#### Supporting Information for

# Cu(I)-Catalyzed Synthesis of Furan-Substituted Allenes Using Conjugated Ene-Yne-Ketones as Carbene Precursors

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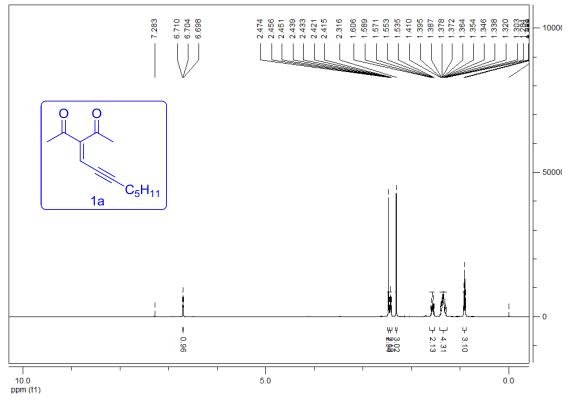
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<sup>‡</sup>School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

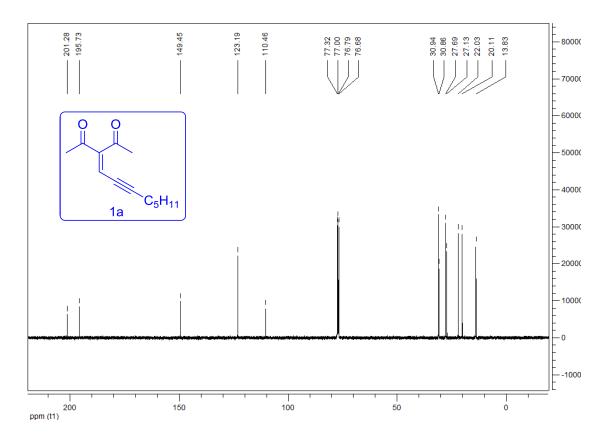
#### Email: wangjb@pku.edu.cn

<sup>1</sup> H and <sup>13</sup> C NMR spectra for compounds <b>1a-l</b>	S2-S13
<sup>1</sup> H and <sup>13</sup> C NMR spectra for compounds <b>4a-p</b>	S14-S29
<sup>1</sup> H and <sup>13</sup> C NMR spectra for compounds <b>5a-j</b>	S30-S39
<sup>1</sup> H and <sup>13</sup> C NMR spectra for compounds <b>6a-p</b>	S40-S55
<sup>1</sup> H and <sup>13</sup> C NMR spectra for compounds <b>7a-i</b>	S56-S67

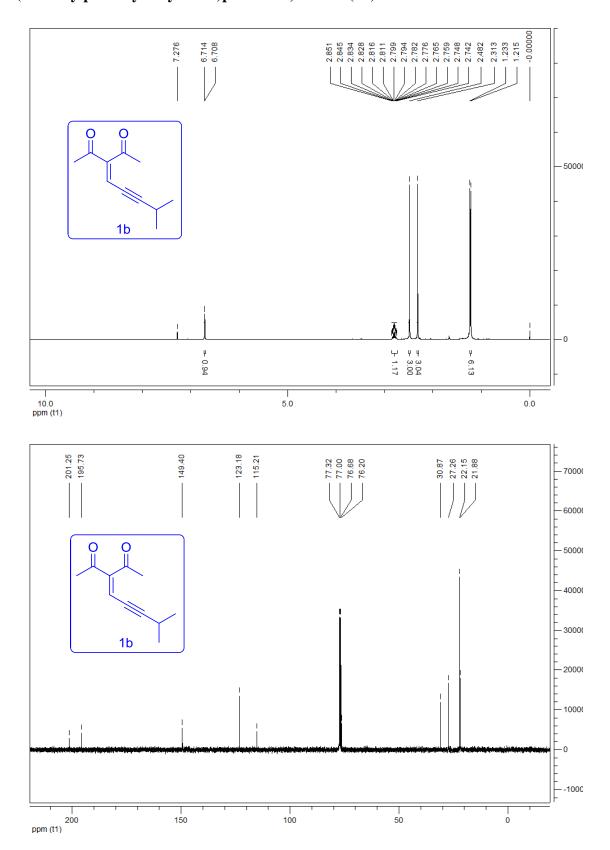
## <sup>1</sup>H and <sup>13</sup>C NMR spectra of substrates and products

## 3-(Oct-2-yn-1-ylidene)pentane-2,4-dione (1a)

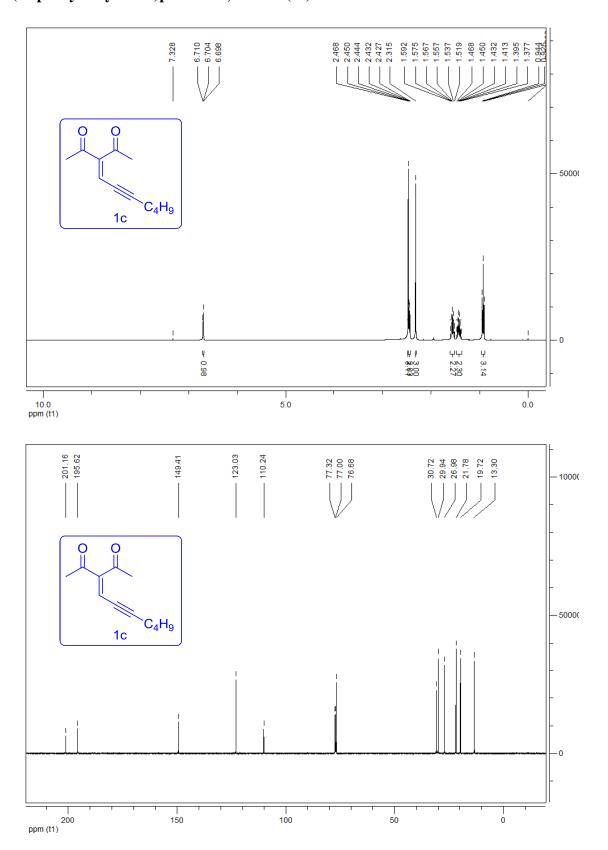




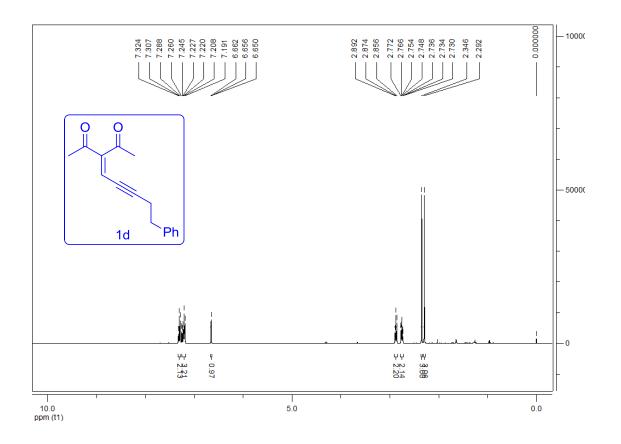
## 3-(4-Methylpent-2-yn-1-ylidene)pentane-2,4-dione (1b)

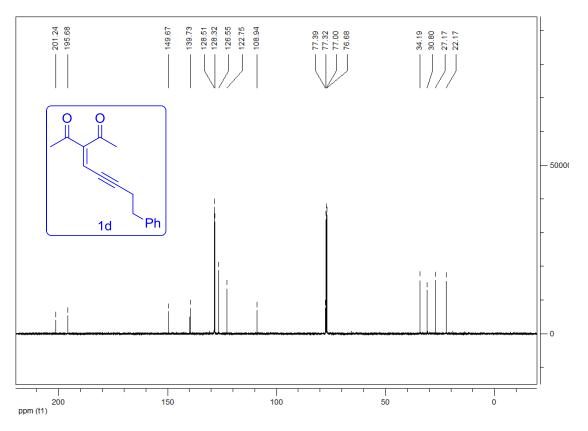


## 3-(Hept-2-yn-1-ylidene)pentane-2,4-dione (1c)

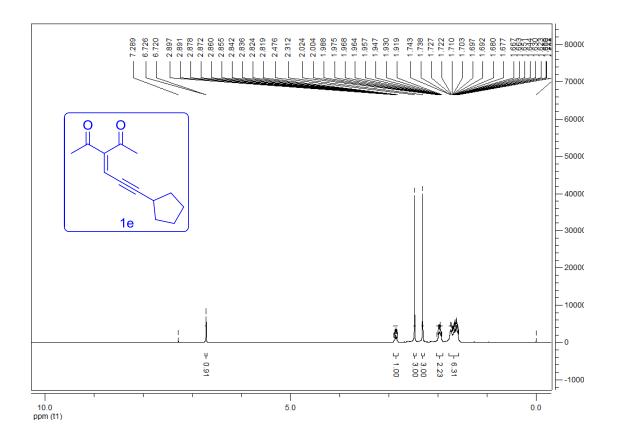


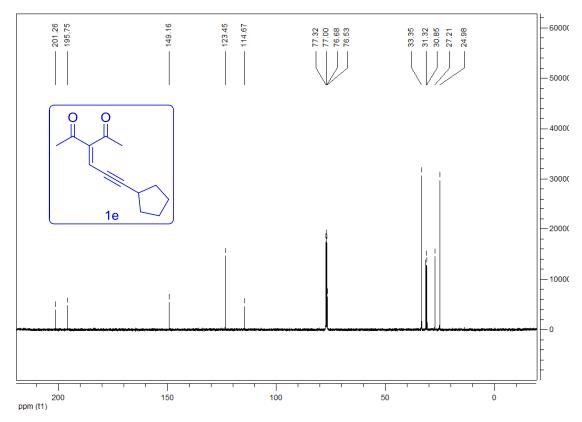
## 3-(5-Phenylpent-2-yn-1-ylidene)pentane-2,4-dione (1d)



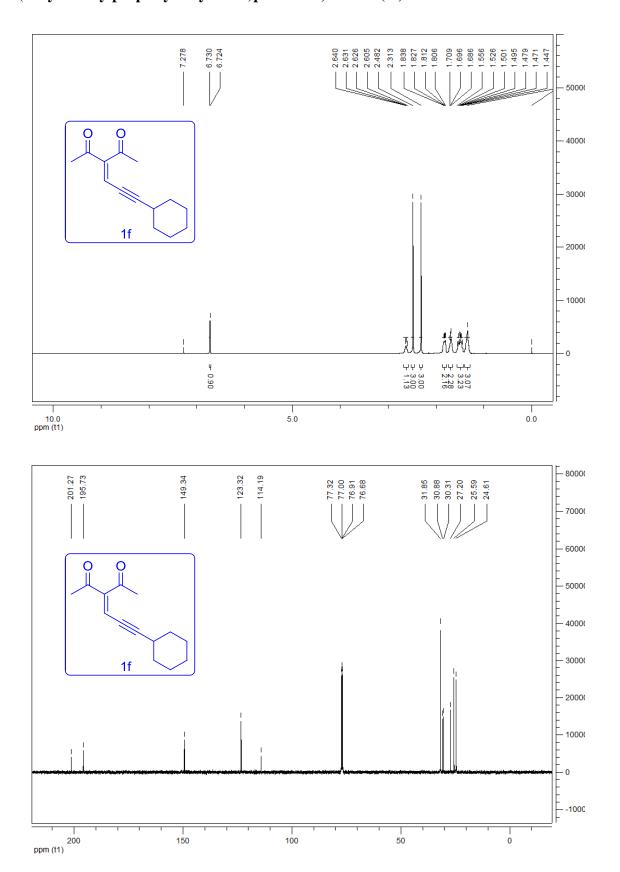


## ${\bf 3\text{-}(3\text{-}Cyclopentylprop-2\text{-}yn\text{-}1\text{-}ylidene)} pentane\text{-}2,\!4\text{-}dione\;(1e)$

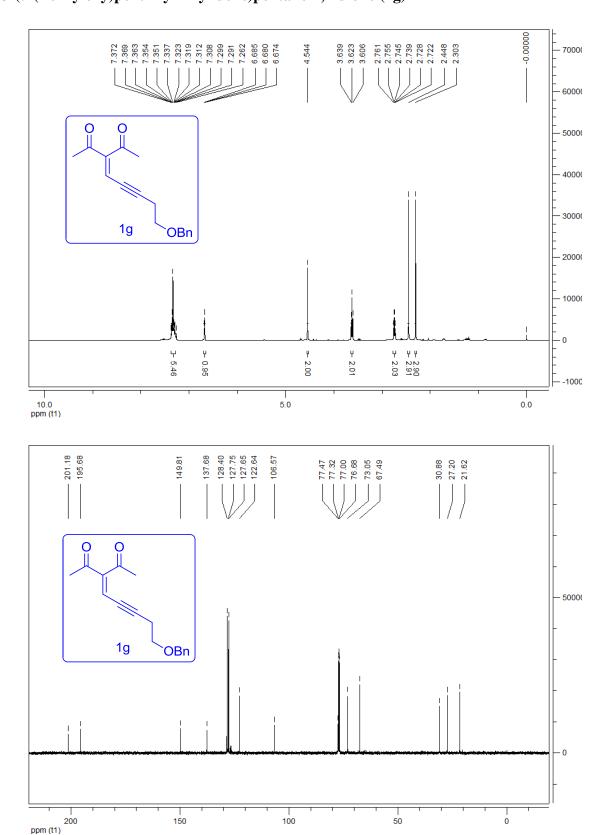




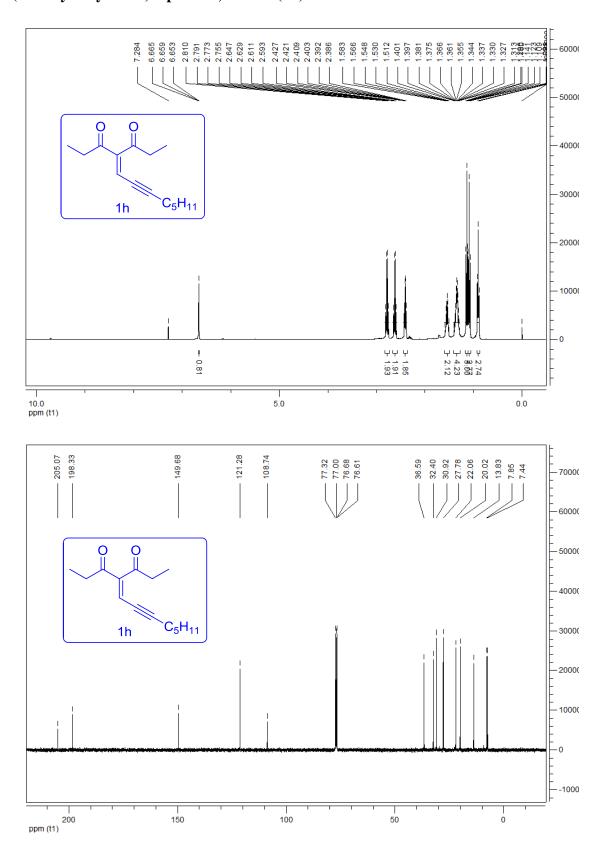
## ${\it 3-} (3-Cyclohexylprop-2-yn-1-ylidene) pentane-2, 4-dione~(1f)$



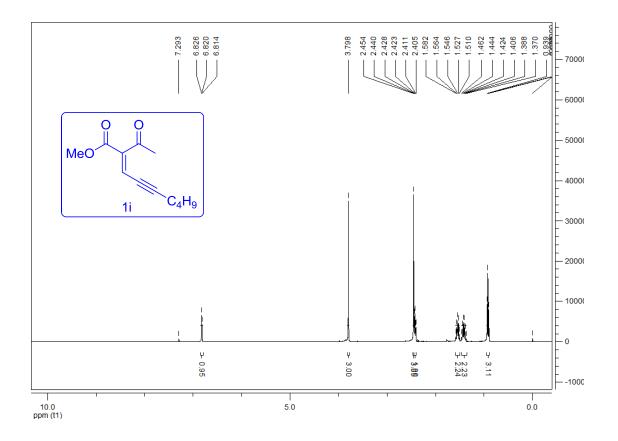
## ${\bf 3\text{-}(5\text{-}(Benzyloxy)pent\text{-}2\text{-}yn\text{-}1\text{-}ylidene)pentane\text{-}2\text{,}4\text{-}dione}\;(1g)$

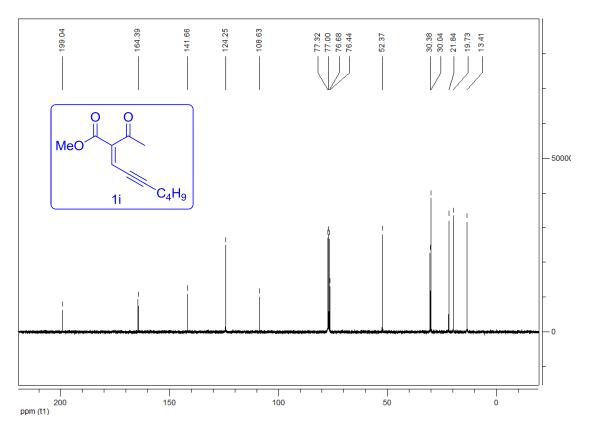


## 4-(Oct-2-yn-1-ylidene)heptane-3,5-dione (1h)

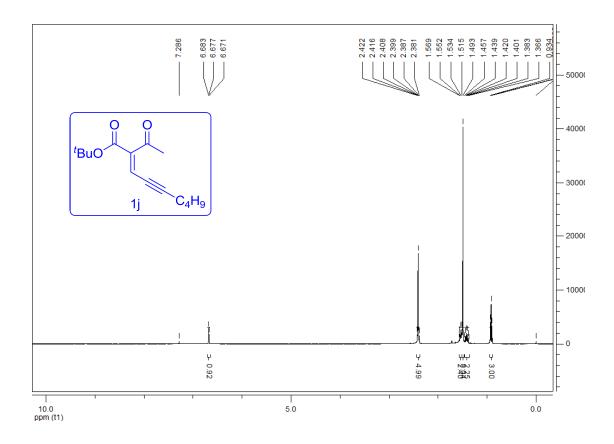


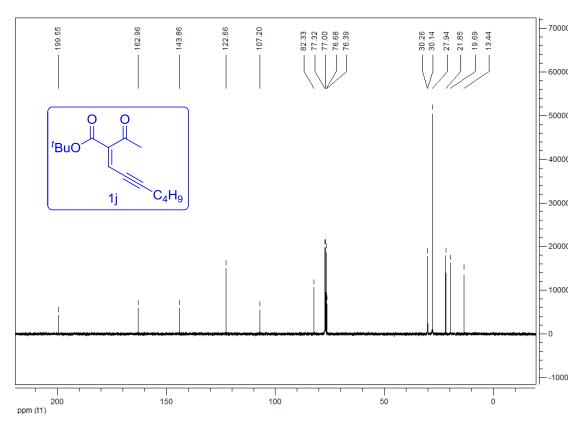
## (E)-Methyl 2-acetylnon-2-en-4-ynoate (1i)



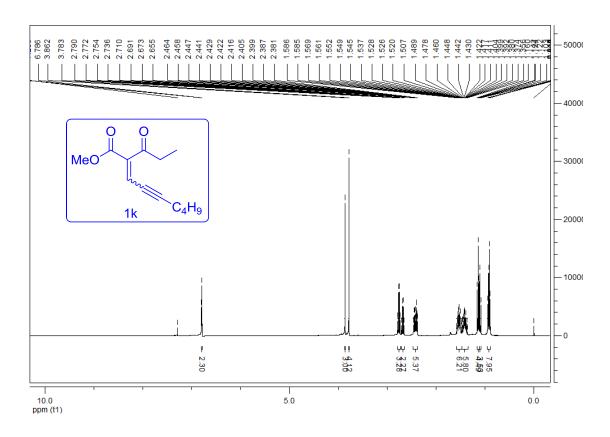


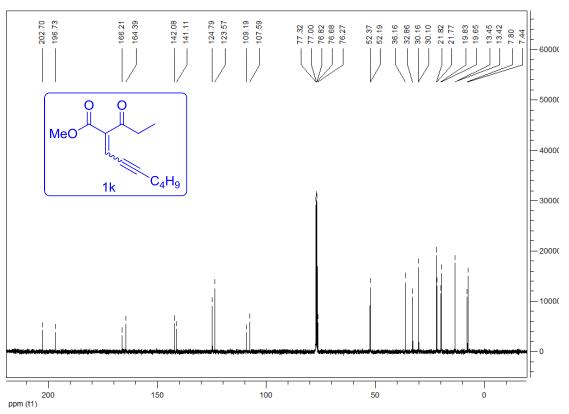
## (E)-tert-Butyl 2-acetylnon-2-en-4-ynoate (1j)



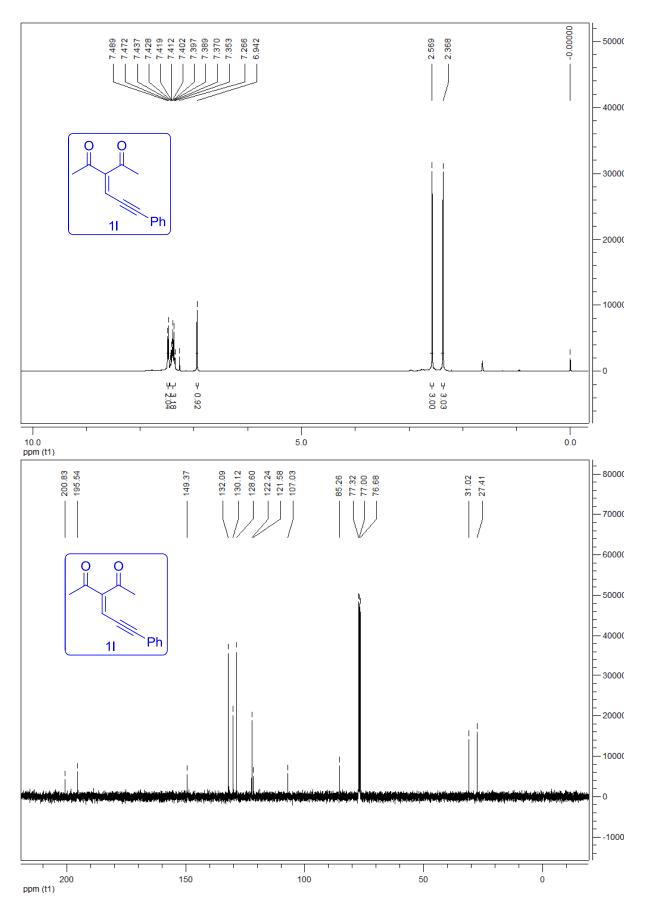


Methyl 2-propionylnon-2-en-4-ynoate (E/Z mixture) (1k)

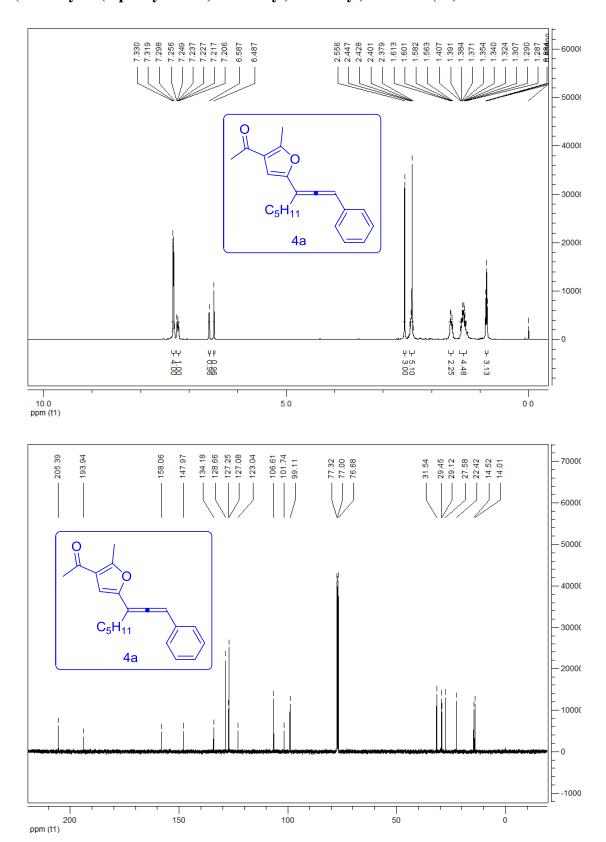




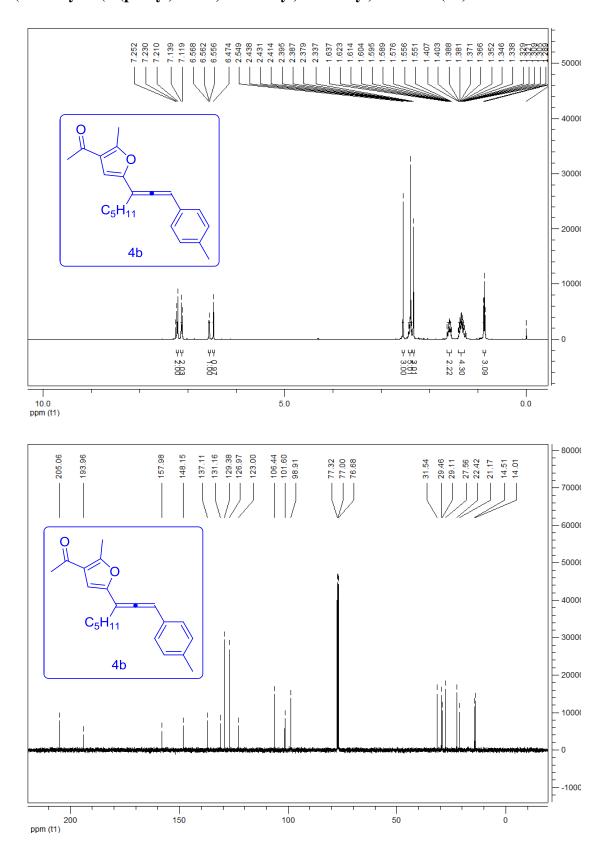
## ${\bf 3\text{-}(3\text{-}phenylprop-2\text{-}yn-1\text{-}ylidene)} pentane-2, {\bf 4\text{-}dione}\;(1l)$



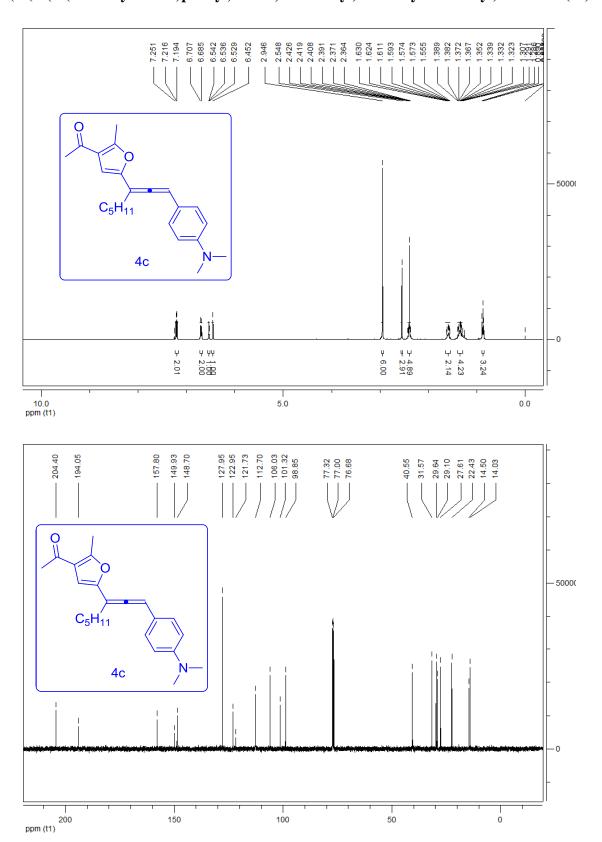
## $1\hbox{-}(2\hbox{-}Methyl\hbox{-}5\hbox{-}(1\hbox{-}phenylocta\hbox{-}1\hbox{,}2\hbox{-}dien\hbox{-}3\hbox{-}yl)furan\hbox{-}3\hbox{-}yl)ethan one \ (4a)$



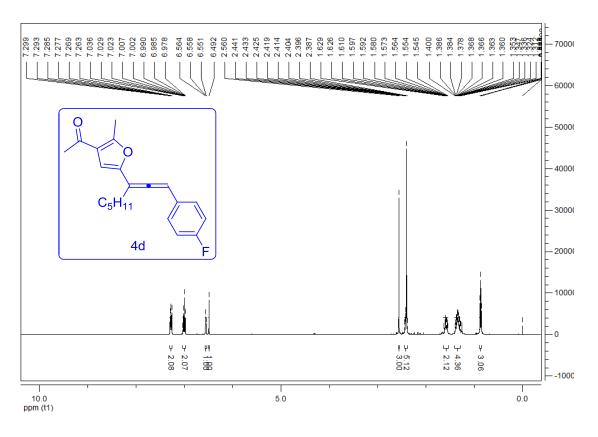
#### $1\hbox{-}(2\hbox{-}Methyl\hbox{-}5\hbox{-}(1\hbox{-}(p\hbox{-}tolyl)octa\hbox{-}1,2\hbox{-}dien\hbox{-}3\hbox{-}yl)furan\hbox{-}3\hbox{-}yl)ethan one \ (4b)$

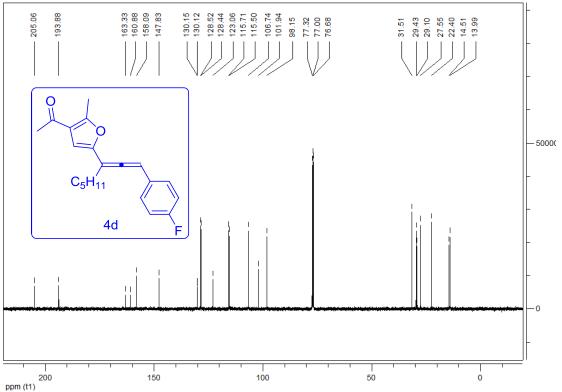


## $1\hbox{-}(5\hbox{-}(1\hbox{-}(4\hbox{-}(Dimethylamino)phenyl)octa-1,}2\hbox{-}dien-3\hbox{-}yl)\hbox{-}2\hbox{-}methylfuran-3\hbox{-}yl)ethanone\ (4c)$

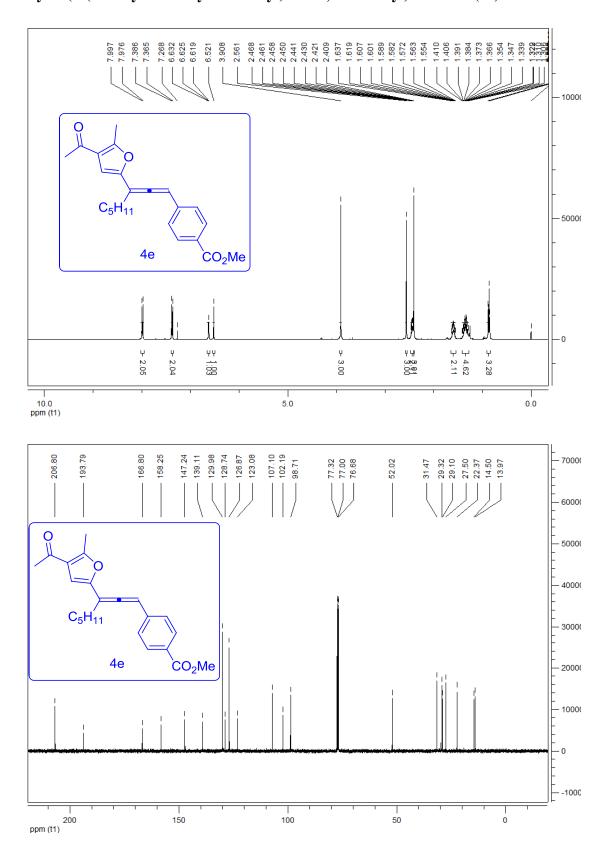


#### 1-(5-(1-(4-Fluorophenyl)octa-1,2-dien-3-yl)-2-methylfuran-3-yl)ethanone (4d)

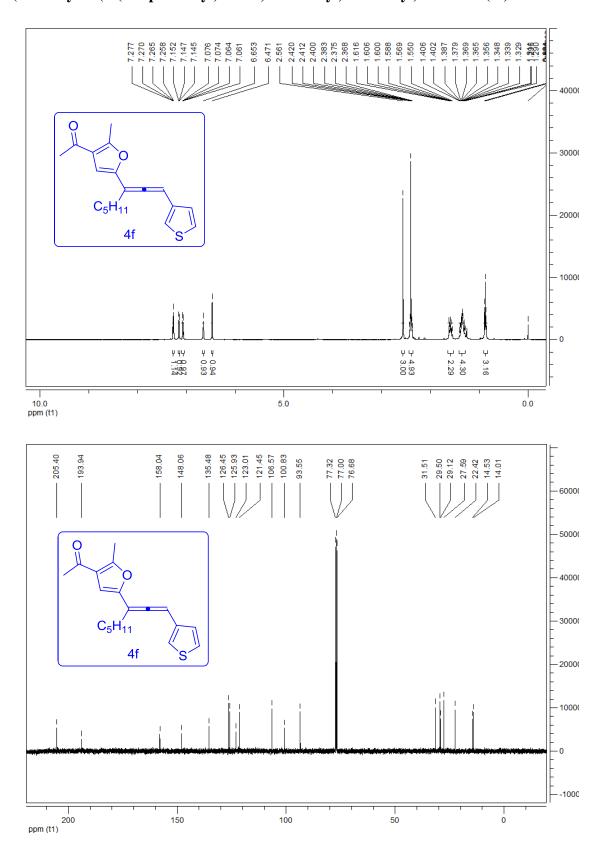




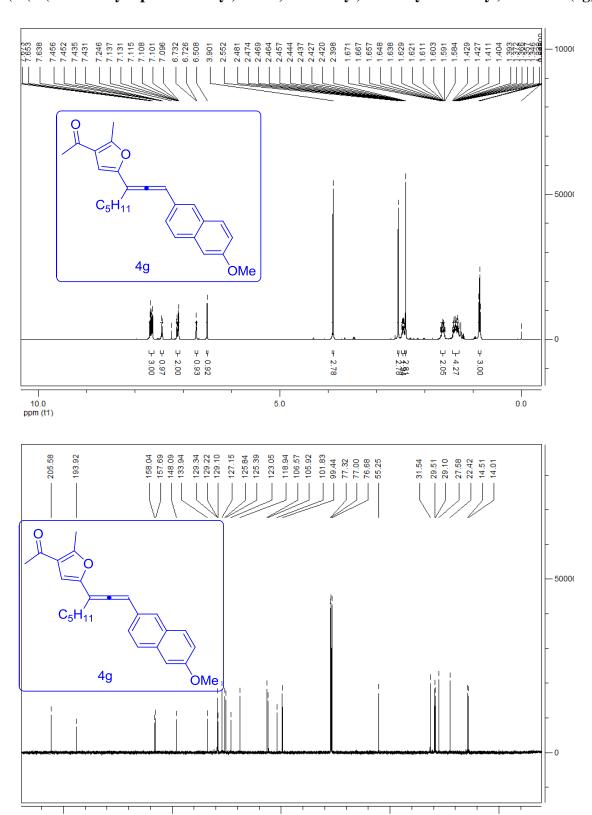
 $Methyl\ 4\hbox{-}(3\hbox{-}(4\hbox{-}acetyl\hbox{-}5\hbox{-}methylfuran\hbox{-}2\hbox{-}yl)octa\hbox{-}1\hbox{,}2\hbox{-}dien\hbox{-}1\hbox{-}yl)benzoate\ (4e)$ 



## $1\hbox{-}(2\hbox{-}Methyl\hbox{-}5\hbox{-}(1\hbox{-}(thiophen\hbox{-}3\hbox{-}yl)octa\hbox{-}1\hbox{,}2\hbox{-}dien\hbox{-}3\hbox{-}yl)furan\hbox{-}3\hbox{-}yl)ethan one \ (4f)$

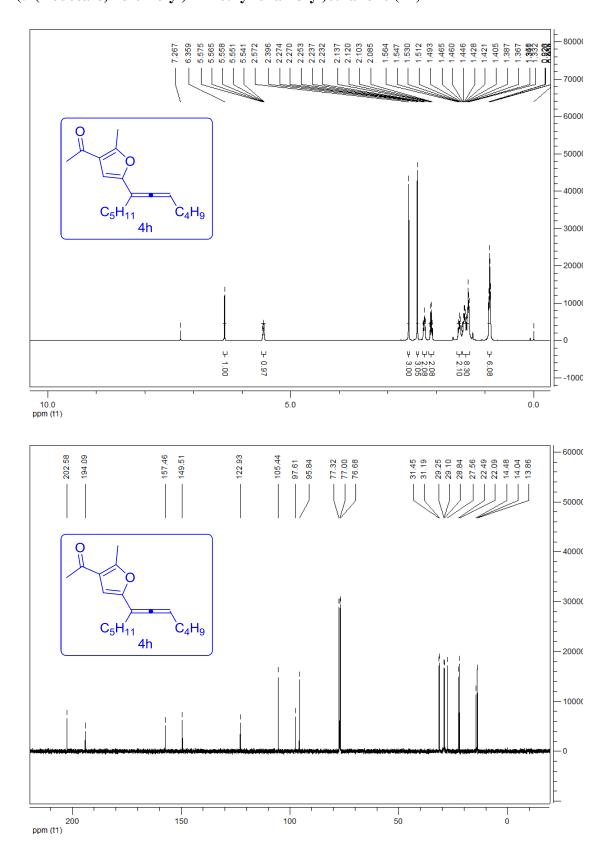


#### 1-(5-(1-(6-Methoxynaphthalen-2-yl)octa-1,2-dien-3-yl)-2-methylfuran-3-yl)ethanone (4g)

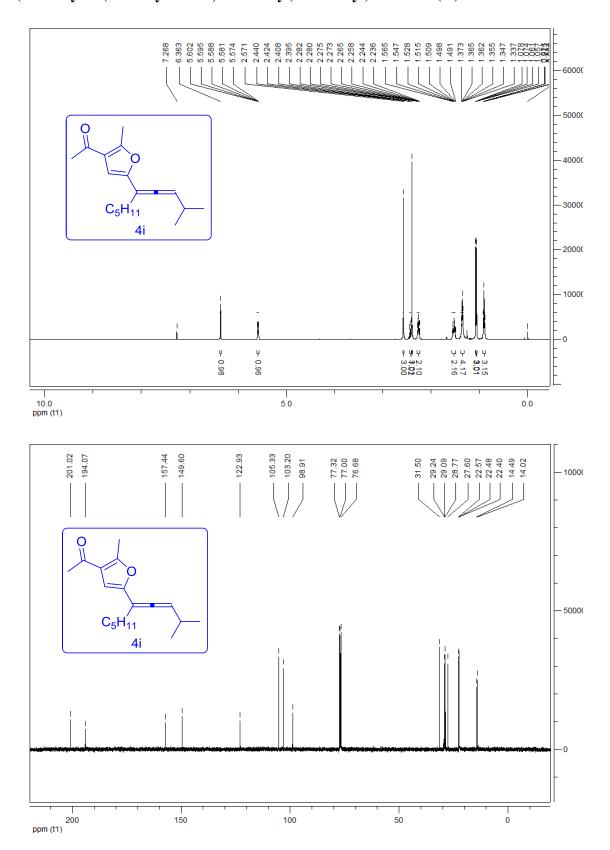


ppm (t1)

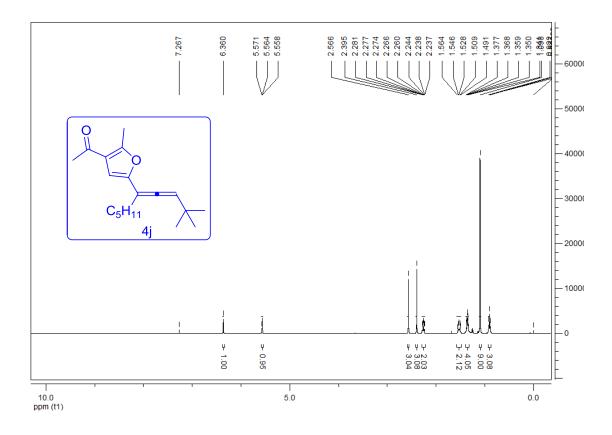
#### $1\hbox{-}(5\hbox{-}(Dodeca\hbox{-}6,7\hbox{-}dien\hbox{-}6\hbox{-}yl)\hbox{-}2\hbox{-}methyl furan\hbox{-}3\hbox{-}yl) ethan one \ (4h)$

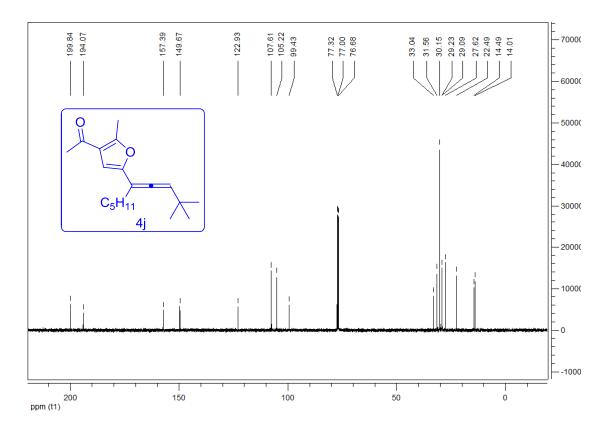


## $1\hbox{-}(2\hbox{-}Methyl\hbox{-}5\hbox{-}(2\hbox{-}methyldeca-3,}4\hbox{-}dien\hbox{-}5\hbox{-}yl) furan\hbox{-}3\hbox{-}yl) ethanone\ (4i)$

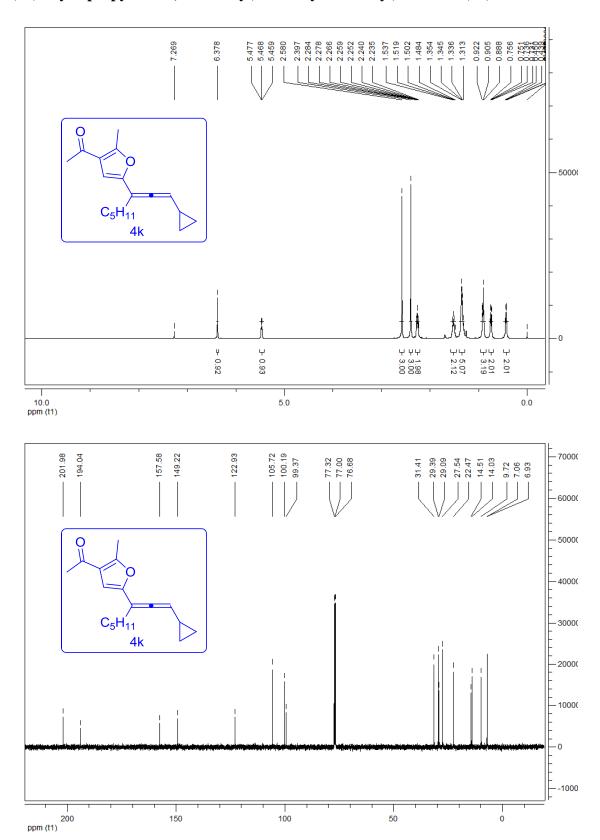


 $1\hbox{-}(5\hbox{-}(2,\!2\hbox{-}Dimethyldeca-3,\!4\hbox{-}dien-5\hbox{-}yl)\hbox{-}2\hbox{-}methylfuran-3\hbox{-}yl)ethan one \ (4j)$ 

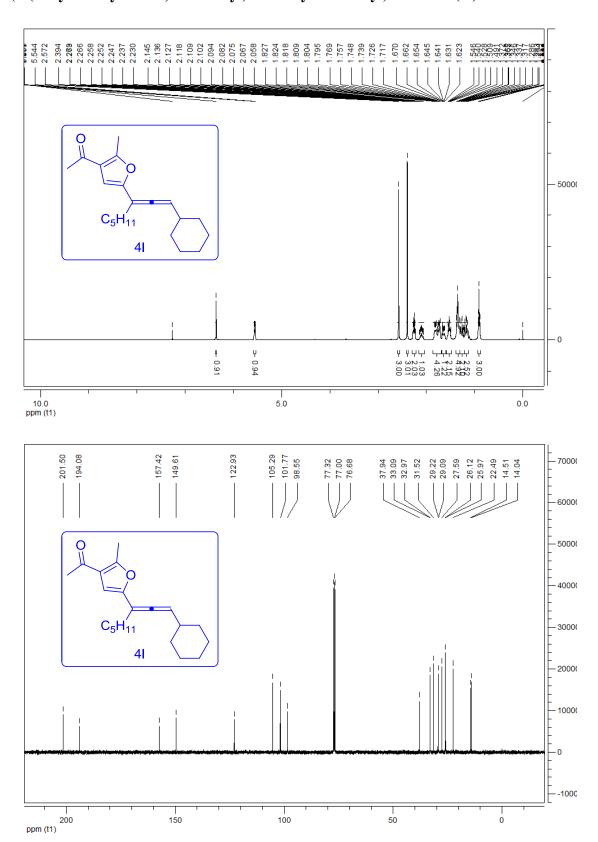




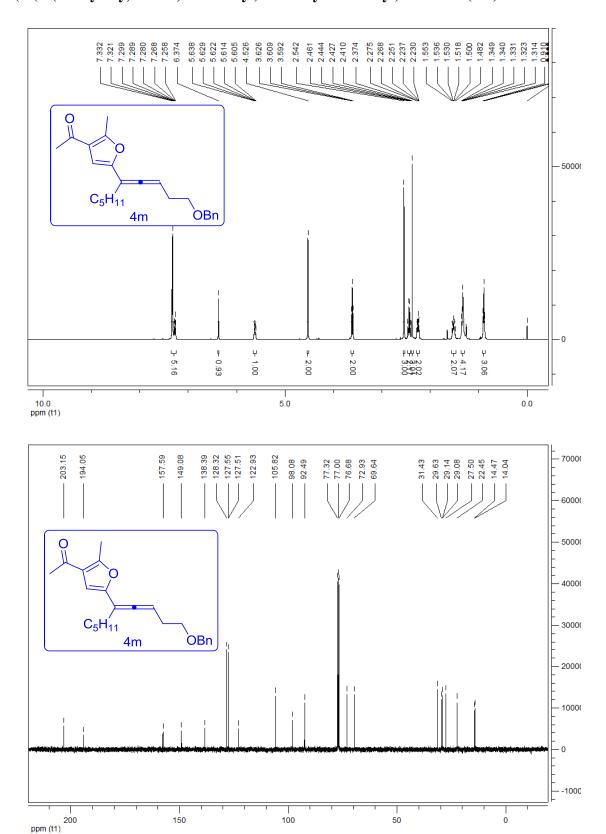
## $1\hbox{-}(5\hbox{-}(1\hbox{-}Cyclopropylocta-1,2\hbox{-}dien-3\hbox{-}yl)\hbox{-}2\hbox{-}methylfuran-3\hbox{-}yl) ethanone \ (4k)$



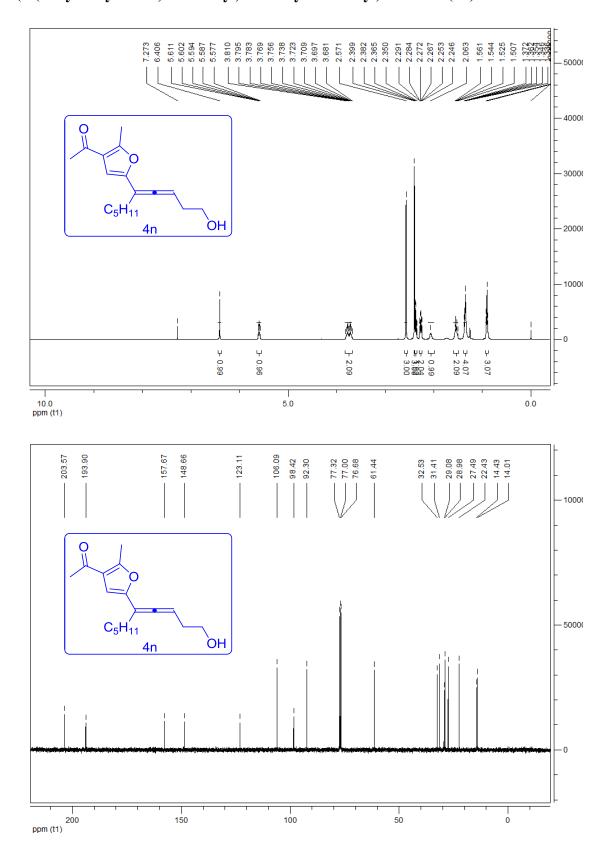
#### 1-(5-(1-Cyclohexylocta-1,2-dien-3-yl)-2-methylfuran-3-yl)ethanone (4l)



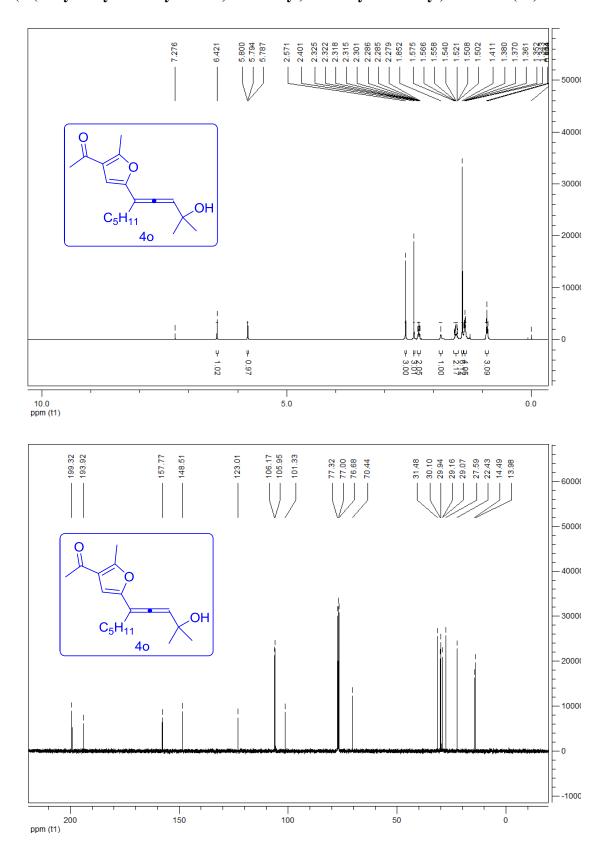
#### 1-(5-(1-(Benzyloxy)deca-3,4-dien-5-yl)-2-methylfuran-3-yl)ethanone (4m)



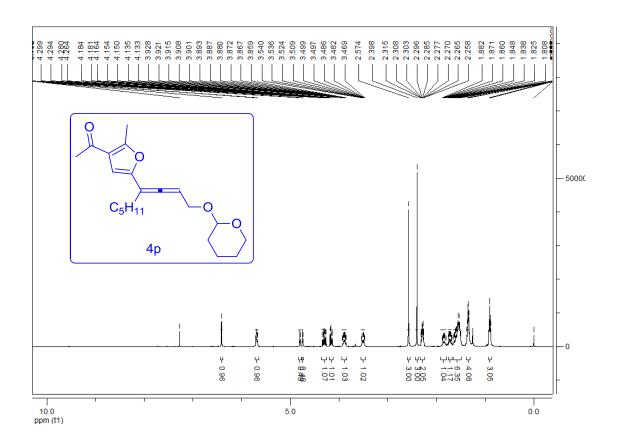
## $1\hbox{-}(5\hbox{-}(1\hbox{-}Hydroxydeca\hbox{-}3,4\hbox{-}dien\hbox{-}5\hbox{-}yl)\hbox{-}2\hbox{-}methylfuran\hbox{-}3\hbox{-}yl)ethan one \ (4n)$

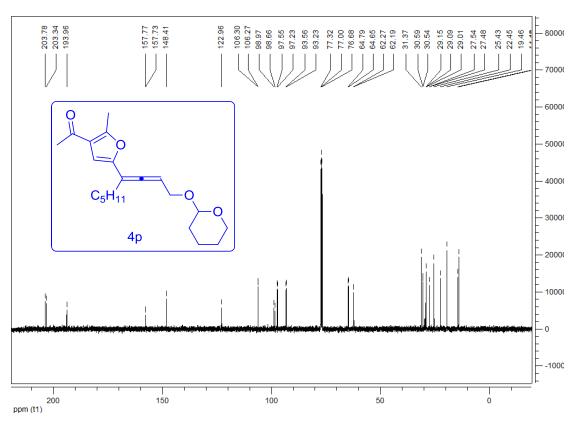


## $1\hbox{-}(5\hbox{-}(2\hbox{-Hydroxy-}2\hbox{-methyldeca-}3, 4\hbox{-dien-}5\hbox{-yl})\hbox{-}2\hbox{-methylfuran-}3\hbox{-yl}) ethan one~(4o)$

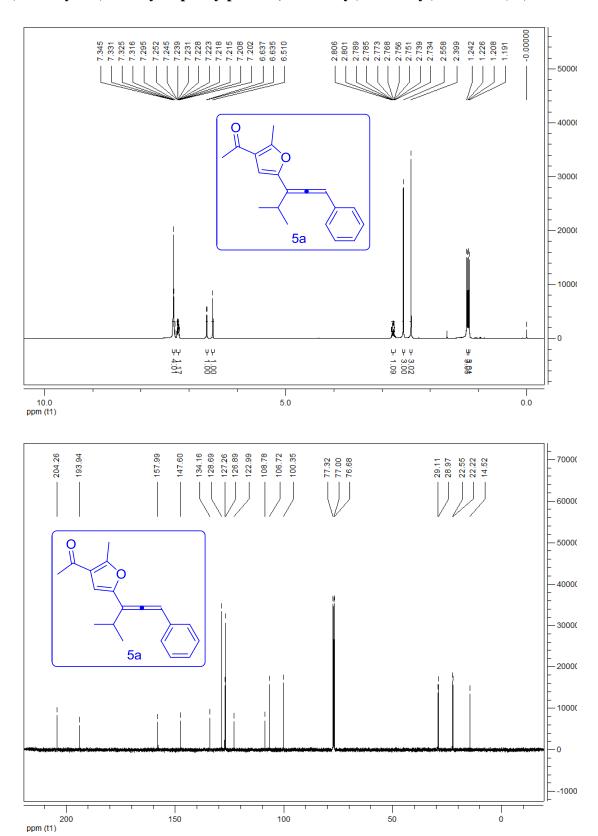


 $1\hbox{-}(2\hbox{-}Methyl\hbox{-}5\hbox{-}(1\hbox{-}((tetrahydro\hbox{-}2H\hbox{-}pyran\hbox{-}2\hbox{-}yl)oxy)nona\hbox{-}2,}3\hbox{-}dien\hbox{-}4\hbox{-}yl)furan\hbox{-}3\hbox{-}yl)ethanon e (4p)$ 

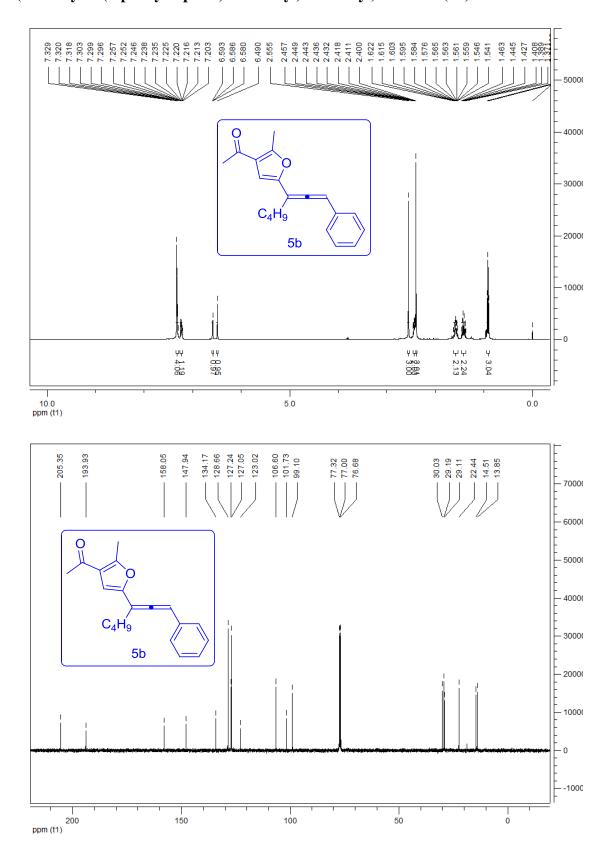




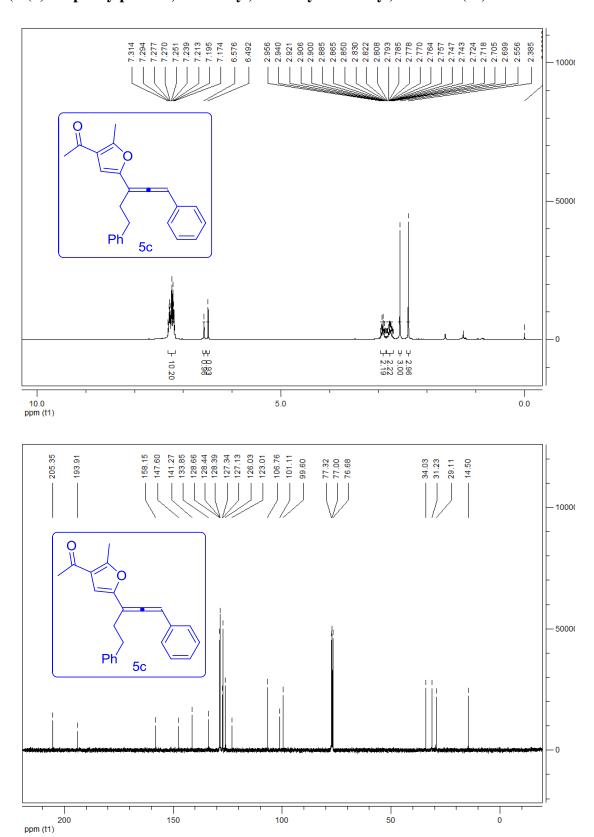
## $1\hbox{-}(2\hbox{-}Methyl\hbox{-}5\hbox{-}(4\hbox{-}methyl\hbox{-}1\hbox{-}phenylpenta\hbox{-}1\hbox{,}2\hbox{-}dien\hbox{-}3\hbox{-}yl)furan\hbox{-}3\hbox{-}yl)ethan one \ (5a)$



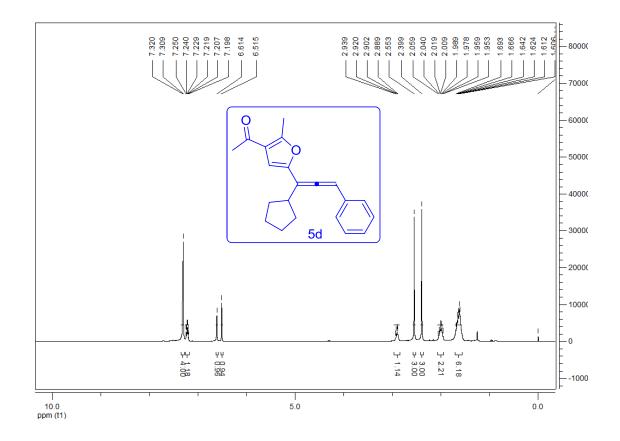
#### 1-(2-Methyl-5-(1-phenylhepta-1,2-dien-3-yl)furan-3-yl)ethanone (5b)

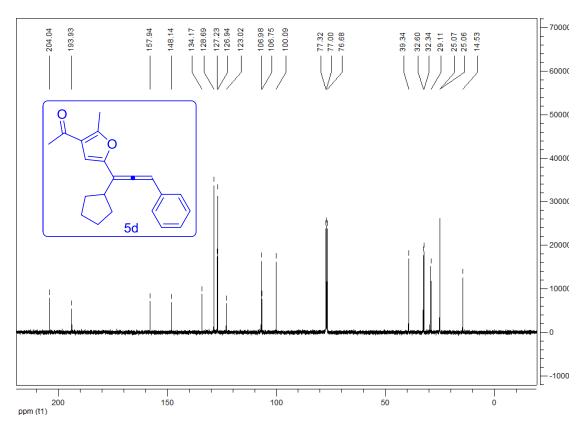


## $1\hbox{-}(5\hbox{-}(1,5\hbox{-}Diphenylpenta-1,2\hbox{-}dien-3\hbox{-}yl)\hbox{-}2\hbox{-}methylfuran-3\hbox{-}yl) ethanone \ (5c)$

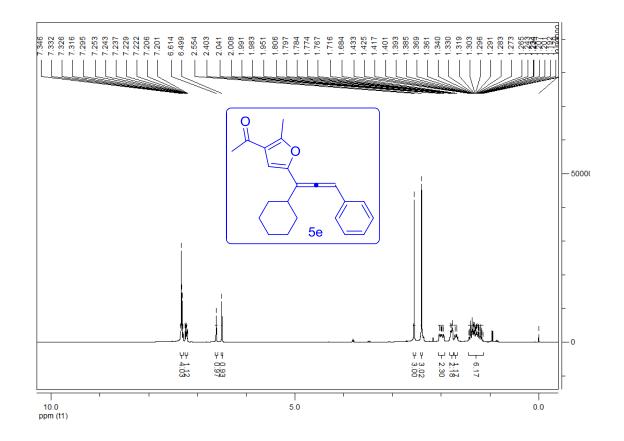


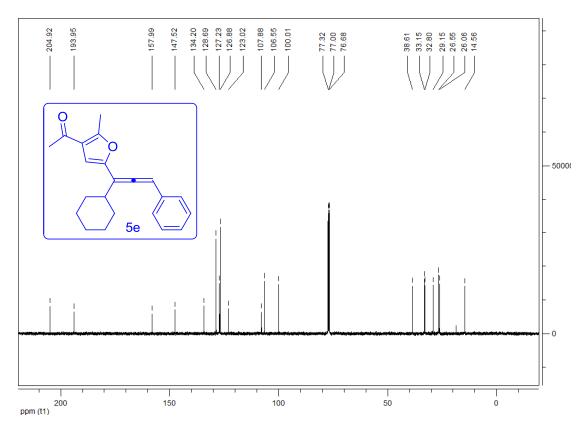
 $1\hbox{-}(5\hbox{-}(1\hbox{-}Cyclopentyl\hbox{-}3\hbox{-}phenylpropa-1,}2\hbox{-}dien\hbox{-}1\hbox{-}yl)\hbox{-}2\hbox{-}methylfuran-3\hbox{-}yl) ethanone~(5d)$ 



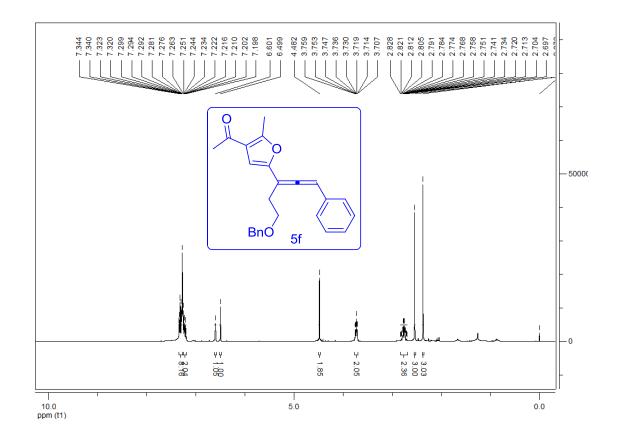


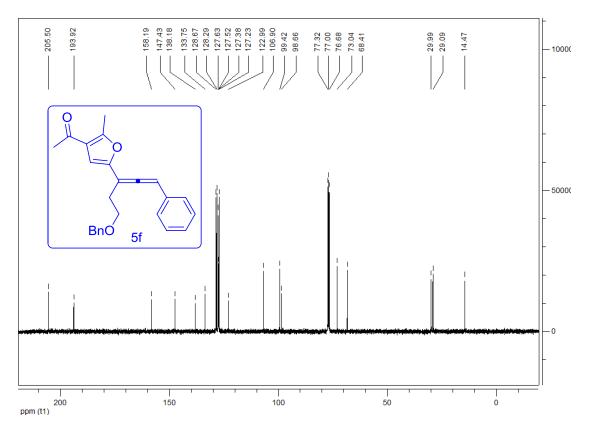
## $1\hbox{-}(5\hbox{-}(1\hbox{-}Cyclohexyl\hbox{-}3\hbox{-}phenylpropa-1,}2\hbox{-}dien\hbox{-}1\hbox{-}yl)\hbox{-}2\hbox{-}methylfuran\hbox{-}3\hbox{-}yl) ethanone \ (5e)$



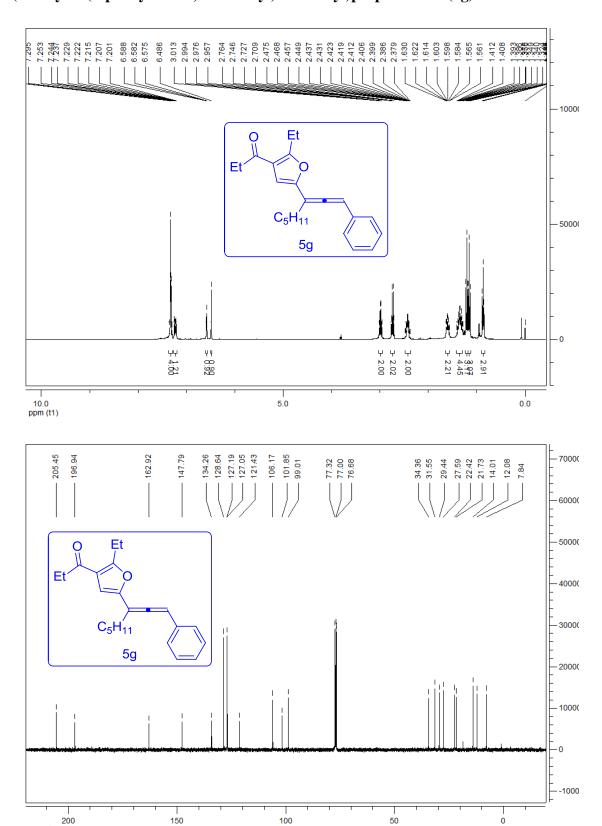


## $1\hbox{-}(5\hbox{-}(5\hbox{-}(Benzyloxy)\hbox{-}1\hbox{-}phenylpenta-1,}2\hbox{-}dien-3\hbox{-}yl)\hbox{-}2\hbox{-}methylfuran-3\hbox{-}yl)ethan one \ (5f)$



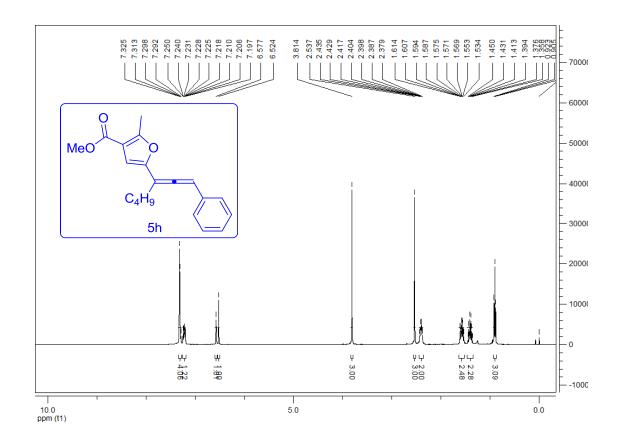


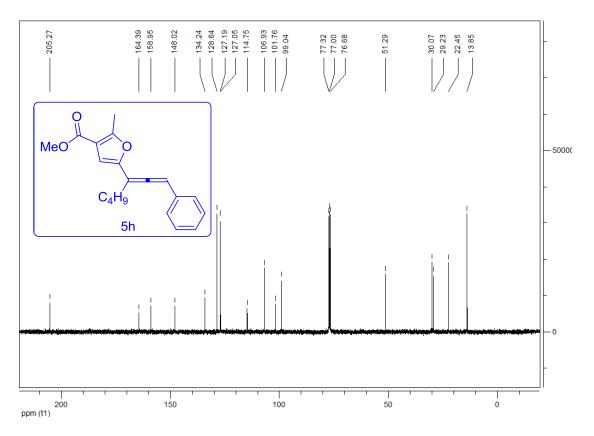
#### 1-(2-Ethyl-5-(1-phenylocta-1,2-dien-3-yl)furan-3-yl)propan-1-one (5g)



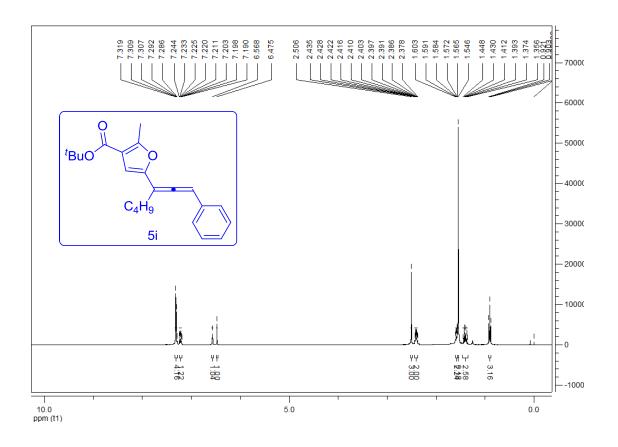
ppm (t1)

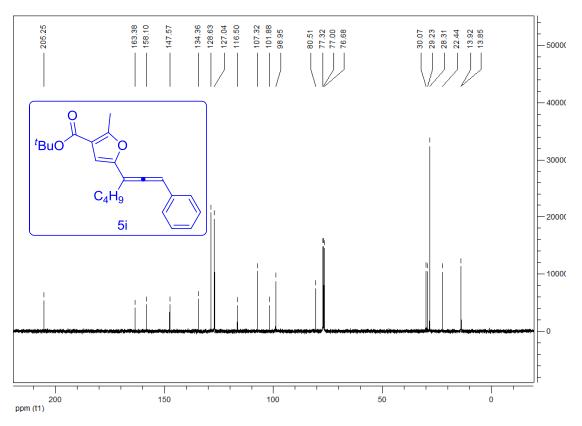
 $Methyl\ 2\text{-methyl-5-} (1\text{-phenylhepta-1,2-dien-3-yl}) furan-3\text{-carboxylate}\ (5h)$ 



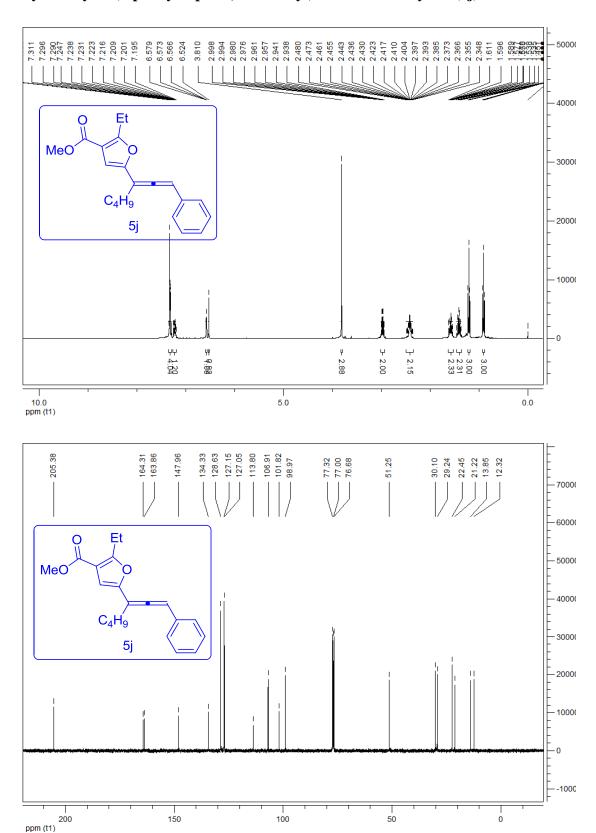


## tert-Butyl 2-methyl-5-(1-phenylhepta-1,2-dien-3-yl) furan-3-carboxylate (5i)

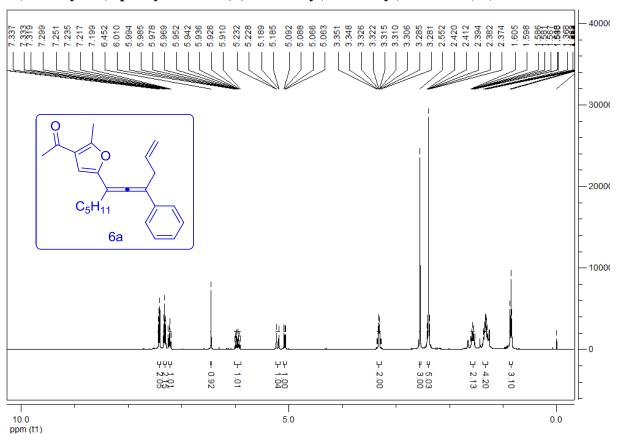


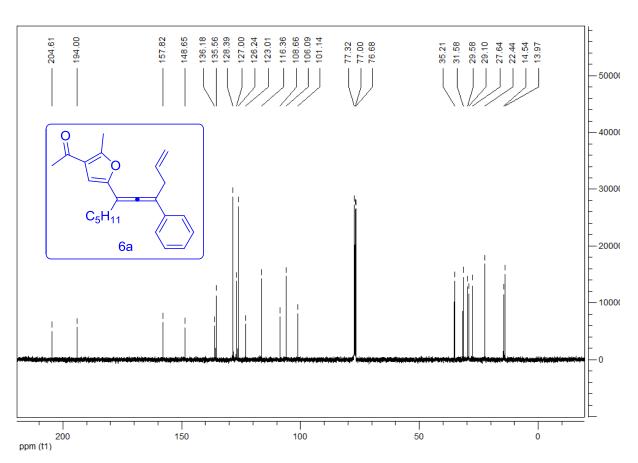


Methyl 2-ethyl-5-(1-phenylhepta-1,2-dien-3-yl)furan-3-carboxylate (5j)

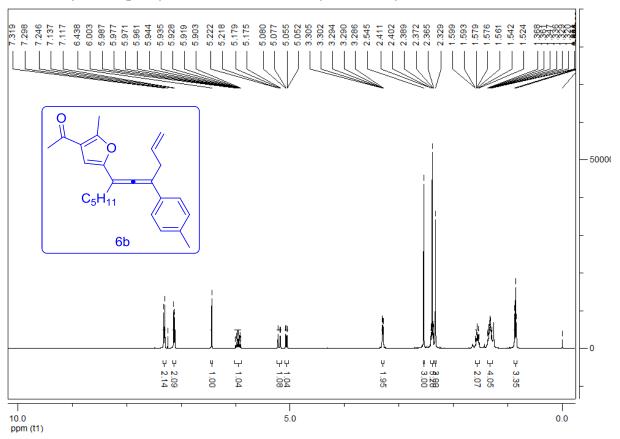


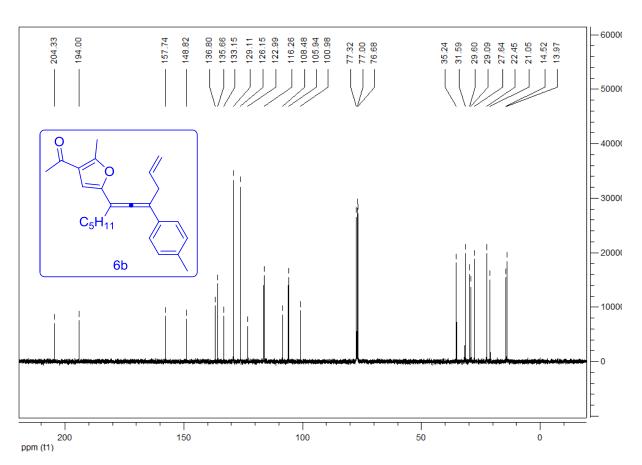
## 1-(2-methyl-5-(4-phenylundeca-1,4,5-trien-6-yl)furan-3-yl)ethanone (6a)



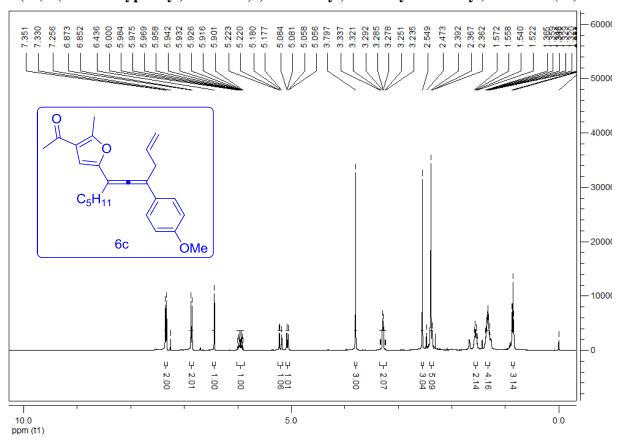


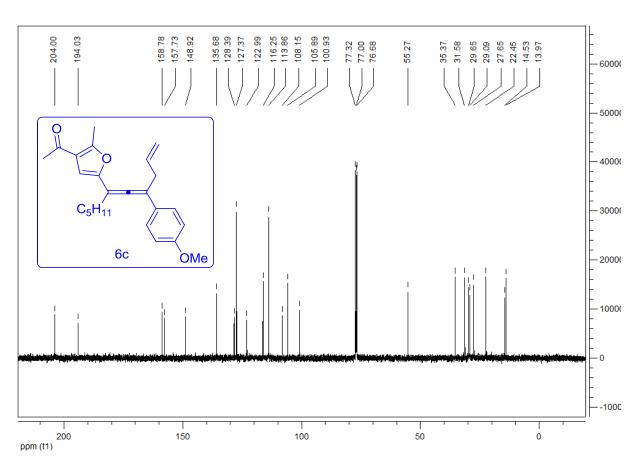
## 1-(2-methyl-5-(4-(p-tolyl)undeca-1,4,5-trien-6-yl)furan-3-yl)ethanone (6b)



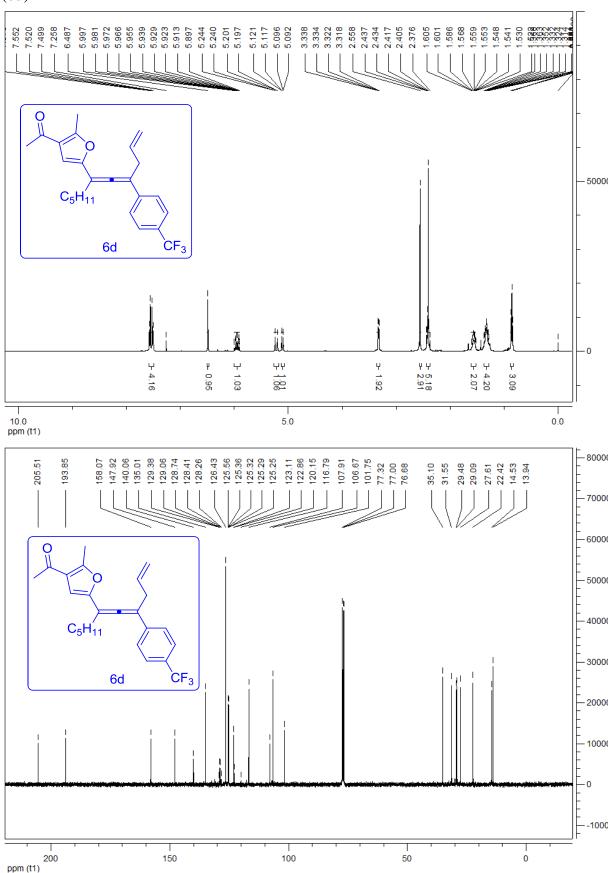


## 1-(5-(4-(4-methoxyphenyl)undeca-1,4,5-trien-6-yl)-2-methylfuran-3-yl)ethanone (6c)

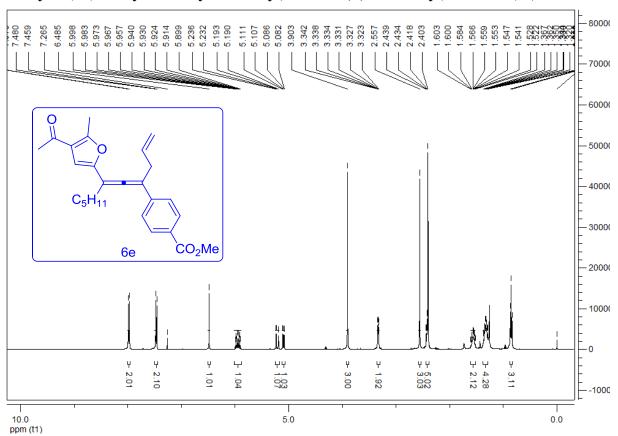


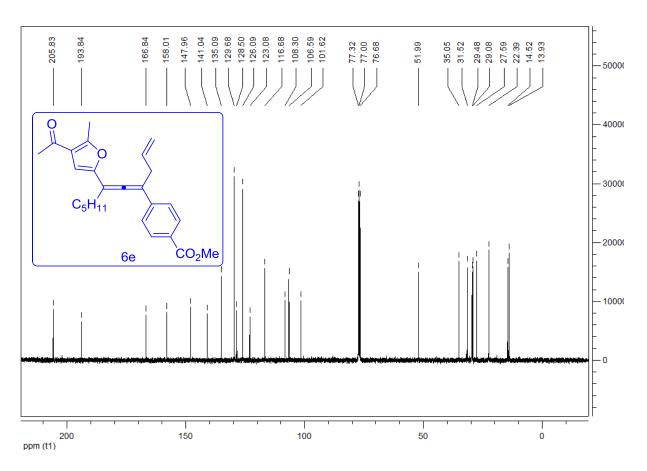


# $1-(2-methyl-5-(4-(4-(trifluoromethyl)phenyl)undeca-1,4,5-trien-6-yl)furan-3-yl)ethanone \\ (6d)$

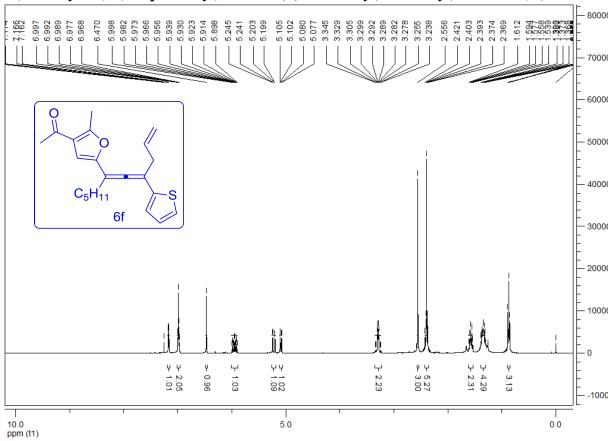


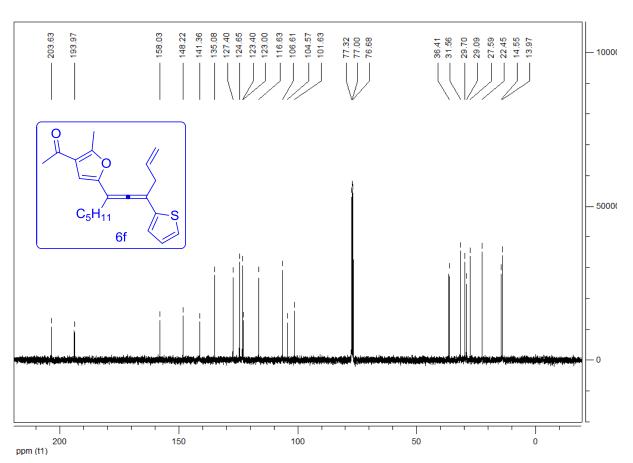
methyl 4-(6-(4-acetyl-5-methylfuran-2-yl)undeca-1,4,5-trien-4-yl)benzoate (6e)



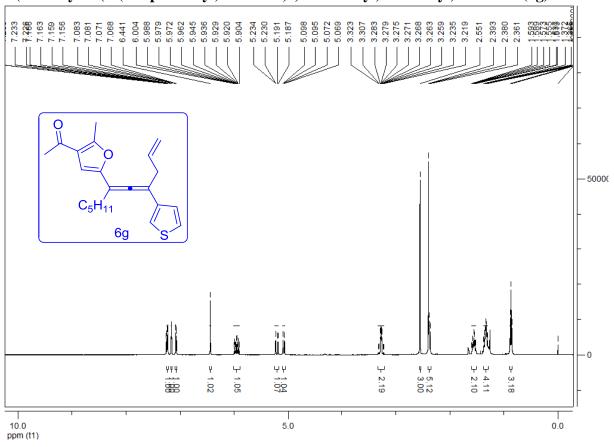


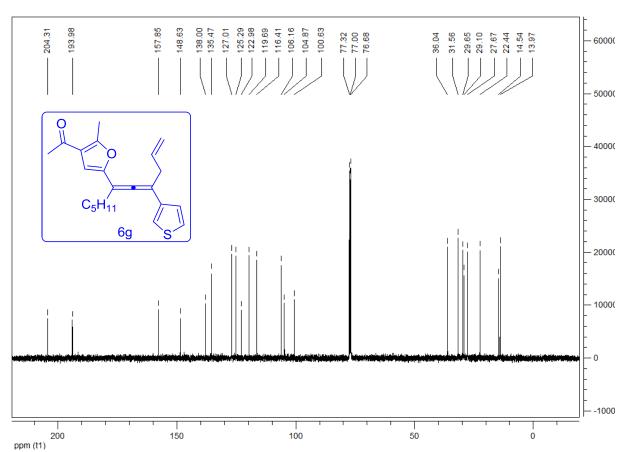
#### 1-(2-methyl-5-(4-(thiophen-2-yl)undeca-1,4,5-trien-6-yl)furan-3-yl)ethanone (6f)



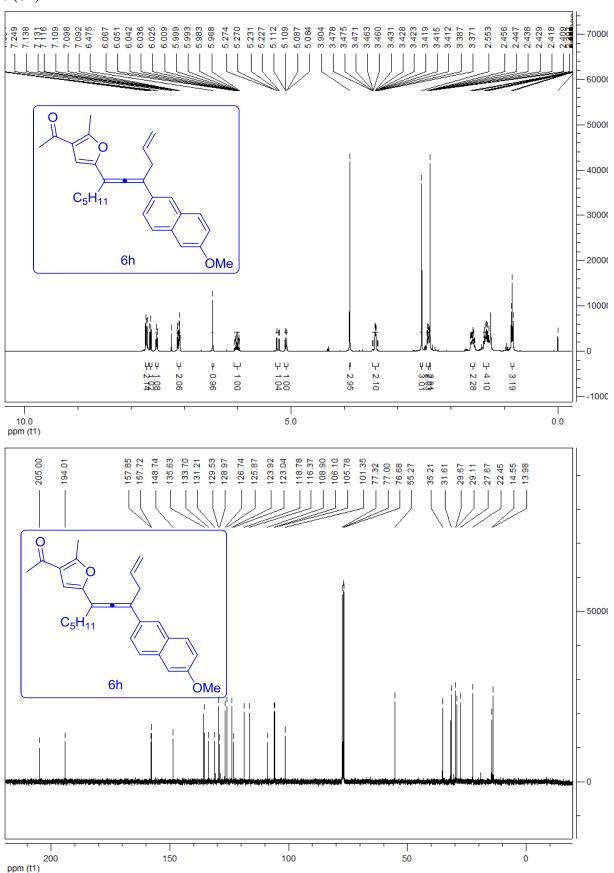


#### 1-(2-methyl-5-(4-(thiophen-3-yl)undeca-1,4,5-trien-6-yl)furan-3-yl)ethanone (6g)

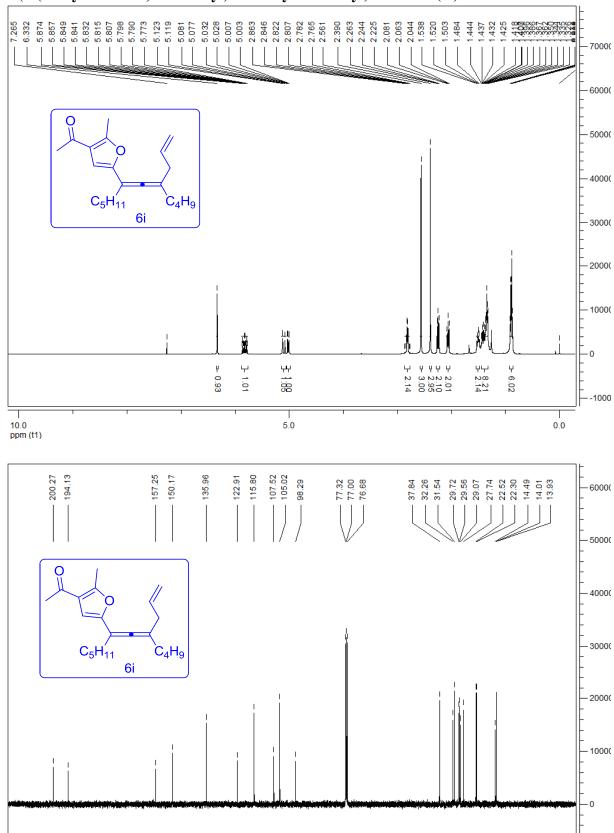




 $1-(5-(4-(6-methoxynaphthalen-2-yl)undeca-1,4,5-trien-6-yl)-2-methylfuran-3-yl)ethanon \\ e~(6h)$ 



#### 1-(5-(8-allyldodeca-6,7-dien-6-yl)-2-methylfuran-3-yl)ethanone (6i)



50

100

150

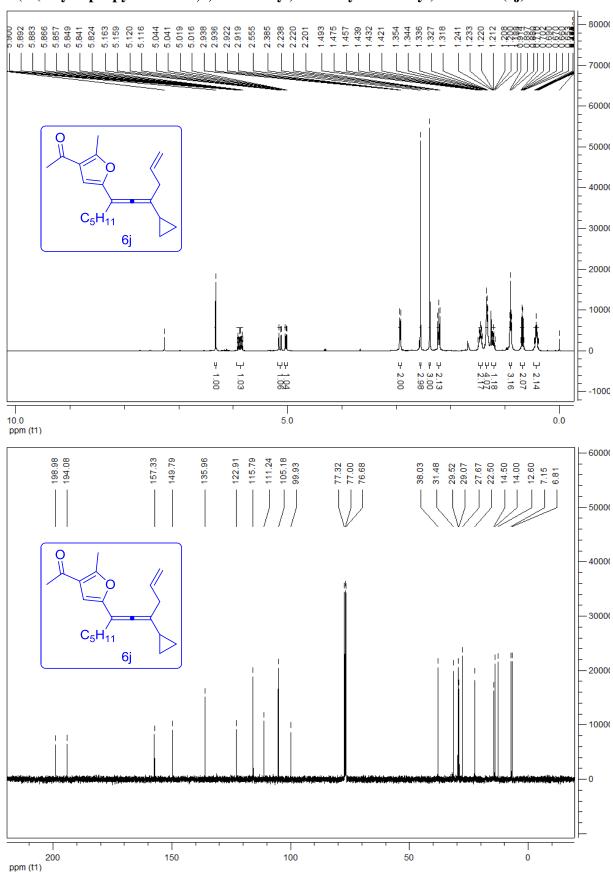
200

ppm (t1)

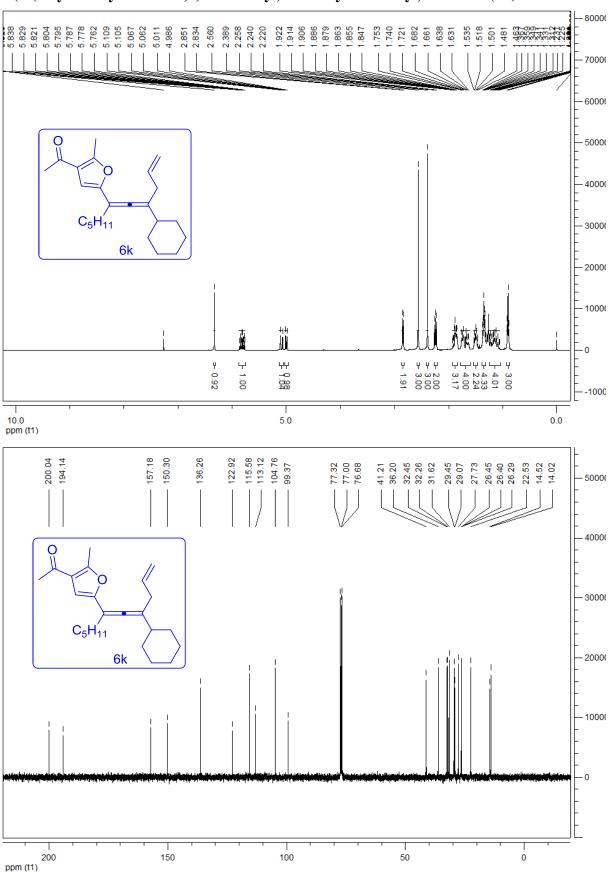
-1000

0

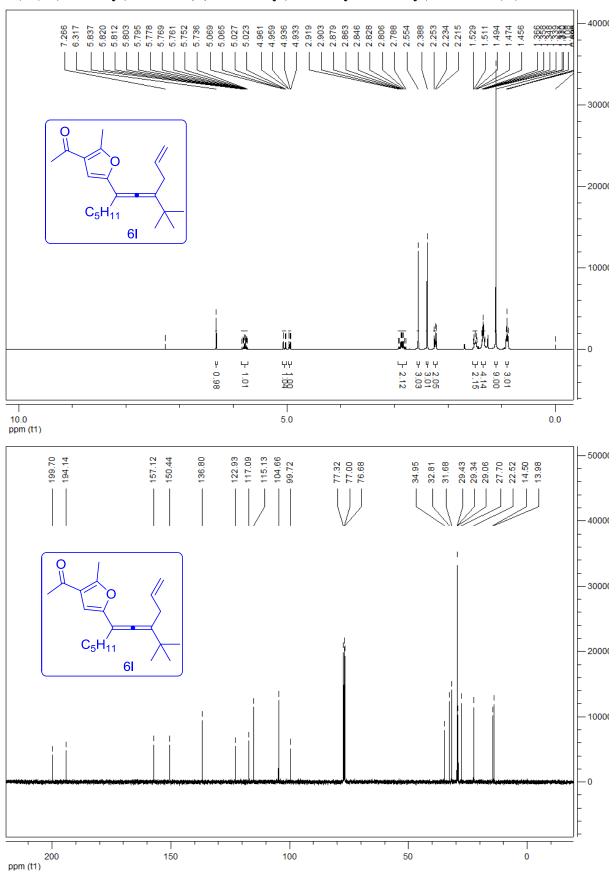
## 1-(5-(4-cyclopropylundeca-1,4,5-trien-6-yl)-2-methylfuran-3-yl)ethanone (6j)



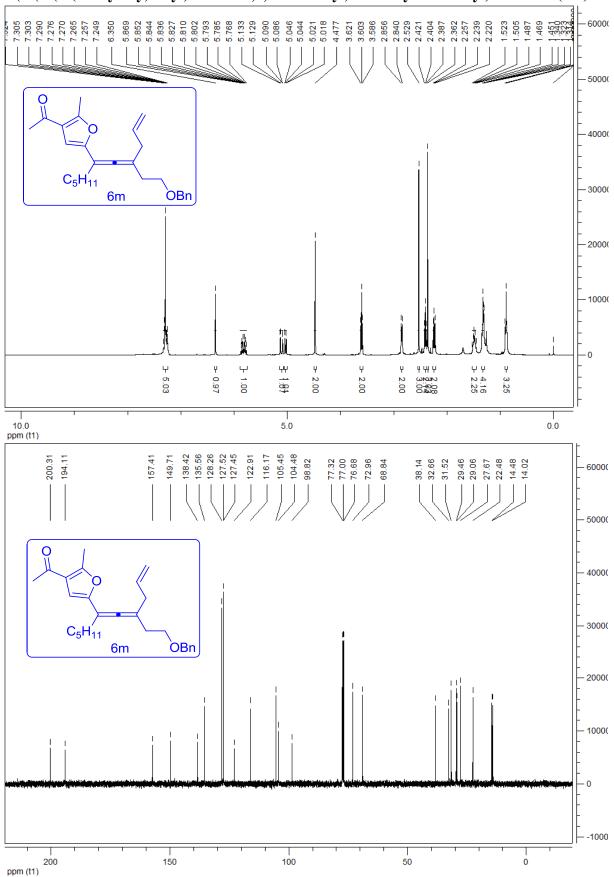
## 1-(5-(4-cyclohexylundeca-1,4,5-trien-6-yl)-2-methylfuran-3-yl)ethanone (6k)



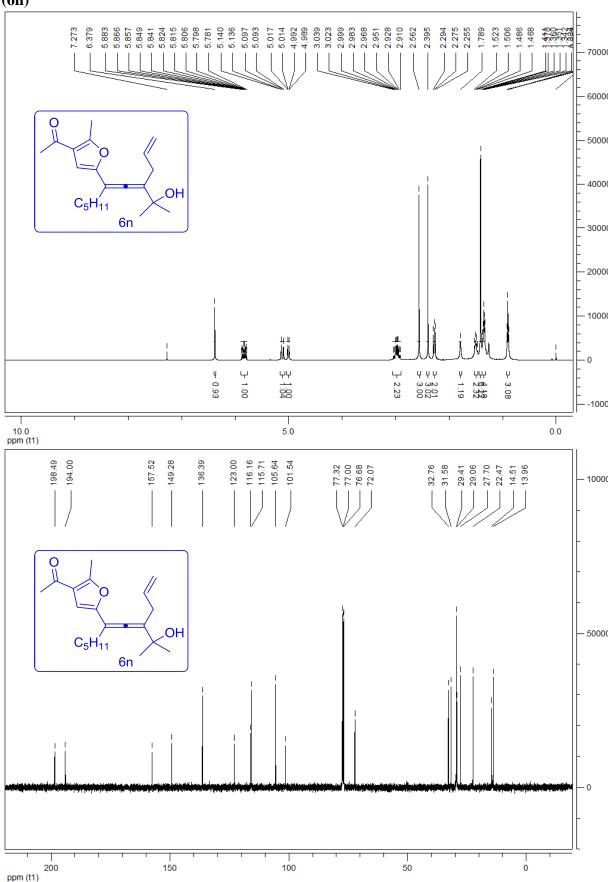
## 1-(5-(4-(tert-butyl)undeca-1,4,5-trien-6-yl)-2-methylfuran-3-yl)ethanone (6l)



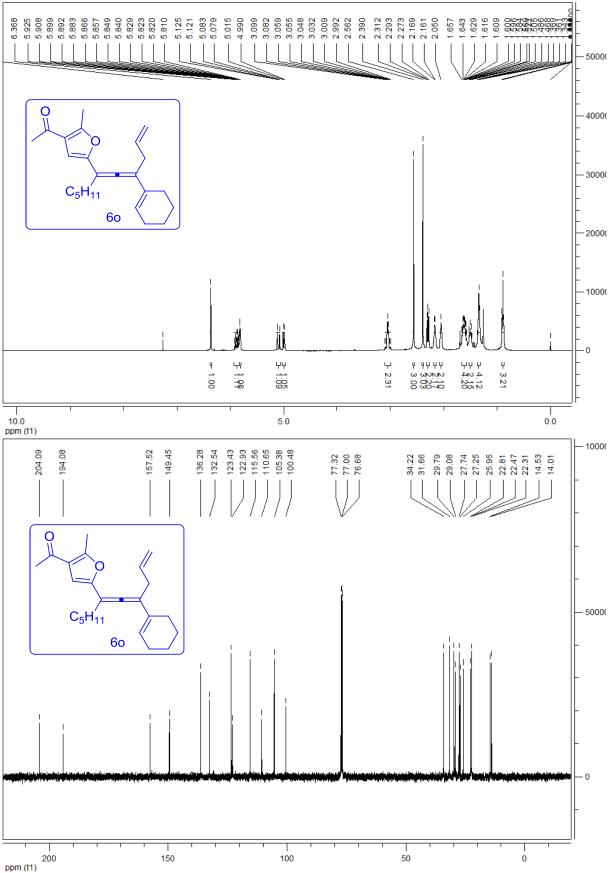
1-(5-(4-(2-(benzyloxy)ethyl)undeca-1,4,5-trien-6-yl)-2-methylfuran-3-yl)ethanone (6m)



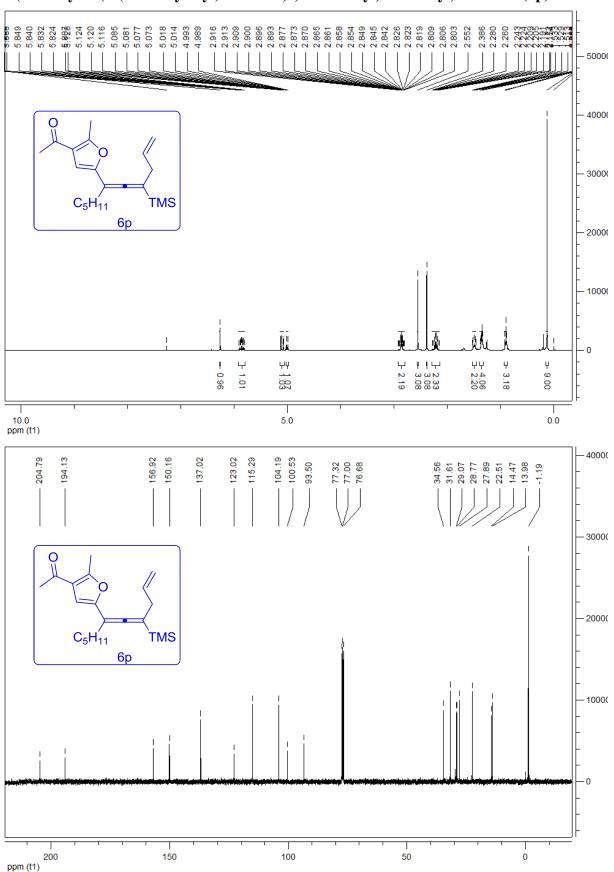
 $1\hbox{-}(5\hbox{-}(4\hbox{-}(2\hbox{-hydroxypropan-2-yl})undeca\hbox{-}1,4,5\hbox{-trien-6-yl})\hbox{-}2\hbox{-methylfuran-3-yl})ethan one \end{substitute}$ 

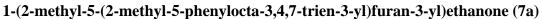


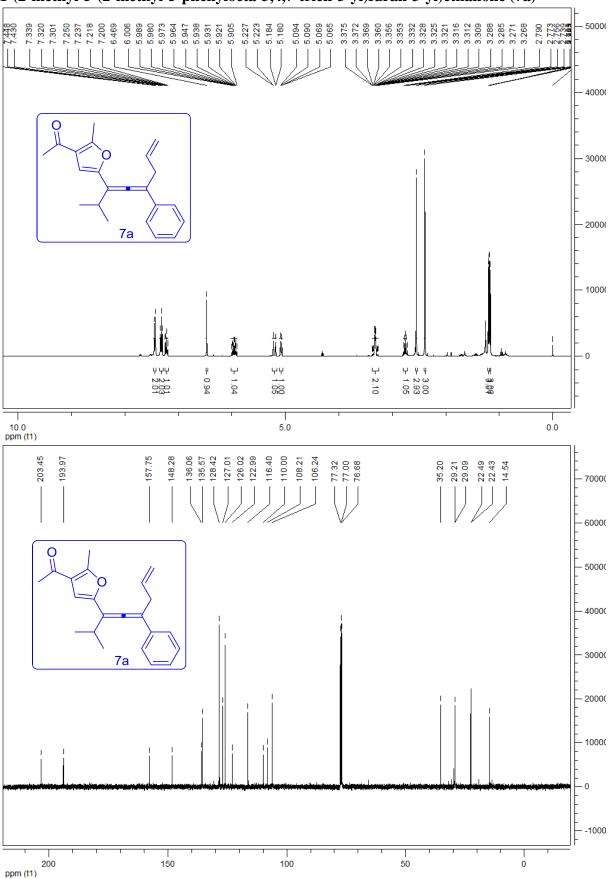




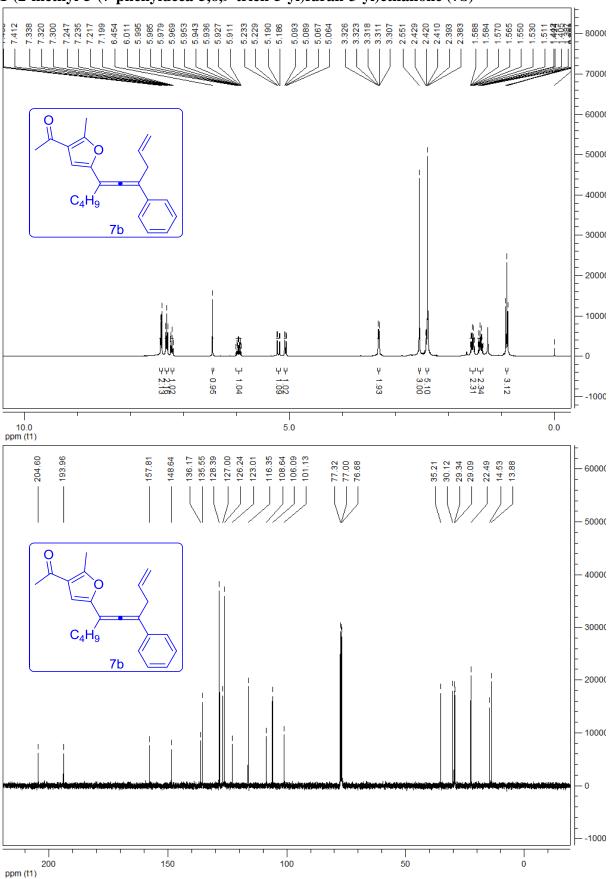
## 1-(2-methyl-5-(4-(trimethylsilyl)undeca-1,4,5-trien-6-yl)furan-3-yl)ethanone (6p)





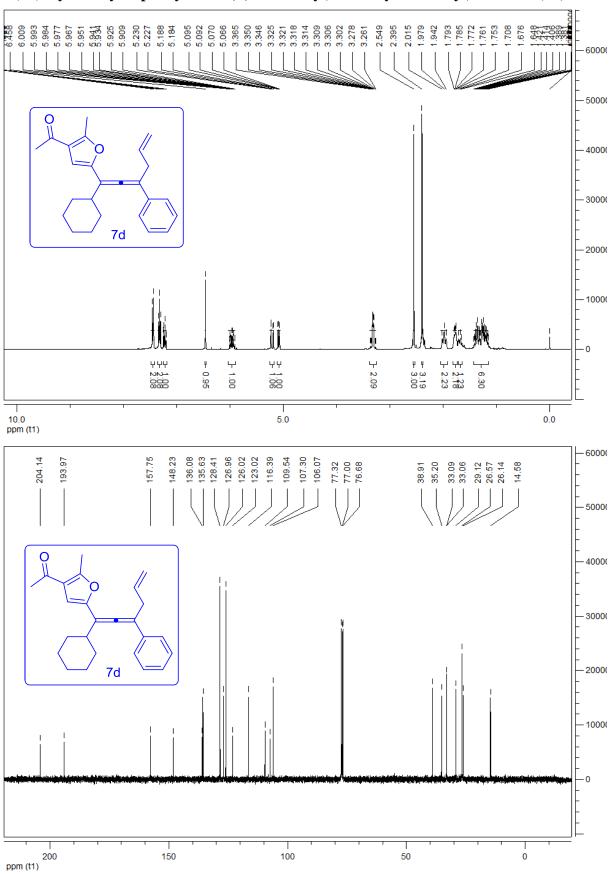


#### 1-(2-methyl-5-(7-phenyldeca-5,6,9-trien-5-yl)furan-3-yl)ethanone (7b)

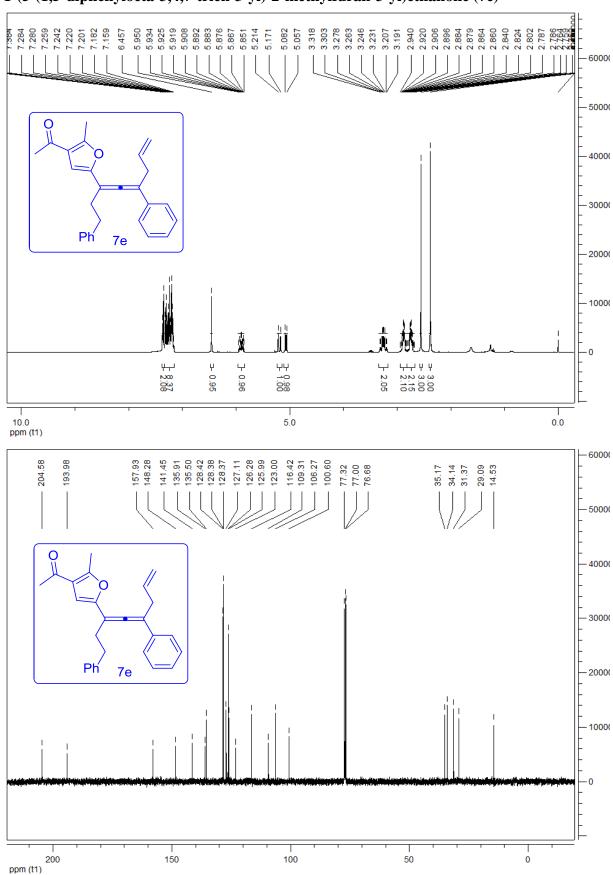


1-(5-(1-cyclopentyl-3-phenylhexa-1,2,5-trien-1-yl)-2-methylfuran-3-yl)ethanone (7c) - 30000 - 20000 7c - 10000 무무 2:03 **ሦ** ሃ 구 1.04 ¥ 3.04 3.00 000 5.0 0.0 10.0 ppm (t1) 157.72 126.98 126.07 123.01 116.38 109.63 106.48 106.17 203.22 193.97 148.82 136.06 135.54 128.41 77.32 77.00 76.68 35.20 32.60 32.38 29.10 25.12 25.09 14.55 - 60000 - 50000 - 40000 - 30000 7c - 20000 — 1000C -1000 200 150 100 ppm (t1)

## 1-(5-(1-cyclohexyl-3-phenylhexa-1,2,5-trien-1-yl)-2-methylfuran-3-yl)ethanone (7d)



**1-**(5-(1,5-diphenylocta-3,4,7-trien-3-yl)-2-methylfuran-3-yl)ethanone (7e)



 $1-(5-(1-(benzyloxy)-5-phenylocta-3,4,7-trien-3-yl)-2-methylfuran-3-yl) ethanone\ (7f)$ - 50000 BnÓ 7f 무무 1.001 051 子 2.16 → 3.01 → 3.00 → 2.21 5.0 0.0 10.0 ppm (t1) 167.95 148.10 138.21 135.39 135.39 127.62 127.62 127.49 126.35 122.99 116.44 116.44 109.14 106.41 98.06 77.00 77.00 77.00 204.71 35.09 30.13 29.07 14.49 - 60000 - 50000 **— 40000** - 30000 BnÓ 7f - 20000 — 1000C

100

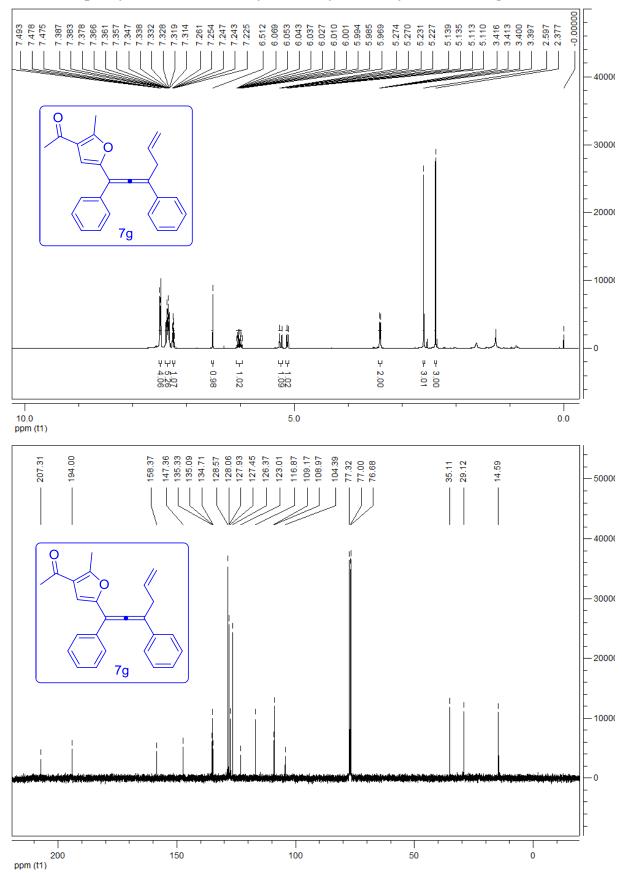
200

ppm (t1)

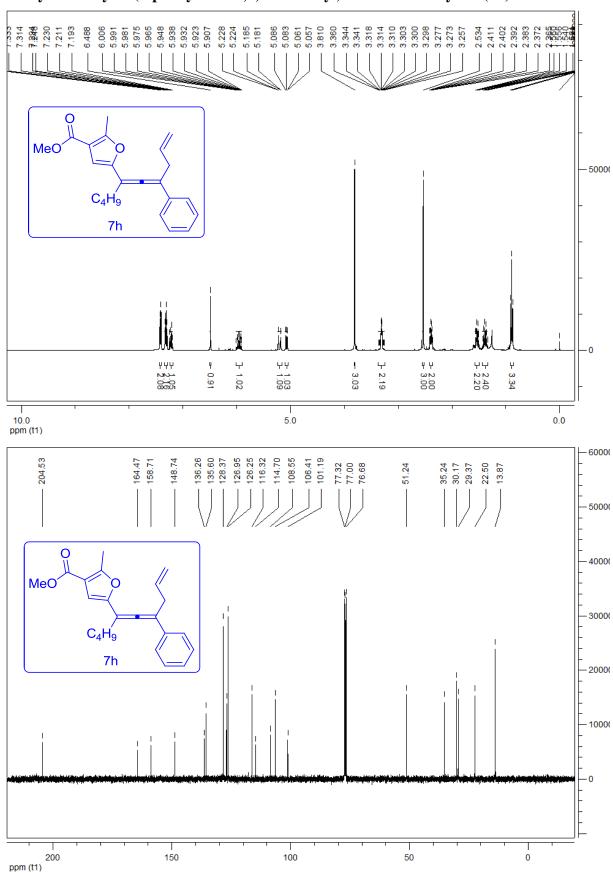
150

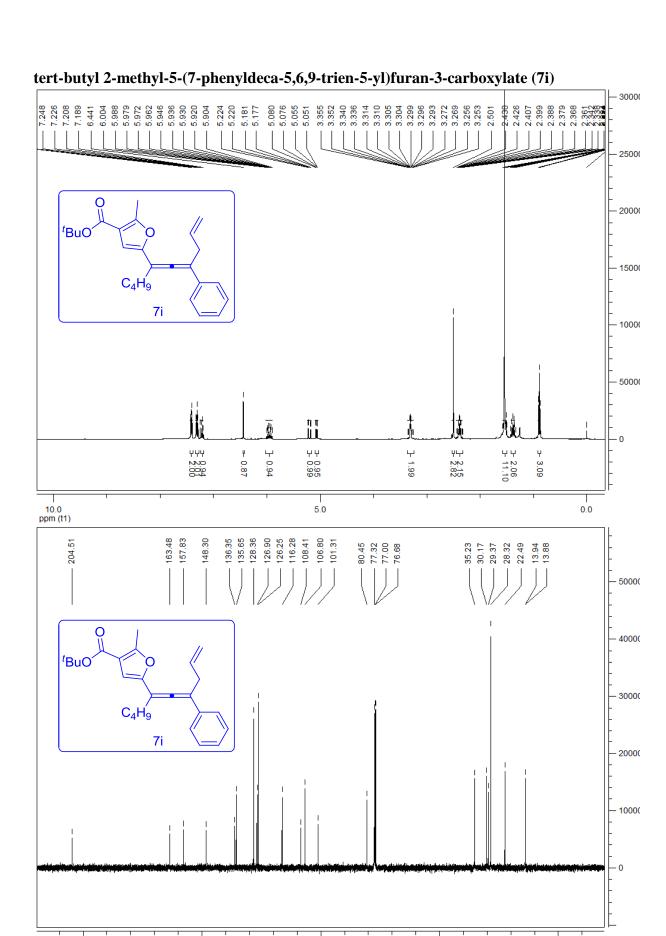
- -1000

**1-**(5-(1,3-diphenylhexa-1,2,5-trien-1-yl)-2-methylfuran-3-yl)ethanone (7g)



methyl 2-methyl-5-(7-phenyldeca-5,6,9-trien-5-yl)furan-3-carboxylate (7h)





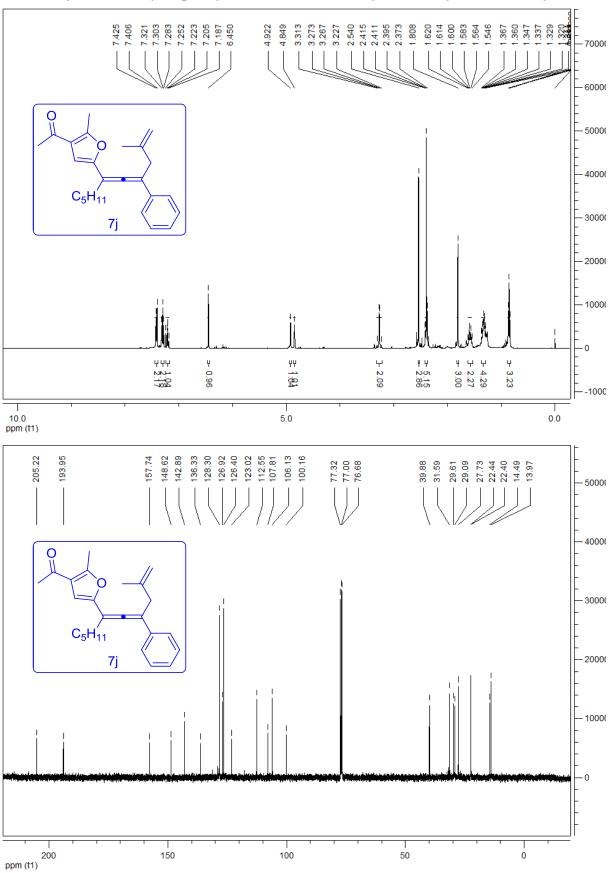
100

200

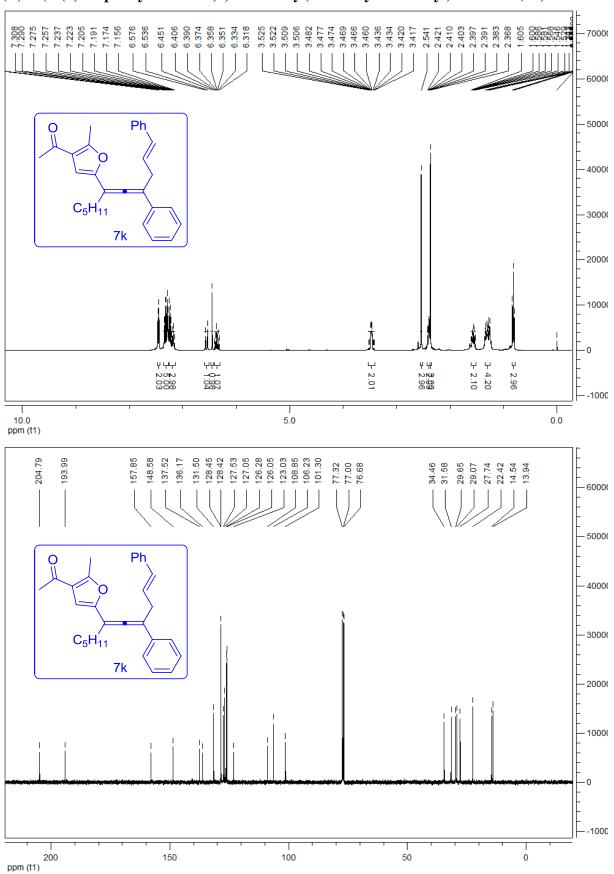
ppm (t1)

150

## 1-(2-methyl-5-(2-methyl-4-phenylundeca-1,4,5-trien-6-yl)furan-3-yl)ethanone (7j)



(E)-1-(5-(1,4-diphenylundeca-1,4,5-trien-6-yl)-2-methylfuran-3-yl)ethanone (7k)



 $1-(5-(1-(cyclohex-2-en-1-yl)-1-phenylocta-1,2-dien-3-yl)-2-methylfuran-3-yl)ethanone \eqno(7l)$ 

