129.68, 128.35, 85.26, 84.39, 66.32, 31.73, 27.72, 25.15, 21.19.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{20}H_{26}NaO_6^+$): m/z 385.1622; found: 385.1631.



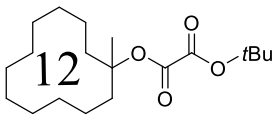
***tert*-Butyl (1-methylcyclopentyl) oxalate**

The title compound was prepared according the general procedure using 1-methylcycloheptan-1-ol (1.28 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (2.31 g, 9.0 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-d): δ 2.21 (dd, *J* = 14.8, 8.5 Hz, 2H), 1.83 - 1.78 (m, 2H), 1.62 - 1.60 (m, 5H), 1.57 (s, 3H), 1.54 (s, 9H), 1.51 - 1.49 (m, 1H), 1.45 - 1.42 (m, 2H).

^{13}C NMR (150 MHz, Chloroform-d): δ 157.93, 157.86, 90.30, 84.08, 39.89, 39.86, 29.28, 29.20, 27.75, 26.56, 22.54.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{14}H_{24}NaO_4^+$): m/z 279.1567; found: 279.1575.



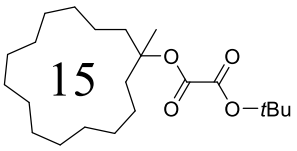
***tert*-Butyl (1-methylcyclododecyl) oxalate**

The title compound was prepared according the general procedure using 1-methylcyclododecan-1-ol (1.98 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 97% yield (3.17 g, 9.7 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-d): δ 2.07 - 1.95 (m, 2H), 1.66 (ddt, *J* = 13.7, 11.7, 4.5 Hz, 2H), 1.53 (d, *J* = 2.1 Hz, 12H), 1.34 (s, 18H).

^{13}C NMR (100 MHz, Chloroform-d): δ 157.60, 89.91, 84.10, 32.76, 27.72, 26.05, 26.00, 23.83, 22.27, 21.85, 19.27.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{19}H_{34}NaO_4^+$): m/z 349.2349; found: 349.2355.



***tert*-Butyl (1-methylcyclopentadecyl) oxalate**

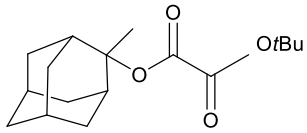
The title compound was prepared according the general procedure using 1-methylcyclopentadecan-1-ol (2.40 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 78% yield (2.87 g, 7.8 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-d): δ 1.98 - 1.93 (m, 2H), 1.74 - 1.69 (m, 2H), 1.55 (s, 3H), 1.54 (s, 9H), 1.37 - 1.34 (m, 12H), 1.31 (m, 12H).

^{13}C NMR (150 MHz, Chloroform-d): δ 157.86, 157.68, 89.68, 84.10, 36.59, 27.77, 27.47, 26.94, 26.68, 26.65, 26.29, 24.23, 23.46, 21.77.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{40}NaO_4^+$): m/z 391.2819; found: 391.2823.

***tert*-Butyl ((1r,3r,5r,7r)-2-methyladamantan-2-yl) oxalate**

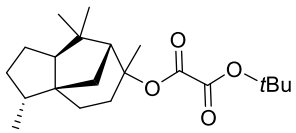


The title compound was prepared according the general procedure using (1r,3r,5r,7r)-2-methyladamantan-2-ol (1.66 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 88% yield (2.59 g, 8.8 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-d): δ 2.34 (s, 2H), 2.06 (d, *J* = 12.7 Hz, 2H), 1.91 - 1.70 (m, 8H), 1.67 (s, 3H), 1.58 (d, *J* = 12.2 Hz, 2H), 1.53 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-d): δ 157.36, 90.96, 84.04, 37.96, 35.96, 34.46, 32.83, 27.73, 27.17, 26.49, 21.93.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{17}H_{26}NaO_4^+$): m/z 317.1723; found: 317.1725.



***tert*-Butyl ((3R,3aR,7R)-3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulen-6-yl) oxalate**

The title compound was prepared according the general procedure using (3R,3aR,7R)-3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulen-6-ol (2.22 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 93% yield (3.26 g, 9.3 mmol) as a white solid.

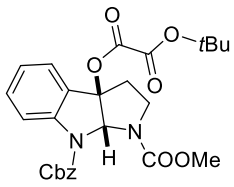
^{1}H NMR (400 MHz, Chloroform-d): δ 2.38 (d, *J* = 5.2 Hz, 1H), 2.17 (dd, *J* = 13.6, 5.7 Hz, 1H),

2.04 (ddd, *J* = 14.2, 12.5, 6.8, 1.1 Hz, 1H), 1.93 - 1.77 (m, 2H), 1.67 (ddt, *J* = 9.0, 6.7, 3.5 Hz, 2H), 1.60 (s, 3H), 1.52 (s, 9H), 1.49 - 1.22 (m, 7H), 1.18 (s, 3H), 0.98 (s, 3H), 0.90 - 0.85 (m, 1H), 0.83 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-d): δ 157.61, 90.33, 83.98, 56.98, 56.65, 53.86, 43.47, 41.21, 41.00, 36.90, 32.73, 31.25, 28.37, 27.72, 26.97, 25.30, 25.24, 15.47.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{21}H_{34}NaO_4^+$): m/z 373.2349; found: 373.2361.

M.P.: 47.2 - 48.3 °C.



8-Benzyl 1-methyl 3a-(2-(tert-butoxy)-2-oxoacetoxy)-2,3,3a,8a-tetrahydropyrrolo[2,3-b] indole-1,8-dicarboxylate

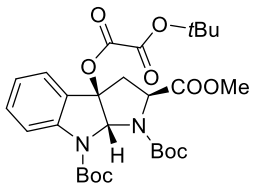
The title compound was prepared according the general procedure using 8-benzyl 1-methyl 3a-hydroxy-2,3,3a,8a-tetrahydropyrrolo[2,3-b] indole-1,8-dicarboxylate [12] (3.68 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 79% yield (3.92 g, 7.9 mmol) as a white solid.

^{1}H NMR (600 MHz, Chloroform-d): δ 7.79 (bs, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 3H), 7.35 - 7.32 (m, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.53 (s, 1H), 5.30 (s, 2H), 4.03 (t, *J* = 8.0 Hz, 1H), 3.52 (bs, 3H), 2.91 (td, *J* = 12.0, 5.4 Hz, 1H), 2.75 (dd, *J* = 12.0, 5.4 Hz, 1H), 2.53 (dt, *J* = 12.0, 8.4 Hz, 1H), 1.52 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-d): δ 156.90, 156.08, 153.08, 144.07, 135.88, 131.42, 128.52, 128.38, 128.24, 127.02, 125.14, 124.03, 116.52, 85.38, 79.78, 67.87, 52.69, 45.08, 27.64.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{26}H_{29}N_2O_8^+$): m/z 497.1918; found: 497.1923.

M.P.: 74.3 - 75.1 °C



1,8-Di-tert-butyl 2-methyl 3a-(2-(tert-butoxy)-2-oxoacetoxy)-2,3,3a,8a-tetrahydropyrrolo [2,3-b] indole-1,2,8-tricarboxylate

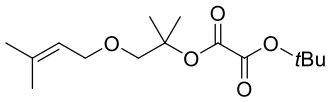
The title compound was prepared according the general procedure using 1,8-di-tert-butyl 2-methyl 3a-hydroxy-2,3,3a,8a-tetrahydro pyrrolo[2,3-b] indole-1,2,8-tricarboxylate [13] (4.34 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 80% yield (4.50 g, 8.0 mmol) as a white solid.

^{1}H NMR (600 MHz, Chloroform-d): δ 7.61 (d, *J* = 6.6 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.40 (s, 1H), 3.97 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.74 (s, 3H), 3.34 (bs, 1H), 2.58 (t, *J* = 11.4 Hz, 1H), 1.58 (s, 9H), 1.49 (s, 9H), 1.41 (bs, 9H).

^{13}C NMR (150 MHz, Chloroform-d): δ 171.84, 156.59, 155.94, 152.21, 144.44, 131.45, 126.09, 123.89, 89.41, 85.19, 82.07, 79.94, 58.90, 52.33, 36.64, 28.23, 27.61.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{28}H_{39}N_2O_{10}^+$): m/z 563.2599; found: 563.2597.

M.P.: 125.3 - 126.2 °C.



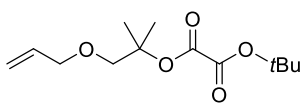
***tert*-Butyl (2-methyl-1-((3-methylbut-2-en-1-yl) oxy) propan-2-yl) oxalate**

The title compound was prepared according the general procedure using 2-methyl-1-((3-methylbut-2-en-1-yl) oxy) propan-2-ol (1.58 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 94% yield (2.69 g, 9.4 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-d): δ 5.33 (t, *J* = 6.8 Hz, 1H), 4.03 (d, *J* = 6.9 Hz, 2H), 3.57 (s, 2H), 1.74 (s, 3H), 1.66 (s, 3H), 1.53 (s, 15H).

^{13}C NMR (100 MHz, Chloroform-d): δ 157.59, 157.39, 137.24, 120.96, 85.26, 84.29, 74.91, 67.98, 27.70, 25.78, 22.95, 18.04.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{15}H_{26}NaO_5^+$): m/z 309.1672; found: 309.1672.



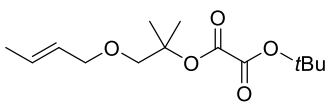
1-(Allyloxy)-2-methylpropan-2-yl *tert*-butyl oxalate

The title compound was prepared according the general procedure using 1-(allyloxy)-2-methylpropan-2-ol (1.30 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 89% yield (2.30 g, 8.9 mmol) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-d): δ 2.00 - 1.67 (m, 4H), 1.51 (m, 10H), 1.45 (s, 3H), 1.35 - 1.22 (m, 2H), 1.19 - 1.10 (m, 2H), 0.90 - 0.81 (m, 9H).

^{13}C NMR (100 MHz, Chloroform-d): δ 157.60, 89.91, 84.10, 32.76, 27.72, 26.05, 26.00, 23.83, 22.27, 21.85, 19.27.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{13}H_{22}NaO_5^+$): m/z 281.1359; found: 281.1367.



(*E*)-1-(but-2-en-1-yloxy)-2-methylpropan-2-yl *tert*-butyl oxalate The title compound was prepared according the general procedure using (*E*)-1-(but-2-en-1-yloxy)-2-methylpropan-2-ol (1.44 g, 10.0 mmol). After purification by a flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether), the title compound was isolated in 78% yield (2.12 g, 7.8 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, Chloroform-d): δ 5.72 - 5.67 (m, 1H), 5.57 - 5.52 (m, 1H), 3.96 (d, *J* = 6.2 Hz, 2H), 3.56 (s, 2H), 1.70 (d, *J* = 6.5 Hz, 3H), 1.52 (d, *J* = 1.6 Hz, 15H).

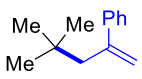
^{13}C NMR (150 MHz, Chloroform-d): δ 157.57, 157.39, 129.44, 127.45, 85.16, 84.24, 74.80, 72.24, 27.70, 22.95, 17.71.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{14}H_{24}NaO_5^+$): m/z 295.1516; found: 295.1524.

Part 6. Allylation of Tertiary Alkyl Oxalates with Allylic Electrophiles.

***Method A*:** To a flame-dried Schlenk tube equipped with a stir bar was loaded zinc power (29.4 mg, 0.45 mmol, 300 mol %), followed by addition of $MgCl_2$ (42.9 mg, 0.45 mmol, 300 mol %), dtbbipy **L1a** (7.9 mg, 0.03 mmol, 20 mol %) and Fe (acac)$_3$ (5.3 mg, 0.015 mmol, 10 mol%). The tube was evacuated and refilled nitrogen (N_2) three time. DMA (1.0 mL) was added via a syringe, followed by addition of *tertiary* alkyl oxalate (0.15 mmol, 100 mol %), and allylic carbonate (0.3 mmol, 200 mol %). After the reaction mixture was allowed to stir for 12 hours under a N_2 atmosphere at 45 °C. The reaction was loaded onto a silica column. Flash column chromatography provided the product as an oil or a solid.

(4,4-Dimethylpent-1-en-2-yl) benzene (3a).



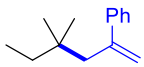
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 84% yield (21.9 mg, 0.126 mmol) as colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.34 (t, *J* = 7.0 Hz, 2H), 7..27 (t, *J* = 7.0 Hz, 1H), 5.29 (d, *J* = 2.0 Hz, 1H), 5.06 (d, *J* = 2.0 Hz, 1H), 2.51 (s, 2H), 0.85 (s, 9H).

^{13}C NMR (125 MHz, Chloroform-*d*): δ 147.58, 143.70, 128.08, 126.91, 126.53, 116.27, 48.91, 31.72, 30.06.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{13}H_{18}Na^+$): m/z 197.1301; found: 197.1309.

(4,4-Dimethylhex-1-en-2-yl) benzene (4)



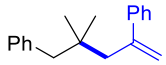
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 71% yield (20.1 mg, 0.107 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.37 (d, *J* = 6.9 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.23 (d, *J* = 2.1 Hz, 1H), 5.02 (dd, *J* = 2.0, 1.0 Hz, 1H), 2.46 (s, 2H), 1.18 (q, *J* = 7.5 Hz, 2H), 0.78 (t, *J* = 7.5 Hz, 3H), 0.72 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.54, 143.99, 128.04, 126.86, 126.55, 116.45, 46.70, 34.86, 34.25, 26.91, 8.45.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{14}H_{20}Na^+$): m/z 211.1457; found: 211.1455.

(2,2-dimethylpent-4-ene-1,4-diyl) dibenzene (5a)



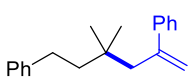
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 85% yield (31.9 mg, 0.128 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.34 - 7.29 (m, 3H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 6.8 Hz, 2H), 5.36 (d, *J* = 2.0 Hz, 1H), 5.13 - 5.10 (m, 1H), 2.63 (s, 2H), 2.56 (s, 2H), 0.80 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.10, 143.75, 139.16, 130.67, 128.15, 127.57, 126.98, 126.50, 125.75, 116.92, 49.63, 48.01, 35.43, 26.84.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{19}H_{22}Na^+$): m/z 273.1614; found: 273.1619.

(3,3-Dimethylhex-5-ene-1,5-diyl) dibenzene (6)



According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate

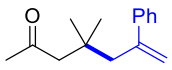
in petroleum ether) provided this compound in 56% yield (22.2 mg, 0.084 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.43 (d, *J* = 7.0 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 - 7.25 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.0 Hz, 2H), 5.29 (d, *J* = 2.0 Hz, 1H), 5.14 - 5.08 (m, 1H), 2.59 (s, 2H), 2.58 - 2.53 (m, 2H), 1.52 - 1.47 (m, 2H), 0.88 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.32, 143.93, 143.32, 128.25, 128.21, 128.17, 126.98, 126.63, 125.45, 116.86, 46.67, 44.62, 34.40, 30.74, 27.74.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{20}H_{24}Na^+$): m/z 287.1770; found: 287.1777.

4,4-Dimethyl-6-phenylhept-6-en-2-one (7)



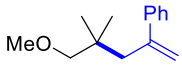
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 80% yield (26.0 mg, 0.12 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.34 (d, *J* = 6.9 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.24 (d, *J* = 2.1 Hz, 1H), 5.05 - 5.00 (m, 1H), 2.66 (s, 2H), 2.20 (s, 2H), 1.87 (s, 3H), 0.91 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 208.67, 147.09, 143.41, 128.25, 127.12, 126.64, 117.23, 53.36, 46.14, 34.14, 31.83, 28.22.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{15}H_{20}NaO^+$): m/z 239.1406; found: 239.1411.

(5-Methoxy-4,4-dimethylpent-1-en-2-yl) benzene (8)



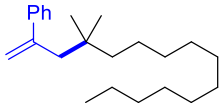
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 56% yield (17.2 mg, 0.084 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.39 (d, *J* = 6.9 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.26 (d, *J* = 2.1 Hz, 1H), 5.06 - 5.02 (m, 1H), 3.10 (s, 3H), 2.87 (s, 2H), 2.54 (d, *J* = 0.9 Hz, 2H), 0.79 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 146.97, 143.43, 128.01, 126.95, 126.53, 116.64, 80.99, 58.69, 43.65, 35.56, 25.28.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{14}H_{20}NaO^+$): m/z 227.1406; found: 227.1411.

(4,4-Dimethylpentadec-1-en-2-yl) benzene (9)



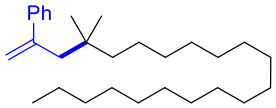
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 67% yield (31.6 mg, 0.1005 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.37 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.23 (d, *J* = 2.1 Hz, 1H), 5.02 (d, *J* = 2.1 Hz, 1H), 2.47 (s, 2H), 1.28 (d, *J* = 5.5 Hz, 14H), 1.14 - 1.08 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 5H), 0.74 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 128.03, 126.84, 126.57, 116.44, 46.87, 46.13, 42.61, 34.19, 32.41, 31.94, 31.93, 30.48, 29.75, 29.70, 29.66, 29.63, 29.61, 29.56, 29.38, 29.36, 27.64, 25.14, 24.10, 22.71, 14.12.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{23}H_{38}Na^+$): m/z 337.2866; found: 337.2871.

(4,4-Dimethylhenicos-1-en-2-yl) benzene (10)



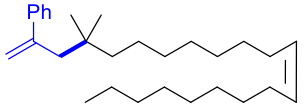
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 56% yield (33.5 mg, 0.084 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.37 (d, *J* = 7.1 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.23 (d, *J* = 2.1 Hz, 1H), 5.02 (d, *J* = 2.0 Hz, 1H), 2.46 (s, 2H), 1.28 (s, 30H), 0.90 (t, *J* = 6.9 Hz, 5H), 0.74 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ147.61, 128.03, 126.85, 126.57, 116.44, 46.87, 42.62, 34.19, 32.41, 31.94, 30.48, 29.73, 29.70, 29.68, 29.38, 27.64, 25.14, 24.11, 22.71, 14.12.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{29}H_{50}Na^+$): m/z 421.3805; found: 421.3808.

(Z)-(4,4-Dimethylhenicosa-1,12-dien-2-yl) benzene (11)



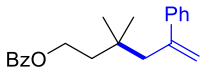
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 61% yield (36.3 mg, 0.0915 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.37 (d, *J* = 6.8 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.38 - 5.36 (m, 2H), 5.23 (d, *J* = 2.1 Hz, 1H), 5.02 (d, *J* = 2.0 Hz, 1H), 2.47 (s, 2H), 2.03 (t, J = 6.7 Hz, 4H), 1.33 - 1.29 (m, 18H), 1.11 (dt, *J* = 11.5, 3.7 Hz, 4H), 0.90 (t, *J* = 6.9 Hz, 5H), 0.74 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 129.89, 128.03, 126.85, 126.57, 116.44, 46.87, 46.12, 42.60, 34.18, 32.40, 31.92, 30.44, 29.78, 29.57, 29.54, 29.44, 29.34, 29.23, 27.64, 27.23, 27.21, 24.09, 22.69, 14.11.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{29}H_{48}Na^+$): m/z 419.3648; found: 419.3654.

3,3-Dimethyl-5-phenylhex-5-en-1-yl benzoate (12a)



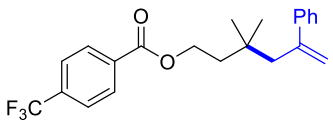
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 78% yield (36.1 mg, 0.117 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.08 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 - 7.39 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 5.33 (d, *J* = 2.0 Hz, 1H), 5.12 (d, *J* = 1.9 Hz, 1H), 4.39 (t, *J* = 7.3 Hz, 2H), 2.61 (s, 2H), 1.73 (t, *J* = 7.3 Hz, 2H), 0.91 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 166.43, 146.66, 143.42, 132.63, 130.34, 129.37, 128.16, 128.08, 126.97, 126.38, 117.01, 62.13, 47.34, 40.19, 33.55, 27.59.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{21}H_{24}NaO_2^+$): m/z 331.1669; found: 331.1677.

3,3-Dimethyl-5-phenylhex-5-en-1-yl 4-(trifluoromethyl) benzoate (13)



According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 71% yield (40.1 mg, 0.107 mmol) as colorless oil.

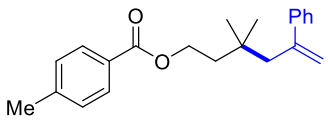
^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.74 - 7.67 (m, 2H), 7.38 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.29 (d, *J* = 1.9 Hz, 1H), 5.10 - 5.05 (m, 1H), 4.36 (t, *J* = 7.3 Hz, 2H), 2.57 (d, *J* = 0.8 Hz, 2H), 1.68 (t, *J* = 7.3 Hz, 2H), 0.87 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*): δ 165.40, 146.71, 143.51, 133.62, 129.89, 128.22, 127.12, 126.50, 125.35 (q, J = 3.6 Hz), 117.24, 62.89, 47.48, 40.11, 33.68, 27.69.

^{19}F NMR (376 MHz, Chloroform-d): δ -62.95.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{23}FNaO_2^+$): m/z 399.1542; found: 399.1548.

3,3-Dimethyl-5-phenylhex-5-en-1-yl 4-methylbenzoate (14)



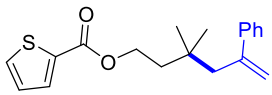
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 70% yield (33.9 mg, 0.105 mmol) as colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 7.1 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.26 - 7.21 (m, 3H), 5.28 (d, *J* = 1.9 Hz, 1H), 5.09 - 5.06 (m, 1H), 4.33 (t, *J* = 7.3 Hz, 2H), 2.57 (s, 2H), 2.41 (s, 4H), 1.68 (t, *J* = 3.7 Hz, 2H), 0.86 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*): δ 166.71, 146.80, 143.56, 143.39, 129.51, 129.00, 128.18, 127.69, 127.05, 126.49, 117.12, 62.08, 47.46, 40.31, 33.67, 27.67, 21.61.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{26}NaO_2^+$): m/z 345.1825; found: 345.1827.

3,3-Dimethyl-5-phenylhex-5-en-1-yl thiophene-2-carboxylate (15)



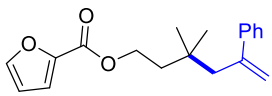
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 62% yield (29.2 mg, 0.093 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.77 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.54 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.37 (d, *J* = 6.9 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 5.28 (d, *J* = 1.9 Hz, 1H), 5.10 - 5.05 (m, 1H), 4.31 (t, *J* = 7.2 Hz, 2H), 2.56 (s, 2H), 1.65 (t, *J* = 7.2 Hz, 2H), 0.85 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-d): δ 162.26, 146.79, 143.57, 134.09, 133.20, 132.15, 128.19, 127.66, 127.07, 126.51, 117.15, 62.48, 47.48, 40.29, 33.69, 27.66.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{19}H_{22}NaO_2S^+$): m/z 337.1233; found: 337.1237.

3,3-Dimethyl-5-phenylhex-5-en-1-yl furan-2-carboxylate (16)



According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 71% yield (31.8

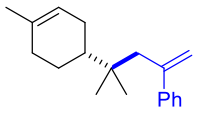
mg, 0.1065 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.57 (s, 1H), 7.37 (d, *J* = 7.0 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.25 - 7.20 (m, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 6.53 - 6.45 (m, 1H), 5.27 (d, *J* = 1.9 Hz, 1H), 5.07 (d, *J* = 1.9 Hz, 1H), 4.32 (t, *J* = 7.4 Hz, 2H), 2.55 (s, 2H), 1.65 (t, *J* = 7.4 Hz, 2H), 0.83 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 158.77, 146.75, 146.17, 144.89, 143.55, 128.20, 127.07, 126.50, 117.64, 117.18, 111.74, 62.31, 47.46, 40.23, 33.66, 27.64.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{19}H_{22}NaO_3^+$): m/z 321.1461; found: 321.1463.

(R)-(4-Methyl-4-(4-methylcyclohex-3-en-1-yl) pent-1-en-2-yl) benzene (17)



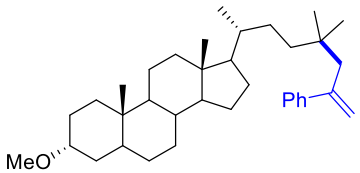
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 79% yield (30.1 mg, 0.119 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 5.37 (d, *J* = 3.6 Hz, 1H), 5.25 (d, *J* = 1.8 Hz, 1H), 5.06 - 5.02 (m, 1H), 2.60 - 2.47 (m, 2H), 2.00 - 1.93 (m, 1H), 1.92 - 1.85 (m, 1H), 1.81 - 1.79 (m, 2H), 1.64 (s, 3H), 1.35 - 1.27 (m, 2H), 1.22 - 1.15 (m, 1H), 0.71 (d, *J* = 4.8 Hz, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.54, 144.14, 133.94, 128.07, 126.85, 126.55, 121.23, 116.79, 44.61, 42.62, 36.19, 31.33, 26.59, 25.24, 24.37, 24.16, 23.32.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{19}H_{26}Na^+$): m/z 277.1927; found: 277.1936.

(3R,10S,13R)-17-((R)-5,5-Dimethyl-7-phenyloct-7-en-2-yl)-3-methoxy-10,13-dimethyl hexadecahydro-1H-cyclopenta[a]phenanthrene (18)



According to *method A*, flash column chromatography (SiO_2: 4% ethyl acetate in petroleum ether) provided this compound in 55% yield (41.6 mg, 0.0825 mmol) as foam solid.

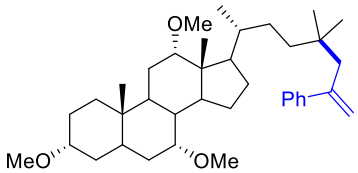
^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.35 (d, *J* = 7.2 Hz, 2H), 2.28 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 5.22 (s, 1H), 5.02 (s, 1H), 3.35 (s, 3H), 3.18 - 3.14 (m, 1H), 2.45 (dd, *J* = 28.2, 13.2 Hz, 2H), 1.93 (d, *J* = 11.4 Hz, 1H), 1.88 - 1.82 (m, 2H), 1.80 - 1.75 (m, 2H), 1.71 (s, 2H), 1.55 (d,

J = 5.4 Hz, 2H), 1.42 - 1.31 (m, 6H), 1.29 - 1.18 (m, 4H), 1.13 - 1.08 (m, 3H), 1.06 - 1.01 (m, 3H), 0.92 (s, 6H), 0.80 (d, *J* = 6.6 Hz, 3H), 0.71 (d, *J* = 2.4 Hz, 5H), 0.65 (s, 1H), 0.61 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.55, 144.00, 128.00, 126.78, 126.52, 116.41, 80.38, 56.41, 55.97, 55.46, 46.99, 42.58, 42.02, 40.30, 40.12, 38.73, 36.16, 35.81, 35.27, 34.84, 34.06, 32.73, 29.70, 28.16, 27.53, 27.50, 27.31, 26.74, 26.38, 24.18, 23.39, 20.76, 18.59, 11.97.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{36}H_{56}NaO^+$): m/z 527.4223; found: 527.4240.

(3R,7R,10S,12S,13R)-17-((R)-5,5-Dimethyl-7-phenyloct-7-en-2-yl)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene (19)



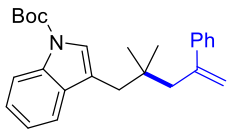
According to *method A*, flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether) provided this compound in 47% yield (39.8 mg, 0.0705 mmol) as foam solid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.35 (s, 2H), 7.28 (s, 2H), 7.22 (s, 1H), 5.21 (s, 1H), 5.01 (s, 1H), 3.37 (s, 1H), 3.33 (s, 3H), 3.25 (s, 3H), 3.21 (s, 3H), 3.14 (s, 1H), 2.99 (s, 1H), 2.44 (dd, *J* = 27.6, 12.6 Hz, 2H), 2.20 (dd, J = 23.4, 11.4 Hz, 1H), 2.09 - 2.04 (m,3H), 1.84 - 1.67 (m, 9H), 1.59 (d, *J* = 10.8 Hz, 2H), 1.51 - 1.45 (m, 3H), 1.34 - 1.14 (m, 10H), 0.98 (m, 4H), 0.89 (s, 6H), 0.80 (s, 3H), 0.71 (s, 5H), 0.62 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.58, 143.99, 127.98, 126.76, 126.52, 116.37, 81.99, 80.69, 76.95, 55.77, 55.64, 55.31, 46.88, 46.32, 45.94, 42.56, 41.92, 39.59, 38.67, 35.94, 35.22, 34.85, 34.38, 34.07.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{38}H_{60}NaO_3^+$): m/z 587.4435; found: 587.4440.

***Tert*-butyl 3-(2,2-dimethyl-4-phenylpent-4-en-1-yl)-1H-indole-1-carboxylate (20)**



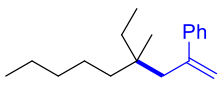
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 70% yield (40.9 mg, 0.105 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.14 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.34 - 7.30 (m, 3H), 7.27 - 7.22 (m, 3H), 5.32 (d, *J* = 1.8 Hz, 1H), 5.09 (d, *J* = 1.8 Hz, 1H), 2.65 (s, 2H), 2.59 (s, 2H), 1.70 (s, 9H), 0.82 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.16, 143.70, 128.17, 127.01, 126.52, 124.34, 123.85, 122.17, 119.73, 117.98, 116.97, 114.98, 47.98, 37.97, 35.64, 28.22, 27.30.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{26}H_{32}NO_2^+$): m/z 390.2428; found: 390.2437.

(4-Ethyl-4-methylnon-1-en-2-yl) benzene (21)



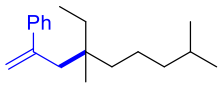
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 78% yield (28.6 mg, 0.117 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.36 (d, *J* = 6.9 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.20 (d, *J* = 2.1 Hz, 1H), 5.03 - 5.01 (m, 1H), 2.45 (s, 2H), 1.22 (p, *J* = 7.5 Hz, 2H), 1.19 - 1.10 (m, 4H), 1.09 - 1.03 (m, 4H), 0.85 (t, *J* = 7.4 Hz, 3H), 0.73 (t, *J* = 7.5 Hz, 3H), 0.65 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.67, 144.31, 127.99, 126.79, 126.60, 116.62, 44.38, 38.61, 36.63, 32.67, 31.60, 24.99, 23.23, 22.69, 14.11, 8.04.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{18}H_{28}Na^+$): m/z 267.2083; found: 267.2091.

(4-Ethyl-4,8-dimethylnon-1-en-2-yl) benzene (22)



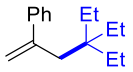
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 67% yield (30.0 mg, 0.1005 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.20 (d, *J* = 1.8 Hz, 1H), 5.02 (m, 1H), 2.45 (s, 2H), 1.49 - 1.42 (m, 1H), 1.22 - 1.16 (m, 2H), 1.15 - 1.09 (m, 2H), 1.07 - 1.03 (m, 2H), 0.98 - 0.92 (m, 2H), 0.83 (dd, *J* = 6.6, 1.2 Hz, 6H), 0.74 (t, *J* = 7.2 Hz, 3H), 0.66 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.67, 144.32, 128.01, 126.79, 126.59, 116.64, 44.38, 39.78, 38.84, 36.68, 31.67, 27.97, 25.00, 22.69, 22.64, 21.29, 8.06.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{19}H_{30}Na^+$): m/z 281.2240; found: 281.2249.

(4,4-Diethylhex-1-en-2-yl) benzene (23)



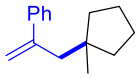
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 61% yield (19.8 mg, 0.092 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.34 (d, *J* = 6.9 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.17 (d, *J* = 2.1 Hz, 1H), 5.08 - 5.03 (m, 1H), 2.40 (d, *J* = 0.9 Hz, 2H), 1.12 (q, *J* = 7.5 Hz, 6H), 0.66 (t, *J* = 7.5 Hz, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.88, 144.65, 127.91, 126.73, 126.66, 116.80, 40.07, 39.32, 27.58, 7.54.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{16}H_{25}^+$): m/z 217.1951; found: 217.1949.

(3-(1-Methylcyclopentyl) prop-1-en-2-yl) benzene (24)



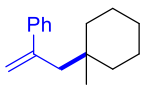
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 76% yield (22.8 mg, 0.114 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 5.21 (d, *J* = 1.8 Hz, 1H), 5.05 (m, 1H), 2.58 (s, 2H), 1.57 - 1.55 (m, 4H), 1.38 - 1.32 (m, 2H), 1.19 - 1.15 (m, 2H), 0.82 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 148.12, 143.76, 128.03, 126.92, 126.63, 115.92, 46.97, 43.05, 39.46, 26.08, 23.84.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{15}H_{20}Na^+$): m/z 223.1457; found: 223.1459.

(3-(1-Methylcyclohexyl) prop-1-en-2-yl) benzene (25)



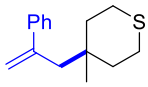
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 79% yield (25.4 mg, 0.119 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 5.23 (d, *J* = 1.8 Hz, 1H), 5.04 - 5.01 (m, 1H), 2.50 (s, 2H), 1.41 (qd, *J* = 8.7, 6.8, 4.2 Hz, 3H), 1.35 (qt, *J* = 10.3, 4.8 Hz, 2H), 1.26 - 1.12 (m, 5H), 0.74 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.19, 144.18, 128.03, 126.84, 126.55, 116.55, 38.22, 34.16, 26.37, 22.12.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{16}H_{22}Na^+$): m/z 237.1614; found: 237.1621.

4-Methyl-4-(2-phenylallyl) tetrahydro-2H-thiopyran (26)



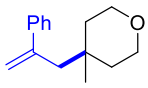
According to *method A*, flash column chromatography (SiO_2: 3% ethyl acetate in petroleum ether) provided this compound in 70% yield (24.4 mg, 0.105 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 5.26 (d, *J* = 2.0 Hz, 1H), 5.04 (m, 1H), 2.62 - 2.58 (m, 2H), 2.51 (s, 2H), 2.49 - 2.45 (m, 2H), 1.59 - 1.55 (m, 2H), 1.52 - 1.48 (m, 2H), 0.77 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 146.08, 143.73, 128.17, 127.06, 126.44, 117.33, 47.53, 38.60, 33.17, 24.41, 23.86.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{15}H_{21}S^+$): m/z 233.1358; found: 233.1368.

4-Methyl-4-(2-phenylallyl) tetrahydro-2H-pyran (27)



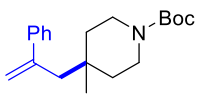
According to *method A*, flash column chromatography (SiO_2: 3% ethyl acetate in petroleum ether) provided this compound in 61% yield (19.8 mg, 0.0915 mmol) as colorless oil.

^{1}H NMR (500 MHz, Chloroform-d) δ 7.37 (d, *J* = 6.9 Hz, 2H), 7.30 (d, *J* = 14.8 Hz, 2H), 7.27 - 7.23 (m, 1H), 5.27 (d, *J* = 2.0 Hz, 1H), 5.07 - 5.03 (m, 1H), 3.65 (dt, *J* = 11.8, 4.6 Hz, 2H), 3.53 (ddd, *J* = 12.0, 9.5, 3.0 Hz, 2H), 2.56 (s, 2H), 1.46 (ddd, *J* = 13.8, 9.5, 4.3 Hz, 2H), 1.21 - 1.14 (m, 2H), 0.86 (s, 3H).

^{13}C NMR (125 MHz, Chloroform-d) δ 146.25, 143.65, 128.17, 127.09, 117.14, 63.91, 37.95, 31.90.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{15}H_{20}NaO^+$): m/z 239.1406; found: 239.1411.

***Tert*-butyl 4-methyl-4-(2-phenylallyl) piperidine-1-carboxylate (28)**



According to *method A*, flash column chromatography (SiO_2: 4% ethyl acetate in petroleum ether) provided this compound in 78% yield (36.9 mg, 0.117 mmol)

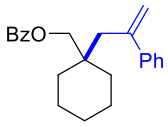
as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.35 (d, *J* = 6.9 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 5.25 (d, *J* = 1.9 Hz, 1H), 5.05 - 5.02 (m, 1H), 3.53 (s, 2H), 3.07 (ddd, *J* = 13.5, 9.8, 3.6 Hz, 2H), 2.57 - 2.47 (m, 2H), 1.43 (s, 9H), 1.35 - 1.29 (m, 2H), 1.17 (d, *J* = 13.2 Hz, 2H), 0.80 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 146.27, 143.59, 128.18, 127.09, 126.44, 117.18, 79.09, 47.24, 32.67, 28.41, 23.55.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{20}H_{29}NNaO_2^+$): m/z 338.2091; found: 338.2096.

(1-(2-Phenylallyl) cyclohexyl) methyl benzoate (29)



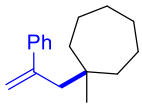
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 63% yield (31.6 mg, 0.0945 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.37 - 7.35 (m, 2H), 7.20 - 7.17 (m, 3H), 5.26 (d, *J* = 1.8 Hz, 1H), 5.09 (d, *J* = 1.8 Hz, 1H), 3.99 (s, 2H), 2.75 (s, 2H), 1.48 - 1.35 (m, 10H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 166.23, 146.18, 143.31, 132.72, 130.54, 129.45, 128.29, 128.09, 127.11, 126.42, 117.41, 37.38, 33.27, 26.05, 21.48.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{23}H_{26}NaO_2^+$): m/z 357.1825; found: 357.1841.

1-Methyl-1-(2-phenylallyl) cycloheptane (30)



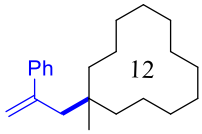
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 92% yield (31.5 mg, 0.138 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.360 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 5.25 (d, *J* = 2.4 Hz, 1H), 5.03 (m, 1H), 2.48 (s, 2H), 1.48 - 1.45 (m, 5H), 1.42 - 1.38 (m, 5H), 1.35 - 1.32 (m, 4H), 1.25 - 1.20 (m, 2H), 0.70 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.45, 144.07, 128.04, 126.83, 126.53, 116.74, 47.75, 40.58, 37.32, 30.92, 28.19, 22.85.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{17}H_{24}Na^+$): m/z 251.1770; found: 251.1777.

1-Methyl-1-(2-phenylallyl) cyclododecane (31)



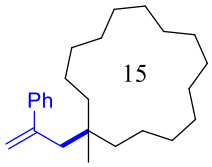
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 52% yield (23.3 mg, 0.078 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.22 (d, *J* = 1.8 Hz, 1H), 5.04 (m, 1H), 2.44 (s, 2H), 1.37 - 1.16 (m, 22H), 0.59 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.51, 144.37, 127.98, 126.80, 126.57, 116.62, 45.92, 36.94, 34.86, 26.99, 26.21, 26.10, 22.89, 22.43, 19.27.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{34}Na^+$): m/z 321.2553; found: 321.2556.

1-Methyl-1-(2-phenylallyl) cyclopentadecanone (32)



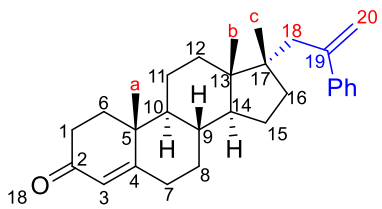
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 61% yield (31.2 mg, 0.0915 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 5.23 (d, *J* = 1.8 Hz, 1H), 5.03 (m, 1H), 2.46 (s, 2H), 1.37 - 1.29 (m, 18H), 1.23 - 1.18 (m, 4H), 1.17 - 1.13 (m, 6H), 0.67 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 147.49, 144.26, 127.97, 126.79, 126.58, 116.59, 46.05, 38.29, 36.68, 27.95, 26.96, 26.85, 26.68, 26.24, 25.93, 21.64.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{25}H_{40}Na^+$): m/z 363.3022; found: 363.3028.

(10R,13S,17R)-10,13,17-Trimethyl-17-(2-phenylallyl)-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (33)



According to *method A*, flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether) provided this compound in 37% yield (22.3 mg, 0.0555 mmol) as colorless oil.

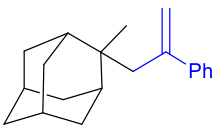
The stereochemistry was assigned based on the weak correlation of Me^a and Me^b, Me^c and H18, Ph and Me^c, and no correlation was detected between H18 and Me^b in the NOSEY spectra.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.35 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.74 (s, 1H), 5.31 (d, *J* = 1.8 Hz, 1H), 5.01 (d, *J* = 1.8 Hz, 1H), 2.57 (d, *J* = 13.2 Hz, 2H, H18), 2.46 - 2.39 (m, 2H), 2.35 (d, *J* = 13.2 Hz, 2H, H18`), 2.30 - 2.26 (m, 1H), 2.06 - 2.03 (m, 1H), 1.86 - 1.83 (m, 1H), 1.75 - 1.69 (m, 2H), 1.65 - 1.58 (m, 4H), 1.53 - 1.47 (m, 2H), 1.45 (d, *J* = 3.0 Hz, 2H), 1.20 (s, 3H), 1.12 - 1.07 (m, 3H), 0.77 (s, 3H), 0.75 (s, 3H, Me^b).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 199.59, 171.57, 128.20, 126.93, 126.27, 123.78, 117.47, 53.98, 50.13, 46.65, 45.71, 40.99, 38.71, 36.48, 35.77, 33.99, 32.99, 32.42, 31.64, 30.88, 24.58, 21.69, 20.76, 17.40, 15.96.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{29}H_{38}NaO^+$): m/z 425.2815; found: 425.2816.

(1R,3S,5r,7r)-2-Methyl-2-(2-phenylallyl) adamantane (34)



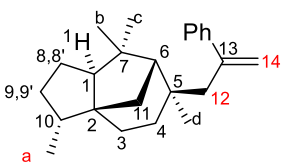
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 63% yield (25.2 mg, 0.0945 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.37 (d, *J* = 7.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 5.19 (d, *J* = 2.1 Hz, 1H), 5.08 - 5.04 (m, 1H), 2.77 (s, 2H), 2.17 (d, *J* = 12.7 Hz, 2H), 2.03 (d, *J* = 12.8 Hz, 2H), 1.82 (d, *J* = 42.7 Hz, 2H), 1.66 (s, 2H), 1.49 (d, *J* = 12.6 Hz, 4H), 1.36 (s, 2H), 0.89 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 148.30, 144.70, 127.94, 126.74, 126.65, 116.62, 43.73, 39.79, 38.95, 36.02, 33.39, 33.10, 28.04, 27.85, 24.05.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{20}H_{26}Na^+$): m/z 289.1927; found: 289.1932.

(3R,3aR,6R,7S)-3,6,8,8-Tetramethyl-6-(2-phenylallyl) octahydro-1H-3a,7-methanoazulene (35)



According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 65% yield (31.4 mg, 0.0975 mmol) as colorless oil.

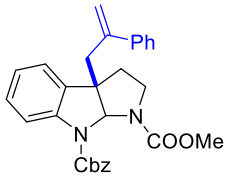
The stereochemistry is assigned based on the correlation between Me^d with Me^c, H12 with H11 and H12 with H6 in the NOESY spectra.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 2H), 5.19 (d, *J* = 1.8 Hz, 1H), 5.04 (d, *J* = 2.4 Hz, 1H), 2.63 (q, *J* = 13.2 Hz, 2H, H12), 1.89 - 1.84 (m, 1H), 1.73 - 1.68 (m, 2H, H6, H11), 1.65 (q, *J* = 6.6 Hz, 1H, H10), 1.53 - 1.47 (m, 2H), 1.46 - 1.43 (m, 2H), 1.41 - 1.40 (m, 1H), 1.39 - 1.37 (m, 2H), 1.28 - 1.27 (m, 1H), 1.26 - 1.25 (m, 1H), 1.16 (s, 3H, Me^c), 0.96 (s, 3H), 0.87 (s, 3H, Me^d), 0.85 (d, *J* = 7.2 Hz, 3H, Me^a).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 148.21, 144.68, 127.98, 126.73, 126.72, 116.99, 58.86, 57.29, 53.56, 46.07, 44.58, 41.82, 40.38, 39.10, 36.77, 32.75, 30.55, 29.85, 29.51, 27.59, 25.29, 15.54.

HRMS (ESI) exact mass calculated for [M+Na^+] ($C_{24}H_{34}Na^+$): m/z 345.2553; found: 345.2555.

8-Benzyl 1-methyl (3aS)-3a-(2-phenylallyl)-2,3,3a,8a-tetrahydropyrrolo[2,3-b] indole-1,8-dicarboxylate (36)



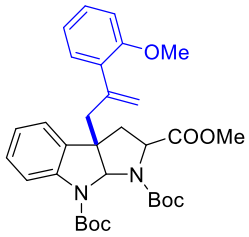
According to *method A*, flash column chromatography (SiO_2: 3% ethyl acetate in petroleum ether) provided this compound in 43% yield (30.2 mg, 0.0645 mmol) as a white foam solid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.62 (bs, 1H), 7.43 (s, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.17 - 7.13 (m, 6H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.02 (s, 1H), 5.24 (s, 2H), 5.15 (s, 1H), 4.93 (s, 1H), 3.70 (s, 1H), 3.47 (s, 3H), 3.02 (d, *J* = 13.8 Hz, 1H), 2.87 (d, *J* = 13.8 Hz, 1H), 2.83 - 2.78 (m, 1H), 1.96 - 1.93 (m, 2H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 154.98, 153.12, 152.89, 144.63, 141.95, 141.43, 136.16, 134.04, 128.38, 128.31, 128.24, 128.11, 128.05, 127.42, 127.28, 126.15, 126.10, 123.27, 117.88, 116.42, 67.35, 52.20, 45.80, 43.18, 43.05.

HRMS (ESI) exact mass calculated for [M+H^+] ($C_{29}H_{29}N_2O_4^+$): m/z 469.2122; found: 469.2131.

1,8-Di-*tert*-butyl 2-methyl (3aS)-3a-(2-(2-methoxyphenyl) allyl)-2,3,3a,8a-tetrahydropyrrolo [2,3-b] indole-1,2,8-tricarboxylate (37)



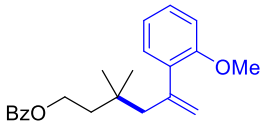
According to *method A*, flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether) provided this compound in 52% yield (44.0 mg, 0.078 mmol) as foam solid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.48 (bs, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.90 (dd, *J* = 18.6, 7.2 Hz, 2H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.02 (s, 1H), 5.09 (s, 1H), 5.07 (s, 1H), 3.79 - 3.75 (m, 4H), 3.67 (s, 3H), 3.14 (d, *J* = 13.8 Hz, 1H), 2.73 (d, *J* = 13.8 Hz, 1H), 2.27 (q, *J* = 6.0 Hz, 1H), 2.01 (t, *J* = 11.4 Hz, 1H), 1.59 (s, 9H), 1.36 (bs, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 172.93, 155.96, 152.32, 144.07, 141.93, 134.83, 131.34, 129.87, 128.52, 128.18, 123.01, 120.60, 119.97, 110.45, 81.15, 80.52, 65.26, 59.39, 55.17, 51.92, 42.91, 41.94, 28.30, 28.17.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{32}H_{41}N_2O_7^+$): m/z 565.2908; found: 565.2929.

5-(2-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl benzoate (12b)



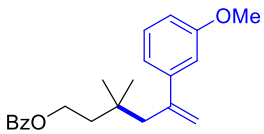
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 57% yield (28.9 mg, 0.0855 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.22 - 7.19 (m, 2H), 6.91 (t, *J* = 1.8 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 5.15 (d, *J* = 2.4 Hz, 1H), 5.13 (d, *J* = 2.4 Hz, 1H), 4.29 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 2.62 (s, 2H), 1.63 (t, *J* = 7.2 Hz, 2H), 0.87 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 166.60, 156.32, 146.39, 133.18, 132.68, 130.51, 130.18, 129.46, 128.23, 120.56, 118.79, 110.61, 62.34, 55.26, 47.94, 40.01, 33.53, 27.73.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{26}NaO_3^+$): m/z 361.1774; found: 361.1786.

5-(3-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl benzoate (12c)



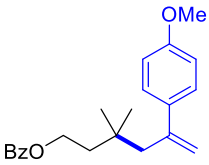
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 66% yield (33.5 mg, 0.099 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.02 (d, *J* = 6.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.99 - 6.97 (m, 1H), 6.93 (t, *J* = 1.8 Hz, 1H), 6.80 - 6.78 (m, 1H), 5.30 (d, *J* = 1.8 Hz, 1H), 5.07 (d, *J* = 1.8 Hz, 1H), 4.35 (t, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 2.55 (s, 2H), 1.69 (t, *J* = 7.2 Hz, 2H), 0.88 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 166.58, 159.41, 146.64, 145.09, 132.72, 130.43, 129.45, 129.11, 128.25, 119.08, 117.17, 112.51, 112.16, 62.25, 55.11, 47.51, 40.22, 33.66, 27.62.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{26}NaO_3^+$): m/z 361.1774; found: 361.1790.

5-(4-Methoxyphenyl)-3,3-dimethylhex-5-en-1-yl benzoate (12d)



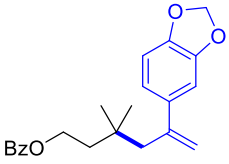
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 63% yield (32.0 mg, 0.0945 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.01 (d, *J* = 6.8 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.22 (d, *J* = 1.9 Hz, 1H), 5.01 - 4.96 (m, 1H), 4.34 (t, *J* = 7.3 Hz, 2H), 3.77 (s, 3H), 2.53 (s, 2H), 1.67 (t, *J* = 7.3 Hz, 2H), 0.86 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 166.66, 158.82, 146.12, 136.01, 132.77, 130.47, 129.49, 128.29, 127.56, 115.78, 113.53, 62.33, 55.17, 47.47, 40.29, 33.66, 27.75.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{26}NaO_3^+$): m/z 361.1774; found: 361.1789.

5-(Benzo[d] [1,3] dioxol-5-yl)-3,3-dimethylhex-5-en-1-yl benzoate (12e)



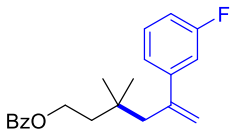
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 67% yield (35.4 mg, 0.1005 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.02 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 6.88 - 6.84 (m, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 2H), 5.20 (d, *J* = 1.9 Hz, 1H), 4.99 (d, *J* = 1.8 Hz, 1H), 4.34 (t, *J* = 7.3 Hz, 2H), 2.49 (s, 2H), 1.68 (t, *J* = 7.3 Hz, 2H), 0.88 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 166.62, 147.50, 146.71, 146.25, 137.86, 132.76, 130.44, 129.48, 128.29, 119.88, 116.26, 107.94, 107.14, 100.94, 62.28, 47.70, 40.25, 33.68, 27.68.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{22}H_{24}NaO_4^+$): m/z 375.1567; found: 375.1574.

5-(3-Fluorophenyl)-3,3-dimethylhex-5-en-1-yl benzoate (12f)



According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 71% yield (34.7 mg, 0.1065 mmol) as colorless oil.

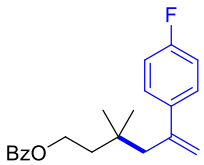
^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.01 (d, *J* = 6.6 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.26 - 7.22 (m, 1H), 7.15 - 7.14 (m, 1H), 7.07 (dt, *J* = 10.2, 1.8 Hz, 1H), 6.93 - 6.90 (m, 1H), 5.30 (d, *J* = 1.8 Hz, 1H), 5.09 (d, *J* = 1.2 Hz, 1H), 4.34 (t, *J* = 7.2 Hz, 2H), 2.52 (s, 2H), 1.67 (t, *J* = 7.2 Hz, 2H), 0.85 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ166.59, 145.89, 145.65, 132.78, 130.39, 129.67, 129.61, 129.47, 128.28, 122.15, 122.13, 118.03, 113.93, 113.79, 113.49, 113.35, 62.16, 47.42, 40.30, 33.70, 27.57.

^{19}F NMR (564 MHz, Chloroform-d): δ -113.50.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{21}H_{23}FNaO_2^+$): m/z 349.1574; found: 349.1588.

5-(4-Fluorophenyl)-3,3-dimethylhex-5-en-1-yl benzoate (12g)



According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 63% yield (30.8 mg, 0.0945 mmol) as colorless oil.

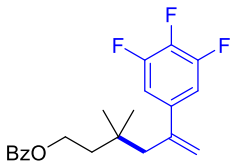
^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.01 (d, *J* = 6.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.34 (dd, *J* = 8.4, 5.4 Hz, 2H), 6.99 (t, *J* = 8.4 Hz, 2H), 5.24 (d, *J* = 1.8 Hz, 1H), 5.06 (m, 1H), 4.34 (t, *J* = 7.2 Hz, 2H), 2.53 (s, 2H), 1.67 (t, *J* = 7.2 Hz, 2H), 0.86 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 166.62, 145.74, 132.80, 130.40, 129.47, 128.30, 128.03, 127.98, 117.16, 115.09, 114.95, 62.20, 47.66, 40.32, 33.69, 27.67.

^{19}F NMR (564 MHz, Chloroform-d): δ -115.71.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{21}H_{23}FNaO_2^+$): m/z 349.1574; found:349.1580.

3,3-Dimethyl-5-(3,4,5-trifluorophenyl) hex-5-en-1-yl benzoate (12h)



According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 65% yield (35.3 mg, 0.0975 mmol) as colorless oil.

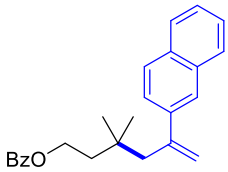
^{1}H NMR (400 MHz, Chloroform-d): δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.04 - 6.94 (m, 2H), 5.29 (d, *J* = 1.3 Hz, 1H), 5.13 (s, 1H), 4.36 (t, *J* = 7.2 Hz, 2H), 2.47 (s, 2H), 1.68 (t, *J* = 7.2 Hz, 2H), 0.86 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d): δ 166.59, 152.18, 144.01, 139.70, 132.87, 130.27, 129.46, 128.33, 118.99, 110.56, 110.50, 110.40, 110.34, 62.00, 47.21, 40.29, 33.75, 27.46.

^{19}F NMR (376 MHz, Chloroform-d): δ -134.43, -162.26.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{21}H_{21}F_3NaO_2^+$): m/z 385.1386; found: 385.1393.

3,3-Dimethyl-5-(naphthalen-2-yl) hex-5-en-1-yl benzoate (12i)



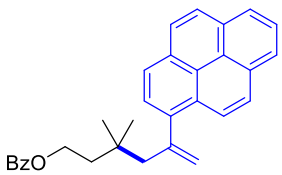
According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 81% yield (43.6 mg, 0.1215 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.85 - 7.75 (m, 4H), 7.54 (t, *J* = 7.3 Hz, 2H), 7.49 - 7.38 (m, 4H), 5.42 (d, *J* = 1.8 Hz, 1H), 5.18 (d, *J* = 1.8 Hz, 1H), 4.36 (t, *J* = 7.3 Hz, 2H), 2.68 (s, 2H), 1.71 (t, *J* = 7.3 Hz, 2H), 0.89 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 146.71, 140.97, 133.34, 132.74, 132.64, 130.41, 129.47, 128.27, 128.04, 127.80, 127.52, 126.07, 125.66, 125.21, 125.00, 117.78, 62.28, 47.48, 40.33, 33.79, 27.75.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{25}H_{26}NaO_2^+$): m/z 381.1825; found: 381.1830.

3,3-Dimethyl-5-(pyren-1-yl) hex-5-en-1-yl benzoate (12j)



According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 48% yield (31.1 mg, 0.072 mmol) as colorless oil.

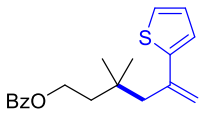
^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.49 (d, *J* = 9.2 Hz, 1H), 8.16 (d, *J* = 7.7 Hz, 2H), 8.12 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 9.2 Hz, 1H), 8.03 - 7.98 (m, 3H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* =

7.2 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 5.63 (d, *J* = 2.1 Hz, 1H), 5.41 (d, *J* = 2.1 Hz, 1H), 4.24 (t, *J* = 7.3 Hz, 2H), 2.86 (s, 2H), 1.69 (t, *J* = 7.3 Hz, 2H), 0.90 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 166.50, 145.87, 139.81, 132.64, 130.92, 130.16, 129.36, 128.17, 127.36, 127.25, 127.11, 125.92, 125.85, 125.37, 125.19, 124.99, 124.73, 124.42, 121.36, 62.13, 51.15, 40.10, 34.19, 27.81.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{31}H_{28}NaO_2^+$): m/z 455.1982; found: 455.1982.

3,3-Dimethyl-5-(thiophen-2-yl) hex-5-en-1-yl benzoate (12k)



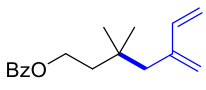
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 43% yield (20.3 mg, 0.0645 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 4.8 Hz, 1H), 7.03 (d, *J* = 3.0 Hz, 1H), 6.95 (t, *J* = 3.0 Hz, 1H), 5.51 (s, 1H), 4.97 (s, 1H), 4.41 (t, *J* = 7.2 Hz, 2H), 2.52 (s, 2H), 1.78 (t, *J* = 7.2 Hz, 2H), 0.97 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 166.64, 147.05, 139.04, 132.79, 130.41, 129.49, 128.30, 127.22, 124.06, 123.71, 115.43, 62.27, 47.74, 40.46, 33.71, 27.41.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{19}H_{22}NaO_2S^+$): m/z 337.1233; found: 337.1238.

3,3-Dimethyl-5-methylenehept-6-en-1-yl benzoate (12l)



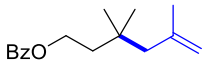
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 38% yield (14.7 mg, 0.057 mmol) as colorless oil. Further purification of the product was performed using a preparation TLC.

^{1}H NMR (600 MHz, Chloroform-d) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 6.40 (dd, *J* = 18.0, 10.8 Hz, 1H), 5.26 (d, *J* = 18.0 Hz, 1H), 5.21 (s, 1H), 5.05 (d, *J* = 10.8 Hz, 1H), 4.96 (s, 1H), 4.42 (t, *J* = 7.3 Hz, 2H), 2.24 (s, 2H), 1.77 (t, *J* = 7.3 Hz, 2H), 0.98 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-d) δ 166.69, 143.45, 140.43, 132.79, 130.47, 129.51, 128.31, 119.03, 113.69, 62.40, 43.04, 40.58, 33.32, 27.47.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{17}H_{22}NaO_2^+$): m/z 281.1512; found: 281.1519.

3,3,5-Trimethylhex-5-en-1-yl benzoate (12m)



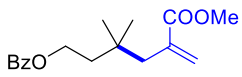
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 43% yield (15.9 mg, 0.0645 mmol) as colorless oil. Further purification of the product was performed using a preparation TLC.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.04 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.59 - 7.52 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.91 - 4.86 (m, 1H), 4.68 (dd, *J* = 1.7, 0.8 Hz, 1H), 4.40 (t, *J* = 7.4 Hz, 2H), 2.04 (d, *J* = 0.7 Hz, 2H), 1.80 (dd, *J* = 1.5, 0.8 Hz, 3H), 1.76 (t, *J* = 7.4 Hz, 2H), 1.01 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 166.71, 143.09, 132.80, 130.44, 129.51, 128.31, 114.63, 62.42, 50.13, 40.37, 33.24, 27.66, 25.44.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{16}H_{22}NaO_2^+$): m/z 269.1512; found: 269.1515.

5-(Methoxycarbonyl)-3,3-dimethylhex-5-en-1-yl benzoate (12n)



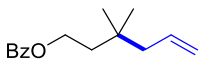
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 57% yield (24.8 mg, 0.0855 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 6.24 (d, *J* = 1.2 Hz, 1H), 5.52 (d, *J* = 1.2 Hz, 1H), 4.41 (t, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 2.39 (s, 2H), 1.71 (t, *J* = 7.2 Hz, 2H), 0.95 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 168.51, 166.62, 137.90, 132.80, 130.40, 129.49, 128.31, 127.99, 62.16, 51.89, 43.10, 39.92, 33.37, 27.71, 26.59.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{17}H_{22}NaO_4^+$): m/z 313.1410; found: 313.1416.

3,3-Dimethylhex-5-en-1-yl benzoate (12o)



To a flame-dried Schlenk tube equipped with a stir bar was loaded zinc power (29.4 mg, 0.45 mmol, 300 mol %), followed by addition of $MgCl_2$ (42.9 mg, 0.45 mmol, 300 mol %), *t*Bu-*ter*-pyridine **L4** (6.0 mg, 0.015 mmol, 10 mol %) and FePc (8.5 mg, 0.015 mmol, 10 mol%). The tube was evacuated and refilled nitrogen (N_2) three time. DMA (0.5 mL) was added via a syringe, followed by addition of *tertiary* alkyl oxalate (0.15 mmol, 100 mol %),

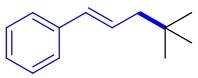
and allyl acetate (0.6 mmol, 400 mol %). After the reaction mixture was allowed to stir for 12 hours under a N_2 atmosphere at 25 °C. The reaction mixture was loaded onto a silica column. Flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 49% yield (17.1 mg, 0.0735 mmol) as colorless oil. Further purification of the product was performed using a preparation TLC.

^{1}H NMR (600 MHz, Chloroform-d) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 5.85 (ddt, *J* = 17.4, 10.3, 7.5 Hz, 1H), 5.07 - 5.03 (m, 2H), 4.39 (t, *J* = 7.2 Hz, 2H), 2.05 (d, *J* = 7.8 Hz, 2H), 1.72 (t, *J* = 7.2 Hz, 2H), 0.98 (s, 6H).

^{13}C NMR (150 MHz, Chloroform-d) δ 166.68, 135.00, 132.78, 130.46, 129.50, 128.30, 117.35, 62.28, 46.87, 39.66, 32.58, 27.14.

HRMS (APCI) exact mass calculated for [M+H$^+$] ($C_{15}H_{21}O_2^+$): m/z 233.1356; found: 233.1597.

(*E*)-(4,4-dimethylpent-1-en-1-yl) benzene (3b)



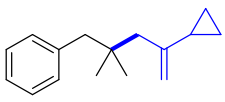
According to *method A*, using methyl (1-phenylallyl) carbonate, flash column chromatography (SiO_2: petroleum ether) provided this compound in 35% yield (9.0 mg, 0.0525 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 6.29 - 6.24 (m, 1H), 2.09 (dd, *J* = 7.6, 0.6 Hz, 2H), 0.95 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-d) δ 137.94, 131.80, 128.45, 128.23, 126.78, 125.97, 47.57, 31.41, 29.39.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{13}H_{18}Na^+$): m/z 197.1301; found: 197.1298.

(4-cyclopropyl-2,2-dimethylpent-4-en-1-yl) benzene (5b)



According to *method A*, flash column chromatography (SiO_2: 1% ethyl acetate in petroleum ether) provided this compound in 26% yield (8.36 mg, 0.039 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.26 (t, *J* = 7.0 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 4.61 (s, 1H), 4.57 (s, 1H), 2.58 (s, 2H), 2.15 (s, 2H), 1.23 - 1.20 (m, 1H), 0.92 (s, 6H), 0.71 - 0.68 (m, 2H), 0.48 - 0.45 (m, 2H).

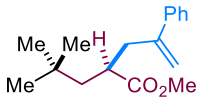
^{13}C NMR (150 MHz, Chloroform-*d*): δ 149.30, 139.37, 130.73, 127.58, 125.74, 108.31, 50.98, 49.59, 34.97, 26.80, 17.49, 8.78.

HRMS (ESI) exact mass calculated for [M+Na^{+}] ($C_{16}H_{22}Na^{+}$): m/z 237.1614; found: 237.1619.

Part 7. Three Component Reaction

***Method B*:** To a flame-dried Schlenk tube equipped with a stir bar was loaded zinc power (58.8 mg, 0.90 mmol, 300 mol %), followed by addition of $MgCl_2$ (85.8 mg, 0.90 mmol, 300 mol %), DtBBipy **L1a** (7.9 mg, 0.03 mmol, 10 mol %) and Fe $(acac)_3$ (5.3 mg, 0.015 mmol, 5 mol%). The tube was evacuated and refilled nitrogen (N_2) three time. DMA (1.0 mL) was added via s syringe, followed by addition of *tertiary* alkyl oxalate (0.30 mmol, 100 mol %), allylic carbonate (0.6 mmol, 200 mol %) and methyl acrylate (0.6 mmol, 200%). After the reaction mixture was allowed to stir for 12 hours under a N_2 atmosphere at 45 °C. The reaction mixture was loaded onto a silica column. Flash column chromatography provided the product as an oil or a solid.

Methyl (S)-2-neopentyl-4-phenylpent-4-enoate (38a)



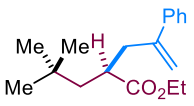
According to *method B*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 49% yield (38.3 mg, 0.147 mmol) as colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.40 - 7.31 (m, 4H), 7.31 - 7.26 (m, 1H), 5.29 (d, *J* = 1.6 Hz, 1H), 5.07 (d, *J* = 1.5 Hz, 1H), 3.58 (s, 3H), 2.88 - 2.76 (m, 1H), 2.60 - 2.49 (m, 2H), 1.79 (dd, *J* = 13.9, 9.4 Hz, 1H), 1.31 (d, *J* = 15.9 Hz, 1H), 0.77 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-d): δ 177.30, 145.86, 140.34, 128.32, 127.55, 126.27, 114.85, 51.34, 45.33, 40.71, 40.53, 30.52, 29.20.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{17}H_{25}O_2^+$): m/z 261.1849; found: 261.1851.

Ethyl (S)-2-neopentyl-4-phenylpent-4-enoate (38b)



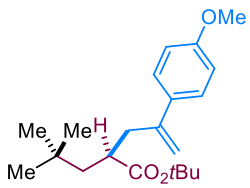
According to *method B*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 42% yield (34.6 mg, 0.126 mmol) as colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.41 - 7.26 (m, 5H), 5.29 (d, *J* = 1.5 Hz, 1H), 5.08 (d, *J* = 1.3 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.88 - 2.77 (m, 1H), 2.60 - 2.46 (m, 2H), 1.80 (dd, *J* = 14.1, 9.9 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 4H), 0.77 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-d): δ 176.86, 145.85, 140.40, 128.30, 127.52, 126.29, 114.83, 60.09, 45.34, 40.73, 40.58, 30.59, 29.26, 14.13.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{18}H_{26}NaO_2^+$): m/z 297.1825; found: 297.1828.

***Tert*-butyl (S)-4-(4-methoxyphenyl)-2-neopentylpent-4-enoate (38c)**



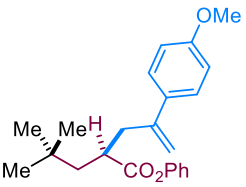
According to *method B*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 46% yield (45.9 mg, 0.138 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.33 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.22 (d, *J* = 1.5 Hz, 1H), 5.00 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H), 2.76 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.46 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.38 (q, *J* = 9.1, 8.4 Hz, 1H), 1.77 (dd, *J* = 14.1, 9.9 Hz, 1H), 1.41 (s, 9H), 1.22 (dd, *J* = 14.1, 1.9 Hz, 1H), 0.78 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 176.17, 159.07, 145.10, 132.96, 127.38, 113.63, 113.22, 79.89, 55.23, 45.24, 41.24, 40.92, 30.61, 29.39, 28.00.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{21}H_{32}NaO_3^+$): m/z 355.2244; found: 355.2250.

Phenyl (S)-4-(4-methoxyphenyl)-2-neopentylpent-4-enoate (38d)



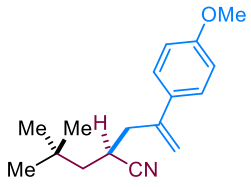
According to *method B*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 45% yield (46.5 mg, 0.132 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.32 (d, *J* = 1.5 Hz, 1H), 5.11 (d, *J* = 1.5 Hz, 1H), 3.82 (s, 3H), 2.96 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.81 - 2.74 (m, 1H), 2.68 (dd, *J* = 13.8, 6.8 Hz, 1H), 1.96 (dd, *J* = 14.2, 10.1 Hz, 1H), 1.42 (dd, *J* = 14.2, 2.0 Hz, 1H), 0.89 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 175.30, 159.25, 150.82, 144.89, 132.60, 129.31, 127.39, 127.19, 125.63, 121.46, 113.82, 113.71, 55.25, 45.64, 40.94, 40.77, 30.76, 29.40.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{23}H_{29}O_3^+$): m/z 353.2111; found: 353.2111.

(S)-4-(4-methoxyphenyl)-2-neopentylpent-4-enenitrile (38e)



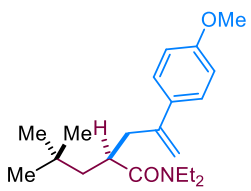
According to *method B*, flash column chromatography (SiO_2: 3% ethyl acetate in petroleum ether) provided this compound in 48% yield (37.1 mg, 0.144 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.29 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 5.33 (d, *J* = 0.6 Hz, 1H), 5.13 (d, *J* = 0.6 Hz, 1H), 3.82 (s, 3H), 2.88 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.65 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.55 - 2.50 (m, 1H), 1.66 (dd, *J* = 14.4, 10.8 Hz, 1H), 1.42 (dd, *J* = 14.4, 2.4 Hz, 1H), 0.88 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 159.47,143.27, 131.62, 127.36, 123.26, 115.03, 113.98, 55.27, 45.42, 40.31, 30.62, 29.22, 25.64.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{17}H_{24}NO^+$): m/z 258.1852; found: 258.1859.

(S)-2-(2,2-Dimethyl-3-phenylpropyl)-N, N-diethyl-4-(4-methoxyphenyl) pent-4-enamide (38f)



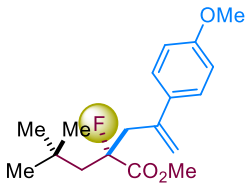
According to *method B*, flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether) provided this compound in 43% yield (42.7 mg, 0.129 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.31 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6Hz, 2H), 5.20 (d, *J* = 1.2 Hz, 1H), 5.02 (s, 1H), 3.82 (s, 3H), 3.37 - 3.32 (m, 1H), 3.31 - 3.25 (m, 1H), 3.21 - 3.11 (m, 2H), 2.71 (dd, *J* = 13.8, 5.4 Hz, 1H), 2.68 - 2.63 (m, 1H), 2.52 (dd, *J* = 13.8, 8.4 Hz, 1H), 1.96 (dd, *J* = 13.8, 9.0 Hz, 1H), 1.32 (dd, *J* = 13.8, 2.4 Hz, 1H), 1.05 (q, *J* = 7.2 Hz, 6H), 0.77 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 175.41, 159.11, 145.56, 133.46, 127.44, 113.74, 113.63, 55.27, 44.91, 41.61, 40.82, 40.10, 35.74, 30.60, 29.73, 14.40, 12.54.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{21}H_{34}NO_2^+$): m/z 332.2584; found: 332.2580.

Methyl 2-fluoro-4-(4-methoxyphenyl)-2-neopentylpent-4-enoate (38g)



According to *method B*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 50% yield (46.3 mg, 0.15 mmol) as colorless oil.

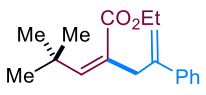
^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.30 (d, *J* = 1.5 Hz, 1H), 5.11 (s, 1H), 3.80 (s, 3H), 3.43 (s, 3H), 3.03 (dd, *J* = 31.2, 14.4 Hz, 1H), 2.93 (t, *J* = 14.1 Hz, 1H), 2.03 (dd, *J* = 39.1, 14.9 Hz, 1H), 1.84 (dd, *J* = 14.9, 6.2 Hz, 1H), 0.92 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 172.03, 171.86, 159.06, 141.68, 133.74, 127.72, 116.94, 113.44, 55.24, 51.76, 50.11, 49.97, 45.58, 45.43, 30.95, 30.26, 30.25.

^{19}F NMR (565 MHz, Chloroform-*d*): δ -165.23.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{18}H_{26}FO_3^+$): m/z 309.1860 found: 309.1861.

Methyl (S)-4-(4-methoxyphenyl)-2-((1-methylcyclopentyl) methyl) pent-4-enoate (38h)



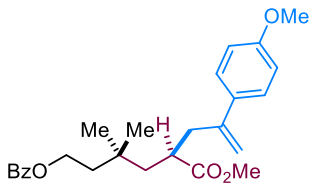
According to *method B*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 27% yield (22.1 mg, 0.081 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.40 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 5.50 (s, 1H), 5.42 - 5.36 (m, 1H), 5.13 (d, *J* = 1.5 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.37 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 9H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 170.17, 145.22, 144.63, 140.80, 128.61, 128.08, 127.35, 126.25, 114.71, 60.37, 42.14, 33.30, 29.76, 14.07.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{18}H_{24}NaO_2^+$): m/z 295.1669; found: 295.1674.

(S)-5-(Methoxycarbonyl)-7-(4-methoxyphenyl)-3,3-dimethyloct-7-en-1-yl benzoate (39)



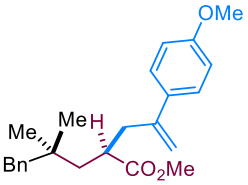
According to *method B*, flash column chromatography (SiO_2: 3% ethyl acetate in petroleum ether) provided this compound in 41% yield (52.2 mg, 0.123 mmol) as colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 5.26 - 5.20 (m, 1H), 5.02 - 4.95 (m, 1H), 4.32 - 4.23 (m, 2H), 3.76 (s, 3H), 3.60 (s, 3H), 2.83 (dd, *J* = 12.8, 6.1 Hz, 1H), 2.63 - 2.46 (m, 2H), 1.89 (dd, *J* = 14.1, 9.6 Hz, 1H), 1.58 (t, *J* = 7.3 Hz, 2H), 1.41 (d, *J* = 14.1 Hz, 1H), 0.85 (s, 3H), 0.81 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-d): δ 177.10, 166.55, 159.14, 144.81, 132.80, 132.35, 130.36, 129.47, 128.29, 127.32, 113.71, 62.05, 55.14, 51.48, 43.41, 40.52, 40.14, 39.90, 32.42, 26.99, 26.72.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{26}H_{32}NaO_5^+$): m/z 447.2142; found: 447.2145.

Phenyl (S)-4-(4-methoxyphenyl)-2-neopentylpent-4-enoate (40)



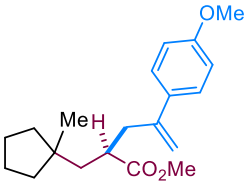
According to *method B*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 43% yield (47.3 mg, 0.129 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.29 (d, *J* = 8.6 Hz, 2H), 7.26 - 7.22 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.20 (d, *J* = 1.5 Hz, 1H), 4.98 (s, 1H), 3.81 (s, 3H), 3.58 (s, 3H), 2.78 (dd, *J* = 13.7, 8.0 Hz, 1H), 2.62 (q, *J* = 8.5, 8.0 Hz, 1H), 2.53 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.40 (s, 2H), 1.84 (dd, *J* = 14.1, 10.3 Hz, 1H), 1.37 (d, *J* = 14.1 Hz, 1H), 0.72 (d, *J* = 16.6 Hz, 6H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 177.23, 159.16, 145.11, 138.79, 130.61, 127.61, 127.36, 125.83, 113.70, 113.48, 55.24, 51.37, 48.65, 44.15, 40.80, 40.53, 34.32, 26.41, 25.90.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{24}H_{31}O_3^+$): m/z 367.2268; found: 367.2267.

Methyl (S)-4-(4-methoxyphenyl)-2-((1-methylcyclopentyl) methyl) pent-4-enoate (41)



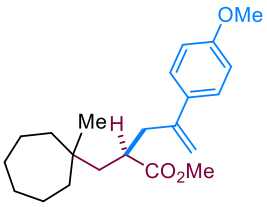
According to *method B*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 56% yield (53.1 mg, 0.168 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.31 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.21 (d, *J* = 1.5 Hz, 1H), 4.99 (d, *J* = 1.5 Hz, 1H), 3.82 (s, 3H), 3.58 (s, 3H), 2.79 (dd, *J* = 12.7, 6.6 Hz, 1H), 2.59 - 2.50 (m, 2H), 1.84 (dd, *J* = 13.9, 9.7 Hz, 1H), 1.59 - 1.52 (m, 4H), 1.46 (dd, *J* = 14.0, 2.2 Hz, 1H), 1.27 - 1.19 (m, 4H), 0.78 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 177.34, 159.13, 145.21, 132.83, 127.32, 113.68, 113.23, 55.24, 51.33, 43.90, 42.10, 41.56, 40.49, 39.66, 39.06, 25.02, 24.12, 23.78.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{20}H_{28}NaO_3^+$): m/z 339.1931; found: 339.1936.

Phenyl (S)-4-(4-methoxyphenyl)-2-neopentylpent-4-enoate (42)



According to *method B*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 52% yield (53.7 mg, 0.156 mmol) as colorless oil.

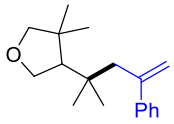
^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.31 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.22 (d, *J* = 1.5 Hz, 1H), 4.99 (s, 1H), 3.82 (s, 3H), 3.59 (s, 3H), 2.80 (q, *J* = 6.0 Hz, 1H), 2.56 - 2.47 (m, 2H), 1.78 (dd, *J* = 14.3, 9.7 Hz, 1H), 1.45 (d, *J* = 4.5 Hz, 4H), 1.35 - 1.29 (m, 6H), 1.21 - 1.18 (m, 3H), 0.68 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 177.53, 159.14, 145.15, 132.72, 127.35, 113.68, 113.39, 55.24, 51.36, 44.17, 40.79, 40.69, 40.16, 40.00, 36.00, 30.75, 30.64, 26.91, 22.82, 22.68.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{22}H_{33}O_3^+$): m/z 345.2424; found: 345.2425.

Part 8. Cyclization/Allylation Reactions

3,3-Dimethyl-4-(2-methyl-4-phenylpent-4-en-2-yl) tetrahydrofuran (43)



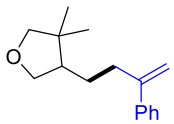
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 61% yield (23.6 mg, 0.0915 mmol) as colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.38 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29 - 7.25 (m, 1H), 5.29 (d, *J* = 1.9 Hz, 1H), 5.07 (d, *J* = 1.9 Hz, 1H), 4.00 (t, *J* = 8.6 Hz, 1H), 3.94 - 3.88 (m, 1H), 3.43 (s, 2H), 2.65 - 2.49 (m, 2H), 1.91 (t, *J* = 9.5 Hz, 1H), 1.17 (s, 3H), 1.11 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 146.80, 143.88, 128.20, 127.04, 126.47, 117.53, 83.36, 69.92, 56.93, 47.63, 41.71, 36.99, 26.89, 26.45, 26.04, 22.99.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{18}H_{26}NaO^+$): m/z 281.1876; found: 281.1883.

3,3-Dimethyl-4-(3-phenylbut-3-en-1-yl) tetrahydrofuran (44)



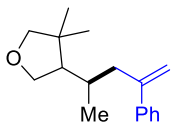
According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 39% yield (13.5 mg, 0.0585 mmol) as colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.41 - 7.26 (m, 5H), 5.28 (d, *J* = 1.4 Hz, 1H), 5.07 (d, *J* = 1.4 Hz, 1H), 4.11 (t, *J* = 8.1 Hz, 1H), 3.57 - 3.43 (m, 3H), 2.55 - 2.37 (m, 2H), 1.91 - 1.79 (m, 1H), 1.59 (dtt, *J* = 10.2, 6.7, 3.6 Hz, 2H), 0.96 (s, 3H), 0.87 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*): δ 148.30, 140.97, 128.32, 127.42, 126.06, 112.55, 81.41, 73.14, 48.38, 40.63, 34.61, 26.21, 24.39, 20.57.

HRMS (ESI) exact mass calculated for [M+H$^+$] ($C_{16}H_{23}O^+$): m/z 231.1743; found: 231.1747.

3,3-Dimethyl-4-((R)-4-phenylpent-4-en-2-yl) tetrahydrofuran (45)



According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 41% yield (15.0 mg, 0.0615 mmol) as colorless oil.

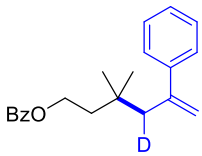
^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.43 - 7.37 (m, 4H), 7.34 - 7.31 (m, 1H), 5.33 (s, 1H), 5.09

(s, 1H), 4.25 (t, *J* = 7.8 Hz, 1H), 3.70 (t, *J* = 7.8 Hz, 1H), 3.53 (s, 2H), 2.67 (d, *J* = 13.8 Hz, 1H), 2.09 (t, *J* = 13.2 Hz, 1H), 1.73 (q, *J* = 9.6 Hz, 1H), 1.65 - 1.61 (m, 1H), 1.12 (s, 3H), 0.97 (s, 3H), 0.95 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, Chloroform-*d*): δ 146.91, 141.07, 128.30, 128.27, 127.35, 126.36, 126.24, 114.54, 82.85, 73.32, 54.51, 42.38, 40.51, 31.93, 25.65, 20.31, 17.95.

HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{17}H_{24}NaO^+$): m/z 267.1719; found: 267.1717.

(S)-3,3-Dimethyl-5-phenylhex-5-en-1-yl-4-d benzoate (12a-*d*)



According to *method A*, flash column chromatography (SiO_2: 2% ethyl acetate in petroleum ether) provided this compound in 72% yield (33.4 mg, 0.108 mmol) as colorless oil.

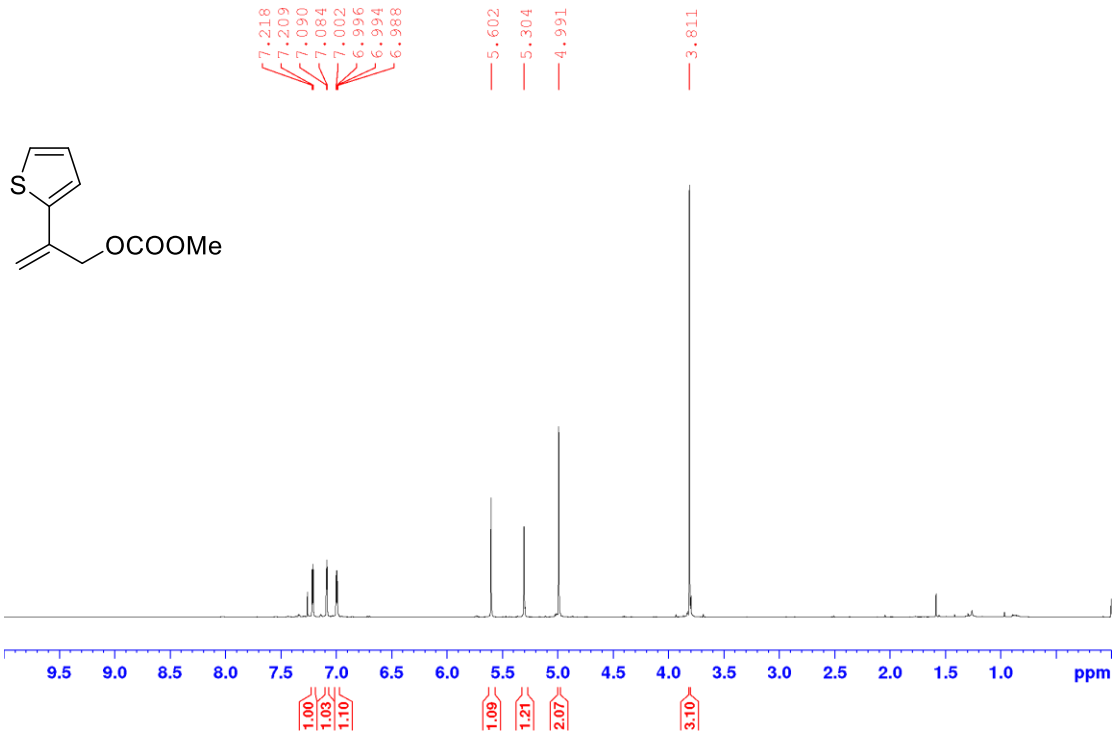
^{1}H NMR (600 MHz, Chloroform-*d*): δ 8.02 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.29 (d, *J* = 1.9 Hz, 1H), 5.08 (d, *J* = 1.1 Hz, 1H), 4.34 (t, *J* = 7.3 Hz, 2H), 2.56 (d, *J* = 10.9 Hz, 1H), 1.68 (t, *J* = 7.3 Hz, 2H), 0.87 (s, 6H).

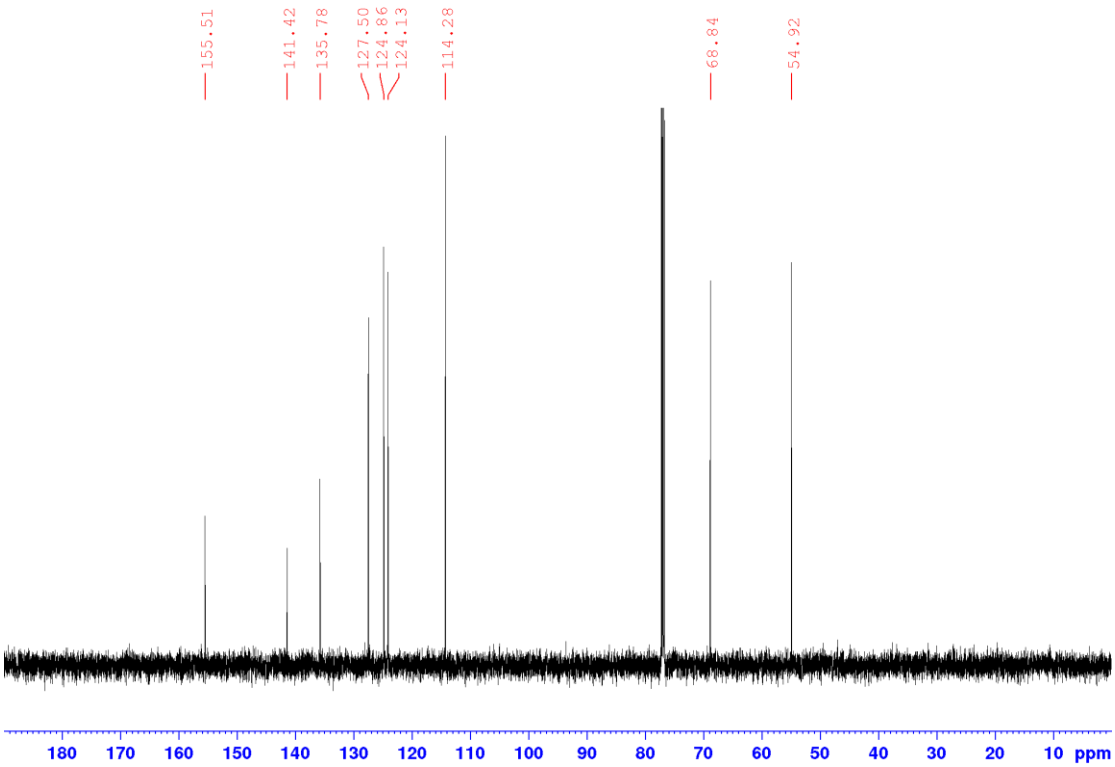
^{13}C NMR (150 MHz, Chloroform-*d*): δ 166.63, 146.76, 143.56, 132.76, 130.45, 129.48, 128.28, 128.19, 127.07, 126.50, 117.10, 62.29, 47.23, 47.11, 46.98, 40.30, 33.60, 27.69, 27.67, 27.65.

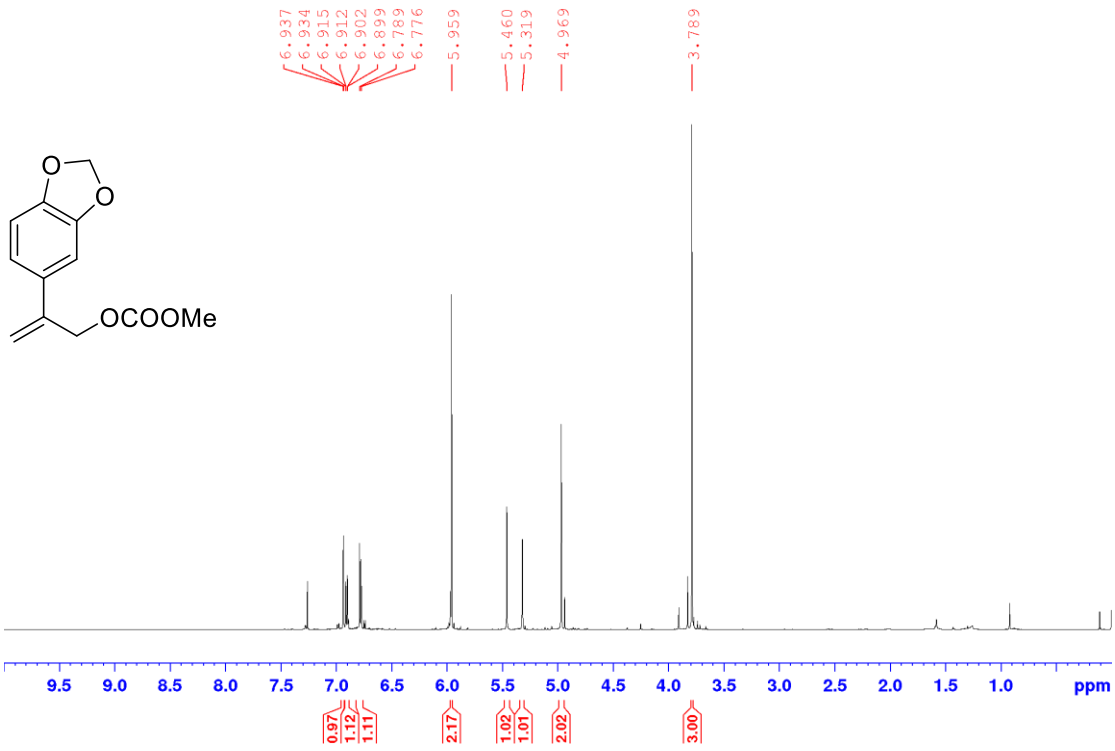
^{2}D NMR (61 MHz, $CHCl_3$) δ 2.58.

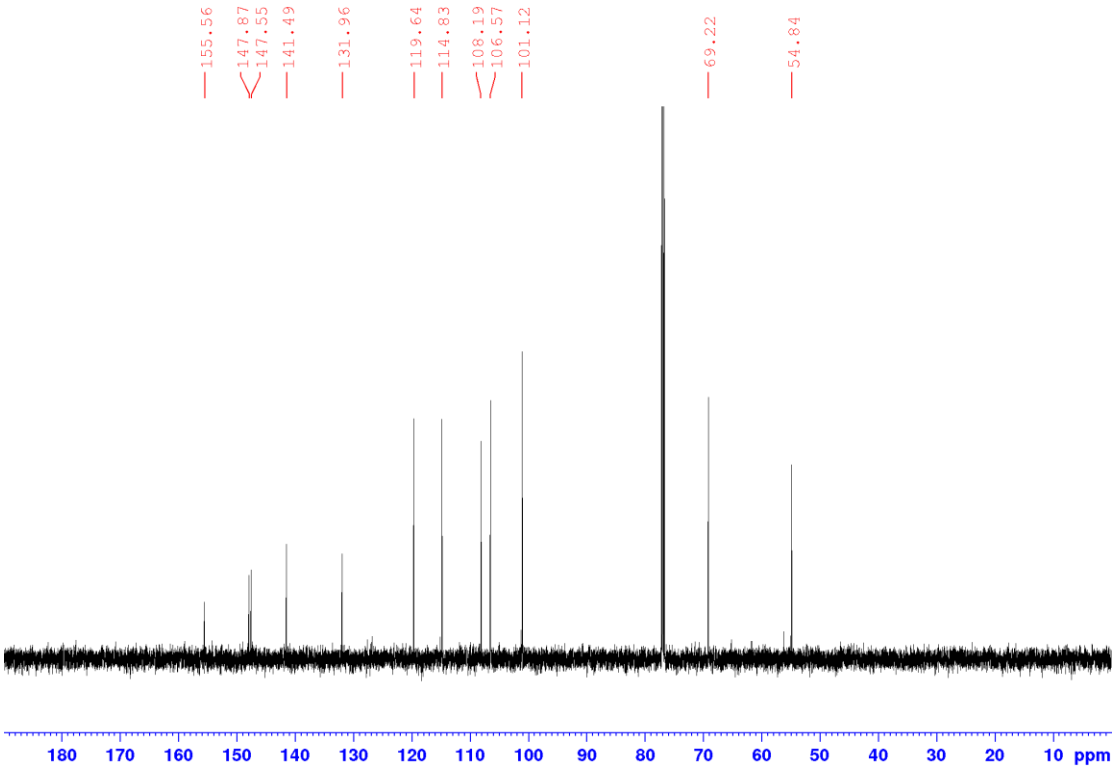
HRMS (ESI) exact mass calculated for [M+Na$^+$] ($C_{21}H_{23}DNaO_2^+$): m/z 332.1731; found: 332.1737.

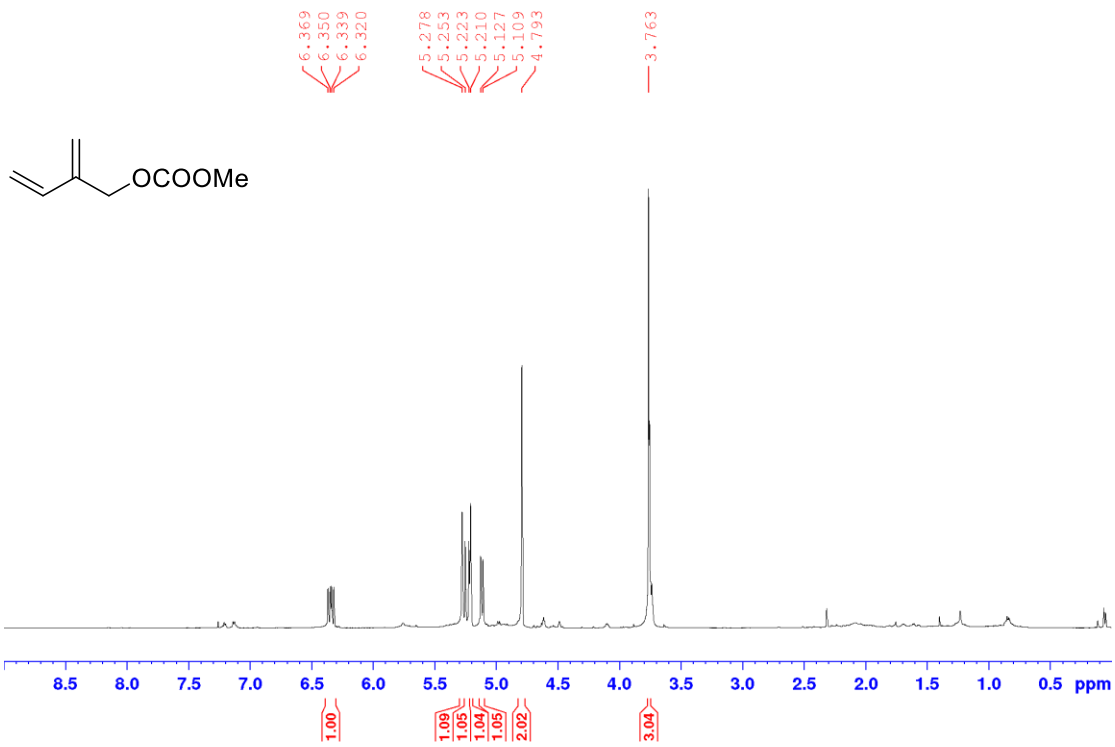
II. Spectral Data for New Compounds

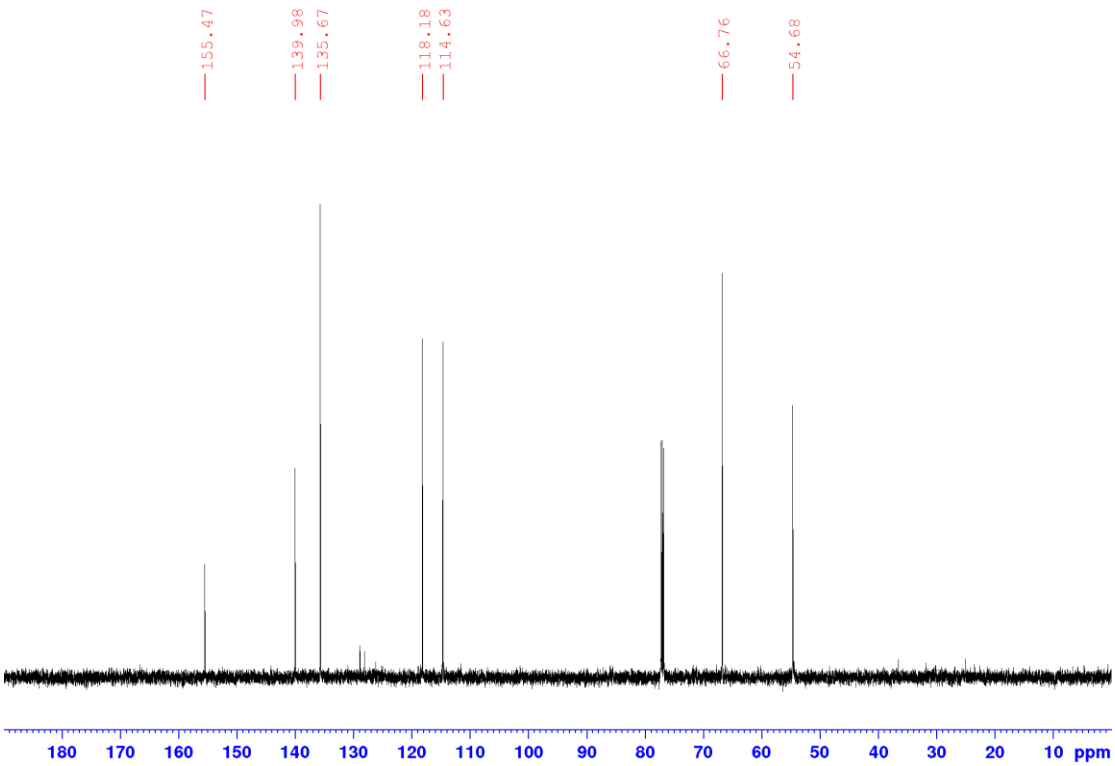


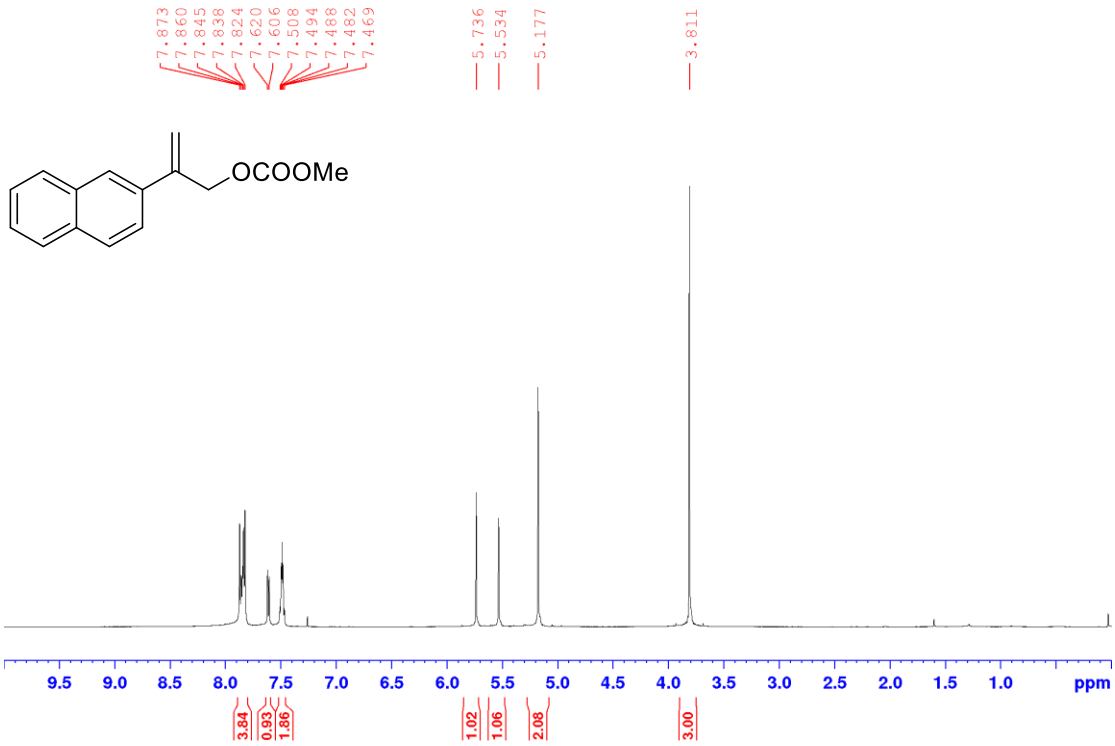


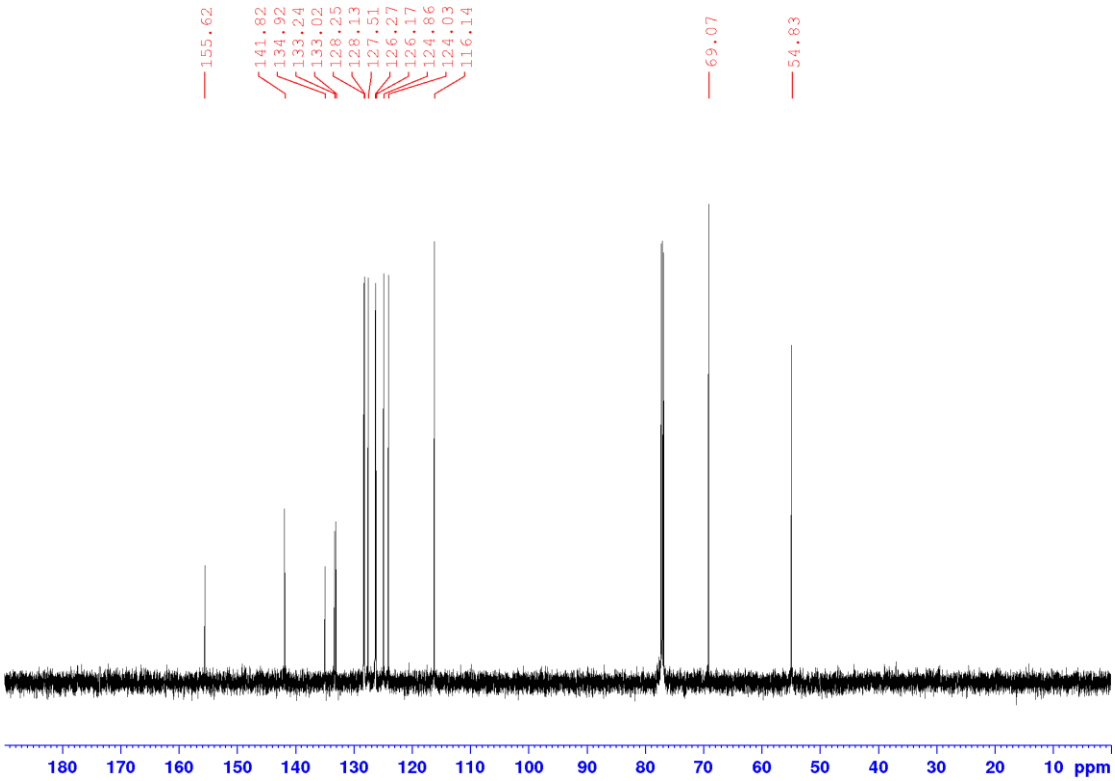

6.937
6.934
6.915
6.912
6.902
6.899
6.789
6.776
5.959
5.460
5.319
4.969
3.789
OCOOMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.97
1.12
1.11
2.17
1.02
1.01
2.02
3.00

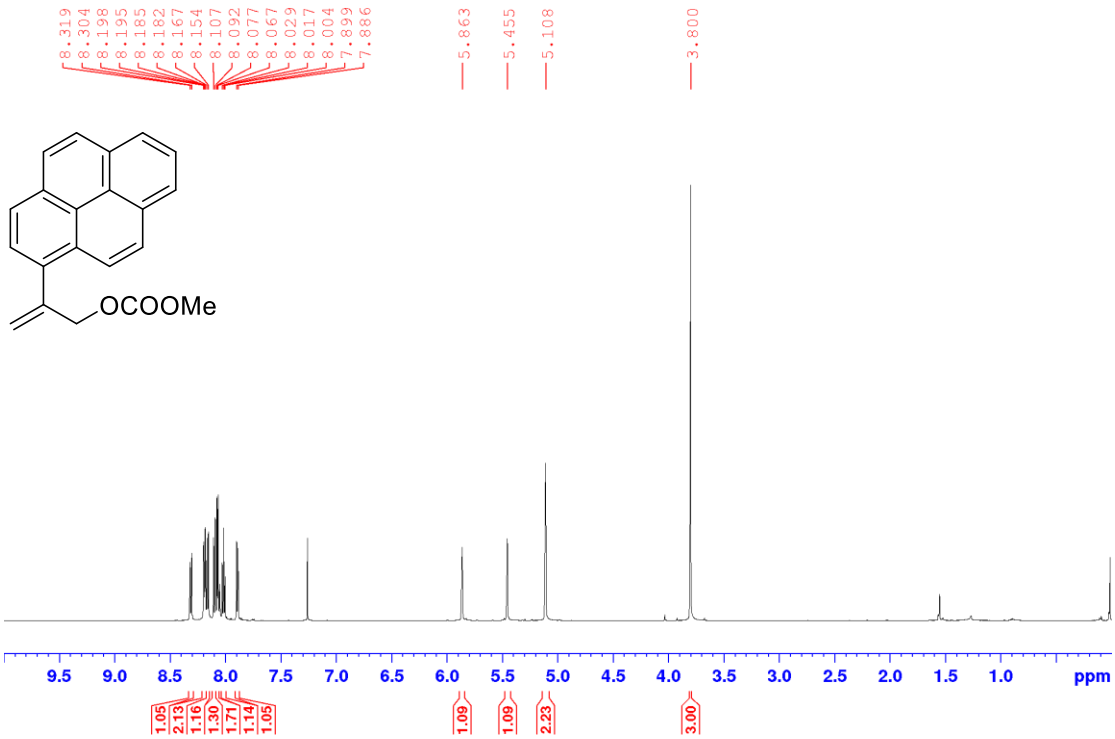

155.56
147.87
147.55
141.49
131.96
119.64
114.83
108.19
106.57
101.12
69.22
54.84
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

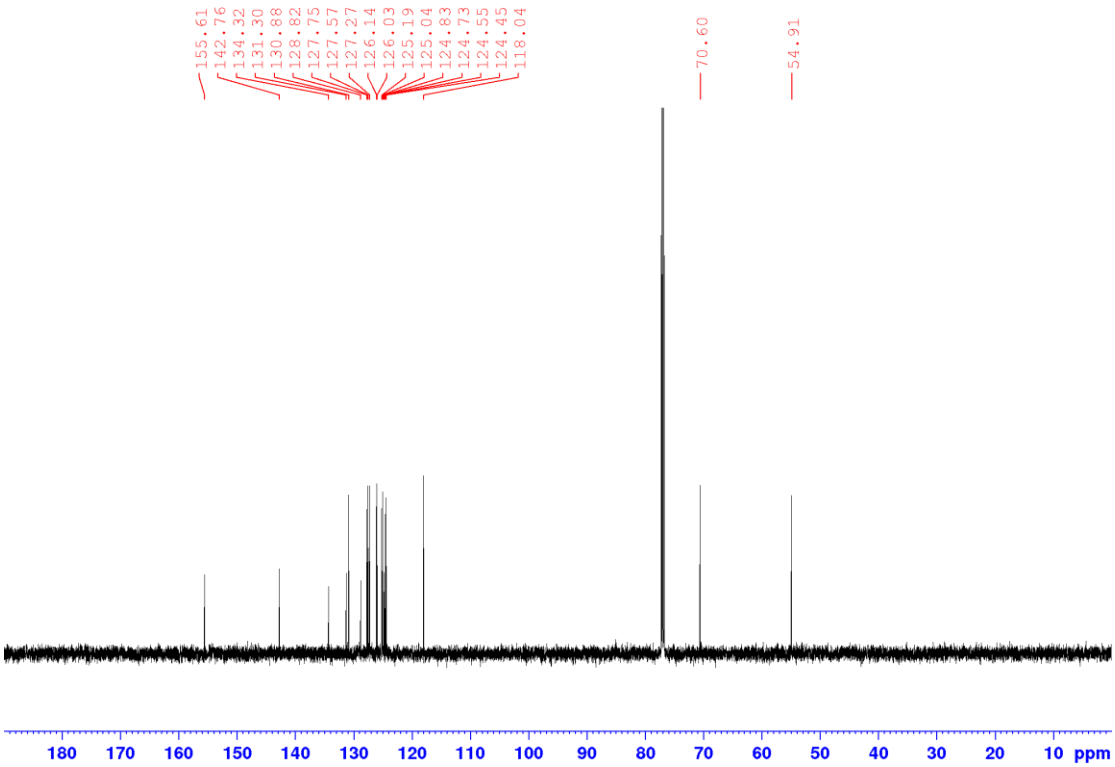

6.369
6.350
6.339
6.320
5.278
5.253
5.223
5.210
5.127
5.109
4.793
3.763
OCOOMe
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.09
1.05
1.04
1.05
2.02
3.04

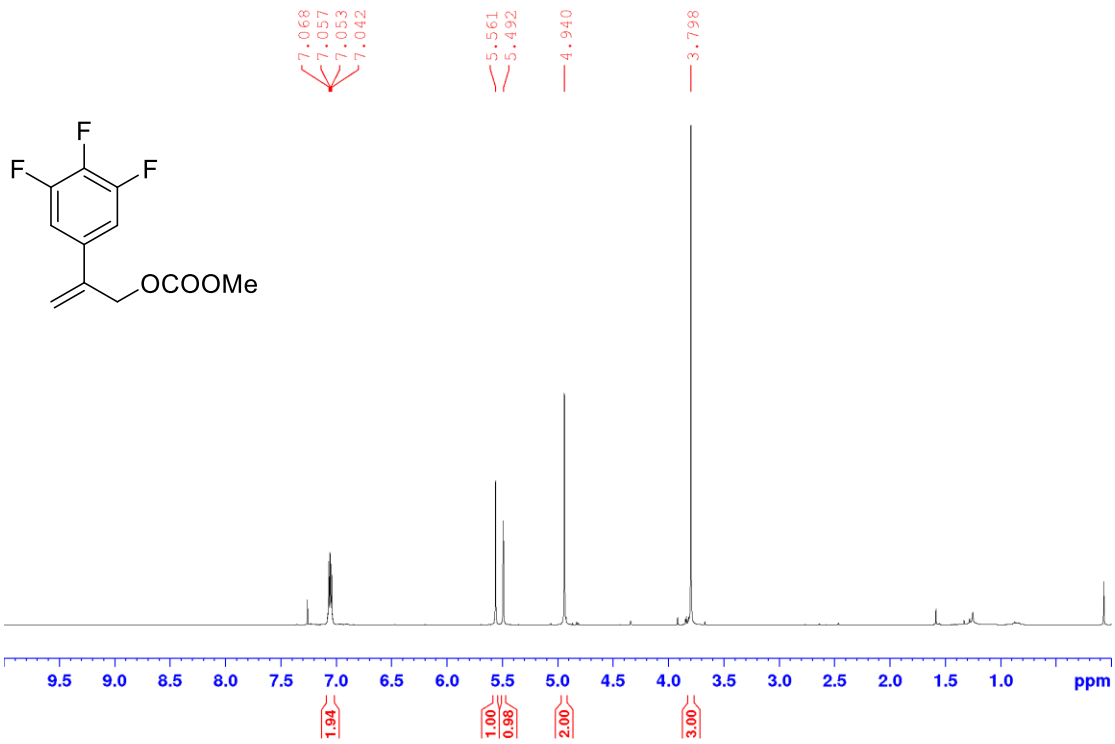

155.47
139.98
135.67
118.18
114.63
66.76
54.68
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

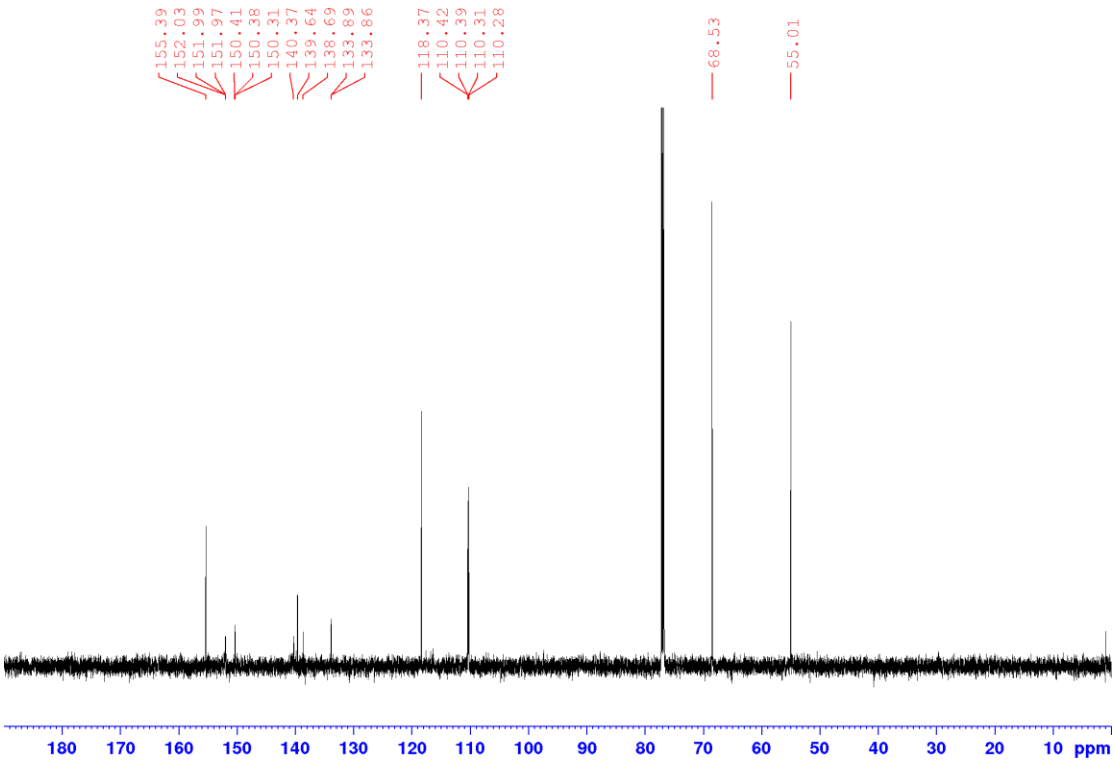

7.873
7.860
7.845
7.838
7.824
7.620
7.606
7.508
7.494
7.488
7.482
7.469
5.736
5.534
5.177
3.811
OCOOMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
3.84
0.93
1.86
1.02
1.06
2.08
3.00

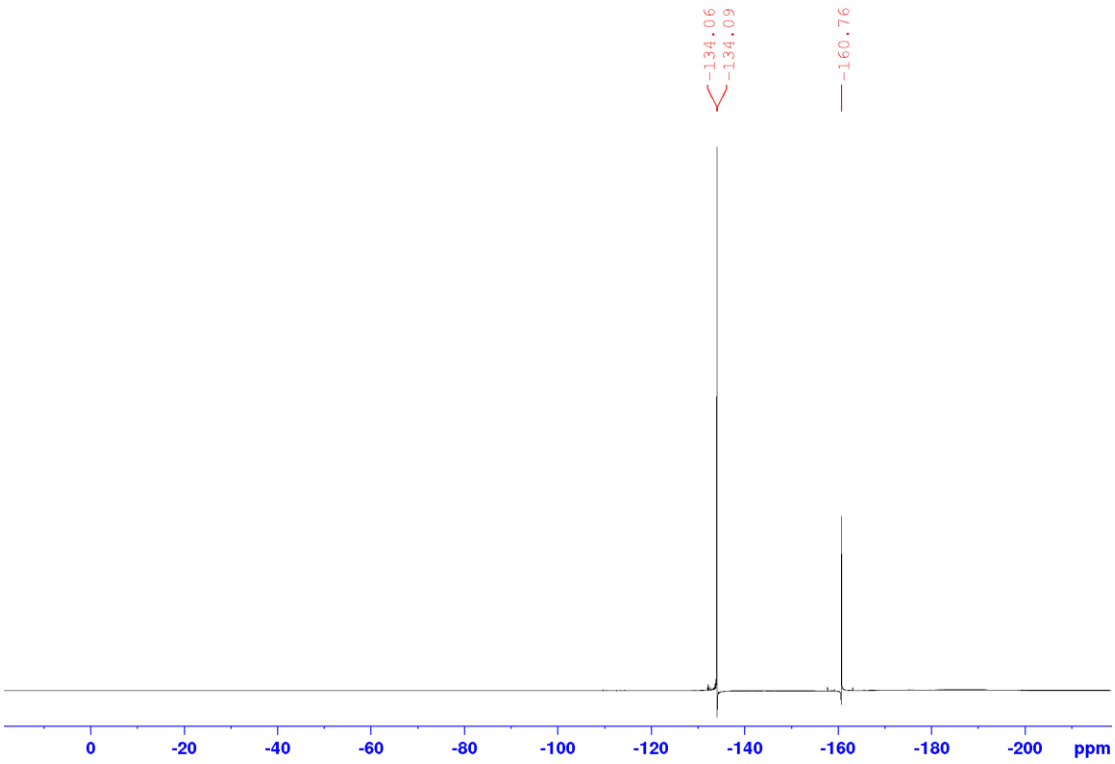

155.62
141.82
134.92
133.24
133.02
128.25
128.13
127.51
126.27
126.17
124.86
124.03
116.14
69.07
54.83
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

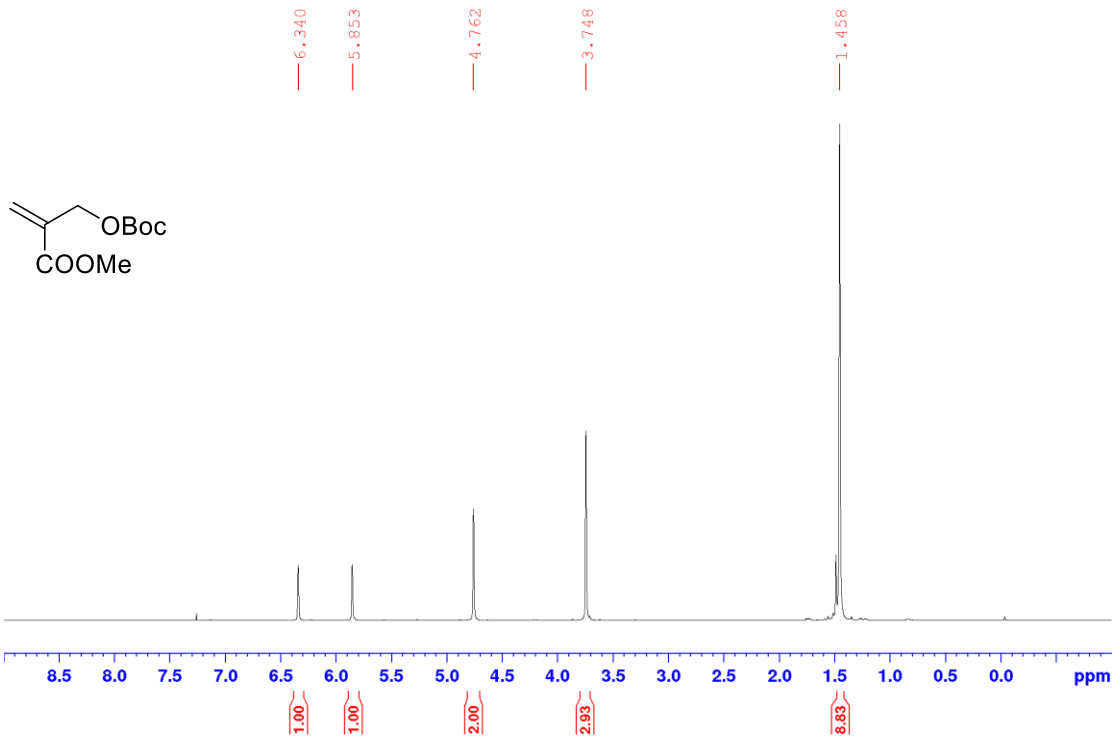

8.319
8.304
8.198
8.195
8.185
8.182
8.167
8.154
8.107
8.092
8.077
8.067
8.029
8.017
8.004
7.899
7.886
5.863
5.455
5.108
3.800
OCOOMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.05 2.13 1.16 1.30 1.71 1.14 1.05 1.09 1.09 2.23 3.00

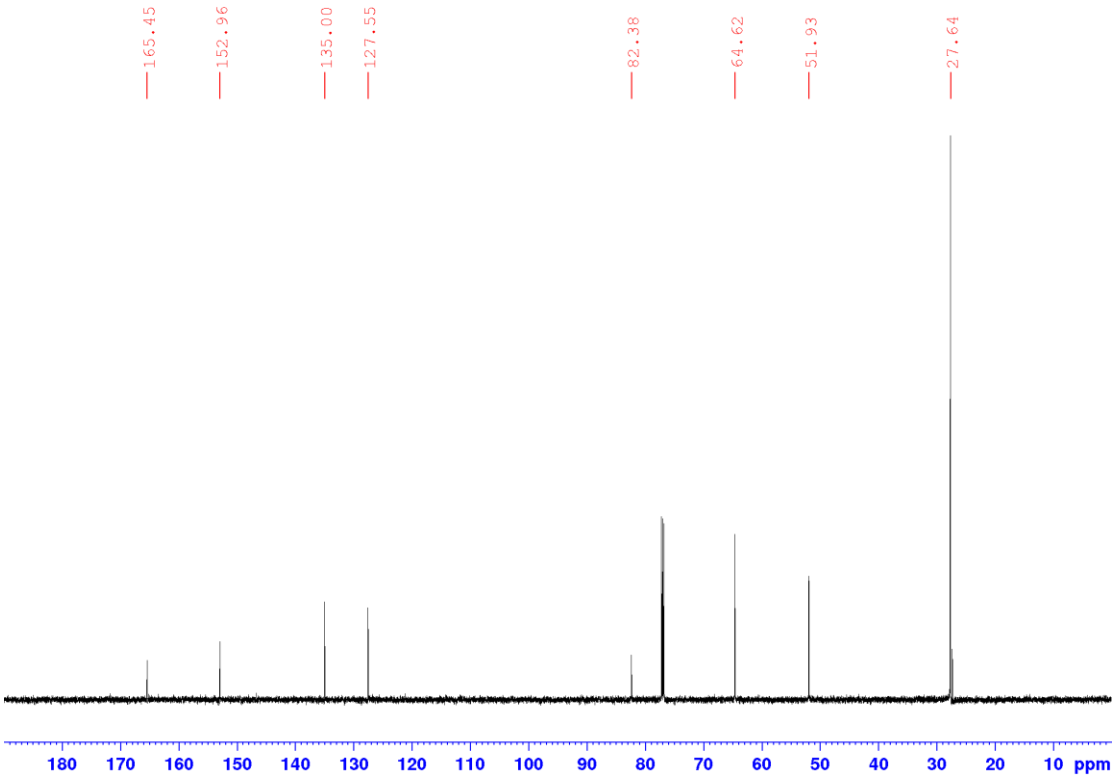

155.61
142.76
134.32
131.30
130.88
128.82
127.75
127.57
127.27
126.14
126.03
125.19
125.04
124.83
124.73
124.55
124.45
118.04
70.60
54.91
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

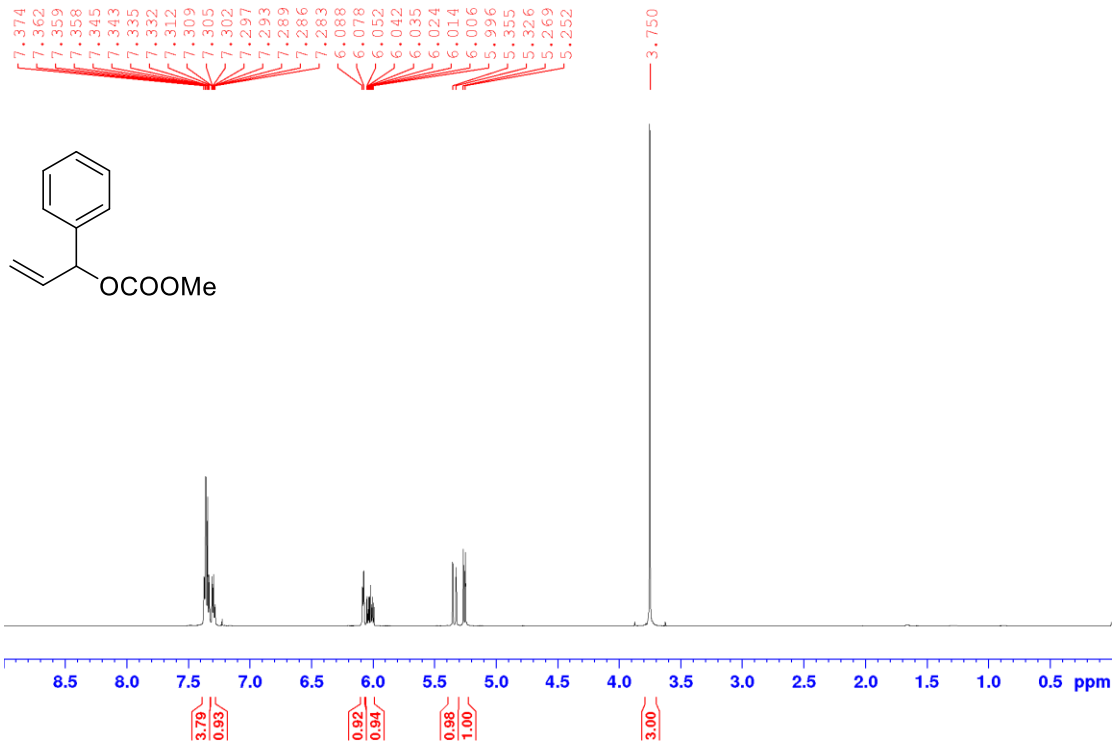

7.068
7.057
7.053
7.042
5.561
5.492
4.940
3.798
F
F
F
OCOOMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.94
1.00
0.98
2.00
3.00

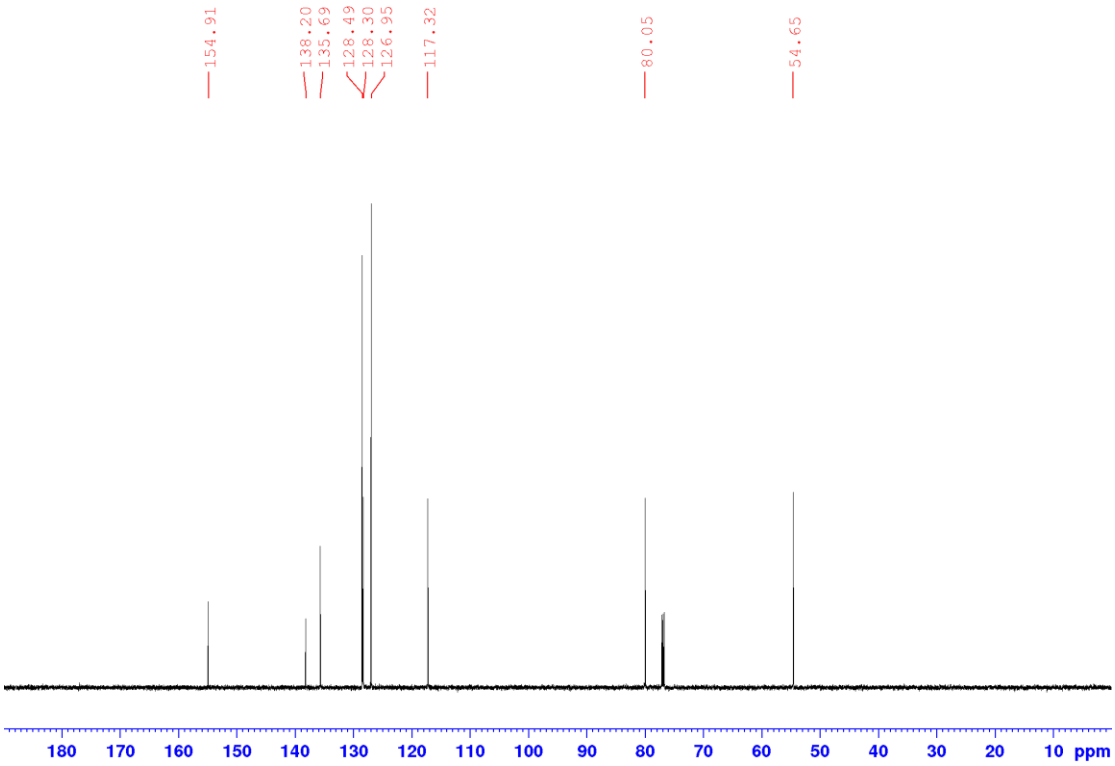

155.39
152.03
151.99
151.97
150.41
150.38
150.31
140.37
139.64
138.69
133.89
133.86
118.37
110.42
110.39
110.31
110.28
68.53
55.01
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

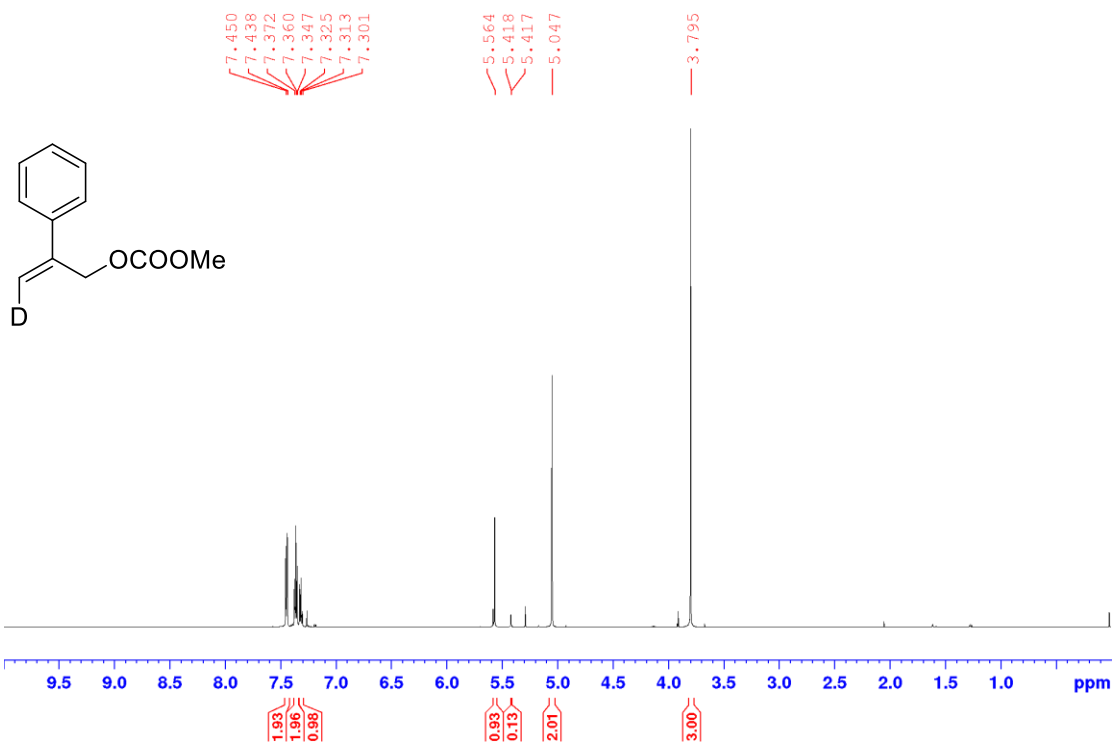

-134.06
-134.09
-160.76
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

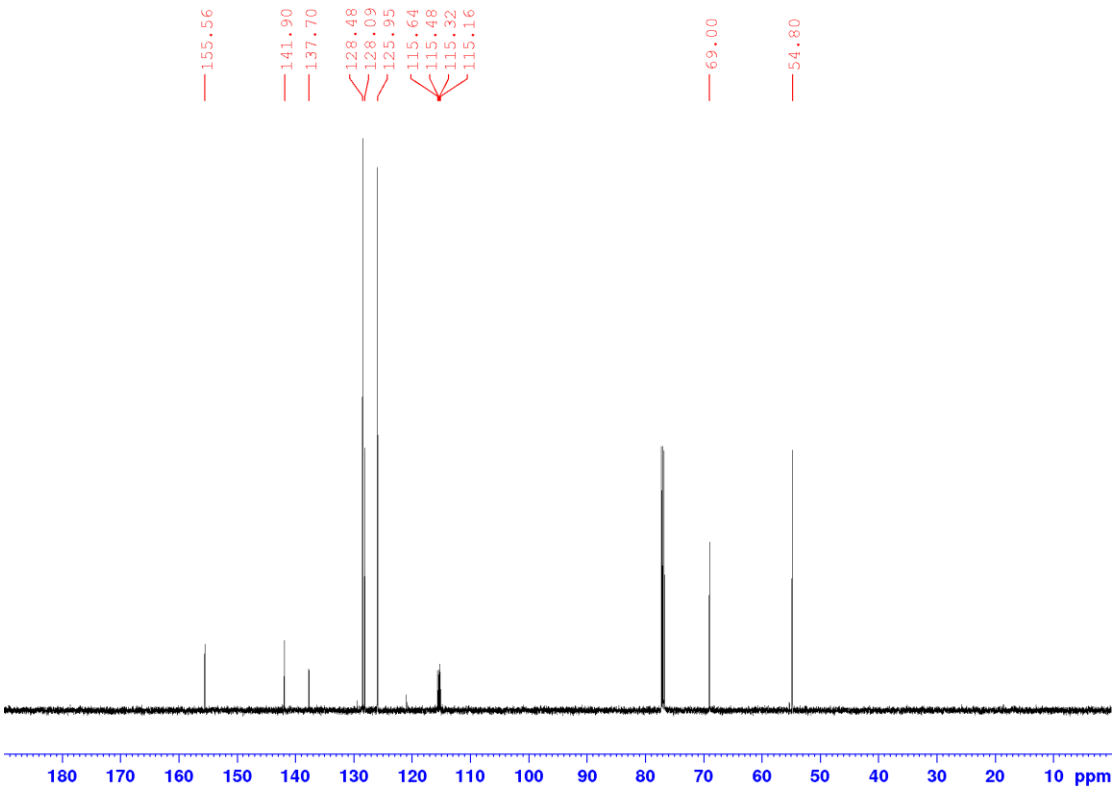

6.340
5.853
4.762
3.748
1.458
OBoc
COOMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.00
2.00
2.93
8.83

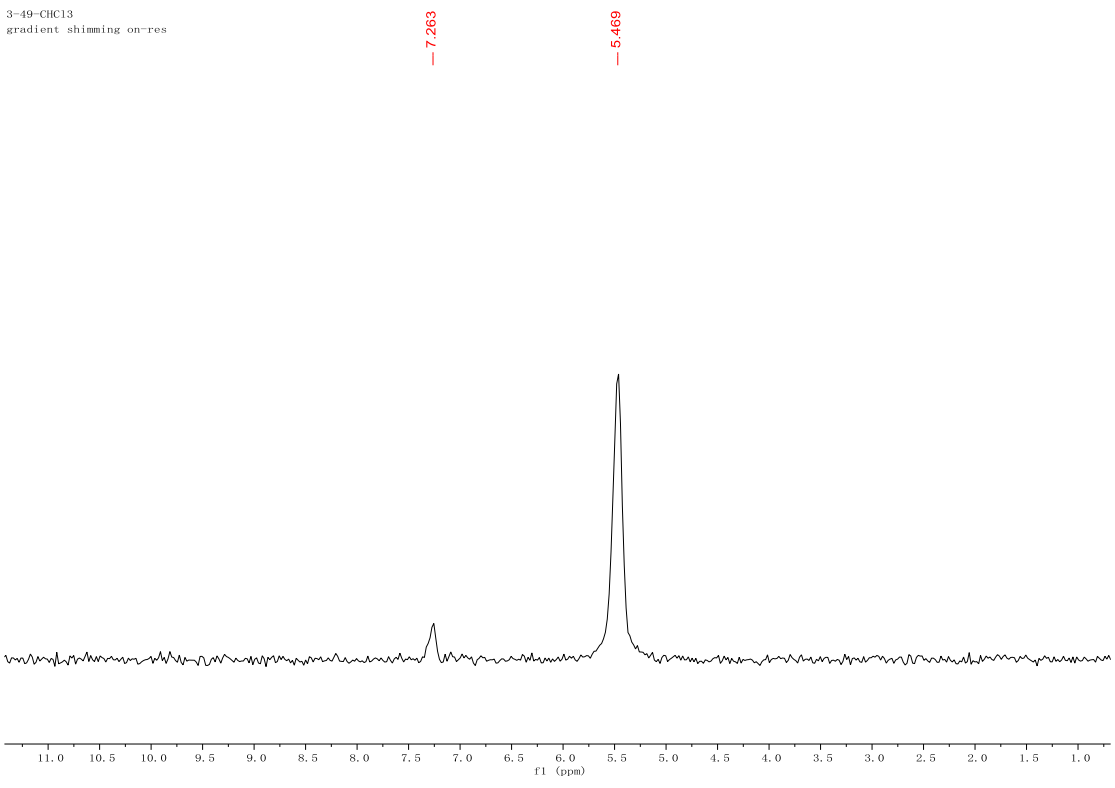

165.45
152.96
135.00
127.55
82.38
64.62
51.93
27.64
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

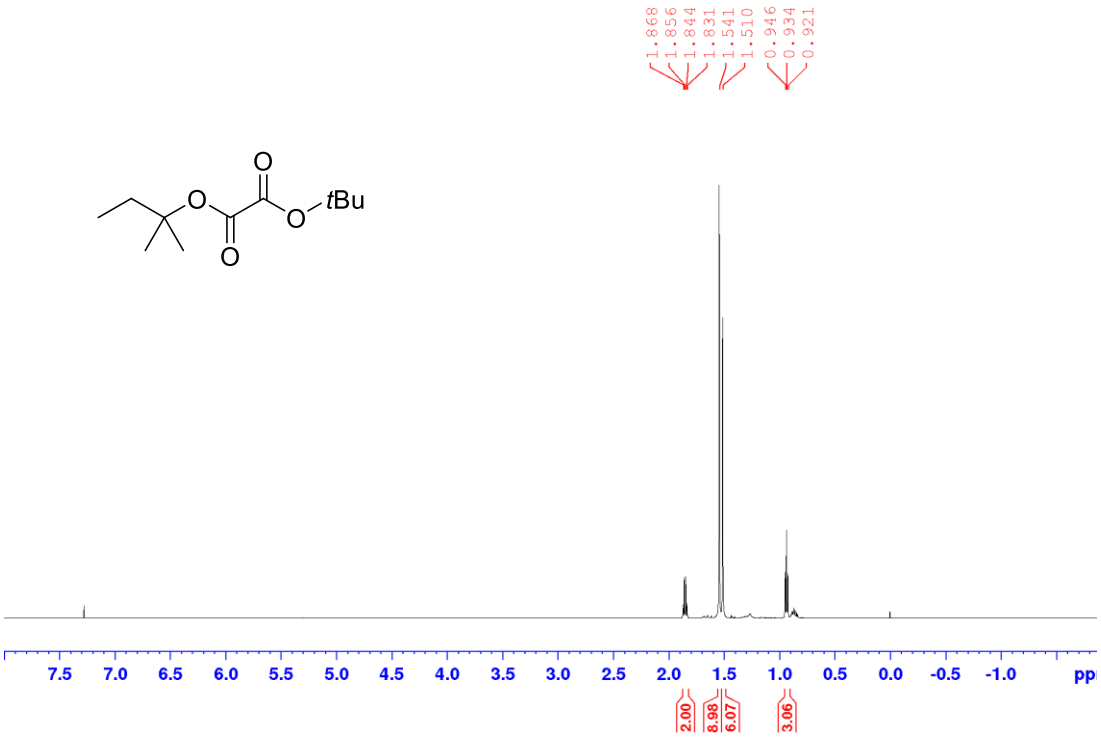

7.374
7.362
7.359
7.358
7.345
7.343
7.335
7.332
7.312
7.309
7.305
7.302
7.297
7.293
7.289
7.286
7.283
6.088
6.078
6.052
6.042
6.035
6.024
6.014
6.006
5.996
5.355
5.326
5.269
5.252
3.750
OCOOMe
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.79
0.93
0.92
0.94
0.98
1.00
3.00

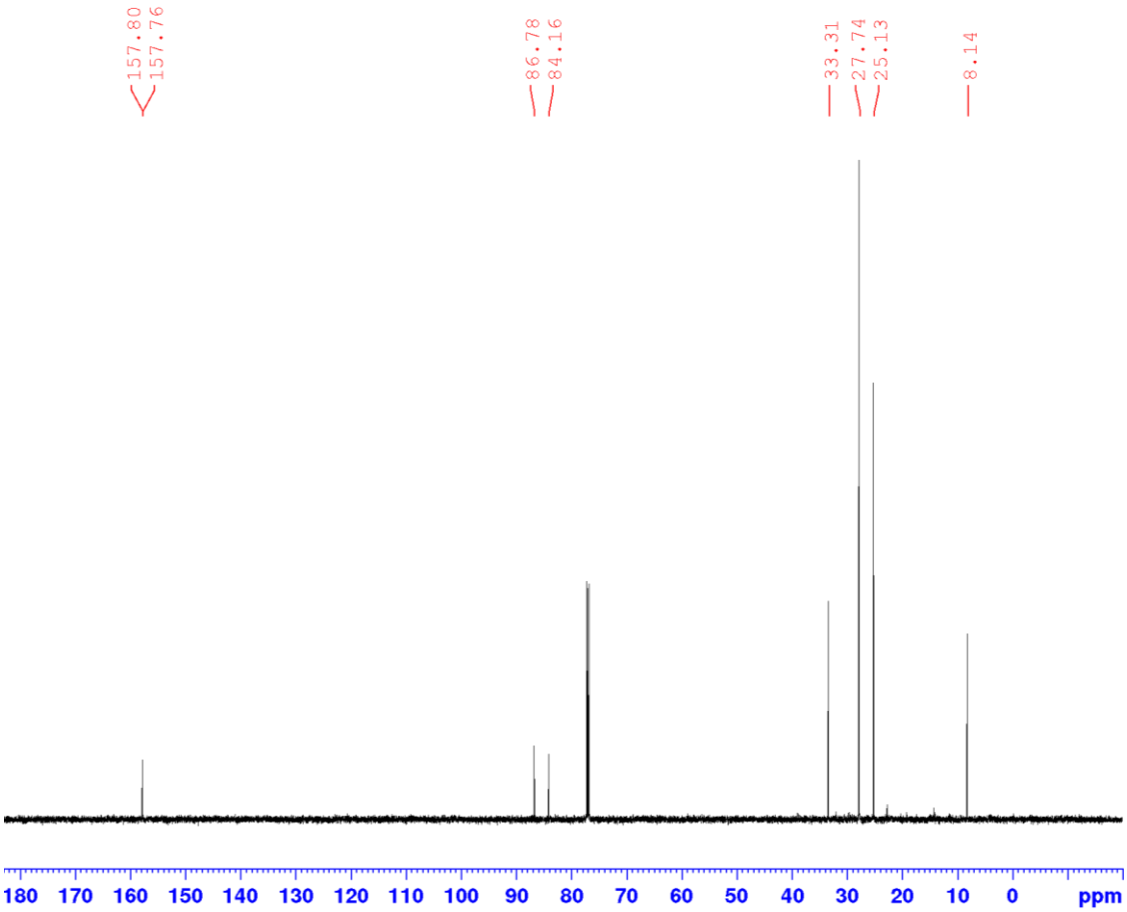

154.91
138.20
135.69
128.49
128.30
126.95
117.32
80.05
54.65
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

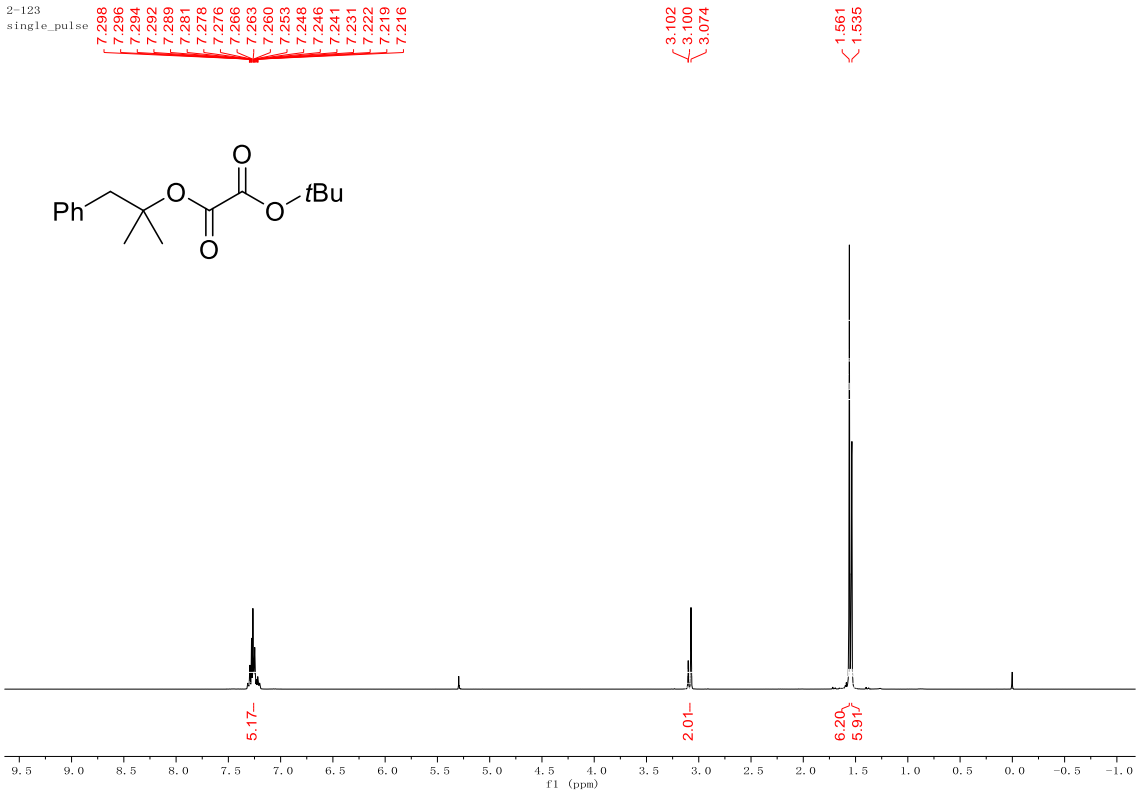

7.450
7.438
7.372
7.360
7.347
7.325
7.313
7.301
5.564
5.418
5.417
5.047
3.795
OCOOMe
D
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.93
1.96
0.98
0.93
0.13
2.01
3.00

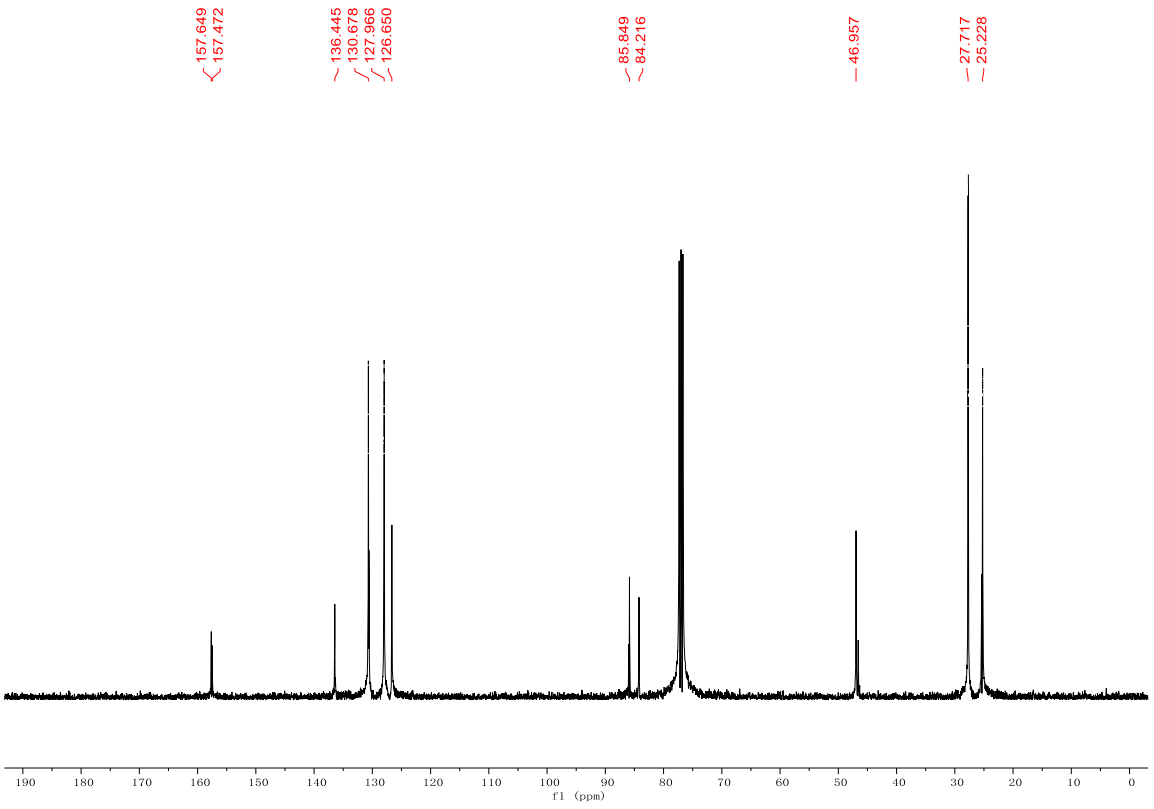

155.56
141.90
137.70
128.48
128.09
125.95
115.64
115.48
115.32
115.16
69.00
54.80
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

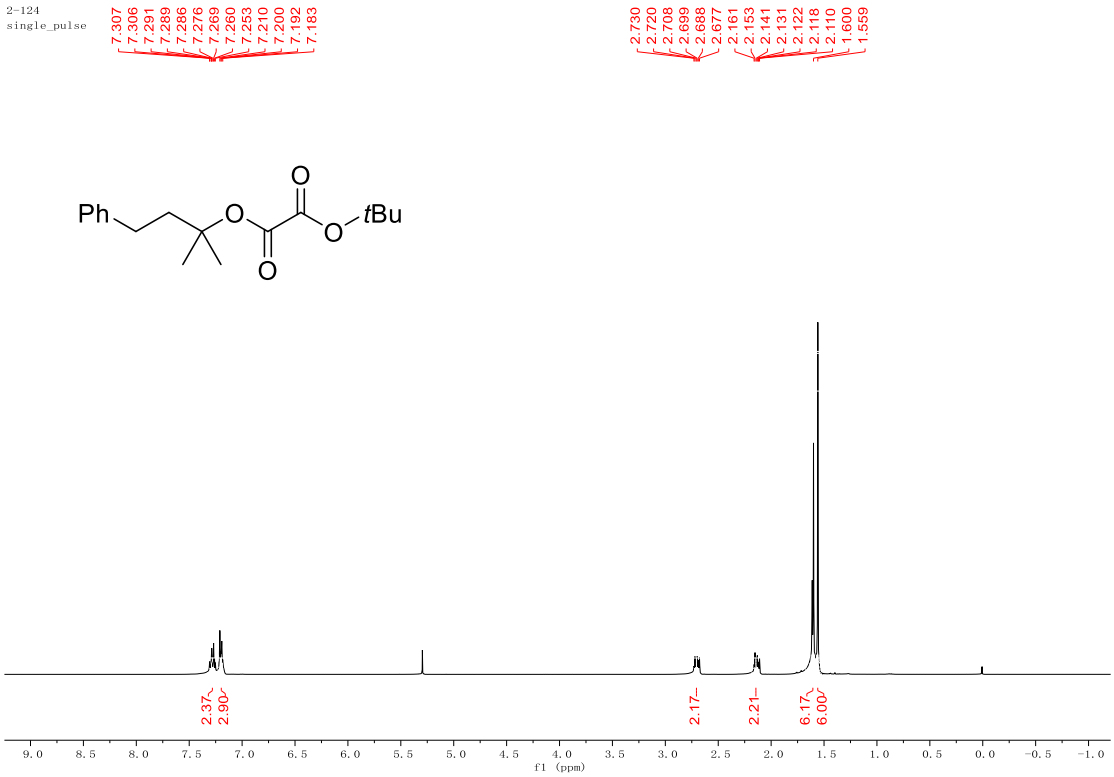

3-49-CHC13
gradient shimming on-res
7.263
5.469
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

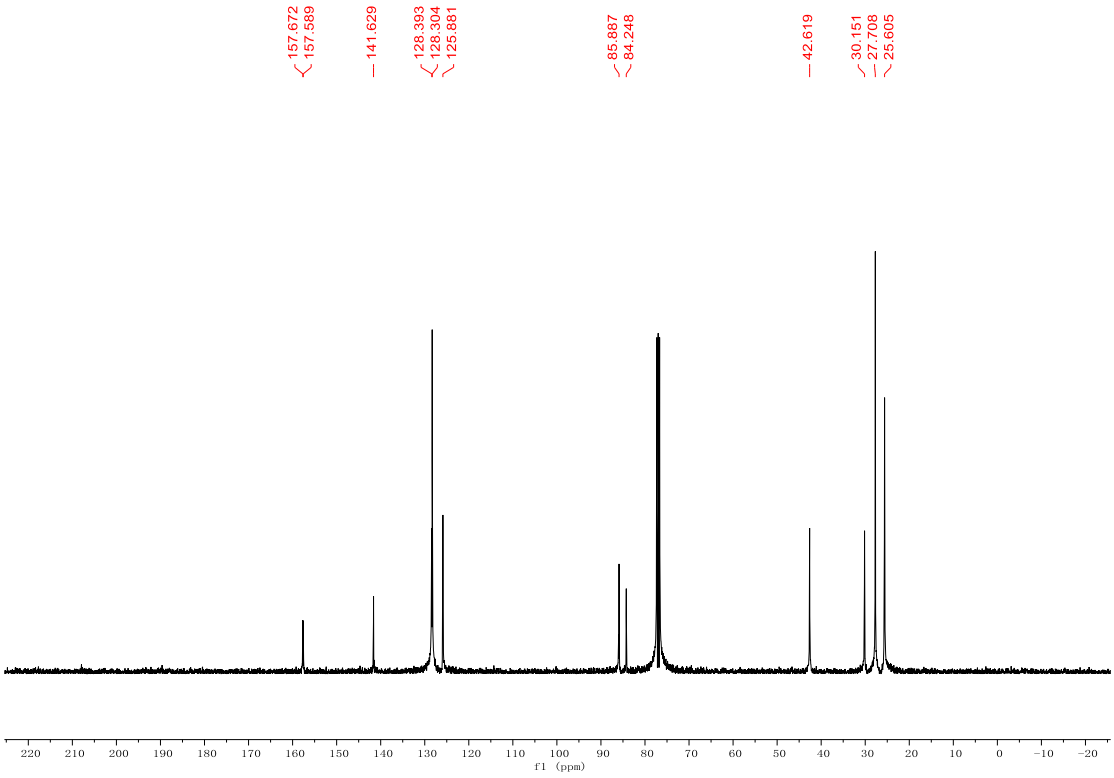

1.868
1.856
1.844
1.831
1.541
1.510
0.946
0.934
0.921
O
O
O
O
tBu
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
2.00
8.98
6.07
3.06


157.80
157.76
86.78
84.16
33.31
27.74
25.13
8.14
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

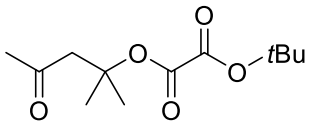

2-123
single_pulse
7.298
7.296
7.294
7.292
7.289
7.281
7.278
7.276
7.266
7.263
7.260
7.253
7.248
7.246
7.241
7.231
7.222
7.219
7.216
3.102
3.100
3.074
1.561
1.535
Ph
O
O
O
O
tBu
5.17
2.01
6.20
5.91
f1 (ppm)

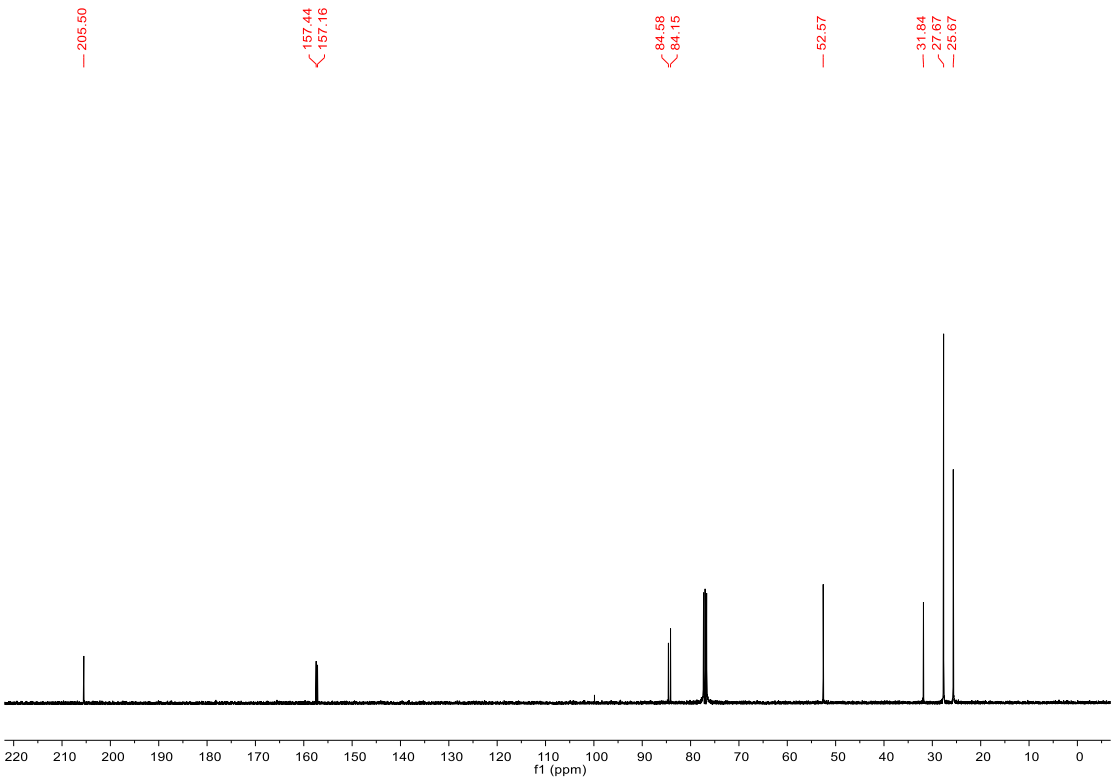

157.649
157.472
136.445
130.678
127.966
126.650
85.849
84.216
46.957
27.717
25.228
f1 (ppm)


2-124
single_pulse
7.307
7.306
7.291
7.289
7.286
7.276
7.269
7.260
7.253
7.210
7.200
7.192
7.183
2.730
2.720
2.708
2.699
2.688
2.677
2.161
2.153
2.141
2.131
2.122
2.118
2.110
1.600
1.559
Ph
O
O
O
O
tBu
2.37
2.90
2.17
2.21
6.17
6.00
f1 (ppm)

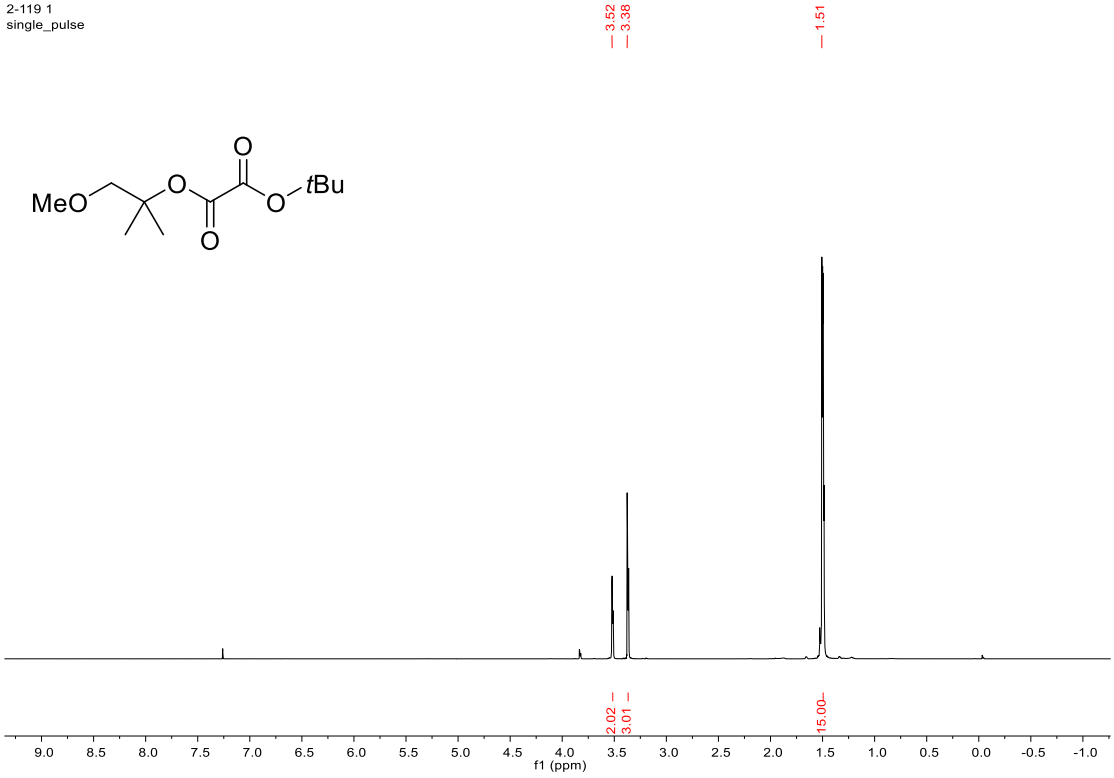


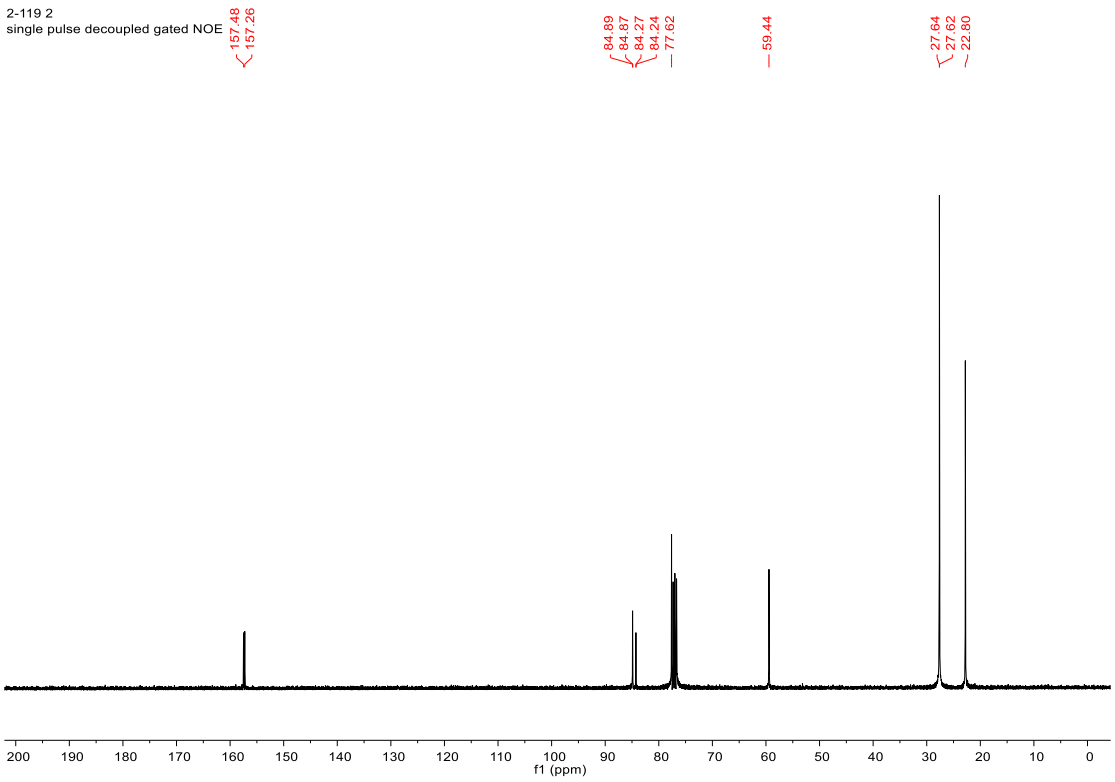
2-120
single_pulse

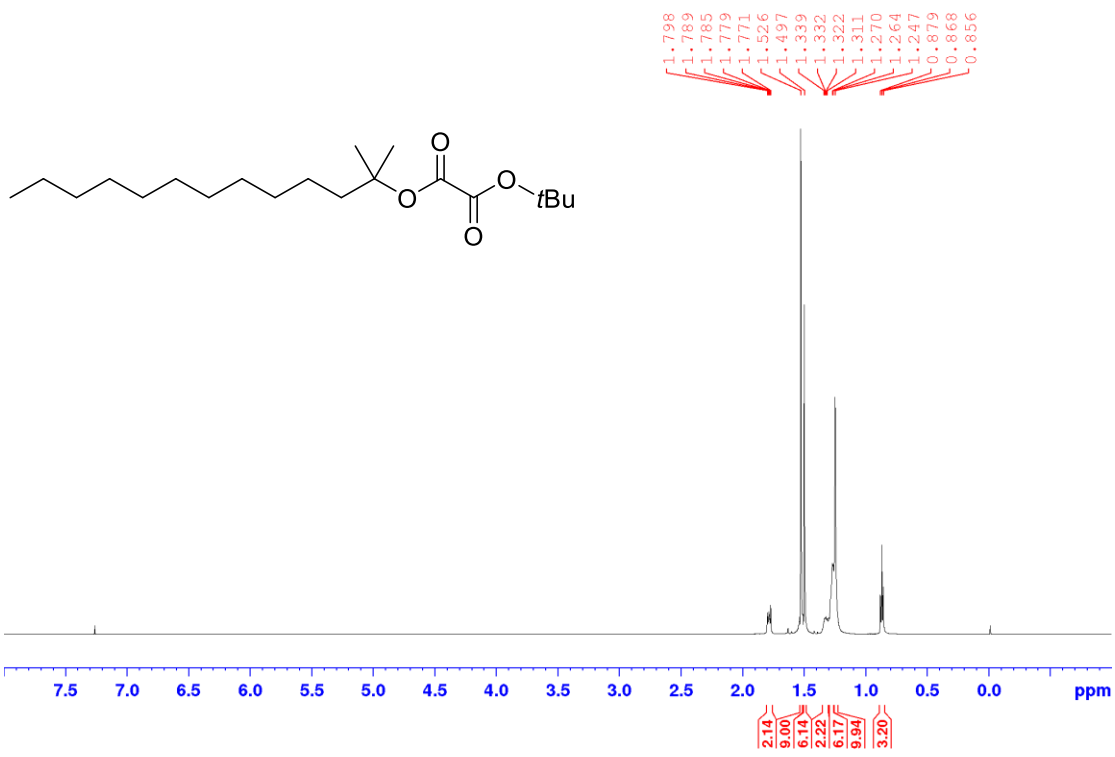


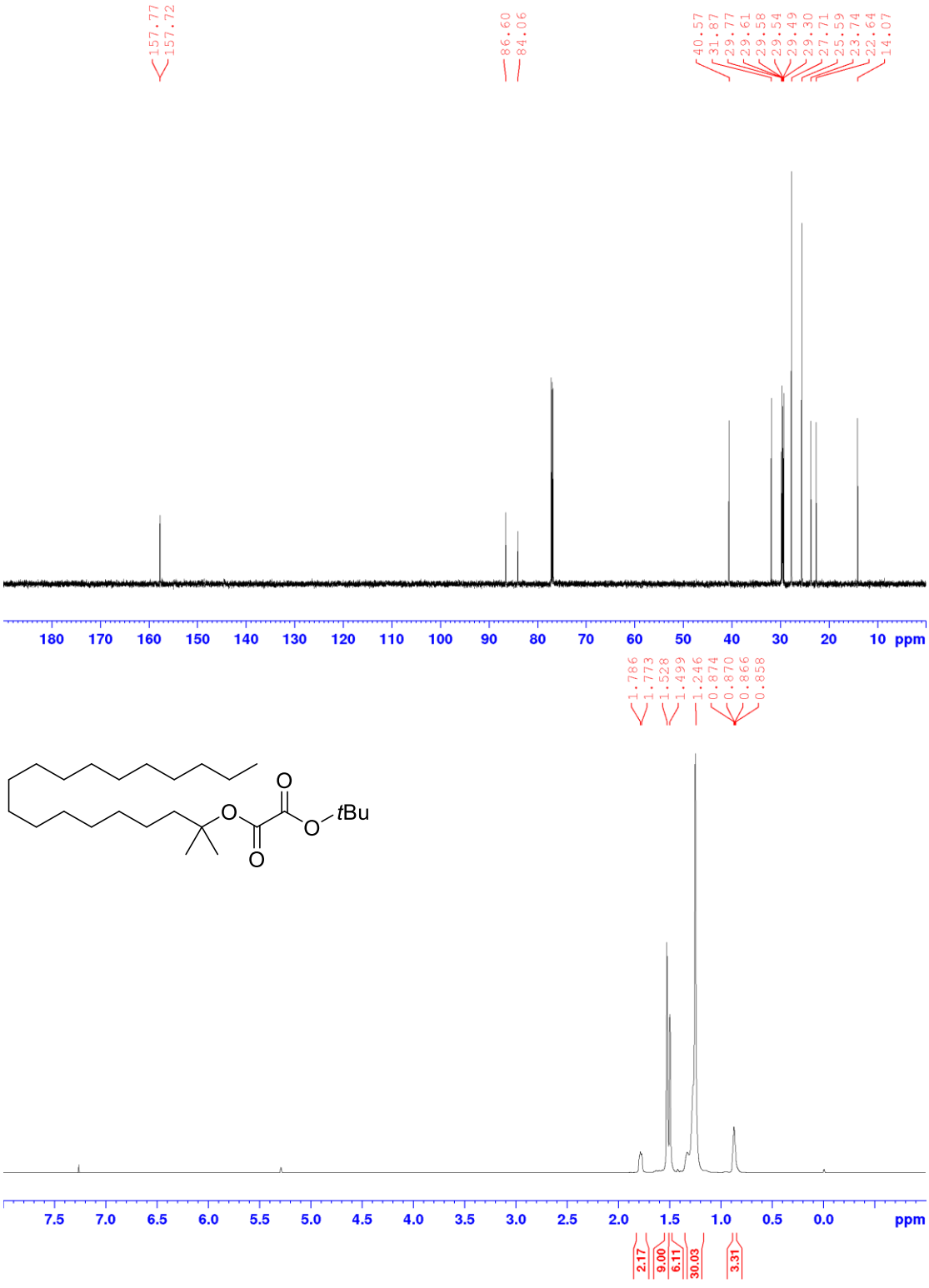


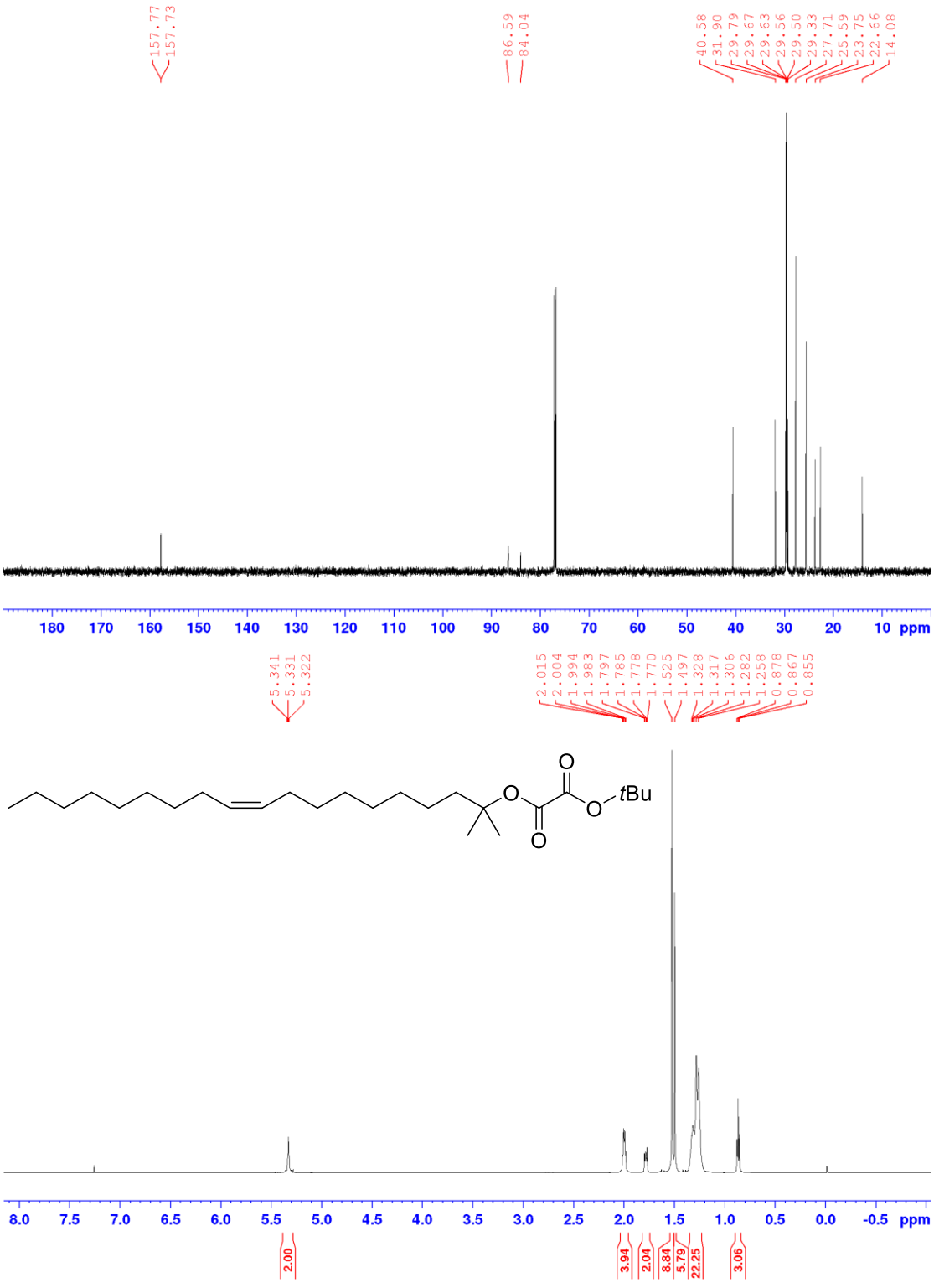
2-119 1
single_pulse

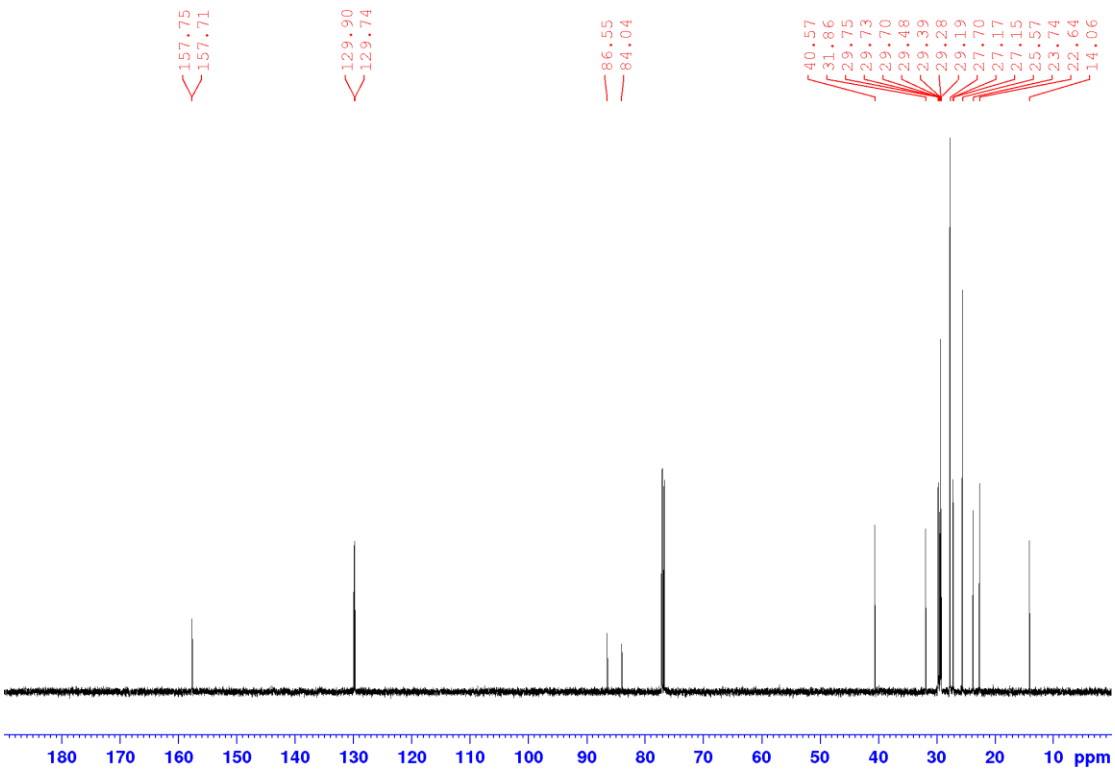


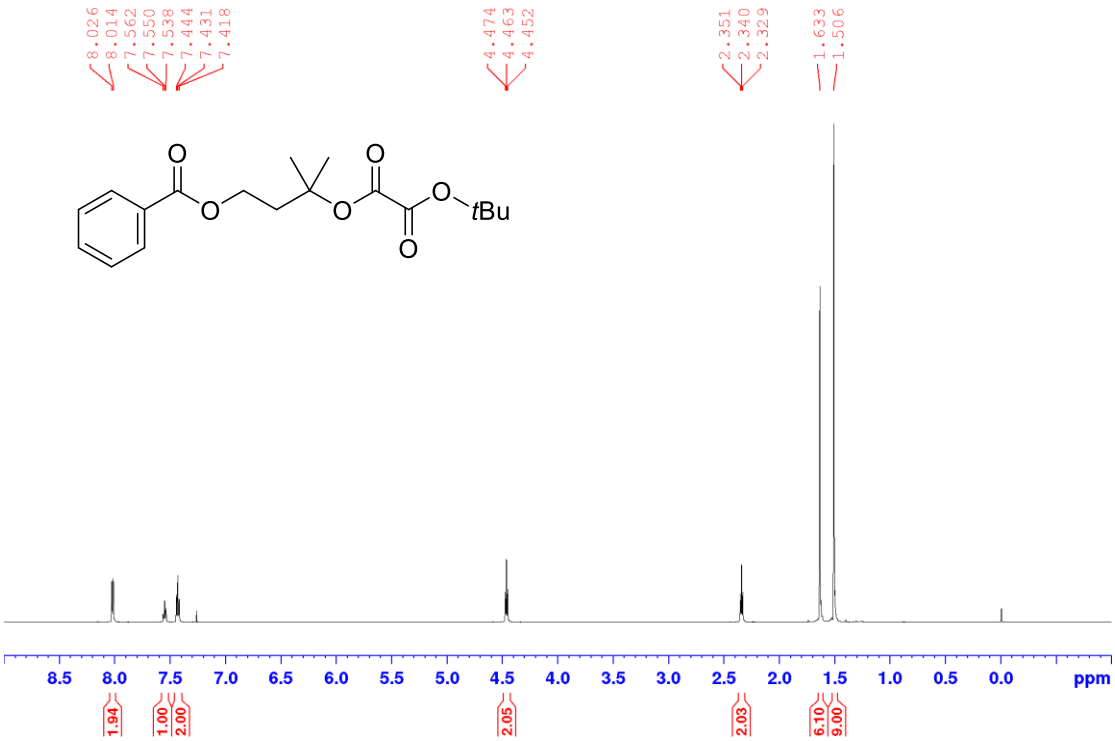

2-119 2
single pulse decoupled gated NOE
157.48
157.26
84.89
84.87
84.27
84.24
77.62
59.44
27.64
27.62
22.80
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

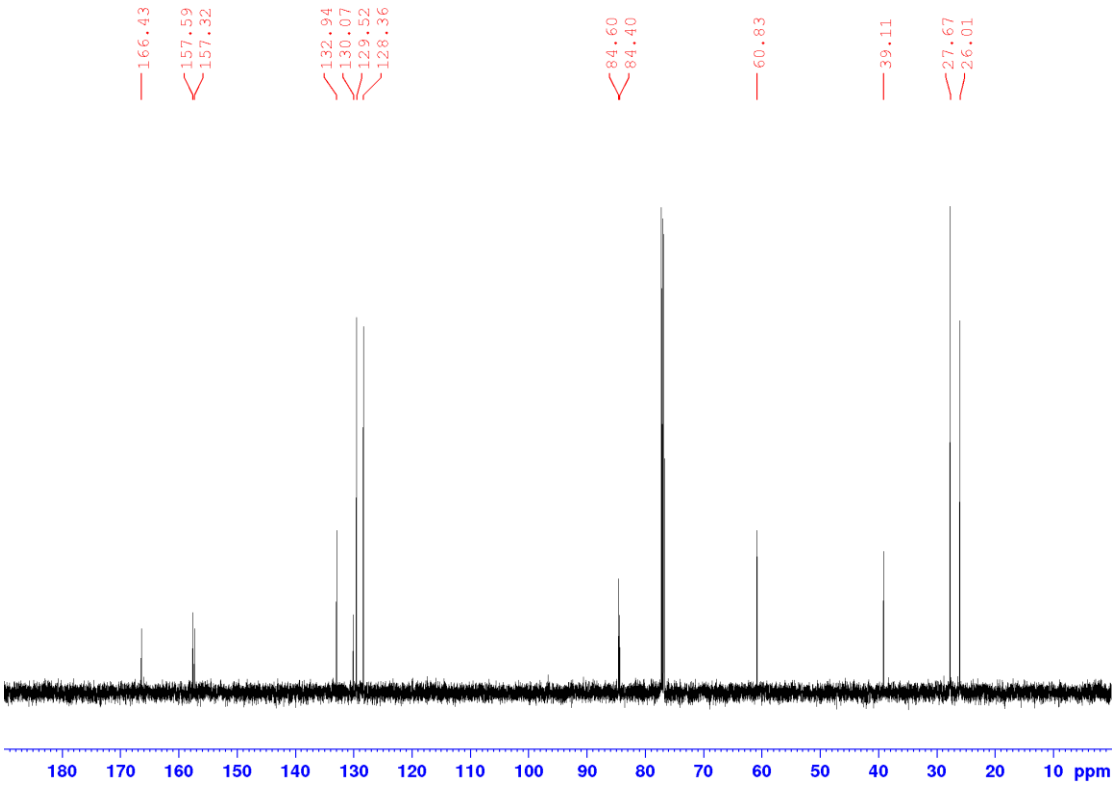

1.798
1.789
1.785
1.779
1.771
1.526
1.497
1.339
1.332
1.322
1.311
1.270
1.264
1.247
0.879
0.868
0.856
O
O
O
O
tBu
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.14
9.00
6.14
2.22
6.17
9.94
3.20

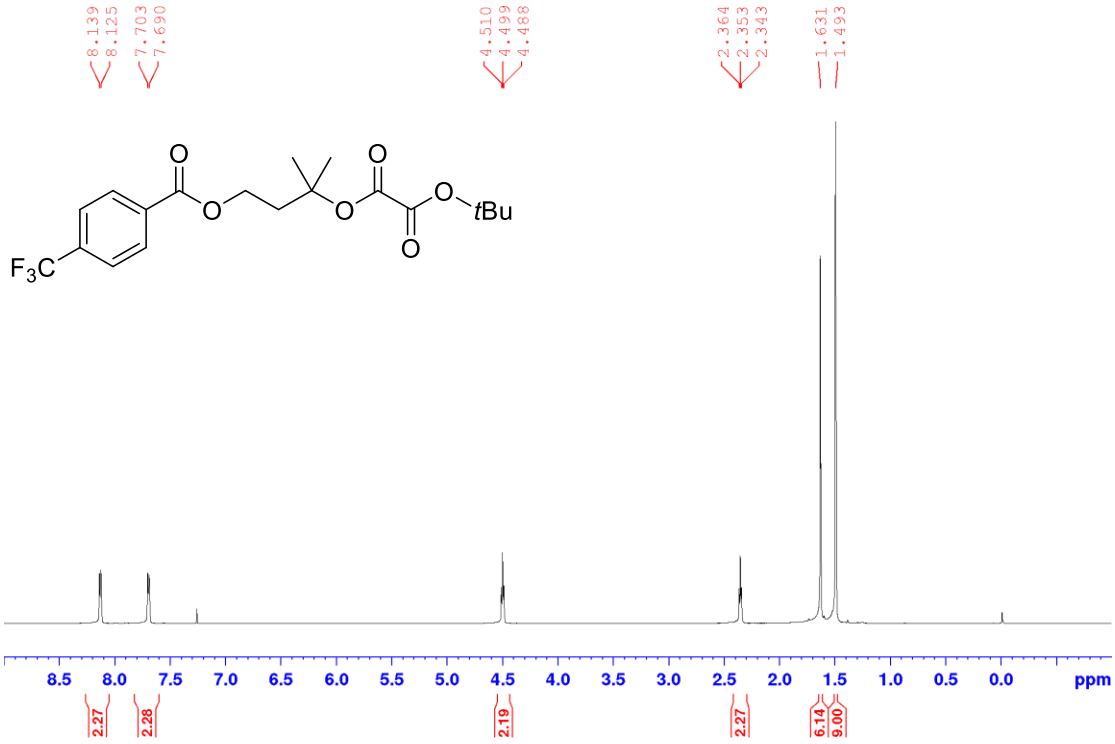

157.77
157.72
86.60
84.06
40.57
31.87
29.77
29.61
29.58
29.54
29.49
29.30
27.71
25.59
23.74
22.64
14.07
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
1.786
1.773
1.528
1.499
1.246
0.874
0.870
0.866
0.858
O
O
O
O
tBu
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.17
9.00
6.11
30.03
3.31

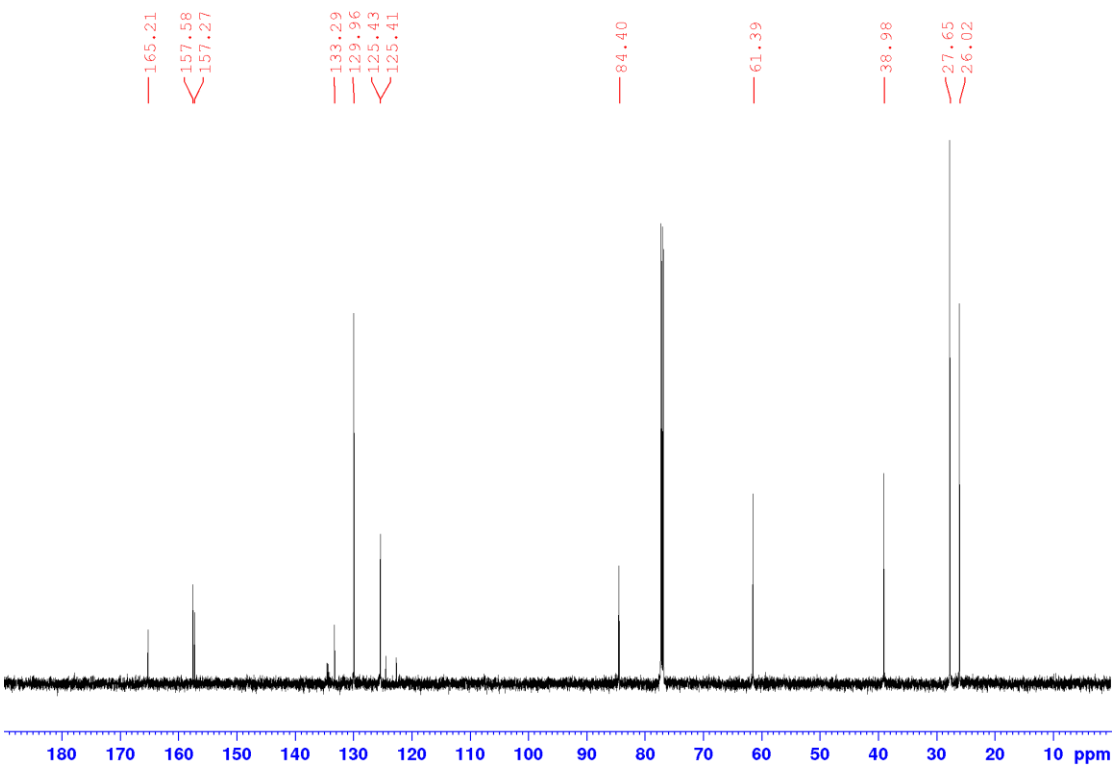

157.77
157.73
86.59
84.04
40.58
31.90
29.79
29.67
29.63
29.56
29.50
29.33
27.71
25.59
23.75
22.66
14.08
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
5.341
5.331
5.322
2.015
2.004
1.994
1.983
1.797
1.785
1.778
1.770
1.525
1.497
1.328
1.317
1.306
1.282
1.258
0.878
0.867
0.855
O
O
O
O
tBu
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 ppm
2.00
3.94
2.04
8.84
5.79
22.25
3.06


157.75
157.71
129.90
129.74
86.55
84.04
40.57
31.86
29.75
29.73
29.70
29.48
29.39
29.28
29.19
27.70
27.17
27.15
25.57
23.74
22.64
14.06
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

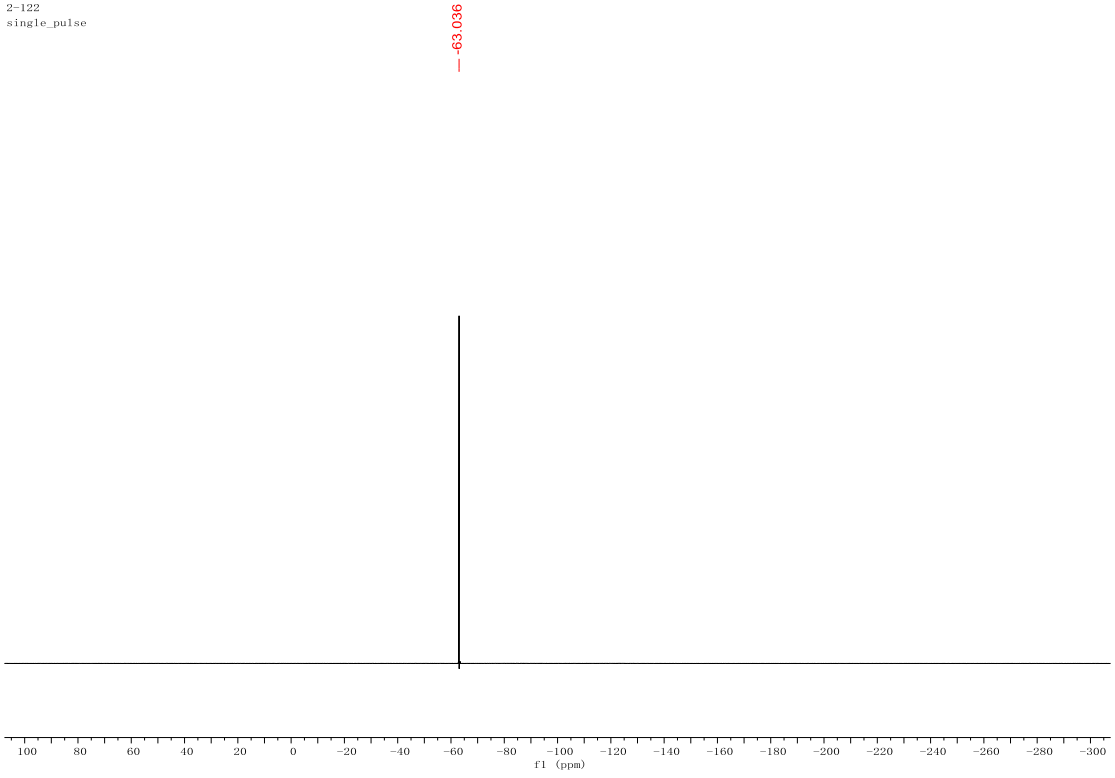

8.026
8.014
7.562
7.550
7.538
7.444
7.431
7.418
4.474
4.463
4.452
2.351
2.340
2.329
1.633
1.506
O
O
O
O
O
O
tBu
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.94
1.00
2.00
2.05
2.03
6.10
9.00

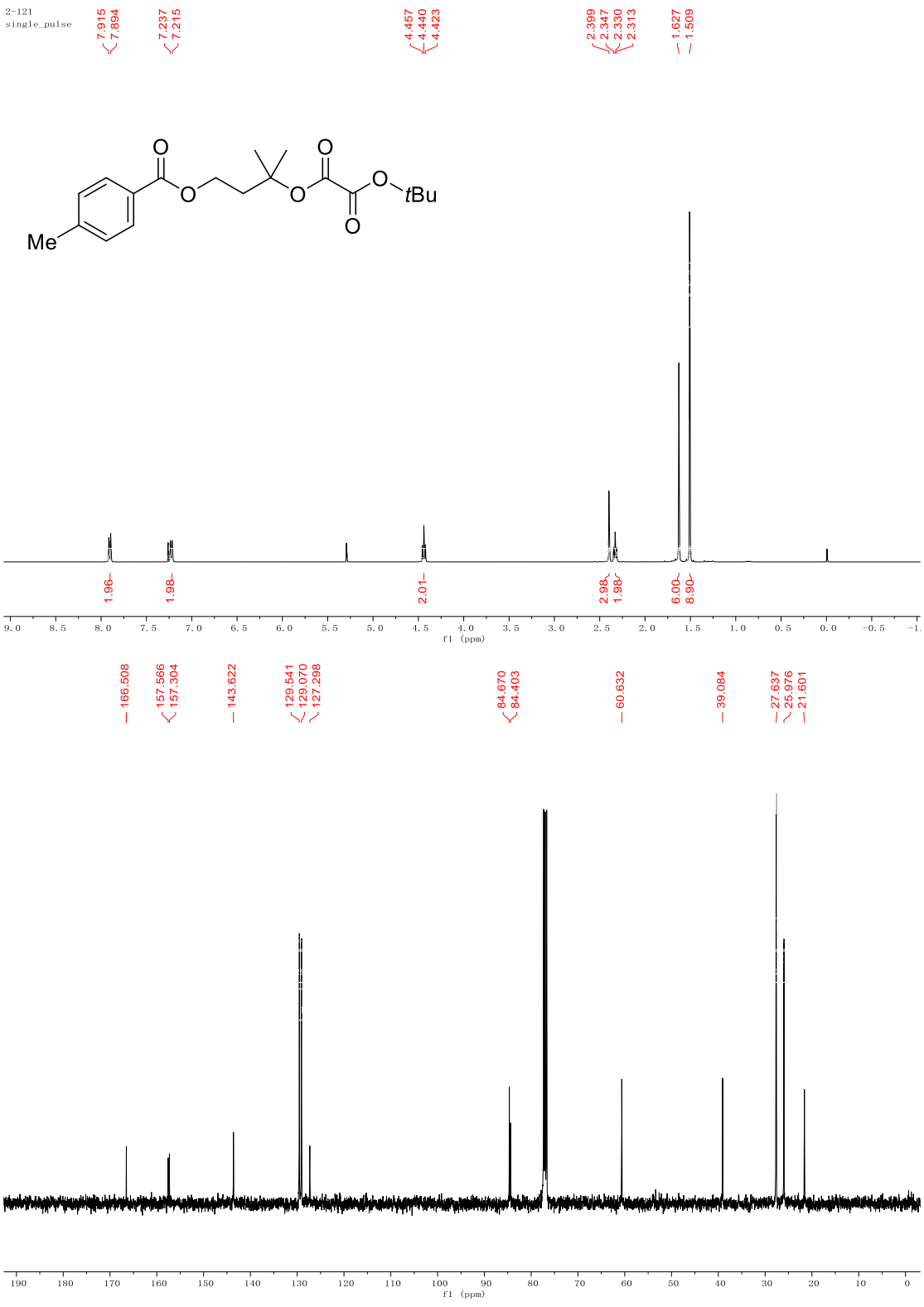

166.43
157.59
157.32
132.94
130.07
129.52
128.36
84.60
84.40
60.83
39.11
27.67
26.01
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

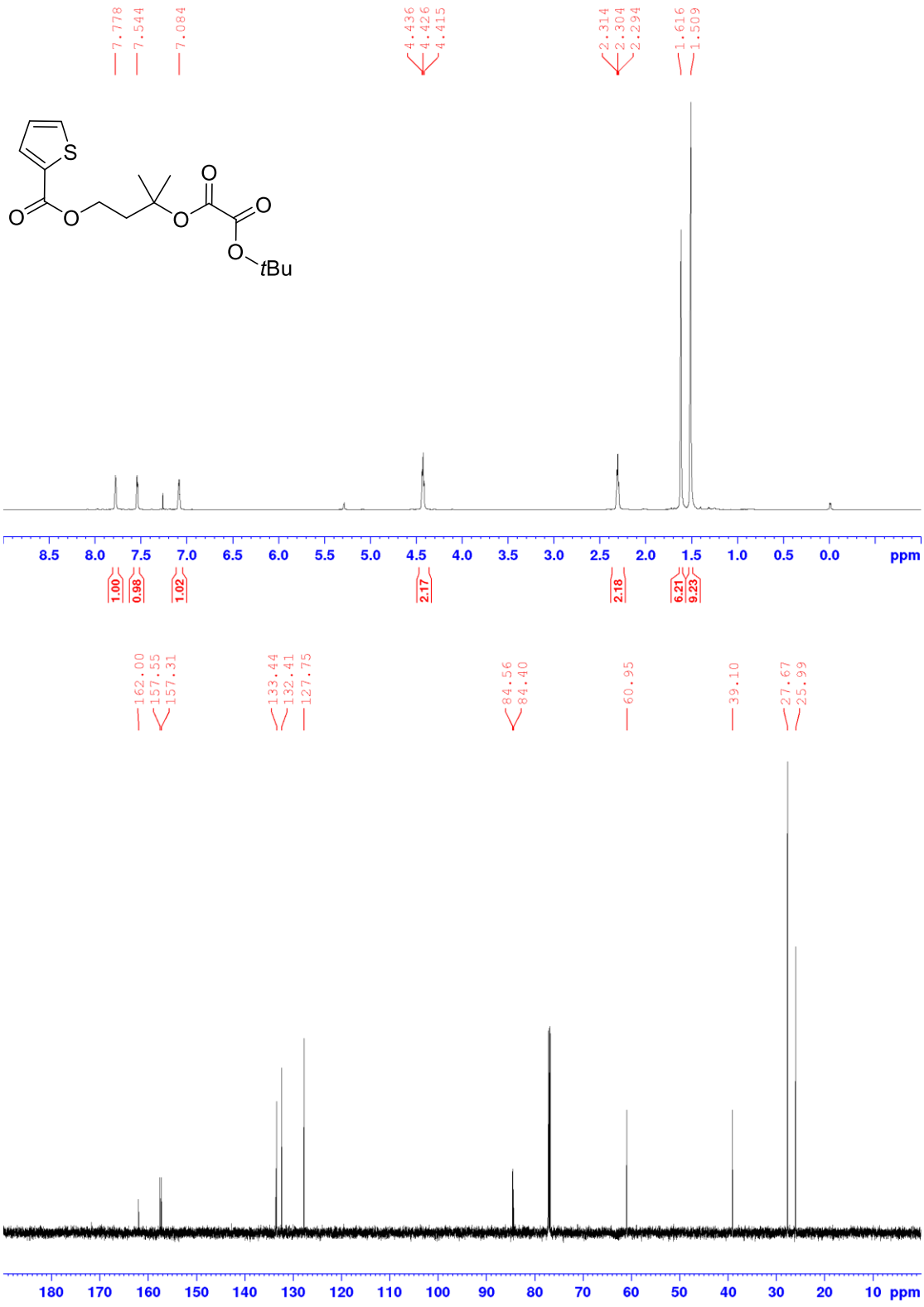

8.139
8.125
7.703
7.690
4.510
4.499
4.488
2.364
2.353
2.343
1.631
1.493
O
O
O
O
O
O
tBu
F3C
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.27
2.28
2.19
2.27
6.14
9.00

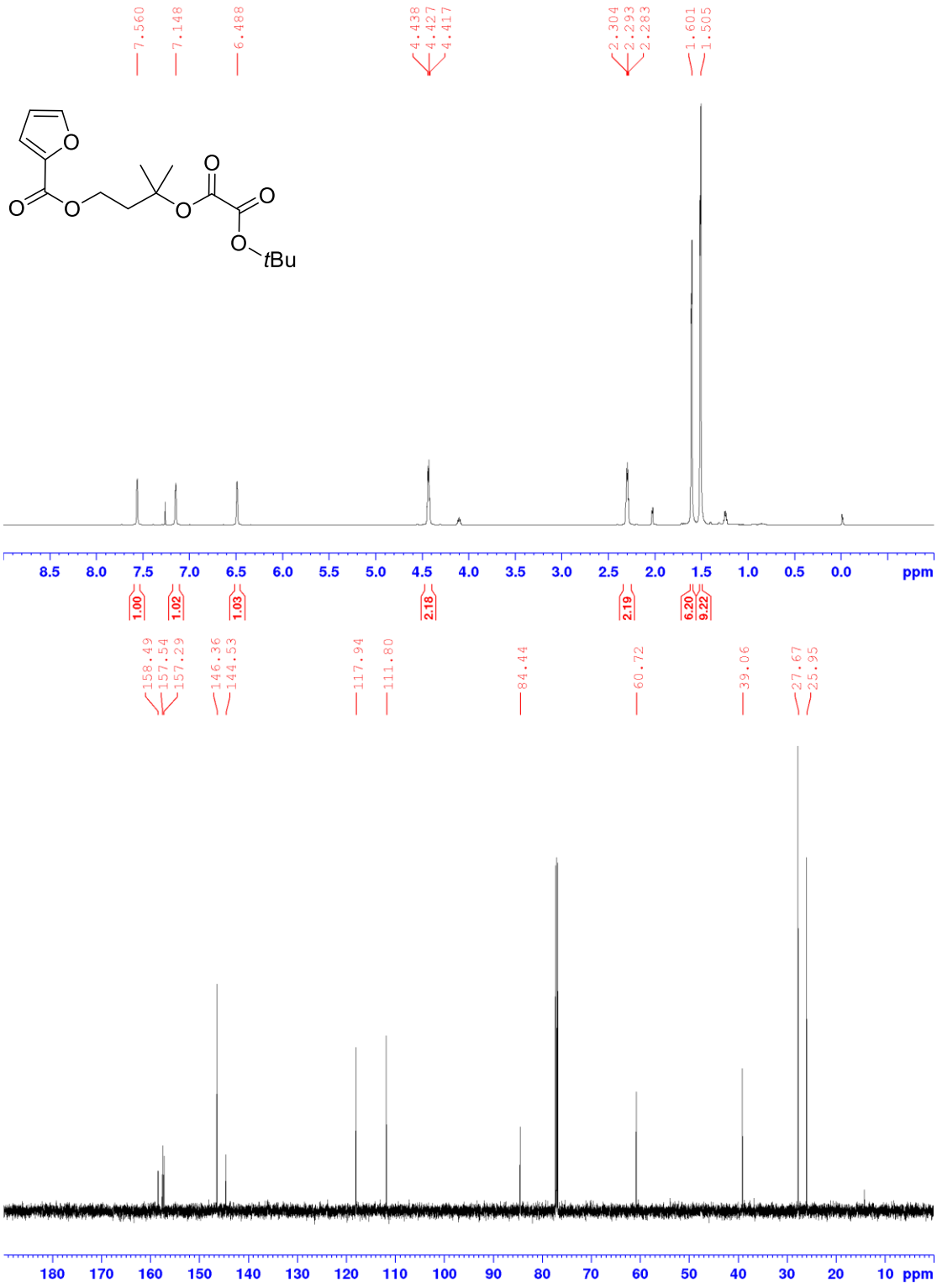


2-122
single_pulse

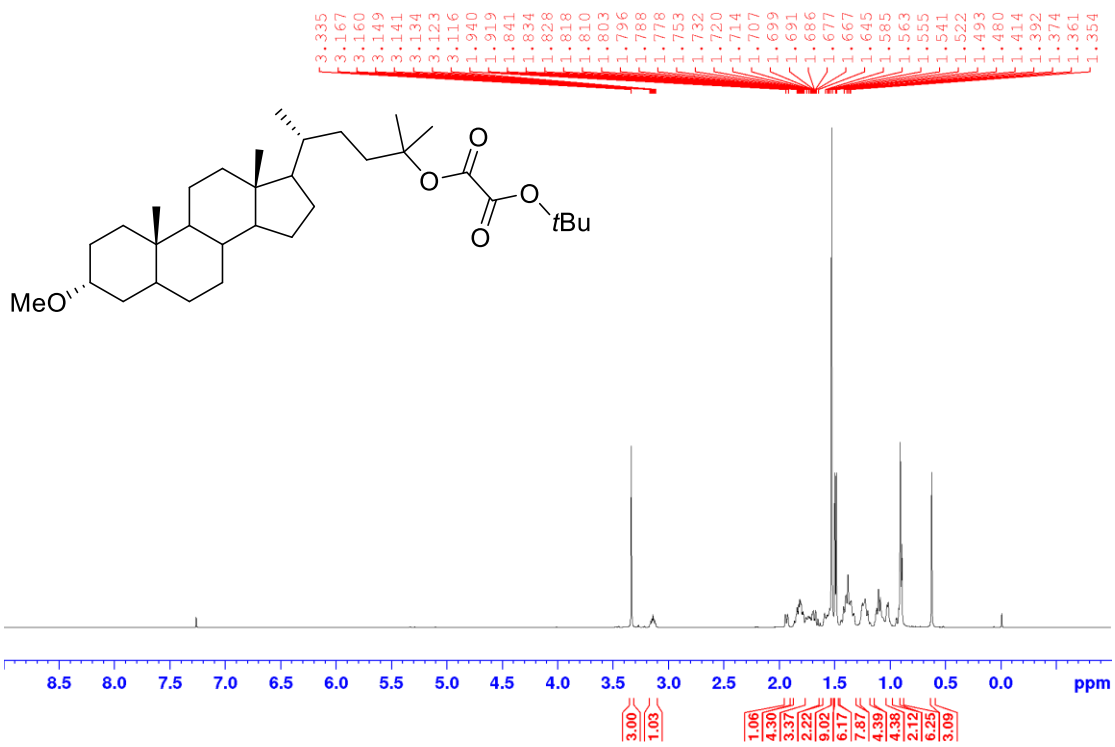


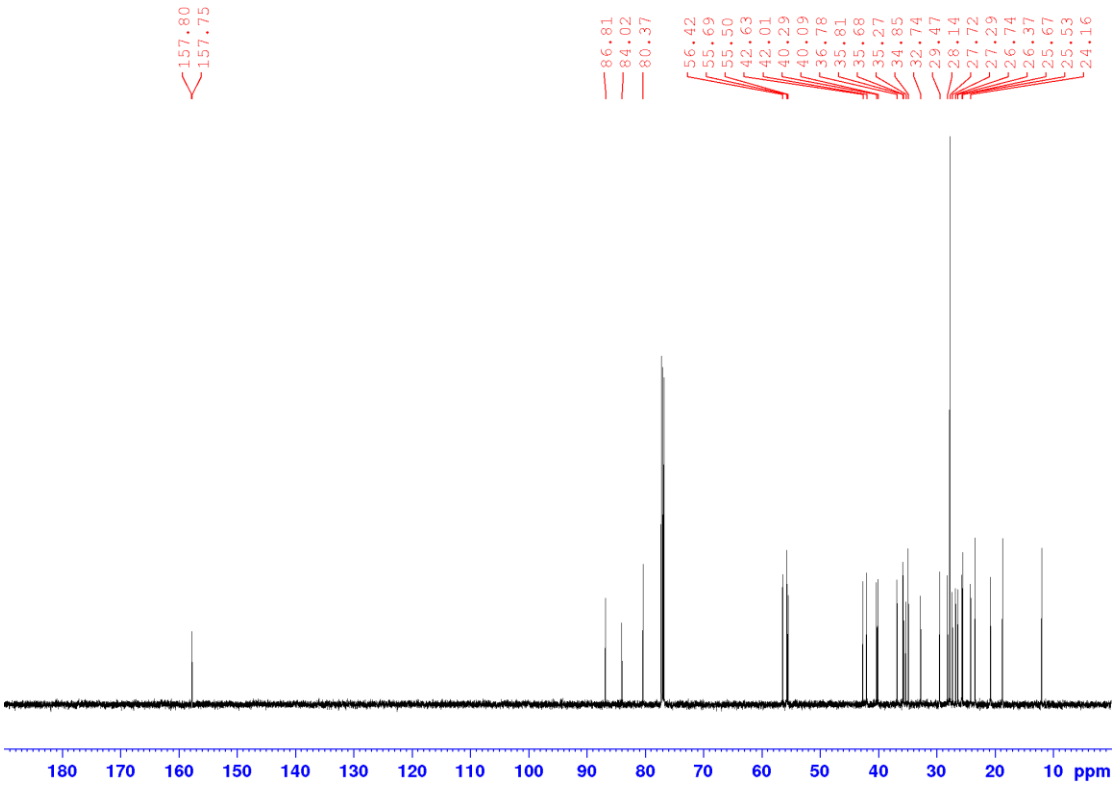

2-121
single_pulse
7.915
7.894
7.237
7.215
4.457
4.440
4.423
2.399
2.347
2.330
2.313
1.627
1.509
Me
tBu
1.96
1.98
2.01
2.98
1.98
6.00
8.90
f1 (ppm)
166.508
157.566
157.304
143.622
129.541
129.070
127.298
84.670
84.403
60.632
39.084
27.637
25.976
21.601
f1 (ppm)

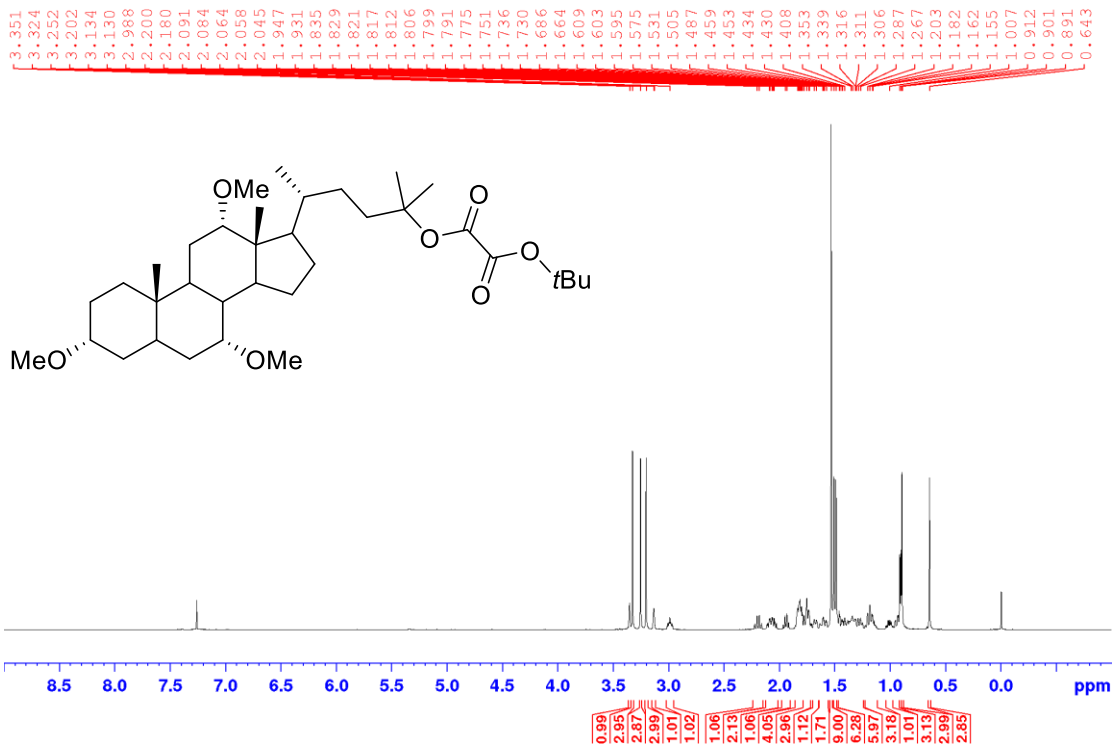

7.778
7.544
7.084
4.436
4.426
4.415
2.314
2.304
2.294
1.616
1.509
S
O
O
O
O
O
O
tBu
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
0.98
1.02
2.17
2.18
6.21
9.23
162.00
157.55
157.31
133.44
132.41
127.75
84.56
84.40
60.95
39.10
27.67
25.99
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

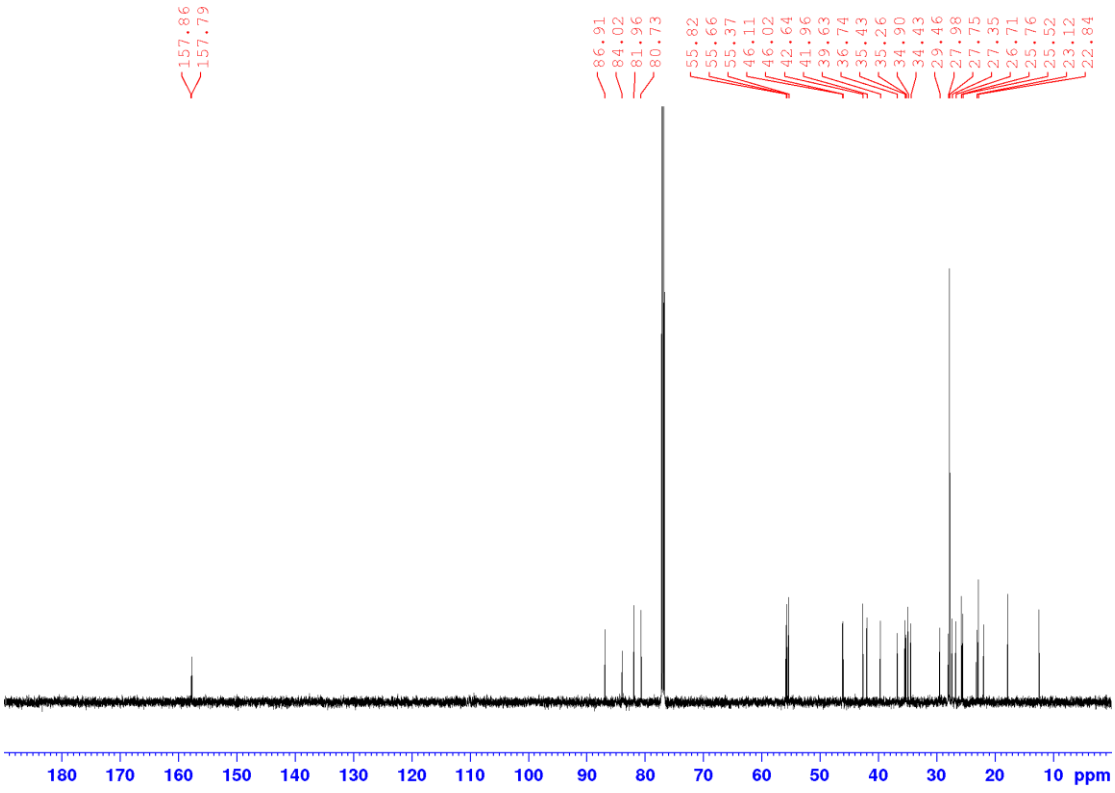

7.560
7.148
6.488
4.438
4.427
4.417
2.304
2.293
2.283
1.601
1.505
O
O
O
O
O
O
O
tBu
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.02
1.03
2.18
2.19
6.20
9.22
158.49
157.54
157.29
146.36
144.53
117.94
111.80
84.44
60.72
39.06
27.67
25.95
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

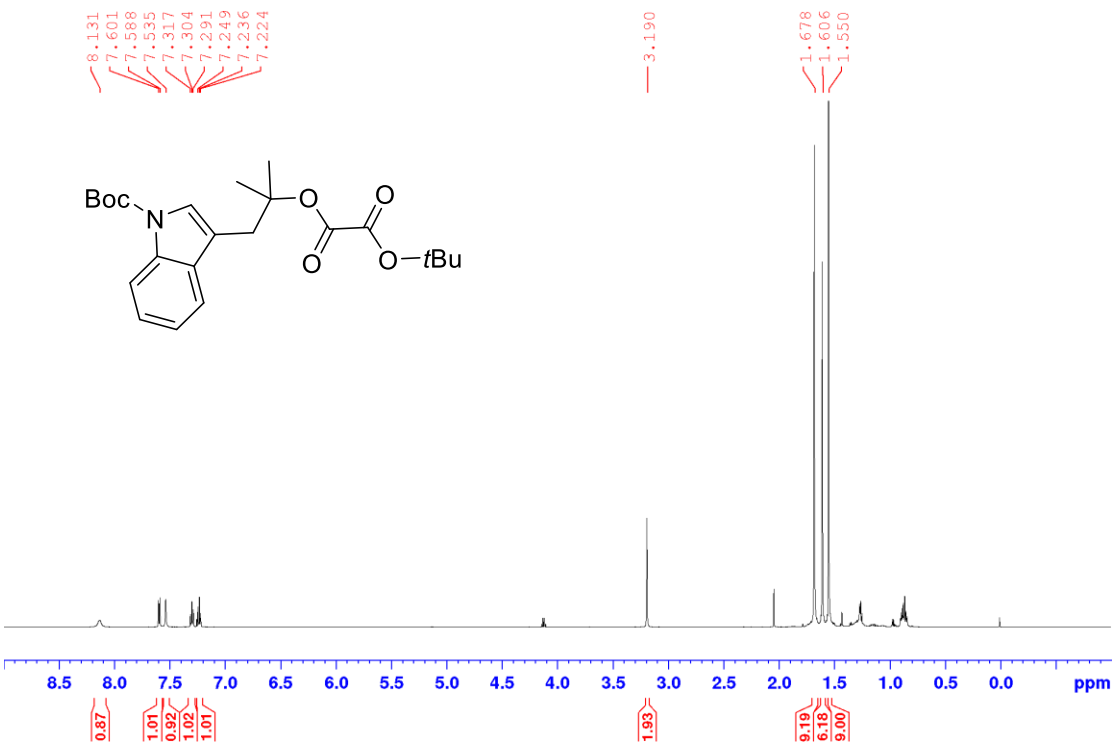

5.363
2.100
2.097
2.077
2.054
2.039
2.014
1.966
1.944
1.884
1.881
1.860
1.841
1.837
1.823
1.820
1.637
1.528
1.518
1.498
1.362
1.353
1.342
1.333
1.321
1.312
1.301
1.292
O
O
O
O
tBu
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
4.40
2.19
3.25
8.68
6.31
1.31
157.79
157.73
133.93
120.03
88.99
84.08
42.69
30.73
27.74
26.27
23.75
23.25
22.96
22.75
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

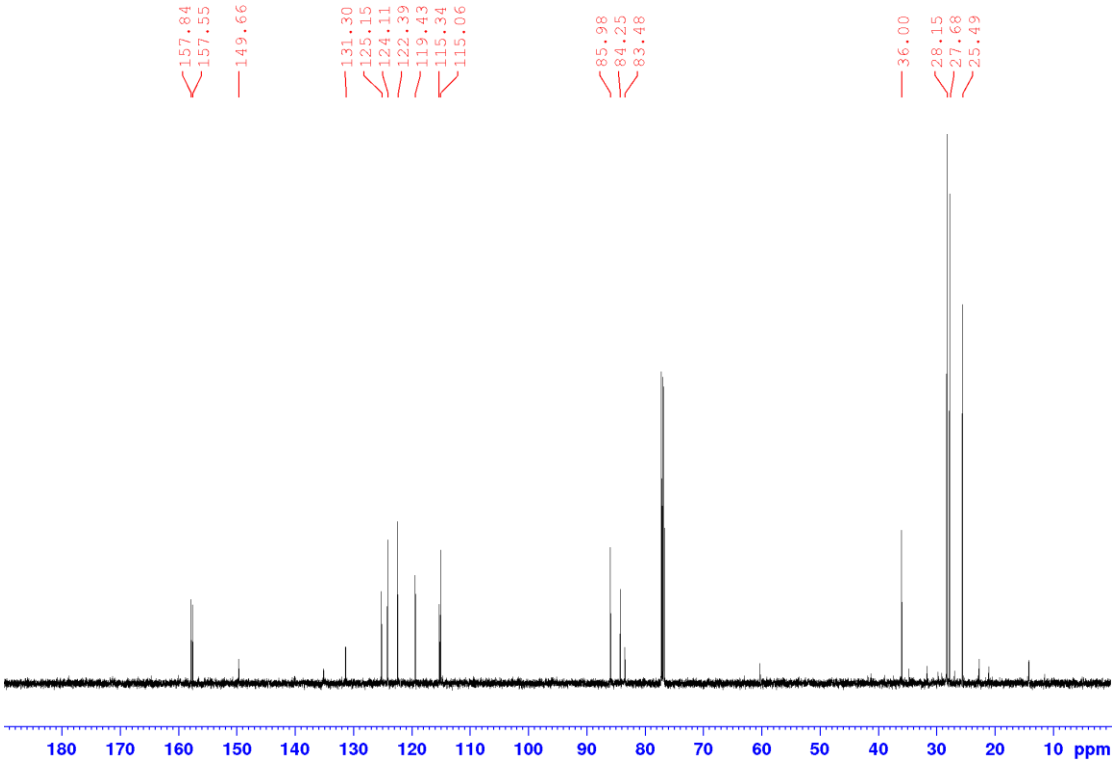

3.335
3.167
3.160
3.149
3.141
3.134
3.123
3.116
1.940
1.919
1.841
1.834
1.828
1.818
1.810
1.803
1.796
1.788
1.778
1.753
1.732
1.720
1.714
1.707
1.699
1.691
1.686
1.677
1.667
1.645
1.585
1.563
1.555
1.541
1.522
1.493
1.480
1.414
1.392
1.374
1.361
1.354
MeO
O
O
O
O
tBu
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.00
1.03
1.06
4.30
3.37
2.22
9.02
6.17
7.87
4.39
4.38
2.12
6.25
3.09

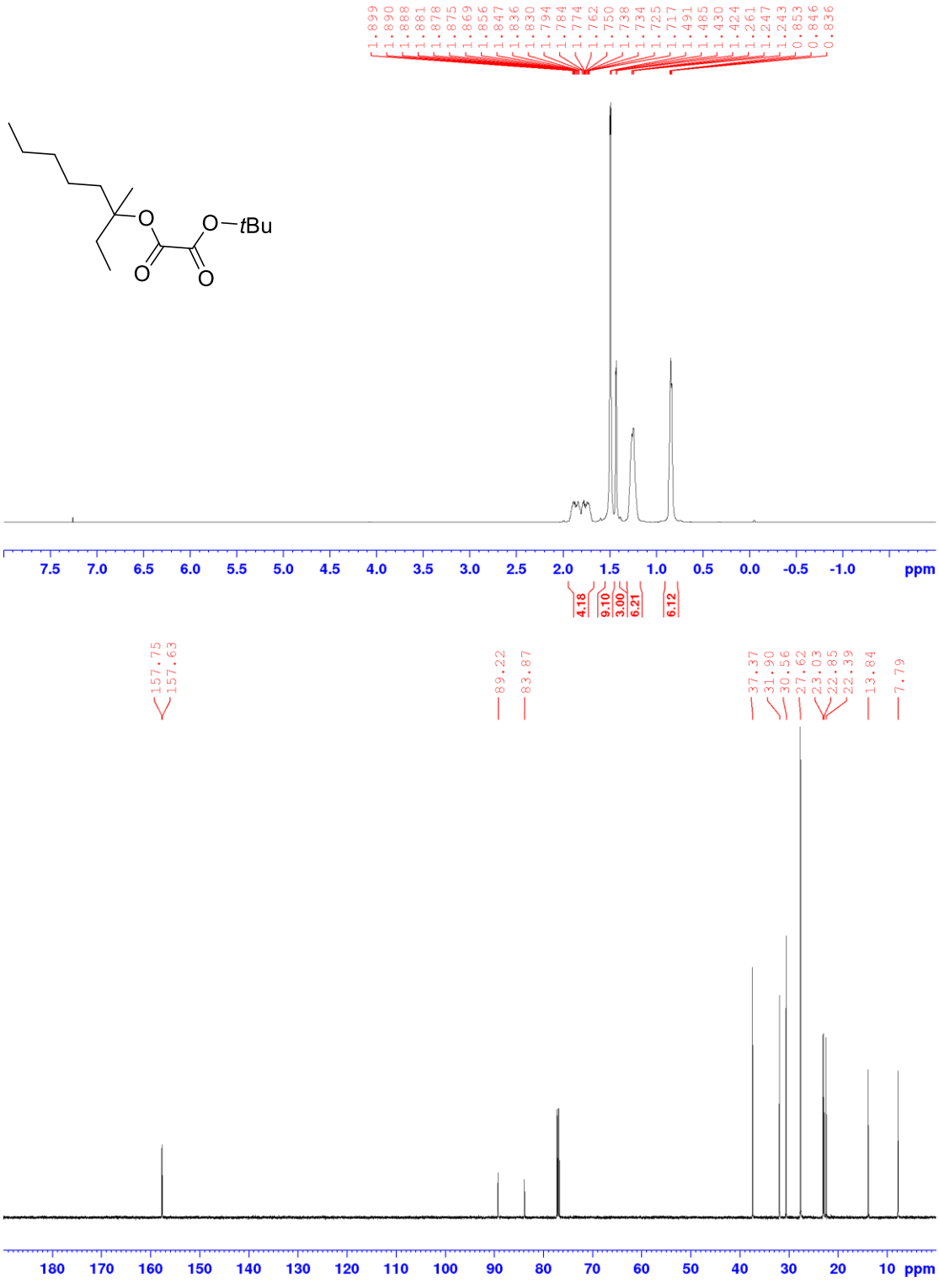

157.80
157.75
86.81
84.02
80.37
56.42
55.69
55.50
42.63
42.01
40.29
40.09
36.78
35.81
35.68
35.27
34.85
32.74
29.47
28.14
27.72
27.29
26.74
26.37
25.67
25.53
24.16
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

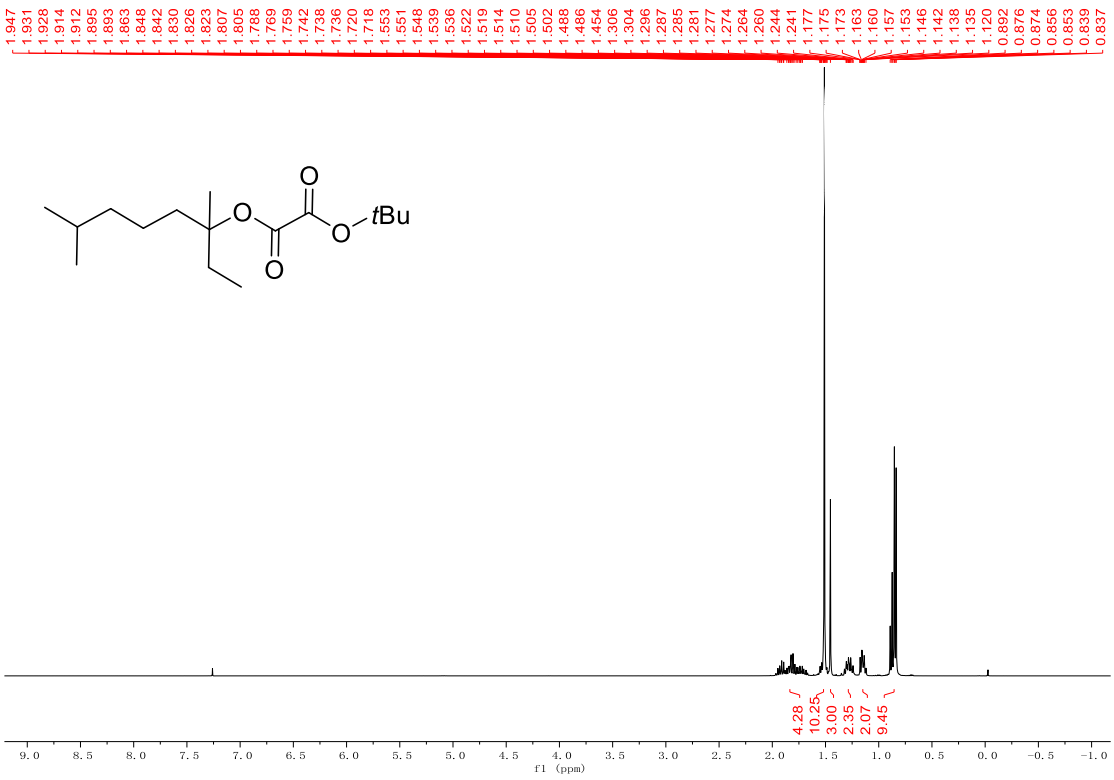

OMe
O
O
O
O
tBu
MeO
OMe
ppm

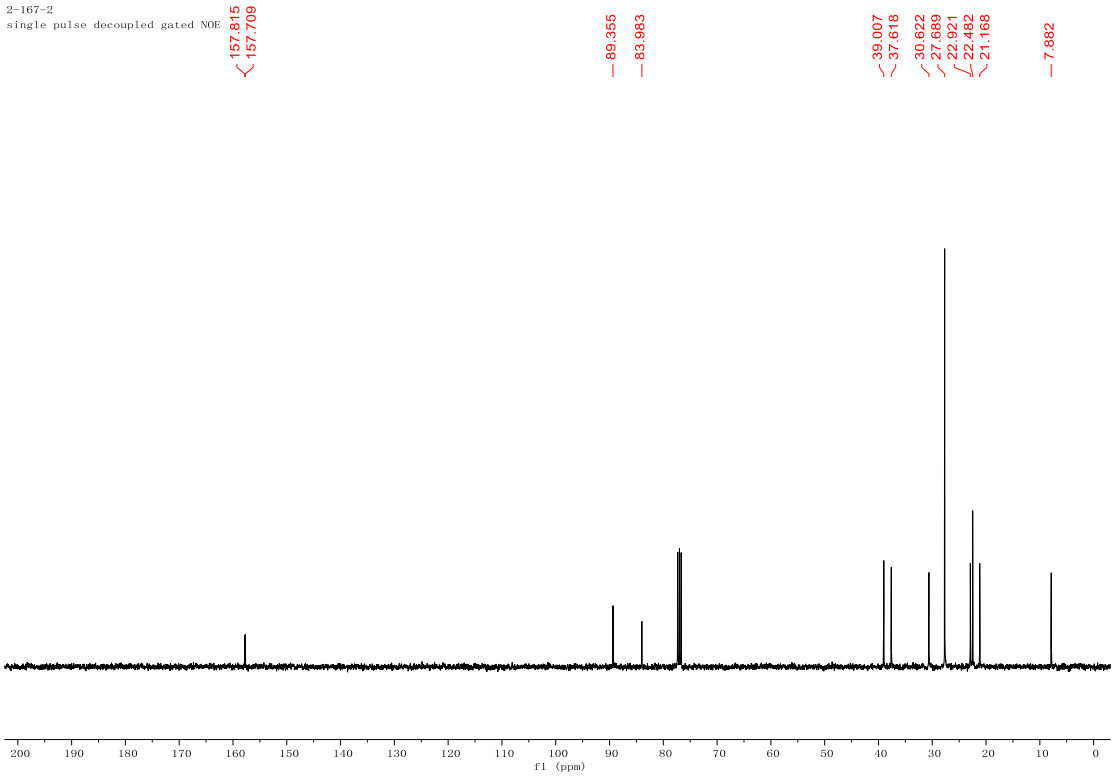

ppm


8.131
7.601
7.588
7.535
7.317
7.304
7.291
7.249
7.236
7.224
3.190
1.678
1.606
1.550
Boc
N
O
O
O
O
O—tBu
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
ppm
0.87
1.01
0.92
1.02
1.01
1.93
9.19
6.18
9.00

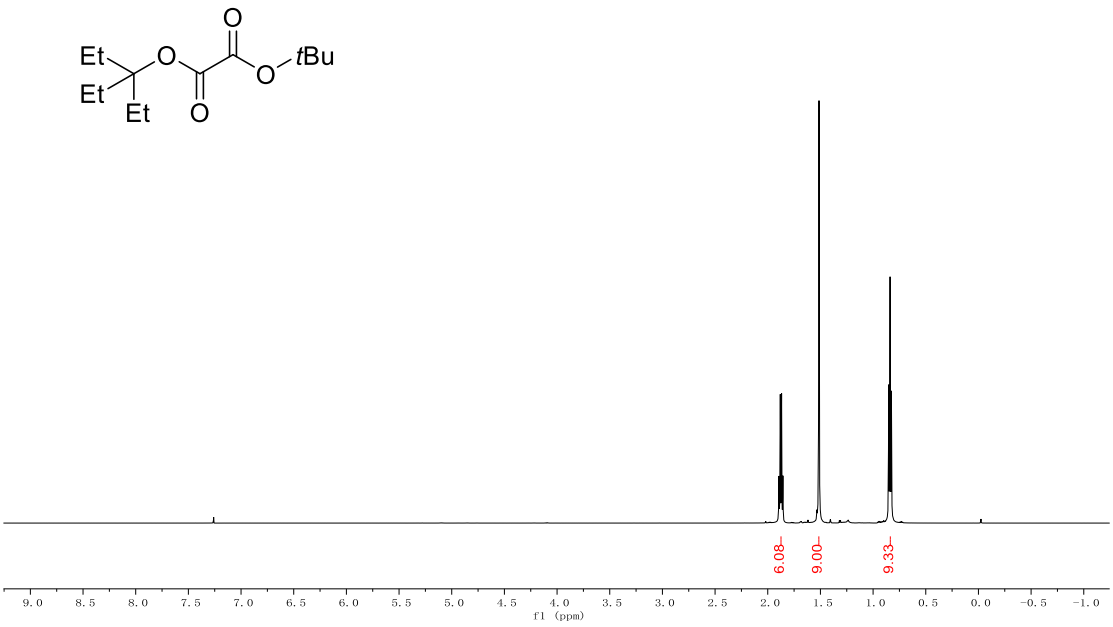

157.84
157.55
149.66
131.30
125.15
124.11
122.39
119.43
115.34
115.06
85.98
84.25
83.48
36.00
28.15
27.68
25.49
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


1.899
1.890
1.888
1.881
1.878
1.875
1.869
1.856
1.847
1.836
1.830
1.794
1.784
1.774
1.762
1.750
1.738
1.734
1.725
1.717
1.491
1.485
1.430
1.424
1.261
1.247
1.243
0.853
0.846
0.836
O
O
O
O
tBu
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 ppm
4.18
9.10
3.00
6.21
6.12
157.75
157.63
89.22
83.87
37.37
31.90
30.56
27.62
23.03
22.85
22.39
13.84
7.79
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

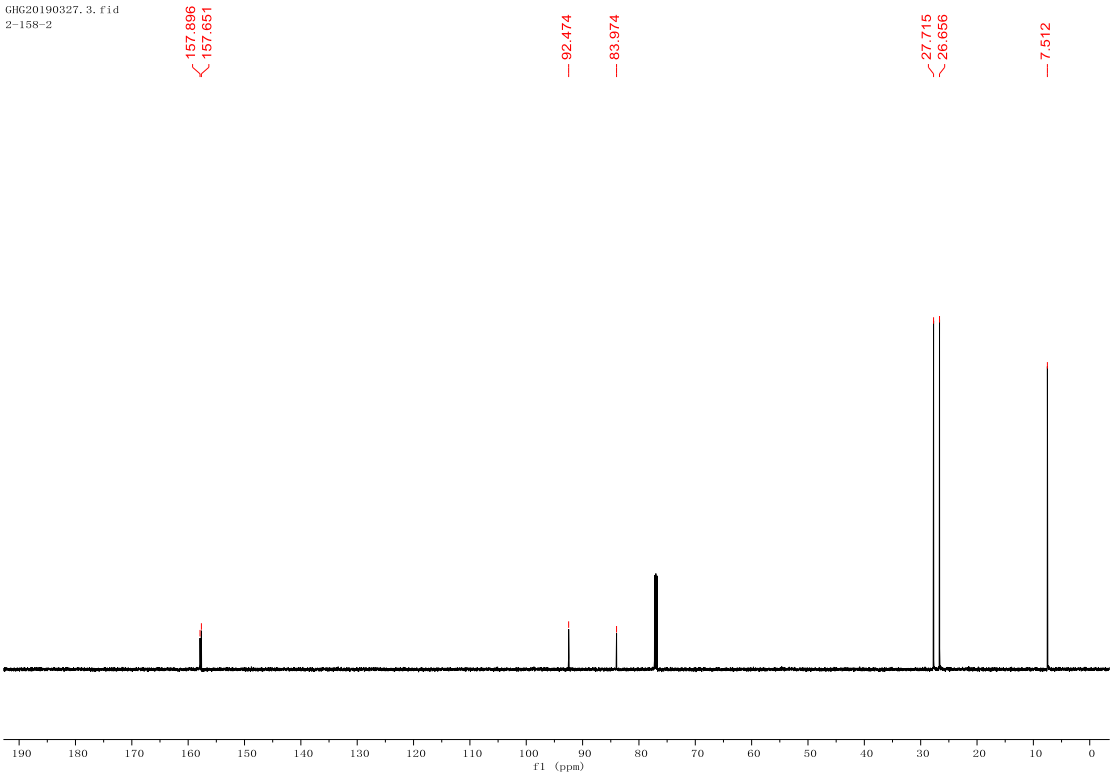

1.947
1.931
1.928
1.914
1.912
1.895
1.893
1.863
1.848
1.842
1.830
1.826
1.823
1.807
1.805
1.788
1.769
1.759
1.742
1.738
1.736
1.720
1.718
1.553
1.551
1.548
1.539
1.536
1.522
1.519
1.514
1.510
1.505
1.502
1.488
1.486
1.454
1.306
1.304
1.296
1.287
1.285
1.281
1.277
1.274
1.264
1.260
1.244
1.241
1.177
1.175
1.173
1.163
1.160
1.157
1.153
1.146
1.142
1.138
1.135
1.120
0.892
0.876
0.874
0.856
0.853
0.839
0.837
O
O
O
O
tBu
4.28
10.25
3.00
2.35
2.07
9.45
f1 (ppm)


2-167-2
single pulse decoupled gated NOE
157.815
157.709
89.355
83.983
39.007
37.618
30.622
27.689
22.921
22.482
21.168
7.882
f1 (ppm)

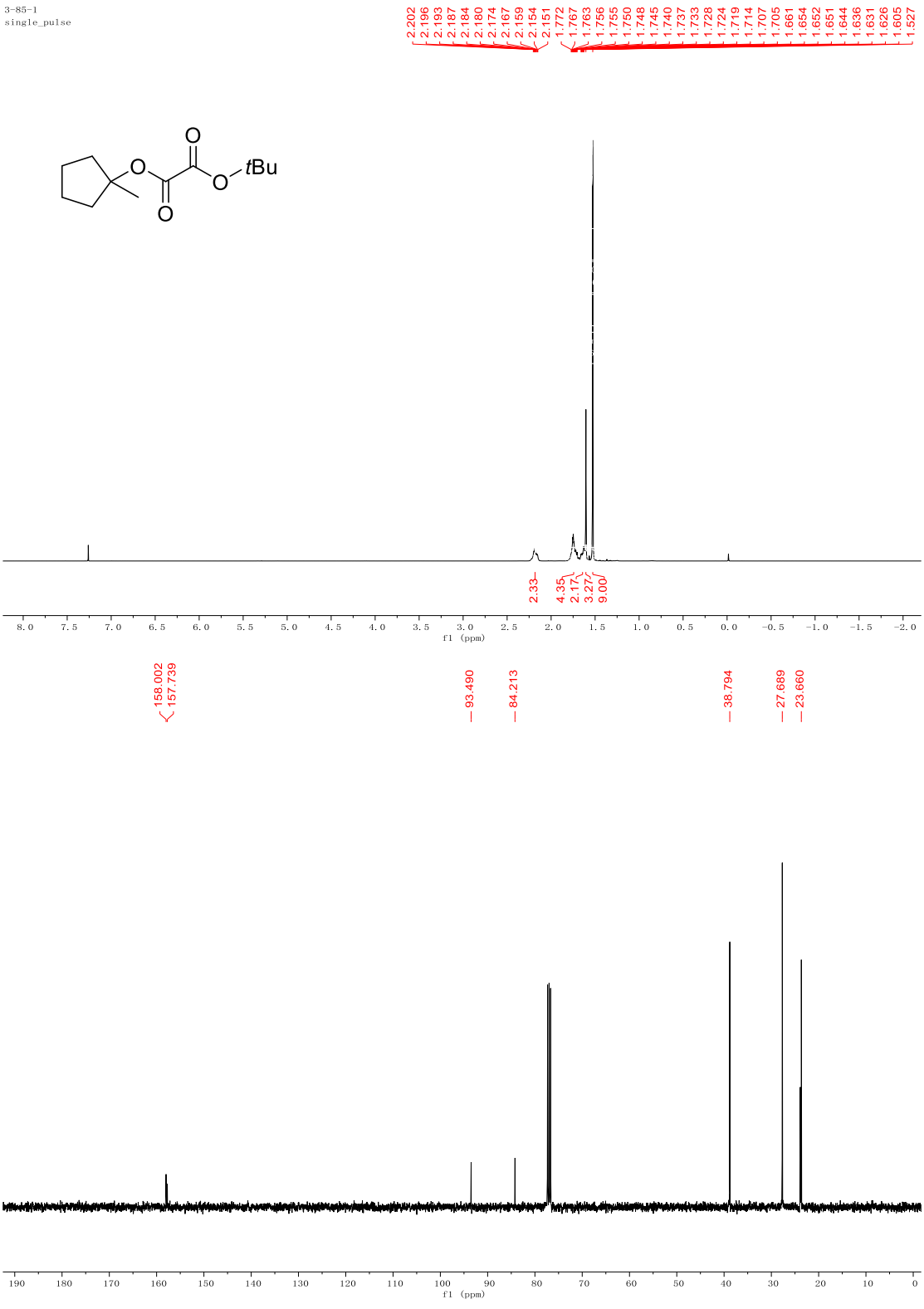
GHG20190327.2.fid
2-158-2

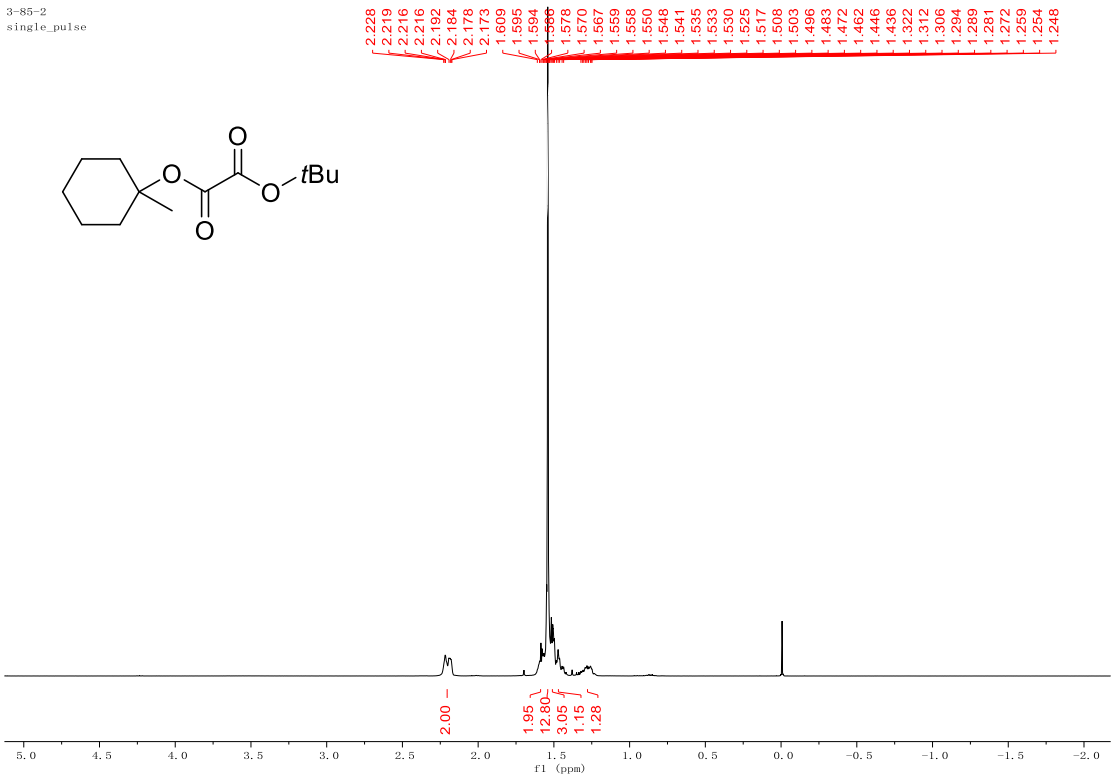


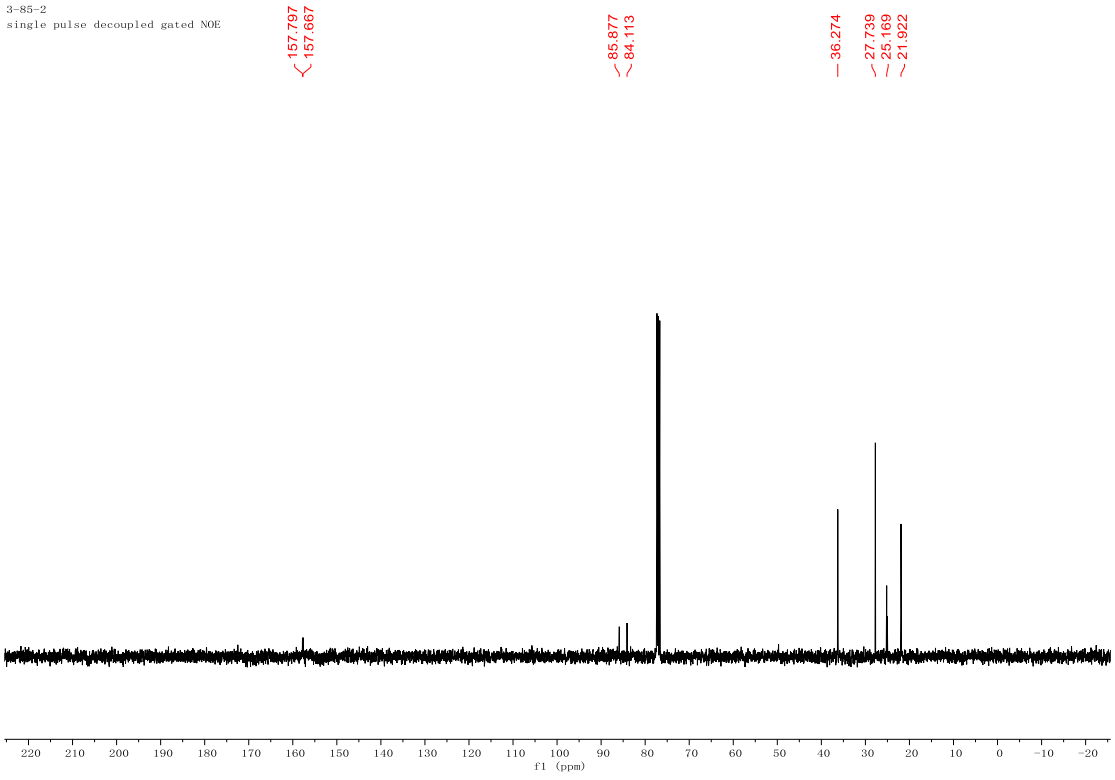
GHG20190327.3.fid
2-158-2

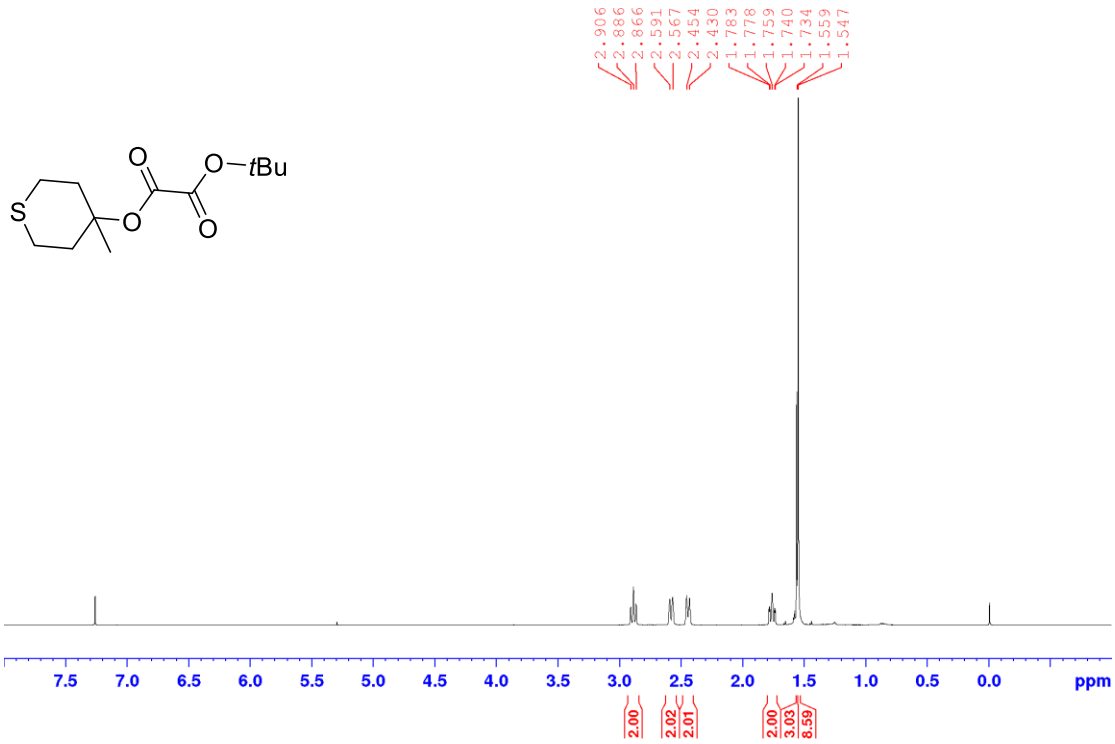


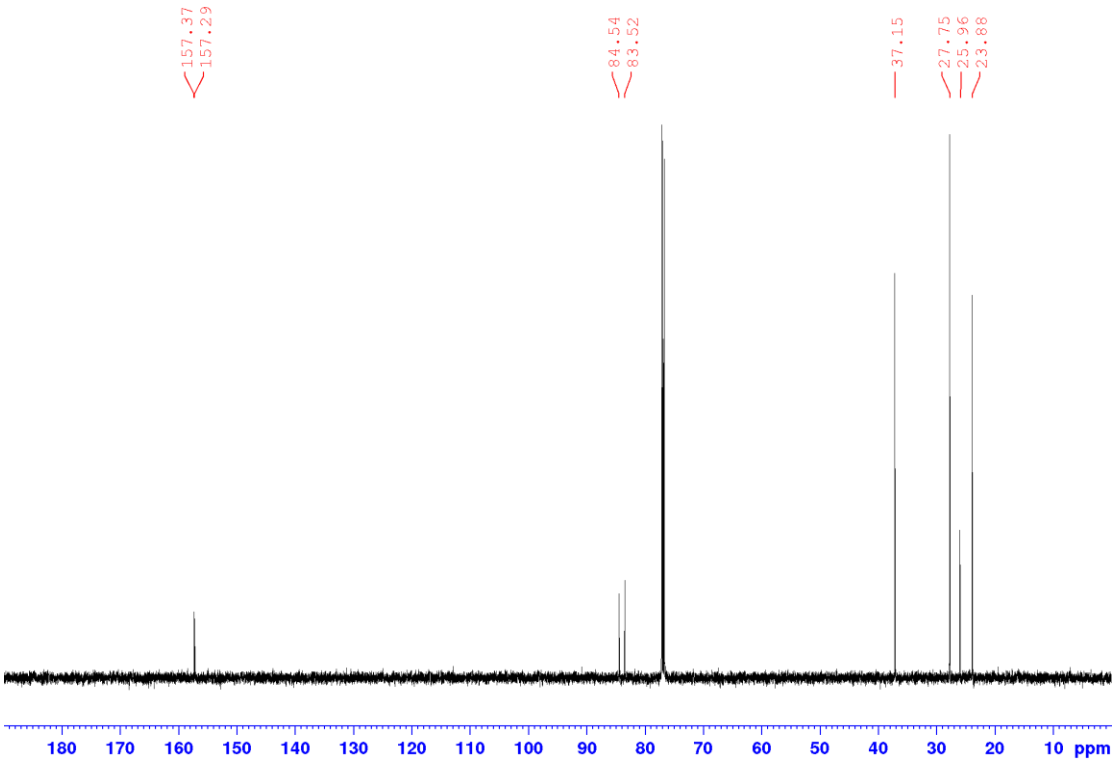
3-85-1
single_pulse

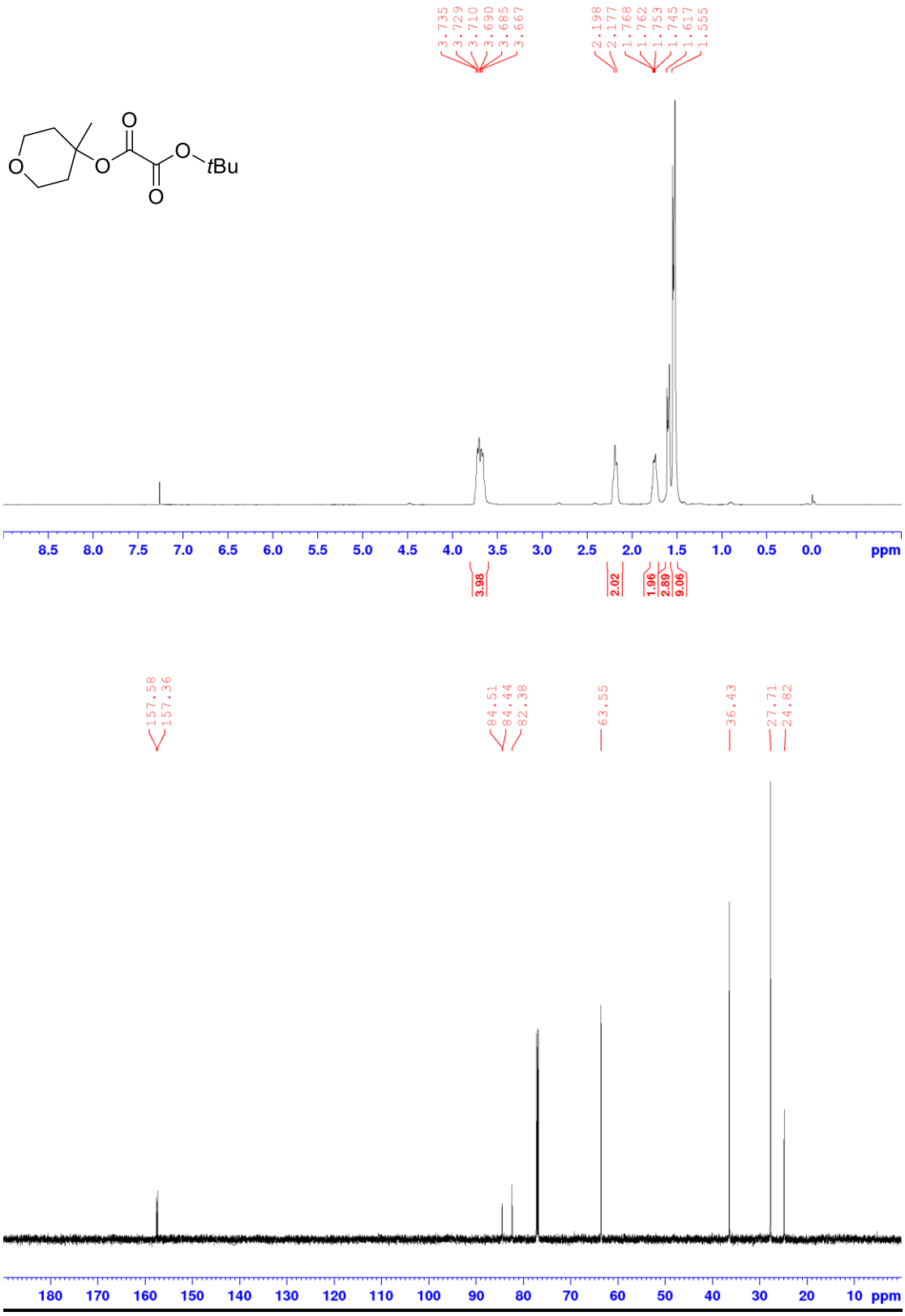



3-85-2
single_pulse
2.228
2.219
2.216
2.216
2.192
2.184
2.178
2.173
1.609
1.595
1.594
1.586
1.578
1.570
1.567
1.559
1.558
1.550
1.548
1.541
1.535
1.533
1.530
1.525
1.517
1.508
1.503
1.496
1.483
1.472
1.462
1.446
1.436
1.322
1.312
1.306
1.294
1.289
1.281
1.272
1.259
1.254
1.248
O
O
O
O
tBu
2.00
1.95
12.80
3.05
1.15
1.28
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2.0
f1 (ppm)


3-85-2
single pulse decoupled gated NOE
157.797
157.667
85.877
84.113
36.274
27.739
25.169
21.922
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

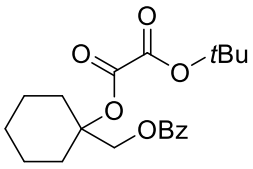

2.906
2.886
2.866
2.591
2.567
2.454
2.430
1.783
1.778
1.759
1.740
1.734
1.559
1.547
O
O
O
O
O
tBu
S
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
2.02
2.01
2.00
3.03
8.59

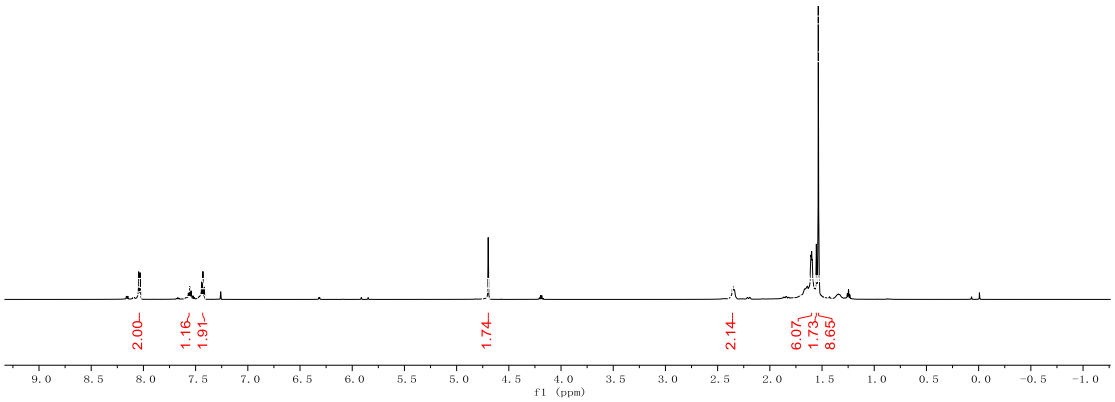

157.37
157.29
84.54
83.52
37.15
27.75
25.96
23.88
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


3.735
3.729
3.710
3.690
3.685
3.667
2.198
2.177
1.768
1.762
1.753
1.745
1.617
1.555
O
O
O
O
tBu
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 ppm
3.98
2.02
1.96
2.89
9.06
157.58
157.36
84.51
84.44
82.38
63.55
36.43
27.71
24.82
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

GHG20181128.10.fid
2-129

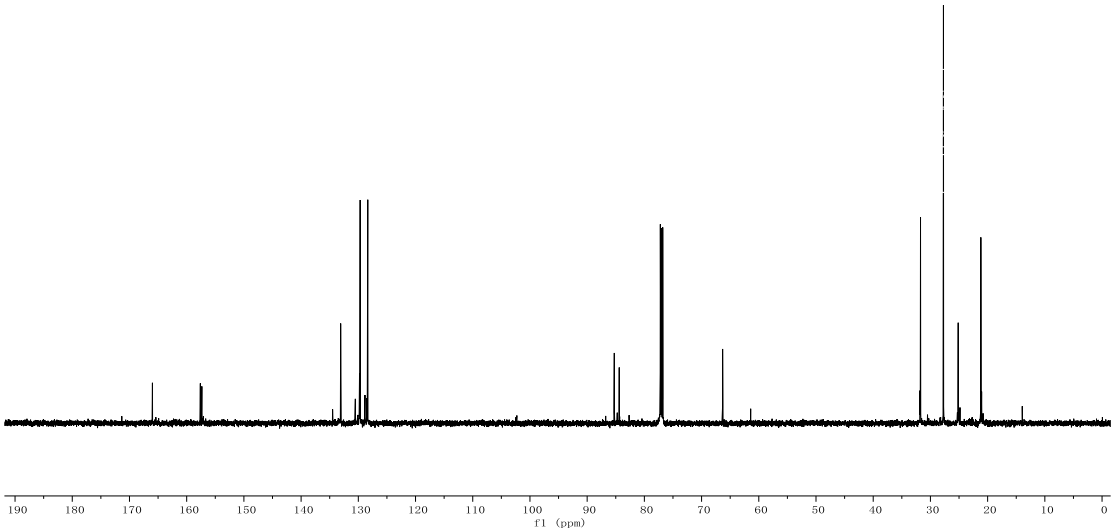
8.045
8.031
7.569
7.557
7.545
7.442
7.430
7.418
4.697
2.354
2.345
2.337
1.607
1.600
1.593
1.554
1.552
1.536

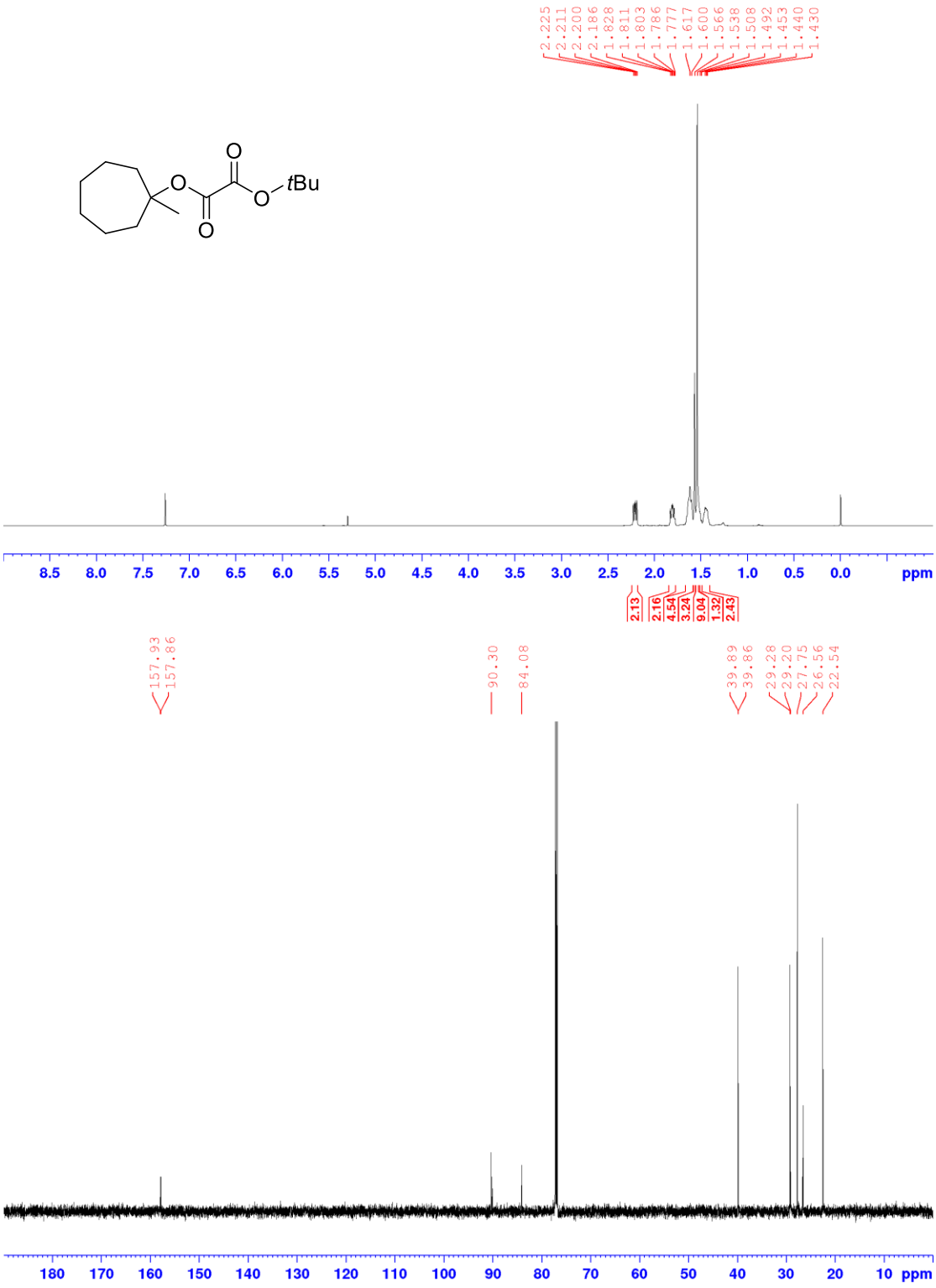


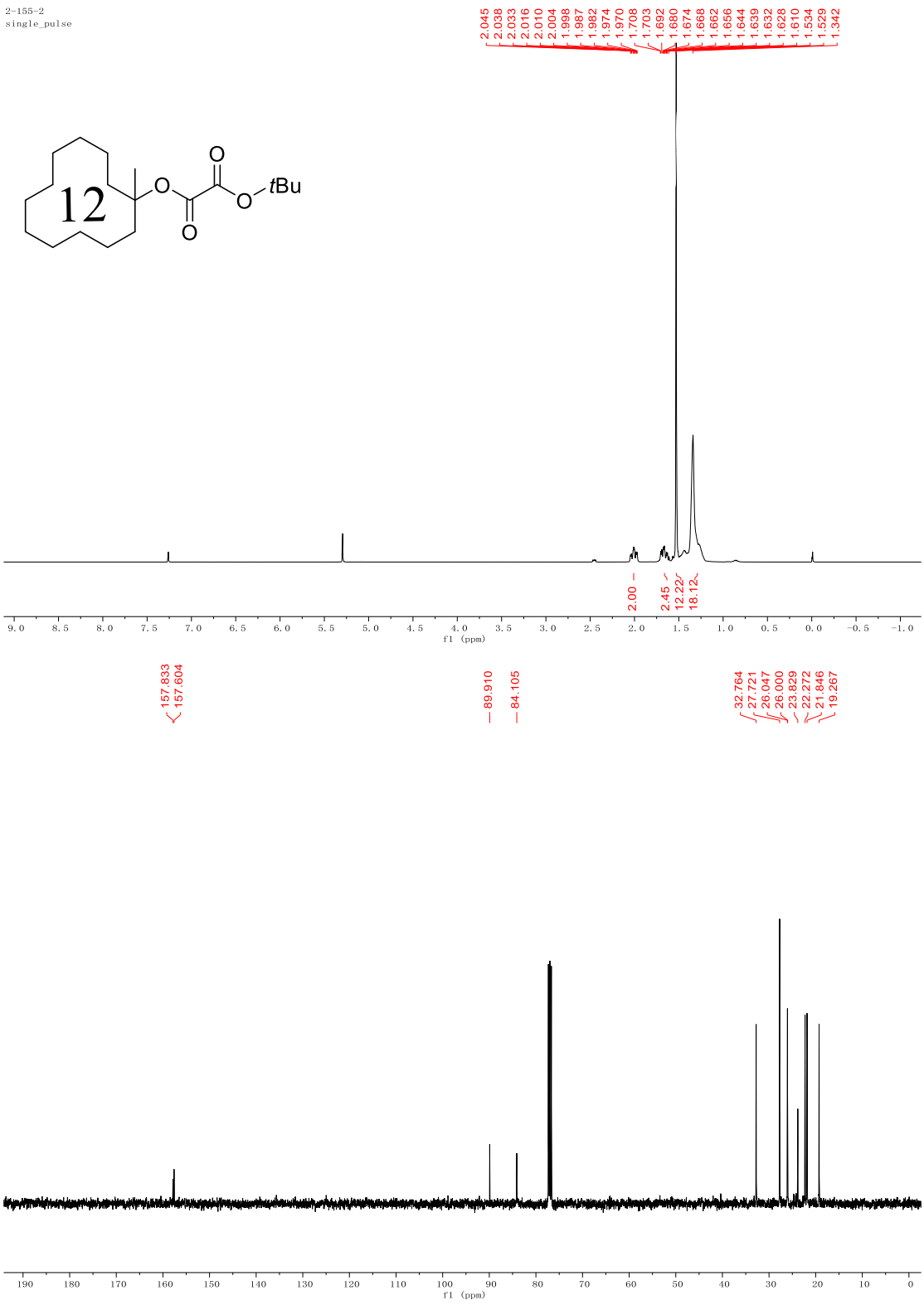


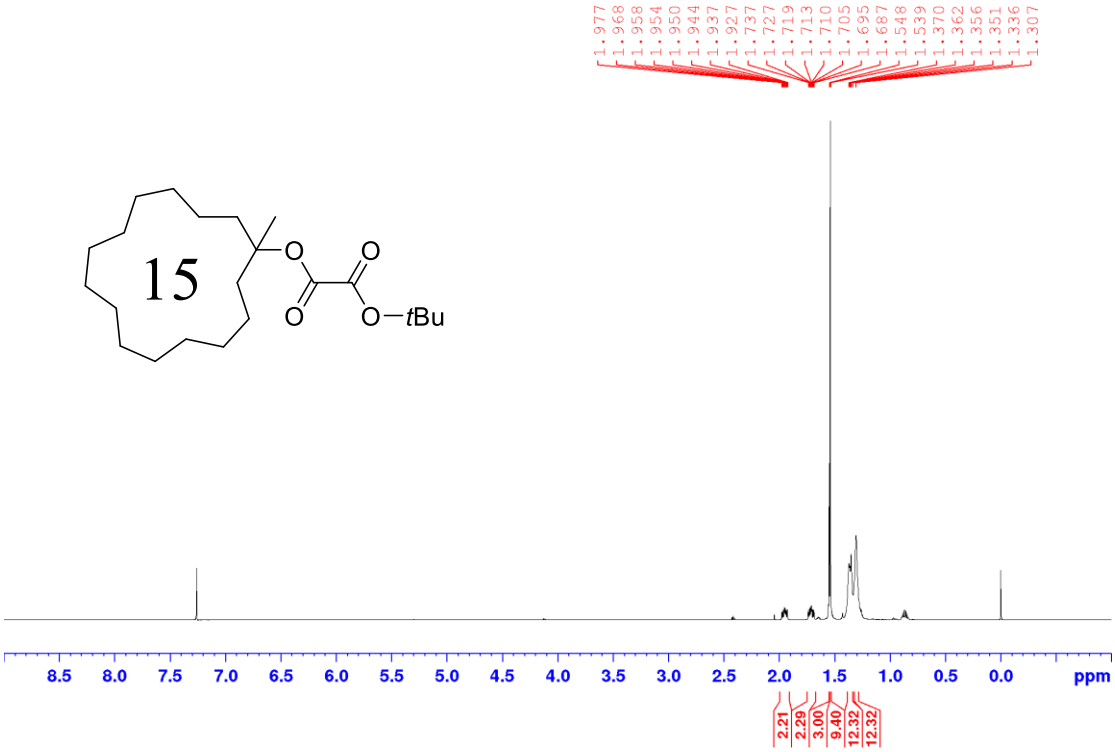
GHG20181128.11.fid
2-129

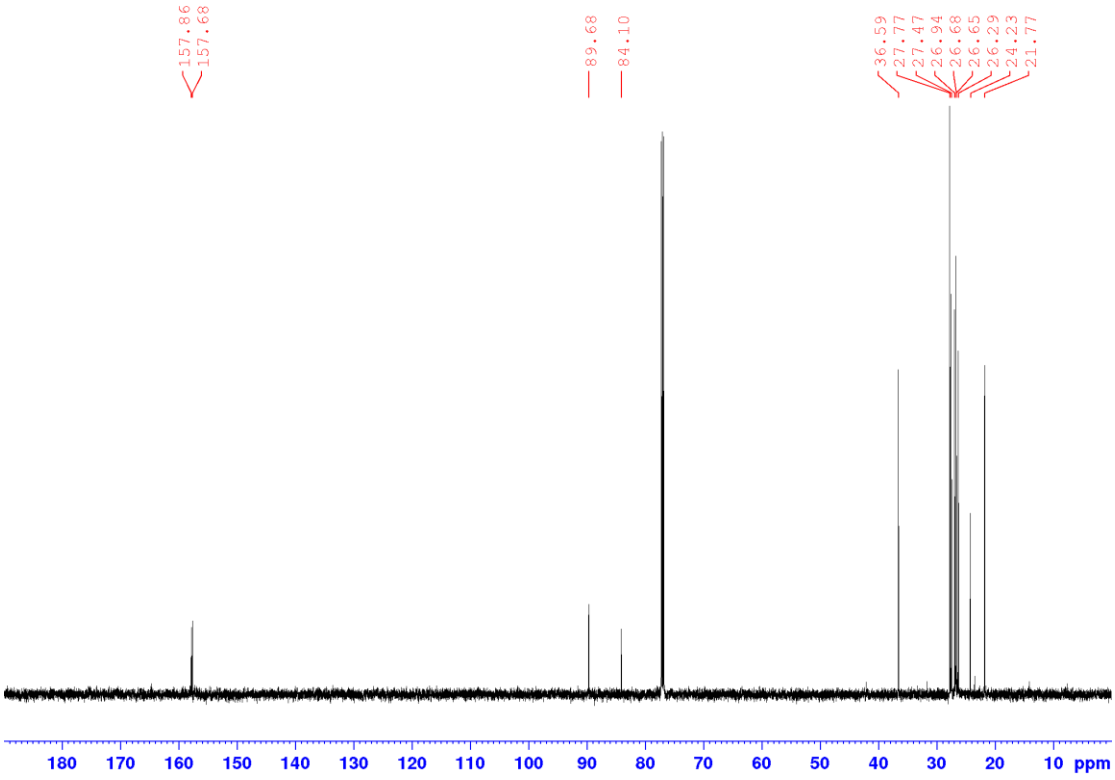
165.988
157.614
157.348
133.083
129.678
128.345
85.258
84.394
66.319
31.732
27.724
25.146
21.185

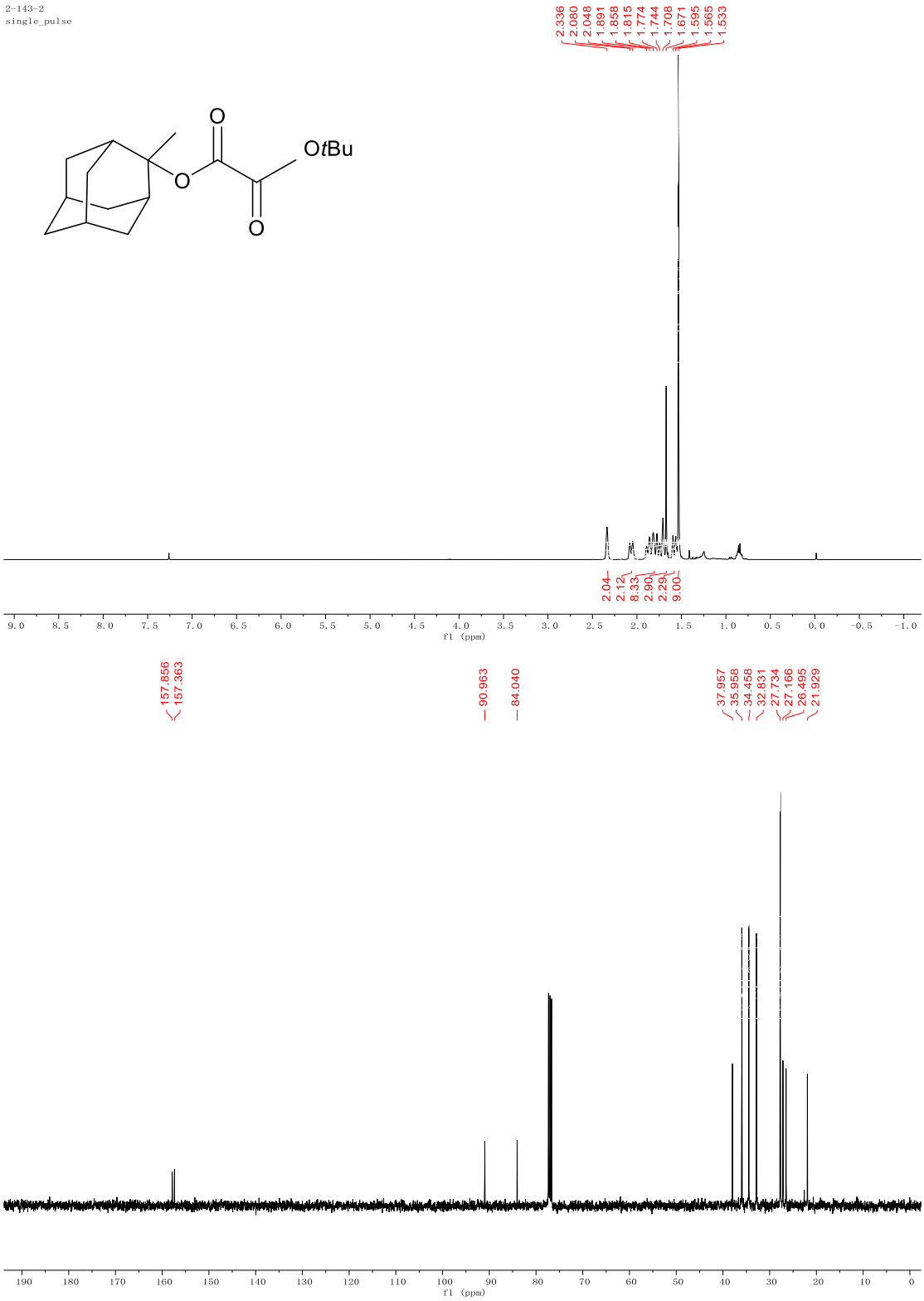


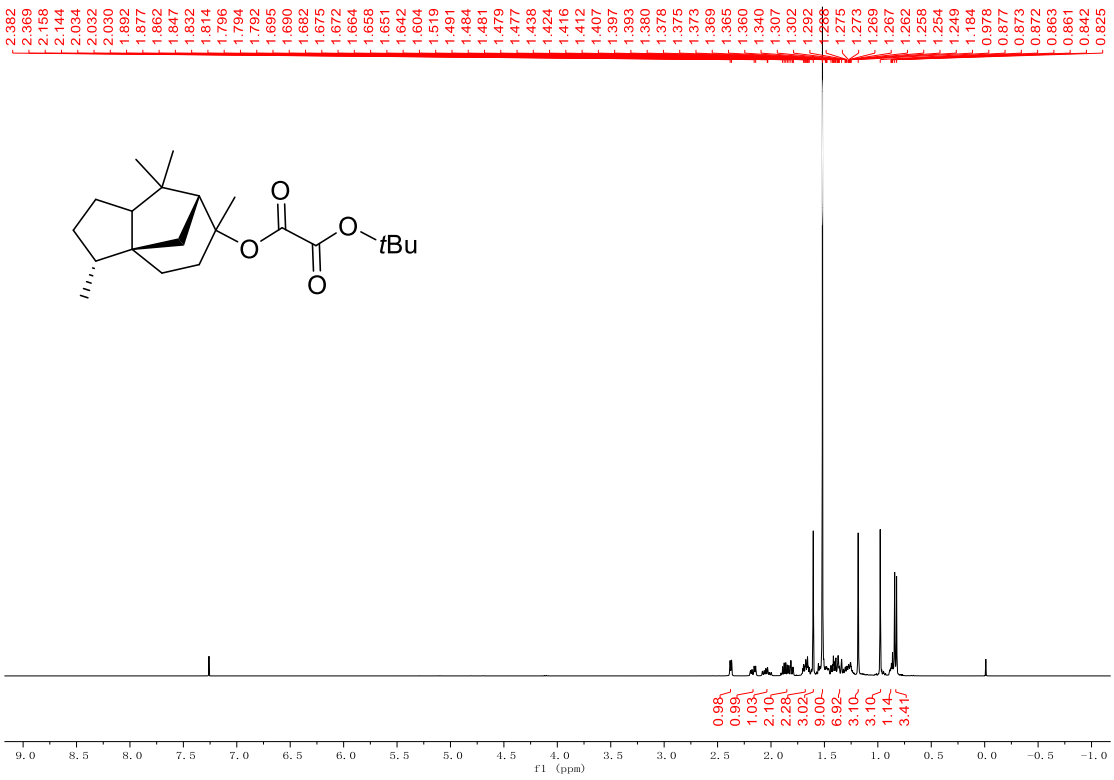

2.225
2.211
2.200
2.186
1.828
1.811
1.803
1.786
1.777
1.617
1.600
1.566
1.538
1.508
1.492
1.453
1.440
1.430
O
O
O
O
tBu
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.13
2.16
4.54
3.24
9.04
1.32
2.43
157.93
157.86
90.30
84.08
39.89
39.86
29.28
29.20
27.75
26.56
22.54
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

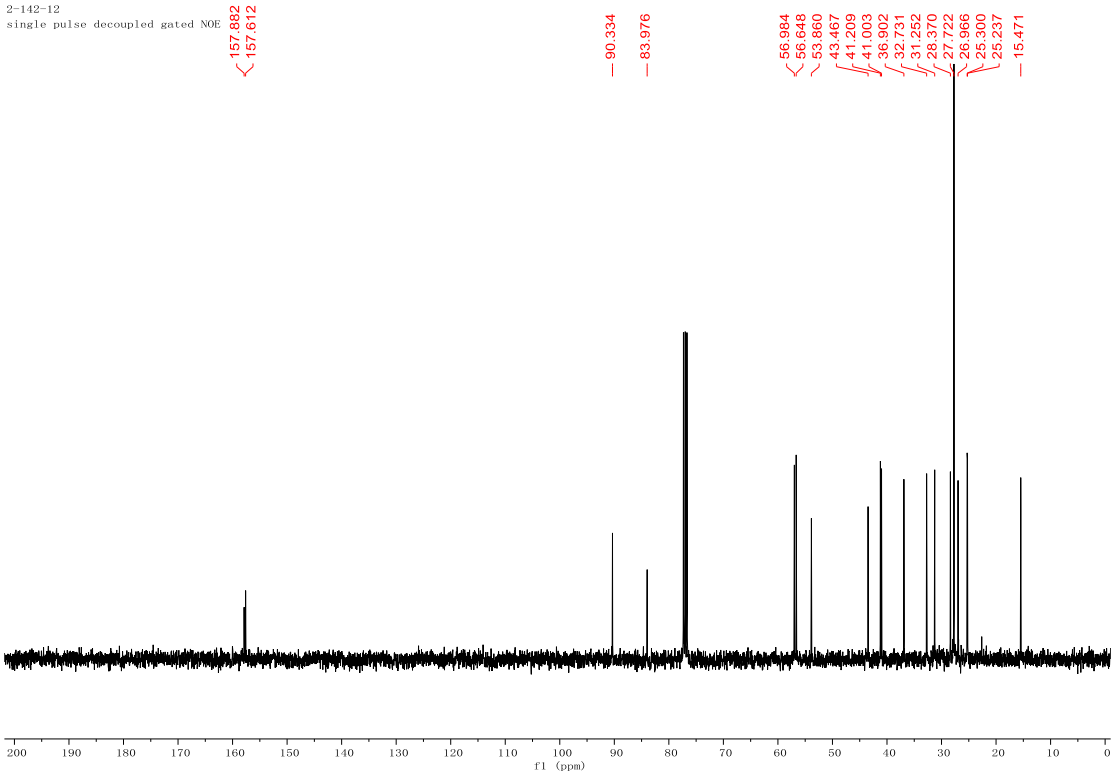

2-155-2
single_pulse
12
O
O
O
O
tBu
2.045
2.038
2.033
2.016
2.010
2.004
1.998
1.987
1.982
1.974
1.970
1.708
1.703
1.692
1.680
1.674
1.668
1.662
1.656
1.644
1.639
1.632
1.628
1.610
1.534
1.529
1.342
2.00
2.45
12.22
18.12
f1 (ppm)
157.833
157.604
89.910
84.105
32.764
27.721
26.047
26.000
23.829
22.272
21.846
19.267
f1 (ppm)

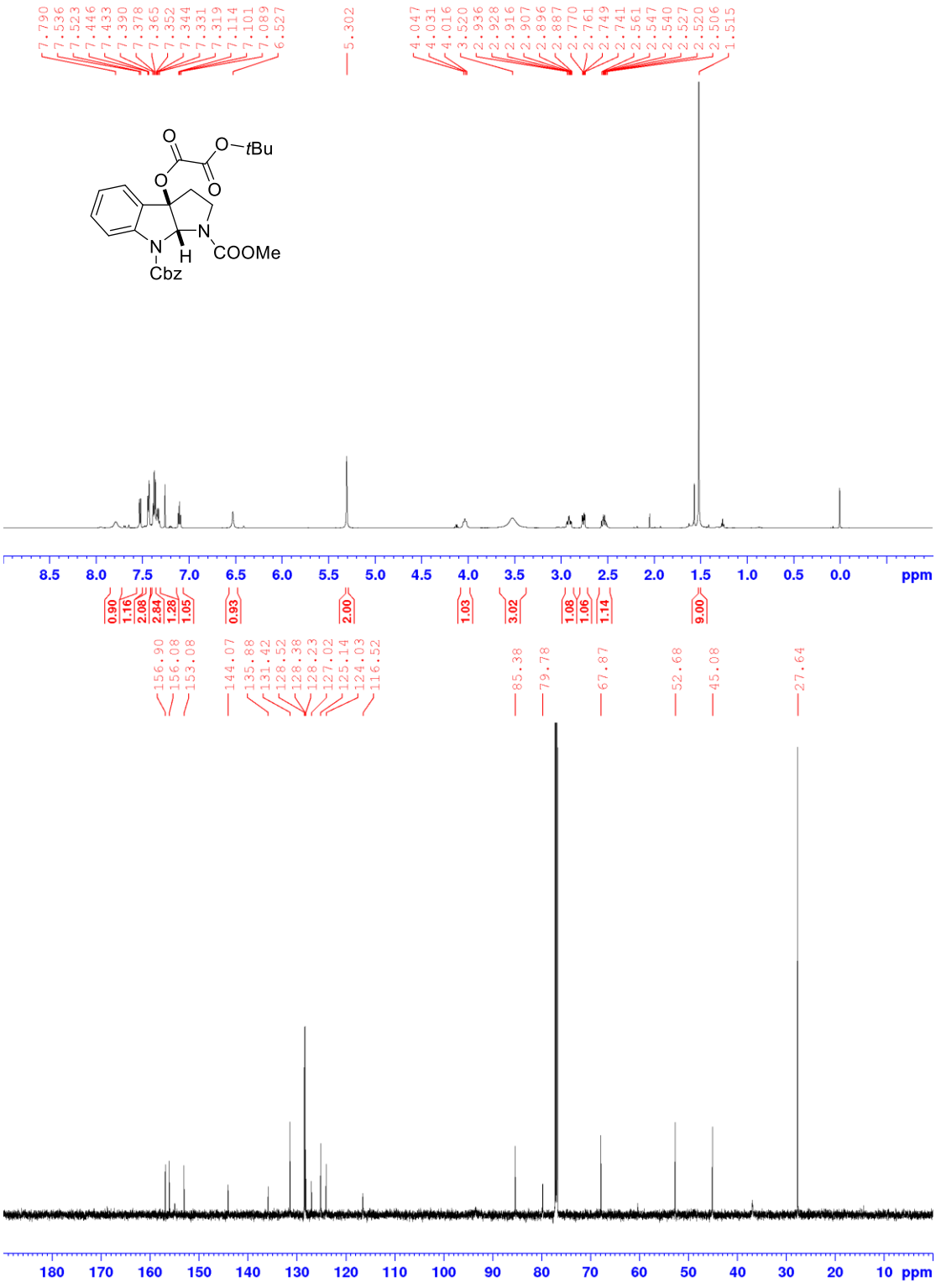

1.977
1.968
1.958
1.954
1.950
1.944
1.937
1.927
1.737
1.727
1.719
1.713
1.710
1.705
1.695
1.687
1.548
1.539
1.370
1.362
1.356
1.351
1.336
1.307
15
O
O
O
O
O—tBu
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.21
2.29
3.00
9.40
12.32
12.32

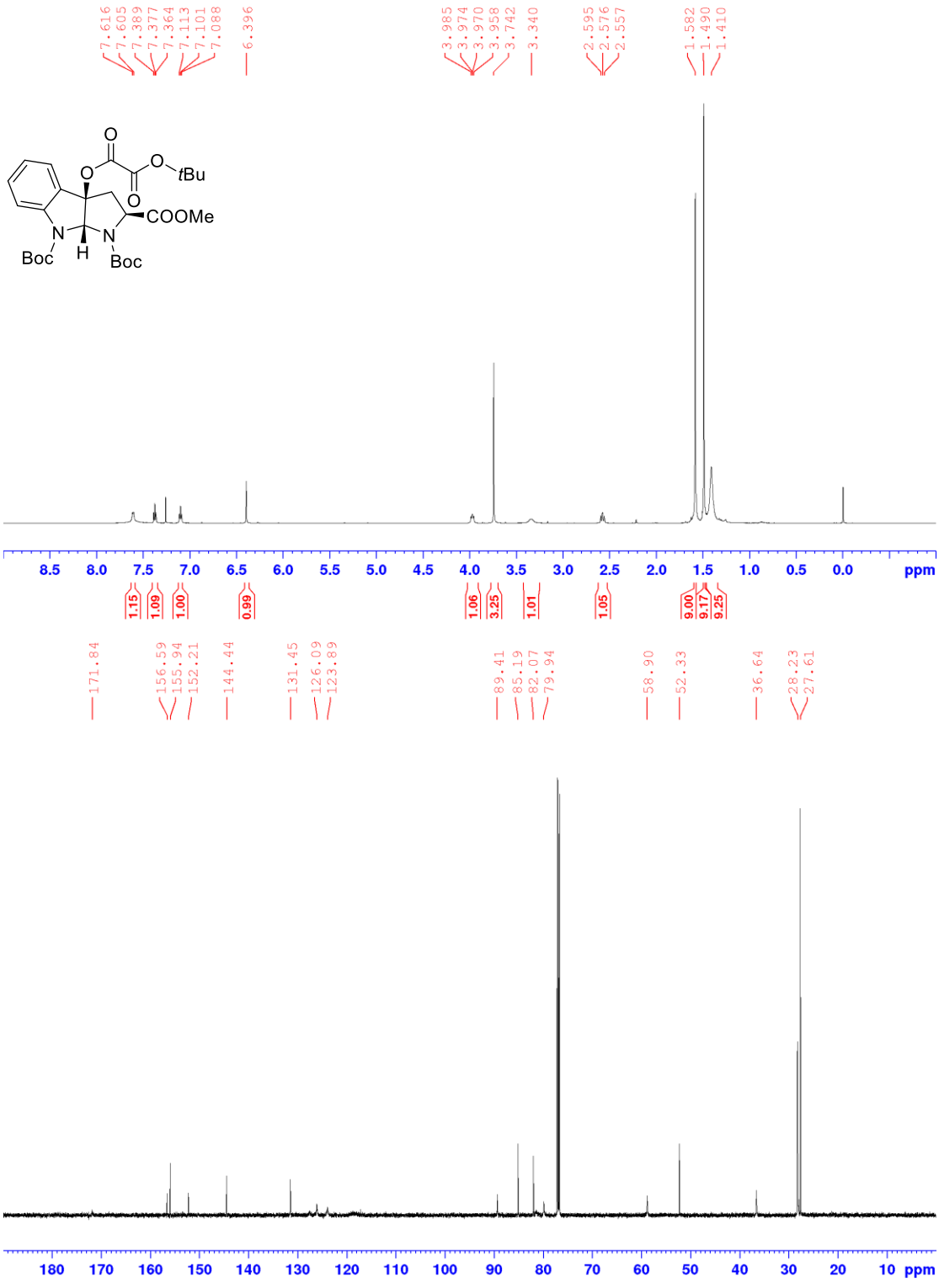

157.86
157.68
89.68
84.10
36.59
27.77
27.47
26.94
26.68
26.65
26.29
24.23
21.77
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

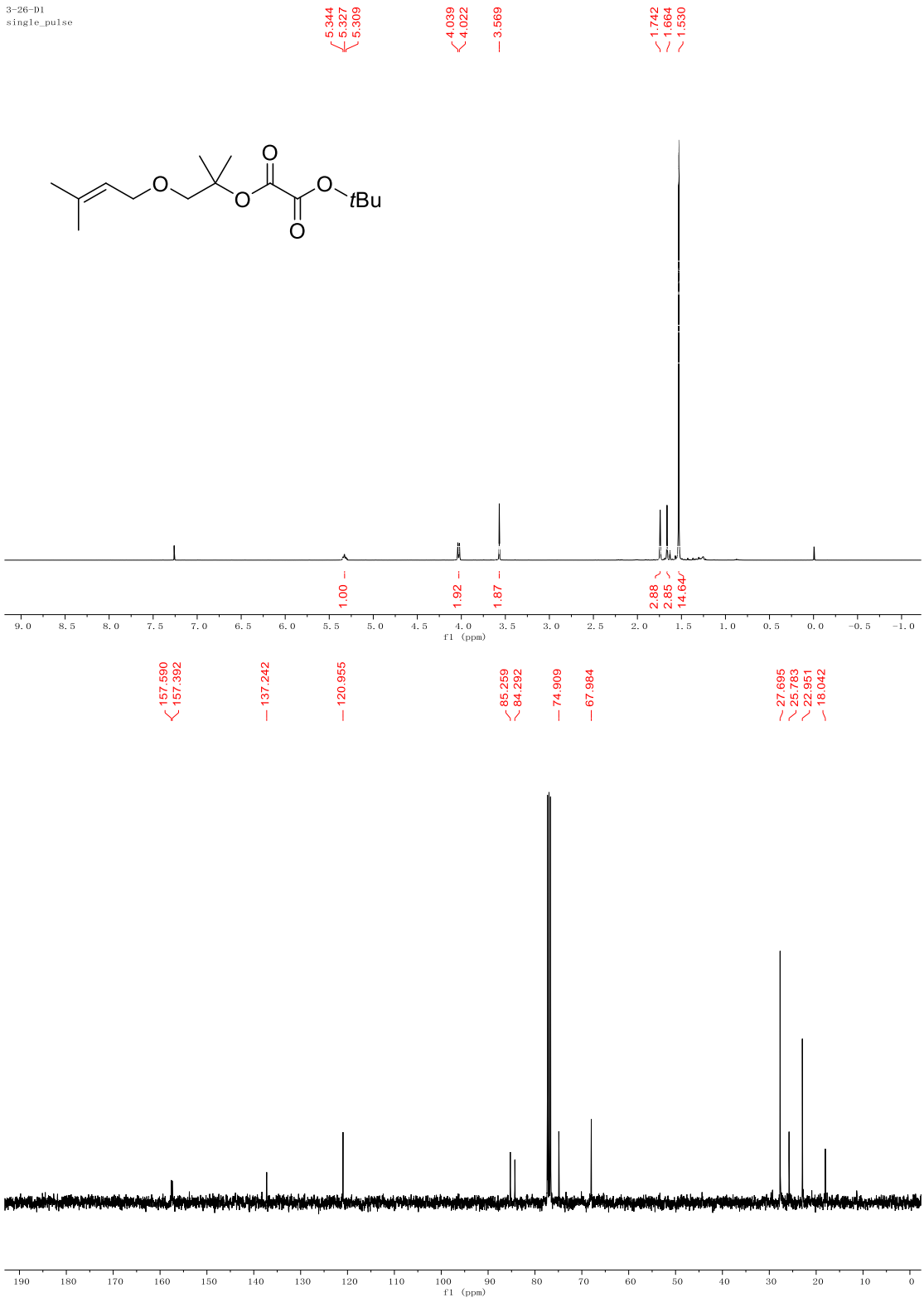

2-143-2
single_pulse
O
O
O
OtBu
2.336
2.080
2.048
1.891
1.858
1.815
1.774
1.744
1.708
1.671
1.595
1.565
1.533
2.04
2.12
8.33
2.90
2.28
9.00
f1 (ppm)
157.856
157.363
90.963
84.040
37.957
35.958
34.458
32.831
27.734
27.166
26.495
21.929
f1 (ppm)


2.382
2.369
2.158
2.144
2.034
2.032
2.030
1.892
1.877
1.862
1.847
1.832
1.814
1.796
1.794
1.792
1.695
1.690
1.682
1.675
1.672
1.664
1.658
1.651
1.642
1.604
1.519
1.491
1.484
1.481
1.479
1.477
1.438
1.424
1.416
1.412
1.407
1.397
1.393
1.380
1.378
1.375
1.373
1.369
1.365
1.360
1.340
1.307
1.302
1.292
1.288
1.275
1.273
1.269
1.267
1.262
1.258
1.254
1.249
1.184
0.978
0.877
0.873
0.872
0.863
0.861
0.842
0.825
O
O
O
O
tBu
0.98
0.99
1.03
2.10
2.28
3.02
9.00
6.92
3.10
3.10
1.14
3.41
f1 (ppm)

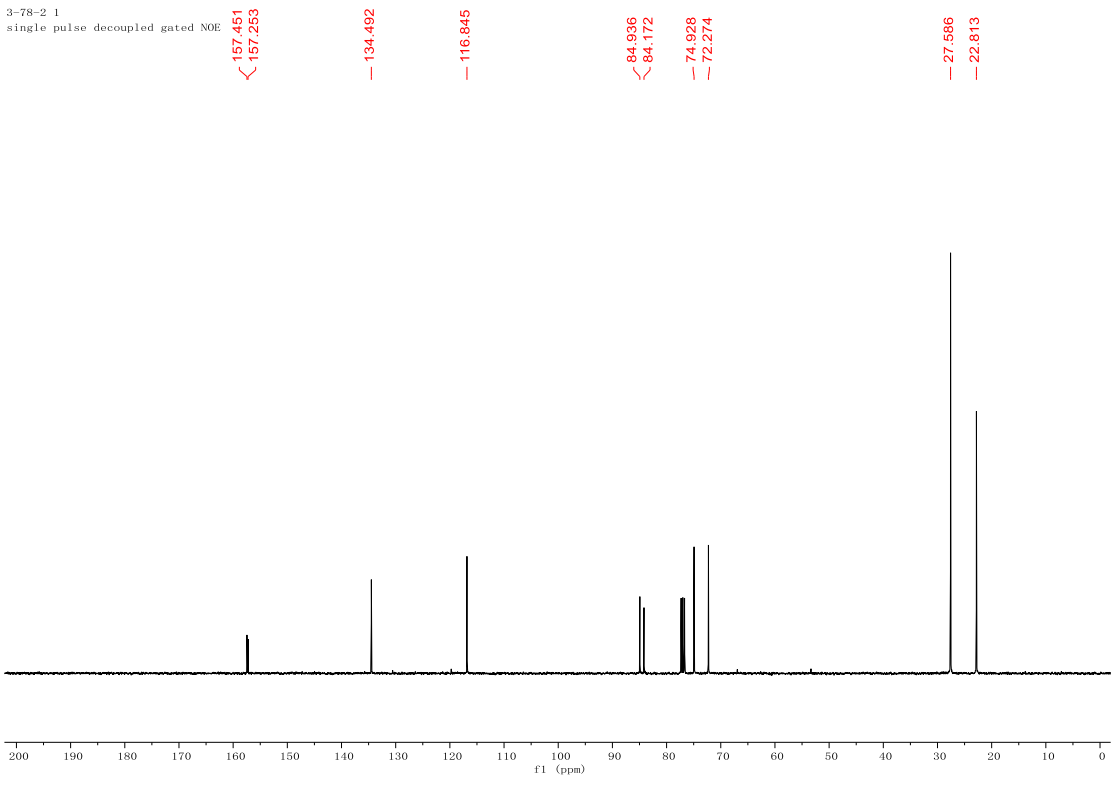

2-142-12
single pulse decoupled gated NOE
157.882
157.612
90.334
83.976
56.984
56.648
53.860
43.467
41.209
41.003
36.902
32.731
31.252
28.370
27.722
26.966
25.300
25.237
15.471
f1 (ppm)

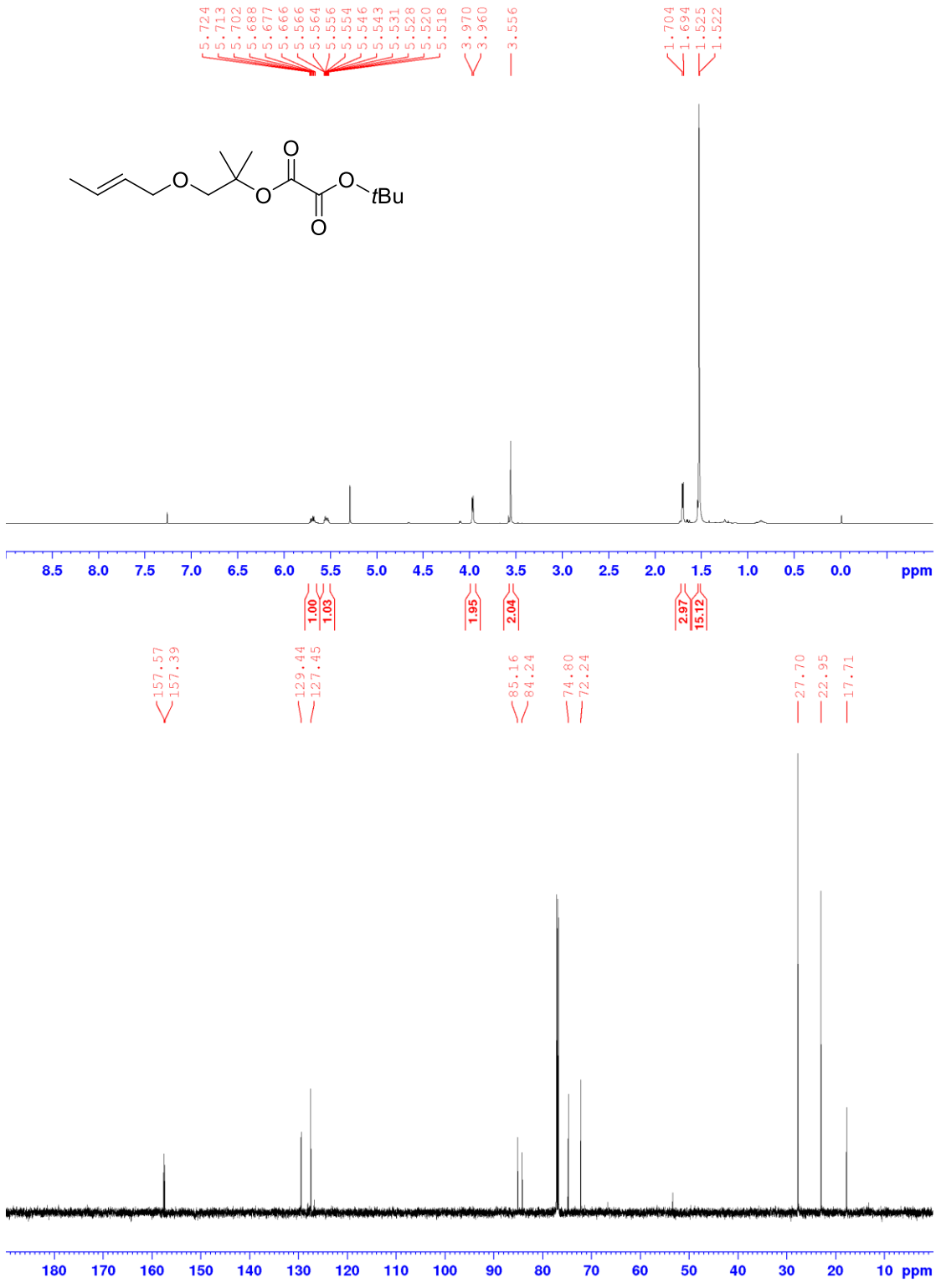

7.790
7.536
7.523
7.446
7.433
7.390
7.378
7.365
7.352
7.344
7.331
7.319
7.114
7.101
7.089
6.527
5.302
4.047
4.031
4.016
3.520
2.936
2.928
2.916
2.907
2.896
2.887
2.770
2.761
2.749
2.741
2.561
2.547
2.540
2.527
2.520
2.506
1.515
O
O
O
O
O
tBu
N
H
N
COOMe
Cbz
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.90
1.16
2.08
2.84
1.28
1.05
0.93
2.00
1.03
3.02
1.08
1.06
1.14
9.00
156.90
156.08
153.08
144.07
135.88
131.42
128.52
128.38
128.23
127.02
125.14
124.03
116.52
85.38
79.78
67.87
52.68
45.08
27.64
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

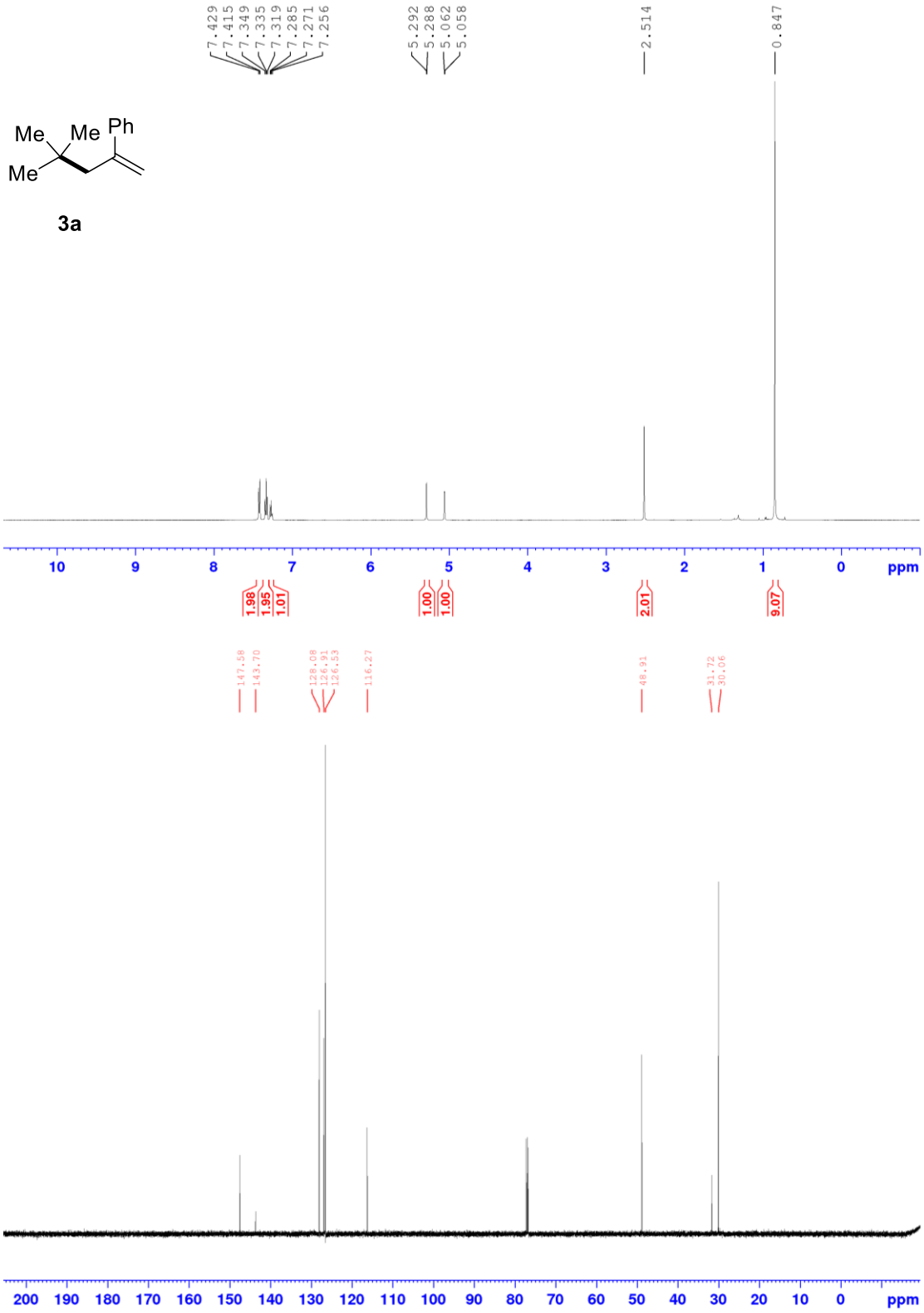

7.616
7.605
7.389
7.377
7.364
7.113
7.101
7.088
6.396
3.985
3.974
3.970
3.958
3.742
3.340
2.595
2.576
2.557
1.582
1.490
1.410
O
O
O
tBu
O
COOMe
N
H
N
Boc
Boc
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.15
1.09
1.00
0.99
1.06
3.25
1.01
1.05
9.00
9.17
9.25
171.84
156.59
155.94
152.21
144.44
131.45
126.09
123.89
89.41
85.19
82.07
79.94
58.90
52.33
36.64
28.23
27.61
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

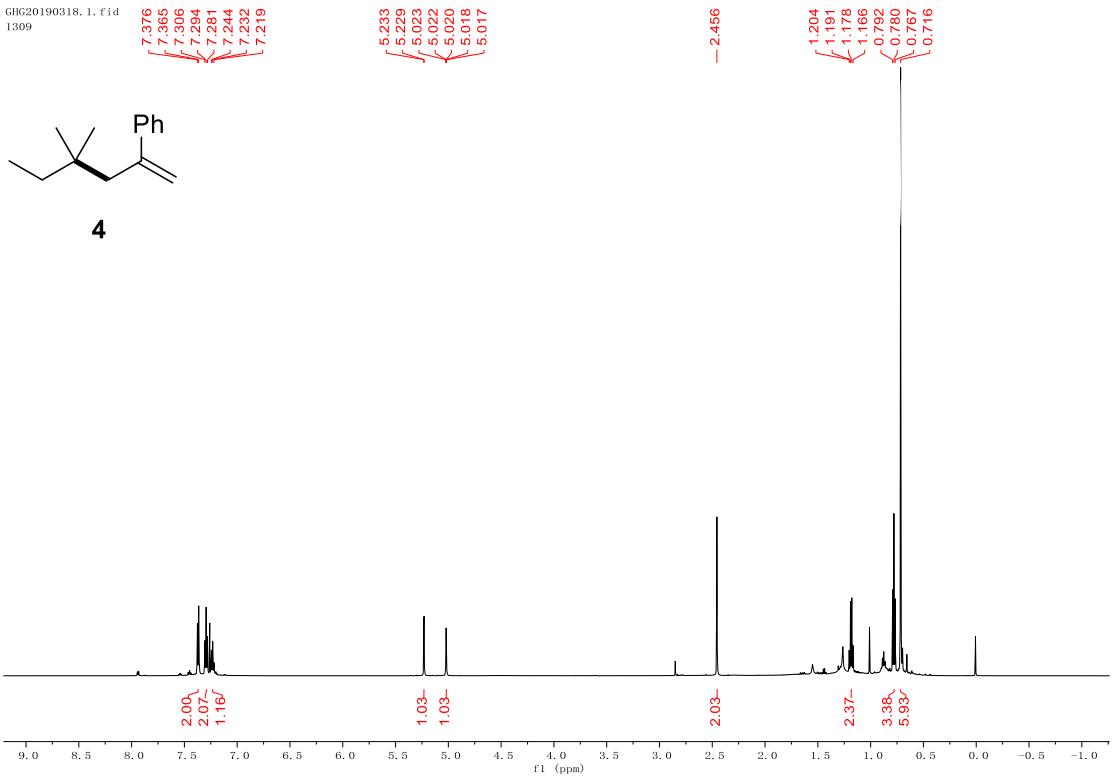

3-26-D1
single_pulse
5.344
5.327
5.309
4.039
4.022
3.569
1.742
1.664
1.530
O
O
O
O
O
tBu
1.00
1.92
1.87
2.88
2.85
14.64
f1 (ppm)
157.590
157.392
137.242
120.955
85.259
84.292
74.909
67.984
27.695
25.783
22.951
18.042
f1 (ppm)

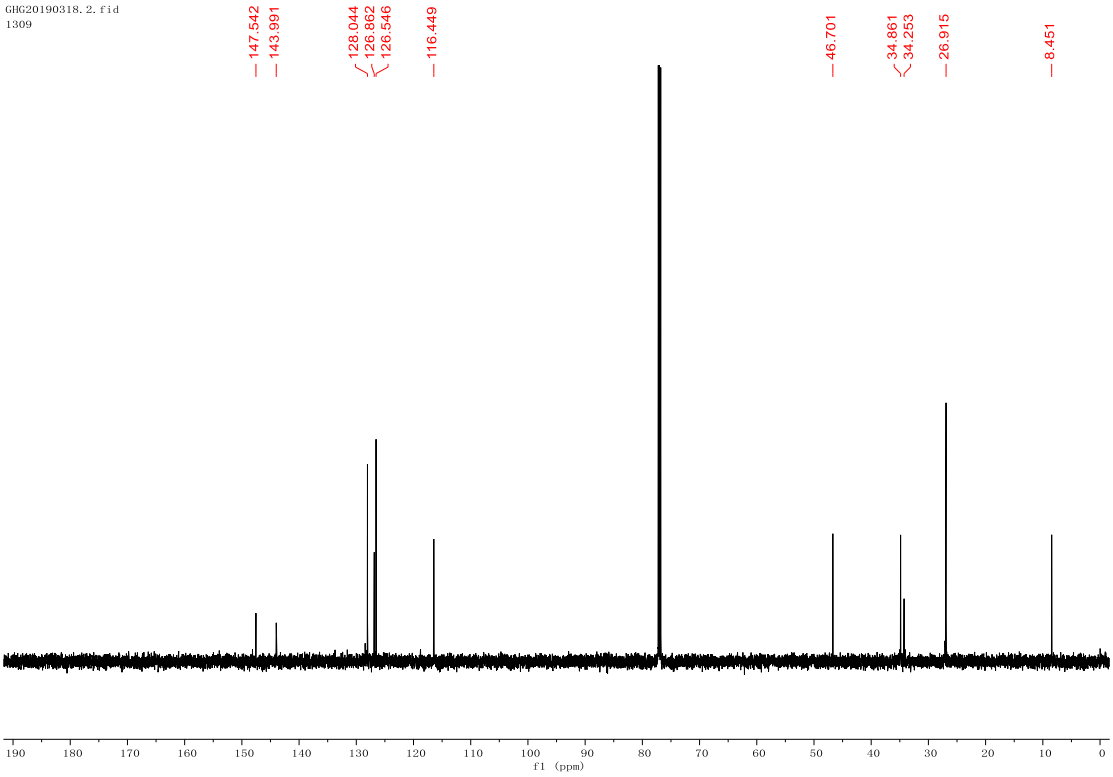

5.930
5.916
5.904
5.903
5.890
5.887
5.877
5.873
5.861
5.860
5.847
5.833
5.303
5.299
5.295
5.293
5.291
5.260
5.256
5.252
5.247
5.191
5.188
5.184
5.180
5.165
5.162
5.158
5.154
4.055
4.051
4.048
4.041
4.038
4.034
3.590
1.535
1.527
O
O
O
O
O
tBu
1.00
1.28
1.04
2.12
2.16
15.01
f1 (ppm)

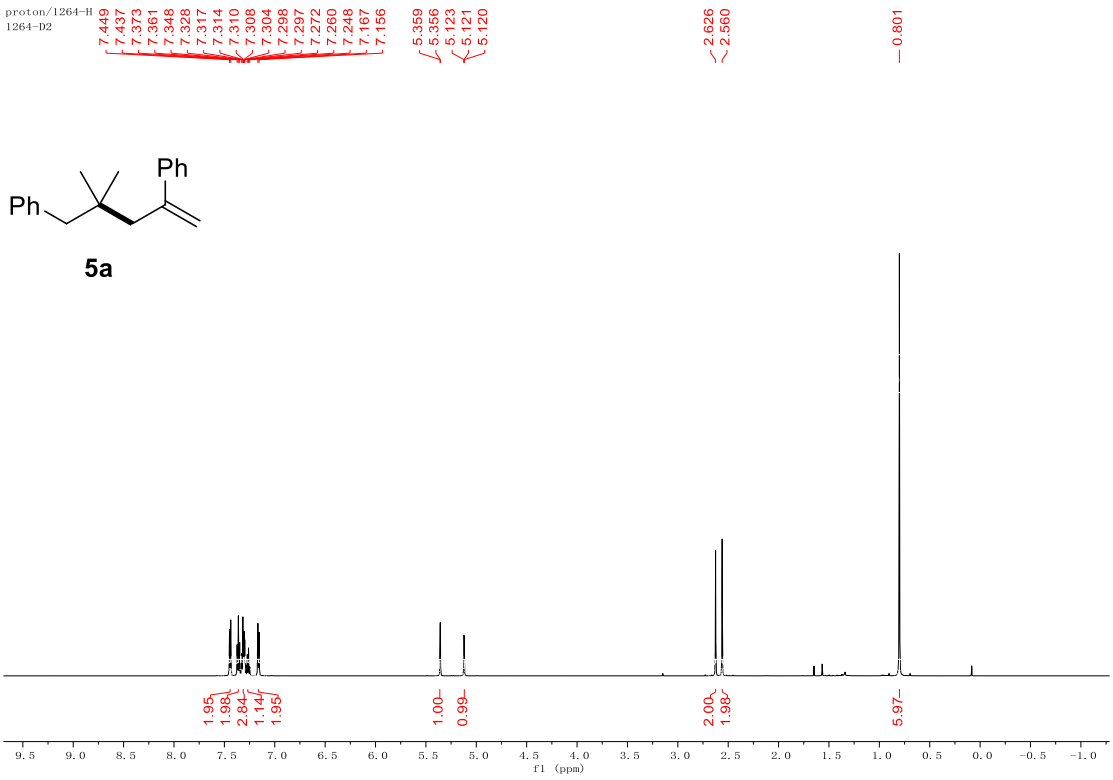

3-78-2 1
single pulse decoupled gated NOE
157.451
157.253
134.492
116.845
84.936
84.172
74.928
72.274
27.586
22.813
f1 (ppm)


5.724
5.713
5.702
5.688
5.677
5.666
5.566
5.564
5.556
5.554
5.546
5.543
5.531
5.528
5.520
5.518
3.970
3.960
3.556
1.704
1.694
1.525
1.522
O
O
O
O
O
tBu
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 ppm
1.00
1.03
1.95
2.04
2.97
15.12
157.57
157.39
129.44
127.45
85.16
84.24
74.80
72.24
27.70
22.95
17.71
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

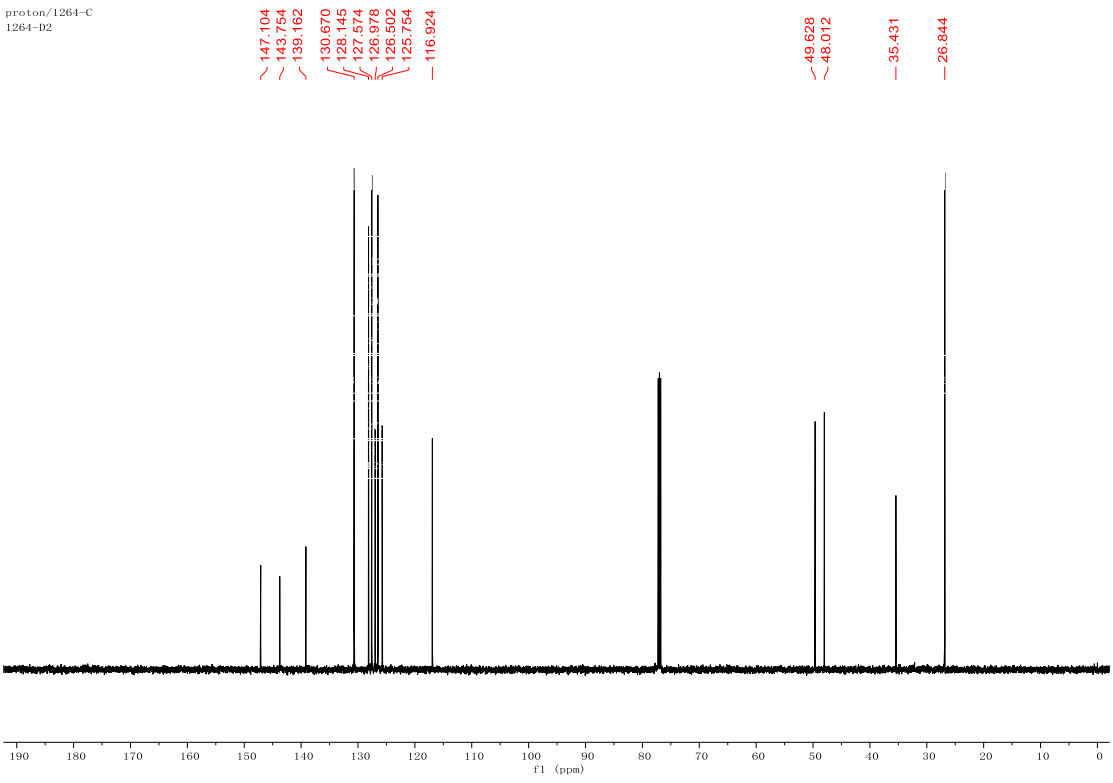

7.429
7.415
7.349
7.335
7.319
7.285
7.271
7.256
5.292
5.288
5.062
5.058
2.514
0.847
Me
Me
Me
Ph
3a
10
9
8
7
6
5
4
3
2
1
0
ppm
1.98
1.95
1.01
1.00
1.00
2.01
9.07
147.58
143.70
128.08
126.91
126.53
116.27
48.91
31.72
30.06
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


GHG20190318.1.fid
1309
7.376
7.365
7.306
7.294
7.281
7.244
7.232
7.219
5.233
5.229
5.023
5.022
5.020
5.018
5.017
2.456
1.204
1.191
1.178
1.166
0.792
0.780
0.767
0.716
Ph
4
2.00
2.07
1.16
1.03
1.03
2.03
2.37
3.38
5.93
f1 (ppm)

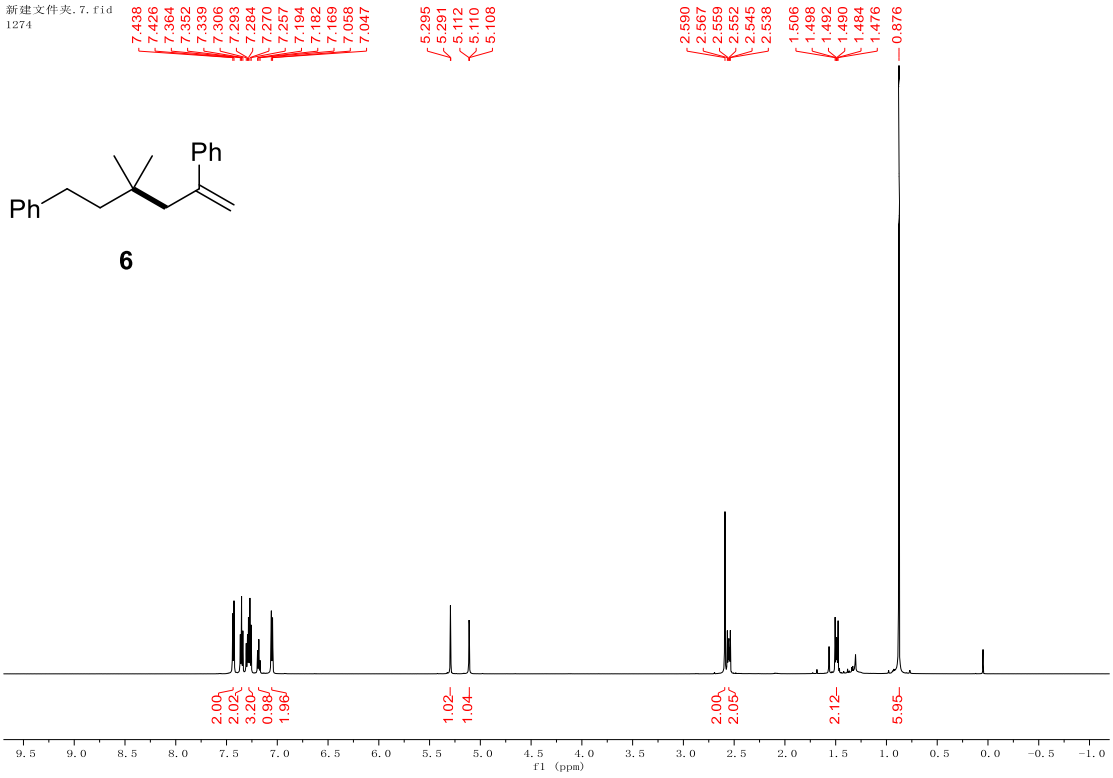

GHG20190318.2.fid
1309
147.542
143.991
128.044
126.862
126.546
116.449
46.701
34.861
34.253
26.915
8.451
f1 (ppm)


proton/1264-H
1264-D2
7.449
7.437
7.373
7.361
7.348
7.328
7.317
7.314
7.310
7.308
7.304
7.298
7.297
7.272
7.260
7.248
7.167
7.156
5.359
5.356
5.123
5.121
5.120
2.626
2.560
0.801
Ph
Ph
1.95
1.96
2.84
1.14
1.95
1.00
0.99
2.00
1.98
5.97
f1 (ppm)

5a


proton/1264-C
1264-D2
147.104
143.754
139.162
130.670
128.145
127.574
126.978
126.502
125.754
116.924
49.628
48.012
35.431
26.844
f1 (ppm)

新建文件夹.7.fid
1274

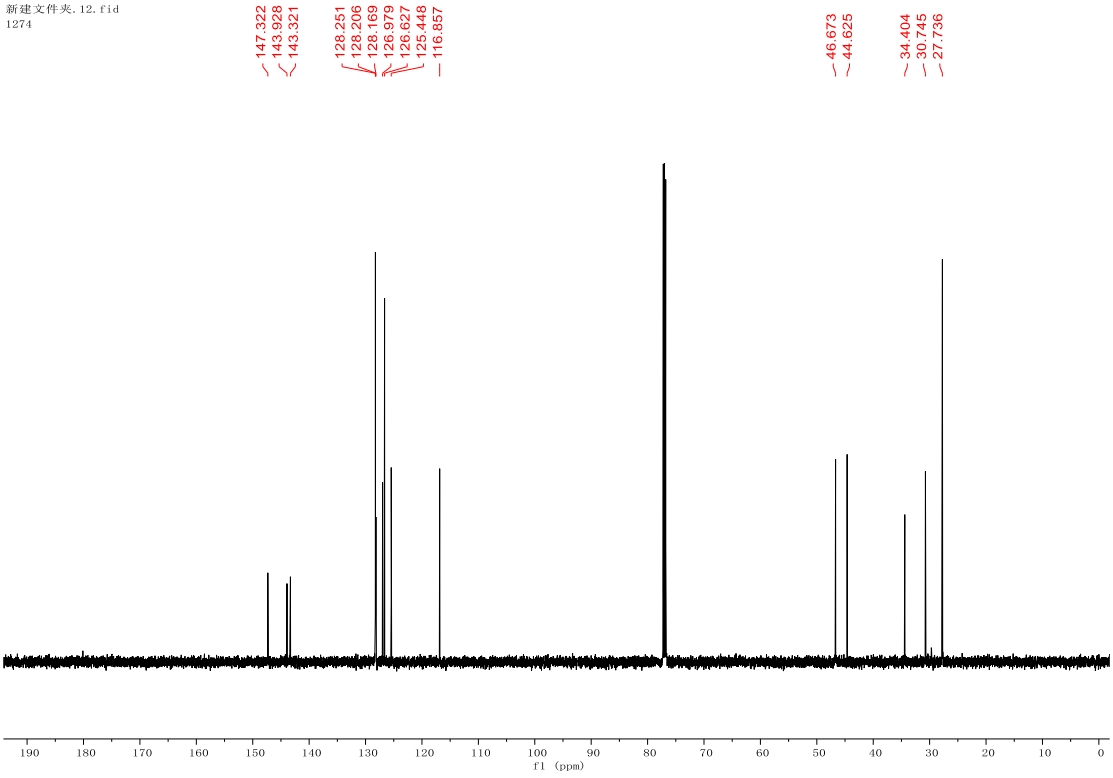


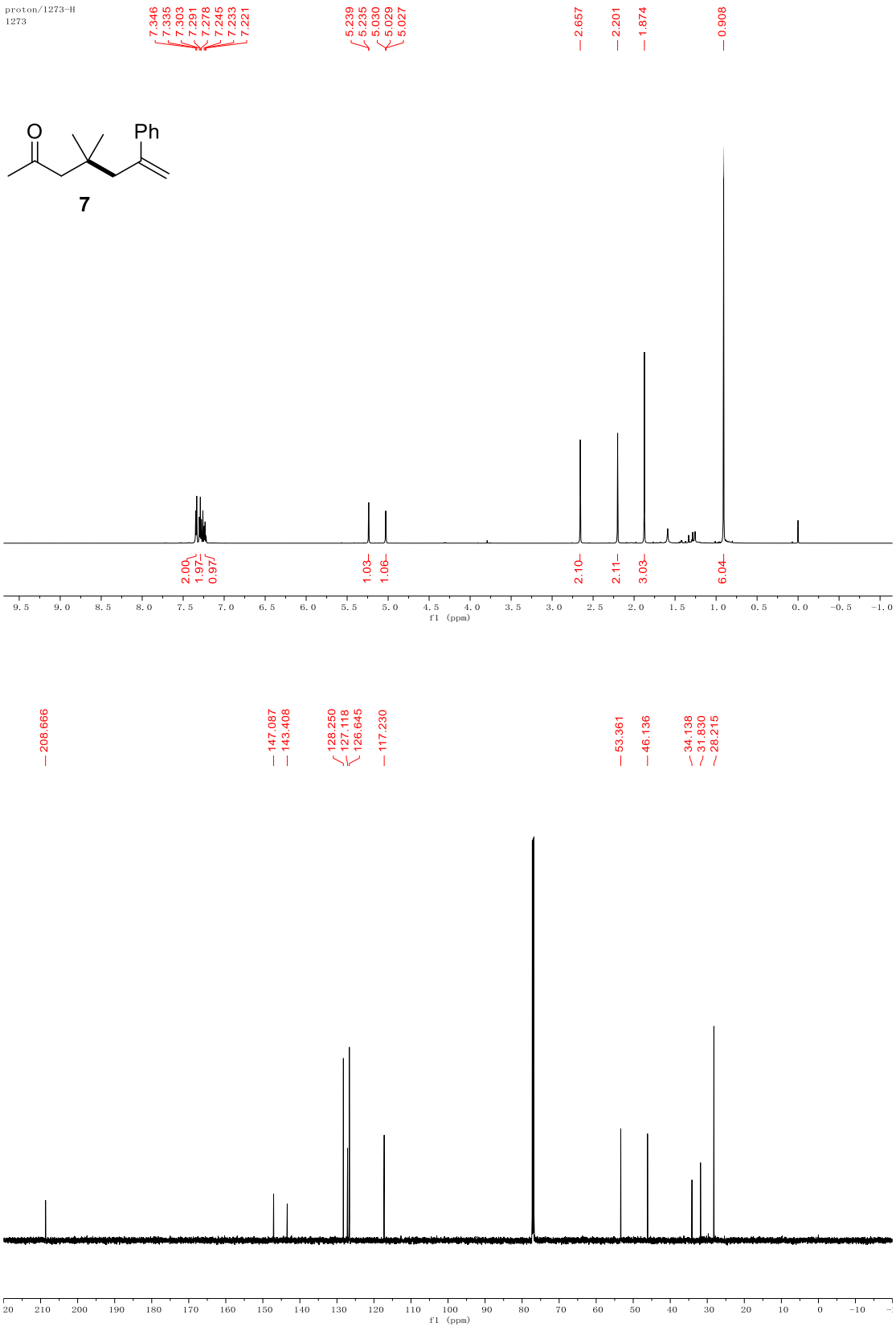
Ph

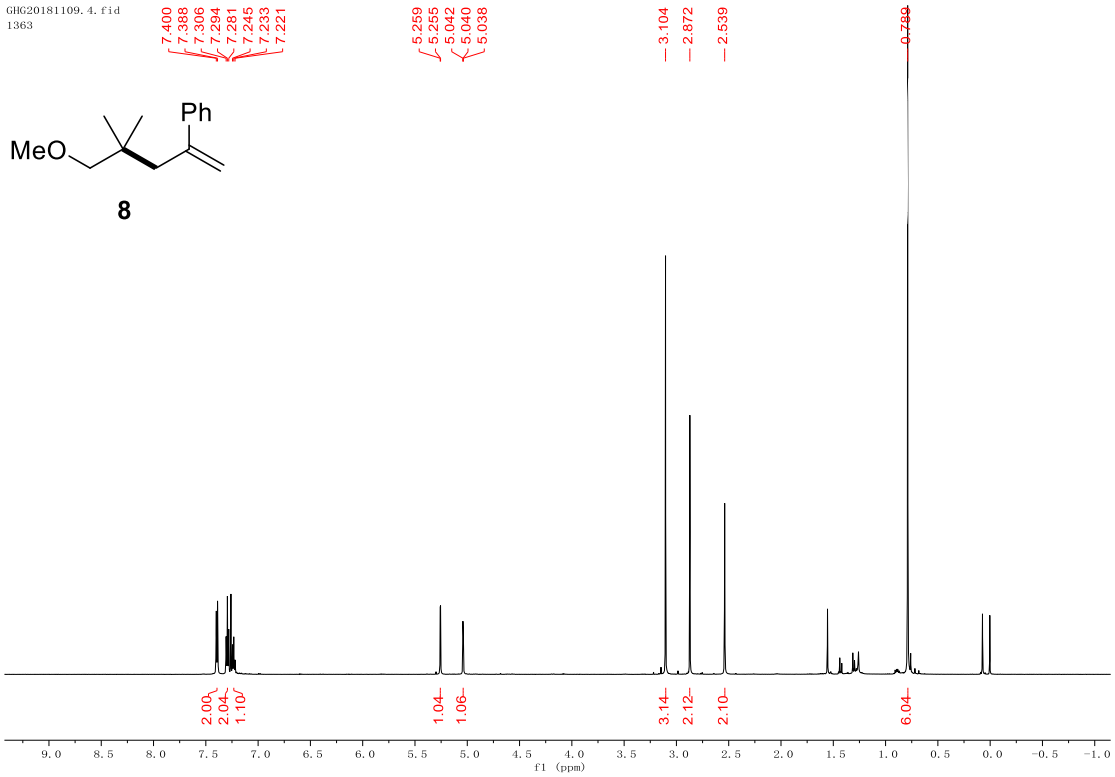
Ph

6

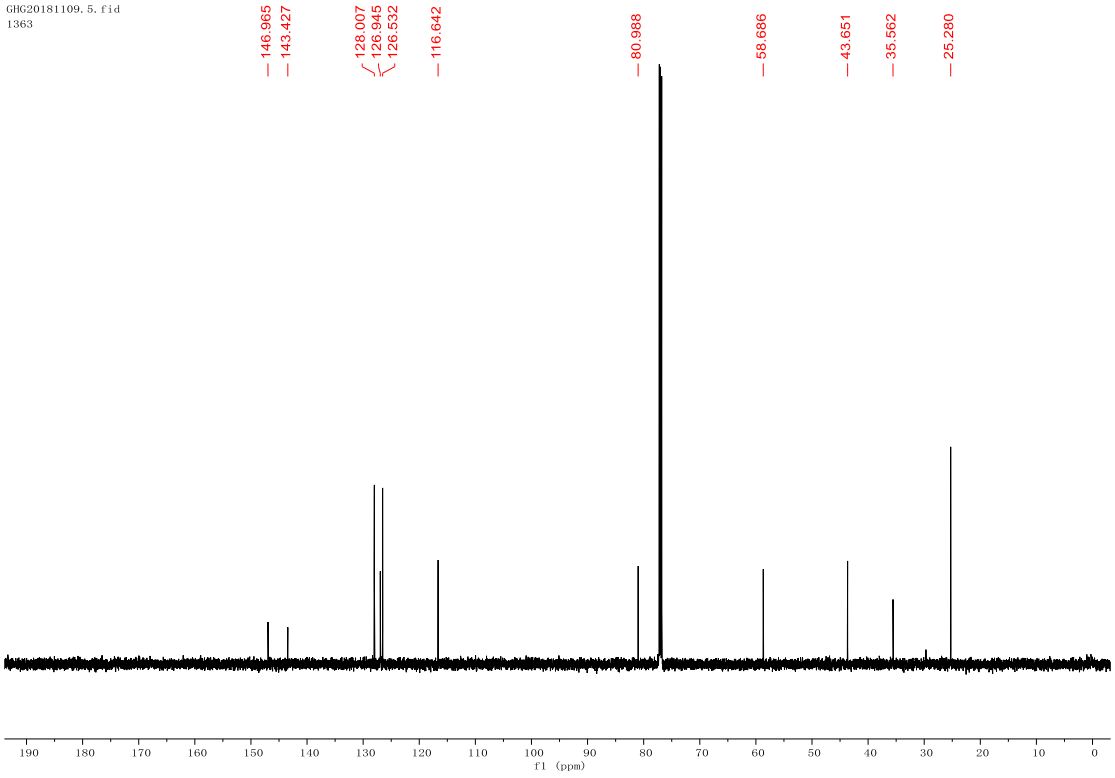
新建文件夹.12.fid
1274

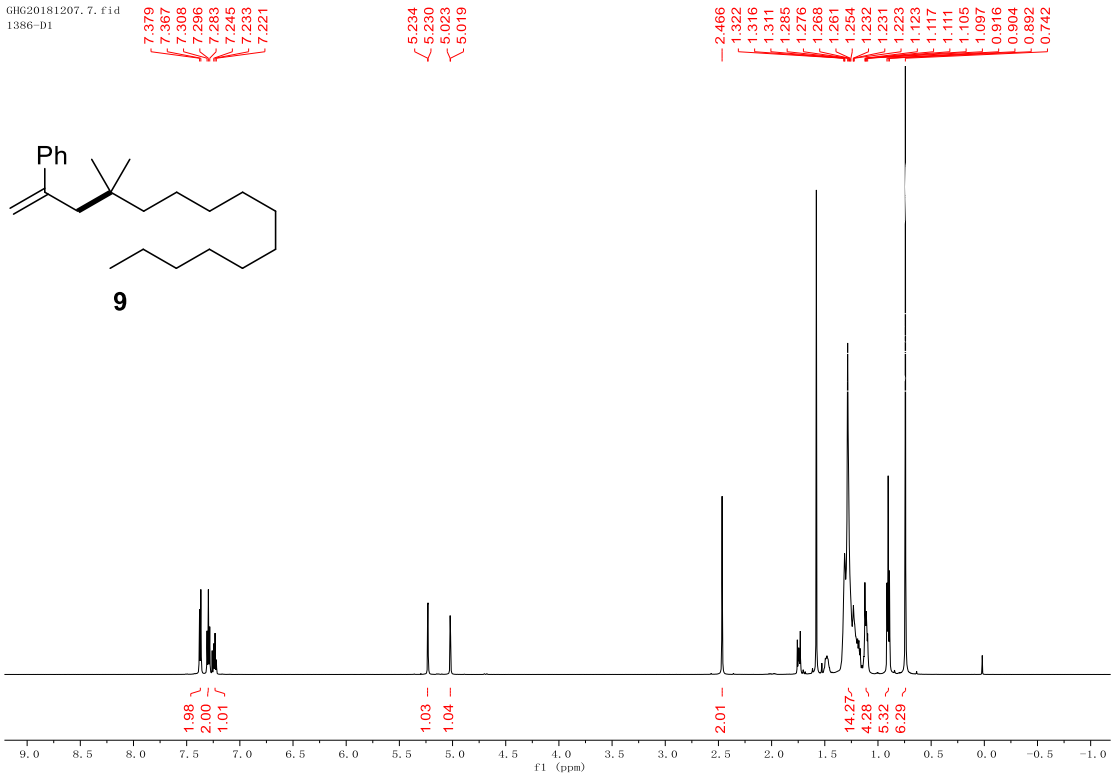


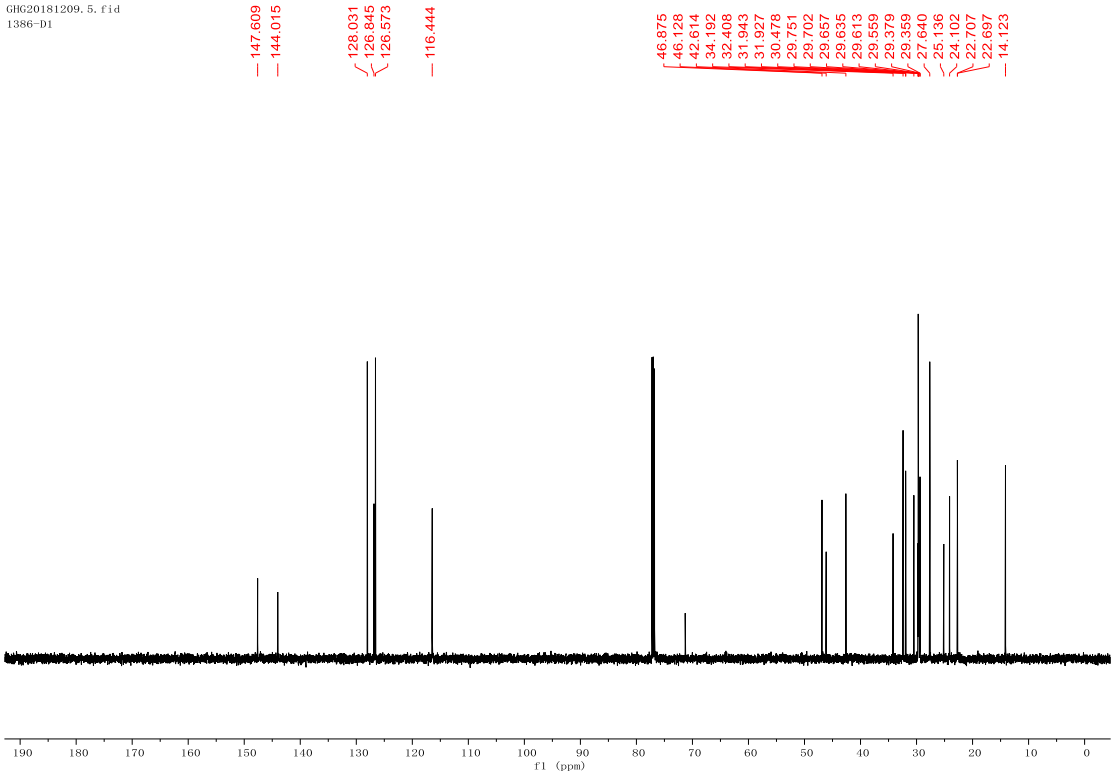

proton/1273-H
1273
7.346
7.335
7.303
7.291
7.278
7.245
7.233
7.221
5.239
5.235
5.030
5.029
5.027
2.657
2.201
1.874
0.908
O
Ph
7
2.00
1.97
0.97
1.03
1.06
2.10
2.11
3.03
6.04
f1 (ppm)
208.666
147.087
143.408
128.250
127.118
126.645
117.230
53.361
46.136
34.138
31.830
28.215
f1 (ppm)

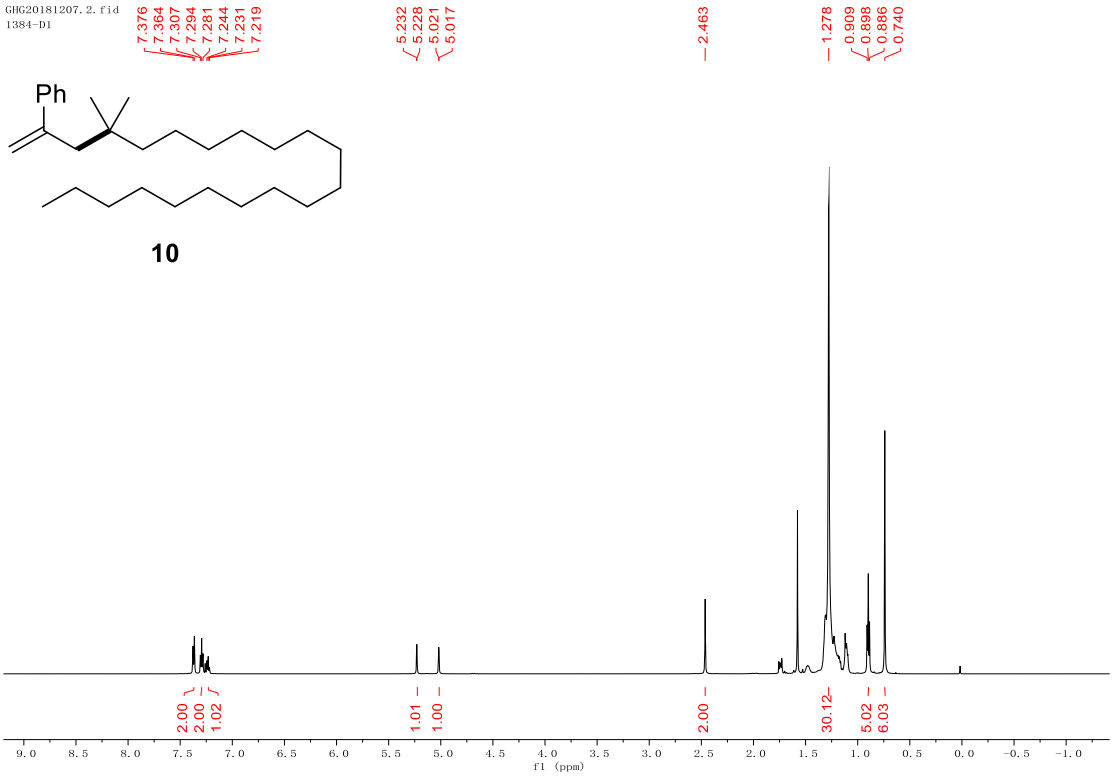

GHG20181109.4.fid
1363
7.400
7.388
7.306
7.294
7.281
7.245
7.233
7.221
5.259
5.255
5.042
5.040
5.038
3.104
2.872
2.539
0.789
Ph
MeO
2.00
2.04
1.10
1.04
1.06
3.14
2.12
2.10
6.04
f1 (ppm)

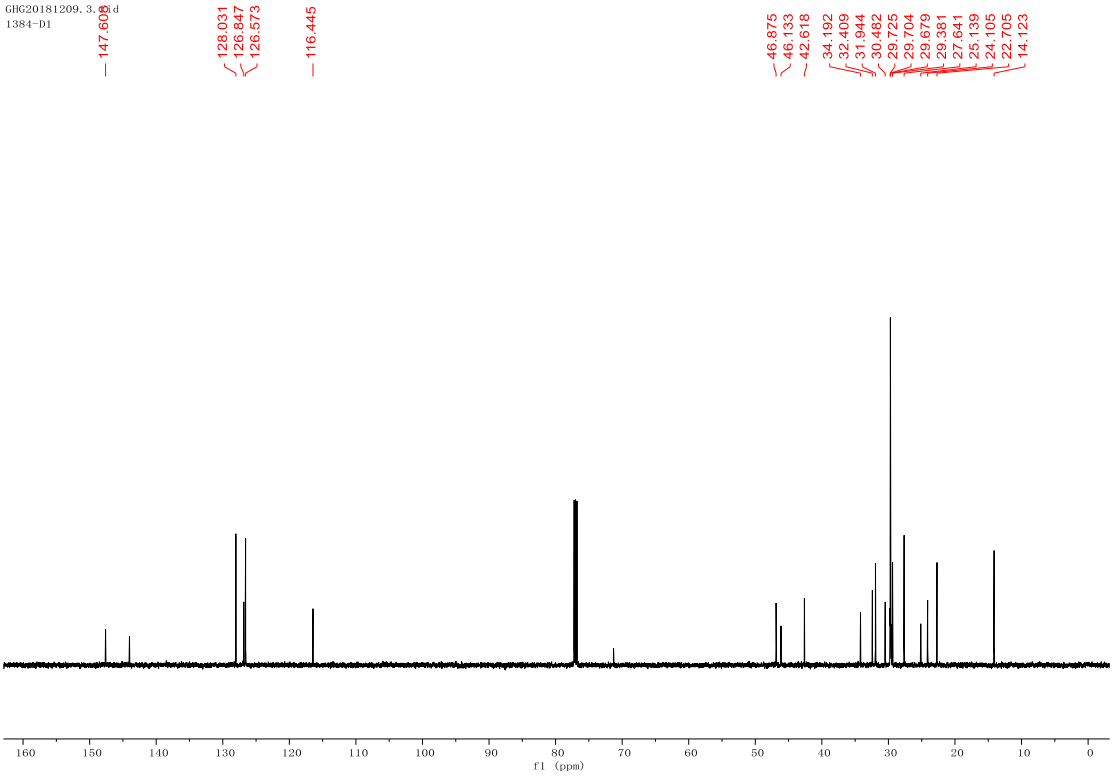
8


GHG20181109.5.fid
1363
146.965
143.427
128.007
126.945
126.532
116.642
80.988
58.686
43.651
35.562
25.280
f1 (ppm)


GHG20181207.7.fid
1386-D1
7.379
7.367
7.308
7.296
7.283
7.245
7.233
7.221
5.234
5.230
5.023
5.019
2.466
1.322
1.316
1.311
1.285
1.276
1.268
1.261
1.254
1.232
1.231
1.223
1.123
1.117
1.111
1.105
1.097
0.916
0.904
0.892
0.742
Ph
9
1.98
2.00
1.01
1.03
1.04
2.01
14.27
4.28
5.32
6.29
f1 (ppm)

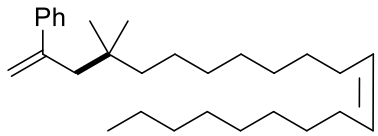

GHG20181209.5.fid
1386-D1
147.609
144.015
128.031
126.845
126.573
116.444
46.875
46.128
42.614
34.192
32.408
31.943
31.927
30.478
29.751
29.702
29.657
29.635
29.613
29.559
29.379
29.359
27.640
25.136
24.102
22.707
22.697
14.123
f1 (ppm)


GHG20181207.2.fid
1384-D1
7.376
7.364
7.307
7.294
7.281
7.244
7.231
7.219
5.232
5.228
5.021
5.017
2.463
1.278
0.909
0.898
0.886
0.740
Ph
10
2.00
2.00
1.02
1.01
1.00
2.00
30.12
5.02
6.03
f1 (ppm)

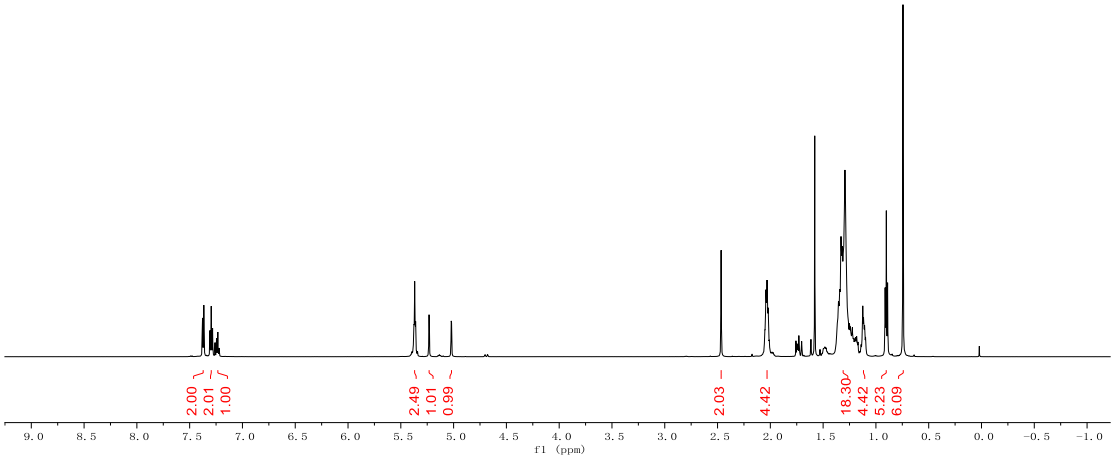

GHG20181209.3.fid
1384-D1
147.609
128.031
126.847
126.573
116.445
46.875
46.133
42.618
34.192
32.409
31.944
30.482
29.725
29.704
29.679
29.381
27.641
25.139
24.105
22.705
14.123
f1 (ppm)

GHG20181207.5.fid
1385-D1

7.378 7.367 7.308 7.296 7.283 7.245 7.233 7.221
5.378 5.375 5.369 5.360
2.466 2.042 2.031 2.020 1.330 1.319 1.308 1.299 1.294 1.289 1.282 1.129 1.125 1.118 1.113 1.107 1.098 1.096 0.912 0.901 0.889 0.744

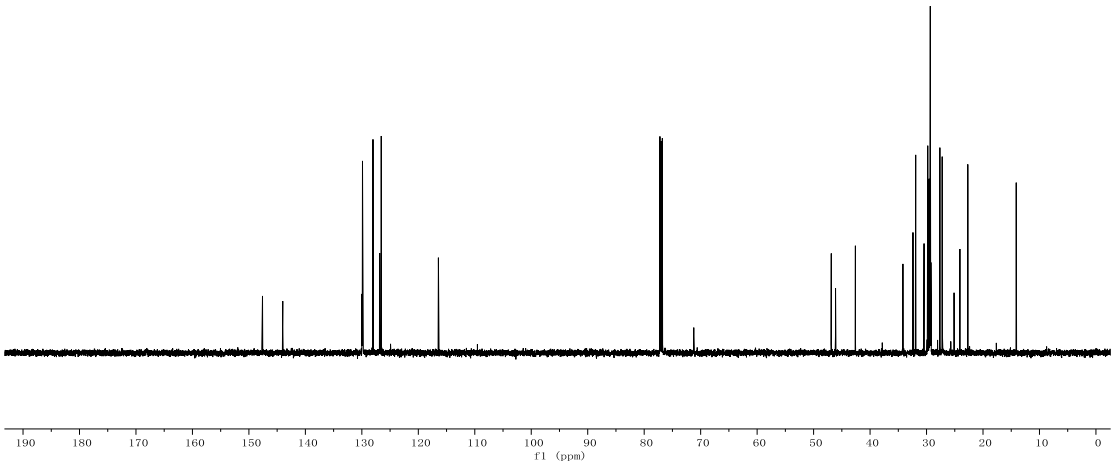


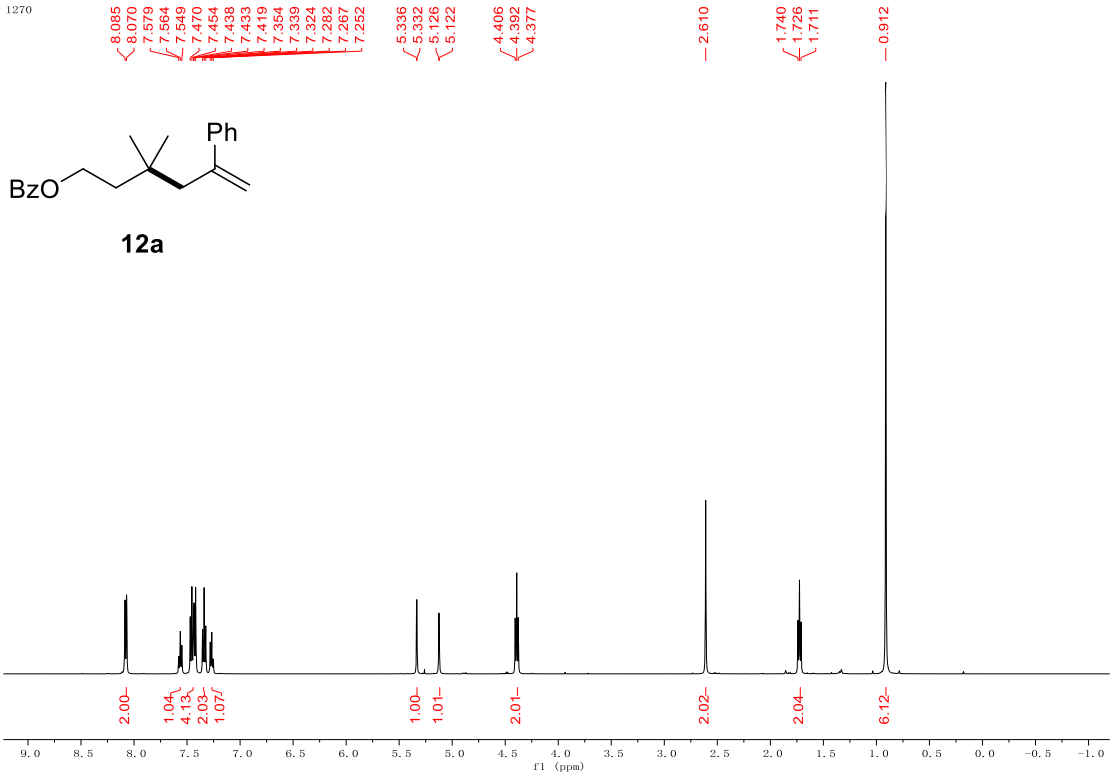
11

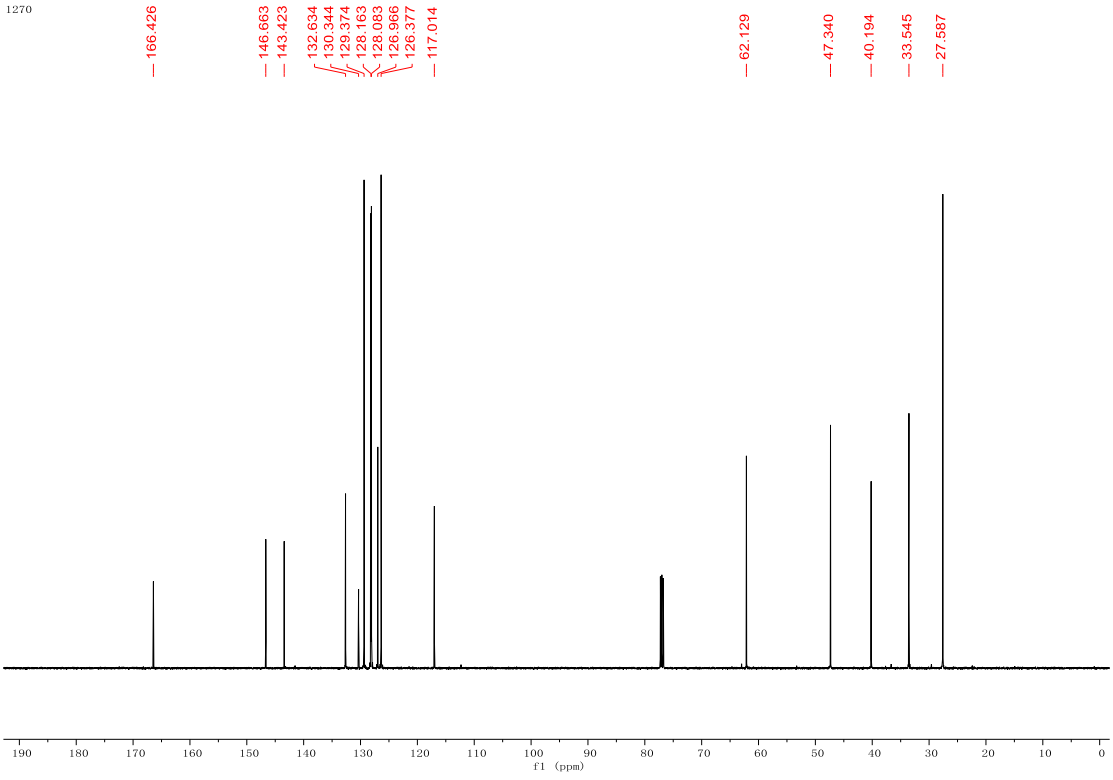


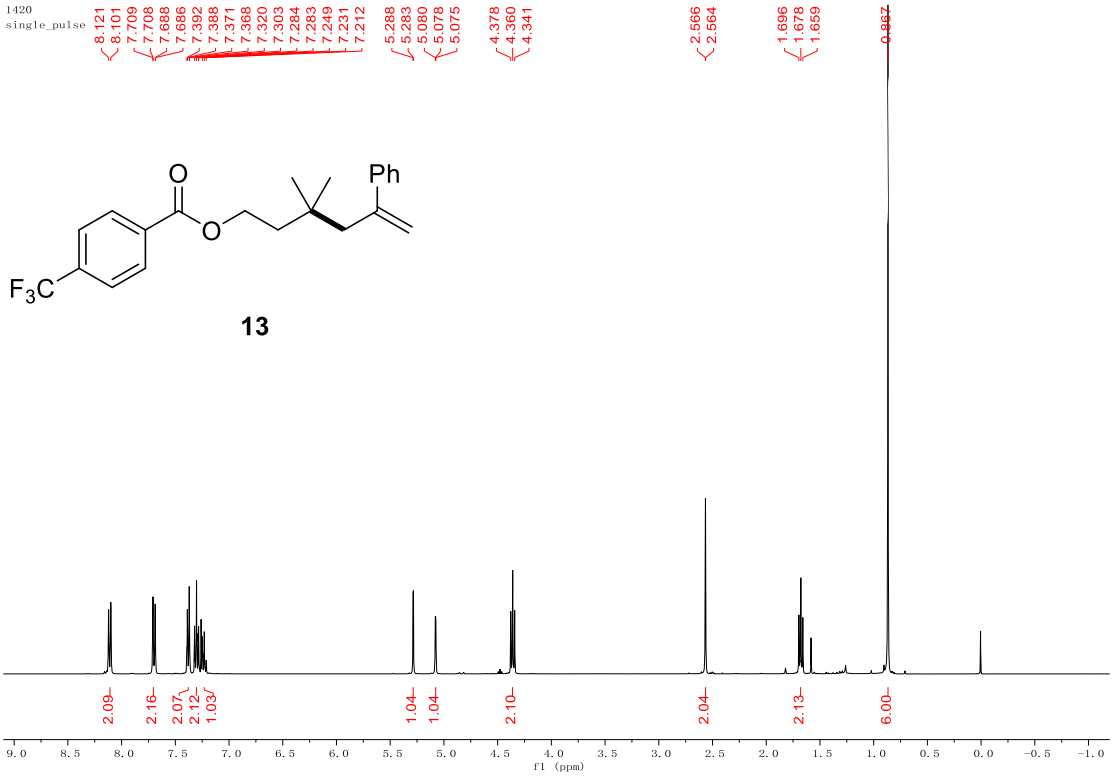
GHG20181209.4.fid
1385-D1

147.593 144.004
129.885 128.027 126.847 126.565
116.445
46.869 46.115 42.599 34.183 32.403 31.920 30.439 29.783 29.740 29.719 29.568 29.540 29.439 29.336 29.235 27.636 27.227 27.211 27.183 25.124 24.092 22.692 14.114

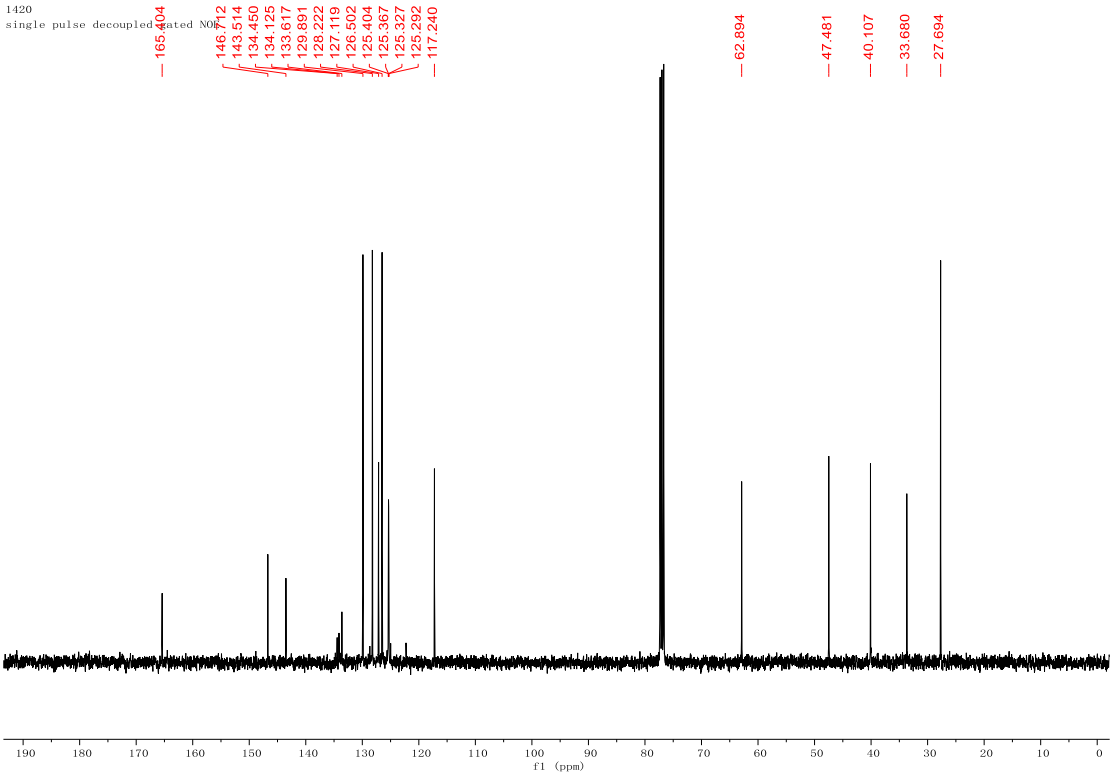


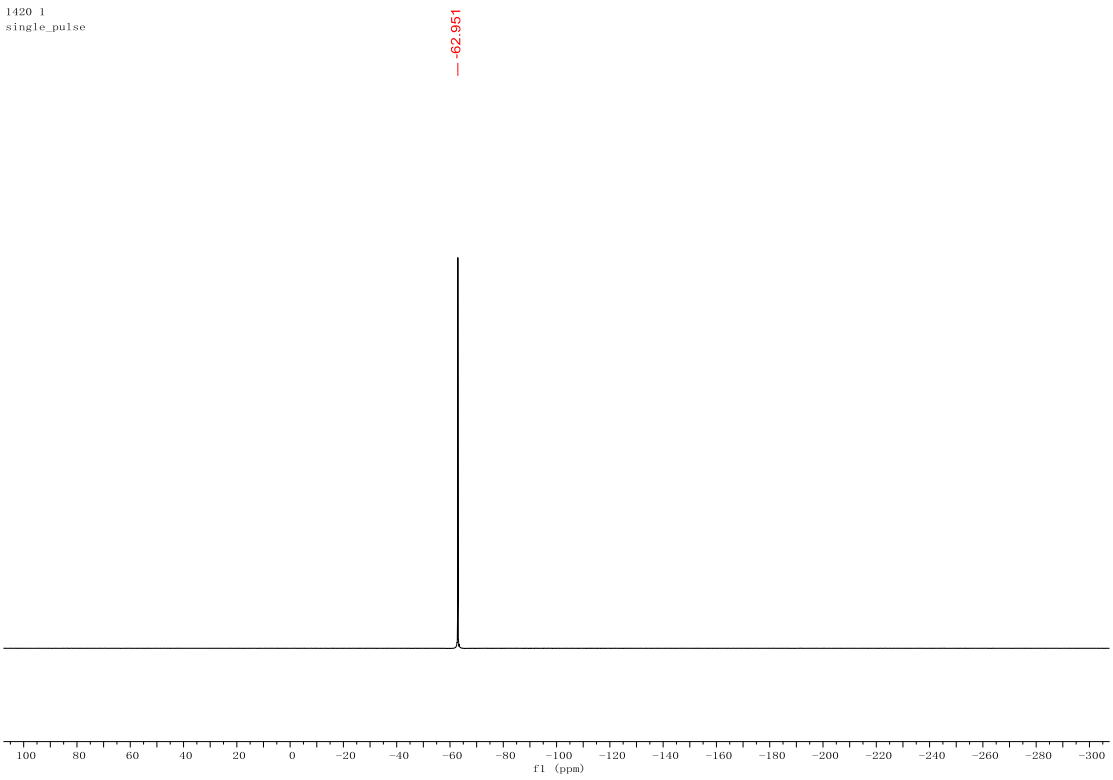

1270
8.085
8.070
7.579
7.564
7.549
7.470
7.454
7.438
7.433
7.419
7.354
7.339
7.324
7.282
7.267
7.252
5.336
5.332
5.126
5.122
4.406
4.392
4.377
2.610
1.740
1.726
1.711
0.912
Ph
BzO
12a
2.00
1.04
4.13
2.03
1.07
1.00
1.01
2.01
2.02
2.04
6.12
f1 (ppm)

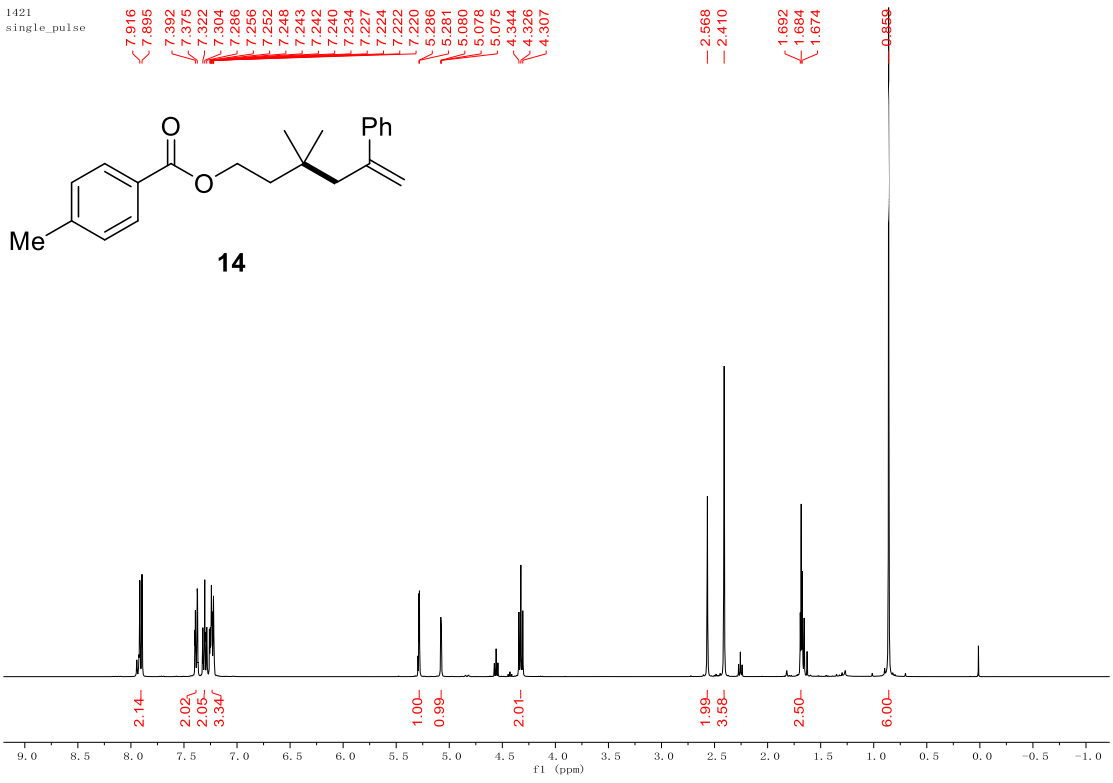

1270
166.426
146.663
143.423
132.634
130.344
129.374
128.163
128.083
126.966
126.377
117.014
62.129
47.340
40.194
33.545
27.587
f1 (ppm)

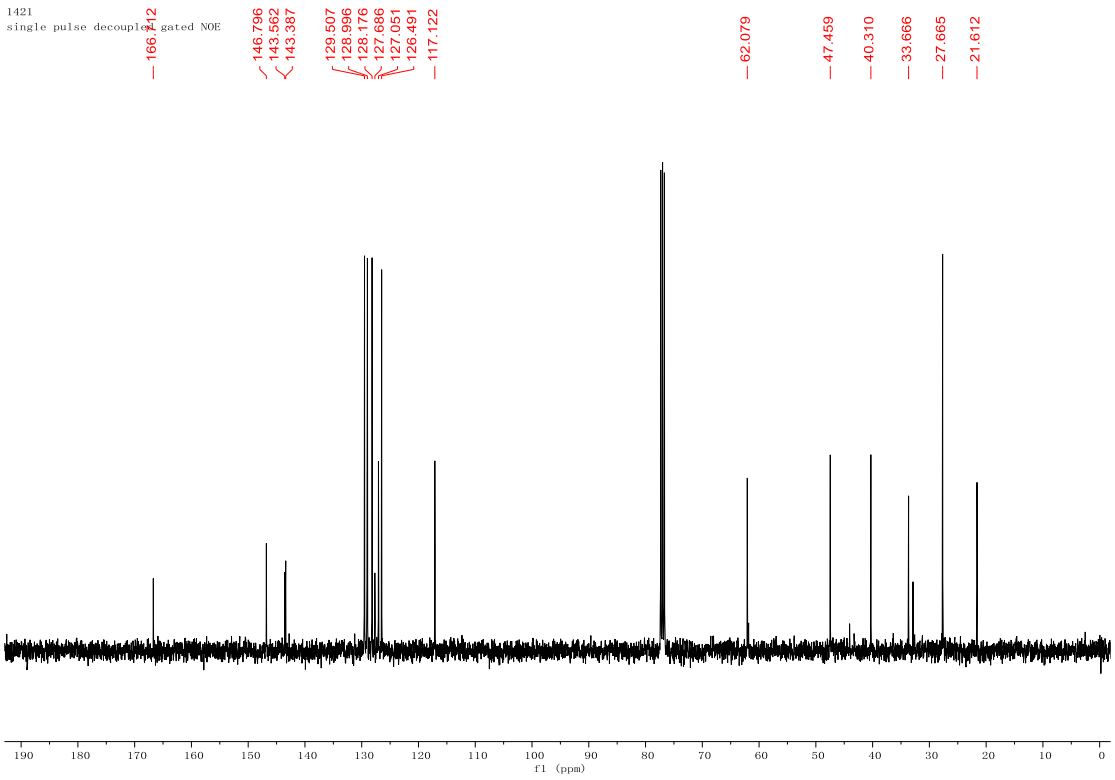

1420
single_pulse
8.121
8.101
7.709
7.708
7.688
7.686
7.392
7.388
7.371
7.368
7.320
7.303
7.284
7.283
7.249
7.231
7.212
5.288
5.283
5.080
5.078
5.075
4.378
4.360
4.341
2.566
2.564
1.696
1.678
1.659
0.867
O
O
Ph
F3C
2.09
2.16
2.07
2.12
1.03
1.04
1.04
2.10
2.04
2.13
6.00
f1 (ppm)

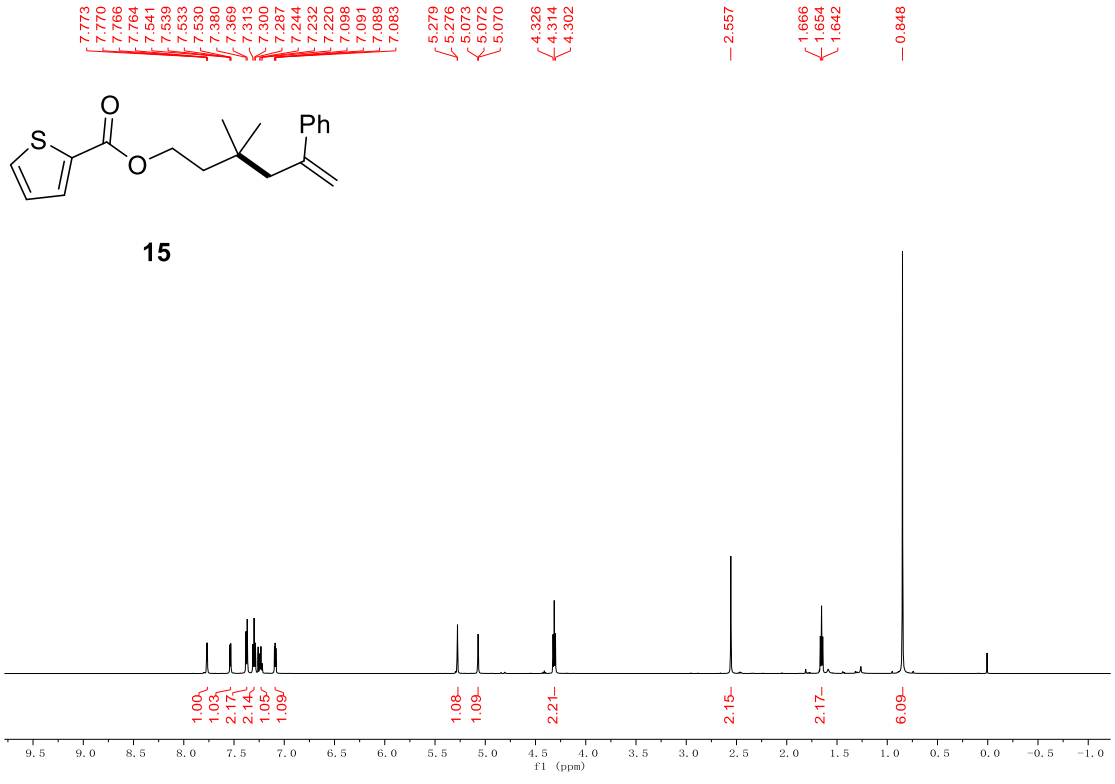
13


1420
single pulse decoupled gated NOE
165.404
146.712
143.514
134.450
134.125
133.617
129.891
128.222
127.119
126.502
125.404
125.367
125.327
125.292
117.240
62.894
47.481
40.107
33.680
27.694
f1 (ppm)


1420 1
single_pulse
-62.951
f1 (ppm)

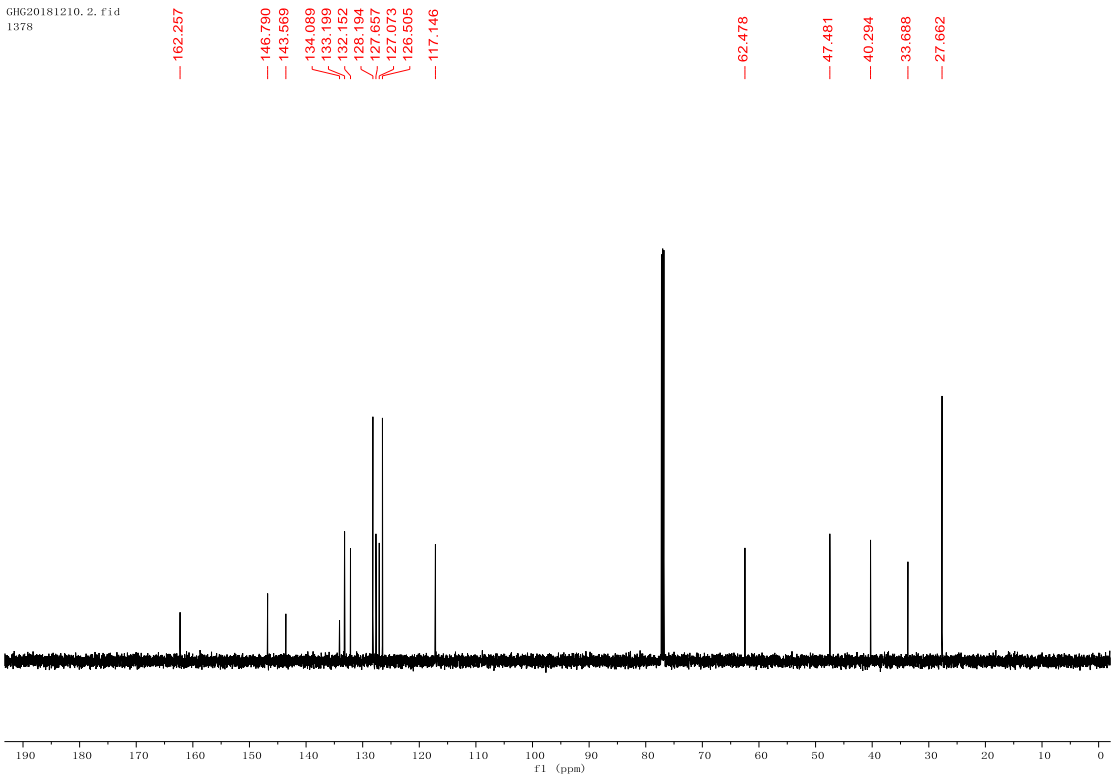

1421
single_pulse
7.916
7.895
7.392
7.375
7.322
7.304
7.286
7.256
7.252
7.248
7.243
7.242
7.240
7.234
7.227
7.224
7.222
7.220
5.286
5.281
5.080
5.078
5.075
4.344
4.326
4.307
2.568
2.410
1.692
1.684
1.674
0.850
O
O
Ph
Me
14
2.14
2.02
2.05
3.34
1.00
0.99
2.01
1.99
3.58
2.50
6.00
f1 (ppm)

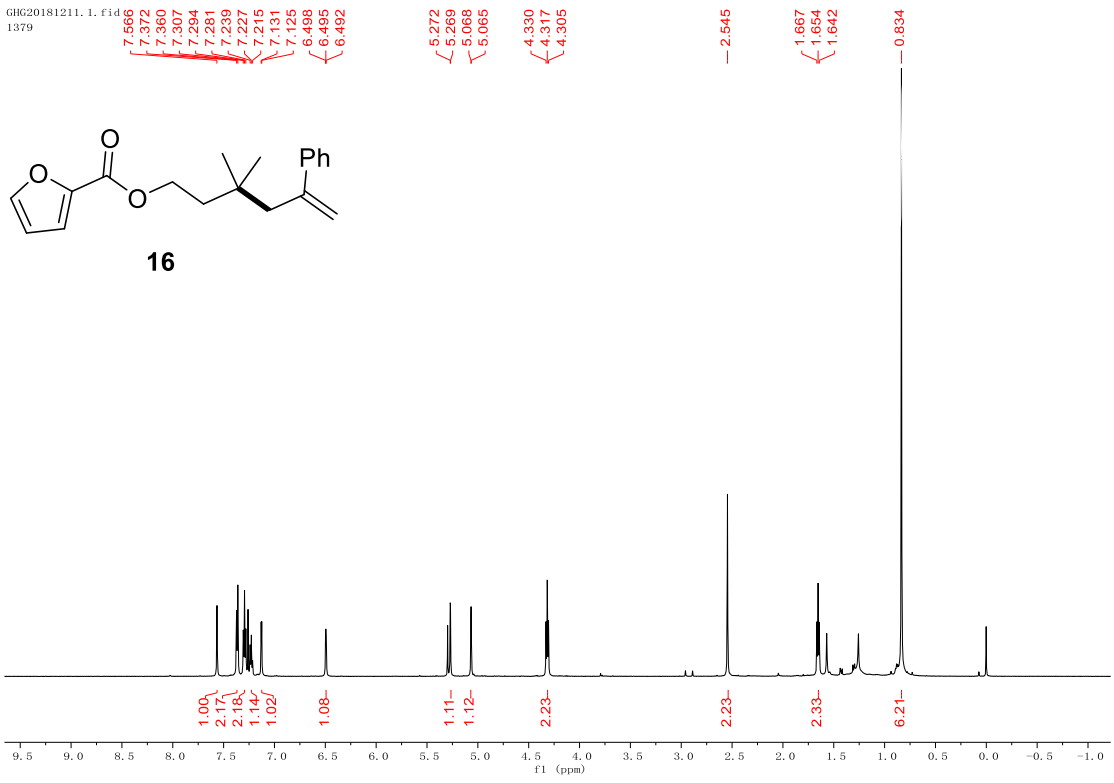

1421
single pulse decoupled gated NOE
166.212
146.796
143.562
143.387
129.507
128.996
128.176
127.686
127.051
126.491
117.122
62.079
47.459
40.310
33.666
27.665
21.612
f1 (ppm)


7.773
7.770
7.766
7.764
7.541
7.539
7.533
7.530
7.380
7.369
7.313
7.300
7.287
7.244
7.232
7.220
7.098
7.091
7.089
7.083
5.279
5.276
5.073
5.072
5.070
4.326
4.314
4.302
2.557
1.666
1.654
1.642
0.848
1.00
1.03
2.17
2.14
1.05
1.09
1.08
1.09
2.21
2.15
2.17
6.09
f1 (ppm)

O
S
O
Ph

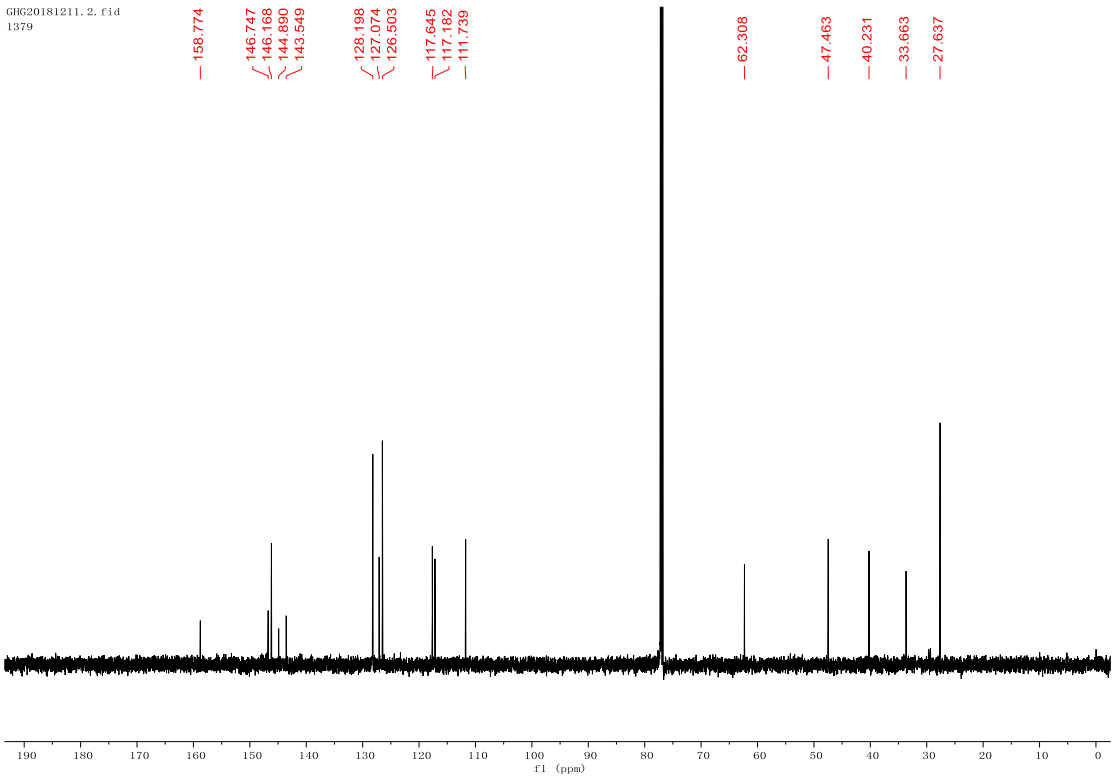
15


GHG20181210.2.fid
1378
162.257
146.790
143.569
134.089
133.199
132.152
128.194
127.657
127.073
126.505
117.146
62.478
47.481
40.294
33.688
27.662
f1 (ppm)

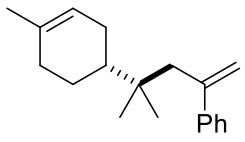

GHG20181211.1.fid
1379
7.566
7.372
7.360
7.307
7.294
7.281
7.239
7.227
7.215
7.131
7.125
6.498
6.495
6.492
5.272
5.269
5.068
5.065
4.330
4.317
4.305
2.545
1.667
1.654
1.642
0.834
1.00
2.17
2.18
1.14
1.02
1.08
1.11
1.12
2.23
2.23
2.33
6.21
f1 (ppm)

O
O
O
Ph

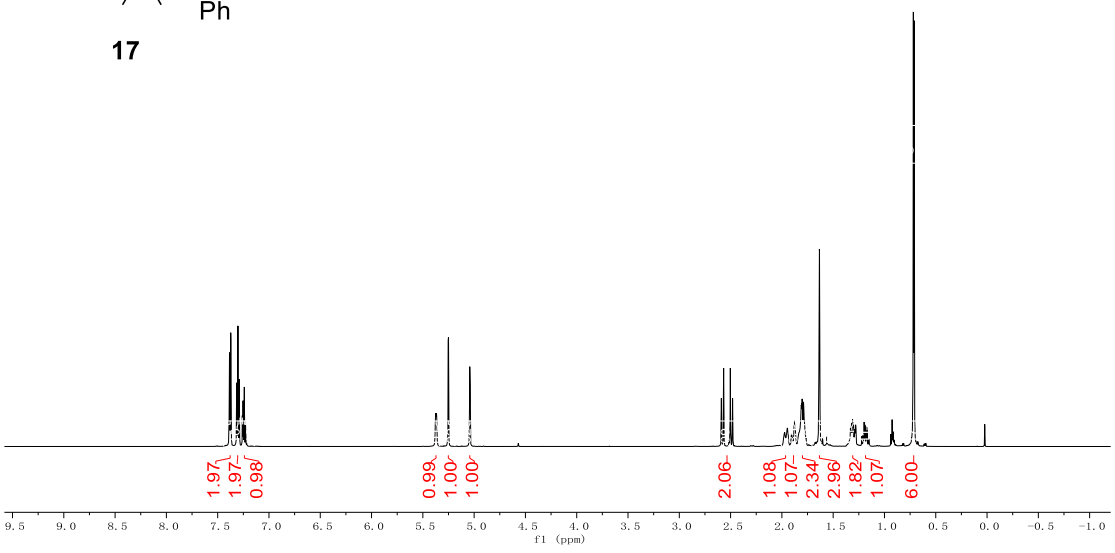
16

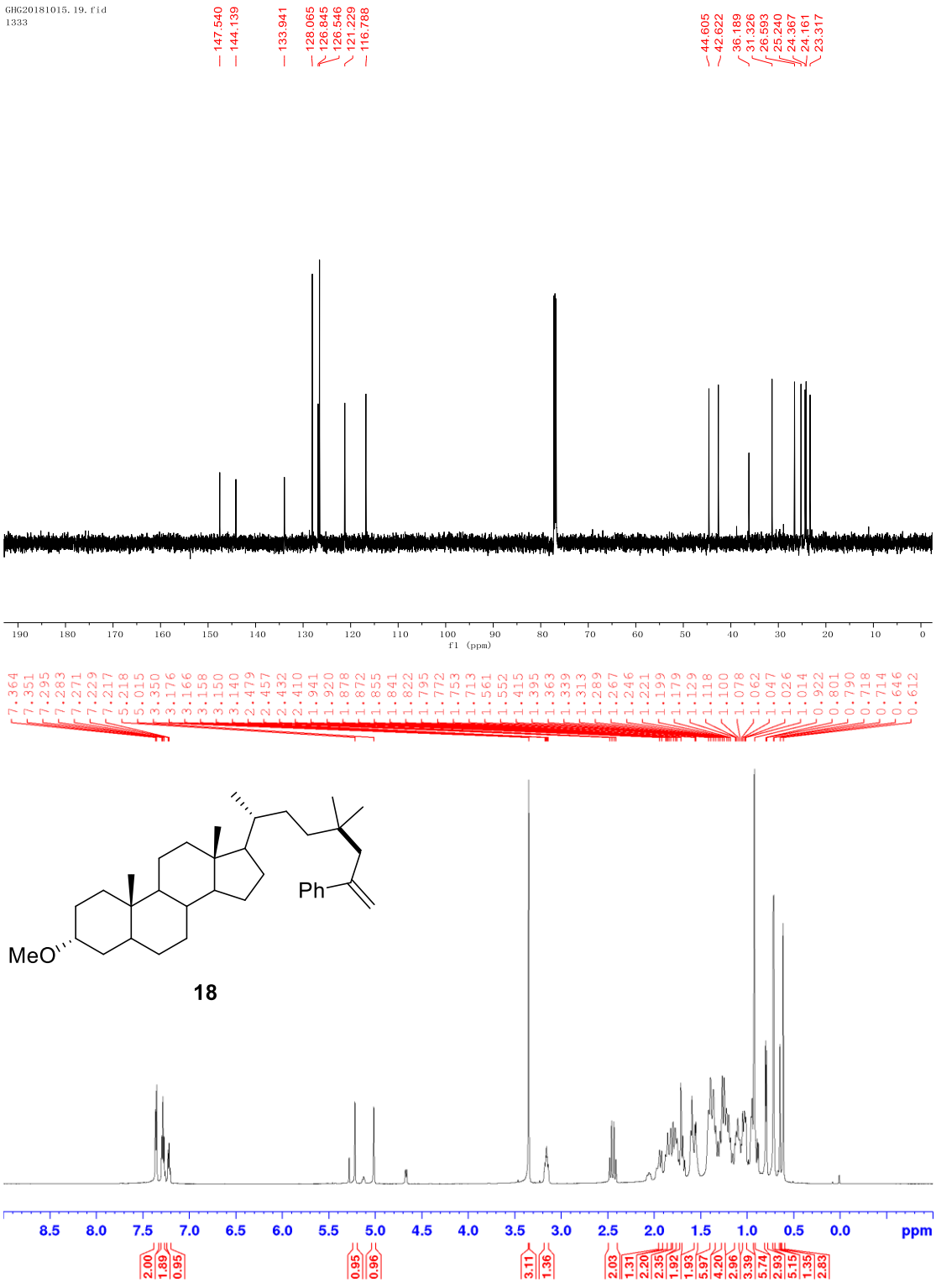

GHG20181211.2.fid
1379
158.774
146.747
146.168
144.890
143.549
128.198
127.074
126.503
117.645
117.182
111.739
62.308
47.463
40.231
33.663
27.637
f1 (ppm)

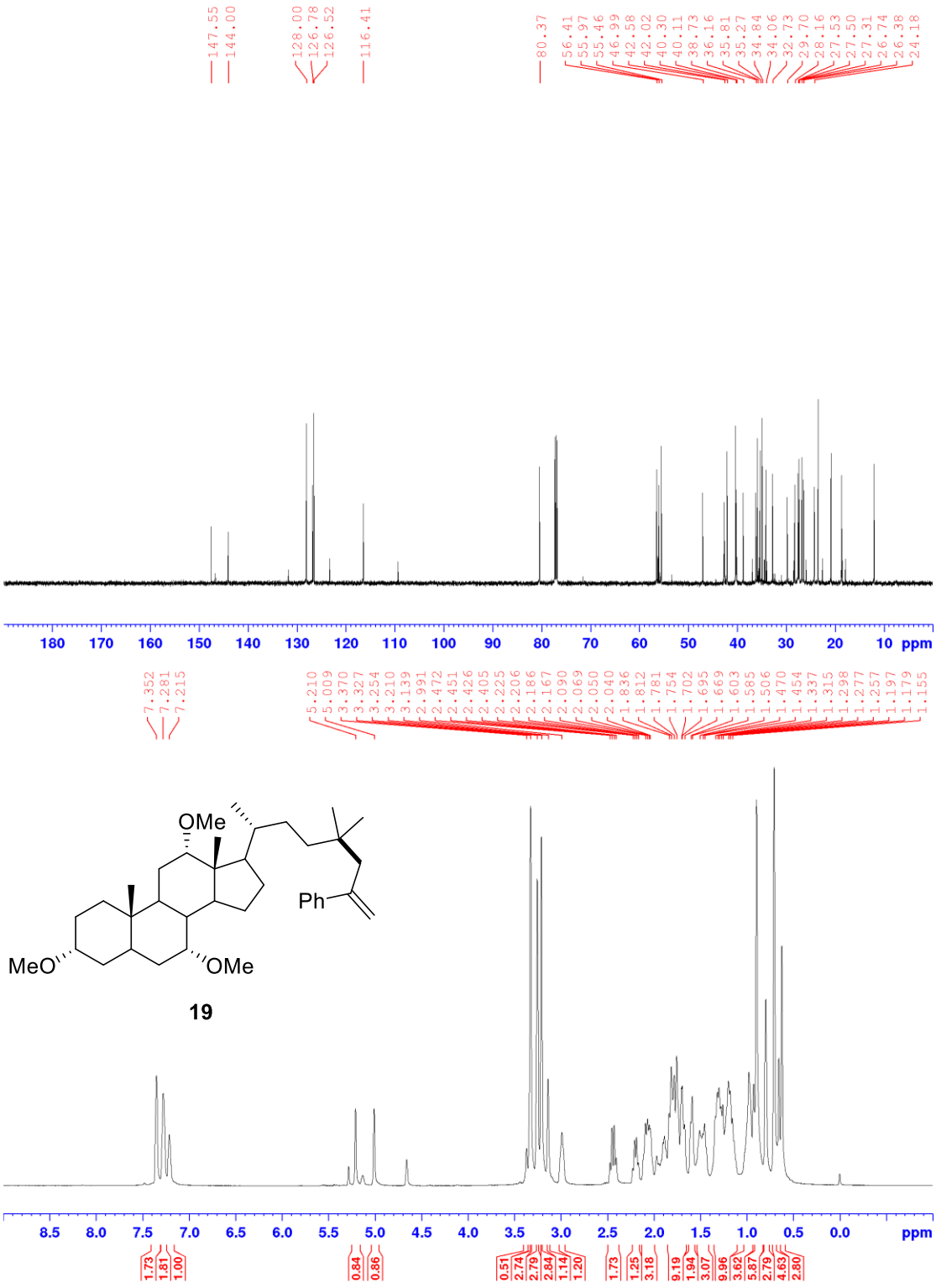

7.385
7.373
7.315
7.303
7.290
7.253
7.240
7.228
5.373
5.367
5.253
5.250
5.043
5.041
5.039
2.590
2.568
2.503
2.481
1.978
1.976
1.973
1.970
1.951
1.948
1.945
1.908
1.904
1.901
1.879
1.873
1.868
1.812
1.809
1.806
1.803
1.799
1.792
1.789
1.786
1.636
1.332
1.329
1.324
1.321
1.315
1.311
1.305
1.303
1.300
1.293
1.290
1.285
1.281
1.278
1.219
1.208
1.198
1.188
1.177
1.169
1.156
1.149
0.719
0.711

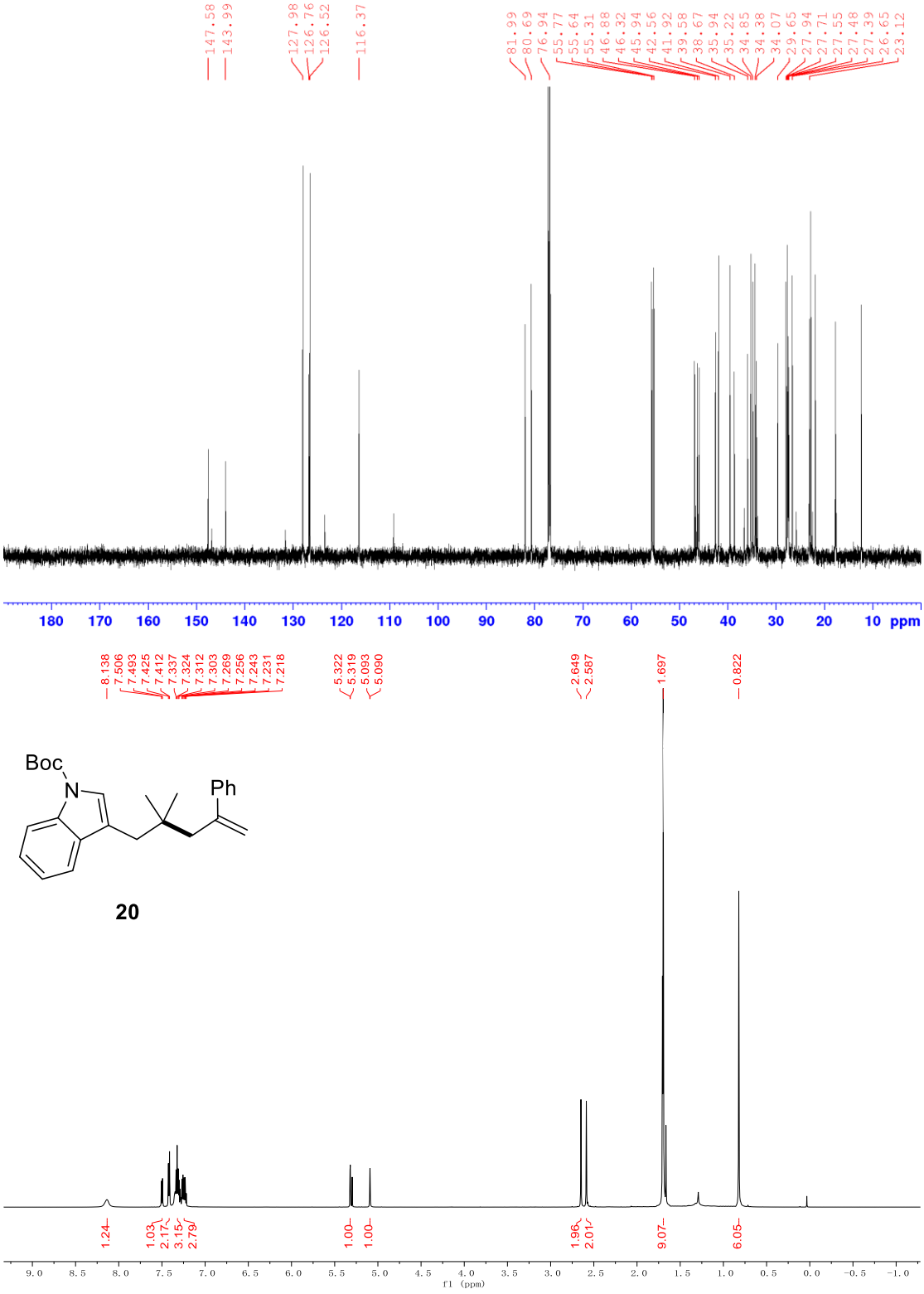

Ph

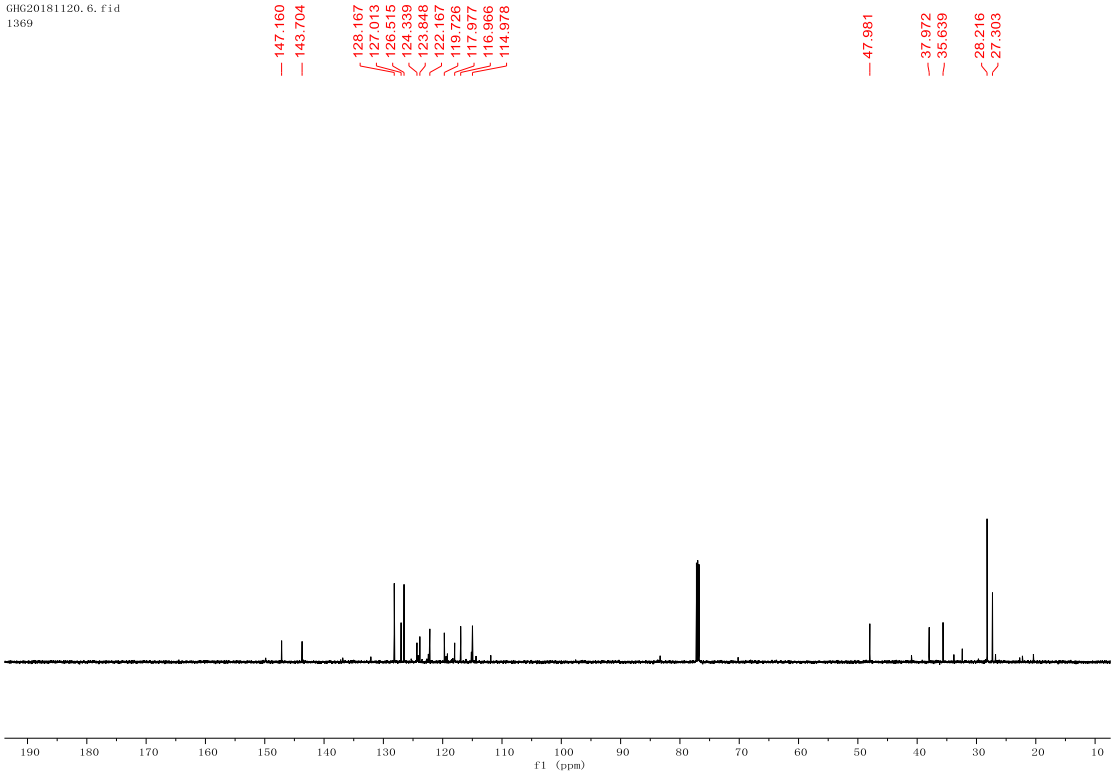
17

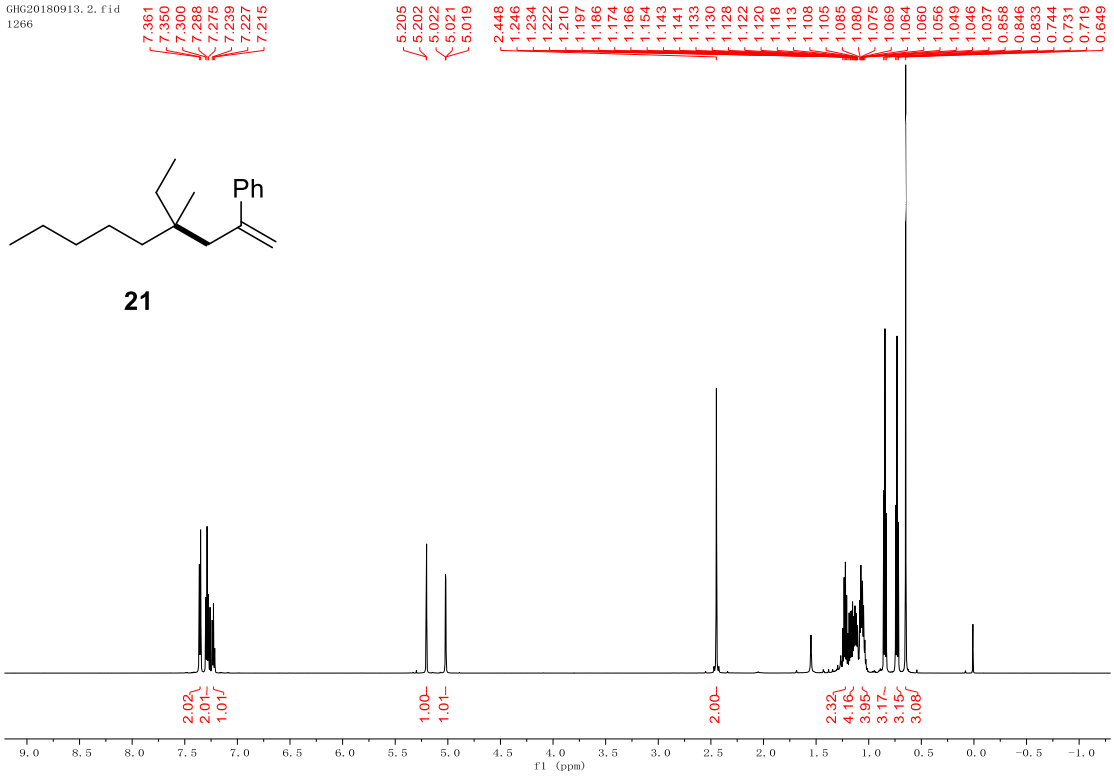

1.97
1.97
0.98
0.99
1.00
1.00
2.06
1.08
1.07
2.34
2.96
1.82
1.07
6.00
f1 (ppm)

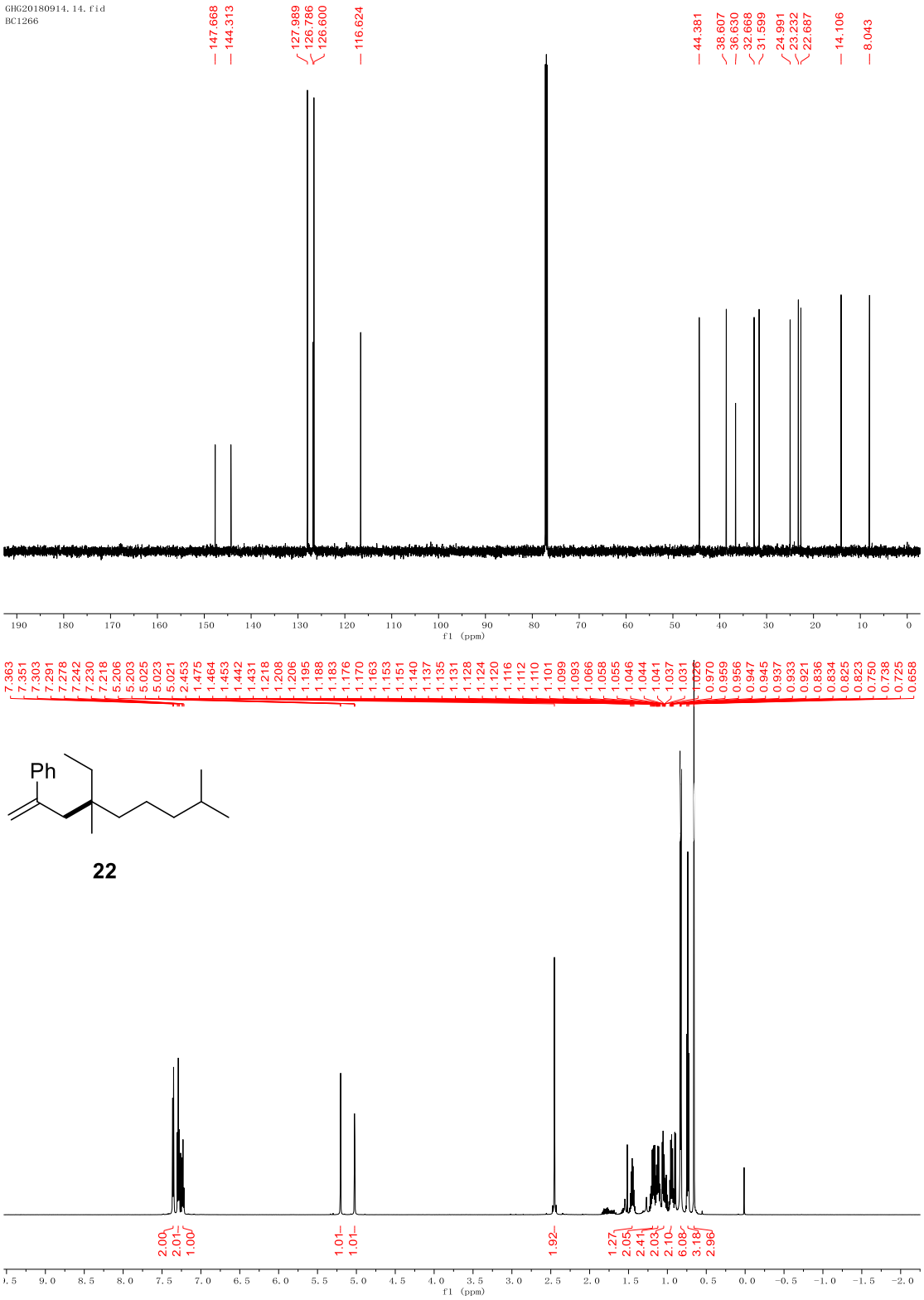

GHG20181015.19.fid
1333
147.540
144.139
133.941
128.065
126.845
126.546
121.229
116.788
44.605
42.622
36.189
31.326
26.593
25.240
24.367
24.161
23.317
f1 (ppm)
MeO
Ph
18
ppm

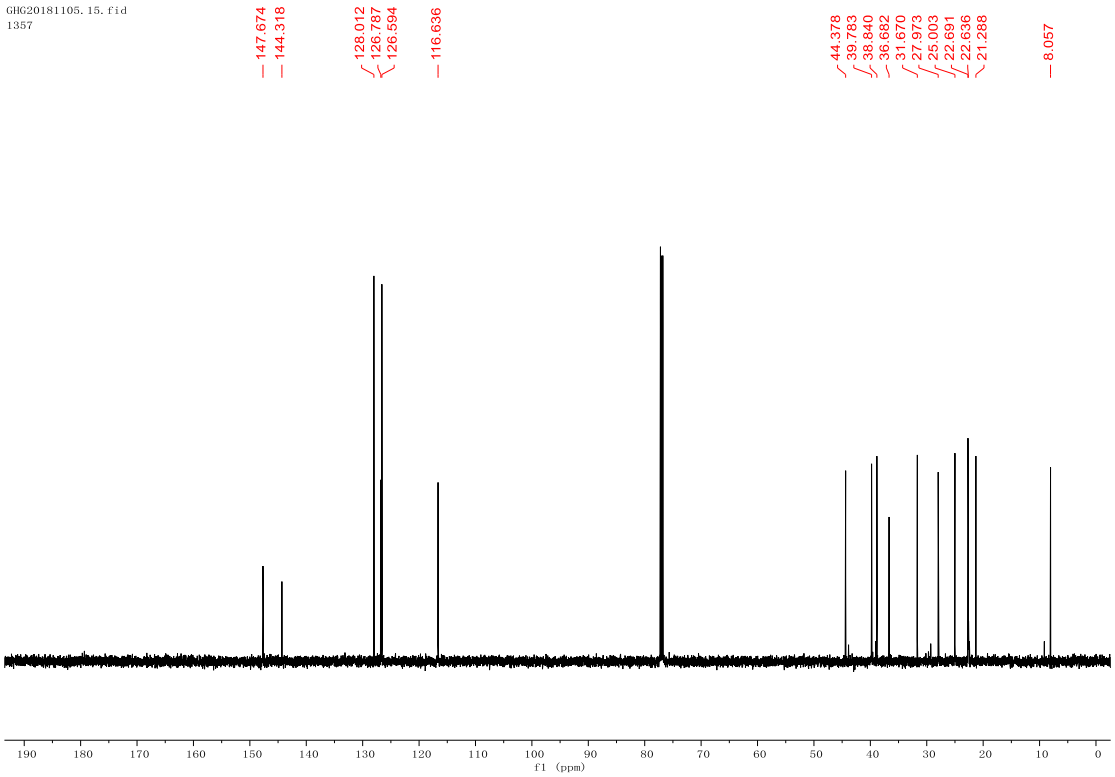

147.55
144.00
128.00
126.78
126.52
116.41
80.37
56.41
55.97
55.46
46.99
42.58
42.02
40.30
40.11
38.73
36.16
35.81
35.27
34.84
34.06
32.73
29.70
28.16
27.53
27.50
27.31
26.74
26.38
24.18
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
7.352
7.281
7.215
5.210
5.009
3.370
3.327
3.254
3.210
3.139
2.991
2.472
2.451
2.426
2.405
2.225
2.206
2.186
2.167
2.090
2.069
2.050
2.040
1.836
1.812
1.781
1.754
1.702
1.695
1.669
1.603
1.585
1.506
1.470
1.454
1.337
1.315
1.298
1.277
1.257
1.197
1.179
1.155
OMe
Ph
MeO
OMe
19
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 ppm
1.73
1.81
1.00
0.84
0.86
0.51
2.74
2.79
2.84
1.14
1.20
1.73
1.25
3.18
9.19
1.94
3.07
9.96
3.62
5.87
2.79
4.63
2.80

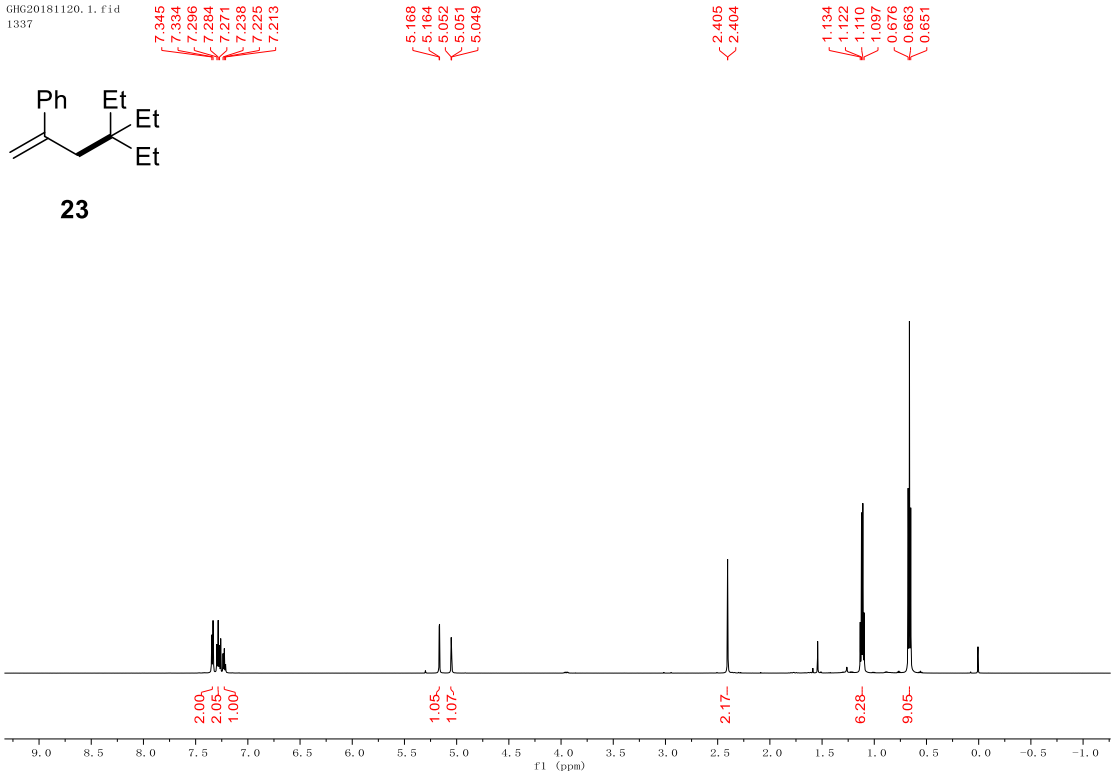

147.58
143.99
127.98
126.76
126.52
116.37
81.99
80.69
76.94
55.77
55.64
55.31
46.88
46.32
45.94
42.56
41.92
39.58
38.67
35.94
35.22
34.85
34.38
34.07
29.65
27.94
27.71
27.55
27.48
27.39
26.65
23.12
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
8.138
7.506
7.493
7.425
7.412
7.337
7.324
7.312
7.303
7.269
7.256
7.243
7.231
7.218
5.322
5.319
5.093
5.090
2.649
2.587
1.697
0.822
Boc
N
Ph
20
1.24
1.03
2.17
3.15
2.79
1.00
1.00
1.96
2.01
9.07
6.05
f1 (ppm)


GHG20181120.6.fid
1369
147.160
143.704
128.167
127.013
126.515
124.339
123.848
122.167
119.726
117.977
116.966
114.978
47.981
37.972
35.639
28.216
27.303
f1 (ppm)


GHG20180913.2.fid
1266
7.361
7.350
7.300
7.288
7.275
7.239
7.227
7.215
5.205
5.202
5.022
5.021
5.019
2.448
1.246
1.234
1.222
1.210
1.197
1.186
1.174
1.166
1.154
1.143
1.141
1.133
1.130
1.128
1.122
1.120
1.118
1.113
1.108
1.105
1.085
1.080
1.075
1.069
1.064
1.060
1.056
1.049
1.046
1.037
0.858
0.846
0.833
0.744
0.731
0.719
0.649
Ph
21
2.02
2.01
1.01
1.00
1.01
2.00
2.32
4.16
3.95
3.17
3.15
3.08
f1 (ppm)

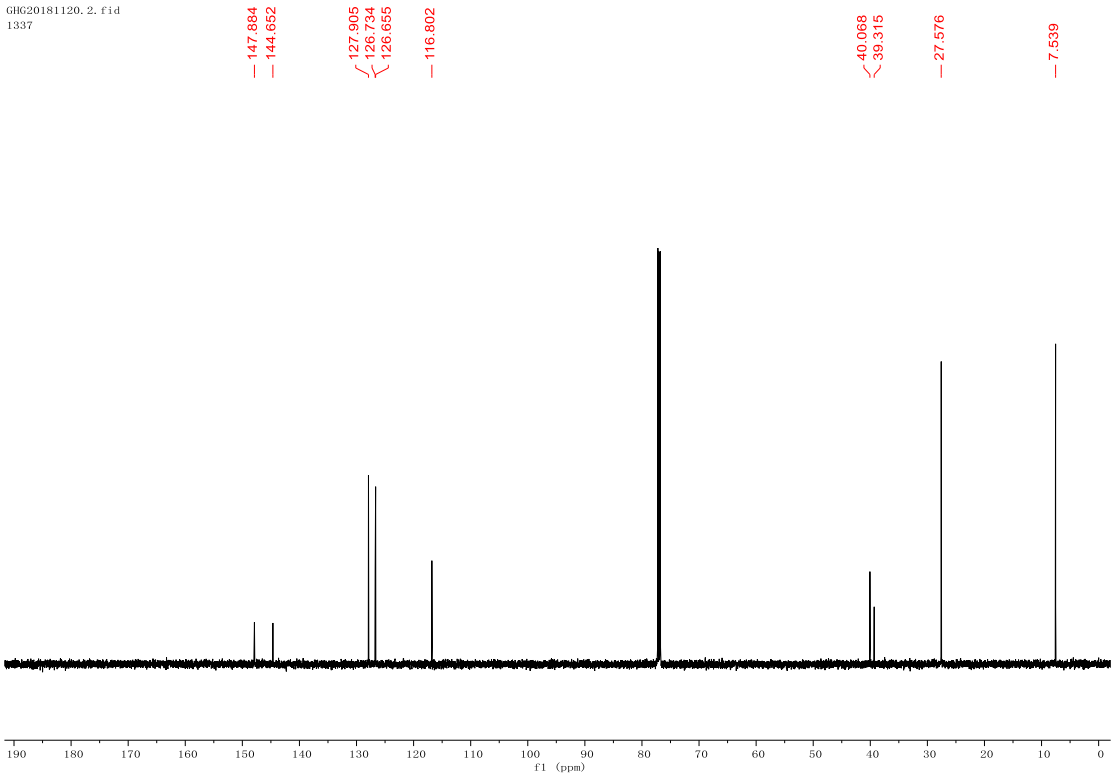

GHG20180914.14.fid
BC1266
147.668
144.313
127.989
126.786
126.600
116.624
44.381
38.607
36.630
32.668
31.599
24.991
23.232
22.687
14.106
8.043
f1 (ppm)
7.363
7.351
7.303
7.291
7.278
7.242
7.230
7.218
5.206
5.203
5.025
5.023
5.021
2.453
1.475
1.464
1.453
1.442
1.431
1.218
1.208
1.206
1.195
1.188
1.183
1.176
1.170
1.163
1.153
1.151
1.140
1.137
1.135
1.131
1.128
1.124
1.120
1.116
1.112
1.110
1.101
1.099
1.093
1.066
1.058
1.055
1.046
1.044
1.041
1.037
1.031
1.026
0.970
0.959
0.956
0.947
0.945
0.937
0.933
0.921
0.836
0.834
0.825
0.823
0.750
0.738
0.725
0.658
Ph
22
2.00
2.01
1.00
1.01
1.01
1.92
1.27
2.05
2.41
2.03
2.10
6.08
3.18
2.96
f1 (ppm)

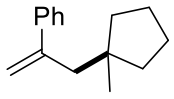

GHG20181105.15.fid
1357
147.674
144.318
128.012
126.787
126.594
116.636
44.378
39.783
38.840
36.682
31.670
27.973
25.003
22.691
22.636
21.288
8.057
f1 (ppm)


GHG20181120.1.fid
1337
7.345
7.334
7.296
7.284
7.271
7.238
7.225
7.213
5.168
5.164
5.052
5.051
5.049
2.405
2.404
1.134
1.122
1.110
1.097
0.676
0.663
0.651
2.00
2.05
1.00
1.05
1.07
2.17
6.28
9.05
f1 (ppm)

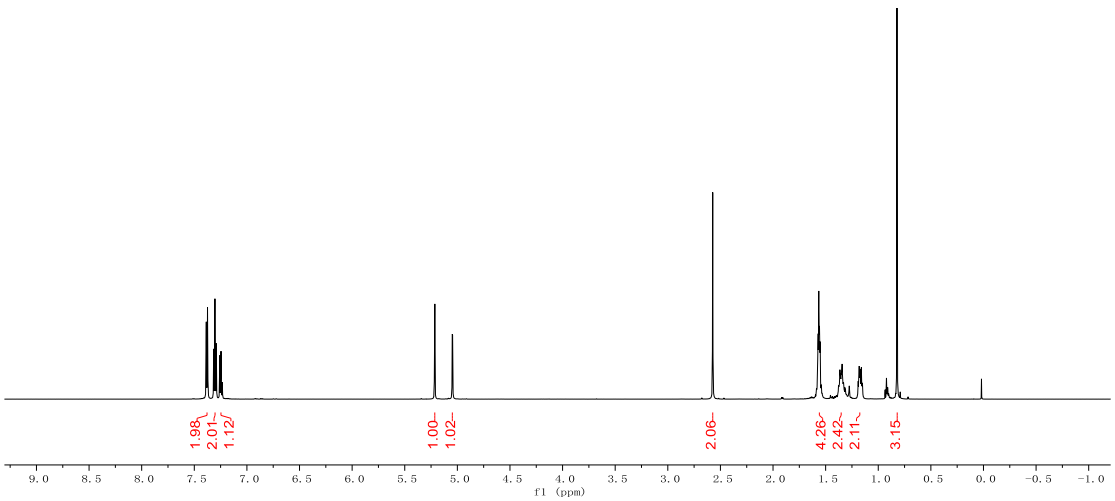
Ph
Et
Et
Et

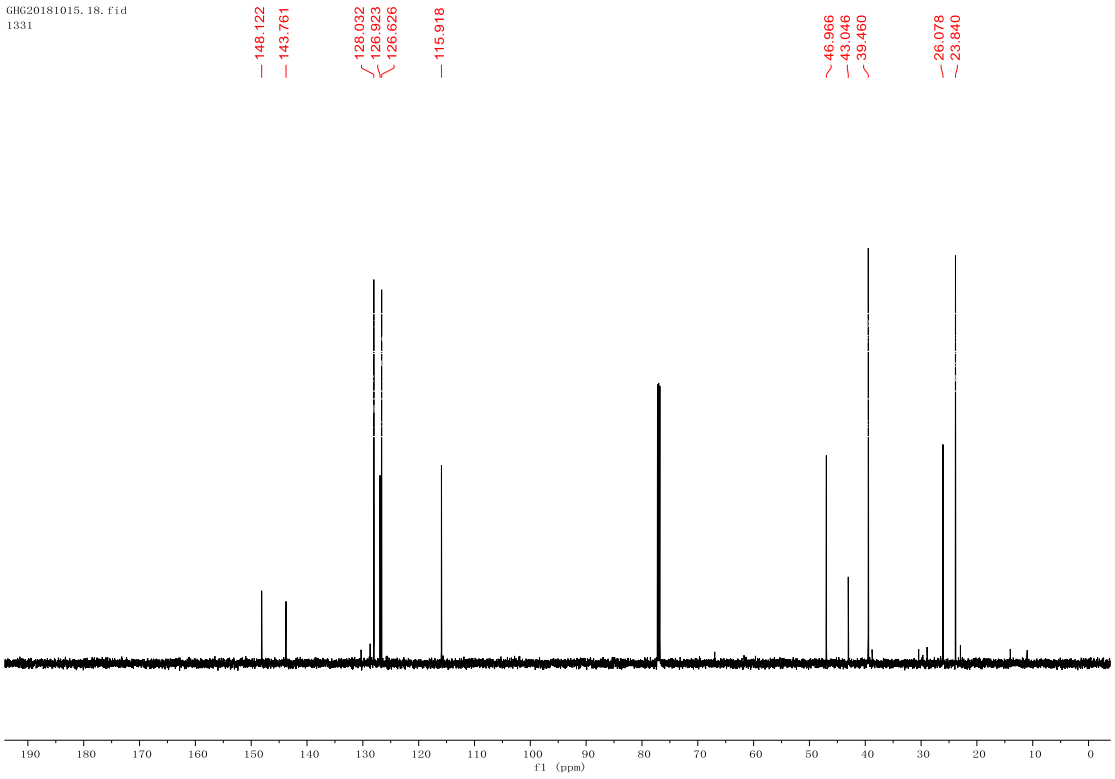
23

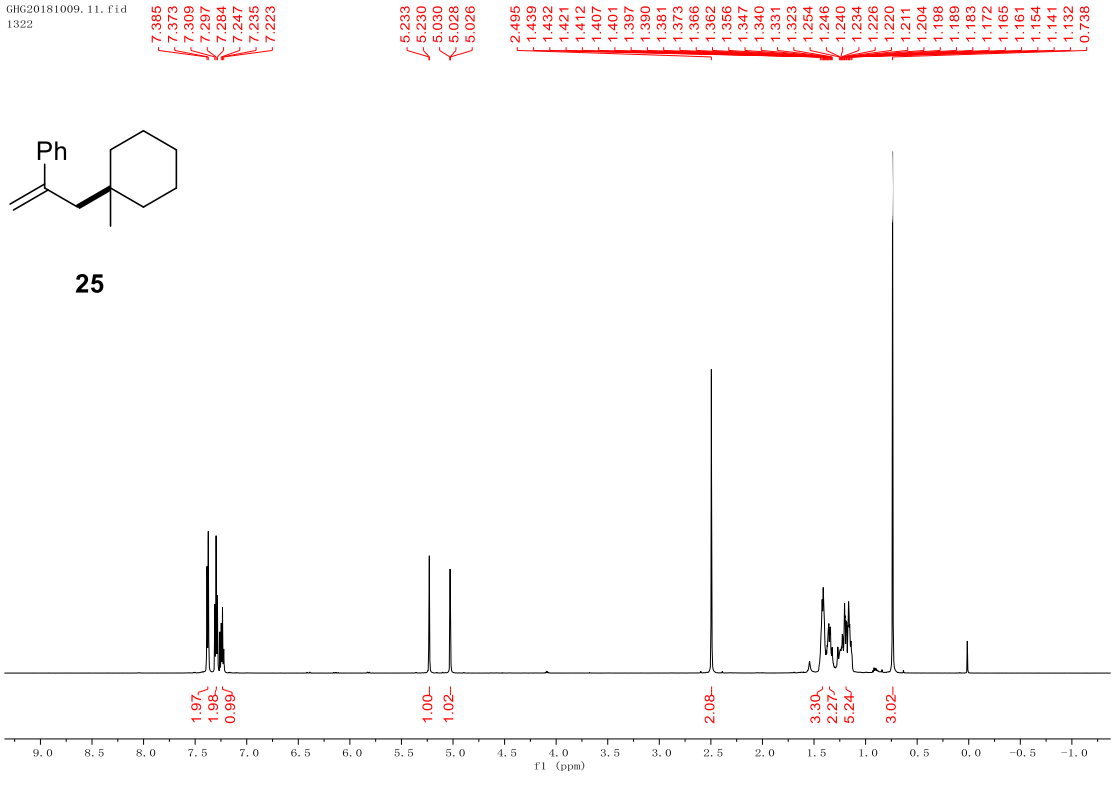

GHG20181120.2.fid
1337
147.884
144.652
127.905
126.734
126.655
116.802
40.068
39.315
27.576
7.539
f1 (ppm)
7.386
7.374
7.316
7.304
7.291
7.258
7.246
7.234
5.217
5.214
5.049
5.047
5.045
2.573
1.571
1.567
1.565
1.563
1.558
1.552
1.378
1.376
1.372
1.368
1.364
1.361
1.357
1.354
1.347
1.343
1.339
1.332
1.330
1.328
1.317
1.192
1.190
1.186
1.184
1.181
1.175
1.171
1.167
1.164
1.160
1.154
1.152
1.149
0.822


Ph

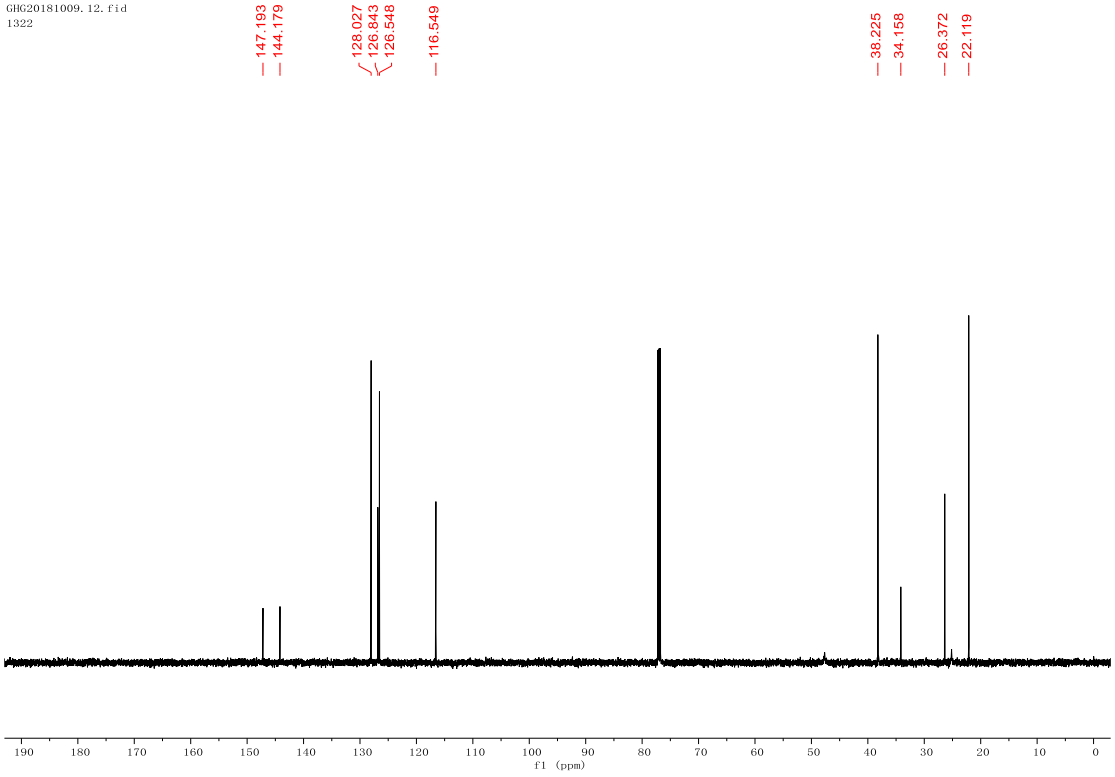
24


1.98
2.01
1.12
1.00
1.02
2.06
4.26
2.42
2.11
3.15
f1 (ppm)

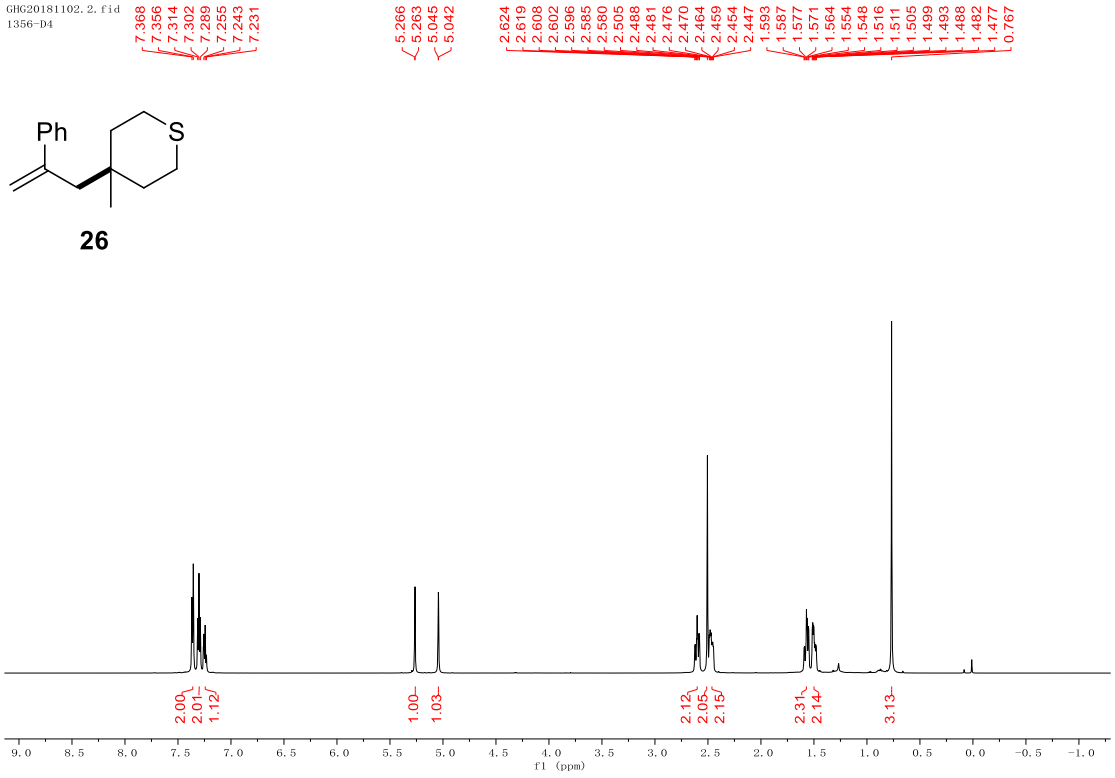

GHG20181015.18.fid
1331
148.122
143.761
128.032
126.923
126.626
115.918
46.966
43.046
39.460
26.078
23.840
f1 (ppm)


GHG20181009.11.fid
1322
7.385
7.373
7.309
7.297
7.284
7.247
7.235
7.223
5.233
5.230
5.030
5.028
5.026
2.495
1.439
1.432
1.421
1.412
1.407
1.401
1.397
1.390
1.381
1.373
1.366
1.362
1.356
1.347
1.340
1.331
1.323
1.254
1.246
1.240
1.234
1.226
1.220
1.211
1.204
1.198
1.189
1.183
1.172
1.165
1.161
1.154
1.141
1.132
0.738
Ph
25
1.97
1.98
0.99
1.00
1.02
2.08
3.30
2.27
5.24
3.02
f1 (ppm)

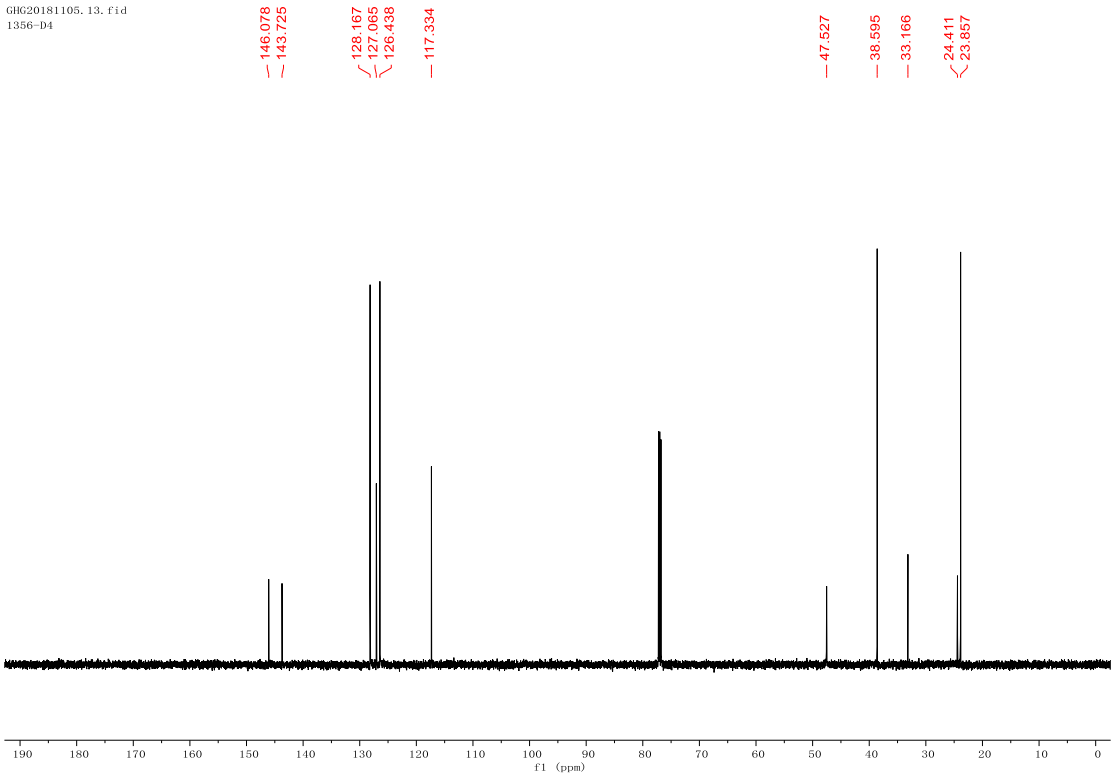
GHG20181009.12.fid
1322

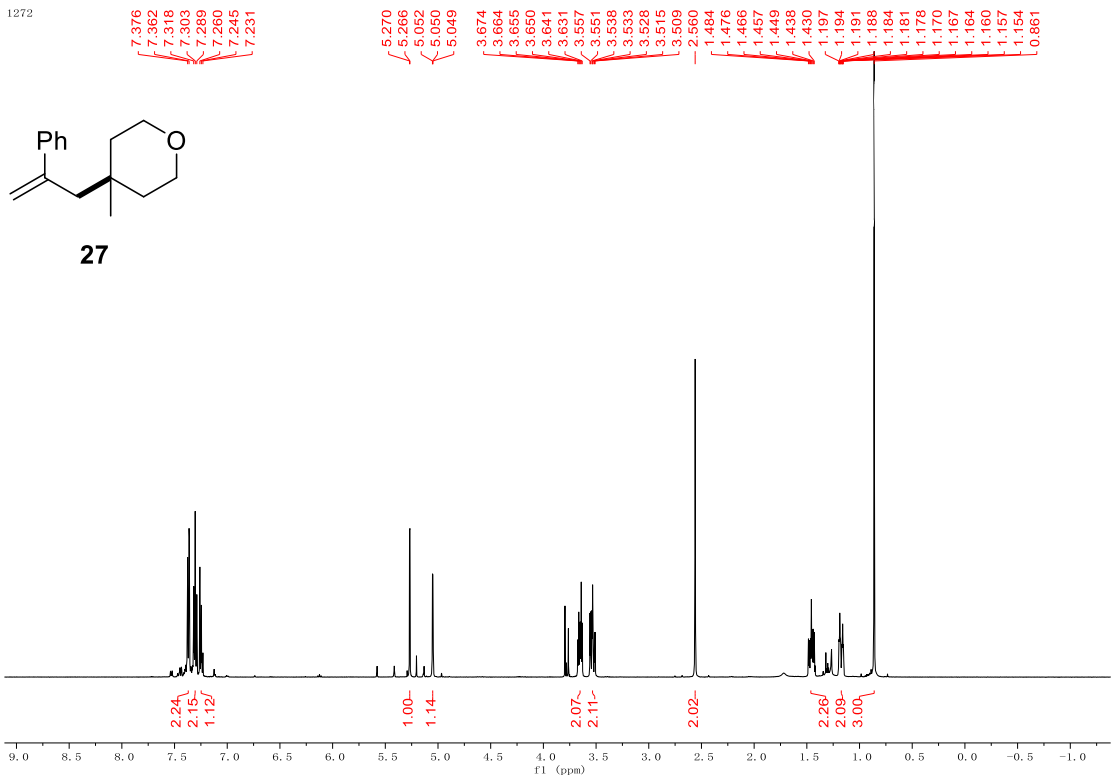


GHG20181102.2.fid
1356-D4



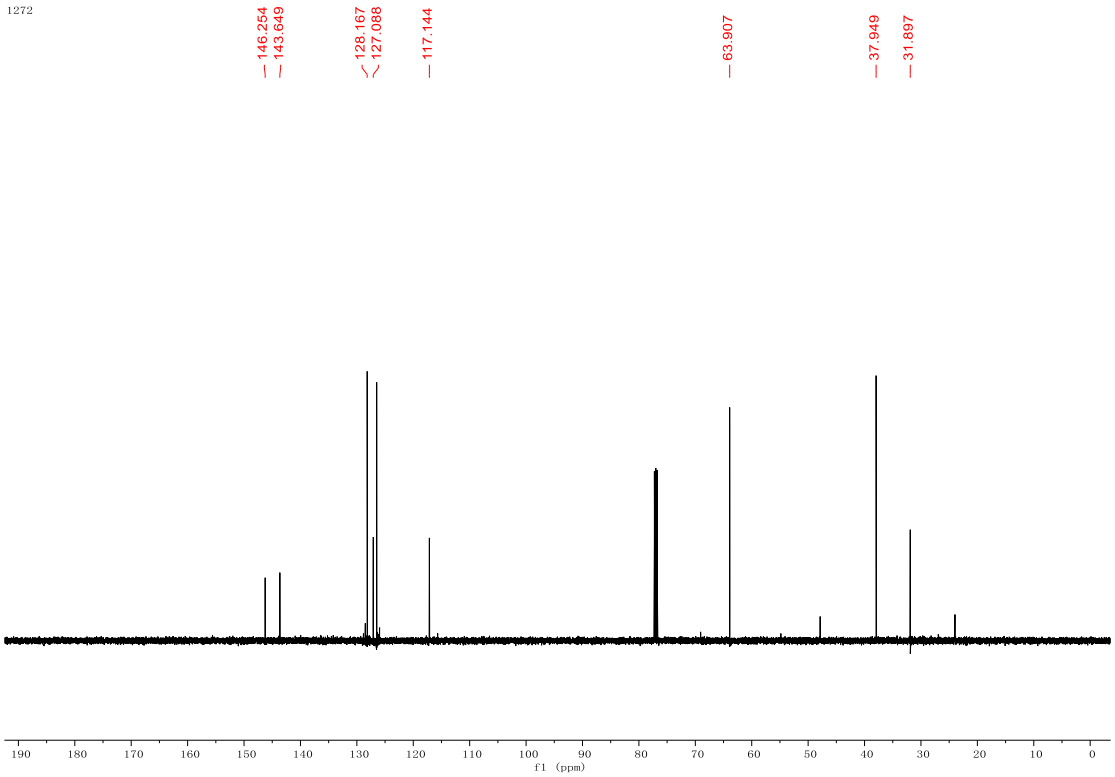
26

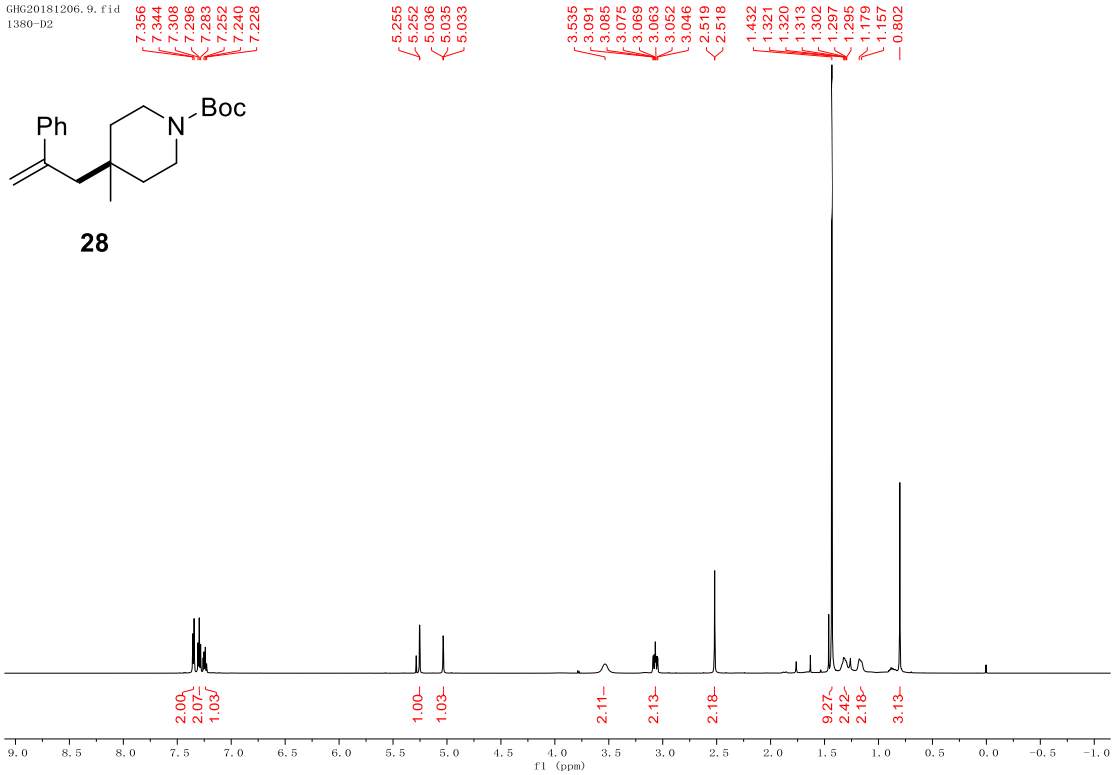

GHG20181105.13.fid
1356-D4
146.078
143.725
128.167
127.065
126.438
117.334
47.527
38.595
33.166
24.411
23.857
f1 (ppm)

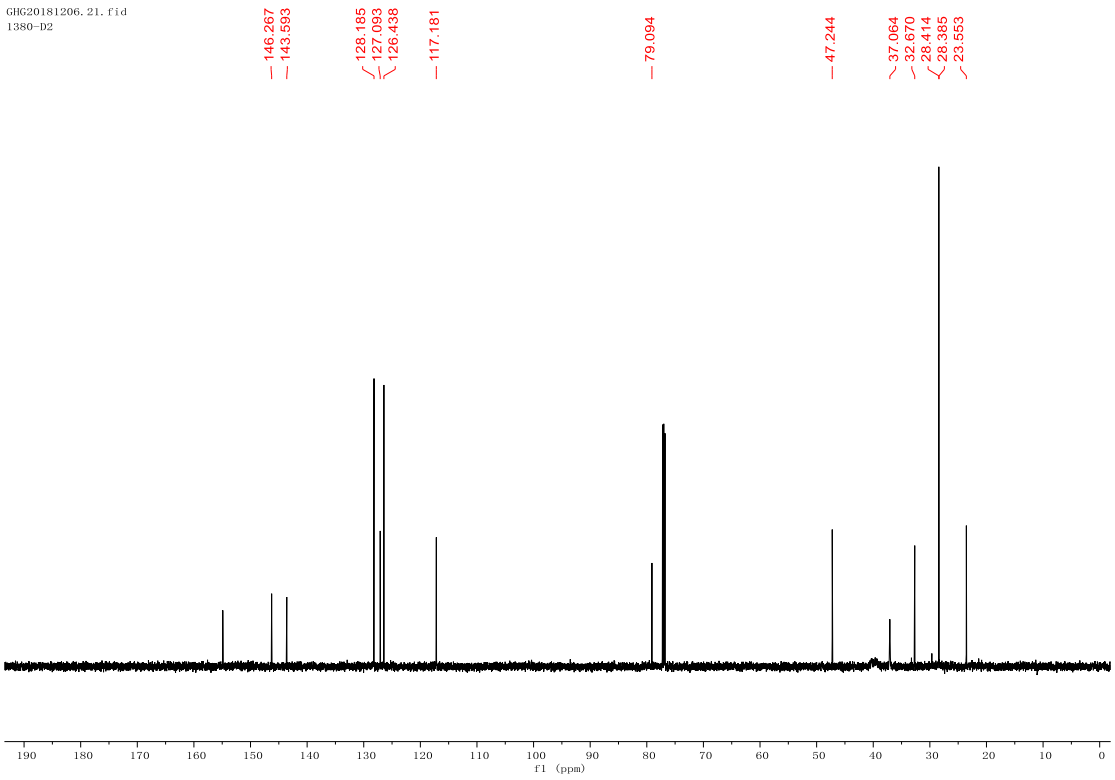

1272
7.376
7.362
7.318
7.303
7.289
7.260
7.245
7.231
5.270
5.266
5.052
5.050
5.049
3.674
3.664
3.655
3.650
3.641
3.631
3.557
3.551
3.538
3.533
3.528
3.515
3.509
2.560
1.484
1.476
1.466
1.457
1.449
1.438
1.430
1.197
1.194
1.191
1.188
1.184
1.181
1.178
1.170
1.167
1.164
1.160
1.157
1.154
0.861
2.24
2.15
1.12
1.00
1.14
2.07
2.11
2.02
2.26
2.09
3.00
f1 (ppm)

Ph
O

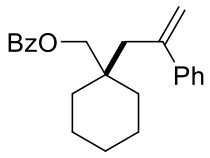
27


1272
146.254
143.649
128.167
127.088
117.144
63.907
37.949
31.897
f1 (ppm)

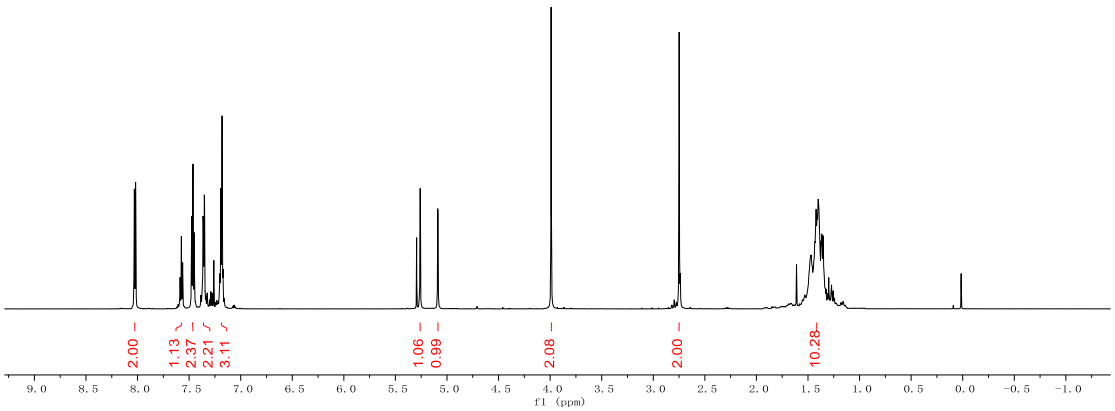

GHG20181206.9.fid
1380-D2
7.356
7.344
7.308
7.296
7.283
7.252
7.240
7.228
5.255
5.252
5.036
5.035
5.033
3.535
3.091
3.085
3.075
3.069
3.063
3.052
3.046
2.519
2.518
1.432
1.321
1.320
1.313
1.302
1.297
1.295
1.179
1.157
0.802
Ph
N
Boc
28
2.00
2.07
1.03
1.00
1.03
2.11
2.13
2.18
9.27
2.42
2.18
3.13
f1 (ppm)

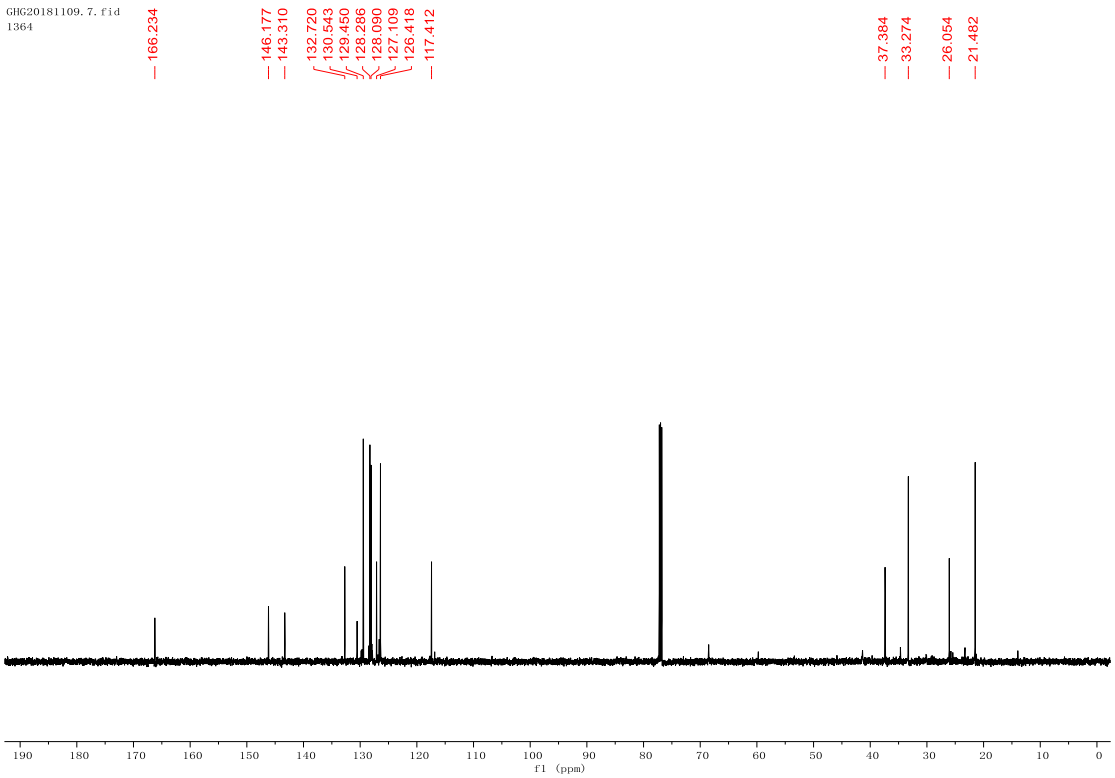

GHG20181206.21.fid
1380-D2
146.267
143.593
128.185
127.093
126.438
117.181
79.094
47.244
37.064
32.670
28.414
28.385
23.553
f1 (ppm)

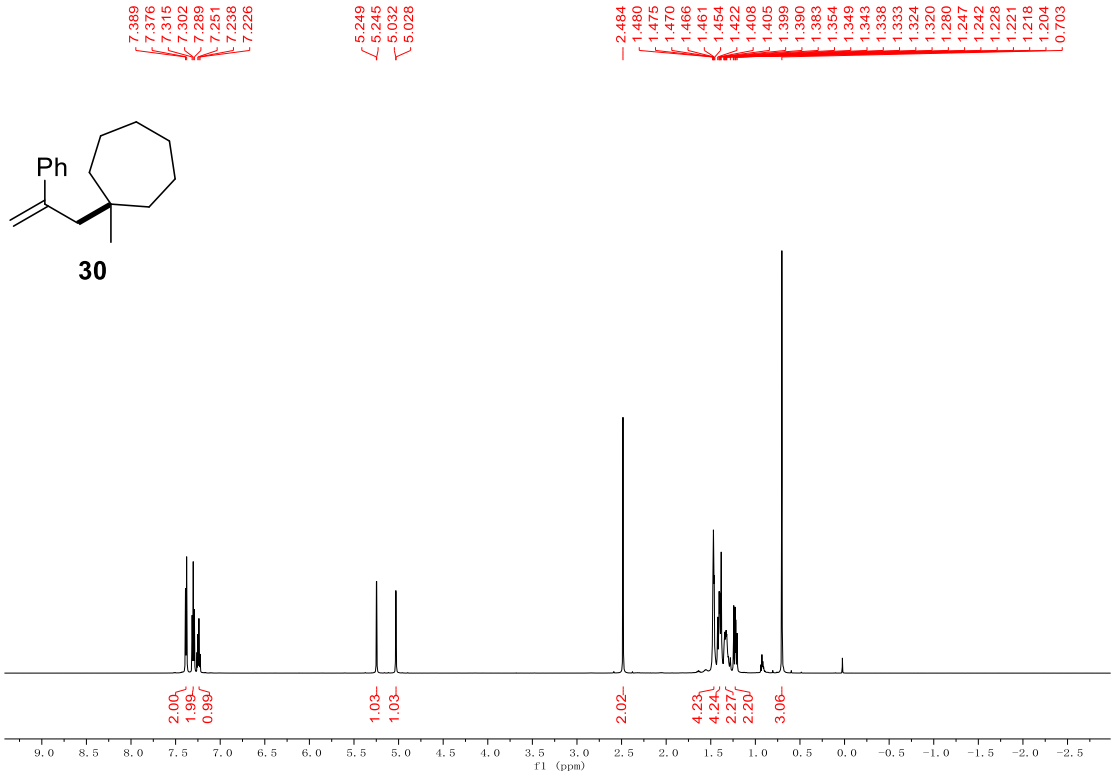

8.031
8.019
7.587
7.575
7.563
7.476
7.463
7.450
7.366
7.362
7.352
7.350
7.202
7.198
7.193
7.190
7.184
7.181
7.172
7.170
5.261
5.258
5.090
5.087
3.990
2.749
1.479
1.470
1.458
1.458
1.451
1.443
1.436
1.433
1.425
1.420
1.412
1.403
1.398
1.391
1.385
1.373
1.366
1.358
1.351

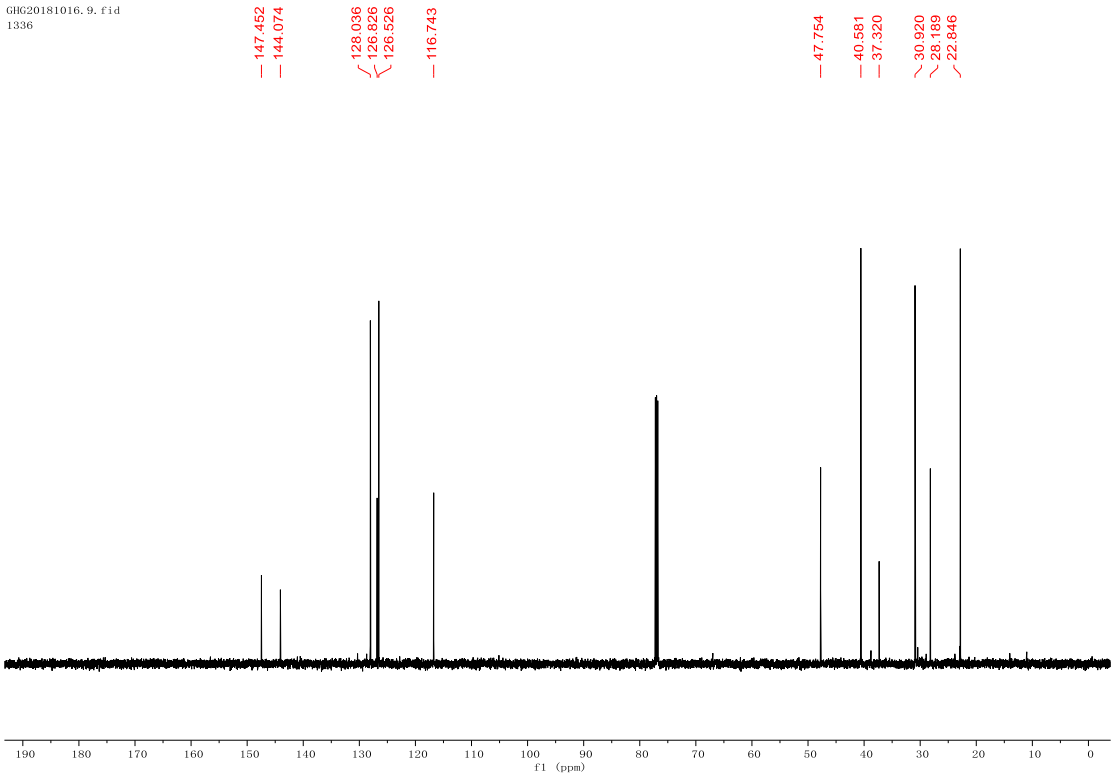

BzO
Ph

29

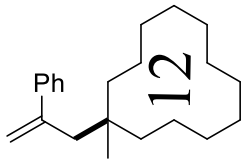

2.00
1.13
2.37
2.21
3.11
1.06
0.99
2.08
2.00
10.28
f1 (ppm)


GHG20181109.7.fid
1364
166.234
146.177
143.310
132.720
130.543
129.450
128.286
128.090
127.109
126.418
117.412
37.384
33.274
26.054
21.482
f1 (ppm)

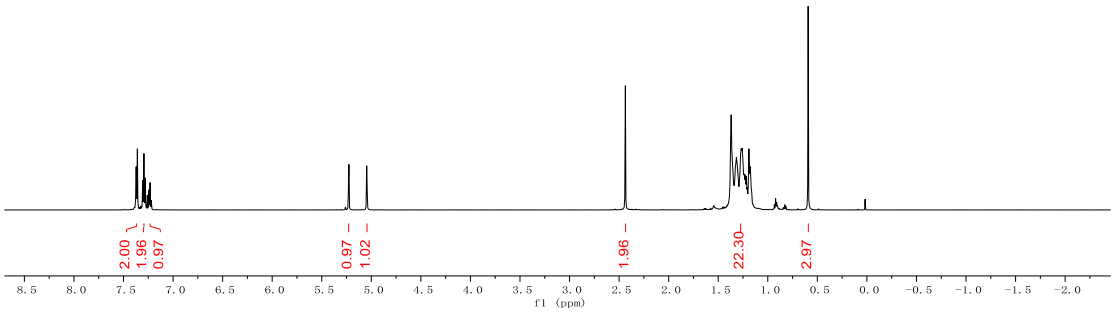

7.389
7.376
7.315
7.302
7.289
7.251
7.238
7.226
5.249
5.245
5.032
5.028
2.484
1.480
1.475
1.470
1.466
1.461
1.454
1.422
1.408
1.405
1.399
1.390
1.383
1.354
1.349
1.343
1.338
1.333
1.324
1.320
1.280
1.247
1.242
1.228
1.221
1.218
1.204
0.703
Ph
30
2.00
1.99
0.99
1.03
1.03
2.02
4.23
4.24
2.27
2.20
3.06
f1 (ppm)

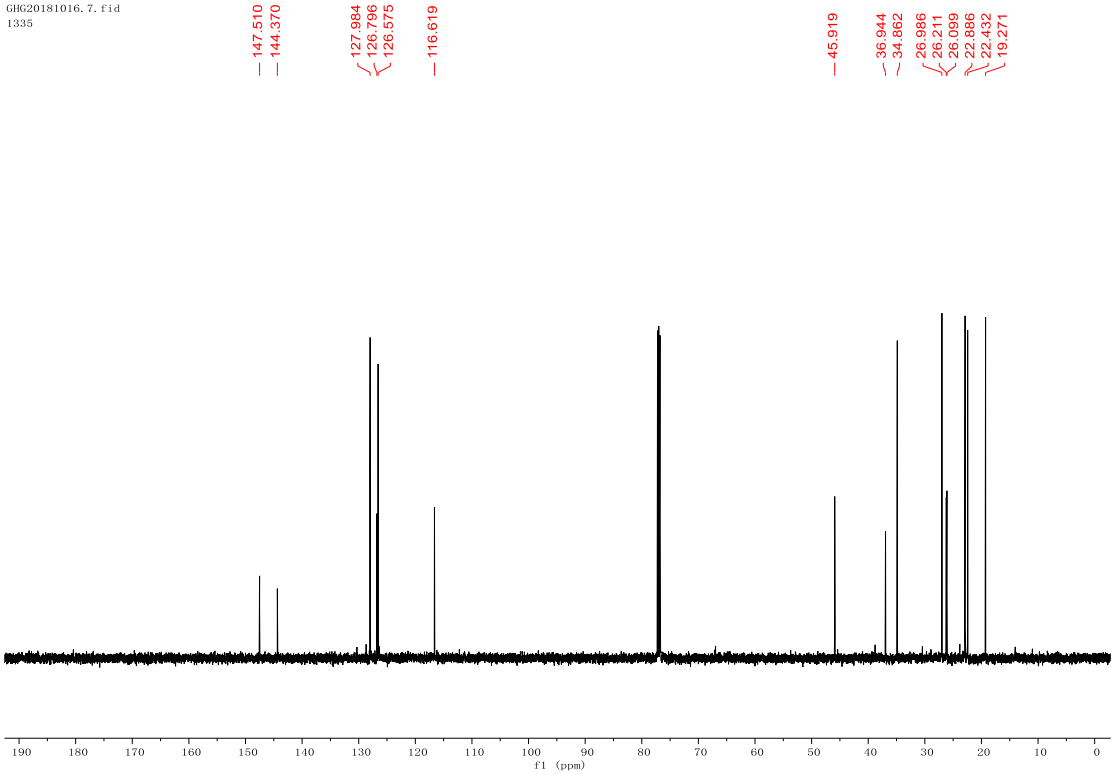

GHG20181016.9.fid
1336
147.452
144.074
128.036
126.826
126.526
116.743
47.754
40.581
37.320
30.920
28.189
22.846
f1 (ppm)

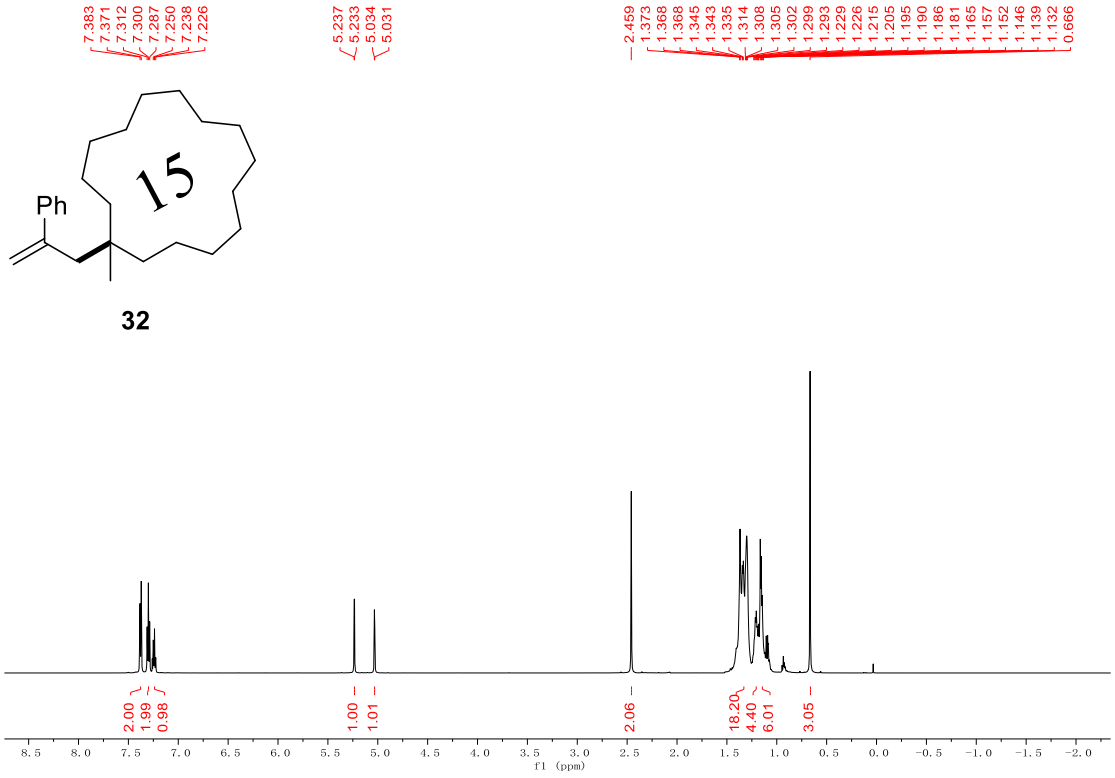

7.373
7.360
7.306
7.294
7.281
7.244
7.232
7.220
5.229
5.226
5.047
5.044
2.437
1.370
1.354
1.326
1.316
1.310
1.306
1.301
1.286
1.278
1.273
1.268
1.263
1.258
1.253
1.248
1.240
1.236
1.230
1.226
1.216
1.208
1.206
1.190
1.177
1.170
1.162
0.593


Ph
12

31

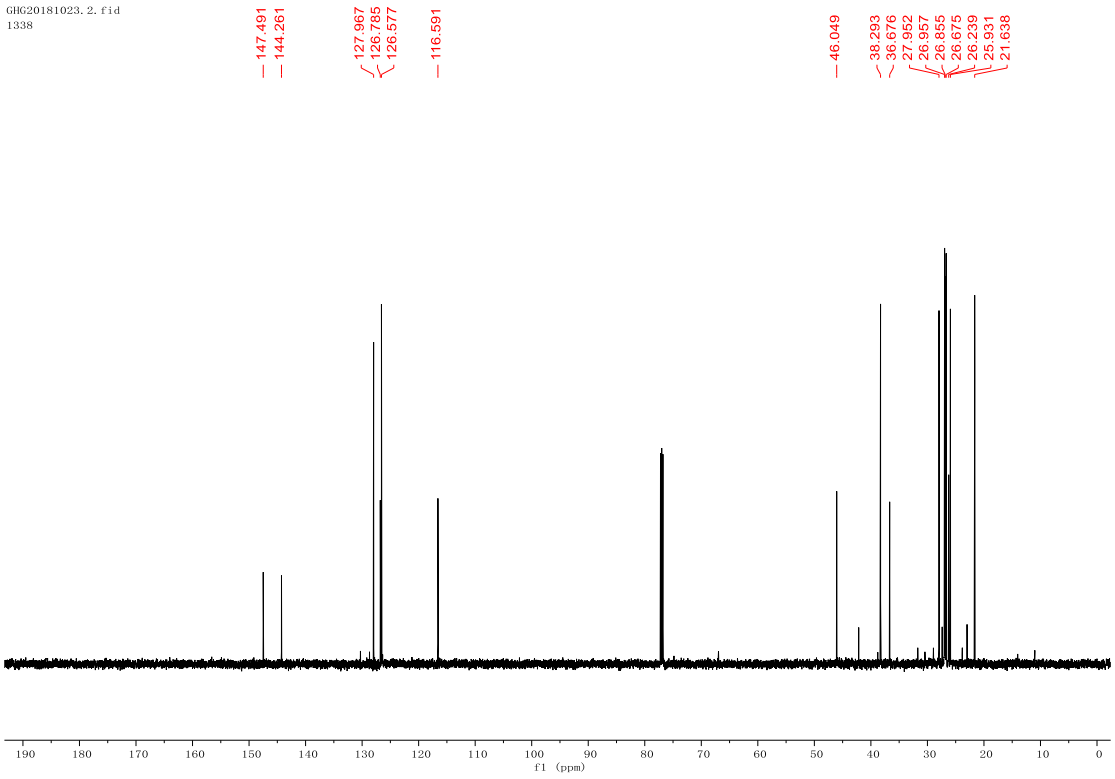

2.00
1.96
0.97
0.97
1.02
1.96
22.30
2.97
f1 (ppm)

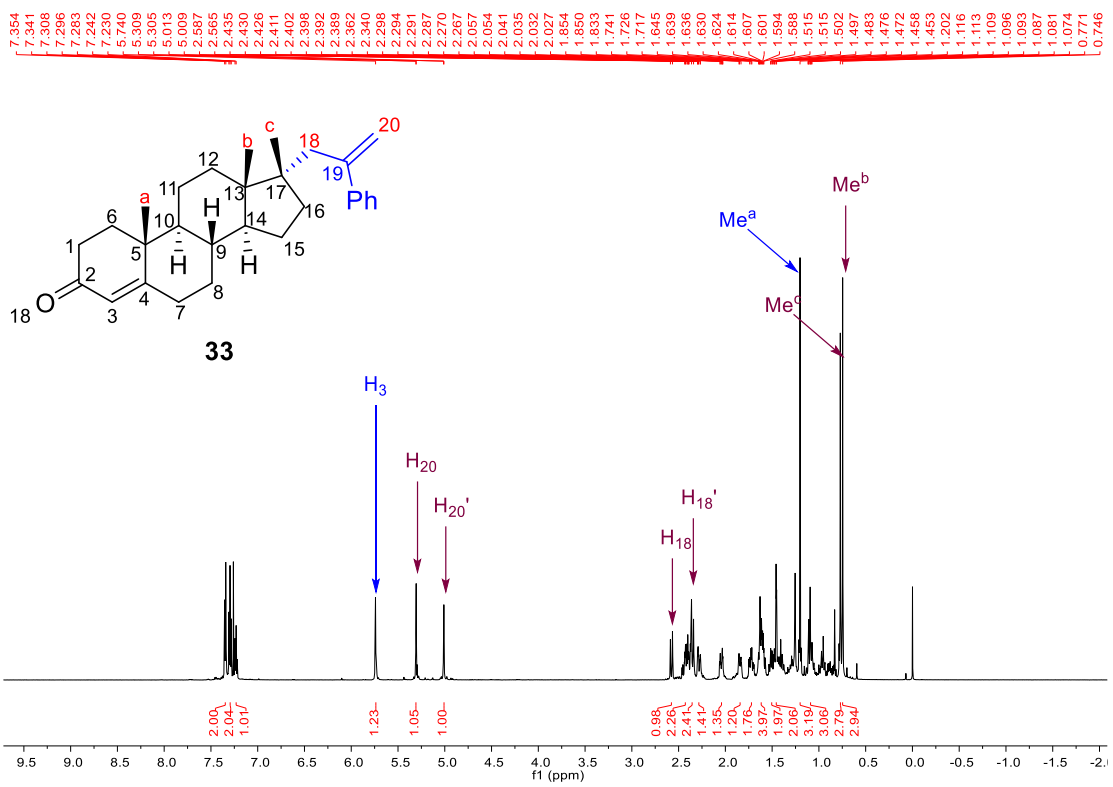

GHG20181016.7.fid
1335
147.510
144.370
127.984
126.796
126.575
116.619
45.919
36.944
34.862
26.986
26.211
26.099
22.886
22.432
19.271
f1 (ppm)

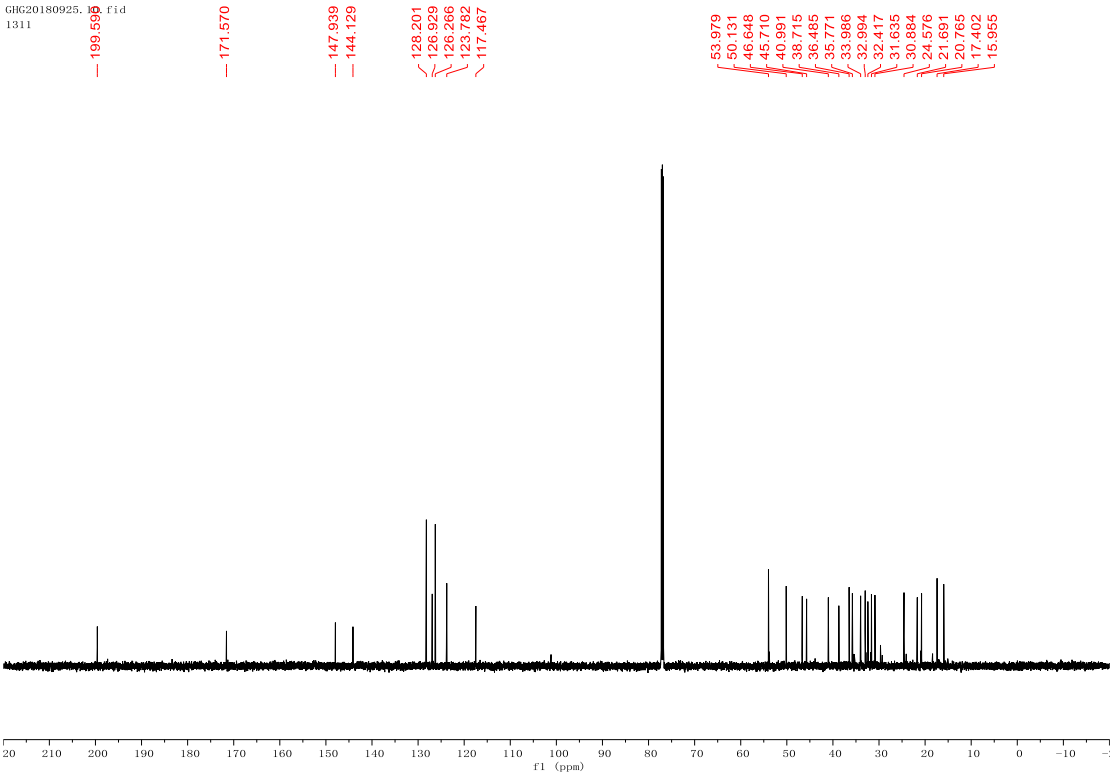

7.383
7.371
7.312
7.300
7.287
7.250
7.238
7.226
5.237
5.233
5.034
5.031
2.459
1.373
1.368
1.345
1.343
1.335
1.314
1.308
1.305
1.302
1.299
1.293
1.229
1.226
1.215
1.205
1.195
1.190
1.186
1.181
1.165
1.157
1.152
1.146
1.139
1.132
0.666
2.00
1.99
0.98
1.00
1.01
2.06
18.20
4.40
6.01
3.05
f1 (ppm)

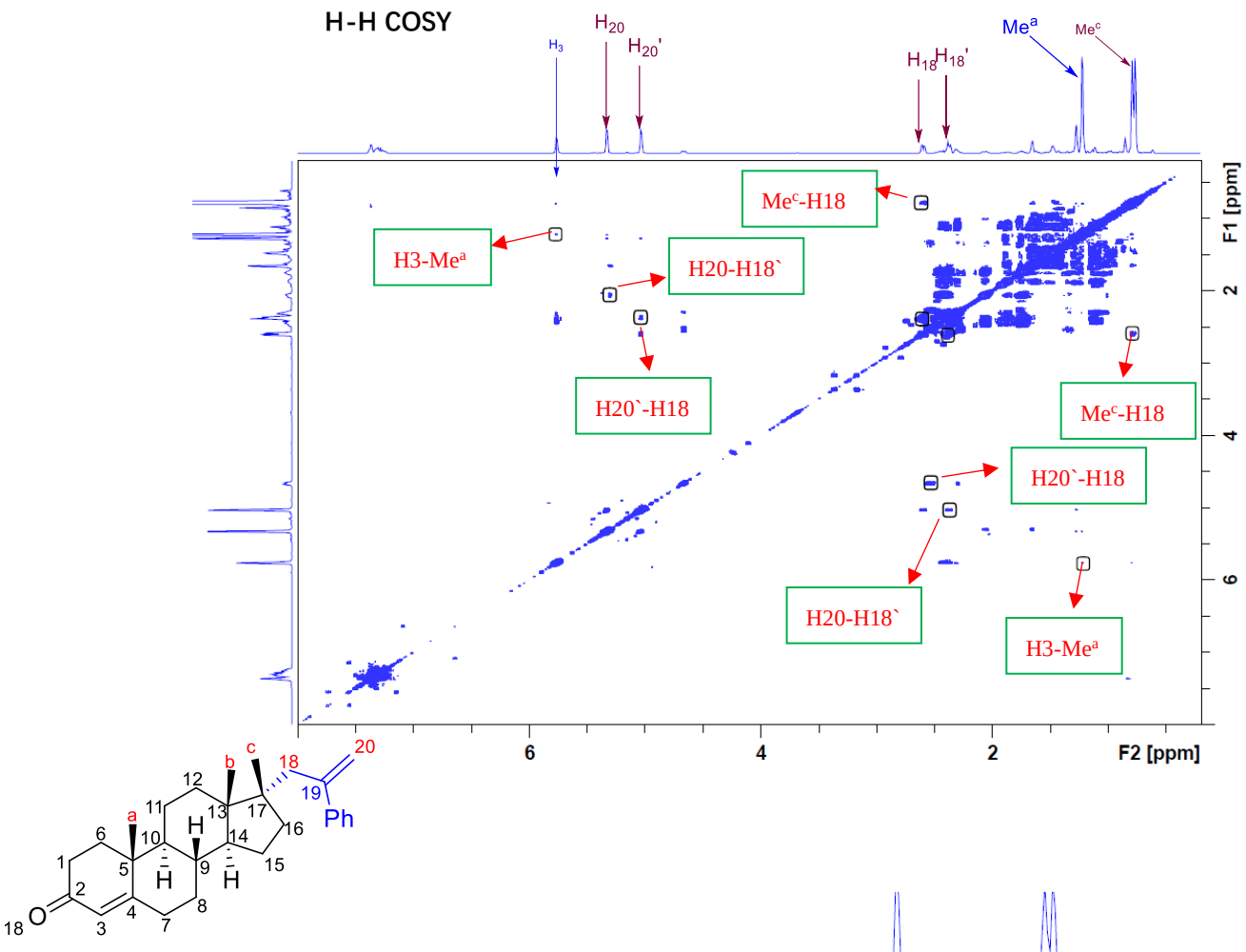
Ph
15

32

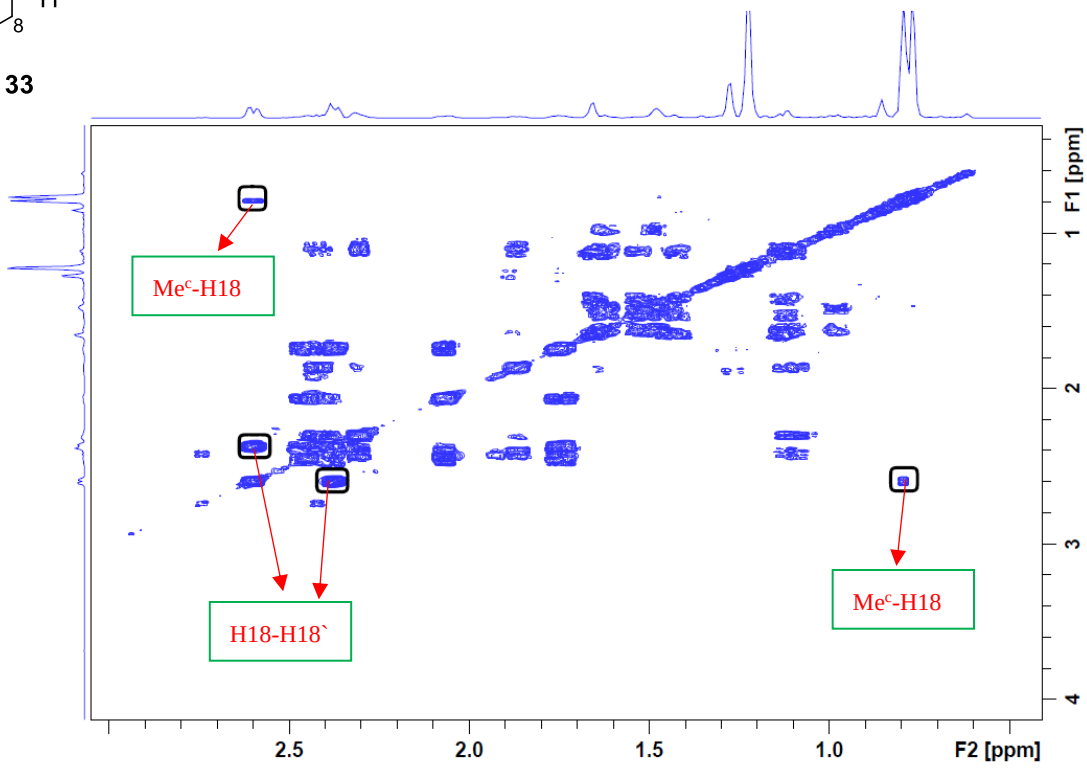

GHG20181023.2.fid
1338
147.491
144.261
127.967
126.785
126.577
116.591
46.049
38.293
36.676
27.952
26.957
26.855
26.675
26.239
25.931
21.638
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


33
Me^a
Me^b
Me^c
H3
H20
H20'
H18
H18'
f1 (ppm)

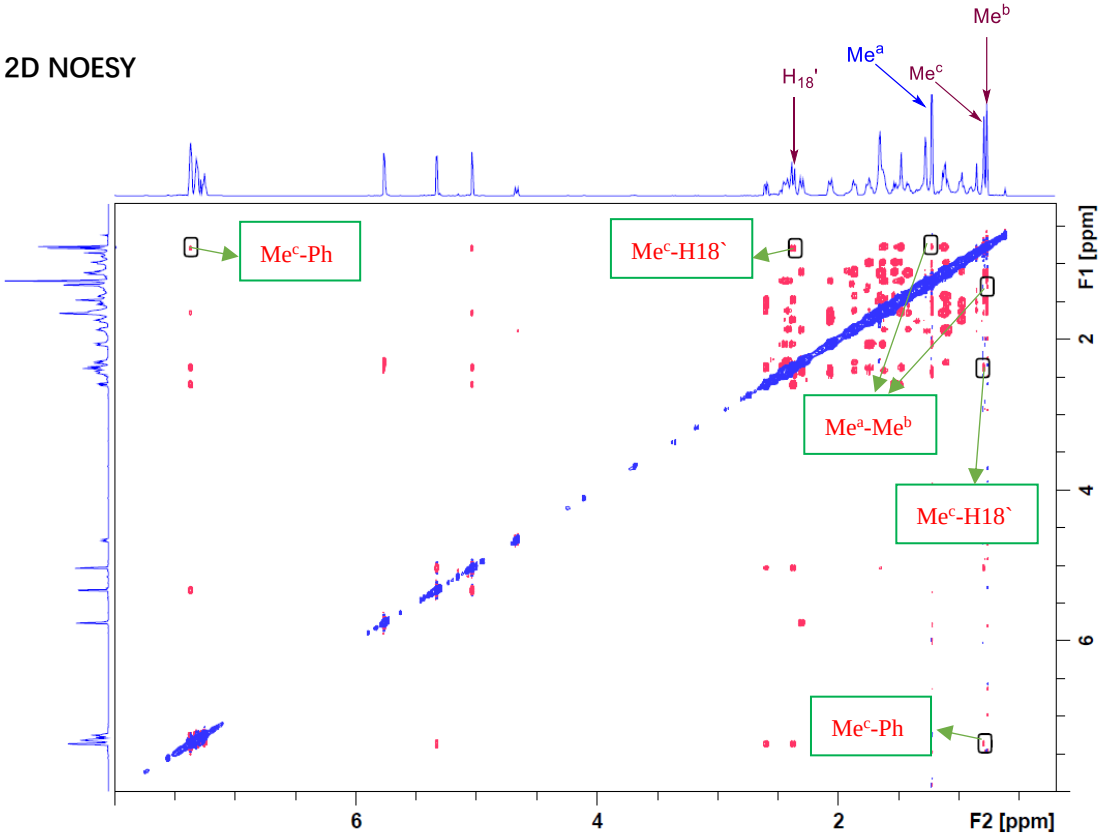

f1 (ppm)

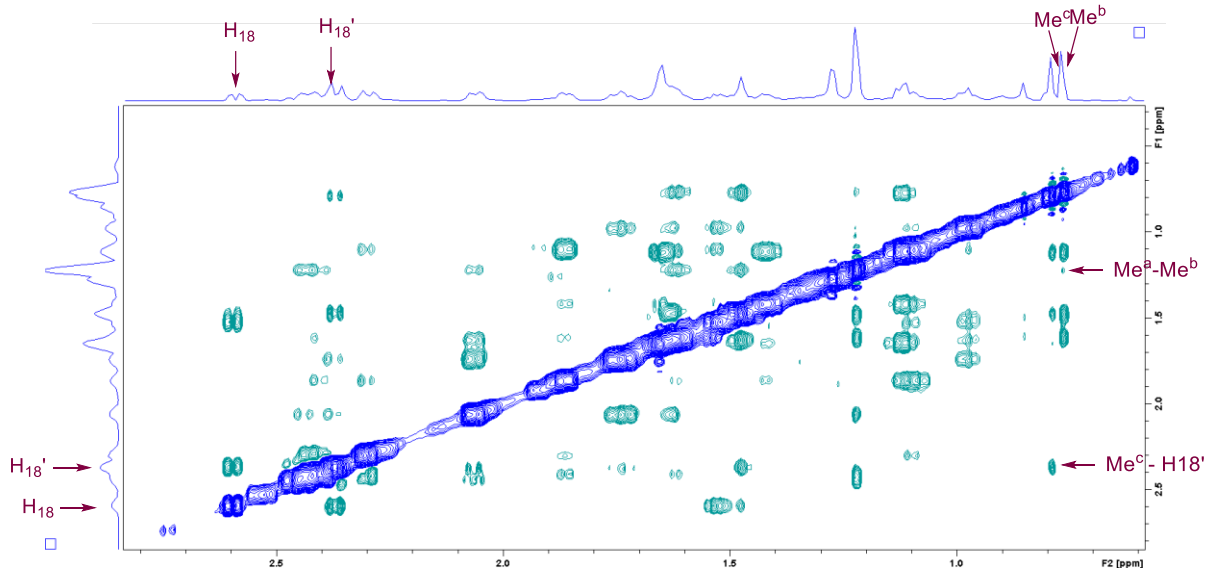

H-H COSY
H3
H20
H20'
H18
H18'
Me^a
Me^c
Me^c-H18
H3-Me^a
H20-H18`
H20`-H18
Me^c-H18
H20`-H18
H20-H18`
H3-Me^a
F1 [ppm]
F2 [ppm]
Ph

33


Me^c-H18
H18-H18`
Me^c-H18
F1 [ppm]
F2 [ppm]

2D NOESY


Me^b
Me^a
Me^c
H18'
Me^c-Ph
Me^c-H18`
Me^a-Me^b
Me^c-H18`
Me^c-Ph
F1 [ppm]
F2 [ppm]
6
4
2


H18
H18'
Me^cMe^b
Me^a-Me^b
H18'
H18
Me^c- H18'
F1 [ppm]
F2 [ppm]

GHG20180928.1.fid
1317

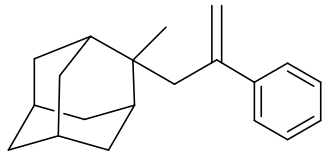
7.372
7.361
7.307
7.295
7.282
7.248
7.235
7.223

5.188
5.185
5.062
5.060
5.058

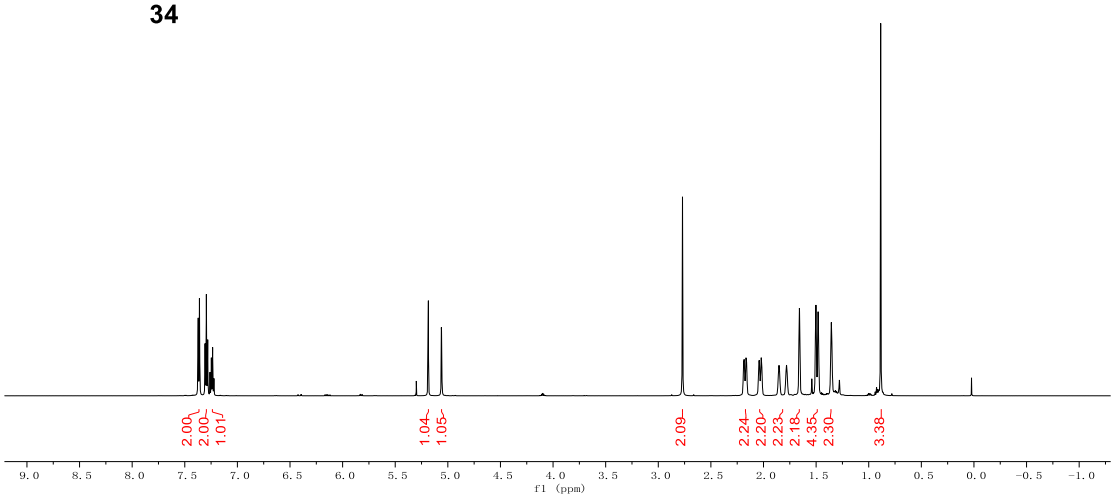
2.770

2.184
2.163
2.043
2.022
1.852
1.781
1.659
1.502
1.481
1.355

0.886



34



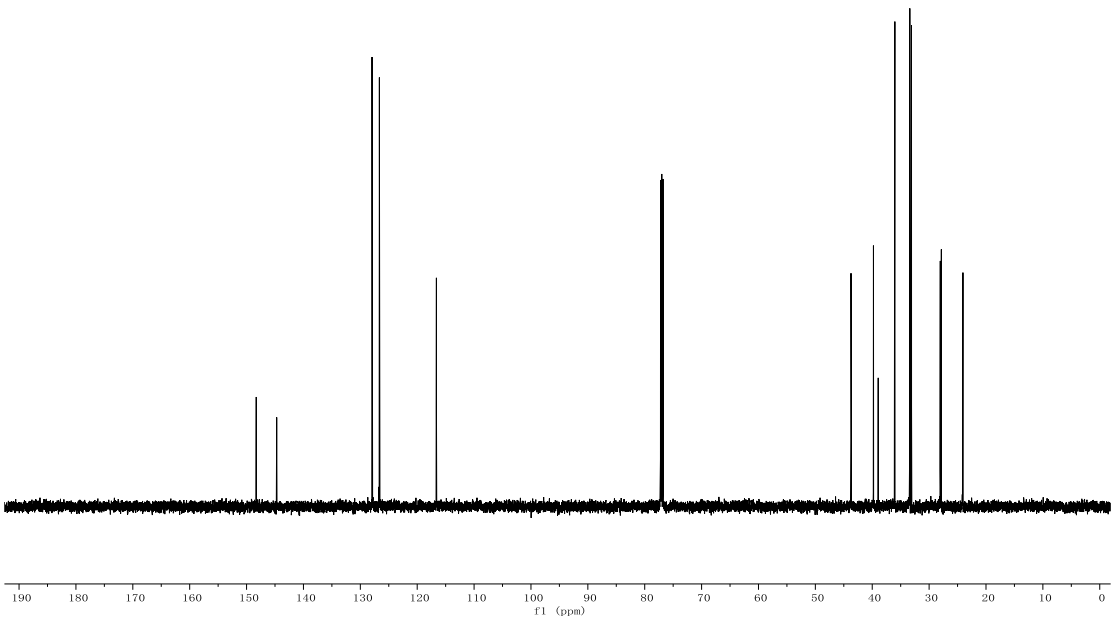
GHG20180928.2.fid
1317

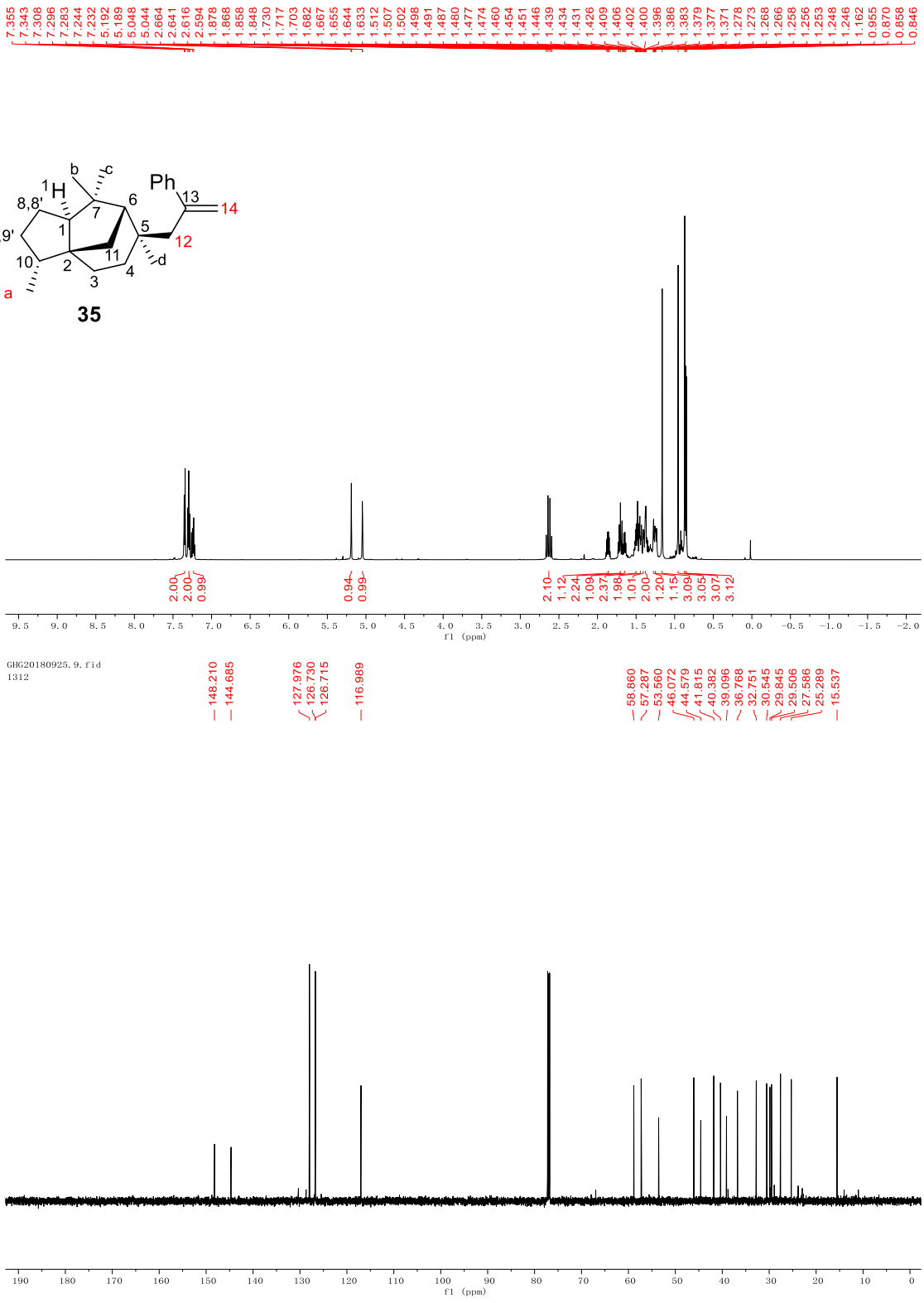
148.301
144.702

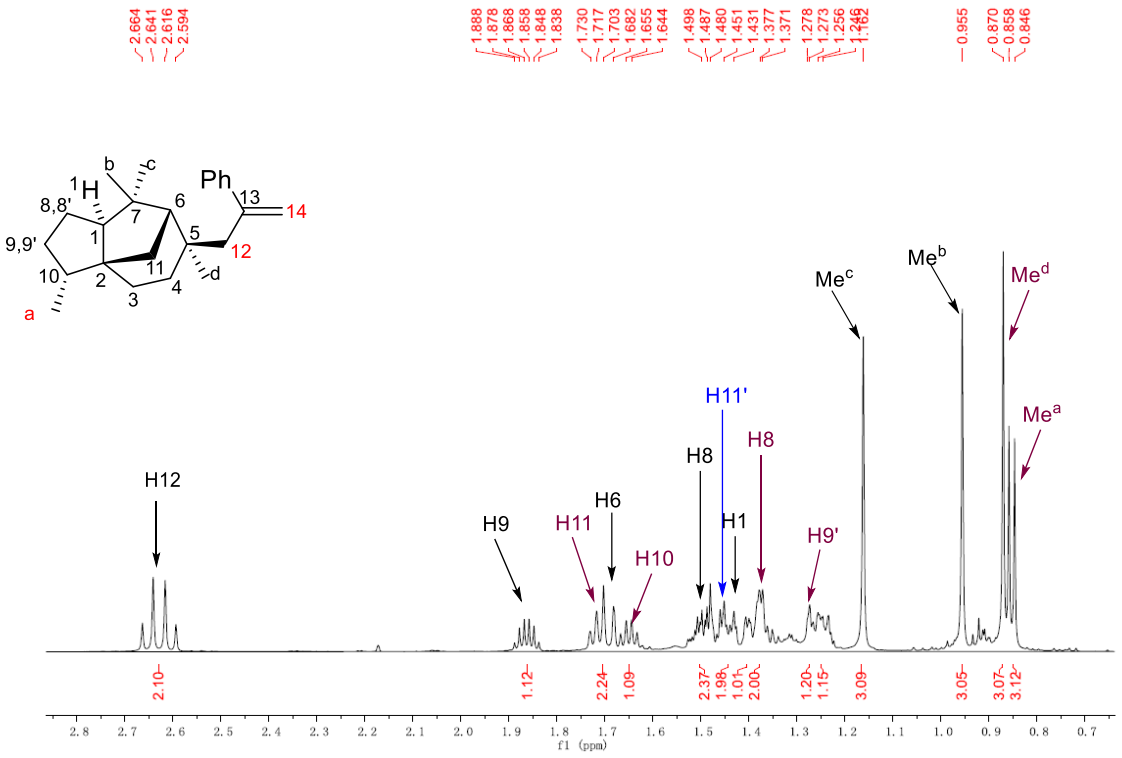
127.944
126.738
126.650

116.623

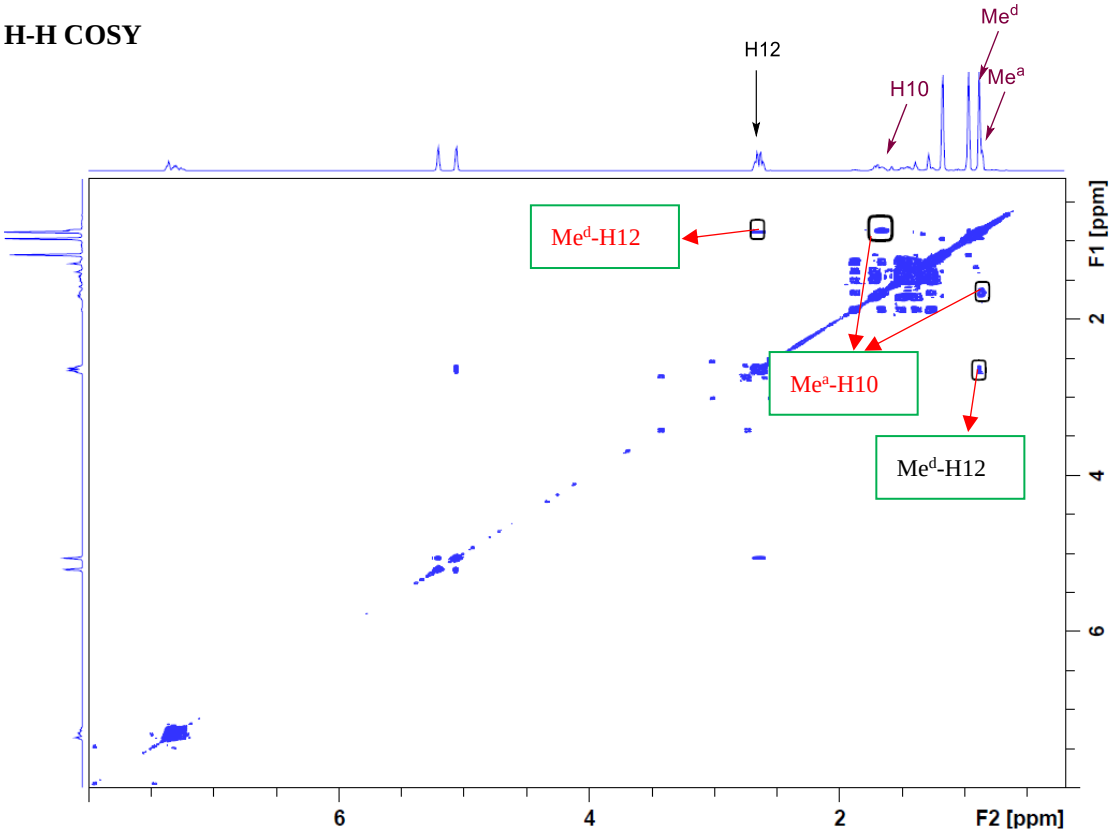
43.732
39.786
38.951
36.020
33.389
33.097
28.037
27.850
24.052

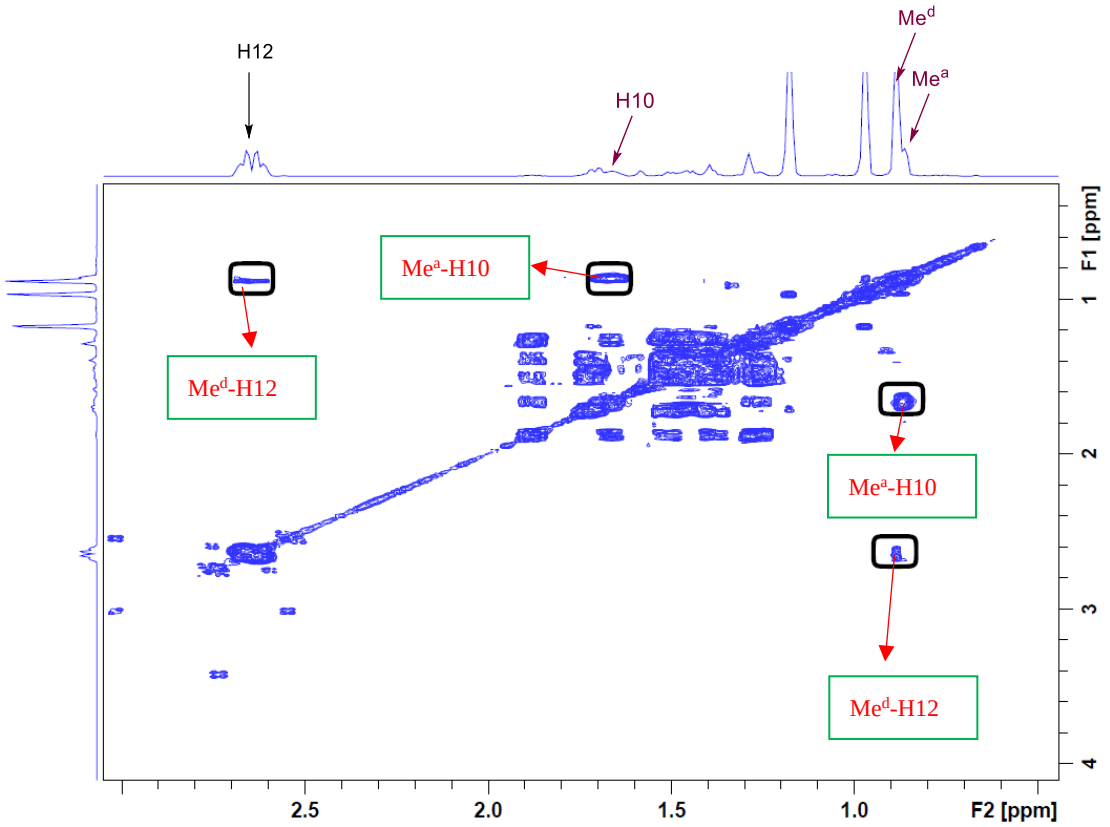


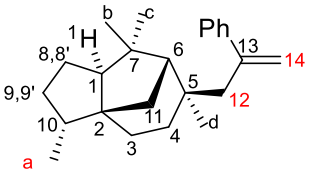

7.355 7.343 7.308 7.296 7.283 7.244 7.232 5.192 5.189 5.048 5.044 2.664 2.641 2.616 2.594 1.878 1.868 1.858 1.848 1.730 1.717 1.703 1.682 1.667 1.655 1.644 1.633 1.512 1.507 1.502 1.498 1.491 1.487 1.480 1.477 1.474 1.460 1.454 1.451 1.446 1.439 1.434 1.431 1.426 1.409 1.406 1.402 1.400 1.396 1.386 1.383 1.379 1.377 1.371 1.278 1.273 1.268 1.266 1.258 1.256 1.253 1.248 1.246 1.162 0.955 0.870 0.858 0.846
Ph
13
14
12
a
b
c
d
1H
8,8'
9,9'
1
2
3
4
5
6
7
10
11
35
2.00 2.00 0.99 0.94 0.99 2.10 1.12 2.24 1.09 2.37 1.98 1.01 2.00 1.20 1.15 3.09 3.05 3.07 3.12
f1 (ppm)
GHG20180925.9.fid
1312
148.210 144.685 127.976 126.730 126.715 116.989 58.860 57.287 53.560 46.072 44.579 41.815 40.382 39.096 36.768 32.751 30.545 29.845 29.506 27.586 25.289 15.537
f1 (ppm)


2.664
2.641
2.616
2.594
1.888
1.878
1.868
1.858
1.848
1.838
1.730
1.717
1.703
1.682
1.655
1.644
1.498
1.487
1.480
1.451
1.431
1.377
1.371
1.278
1.273
1.256
0.955
0.870
0.858
0.846
1H
8,8'
9,9'
10
1
2
3
4
5
6
7
11
12
13
14
Ph
a
b
c
d
H12
H9
H11
H6
H10
H8
H11'
H8
H1
H9'
Mec
Meb
Med
Mea
2.10
1.12
2.24
1.09
2.37
1.98
1.01
2.00
1.20
1.15
3.09
3.05
3.07
3.12
f1 (ppm)

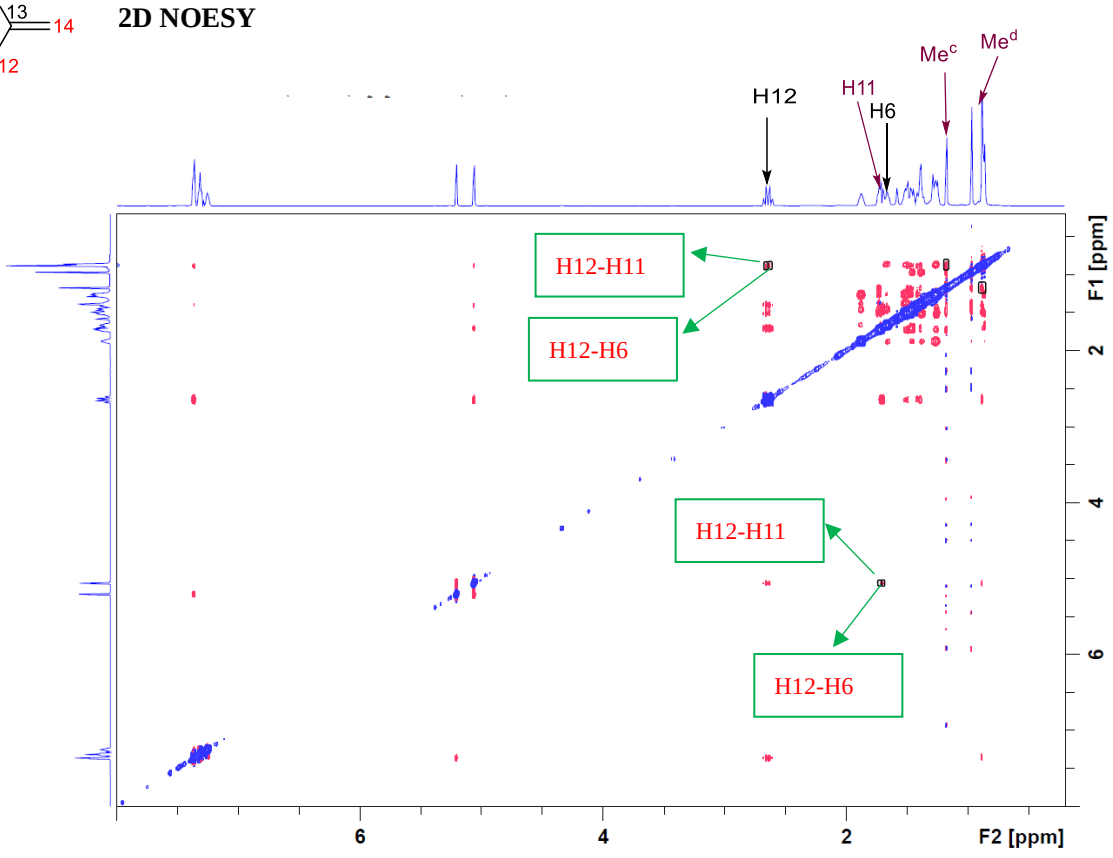
H-H COSY

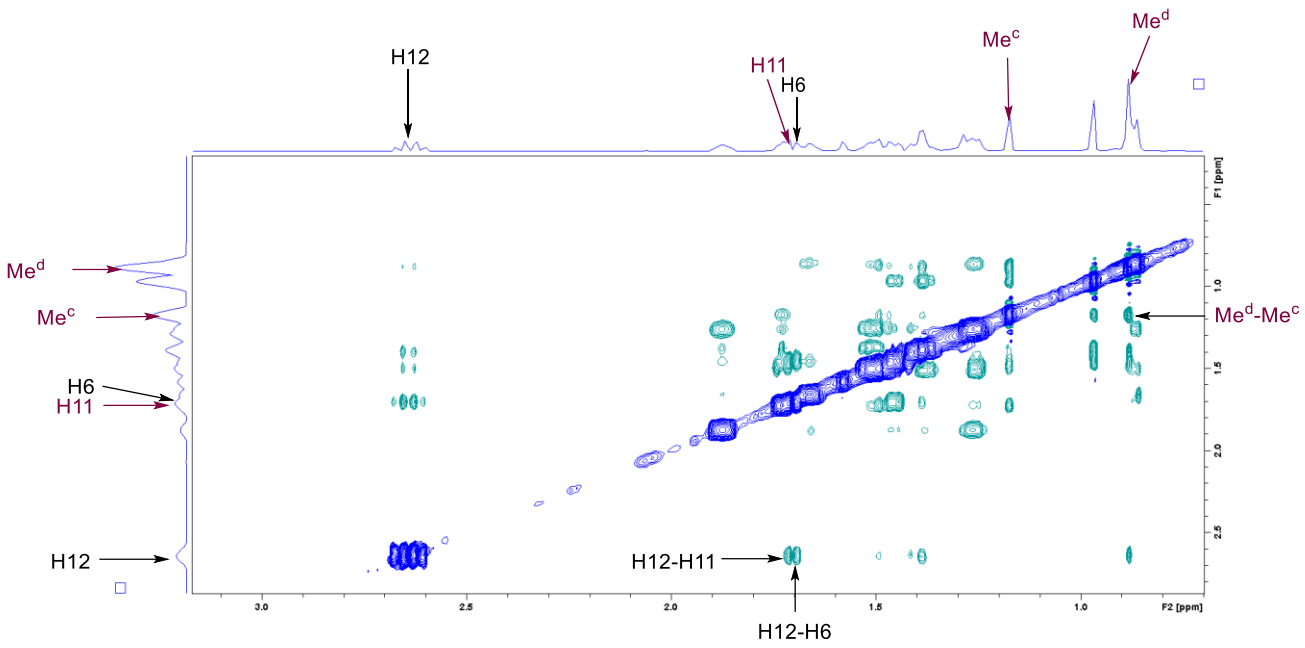

H12
Med
Mea
H10
Med-H12
Mea-H10
Med-H12
F1 [ppm]
F2 [ppm]
2
4
6


H12
H10
Me^d
Me^a
Me^a-H10
Me^d-H12
Me^a-H10
Me^d-H12
F1 [ppm]
F2 [ppm]
2.5
2.0
1.5
1.0

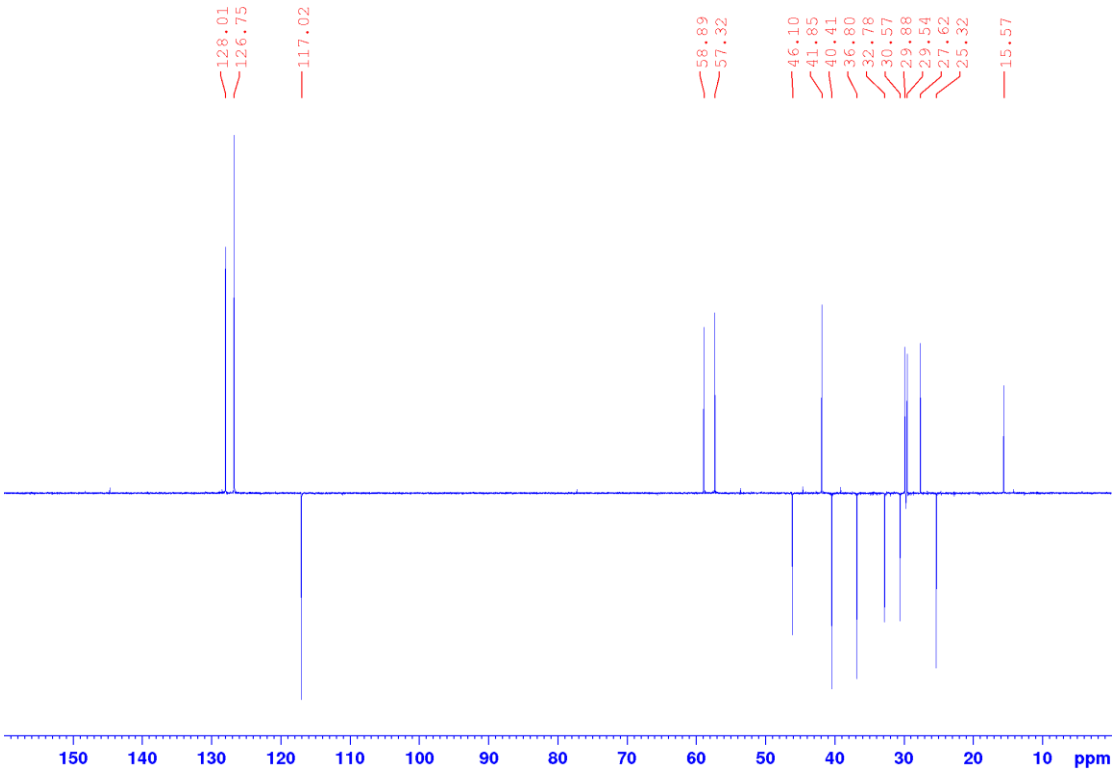

1H
8,8'
9,9'
10
a
b
c
d
Ph
12
13
14

2D NOESY

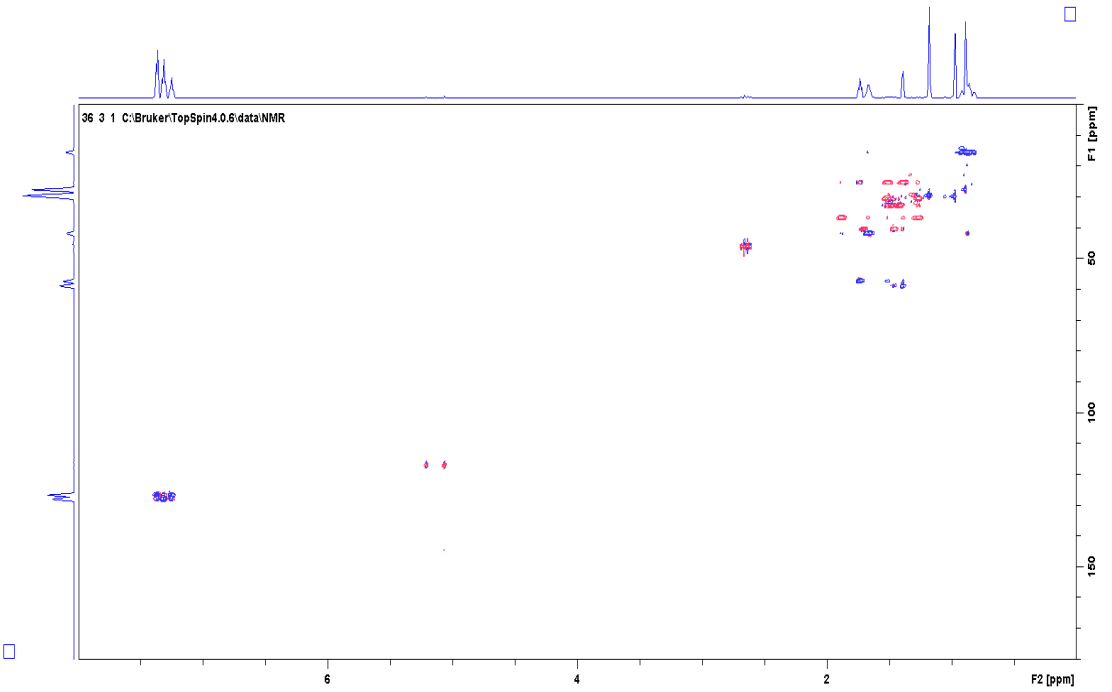

H12
H11
H6
Me^c
Me^d
H12-H11
H12-H6
H12-H11
H12-H6
F1 [ppm]
F2 [ppm]
6
4
2

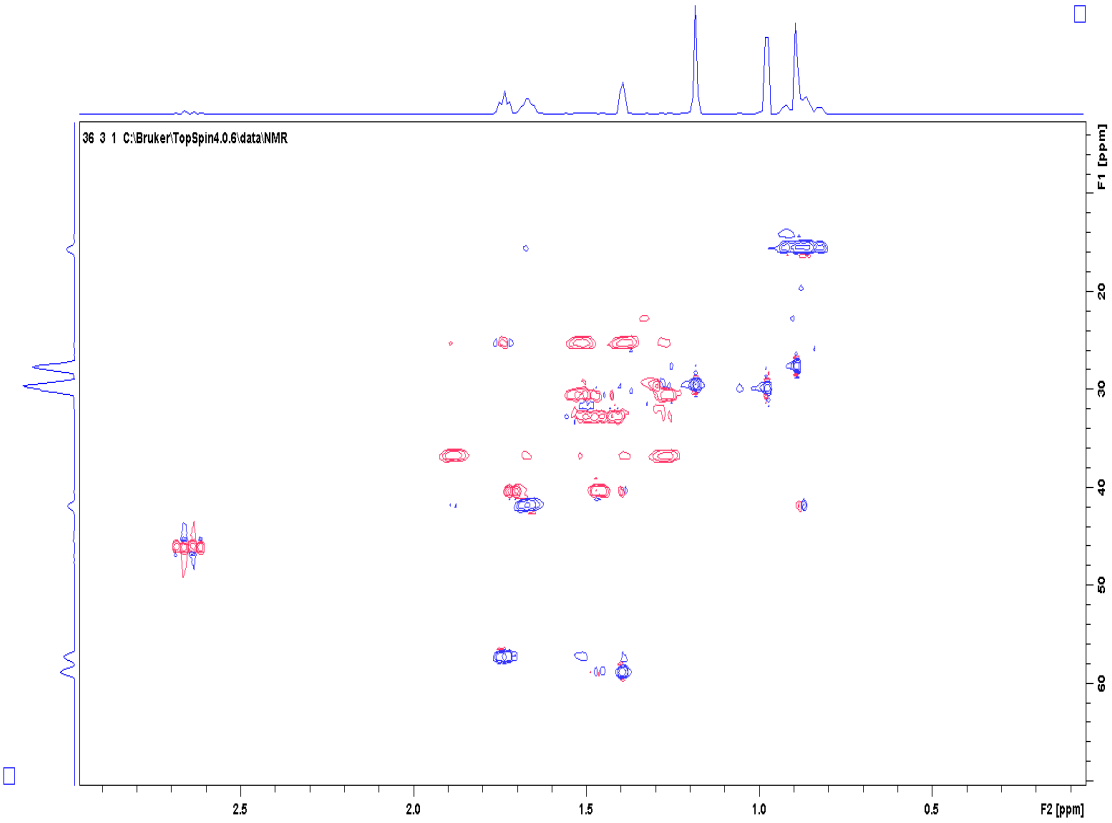

H12
H11
H6
Me^c
Me^d
Me^d
Me^c
H6
H11
H12
Me^d-Me^c
H12-H11
H12-H6
F1 [ppm]
F2 [ppm]

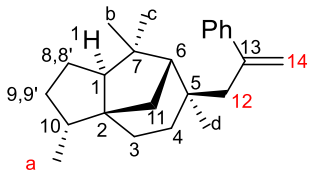
DEPT-135


128.01
126.75
117.02
58.89
57.32
46.10
41.85
40.41
36.80
32.78
30.57
29.88
29.54
27.62
25.32
15.57
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

HMQC

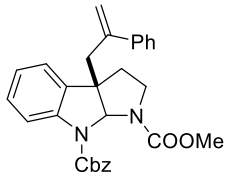

36 3 1 C:\Bruker\TopSpin4.0.6\data\NMR
F1 [ppm]
50
100
150
6
4
2
F2 [ppm]


36 3 1 C:\Bruker\TopSpin4.0.6\data\NMR
F1 [ppm]
20
30
40
50
60
2.5
2.0
1.5
1.0
0.5
F2 [ppm]



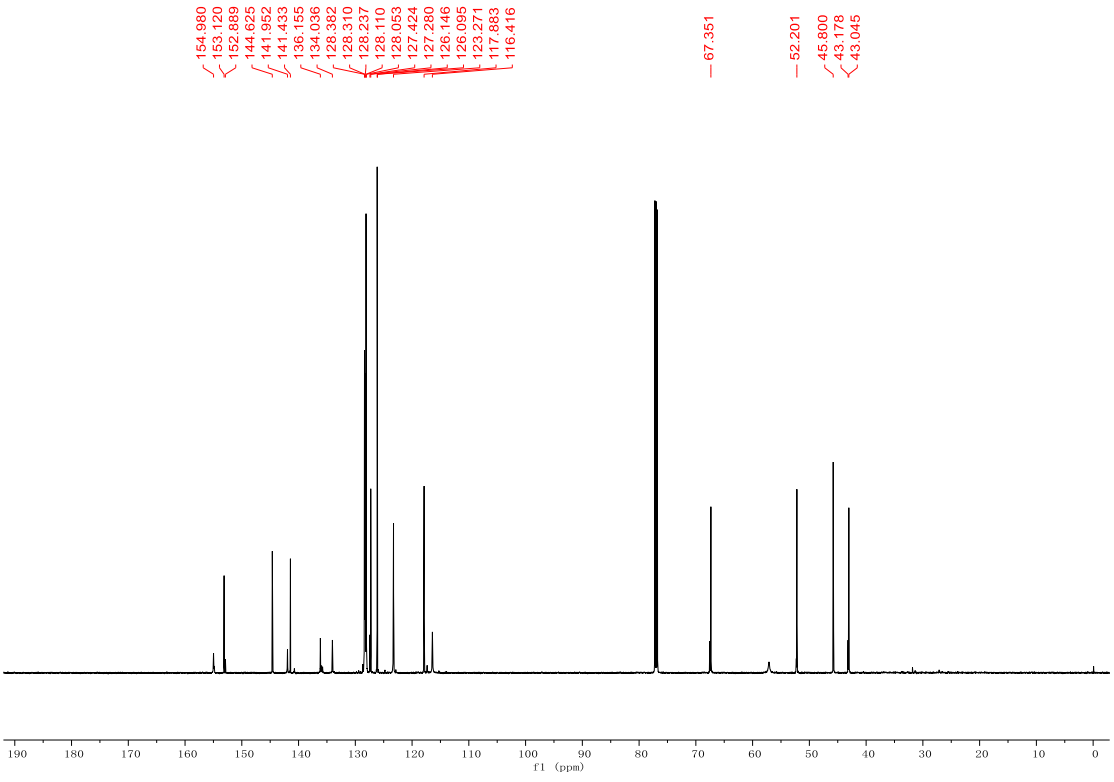
35

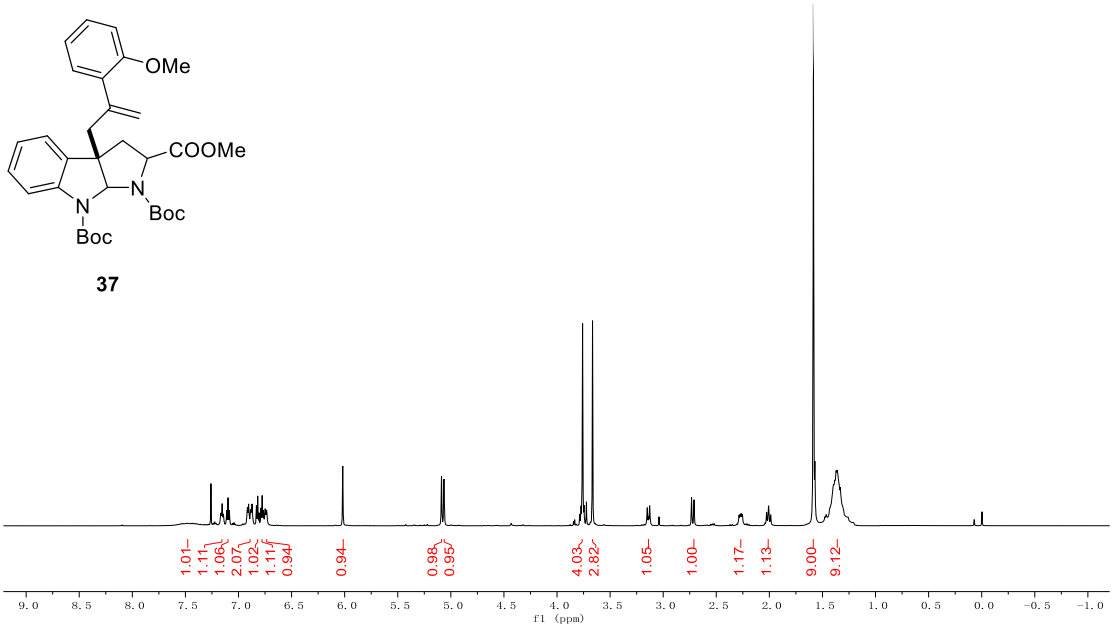
	^{13}C	^{1}H	DEPT 135
C1	58.9 ppm	1.45 ppm	+
C8	25.3 ppm	~1.39 ppm ~1.51 ppm	-
C3 or C4	30.6 ppm	~1.26 ppm ~1.51 ppm	-
	32.8 ppm	~1.41 ppm 1.49 ppm	-
C6	57.3 ppm	1.7 ppm	+
C9	36.8 ppm	~1.27 ppm 1.88 ppm	-
C10	41.9 ppm	1.65 ppm	+
C11	40.4 ppm	1.47 ppm 1.71 ppm	-
Me^{b}	29.5 ppm	0.96 ppm	+
or Me^{c}	29.8 ppm	1.16 ppm	+
C12	46.1 ppm	2.62 ppm (ab)	-

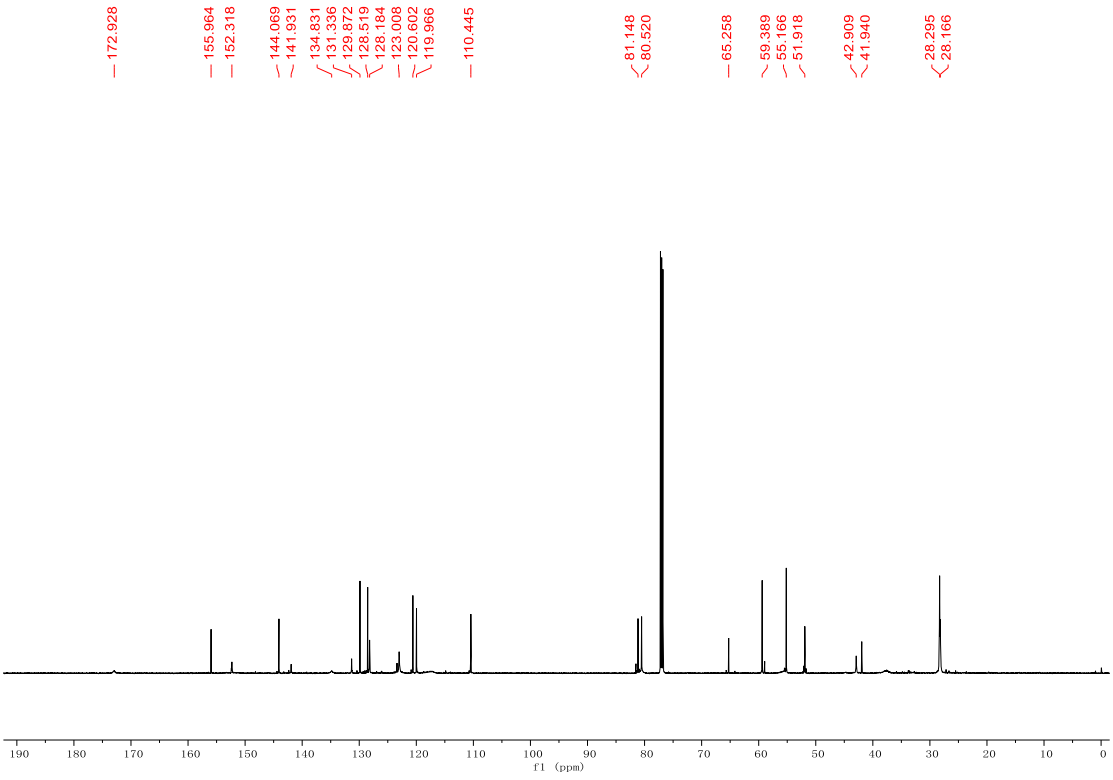

Ph
N
N
COOMe
Cbz

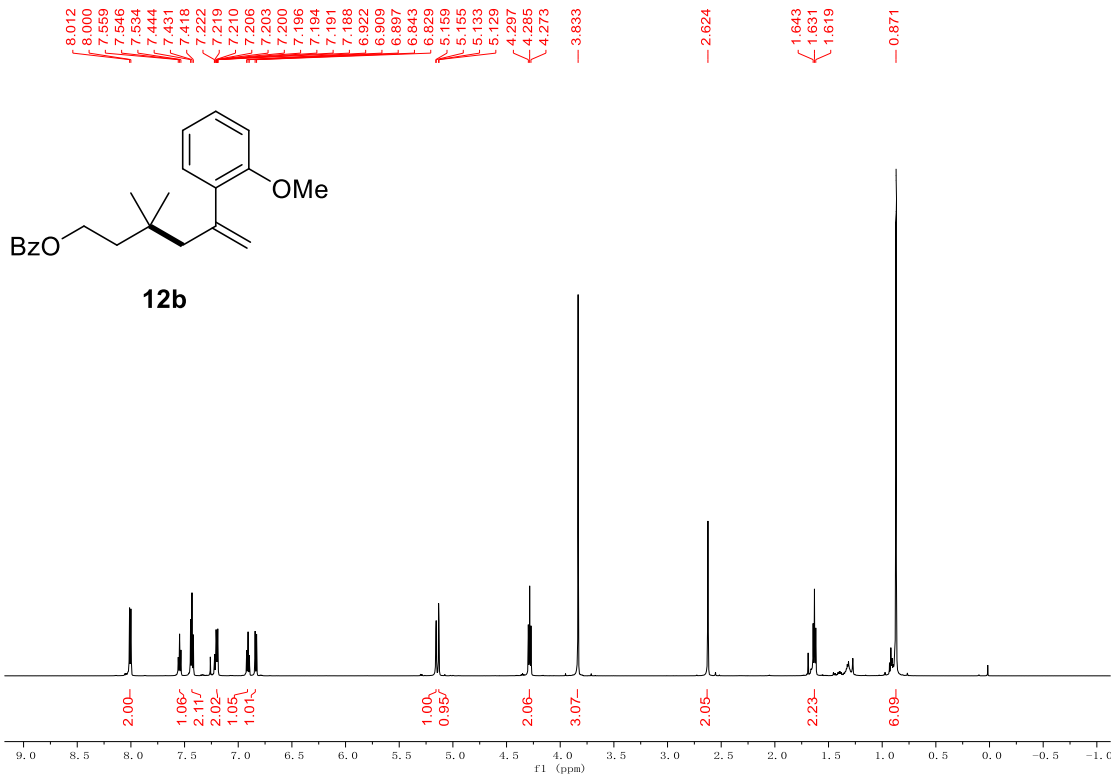
36

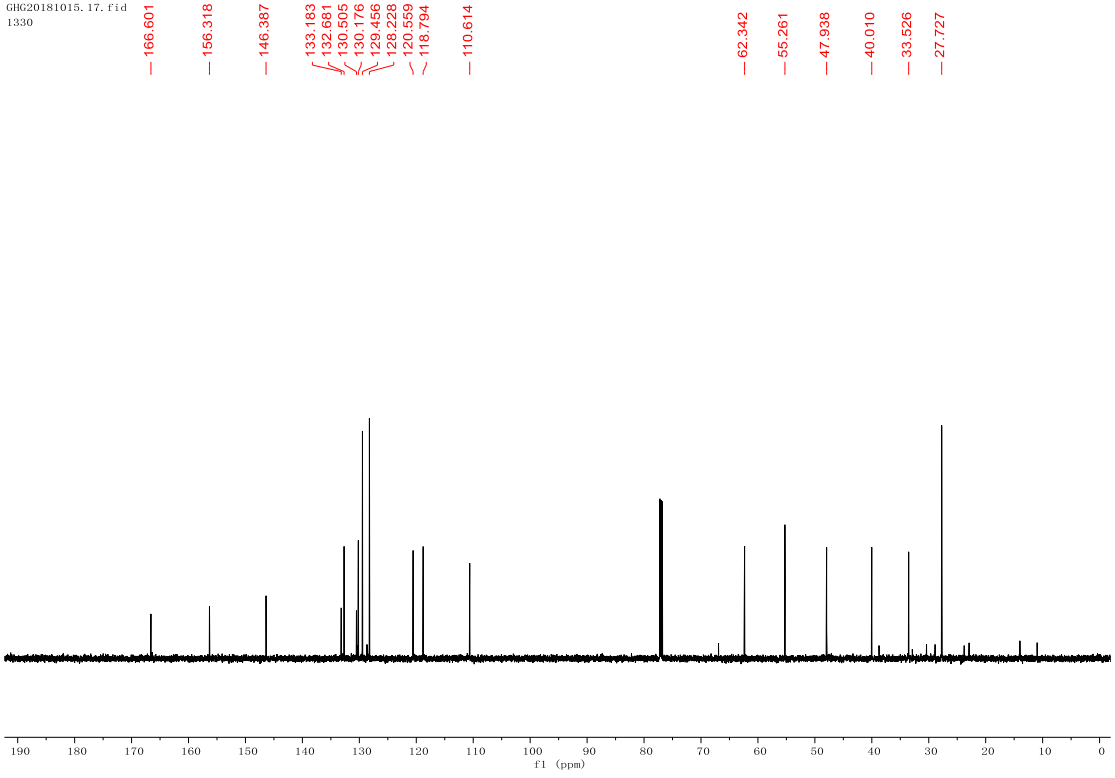
7.619
7.429
7.401
7.389
7.376
7.350
7.338
7.173
7.161
7.137
7.125
7.013
7.001
6.931
6.919
6.908
6.019
5.240
5.145
4.928
3.697
3.468
3.032
3.009
2.880
2.857
2.833
2.827
2.817
2.808
2.798
2.791
2.780
1.962
1.951
0.86
1.98
2.33
1.13
6.06
0.94
1.07
1.00
2.16
1.12
0.91
1.28
3.06
1.02
1.05
1.19
1.83
f1 (ppm)

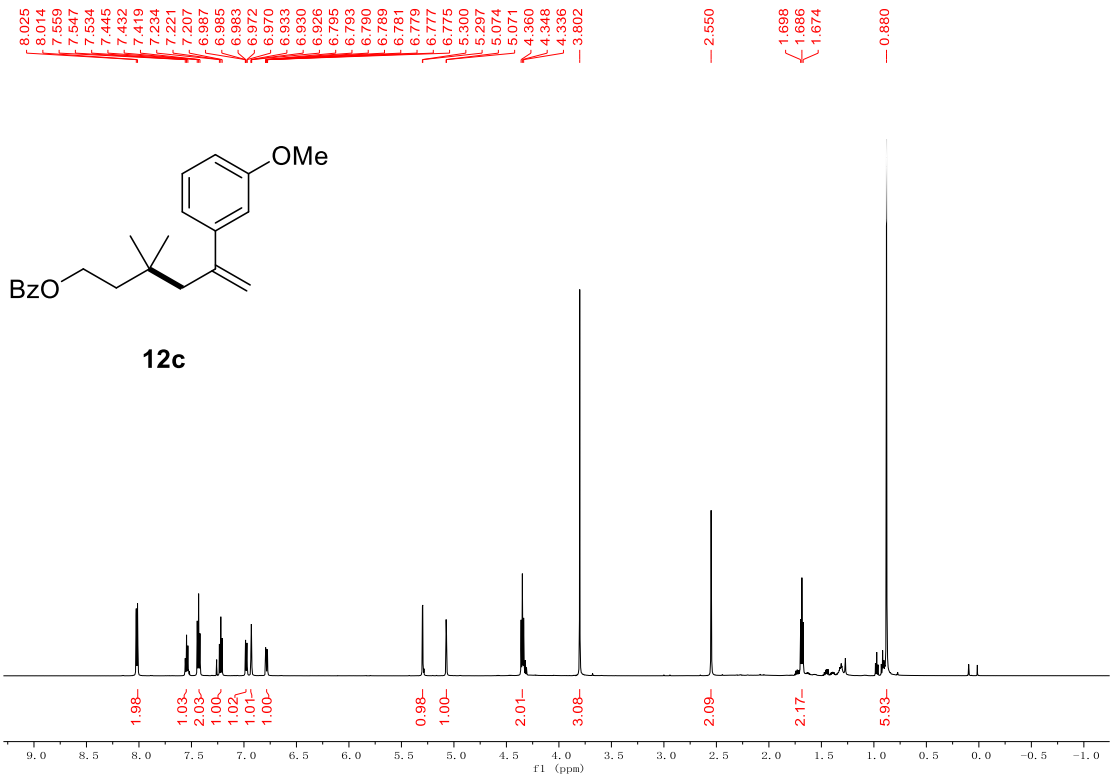

154.980
153.120
152.889
144.625
141.952
141.433
136.155
134.036
128.382
128.310
128.237
128.110
128.053
127.424
127.280
126.146
126.095
123.271
117.883
116.416
67.351
52.201
45.800
43.178
43.045
f1 (ppm)

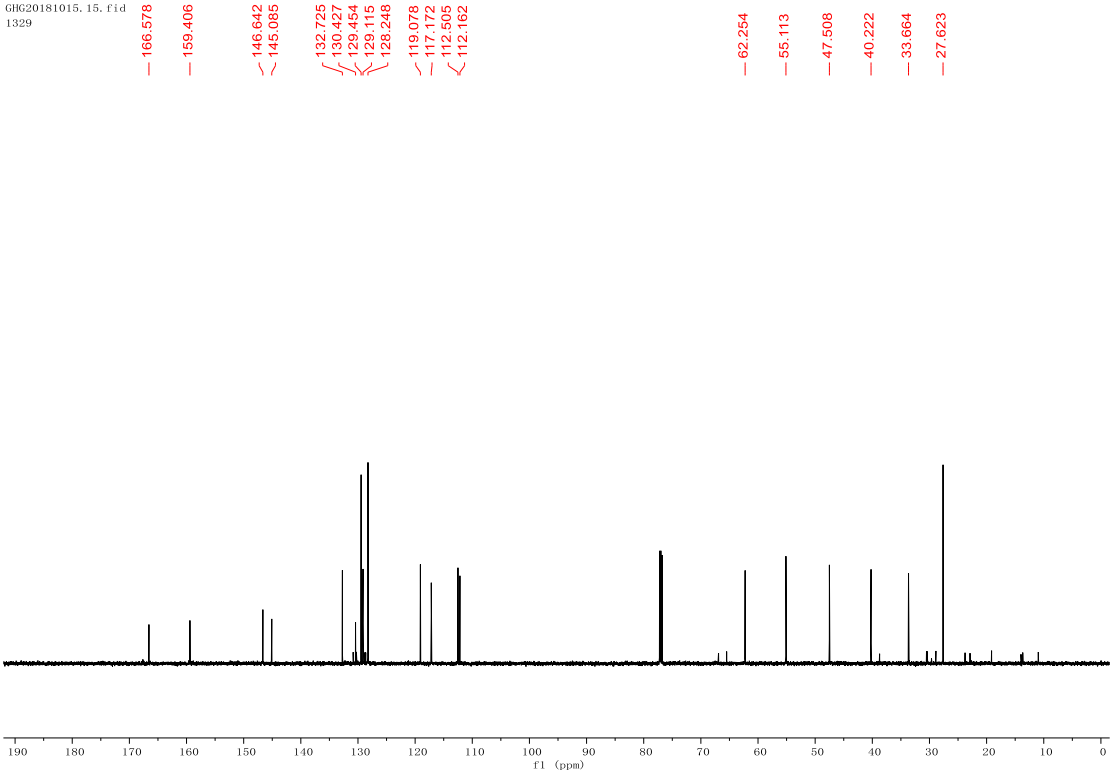

7.478
7.166
7.154
7.142
7.111
7.099
7.086
6.916
6.905
6.885
6.873
6.831
6.819
6.807
6.789
6.777
6.765
6.748
6.735
6.018
5.088
5.065
3.786
3.774
3.759
3.746
3.665
3.150
3.127
2.733
2.710
2.285
2.275
2.265
2.255
2.026
2.007
1.988
1.585
1.362
OMe
COOMe
N
Boc
N
Boc
37
1.01
1.11
1.06
2.07
1.02
1.11
0.94
0.94
0.98
0.95
4.03
2.82
1.05
1.00
1.17
1.13
9.00
9.12
f1 (ppm)

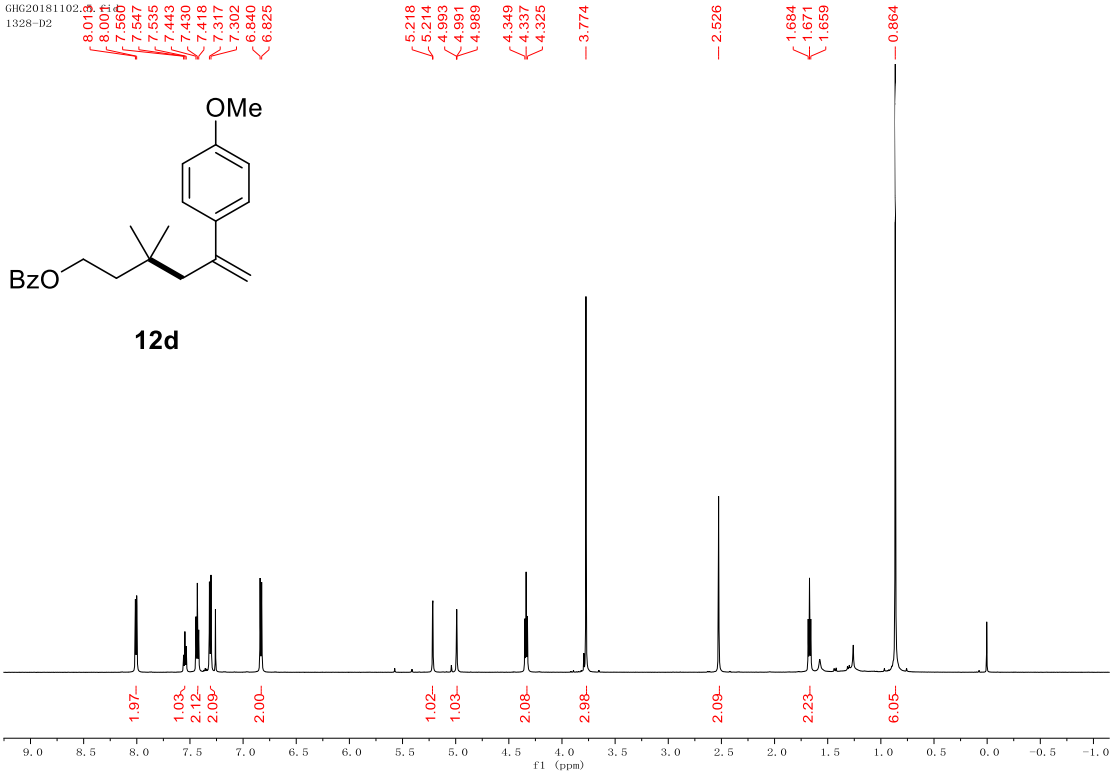

172.928
155.964
152.318
144.069
141.931
134.831
131.336
129.872
128.519
128.184
123.008
120.602
119.966
110.445
81.148
80.520
65.258
59.389
55.166
51.918
42.909
41.940
28.295
28.166
f1 (ppm)

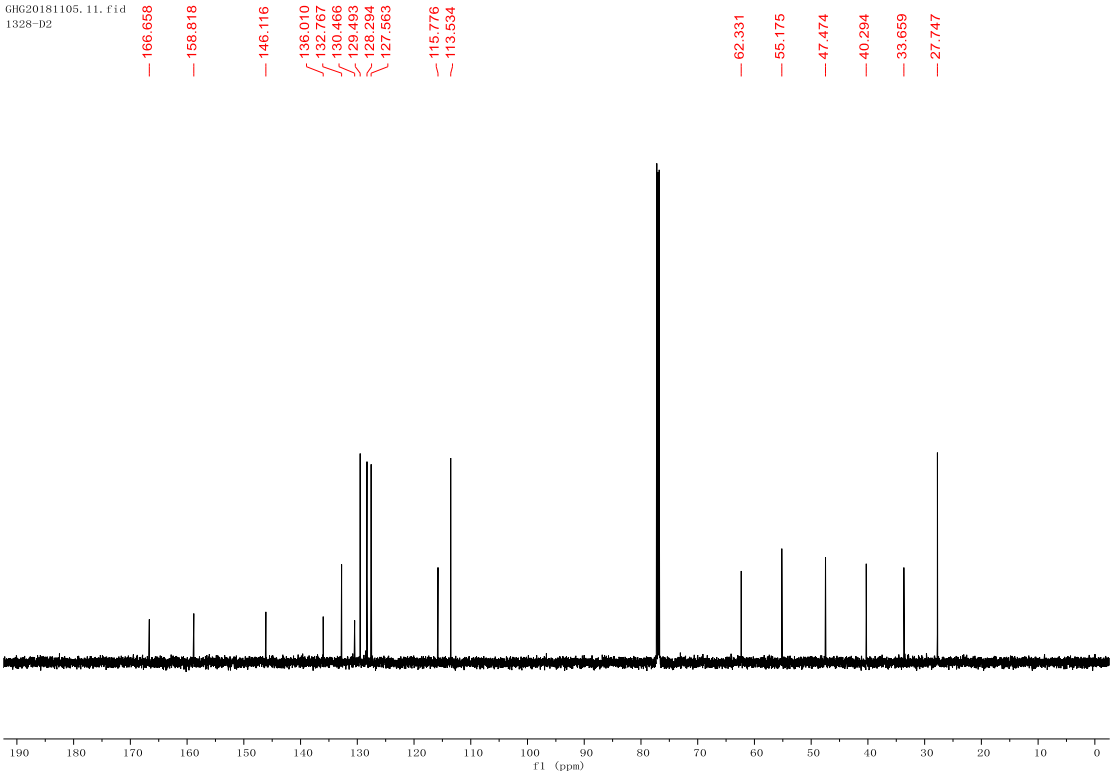

8.012
8.000
7.559
7.546
7.534
7.444
7.431
7.418
7.222
7.219
7.210
7.206
7.203
7.200
7.196
7.194
7.191
7.188
6.922
6.909
6.897
6.843
6.829
5.159
5.155
5.133
5.129
4.297
4.285
4.273
3.833
2.624
1.643
1.631
1.619
0.871
OMe
BzO
12b
2.00
1.06
2.11
2.02
1.05
1.01
1.00
0.95
2.06
3.07
2.05
2.23
6.09
f1 (ppm)

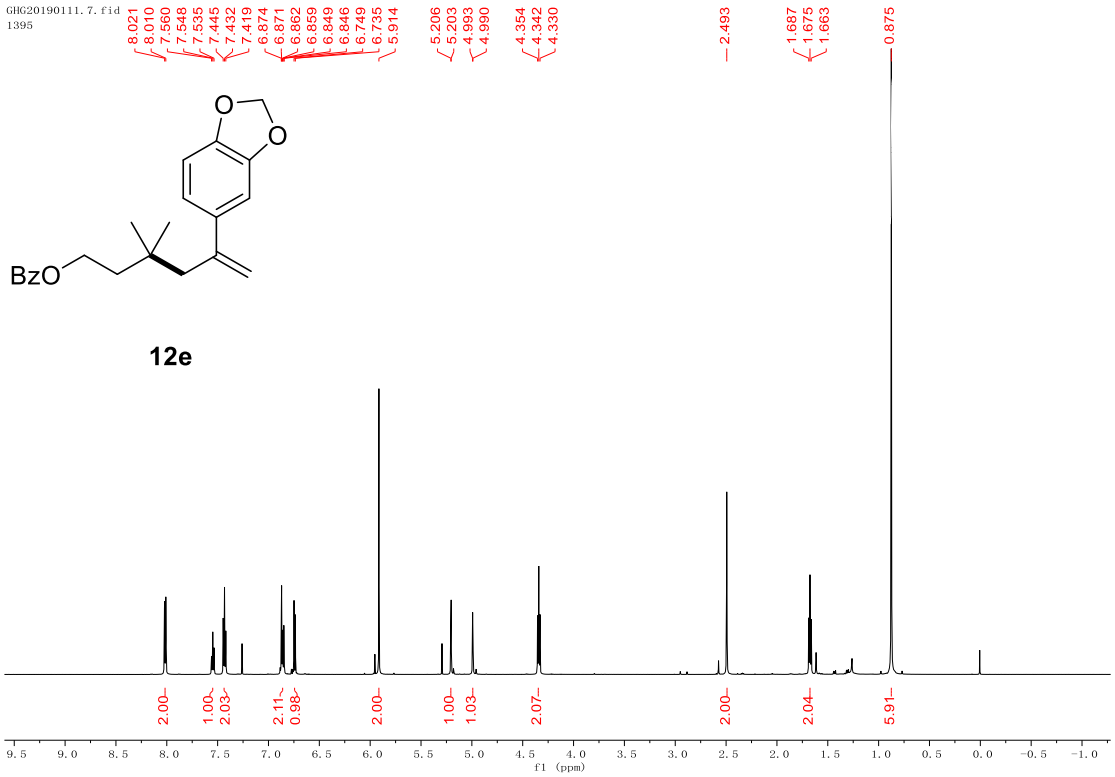

GHG20181015.17.fid
1330
166.601
156.318
146.387
133.183
132.681
130.505
130.176
129.456
128.228
120.559
118.794
110.614
62.342
55.261
47.938
40.010
33.526
27.727
f1 (ppm)


8.025
8.014
7.559
7.547
7.534
7.445
7.432
7.419
7.234
7.221
7.207
6.987
6.985
6.983
6.972
6.970
6.933
6.930
6.926
6.795
6.793
6.790
6.789
6.781
6.779
6.777
6.775
5.300
5.297
5.074
5.071
4.360
4.348
4.336
3.802
2.550
1.698
1.686
1.674
0.880
OMe
BzO
12c
1.98
1.03
2.03
1.00
1.02
1.01
1.00
0.98
1.00
2.01
3.08
2.09
2.17
5.93
f1 (ppm)

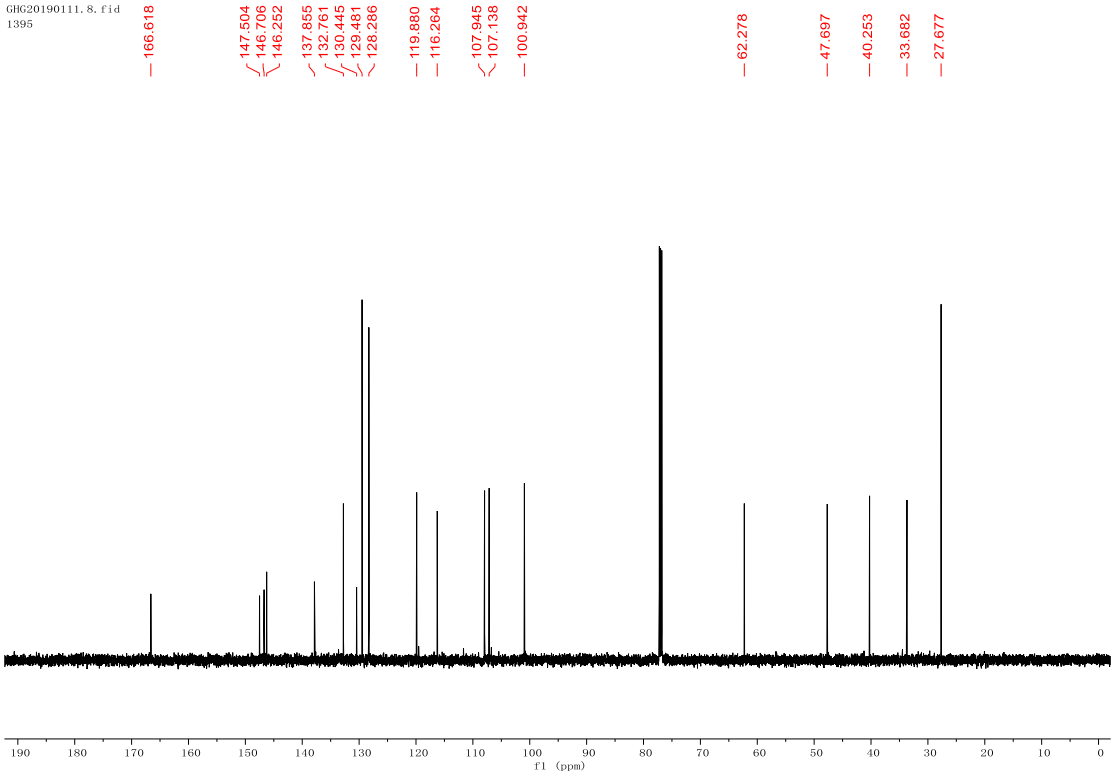

GHG20181015.15.fid
1329
166.578
159.406
146.642
145.085
132.725
130.427
129.454
129.115
128.248
119.078
117.172
112.505
112.162
62.254
55.113
47.508
40.222
33.664
27.623
f1 (ppm)


GHG20181102.9.1
1328-D2
8.015
8.001
7.566
7.547
7.535
7.443
7.430
7.418
7.317
7.302
6.840
6.825
5.218
5.214
4.993
4.991
4.989
4.349
4.337
4.325
3.774
2.526
1.684
1.671
1.659
0.864
OMe
BzO
12d
1.97
1.03
2.12
2.09
2.00
1.02
1.03
2.08
2.98
2.09
2.23
6.05
f1 (ppm)

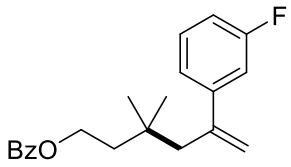

GHG20181105.11.fid
1328-D2
166.658
158.818
146.116
136.010
132.767
130.466
129.493
128.294
127.563
115.776
113.534
62.331
55.175
47.474
40.294
33.659
27.747
f1 (ppm)


GHG20190111.7.fid
1395
8.021
8.010
7.560
7.548
7.535
7.445
7.432
7.419
6.874
6.871
6.862
6.859
6.849
6.846
6.749
6.735
5.914
5.206
5.203
4.993
4.990
4.354
4.342
4.330
2.493
1.687
1.675
1.663
0.875
O
O
BzO
2.00
1.00
2.03
2.11
0.98
2.00
1.00
1.03
2.07
2.00
2.04
5.91
f1 (ppm)

12e

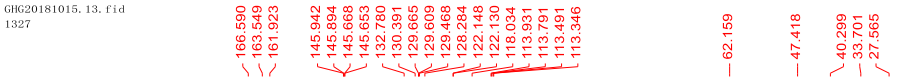

GHG20190111.8.fid
1395
166.618
147.504
146.706
146.252
137.855
132.761
130.445
129.481
128.286
119.880
116.264
107.945
107.138
100.942
62.278
47.697
40.253
33.682
27.677
f1 (ppm)

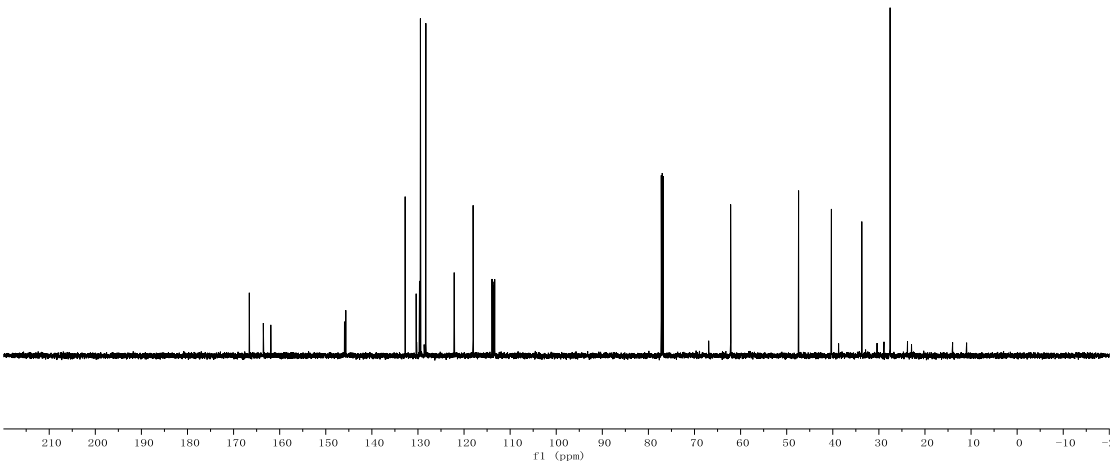

8.010
7.999
7.546
7.534
7.522
7.432
7.419
7.406
7.260
7.250
7.247
7.244
7.237
7.233
7.223
7.152
7.150
7.148
7.137
7.080
7.077
7.073
7.063
7.060
7.056
6.930
6.928
6.925
6.924
6.916
6.914
6.911
6.910
6.902
6.900
6.897
6.896
5.299
5.296
5.096
5.094
4.349
4.337
4.325
2.524
1.682
1.670
1.657
0.853

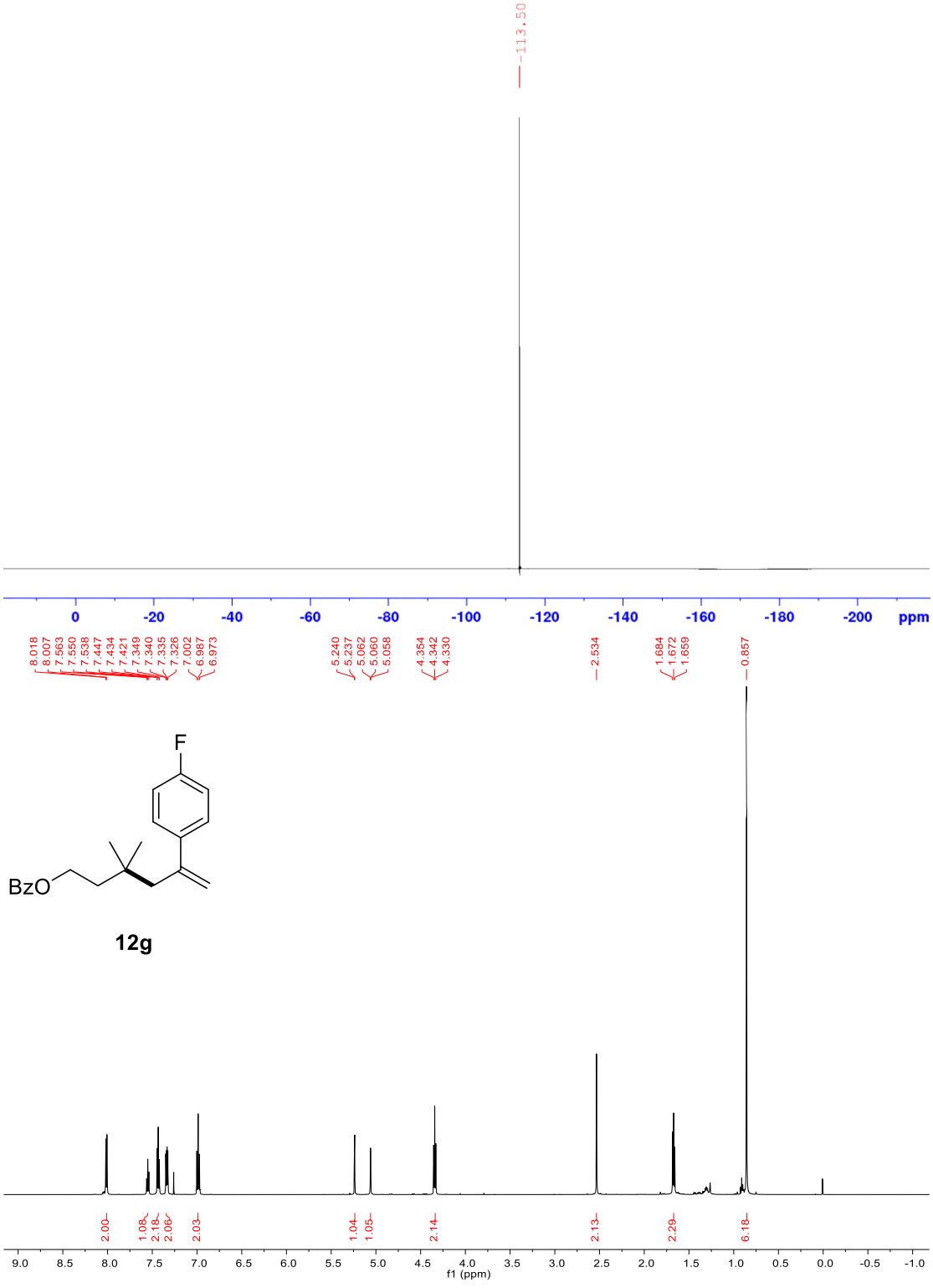

F
BzO

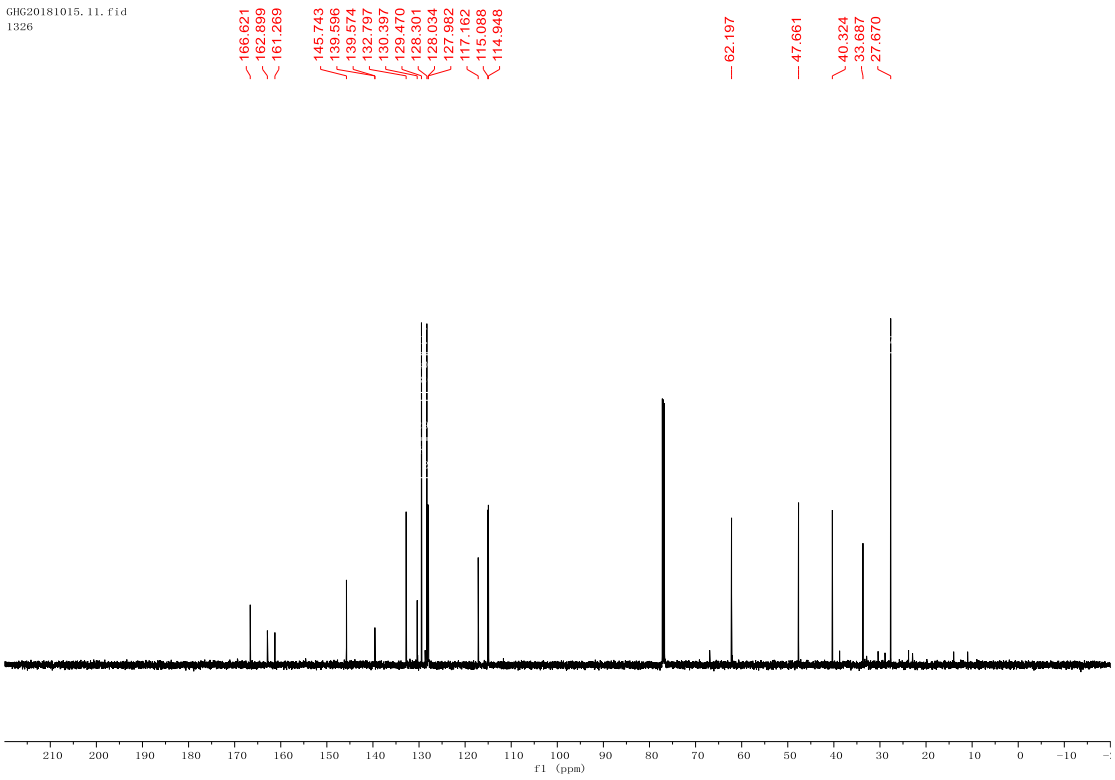
12f

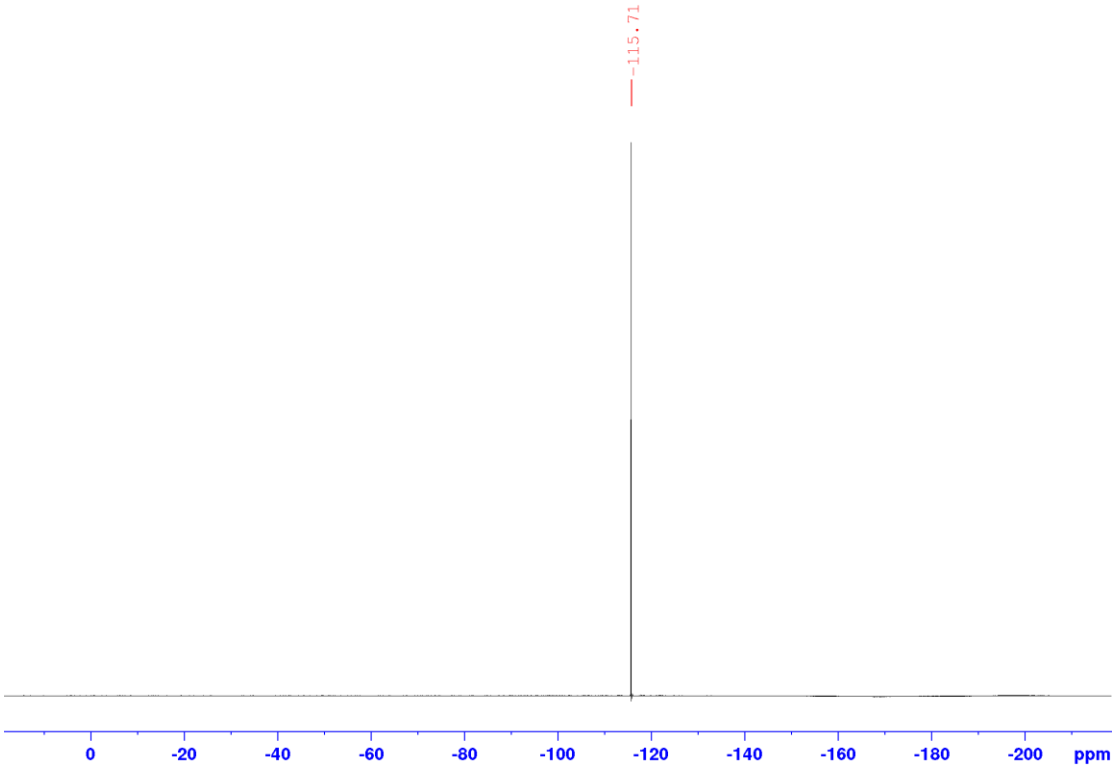
1.93
1.00
2.01
1.08
0.98
0.98
0.96
1.02
1.01
2.05
2.04
2.14
5.83
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)

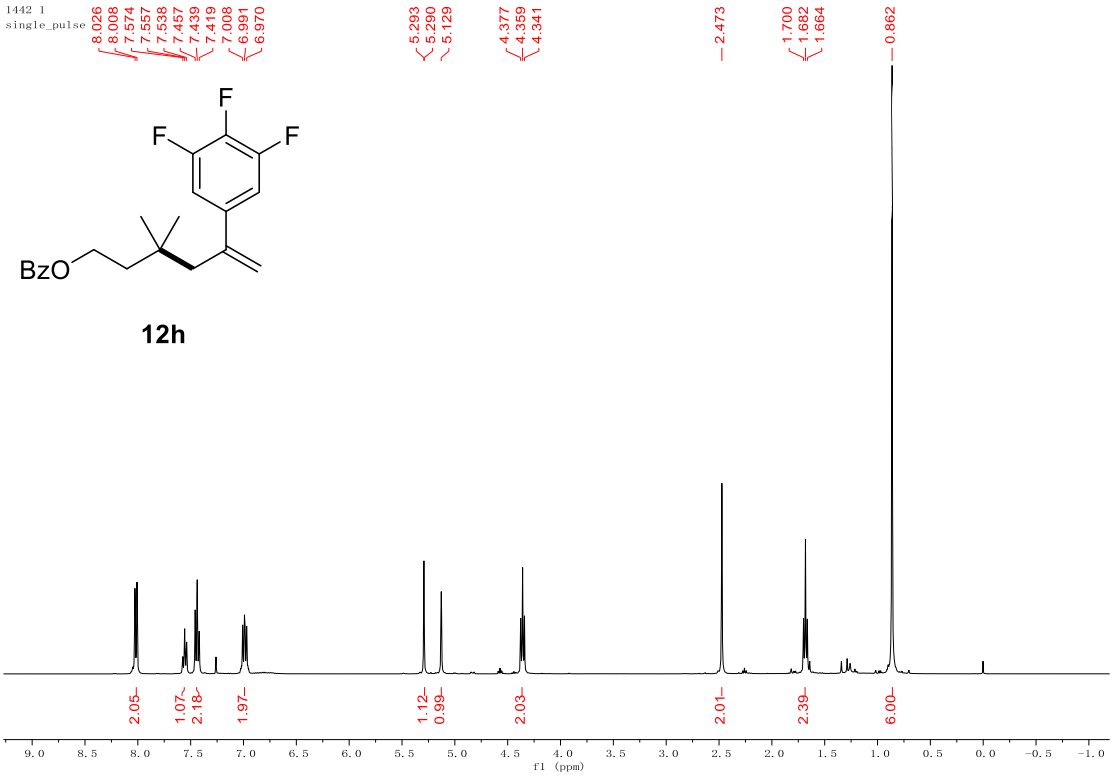

GHG20181015.13.fid
1327
166.590
163.549
161.923
145.942
145.894
145.668
145.653
132.780
130.391
129.665
129.609
129.468
128.284
122.148
122.130
118.034
113.931
113.791
113.491
113.346
62.159
47.418
40.299
33.701
27.565


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)

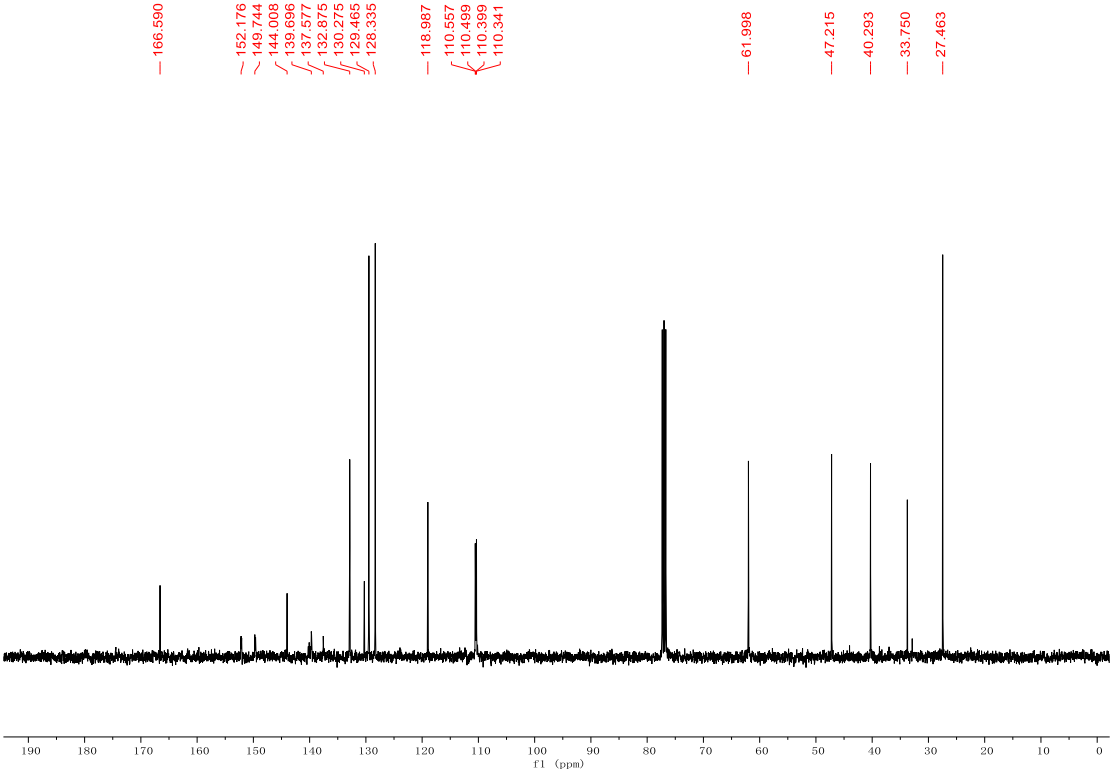

-113.50
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
8.018
8.007
7.563
7.550
7.538
7.447
7.434
7.421
7.349
7.340
7.335
7.326
7.002
6.987
6.973
5.240
5.237
5.062
5.060
5.058
4.354
4.342
4.330
2.534
1.684
1.672
1.659
0.857
F
BzO
12g
2.00
1.08
2.18
2.06
2.03
1.04
1.05
2.14
2.13
2.29
6.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

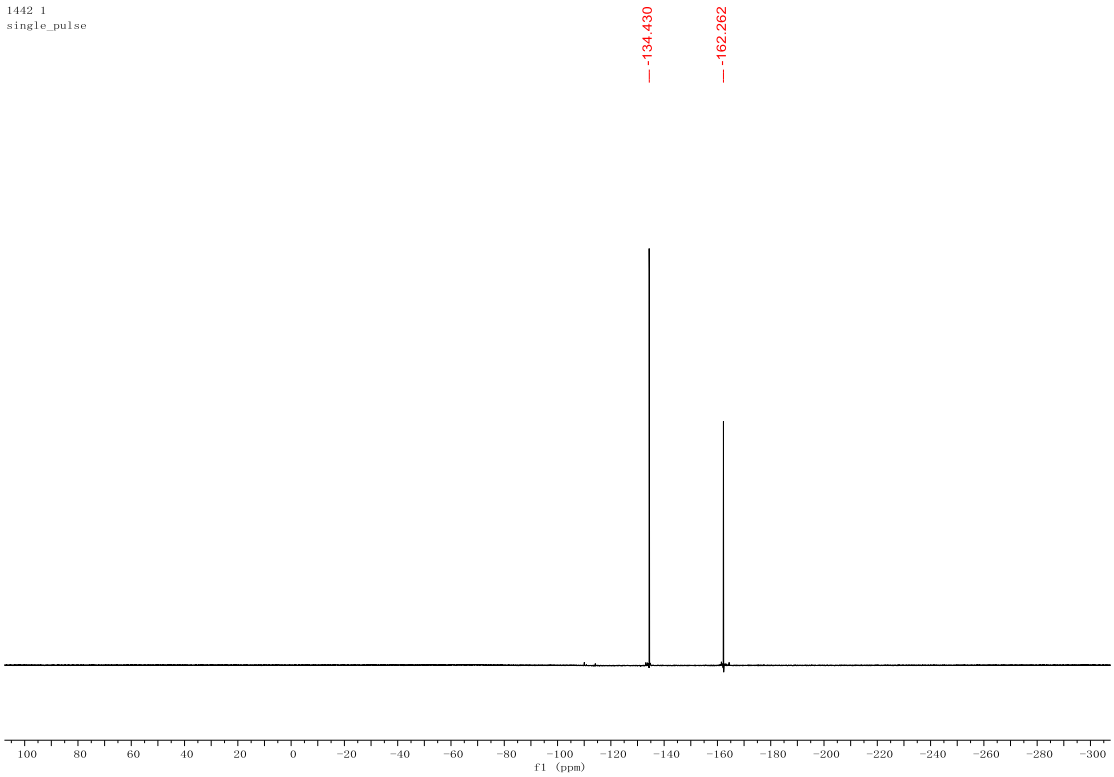

GHG20181015.11.fid
1326
166.621
162.899
161.269
145.743
139.596
139.574
132.797
130.397
129.470
128.301
128.034
127.982
117.162
115.088
114.948
62.197
47.661
40.324
33.687
27.670
f1 (ppm)

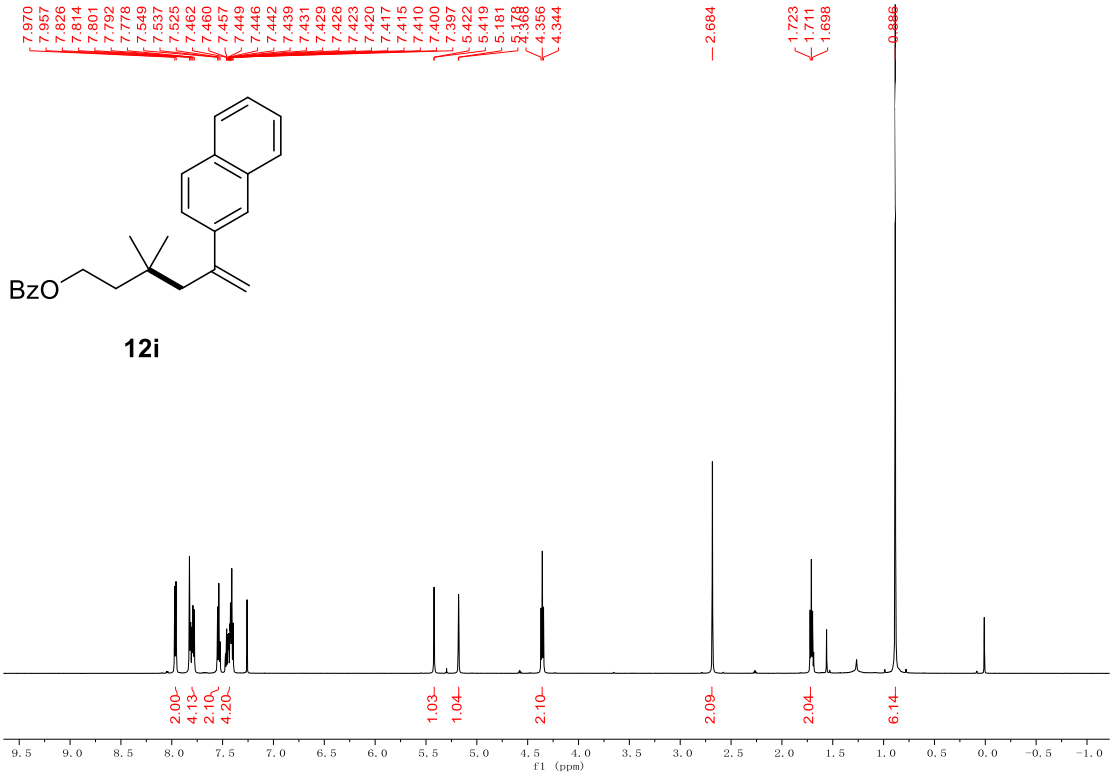

-115.71
ppm


1442 1
single_pulse
8.026
8.008
7.574
7.557
7.538
7.457
7.439
7.419
7.008
6.991
6.970
5.293
5.290
5.129
4.377
4.359
4.341
2.473
1.700
1.682
1.664
0.862
F
F
F
BzO
2.05
1.07
2.18
1.97
1.12
0.99
2.03
2.01
2.39
6.00
f1 (ppm)

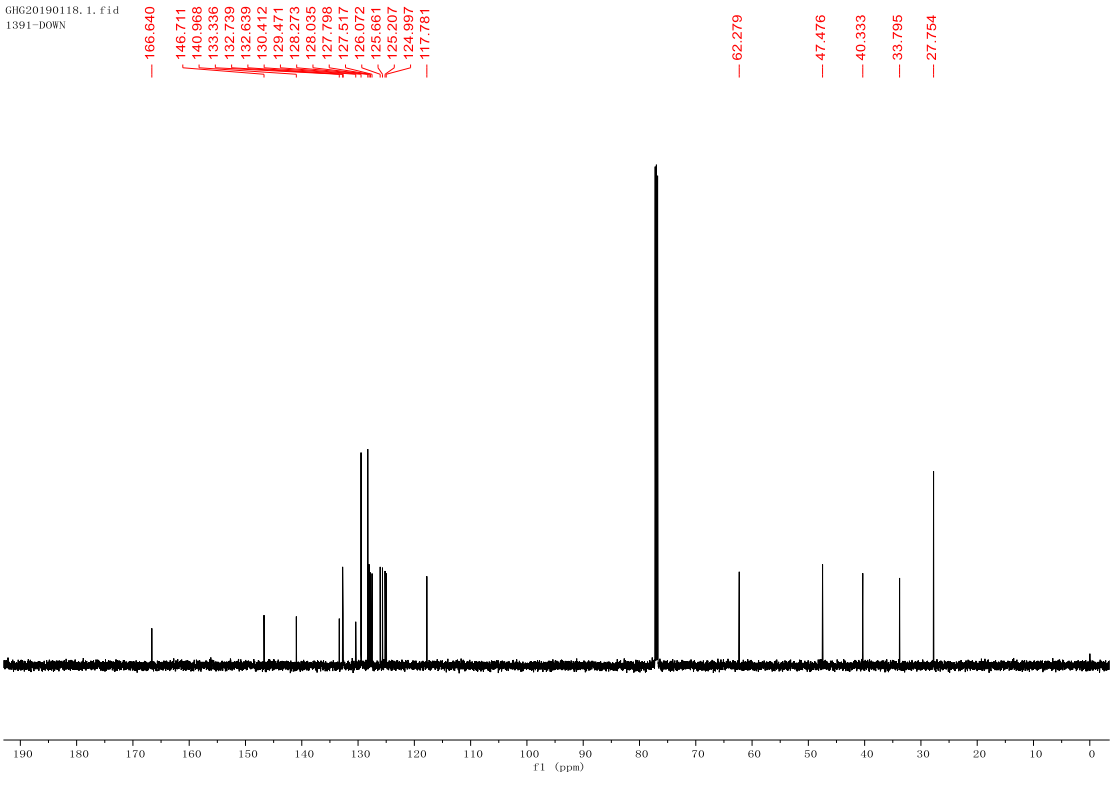
12h

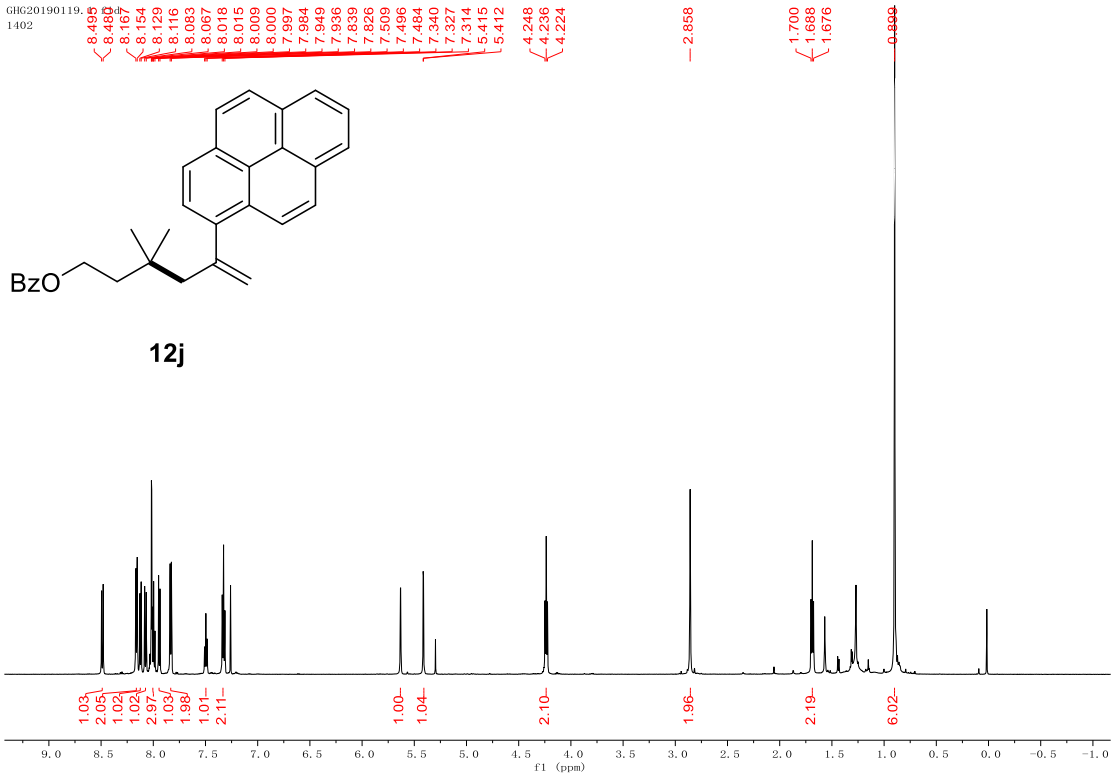

166.590
152.176
149.744
144.008
139.696
137.577
132.875
130.275
129.465
128.335
118.987
110.557
110.499
110.399
110.341
61.998
47.215
40.293
33.750
27.463
f1 (ppm)


1442 1
single_pulse
-134.430
-162.262
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)

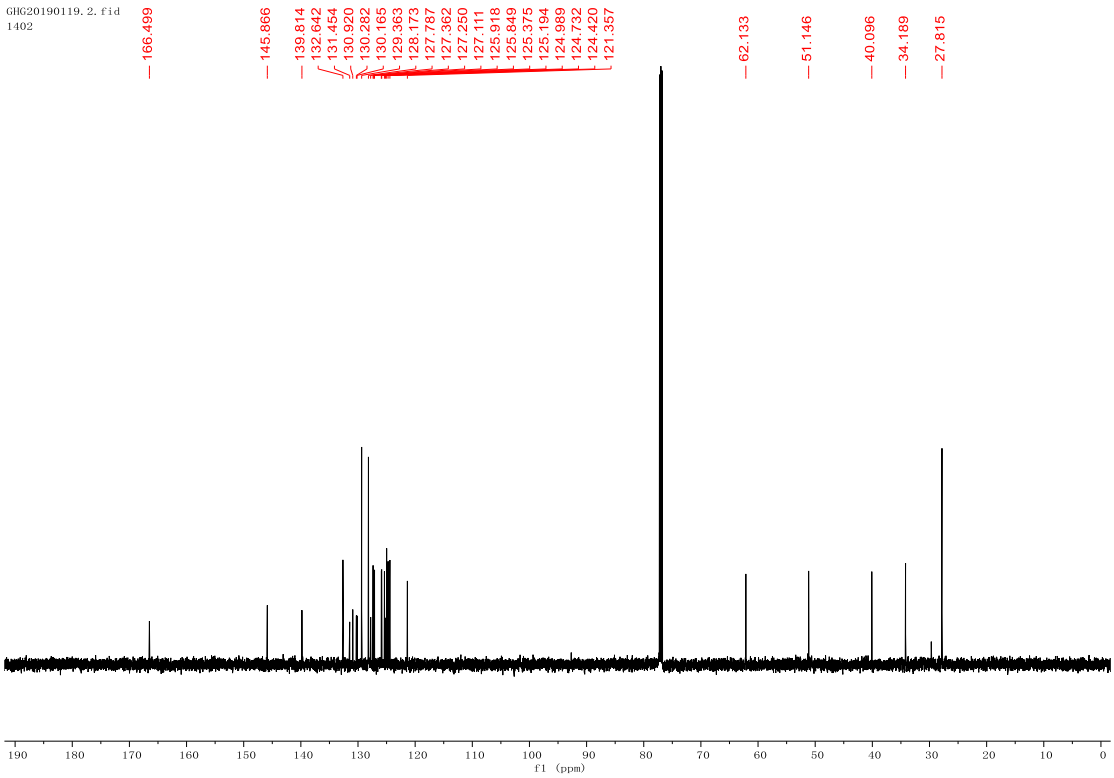

7.970
7.957
7.826
7.814
7.801
7.792
7.778
7.549
7.537
7.525
7.462
7.460
7.457
7.449
7.446
7.442
7.439
7.431
7.429
7.426
7.423
7.420
7.417
7.415
7.410
7.400
7.397
5.422
5.419
5.181
5.178
4.368
4.356
4.344
2.684
1.723
1.711
1.698
0.886
BzO
2.00
4.13
2.10
4.20
1.03
1.04
2.10
2.09
2.04
6.14
f1 (ppm)

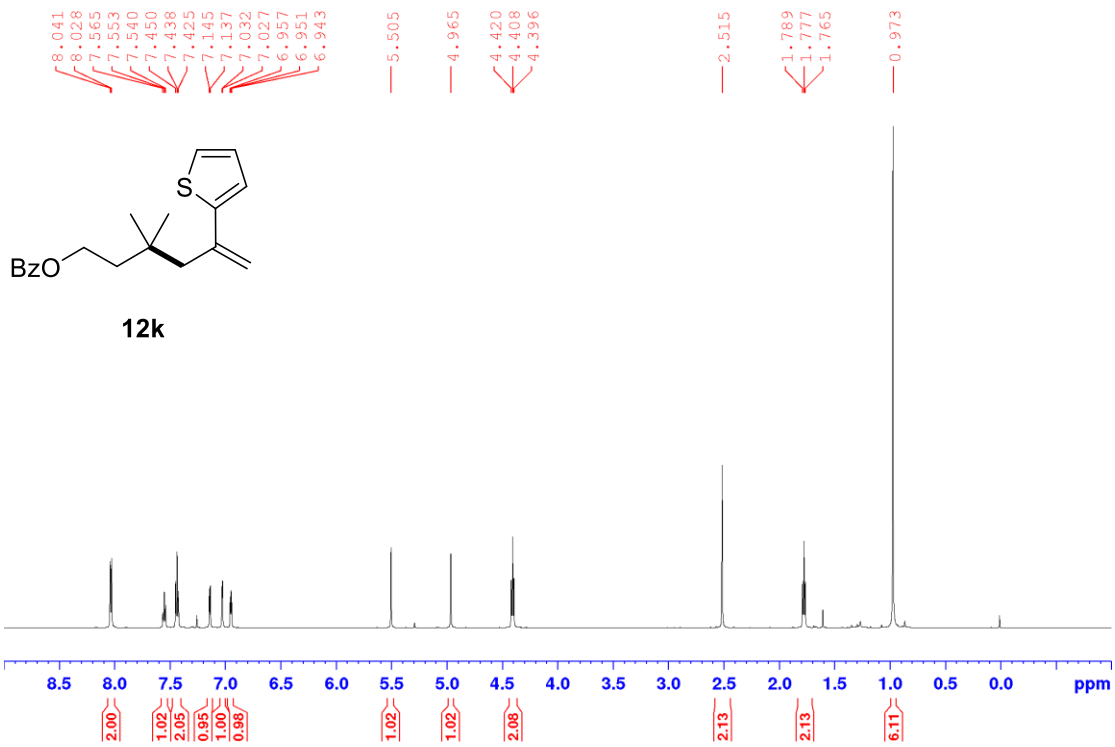
12i


GHG20190118.1.fid
1391-DOWN
166.640
146.711
140.968
133.336
132.739
132.639
130.412
129.471
128.273
128.035
127.798
127.517
126.072
125.661
125.207
124.997
117.781
62.279
47.476
40.333
33.795
27.754
f1 (ppm)

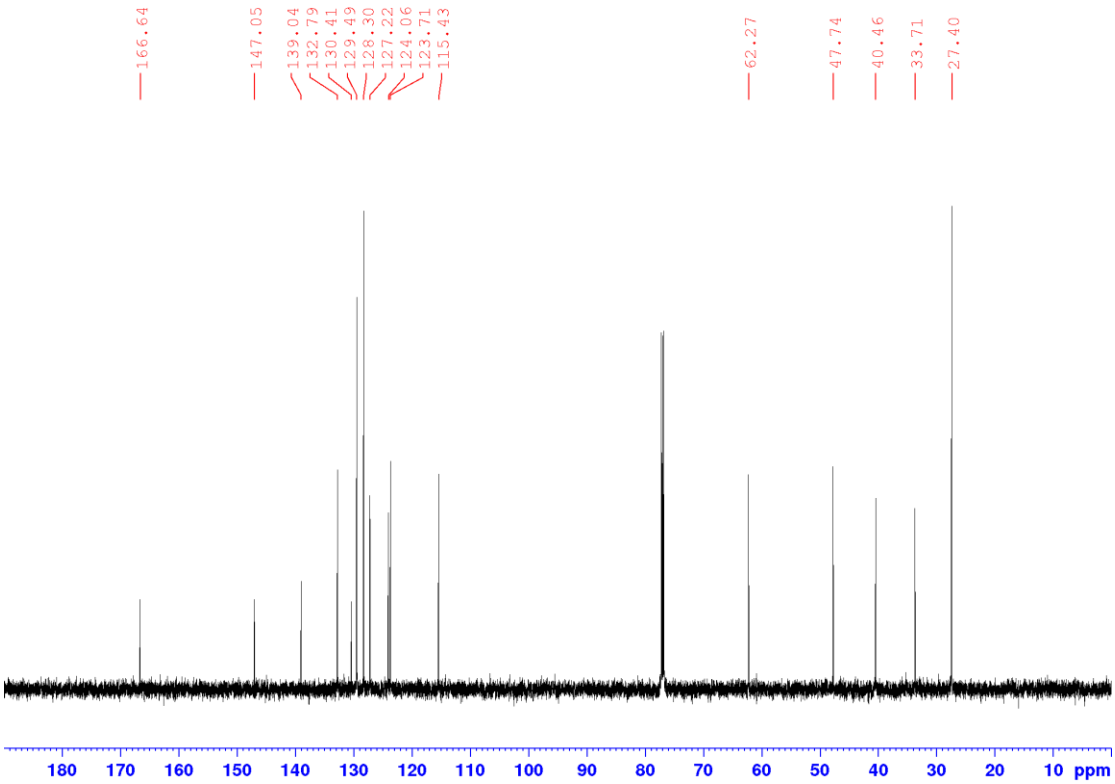

GHG20190119.
1402
8.495
8.480
8.167
8.154
8.129
8.116
8.083
8.067
8.018
8.015
8.009
8.000
7.997
7.984
7.949
7.936
7.839
7.826
7.509
7.496
7.484
7.340
7.327
7.314
5.415
5.412
4.248
4.236
4.224
2.858
1.700
1.688
1.676
0.899
BzO
1.03
2.05
1.02
1.02
2.97
1.03
1.98
1.01
2.11
1.00
1.04
2.10
1.96
2.19
6.02
f1 (ppm)

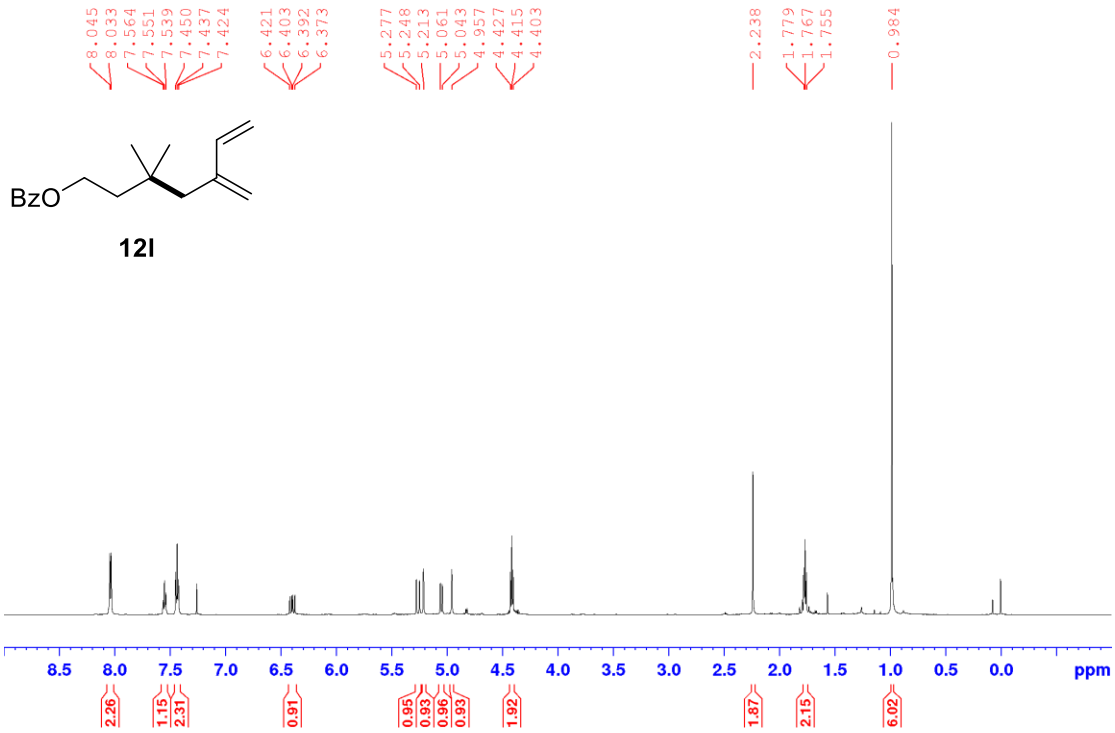
12j


GHG20190119.2.fid
1402
166.499
145.866
139.814
132.642
131.454
130.920
130.282
130.165
129.363
128.173
127.787
127.362
127.250
127.111
125.918
125.849
125.375
125.194
124.989
124.732
124.420
121.357
62.133
51.146
40.096
34.189
27.815
f1 (ppm)

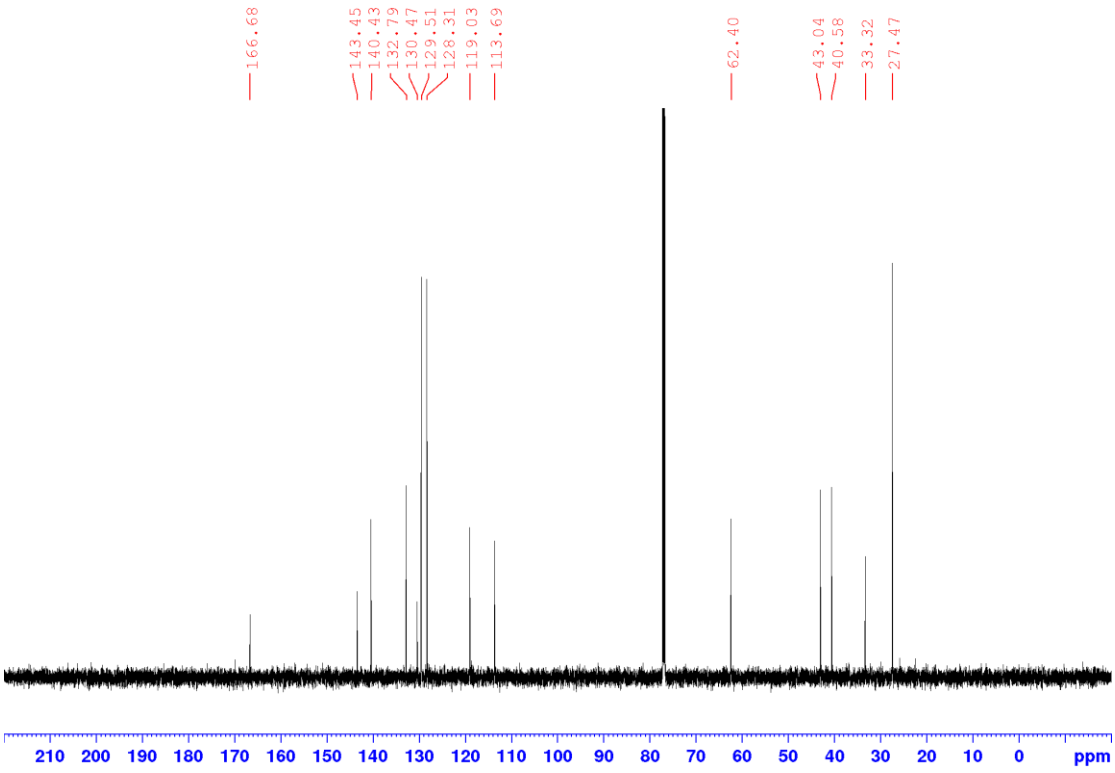

8.041
8.028
7.565
7.553
7.540
7.450
7.438
7.425
7.145
7.137
7.032
7.027
6.957
6.951
6.943
5.505
4.965
4.420
4.408
4.396
2.515
1.789
1.777
1.765
0.973
S
BzO
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.02
2.05
0.95
1.00
0.98
1.02
1.02
2.08
2.13
2.13
6.11

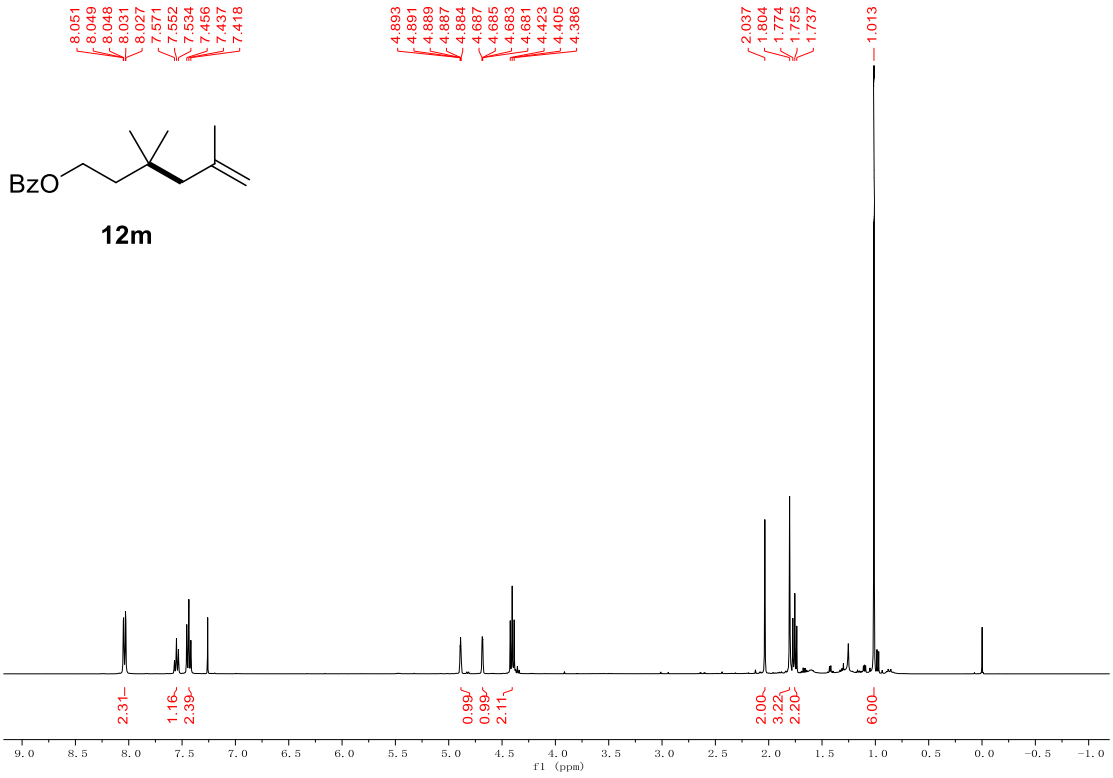
12k

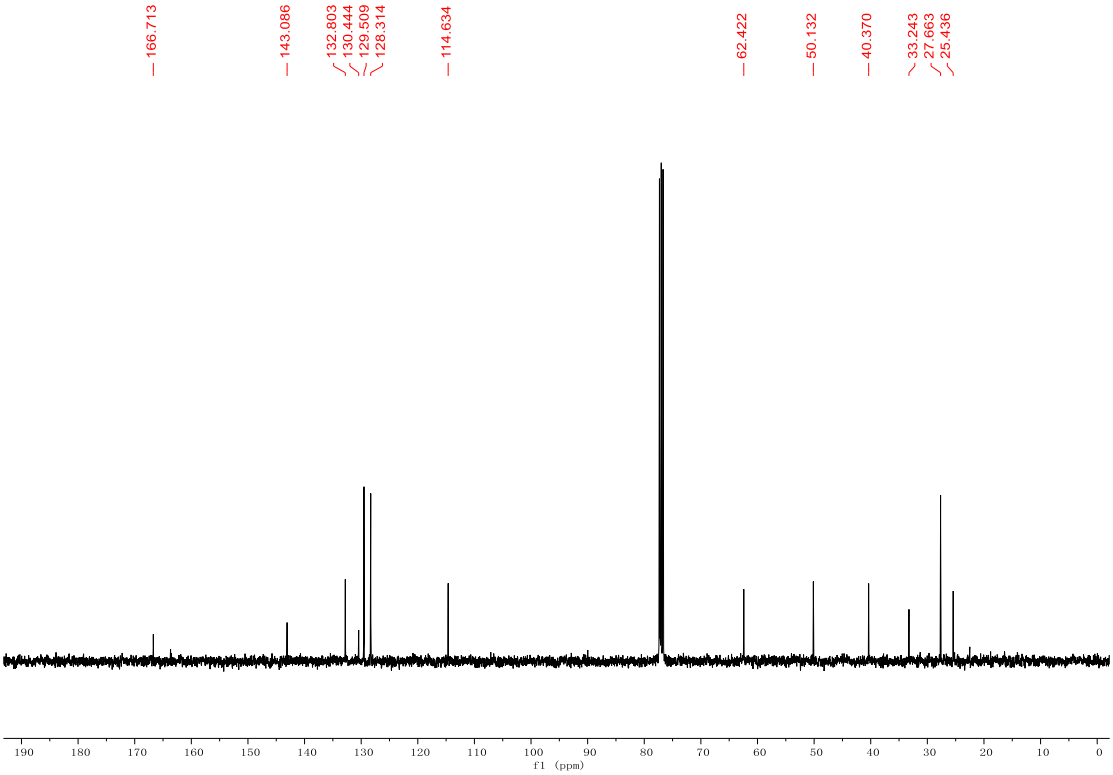

166.64
147.05
139.04
132.79
130.41
129.49
128.30
127.22
124.06
123.71
115.43
62.27
47.74
40.46
33.71
27.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

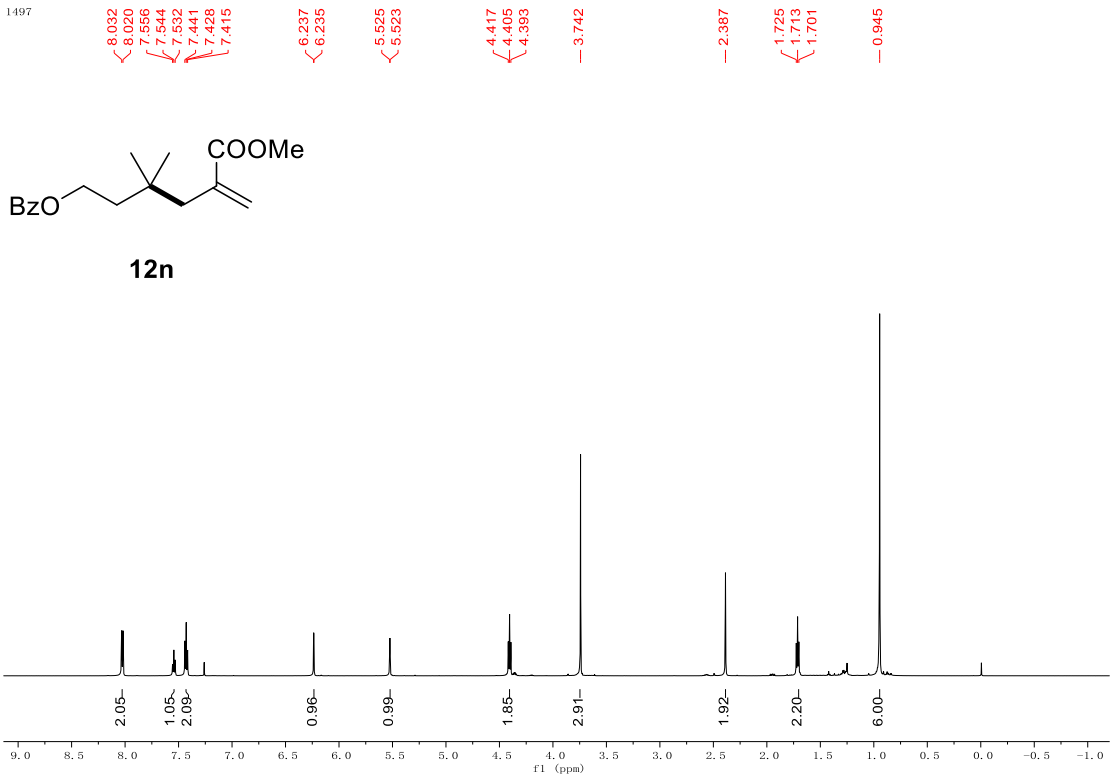

8.045
8.033
7.564
7.551
7.539
7.450
7.437
7.424
6.421
6.403
6.392
6.373
5.277
5.248
5.213
5.061
5.043
4.957
4.427
4.415
4.403
2.238
1.779
1.767
1.755
0.984
BzO
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.26
1.15
2.31
0.91
0.95
0.93
0.96
0.93
1.92
1.87
2.15
6.02

12l

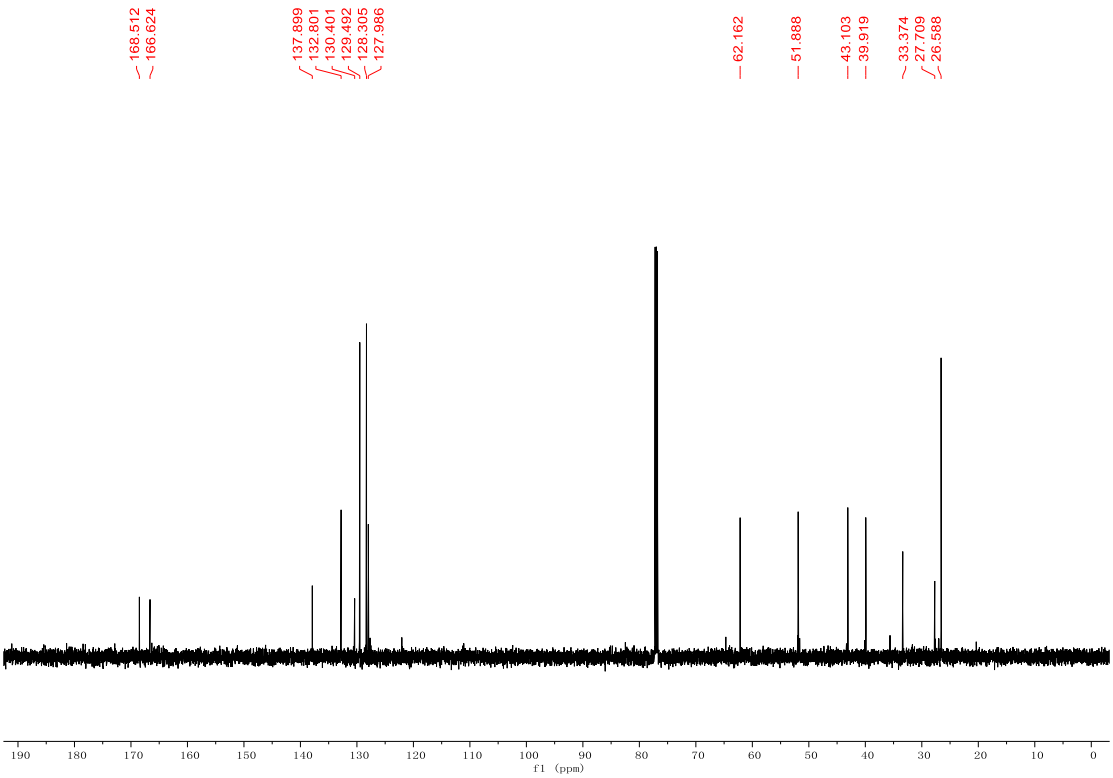

166.68
143.45
140.43
132.79
130.47
129.51
128.31
119.03
113.69
62.40
43.04
40.58
33.32
27.47
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

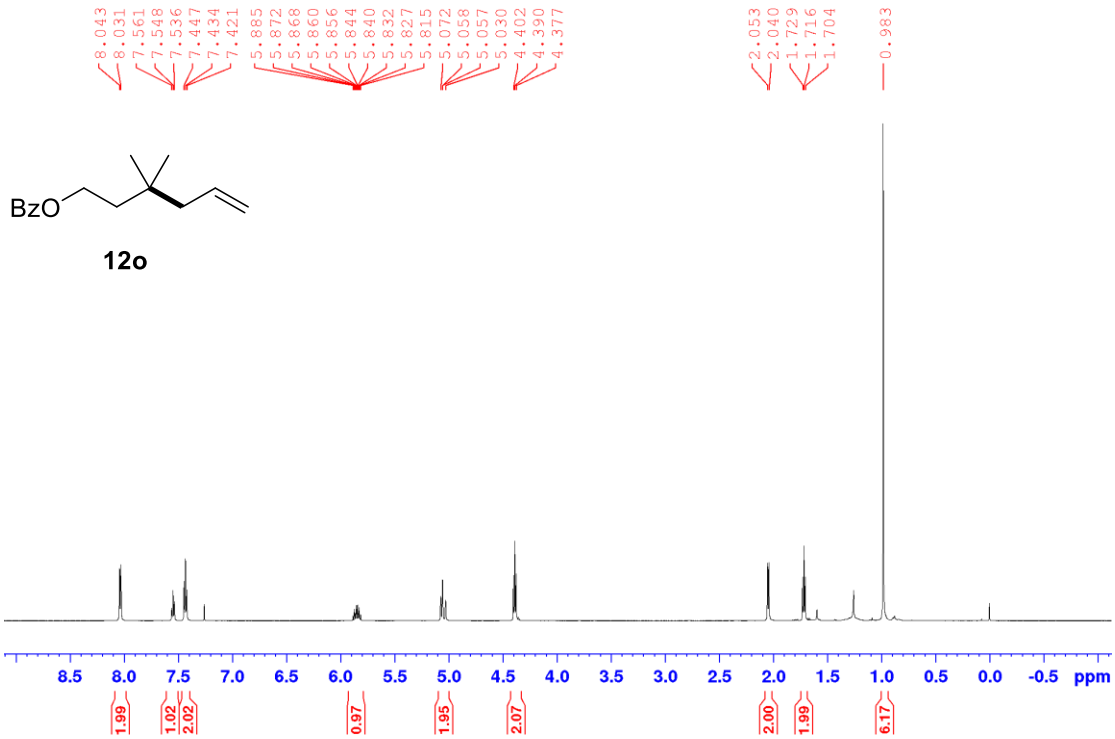

8.051
8.049
8.048
8.031
8.027
7.571
7.552
7.534
7.456
7.437
7.418
4.893
4.891
4.889
4.887
4.884
4.687
4.685
4.683
4.681
4.423
4.405
4.386
2.037
1.804
1.774
1.755
1.737
1.013
BzO
12m
2.31
1.16
2.39
0.98
0.99
2.11
2.00
3.22
2.20
6.00
f1 (ppm)


166.713
143.086
132.803
130.444
129.509
128.314
114.634
62.422
50.132
40.370
33.243
27.663
25.436
f1 (ppm)

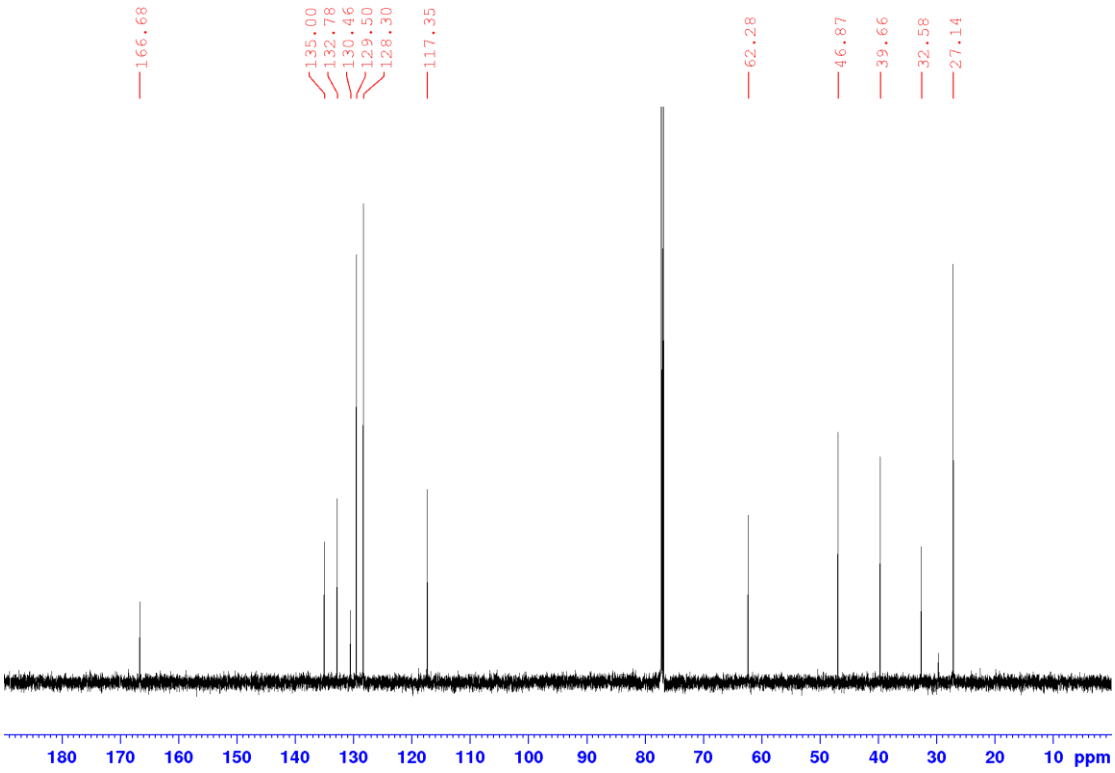

1497
8.032
8.020
7.556
7.544
7.532
7.441
7.428
7.415
6.237
6.235
5.525
5.523
4.417
4.405
4.393
3.742
2.387
1.725
1.713
1.701
0.945
COOMe
BzO
2.05
1.05
2.09
0.96
0.99
1.85
2.91
1.92
2.20
6.00
f1 (ppm)

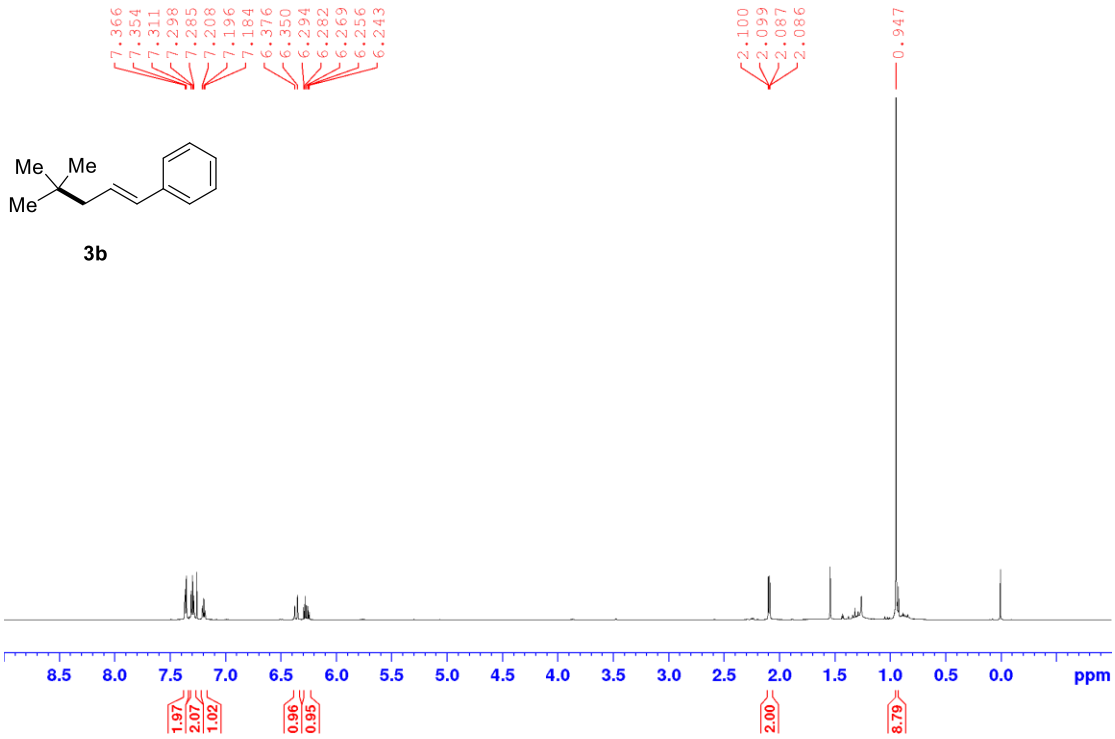
12n

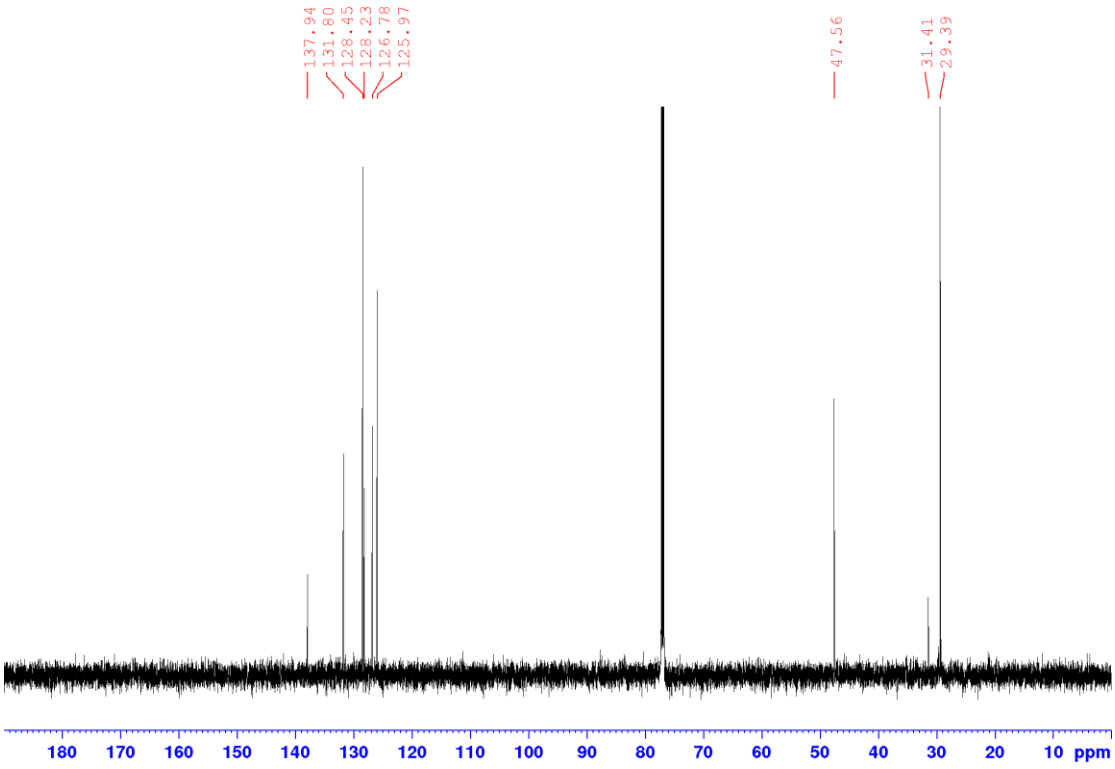

168.512
166.624
137.899
132.801
130.401
129.492
128.305
127.986
62.162
51.888
43.103
39.919
33.374
27.709
26.588
f1 (ppm)

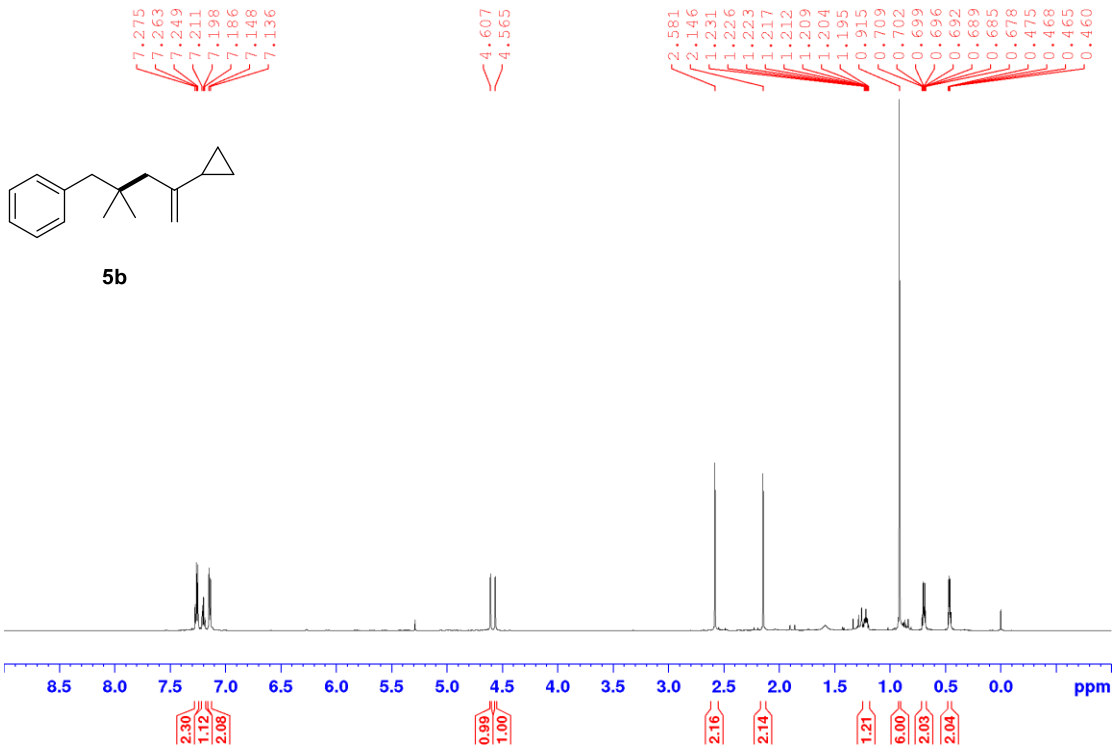

8.043
8.031
7.561
7.548
7.536
7.447
7.434
7.421
5.885
5.872
5.868
5.860
5.856
5.844
5.840
5.832
5.827
5.815
5.072
5.058
5.057
5.030
4.402
4.390
4.377
2.053
2.040
1.729
1.716
1.704
0.983
BzO
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.99
1.02
2.02
0.97
1.95
2.07
2.00
1.99
6.17

12o

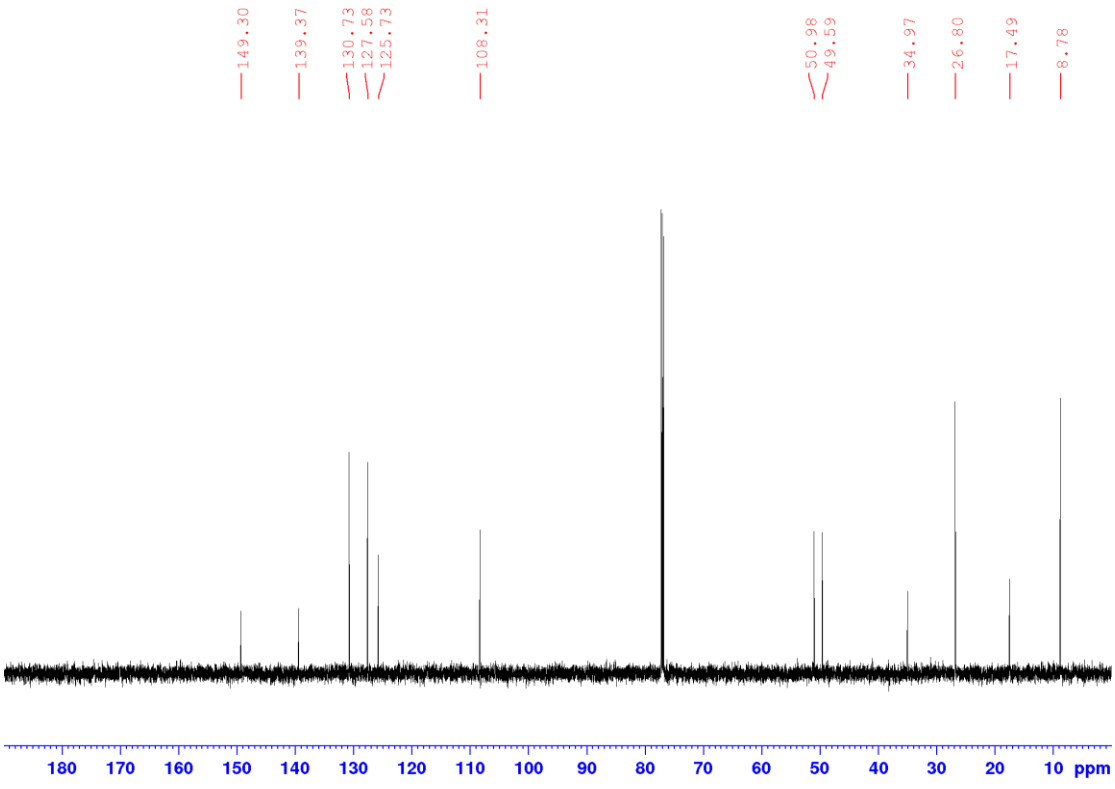

166.68
135.00
132.78
130.46
129.50
128.30
117.35
62.28
46.87
39.66
32.58
27.14
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

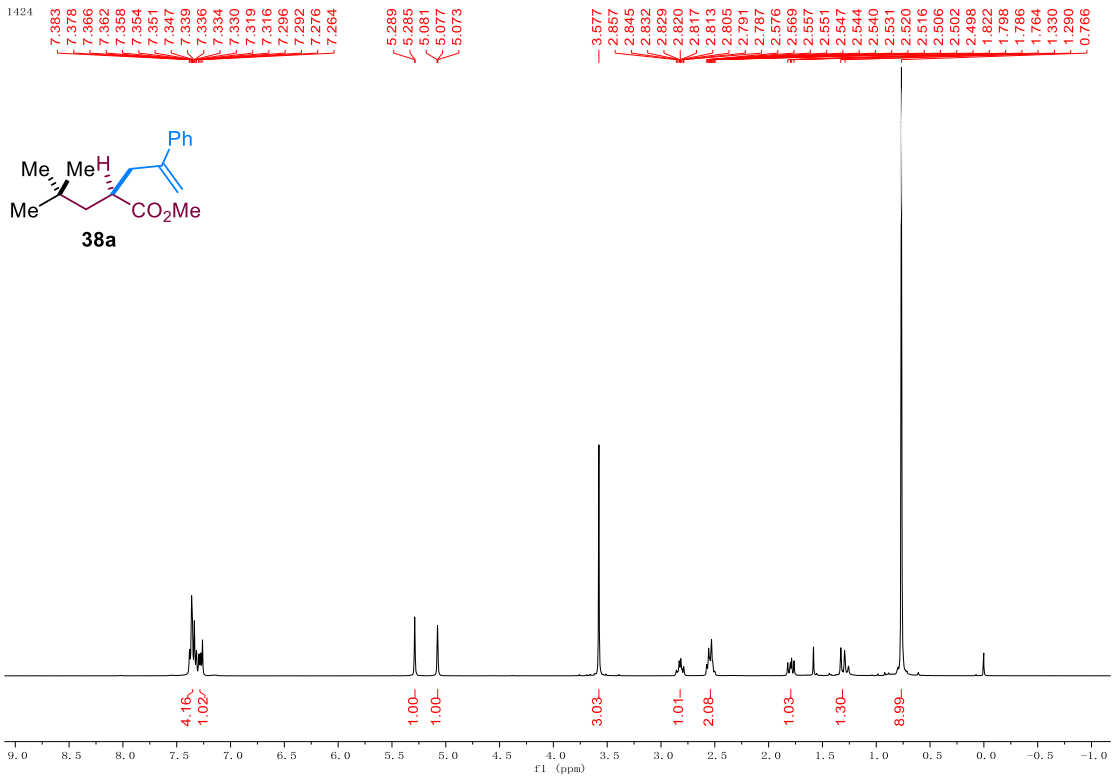

7.366
7.354
7.311
7.298
7.285
7.208
7.196
7.184
6.376
6.350
6.294
6.282
6.269
6.256
6.243
2.100
2.099
2.087
2.086
0.947
Me
Me
Me
3b
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.97
2.07
1.02
0.96
0.95
2.00
8.79

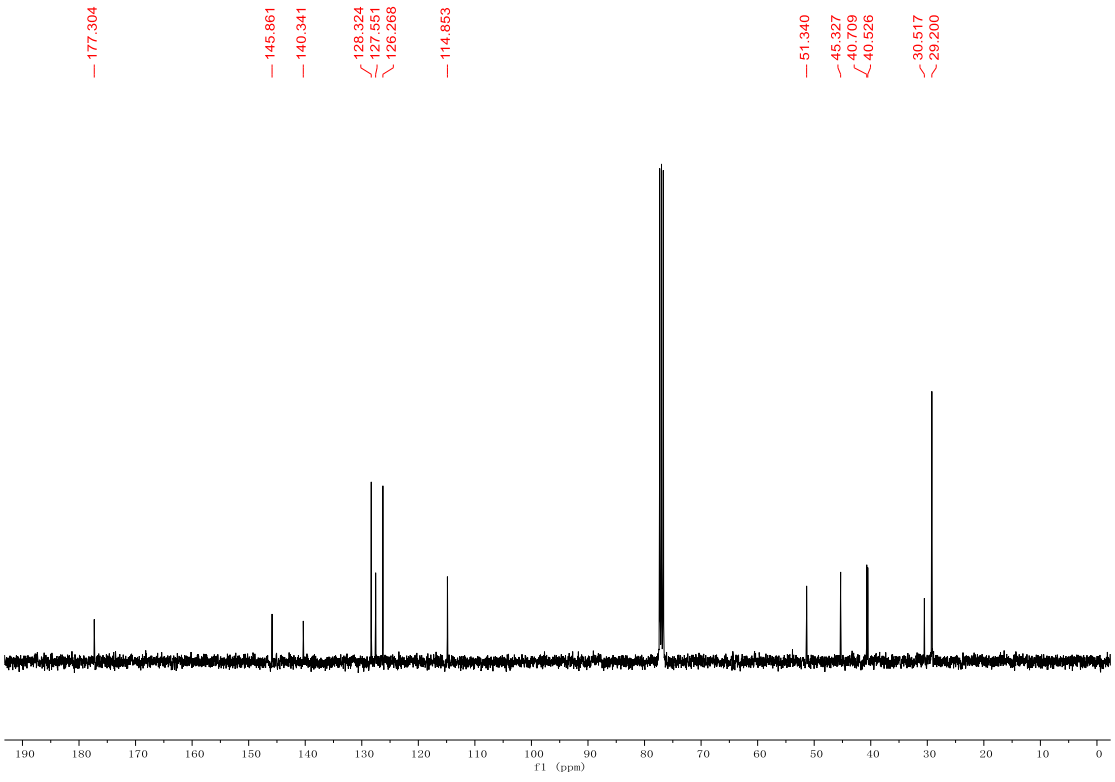

137.94
131.80
128.45
128.23
126.78
125.97
47.56
31.41
29.39
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

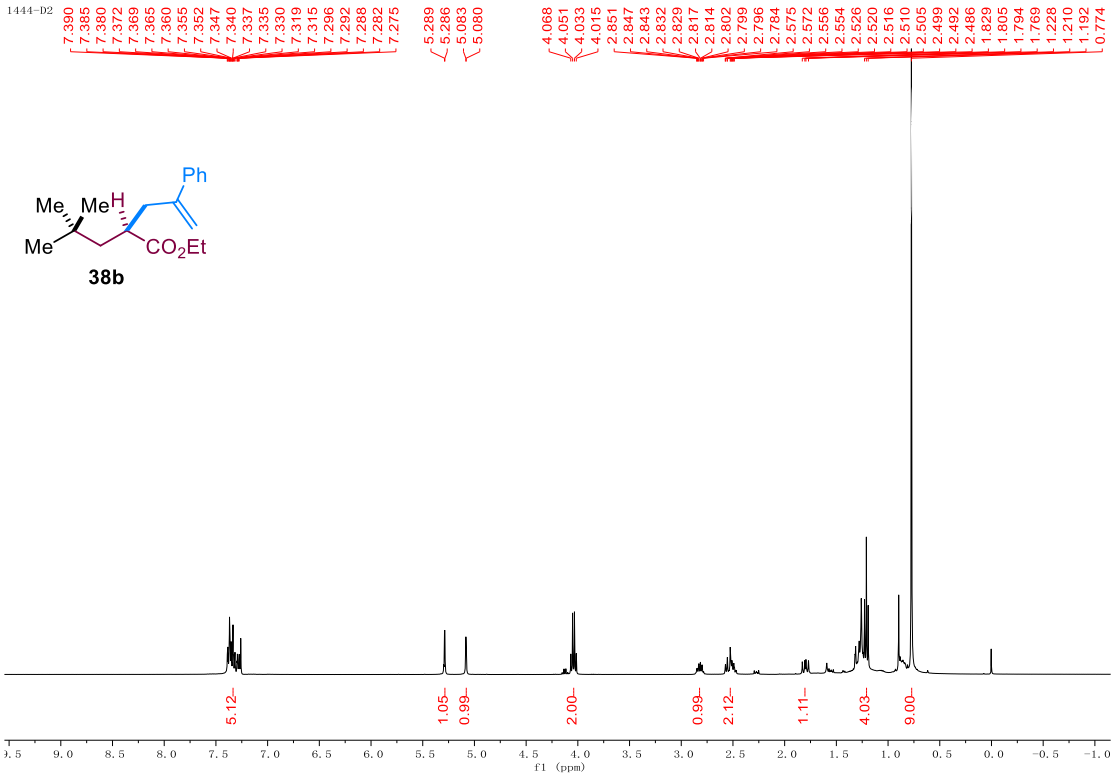

7.275
7.263
7.249
7.211
7.198
7.186
7.148
7.136
4.607
4.565
2.581
2.146
1.231
1.226
1.223
1.217
1.212
1.209
1.204
1.195
0.915
0.709
0.702
0.699
0.696
0.692
0.689
0.685
0.678
0.475
0.468
0.465
0.460
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.30
1.12
2.08
0.99
1.00
2.16
2.14
1.21
6.00
2.03
2.04

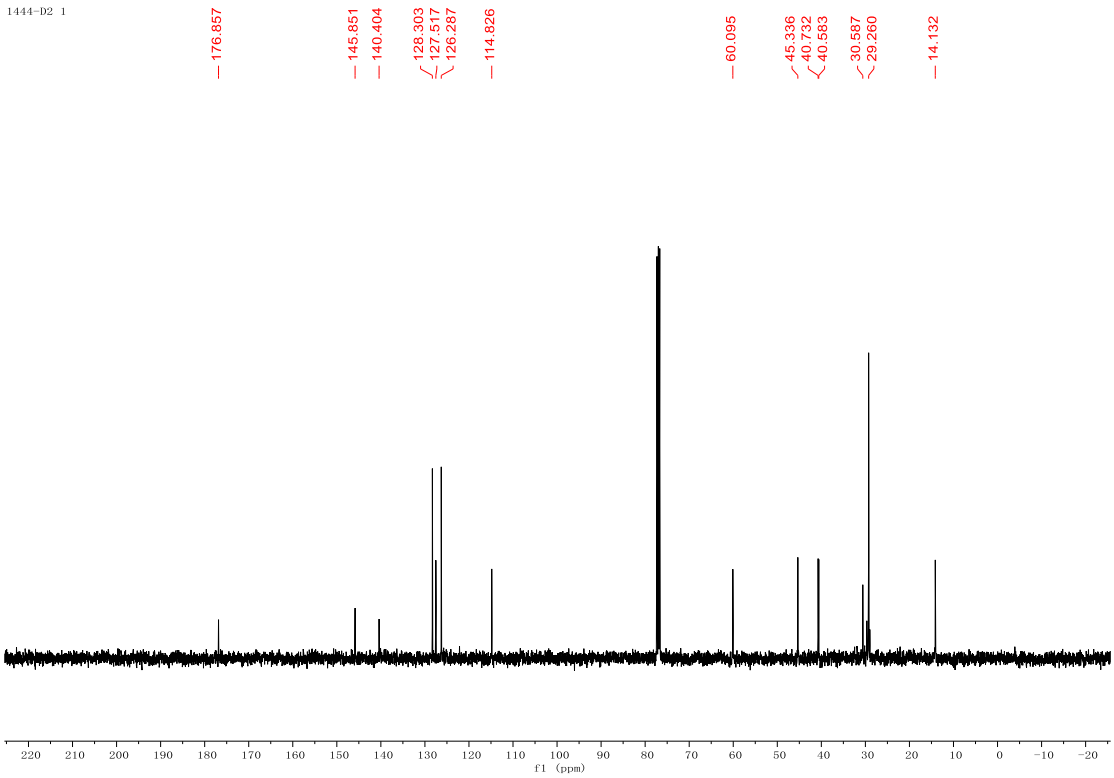
5b

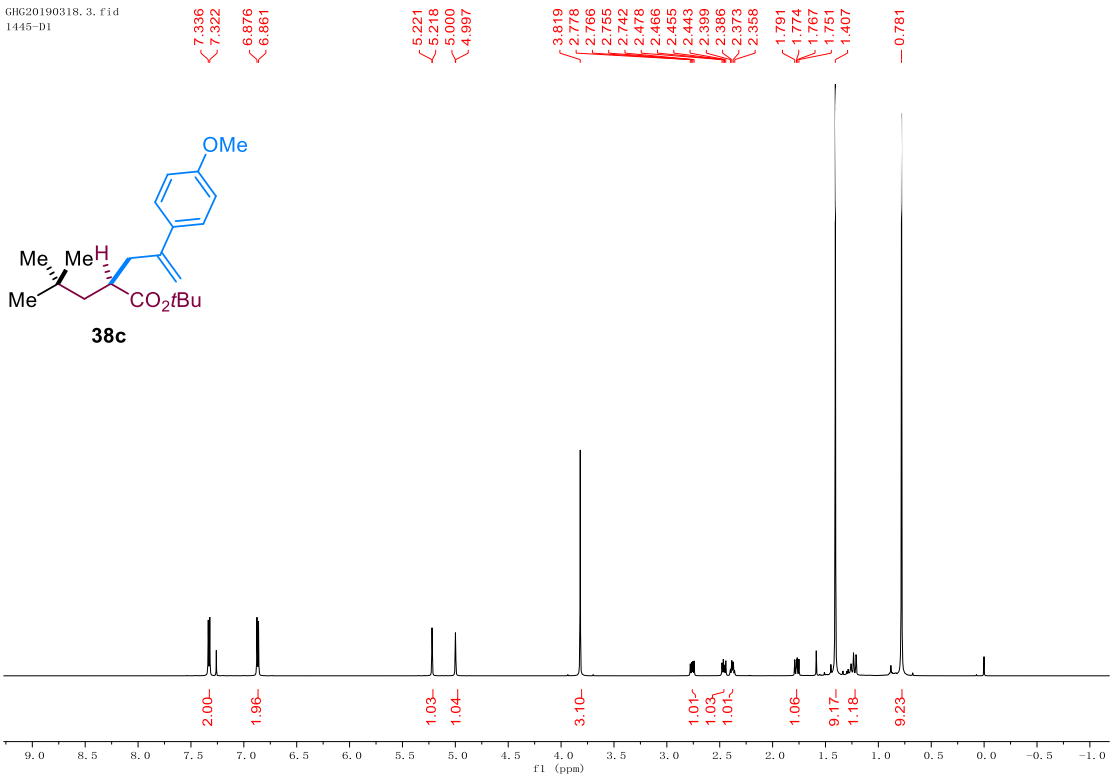

149.30
139.37
130.73
127.58
125.73
108.31
50.98
49.59
34.97
26.80
17.49
8.78
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

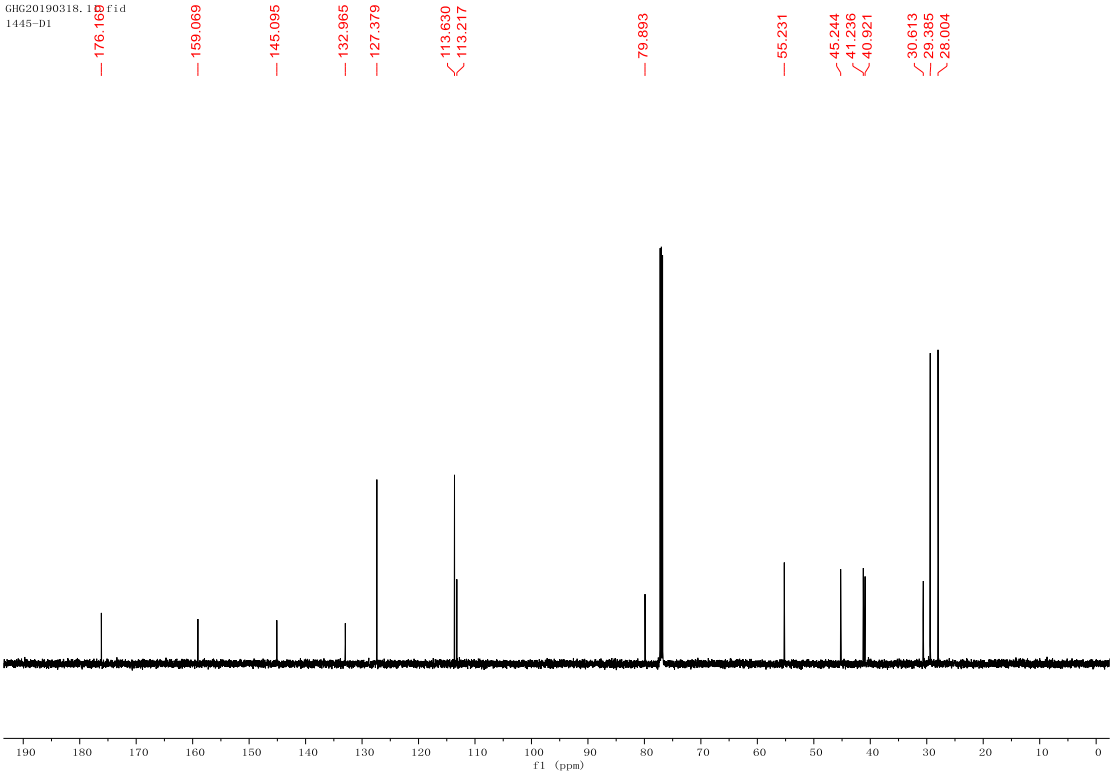

1424
7.383
7.378
7.366
7.362
7.358
7.354
7.351
7.347
7.339
7.336
7.334
7.330
7.319
7.316
7.296
7.292
7.276
7.264
5.289
5.285
5.081
5.077
5.073
3.577
2.857
2.845
2.832
2.829
2.820
2.817
2.813
2.805
2.791
2.787
2.576
2.569
2.557
2.551
2.547
2.544
2.540
2.531
2.520
2.516
2.506
2.502
2.498
1.822
1.798
1.786
1.764
1.330
1.290
0.766
Ph
Me
Me
H
Me
CO2Me
38a
4.16
1.02
1.00
1.00
3.03
1.01
2.08
1.03
1.30
8.99
f1 (ppm)


177.304
145.861
140.341
128.324
127.551
126.268
114.853
51.340
45.327
40.709
40.526
30.517
29.200
f1 (ppm)

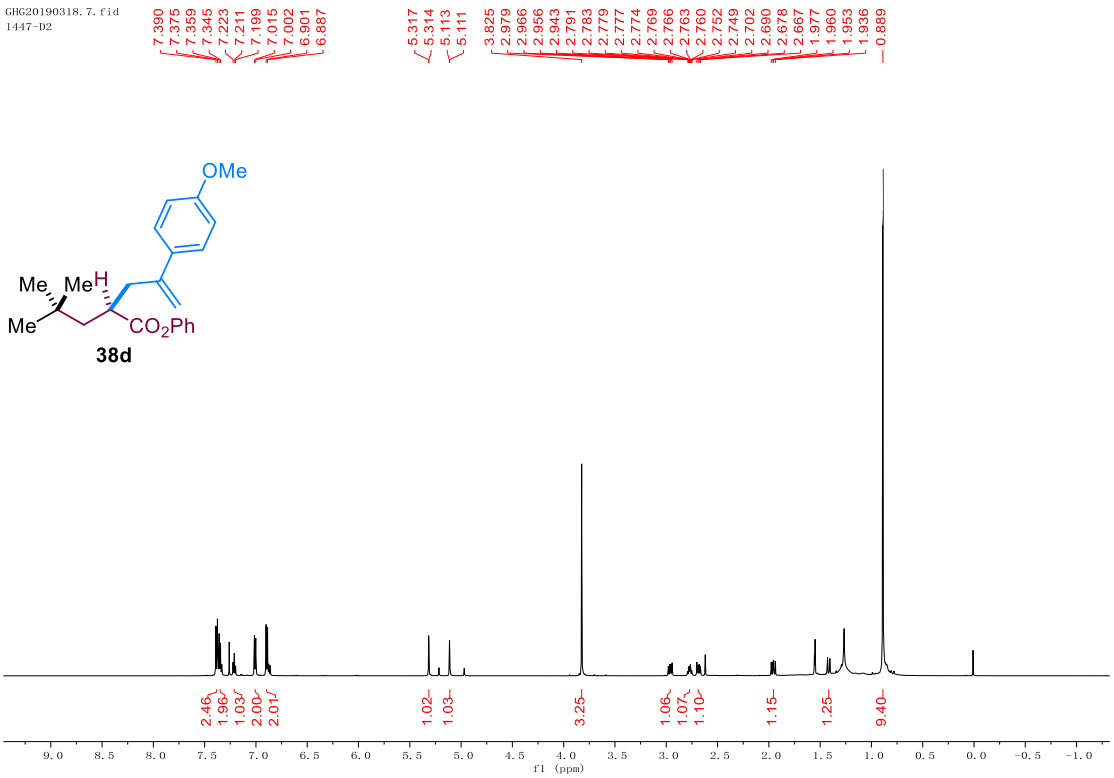

1444-D2
7.390
7.385
7.380
7.372
7.369
7.365
7.360
7.355
7.352
7.347
7.340
7.337
7.335
7.330
7.319
7.315
7.296
7.292
7.288
7.282
7.275
5.289
5.286
5.083
5.080
4.068
4.051
4.033
4.015
2.851
2.847
2.843
2.832
2.829
2.817
2.814
2.802
2.799
2.796
2.784
2.575
2.572
2.556
2.554
2.526
2.520
2.516
2.510
2.505
2.499
2.492
2.486
1.829
1.805
1.794
1.769
1.228
1.210
1.192
0.774
Ph
Me
Me
H
Me
CO2Et
38b
5.12
1.05
0.99
2.00
0.99
2.12
1.11
4.03
9.00
f1 (ppm)


1444-D2 1
176.857
145.851
140.404
128.303
127.517
126.287
114.826
60.095
45.336
40.732
40.583
30.587
29.260
14.132
f1 (ppm)

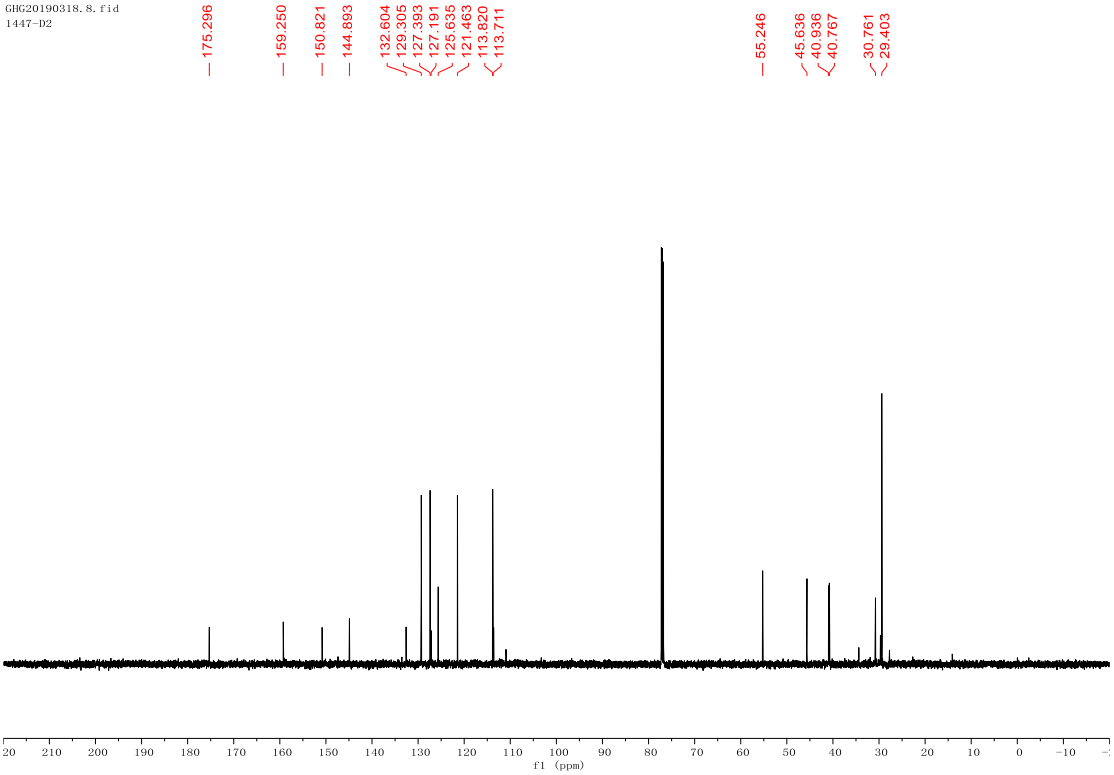

GHG20190318.3.fid
1445-D1
7.336
7.322
6.876
6.861
5.221
5.218
5.000
4.997
3.819
2.778
2.766
2.755
2.742
2.478
2.466
2.455
2.443
2.399
2.386
2.373
2.358
1.791
1.774
1.767
1.751
1.407
0.781
OMe
Me
Me
H
CO2tBu
38c
2.00
1.96
1.03
1.04
3.10
1.01
1.03
1.01
1.06
9.17
1.18
9.23
f1 (ppm)

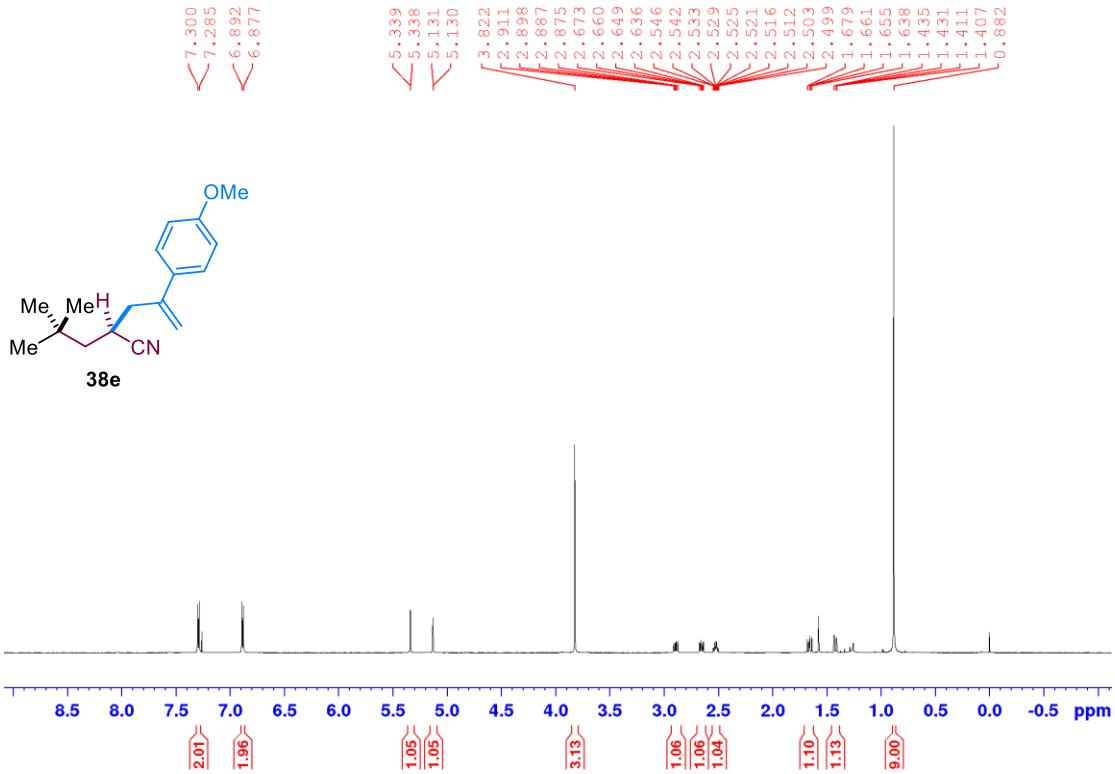

GHG20190318.1?.fid
1445-D1
176.169
159.069
145.095
132.965
127.379
113.630
113.217
79.893
55.231
45.244
41.236
40.921
30.613
29.385
28.004
f1 (ppm)

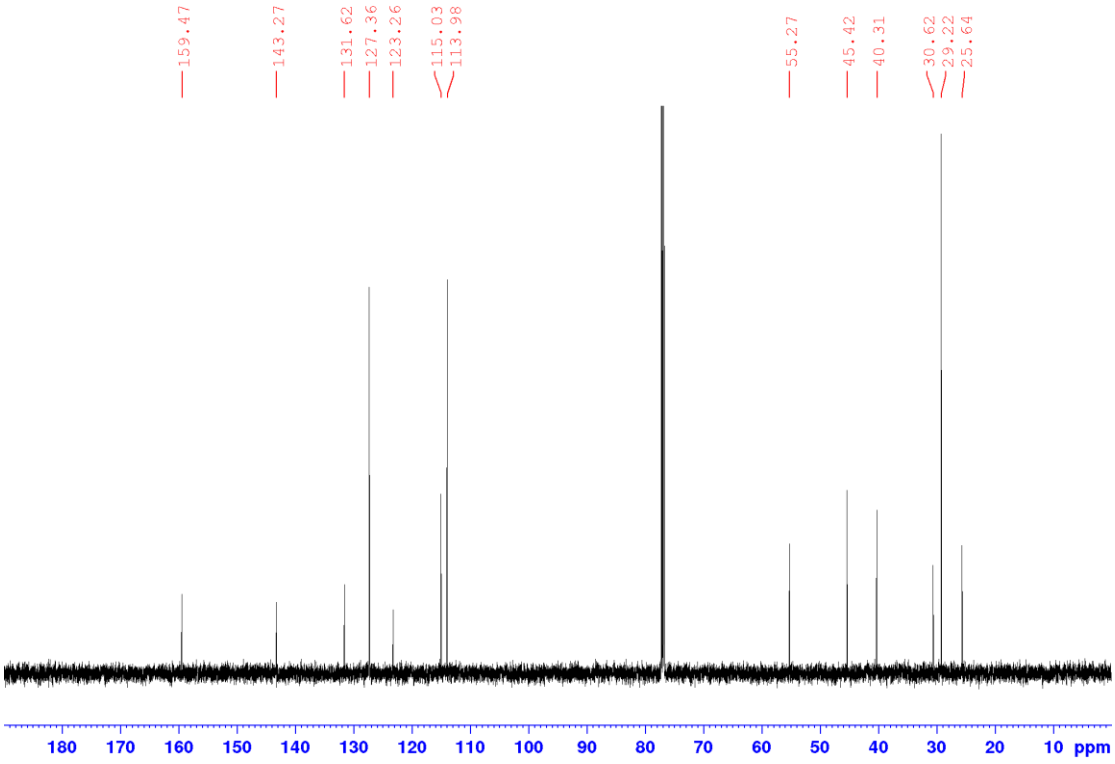
GHG20190318.7.fid
1447-D2

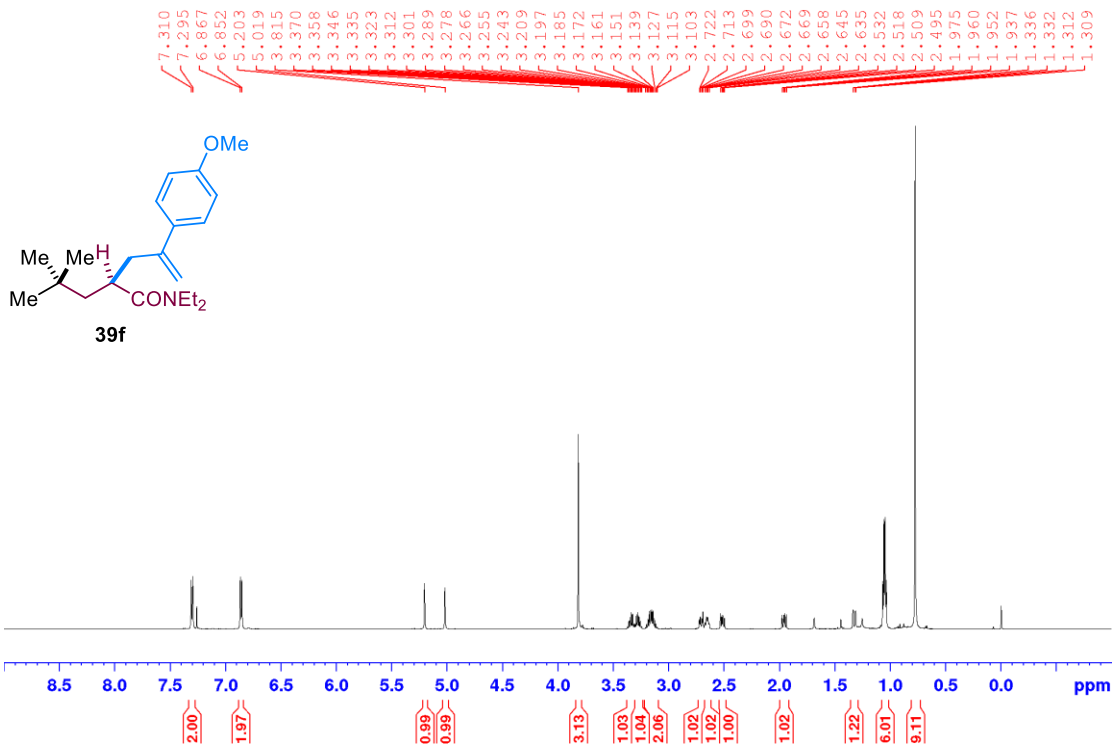


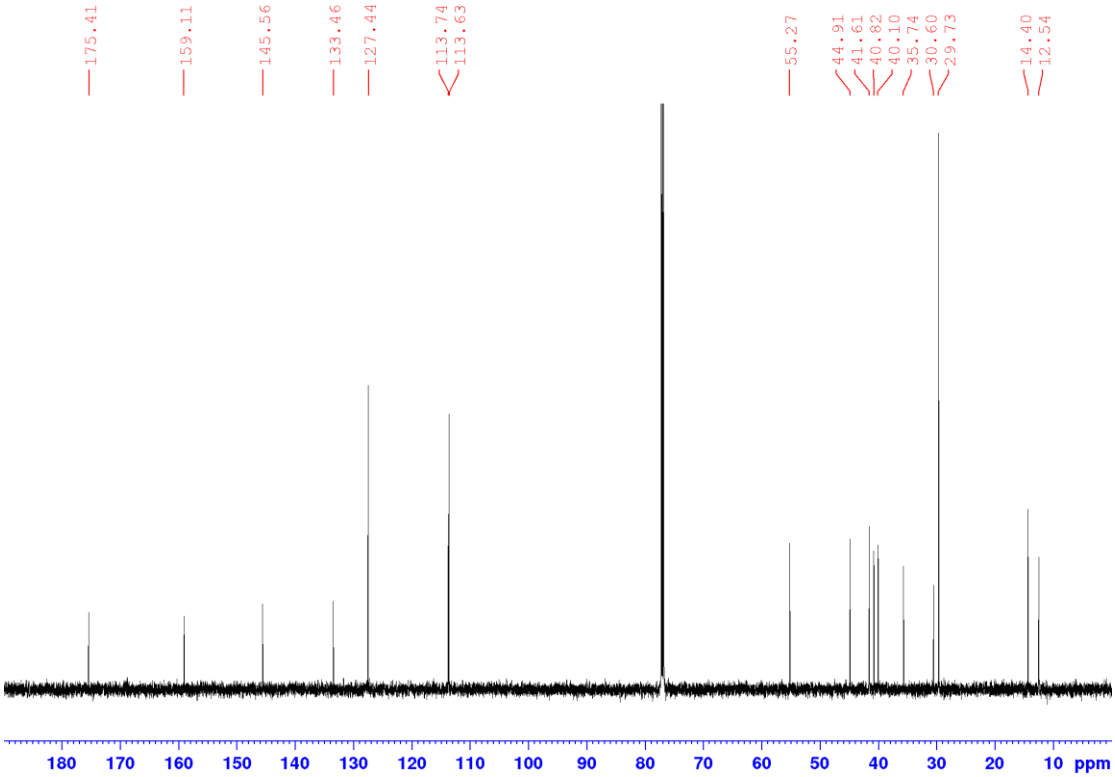
GHG20190318.8.fid
1447-D2

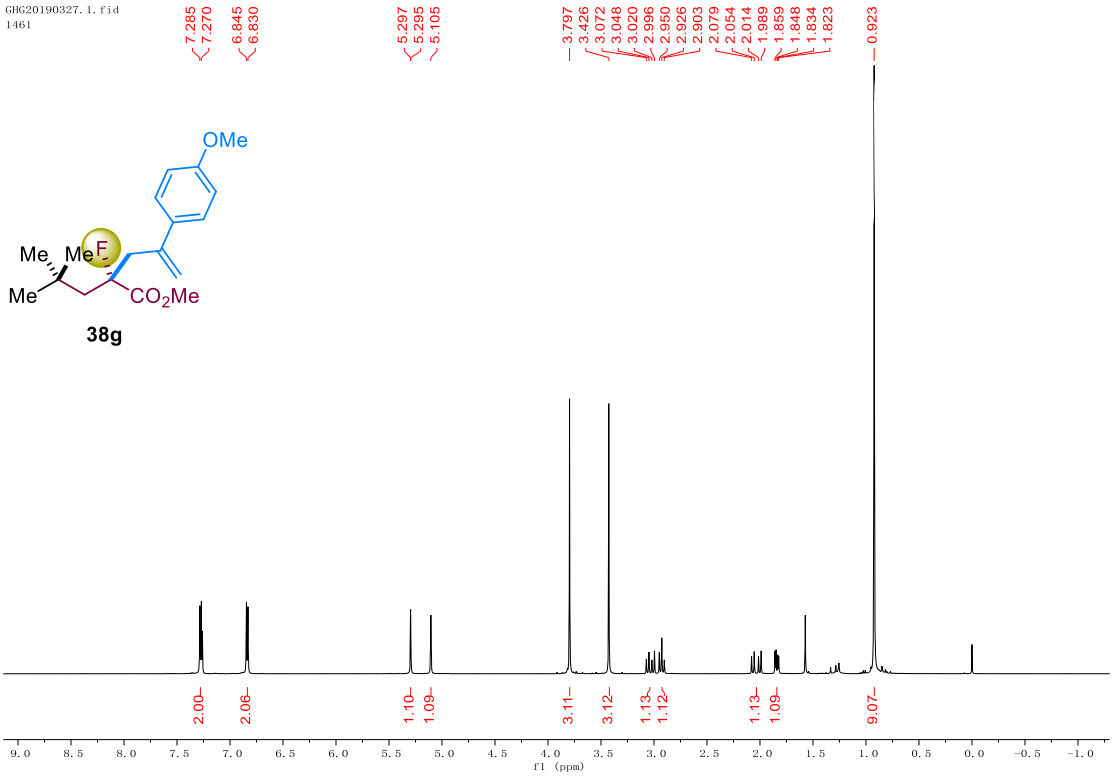


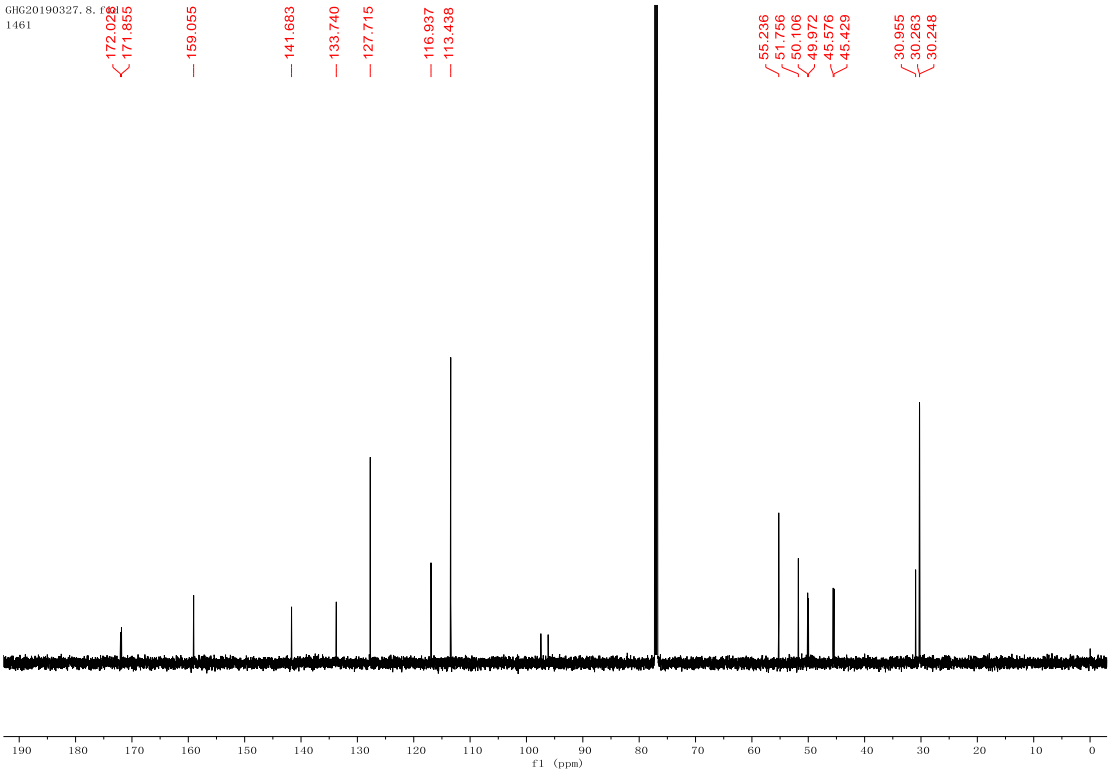

7.300
7.285
6.892
6.877
5.339
5.338
5.131
5.130
3.822
2.911
2.898
2.887
2.875
2.673
2.660
2.649
2.636
2.546
2.542
2.533
2.529
2.525
2.521
2.516
2.512
2.503
2.499
1.679
1.661
1.655
1.638
1.435
1.431
1.411
1.407
0.882
OMe
Me
Me
H
CN
38e
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
2.01
1.96
1.05
1.05
3.13
1.06
1.06
1.04
1.10
1.13
9.00

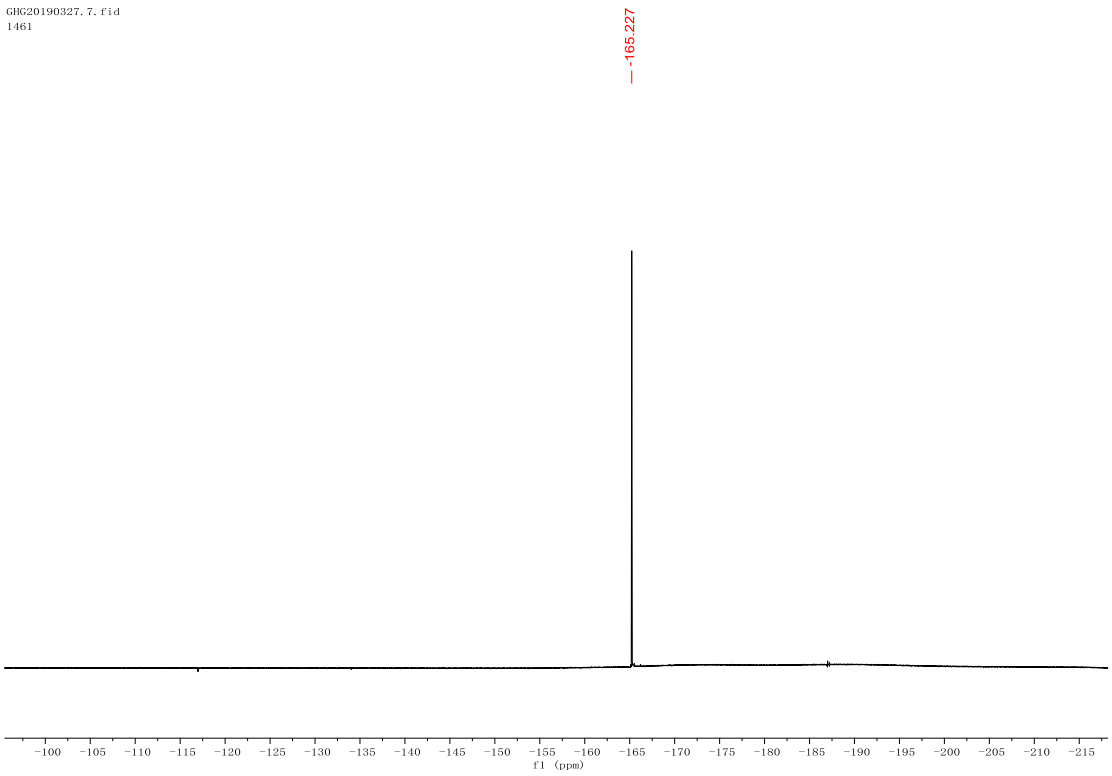

159.47
143.27
131.62
127.36
123.26
115.03
113.98
55.27
45.42
40.31
30.62
29.22
25.64
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

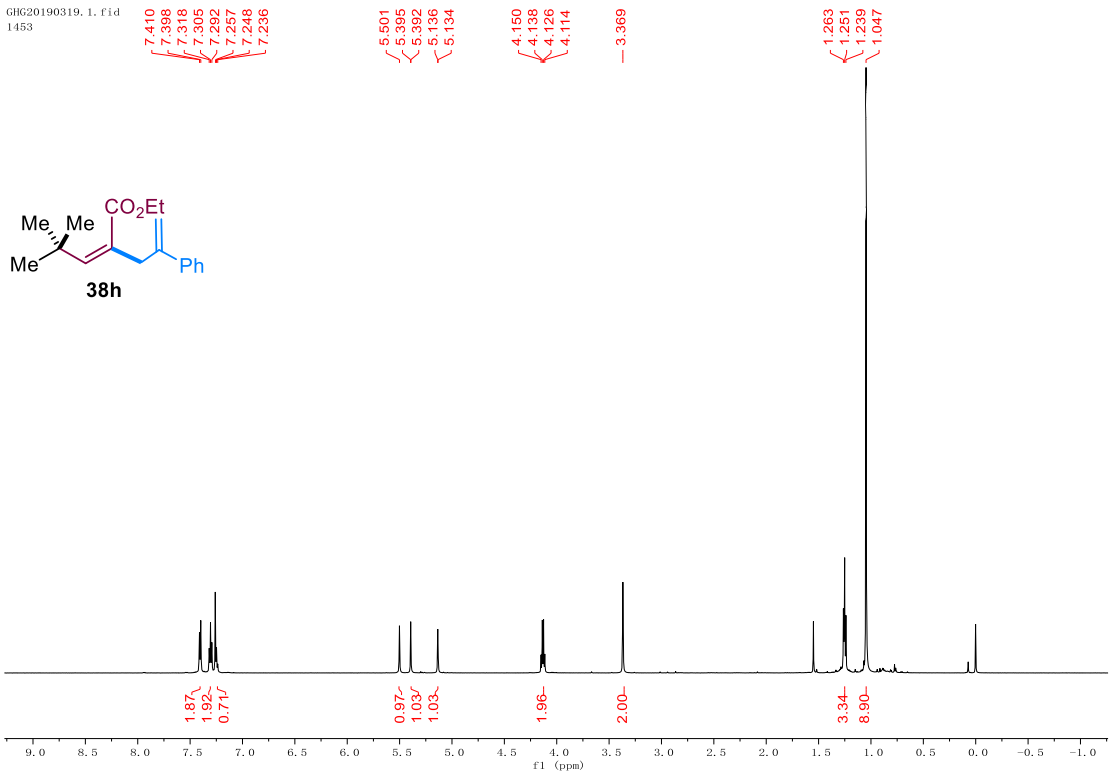

7.310
7.295
6.867
6.852
5.203
5.019
3.815
3.370
3.358
3.346
3.335
3.323
3.312
3.301
3.289
3.278
3.266
3.255
3.243
3.209
3.197
3.185
3.172
3.161
3.151
3.139
3.127
3.115
3.103
2.722
2.713
2.699
2.690
2.672
2.669
2.658
2.645
2.635
2.532
2.518
2.509
2.495
1.975
1.960
1.952
1.937
1.336
1.332
1.312
1.309
OMe
Me
Me
H
CONEt2
39f
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
ppm
2.00
1.97
0.99
0.99
3.13
1.03
1.04
2.06
1.02
1.02
1.00
1.02
1.22
6.01
9.11


175.41
159.11
145.56
133.46
127.44
113.74
113.63
55.27
44.91
41.61
40.82
40.10
35.74
30.60
29.73
14.40
12.54
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


GHG20190327.1.fid
1461
7.285
7.270
6.845
6.830
5.297
5.295
5.105
3.797
3.426
3.072
3.048
3.020
2.996
2.950
2.926
2.903
2.079
2.054
2.014
1.989
1.859
1.848
1.834
1.823
0.923
OMe
Me
Me
F
Me
CO2Me
38g
2.00
2.06
1.10
1.09
3.11
3.12
1.13
1.12
1.13
1.09
9.07
f1 (ppm)

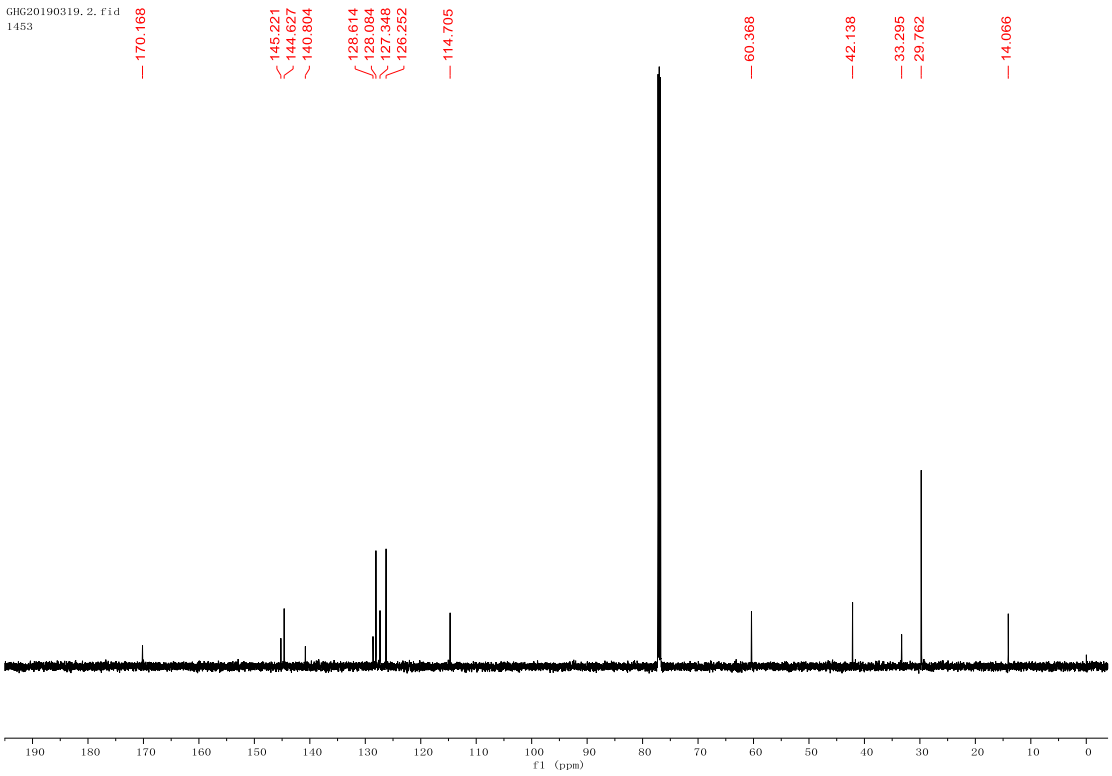

GHG20190327.8.fid
1461
172.028
171.855
159.055
141.683
133.740
127.715
116.937
113.438
55.236
51.756
50.106
49.972
45.576
45.429
30.955
30.263
30.248
f1 (ppm)

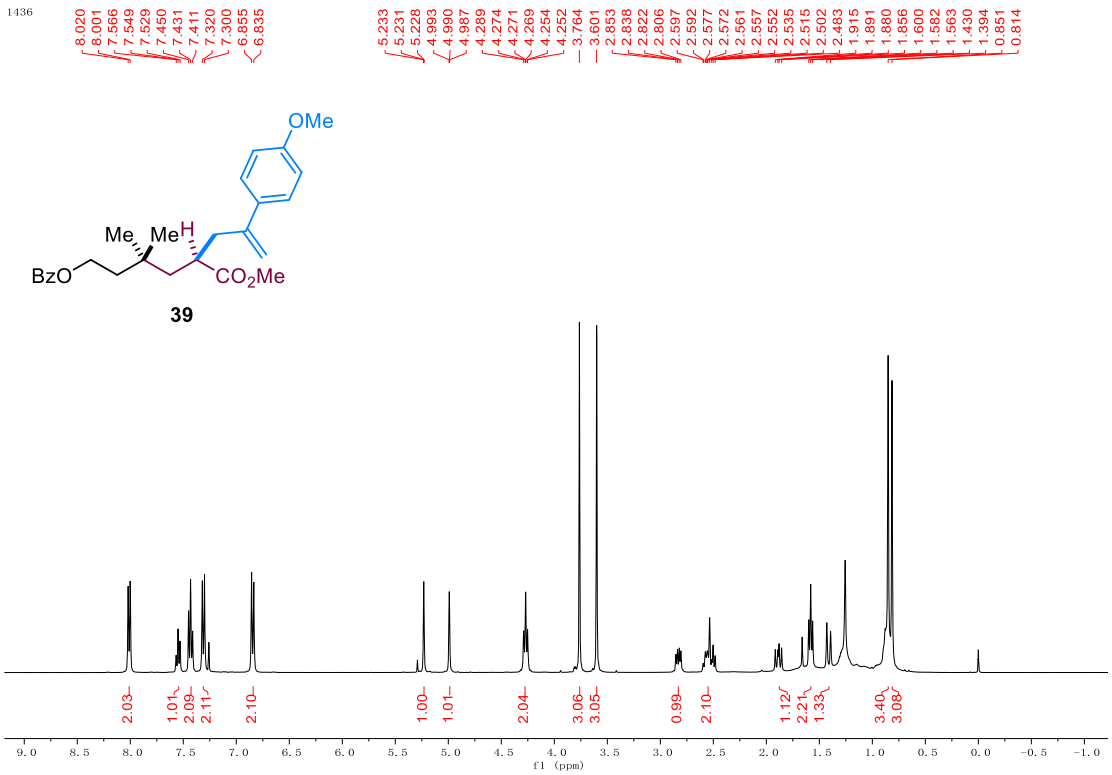

GHG20190327.7.fid
1461
-165.227
f1 (ppm)

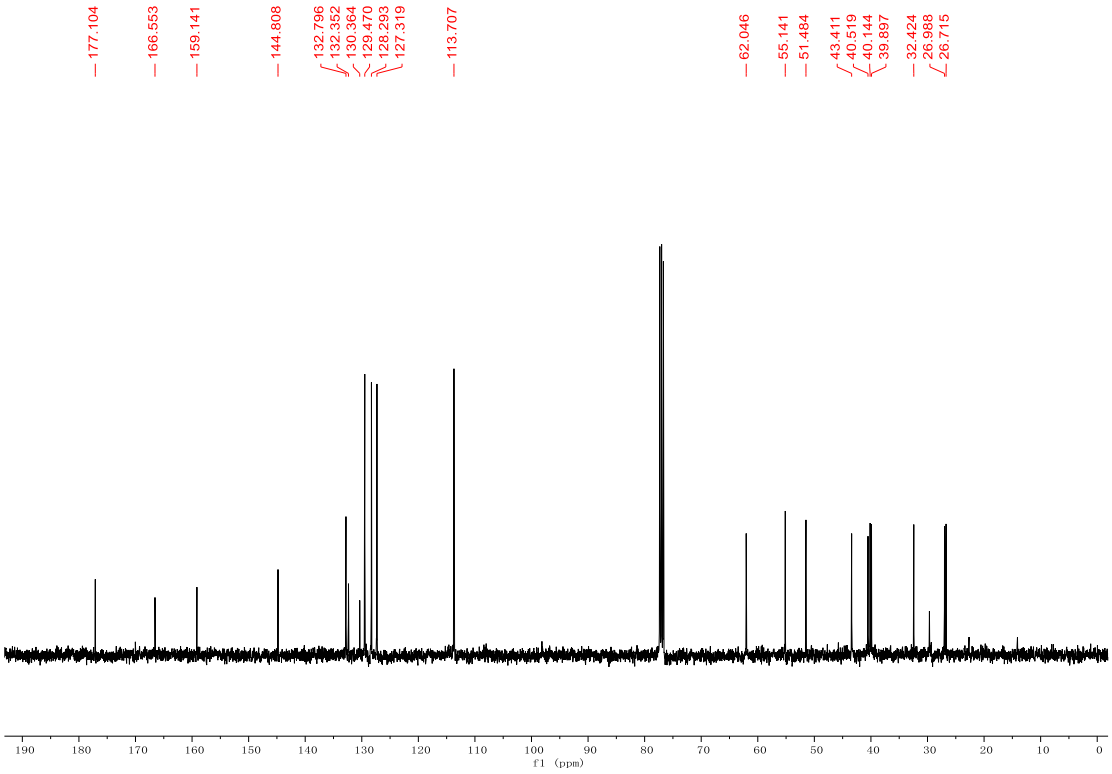

GHG20190319.1.fid
1453
7.410
7.398
7.318
7.305
7.292
7.257
7.248
7.236
5.501
5.395
5.392
5.136
5.134
4.150
4.138
4.126
4.114
3.369
1.263
1.251
1.239
1.047
1.87
1.92
0.71
0.97
1.03
1.03
1.96
2.00
3.34
8.90
f1 (ppm)

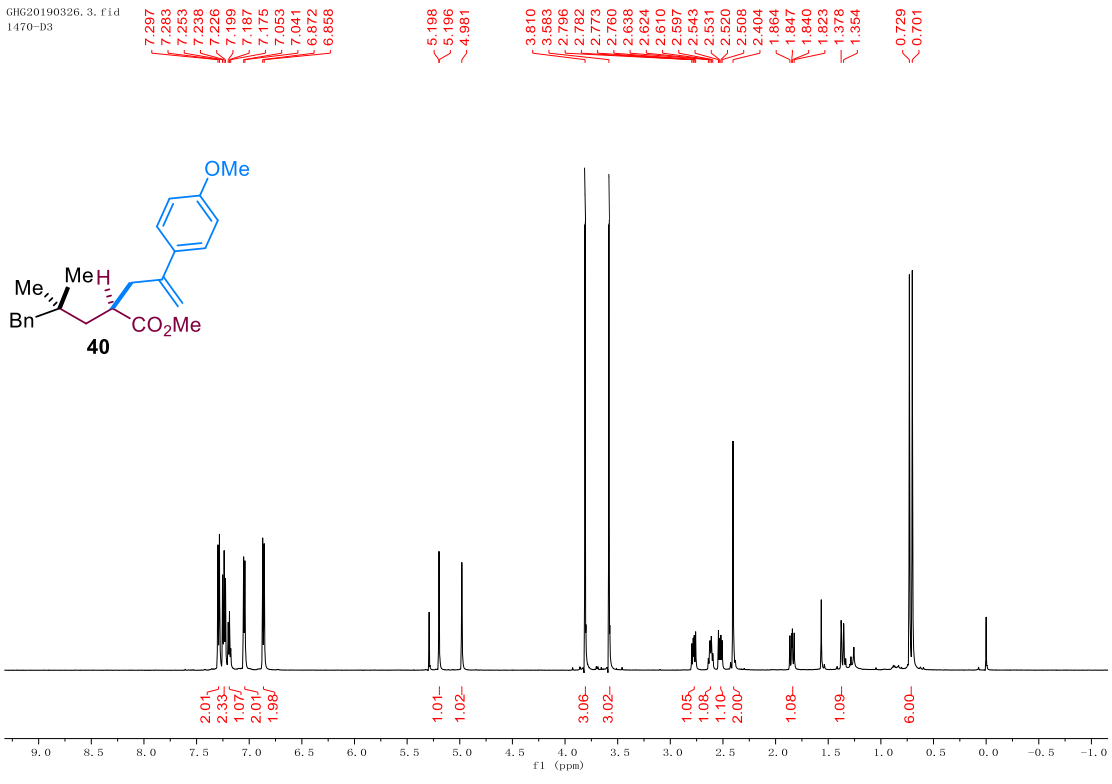
CO2Et
Me
Me
Me
Ph

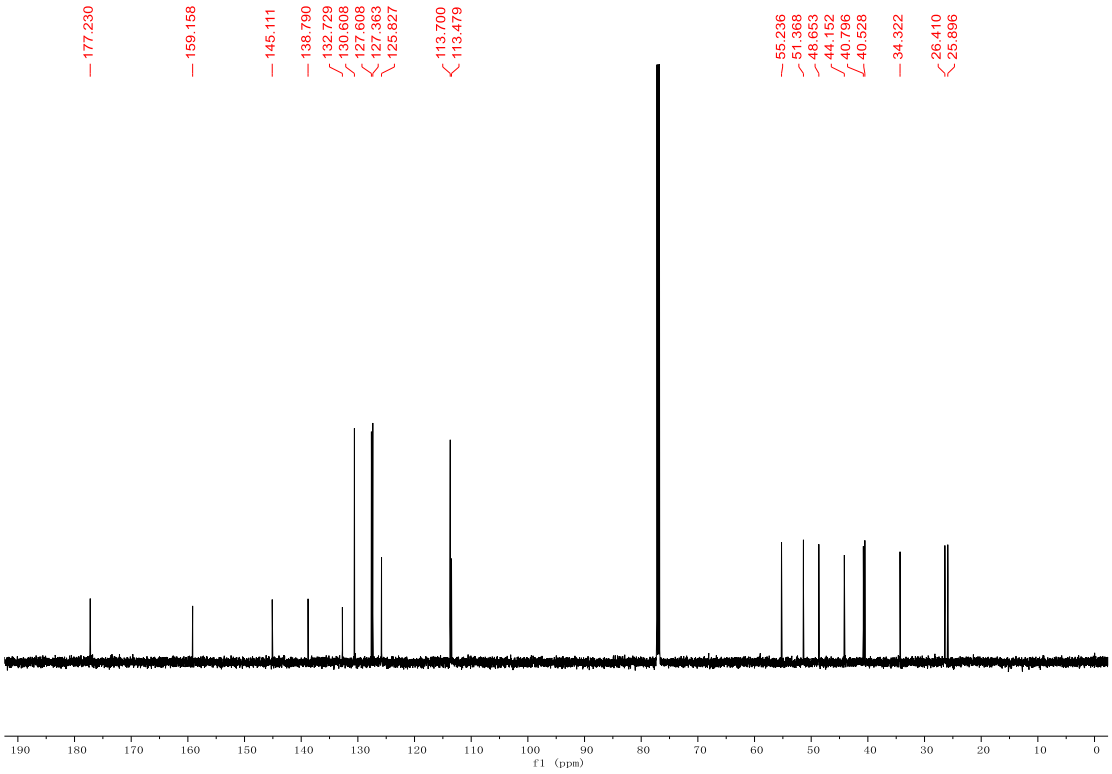
38h

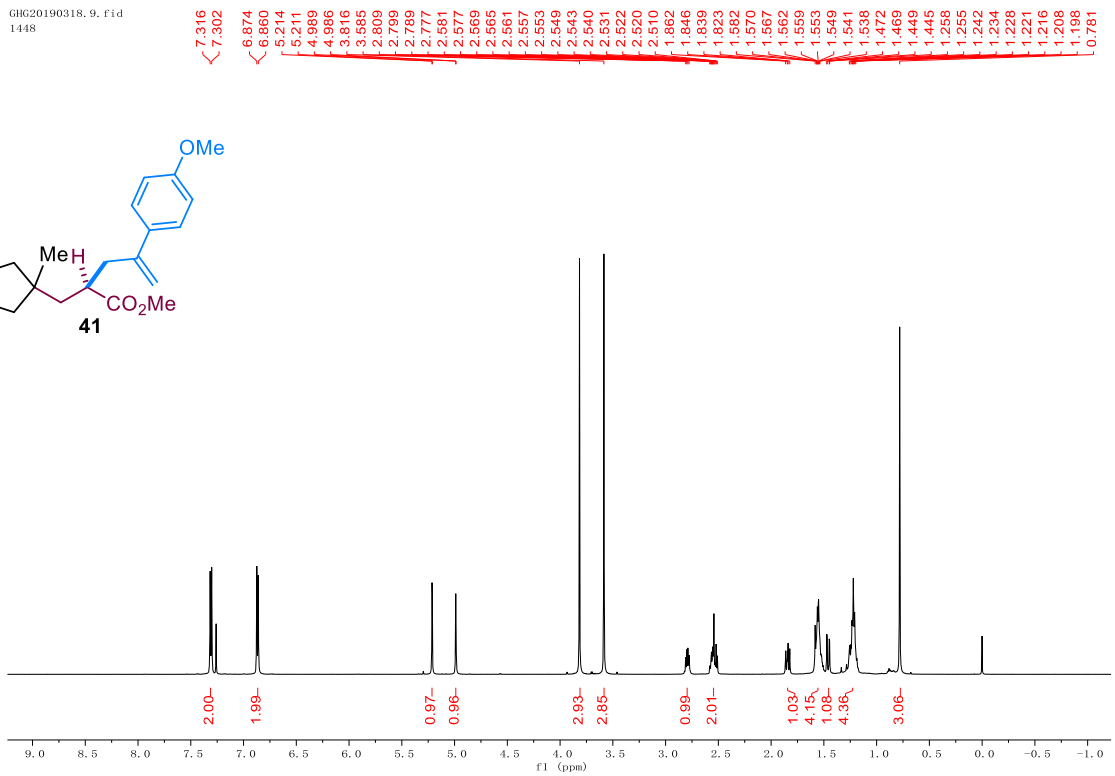

GHG20190319.2.fid
1453
170.168
145.221
144.627
140.804
128.614
128.084
127.348
126.252
114.705
60.368
42.138
33.295
29.762
14.066
f1 (ppm)

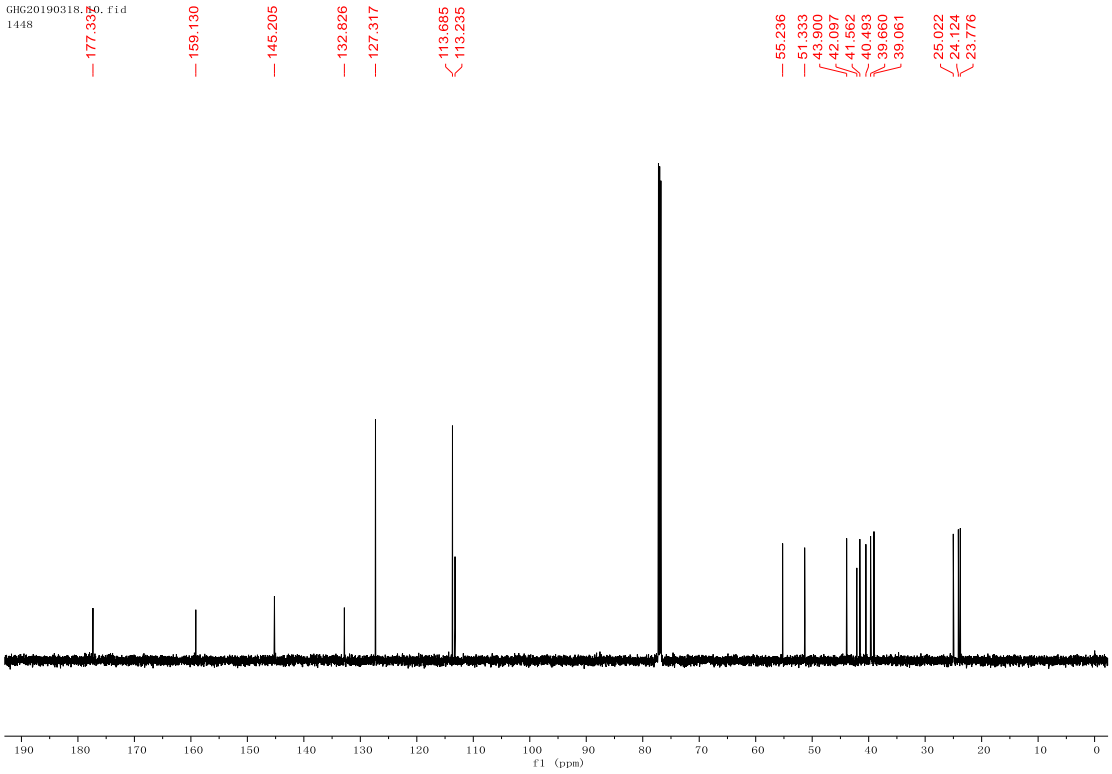

1436
8.020
8.001
7.566
7.549
7.529
7.450
7.431
7.411
7.320
7.300
6.855
6.835
5.233
5.231
5.228
4.993
4.990
4.987
4.289
4.274
4.271
4.269
4.254
4.252
3.764
3.601
2.853
2.838
2.822
2.806
2.597
2.592
2.577
2.572
2.561
2.557
2.552
2.535
2.515
2.502
2.483
1.915
1.891
1.880
1.856
1.600
1.582
1.563
1.430
1.394
0.851
0.814
OMe
Me
Me
H
BzO
CO2Me
39
2.03
1.01
2.09
2.11
2.10
1.00
1.01
2.04
3.06
3.05
0.99
2.10
1.12
2.21
1.33
3.40
3.08
f1 (ppm)

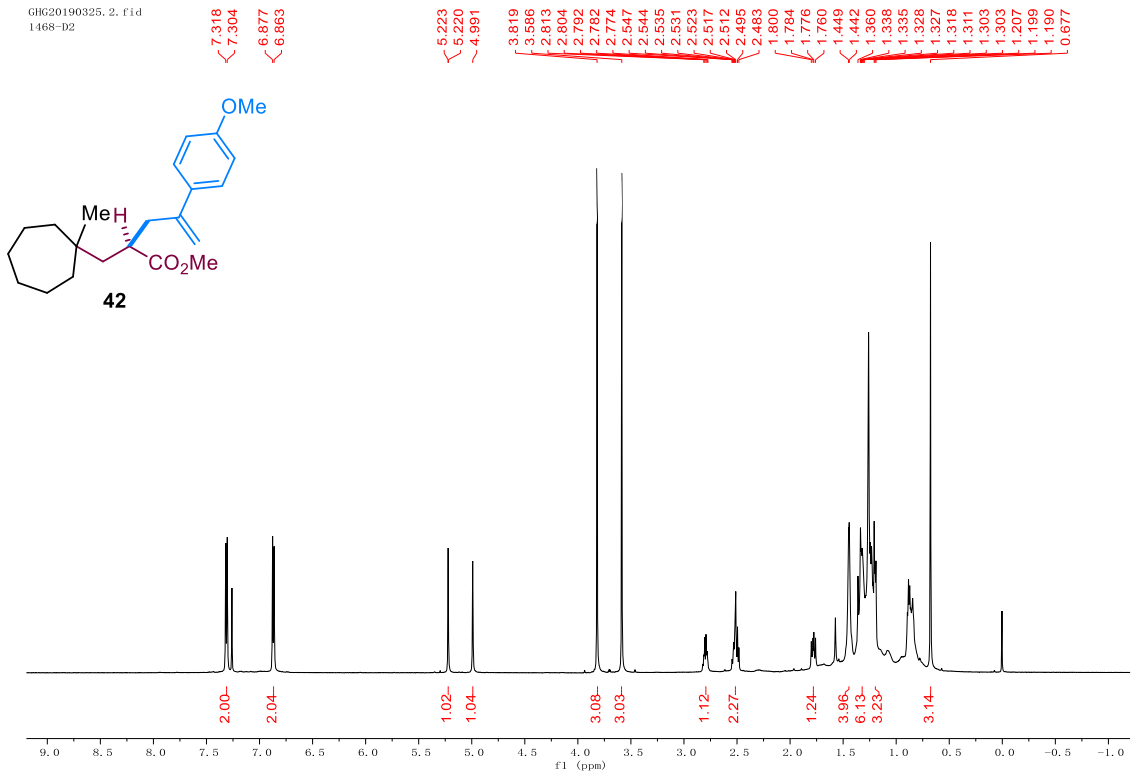

177.104
166.553
159.141
144.808
132.796
132.352
130.364
129.470
128.293
127.319
113.707
62.046
55.141
51.484
43.411
40.519
40.144
39.897
32.424
26.988
26.715
f1 (ppm)

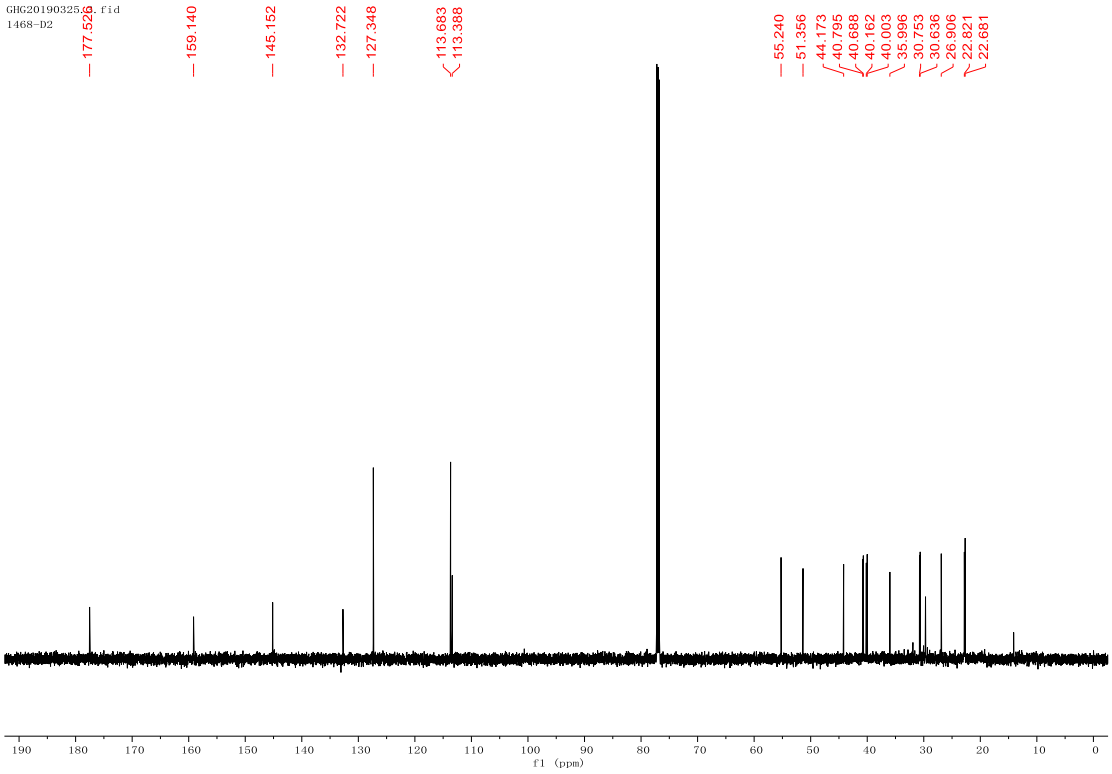

GHG20190326.3.fid
1470-D3
7.297
7.283
7.253
7.238
7.226
7.199
7.187
7.175
7.053
7.041
6.872
6.858
5.198
5.196
4.981
3.810
3.583
2.796
2.782
2.773
2.760
2.638
2.624
2.610
2.597
2.543
2.531
2.520
2.508
2.404
1.864
1.847
1.840
1.823
1.378
1.354
0.729
0.701
OMe
Me
H
Me
Bn
CO2Me
40
2.01
2.33
1.07
2.01
1.98
1.01
1.02
3.06
3.02
1.05
1.08
1.10
2.00
1.08
1.09
6.00
f1 (ppm)

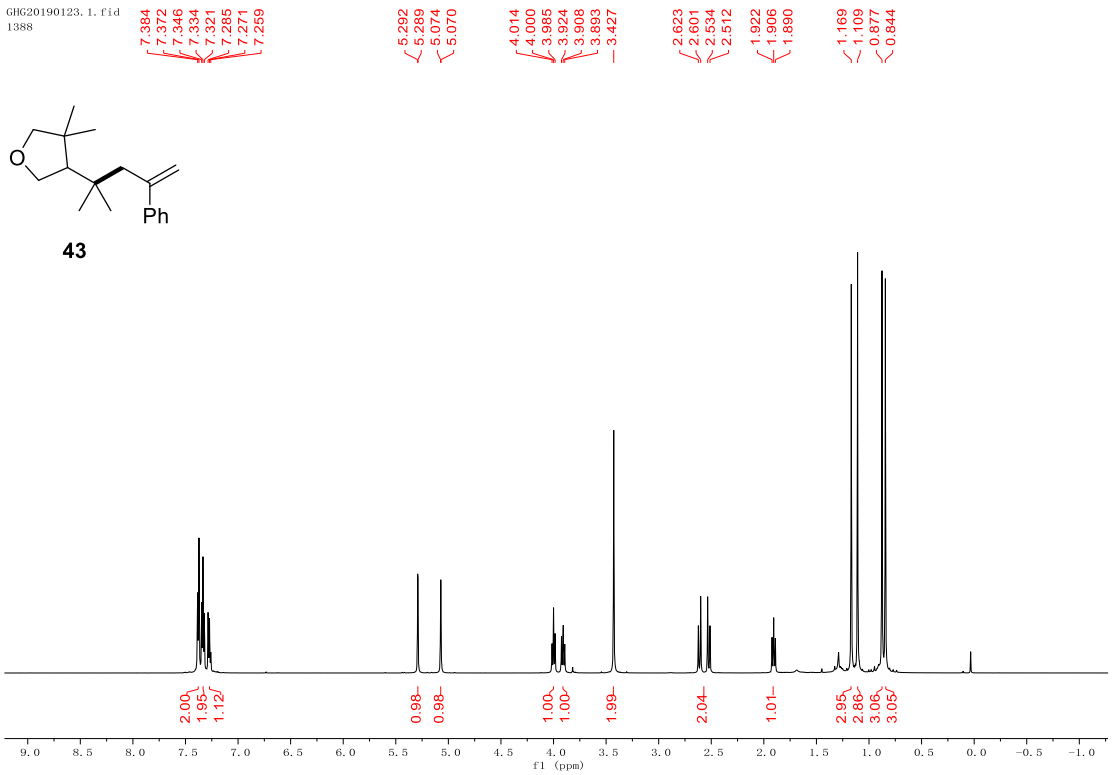

177.230
159.158
145.111
138.790
132.729
130.608
127.608
127.363
125.827
113.700
113.479
55.236
51.368
48.653
44.152
40.796
40.528
34.322
26.410
25.896
f1 (ppm)


GHG20190318.9.fid
1448
7.316
7.302
6.874
6.860
5.214
5.211
4.989
4.986
3.816
3.585
2.809
2.799
2.789
2.777
2.581
2.577
2.569
2.565
2.561
2.557
2.553
2.549
2.543
2.540
2.531
2.522
2.520
2.510
1.862
1.846
1.839
1.823
1.582
1.570
1.567
1.562
1.559
1.553
1.549
1.541
1.538
1.472
1.469
1.449
1.445
1.258
1.255
1.242
1.234
1.228
1.221
1.216
1.208
1.198
0.781
OMe
MeH
CO2Me
41
2.00
1.99
0.97
0.96
2.93
2.85
0.99
2.01
1.03
4.15
1.08
4.36
3.06
f1 (ppm)


GHG20190318.10.fid
1448
177.335
159.130
145.205
132.826
127.317
113.685
113.235
55.236
51.333
43.900
42.097
41.562
40.493
39.660
39.061
25.022
24.124
23.776
f1 (ppm)

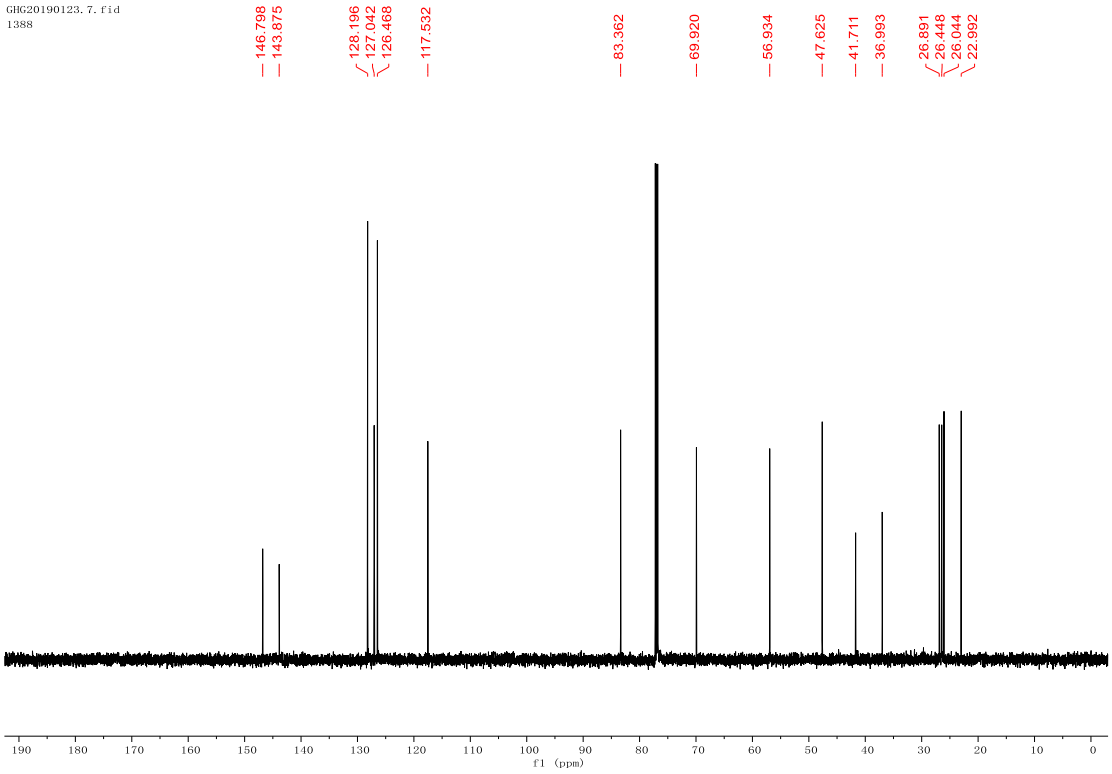

GHG20190325.2.fid
1468-D2
7.318
7.304
6.877
6.863
5.223
5.220
4.991
3.819
3.586
2.813
2.804
2.792
2.782
2.774
2.547
2.544
2.535
2.531
2.523
2.517
2.512
2.495
2.483
1.800
1.784
1.776
1.760
1.449
1.442
1.360
1.338
1.335
1.328
1.327
1.318
1.311
1.303
1.303
1.207
1.199
1.190
0.677
OMe
Me
H
CO2Me
42
2.00
2.04
1.02
1.04
3.08
3.03
1.12
2.27
1.24
3.96
6.13
3.23
3.14
f1 (ppm)


GHG20190325.5.fid
1468-D2
177.526
159.140
145.152
132.722
127.348
113.683
113.388
55.240
51.356
44.173
40.795
40.688
40.162
40.003
35.996
30.753
30.636
26.906
22.821
22.681
f1 (ppm)

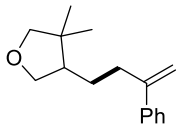

GHG20190123.1.fid
1388
7.384
7.372
7.346
7.334
7.321
7.285
7.271
7.259
5.292
5.289
5.074
5.070
4.014
4.000
3.985
3.924
3.908
3.893
3.427
2.623
2.601
2.534
2.512
1.922
1.906
1.890
1.169
1.109
0.877
0.844
2.00
1.95
1.12
0.98
0.98
1.00
1.00
1.99
2.04
1.01
2.95
2.86
3.06
3.05
f1 (ppm)

O
Ph

43

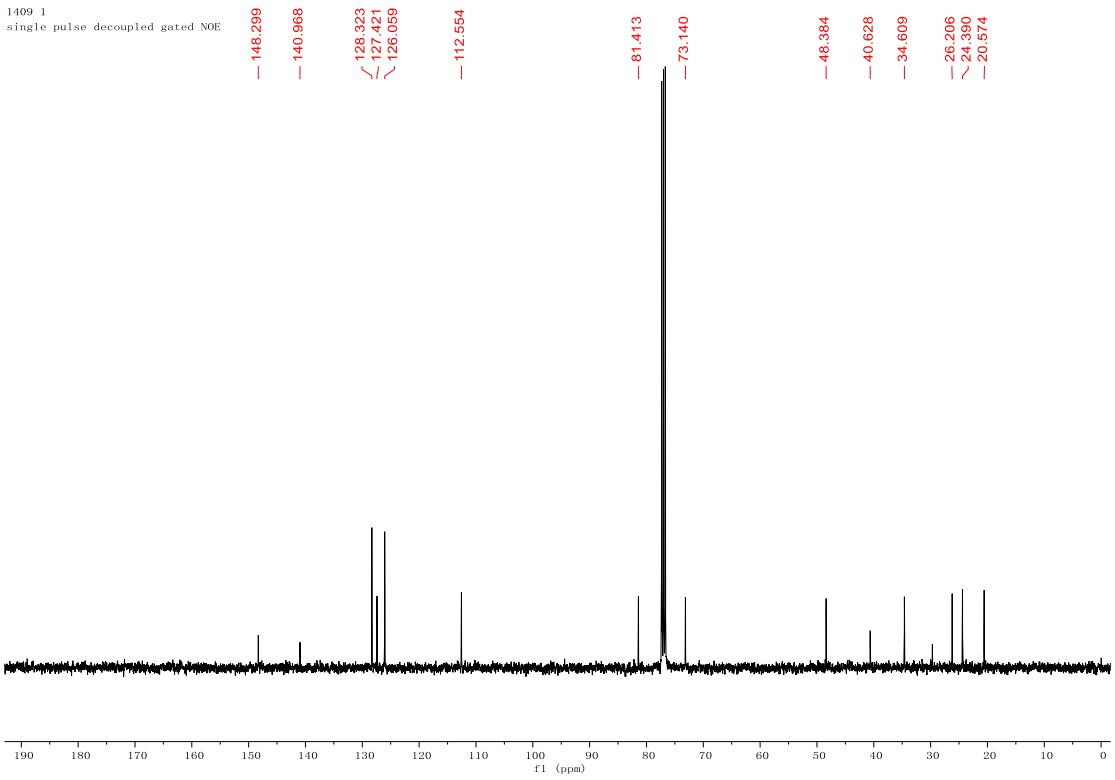

GHG20190123.7.fid
1388
146.798
143.875
128.196
127.042
126.468
117.532
83.362
69.920
56.934
47.625
41.711
36.993
26.891
26.448
26.044
22.992
f1 (ppm)


7.396
7.392
7.387
7.379
7.375
7.371
7.366
7.355
7.352
7.347
7.340
7.337
7.335
7.330
7.320
7.316
7.295
7.291
7.287
7.280
7.274
5.280
5.277
5.071
5.067
4.132
4.112
4.091
3.543
3.523
3.513
3.493
3.489
3.468
3.448
2.501
2.499
2.497
2.487
2.484
2.477
2.473
2.464
2.461
2.447
2.444
2.441
2.438
2.424
2.421
1.867
1.863
1.859
1.857
1.846
1.842
1.837
1.833
1.622
1.613
1.605
1.603
1.597
1.588
1.580
1.572
1.564
1.555

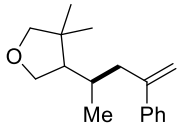

O
Ph

44

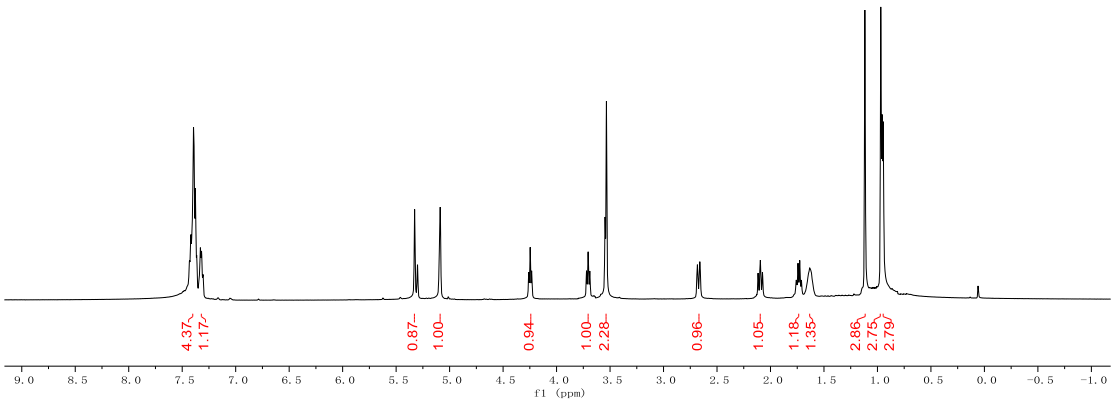
5.19
0.98
0.99
1.00
3.13
2.04
1.05
2.25
3.00
3.35
f1 (ppm)

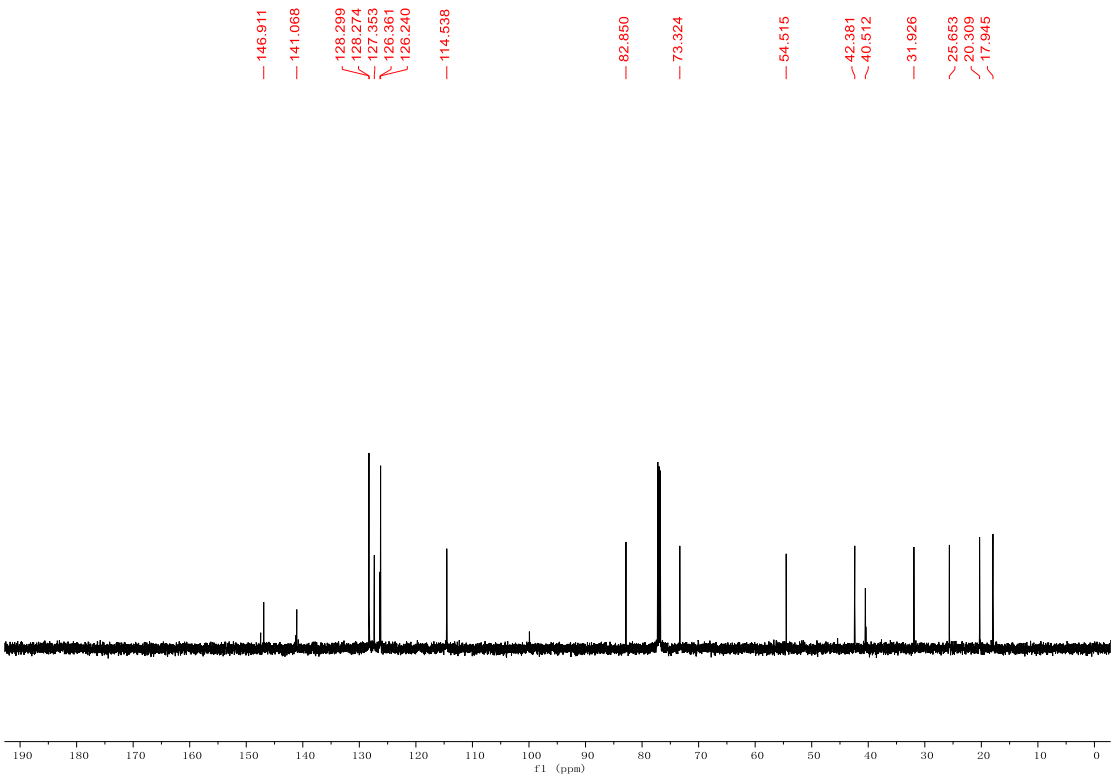

1409 1
single pulse decoupled gated NOE
148.299
140.968
128.323
127.421
126.059
112.554
81.413
73.140
48.384
40.628
34.609
26.206
24.390
20.574
f1 (ppm)

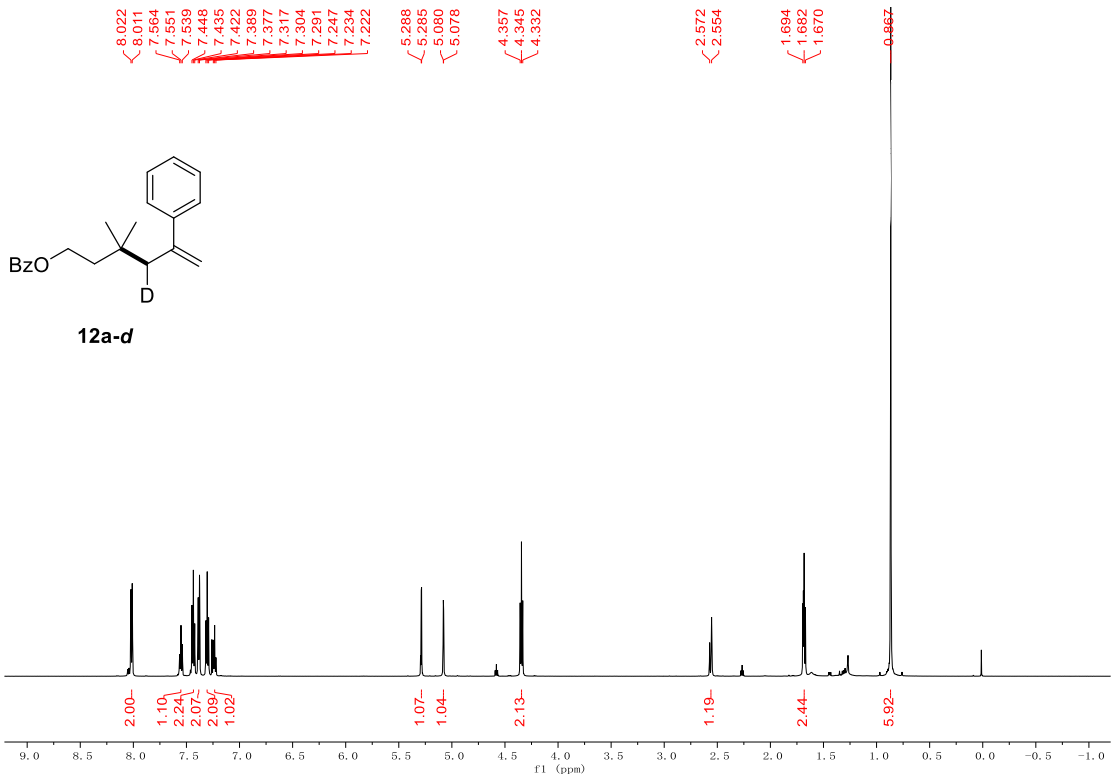

7.433
7.420
7.408
7.396
7.389
7.376
7.364
7.342
7.330
7.319
7.305
5.327
5.088
4.260
4.246
4.233
3.720
3.704
3.690
3.534
2.683
2.660
2.116
2.094
2.075
1.758
1.742
1.727
1.711
1.652
1.646
1.640
1.635
1.629
1.623
1.618
1.612
1.118
0.969
0.958
0.946


O
Me
Ph

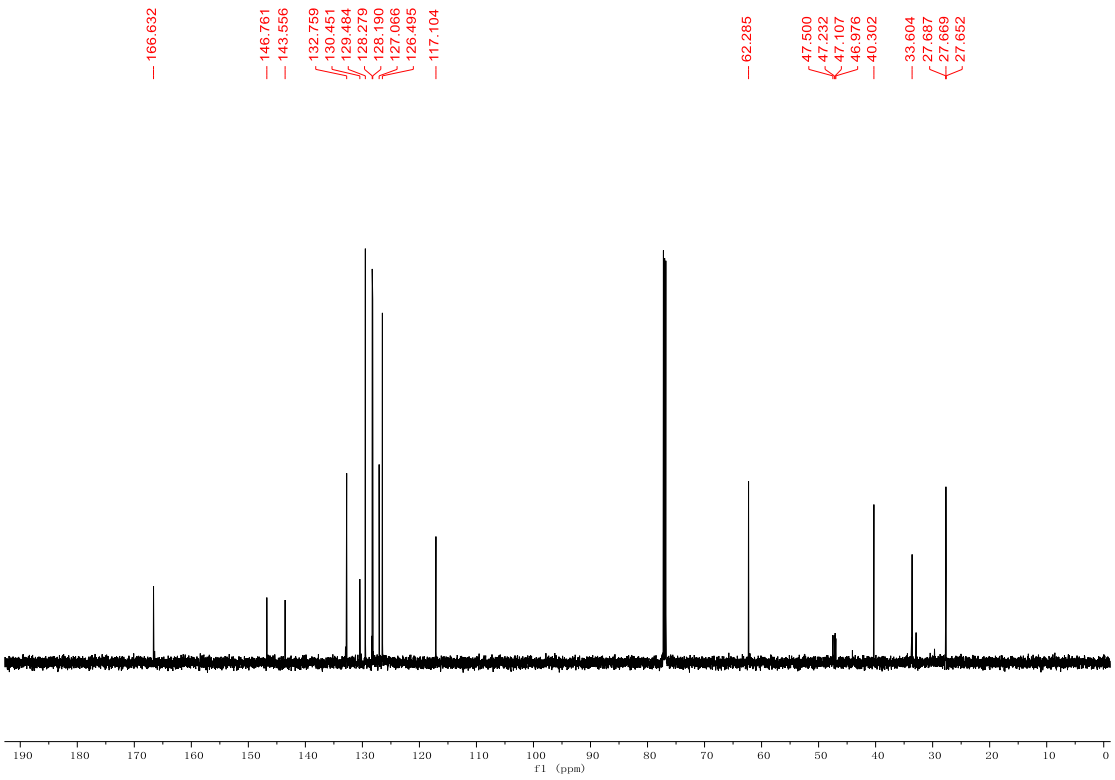
45


4.37
1.17
0.87
1.00
0.94
1.00
2.28
0.96
1.05
1.18
1.35
2.86
2.75
2.79
f1 (ppm)

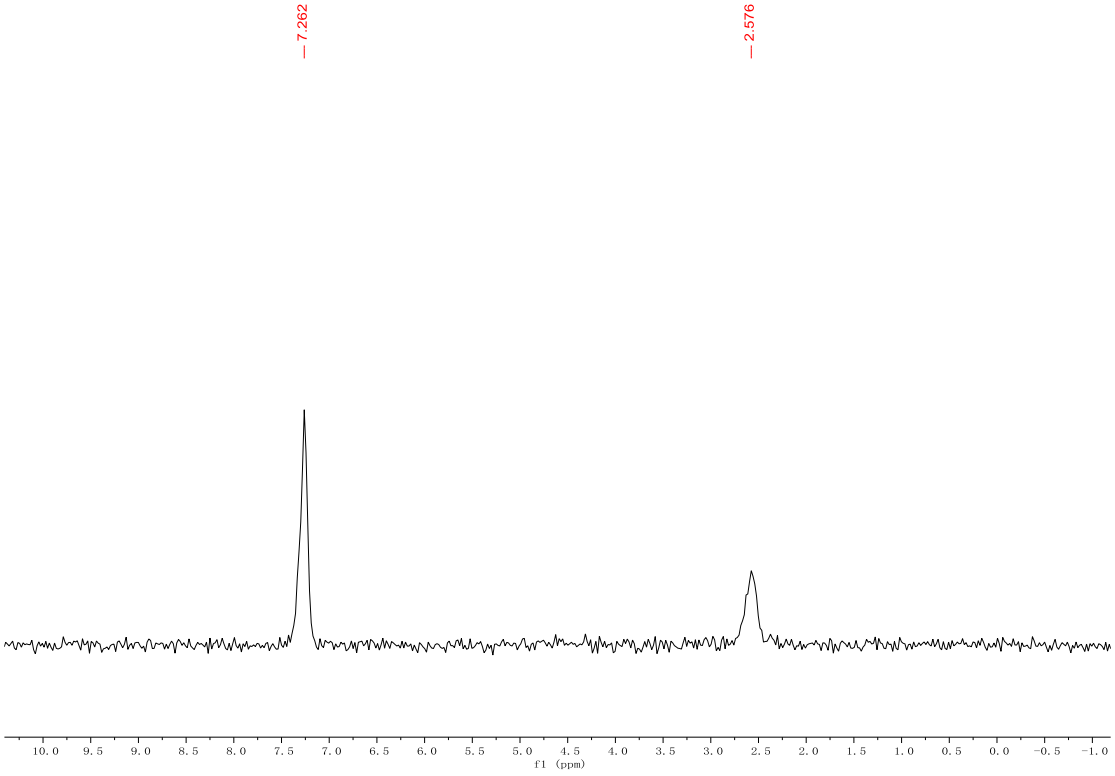

146.911
141.068
128.299
128.274
127.353
126.361
126.240
114.538
82.850
73.324
54.515
42.381
40.512
31.926
25.653
20.309
17.945
f1 (ppm)


8.022
8.011
7.564
7.551
7.539
7.448
7.435
7.422
7.389
7.377
7.317
7.304
7.291
7.247
7.234
7.222
5.288
5.285
5.080
5.078
4.357
4.345
4.332
2.572
2.554
1.694
1.682
1.670
0.867
BzO
D
2.00
1.10
2.24
2.07
2.09
1.02
1.07
1.04
2.13
1.19
2.44
5.92
f1 (ppm)

12a-*d*


166.632
146.761
143.556
132.759
130.451
129.484
128.279
128.190
127.066
126.495
117.104
62.285
47.500
47.232
47.107
46.976
40.302
33.604
27.687
27.669
27.652
f1 (ppm)

^{2}D NMR


7.262
2.576
f1 (ppm)

III. References

(1) (a) Zheng, M.; Xue, W.; Xue, T.; Gong, H. Ester Formation via Nickel-Catalyzed Reductive Coupling of Alkyl Halides with Chloroformates. *Org. Lett.* **2016**, *18*, 6152. (b) Wu, F.; Lu, W.; Qian, Q.; Ren, Q.; Gong, H. Ketone Formation via Mild Nickel-Catalyzed Reductive Coupling of Alkyl Halides with Aryl Acid Chlorides. *Org. Lett.* **2012**, *14*, 3044. (c) Yin, H.; Zhao, C.; You, H.; Lin, Q.; Gong, H. Mild ketone formation via Ni-catalyzed reductive coupling of unactivated alkyl halides with acid anhydrides. *Chem. Comm.* **2012**, *48*, 7034. (d) Xu, H.; Zhao, C.; Qian, Q.; Deng, W.; Gong, H. Nickel-catalyzed cross-coupling of unactivated alkyl halides using bis(pinacolato)diboron as reductant. *Chem. Sci.* **2013**, *4*, 4022. (e) Wang, S.; Qian, Q.; Gong, H. Nickel-Catalyzed Reductive Coupling of Aryl Halides with Secondary Alkyl Bromides and Allylic Acetate. *Org. Lett.* **2012**, *14*, 3352. (f) Yu, X.; Yang, T.; Wang, S.L.; Xu, H.; Gong, H. Nickel-Catalyzed Reductive Cross-Coupling of Unactivated Alkyl Halides. *Org. Lett.* **2011**, *13*, 2138.

(2) (a) Chen, H.; Jia, X.; Yu, Y.; Qian, Q.; Gong, H. Nickel-Catalyzed Reductive Allylation of Tertiary Alkyl Halides with Allylic Carbonates. *Angew. Chem. Int. Ed.* **2017,** *56*, 13103. (b) Yu, Y.; Chen, H.; Qian, Q.; Yao, K.; Gong, H. An extension of nickel-catalyzed reductive coupling between tertiary alkyl halides with allylic carbonates. *Tetrahedron*, **2018**, *74*, 5651.

(3) (a) Kulinkovich, O. G.; Kananovich, D. G. Advanced Procedure for the Preparation of cis-1,2-Dialkylcyclopropanols–Modified Ate Complex Mechanism for Titanium-Mediated Cyclopropanation of Carboxylic Esters with Grignard Reagents. *Eur. J. Org. Chem.* **2007**, 2121. (b) Atack, T.; Cook, S.; Manganese-Catalyzed Borylation of Unactivated Alkyl Chlorides. *J. Am. Chem. Soc.* **2016**, *138*, 6139. (c) Kuhn, M.; Ludwig, J.; Marszalek, T.; Adermann, T.; Pisula, W.; Mullen, Colsmann, K.; Hanburger, A.; M. Tertiary Carbonate Side Chains: Easily Tunable Thermo-Labile Breaking Points for Controlling the Solubility of Conjugated Polymers. *Chem. Mater.* **2015**, *27*, 2678. (d) Drescher, K.D.; Hans, H.; Heinz, F. K. Synthese einiger Derivate des Hämatoxylins. *Chemische Berichte* **1968**, *101*, 2494. (e) Ye, Y.; Chen, H.F.; Sessler, J. L.; Gong, H. Zn-Mediated Fragmentation of Tertiary Alkyl Oxalates Enabling Formation of Alkylated and Arylated Quaternary Carbon Centers. *J. Am. Chem. Soc.*, **2019**, *141*, 820. (f) Wang, X.; Wang, S.L.; Xue, W.C.; Gong, H. Nickel-Catalyzed Reductive Coupling of Aryl Bromides with Tertiary Alkyl Halides. *J. Am. Chem. Soc.*, **2015,** *137*, 11562.

(4) Jin, W.; Yang, Q.; Wu, P.; Chen, J.; Yu, Z. Palladium-Catalyzed Oxidative Heck-Type Allylation of β, β-Disubstituted Enones with Allyl Carbonates. *Adv. Synth. Catal.* **2014,** *356*, 2097.

(5) Dieckmann, M.; Jang, Y.; Cramer, N. Chiral Cyclopentadienyl Iridium (III) Complexes Promote Enantioselective Cycloisomerizations Giving Fused Cyclopropanes. *Angew. Chem. Int. Ed.* **2015**, *54*, 12149.

(6) Schwarz, K.J.; Pearson, C.; Rosado, G. A. C.; Liu, P.; Snaddon, T. N. Traversing Steric Limitations by Cooperative Lewis Base/Palladium Catalysis: An Enantioselective Synthesis of α-Branched Esters Using 2-Substituted Allyl Electrophiles. *Angew. Chem. Int. Ed.* **2018**, *57*, 7800.

(7) Tian, P.; Wang, C.; Cai, S.; Song, S.; Ye, L.; Feng, C.; Loh, T.-P. F^- Nucleophilic-Addition-Induced Allylic Alkylation. *J. Am. Chem. Soc.* **2016,** *138*, 15869.

(8) Nagasawa, S.; Sasano, Y.; Iwabuchi, Y. Synthesis of 1,3-Cycloalkadienes from Cycloalkenes:

Unprecedented Reactivity of Oxoammonium Salts. *Angew. Chem. Int. Ed.* **2016**, *55*, 13189.

(9) Dong, X.; Han, Y.; Yan, F.; Liu, Q.; Wang, P.; Chen, K.; Li, Y.; Zhao, Z.; Dong, Y.; Liu, H. Palladium-Catalyzed 6-Endo Selective Alkyl-Heck Reactions: Access to 5-Phenyl-1,2,3,6-tetrahydropyridine Derivatives. *Org. Lett.* **2016**, *18*, 3774.

(10) (a) Nawrat, C. C.; Jamison, C. R.; Slutskyy, Y.; MacMillan, D. C.; Overman, L. E.; Oxalates as Activating Groups for Alcohols in Visible Light Photoredox Catalysis: Formation of Quaternary Centers by Redox-Neutral Fragment Coupling. *J. Am. Chem. Soc.* **2015**, *137*, 11270. (b) Rackl, D.; Kais, V.; Lutsker, E.; Reiser, O. Synthesis of Chiral Tetrahydrofurans and Pyrrolidines by Visible-Light-Mediated Deoxygenation. *Eur. J. Org. Chem.* **2017**, 2130. (c) Abbas, S.; Zhao, P.; Overman, L. E. 1,6-Addition of Tertiary Carbon Radicals Generated from Alcohols or Carboxylic Acids by Visible-Light Photoredox Catalysis. *Org. Lett.* **2018**, *20*, 868.

(11) Seki, Y.; Tanabe, K.; Sasaki, D.; Sohma, Y.; Oisaki, K.; Kanai, M. Serine-Selective Aerobic Cleavage of Peptides and a Protein Using a Water-Soluble Copper-Organoradical Conjugate. *Angew. Chem. Int. Ed.* **2014**, *53*, 6501.

(12) Adhikari, A.A.; Chisholm, J. D. Lewis Acid Catalyzed Displacement of Trichloroacetimidates in the Synthesis of Functionalized Pyrroloindolines. *Org. Lett.* **2016**, *18*, 4100.

(13) Lorenzo, P.; Álvarez, R.; de Lera, Ángel R. Total Synthesis and Structural Revision of (–)-Protubonine A and (–)-Protubonine B. *Eur. J. Org. Chem.* **2014**, 2557.