$CoCl(PPh_3)_3$ as Cyclotrimerization Catalyst for Functionalized Triynes under Mild Conditions

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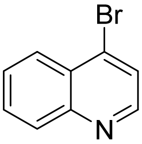
Supporting Information

Table of Contents

1. Overview of compounds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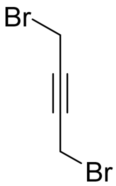
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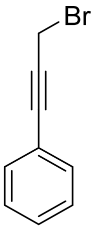
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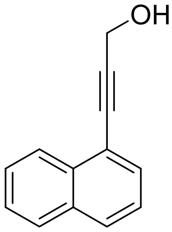
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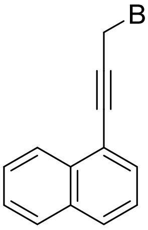
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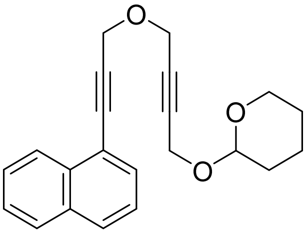
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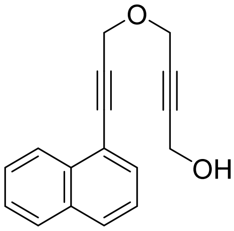
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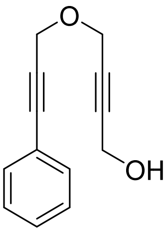
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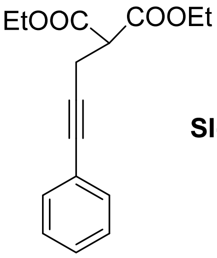
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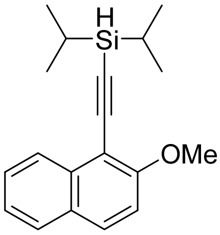
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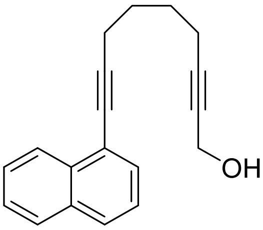
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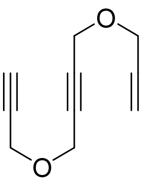
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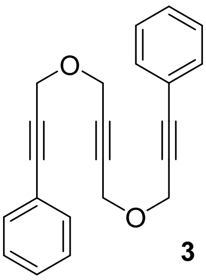
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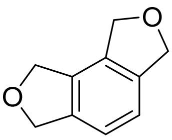
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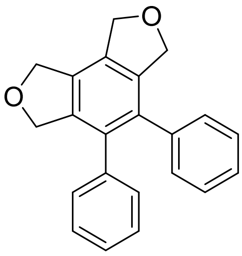
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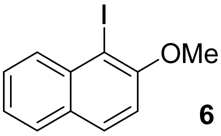
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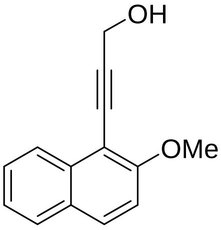
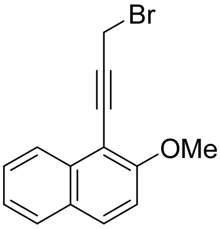

7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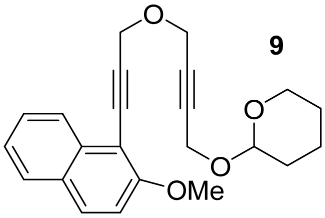
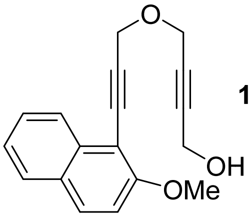
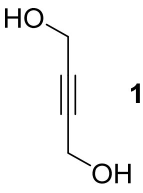
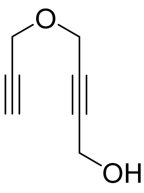
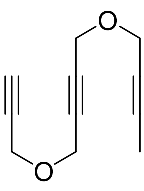

9


10


11


12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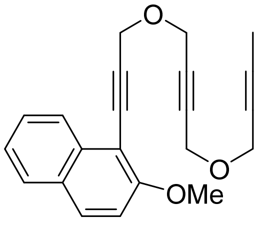
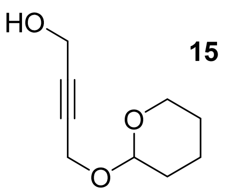
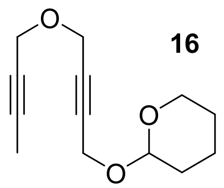


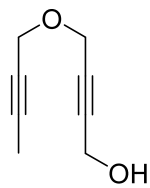
14



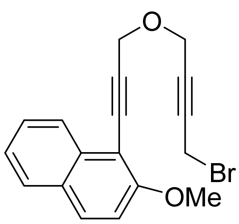
15



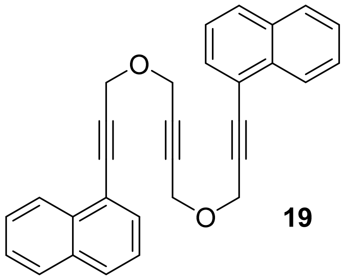
16



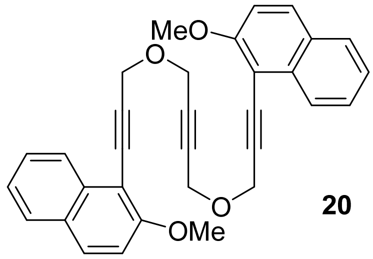
17



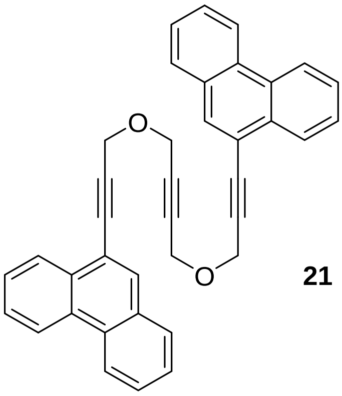
18



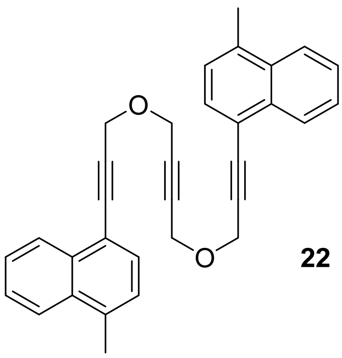
19



20



21



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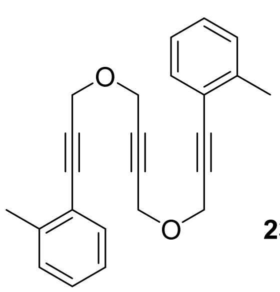
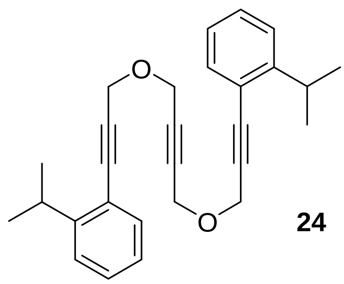
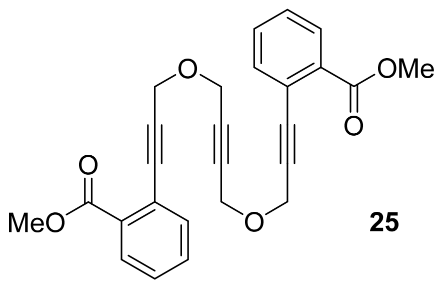


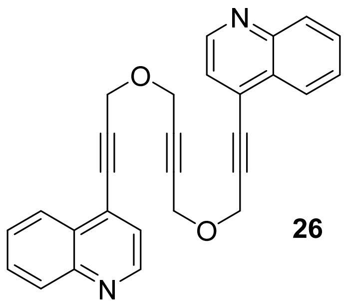
23



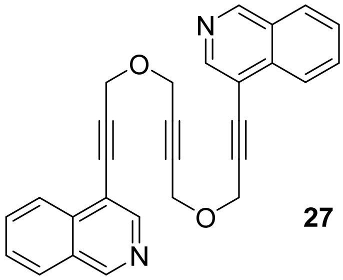
24



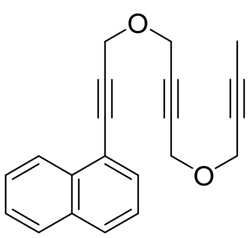
25



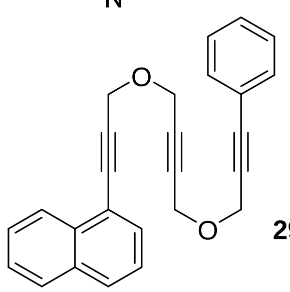
26



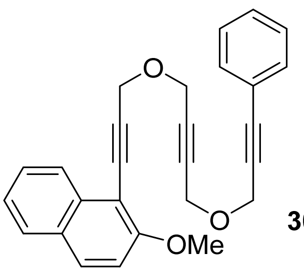
27



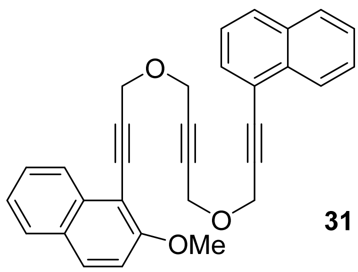
28



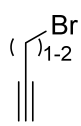
29



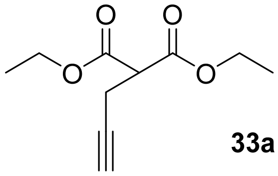
30



31



32



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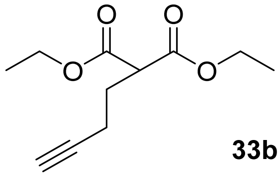

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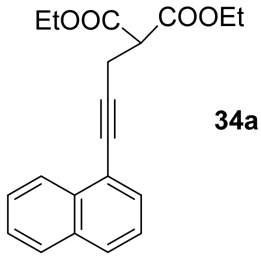

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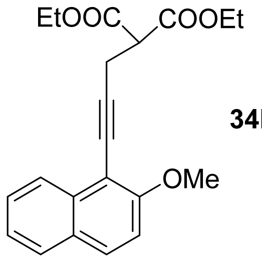

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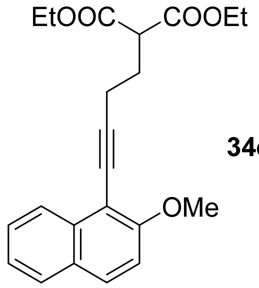

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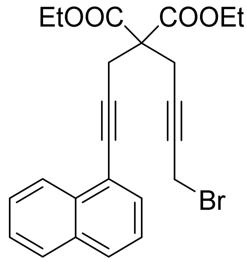

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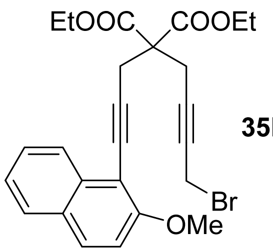

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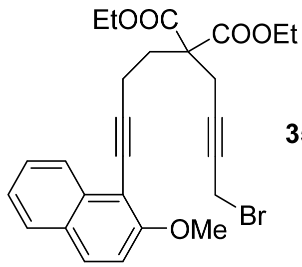

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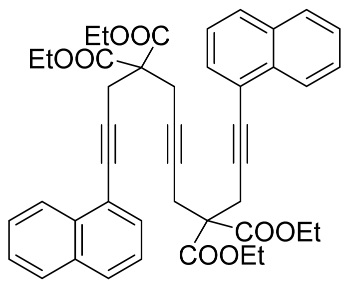

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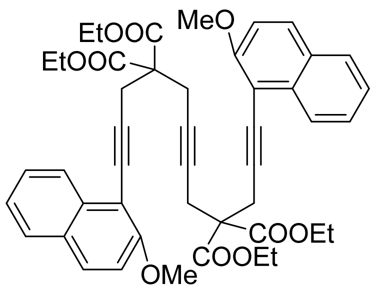

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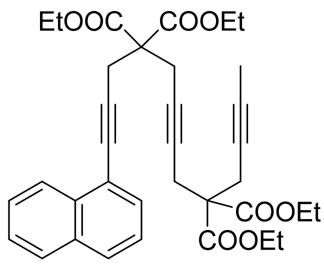

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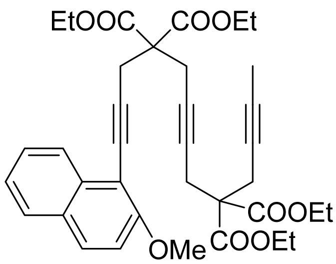

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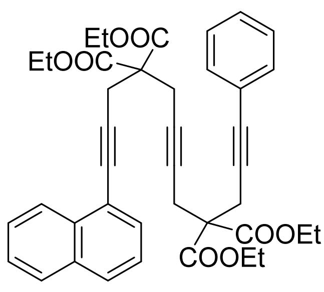

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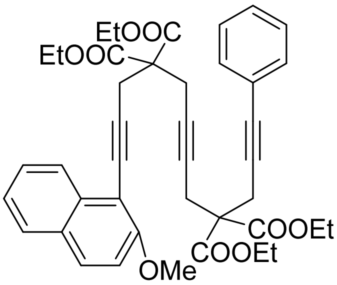
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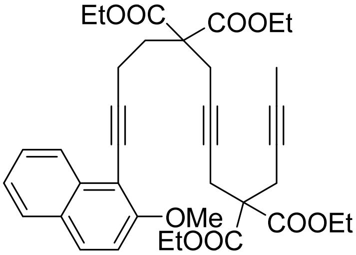
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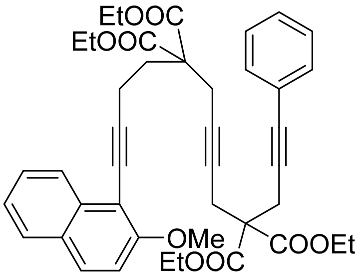
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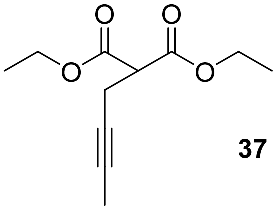
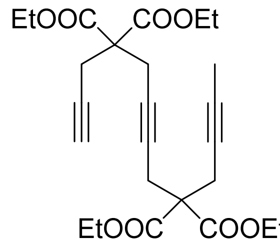
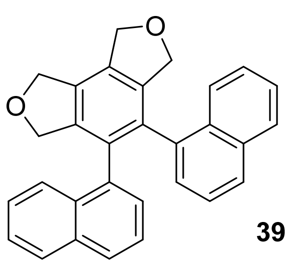
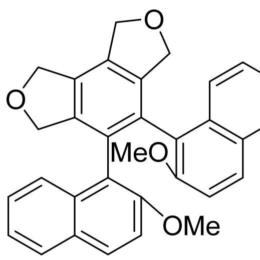
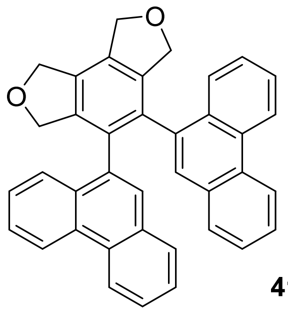
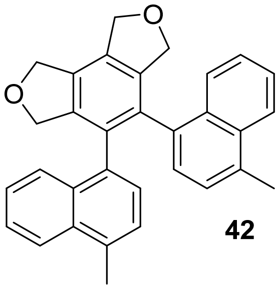

37

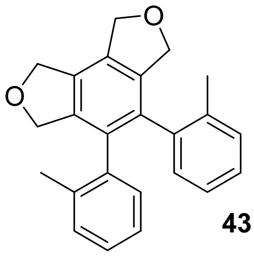

38

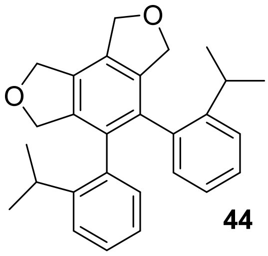

39

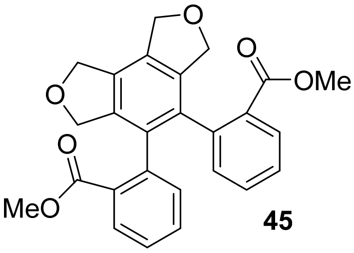

40

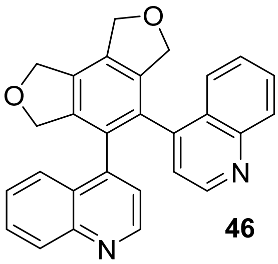

41

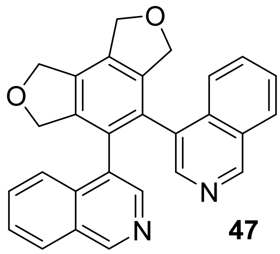

42

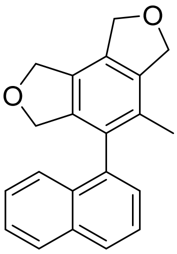

43

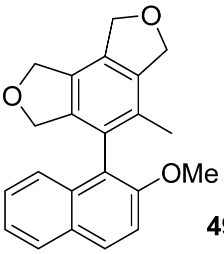

44

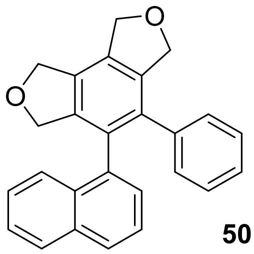

45

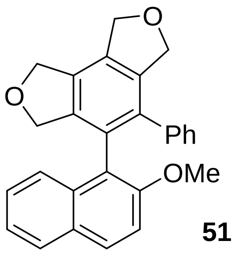

46

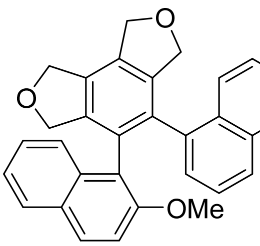

47


48

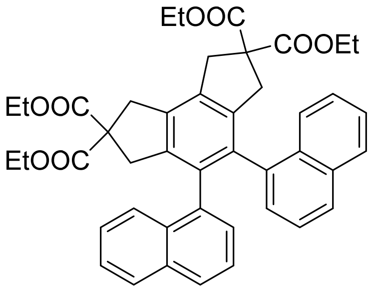

49


50


51



52



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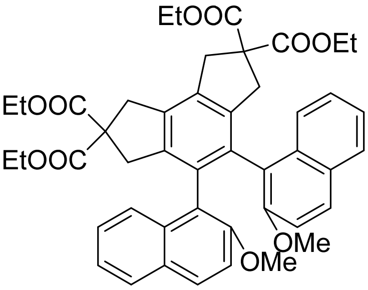

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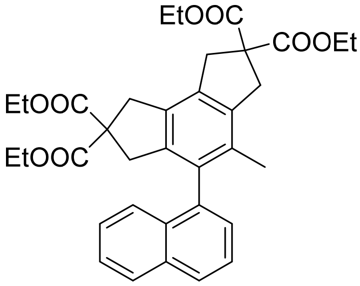

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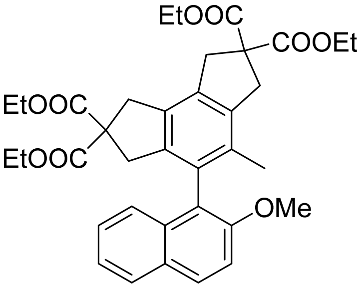

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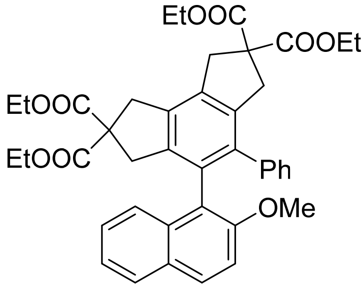

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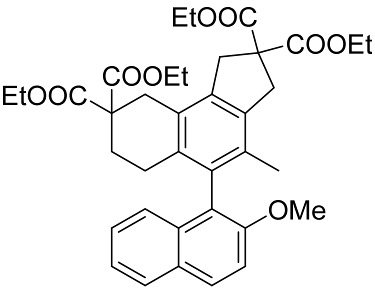

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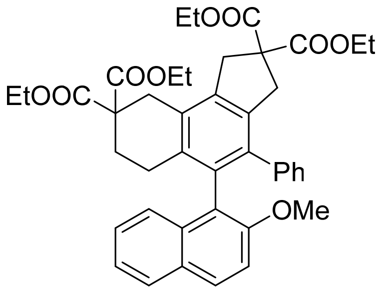

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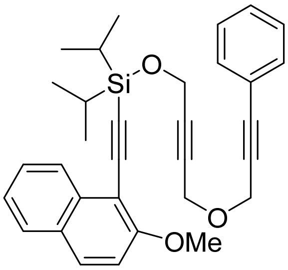

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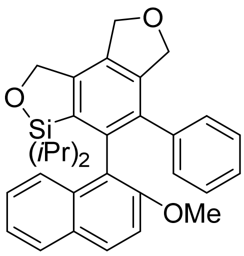

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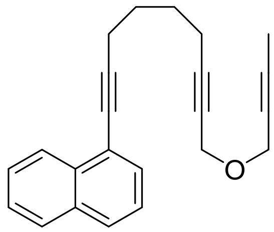

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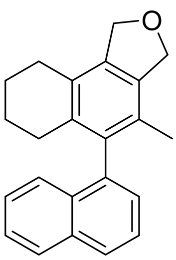
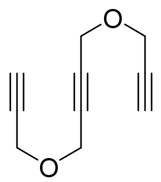


57

2. Literature synthesis procedures

1,4-Bis(prop-2-yn-1-yloxy)but-2-yne (2):

Literature procedure:[1]

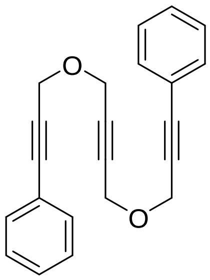


2

Spectral data are according to the literature.[2]

1,4-Bis((3-phenylprop-2-yn-1-yl)oxy)but-2-yne (3):

Literature procedure:[1]

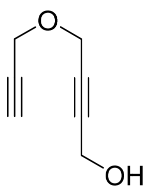


3

Spectral data are according to the literature.[2]

4-(Prop-2-yn-1-yloxy)but-2-yn-1-ol (12):

Literature procedure:[3]

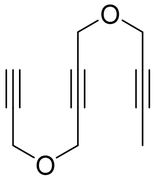


12

Spectral data are according to the literature.[4]

1-(But-2-yn-1-yloxy)-4-(prop-2-yn-1-yloxy)but-2-yne (13):

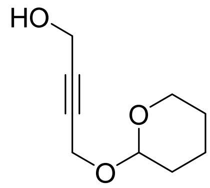
Literature procedure:[2]



13

4-((Tetrahydro-2H-pyran-2-yl)oxy)but-2-yn-1-ol (15):

Literature procedure:[5]

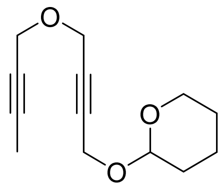


15

Spectral data are according to the literature.[6]

2-((4-(But-2-yn-1-yloxy)but-2-yn-1-yl)oxy)tetrahydro-2H-pyran (16):

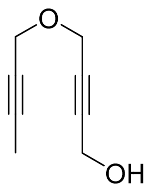
Literature procedure:[7]



16

4-(But-2-yn-1-yloxy)but-2-yn-1-ol (17):

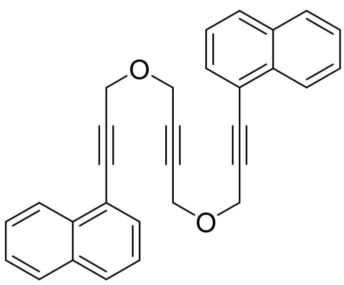
Literature procedure:[7]



17

1,4-Bis((3-(naphthalen-1-yl)prop-2-yn-1-yl)oxy)but-2-yne (19):

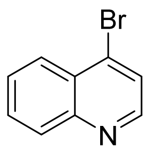
Literature procedure:[8]



19

4-Bromoquinoline (SI-I):

Literature procedure:[9]

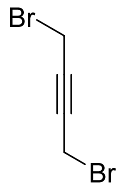


SI-I

Spectral data are according to the literature.[10]

1,4-Dibromobut-2-yne (SI-II):

Literature procedure:[3]

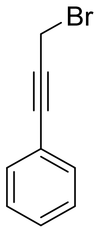


SI-II

Spectral data are according to the literature.[11]

(3-Bromoprop-1-yn-1-yl)benzene (SI-III):

Literature procedure:[12]

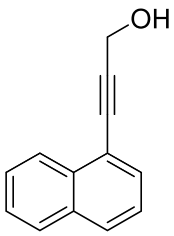


SI-III

Spectral data are according to the literature.[13]

3-(Naphthalen-1-yl)prop-2-yn-1-ol (SI-IV):

Literature procedure:[14]

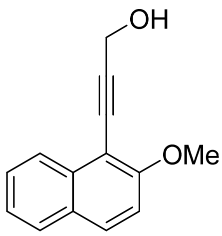


SI-IV

Spectral data are according to the literature. [15]

3-(2-Methoxynaphthalen-1-yl)prop-2-yn-1-ol (7):

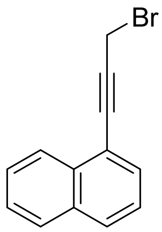
Literature procedure:[16]



7

1-(3-Bromoprop-1-yn-1-yl)naphthalene (SI-V):

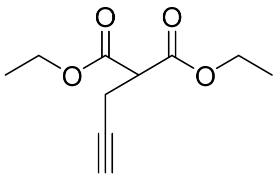
Literature procedure:[17]



SI-V

Diethyl-2-(prop-2-yn-1-yl)malonate (33a):

Literature procedure:[18]

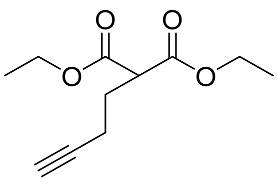


33a

Spectral data are according to the literature.[19]

Diethyl-2-(but-3-yn-1-yl)malonate (33b):

Literature procedure:[20]

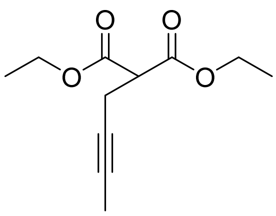


33b

Spectral data are according to the literature.[21]

Diethyl-2-(but-2-yn-1-yl)malonate (37):

Literature procedure:[22]



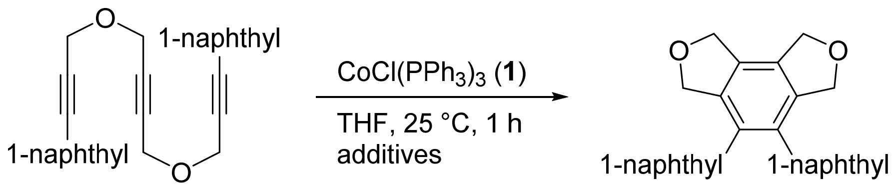
37

3. Procedure and results for cyclizations with chiral anions as additives

Reaction procedure:

The respective triyne (**19**, 1 mmol), $CoCl(PPh_3)_3$ (**1**, 5 mol% with regard to the triyne) and the respective chiral anion (5 mol% with regard to the triyne) were dissolved in THF (3 mL). NEt_3 (3 drops) was added to the reaction mixture before the solution was stirred at 25 °C for 1 h. At the end of the reaction, the solvent was removed under reduced pressure and the residue purified by column chromatography using *n*-hex/EE (1:1) as the eluent to yield triaryl compound **39**. The *ee* values were determined by chiral HPLC-analysis (Cellulose 2, *n*-heptane/isopropanol 95:5, v/v, 1 mL/min or Cellulose 4, *n*-heptane/ethanol 98:2, v/v, 1 mL/min).

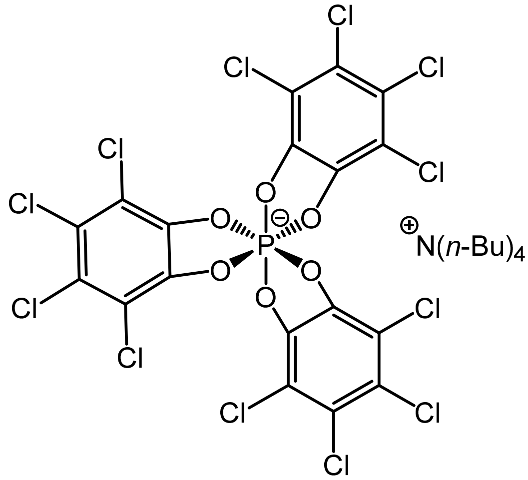
Table SI1: Screening of catalytic activity for 1 and *in situ* generated catalysts in combination with various chiral anion additives



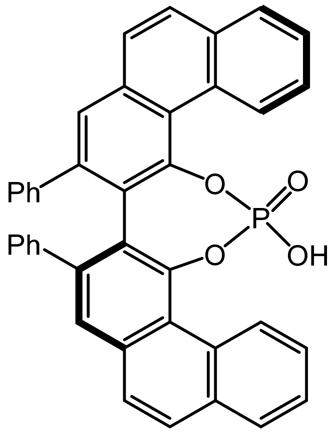
19 **39**

#	Catalyst system	yield	d/l : meso
1	**1**, no chiral anion	59%	1.1 : 1
2	**1** + **L1**	73%	1.3 : 1
3	**1** + **L1**/AgOTf	0%	--
4	**1** + **L2**/NEt_3	67%	1.1 : 1
5	**1** + **58**/NEt_3	94%	2.2 : 1
6	**1** + **59**/NEt_3	76%	1.2 : 1
7	$CoBr_2$/dppe/Zn/ZnI_2/**L2**/NEt_3	41%	1: 2.2

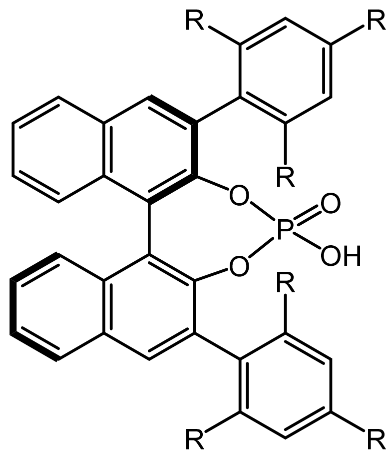
Investigated chiral anions:



Δ-TRISPHAT tetrabutylammonium salt (**L1**)



(*R*)-(-)-VAPOL hydrogen phosphate (**L2**)



TRIP derivatives

58: R = *i*-Pr

59: R = CF_3

4. References

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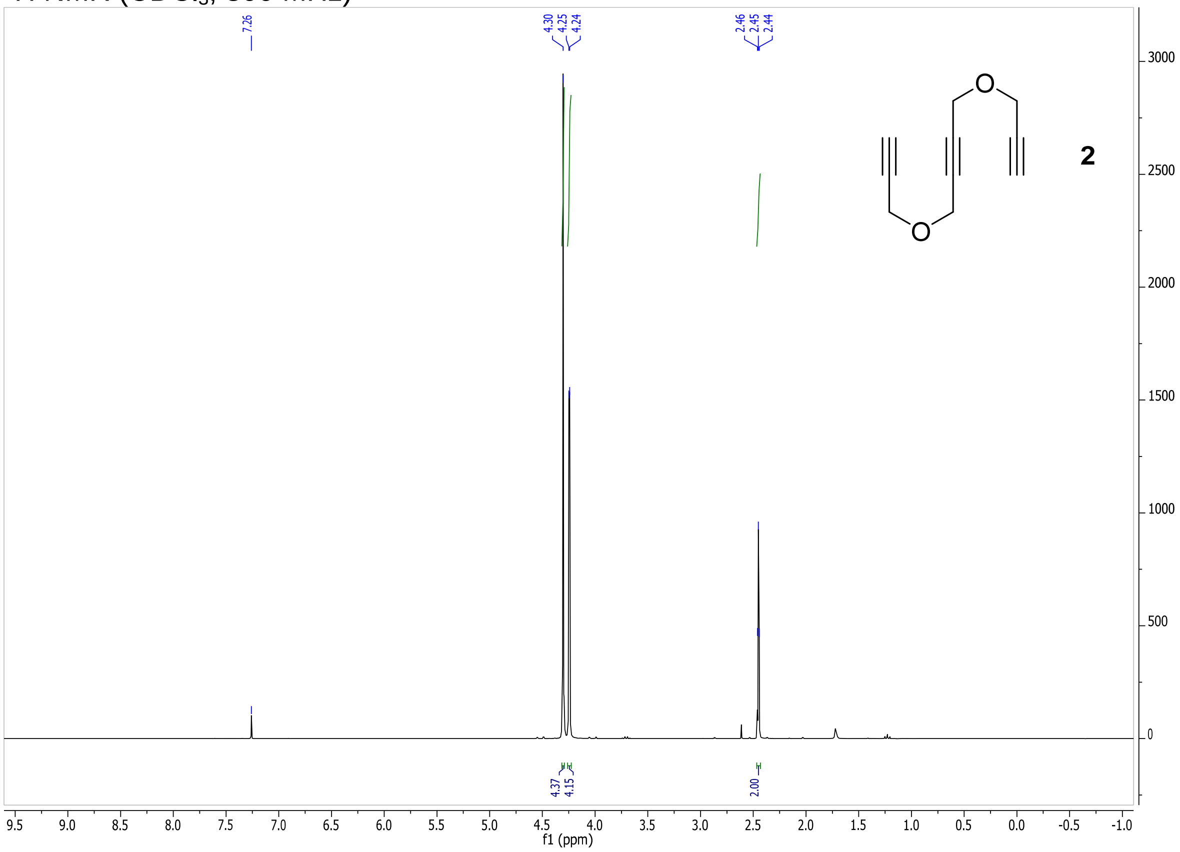
5. NMR Spectra

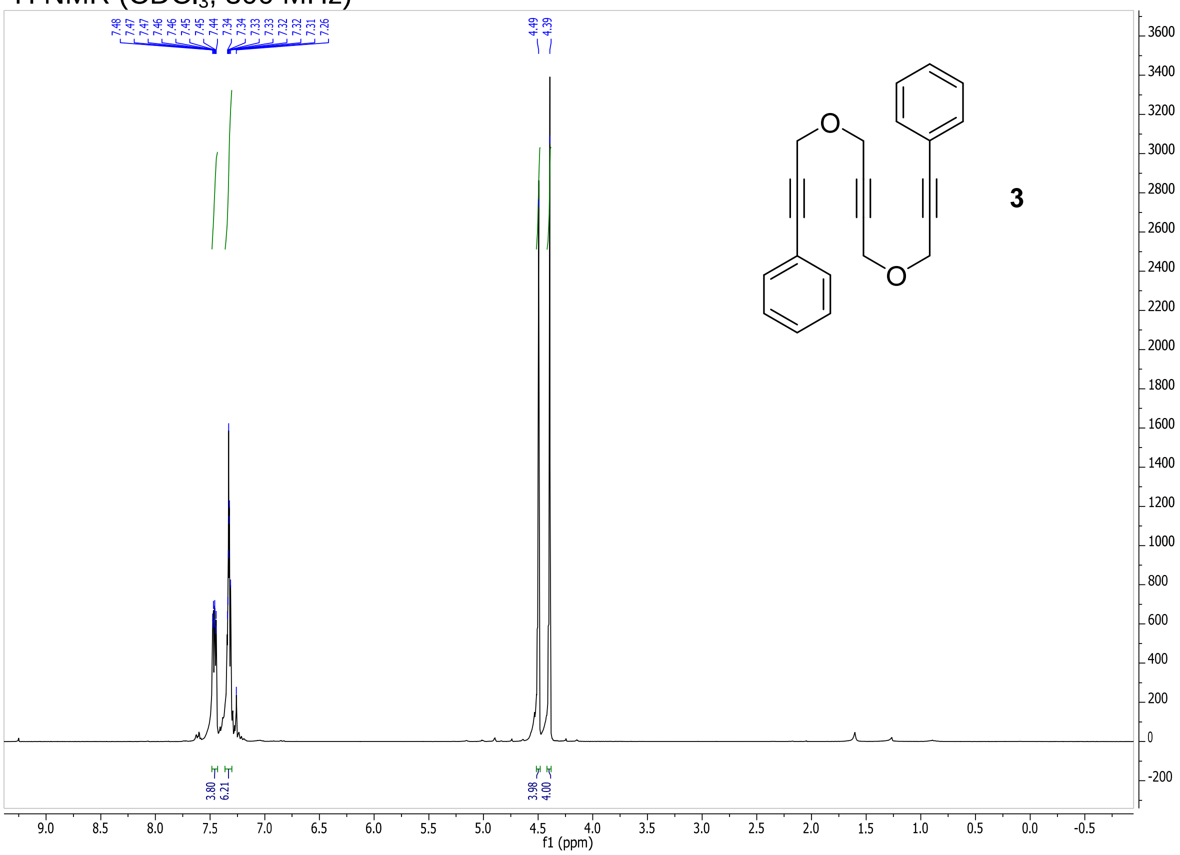
Compound 2:

^{1}H NMR ($CDCl_3$, 300 MHz)



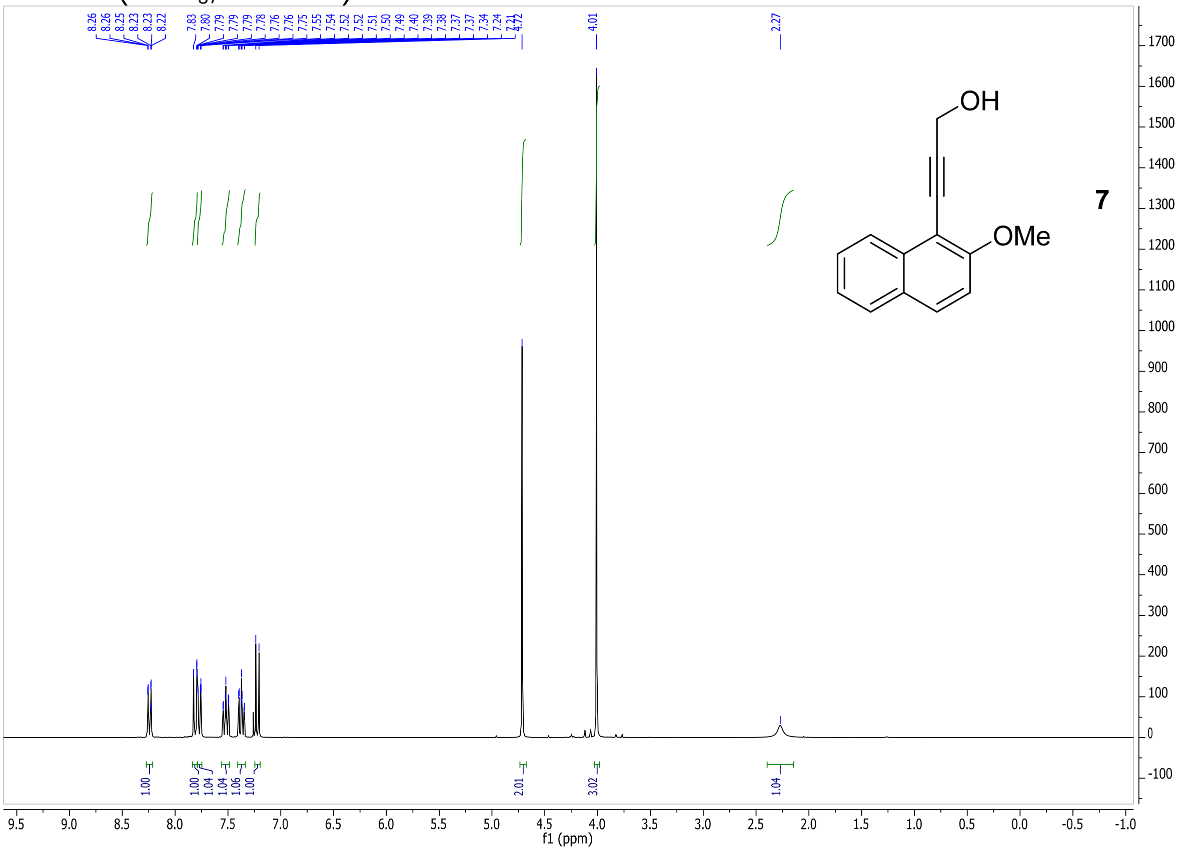
Compound 3:

^{1}H NMR ($CDCl_3$, 300 MHz)



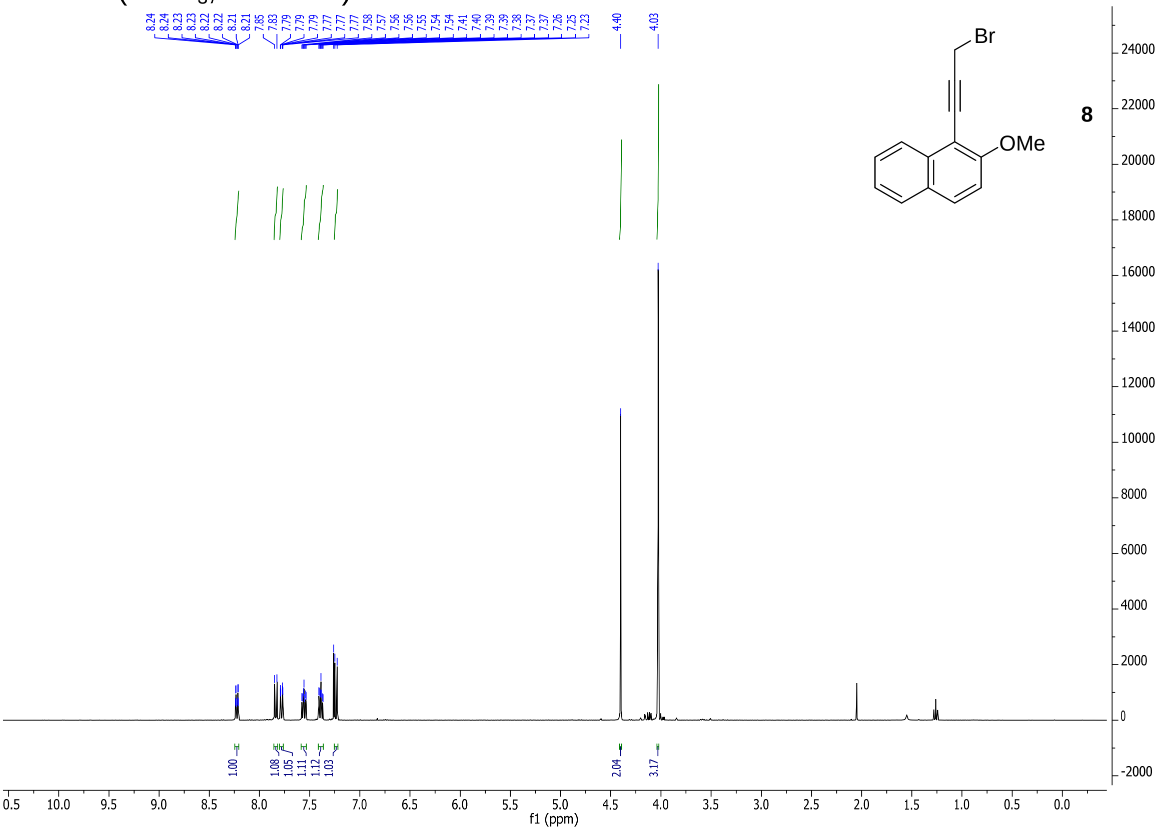
Compound 7:

^{1}H NMR ($CDCl_3$, 300 MHz)

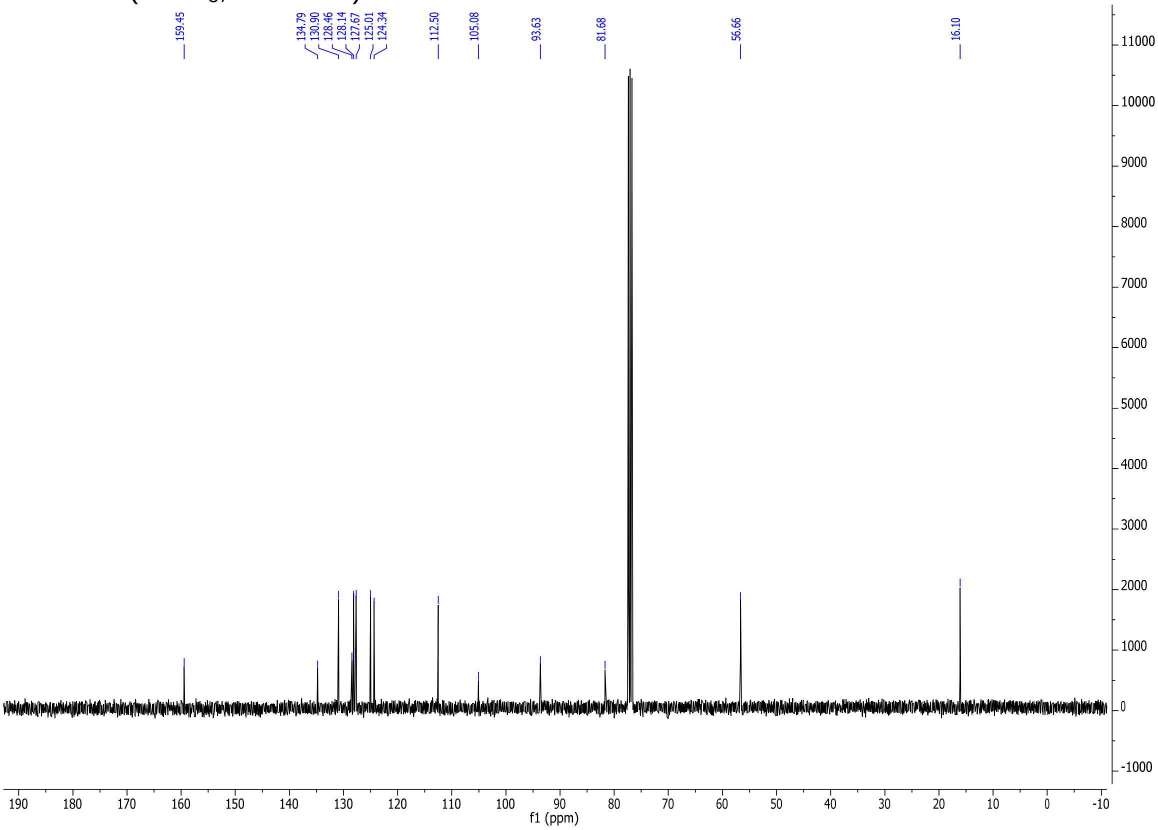


Compound 8:

^{1}H NMR ($CDCl_3$, 400 MHz)

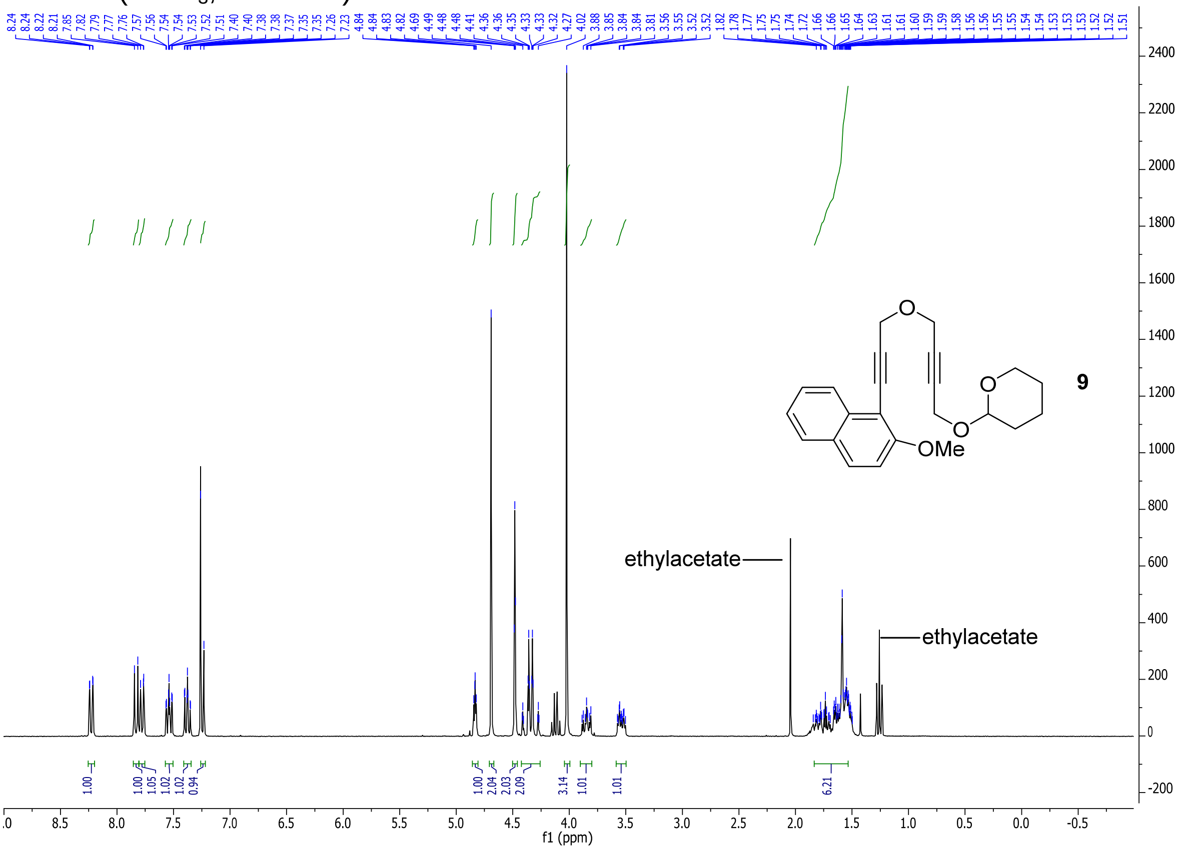


^{13}C NMR ($CDCl_3$, 100 MHz)

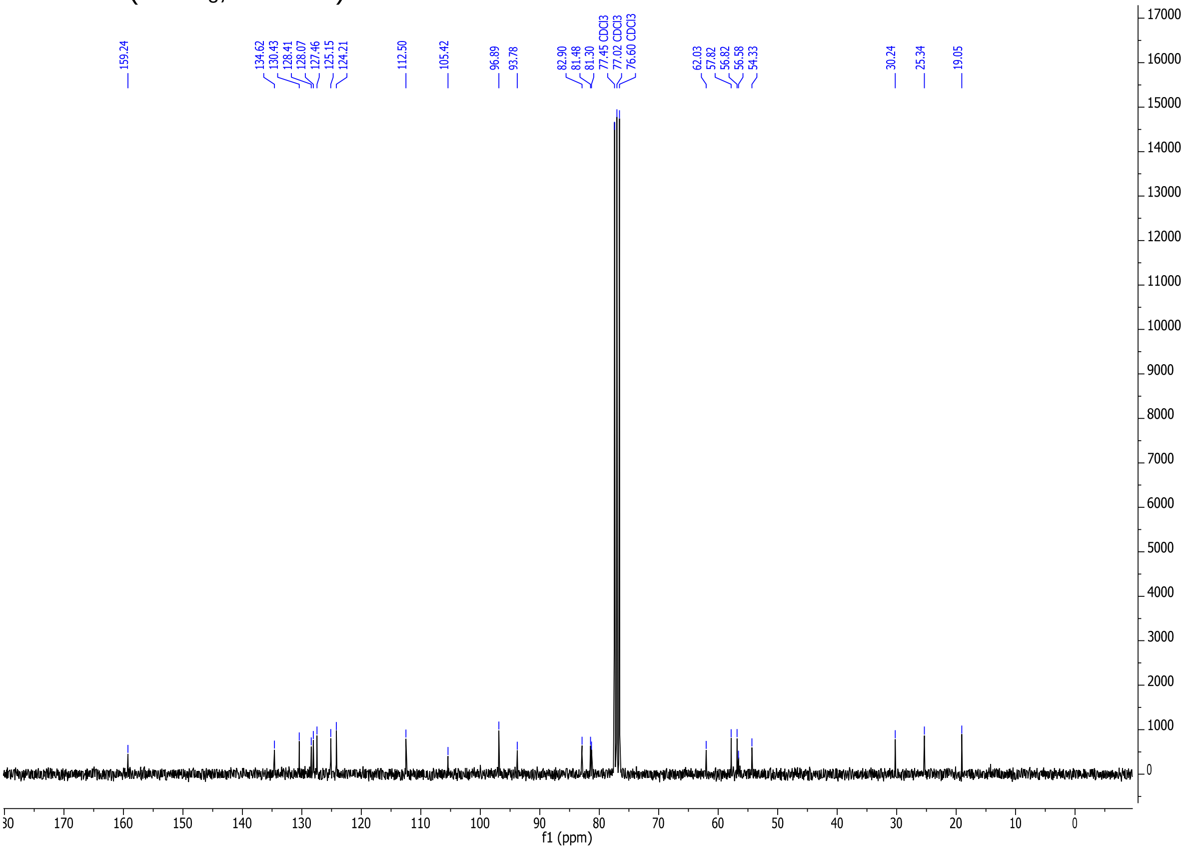


Compound 9:

^1H NMR ($CDCl_3$, 300 MHz)

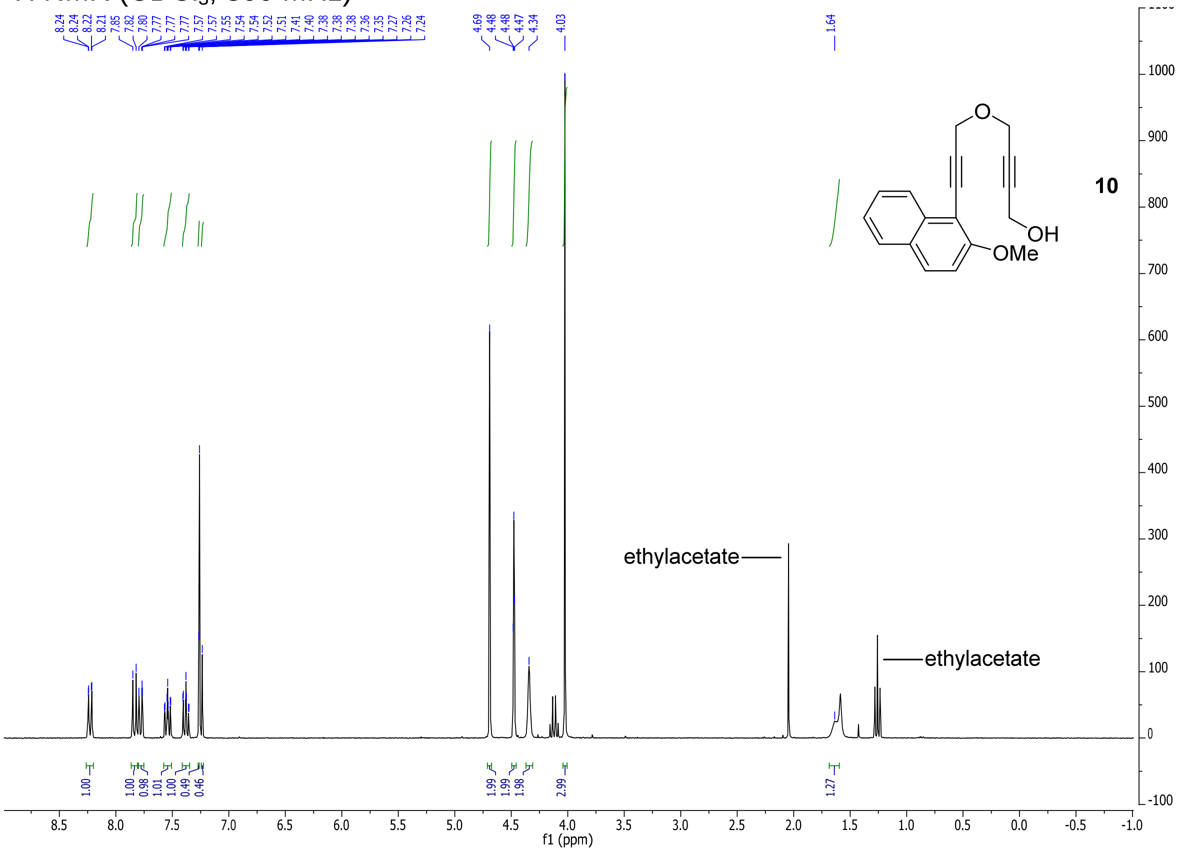


^{13}C NMR ($CDCl_3$, 75 MHz)

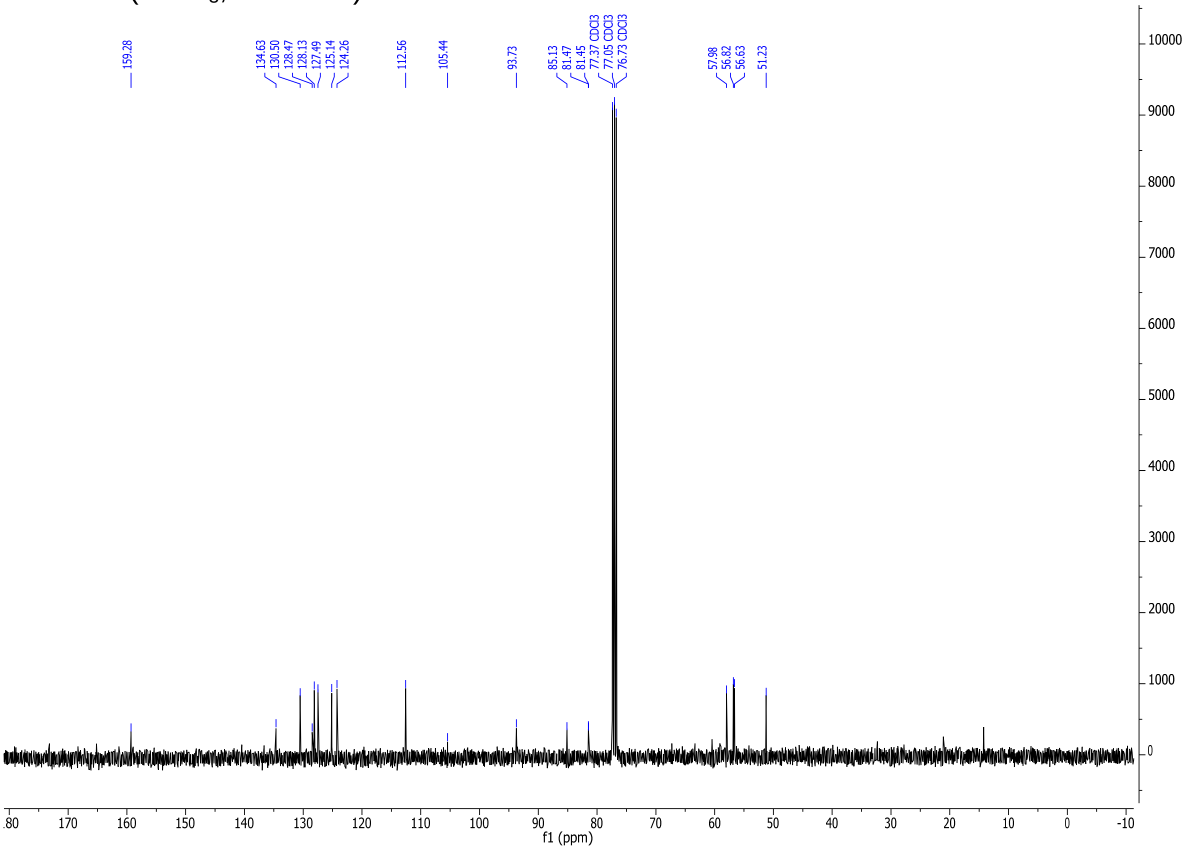


Compound 10: pathway A

^{1}H NMR ($CDCl_3$, 300 MHz)

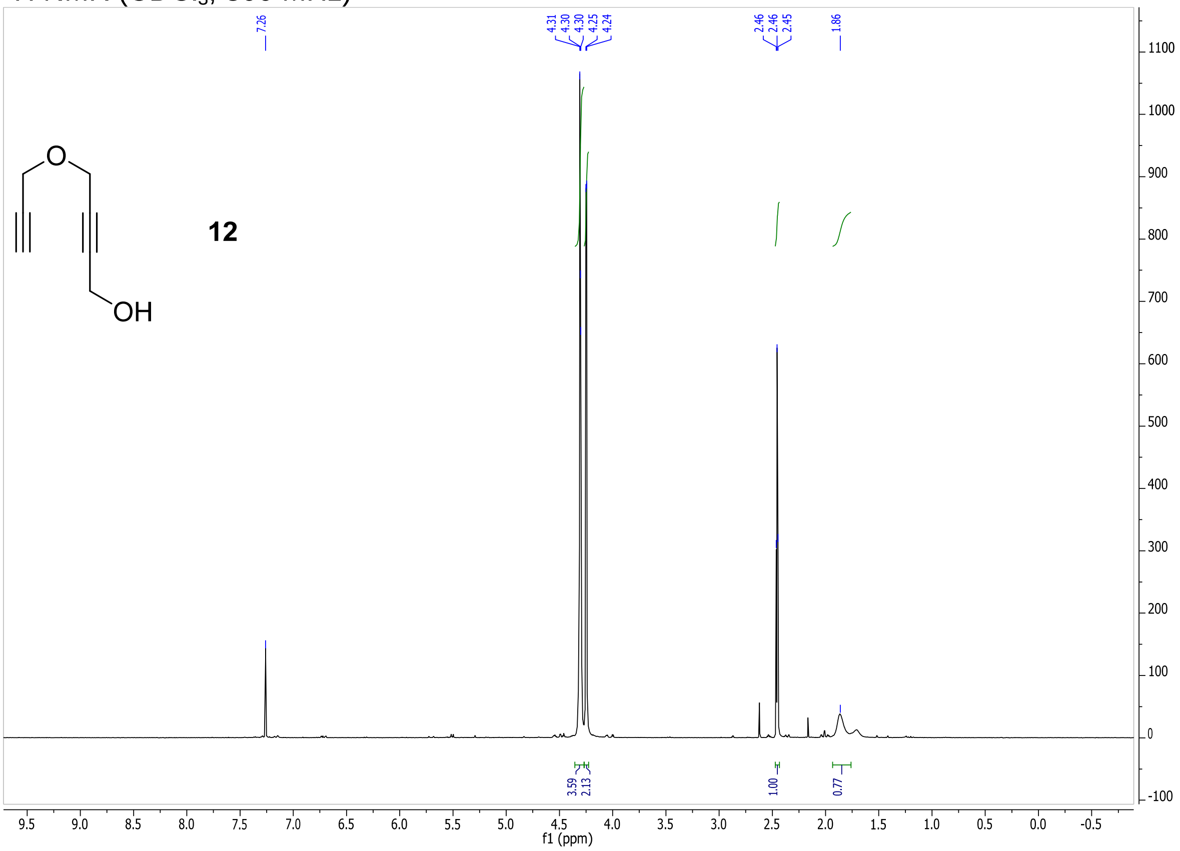


^{13}C NMR ($CDCl_3$, 100 MHz)



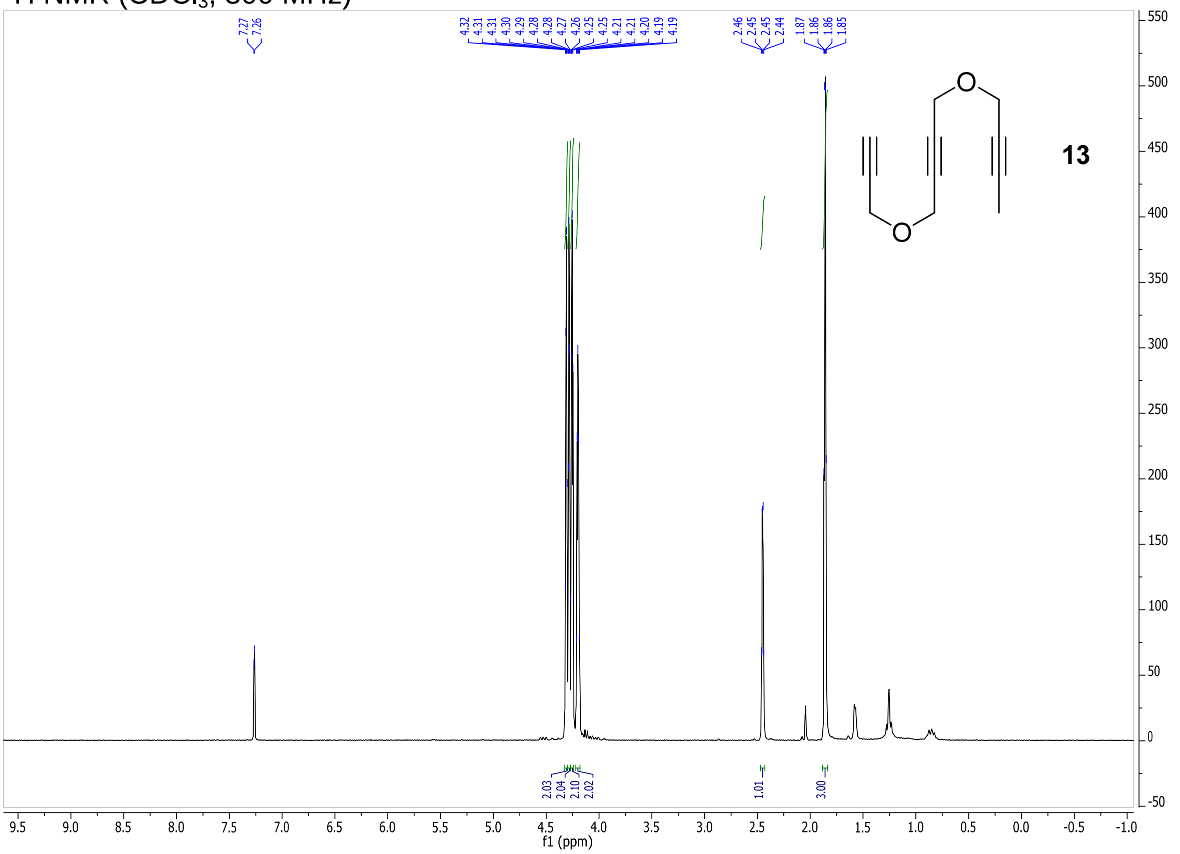
Compound 12:

^{1}H NMR ($CDCl_3$, 300 MHz)



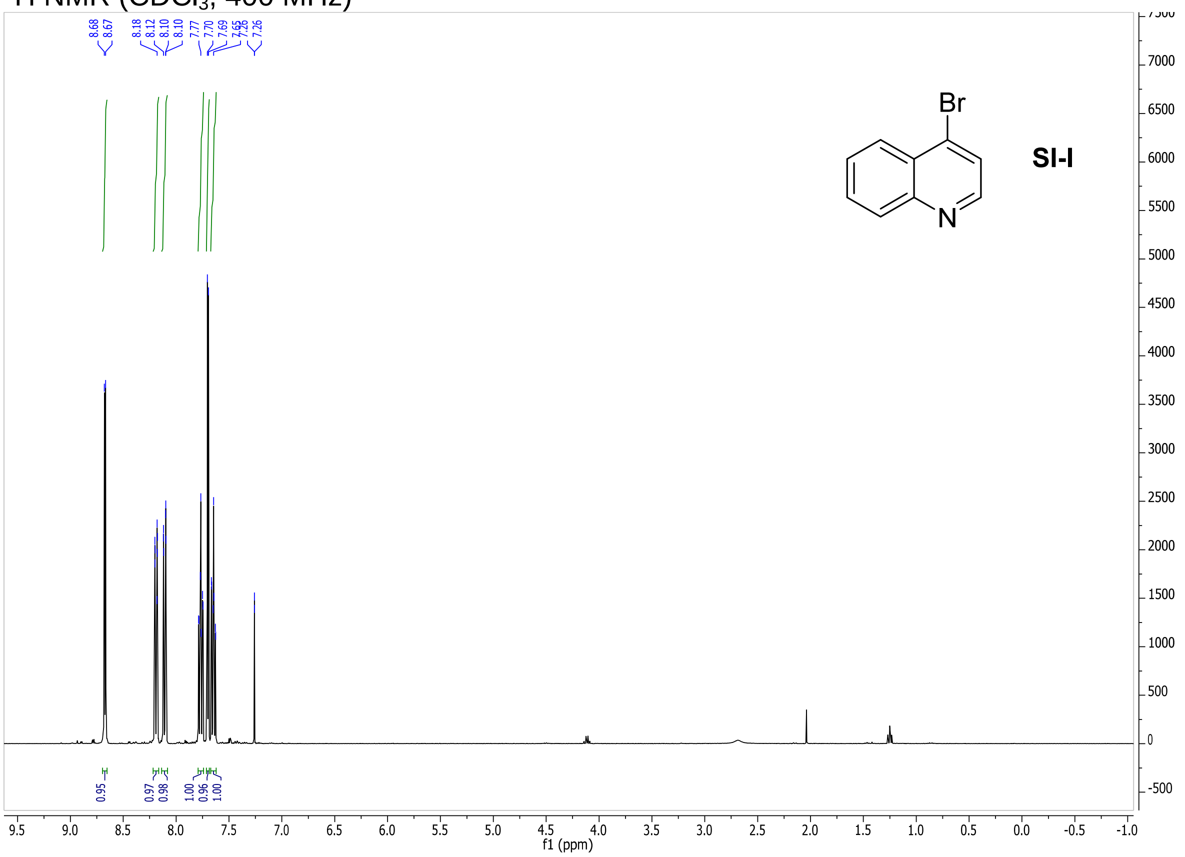
Compound 13:

^{1}H NMR ($CDCl_3$, 300 MHz)



Compound SI-I:

^{1}H NMR ($CDCl_3$, 400 MHz)



Compound SI-II:

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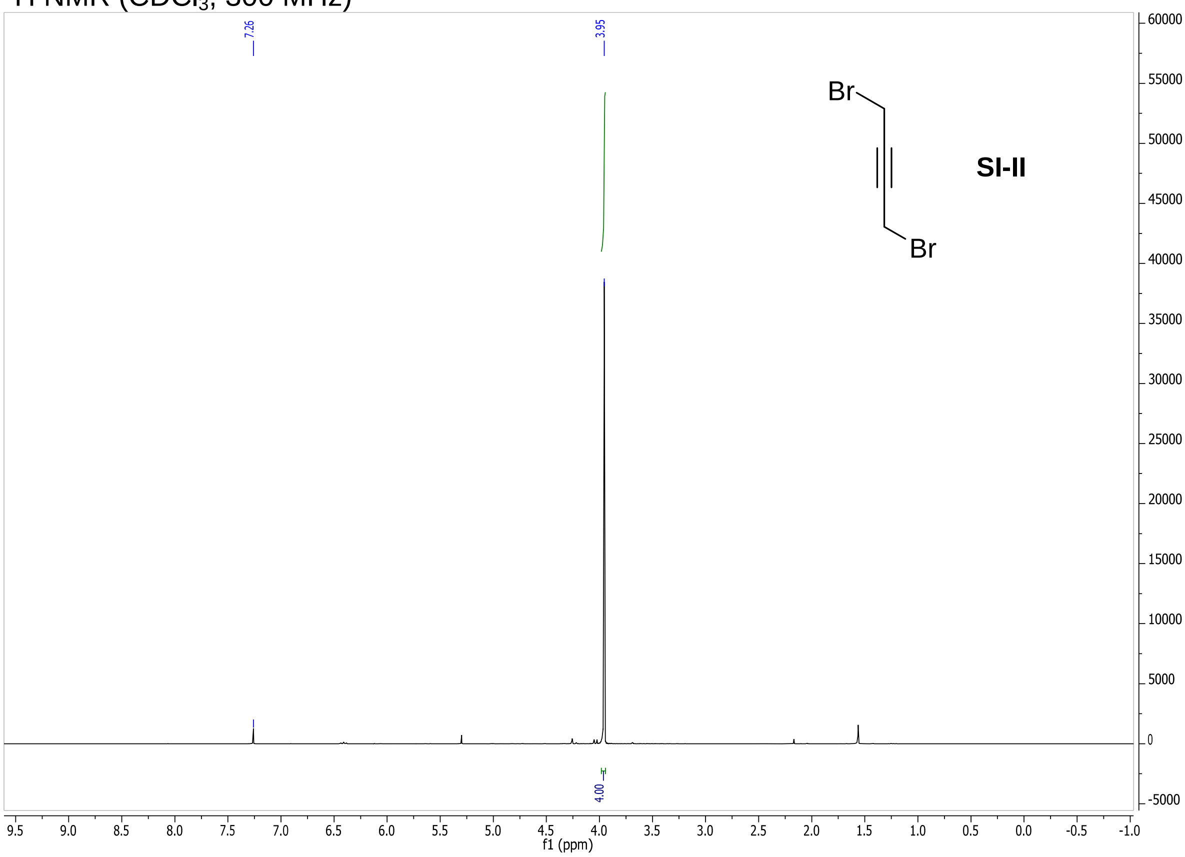

Compound SI-III:

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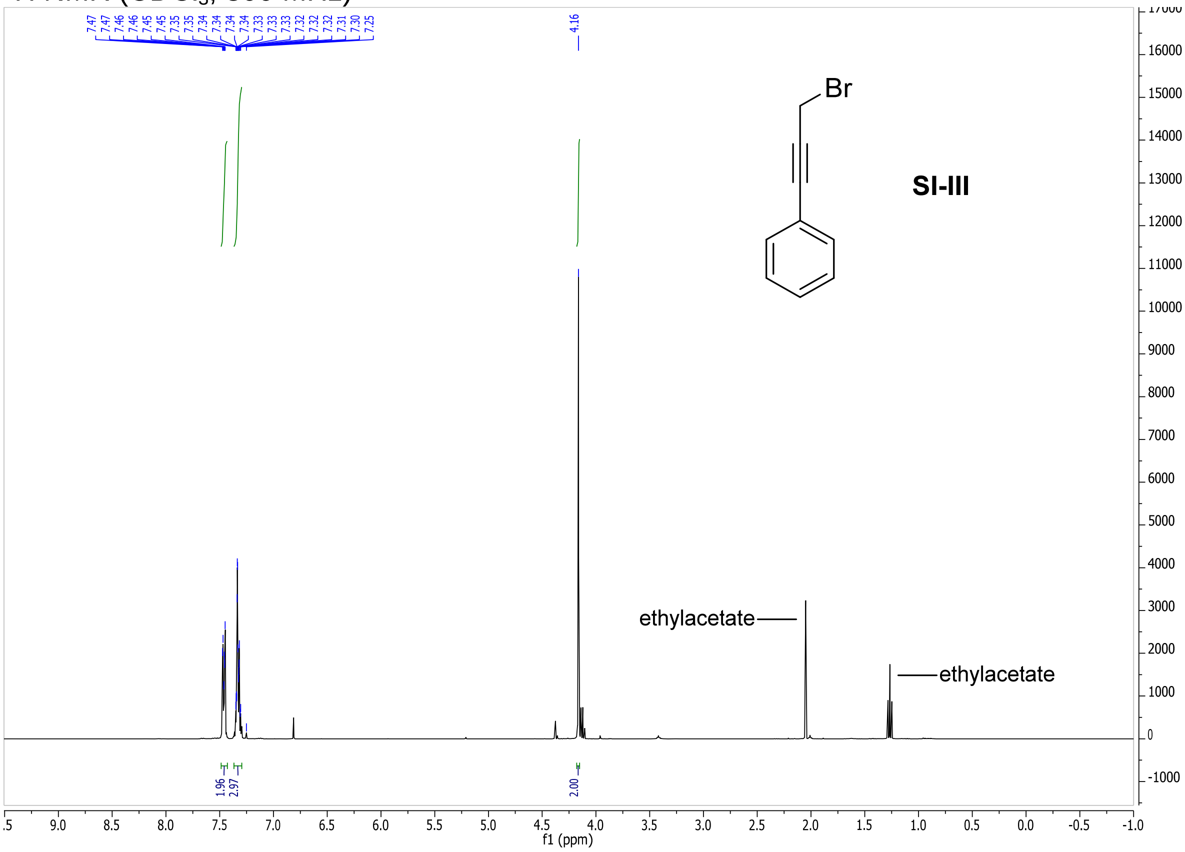

Compound SI-IV:

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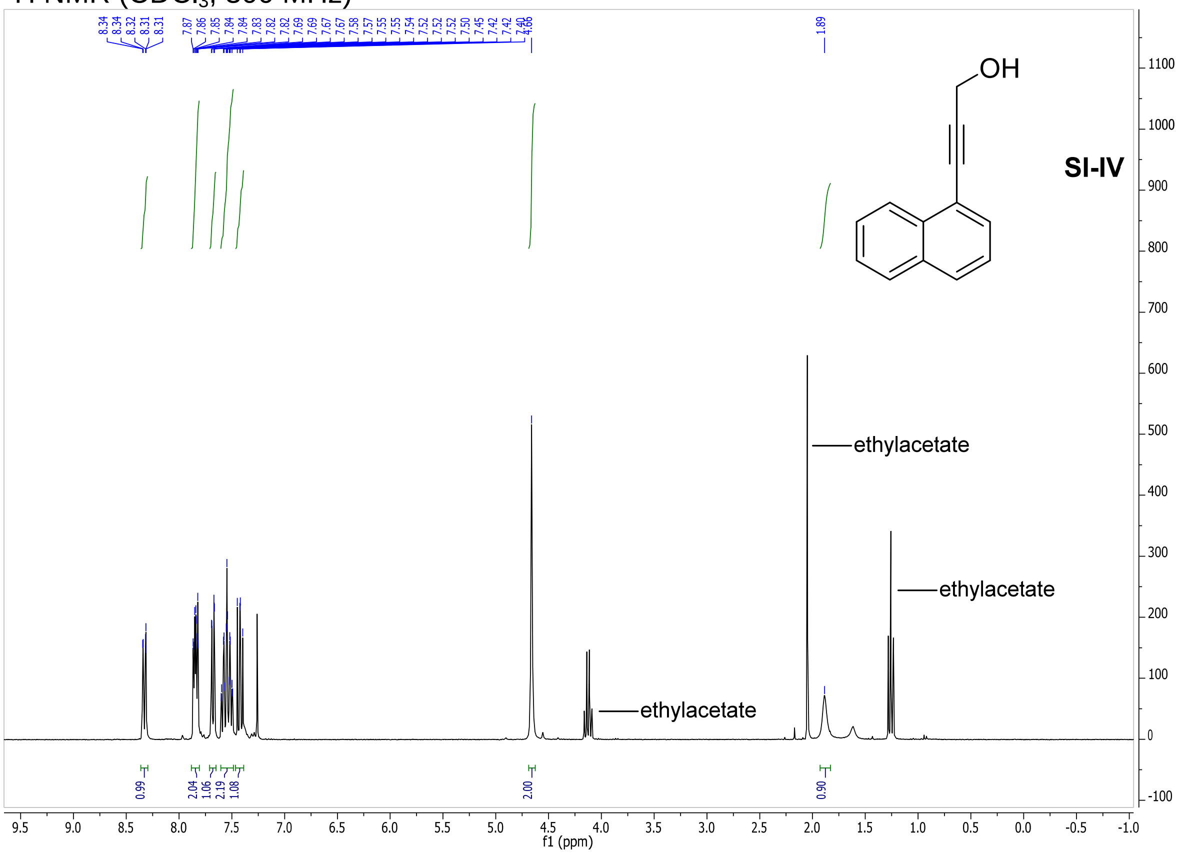

Compound SI-V:

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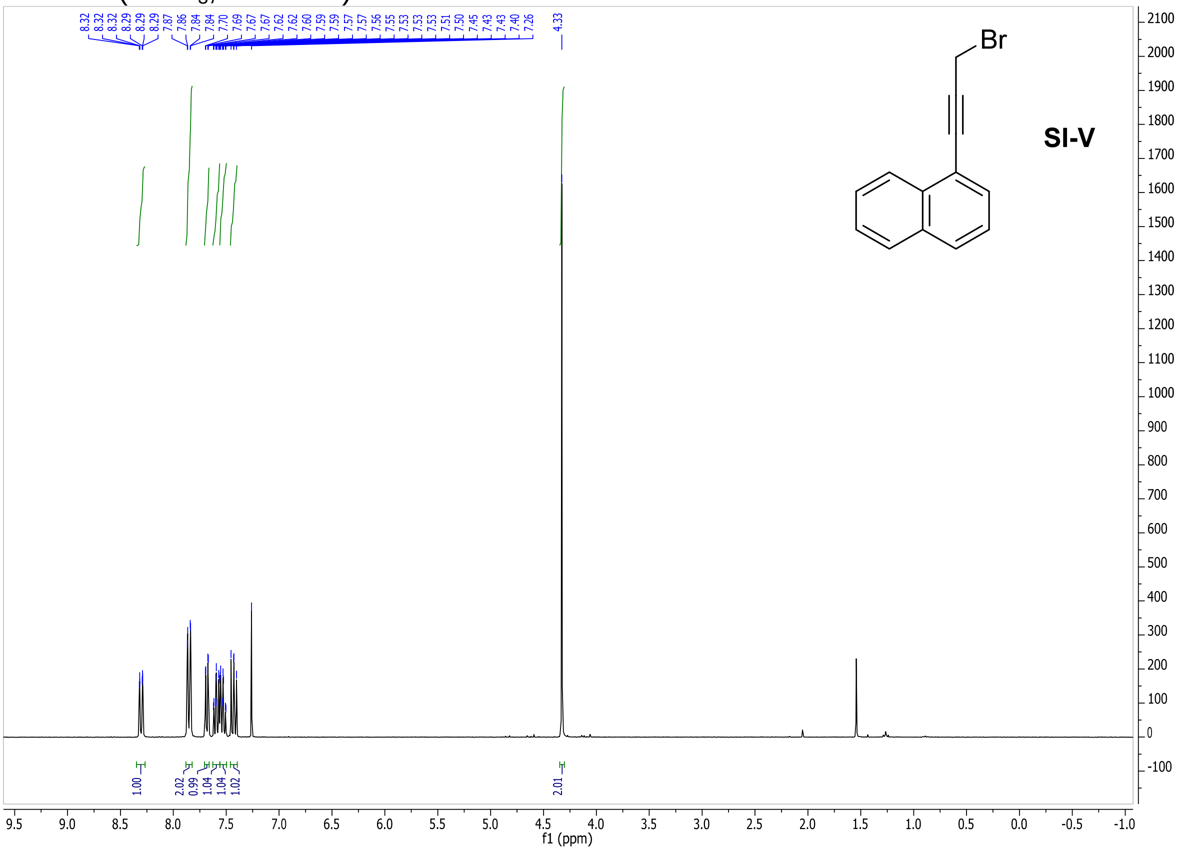

Compound SI-VI:

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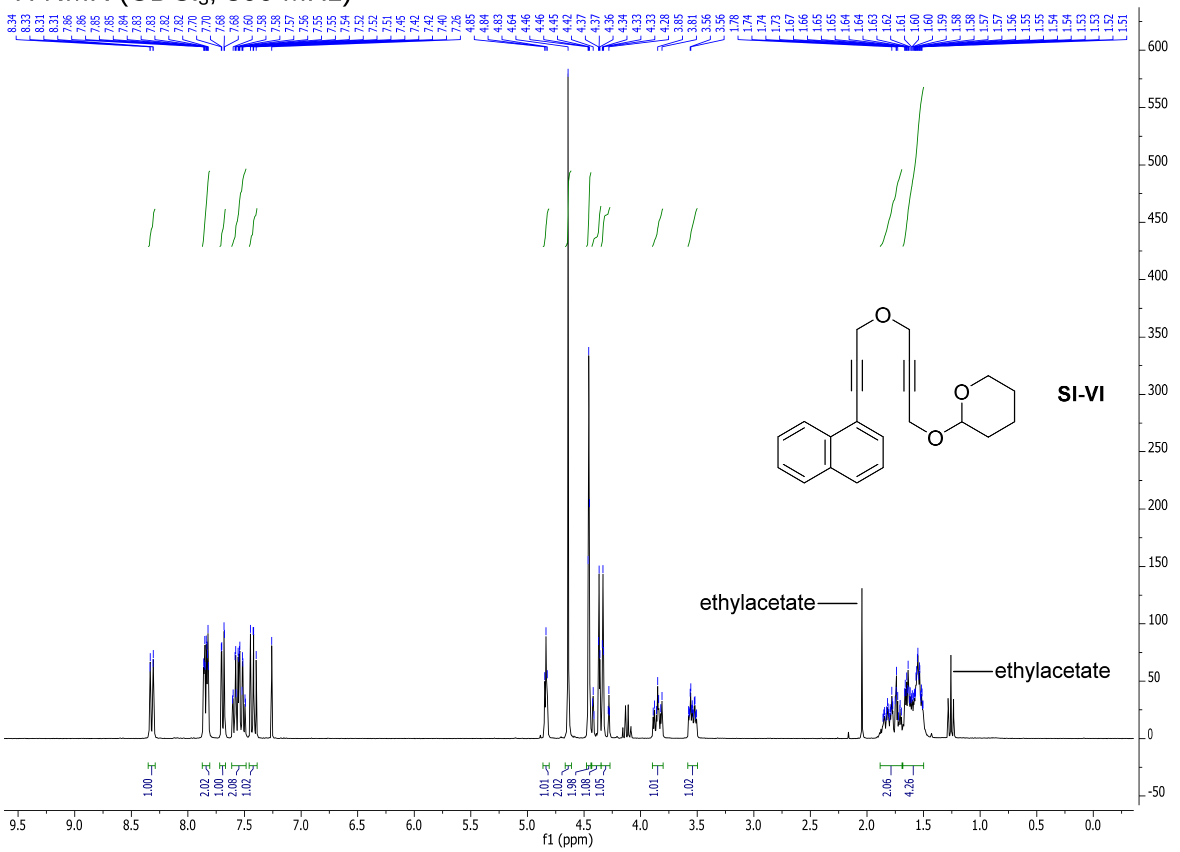
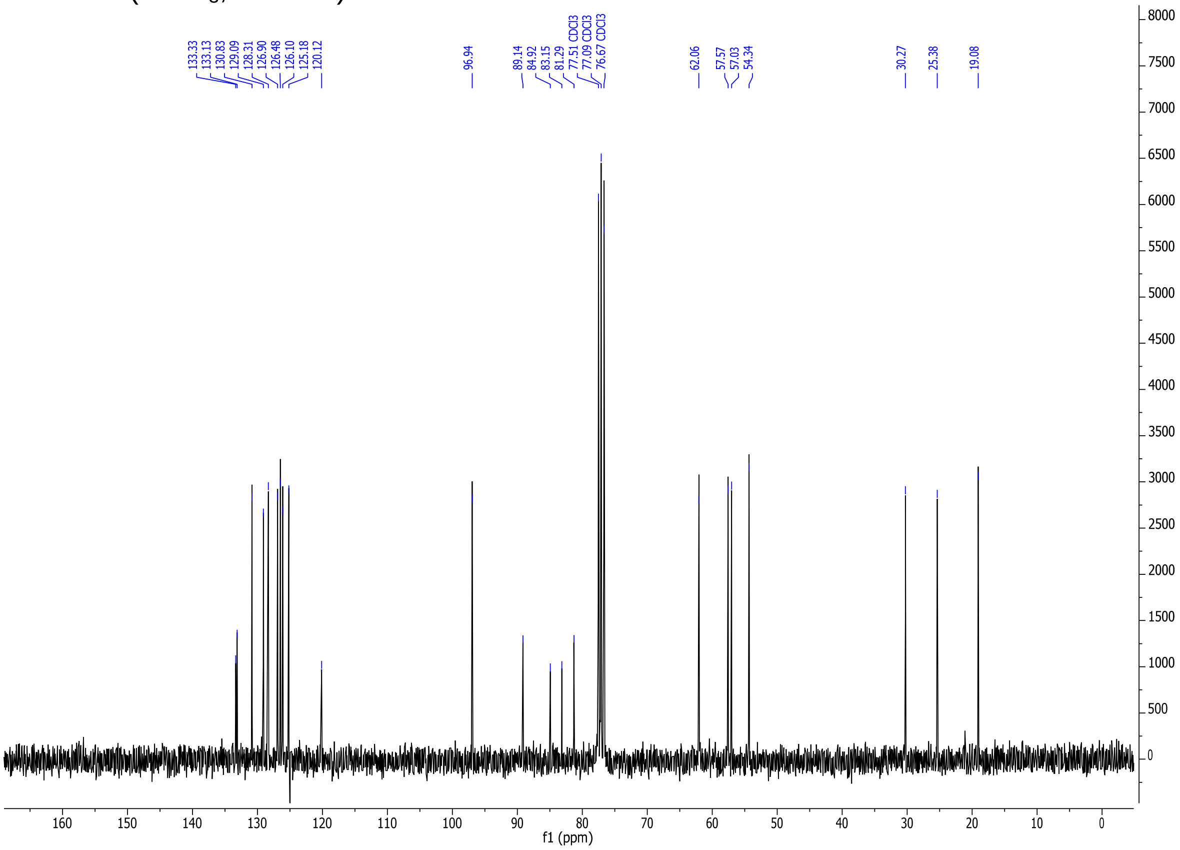
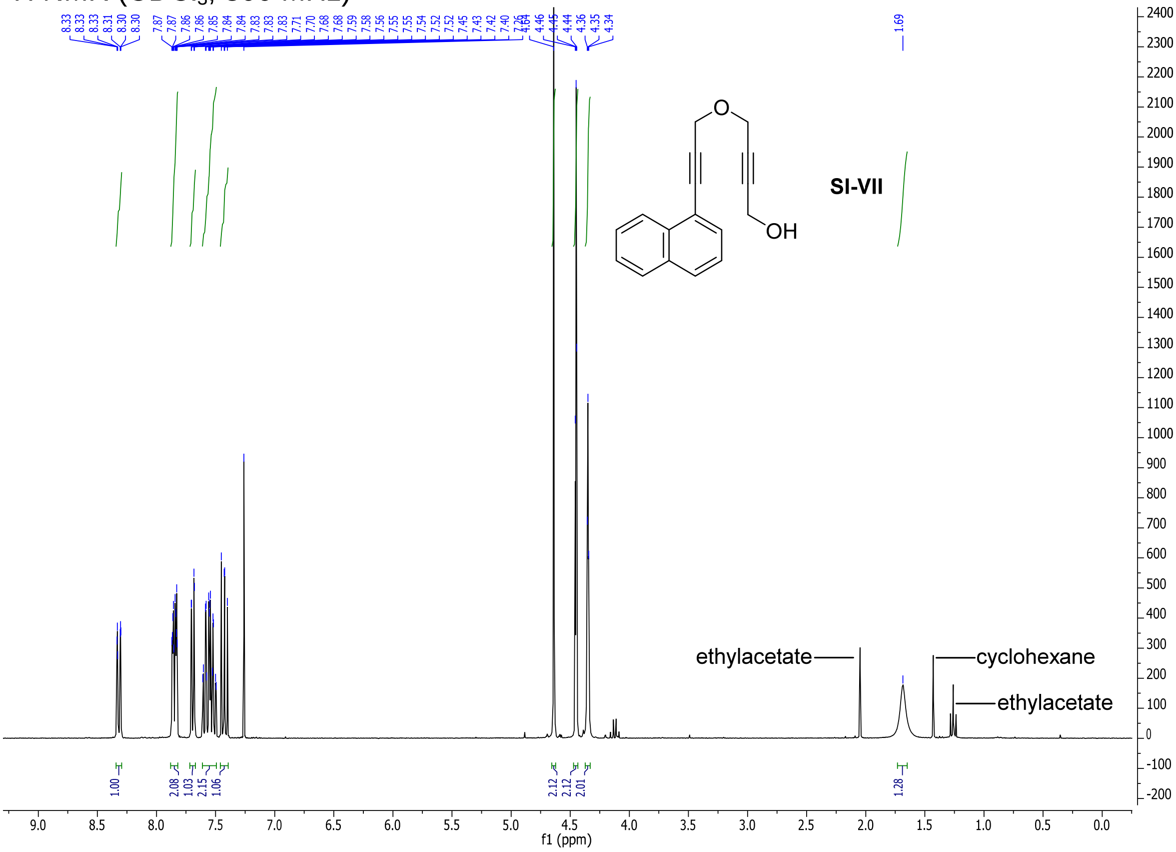


^{13}C NMR ($CDCl_3$, 75 MHz)

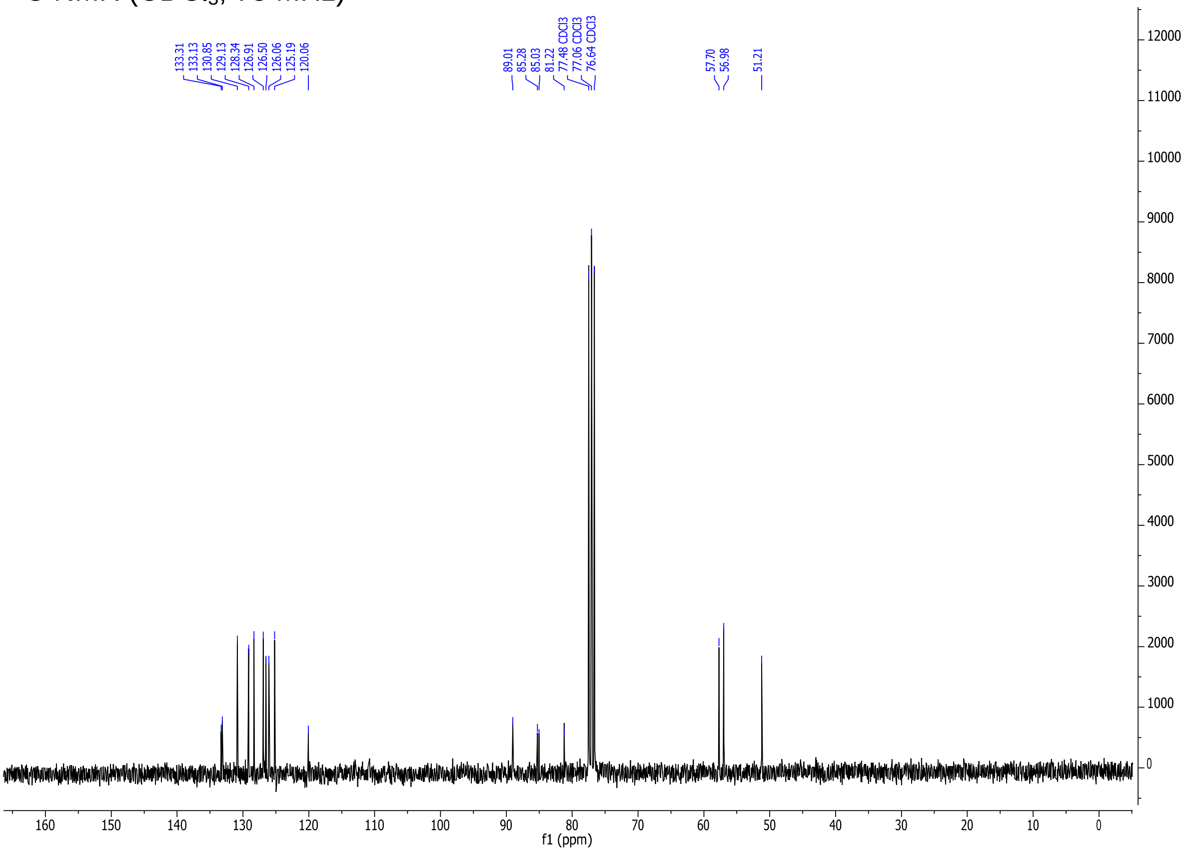


Compound SI-VII: pathway A

^1H NMR ($CDCl_3$, 300 MHz)

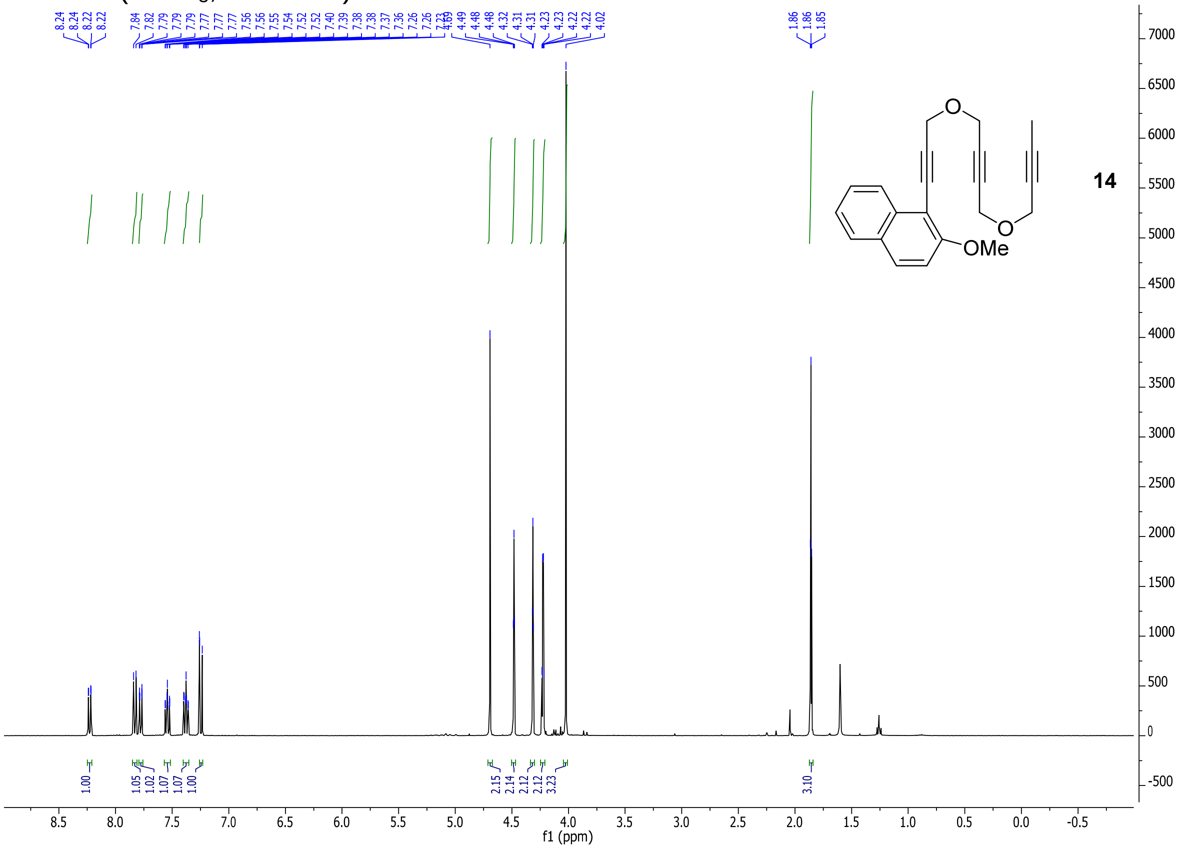


^{13}C NMR ($CDCl_3$, 75 MHz)

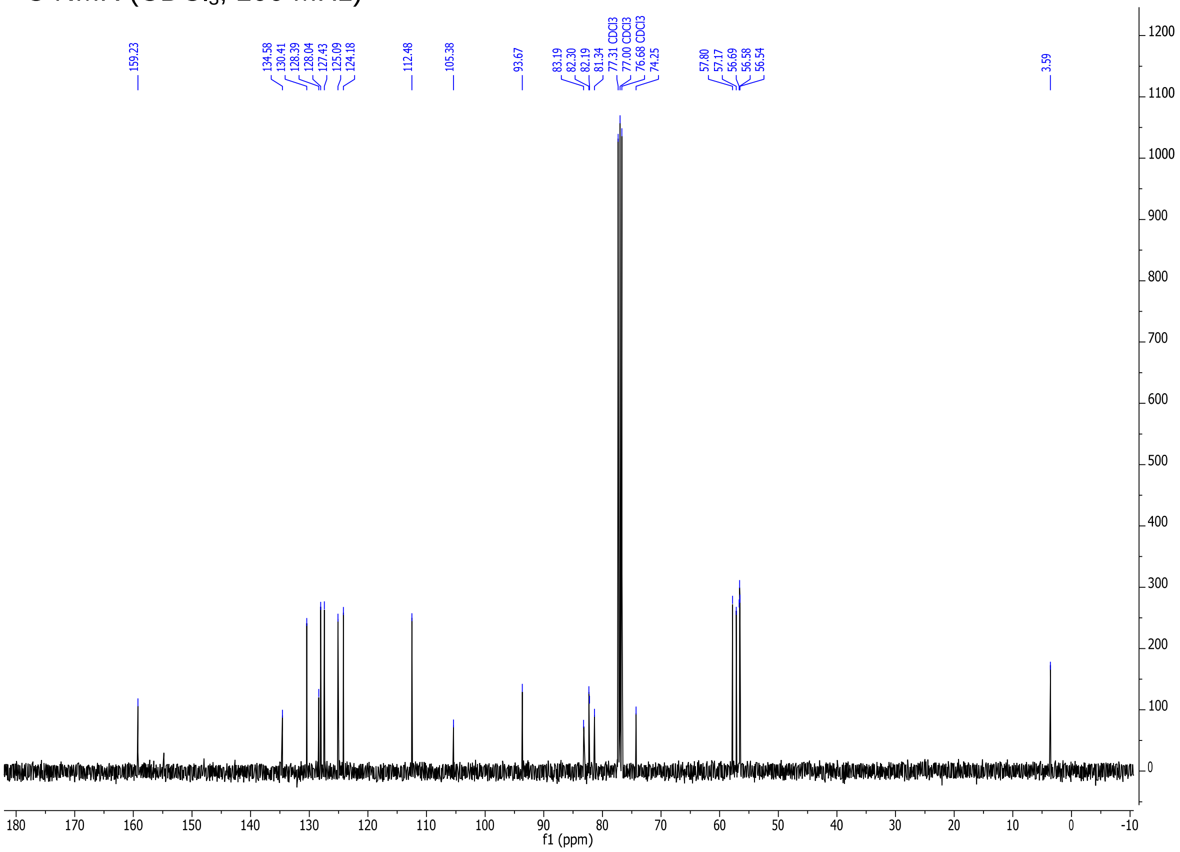


Compound 14: pathway B

^{1}H NMR ($CDCl_3$, 400 MHz)

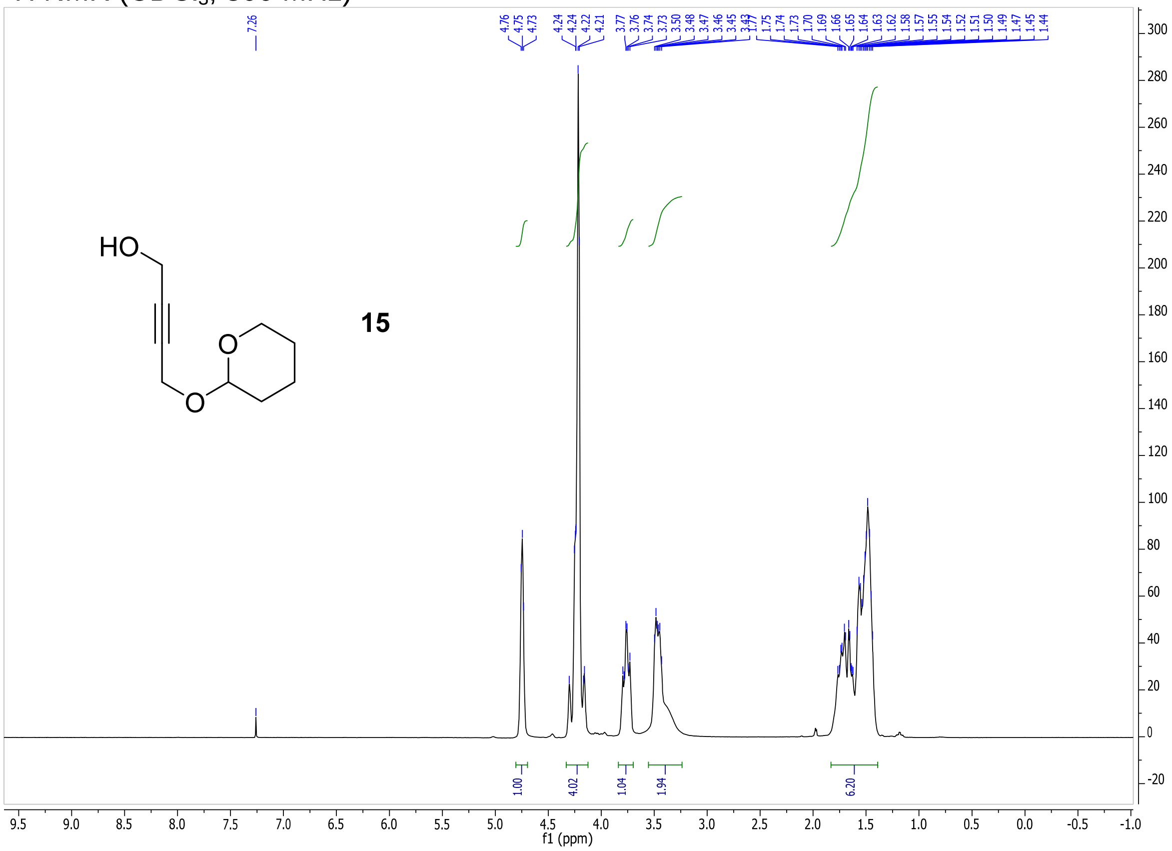


^{13}C NMR ($CDCl_3$, 100 MHz)



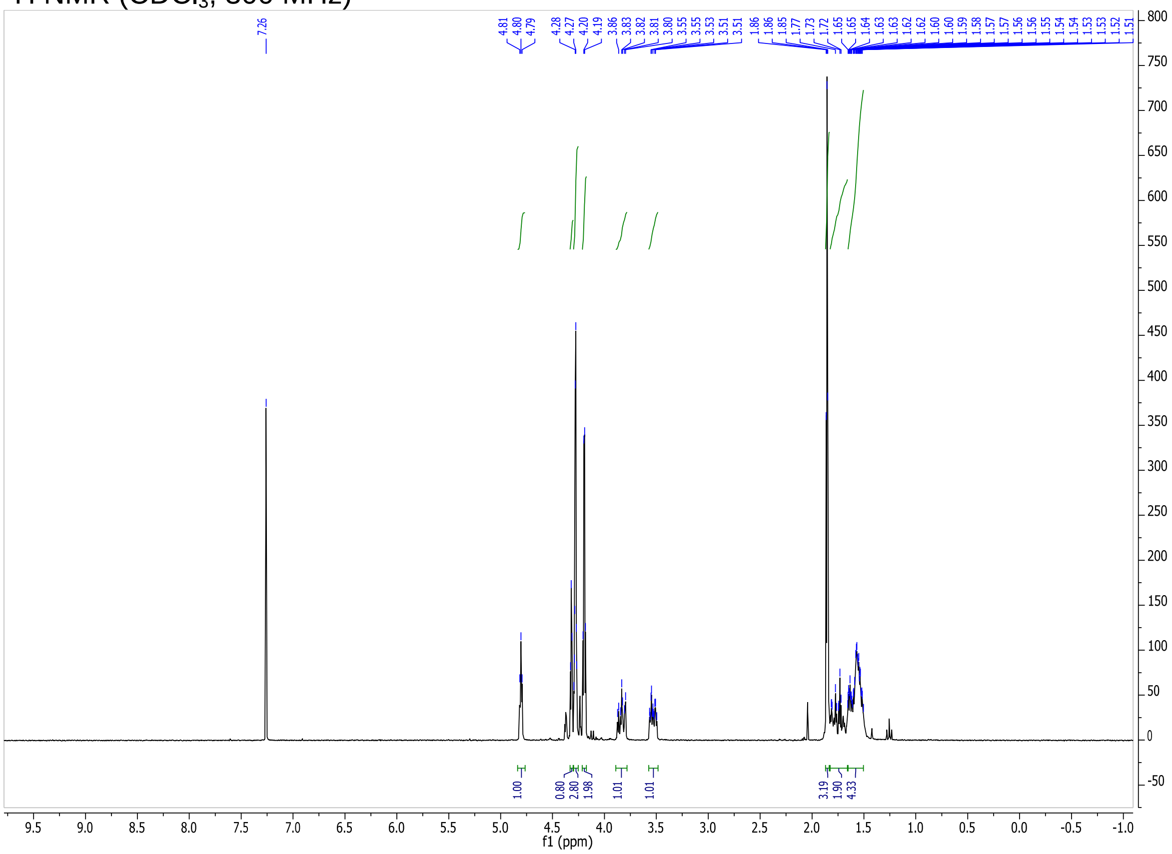
Compound 15:

^{1}H NMR ($CDCl_3$, 300 MHz)



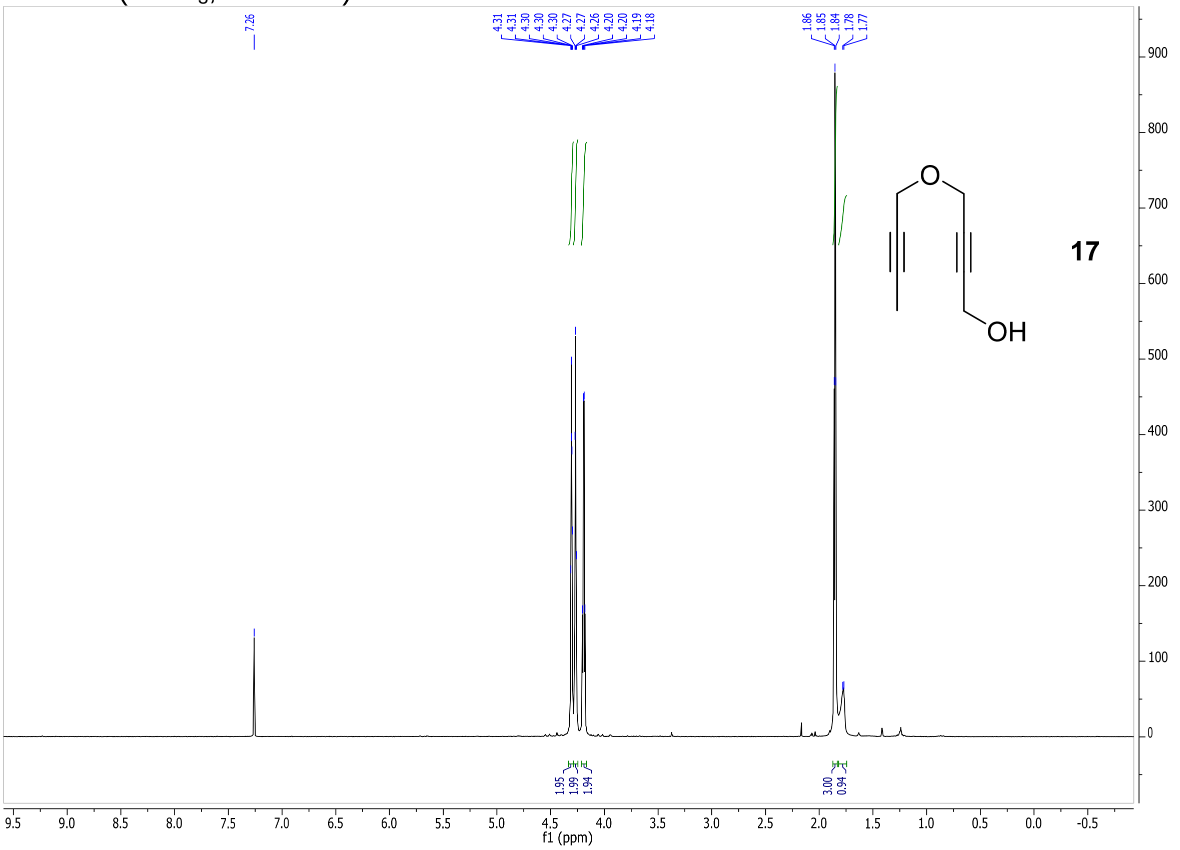
Compound 16:

^{1}H NMR ($CDCl_3$, 300 MHz)



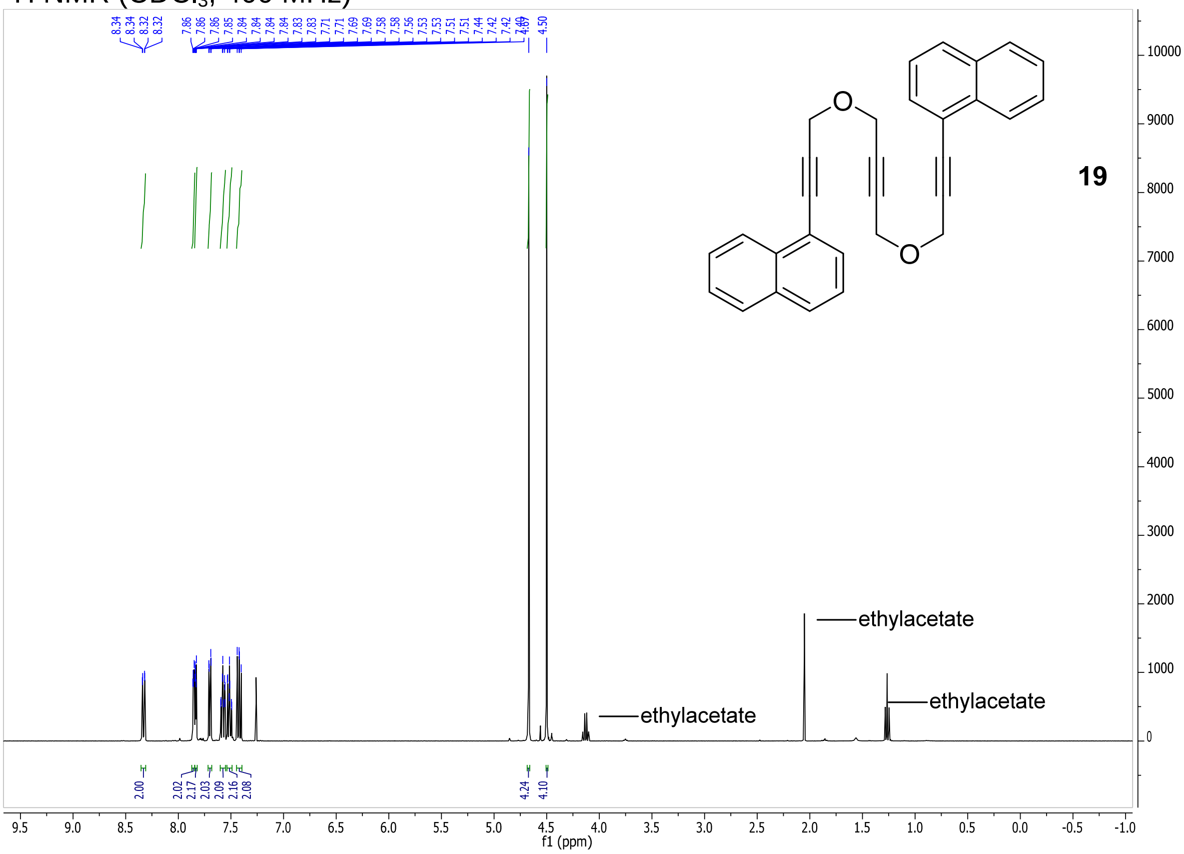
Compound 17:

^{1}H NMR ($CDCl_3$, 300 MHz)



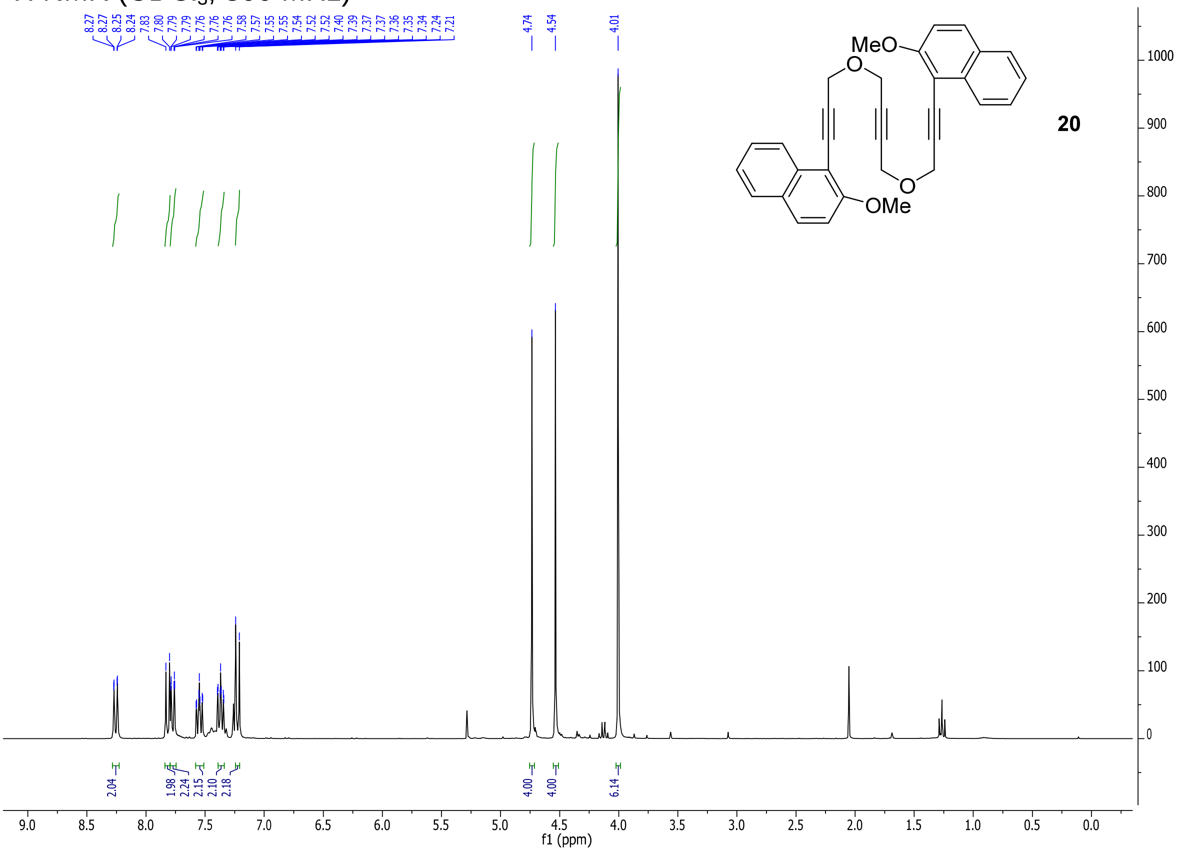
Compound 19:

^{1}H NMR ($CDCl_3$, 400 MHz)

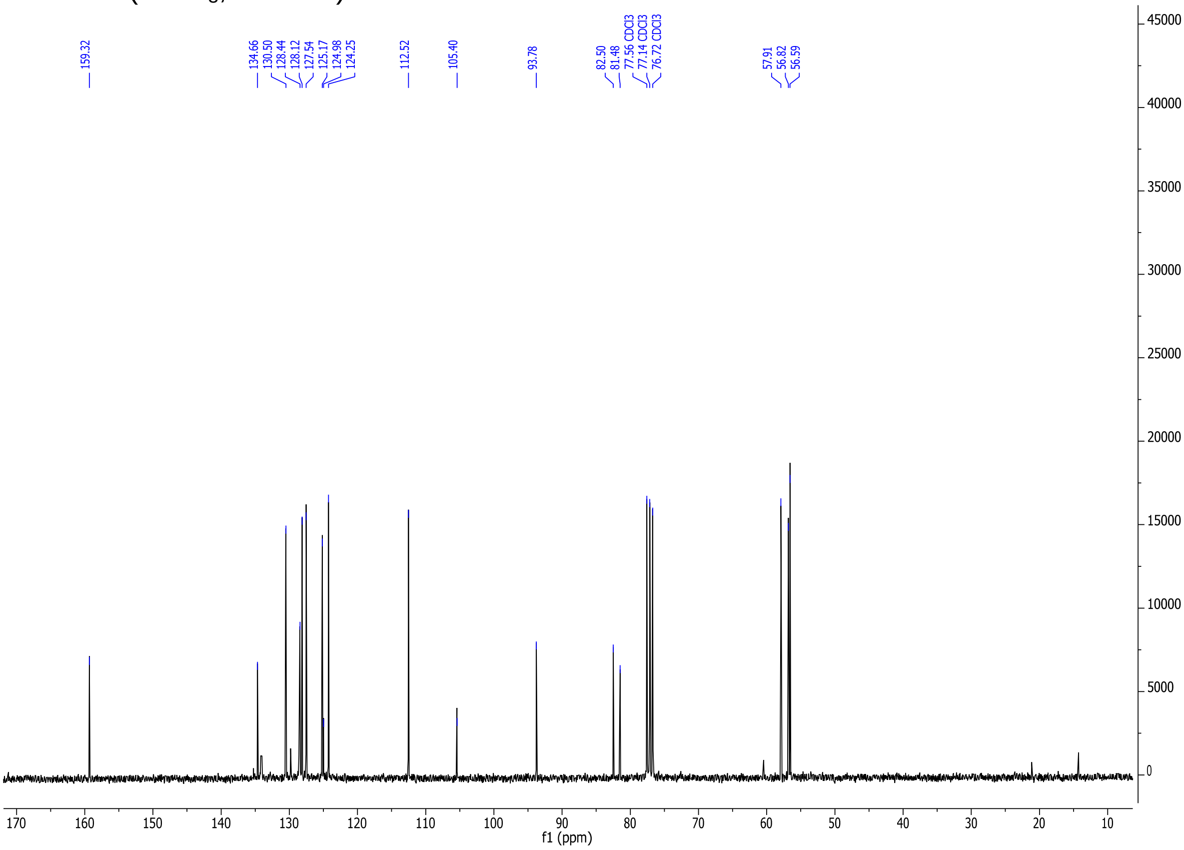


Compound 20:

^{1}H NMR ($CDCl_3$, 300 MHz)

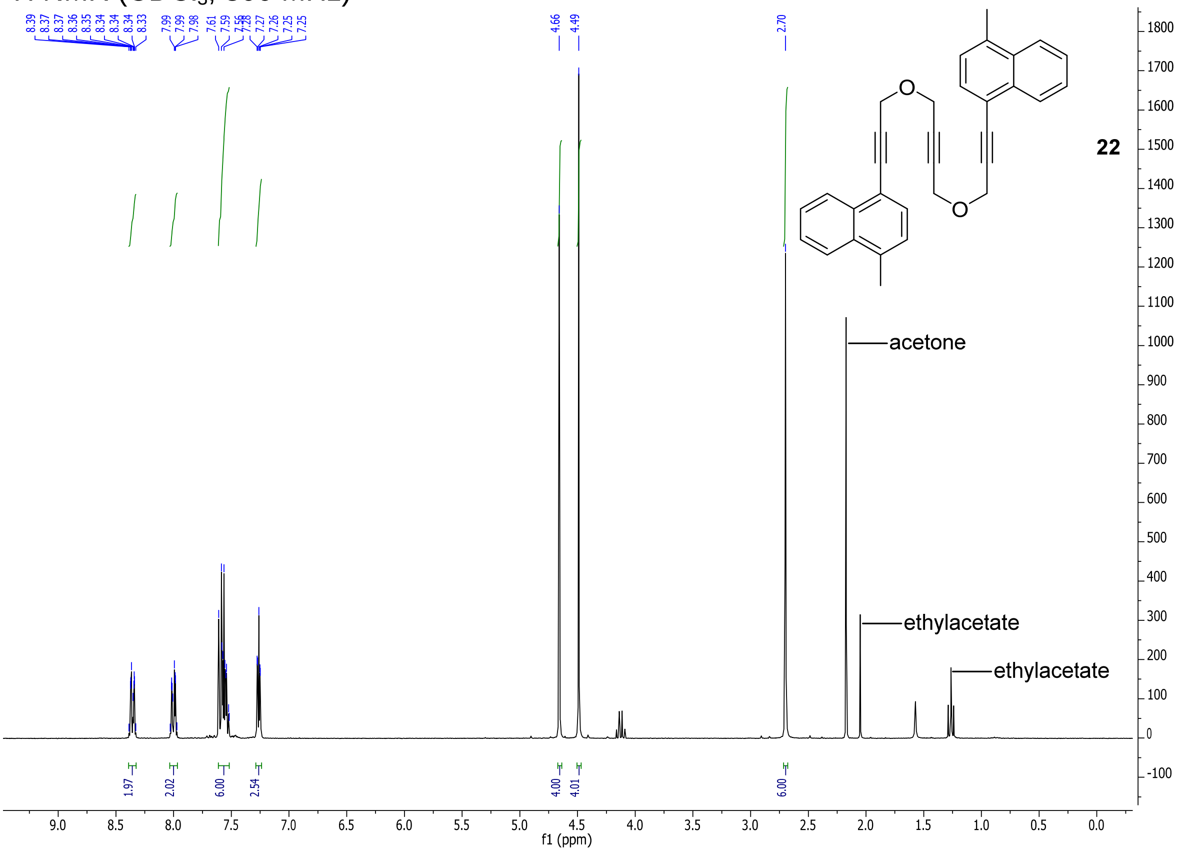


^{13}C NMR ($CDCl_3$, 75 MHz)

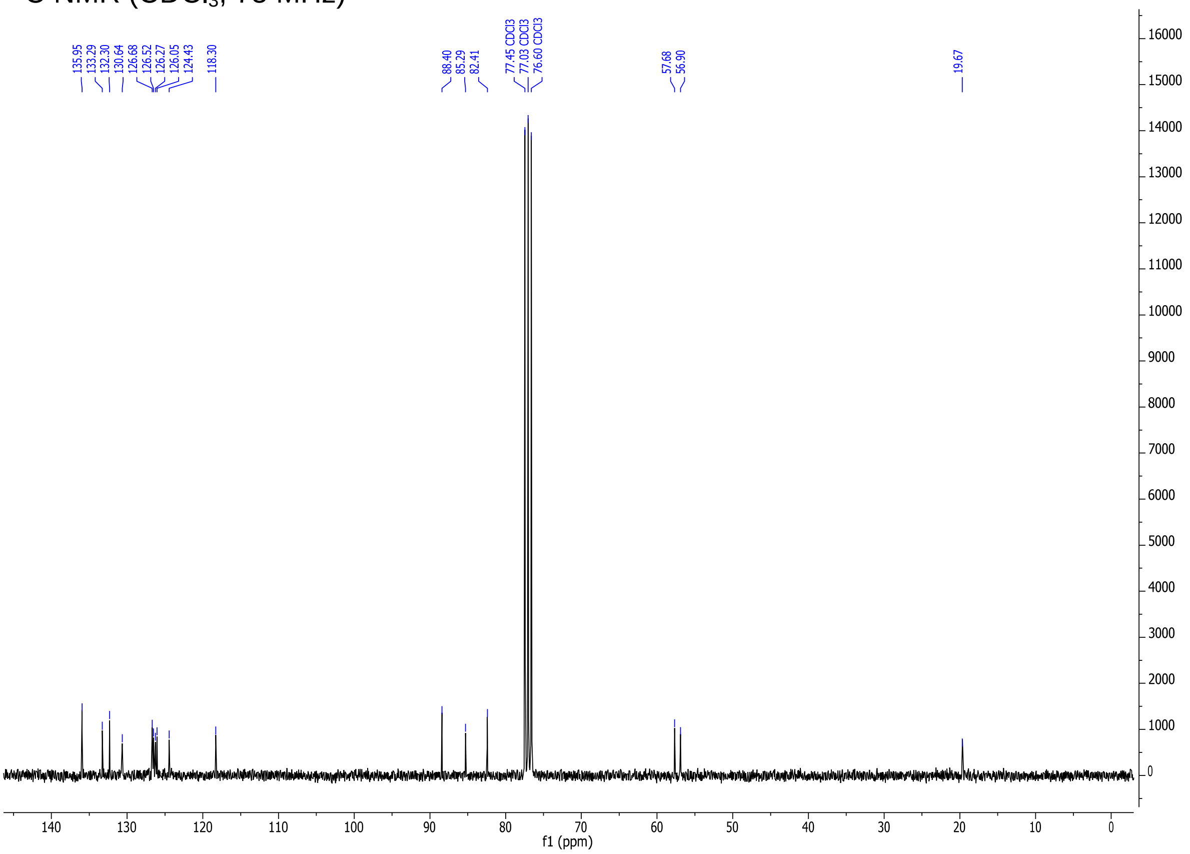


Compound 22:

^{1}H NMR ($CDCl_3$, 300 MHz)

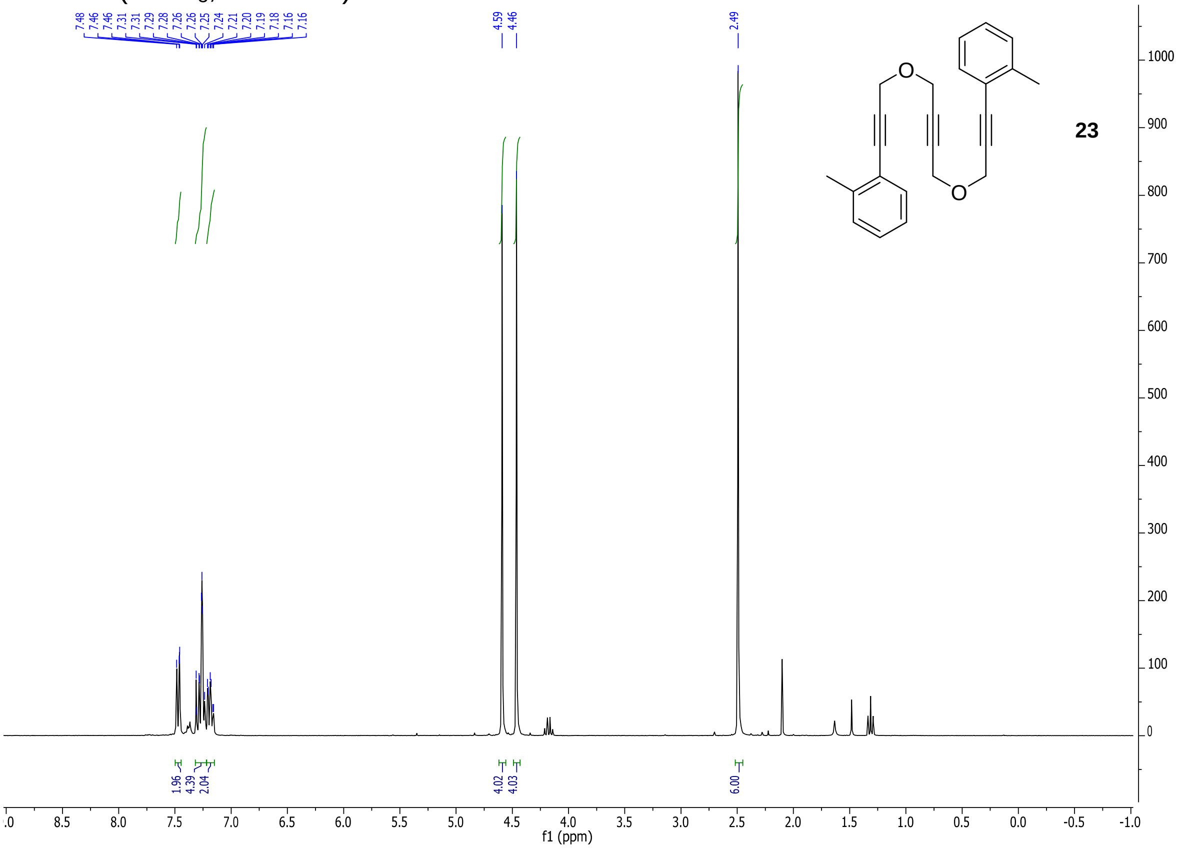


^{13}C NMR ($CDCl_3$, 75 MHz)



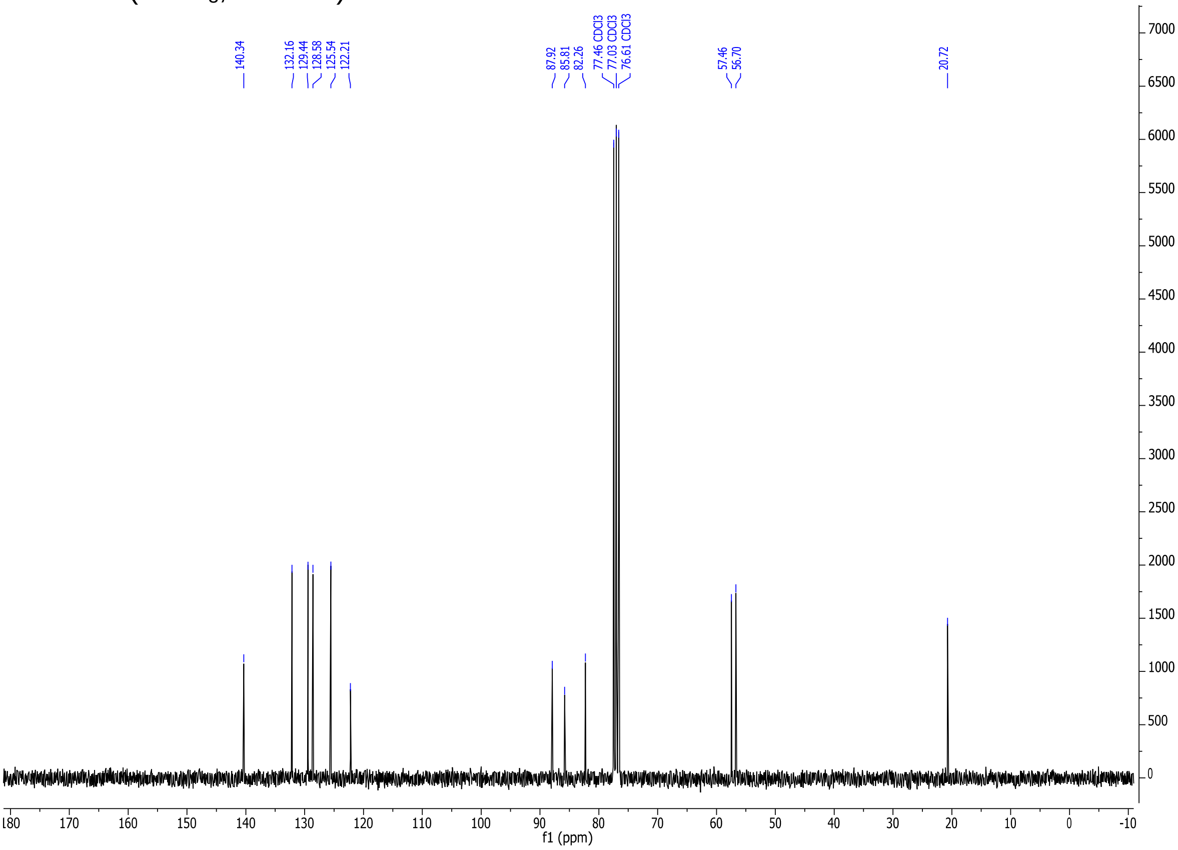
Compound 23:

^{1}H NMR ($CDCl_3$, 300 MHz)



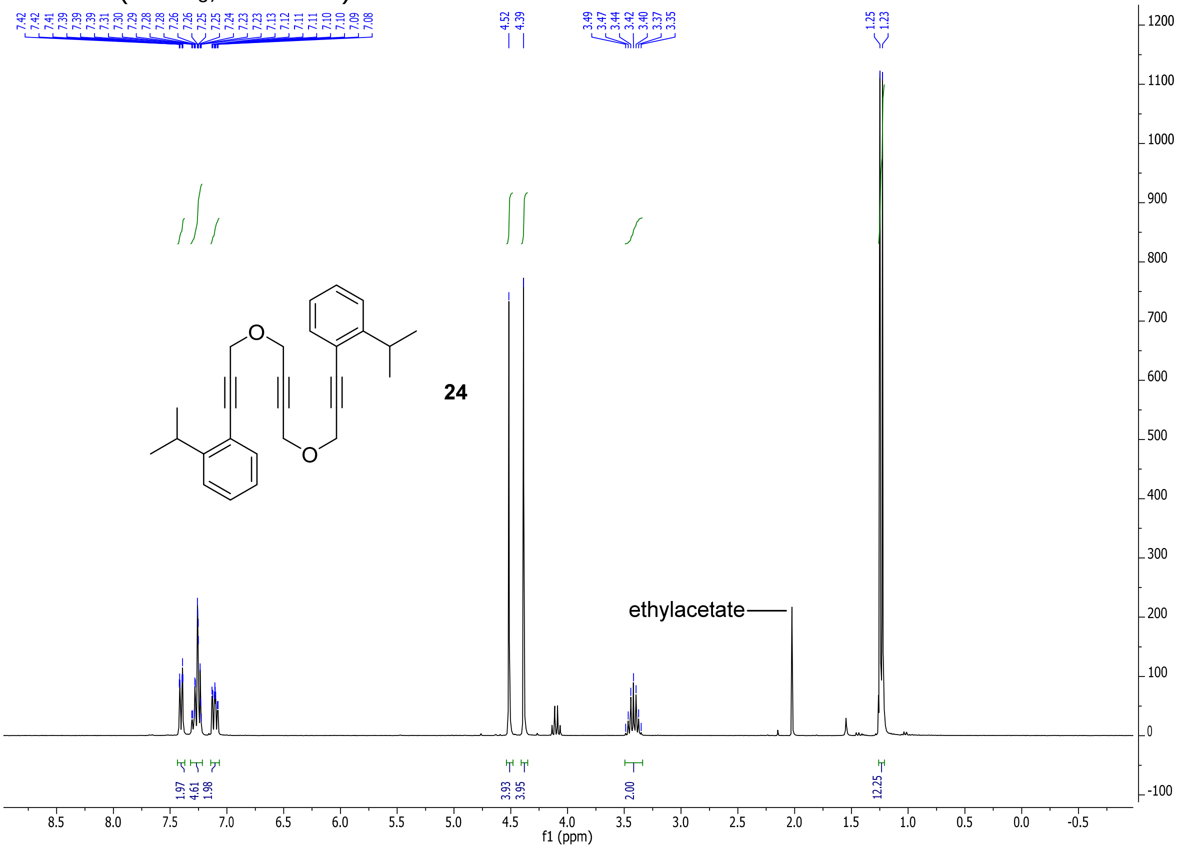
23

^{13}C NMR ($CDCl_3$, 75 MHz)

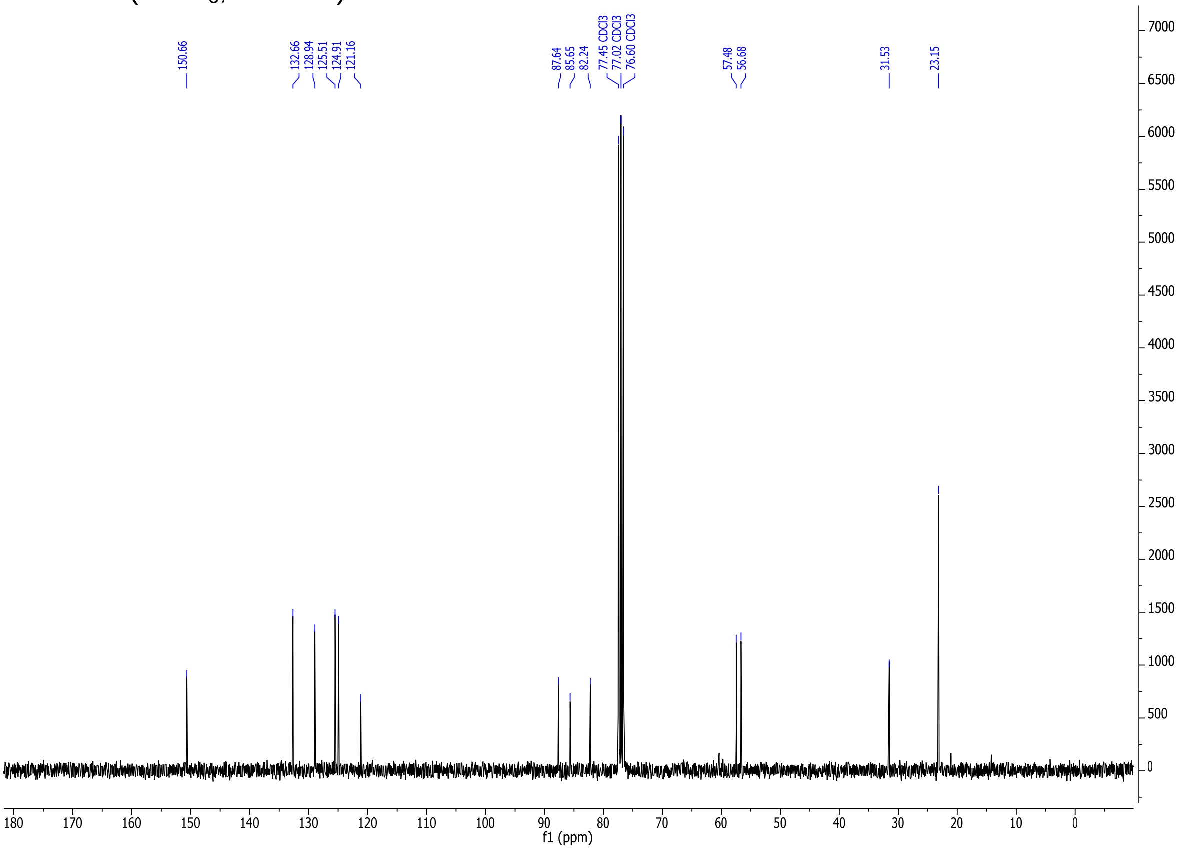


Compound 24:

^{1}H NMR ($CDCl_3$, 300 MHz)

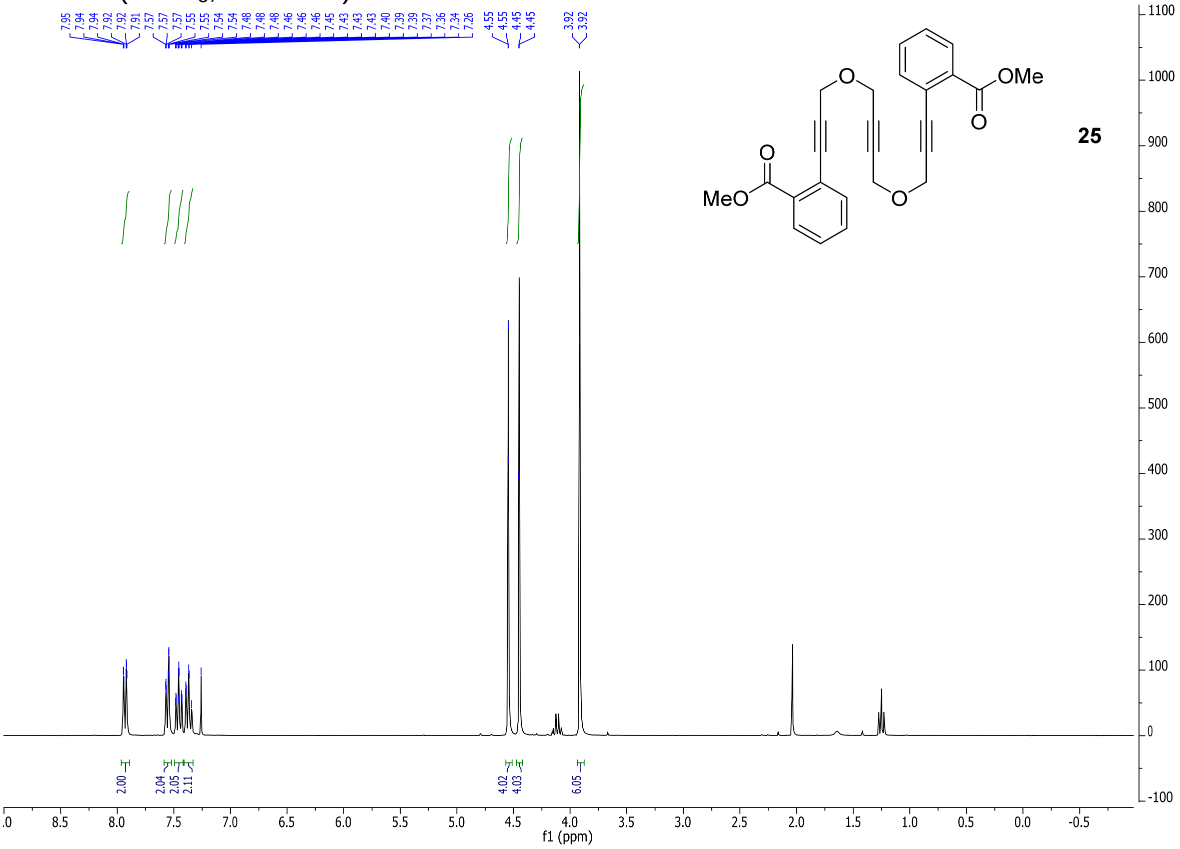


^{13}C NMR ($CDCl_3$, 75 MHz)

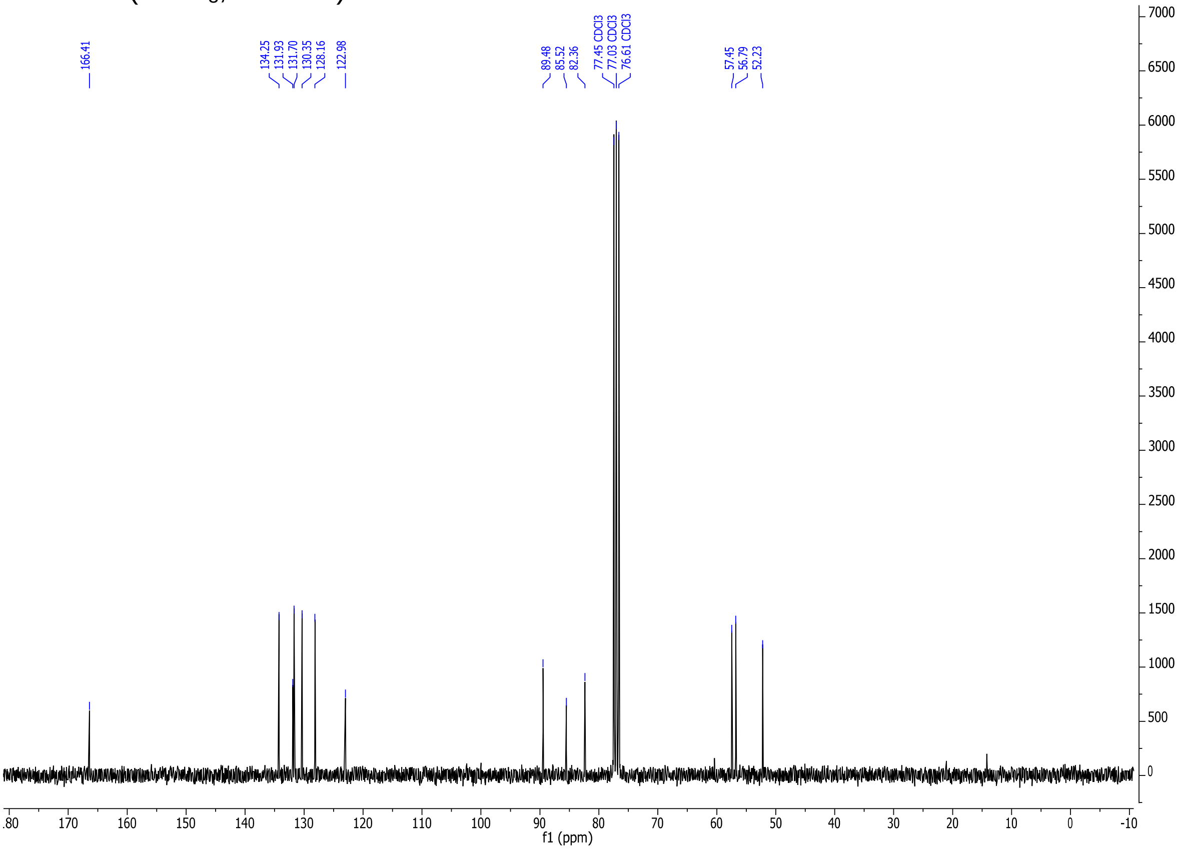


Compound 25:

^{1}H NMR ($CDCl_3$, 300 MHz)

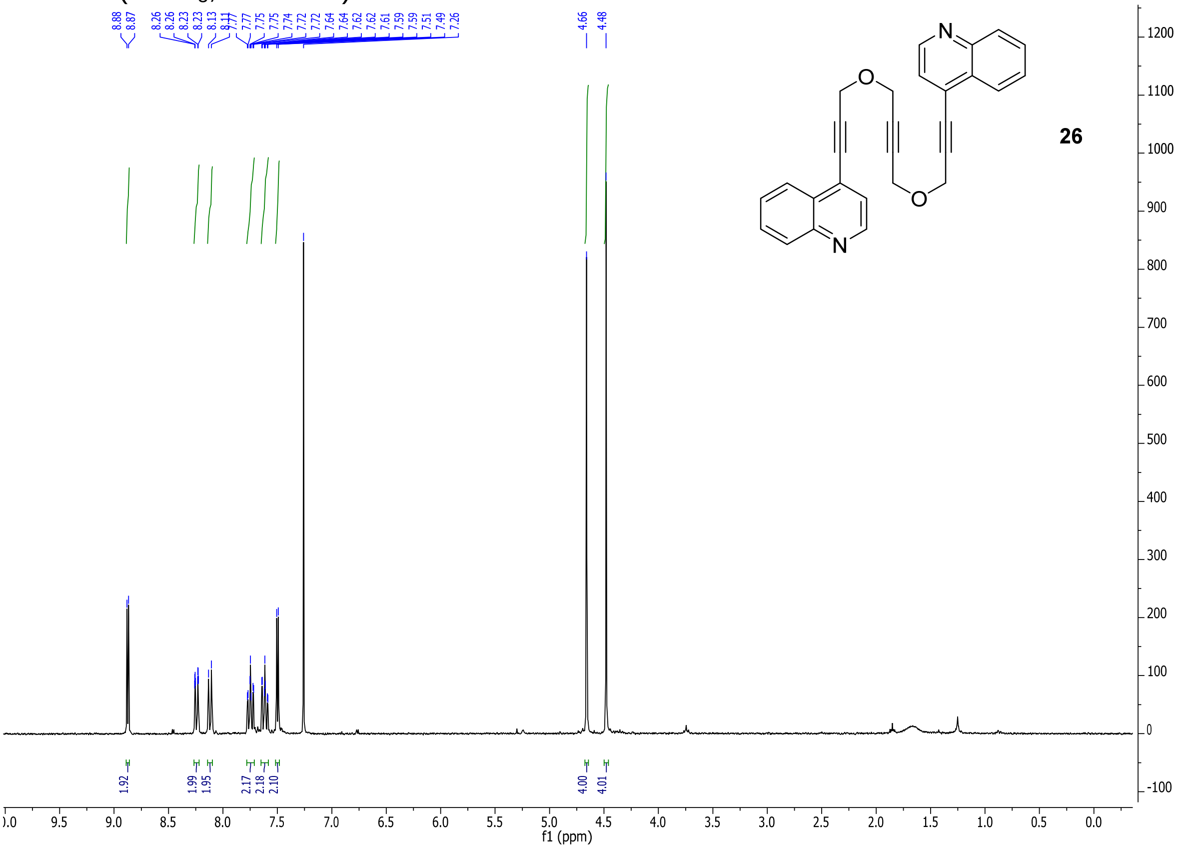


^{13}C NMR ($CDCl_3$, 75 MHz)

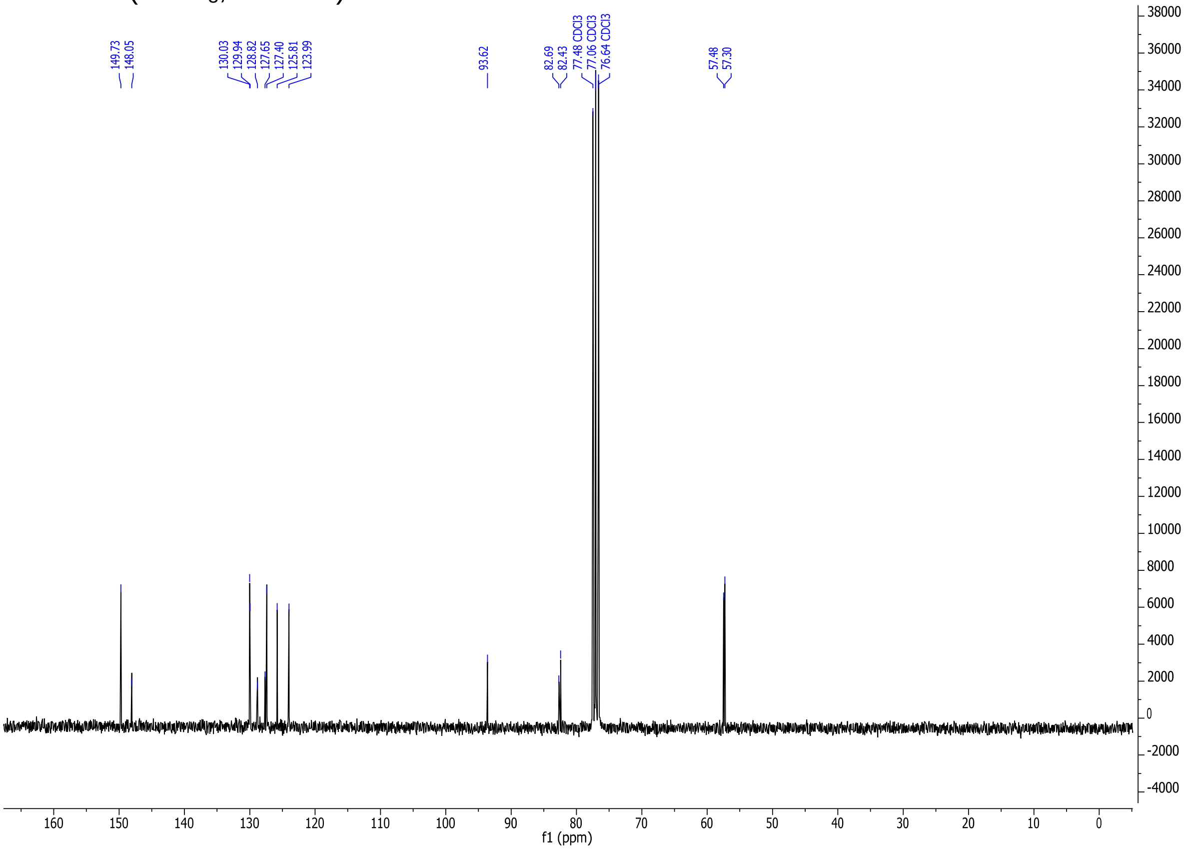


Compound 26:

^{1}H NMR ($CDCl_3$, 300 MHz)

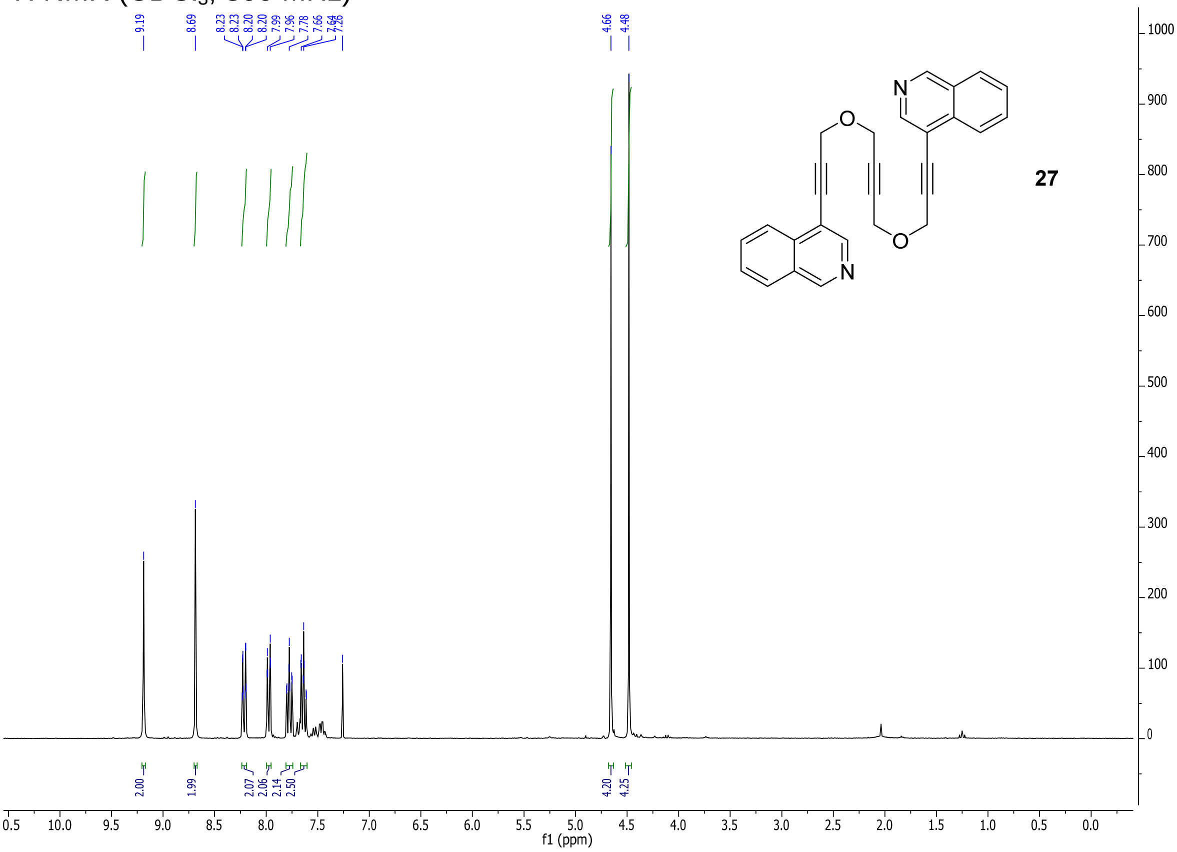


^{13}C NMR ($CDCl_3$, 75 MHz)



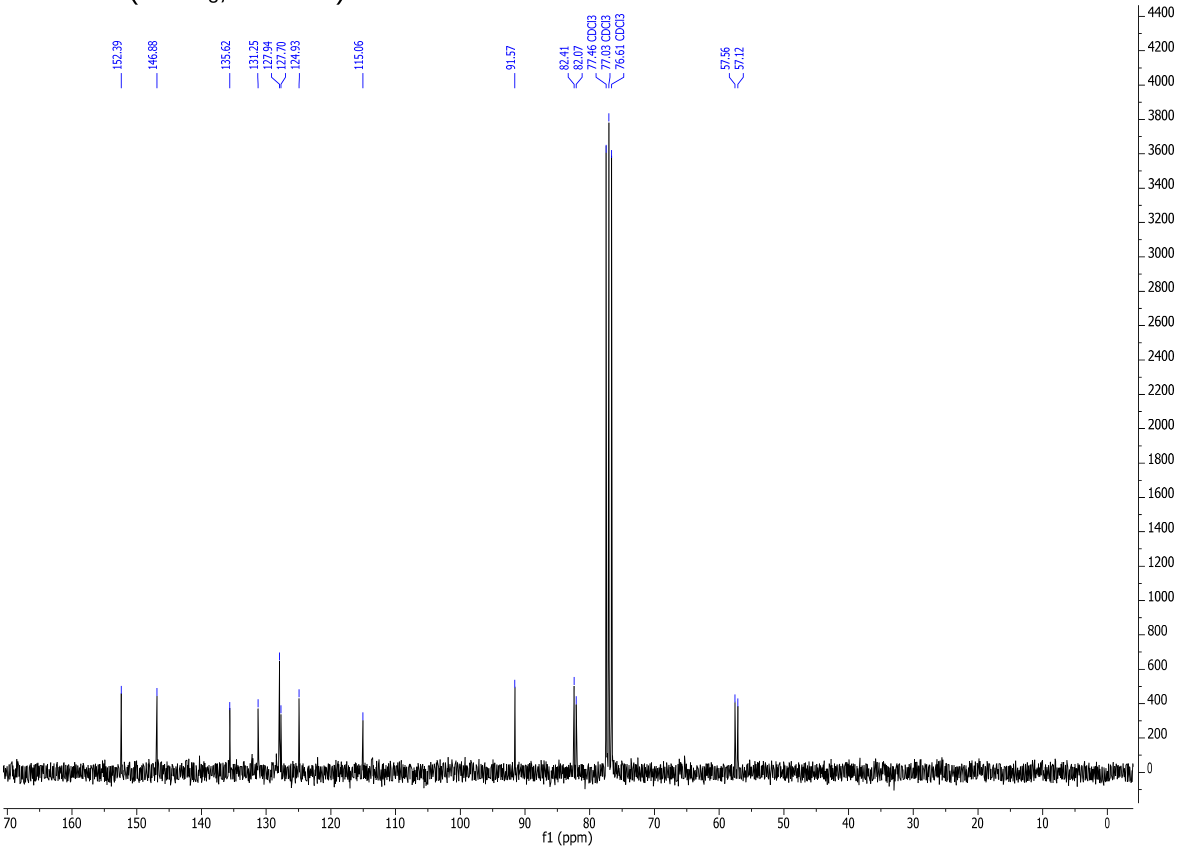
Compound 27:

^{1}H NMR ($CDCl_3$, 300 MHz)



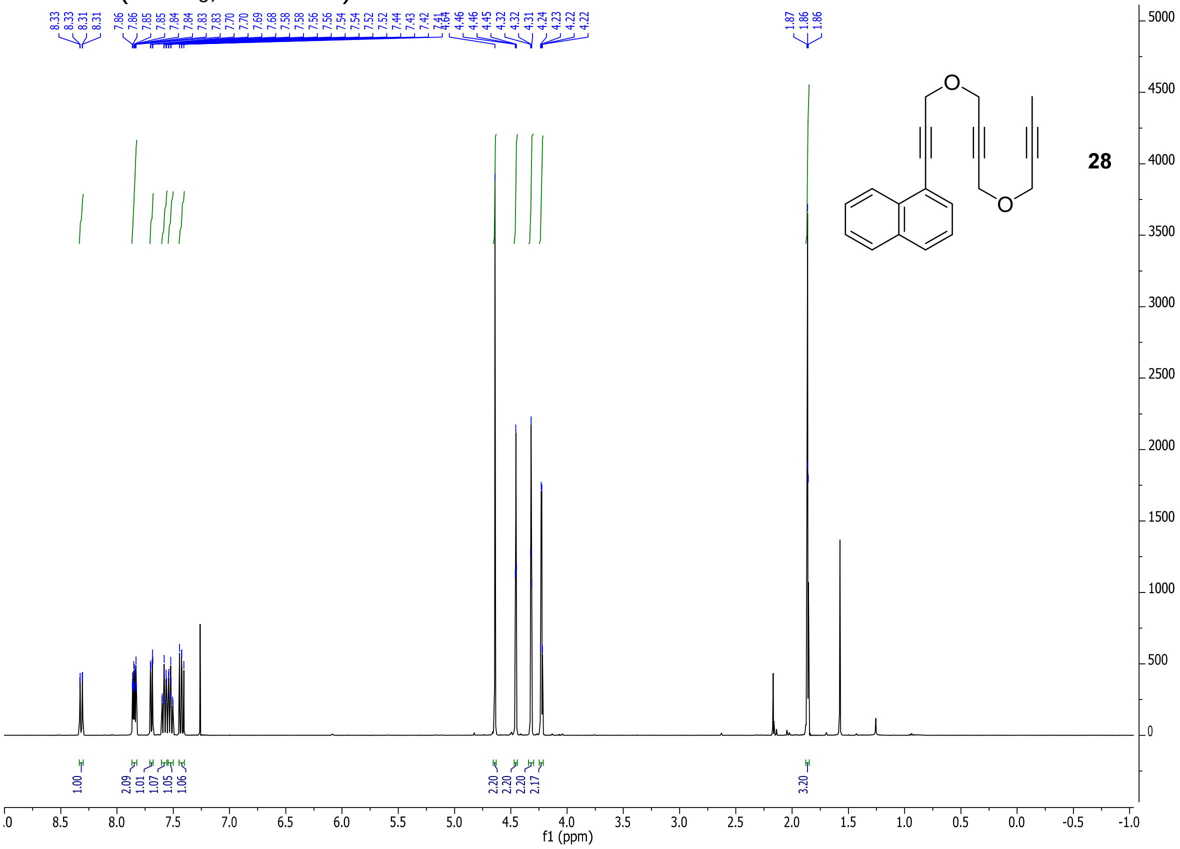
27

^{13}C NMR ($CDCl_3$, 75 MHz)

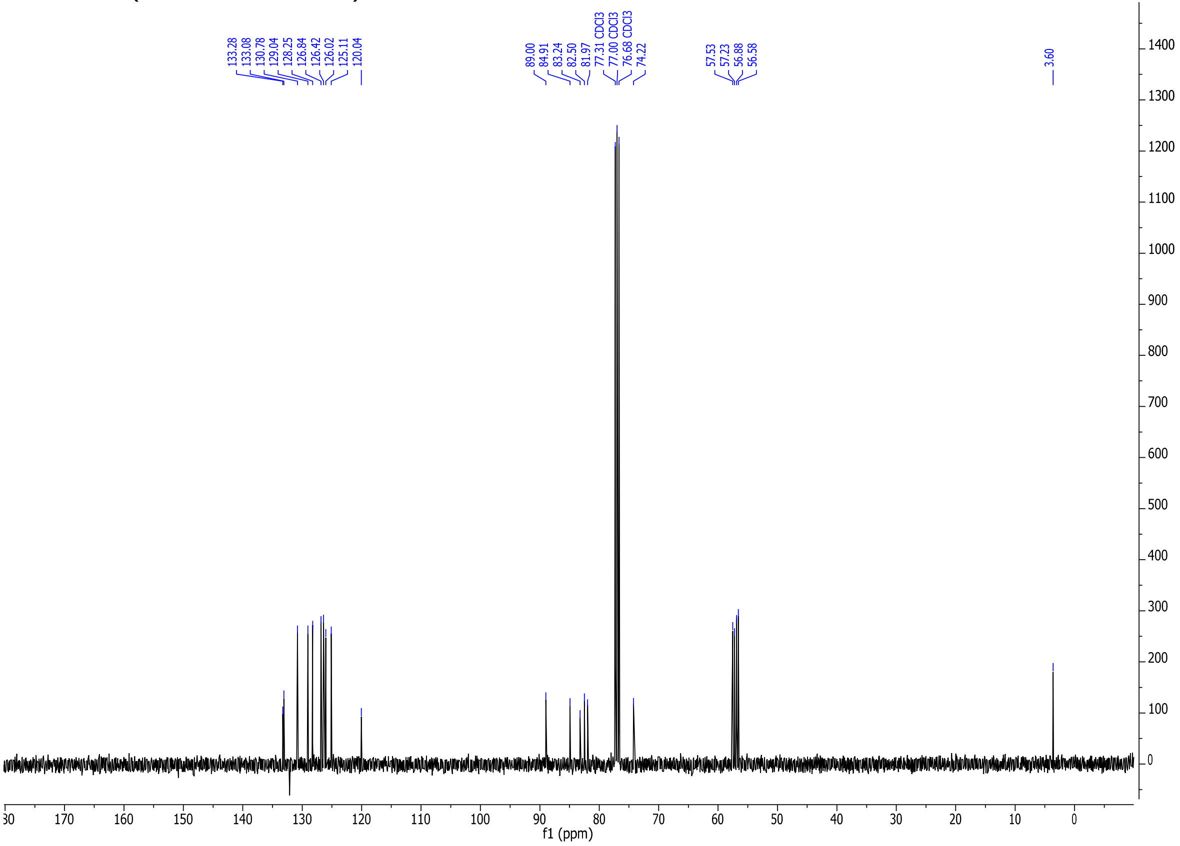


Compound 28: pathway B

^{1}H NMR ($CDCl_3$, 400 MHz)

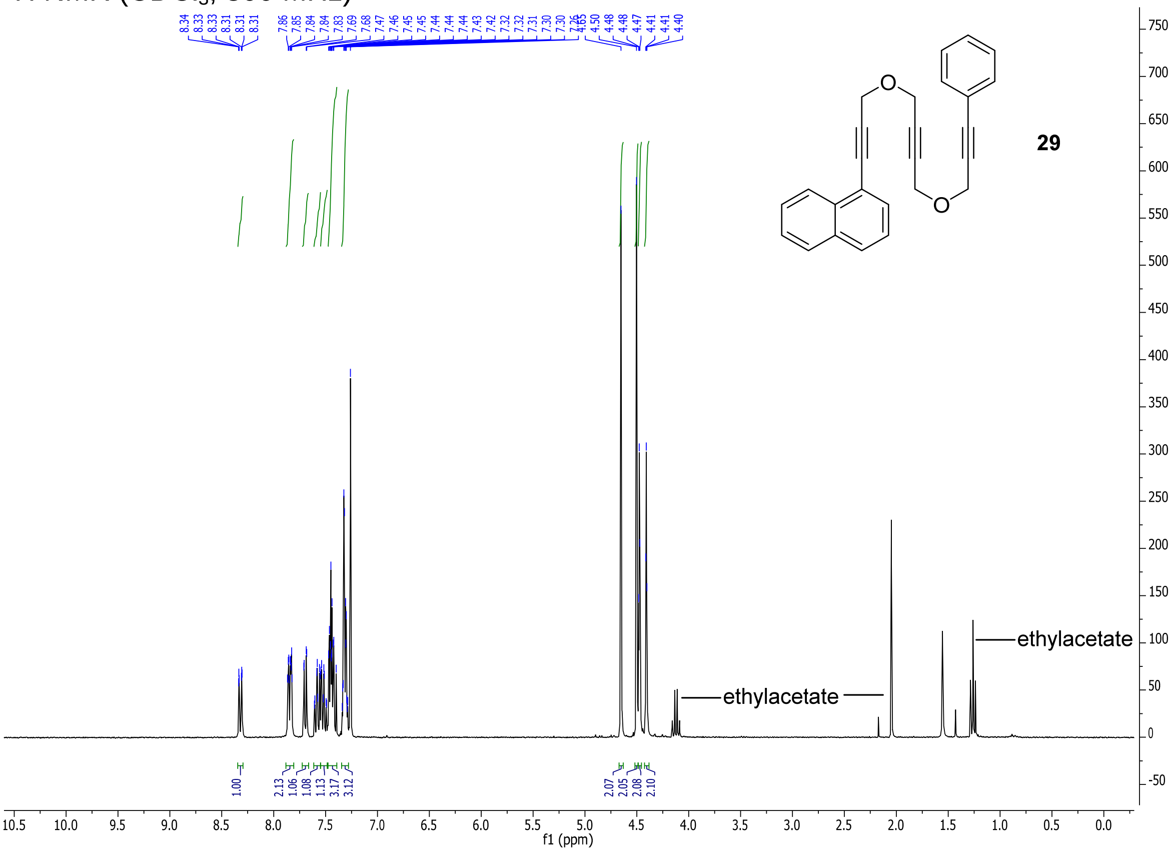


^{13}C NMR ($CDCl_3$, 100 MHz)

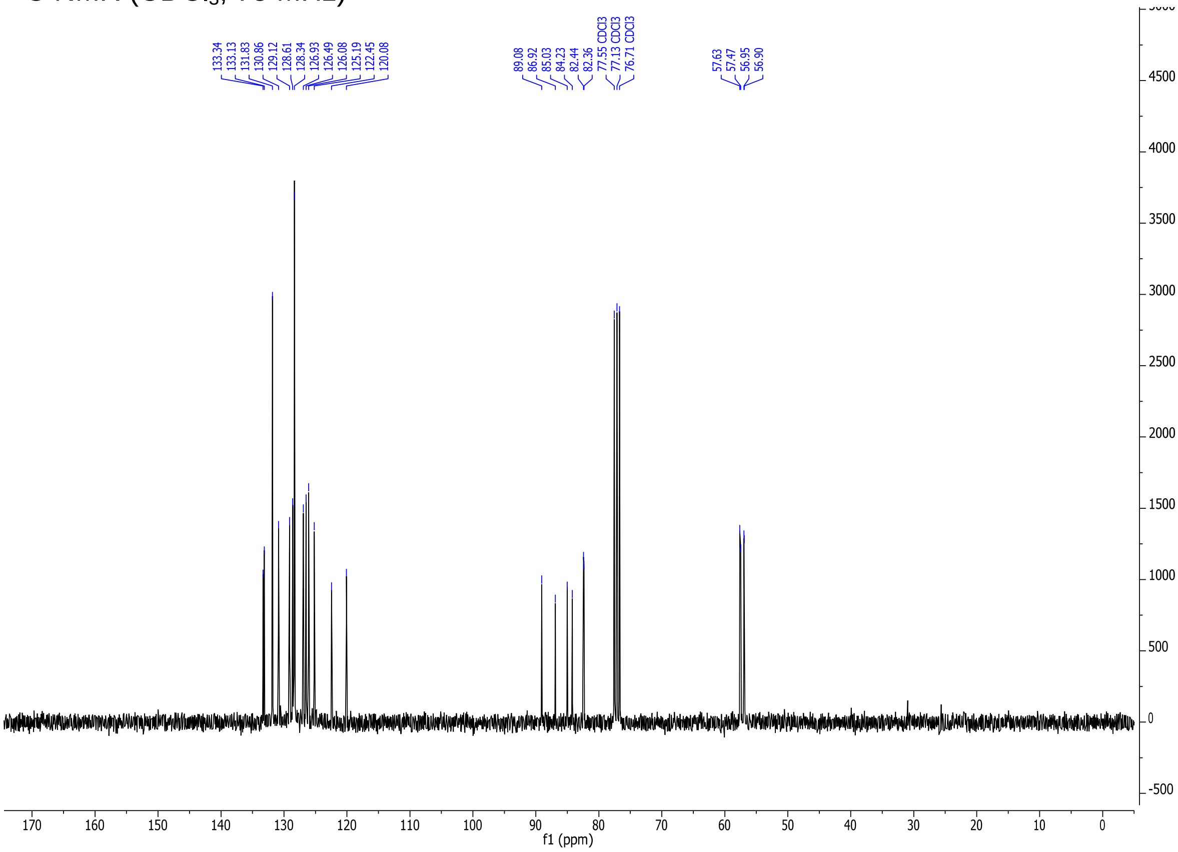


Compound 29: pathway A

^1H NMR ($CDCl_3$, 300 MHz)

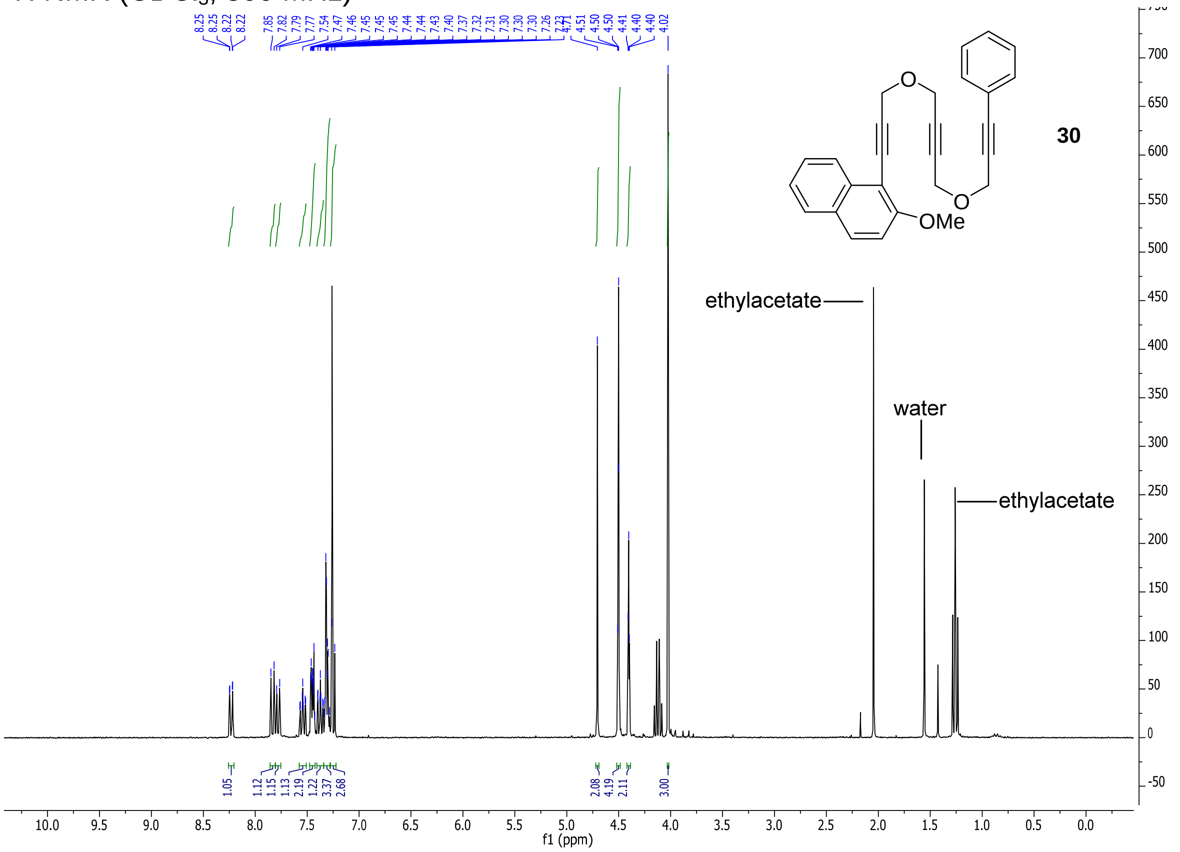


^{13}C NMR ($CDCl_3$, 75 MHz)

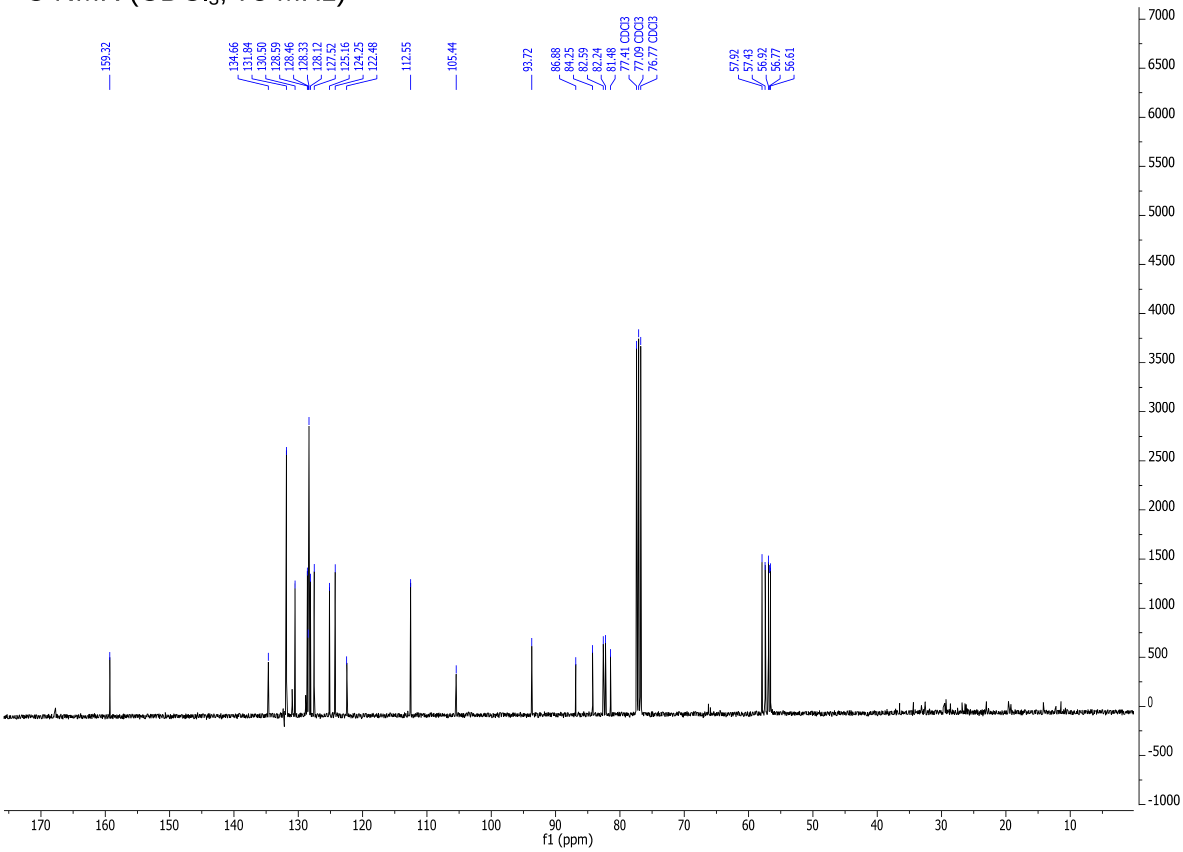


Compound 30: pathway A

^{1}H NMR ($CDCl_3$, 300 MHz)

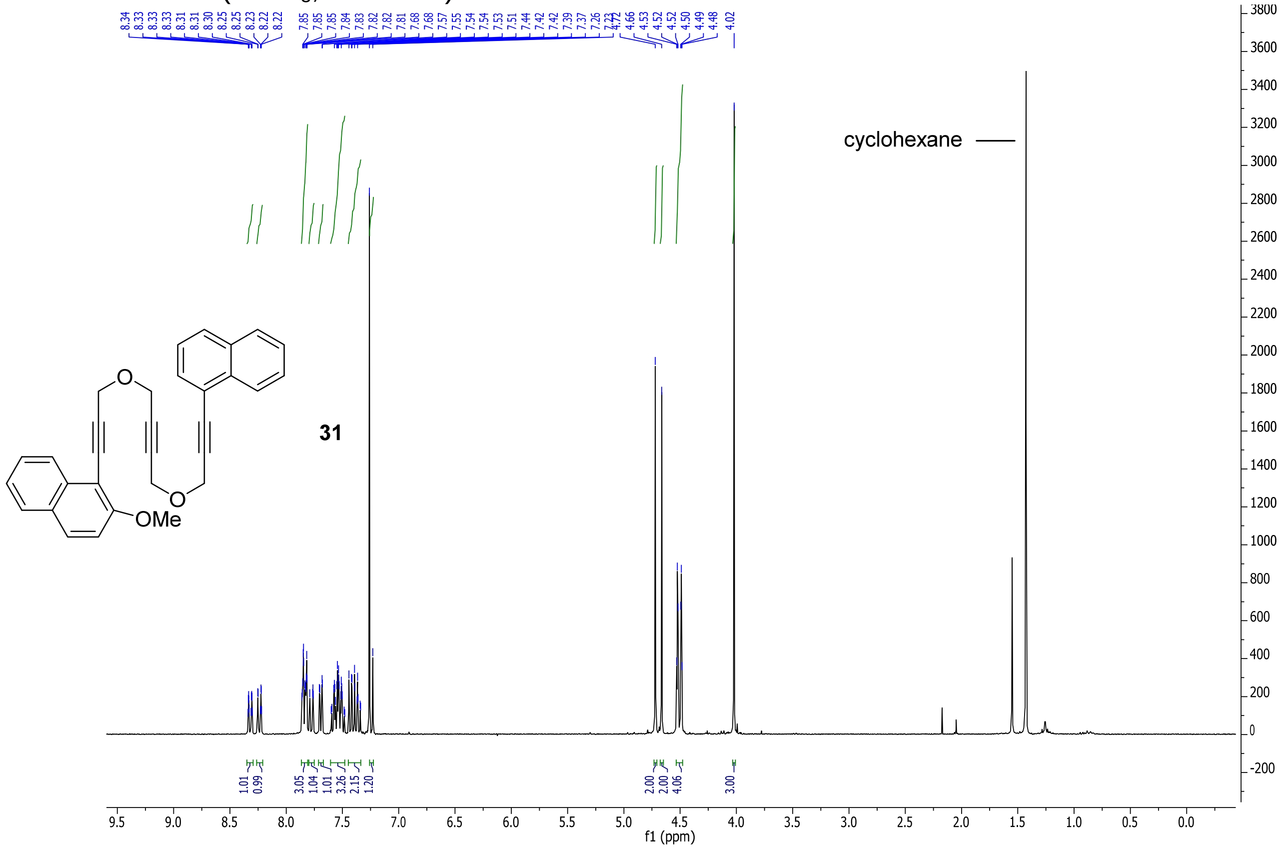


^{13}C NMR ($CDCl_3$, 75 MHz)

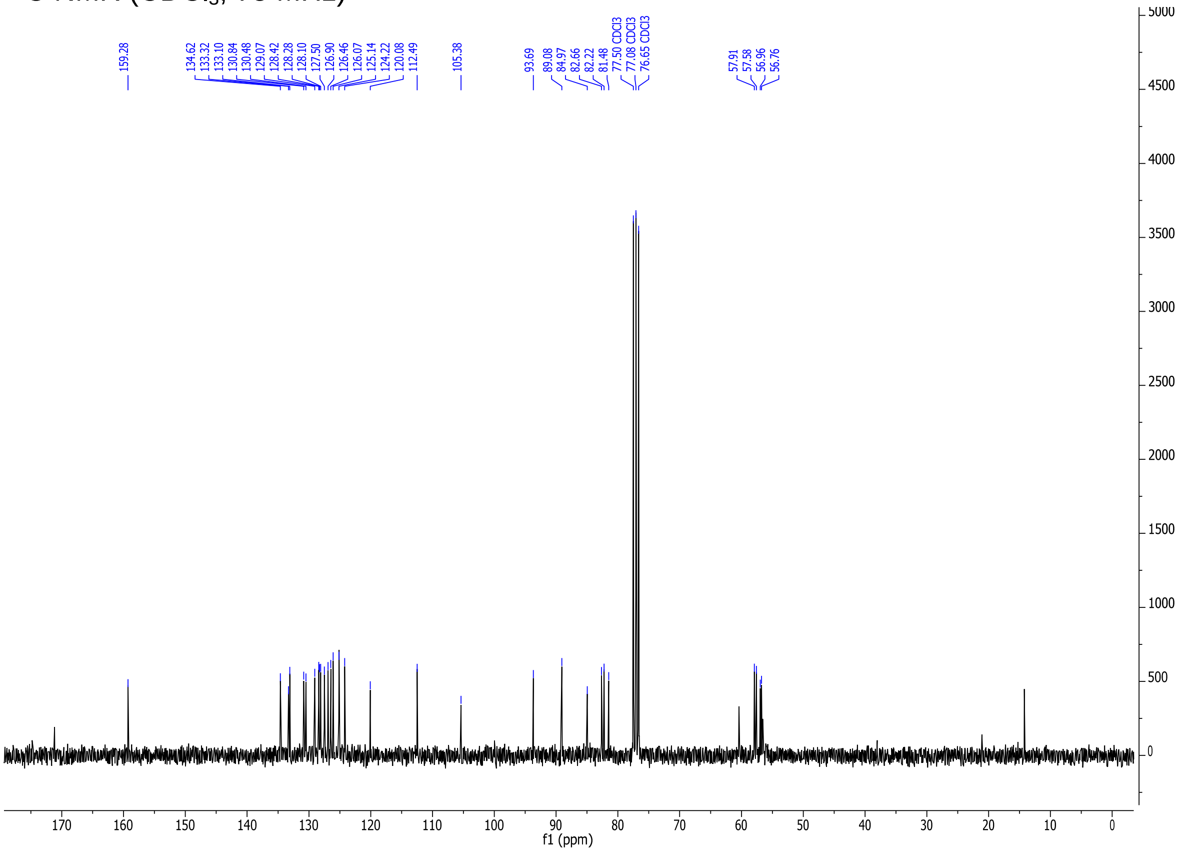


Compound 31: pathway A

^{1}H NMR ($CDCl_3$, 300 MHz)

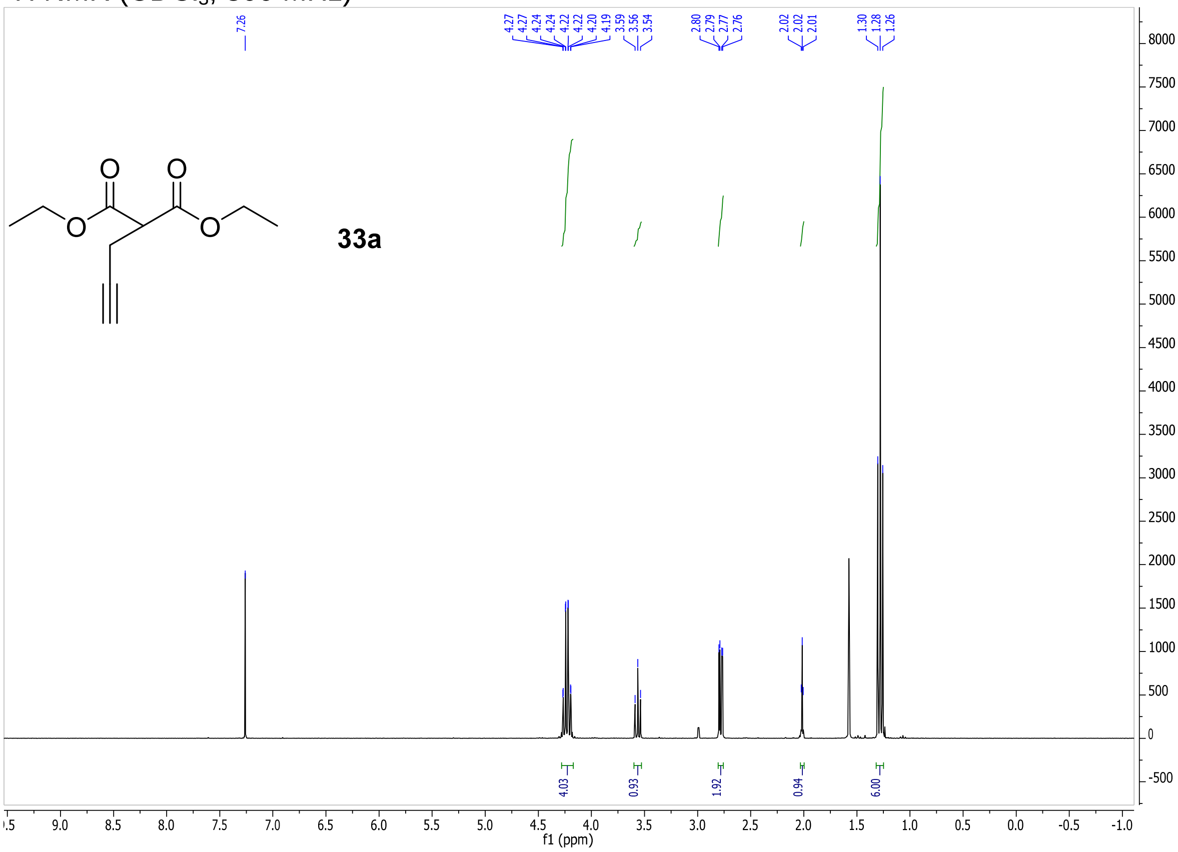


^{13}C NMR ($CDCl_3$, 75 MHz)



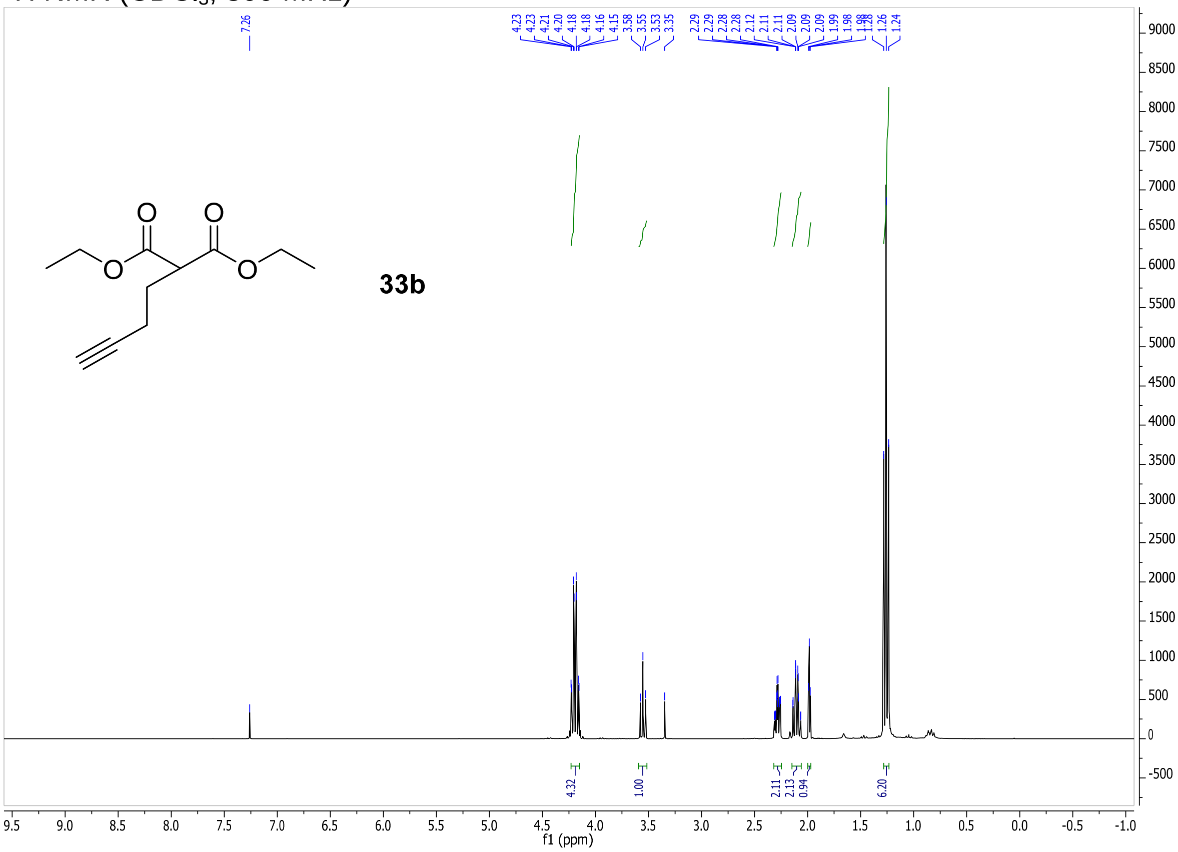
Compound 33a:

^1H NMR ($CDCl_3$, 300 MHz)



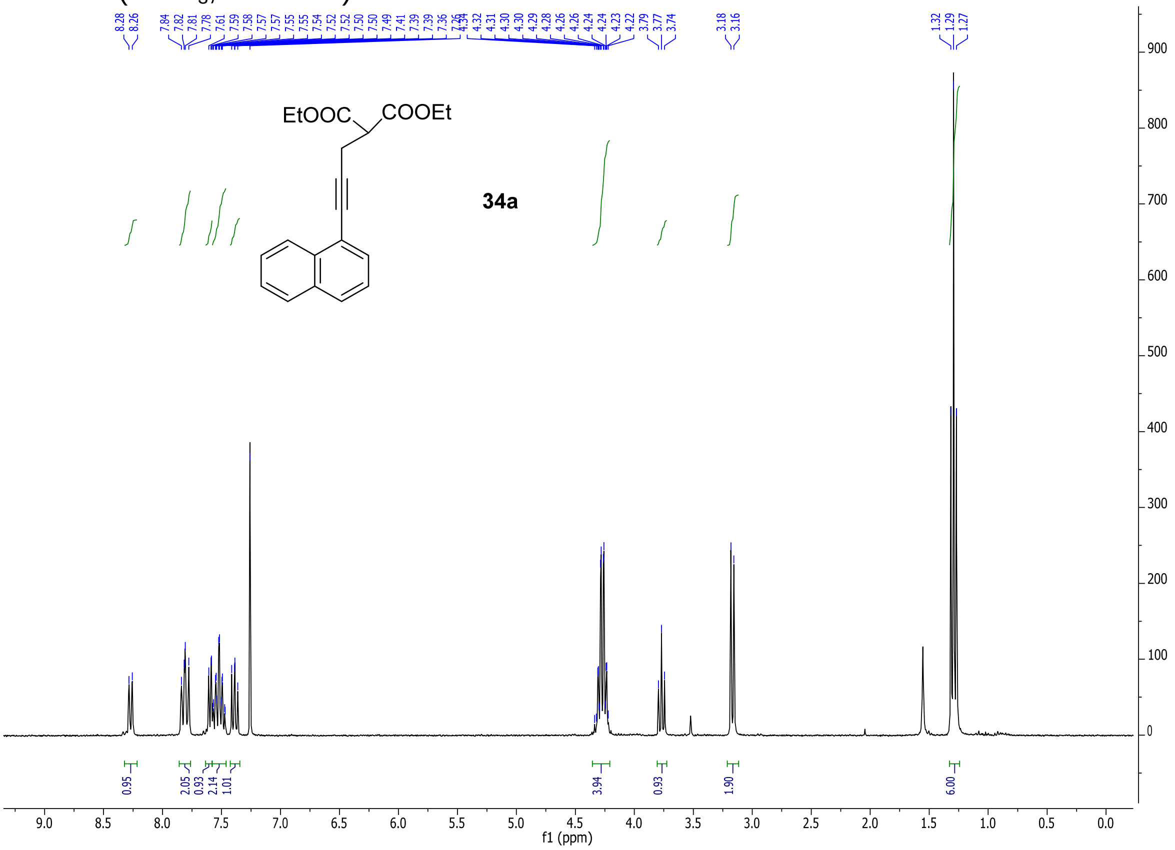
Compound 33b:

^1H NMR ($CDCl_3$, 300 MHz)

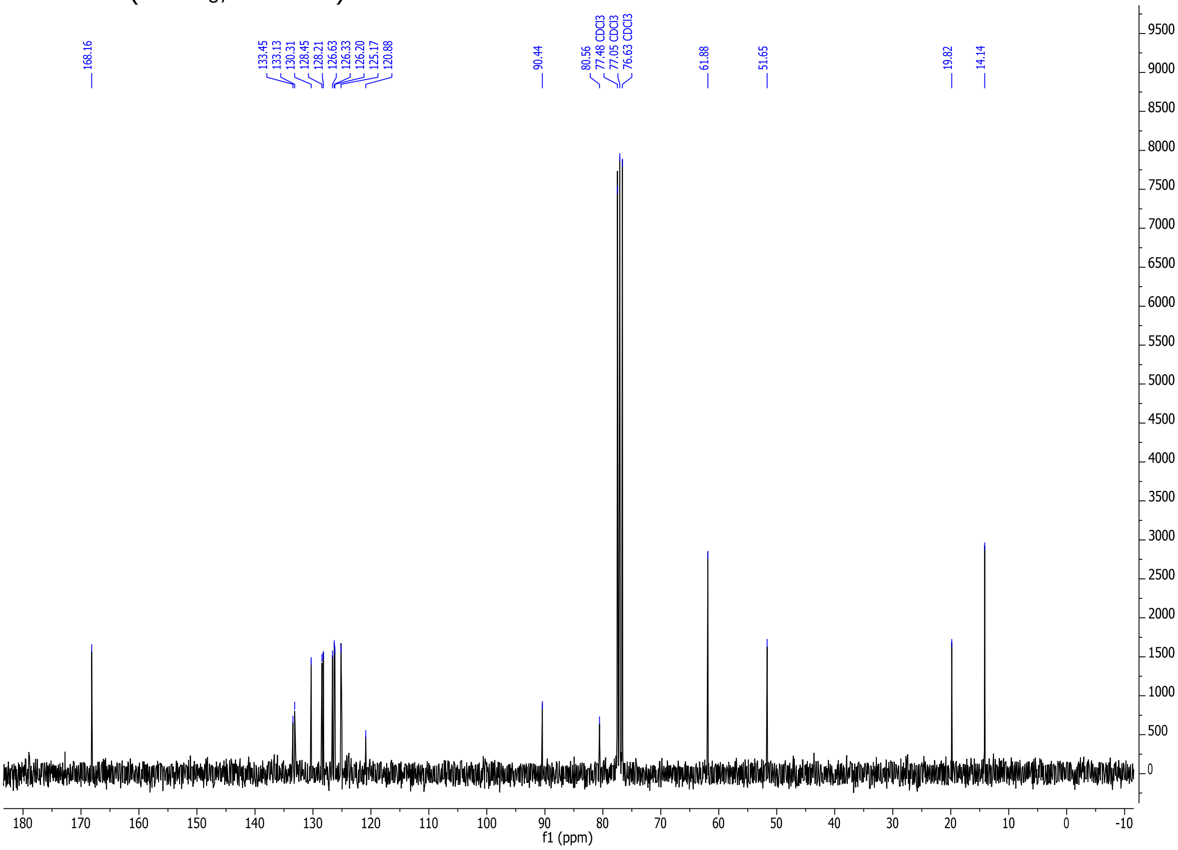


Compound 34a:

^{1}H NMR ($CDCl_3$, 300 MHz)

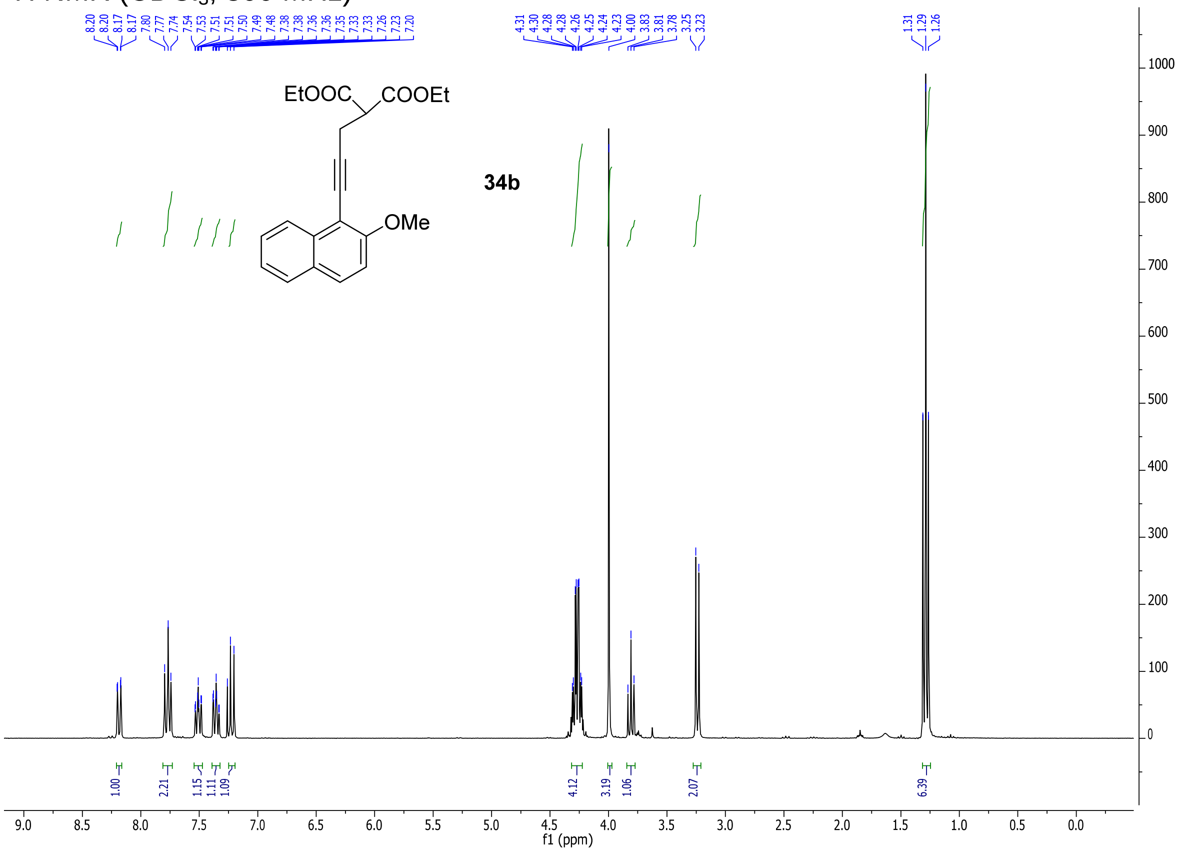


^{13}C NMR ($CDCl_3$, 75 MHz)

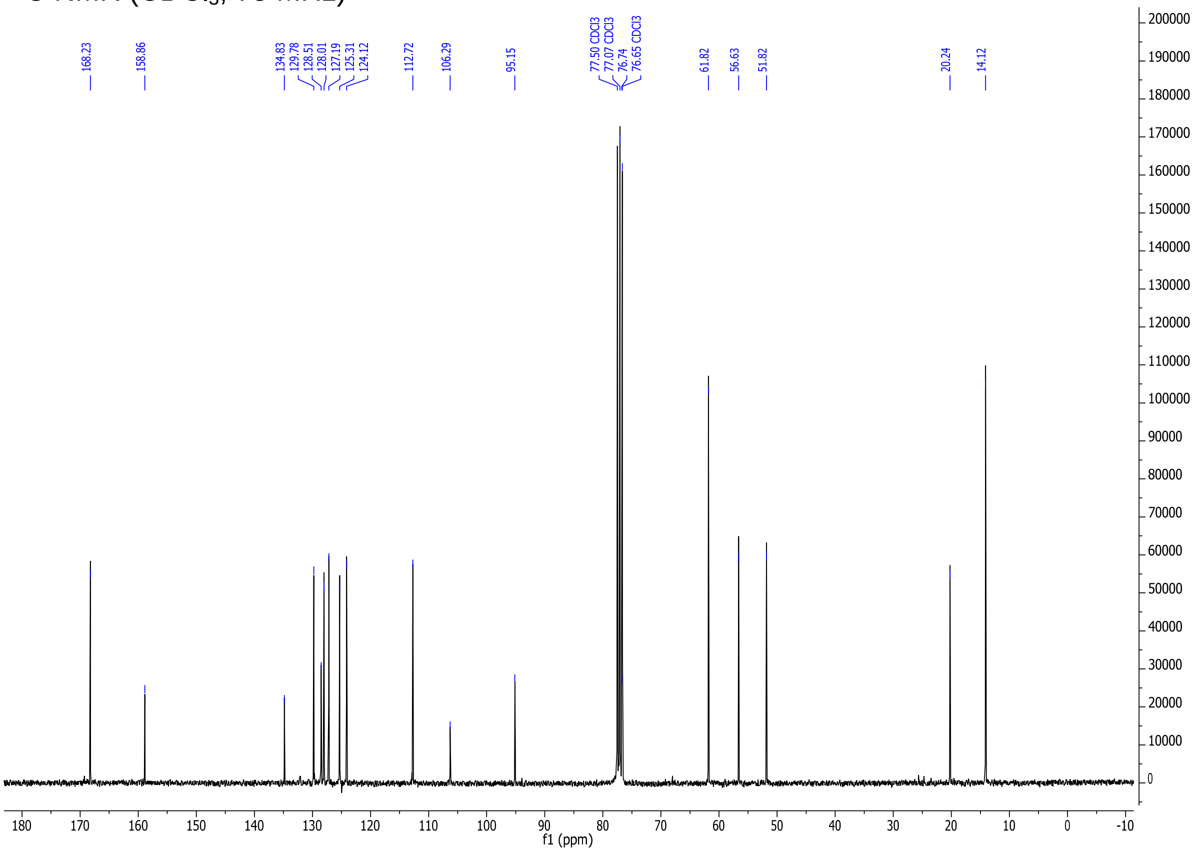


Compound 34b:

^{1}H NMR ($CDCl_3$, 300 MHz)

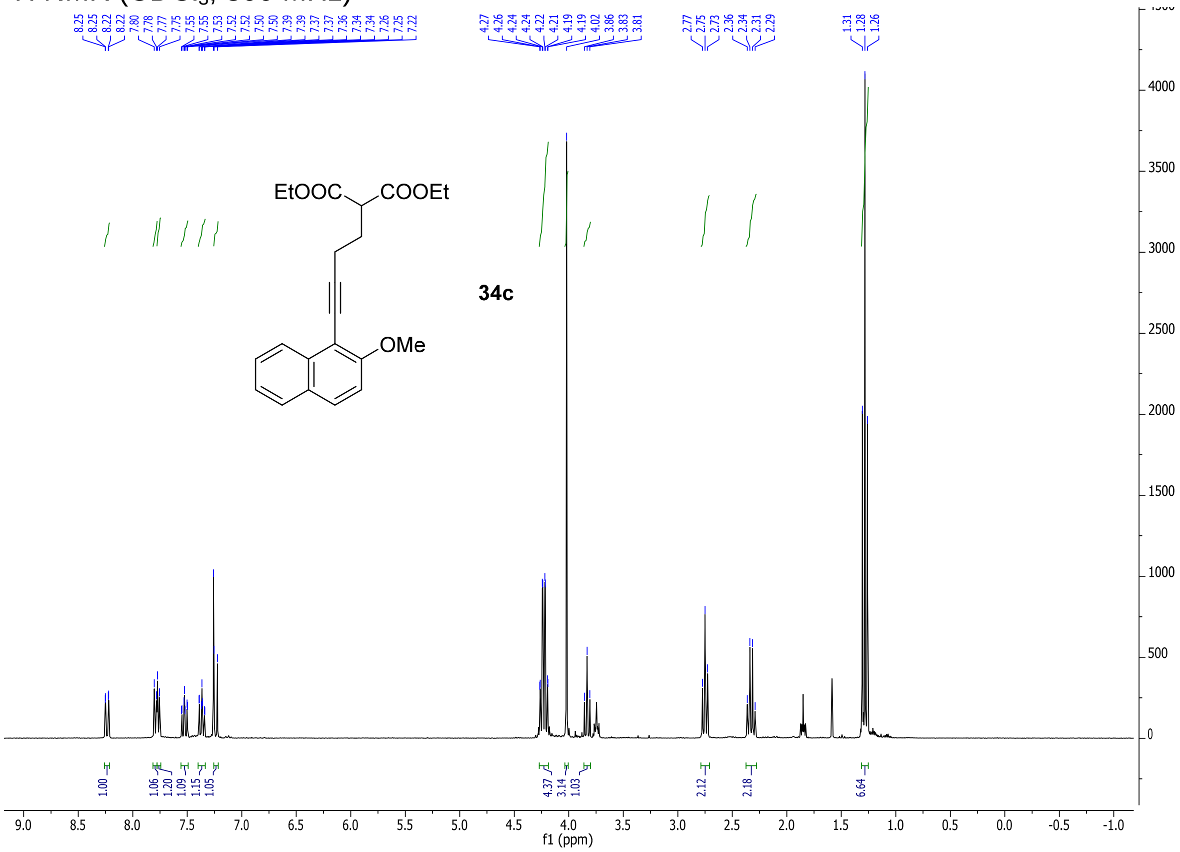


^{13}C NMR ($CDCl_3$, 75 MHz)

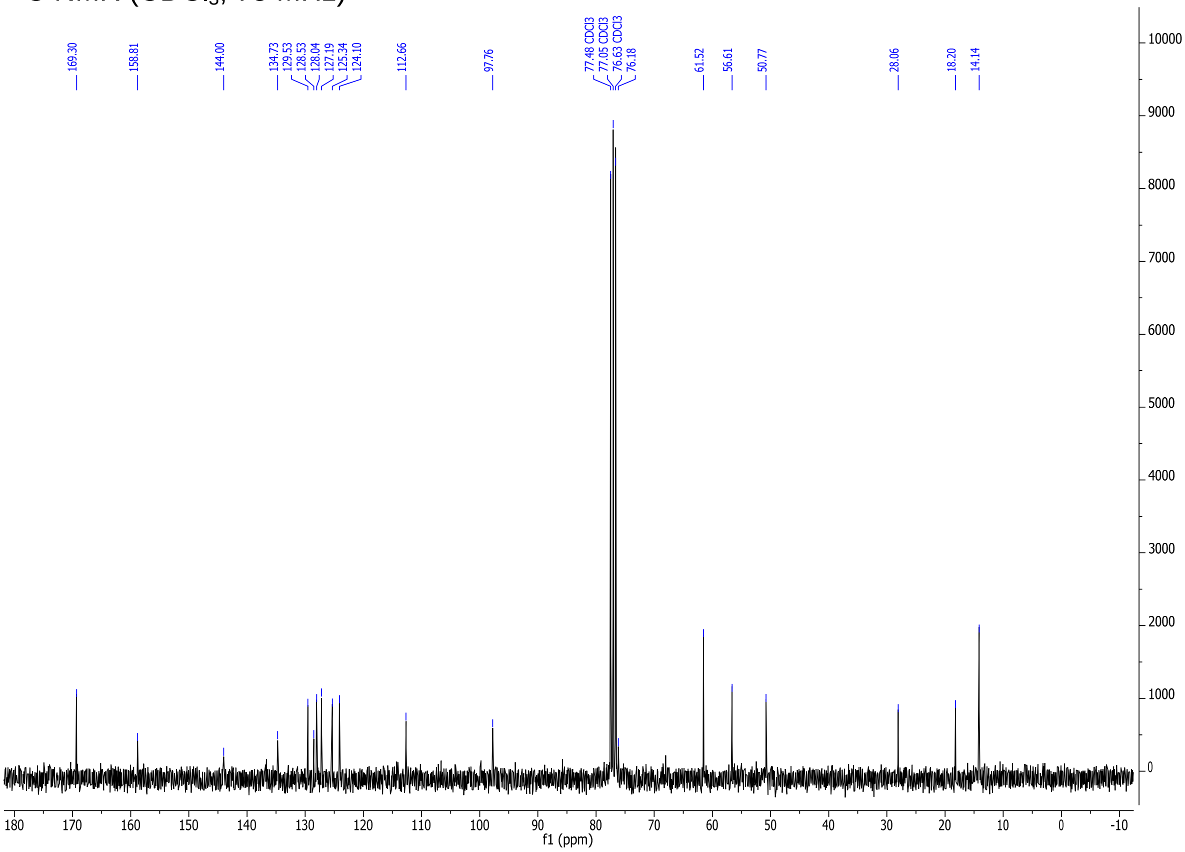


Compound 34c:

^{1}H NMR ($CDCl_3$, 300 MHz)

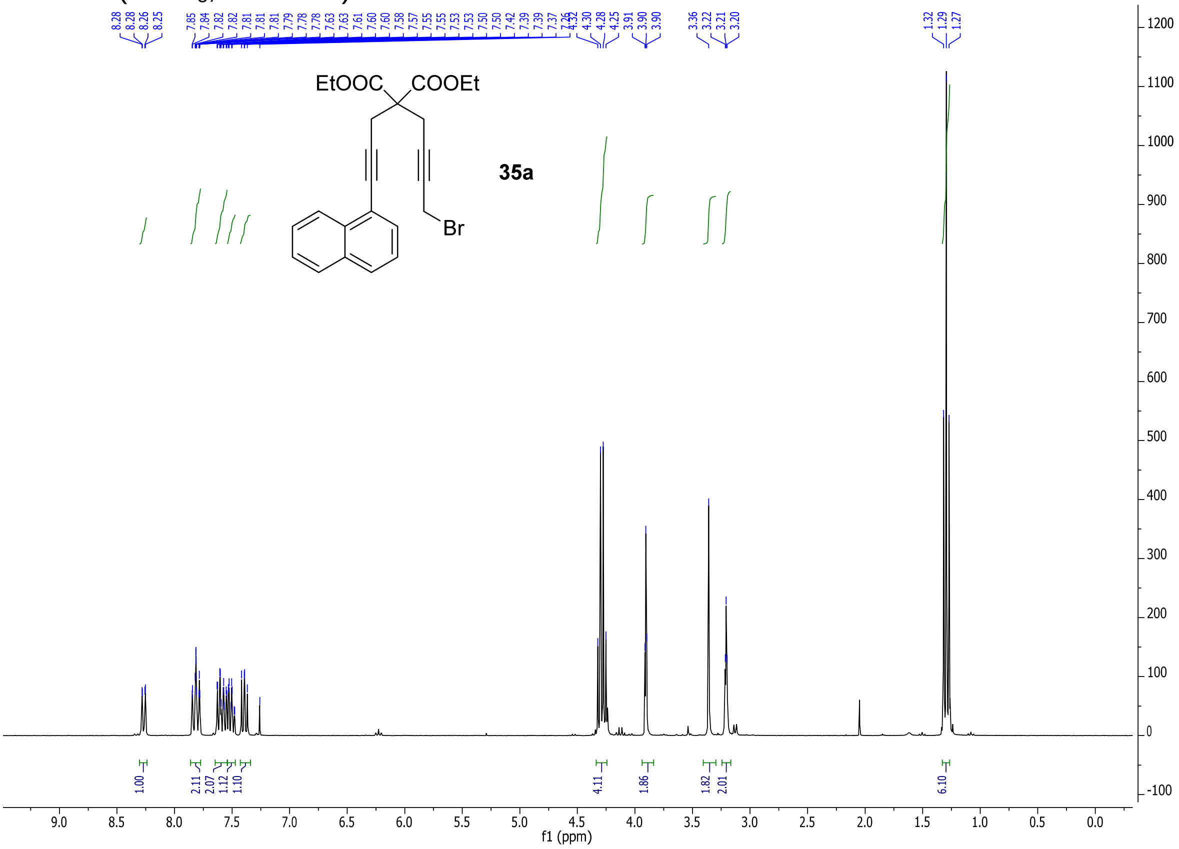


^{13}C NMR ($CDCl_3$, 75 MHz)

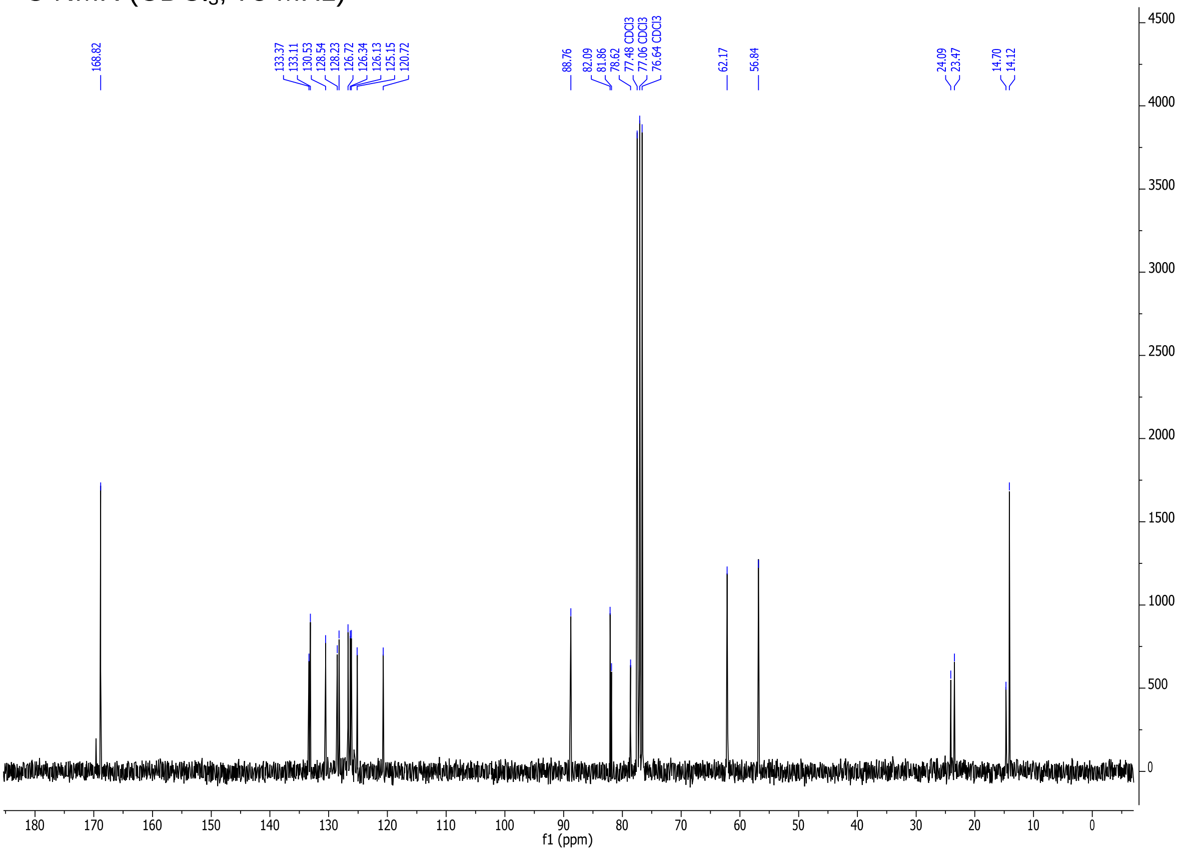


Compound 35a:

^{1}H NMR ($CDCl_3$, 300 MHz)

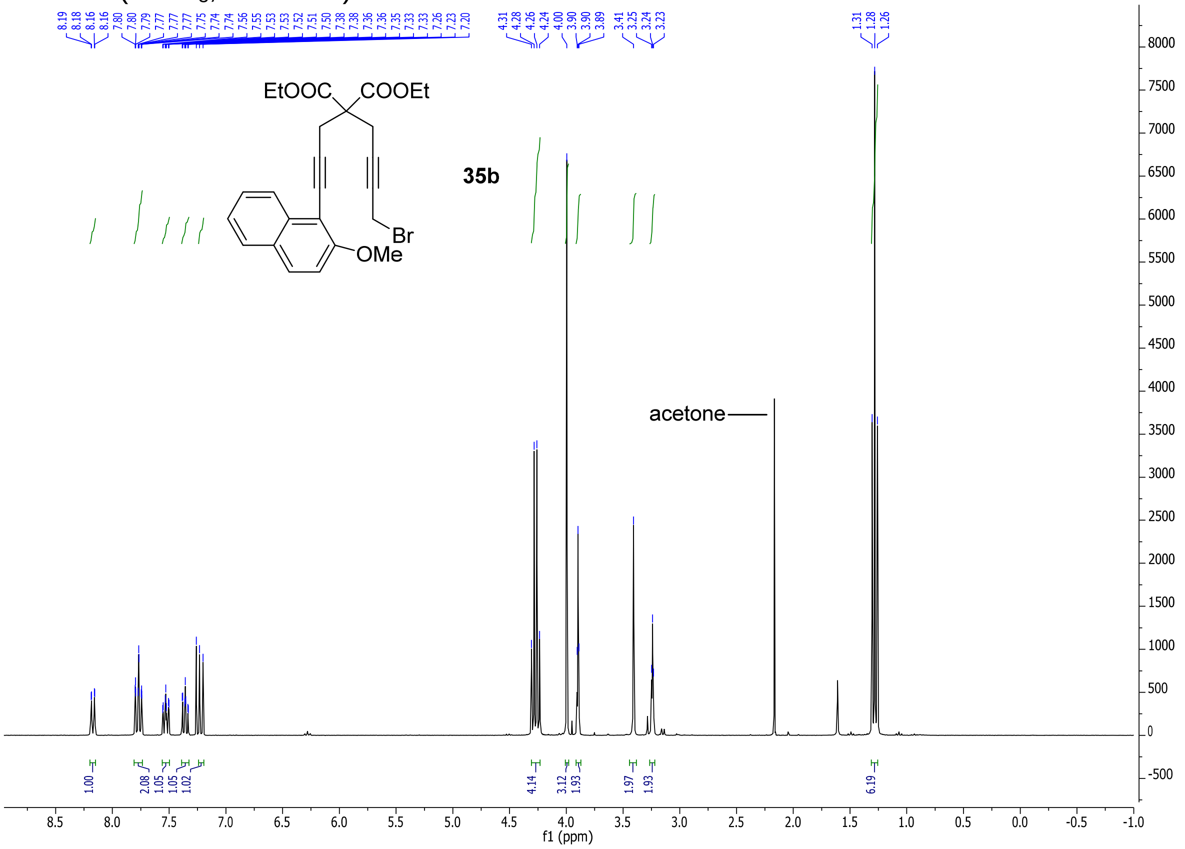


^{13}C NMR ($CDCl_3$, 75 MHz)

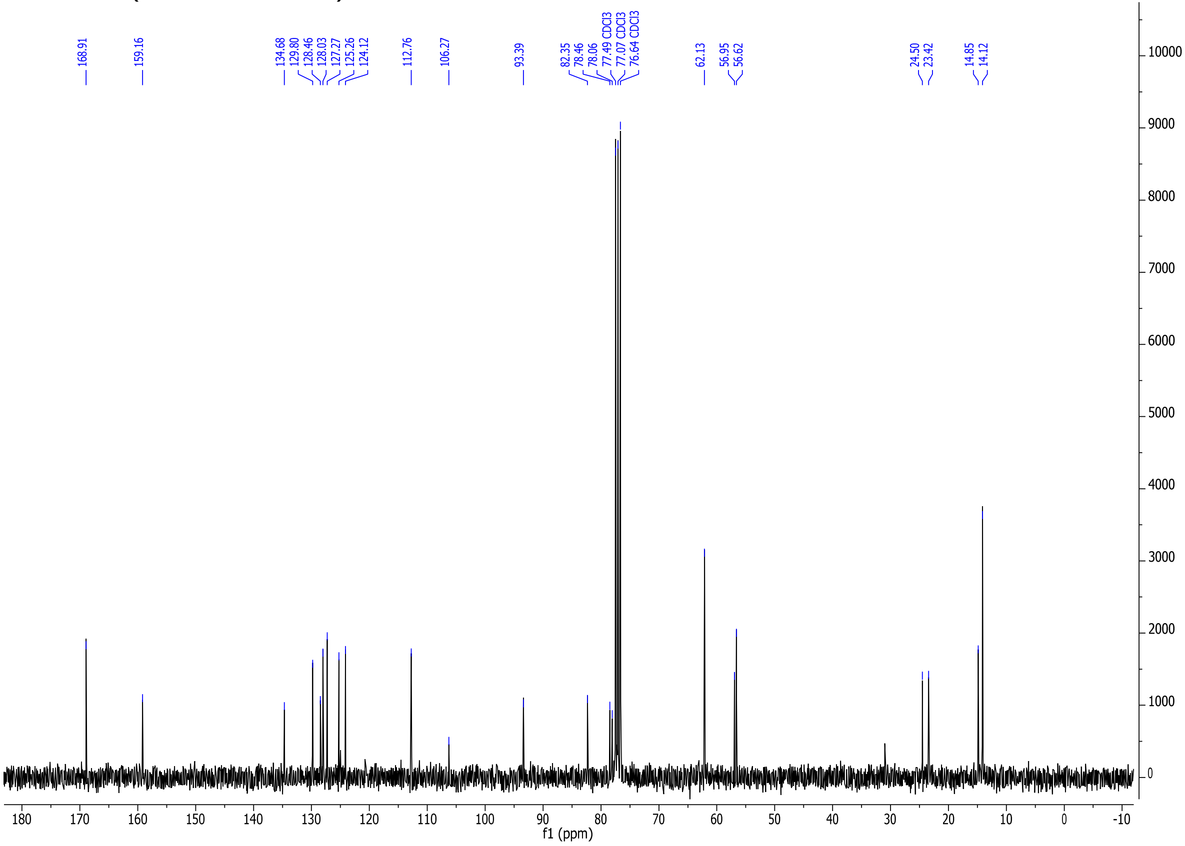


Compound 35b:

^{1}H NMR ($CDCl_3$, 300 MHz)

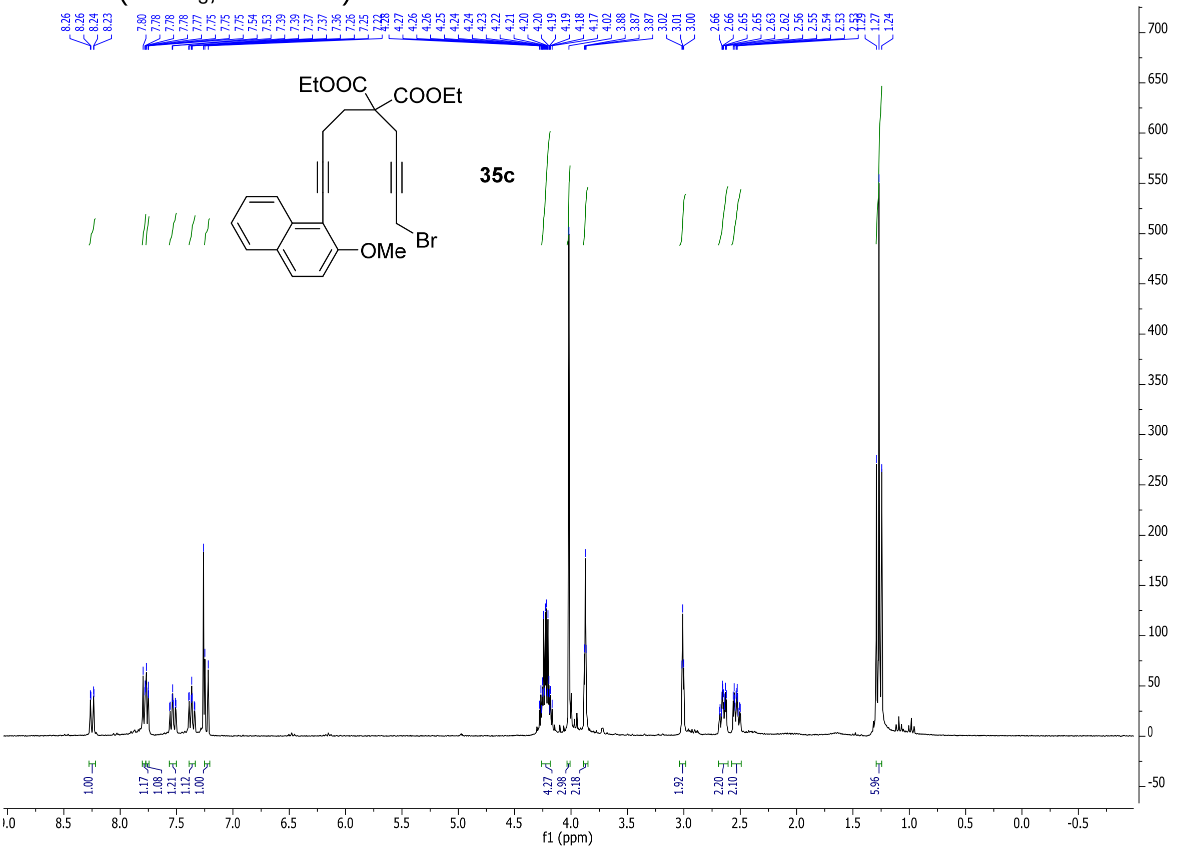


^{13}C NMR ($CDCl_3$, 75 MHz)

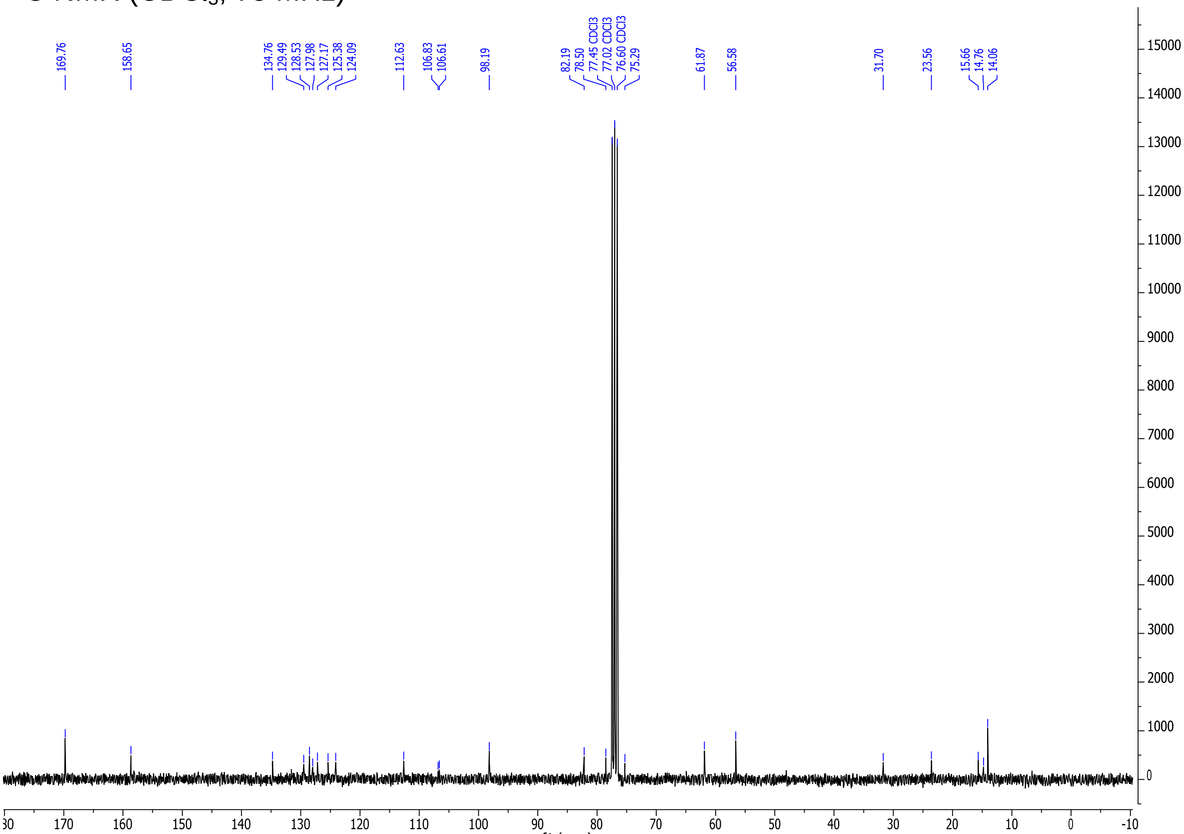


Compound 35c:

^{1}H NMR ($CDCl_3$, 300 MHz)

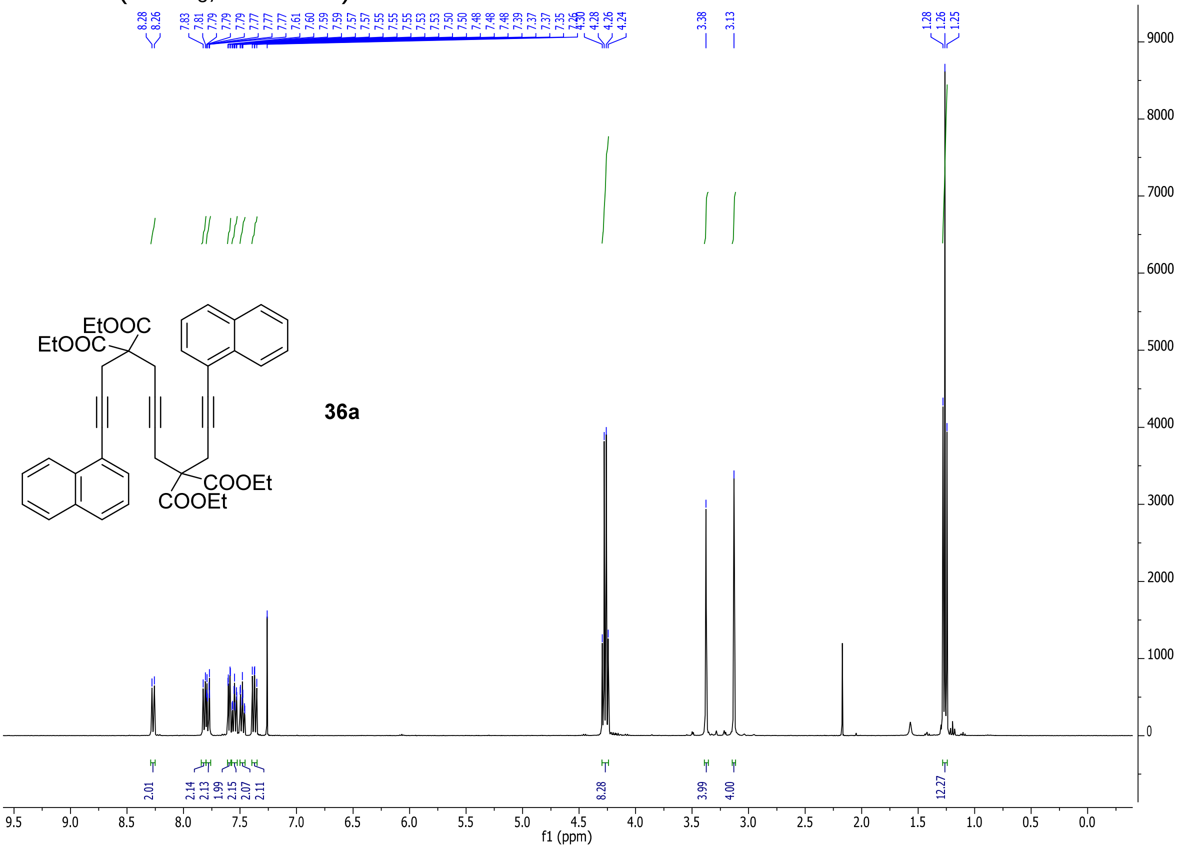


^{13}C NMR ($CDCl_3$, 75 MHz)



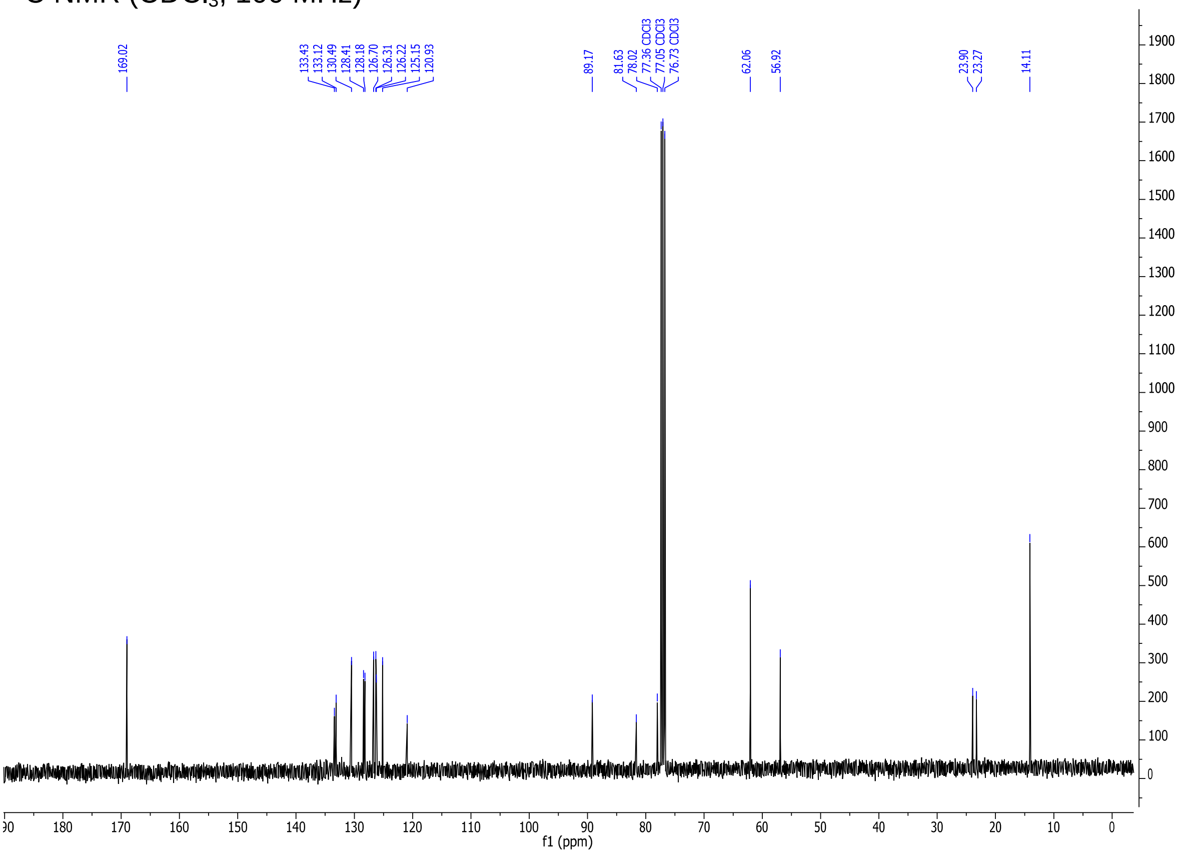
Compound 36a:

^1H NMR ($CDCl_3$, 400 MHz)



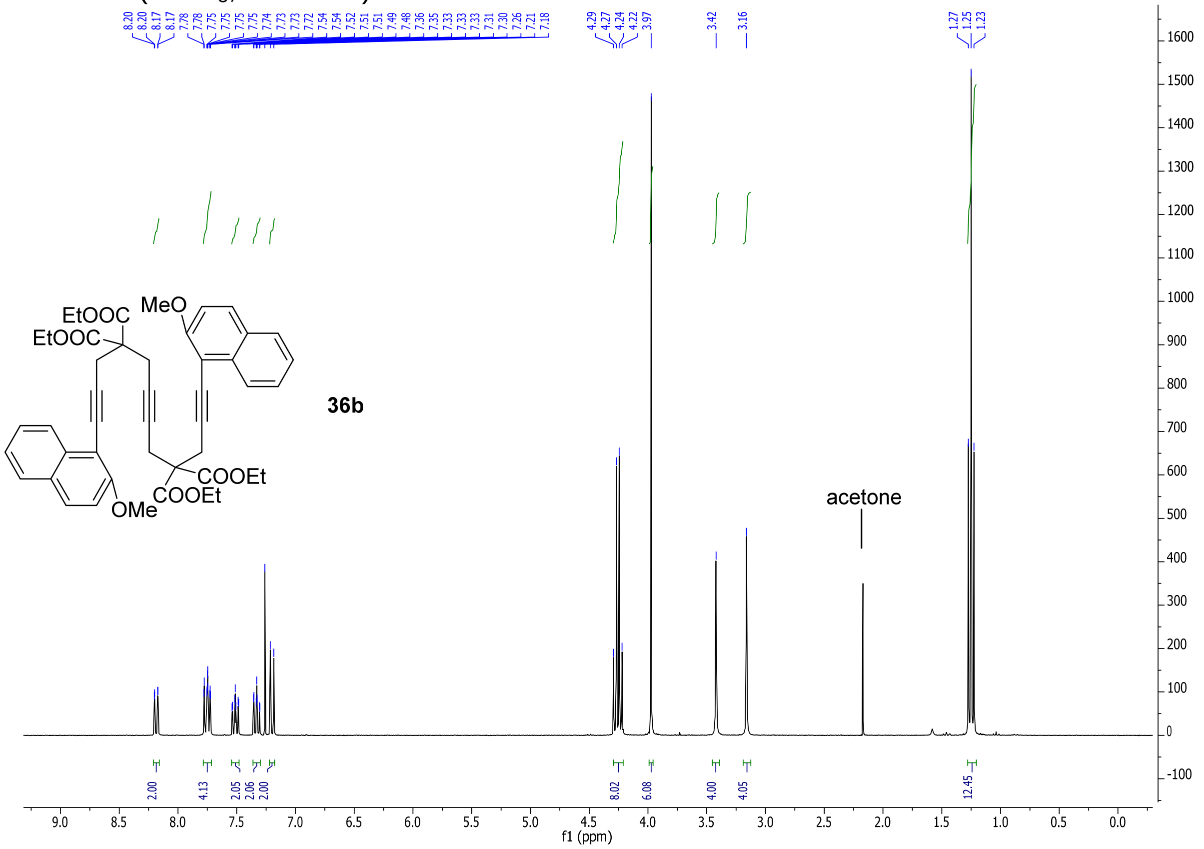
36a

^{13}C NMR ($CDCl_3$, 100 MHz)

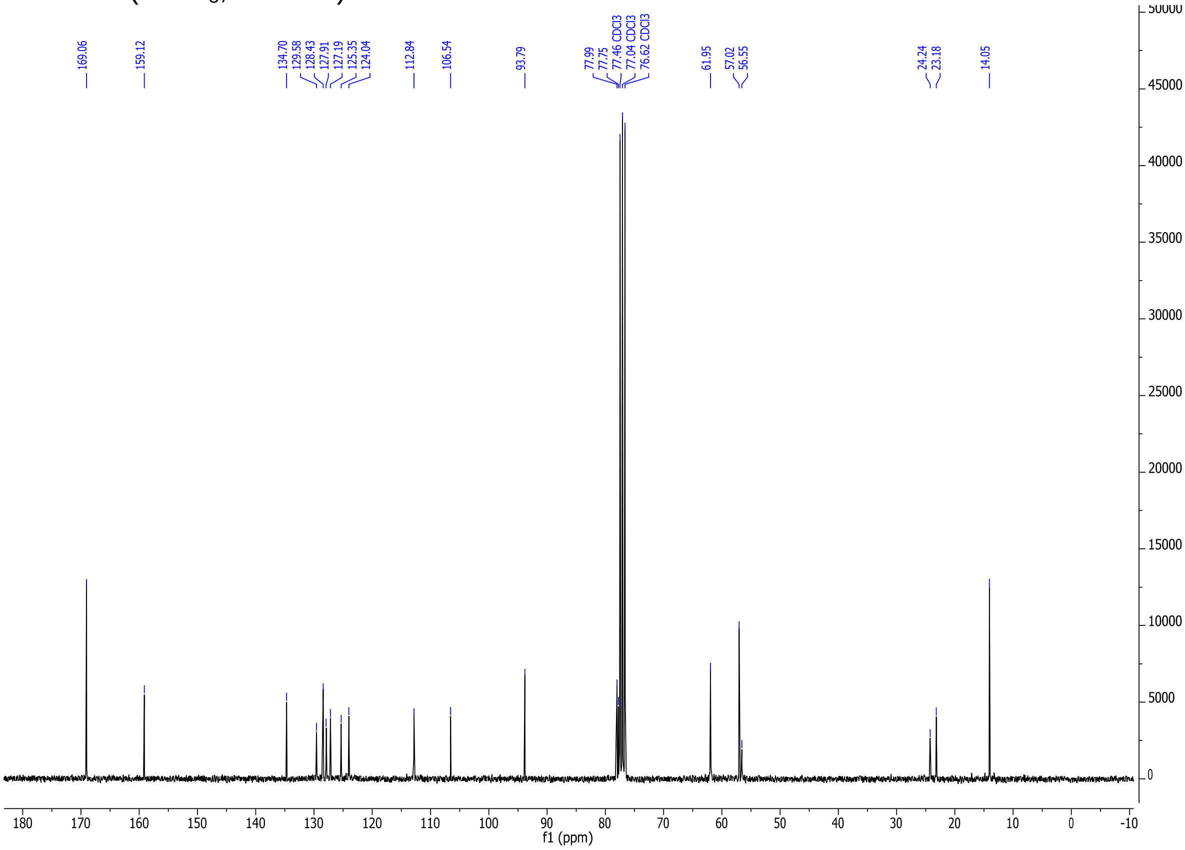


Compound 36b:

^{1}H NMR ($CDCl_3$, 300 MHz)

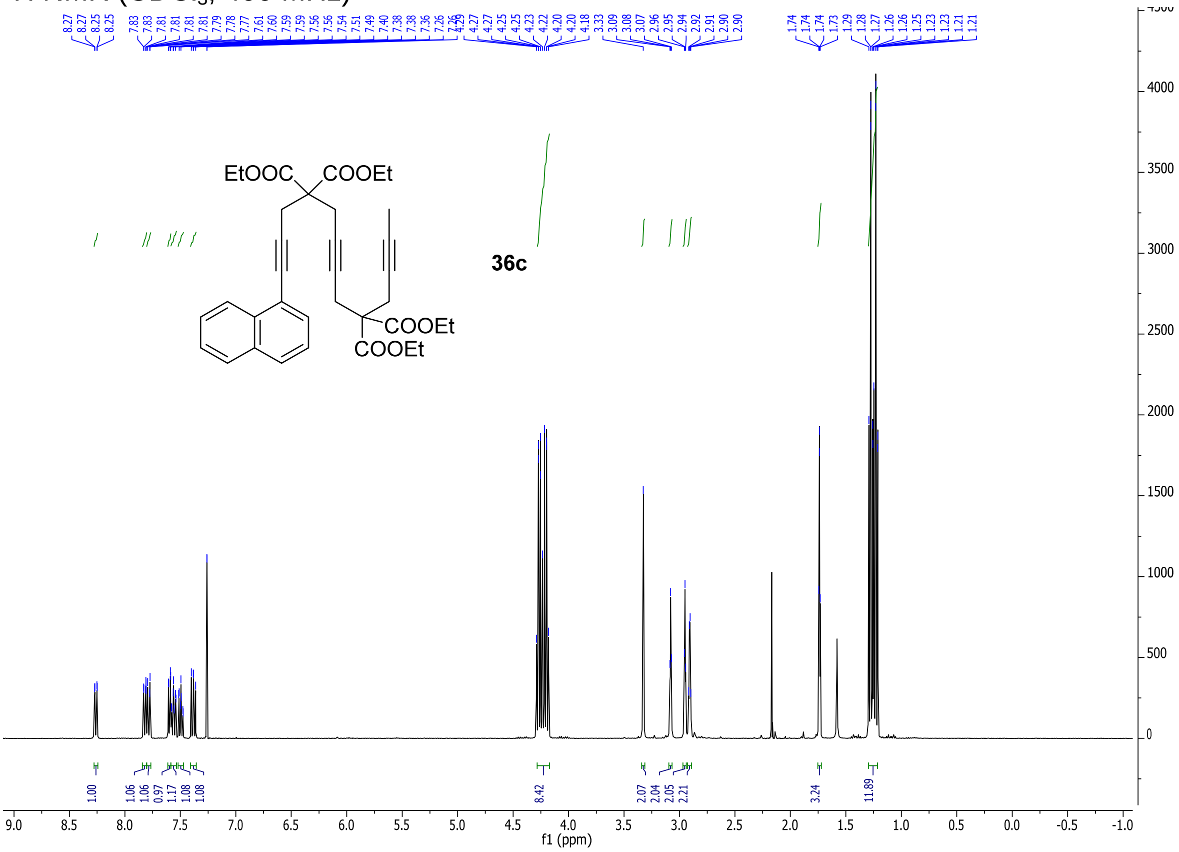


^{13}C NMR ($CDCl_3$, 75 MHz)



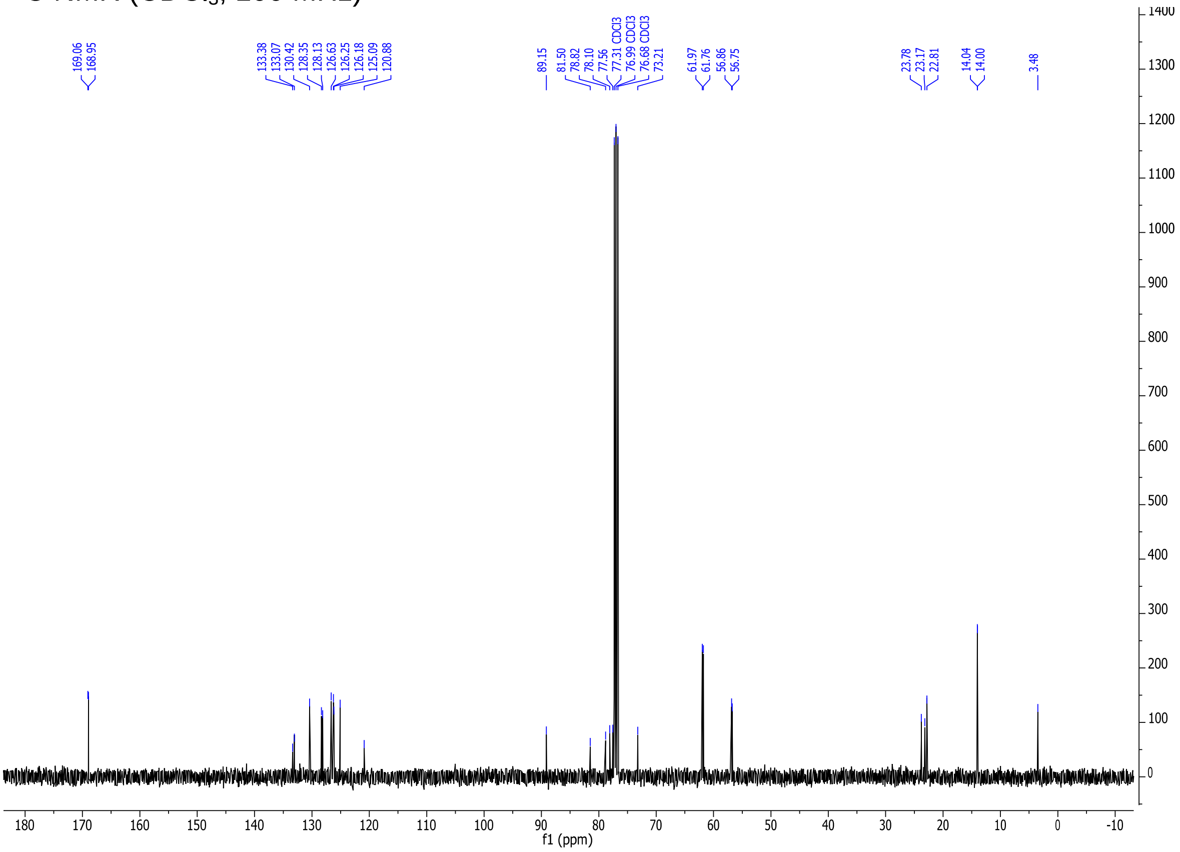
Compound 36c:

^{1}H NMR ($CDCl_3$, 400 MHz)



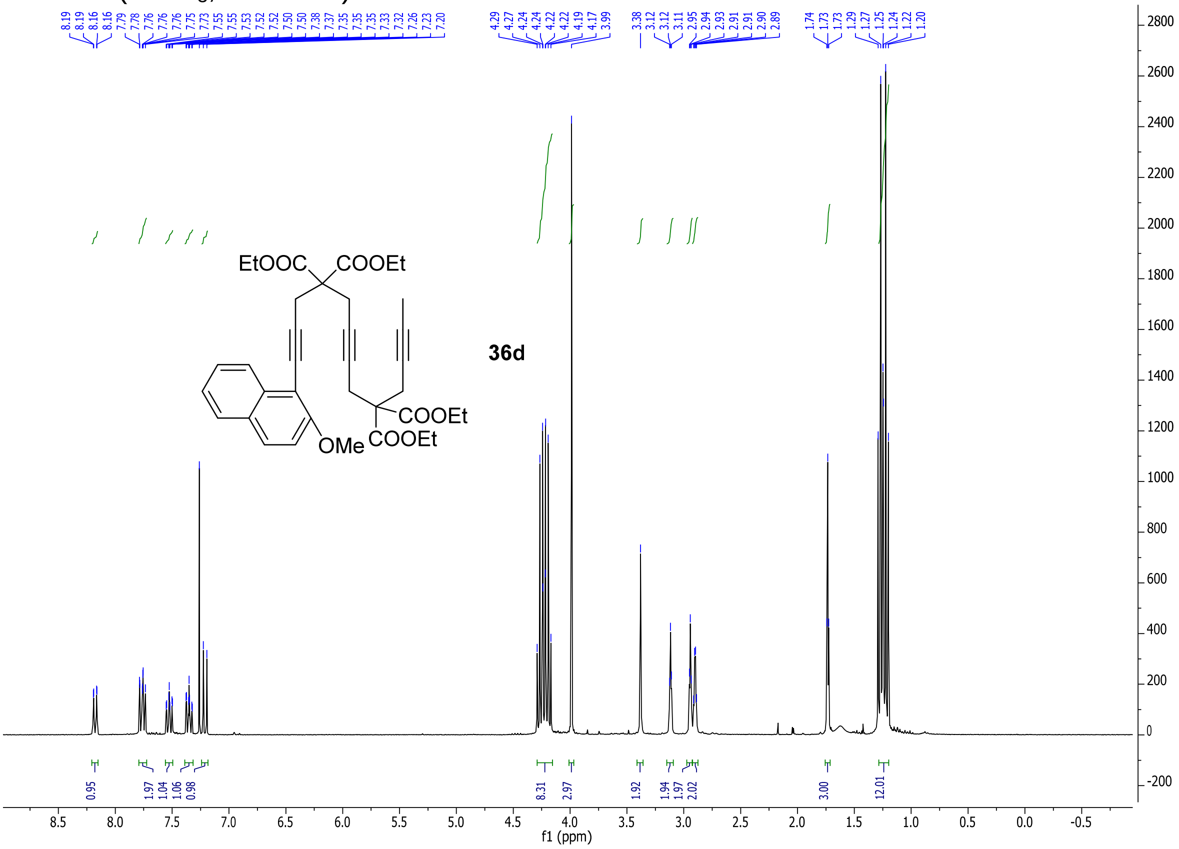
36c

^{13}C NMR ($CDCl_3$, 100 MHz)

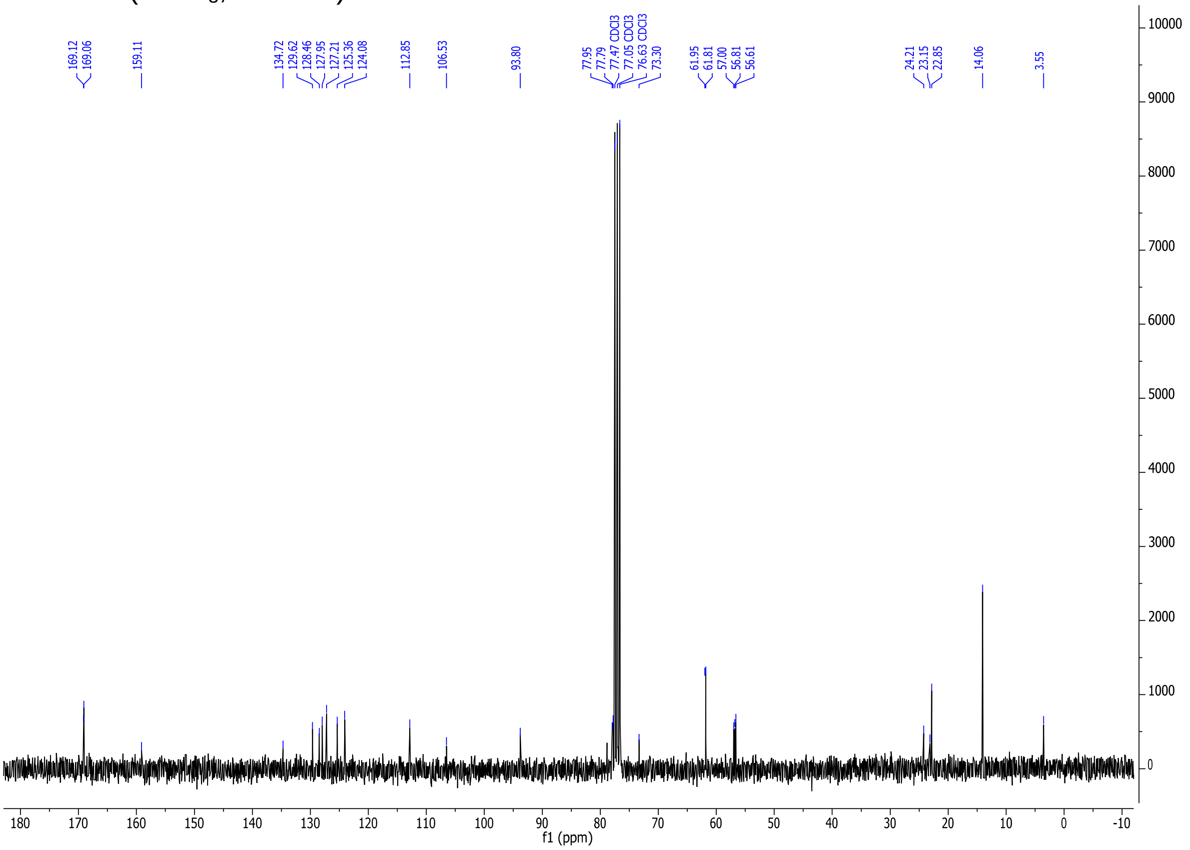


Compound 36d:

^{1}H NMR ($CDCl_3$, 300 MHz)

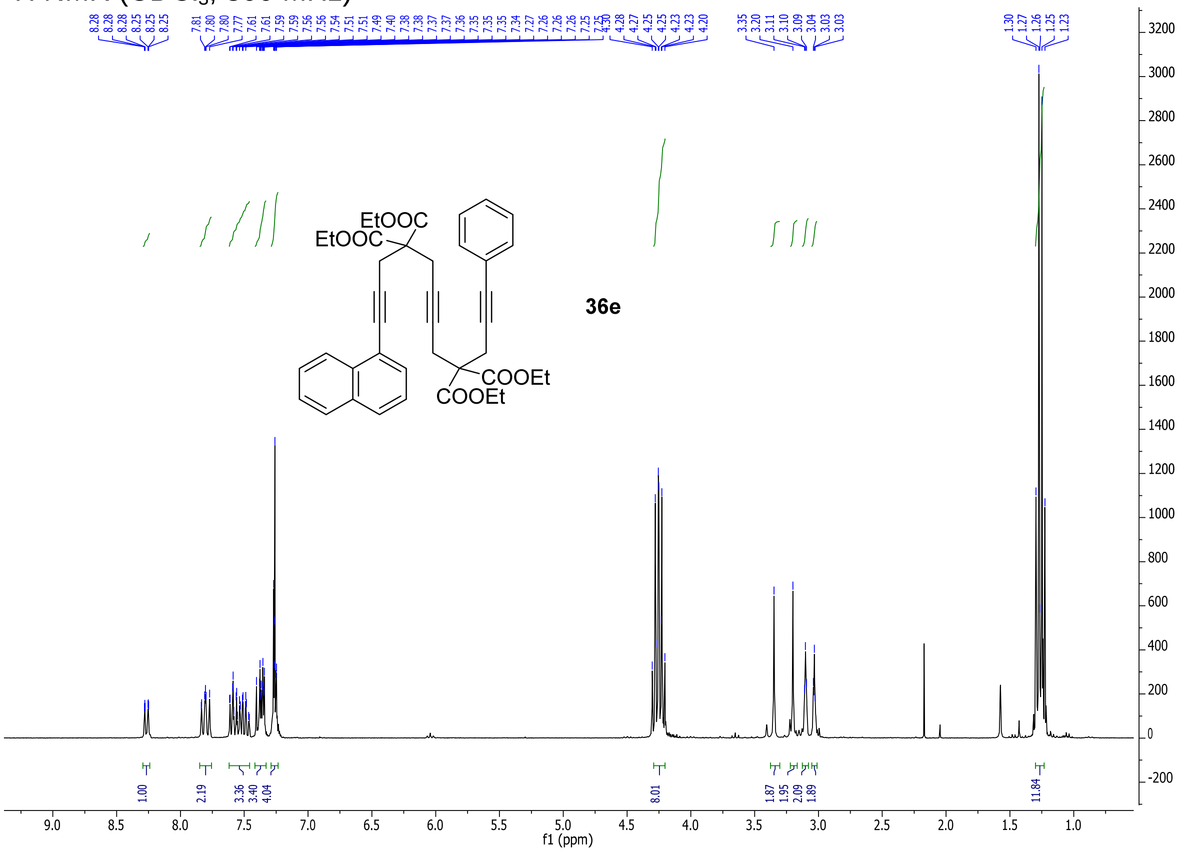


^{13}C NMR ($CDCl_3$, 75 MHz)

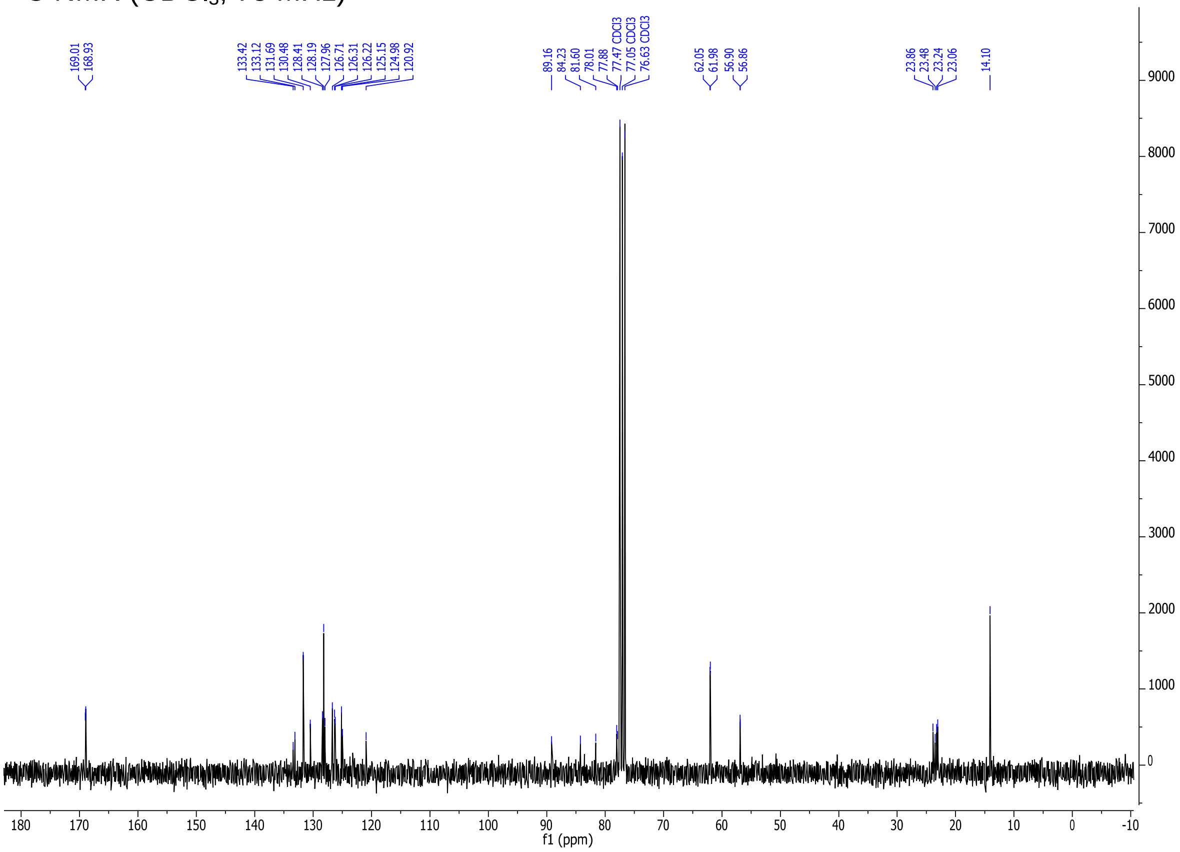


Compound 36e:

^{1}H NMR ($CDCl_3$, 300 MHz)

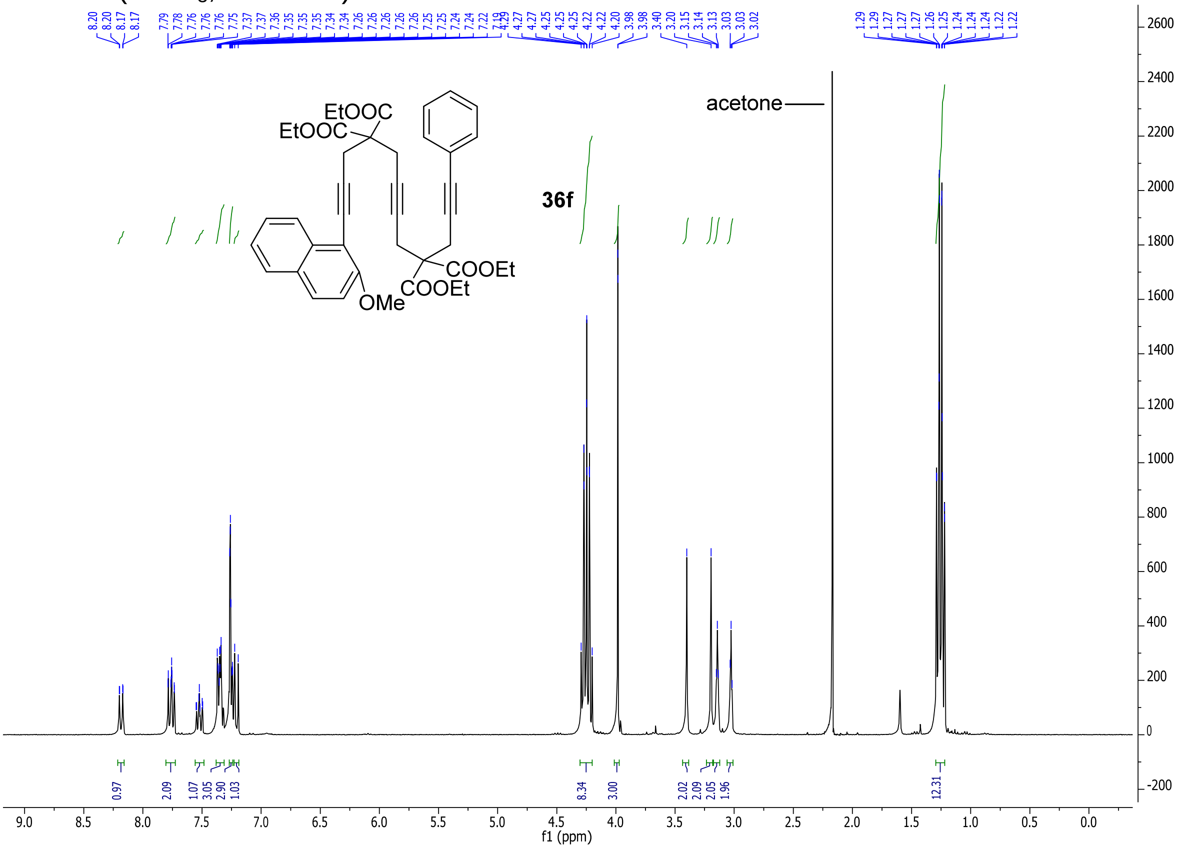


^{13}C NMR ($CDCl_3$, 75 MHz)

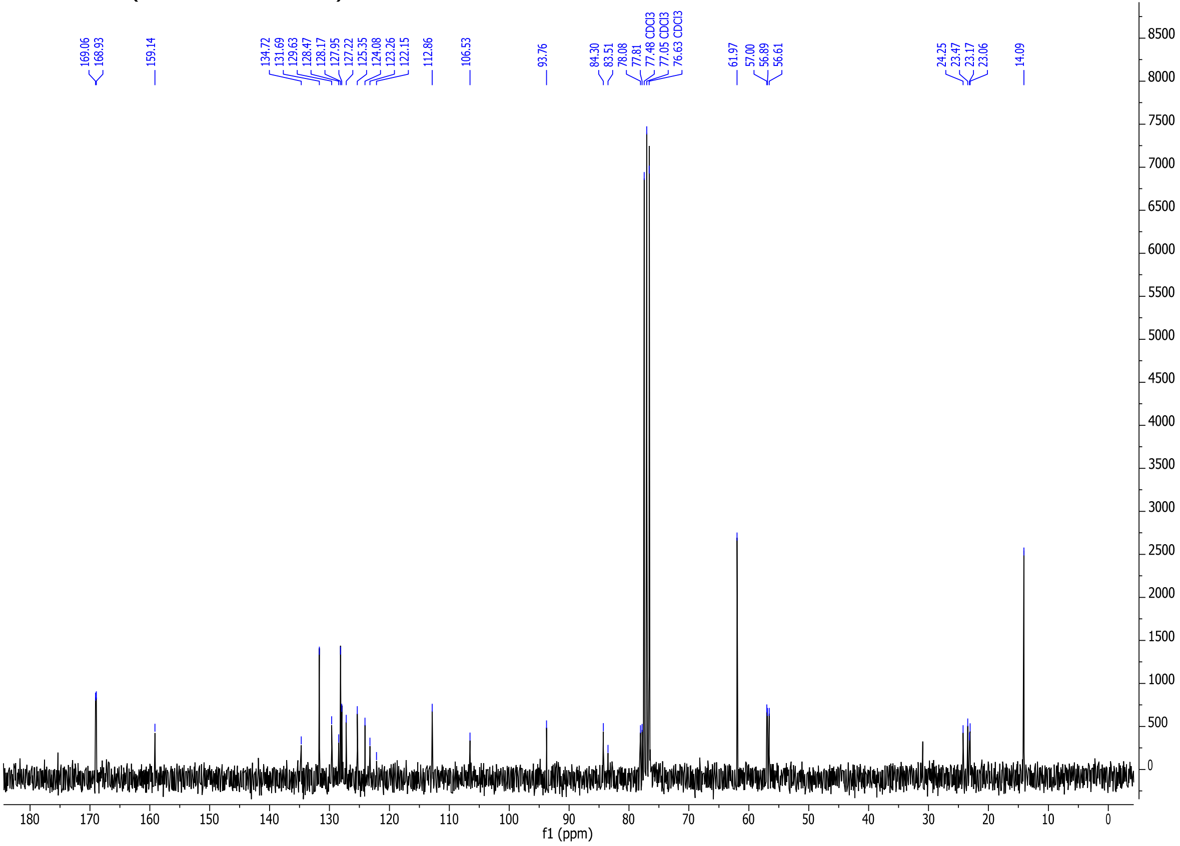


Compound 36f:

^{1}H NMR ($CDCl_3$, 300 MHz)

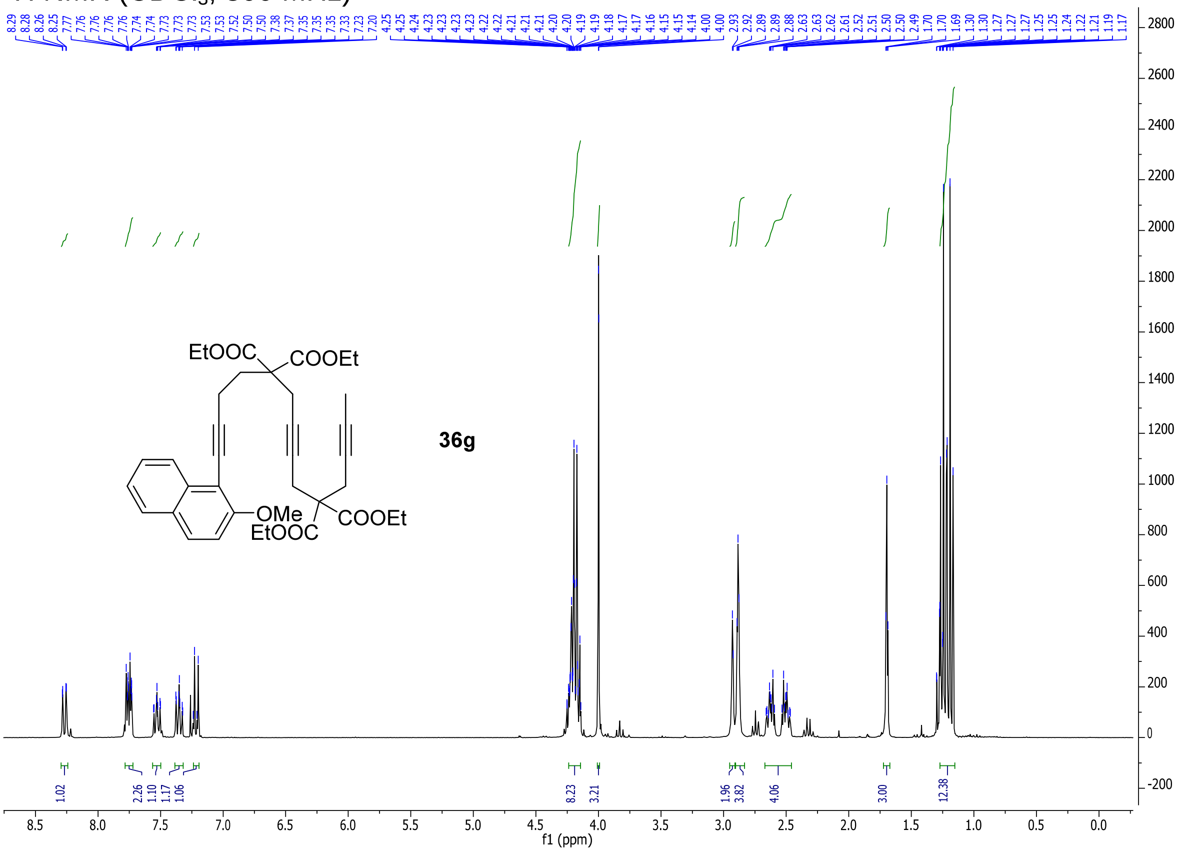


^{13}C NMR ($CDCl_3$, 75 MHz)

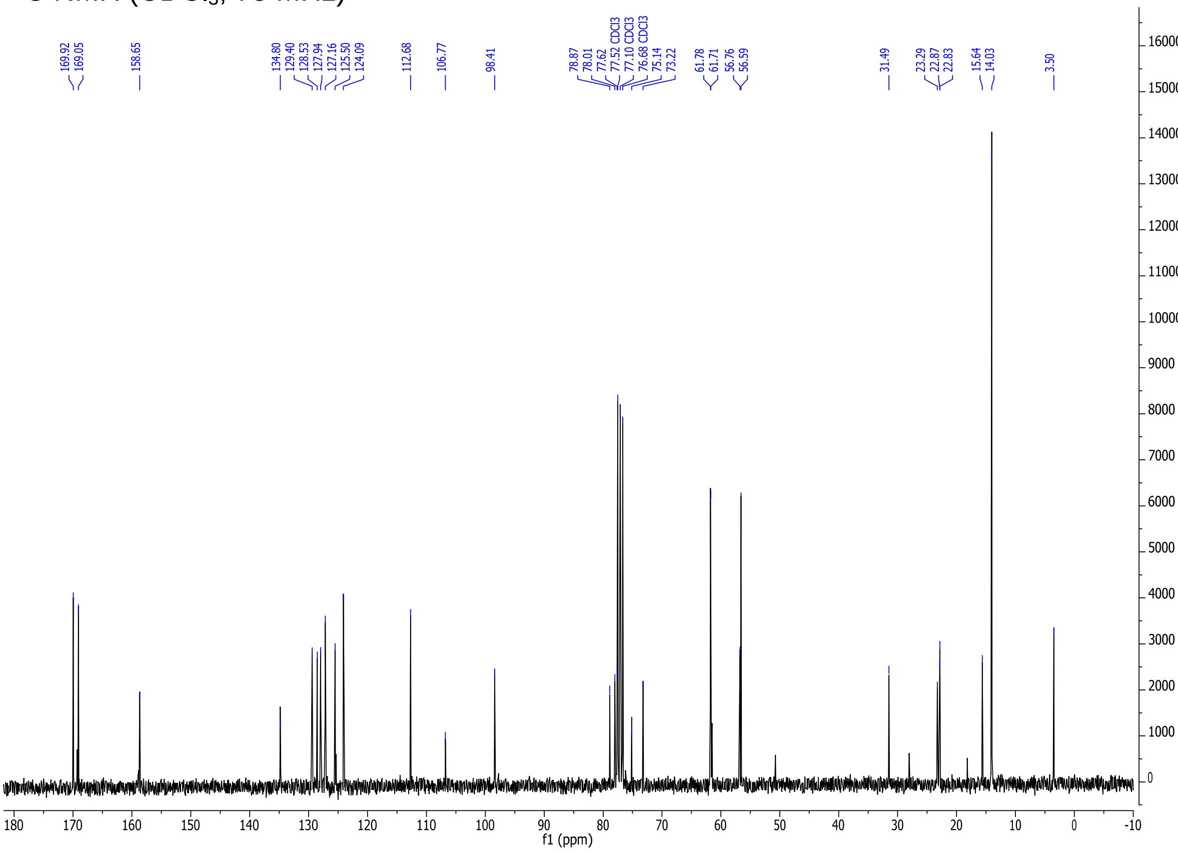


Compound 36g:

^{1}H NMR ($CDCl_3$, 300 MHz)

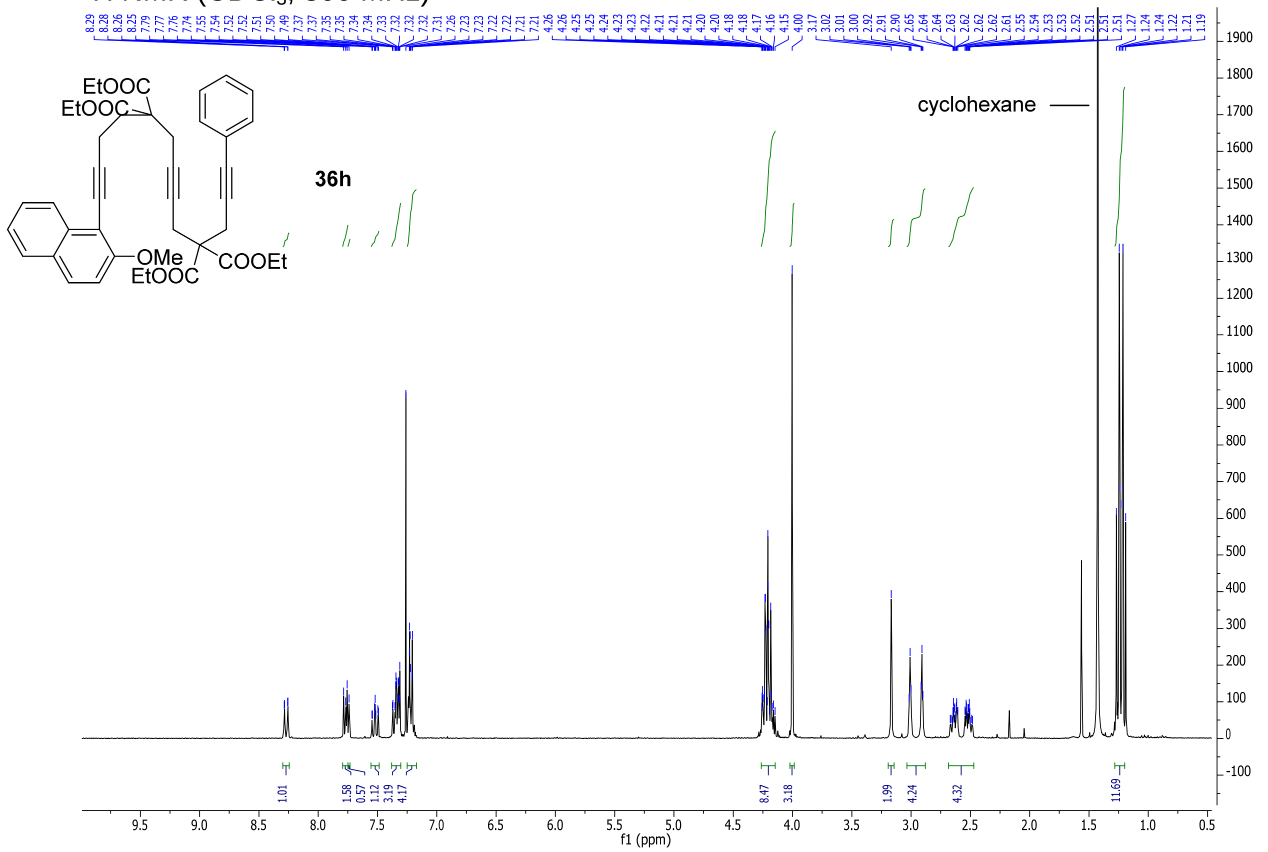


^{13}C NMR ($CDCl_3$, 75 MHz)

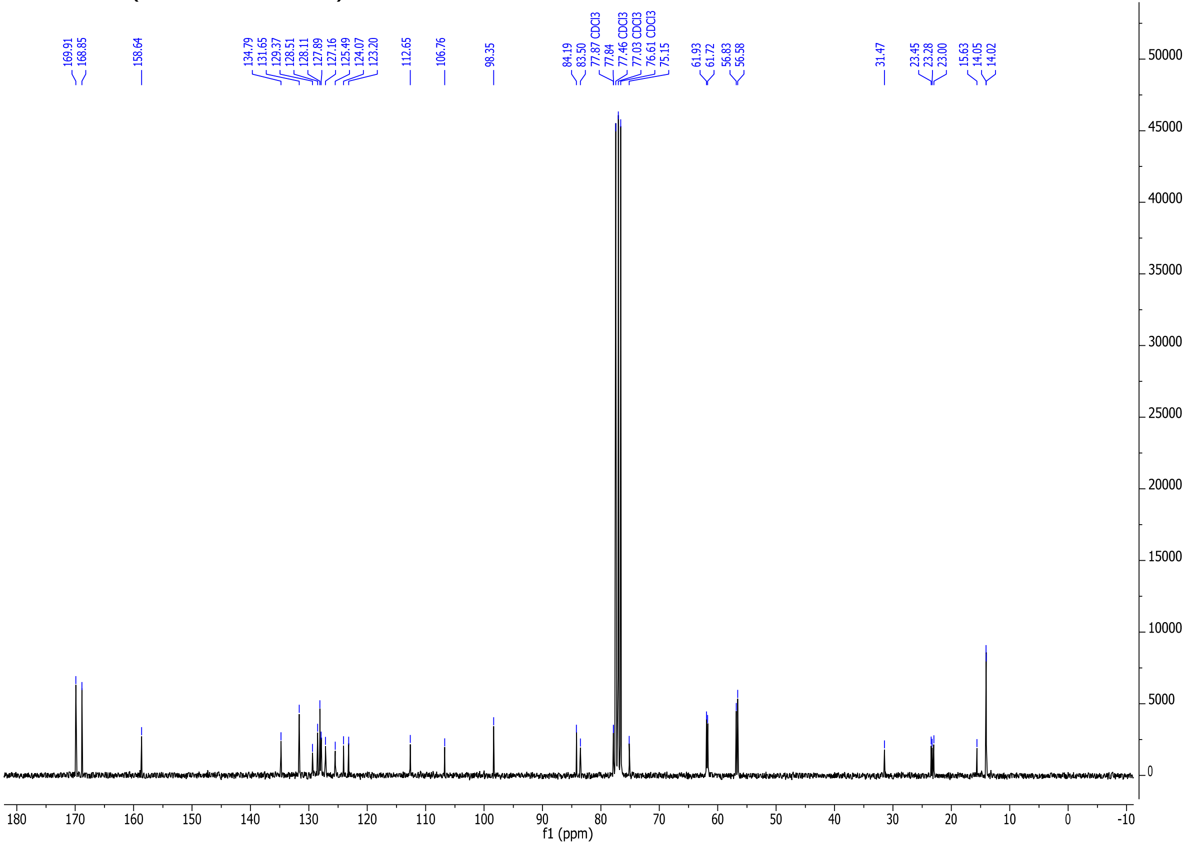


Compound 36h:

^1H NMR ($CDCl_3$, 300 MHz)

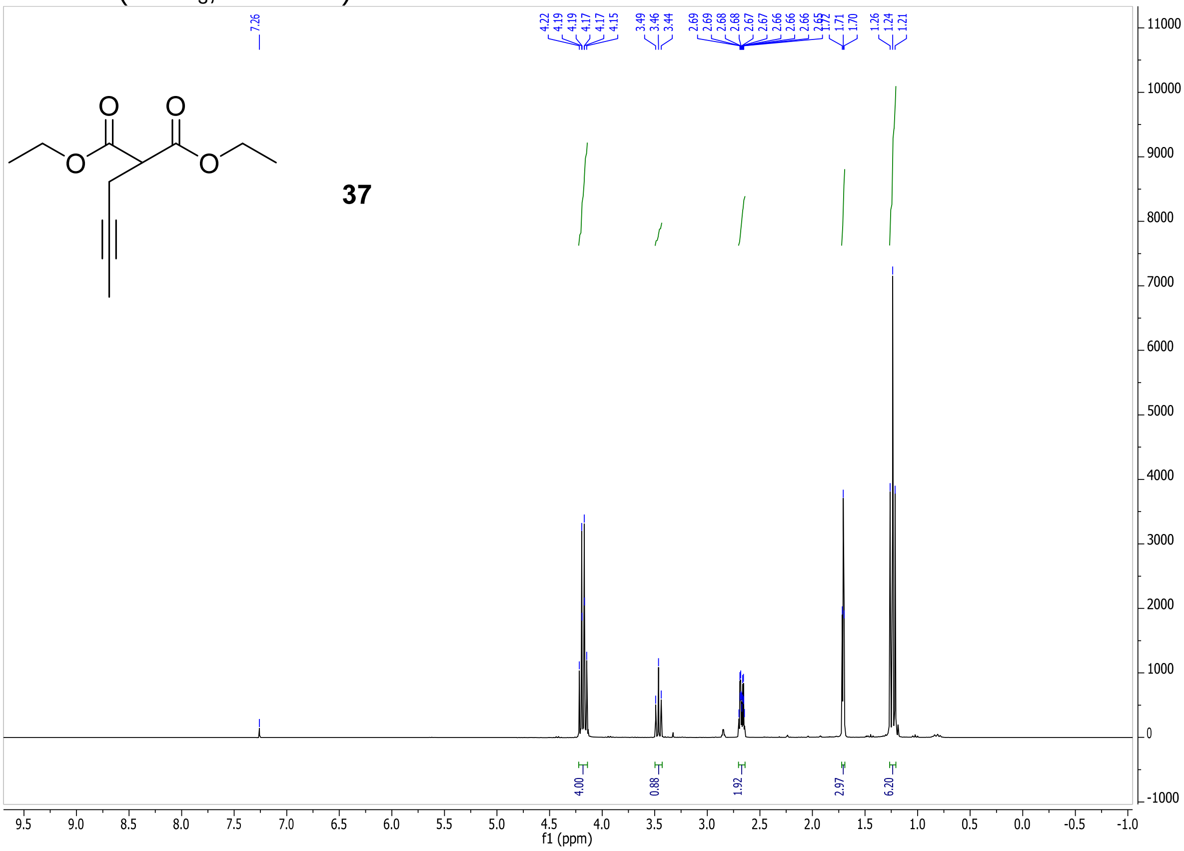


^{13}C NMR ($CDCl_3$, 75 MHz)



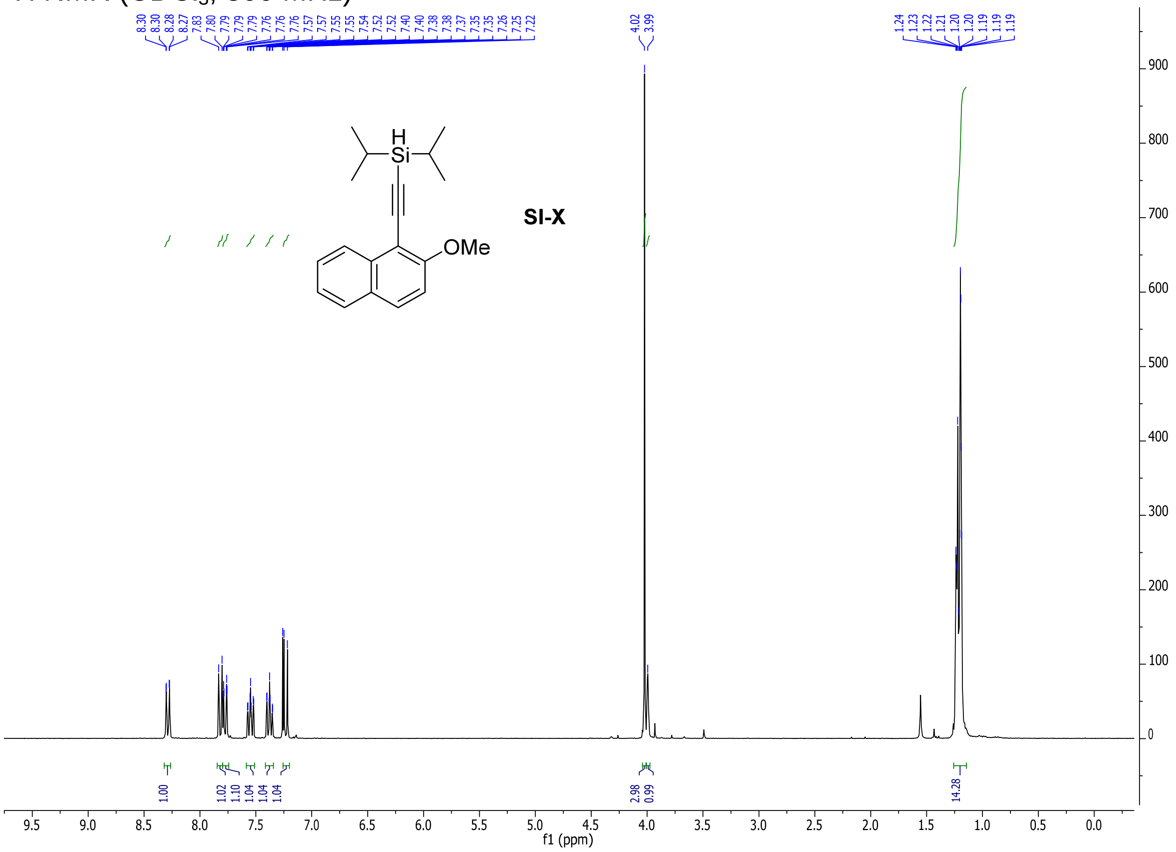
Compound 37:

^{1}H NMR ($CDCl_3$, 300 MHz)

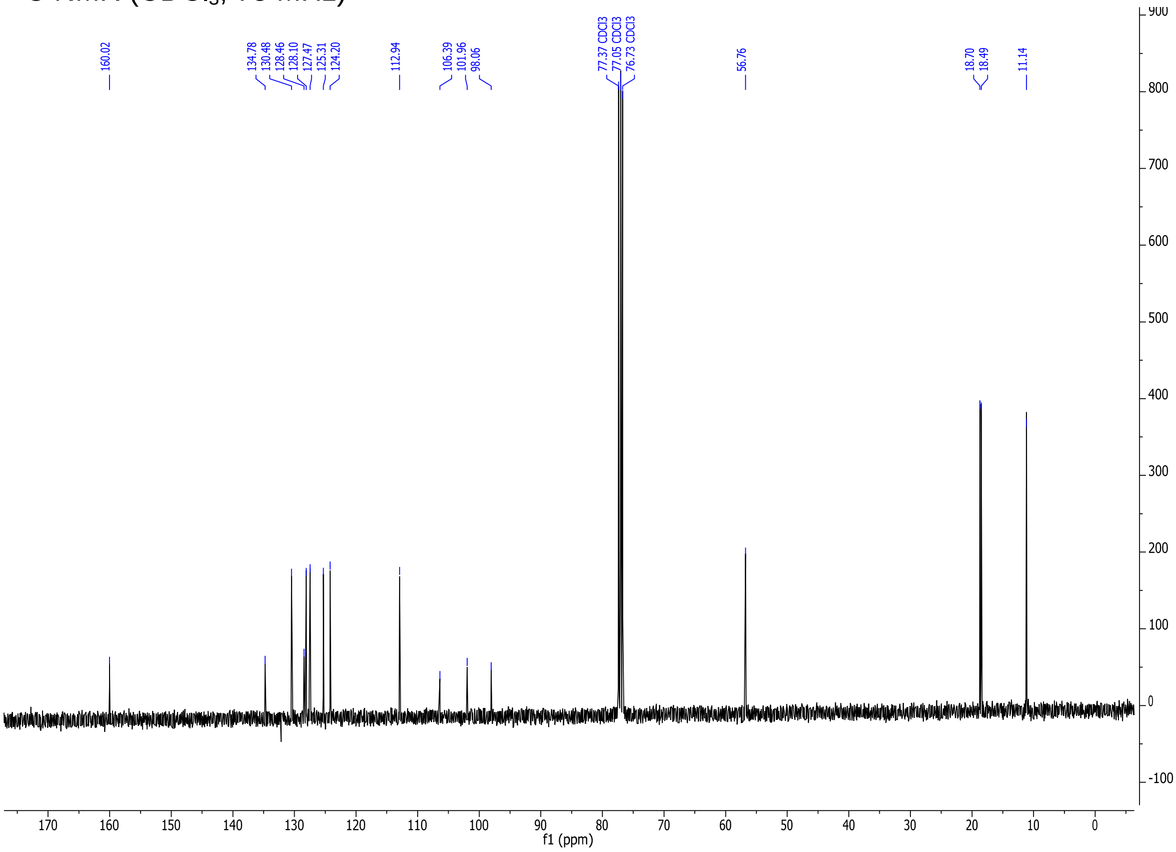


Compound SI-X:

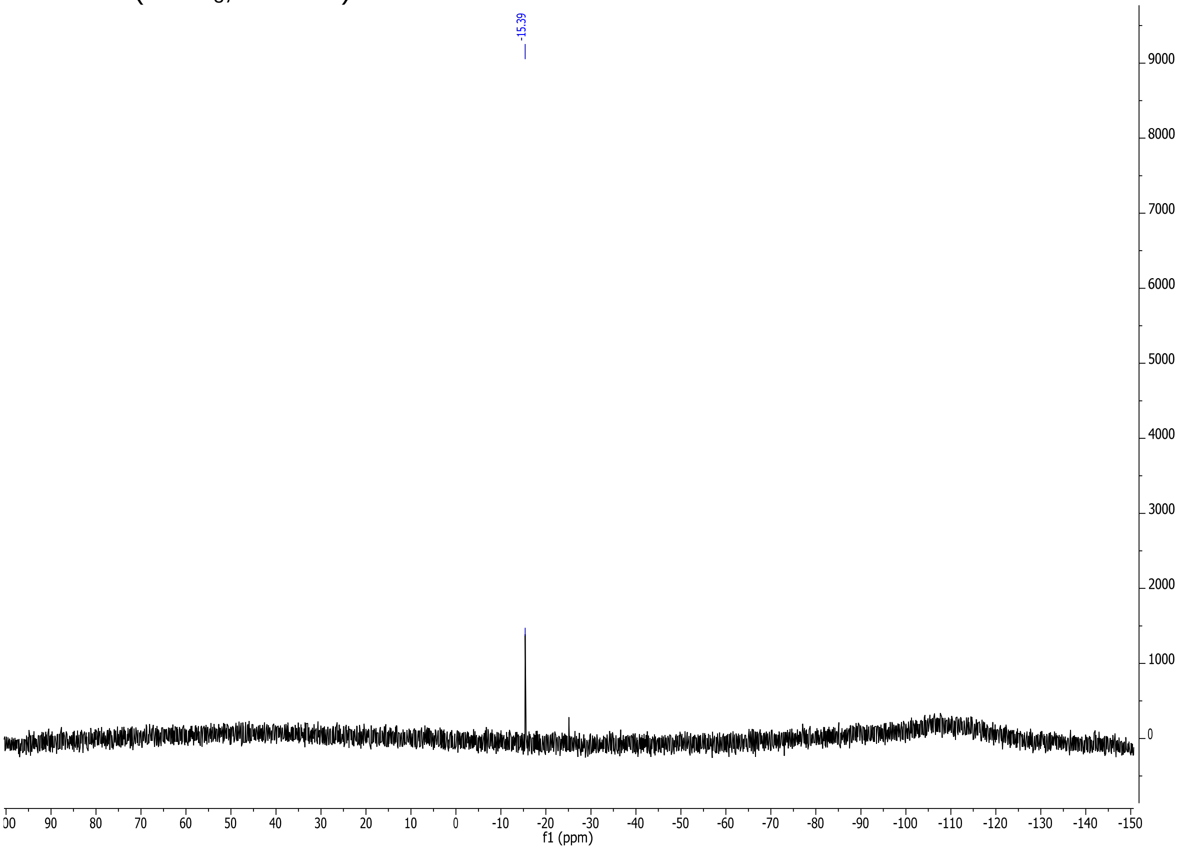
^{1}H NMR ($CDCl_3$, 300 MHz)



^{13}C NMR ($CDCl_3$, 75 MHz)

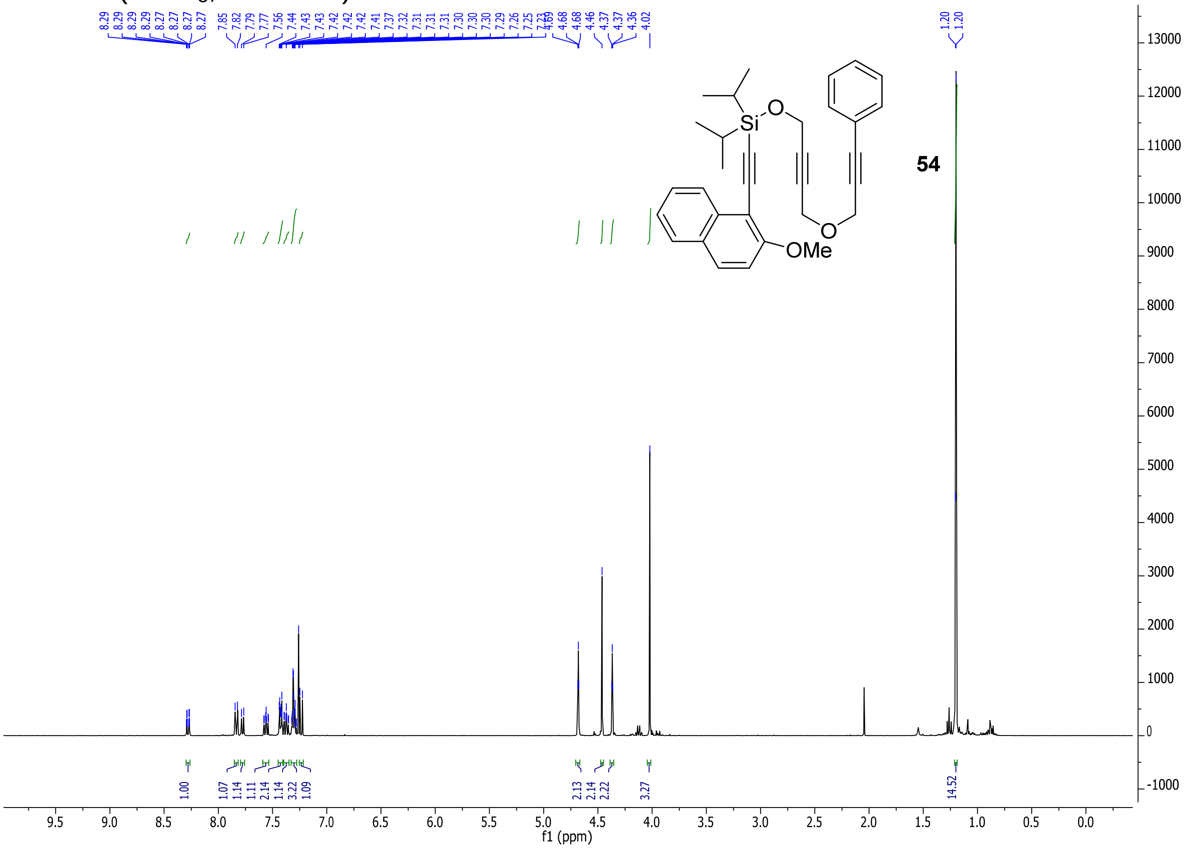


^{29}Si NMR ($CDCl_3$, 79 MHz)

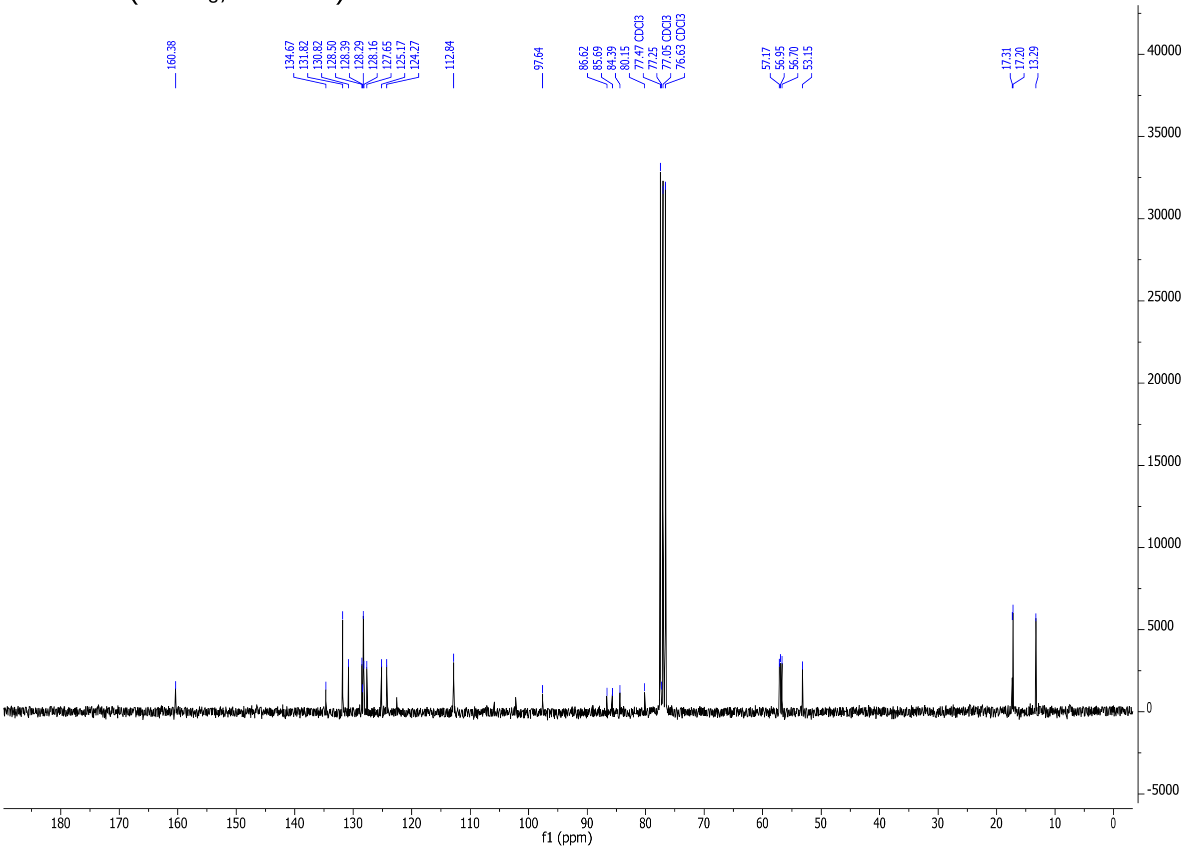


Compound 54:

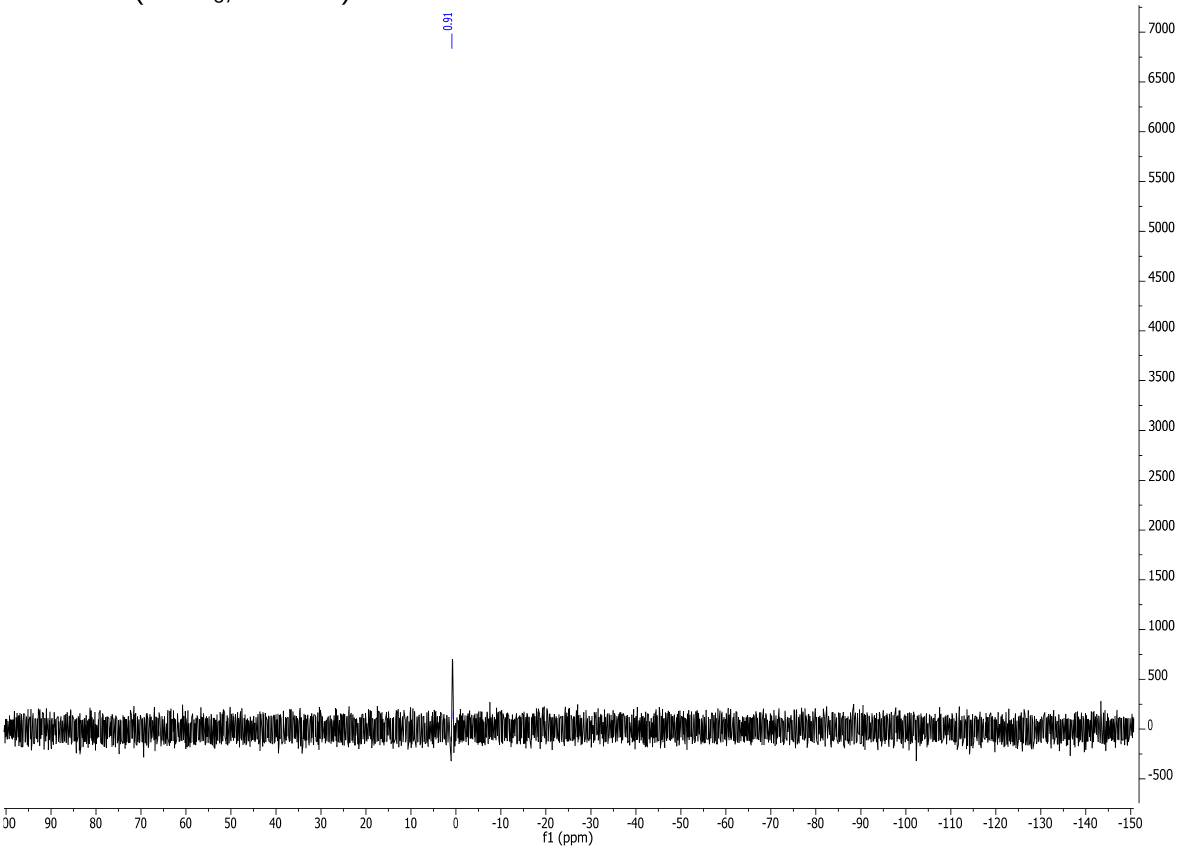
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 75 MHz)

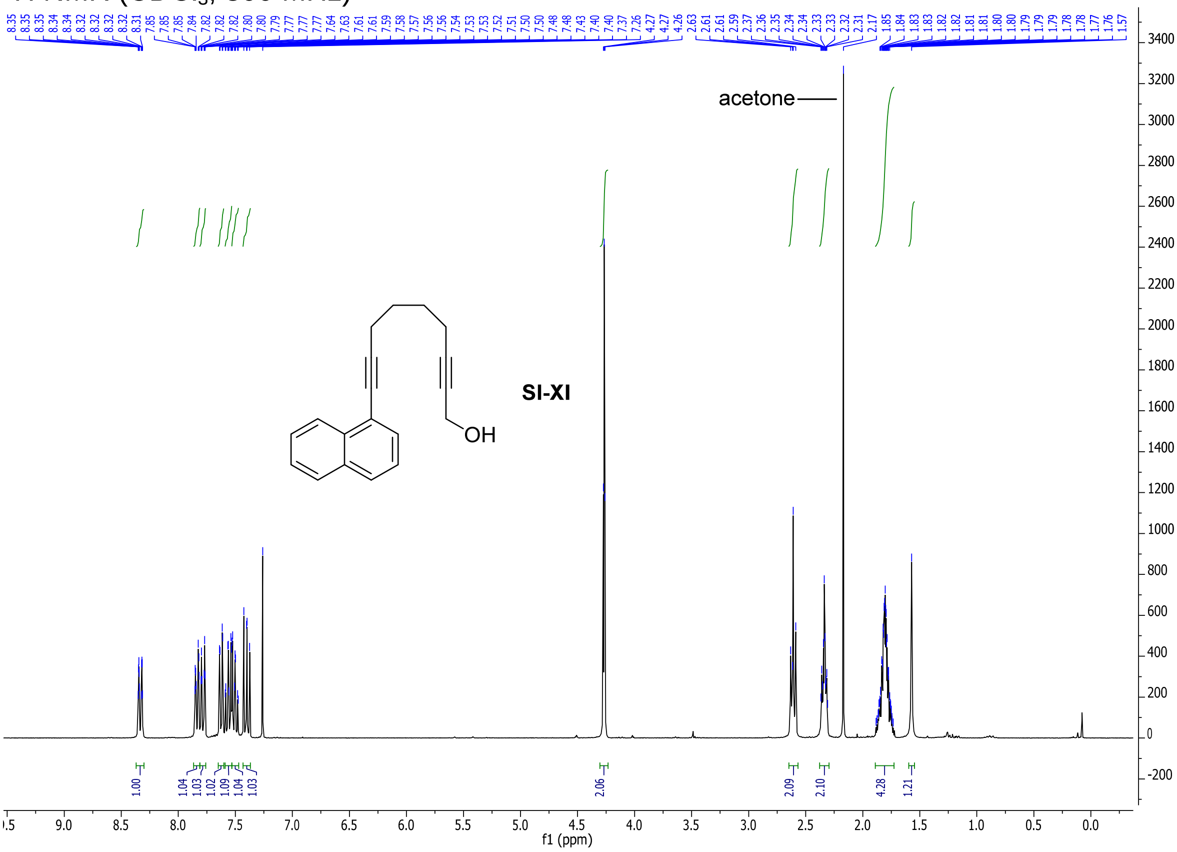


^{29}Si NMR ($CDCl_3$, 79 MHz)

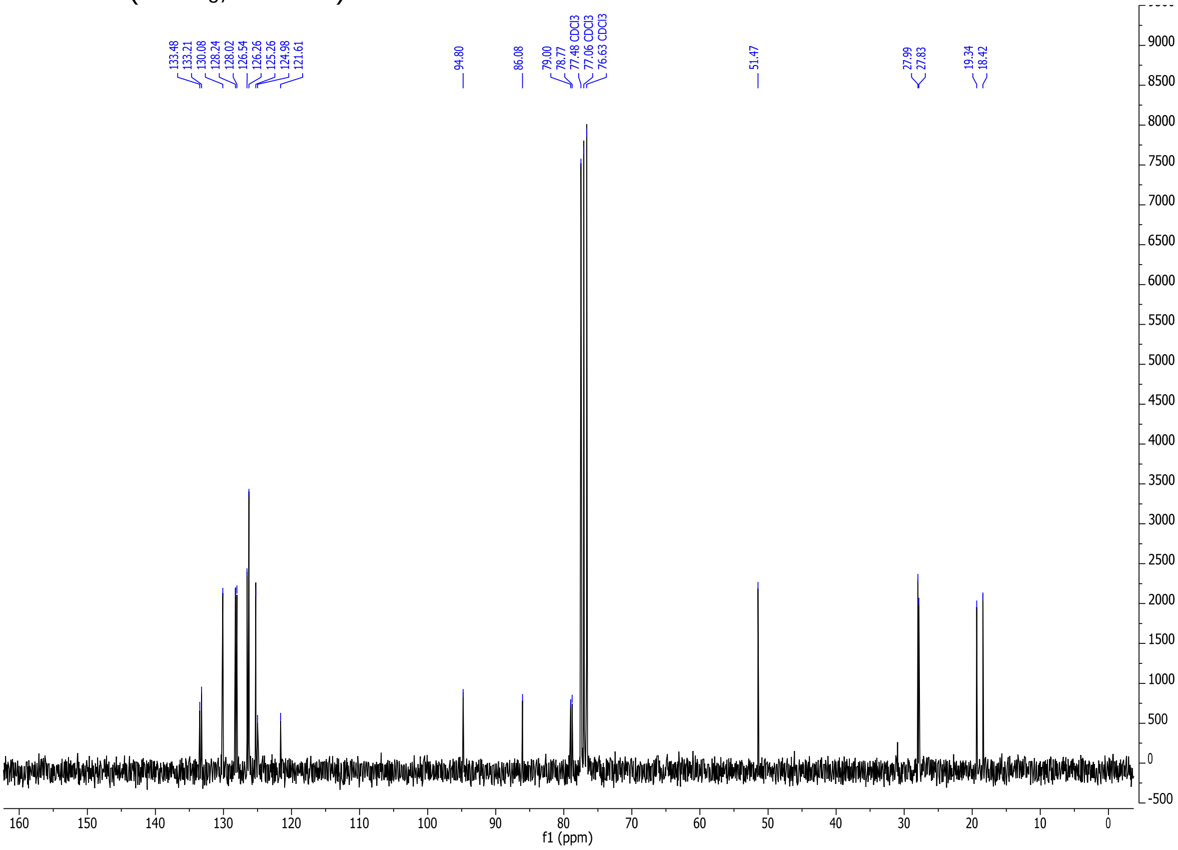


Compound SI-XI: pathway D

^{1}H NMR ($CDCl_3$, 300 MHz)

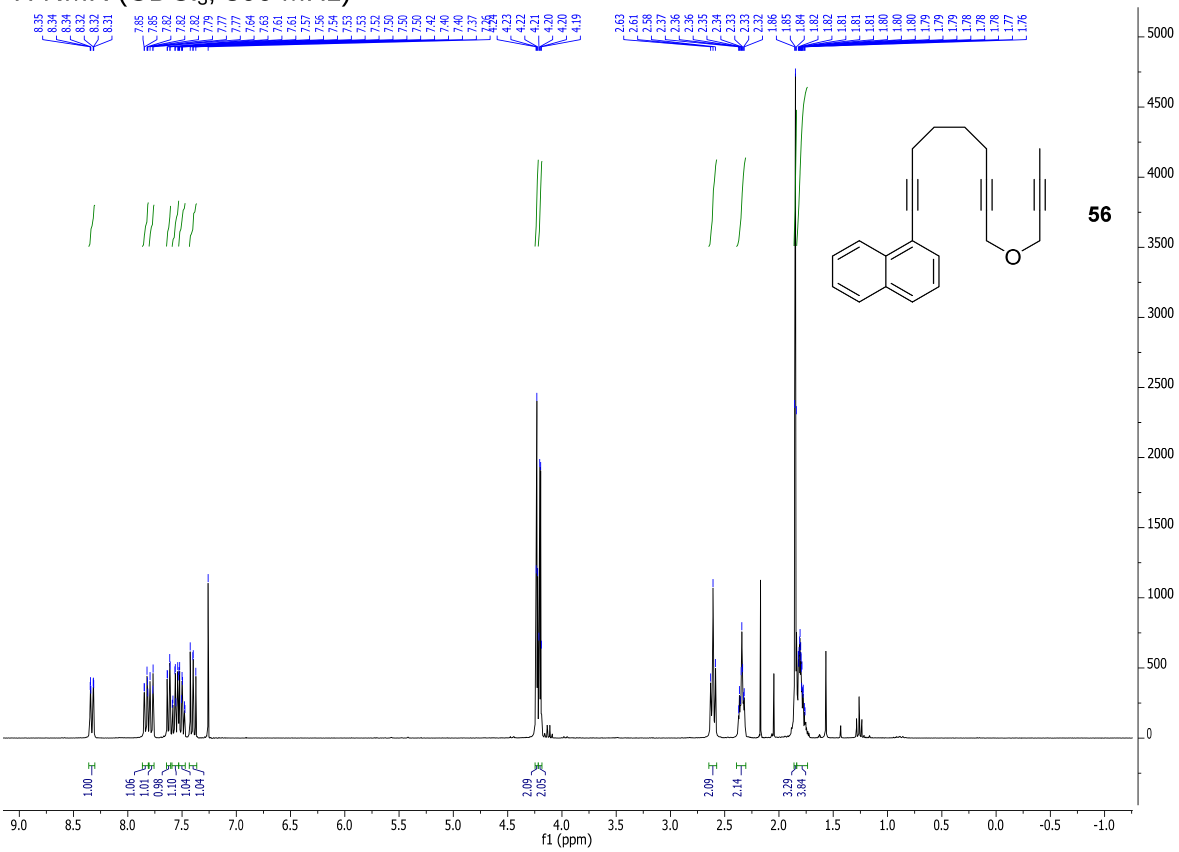


^{13}C NMR ($CDCl_3$, 75 MHz)



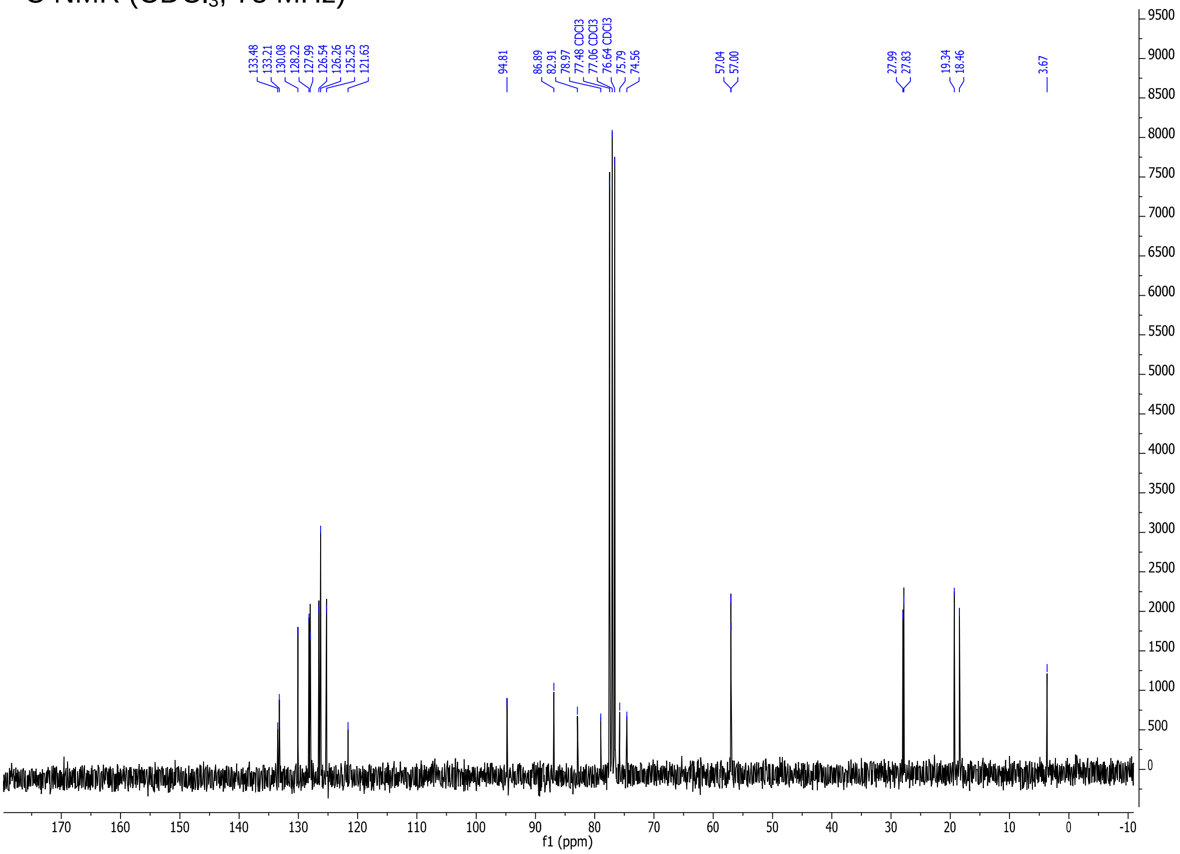
Compound 56: pathway D

^{1}H NMR ($CDCl_3$, 300 MHz)



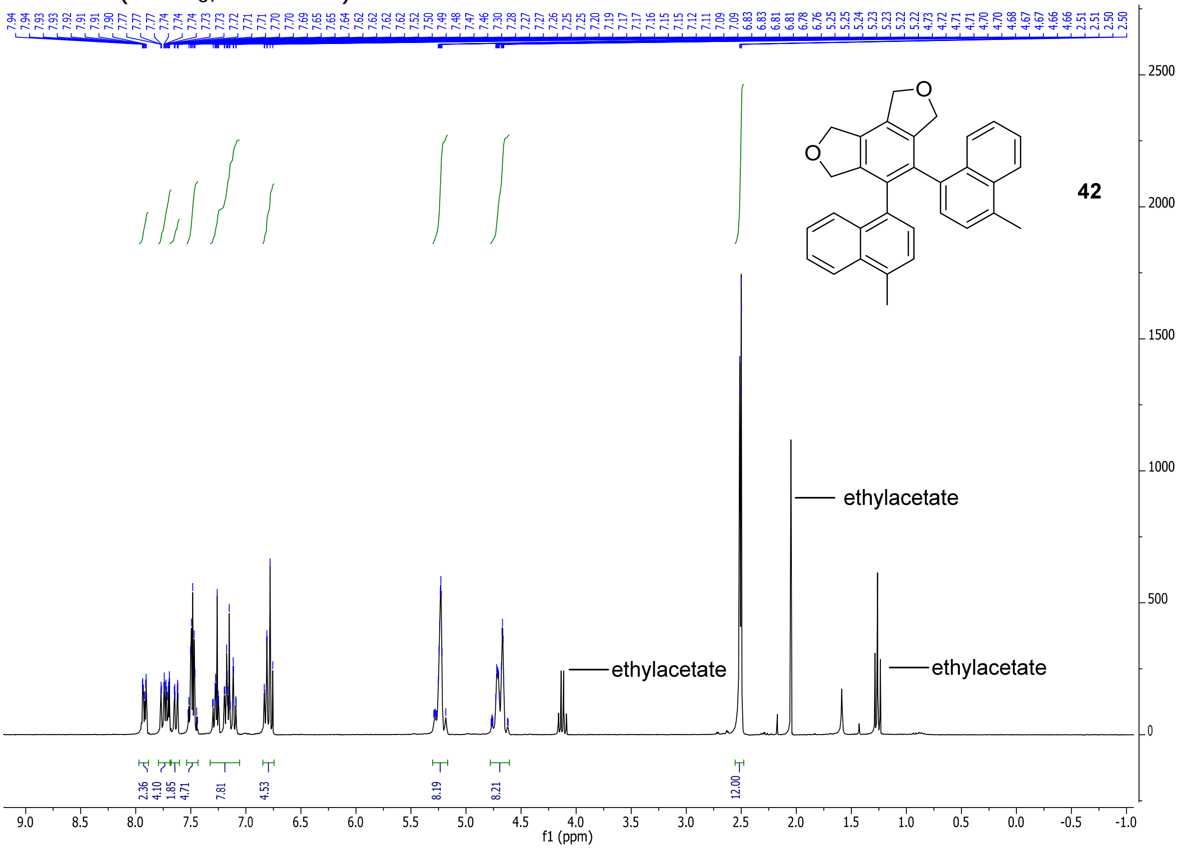
56

^{13}C NMR ($CDCl_3$, 75 MHz)

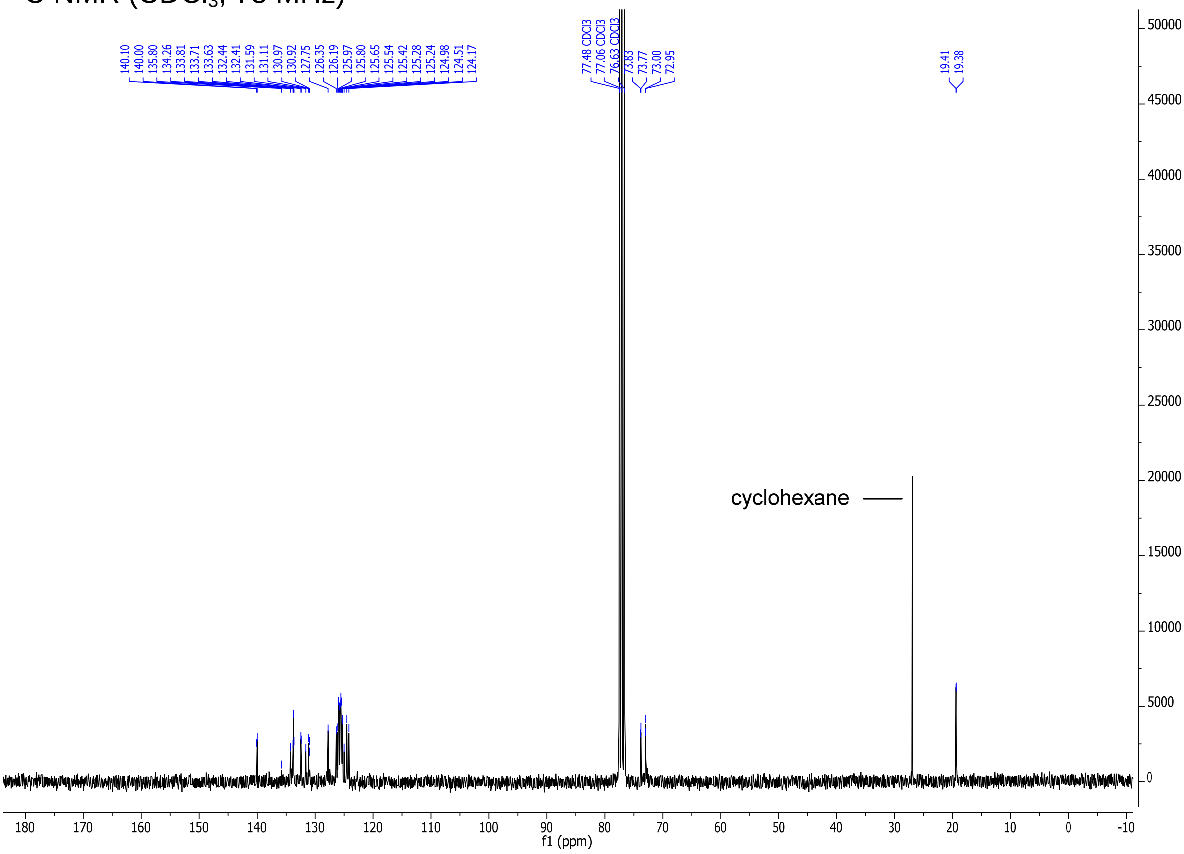


Compound 42:

^{1}H NMR ($CDCl_3$, 300 MHz)

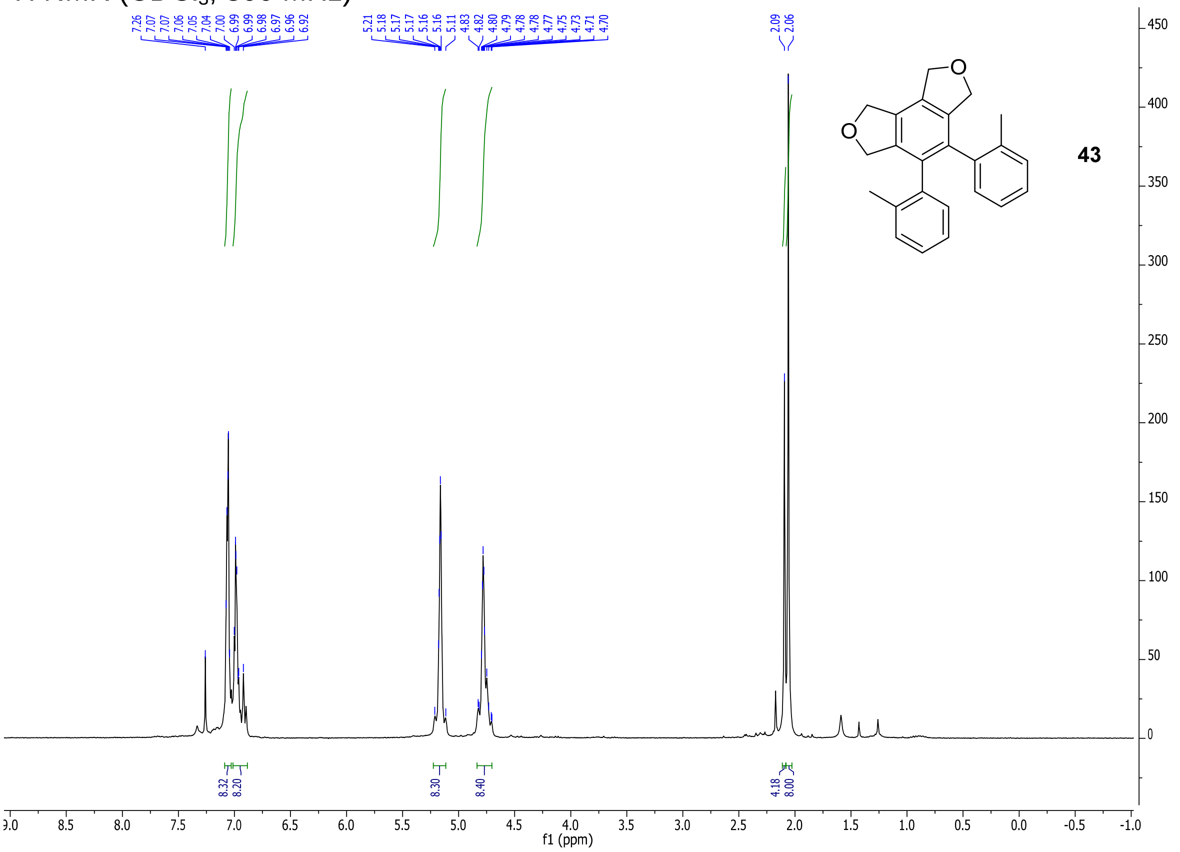


^{13}C NMR ($CDCl_3$, 75 MHz)

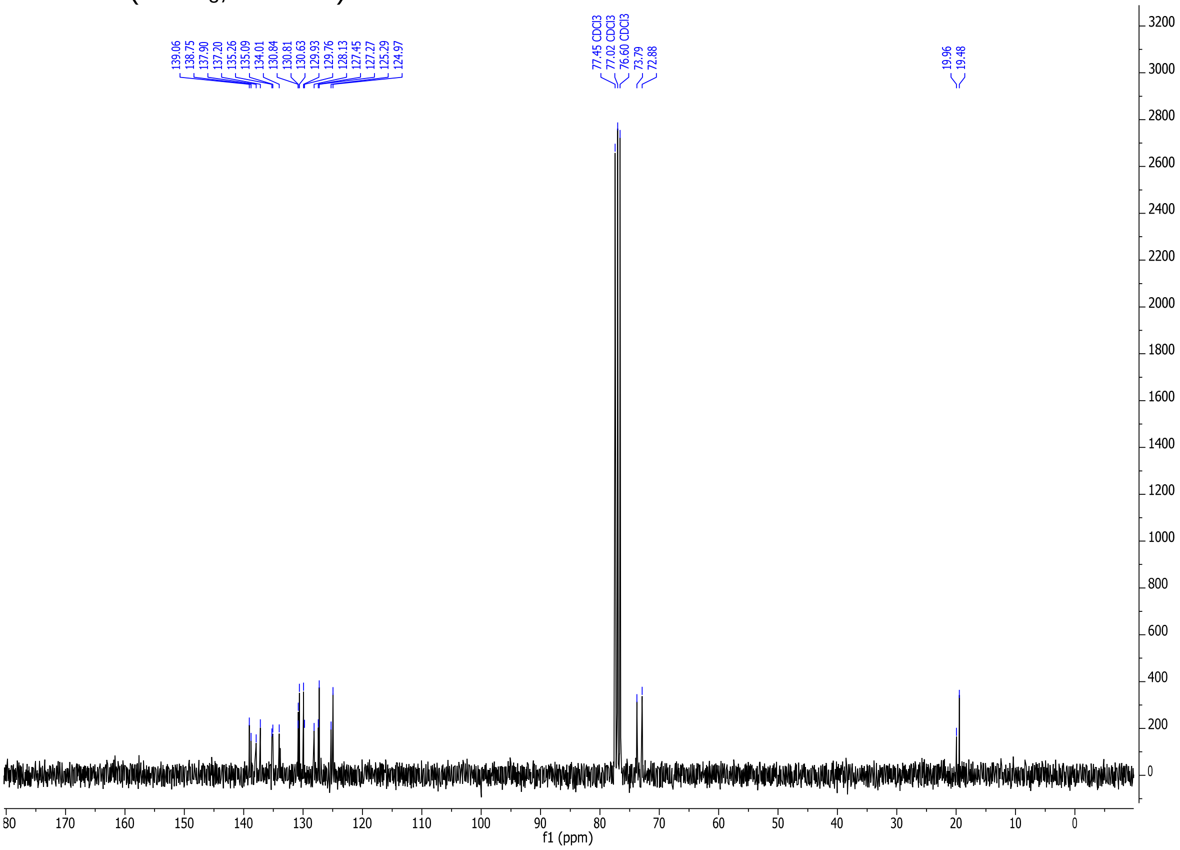


Compound 43:

[1]H NMR ($CDCl_3$, 300 MHz)

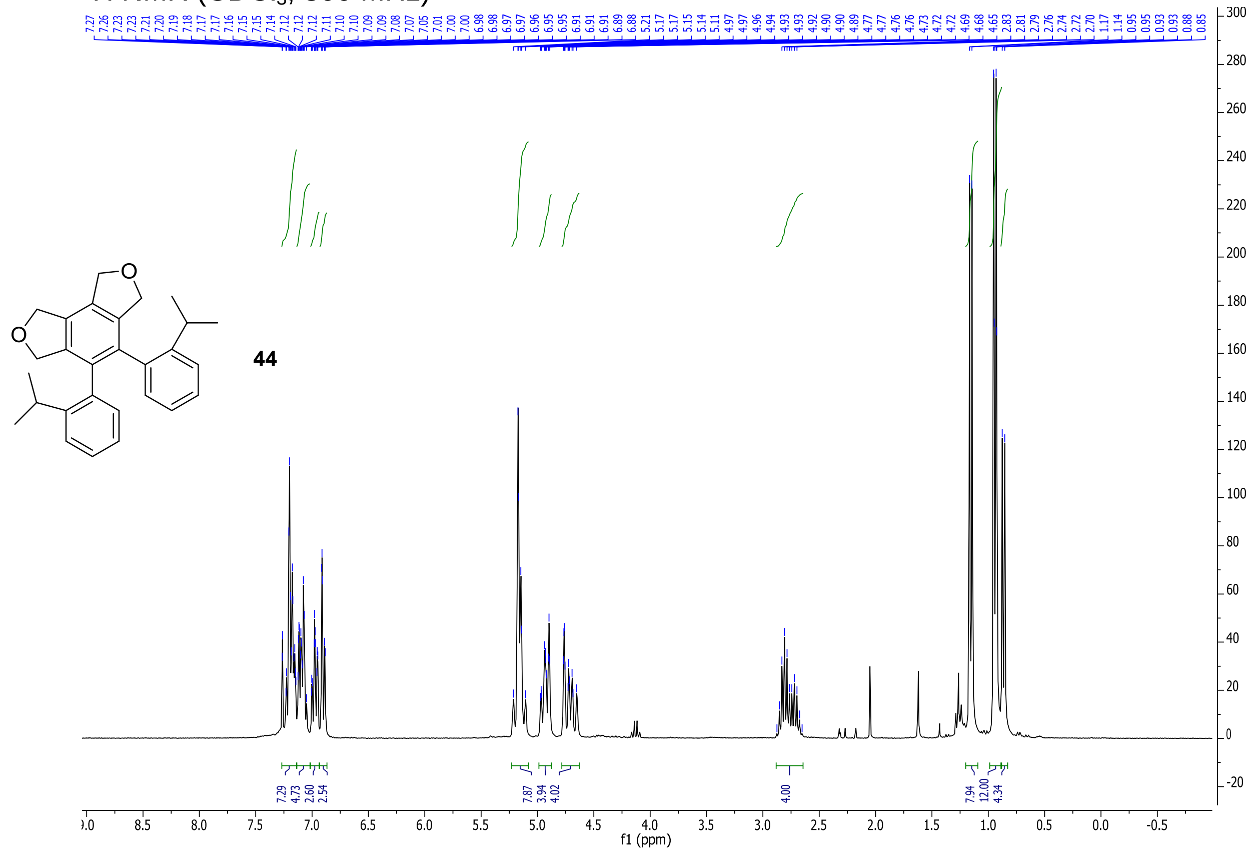


[13]C NMR ($CDCl_3$, 75 MHz)



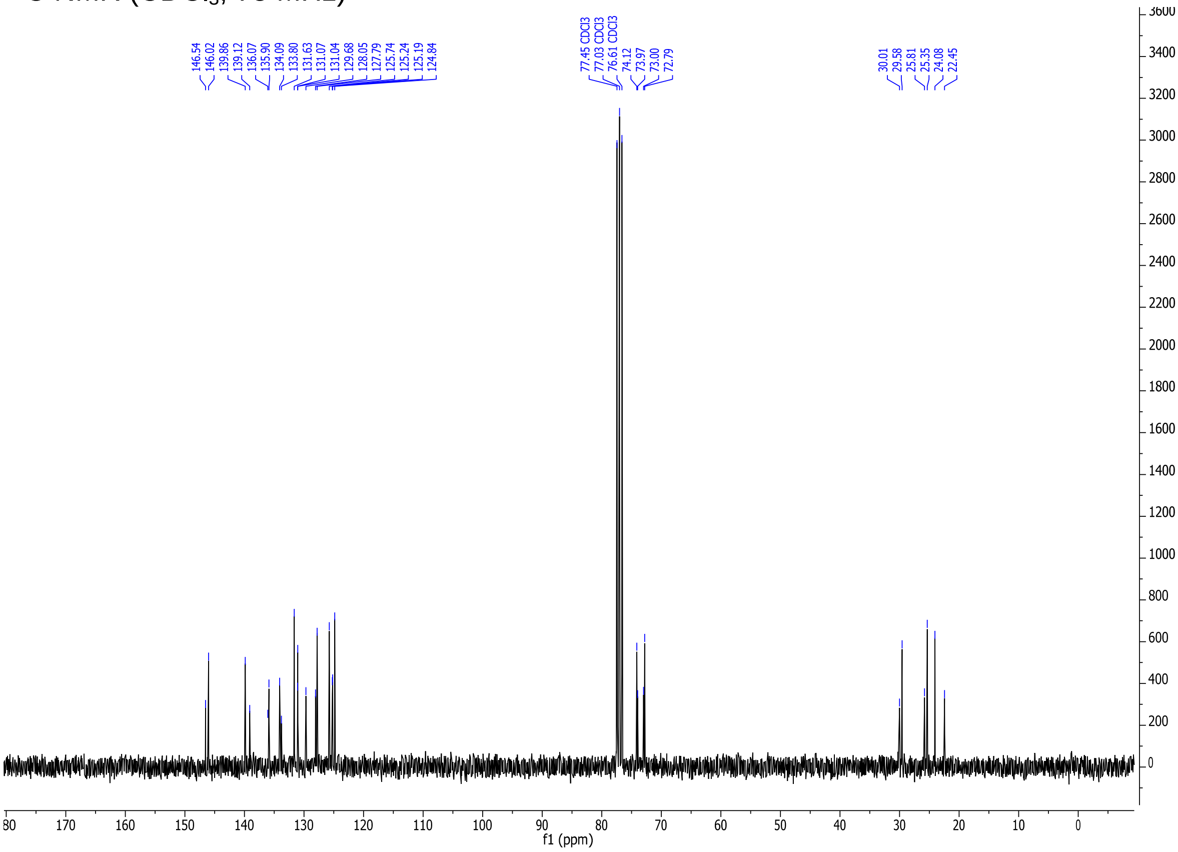
Compound 44:

^{1}H NMR ($CDCl_3$, 300 MHz)



44

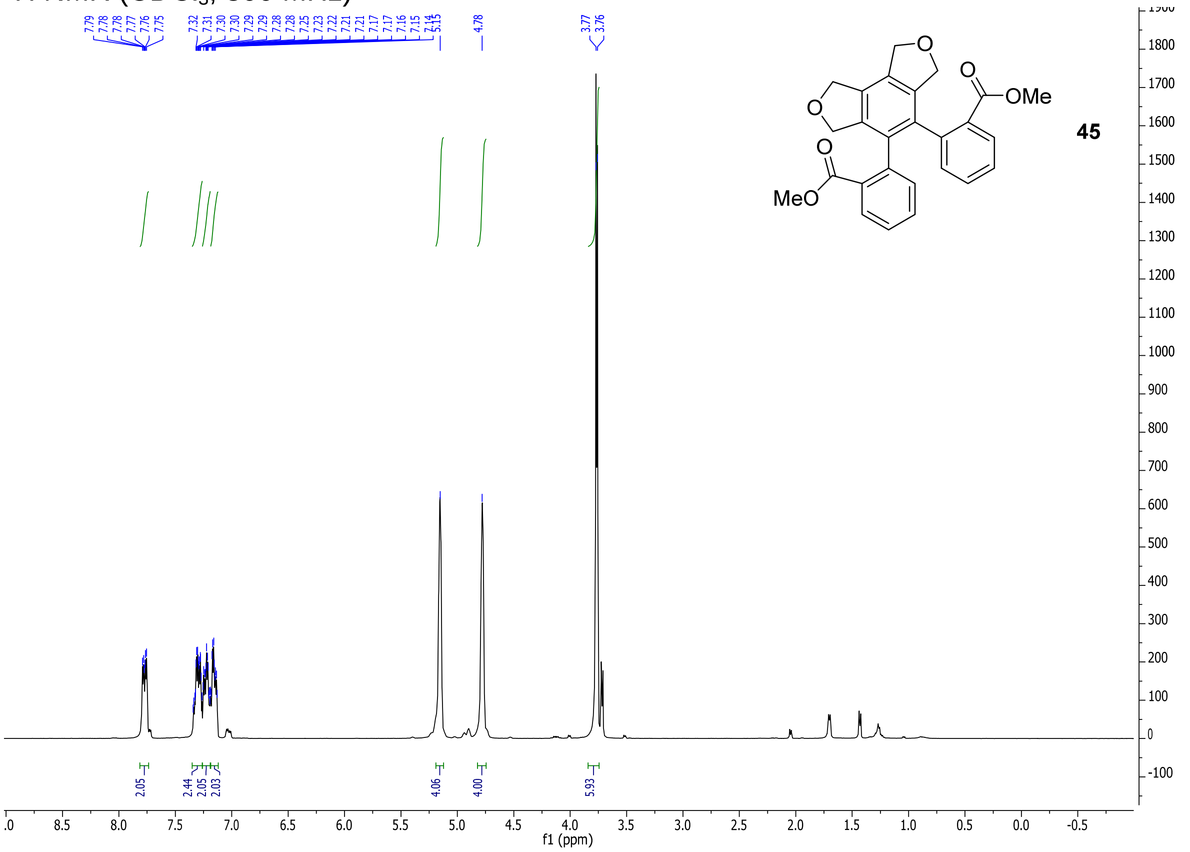
^{13}C NMR ($CDCl_3$, 75 MHz)



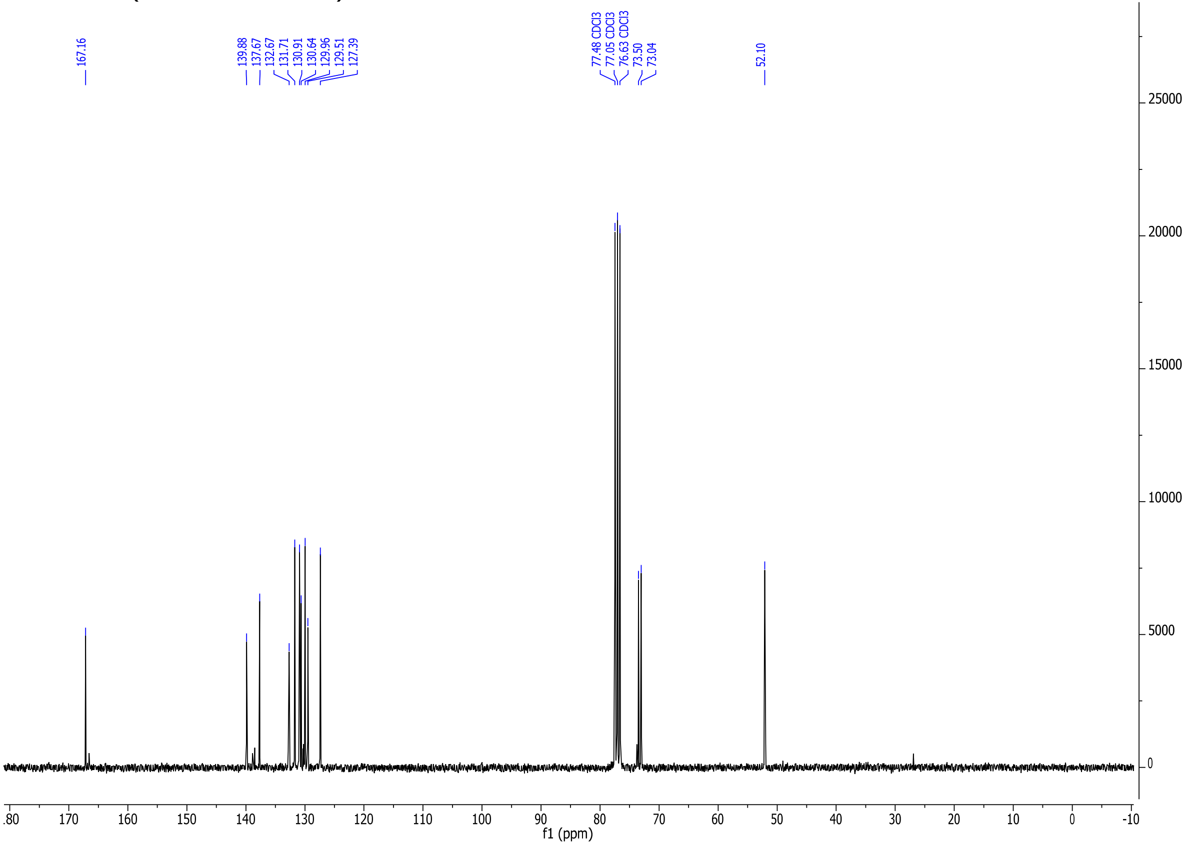
Compound 45:

d/l-form

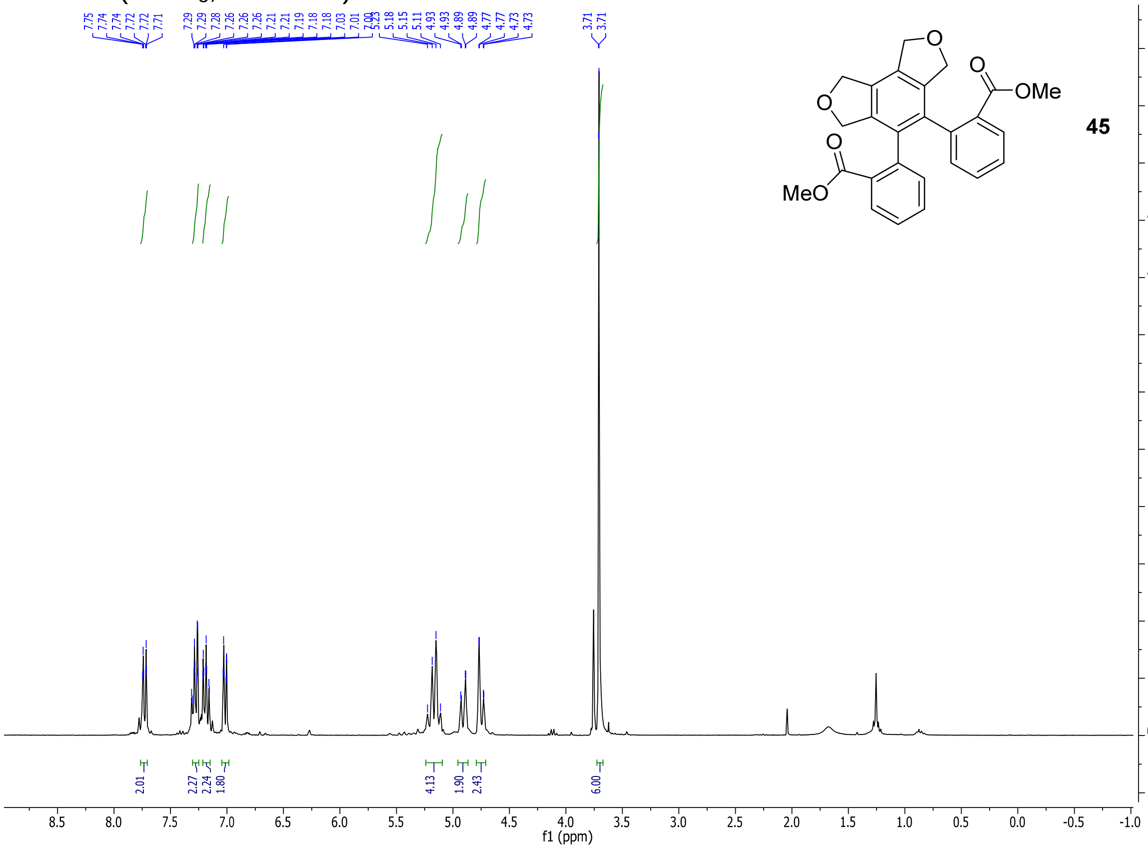
^{1}H NMR ($CDCl_3$, 300 MHz)



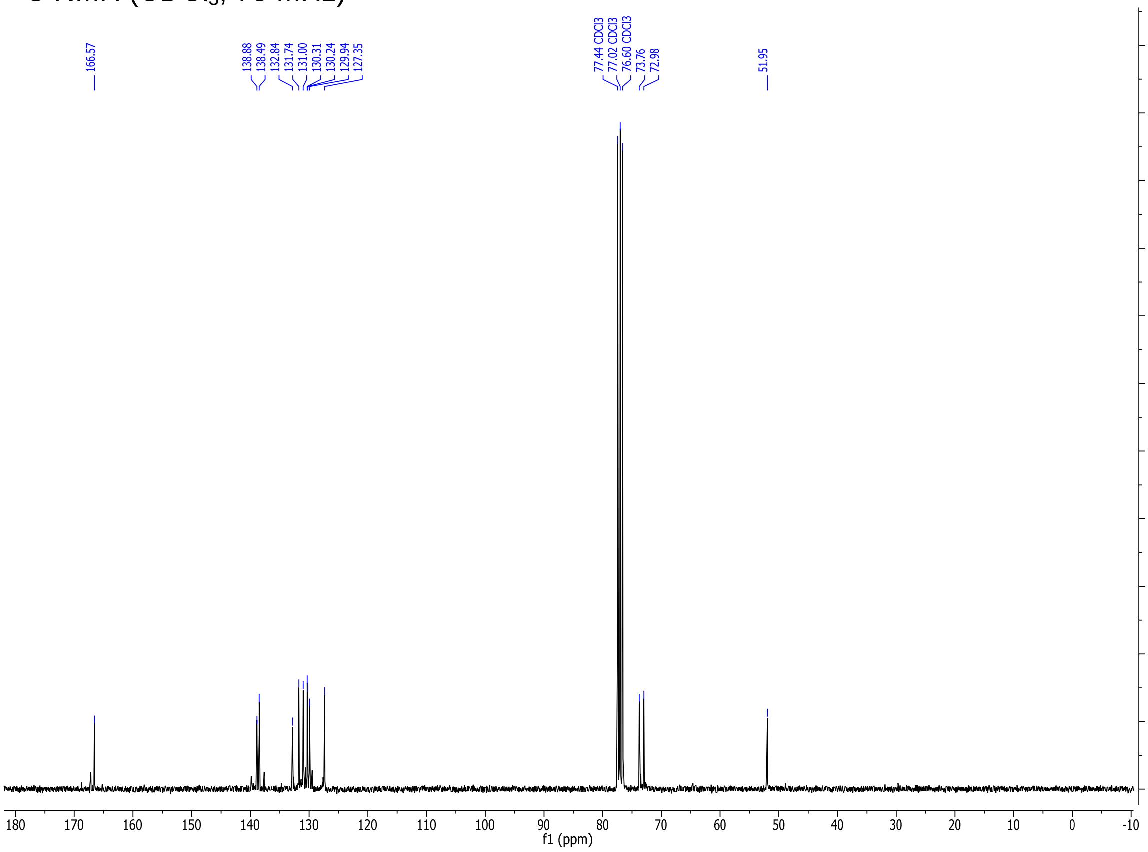
^{13}C NMR ($CDCl_3$, 75 MHz)



Compound 45:
meso-form
^{1}H NMR ($CDCl_3$, 300 MHz)



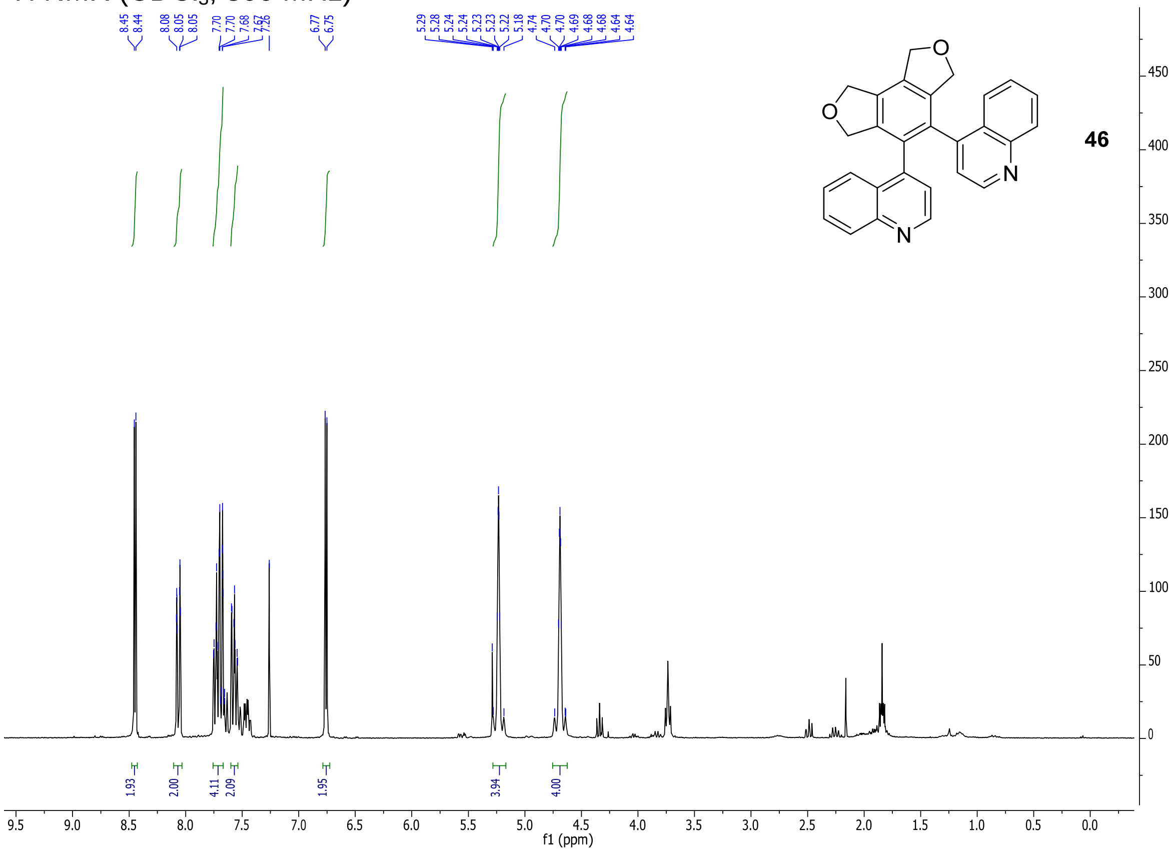
^{13}C NMR ($CDCl_3$, 75 MHz)



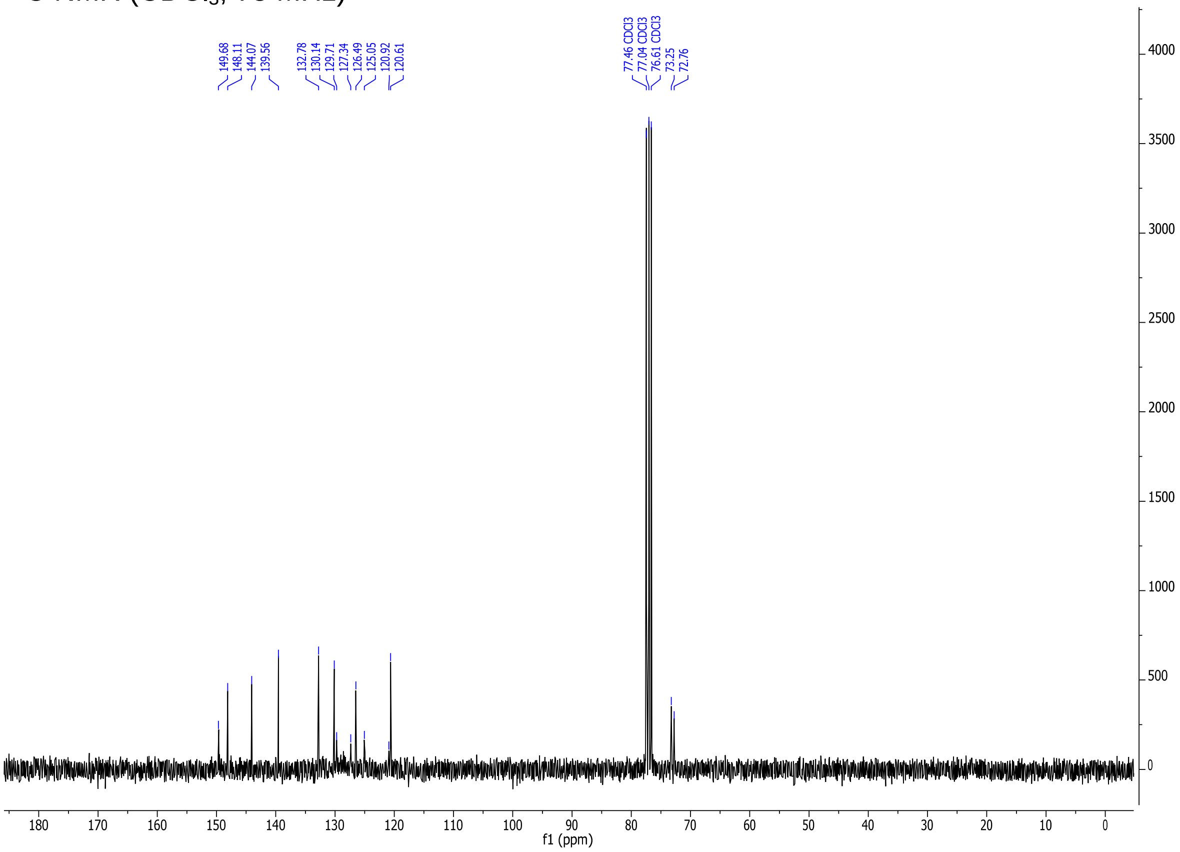
Compound 46:

d/l-form

^{1}H NMR ($CDCl_3$, 300 MHz)

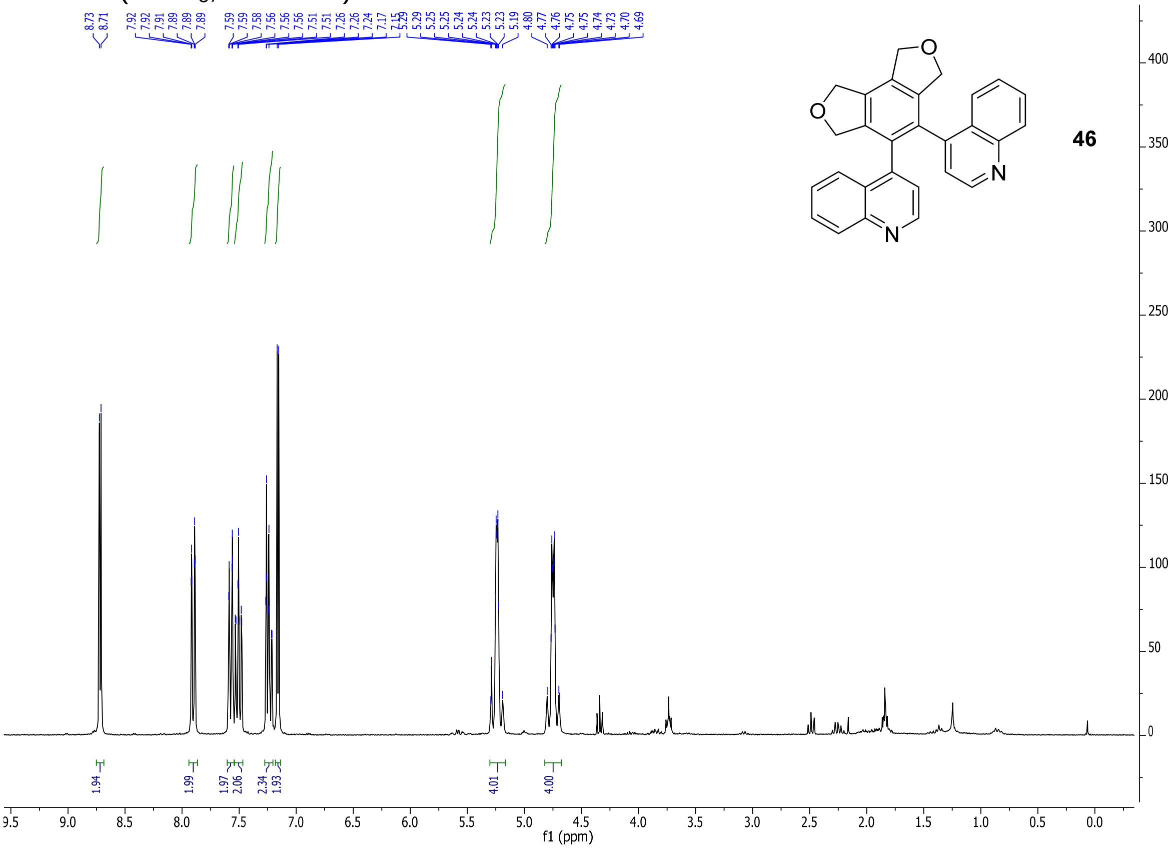


^{13}C NMR ($CDCl_3$, 75 MHz)

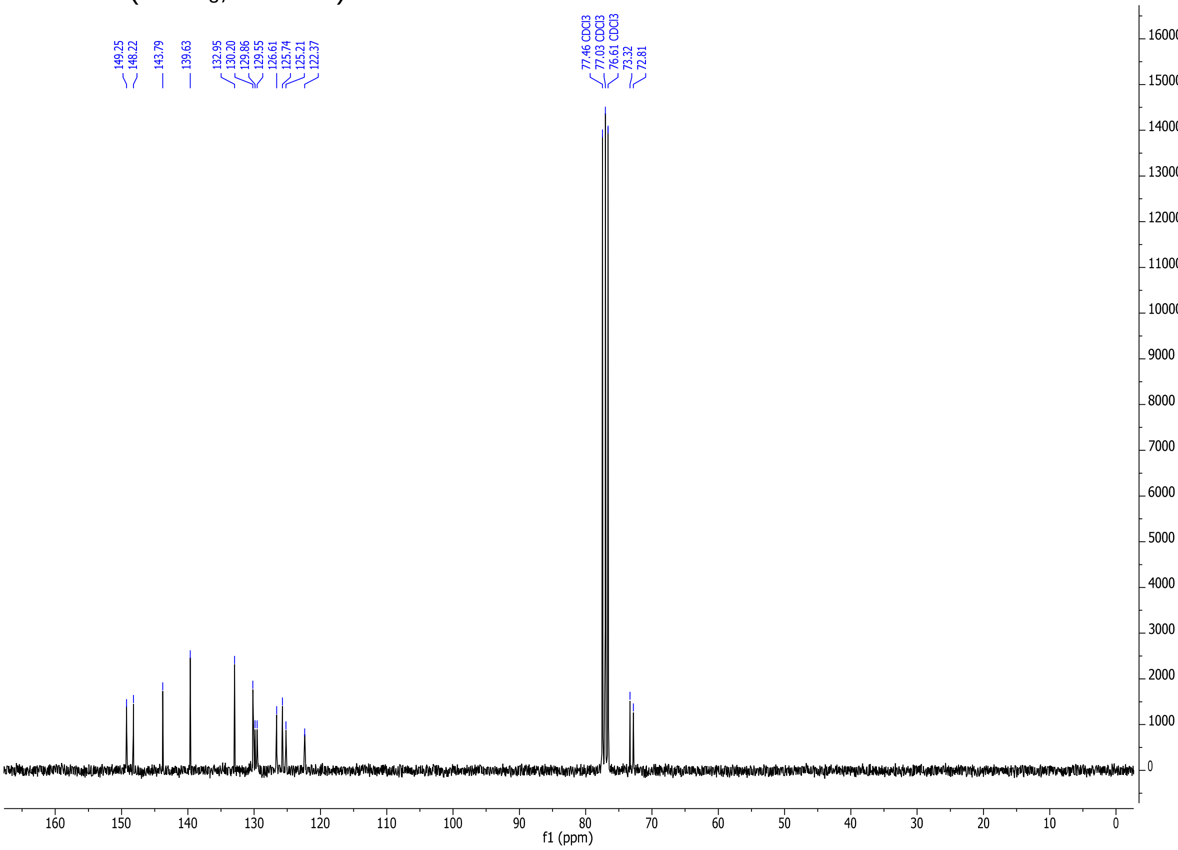


Compound 46:
meso-form
^{1}H NMR ($CDCl_3$, 300 MHz)

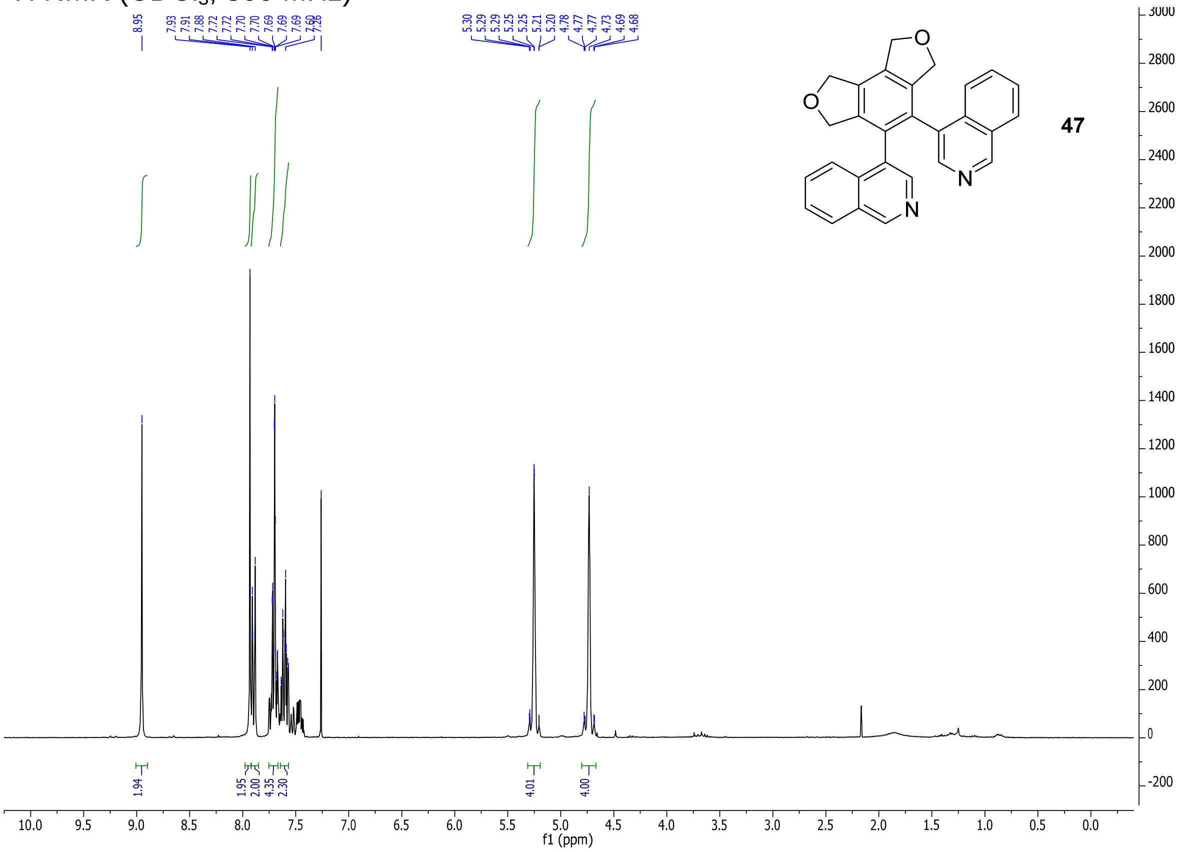
46



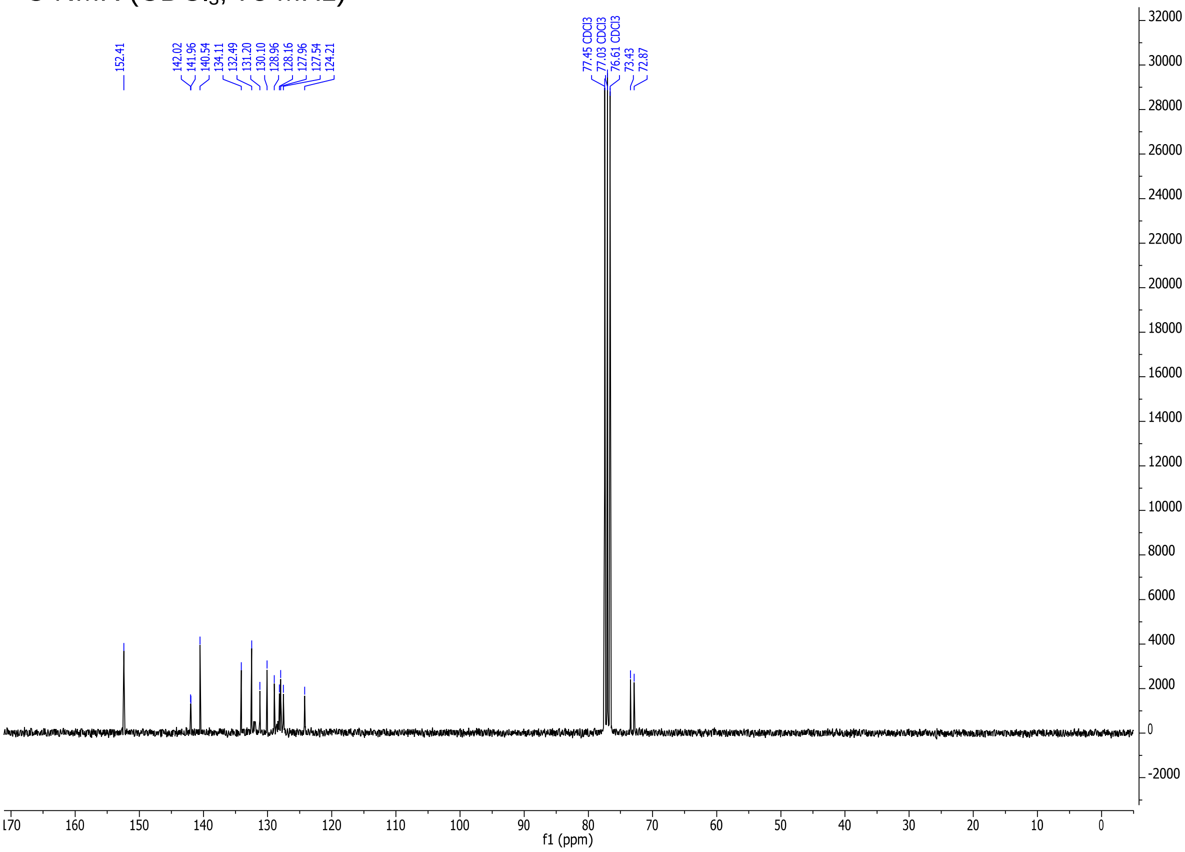
^{13}C NMR ($CDCl_3$, 75 MHz)



Compound 47:
d/l-form
^1H NMR ($CDCl_3$, 300 MHz)



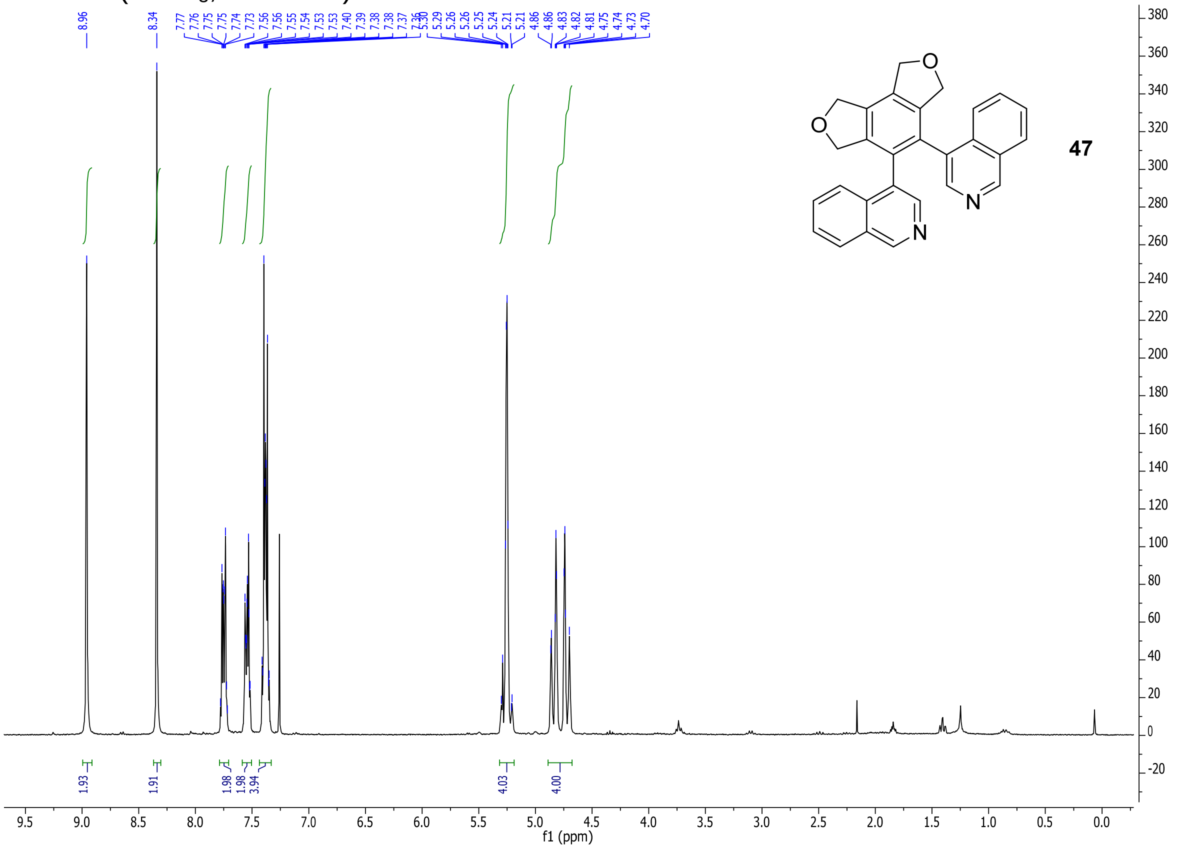
^{13}C NMR ($CDCl_3$, 75 MHz)



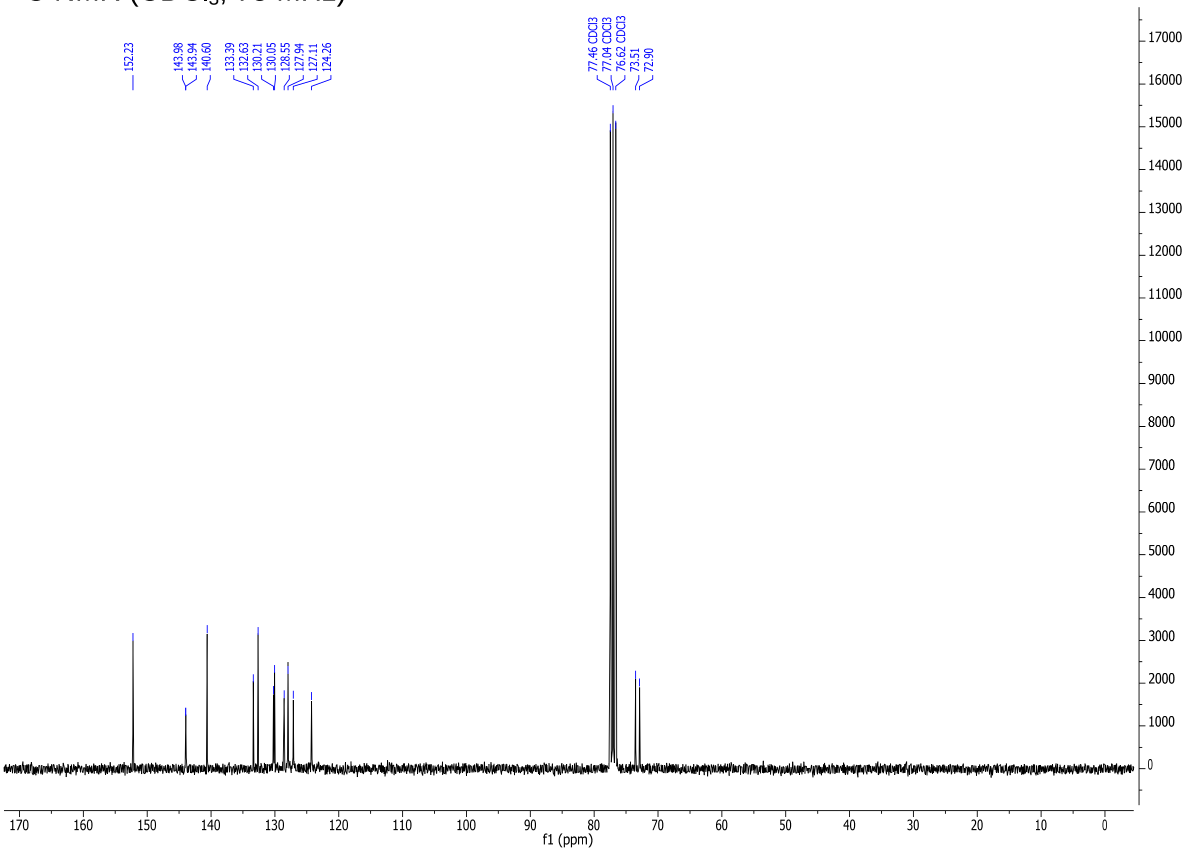
Compound 47:

meso-form

^{1}H NMR ($CDCl_3$, 300 MHz)

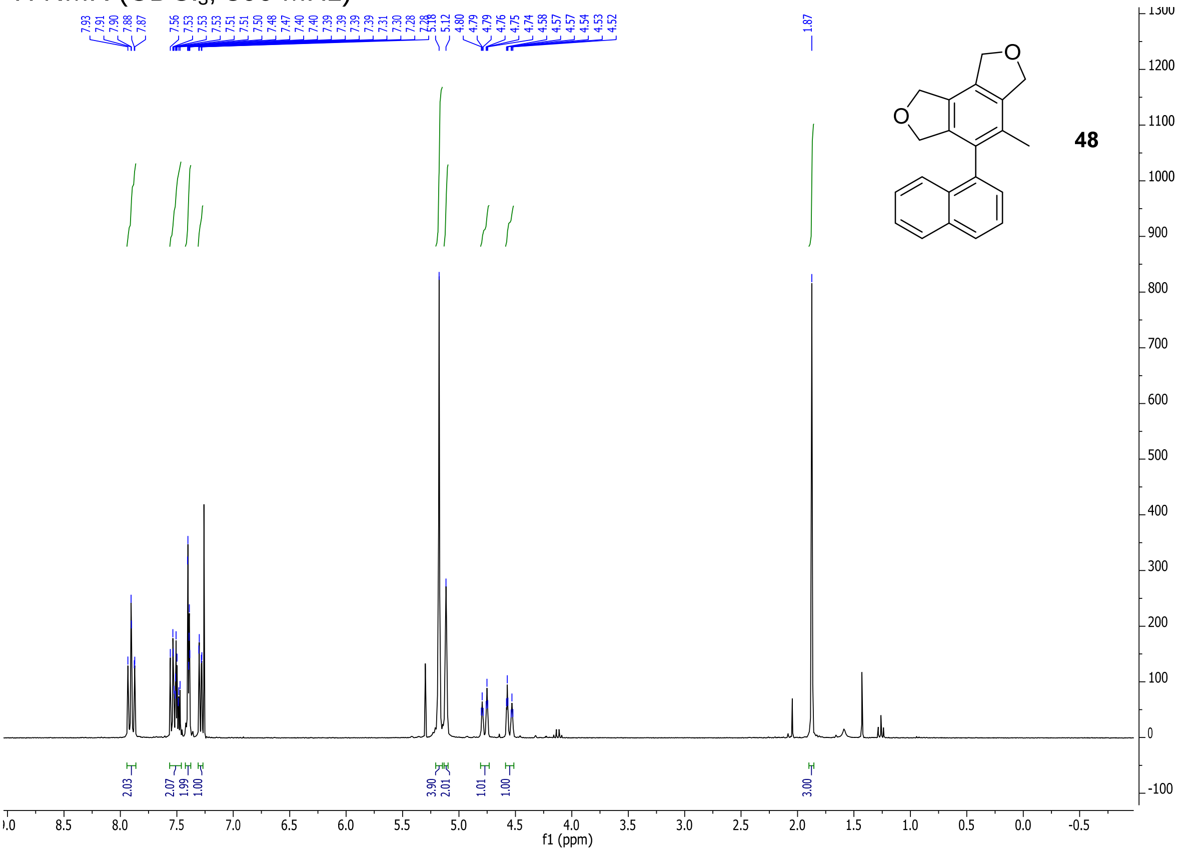


^{13}C NMR ($CDCl_3$, 75 MHz)

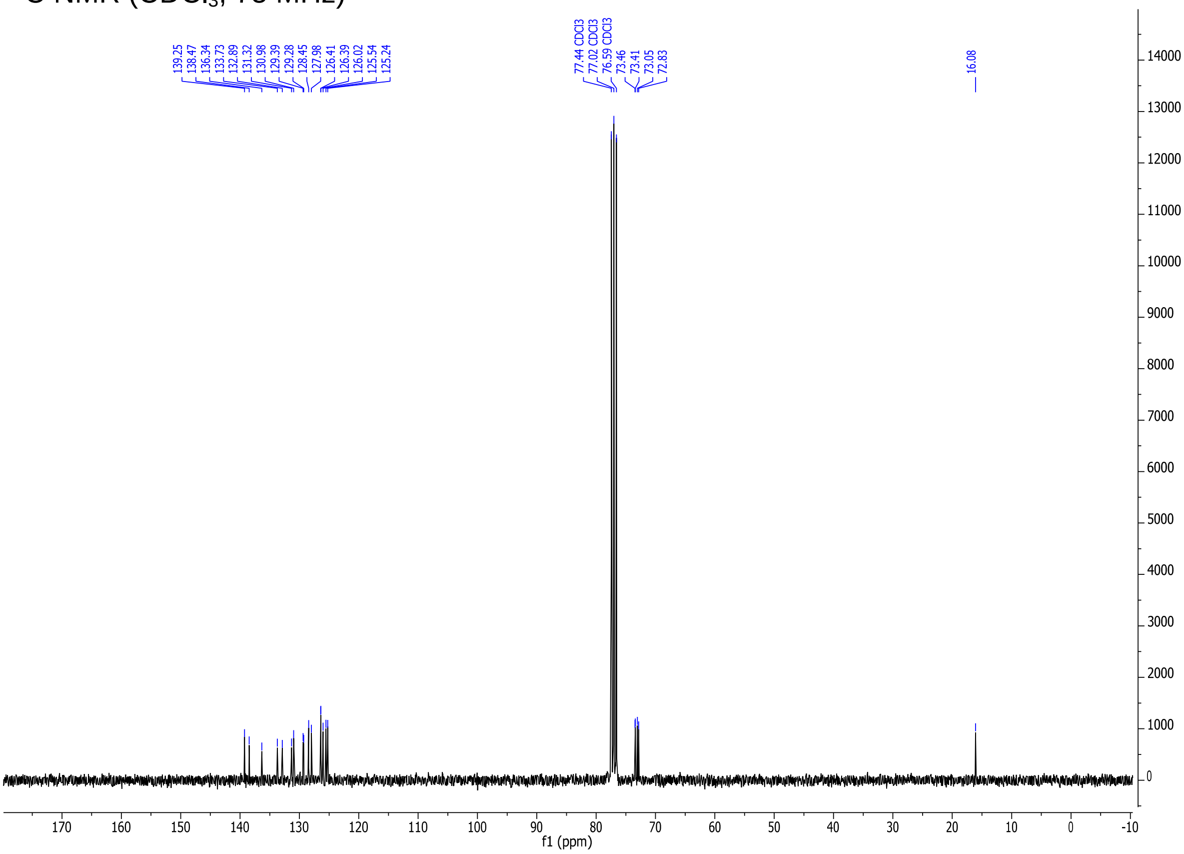


Compound 48:

^{1}H NMR ($CDCl_3$, 300 MHz)

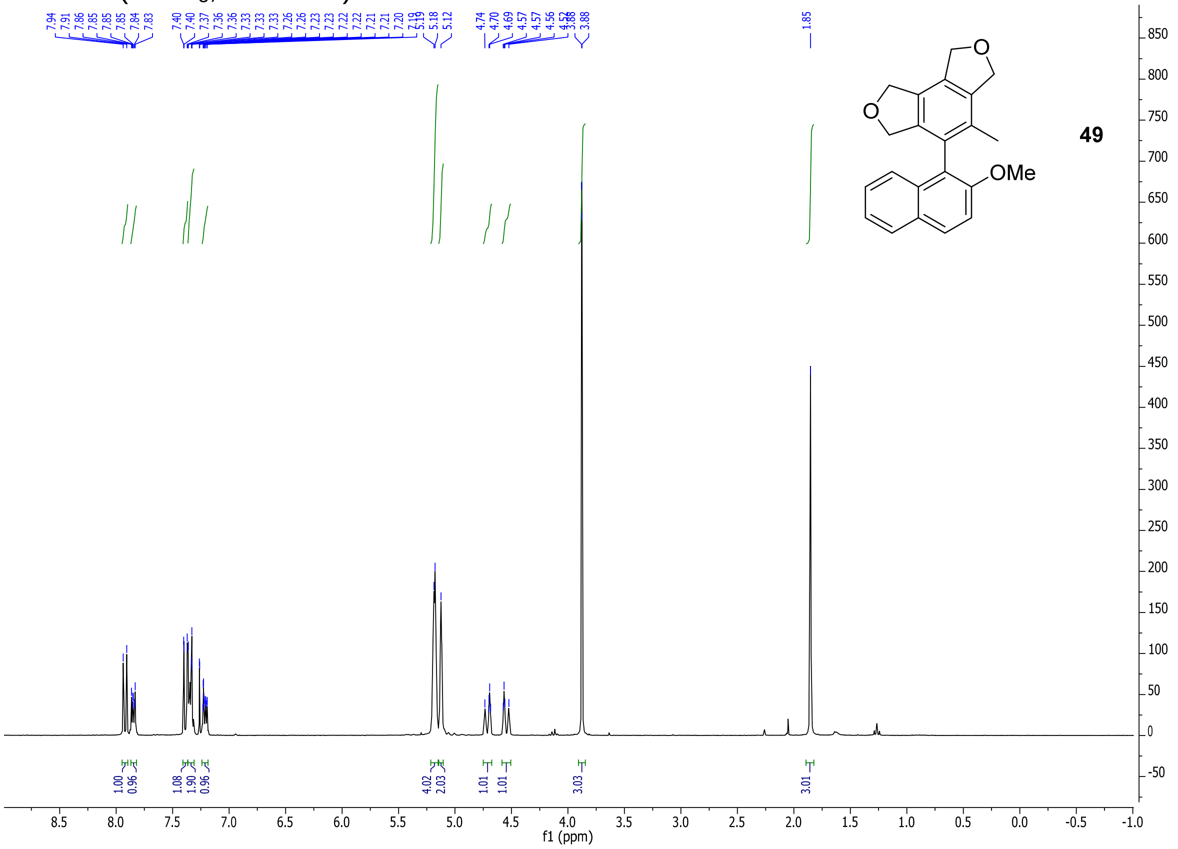


^{13}C NMR ($CDCl_3$, 75 MHz)

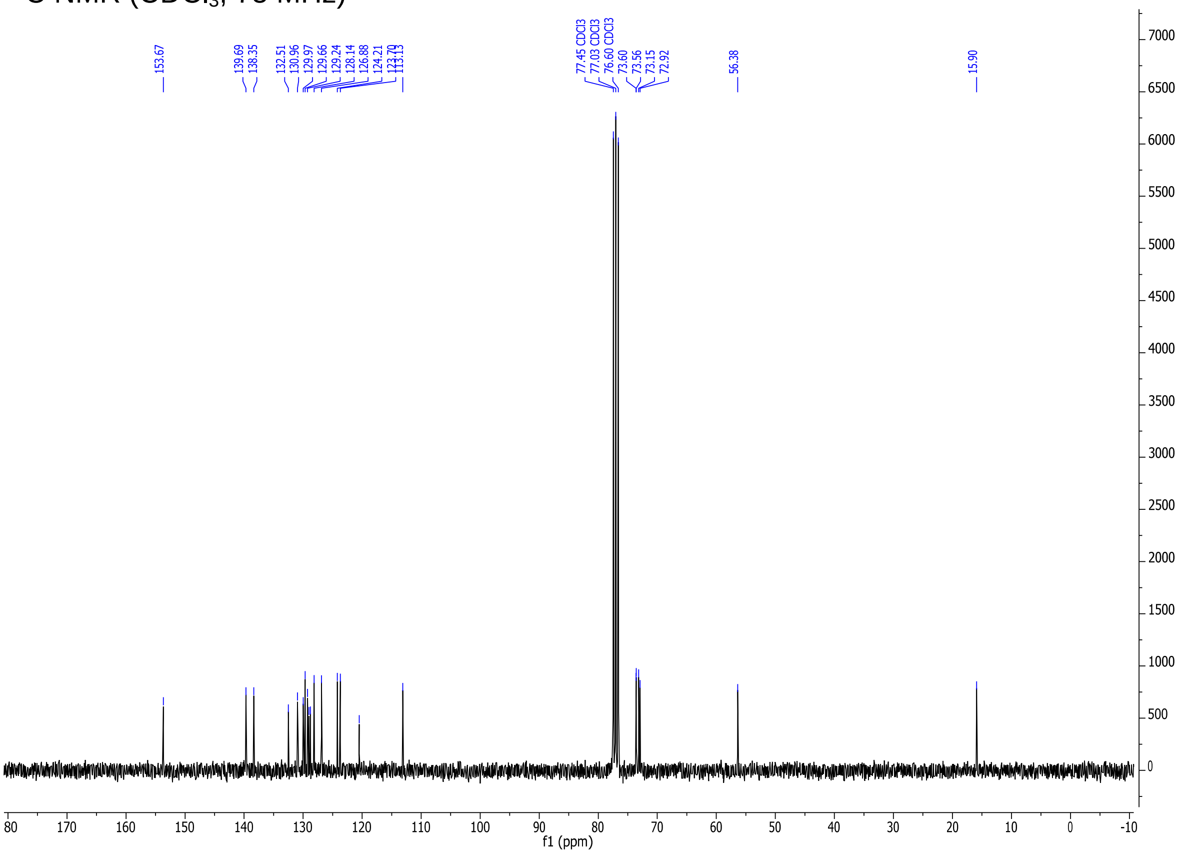


Compound 49:

¹H NMR ($CDCl_3$, 300 MHz)

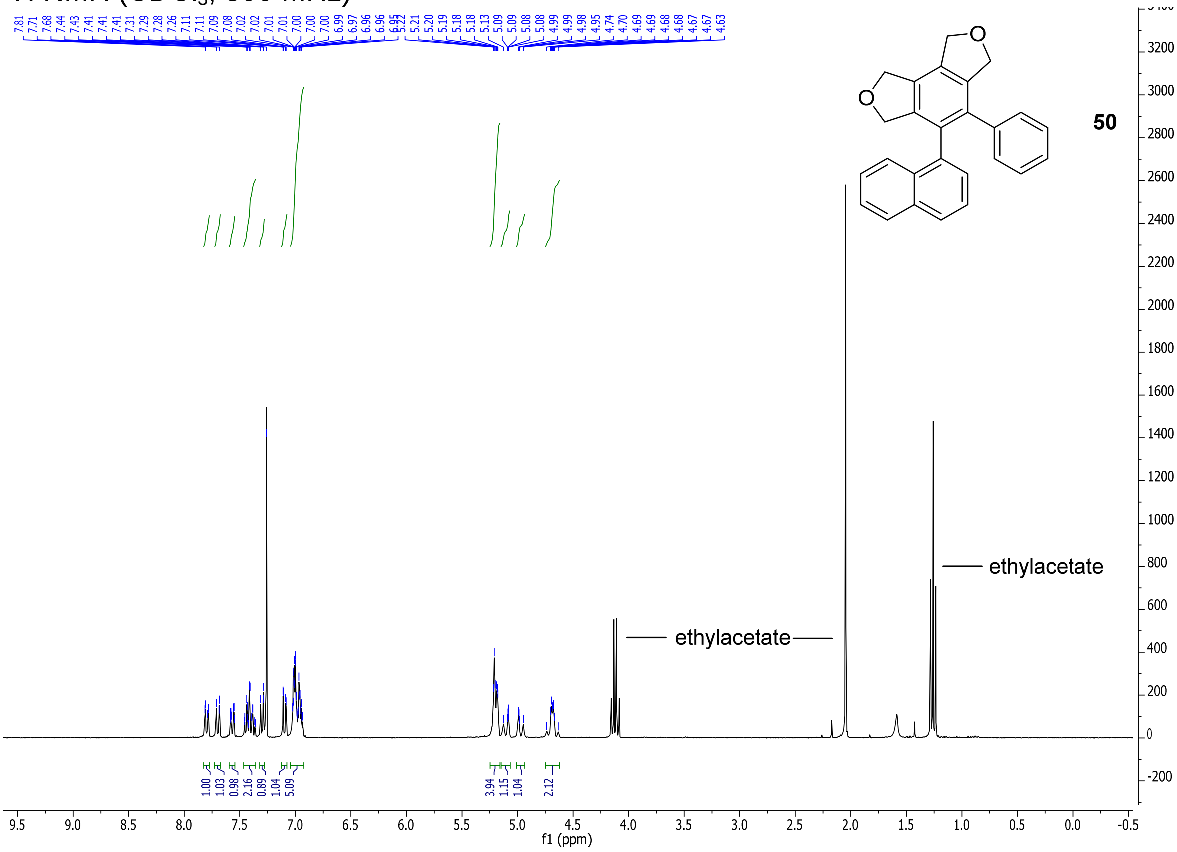


¹³C NMR ($CDCl_3$, 75 MHz)

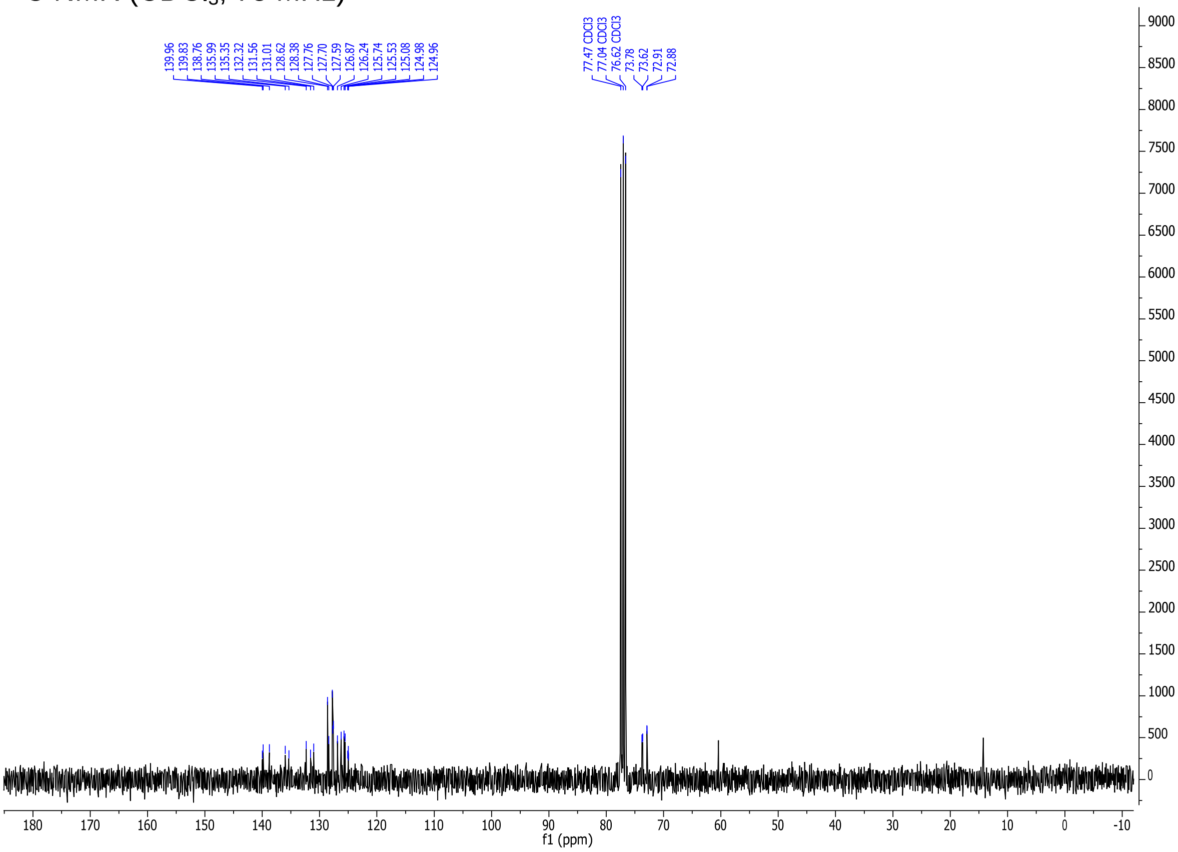


Compound 50:

^{1}H NMR ($CDCl_3$, 300 MHz)

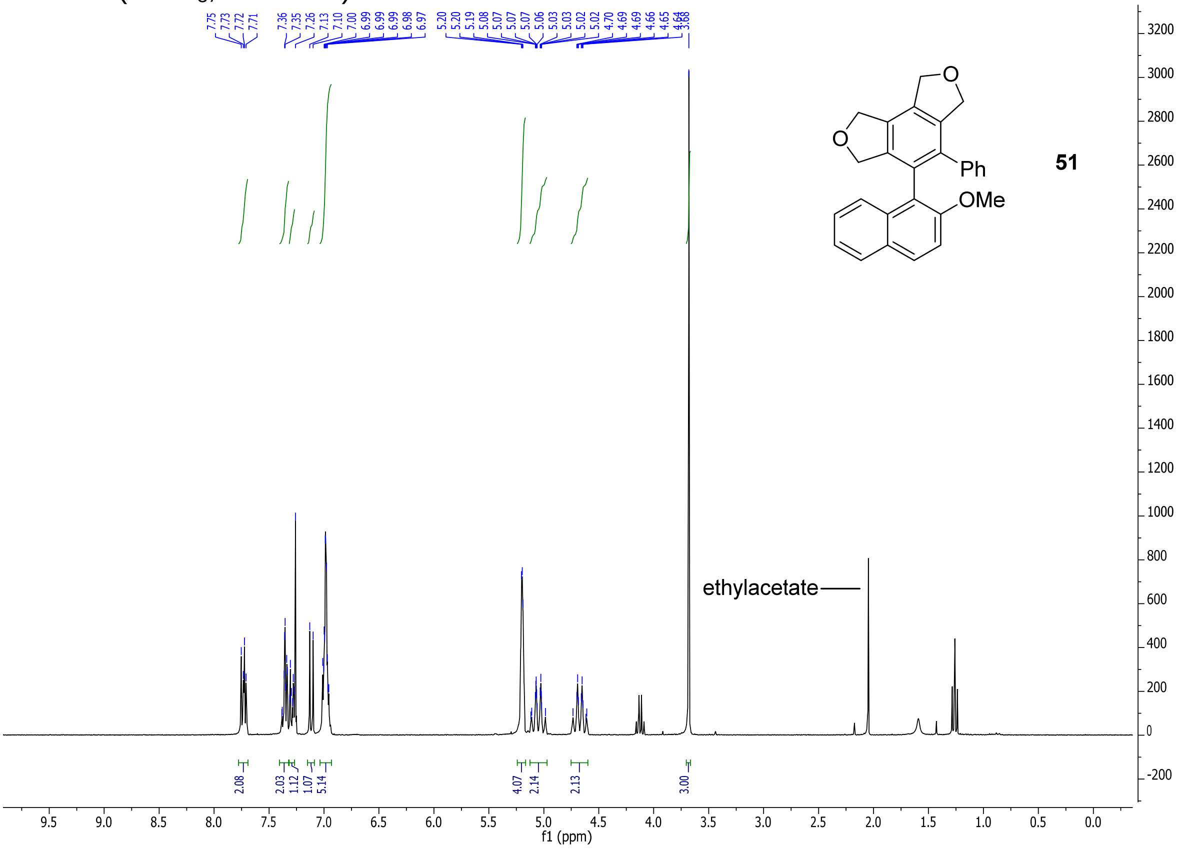


^{13}C NMR ($CDCl_3$, 75 MHz)



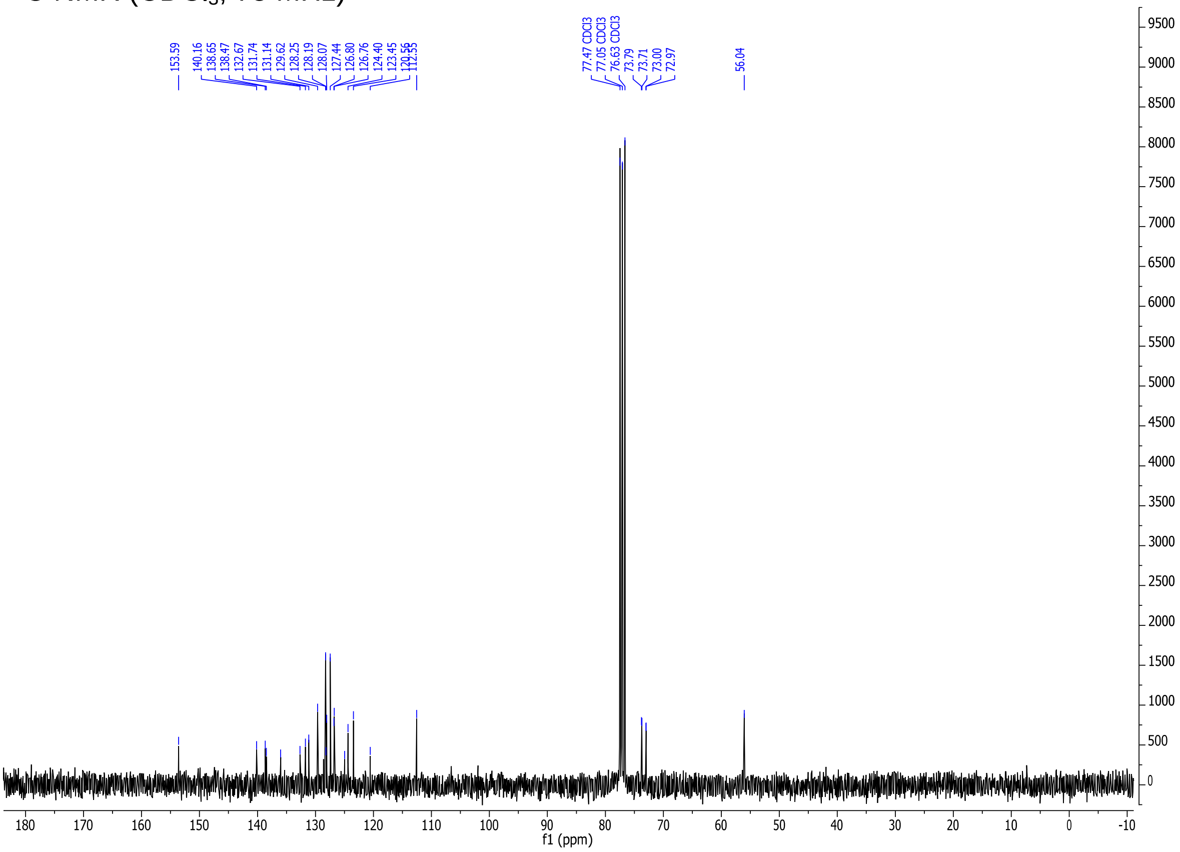
Compound 51:

^1H NMR ($CDCl_3$, 300 MHz)



51

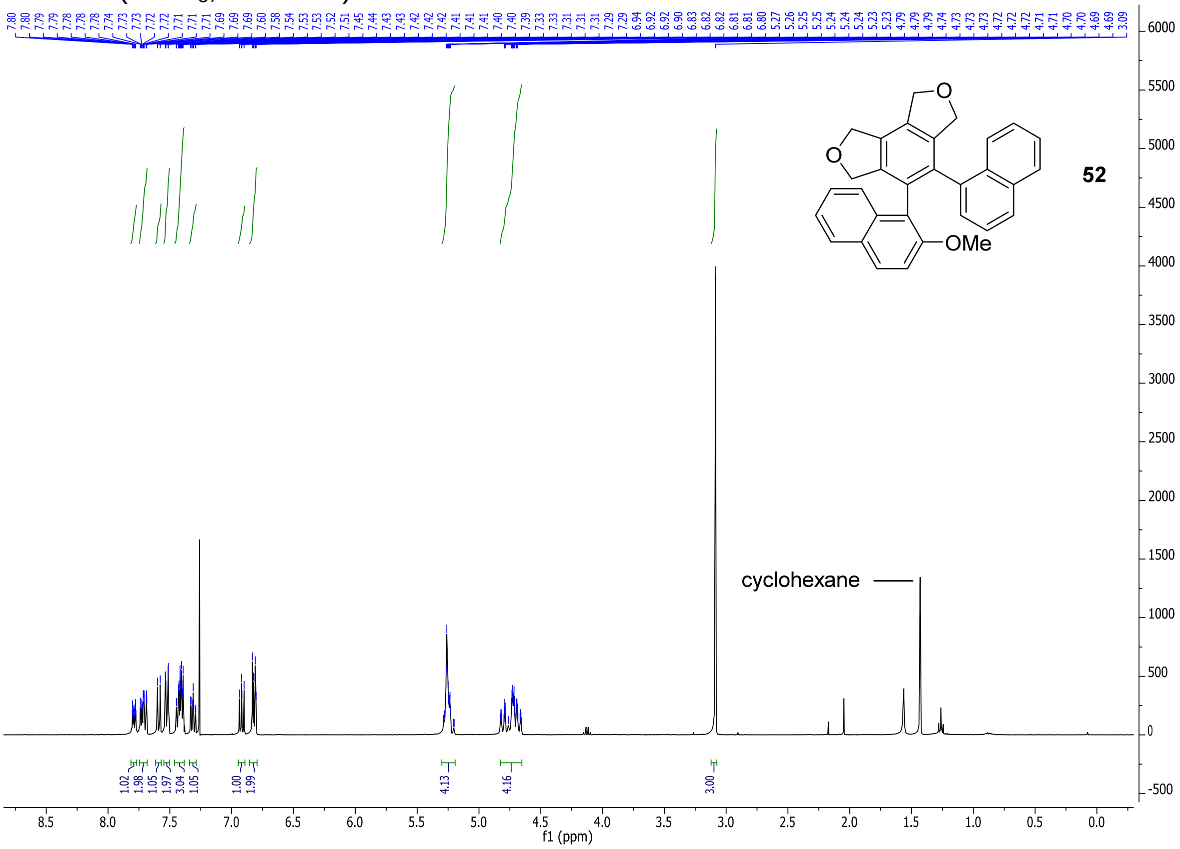
^{13}C NMR ($CDCl_3$, 75 MHz)



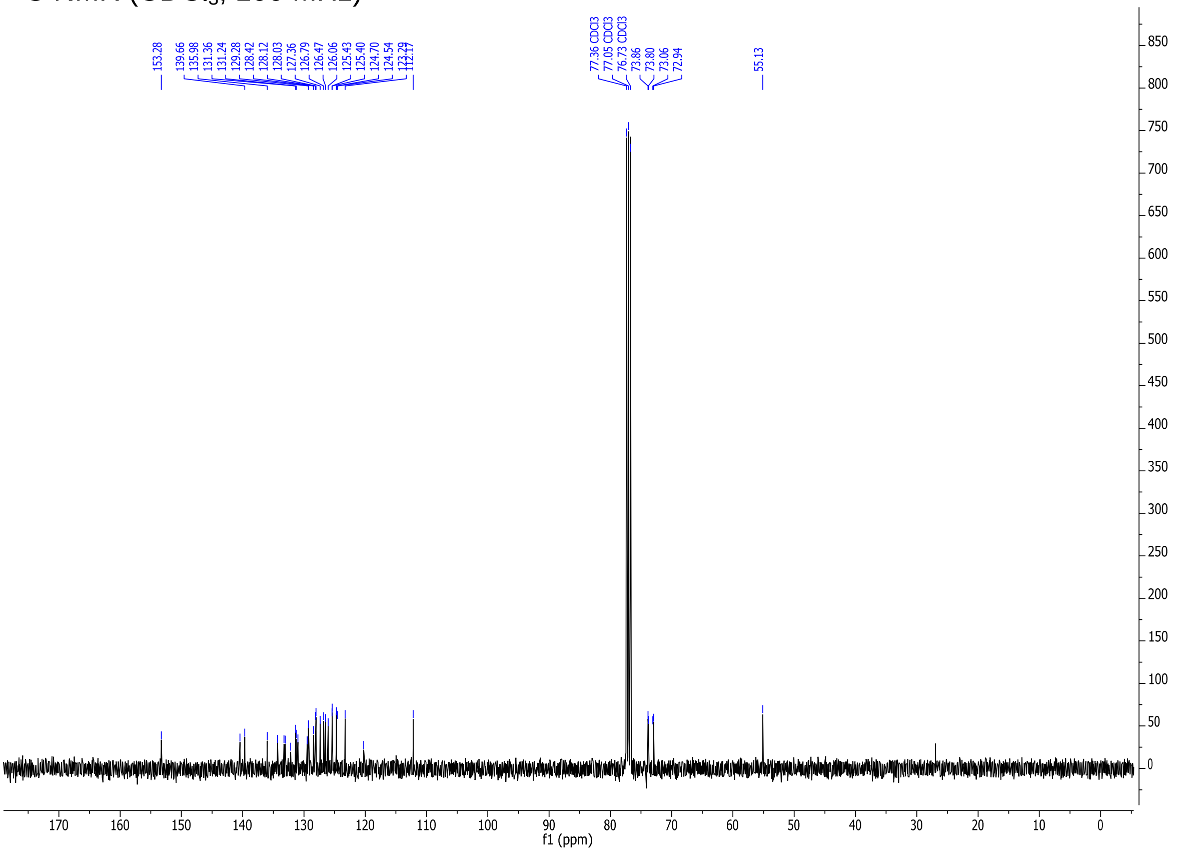
Compound 52:

fraction 1:

^{1}H NMR ($CDCl_3$, 400 MHz)



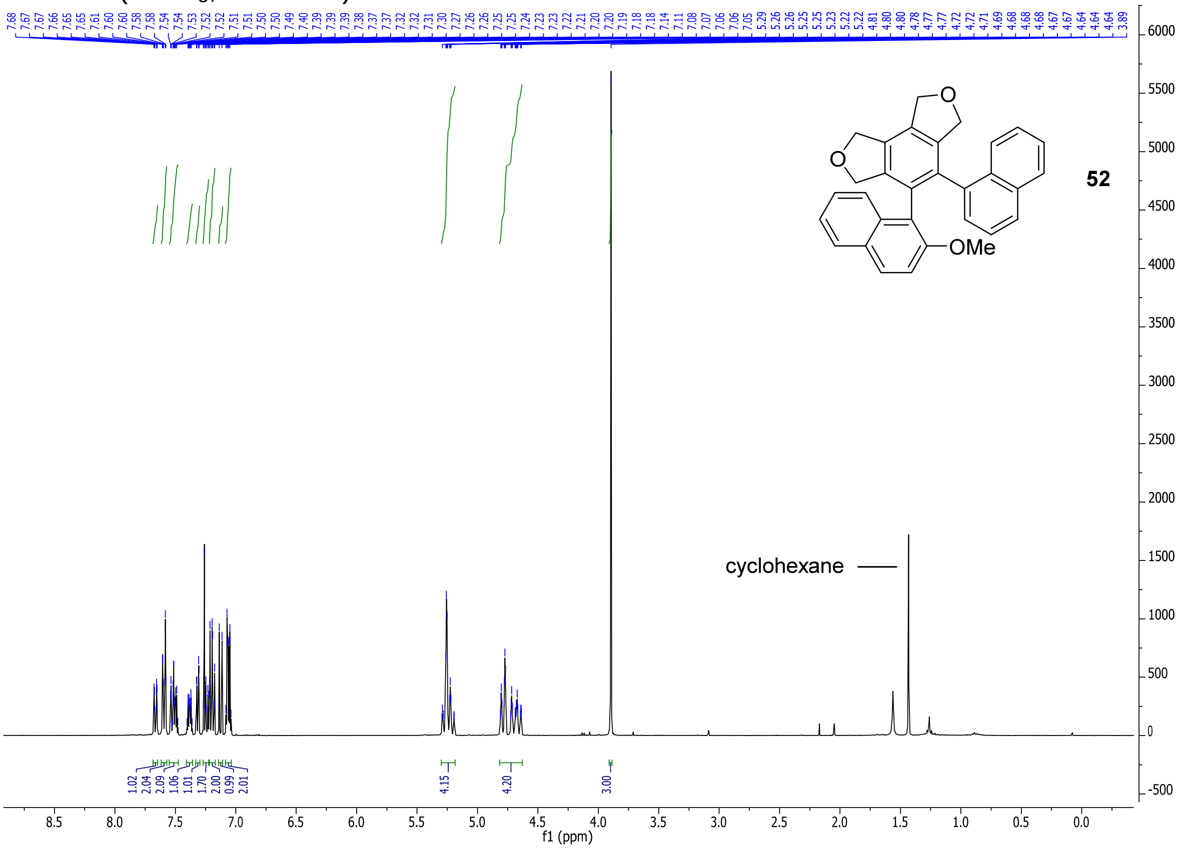
^{13}C NMR ($CDCl_3$, 100 MHz)



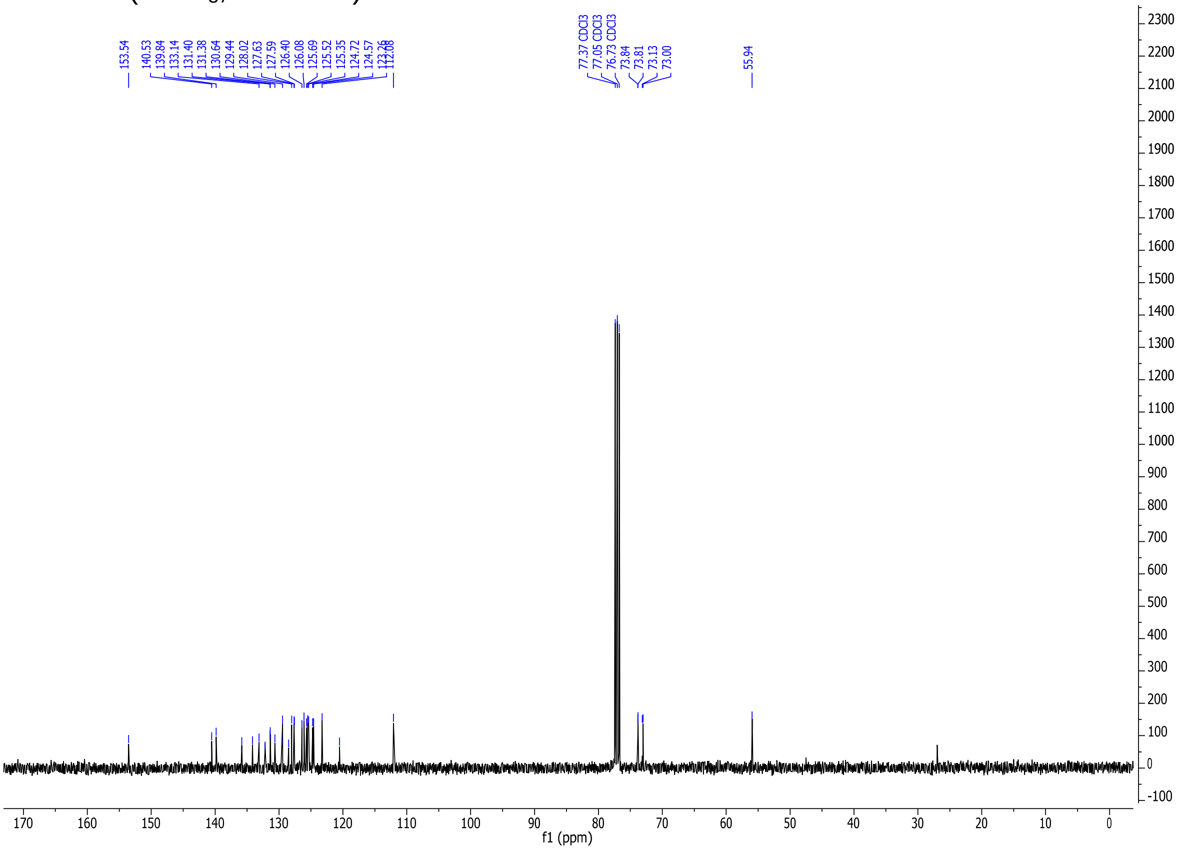
Compound 52:

fraction 2:

^{1}H NMR ($CDCl_3$, 400 MHz)

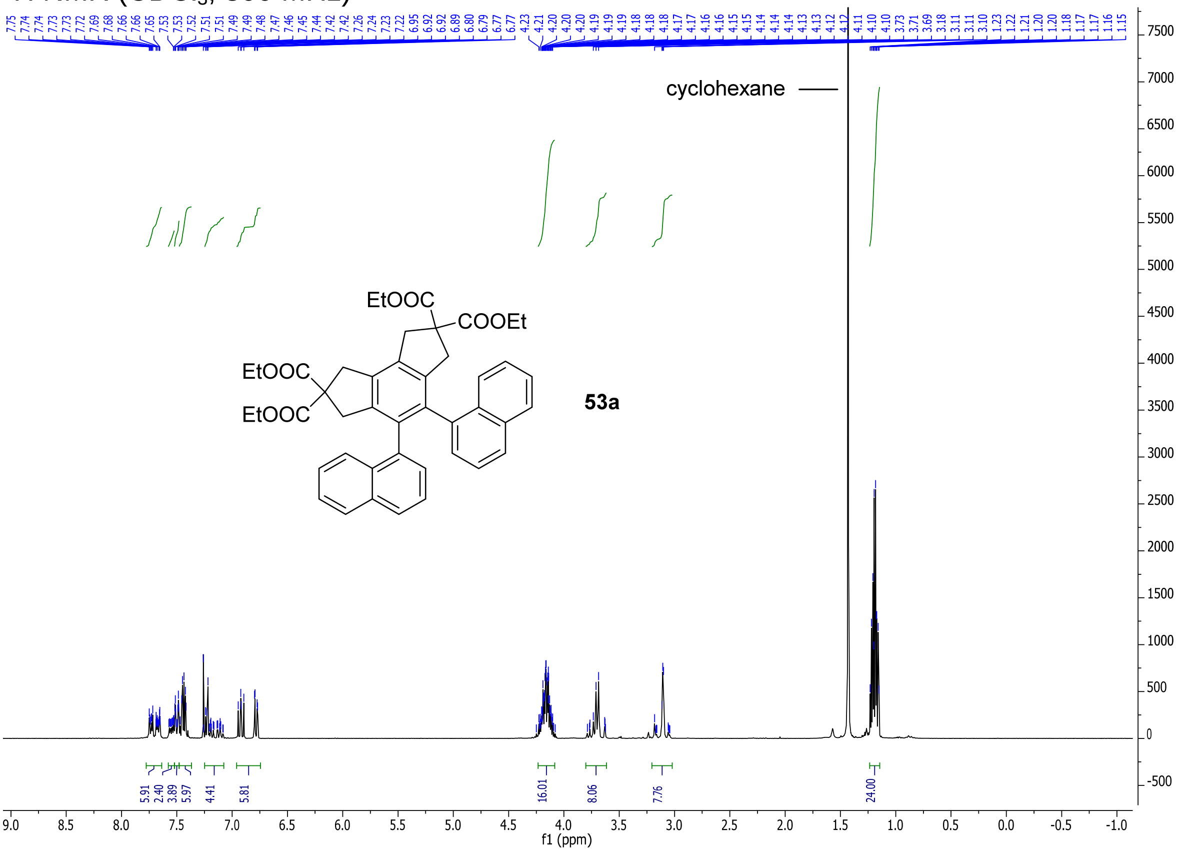


^{13}C NMR ($CDCl_3$, 100 MHz)

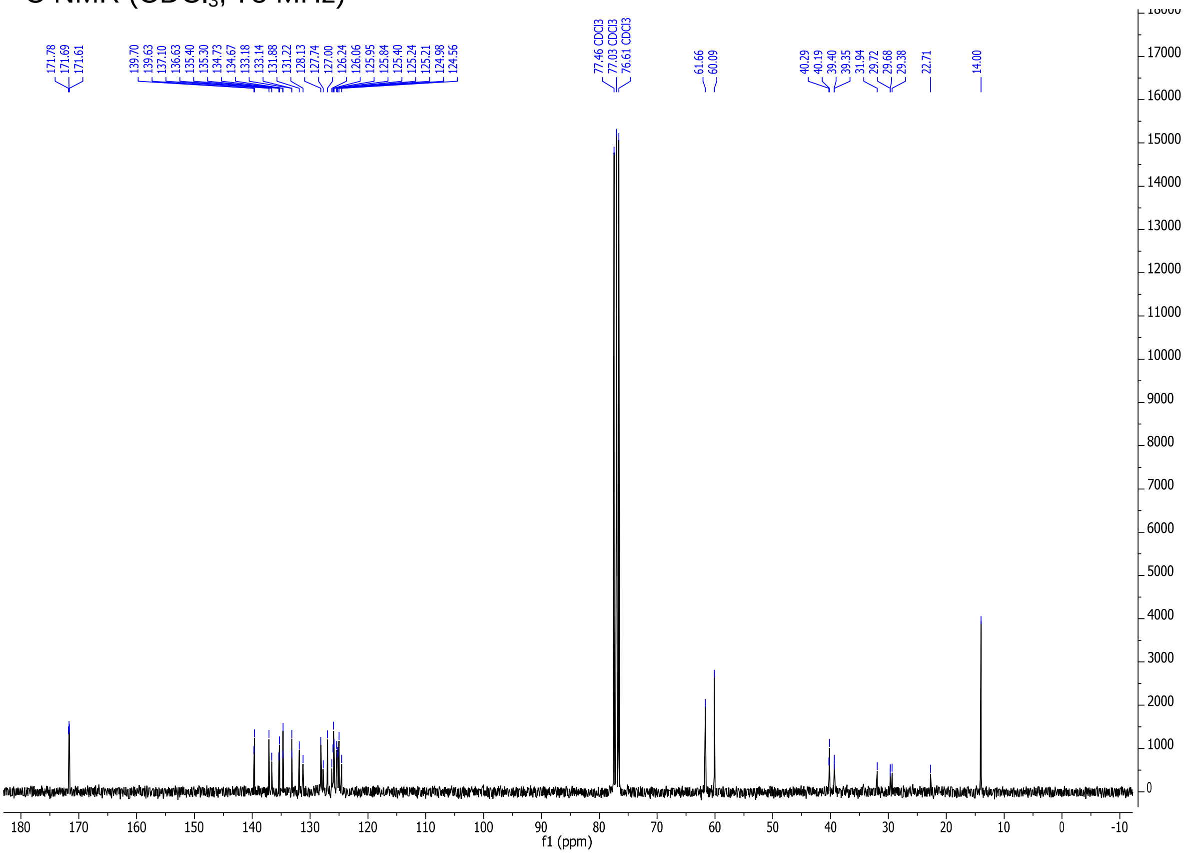


Compound 53a:

^{1}H NMR ($CDCl_3$, 300 MHz)

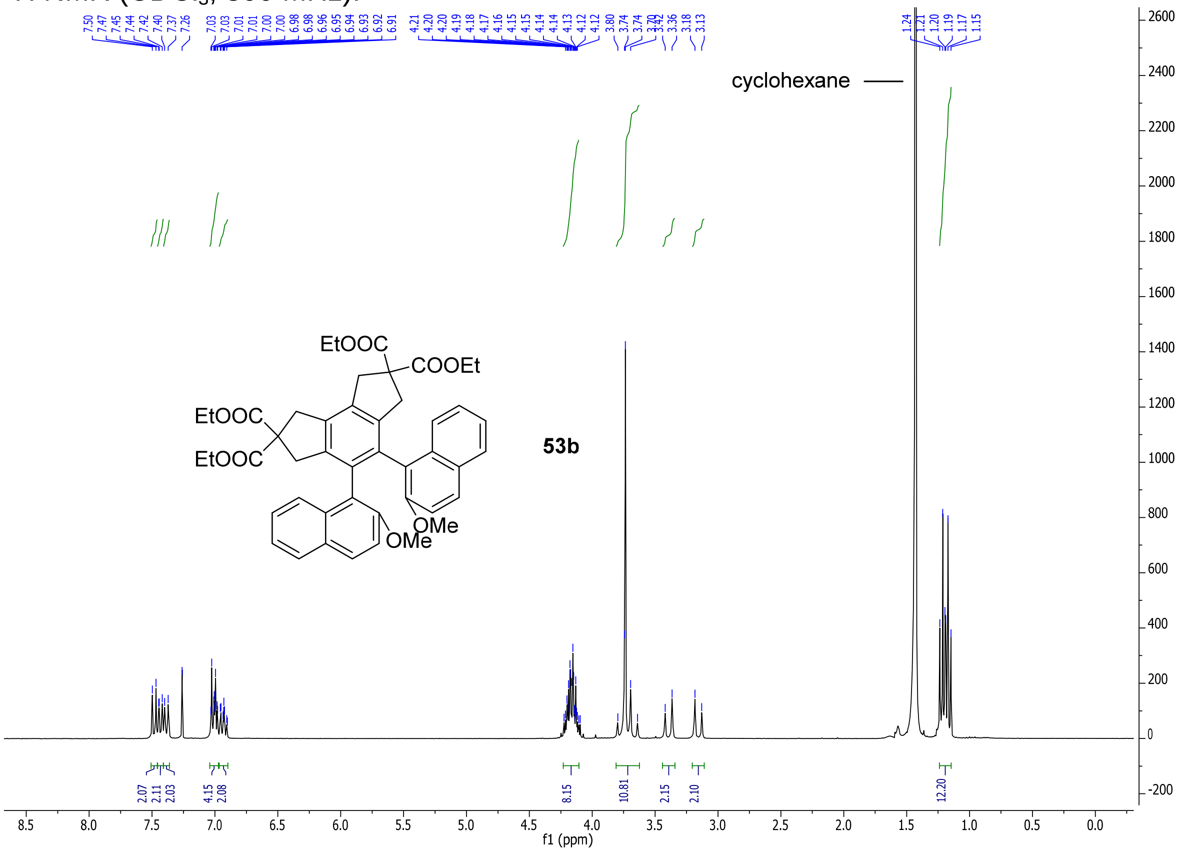


^{13}C NMR ($CDCl_3$, 75 MHz)

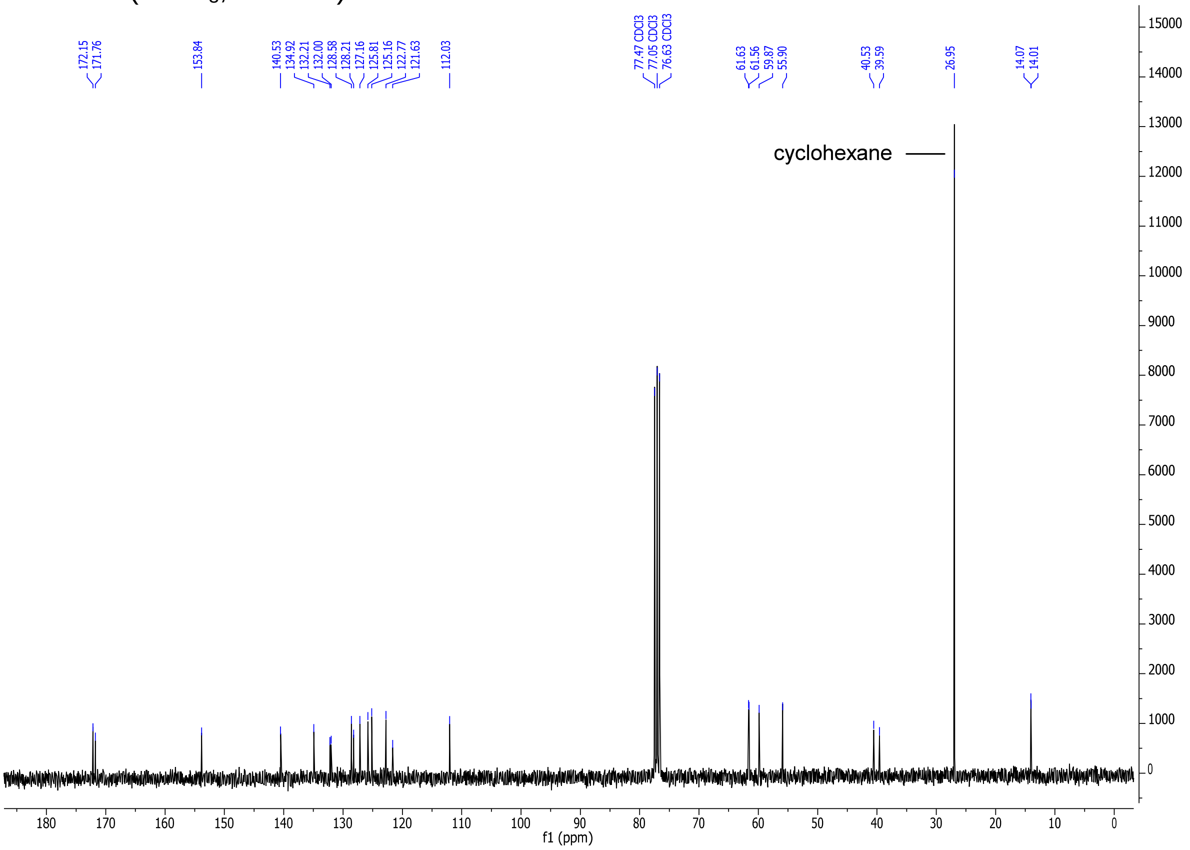


Compound 53b:

^{1}H NMR ($CDCl_3$, 300 MHz):

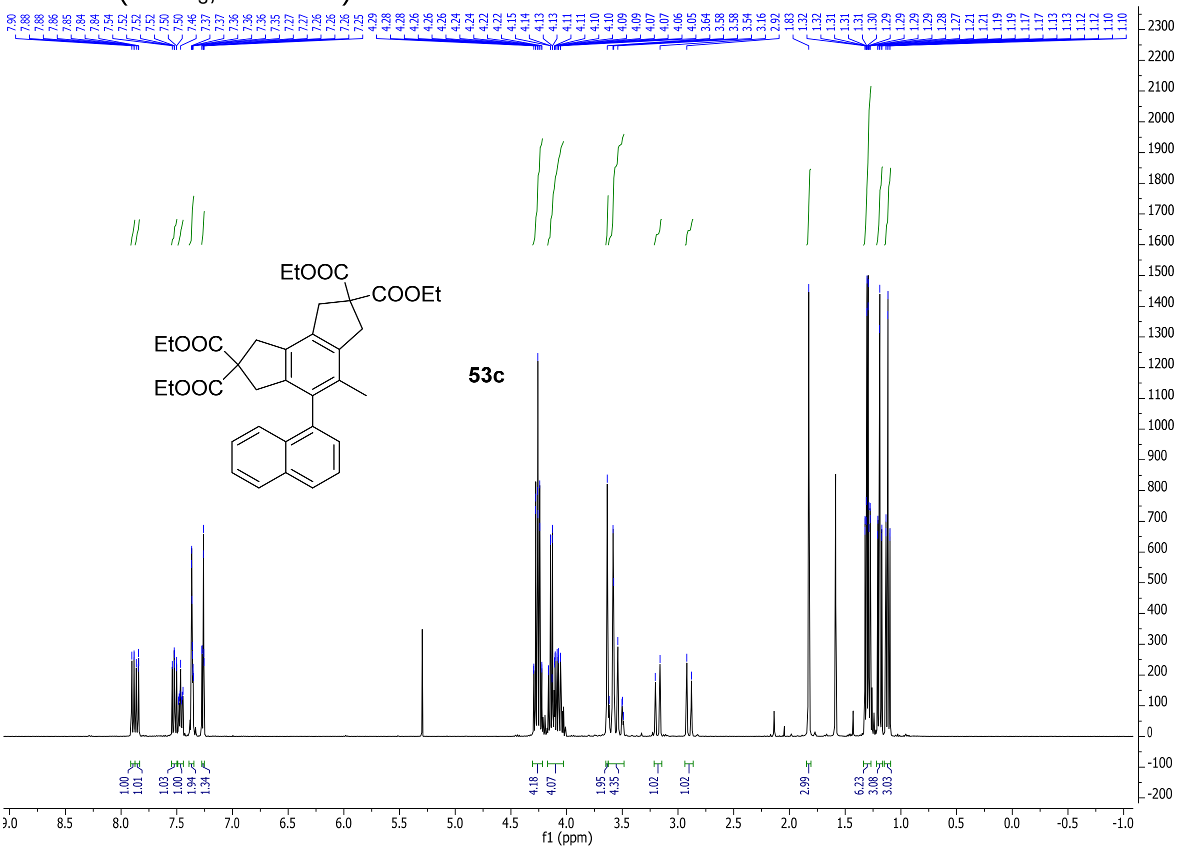


^{13}C NMR ($CDCl_3$, 75 MHz):



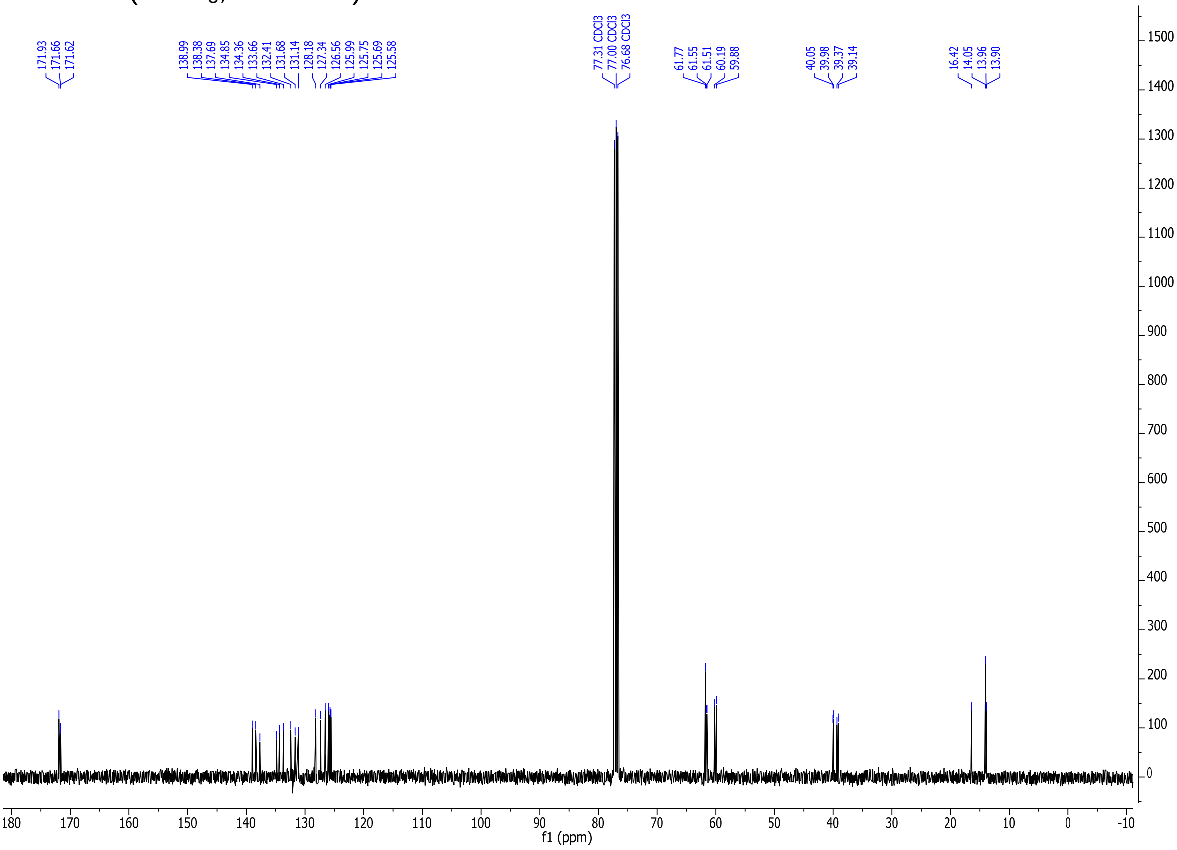
Compound 53c:

^{1}H NMR ($CDCl_3$, 400 MHz)



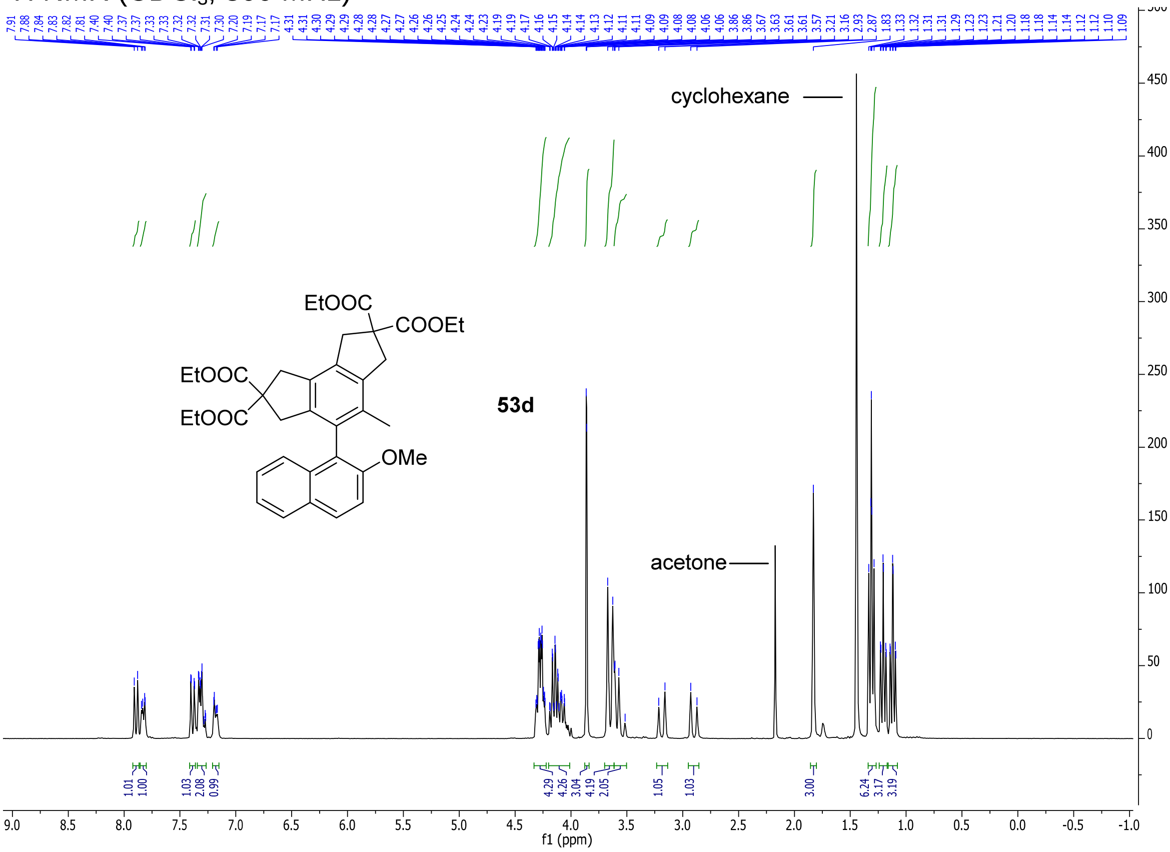
53c

^{13}C NMR ($CDCl_3$, 100 MHz):

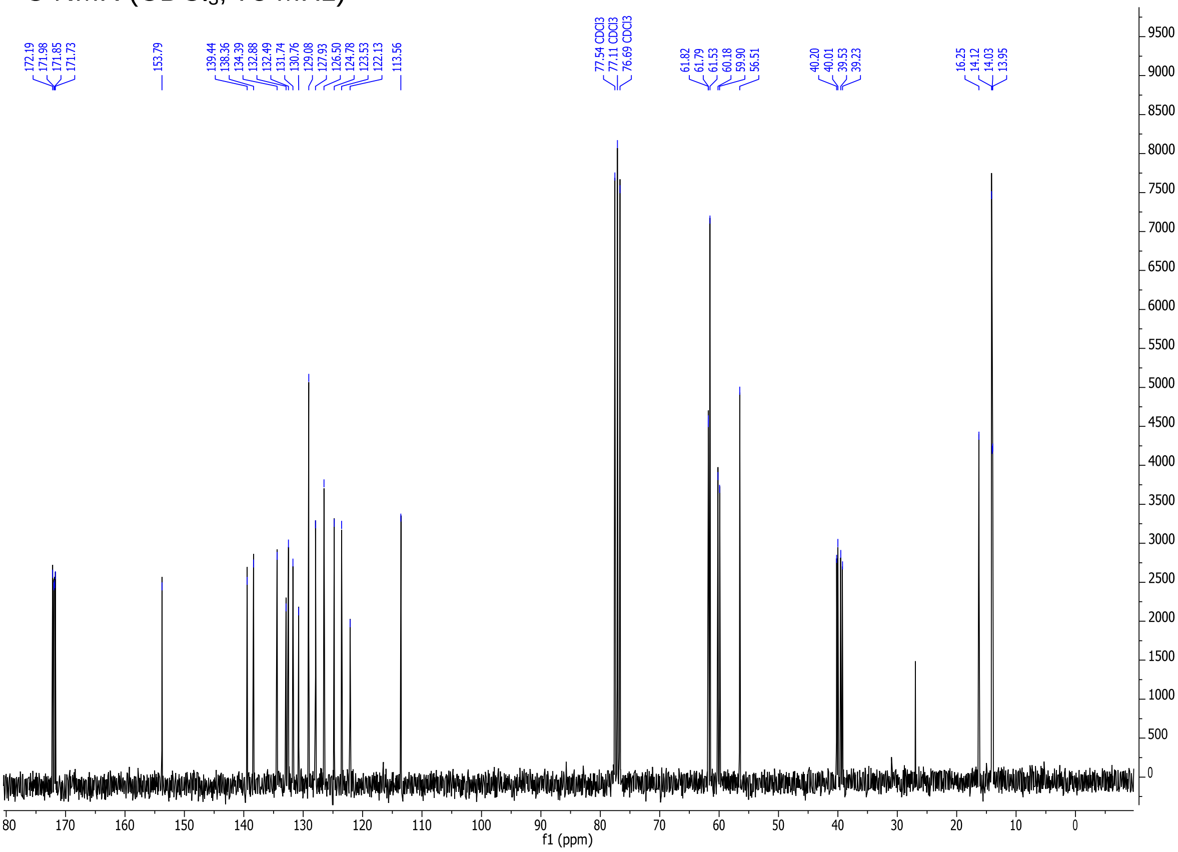


Compound 53d:

[1]H NMR ($CDCl_3$, 300 MHz)

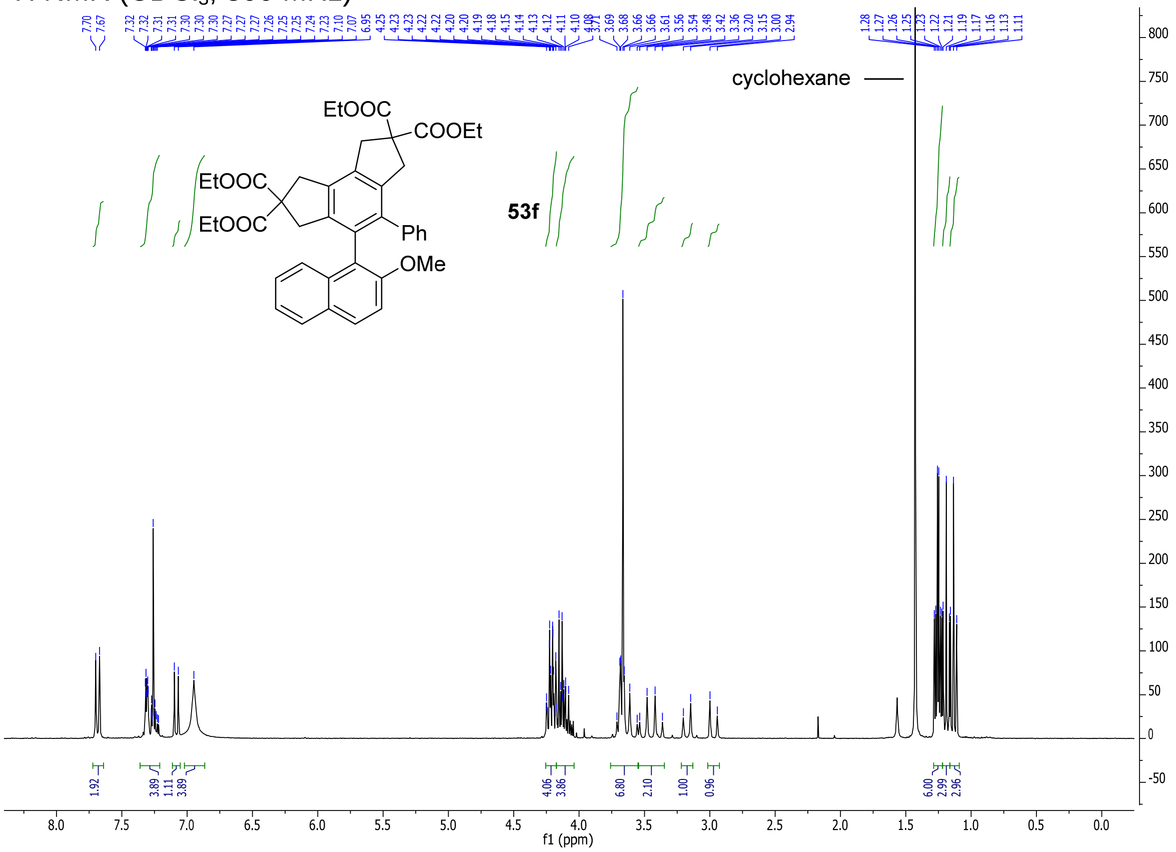


[13]C NMR ($CDCl_3$, 75 MHz)

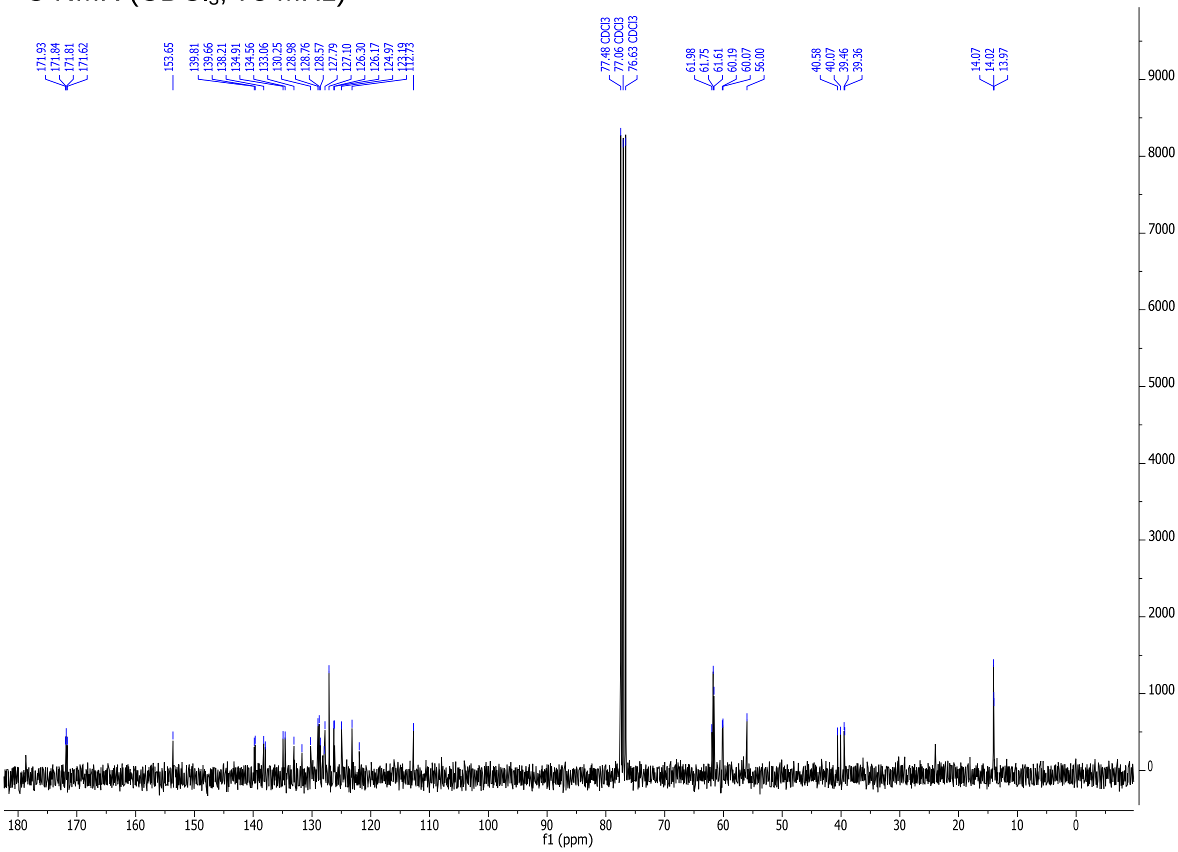


Compound 53f:

^{1}H NMR ($CDCl_3$, 300 MHz)

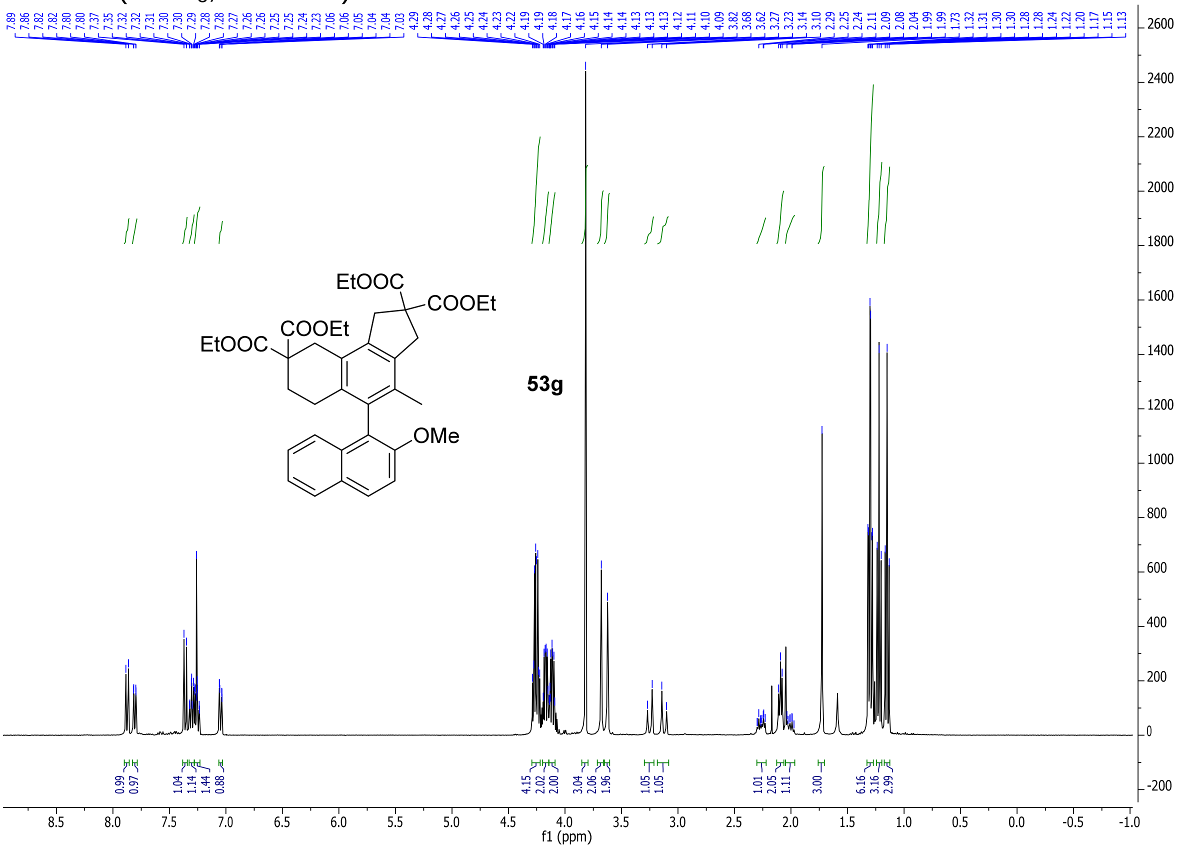


^{13}C NMR ($CDCl_3$, 75 MHz)

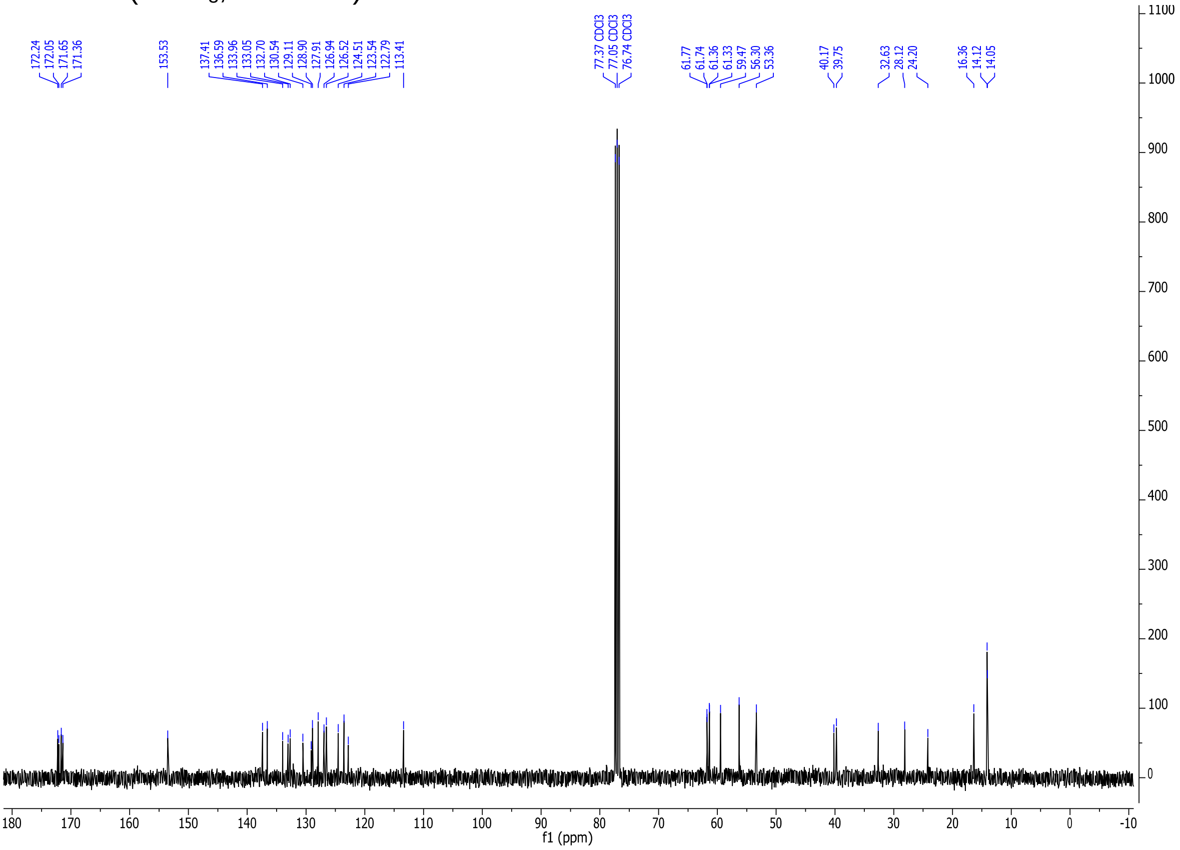


Compound 53g:

^{1}H NMR ($CDCl_3$, 400 MHz)

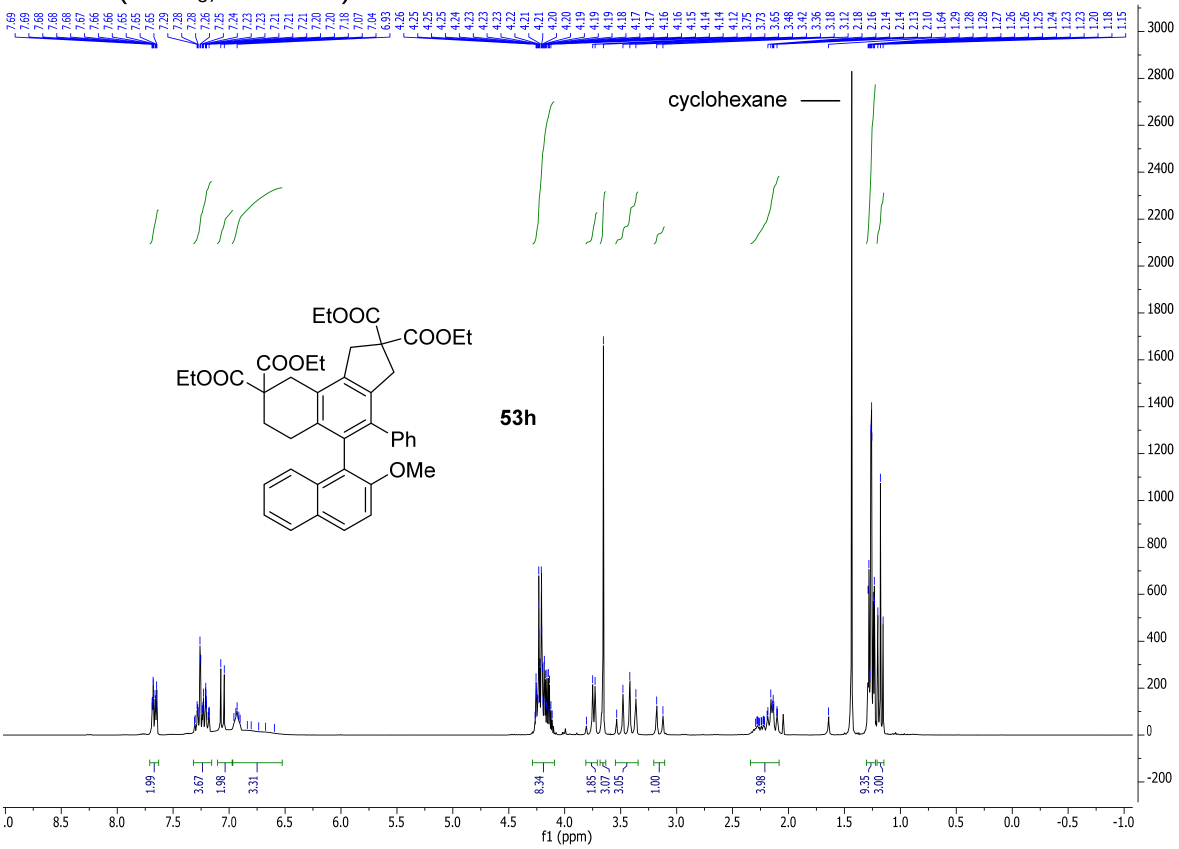


^{13}C NMR ($CDCl_3$, 100 MHz)

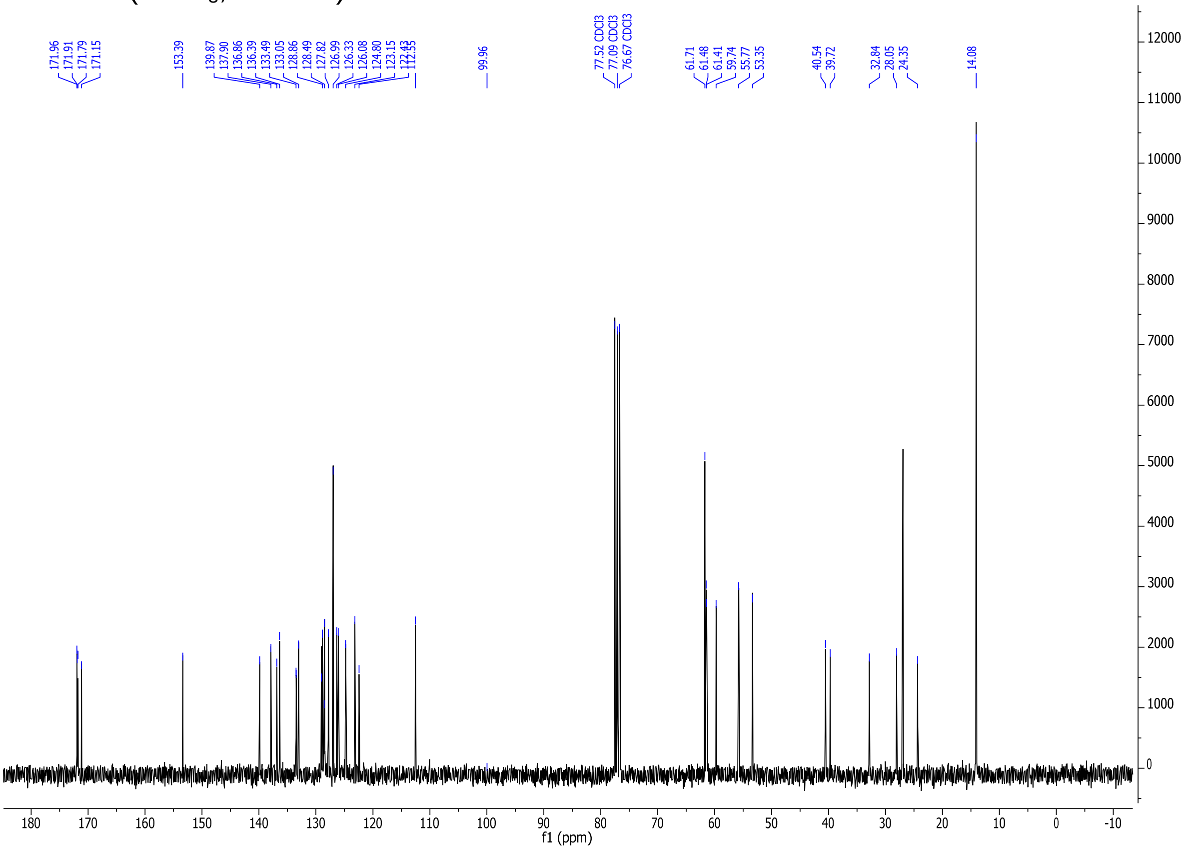


Compound 53h:

^{1}H NMR ($CDCl_3$, 300 MHz)

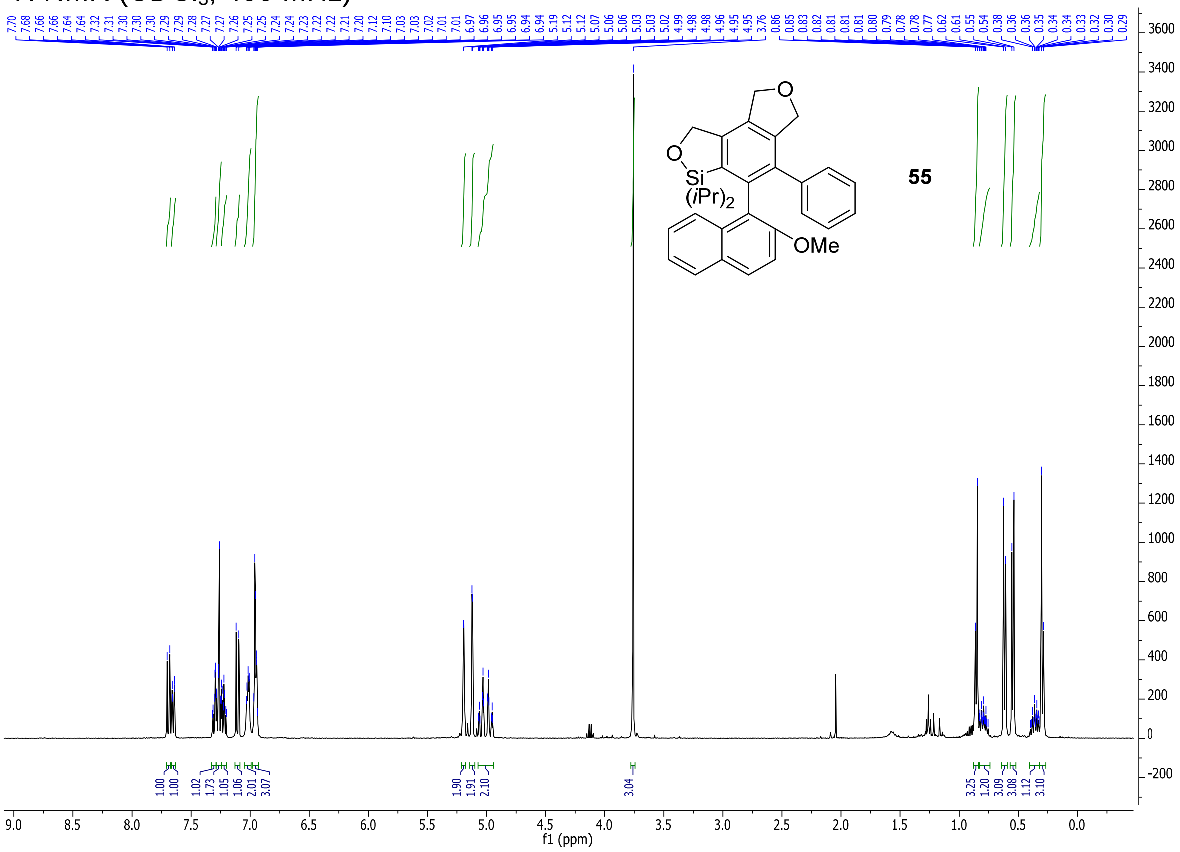


^{13}C NMR ($CDCl_3$, 75 MHz)

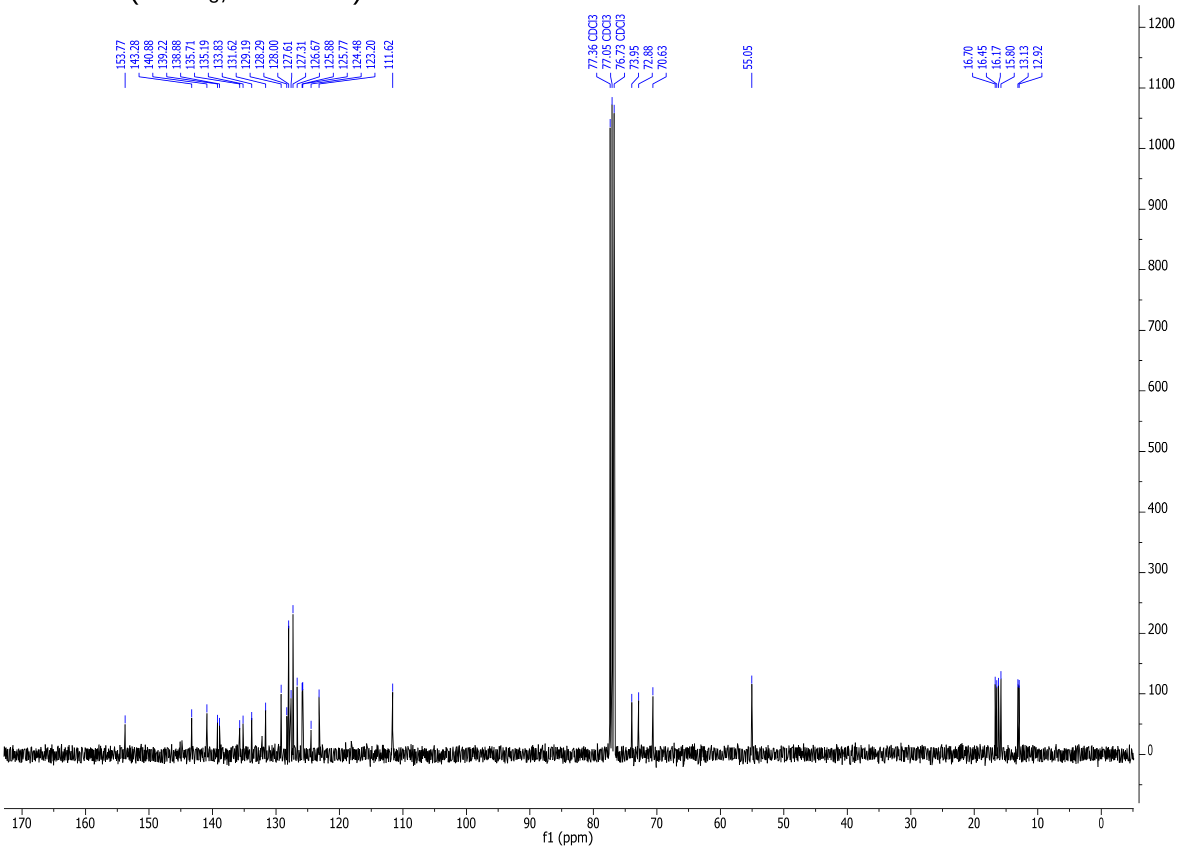


Compound 55:

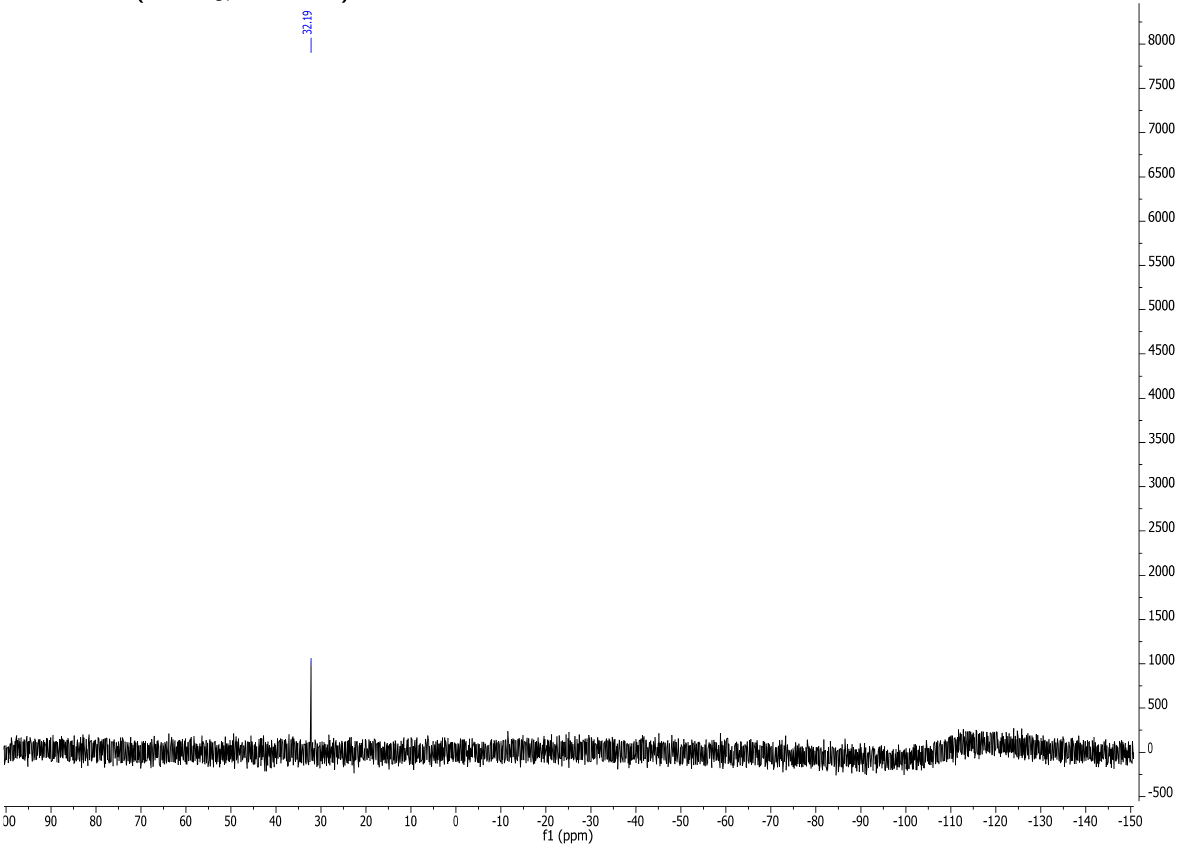
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 100 MHz)

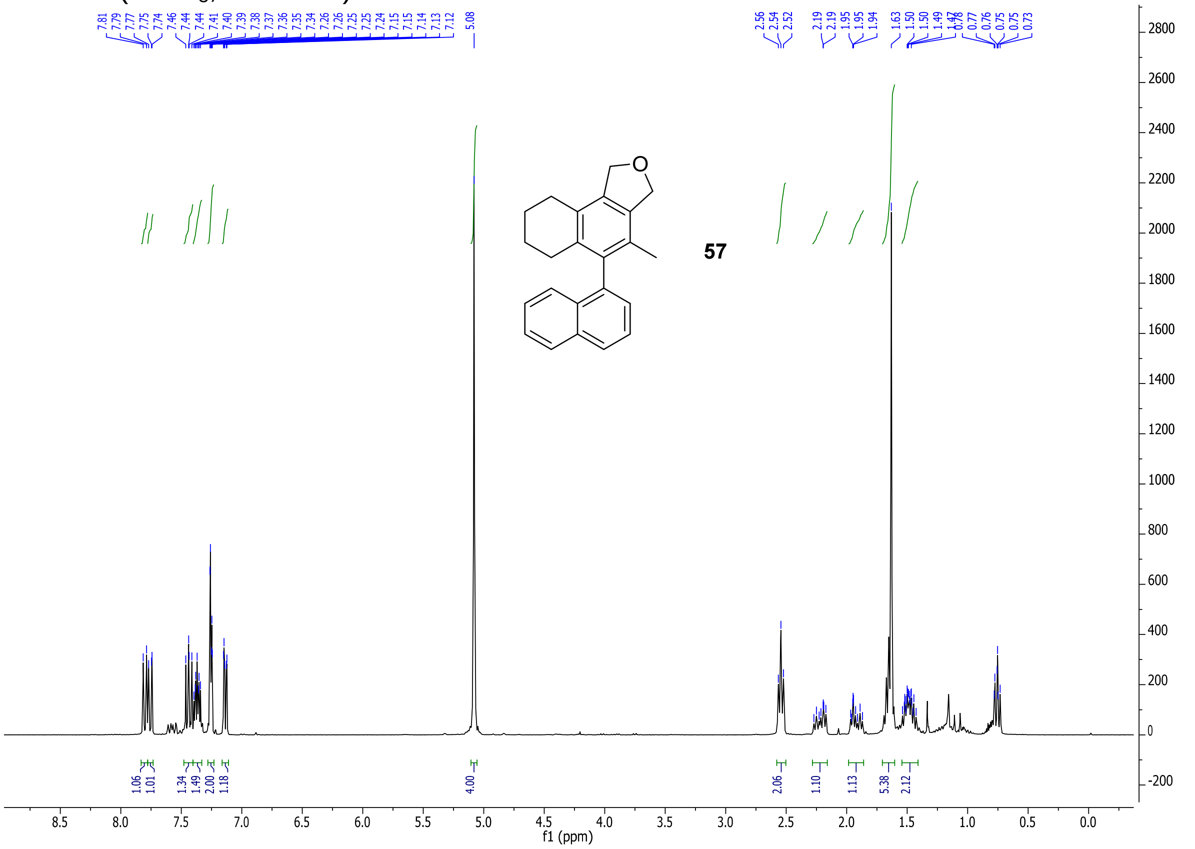


^{29}Si NMR ($CDCl_3$, 79 MHz)



Compound 57:

^{1}H NMR ($CDCl_3$, 300 MHz)



^{13}C NMR ($CDCl_3$, 75 MHz)