



Gold-Catalyzed Cycloisomerization of [3]-Cumulenols

Laura Ferrand, Nicolas das Neves, Max Malacria, Virginie Mouriès-Mansuy,
Cyril Ollivier, Louis Fensterbank

► To cite this version:

Laura Ferrand, Nicolas das Neves, Max Malacria, Virginie Mouriès-Mansuy, Cyril Ollivier, et al.. Gold-Catalyzed Cycloisomerization of [3]-Cumulenols. *Journal of Organometallic Chemistry*, 2015, *The Organometallic Chemistry of Gold*, 795, pp.53-57. 10.1016/j.jorganchem.2015.02.003 . hal-01117118

HAL Id: hal-01117118

<https://hal.sorbonne-universite.fr/hal-01117118>

Submitted on 16 Feb 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Gold-Catalyzed Cycloisomerization of [3]-Cumulenols

Laura Ferrand,^{†,‡} Nicolas Das Neves,^{†,‡} Max Malacria,^{†,‡} Virginie Mouriès-Mansuy,^{†,‡} Cyril Ollivier^{†,‡,*}, Louis Fensterbank^{†,‡,*}

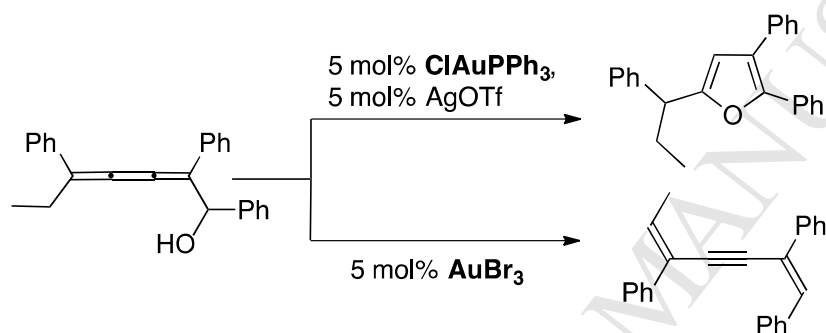
[†] Sorbonne Universités, UPMC Univ Paris 06, UMR 8232, Institut Parisien de Chimie Moléculaire, F-75252 Paris Cedex 05, France.

[‡] CNRS, UMR 8232, Institut Parisien de Chimie Moléculaire, F 75252 Paris Cedex 05, France.

cyril.ollivier@upmc.fr; louis.fensterbank@upmc.fr

Tel: 00 33 1 44 27 38 47; Fax: 00 33 1 44 27 73 60

Abstract. The gold-catalyzed cycloisomerization of tetrasubstituted [3]-cumulenols has been investigated. Overall, two main pathways are followed. In the presence of a gold(III) catalyst, a dehydration process prevails giving diastereomerically pure dienynes while gold(I) catalysts favor the cycloisomerization to provide trisubstituted furan derivatives.

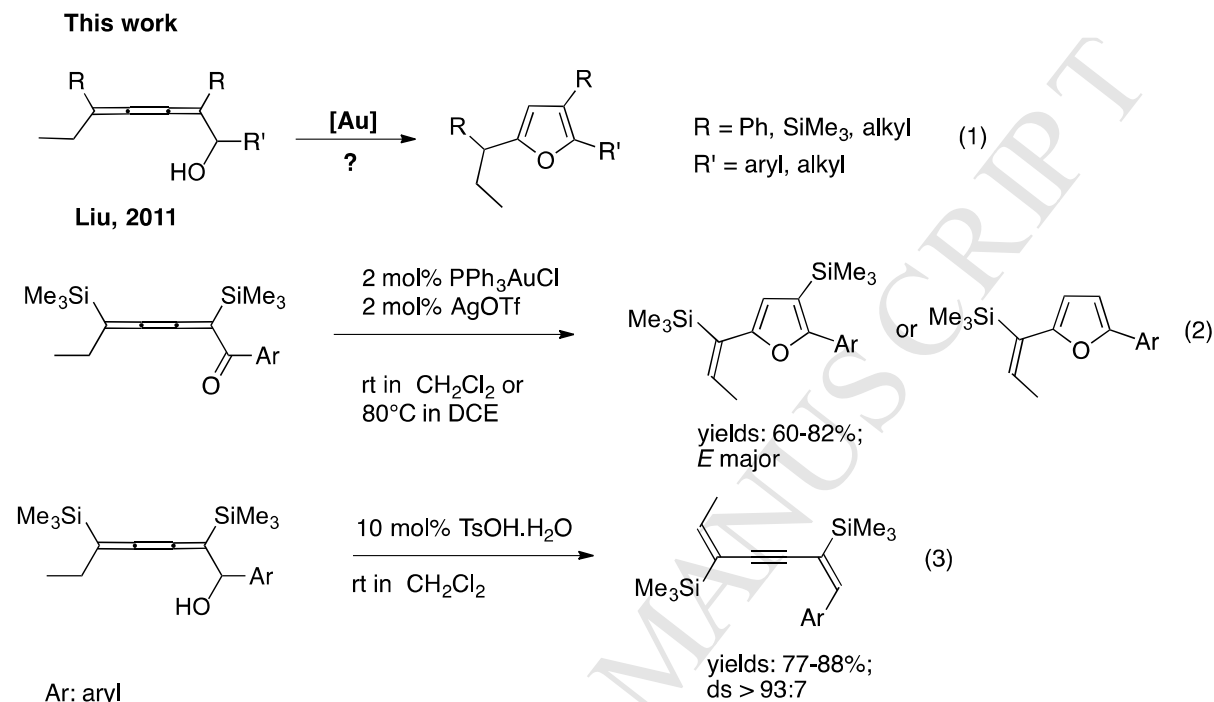


1. Introduction

[n]-Cumulenes are fascinating molecules.[1] Their extreme level of unsaturation bodes well for intriguing reactivities, especially in the presence of metallic species.[2] Nevertheless, the game can be played only when the starting cumulene is readily available and stable enough to be further engaged. Tetrasubstituted [3]-cumulenes meet these criteria and when armed with a side hydroxy function, the corresponding 2,3,4-trien-1-ol systems become interesting substrates to examine for electrophilic gold catalysis.[3] Assuming a preliminary electrophilic activation of the π -system of the cumulene network, intramolecular nucleophilic attack from the pendant hydroxy function is anticipated and should deliver an oxygen unsaturated heterocycle presumably of furan type (eq. 1, Scheme 1).[4] Gold catalysis has provided several versatile routes to furanic systems, most of them relying on a key C-O bond formation from different type of unsaturated precursors bearing an alcohol or a ketone function.[5] Furan moieties are widespread in natural products with relevant biological properties such as kallolide A[6] and (–)-deoxypukalide.[7] They are also found in numerous drugs, for instance the anti-ulcer drug ranitidine or the anti-bacterial furazilidone and have proven to be valuable synthons for further elaboration.[8]

Closest to our approach is the report by Y. Liu who has recently examined the gold-catalyzed cycloisomerization of [3]-cumulenones, obtained from diyne precursors, to provide furan derivatives (eq. 2, Scheme 1).[2g] The same report also described the Brønsted catalyzed dehydration of the arylcumulenols to give the corresponding dienynes in good yields (eq. 3, Scheme 1). It should also be mentioned that Skrydstrup developed a gold(I)-catalyzed double hydration of diyne substrates delivering 2,5-symmetrically substituted furans.[9] In this context, our objective was to devise an access to trisubstituted furan derivatives directly from

[3]-cumulenols. This implied to find the proper gold-based catalytic system which would be compatible with the hydroxy function of the cumulenol system and not trigger a dehydrative process. Indeed, this could be quite challenging since gold(III) salts have for instance been shown to catalyze the nucleophilic substitution of propargylic alcohols.[10] Moreover, we wanted to broaden the scope of the substituents on the final furanic products which implied to engage diversely substituted cumulenols.



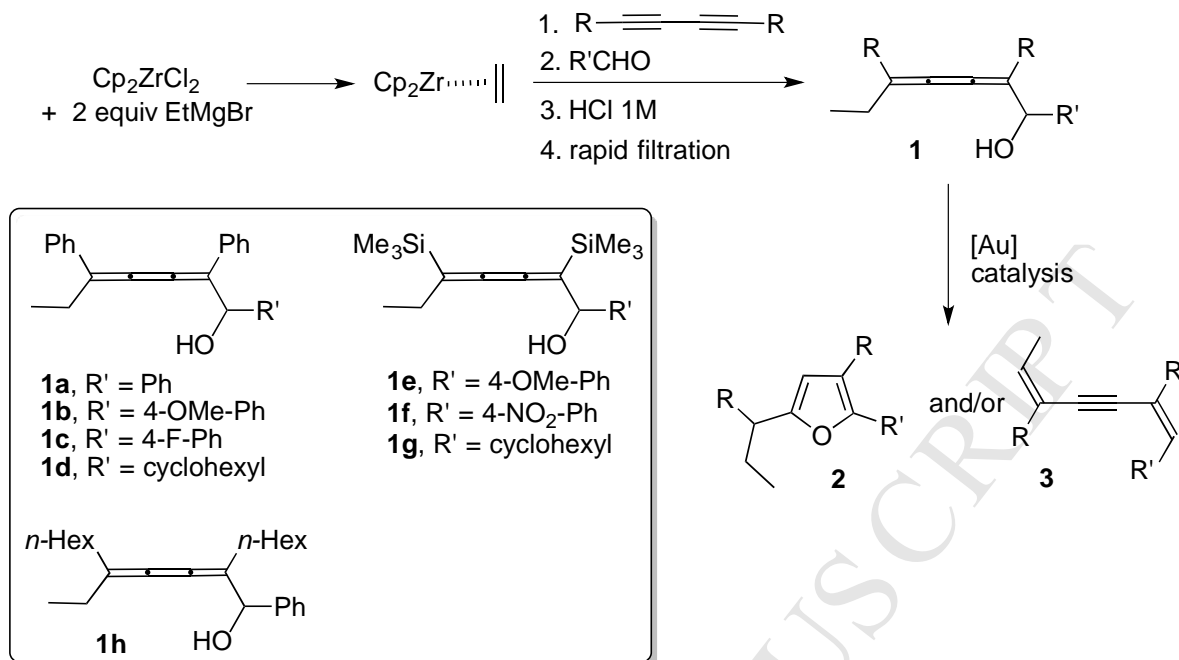
Scheme 1. Context of the [3]-cumulenol gold-catalyzed cycloisomerization

2. Results and discussion

2.1. Synthesis of precursors

For that purpose, we relied on the synthesis of [3]-cumulenols also documented by Y. Liu,[11] who developed a zirconium-mediated coupling of 1,3-butadiynes with aldehydes. In this work, we used bis-trimethylsilyl, bis-phenyl and bis-*n*-hexyl diynes as butadiynyl substrates combined with cyclohexylaldehyde and various aryl aldehydes as electrophilic partners. The expected representative [3]-cumulenols were produced satisfactorily as judged from the examination of the ¹H NMR spectra of the crude products (Scheme 2). Nevertheless, we faced some difficulties at the purification stage in some cases. Chromatography of some substrates, even with neutralized silica gel, leads to dehydration products **3** accompanied by decomposition products. We thus devised a one pot sequence consisting of the synthesis of the precursor **1** followed by a rapid filtration over silica gel neutralized by sodium carbonate. The resulting product showed sufficient purity to be engaged in the cycloisomerization step with gold catalysis.

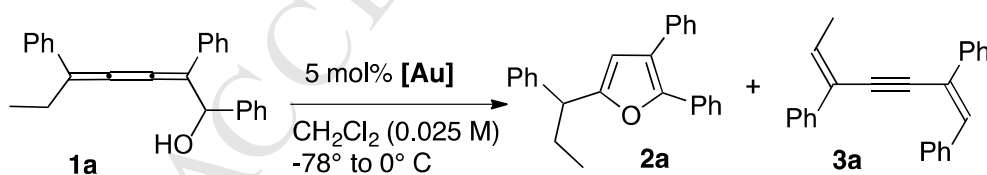
One pot sequence



Scheme 2. One pot sequence: [3]-cumulenol synthesis - gold-catalyzed step

2.2. Preliminary catalyst screening

Our preliminary catalyst screening was achieved with substrate **1a** (Table 1) and provided useful trends. Not surprisingly, the more electrophilic and oxophilic gold (III) salts[10,12,13] favored the dehydration product **3a** (entries 2-3). Same result was obtained with the oxophilic AgOTf (entry 1).[14] In sharp contrast, gold (I) salt AuCl (entry 6) allowed to retrieve the expected carbophilic activation favoring the exclusive formation of **2a**. In the same line, a complete selectivity was also observed with cationic gold(I) complexes (entries 7-9). Interestingly, a better yield was observed with a triflate counter ion compared to a hexafluoroantimonate (entry 7 vs. 8) which would be consistent with the fact that a triflate anion has already been claimed as an efficient proton shuttle.[15] To pursue our study, we selected AuBr₃ to provide diyne **3a** and the AuClPPh₃-AgOTf mixture as a privileged catalytic system since it provided the best yield of **2a** in the shortest reaction time.



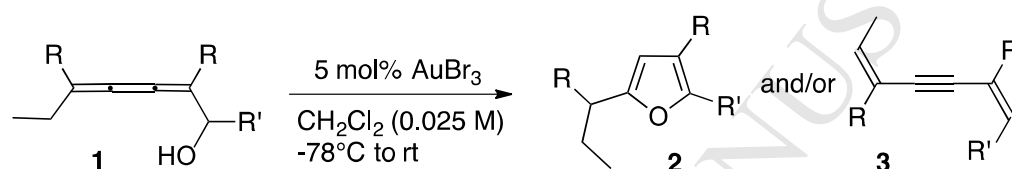
Entry	Catalyst	Conversion	Yield ^[a]	2 : 3 ratio
1	AgOTf	100 % after 18 h	51%	0 : 100
2	AuBr ₃	100 % after 18 h	59 %	0 : 100
3	AuCl ₃	100 % after 18 h	46 %	20 : 80
4	AuCN	None after 24 h	-	-
5	AuClPPh ₃	None after 24 h	-	-
6	AuCl	100 % after 56 h	53%	100 : 0
7	AuClPPh ₃ +AgOTf	100% after 10 h	59%	100 : 0
8	AuClPPh ₃ +AgSbF ₆	33% after 18 h	27%	100 : 0
9	[JohnPhosAu(NCMe)]SbF ₆	100% after 42 h	47%	100 : 0

^[a] Overall yield from butadiyne precursor ; sequence run on a 1 mmol scale.

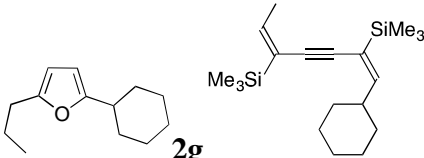
Table 1. Preliminary catalytic screening

2.3. Dehydration process

It appeared interesting to examine the possibility to develop a versatile access to dienyne products **3**. For that purpose, we submitted various cumulenols to gold(III) catalysis (Table 2). As expected, bis-aryl cumulenol derivatives provided exclusively the dehydration products **3** in moderate to fair yields. Not surprisingly, para-fluoro substituted precursor (**1c**, entry 3) resulted in a poorer reaction. In contrast, bis-TMS precursors gave inseparable mixtures of products **2** and **3**, featuring a significant influence of the R' substituent (entries 5 vs. 6). Partial desilylation on **2f** or total one on **2g** was observed which can be ascribed to the presence of protic sources originating from the dehydration process. The more-electron donating cyclohexyl resulted indeed in a logical higher yield of dienyne **3g**. All dienyne **3** were isolated as single diastereomers.[16] Their structures were assigned by analogy with the one of **3b** which was secured by X-ray crystallography (Figure 1).[17]



Entry	Cumulenols	Products	Yield ^[a] , 2 : 3 ratio
1	1a	 3a	59%, 0 : 100
2	1b	 3b	45%, 0 : 100
3	1c	 3c	38%, 0 : 100
4	1d	 3d	56%, 0 : 100
5	1f ^[b]	 2f and 3f	52%, 62 : 38

6 ^[b]	1g ^[b]		69%, 23 : 77
------------------	-------------------	---	--------------

^[a] Overall yield from butadiyne precursor ; sequence run on a 1 mmol scale. ^[b] Reaction run at 0.05 M.

Table 2. Gold (III)-catalyzed dehydration reaction

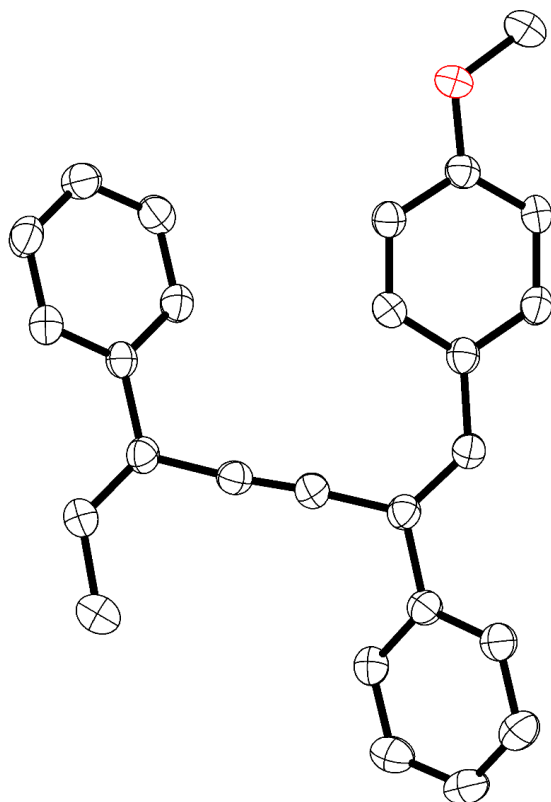
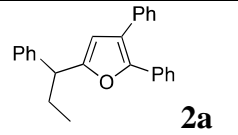
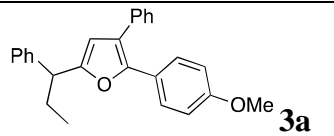
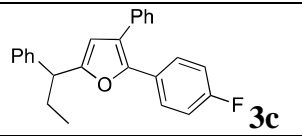
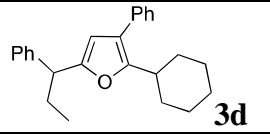
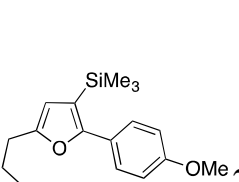
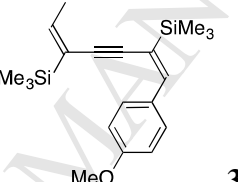
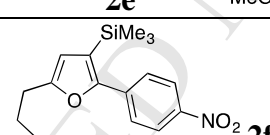
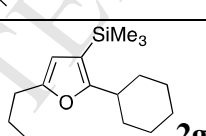
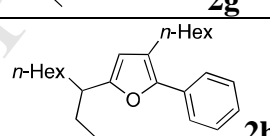


Figure 1. ORTEP diagram of **3b**.

2.4. Cycloisomerization process

We then examined the behavior of these substrates when exposed to gold(I) catalysis anticipating a higher π -activation of the cumulene moiety. We selected the 1:1 AuClPPH₃/AgOTf mixture as catalytic system. Gratifyingly, our working hypothesis proved to be correct since bis-phenyl precursors **1a-1d** cleanly afforded the corresponding furan products in satisfactory yields, taking into account that it is an overall yield from the diyne substrate. Here also, bis-TMS precursors gave contrasted results. Electron-rich substrate **1e** resulted in an equimolar mixture of products **2e** and **3e**, while precursors **1f** and **1g** gratifyingly provided monodesilylated furans **2f** and **2g**. In three instances, we used Echavarren's catalyst (entries 2, 3 and 6) but no improvement in the reaction outcome was observed. Finally, dialkylsubstrate **1h** also afforded a good yield of furan product **2h**.

Entry	Cumulenols	Products	Yield ^[a] , 2 : 3 ratio
1	1a	 2a	59%, 100 : 0 47% ^[b] , 100 : 0
2	1b	 3a	47%, 100 : 0 34% ^[b] , 100 : 0
3	1c	 3c	57%, 100 : 0
4	1d	 3d	59%, 100 : 0
6	1e ^[c]	 2e and  3e	55%, 50 : 50 complex mixture ^[b]
7	1f ^[c]	 2f	36%, 100 : 0
8	1g ^[c]	 2g'	50%, 100 : 0
9	1h	 2h	52 %, 100 : 0

^[a] Overall yield from butadiyne precursor ; sequence run on a 1 mmol scale.

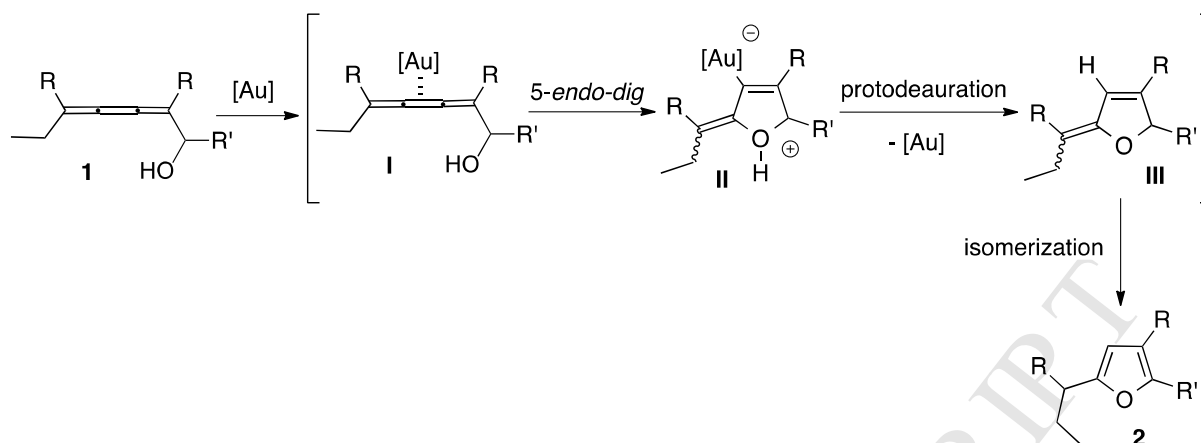
^[b] Reaction run with 5 mol% [JohnPhosAu(NCMe)]SbF₆.

^[c] Reaction run at 0.05 M.

Table 3. Gold (I)-catalyzed cycloisomerization

2.5. Mechanism proposal for the furan formation

A plausible mechanism for the furan formation can be proposed based on literature data (Scheme 3). As for allenes,^[18] preliminary π -activation of the cumulene moiety as in **I** would generates a highly electrophilic complex that undergoes a 5-*endo-dig* cyclization. The resulting vinylgold **II** intermediate then undergoes protodeauration, liberating the gold catalyst and diene **III**. The latter then isomerizes to the aromatic furan substrates **2**.



Scheme 3. Mechanism proposal for the formation of furans

3. Conclusion

We have explored the reactivity of cumulenols towards gold catalysis. Because of the acidic lability of the cumulenol substrates, we have worked out a multi-step reaction starting from the zirconium mediated formation of the cumulenol from a diyne precursor, followed by rapid filtration and the gold-catalyzed step. Overall, two main pathways are followed. In the presence of gold(III) catalysts, a dehydration process takes place delivering diastereomerically pure dienynes. In contrast, gold(I) catalysis offers an access to variously trisubstituted furans. These findings illustrate the synthetic potential of the use of cumulenes as partners in organometallic catalysis and more specifically upon π -activation of the cumulene moiety. They also illustrate the fine tuning of catalysis provided by gold complexes just by playing with the oxidation degree.

4. Experimental

General procedure of furan synthesis

EtMgBr (1.0 M in THF solution, 2.5 mL, 2.5 mmol) was added to a solution of ZrCp_2Cl_2 (0.365 g, 1.25 mmol) in THF (5 mL) at -50°C . The reaction mixture was stirred for 1 h at the same temperature. Then, the diyne (1 mmol) was added and the reaction mixture was warmed to room temperature and stirred for 2 h. Distilled aldehyde (1 mmol) was added; then the reaction mixture was stirred overnight and monitored by TLC (*n*-Pentane/EtOAc) before being quenched with HCl 1M (3 mL). The aqueous layer was extracted with diethyl ether. The combined organic layers were then washed with brine, dried over Na_2SO_4 , filtered and the solvent was evaporated under reduced pressure at 20°C . The crude residue was finally filtered on silica gel neutralized with Na_2CO_3 to yield the [3]-cumulenol **1**.

A solution of AuClPPh_3 (24.7 mg, 0.05 mmol) and AgOTf (12.8 mg, 0.05 mmol) in CH_2Cl_2 (30 mL) was stirred for 5 min at room temperature and then cooled to -78°C . A solution of the crude [3]-cumulenol **1** (ca. 1 mmol) in CH_2Cl_2 (10 mL) was added and the resulting mixture was warmed to room temperature. The completion of the reaction was monitored by TLC (*n*-Pentane/ Et_2O), the reaction mixture was filtered and the solvent was removed under reduced pressure. Purification of the residue by flash chromatography (*n*-Pentane/EtOAc) afforded the desired furan **2**.

Acknowledgments. We thank the MRES, the CNRS, the IUF and the ANR Blan 0302 “Allènes” for financial support. Special thanks to Geoffrey Gontard (UPMC) for the X-ray

structure determination of **3b**. We also thank Lucas Defaut and Alexander V. Belovodski for some experiments and Prof. Liu (Shanghai Institute of Organic Chemistry) for helpful discussions.

Appendix A. Supplementary material

a) General procedures, characterization and spectral data (^1H and ^{13}C NMR spectra) of all new compounds.

b) CCDC 1035348 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found in online version at doi:

References

- [1] For reviews, see: (a) L. Leroyer, V. Maraval, R. Chauvin, *Chem. Rev.* 112 (2012) 1310. (b) J. A. Januszewski, R. R. Tykwinski, *Chem. Soc. Rev.* 43 (2014) 3184. (c) M. Ogasawara, in *Science of synthesis. Cumulenes and allenes*, ed. D. Bellus, Georg Thieme Verlag (2008), vol. 44.1, pp. 9. (d) C. Bruneau, J.-L. Renaud, in *Compr. Org. Funct. Group Transform. II*, ed. A. R. Katritzky and R. J. K. Taylor, Elsevier, Oxford (2005) vol. 1.20, pp. 1019.
- [2] (a) P. J. Stang, M. R. White, G. Maas, *Organometallics* 2 (1983) 720. (b) M. Iyoda, S. Tanaka, H. Otani, M. Nose, M. Oda, *J. Am. Chem. Soc.* 110 (1988) 8494. (c) S. Hashmi, K. Polborn, G. Szeimies, *Chem. Ber.* 122 (1989) 2399. (d) N. Suzuki, M. Nishiura, Y. Wakatsuki, *Science* 295 (2002) 660. (e) T. Furuta, T. Asakawa, M. Iiumina, S. Fujii, K. Tanaka, T. Kan, *Chem. Commun.* (2006) 3648. (f) N. Suzuki, Y. Fukuda, C. E. Kim, H. Takahara, M. Iwasaki, M. Saburi, M. Nishiura, Y. Wakatsuki, *Chem. Lett.* 32 (2003) 16. (g) E. Wang, X. Fu, X. Xie, J. Chen, H. Gao, Y. Liu, *Tetrahedron Lett.* 52 (2011) 1968.
- [3] For recent monographs covering most aspects of gold catalysis, see: (a) *Modern Gold Catalyzed Synthesis*; Hashmi, A. S. K., Toste, F. D., Eds.; Wiley-VCH: Weinheim, Germany, 2012. (b) *Gold Catalysis: An Homogenous Approach*; Toste, F. D., Michelet, V., Eds.; Imperial College Press: London, 2014.
- [4] For recent reviews on mechanistic aspects of gold-catalyzed reactions, see: (a) A. Fürstner, *Chem. Soc. Rev.* 38 (2009) 3208. (b) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* 49 (2010) 5232. (c) C. Obradors, A. E. Echavarren, *Acc. Chem. Res.* 47 (2014) 902. (d) L. Fensterbank, M. Malacria, *Acc. Chem. Res.* 47 (2014) 953. (e) A. S. K. Hashmi, *Acc. Chem. Res.* 47 (2014) 864.
- [5] For seminal works, see: (a) A. S. K. Hashmi, L. Schwartz, J.-H. Choi, T. M. Frost, *Angew. Chem. Int. Ed.* 39 (2000) 2285. (b) T. Schwier, A. W. Sromek, D. M. L. Yap, D. Chernyak, V. Gevorgyan, *J. Am. Chem. Soc.* 129 (2007) 9868. (c) A. S. Dudnik, V. Gevorgyan, *Angew. Chem. Int. Ed.* (2007) 46, 5195. (d) A. S. K. Hashmi, T. Häfner, M. Rudolph, F. Rominger, *Eur. J. Org. Chem.* (2011) 667. For reviews, see: (d) A. V. Gulevich, A. S. Dudnik, N. Chernyak, V. Gevorgyan, *Chem. Rev.* 113 (2013) 3084. (e) N. Krause, C. Winter, *Chem. Rev.* 111 (2011) 1994. (f) A. Corma, A. Leyva-Perez, M. J. Sabater, *Chem. Rev.* 111 (2011) 1657. (g) M. Rudolph, A. S. K. Hashmi, *Chem. Commun.* 47 (2011) 6536. For recent developments, see: (h) T. Wang, S. Shi, M. Rudolph, A. S. K. Hashmi, *Adv. Synth. Catal.* 356 (2014) 2337. (i) T. Wang, S. Shi, M. M. Hansmann, E. Rettenmeier, M. Rudolph, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* 53 (2014) 3715. (j) S. Kramer, T. Skrydstrup, *Angew. Chem. Int. Ed.* 51 (2012) 4681. (k) X. Huang, B. Peng, M. Luparia, L. Gomes, L. F. Veiros, N. Maulide, *Angew. Chem. Int. Ed.* 51 (2012) 8886.
- [6] S. A. Look, M. T. Burch, W. Fenical, Z. Qi-tai, J. Clardy *J. Org. Chem.* 50 (1985) 5741.
- [7] T. J. Donohoe, A. Ironmonger, N. M. Kershaw, *Angew. Chem. Int. Ed.* 47 (2008) 7314.
- [8] (a) D. L. Wright, *Prog. Het. Chem.* 17 (2005) 1. (b) B. H. Lipschutz, *Chem. Rev.* 86 (1986) 795. (c) B. A. Keay, *Chem. Soc. Rev.* 28 (1999) 209. (d) X. L. Hou, H. Y. Cheung, T. Y. Hon, P. L. Kwan, T. H. Lo, S. Y. Tong, H. N.C. Wong, *Tetrahedron* 54 (1998) 1955.
- [9] S. Kramer, J. L. H. Madsen, M. Rottländer, T. Skrydstrup, *Org. Lett.* 12 (2010) 2758.
- [10] M. Georgy, V. Boucard, J.-M. Campagne, *J. Am. Chem. Soc.* 127 (2005) 14180-14181.
- [11] Y. Liu, H. Gao, S. Zhou, *Angew. Chem. Int. Ed.* 45 (2006) 4163;
- [12] For an evaluation of the Lewis acidity of various salts, see : Y. Yamamoto, *J. Org. Chem.* 72 (2007) 7817.
- [13] For examples of oxidation state dependent dichotomy in gold catalysis, see: (a) A. W. Sromek, M. Rubina, V. Gevorgyan, *J. Am. Chem. Soc.* 127 (2005) 10500. (b) A. S. Dudnik, A. W. Sromek, M. Rubina, J. T. Kim, A. V. Kel'in, V. Gevorgyan, *J. Am. Chem. Soc.* 130 (2008) 1440. (c) A. S. K. Hashmi, J. Hofmann, S. Shi, A.

- Schütz, M. Rudolph, C. Lothschütz, M. Wietek, M. Bührle, M. Wölfle, F. Rominger, *Chem. Eur. J.* 19 (2013) 382.
- [14] Y. Su, Y. Zhang, N. G. Akhmedov, J. L. Petersen, X. Shi, *Org. Lett.* 16 (2014) 2478.
- [15] (a) J. Zhang, W. Shen, L. Li, M. Li, *Organometallics* 28 (2009) 3129 (b) C. M. Krauter, A. S. K. Hashmi, M. Pernpointner, *ChemCatChem* 2 (2010) 1226 (c) M. Jiang, L.-P. Shi, Y. Li, *Org. Lett.* 12 (2010) 116. (d) A. S. Dudnik, Y. Xia, Y. Li, V. Gevorgyan, *J. Am. Chem. Soc.* 132 (2010) 7645. (e) A. Zhdanko, M. E. Maier, *ASC Cat.* 4 (2014) 2770.
- [16] Minor diastereomers (< 5 %) were detected on the ^1H NMR of the crude product.
- [17] CCDC 1035348.
- [18] (a) B. Gockel, N. Krause, *Org. Lett.* 8 (2006) 4485. (b) R. Zriba, V. Gandon, C. Aubert, L. Fensterbank, M. Malacria, *Chem. Eur. J.* 14 (2008) 1482. For reviews: (c) M. Malacria, L. Fensterbank, V. Gandon, *Top. Curr. Chem.* 302 (2011) 157. (d) E. Soriano, I. Fernandez, *Chem. Soc. Rev.* 43 (2014) 3041.

Highlights:

- First gold-catalyzed cycloisomerization of cumulenols
- Reaction outcome dependent from the gold oxidation state
- A new access to trisubstituted furan derivatives
- Gold(I) π -activation of the cumulene moiety

SUPPORTING INFORMATION

Gold-Catalyzed Cycloisomerization of [3]-Cumulenols

Laura Ferrand,^{†,‡} Nicolas Das Neves,^{†,‡} Max Malacria,^{†,‡} Virginie Mouriès-Mansuy,^{†,‡} Cyril Ollivier^{†,‡,*}, Louis Fensterbank^{†,‡,*}

[†] Sorbonne Universités, UPMC Univ Paris 06, UMR 8232, Institut Parisien de Chimie Moléculaire, F-75252 Paris Cedex 05, France.

[‡] CNRS, UMR 8232, Institut Parisien de Chimie Moléculaire, F 75252 Paris Cedex 05, France.

Contents

1. General information	2
2. General procedures	3
3. Characterization data	4 -16
4. Spectral data	17 - 35
5. Crystal structure	36

1. General information

Unless special mention, all reactions were carried out in oven-dried glassware under argon atmosphere with magnetic stirring. All commercially available compounds were used as received when not precised. Ethylmagnesium bromide was titrated with iodine in a 0.5 M solution of lithium chloride in THF.^[13]

Purifications

THF was purified either by distillation over Na/benzophenone or with the Puresolv Micro solvent purification system, and CH₂Cl₂ was purified by distillation over CaH₂. They all were transferred under argon atmosphere.

Thin Layer Chromatography (TLC) was performed on Merck 60 F254 silica gel and revealed with either a UV lamp ($\lambda = 254$ nm) or a specific color reagent (p-anisaldehyde). Davisil LC 60 A silica gel (40-63 μ m) was used for flash chromatography.

Analyses

Melting points (m.p.) were measured on a Bibby Stuart Scientific melting point apparatus SMP3 and were uncorrected.

IR spectra were recorded on a Bruker Tensor 27 ATR diamond PIKE Spectrophotometer. Wavenumbers (ν) are given in cm⁻¹.

NMR ¹H, ¹³C, ¹⁹F spectra were recorded at 400, 100 and 376 MHz, respectively, using a Bruker AVANCE 400 MHz spectrometer equipped with a BBFO probe. Some NMR ¹H, ¹³C were recorded at 300 and 75 MHz respectively, using a Bruker AVANCE 300 MHz spectrometer. Chemical shifts (δ) are reported in ppm, using, for ¹H and ¹³C, solvent residual peak as internal standard references (CDCl₃ : ¹³C = 77.16 ppm ; Residual CHCl₃ in CDCl₃ : ¹H = 7.26 ppm) and using for ¹⁹F, trifluorotoluene as internal reference (C₆H₅CF₃ : ¹⁹F = – 63.72 ppm). Signals were attributed with the help of ¹H, ¹³C, DEPT-135, and HSQC experiments. The letters m, s, d, t, sp and q stand for multiplet, singlet, doublet, triplet, sextuplet and quartet, respectively. The letters b indicate that the signal is broad.

High resolution mass spectrometry (HRMS) analyses were performed at the IPCM on a Bruker MicroTof mass spectrometer.

2. General procedures

Typical procedure A for the synthesis of [3]-cumulenol

EtMgBr (1.0 M in THF solution, 2.5 mL, 2.5 mmol) was added to a solution of ZrCp_2Cl_2 (0.365 g, 1.25 mmol) in THF (5 mL) at -50°C . The reaction mixture was stirred for 1 h at the same temperature. Then, the diyne (1 mmol) was added and the reaction mixture was warmed to room temperature and stirred for 2 h. Distilled aldehyde (1 mmol) was added; then the reaction mixture was stirred overnight and monitored by TLC (*n*-Pentane/EtOAc) before being quenched with HCl 1M (3 mL). The aqueous layer was extracted with diethyl ether (3×10 mL). The combined organic layers were then washed with brine (3×10 mL), dried over Na_2SO_4 , filtered and the solvent was evaporated under reduced pressure at 20°C . The crude residue was finally filtered through a pad of silica gel neutralised with Na_2CO_3 to yield [3]-cumulenol. Analytical sample was purified for characterization.

Typical procedure B for the AuBr_3 -catalyzed reaction on [3]-cumulenol :

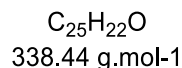
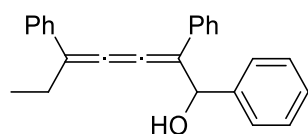
The crude [3]-cumulenol (ca. 1 mmol) was dissolved in CH_2Cl_2 (40 or 20 mL) and the solution was cooled to -78°C , before AuBr_3 (21.8 mg, 0.05 mmol) was added. The reaction mixture was warmed to room temperature and stirred overnight. Then, the mixture was filtered and the solvent was removed under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-Pentane/EtOAc) affording the pure dienyne.

Typical procedure C for the AuPPh_3OTf -catalyzed reaction on [3]-cumulenol :

A solution of AuClPPh_3 (24.7 mg, 0.05 mmol) and AgOTf (12.8 mg, 0.05 mmol) in CH_2Cl_2 (30 or 10 mL) was stirred for 5 min at room temperature and then cooled to -78°C . A solution of crude [3]-cumulenol (ca. 1 mmol) in CH_2Cl_2 (10 mL) was added and the resulting mixture was warmed to room temperature and stirred for 10 h. After completion of the reaction (monitored by TLC), the reaction mixture was filtered and the solvent was removed under reduced pressure. Purification of the residue by flash chromatography (*n*-Pentane/EtOAc) afforded the desired furan.

3. Characterization Data for the Products

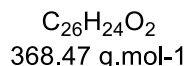
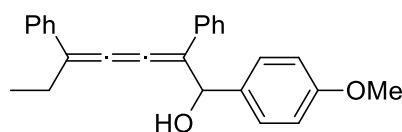
(*E*)-1,2,5-Triphenylhepta-2,3,4-trien-1-ol (**1a**)



Following general procedure **A**, using 1,4-diphenylbuta-1,3-diyne (0.202 g, 1 mmol) and distilled benzaldehyde (0.10 mL, 1 mmol), [3]-cumulenol **1a** was obtained as a brown oil.

¹H NMR (300 MHz, CDCl₃) : δ = 7.65 (2H, m), 7.55 (2H, m), 7.42-7.21 (11H, m), 5.97 (1H, s), 2.64 (2H, q, J = 7.4 Hz), 2.58 (1H, bs), 1.18 (3H, t, J = 7.3 Hz); **¹³C NMR (100 MHz, CDCl₃)** : δ = 154.8 (C), 154.6 (C), 142.6 (C), 138.5 (C), 137.3 (C), 128.7 (2 \times CH), 128.7 (2 \times CH), 128.7 (2 \times CH), 128.1 (CH), 128.0 (CH), 127.6 (CH), 127.5 (2 \times CH), 127.1 (2 \times CH), 127.0 (2 \times CH), 125.2 (C), 121.3 (C), 73.9 (CH), 26.5 (CH₂), 13.1 (CH₃). ¹H and ¹³C NMR data matched those reported in the literature.^[10]

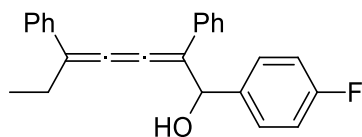
(*E*)-1-(4-Methoxyphenyl)-2,5-diphenylhepta-2,3,4-trien-1-ol (**1b**)



Following general procedure **A**, using 1,4-diphenylbuta-1,3-diyne (0.202 g, 1 mmol) and distilled *p*-anisaldehyde (0.12 mL, 1 mmol), [3]-cumulenol **1b** was obtained as a yellow oil.

¹H NMR (400 MHz, CDCl₃) : δ = 7.66 (2H, d, J = 7.2 Hz), 7.60 (2H, d, J = 7.6 Hz), 7.46 (2H, d, J = 8.4 Hz), 7.40 (2H, t, J = 7.2 Hz), 7.33-7.31 (4H, m), 6.89 (2H, d, J = 8.8 Hz), 5.90 (1H, s), 3.80 (3H, s), 2.68 (2H, q, J = 7.2 Hz), 2.55 (1H, bs), 1.23 (3H, t, J = 7.2 Hz); **¹³C NMR (100 MHz, CDCl₃)** : δ = 159.5 (C), 154.8 (C), 154.4 (C), 138.6 (C), 137.3 (C), 134.8 (C), 128.7 (4 \times CH), 128.5 (2 \times CH), 128.1 (CH), 127.6 (CH), 127.5 (2 \times CH), 127.0 (2 \times CH), 124.9 (C), 121.6 (C), 114.2 (2 \times CH), 73.5 (CH), 55.4 (CH₃), 26.5 (CH₂), 13.1 (CH₃); **HRMS (ESI)** : calcd for $C_{26}H_{24}NaO_2$ [M + Na]⁺: 391.1669; found 391.1683; **IR (ATR)** : ν = 3425, 3060, 2969, 1678, 1646, 1612, 1512, 1491, 1447, 1248, 1175, 1031, 834, 754, 691 cm⁻¹.

(E)-1-(4-Fluorophenyl)-2,5-diphenylhepta-2,3,4-trien-1-ol (1c)

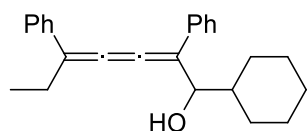


$C_{25}H_{21}FO$
356.43 g.mol⁻¹

Following general procedure **A**, using 1,4-diphenylbuta-1,3-diyne (0.202 g, 1 mmol) and 4-fluorobenzaldehyde (0.11 mL, 1 mmol), [3]-cumulenol **1c** was obtained as a yellow oil.

¹H NMR (400 MHz, CDCl₃) : δ = 7.66-7.60 (4H, m), 7.53-7.48 (2H, m), 7.42-7.23 (6H, m), 7.08-7.02 (2H, m), 5.95 (1H, s), 2.64 (2H, q, J = 7.2 Hz), 2.64 (1H, bs), 1.18 (3H, t, J = 7.2 Hz); **¹³C NMR (100 MHz, CDCl₃)** : δ = 162.6 (C, d, J = 245 Hz), 154.8 (C), 154.5 (C), 138.4 (C), 138.3 (C, d, J = 4.0 Hz), 137.1 (C), 128.9 (2 \times CH, d, J = 9.0 Hz), 128.8 (2 \times CH), 128.7 (2 \times CH), 128.2 (CH), 127.8 (CH), 127.5 (2 \times CH), 127.1 (2 \times CH), 125.6 (C), 121.0 (C), 115.5 (2 \times CH, d, J = 21.0 Hz), 73.3 (CH), 26.5 (CH₂), 13.0 (CH₃); **¹⁹F NMR (376 MHz, CDCl₃)** : δ = -115.7; **HRMS (ESI)** : calcd for $C_{25}H_{21}FNaO$ [M + Na]⁺: 379.1469; found 379.1478; **IR (ATR)** : ν = 3380, 3059, 2970, 1684, 1647, 1601, 1509, 1491, 1448, 1221, 1157, 841, 754, 690 cm⁻¹.

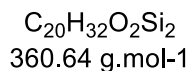
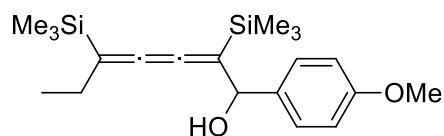
(E)-1-Cyclohexyl-2,5-diphenylhepta-2,3,4-trien-1-ol (1d)



$C_{25}H_{28}O$
344.49 g.mol⁻¹

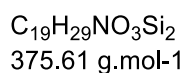
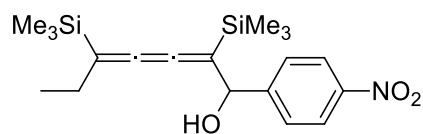
Following general procedure **A**, using 1,4-diphenylbuta-1,3-diyne (0.202 g, 1 mmol) and distilled cyclohexane carboxaldehyde (0.12 mL, 1 mmol), [3]-cumulenol **1d** was obtained as a yellow oil.

¹H NMR (400 MHz, CDCl₃) : δ = 7.64 (4H, dd, J = 8.4, 1.2 Hz), 7.41-7.36 (4H, m), 7.29 (1H, bt, J = 1.2 Hz), 7.27 (1H, bt, J = 1.6 Hz), 4.66 (1H, bd, J = 5.6 Hz), 2.77 (2H, qd, J = 7.2, 2.0 Hz), 2.11-1.91 (2H, m), 1.85-1.59 (6H, m), 1.37 (3H, t, J = 7.2 Hz), 1.32-1.10 (6H, m); **¹³C NMR (100 MHz, CDCl₃)** : δ = 154.6 (C), 153.5 (C), 138.7 (C), 138.0 (C), 128.8 (2 \times CH), 128.7 (2 \times CH), 127.9 (CH), 127.7 (CH), 127.5 (2 \times CH), 126.9 (2 \times CH), 123.8 (C), 122.1 (C), 75.9 (CH), 43.6 (CH), 30.4 (CH₂), 27.4 (CH₂), 26.6 (CH₂), 26.5 (CH₂), 26.4 (CH₂), 26.2 (CH₂), 13.2 (CH₃); **HRMS (ESI)** : calcd for $C_{25}H_{28}NaO$ [M + Na]⁺: 367.2032; found 367.2025; **IR (ATR)** : ν = 3440, 3059, 2930, 1650, 1595, 1492, 1448, 1262, 1077, 754, 690 cm⁻¹.

(Z)-1-(4-Methoxyphenyl)-2,5-bis(trimethylsilyl)hepta-2,3,4-trien-1-ol (1e)

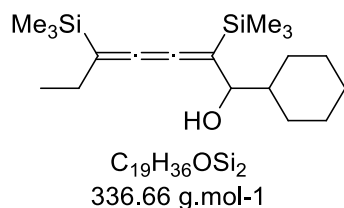
Following general procedure **A**, using 1,4-bis(trimethylsilyl)buta-1,3-diyne (0.198 g, 1 mmol) and distilled *p*-anisaldehyde (0.12 mL, 1 mmol), [3]-cumulenol **1e** was obtained as a yellow oil.

¹H NMR (400 MHz, CDCl₃) : δ = 7.29 (2H, d, J = 8.6 Hz), 6.87 (2H, d, J = 8.6 Hz), 5.34 (1H, d, J = 5.2 Hz), 3.79 (3H, s), 2.86 (1H, d, J = 5.4 Hz), 2.37 (2H, q, J = 7.2 Hz), 1.12 (3H, t, J = 7.2 Hz), 0.21 (9H, s), 0.04 (9H, s); **¹³C NMR (100 MHz, CDCl₃)** : δ = 170.8 (C), 170.0 (C), 159.4 (C), 135.3 (C), 134.0 (C), 130.3 (C), 128.8 (2 × CH), 113.9 (2 × CH), 75.8 (CH), 55.3 (CH₃), 29.0 (CH₂), 13.5 (CH₃), −0.6 (3 × CH₃), −1.3 (3 × CH₃). ¹H and ¹³C NMR data matched those reported in the literature.^[10]

(Z)-1-(4-Nitrophenyl)-2,5-bis(trimethylsilyl)hepta-2,3,4-trien-1-ol (1f)

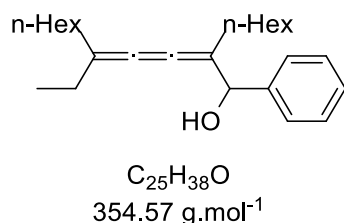
Following general procedure **A**, using 1,4-bis(trimethylsilyl)buta-1,3-diyne (0.198 g, 1 mmol) and 4-nitrobenzaldehyde 98 % (0.153g, 1 mmol), [3]-cumulenol **1f** was obtained as a yellow oil.

¹H NMR (300 MHz, CDCl₃) : δ = 8.20 (2H, d, J = 8.7 Hz), 7.54 (2H, d, J = 8.7 Hz), 5.50 (1H, d, J = 4.9 Hz), 2.80 (1H, d, J = 5.1 Hz), 2.34 (2H, q, J = 7.2 Hz), 1.02 (3H, t, J = 7.2 Hz), 0.19 (9H, s), 0.09 (9H, s); **¹³C NMR (75 MHz, CDCl₃)** : δ = 173.5 (C), 169.7 (C), 150.6 (C), 147.5 (C), 137.5 (C), 128.0 (2 × CH), 127.9 (C), 123.7 (2 × CH), 75.6 (CH), 29.3 (CH₂), 13.37 (CH₃), −0.42 (3 × CH₃), −1.27 (3 × CH₃). ¹H and ¹³C NMR data matched those reported in the literature.^[10]

(Z)-1-Cyclohexyl-2,5-bis(trimethylsilyl)hepta-2,3,4-trien-1-ol (1g)

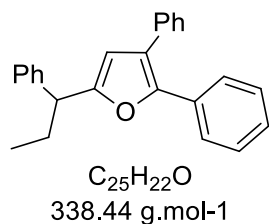
Following general procedure **A**, using 1,4-bis(trimethylsilyl)buta-1,3-diyne (0.198 g, 1 mmol) and distilled cyclohexane carboxaldehyde (0.12 mL, 1 mmol), [3]-cumulenol **1g** was obtained as a yellow oil.

¹H NMR (400 MHz, CDCl₃) : δ = 4.16 (1H, m), 2.36 (2H, qd, J = 7.2, 1.2 Hz), 2.06 (1H, d, J = 6.8 Hz), 1.78-1.61 (5H, m), 1.60-1.53 (1H, m), 1.35-0.97 (5H, m), 1.13 (3H, t, J = 7.2 Hz), 0.19 (9H, s), 0.18 (9H, s); **¹³C NMR (100 MHz, CDCl₃)** : δ = 171.1 (C), 170.9 (C), 133.6 (C), 130.4 (C), 78.2 (CH), 44.1 (CH), 30.8 (CH₂), 29.0 (CH₂), 26.8 (CH₂), 26.6 (CH₂), 26.4 (CH₂), 26.2 (CH₂), 13.5 (CH₃), -0.5 (3 \times CH₃), -1.2 (3 \times CH₃); **HRMS (ESI)** : calcd for C₁₉H₃₆NaOSi₂ [M + Na]⁺: 359.2197; found 359.2203; **IR (ATR)** : ν = 3460, 2924, 1677, 1586, 1245, 833 cm⁻¹.

(E)-5-Ethyl-2-hexyl-1-phenylundeca-2,3,4-trien-1-ol (1h)

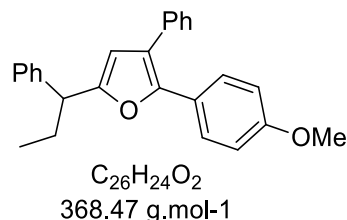
Following general procedure **A**, using 7,9-hexadecadiyne (0.26 mL, 1 mmol) and distilled benzaldehyde (0.10 mL, 1 mmol), [3]-cumulenol **1a** was obtained as a yellow oil. Purification by flash chromatography for characterization afforded the [3]-cumulenol as a white solid.

m.p. = 44 °C; **¹H NMR (400 MHz, CDCl₃)** : δ = 7.40-7.32 (4H, m), 7.27 (1H, m), 5.15 (1H, bd, J = 4.4 Hz), 2.60 (1H, d, J = 4.8 Hz), 2.21-2.17 (4H, m), 2.03 (2H, m), 1.60-1.49 (4H, m), 1.41-1.17 (12H, m), 1.11 (3H, t, J = 7.6 Hz), 0.93-0.82 (6H, m); **¹³C NMR (100 MHz, CDCl₃)** : δ = 156.7 (C), 154.7 (C), 142.6 (C), 128.5 (2 \times CH), 127.8 (CH), 127.0 (2 \times CH), 123.8 (C), 119.7 (C), 76.3 (CH), 36.4 (CH₂), 32.0 (CH₂), 31.9 (2 \times CH₂), 29.5 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 28.0 (CH₂), 27.9 (CH₂), 22.8 (CH₂), 22.7 (CH₂), 14.2 (2 \times CH₃), 12.5 (CH₃); **HRMS (ESI)** : calcd for C₂₅H₃₈NaO [M + Na]⁺: 377.2815; found 377.2802; **IR (ATR)** : ν = 3375, 3029, 2927, 1620, 1467, 1039, 764, 700 cm⁻¹.

2,3-Diphenyl-5-(1-phenylpropyl)furan (2a)

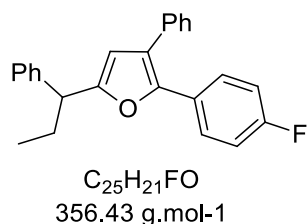
Following general procedure **C** on [3]-cumulenol **1a** in CH₂Cl₂ (40 mL), the furan **2a** was obtained after flash chromatography on silica gel (*n*-Pentane/EtOAc, 99/1 to 98/2) as a yellow oil (0.199 g, 0.59 mmol, 59 %).

¹H NMR (400 MHz, CDCl₃) : δ = 7.59-7.56 (2H, m), 7.49-7.46 (2H, m), 7.43-7.7.37 (6H, m), 7.35-7.29 (4H, m), 7.25 (1H, m), 6.26 (1H, d, J = 0.8 Hz), 3.97 (1H, t, J = 7.7 Hz), 2.32 (1H, m), 2.07 (1H, m), 1.05 (3H, t, J = 7.2 Hz) ; **¹³C NMR (100 MHz, CDCl₃)** : δ = 157.4 (C), 147.2 (C), 142.6 (C), 134.8 (C), 131.6 (C), 128.8 (2 \times CH), 128.7 (2 \times CH), 128.6 (2 \times CH), 128.4 (2 \times CH), 128.2 (2 \times CH), 127.2 (CH), 127.1 (CH), 126.7 (CH), 126.1 (2 \times CH), 123.0 (C), 110.1 (CH), 47.4 (CH), 28.1 (CH₂), 12.6 (CH₃) ; **HRMS (ESI)** : calcd for C₂₅H₂₂NaO [M + Na]⁺: 361.1563; found 361.1585 ; **IR (ATR)** : ν = 3028, 2964, 1600, 1553, 1503, 1451, 1253, 763, 696 cm⁻¹.

2-(4-Methoxyphenyl)-3-phenyl-5-(1-phenylpropyl)furan (2b)

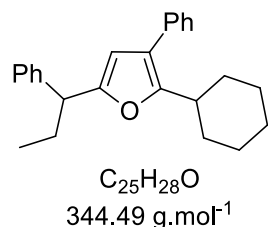
Following general procedure **C** on [3]-cumulenol **1b** in CH₂Cl₂ (40 mL), the furan **2b** was obtained after flash chromatography on silica gel (*n*-Pentane/EtOAc, 98/2) as a yellow oil (0.173 mg, 0.47 mmol, 47 %).

¹H NMR (400 MHz, CDCl₃) : δ = 7.47-7.40 (4H, m), 7.39-7.32 (6H, m), 7.30-7.25 (2H, m), 7.25 (12H, m), 6.84 (2H, d, J = 8.8 Hz), 6.21 (1H, d, J = 0.8 Hz), 3.91 (1H, bt, J = 7.6 Hz), 3.81 (3H, s), 2.27 (1H, m), 2.02 (1H, m), 1.00 (3H, t, J = 7.6 Hz) ; **¹³C NMR (100 MHz, CDCl₃)** : δ = 159.0 (C), 156.8 (C), 147.3 (C), 142.7 (C), 135.0 (C), 128.7 (2 \times CH), 128.6 (4 \times CH), 128.2 (2 \times CH), 127.7 (2 \times CH), 126.9 (CH), 126.7 (CH), 124.5 (C), 121.5 (C), 113.9 (2 \times CH), 109.7 (CH), 55.4 (CH₃), 47.4 (CH), 28.1 (CH₂), 12.6 (CH₃) ; **HRMS (ESI)** : calcd for C₂₆H₂₄NaO₂ [M + Na]⁺: 391.1669; found 391.1661 ; **IR (ATR)** : ν = 3028, 2962, 1598, 1511, 1463, 1248, 832, 729, 698 cm⁻¹.

2-(4-Fluorophenyl)-3-phenyl-5-(1-phenylpropyl)furan (2c)

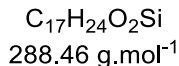
Following general procedure **C** on [3]-cumulenol **1c** in CH₂Cl₂ (40 mL), the furan **2c** was obtained after flash chromatography on silica gel (*n*-Pentane/EtOAc, 99/1 to 98/2) as a yellow oil (0.203 g, 0.57 mmol, 57 %).

¹H NMR (400 MHz, CDCl₃) : δ = 7.44 (2H, m), 7.39-7.22 (10H, m), 6.95 (2H, m), 6.18 (1H, d, *J* = 0.6 Hz), 3.88 (1H, t, *J* = 7.7 Hz), 2.23 (1H, m), 1.99 (1H, m), 0.97 (3H, t, *J* = 7.4 Hz) ; **¹³C NMR (100 MHz, CDCl₃)** : δ = 162.0 (C, d, *J* = 246 Hz), 157.4 (C), 146.3 (C), 142.4 (C), 134.6 (C), 128.7 (2 × CH), 128.7 (2 × CH), 128.6 (2 × CH), 128.2 (2 × CH), 127.9 (2 × CH, d, *J* = 8 Hz), 127.8 (C, d, *J* = 3 Hz), 127.2 (CH), 126.8 (CH), 122.7 (C), 115.4 (2 × CH, d, *J* = 21 Hz), 110.0 (CH), 47.4 (CH), 28.1 (CH₂), 12.6 (CH₃) ; **¹⁹F NMR (376 MHz, CDCl₃)** : δ = -115.4 ; **HRMS (ESI)** : calcd for C₂₅H₂₁FKO [*M* + K]⁺: 395.1208; found 395.1198 ; **IR (ATR)** : ν = 3029, 2964, 1602, 1555, 1510, 1489, 1451, 1235, 1158, 838, 764, 699 cm⁻¹.

2-Cyclohexyl-3-phenyl-5-(1-phenylpropyl)furan (2d)

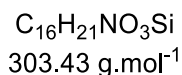
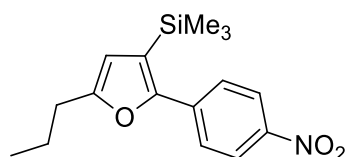
Following general procedure **C** on [3]-cumulenol **1d** in CH₂Cl₂ (40 mL), the furan **2d** was obtained after flash chromatography on silica gel (*n*-Pentane/EtOAc, 98/2) as a yellow oil (0.203 g, 0.59 mmol, 59 %).

¹H NMR (400 MHz, CDCl₃) : δ = 7.38-7.17 (10H, m), 6.06 (1H, s), 3.81 (1H, t, *J* = 7.6 Hz), 2.84 (1H, tt, *J* = 11.9, 3.3 Hz), 2.17 (1H, m), 2.0-1.74 (5H, m), 1.74-1.52 (3H, m), 1.24-1.33 (3H, m), 0.93 (3H, t, *J* = 7.2 Hz) ; **¹³C NMR (100 MHz, CDCl₃)** : δ = 155.6 (C), 154.5 (C), 143.1 (C), 135.0 (C), 128.6 (2 × CH), 128.5 (2 × CH), 128.2 (2 × CH), 128.0 (2 × CH), 126.5 (CH), 126.2 (CH), 119.8 (C), 107.2 (CH), 47.4 (CH), 36.5 (CH), 32.1 (CH₂), 32.0 (CH₂), 28.3 (CH₂), 26.6 (CH₂), 26.5 (CH₂), 26.1 (CH₂), 12.6 (CH₃) ; **HRMS (ESI)** : calcd for C₂₅H₂₉O [*M* + H]⁺: 345.2213; found 345.2211 ; **IR (ATR)** : ν = 3028, 2929, 2853, 1600, 1560, 1494, 1449, 1219, 976, 763, 698 cm⁻¹.

(2-(4-Methoxyphenyl)-5-propylfuran-3-yl)trimethylsilane (2e)

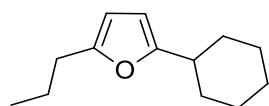
Following general procedure **C** on [3]-cumulenol **1e** in CH_2Cl_2 (20 mL), the furan **2e** was obtained after flash chromatography on silica gel (*n*-Pentane/EtOAc, 98/2) as a yellow oil corresponding to an inseparable mixture with dienyne **3e** (0.173 g, 0.55 mmol, 55 % with a ratio **2e/3e** of 50/50).

^1H NMR (400 MHz, CDCl_3) : δ = 7.52 (2H, d, J = 8.8 Hz), 6.93 (2H, d, J = 8.4 Hz), 6.04 (1H, d, J = 1.2 Hz), 3.85 (3H, s), 2.65 (2H, t, J = 7.6 Hz), 1.73 (2H, sp, J = 7.2 Hz), 1.02 (3H, t, J = 7.2 Hz), 0.24 (9H, s) ; **^{13}C NMR (100 MHz, CDCl_3)** : δ = 159.2 (C), 157.1 (C), 155.3 (C), 130.4 (C), 128.6 (2 \times CH), 126.0 (C), 113.7 (2 \times CH), 111.7 (CH), 55.4 (CH_3), 30.1 (CH_2), 21.6 (CH_2), 14.1 (CH_3), 0.1 (3 \times CH_3) ; **HRMS (ESI)** : calcd for $\text{C}_{17}\text{H}_{25}\text{O}_2\text{Si}$ [$M + \text{H}$] $^+$: 289.1618 ; found 289.1623.

Trimethyl(2-(4-nitrophenyl)-5-propylfuran-3-yl)silane (2f)

Following general procedure **C** on [3]-cumulenol **1f** in CH_2Cl_2 (20 mL), the furan **2f** was obtained after flash chromatography on silica gel (*n*-Pentane/EtOAc, 98/2) as a yellow oil (0.109 g, 0.36 mmol, 36 %).

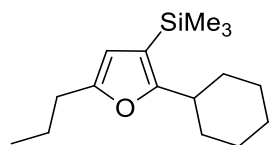
^1H NMR (400 MHz, CDCl_3) : δ = 8.26 (2H, d, J = 8.8 Hz), 7.77 (2H, d, J = 8.8 Hz), 6.16 (1H, t, J = 0.8 Hz), 2.70 (2H, t, J = 7.2 Hz), 1.76 (2H, sp, J = 7.6 Hz), 1.04 (3H, t, J = 7.4 Hz), 0.33 (9H, s) ; **^{13}C NMR (100 MHz, CDCl_3)** : δ = 157.9 (C), 154.1 (C), 146.3 (C), 138.7 (C), 126.4 (2 \times CH), 123.9 (2 \times CH), 120.2 (C), 113.5 (CH), 30.0 (CH_2), 21.5 (CH_2), 14.0 (CH_3), -0.1 (3 \times CH_3) ; **HRMS (ESI)** : calcd for $\text{C}_{16}\text{H}_{21}\text{LiNO}_3\text{Si}$ [$M + \text{Li}$] $^+$: 310.1446; found 310.1453 ; **IR (ATR)** : ν = 2960, 1598, 1579, 1513, 1333, 1251, 1109, 836, 753, 696 cm^{-1} .

2-Cyclohexyl-5-propylfuran (2g)

$C_{13}H_{20}O$
192.30 g.mol⁻¹

Following general procedure **B** on [3]-cumulenol **1g** in CH₂Cl₂ (20 mL), the furan **2g** was obtained after flash chromatography on silica gel (*n*-Pentane to *n*-Pentane/EtOAc, 98/2) as a yellowish oil corresponding to a mixture with dienyne **3g** (0.198 g, 0.69 mmol, 69 % with a ratio **2g/3g** of 23/77).

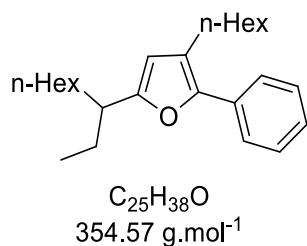
¹H NMR (400 MHz, CDCl₃) : δ = 5.85 (1H, d, J = 2.8 Hz), 5.81 (1H, d, J = 2.8 Hz), 2.60-2.53 (3H, m), 2.07-1.95 (2H, m), 1.82-1.59 (5H, m), 1.42-1.21 (5H, m), 0.95 (3H, t, J = 7.4 Hz) ; **¹³C NMR (100 MHz, CDCl₃)** : δ = 159.4 (C), 154.4 (C), 104.9 (CH), 102.9 (CH), 37.4 (CH), 31.8 (2 × CH₂), 30.3 (CH₂), 26.3 (CH₂), 26.1 (2 × CH₂), 21.6 (CH₂), 13.9 (CH₃) **IR (ATR)** : ν = 2928, 1564, 1450, 1248cm⁻¹.

(2-Cyclohexyl-5-propylfuran-3-yl)trimethylsilane (2g')

$C_{16}H_{28}OSi$
264.48 g.mol⁻¹

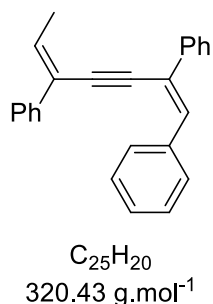
Following general procedure **C** on [3]-cumulenol **1g** in CH₂Cl₂ (20 mL), the furan **2g'** was obtained after flash chromatography on silica gel (*n*-Pentane) as a yellowish oil (0.132 g, 0.50 mmol, 50 %).

¹H NMR (400 MHz, CDCl₃) : δ = 5.81 (1H, t, J = 0.9 Hz), 2.63 – 2.53 (3H, m), 1.85-1.60 (9H, m), 1.35-1.28 (3H, m), 0.98 (3H, t, J = 7.4 Hz), 0.21 (9H, s) ; **¹³C NMR (100 MHz, CDCl₃)** : δ = 163.8 (C), 154.1 (C), 110.9 (C), 109.0 (CH), 39.2 (CH), 32.5 (2 × CH₂), 30.1 (CH₂), 26.8 (2 × CH₂), 26.1 (CH₂), 21.6 (CH₂), 14.1 (CH₃), 0.1 (3 × CH₃) ; **IR (ATR)** : ν = 2958, 2930, 2852, 1552, 1450, 1247cm⁻¹.

3-Hexyl-5-(nonan-3-yl)-2-phenylfuran (2h)

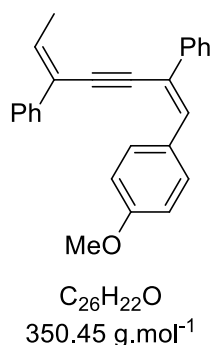
Following general procedure **C** on [3]-cumulenol **1h** in CH₂Cl₂ (20 mL), the furan **2h** was obtained after flash chromatography on silica gel (*n*-Pentane) as a yellow oil (0.185 g, 0.52 mmol, 52 %).

¹H NMR (400 MHz, CDCl₃) : δ = 7.58 (2H, d, J = 8.0 Hz), 7.38 (2H, t, J = 7.6 Hz), 7.21 (1H, t, J = 7.2 Hz), 5.97 (1H, s), 2.65-2.55 (3H, m), 1.69-1.60 (6H, m), 1.45-1.23 (14H, m), 0.91-0.86 (9H, m) ; **¹³C NMR (100 MHz, CDCl₃)** : δ = 157.9 (C), 146.3 (C), 132.6 (C), 128.6 (2 \times CH), 126.2 (CH), 125.2 (2 \times CH), 122.4 (C), 109.1 (CH), 40.8 (CH), 33.8 (CH₂), 32.0 (CH₂), 31.9 (CH₂), 30.1 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 27.5 (CH₂), 27.2 (CH₂), 26.3 (CH₂), 22.8 (2 \times CH₂), 14.2 (2 \times CH₃), 12.0 (CH₃) ; **HRMS (ESI)** : calcd for C₂₅H₃₈NaO [M + Na]⁺: 377.2815; found 377.2828 ; **IR (ATR)** : ν = 3060, 2927, 1599, 1552, 1491, 1465, 1069, 761, 692 cm⁻¹.

(1Z,5Z)-Hepta-1,5-dien-3-yne-1,2,5-triyltribenzene (3a)

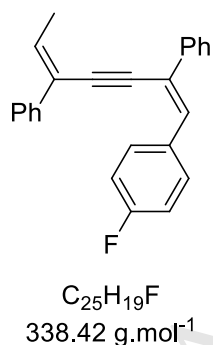
Following general procedure **B** on [3]-cumulenol **1a** in CH₂Cl₂ (40 mL), the dienyne **3a** was obtained after flash chromatography on silica gel (*n*-Pentane/EtOAc, 95/5) as a yellowish solid (0.189 g, 0.59 mmol, 59 %).

m.p. = 88 °C ; **¹H NMR (400 MHz, CDCl₃)** : δ = 8.01 (2H, d, J = 7.2 Hz), 7.80 (2H, d, J = 7.6 Hz), 7.63 (2H, d, J = 7.6 Hz), 7.41 (2H, t, d, J = 7.2 Hz), 7.36-7.26 (7H, m), 7.21 (1H, s), 6.54 (1H, q, J = 6.8 Hz), 2.15 (3H, d, J = 7.1 Hz) ; **¹³C NMR (100 MHz, CDCl₃)** : δ = 140.2 (C), 138.5 (C), 136.8 (C), 134.8 (CH), 134.3 (CH), 129.2 (2 \times CH), 128.6 (2 \times CH), 128.5 (2 \times CH), 128.4 (3 \times CH), 128.0 (CH), 127.6 (CH), 126.8 (2 \times CH), 126.3 (2 \times CH), 125.1 (C), 122.4 (C), 94.8 (C), 94.6 (C), 17.2 (CH₃) ; **HRMS (ESI)** : calcd for C₂₅H₂₀Na [M + Na]⁺: 343.1457; found 343.1455 ; **IR (ATR)** : ν = 3060, 1595, 1488, 1447, 760, 689 cm⁻¹.

((1Z,5Z)-1-(4-Methoxyphenyl)hepta-1,5-dien-3-yne-2,5-diyl)dibenzene (3b)

Following general procedure **B** on [3]-cumulenol **1b** in CH₂Cl₂ (40 mL), the dienyne **3b** was obtained after flash chromatography on silica gel (*n*-Pentane to *n*-Pentane/EtOAc 95/5) as an orange oil (0.157 g, 0.45 mmol, 45 %). Suitable X-ray crystals were obtained by crystallization in *n*-Pentane.

m.p. = 114 °C ; **¹H NMR (400 MHz, CDCl₃)** : δ = 8.01 (2H, d, *J* = 8.4 Hz), 7.81 (2H, d, *J* = 7.2 Hz), 7.67 (2H, d, *J* = 7.2 Hz), 7.49-7.28 (6H, m), 7.17 (1H, s), 6.89 (2H, d, *J* = 8.8 Hz), 6.55 (1H, q, *J* = 7.2 Hz), 3.85 (3H, s), 2.18 (3H, d, *J* = 7.2 Hz) ; **¹³C NMR (100 MHz, CDCl₃)** : δ 159.8 (C), 140.4 (C), 138.6 (C), 134.4 (CH), 133.9 (CH), 130.7 (2 × CH), 129.7 (C), 128.6 (2 × CH), 128.5 (2 × CH), 127.7 (CH), 127.6 (CH), 126.6 (2 × CH), 126.4 (2 × CH), 125.2 (C), 120.0 (C), 113.8 (2 × CH), 94.9 (C), 94.4 (C), 55.4 (CH₃), 17.3 (CH₃) ; **HRMS (ESI)** : calcd for C₂₆H₂₃O [*M* + H]⁺: 351.1743; found 351.1750 ; **IR (ATR)** : ν = 3005, 2902, 2835, 1600, 1505, 1446, 1244, 864, 832, 802, 765, 750, 692 cm⁻¹.

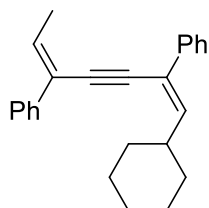
((1Z,5Z)-1-(4-Fluorophenyl)hepta-1,5-dien-3-yne-2,5-diyl)dibenzene (3c)

Following general procedure **B** on [3]-cumulenol **1c** in CH₂Cl₂ (40 mL), the dienyne **3c** was obtained after flash chromatography on silica gel (*n*-Pentane to *n*-Pentane/EtOAc, 95/5) as a white solid (0.136 g, 0.38 mmol, 38 %).

m.p. = 94 °C ; **¹H NMR (300 MHz, CDCl₃)** : δ = 7.97 (2H, dd, *J* = 8.7, 5.4 Hz), 7.78 (2H, d, *J* = 7.2 Hz), 7.59 (2H, d, *J* = 6.9 Hz), 7.43-7.29 (6H, m), 7.15 (1H, s), 7.01 (2H, t, *J* = 8.7 Hz), 6.54 (1H, q, *J* = 6.9 Hz), 2.14 (3H, d, *J* = 6.9 Hz) ; **¹³C NMR (100 MHz, CDCl₃)** : δ = 162.5 (C, d, *J* = 248 Hz) , 140.0 (C), 138.4 (C), 134.4 (CH), 133.4 (CH), 133.0 (C, d, *J* = 3 Hz),

131.0 (2 × CH, d, $J = 8.0$ Hz), 128.6 (2 × CH), 128.5 (2 × CH), 128.1 (CH), 127.7 (CH), 126.7 (2 × CH), 126.3 (2 × CH), 125.0 (C), 122.1 (C, d, $J = 2.0$ Hz), 115.3 (2 × CH, d, $J = 22.0$ Hz), 94.8 (C), 94.4 (C), 17.2 (CH₃) ; **¹⁹F NMR (376 MHz, CDCl₃)** : $\delta = -113.3$; **HRMS (ESI)** : calcd for C₂₅H₁₉FNa [$M + Na$]⁺: 361.1363; found 361.1366 ; **IR (ATR)** : $\nu = 3034, 2940, 1599, 1507, 1448, 1233, 1159, 830, 759, 693$ cm⁻¹.

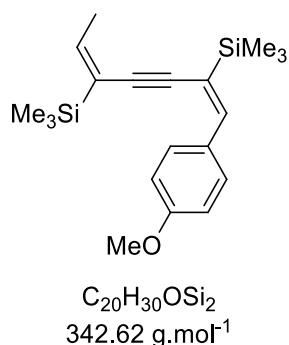
((1Z,5Z)-1-Cyclohexylhepta-1,5-dien-3-yne-2,5-diyl)dibenzene (3d)



C₂₅H₂₆
326.47 g.mol⁻¹

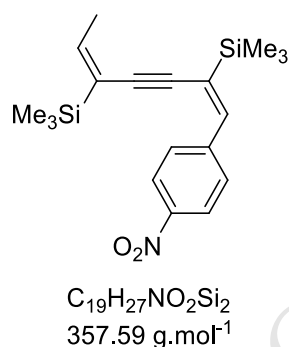
Following general procedure **B** on [3]-cumulenol **1d** in CH₂Cl₂ (40 mL), the dienyne **3d** was obtained after flash chromatography on silica gel (*n*-Pentane to *n*-Pentane/EtOAc, 95/5) as a yellowish oil (0.183 g, 0.56 mmol, 56 %).

¹H NMR (400 MHz, CDCl₃) : $\delta = 7.67$ (4H, m), 7.37-7.27 (6H, m), 6.54 (1H, q, $J = 7.2$ Hz), 6.31 (1H, d, $J = 9.3$ Hz), 2.91 (1H, m), 2.18 (3H, d, $J = 7.2$ Hz), 1.91-1.70 (5H, m), 1.43-1.20 (5H, m) ; **¹³C NMR (75 MHz, CDCl₃)** : $\delta = 144.1$ (CH), 138.7 (2 × C), 132.8 (CH), 128.5 (4 × CH), 127.5 (2 × CH), 126.2 (2 × CH), 126.1 (2 × CH), 125.1 (C), 122.2 (C), 93.4 (C), 92.3 (C), 40.7 (CH), 32.7 (2 × CH₂), 26.2 (CH₂), 26.0 (2 × CH₂), 17.2 (CH₃) ; **HRMS (ESI)** : calcd for C₂₅H₂₆Na [$M + Na$]⁺: 349.1927; found 349.1922 ; **IR (ATR)** : $\nu = 3028, 2923, 1598, 1493, 1447, 758, 692$ cm⁻¹.

((1E,5E)-1-(4-Methoxyphenyl)hepta-1,5-dien-3-yne-2,5-diyl)bis(trimethylsilane) (3e)

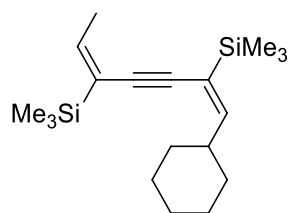
Following general procedure **C** on [3]-cumulenol **1e** in CH₂Cl₂ (20 mL), the diyne **3e** was obtained after flash chromatography on silica gel (*n*-Pentane/EtOAc, 98/2) as a yellow oil corresponding to an inseparable mixture with furan **2e** (0.173 g, 0.55 mmol, 55 % with a ratio **2e/3e** of 50/50).

¹H NMR (400 MHz, CDCl₃) : δ = 7.99 (2H, d, J = 8.4 Hz), 6.87 (2H, d, J = 8.4 Hz), 6.73 (1H, s), 6.23 (1H, q, J = 6.6 Hz), 3.83 (1H, s), 2.04 (3H, d, J = 6.8 Hz), 0.27 (9H, s), 0.21 (9H, s) ; **¹³C NMR (75 MHz, CDCl₃)** ; δ = 159.6 (C), 144.4 (CH), 141.7 (CH), 131.3 (C), 130.4 (2 \times CH), 126.7 (C), 121.9 (C), 113.6 (2 \times CH), 100.2 (C), 98.4 (C), 55.4 (CH₃), 18.6 (CH₃), -1.53 (6 \times CH₃). ¹H and ¹³C NMR data matched those reported in the literature. ^[2]

((1E,5E)-1-(4-Nitrophenyl)hepta-1,5-dien-3-yne-2,5-diyl)bis(trimethylsilane) (3f)

Following general procedure **B** on [3]-cumulenol **1f** in CH₂Cl₂ (20 mL), the diyne **3f** was obtained after flash chromatography on silica gel (*n*-Pentane to *n*-Pentane/EtOAc, 98/2) as a yellow oil corresponding to a mixture with furan **2f** (0.170 g, 0.52 mmol, 52 % with a ratio **3f/2f** of 38/62).

¹H NMR (400 MHz, CDCl₃) : δ = 8.20-8.15 (2H, m), 8.14-8.08 (2H, m), 6.81 (1H, s), 6.28 (1H, q, J = 6.6 Hz), 2.01 (3H, d, J = 6.6 Hz), 0.29 (9H, s), 0.19 (9H, s) ; **¹³C NMR (100 MHz, CDCl₃)** : δ = 146.7 (C), 145.8 (CH), 143.8 (C), 139.0 (CH), 131.6 (C), 129.1 (2 \times CH), 126.1 (C), 123.6 (2 \times CH), 104.3 (C), 97.4 (C), 18.7 (CH₃), -0.2 (3 \times CH₃), -0.2 (3 \times CH₃). ¹H and ¹³C NMR data matched those reported in the literature. ^[2]

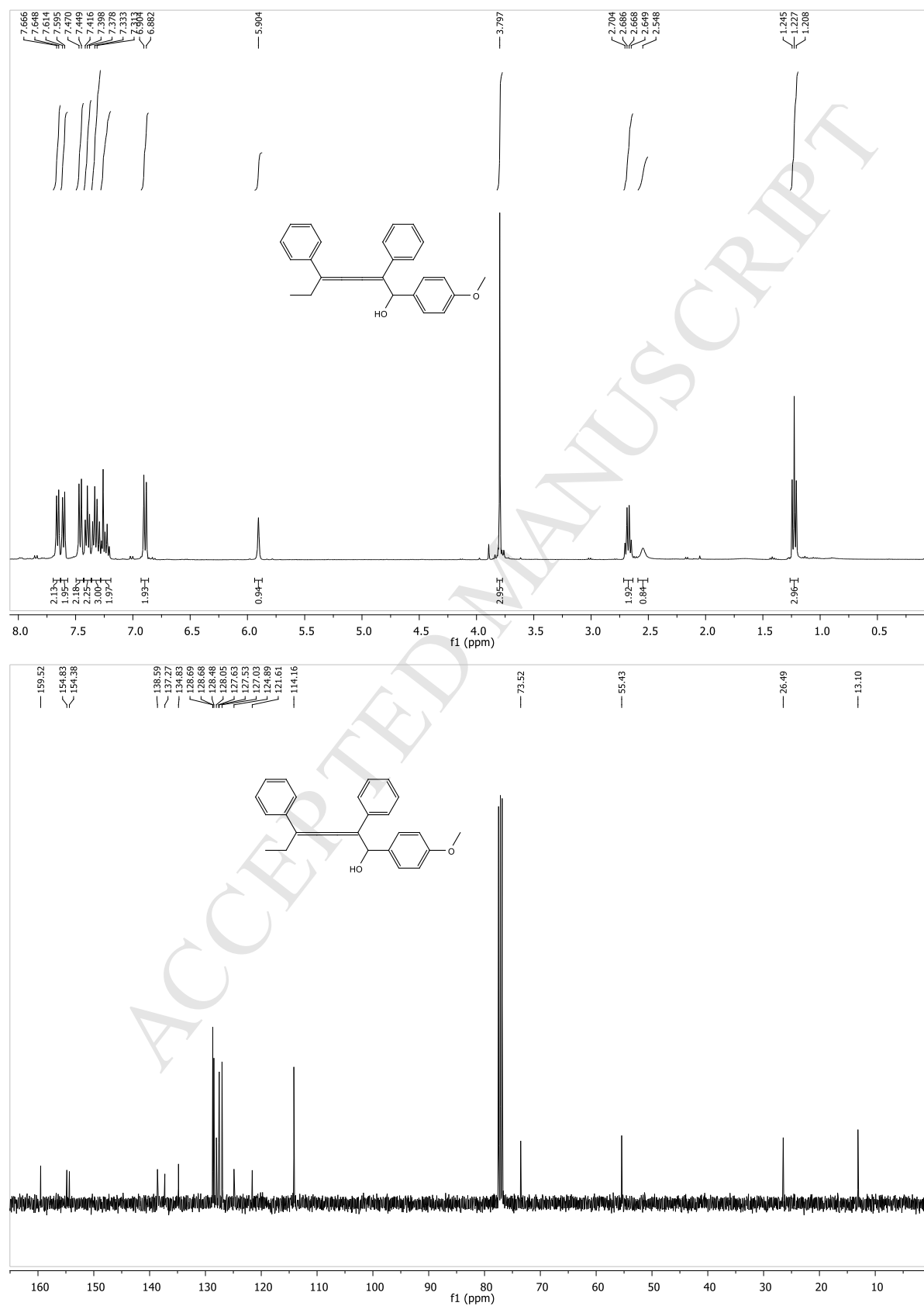
((1E,5E)-1-Cyclohexylhepta-1,5-dien-3-yne-2,5-diyl)bis(trimethylsilane) (3g)

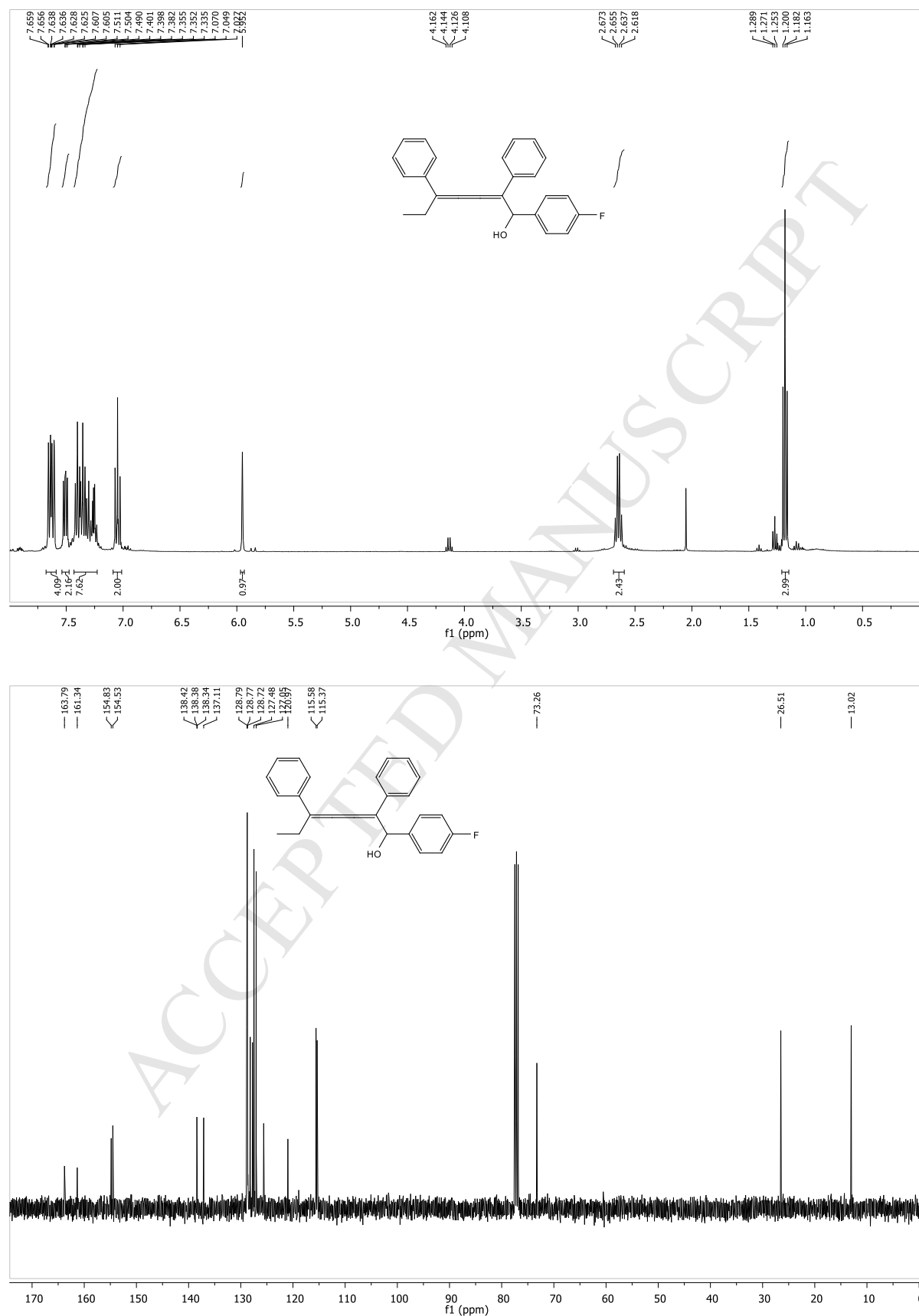
$C_{19}H_{34}Si_2$
318.64 g.mol⁻¹

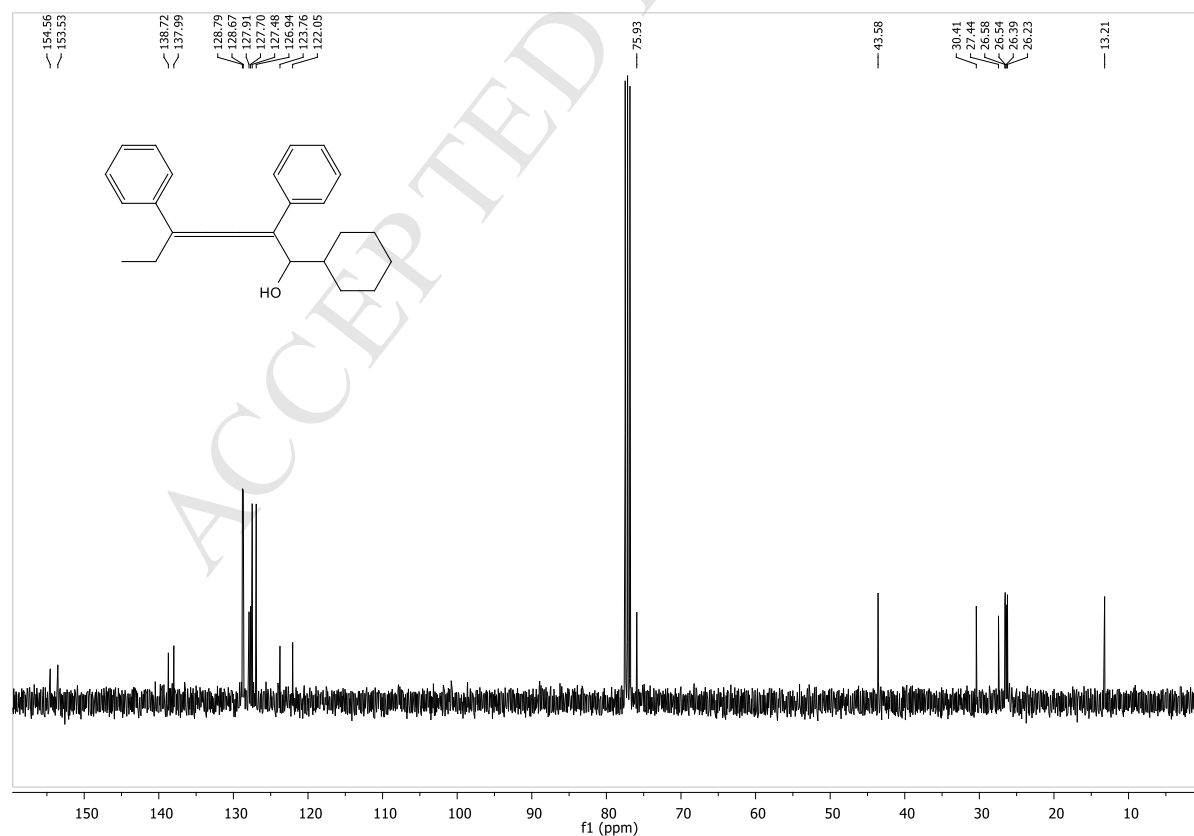
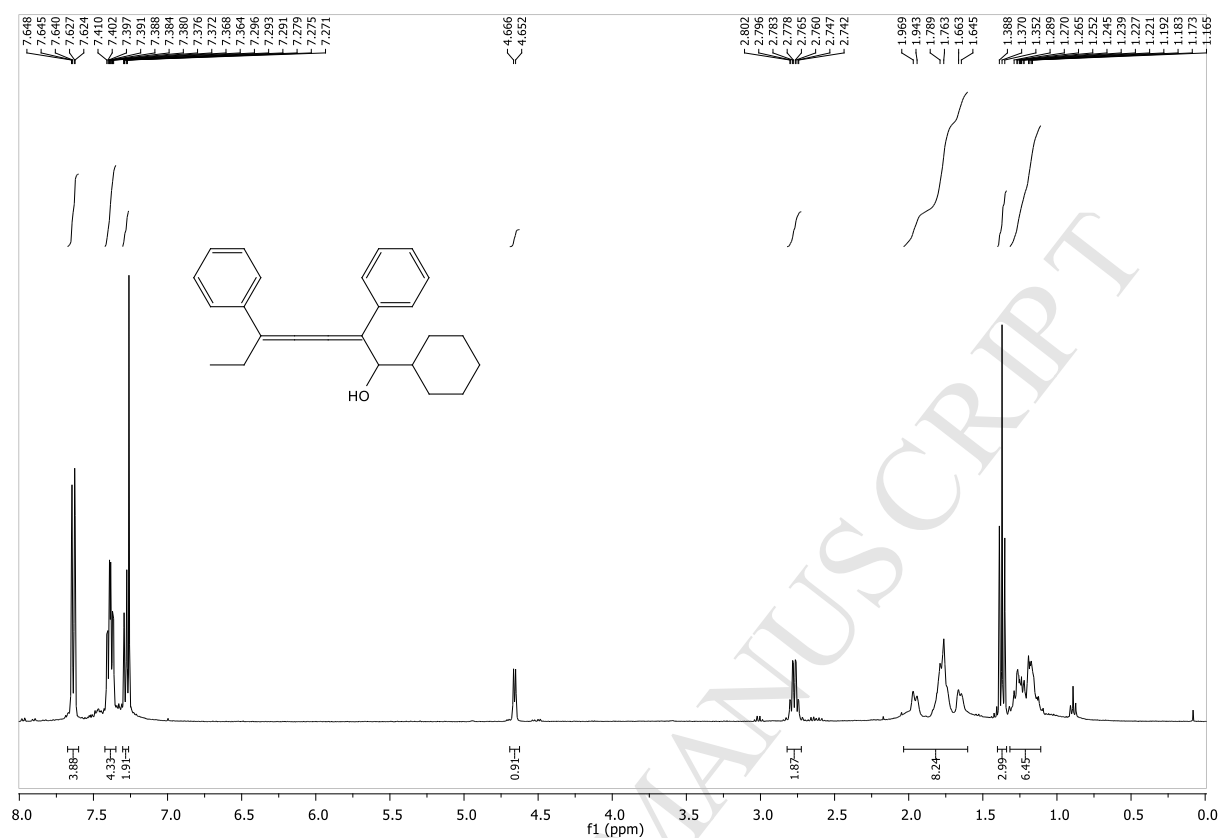
Following general procedure **B** on [3]-cumulenol **1g** in CH₂Cl₂ (20 mL), the diyne **3g** was obtained after flash chromatography on silica gel (*n*-Pentane to *n*-Pentane/EtOAc, 98/2) as a yellowish oil corresponding to a mixture with furan **2g** (0.198 g, 0.69 mmol, 69 % with a ratio **3g/2g** of 77/23).

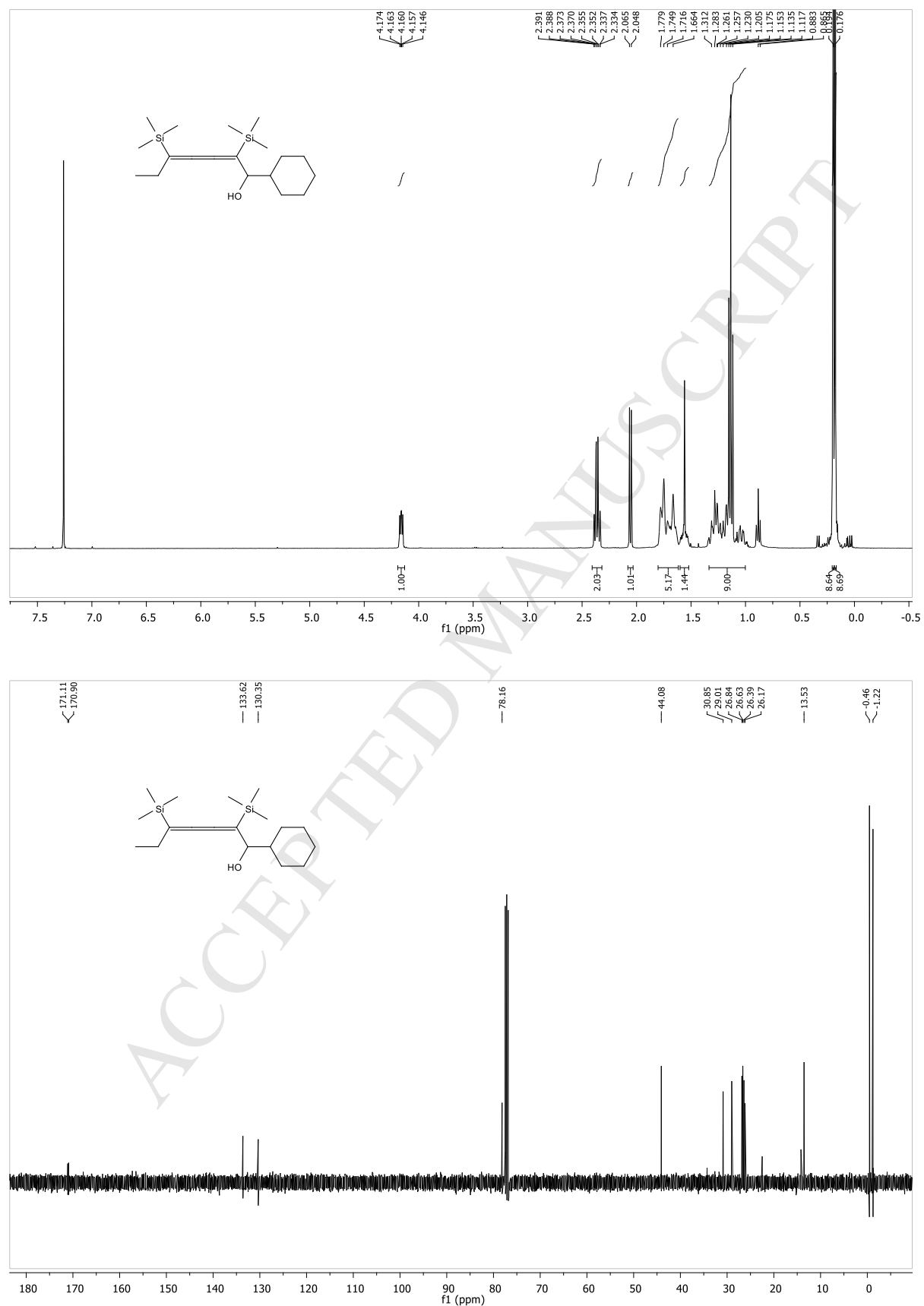
¹H NMR (400 MHz, CDCl₃) : δ = 6.16 (1H, q, *J* = 6.5 Hz), 5.89 (1H, d, *J* = 8.4 Hz), 2.74 (1H, m), 1.98 (3H, d, *J* = 6.4 Hz), 1.75-1.63 (5H, m), 1.36-1.03 (5H, m), 0.16 (9H, s), 0.15 (9H, s) ; **¹³C NMR (75 MHz, CDCl₃)** : δ = 155.4 (CH), 144.0 (CH), 126.6 (C), 123.1 (C), 97.2 (C), 95.7 (C), 41.6 (CH), 32.4 (2 × CH₂), 26.3 (CH₂), 26.1 (2 × CH₂), 18.4 (CH₃), -1.6 (CH₃), -1.7 (CH₃) ; **HRMS (ESI)** : calcd for C₁₉H₃₄KS₂ [*M* + *K*]⁺: 357.1831; found 357.1829 ; **IR (ATR)** : ν = 2924, 1572, 1246, 834, 752 cm⁻¹.

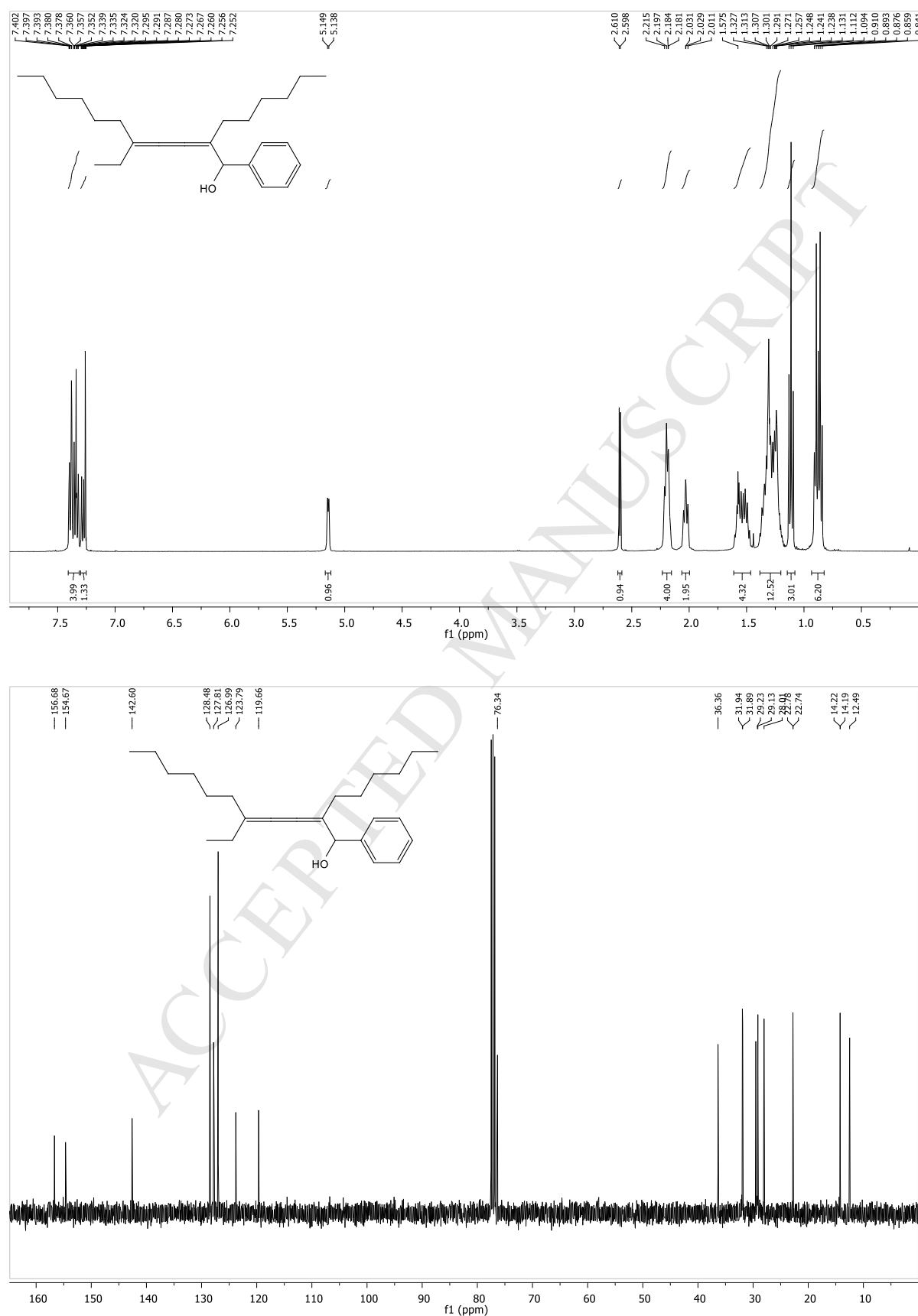
4. Spectral Data

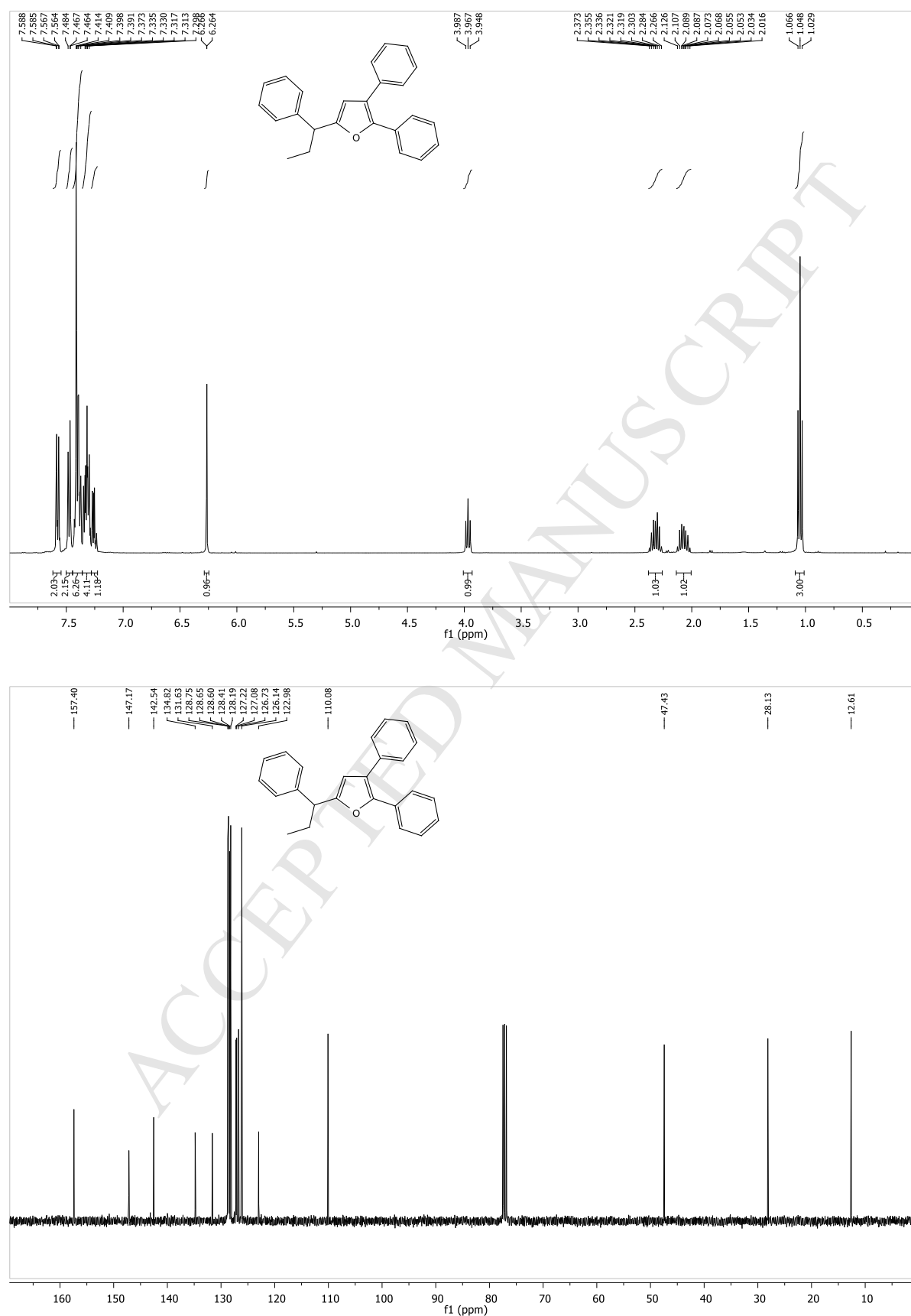
(E)-1-(4-Methoxyphenyl)-2,5-diphenylhepta-2,3,4-trien-1-ol (1b)

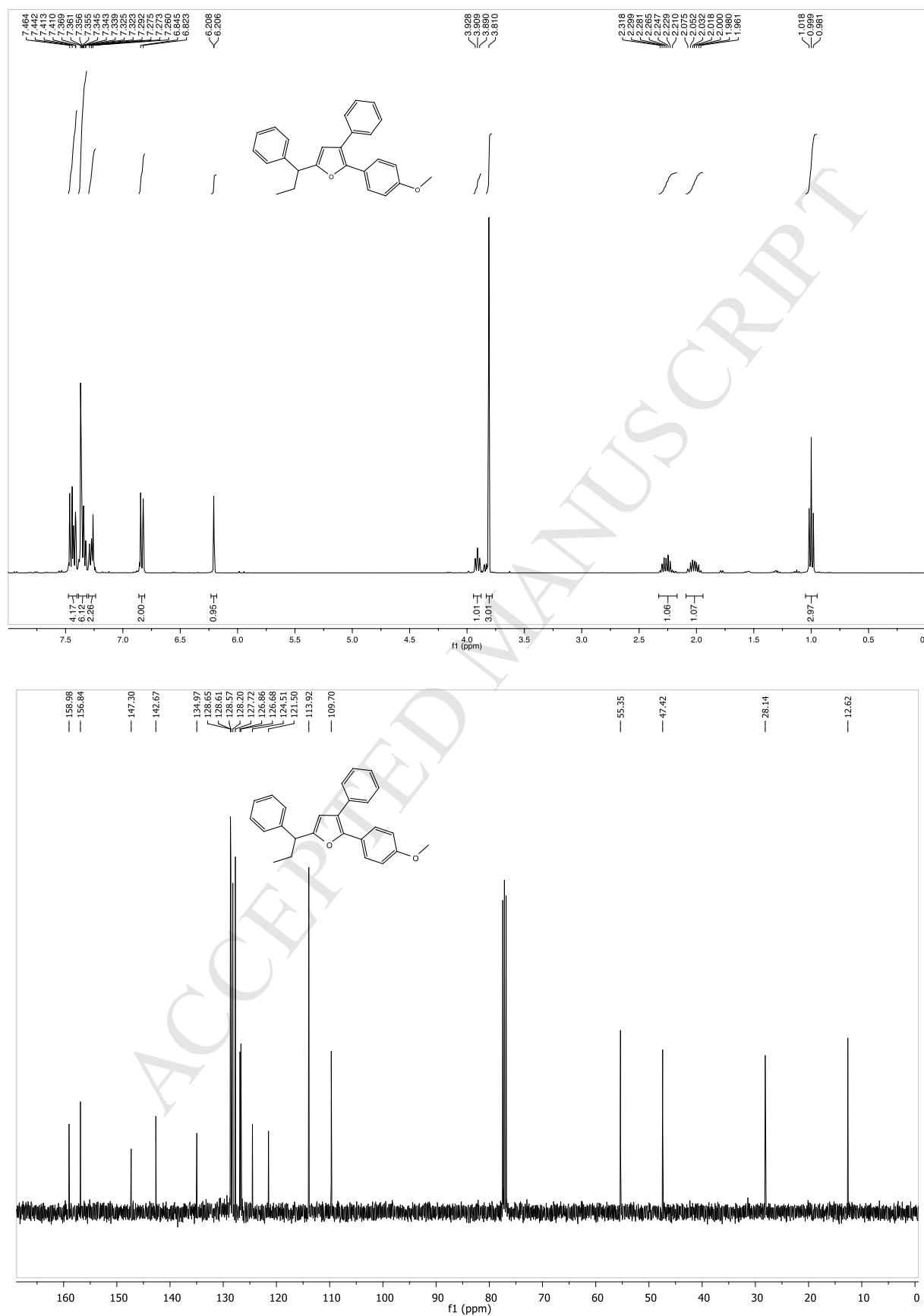
(E)-1-(4-Fluorophenyl)-2,5-diphenylhepta-2,3,4-trien-1-ol (1c)

(E)-1-Cyclohexyl-2,5-diphenylhepta-2,3,4-trien-1-ol (1d)

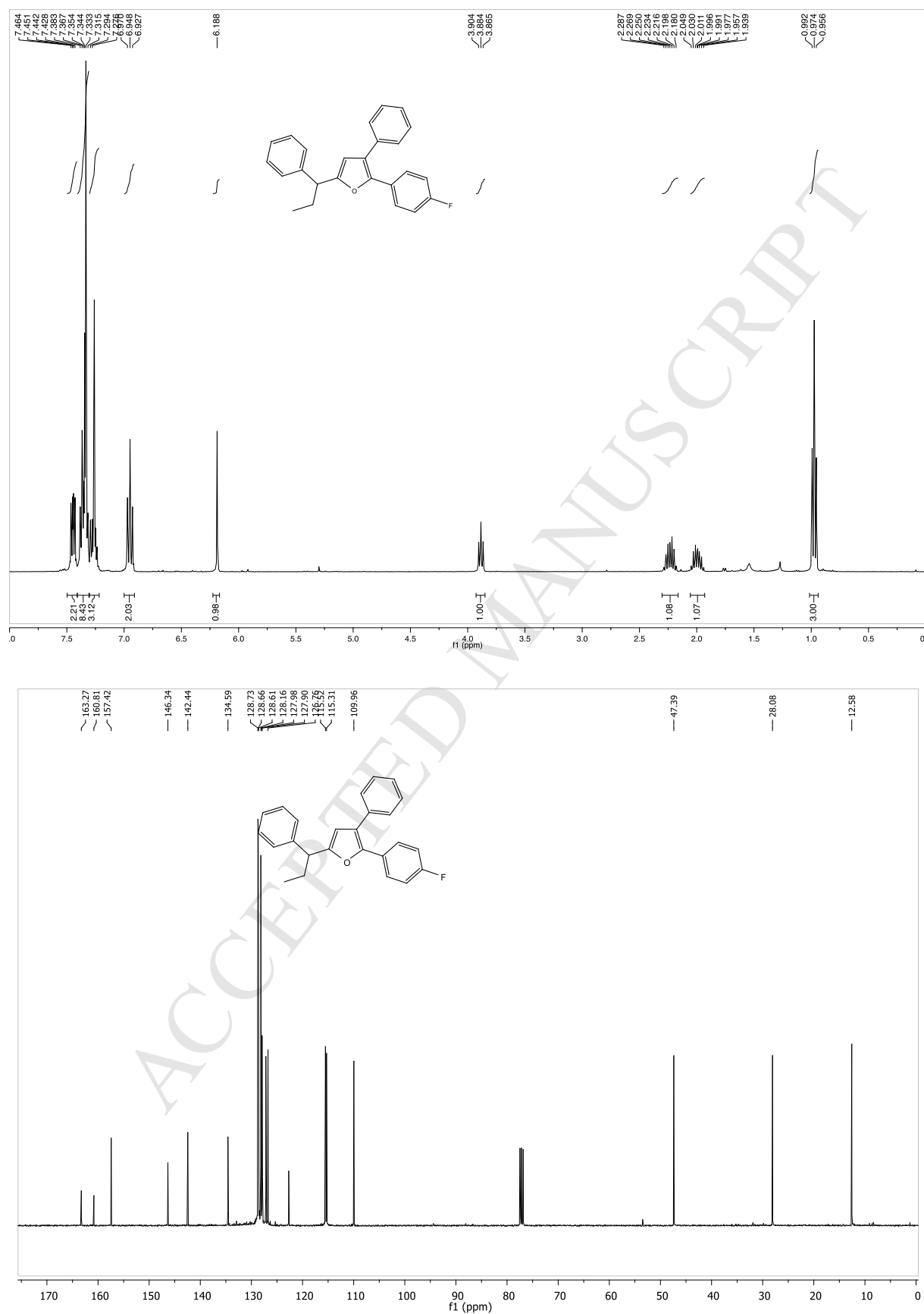
(Z)-1-Cyclohexyl-2,5-bis(trimethylsilyl)hepta-2,3,4-trien-1-ol (1g)

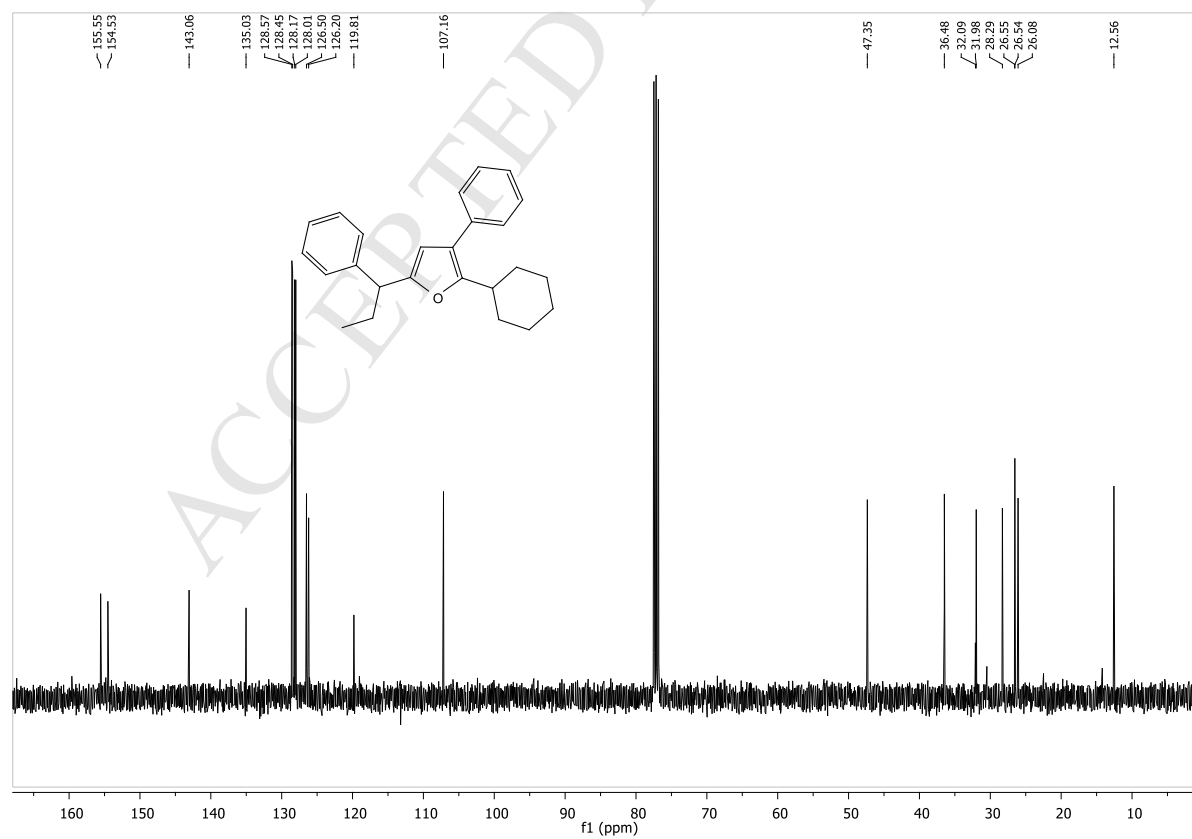
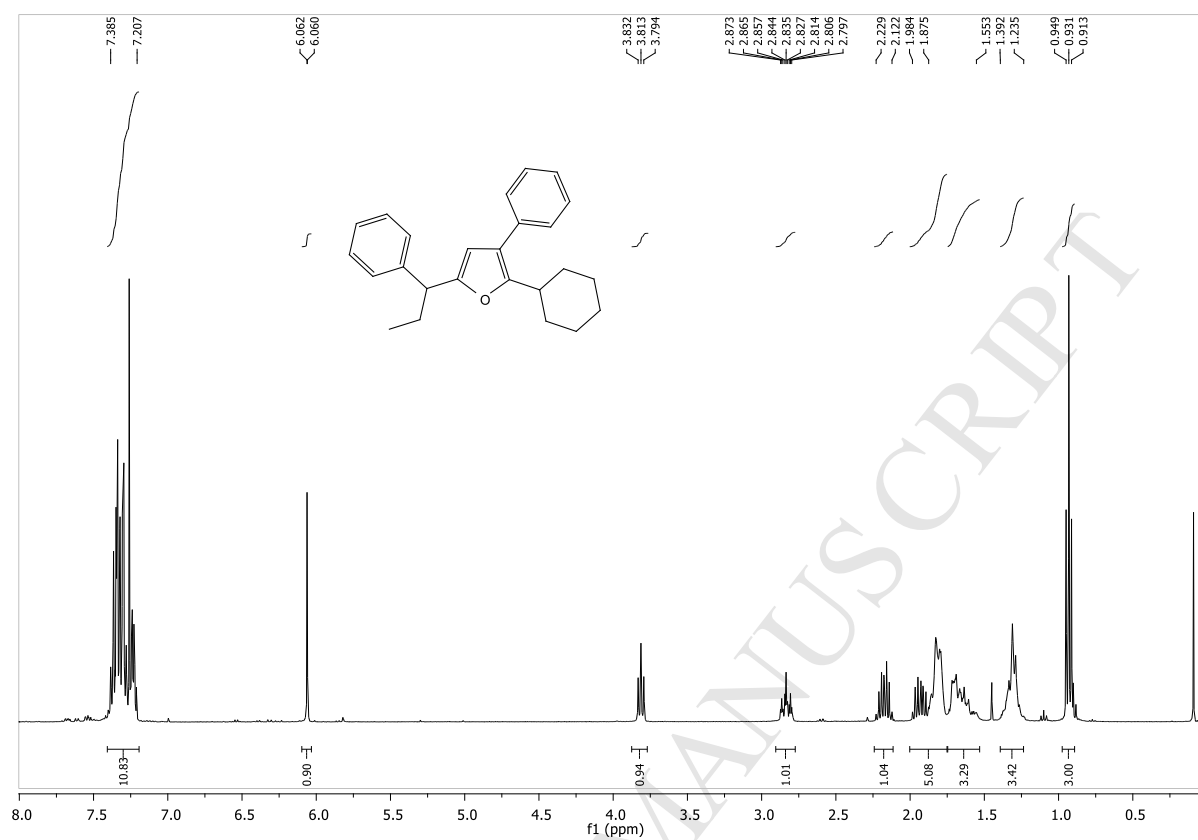
(E)-5-Ethyl-2-hexyl-1-phenylundeca-2,3,4-trien-1-ol (1h)

2,3-Diphenyl-5-(1-phenylpropyl)furan (2a)

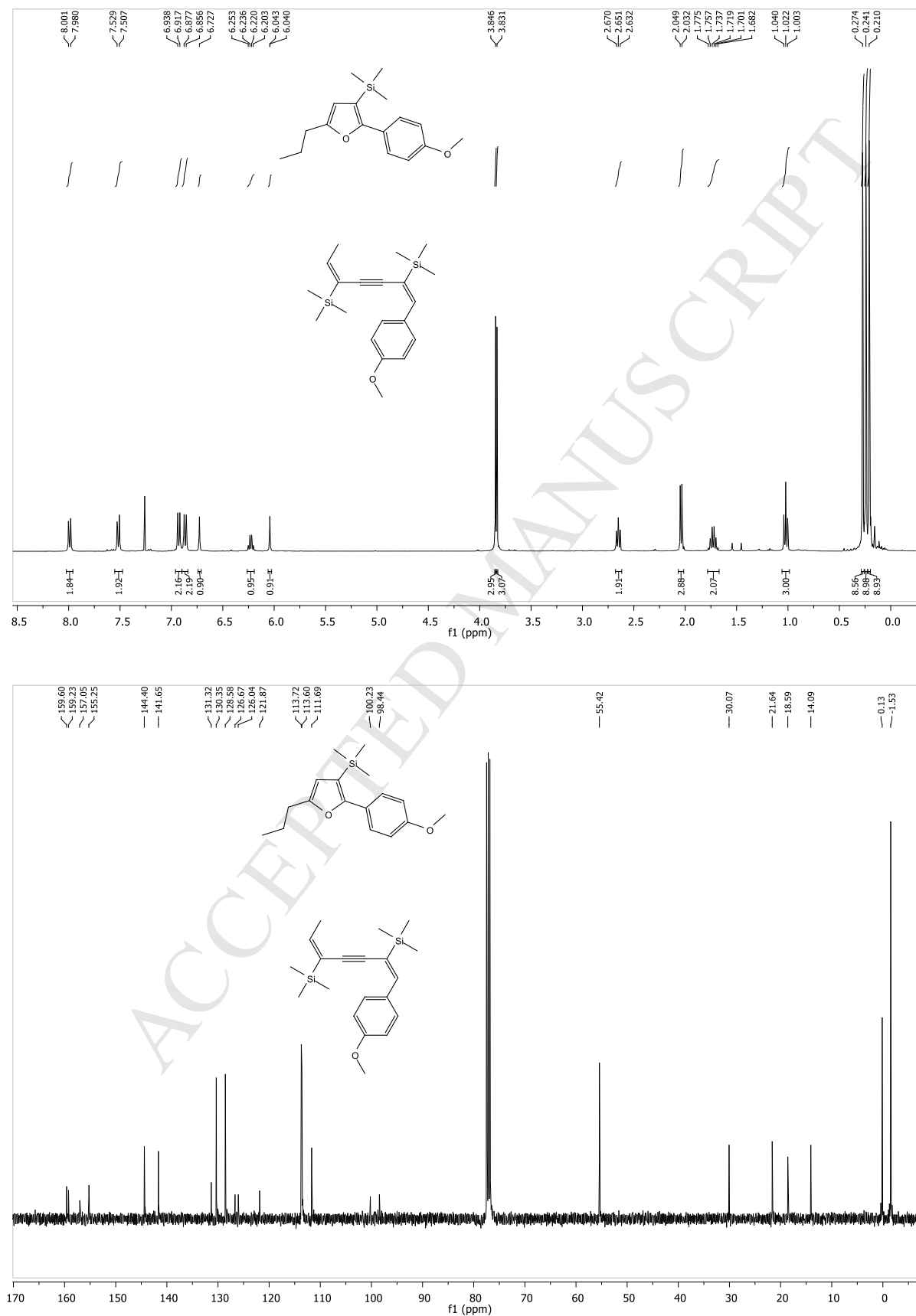
2-(4-Methoxyphenyl)-3-phenyl-5-(1-phenylpropyl)furan (2b)

2-(4-Fluorophenyl)-3-phenyl-5-(1-phenylpropyl)furan (2c)

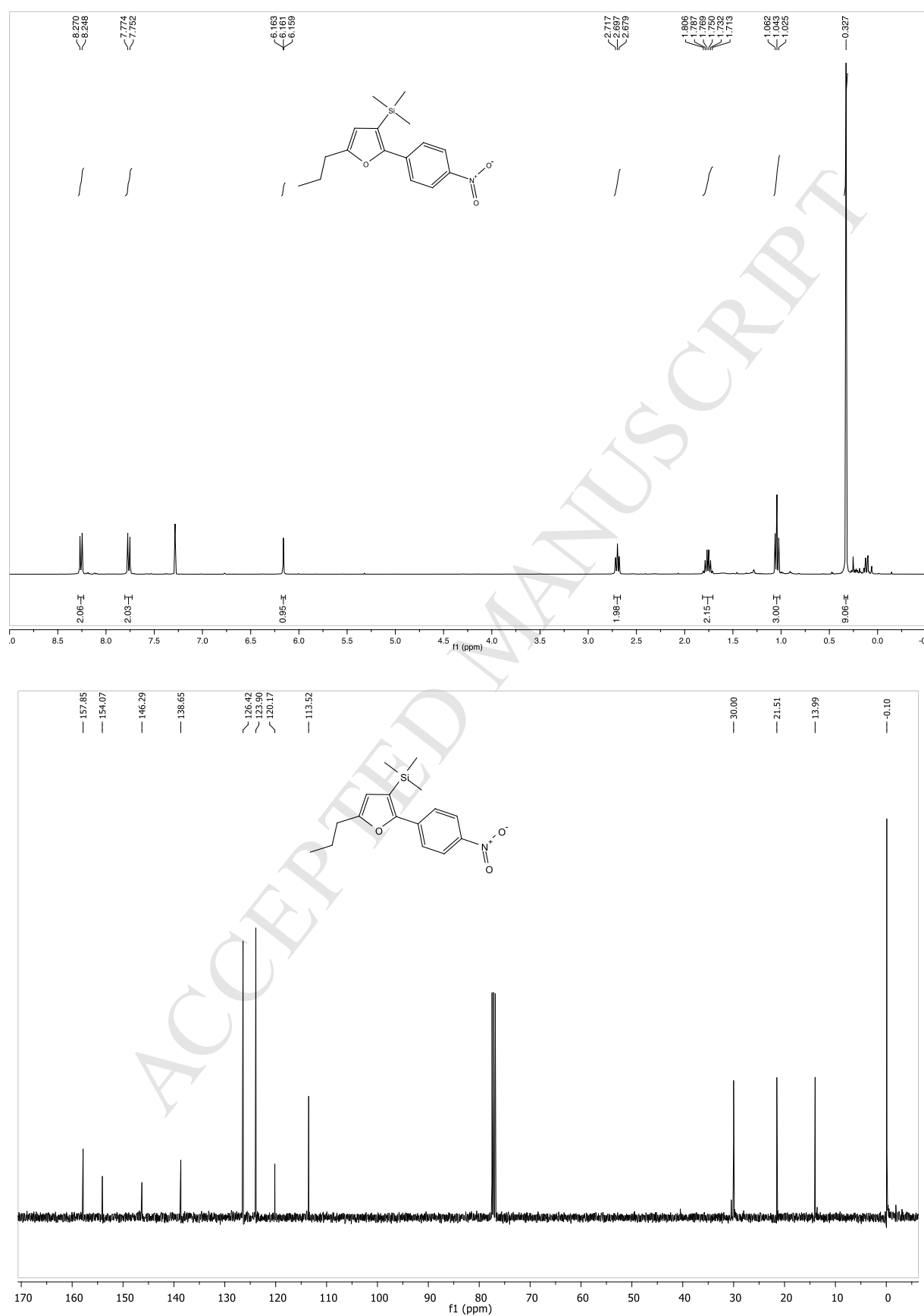


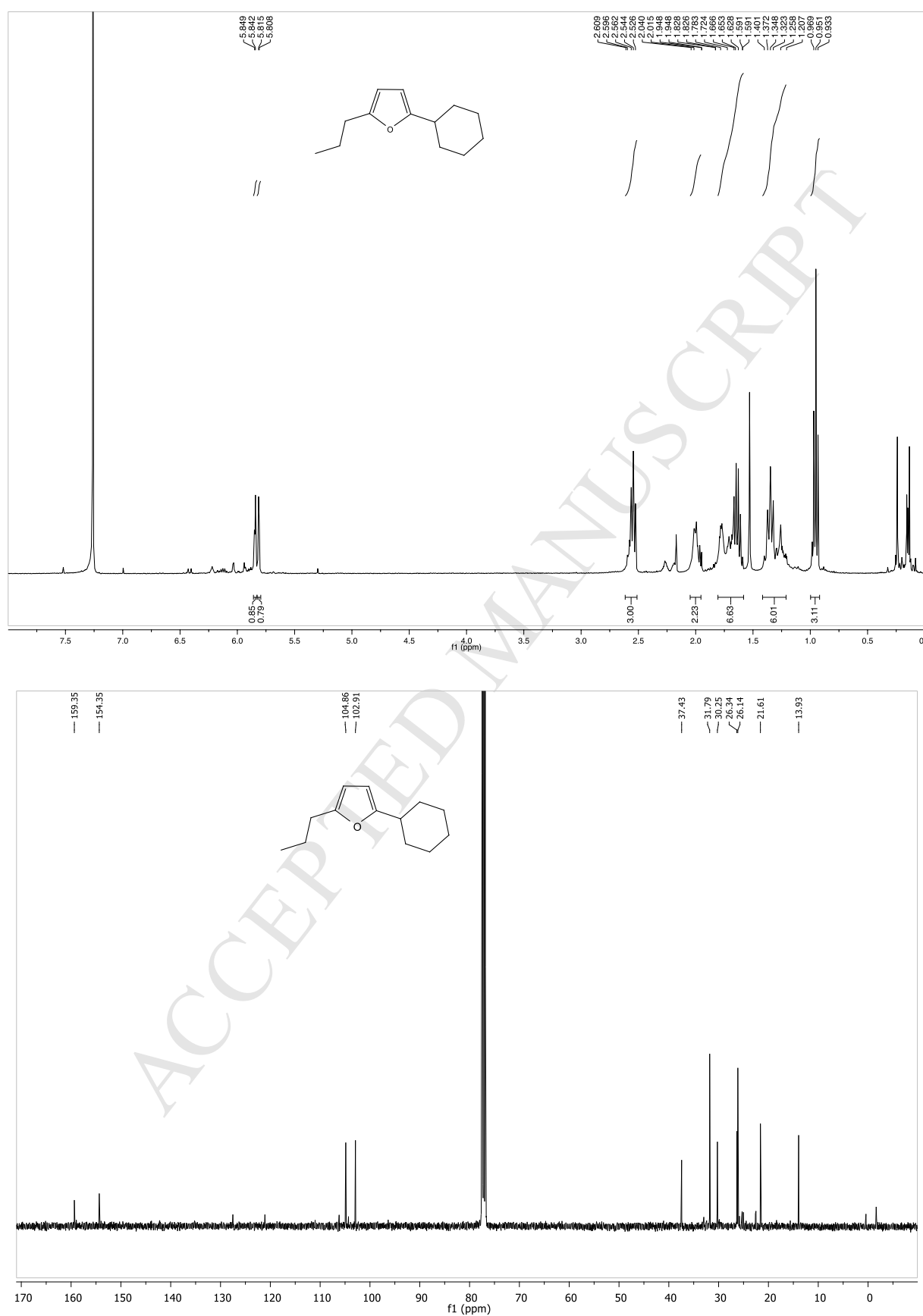
2-Cyclohexyl-3-phenyl-5-(1-phenylpropyl)furan (2d)

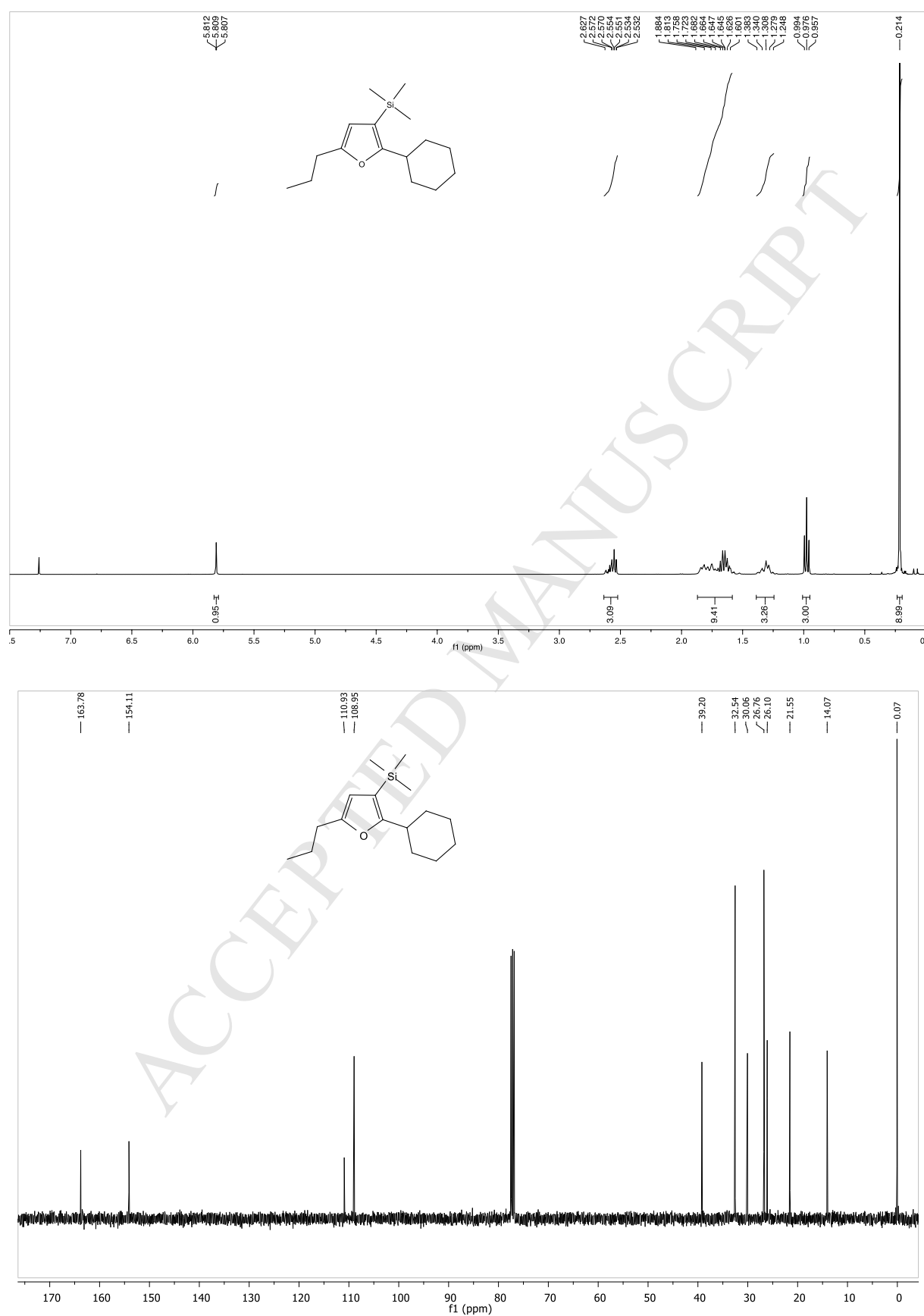
Mixture of (2-(4-methoxyphenyl)-5-propylfuran-3-yl)trimethylsilane (2e) and ((1E,5E)-1-(4-methoxyphenyl)hepta-1,5-dien-3-yne-2,5-diyl)bis(trimethylsilane) (3e)

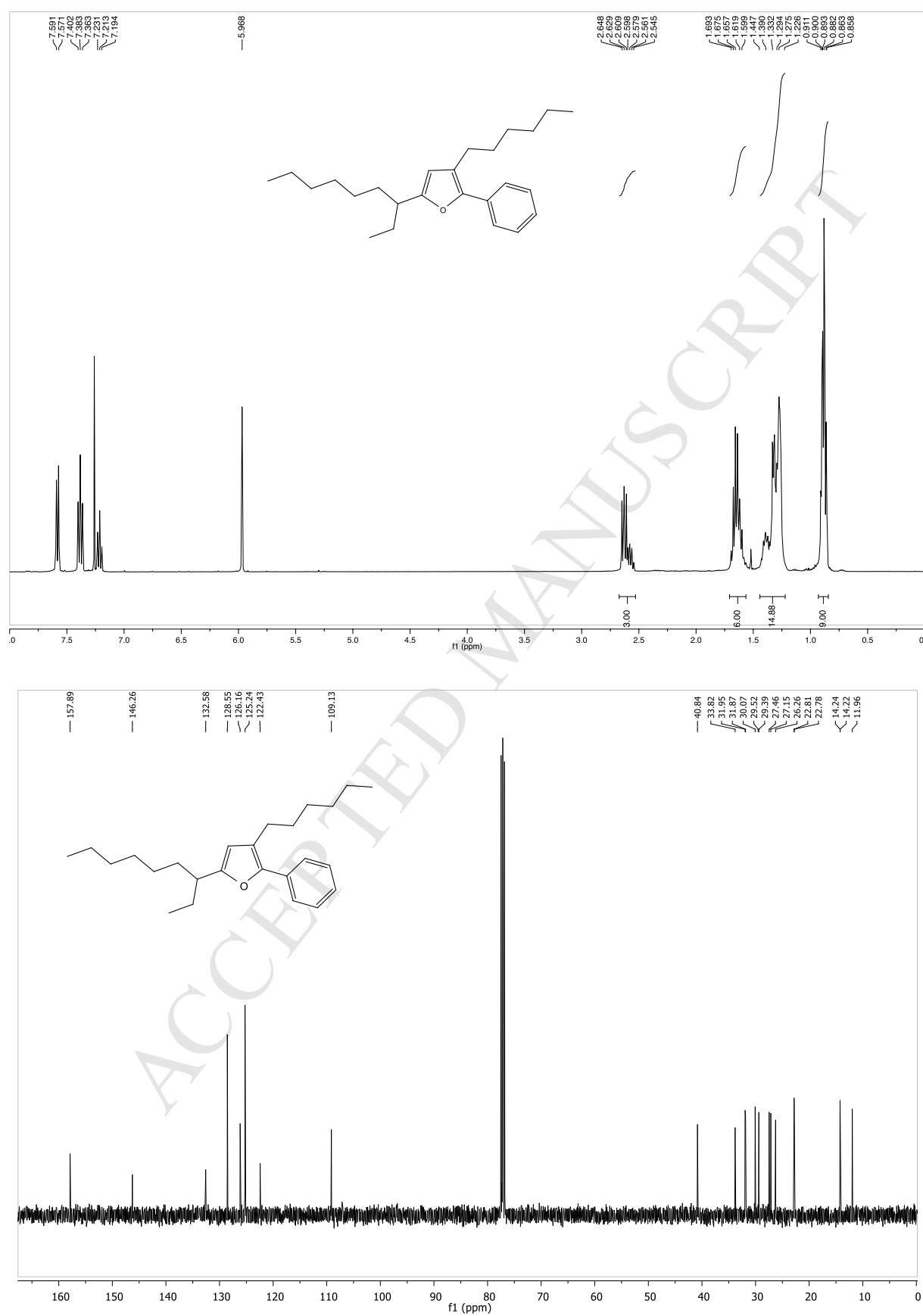


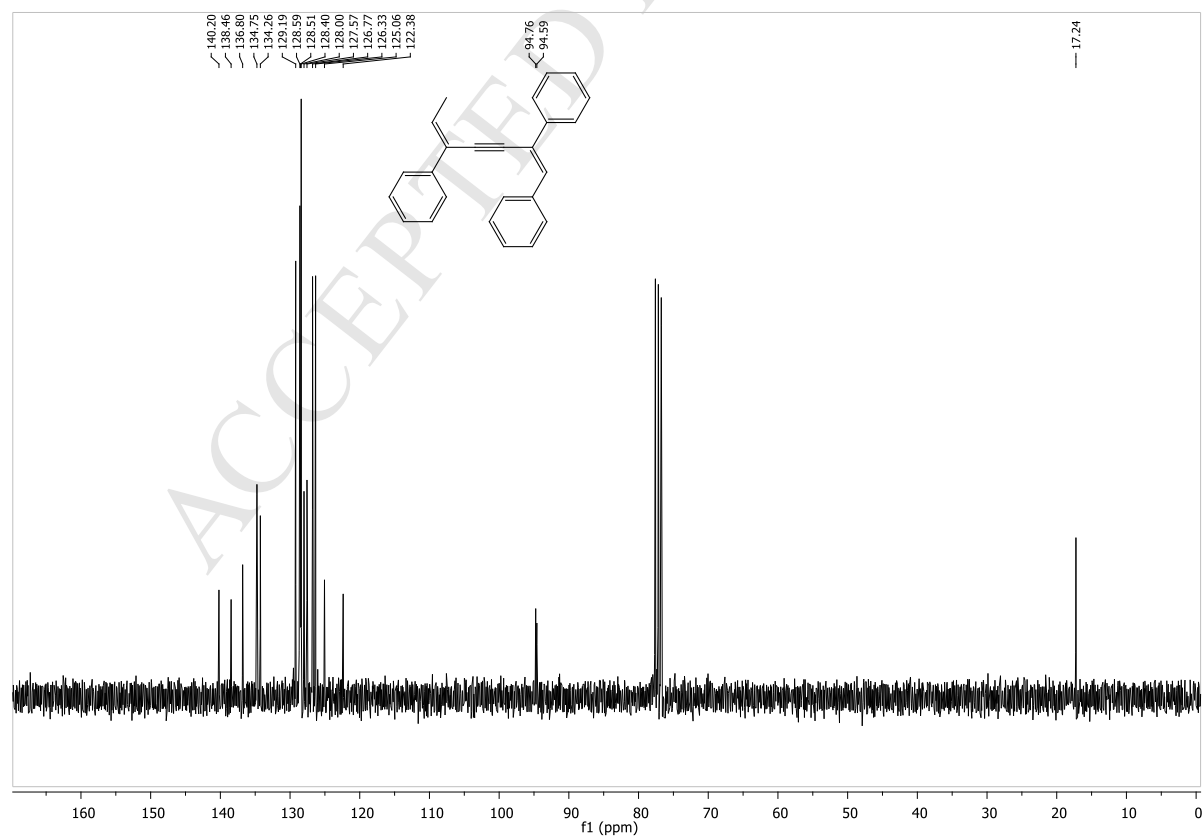
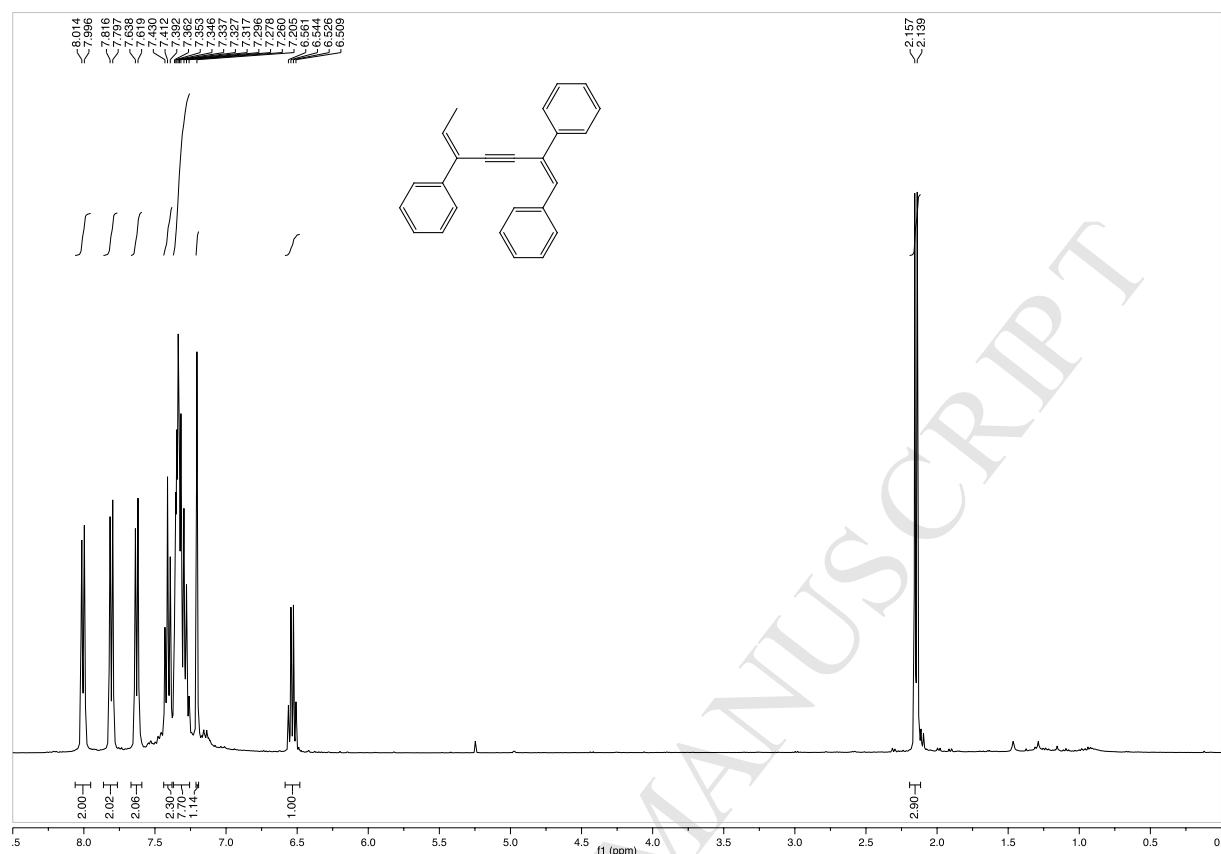
Trimethyl(2-(4-nitrophenyl)-5-propylfuran-3-yl)silane (2f)

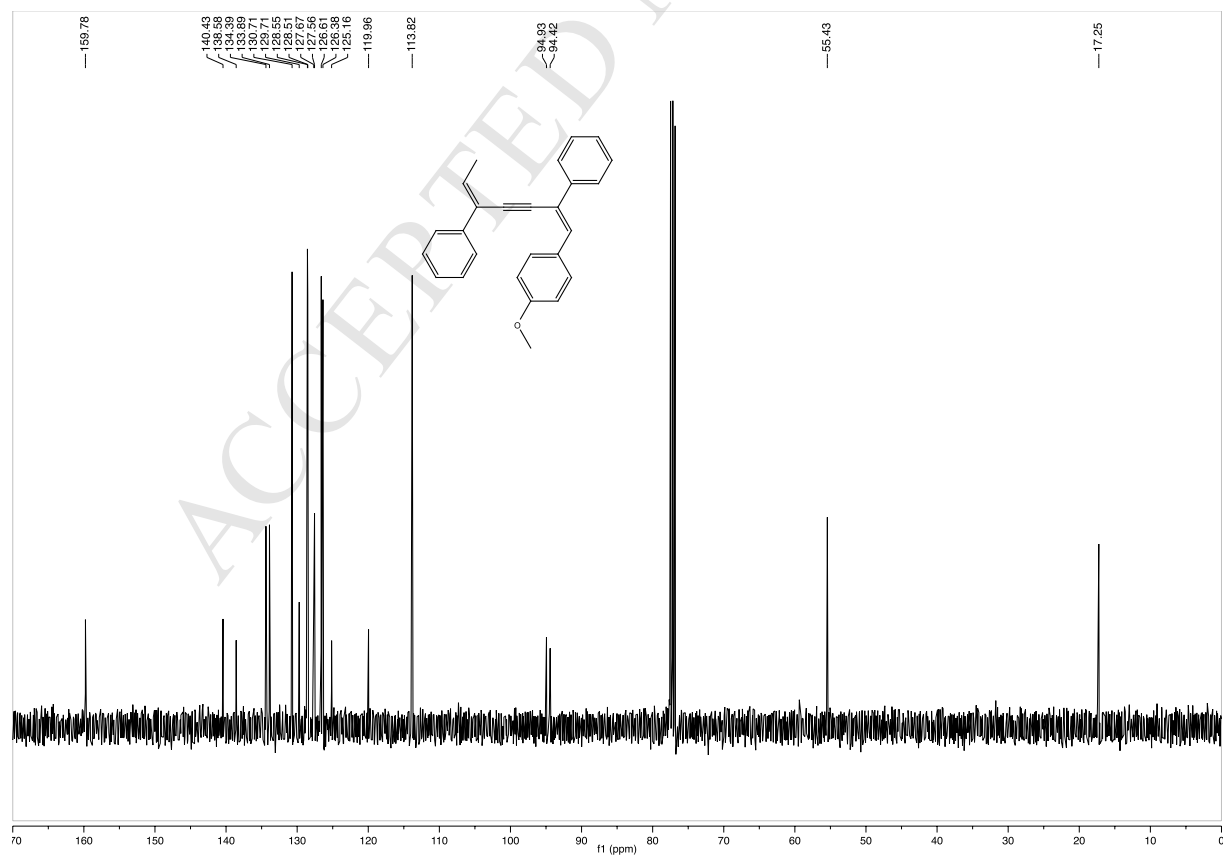
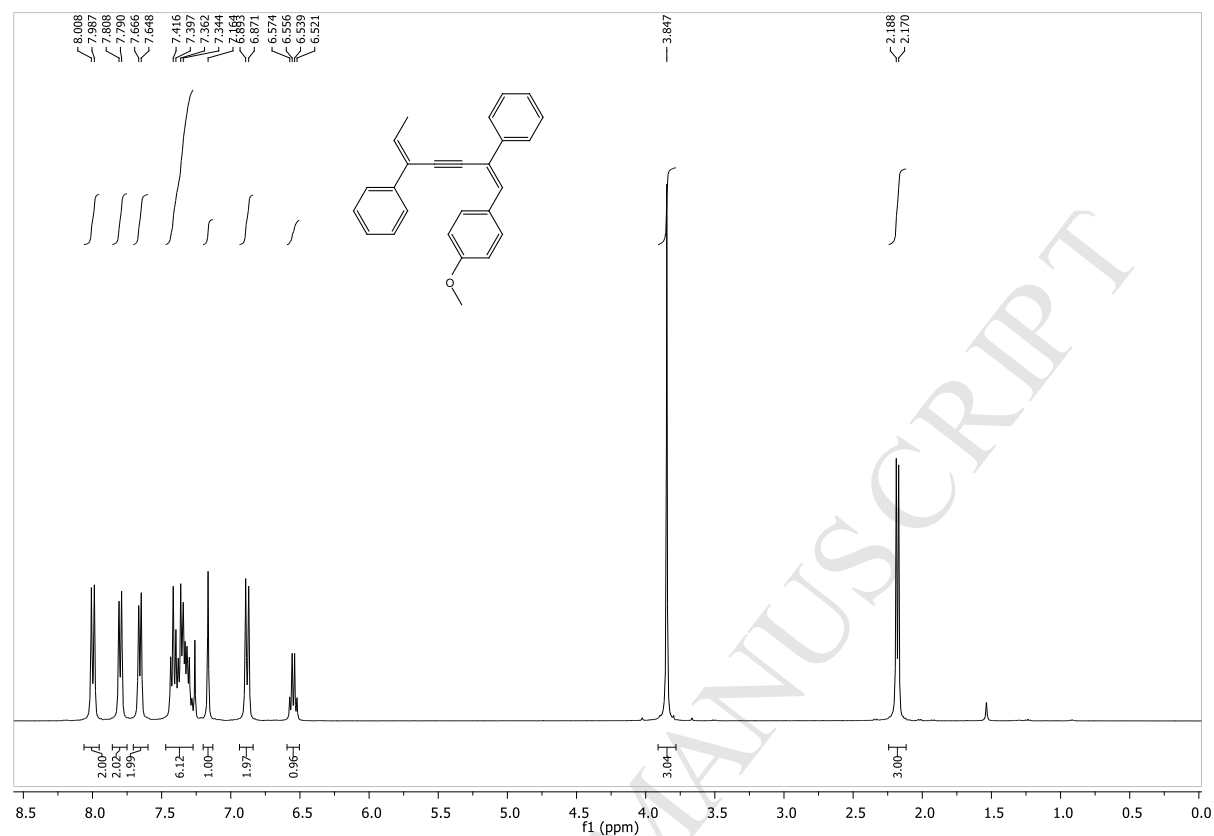


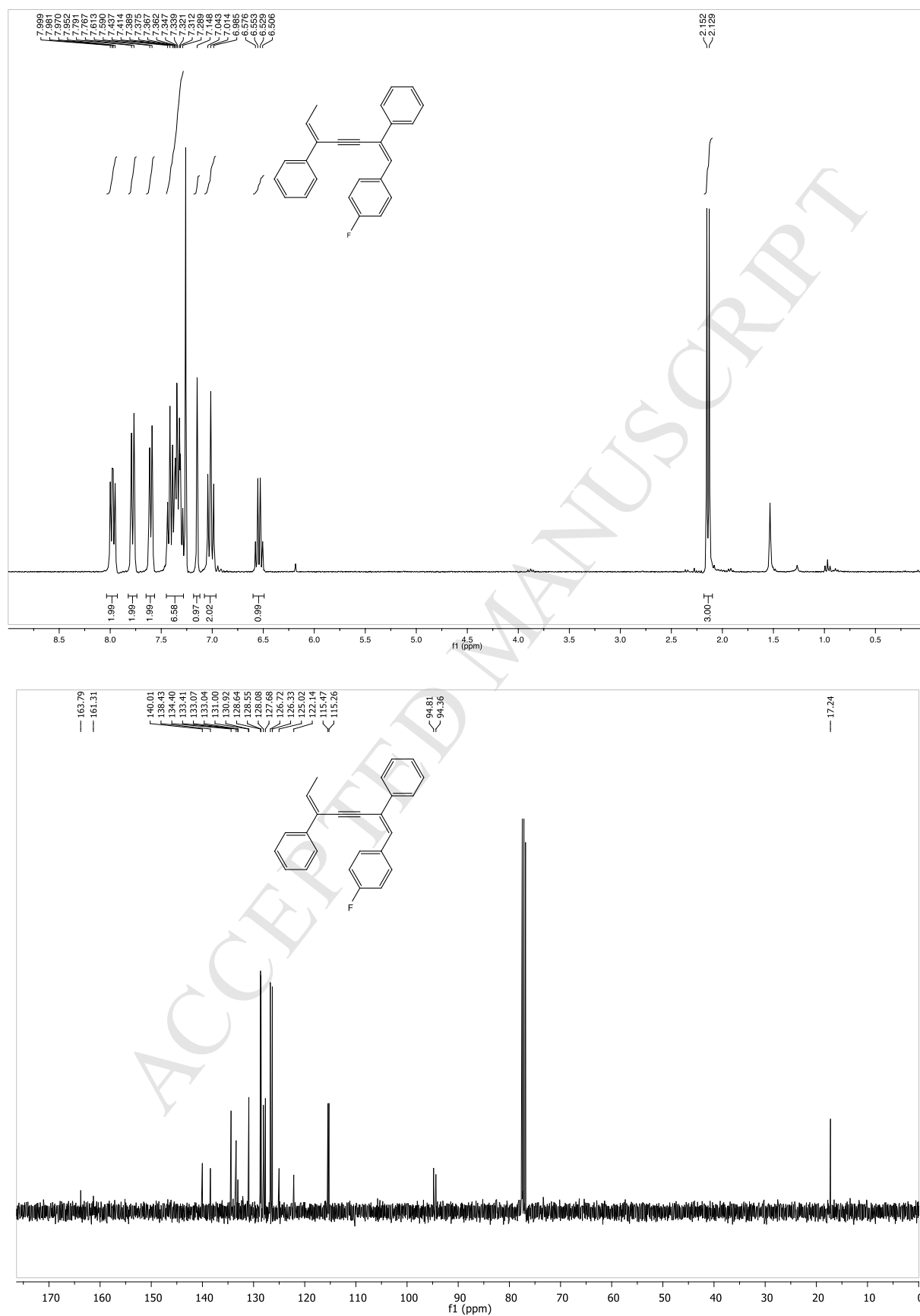
2-Cyclohexyl-5-propylfuran (2g)

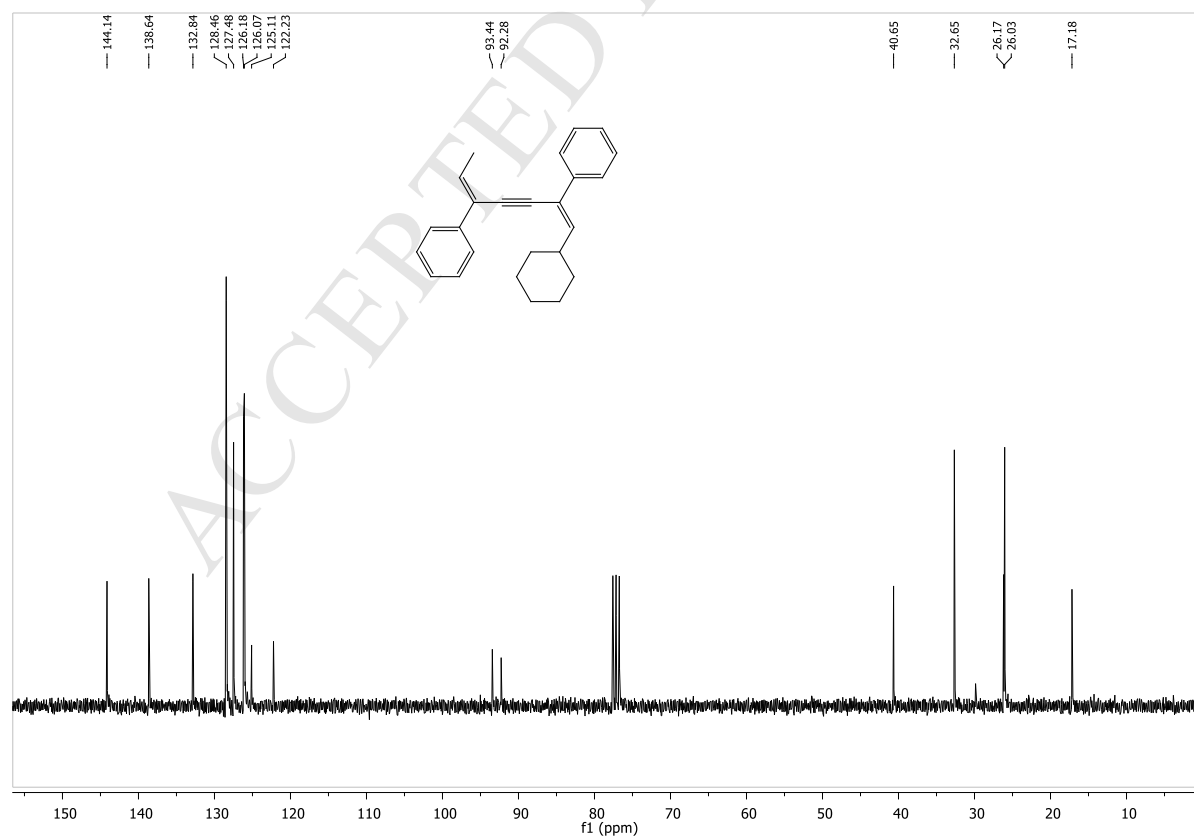
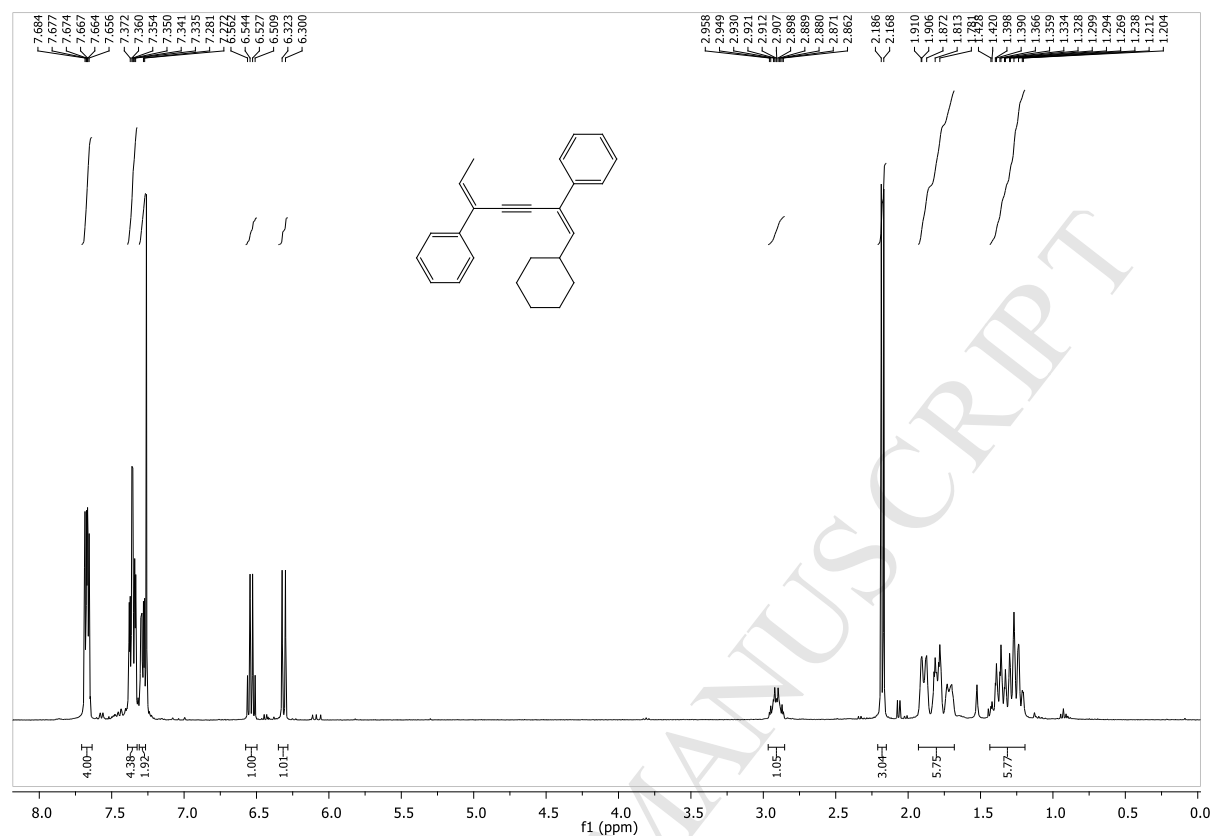
(2-Cyclohexyl-5-propylfuran-3-yl)trimethylsilane (2g')

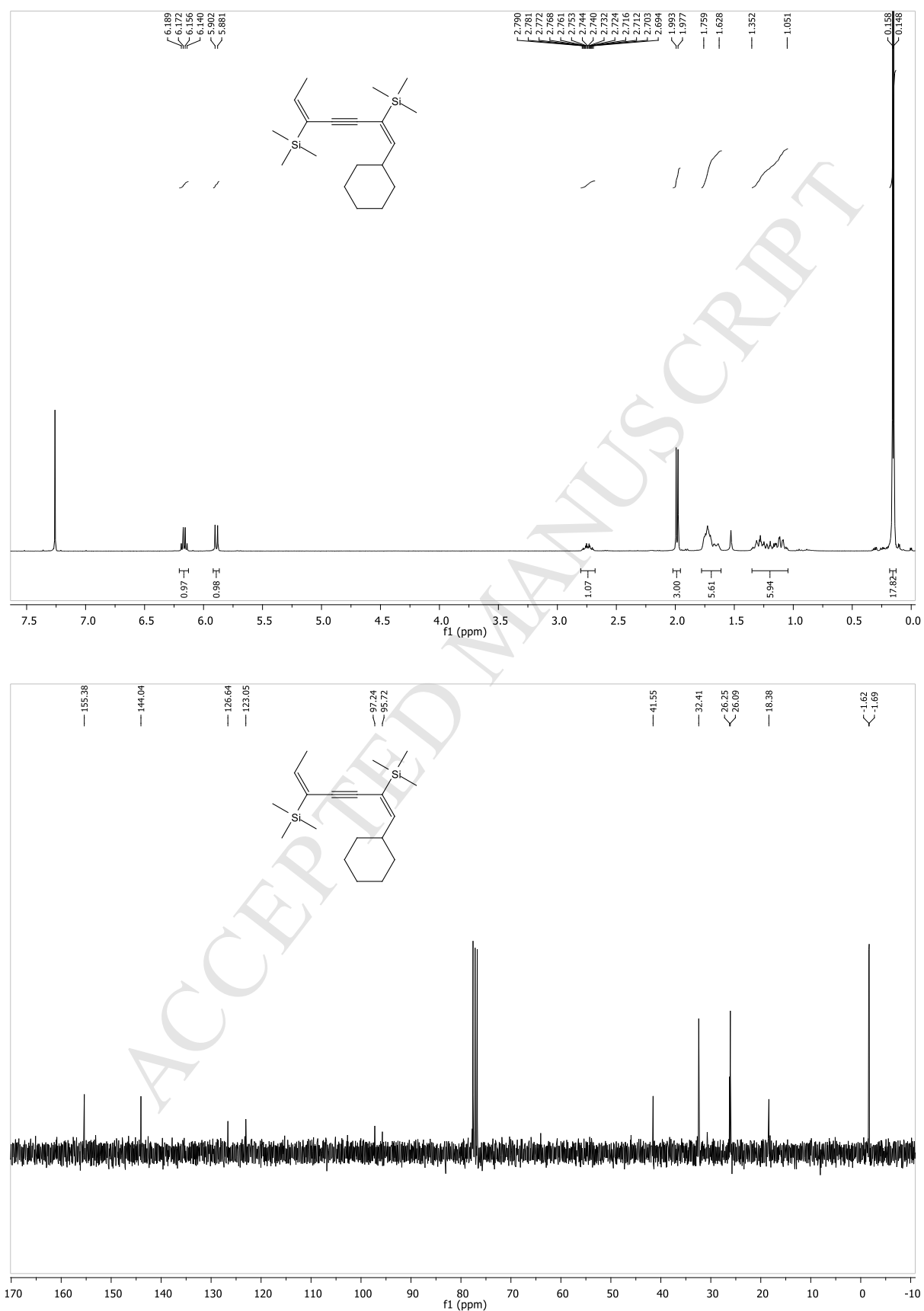
3-Hexyl-5-(nonan-3-yl)-2-phenylfuran (2h)

(1Z,5Z)-Hepta-1,5-dien-3-yne-1,2,5-triyltribenzene (3a)

((1*Z*,5*Z*)-1-(4-Methoxyphenyl)hepta-1,5-dien-3-yne-2,5-diyl)dibenzene (3b)

((1*Z*,5*Z*)-1-(4-Fluorophenyl)hepta-1,5-dien-3-yne-2,5-diyl)dibenzene (3c)

((1*Z*,5*Z*)-1-Cyclohexylhepta-1,5-dien-3-yne-2,5-diyl)dibenzene (3d)

((1*E*,5*E*)-1-Cyclohexylhepta-1,5-dien-3-yne-2,5-diyl)bis(trimethylsilane) (3g)

5. Crystal structure

((1*Z*,5*Z*)-1-(4-Methoxyphenyl)hepta-1,5-dien-3-yne-2,5-diyl)dibenzene (3b)

