The Rh(I)-Catalyzed Cyclocarbonylation of Allenol Esters to Prepare α-Acetoxy 4-Alkylidene Cyclopent-3-en-2-ones

by

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B.S., Chemistry, Hope College, 2004

Submitted to the Graduate Faculty of

Arts and Sciences in partial fulfillment

of the requirements for the degree of

Master of Science

University of Pittsburgh

2009

UNIVERSITY OF PITTSBURGH

ARTS AND SCIENCES

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The Rh(I)-catalyzed allenic cyclocarbonylation reaction is an effective method for forming 4-alkylidene cyclopentenones. The scope of this methodology was expanded to include the cyclocarbonylation of allenol acetates to provide α-acetoxy-4-alkylidene cyclopentenones. The diastereoselectivity of the [3,3]-sigmatropic rearrangement to form the allenol acetates and cyclocarbonylation reaction were examined. During the course of the Rh(I)-catalyzed cyclocarbonylation reaction two rhodium metallocycle intermediates were observed and structures are postulated based upon ^{1}H and ^{13}C NMR data. Liberation of the acetate to the free alcohol was also accomplished yielding α-hydroxy-4-alkylidene cyclopentenones.

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ACKNOWLEDGEMENTS

I would like to thank my research advisor Professor Kay M. Brummond for the time and support she has given me throughout my graduate career. I also would like to thank Dr. Curran and Dr. Meyer for serving on my committee for both my comprehensive and masters examinations. Thanks to all Brummond group members past and present for their advice and support. You guys have been great and I really appreciate the good times we've had together. I would like to thank my parents for supporting me in whatever I do. Finally I would like to thank my wife Kathy for her near infinite support and patience. Graduate school would have been a much sadder place without you.

ABBREVIATIONS

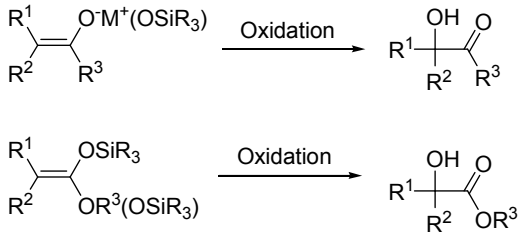
Ac	Acetyl
AcCl	Acetyl Chloride
Ac_2O	Acetic Anhydride
aq	Aqueous
atm	Atmosphere
Bz	Benzoyl
calcd	Calculated
cm^{-1}	Wavenumbers
δ	Chemical Shift
DMAP	4-*N,N*-Dimethylaminopyridine
DMF	*N*,*N*-Dimethylformamide
DMSO	Dimethylsulfoxide
dr	Diastereomeric Ratio
ee	Enantiomeric Excess
EI	Electron Impact
ESI	Electrospray Ionization
Et	Ethyl
EtOAc	Ethyl Acetate

h	hour(s)
IR	infrared
J	coupling constant (in NMR spectroscopy)
LDA	lithium diisopropylamide
liq	Liquid
Me	Methyl
min	Minutes
n-Bu	Normal Butyl
n-Pr	Normal Propyl
NMO	*N*-Methylmorpholine-*N*-Oxide
NMR	Nuclear Magnetic Resonance
nOe	Nuclear Overhauser Effect
Ph	Phenyl
Piv	Pivaloyl
PNB	*para*-Nitro Benzoyl
ppm	Parts Per Million
rt	Room Temperature
T	Temperature
Tf	Trifluoromethanesulfonyl
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	Trimethylsilyl

1.0 INTRODUCTION

1.1 ALPHA-HYDROXY CARBONYLS

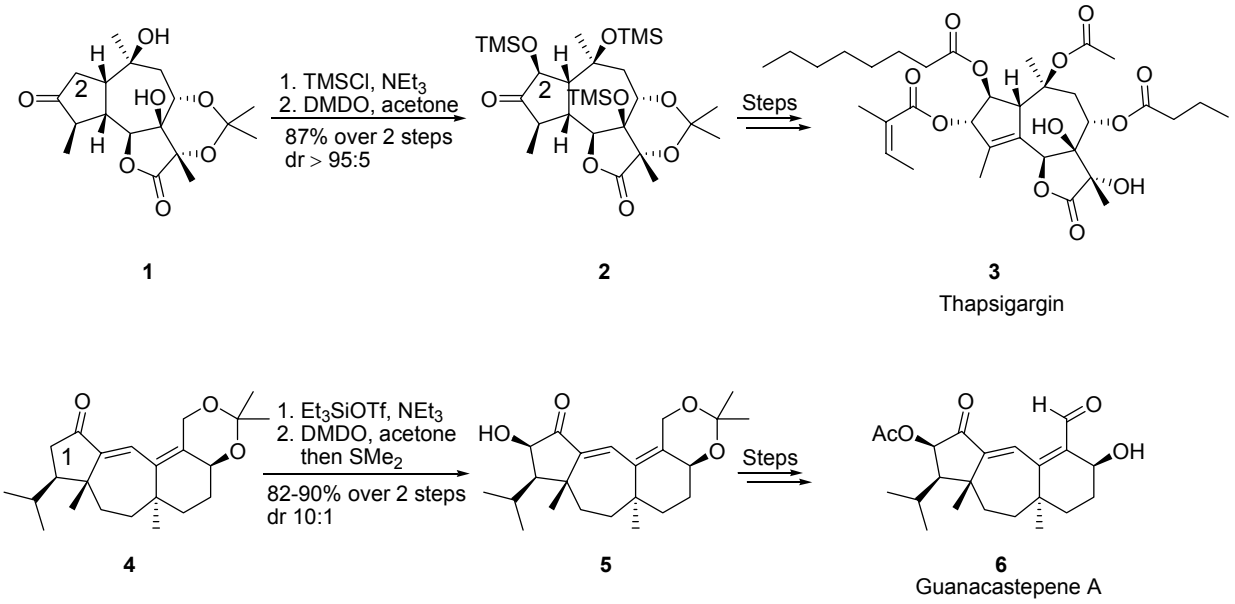
α-Hydroxy carbonyls are important building blocks in organic synthesis and are present in a number of biologically active compounds.[1] A variety of methods exist to prepare α-hydroxy carbonyls, and the most commonly used protocol is the oxidation of enolates or silyl enol ethers (Scheme 1).[2] In view of the incompatibilities of some functional groups to these enolization/oxidation conditions and in consideration of redox economy,[3] synthetic alternatives to this late-stage oxidation strategy would be useful.



Scheme 1. Formation of α-Hydroxy Carbonyl Compounds

Representative examples of biologically active molecules that would benefit from efficient synthetic access to α-hydroxy carbonyls are the thapsigargin guaianolides and the guanacastepene diterpenes. Relevant examples of each family are thapsigargin (**3**) and guanacastepene A (**6**) (Scheme 2). Thapsigargin is a potent histamine liberator and has proven useful in the study of Ca^{2+} signaling pathways.[4] Guanacastepene A has shown activity against

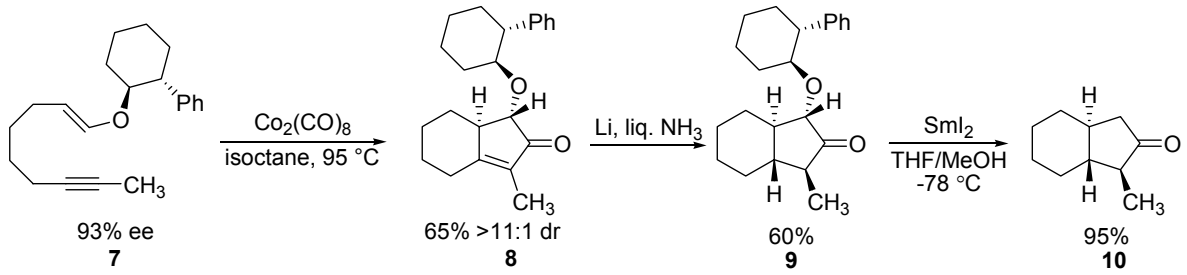
drug resistant strains of *Staphylococcus aureus* and *Enterococcus faecalis*.[5] In the synthesis of thapsigargin, installation of the C-2 siloxy group of **2** was accomplished via a Rubottom oxidation of the corresponding silyl enol ether of ketone **1**.[6] The high diastereoselectivity of this transformation (dr 95:5) results from the approach of dimethyldioxirane from the less sterically hindered face of the silyl enol ether. For the synthesis of guanacastepene A, conversion of ketone **4** to the α-hydroxy ketone **5** is accomplished in an analogous manner;[7] however, the diastereoselectivity results from equilibration of the α-hydroxy carbonyl carbon C-1. An alternative approach to the stereoselective synthesis of α-hydroxy carbonyls is needed whereby reagent control is used.



Scheme 2. Synthesis of Thapsigargin and Guanacastepene A

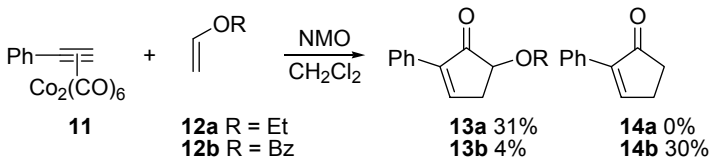
1.2 CYCLOCARBONYLATION REACTIONS OF ENOL ETHERS AND ENOL ESTERS

Since its discovery in 1973,[8] the Pauson-Khand cyclocarbonylation reaction has proven to be a powerful method for the formation of functionalized cyclopentenone containing compounds.[9] However, missing from the cyclocarbonylation reaction arsenal is efficient access to an α-hydroxy carbonyl via an enol ether or enol ester precursor. Schore demonstrated that α-alkoxy cyclopentenones could be prepared from enol ether precursors using a Pauson-Khand reaction[10] and subsequently a number of groups have rendered the reaction asymmetric.[11] However, relatively harsh conditions are required for the conversion of an α-alkoxy cyclopentenone to an α-hydroxy cyclopentenone. Thus after serving as a control element in the reaction, the alkoxy group is typically removed reductively (Scheme 3).[12]



Scheme 3. Pauson-Khand Reaction of Chiral Enol Ethers

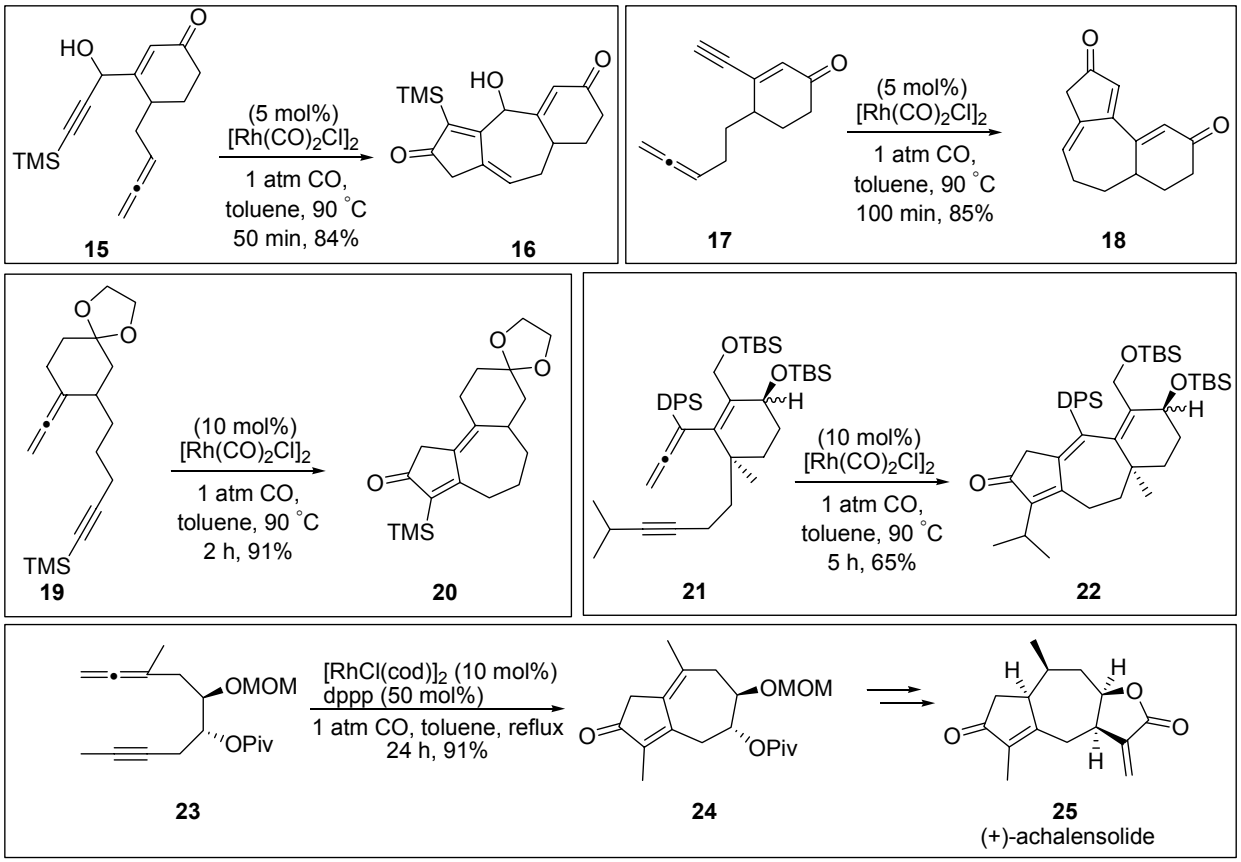
The $Co_2(CO)_8$-mediated Pauson–Khand reaction of vinyl ether **12a** gave a 31% yield of α-ethoxy cyclopentenone **13a**. Reaction of analogous vinyl ester **12b** to form an α-benzyloxy cyclopentenone results in concurrent loss of the ester through a proposed single electron transfer process (Scheme 4).[13]



11 **12a** R = Et, **12b** R = Bz → **13a** 31%, **13b** 4%; **14a** 0%, **14b** 30%

Scheme 4. Pauson-Khand Reaction of Enol Ethers and Enol Esters

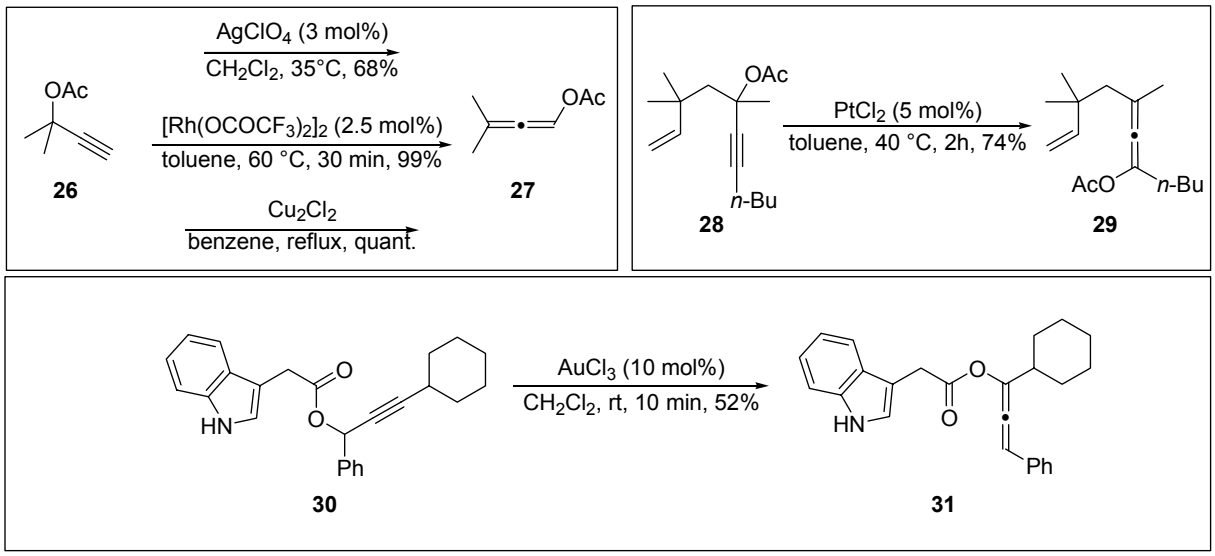
It was hypothesized that a Rh(I)-catalyzed cyclocarbonylation of the related allenol esters to afford α-acetoxy cyclopentadienones would be possible due to the mildness of the reaction conditions and the unlikelihood of a rhodium catalyst to undergo a single electron transfer.[14] Using conditions developed by Narasaka,[15] Brummond and coworkers have demonstrated a selective cyclocarbonylation reaction with the distal double bond of the allene.[16] Subsequently, the allenic Rh(I)-catalyzed cyclocarbonylation reaction was demonstrated as an efficient method to synthesize a variety of alkylidene cyclopentenones including bicyclo[5.3.0]undecadienones **16**, **18**, and **20**;[17] a long sought after ring system previously inaccessible to cyclocarbonylation methodology (Scheme 5).[18] In addition, this methodology was applied to the synthesis of the carbocyclic core of guanacastepene A (**22**).[19] Furthermore, the utility of this methodology was demonstrated by Mukai and coworkers in the total synthesis of (+)-achalensolide (**25**).[20]



Scheme 5. Formation of Bicyclo[5.3.0]undecadienones

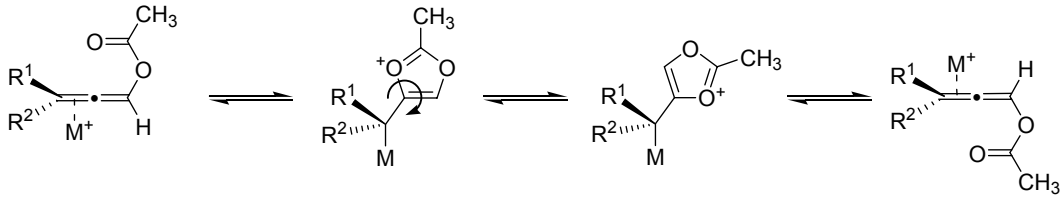
1.3 SYNTHETIC AVAILABILITY OF ALLENOL ACETATES

Allenol esters are often prepared from propargyl acetates via a formal [3,3]-sigmatropic rearrangement using a variety of transition metal catalysts, such as Ag,[21] Rh,[22] Cu,[23] Pt,[24] and Au[25] (Scheme 6).



Scheme 6. Transition Metal Catalyzed Rearrangement of Propargyl Acetates to Allenol Acetates

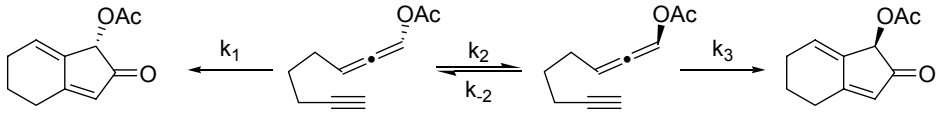
This is an atom economical alternative to a more common method of forming allenes via an S_N2' reaction of a propargyl ester, which results in loss of the ester.[26] A potential disadvantage to preparing allenol acetates via transition metal catalysis, is the rapid isomerization of allenol acetates under metal catalysis (Scheme 7).[27]



Scheme 7. Metal-Catalyzed Isomerization of Allenol Acetates

We envisioned that the rapid isomerization could be exploited in asymmetric synthesis via a dynamic kinetic resolution if k_2 or k_{-2} is faster than either k_1 or k_3 (Scheme 8). Furthermore, it is predicted that the use of a chiral rhodium catalyst will preferentially give one isomer over

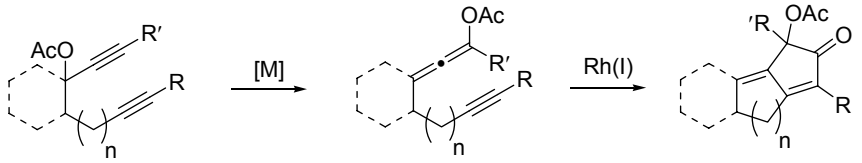
the other (i.e. $k_1 > k_3$ or $k_3 > k_1$).[28,29] While the use of dynamic kinetic asymmetric transformations (DYKAT) are becoming more commonplace, there are few examples involving allenes.[30-33]



Scheme 8. Dynamic Kinetic Resolution

1.4 SUBSTRATE DESIGN

Once the feasibility of the cyclocarbonylation reaction of allenol acetates to produce α-acetoxy carbonyls was established, several cyclocarbonylation substrates were examined. Guided by a number of natural product substructures the scope of the cyclocarbonylation reaction was explored as follows: 1) The chain length of the tether between the allene and alkyne was varied (n = 1-4); 2) Substitution on the allene and the tether were altered (Scheme 9). The stereochemical consequences of the [3,3]-sigmatropic rearrangement of propargyl acetate **32** to allenol acetate **33** and the cyclocarbonylation reaction to give **34** were examined by imbedding the allene into a conformationally anchored cyclohexane ring.

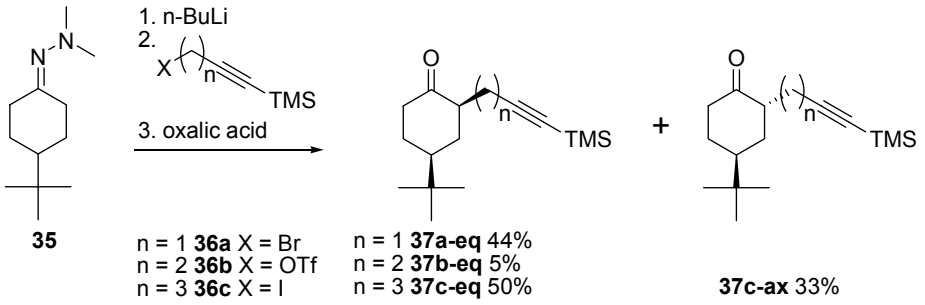


Scheme 9. Substrate Design

2.0 RESULTS AND DISCUSSION

2.1 PREPARATION OF PROPARGYL ACETATES

Preparation of cyclohexane-based substrates began by alkylating the lithium enolate of dimethyl hydrazone **35**[34] with alkynyl halides or triflates (**36a-c**) (Scheme 10). Acidic hydrolysis[35] gave ketones **37a-eq**, **37c-eq**, and **37c-ax** (n = 1, 3) in 44%, 50%, and 33% yields. Ketone **37b-eq** was obtained in only 5% yield, possibly due to a competing E2 elimination of the triflate to form a conjugated enyne prior to alkylation. The diastereomers of **37c** were separated via column chromatography and the major diastereomer was carried forward.



Scheme 10. Preparation of Ketones 37a-c

The major diastereomer of **37a-eq** was assigned as having a chair conformation with the alkyne side chain equatorial based on ^{1}H NMR and ^{1}H-^{1}H COSY experiments (Figure 1). Proton resonance G is assigned as being adjacent to the *t*-Bu group based on the two large (12.0 Hz) coupling constants consistent with axial-axial coupling and two smal (3.0 Hz) coupling constants consistent with axial-equatorial coupling. COSY correlation was observed between H_G and

proton resonances H_B, H_F, H_H, and H_I indicating that they are on carbons adjacent to H_G. Resonances H and I proved most informative. Resonance H was assigned based on the three large (12.0 Hz) couplings attributed to two axial-axial and one geminal coupling and a small (3.0 Hz) coupling attributed to an axial-equatorial coupling. Resonance I was assigned based on the three large (2×12.5 Hz and 14.0 Hz) couplings attributed to two axial-axial and one geminal coupling. The three large coupling constants observed for H_I support the side chain having an equatorial orientation. If the side chain was axial, then H_I would have two large coupling constants from an axial-axial and a geminal coupling along with a smaller constant for an axial-equatorial coupling. The same rationale was applied to assign the stereochemistry of ketones 37b-eq and 37c-eq.

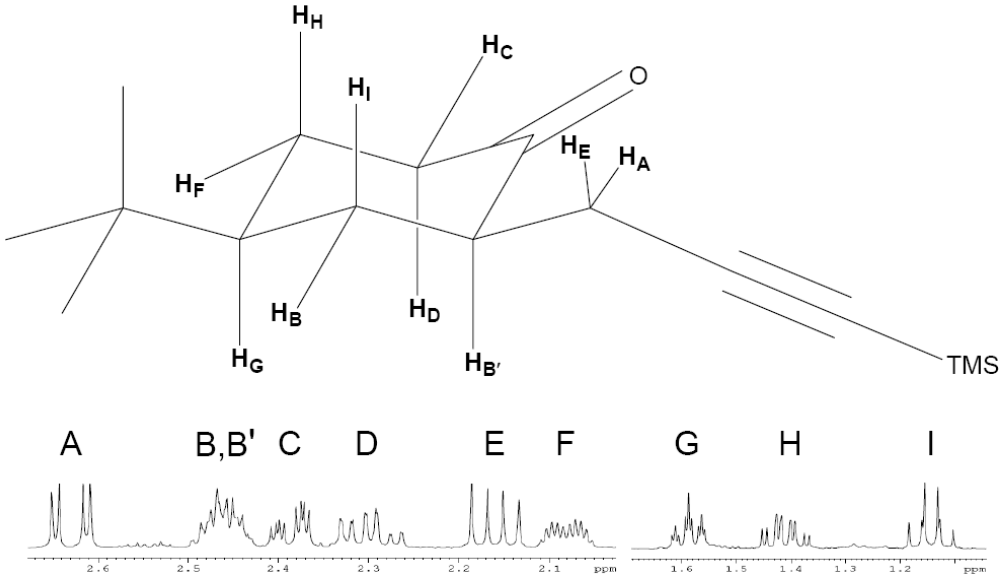
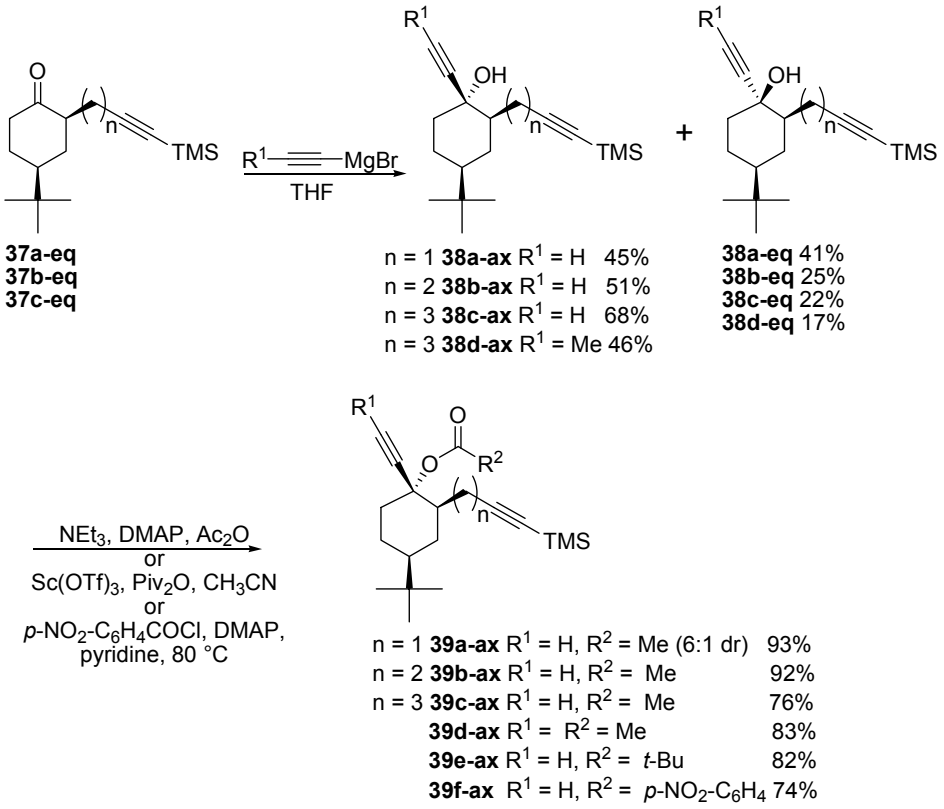


Figure 1. Stereochemical Assignment of the Major Diastereomer of 37a-eq

Addition of ethynyl or 1-propynylmagnesium bromide to **37a-c-eq** gave the propargyl alcohols resulting from axial addition of the Grignard reagent **38a-d-ax** in 45-68% yields and the propargyl alcohols resulting from equatorial addition **38a-d-eq** in 17-41% yields (Scheme 11). The major diastereomers were assigned based on the predisposition of small nucleophiles to add

axially to substituted cyclohexanones.[36] Separation of the two diastereomers of **38** was readily accomplished via column chromatography. The major diastereomers were acetylated using triethylamine, DMAP, and acetic anhydride yielding a single diastereomer of propargyl acetates **39a-d-ax** in 71-93% yield. Two substrates were prepared to examine the electronic and steric effects of the carboxy group. A bulky pivaloyl group was appended to the corresponding propargyl alcohol using trimethylacetic anhydride and catalytic $Sc(OTf)_3$ to give **39e-ax** in 82% yield.[37] An electron withdrawing *p*-nitrobenzoate was attached to propargyl alcohol **38c-ax** using 4-nitrobenzoyl chloride and DMAP to give **39f-ax** in 74% yield.[38]

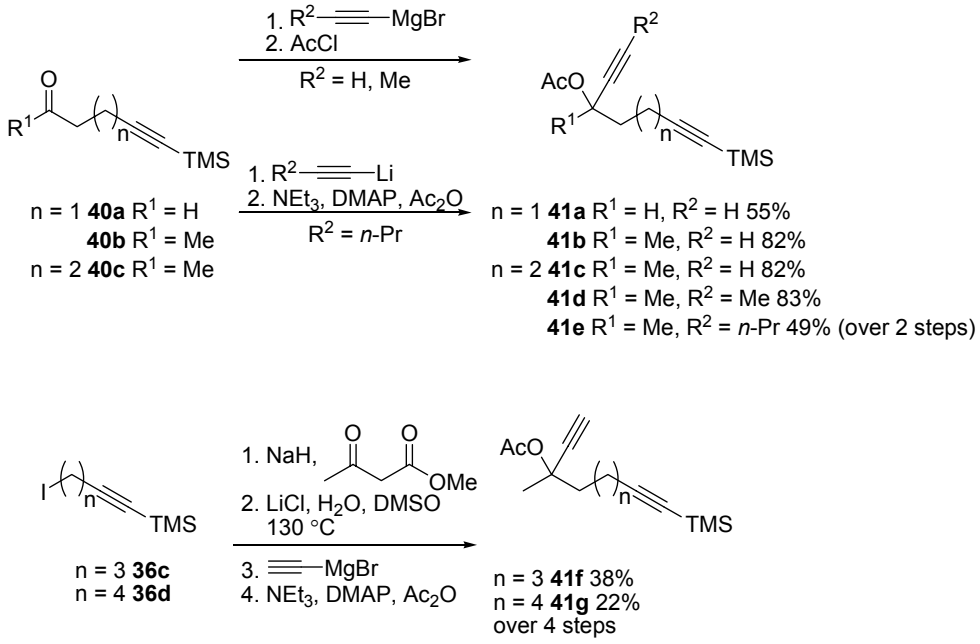


Scheme 11. Preparation of Propargyl Acetates 39a-f

Propargyl acetates containing a simple alkyl chain were prepared using two different methods (Scheme 12). Propargyl acetates **41a-d** (n = 1, 2) were prepared by addition of ethynylmagnesium bromide or 1-propynylmagnesium bromide to aldehyde **40a** or ketones **40b-**

c[39] followed by in situ acetylation with acetyl chloride furnishing the desired products in 55-82% yields. For propargyl acetate **41e** (R^2 = *n*-Pr) addition of the lithiate of 1-pentyne to ketone **55c** gave the propargyl alcohol, which was then acetylated using triethylamine, DMAP, and acetic anhydride to obtain propargyl acetate **41e** in 49% yield over two steps.

Propargyl acetates **41f-g** (n = 3, 4) were prepared by reacting a slight excess of the sodium salt of methyl acetoacetate with iodides **36c** and **36d**.[40-42] After aqueous workup, the crude material still containing a small amount of methyl acetoacetate, was subjected to Krapcho decarboxylation by heating the ketoester to 130 °C with lithium chloride in wet DMSO to obtain 8-(trimethylsilyl)oct-7-yn-2-one and 9-(trimethylsilyl)non-8-yn-2-one.[43] Subjecting the crude 8-(trimethylsilyl)oct-7-yn-2-one and 9-(trimethylsilyl)non-8-yn-2-one to ethynylmagnesium bromide proved more straight forward than isolating the ketones. After chromatographic purification, the resulting propargyl alcohols were acetylated using triethylamine, DMAP, and acetic anhydride to obtain propargyl acetates **41f** and **41g** in 38% and 22% yields over 4 steps.

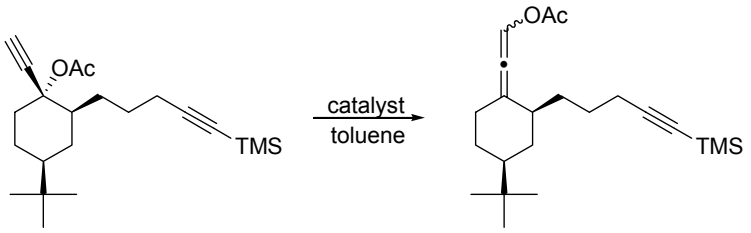


Scheme 12. Preparation of Propargyl Acetates 41a-g

2.2 FORMATION OF ALLENOL ACETATES FROM PROPARGYL ACETATES.

Previously reported conditions to form allenol acetates were screened for efficiency and diastereospecificity. Treating **39c-ax** with $AuCl_3$ at 60 °C (Table 1, entry 1) gave complete conversion of allene-yne **39c-ax** to **42c** in 30 min as 1:1 ratio of diastereomers.[22] Performing the same reaction at room temperature gave **42c** as a 1:1 mixture of diastereomers in 30 min (entry 2). Lowering the temperature to -30 °C resulted in an incomplete reaction after 5 h and afforded a 1:1 diastereomeric mixture of **42c** (entry 3). Increasing the temperature to 90 °C decreased the reaction time giving full conversion to allenol acetate **42c** in 12 min and a 1:1 dr (entry 4). Two Ag(I) catalysts ($AgBF_4$ and $AgSbF_6$) were examined (entries 5-8) with no significant changes in stereoselectivity, but significant loss of the TMS group was observed.[44,45] $[Rh(OCOCF_3)_2]_2$ gave only a trace amount of product after 14 h (entry 9).[22] Using the $PtCl_2$ conditions reported by Malacria,[24] clean conversion to **42c** was observed, with a 1:1 dr and required prolonged reaction times (entry 10). Among the conditions examined, $AuCl_3$ afforded the allenol acetates in the highest yields and the shortest reaction times. The reaction temperature had a marginal effect on the diastereoselectivity.

Table 1. Catalyst Screening for Rearrangement



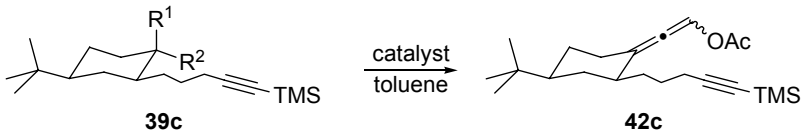
39c-ax **42c**

entry	catalyst	mol %	T (°C)	time (h)	Conversion%[a] (isolated yield %)	dr[b]
1	$AuCl_3$	10	60	0.5	100 (71)	1:1
2	$AuCl_3$	10	rt	0.5	100 (74)	1:1
3	$AuCl_3$	20	-30	5	55	1:1
4	$AuCl_3$	10	90	0.2	100 (62)	1:1
5	$AgBF_4$	50	rt	4	84[c]	1:1
6	$AgSbF_6$	10	60	3	83	2:1
7	$AgSbF_6$	10	rt	19	90[c]	1:1
8	$AgSbF_6/PPh_3$	20	rt	17	73	1:1
9	$[Rh(OCOCF_3)_2]_2$	2	60	14	2	1:1
10	$PtCl_2$	10	40	96	100	1:1

[a]Conversion determined by ^{1}H NMR, [b] Diastereomeric ratio determined by comparing the allenyl protons in the ^{1}H NMR, [c]Significant loss of TMS observed by ^{1}H NMR

Interestingly, while reacting both **39c-ax** and **39c-eq** independently with $AuCl_3$ at room temperature showed little difference in reaction time, yield, or dr (entries 1 and 2, Table 2), when $[Rh(OCOCF_3)_2]_2$ was used significant differences in reaction times for the two diastereomers were observed (compare entries 3 and 4). With the alkyne cis to the *t*-butyl group **39c-ax** only trace amounts of product were observed after 72 h (entry 3). Conversely, the other diastereomer**39c-eq** (entry 4) showed complete conversion to **42c** in 4 h in 94% yield.

Table 2. Rearrangement of 39c-ax and 39c-eq

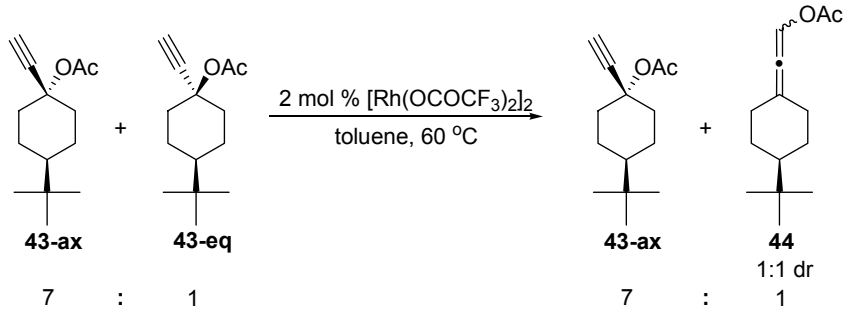


39c **42c**

entry	R^1	R^2	catalyst (mol %)	time (h)	yield (%)	dr
1	CCH	OAc	$AuCl_3$ (10)	0.5	74	1:1
2	OAc	CCH	$AuCl_3$ (10)	0.5	80	1:1
3	CCH	OAc	$[Rh(OCOCF_3)_2]_2$ (2)	72	2[a]	1:1
4	OAc	CCH	$[Rh(OCOCF_3)_2]_2$ (2)	4	94	1:1

[a]Approximate conversion by ^{1}H NMR

Similar results were seen when **43** (7:1 dr) was reacted with $[Rh(OCOCF_3)_2]_2$ (Scheme 13). After 5 h at 60 °C, the minor diastereomer possessing a trans relationship between the alkyne and the *t*-butyl group was completely converted to product **44**, and no change was observed for the major diastereomer of **43-ax**, based on ^{1}H NMR. Thus, the stereochemistry of the propargyl acetate significantly impacts the reaction time of the rearrangement when using $[Rh(OCOCF_3)_2]_2$ with the axially oriented alkyne being slowest. It is postulated that developing 1,3-diaxial interactions of the alkyne coordinated to $[Rh(OCOCF_3)_2]_2$ slows this reaction.

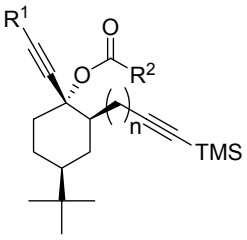
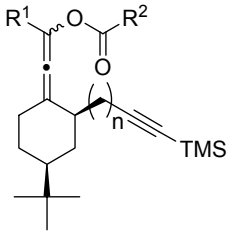
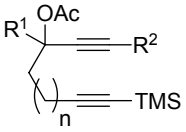
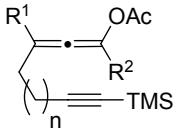
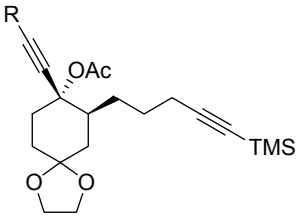
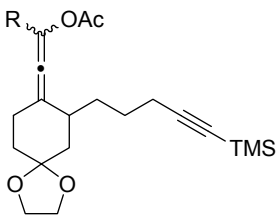


Scheme 13. $[Rh(OCOCF_3)_2]_2$ Catalyzed Rearrangement of 43

With $AuCl_3$-catalyzed rearrangement conditions in hand, propargyl acetates **39a-c-ax** were transformed to the trisubstituted allenol acetates **42a-c** using $AuCl_3$ in 74–84% yield as ~1:1 mixtures of diastereomers (Table 3, entries 1-3). Tetrasubstituted allenol acetate **42d** was

isolated in 53% yield (entry 4) due to the incomplete consumption of starting material and the instability of **42d**. (Decomposition products were observed within 4 h of **42d** standing in $CDCl_3$ at rt.) Treating sterically demanding propargyl ester **39e-ax** to $AuCl_3$ readily formed allene-yne **42e** in 1 h (91%, 2:1 dr) (entry 5). Subjecting *p*-nitrobenzoate ester **39f-ax** to $AuCl_3$-catalyzed conditions gave allene-yne **42f** in 87% yield in a 1.4:1 dr (entry 6). Reacting the secondary propargyl acetate **41a** to the $AuCl_3$-catalyzed reaction conditions yielded only trace amounts of the 1,3-disubstituted allene (entry 7). The temperature was increased to 60 °C using $AuCl_3$ and the $[Rh(OCOCF_3)_2]_2$ and $PtCl_2$ conditions gave no improvement. Tertiary propargyl acetates **41b** and **41c** (entries 8 and 9) rearranged to give the desired allenol acetates **45b** and **45c** in 46% and 67% yields. Longer reaction times were required compared to the analogous cyclohexane based propargyl acetates (compare entries 1 and 2 to entries 8 and 9). Substituting an alkyl group for the proton on the terminus of the alkyne had little effect on the yield for the rearrangement of the linear system compared to the analogous cyclohexane based system (compare entries 9 and 10 to 3 and 4). Propargyl acetates **41f** and **41g** (n = 3, 4) reacted in significantly shorter reaction times and gave both **45f** and **45g** in 79% and 77% yields respectively (entries 12 and 13). It is possible that the remoteness of the appending alkyne minimizes coordination of the gold catalyst allowing for more rapid catalyst turnover, and limits potential side reactions. Reacting propargyl acetate **46a** (R = H)[17] to $AuCl_3$ gave allene-yne **47a** in near quantitative yield as a 1.3:1 dr (entry 14). However, treating propargyl acetate **46b** (R = Me)[17] to $AuCl_3$ gave allene-yne **47b** in a 43% yield (entry 15). (After 19 h propargyl acetate **46b** was still observed in the crude ^1H NMR along with the appearance of a byproduct containing alkene resonances by ^1H NMR.)

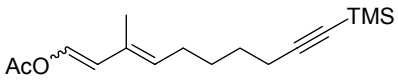
Table 3. Preparation of Allenol Acetates[a]

entry	propargyl acetate	time (h)	yield (%)	dr[c]
	 **39-ax**		 **42**	
1[b]	**39a-ax**, n = 1 R^1 = H, R^2 = Me	3	84	1:1
2[c]	**39b-ax**, n = 2 R^1 = H, R^2 = Me	0.5	80	1.1:1
3[c]	**39c-ax**, n = 3 R^1 = H, R^2 = Me	0.5	74	1:1
4[c]	**39d-ax**, n = 3 R^1 = Me, R^2 = Me	5	53	1.2:1
5[c]	**39e-ax**, n = 3 R^1 = H, R^2 = *t*-Bu	0.8	91	2:1
6[c]	**39f-ax**, n = 3 R^1 = H, R^2 = *p*-NO_2-C_4H_4	16	87	1.4:1
	 **41**		 **45**	
7	**41a**, n = 1, R^1 = H, R^2 = H	20	trace[d]	NA
8	**41b**, n = 1, R^1 = Me, R^2 = H	19	46	NA
9	**41c**, n = 2, R^1 = Me, R^2 = H	4	67[e]	NA
10	**41d**, n = 2, R^1 = Me, R^2 = Me	1.5	64	NA
11	**41e**, n = 2, R^1 = Me, R^2 = *n*-Pr	1.5	58	NA
12	**41f**, n = 3, R^1 = Me, R^2 = H	0.5	79	NA
13	**41g**, n = 4, R^1 = Me, R^2 = H	0.5	77	NA
	 **46-ax**		 **47**	
14[f]	**46a**, R = H	4	100	1.3:1
15[g]	**46b**, R = Me	19	43	1.5:1

[a]Conditions: $AuCl_3$ (10 mol %), toluene, rt, [b]Reacted as a 6:1 dr (major diastereomer is shown), [c]Reacted as a single diastereomer, [d]Observed by ^{1}H NMR, [e]Contaminated with unknown impurity, [f]Reacted as a 4:1 dr (major diastereomer is shown), [g]Reacted as a 5:1 dr (major diastereomer is shown).

2.3 RHODIUM(I)-CATALYZED CYCLOCARBONYLATION REACTION OF ALLENOL ACETATES TO FORM ALPHA-ACETOXY CYCLOPENTADIENONES.

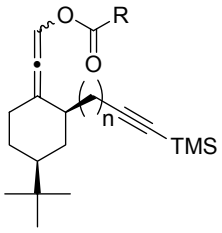
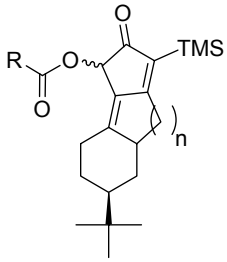
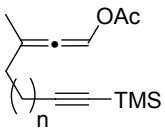
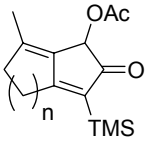
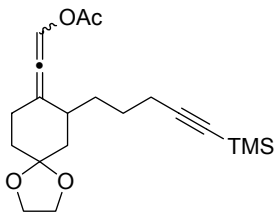
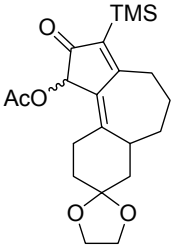
Next the scope and limitations of the Rh(I)-catalyzed cyclocarbonylation reaction of allenol acetates for the formation of bi- and tricyclic ring systems were explored (Table 4). Previously optimized conditions were used to effect the cyclocarbonylation reaction of allenol acetates.[17] Reaction of allenol acetate **42a** to the standard Rh(I) cyclocarbonylation conditions gave only a 19% yield of **48a** in 8 h (entry 1). Allene-ynes **42b** (entry 2) and **42c** (entry 3), underwent cyclocarbonylation to produce **48b** and **48c** in 67% and 76% yields respectively. Formation of the [6-7-5] ring system took significantly longer (17 h, entry 3) than the analogous [6-6-5] ring system (1 h, entry 1). Subjecting **42e** to cyclocarbonylation conditions gave a 2.6:1 dr of α-pivaloxy 4-alkylidene cyclopentadione **48e** in 51% yield (entry 4). Cyclocarbonylation of **42f** gave the cyclized product **48f** as a 1.8:1 mixture of diastereomers in 35% yield (entry 5). Thus, it appears that neither steric nor electronic changes significantly impact the diastereomeric ratio of the products. Reaction of linear allene-yne **45b** (entry 6) gave **49b** in 28% yield along with significant decomposition, indicating that [5-5] ring systems are not efficiently prepared via this methodology. Cyclocarbonylation of allene-yne **45c** and **45f** was readily accomplished giving **49c** and **49f** in 53% and 62% yields (entry 7 and 8). The reaction of **45g** to produce an [8-5] ring system resulted in only trace amounts of the product with the majority of allenol ester rearranging into the conjugated dienol acetate **50** in an ~1:1 *Z* to *E* ratio (entry 10 and Figure 2). Cyclocarbonylation of allenol-acetate **47a** gave the α-acetoxy 4-alkylidene cyclopentenone **51a** in 19 h and 74% yield.



50

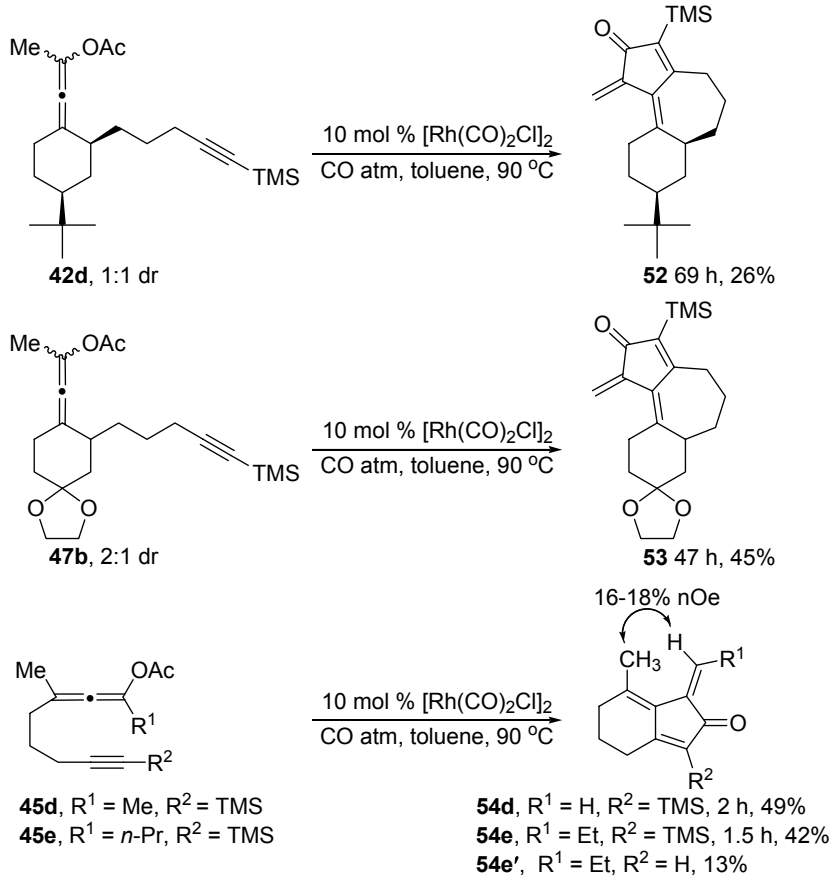
Figure 2. Conjugated Dienol Acetate 50

Table 4. $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reactions[a]

entry	allene-yne	time (h)	yield (%)	dr[b]
	 **42**		 **48**	
1	**42a**, n = 1, R = Me 1:1 dr	8	19	1.3:1
2	**42b**, n = 2, R = Me1.1:1 dr	1	67	1.2:1
3	**42c**, n = 3, R = Me 1:1 dr	17	76	1.9:1
4	**42e**, n = 3, R = *t*-Bu 2:1 dr	18	51	2.3:1
5	**42f**, n = 3, R = *p*-NO_2-C_6H_4 1.4:1 dr	18	35	1.8:1
	 **45**		 **49**	
6	**45b**, n = 1	22	28	NA
7	**45c**, n = 2	2	53	NA
8	**45f**, n = 3	46	62	NA
9	**45g**, n = 4	120	trace[c]	NA
	 **47**		 **51**	
10	**47a**, 1.3:1 dr	19	74	2.3:1

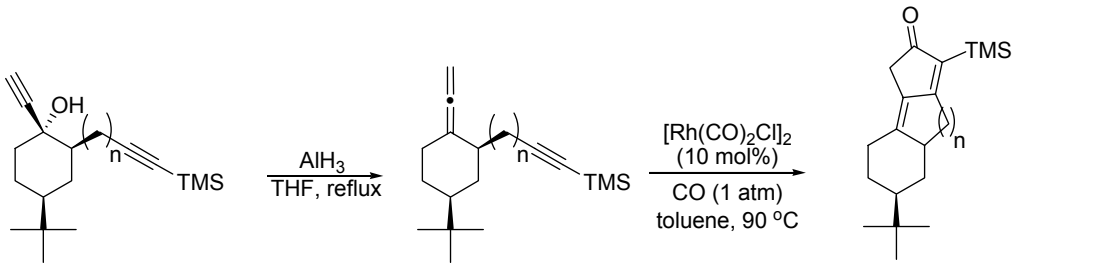
[a]Conditions: $[Rh(CO)_2Cl]_2$ (10 mol %), CO(g) (1 atm), toluene, 90 °C, [b]Diastereomeric ratio determined comparing proton resonances by ^{1}H NMR, [c]Observed by ^{1}H NMR.

Cyclocarbonylation reactions of tetrasubstituted allene **42d** afforded a 26% yield of **52** in 69 h and **47b** gave a 45% yield of **53** in 47 h via cyclocarbonylation followed by loss of acetic acid (Scheme 14). Linear allenol acetate **45d** gave a 49% yield of trienone **54d**, along with a trace amount of the desilyated product observed in the crude ^{1}H NMR. Similarly, allenol acetate **45e** afforded triene **54e** in 42% yield along with desilyated **54e'** in 13% yield. Compounds **52**, **53**, and **54d,e** proved relatively unstable with observable decomposition by ^{1}H NMR within 24 h in a freezer. *Nonetheless, these examples have provided access to the products of a cyclocarbonylation between an alkyne and a cumulene.*



Scheme 14. The $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction of Tetrasubstituted Allenol Esters

The cyclocarbonylation of allene-ynes **55a** and **55c** gave cycloadducts **56a** and **56c** in 32% and 70% yields (Scheme 15), paralleling the yields obtained for analogous [6-5-5] and [6-7-5] ring systems **48a** and **48c** (Table 4, entries 1 and 3), suggesting that the acetoxy group has little influence on the yields of the cyclocarbonylation reaction. Conversely, the reaction times for the cyclocarbonylation of **55a** and **55c** were 30 and 40 min, compared to 8 and 17 h for **48a** and **48c** suggesting that the acetoxy group has a large effect on the reaction time.



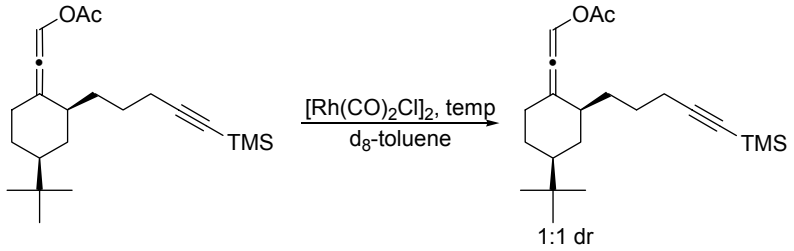
Scheme 15. Preparation and Cyclocarbonylation of Allene-ynes 55a and 55c

2.4 DIASTEREOSELECTIVE CONSIDERATIONS

To probe the origin of the slight increase in dr (1:1 to 2:1) for the transformation of **42c** to **48c**, the cyclocarbonylation of diastereomerically enriched allene-yne **42c** was performed in d_8-toluene and monitored via ^{1}H NMR (Table 5). Starting with 3:1 dr of **42c**, rapid isomerization of the allenol acetate was observed giving a 1:1 dr of allenol acetates in 40 min with no evidence of cyclocarbonylation products (entries 1 and 2). Performing the reaction at room temperature slowed the rate of isomerization but still resulted in a 1:1 dr of allenes after 7 h with no evidence of cyclocarbonylation products (entries 3 and 4). Heating allene **42c** in the absence of rhodium catalyst for 24 h at 90 °C resulted in no change in dr. Additionally subjecting a 5:1 dr of

cyclocarbonylation product **48c** to reaction conditions resulted in no change in dr after three days. Thus, under the Rh(I)-catalyzed cyclocarbonylation conditions rapid isomerization of the allenol acetates is occurring prior to cyclcocarbonylation.

Table 5. Isomerization of Allenol Acetate 42c



42c **42c**

entry	starting dr (major/minor)	$[Rh(CO)_2Cl]_2$ (mol %)	T (°C)	time[a]
1	3:1	10	90	40 min[b]
2	1:3	10	90	40 min[b]
3	3:1	10	rt	7 h[b]
4	1:3	10	rt	7 h[b]
5	3:1	0	90	24[c]
6	1:3	0	90	24[c]

[a]Time until 1:1 dr was observed. [b]Run under CO atm, [c]No epimerization observed after 24 h under Ar.

During the course of our studies of the isomerization of allenol acetates, we noted by ^{1}H NMR, the formation of new resonances not characteristic of starting material **42c** or product **48c**. It was postulated that these new resonances may be a rhodium metallocycle stabilized by coordination of the acetoxy carbonyl. This hypothesis was supported by the disappearance of these resonances and a decrease to 1:1 dr from 2:1 dr observed for **48c** performing the reaction with 10 mol% triphenylphosphine, a competing coordinating ligand.

To further probe and characterize the postulated metallocycle intermediate, allenol ester **42c** (1:1 dr) was reacted with a full equivalent of $[Rh(CO)_2Cl]_2$ in d_8-toluene and the reaction progress was monitored by ^{1}H NMR and the resulting products were characterized by ^{13}C NMR

(Figure 3a-d). After 20 h at rt under argon the resonances for the starting material (Figure 3a) were gone and pairs of new resonances appeared in a 1:1 ratio (Figure 3b). The appearance of resonances at 211.0 (d, $J_{Rh\text{-}C}$ = 27.0 Hz) and 211.4 (d, $J_{Rh\text{-}C}$ = 26.3 Hz) suggest two diastereomeric carbonyl carbons attached to the rhodium[46,47] and the resonances at 182.8 (d, $J_{Rh\text{-}C}$ = 86.3 Hz, 2C) and 183.5 (d, $J_{Rh\text{-}C}$ = 86.3 Hz) suggest diastereomeric rhodium bound carbon monoxides.[48] Disappearance of the resonances for the alkyne carbons of the two diastereomers of **42c** at 108.3, 108.3, 85.1, and 84.9 ppm were also observed. Furthermore, the signals at 102.4 (d, $J_{Rh\text{-}C}$ = 27.2 Hz) and 102.2 (d, $J_{Rh\text{-}C}$ = 26.8 Hz) are consistent with a carbon attached to both a rhodium and an acetoxy group.[47]

Heating this same NMR sample at 90 °C under argon produced new resonances in an apparent 1:1 ratio (Figure 3c) that were not consistent with either starting material **42c** (Figure 3a) or cyclocarbonylation product **48c** (Figure 3d). Disappearance of the resonances at 211.0 (d, $J_{Rh\text{-}C}$ = 27.0 Hz) and 211.4 (d, $J_{Rh\text{-}C}$ = 26.3 Hz) and new resonances at 180.1 (d, $J_{Rh\text{-}C}$ = 73.4 Hz), δ = 184.6 (d, $J_{Rh\text{-}C}$ = 81.4 Hz) and 184.5 (d, $J_{Rh\text{-}C}$ = 81.2 Hz) were observed. Additional resonances proposed to result from sp^2 hybridized carbons at 158.9 (d, $J_{Rh\text{-}C}$ = 24.8 Hz) and 159.3 (d, $J_{Rh\text{-}C}$ = 27.5 Hz), resonances at 144.4 (d, $J_{Rh\text{-}C}$ = 2.4 Hz), 143.4 (d, $J_{Rh\text{-}C}$ = 2.6 Hz), 141.2 (d, $J_{Rh\text{-}C}$ = 1.8 Hz), 140.5 (d, $J_{Rh\text{-}C}$ = 1.4 Hz) were observed with significantly smaller ^{103}Rh coupling constants suggesting a greater distance from the rhodium. The ^{13}C signals at 106.2 (d, $J_{Rh\text{-}C}$ = 24.9 Hz) and 106.0 (d, $J_{Rh\text{-}C}$ = 25.0 Hz) appear to still be consistent with a carbon attached to both a rhodium and an acetoxy group. Based upon these experiments, compounds **57** and **58** (Table 6) are proposed as intermediates corresponding to the spectra in Figure 3b and 3c, respectively.

These postulated intermediates are further supported by the following experiments: 1) Changing the atmosphere in the NMR tube from argon to CO and allowing to react for an additional 19 h at rt resulted in reappearance of the peaks for the first intermediate in a 1:1 ratio (figure 3b); 2) Heating, the resultant mixture at 90 °C under CO led to the appearance of resonances consistent with cyclocarbonylation product **48c** in a 2:1 dr (Figure 3d). After approximately 75% conversion to **48c**, the resonances for the postulated rhodium intermediate **57** had changed to a 3:1 ratio by ^{1}H NMR indicating that one diastereomer was reacting preferentially over the other. This rare example of a trapped Rh(III) intermediate in the cyclocarbonylation reaction is most likely enabled by the coordination of the appending acetoxy ligand.

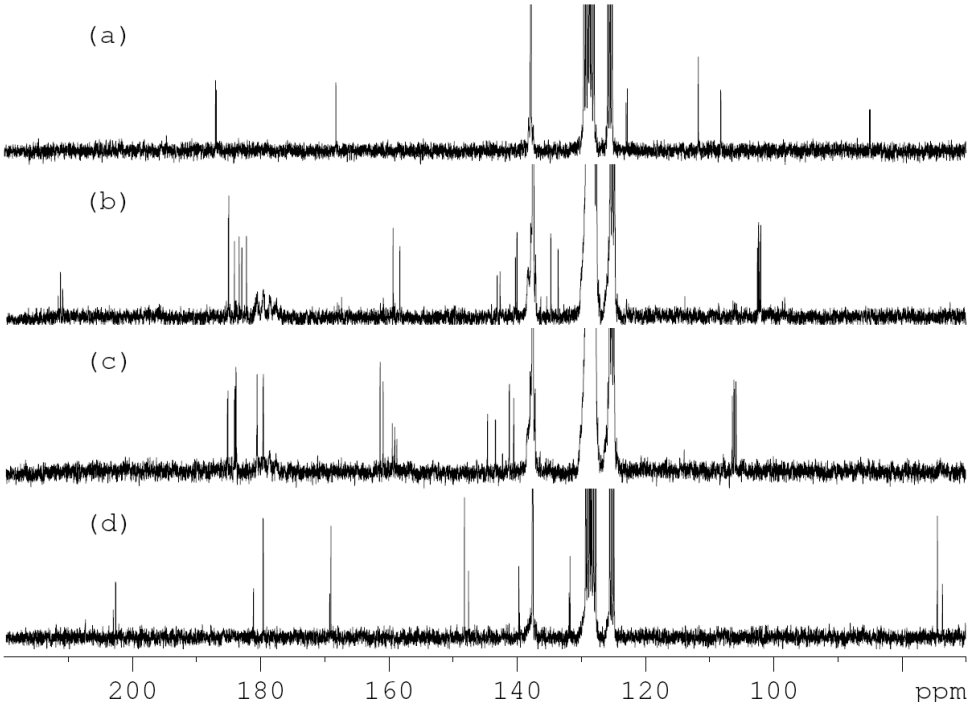
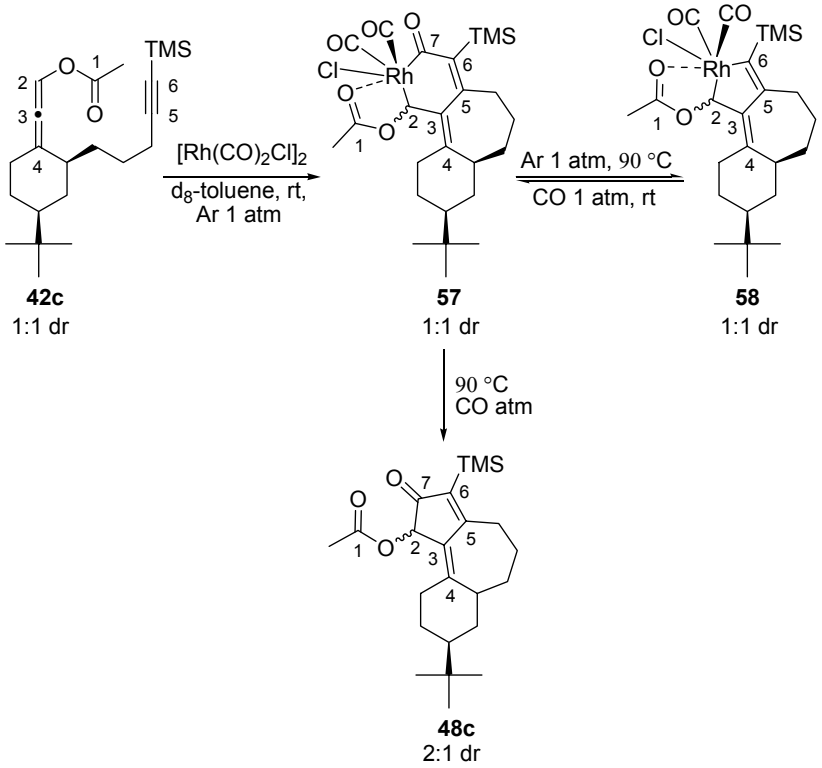


Figure 3. ^{13}C NMR spectrum (in d_8-toluene at 23 °C) (a) 42c, (b) 42c and $[Rh(CO)_2Cl]_2$ after 20 h at rt under Ar, proposed as 57, (c) 42c and $[Rh(CO)_2Cl]_2$ after stirring an additional 17 h at 90 °C under Ar, proposed as 58, (d) Spectrum of isolated 48c.

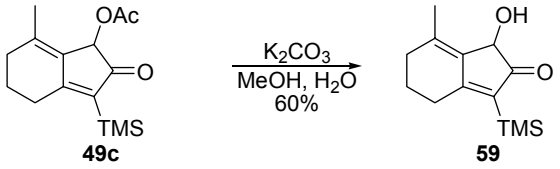
Table 6. ^{13}C Chemical Shifts of 42c, 57, 58, and 48c in d_8-toluene (δC, mult, J_{Rh-C} in Hz)



Position	**42c**	**57**	**58**	**48c**
1	168.3, s	184.9, s	183.9, s	169.0, s
1[a]	168.3, s	185.0, s	183.8, s	169.2, s
2	111.8, s	102.2, d, 26.8	106.0, d, 25.0	74.4, s
2[a]	111.8, s	102.4, d, 27.2	106.2, d, 24.9	73.6, s
3	187.0, s	159.4, s[b]	141.2, d, 1.4	131.8, s
3[a]	186.9, s	158.3, s[b]	140.5, d, 1.8	131.9, s
4	122.8, s	142.7, s[b]	161.4, s	148.2, s
4[a]	123.0, s	143.1, s[b]	160.9, s	147.6, s
5	84.9, s	140.0, s[b]	143.4, d, 2.6	179.6, s
5[a]	85.1, s	140.3, s[b]	144.6, d, 2.4	181.2, s
6	108.3, s	134.8, s[b]	159.3, d, 27.5	139.7, s
6[a]	108.3, s	133.6, s[b]	158.9, d, 24.8	139.6, s
7	–	211.0, d, 27.0	–	202.6, s
7[a]	–	211.4, d, 26.3	–	203.0, s
CO	–	182.8, d, 86.3	184.5, d, 81.2	–
CO[a]	–	183.5, d, 86.3	184.6, d, 81.4	–
CO	–	–	180.1, d, 73.7	–

[a]Minor diastereomer, [b]Carbon assignment is interchangeable.

Removal of the acetate group was achieved. Subjecting acetate **49c** to K_2CO_3 in MeOH/H_2O gave alcohol **59** in 60% yield (Scheme 16). This demonstrates the synthetic utility of the Rh(I)-catalyzed allenic cyclocarbonylation reaction for accessing α-hydroxy containing cyclopentadienones.



Scheme 16. Deprotection of 49c

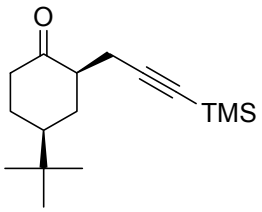
3.0 CONCLUSION

We have demonstrated the first Rh(I)-catalyzed cyclocarbonylation reaction for the formation of α-acetoxy 4-alkylidene cyclopentenones from allenol acetates. Both cyclohexane and linear allene-ynes [6-5] and [7-5] ring systems were prepared in good yields, however [5-5] ring systems proved less successful. The α-acetoxy cyclopentadienone product was prepared from trisubstituted allenol acetates, while tetrasubstituted allenol acetates gave elimination products. Intermediate rhodium(III) metallocycles were characterized by ^{13}C and ^{1}H NMR; representing a rare example of trapping a cyclocarbonylation intermediate. Liberation of the acetate from the α-acetoxy-4-alkylidene cyclopentadienone was readily accomplished yielding an α-hydroxy ketone. Studies are underway to expand the scope of this reaction and increase the stereoselectivity of this reaction.

4.0 EXPERIMENTAL

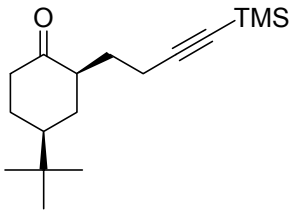
General Methods

Unless otherwise noted, all reactions were performed under a nitrogen atmosphere using standard syringe, cannula, and septum techniques. All commercially available compounds were used as received unless otherwise noted. Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purified using a solvent purification system passing through a column containing Q5 reagent and a column containing activated alumina for THF and passing through a column containing activated alumina for CH_2Cl_2. Toluene, triethylamine (NEt_3), and diisopropylamine were freshly distilled from CaH_2 prior to use. Acetic anhydride (Ac_2O) was distilled from P_2O_5 and stored over 4 Å molecular sieves. Flash chromatography was performed using silica gel (32-63 μm particle size, 60 Å pore size). Thin layer chromatography (TLC) was performed using silica gel plates (60 F_{254}, 250 μm). All ^1H and ^{13}C NMR spectra were obtained on 300 MHz instruments at room temperature unless otherwise specified. Chemical shifts (δ) are reported relative to tetramethylsilane ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.27 ppm). IR spectra were obtained using an FT-IR instrument as a thin film. Diastereomers were not separated for characterization unless stated otherwise. Diastereomeric ratios were assigned using ^1H NMR integrations.



37a-eq

4-Tert-butyl-2-(3-(trimethylsilyl)prop-2-ynyl)cyclohexanone (37a-eq). A flame-dried, 15 mL single-necked round-bottomed flask equipped with a stir-bar was charged with 4-tert-butylcyclohexanone *N*,*N*-dimethylhydrazone[34] (169 mg, 0.861 mmol) and THF (4.3 mL). The solution was cooled in an ice/H_2O bath and *n*-BuLi (0.64 mL, 1.6 M in hexanes, 1.0 mmol) was added dropwise via syringe forming a canary yellow solution. After 1 h in an ice/H_2O bath, 3-(trimethylsilyl)propargyl bromide (0.15 mL, 1.1 mmol) was added dropwise via syringe. The resulting solution was warmed to rt and stirred overnight. The reaction was diluted with Et_2O and H_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were concentrated in vacuo in a 10 mL round-bottomed flask. The residue was diluted with Et_2O (3.3 mL) and a stir-bar was added to the flask. A saturated aq oxalic acid solution (1.3 mL) was added with vigorous stirring at rt; after 6 h, the reaction was diluted with H_2O and Et_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 95:5, v/v) affording the title compound (100 mg, 44%) as a slightly yellow oil as a single diastereomer. **37a-eq** R_f = 0.50 (hexanes/EtOAc, 90:10, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.63 (dd, *J* = 17.0, 4.0 Hz, 1H), 2.49-2.43 (m, 2H), 2.39 (ddd, *J* = 13.5, 4.0, 2.5 Hz, 1H), 2.30 (tdd, *J* = 14.0, 6.0, 1.0 Hz, 1H), 2.16 (dd, *J* = 17.5, 9.0 Hz, 1H), 2.10-2.06 (m, 1H), 1.59, (tt, *J* = 12.0, 3.0 Hz, 1H), 1.41 (qd, *J* = 13.0, 4.5 Hz, 1H), 1.14 (dt, *J* = 12.5, 14.0 Hz, 1H), 0.91 (s, 9H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 210.9, 105.4, 85.9, 48.7, 46.9, 41.2, 34.0, 32.5, 28.5, 27.5, 20.1, 0.0; IR: 2959, 2176, 1716, 1249, 843 cm^{-1}; MS *m/z* (relative intensity): 264 (8%, M^+), 249 (52%), 74, (46%), 72 (91%), 55 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{28}OSi$, 264.1909; found, 264.1907.

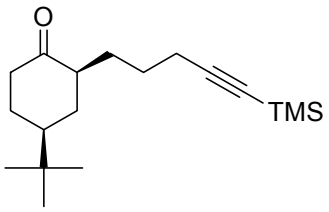


37b-eq

4-Tert-butyl-2-(4-(trimethylsilyl)but-3-ynyl)cyclohexanone (37b-eq).

A flame-dried, single-necked 50 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with 4-tert-butylcyclohexanone *N*,*N*-dimethylhydrazone (500 mg, 2.55 mmol) and THF (12.8 mL). The solution was cooled to -78 °C and *n*-BuLi (1.9 mL, 1.6 M in hexanes, 3.0 mmol) was added dropwise via syringe. The reaction was stirred at -78 °C for 6 h and freshly prepared 4-trimethylsilyl-3-butyn-1-yl triflate (1.05 g, 3.8 mmol) in THF (3.8 mL) was added via cannula at -78 °C. The solution was stirred at -78 °C for 16 h then warmed to -40 °C over 3.5 h and saturated aq NH_4Cl was added. The solution was diluted with Et_2O and H_2O and warmed to rt. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were concentrated in vacuo in a 100 mL round-bottomed flask. The residue was diluted with Et_2O (10 mL) and a stir-bar was added to the flask. A saturated aq oxalic acid solution (3.8 mL) was added with vigorous stirring at rt; after 1 h the reaction was diluted with H_2O and Et_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was taken up in pentanes and filtered. Following concentration in vacuo the crude oil was purified via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v then hexanes/CH_2Cl_2, 7:3 to 1:0, v/v) affording the title compound (36 mg, 5%) as a colorless oil as a single diastereomer. R_f = 0.63 (hexanes/EtOAc, 90:10, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.52-2.40 (m, 1H), 2.40-2.33 (m, 2H), 2.29 (t, *J* = 7.2 Hz, 2H), 2.19-1.97 (m, 3H), 1.60 (tt, *J* = 12.0, 3.0 Hz, 1H), 1.52-1.29 (m, 2H), 1.14 (q, *J* = 12.3 Hz, 1H), 0.92 (s, 9H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 213.0, 107.0, 84.8, 48.4, 47.2, 41.7, 35.0, 32.4, 28.8, 28.1, 27.6, 17.6, 0.2; IR: 2958, 2174, 1714, 1365,

1249, 842 cm^{-1}; MS *m/z* (relative intensity): 278 (45%, M^+), 263 (30%), 154 (68%), 139 (83%), 97 (53%), 74 (90%), 72 (98%), 55 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{17}H_{30}OSi$, 278.2066; found, 278.2063.



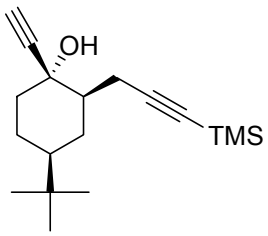
37c-eq

4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexanone (37c).

A flame-dried, 100 mL single-necked round-bottomed flask equipped with a stir-bar was charged with 4-tert-butylcyclohexanone *N*,*N*-dimethylhydrazone (1.02 g, 5.20 mmol) and THF (26 mL). The solution was cooled in an ice/H_2O bath. and *n*-BuLi (5.3 mL, 1.6 M in hexanes, 8.5 mmol) was added dropwise via syringe forming a canary yellow solution. After stirring for 1 h in an ice/H_2O bath, 1-iodo-5-(trimethylsilyl)-4-pentyne (1.70 g, 6.38 mmol) was added dropwise via syringe. The resulting solution was warmed to rt and stirred overnight. The reaction was quenched with a saturated aq NH_4Cl solution and diluted with Et_2O, H_2O, and brine. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were concentrated in vacuo in a 200 mL round-bottomed flask. The residue was diluted with Et_2O (20 mL) and a stir-bar was added to the flask. A saturated aq oxalic acid solution (8 mL) was added with vigorous stirring at rt; after 1 h the reaction was diluted with H_2O and Et_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was taken up in pentanes, filtered, and concentrated in vacuo. The crude material was purified via flash chromatography (pentanes/Et_2O, 95:5 to 8:2, v/v) affording 597 mg **37c-eq**, 219 mg (**37c-eq**/**37c-ax** 1.2:1), 442 mg **37c-ax** with a combined mass of 1.258 g (83%) as a slightly yellow oil as an ~1.5:1 dr. **37c-eq**: R_f = 0.61 (hexanes/EtOAc,

90:10, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.39 (ddd, *J* = 13.5, 5.0, 3.0 Hz, 1H), 2.33 (ddd, *J* = 13.5, 6.0, 1.5 Hz, 1H), 2.31-2.28 (m, 1H), 2.22 (m, 2H), 2.15-2.07 (m, 2H), 1.88-1.82 (m, 1H), 1.61-1.50 (m, 3H), 1.44 (qd, *J* = 13.0, 4.5 Hz, 1H), 1.29-1.23 (m, 1H), 1.15 (q, *J* = 12.5 Hz, 1H), 0.91 (s, 9H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 213.1, 107.3, 84.4, 49.2, 47.1, 41.7, 35.2, 32.4, 28.7, 27.6, 26.3, 20.1, 0.13; IR: 2957, 2174, 1715, 1249, 842 cm^{-1}; MS *m/z* (relative intensity): 292 (13%, M^+), 277 (17%), 235 (14%), 179 (21%), 154 (37%), 138 (41%), 109 (40%), 75 (84%), 73 (88%), 57 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{18}H_{32}OSi$, 292.2222; found, 292.2215.

37c-ax R_I = 0.58 (hexanes/EtOAc, 90:10, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.37 (ddd, *J* = 15.0, 14.0, 6.0 Hz, 1H), 2.35-2.31 (m, 1H), 2.26-2.22 (m, 1H), 2.18 (t, *J* = 7.0 Hz, 2H), 1.98-1.94 (m, 1H), 1.81-1.75 (m, 2H), 1.63-1.44 (m, 4H), 1.43-1.36 (2H), 0.86 (s, 9H), 0.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 215.1, 106.6, 84.7, 48.6, 41.1, 38.2, 32.1, 31.6, 30.3, 27.3, 26.9, 26.0, 19.5, 0.0



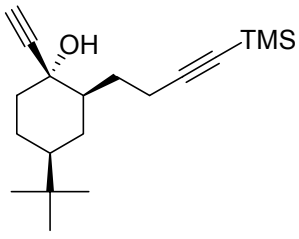
38a-ax

4-Tert-butyl-1-ethynyl-2-(3-(trimethylsilyl)prop-2-ynyl)cyclohexanol (38a).

A flame-dried, single-necked 10 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with the major diastereomer of **37a-eq** (100 mg, 0.378 mmol) and THF (1.9 mL). The solution was cooled in an ice/H_2O bath and ethynylmagnesium bromide (2.3 mL, 0.5 M in THF, 1.2 mmol) was added rapidly via syringe and the solution was allowed to warm to rt. After 90 min, the reaction was complete by TLC and the solution was diluted with Et_2O and H_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and

concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded 32 mg **54a-ax**, 19 mg (**54a-ax**/**54a-eq** 1.5:1), 45 mg **54a-eq** with a combined mass of 95 mg (86%) as off white solids in an ~1.1:1 dr. **38a-ax**: R_f = 0.13 (hexanes/EtOAc, 95:5, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.18 (bs, 1H), 2.67 (dd, *J* = 17.0, 7.0 Hz, 1H), 2.52 (s, 1H), 2.20 (dd, *J* = 17.0, 7.5 Hz, 1H), 2.08 (dt, *J* = 12.5, 3.0 Hz, 1H), 1.88 (dq, *J* = 13.0, 3.0 Hz, 1H), 1.78-1.71 (m, 2H), 1.56 (td, *J* = 12.5, 3.5 Hz, 1H), 1.33 (qd, *J* = 12.0, 3.5 Hz, 1H), 1.10 (tt, *J* = 12.0, 3.0 Hz, 1H), 0.98 (q, *J* = 13.0 Hz, 1H), 0.87 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 106.6, 86.9, 84.1, 74.7,73.0, 47.2, 46.9, 40.7, 32.3, 30.8, 27.5, 24.4, 22.4, 0.0; IR: 3295, 2956, 2175, 1250, 841 cm^{-1}; MS *m/z* (relative intensity): 290 (8%, M^+), 275 (11%), 233 (23%), 74 (97%), 72 (96%), 55 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{18}H_{30}OSi$, 290.2066; found, 290.2074.

38a-eq: R_f = 0.18 (hexanes/EtOAc, 95:5, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.64 (dd, *J* = 17.0, 4.0 Hz, 1H), 2.54 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.46 (s, 1H), 2.34 (s, 1H), 2.10 (dt, *J* = 14.0, 3.5 Hz, 1H), 1.85 (dq, *J* = 13.0, 2.0 Hz, 1H), 1.75-1.55 (m, 3H), 1.38 (qd, *J* = 12.5, 3.0 Hz, 1H), 1.29 (q, *J* = 12.5 Hz, 1H), 1.12 (tt, *J* = 12.0, 3.0 Hz, 1H), 0.89 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 106.3, 87.7, 87.2, 71.7, 69.1, 47.4, 45.1, 40.4, 32.6, 27.4, 26.5, 22.2, 21.5, 0.0



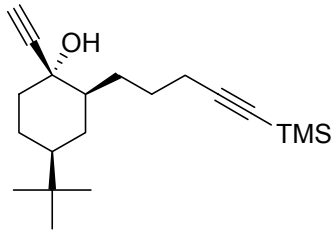
38b-ax

4-Tert-butyl-1-ethynyl-2-(4-(trimethylsilyl)but-3-ynyl)cyclohexanol (38b).

A flame-dried, single-necked 10 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with a single diastereomer of **37b-eq** (34 mg, 0.12 mmol) and THF (0.61 mL). The solution was cooled in an ice/H_2O bath and ethynylmagnesium bromide (0.73 mL, 0.5 M in THF, 0.37 mmol) was added rapidly via syringe

and the solution was allowed to warm to rt. After 40 min the reaction was complete by TLC and the solution was diluted with Et_2O and H_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded 21 mg **37b-ax** and 7 mg **37b-eq** with a combined mass of 28 mg (76%) as a slightly yellow oil as a 2.6:1 dr. Diastereomers were separated by flash chromatography. **38b-ax**: R_f = 0.45 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.49 (s, 1H), 2.44-2.21 (m, 2H), 2.18 (s, 1H), 2.13-2.02 (m, 2H), 1.82-1.25 (m, 6H), 1.12-0.94 (m, 2H), 0.87 (s, 9H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 107.6, 84.9, 84.8, 74.3, 72.6, 47.2, 47.0, 41.4, 32.3, 30.2, 29.9, 27.6, 24.7, 18.3, 0.2; IR: 3469, 3308, 2954, 2173, 1366, 1249, 843; MS *m/z* (relative intensity): 304 (36%, M^+), 289 (50%), 286 (78%), 271 (39%), 261 (39%), 74 (90%), 72 (98%), 55 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{19}H_{32}OSi$, 304.2222; found, 304.2210.

38b-eq: R_f = 0.51 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.44 (s, 1H), 2.42-2.07 (m, 4H), 1.78-1.68 (m, 2H), 1.62 (s, 1H), 1.63-1.26 (m, 4H), 1.12-0.92 (m, 2H), 0.87 (s, 9H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 107.4, 88.2, 84.7, 71.5, 69.2, 47.3, 45.4, 40.7, 32.5, 30.2, 27.5, 26.8, 21.6, 18.1, 0.2.



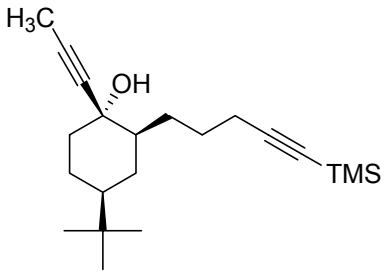
38c-ax

4-Tert-butyl-1-ethynyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexanol (38c).

A flame-dried, single-necked 50 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with the major diastereomer **37c-eq** (597 mg, 2.04 mmol) and THF (10 mL). The solution was cooled in an ice/H_2O bath and ethynylmagnesium bromide (12.2 mL, 0.5 M in THF, 6.10 mmol) was added

rapidly via syringe and the solution was allowed to warm to rt. After 1.5 h the reaction was complete by TLC and the solution was quenched with saturated aq NH_4Cl solution. The volume was reduced in vacuo and the remaining solution was diluted with Et_2O and H_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude oil (2:1 dr by crude ^1H NMR) via flash chromatography (hexanes/EtOAc, 97.5:2.5 to 8:2 v/v) afforded 146 mg **38c-ax** and 439 mg **38c-eq** with a combined mass of 585 mg (90%) as a slightly yellowish oil. **38c-ax**: R_f = 0.50 (hexanes/EtOAc, 80:20, v/v); ^1H NMR (500 MHz, $CDCl_3$) δ: 2.46 (s, 1H), 2.26-2.21 (m, 2H), 2.17 (s, 1H), 2.05 (dt, *J* = 12.0, 3.5 Hz, 1H), 1.92-1.85 (m, 1H), 1.80 (dq, *J* = 13.0, 3.0 Hz, 1H), 1.74-1.67 (m, 2H), 1.52 (td, *J* = 13.0, 3.5 Hz, 1H), 1.52-1.43 (m, 1H), 1.37 (tt, *J* = 10.0, 3.0 Hz, 2H), 1.32-1.28 (m, 1H), 1.04 (tt, *J* = 12.0, 3.0 Hz, 1H), 0.95 (q, *J* = 12.0 Hz, 1H), 0.86 (s, 9H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 107.6, 85.0, 84.5, 74.1, 72.6, 47.1, 47.0, 41.2, 32.2, 30.1, 29.8, 27.6, 26.7, 24.6, 20.6, 0.1; IR: 3518, 3309, 2952, 2174, 1366, 1249, 844 cm^{-1}; MS *m/z* (relative intensity): 318 (16%, M^+), 285 (12%), 261 (20%), 245 (29%), 149 (27%), 75 (38%), 73 (100%), 57 (70%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{20}H_{34}OSi$, 318.2379; found, 318.2365.

38c-eq: R_f = 0.57 (hexanes/EtOAc, 80:20, v/v); ^1H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 1H), 2.27-2.23 (m, 2H), 2.10 (dt, *J* = 14.0, 3.0 Hz, 1H), 2.04-1.96 (m, 1H), 1.73-1.66 (m, 3H), 1.63 (s, 1H), 1.57-1.43 (m, 3H), 1.34-1.26 (m, 2H), 1.04 (tt, *J* = 9.5, 2.5 Hz, 1H), 0.99 (q, *J* = 11.5 Hz, 1H), 0.86 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 107.5, 88.4, 84.4, 71.2, 69.4, 47.3, 45.7, 40.5, 32.5, 30.5, 27.5, 27.0, 27.0, 21.6, 20.2, 0.2



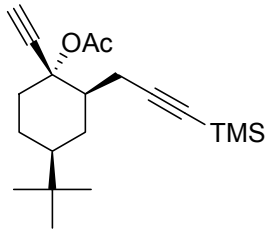
38d-ax

4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)-1-(prop-1-ynyl)cyclohexanol (38d).

A flame-dried, single-necked 15 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with the major diastereomer of **37c** (351 mg, 1.19 mmol) and THF (4 mL). The solution was cooled in an ice/H_2O bath and 1-propynylmagnesium bromide (4.8 mL, 0.5 M in THF, 2.4 mmol) was added rapidly via syringe and the solution was allowed to warm to rt. After 2.5 h the reaction was complete by TLC and the reaction was diluted with H_2O, Et_2O, and brine (to break up the emulsion). The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude (3:1 dr by crude ^{1}H NMR) oil via flash chromatography (hexanes/EtOAc, 95:5 to 8:2 v/v) afforded 186 mg **54d-ax** and 70 mg **54d-eq** separate diastereomers of the title compound with a combined mass of 256 mg (63%) as a faintly yellow oil. **38d-ax**: R_f = 0.52 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.25-2.20 (m, 2H), 2.07 (bs, 1H), 1.98 (dt, *J* = 12.5, 3.5 Hz, 1H), 1.88-1.81 (m, 1H), 1.84 (s, 3H), 1.75 (dq, *J* = 13.0, 2.5 Hz, 1H), 1.70-1.64 (m, 2H), 1.50-1.44 (m, 2H), 1.34-1.20 (m, 3H), 1.01 (tt, *J* = 12.0, 3.5 Hz, 1H), 0.90 (q, *J* = 12.5 Hz, 1H), 0.85 (s, 9H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 107.7, 84.4, 81.9, 80.2, 72.9, 47.5, 47.2, 41.6, 32.3, 30.3, 30.0, 27.6, 26..8, 24.9, 20.3, 3.5, 0.1; IR: 3406, 2951, 2866, 2246, 2174, 1366, 1249, 1031, 843 cm^{-1}; MS *m/z* (relative intensity): 332 (6%, M^+), 317 (9%), 275 (20%), 259 (24%), 167 (46%), 95 (63%), 74 (84%), 72 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{21}H_{36}O_1Si$, 332.2535; found, 332.2522.

38d-eq: R_f = 0.61 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.26-2.23 (m, 2H), 2.04 (dt, *J* = 14.0, 3.0 Hz, 1H), 1.99-1.92 (m, 1H), 1.83 (s, 3H), 1.74-1.61 (m, 3H), 1.55-

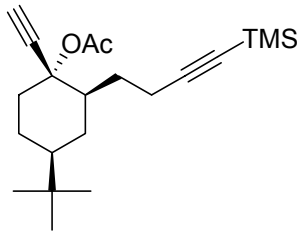
1.45 (m, 3H), 1.41-1.20 (m, 3H), 1.04-0.03 (m, 2H), 0.85 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 107.7, 84.2, 84.0, 79.0, 69.5, 47.4, 46.1, 41.0, 32.5, 30.7, 27.5, 27.3, 27.1, 21.8, 20.3, 3.6, 0.2



39a-ax major diastereomer

4-Tert-butyl-1-ethynyl-2-(3-(trimethylsilyl)prop-2-ynyl)cyclohexyl acetate (39a-ax).

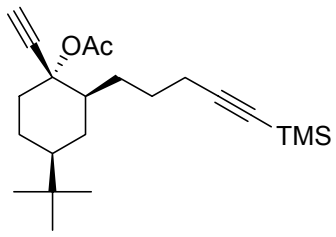
A flame-dried, single-necked 5 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with **38a** (45 mg, 0.16 mmol) ~7:1 **38a-ax/38a-eq**, *N*,*N*-dimethyl-4-aminopyridine (20 mg, 0.16 mmol), and NEt_3 (0.21 mL, 1.5 mmol). The solution was cooled in an ice/H_2O bath and acetic anhydride (0.07 mL, 0.7 mmol) was added via syringe. The solution was warmed to rt. After 19 h the mixture was diluted with Et_2O and passed through a plug of silica gel. The filtrate was concentrated in vacuo the crude oil was purified via flash chromatography (hexanes/EtOAc, 95:5, v/v) affording the title compound (48 mg, 93%) as a slightly yellow oil in ~6:1 dr. **39a-ax**: R_f = 0.57 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.88-2.84 (m, 1H), 2.97 (dd, *J* = 16.8, 3.6 Hz, 1H), 2.62 (s, 1H), 2.22 (dd, *J* = 16.8, 10.8 Hz, 1H), 2.26-2.09 (m, 1H), 2.02 (s, 3H), 1.98-1.85 (m, 1H), 1.77-1.56 (m, 1H), 1.46-1.41 (m, 2H), 1.23-1.03 (m, 2H), 1.87 (s, 9H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.2, 106.1, 85.7, 79.7, 79.0, 77.1, 46.8, 46.0, 36.0, 32.3, 29.0, 27.4, 24.3, 21.9, 21.4; IR: 3273, 2958, 2175, 1749, 1367, 1230, 843 cm^{-1}; MS *m/z* (relative intensity): 332 (8%, M^+), 317 (8%), 257 (22%), 215 (27%), 117 (89%), 74 (86%), 72 (100%), 55 (98%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{20}H_{32}O_2Si$, 332.2172; found, 332.2176.



39b-ax

4-Tert-butyl-1-ethynyl-2-(4-(trimethylsilyl)but-3-ynyl)cyclohexyl acetate (39b-ax).

A flame-dried, single-necked 5 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with an 8:1 mixture of **54b-ax/54b-eq** (21 mg, 0.069mmol), *N*,*N*-dimethyl-4-aminopyridin*e* (9 mg, 0.07 mmol), and NEt_3 (0.2 mL, 1.4 mmol). The flask was cooled in an ice/H_2O bath and acetic anhydride (0.26 mL, 2.8 mmol) was added via syringe. The solution was warmed to rt and stirred for 17 h. The solution was diluted with Et_2O, passed through a plug of silica gel, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (22 mg, 92%) as a slightly yellow oil as single diastereomer. **39b-ax**: R_f = 0.60 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.89-2.84 (m, 1H), 2.62 (s, 1H), 2.42-2.16 (m, 2H), 2.10-2.02 (m, 1H), 2.04 (s, 3H), 1.86-1.68 (m, 3H), 1.52-1.37 (m, 3H), 1.18-1.02 (m, 2H), 0.87 (s, 9H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.3, 107.4, 84.6, 80.6, 79.7, 76.5, 46.9, 45.5, 36.2, 32.3, 29.8, 29.4, 27.5, 24.2, 22.1, 18.1, 0.2; IR: 3278, 2957, 2174, 1747, 1367, 1233, 843 cm^{-1}; MS *m/z* (relative intensity): 346 (4%, M^+), 331 (57%), 117 (72%), 72 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{21}H_{34}O_2Si$, 346.2328; found, 346.2329.



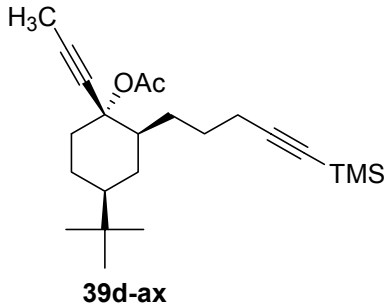
39c-ax

4-Tert-butyl-1-ethynyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexyl acetate (39c).

A flame-dried, single-necked 25 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with the major diastereomer of **38c-ax** (390 mg, 1.22 mmol), THF (12.2mL), *N*,*N*-dimethyl-4-aminopyridine (80 mg, 0.65 mmol), and NEt_3 (0.94 mL, 6.7 mmol). The solution was cooled in an ice/H_2O bath

and acetic anhydride (0.57 mL, 6.0 mmol) was added via syringe. The solution was allowed to return to rt and stirred for 4 d, whereupon consumption of **33c** was observed by TLC brine and saturated aq NH_4Cl were added. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 9:1 v/v) afforded the title compound (335 mg, 76%) as a slightly yellow oil as a single diastereomer. **39c-ax**: R_f = 0.44 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.86-2.81 (m, 1H), 2.59 (s, 1H), 2.23 (t, *J* = 7.2 Hz, 2H), 2.03 (s, 3H), 1.90-1.78 (m, 2H), 1.72-1.61 (m, 3H), 1.55-1.37 (m, 3H), 1.33-1.21 (m, 1H), 1.15-1.04 (m, 2H), 0.86 (s, 9H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.2, 107.5, 84.4, 80.6, 80.0, 76.3, 46.9, 45.7, 36.2, 32.3, 30.0, 29.7, 27.5, 26.8, 24.2, 22.0, 20.1, 0.2; IR: 3309, 2954, 2174, 1747, 1230, 844 cm^{-1}; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{22}H_{36}O_2NaSi$, 383.2382; found, 383.2376.

39c-eq: R_f = 0.60 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.02 (dt, *J* = 14.5, 3.5 Hz, 1H), 2.53 (s, 1H), 2.31-2.20 (m, 2H), 2.05 (s, 3H), 2.07-2.00 (m, 1H), 1.77-1.63 (m, 2H), 1.62-1.55 (2 H), 1.54-1.44 (m, 2H), 1.40-1.31 (m, 1H), 1.14-1.05 (m, 3H), 0.87 (s, 9H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.3, 107.5, 84.5, 84.0, 76.4, 73.4, 46.9, 46.8, 35.4, 32.4, 30.4, 27.4, 27.3, 27.0, 21.7, 21.6, 20.2, 0.2.

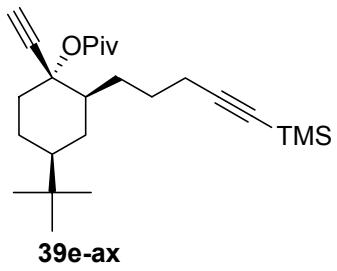


39d-ax

4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)-1-(prop-1-ynyl)cyclohexyl acetate (39d-ax).

A flame-dried, single-necked 5 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with the major diastereomer of **38d-ax** (186 mg, 0.560 mmol), NEt_3 (0.78 mL, 5.6 mmol), and *N*,*N*-dimethyl-4-aminopyridine (69 mg, 0.56 mmol). The solution was

cooled in an ice/H_2O bath and acetic anhydride (0.26 mL, 2.8 mmol) was added via syringe. The solution was warmed to rt and stirred 21 h. The solution was transferred to a separatory funnel and diluted with Et_2O and H_2O. The organic layer was separated and washed with saturated aq NH_4Cl, brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (174 mg, 83%) as a slightly yellow oil as single a diastereomer. R_f = 0.67 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.73 (dt, *J* = 12, 3.5 Hz, 1H), 2.23-2.19 (m, 2H), 1.98 (s, 3H), 1.86 (s, 3H), 1.86-1.77 (m, 1H), 1.75-1.71 (m, 1H), 1.67-1.58 (m, 3H), 1.49-1.30 (m, 3H, 1.26-1.18 (m, 1H), 1.07-9.98 (m, 2H), 0.84 (s, 9H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.3, 107.6, 84.2, 84.1, 80.8, 76.0, 46.8, 46.0, 36.4, 32.2, 30.1, 29.8, 27.5, 26.8, 24.3, 22.1, 20.2, 3.6, 0.1; IR: 2954, 2250, 2174, 1745, 1366, 1235, 1019, 843; 374 MS *m/z* (relative intensity): (5%, M^+), 359 (4%), 331 (24%), 317 (20%), 275 (34%), 257 (39%), 219 (54%), 194 (68%), 117 (100%), 74 (89%), 72 (95%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{23}H_{38}O_2Si$, 374.2641; found, 374.2631.

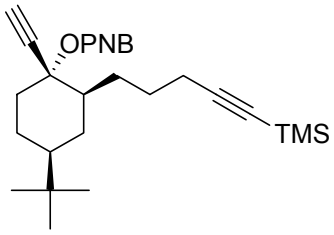


39e-ax

(1S,2S,4S)-4-Tert-butyl-1-ethynyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexyl pivalate (39e-ax).

To a flame-dried, 5 mL round-bottomed flask containing a Teflon-coated stir-bar was added the major diastereomer of **38c-ax** (185 mg, 0.581 mmol), CH_3CN (2.3 mL), and trimethylacetic anhydride (0.17 mL, 0.84 mmol). A solution of $Sc(OTf)_3$ (0.06 mL, 0.1 M in CH_3CN, 0.006 mmol) was added via syringe, immediately the reaction turned a reddish color. After 20 min at rt, consumption of **38c-ax** was observed via TLC. The reaction was then quenched with saturated aq $NaHCO_3$ and diluted with H_2O and Et_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers

were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (191 mg, 82%) as a solid as a single diastereomer. R_f = 0.78 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500) MHz, $CDCl_3$) δ: 2.87-2.79 (m, 1H), 2.55 (s, 1H), 2.22 (t, *J* = 7.0 Hz, 2H), 1.90-1.82 (m, 1H), 1.82-1.77 (m, 1H), 1.72-1.60 (m, 3H), 1.53-1.42 (m, 1H), 1.41-1.32 (m, 2H), 1.31-1.22 (m, 1H), 1.17 (s, 9H), 1.12-1.01 (m, 2H), 0.85 (s, 9H), 0.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.4, 107.4, 84.3, 80.7, 79.2, 76.0, 46.9, 45.9, 39.2, 36.1, 32.2, 30.0, 29.5, 27.5, 27.1, 26.8, 24.2, 20.2, 0.1; IR: 3311, 2957, 2869, 2174, 1739, 1478, 1366, 1249, 1155, 843 cm^{-1}; MS *m/z* (relative intensity): 402 (13%, M^+), 387 (43%), 301 (49%), 243 (44%), 227 (45%), 171 (61%), 159 (84%), 73 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{25}H_{42}O_2Si$, 402.2954; found, 402.2950.

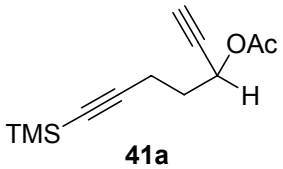


39f-ax

(1S,2S,4S)-4-Tert-butyl-1-ethynyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexyl 4-nitrobenzoate (39f-ax).

To a flame-dried 5 mL round-bottomed flask containing a Teflon-coated stir-bar was added the major diastereomer of **38c-ax** (103 mg, 0.323 mmol), *N*,*N*-dimethyl-4-aminopyridine (10 mg, 0.08 mmol), and 4-nitrobenzoyl chloride (92 mg, 1.1 mmol). Pyridine (1.6 mL) were added, the flask was equipped with an internal reflux condenser, and placed in a 80 °C oil bath. After 23 h at 80 °C consumption of starting material was observed via TLC. The majority of the solvent was removed in vacuo. The residue was dissolved with CH_2Cl_2 and saturated aq $NaHCO_3$, brined, and H_2O were added. The mixture was shaken and the organic layer was separated. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (112 mg, 74%). R_f = 0.64 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.31-8.27 (m, 2H), 8.18-8.15 (m, 2H), 2.99 (dt, *J* = 12.0, 3.5 Hz, 1H), 2.71

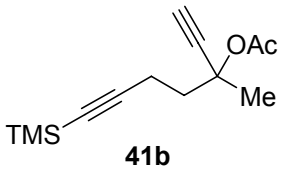
(s, 1H), 2.29 (t, J = 7.0 Hz, 2H), 2.01-1.86 (m, 3H), 1.83-1.70 (m, 2H), 1.66-1.37 (m, 4H), 1.23-1.09 (m, 2H), 0.90 (s, 9H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 162.8, 150.4, 136.4, 130.6, 123.5, 107.2, 84.7, 82.0, 79.9, 77.3, 46.8, 46.0, 36.3, 32.3, 30.3, 29.8, 27.5, 26.8, 24.3, 20.4, 0.1; IR: 3300, 2956, 2867, 2173, 1731, 1530, 1348, 1282, 1261, 1098, 842 cm^{-1}; MS *m/z* (relative intensity): 467 (13%, M^+), 452 (34%), 300 (30%), 224 (91%), 150 (77%), 73 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{27}H_{37}NO_4Si$, 467.2492; found, 467.2500.



41a

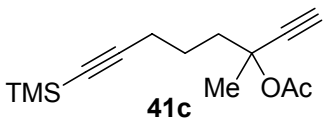
7-(Trimethylsilyl)hepta-1,6-diyn-3-yl acetate (41a).

A flame-dried, single-necked 25 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with 5-(trimethylsilyl)pent-4-ynal (250 mg, 1.62 mmol) and THF (5.4 mL). The solution was cooled in an ice/H_2O bath and ethynylmagnesium bromide (9.7 mL, 0.5 M in THF, 4.9 mmol) was added rapidly via syringe. After 1 h in an ice/H_2O bath, consumption of 5-(trimethylsilyl)pent-4-ynal was observed by TLC and acetyl chloride (0.58 mL, 8.1 mmol) was added via syringe. After stirring 1 h, the reaction was complete by TLC and the solution was diluted with Et_2O, H_2O, and brine. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (197 mg, 55%) as a slightly yellow oil. R_f = 0.59 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.36 (td, J = 6.3, 1.8 Hz, 1H), 2.45 (d, J = 2.1 Hz, 1H), 2.33 (t, J = 7.2 Hz, 2H), 2.02 (s, 3H), 1.98-1.90 (m, 2H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.4, 104.8, 85.4, 80.3, 74.0, 62.3, 33.3, 20.7, 15.6, -0.1; IR: 3290, 2961, 2177, 2123, 1747, 1372, 1230, 1047, 845, 761 cm^{-1}; MS *m/z* (relative intensity): 207 (46%, M^+), 147 (68%), 117 (89%), 74 (98%), 72 (100%); HRMS-EI (*m/z*): $[M - CH_3]^+$ calcd for $C_{11}H_{15}O_2Si$, 207.0841; found, 207.0841.



41b

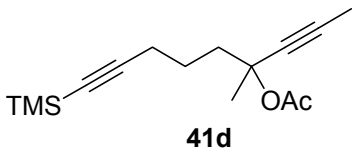
3-Methyl-7-(trimethylsilyl)hepta-1,6-diyn-3-yl acetate (41b). A flame-dried, single-necked 10 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with 6-(trimethylsilyl)hex-6-yn-2-one (80 mg, 0.48 mmol) and THF (1.6 mL). The solution was cooled in an ice/H_2O bath and ethynylmagnesium bromide (2.8 mL, 0.5 M in THF, 1.4 mmol) was added rapidly via syringe. The solution was allowed to slowly warm to rt . After 40 min consumption of 6-(trimethylsilyl)hex-6-yn-2-one was observed by TLC and acetyl chloride (0.17 mL, 2.4 mmol) was added via syringe. After stirring 1 h the reaction was complete by TLC and the solution was diluted with Et_2O and the solvent was removed in vacuo. The residue was diluted with Et_2O and H_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (93 mg, 82%) as a slightly yellow oil. R_f = 0.60 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.54 (s, 1H), 2.41 (t, J = 8.1 Hz, 2H), 2.22-2.12 (m, 1H), 2.06-2.41 (m, 1H), 1.99 (s, 3H), 1.66 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.0, 106.0, 84.7, 82.7, 73.9, 73.8, 40.5, 26.2, 21.7, 15.1, -0.01; IR: 3284, 2960, 2177, 1748, 1248, 1087, 845 cm^{-1}; MS *m/z* (relative intensity): 221 (44%, M – CH_3), 193 (25%), 161 (29%), 117 (90%), 74 (95%), 72 (100%); HRMS-EI (*m/z*): $[M - CH_3]^+$ calcd for $C_{12}H_{17}O_2Si$, 221.0998; found, 221.0989.



41c

3-Methyl-8-(trimethylsilyl)octa-1,7-diyn-3-yl acetate (41c). A flame-dried, single-necked 10 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with 7-(trimethylsilyl)hept-6-yn-2-one (181 mg, 0.993 mmol) and THF (3.3 mL). The solution was cooled in an ice/H_2O bath and ethynylmagnesium

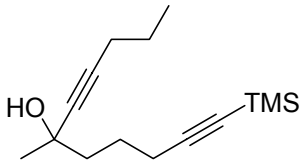
bromide (6.0 mL, 0.5 M in THF, 3.0 mmol) was added rapidly via syringe. After 30 min in an ice/H_2O bath, consumption of 7-(trimethylsilyl)hept-6-yn-2-one was observed by TLC and acetyl chloride (0.35 mL, 4.9 mmol) was added via syringe. After stirring an additional 75 min, the reaction was complete by TLC and the solution was diluted with Et_2O, H_2O, and brine. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine (2×), dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (204 mg, 82%) as a slightly yellow oil. R_f = 0.57 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.53 (s, 1H), 2.22 (t, *J* = 7.2 Hz, 2H), 2.04-1.93 (m, 1H), 1.98 (s, 3H), 1.90-1.78 (m, 1H), 1.71-1.57 (m, 2H), 1.64 (s, 3H), 0.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.1, 106.6, 84.8, 83.4, 74.3, 73.4, 40.5, 26.3, 23.4, 21.8, 19.6, 0.0; IR: 3286, 2959, 2174, 1747, 1369, 1249, 844 cm^{-1}; MS *m/z* (relative intensity): 235 (50%, M – CH_3), 175 (60%), 117 (99%), 75 (95%), 73 (100%); HRMS-EI (*m/z*): $[M - CH_3]^+$ calcd for $C_{13}H_{19}O_2Si$, 235.1154; found, 235.1161.



41d

4-Methyl-9-(trimethylsilyl)nona-2,8-diyn-4-yl acetate (41d). To a flame-dried, 25 mL round-bottomed flask equipped with a Teflon-coated stir-bar was added 7-(trimethylsilyl)hept-6-yn-2-one (318 mg, 1.74 mmol) and THF (5.8 mL). The solution was cooled in an ice/H_2O bath and 1-propynylmagnesium bromide (10.5 mL, 0.5 M in THF, 5.25 mmol) was added via syringe. The reaction was stirred for 1h in an ice/H_2O bath until consumption of starting material was observed via TLC. Acetyl chloride (0.62 mL, 8.7 mmol) was added via syringe and the reaction was warmed to rt. After 2 h at rt, the starting material was consumed by TLC and the reaction was diluted with Et_2O and H_2O. The aq layer was separated and extracted with Et_2O (2×). The

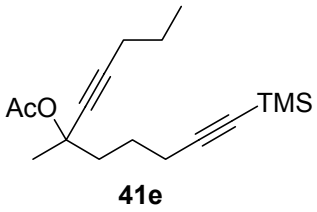
combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 90:10, v/v) afforded the title compound (380 mg, 83%). R_f = 0.58 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.23 (t, *J* = 6.9 Hz, 2H), 2.05-1.91 (m, 1H), 1.98 (s, 3H), 1.86-1.77 (m, 1H), 1.82 (s, 3H), 1.75-1.62 (m, 2H), 1.62 (s, 3H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.3, 106.9, 84.7, 81.3, 79.2, 75.4, 41.0, 26.7, 23.7, 22.0, 19.8, 3.6, 0.1; IR: 2959, 2921, 2250, 2175, 1745, 1369, 1247, 1169, 1017, 844.1 cm^{-1}. MS *m/z* (relative intensity): 264 (46%, M^+), 250 (35%), 223 (96%), 149 (95%), 148 (97%), 96 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{15}H_{24}O_2Si$, 264.1546; found, 264.1542.



60e

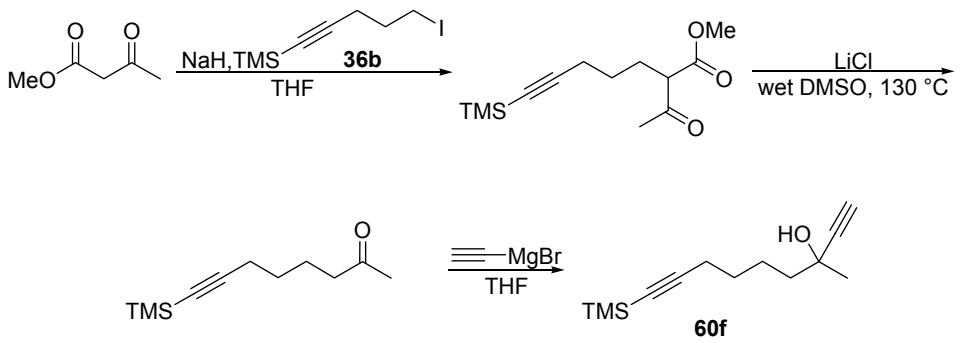
6-Methyl-1-(trimethylsilyl)undeca-1,7-diyn-6-ol (60e). To a flame-dried 50 mL round-bottomed flask equipped with a Teflon-coated stir-bar was added THF (13.4 mL) and 1-pentyne (0.66 mL, 6.7 mmol). The solution was cooled to -78 °C and *n*-BuLi (0.79 ml, 1.6 M in hexanes, 1.3 mmol) was added via syringe. The reaction was stirred 30 min at -78 °C and a solution of 7-(trimethylsilyl)hept-6-yn-2-one (153 mg, 0.840 mmol) in THF (0.8 mL) was added via syringe. The solution was warmed to rt. After 1 h at rt, consumption of starting material was observed via TLC and the reaction was quenched with saturated aq NH_4Cl and diluted with Et_2O and H_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. Purification of the crude material via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (141 mg, 67%). R_f = 0.56 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.27-2.19 (m, 2H), 2.16 (s, 1H), 2.13 (t, *J* = 6.9 Hz, 2H), 1.76-1.64 (m, 4H), 1.48 (sext, *J* = 7.2 Hz, 2 H), 1.43 (s, 3H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.11 (s 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 107.1, 84.6,

83.9, 83.7, 67.9, 43.0, 30.2, 24.1, 22.0, 20.5, 19.9, 13.4, 0.1; IR: 3407, 2961, 2241, 2174, 1458, 1250, 842 cm^{-1}; MS *m/z* (relative intensity): 235 (41%, M – CH_3), 233 (53%, M – OH), 219 (39%), 159 (88%), 125 (76%), 96 (98%), 83 (81%), 69 (100%); HRMS-EI (*m/z*): $[M - CH_3]^+$ calcd for $C_{14}H_{23}OSi$: 235.1518; found: 235.1521.



41e

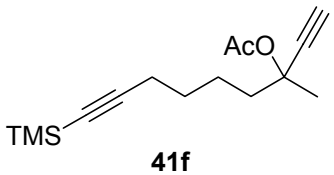
6-Methyl-1-(trimethylsilyl)undeca-1,7-diyn-6-yl acetate (41e). To a flame-dried, 5 mL round-bottomed flask equipped with a stir-bar was added **60e** (141 mg, 0.563 mmol), CH_2Cl_2 (1.1 mL), NEt_3 (0.31 mL, 2.2 mmol), and *N*,*N*-dimethyl-4-aminopyridine (22 mg, 0.18 mmol). The mixture was cooled in an ice/H_2O bath and acetic anhydride (0.11 mL, 1.2 mmol) was added via syringe. The reaction was warmed to rt and stirred for 11 h. The solution was then diluted with H_2O and Et_2O and quenched with the addition of saturated aq NH_4Cl. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brined, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude material via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (120 mg, 73%). R_f = 0.64 (hexanes/EtOAc, 80:20, v/v); ^1H NMR (500 MHz, $CDCl_3$) δ: 2.27-2.22 (m, 2H), 2.17 (t, *J* = 7.0 Hz, 2H), 2.01-1.95 (m, 1H), 1.99 (s, 3H), 1.86-1.80 (m, 1H), 1.73-1.66 (m, 2H), 1.64 (s, 3H), 1.51 (sext, *J* = 7.0 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.2, 107.0, 85.7, 85.0, 80.3, 75.5, 41.0, 26.8, 23.8, 22.0, 20.6, 19.8, 13.4, 0.1; IR: 2961, 2873, 2245, 2175, 1746, 1368, 1246, 843 cm^{-1}; MS *m/z* (relative intensity): 292 (3%, M^+), 291 (6%), 277 (32%), 250 (24%), 126 (45%), 117 (100%), 111 (70%), 96 (47%). 83 (69%); HRMS-EI (*m/z*): $[M - CH_3]^+$ calcd for $C_{16}H_{25}O_2Si$, 277.1624; found, 277.1625.



3-Methyl-9-(trimethylsilyl)nona-1,8-diyn-3-ol (60f).

To a flame-dried, 50 mL round-bottomed flask containing a Teflon-coated stir-bar was added NaH (426 mg, 60% dispersion in mineral oil, 10.7 mmol) and THF (7.6 mL). The resulting suspension was cooled in an ice/H_2O bath and methyl acetoacetate (1.39 mL, 11.4 mmol) was added via syringe. The reaction was stirred 5 min in an ice/H_2O bath and then warmed to rt. After 10 min at rt a solution of 5-iodo-1-(trimethylsilyl)-1-pentyne (2.024 g, 7.60 mmol) in DMF (7.6 mL) was added via syringe. The reaction was stirred 16 h at rt and then diluted with H_2O and Et_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine (3×), dried over $MgSO_4$, filtered, and concentrated in vacuo for 2.282 g. The residue was transferred to a 100 mL round-bottomed flask containing a Teflon-coated stir-bar along with DMSO (38 mL), H_2O (0.16 mL, 8.9 mmol), and LiCl (979 mg, 23.1 mmol). The flask was equipped with a coil type reflux condenser that was open to the atmosphere and placed in a preheated 130 °C oil bath. After 23 h no starting material (R_f = 0.51 (hexanes/EtOAc, 80:20, v/v)) was observed by TLC. The reaction was cooled to rt and diluted with H_2O and Et_2O. The aq layer was separated and extracted with Et_2O (4×). The combined organic layers were washed with brine (4×), dried over $MgSO_4$, filtered, and concentrated in vacuo yielding 1.315 g of 8-(trimethylsilyl)oct-7-yn-2-one. To a flame-dried 100 mL flask containing a Teflon-coated stir-bar was added 697 mg of the crude material and THF (36 mL). The solution was cooled in an

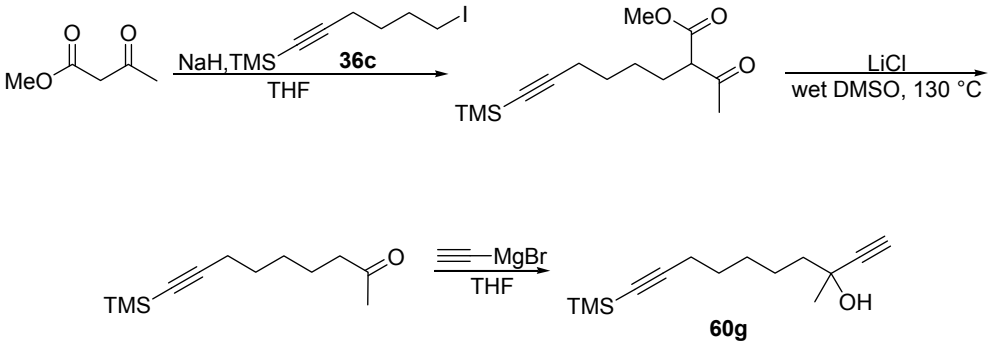
ice/H_2O bath and ethynylmagnesium bromide (21 mL, 0.5 M in THF, 11 mmol) was added via syringe. After 1 h in an ice/H_2O bath consumption of the ketone (R_f = 0.58 (hexanes/EtOAc, 80:20, v/v)) was observed by TLC and the reaction was quenched with saturated aq NH_4Cl. The reaction mixture was diluted with Et_2O and H_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 9:1 v/v) affording the title compound (529 mg, 59%). R_f = 0.49 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.42 (s, 1H), 2.25 (bs, 1H), 2.23 (t, *J* = 6.3 Hz, 2H), 1.69-1.51 (m, 6H), 1.47 (s, 3H), 0.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 107.2, 87.6, 84.6, 71.3, 67.9, 42.8, 29.6, 28.5, 23.7, 19.7, 0.1; IR: 3288, 2955, 2174, 1747, 1246, 844 cm^{-1} 3403, 3307, 2950, 2866, 2173, 1372, 1250, 844, 760; MS *m/z* (relative intensity): 222 (37%, M^+), 207 (82%), 189 (45%), 139 (48%), 75 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{13}H_{22}OSi$, 222.1440; found, 222.1439.



41f

3-Methyl-9-(trimethylsilyl)nona-1,8-diyn-3-yl acetate (41f). To a flame-dried 5 mL round-bottomed containing a Teflon-coated stir-bar was added **60f** (200 mg, 0.899 mmol), CH_2Cl_2 (1.8 mL), NEt_3 (0.50 mL, 3.6 mmol), and *N*,*N*-dimethyl-4-aminopyridine (32 mg, 0.26 mmol). The mixture was cooled in an ice/H_2O bath and acetic anhydride (0.17 mL, 1.8 mmol) was added via syringe. The reaction was warmed to rt and stirred for 22 h until no starting material was observed by TLC. The reaction was opened and diluted with H_2O and Et_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brined, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 95:5 v/v) affording the title compound (155 mg, 65%). R_f =

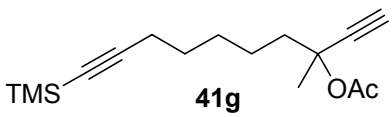
0.64 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.53 (s, 1H), 2.24 (t, *J* = 6.9 Hz, 2H), 2.01 (s, 3H), 1.98-1.87 (m, 1H), 1.86-1.76 (m, 1H), 1.67 (s, 3H), 1.65-1.48 (m, 4H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.2, 107.0, 84.7, 83.8, 74.7, 73.2, 40.8, 28.3, 26.3, 23.2, 21.8, 19.7, 0.1; IR: 3288, 2955, 2868, 2174, 1747, 1369, 1246, 844cm^{-1}; MS *m/z* (relative intensity): 249 (51%, M -CH_3), 207 (36%), 189 (90%), 148 (75%), 118 (87%), 83 (91%), 59 (100%); HRMS-EI (*m/z*): $[M - CH_3]^+$ calcd for $C_{14}H_{21}O_2Si$, 249.1311; found, 249.1310.



3-Methyl-10-(trimethylsilyl)deca-1,9-diyn-3-ol (60g).

To a flame-dried, 25 mL round-bottomed flask containing a Teflon-coated stir-bar was added NaH (231 mg, 60% dispersion in mineral oil, 5.78 mmol) and THF (4.3 mL). The resulting suspension was cooled in an ice/H_2O bath and methyl acetoacetate (0.69 mL, 6.4 mmol) was added via syringe. The reaction was warmed to rt. After stirring 40 min a solution of 6-iodo-1-(trimethylsilyl)-1-hexyne (1.20 g, 4.3 mmol) in DMF (4.3 mL) was added via syringe. The reaction was stirred 15 h and then diluted with H_2O and Et_2O. The aq layer was separated and extracted with Et_2O (2×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo for 1.042 g. The ketoester (737 mg) was transferred to a 25 mL round-bottomed flask containing a Teflon-coated stir-bar along with DMSO (12 mL), H_2O (0.06 mL, 3.3 mmol), and LiCl (364 mg, 8.59 mmol). The flask was equipped with a coil type reflux condenser open to the atmosphere and placed in a preheated 130 °C oil bath. After 21

h stirring no starting material (R_f = 0.53 (hexanes/EtOAc, 80:20, v/v)) was observed by TLC. The reaction was cooled to rt and diluted with H_2O and Et_2O. The aq layer was separated and extracted with Et_2O (4×). The combined organic layers were washed with brine (4×), dried over $MgSO_4$, filtered, and concentrated in vacuo in a 50 mL round-bottomed flask yielding 521 mg of 9-(trimethylsilyl)non-8-yn-2-one. To the 50 mL flask was added a stir-bar and THF (11.2 mL). The solution was cooled in an ice/H_2O bath and ethynylmagnesium bromide (13.4 mL, 0.5 M in THF, 6.7 mmol) was added via syringe. After 1 h in an ice/H_2O bath consumption of the crude ketone (R_f = 0.66 (hexanes/EtOAc, 80:20, v/v)) was observed by TLC and the reaction was quenched with saturated aq NH_4Cl. The reaction mixture was diluted with Et_2O and H_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine (2×), dried over $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 9:1 v/v) affording the title compound (204 mg, 28% over three steps). R_f = 0.53 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.42 (s, 1H), 2.22 (t, *J* = 7.2 Hz, 2H), 2.17 (s, 1H), 1.69-1.38 (m, 9H), 1.48 (s, 3H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 107.4, 87.7, 84.4, 71.3, 67.9, 43.2, 29.7, 28.7, 28.4, 24.0, 19.7, 0.1; IR: 3394, 3307, 2940, 2862, 2173, 1371, 1250, 1114, 843, 760 cm^{-1}; MS *m/z* (relative intensity): 221 (44%, M –CH_3]) 203 (21%), 153 (24%), 145 (35%), 109 (100%), 96 (85%); HRMS-EI (*m/z*): [M – CH_3]$^+$ calcd for $C_{13}H_{21}OSi$, 221.1361; found, 221.1355.

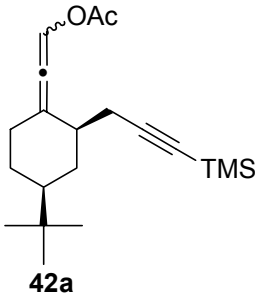


41g

3-Methyl-10-(trimethylsilyl)deca-1,9-diyn-3-yl acetate (41g). To a 15 mL round-bottomed flask containing a Teflon-coated stir-bar was added **60g** (204 mg, 0.863 mmol), CH_2Cl_2 (1.7 mL), NEt_3 (0.48 mL, 3.4 mmol), and *N*,*N*-dimethyl-4-aminopyridine (31 mg, 0.26 mmol). The mixture was cooled in an ice/H_2O bath and acetic anhydride (0.16 mL, 1.7 mmol) was added via syringe. The reaction was warmed to rt.

After 17 h further consumption of **60g** was no longer observed by TLC. The reaction was diluted with H_2O and Et_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 95:5 v/v) affording the title compound (184 mg, 77%). R_f = 0.69 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.52 (s, 1H), 2.20 (t, *J* = 6.9 Hz, 2H), 1.99 (s, 3H), 1.97-1.87 (m, 1H), 1.82-1.72 (m, 1H), 1.63 (s, 3H), 1.56-1.37 (m 6H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.2, 107.3, 84.4, 83.8, 74.7, 73.1, 41.1, 28.5, 28.3, 26.3, 23.5, 21.8, 19.7, 0.1; IR: 3287, 2942, 2864, 2173, 2118, 1747, 1369, 1244, 1042, 844 cm^{-1}; MS *m/z* (relative intensity): 279 (9%, M+1), 263 (32%), 235 (72%), 203 (86%), 97 (100%), 79 (98%).

General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation: A flame-dried, 5 mL round-bottomed flask equipped with a Teflon-coated stir-bar was charged with $AuCl_3$ (0.1 equiv) in a glove box. The flask was removed from the glove box, wrapped in aluminum foil, and placed under N_2. A solution of propargyl acetate in toluene (0.2 M, toluene degassed by bubbling with nitrogen for ~5 min) was added rapidly via cannula. The reaction was stirred at rt in a darkened hood. When the reaction was complete as observed by TLC, the mixture was passed through a plug of silica gel using hexanes/EtOAc and concentrated in vacuo. The crude material was purified via flash chromatography.



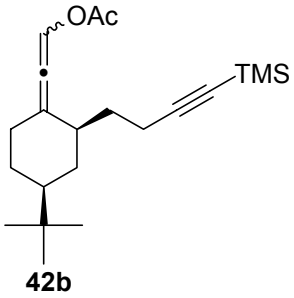
42a

2-(4-Tert-butyl-2-(3-(trimethylsilyl)prop-2-ynyl)cyclohexylidene)vinyl acetate (42a).

Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Acetate Formation, $AuCl_3$ (2 mg, 0.01 mmol) and propargyl acetate **39a-ax** (19 mg, 0.057 mmol, ~6:1 dr (major/minor)) were reacted in toluene (0.29 mL) for 3 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (16 mg, 84%) as a colorless oil in an ~1:1 dr. R_f = 0.67 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39* (t, *J* = 2.1 Hz, 0.5H), 7.34** (t, *J* = 2.4, 0.5H), 2.50-2.43 (m, 2H), 2.34-1.88 (m, 4H), 2.21-2.03 (m, 2H), 2.14 (s, 1.5H), 2.13 (s, 1.5H), 1.31-1.10 (m, 2H), 0.97-0.82 (m, 1H), 0.90* (s, 4.5H), 0.89** (s, 4.5H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 185.6*, 185.5**, 168.7, 121.7*, 121.7**, 111.4**, 111.1*, 105.9**, 105.9*, 86.0, 47.6**, 47.4*, 40.5*, 40.4**, 34.0, 32.3**, 33.1*, 32.6**, 32.6*, 28.2*, 28.0*, 27.5*, 27.5**, 24.7*, 24.6**, 21.0**, 20.9*, 0.13; IR: 2957, 2175, 1976, 1757, 1367, 1213, 1036, 842 cm^{-1}; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{20}H_{32}O_2NaSi$, 355.2069; found, 355.2062.

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~1:1 mixture of diastereomers



42b

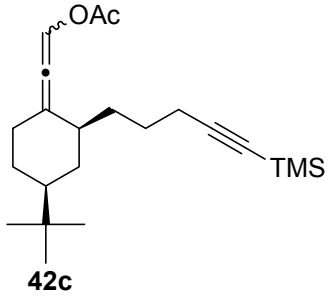
2-(4-Tert-butyl-2-(4-(trimethylsilyl)but-3-ynyl)cyclohexylidene)vinyl acetate (42b).

Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (2 mg, 0.01 mmol) and propargyl acetate **39b-ax** (20 mg, 0.058 mmol) were reacted in toluene (0.29 mL) for 40 min. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (16 mg, 80%) as a colorless oil in an ~1:1 dr. R_f = 0.71 (hexanes/EtOAc, 80:20, v/v);

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38* (t, *J* = 2.5 Hz, 0.5H), 7.36** (t, *J* = 2.5 Hz, 0.5H), 2.51-2.46 (m, 1H), 2.31-2.27 (m, 2H), 2.18-2.12 (m, 1H), 2.15** (s, 1.5H), 2.15* (s, 1.5H), 2.11-2.05 (m, 1H), 2.05-1.96 (m, 1H), 1.96-1.90 (m, 1H), 1.84-1.74 (m, 1H), 1.48-1.40 (m, 1H), 1.23-1.11 (m, 2H), 0.95-0.81 (m, 1H), 0.89** (s, 4.5H), 0.88* (s, 4.5H), 0.16* (s, 4.5H), 0.15** (s, 4.5H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186*, 185**, 168.8, 122.9*, 122.8**, 110.9*, 110.8**, 107.4*, 107.3**, 84.6, 47.8**, 47.7*, 40.3**, 40.2*, 34.7*, 34.5**, 33.6*, 33.6**, 32.5*, 32.5*, 32.3, 28.5**, 28.4*, 27.6*, 27.6**, 21.1**, 21.0*, 17.6**, 17.5*, 0.2; IR: 2953, 2173, 1974, 1756, 1367, 1214, 1035, 842 cm^{-1}; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{21}H_{34}O_2NaSi$, 369.2226; found, 369.2211.

Spectra Recorded as ~1:1 mixture of diastereomers

*diastereomer 1; **diastereomer 2



42c

2-(4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexylidene)vinyl acetate (42c).

Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (4 mg, 0.01 mmol) and propargyl acetate **38c** (58 mg, 0.16 mmol) were reacted in toluene (0.81 mL) for 40 min. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (33 mg, 74%) as a colorless oil in an ~1:1 dr. Diastereomers were separated via flash chromatography (hexanes/CH_2Cl_2/benzene, 16:4:1 v/v/v). Major Diastereomer **42c**: R_f = 0.17 (hexanes/CH_2Cl_2/benzene, 16:4:1 v/v/v); ^{1}H NMR (500) MHz, $CDCl_3$) δ: 7.37* (t, *J* = 2.5 Hz, 0.75H), 7.35** (t, *J* = 3 Hz, 0.25H), 2.50-2.45 (m, 1H), 2.23-2.19 (m, 2H), 2.15** (s, 0.75H), 2.14* (s, 2.25H), 2.16-1.89 (m, 5H), 1.67-1.53 (m, 4H), 1.36-1.09 (m, 3H), 0.95-0.74 (m, 1H), 0.88** (s, 2.25H), 0.87* (s, 6.75), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 185.9, 168.8,

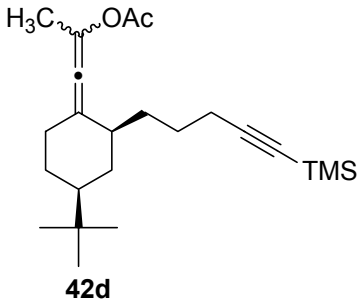
123.2, 110.8, 107.5, 84.3, 47.7, 40.9, 35.1, 33.7, 33.2, 32.5, 28.4, 27.6, 26.3, 20.9, 20.1, 0.2; IR: 2954, 2174, 1975, 1751, 1367, 1215, 1036, 842 cm^{-1}; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{22}H_{26}O_2NaSi$, 383.2382; found, 383.2354.

Spectra Recorded as ~3:1 mixture of diastereomers

Minor Diastereomer **42c**: R_f = 0.17 (hexanes/CH_2Cl_2/benzene, 16:4:1 v/v/v); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.37* (t, *J* = 2.5 Hz, 0.25H), 7.35 (t, *J* = 2.5 Hz, 0.75H), 2.51-2.44 (m, 1H), 2.26-2.18 (m, 2H), 2.15** (s, 2.25H), 2.14* (s, 0.75H), 2.12-1.89 (m, 4H), 1.68-1.52 (m, 4H), 1.35-1.11 (m, 4H), 0.96-0.82 (m, 1H), 0.89** (s, 2.25H), 0.87* (s, 6.75H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 185.7, 168.8, 123.2, 110.7, 107.6, 84.4, 47.9, 40.9, 34.9, 33.6, 33.0, 32.5, 28.5, 27.6, 26.3, 21.1, 20.1, 0.2

Spectra Recorded as ~1:3 mixture of diastereomers

*diastereomer 1; **diastereomer 2



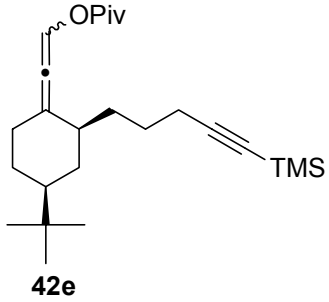
42d

1-(4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexylidene)prop-1-en-2-yl acetate (42d). Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (3 mg, 0.01 mmol) and propargyl acetate **39d-ax** (56 mg, 0.15 mmol, major diastereomer) were reacted in toluene (0.75 mL) for 5 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (30 mg, 54%) as a colorless oil in an ~1:1 dr. R_f = 0.67 (hexanes/EtOAc, 80:20, v/v); ^1H NMR (300 MHz, $CDCl_3$) δ: 2.50-2.40 (m, 1H), 2.28-2.15 (m, 2H), 2.11* (s, 1.5H), 2.10** (s, 1.5H), 2.05-1.86 (m, 4H), 1.97** (s, 1.5H), 1.95* (s, 1.5H), 1.69-1.48 (m, 3H), 1.34-1.23 (m, 1H), 1.23-1.00 (m, 2H), 0.93-0.80 (m, 1H), 0.87* (s, 4.5H), 0.86**

(s, 4.5H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 187.7, 169.1*, 169.0**, 120.2**, 120.0*, 118.7**, 118.6*, 107.8**, 107.8*, 48.0*, 47.8**, 41.3*, 40.9**, 35.4*, 35.1**, 33.3**, 33.2*, 33.2*, 33.2**, 32.5, 28.6*, 28.6**, 27.6*, 27.6**, 26.6*, 26.3**, 21.3*, 21.1**, 20.1**, 20.0*, 18.7**, 18.4*, 0.2; IR: 2954, 2174, 1981, 1750, 1366, 1221, 1125, 842 cm^{-1}; MS *m/z* (relative intensity): 374 (7%, M^+), 359 (49%), 358 (53%), 331 (29%), 194 (100%), 117 (39%), 75 (34%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{23}H_{38}O_2Si$, 374.2641; found, 374.2639.

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~1:1 mixture of diastereomers



42e

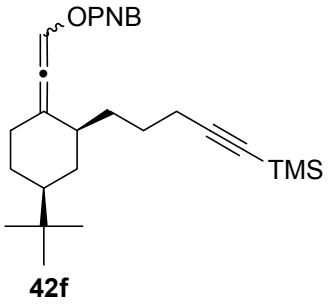
2-((2S,4S)-4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexylidene)vinyl pivalate (42e).

Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (2 mg, 0.01 mmol) and propargyl acetate **39e-ax** (39 mg, 0.097 mmol, 1diastereomer) were reacted in toluene (0.48 mL) for 50 min. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (35 mg, 91%) as a colorless oil in an ~2:1 dr. R_f = 0.81 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34* (t, *J* = 2.0 Hz, 0.66H), 7.30** (t, *J* = 2.5 Hz, 0.33H), 2.51-2.45 (m, 1H), 2.26-1.84 (m, 6H), 1.66-1.48 (m, 3H), 1.38-1.09 (m, 3H), 1.26** (s, 3H), 1.25* (s, 6H), 0.96-0.83 (m, 1H), 0.89** (s, 3H), 0.87* (s, 6H), 0.15** (s, 3H), 0.14* (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.0*, 186.0**, 176.4**, 176.4*, 122.3, 110.9*, 110.8**, 107.6**, 107.5*, 84.3**, 84.1*, 47.9**, 47.8*, 41.2*, 40.8**, 39.0*, 38.9**, 35.8*, 34.7**, 34.6**, 33.6*, 33.5*, 33.4**, 32.8**, 32.5**, 32.5*, 31.6*, 28.6*, 28.4**, 27.6**, 27.6*, 27.1, 26.4*, 25.9**, 25.3**, 22.6*, 20.7**, 20.1**, 20.1*, 14.1*, 0.2 ; IR: 3066, 2958, 2867, 2174, 1990, 1741, 1480, 1249, 1133, 843 cm^{-1}; MS *m/z* (relative intensity): 402

(12%, M^+), 387 (15%), 263 (20%), 180 (62%), 159 (54%), 119 (65%), 117 (66%), 85 (71%), 73 (100%), 57 (97%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{25}H_{42}O_2Si$, 402.2954; found, 402.2940.

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~2:1 mixture of diastereomers

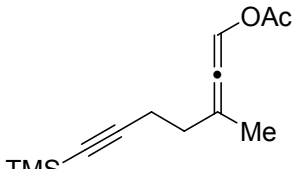


42f

2-((2S,4S)-4-Tert-butyl-2-(5-(trimethylsilyl)pent-4-ynyl)cyclohexylidene)vinyl 4-nitrobenzoate (42f). Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (2 mg, 0.01 mmol) and propargyl acetate **39f-ax** (40 mg, 0.086 mmol, 1 diastereomer) were reacted in toluene (0.43 mL) for 16 h. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (35 mg, 87%) as a colorless oil in an ~1:1 dr. R_f = 0.78 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.33-8.26 (m, 4H), 7.60* (t, *J* = 2.0 Hz, 0.5H), 7.57** (t, *J* = 3.0 Hz, 0.5H), 2.56-2.52 (m, 1H), 2.28-1.93 (m; 6H), 1.73-1.55 (m, 3H), 1.41-1.32 (m, 1H), 1.31-1.14 (m, 2H), 1.02-0.06 (m, 1H), 0.91** (s, 4.5H), 0.87* (s, 4.5H), 0.12** (s, 4.5H), 0.09* (s, 4.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.3*, 186.2**, 162.6**, 162.6*, 150.6, 135.1**, 135.0*, 131.0**, 131.0*, 124.3**, 124.2*, 123.6, 111.2*, 111.1**, 107.4**, 107.3*, 84.5**, 84.4*, 47.8**, 47.7*, 41.0, 35.2*, 34.8**, 33.6*, 33.5**, 33.2*, 33.0**, 32.5**, 32.5**, 28.5, 27.6**, 27.6*, 26.3*, 26.2**, 20.6, 0.1; IR: 2953, 2863, 2173, 1982, 1733, 1531, 1279, 1250, 1100, 845 cm^{-1}; MS *m/z* (relative intensity): 467 (35%, M^+), 452 (55%), 329 (82%), 300 (92%), 224 (84%), 171 (67%), 104 (86%), 73 (100%), 58 (95%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{27}H_{37}NO_4Si$, 467.2492; found, 467.2512.

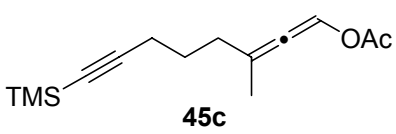
*diastereomer 1; **diastereomer 2

Spectra Recorded as ~1:1 mixture of diastereomers



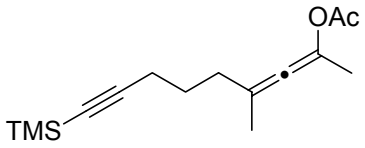
45b

3-Methyl-7-(trimethylsilyl)hepta-1,2-dien-6-ynyl acetate (45b). Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (4 mg, 0.01 mmol) and propargyl acetate **41b** (28 mg, 0.12 mmol) were reacted in toluene (0.60 mL) for 19 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (13 mg, 46%) as a colorless oil. R_f = 0.65 (hexanes/EtOAc, 90:10, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.33 (q, *J* = 2.1 Hz, 1H), 2.41-2.25 (m, 4H), 2.14 (s, 3H), 1.86 (d, *J* = 2.1 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.2, 169.3, 115.1, 111.1, 106.9, 85.6, 34.7, 21.5, 21.1, 18.9, 0.7; IR: 2959, 2176, 1979, 1752, 1214, 1051, 842 cm^{-1}; HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{13}H_{20}O_2Si$, 236.1232; found, 236.1234.



45c

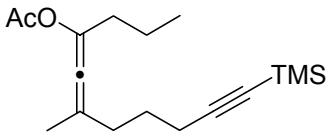
3-Methyl-8-(trimethylsilyl)octa-1,2-dien-7-ynyl acetate (45c). Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (7 mg, 0.02 mmol) and propargyl acetate **41c** (39 mg, 0.16 mmol) were reacted in toluene (0.78 mL) for 4 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (27 mg, 67%) as a colorless oil. R_f = 0.68 (hexanes/EtOAc, 90:10, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32 (q, *J* = 2.1 Hz, 1H), 2.27 (t, *J* = 6.9 Hz, 2H), 2.22-2.08 (m, 2H), 2.14 (s, 3H), 1.85 (d, *J* = 2.1Hz, 3H), 1.68 (quint *J* = 7.5 Hz, 2H) 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 189.4, 168.8, 115.3, 110.0, 106.8, 84.9, 34.0, 26.1, 20.9, 20.6, 19.3, 0.1; IR: 2956, 2174, 1976, 1750, 1250, 1215, 1056, 843 cm^{-1}.



45d

4-Methyl-9-(trimethylsilyl)nona-2,3-dien-8-yn-2-yl acetate (45d).

Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (3 mg, 0.01 mmol) and propargyl acetate **41d** (42 mg, 0.16 mmol) were reacted in toluene (0.80 mL) for 1.5 h. Purification via flash chromatography (hexanes/EtOAc, 95: 5, v/v) afforded the title compound (27 mg, 64%) as a colorless oil. R_f = 0.66 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.25 (t, *J* = 6.9 Hz, 2H), 2.13 (td, *J* = 7.5, 3.0 Hz, 2H), 2.10 (s, 3H), 1.93 (s, 3H), 1.79 (s, 3H), 1.68 (quint, *J* = 7.2 Hz, 2H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.4, 168.9, 119.2, 110.7, 107.1, 84.7, 33.9, 26.1, 21.1, 20.2, 19.2, 18.4, 0.1; IR: 2956, 2901, 2174, 1983, 1753, 1433, 1368, 1249, 1220, 1126, 843 cm^{-1}; MS *m/z* (relative intensity): 264 (14%, M^+), 263 (45%), 222 (54%), 221 (50%), 149 (60%), 117 (62%), 98 (100%), 83 (80%), 73 (98%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{15}H_{24}O_2Si$, 264.1546; found, 264.1539.

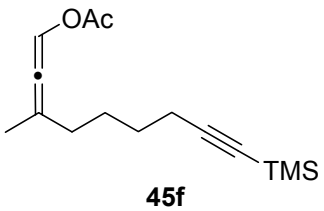


45e

6-Methyl-11-(trimethylsilyl)undeca-4,5-dien-10-yn-4-yl acetate (45e).

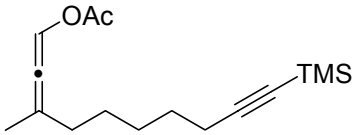
Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (12 mg, 0.04 mmol) and propargyl acetate **41e** (120 mg, 0.41 mmol) were reacted in toluene (2.0 mL) for 80 min. Purification via flash chromatography (hexanes/EtOAc, 99:1, v/v) afforded the title compound (69 mg, 58%) as a colorless oil. R_f = 0.67 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.25 (t, *J* = 6.9 Hz, 2H), 2.20-2.12 (m, 4H), 2.10 (s, 3H), 1.80 (s, 3H), 1.69 (quint, *J* = 6.9, 2H), 1.43 (sext, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.1, 168.9, 122.8, 111.7, 107.1, 84.7, 34.0, 33.8, 26.2, 21.1, 20.3, 19.7, 19.4, 13.6, 0.1; IR: 2959, 2174, 1979, 1753, 1367,

1214, 842.3 cm^{-1}; MS *m/z* (relative intensity): 277 (8%, M – CH_3), 250 (38%), 249 (41%), 177 (39%), 117 (68%), 83 (98%), 73 (100%); HRMS-EI (*m/z*): $[M - CH_3]^+$ calcd for $C_{16}H_{25}O_2Si$, 277.1624; found, 277.1621.



45f

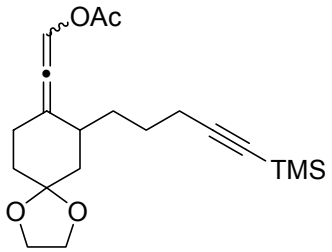
3-Methyl-9-(trimethylsilyl)nona-1,2-dien-8-ynyl acetate (45f). Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (4 mg, 0.01 mmol) and propargyl acetate **41f** (32 mg, 0.12 mmol) were reacted in toluene (0.61 mL) for 30 min. Purification via flash chromatography (hexanes/EtOAc, 9:1, v/v) afforded the title compound (25 mg, 79%) as a colorless oil. R_f = 0.69 (hexanes/EtOAc, 80:20, v/v); ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (sext, *J* = 2.1Hz, 1H), 2.26-2.20 (m, 2H), 2.16-2.02 (m, 2H), 2.13 (s, 3H), 1.83 (d, *J* = 2.1 Hz, 3H), 1.61-1.49 (m, 4H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 168.8, 115.7, 109.7, 107.2, 84.6, 34.6, 28.0, 26.3, 20.9, 20.4, 19.6, 0.1; IR: 3065, 2943, 2862, 2174, 1976, 1750, 1456, 1369, 1249, 1215, 1066, 1039, 843 cm^{-1}; MS *m/z* (relative intensity): 249 (36%, M-CH_3), 222 (26%), 117 (100%), 84 (88%), 75 (79%), 73 (95%); HRMS-EI (*m/z*): $[M - CH_3]^+$ calcd for $C_{14}H_{21}O_2Si$, 249.1311; found, 249.1308.



45g

3-Methyl-10-(trimethylsilyl)deca-1,2-dien-9-ynyl acetate (45g). Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (5 mg, 0.02 mmol) and propargyl acetate **41g** (37 mg, 0.13 mmol) were reacted in toluene (0.66 mL) for 30 min. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (28 mg, 77%) as a colorless oil. R_f = 0.63 (hexanes/EtOAc, 80:20, v/v); ^1H NMR (300 MHz, $CDCl_3$) δ: 7.29 (sext, *J* = 2.1 Hz, 1H), 2.22 (t, *J* = 6.9 Hz, 2H), 2.13 (s, 3H), 2.16-2.01 (m, 2H), 1.83 (d, *J* = 2.1 Hz,

3H), 1.60-1.37 (m, 6H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 189.3, 168.8, 115.9, 109.7, 107.5, 84.4, 34.9, 28.4, 28.3, 26.6, 20.9, 20.5, 19.8, 0.2; IR: 3065, 2935, 2859, 2174, 1976, 1750, 1457, 1368, 1249, 1215, 1068, 1041, 842 cm^{-1}; MS *m/z* (relative intensity): 278 (26%, M^+), 263 (13%), 249 (20%), 236 (100%), 218 (64%), 145 (65%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{26}O_2Si$, 278.1702; found, 278.1702.



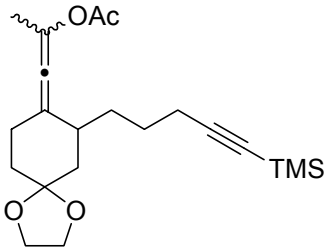
47a

2-(2-(5-(Trimethylsilyl)pent-4-ynyl)-4-oxocyclohexylidene)vinyl acetate-4-monoethylene ketal (47a).

Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (2 mg, 0.007 mmol) and propargyl acetate **45a** (27 mg, 0.074 mmol, 4:1 dr (major/minor)) were reacted in toluene (0.37 mL) for 4 h. Purification via flash chromatography (hexanes/EtOAc, 9:1, v/v) afforded the title compound (27 mg, quant) as a colorless oil in an ~1:1 dr. R_f = 0.44 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.41* (s, 0.5H), 7.38** (t, *J* = 2.4 Hz, 0.5H),4.03-3.98 (m, 4H), 2.44-2.35 (m, 3H), 2.24-2.18 (m, 2H), 2.15 (s, 3H), 1.96-1.86 (m, 2H), 1.79-1.27 (m, 6H), 0.13 (9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.9, 168.7, 120.7, 111.2*, 111.0**, 108.4**, 108.3*, 107.3, 84, 64.5, 41.8*, 41.5**, 38.0**, 37.9*, 35.3, 32.5*, 32.2**, 30.0, 26.1, 20.9, 19.9, 0.2; IR: 2954, 2173, 1976, 1751, 1368, 1215, 1060, 843 cm^{-1}; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{20}H_{30}O_4NaSi$, 385.1811; found, 385.1809.

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~1:1 mixture of diastereomers



47b

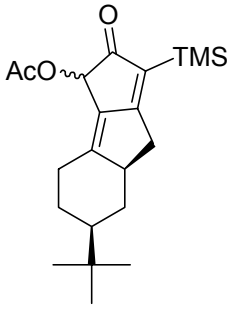
1-(2-(5-(Trimethylsilyl)pent-4-ynyl)-4-oxocyclohexylidene)prop-1-en-2-yl acetate-4-monoethylene ketal (47b).

Following the General Procedure for the $AuCl_3$ Catalyzed Allenol Ester Formation, $AuCl_3$ (7 mg, 0.02 mmol) and propargyl acetate **46b** (106 mg, 0.281 mmol, 5:1 dr) were reacted in toluene (1.4 mL) for 19 h. Purification via flash chromatography (hexanes/EtOAc, 90:10, v/v) afforded the title compound (45 mg, 43%) as a colorless oil in an ~1.5:1 dr. R_f = 0.43 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.00-3.93 (m, 4H), 2.42-2.36 (m, 1H), 2.34-2.17 (m, 4H), 2.10 (s, 3H), 1.96* (s, 1.76), 1.95** (s, 1.14H), 1.93-1.81 (m, 2H), 1.70-1.59 (m, 2H), 1.58-1.47 (m, 2H), 1.47-1.28 (m, 2H), 0.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.7**, 188.6*, 168.9*, 168.8**, 120.5*, 120.3**, 116.1*, 116.0**, 108.5**, 108.4*, 107.6, 84.2, 64.4, 42.0**, 41.7*, 35.5*, 35.4**, 32.4**, 32.3*, 29.7**, 29.5*, 26.4**, 26.1*, 21.2**, 21.1*, 19.9*, 19.9**, 18.7*, 18.3**, 0.2; IR: 2954, 2173, 1982, 1751, 1438, 1369, 1249, 1221, 1123, 843 cm^{-1}; MS *m/z* (relative intensity): 376 (35%, M^+), 360 (31%), 333 (76%), 158 (86%), 110 (95%), 99 (78%), 87 (88%), 73 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{21}H_{32}O_4Si$, 376.2070; found, 376.2069.

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~1.5:1 mixture of diastereomers

General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction: A flame-dried, test tube (10 × 100 mm) equipped with a Teflon-coated stir-bar was charged with allene-yne and toluene (0.1 M). The tube was evacuated for 3-5 s (via a needle through the septa) and refilled with CO(g) (from a balloon) (3×). To the allene-yne solution was added $[Rh(CO)_2Cl]_2$ (0.10 equiv) in one portion and the test tube was evacuated and refilled with CO(g) (3×). The test tube was placed in a preheated 90 ^oC oil bath and stirred under CO(g). After the reaction was complete by TLC, the mixture was cooled to rt, passed through a short plug of silica gel using hexanes/EtOAc and concentrated in vacuo. The crude material was purified by flash chromatography.



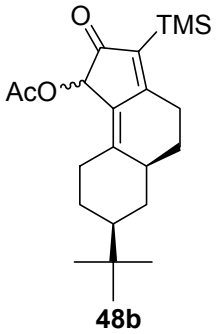
48a

6-Tert-butyl-2,3,4,5,6,7,7a,8-octahydro-1-(trimethylsilyl)-2-oxocyclopenta[a]inden-3-yl acetate (48a).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **42a** (19 mg, 0.057 mmol, ~1:1 dr) and $[Rh(CO)_2Cl]_2$ (2 mg, 0.005 mmol) were reacted in toluene (0.57 mL) for 8 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (4 mg, 19%) as a slightly yellowish oil in an ~2:1 dr. R_f = 0.47 (hexanes/EtOAc, 80:20, v/v); ^1H NMR (300 MHz, $CDCl_3$) δ: 5.66* (s, 0.6H), 5.62** (s, 0.4H), 3.07** (d, J = 19.2 Hz, 0.4H), 3.05* (d, J = 19.5 Hz, 0.6H), 2.98-2.84 (m, 1H), 2.72-2.64 (m, 1H), 2.44-2.31 (m, 1H), 2.26-1.94 (m, 3H), 2.17** (s, 1.2H), 2.15* (s, 1.8H), 1.33-1.25 (m, 1H), 1.19-0.88 (m, 2H), 0.89 (s, 9H), 0.21 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 206.8, 194.2**, 193.7*, 170.5, 154.2**, 153.7*, 136.3*, 135.6**, 135.6*, 127.9**, 127.8*, 69.3*, 69.1**, 50.1**, 49.1*, 47.5**, 47.2*, 36.2**, 36.0*, 35.3*, 35.0**, 32.5*, 28.1**, 22.7**, 27.6*, 27.6*, 27.5**, 20.8**, 20.8*, -1.3; IR: 2953, 1746, 1701, 1559, 1230, 842 cm^{-1}.

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~2:1 mixture of diastereomers



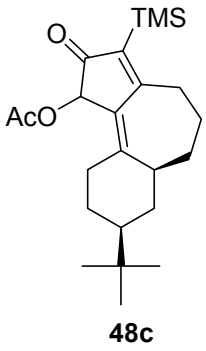
48b

7-Tert-butyl-2,4,5,5a,6,7,8,9-octahydro-3-(trimethylsilyl)-2-oxo-1H-cyclopenta[a]naphthalen-1-yl acetate (48b).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **42b** (14 mg, 0.040 mmol) and $[Rh(CO)_2Cl]_2$ (2 mg, 0.005 mmol) were reacted in toluene (0.39 mL) for 1 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (10 mg, 67%) as a slightly yellow oil in an ~1:1 dr. R_f = 0.55 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.75** (s, 0.5H), 5.71* (d, *J* = 1.0 Hz, 0.5H), 2.92* (dt, *J* = 16.5, 4.0 Hz, 0.5H), 2.83** (dt, *J* = 17.0, 5.5 Hz, 0.5H), 2.60** (ddd, *J* = 17.0, 10.5, 5.0, Hz, 0.5H), 2.54* (ddd, *J* = 14.5, 6.3, 3.0 Hz, 0.5H), 2.46-2.37 (m, 1H), 2.32-2.19 (m, 1H), 2.17* (s, 1.5H), 2.14** (s, 1.5H), 2.11-1.98 (m, 4H), 1.57-1.49** (m, 0.5H), 1.46-1.37* (m, 0.5H), 1.13-0.95 (m, 2H), 0.89** (s, 4.5H), 0.88* (s, 4.5H), 0.94-0.82 (m, 1H), 0.24** (s, 4.5H), 0.23* (s, 4.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 204.6, 178.4*, 178.2**, 170.1**, 170.0*, 145.8**, 145.4*, 134.1**, 133.4*, 129.7*, 129.3**, 70.7**, 70.5*,47.1**, 47.1*, 37.9*, 37.4**, 36.0*, 35.2**, 32.4, 30.8**, 30.7**, 29.3*, 29.0**, 27.7**, 27.5*, 27.5, 27.0*, 26.1**, 20.9*, 20.8**,-0.6; IR: 2952, 1745, 1699, 1543, 1367, 1245, 844 cm^{-1}; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{22}H_{34}O_3NaSi$: 397.2175; found: 397.2158.

Spectra Recorded as ~1:1 mixture of diastereomers

*diastereomer 1; **diastereomer 2



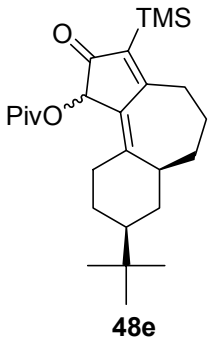
48c

(10aE)-8-Tert-butyl-1,2,4,5,6,6a,7,8,9,10-decahydro-3-(trimethylsilyl)-2-oxobenzo[e]azulen-1-yl acetate (48c).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **42c** (16 mg, 0.044 mmol, ~1:1 dr) and $[Rh(CO)_2Cl]_2$ (3 mg, 0.006 mmol) were reacted in toluene (0.91 mL) for 17 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (13 mg, 76%) as a slightly yellowish oil in an ~2.3:1 dr. R_f = 0.58 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.82* (s, 0.7), 5.77 (s, 0.3H), 3.02** (t, *J* = 5.4 Hz, 0.3H), 2.96* (t, *J* = 5.4 Hz, 0.7H), 2.86* (dd, *J* = 9.9, 4.5 Hz, 0.7H), 2.79** (dd, *J* = 11.4, 5.0 Hz, 0.3H), 2.58-2.34 (m, 2H), 2.15* (s, 2.1H), 2.14 (m, 0.9H), 2.02-1.57 (m, 7H), 1.52-1.04 (m, 5H), 0.94-0.81 (m, 1H), 0.86 (s, 9H), 0.26 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 203.8**, 203.6*, 182.5**, 181.3*, 170.0**, 169.9*, 149.7*, 149.0**, 139.3*, 139.1**, 130.6**, 130.4*, 74.4*, 73.5**, 47.4*, 46.9**, 46.2*, 43.7**, 37.9*, 35.4*, 35.2*, 35.1*, 35.0**, 34.6**, 34.4*, 33.1**, 32.5**, 32.4*, 28.4*, 27.8**, 27.5*, 27.4**, 23.0*, 21.7**, 20.9*, 0.3; IR: 2942, 1746, 1695, 1510, 1367, 1228, 843 cm^{-1}; HRMS-EI (*m/z*): $[M + Na]^+$ calcd for $C_{23}H_{36}O_3NaSi$, 411.2331; found, 411.2308.

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~2.3:1 mixture of diastereomers



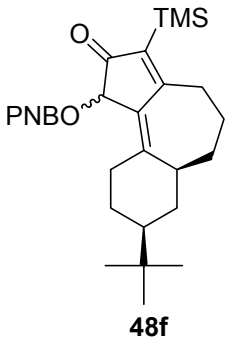
48e

(8S,10aE)-8-Tert-butyl-1,2,4,5,6,6a,7,8,9,10-decahydro-3-(trimethylsilyl)-2-oxobenzo[e]azulen-1-yl pivalate (48e).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **42e** (35 mg, 0.087 mmol, ~2:1 dr) and $[Rh(CO)_2Cl]_2$ (4 mg, 0.01 mmol) were reacted in toluene (0.86 mL) for 18 h. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (19 mg, 51%) as a slightly yellow oil in an ~2.6:1 dr. R_f = 0.70 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.85* (s, 0.65H), 5.75** (s, 0.25), 3.03-2.93 (m, 1H), 2.87-2.78 (m, 1H), 2.56-2.47 (m, 1H), 2.42-2.32 (m, 1H), 2.07-1.60 (m, 7H), 1.55-1.46 (m, 1H), 1.36 (tt, *J* = 8.0, 3.5 Hz, 1H), 1.32-1.13 (m, 2H), 1.26* (s, 6.5H) 1.24** (s, 2.4H), 0.86** (s, 2.2H), 0.85 (s, 6.4H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 203.8**, 203.4*, 181.7**, 180.6*, 177.6*, 177.5**, 149.2*, 148.5**, 139.0*, 138.8**, 130.8**, 130.7*, 74.5*, 73.7**, 47.3*, 46.8**, 45.8*, 43.6**, 38.9**, 38.8*, 37.7*, 35.2*, 35.0*, 34.8**, 34.7*, 34.4**, 34.3**, 32.9**, 32.5**, 32.4*, 28.7*, 27.8**, 27.4*, 27.3, 27.2**, 23.2*, 21.7**, -0.2; IR: 2954, 2866, 1734, 1695, 1510, 1478, 1248, 1142, 843 cm^{-1}; MS *m/z* (relative intensity): 430 (33%, M^+), 415 (15%), 345 (43%), 328 (71%), 313 (60%), 271 (44%), 159 (45%), 121 (89%), 75 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{26}H_{42}O_3Si$, 430.2903; found, 430.2902.

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~2.6:1 mixture of diastereomers



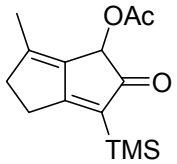
48f

(8S,10aE)-8-Tert-butyl-1,2,4,5,6,6a,7,8,9,10-decahydro-3-(trimethylsilyl)-2-oxobenzo[e]azulen-1-yl 4-nitrobenzoate (48f).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **42f** (35 mg, 0.075 mmol, ~1:1 dr) and $[Rh(CO)_2Cl]_2$ (3 mg, 0.01 mmol) were reacted in toluene (0.74 mL) for 18 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5 to 80:20, v/v) afforded the title compound (13 mg, 35%) as a slightly yellowish oil in an ~2:1 dr. R_f = 0.65 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.30-8.10 (m, 4H), 6.06* (s, 0.66H), 6.01 (s, 0.33H), 3.08-3.00 (m, 1H), 2.93-2.86 (m, 1H), 2.59-2.36 (m, 2H), 2.09-1.62 (m, 8H), 1.56-1.46 (m, 1H), 1.38-1.18 (m, 2H), 1.10 (q, *J* = 12.5, 1H), 1.05-0.82 (m, 3H), 0.84** (s, 0.33H), 0.75* (s, 0.66H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 203.0**, 202.7*, 182.6**, 181.4*, 163.9**, 163.7*, 150.6**, 150.6**, 150.4*, 149.6*, 139.5*, 139.3**, 135.3**, 135.3*, 131.0, 130.2**, 129.9*, 123.4, 75.8*, 75.0**, 47.2*, 47.0**, 46.4*, 43.8**, 38.0*, 35.5*, 35.3*, 35.0*, 35.0**, 34.7**, 34.4**, 33.2**, 32.5**, 32.3*, 28.6*, 27.8**, 27.3, 23.0*, 21.7**, -0.3; IR: 2949, 2865, 1731, 1693, 1345, 1320, 1261, 1120, 1100, 844, 718 cm^{-1}; MS *m/z* (relative intensity): 495 (14%, M^+), 480 (12%), 329 (62%), 271 (48%), 104 (100%), 91 (98%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{20}H_{37}NO_5Si$, 495.2441; found, 495.2440.

*diastereomer 1; **diastereomer 2

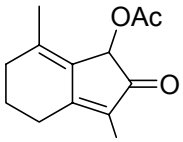
Spectra Recorded as ~2:1 mixture of diastereomers



49b

1,2,4,5-Tetrahydro-6-methyl-3-(trimethylsilyl)-2-oxopentalen-1-yl acetate (49b).

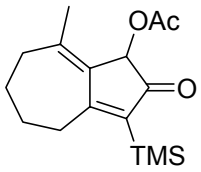
Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **45b** (13 mg, 0.055 mmol) and $[Rh(CO)_2Cl]_2$ (3 mg, 0.006 mmol) were reacted in toluene (0.56 mL) for 22 h. Purification via flash chromatography (hexanes/EtOAc, 9:1, v/v) afforded the title compound (4 mg, 28%) as a slightly yellow oil. R_f = 0.35 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.65 (s, 1H), 2.85-2.72 (m, 4H), 2.17 (s, 3H), 1.95 (s, 3H), 0.21 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 194.8, 170.4, 147.2, 140.1, 127.8, 124.8, 69.4, 40.4, 27.8, 20.7, 15.5, -1.3; IR: 2955, 2918, 1745, 1699, 1558, 1229, 839 cm^{-1}; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{14}H_{20}O_3NaSi$: 287.1079; found: 287.1080.



49c

1,2,4,5,6-Pentahydro-7-methyl-3-(trimethylsilyl)-2-oxo-2H-inden-1-yl acetate (49c).

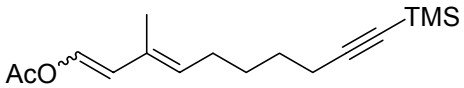
Following the General Procedure for $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **45c** (22 mg, 0.088 mmol) and $[Rh(CO)_2Cl]_2$ (3 mg, 0.006 mmol) were reacted in toluene (0.87 mL) for 1.5 h. Purification via flash chromatography (hexanes/EtOAc, 9:1, v/v) afforded the title compound (13 mg, 53%) as a slightly yellowish oil. R_f = 0.36 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.73 (s, 1H), 2.79 (dd, *J* = 17.1, 6.0, 4.8 Hz, 1H), 2.58 (ddd, *J* = 16.8, 10.2, 4.8 Hz, 1H), 2.32-2.19 (m, 2H), 2.16 (s, 3H), 1.96-1.72 (m, 2H), 1.83 (s, 3H), 0.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.3, 177.7, 170.0, 139.6, 133.4, 131.7, 70.6, 31.3, 27.3, 21.8, 20.7, 20.4, -0.6; IR: 2951, 1746, 1696, 1542, 1223, 841 cm^{-1}; MS *m/z* (relative intensity): 278 (15%, M^+), 236 (35%), 235 (32%), 220 (56%), 218 (72%), 117 (71%), 74 (82%), 72 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{15}H_{22}O_3Si$, 278.1338; found, 278.1327.



49f

(8E)-1,2,4,5,6,7-Hexahydro-8-methyl-3-(trimethylsilyl)-2-oxoazulen-1-yl acetate (49f).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **45f** (27 mg, 0.10 mmol) and $[Rh(CO)_2Cl]_2$ (3 mg, 0.008 mmol) were reacted in toluene (1.0 mL) for 46 h. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (18 mg, 62%) as a slightly yellow oil. R_f = 0.43 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.73 (s, 1H), 2.87 (dt, *J* = 14.7, 5.4 Hz, 1H), 2.81-2.70 (m, 1H), 2.51-2.32 (m, 2H), 2.15 (s, 3H), 1.94-1.72 (m, 4H), 1.85 (s, 3H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 204.4, 181.8, 170.0, 143.5, 136.8, 134.5, 73.5, 34.1, 30.6, 25.9, 24.1, 23.7, 20.7, -0.2; IR: 2937, 2865, 1746, 1697, 1528, 1369, 1246, 1224, 1049, 842.1 cm^{-1}; MS *m/z* (relative intensity): 292 (14%, M^+), 266 (24%), 249 (21%), 232 (71%), 217 (28%), 117 (51%), 75 (88%), 73 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{24}O_3Si$, 292.1495; found, 292.1485.



50

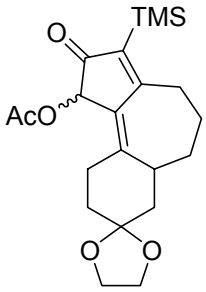
3-Methyl-10-(trimethylsilyl)deca-1,3-dien-9-ynyl acetate (50).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **45g** (26 mg, 0.093 mmol) and $[Rh(CO)_2Cl]_2$ (4 mg, 0.01 mmol) were reacted in toluene (0.99 mL) for 120 h. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (3 mg, 12%) as a slightly yellow colored oil. R_f = 0.71 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30* (d, *J* = 13.0 Hz, 0.5H), 6.90** (d, *J* = 7.0 Hz, 0.5H), 6.08* (d, *J* = 12.5 Hz, 0.5H), 5.53* (t, *J* = 7.5Hz, 0.5H), 5.44** (t, *J* = 7.0 Hz, 0.5H), 5.28** (d, *J* = 7.5 Hz, 0.5H), 2.26-2.21 (m, 1H), 2.18-2.10 (m, 2H), 2.17* (s,

0.5H), 2.15** (s, 0.5H), 1.95* (s, 1.5H), 1.74**(s, 1.5H), 1.55-1.45 (m, 4H), 0.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2*, 167.6**, 134.2**, 133.0**, 132.2*, 131.0*, 130.8**, 130.0*, 120.5*, 116.6**, 107.3*, 107.3**, 84.5, 28.5**, 28.6*, 28.2*, 28.2**, 27.5**, 27.4*, 20.8**, 20.8*, 19.7, 15.6*, 12.5**; IR: 2923, 2852, 2174, 1760, 1459, 1369, 1213, 842 cm^{-1}; MS *m/z* (relative intensity): 278 (8%, M^+), 263 (37%, M+1), 249 (30%), 203 (48%), 131 (50%), 119 (79%), 117 (80%), 86 (66%), 84 (88%), 75 (60%), 73 (100%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{26}O_2Si$, 278.1702; found: 278.1700.

*E isomer; **Z isomer

Spectra Recorded as ~1:1 mixture of E/Z isomers



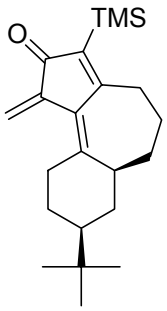
51a

(51a).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **47a** (25 mg, 0.069 mmol, ~1:1 dr) and $[Rh(CO)_2Cl]_2$ (4 mg, 0.01 mmol) were reacted in toluene (0.68 mL) for 18 h. Purification via flash chromatography (hexanes/EtOAc, 8:2, v/v) afforded the title compound (20 mg, 74%) as a slightly yellowish oil in an ~2:1 dr. R_f = 0.13 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.82* (s, 0.7H), 5.76** (s, 0.3H), 4.04-3.93 (m, 4H), 3.04-2.64 (m, 3H), 2.44-2.17 (m, 2H), 2.14 (s, 2.1H)*, 2.13** (s, 0.9H), 2.00-1.40 (m, 8H), 0.26 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 203.5**, 203.3*, 181.7**, 180.3*, 170.0**, 169.0*, 146.7*, 145.8**, 140.0**, 139.8*, 132.5*, 132.0**, 108.4*, 108.4**, 74.3*, 73.5**, 64.5, 64.4*, 64.3**, 43.6, 41.6*, 41.5**, 39.9, 35.3*, 35.2**, 34.4*, 34.4**, 34.3*, 33.8**, 31.5*, 3.3**, 23.0, 21.6**, 20.8*, -0.3; IR: 2947, 2055, 1744, 1695, 1227, 843 cm^{-1}; HRMS-EI (*m/z*): $[M + Na]^+$ calcd for $C_{21}H_{30}O_5NaSi$, 413.1760; found, 413.1752.

*diastereomer 1; **diastereomer 2

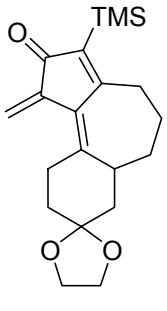
Spectra Recorded as ~2:1 mixture of diastereomers



52

8-Tert-butyl-4,5,6,6a,7,8,9,10-octahydro-1-methylene-3-(trimethylsilyl)benzo[e]azulen-2(1H)-one (52).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **42d** (39 mg, 0.10 mmol, ~1:1 dr) and $[Rh(CO)_2Cl]_2$ (4 mg, 0.01 mmol) were reacted in toluene (1.1 mL) for 69 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5, v/v) afforded the title compound (9 mg, 26%) as a slightly yellow oil. R_f = 0.69 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.06 (s, 1H), 5.57 (s, 1H), 2.95 (ddd, *J* = 16.0, 6.0, 4.5 Hz, 1H), 2.83-2.77 (m, 2H), 2.68-2.61 (m, 1H), 2.55 (ddd, *J* = 14.5, 6.5, 5.0 Hz, 1H), 1.92-1.81 (m, 2H), 1.78-1.67 (m, 3H), 1.64-1.56 (m, 1H), 1.51-1.37 (m, 2H), 1.24 (q, *J* = 12.5 Hz, 1H), 0.89 (s, 9H), 0.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 198.6, 180.4, 150.4, 143.2, 136.9, 131.6, 115.0, 45.1, 42.3, 34.4, 34.0, 32.9, 32.3, 30.6, 27.2, 25.2, 23.1, 0.0; IR: 2951, 2865, 1754, 1683, 1625, 1529, 1366, 1247, 842 cm^{-1}.

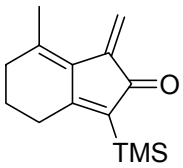


53

(10aZ)-5,6,6a,7,9,10-Hexahydro-1-methylene-3-(trimethylsilyl)benzo[e]azulene-2,8(1H,4H)-dione-8-monoethylene ketal (53).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **47b** (36 mg, 0.096 mmol, 1.5:1 dr) and $[Rh(CO)_2Cl]_2$ (4 mg, 0.01 mmol) were reacted in toluene (0.68 mL) for 47 h. Purification via flash chromatography (hexanes/EtOAc, 85:15, v/v) afforded the title compound (15 mg, 45%) as a slightly yellow oil. R_f = 0.30 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.07 (s, 1H), 5.55 (s, 1H), 4.02-3.91 (m, 4H), 2.97 (dt, *J* = 15.0, 4.5 Hz, 1H)

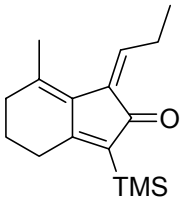
2.96-2.88 (m, 1H), 2.82-2.69 (m, 3H), 1.95 (dt, *J* = 14.0, 5.5 Hz, 1H), 1.92-1.61 (m, 7H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.4, 179.5, 147.9, 142.6, 137.5, 133.5, 115.5, 108.8, 64.2, 64.1, 41.1, 37.2, 34.2, 33.6, 31.2, 28.7, 23.3, -0.0; IR: 2949, 2893, 1683, 1624, 1530, 1247, 1120, 842 cm^{-1}; MS *m/z* (relative intensity): 360 (9%, M + 16), 344 (16%, M^+), 99 (100%), 86 (54%), 73 (66%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{20}H_{28}O_3Si$, 344.1808; found, 344.1811.



54d

5,6-Dihydro-7-methyl-1-methylene-3-(trimethylsilyl)-1H-inden-2(4H)-one (54d).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **45d** (21 mg, 0.079 mmol) and $[Rh(CO)_2Cl]_2$ (2 mg, 0.005 mmol) were reacted in toluene (0.80 mL) for 2.5 h. Purification via flash chromatography (hexanes/EtOAc, 95:5 to 80:20, v/v) afforded the title compound (9 mg, 49%) as a slightly yellow oil. R_f = 0.65 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.06 (s, 1H), 5.61 (s, 1H), 2.72 (t, *J* = 6.3 Hz, 2H), 2.35 (t, *J* = 5.7 Hz, 2H), 2.12 (s, 3H), 1.83 (quint, *J* = 6.3 Hz, 2H), 0.23 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 198.4, 175.2, 140.0, 139.2, 132.8, 130.4, 114.6, 33.3, 27.3, 21.9, 21.3, -0.4; IR: 2951, 2823, 1685, 1647, 1545, 1246, 842 cm^{-1}; MS *m/z* (relative intensity): 248 (14%, M + 16), 232 (38%, M^+), 217 (100%), 191 (12%), 167 (34%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{14}H_{20}OSi$, 232.1283; found, 232.1281.

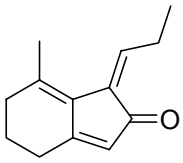


54e

(1Z)-5,6-Dihydro-7-methyl-3-(trimethylsilyl)-1-propylidene-1H-inden-2(4H)-one (54e).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction allene-yne **45e** (35 mg, 0.12 mmol) and

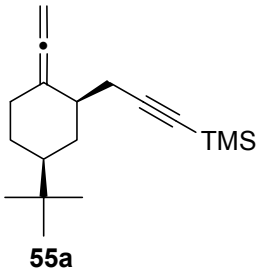
$[Rh(CO)_2Cl]_2$ (4 mg, 0.010 mmol) were reacted in toluene (1.2 mL) for 1.5 h. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5 to 90:10, v/v) afforded **53e** (13 mg, 42%) and **53e'** (3 mg, 13 %) as yellow oils. **53e**: R_f = 0.73 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.40 (t, *J* = 7.5 Hz, 1 H), 2.92 (quint, *J* = 7.5 Hz, 2H), 2.67 (t, *J* = 6.5 Hz, 2H), 2.31 (t, *J* = 6.0 Hz, 2H), 2.09 (s, 3H), 1.79 (quint, *J* = 6.0 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 200.6, 172.5, 141.2, 136.4, 134.3, 132.1, 131.7, 33.9, 27.2, 22.0, 21.6, 21.1, 14.2, -0.2; IR: 2954, 2870, 1674, 1640, 1553, 1246, 840 cm^{-1}; MS *m/z* (relative intensity): 276 (24% M + 16), 260 (58%, M^+), 244 (100%), 229 (29%), 215 (27%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{24}OSi$, 260.1596; found, 260.1590.



54e'

(1Z)-5,6-Dihydro-7-methyl-1-propylidene-1H-inden-2(4H)-one (54e').

R_f = 0.44 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.46 (t, *J* = 7.5 Hz, 1 H), 5.84 (s, 1H), 2.93 (quint, *J* = 7.5 Hz, 2H), 2.61 (t, *J* = 6.0 Hz, 2H), 2.32 (t, *J* = 5.5 Hz, 2H), 2.10 (s, 3H), 1.80 (quint, *J* = 6.0 Hz, 2H), 1.11 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 196.4, 165.6, 142.1, 136.8, 131.8, 130.2, 124.7, 34.0, 26.1, 21.9, 21.4, 21.1, 14.1; IR: 2932, 2872, 1695, 1583, 1456, 1372, 1247, 1179, 844 cm^{-1}; MS *m/z* (relative intensity): 188 (100%, M^+), 173 (52%), 91 (41%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{13}H_{16}O$, 188.1201; found, 188.1195.

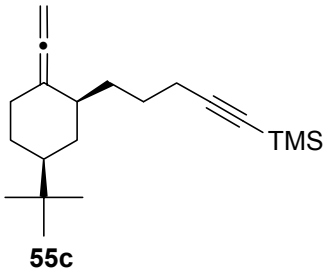


55a

(3-(5-Tert-butyl-2-vinylidenecyclohexyl)prop-1-ynyl)trimethylsilane (55a).

A flame-dried, 25 mL, 2-necked round-bottomed flask containing a Teflon-coated stir-bar was equipped with an internal condenser and $AlCl_3$ (49 mg, 0.37 mmol) was added. The flask was flushed with N_2 and THF (9.3 mL) was added. The solution was cooled in an ice/H_2O bath and lithium aluminum hydride was added (1.1 mL,

1.0 M in Et_2O, 1.1 mmol) via syringe. After 15 min in an ice/H_2O bath, a solution of **38a** (154 mg, 0.530 mmol) ~2:1 dr (**38a-eq**/**38a-ax**) in THF (5.3 mL) was added dropwise via cannula, then heated to reflux. After 3.5 h consumption of starting material was observed via TLC and the reaction was cooled in an ice/H_2O bath The reaction was carefully quenched by the addition of saturated aq Rochelle's salt and diluted with Et_2O and H_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 95:5, v/v) affording the title compound (47 mg, 33%) as a single diastereomer. R_f = 0.91 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.74-4.64 (m, 2H), 2.45-2.37 (m, 2H), 2.24-1.82 (m, 5H), 1.21-1.02 (m, 2H), 0.87-0.77 (m, 1H), 0.88 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 202.0, 106.7, 104.9, 85.7, 76.2, 47.7, 38.4, 33.8, 32.6, 31.8, 27.9, 27.5, 24.8, 0.2; IR: 2957, 2863, 2176, 1960, 1440, 1249, 843 cm^{-1}; MS *m/z* (relative intensity): 274 (20%, M^+), 259 (38%), 217 (50%), 86 (79%), 84 (87%), 73 (100%), 59 (66%), 57 (93%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{18}H_{30}Si$, 274.2117; found, 274.2111.

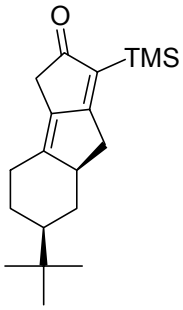


55c

(5-((1S,5S)-5-Tert-butyl-2-vinylidenecyclohexyl)pent-1-ynyl)trimethylsilane (55c).

A flame-dried 15 mL 2 neck round-bottomed flask containing a Teflon-coated stir-bar equipped with an internal condenser and $AlCl_3$ (18 mg, 0.13 mmol) was added. The flask was flushed with N_2 and THF (3.1 mL) was added. The solution was cooled in an ice/H_2O bath and lithium aluminum hydride was added (0.35 mL, 1.0 M in Et_2O, 0.35 mmol) via syringe. The solution was stirred 15 min in an ice/H_2O bath. A solution of **38c-ax** (56 mg, 0.18 mmol) in THF (1.8 mL) was added dropwise via cannula. The

solution was then heated to reflux. After 5 h consumption of starting material was observed via TLC and the reaction was cooled in an ice/H_2O bath. The reaction was quenched with the addition of saturated aq Rochelle's salt and diluted with Et_2O and H_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude material was purified via flash chromatography (hexanes/EtOAc, 97.5:2.5 to 90:10, v/v) affording the title compound (15 mg, 28%) as a single diastereomer. R_f = 0.92 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300) MHz, $CDCl_3$) δ: 4.67 (t, *J* = 3.9 Hz, 2H); 2.38 (dt, *J* = 12.9, 2.7 Hz, 1H), 2.22 (t, *J* = 7.2 Hz, 2H), 2.03-1.74 (m, 4H) 1.68-1.53 (m, 2H), 1.35-1.02 (m, 4H), 0.92-0.78 (m, 1H), 0.87 (s, 9H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 202.4, 107.8, 106.0, 84.3, 75.4, 48.0, 38.9, 35.0, 33.4, 32.5, 32.3, 28.3, 27.6, 26.6, 20.1, 0.2; IR: 2953, 2854, 2175, 1958, 1441, 1365, 1249, 841cm^{-1}; MS *m/z* (relative intensity): 302 (34%, M^+), 171 (32%), 73 (100%), 57 (82%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{20}H_{34}Si$, 302.2430; found, 302.2421.

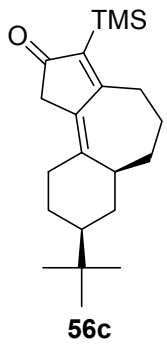


56a

6-Tert-butyl-4,5,6,7,7a,8-hexahydro-1-(trimethylsilyl)cyclopenta[a]inden-2(3H)-one (56a).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **55a** (14 mg, 0.051 mmol) and $[Rh(CO)_2Cl]_2$ (2 mg, 0.005 mmol) reacted in toluene (0.5 mL) for 30 min. Purification via flash chromatography (hexanes/EtOAc, 97.5:2.5 to 95:5, v/v) afforded the title compound (5 mg, 32%) as a slightly yellowish oil. R_f = 0.57 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.03 (dd, *J* = 18.9, 6.3 Hz, 1H), 2.86-2.80 (m, 1H), 2.82 (1/2 ABq, *J* = 18.0 Hz, 1H), 2.68 (1/2 ABq, *J* = 18.0 Hz, 1H), 2.64 (ddd, *J* = 13.5, 3.9, 2.4 Hz, 1H), 2.35 (d,

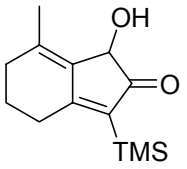
J = 19.2, 1H), 2.23-2.08 (m, 2H), 2.05-1.94 (m, 1H), 1.30 (tt, *J* = 12.0, 2.7 Hz, 1H), 1.09 (td, *J* = 12.6, 4.2 Hz, 1H), 0.96-0.84 (m, 1H), 0.89 (s, 9H), 0.21 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 212.0, 194.3, 150.1, 137.3, 130.1, 49.8, 47.5, 36.1, 35.5, 35.0, 32.5, 28.1, 27.8, 27.7, -1.1; IR: 2951, 2864, 1690, 1563, 1244, 1205, 840 cm^{-1}; MS *m/z* (relative intensity): 303 (15%, M + 1), 302 (49%, M^+), 218 (8%), 84 (77%), 73 (30%) HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{19}H_{30}OSi$, 302.2066; found, 302.2064.



56c

(5-((1S,5S)-5-Tert-butyl-2-vinylidenecyclohexyl)pent-1-ynyl)trimethylsilane (56c).

Following the General Procedure for the $[Rh(CO)_2Cl]_2$ Catalyzed Cyclocarbonylation Reaction, allene-yne **55c** (13 mg, 0.043 mmol) and $[Rh(CO)_2Cl]_2$ (2 mg, 0.005 mmol) was reacted in toluene (0.43 mL) for 40 min. Purification via flash chromatography (hexanes/EtOAc, 95:5, v/v) afforded the title compound (10 mg, 70%) as a slightly yellowish oil. R_f = 0.63 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300) MHz, $CDCl_3$) δ: 3.05 (1/2 ABq, *J* = 18.0 Hz, 1H), 2.96 (1/2 ABq, *J* = 18.0 Hz, 1H), 2.91-2.84 (m, 2H), 2.57 (dt, *J* = 13.8, 3.9 Hz, 1H), 2.44-2.33 (m, 1H), 2.06-1.93 (m, 2H), 1.93-1.58 (m, 5H), 1.57-1.26 (m, 3H), 1.24-1.06 (m, 2H), 0.96-0.87 (m, 1H), 0.87 (s, 9H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 208.8, 181.3, 144.7, 142.8, 130.5, 47.6, 44.8, 43.6, 37.3, 36.0, 35.5, 35.4, 32.4, 28.1, 27.5, -0.1; IR: 2939, 2863, 1680, 1515, 1246, 842 cm^{-1}; MS *m/z* (relative intensity): 330 (64%, M^+), 315 (100%), 73 (68%), 57 (53%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{21}H_{34}OSi$, 330.2379; found, 330.2383.

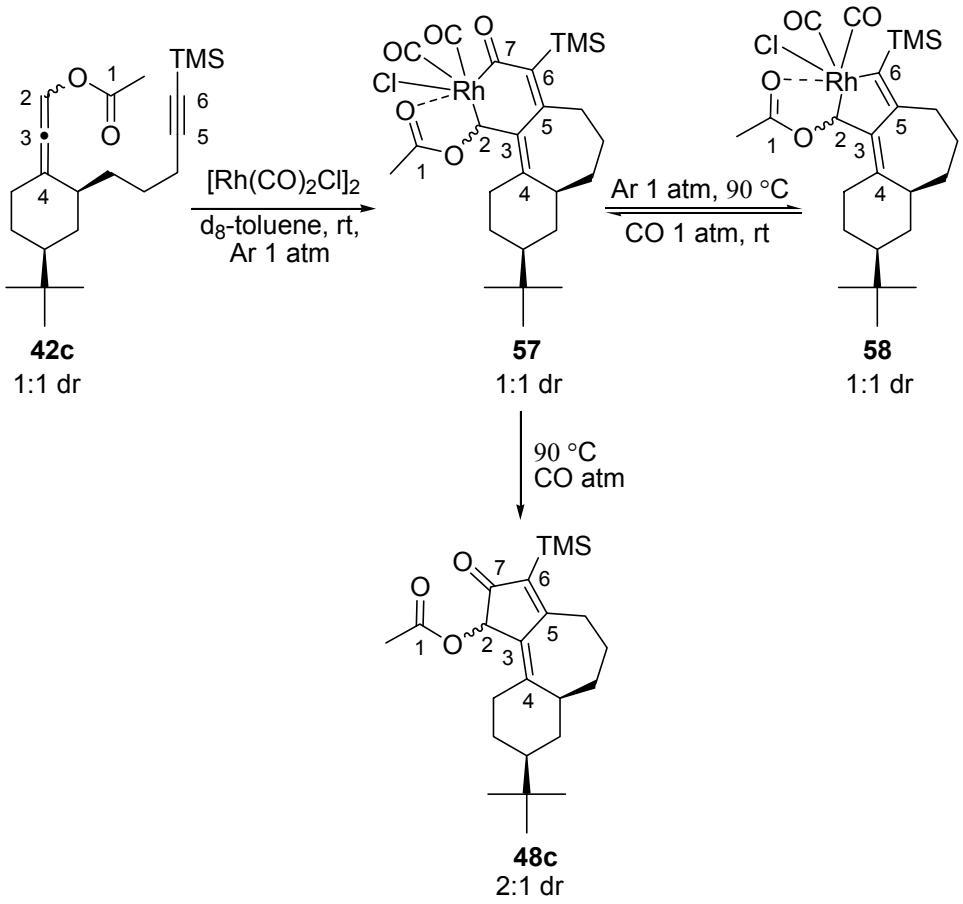


59

5,6-Dihydro-1-hydroxy-7-methyl-3-(trimethylsilyl)-1H-inden-2(4H)-one (59).

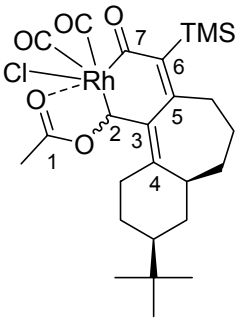
To a flame-dried, 5 mL round-bottomed flask equipped with a stir-bar was added **22c** (12 mg, 0.043 mmol), MeOH (0.44 mL). K_2CO_3 (8 mg, 0.06 mmol), and H_2O (0.44 mL). After 16 h at rt, consumption of **49c** was observed via TLC. The reaction mixture was diluted with Et_2O and quenched by the addition of saturated aq NH_4Cl. The solution was diluted with H_2O and Et_2O. The aq layer was separated and extracted with Et_2O (3×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude oil via flash chromatography (hexanes/EtOAc, 80:20, v/v) afforded the title compound (6 mg, 60%) as an off-white solid. R_f = 0.24 (hexanes/EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.42 (s, 1H), 2.77 (ddd, *J* = 17.1, 6.0, 4.8 Hz, 1H), 2.69 (bs, 1H), 2.57 (ddd, *J* = 16.8, 10.2, 4.8 Hz, 1H), 2.31-2.18 (m, 2H), 2.03 (s, 3H), 1.96-1.72 (m, 2H), 0.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 210.0, 178.3, 140.3, 134.0, 131.9, 70.9, 31.2, 27.4, 21.9, 20.6, -0.6; IR: 3348, 2948, 2905, 1666, 1532, 1429, 837 cm^{-1}. MS *m/z* (relative intensity): 237 (19%), 236 (100%, M^+), 235 (54%), 221 (77%), 117 (72%); HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{13}H_{20}O_2Si$, 236.1233; found, 236.1235.

Preparation and Characterization of Rhodocycle Intermediates



d_8-Toluene was obtained from a freshly opened bottle and deoxygenated by bubbling with N_2 ~5 min prior to use. An oven dried NMR tube, equipped with septa was evacuated and refilled with Ar (3×). A solution of allene-yne **42c** (0.56 mL, 0.1 M in d_8-toluene [prepared by dissolving 40 mg **41c** in d_8-toluene (1.11 ml)], 0.56 mmol) was added via syringe followed by $[Rh(CO)_2Cl]_2$ (0.56 mL, 0.1 M in d_8-toluene [prepared by sonicating 34 mg $[Rh(CO)_2Cl]_2$ in d_8-toluene (0.87 ml)], 0.56 mmol). The tube was shaken and allowed to stand at rt in a darkened hood under Ar. Progress of the reaction was monitored by ^{1}H NMR, for the disappearance of resonances corresponding to the allene protons of **42c** at δ = 7.60 (bs) and 7.58 (bs) ppm and the appearance of new resonances at δ = 7.50 (d, *J* = 3.0 Hz) and 7.40 (d, *J* = 3.0 Hz) ppm. After 20 h complete consumption of **42c** was observed and the tube was placed in a 90 °C oil bath under Ar. The

reaction was monitored periodically by ^{1}H NMR, showing disappearance of (δ = 7.50 (d, *J* = 3.0 Hz) and 7.40 (d, *J* = 3.0 Hz) ppm) and appearance of new resonances at (δ = 7.17 (d, *J* = 3.0 Hz) and 6.98 (d, *J* = 3.0 Hz) ppm) by ^{1}H NMR. The transformation was complete after 17 h. The NMR tube was then evacuated and refilled with CO (3×), vigorously shaken, and sonicated for 2 min. The solution was maintained under CO atmosphere at rt periodically shaking, monitoring for disappearance of (δ = 7.17 (d, *J* = 3.0 Hz) and 6.98 (d, *J* = 3.0 Hz) ppm) and reappearance of (δ = 7.50 (d, *J* = 3.0 Hz) and 7.40 (d, *J* = 3.0 Hz) ppm) by ^{1}H NMR. After 17 h the transformation was complete. The NMR tube was then placed in a 90 °C oil bath under CO, shaking each time the CO balloon was refilled, monitoring for disappearance of (δ = 7.50 (d, *J* = 3.0 Hz) and 7.40 (d, *J* = 3.0 Hz) ppm) and appearance of **48c** resonances (δ = 5.86 (s) and 5.79 (s) ppm) by ^{1}H NMR. After 80 h 74% conversion was observed by comparing the integrations of protons for **57** (δ = 7.50 (d, *J* = 3.0 Hz) and 7.40 (d, *J* = 3.0 Hz) ppm in a 3:1 ratio) and **48c** (δ = 5.86 ppm (s) and 5.79 ppm (s) in a 1:2 ratio)



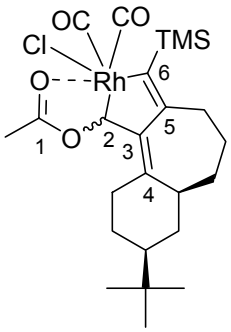
57
1:1 dr

57

^{13}C NMR (75 MHz, $CDCl_3$) δ 211.4** (d, *J* = 26.3 Hz), 211.0* (d, *J* = 27.0 Hz), 185.0**, 184.9*, 183.5** (d, *J* = 86.3 Hz), 182.8* (d, *J* = 86.3 Hz), 159.4*, 158.3**, 143.1**, 142.7*, 140.3**, 140.0*, 134.8*, 133.6**, 102.4** (d, *J* = 27.2 Hz), 102.2* (d, *J* = 26.8 Hz), 48.3**, 47.4*, 47.3**, 43.9*, 38.6, 35.3, 33.5, 32.4, 32.3*, 30.9, 30.4**, 29.6, 28.4**, 28.3*, 27.5, 25.3*, 24.8**, 17.9*, 17.9**, 0.6*, 0.5**

*diastereomer 1; **diastereomer 2

Spectra Recorded as ~1:1 mixture of diastereomers



58

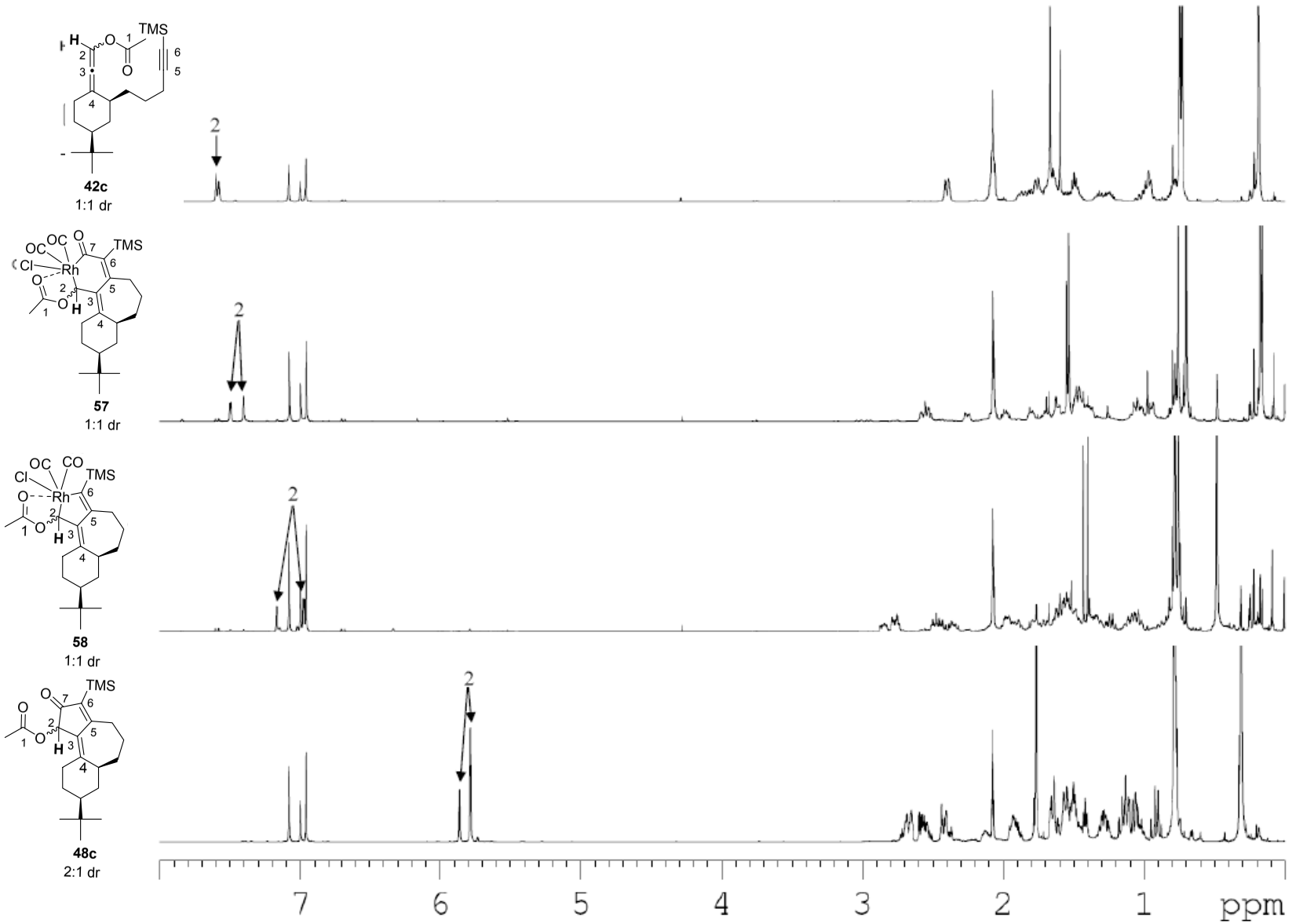
1:1 dr

58

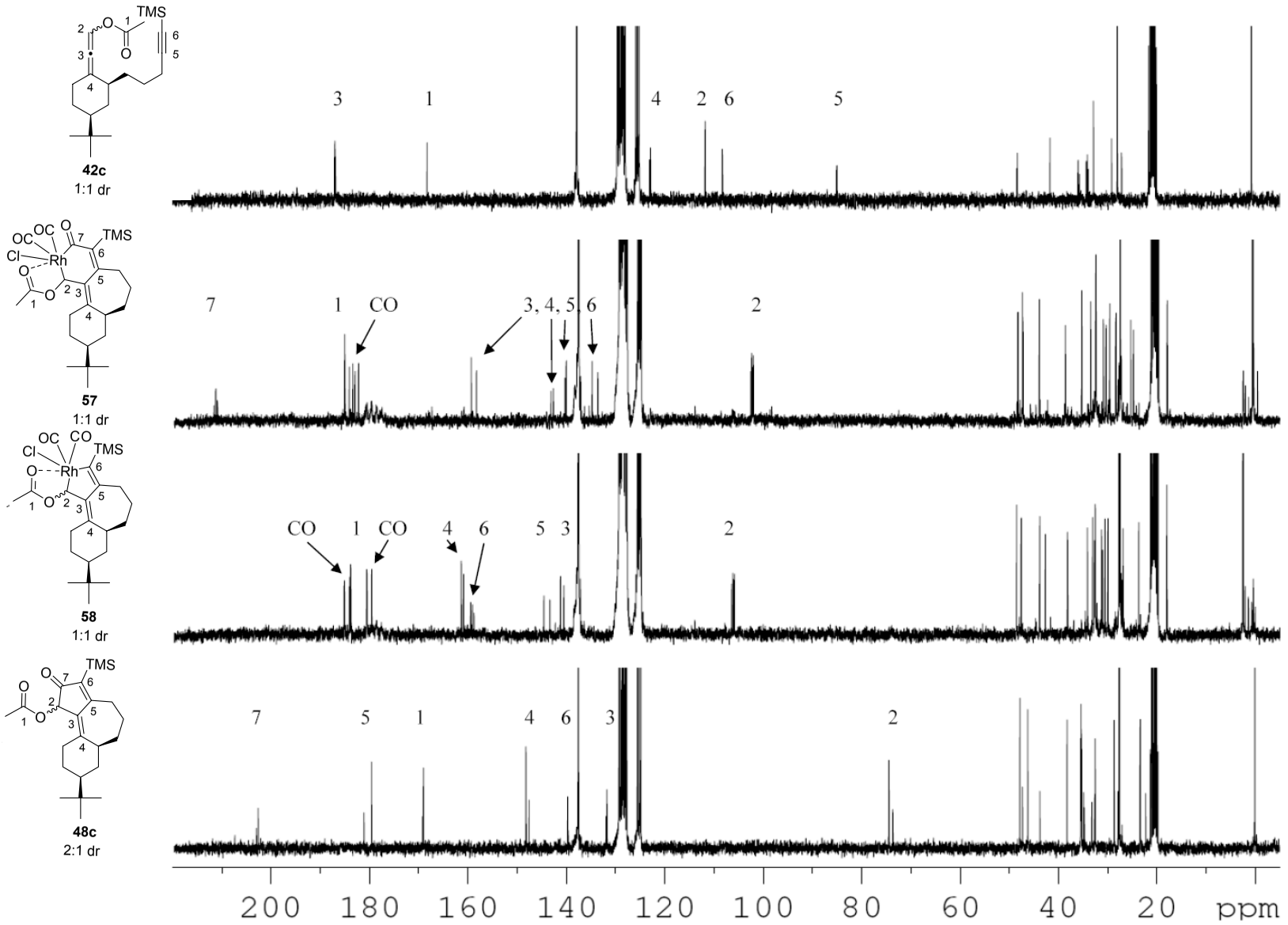
^{13}C NMR (75 MHz, $CDCl_3$) δ 184.6** (d, *J* = 81.4 Hz), 184.5* (d, *J* = 81.2 Hz), 183.9*, 183.8**, 180.1 (d, *J* = 73.7 Hz), 161.4*, 160.9**, 159.3* (d, *J* = 27.5 Hz), 158.9** (s, *J* = 24.8 Hz), 144.6** (d, *J* = 2.4 Hz), 143.4* (d, *J* = 2.6 Hz), 141.2* (d, *J* = 1.4 Hz), 140.5** (d, *J* = 1.8 Hz), 106.2** (d, *J* = 24.9 Hz), 106.0* (d, *J* = 25.0 Hz), 48.5*, 47.6**, 43.8*, 42.7**, 38.1, 34.1**, 33.1*, 32.6*, 32.5**, 31.3*, 31.1**, 30.6*, 30.0**, 27.8**, 27.6*, 27.5**, 26.9**, 23.7, 18.0, 2.6**, 2.5*.

*diastereomer 1; **diastereomer 2

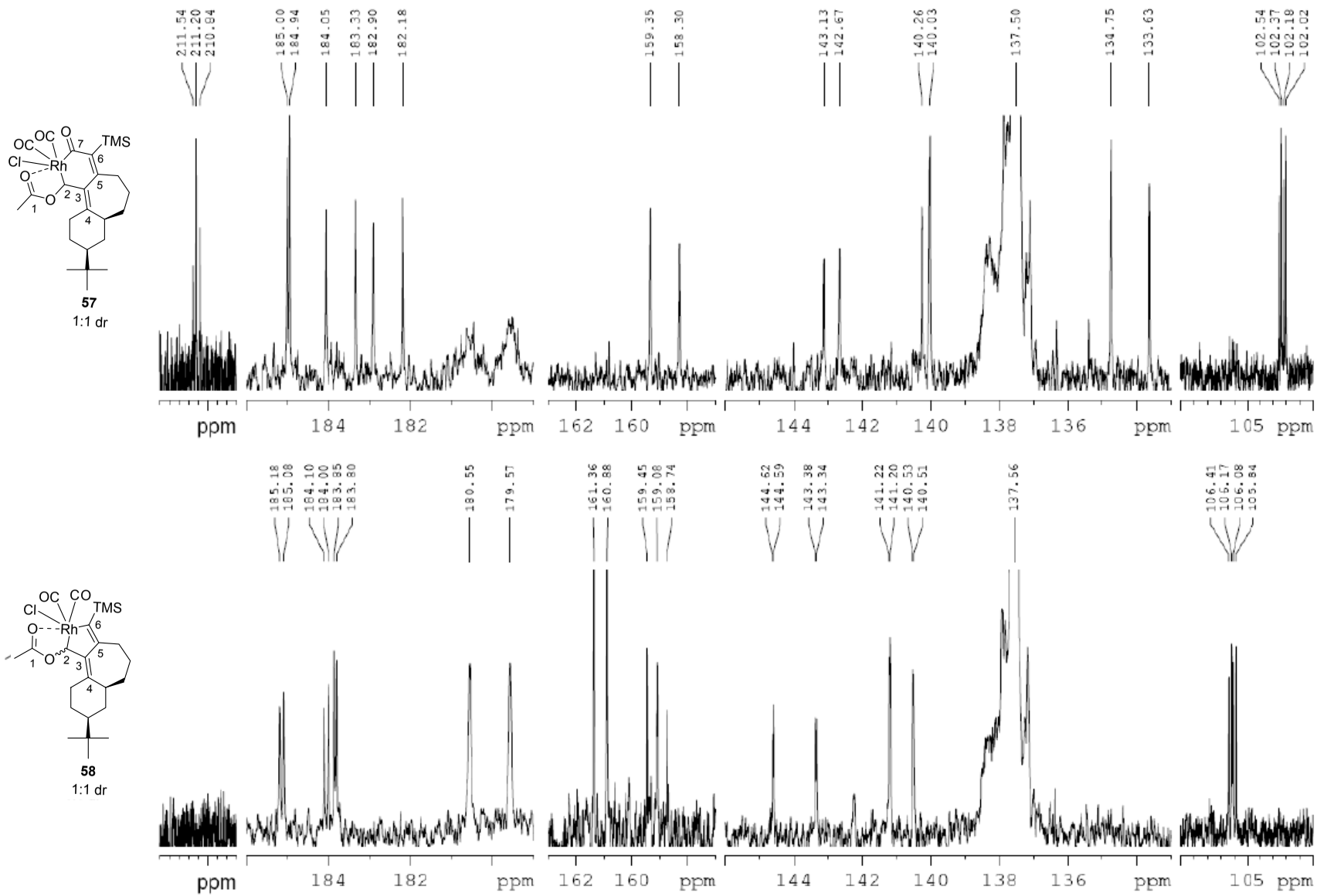
Spectra Recorded as ~1:1 mixture of diastereomers



^{1}H Spectra Recorded at 500 MHz in d_8-toluene at Room Temperature



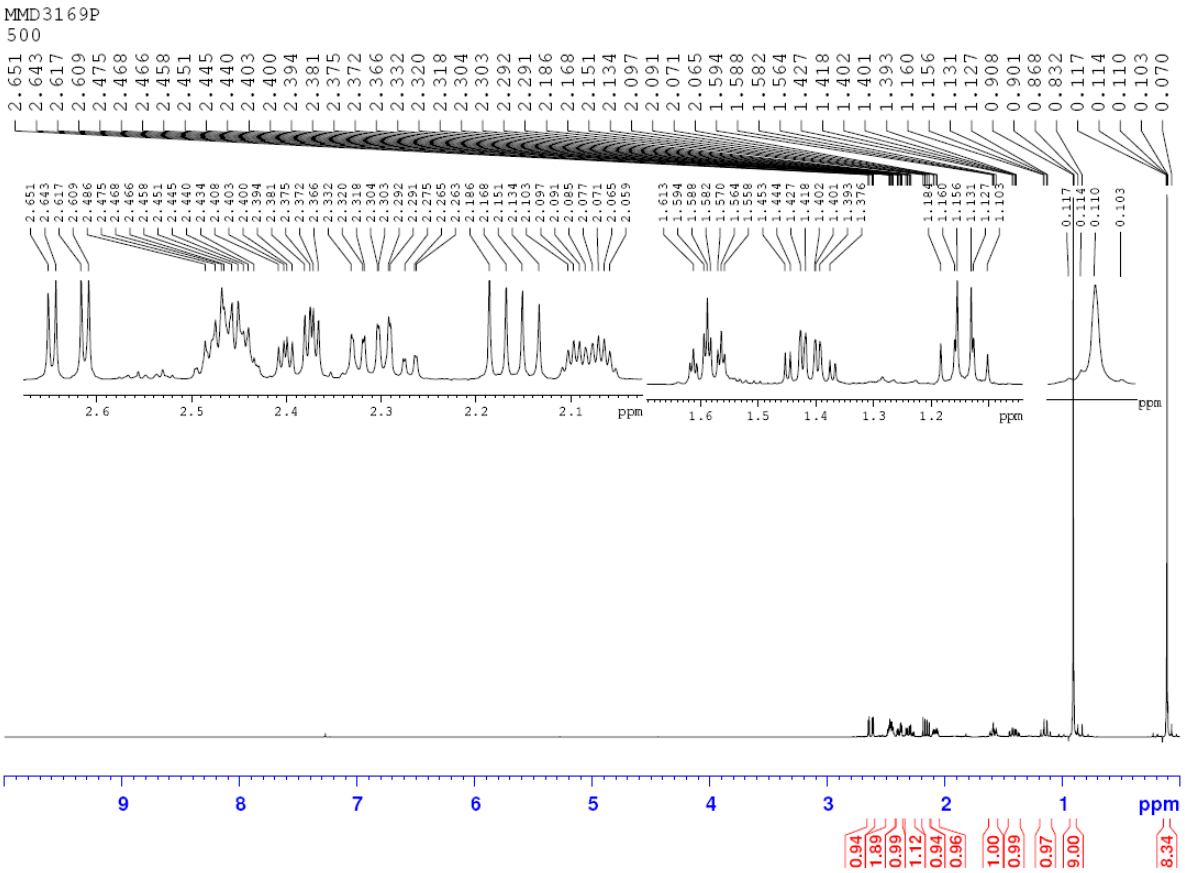
^{13}C Spectra Recorded at 75 MHz in d_8-toluene at Room Temperature

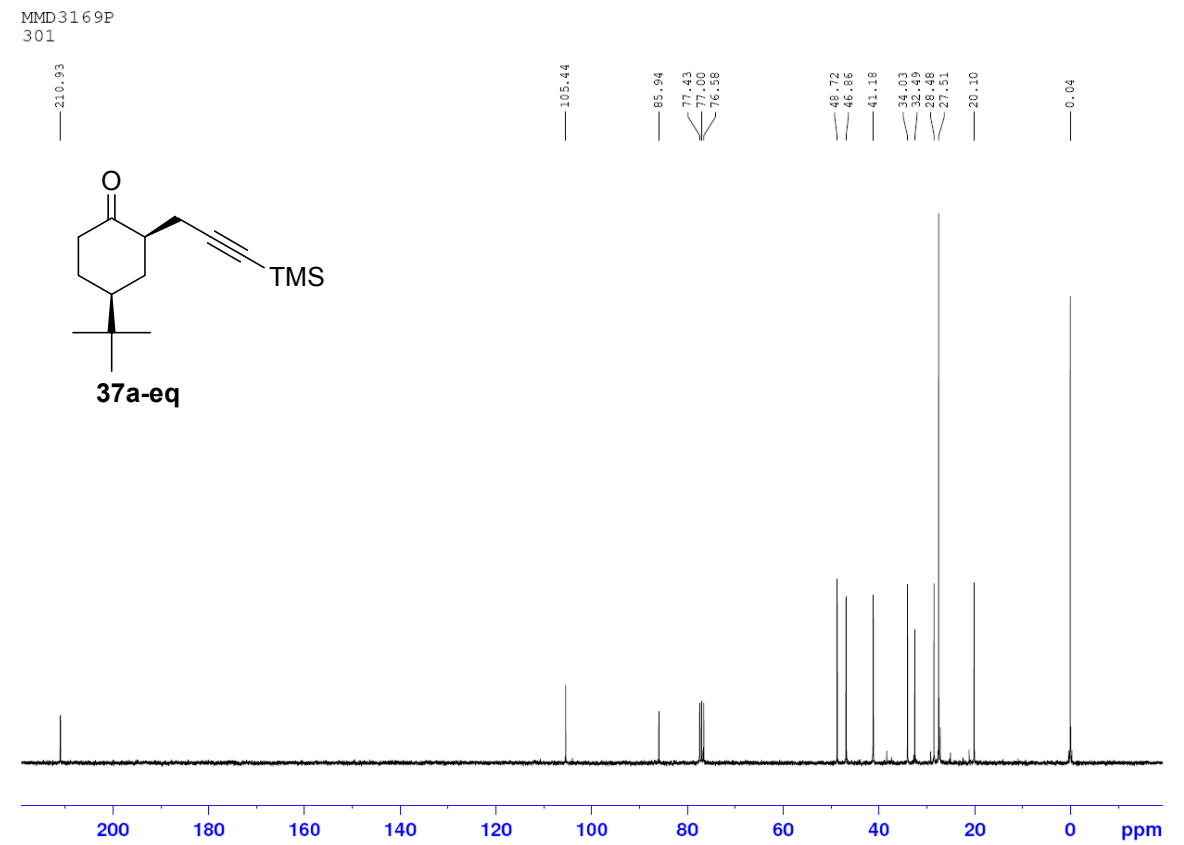


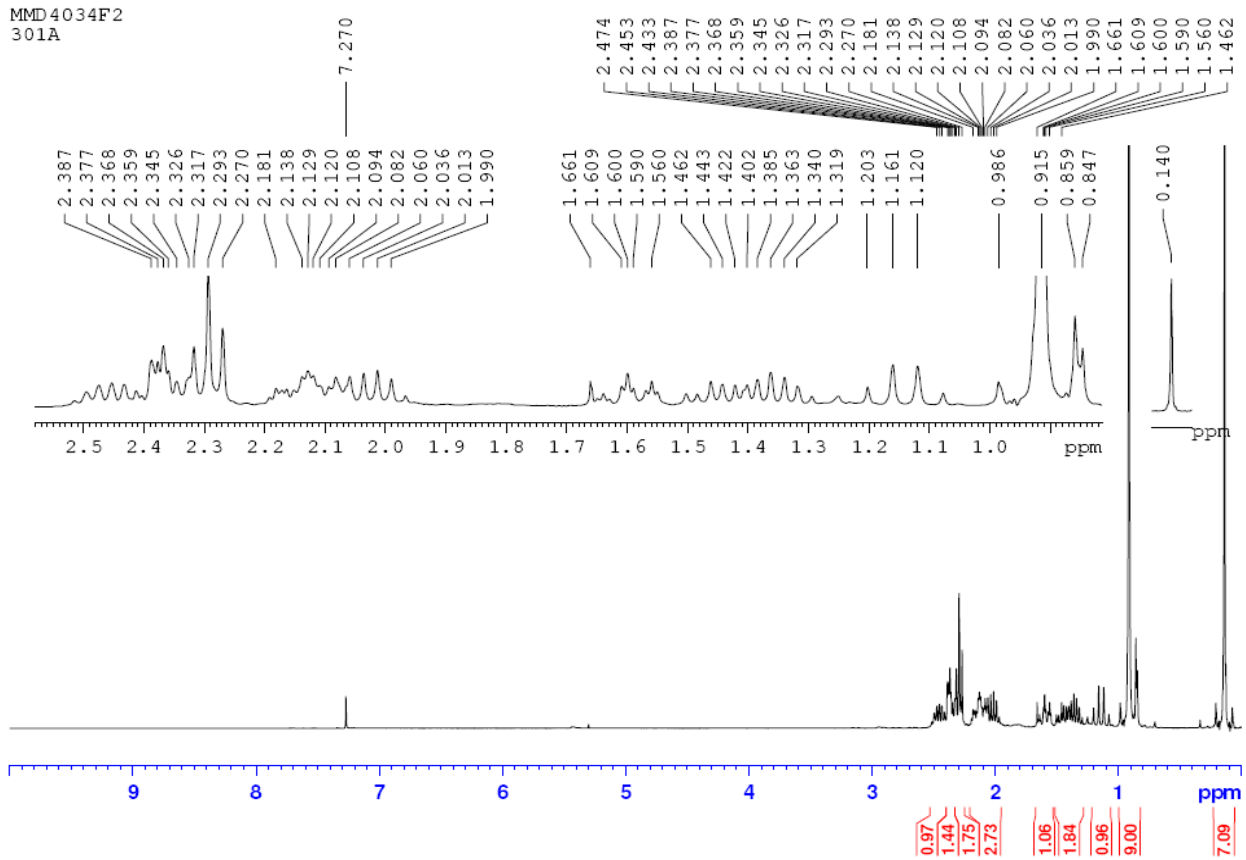
Expansions of ^{13}C NMR Spectra Recorded at 75 MHz in d_8-toluene at Room Temperature

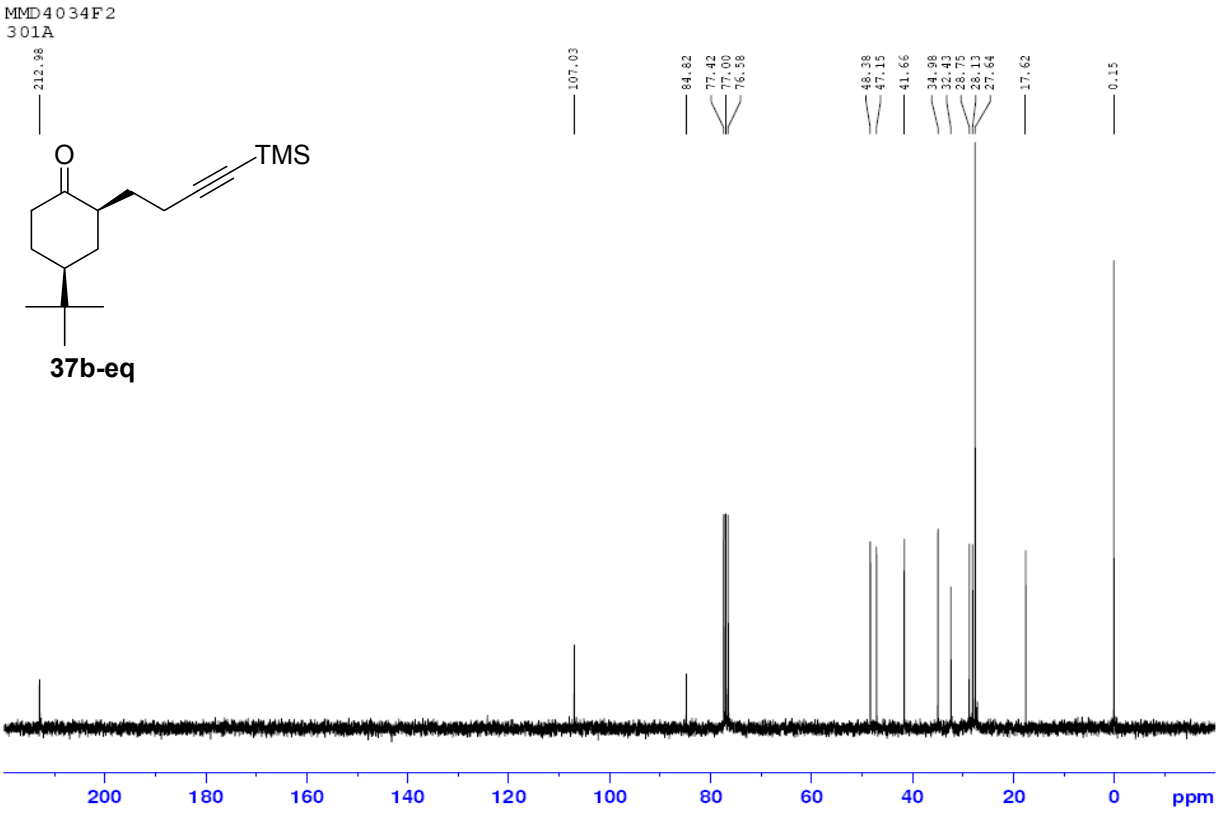
APPENDIX A

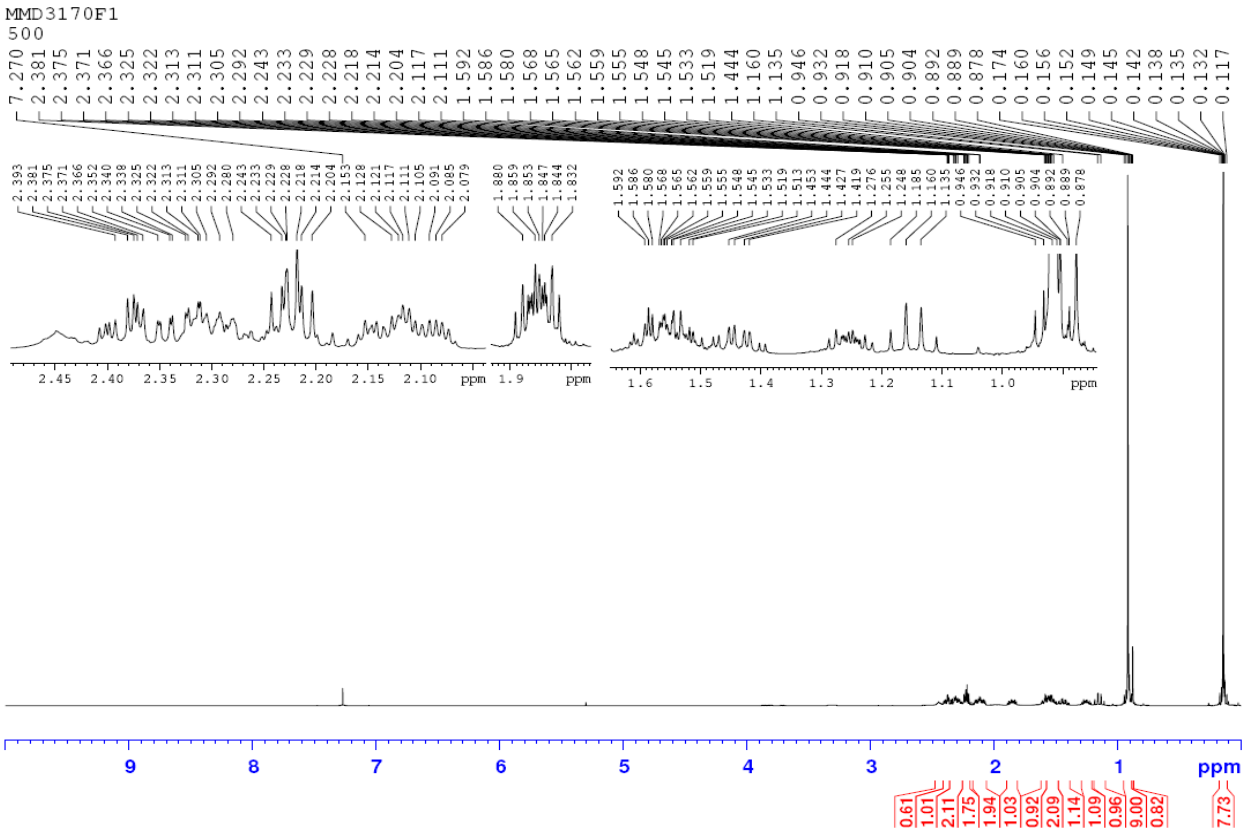
^{1}H AND ^{13}C SPECTRA FOR NEW COMPOUNDS

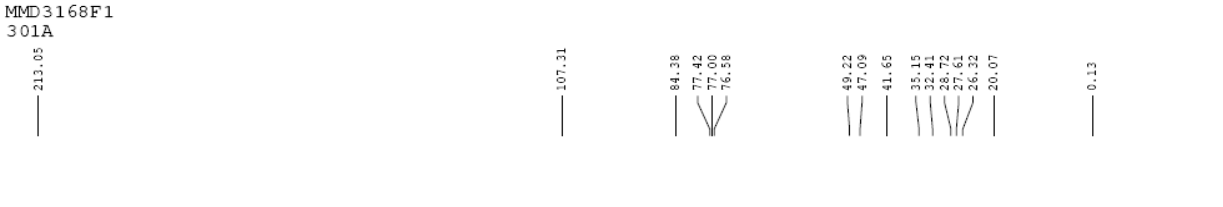

MMD3169P
500
ppm

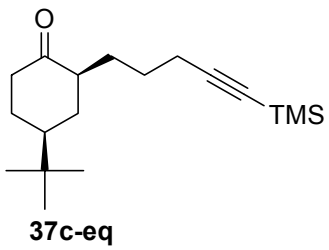

MMD3169P
301
TMS
37a-eq
ppm


MMD4034F2
301A
7.270
2.474 2.453 2.433 2.387 2.377 2.368 2.359 2.345 2.326 2.317 2.293 2.270 2.181 2.138 2.129 2.120 2.108 2.094 2.082 2.060 2.036 2.013 1.990 1.661 1.609 1.600 1.590 1.560 1.462 1.443 1.422 1.402 1.385 1.363 1.340 1.319 1.203 1.161 1.120 0.986 0.915 0.859 0.847 0.140
2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 ppm
ppm
9 8 7 6 5 4 3 2 1 ppm
0.97 1.44 1.75 2.73 1.06 1.84 0.96 9.00 7.09

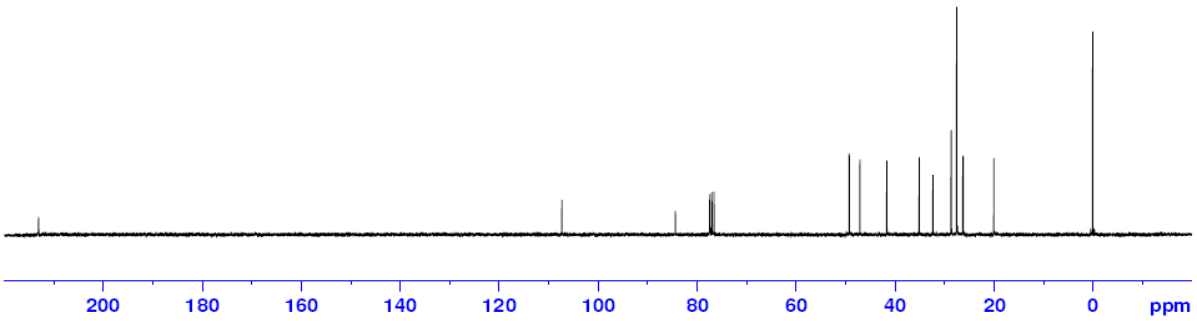

MMD4034F2
301A
212.98
107.03
84.82
77.42
77.00
76.58
48.38
47.15
41.66
34.98
32.43
28.75
28.13
27.64
17.62
0.15
O
TMS
37b-eq
200 180 160 140 120 100 80 60 40 20 0 ppm

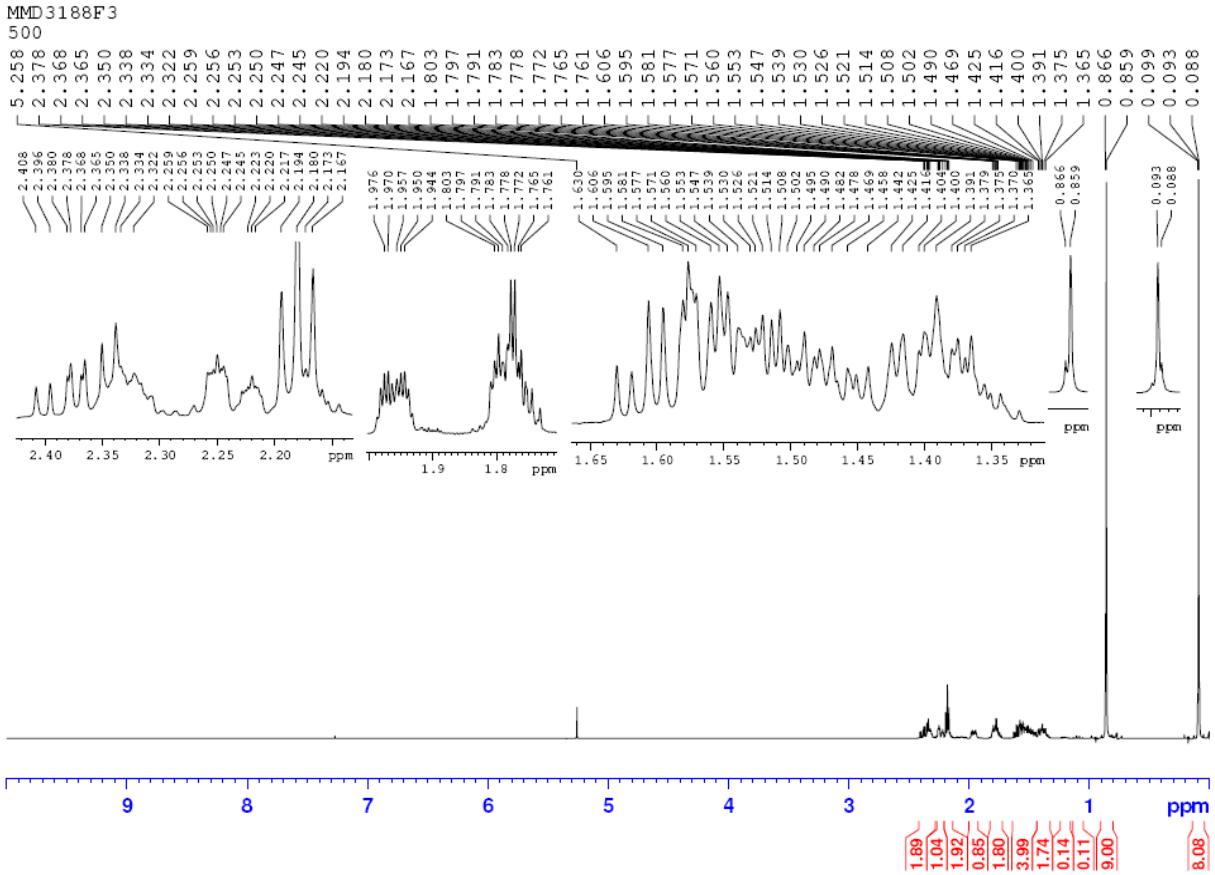


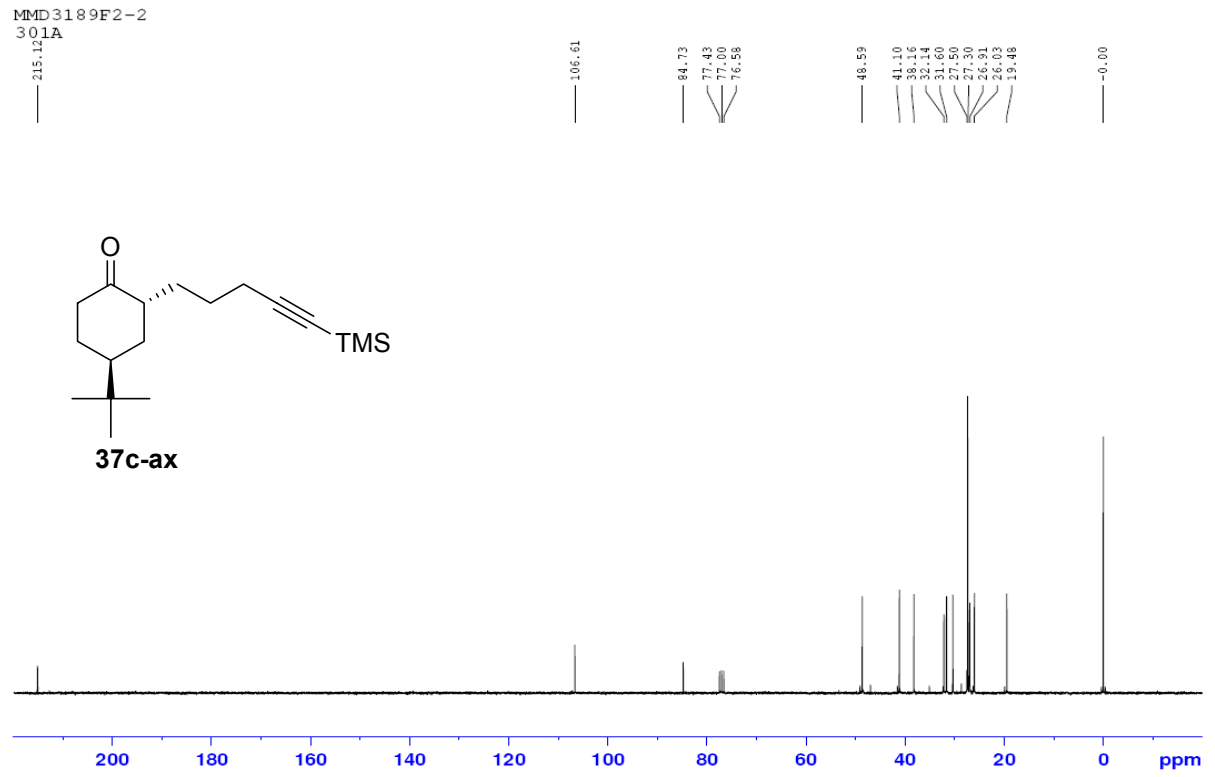


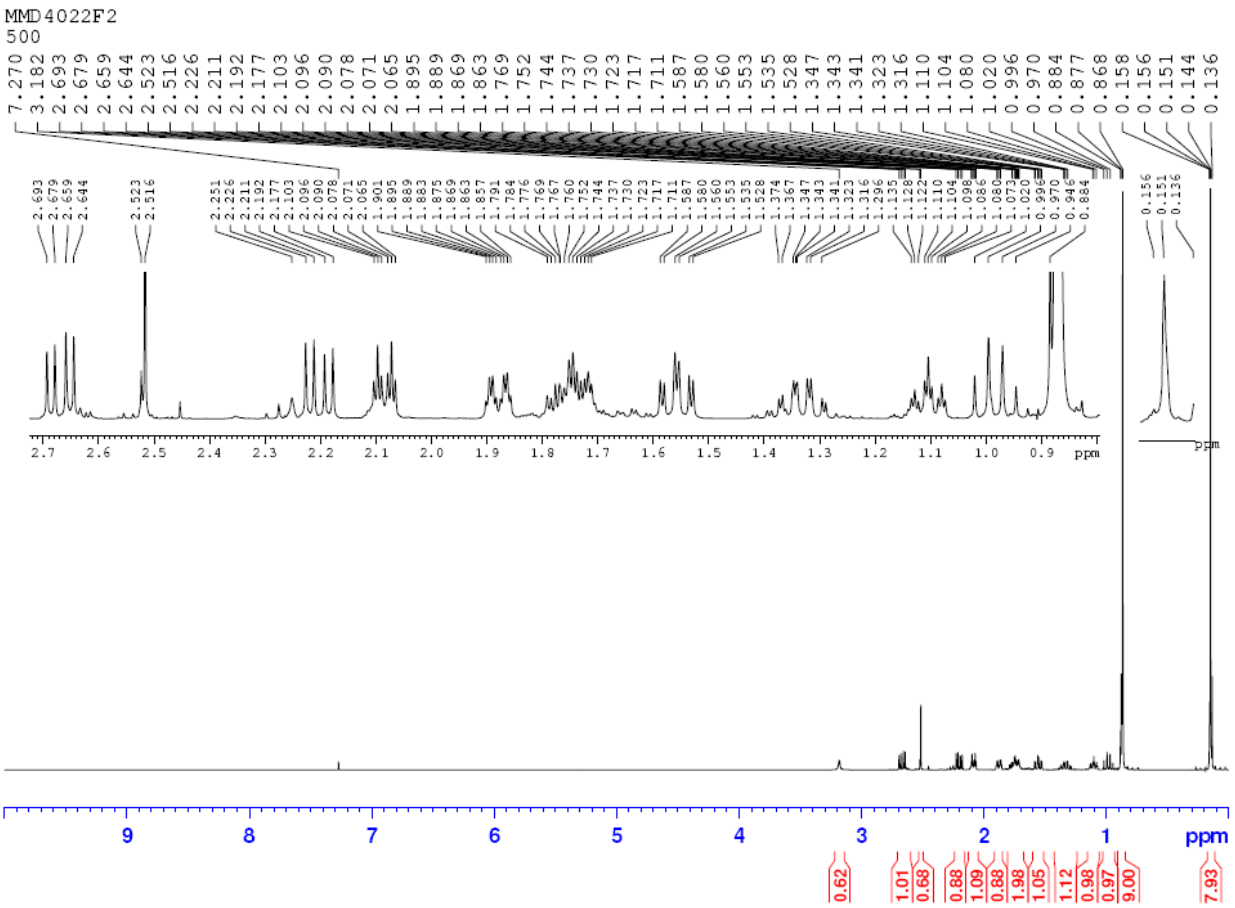


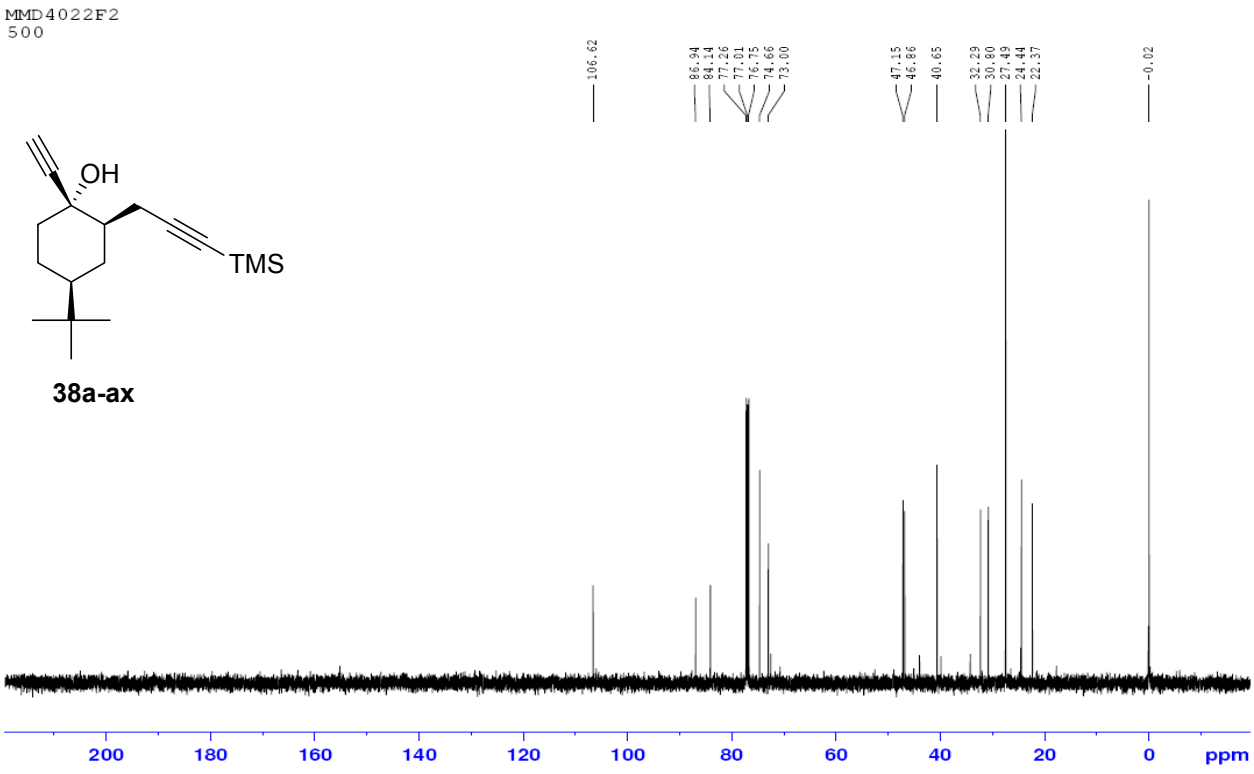
37c-eq



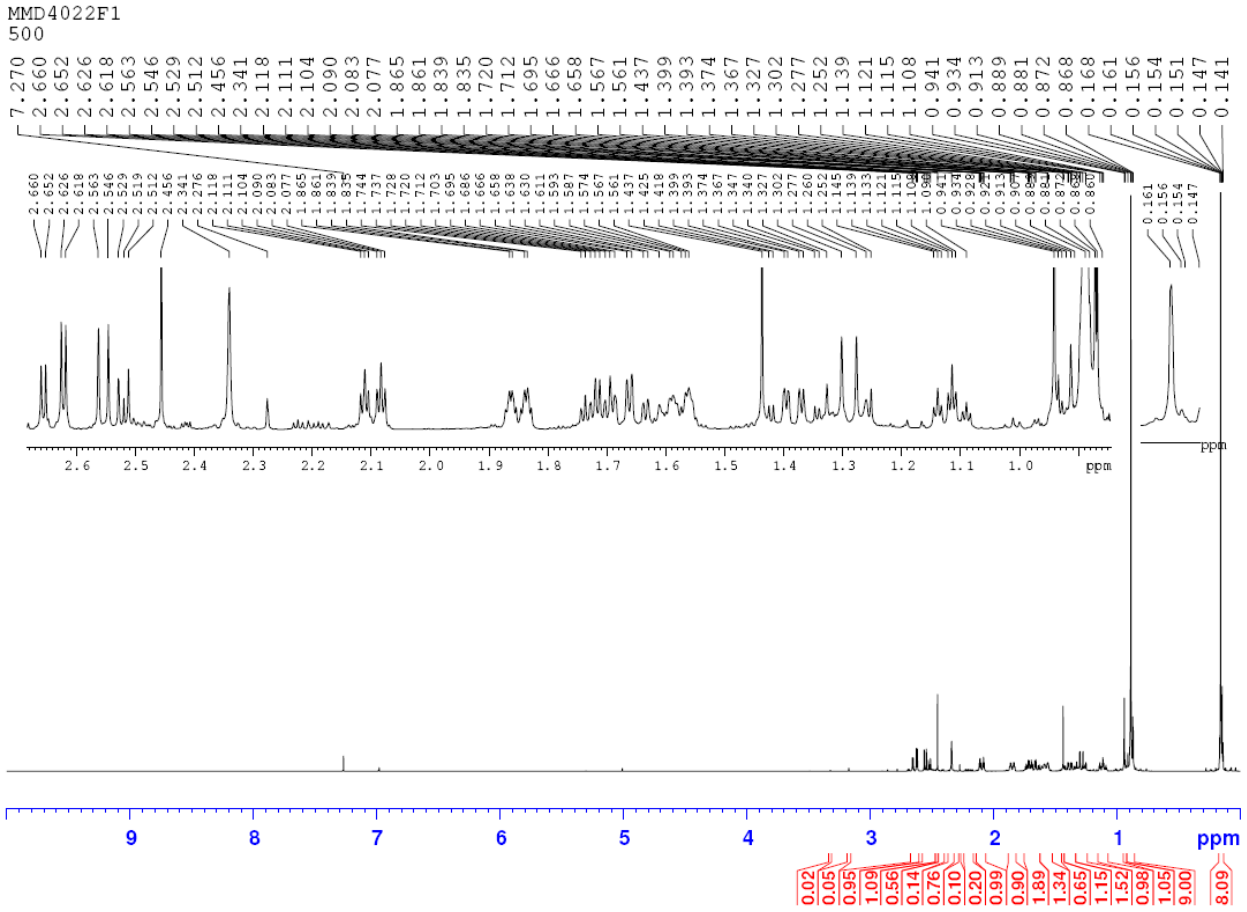

MMD3188F3
500
ppm


MMD3189F2-2
301A
TMS
37c-ax
ppm





38a-ax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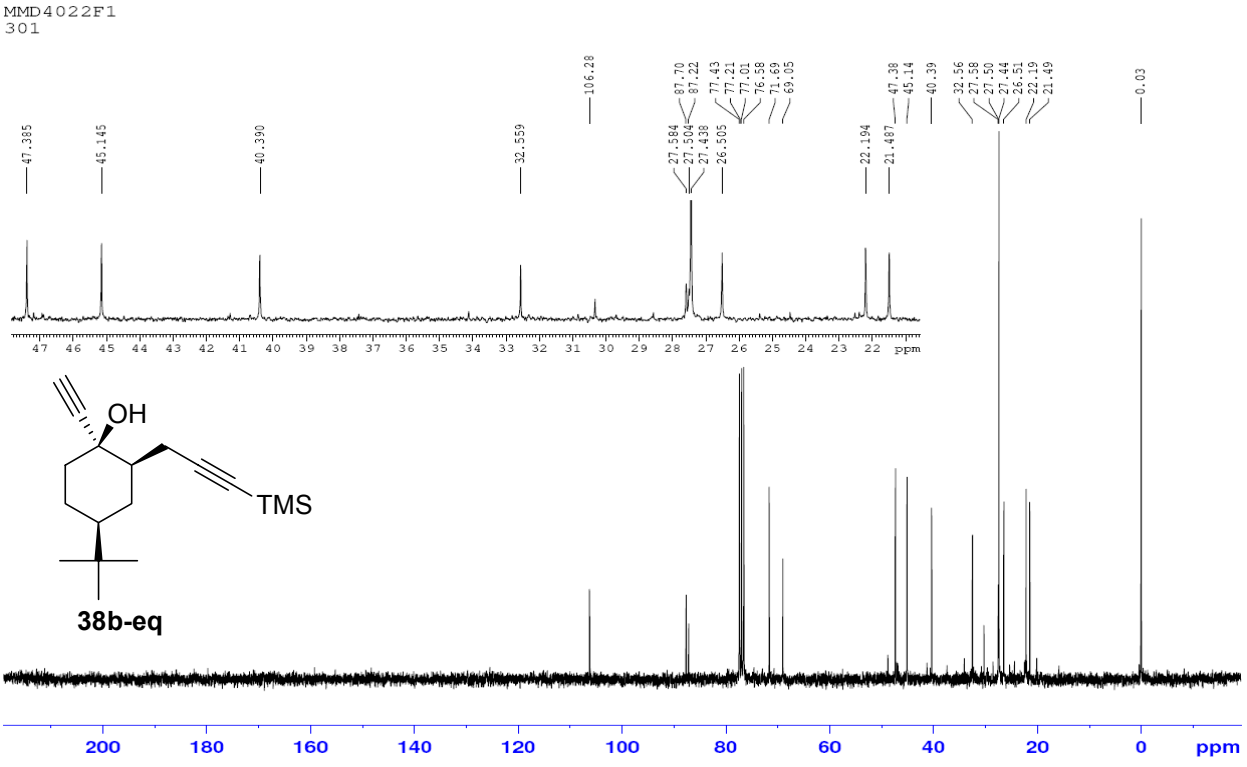
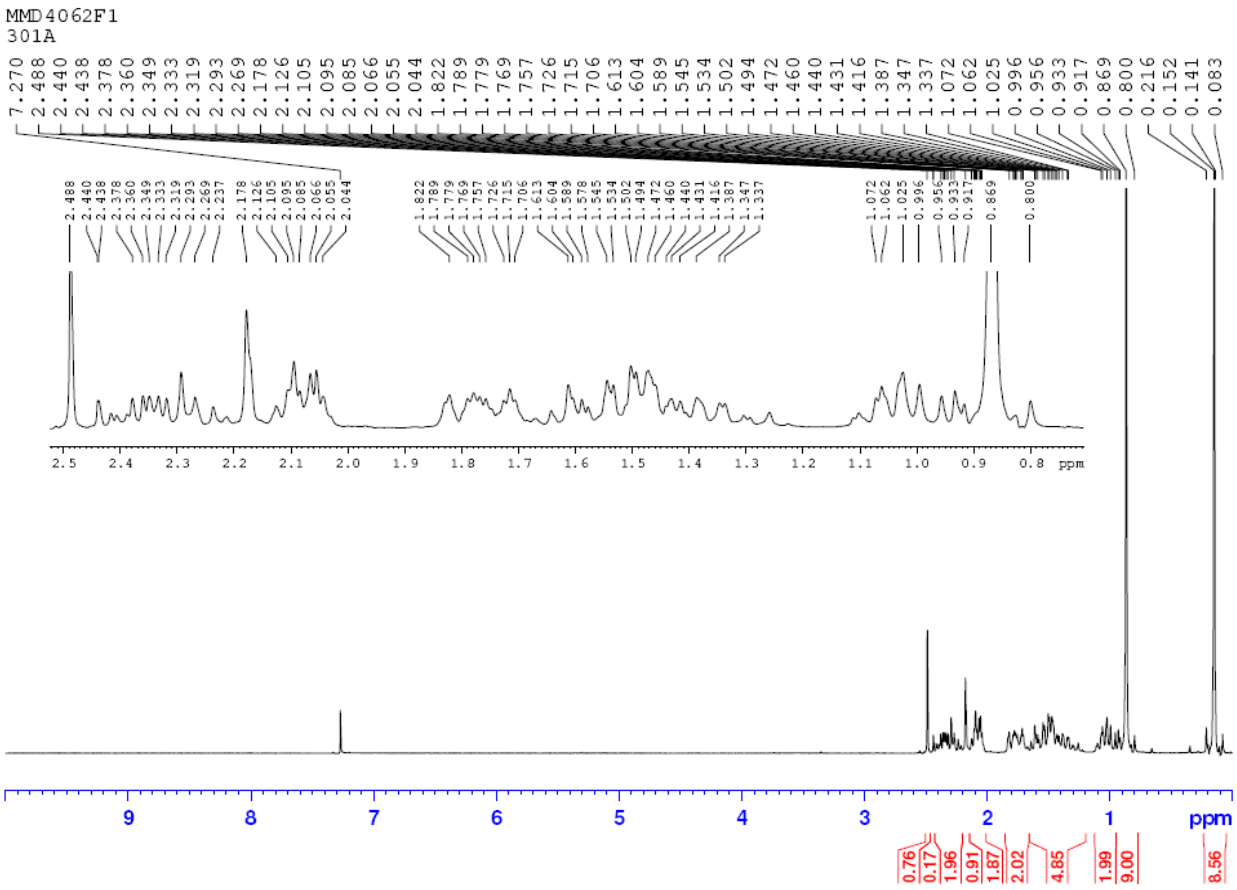
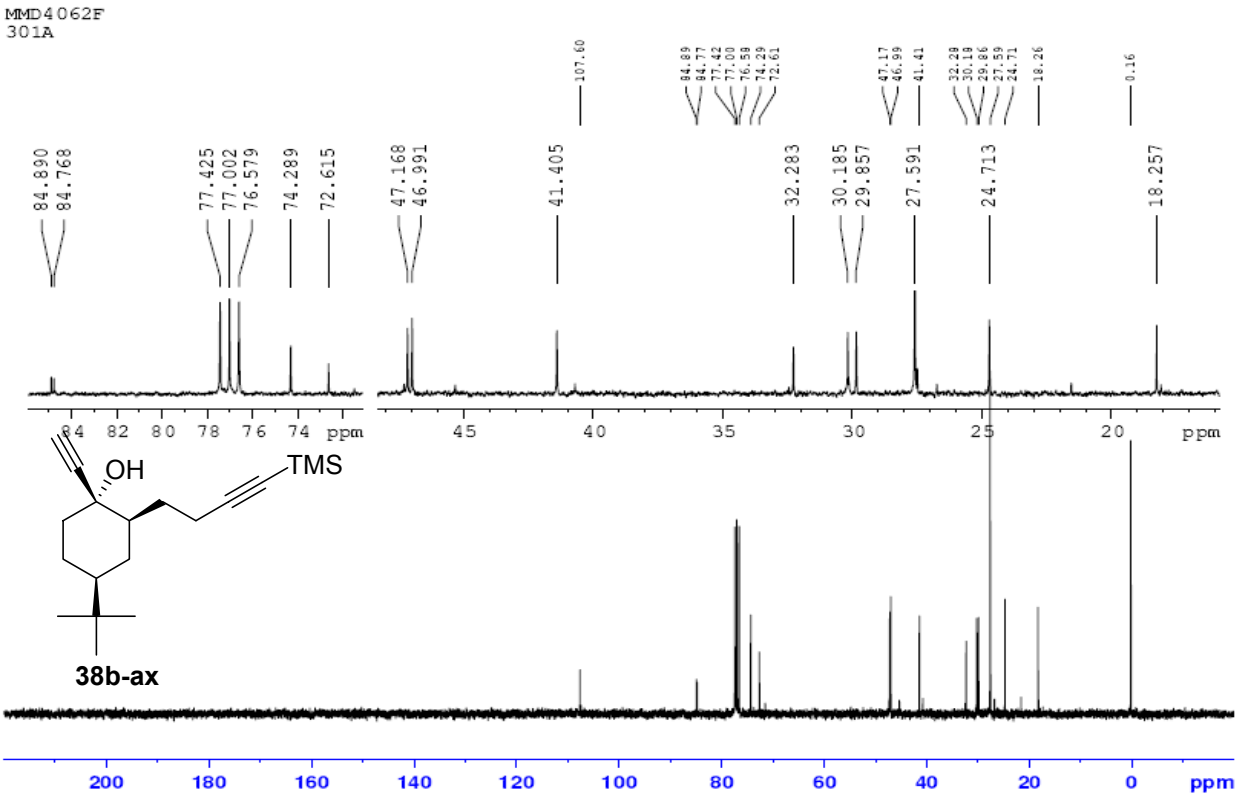
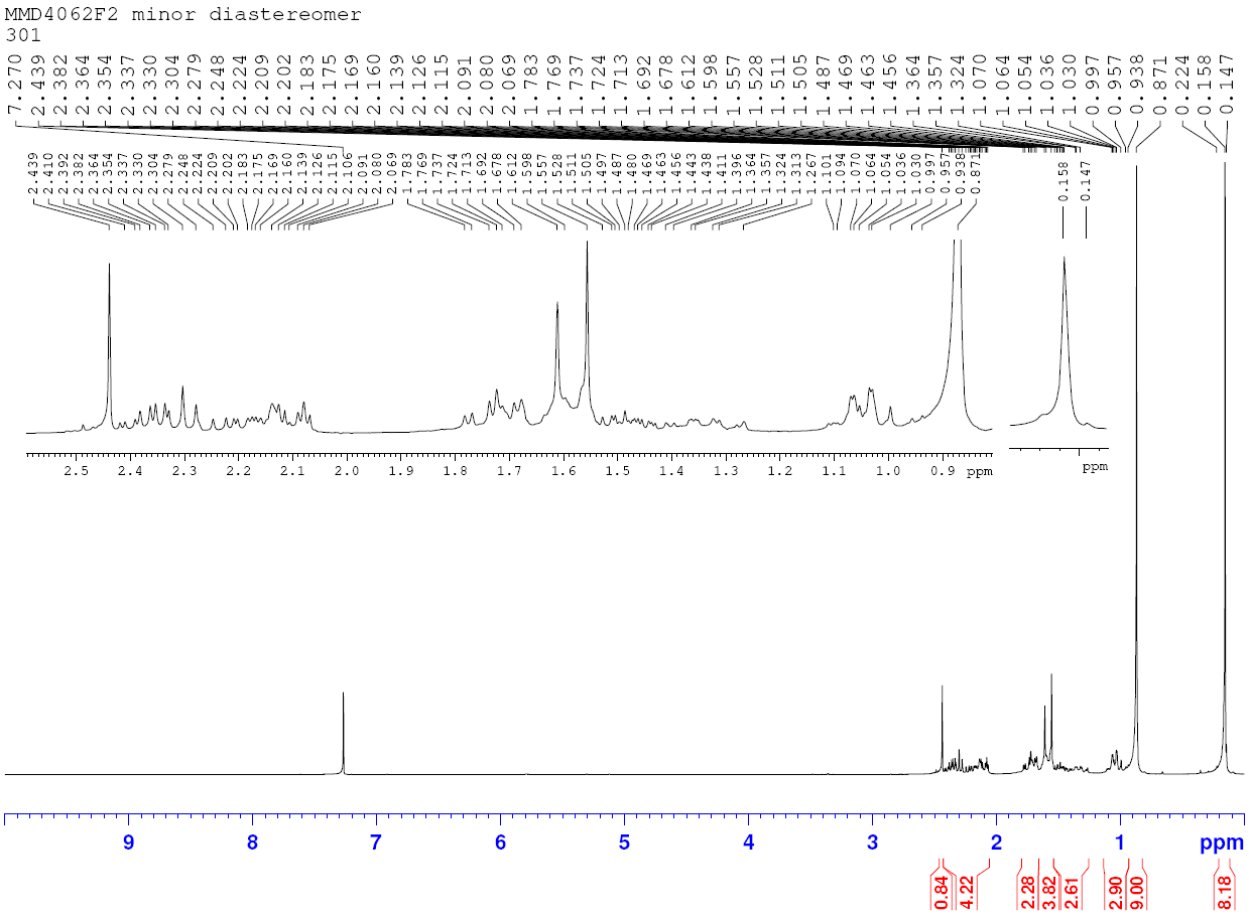
ppm


MMD4022F1
301
OH
TMS
38b-eq
ppm


MMD4062F1
301A
ppm


MMD4062F
301A
OH
TMS
38b-ax
ppm


MMD4062F2 minor diastereomer
301
ppm
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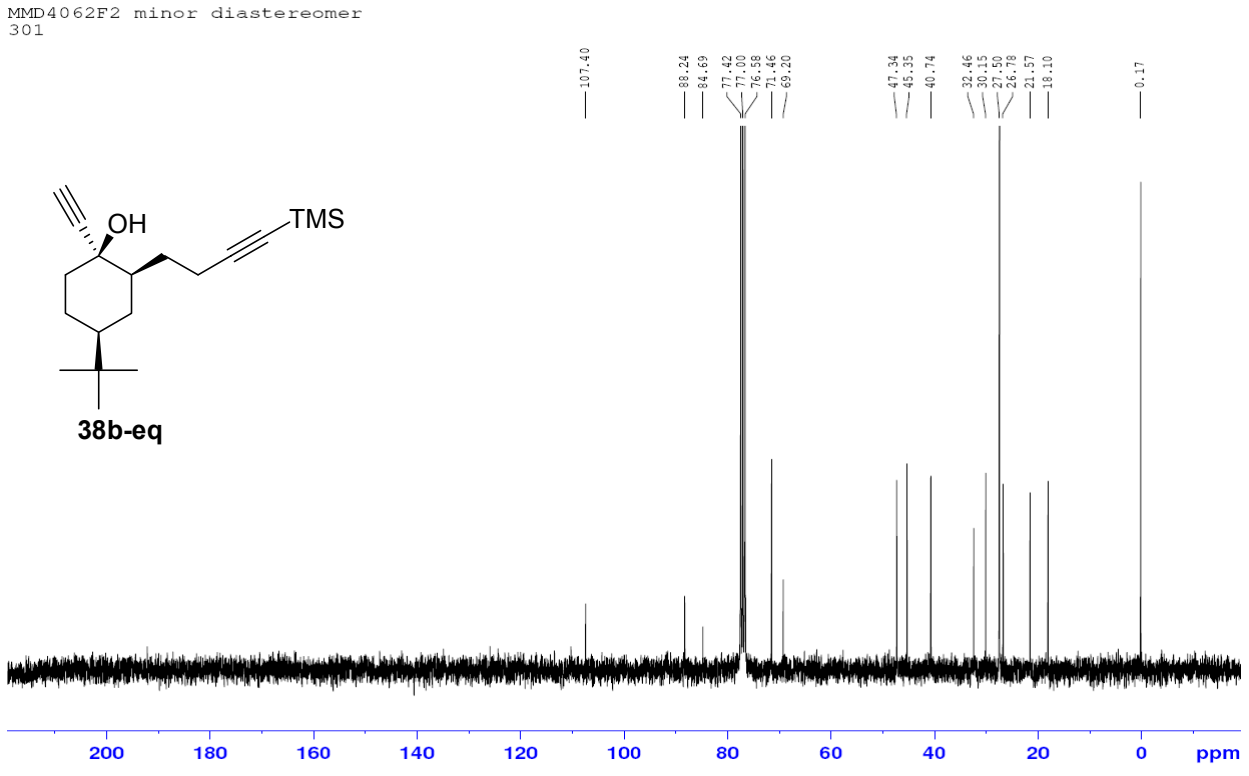
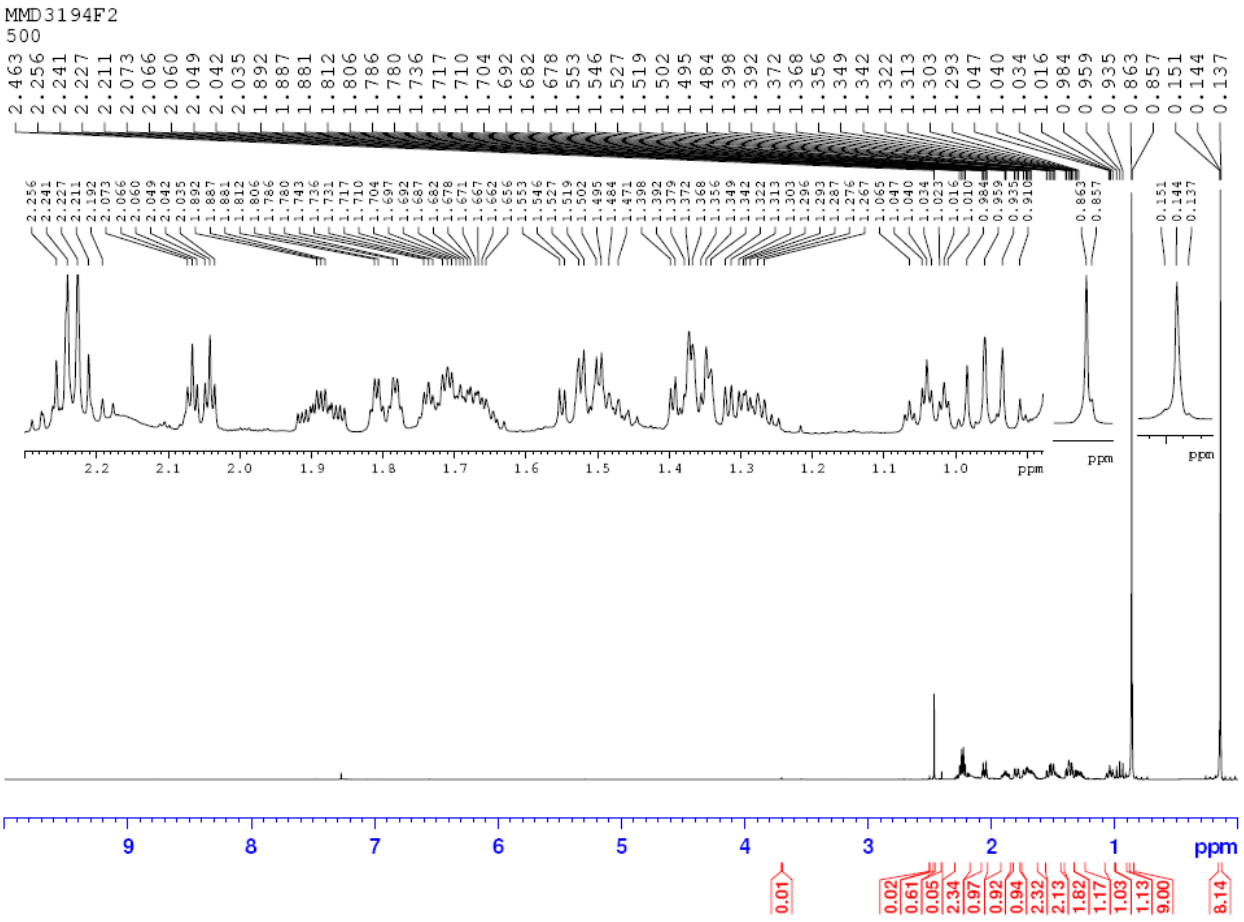
4.22
2.28
3.82
2.61
2.90
9.00
8.18


MMD4062F2 minor diastereomer
301
OH
TMS
38b-eq
ppm


MMD3194F2
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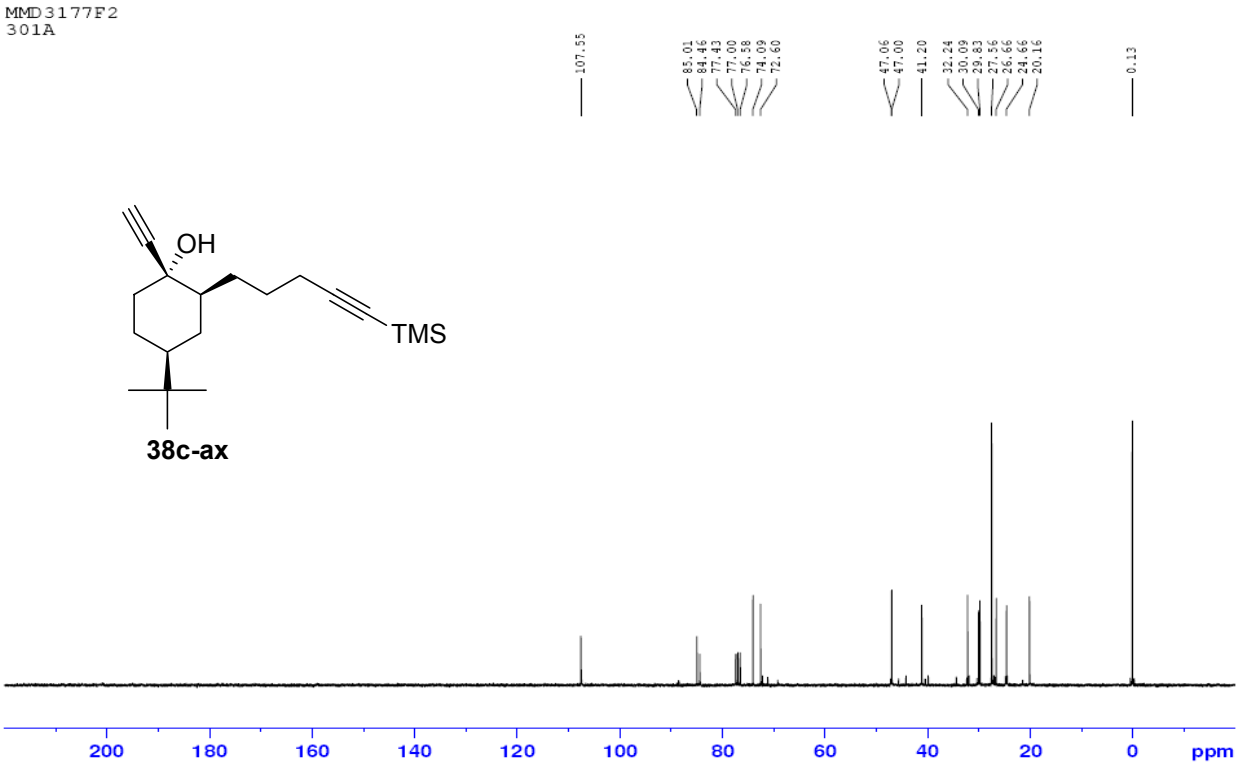
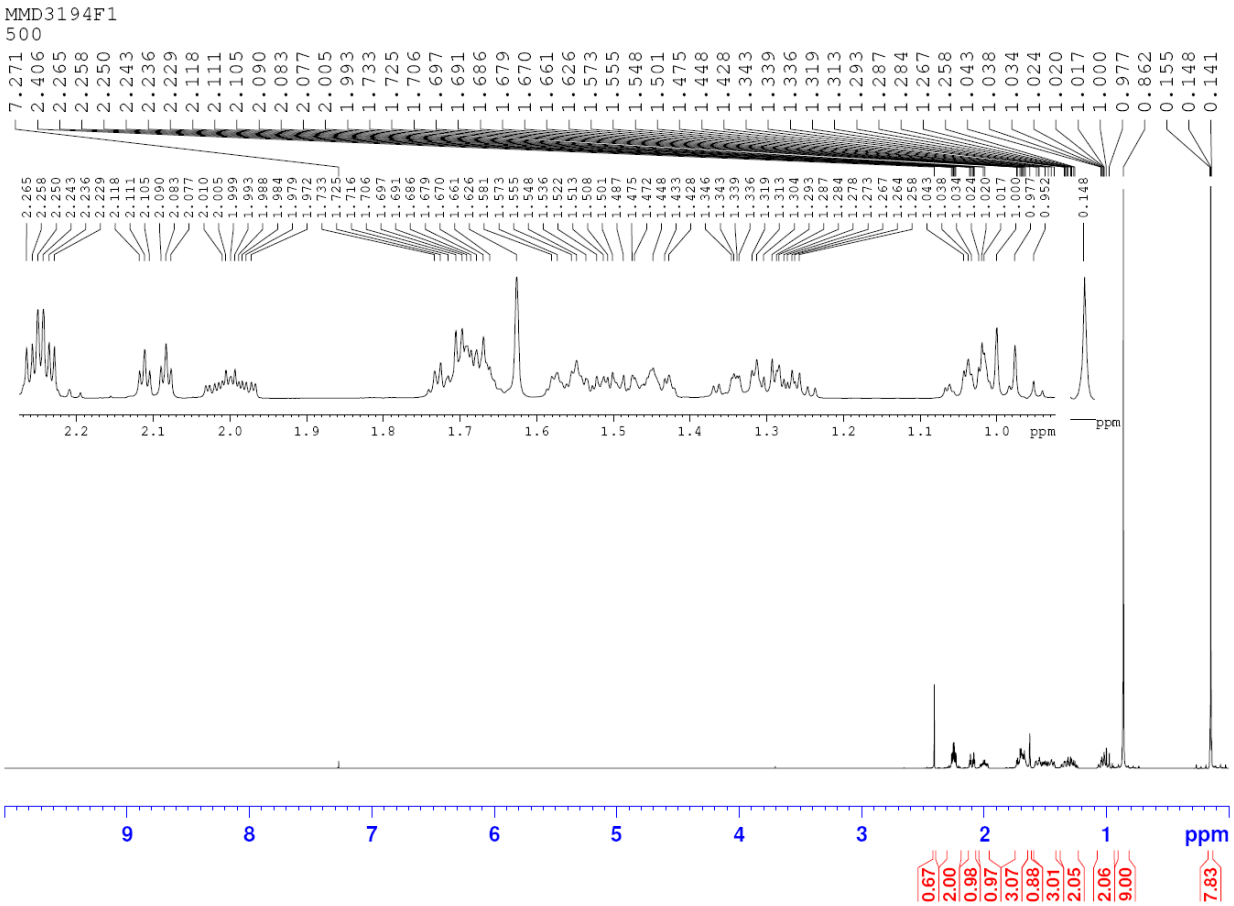
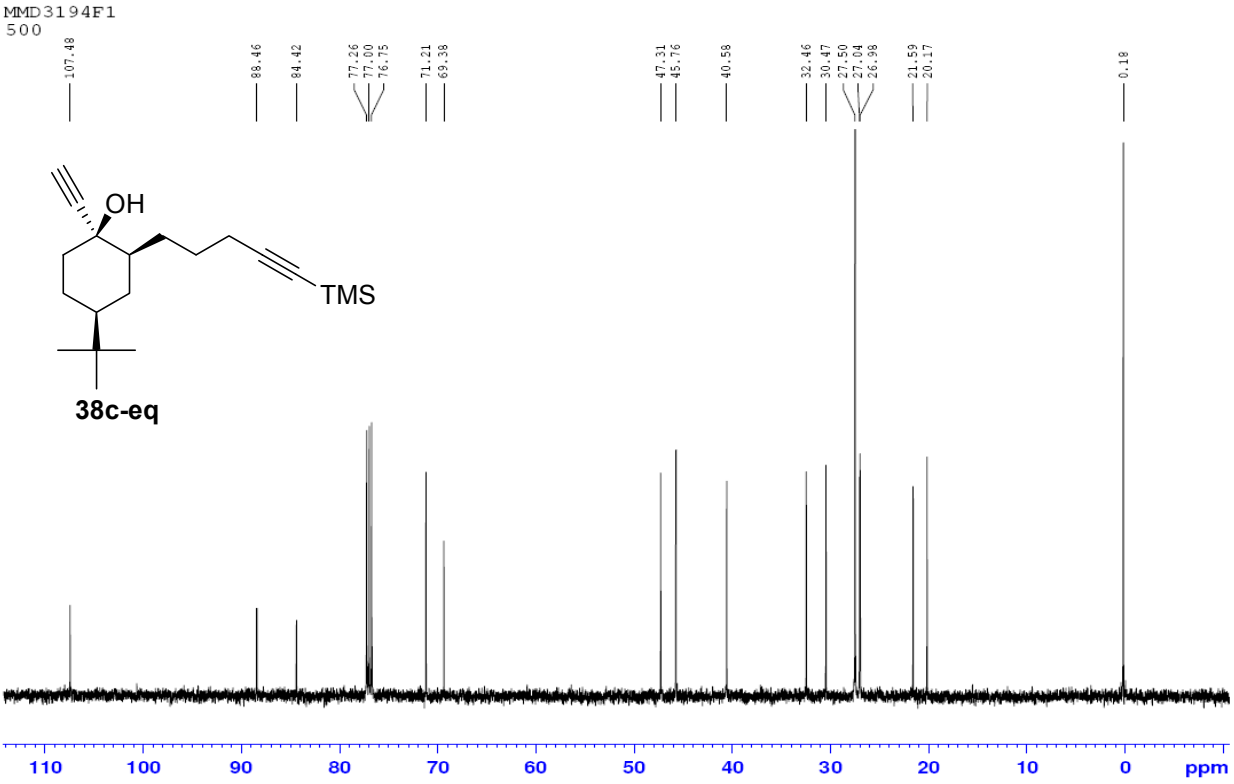
ppm


MMD3177F2
301A
OH
TMS
38c-ax
ppm


MMD3194F1
500
ppm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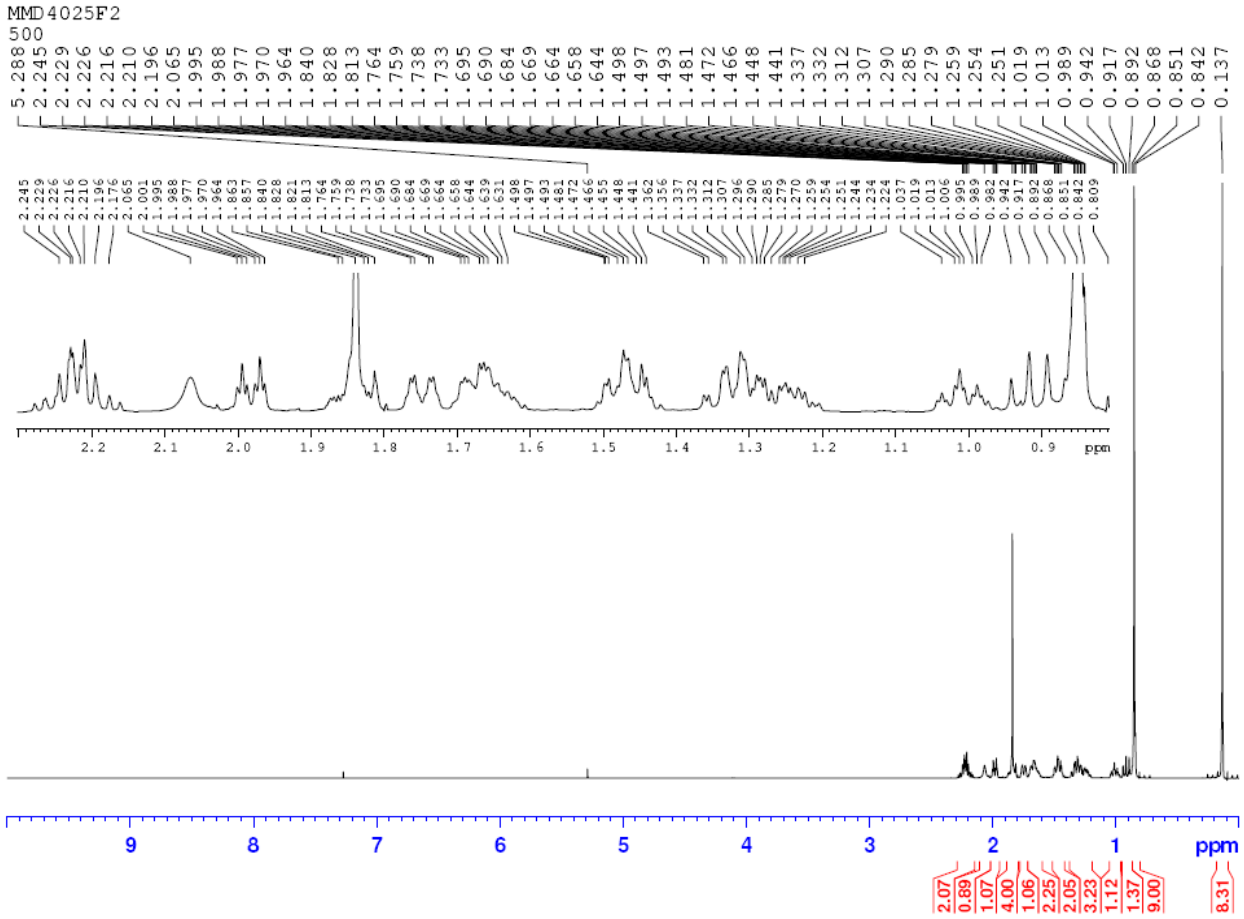
500
OH
TMS
38c-eq
ppm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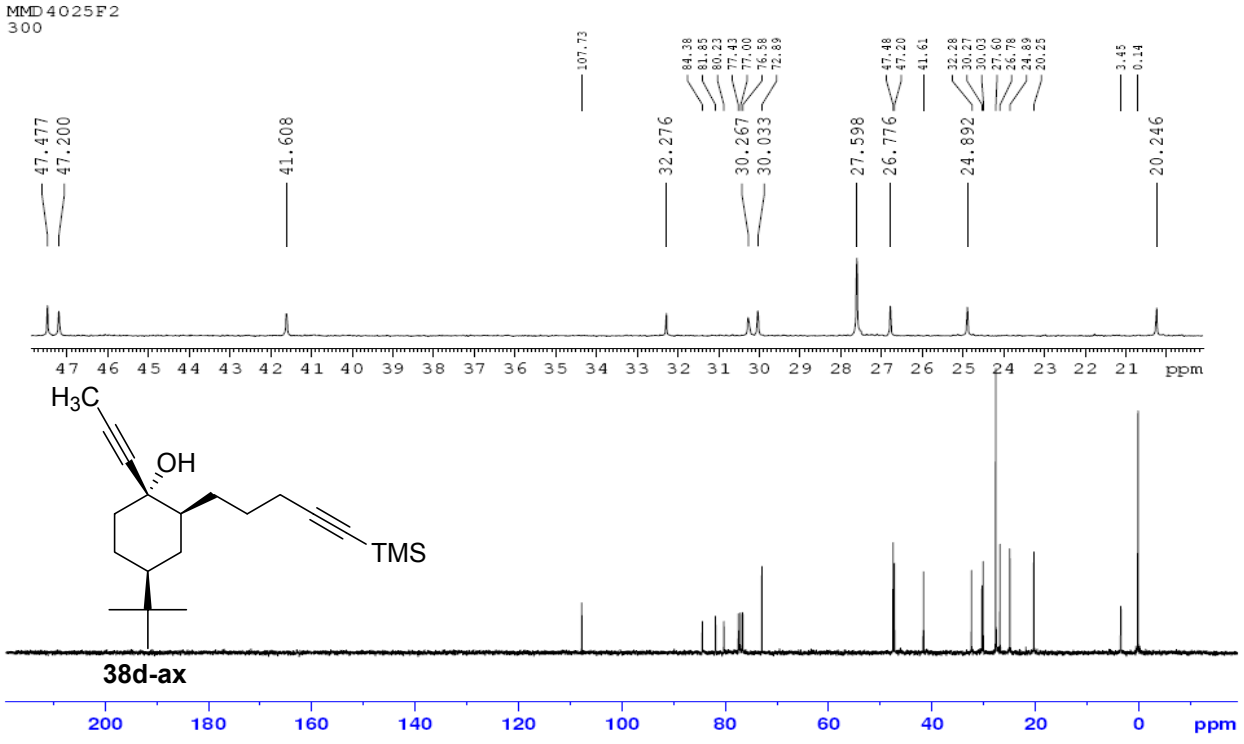
500
ppm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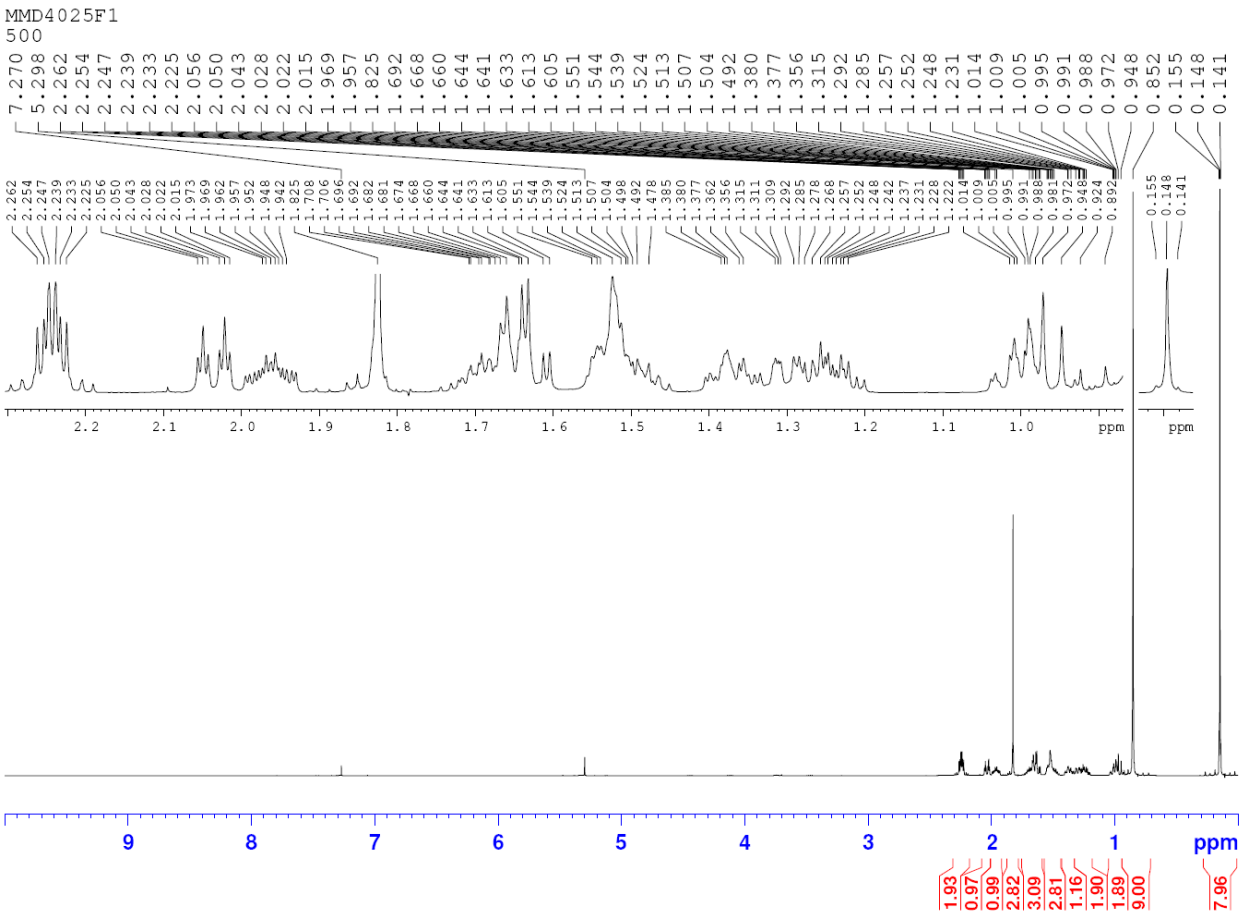
300
H3C
OH
TMS
38d-ax
ppm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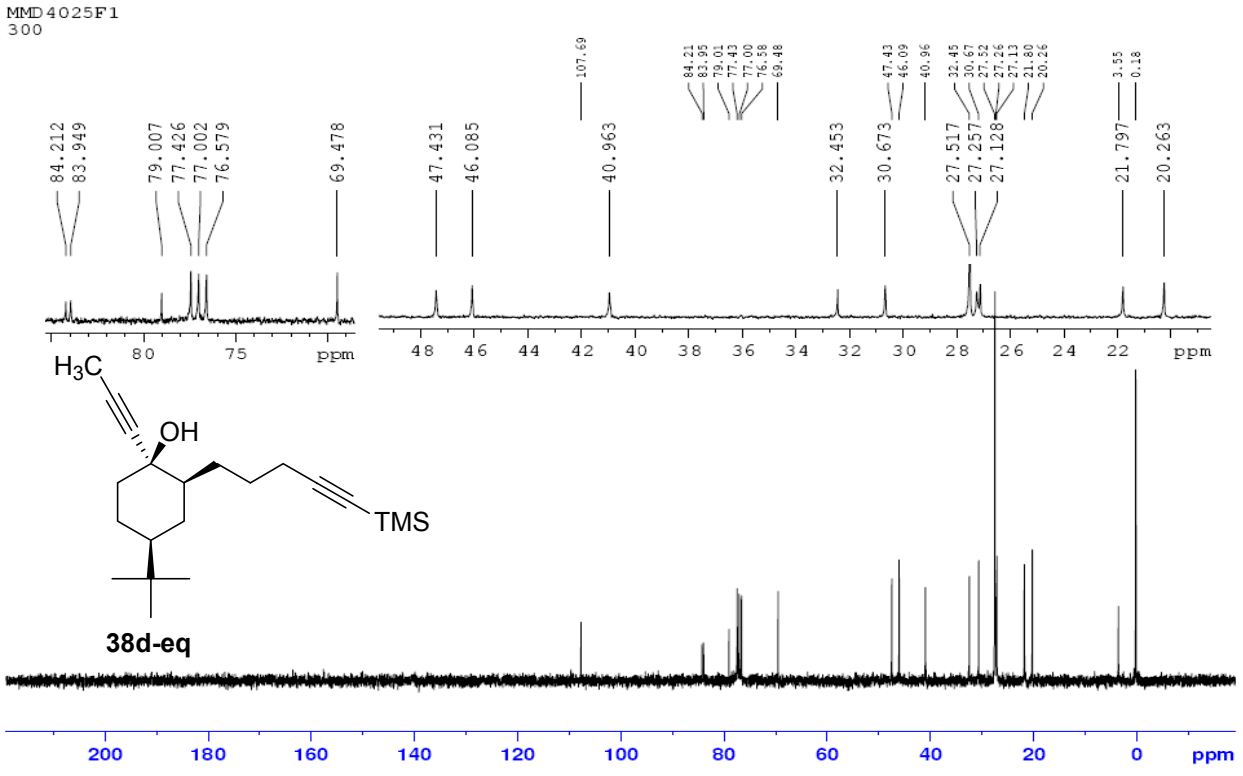
500
ppm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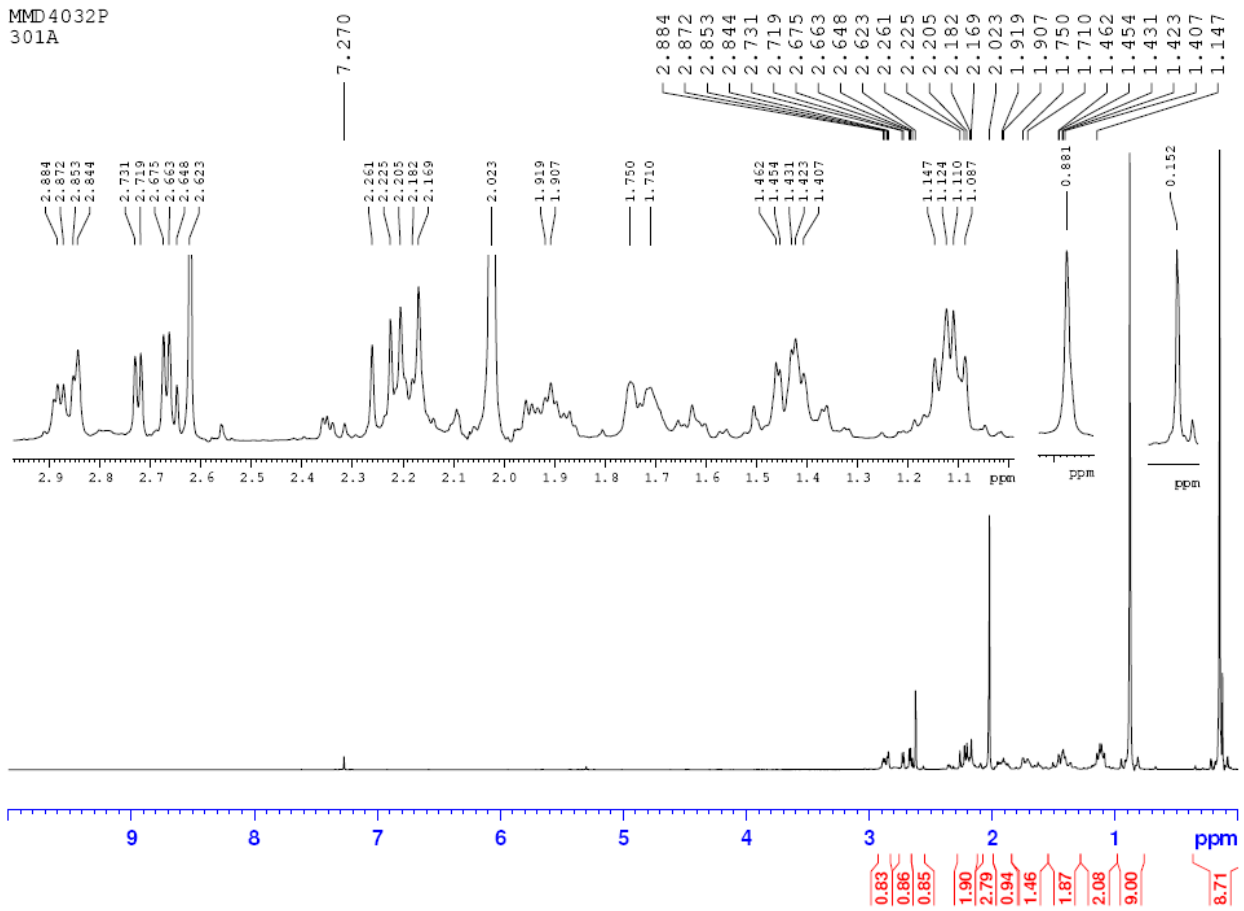
300
ppm
H3C
OH
TMS
38d-eq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301A
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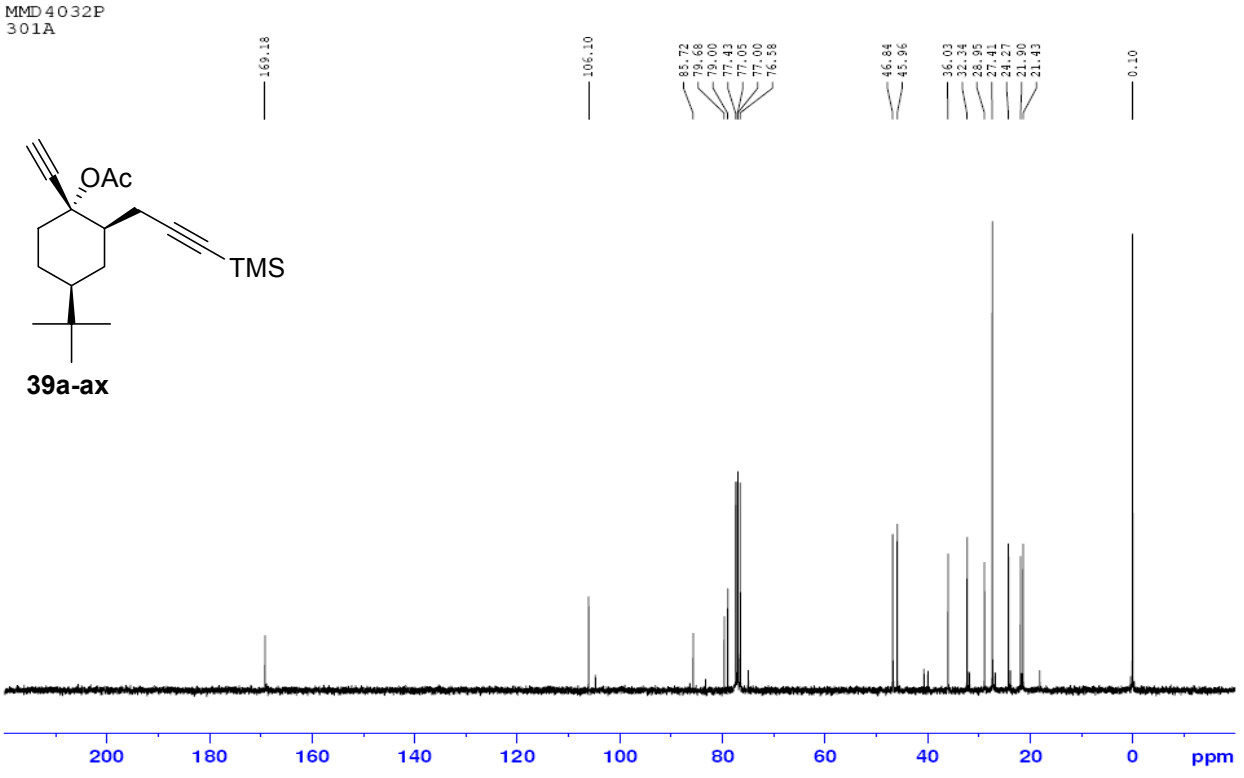
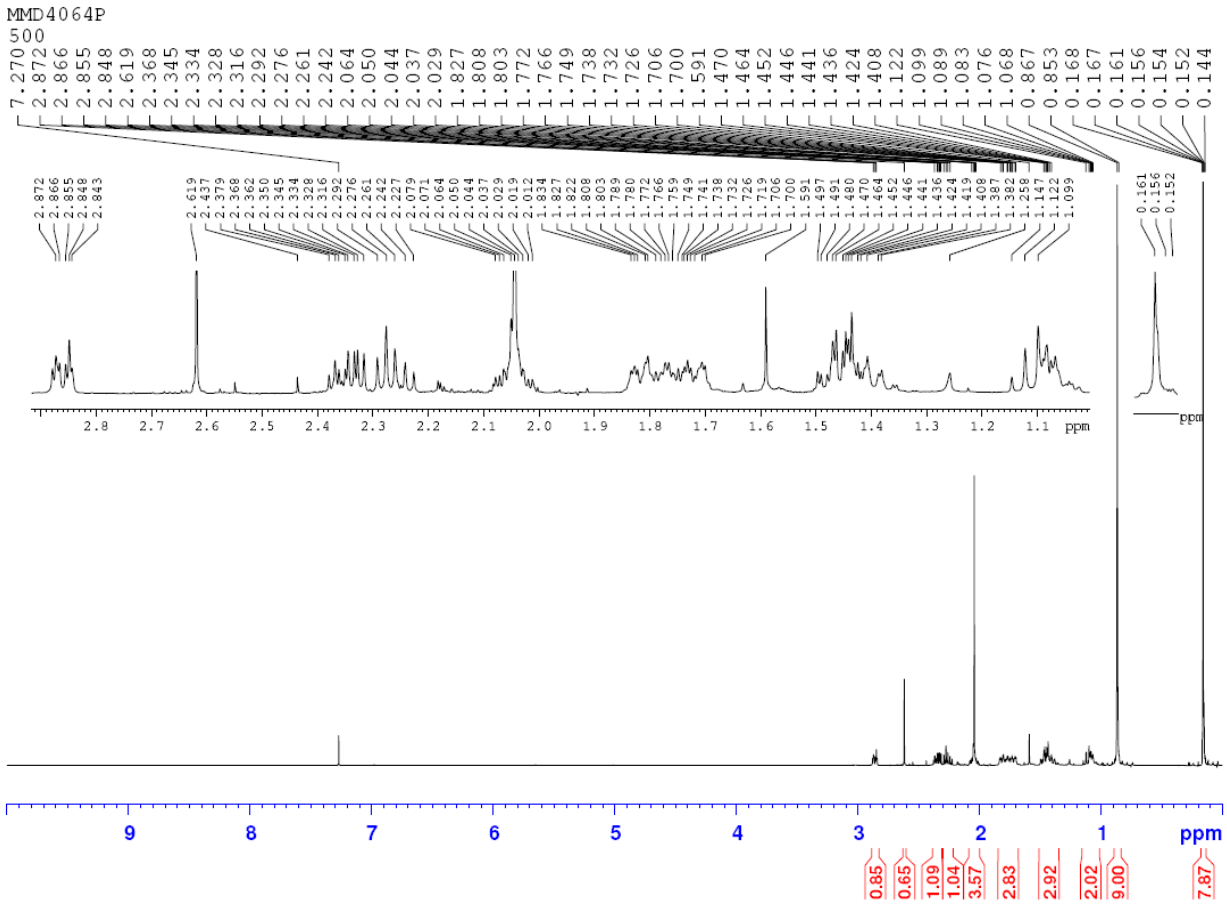
2.884
2.872
2.853
2.844
2.731
2.719
2.675
2.663
2.648
2.623
2.261
2.225
2.205
2.182
2.169
2.023
1.919
1.907
1.750
1.710
1.462
1.454
1.431
1.423
1.407
1.147
1.124
1.110
1.087
0.881
0.152
ppm
9
8
7
6
5
4
3
2
1
ppm
0.83
0.86
0.85
1.90
2.79
0.94
1.46
1.87
2.08
9.00
8.71


MMD4032P
301A
169.18
106.10
85.72
79.68
79.00
77.43
77.05
77.00
76.58
46.84
45.96
36.03
32.34
28.95
27.41
24.27
21.90
21.43
0.10
OAc
TMS
200
180
160
140
120
100
80
60
40
20
0
ppm

39a-ax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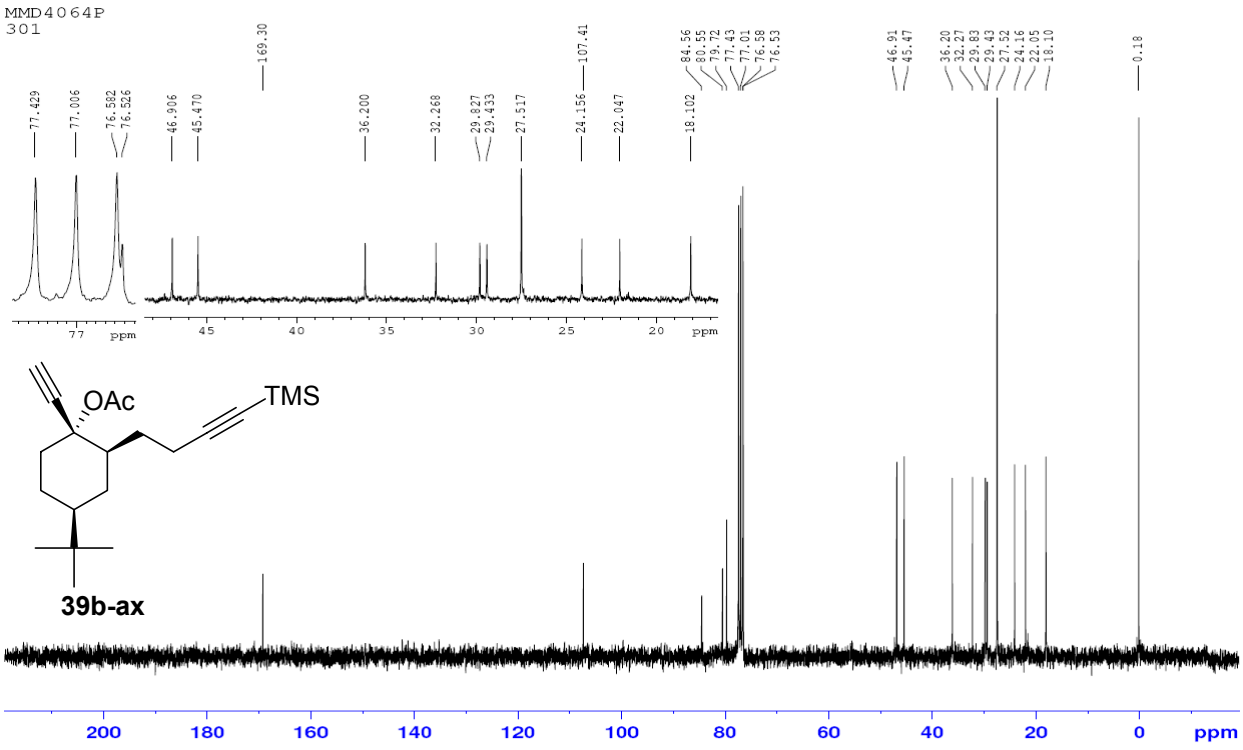
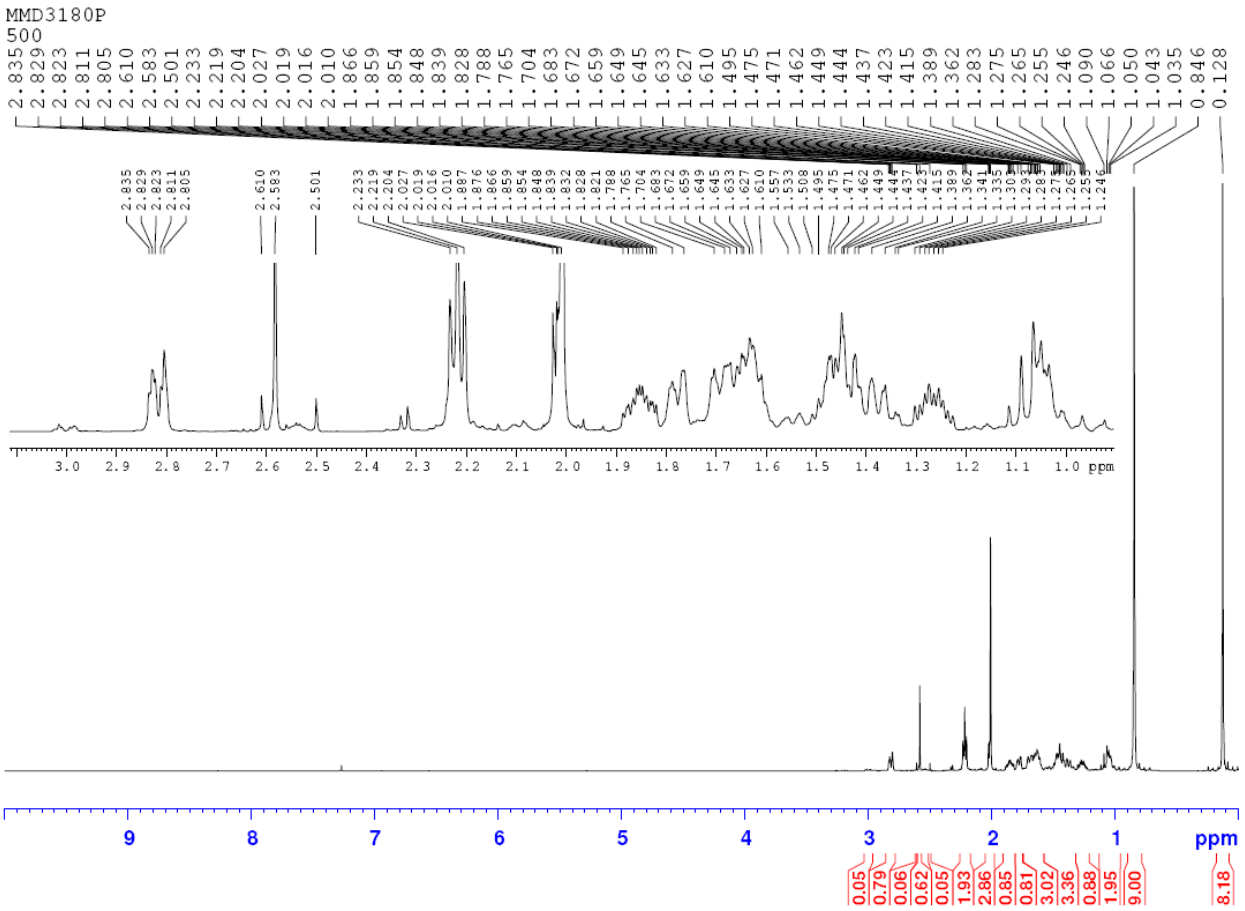
500
ppm
0.85
0.65
1.09
1.04
3.57
2.83
2.92
2.02
9.00
7.87


MMD4064P
301
OAc
TMS
39b-ax
ppm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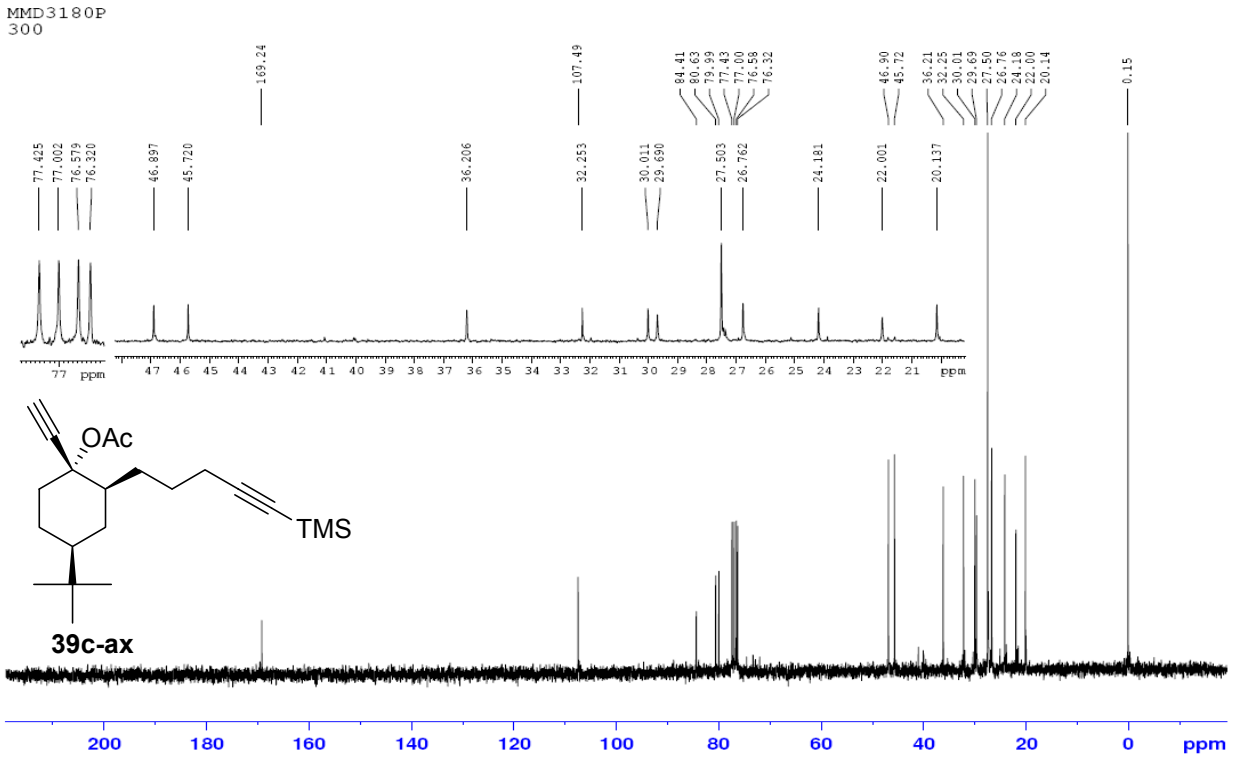
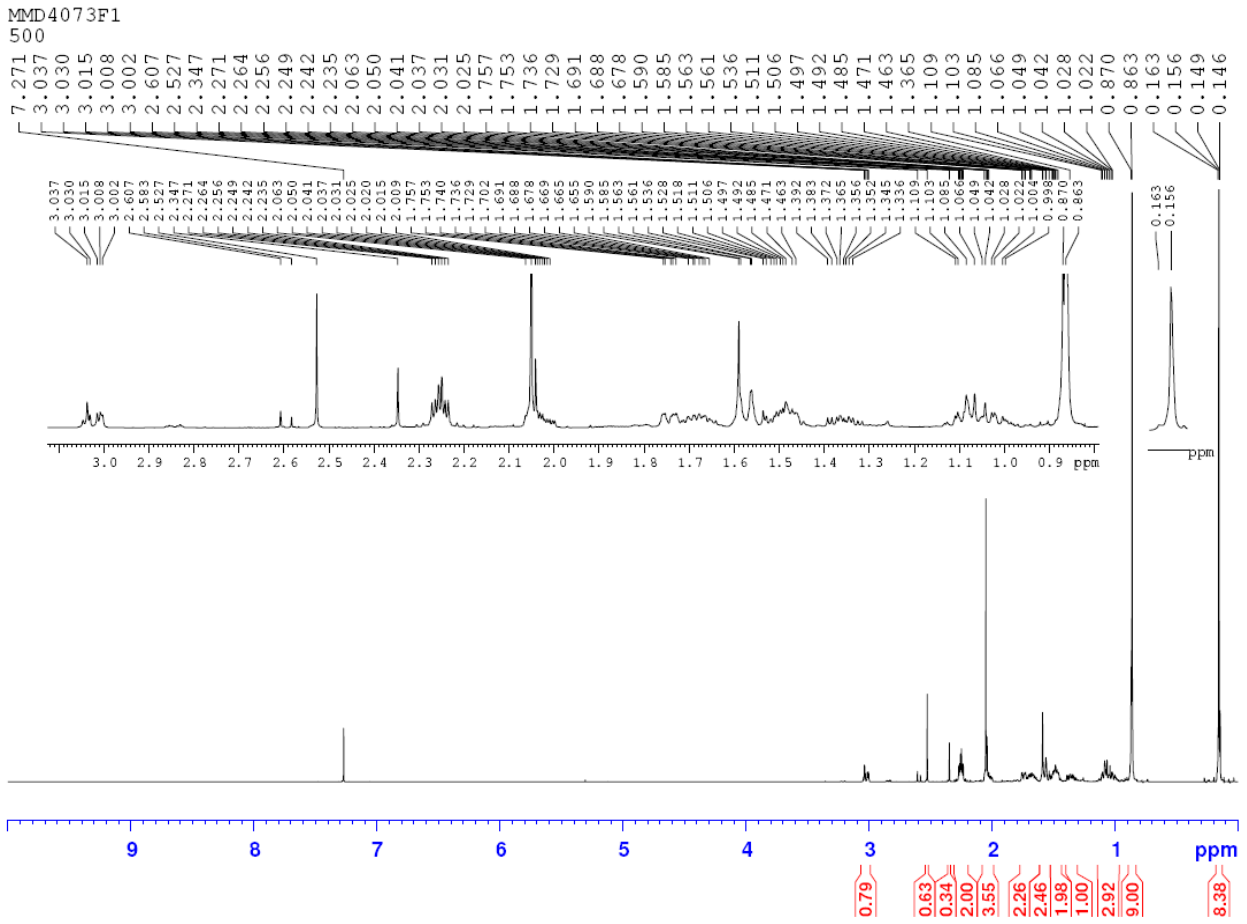
500
ppm


MMD3180P
300
OAc
TMS
39c-ax
ppm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500
ppm
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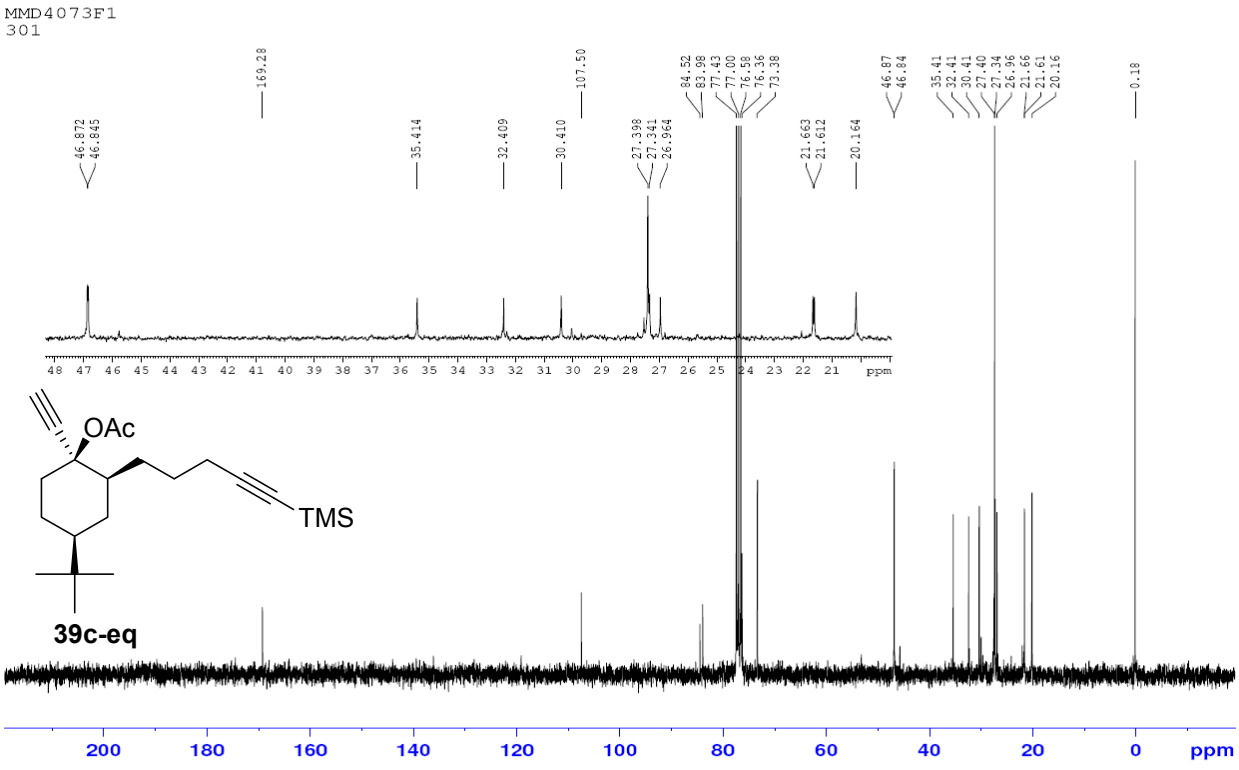
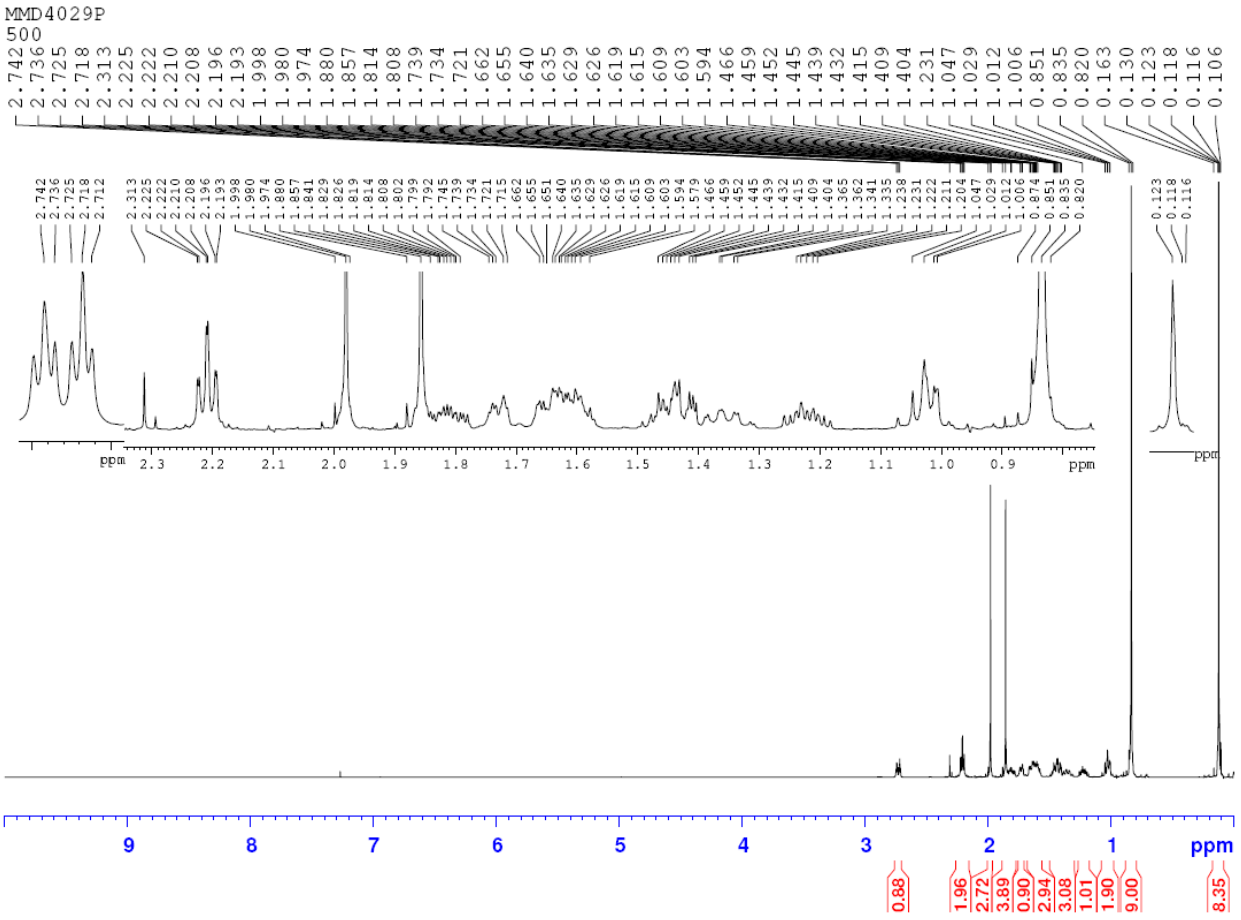
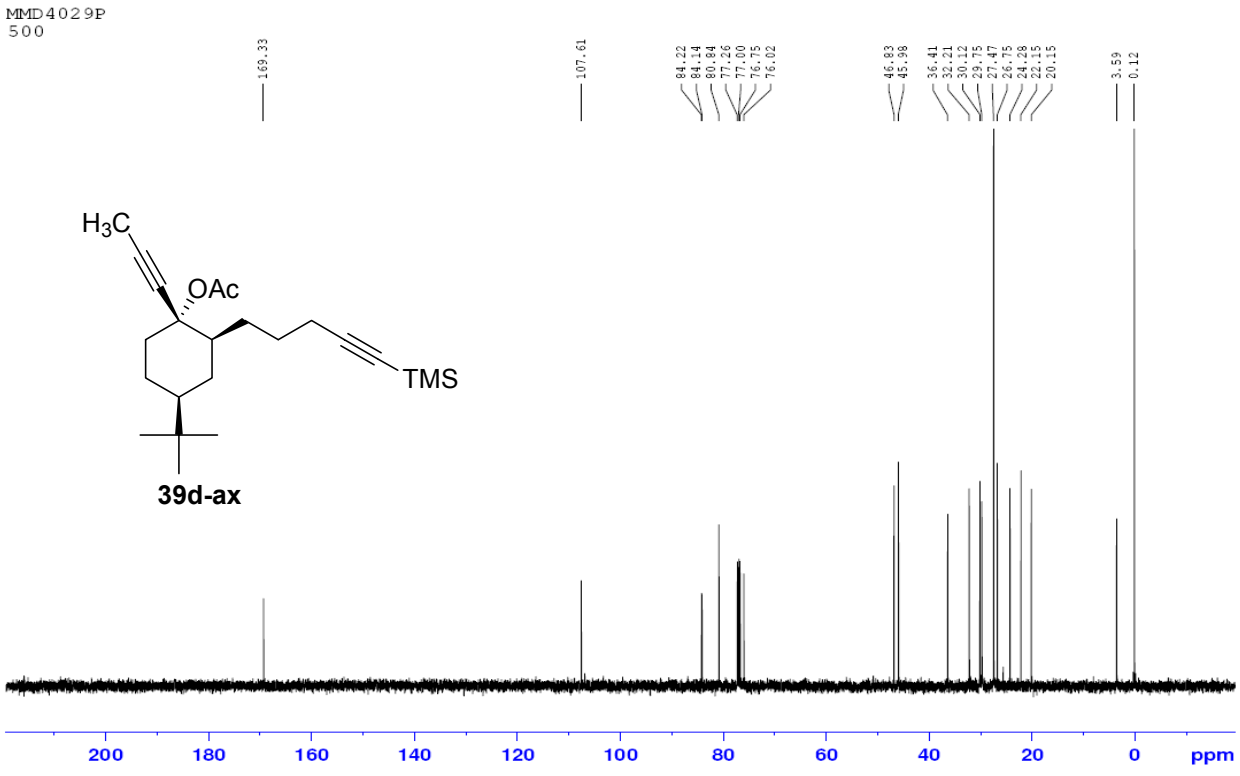
0.63
0.34
2.00
3.55
2.26
2.46
1.98
1.00
2.92
9.00
8.38

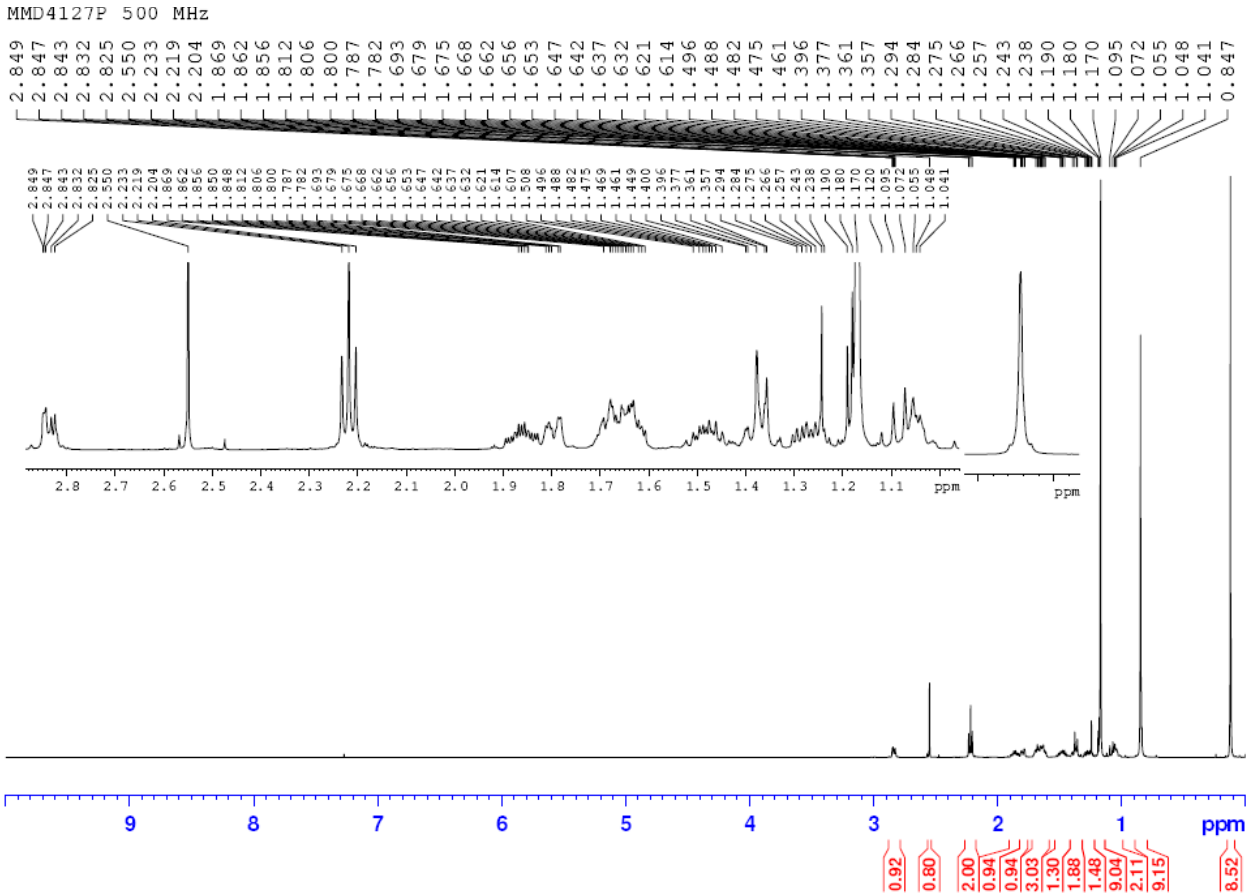

MMD4073F1
301
OAc
TMS
39c-eq
ppm

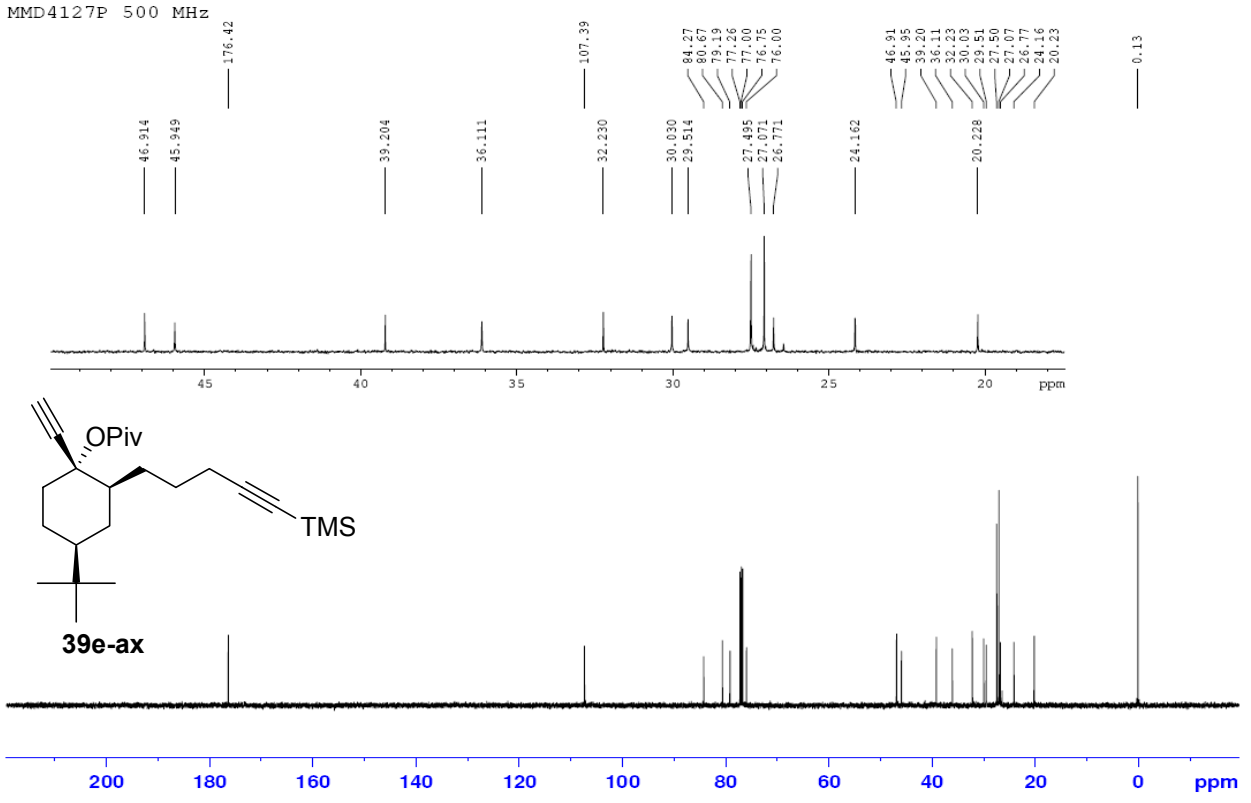

MMD4029P
500
ppm
0.88
1.96
2.72
3.89
0.90
2.94
3.08
1.01
1.90
9.00
8.35

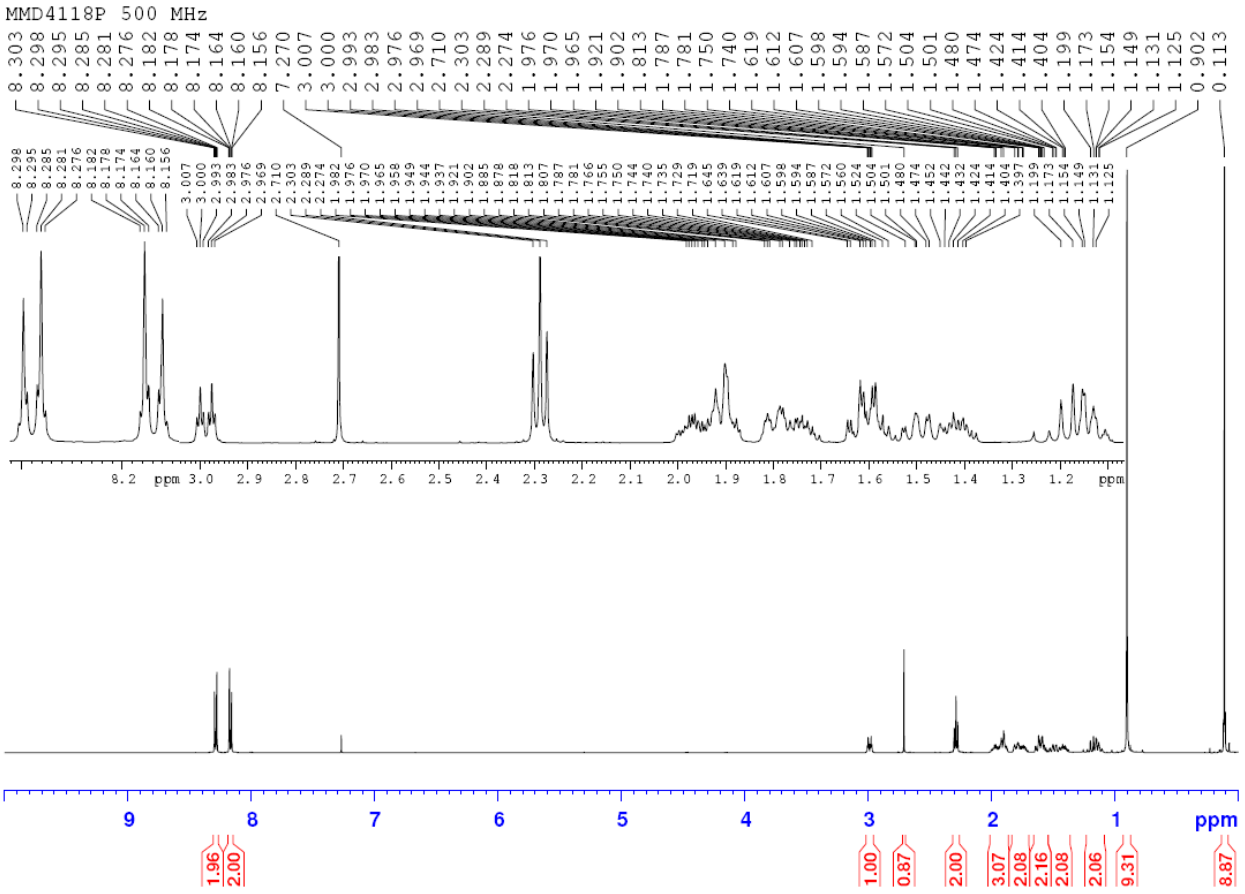

MMD4029P
500
ppm

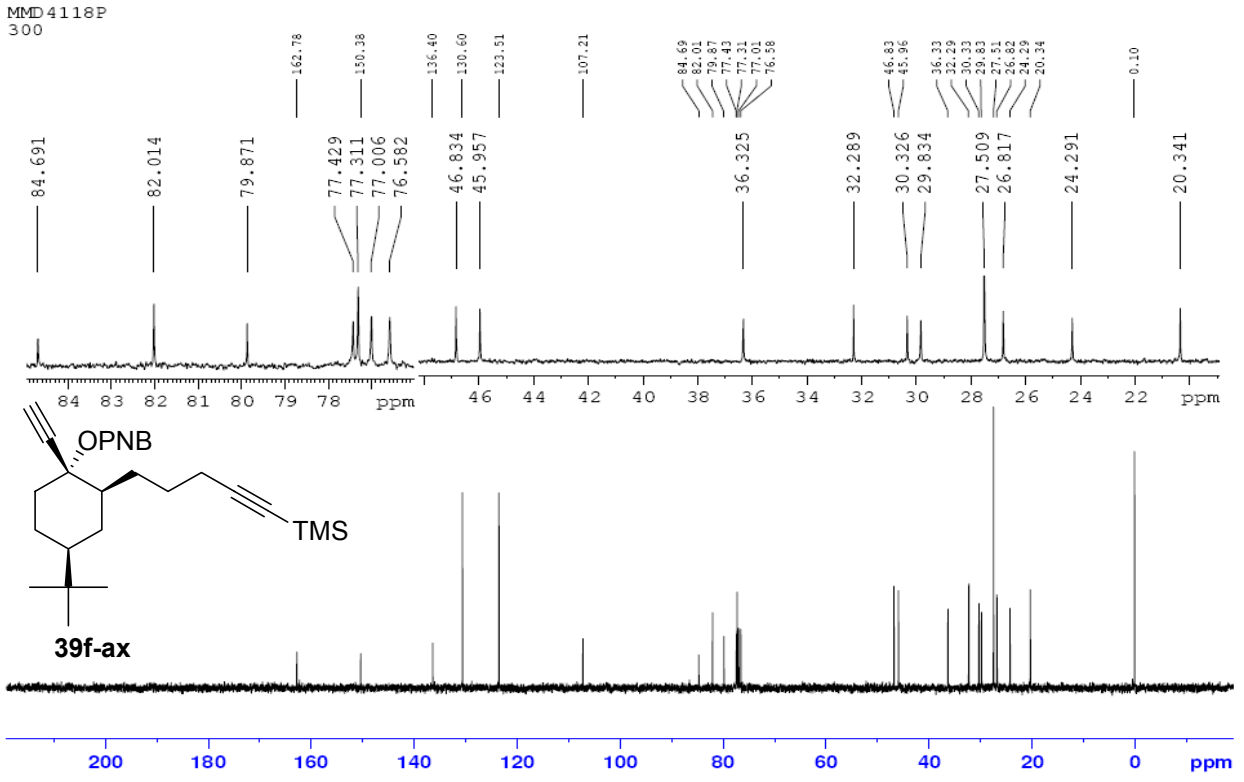
H3C
OAc
TMS

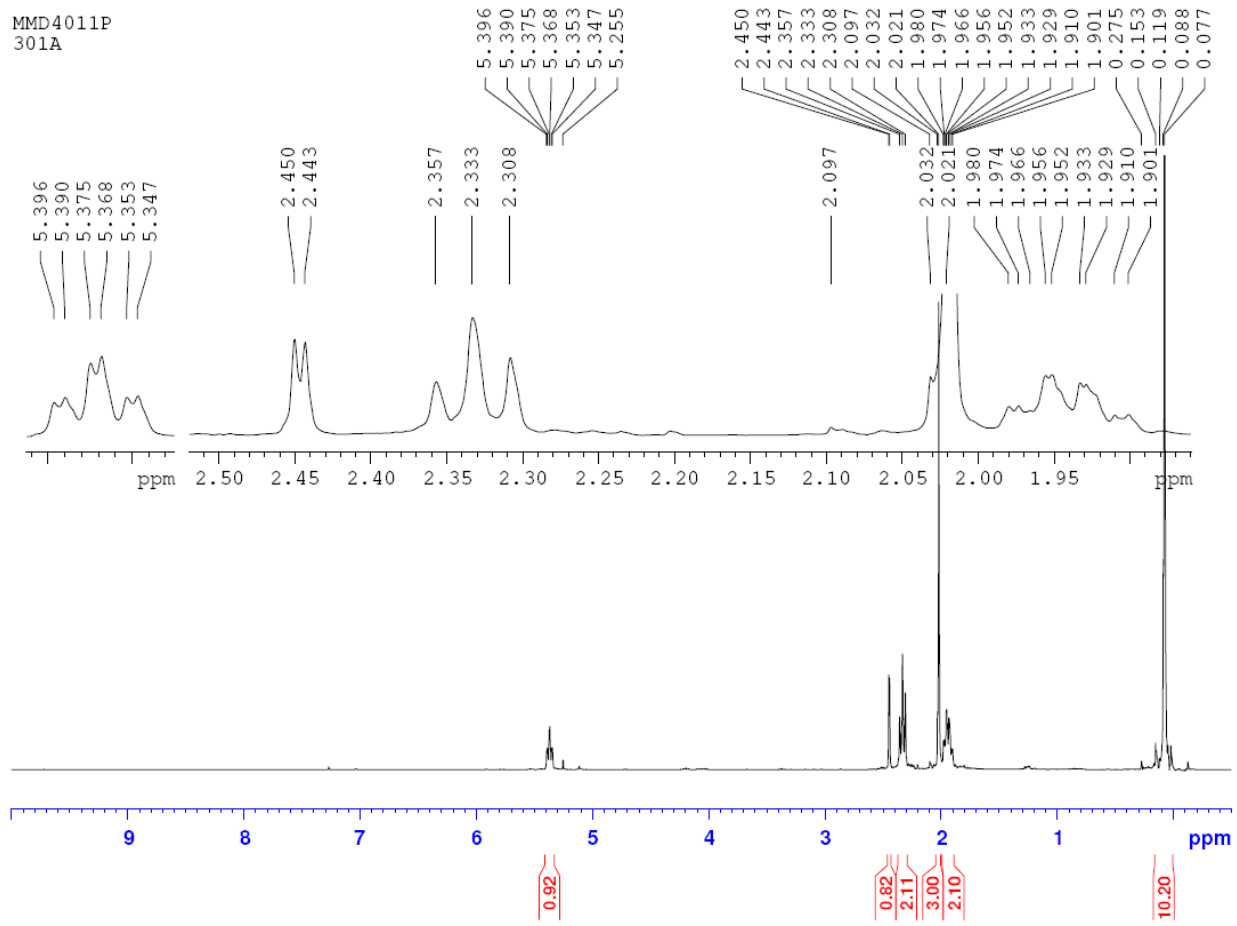
39d-ax

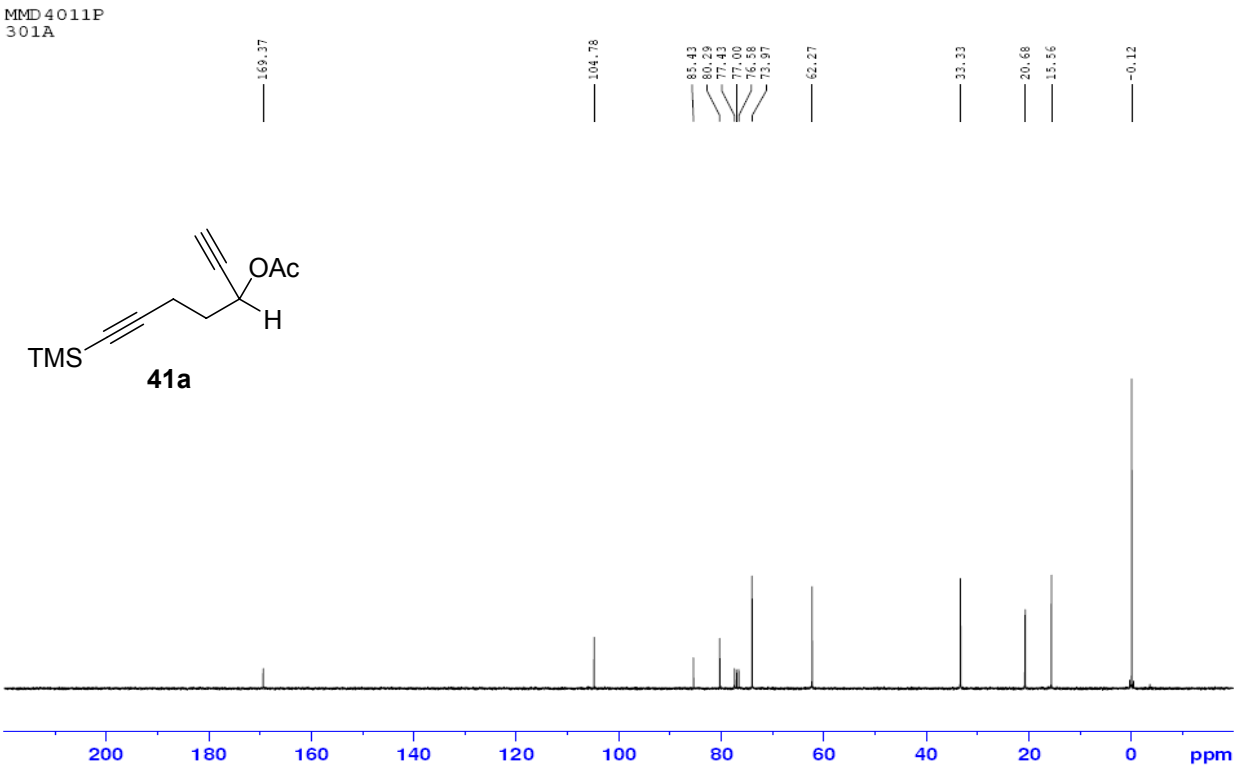

MMD4127P 500 MHz
ppm
0.92
0.80
2.00
0.94
0.94
3.03
1.30
1.88
1.48
9.04
2.11
9.15
8.52


MMD4127P 500 MHz
OPiv
TMS
39e-ax
ppm


MMD4118P 500 MHz
ppm
1.96
2.00
1.00
0.87
2.00
3.07
2.08
2.16
2.08
2.06
9.31
8.87

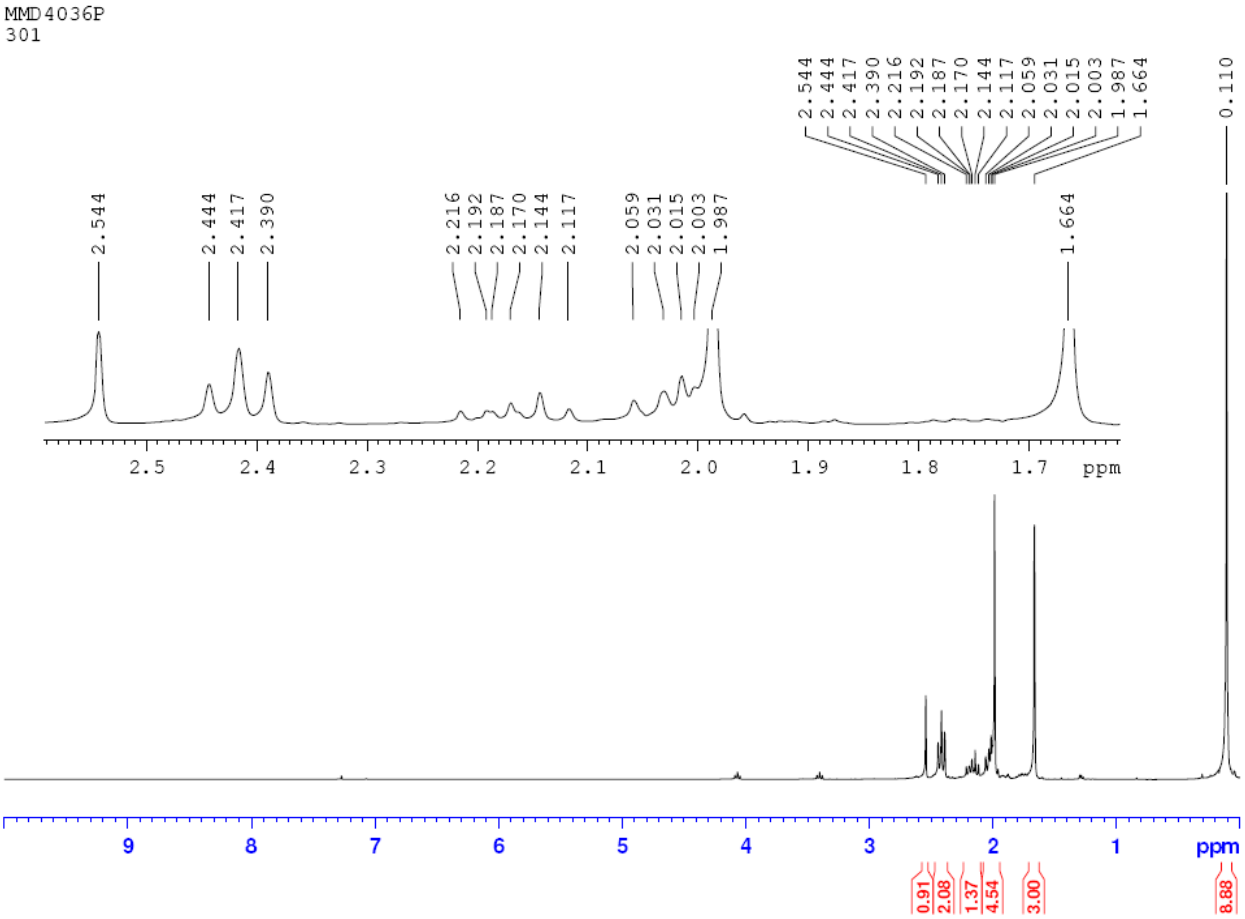

MMD4118P
300
84.691
82.014
79.871
77.429
77.311
77.006
76.582
46.834
45.957
36.325
32.289
30.326
29.834
27.509
26.817
24.291
20.341
ppm
OPNB
TMS
39f-ax

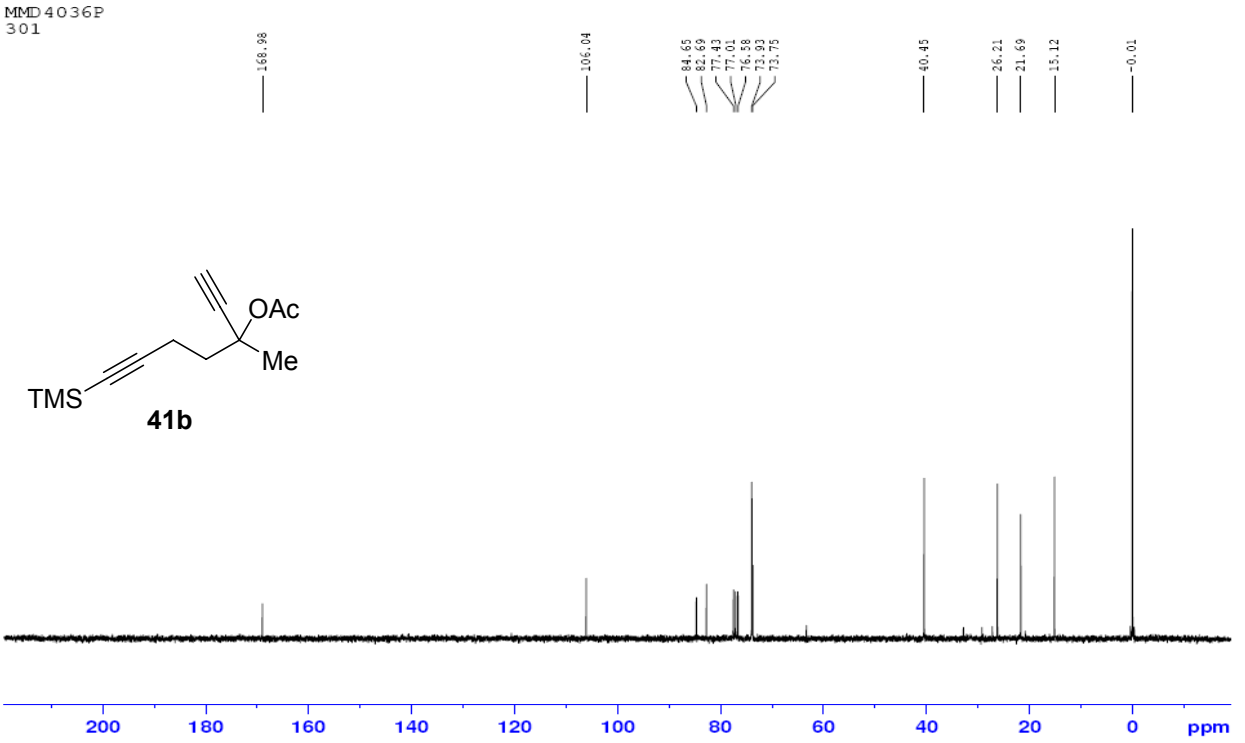

MMD4011P
301A
5.396
5.390
5.375
5.368
5.353
5.347
5.255
2.450
2.443
2.357
2.333
2.308
2.097
2.032
2.021
1.980
1.974
1.966
1.956
1.952
1.933
1.929
1.910
1.901
0.275
0.153
0.119
0.088
0.077
ppm
2.50
2.45
2.40
2.35
2.30
2.25
2.20
2.15
2.10
2.05
2.00
1.95
9
8
7
6
5
4
3
2
1
0.92
0.82
2.11
3.00
2.10
10.20


MMD4011P
301A
169.37
104.78
85.43
80.29
77.43
77.00
76.58
73.97
62.27
33.33
20.68
15.56
-0.12
200
180
160
140
120
100
80
60
40
20
0
ppm

OAc
H
TMS

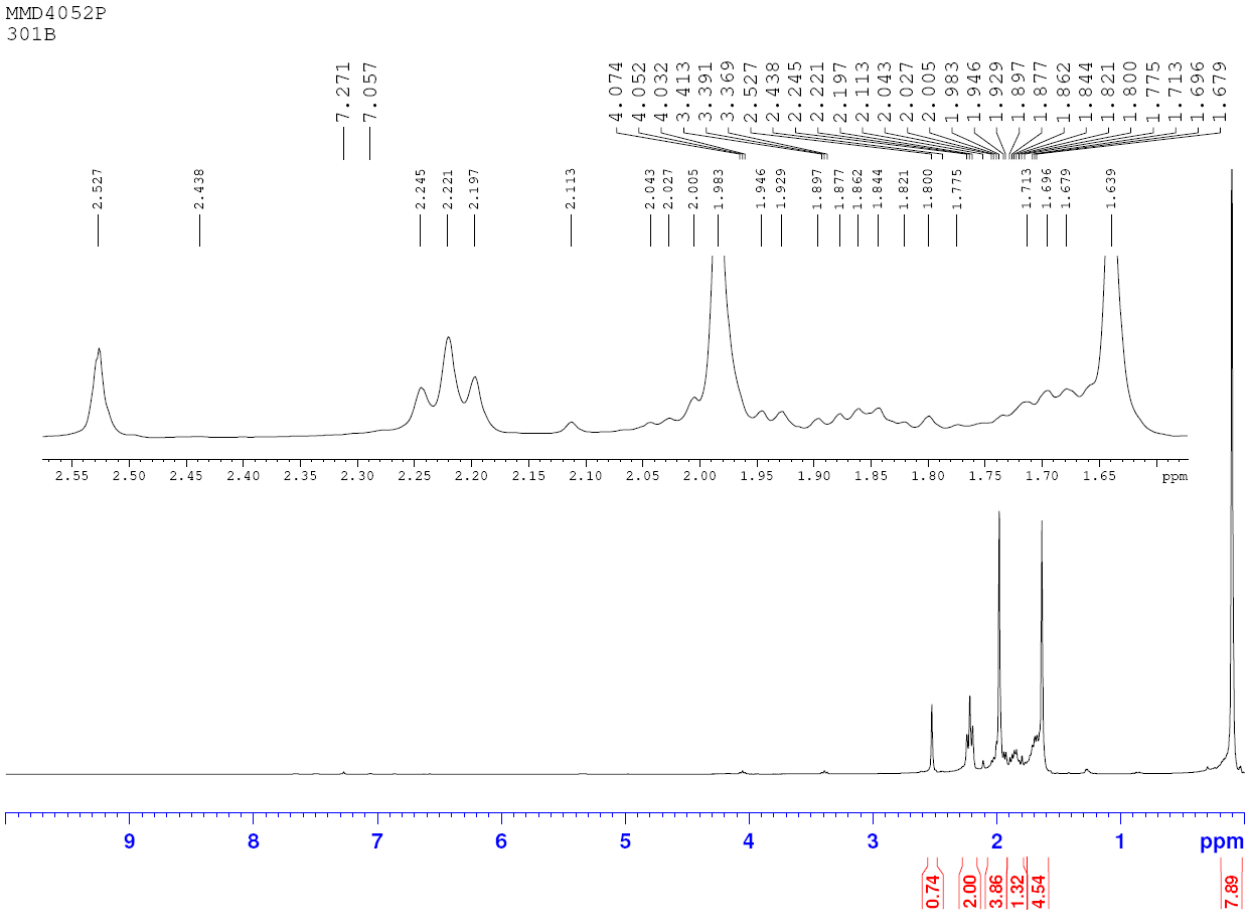
41a

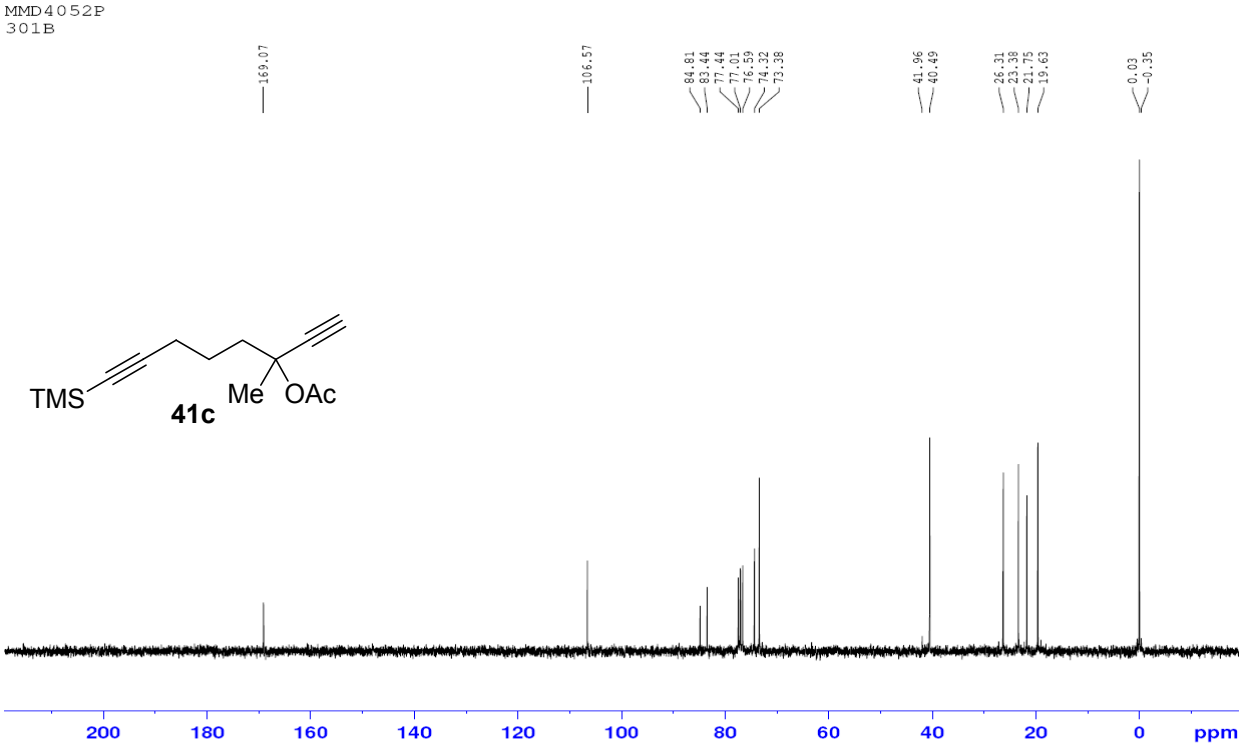

MMD4036P
301
2.544
2.444
2.417
2.390
2.216
2.192
2.187
2.170
2.144
2.117
2.059
2.031
2.015
2.003
1.987
1.664
0.110
ppm
0.91
2.08
1.37
4.54
3.00
8.88

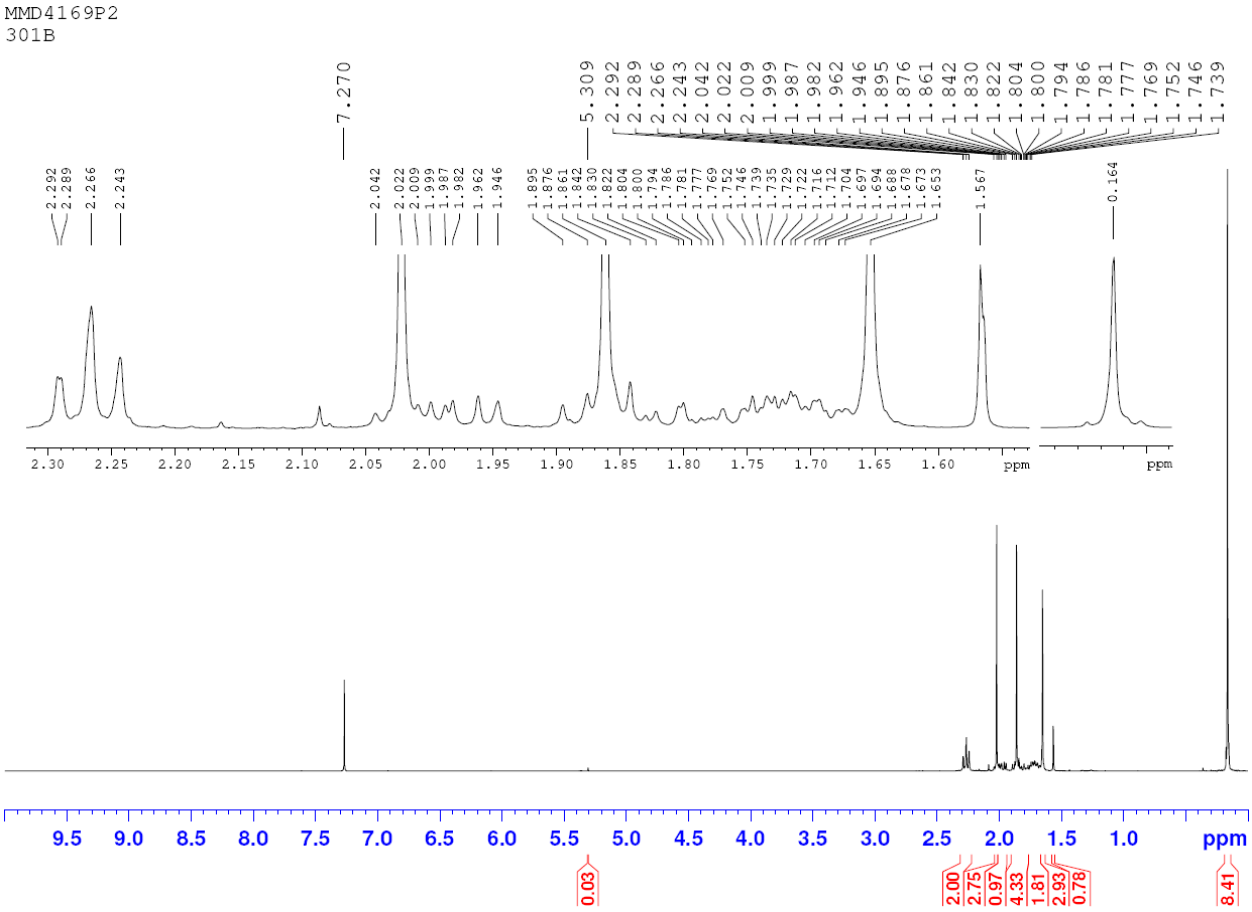

MMD4036P
301
168.98
106.04
84.65
82.69
77.43
77.01
76.38
73.93
73.75
40.45
26.21
21.69
15.12
-0.01
ppm

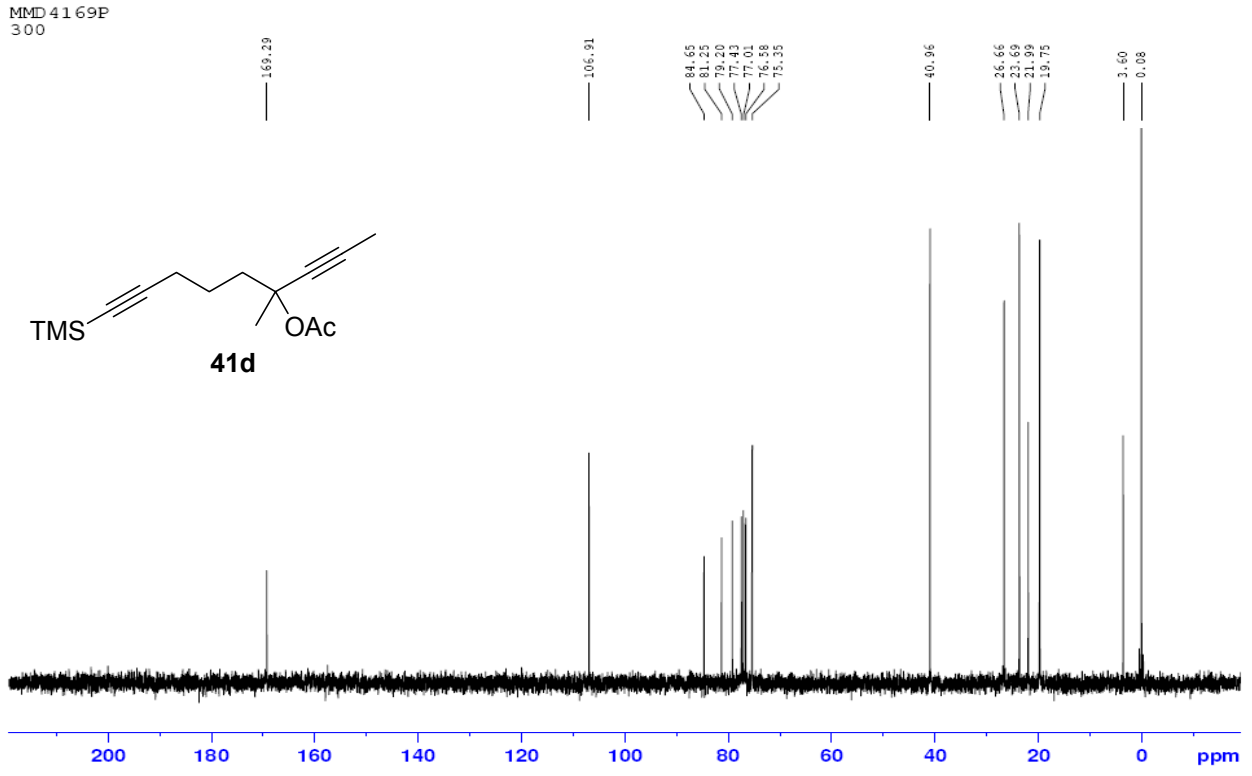
OAc
Me
TMS

41b

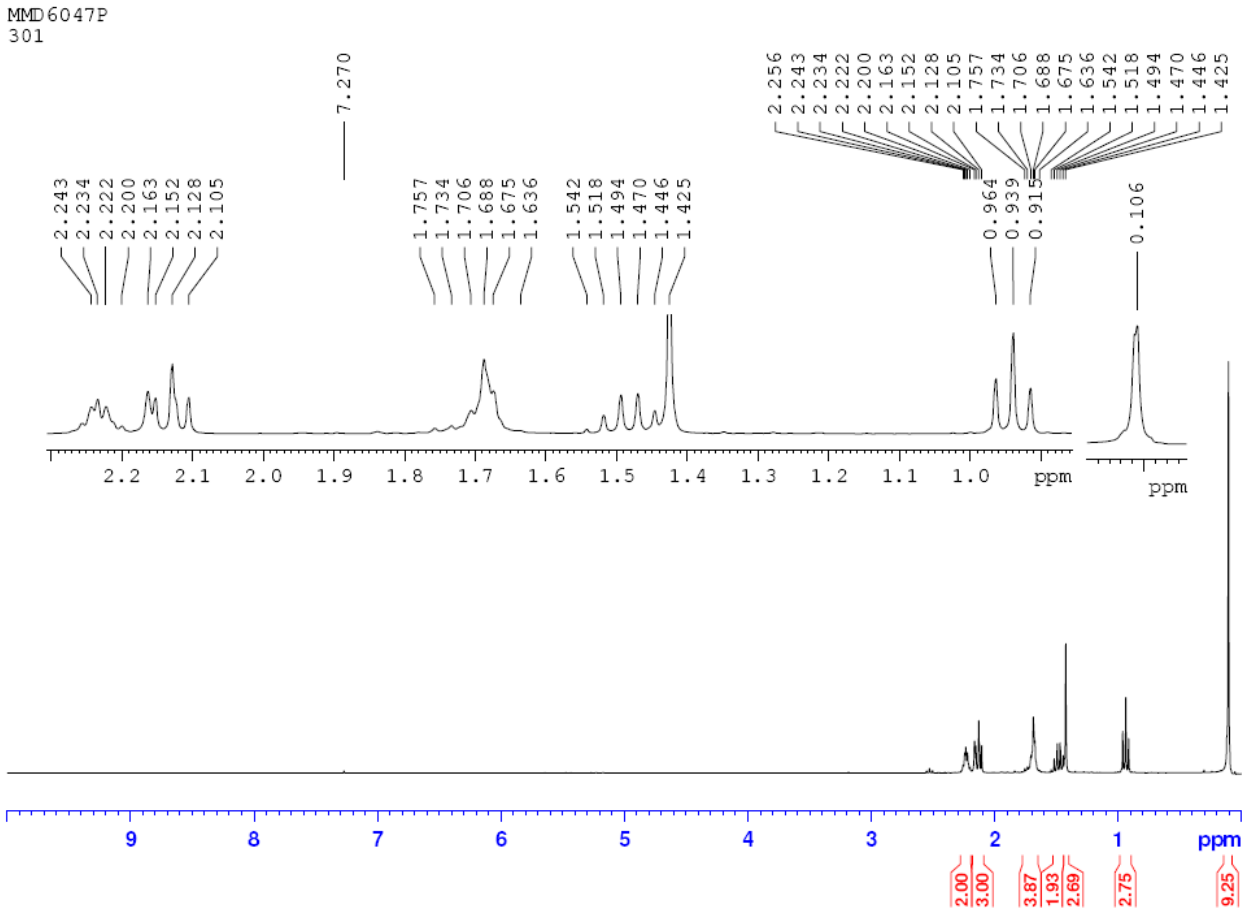

MMD4052P
301B
7.271
7.057
4.074
4.052
4.032
3.413
3.391
3.369
2.527
2.438
2.245
2.221
2.197
2.113
2.043
2.027
2.005
1.983
1.946
1.929
1.897
1.877
1.862
1.844
1.821
1.800
1.775
1.713
1.696
1.679
1.639
ppm
0.74
2.00
3.86
1.32
4.54
7.89

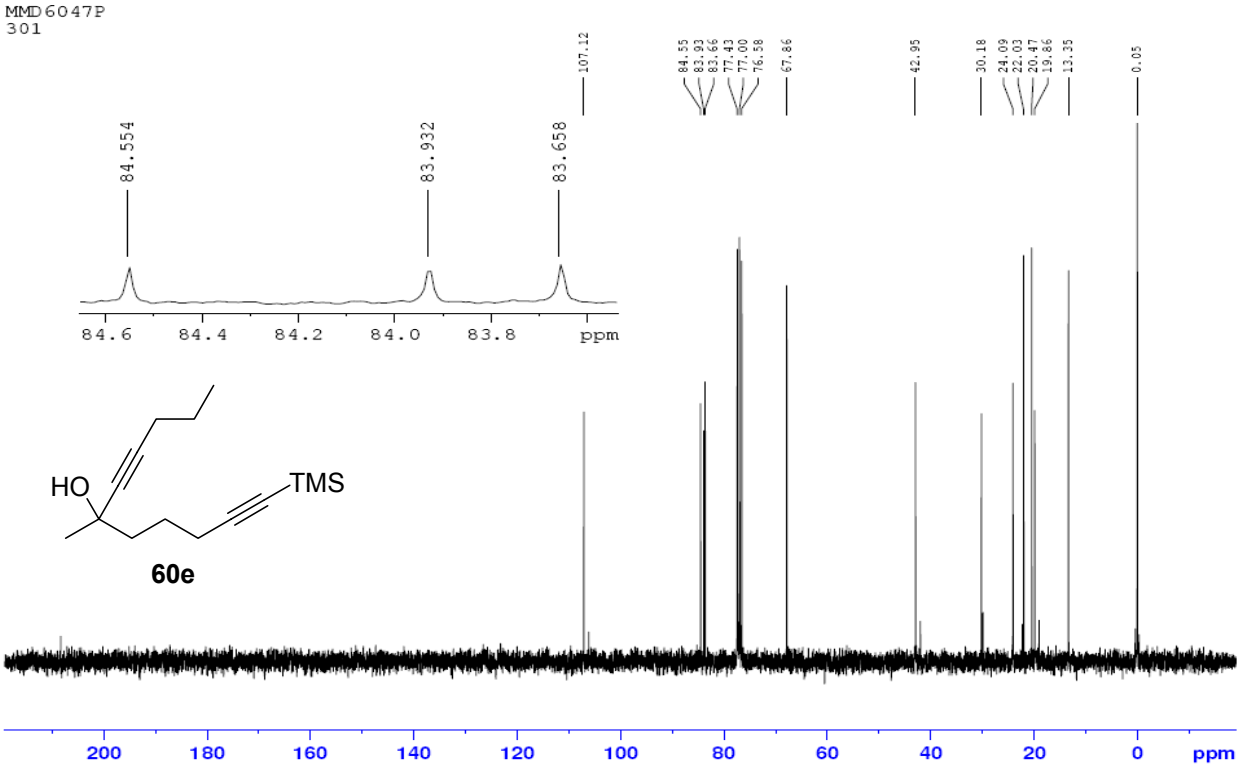

MMD4052P
301B
169.07
106.57
84.81
83.44
77.44
77.01
76.59
74.32
73.38
41.96
40.49
26.31
23.38
21.75
19.63
0.03
-0.35
TMS
Me
OAc
41c
ppm

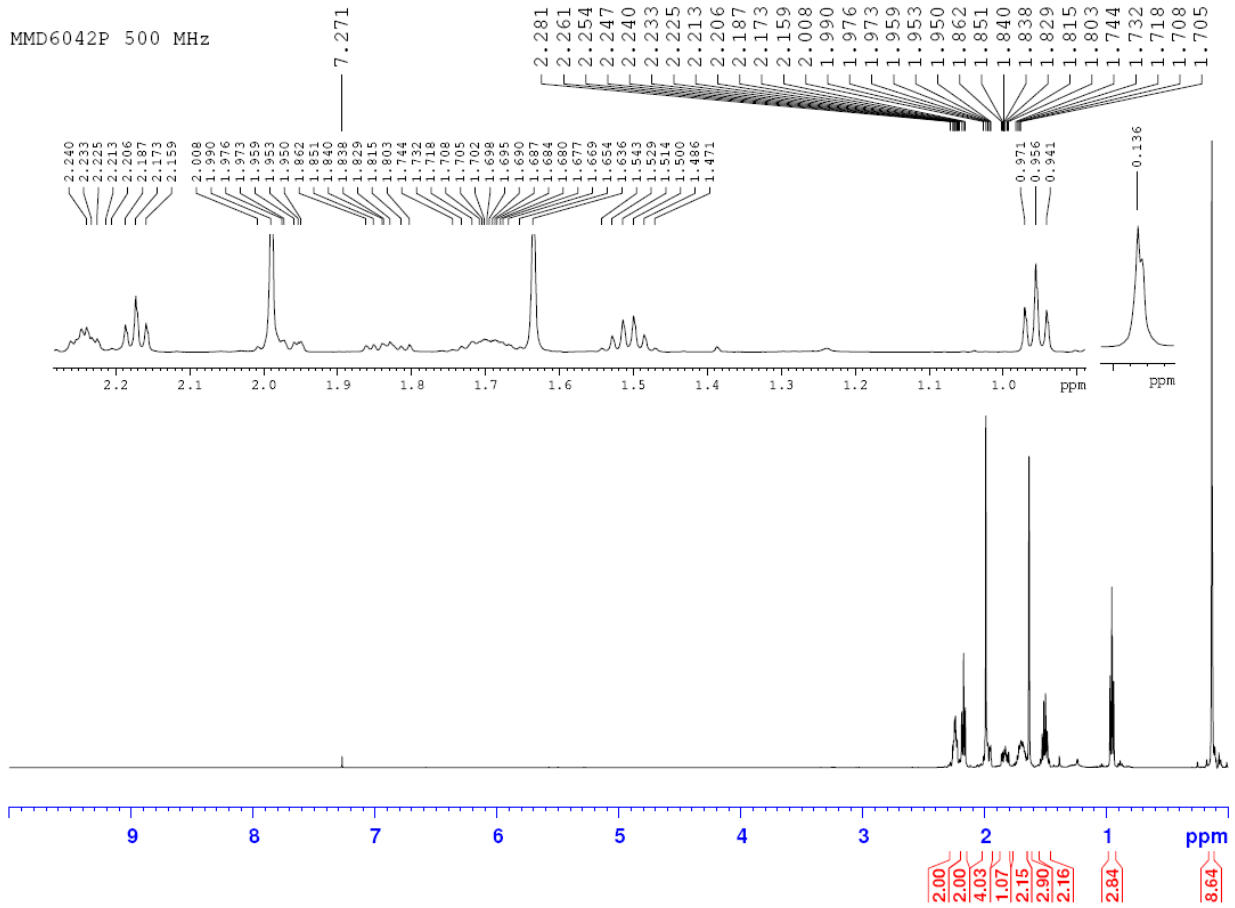

MMD4169P2
301B
7.270
5.309
2.292
2.289
2.266
2.243
2.042
2.022
2.009
1.999
1.987
1.982
1.962
1.946
1.895
1.876
1.861
1.842
1.830
1.822
1.804
1.800
1.794
1.786
1.781
1.777
1.769
1.752
1.746
1.739
1.735
1.729
1.722
1.716
1.712
1.704
1.697
1.694
1.688
1.678
1.673
1.653
1.567
0.164
ppm
9.5 9.0 8.5 8.0 7.5 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
0.03
2.00
2.75
0.97
4.33
1.81
2.93
0.78
8.41

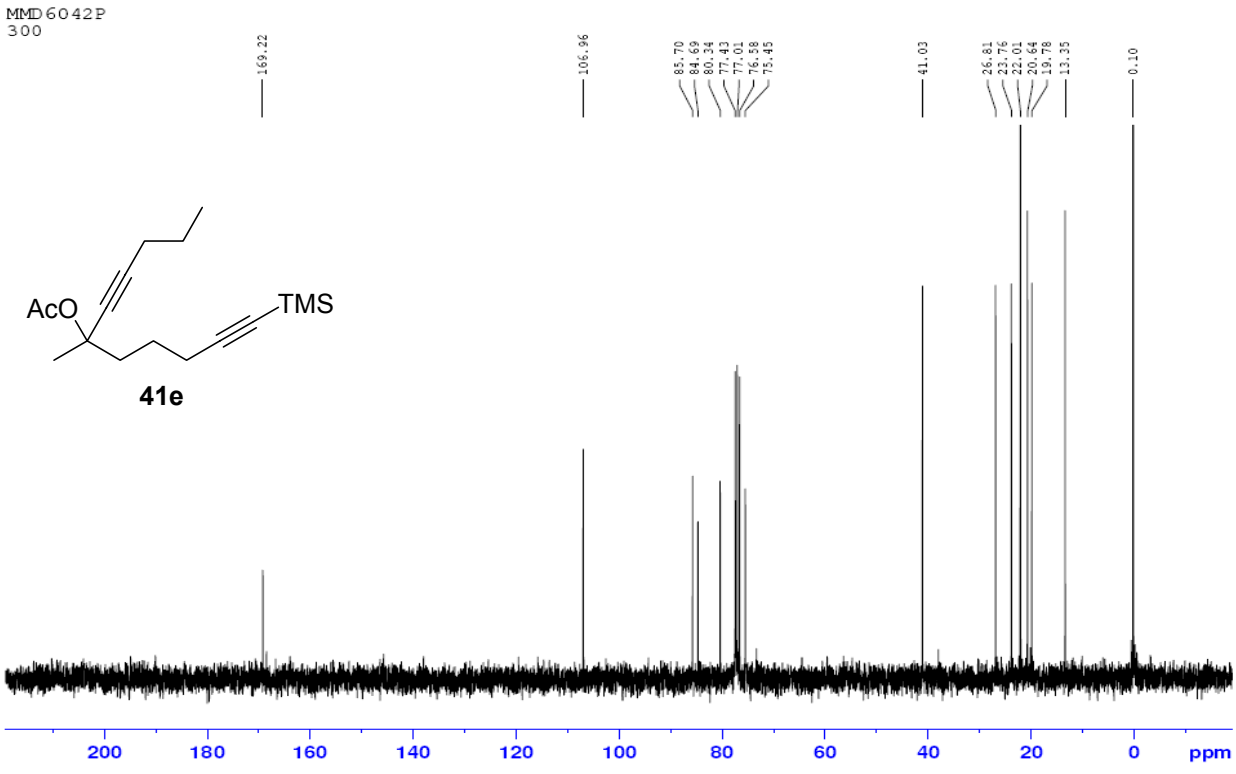

MMD4169P
300
169.29
106.91
84.65
81.25
79.20
77.43
77.01
76.58
75.35
40.96
26.66
23.69
21.99
19.75
3.60
0.08
TMS
OAc
200 180 160 140 120 100 80 60 40 20 0 ppm

41d

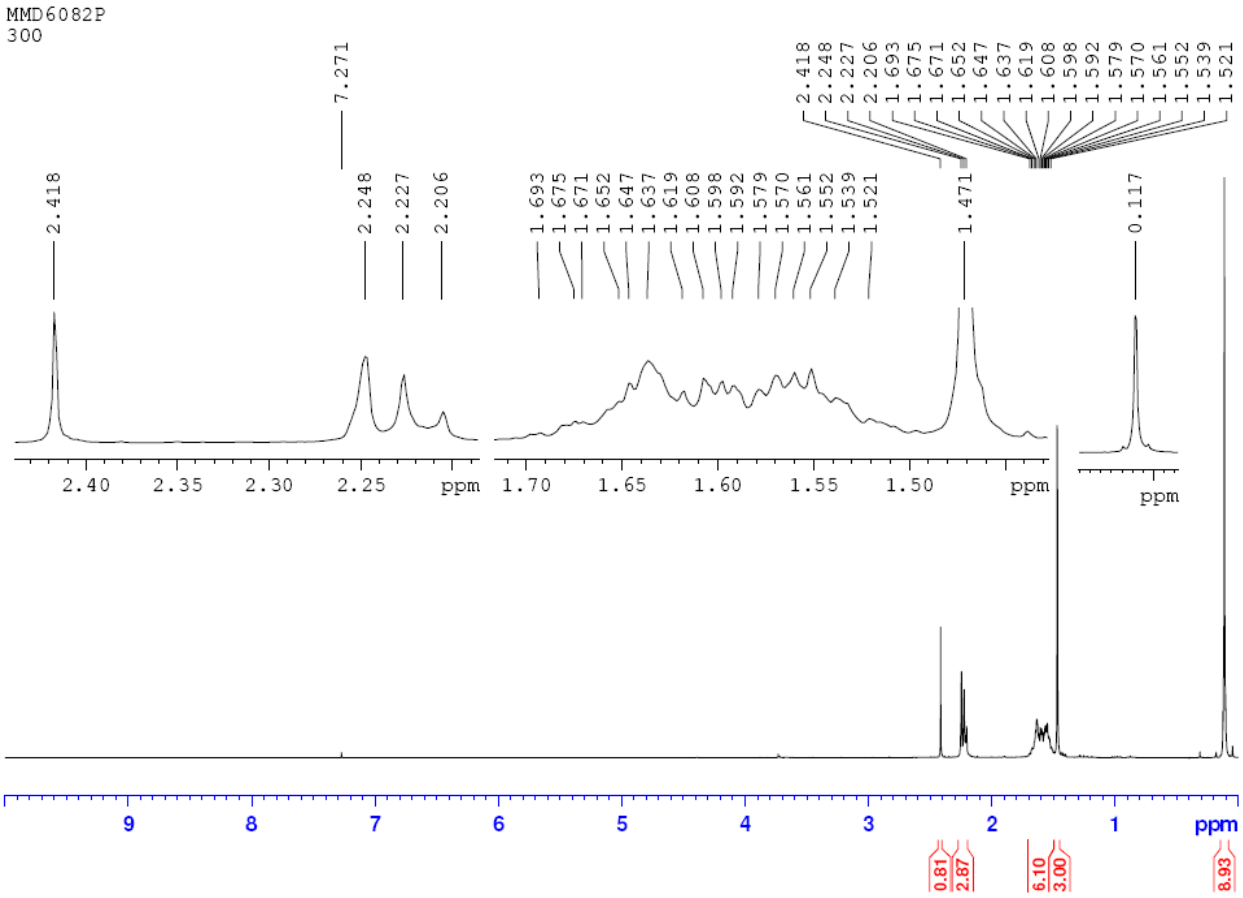

MMD6047P
301
7.270
2.256
2.243
2.234
2.222
2.200
2.163
2.152
2.128
2.105
1.757
1.734
1.706
1.688
1.675
1.636
1.542
1.518
1.494
1.470
1.446
1.425
0.964
0.939
0.915
0.106
ppm
2.00
3.00
3.67
1.93
2.69
2.75
9.25

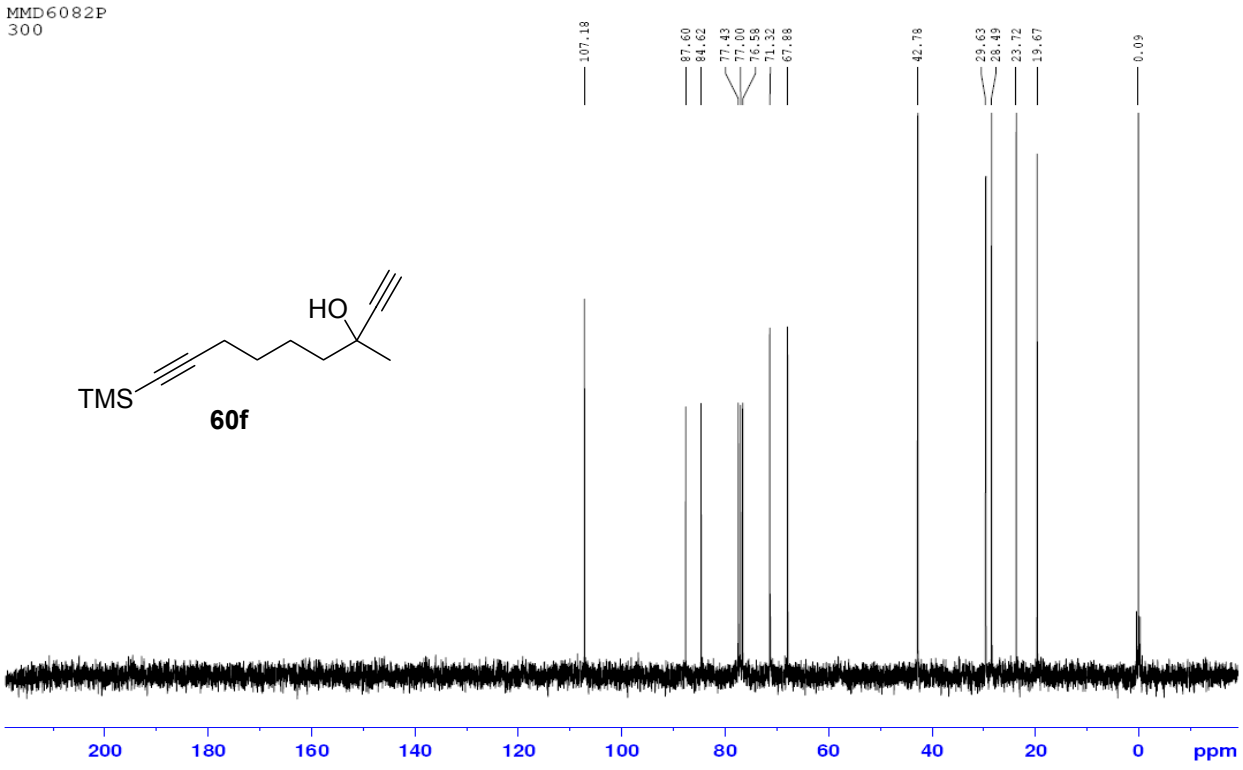

MMD6047P
301
84.554
83.932
83.658
107.12
84.55
83.93
83.66
77.43
77.00
76.58
67.86
42.95
30.18
24.09
22.03
20.47
19.86
13.35
0.05
ppm
HO
TMS
60e


MMD6042P 500 MHz
7.271
2.281
2.261
2.254
2.247
2.240
2.233
2.225
2.213
2.206
2.187
2.173
2.159
2.008
1.990
1.976
1.973
1.959
1.953
1.950
1.862
1.851
1.840
1.838
1.829
1.815
1.803
1.744
1.732
1.718
1.708
1.705
0.971
0.956
0.941
0.136
ppm
9
8
7
6
5
4
3
2
1
ppm
2.00
2.00
4.03
1.07
2.15
2.90
2.16
2.84
8.64


MMD6042P
300
169.22
106.96
85.70
84.69
80.34
77.43
77.01
76.58
75.45
41.03
26.81
23.76
22.01
20.64
19.78
13.35
0.10
AcO
TMS
200
180
160
140
120
100
80
60
40
20
0
ppm

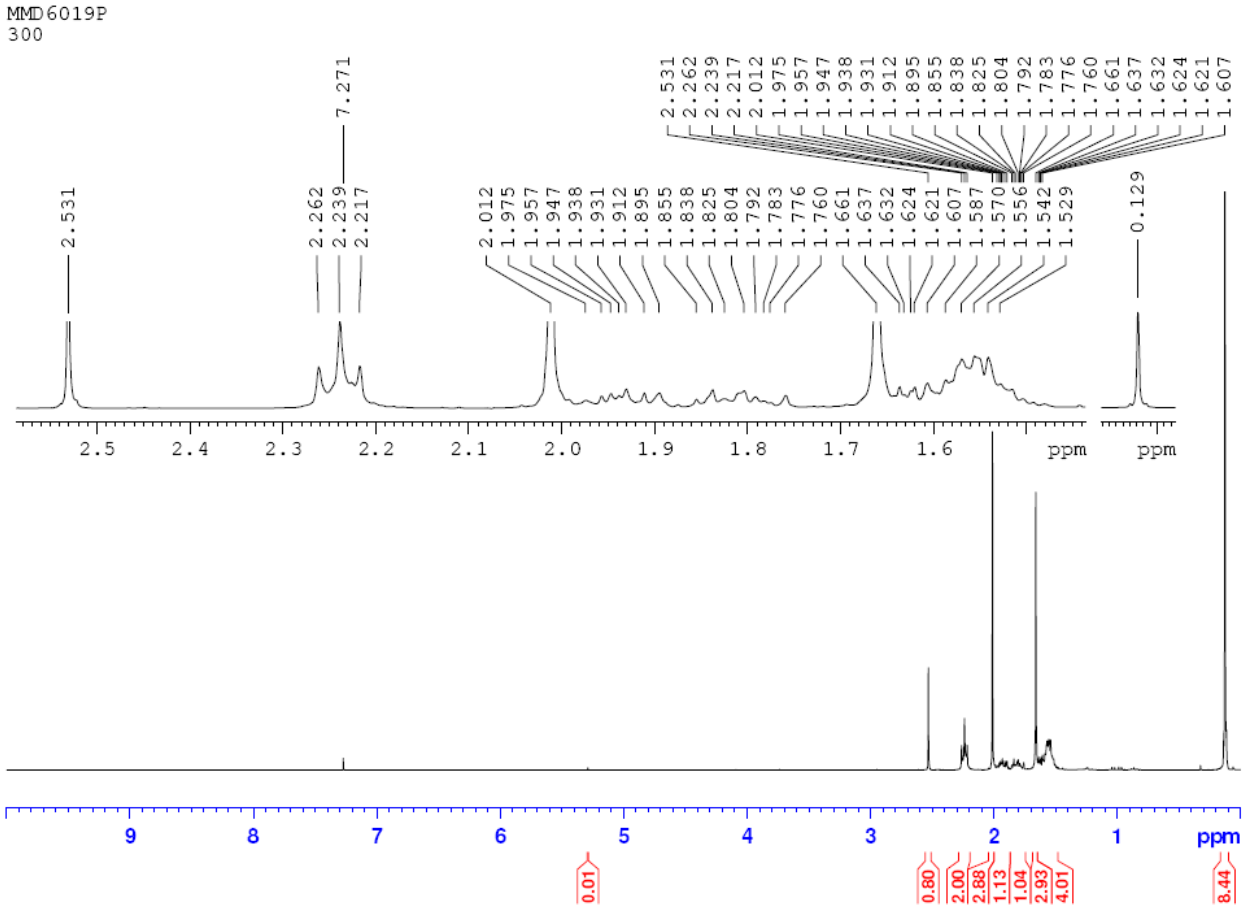
41e

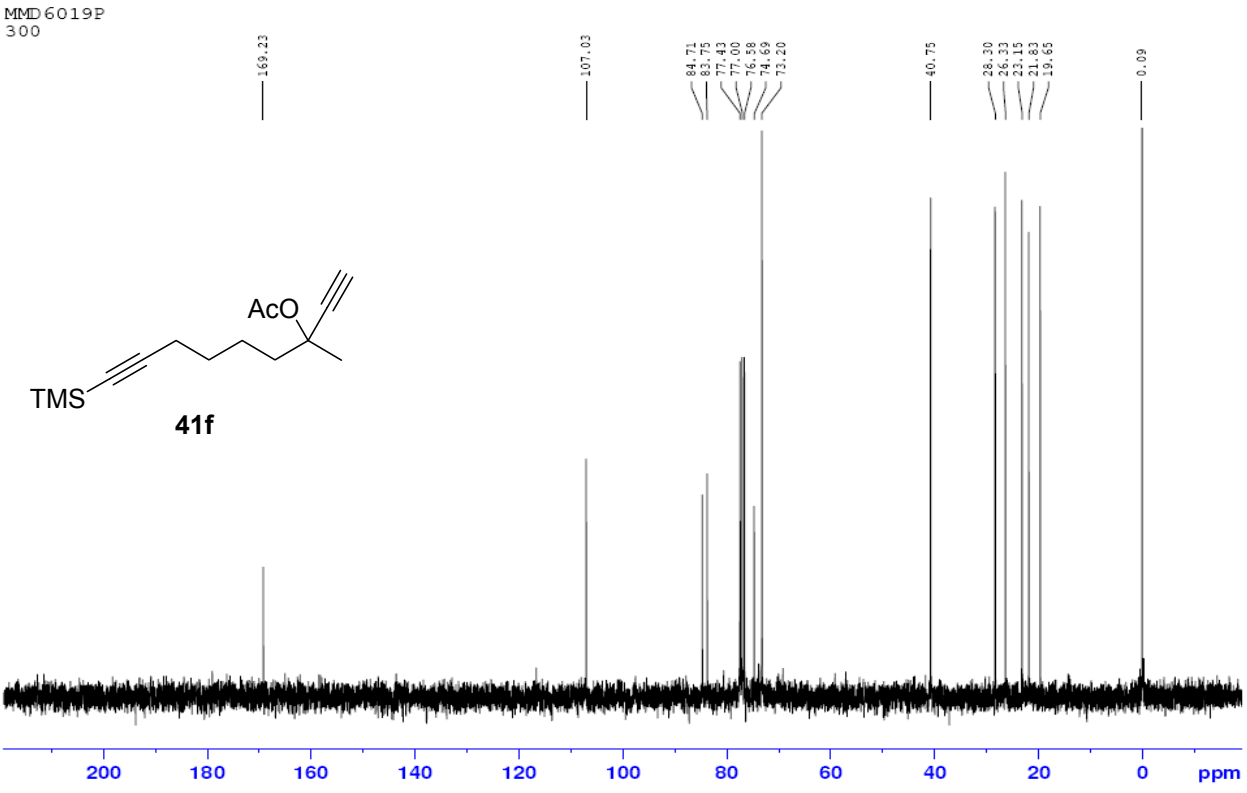

MMD6082P
300
7.271
2.418
2.248
2.227
2.206
1.693
1.675
1.671
1.652
1.647
1.637
1.619
1.608
1.598
1.592
1.579
1.570
1.561
1.552
1.539
1.521
1.471
0.117
ppm
9
8
7
6
5
4
3
2
1
0.81
2.87
6.10
3.00
8.93


MMD6082P
300
107.18
87.60
84.62
77.43
77.00
76.58
71.32
67.88
42.78
29.63
28.49
23.72
19.67
0.09
200
180
160
140
120
100
80
60
40
20
0
ppm

HO
TMS

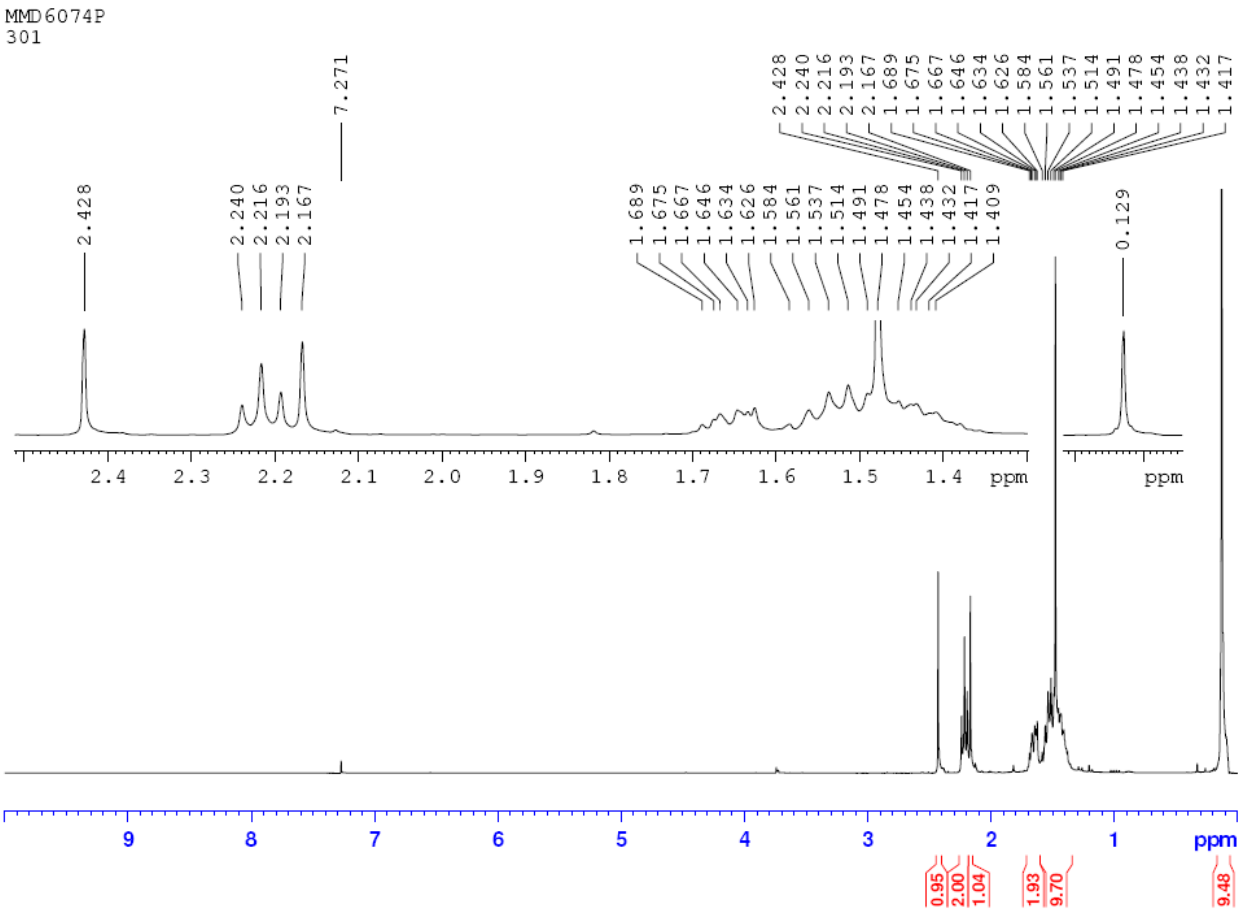
60f

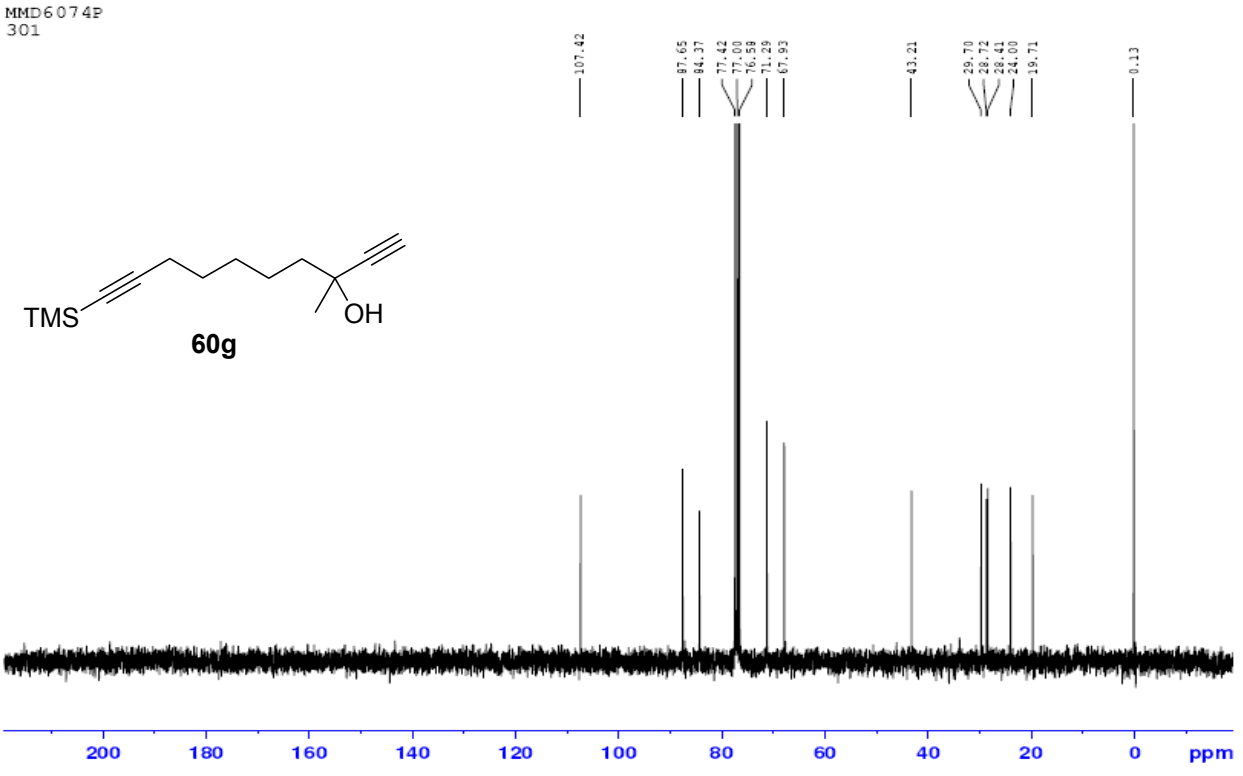

MMD6019P
300
2.531
2.262
2.239
2.217
2.012
1.975
1.957
1.947
1.938
1.931
1.912
1.895
1.855
1.838
1.825
1.804
1.792
1.783
1.776
1.760
1.661
1.637
1.632
1.624
1.621
1.607
1.587
1.570
1.556
1.542
1.529
0.129
7.271
ppm
0.01
0.80
2.00
2.88
1.13
1.04
2.93
4.01
8.44


MMD6019P
300
169.23
107.03
84.71
83.75
77.43
77.00
76.58
74.69
73.20
40.75
28.30
26.33
23.15
21.83
19.65
0.09
ppm

AcO
TMS

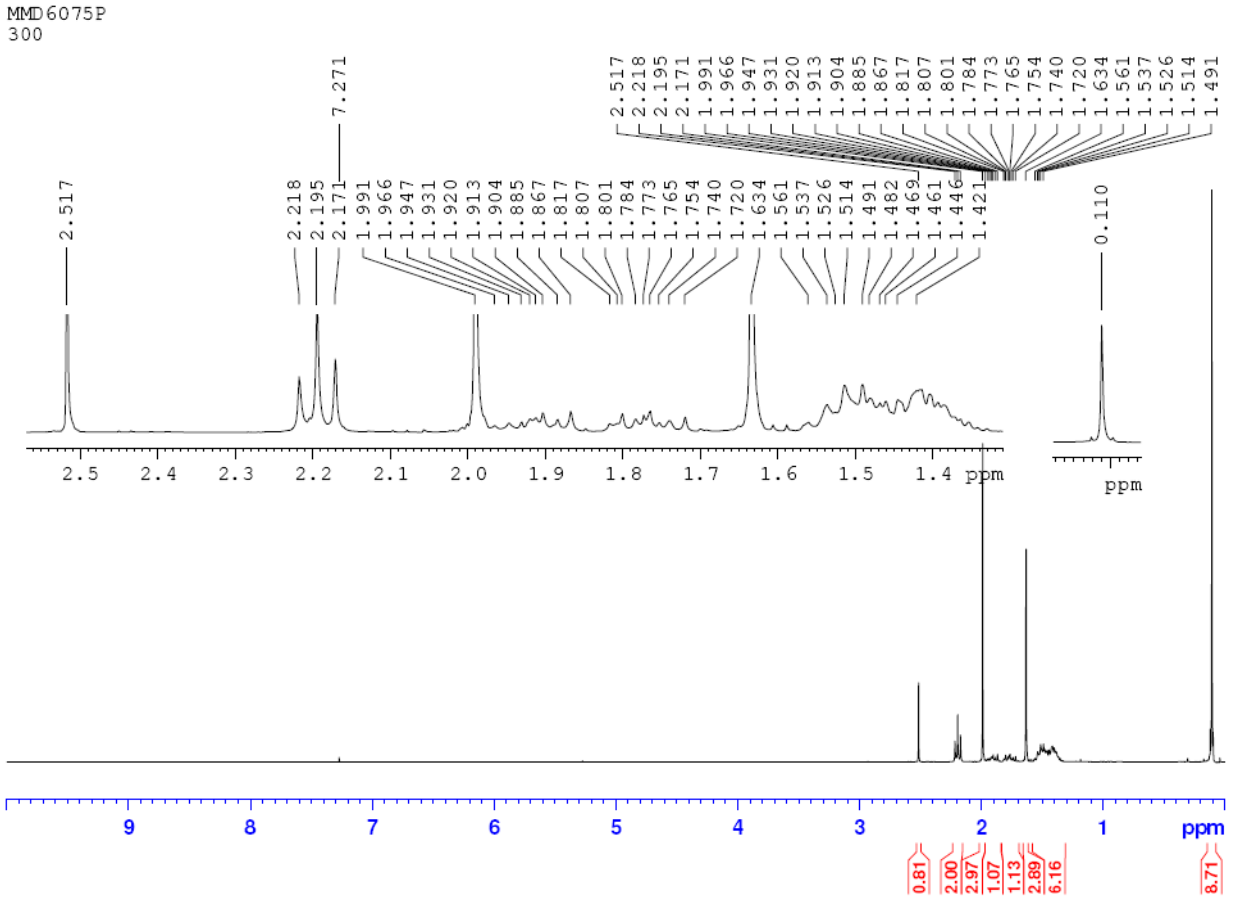
41f

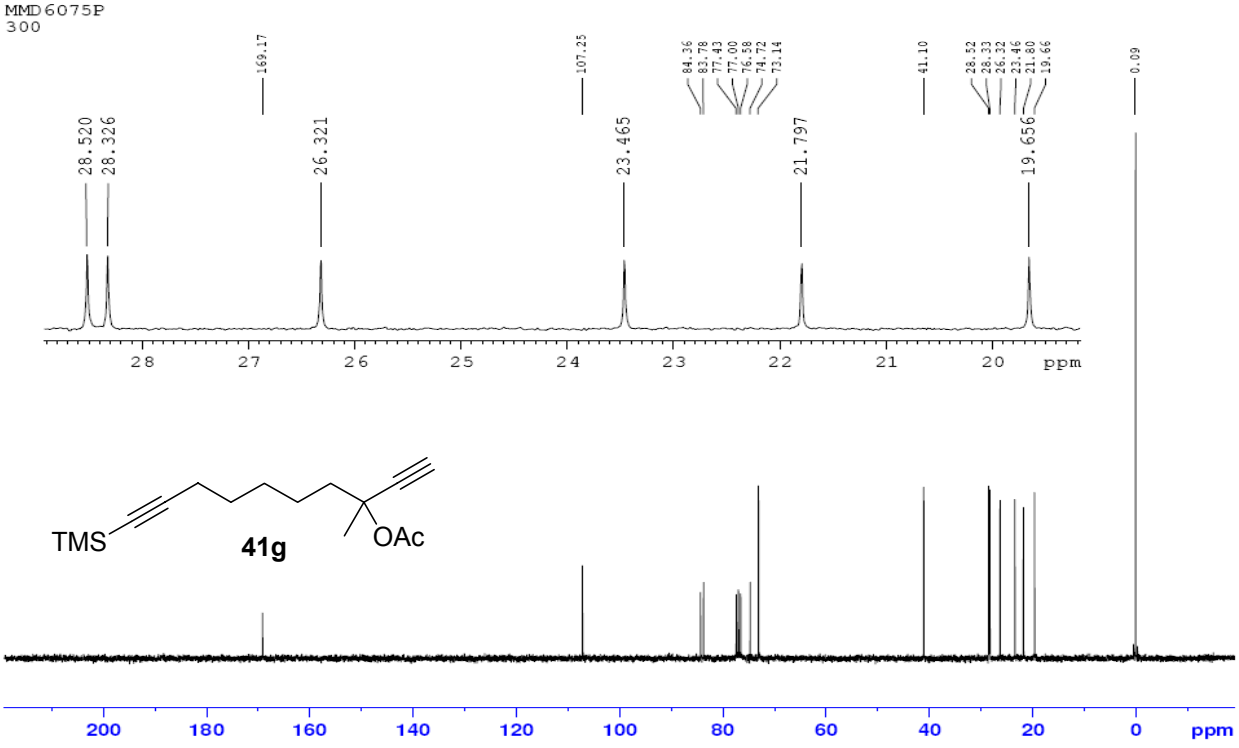

MMD6074P
301
2.428
2.240
2.216
2.193
2.167
7.271
1.689
1.675
1.667
1.646
1.634
1.626
1.584
1.561
1.537
1.514
1.491
1.478
1.454
1.438
1.432
1.417
1.409
0.129
ppm
0.95
2.00
1.04
1.93
9.70
9.48

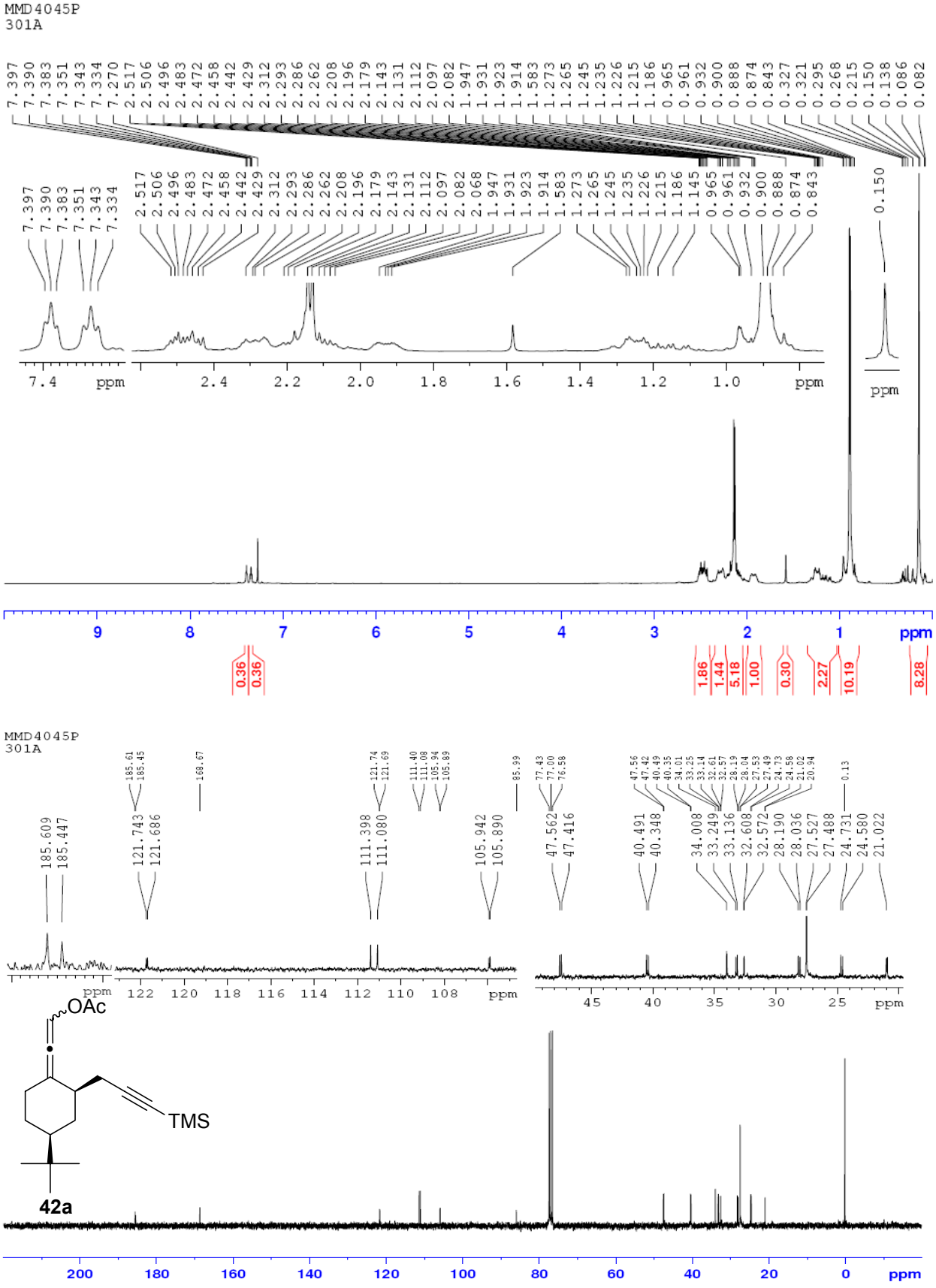

MMD6074P
301
107.42
87.65
84.37
77.42
77.00
76.58
71.29
67.93
43.21
29.70
28.72
28.41
24.00
19.71
0.13
ppm

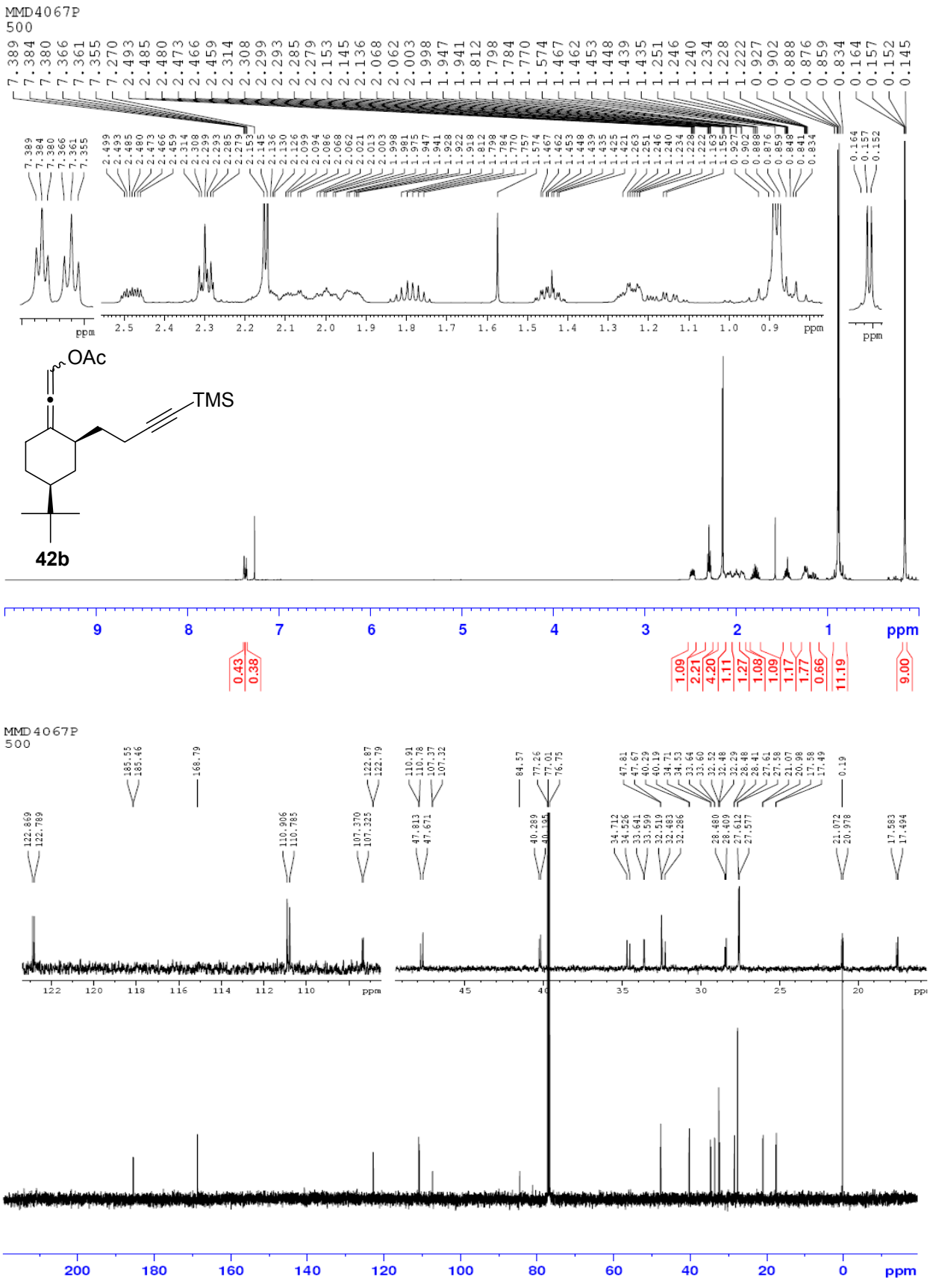
TMS
OH

60g

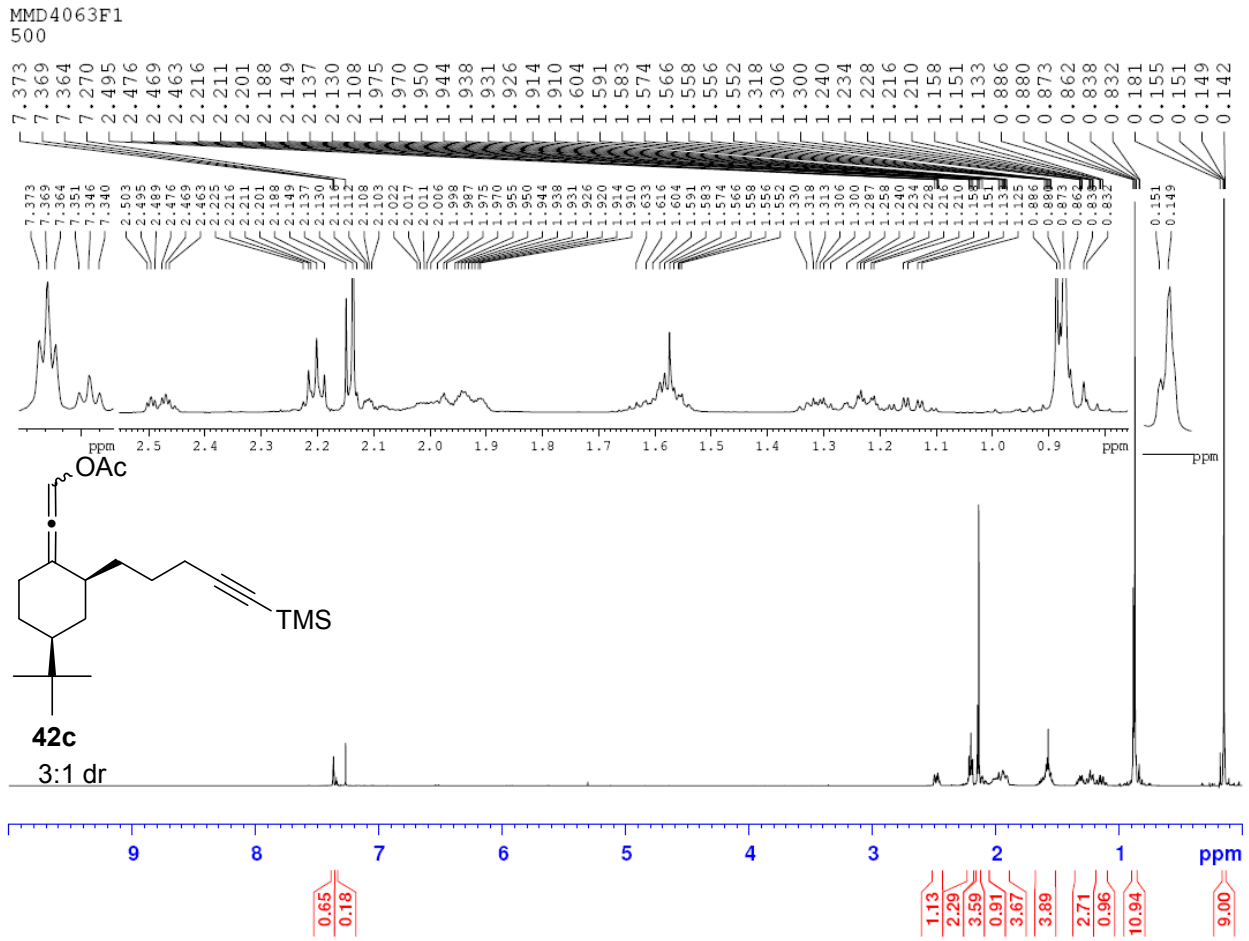

MMD6075P
300
2.517
7.271
0.110
ppm
0.81
2.00
2.97
1.07
1.13
2.89
6.16
8.71

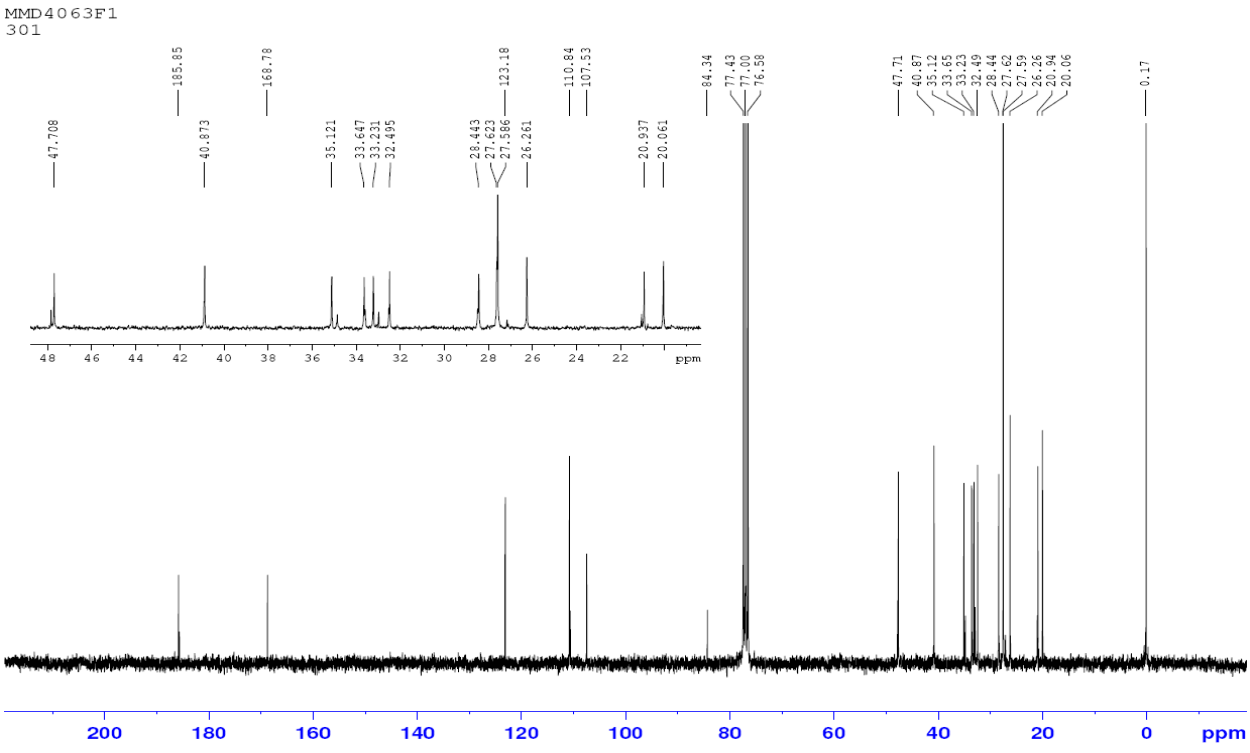

MMD6075P
300
28.520
28.326
26.321
23.465
21.797
19.656
ppm
TMS
OAc
41g

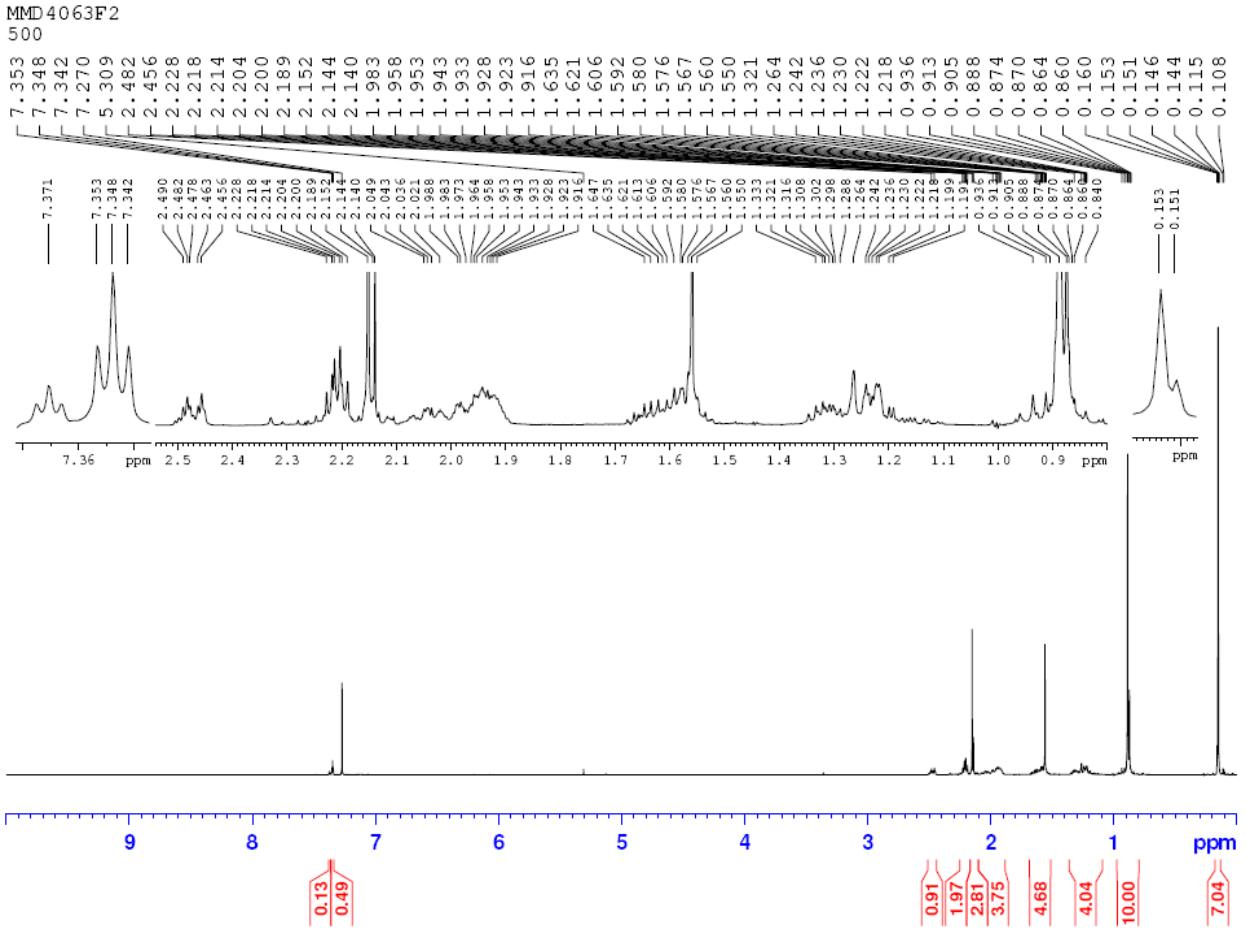

MMD4045P
301A
OAc
TMS
42a

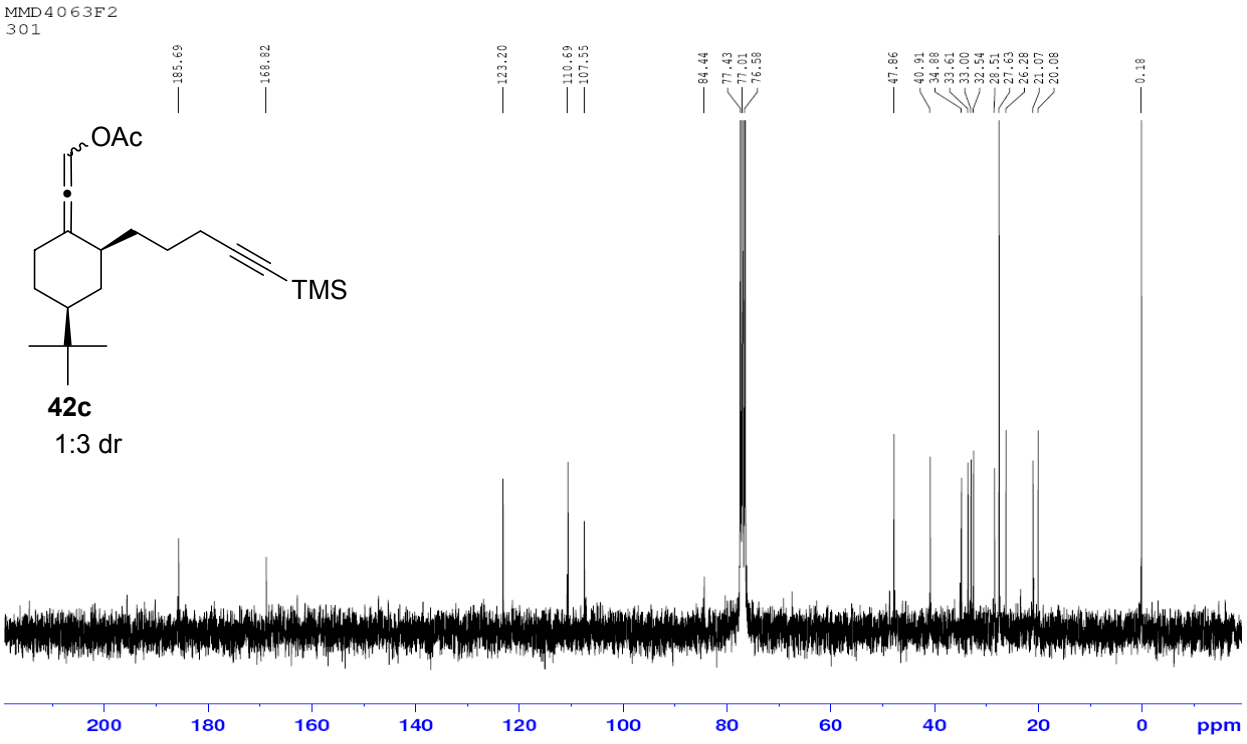

MMD4067P
500
OAc
TMS
42b
ppm

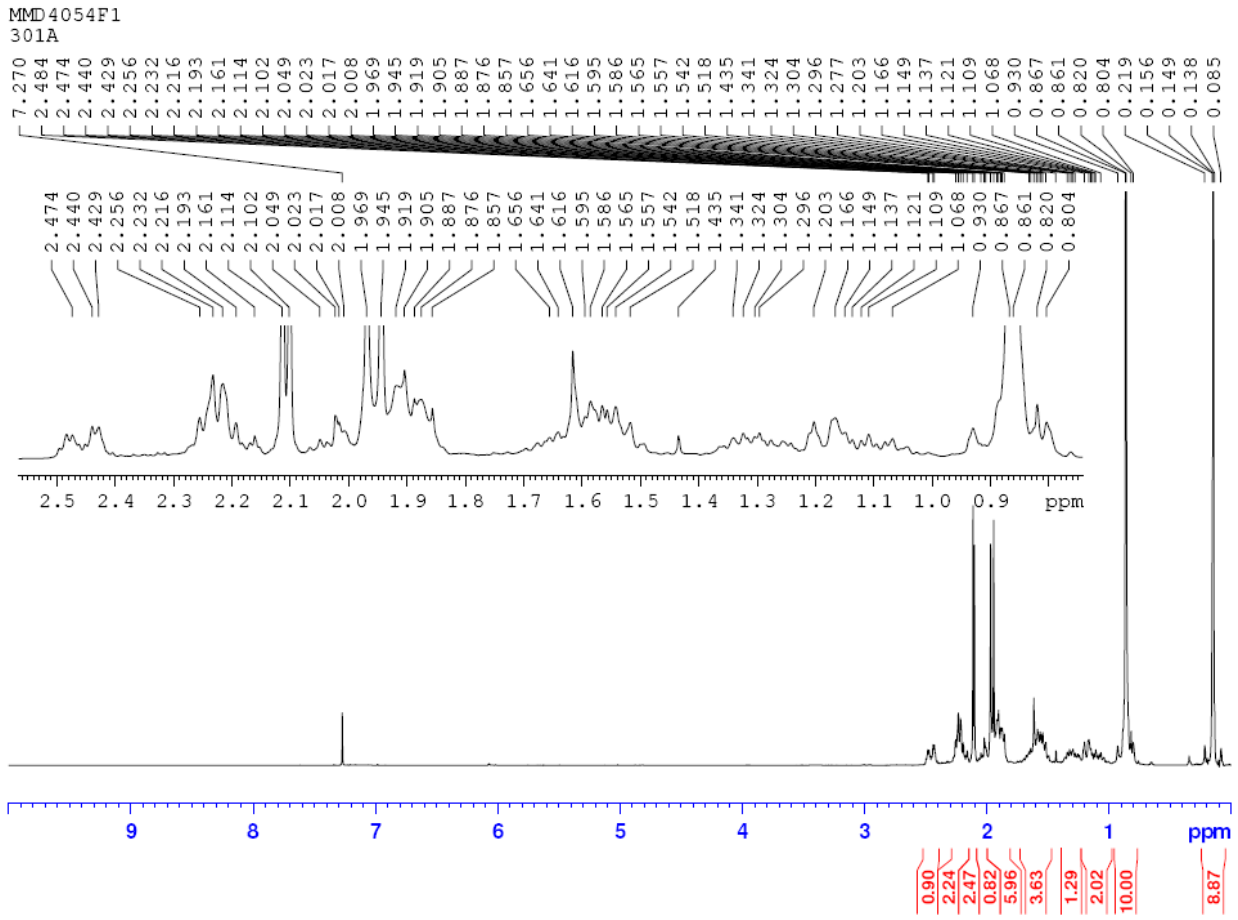
MMD4067P
500
ppm

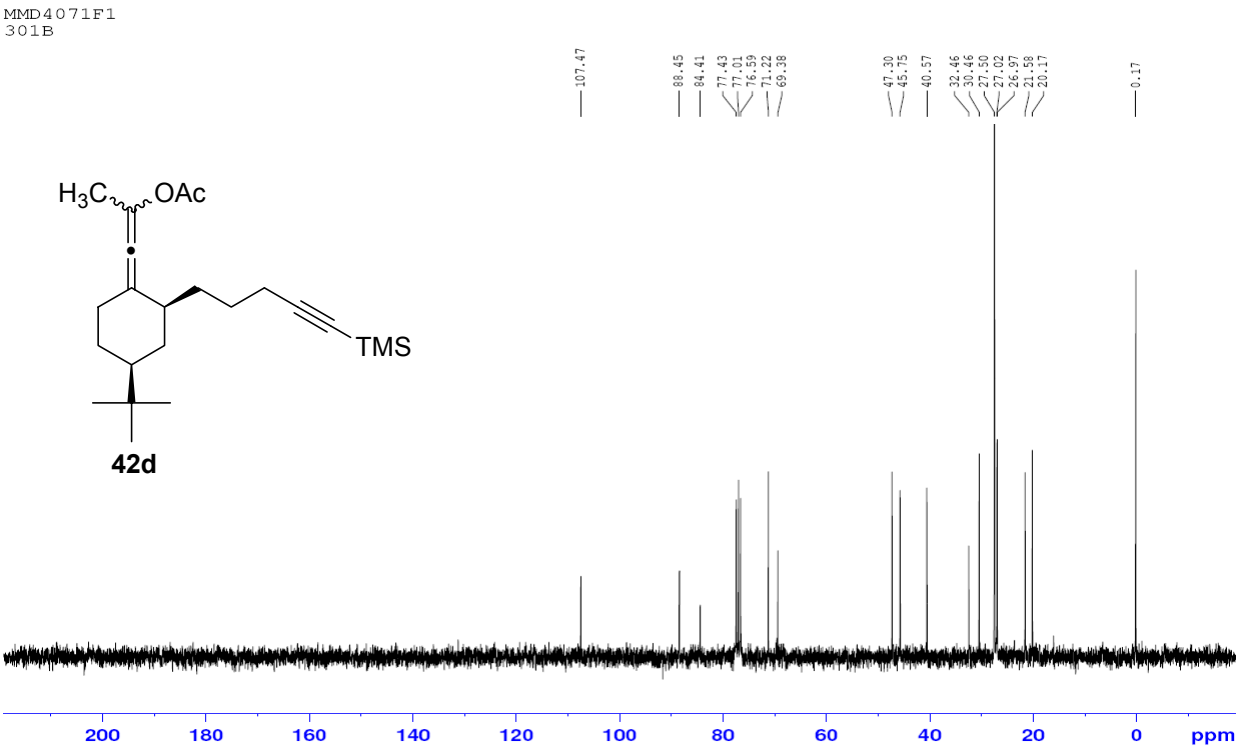

MMD4063F1
500
OAc
TMS
42c
3:1 dr

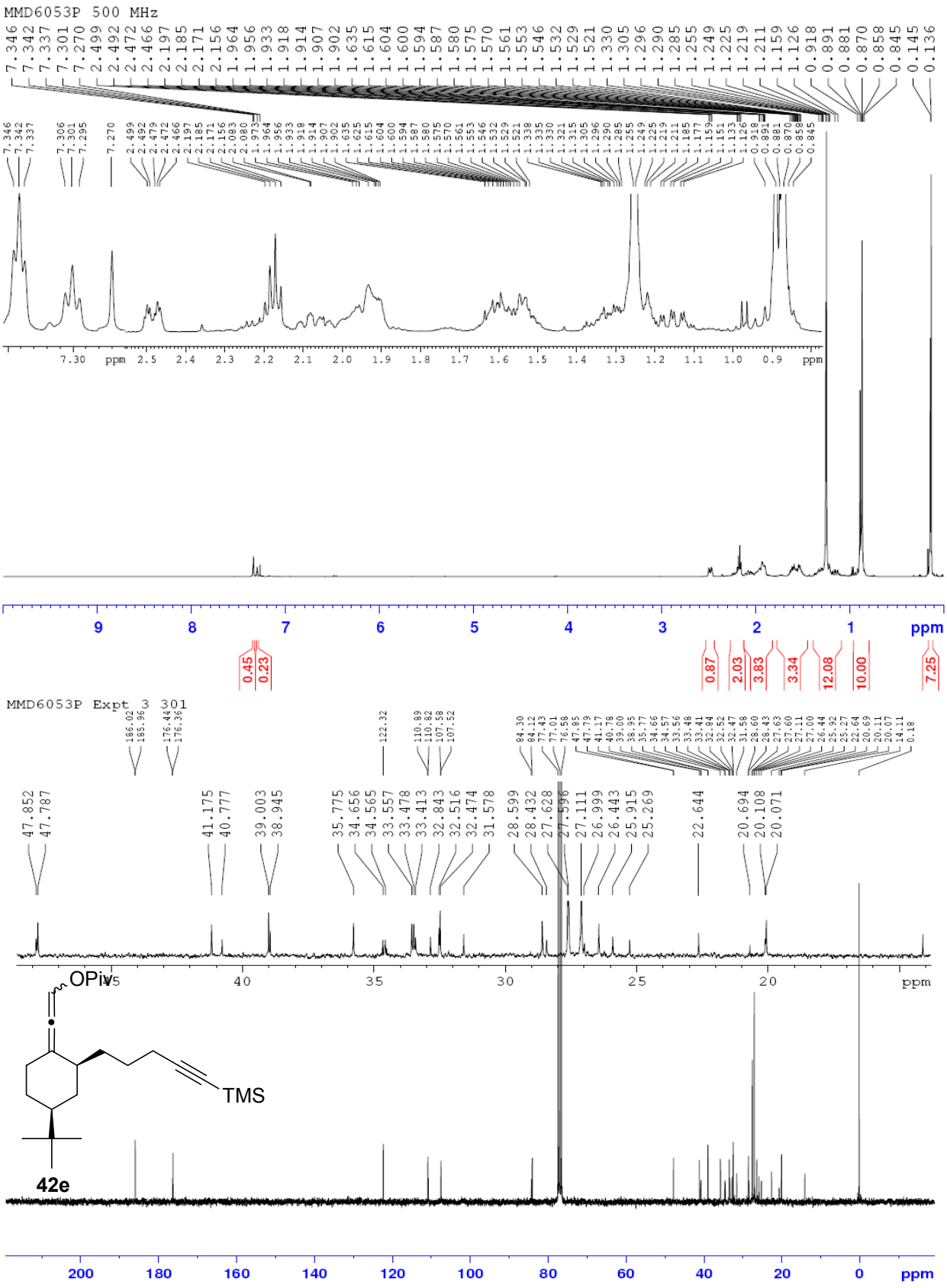

MMD4063F1
301

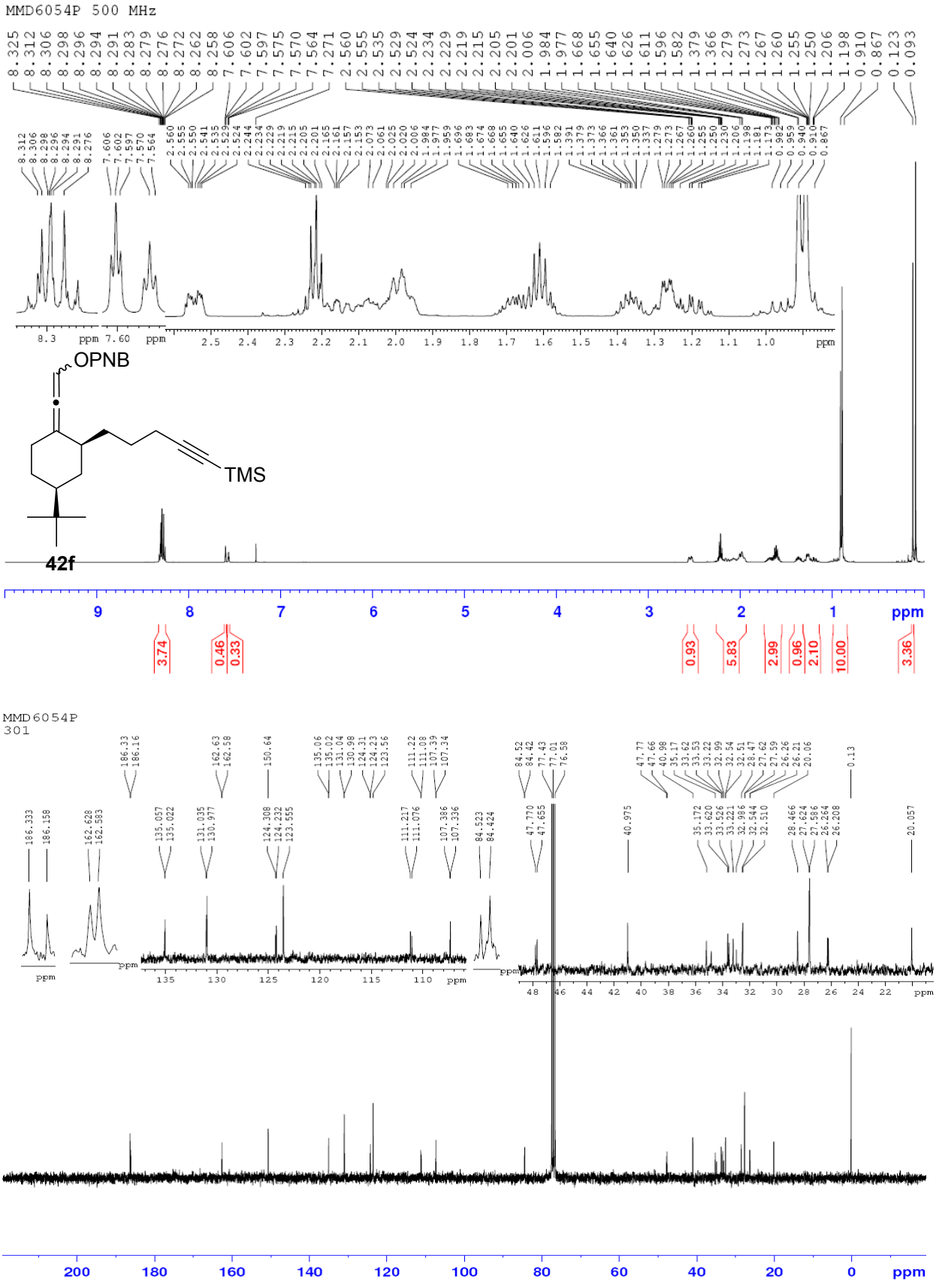

MMD4063F2
500
ppm
0.13
0.49
0.91
1.97
2.81
3.75
4.68
4.04
10.00
7.04

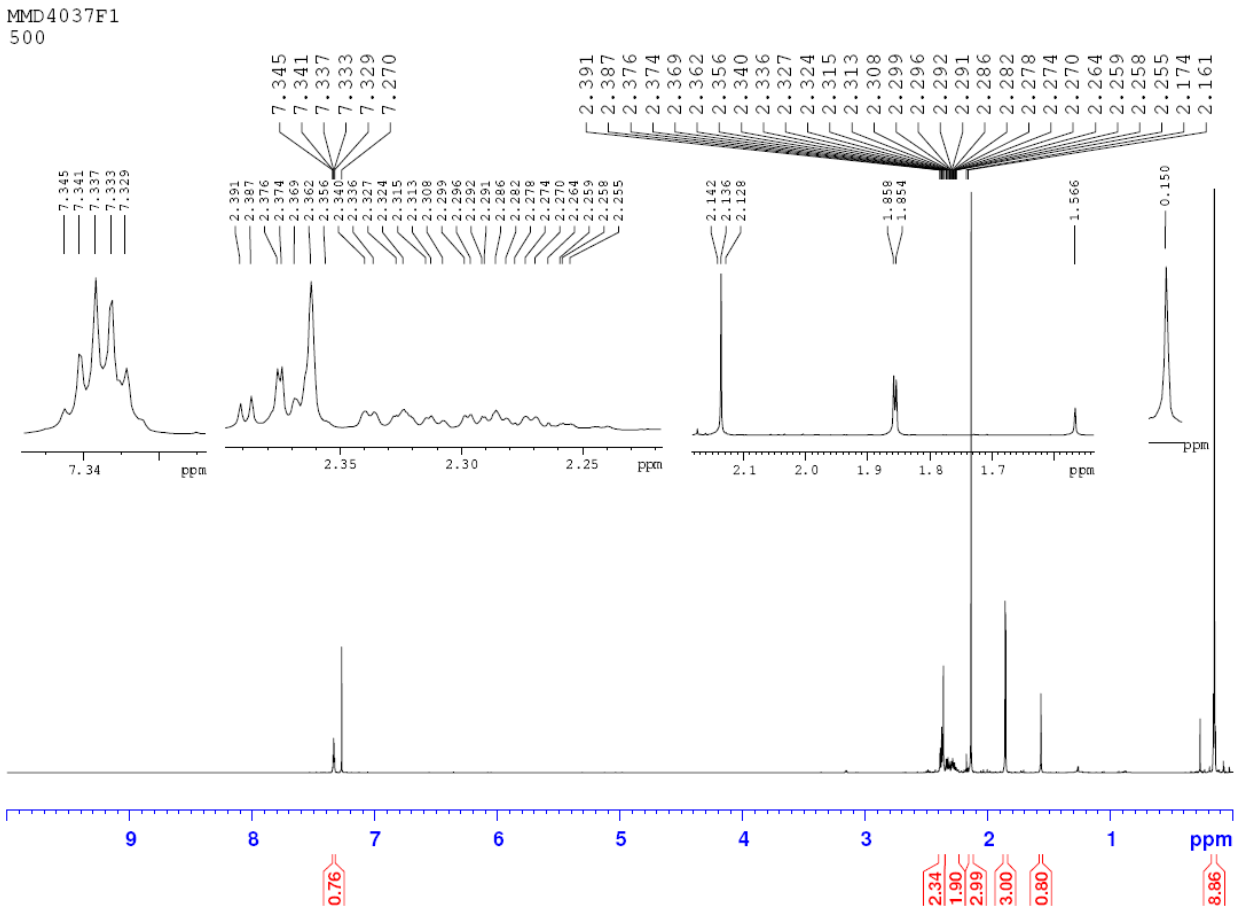

MMD4063F2
301
OAc
TMS
42c
1:3 dr
ppm

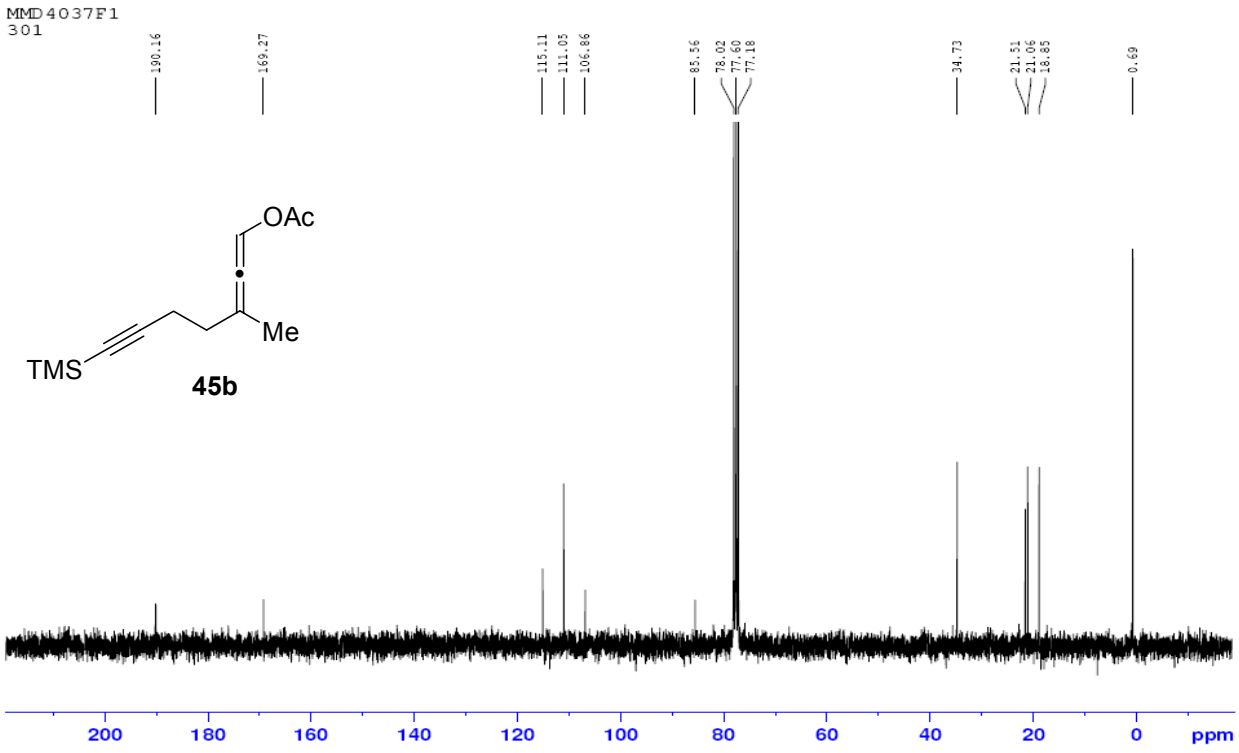

MMD4054F1
301A
ppm

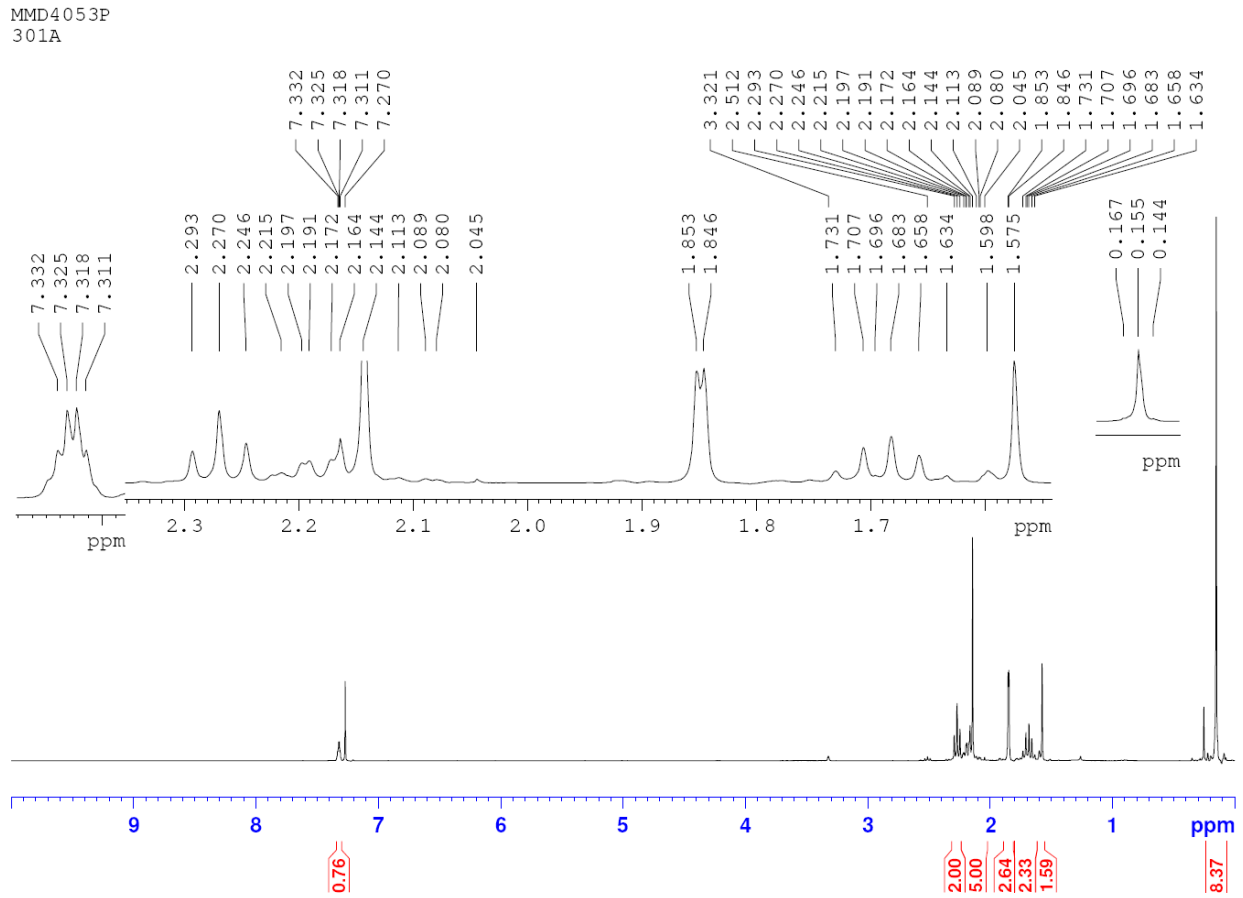

MMD4071F1
301B
H3C
OAc
TMS
42d
ppm

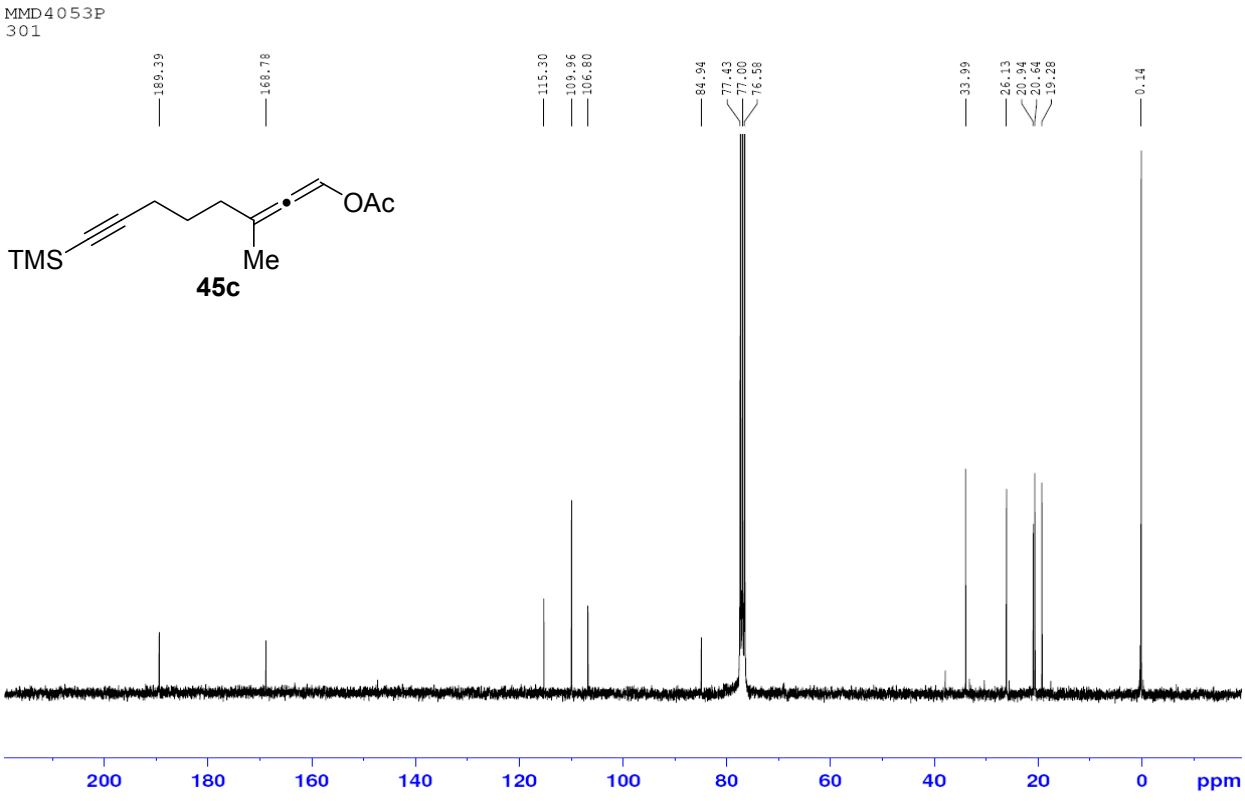

MMD6053P 500 MHz
MMD6053P Expt 3 301
OPiv
TMS
42e

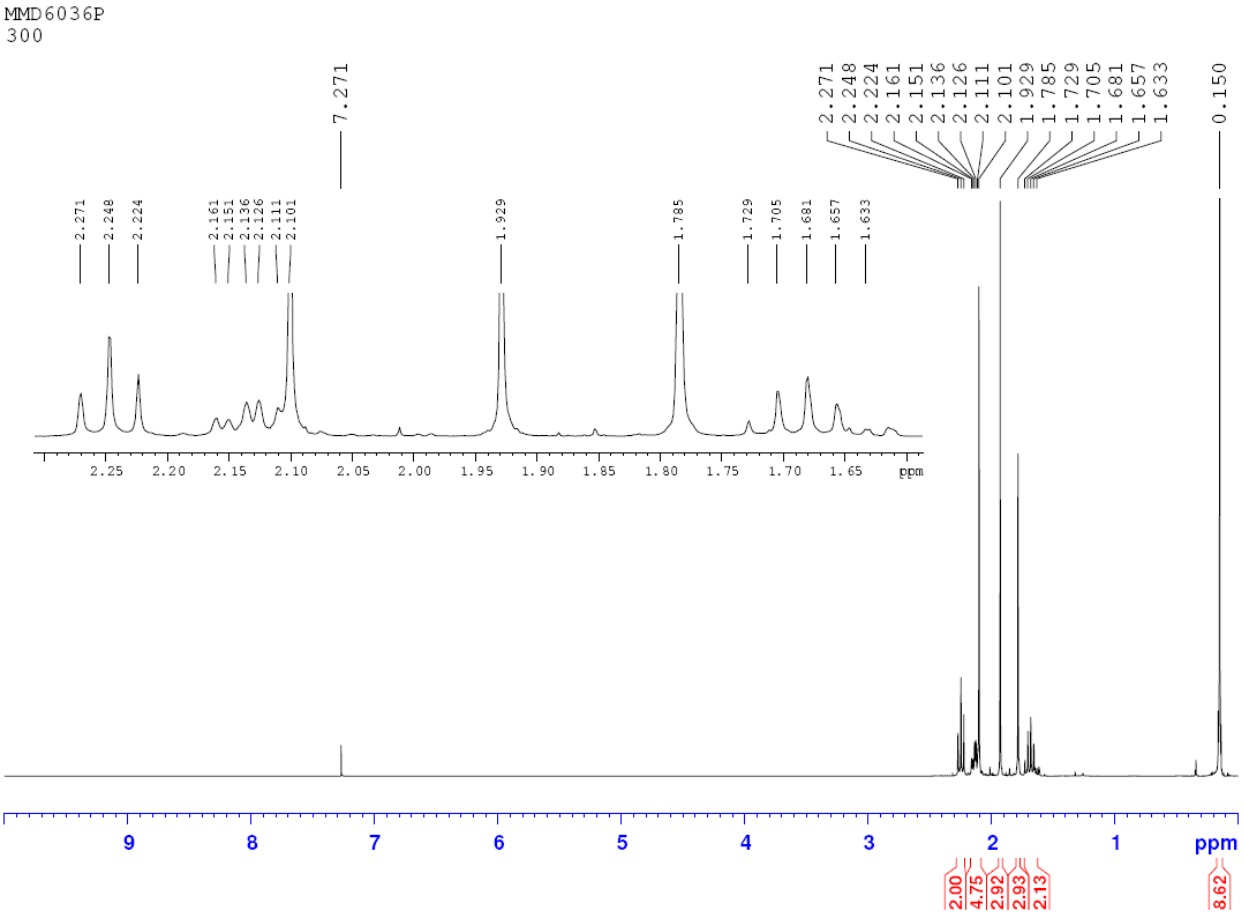

MMD6054P 500 MHz
OPNB
TMS
42f
MMD6054P
301

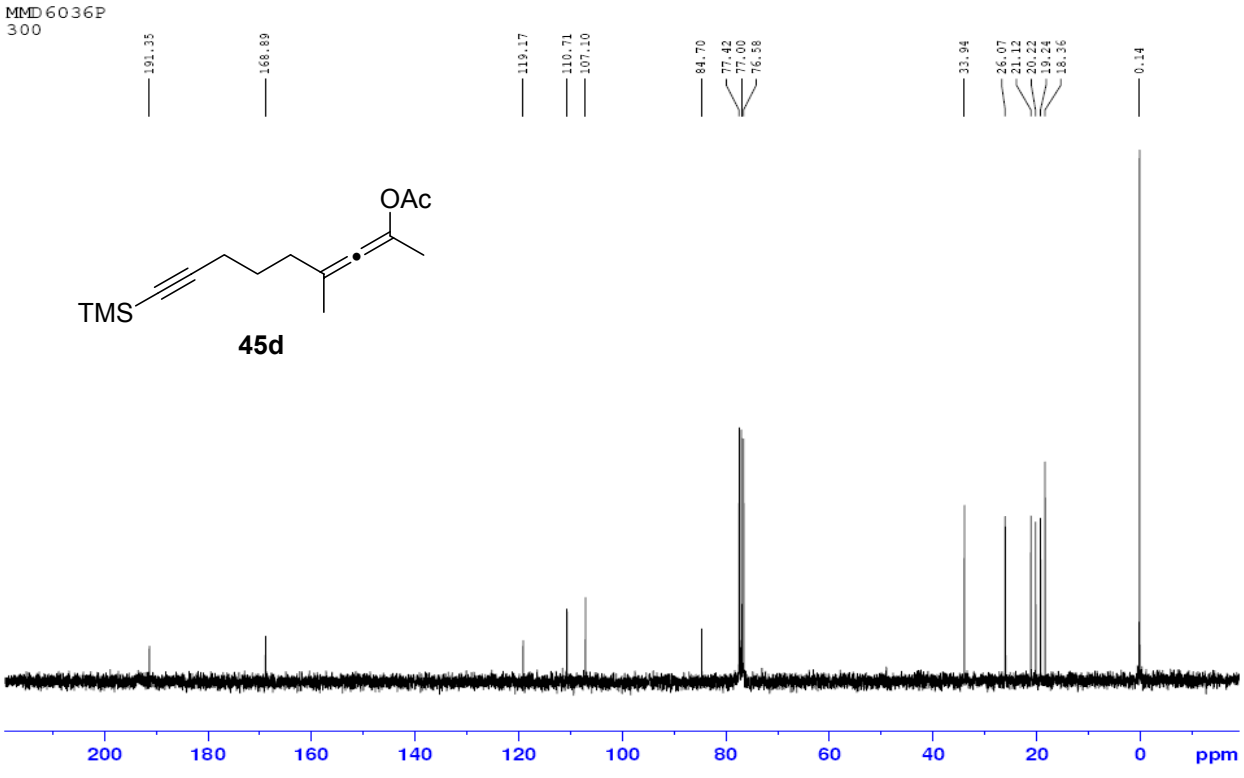

MMD4037F1
500
7.345
7.341
7.337
7.333
7.329
7.270
2.391
2.387
2.376
2.374
2.369
2.362
2.356
2.340
2.336
2.327
2.324
2.315
2.313
2.308
2.299
2.296
2.292
2.291
2.286
2.282
2.278
2.274
2.270
2.264
2.259
2.258
2.255
2.174
2.161
2.142
2.136
2.128
1.858
1.854
1.566
0.150
ppm
9
8
7
6
5
4
3
2
1
ppm
0.76
2.34
1.90
2.99
3.00
0.80
8.86

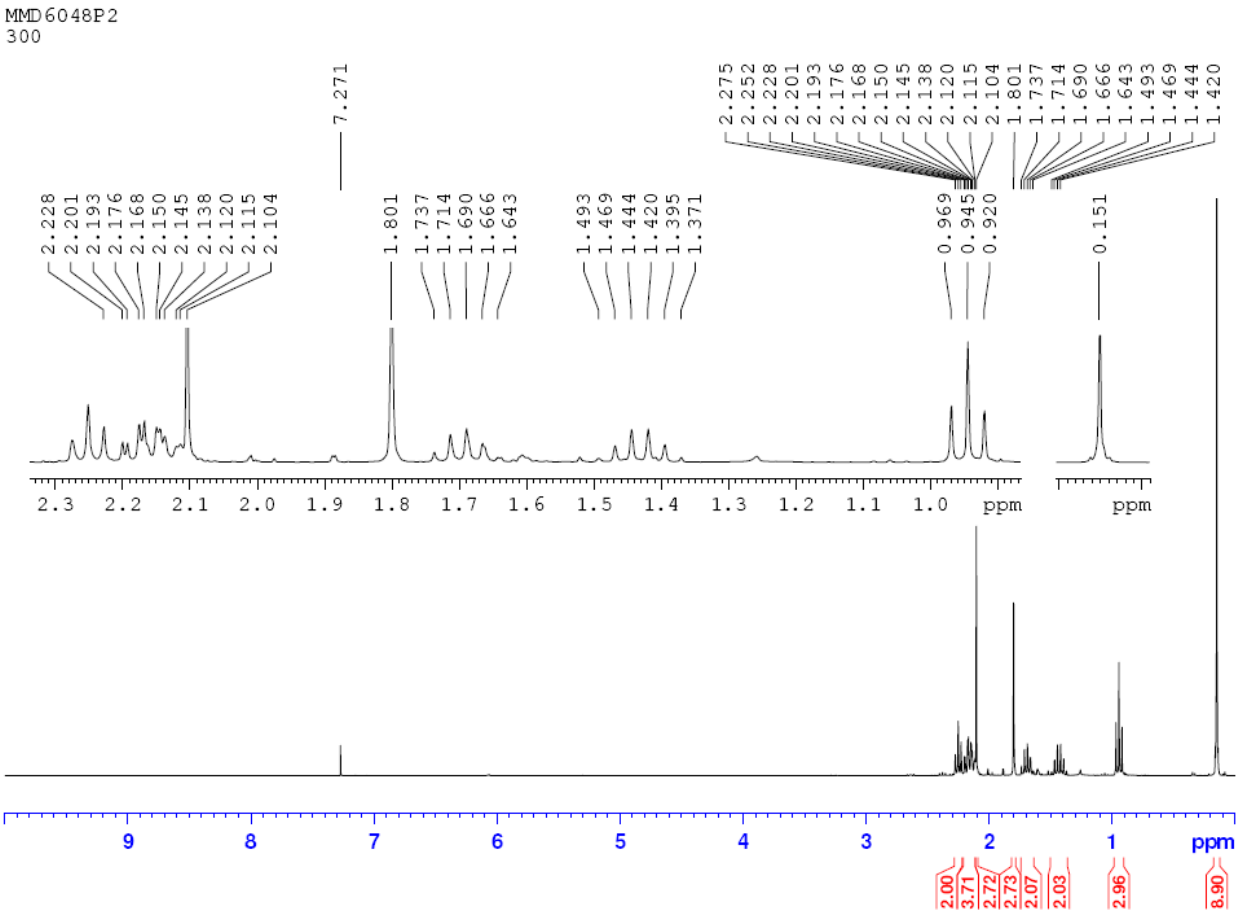

MMD4037F1
301
190.16
169.27
115.11
111.05
106.86
85.56
78.02
77.60
77.18
34.73
21.51
21.06
18.85
0.69
OAc
Me
TMS
45b
200
180
160
140
120
100
80
60
40
20
0
ppm

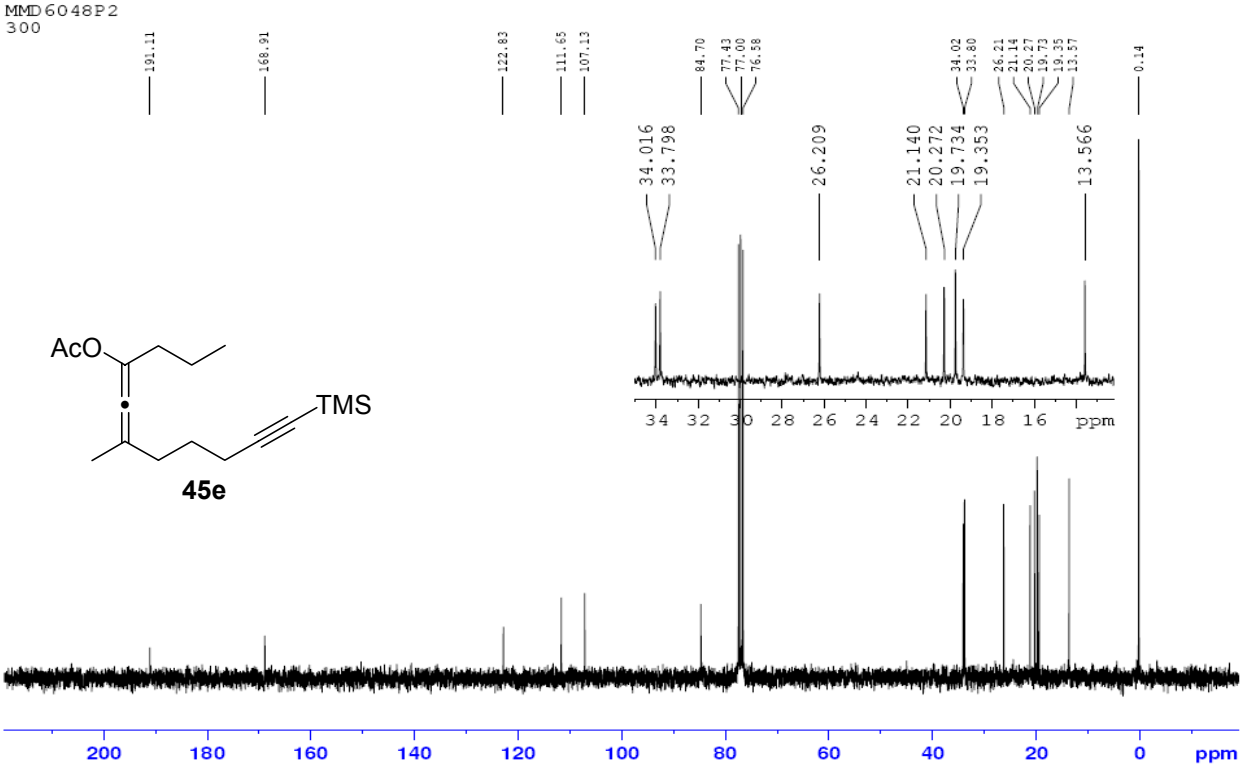

MMD4053P
301A
7.332
7.325
7.318
7.311
7.270
3.321
2.512
2.293
2.270
2.246
2.215
2.197
2.191
2.172
2.164
2.144
2.113
2.089
2.080
2.045
1.853
1.846
1.731
1.707
1.696
1.683
1.658
1.634
1.598
1.575
0.167
0.155
0.144
ppm
9
8
7
6
5
4
3
2
1
0.76
2.00
5.00
2.64
2.33
1.59
8.37

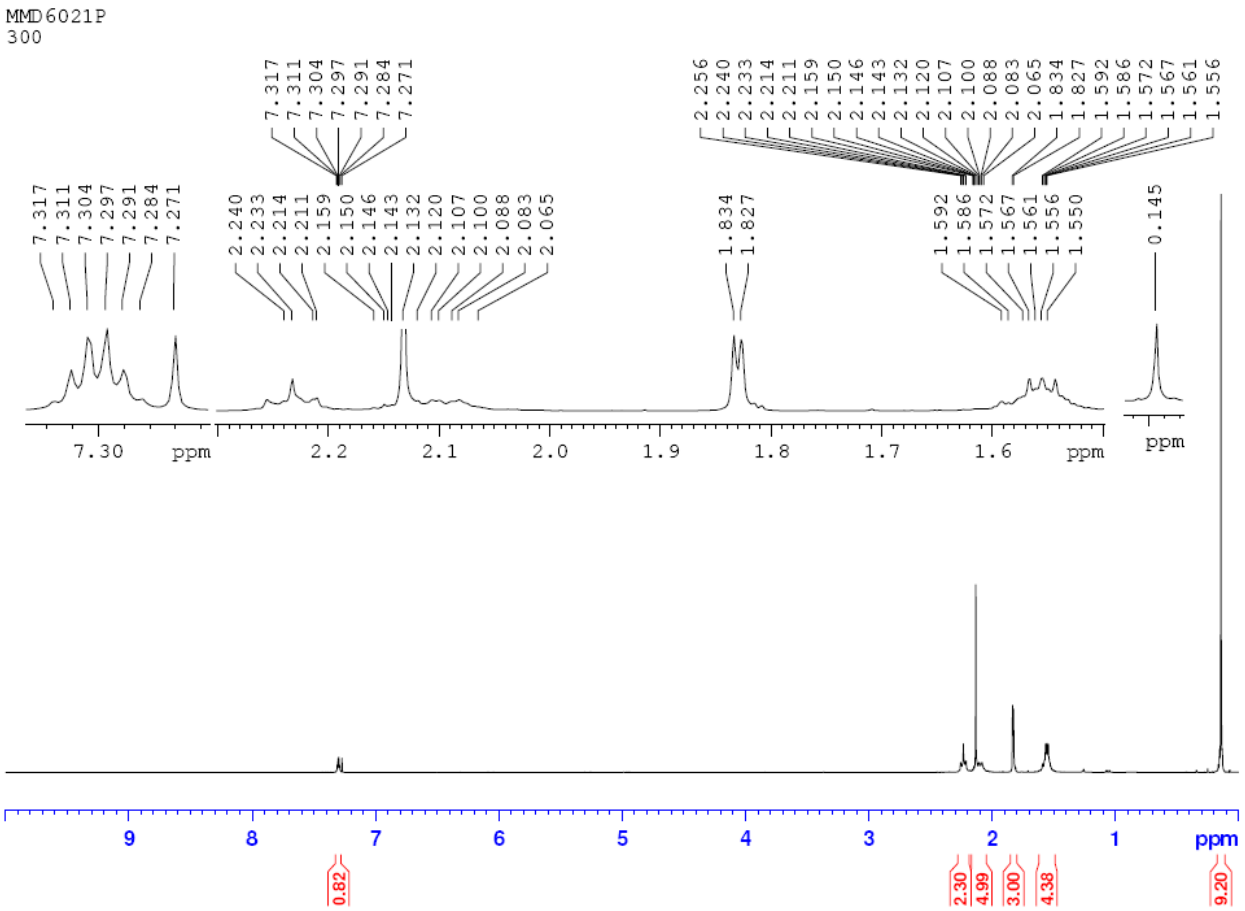

MMD4053P
301
189.39
168.78
115.30
109.96
106.80
84.94
77.43
77.00
76.58
33.99
26.13
20.94
20.64
19.28
0.14
OAc
TMS
Me
45c
200
180
160
140
120
100
80
60
40
20
0
ppm

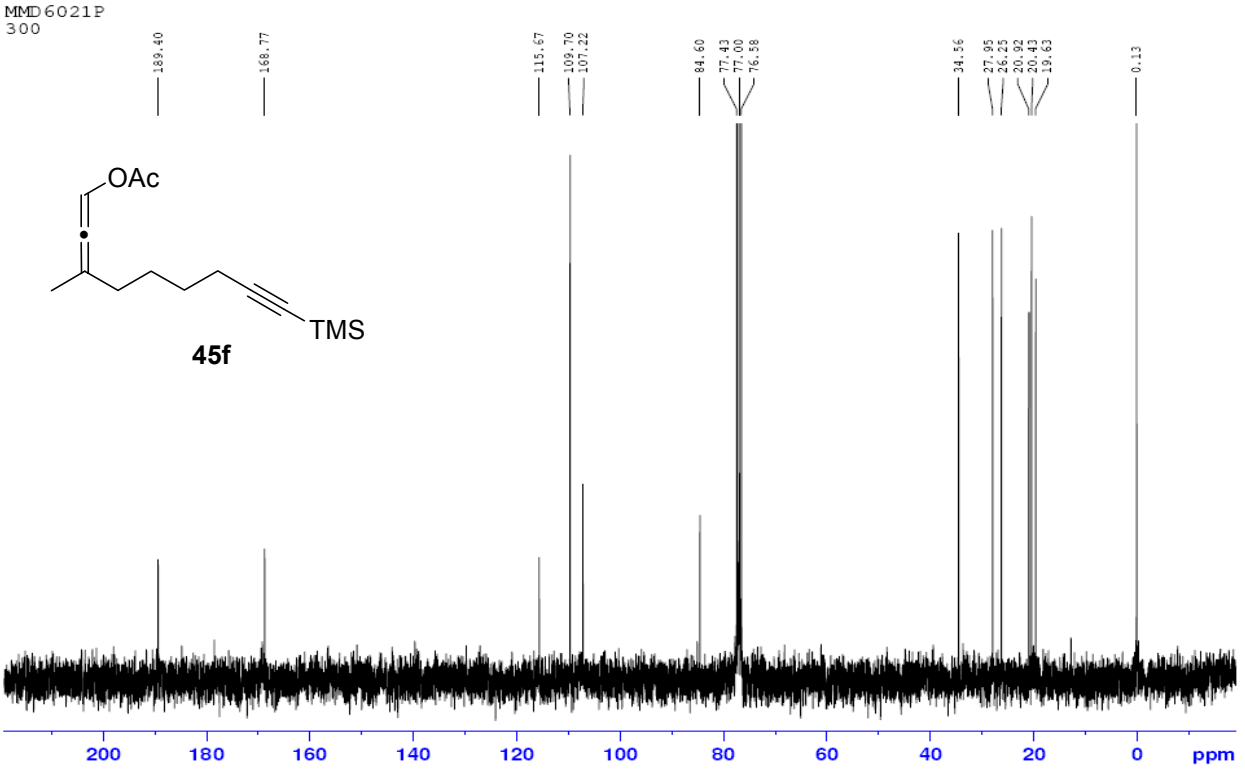

MMD6036P
300
7.271
2.271
2.248
2.224
2.161
2.151
2.136
2.126
2.111
2.101
1.929
1.785
1.729
1.705
1.681
1.657
1.633
0.150
ppm
2.00
4.75
2.92
2.93
2.13
8.62

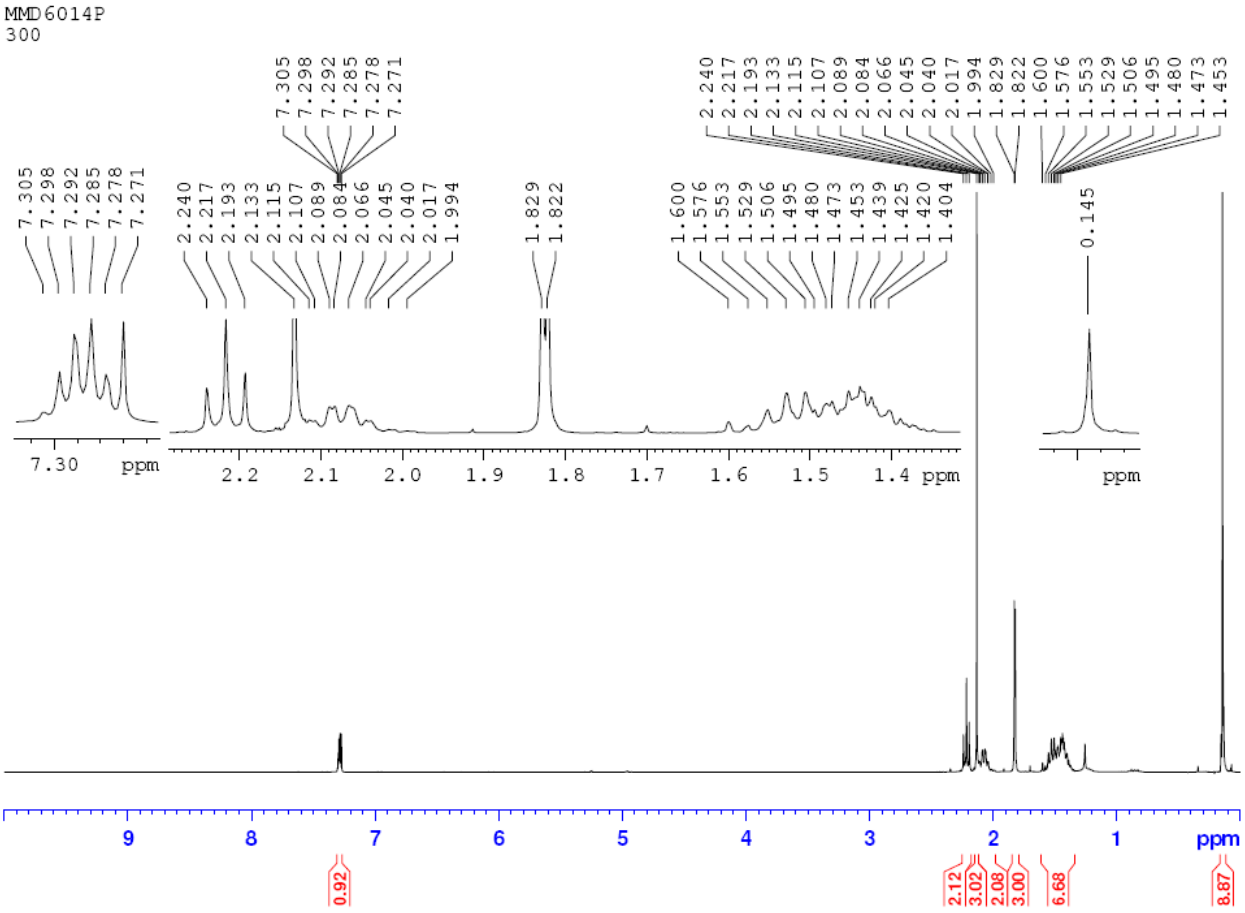

MMD6036P
300
191.35
168.89
119.17
110.71
107.10
84.70
77.42
77.00
76.58
33.94
26.07
21.12
20.22
19.24
18.36
0.14
OAc
TMS
45d
ppm

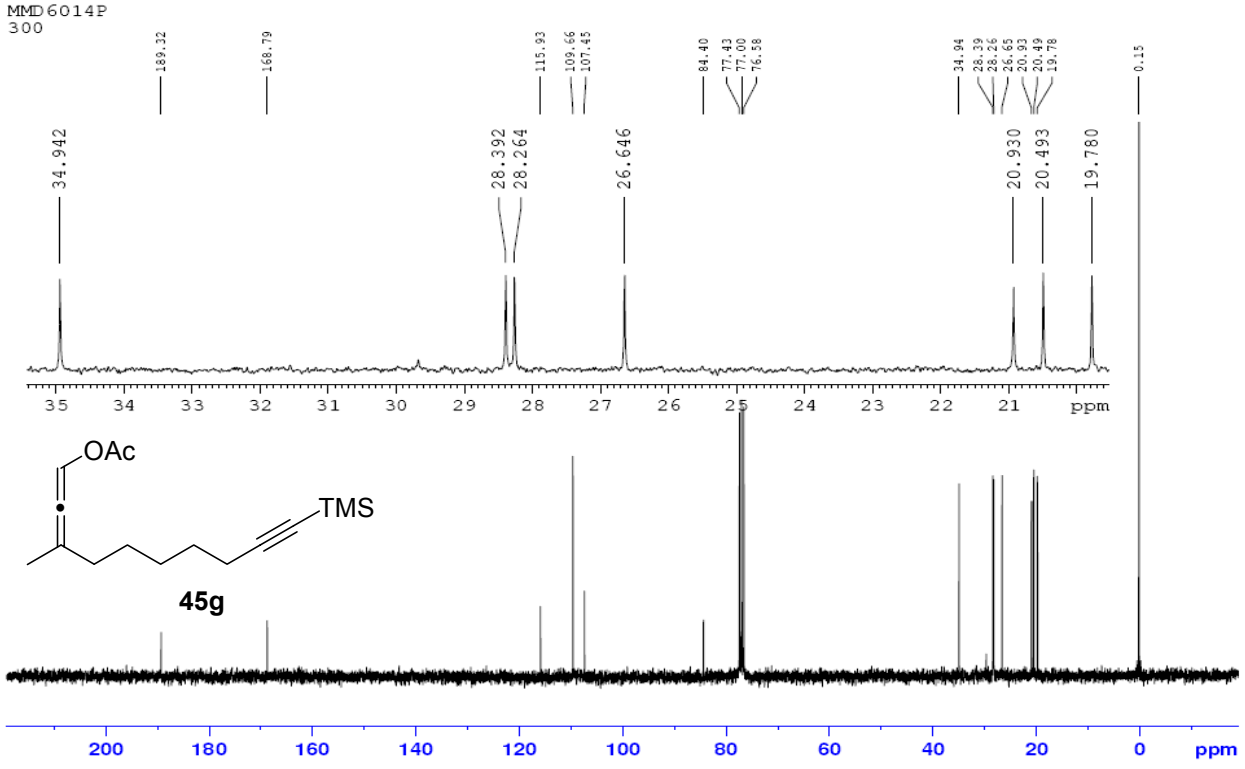

MMD6048P2
300
7.271
2.275 2.252 2.228 2.201 2.193 2.176 2.168 2.150 2.145 2.138 2.120 2.115 2.104 1.801 1.737 1.714 1.690 1.666 1.643 1.493 1.469 1.444 1.420 1.395 1.371 0.969 0.945 0.920 0.151
2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 ppm
ppm
9 8 7 6 5 4 3 2 1 ppm
2.00 3.71 2.72 2.73 2.07 2.03 2.96 8.90

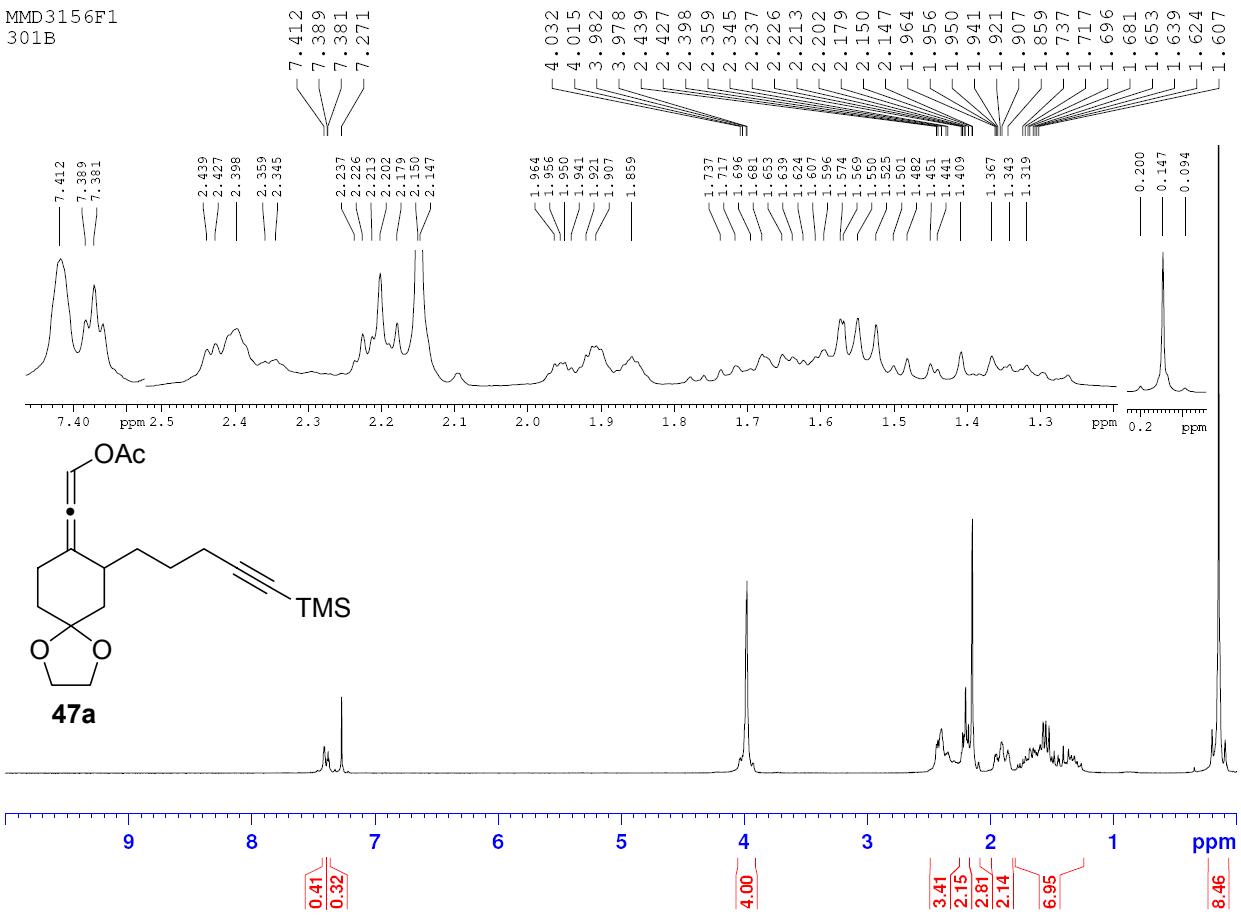

MMD6048P2
300
191.11 168.91 122.83 111.65 107.13 84.70 77.43 77.00 76.58 34.02 33.80 26.21 21.14 20.27 19.73 19.35 13.57 0.14
34.016 33.798 26.209 21.140 20.272 19.734 19.353 13.566
34 32 30 28 26 24 22 20 18 16 ppm
AcO
TMS
45e
200 180 160 140 120 100 80 60 40 20 0 ppm

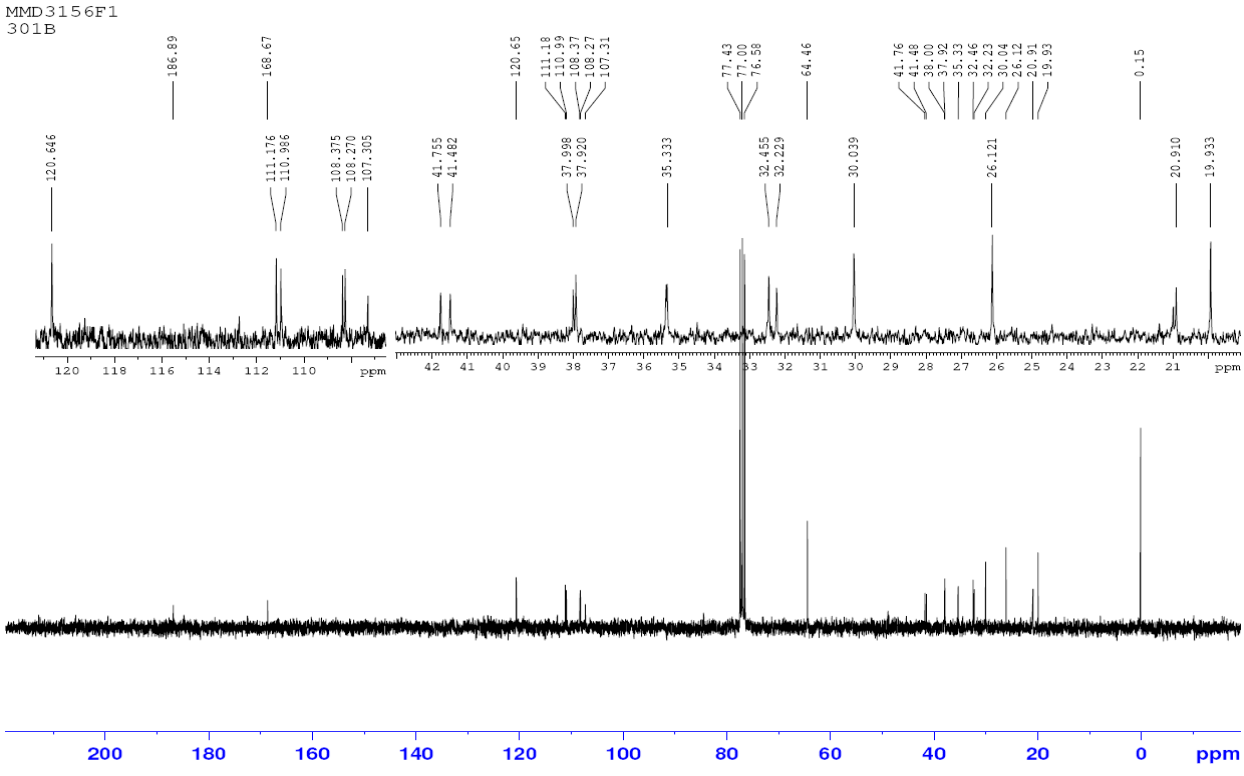

MMD6021P
300
7.317
7.311
7.304
7.297
7.291
7.284
7.271
2.240
2.233
2.214
2.211
2.159
2.150
2.146
2.143
2.132
2.120
2.107
2.100
2.088
2.083
2.065
1.834
1.827
1.592
1.586
1.572
1.567
1.561
1.556
1.550
0.145
2.256
1.592
1.586
1.572
1.567
1.561
1.556
1.834
1.827
1.592
1.586
1.572
1.567
1.561
1.556
ppm
0.82
2.30
4.99
3.00
4.38
9.20

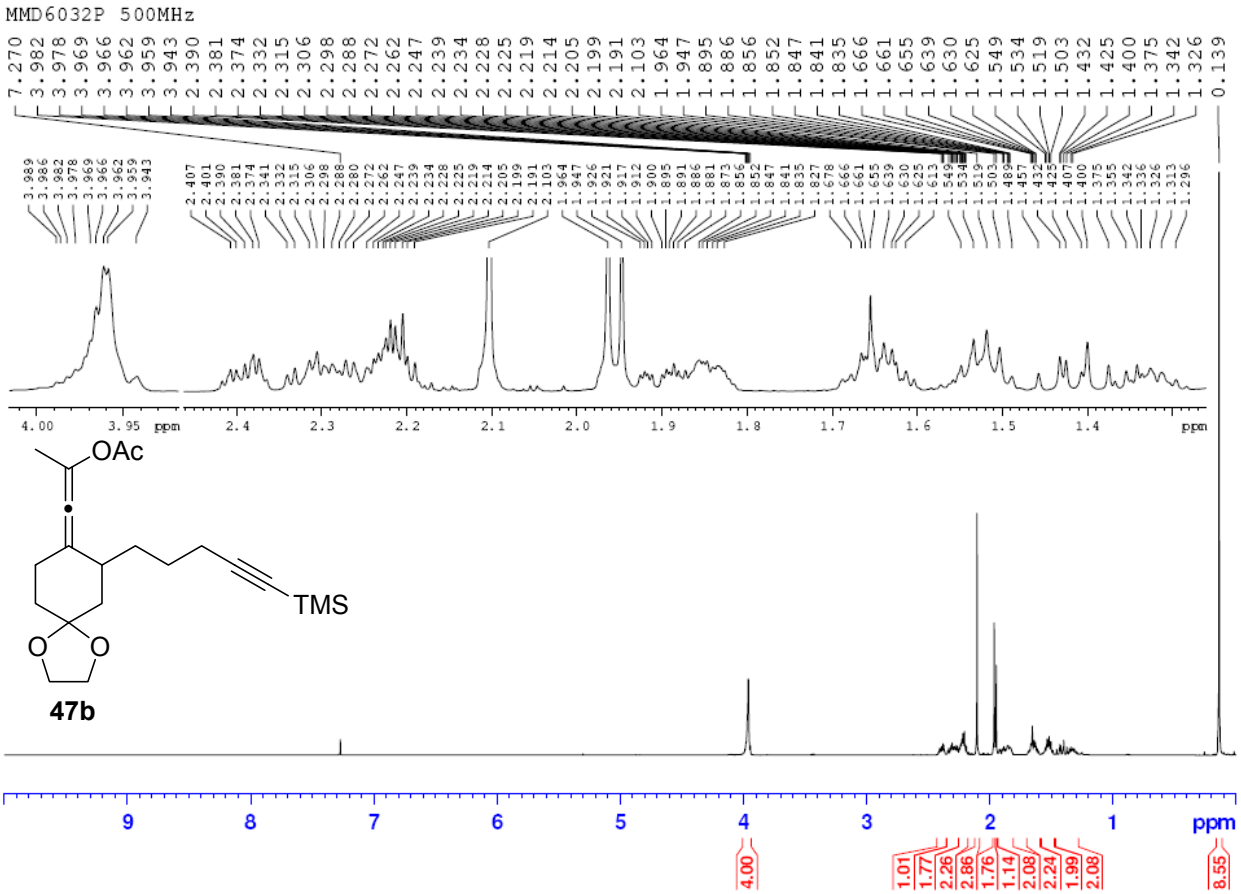

MMD6021P
300
189.40
168.77
115.67
109.70
107.22
84.60
77.43
77.00
76.58
34.56
27.95
26.25
20.92
20.43
19.63
0.13
OAc
TMS
45f
ppm


MMD6014P
300
7.305
7.298
7.292
7.285
7.278
7.271
2.240
2.217
2.193
2.133
2.115
2.107
2.089
2.084
2.066
2.045
2.040
2.017
1.994
1.829
1.822
1.600
1.576
1.553
1.529
1.506
1.495
1.480
1.473
1.453
1.439
1.425
1.420
1.404
0.145
7.30 ppm
2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 ppm
ppm
9 8 7 6 5 4 3 2 1 ppm
0.92
2.12
3.02
2.08
3.00
6.68
8.87

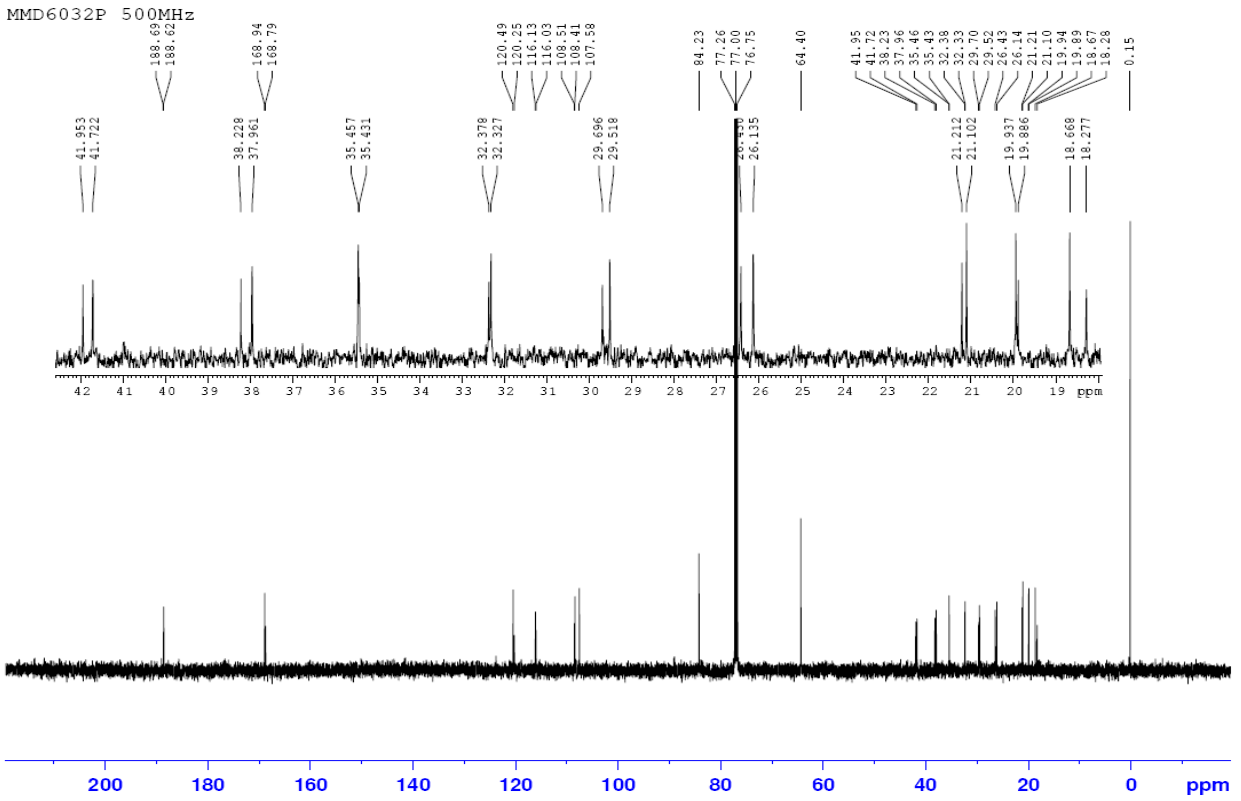

MMD6014P
300
189.32
168.79
115.93
109.66
107.45
84.40
77.43
77.00
76.58
34.94
28.39
28.26
26.65
20.93
20.49
19.78
0.15
34.942
28.392
28.264
26.646
20.930
20.493
19.780
35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 ppm
OAc
TMS
45g
200 180 160 140 120 100 80 60 40 20 0 ppm


MMD3156F1
301B
OAc
TMS
O
O
47a
ppm
0.41
0.32
4.00
3.41
2.15
2.81
2.14
6.95
8.46

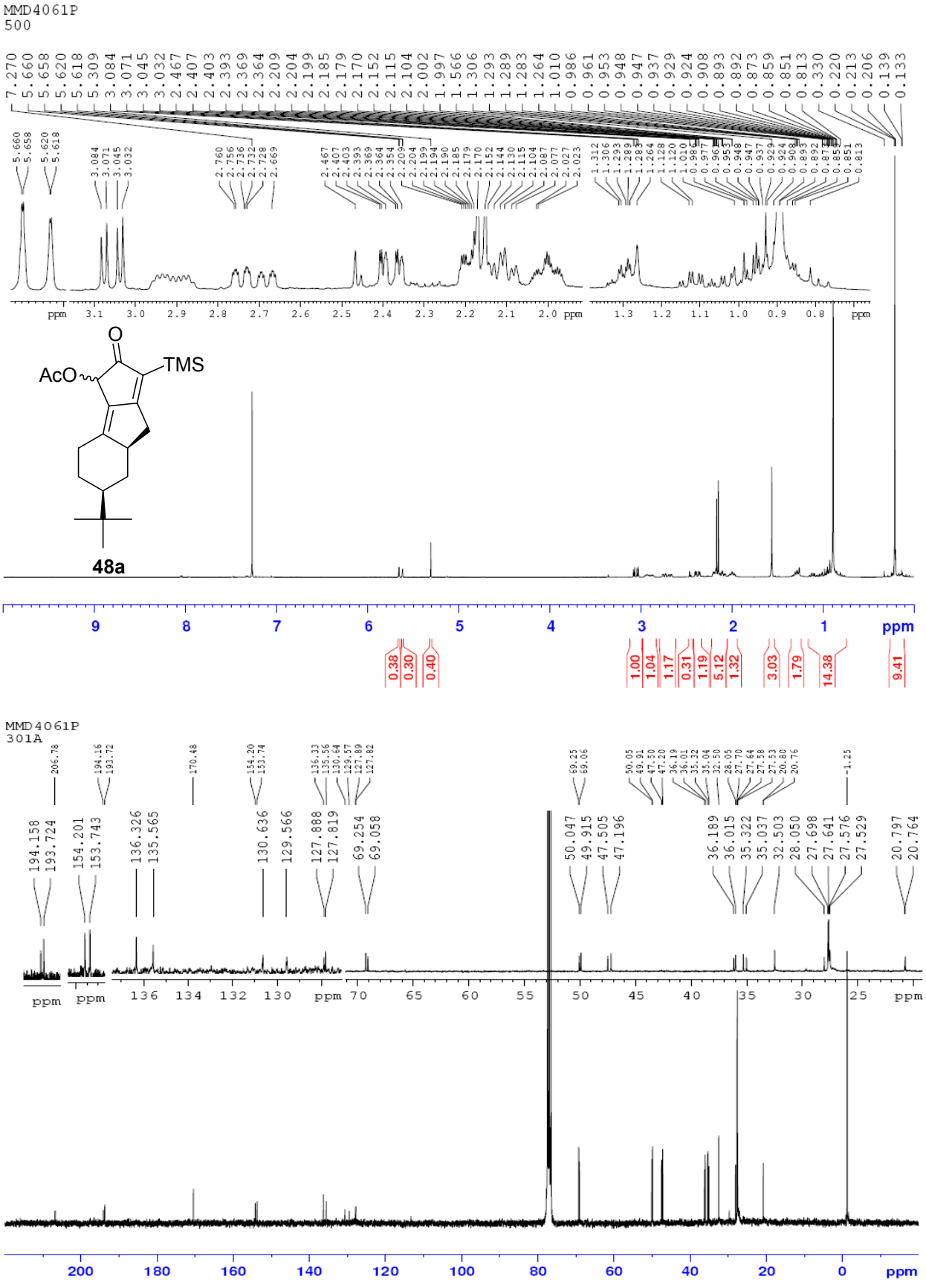

MMD3156F1
301B
ppm

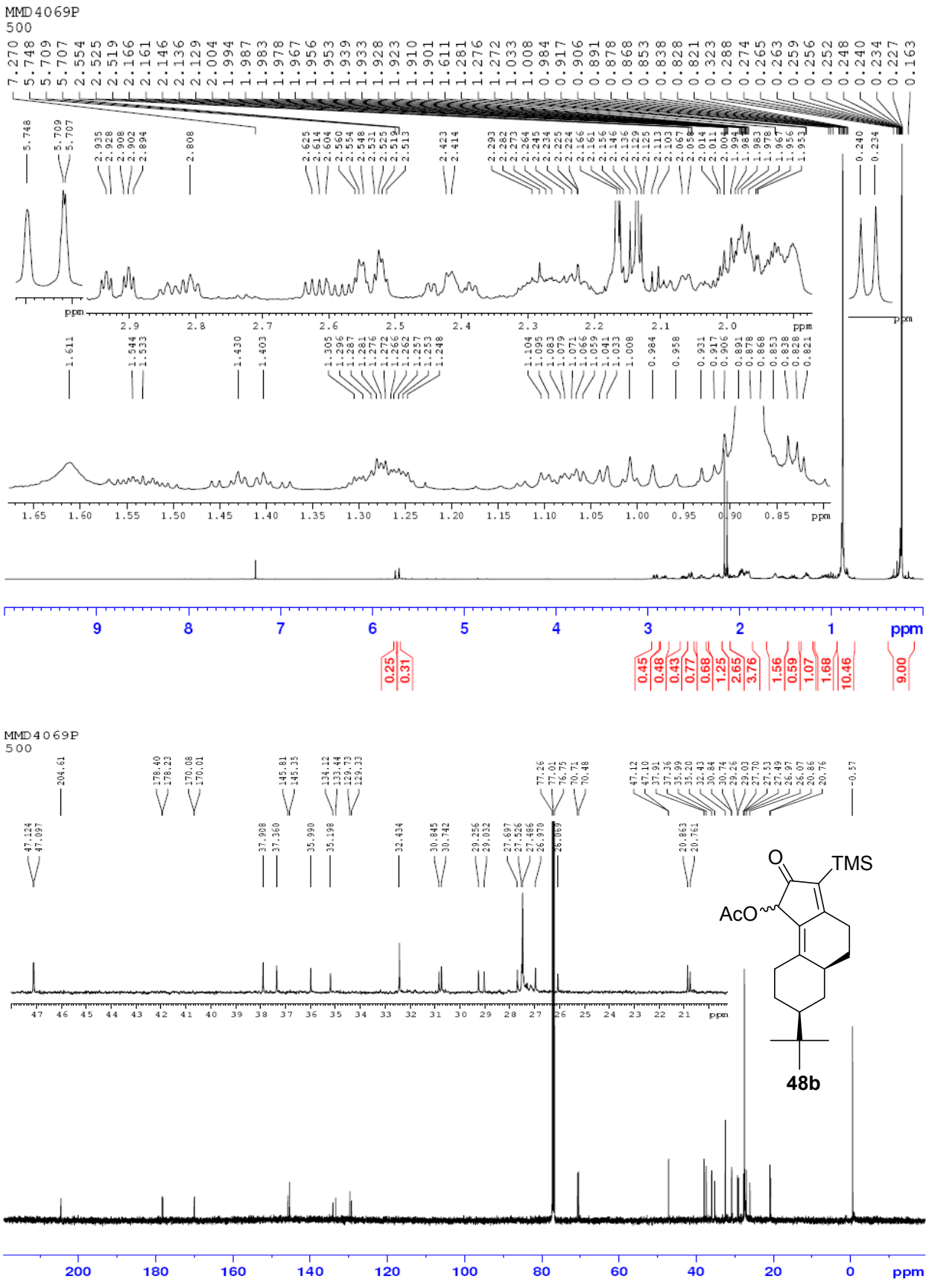

MMD6032P 500MHz
OAc
TMS
O
O
47b
ppm

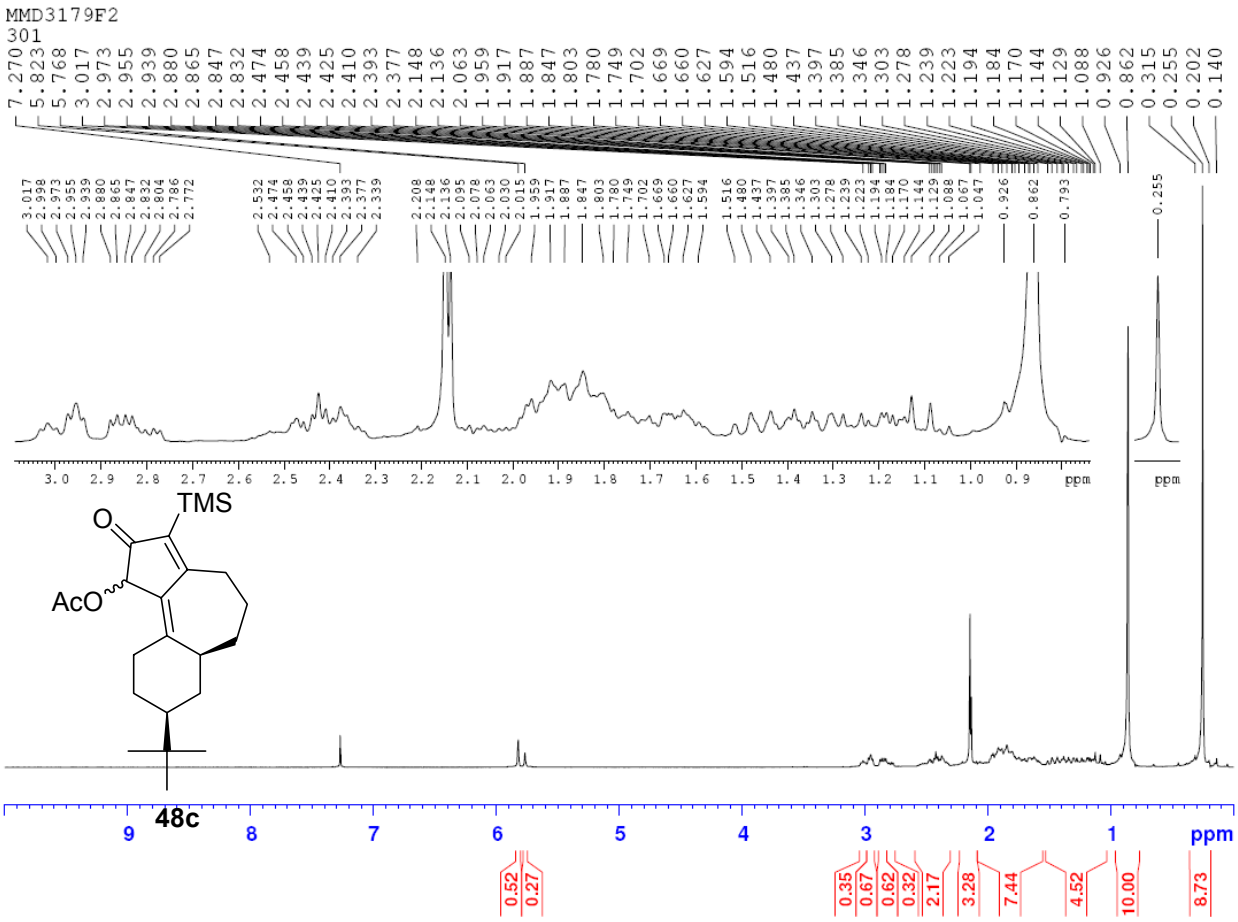
9
8
7
6
5
4
3
2
1
ppm
4.00
1.01
1.77
2.26
2.86
1.76
1.14
2.08
2.24
1.99
2.08
8.55

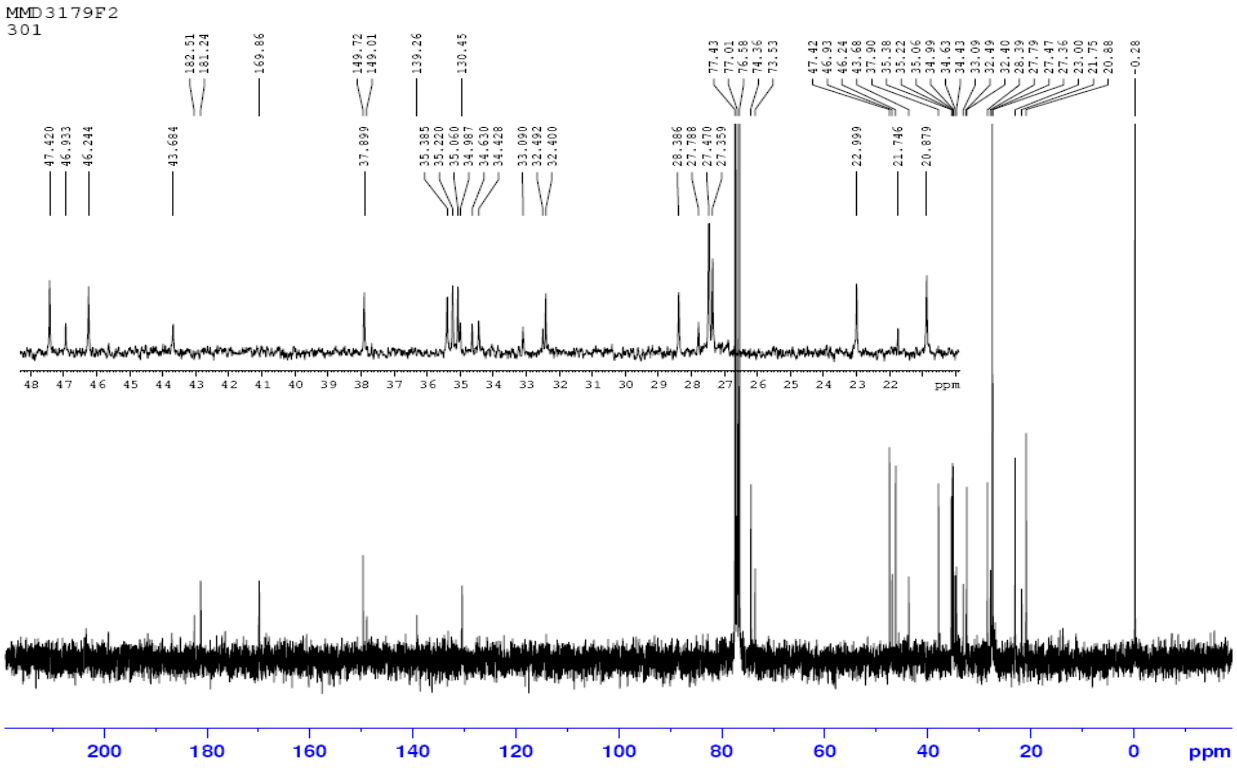

MMD6032P 500MHz
ppm

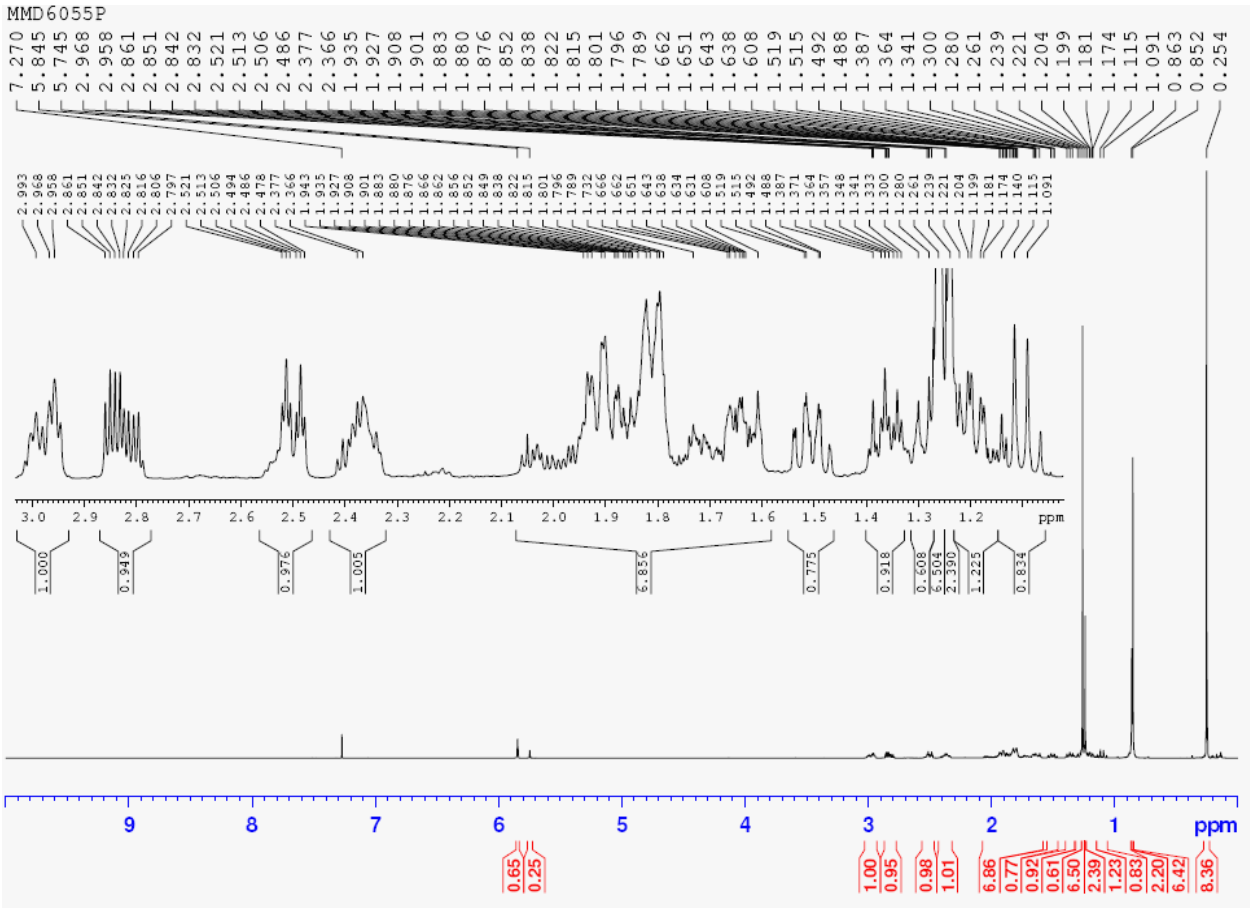
200
180
160
140
120
100
80
60
40
20
0
ppm

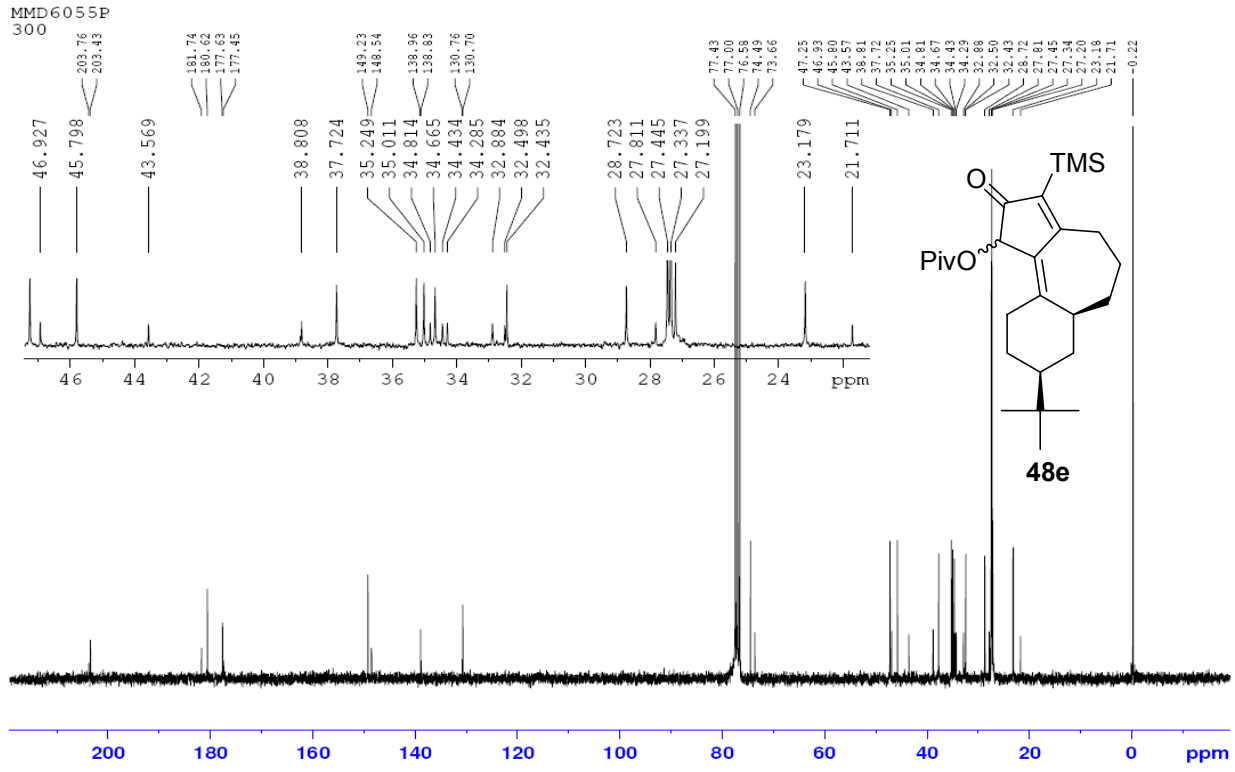

MMD4061P
500
AcO
TMS
O
48a
MMD4061P
301A

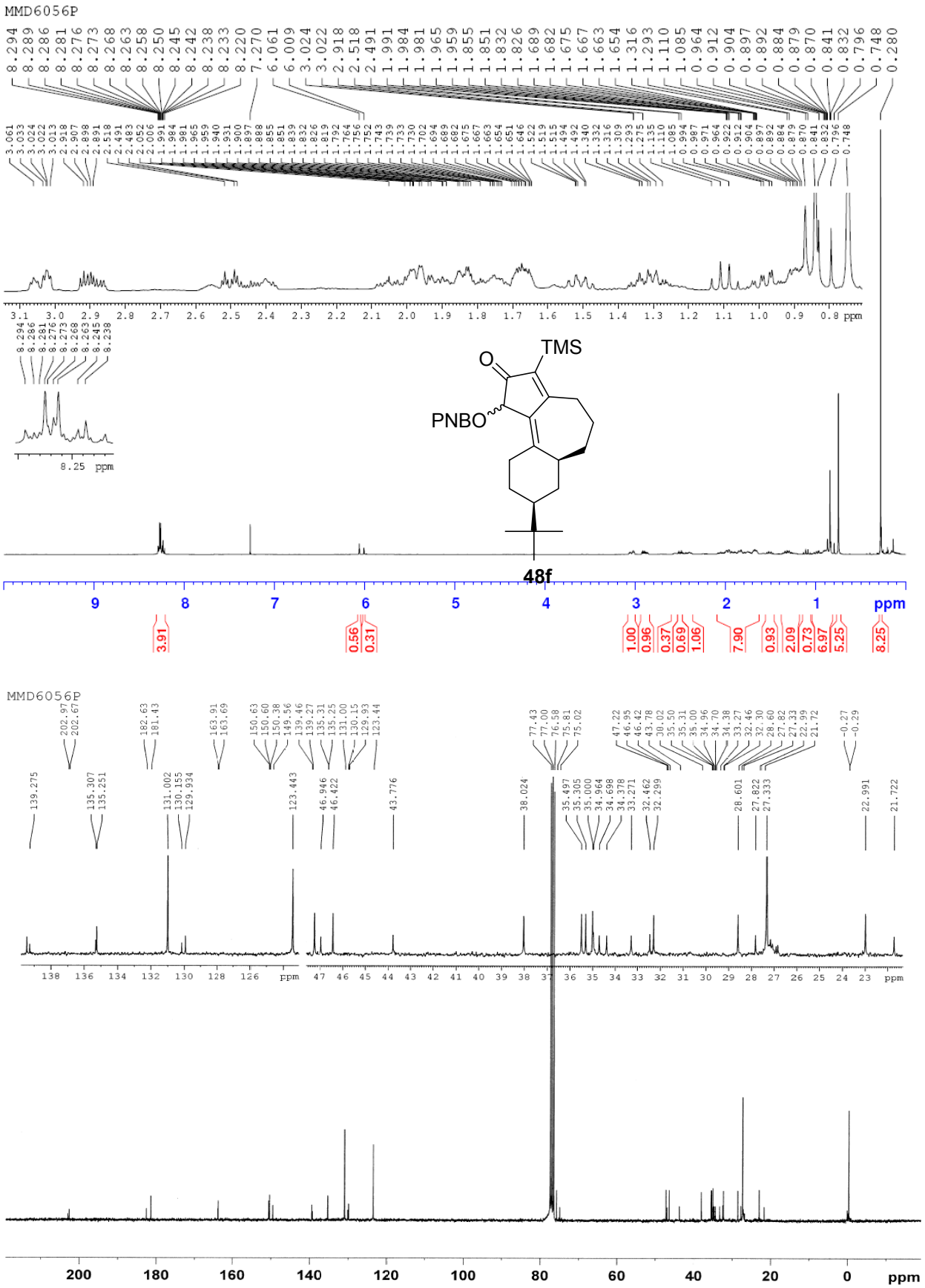

MMD4069P
500
MMD4069P
500
TMS
AcO
O
48b

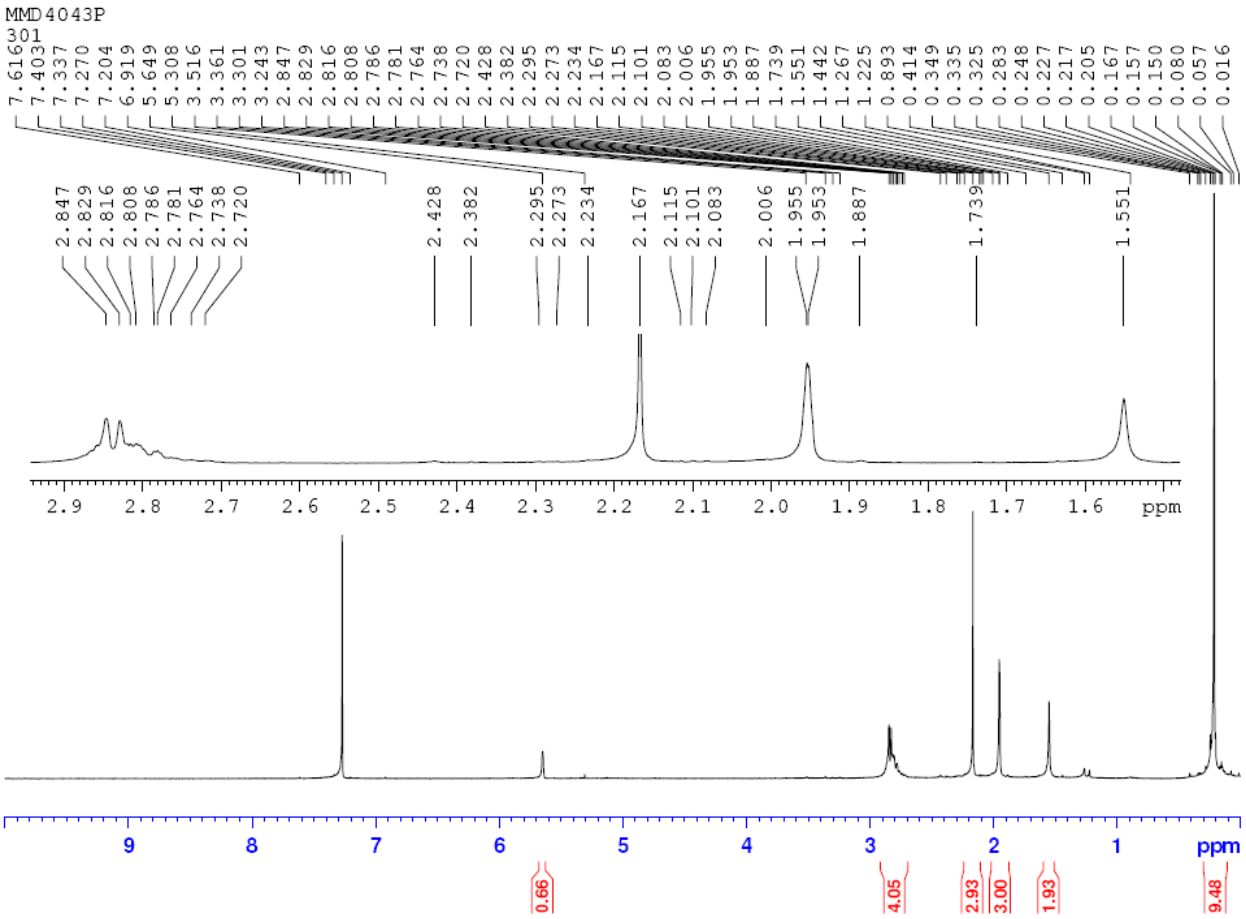

MMD3179F2
301
TMS
O
AcO
48c
ppm

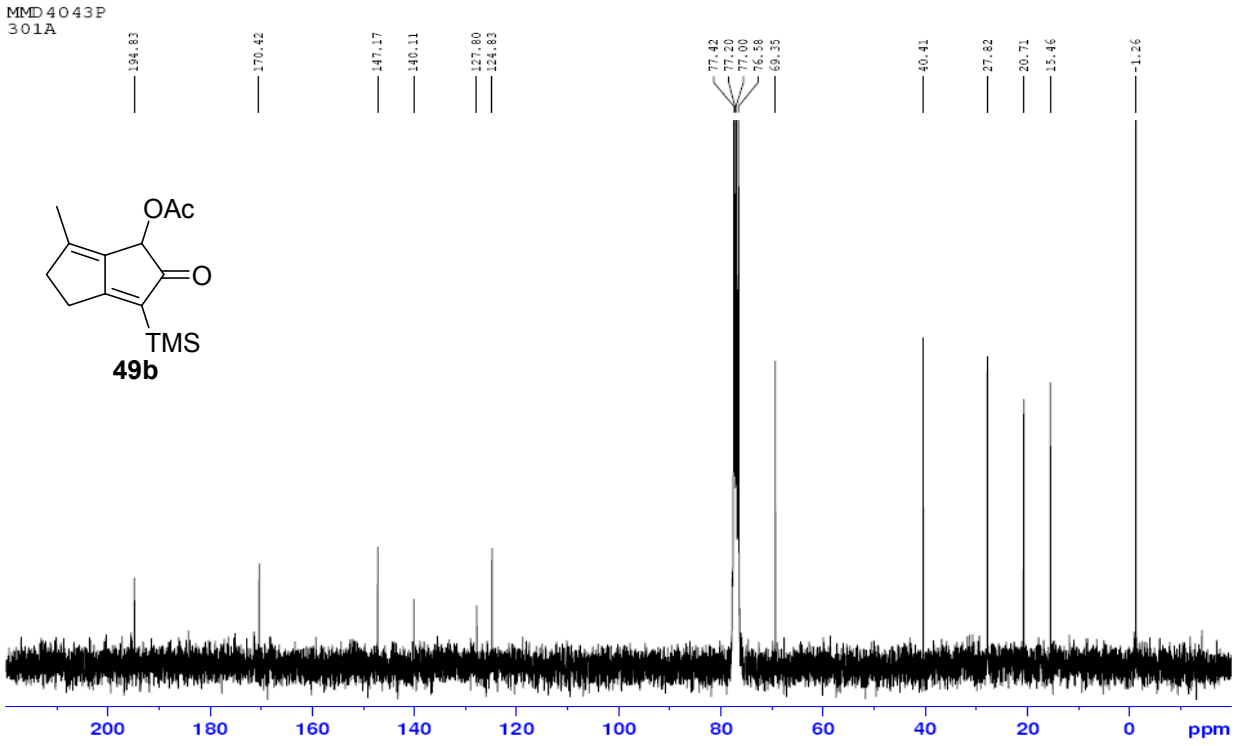

MMD3179F2
301
ppm

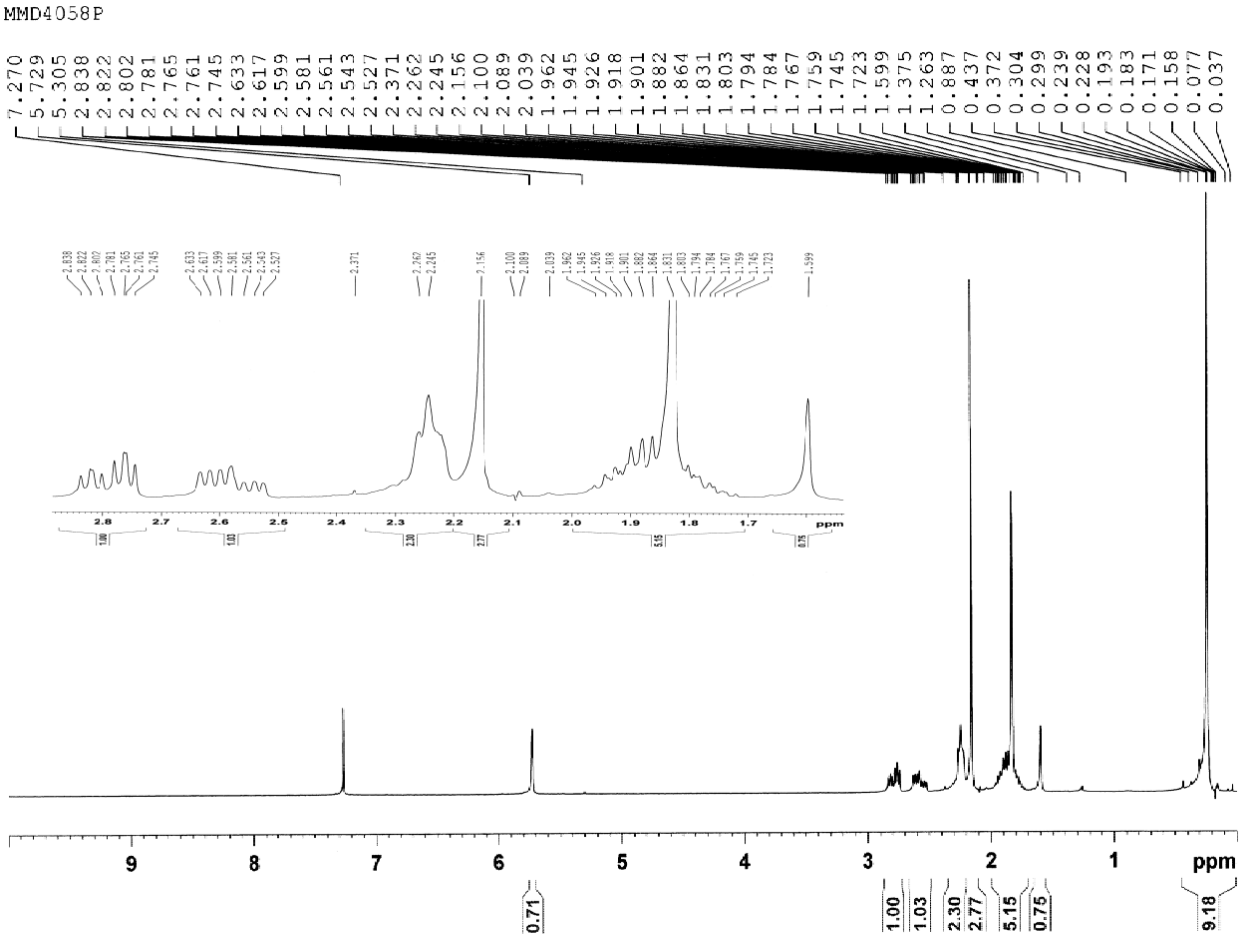

MMD6055P
ppm

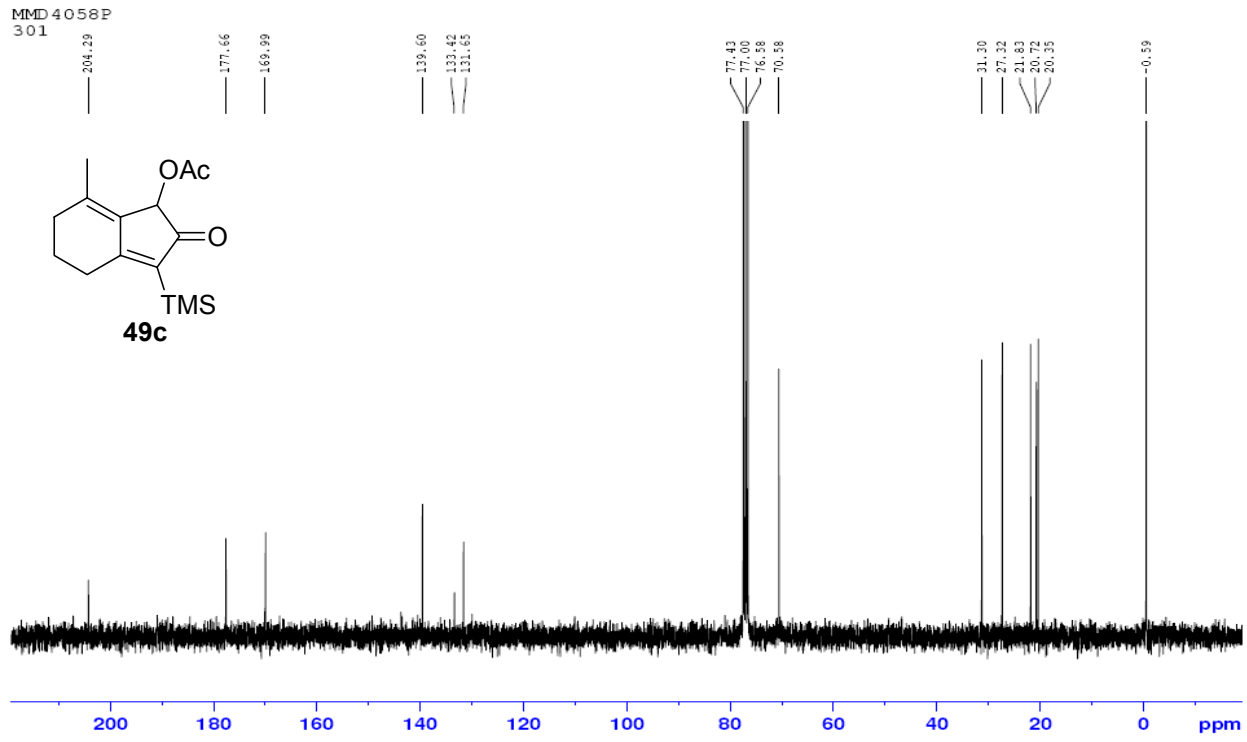

MMD6055P
300
TMS
O
PivO
48e
ppm

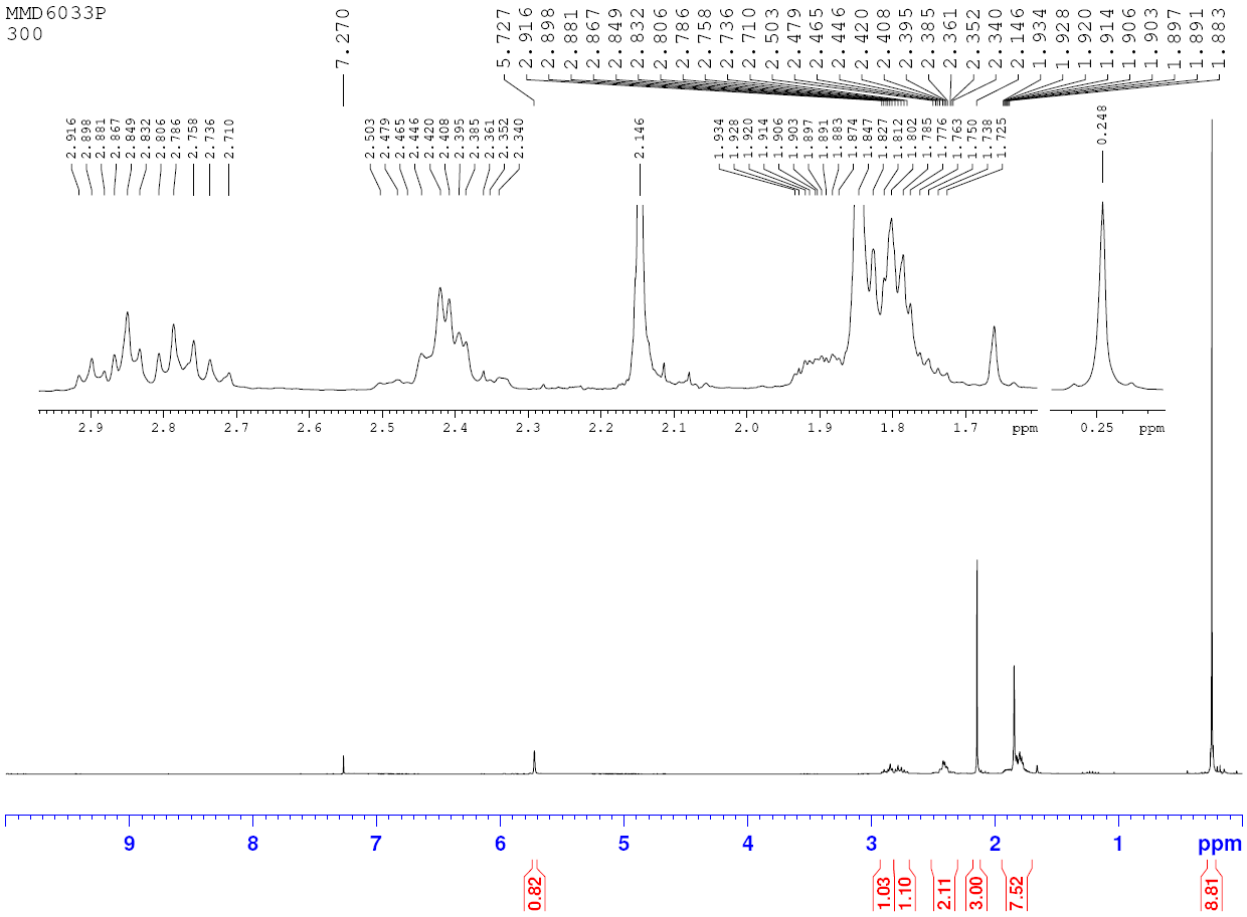

MMD6056P
TMS
O
PNBO
48f
ppm
MMD6056P
ppm

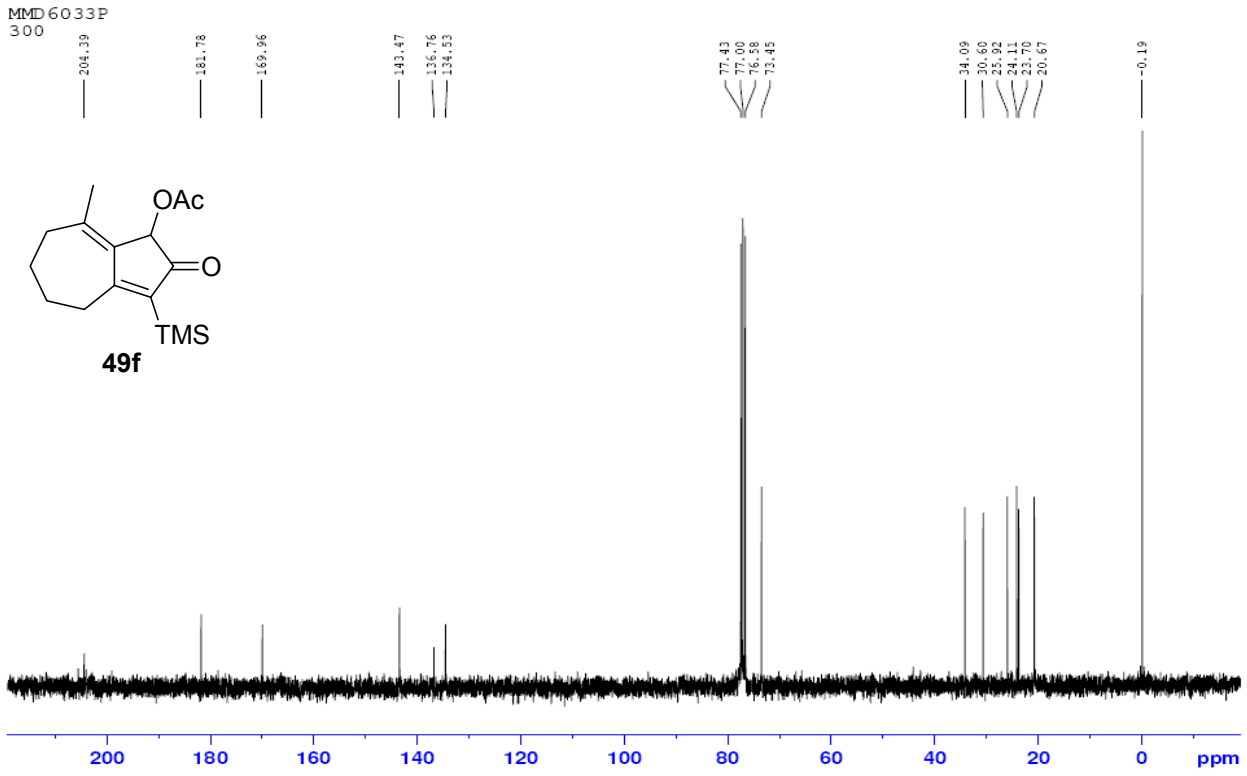

MMD4043P
301
ppm
0.66
4.05
2.93
3.00
1.93
9.48

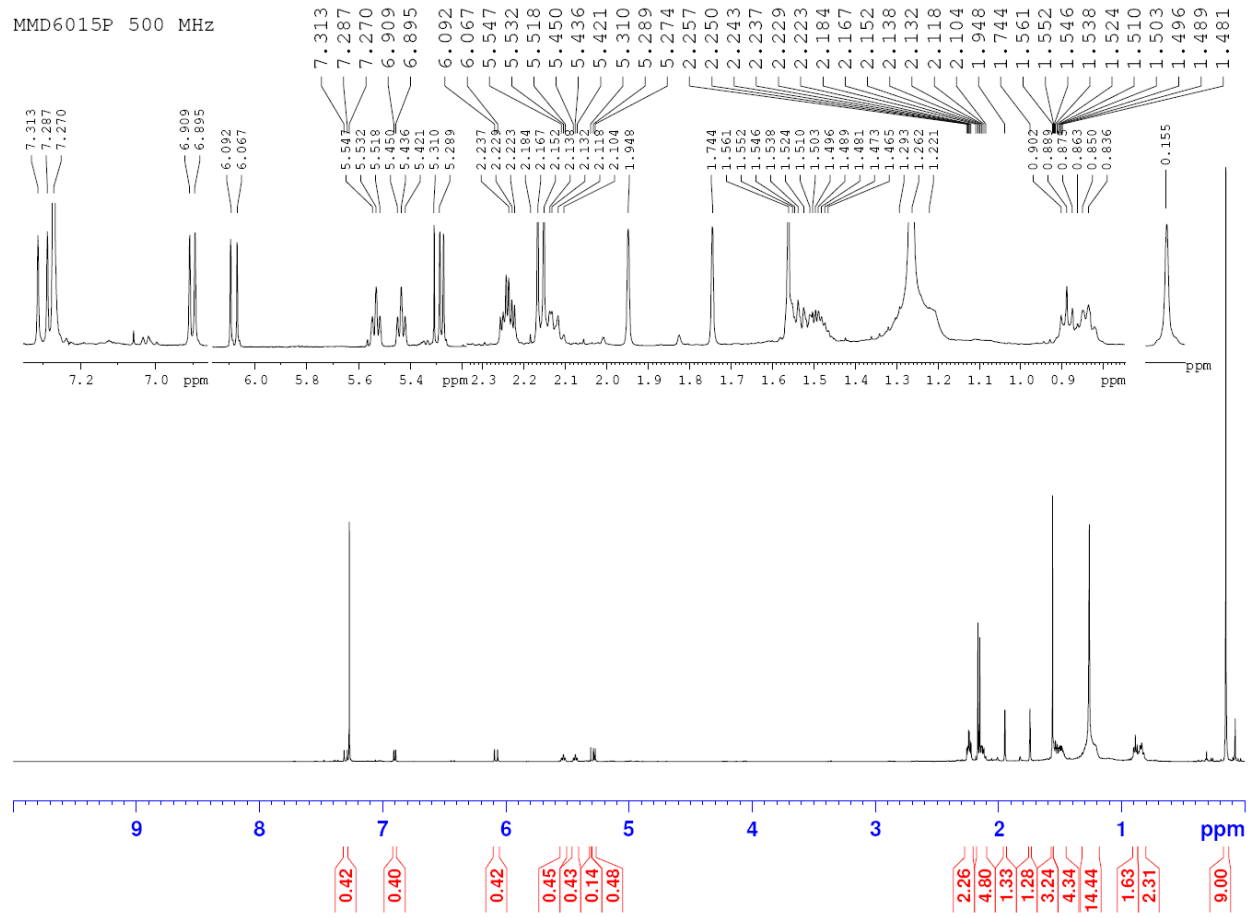

MMD4043P
301A
OAc
O
TMS
49b
ppm

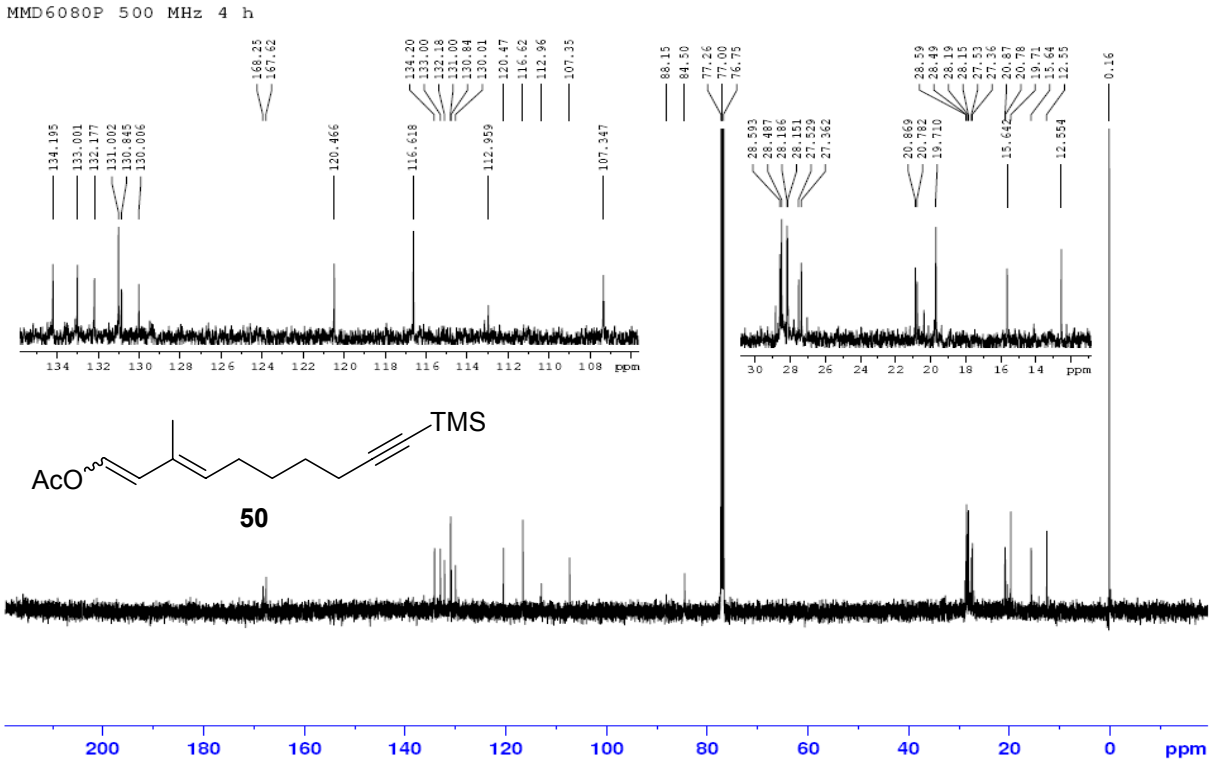

MMD4058P
7.270
5.729
5.305
2.838
2.822
2.802
2.781
2.765
2.761
2.745
2.633
2.617
2.599
2.581
2.561
2.543
2.527
2.371
2.262
2.245
2.156
2.100
2.089
2.039
1.962
1.945
1.926
1.918
1.901
1.882
1.864
1.831
1.803
1.794
1.784
1.767
1.759
1.745
1.723
1.599
1.375
1.263
0.887
0.437
0.372
0.304
0.299
0.239
0.228
0.193
0.183
0.171
0.158
0.077
0.037
ppm
0.71
1.00
1.03
2.30
2.77
5.15
0.75
9.18


MMD4058P
301
204.29
177.66
169.99
139.60
133.42
131.65
77.43
77.00
76.58
70.58
31.30
27.32
21.83
20.72
20.35
-0.59
OAc
O
TMS
49c
ppm


MMD6033P
300
ppm


MMD6033P
300
OAc
O
TMS
49f
ppm


MMD6015P 500 MHz
7.313
7.287
7.270
6.909
6.895
6.092
6.067
5.547
5.532
5.518
5.450
5.436
5.421
5.310
5.289
2.237
2.223
2.184
2.167
2.152
2.138
2.132
2.118
2.104
1.948
1.744
1.561
1.552
1.546
1.538
1.524
1.510
1.503
1.496
1.489
1.481
1.465
1.293
1.262
1.221
0.902
0.889
0.875
0.863
0.850
0.836
0.155
ppm
9
8
7
6
5
4
3
2
1
ppm
0.42
0.40
0.42
0.45
0.43
0.14
0.48
2.26
4.80
1.33
1.28
3.24
4.34
14.44
1.63
2.31
9.00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107.35
88.15
84.50
77.26
77.00
76.75
28.59
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28.19
28.15
27.53
27.36
20.87
20.78
19.71
15.64
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131.002
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112.959
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19.710
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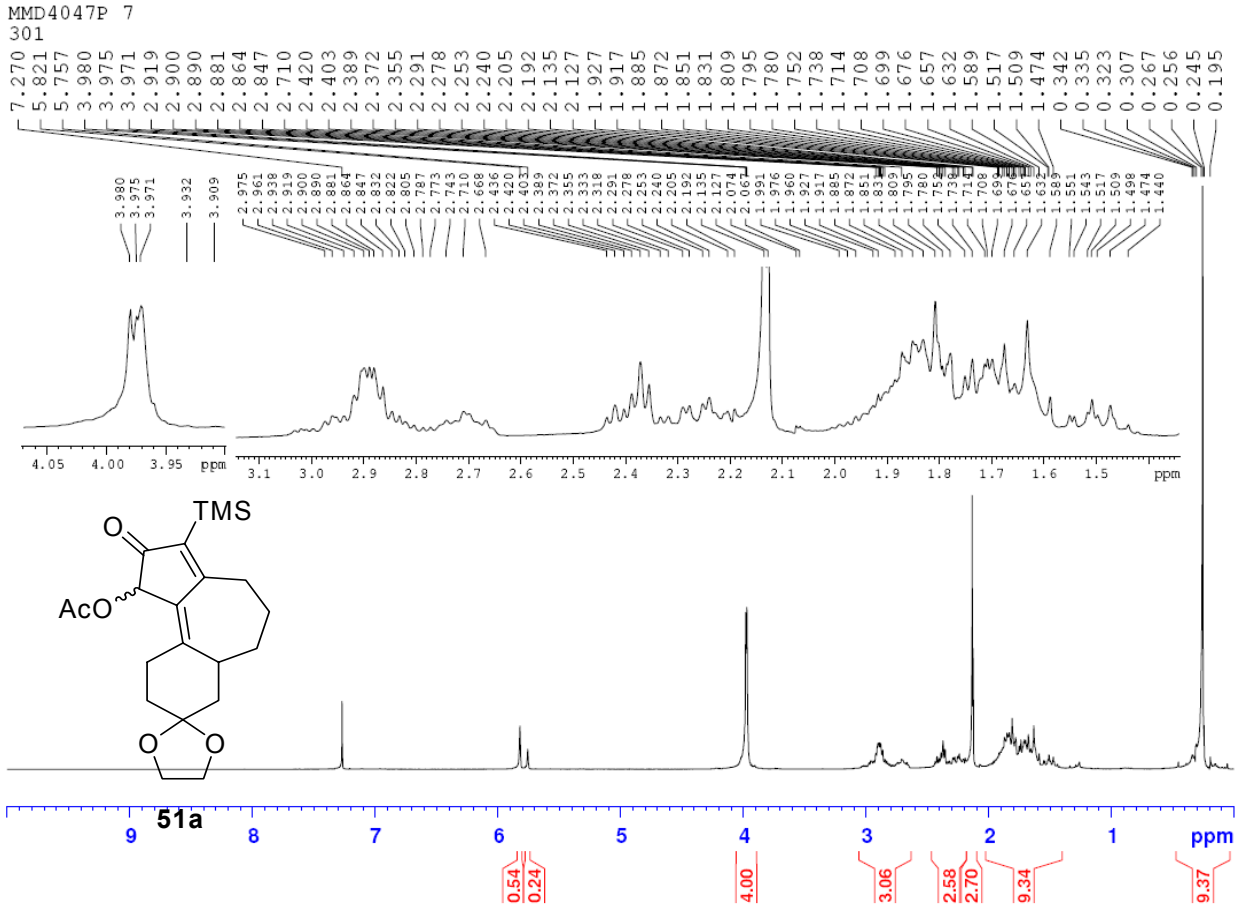
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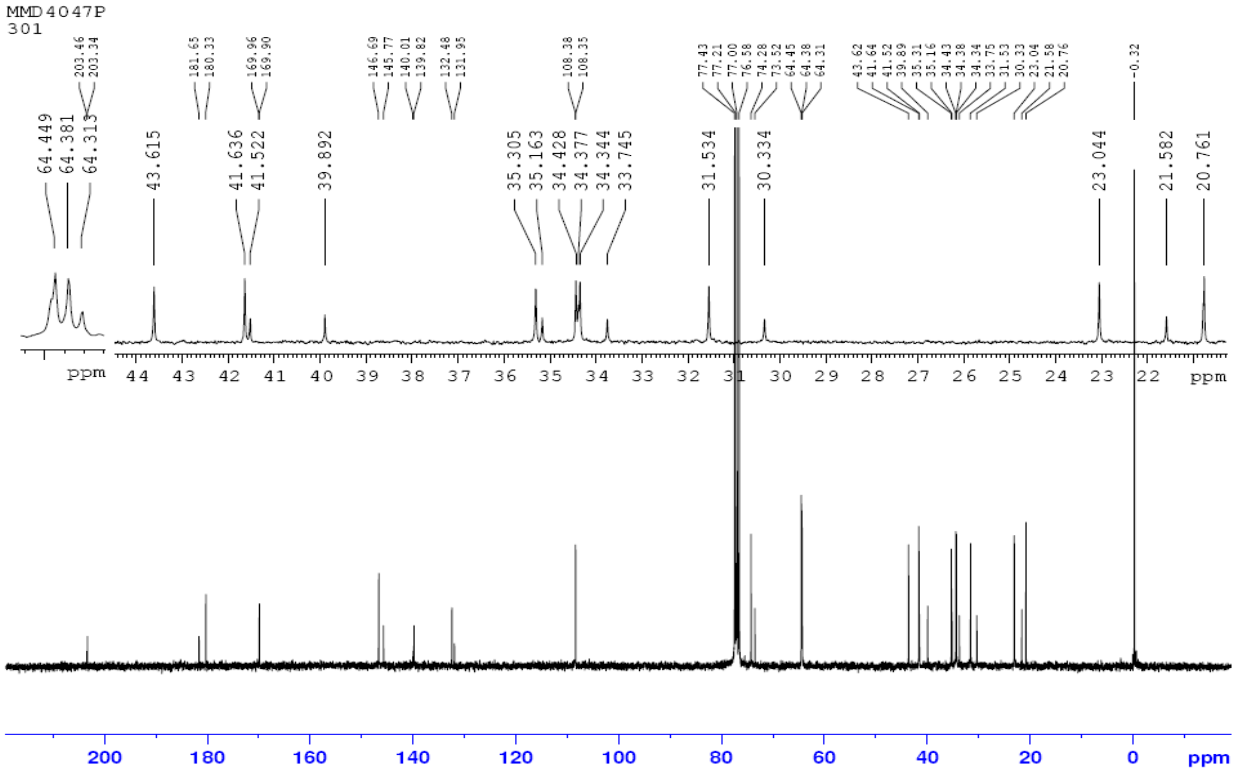
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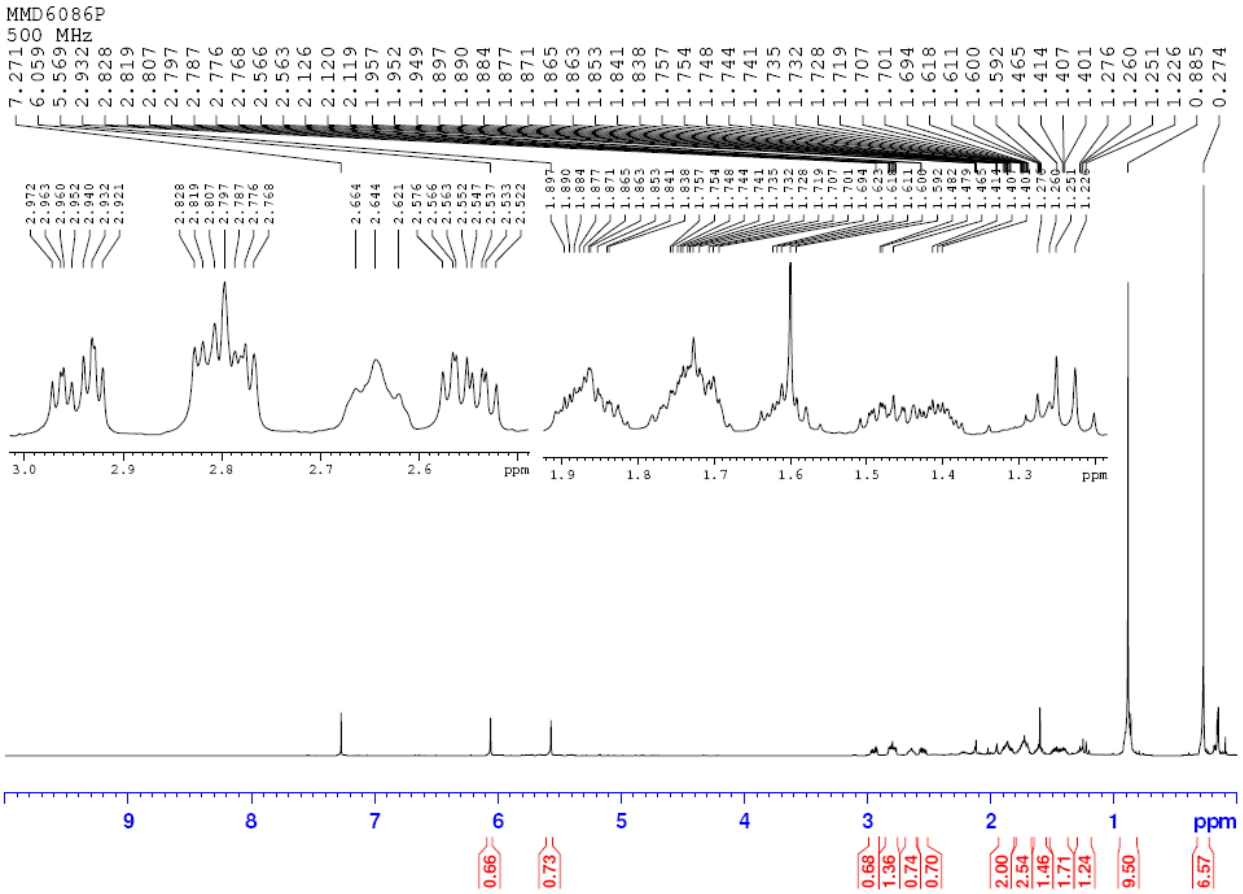
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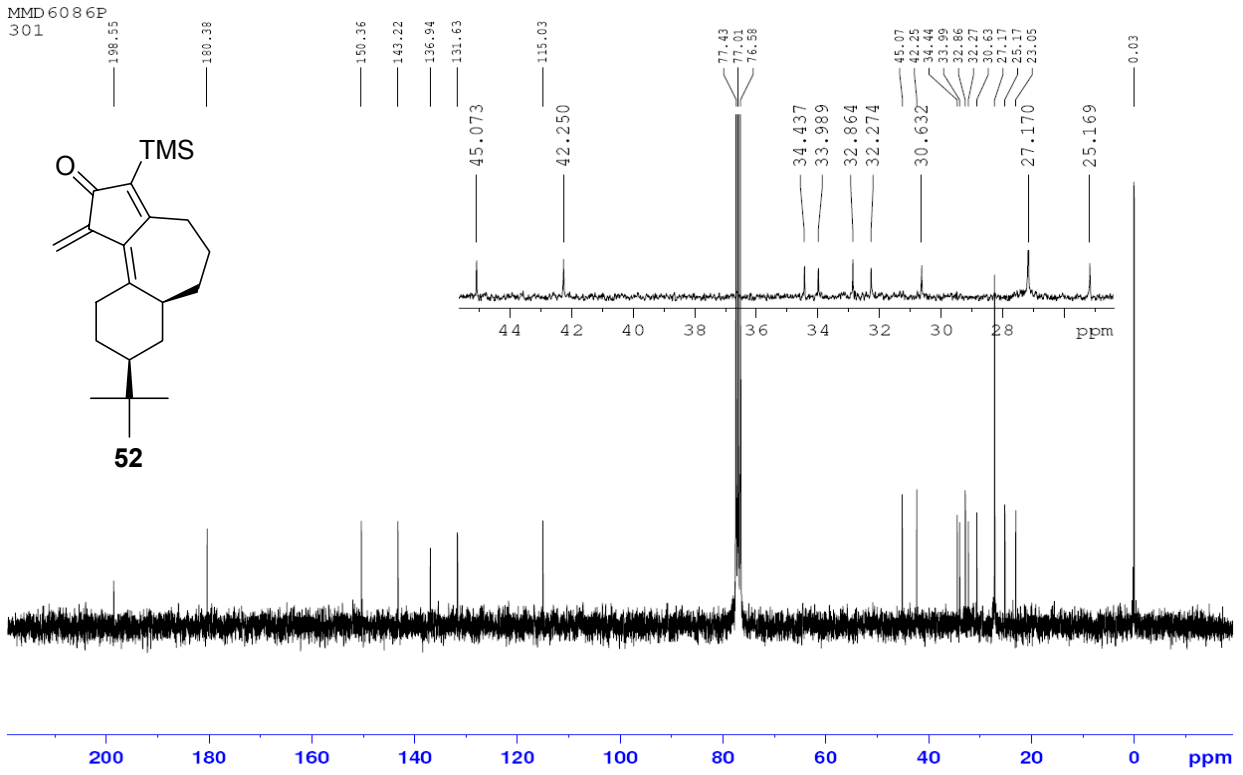
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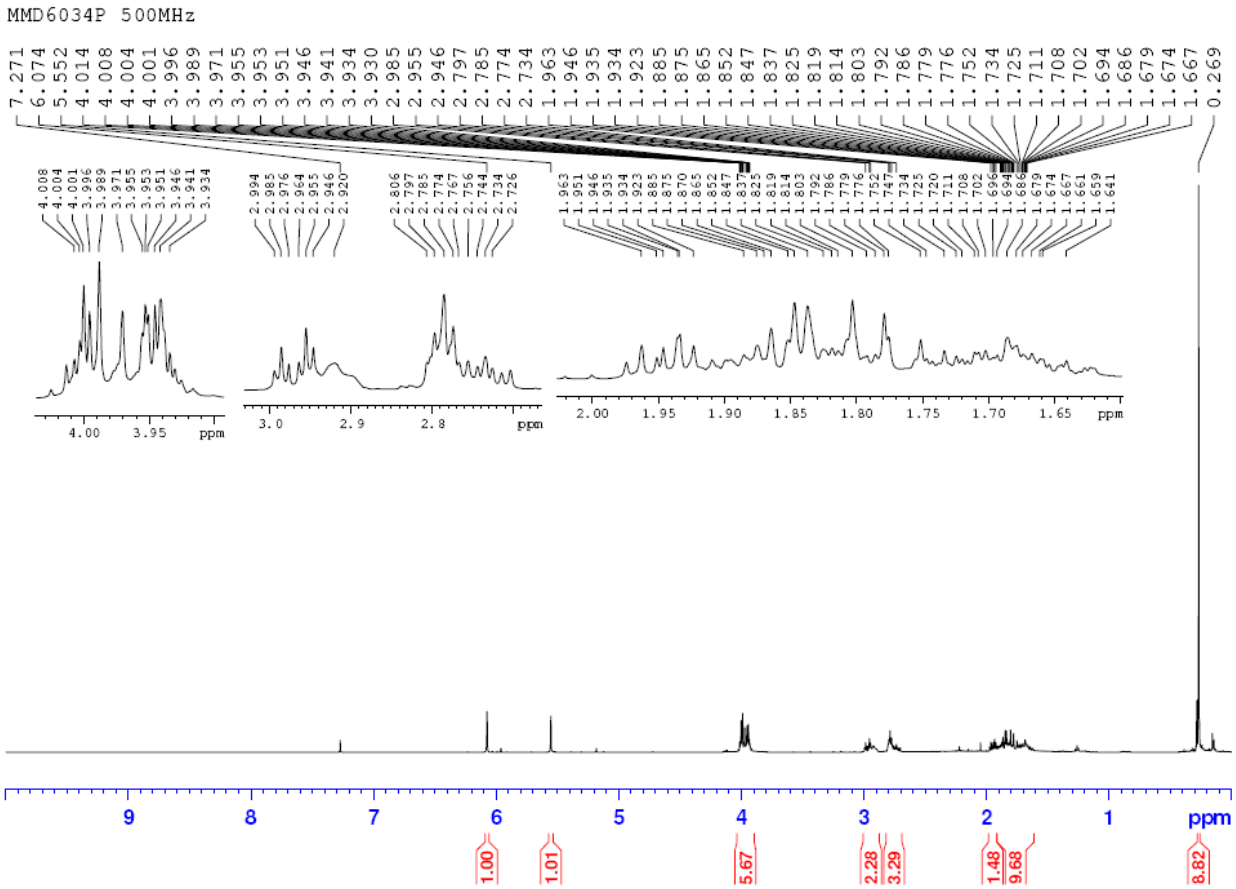

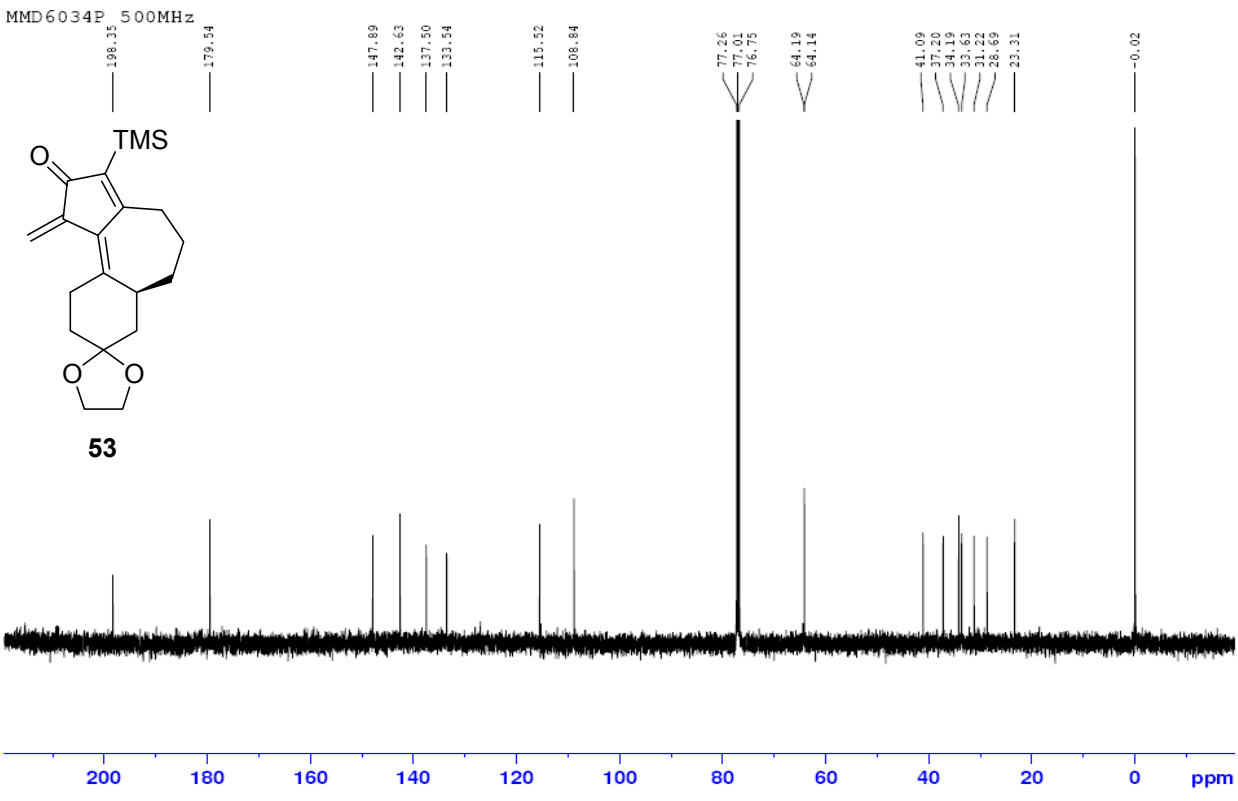

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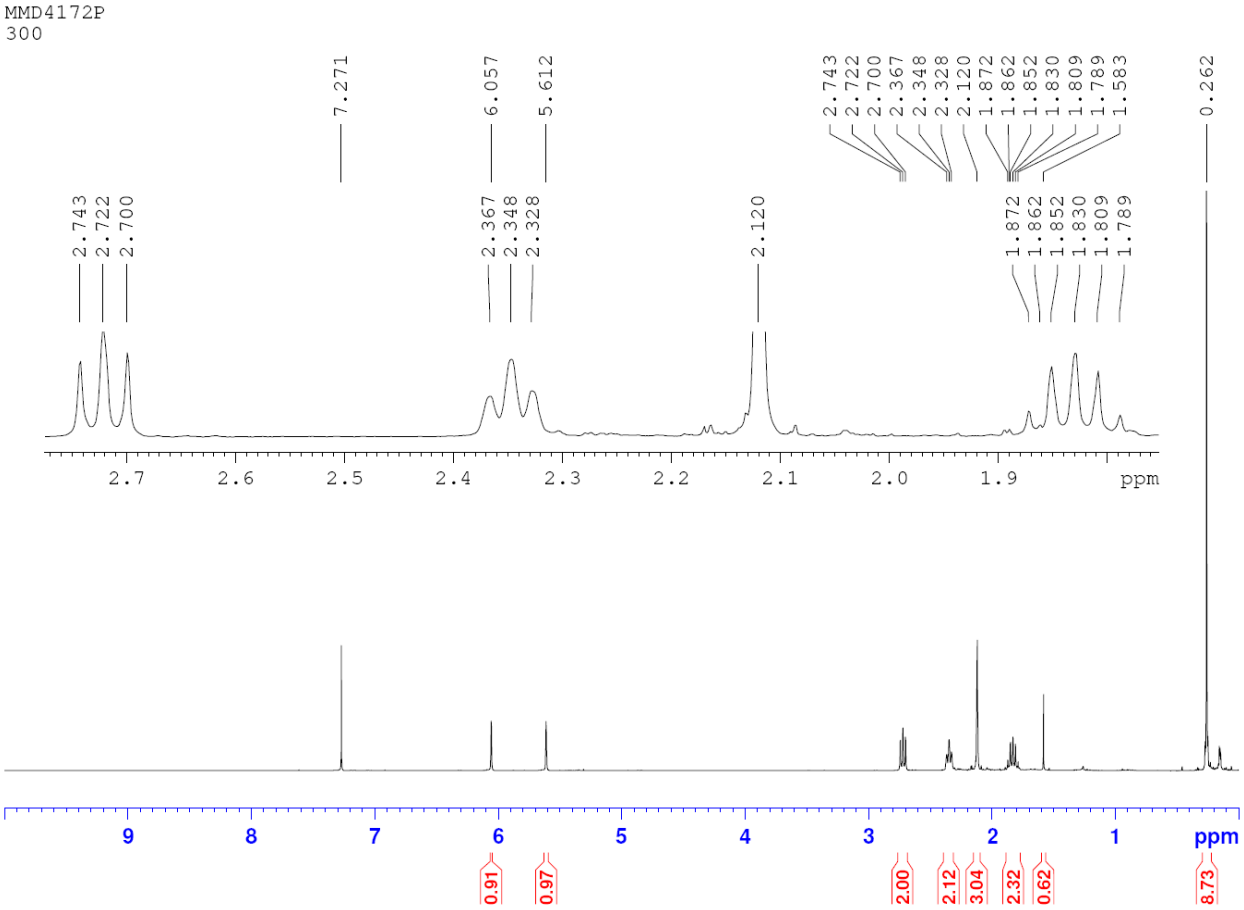
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1.862
1.852
1.830
1.809
1.789
1.583
0.262
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
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ppm
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7
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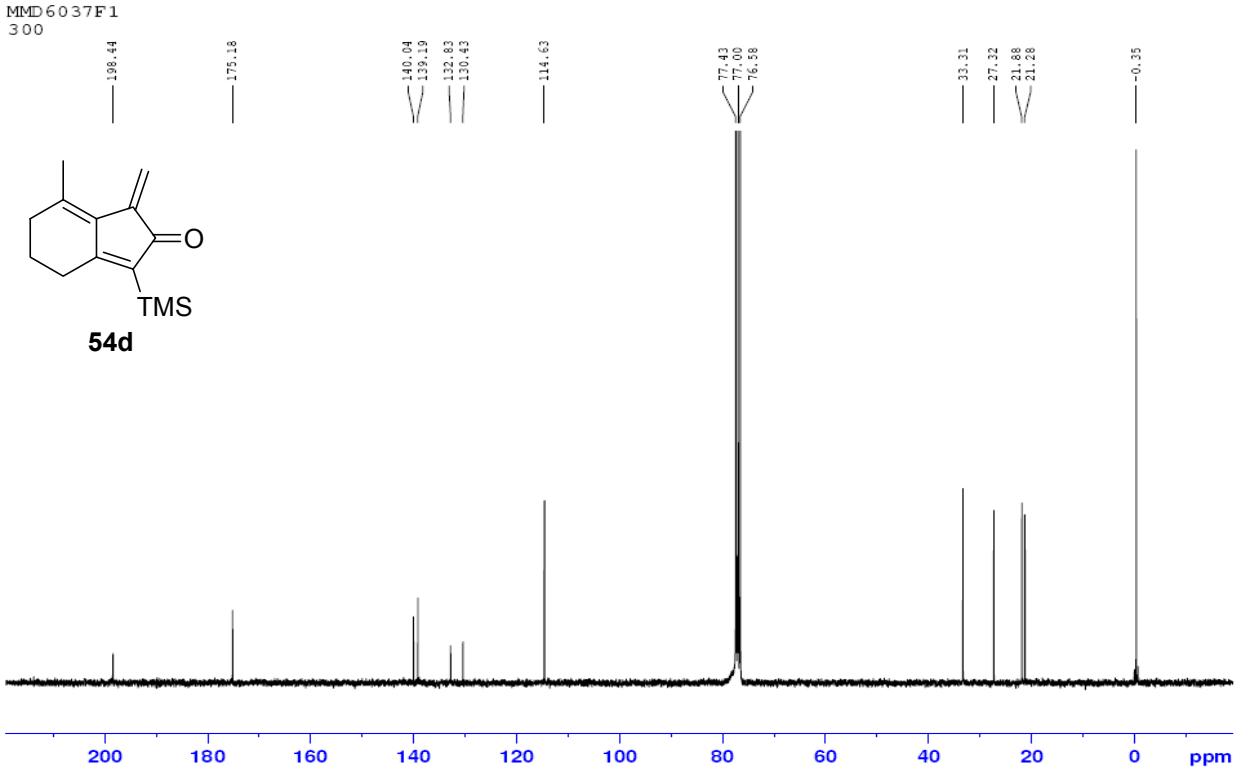
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O
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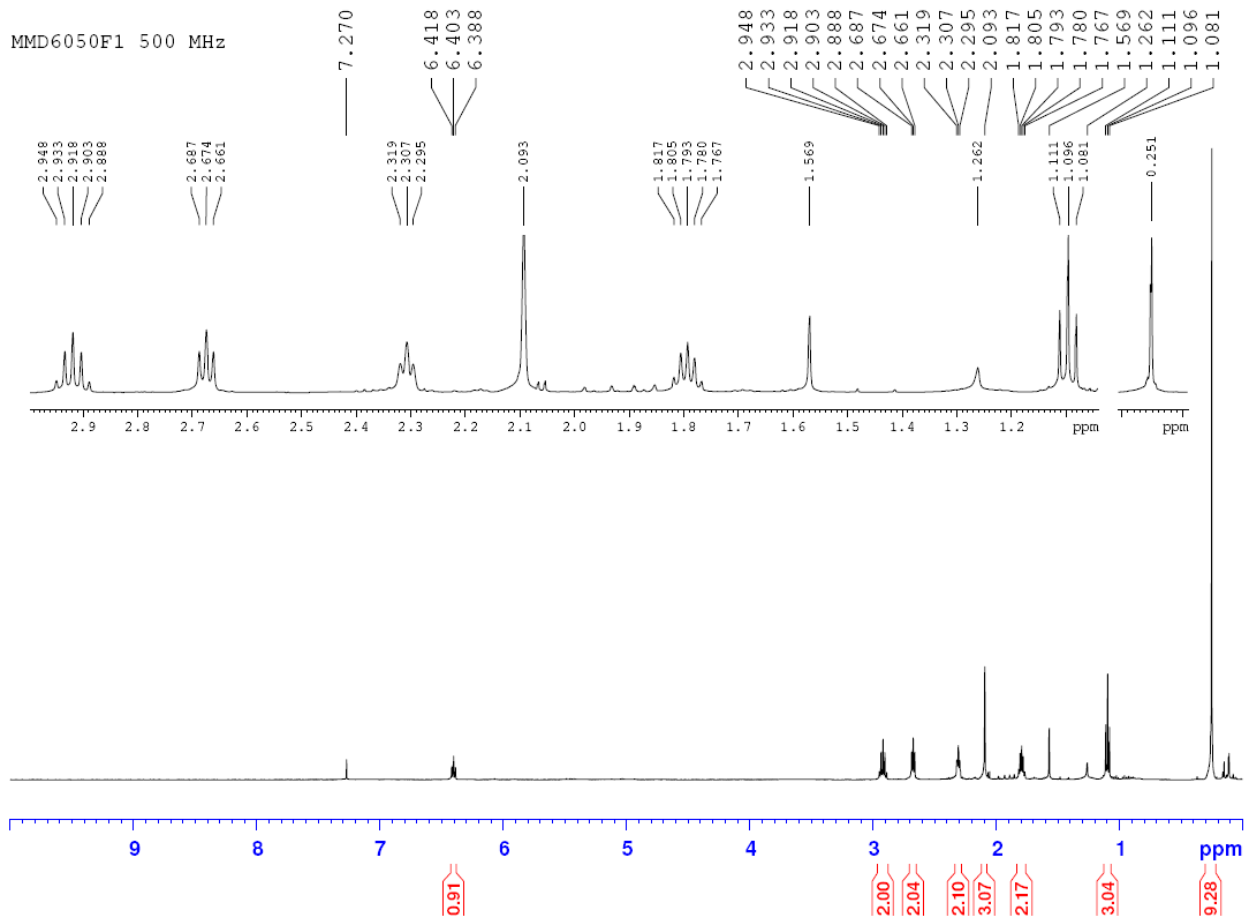
20
0
ppm

54d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2.661
2.319
2.307
2.295
2.093
1.817
1.805
1.793
1.780
1.767
1.569
1.262
1.111
1.096
1.081
0.251
ppm
9
8
7
6
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4
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2
1
ppm
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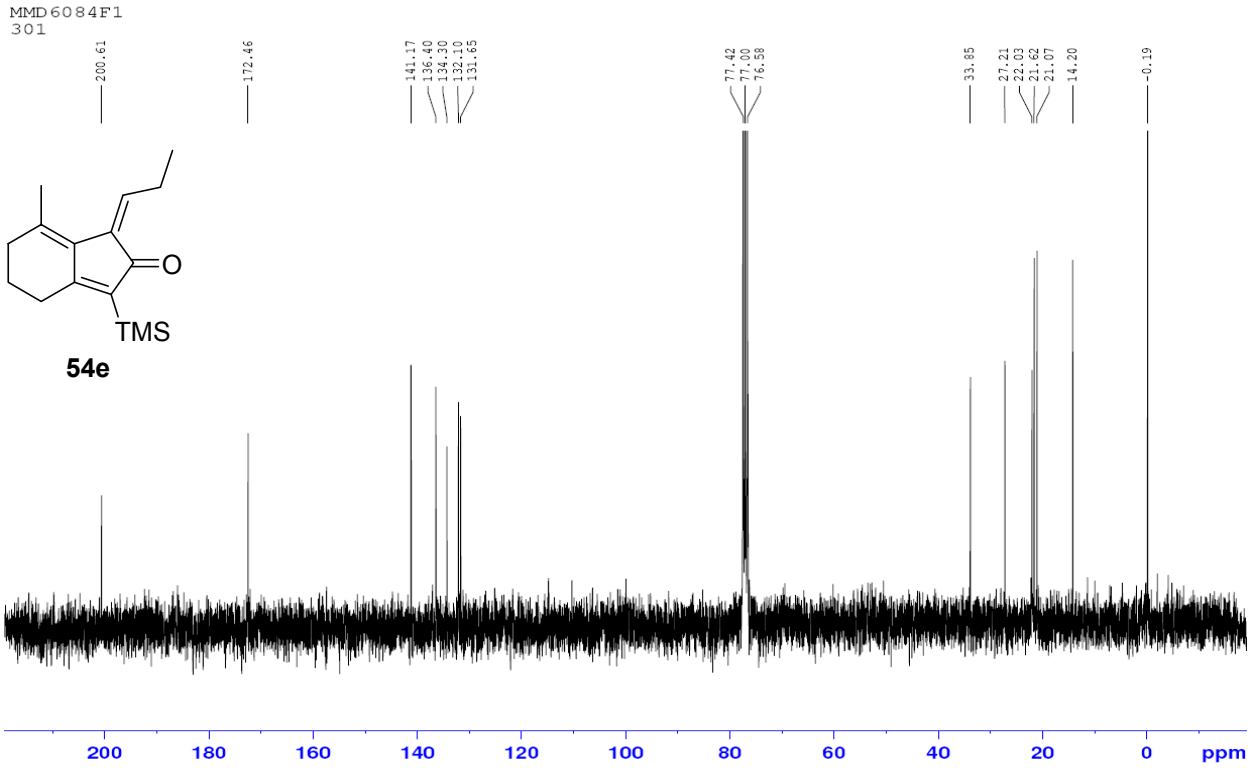
3.04
9.28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132.10
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77.42
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76.58
33.85
27.21
22.03
21.62
21.07
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O
TMS
200
180
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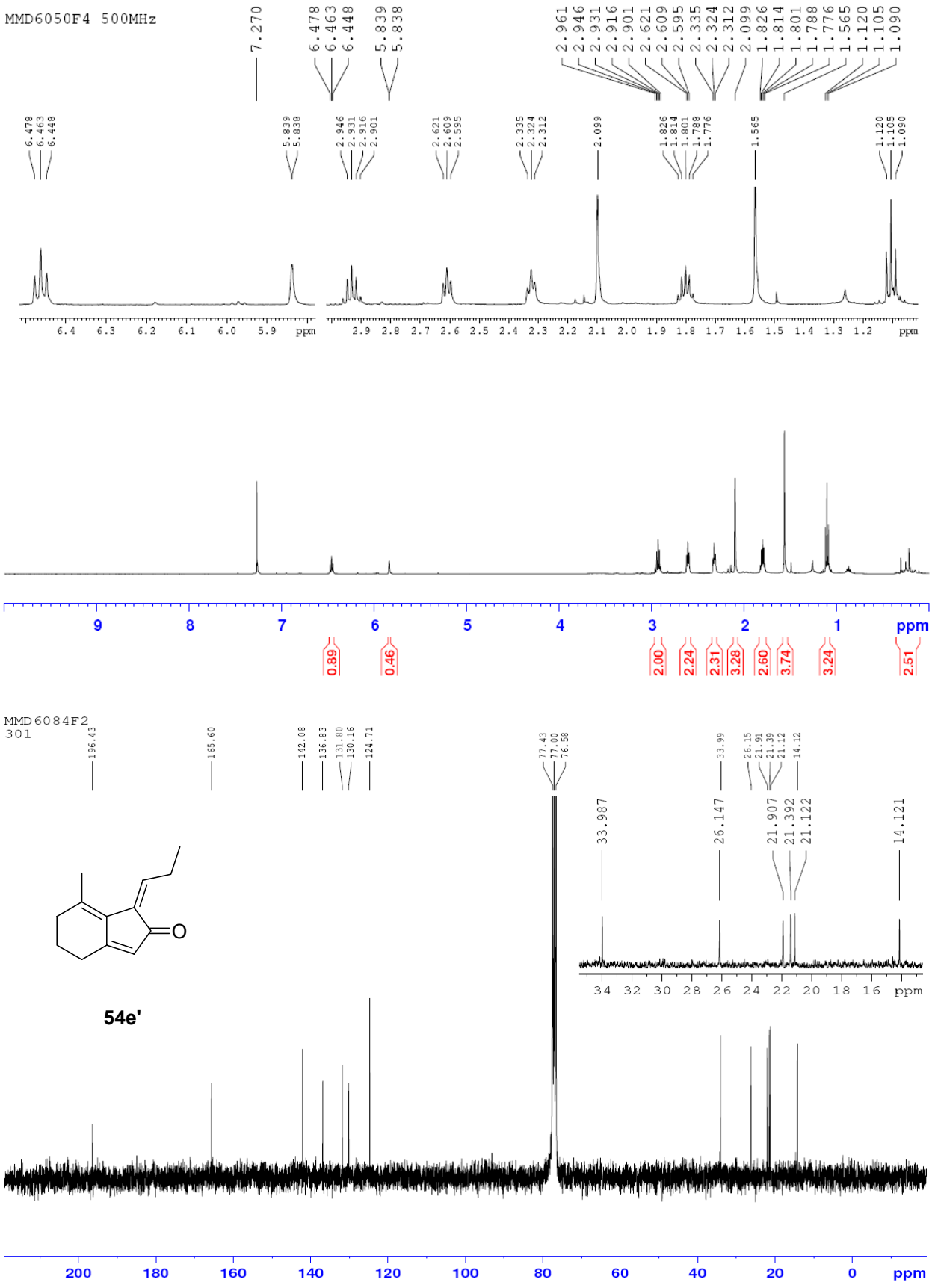
140
120
100
80
60
40
20
0
ppm

54e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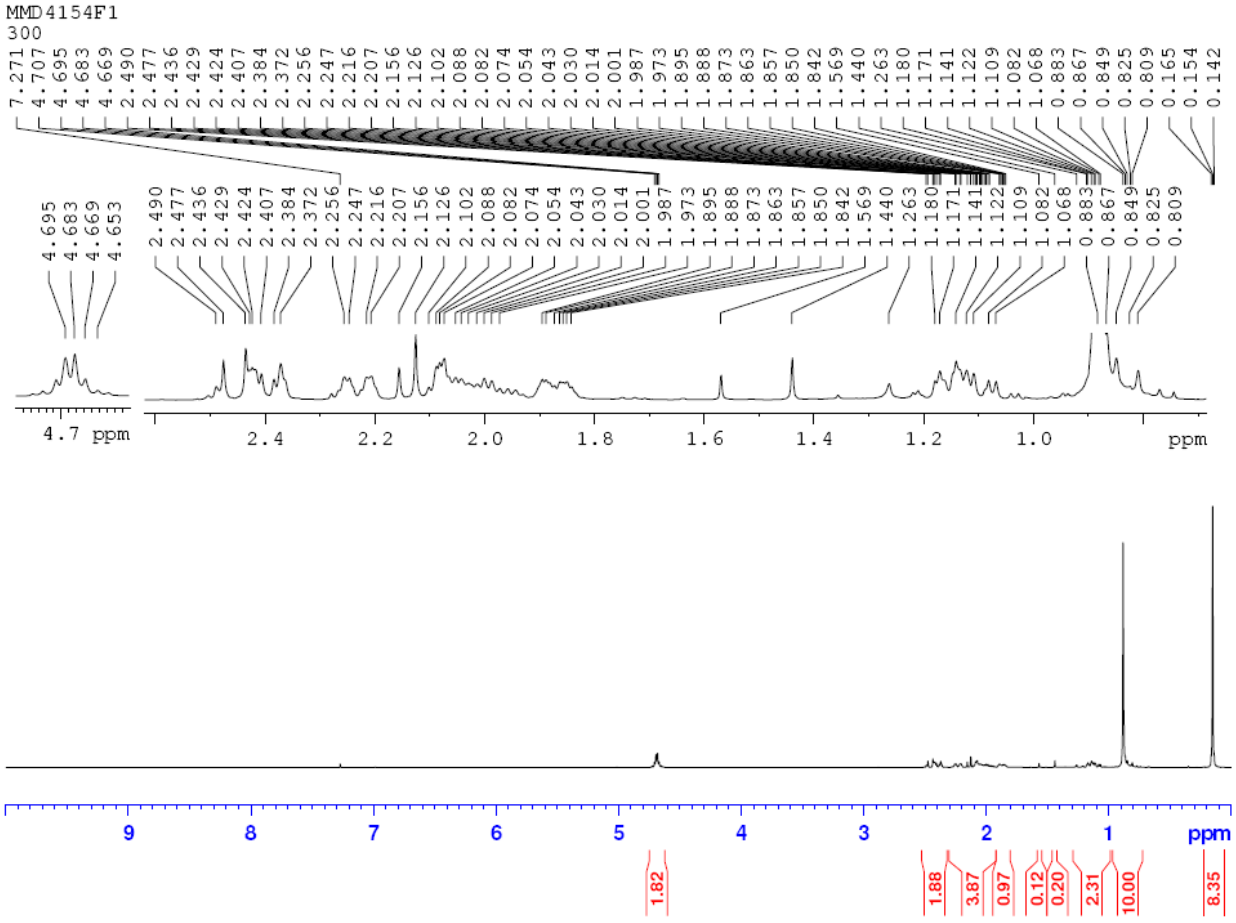
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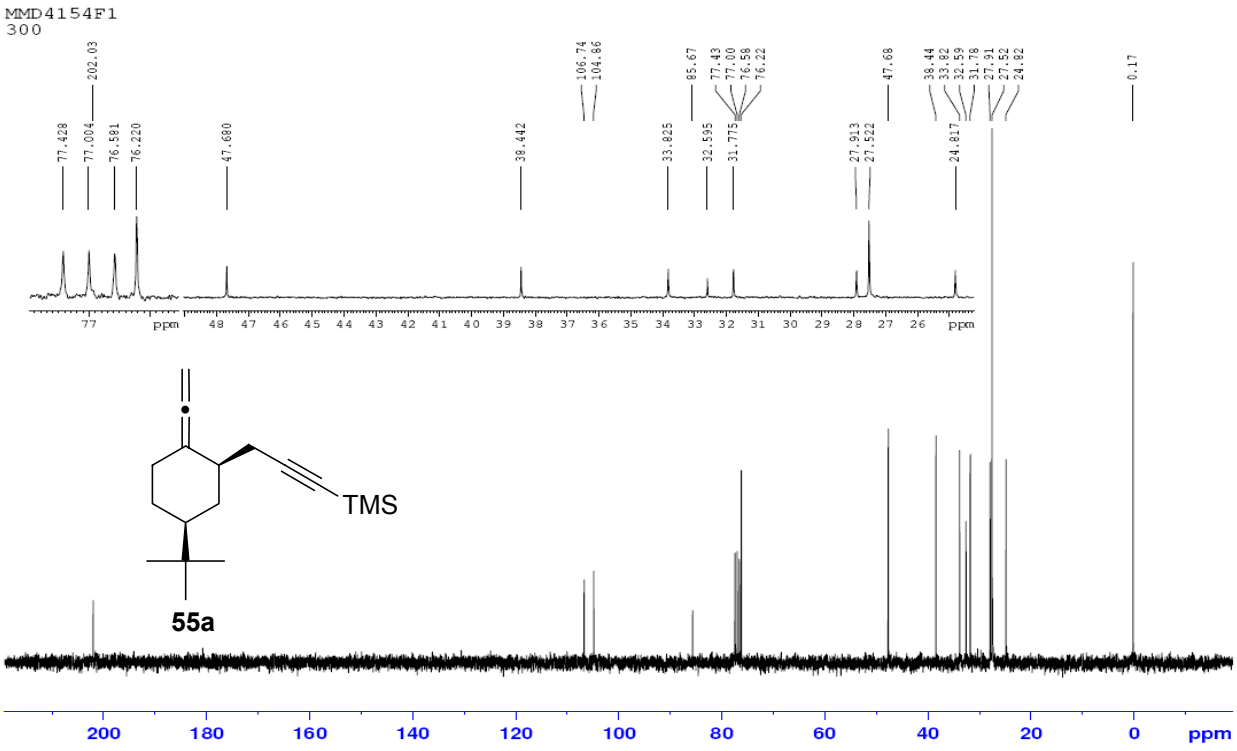
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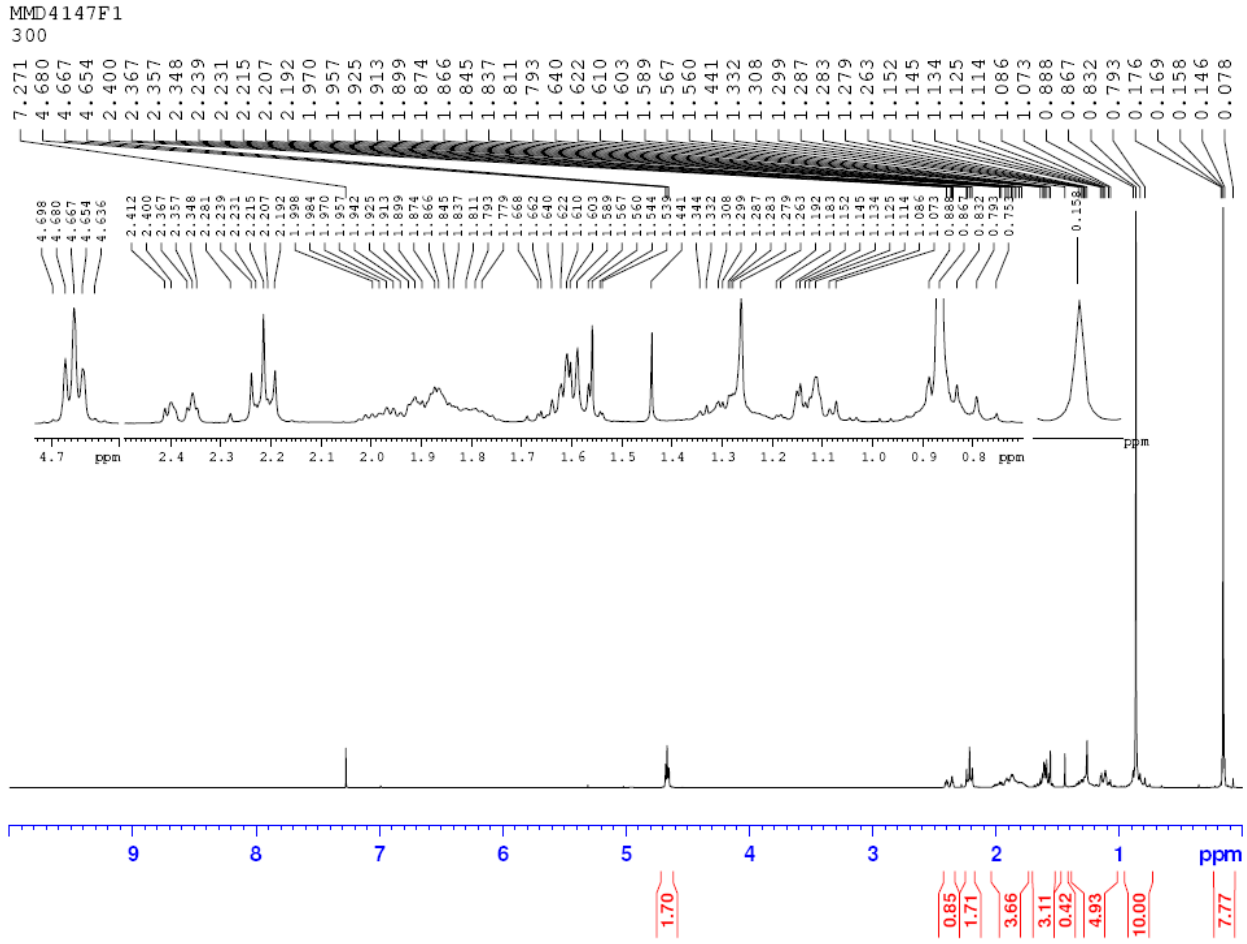
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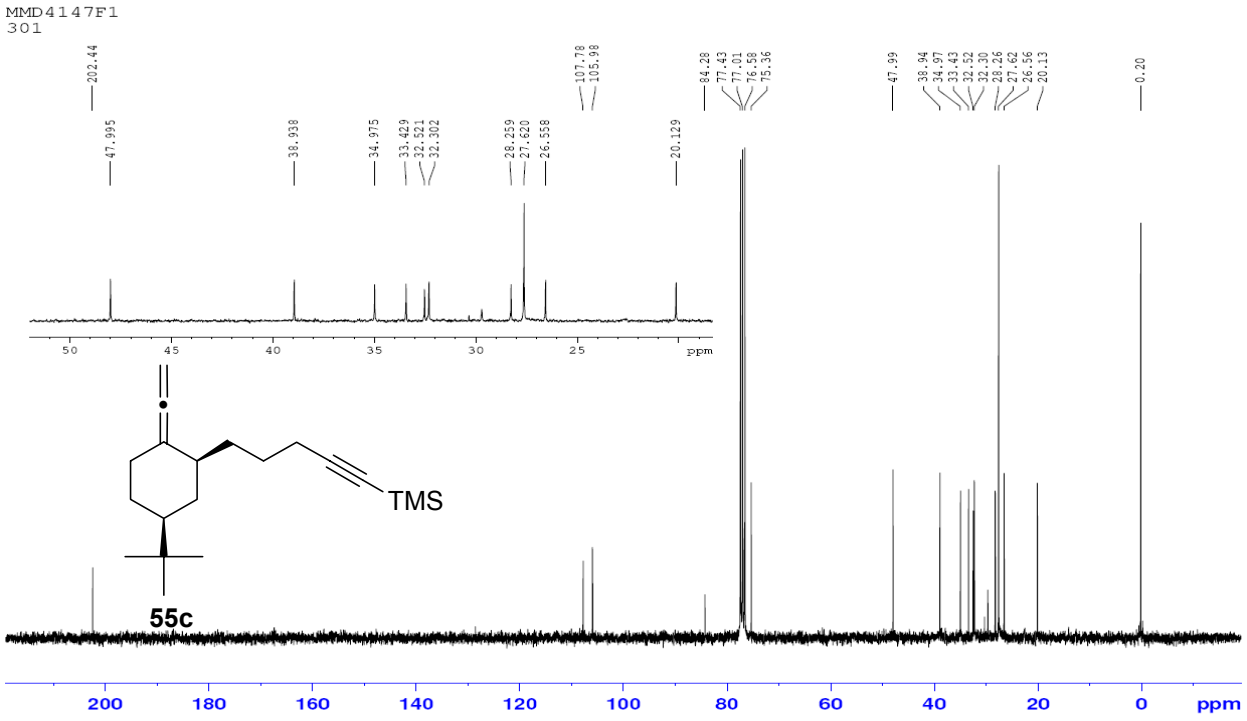
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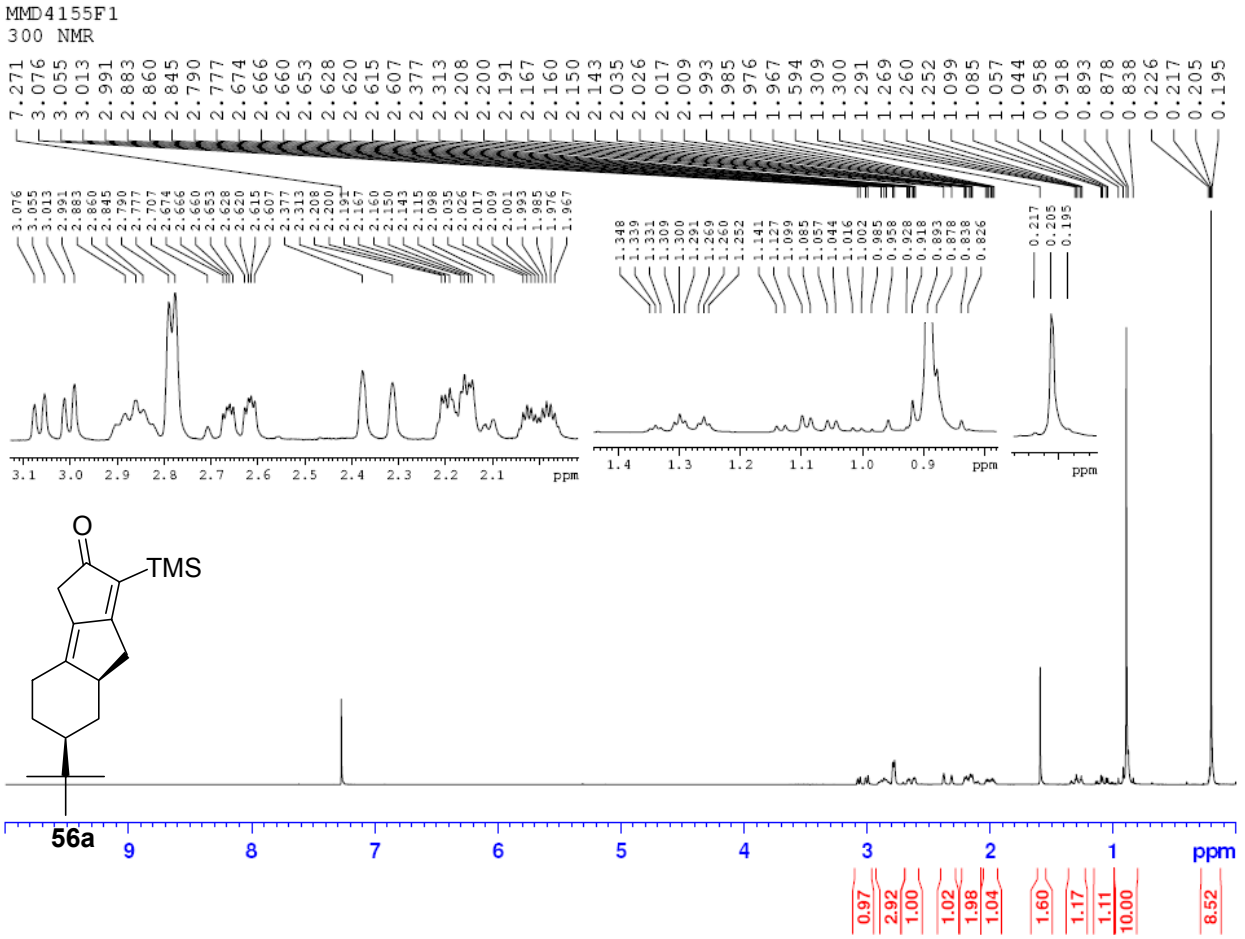
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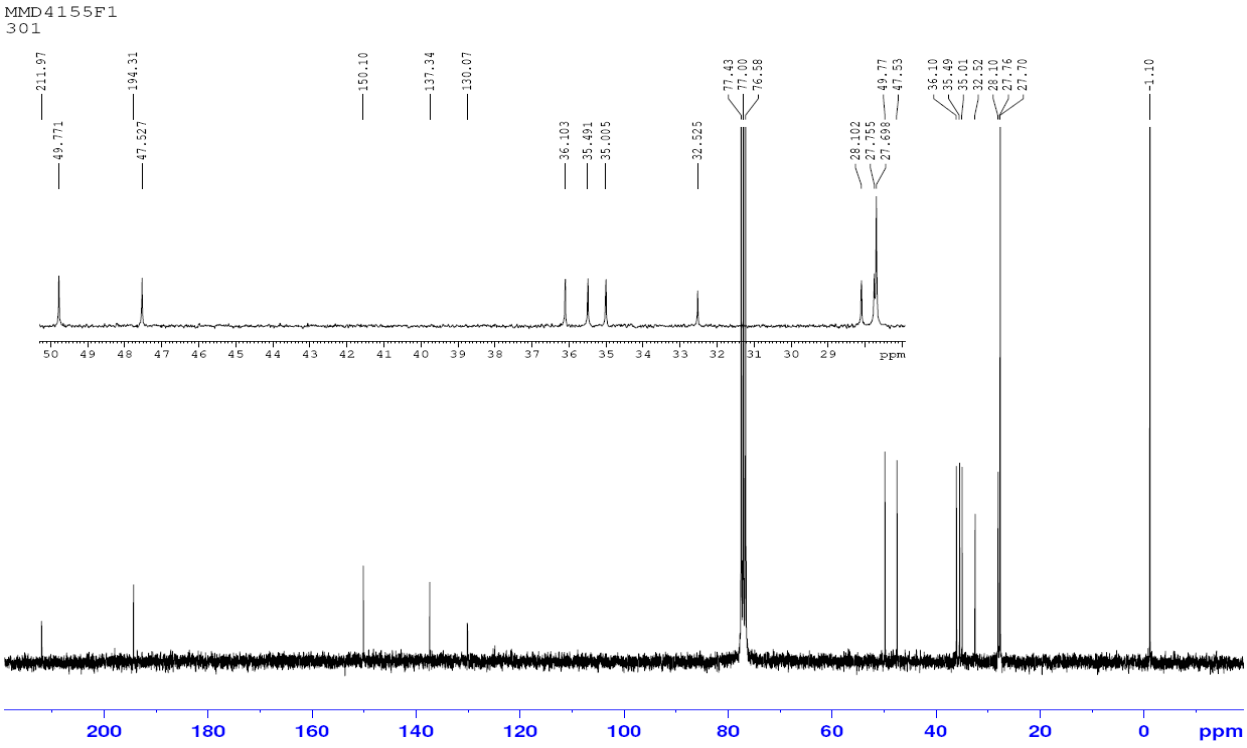
56a
ppm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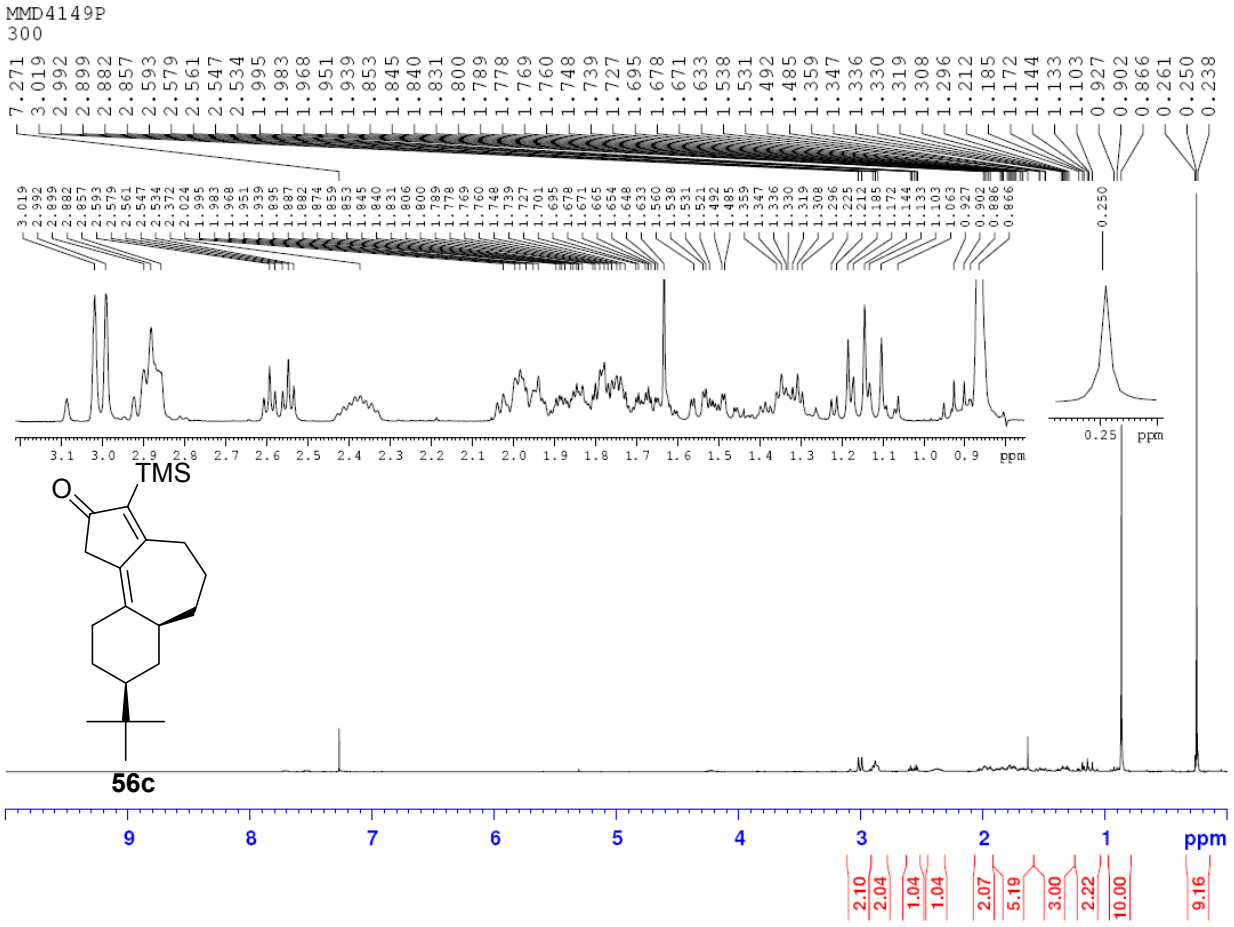
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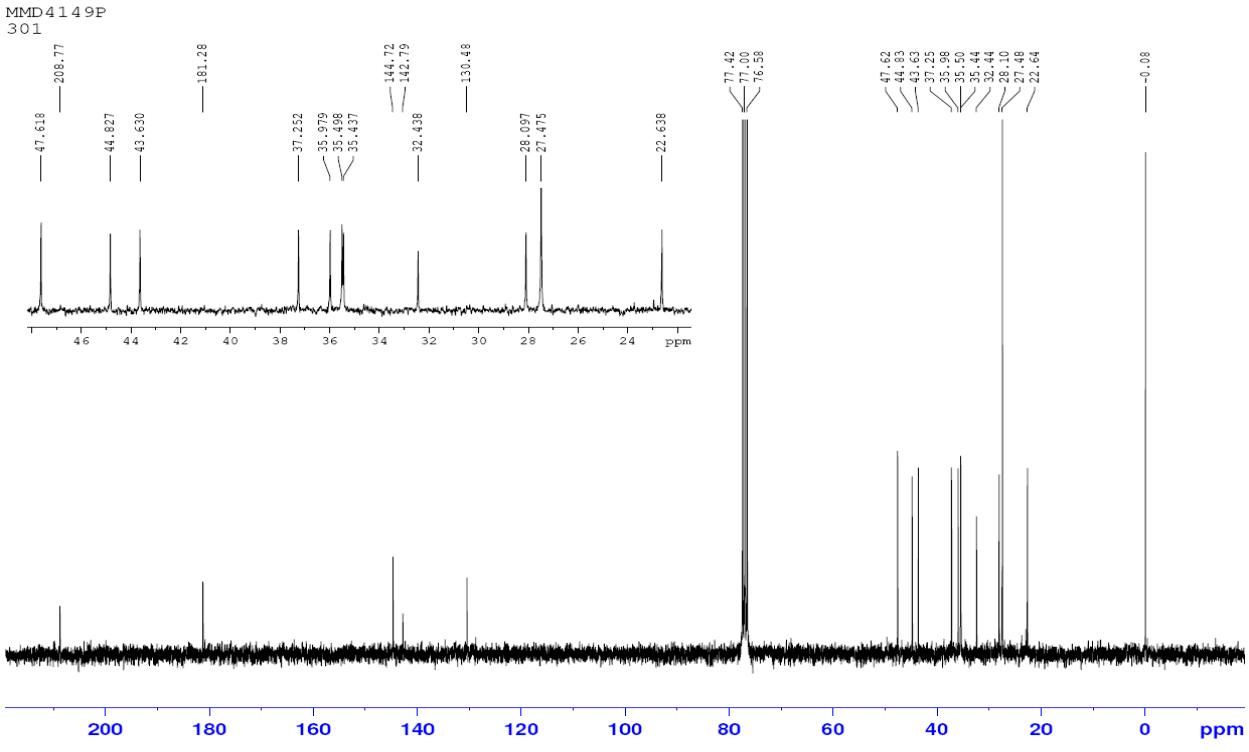
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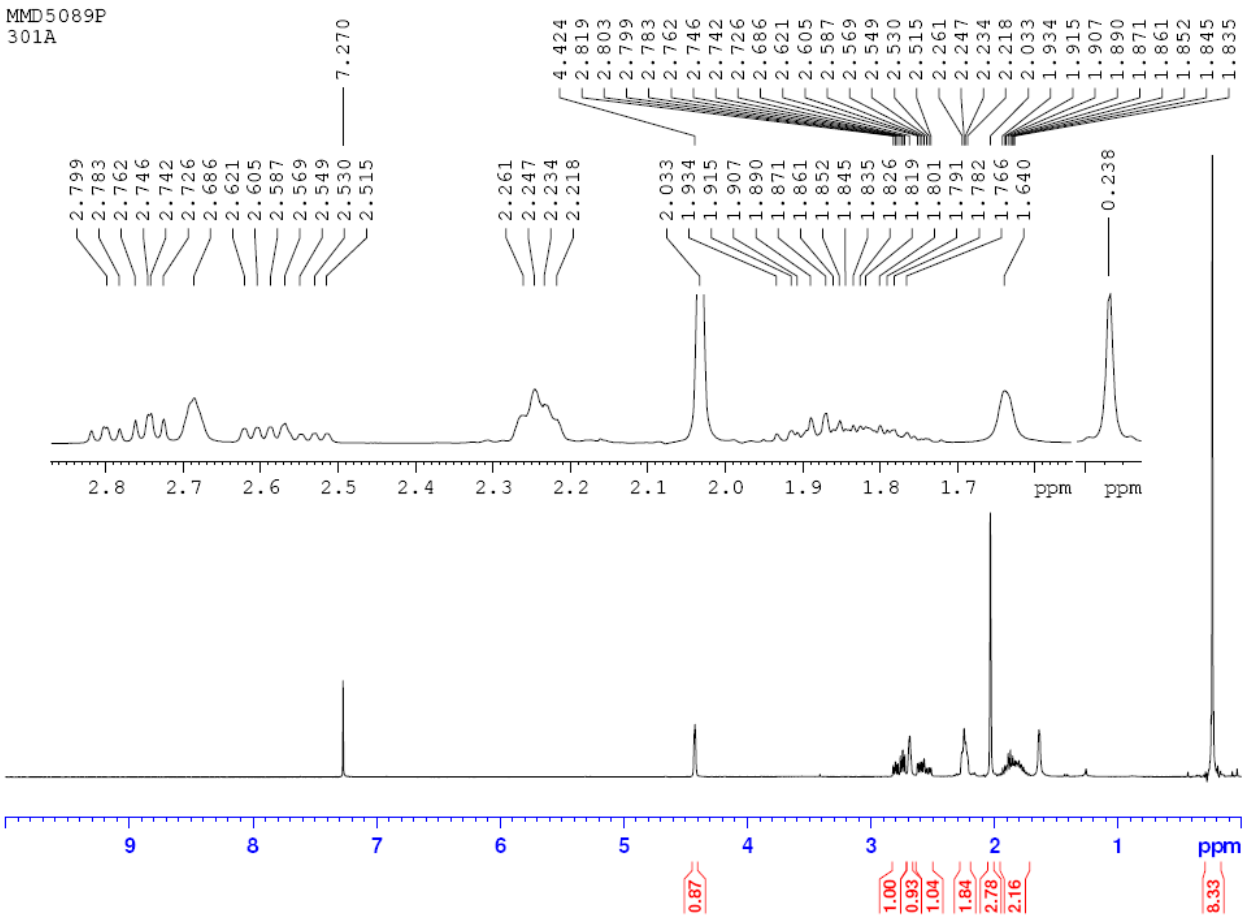
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2.799 2.783 2.762 2.746 2.742 2.726 2.686 2.621 2.605 2.587 2.569 2.549 2.530 2.515
2.261 2.247 2.234 2.218
2.033 1.934 1.915 1.907 1.890 1.871 1.861 1.852 1.845 1.835 1.826 1.819 1.801 1.791 1.782 1.766 1.640
0.238
2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 ppm
9 8 7 6 5 4 3 2 1 ppm
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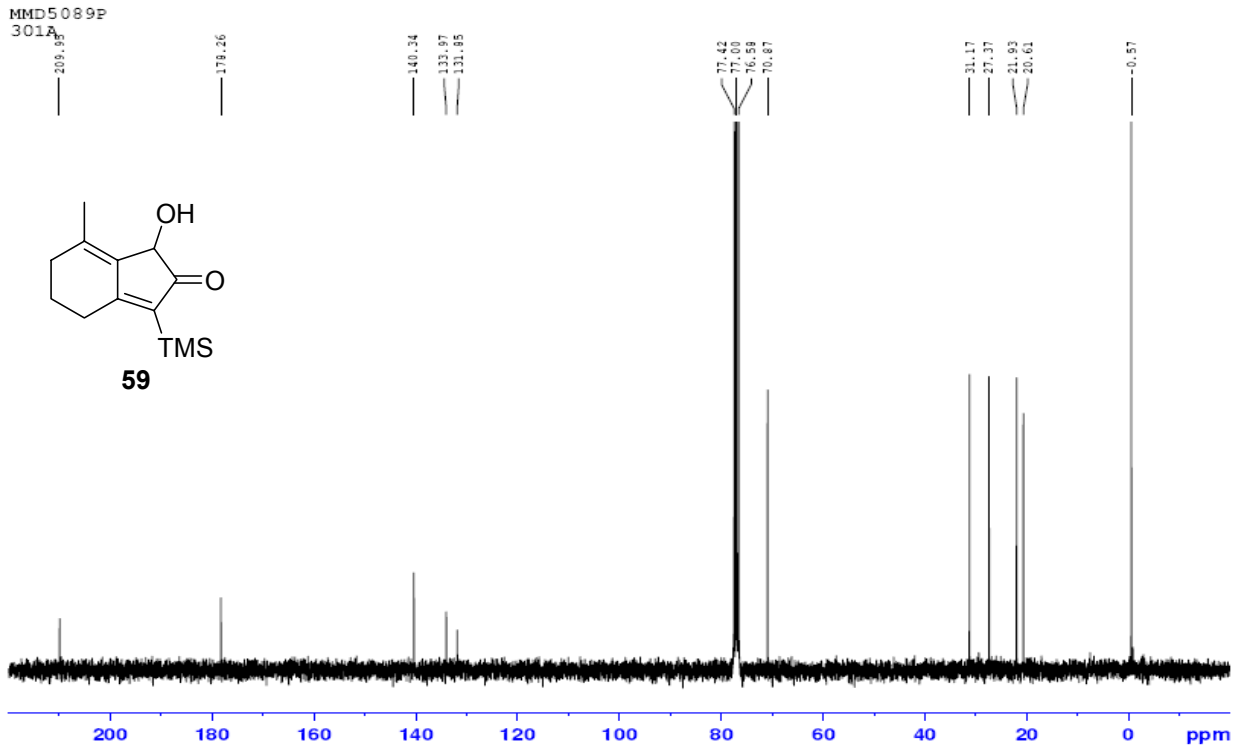
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77.42
77.00
76.58
70.87
31.17
27.37
21.93
20.61
-0.57
OH
O
TMS
200 180 160 140 120 100 80 60 40 20 0 ppm

59

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