Synthesis and application of 4,5-disubstituted carbazoles

by

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A thesis submitted to

The University of Birmingham

For a degree of

DOCTOR OF PHILOSOPHY



School of Chemistry

College of Engineering and Physical Sciences

The University of Birmingham

October 2022

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Dedication

I dedicate this thesis first to two special people who set me off on the road to this PhD a long time ago, my mother and my father. Second, this thesis is for everyone who put in time, effort and energy to be chemists in this world.

Acknowledgments

First and foremost, I thank the Almighty Allah for his abundant grace in getting me through this process.

Next, I am grateful to the generous support from the Prince Sattam bin Abdulaziz University for funding my research.

There are so many people without whom this endeavour would have been impossible. I owe very warm thanks to Dr Grainger. I am grateful for his patience, guidance, support, encouragement, enthusiasm and constructive feedback throughout this project.

Thank you also to my second supervisors, Paul Davies and the late Professor John Fossey who sadly passed away this year. Words cannot express my gratitude to staff and people in the School of Chemistry at the University of Birmingham.

Special thanks go to members of the analytical facility: Dr Louise Male, Dr Cécile Le Duff, Christopher Williams, Dr John Wilkie, Ian Wilkinson, Katherine Webb, Richard Petford, Trevor Hardy, and Nicky Gillece. I would like to extend my sincere thanks to Dr Liam Cox and his group. I am also grateful to Dr Holly Adcock for her help and moral support.

Thanks, should also go to Jon Preece's group, especially Dr Owen Jones and Dr Michael Butlin whose help in photophysical concepts has been instrumental. Also, I am grateful to Dr Alexander Quy for sharing his knowledge and experience of boronic compounds.

Thanks also to the Neil Champness group, especially Asia Almhuna and Dr Nicholas Pearce for help with X-ray analysis.

Moreover, I am indebted to the Grainger Group for their support. I would especially like to thank Dr Sanaz Ahmadipour, Dr Nicholas Cundy, Dr Connor Prior, Dr Charlotte Farrow, Dr Ian Pocock, and Isobel Barker and other members. Special thanks are also owed to Prof. Jim Tucker group, namely Dr Media Ismail, Dr Francia Allabush and Dr Klaudia Englert and Jack Dismorr, and other members. I would like to thank them all for their support, enlightening discussions, and the collegiality.

Finally, I am eternally grateful to my family for their love, their belief in me and their unconditional support. My husband, and my son Muteb, have been exceptionally patient and very encouraging throughout the PhD process. To Faisal and Njood, I would like to say thank you for being there from the beginning to the end of my Ph.D. journey.

My biggest thanks go to my parents and my siblings in Saudi Arabia. Their belief in me has kept my spirits and motivation high during this process. Also, I would like to thank my lovely friends and neighbours in Birmingham - Alya Alqhtani for help and support during my PhD journey and Ahad Alotaibi for her support and help through my writing up stage. Additional third-party editorial assistance from Linda Kirby and Aaliya Ragah is also acknowledged.

Abstract

Carbazoles are widely exploited for their interesting photophysical and electronic properties. However, (4,5-) functionalisation is challenging, and previously inaccessible through carbazole C-H activation. There is limited literature on the direct synthesis of substituted carbazoles, in particular at the 4,5 positions. In 2021, the Grainger group reported a direct and convenient method to synthesise 4,5-disubstituted carbazoles.

This thesis expands on this new protocol for the regioselective synthesis of 4,5-disubstituted carbazoles, and extends it to fluorenes, through direct C-H functionalization.

4,5-Disubstituted carbazoles and fluorenes were synthesised from *N*-TIPS carbazole **56** and 9,9-dimethyl fluorene **176** using a dilithiation methodology (*n*-BuLi and TMEDA) and quenching with different electrophiles. Subsequent reactions towards potential applications of these compounds were investigated. The novel 4,5 disubstituted carbazoles obtained are potentially useful in a range of fields.

X-ray crystal structures of select 4,5-disubstituted carbazole derivatives were obtained, and data analysed with respect to potential twisting and other deviations from the planar aromatic carbazole ring system. Photophysical properties were investigated for sulfur and selenium functionalised 4,5-disubstituted carbazoles and compared with the corresponding 3,6- disubstituted carbazoles.

4,5-Disubstituted dicarboxylate dibenzyl ammonium carbazole and fluorene salts were synthesized and crystallised.

Abbre*via*tions

Å	Angstrom
Ac	Acetyl
ap.	Apparent
aq.	Aqueous
Bn	Benzyl
br	Broad
Bu	Butyl
B_2pin_2	Bis(pinacolato)diboron
cat.	Catalytic
°C	Celsius
CTAB	Cetyltrimethylammonium bromide
conc.	Concentrated
d	Doublet
DMEDA	1,2-dimethylethylenediamine
DMF	*N,N*-dimethylformamide
DMSO	Dimethylsulfoxide
EDG	electron-donating group
eq.	Equivalent
ESI	electrospray ionisation
Et	Ethyl
EWG	electron-withdrawing group
g	gram(s)
h	hour(s)
Hz	Hertz
i	Iso
IR	Infrared
J	coupling constant (in NMR)
L	Litre
LiHMDS	Lithium bis(trimethylsilyl)amide
m	Multiplet
M	Molar
M	*Meta*
m-CPBA	*meta*-chloroperoxybenzoic acid
Me	Methyl
min	minute(s)
mol	Moles
mp	melting point
m/z	mass/charge
n	Normal
n/d	Not determined
NBS	*N*-bromosuccinimide
NMO	*N*-methylmorpholine-*N*-oxide
NMR	nuclear magnetic resonance
[O]	Oxidation

O	*Ortho*
p	*Para*
o/n	*Overnight*
Ph	Phenyl
ppm	part(s) per million
Pr	Propyl
Piv	Pivalyl or pivaloyl group
PAH's	polycyclic aromatic hydrocarbons
q	Quartet
quant.	Quantitative
rt	room temperature
Sat	Saturated
s	Singlet
t	*Tert*
Temp	Temperature
t	Triplet
TBAF	tetrabutylammonium fluoride
THF	Tetrahydrofuran
TIPS	Triisopropylsilyl
TLC	thin layer chromatography
TMEDA	*N*, *N*, *N*', *N*'-Tetramethylethylenediamine
u	atomic mass unit
UV	Ultraviolet
vs.	Versus
v	Frequency

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Chapter 1: Synthetic approaches to disubstituted carbazoles

1.1 Carbazole structure and importance

Carbazoles are a group of natural compounds found in a wide range of higher plants. The first simple carbazole from plant sources was identified from coal tar in 1872 by Graebe and Glaser.[1] However, this natural chemical was not discovered until the 1960s.[1] Natural sources have yielded a vast number of biologically active carbazole alkaloids.

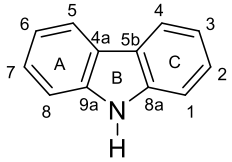


Figure 1: Chemical structure of carbazole **1**

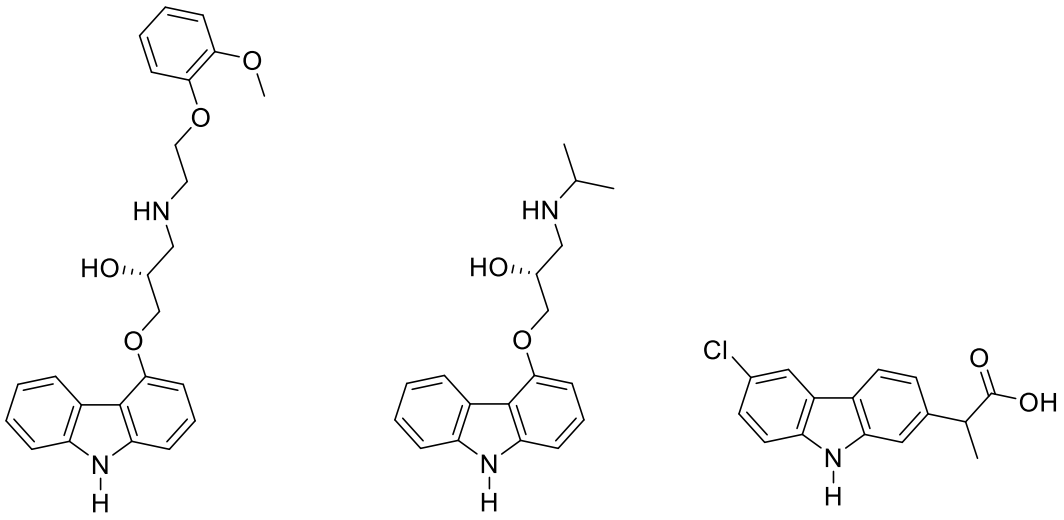
Carbazole is the generic name for 9H-carbazole **1**, a tricyclic structure containing a pyrrole ring bonded to benzene rings on both sides (**Figure 1**).

The chemistry of carbazole has been investigated for many years. Carbazole and its derivatives are known to have important photophysical and biological properties. Four fundamental advantages of carbazole as an organic material have been highlighted: (1) low cost; (2) ease of functionalisation at the nitrogen atom, allowing property modification without changing the backbone; (3) multiple linkage positions on its backbone; and (4) aromatic properties that confer stability under a wide range of conditions.[2]

In recent years, carbazoles have attracted great attention for a variety of applications in organic and medicinal chemistry as well as in materials science.[3]

Carbazole analogues are utilised for a range of biological responses such as antitubercular,[4, 5] antibacterial,[6] [7]antifungal,[7] antitumor,[8] [9]and antialzheimer.[10] The carbazole skeleton can be seen in several drugs on the market including carvedilol **2**, carazolol **3**, and carprofen **4** (**Figure 2**). Carvedilol

is a non-selective β-1, and β-2 adrenergic blocker used in the treatment of congestive heart failure.[11] Carazolol is also a β-adrenergic blocker which is employed in non-human mammals to treat cardiovascular disease.[12] Carprofen is a non-steroidal anti-inflammatory drug used as a non-selective inhibitor of cyclooxygenase-1 (COX-1) and cyclooxygenase-2 (COX-2) to relieve pain and inflammation in animals.[13] Compounds with a carbazole nucleus have a lot of potential for therapeutic development. As a result, using the structure activity relationship (SAR) to manipulate substitutions and linkers at different places in the carbazole nucleus can be beneficial for the development of new therapeutic compounds.[5]

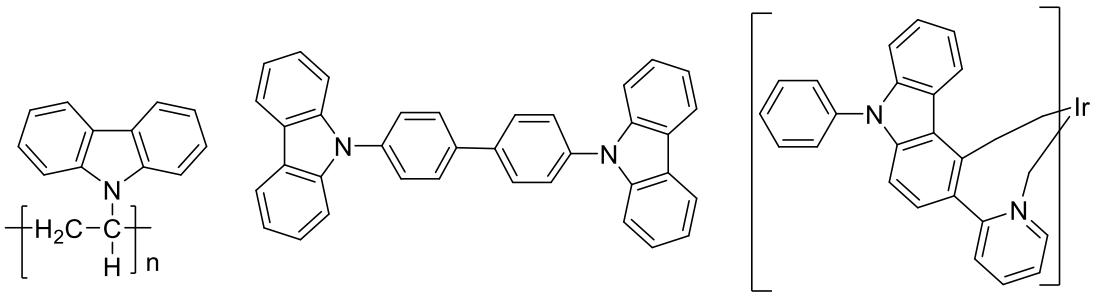


Carvedilol **2** Carazolol **3** Carprofen **4**

Figure 2: Carbazole scaffold-containing medications on the market

1.2 Application of carbazole derivatives

Carbazole chemistry has been studied for many years. However, in recent years, carbazole and carbazole-derived compounds, such as polymers, have received significant attention since they are particularly valuable in electronic materials such as photoconducting polymers and organic optoelectronic materials (**Figure 3**).[3, 14-18]

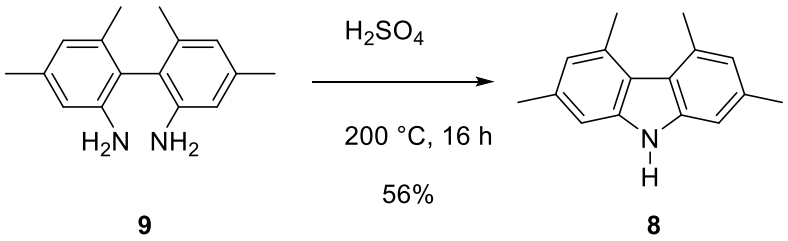


Photoconducting polymer **5** Green host materials Phosphorescent OLEDs **6** Electrophosphors **7**

Figure 3: Carbazole scaffold-containing electronic materials.

1.3 Synthesis of 4,5-disubstituted carbazoles

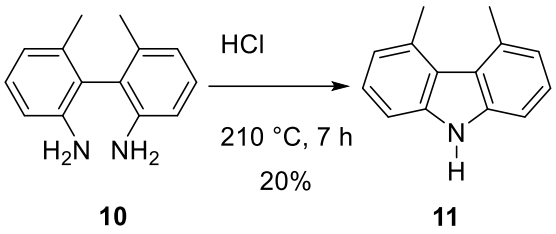
In view of the increasing significance of carbazoles, numerous routes to synthesise the carbazole ring system have been reported in the literature. Most of these strategies start from non-carbazole precursors.[19, 20] 4,5-Disubstituted carbazoles are important intermediates in the synthesis of natural products and materials. In 1890, Ernst Täuber used the acid-promoted, high-temperature conversion of 2,2'-diaminobiphenyls to carbazoles.[21] Robert B. Carlin and William O. Forshey reported the synthesis of 2,4,5,7-tetramethylcarbazole **8** in 56% yield *via* a Täuber Carbazole Synthesis. Diaminotetramethylbiphenyl **9** was heated with sulfuric acid, as shown (**Scheme 1**). [22]



9 **8**

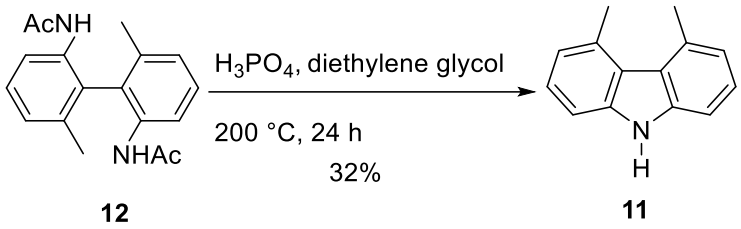
Scheme 1: Täuber Carbazole Synthesis

Cyclisation of 2,2'-diamino-6,6'dimethylbiphenyl **10** in hydrochloric acid gave 4,5-dimethylcarbazole **11** in 20% yield (**Scheme 2**).[23]



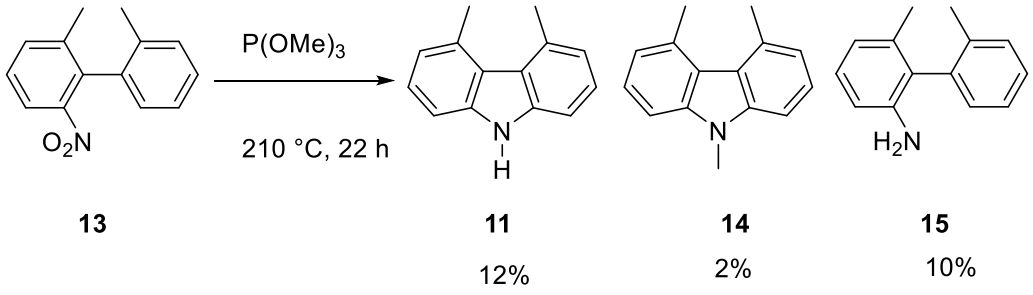
Scheme 2: Synthesis of 4,5-dimethylcarbazole **11**

When 2,2'-bis(acetamido)biphenyl **12** was heated with H_3PO_4 and diethylene glycol was used in the ring closure reaction to synthesise **11**, a 32% yield resulted from this method (**Scheme 3**).[24] Strongly acidic conditions and high reaction temperatures are necessary for each of these procedures.



Scheme 3: Acid-mediated intramolecular amination for synthesis of 4,5 dimethylcarbazole **11**

4,5-Dimethylcarbazole **11** was also prepared *via* the Cadogan cyclisation.[25] This method involved reductive cyclisation of 2,2'-dimethyl-6-nitrobiphenyl **13** by trimethyl phosphite (**Scheme 4**).[23]

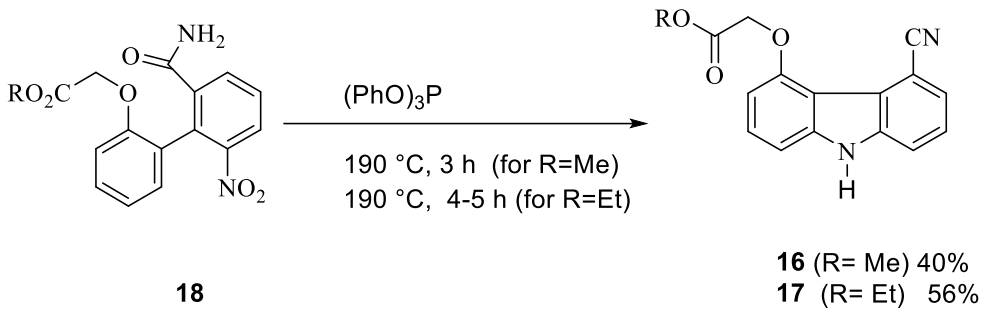


Scheme 4: Cadogan cyclisation of 2,2'-dimethyl-6-nitrobiphenyl **13** to give 4,5-dimethylcarbazole **11**

The low yields of 4,5-dimethylcarbazole **11** are probably caused by the unfavourable conformations of the nitro-compound and nitrene for ring closure. [23]

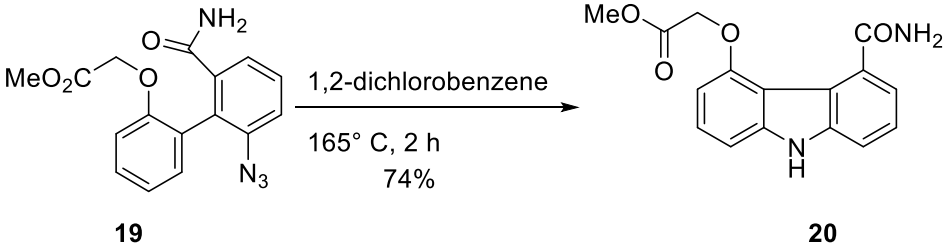
May et *al*. used the Cadogan cyclisation to synthesise 4,5-disubstituted carbazole **16**, **17** .[26]

The reactions were conducted **18** in triphenylphosphite and gave 4,5-disubstituted carbazoles **16** in 40 % and **17** in 56% yield respectively (**Scheme 5**).[26]



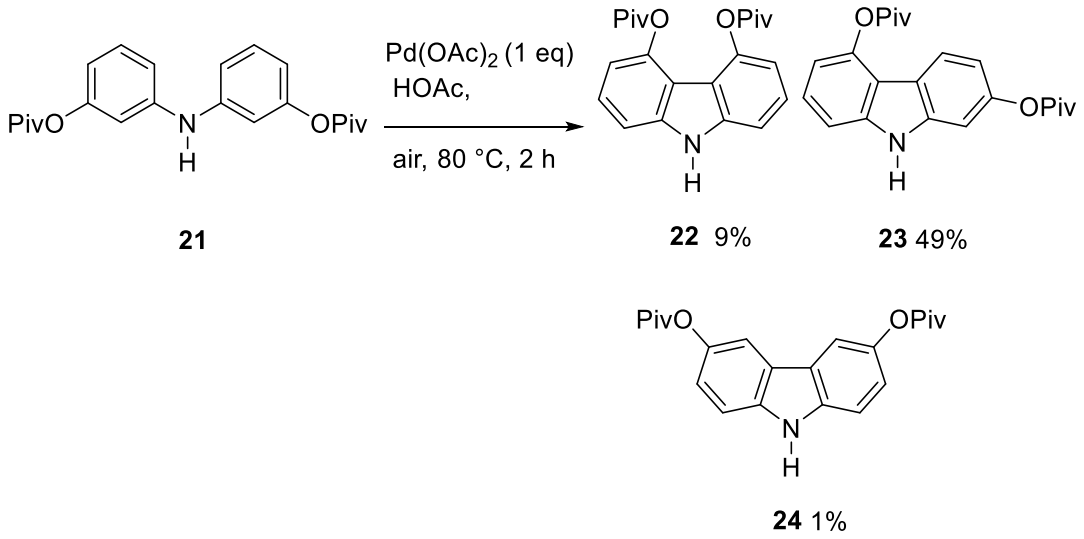
Scheme 5: Cadogan cyclisation to give 4,5-disubstituted carbazole **16** and **17**

The thermal decomposition of azide **19** afforded **20** in 74% yield (**Scheme 6**).[26] This reaction is less appealing due to the risks in the use of an azide.



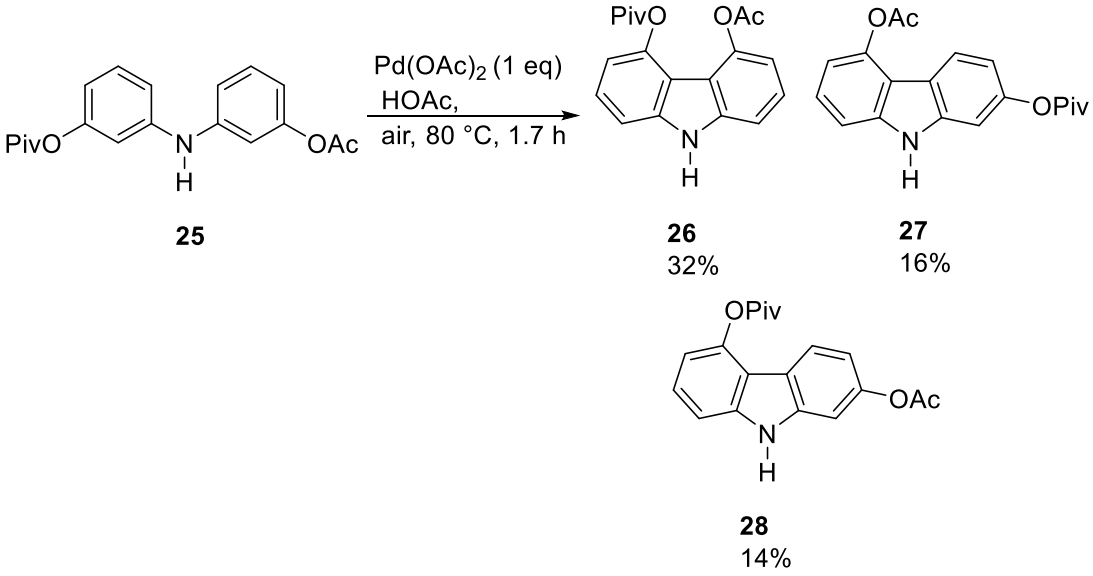
Scheme 6: Azide **19** decomposition to give carbazole **20**

In 1975, Akermark *et al*. reported the transformation of diarylamines to a carbazole *via* palladium-mediated oxidative cyclisation.[27] Recently, this method was used to form 4,5-disubstituted carbazoles .[28] The oxidative cyclisation of compound **21** gave 4,5-disubstituted carbazole **22** in a 9% yield, but also gave the 2,5-disubstituted carbazoles **23** and 3,6-disubstituted carbazoles **24** in 49% and 1% yield respectively (**Scheme 7**).



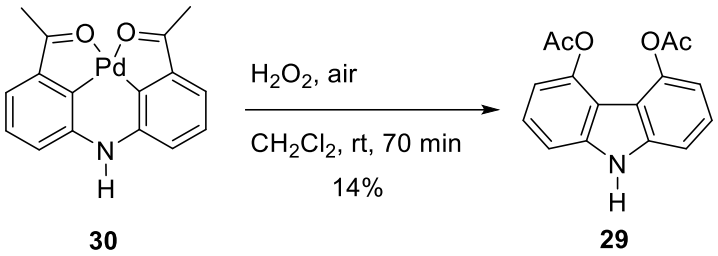
Scheme 7: Synthesis of 4,5-disubstituted carbazoles

A significant regiodirecting effect of the substituents was confirmed by mechanistic studies. An acetyl group was substituted for one of the pivaloyl groups to enable an improvement in the production of a 4,5-disubstituted isomer.[28] The oxidative cyclisation of compound **25** was also giving **26** in 32% yield along with other regioisomers **27** and **28** (**Scheme 8**).[28]



Scheme 8: Palladium (II)-catalysed oxidative cyclisation of diarylamines for carbazole synthesis.

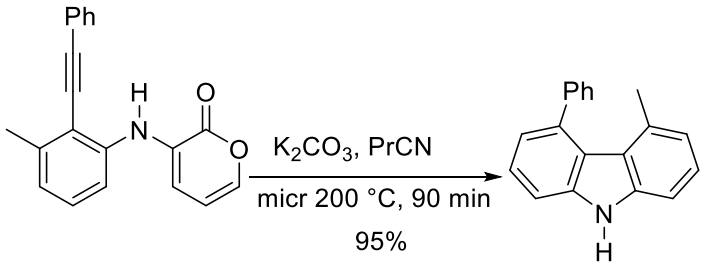
Also, 4,5-diacetyl carbazole **29** was synthesised from the direct reductive elimination of diarylpalladium(II) complex **30** (**Scheme 9**).[29]



30 **29**

Scheme 9: Synthesis of 4,5 diacetyl carbazole **29** by reductive elimination of diarylpalladium(II) complex **30**

In 2021, Beaudry *et al*. reported a new regioselective carbazole synthesis .[30] The diarylamine **31** was heated *via* microwave radiation in the presence of a base to give 4-methyl-5-phenyl-9H-carbazole **32** in 95% yield (**Scheme 10**).[30]



31 **32**

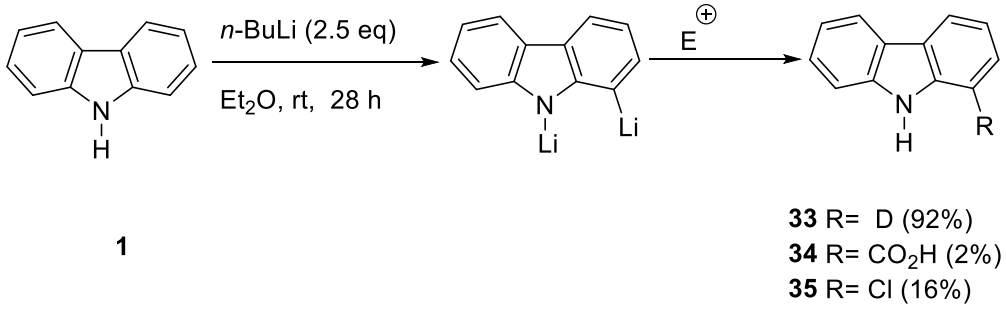
Scheme 10: Synthesis of 4-methyl-5-phenyl-9H-carbazole **32**

In this reaction intramolecular cycloadditions of alkyne-tethered 3-anilido-2-pyrones **31** associated with loss CO_2 to form substituted carbazoles **32** in high yield.

All the previous cited methods used to prepare 4,5-disubstituted carbazoles have some limitations. For instance, all these methods do not start with carbazole. In addition, some of them used harsh conditions to promote the reaction.

1.4 Direct functionalisation of carbazole

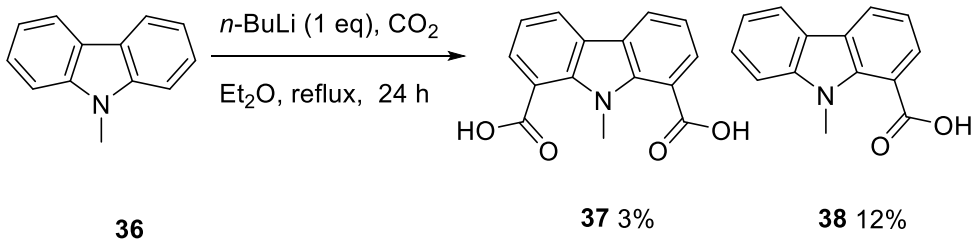
Metalation of carbazole with lithium, sodium, potassium, calcium or mercury has been reported in the literature.[31, 32] In 1988 Katritzky and co-workers, were reported the lithiation of carbazole **1**.[33] Using 2.5 equiv of *n*-butyllithium in diethyl ether at room temperature for 28 hours and quenching with different electrophiles (**Scheme 11**).[33]



Scheme 11: The lithiation of carbazole **1** with different electrophiles

1.4.1 Lithiation of protected N-carbazoles

In 1952, Gilman *et al*. described lithiation of carbazoles to synthesise carbazole derivatives.[34] The *N*-methylcarbazole reacted with *n*-BuLi followed by carbonation to give mono-carboxylic acid **38** in 12% yield and dicarboxylic acid **37** in 3% yield (**Scheme 12**).[34]

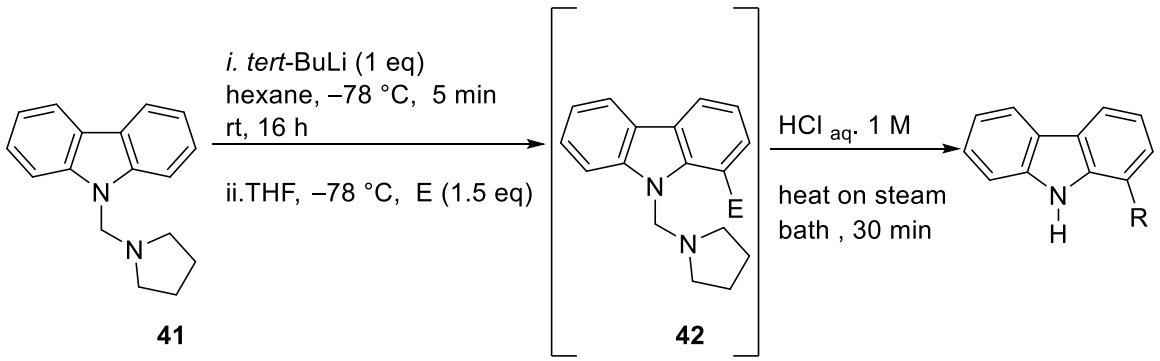


Scheme 12: Lithiation of *N*-methylcarbazole **36**

Only mono-carboxylic acid **39**, was produced when the identical reaction conditions were applied to *N*-ethylcarbazole **40**. [35] This was explained by the fact that dimetalation was more challenging due to the bigger ethyl group. However, only 1,8 position of the carbazole can be synthesised by these lithium mediated metalations.[32, 33, 36]

In 1987, Katritzky *et al*. used lithiation of 9-(l-pyrrolidinomethyl) protected carbazole **41** with a range of electrophiles to synthesise 1-functionalised carbazoles in good yield (**Table1**).[33] Additionally, the lithiation of other carbazole derivatives gave also 1-position carbazole derivatives.[35]

Table 1: Lithiation of *N*-protected carbazole with a range of electrophiles



41 **42**

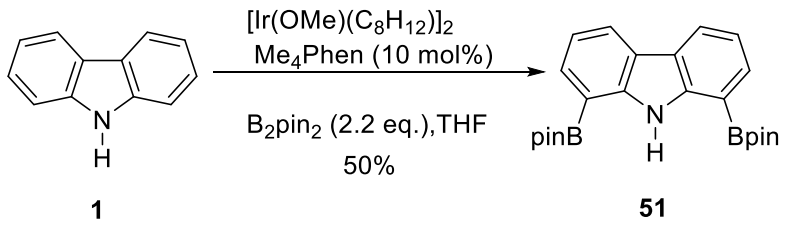
Electrophile	**R**	**Yield %**
CO_2	CO_2H	**43** (86)
C_2Cl_6	Cl	**44** (100)
CH_3I	CH_3	**45** (70)
$CH_3(CH_2)_3I$	$CH_3(CH_2)_3$	**46** (68)
$[(CH_3)_3SiO]$	OH	**47** (40)
C_6H_5CHO	C_6H_5CO	**48** (63)
$C_6H_5COCH_2CH_3$	C_6H_5CO	**49** (36)
$(C_6H_5)_2CO$	$(C_6H_5)_2COH$	**50** (75)

1.4.2 Position selectivity in carbazole functionalisation

Over the past decade, transition-metal catalysts (e.g., Rh, Ru, Pd, Cu, and Fe) have been developed for the activation and functionalisation of carbon-hydrogen bonds (C–H) to access a remarkable range of organic compounds.[37-43] A C–H activation protocol has become one of the most powerful tools for constructing carbon-carbon bonds and carbon-heteroatom bonds (such as C–X, X = N, O, S, B, and Si). This promising field is enriched by the works of Suzuki and Miyaura,[44-47] Yu, [48-51] Buchwald and Hartwig,[52-56] and others.[57-60] Recently, metalcatalysis has offered a new synthetic route for the synthesis of substituted carbazoles given that direct C–H functionalisation of carbazoles is difficult.[60]

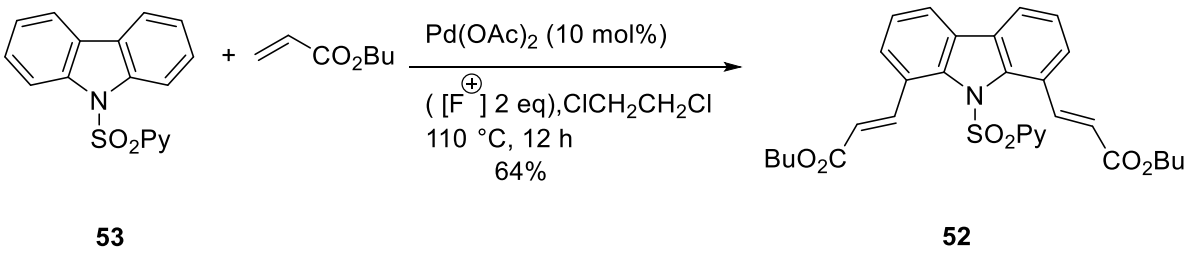
1.4.2.1 1,8-Substituted carbazole

There have been many methods developed for the 1,8 function of carbazole. The two examples below are representative. Sperry and co- workers used the iridium-catalysed C–H borylation of carbazole at C-1-H and C-8-H (**Scheme 13**).[61] There was no protecting or directing group in this method.



Scheme 13: Iridium-catalysed synthesis of 1, 8- disubstituted carbazole **51**

Carretero *et al*. prepared 1, 8-disubstiuted carbazoles **52** using a palladium(II)-catalysed reaction (**Scheme 14**).[62]

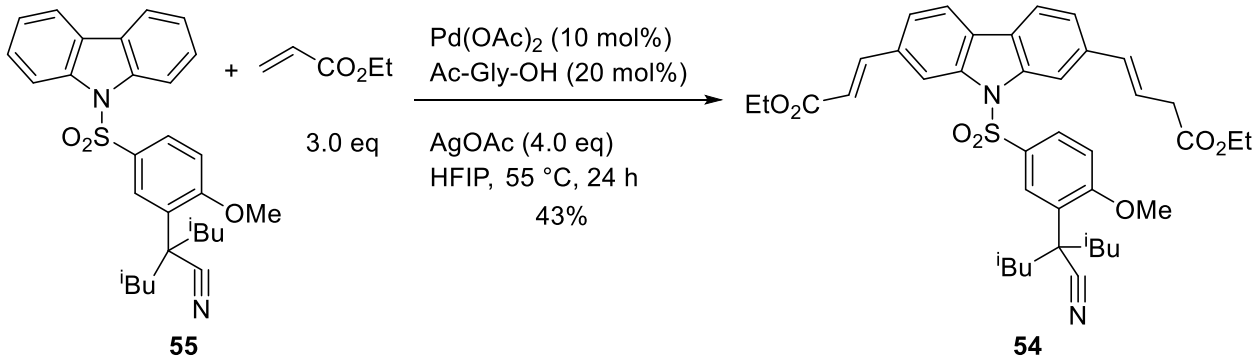


53 **52**

Scheme 14: Synthesis of 1,8 disubstituted carbazole **52**

1.4.2.2 2,7-Substituted carbazoles

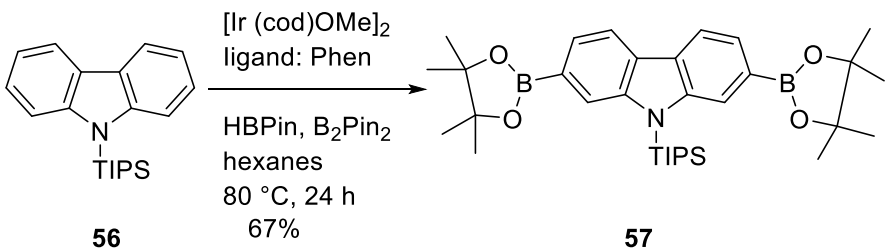
Movassaghi *et al*. reported the synthesis of 2,7-disubstituted carbazole.[63] The Pd (II)-catalysed meta-selective C–H olefination reaction was used to synthesise C-2, C-7-bis-borylated product **54** in 43% yield (**Scheme 15**) .



55 **54**

Scheme 15: Synthesis of 2,7-disubstituted carbazole **54**

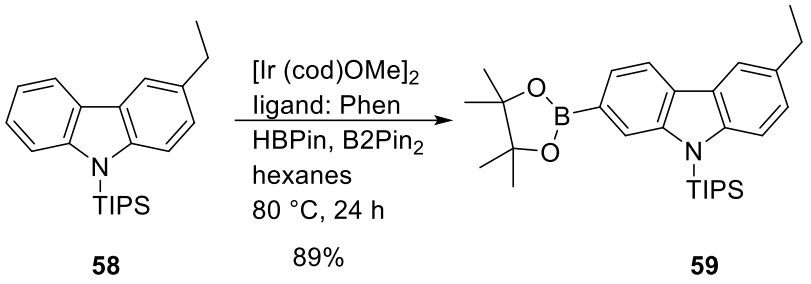
Baran *et al*. reported the synthesis of 2,7 disubstituted **57** from the borylation of *N*-TIPS carbazole **56** (**Scheme 16**). [64]



56 **57**

Scheme 16: Synthesis of 2,7-disubstituted carbazole **57**

Moreover, C-3-ethylated *N*-TIPS carbazole **58** was synthesised by borylation to give C-7-monoborylated product **59** (**Scheme 17**).[64]

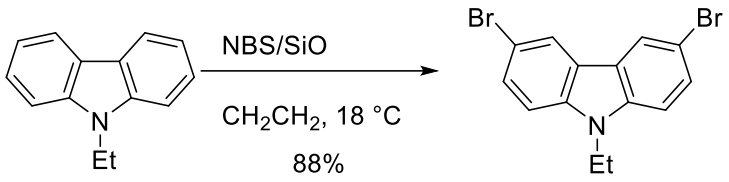


58 **59**

Scheme 17: Synthesis of 7-mononborylated carbazole **59**

1.4.2.3 3,6-Substituted carbazoles

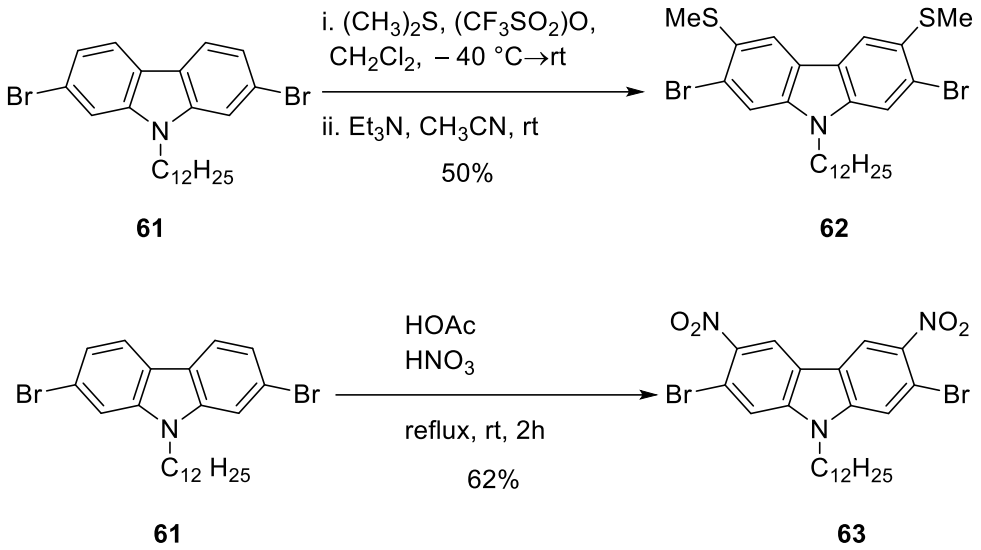
3,6-Substituted carbazoles are relatively easy to prepare through electrophilic aromatic substitution.[65-67] For example, the bromination of carbazole **40** to prepare the 3,6-dibromo carbazole **60** reported in the literature used *N*-bromosuccinimide and silica gel (**Scheme 18**).[65]



40 **60**

Scheme 18: Synthesis of 3,6-dibromocarbazole **60**

2,7-Dibromo-9-dodecyl-9H-carbazole **61** was reported in the literature and is used to synthesise 3,6-disubstituted carbazoles **62** and **63**,through electrophilic aromatic substitution (**Scheme 19**).[66, 67]

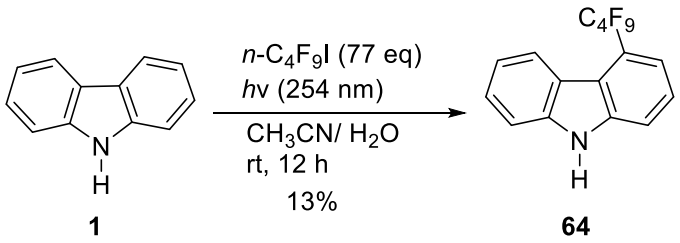


Scheme 19: Synthesis of 3,6-disubstituted carbazoles

1.4.2.4 4,5-Substituted carbazoles

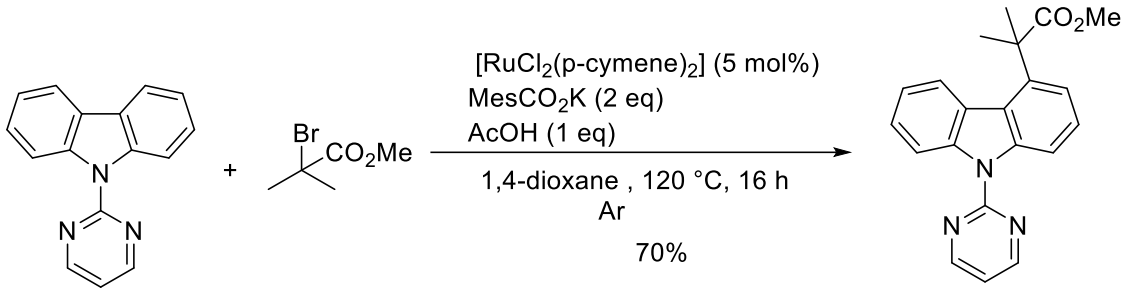
4,5-Disubstituted carbazoles derivatives from carbazole precursors have not yet been reported. However, the C-4 position of carbazole and the *N*-trichlorobenzoylation of 4-substituted carbazoles have been studied.[68]

The 4-(1,1,2,2,3,3,4,4,4-nonafluorobutyl)carbazole **64** was synthesised *via* a photochemical method in aqueous media (**Scheme 20**).[68, 69]



Scheme 20: Synthesis of 4-substituted carbazole **64** *via* photochemical method

Frost *et al*. described the C4-selective C–H alkylation of carbazole derivatives *via* ruthenium catalysed α-activation methodology (**Scheme 21**).[69]



66 **65**

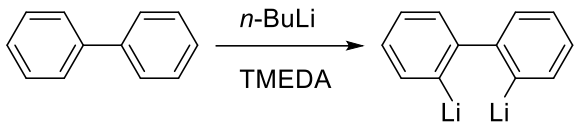
Scheme 21: Synthesis of 4-substituted carbazole **65**

The previous methods only worked for the synthesis of 4-monosubstituted carbazoles. The direct synthesise of 4,5-disubstituted carbazoles has not yet been reported in the literature.

1.5 Double lithiation of aromatic systems using n-BuLi -TMEDA

The bay-region - disubstituted for polycyclic aromatic hydrocarbon (PAHs) - is a unique aromatic position due to the strain from the close proximity effect on the properties of compounds, thus providing useful in applications. One of the most common methods for accessing these positions is by means of a lithium-halogen exchange using butyllithium (*n*-BuLi) and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA).[70]

In recent years, di-lithio compounds derived from polycyclic aromatic hydrocarbons (PAHs) have attracted considerable attention. [70-74] Lithium-directed metalations of aromatic compounds have been extensively studied.[71] According to Schleyer and co-workers, this double lithium bridging provides thermochemical energy to achieve the ortho-dilithiation of biphenyl **68** in *n*-BuLi with the TMEDA/hexane (**Scheme 22**), which would be otherwise difficult to accomplish.[72]

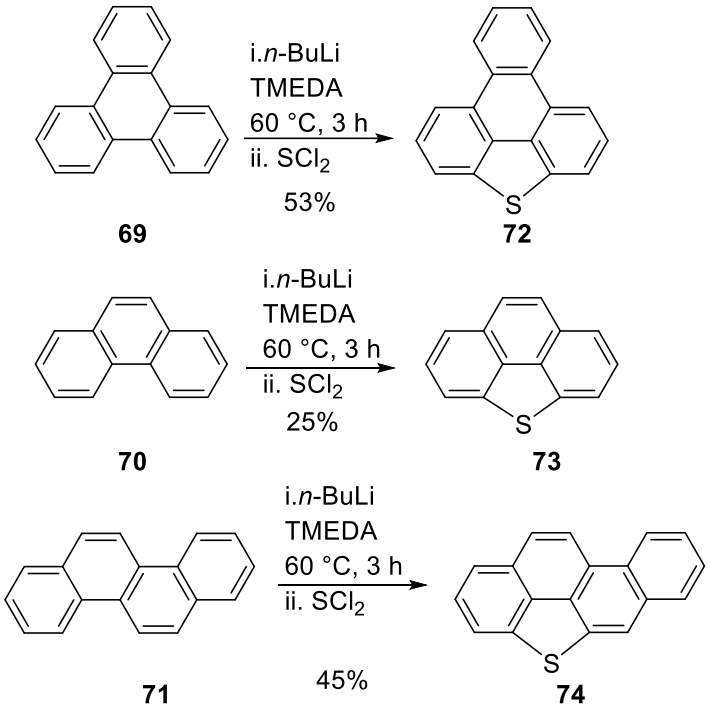


67 **68**

Scheme 22: Lithiation of biaryl **67**

The mechanism and structure of dilithium species has been reported in the literature.[75]

Dilithiation of a number of polycyclic aromatic hydrocarbons (PAH's) has been described.[71] Ashe *at al*. demonstrated the dilithiation of triphenylene **69**, phenanthrene **70**,[76] and chrysene **71**, and quenching with SCl_2 to provide the corresponding fused thiophene products (**Scheme 23**).[70, 71]

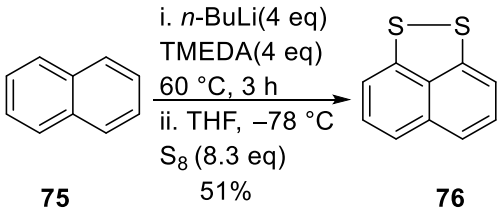


69 **72** **70** **73** **71** **74**

Scheme 23: Synthesis of triphenyleno [4,5-bed] thiophene **72**,[77] fused thiophenes **73**,[78, 79] and **74**, [80] by dilithiation methodology.

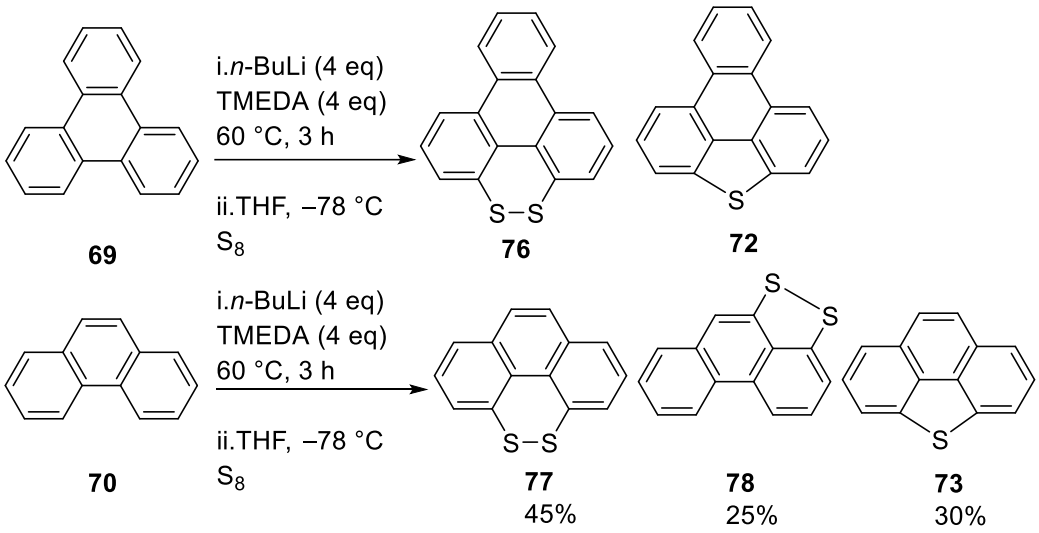
Naphthalene **75** is the simplest PAHs chosen for dilithiation due to several reported lithiation conditions.[73-75, 81]

In 1994, Ashe *at al*.[70] investigated the synthesis of the naphthalene disulfide **76**, using 4 equivalents of *n*-BuLi/ TMEDA heated at 60 °C for 3 hours. The dilithio-species were quenched with sulfur to afford the corresponding disulfide products (**Scheme 24**).[70]



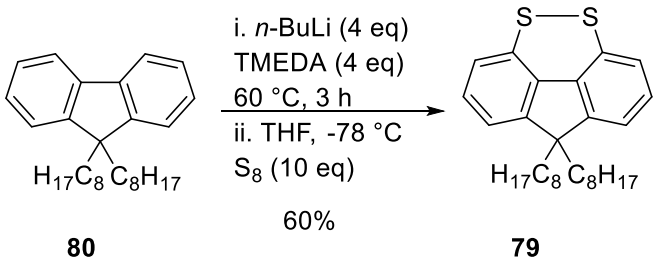
Scheme 24: Ashe III *et al*. conditions for the synthesis of naphthalene disulfide **75**

Under the same conditions as above,[70] the dilithiation of triphenylene **69** and phenanthrene **70**,[76] gave the corresponding disulfide products (**Scheme 25**).[70]



Scheme 25: Synthesis of the triphenyleno [4,5-bed] thiophene **72**,[77] and triphenyleno-[1,12-cde][l,2]dithiin **76**, [70] fused thiophenes **73**, [78, 79], phenanthro[4,5-cde] [I ,2]dithiin **77**,[70] and phenanthro[I ,I O-cd]-l,2-dithiole **78**,[70] by Ashe III *et al*. conditions.

In 2010, Bonifácio and co-workers synthesised fluorene disulfide **79** *via* Ashe III's procedure. [70,82] 9,9'-Dioctylfluorene **80** was treated with TMEDA and *n*-BuLi followed by quenching with sulfur to form 4,5-disulfide-9,9'-dioctylfluorene **79** in a 60% yield (**Scheme 26**).



80 **79**

Scheme 26: Synthesis of 4,5-disulfide fluorene **79**

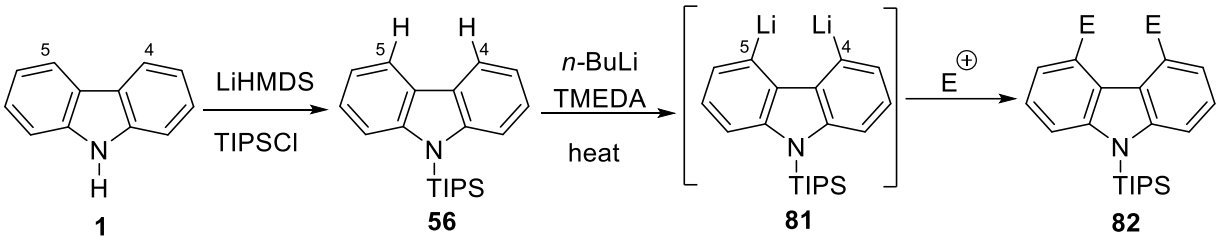
Currently, only this example of a directed lithiation on fluorene has been reported in the literature.[82] The previous lithiation conditions of polycyclic aromatic hydrocarbons (PAH's), exhibited the directed efficient method for the preparation of the selective functionalisation in the bay region of the PAHS. Recent studies have focused on carbazoles due to its photophysical properties.[83-87] The 1,8 substituted carbazoles were synthesised using the directed lithiation method after protection of nitrogen with a bulky grup.[32, 34, 35, 88]

The dilithiation of 4,5-position of carbazole has not been reported. The limitations of 4,5-disubstituted carbazole synthesis in the literature led the Grainger group to find a more direct, selective and convenient method to functionalise 4,5-disubstituted carbazole.

In 2021, the Grainger group published a paper which established a method to dilithiate the 4,5-positions of carbazole.[89] According to our hypothesis, a protecting group that is capable of blocking both the C-1 and C-8 positions of carbazole and withstand the harsh conditions of *n*-BuLi at 60 °C could allow the lithium atoms to migrate to the 4,5-position in the presence of TMEDA.

1.6 Previous group work

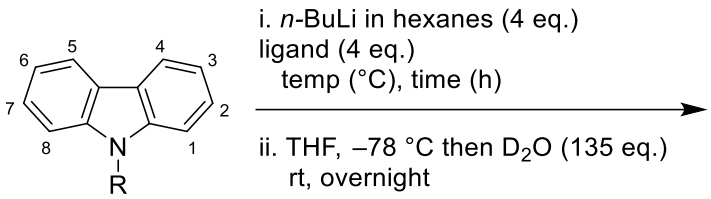
The Grainger group has previously introduced the first methodology for the direct functionalisation at both the C-4 and C-5 positions of carbazole,[89] using the combination of a bulky silyl protecting group on the carbazole nitrogen (to prevent C-1/C-8-lithiation) and *n*-BuLi–TMEDA (to dilithiate at C-4 and C-5). This methodology was considered a simple and appropriate approach to 4,5-difunctionalized carbazoles upon electrophilic trapping (**Scheme 27**).



Scheme 27: Synthesis of 4,5-disubstituted carbazoles

The optimisation of the method to synthesise 4,5 disubstituted carbazoles was carried out by Ian A. Pocock.[89] The reaction was investigated under various conditions. The best conditions for the dilithiation of 4,5-carbazole required firstly placing a triisopropylsilyl (TIPS) group on carbazole nitrogen to prevent C-1 and C-8 lithiation and secondly, using 4 equivalents each of *n*-BuLi and TMEDA at 60 °C for 6 h (**Table 2**).

Table 2: Deprotonation screen of carbazole via double lithiation method

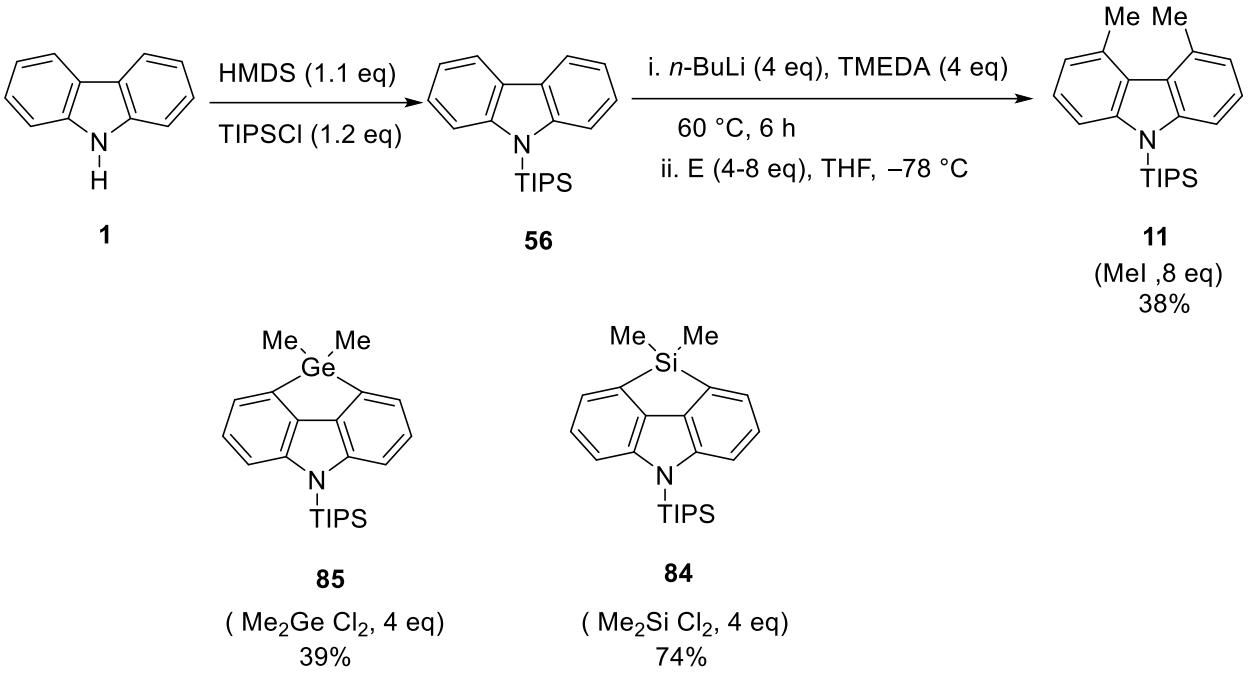


[a] R = TIPS; [b] R = H; [c] R = TES

Entry	Carbazole (R)	Ligand	Time (h)	Temp (°C)	Percentage deuteration (%)[a] C1/8	C2/5	C3/6	C4/5
1	**56** (TIPS)	TMEDA	3	60	-	-	-	70
2	**56** (TIPS)	TMEDA	6	60	-	-	-	83
3	**56** (TIPS)	TMEDA	9	60	-	-	-	75
4	**56** (TIPS)	TMEDA	3	68	-	-	-	83
5	**56** (TIPS)	TMEDA	6	68	-	-	-	79
6	**1** (H)	TMEDA	6	60	57	-	-	12
7	**83** (TES)	TMEDA	6	60	100% desilylation			
10	**56** (TIPS)	PMDTA	6	60	decomposition			

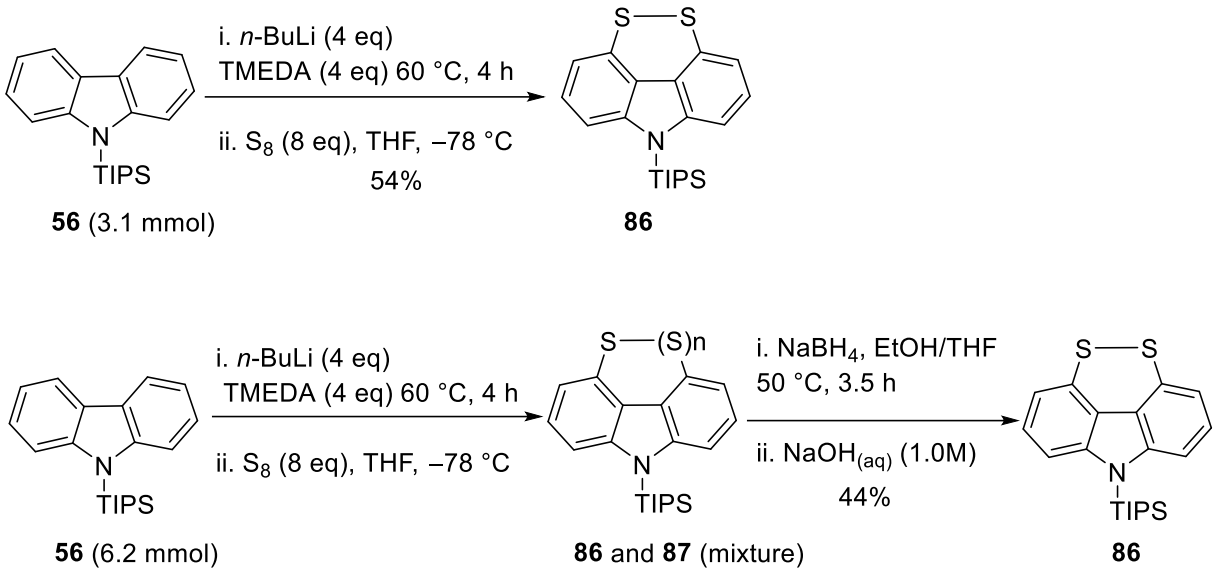
[a] determined by relative integration of aromatic hydrogen signals in ^{1}H-NMR

4,5-Dimethylcarbazole **11** was synthesised in 38% yield by alkylation (using iodomethane). The use of dimethyldichlorosilane as an electrophile gave silafluorene **84** in 74% yield. Similarly, germa-fluorene **85** was prepared in 39% yield (**Scheme 28**).



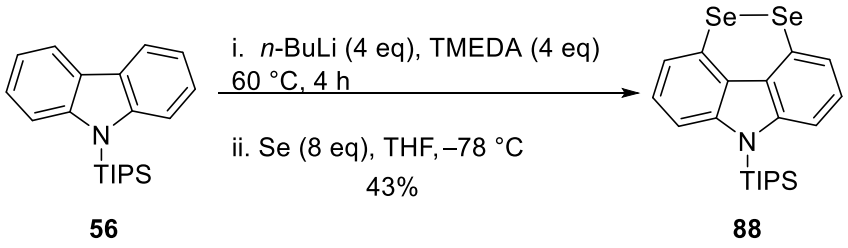
Scheme 28: Synthesis of 4,5-disubstituted carbazole **11**, **85**, and **84**

The Grainger group's interest in *peri*-substituted naphthalene disulfides and diselenides directed us to examine sulfur and selenium at C-4 and C-5. Therefore, Connor Prior conducted the reaction of *N*-TIPS carbazole **56** with elemental sulfur which gave disulfide **86** in 54% yield on a small scale (3.1 mmol scale). On a larger scale (6.2 mmol), mixtures of disulfide **86** and trisulfide **87** were obtained. Treatment of this mixture with Sodium borohydride converted it to disulfide **86** in 44% overall yield (**Scheme 29**).[89, 90]



Scheme 29 Synthesis of 4,5- disulfide **86**, and 4,5-trisulfide carbazole **87**

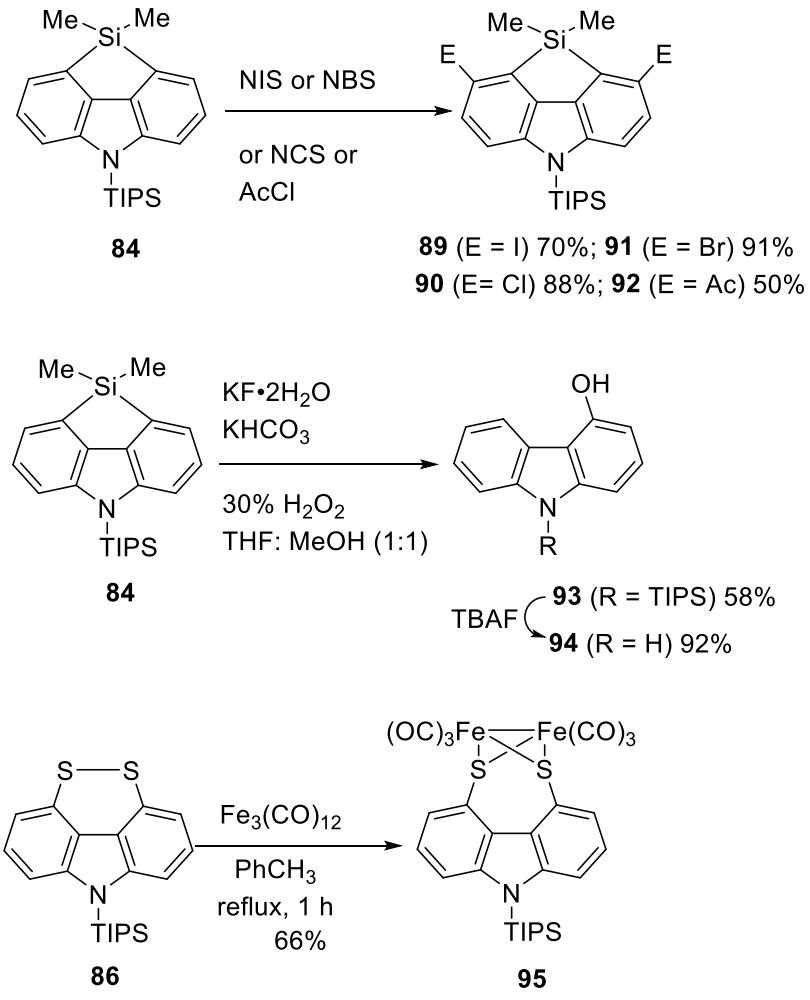
In addition, carbazole diselenide **88** was synthesised by Kesar Jagdev. The *N*-TIPS carbazole **56** was lithiated and followed by quenching with elemental selenium gave only carbazole diselenide **88** in 43% yield (**Scheme 30**).[89, 91]



Scheme 30: Synthesis of 4,5-diselenide carbazole **88**

As a result of further manipulation of the functionality built into these unique 4,5-disubstituted carbazoles, a broad selection of carbazoles are now accessible using this technology (**Scheme 27**). The corresponding 3,6-disubstituted carbazoles **89**-**92** were produced *via* the regioselective electrophilic aromatic substitution of the fused carbazole–silafluorene **84**. Silafluorenes are widely used in materials,[92] and synthesis.[93] The efficient synthesis of the dihalides **89**-**92** allows for future

cross coupling processes to investigate these unique heteroatom-bridged heterofluorenes.[94] Under Dudley's conditions, **84** was oxidised to produce the desymmetrized carbazole monoalcohol **93**.[95] A well-known starting point for the synthesis of natural products, 4-hydroxycarbazole **94** was produced by *N*-desilylation of **93** with TBAF.[96] The $Fe_2(CO)_6$ complex **95**, was produced by the oxidative insertion of $Fe_3(CO)_{12}$ into the disulfide **86** (**Scheme 31**).



Scheme 31: Previous transformation of 4,5-disubstituted carbazoles

1.7 Aims and objectives

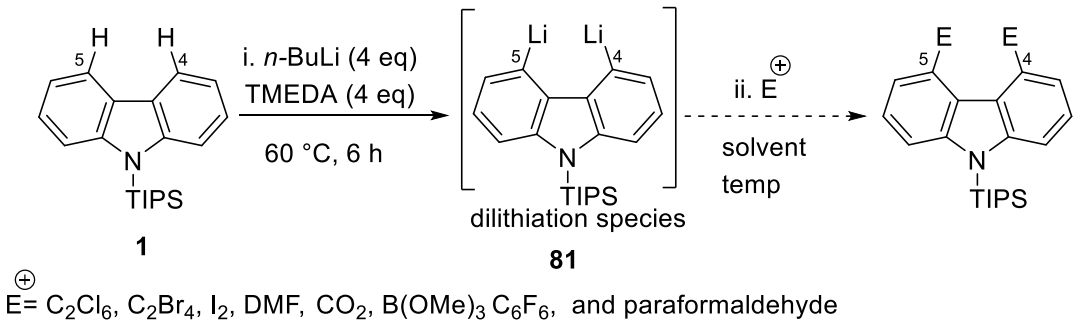
As discussed in the literature review above, the relatively few known examples of 4,5-disubstituted carbazoles are prepared from non-carbazole precursors. Also, there is only one method for C–H activation at C-4, through the coupling of *N*-pyrimidinyl carbazoles with tertiary α-bromoesters under Ru catalysis. These limitations are a driver to find a simple and direct method to derivatise both the 4- and 5-positions of carbazole.

The Grainger group solved this limitation by utilising the combination of a bulky silyl protecting group on the nitrogen group of carbazole and *n*-BuLi–TMEDA for dilithiation at C-4 and C-5. This methodology was successfully applied to the synthesis of 4,5-dimethylcarbazole **11**, silafluorene **84**, germa-fluorene **85**, disulfide **86**, and diselenide **88**.

The primary aim of this research is to increase the range of novel 4,5-substituted carbazoles that can be prepared using the Grainger group methodology, and to investigate their subsequent transformations and photophysical properties.

Based on the above aim, the following research objectives were proposed:

1. Quench the dilithiation species **81** with a range of different electrophiles.



Scheme 32: Proposed quench of the dilithiation species with other electrophiles

2- Increase the range of 4,5-disubstituted carbazoles by further transformations.

3- Study the fundamental photophysics and electronic spectroscopy (UV and fluorescence) of the 4,5-Se/S carbazole derivatives.

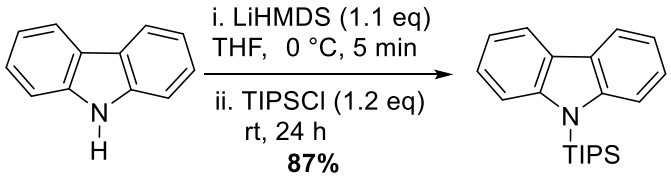
Chapter 2: Synthesis of 4,5-disubstituted carbazoles and their X-ray analysis

This chapter describes the synthesis of a series of 4,5-disubstituted carbazoles based on previous work within the Grainger group (Chapter 1), following their dilithiation methodology of *N*-TIPS-carbazole **56** with a range of electrophiles. Furthermore, additional transformations of the unique 4,5-disubstituted carbazoles to boost the accessibility of 4,5-disubstituted carbazoles are detailed. The structure for several 4,5-disubstituted carbazole compounds will be confirmed by the X-ray analysis and their planarity examined. Finally, the basic electronic spectroscopy (UV and fluorescence) of the 4,5- disubstituted carbazoles will be determined and discussed.

2.1 Methodology development and reaction scope

2.1.1 Synthesis of *N*-TIPS carbazole

The literature procedure for the synthesis of triisopropylsilyl carbazole **56**,[64] had been modified by a past member of the Grainger group. The change of base from *n*-BuLi to lithium hexamethyldisilazide resulted in reproducible yields between 60% and 90%. Repetition of the new group procedure was successful giving **56** in 87% yield after purification by column chromatography (**Scheme 33**).

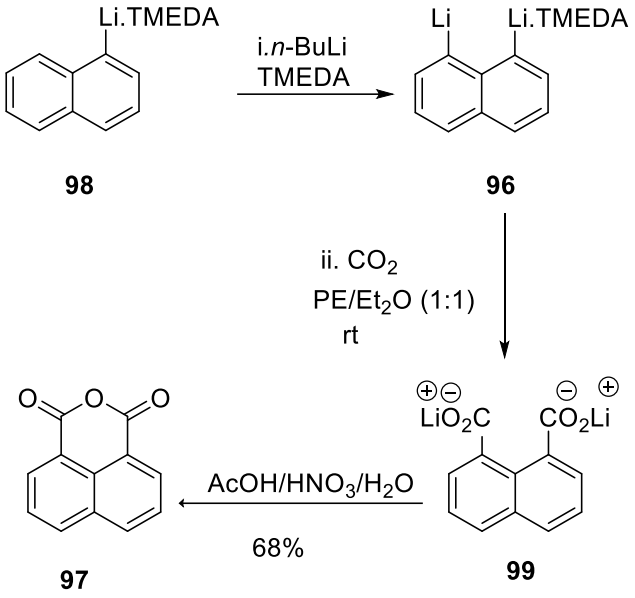


1 **56**

Scheme 33: Synthesis of *N*-TIPS carbazole **56**

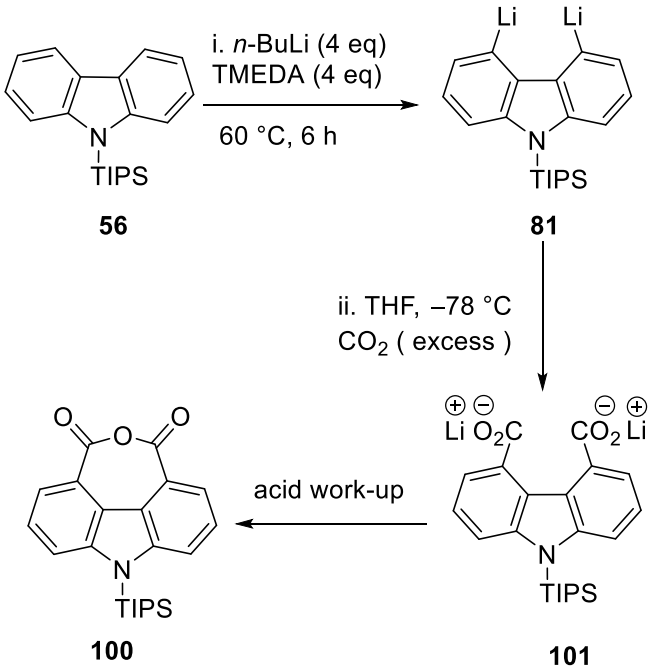
2.1.2 Quenching with carbon dioxide

In the literature, quenching of 1,8 dilithionaphthalene **96** with CO_2 gave the product 1, 8- anhydride **97** (**Scheme 34**).[73]



Scheme 34: Synthesis of 1H,3H-benzo[de]isochromene-1,3-dione **97** using CO_2

N-TIPS carbazole **56** was treated with *n*-BuLi and TMEDA; subsequent quenching with CO_2 gave anhydride **100** in a pleasing 67% yield after purification by trituration with *n*-hexane (**Scheme 35**).

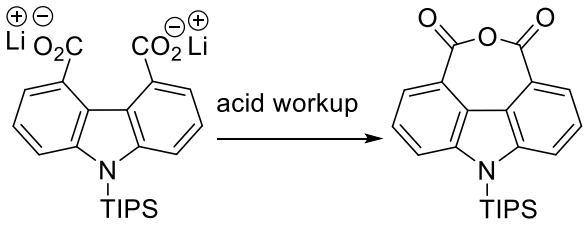


Scheme 35: Synthesis of 4,5- carbazole anhydride **100** using CO_2

The product was identified as anhydride **100**, not the di-acid, due to the IR spectra showing no carboxylic acids (COOH) peak absorptions between 2500 cm^{-1} to 3300 cm^{-1}. Also, in the ^{1}H-NMR spectrum the COOH peak was not observed.

The acidic work-up step was investigated with different acids (**Table 3**).

Table 3: Work-up optimisation for the formation of *N*-TIPS carbazole anhydride **100**



101 **100**

Entry	Acid Work-up condition	Yield [a]
1	$HCl_{(aq)}$ (1M), 1 h, at 0° C	31%
2	$HNO_{3\,(l)}$ (15.8 M), 1 h, at 0 °C	45%
3	$AcOH_{(l)}$ (17.6 M), 1 h, at 60 °C	41%
4	$HCl_{(l)}$ (12.1 M), 1 h, at 0 °C	67%

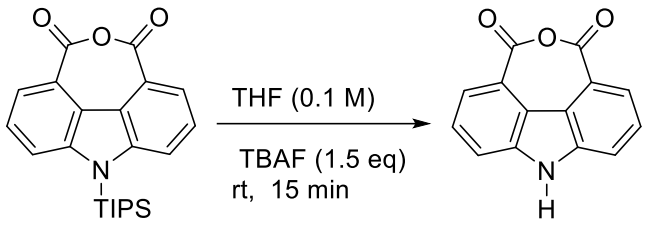
[a] Isolated yield after purification by trituration with n-hexane.

The use of aqueous hydrochloric acid gave **100** in 31% yield (entry 1). Nitric acid and acetic acid gave 45% and 41% yields respectively (entries 2 and 3). The highest yield of 67% of the anhydride **100** was obtained when using concentrated hydrochloric acid (entry 4).

The purification of the *N*-TIPS carbazole anhydride **100** was the most challenging step. Initially, flash column chromatography was used to purify **100**. Unfortunately, this was effective only on small scales; on larger scales, the anhydride **100** was trapped or decomposed on silica during the

purification stage. For this reason, the *N*-TIPS carbazole anhydride **100** was purified by trituration with *n*-hexane to give an analytically pure solid.

The removal of the tri(isopropyl)silyl protecting group from anhydride **100** was examined.[96] The anhydride **100** was treated with TBAF in THF at room temperature to give carbazole anhydride **102** in 56% yield (**Scheme 36**).



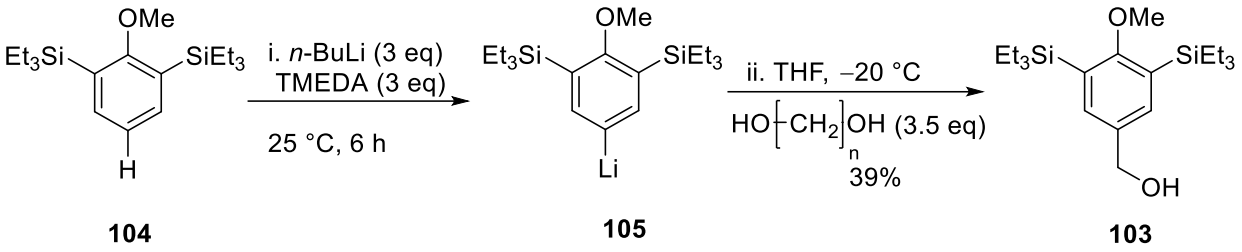
100 **102**

Scheme 36: Deprotection of *N*-TIPS carbazole anhydride **100**

Due to the high polarity and sensitivity of the anhydride **102** towards silica, it was expected to decompose using flash column chromatography. The ^{1}H-NMR spectrum showed the product to be sufficiently pure with slight impurity in the up-field region after work-up.

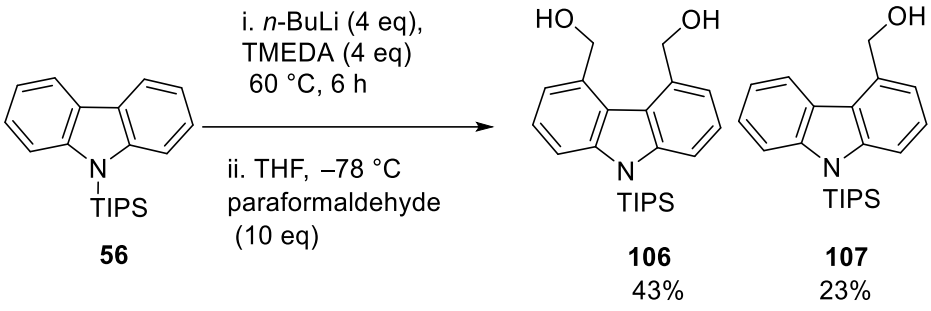
2.1.3 Quenching with paraformaldehyde

In the literature, in Paul Knochel's work,[97] lithiation of anisole derivative **104** and trapping with paraformaldehyde gave [4-methoxy-3,5-bis(triethylsilyl)phenyl]methanol **103** in 39% yield (**Scheme 37**).[97]



Scheme 37: Synthesis of 4-methoxy-3,5-bis(triethylsilyl)phenyl]methanol **103** using paraformaldehyde

N-TIPS carbazole **56** trapping with paraformaldehyde gave *N*-TIPS carbazole diol **106** in 43% yield, along with 23% of the monomethanol **93** (**Scheme 38**).



Scheme 38: Trapping of *N*-TIPS carbazole **56** with paraformaldehyde

^{1}H-NMR analysis showed the CH_2 signal which appeared as one signal at δ_H 5.22 or TIPS carbazole diol **106** while OH signal appeared as broad at δ_H 3.47, the X-ray structure of **106** was obtained (**Section 2.3**). The literature indicates that paraformaldehyde ($HO(CH_2O)_nH$) reacts with organolithium compounds to form primary alcohols in good yields. Mono formaldehyde HCOH is favoured in most organic syntheses but not for metalation.[98] For this reason, it was decided to investigate the use of paraformaldehyde and mono formaldehyde to compare the results with literature (**Table 4**).[98] Firstly, trapping with paraformaldehyde gave *N*-TIPS carbazole diol **106** in 43% yield, along with 23% of the monoalcohol **107** (entry 1). On increasing the amount of paraformaldehyde from 10 to 20 equivalents, the yield decreased for the diol **106** from 43% to 5% and the monoalcohol **107** from 23% to 14% (entry 2). Following a literature procedure, the

monomeric formaldehyde in ethereal solution was prepared.[98] On examination, it was found that the trapping of the lithiation species of *N*-TIPS carbazole **56** with formaldehyde (0.5 M in THF) gave *N*-TIPS carbazole diol **106** in 5% yield, along with 10% of the monoalcohol **107**, and starting material was recovered in 29% (entry 3). In summary, quenching the dilithio of *N*-TIPS carbazole **81** with paraformaldehyde as electrophile works better than formaldehyde to give the primary alcohol.[98]

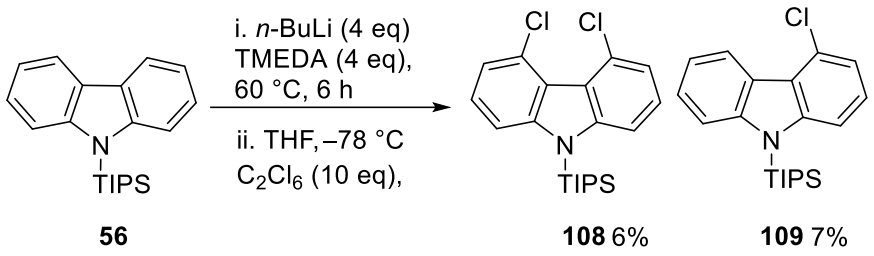
Table 4: The optimisation for synthesis of *N*-TIPS carbazole diol **106**

Entry	Aldehyde	No of eq	Product	Yield[a]
1	paraformaldehyde	10	**106**	43%
			107	23%
			S.M.	6%
2	paraformaldehyde	20	**106**	5%
			107	14%
			S.M.	18%
3	formaldehyde in THF (0.5 M)	10	**106**	5%
			107	10%
			S.M.	29%

[a] Isolated yield after purification by column chromatography

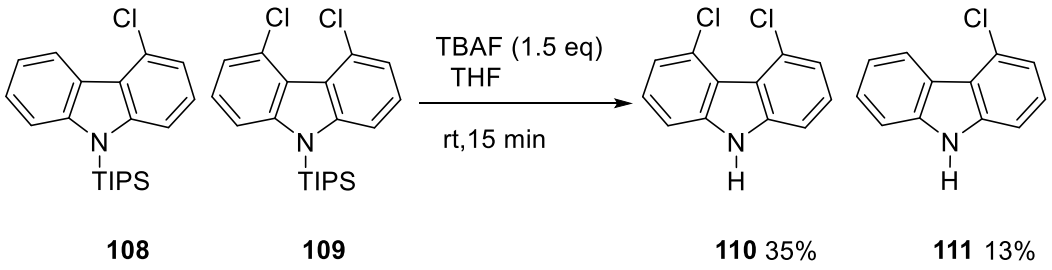
2.1.4 Quenching with halide sources

In addition, trapping **81** with heteroatom electrophiles was also explored. Firstly, chlorination of **56** using hexachloroethane,[99] gave a mixture of dichloride *N*-TIPS carbazole **108** and monochloride **109** which were difficult to separate with low yield 8% and 6% respectively (**Scheme 39**).



Scheme 39: Synthesis of the chlorocarbazoles **108** and **109**

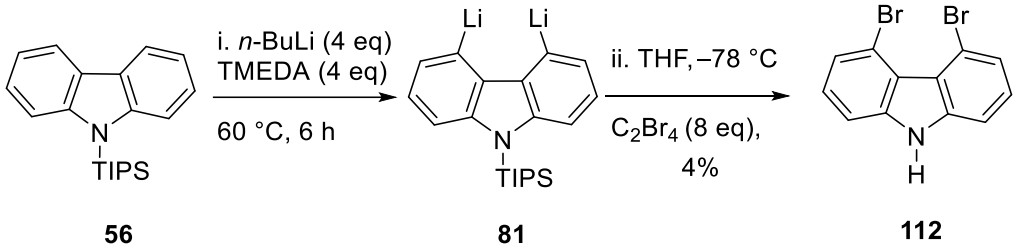
However, deprotecting the mixture of mono and dichloride *N*-TIPS carbazole **56** allowed them to be easily separated. Removal of the TIPS group from the crude mixture of mono and di- chloride TIPS carbazole **108** and **109** using TBAF,[96] gave the dichloride carbazole **110** in 35% yield, along with 13% of the 4-chloro-9H-carbazole **111** (**Scheme 40**). [100]



Scheme 40: Synthesis of the dichloride carbazole **110**

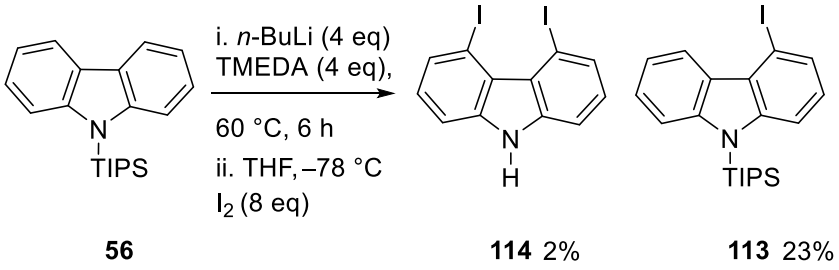
The dichloro- *N*-TIPS carbazole **110** structure was confirmed by X-ray crystallography (**Section 2.3**).

Attempted bromination of **56** using tetrabromoethylene,[101] gave 4,5-dibromocarbazole **112** without TIPS group in low yield 4% (**Scheme 41**). The structure of compound **112** was assigned by ^{1}H-NMR and mass spectrometry. Unfortunately, complete characterisation of compound **112** was not possible due to insufficient material.



Scheme 41: Synthesis of 4,5-dibromocarbazole **112**

Iodination of **56** using iodine, [102] was carried out which gave a mixture of monoiodo carbazole **113** containing the TIPS group in 23% yield, and the diiodine carbazole **114** without the TIPS group in a very low yield of 2% (**Scheme 42**).

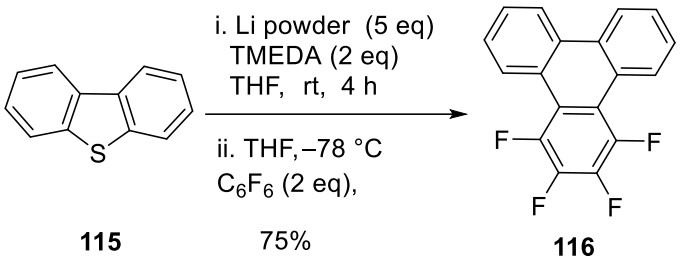


Scheme 42: Synthesis of 4,5-diiodocarbazole **114**

The difficulties of combining two groups in close proximity in the carbazole bay region were heightened by attempts to incorporate larger bromine or iodine, which yielded very poor yields along with removed of the TIPS group.

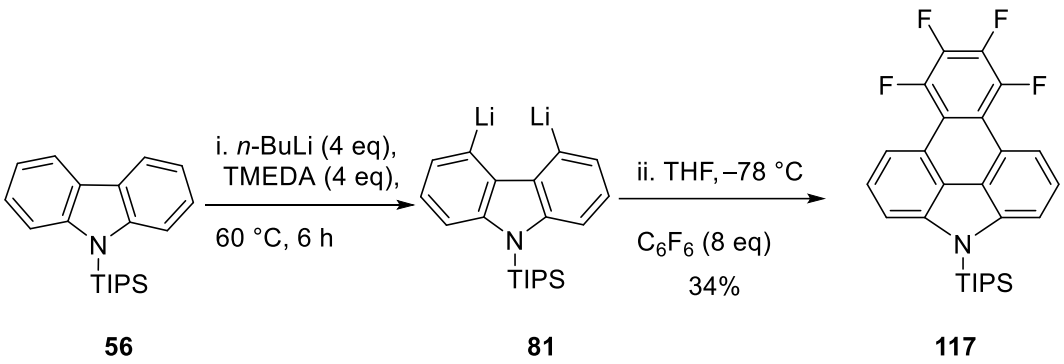
2.1.5 Quenching with hexafluorobenzene

In 2021, Hideki Yorimitsu and co-workers demonstrated that dilithiation of dibenzothiophene **115** and subsequent trapping with hexafluorobenzene to give 1,2,3,4-tetrafluorotriphenylene **116** in a 75% yield (**Scheme 43**).[103]



Scheme 43: Synthesis of 1,2,3,4-tetrafluorotriphenylene **116**

Based on this methodology, it was decided to investigate trapping dilithiated *N*-TIPS carbazole **81** with hexafluorobenzene. The result was the 4H-naphtho[1,2,3,4-def]carbazole **117** in 34% yield (**Scheme 44**).



Scheme 44: Synthesis of the 4H-naphtho[1,2,3,4-def]carbazole **117**

In the ^{13}C-NMR, the C-3/C-6 signal appears as a multiplet at δc 117.5 due to splitting by F (**Figure 4**). The C-10/C-11 signal appears as a multiplet at δc 117.9, and C-12/C-15-F and C-13/C-14-F appear as double-multiplets at δc 139.02 and 147.4 respectively, with *J* values of 253.02 Hz and 250.05.

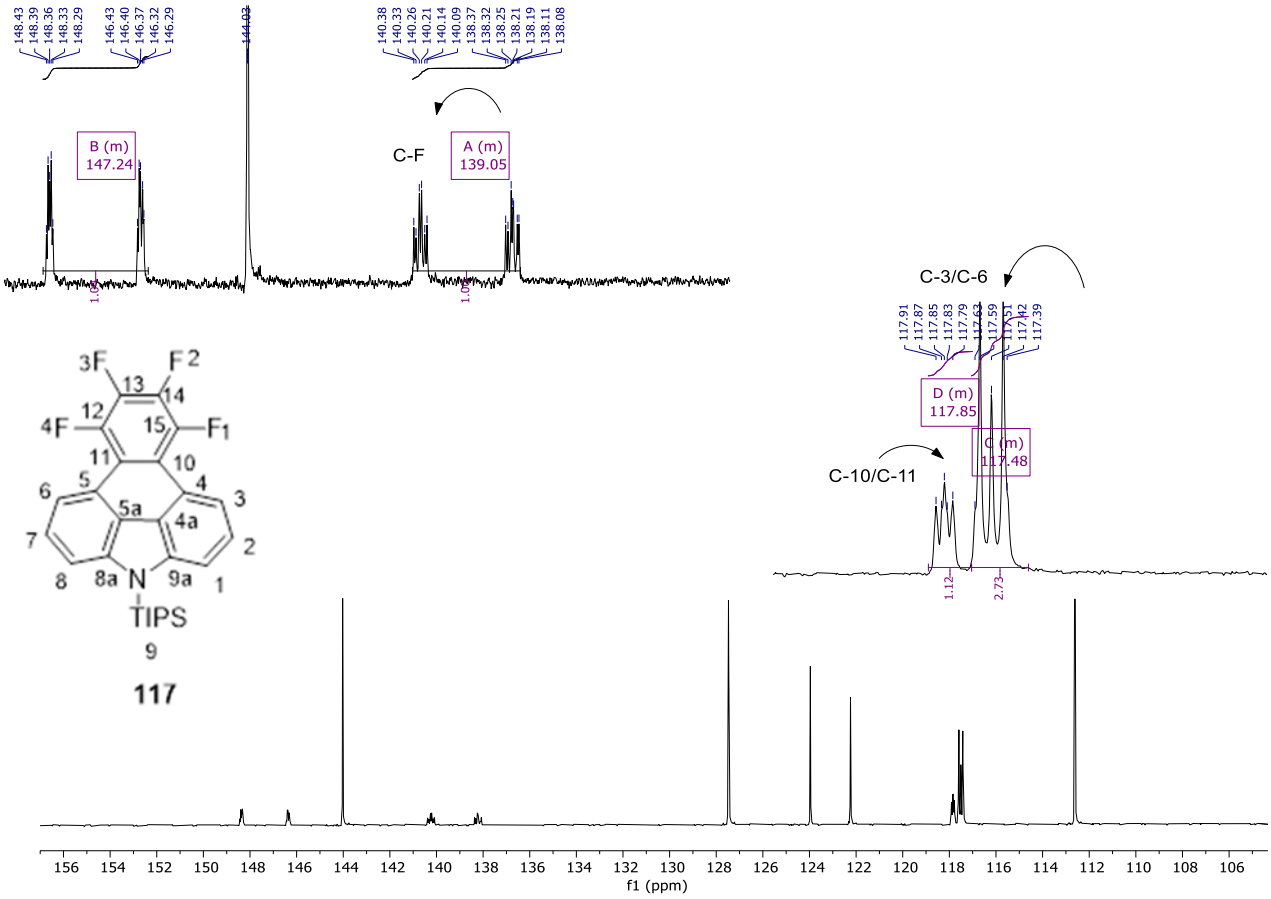


Figure 4: ^{13}C-NMR spectrum ($CDCl_3$, 500 MHz) of compound **117**

The ^{19}F-NMR showed that the F signals appear as doublets, which confirms the two fluorine environments (**Figure 5**).

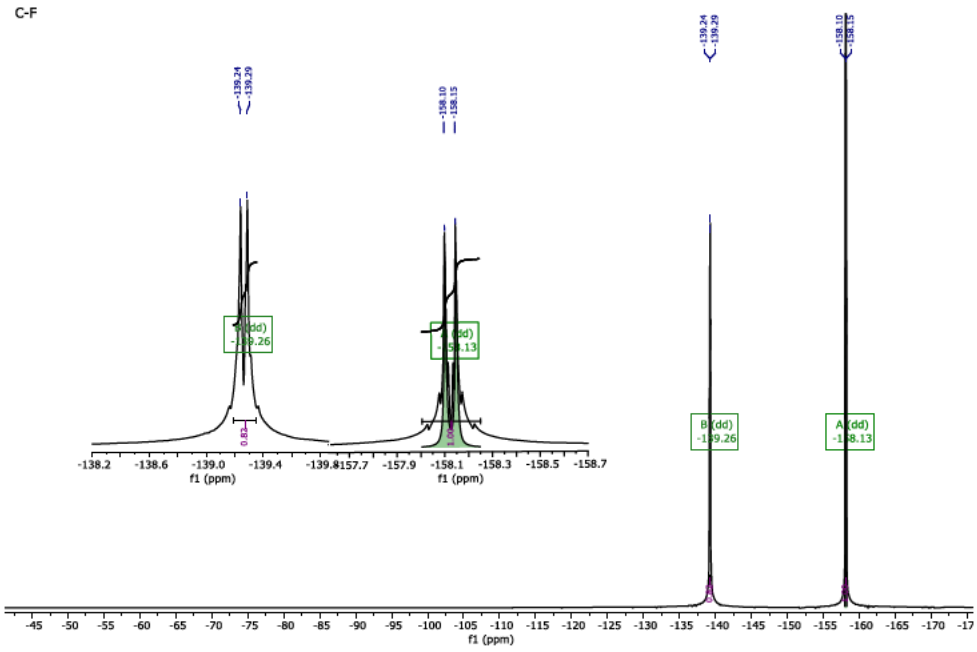


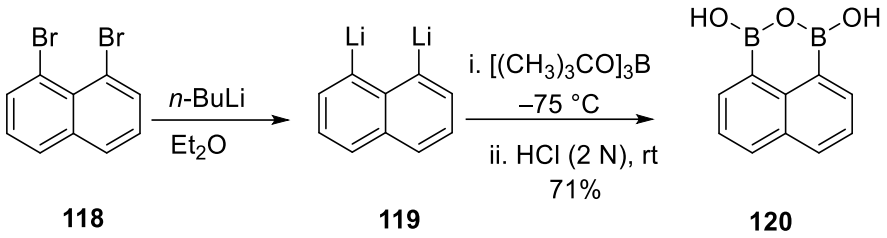
Figure 5: ^{19}F-NMR spectrum ($CDCl_3$, 500 MHz) of compound **117**

The-X- ray structure of compound **117** was grown by slow evaporation from chloroform solution (**Section 2.3**).

2.1.6 Borylation of *N*-TIPS carbazole

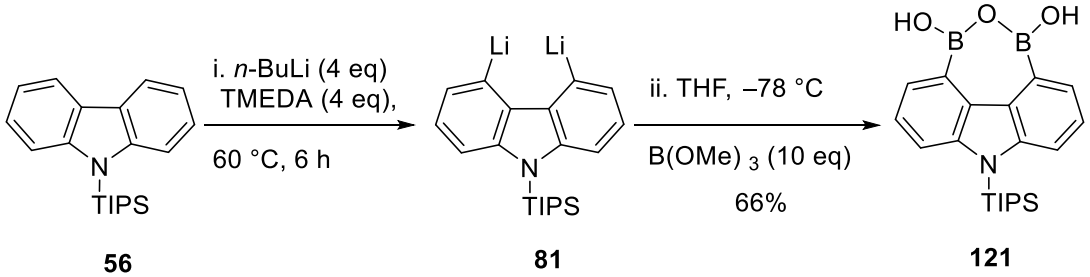
Boron containing compounds are used in a variety of technologies, including anticancer medications (such as Velacade, a boronic-acid-based multiple myeloma treatment) and OLED displays and solar cells. [104, 105]

In the literature *n*-BuLi and 1,8-dibromonaphthalene **118** were used in a metal-halogen exchange process to produce 1,8-dilithionaphthalene **119**. This product was then treated with *n*-butyl borate and hydrolysed to produce 1, 8- naphthalene boronic anhydride **120** in 71% yield after drying (**Scheme 45**).[106]



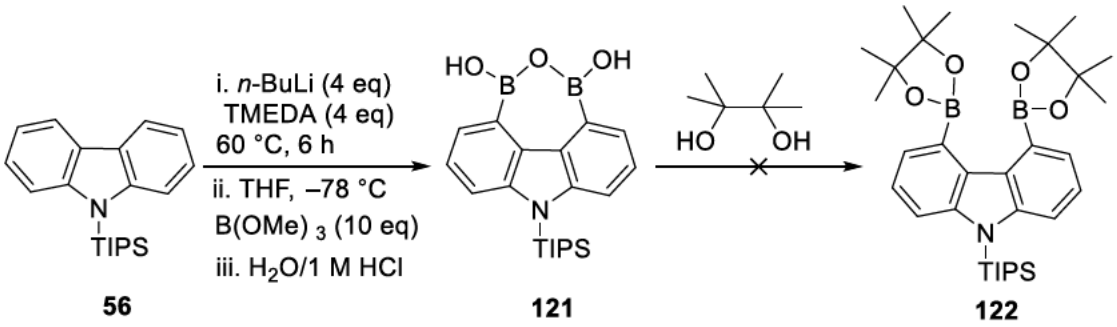
Scheme 45: Synthesis of 1,8 naphthalene boronic anhydride **120** from 1,8 dibromonaphthalene **118**

Borylation of *N*-TIPS carbazole **56** was investigated using two methods. Initially, **81** was trapped with trimethyl borate $B(OMe)_3$. [106, 107] After acidic work-up (3 M HCl stirred vigorously for three hours at room temperature), the *N*-TIPS carbazole diboronic anhydride **121** was obtained in 67% yield after purification by trituration with *n*-hexane (**Scheme 46**). The ^{1}H-NMR showed an OH signal at δ_H 4. 74 which appears as singlet. The ^{11} B-NMR confirmed the C-B bond, the chemical shift value at 28.8 ppm which was expected.[107]



Scheme 46: Synthesis of the diboronic anhydride carbazole **121**

The second way was to trap **81** with $B(OMe)_3$ followed by the addition of pinacol (5 eq) and 1:1 HCl /Et_2O heating to 65 °C (**Scheme 47**).



Scheme 47: Attempted of formation of diboronic ester **122**

^{1}H-NMR of the crude mixture showed a mixture of compounds. The desired product **122** could not be separated from starting materials by FCC (**Figure 6**).

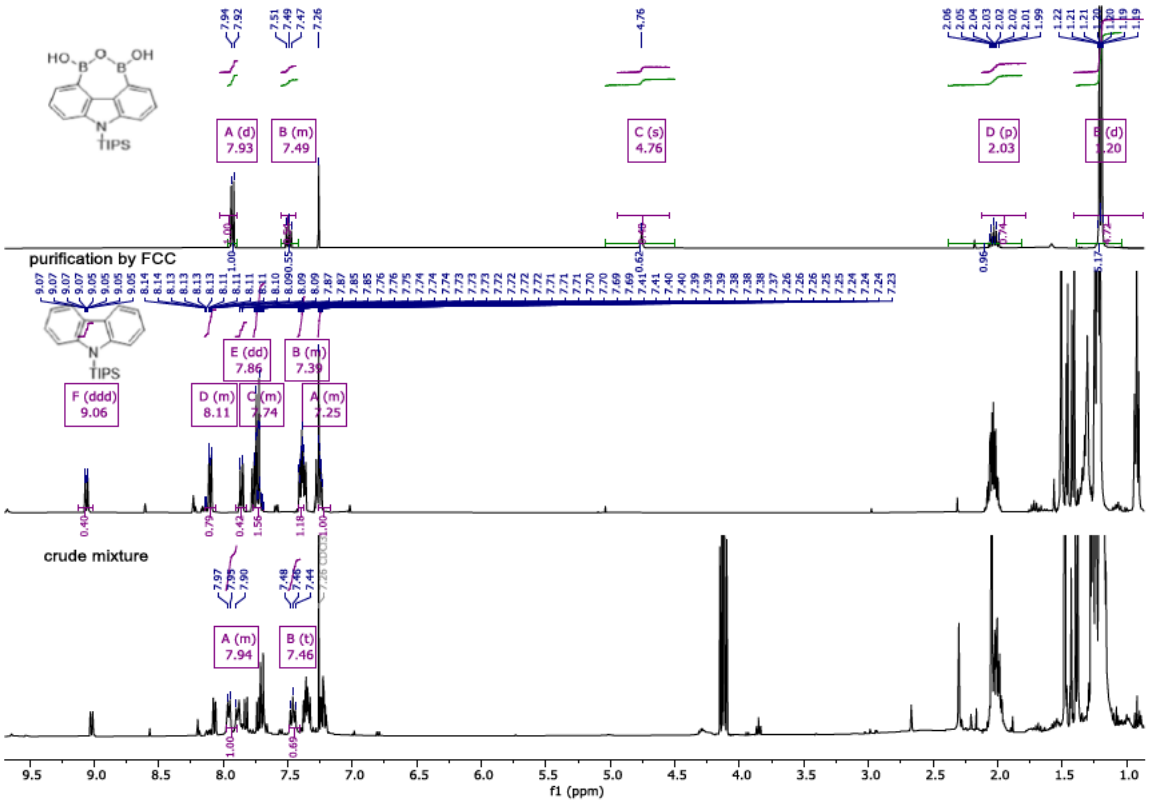
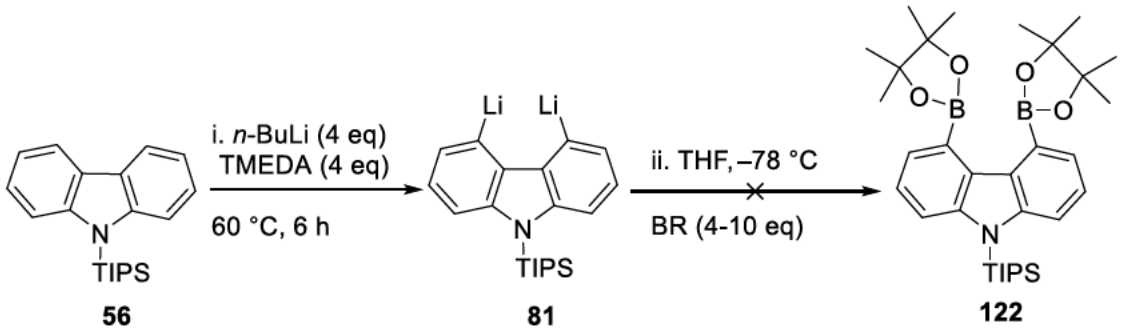


Figure 6: ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of crude mixture in formation of diboronic ester **122**

Attempts were made to trap **81** with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [107] followed by an acidic work-up and an attempt at purification (**Scheme 48**).



BR: 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Scheme 48: Attempted of formation diboronic ester **122** by trapping dilithio **81** with BR

However, the crude ^{1}H-NMR as before showed *N*-TIPS carbazole diboronic anhydride **121** and the starting material (**Figure 7**).

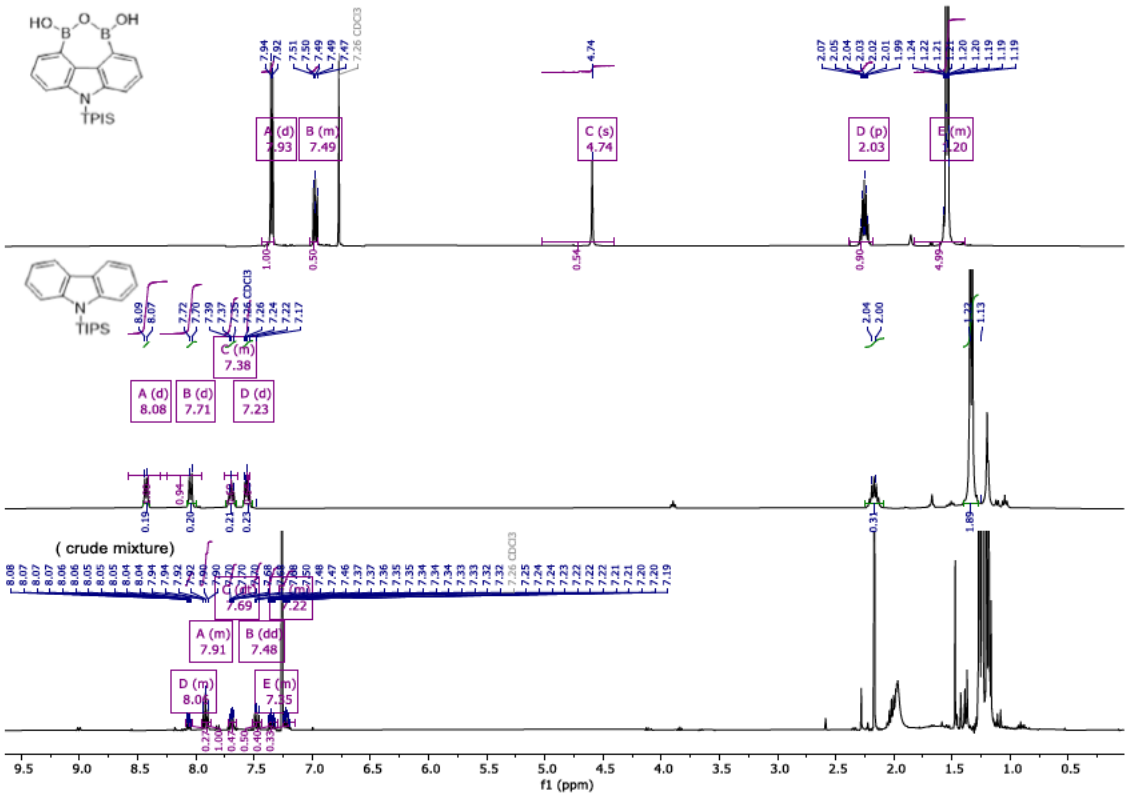
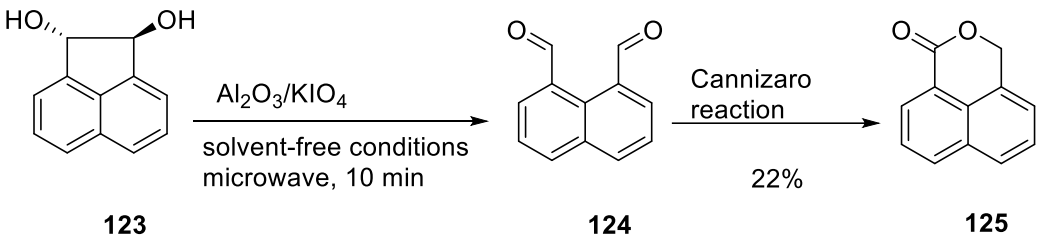


Figure 7: The ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of the synthesis of diboronic ester **122**

The synthesis of the diboronic ester **122** was unsuccessful; however, the diboronic acid anhydrides **121** with a preorganized B−O−B motif was achieved in 67% yield with a simple and convenient method. The difficulties of incorporations two groups in close proximity in the carbazole bay region were further underlined by attempting with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

2.1.7 Formylation of N-TIPS carbazole

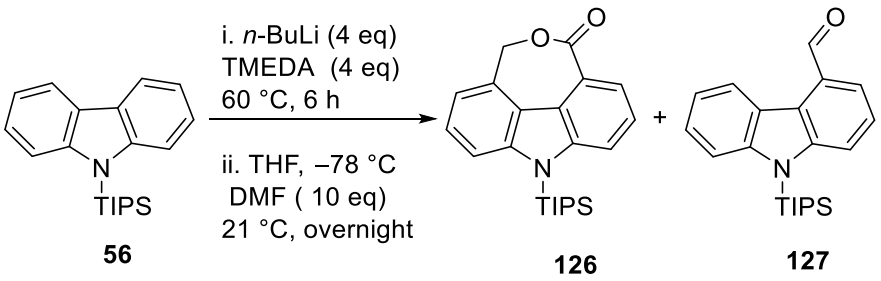
In the literature, it was found that the 1,2-dihydroacenaphthylene-1,2-diol **123** was cleaved into a dialdehyde **124** which was immediately engaged in a Cannizzaro reaction giving lactone **125** in 22% yield (**Scheme 49**). [108]



Scheme 49: Intramolecular Cannizzaro reactions of naphthalene dialdehyde **124**

Trapping of the lithiated species of *N*-TIPS carbazole **81** with dimethylformamide, [109] was examined (**Table 5**).

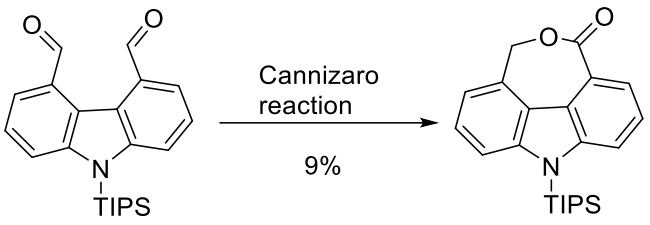
Table 5: The formylation of the *N*-TIPS carbazole **56**



56 **126** **127**

Entry	DMF (no of eq)	Product	Yield
1	DMF (4 eq)	**126**	9%
		127	n/d
2	DMF (10 eq)	**126**	5%
		127	11%
3	DMF (10 eq)	**126**	5%
		127	4%
4	DMF (10 eq)	**126**	9%
		127	2%
5	DMF (20 eq)	**126**	5%
		127	22
		129-130	n/d

The formylating agent was very reactive and gave more than one product. Purification by flash column chromatography gave *N*-TIPS carbazole lactone **126** in 9% yield, along with *N*-TIPS carbazole monoaldehyde **127** (entry 1). This product was related to Cannizzaro's reaction (**Scheme 50**).[108]



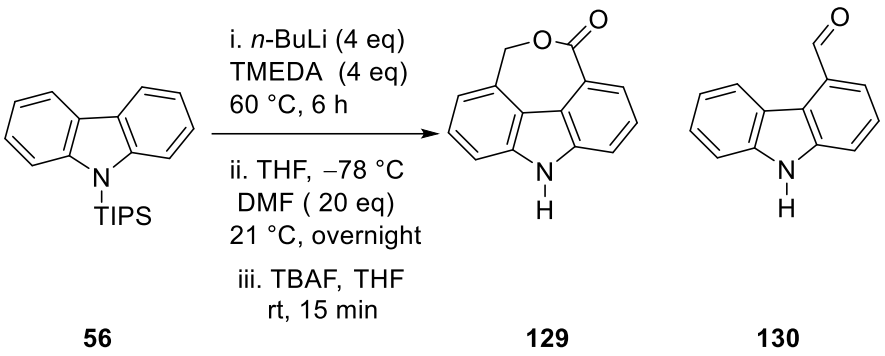
128 **126**

Scheme 50: The Cannizaro reaction of *N*-TIPS-carbazole dialdehyde **128**

Even though DMF is generally a reactive electrophile towards organolithiums, a low yield was observed in the trapping stage to form the product. The amount of the DMF was increased and the work-up was changed. However, this did not improve the yield of *N*-TIPS carbazole lactone **126** (entries 2,3). The desired dialdehyde **128** was observed to be impure and formed in low yield. Increasing the amount of DMF to 20 equivalents also resulted in removed of TIPS group and gave a mixture of compounds with and without TIPS (entry 5).

Deprotection of the *N*-TIPS carbazole lactone **126,** as both a crude mixture and pure, was explored (**Table 6**). After the lithiation stage and work-up, the crude mixture was taken to remove TIPS group using TBAF,[96] resulting in 10% **129** and mono aldehyde **130** in 18% yield (entry 1). Moreover, deprotection of *N*-TIPS carbazole lactone **126** as a pure compound using TBAF gave the carbazole lactone **129** in 29% yield (entry 2).

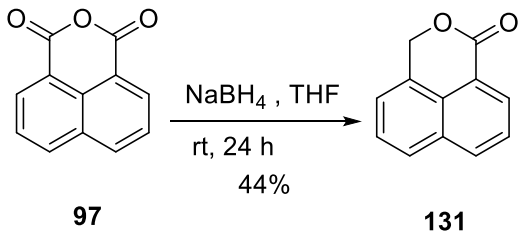
Table 6: Deprotection of *N*-TIPS carbazole lactone **126**



Entry	Reaction conditions	Product	Yield
1	i. lithiation (DMF 20 eq) ii. TBAF (1.5 eq) in THF rt, 15 min	**129** **130**	10% 18%
2	i. lithiation (DMF 20 eq) ii. TBAF (1.5 eq) in THF rt, 15 min	**129**	29%

2.1.7.1 Synthesis of N-TIPS carbazole lactone 126

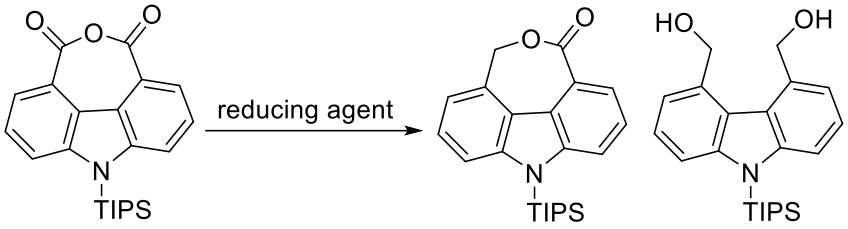
To improve the yield of **126**, the synthesis of *N*-TIPS carbazole lactone was investigated, using an alternative method. The reduction of naphthalic anhydride **97** to naphthalene lactone **131** was reported in the literature (**Scheme 51**). [110]



Scheme 51: Reduction of anhydride naphthalene **79** to lactone **131**

The synthesis of *N*-TIPS carbazole lactone **126** by reduction of anhydride **100** was investigated (**Table 7**).

Table 7: Attempts to synthesise of *N*-TIPS carbazole lactone**126** from the reduction of the *N*-TIPS carbazole anhydride **100**



100 **126** **106**

Entry	Reducing agent	Solvent	Temperature	Time	Result	Yield[a]
1	$NaBH_4$(0.626 eq)	THF	rt	48 h	n/r	
2	$NaBH_4$ (1.0 eq)	THF	rt	2 h	n/r	
			50 °C	2 h		
			reflux	7 h		
3	$NaBH_4$ (1.9 eq)	DMF	rt	2 h	n/r	
			100 °C	24 h		
4	$LiAlH_4$ (3.0 eq)	THF	0 °C	2 h	**126**	13%
					106	7%
5[b]	$LiAlH_4$ (3.0 eq)	THF	0 °C	4 h	**126**	9%
					106	3%
6[b]	$LiAlH_4$ (3.0 eq)	THF	0 °C	6 h	**126**	8%
					106	9%
7[b]	$LiAlH_4$ (1.5 eq)	THF	0 °C	6 h	**126**	6%

[a]Isolated yield after purification by flash column chromatography. BnNH carbazole observed.

Initially, the method of Fuson and Munn was examined,[111] using sodium borohydride ($NaBH_4$) to reduce the anhydride **100** at different temperatures, times, and using different solvents

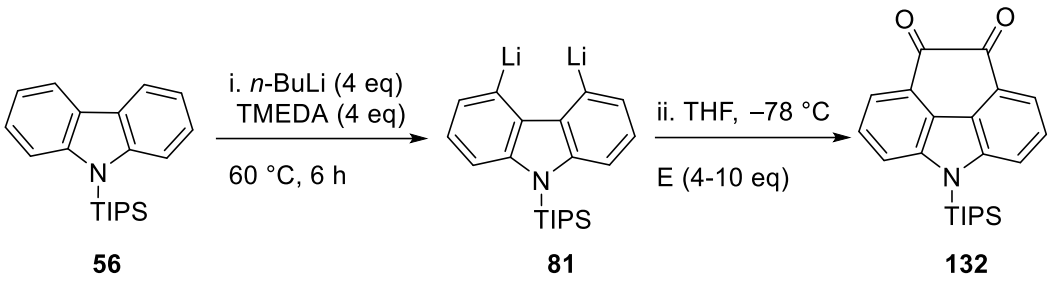
Unfortunately, in every case there was no reaction (entries 1,2 and 3). The reduction of *N*-TIPS carbazole anhydride **100** was achieved by the literature procedure, [112] using lithium aluminium hydride ($LiAlH_4$) as a reducing agent, which gave *N*-TIPS carbazole lactone **126** in low yield along with *N*-TIPS carbazole diol **106**.[89] Attempts were made to optimise the reaction. Firstly, 3 equivalents of $LiAlH_4$ in THF were used in an ice bath for two hours and gave *N*-TIPS carbazole lactone **126** in 13% yield, along with *N*-TIPS carbazole diol **106** in 7% yield. Starting materials without TIPS were recovered (entry 4). The reaction time was increased from 2 to 4, to 6, hours in an attempt to improve the yield, but this did not work and gave low yields for **126**, **106**, and also resulted in the removal of the TIPS group (entries 5 and 6). Trying to decrease the amount of $LiAlH_4$ to half and leaving the reaction for 6 hours also did not improve the yield and gave a mixture of product with and without the TIPS group (entry 7).

2.1.8 Quenching with oxalate

It was proposed that treatment with an oxalate derivative would form a cyclic 1,2 diketone, alerting potential peri-like interaction.

In Table 8, when trapping **81** with oxalyl chloride, no reaction occurred, and the starting material was recovered in 23% yield (entry 1). Secondly, trapping with dimethylcarbamoyl chloride also recovered starting material in 9% yield (entry 2). Use of diethyloxalate also gave recovered starting materials (entry 3). Trapping **81** with ethyl chlorooxoacetate, [113] worked and gave *N*-TIPS carbazole diketone **132** in a low 4% yield and 22% recovered starting materials (entry 4). Moreover, increasing the amount of ethyl chlorooxoacetate from 2 to 10 equivalent causes the decomposition of the product **132** after purification by flash column chromatography (entry 5).

Table 8: Attempts to synthesise diketone carbazole **132**



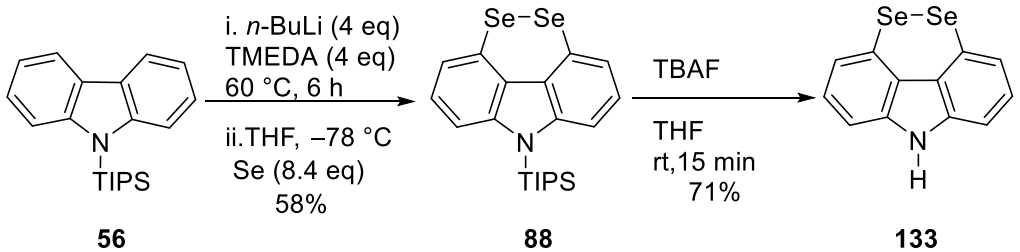
56 **81** **132**

Entry	Electrophiles	No of eq	Result	Yield[a]
1	oxalyl chloride	2	S.M.	23%
2	dimethylcarbamoyl chloride	2	S.M.	9%
3	diethyloxalate	2	S.M.	n/d
4	ethyl chlorooxoacetate	2	**132**	4%
5	ethyl chlorooxoacetate	10	S.M. decomposed product	22%

[a] Isolated yield after purification by flash column chromatography.

2.1.9 Synthesis of carbazole diselenide 88

The Grainger group synthesis of *N*-TIPS carbazole diselenide **88**[89, 91] was repeated, affording **88** in 58% yield. The diselenide **88** was deprotected using TBAF in THF at room temperature for 15 minutes to give carbazole diselenide **133**,[89, 91] in 71% yield (**Scheme 52**).

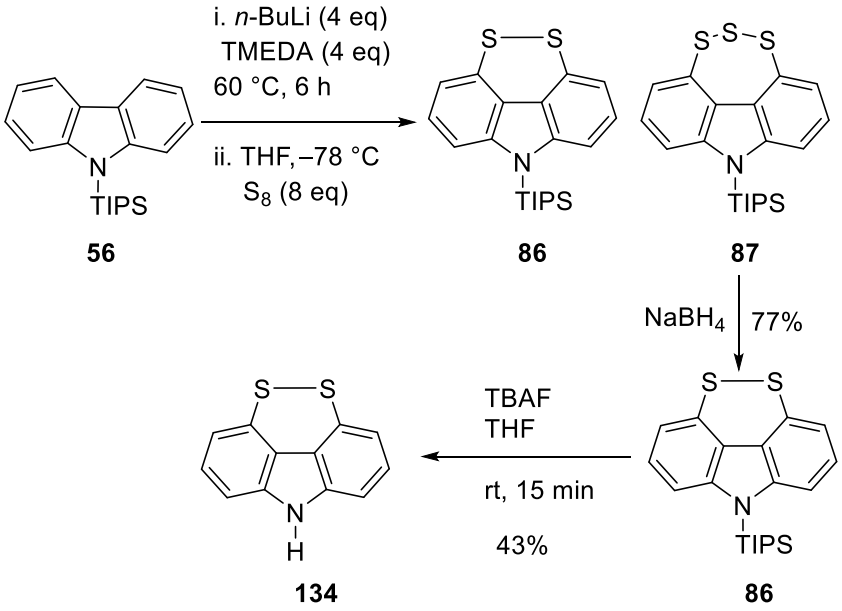


56 **88** **133**

Scheme 52: Synthesis of 4,5-diselenide carbazole **88**

2.1.10 Synthesis of carbazole disulfide 86

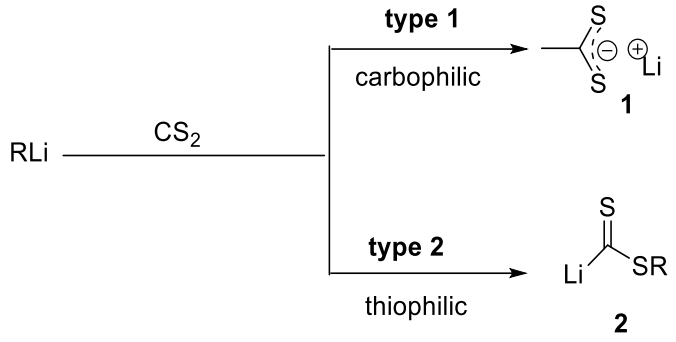
The *N*-TIPS carbazole disulfide **86**, [89, 90] was also prepared on small scales (1.23 mmol), the reaction gave *N*-TIPS carbazole disulfide **86** in 51% yield. However, on large scales (3.31 mmol), the reaction gave a mixture of *N*-TIPS carbazole disulfide **86** and *N*-TIPS carbazole trisulfide **87**. The *N*-TIPS carbazole trisulfide **87** was converted to *N*-TIPS carbazole disulfide **86** *via* treatment of the mixture with $NaBH_4$, which gave **86**,[89] in 77 % overall yield. The *N*-TIPS carbazole disulfide **86** was deprotected using TBAF to get carbazole disulfide **134**,[89, 90] in 43% yield (**Scheme 53**).



Scheme 53: Synthesis of *N*-TIPS carbazole disulfide **86** and carbazole disulfide **134**

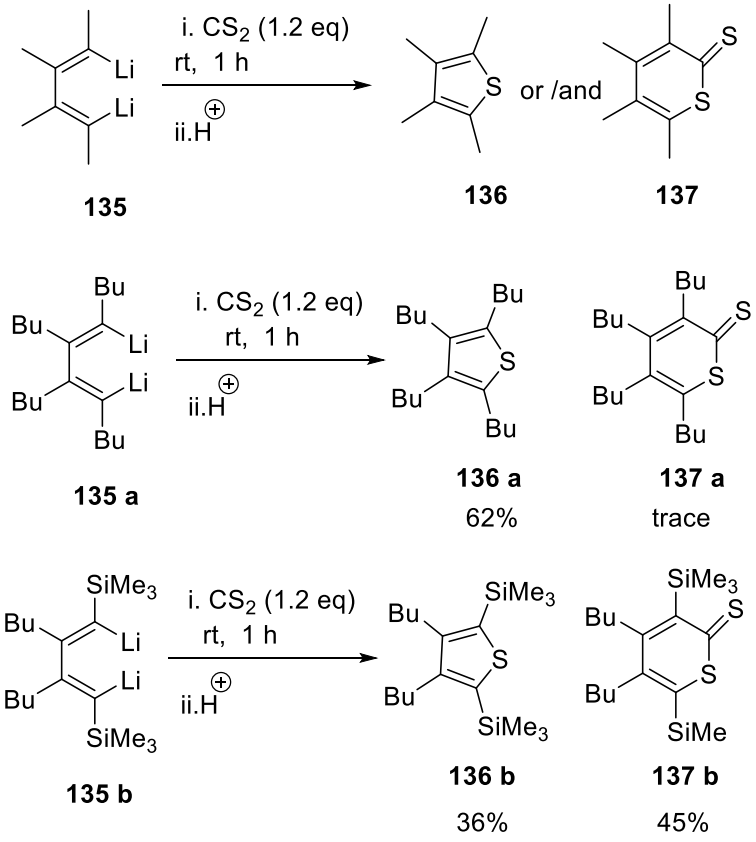
2.1.11 Quenching with carbon disulfide

In the literature, carbon disulfide was used as an electrophile in the trapping of dilithiated compounds *via* both carbophilic addition and thiophilic addition to give one product or a mixture of product (**Scheme 54**).[114, 115]



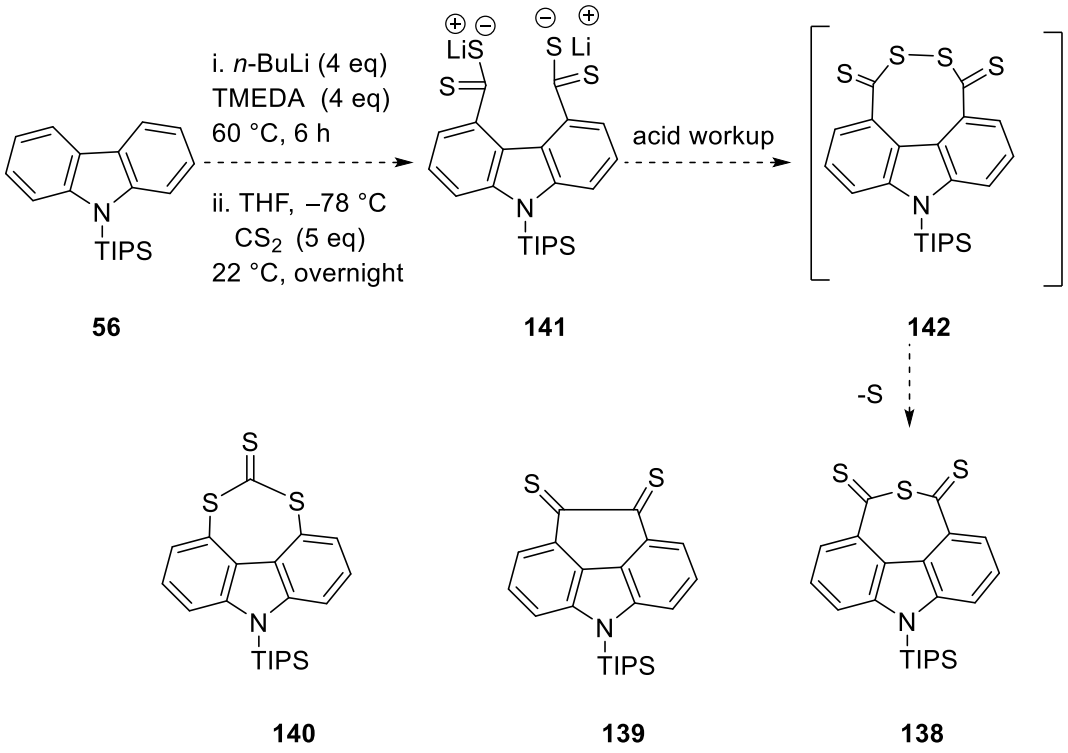
Scheme 54: Reaction patterns of CS_2 with organolithium compounds

For example, reaction of 1,4-dilithio-1,3-dienes **135** with carbon disulfide gave a single product of **136** or mixture of **136**, and **137** (**Scheme 55**).[115]



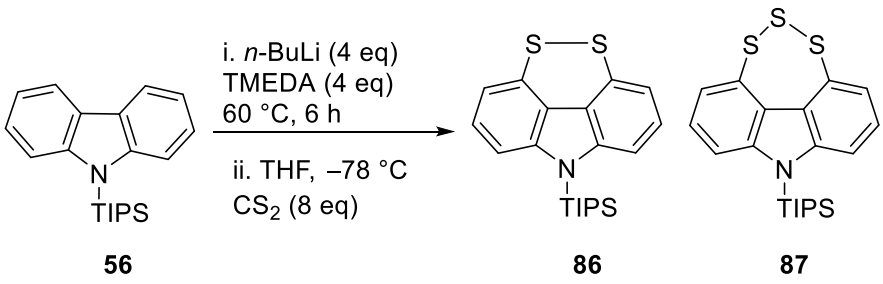
Scheme 55: Example of the reaction of CS_2 with **133**

This led to the examination of the lithiation of *N*-TIPS carbazole **56** and trapping with CS_2. It was proposed that trapping of **56** with CS_2 may result in the formation of three compounds **138**, **139** and **140** (**Scheme 56**).



Scheme 56: The proposal of the trapping of lithiation species of *N*-TIPS carbazole **56** with CS_2

The trapping of *N*-TIPS carbazole **56** with CS_2 was demonstrated. The products were a mixture of disulfide **86**,[89] and trisulfide **87**,[89] in less than 5% yield (**Scheme 57**).



Scheme 57: Reaction of the CS_2 with carbazole **56**

The ^{1}H-NMR showed the presence of *N*-TIPS carbazole disulfide **86** and *N*-TIPS carbazole **56** after multiple purifications by flash column chromatography (**Figure 8**).

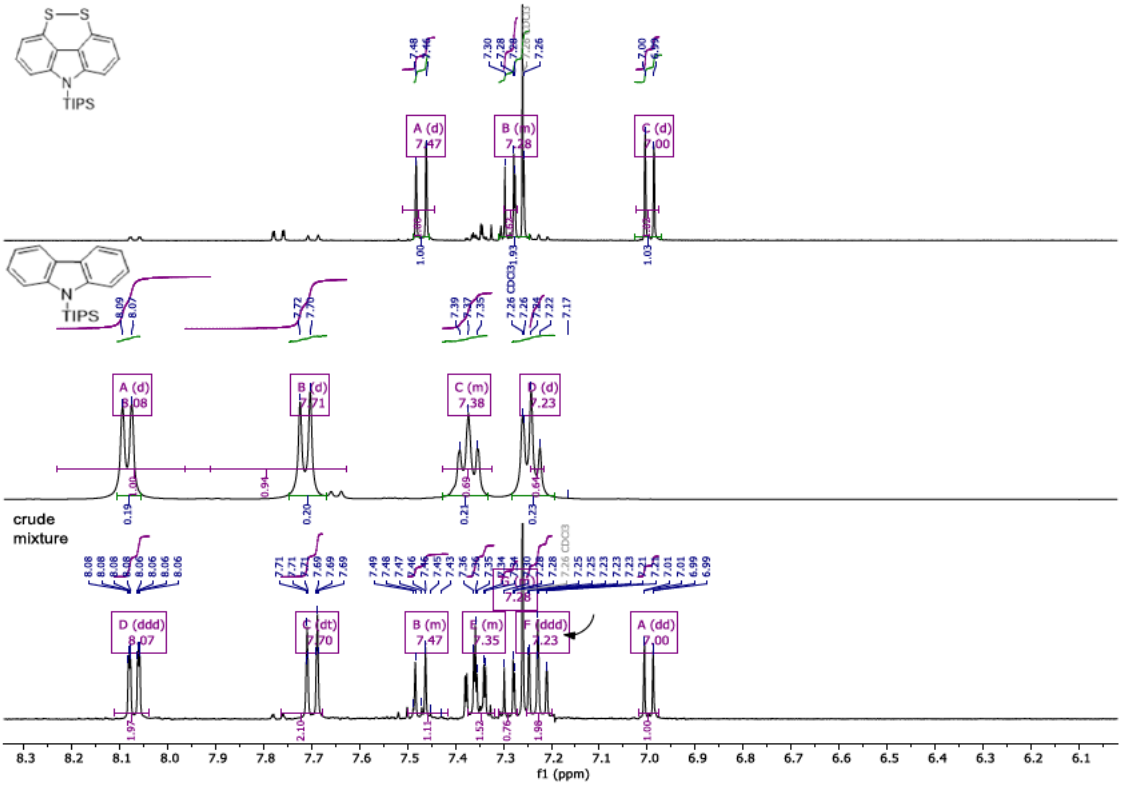


Figure 8: The ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) for the reaction of *N*-TIPS carbazole **56** with CS_2

After deprotecting the reaction mixture, ^{1}H-NMR showed the mixture of the carbazole disulfide **134**,[89] and carbazole trisulfide **143**[89] (**Figure 9**).

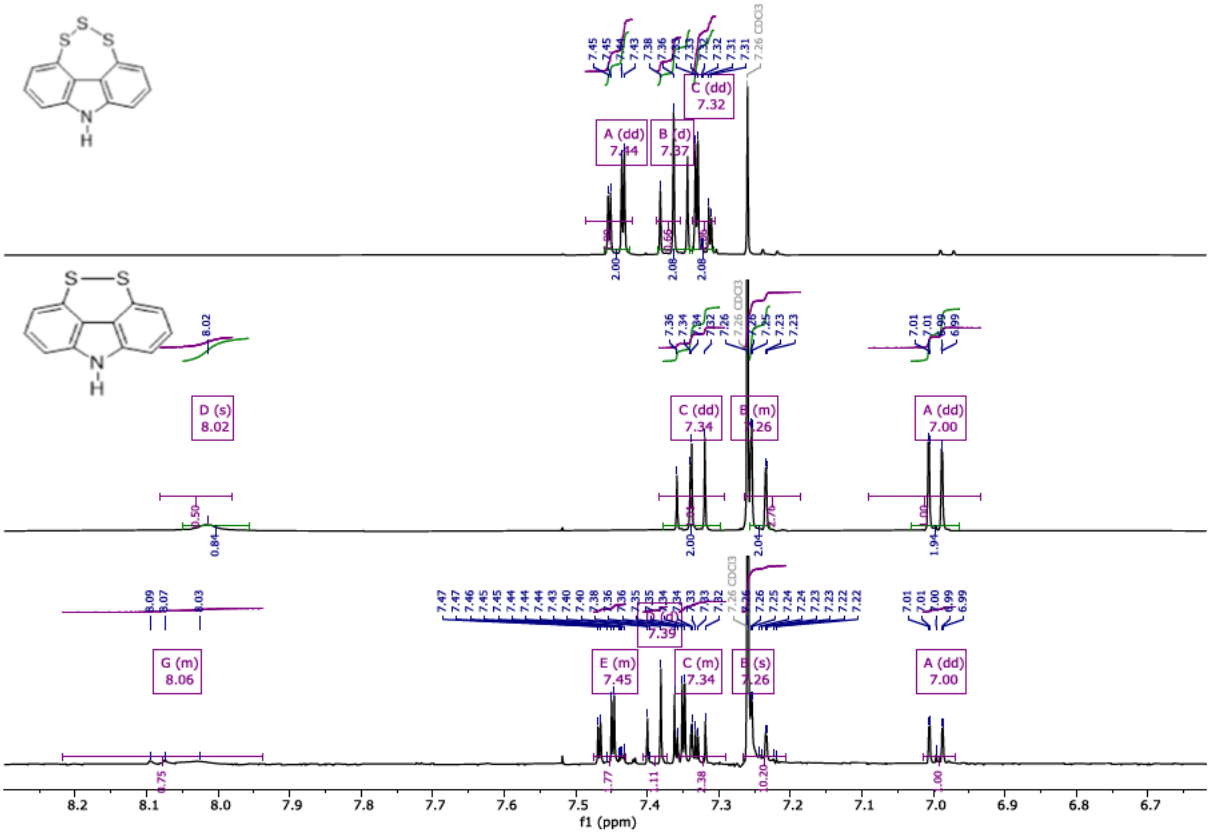
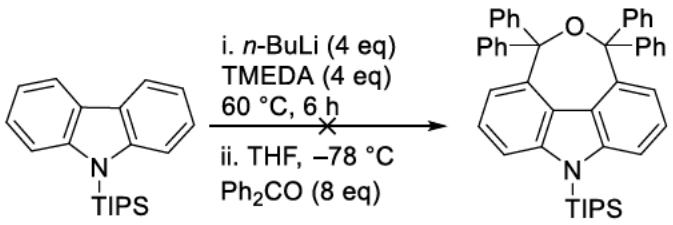


Figure 9: The ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of the mixture of disulfide **134** and trisulfide **143**

2.1.12 Quenching with benzophenone

Quenching with benzophenone was also examined.[116] However, the reaction was unsuccessful **(Scheme 58)**.

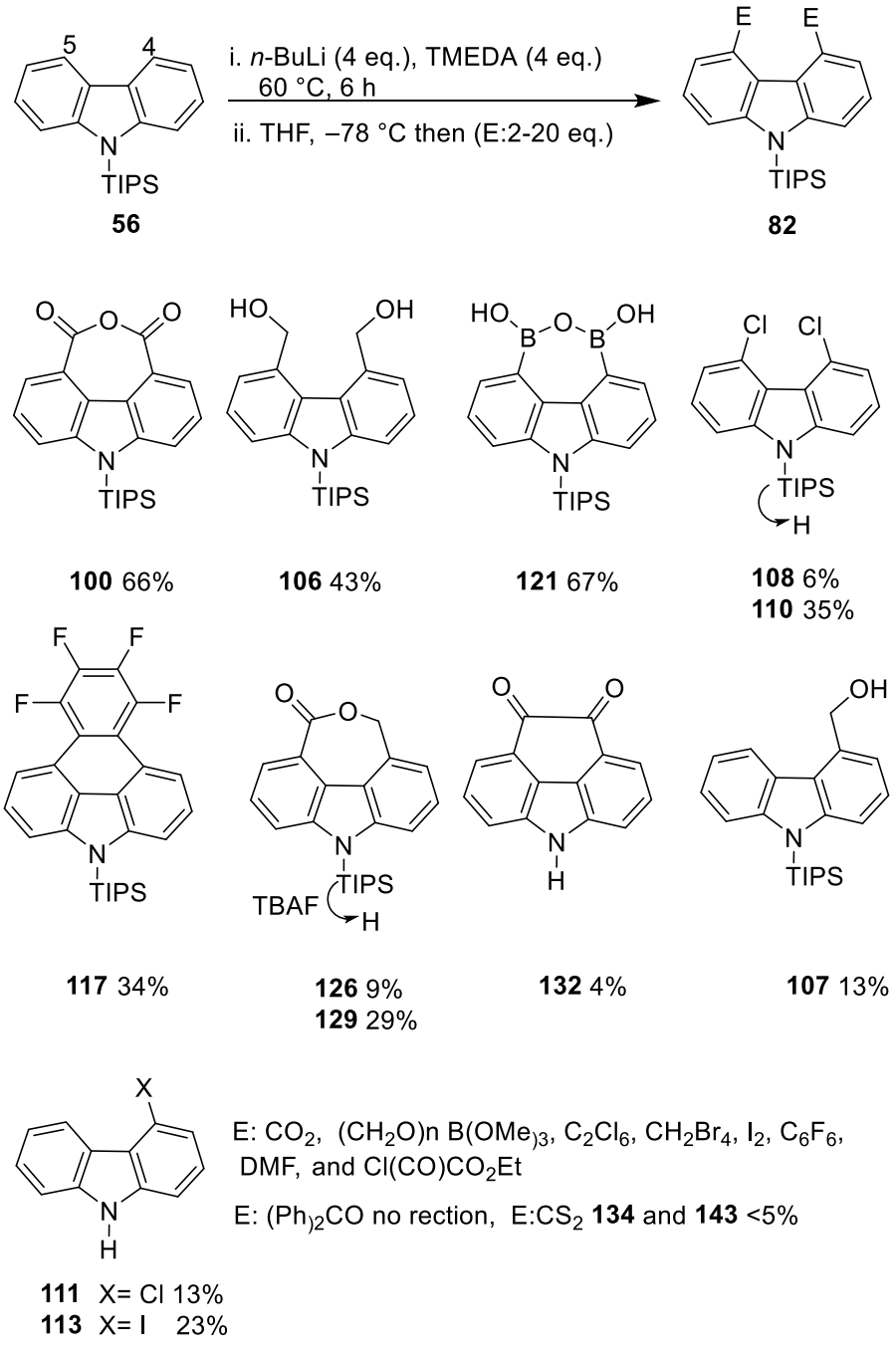


56 **144**

Scheme 58: The reaction of benzophenone with *N*-TIPS carbazole **56**

The result showed no appreciable reaction and starting material was evident in the ^{1}H-NMR of the crude reaction mixture. This may be due to the size of the benzophenone to access the bay region of carbazole.

In summary, the synthesis of 4,5-disubstituted carbazoles was obtained and successful where the electrophile was particularly small, or where a ring could be formed in situ, relieving potential *peri*-like steric and electronic repulsions in the hindered carbazole bay region. The synthesis of *N*-TIPS carbazoles was achieved for *N*-TIPS carbazole anhydride **100** in 66% yield, *N*-TIPS carbazole diboronic anhydride **121** in 67% yield, the *N*-TIPS carbazole diol **106** 43%, 4H-naphtho[1,2,3,4-def]carbazole **117** in 34% yield, dichloride carbazole **110** in 35% yield, carbazole lactone **126** in 29% yield (**Scheme 59**).



Scheme 59: 4,5-Dilithiation and electrophilic trapping of *N*-TIPS carbazole **56**

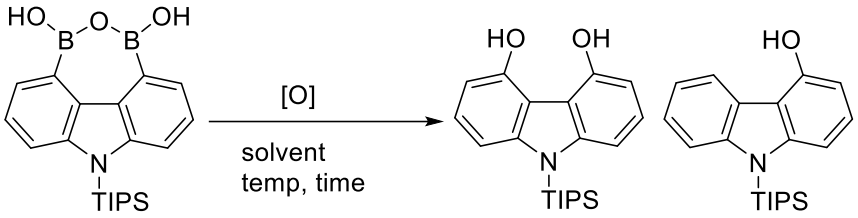
2.2 Synthetic applications

The functionality in unique 4,5-disubstituted carbazoles can be further modified, expanding the range of carbazoles. Further transformations of the 4,5-disubstituted carbazoles were investigated.

2.2.1 Oxidation of *N*-TIPS carbazole boronic anhydride 121

The oxidation of *N*-TIPS carbazole boronic anhydride **121** was examined with various oxidising agents (**Table 9**).

Table 9: Screen of the oxidation of *N*-TIPS carbazole diboronic acid **121**



121 **145** **93**

Entry	Oxidising agent	Solvent	Temperature	Time	Products	Yield[a]
1	H_2O_2 60% w/v (4.0 eq.)	THF	rt	24 h	n/r	
2	*m*-CPBA (2.4 eq.)	CH_2Cl_2	rt	2 h	**145**	16%
			60 °C	2 h	**93**/S.M.	n/d
			reflux	2 h		
3	NMO (5.0 eq.)	CH_3CN	reflux	3 h	**145**	31%
					93	13%
4	NMO (5.0 eq.)	CH_3CN	reflux	12 h	**145**	6%
					93	13%
5	NMO (10.0 eq.)	CH_3CN	reflux	3 h	**145**	29%
					93	14%

[a] Isolated yield after purification by flash column chromatography.

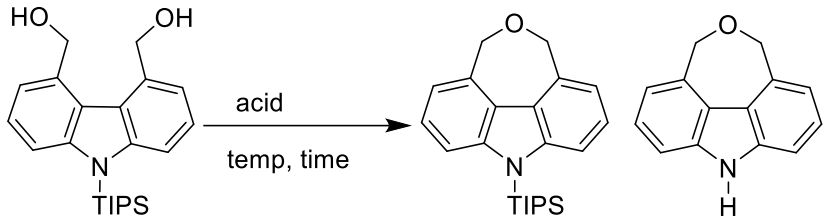
Firstly, using hydrogen peroxide,[82] in THF at room temperature, no reaction was observed after 24 hours (entry 1). Secondly, the use of m-chloroperoxybenzoic acid was examined. ^{1}H-NMR of the crude reaction mixture showed the presence of 4,5-dihydroxy-*N*-TIPS carbazole **145** and 4-monohydroxy-*N*-TIPS carbazole **93**.[89] The crude material was purified by flash column

chromatography to afford the 4,5-dihydroxy-*N*-TIPS carbazole **145** in 16% yield and a mixture of 4-monohydroxy-*N*-TIPS carbazole **93** and starting materials (entry 2). The oxidation of diboronic anhydride **121** using *N*-methylmorpholine-*N*-oxide in refluxing CH_3CN for 3 hours gave the 4,5-dihydroxy -*N*-TIPS carbazole **145** in 31% yield along with 4-monohydroxy-*N*- TIPS carbazole **93** in 13% yield (entry 3).[89, 117] Increasing the time at reflux from 3 to 12 hours decreased the yield of **145** to 6% (entry 4). Increasing the amount of *N*-methylmorpholine-*N*-oxide resulted in a decrease in yield of 4,5-dihydroxy-*N*-TIPS carbazole **145** (entry 5). In summary, the best yield for the 4,5-dihydroxy-*N*-TIPScarbazole **145** was 31% along with 4-monohydroxy **93** in 13%. Complementary to the oxidation of silane **84,** the 4,5-dihydroxy-*N*-TIPS carbazole **145** was the major product formed in the oxidation of the *N*-TIPS carbazole diboronic anhydride **121** using NMO oxidising agent. [89, 117]

2.2.2 Cyclisation of *N*-TIPS carbazole diol 106

The cyclisation of diol **106** to cyclic ether **146** was accomplished using H_3PO_4.[118] Reaction optimisation was investigated with different acids, times and temperatures (**Table 10**). Initially, using concentrated HCl at room temperature for 7 hours gave *N*-TIPS carbazole cyclic ether **146** in 2% yield and deprotected cyclic ether **147** in 17% yield (entry 1). Using H_3PO_4 50% at room temperature for 11 hours resulted in no product being formed (entry 2). Refluxing the mixture for 1 hour gave the desired product **146** in 18% yield along with 33% deprotected product **147** (entry 3). Increasing the reaction time from 1 hour to 3 hours led to a decrease in isolated products, *N*-TIPS carbazole cyclic ether **146** in 4% yield and **147** in 18% yield (entry 4).

Table 10: Optimisation of the dehydration of *N*-TIPS carbazole diol **106** to cyclic ether **146**



106 **146** **147**

Entry	Acid	Temperature	Time	Products	Yield[a]
1	HCl (Conc.)	rt	1 h	**146**	2%
				147	17%
2	H_3PO_4 50%	rt	11 h	n/r	
3	H_3PO_4 50%	reflux	3 h	**146**	4%
4	H_3PO_4 50%	reflux	1 h	**147**	18%
5	H_3PO_4 50%	60 °C	7 h	**146**	28%
		75-80 °C	4 h	**147**	4%
		90 °C	7 h		
6	H_3PO_4 50%	90 °C	11 h	**146**	56%
				S.M.	11%

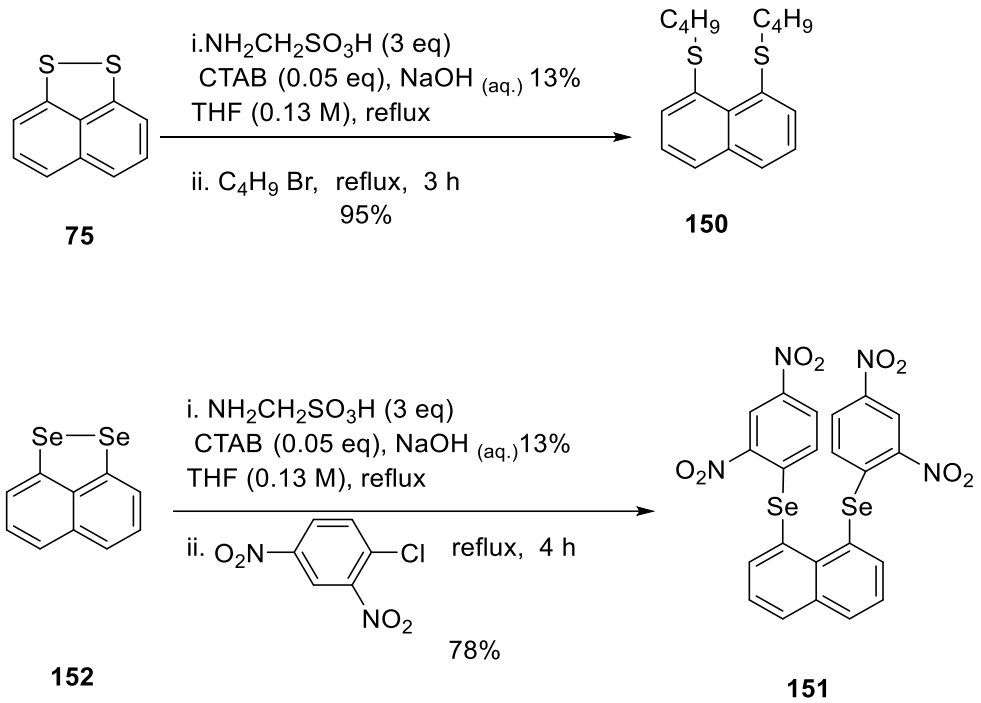
[a] isolated yield after purification by column chromatography.

The reaction was heated at different temperatures 60 °C ,75 °C, and 90 °C after 18 hours gave *N*-TIPS carbazole cyclic ether **146** in 28% yield (entry 5). As a result, the optimal temperature and time for the reaction was found to be 90 °C for 11 hours, providing the best yield of **146** (56%), after purification by flash column chromatography (entry 6).[89] The *X*-ray crystal structure of **146** was grown by slow evaporation from ethyl acetate solution (**Section 2.3**).

2.2.3 Reduction and methylation of di S/Se carbazole

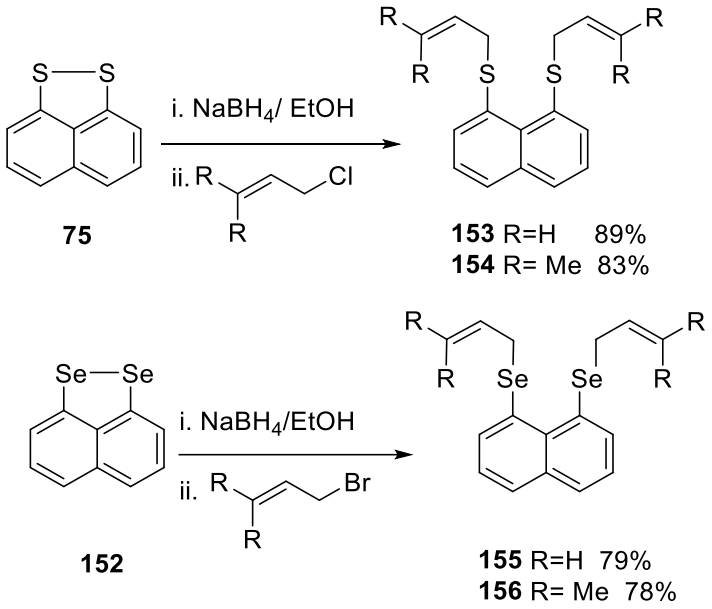
In order to compare the photophysical properties of 3,6-bismethyl sulfide carbazole **148** and 3,6-bismethyl selenide carbazole **149**, [119] with 4,5-bismethyl(S/Se)-substituted carbazoles (**Sections 2.4**), the reduction and methylation of 4,5-disulfide carbazole **86** and 4,5-diselenide carbazole **88** were investigated .

In the literature, Ferreira and co-workers,[120] synthesised arylalkyl chalcogenides, diaryl chalcogenides, and dialkyl chalcogenides under phase transfer conditions. The reduction of the dichalcogenides by aminoiminomethanesulfinic acid (thiourea dioxide) was achieved in an alkaline medium and catalysed by a quaternary ammonium salt. The intermediate arylthiolates and arylselenolates were quenched by alkyl and activated aryl halides to give the corresponding sulfide **150** and selenide **151** in high yield (77-97%) (**Scheme 60**).[120]



Scheme 60: Synthesis of dialkylchalcogenides **150** and **151**

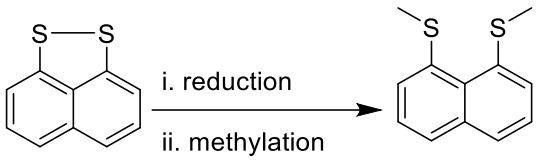
In 1995, Furukawa and co-workers,[121] prepared allyl 1,8-dichalcogen-substituted naphthalene through reduction of the disulfide **75** or diselenide **152** with $NaBH_4$ followed by addition of an allylic halide (**Scheme 61**). [122,123 121]



Scheme 61: Synthesis of allyl 1,8-dichalcogen-substituted naphthalene

In order to determine appropriate conditions for carbazole, the naphthalene disulfide **75** was investigated (**Table 11**). Firstly, the Ferreira method,[120, 124] was followed and resulted in the product **157**,[122] in 21% yield (entry 1). Secondly, the Furukawa literature followed and resulted in the product **157**, [122, 125] in 25% yield after purification by column chromatography (entry 2).[121]

Table 11: The reduction and methylation of the naphthalene **75**.



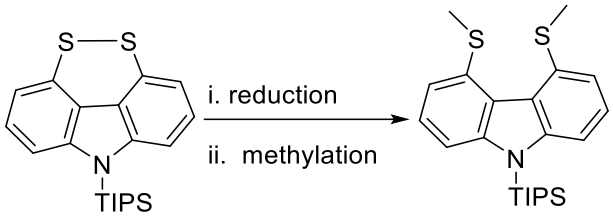
75 **157**

Entry	Reaction conditions	Temp	Time	Yield[a]
1	$NaOH_{(aq.)}$ (6%), THF (0.13 M) $NH_2CH_2SO_3H$ (3.0 eq), CTAB (0.05 eq) MeI (6.0 eq)	reflux	6 h	21%
2	$NaBH_4$/ EtOH MeI (5.0 eq) in THF	rt	2 h	25%

[a]Isolated yield after purification by column chromatography.

Reduction and methylation of the *N*-TIPS carbazole 4,5-dichalcogen was then investigated (**Table 12**). Firstly, no reaction occurred when the Ferreira procedure was used (entry 1). As a result, the Furukawa procedure was applied and gave **158** in 32% yield (entry 2). The mixture of disulfide **86** and trisulfide **87** from the quenching reaction (**Scheme 53**) was reduced by $NaBH_4$ and heated to 50 °C for 2 hours, followed by the addition of MeI at room temperature for 1 hour, gave the **158** in 33% yield (entry 3). The best results were when the pure disulfide **86** was heated at 50 °C and the amount of the MeI was increased to 20 equivalents, the yield of **158** (44%) (entry 4).

`Table 12: The reduction and methylation of the *N*-TIPS carbazole disulfide **86**

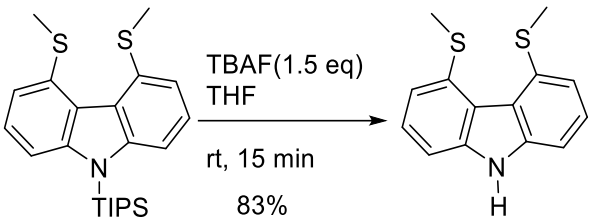


86 **158**

Entry	Reaction condition	Temp	Time	Yield[a]
1	$NaOH_{(aq.)}$ (6%), THF, $NH_2CH_2SO_3H$ (4.0 eq), CTAB (0.05 eq) MeI (8.0 eq) reflux, 6 h	80 °C	6 h	n/r
2	$NaBH_4$/ EtOH MeI (5.0 eq) in THF	25 °C	2 h	32%
3	$NaBH_4$ (2.5 eq for S-S)/ EtOH (0.5) MeI (20.0 eq)	50 °C rt	1 h 1 h	33%
4	$NaBH_4$ / EtOH MeI (20.0 eq) in THF	50 °C rt	2 h o/n	44%

[a] Isolated yields after purification by column chromatography.

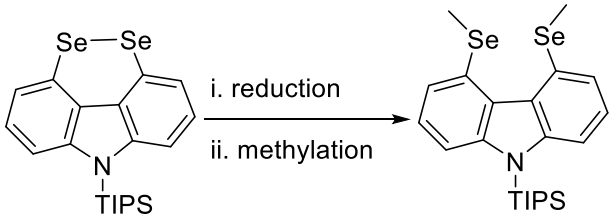
The 4,5-bismethylsulfide *N*-TIPS carbazole **158** was deprotected using TBAF in THF at room temperature for 15 minutes and gave the 4,5-bismethyl sulfide carbazole **159** in 83% yield (**Scheme 62**). The X-ray structure of the 4,5-bismethyl sulfide carbazole **159** was grown by slow evaporation from ethanolic solution (**Section 2.3**).



Scheme 62: Deprotection of 4,5-bismethyl sulfide *N*-TIPS carbazole **158**

Furthermore, the 4,5-bismethyl selenide *N*-TIPS carbazole **160** was optimised utilising the Furukawa procedure (**Table 13**).

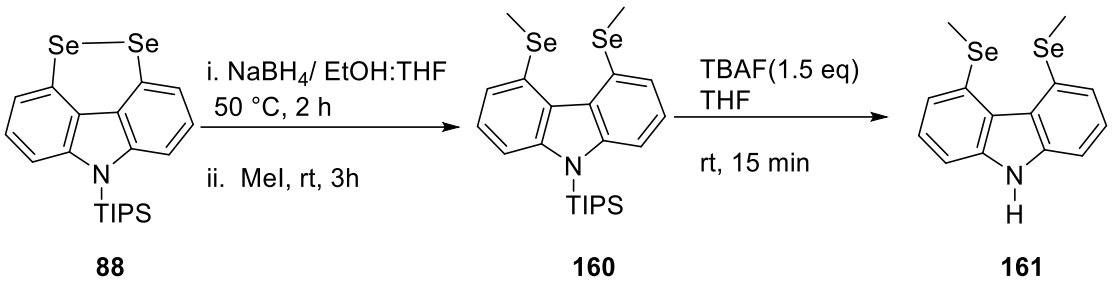
Table 13: Optimisation of the synthesis of 4,5-bimethyl selenide-*N*-TIPS carbazole **160**



Entry	Reaction condition	Time	Temp	Yield[a]
1	i. $NaBH_4$/ EtOH ii. MeI (5.0 eq) in THF	rt	4 h	11%
2	i. $NaBH_4$(3.0 eq)/ EtOH ii. MeI (20.0 eq) in THF	50 °C rt	3 h o/n	41%

[a] Isolated yields after purification by column chromatography.

The TIPS group was removed from 4,5-bismethyl selenide *N*-TIPS carbazole **160** using the TBAF,[96, 126] to give 4,5-bismethyl selenide carbazole **161** in 48% yield over two steps (**Scheme 63**). The X-ray structure of the 4,5-bismethylselenide carbazole **161** was grown by slow evaporation from dichloromethane solution (**Section 2.3**).



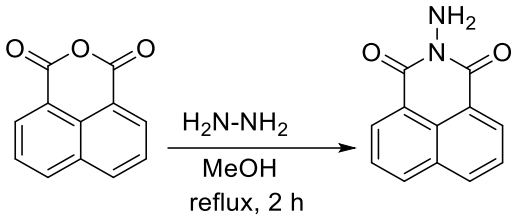
88 **160** **161**

Scheme 63: Synthesis of 4,5-bismethyl selenide carbazole **161**

2.2.4 Transformation of *N*-TIPS carbazole anhydride 100 to form a CO-N(R)-CO imide functionality

2.2.4.1 Using hydrazines

The synthesis of *N*-amino-1,8-naphthalimide **162** was reported by Bojinov *et. al*. The naphthalic anhydride **97** was treated with hydrazine monohydrate in methanol to give *N*-amino-1,8-naphthalimide **162** in 91% yield (**Scheme 64**).[127]

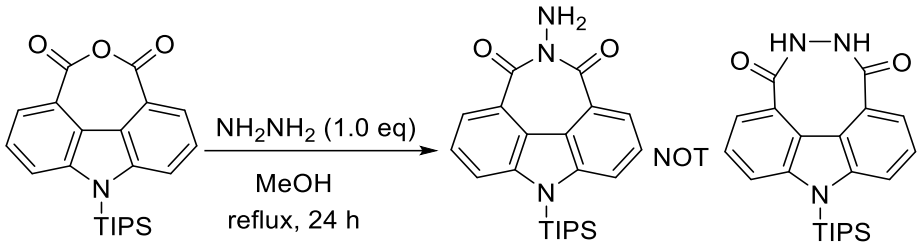


97 91% **162**

Scheme 64: Synthesis of *N*-amino-1,8-naphthalimide **162**

The analogous transformation of the *N*-TIPS carbazole anhydride **100** to form a CO-N(R)-CO functionality was examined with a range of reagents (**Table 14**).

Table 14: Attempted formation of hydrazine *N*-TIPS carbazole **163**



100 **163** **164**

Entry	Hydrazine	Solvent	Temp	Time	Result	Yield[a]
1	NH_2-NH_2 (2.0 eq)	$CHCl_3$	reflux	24 h	**163** S.M.	35%[b] n/d
2	NH_2-NH_2 (1.0 eq)	MeOH	reflux	24 h	**163** S.M.	38%[b]
3	NH_2-NH_2 (1.4 eq)	MeOH	reflux	24 h	**163** **102**	30% n/d
4	NH_2-NH_2 (1.0 eq)	MeOH	sealed tube at 90 °C	6 h	**163** S.M.	17% n/d
5	NH_2-NH_2 (1.0 eq)	EtOH	reflux	48 h	S.M.	n/d
6	$(Me)_2NNH_2$ (2.0 eq)	MeOH	reflux	24 h	S.M.	n/d
7	$(Me)_2NNH_2$ (2.0 eq)	$CHCl_3$	reflux	24 h	S.M.	n/d
8	$PhNHNH_2$ (1.0 eq)	MeOH	reflux		S.M.	n/d

[a] the isolated yield after filtration and washed by solvent.

[b] isolated yield with impurity (S.M.)

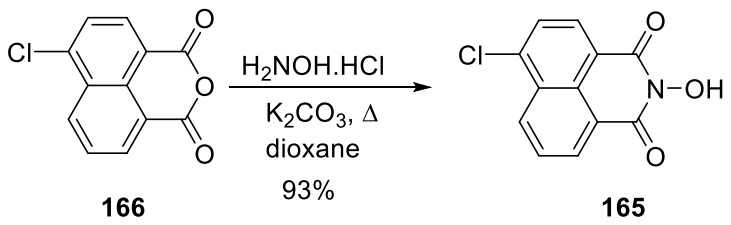
Hydrazine hydrate was dissolved in $CHCl_3$ and the mixture was heated at reflux for 24 hours to give an impure solid precipitate of the hydrazine carbazole **163** in 35% yield. The filtrate contained starting material recovered (entry 1).[128] The impure product was difficult to dissolve in organic solvent, which led to difficulties in purification. Subsequently, the solvent was changed to CH_3OH and the reaction was heated at reflux for 24 hours to afford the pure hydrazine product **163** in 38% yield (entry 2).[89, 127] To improve the yield, the amount of hydrazine hydrate was increased from 1 to 1.4 equivalents; however, this led to the *N*-deprotection of the anhydride **102** (entry 3). The reaction was carried out in a sealed glass tube to increase the temperature to 90 °C, however this gave product **163** in decreased yield (17%) (entry 4). When the solvent was changed from methanol to ethanol and the reaction heated at reflux for 48 hours, no reaction occurred, and the starting material was recovered (entry 5).

When *N*,*N*-dimethylhydrazine was examined under the same conditions, no reaction occurred in methanol, or in chloroform (entries 6, 7).[129] Additionally, using phenyl hydrazine under the same conditions was unproductive and starting materials was recovered (entry 8).

The structure of the product was assigned as imide **163** rather than hydrazine amide **164** based on the IR spectrum that showed weak bands in the 3656, 3356 and 3269 cm^{-1} regions, which represent the NH_2 stretches of primary group. The IR also showed N-C=O stretch at 1694 and 1573 cm^{-1}, analogous were used in the literature to assign the structure of *N*-amino-1,8-naphthalimide**162**.[127] In addition *N*-benzoylbenzohydrazide (PhC(O)NHNH(O)CPh) **164** in the literature shows NH stretches at 3201 and 3001 cm^{-1}.[130]

2.2.4.2 Using hydroxylamine

In the literature, the 2-hydroxy-6-chloro-benzo[de]isoquinoline-1,3-dione **165** was synthesised by the direct reaction of 4-chloro-1,8-naphthalic anhydride **166** with hydroxylamine hydrochloride in the presence of a base (**Scheme 65**).[131]



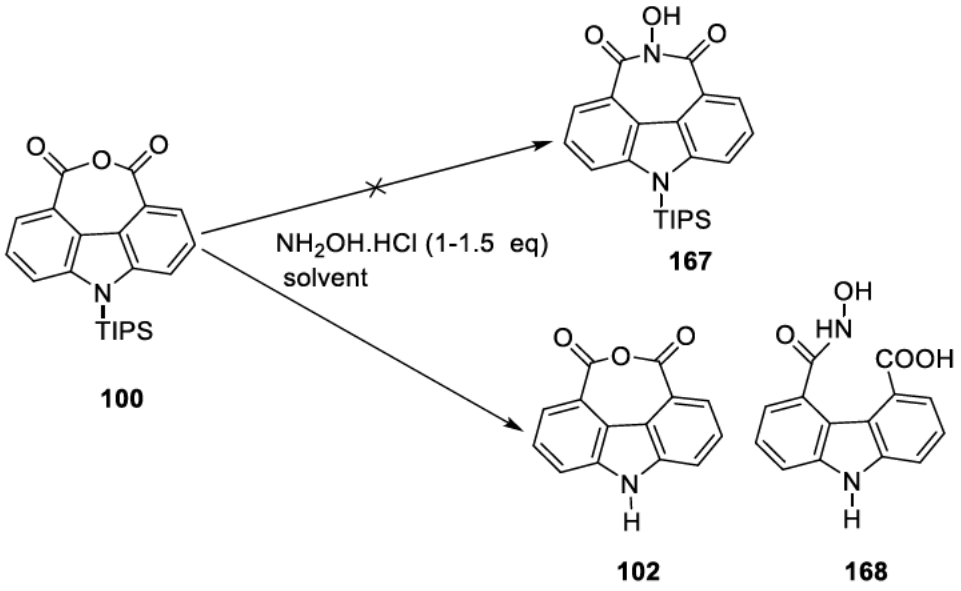
166 **165**

Scheme 65: Reaction of the naphthalene anhydride **165** with hydroxylamine

It was decided to introduce hydroxyl amine (N-OH) to *N*-TIPS carbazole anhydride **100**. The reaction of *N*-TIPS carbazole anhydride **100** with hydroxylamine was investigated (**Table 15**).

Firstly, the reaction was carried out in EtOH as solvent with Et_3N and heating at reflux for 24 hours;[132] starting materials were recovered (entry 1). Changing the base to $NaHCO_3$ did not have any effect (entry 2). The use of DMF as solvent with $NaHCO_3$ with *N*-TIPS carbazole anhydride **100** gave starting matirals (entry 3). The use of NaOH in H_2O and heating at reflux for 24 hours,[132] did not lead to any reaction (entry 4). According to literature procedure for related naphthalene anhydride **97**,[133] 1,4 dioxane was used as solvent with K_2CO_3 as base, heating at reflux for 24 hours and gave deprotecting anhydride **102** (entry 5). Using pyridine as solvent and base at room temperature for 38 hours, also heating at reflux for 5 hours resulted deprotecting anhydride **102** (entries 6 and 7).[134, 135] The reaction was carried out in a sealed glass tube, and temperature was increased to 150 °C for 2 and 6 hours and gave the unexpected compound 5-(hydroxycarbanoyl)-9H-carbazole-4-carboxylic acid **168** in 7% yield (entry 8). The reaction was repeated, and a time increase to 6 hours gave **168** in 14% yield along with anhydride **102** (entry 9).

Table 15: Screening the formation of the hydroxyl carbazole **167**

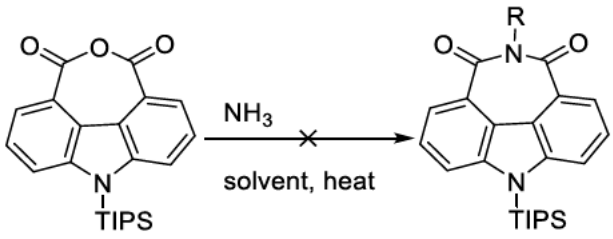


Entry	$NH_2OH.HCl$	Solvent	Base	Temp	Time	Results
1	1.0 eq	EtOH	Et_3N (0.65 eq)	reflux	24 h	S.M.
2	1.5 eq	EtOH	$NaHCO_3$ (1.5 eq)	reflux	24 h	S.M.
3	1.5 eq	DMF	$NaHCO_3$ (1.5 eq)	reflux	24 h	S.M.
4	1.2 eq	H_2O	NaOH (1.0 eq)	reflux	24 h	S.M.
5	1.4 eq	1,4 dioxane	K_2CO_3	reflux	24 h	S.M. **102** n/d
6	1.09 eq	Pyridine	-	rt	38 h	**102** n/d
7	1.09 eq	Pyridine	-	reflux	5 h	**102** 68%
8	1.09 eq	Pyridine	-	150 °C	2 h	**168** 7%
9	1.09 eq	Pyridine	-	150 °C	6 h	**168** 14% **102** n/d

2.2.4.3 Using ammonia

The reaction of *N*-TIPS carbazole anhydride **100** with ammonia was studied (**Table 15**).

Table 15: The reaction of the *N*-TIPS carbazole anhydride **100** with ammonia



100 **169**

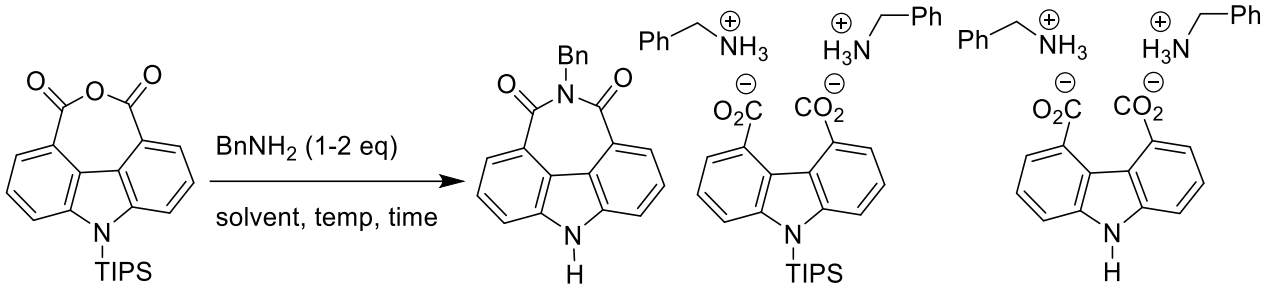
Entry	Solvent	Tempe	Time	Result
1	NH_3 in EtOH (2.0 M) 20.0 eq	reflux	20 h	S.M.
2	NH_3 in H_2O (35%w/w) 20.0 eq	80 °C	14 h	S.M.

Firstly, an attempt was made using ammonia in ethanol, heating at reflux for 20 hours. However, only starting materials were recovered. Similarly using ammonia in H_2O at 80 °C for 14 hours also resulted in no reaction.

2.2.4.4 Using benzylamine

The reaction of *N*-TIPS-carbazole anhydride **100** with benzylamine was investigated (**Table 16**). When the anhydride **100** was treated with benzylamine in EtOH, and heating at reflux for 14 hours, the starting materials were recovered (entry 1). If the solvent was changed to DMF and heated at reflux for 18 hours, the *N*-TIPS carbazole **56** was recovered after purification (entry 2). Moreover, using acetic acid as the solvent, the reaction mixture was heated at 80 °C for 6 hours, and then heated at reflux for 6 hours, caused only the removal of the TIPS group from the starting material (entry 3). Using methanol as solvent with $BnNH_2$, the reaction mixture was heated at reflux for 48 hours, followed by removal TIPS group, after the crude mixture was purified by flash column

Table 16: The screen of treatment **100** with benzylamine



100 **170** **171** **172**

Entry	$BnNH_2$ (eq)	Solvent	Temp	Time	Deprotection step	Result	Yield[a]
1	1.6	EtOH	reflux	14 h	-	n/r	
2	1.6	DMF	reflux	18 h	-	S.M.	
3	1.6	AcOH	80 °C reflux	6 h 6 h	-	**100**+**102**	n/d
4	1.0	MeOH	reflux	48 h	TBAF (1.5 eq) in THF (0.1 M) rt, 15 min	**170** S.M.	**<5%**[b]
5	1.5	MeOH	reflux	48 h	-	**171** **172**	20% 27%
6	1.0	MeOH	reflux	24 h	pyridine (2.0 eq) MeOH rt, 16 h	**171** **172**	22%[b] 29%[b]
7	1.0	MeOH	reflux	24 h	TBAF (3.0 eq) MeOH rt, o/n	**172**	47%[b]
8	2.0	MeOH	reflux	24 h	-	**171** **172**	48% 29%
9	2.0	MeOH	reflux	2 h	TBAF (1.5 eq), THF rt, 30 min	**172**	68%[b]
10	1.0	MeOH	rt	2 h	-	**171** S.M.	26% 47%
11	2.0	MeOH	rt	5-10 min		**171**	57%

[a] Isolated yield after purification by FCC. [b] Isolated yield over two steps.

chromatography gave the desired product carbazole imide **170** in less than 5% yield, the rest was a mixture starting materials.

The compound was confirmed by ^{1}H-NMR which showed the right signal for the carbazole imide **170** (**Figure 10**).

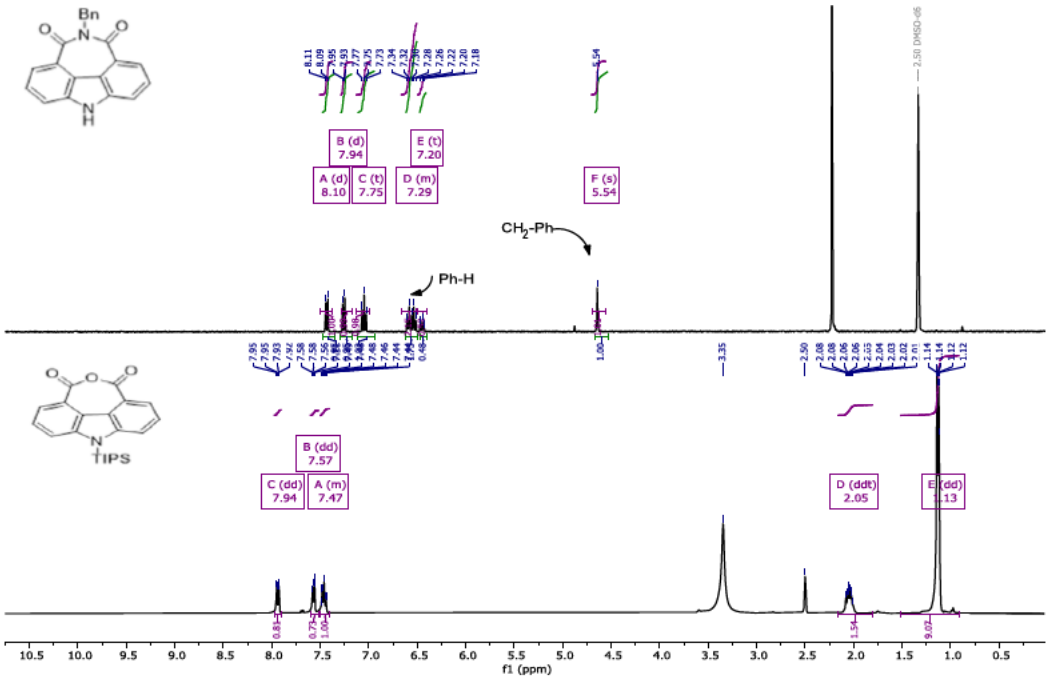


Figure 10: ^{1}H-NMR spectrum (DMSO-d6, 400 MHz) for the carbazole imide **170**

Due to unsatisfactory yield the other analytical data to confirm and identify the product was not collected (entry 4). In spite of this limitation, increasing the $BnNH_2$ amount to 1.5 equivalents and heated at reflux for 48 hours gave the *N*-TIPS carbazole-4,5-dicarboxylate benzylammonium salt **171** in 20% yield, carbazole-4,5-dicarboxylate benzylammonium salt **172** in 27% yield (entry 5). It was decided to remove the TIPS group using two ways to improve the reaction. Firstly, after the *N*-TIPS carbazole anhydride **100** was treated with 1 equivalent of $BnNH_2$ in MeOH and heated at reflux for

24 hours, the crude mixture was taken directly to remove the TIPS group using 2 equivalents of pyridine at room temperature for 16 hours.

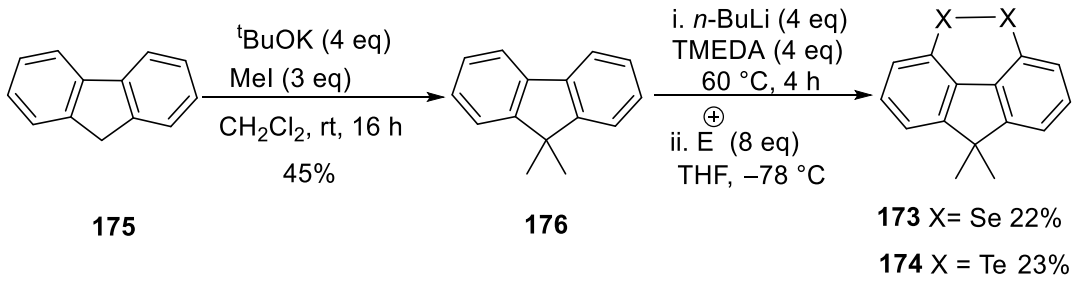
The crude mixture was purified by flash column chromatography to give the *N*-TIPS carbazole-4,5-dicarboxylate benzylammonium salt **171** in 22% yield, and carbazole-4,5-dicarboxylate benzylammonium salt **172** in 29% yield (entry 6). Secondly, the crude mixture was treated with TBAF in MeOH at room temperature for 15 minutes and after the purification by flash column chromatography resulted carbazole-4,5-dicarboxylate benzylammonium salt **172** in 47% yield (entry 7). Additionally, the synthesis of *N*-TIPS carbazole-4,5-dicarboxylate benzylammonium salt **171** was optimised to improve the yield. Initially, increasing the amount of $BnNH_2$ resulted *N*-TIPS carbazole-4,5-dicarboxylate benzylammonium salt **171** in 48% yield along with carbazole-4,5-dicarboxylate benzylammonium salt **172** in 29% yield (entry 8). However, removing the TIPS group gave the carbazole-4,5-dicarboxylate benzylammonium salt **172** in 68% yield (entry 9). The amount of $BnNH_2$ and time of reflux were decreased, which resulted in the *N*-TIPS carbazole-4,5-dicarboxylate benzylammonium salt **171** in 26% yield and starting material was recovered in 47% yield (entry 10). When **100** was treated with 2 equivalents of $BnNH_2$ at room temperature for 10 minutes resulted the *N*-TIPS carbazole-4,5-dicarboxylate benzylammonium salt **171** in 57% yield, which was the best condition to synthesise **171** (entry 11). The formation of the *N*-TIPS carbazole-4,5-dicarboxylate benzylammonium salts **171** depended on the amount of reagent, and reaction time. The X-ray structure for the carbazole-4,5-dicarboxylate benzylammonium salt **172** was obtained by slow evaporation from methanol (**Section 2.3**).

2.3 Comparison of fluorene anhydride and *N* -TIPS carbazole anhydride

In order to compare the reaction of *N*-TIPS carbazole with benzylamine with other analogous fluorene anhydride, the synthesis of 4,5-substituted fluorenes was investigated.

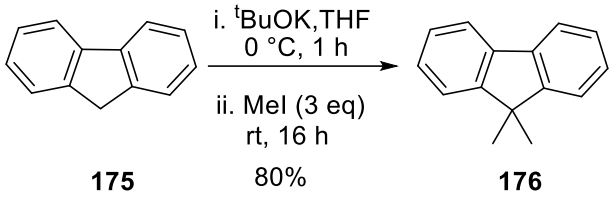
2.3.1 Synthesis of 4,5-disubstiuted 9,9-dimethylfluorenes

The synthesis of dimethyl fluorene diselenide **173** and dimethyl fluorene ditelluride **174** has been previously investigated by the Grainger group (**Scheme 66**). [91, 136] The synthesis began with demethylation of fluorene according to literature procedures,[137] to give the 9,9-dimethyl-*9H*-fluorene **176** in 45% yield. Fluorene **176** was dilithiated and quenched with selenium to give the demethylated fluorene diselenide **173** in 22% yield. It was also intended to use a similar approach to reach the disulfide and trisulfide**.**



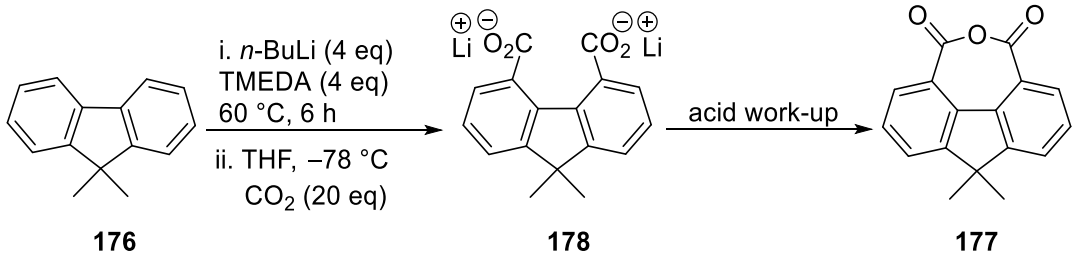
Scheme 66: Synthesis of 9,9-dimethyl-9H-fluorene **176** and 4,5 disubstituted 9,9-dimethyl-*9H*-fluorenes

Following this literature precedent, the 9,9-dimethyl-*9H*-fluorene **176** was synthesised in 80% yield (**Scheme 67**).[82]



Scheme 67: Formation of 9,9-dimethyl-9H-fluorene **176**

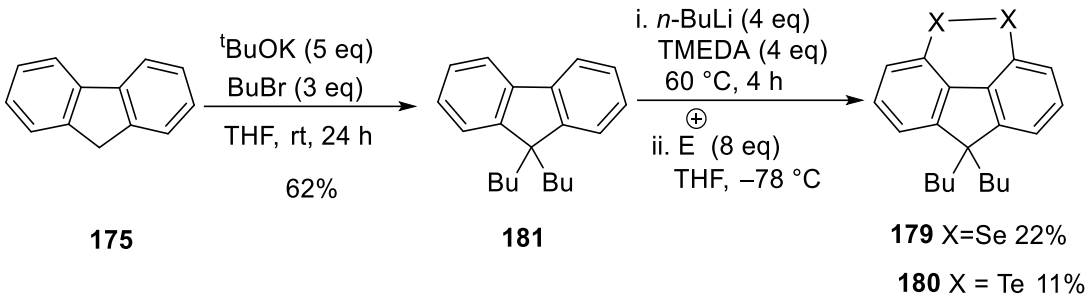
The 9,9-dimethyl-9H-fluorene **176** was dilithiated and trapped with dry ice (CO_2) to give 4,4-dimethyl-4H-fluoreno[4,5-cde]oxepine-8,10-dione **177** in 41% yield after purification by trituration with *n*-hexane **(Scheme 68**).



Scheme 68: Synthesis of fluorene anhydride **177**

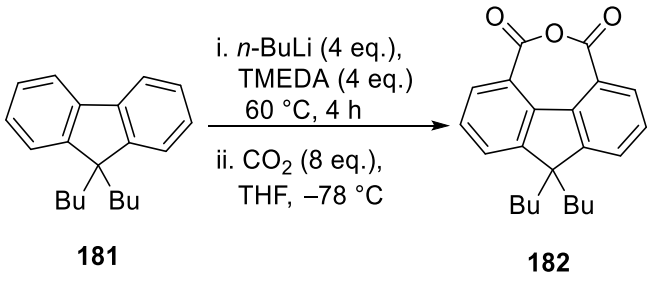
2.3.2 Synthesis of 4,5-disubstituted dibutylfluorene

The Grainger group has previously synthesized dibutylfluorene diselenide **179** and dibutylfluorene ditelluride **180.**[91, 136, 138] The synthesis began with alkylation of fluorene **175** using ^{t}BuOK in the presence of BuBr to give dibutylfluorene **181** in a 62% yield (**Scheme 69**).[139] According to Bonifácio's procedure,[82] the dibutylfluorene **181** was lithiated and quenched with selenium to give dibutylfluorene diselenide **179** in 22% yield. **181** was also lithiated and quenched with tellurium to give dibutylfluorene ditelluride **180** in 11% yield in scheme 69. [91, 136]



Scheme 69: Synthesis of dibutylfluorene diselenide **179** and dibutylfluorene ditelluride **180**

The dibutylfluorene **181** was dilithiated and quenched with carbon dioxide (**Scheme 70**). The crude material was partially purified by titration *via n*-hexane to give the desired product **182** (70% based on the purity of NMR analysis) however, the product is impure.



Scheme 70: Attempt at synthesising compound **182**

The ^{1}H-NMR shows the presence of compound **182** along with impurities (**Figure 11**). Previously, the Grainger group found that *n*-butyl chains led molecules to become more lipophilic and less amenable to crystallography in the synthesis of **179** and **180** compared with 9,9-dimethyl substituted fluorenes.

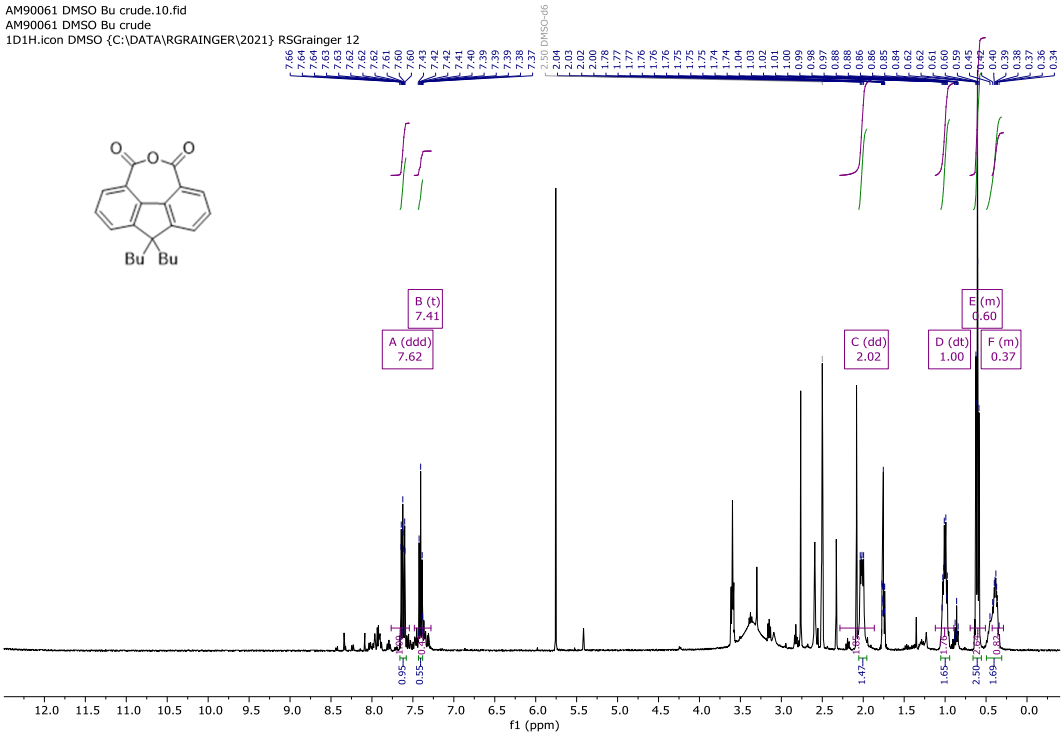
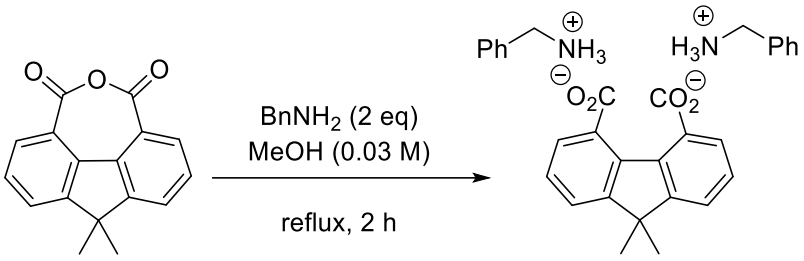


Figure 11: ^{1}H-NMR spectrum(DMSO-d6, 400 MHz) of compound **182**

2.3.3 Reaction of dimethyl fluorene anhydride with benzylamine

The reaction of dimethyl fluorene anhydride **177** with $BnNH_2$ was investigated (**Table 17**).

Table 17: The formation of dimethyl fluorene 4,5-dicarboxylate benzylammonium salt **183**



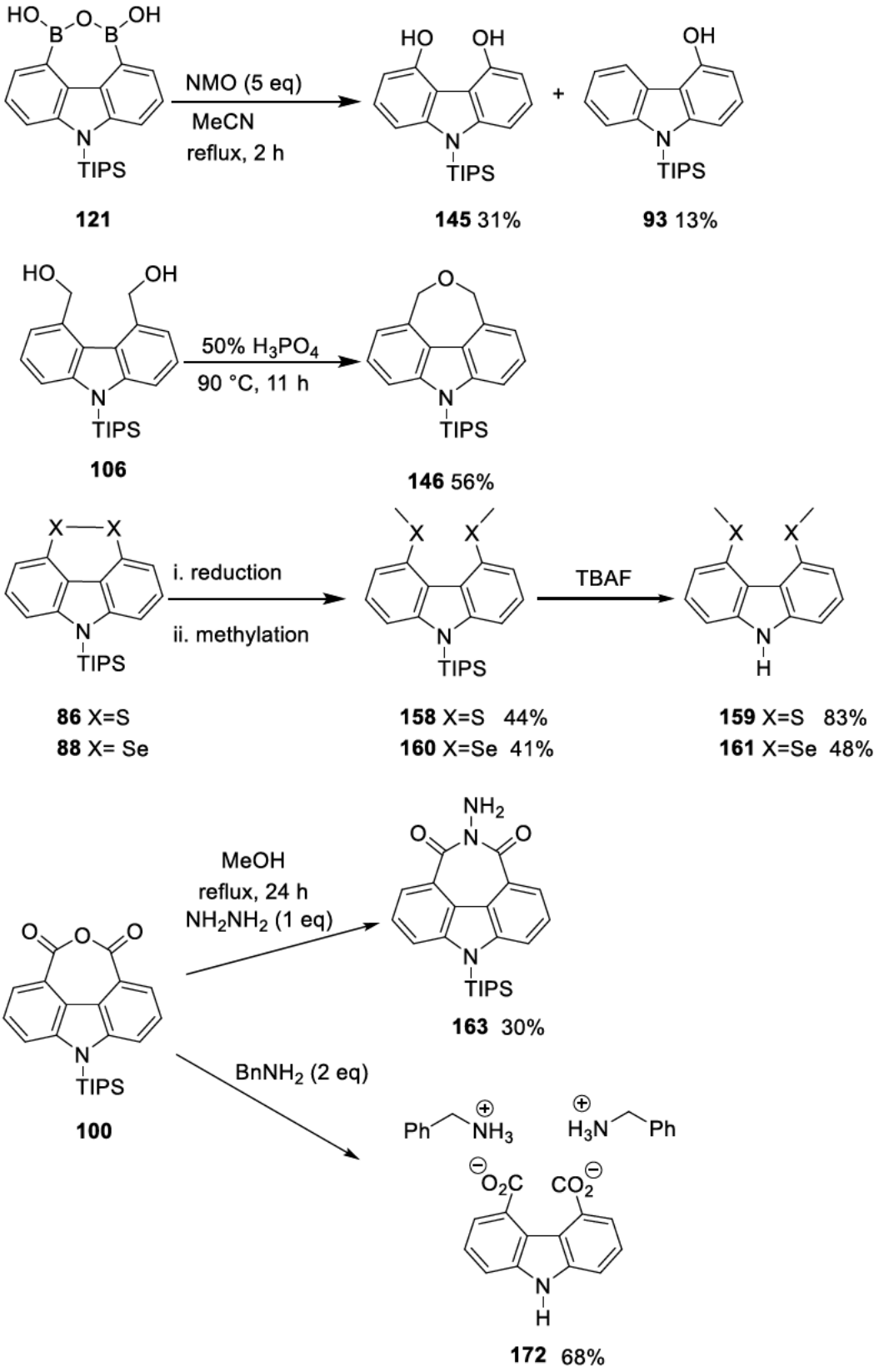
177 **183**

Entry	$BnNH_2$ (eq)	Time (h)	Products	Yield[a]
1	1	24	**183**	17%
2	2	2	**183**	63%

[a] isolated yield after second purification.

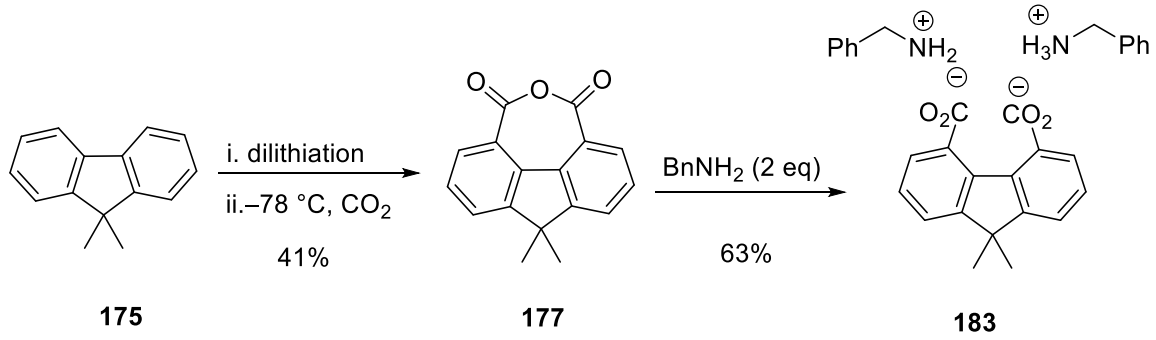
When **177** was treated with $BnNH_2$ in MeOH, and heated at reflux for 24 hours, the dimethyl fluorene 4,5-dicarboxylate benzylammonium salt **183** was formed in 17% yield (entry 1). If the amount of the $BnNH_2$ was increased to 2 equivalents and the time at reflux was reduced to 2 hours, the reaction gave **183** in 63% yield (entry 2). The X-ray structure for the dimethyl fluorene 4,5-dicarboxylate benzylammonium salt **183** was obtained (**Section 2.3**).

To conclude, further transformations of the 4,5-disubstituted carbazoles were achieved. *N*-TIPS carbazole boronic anhydride **121** was oxidised to 4,5-dihydroxycarbazole **145** in 31% yield, *N*-TIPS carbazole diol **106** was cyclised to the cyclic ether **146** in 56% yield. In addition, the reduction and methylation of the sulfide **86** and selenide **88** to the corresponding bismethyl sulfide carbazole**159** and bismethyl selenide carbazole **161** were successful in 83% and 48% yield respectively. Moreover, the *N*-TIPS carbazole anhydride **100** transformation to *N*-TIPS carbazole imide **163** was achieved in 30% yield, and to carbazole-4,5-dicarboxylate benzylammonium salt **172** in 68% yield (**Scheme 71**).



Scheme 71: Further transformations of 4,5-disubstituted carbazoles

Finally, the 4,4-dimethyl-4H-fluoreno[4,5-cde]oxepine-8,10-dione **177** was prepared in 41% yield and transformation to salt **183** in 63% yield (**Scheme 72**) .



Scheme 72: Synthesis of 4,5-disubstituted fluorene anhydride **177** and reaction with benzylamine

2.4 X-ray Structure Analysis

To allow for comparisons between structures, some of the parameters that are used to define 4,5-disubstituted carbazole structures are described. Firstly, the IUPAC system of numbering the atoms of carbazole and dimethyl fluorene was adapted to make the comparisons easier for the reader in this thesis (**Figure 12**). Locations across the '*peri*-like' positions of carbazole and fluorene (positions 4 and 5) are referred to as the bay region.[89, 140]

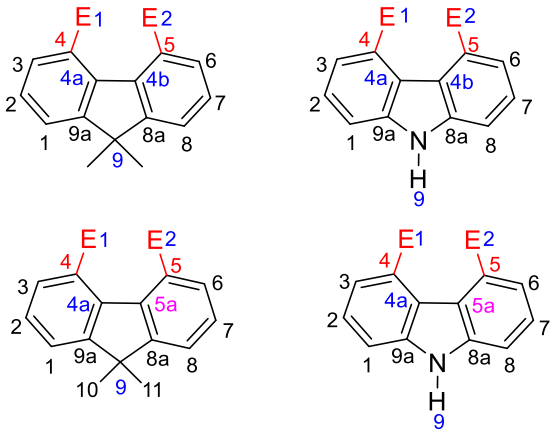


Figure 12: The standard IUPAC numbering system (top) and alternative numbering (bottom) used in this thesis for carbazole **1** and dimethyl fluorene **176**

The structures that had previously been assigned based on ^{1}H- and ^{13}C-NMR data were further confirmed by single crystal X-ray diffraction. Previous work, conducted by Connor Prior, [90] comprehensively analysed the various structural concepts that can influence the strain around the bay region for 4,5-substituted molecules based upon carbazole and fluorene skeletons.

Splay angle:

The inward or outward tilting is a measure of the deviation in the angle between the bay-region substituents when compared to the unsubstituted parent molecule. This is termed the 'splay angle' (**Figure 13**).

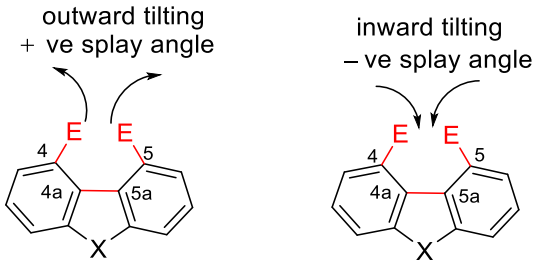


Figure 13: Tilting in the bay-region.

For the fluorene and carbazole structures, the splay angles will be determined as deviations from their parent hydrocarbons.[90] Neutron diffraction should ideally be used to examine the crystal for an accurate representation of the bay region angles, since X-ray diffraction is unable to accurately determine the position of hydrogen atoms. Because neutron diffraction studies were beyond the scope of this research, the bay angles of TIPS-carbazole **56** and dimethyl fluorene **176** were determined , using SCXRD. [90]The final H-4—C-4—C-4a and H-5—C-5—C-5a angles were determined by halving the C-3—C4—C-4a and C-6—C-5—C-5a external angles respectively, yielding the predicted positions of the hydrogen atoms H-4 and H-5. The total bay region angles estimated for *N*-TIPS-carbazole **56** and 9,10-di methyl fluorene **176** are shown below.[90, 141]

Splay angle of bay system= $\sum bay\ region\ angles\ of\ substituted\ scaffold\ -$
$\sum bay\ region\ angles\ of\ unsubstituted\ scaffold$

$$\sum bay\ region\ angles\ of\ carbazole = 131.9° + 132.5° + 120.55° + 120.55° = 505.50\ °$$

$$\sum bay\ region\ angles\ of\ fluorene\ = 130.87° + 131.10° + 120.64° + 120.73° = 503.34\ °$$

When the value of the splay angle is positive, the E groups experience an outward tilting effect; if the value is negative, the splay angle is less than for the unsubstituted scaffold, resulting in an inward tilting action of the E groups. [90]

Torsion angle:

A torsion angle which represents the deviation from planarity, is the C-4—C-4a—C-5a—C5 dihedral angle (**Figure 14**).[90]

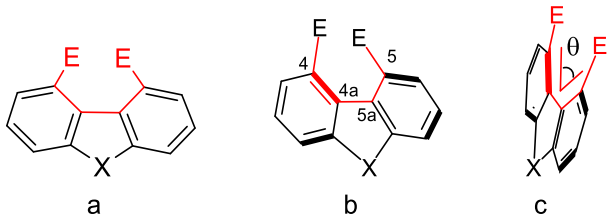


Figure 14: Views of the torsion angle of the bay region

For dibromonaphthalene **118**, [142] dibromoacenaphthene **184**,[143] and dibromoacenaphthylene **185**, [144] compounds were compared and the strain and splay angle found. Connor Prior compared the disulfide carbazole **86**, [89] and fluorene **186**, [136] with disulfide naphthalene **75** ,[145] and observed that the bayregion-substituted scaffolds are more strained from the *peri*-substituted scaffolds.[90]

In 2012, Knolker and co-workers reported the X-ray structure for the 4,5- bis(pivaloyloxy)carbazole **22** (**Figure 15**).[28] The pivaloyloxy group in the bay region caused the distortion on the bond and torsion angles C-3—C-4—C4a 121.10(16), C-3—C4—O1 117.10(15), C-4a—C4—O1 121.53(15), and C-4—C-4a—C-4b—C5 17.7(4)

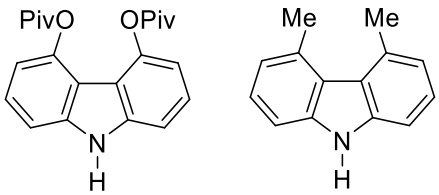


Figure 15: 4,5-Disubstituted carbazoles where X-ray crystallography is reported.

Also, in 2022, Knolker and co-workers reported the X-ray structure of 4,5-dimethylcarbazole **11**. [146] They found that the molecules were perfectly planar. The methyl groups in the bay region do not affect the aromatic plane but do caused distortion of the bond angles in Figure 15. The methyl groups are outwardly displaced, the inner bond angles for C-4a—C-4—Me (125) and C-4b—C-4—Me (125.5) compared with outer bond angles C-3—C-4—Me (117) and C-6—C-5—Me (116).[146]

2.4.1 X-ray Analysis of 4,5-disubstituted carbazole compounds

The crystal structure of *N*-TIPS carbazole -4,5-diol **106** was obtained by slow evaporation from ethanol solution of the compound (Figure 16). The X-ray crystal structure of *N*- TIPS carbazole diol **106** shows that one CH_2–OH group C-(13) —O(1) / C-(13A) —O(1A) is disordered over two positions with a refined percent occupation ratio of 59 (2) : 49 (2).

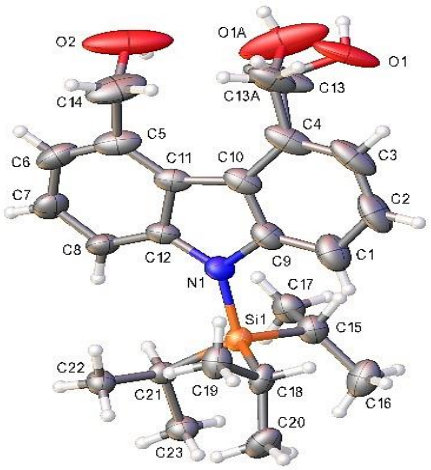


Figure 16: X-ray Crystal structure of *N*-TIPS carbazole diol **106**

The structure of 4,5-dichlororcarbazole **110** was confirmed by X-ray analysis after obtaining single crystals through slow evaporation from CH_2Cl_2 solution (**Figure 17**).

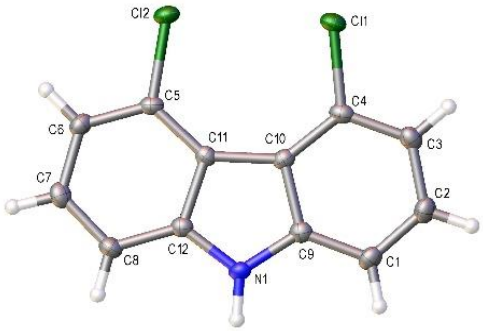


Figure 17: X-ray Crystal structure of 4,5-dichlorocarbazole **110**

The single crystal of 4,5-bismethyl sulfide carbazole **159** was grown by slow evaporation from ethanolic solution (**Figure 18**), whereas the 4,5-bismethyl selenide carbazole **161** was obtained by slow evaporation from a CH_2Cl_2 solution of the compound (**Figure 19**).

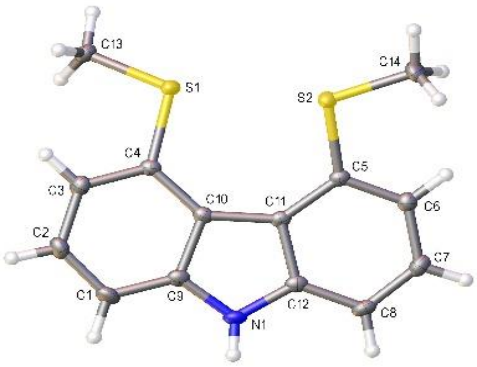


Figure 18: X-ray Crystal structure of compound **159**

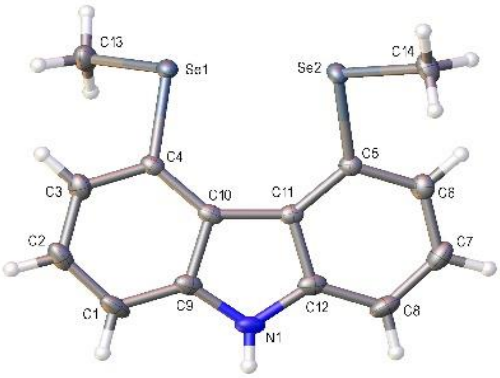
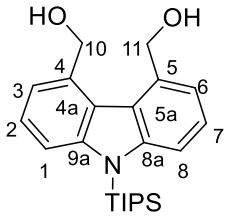
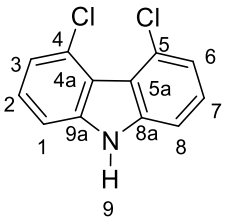
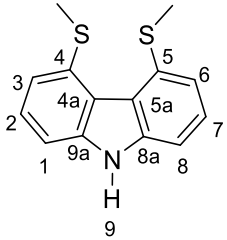
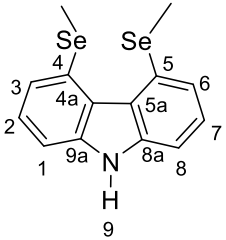
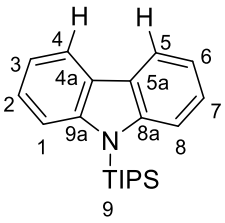


Figure 19: X-ray Crystal structure of compounds **161**

The crystallographic data of the 4,5-disubstituted carbazole compounds **106**, **110**, **159**, and **161** are compared with the *N*-TIPS carbazole **56** (**Table 18**). The data for dichlorocarbazole **110**, *N*-TIPS carbazole diol **106** and 4,5-bismethyl sulfide carbazole **159** and 4,5-bismethyl selenide carbazole **161** are shown in Table 18. It can be seen that the distance between C-4 and C-5 in all 4,5-disubstituted compounds was longer than in unsubstituted carbazole **56** (entry 4). In contrast, the distance between C-1 and C-8 is shorter than in unsubstituted carbazole **56** (entry 5). The distance between C-1…C-8 decreases. Likewise, the bond lengths (C-9a—N-1) and (C-8a—N-1) were decreased for the substituted carbazole compounds (entries 6 and 7 respectively). Similarly, the distance between C-9a and C-8a also decreases with 4,5-substitution (entry 8). The C-5—C5a—C-4a and C-4—C-4a—C-5a bond angles increased in 4,5-dichlorocarbazole **110**, 4,5- bismethyl sulfide carbazole **159**, 4 ,5-bismethylselenide carbazole **161** and 4,5-diol **106** (entries 9 and 10 respectively). This increase is due to the atoms in the substituent groups repelling each other. In the case of the chloro atom substituents, this angle is the greatest at 139.2(2) °. (entry 10). The dihedral angle (C-4—C-4a—C-5a—C5) increased more in 4,5-bis-methyl selenide **161** than in 4,5-bis-methylsulfide **159** (entry 11). 4,5-bismethyl selenide carbazole **161** is out of the plane by 15°, in contrast to the 4,5-dichlorocarbazole **110**, deviated by only 1.9°. All 4,5-disubstituted carbazoles showed deviation from the planarity of parent carbazole **56**. Finally, the splay angles were positive for all disubstituted compounds, indicating that an outward tilting action is present (entry 12).

Table 18: Comparison of crystallographic data of 4,5-disubstituted compounds **106**, **110**, **159** and **161** with *N*-TIPS carbazole **56**

Entry		**106**	**110**	**159**	**161**	**56**
1	structure and numbering					
2	formula weight	383.59	236.09	259.37	353.17	323.54
3	crystal system	hexagonal	Orthorhombic	monoclinic	trigonal	monoclinic
4	distance C-4…C-5/Å	3.481	3.588	3.588	3.538	3.308
5	distance C-1…C-8/Å	4.932	4.897	4.887	4.904	4.974
6	bond length (C-9a—N-1)/Å	1.403(7)	1.376(3)	1.376 (19)	1.372(3)	1.416(3)
7	bond length (C-8a—N-1)/Å	1.409(6)	1.370(4)	1.368 (19)	1.373(2)	1.413(3)
8	distance C-9a…C-8a/Å	2.244	2.245	2.248	2.250	2.252
9	bond angle C5-C5a-C4a /°	135.1(6)	138.7(2)	137.79(13)	136.88 (16)	132.4(2)
10	bond angle C-4—C4a—C-5a /°	135.9 (5)	139.2(2)	137.79(13)	137.27(15)	132.0(2)
11	planarity torsion C-4—C-4a—C-5a—C5/°	-15.9(10)	1.9(7)	11.3(3)	15.4(3)	-0.8(5)
12	splay angle/°	16	21.1	12.43	14.85	505.50

A single crystal of the carbazole cyclic ether **146**, was grown by slow evaporation from ethyl acetate solution. The resulting structure shows a 7-membered dihydrooxepine ring fused to the carbazole from C-4 to C-5 (**Figure 20**).

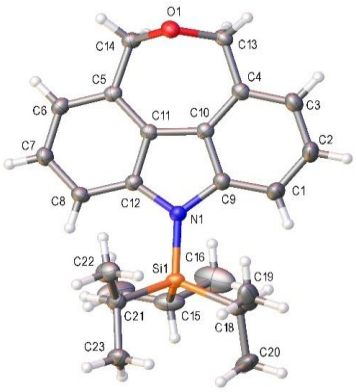
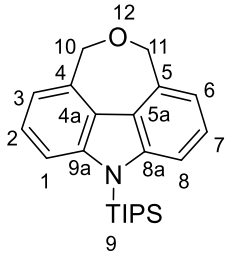
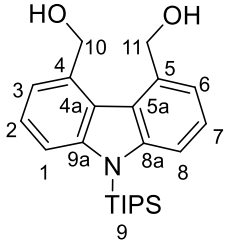


Figure 20: X-ray Crystal structure of carbazole cyclic ether **146**

The carbazole cyclic ether **146** was compared with the related carbazole diol **106** (**Table 19**). The bond distance C-4—C-10 and C-4—C-4a in cyclic ether **146** is shorter than carbazole diol **106** (entries 4 and 5). The C-4—C-5 distance is shorter in cyclic ether **146** than diol **106** (entry 6). The (C-9a—N-1) bond length in cyclic ether **146** is longer than diol **106** (entries 7 and 8). The distance between C-9a and C-8a is longer (2.258 Å) in cyclic ether **146** than diol **106** (2.248 Å) (entry 9). Also, in 4,5-disubstituted carbazole systems, the C-4 and C-5 positions shift further apart when the C-9a and C8-a positions are pinched together.[3] Moreover, the bond angle C-5—C-5a—C-4a is smaller in cyclic ether **146** than in diol **106** (entries 10 and 11). The torsion angle C-4—C-4a—C-5a—C-5 for cyclic ether **146** and diol **106** are very different (entry 12). For the carbazole cyclic ether **146** the splay angle was very small and negative, an inward titling

effect. The differences between the cyclic ether **146** and the diol **106** were significant due to the bay region decreasing.

Table 19: Comparison of crystallographic data of diol **106** and cyclic ether **146**

Entry		**146**	**106**
1	structure and numbering		
2	formula weight	365.58	383.59
3	crystal system	orthorhombic	hexagonal
4	distance C-4…C-10 /A°	1.507(2)	1.517(8)
5	bond length C-4—C-4a /A°	1.384 (2)	1.398 (9)
6	distance C-4…C-5 /A°	3.287	3.485
7	bond length (C-9a— N-1) /A°	1.417(19)	1.403 (7)
8	bond length (C-8a— N-1) /A°	1.415 (19)	1.409 (6)
9	distance C-9a… C-8a /A°	2.258	2.248
10	bond angle C-5—C-5a— C-4a /°	131.7(14)	135.1 (6)
11	bond angle C-4—C-4a—C-5a /°	131.2(14)	135.9 (5)
12	planarity torsion C-4—C-4a—C-5a—C-5 /°	3.2(3)	-15.9(10)
13	splay angle / °	-0.32	16

The crystal structure of tetrafluoro naphthocarbazole **117** was obtained by slow evaporation from chloroform (**Figure 21**).

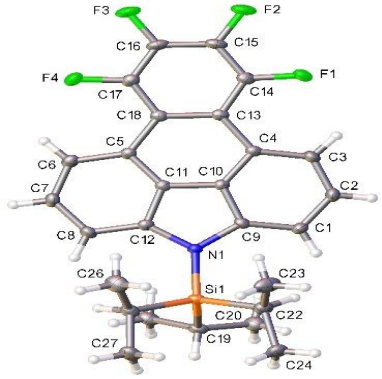
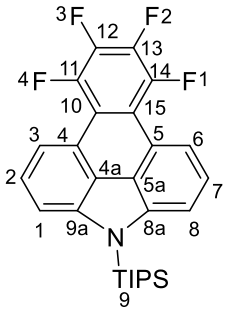


Figure 21: X-ray Crystal structure tetrafluoro naphthocarbazole **117**

*S*elected bond lengths and bond angles for **117** are shown in Table 20.

Table 20: Crystallographic data of 4,5- tetrafluoro naphthocarbazole **117**

Entry		**117**
1	structure and numbering	
2	formula weight	469.58
3	crystal system	Monoclinic
4	bond length C-5—C-5a/A°	1.394(2)
5	bond length C-5—C-15/A°	1.471(2)
6	bond length (C-9a …N1)/A°	1.425(2)
7	bond length (C-8a …N-1)/A°	1.424(2)
8	bond angle C-5a—C5—C-15/°	114.3(14)
9	bond angle C-4a-C-4—C-10/°	114.0(14)
10	bond angle F-1—C-14—C-15 /°	120.4(14)
11	bond angle F-1—C-14—C-13/°	116.6(14)
12	bond angle F-2—C-15—C-14 /°	119.9(15)
13	bond angle F-2—C-13—C-12 /°	120.7(15)
14	planarity torsion C-4—C-4a—C-5a—C-5 /°	-0.1(2)
15	splay angle /°	-28.25

The **117** has the highest planarity 4,5-disubstituted carbazole which is -0.1 ° (entry 14). The aromatic system in the tetrafluoro naphthocarbazole **117** increased more than carbazole system, due to the **117** is a more planar. The splay angle value is the largest inward tilting effect (-28.25°) compared with other structures (entry 15).

2.4.2 X-ray analysis of 4,5-dicarboxylate benzylammonium salt carbazole and fluorene

The crystal structure of carbazole -4,5-dicarboxylate benzylammonium salt **172** was obtained by slow evaporation from methanol (**Figure 22**). The crystal structure of compound **172** contains two crystallographically distinct carbazole-4,5-dicarboxylate units, four benzylammonium ions and three molecules of water.

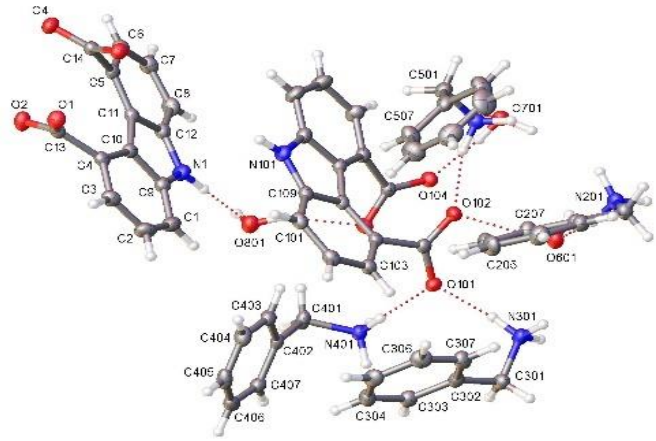


Figure 22: X-ray Crystal structure of carbazole -4,5-dicarboxylate benzylammonium salt **172**

The crystal structure of fluorene-4,5-bis(carboxylate) benzylammonium salt **183** was also obtained by slow evaporation from methanol (**Figure 23**). The unit cell/asymmetric unit shows the salt with two crystallographically-separate benzylammonium cations and dicarboxylate fluorene anions and two molecules of water.

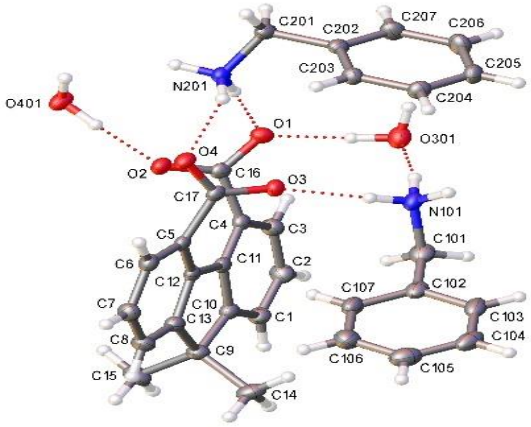


Figure 23: X-ray Crystal structure of fluorene-4,5-dicarboxylatebenzylammonium salt **183**

Selected bond lengths and bond angles of carbazole salt **172** and fluorene salt **183** are compared (**Table 21**). Initially, the structure and intramolecular distances for both salts were compared. First, the values of bonds and angles of carbazole salt **172** are similar to other of substituted carbazoles **106**, **110**, **126, 148**, and **149**. For example, the intramolecular distance C-4 …C-5 also is longer in the **172** than the carbazole system **56** (entry 6).

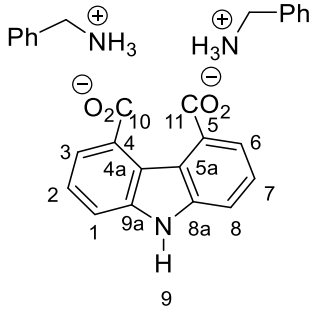
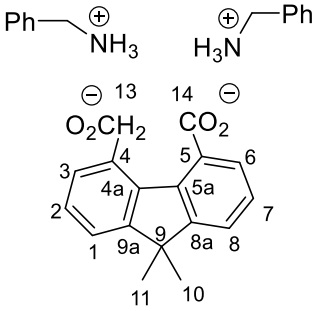
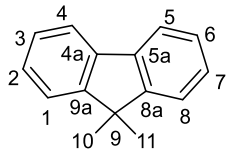
Second, the fluorene salt **183** was compared with fluorene system **176**,[141] the X-ray structures show that the bond length C-5—C-5a is longer in the **183** than in the fluorene **176** (entries 4 and 5). The intramolecular distance C-4 …C-5 also is longer in the **183** than the fluorene **176**. In the compound **183** torsion angle C-4—C4a—C5a—C5 is 12° and 0.9 in the **176** (entry 11). The fluorene salt **183** has shorter bond length (C-8a —C-9 and/or C-9a —C-9) and distance C-8a…C-9a than fluorene **176** (entries 17, 18, and 19).

The substitutions in C-4 and C-5 positions in **183** effect to increase the distance of C-4…C-5 and decrease bond length C-8a —C-9 and/or C-9a —C-9 when comparing with unsubstituted fluorene **176**. The value of splay angle of compound **183** is positive (entry 12).

The X-ray structures show that the bond length C-5—C-5a is longer in the carbazole system than in the analogous fluorene system (entries 4 and 5). The intramolecular distance C-4 …C-5 also is longer in the carbazole system than the fluorene system (entry 6). This related to decrease nitrogen -carbon bond in five-member ring in carbazole system more than carbon-carbon bond in fluorene system.

The torsion angle is small in the carbazole system compared to the fluorene system. (entry 11). Also, an outward titling effect is found in both salts, with positive values for the splay angles (entry 12). Table 21 shows some of the intermolecular hydrogen bonds present for both crystal systems. The shortest hydrogen bonds are found in fluorene salt **183** between COO…HOH bond, distance is 1.75 Å (entry 14). In general, the fluorene **183** salt displays shorter H-bond donor-acceptor distances than the salt carbazole **172**. Also, the carbazole NH group is also able to participate in hydrogen bonding (entry 16).

Table 21: Crystallographic data of 4,5-bis(carboxylate) benzylammonium salt for carbazole and fluorene system.

Entry		172	183	167[141]
1	structure and numbering			
2	formula weight	496.55	532.62	194.26
3	crystal system	Monoclinic	Triclinic	tetragonal
4	bond length C-5—C-5a/A°	1.410(16)	1.406(17)	1.3914(14)
5	bond length C-4—C-4a/A°	1.413(17)	1.409(16)	1.3897(14)
6	distance C-4…C-5/A°	3.459	3.415	3.313
7	hydrogen bond O701…H70A…O104 (H…OH…OOC)/A°	174.5(18)	175(2)	—
8	hydrogen bond N301…H30D…O101 (NH_3…OOC)/A°	172.1(15)	153.7(14)	—
9	N1…H1A…O801 (NH…OH_2)/A°	176.2(16)	-	—
10	bond angle C-5—C-5a—C4a/°	135.27(11)	132.99(10)	131.09(9)
11	planarity torsion C-4—C4a—C5a—C5/°	11.5(2)	-12.3(2)	-0.9
12	splay angle / °	10.34	8.1	503.34

13	hydrogen bond COO…H-NH_2-Bn/A°	1.864(15)	1.85(2)	__
14	hydrogen bond COO…H-OH /A°	1.845(19)	1.75(2)	__
15	hydrogen bond H_2NH… OH_2/ A°	1.923(17)	1.847(15)	__
16	hydrogen bond H_2O…H-N-Cz/ A°	2.021(17)	-	__
17	Distance C-9a… C-8a/A°	2.237	2.340	
18	Bond length (C-8a —N-1) or C-8a —C-9/A°	1.375(16)	1.512(17)	1.5167(14)
19	Bond length (C-9a —N1) or C-9a —C-9 /A°	1.373(17)	1.516(16)	1.5186(14)

In conclusion, the functionality at the 4,5-positions has an effect on the C-9a…C-8a distance and the planarity of carbazole scaffolds (Table 18). The shortest C-9a…C-8a distance was obtained for carbazole cyclic ether **146** at 3.287 Å; this was related to the effect of the cyclisation on the bay region. (**Table 19**). The influences on the bay region are observed with an increase in size of angle C-5—C-5a—C-4a (**Table 18**, entries 9 and 10). From the comparison of the bis-salt of fluorene and carbazole crystallographic data, it was found that the C-4…C-5 bonds are longer in carbazole **172** than the corresponding C-4…C-5 bonds in fluorene **183** (**Table 21**, entry 6). Presently, there is a lack of literature that examines the influence of bay substitution upon carbazole and fluorene scaffolds. The X-ray structures presented in this section offer a valuable opportunity to examine this influence and can be used to conduct further studies.

Chapter 3: photophysical properties of 4,5-disubstituted carbazole

3.1 Photophysical properties of carbazole compounds

Carbazoles and polycarbazoles have a variety of properties that can be applied to optoelectronics. For compounds found in optoelectronic materials, high electrical conductivity, a defined HOMO-LUMO band gap, and a properly balanced technique of introducing charge carriers are all required, allowing for significant increases in system efficiency. Despite the high demand for such materials, no organic compound currently fits all of these requirements, therefore novel materials are continually being investigated.[147] Carbazole-based compounds are appealing as photoconductors or charge-transporting materials for the following reasons: carbazolyl groups produce a radical cation that is relatively stable, carbazole-containing compounds have good thermal and photochemical stability,[148] different substituents can be easily introduced into the carbazole ring, carbazole-containing compounds have comparatively high charge carrier mobilities and carbazole is a low-cost raw material produced by distilling coal tar. [15, 147, 148] [15] The first investigation for the novel organic compounds is the study of their basic photophysics properties. The photophysics of a molecule is defined and characterised by six main parameters:[149]

i. absorption wavelength maxima (λ_{max}),

ii. extinction coefficients or molar absorptivity (ϵ),

iii. emission wavelength maxima (λ_{max})

iv. Stokes shift (SS), also known as *pseudo* Stokes shift (PSS), is defined as the differences between positions of the band maxima absorbance and the maximum emission for the molecules of wavelength or wavenumber ($\lambda_{max\ Abs}$- $\lambda_{max\ Em}$).

v. quantum yield (ϕ)

vi. lifetime (τ).

The basic photophysical properties for the selected 4,5 S/Se disubstituted compounds were determined (**Figure 24**). These derivatives of carbazoles range from bright to deep red in colour.

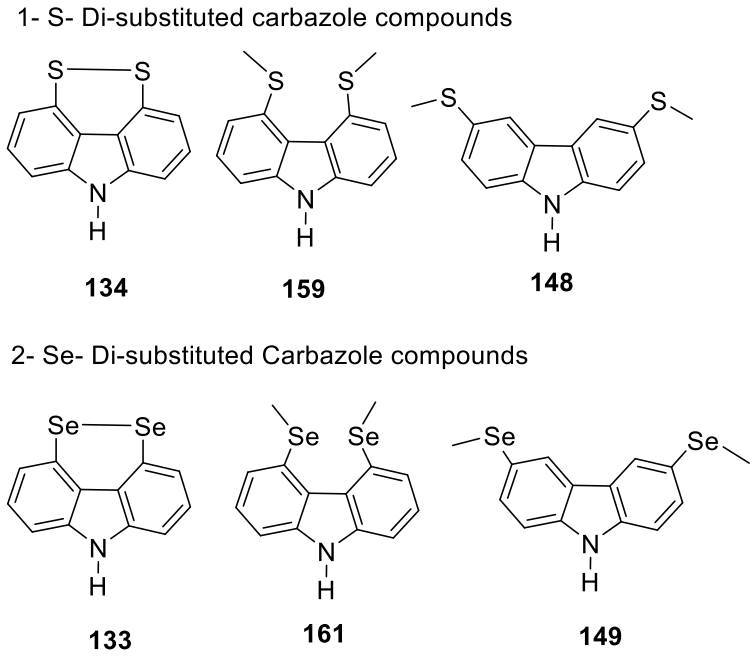


Figure 24: Selected S/Se disubstituted carbazoles compounds for photophysical investigations

The 4,5 -bismethyl S/Se-disubstituted carbazole compounds **159** and **161** were synthesised as described in the previous section. The 4,5-diS/Se carbazoles **133** and **134** were synthesised according to the Grainger group reported method.[89] The 3,6-bismethyl S/Se-disubstituted carbazole compounds **148** and **149** were synthesised and obtained from the Bryce group at Durham university.[119] Firstly, the S/Se substituted carbazole, were divided into two classes. The first class was the S- disubstituted carbazole compounds **134**, **159**, and **148**, and the second class was the Se- disubstituted carbazole compounds **133**, -**161** and **149**. All the

compounds were also compared with reported data of carbazole **1**.[150] The absorbance of the of S/Se substituted carbazoles were determined using UV-VIS spectrum (**Figure 25**)

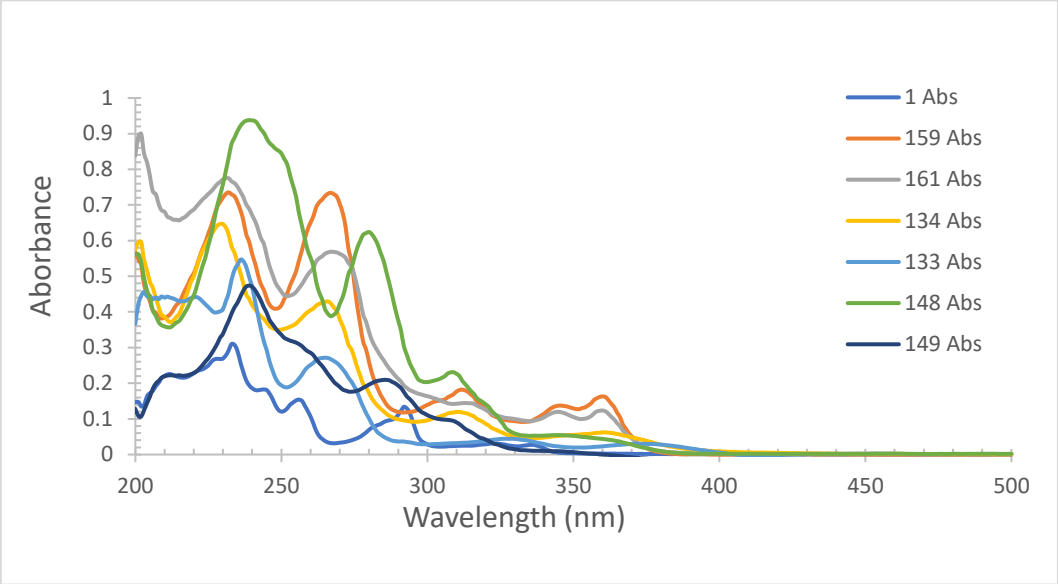


Figure 25: UV-Vis absorption of S/Se-substituted carbazoles in EtOH (Conc. ≈ 0.05 M)

3.1.1 UV Studies of the S-disubstituted carbazoles

The absorption spectra of S-disubstituted carbazoles **134**,**159**, and **148** in EtOH are shown in Figures 26**.**

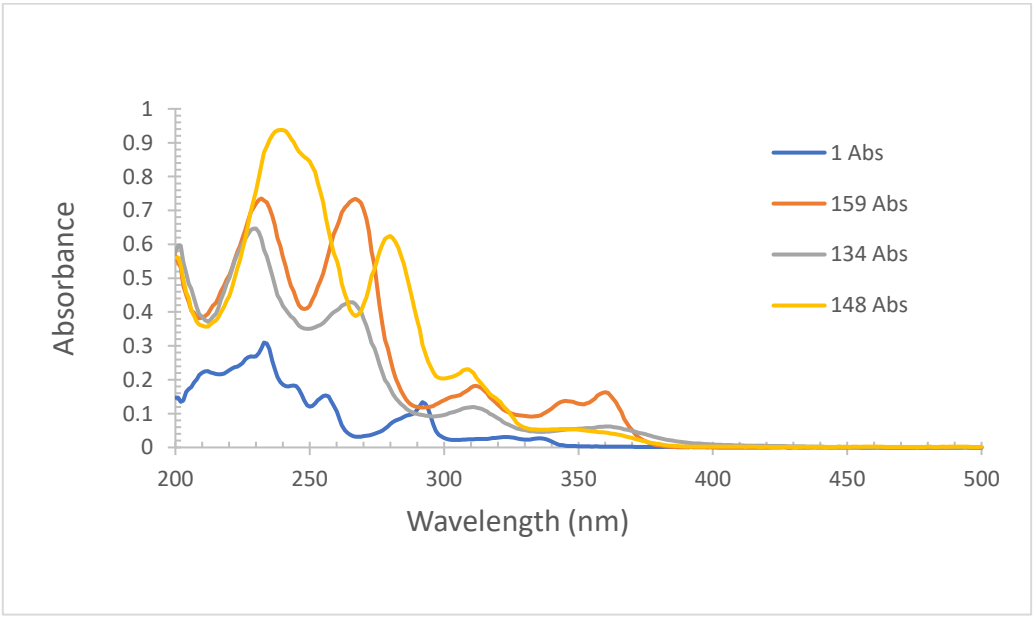


Figure 26: UV-Vis absorption spectra of S--disubstituted carbazoles in EtOH (Conc. ≈0.05 M)

The absorption maxima of all derivatives were observed in the 226–365 nm range (**Table 22**). The compounds that have the disulfide group **134** and bis-methyl disulfide **159** and **148** are comparable to carbazole **1** in that they each have two absorption maxima (λ_{max} ~226-295 nm and λ_{max} ~311-365 nm). The π-π* transition is responsible for the maximum absorbance (λ_{max} ~311-365 nm) (**Figure 26**). Absorption for the low energy (λ_{max} ~380-420 nm) was not observed, this mean the formation of the intramolecular charge-transfer (ICT) transition, was not observed in the S-compounds. [151-153]

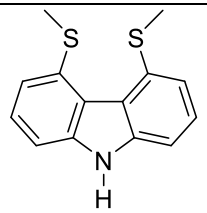
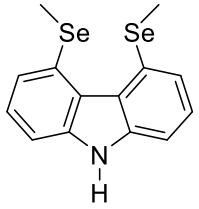
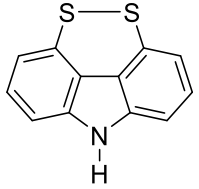
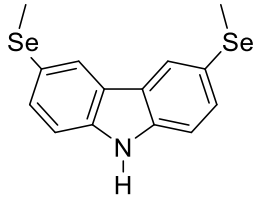
The extinction coefficients (ϵ) of absorption is an intrinsic characteristic of compounds that is dependent on their chemical composition and structure. The molar absorptivity (ϵ) for the compounds **134, 159,** and **148** was calculated using the Beer-Lambert law (Equation 1).[154]

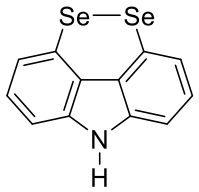
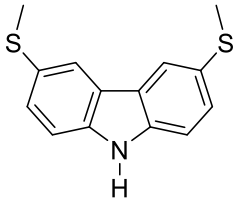
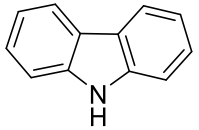
$$A = \epsilon c l$$

Equation 1: The Beer-Lambert Law for calculating molar absorptivity.

In this equation, A is absorbance, ϵ is molar absorptivity, c is the concentration of the sample, l is the path length of the cuvette cell which is 1 cm. The absorption extinction coefficients (ϵ) at the peak corresponding to the π-π* transition ranged from 12 500 to 48 000 $mM^{-1}\,cm^{-1}$. [155] The ϵ values for the S- compounds (54000, 175000 and 32250 $mM^{-1}.cm^{-1}$, respectively) were much higher (**Table 22**). The highest ϵ value was for 4,5-bismethyl sulfide carbazole **159**, then 3,6 -bismethyl sulfide carbazole **148**. The carbazole disulfide **134** had the lowest value from the first-class S-carbazole compounds and was similar to the value carbazole **1** which is 3100 $mM^{-1}.cm^{-1}$. The individual UV-Vis spectra for S-carbazoles **134**, **148**, and **159** are shown in the experimental section.

Table 22: The photophysical properties of of the S/Se disubstituted carbazole recorded in EtOH.

Compound name and structure	Molar absorptivity (ϵ)/$mM^{-1}.cm^{-1}$	λ_{abs}/nm	λ_{em}/nm	(V_{abs}-V_{em})/cm^{-1}	$FWHM_{em}$/cm^{-1}	Φ_f (+-10%)
 **159**	54000	233 nm	391 nm	17343 cm^{-1} 158 nm	125 nm	0.003
 **161**	10.000	233 nm	388 nm	42918.45 cm^{-1} 155 nm	40 nm	0.07
 **134**	17500	228 nm	335 nm	14,008 cm^{-1} 105 nm	85 nm	0.001
 **149**	32250	240 nm	392 nm	16,330 cm^{-1} 152 nm	46 nm	0.006

 **133**	2750	238 nm	433 nm	18922 cm^{-1} 195 nm	17 nm	0.05
 **148**	32250	240 nm	409 nm	17216 cm^{-1} 169 nm	46 nm	0.03
 **1**	3100	234 nm	358 nm	14,802cm^{-1} 124 nm	30 nm	0.36

3.1.2 UV Studies of Se-disubstituted carbazoles compounds

The absorbance spectrum of Se-disubstituted carbazoles **133**, **161** and **149** in EtOH are shown in Figure 27.

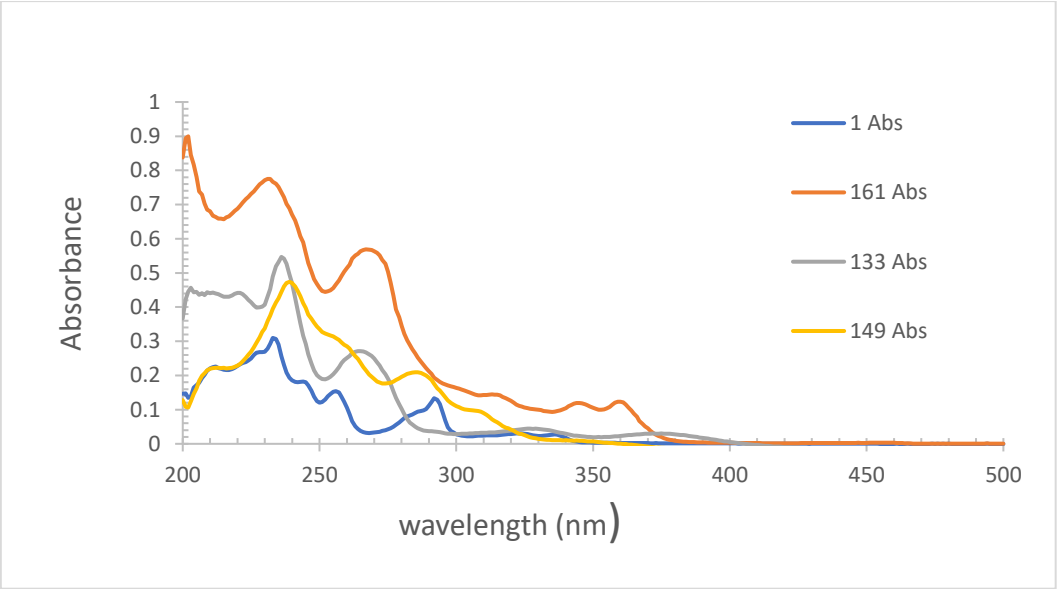


Figure 27: UV-vis absorption spectra of Se-disubstituted carbazoles in EtOH (Conc. ≈0.05 M)

The absorption maxima of the all Se- compounds were observed in the 215–385 nm range (**Figure 27**). The 4,5-bismethyl selenide carbazole **149,** carbazole diselenide **133** and 3,6-bis-methylselenide carbazole **161**, are comparable to carbazole **1,** each has two absorption maxima (λ_{max} ~226-290 nm and λ_{max} ~311-390 nm). An additional absorption to the π-π* transition was observed at low energy wavelength (λ_{max}~380-390 nm), due to an intramolecular charge-transfer (ICT) transition in the Se-compounds**.** The extinction coefficients (ϵ) for Se- compounds were 10000, 32250, and 2750 $mM^{-1}.cm^{-1}$, respectively for **161**, **149** and **133**. The ε values of Se- compounds were low. The 3,6 -bis-methylselenide carbazole **149** had highest value of ϵ in the Se-compounds. However, the 4, 5-diselenide **133** was lowest values in all cases.

Individual absorbance spectra of each compound **134**, **149** and **161** in EtOH were recorded (**Experimental Chapte**r).

3.1.3 Fluorescence studies of S/Se disubstituted carbazoles compounds

Substituted of carbazoles are well-known for extreme luminescence and are commonly utilised as blue, green, red, and white emitters in organic light-emitting diodes (OLEDs).[155]

The emission properties of substituted carbazole inspired detailed investigation of S/Se-compounds **133**, **134**, **148**,**149**,**159**, and **161** to better understand their photophysical properties and structure-property correlations. The emission features of S/Se substituted carbazoles were determined using fluorescence spectroscopy.

The 0.05 M solutions of S/Se-disubstituted carbazoles were excited at wavelengths at 350 nm. The emission spectra and their maximum emission wavelengths were recorded (**Figure 28**).

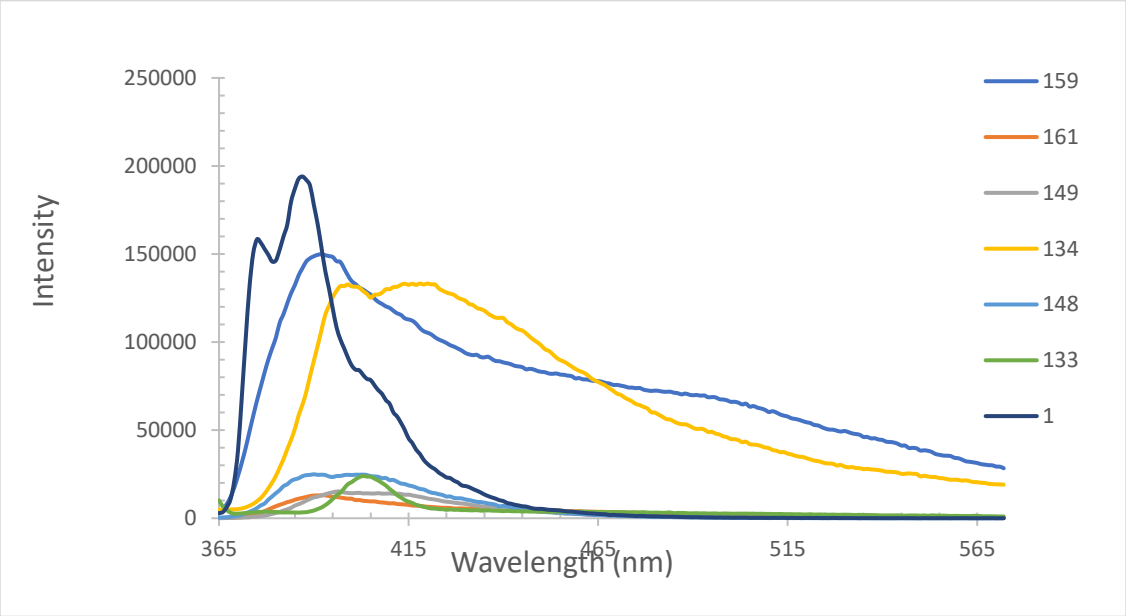


Figure 28: Fluorescence spectra of S/Se-compounds in EtOH (Conc. ≈0.05 M), at the exciting wavelength ≈350 nm. (**1** at λ_{ex}=326 nm and **133** at λ_{ex}= 383nm)

For the first class shown in Figure 29, the maximum emission wavelengths of **134**, **148** and **159** are in the range of 396–531 nm, that is blue and green light emissions.

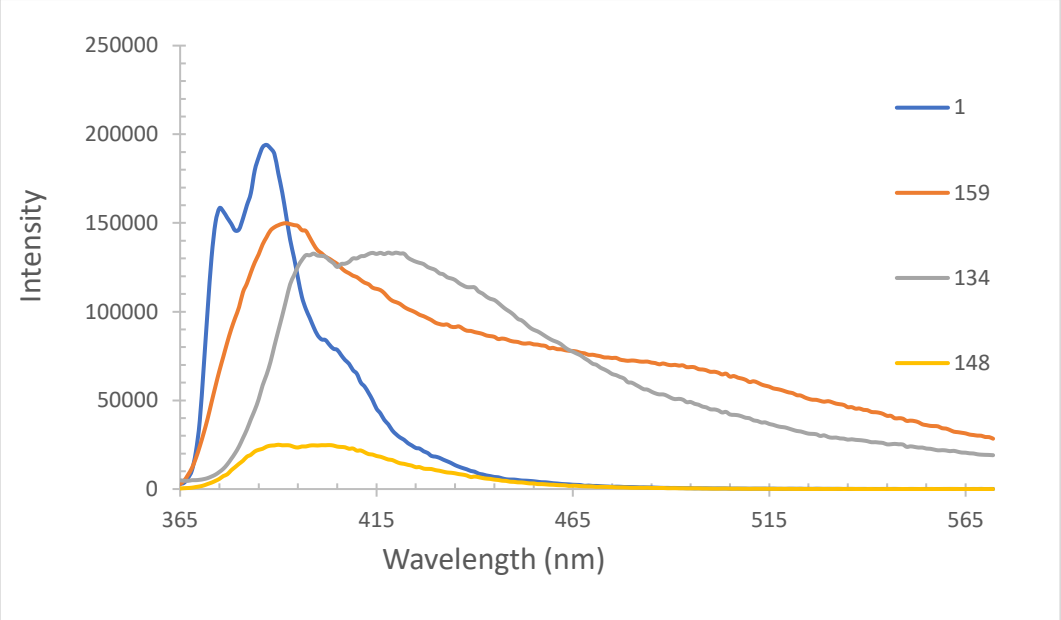


Figure 29: Fluorescence spectra of S-compounds in EtOH (Conc. ≈0.05 M), at the exciting wavelength ≈350 nm. (carbazole at λ_{ex}=326 nm)

The 3,6-bis-methyl sulfide carbazole **159** has the longest wavelength absorption maxima in EtOH (240 nm) and has the longest emission maxima in EtOH at 403 nm. As a result, the greatest Stokes shift for **148** in EtOH is 169 nm, as shown in Table 22. However, the emission maximum value for the 4,5-bis-methyl sulfide carbazole **159** is observed as broad from 390 to 500 nm. The Stokes shift for **159** is 158 nm, as shown in Table 22. The carbazole disulfide **134** emission maxima is observed as low bands at 403-423 nm.

Emission spectra and maximum emission wavelengths for the Se-containing compounds are shown in Figure 30.

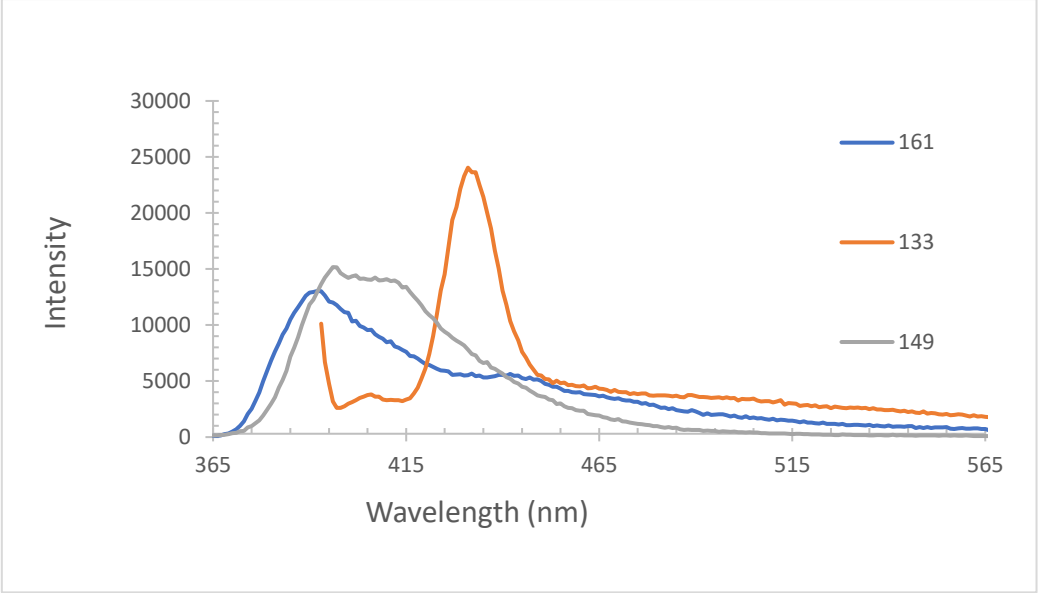


Figure 30: Fluorescence spectra of Se-compounds in EtOH (Conc. ≈0.05 M), at the λ_{ex}≈350 nm. (**133** at λ_{ex}= 383 nm)

The maximum emission wavelengths of **133**, **149**, and **161** are in the range of 385–550 nm and were narrower. The carbazole diselenide **133** exhibits the largest wavelength absorption maxima (283 nm) and the longest and narrow wavelength emission maxima at 403 nm. As a result, as indicated in Table 22, the highest Stokes shift for **133** is 195 nm. However, the emission maximum value of the 4,5-bismethyl selenide carbazole **161** can be seen as broad with two bands at 388 nm and 433 nm, with a Stokes shift value of 155 nm, as indicated in Table 22. On the other hand, the 3,6-bismethyl selenide carbazole **149** emission peaks observed as one broad band from 398 to 414 nm with a Stokes shift of 154 nm.

Literature[155] suggests that the presence of the ethynylphenyl group or carbaldehyde para to nitrogen in carbazole moiety compounds **187**-**189** (**Figure 31**) would increase the effective conjugation length. However, maximum wavelengths of **187**-**198** (λ_{max}) 392-405 nm were found, indicating that replacement of carbazole with a smaller carbaldehyde or ethynylphenyl groups at the 3 or 6 position did not extend conjugation.[155] Incorporation of either SMe or SeMe groups the 3,6-positions of carbazole cause no significant red shift (**Table 22**)

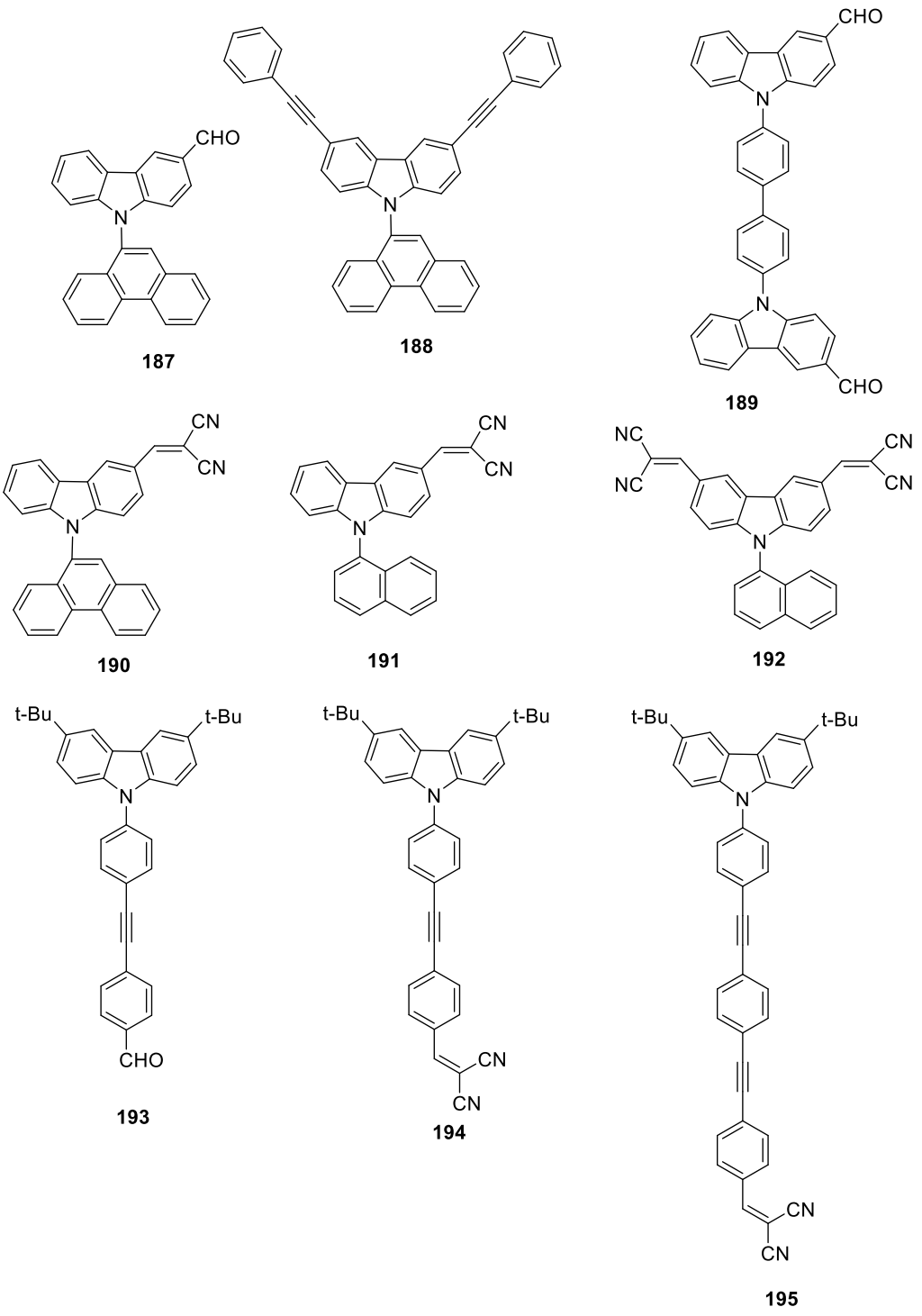


Figure 31: Examples of 3,6 substituted carbazoles in the literature[155]

3.1.4 Quantum yield

Carbazoles are one of the important classes of compounds that have been intensively pursued for use in OLEDs and other optoelectronic devices due to their light-emitting feature mixed with their hole-transporting capabilities.[147] Although there have been a few studies on carbazoles in the literature in recent years.[3, 14-18, 109, 147] They have largely focused on their use as materials and applications in devices. [155]. One of the most crucial photophysical factors to consider when describing luminous molecules and materials is quantum yield. For a variety of applications, such as lasers, bioimaging, and solar cells, high quantum yields are essential.

Interestingly the new series of 4,5 S/Se carbazoles derivatives (**Figure 24**) that emit steady blue, and green emission may find application in devices.

The quantum yield values of S/Se disubstituted carbazole in EtOH was determined. The quantum yields (Φ_f) were computed using absorption and emission spectra, as well as a reference with a known compound; the quantum yields (Φ_f) anthracene was used as reference (Φ_f = 0.27 in EtOH).[156] The quantum yields (Φ_f) were calculated by the equation **2**.[157]

$$\Phi_X = \Phi_R \frac{D_X}{D_R} \frac{A(\lambda_{ex,R})}{A(\lambda_{ex,X})} \frac{n_X^2}{n_R^2} \frac{I(\lambda_{ex,R})}{I(\lambda_{ex,X})}$$

Equation 2: Equation for quantum yields calculation.

In this equation, R refers to standard reference and X to unknown sample, Φ is the quantum yield, D is referring to area under emission curve, A is the absorbance at λ_{ex} excitation wavelength, n is the refractive index of solvent, I indicates excitation light intensity at λ_{ex} excitation wavelength.

The fluorescence quantum yields (Φ_f) of the compounds from **133**, **134**, **148**, **149**, **159**, and **161**, determined in EtOH are presented in Table 22, along with full width at half maximum

(FWHM). The fluorescence quantum yield in EtOH is strongly quenched by the presence of S/Se and their substitution positions on the carbazole molecule. The S- compounds showed poor fluorescence quantum yields. The fluorescence quantum yield of the 4,5-bismethyl sulfide **159** (Φ_f ~0.003) can be compared with 3,6-bismethyl sulfide **148** which is 10 times greater (Φ_f ~0.03). Moreover, the absence of the Me group quenched the fluorescence quantum yield in the carbazole disulfide **134** (Φ_f ~0.001). The FWHM values presented in the table decreased with increased Φ_f values, and narrow peaks appeared.

The fluorescence quantum yields of Se-derivatives **133**, **149**, and **161** are shown in table 22. The fluorescence quantum yield of 4,5-bismethyl selenide carbazole **161** (Φ_f ~0.07) is ten times higher than the fluorescence quantum yield for 3,6-position **149** which is (Φ_f 0.006). In contrast, the fluorescence quantum yields value of the carbazole diselenide **133** is (Φ_f 0.05), which is higher than carbazole disulfide **134**. Table 22 shows that the FWHM values decrease with increased Φ_f values and peaks appeared narrow. The fluorescence quantum yield of carbazole **1** is greater than the new S/Se carbazole derivatives (**Table 22**).

The S/Se carbazole showed very low Φ_f values, demonstrating that the presence of S and Se group and S/Se Me group on the carbazole moiety significantly reduces fluorescence. However, this suggests that the presence of these groups quench fluorescence in the polar solvent which was EtOH. The solvatochromic effect can be attributed to a decrease in the energy of the singlet excited states as a function of an increase in the polarity of the solvents. Based on the literature, the Φ_f values for **187**, **190**, and **194** in Figure 31, three examples were determined in polar and non-polar solvents.[155] When switching from a nonpolar to a polar solvent, the Φ_f values decrease slightly. For example, the Φ_f value of **187** in pentane (0.025) was somewhat higher than that in acetonitrile (0.015). In acetonitrile, the Φ_f value of **194**

reduced from 0.50 in pentane to 0.33.[155] Unfortunately, the solvatochromic effect was not studied for these compounds. However, the effect was moderate in the literature for the **187** and **189** to**195** .[155]

3.1.5 Emission of S/Se-disubstituted carbazoles and Kasha-Vavilov's rule.

Among the most important rules in organic photophysics and photochemistry is the Kasha-Vavilov's rule. As Kasha's rule states, photons in molecular systems are always emitted from their lowest excited states and emission quantum yields are independent of excitation wavelength. In other words, the emission spectra are independent of the excitation wavelength.[158] Most molecular systems follow these rules, but violations are reported for molecular systems. Azulene is the prototypical example of Kasha's rule violation.[158]

The effect of different excitation wavelengths was investigated, at constant concentration. Excitation of carbazole disulfide **134** at 315 nm showed emission at 377 and 423 nm. However, when excited at 350 nm, **134** emits as two peaks at 395 nm and at 418 nm. However, at the same concentration, the maximum fluorescence intensity was achieved with increased excitation wavelength and the emission wavelength was longer. This compound **134** is breaking Kasha's rule (**Figure 32**). The compound **134** emitted at a different wavelength with each excitation wavelength.

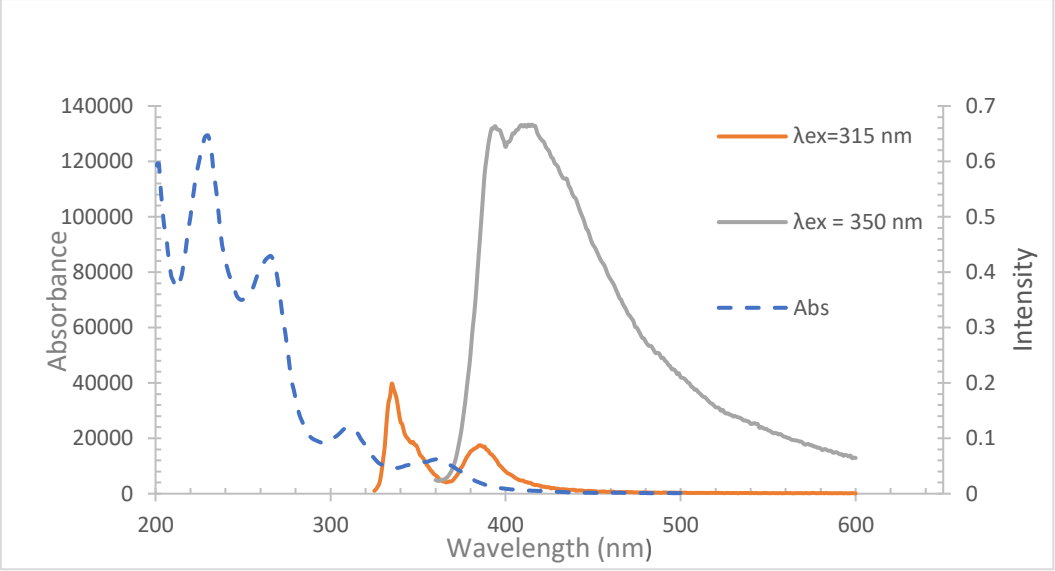


Figure 32: Absorbance and emission spectra of **134** recorded in EtOH at (λ_{ex} 315 and 350 nm)

The 4,5-bismethyl sulfide carbazole **159** showed no change in emission even at different excitation wavelengths (**Figure 33**). For compound **159**, the fluorescence was in the same region even though excited at different wavelengths, meaning that the compound followed Kasha's rule. With 350 nm excitation, a very high intensity and single emission peak was observed around 405 nm.

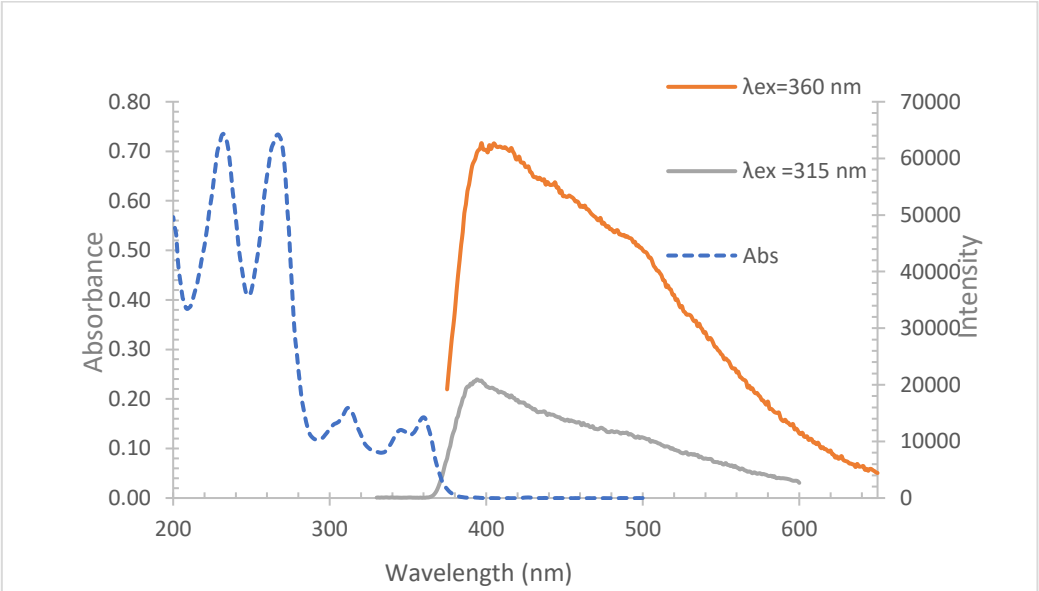


Figure 33: Absorbance and emission spectra of **159** recorded in EtOH at (λ_{ex} 315 and 360 nm)

The compound **148** was excited at 311 nm two sharp peaks were observed at about 396 and 411nm (**Figure 34 (A)**). However, when **148** was excited at 358 nm, a very high intensity and sharp double emission peak was observed (**Figure 34 (B)**).

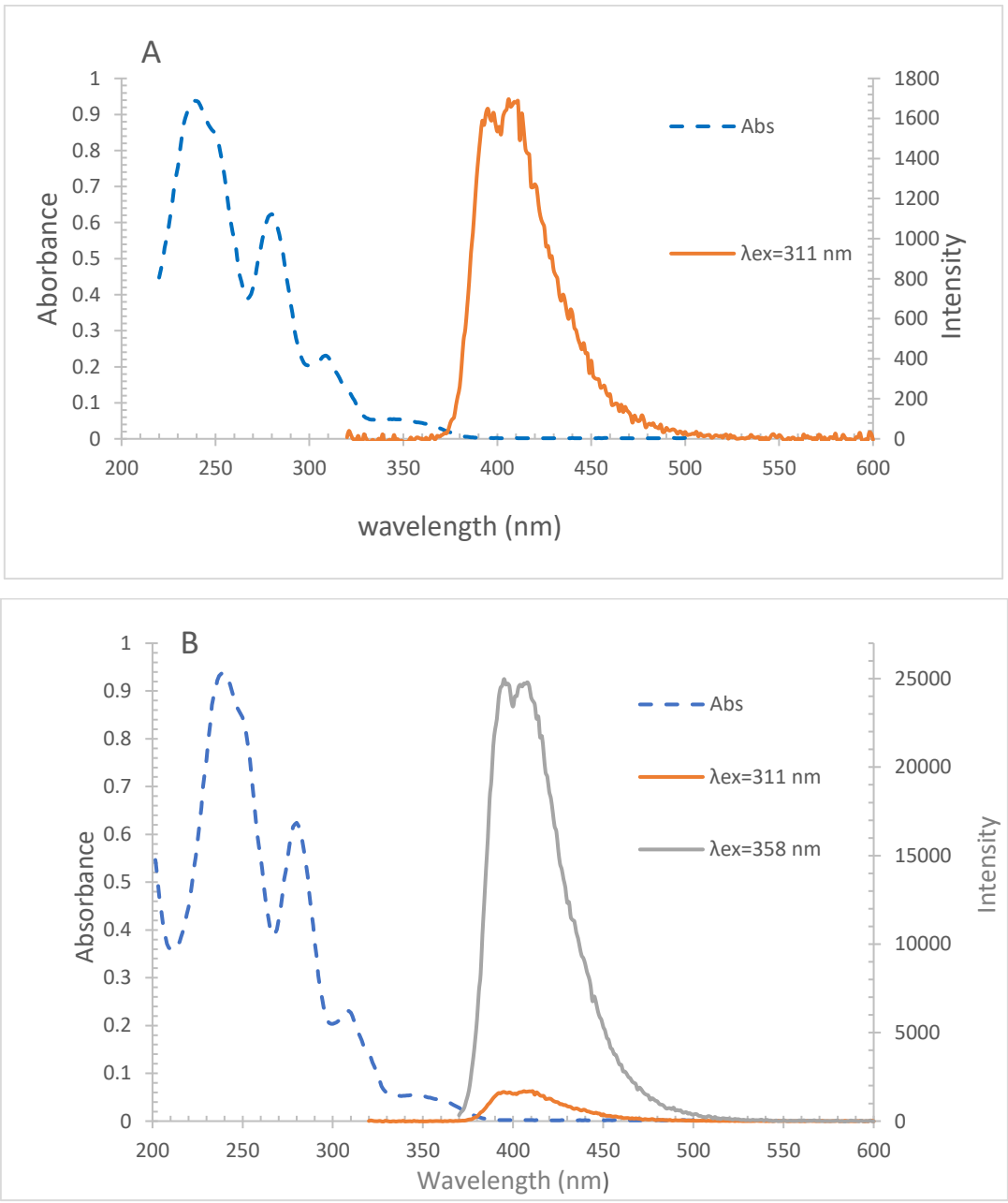


Figure 34: Absorbance and emission spectra of **148** recorded in EtOH at (λ_{ex} 311and 358 nm)

Excitation of carbazole diselenide **133** at 331 nm showed emission at 348 nm and a broad peak at 425 nm. On the other hand, when excited at 383 nm the emission intensity was

increased at long excitation wavelength and a narrow fluorescence peak was observed at 433 nm (**Figure 35**). As result, from the emission spectrum the compound **133** does not obey the Kasha rule. The emission wavelength is dependent on the electronic configuration of the excited state.

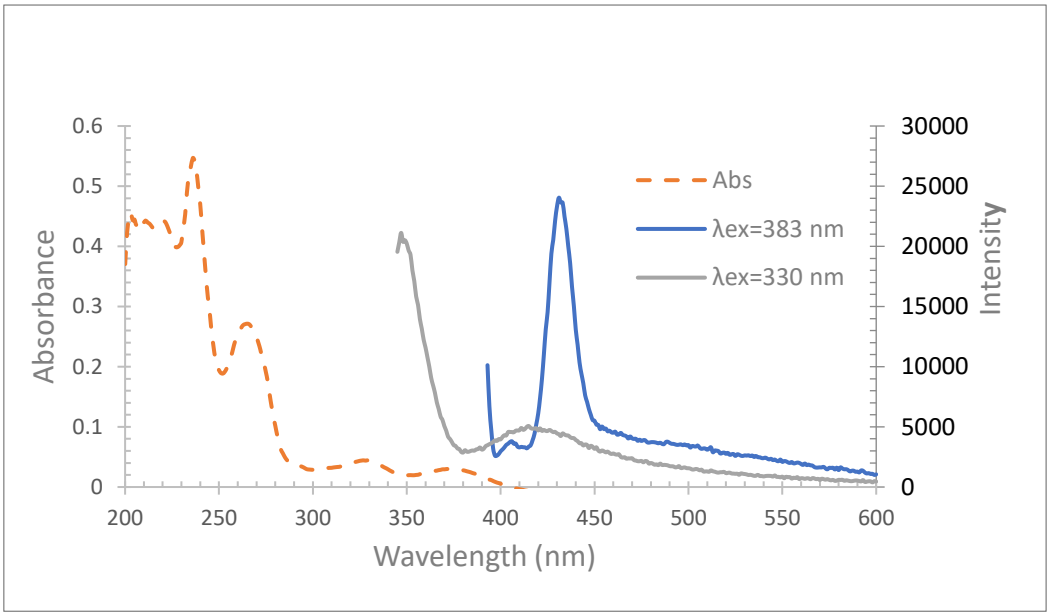


Figure 35: Absorbance and emission spectra of **133** recorded in EtOH at (λ_{ex} 330 and 383 nm)

The 4,5-bismethyl selenide carbazole **161** emitted in the violet-blue region. The excitation of **161** was investigated at two different excitation wavelengths, 318 and 347 nm (**Figure 36**). The spectra showed emission of two peaks, a larger one at 385 nm, and a second smaller peak at 438 nm. At the same concentration, the excitation wavelength at 347 nm is more effective for fluorescence intensity than 318 nm.

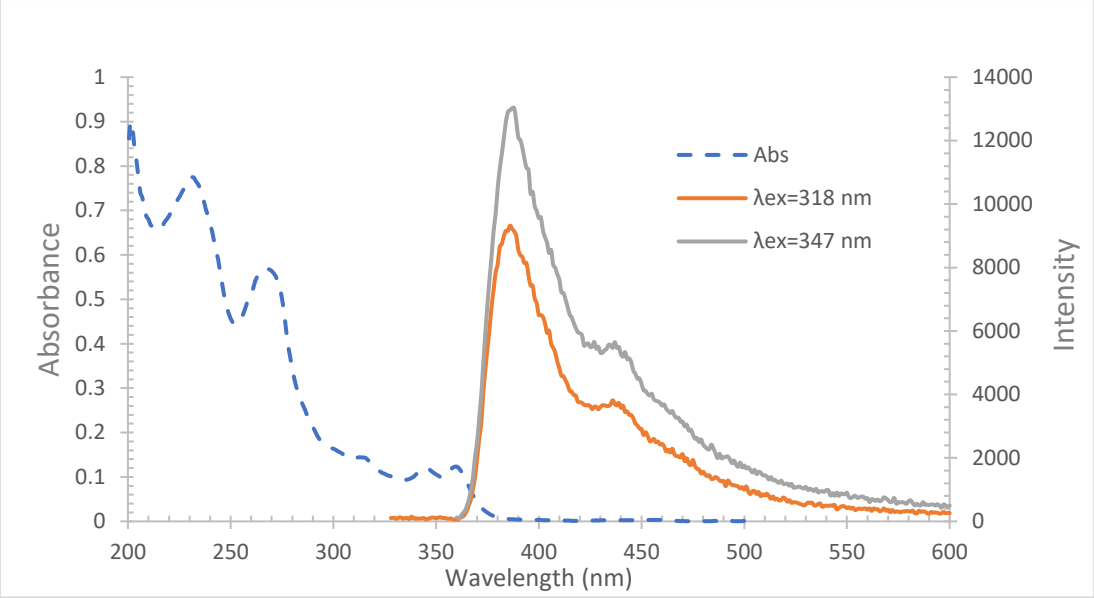


Figure 36: Absorbance and emission spectra of **161** recorded in EtOH at (λ_{ex} 318 and 347 nm)

The 3,6-bismethyl selenide carbazole **149** absorbance and emission spectrum are shown below (**Figure 37**). At an excitation wavelength 311 nm, **149** emitted at 401 nm, as shown in Figure 34, but when the excitation wavelength was 350 nm the emission intensity is increased.

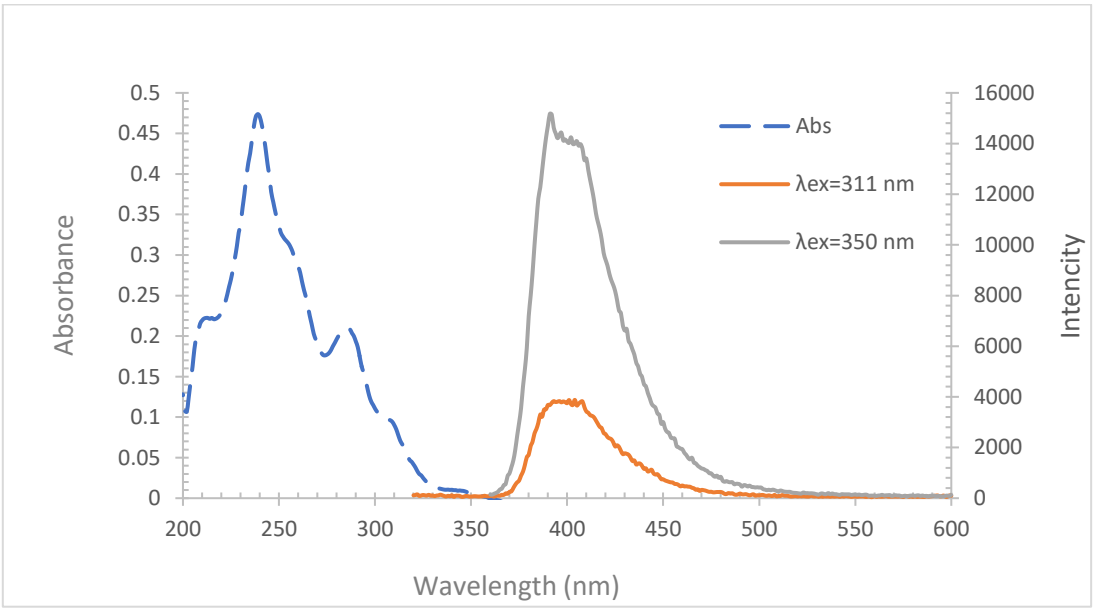


Figure 37: Emission spectra of **149** recorded in EtOH at (λ_{ex} 311 and 350 nm)

In conclusion, a photophysical study of blue and green light-emitting carbazoles (S/Se compounds **133**, **134**, **148**, **149**, **159** and **161**) was carried out. Each compound showed an absorbance and emission in the blue-green region. The substitution pattern on the carbazole showed no significant effect on the absorbance and emission spectra for all compounds, except for carbazole diselenide **134** whose absorbance maxima was 380 nm and the emission maxima 433 nm. The Se-compounds **133**, **149**, and **161** are slightly less than the extinction coefficients (ε) values compared with S-compounds **134**, **148**, and **159**. The Φ_f values of Se-compounds were low (0.006-0.1), and the Φ_f values of S-compounds were extremely low (0.001-0.03), indicating that the S and SMe groups effectively quench the fluorescence in ethanol solvent. The highest Φ_f value was 0.1 for the 4,5 -bismethyl selenide carbazole **161** in ethanol. The solvometric effect was not studied in this investigation. The literature showed an increase in the quantum yield in non-polar solvent.[155]

3.2 Overall conclusions and future work

Treatment of *N*-TIPS carbazole with the combination of *n*-BuLi /TMEDA and quenching the dilithium species with different electrophiles, represents the first direct and convenient methodology for the synthesis of 4,5-disubstituted carbazoles in one step. Lithiation of 1,8-positions of the carbazole are avoided by using the TIPS protective group. The TIPS protecting group is simple to remove. Some electrophiles work in less than 10% yield, such as dichloro *N*-TIPS carbazole **108**, dibromocarbazole **112** diiodocarbazole **114** lactone **126**, diketone **132** and (**Scheme 39**, **41**, and **42**, **Table 5** and **8**). Moreover, some electrophiles gave undesired products, such as with carbon disulfide (**Scheme 57**) or did not react, such as benzophenone (**Scheme 58**). Subsequent reactions for these novel compounds were demonstrated. The oxidation of the diboronic anhydride **121** gave dihydroxy carbazole **145**. The diol **106** was cyclised to cyclic ether **146**. The reduction and methylation of the disulfide **86** and diselenide **88** to the corresponding 4,5-bis methyl sulfide **159** and selenide **161** respectively gave good yields (**Scheme 62** and **63**). The compounds **86**, **88**, **100**, **108**, **126**, **158** and **160** were TIPS group deprotected in satisfactory yields. The anhydride **100** was converted to hydrazine **163**. Salts **171** and **172** were formed from the reaction of benzylamine and anhydride. The dimethyl fluorene anhydride **177** was synthesised using a similar procedure, the dimethyl fluorene bissalt **183** was similar synthesised. The X-ray structure for compounds **106**, **110**, **159**, **161** and **146** were reported, and the crystallographic data analysis was compared with the carbazole scaffold. The effect of the different substituted groups in the bay region was investigated; deviations in carbazole and the splay angle were determined. A comparison was made of the photophysical properties of disulfide carbazole **134**, diselenide **133** with the 4,5-

bismethyl sulfide **159**, methyl selenide **161**, and the corresponding 3,6-disubstituted systems **148** and **149** according to the literature.

Future work could be conducted to make asymmetric 4,5-disubstituted carbazoles through sequential trapping of the intermediate dilithium. Optimisation using different electrophiles can be carried out in the quenching step. Determination of the fluorescence quantum yield can be carried out in different solvents especially in non-polar solvents to increase the values. The lithiation methodology could also be further extended to make 4,5-disubstituted fluorenes with a wider range of electrophiles.

Chapter 4: Experimental Procedures

4.1 General Experimental

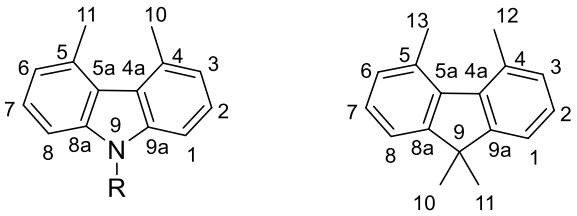
All reagents and solvents obtained from standard providers and used without additional purification. All dry solvents were collected from a Solv-MD solvent purifier or dried over 4 Å molecular sieves and purged under argon for 15 minuities prior to use. All reactions were carried out in glassware that had been oven-dried and under an argon atmosphere, unless otherwise stated. Solutions of *n*-butyllithium in hexanes were purchased from Sigma Aldrich at 2.5 M concentration and titrated in THF (anhydrous) with menthol in the presence of 1-(biphenyl-4-yl)-3-phenyl-2-azapropene("Blue").[159, 160] N,N,N',N'-Tetramethylethylenediamine was distilled from calcium hydride and kept over KOH pellets in dark place. Lithium bis(trimethylsilyl)amide was purchased as a 1 M solution in THF. Elemental sulfur was recrystallised from hot toluene and dried under vacuum.

All column chromatography was performed under pressure (flash column chromatography – FCC) with Sigma-Aldrich silica gel, 60 Å pore size, 230 – 400 mesh, 40 – 63 µm. All compounds were dry-loaded onto silica on the minimum amount of silica that was required (minimum amount refers the minimum amount of silica required in order for the silica to be free flowing when doped with the compound). All TLC analysis was performed using silica gel on Merck aluminium TLC silica gel plates, 60 with 254 nm fluorescent indicator, with visualisation using 254 nm UV light and curcumin dip.[161] Nuclear magnetic resonance (^{1}H and ^{13}C) was detected by a Bruker Avance NEO 400 or Bruker 300 MHz AVIII spectrometer (^{1}H – 400 MHz and ^{13}C 101 MHz). most of the spectra were recorded in $CDCl_3$ and referenced to the residual $CHCl_3$ (^{1}H – 7.26 ppm and ^{13}C – 77.16 ppm) unless otherwise stated. Chemical shifts are reported in ppm and coupling constants, J, are reported in Hz. The following abbre*via*tions are used to describe multiplicity; s – singlet, d

– doublet, dd – doublet of doublets, ddd – doublet of doublets of doublets, t – triplet, q – quartet, hept – heptet, m – multiplet, app – apparent and st – stack. All coupling constants are reported as observed not averaged. All assignments were made using analysis of 2D NMR (COSY, NOESY, HSQC, HMBC). Mass spectrometry was recorded using GCMS on a Water micro mass GC-ToF Premier/Agilent 7890A with a Phenomenex ZB-5 column 30 m × 0.25 mm ID × 0.25 µm film thickness or ASAPs Waters Xevo G2-XSToF and are reported as (m/z%). IR spectra were recorded neat, unless otherwise specified, on a Perkin Elmer spectrum 100 FT-IR spectrometer. UV/Vis absorption spectra were obtained. Using on a Varian Cary 50 spectrometer at a scan rate of 600 nm min^{-1}. Baseline corrections were performed for the EtOH solvent system and quartz cuvette with a 1 cm path length was used. Fluorescence spectra and data were obtained by either Fluorescence spectrometer Jasco FP-8500 and Horiba Fluorolog-3 (L-configuration) equipped with a 450 W Xenon light source, R928P photomultiplier tube and double monochromators. The quantum yields of samples and references in EtOH were measured using Horiba Fluorolog-3.

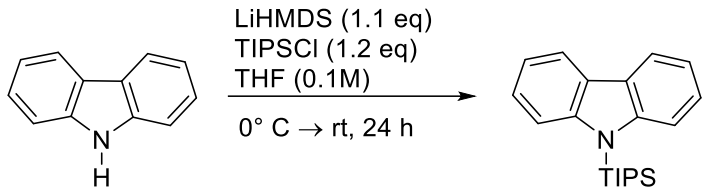
Compound numbering

For NMR assignment, the following numbering convention is adopted:



4.2 Synthetic procedures and analytical data

4.2.1 Synthesis of 9-(triisopropylsilyl)-9H-carbazole 56



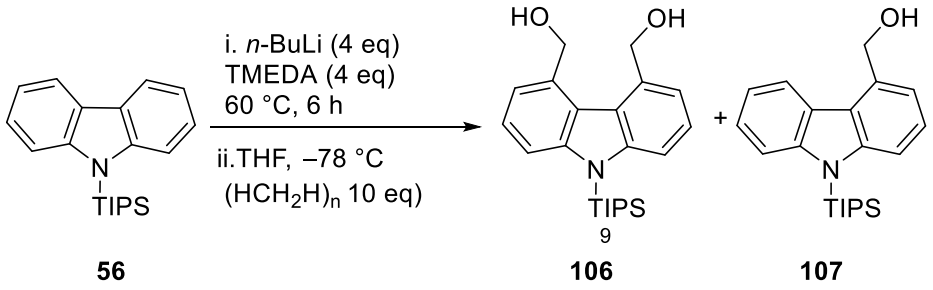
1 **56**

9-(triisopropylsilyl)-9H-carbazole **56** was synthesised following a literature procedure.[64]

A solution of LiHMDS in THF (1.0 M, 9.80 mL, 9.88 mmol) was added dropwise to a solution of carbazole (1500 mg, 8.97 mmol) in anhydrous THF (90 mL, 0.1 M) at 0°C, over 5 min. The reaction mixture was allowed to stir at 0 °C for 15 min. TIPSCl (2.3 mL, 10.76 mmol) was added in one portion and the reaction mixture was allowed to stir at 0 °C for a further 15 min. The cooling bath was removed, and the reaction was stirred at room temperature for 24 h. The solvent was removed from the reaction mixture under reduced pressure and re-dissolved in EtOAc (50 mL) and separated with water (50 mL). The aqueous layer was extracted with EtOAc (50 mL × 2), and the combined organics were washed with water (50 mL) and brine (50 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield a beige solid. The crude mixture was dry-loaded onto silica and purified by FCC (*n*- hexane 100%) to yield a white solid (2489 mg, 86%). R_f 0.3 (*n*-hexane 100%); ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.08 (2 H, dd, *J* 7.7, 0.8 Hz), 7.71 (2 H, d, *J* 8.4 Hz), 7.36 (2 H, ddd, *J* 8.5, 7.1, 1.4 Hz), 7.23 (2 H, d, *J* 7.1 Hz) 2.02 (3 H, hept, *J* 7.5 Hz), 1.20 (18 H, d, *J* 7.5 Hz); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 145.2 (C,), 126.6 (C), 125.4 (CH), 119.8 (CH), 119.6 (CH), 114.2 (CH), 18.6 (CH_3), 13.7 (CH(LRMS, TOF ASAP+) 326.2165 (10),

325.2180 (22), 324.2155 ([M + H]$^+$, 100%). This data is in agreement with that given in the literature. [64, 90, 91]

4.2.2 Synthesis of 9-(triisopropylsilyl)-9H-carbazole-4,5-diyl)dimethanol 106



56 **106** **107**

Novel compounds **106** and **107**, [89] were synthesized according to the procedure found in the literature after modifications.[97]

n-BuLi (2.38 M in *n*-hexanes, 10.86 mL, 25.84 mmol) was added dropwise over 10 min to a solution of compound **56** (2091 mg, 6.46 mmol) in TMEDA (3.88 mL, 25.84 mmol) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C and THF (27 mL, 0.24 M) was added to the mixture, followed by the addition of paraformaldehyde (1940 mg, 64.62 mmol) as a single portion. The reaction mixture was allowed to warm to room temperature and left to stir for 16 h. Sat. $NH_4Cl_{(aq)}$ (100 mL) was added to the reaction mixture and then the resulting mixture was extracted with EtOAc (80 mL × 3). The combined organic extracts were washed brine (80 mL × 3) dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give an orange oil. The orange oil was purified by FCC (*n*-hexane: EtOAc, 3:1 to 1:1) to give first **107** (524 mg, 23%) as a yellow oil followed by **106** (1047 mg, 43%) as an off-white crystalline solid.

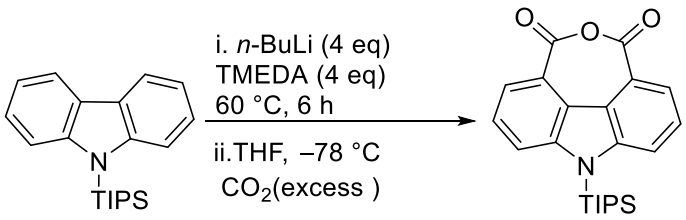
Analytical data for compound 107

R_f = 0.31 (*n*-hexane: EtOAc, 3:1); V_{max} (oil, cm^{-1}) 3357 br, 2949 m, 2868 m, 1725 w, 1588 w, 1450 s, 1427 s, 1265 s, 1209 s, 1002 s, 881 s, 726 s, 682 m; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.24 (1H, dd, *J* 7.9, 0.7 Hz, H-5), 7.76 (1H, d, *J* 8.5 Hz, H-8), 7.71 (1 H, d, *J* 8.3 Hz, H-1), 7.42 – 7.34 (2 H, stack, H-2 and H-3), 7.30–7.25 (2 H, stack, H-6/H-7), 5.29 (2H, s, CH_2-10), 2.02 (3 H, hept, *J* 7.5 Hz, SiC*H*), 1.21 (18 H, d, *J* 7.6 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 145.7 (C, C-8a), 145.4 (C, C-9a), 134.9 C, C-4), 125.8 (C, C-5a), 125.2 (CH, C-7), 125.0 (CH, C-5), 124.0 (C, C-4a), 123.0 (CH, C-3), 120.0 (CH, C-8), 119.3 (CH, C-1), 114.1 (CH, C-2), 114.0 (CH, C-6), 64.7 (CH_2, C-10), 18.8 (CH_3, SiCH*C*H$_3$), 14.0 (CH, Si*C*H); m/z (HRMS, TOF MS Cl^+) calculated for $C_{22}H_{35}N_2OSi$ $[M+NH_4]^+$; 371.2519, found 371.2533 (PPM error 3.8).

Analytical data for compound 106

R_f = 0.30 (*n*-hexane: EtOAc, 1:1); mp 95 – 96 °C (*n*-hexane); V_{max} (solid, cm^{-1}) 3304 br, 2948 m, 2869 m, 1604 w, 1585 m, 1464 m, 1420 s, 1272 s, 1236 m, 1037 w, 1010 s, 982 m, 883 m, 846 m, 778 s, 728 s, 719 s, 682 s; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 7.74 (2 H, dd, *J* 8.4 Hz, 0.9 Hz, H-2/H-7), 7.34 (2 H, dd, *J* 8.4, 7.3 Hz, H-1/H-8), 7.24 (2 H, dd, *J* 7.2 Hz, 0.8 Hz, H-3/H-6), 5.22 (4 H,s, H-10/H-11), 3.47 (2 H, br s, OH), 1.99 (3 H, hept, *J* 7.5 Hz, SiC*H*), 1.17 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 146.7 (C, C-8a/C9a), 134.7 (C, C-4a/C-5a), 124.8 (CH, C-1/C-8), 123.8 (C, C-4/C-5), 122.9 (CH, C-3/C-6), 114.1 (CH, C-2/C-7), 67.0 (CH_2, C-10/C-11), 18.6 (CH_3, SiCHCH_3), 13.9 (CH, Si*C*H); m/z (HRMS, TOF ES+) calculated for $C_{23}H_{33}NO_2SiNa$ $[M+Na]^+$; 406.2178, found 406.2190 (PPM error −3.0). Single crystals of **106** suitable for X-ray structure analysis were obtained by slow evaporation of a methanol solution (appendix X-ray).

4.2.3 Synthesis of 4-(triisopropylsilyl)-4H-oxepino[3,4,5,6-def]carbazole-8,10-dione 100



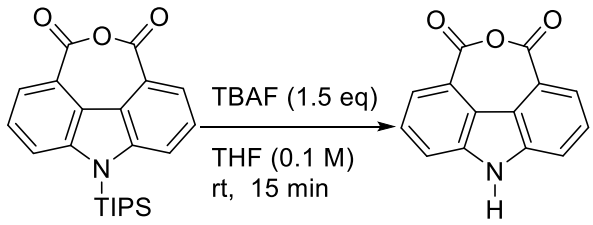
56 **100**

Novel compound **100**,[89] was synthesised using modified literature procedure.

n-BuLi (2.01 M in hexanes, 9.45 mL, 19.01 mmol) was added dropwise over 10 min to a solution of compound **56** (1538 mg, 4.75 mmol) in TMEDA (2.85 mL, 19.01 mmol) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C and THF (19.8 mL, 0.24 M) was added to the mixture, followed by the addition of carbon dioxide (dry ice in excess 20 eq) as a single portion and allowing venting of the excess CO_2 gas using multiple needles in the rubber septum of the reaction flask. The reaction mixture was allowed to warm to room temperature and left to stir for 16 h. After addition of Conc. HCl (37 w/w%, 8 mL) at 0 °C, the reaction mixture was allowed to stir at this temperature for 1 h prior to diluting with H_2O (80 mL) and extracting with CH_2Cl_2 (80 mL× 3). The combined organic extracts were washed with brine (80 mL × 3), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a brown solid. The brown solid was purified by trituration with *n*-hexane, to give **100** (1170 mg, 63%) as a beige solid. R_f =0.29 (CH_2Cl_2: MeOH, 9:1); mp 207 – 209 °C (*n*-hexane); V_{max} (solid, cm^{-1}) 2951 br, 2869 br, 1692 s, 1421 m, 1302 s, 1263 s, 1028 w, 880 w, 754 w, 735 w; ^{1}H-NMR (400 MHz ,$CDCl_3$, 7.26 ppm) δ_H 7.96 (2 H, d, *J* 8.5 Hz, H-2/H-7), 7.77 (2 H, d, *J*

7.3 Hz, H-3/H-6), 7.45 (2 H, dd, *J* 8.4 Hz, 7.6 Hz, H-1/H-8), 2.02 (3 H, hept, *J* 7.5 Hz, SiC*H*), 1.22 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 176.6 (C, C-10/C-11), 146.5 (C, C4a-C-5a), 127.5 (C, C-4/C-5), 125.2 (C, C-8a/C-9a), 122.2 (CH, C-3/C-6), 122.0 (CH, C-1/C-8), 118.4 (CH,C-2/C-7), 18.7 (CH_3, SiCH*C*H$_3$), 14.1 (CH, Si*C*H); m/z (HRMS, TOF ES+) calculated for $C_{23}H_{28}NO_3Si$ [M+H]+; 394.1838, found 394.1839 (PPM error 0.3).

4.2.4 Synthesis of 4H-oxepino[3,4,5,6-def]carbazole-8,10-dione 102



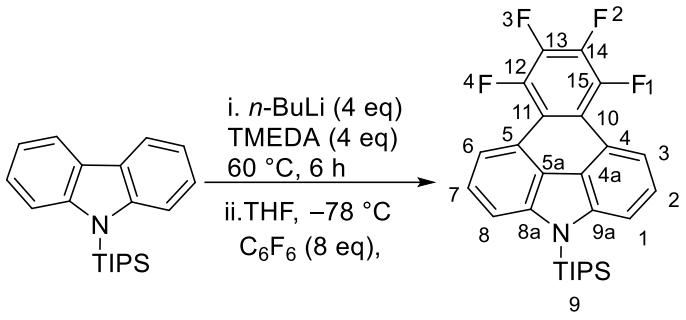
100 **102**

The compound **102** was synthesised following the literature procedure. [96]

Tetrabutylammonium fluoride solution (1 M in THF, 0.20 mL, 0.20 mmol, 1.5 eq) was added to a solution of *N*-TIPS-carbazole anhydride **100** (53 mg, 0.14 mmol) in THF (1.35 mL, 0.1 M). The mixture was stirred at room temperature for 15 min. After that, the reaction mixture was concentred under reduced pressure. The residue was dissolved in EtOAc (4 mL) and washed sequentially with water (4 mL × 2) and brine (4 mL × 2). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give **102** (18 mg, 56% impure) as a beige solid. R_f = 0.29 (CH_2Cl_2: MeOH, 8:2); V_{max} (solid, cm^{-1}) 3354 w, 2920 m, 2871 m, 1686 s, 1613 m, 1598 m, 1572 m, 1463 m, 1317 s, 1282 m, 1258 s, 1171 m, 805 m, 747 s, 719 s, 662 m;

^{1}H NMR (400 MHz, DMSO-d_6, 2.50 ppm) δ_H 11.78 (1 H, s, NH), 7.69 (2 H, dd, *J* 7.8, 1.4 Hz, H-3/H-6), 7.53 – 7.41 (4 H, m, H-2/H-7and H-1/H-8); ^{13} C-NMR (101 MHz, DMSO-d_6, 39.5 ppm) δ_C 169.6 (C, C-10/C-11), 140.6 (C, C-8a/C-9a), 129.6 (C, C-4a/C-5a), 125.2 (CH, C-2/C-7), 120.3 (CH, C-1/C-8), 118.8 (C, C-4/C-5), 114.3 (CH, C-3/C-6); m/z (HRMS, TOF ASAP+) calculated for $C_{14}H_8O_3N$ $[M+H]^+$; 238.0504, found 238.0510 (PPM error 2.5).

4.2.5 Synthesis of 8,9,10,11-tetrafluoro-4-(triisopropylsilyl)-4H-naphtho[1,2,3,4-def]carbazole 117



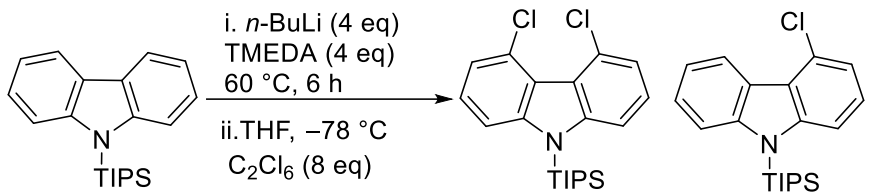
56 **117**

The novel compound **117**,[89] was synthesised using modified literature procedure.[103]

n-BuLi (2.38 M in *n*-hexanes, 1.1 mL, 2.59 mmol, 4 eq) was added dropwise over 10 min to a solution of compound **56** (209 mg, 0.65 mmol) in TMEDA (0.38 mL, 2.16 mmol) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C and THF (2.7 mL, 0.24 M) was added to the mixture, followed by the addition of hexafluorobenzene (0.59 mL, 5.18 mmol, 8 eq) as a single portion. The reaction mixture was

allowed to warm to room temperature and left to stir for 16 h. The mixture was poured into ice/water (8 mL) and extracted with EtOAc (10 mL× 3). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give an orange solid. The crude material was purified by FCC (*n*-hexane) to give **117** (103.6 mg, 34%) as a white solid. R_f = 0.31 (*n*-hexane); mp 207 − 208 °C (*n*-hexane); V_{max} (solid, cm^{-1}) 2950 m, 2870 m, 1570 m, 1489 s, 1451 s, 1369 m, 1256 m, 1112 m, 952 s, 864 s, 778 s, 767 s, 718 s; ^{1}H-NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.45 (2H, d, *J* 7.7 Hz, H-3/H-6), 7.88 (2 H, d, *J* 8.0 H*z,* H-1/H-8), 7.81 (2 H, t, *J* 7.9 Hz, H-2/H-7), 2.12 (3 H, hept, *J* 7.5 Hz, SiC*H*), 1.27 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (126 MHz, $CDCl_3$, 77.16 ppm) δc 147.4 (C, dm, *J* 250.5 Hz, C-13/C-14), 144.0 (C, C-4a/C-5a), 139.2 (C, dm, *J* 253.1 Hz, C-12/C-15), 127.5 (CH, C-1/C-8), 124.0 (C, C-8a/C-9a), 122.2 (C, C-4/C-5), 117.9 (C, m, C-10/C-11) 117.5 (CH, m, C-3/C-6), 112.6 (CH, C-2/C-7), 18.6 (CH_3, SiCH*C*H$_3$), 13.8 (CH, Si*CH*); ^{19}F NMR (471 MHz, $CDCl_3$) δ_F -139.3 (F, d, *J* 16.5 Hz, F-1/F-4), -158.1 (F, d, *J* 16.4 Hz, F-2/F-3); m/z (HRMS, TOF ASAP+) calculated for $C_{27}H_{28}NSiF_4$ $[M+H]^+$;470.1927, found 470.1937 (PPM error 2.1). Single crystals of **117** suitable for X-ray structure analysis were obtained by slow evaporation of a methanol solution (appendix X-ray).

4.2.6 Synthesis of 4,5-dichloro-TIPS-carbazole 108



56 **108** **109**

The novel compounds **108** and **109** were synthesised following a procedure for quenching organolithiums with C_2Cl_6. [89, 99]

n-BuLi (1.68 M in hexanes, 2.2 mL, 3.70 mmol, 4 eq) was added dropwise over 10 min to a solution of compound **56** (301 mg, 0.93 mmol) in TMEDA (0.58 mL, 3.90 mmol, 4 eq) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C and THF (6 mL, 0.24 M) was added to the mixture, followed by the addition of hexachloroethane (2200 mg, 9.30 mmol, 10 eq) as a single portion. The reaction mixture was allowed to warm to room temperature and left to stir for 16 h. The reaction mixture was poured into H_2O (10 mL) and extracted with Et_2O (10 mL × 3). The combined organic extracts were washed with 10 w/w% $NaHCO_{3(aq)}$ (20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a brown oil. The brown oil was purified by FCC (*n*-hexane 100%) to give first compound **109** (23 mg, 7%) as an off-white solid, then followed by compound **108** (22 mg, 6% based on approx. 90% purity by NMR analysis) as a white solid.

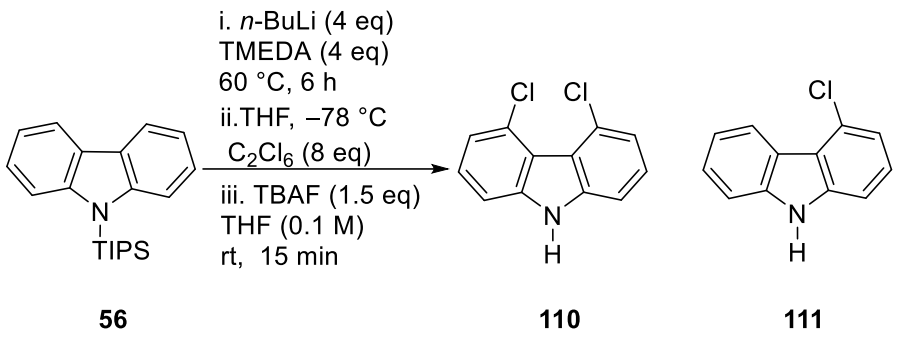
Partial date analysis for compounds 109:

V_{max} (Solid, cm^{-1}) 2953 m, 2926 m, 2868 m, 1587 w, 1471 w, 1444 m, 1420 s, 1263 m, 1215 w, 979 s, 880 s, 757 s; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.70 (1H, d, *J* 8.8 Hz,), 7.72 (1 H, d, *J* 8.5 Hz), 7.62 (1 H, dd, *J* 8.0, 1.2 Hz), 7.46 – 7.35 (1 H, m), 7.32 – 7.17 (3 H, m), 2.0 (3 H, hept, *J* 7.5 Hz ,SiC*H*), 1.19 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δc 146.5 (C), 145.4 (C), 128.5 (C), 125.9 (CH), 125.5 (C), 125.3 (CH), 123.5 (C), 123.1 (CH), 120.8 (CH), 119.9 (CH), 113. 9 (CH), 112.4 (CH), 18.7 (CH_3, SiCH*C*H_3), 13.9 (CH, Si*C*H). m/z (HRMS, TOF EI+) calculated for $C_{21}H_{28}{}^{35}$Cl NSi [M]+, 357.1680, found 357.1684 (PPM error 1.1).

Partial date analysis for compounds 108:

V_{max} (Solid, cm^{-1}) 2988 m, 2901 m, 1417 w, 1275 w, 1066 s, 995 s, 773 m; ^{1}H-NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ_H7.60 (2 H, *J* 7.6 Hz, H-3/H-6), 7.27-7.21 (4 H, m, H-1/H-8 and H-2/ H-7), 1.93 (3 H, hept, *J* 7.5 Hz, SiC*H*), 1.12 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_c 147.5 (C), 127.6 (C), 125.9 (CH), 123.3 (CH), 122.7 (C), 112.4 (CH), 18.7 (CH_3-SiCH*C*H_3), 14.0 (CH, Si*C*H); m/z (HRMS, TOF EI+) calculated for $C_{21}H_{27}{}^{35}Cl_2$NSi $[M]^+$, 391.1290, found 391.1286 (PPM error -1.0).

4.2.7 Synthesis of 4,5-dichloro-9H-carbazole 110



56 **110** **111**

The novel compounds **110** and *111* were synthesised following the literature procedure.[89]

n-BuLi (2.35 M in hexanes, 1.68 mL, 2.55 mmol, 4 eq) was added dropwise over 10 min to a solution of compound **56** (207 mg, 0.64 mmol) in TMEDA (0.38 mL, 2.55 mmol, 4 eq) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to -78 °C and THF (8 mL) was added to the mixture, followed by the addition of hexachloroethane (1512 mg, 6.39 mmol, 10 eq) as a single portion. The reaction mixture was allowed to warm to room temperature and left to stir for 16 h. The reaction mixture was poured into H_2O (20 mL) and extracted with EtOAc (20 mL × 3). The combined organic extracts were washed with 10 w/w% $NaHCO_{3(aq)}$ (40 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a brown oil. The brown oil was dissolved in THF (6.4 mL, 0.1 M), treated with tetrabutylammonium fluoride solution (1.0 M in THF, 0.96 mL, 0.96 mmol, 1.5 eq), and allowed to stir for 15 min at room temperature. The solvent was removed under reduced pressure and the residue dissolved in EtOAc (10 mL). The mixture was sequentially washed with H_2O (10 mL × 2) and brine (10 mL × 2), and the organic extracts dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a brown oil. The brown oil was purified by FCC (*n*-

hexane: EtOAc, 95:5) to give 4-chloro-9H-carbazole **111**,[100, 162, 163] (16.4 mg, 13%) as a yellow solid followed by compound **110** (52.6 mg, 35%) as a beige crystalline solid.

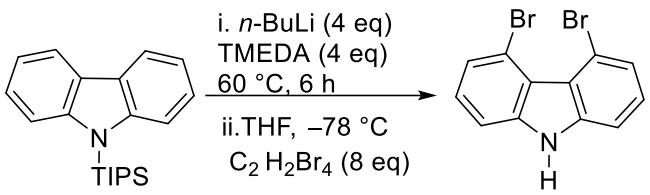
Analytical data for compound 111

V_{max} (Solid, cm^{-1}) 3415 s, 3058w, 2927 w, 1607 m, 1567 w, 1491 m, 1453 s, 1432 s, 1324 s, 1281 m, 1176 m, 1152 w, 945 w, 780 m, 750 m, 720 s; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm), δ_H 8.59 (1H, d, *J* 9.0, Hz), 8.18 (1H, br), 7.50 – 7.43 (2 H, m), 7.35 – 7.27 (3 H, m), 7.22 (1 H, dd, *J* 6.3, 2.3 Hz); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δc 140.6, 139.6, 128.9, 126.5, 126.3, 123.2, 122.5, 120.8, 120.4, 119.9, 110.5, 109.0; m/z (HRMS, TOF EI^+) calculated for $C_{12}H_8N\ ^{35}Cl[M]^+$; 201.0,345 found 201.0346 (PPM error 0.5).The data are agreement with literature.[100, 162, 163]

Analytical data for compound 110

R_f = 0.30 (*n*-hexane: EtOAc, 85:15); mp 173 – 175 °C (*n*-hexane); V_{max} (solid, cm^{-1}) 3417 s, 2957 w, 2925 w, 2855 m, 1603 m, 1561 m, 1493 w, 1476 m, 1427 s, 1380 w, 1305 s, 1148 m, 1133 m, 934 m, 845 w, 765 s, 712 s; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.33 (1 H, br s, NH), 7.35 – 7.33 (4 H, m, H-1/H-8 and H-2/H-7), 7.33 – 7.29 (2 H, m, H-3/H-6); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 141.3 (C, C-8a/C-9a), 128.1 (C, C-4/C-5), 127.0(CH, C-2/C-7), 123.0 (CH, C-3/C-6), 119.9 (C, C-4a/C-5a), 109.2 (CH, C1/C-8); m/z (HRMS, TOF ES+) calculated for $C_{12}H_7{}^{35}Cl_2N\ [M+]^+$; 234.9956, found 234.9955 (PPM error −0.4). Single crystals of **110** suitable for X-ray structure analysis were obtained by slow evaporation of a methanol solution (appendix X-ray).

4.2.8 Synthesis of 4,5-dibromo-9H-carbazole 112



56 **112**

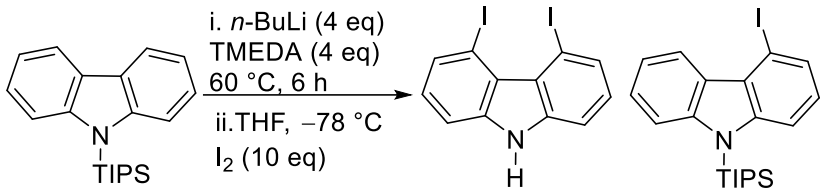
The novel compounds **112** was synthesised following the literature procedure.[89, 101]

n-BuLi (2.32 M, 1.63 mL, 3.8 mmol, 4 eq.) was added to a solution of compound **56** (307 mg, 0.948 mmol) in TMEDA (0.6 mL, 3.8 mmol, 4 eq) and the reaction mixture was heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C and THF (6.4 mL, 0.24 M) was added to the mixture, followed by the addition, of 1,1,2,2-tetrabromoethane (0.9 ml, 7.6 mmol, 8 eq) in one portion. After stirring at –78 ˚C for 1 h. The reaction was allowed to stir at room temperature for 16 h. After that, the reaction mixture was quenched with water and diluted with further Et_2O. After being washed with water and 10% Na_2CO_3 solution, the solution was dried with $MgSO_4$ and the Et_2O was removed under reduced pressure. The crude material was purified using FCC (*n*-hexane: EtOAc, 7:3) to produce 4,5-dibromo-9H-carbazole XX (6 mg, 2%) as an orange solid.

Partial data for compound 112

^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.33 (1 H, s, NH), 7.55 (2 H, dd, *J* 7.7, 1.0 Hz), 7.39 (2 H, dd, *J* 8.1, 1.1 Hz), 7.26 (2 H, t, *J* 7.9 Hz); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δc 141.5 (C), 134.5 (C), 127.3(CH), 127.2(CH), 109.8 (CH), 107.4 (C); m/z (HRMS, TOF ASAP+) calculated for $C_{12}H_8Br_2N$ $[M+H]^+$; 323.9024, found 323. 9020 (PPM error −1.2).

4.2.9 Synthesis of 4,5-diiodo-9H-carbazole 114



56 **114** **113**

The novel compounds **113** and **114** were synthesised following the literature procedure.[89, 102]

n-BuLi (2.65 M in *n*-hexanes, 1.08 mL, 2.55 mmol 4 eq) was added dropwise over 10 min to a solution of compound X X (206 mg, 0.64 mmol) in TMEDA (0.38 mL, 2.55 mmol, 4 eq) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C, and THF (8 mL) was added to the reaction mixture, followed by the addition of iodine (1619 mg 6.38 mmol, 10 eq) as a single portion. The reaction mixture was allowed to warm to room temperature and left to stir for 16 h. The reaction mixture was quenched with $Na_2S_2O_3$ (10 mL) and extracted with EtOAc (20 mL × 2). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give as dark brown solid. The brown solid was purified by FCC (*n*-hexane: EtOAc, 95:5) to give 4-iodo-9-(triisopropylsilyl)-9H-carbazole **113** (49.8 mg, 18 %) as a beige solid, then, after further elution with *n*-hexane: EtOAc (80:20), 4,5-diiodo-9H-carbazole **114** (5.5 mg, 2%) as a brawn solid.

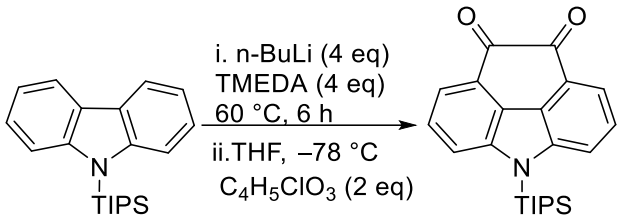
Partial analytical data for compound 113

^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 9.12 (1H, dd, *J* 8.1, 1.4 Hz, H-5), 7.77 – 7.70 (3 H, m, H-1/H-3/H-7), 7.45 (1 H ddd, *J* 8.5, 7.1, 1.5 Hz, H-8), 7.33 (1 H, ddd, *J* 8.0, 7.1, 1.0 Hz, H-2), 7.04 (1 H, dd, *J* 8.4, 7.6 Hz, H-6), 2.00 (3 H, hept, *J* 7.5 Hz, SiC*H*), 1.19 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δc 146.3 (C, C-8a), 145.8 (C, C-9a), 131.4 (CH, C-3), 127.1(C, C-5a), 126.6 (C, C-4a), 126.1 (CH, C-2), 125.9(CH, C-7), 121.6 (CH, C-5), 118.9 (CH, C-6), 113.9(CH, C-8), 113.8 (CH, C-1), 87.1 (C, C-4), 18.6 (CH_3, SiCHC*H*$_3$), 13.9 (CH, Si*C*H).

Partial analytical data for compound 114

V_{max} (solid, cm^{-1}) 3373 m, 2926 w, 2850 w, 1686 w, 1679 m, 1597 s, 1549 w, 1457 m, 1409 m, 1099 m, 897 m, 746 s; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.19 (1 H, s, NH), 7.90 (2 H, dd, *J* 7.6, 1.0 Hz, H-1/H-8), 7.41 (2 H, dd, *J* 8.0, 1.0 Hz, H-3/H-6), 7.09 (2 H, t, *J* 7.8 Hz, H-2/H-7); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δc 141.3 (C, C-8a/C-9a), 134.9 (CH, C-1/C-8), 127.6 (CH, C-2/C-7), 125.8 (C, C-4a/C-5a), 110.4 (CH, C-3/C-6), 85.8 (C, C-4/C-5).

4.2.10 Synthesis of 4-(triisopropylsilyl)-4H-benzo[def]carbazole-8,9-dione 132



56 **132**

Compound **132** is a novel compound and was synthesised from a modified literature procedure.[113]

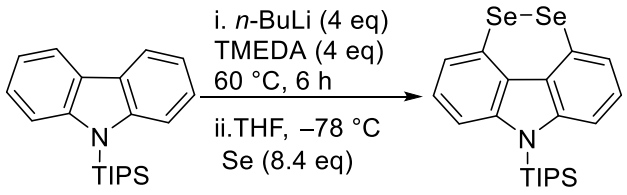
n-BuLi (2.32 M in *n*-hexanes, 1.07 mL, 2.48 mmol) was added dropwise over 10 min to a solution of compound **56** (201 mg, 0.62 mmol) in TMEDA (0.37 mL, 2.48 mmol) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C and THF (2.6 mL, 0.24 M) was added to the mixture, followed by the addition of ethylchlorooxalate (0.14 mL,1.24 mmol, 2 eq). The reaction mixture was allowed to warm to room temperature and left to stir for 16 h. The reaction mixture was poured into sat. $NH_4Cl_{(aq)}$ (10 mL) and extracted with Et_2O (20 mL × 3). The combined organic extracts were washed brine (10 mL × 2), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give an orange oil. The orange oil was purified by FCC (*n*-hexane: EtOAc, 95:5) to give (9 mg, 4%); as an orange oil.

Partial data for Compound 132:

^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H δ 7.82-7.79 (4 H, m, H-3/H-6/ H-2/H-7), 7.53-7.46 (2 H, m, H-1/ H- 8), 1.96 (3 H, hept, *J* 7.6 Hz, SiC*H*), 1.22 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101

MHz, $CDCl_3$, 77.16 ppm) δ_C 180.4 (2 × C, C=O), 144.1 (C, C-8a/C-9a), 128.6 (C, C-4a/C-4b), 128.2 (CH, C-2/C-7), 127.2 (CH, C-4/C-5), 121.2 (CH, C-1/C-8), 120.5 (CH, C-3/C-6) 18.5 (CH_3, SiCHC*H*$_3$), 13.7 (CH, Si*C*H); m/z (HRMS, TOF MS+) calculated for $C_{23}H_{28}NO_2Si$ [M]+; 378.1884, found 378.1888 (PPM error -1.1).

4.2.11 Synthesis of 9-(triisopropylsilyl)-9H-[1,2]diselenino[3,4,5,6-def]carbazole 88



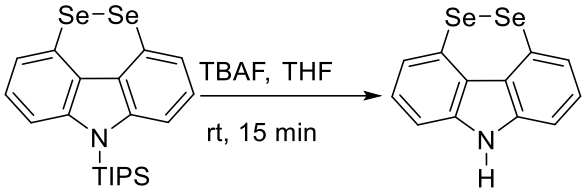
56 **88**

Known compound **88** was prepared according to a literature procedure.[89]

n-BuLi (2.38 M in *n*-hexanes, 10.5 mL, 24.93 mmol, 4 eq) was added dropwise over 10 min to a solution of compound **X** (2018 mg, 6.24 mmol, 4 eq) in TMEDA (3.73 mL, 24.94 mmol, 4 eq) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C and THF (26 mL, 0.24 M) was added to the mixture, followed by the addition of selenium (4084 mg, 51.733 mmol, 8.3 eq) as a single portion and stirred at –78 C for 1 h. The reaction mixture was allowed to warm to room temperature and left to stir for 16 h. H_2O (100 mL) was added to the reaction mixture and then the resulting mixture was extracted with CH_2Cl_2 (80 mL× 3). The combined organic layers were washed with brine (100 ml) dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by FCC (*n*-hexane 100%), diselenide **88** (1753 mg, 58%) was obtained as a dark burgundy crystalline solid. R_f 0.4 (*n*-hexane); V_{max} (solid, cm^{-1}) 2944 m, 2864 m, 16021 w, 1577 w, 1551 m, 1461 m, 1419 s,

1408 s, 1256 s, 1185 m, 989 s, 880 m, 764 s, 712.4 s; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 7.50 (2 H, dd, *J* 8.5, 0.7 Hz), 7.27 (2 H, *J* 8.5, 7.4 Hz), 7.14 (2 H, dd, *J* 7.4, 0.6 Hz), 1.95 (3H, hept, *J* 7.5 Hz), 1.19 (18 H, d, *J* 7.5 Hz); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δc 144.8, 127.3, 125.5, 119.4, 116.7, 113.9, 18.7, 13.9. Data are agreement with Grainger and co-worker.[89, 91]

4.2.12 Synthesis of 9H-[1,2]diselenino[3,4,5,6-def]carbazole 133



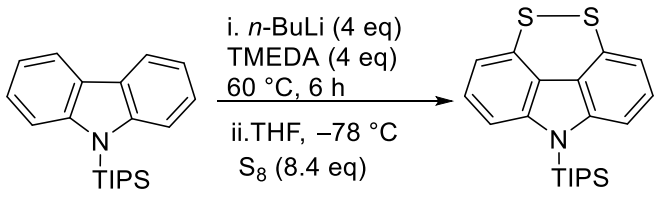
88 **133**

Known compound **133**, was prepared according to the literature procedure.[89, 96]

Tetrabutylammonium fluoride solution (1 M in THF, 11.99 mL, 11.99 mmol, 1.5 eq) was added to a solution of **88** (575 mg, 1.19 mmol) in THF (24 mL, 0.1 M). The mixture was allowed to stir for 20 min then treated with H_2O (18 mL) and extracted with Et_2O (30 mL× 2). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give **133** (274 mg, 71%) as a red crystalline solid. R_f = 0.43 (*n*-hexane: Et_2O, 4:1); V_{max}(solid, cm^{-1}) 3396 s, 3054 w, 29234 w, 1587 m, 1426 m, 1420 m, 1307 s, 1169 m, 890 m, 758 s, 711 s; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.08 (1 H, br), 7.33 (2 H, dd, *J* 8.1, 7.4 Hz), 7.24 (2 H, d, *J*, 0.7 Hz), 7.13 (2 H, dd, *J* 7.4, 0.6 Hz); ^{13}C-NMR(101 MHz, $CDCl_3$, 77.16 ppm) δ_C 138.6, 128.1 , 123.0, 118.8, 116.9, 110.2.Data are agreement with Grainger and co-worker.[89, 91]

4.2.13 Synthesis of 9-(triisopropylsilyl)-9H-[1,2]dithiino[3,4,5,6-def]carbazole (88)

4.2.13.1 Procedure on small scales (less than 3 mmol of starting materials)



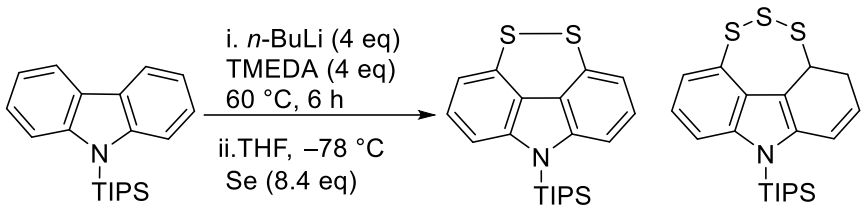
56 **86**

9-(triisopropylsilyl)-9H-[1,2]dithiino[3,4,5,6-def]carbazole **86** was synthesised from a literature procedure.[89, 90]

n-BuLi (1.9 M, 2.60 mL, 4.94 mmol, 4 eq) was added to a solution of *N*-TIPS-carbazole **56** (400 mg, 1.23 mmol) in TMEDA (0.74 mL, 4.94 mmol, 4 eq) and the reaction mixture was heated at 60 °C for 6 h. The reaction mixture was cooling to −78 °C and dilution with anhydrous THF (5 mL, 0.24 M). Sulfur (328 mg, 10.25 mmol, 8.3 eq.) was added. After 1 h at –78 °C the reaction allowed to equilibrate to room temperature for 16 h. The reaction mixture was quenched with 1 M $HCl_{(aq)}$ (20 mL) and opened to the atmosphere (air) and air was forcefully bubbled through the reaction mixture for 1 h. The reaction mixture was extracted using CH_2Cl_2 (40 mL × 3) and the combined organics were washed with brine (40 mL × 3), dried over $MgSO_4$, filtered, and concentrated under reduced pressure yielding a brown oil. The brown oil was purified by FCC (*n*-hexane 100%) to give compound **86** (614 mg, 51%) as a yellow solid. R_f= 0.46 (*n*-hexane); V_{max} (solid,cm^{-1}) 2946 m, 2865 m, 1446 m, 1425 s, 1411 s, 1253 s, 1183 m, 1004 s, 996 s, 881 m, 765 s, 754 s, 719 s, 707 s; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 7.47 (2 H, d, *J* 8.3 Hz), 7.30 (2 H, d, *J* 7.4 Hz), 7.00 (2 H, d, *J* 7.4 Hz), 1.95 (3 H, hept, *J* 7.5 Hz), 1.19 (18 H, d, *J* 7.5 Hz); ^{13} C-NMR (101 MHz, $CDCl_3$, 77.16 ppm)

δ_C 144.2 , 127.5, 124.3, 123.6, 117.0 113.8 ,18.6 , 13.9. Data are agreement with Grainger and co-workers.[89, 90]

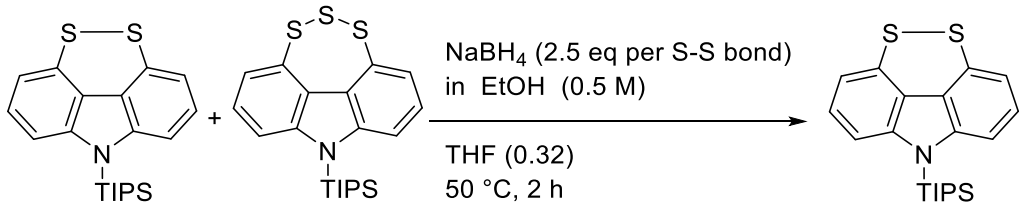
4.2.13.2 Procedure on large scales (more than 3 mmol of starting materials)



56 **86** **87**

n-BuLi (2.18 M, 6.0 mL, 13.25 mmol, 4 eq) was added to a solution of *N*-TIPS-carbazole **56** (1072 mg, 3.31 mmol) in TMEDA (1.98 mL, 13.25 mmol, 4 eq) and the reaction mixture was heated at 60 °C for 6 h. The reaction mixture was cooling to –78 °C and dilution with anhydrous THF (13. 8 mL, 0.24 M). Sulfur (881 mg, 27.49 mmol, 8.3 eq.) was added. After 1 h at –78 °C the reaction allowed to equilibrate to room temperature for 16 h. The reaction mixture was quenched with 1 M $HCl_{(aq)}$ (60 mL) and opened to the atmosphere (air) and air was forcefully bubbled through the reaction mixture for 1 h. The reaction mixture was extracted using CH_2Cl_2 (60 mL × 3) and the combined organics were washed with brine (60 mL × 3), dried over $MgSO_4$, filtered, and concentrated under reduced pressure yielding a brown oil. The brown oil was purified by FCC (*n*-hexane 100%) to give a yellow solid (602 mg) mixture of disulfide **86** and trisulfide **87** which was showed by $^{1-}$HNMR indicated it to be a 4.0:1.0 ratio of disulfide **86** to trisulfide **87**.[89, 90]

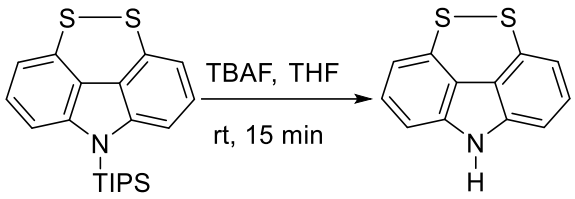
Reduction of 9-(triisopropylsilyl)-9H-[1,2]dithiino[3,4,5,6-def]carbazole 86 /4-(triisopropylsilyl)-4H-[1,2,3]trithiepino[4,5,6,7-def]carbazole 87 mixture to 9-(triisopropylsilyl)-9H-[1,2]dithiino[3,4,5,6-def]carbazole 86



86 **87** **86**

A solution of *N*-TIPS carbazole disulfide **86** and trisulfide **87**mixture (602 mg 1.39 mmol of disulfide **86** and 0.15 mmol of trisulfide **87**) in THF (4.2mL, 0.32 M) was added to a solution of $NaBH_4$ (161 mg, 4.25 mmol, 2.5 eq per S-S bond) in EtOH (8.5 mL, 0.5 M) at room temperature. Once effervescence had stopped, the reaction mixture was heated at 50 °C for 2 h. The reaction mixture was allowed to warm to room temperature. After that, the reaction mixture was quenched with 1 M $NaOH_{(aq)}$ (11 mL) and a force flow of air was bubbled through the reaction mixture for 1.5 h. The reaction mixture was extracted with Et_2O (50 mL × 3). The combined organic layers were washed with brine (50 mL ×2), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield (460 mg, 77%) a yellow solid, without any further purification. Data are agreement with Grainger and co-workers.[89, 90]

4.2.14 9H-[1,2]dithiino[3,4,5,6-def]carbazole 134

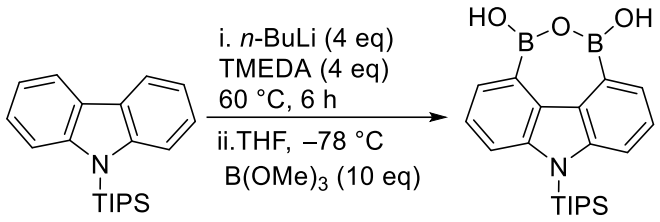


86 **134**

Known compound **134**, was prepared according to the literature procedure.[89, 96]

Tetrabutylammonium fluoride solution (1 M in THF, 2.61 mL, 2.61 mmol, 1.5 eq) was added to a solution of disulfide **86** (403 mg, 1.05 mmol) in THF (11 mL, 0.1 M). The mixture was stirred at room temperature for 15 min. After that, the reaction mixture was concentred under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL) and washed sequentially with water (20 mL × 2) and brine (20 mL × 2). The layers organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give orange solid. The orange solid was purified by FCC (*n*-hexane: EtOAc, 9:1) to give **134** (102 mg, 43%) as a yellow solid. V_{max} (solid, cm^{-1}) 3410 s, 1593 m, 1432 m, 1311 m, 1189 m, 1179 m, 765 s, 715 s; 1-H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.01 (1 H, s), 7.34 (2 H, dd, *J* 8.2, 7.4 Hz), 7.24 (2 H, dd, *J* 8.2, 0.6 Hz), 6.99 (2 H, dd, *J* 7.4, 0.6 Hz); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 138.1, 128.2, 124.6, 120.9, 116.5, 110.2. Data are agreement with Granger and co-worker.[89, 90]

4.2.15 Synthesis of 4-(triisopropylsilyl)-4H-[1,2,7]oxadiborepino[3,4,5,6-def]carbazole-8,10-diol 121



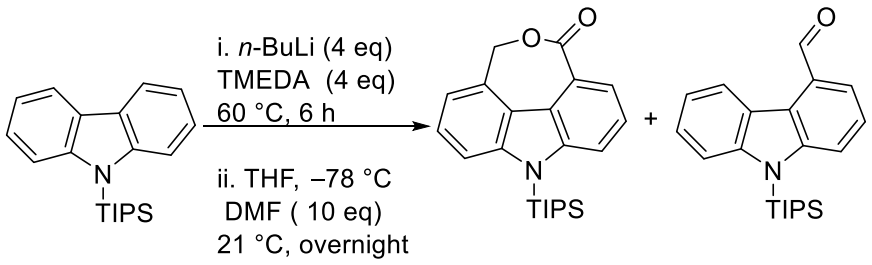
56 **121**

Compound **121** is a novel compound and was synthesised from literature procedure. [106, 107]

n-BuLi (2.0 M in hexanes, 5.0 mL, 9.93 mmol, 4 eq) was added dropwise over 10 min to a solution of compound **56** (151 mg, 4.67 mmol) in TMEDA (1.5 mL, 9.93 mmol, 4 eq) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C and THF (8 mL) was added to the mixture, followed by the addition of trimethyl borate (485.5 mg, 46.73 mmol, 10 eq) as a single portion. The reaction mixture was allowed to warm to room temperature and left to stir for 16 h. The reaction mixture was poured into 3 M $HCl_{(aq)}$ (80 mL) and allowed to stir for 3 h at room temperature. The mixture was diluted with H_2O (100 mL) and extracted with EtOAc (100 mL× 3). The combined organic extracts were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by trituration using **n**-hexane to give **121** (121 mg, 66%) as a beige solid. R_f = 0.29 (*n*-hexane: EtOAc, 7:3); mp 175 – 177 °C (*n*-hexane); V_{max} (solid, cm^{-1}) 2947 br, 2867 br, 1595 w, 1294 w, 1331 w, 1258 s, 1016 w, 957 w, 919 w, 879 s, 732 s, 638 m; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 7.93 (4 H, app d, *J* 7.8 Hz, H-2/H7- and H-3/H-6), 7.49 (2 H, app t, *J* 7.8 Hz, H-1/H-8), 4.74 (2 H, s, OH), 2.03 (3 H, hept, *J* 7.5 Hz, SiC*H*),

1.20 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCL_3$, 77.16 ppm) δ_C 145.0 (C, C-8a/C-9a), 132.2 (C, C-4a/C-5a), 127.8 (CH, C-2/C-7), 125.2 (CH, C-1/C-8), 117.4 (CH, C-3/C-6), 18.7 (CH_3 , SiCH*C*H$_3$) , 14.0 (CH, Si*C*H), missing one quaternary carbon signal; ^{11}B-NMR (128.37 MHz, $CDCl_3$) δ_B 28.5 (C-B); m/z (HRMS, TOF ES+) calculated for $C_{21}H_{30}{}^{10}B^{11}BNO_3Si$ $[M+H]^+$; 393.2217, found 393.2228 (PPM error 2.8).

4.2.16 Formylation of *N*-TIPS carbazole 56 (Table 5, entry 2)



56 **126** **127**

Novel compounds **126** and **127** were synthesised using modified literature procedure.[109]

n-BuLi (1.68 M in hexanes, 3. 7 mL, 6.2 mmol, 4 eq) was added dropwise over 10 min to a solution of compound **56** (501 mg, 1.55 mmol) in TMEDA (0.97 mL, 6.2 mmol, 4 eq) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C and THF (10 mL, 0.24 M) was added to the mixture, followed by the addition of dimethylformamide (1.2 mL, 15.50 mmol, 10 eq) as a single portion. The reaction mixture was allowed to warm to room temperature and left to stir for 16 h. The reaction mixture was poured into sat. $NH_4Cl_{(aq)}$ (10 mL) and extracting with Et_2O(15 mL × 3). The combined organic extracts were washed with brine (10 mL × 2), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give orange oil .The orang oil was purified by FCC in (*n*-hexane: Et_2O,

98:2), to give mono aldehyde **127** (55 mg, 11%)as a bright yellow, then followed in *(n*-hexane: Et_2O, 8:2), to give lactone **126** (28 mg, 5%) as beige solid .

Partial analytical data for compound 127

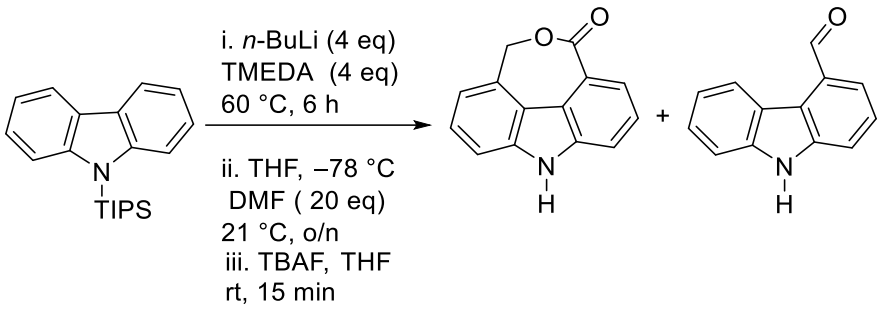
V_{max} (solid, cm^{-1}) 3330 s, 2969 w, 2857 w, 1667 s, 1621 m, 1595 s, 1580 s, 1462 m, 1446 m, 1333 m, 1235 s, 1221 m, 1197 s, 1171 s, 1124 s, 893 m, 849 m, 816 s, 750 s, 728 s, 655 m; ^{1}H-NMR (400 MHz, $CDCl_3$,7.26 ppm) δ_H 10.10 (1 H, s, CHO), 8.58 (1 H, dd, *J* 1.8, 0.6 Hz, H-5), 8.14 (1H, ddd, *J* 7.7, 1.5, 0.7 Hz, 6-H) 7.91 (1 H, dd, *J* 8.7, 1.8 Hz, H-7), 7.80- 7.70 (2 H, m, H-2 and H-8), 7.43 (2 H, ddd, *J* 8.5, 7.1, 1.4 Hz, H-1), 7.32 (1 H, ddd, *J* 7.9, 7.1, 0.8 Hz, H-3), 2.02 (3 H, hept, *J* 7.5 Hz, SiC*H*), 1.20 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 191.9 (C,C-11) 149.5 (C, C-8a), 145.9 (C, C-9a), 129.0 (C, C-4), 126.9 (C, C-5a), 126.7 (CH,C-7), 126.5 (CH, C-), 126.2 (C, C-4a), 123.0 (CH, C-2), 120.9 (CH, C-3), 120.3 (CH, C-5-), 114.7 (CH, C-6), 114, 3 (CH, C-8) 18.7 (CH_3, SiCH*C*H_3),13.9 (CH, Si*C*H); m/z (HRMS, TOF ASAP+) calculated for $C_{22}H_{30}NOSi$ [M+H]+; 352.2079 found 352. 2101 (PPM error 1.1).

Analytical data fo compound 126

R_f= 0.30 (*n*-hexane: EtOAc, 8: 2); mp 136-137 °C; V_{max} (solid, cm^{-1}) 2958 s, 1706 m, 1581s, 1265 m, 914 m, 743 s; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.17 (1H, dd, *J* 7.7, 0.5 Hz, H-3), 7.95 (1 H, dd, *J* 8.4, 0.7 Hz, H-6) 7.72 (1 H, d, *J* 8.5 Hz, H-8), 7.52 (1 H, dd, *J* 8.3 , 7.7 Hz, H- 7), 7.45 (1 H, dd, *J* 8.6, 7.2 Hz, H-1), 7.16 (1H, dd, *J* 7.2, 0.8 Hz, H- 2), 5.51 (2 H, s, C-10), 2.01 (3 H, hept, *J* 7.5 Hz, SiC*H*), 1.12 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 169.4 (C, C-11), 145.1 (C, C-8a), 144.9 (C, C-9a), 131.4 (C, C-4-), 127.4 (CH, C-7), 125.9 (CH, C- 2), 125.8 (C, C-4a), 125.5 (CH,C-3), 125.3 (C, C-5a), 123.9 (C, C-5), 118.9 (CH, C-6-), 116.7(CH, C-1), 114.5

(CH, C-8), 69.6 (CH_2-C-10), 18.6 (CH_3, SiCH*C*H_3), 13.9 (CH, Si*C*H); m/z (HRMS, TOF ES+) calculated for $C_{23}H_{30}NO_2Si$ [M]+; 380.2046, found 380.2049 (PPM error 0.8).

4.2.17 Formylation of *N*-TIPS carbazole 56 with TBAF work-up (Table 6, entry 1)



n-BuLi (2.25 M in *n*-hexanes, 2.8 mL, 6.29 mmol, 4 eq) was added dropwise over 10 min to a solution of compound **56** (509 mg, 1.57 mmol) in TMEDA (0.94 mL, 6.29 mmol, 4 eq) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C and THF (6.5 mL, 0.24 M) was added to the mixture, followed by the addition of dimethylformamide (2.43 mL, 31.46 mmol, 20 eq) as a single portion. The reaction mixture was allowed to warm to room temperature and left to stir for 16 h. The reaction mixture was poured into conc HCl (37 w/w%, 2 mL) at 0 °C and allowed to stir at this temperature for 1 h prior to diluting with H_2O (80 mL) and extracting with CH_2Cl_2 (10 mL × 3). The combined organic extracts were washed with brine (10 mL × 2), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give orange oil. The orang oil was dissolved in THF (15.4 mL, 0.1 M), treated with tetrabutylammonium fluoride solution (1.0 M in THF, 2.3 mL, 2.3 mmol, 1.5 eq), and allowed to stir for 15 min at room temperature. The solvent was removed under reduced pressure and the residue dissolved in EtOAc (10 mL). The mixture was sequentially washed with

H_2O (10 mL × 2) and brine (10 mL × 2), and the organic extracts dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a brown solid. The crude was purified by FCC in (CH_2Cl_2 100%), to give mono aldehyde**130** (54 mg, 18%) as a bright yellow, then followed in (CH_2Cl_2: EtOAc, 9:1), to give lactone **129** (33 mg, 10%) as beige solid.

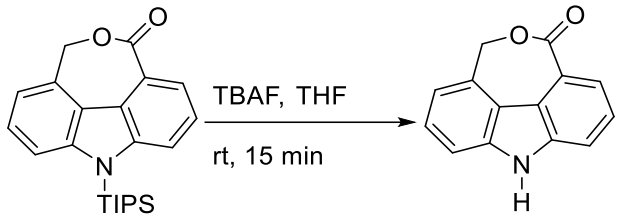
Partial analytical data for compound 130

V_{max} (solid, cm^{-1}) 3227 m, 3193 m, 2738 w, 1677 s, 1622 w, 1603 m, 1561 m, 1509 m, 1455 m, 1441 m, 1323 m, 1308 m, 1286 m, 1145 m, 1048 s, 786 s, 718 s, 693 m; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 10.51 (1 H, s, CHO), 9.09 (1 H, d, *J* 8.2 Hz,), 8.36 (1 H, s, NH), 7.80 (1 H, dd, *J* 7.4, 1.1 Hz), 7.74 (1 H, dd, *J* 8.1, 1.1 Hz), 7.59 (1 H, dd, *J* 8.1, 7.4 Hz), 7.56 – 7.47 (2 H, m), 7.33 (1 H, ddd, *J* 8.2, 6.6, 1.6 Hz); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_c 193.3 (C, C-10), 140.4 (C, C-4a), 140.2 (C, C-8a), 131.9 (C, C-4), 127.6 (CH, C-2), 127.5 (CH,C-8), 126.3 (CH, C-1), 125.1(CH, C-6), 122.4 (C, C-5a), 121.4 (C, C-9a), 120.2 (CH, C-7), 116.9 (CH, C-3), 110.7 (CH, C-5); m/z (HRMS, TOF ASAP+) calculated for $C_{13}H_9NO$[M+H]+; 196.0762, found 196.0771 (PPM error 4.6).

Analytical data for compound 129

R_f = 0.3 (*n* hexane: CH_2Cl_2, 1:2); V_{max} (solid, cm^{-1}); ^{1}H-NMR (400 MHz, DMSO-d_6, 2.50 ppm) δ_H11.73 (1 H, s, NH), 7.92 (1 H, dd, *J* 7.6, 0.8 Hz, H-6), 7.85 (1H, dd, *J* 8.0, 0.8 Hz, H-7), 7.59 (1 H, t, *J* 7.9 Hz, H-2), 7.56-7.47 (2 H, m, H-8 and H-1), 7.17 (1 H, dd, *J* 6.9, 1.0 Hz, H-3), 5.64 (2 H, s, CH_2-10); ^{13}C-NMR (101 MHz, DMSO-d_6, 39.52) δc 168.6(C, C-10), 139.6 (C, C-8a), 139.2(C, C-9a), 131.8(CH, C-5), 127.7 (CH, C-8), 125. 8 (CH, C-2), 123.6 (CH, C-6), 123.6 (C, C-4), 121.6 (C, C-5a), 121.1 (C, C-4a), 116.3 (CH, C-7), 115.2 (CH, C-3), 111.2 (CH, C1), 69.4 (CH_2, C-9); m/z (HRSM, TOF ASAP+) calculated for $C_{14}H_{10}NO_2$[M+H]+; 224.0712, found 224.0720 (PPM error 3.6)

4.2.18 Synthesis of 4,10-dihydro-8H-oxepino[3,4,5,6-def]carbazol-8-one 129

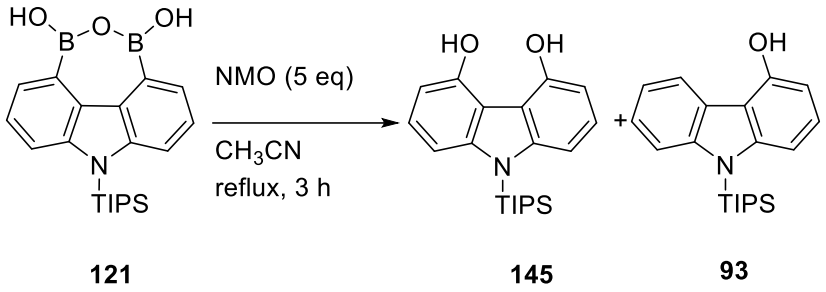


126 **129**

The novel compound **129** was synthesise following the literature procedure.[96]

Tetrabutylammonium fluoride solution (1 M in THF, 0.11mL, 0.20 mmol, 1.5 eq) was added to a solution of lactone **126** (29 mg, 0.08 mmol) in THF (0.75 mL, 0.1 M). The mixture was stirred at room temperature for 15 min. After that, the reaction mixture was concentred under reduced pressure. The residue was dissolved in EtOAc (2 mL) and washed sequentially with water (2 mL × 2) and brine (2 mL × 2). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow solid. The yellow solid was purified by FCC in (*n*- hexane: CH_2Cl_2, 1:1) to give **129** (5 mg, 29%) as yellow solid. Analytical data for **129** are provided in Section 3.1.17.

4.2.19 Synthesis of *N*-(triisopropylsilyl)-9H-carbazole-4,5-diol 145



121 **145** **93**

The novel compound **145**, [89] was synthesised from a literature procedure. [117]

N-methylmorpholine *N*-oxide (207 mg, 1.768 mmol, 5 eq) was added to a suspension of **121** (139.1 mg, 0.353 mmol) in anhydrous acetonitrile (2.7 mL, 0.13 M) and the mixture heated to reflux for 3 h. The reaction was monitored by TLC, which showed that all the starting material was consumed, using curcumin dip,[161] with heating to visualize disappearance of the boronic anhydride **121**, R_f (boronic anhydride **121**) = 0.31 (*n*-hexane: EtOAc 7:3), orange spot. The mixture was then concentrated under reduced pressure and the resulting residue purified by FCC (*n*-hexane: EtOAc, 9:1) to give **93** (15.8 mg, 13%) as a colourless oil followed by **145 (**39.1 mg, 31%) as a beige solid.

Analytical data for 145

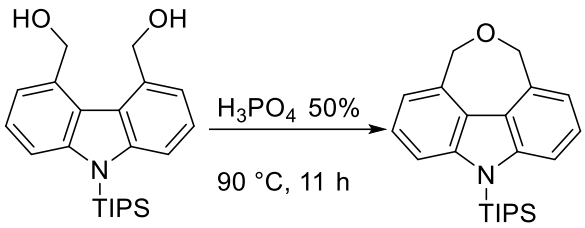
R_f = 0.30 (*n*-hexane: EtOAc, 85:15); mp 156 – 158 °C (*n*-hexane); V_{max} (solid, cm^{-1}) 3212 br, 2950 m, 2869 m, 1610 m, 1585 m, 1446 s, 1393 w, 1271 w, 1237 m, 1092 m, 1062 m, 1036 w, 900 w, 770 m, 718 s; ^{1}H-NMR ($CDCl_3$, 400 MHz, 7.26 ppm) δ_H 8.26 (2H, s, OH), 7.28 (2 H, dd, *J* 8.4, 0.5 Hz, H-1/H-8), 7.21 (2H, dd, *J* 8.4, 7.7 Hz, H-2/H-7), 6.70 (2H, dd, *J* 7.6, 0.5 Hz, H-3/H-6), 1.98 (3 H, hept, *J* 7.5 Hz, CH-1`), 1.19 (18 H, d, *J* 7.5 Hz, CH_3-2'); ^{13}C-NMR (101 MHz, $CDCl_3$) δ_C 149.2 (C, C-4/C-5), 146.8 (C, C-8a/C-9a), 126.1 (CH, C-2/C-7), 113.5 (C, C4a/C5a), 107.0 (CH, C-1/C-8), 105.9 (CH, C-

3/C-6), 18.8 (CH_3, CH_3-2'), 14.0 (CH, CH-1'); m/z (HRMS, TOF ES−) calculated for $C_{21}H_{28}NO_2Si$ $[M-H]^-$; 354.1889, found 354.1891 (PPM error 0.6).

Analytical data for 93

R_f = 0.29 (*n*-hexane: EtOAc, 9:1); V_{max} (oil, cm^{-1}) 3516 br, 2948 br, 2867 br, 1630 w, 1580 w, 1437 s, 1242 m, 1047 s, 880 m, 785 m, 754 s, 717 s, 645 m; ^{1}H-NMR (400 MHz $CDCl_3$, 7.26 ppm) δ_H 8.36 (1H, ddd, *J* 7.7 Hz, 1.5, 0.9 Hz, H-5), 7.68 (1H, d, *J* 8.4 Hz, H-8), 7.34 (2 H, ddd, *J* 8.4 Hz, 7.2, 1.5 Hz, H-7), 7.29 (1 H, d, *J* 8.4 Hz, H-1), 7.24 (1 H, ddd, *J* 7.9, 7.0, 0.9 Hz, H-6), 7.18 1 H, dd, *J* 8.4, 7.8 Hz, H-2), 6.58 (1 H, d, *J* 7.5 Hz, H-3), 5.24 (1 H, s, OH), 1.99 (3 H, hept, *J* 7.6 Hz, SiC*H*), 1.20 (18 H, d, *J* 7.6 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 7.26 ppm) δ_C 151.8 (C, C-4), 147.2 (C, C-8a), 144.6 (C, C-9a), 133.7 (C, C-4a), 125.7 (CH,C-2), 124.6 (CH, C-7), 122.8 (CH, C-5), 119.8 (CH, C-6), 114.9(C, C-5a), 113.6 (CH, C-8), 107.2 (CH, C-1), 105.4 (CH, C-3), 18.7 (CH_3, SiCH*C*H_3), 14.0 (CH, Si*C*H); m/z (HRMS, TOF MS Cl+) calculated for $C_{21}H_{29}NOSi$ $[M+H]+$; 340.2097, found 340.2103 (PPM error 1.8).

4.2.20 Synthesis of 4-(triisopropylsilyl)-8,10-dihydro-4H-oxepino[3,4,5,6-def]carbazole 146



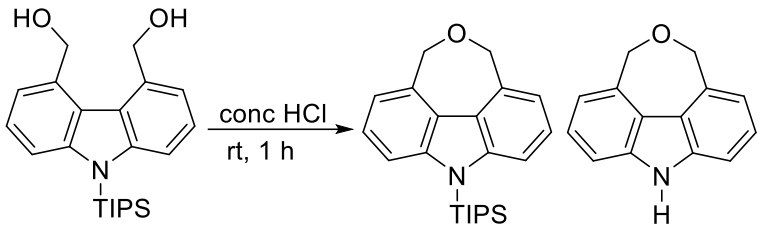
106 **146**

A novel compound **146** was synthesised using a literature procedure.[118]

Diol **106** (131.0 mg, 0.34 mmol) was suspended in 50% $H_3PO_{4(aq)}$ (2 mL) and heated at 90 °C for 11 h. The mixture was cooled to room temperature, diluted with H_2O (10 mL) and extracted by EtOAc (10 mL× 3). The combined organic extracts were washed with sat. $NaHCO_{3(aq)}$ (20 mL), and dried over Na_2SO_4, filtered and the solvent removed under reduced pressure to afford an off-white solid, which was purified by automated flash column chromatography (*n*-hexane: EtOAc, 95:5) to give **146** (69.2 mg, 56%) as an off-white crystalline solid. R_f = 0.31 (*n*-hexane: EtOAc, 95:5); mp 133 − 134 °C (*n*-hexane); V_{max} (solid, cm^{-1}) 2946 m, 2866 m, 1610 w, 1583 w, 1464 m, 1433 s, 1375 m, 1308 m, 1287 m, 1262 s, 1244 s, 1112 m, 1069 m, 1016 m, 879 s, 768 s, 729 s, 676 s, 668 s; ^{1}H-NMR (400 MHz ,$CDCl_3$, 7.26 ppm) δ_H 7.59 (2 H, dd, *J* 8.5 Hz H-2/H-7), 7.27 (2 H, dd, *J* 8.4, 7.3 Hz, H-1/H-8), 6.94 (2H, dd, *J* 7.2, 0.5 Hz, H-3/H-6), 5.31 (4 H, s, CH_2-9/CH_2-10), 2.01 (3 H, hept, *J* 7.5 Hz, Si*CH*), 1.20 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 145.2 (C, C-8a/C-9a), 136.2 (C, C4a-/C-5a), 125.1 (CH, C-1/C-8), 124.2(C, C-4/C-5), 116.1(CH, C-3/C-6), 112.9 (CH, C-2/C-7), 77.6 (CH_2, C-9/C-10), 18.7(CH_3, SiCH*C*H**3**), 14.0 (CH, Si*C*H); m/z (HRMS, TOF MS+) calculated for $C_{23}H_{32}NOSi$ $[M+H]^+$; 366.2253, found 366.2264

(PPM error 3.0). Single crystals of **146** suitable for X-ray structure analysis were obtained by slow evaporation of a methanol solution (appendix X-ray).

4.2.21 Cyclization of diol 106 using HCl (Table 10, entry 1)

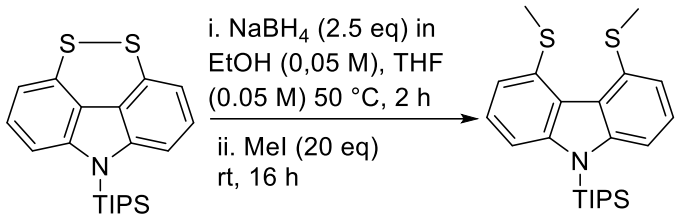


106 **146** **147**

A novel compounds **146**, and **147** were synthesised using modified literature procedure.[118]

Diol **106** (120. mg, 0.31 mol) was suspended in 0.7 M $HCl_{(aq)}$ (0.5 mL) and stirred at room temperature for 1 h. The mixture was diluted with H_2O (2 mL) and extracted by Et_2O (5 mL× 3). The combined organic extracts were washed with sat. $NaHCO_{3(aq)}$ (20 mL), and dried over Na_2SO_4, filtered and the solvent removed under reduced pressure to afford a colour less oil, which was purified by FCC (*n*-hexane: EtOAc, 95:5) to give first **146** (2 mg, 2%) then **147** (11.4 mg, 17%) as white solid. R_f = 0.31 (*n*-hexane: EtOAc, 80:20); V_{max} (solid, cm^{-1}) 2944 m, 2865 m, 1610 w, 1583 w, 1434 s, 1376 s, 1262 s, 1243 s, 1111 s, 1021s, 923 s, 877 s, 768 s, 721 s, 677 s; ^{1}H-NMR (400 MHz ,$CDCl_3$, 7.26 ppm) δ_H 8.12 (1H, s, NH), 7.37-7.28 (4 H, m, H-2/H-7 and H-1/H-8), 7.01-6.92 (2 H, m, H-3/H-6), 5.33 (4 H, s, CH_2-10/CH_2-11), ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 139.4 (C, C-8a/C-9a), 136.8 (C, C4a-/C-5a), 125.9 (CH, C-1/C-8), 121.4 (C, C-4/C-5), 115.7 (CH, C-3/C-6), 109.3 (CH, C-2/C-7), 77.4 (CH_2, C-10/C-11); m/z (HRMS, TOF MS Cl^+) calculated for $C_{14}H_{15}N_2O$ $[M+NH_4]^+$; 227.1184, found 227.1195 (PPM error 4.8).

4.2.22 Synthesis of 4,5-bis(methylthio)-9-(triisopropylsilyl)-9H-carbazole 158



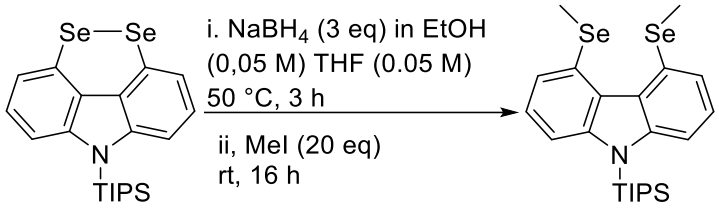
86 **158**

The novel compound **158** was synthesised from a modified literature procedure.[121]

To a solution of $NaBH_4$ (220 mg, 0.54 mmol, 2.5 eq) in EtOH (4 ml, 0.05 M), a solution of disulfide TIPS carbazole **86** (83.50 mg, 0. 25 mmol) in THF (4 ml, 0.05 m) was added at room temperature. The reaction mixture was heated at 50 °C for 2 h. After the reaction mixture cooled down to room temperature, methyl iodide (0.27 ml, 4.23 mmol, 20 eq) was added slowly over 5 min, the reaction mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure. The residues were quenched by H_2O (4 mL) and extracted with EtOAc (10 mL x 3). The organic layers were washed with brine (20 ml), dried over Na_2SO_4, filtered and the solvent was evaporated. The residue was purified by FCC (*n*-hexane: CH_2Cl_2, 7:3) to give *N*-TIPS carbazole 4,5-bismethyl sulfide **158** (39.8 mg, 44%) as beige crystal. R_f = 0.31 (*n*-hexane/CH_2Cl_2, 7:3) ; mp 92-93°C; V_{max} (solid, cm^{-1}) 2947 s, 2918 s, 2867 s, 1593 w, 1564 m, 1461m, 1410 s, 1268 s, 1167 w, 996 s, 940 w, 880 m, 770s, 717 m,677 m; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 7.54 (2 H, dd, *J* 8.2, 1.0 Hz, H-2/H-7), 7.33 (2 H, dd, 8.2, 7.6 Hz, H-1/H-8), 7.27 (2 H, dd, *J* 7.6, 0.9 Hz, H-3/H-6), 2.51 (6 H, s, CH_3-10/CH_3-11), 1.98 (3 H, hept, *J* 7.5 Hz, SiC*H*), 1.17 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCL_3$, 77.16 ppm) δ_C 146.1 (C, C-8a/C- 9a), 132.8 (C, C-4-/C-5), 125.5 (C, C-4a/ C-5a), 125.4 (CH, C-2/C-7), 121.7 (CH, C-1/C- 8), 111.3 (CH, C-3/C- 6), 21.2

(CH_3, CH_3-10/CH_3-11), 18.8 (CH_3, SiCH*C*H_3), 14.1 (CH, Si*C*H); m/z (HRMS, TOF ASPS+) calculated for $C_{23}H_{33}NS_2$ Si $[M+H]^+$, 416.1902, found 416.1897 (PPM error -1.2).

4.2.23 Synthesis of 4,5-bis(methylselanyl)-9-(triisopropylsilyl)-9H-carbazole 160



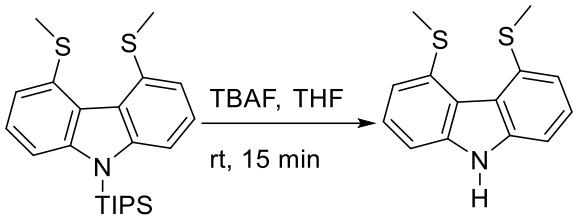
88 **160**

The novel compound **160** was synthesised from a modified literature procedure. [121]

To a solution of $NaBH_4$ (100 mg, 2.53 mmol, 3 eq) in EtOH (17 ml, 0.05M) a solution of *N*-TIPS carbazole diselenide **88** (406 mg, 0.85 mmol) in THF (17 ml, 0.05 M) was added at room temperature. The reaction mixture was heated at 50 ^{o} C for 3 h. After the reaction mixture cooled down to room temperature, methyl iodide (1.05 ml, 16.9 mmol, 20 eq) was added slowly over 5 min, the reaction mixture was stirred at room temperature for 16 h. The solvents were removed under reduced pressure. The residues were quenched by H_2O and extracted with EtOAc (20 mL x 3). The organic layers were washed with brine (20 ml), dried over $MgSO_4$, filtered, and the solvent was evaporated. The residue was purified by FCC using (*n*-hexane: Et_2O, 98:2) to give *N*-TIPS carbazole 4,5-bismethyl selenide **160** (174 mg, 40%) as white solid. R_f = 0.35 (*n*-hexane: Et_2O, 98: 2); mp 71– 72 °C ; V_{max} (solid, cm^{-1}) 2947 m, 2923 m, 2867 m, 1594 w, 1569 w, 1463 m, 1410 s, 1264 s, 979 s, 882 m, 770 s, 723 w, 672 w ; ^{1}H-NMR (400 MHz, $CDCl_3$,7.26 ppm) δ_H δ 7.62 (2H, dd, *J* 8.4, 0.9 Hz, H-3/H-6), 7.49 (2H, dd, *J* 7.5 , 0.9 Hz,H-2/H-7), 7.31 (2H, dd, *J* 8.4 ,7.6 Hz, H-1/H-8), 2.24 (6 H, s, CH_3-10/CH_3-11), 1.99 (3H, hept, *J* 7.5 Hz, SiC*H*),

1.18 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 145.8 (C, C-8a/C-9a), 128.3 (C, C-4/C-5), 125. 9 (CH, CH-2/CH-7), 125.8 (CH, CH-3/CH-6), 125. 5 (C, C4a/C-5a), 112.3 (CH, CH-1/CH-8), 18.8 (CH_3, SiCH*C*H$_3$), 14.3 (CH, Si*C*HC), 14.0 (CH_3, C-10/C-11); m/z (HRMS, TOF ASAP+) calculated for $C_{23}H_{34}N$ $^{76}Se^{78}$ Se Si [M+H]+; 506.0826, found 506.0815 (PPM error -2.2).

4.2.24 Synthesis of 4,5-bis(methylthio)-9H-carbazole 159



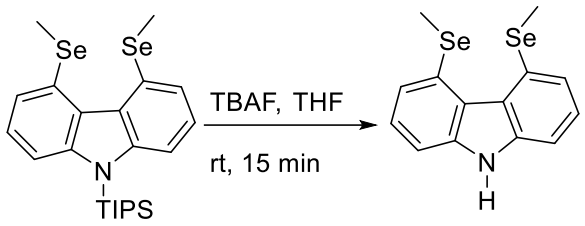
158 **159**

The novel compound **159** was synthesised from a literature procedure.[96]

To a solution of *N*-TIPS carbazole 4,5-bis methyl sulfide **158** (74 mg, 0.18 mmol) in THF (0.74mL, 0.1 M) was added TBAF (1.0 M solution in THF; 0.27 mL,0.267 mmol, 1.5 eq). The mixture was stirred at room temperature for 15 min. The solvent was removed under reduced pressure. The residues were diluted with EtOAc (3 mL) and washed with H_2O (3 mL × 2) then with brine (3 mL × 2). The combined organic layers were dried under over $MgSO_4$, filtered, and concentrated under reduced pressure. A residue was purified by FCC (*n*-hexane: Et_2O, 7:3) as an eluent to give carbazole 4,5-bismethyl sulfide **159** (38 mg, 83%) as light brown solid. R_f = 0.31 (*n*-hexane: Et_2O, 7:3); mp 103-104 °C; V_{max} (solid, cm^{-1}) 3396 s, 3055 w, 2978 w, 2914 w, 1594 m, 1557s, 1434 m, 1415 s, 1306 s, 1155 s, 1141 m, 987 w, 770 s, 943 w, 769 s, 719 s; $_1$H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.23 (1 H, s, NH), 7.38 (2 H, dd, *J* 8.1, 7.5 Hz, H-1/H-8), 7.22 (4 H, d, *J* 7.6 Hz, , H-2/H-7andH-3/H-6), 2.56 (6 H, s, C-10/C-11); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_H 140.2 (C, C-

4a/C-5a), 133.4 (C, C-4/C-5), 126.3(CH, C-1/C-8), 122.5(C, C-8a/C-9a), 120.5 (CH, C-3/C-6), 108.0 (CH,C-2/C-7), 20.3(CH_3, C-10/C-11); m/z (HRMS, TOF ASAP+) calculated for $C_{14}H_{13}NS_2$ $[M+H]^+$; 260.0568, found 260.0579 (PPM error 4.2). Single crystals of **159** suitable for X-ray structure analysis were obtained by slow evaporation of a methanol solution (appendix X-ray).

4.2.25 Synthesis of 4,5-bis(methylselanyl)-9H-carbazole 161



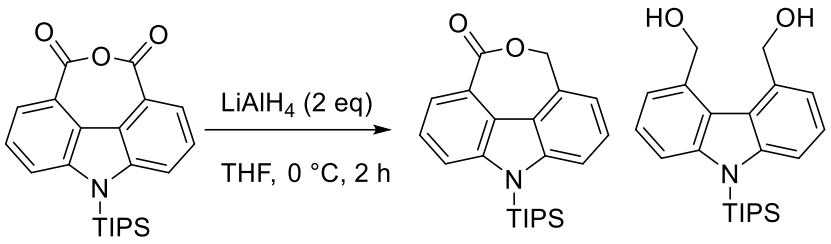
160 **161**

The novel compound **161** was synthesised from literature procedure.[96]

To a solution of crude of *N*-TIPS carbazole 4,5 bismethyl selenide **161** (492 mg, 1.03 mmol) in THF (10.3 mL, 1M) was added TBAF (1.0 M solution in THF, 1.54 mL, 1.54 mmol, 1.5 eq). The mixture was stirred at room temperature for 15 min. The solvent was removed under reduced pressure. The residues were diluted with EtOAc (20 mL) and washed with H_2O (20 mL × 2) first then brine (20 mL × 2). The combined organic layers were dried under over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by FCC with (*n*-hexane: CH_2Cl_2, 1:1) as an eluent to give 4,5 -bismethyl selenide carbazole **161** (170 mg, 48%) as node solid. R_f = 0.3 (*n*-hexane :CH_2CL_2, 1:1); mp 113–114 °C; V_{max} (solid, cm^{-1}) 3391 s, 3048 w, 2925 w, 1594 s, 1552 m, 1481 m, 1464 m, 1414 s, 1363 m, 1310 s, 1266 m, 1194 w, 1155 s, 988 m, 910 m, 788m, 777 s, 722 s; ^{1}H-NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ_H 8.17 (1H, s, NH), 7.44 (2 H, dd, *J* 7.5, 1.1 Hz, H-1/H-8), 7.35 (2H, app t, *J* 7.7 Hz, H-3/H-6), 7.27 (2 H, dd, *J* 7.9, 1.1 Hz, H-2/H-

7), 2.31 (6 H, s, CH_3-10/CH_3-11); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.16 ppm) δ_C 139.9 (C, C-8a/C-9a), 126.7 (CH,C-3/C-6), 126.2 (C,C-4/C-5), 125.1(C, C-4a/C-5a), 125.0 (CH,C-1/C-8), 108.9 (CH,C-2/C-7), 13.6 (CH_3, C-10/C-11); m/z (HRMS, TOF ASAP+) calculated for $C_{14}H_{14}N$ ^{78}Se ^{80} Se[M+H]$^+$; 353.9465, found 353.9442 (PPM error –6.5). Single crystals of **161** suitable for X-ray structure analysis were obtained by slow evaporation of a methanol solution (appendix X-ray).

4.2.26 Synthesis of lactone 126 *via* reduction of anhydride carbazole 100 by $LiAlH_4$

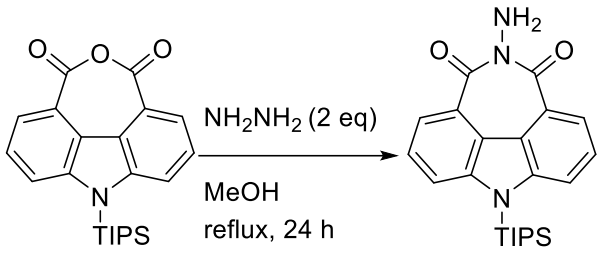


100 **126** **106**

Reduction of *N*-TIPS carbazole anhydride **100** to synthesis lactone **126** using a literature procedure.[112]

$LiAlH_4$ (371 mg, 0.98 mmol, 3 eq), in dry THF (1.5 mL, 0.65 M) was cooled to about 0°C with an ice bath and mounted over a magnetic stirrer. The solution of *N*-TIPS carbazole anhydride **100** (128 mg, 0.35 mmol) in THF (2.5 mL, 0.13 M) was added into the flask slowly over 5 min. After 2 h, the reaction mixture was quenched by addition of ice water (5 mL) to destroy excess $LiAlH_4$. 1 M $HCl_{(aq)}$ (2 mL) was added, and the reaction extracted with EtOAc (20 mL × 3) followed by washing with brine (20 mL). After drying over MgSO4, the solvent was evaporated and the crude mixture purified by FCC (n-hexane: EtOAc, 9:1) to give 4-(triisopropylsilyl)-4,10-dihydro-8H-oxepino[3,4,5,6-def]carbazol-8-one **126** (15.5 mg, 13%) as a white solid, then (9-(triisopropylsilyl)-9H-carbazole-4,5-diyl)dimethanol **106** (9 mg, 7%) as a beige solid. Analytical data are provided in Section **3.1.2** and **3.1.16**.

4.2.27 Synthesise of 9-amino-4-(triisopropylsilyl)azepino[3,4,5,6-def]carbazole-8,10(4H,9H)-dione 163

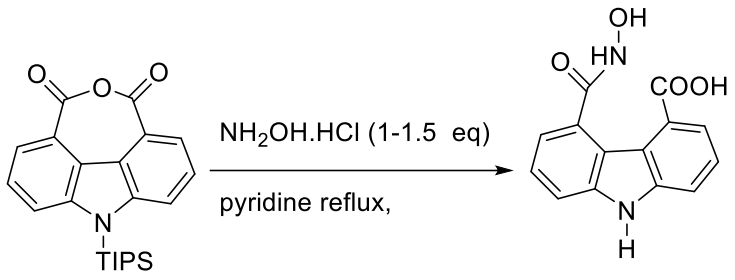


100 **163**

9-amino-4-(triisopropylsilyl)azepino[3,4,5,6-def]carbazole-8,10(4H,9H)-dione **163**, [4] is a novel compound and synthesised using a literature procedure.[89, 127]

Hydrazine monohydrate (0.02 mL, 0.41 mmol) was added to a solution of **163** (115.2 mg, 0.29 mmol) in MeOH (9 mL) and the mixture heated at reflux for 24 h. The mixture was allowed to cool and the resulting precipitate was filtered, washed with MeOH and dried under reduced pressure to give **163** (36 mg, 30%) as a white powder which required no further purification. R_f = 0.31 (CH_2Cl_2: EtOAc, 2:8); mp 169 − 170 °C (MeOH); V_{max} (solid, cm^{-1}) 3624 w br, 3356 w, 3269 w, 2949 m, 2866 m, 1695 m, 1574 m, 1464 w, 1421 w, 1381 w, 1263 s, 1031 s, 990 m, 878 m, 842 m, 807 s, 756 s; ^{1}H-NMR (500 MHz DMSO-d_6, 2.50 ppm) δ_H 7.80 (2 H, d, *J* 8.0 Hz, H-3/H-6), 7.48 (2 H, d, *J* 6.8 Hz, H-1/H-8), 7.37 (2 H, app t, *J* 7.3 Hz, H-2/H-7), 9 − 6.5 (2H, br, NH_2), 2.05 (3 H, hept, *J* 6.9 Hz, SiC*H*), 1.16 (18 H, d, *J* 6.7 Hz, SiCHC*H*$_3$); ^{13}C-NMR (126 MHz, DMSO-d_6, 39.52 pm) δ_C 172.4 (C, C=O), 145.4 (C, C-8a/C-9a), 134.1 (C, C-4a/C-5a), 124.4 (CH, C-2/C-7), 122.7 (C, C-4/C-5), 120.1 (CH, C-1/C-8), 115.0(CH, C-3/C-6), 18.4 (CH_3, SiCH*C*H_3), 13.2 (CH, Si*C*H); m/z (HRMS, TOF ASAP+) calculated for $C_{23}H_{30}N_3O_2Si$ $[M+H]^+$;408.2107, found 408.2097 (PPM error – 2.4).

4.2.28 Synthesise of 5-(hydroxycarbamoyl)-9H-carbazole-4-carboxylic acid 168

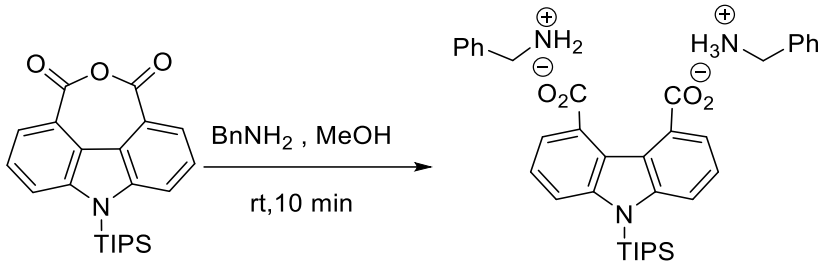


100 **168**

The **168** is a novel compound and synthesised using a literature procedure.[135]

The hydroxylamine hydrochloride (27 mg, 0.389 mmol, 1.09 eq) is dissolved in (4 ml, 0.1 M) of pyridine. (140 mg, 0.356 mmol) of anhydride **100** is added to the solution. The reaction was carried out in a sealed glass tube and heated at 150 °C for 6 h. The precipitated residue is filtered off and washed with 1M HCl and also with water to give (13.5 mg, 14%) as a brown solid. ^{1}H-NMR (300 MHz, DMSO-d_6, 2.50 ppm) δ_H 12.16 (1 H,s, COO*H*), 12.10 (1H, s, N*H*-OH), 11.12 (1H, s, NH-OH), 10.54 (1 H, s, CzN*H*), 8.22 – 7.89 (4 H, m,), 7.86 – 7.69 (2 H, m,); 13C NMR (101 MHz, DMSO-d_6, 39.52 pmm) δ_C 164.89, 162.92, 140.07, 139.87, 127.55, 127.22, 123.91, 122.10, 122.01, 121.65, 118.99, 118.10, 116.23, 115.99.

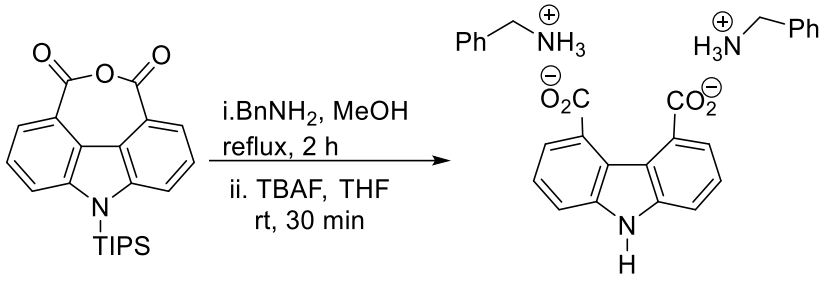
4.2.29 Synthesis of N-TIPS-carbazole-4,5-dicarboxylate benzylammonium 171



100 **171**

N-TIPS carbazole anhydride **100** (102 mg, 0.259 mmol) was dissolved in anhydrous MeOH (8 mL, 0.032 M) and treated with benzylamine (0.056 mL, 0.518 mmol, 2 eq) at room temperature. The reaction mixture was stirred at room temperature for 5-10 min and the solvent was removed under reduced pressure. The resulting yellow oil was purified by FCC (CH_2Cl_2: MeOH, 9:1) to give *N*-TIPS-carbazole-4,5-dicarboxylate benzylammonium **171** (92.3 mg, 57%) as an off-white crystalline solid. R_f = 0.29 (CH_2Cl_2: MeOH, 95: 5); mp: 154– 155 °C; V_{max} (solid, cm^{-1}) 2944 br, 2866 s, 1586 m, 1545 s, 1457 m, 1393 s, 1257 m, 1036 s, 880 w, 757 m, 795 m, 694 s; ^{1}H-NMR (400 MHz, CD_3OD, 3.31 ppm) δ_H 7.82 (2 H, dd, *J* 8.5, 1.0 Hz, H-1/H-8), 7.52 (2 H, d, *J* 6.9 Hz, H-3/H-6), 7.37 (2 H, d, *J* 8.5 Hz, H-2/H-7), 7.34-7.31 (10 H, m, Ph-H), 3.88 (4 H, s, C*H*$_2$-Ph), 2.01 (3 H, hept, *J* 7.5 Hz, SiC*H*), 1.19 (18 H, d, *J* 7.5 Hz, SiCHC*H*$_3$); ^{13}C-NMR (101 MHz, CD_3OD, 49.0 ppm) δ_C 178.0 (C, C=O), 147.4 (C, C-4/C-5), 137.6 (C, C-4a/C-5a), 135.9 (C, C-Ph), 129.9 (CH, C-Ph-), 129.8 (CH, C-Ph), 129.5 (CH, C-Ph), 125.4 (CH, C-2/C-7), 124.1(C, C-8a/C-9a), 121.5 (CH, C-3/C-6), 116.0 (CH, C-1/C-8), 44,1 (CH_2, C-12), 19.1 (CH_3, SiCH*C*H$_3$), 15.1(CH, Si*C*H); *m/z* (HRMS, TOF ES+) calculated for $C_{23}H_{29}NO_4Si$ (M+Na-cation)$^-$ 434.1764, found 434.1761. (PPM error-0.7).

4.2.30 Synthesis of 9H-carbazole-4,5-dicarboxylate benzylammonium 172

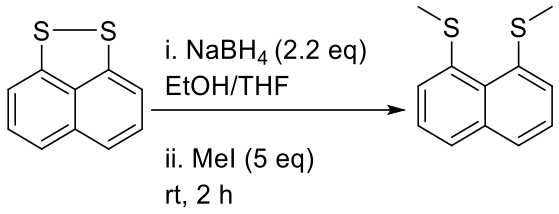


100 **172**

N-TIPS carbazole anhydride **100** (153 mg, 0.39 mmol) was dissolved in anhydrous MeOH (12 mL, 0.03 M), benzylamine (0.08 mL, 0.78 mmol, 2 eq) was added. The reaction mixture was heated at reflux for 2 h. The reaction was followed by crude ^{1}H-NMR. The solvent was removed under reduced pressure. The yellow oil was dissolved in THF (4 mL, 01 M) at room temperature and treated with tetrabutylammonium fluoride solution (1 M in THF, 0.58 mL, 0.58 mmol, 1.5 eq) and allowed to stir at room temperature for 15 min. The solvent was removed under reduced pressure and the residue dissolved in EtOAc (10 mL) which was sequentially washed with H_2O (6 mL × 2) and then brine (6 mL × 2). The organic extracts layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting brown oil was purified by FCC (CH_2Cl_2: MeOH, 9:1) to give 9H-carbazole-4,5-dicarboxylate benzylammonium **172** (123 mg, 68%) as beige crystalline solid . R_f =0.29 (CH_2Cl_2: MeOH, 9:1); mp: 182 – 183°C; V_{max} (solid, cm^{-1}) 3030 w, 2618 w, 1538 s, 1455 w, 1393 s, 1317s, 1257 m, 1180 s, , 810 w, 764 s, 749 s, 739 s, 692 s; ^{1}H-NMR (400 MHz, CD_3OD, 3.31ppm) δ_H 7.51-7.41 (4 H, m, H-1/H-8 and H-2/H-7), 7.36 (2 H, d, *J* 7.7 Hz, H-3/H-6), 7.34-7.28 (10 H, m, *H*-Ph), 3.88 (4 H, s, C*H*$_2$-Ph); ^{13}C-NMR (101 MHz, CD_3OD, 49.0 ppm) δ_C 178.6 (C, C=O), 142.5 (C, C-4/C-5), 137.6 (C, C-4a/C-5a), 135.9 (C, *C*-Ph), 129.9 (CH, *C*H-Ph), 129.7(CH, *C*H-Ph), 129.5 (CH, *C*H-Ph), 125.9 (CH, C-2/C-7), 120.5 (C, C-8a/C-9a), 120.2 (CH,

C-3/C-6), 112.8 (CH, C-1/C-8), 44,1 (CH_2, *C*H_2-Ph); *m/z* (HRMS, TOF ES+) calculated for $C_{21}H_{19}N_2O_4$ $(M\text{-cation})^+$ 363.1336, found 363.1339 (PPM error-1.7). Single crystals of **172** suitable for X-ray structure analysis were obtained by slow evaporation of a methanol solution (appendix X-ray).

4.2.31 1,8-bis(methylthio)naphthalene 157



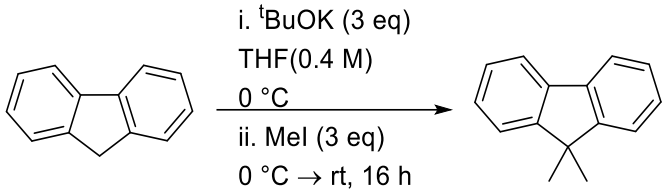
75 **157**

The disulfide naphthalene **75**, was prepare by past a member of Grainger group.[90, 123, 164] 1,8-bis(methylthio)naphthalene **157**, [122, 125] was synthesised by following the literature procudure.[121]

To a solution of $NaBH_4$ (50 mg, 1.27 mmol, 2.2 eq) in EtOH (12 ml, 0.05 M) a solution of disulfide naphthalene **75** (83 mg, 0. 25 mmol) in THF (4 ml, 0.005 M) was added at room temperature. The reaction mixture was stirred for 15 min. The methyl iodide (0.18 ml, 2.90 mmol, 5 eq) was added slowly over 5 min, the reaction mixture was stirred at room temperature for 2 h. The reaction is followed by TLC, after completed the solvent was removed under reduced pressure. The residues were quenched by H_2O (10 mL) and extracted with EtOAc (20 ml x 3). The organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and the solvent was evaporated. The residue was purified by FCC (*n*-hexane: CH_2Cl_2, 70:30) to give bismethyl sulfide naphthalene **157** (31 mg, 24%) as an off-white solid. R_f = 0.31 (*n*-hexane); V_{max} (solid, cm^{-1}) 2915 w, 1725 w, 1549 m, 1421 m, 1201 m, 974 m, 877 m, 811 s, 760 s; ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26

ppm) δ_H 7.65 (2 H, dd, *J* 8.2, 1.3 Hz), 7.50 (2 H, dd, *J* 7.4, 1.3 Hz), 7.38 (2 H, dd, *J* 8.1, 7.4 Hz), 2.55 (3 H, s); ^{13}C-NMR (101 MHz, $CDCl_3$, 77.61 ppm) δc 136.9, 135.9, 132.4, 128.1, 127.6, 125.7, 20.8; m/z (HRMS, TOF ASAP+) calculated for $C_{12}H_{13}S_2$ [M+H]+; 221.0459, found 221.0463 (PPM error −0.9). The IR and ^{1}H-NMR data matched that by Glass and co-worker,[15] and ^{12313}C-NMR data matches the Grainger group unpublished work.

4.2.32 Synthesis of 9,9-dimethyl-9H-fluorene 176



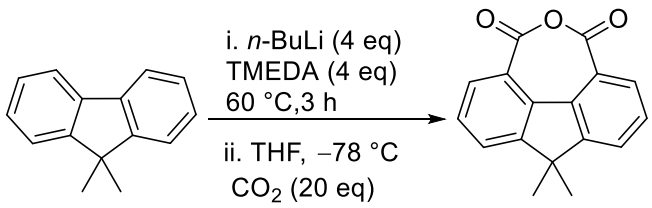
175 **176**

The 9,9-dimethyl-9H-fluorene **176** was synthesised using an improved literature procedure.[137]

Fluorene **175** (3000 mg, 18.09 mmol) was dissolved in THF (44.0 mL, 0.41 M) and cooled to 0 °C. ^{t}BuOK (6080 mg, 254.25 mmol, 3 eq.) was added portion-wise over 8 min. Once all ^{t}BuOK had been added, the reaction stirred for a further 5 min at 0 °C. The reaction mixture allowed to equilibrate to room temperature for 1 h. The mixture which is orange solution was then cooled to 0 °C, MeI (7700 mg, 3.37 mL, 54.25 mmol, 3 eq.) was added and the reaction mixture turned turquoise, and a significant amount of KI precipitated out. The reaction mixture was stirred for a further 15 min at 0 °C the reaction mixture allowed to equilibrate to room temperature for 16 h. The reaction mixture was filtered through a silica pad and the filtrate was concentrated under reduced pressure yielding an orange oil. The orange oil was dry-loaded onto silica and purified by FCC (*n*-hexane 100%) giving compound **176** (281 mg, 80%) as white crystal. R_f =0.36 (*n*-hexane

100%); ^{1}H-NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ_H 7.77 – 7.70 (2 H, m), 7.48 – 7.42 (2 H, m), 7.37 – 7.30 (4 H, m), 1.50 (6 H, s); m/z (LRMS, TOF ASAP+) 195.1149 (22%), 194.1095 ([M + H]+, 100%). The data matches that by Skabara and co-workers.[137]

4.2.33 Synthesis of 4,4-dimethyl-4H-fluoreno[4,5-cde]oxepine-8,10-dione 177

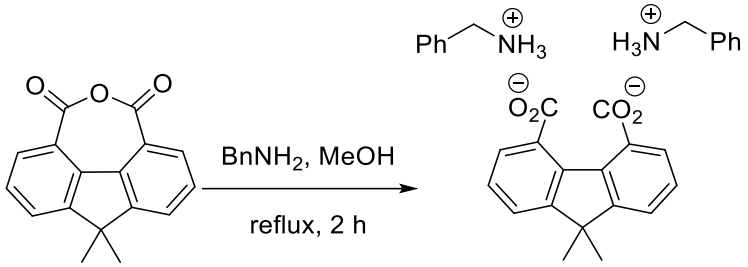


176 **177**

n-BuLi (2.96 ml, 7.42 mmol, 4 eq) was added dropwise over 10 min to a solution of 9,9-dimethyl-9H-fluorene **177** (360 mg, 1.85 mmol) in TMEDA (1.11 mL, 7.4202 mmol, 4 eq) at room temperature. The reaction mixture was then heated at 60 °C for 6 h. The reaction mixture was cooled to –78 °C and THF (8 mL 0.24 M) was added to the mixture, followed by the addition of carbon dioxide (dry ice, in excess 20 eq) as a single portion allowing venting of the excess CO_2 gas using multiple needles in the rubber septum of the reaction flask. The reaction mixture was allowed to warm to room temperature and left to stir for 16 h. After addition of Conc. HCl (37 w/w%, 8 mL) at 0 °C, the reaction mixture was allowed to stir at this temperature for 1 h prior to diluting with H_2O (80 mL) and extracting with CH_2Cl_2 (20 mL × 3). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a brown solid. The brown solid was purified by trituration with *n*-hexane to give fluorene anhydride **177** (350 mg, 41%) as a beige solid. R_f = 0.29 (CH_2Cl_2: MeOH, 9:1); mp 215 – 216 °C (*n*-hexane); V_{max} (solid, cm^{-1}) 2954 s, 2869 br, 2675 w, 2572 w, 1697 s, 1592 w, 1417 m, 1306 s, 1182 m, 1154 w, 912 w, 819 w, 755 s, 731 s, 722 w; ^{1}H-NMR (400 MHz, DMSO-d_6, 2.50

ppm) δ_H 7.74 (2H, dd, *J* 7.5, 1.2 Hz,H-1/H-8), 7.65 (2 H, dd, *J* 7.6, 1.2 Hz,H-3/H-6), 7.42 (2 H, t, *J* 7.6 Hz, H-2/H-7), 1.45 (6 H, s, CH_3- 10/ 11); ^{13}C-NMR (101 MHz, DMSO-d_6, 39.52 ppm) δc 169.1 (C, C=O), 155.2 (C, C-9a/C-8a), 136.3 (C, C-4/C-5), 130.5 (CH, C-3/ C-6), 127.9 (C, C-4a/C-5a), 127.4 (CH, C-2/C-7), 125.2 (CH, C-1/C-8), 45.9 (C, C-9), 26.8 (CH_3, C-10/C-11).; m/z (HRMS, TOF ASAP+) calculated for $C_{17}H_{12}O_3$ [M+H]+ ; 265.0865, found 265.0867 (PPM error 4.1).

4.2.34 Synthesise of 9,9-dimethyl-9H-fluorene-4,5-dicarboxylatedibezylammonium 183



177 **183**

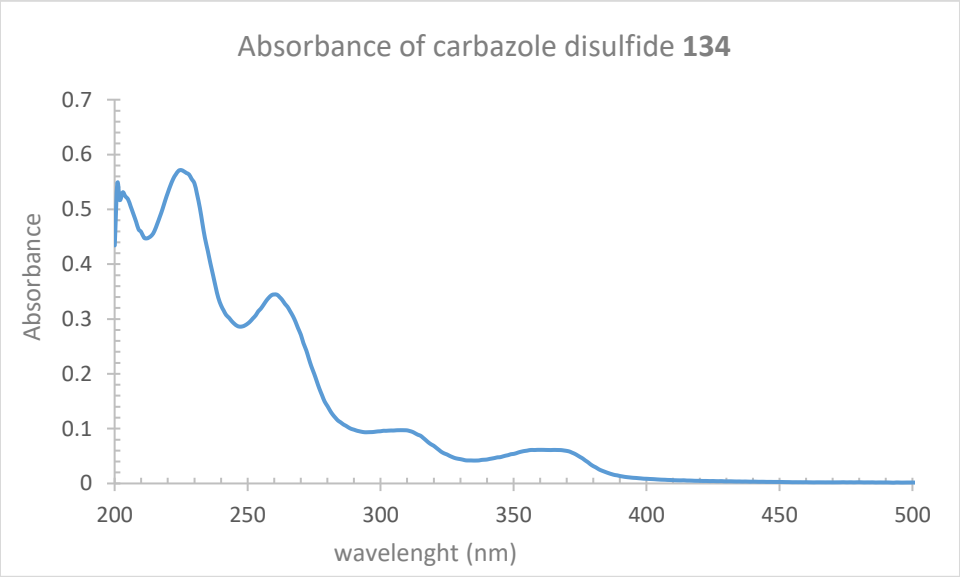
9,9-Dimethyl-9H-fluorene anhydride **177** (19 mg, 0.07 mmol) was dissolved in anhydrous MeOH (2 mL), and treated with benzylamine (0.06 mL, 0.14 mmol) at room temperature. The reaction mixture was heated at reflux for 2 h. The solvent was removed under reduced pressure to give a yellow oil. The resulting yellow oil was purified by FCC (CH_2Cl_2 : MeOH, 9:1) to give product **183** as a beige crystal (22.9 mg, 69%). R_f = 0.29 (CH_2Cl_2: MeOH, 9:1); mp 115– 116 °C ; V_{max} (solid, cm^{-1}) 2958 w, 2637 w, 1596 m, 1545s, 1456 m ,1390 s, 1294 w, 768 m, 736 m, 697 m; ^{1}H-NMR (400 MHz, CD_3OD, 3.31 ppm) δ_H 7.61 (2 H, d, *J* 6.5 Hz, H-3/H-6), 7.48 (2 H, dd, *J* 7.5, 1.2 Hz, H-4/H-5), 7.45 – 7.33 (10 H, m, H-Ph), 7.29 (2 H, t, *J* 7.5 Hz, H-1/H-8), 4.03 (4 H, s, CH_2-Ph), 1.47 (6 H, s, CH_3-C-10/C-11); ^{13}C-NMR (101 MHz, CD_3OD, 49.0 ppm) δ_C 177.7 (C, C=O), 156.3 (C, C-9a/C-8a), 138.9

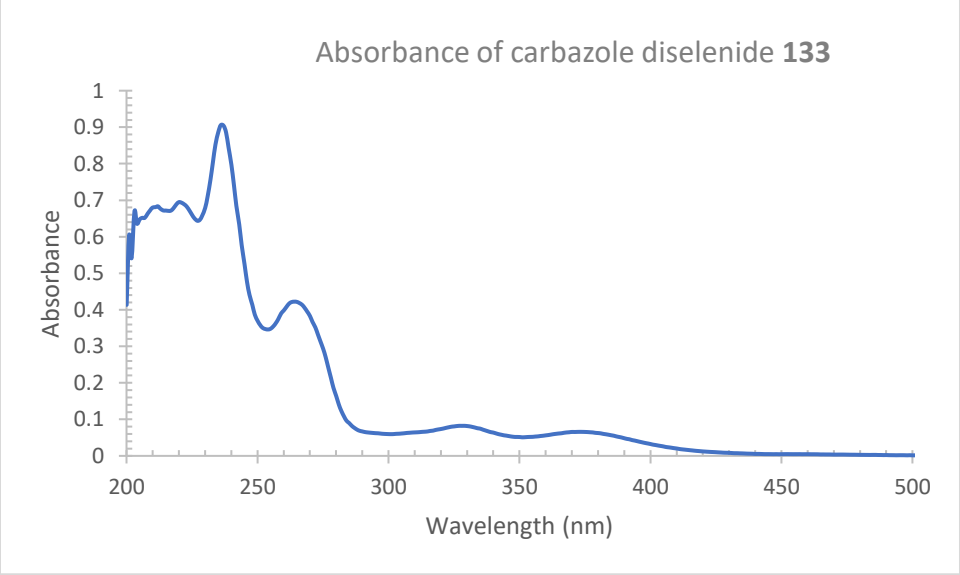
(C, C-4a/C-5a), 137.8 (C, C-4/C5), 136.3 (C, *C*-Ph), 130.0 (CH, *C*H-Ph), 129.7 (CH, *C*H-Ph), 129.6 (CH, *C*H-Ph), 128.4 (CH, C-3/C-6), 127.6 (CH, C-1/ C-8), 123.9 (CH, C-2/C-7), 46.9 (C, C-9), 44.4 (CH_2, *C*H_2-Ph), 27.8 (CH_3, C-10/C-11); m/z (HRMS, TOF ES+) calculated for C_{17} H_{14} O_4 Na $[M-+2H+Na]^+$; 305.0790, found 305.0788 (PPM error -0.7). Single crystals of **183** suitable for X-ray structure analysis were obtained by slow evaporation of a methanol solution (appendix X-ray).

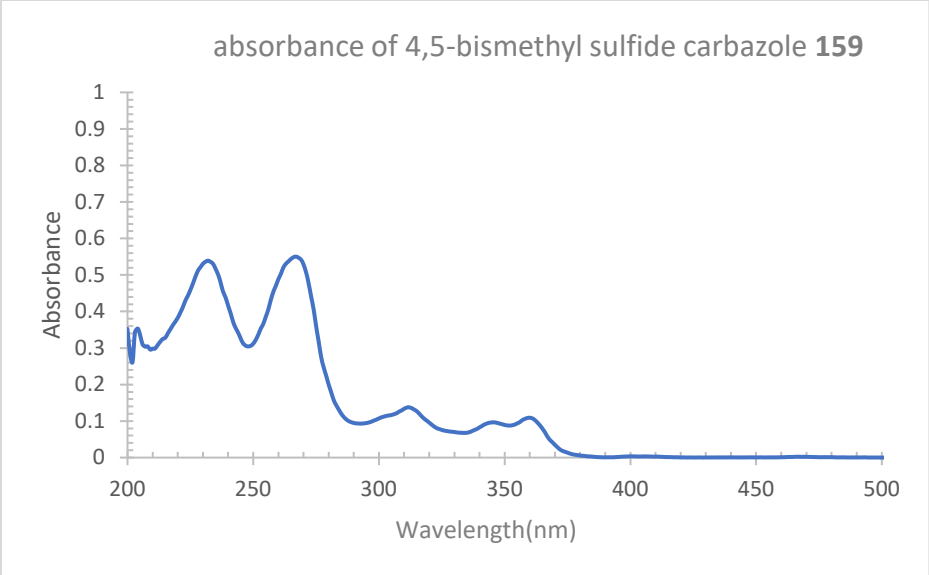
4.3 Experimental Section UV and Fluorescence spectrum

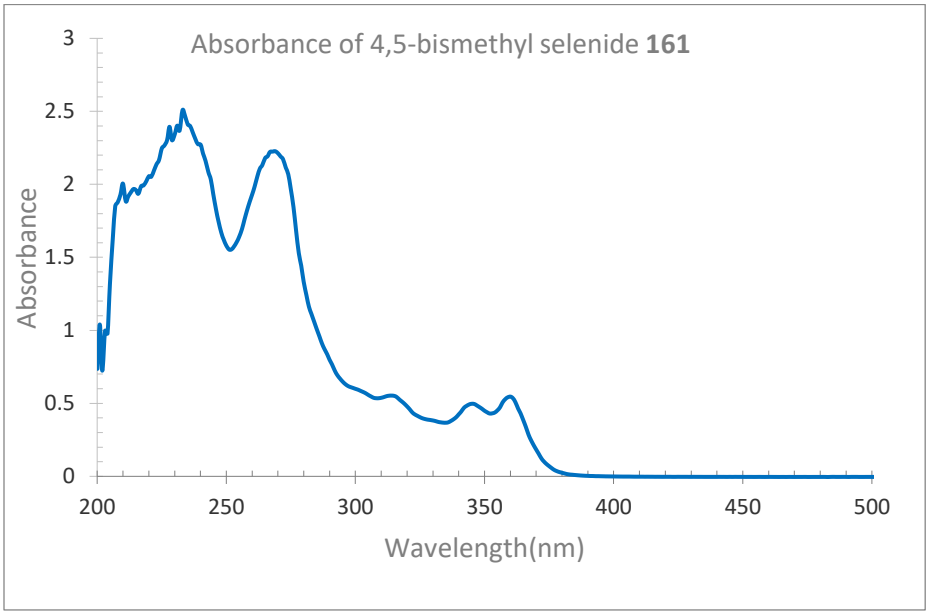
4.3.1 UV- spectrum

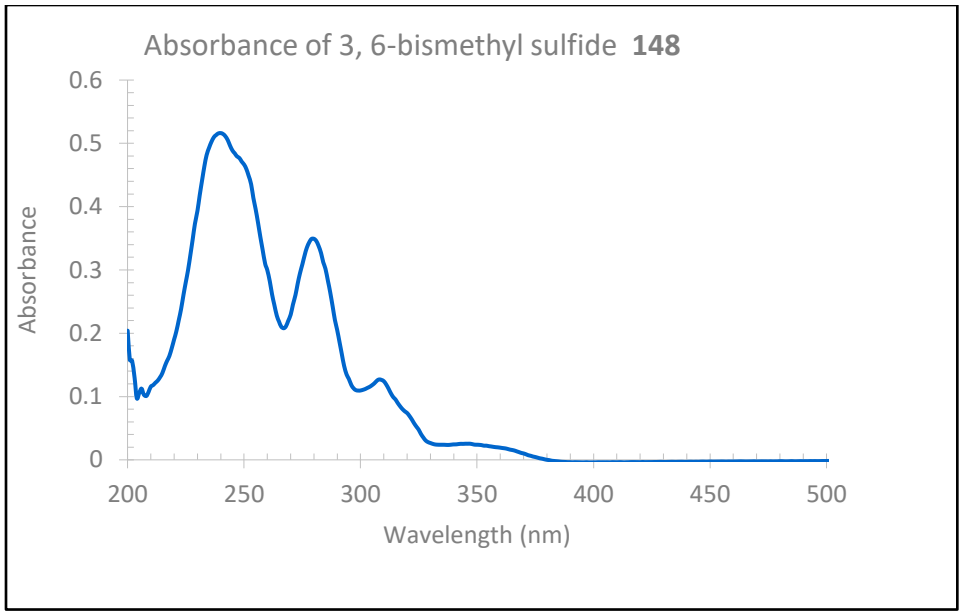
Absorption spectra of compounds recorded in EtOH and concentration (≈0.05 M)

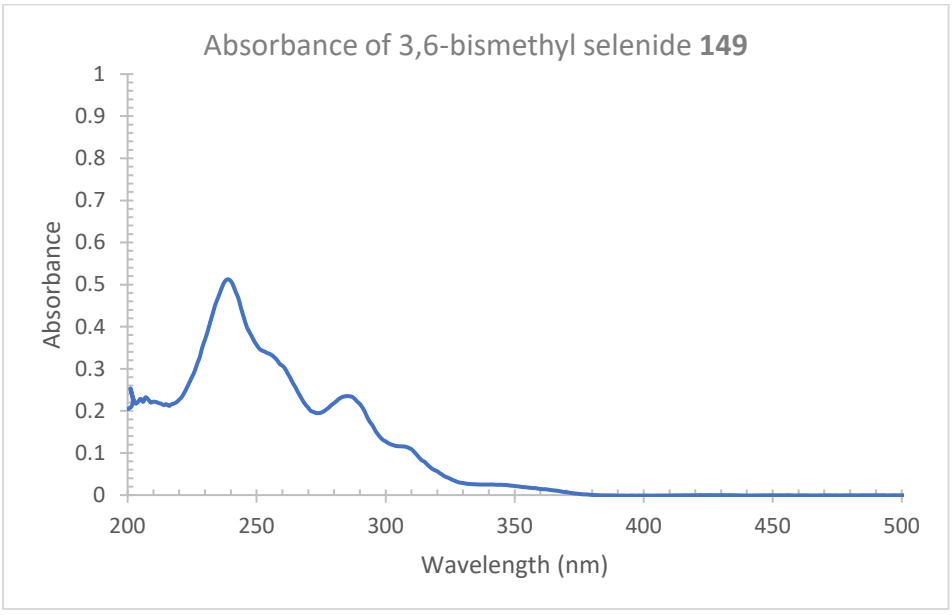


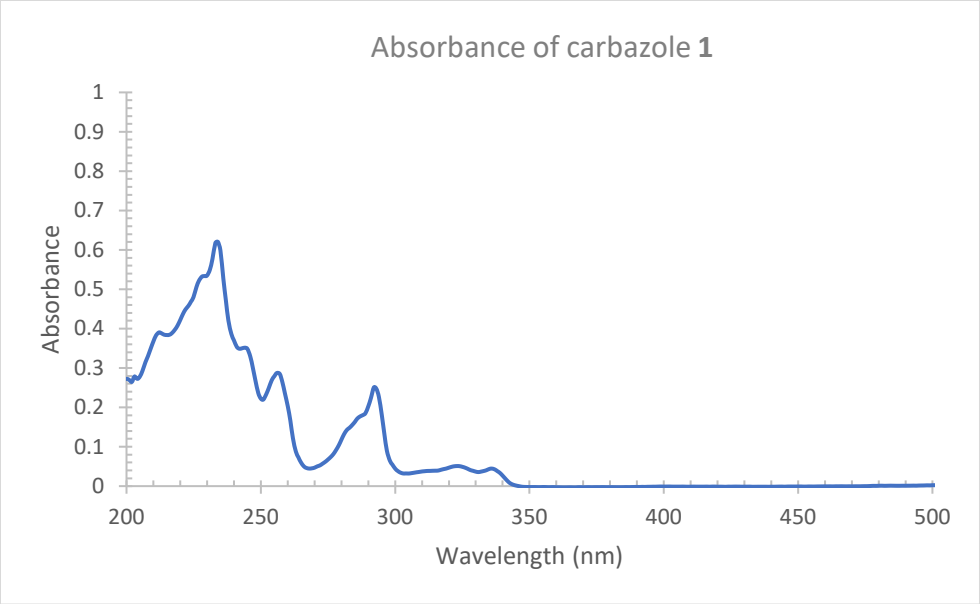



absorbance of 4,5-bismethyl sulfide carbazole 159
Absorbance
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200
250
300
350
400
450
500
Wavelength(nm)


Absorbance of 4,5-bismethyl selenide 161
Absorbance
3
2.5
2
1.5
1
0.5
0
200
250
300
350
400
450
500
Wavelength(nm)


Absorbance of 3, 6-bismethyl sulfide 148
Absorbance
0.6
0.5
0.4
0.3
0.2
0.1
0
200
250
300
350
400
450
500
Wavelength (nm)

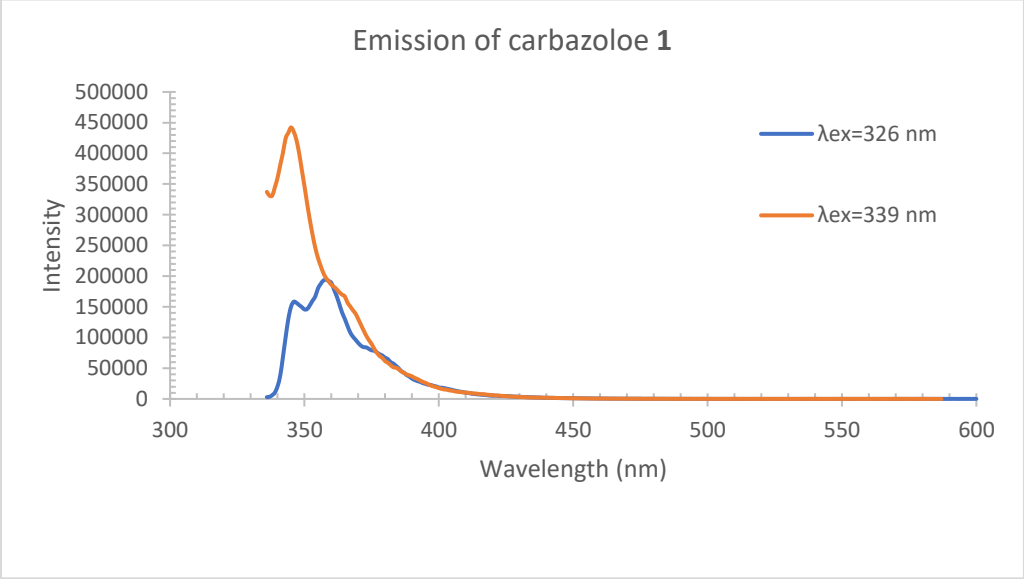

Absorbance of 3,6-bismethyl selenide 149
Absorbance
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200
250
300
350
400
450
500
Wavelength (nm)

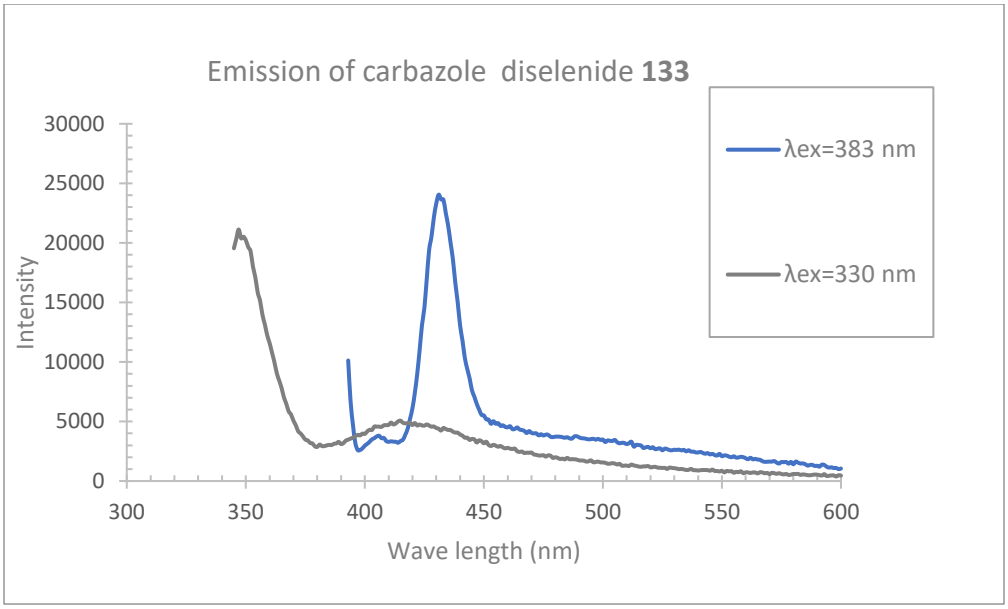

Absorbance of carbazole 1
Absorbance
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200
250
300
350
400
450
500
Wavelength (nm)

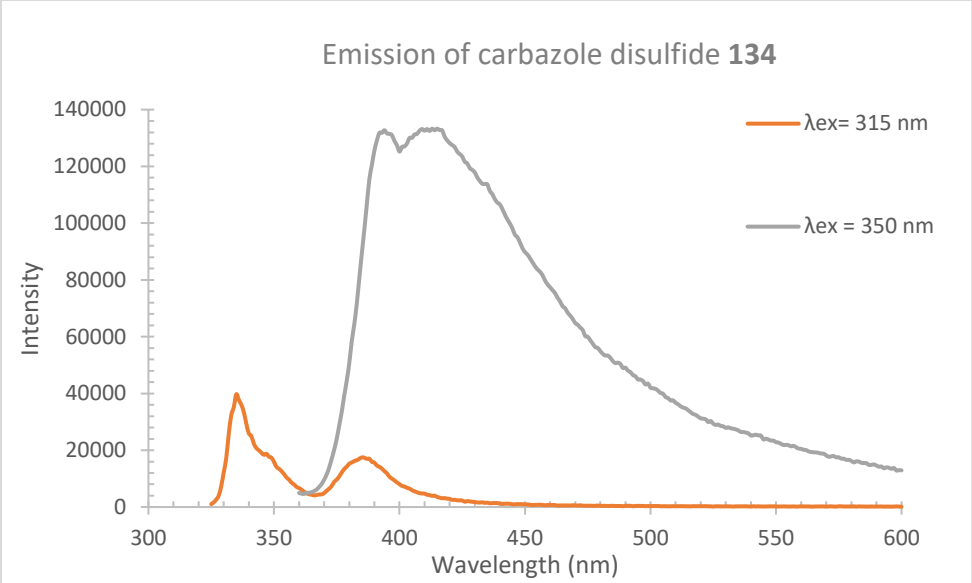
4.3.2 Fluorescence spectrum

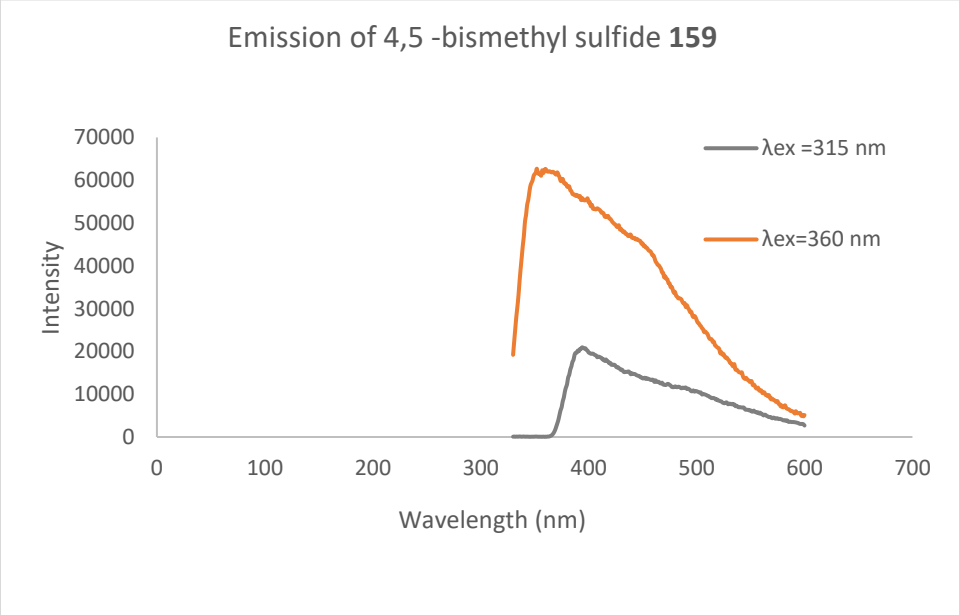
Using Edinburgh Instrument- FLSP920

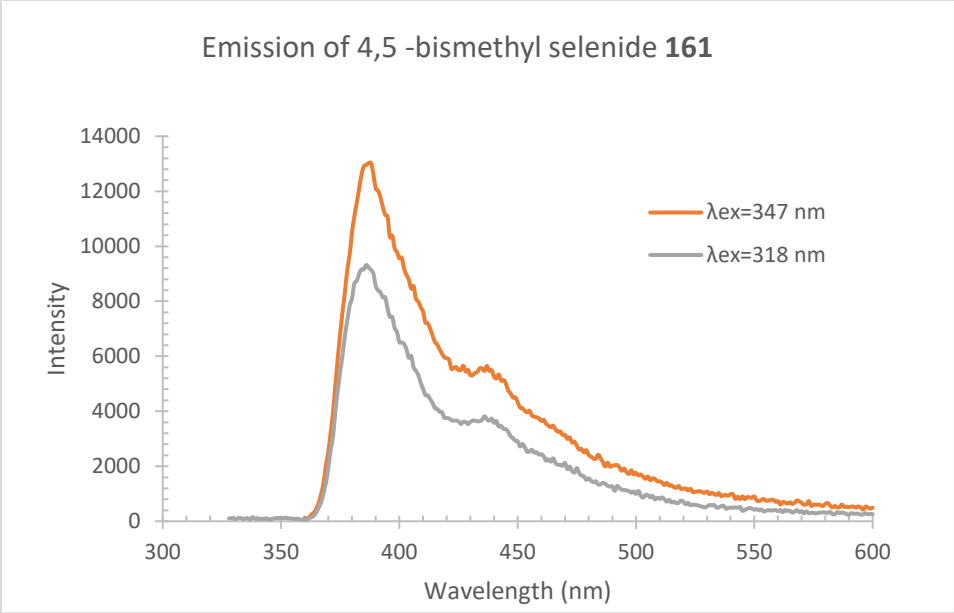
Emission spectra recorded in EtOH at different excitation wavelength.

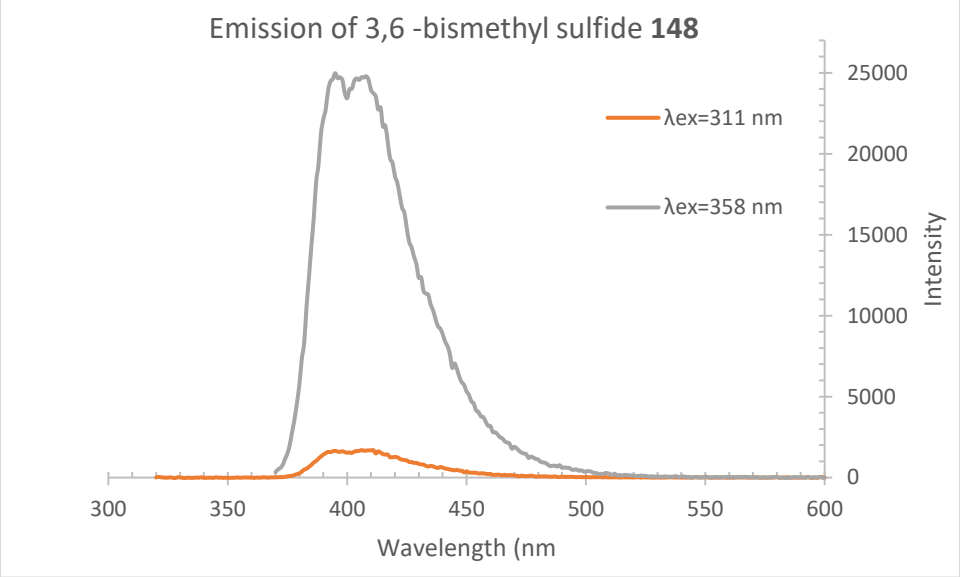


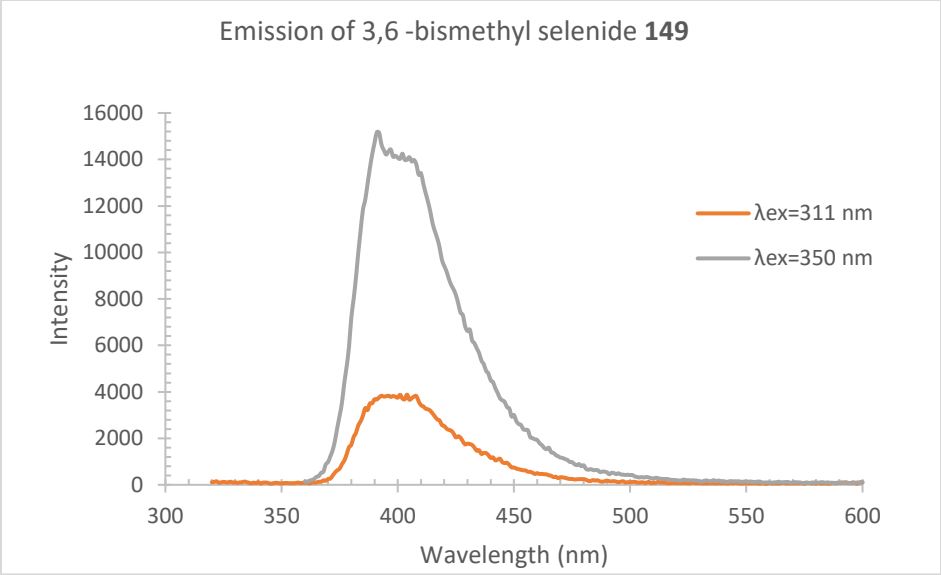



Emission of carbazole disulfide **134**
140000
120000
100000
80000
60000
40000
20000
0
Intensity
300
350
400
450
500
550
600
Wavelength (nm)
λex= 315 nm
λex = 350 nm


Emission of 4,5 -bismethyl sulfide **159**
70000
60000
50000
40000
30000
20000
10000
0
Intensity
0
100
200
300
400
500
600
700
Wavelength (nm)
λex =315 nm
λex=360 nm


Emission of 4,5 -bismethyl selenide **161**
14000
12000
10000
8000
6000
4000
2000
0
Intensity
300
350
400
450
500
550
600
Wavelength (nm)
λex=347 nm
λex=318 nm


Emission of 3,6 -bismethyl sulfide **148**
25000
20000
15000
10000
5000
0
Intensity
300
350
400
450
500
550
600
Wavelength (nm
λex=311 nm
λex=358 nm


Emission of 3,6 -bismethyl selenide **149**
16000
14000
12000
10000
8000
6000
4000
2000
0
Intensity
300
350
400
450
500
550
600
Wavelength (nm)
λex=311 nm
λex=350 nm

4.3.3 Determination of Fluorescence Quantum Yields (Φ_F)

Fluorescence Quantum Yields (Φ_F) values in EtOH were measured following a general producer. The anthracene (Φ_F) 0.27 in EtOH) used as the reference.[156] the compounds **1**, **133**, **134**, **148**, **149**, **158**, **160**, were diluted in EtOH as solvent. Samples were taken in quartz cuvettes. Absorbance spectra of all compounds were recorded at different concentrations five sample for every compound (10µm to 50 µM). The fluorescence spectra of each concentration were recorded also and an average value of integrated areas of fluorescence used for the calculation of Φ_F in solution**.** The equation was used and data were obtained were reported in (**Chapter 2, Table 22**).

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Appendices

X-ray Crystallographic Data

The datasets for **106**, **110**, **146**, **159**, **161**, **172**, and **183**, were reported. Figures and reports were produced using OLEX2.[165]

None of the structures reported contain a stereocentre. For compounds that incorporate a twist in the molecule, there are two possibilities. In some cases (compounds **146**, **159**, **161**, **172**, and **183**), the compound crystallises in a centrosymmetric space group, (one that includes an inversion centre), and as such, there is a 50:50 mixture of twist directions, (see **Figure 7**, compound **159**). In other cases (compounds **106** and **110**), the compound crystallises in a chiral space group with Flack parameters of zero, meaning that there is only one twist direction represented, (see **Figure 3**, compound **110**).

Crystal Structure of 9-(triisopropylsilyl)-9H-carbazole-4,5-diyl)dimethanol 106

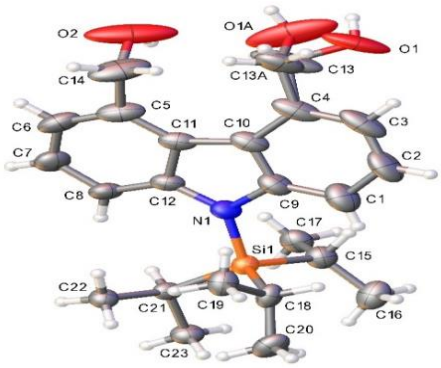


Figure 1: *AM80038-3.jpg: Crystal structure of* ***106*** *with ellipsoids drawn at the 50 % probability level.*

Notes:

The CH_2-OH group C(13)-O(1) / C(13A)-O(1A) is disordered over two positions, at a refined percentage occupancy ratio of 59 (2) : 41 (2).

The hydrogen atoms were fixed as riding models with the isotropic thermal parameters (U_{iso}) based on the U_{eq} of the parent atom. Hydrogen bonding is detailed in Table 6 of the AM80038-3_Tables.html report.

The AM80038-3_Tables.html report contains tables of bond lengths, angles and torsion angles with standard de*via*tions given in brackets.

Table 1 Crystal data and structure refinement for AM80038-3.

Identification code	AM80038-3
Empirical formula	$C_{23}H_{33}NO_2Si$
Formula weight	383.59
Temperature/K	100.00(10)
Crystal system	Hexagonal
Space group	$P6_1$
a/Å	19.2612(6)
b/Å	19.2612(6)
c/Å	9.9892(5)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	3209.4(3)
Z	6
ρ_{calc}g/cm^3	1.191
μ/mm^{-1}	1.092
F(000)	1248.0
Crystal size/mm^3	0.234 × 0.089 × 0.075
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.182 to 140.086
Index ranges	$-23 \leq h \leq 21$, $-23 \leq k \leq 23$, $-11 \leq l \leq 10$
Reflections collected	18641
Independent reflections	3827 [R_{int} = 0.0319, R_{sigma} = 0.0270]
Data/restraints/parameters	3827/50/272
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0611, wR_2 = 0.1663
Final R indexes [all data]	R_1 = 0.0684, wR_2 = 0.1764
Largest diff. peak/hole / e Å^{-3}	1.25/-0.41
Flack parameter	0.00(2)

Crystal Structure of 4,5-dichloro-9H-carbazole 110

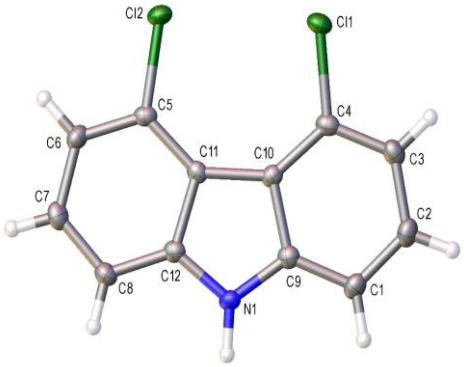


Figure 2 Crystal structure of **110** with ellipsoids drawn at the 50 % probability level.

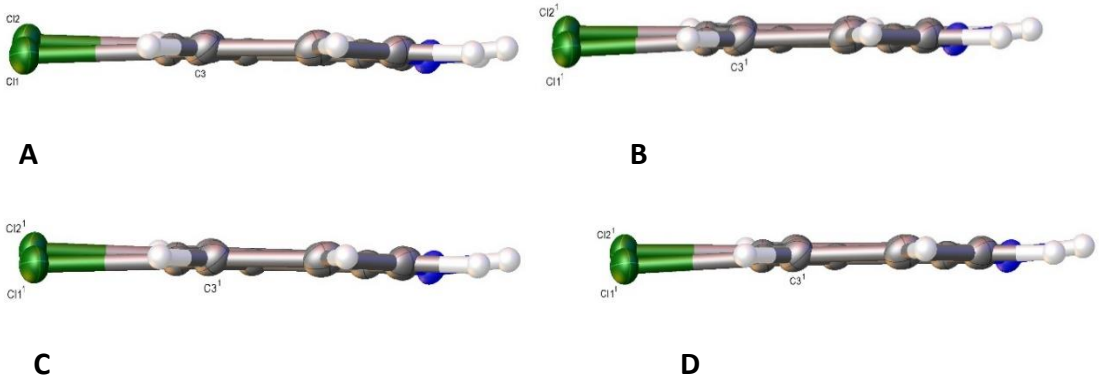


Figure 3: (A): Crystal structure of AM80056-4_DCM with ellipsoids drawn at the 50 % probability level, (B): Symmetry code used to generate equivalent atoms: $1 1 - x, ½ + y, ½ - z , (C): Symmetry code used to generate equivalent atoms: $1 ½ - x, 1 - y, ½ + z , (D): Symmetry code used to generate equivalent atoms: $1 ½ + x, ½ - y, 1 – z. The structure occupies a chiral space group, and as such all four molecules in the unit cell (represented) twist in the same direction.

Notes:

The hydrogen atom bonded to N(1) was located in the electron density and was freely refined. The remaining hydrogen atoms were fixed as riding models with the isotropic thermal parameters (U_{iso}) based on the U_{eq} of the parent atom. Hydrogen bonding is details in Table 6 of the AM80056-4_DCM_Tables.html report.

Table 2 Crystal data and structure refinement for AM80056-4_DCM.

Identification code	AM80056-4_DCM
Empirical formula	$C_{12}H_7Cl_2N$
Formula weight	236.09
Temperature/K	100.00(10)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	3.8267(2)
b/Å	14.2898(6)
c/Å	17.5522(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	959.80(7)
Z	4
ρ_{calc}g/cm^3	1.634
μ/mm^{-1}	5.725
F(000)	480.0
Crystal size/mm^3	0.205 × 0.087 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.978 to 145.682
Index ranges	$-3 \leq h \leq 4$, $-17 \leq k \leq 17$, $-21 \leq l \leq 21$
Reflections collected	9168
Independent reflections	1895 [R_{int} = 0.0352, R_{sigma} = 0.0257]
Data/restraints/parameters	1895/0/140
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0270, wR_2 = 0.0664
Final R indexes [all data]	R_1 = 0.0298, wR_2 = 0.0683
Largest diff. peak/hole / e Å^{-3}	0.21/-0.25
Flack parameter	-0.045(10)

Crystal Structure of 8,9,10,11-tetrafluoro-4-(triisopropylsilyl)-4H-naphtho[1,2,3,4-def]carbazole compound 117

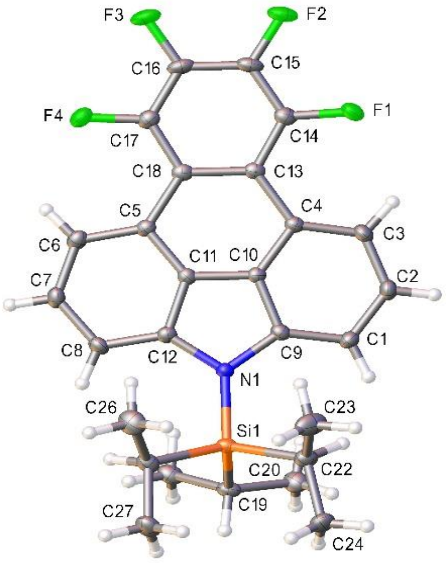


Figure 4: AM90030-1_CDCl3.jpg: crystal structure of **117** with ellipsoids drawn at the 50 % probability level.

Notes:

The hydrogen atoms were fixed as riding models with the isotropic thermal parameters (Uiso) based on the Ueq of the parent atom.

The AM90030-1_CDCl3_Tables.html report contains tables of bond lengths, angles and torsion angles with standard deviations given in brackets.

Table 3 Crystal data and structure refinement for AM90030-1_CDCl3.

Identification code	AM90030-1_$CDCl_3$
Empirical formula	$C_{27}H_{27}F_4NSi$
Formula weight	469.58
Temperature/K	100.01(10)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	8.2725(4)
b/Å	19.9141(9)
c/Å	13.8083(7)
α/°	90
β/°	101.265(5)
γ/°	90
Volume/$Å^3$	2230.95(19)
Z	4
$\rho_{calc}g/cm^3$	1.398
μ/mm^{-1}	1.359
F(000)	984.0
Crystal size/mm^3	0.244 × 0.162 × 0.124
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.896 to 146.254
Index ranges	$-10 \leq h \leq 8$, $-24 \leq k \leq 21$, $-16 \leq l \leq 16$
Reflections collected	8851
Independent reflections	4330 [R_{int} = 0.0280, R_{sigma} = 0.0344]
Data/restraints/parameters	4330/0/304
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0377, wR_2 = 0.0961
Final R indexes [all data]	R_1 = 0.0451, wR_2 = 0.1036
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.30

Crystal Structure of c4-(triisopropylsilyl)-8,10-dihydro-4H-oxepino[3,4,5,6-def]carbazole 146



Figure 5: Crystal structure of **146** with ellipsoids drawn at the 50 % probability level.

Notes:

The hydrogen atoms were fixed as riding models with the isotropic thermal parameters (U_{iso}) based on the U_{eq} of the parent atom.

The AM80057-1_Tables.html report contains tables of bond lengths, angles and torsion angles with standard de*via*tions given in brackets.

Table 4 Crystal data and structure refinement for AM80057-1.

Identification code	AM80057-1
Empirical formula	$C_{23}H_{31}NOSi$
Formula weight	365.58
Temperature/K	100.01(10)
Crystal system	Orthorhombic
Space group	Pbca
a/Å	9.0996(3)
b/Å	14.8381(5)
c/Å	29.5722(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3992.9(2)
Z	8
ρ_{calc}g/cm^3	1.216
μ/mm^{-1}	1.109
F(000)	1584.0
Crystal size/mm^3	0.21 × 0.109 × 0.095
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	11.418 to 146.074
Index ranges	$-11 \leq h \leq 8$, $-12 \leq k \leq 18$, $-20 \leq l \leq 36$
Reflections collected	9832
Independent reflections	3879 [R_{int} = 0.0278, R_{sigma} = 0.0285]
Data/restraints/parameters	3879/0/241
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0409, wR_2 = 0.1093
Final R indexes [all data]	R_1 = 0.0470, wR_2 = 0.1159
Largest diff. peak/hole / e Å^{-3}	0.46/-0.20

Crystal Structure of 4,5-bis(methylthio)-9-(triisopropylsilyl)-9H-carbazole 159

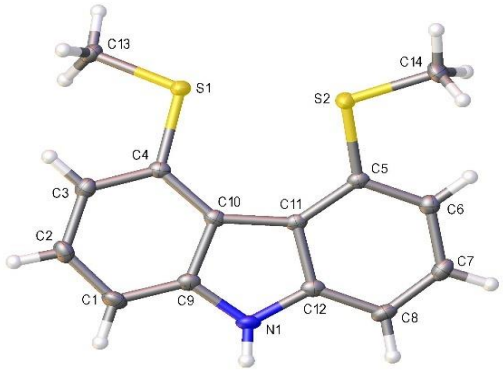


Figure 6: Crystal structure of **159** with ellipsoids drawn at the 50 % probability level.

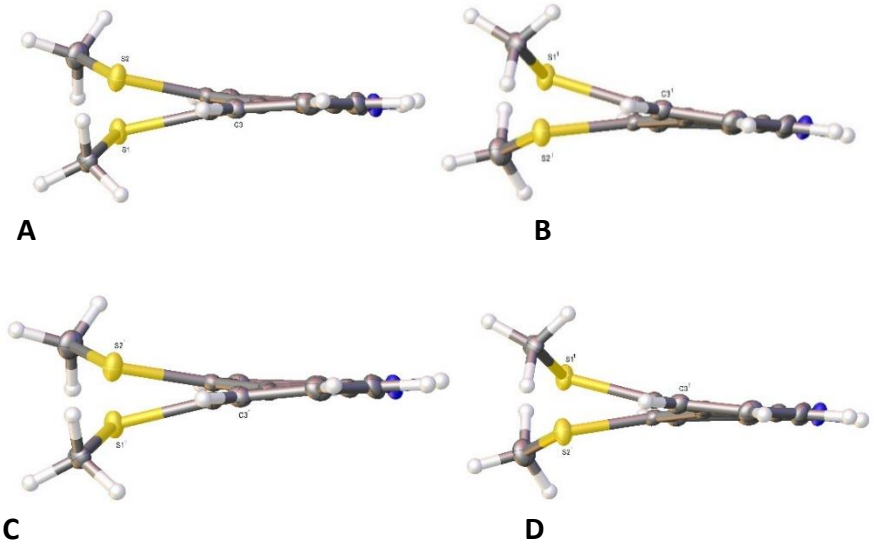


Figure 7: (A) Crystal structure of AM70050-1 with ellipsoids drawn at the 50 % probability level. (B): Symmetry code used to generate equivalent atoms: $1 x, ½ - y, ½ + z.(C): Symmetry code used to generate equivalent atoms: $1 1 - x, ½ + y, ½ - z. (D): Symmetry code used to generate equivalent atoms: $1 1 - x, 1 - y, 1 – z. The structure occupies a centrosymmetric space group, and as such two of the molecules in the unit cell (represented) twist in the opposite direction compared with the other two.

Notes:

The hydrogen atom bonded to N(1) was located in the electron density and freely refined. All remaining hydrogen atoms were fixed as riding models with the isotropic thermal parameters (U_{iso}) based on the U_{eq} of the parent atom.

The AM70050-1_Tables.html report contains tables of bond lengths, angles and torsion angles with standard de*via*tions given in brackets.

Table 5 Crystal data and structure refinement for AM70050-1.

Identification code	AM70050-1
Empirical formula	$C_{14}H_{13}NS_2$
Formula weight	259.37
Temperature/K	100.01(10)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	8.9361(3)
b/Å	18.7321(6)
c/Å	7.4875(2)
α/°	90
β/°	103.995(3)
γ/°	90
Volume/Å^3	1216.14(7)
Z	4
ρ_{calc}g/cm^3	1.417
μ/mm^{-1}	3.743
F(000)	544.0
Crystal size/mm^3	0.329 × 0.206 × 0.054
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.442 to 148.924
Index ranges	$-11 \leq h \leq 4$, $-23 \leq k \leq 20$, $-9 \leq l \leq 9$
Reflections collected	4640
Independent reflections	2399 [R_{int} = 0.0179, R_{sigma} = 0.0229]
Data/restraints/parameters	2399/0/160
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0275, wR_2 = 0.0694
Final R indexes [all data]	R_1 = 0.0299, wR_2 = 0.0712
Largest diff. peak/hole / e Å^{-3}	0.29/-0.22

Crystal Structure of 4,5-bis(methylselanyl)-9-(triisopropylsilyl)-9H-carbazole 161

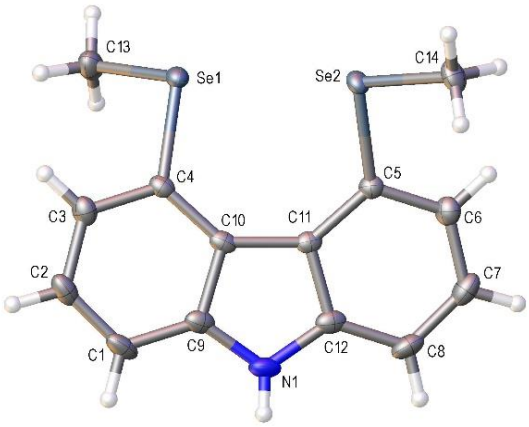


Figure 8: Crystal structure of **161** with ellipsoids drawn at the 50 % probability level.

Notes:

The hydrogen atom bonded to N(1) was located in the electron density and freely refined. All remaining hydrogen atoms were fixed as riding models with the isotropic thermal parameters (Uiso) based on the Ueq of the parent atom.

The AM70053-2_Tables.html report contains tables of bond lengths, angles and torsion angles with standard de*via*tions given in brackets.

Table 6 Crystal data and structure refinement for AM70053-2.

Identification code	AM70053-2
Empirical formula	$C_{14}H_{13}NSe_2$
Formula weight	353.17
Temperature/K	100.01(10)
Crystal system	Trigonal
Space group	R-3
a/Å	25.9500(5)
b/Å	25.9500(5)
c/Å	10.1141(2)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	5898.4(3)
Z	18
ρ_{calc}g/cm^3	1.790
μ/mm^{-1}	6.848
F(000)	3096.0
Crystal size/mm^3	0.193 × 0.13 × 0.085
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.59 to 148.43
Index ranges	$-30 \leq h \leq 27$, $-20 \leq k \leq 31$, $-11 \leq l \leq 12$
Reflections collected	7974
Independent reflections	2613 [R_{int} = 0.0170, R_{sigma} = 0.0161]
Data/restraints/parameters	2613/0/160
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0179, wR_2 = 0.0440
Final R indexes [all data]	R_1 = 0.0196, wR_2 = 0.0448
Largest diff. peak/hole / e Å^{-3}	0.32/-0.29

Crystal Structure of 9H-carbazole-4,5-dicarboxylate benzylammonium 172

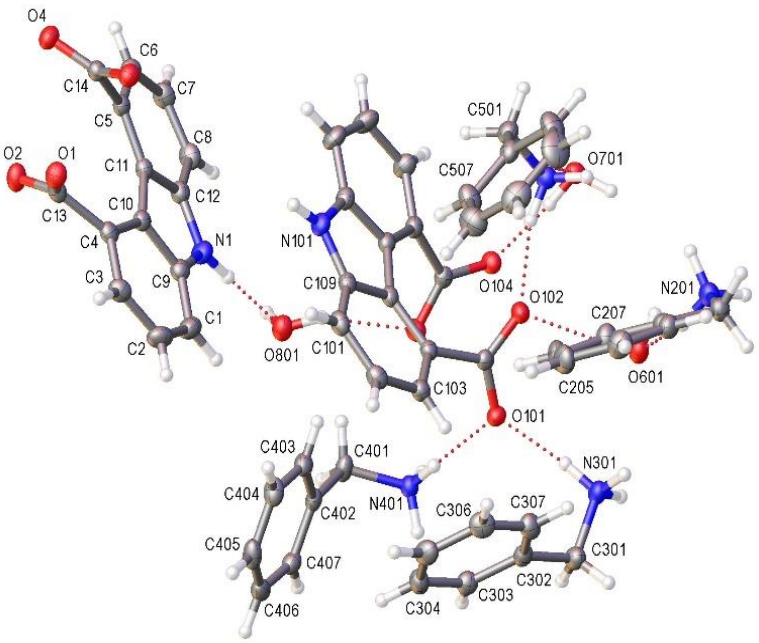


Figure 9: Crystal structure of **172** AM100015-3_MeOH with ellipsoids drawn at the 50 % probability level. Hydrogen bonding between entities in the asymmetric unit is shown using dotted lines.

Notes:

The structure is a salt with two crystallographically-independent anions, for cations and three molecules of water.

The hydrogen atoms bonded to nitrogen and oxygen atoms were located in the electron density and freely refined. All remaining hydrogen atoms were fixed as riding models with the isotropic thermal parameters (U_{iso}) based on the U_{eq} of the parent atom. Hydrogen bonding is detailed in Table 7 of the AM100015-3_MeOH_tables.html report.

Table 7 Crystal data and structure refinement for AM100015-3_MeOH.

Identification code	AM100015-3_MeOH
Empirical formula	$C_{28}H_{30}N_3O_{5.5}$
Formula weight	496.55
Temperature/K	100.00(10)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	13.31620(10)
b/Å	15.39940(10)
c/Å	24.6101(2)
α/°	90
β/°	102.8650(10)
γ/°	90
Volume/Å^3	4919.90(7)
Z	8
ρ_{calc}g/cm^3	1.341
μ/mm^{-1}	0.769
F(000)	2104.0
Crystal size/mm^3	0.143 × 0.103 × 0.066
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.808 to 157.516
Index ranges	$-16 \leq h \leq 16$, $-18 \leq k \leq 18$, $-29 \leq l \leq 31$
Reflections collected	91413
Independent reflections	10099 [R_{int} = 0.0365, R_{sigma} = 0.0191]
Data/restraints/parameters	10099/0/738
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0347, wR_2 = 0.0886
Final R indexes [all data]	R_1 = 0.0394, wR_2 = 0.0914
Largest diff. peak/hole / e Å^{-3}	0.20/-0.23

Crystal Structure of 9,9-dimethyl-9H-fluorene-4,5- dicarboxylatedibezylammonium 183

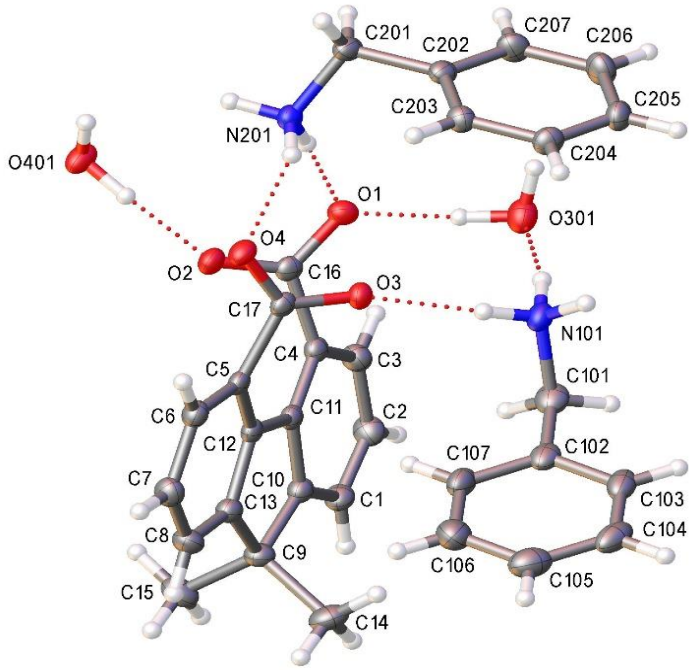


Figure 10: *Crystal structure of **183** AM90064-3_MeOH with ellipsoids drawn at the 50 % probability level. Hydrogen bonding between entities in the asymmetric unit is shown using dotted lines.*

Notes:

The structure is a salt with two crystallographically-independent cations and anions and two molecules of water.

The hydrogen atoms bonded to N(101), N(201) and both water molecules were located in the electron density and freely refined. All remaining hydrogen atoms were fixed as riding models with the isotropic thermal parameters (U_{iso}) based on the U_{eq} of the parent atom. Hydrogen bonding is detailed in Table 6 of the AM90064-3_MeOH_tables.html report.

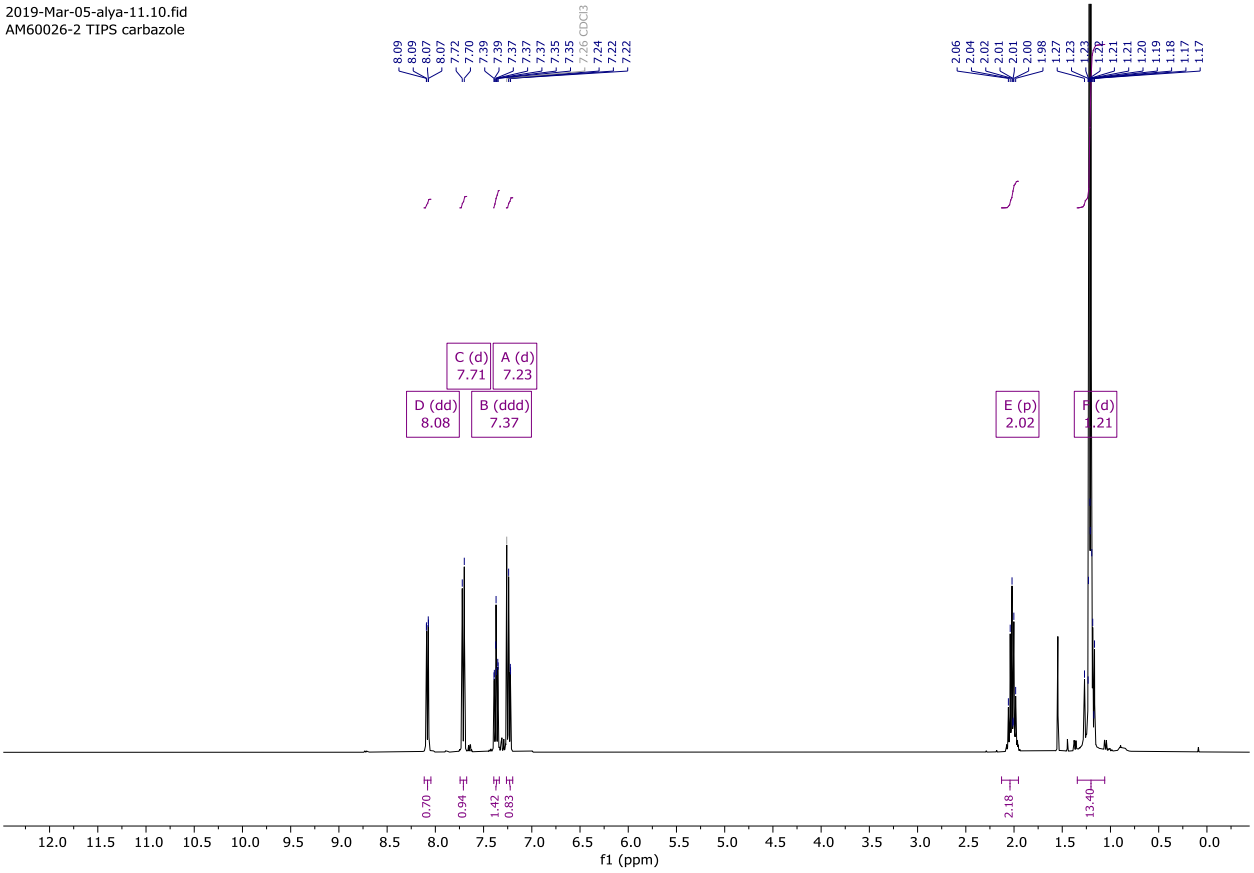
Table 8 Crystal data and structure refinement for AM90064-3_MeOH.

Identification code	AM90064-3_MeOH
Empirical formula	$C_{31}H_{36}N_2O_6$
Formula weight	532.62
Temperature/K	100.00(10)
Crystal system	Triclinic
Space group	P-1
a/Å	9.49130(10)
b/Å	10.15330(10)
c/Å	15.6152(2)
α/°	95.8600(10)
β/°	103.2770(10)
γ/°	103.5430(10)
Volume/Å^3	1404.41(3)
Z	2
ρ_{calc}g/cm^3	1.260
μ/mm^{-1}	0.709
F(000)	568.0
Crystal size/mm^3	0.144 × 0.107 × 0.068
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.084 to 156.946
Index ranges	$-12 \leq h \leq 12$, $-10 \leq k \leq 12$, $-19 \leq l \leq 19$
Reflections collected	26708
Independent reflections	5719 [R_{int} = 0.0417, R_{sigma} = 0.0319]
Data/restraints/parameters	5719/0/394
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.0941
Final R indexes [all data]	R_1 = 0.0408, wR_2 = 0.0970
Largest diff. peak/hole / e Å^{-3}	0.20/-0.21

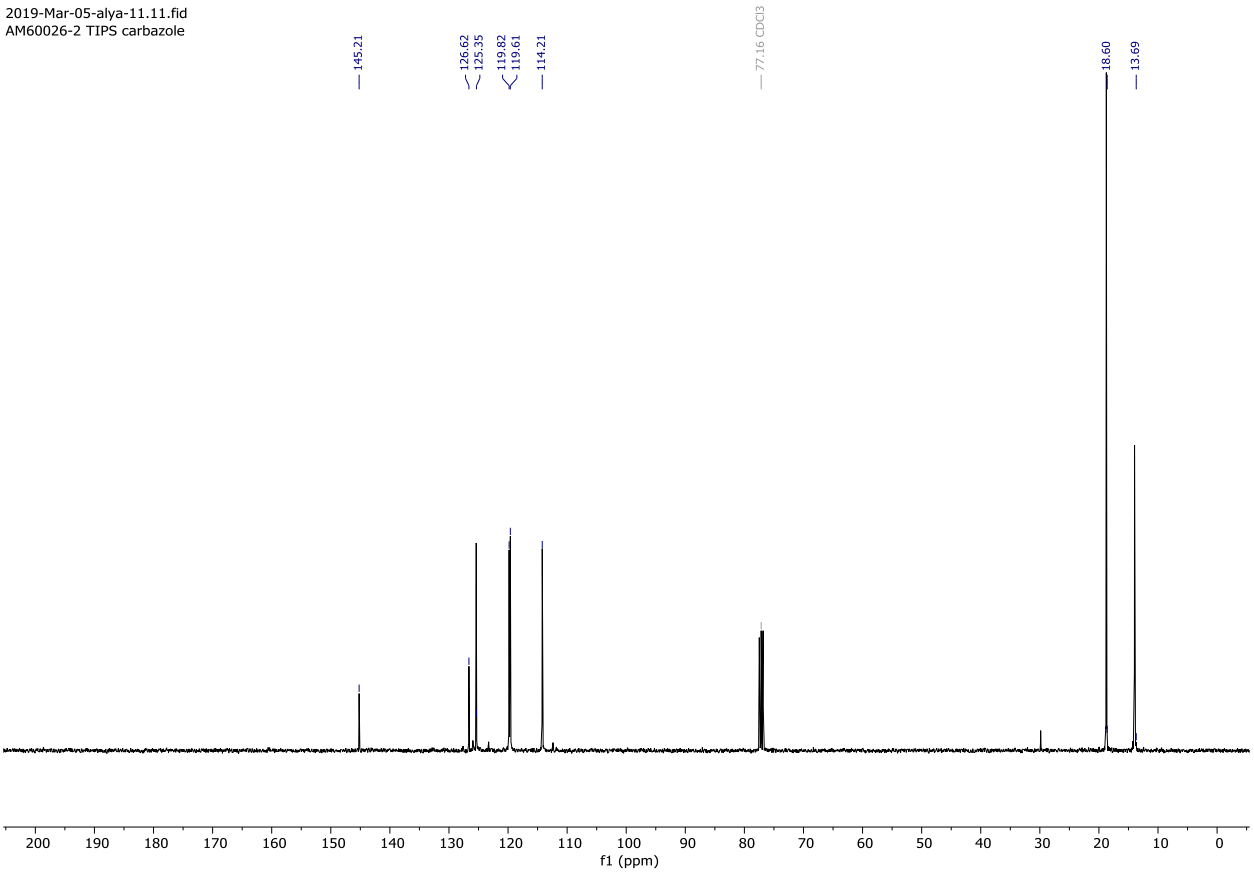
These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Copies of ^{1}H-NMR& ^{13}C-NMR

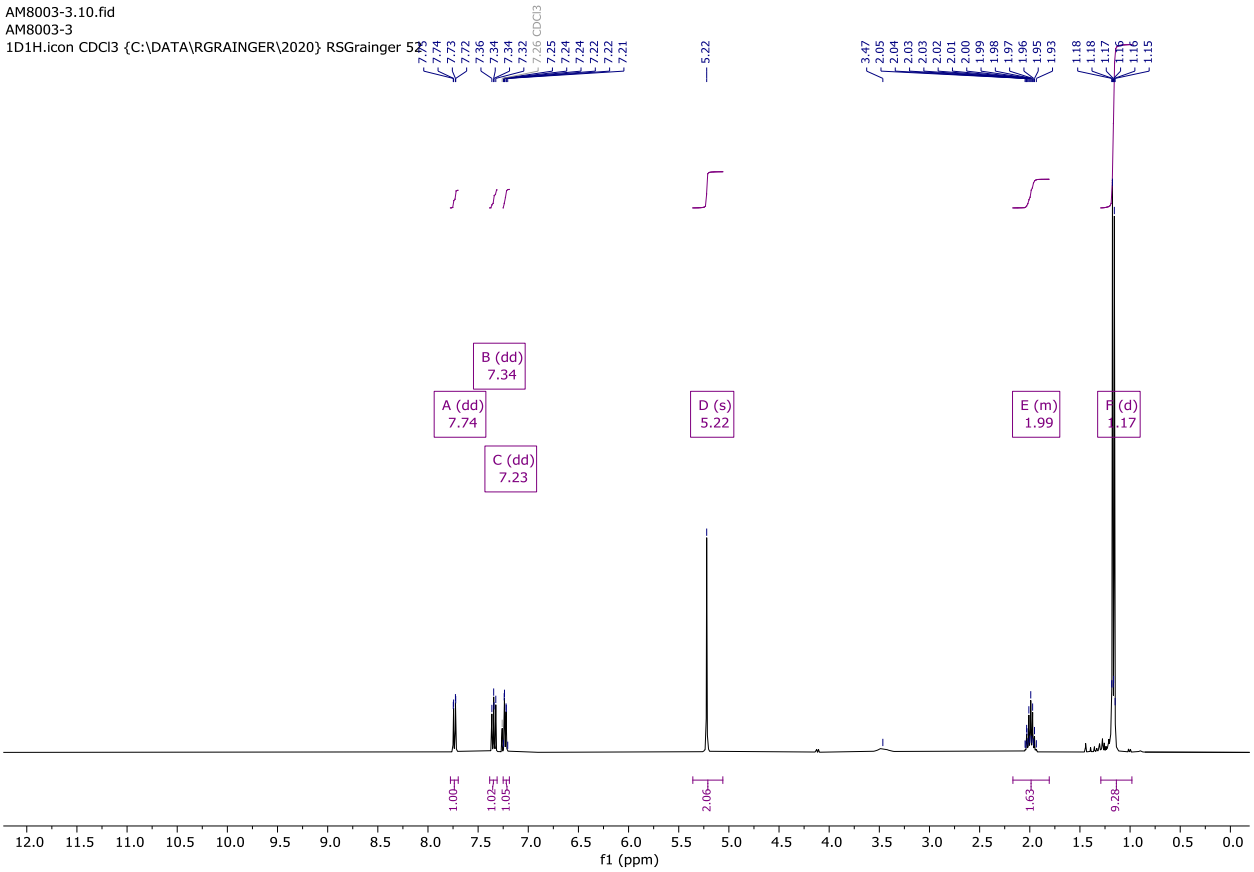
^{1}H-NMR data for 9-(triisopropylsilyl)-9H-carbazole 56



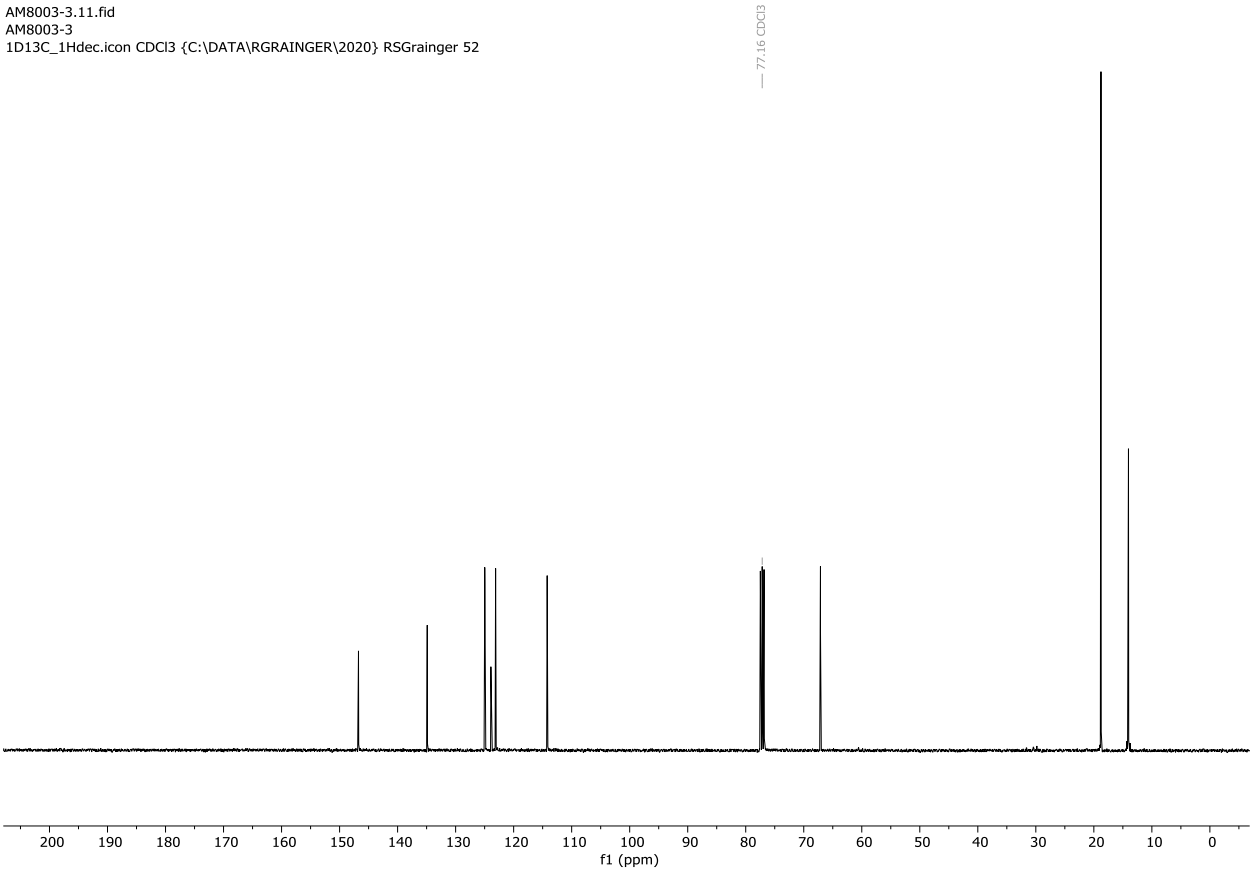
^{13}C-NMR data for 9-(triisopropylsilyl)-9H-carbazole 56



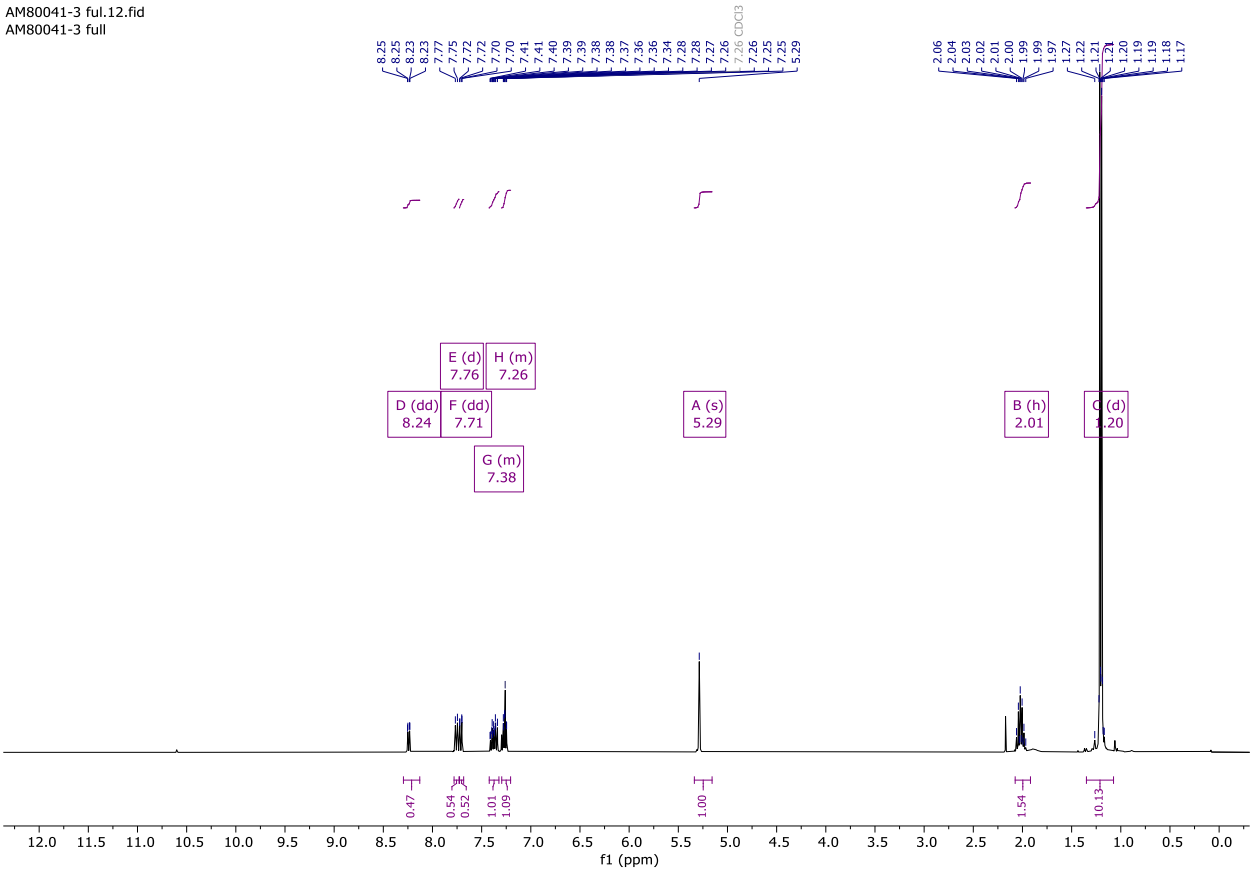
^{1}H-NMR data of 9-(triisopropylsilyl)-9H-carbazole-4,5-diyl)dimethanol 106



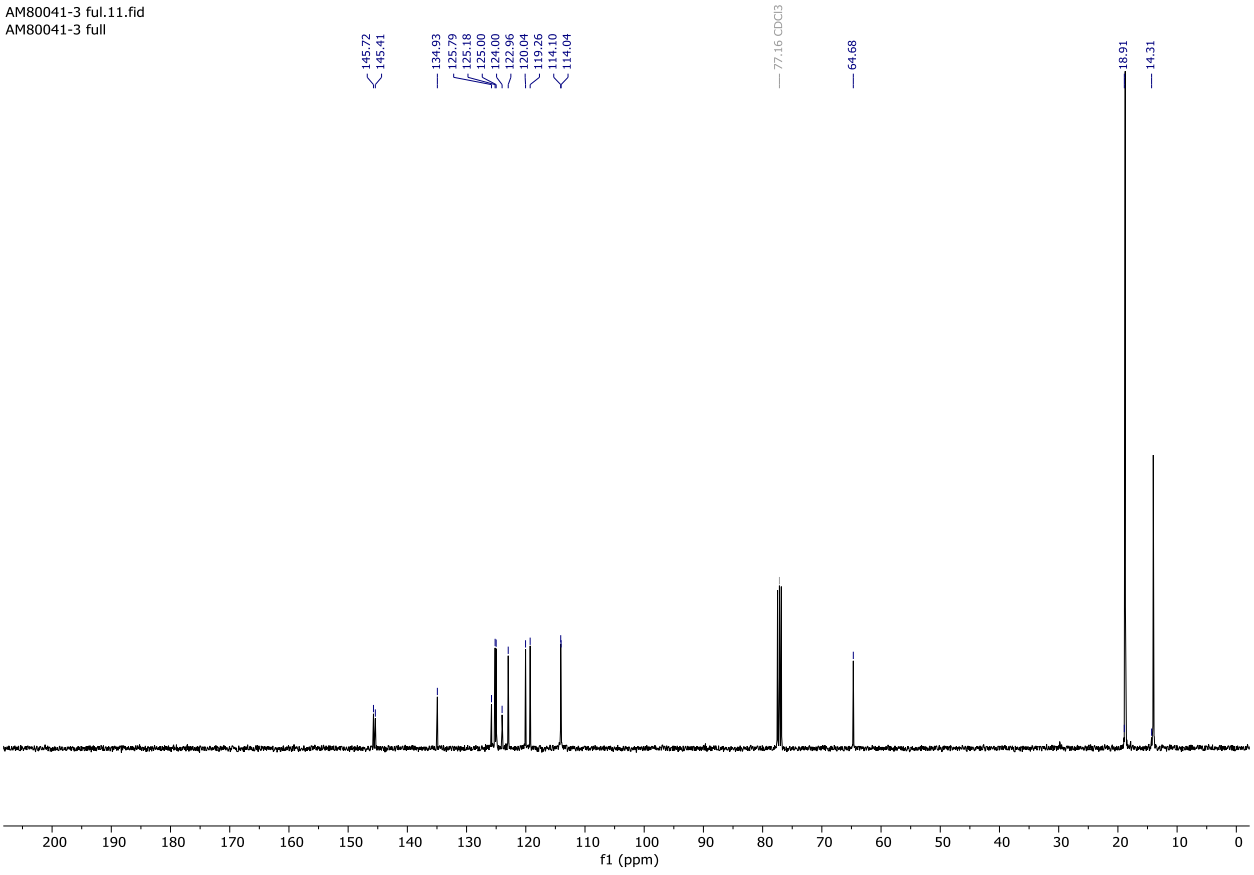
^{13}C-NMR data of 9-(triisopropylsilyl)-9H-carbazole-4,5-diyl)dimethanol 106



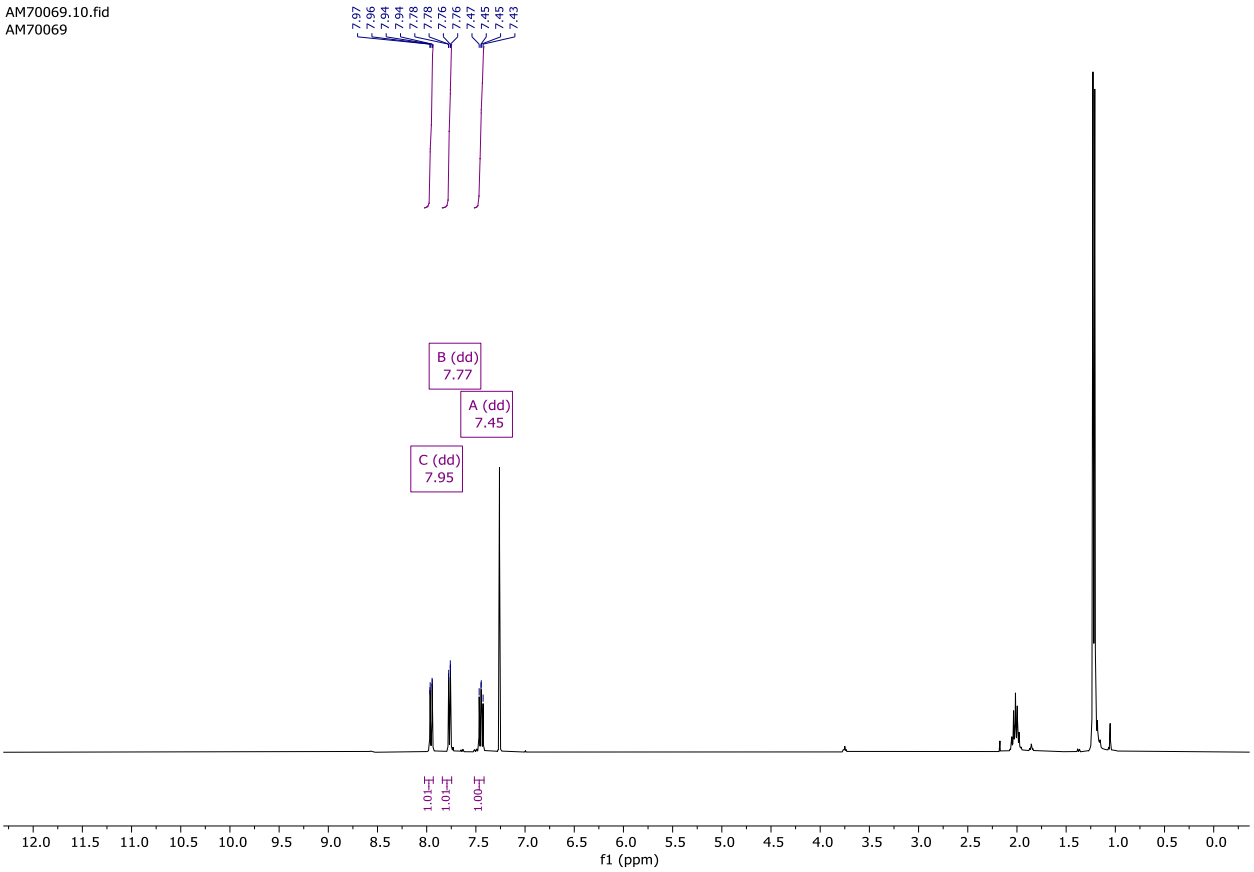
^{1}H-NMR data for 9-(triisopropylsilyl)-9H-carbazol-4-yl) methanol 107



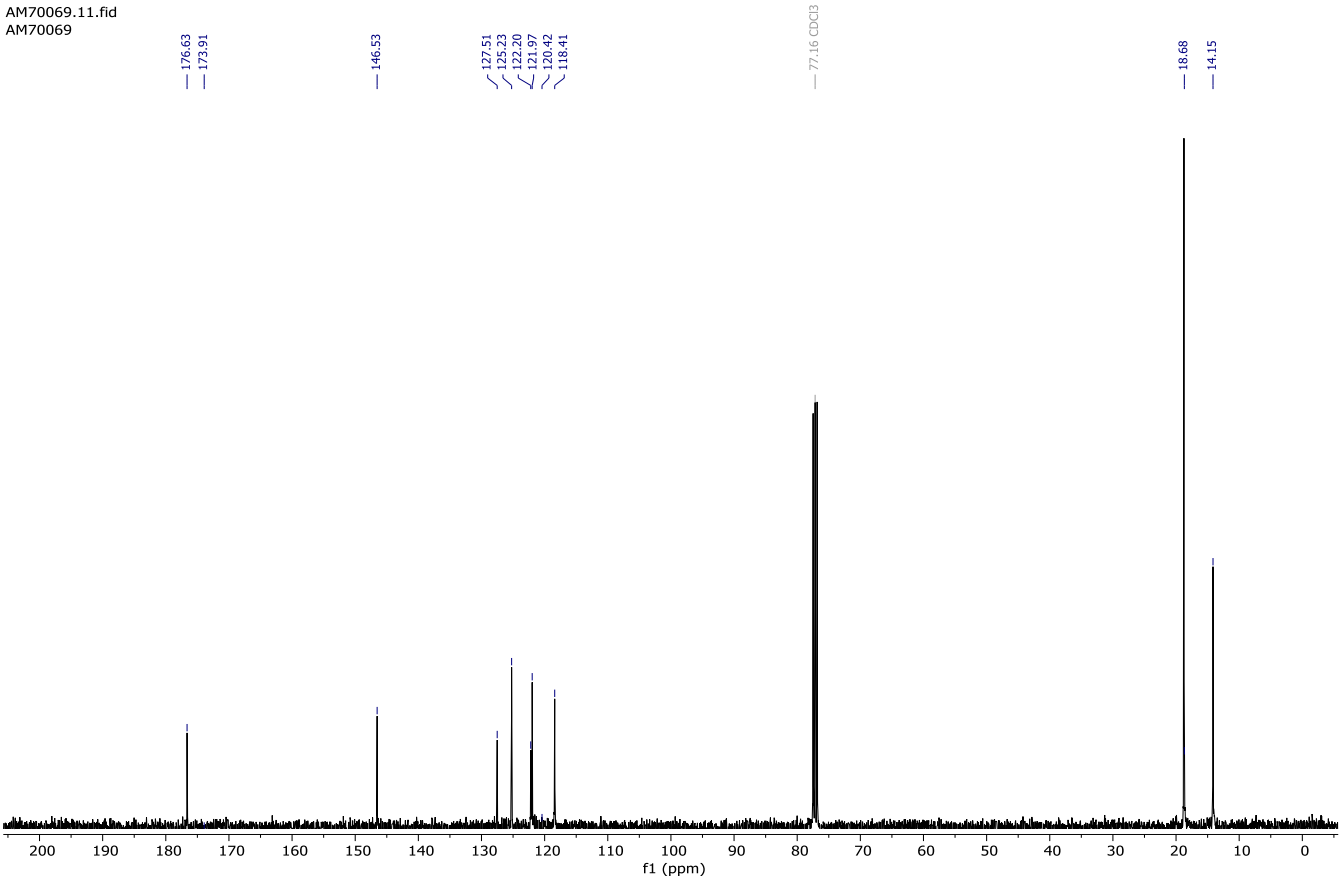
^{13}C-NMR data for9-(triisopropylsilyl)-9H-carbazol-4-yl) methanol 107



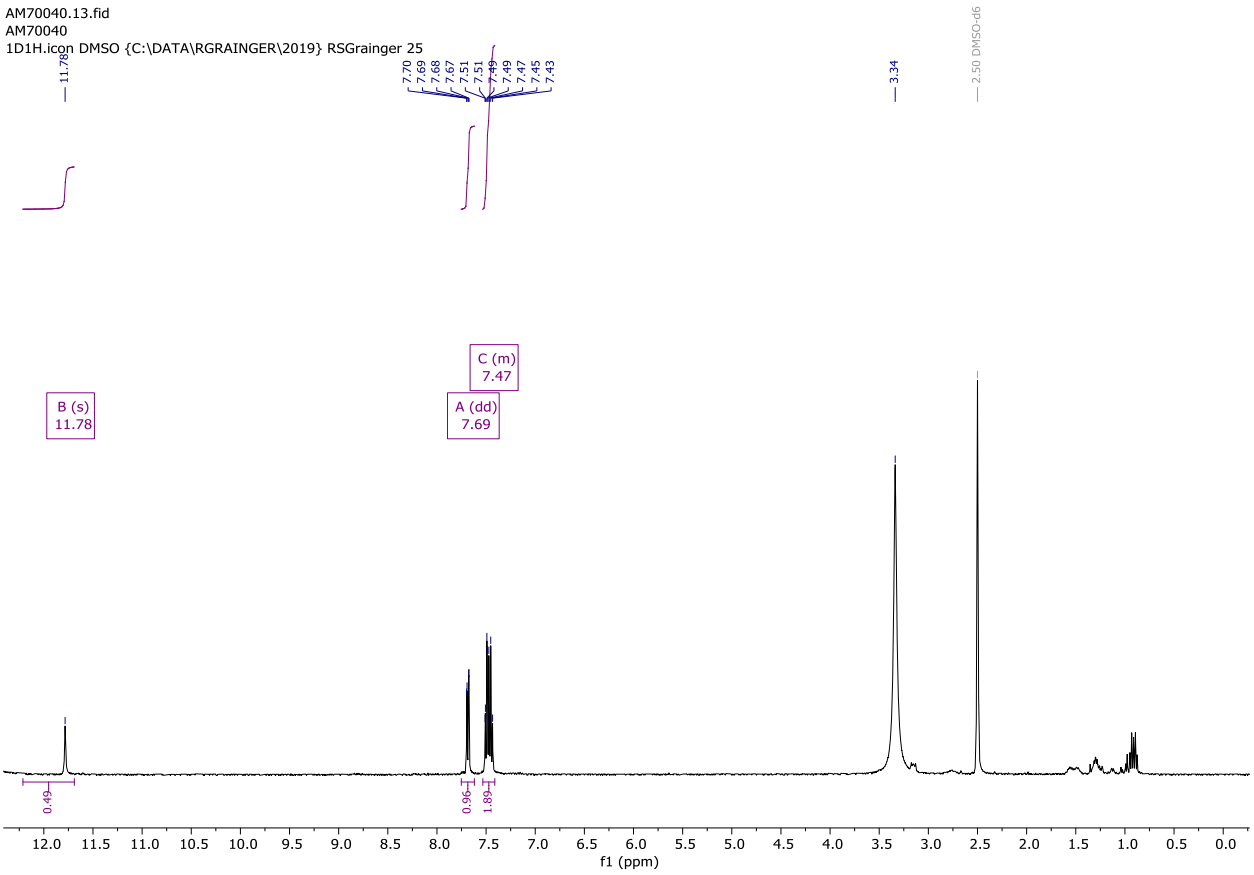
^{1}H-NMR data for 4-(triisopropylsilyl)-4H-oxepino[3,4,5,6-def]carbazole-8,10-dione 100



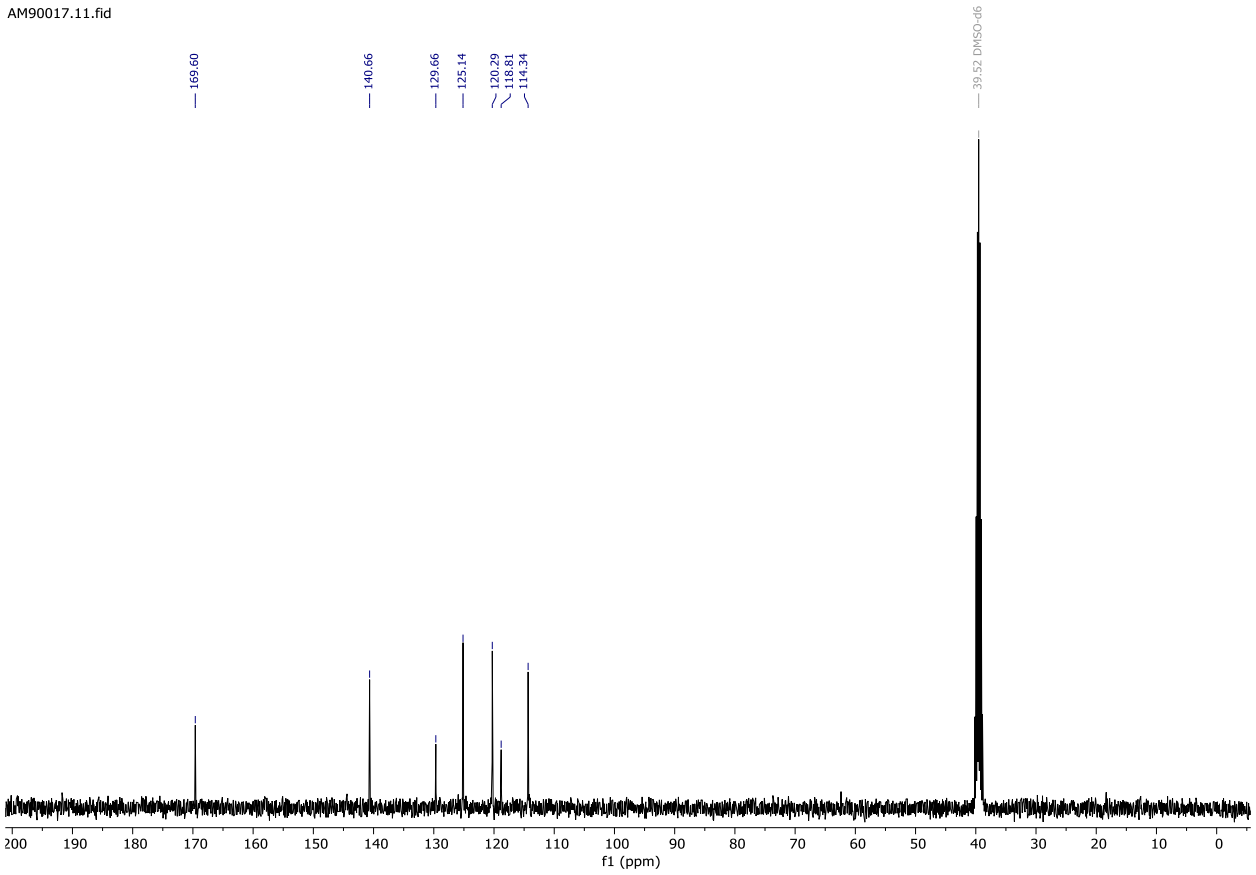
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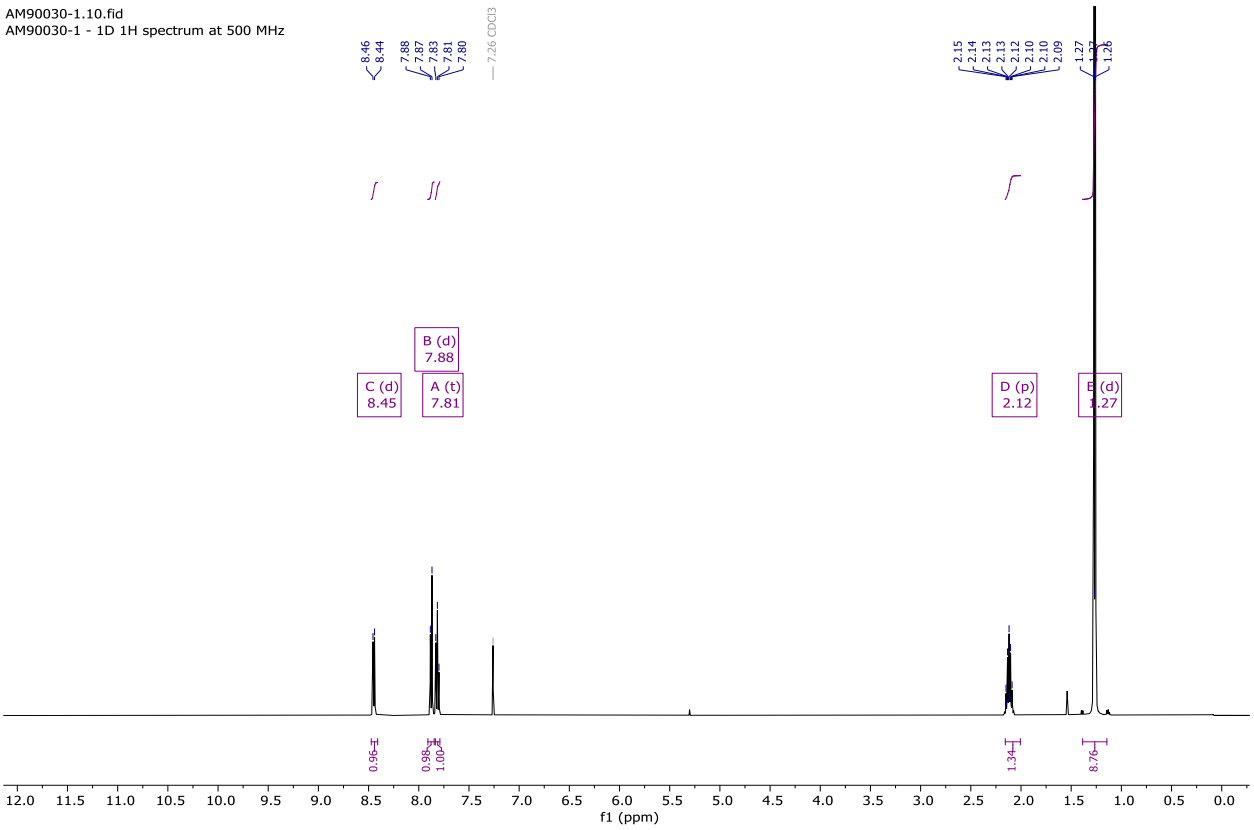
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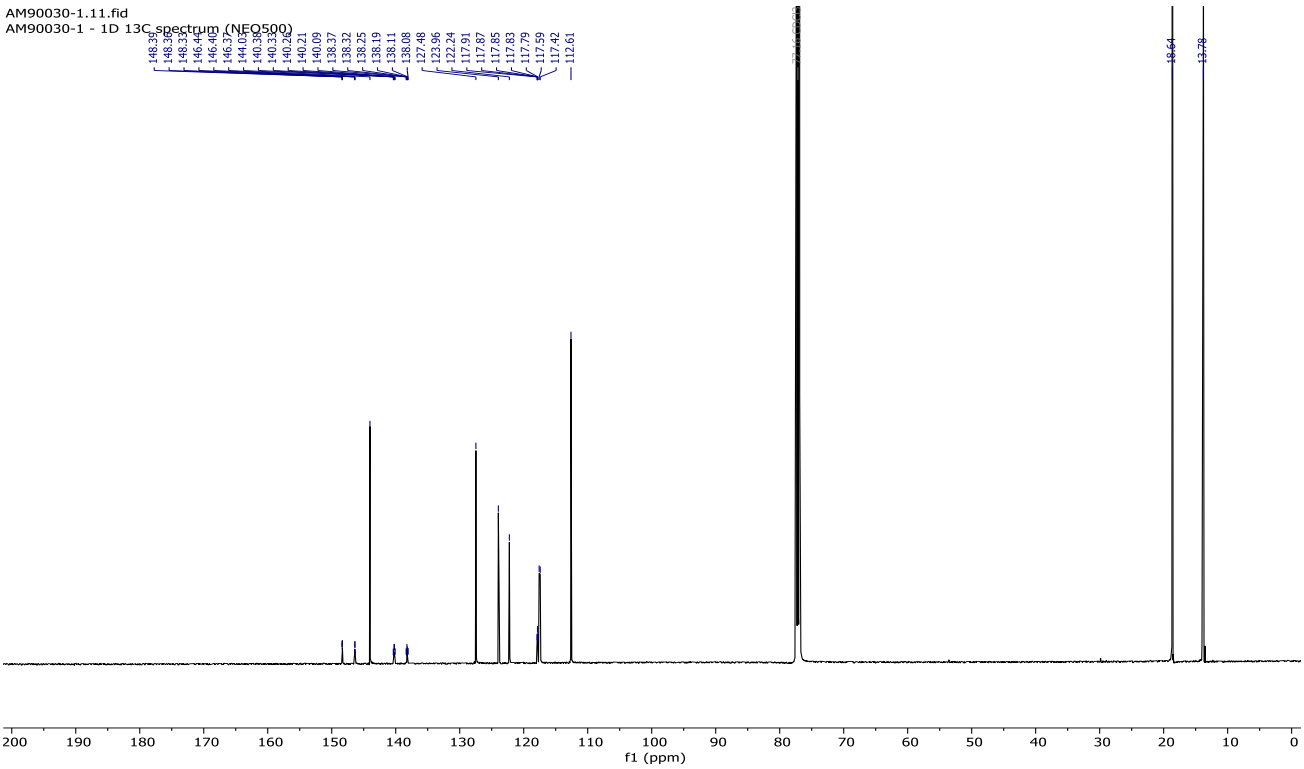
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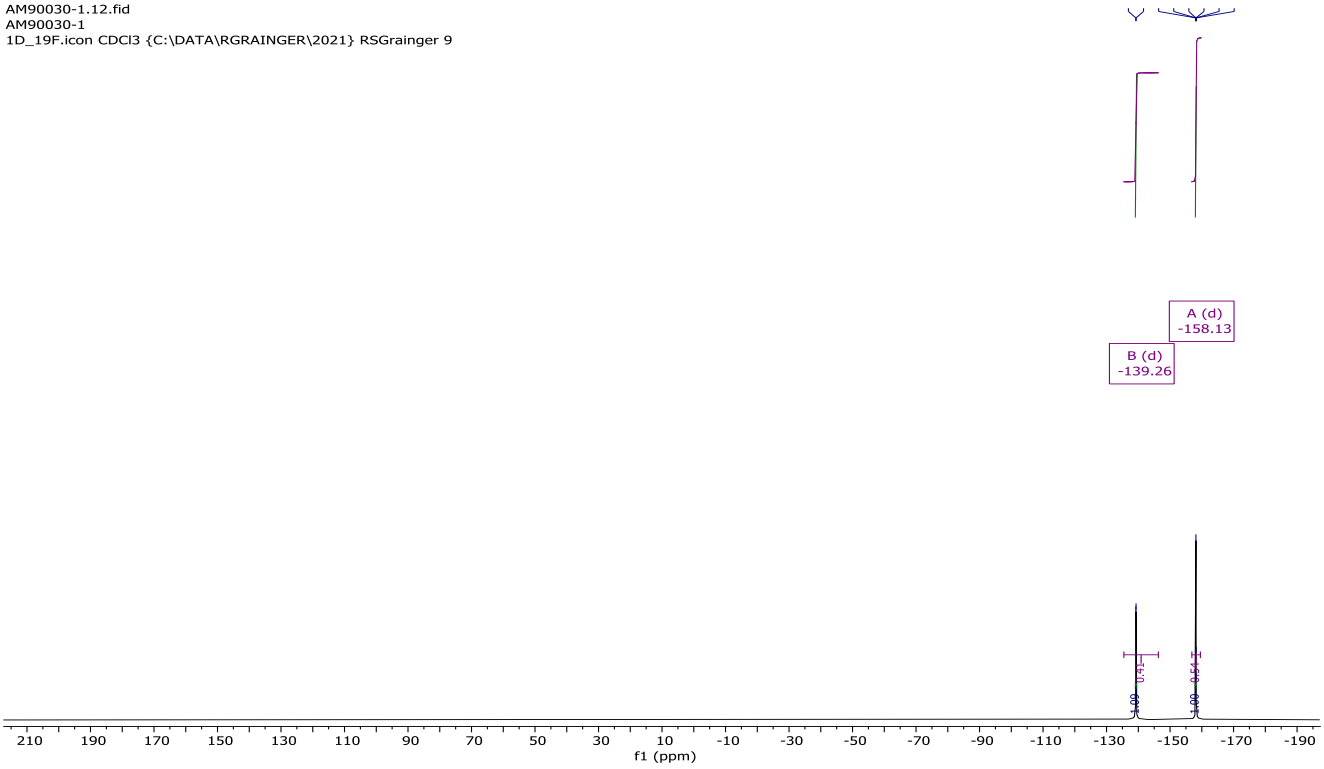
^{1}H-NMR data for 8,9,10,11-tetrafluoro-4-(triisopropylsilyl)-4H-naphtho[1,2,3,4-def]carbazole 117



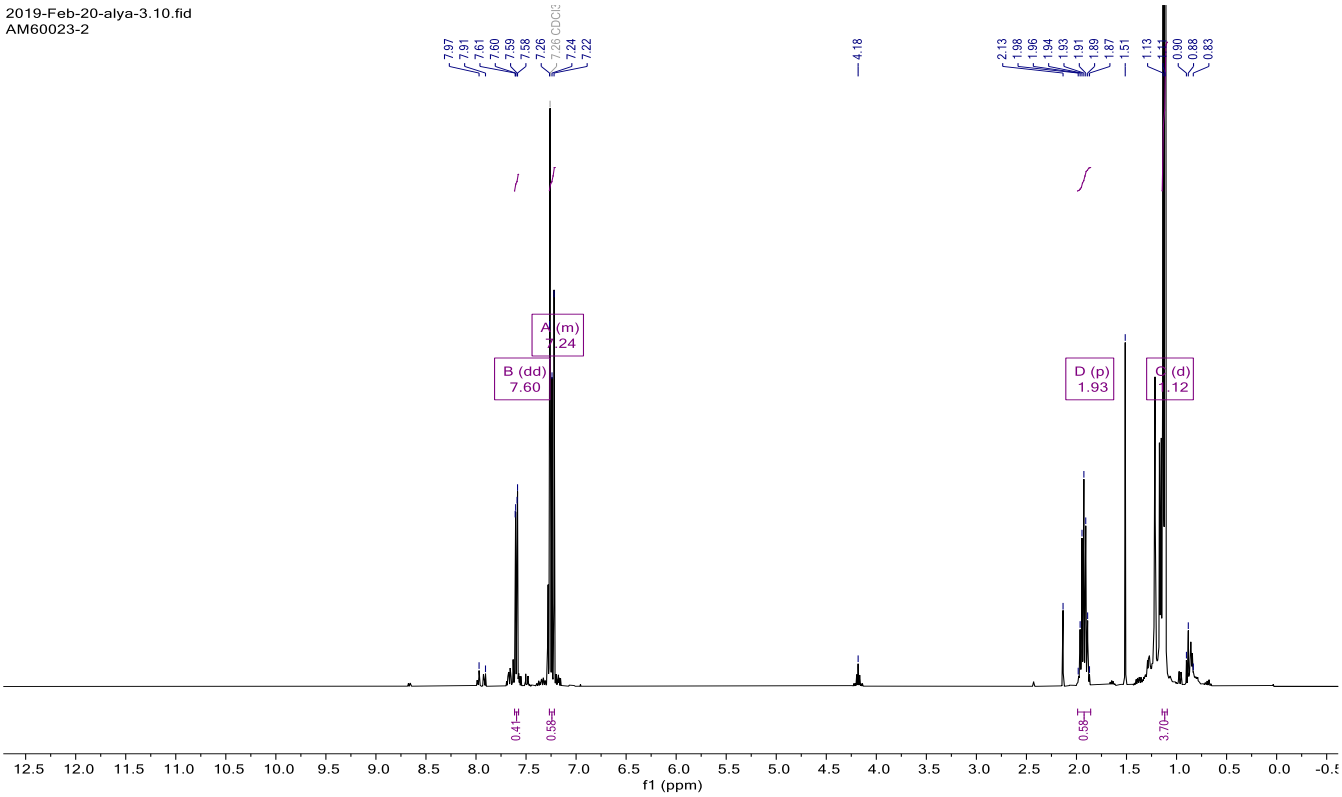
^{13}C-NMR data for 8,9,10,11-tetrafluoro-4-(triisopropylsilyl)-4H-naphtho[1,2,3,4-def]carbazole 117



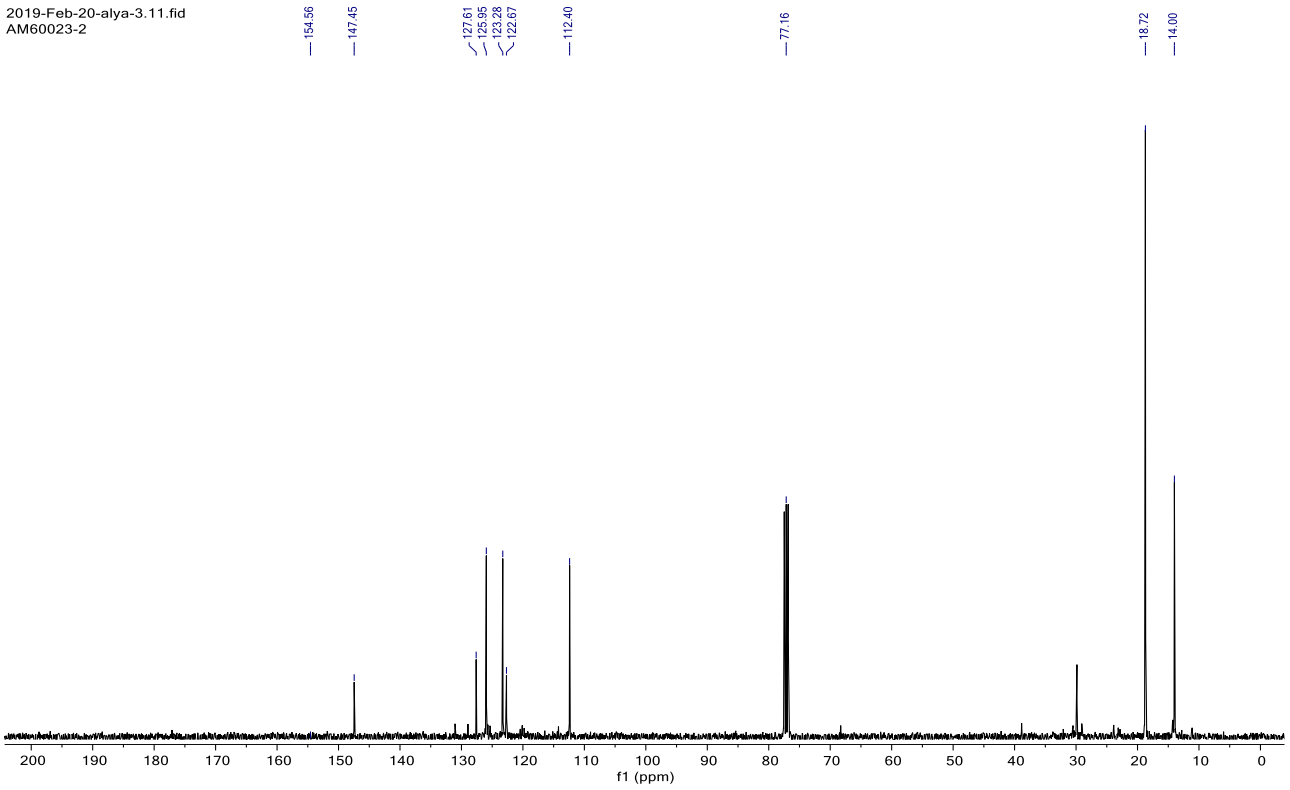
^{19}F-NMR data for 8,9,10,11-tetrafluoro-4-(triisopropylsilyl)-4H-naphtho[1,2,3,4-def]carbazole 117



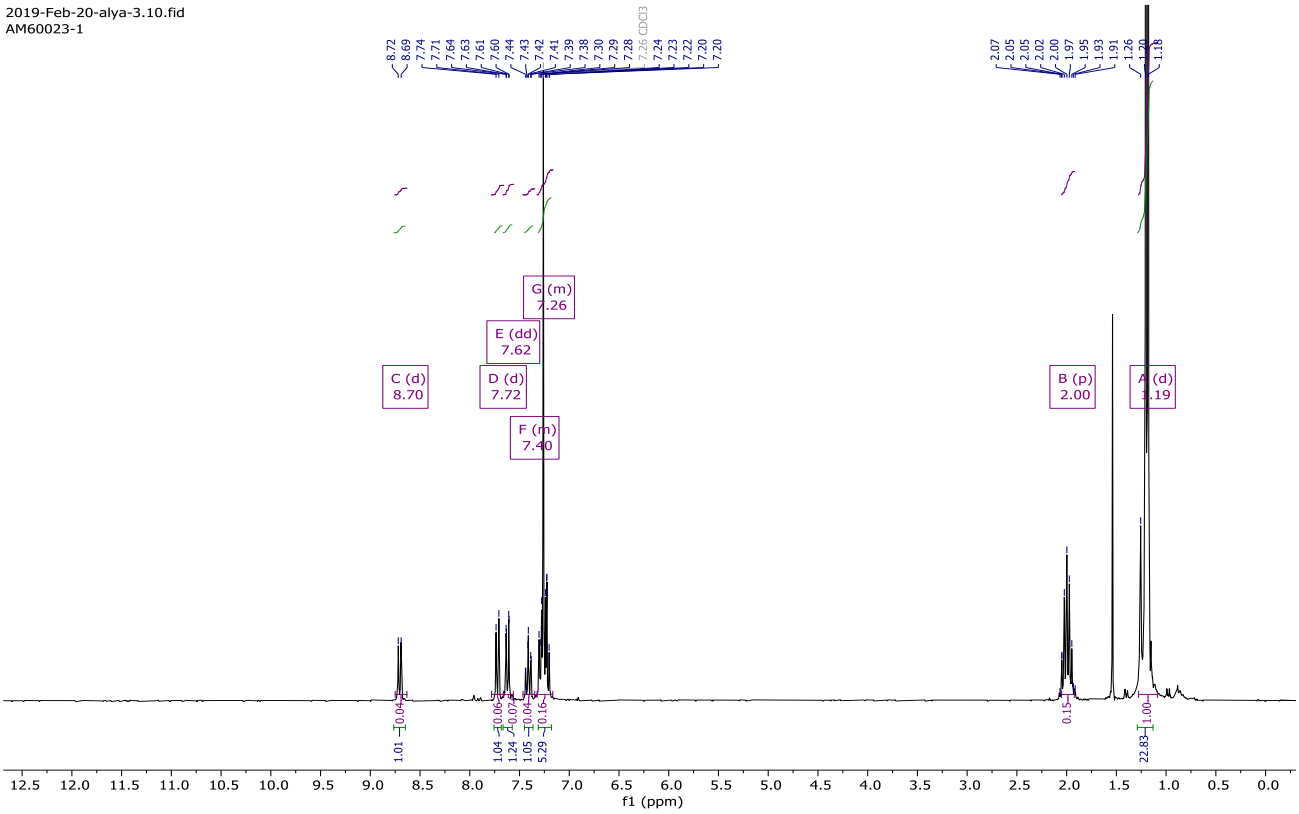
^{1}H-NMR data for 4,5-dichloro-TIPS-carbazole 108



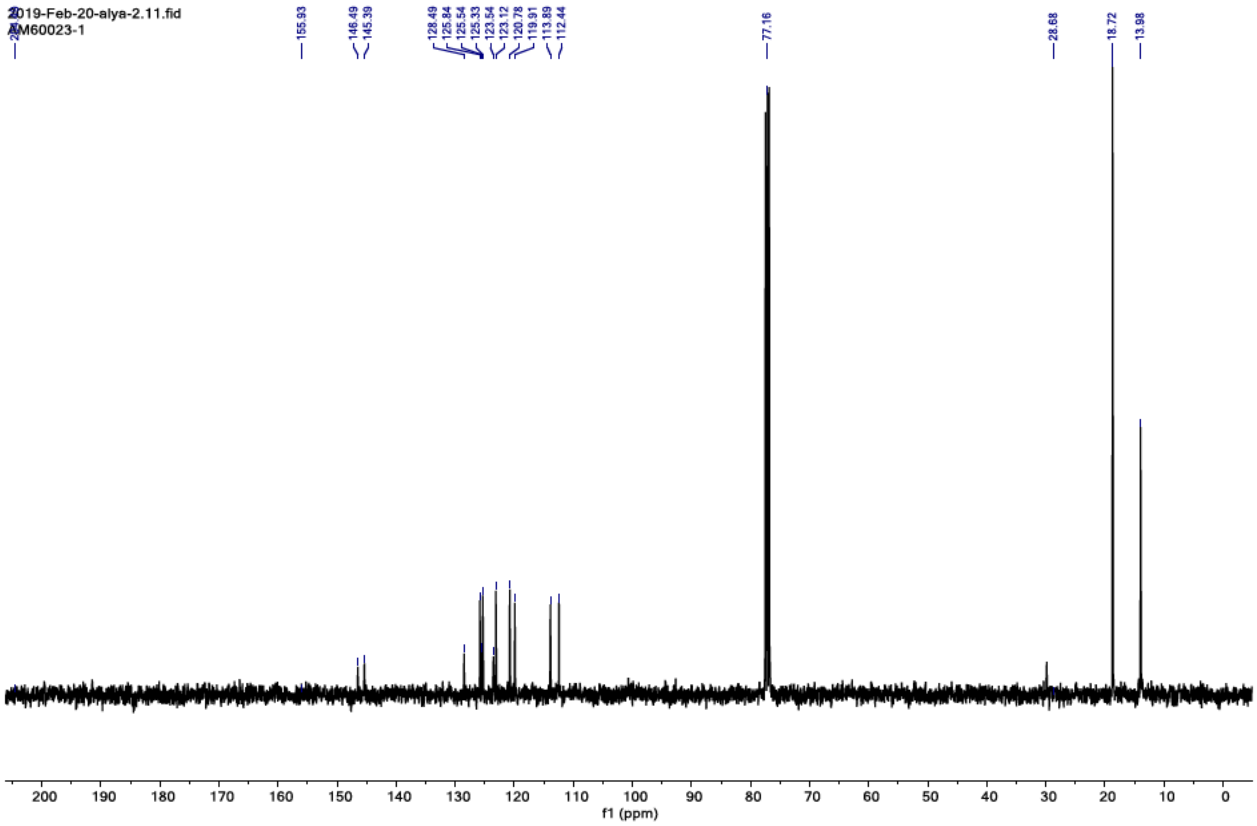
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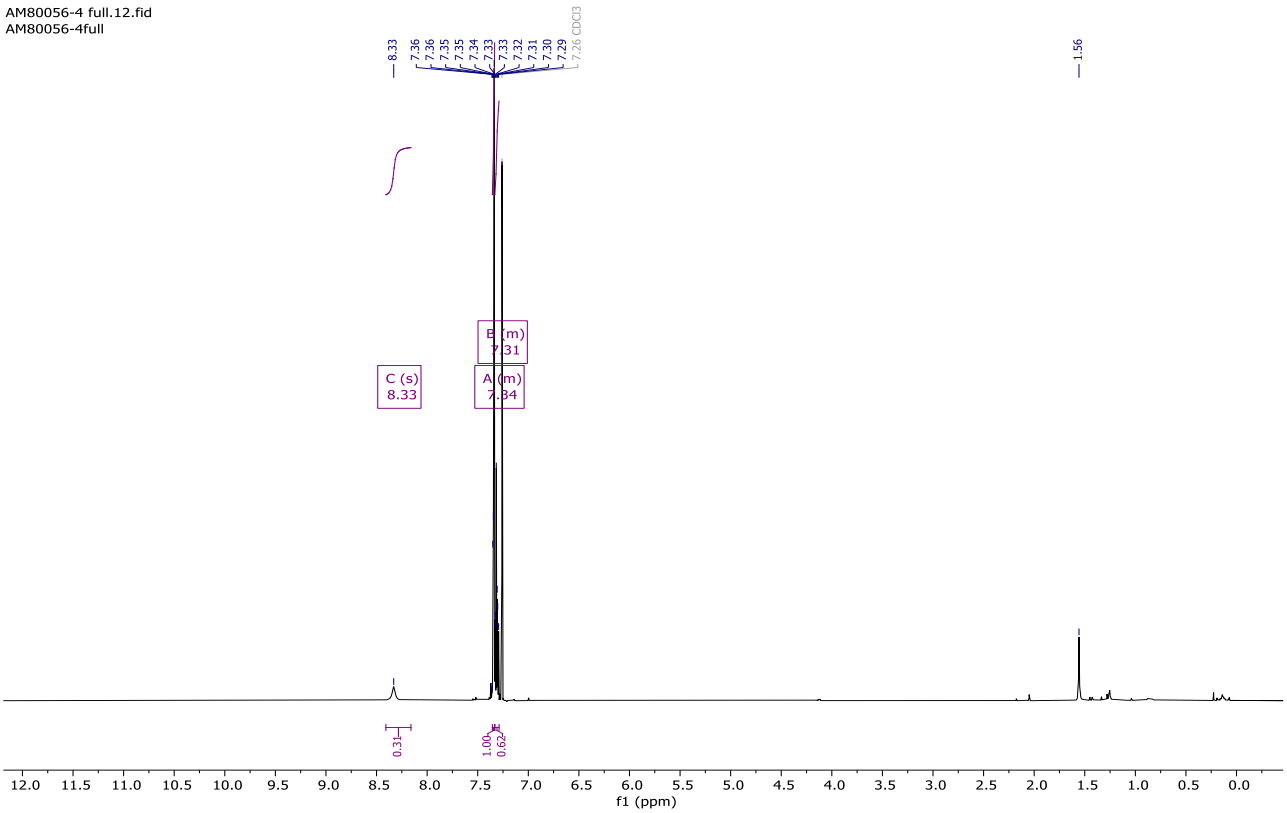
^{1}H-NMR data for 4-Chloro-9-(triisopropylsilyl)-9H-carbazole 109



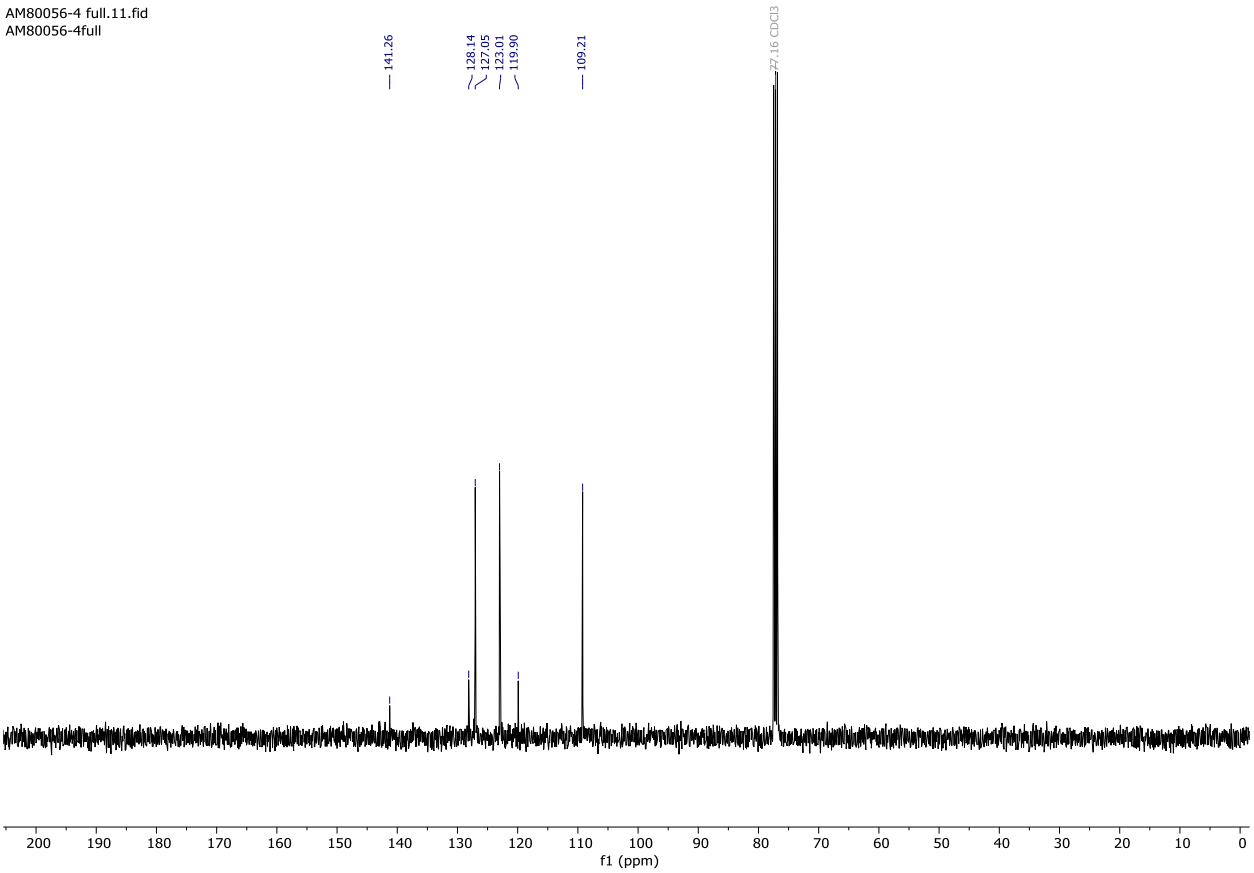
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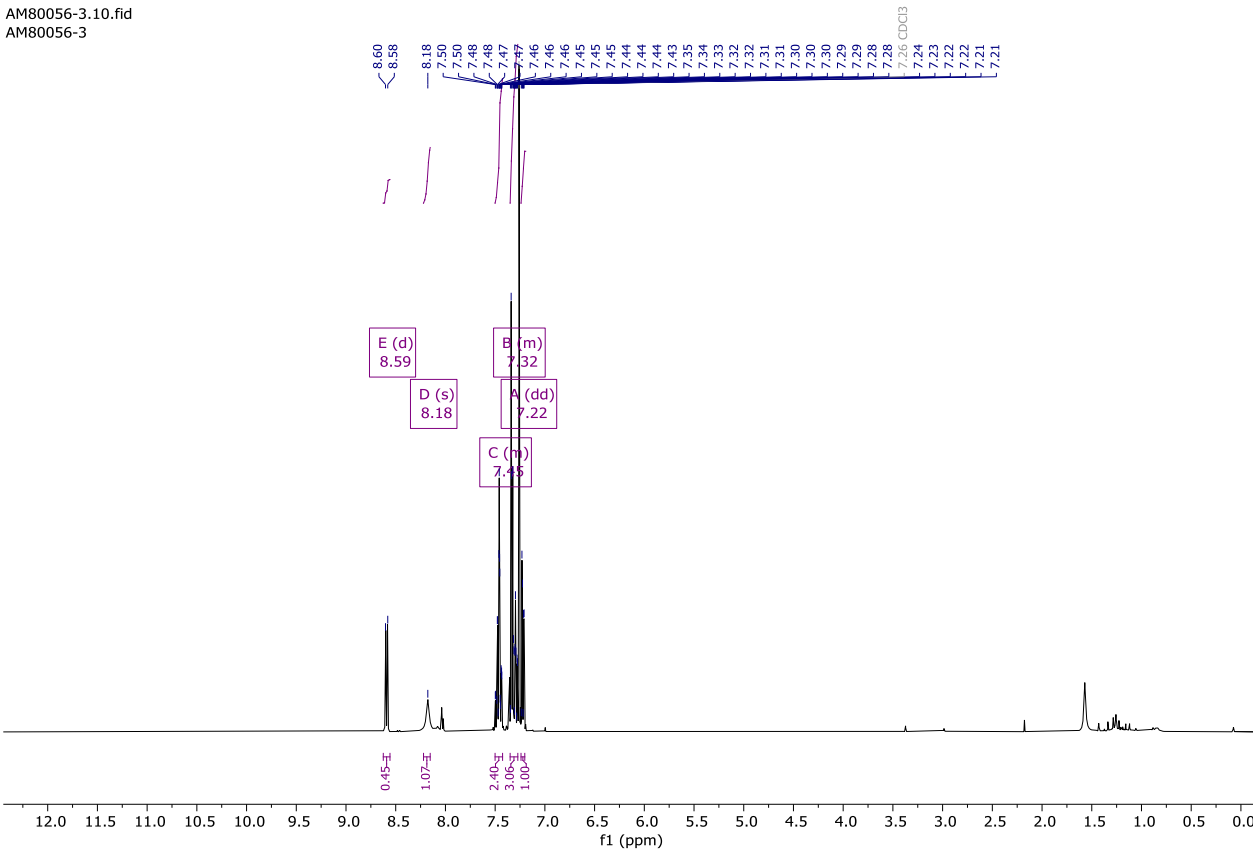
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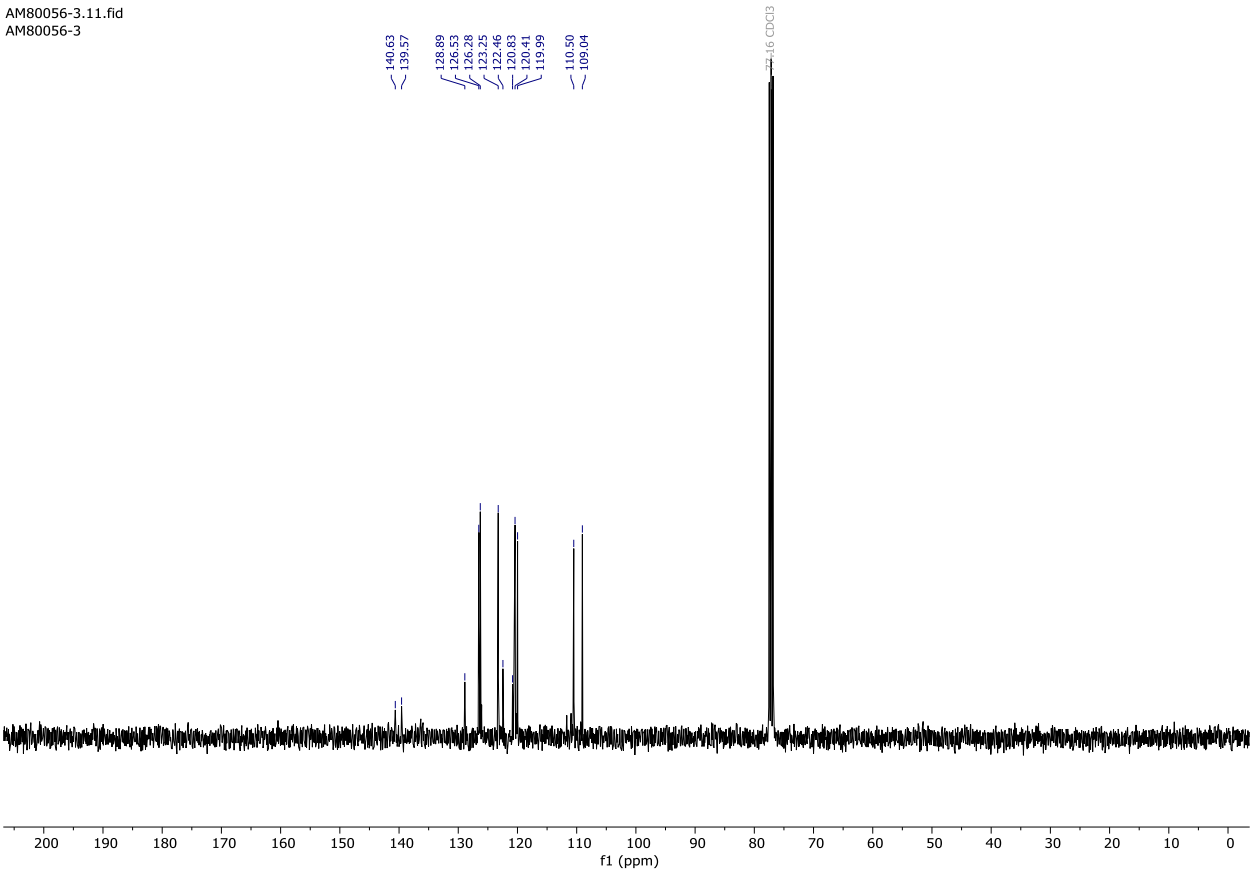
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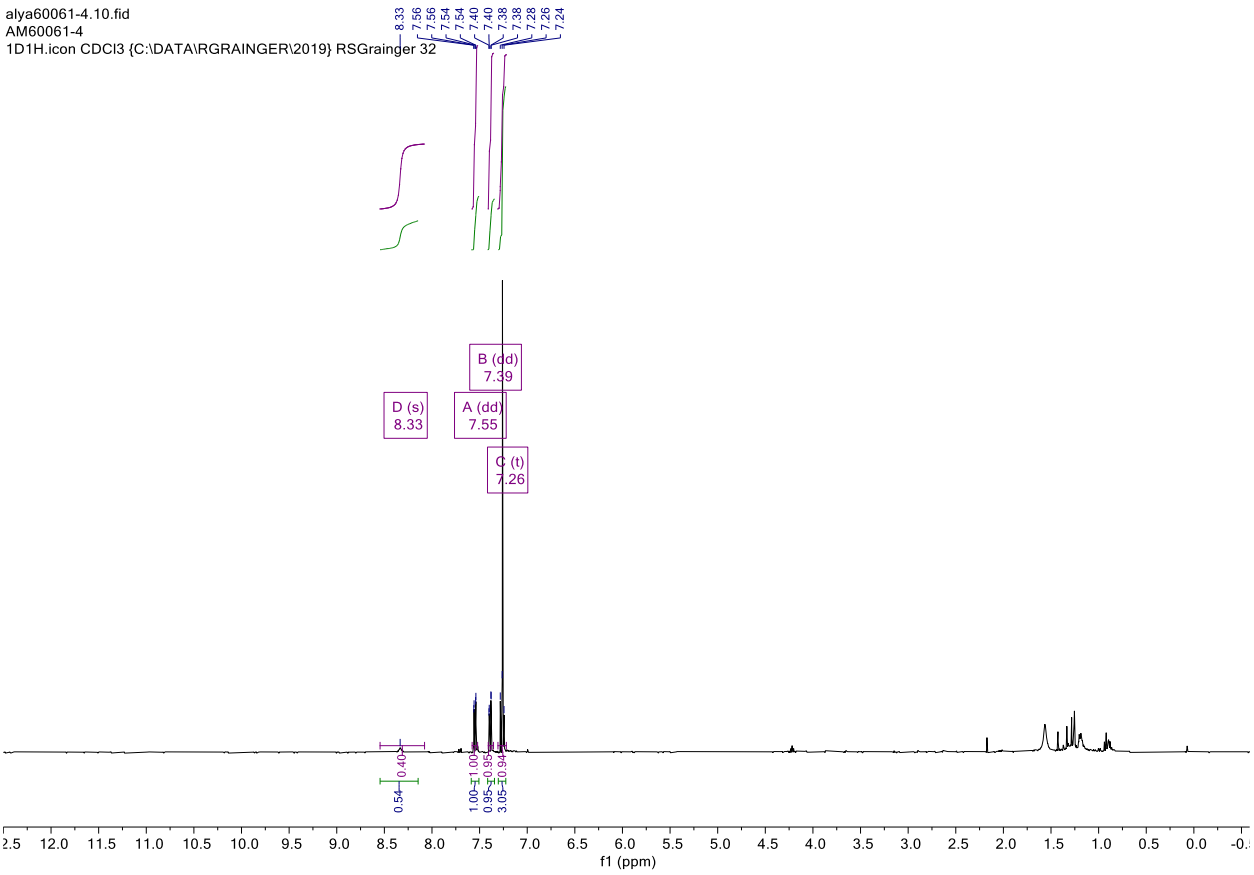
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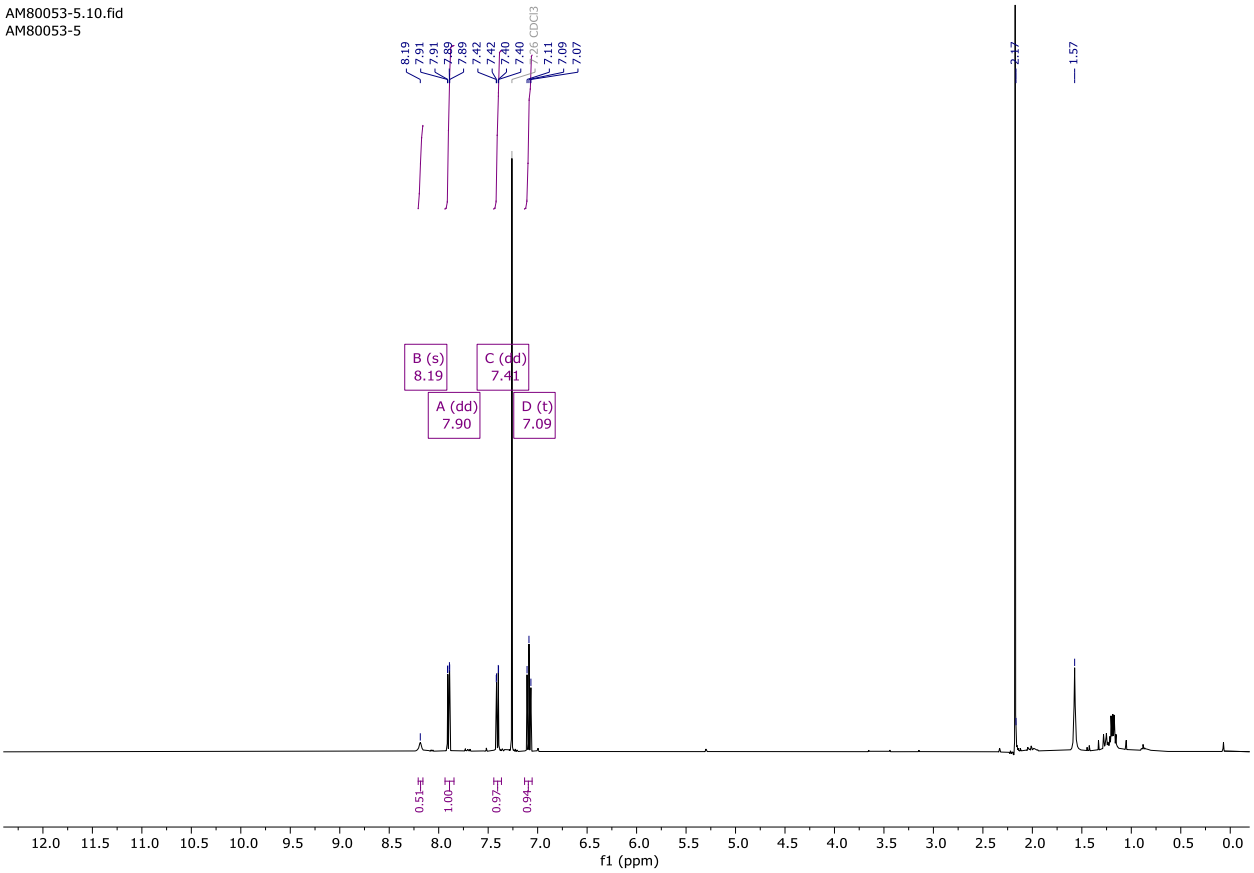
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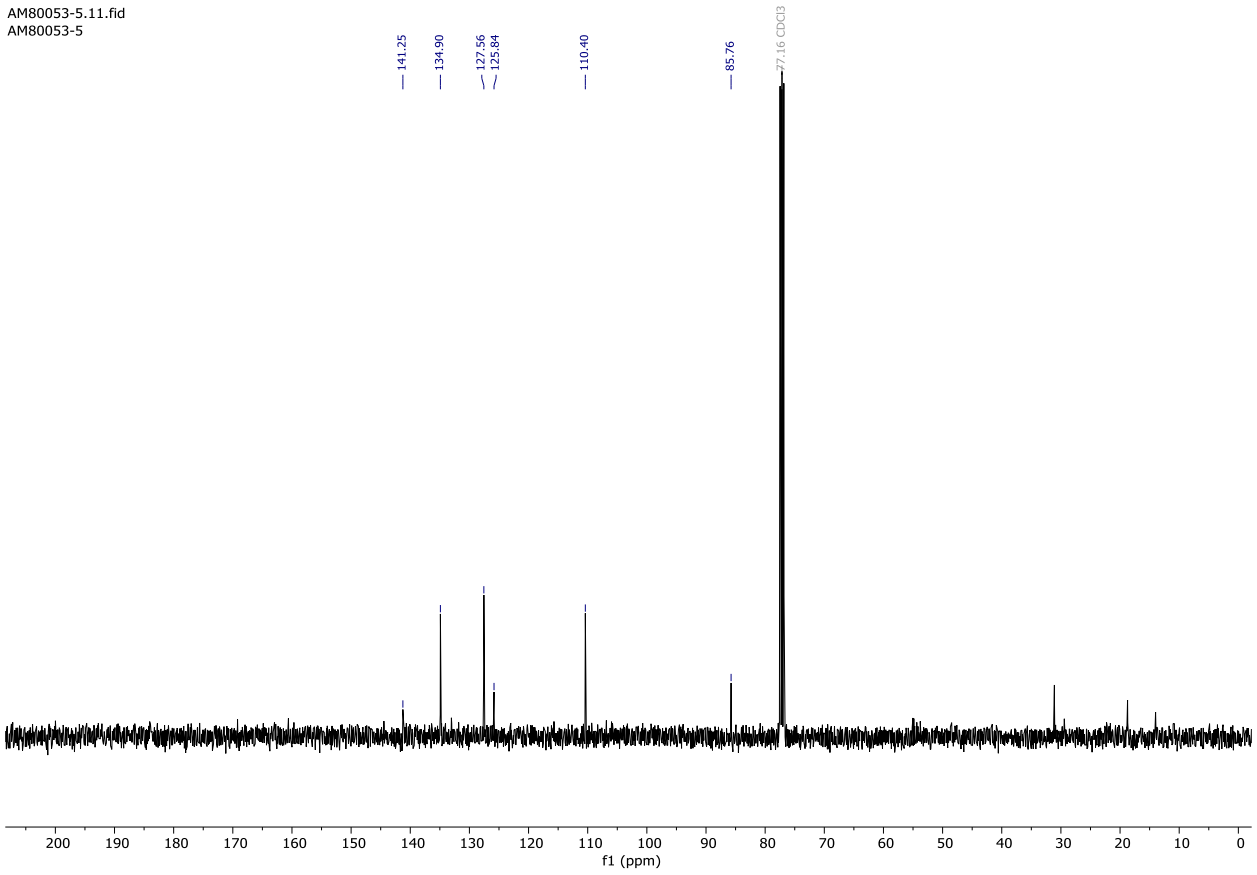
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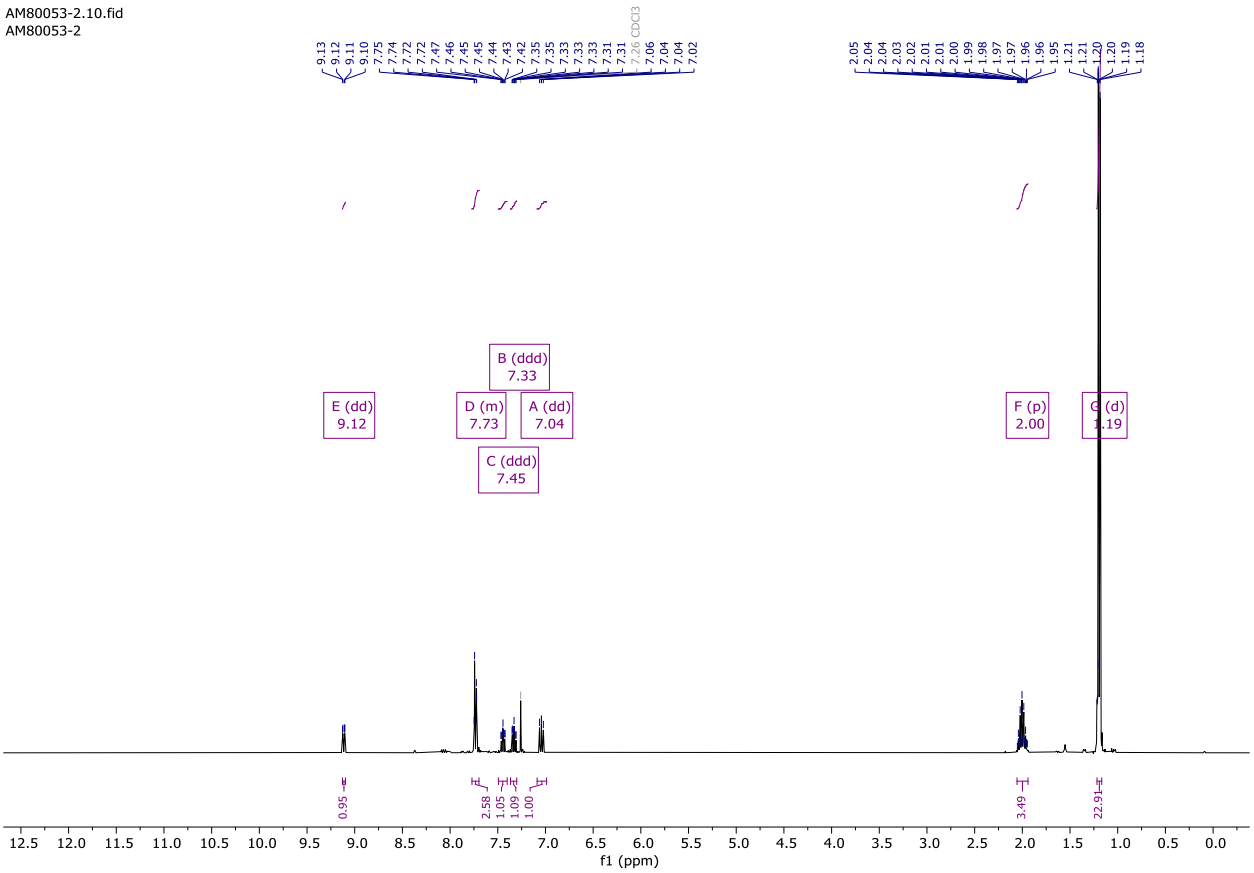
^{1}H-NMR data for 4,5-diiodo-9H-carbazole 114



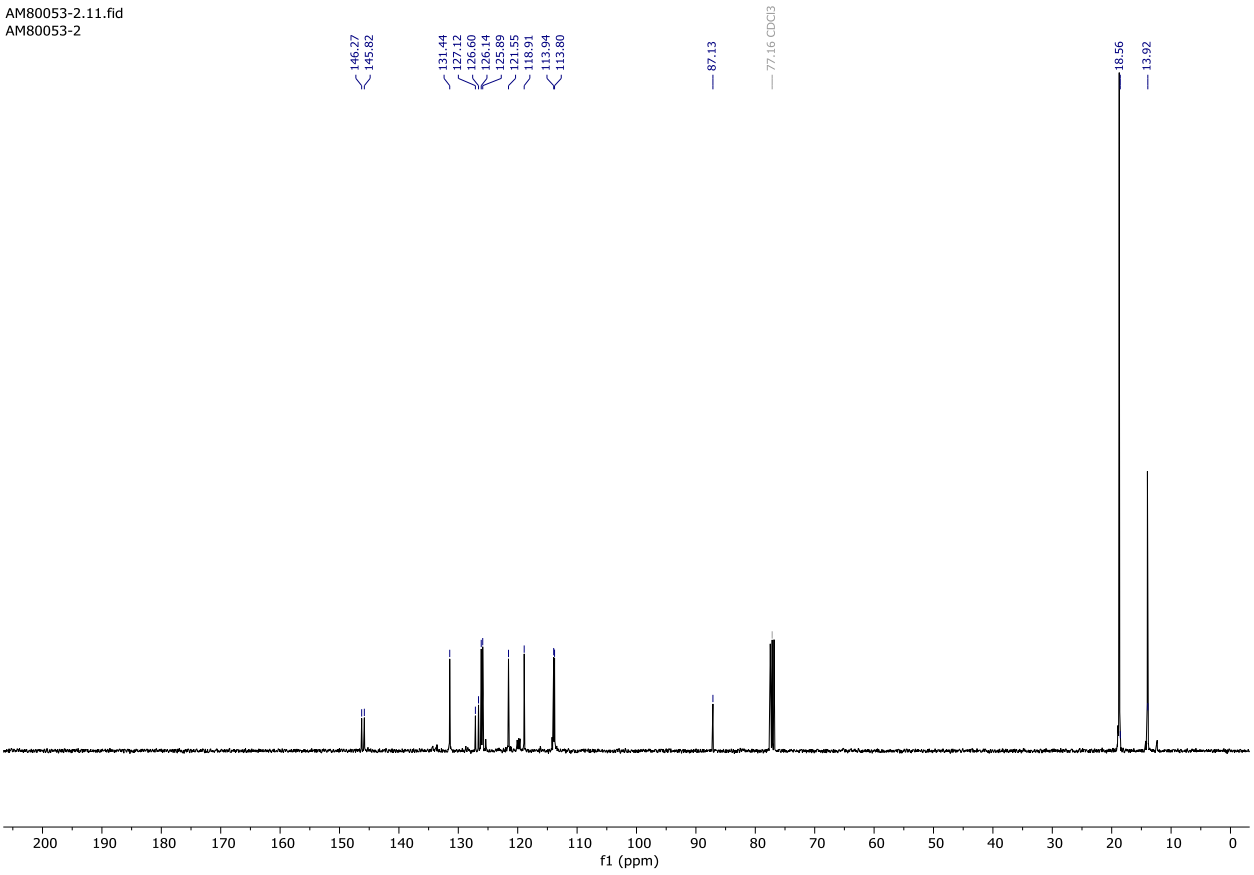
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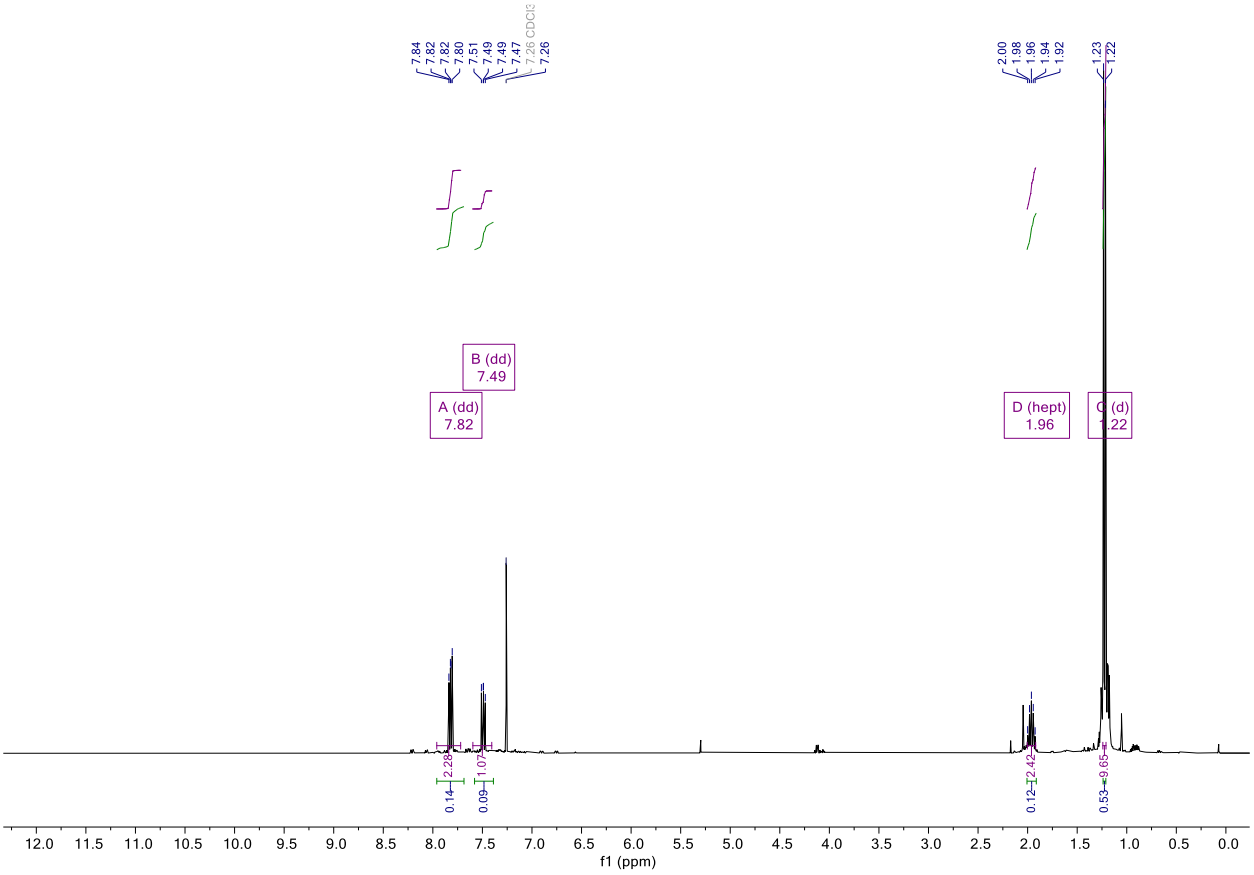
^{1}H-NMR data of 4-Iodo-9-(triisopropylsilyl)-9H-carbazole 113



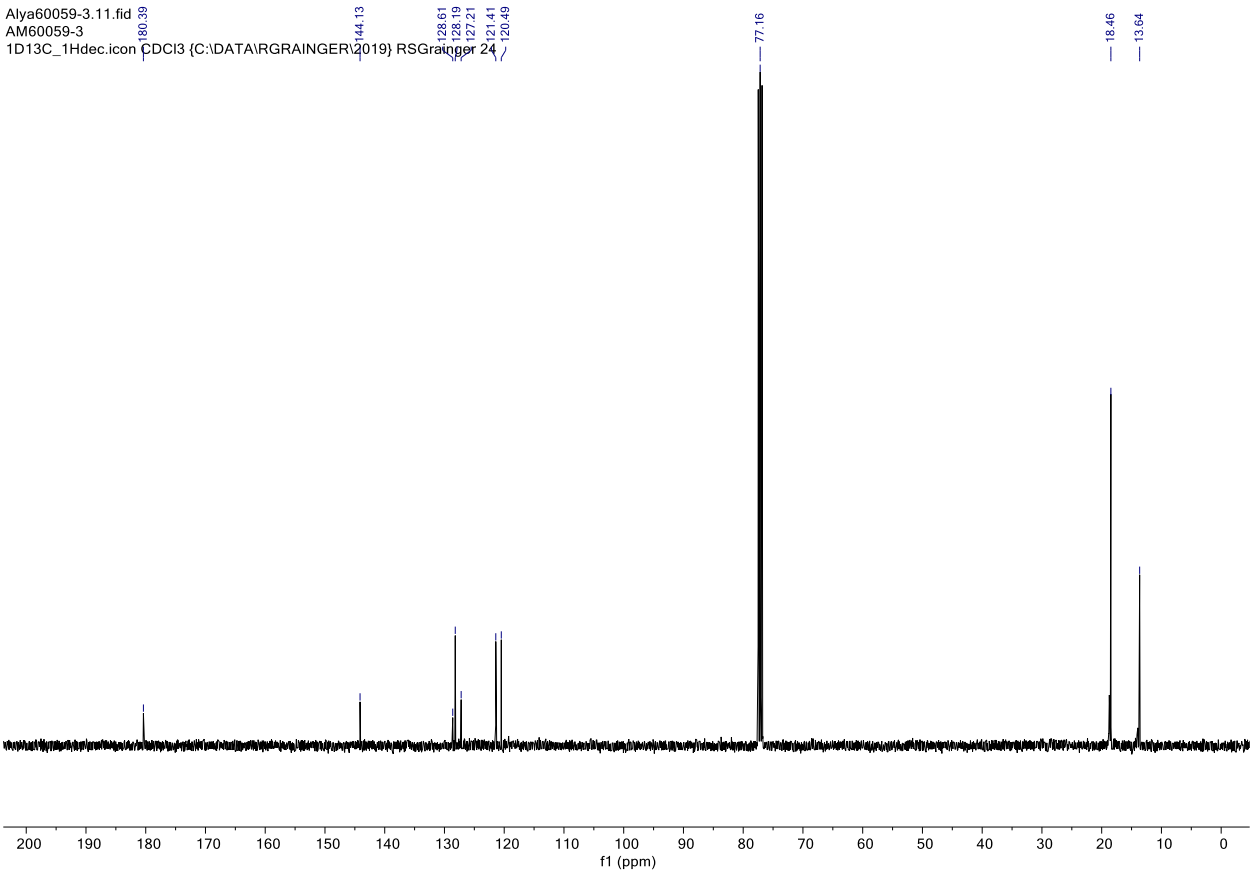
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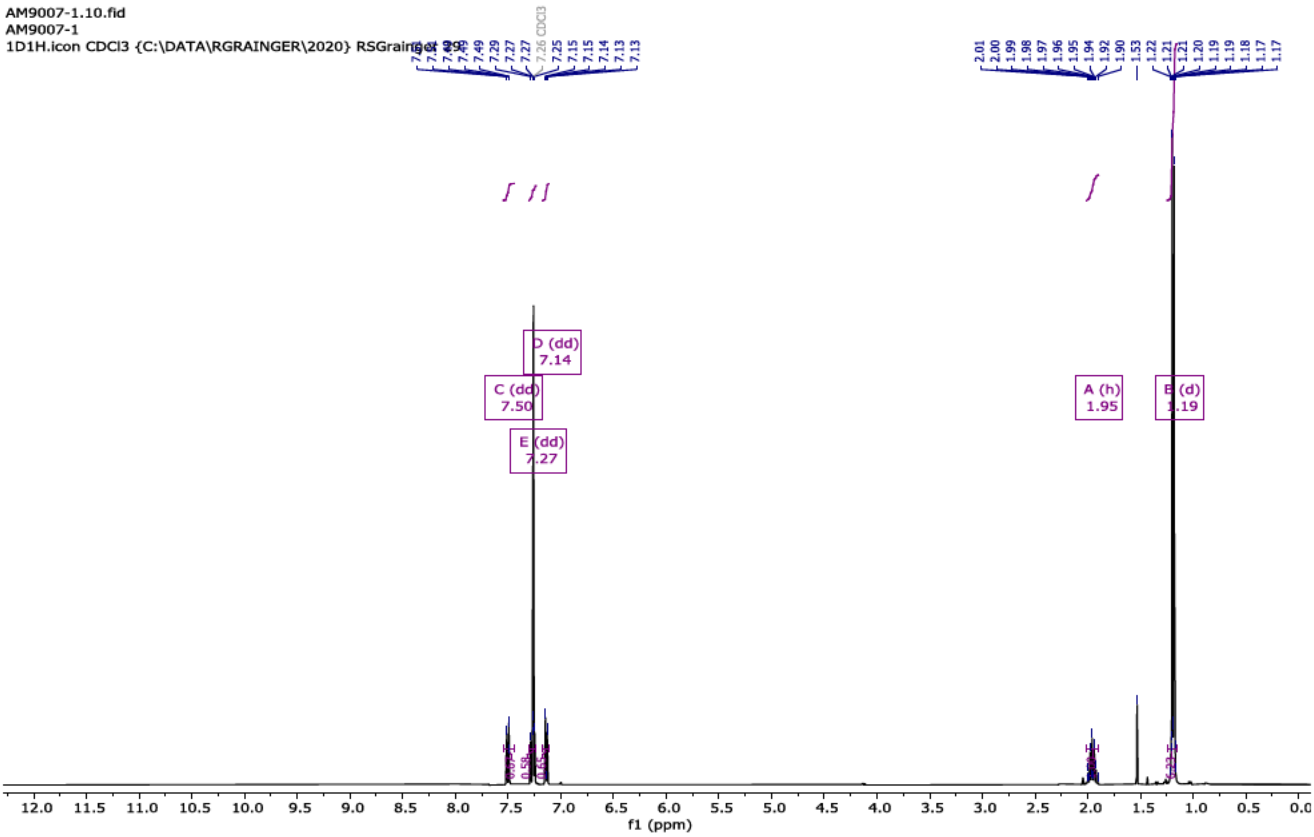
^{1}H-NMR data for 4-(triisopropylsilyl)-4H-benzo[def]carbazole-8,9-dione 114



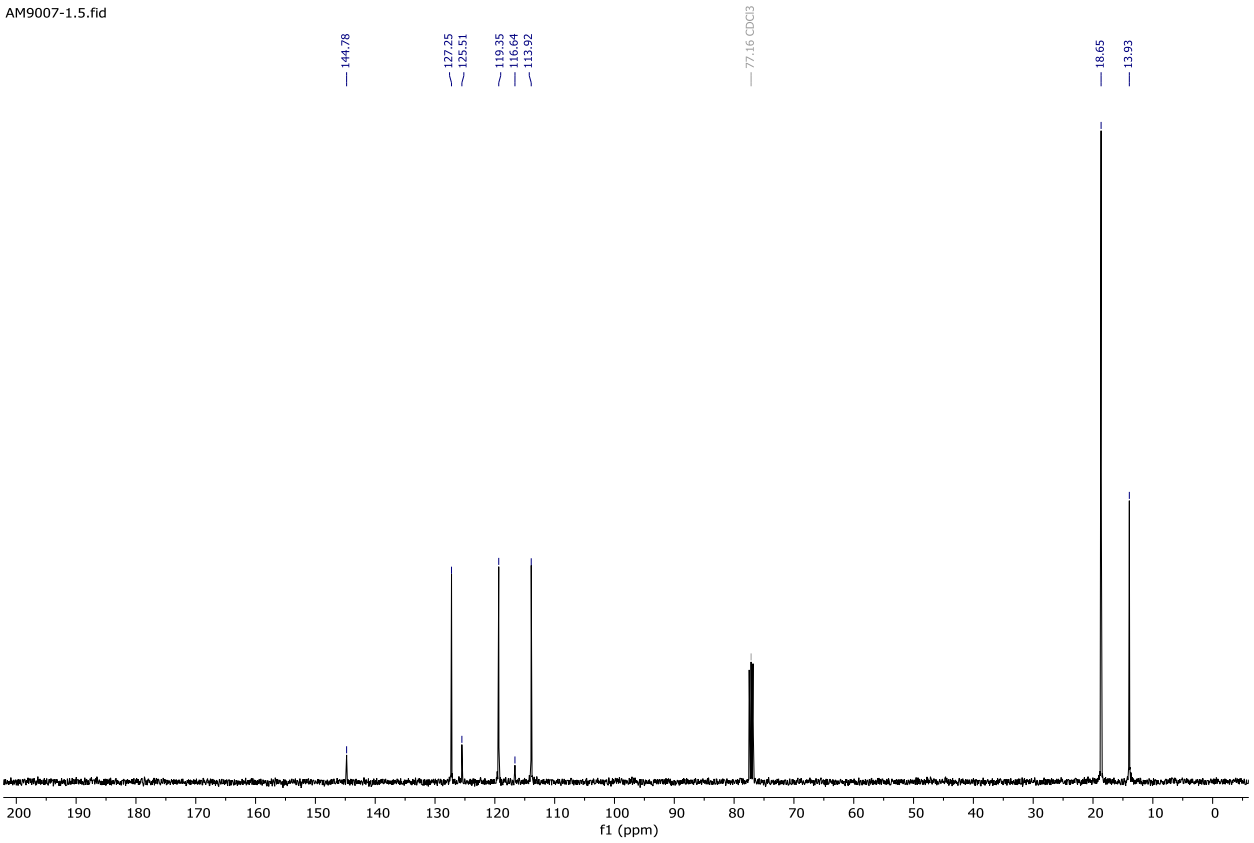
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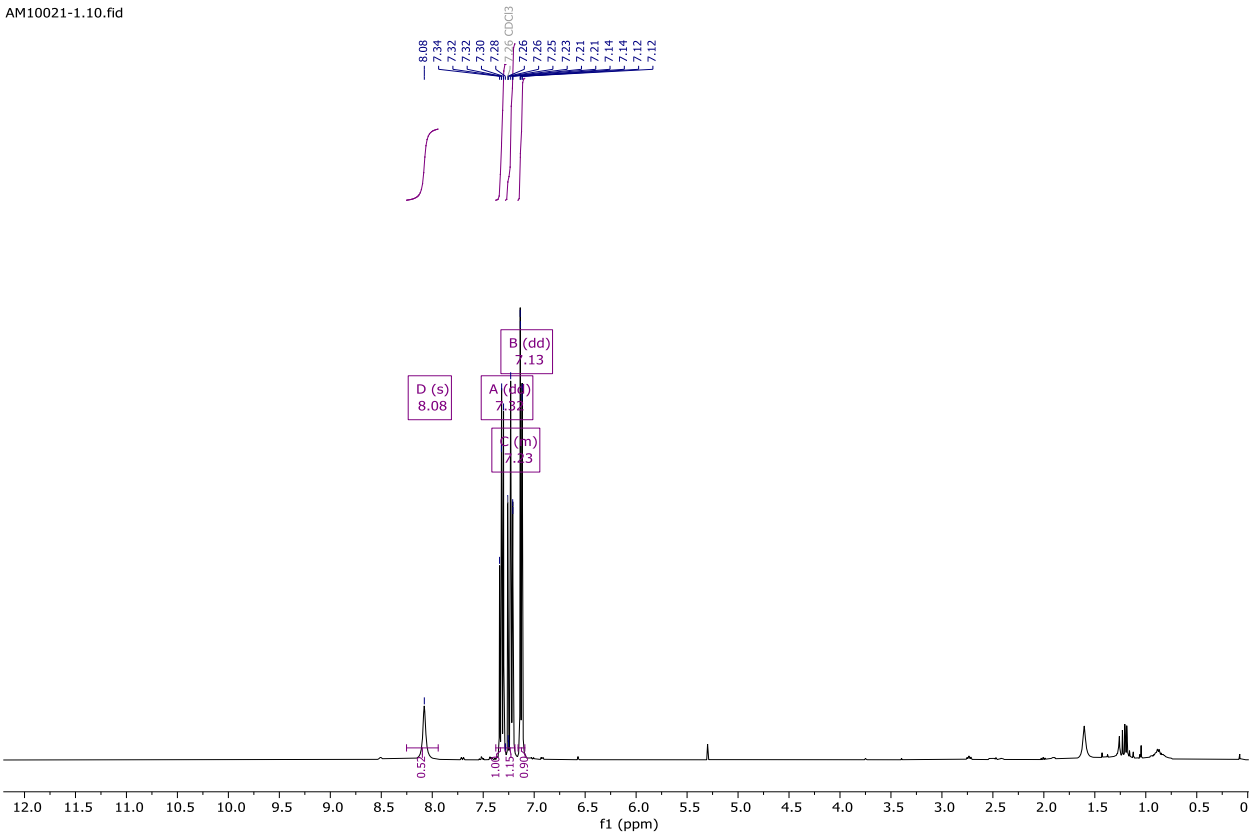
^{1}H-NMR data for 9-(triisopropylsilyl)-9H-[1,2]diselenino[3,4,5,6-def]carbazole 88



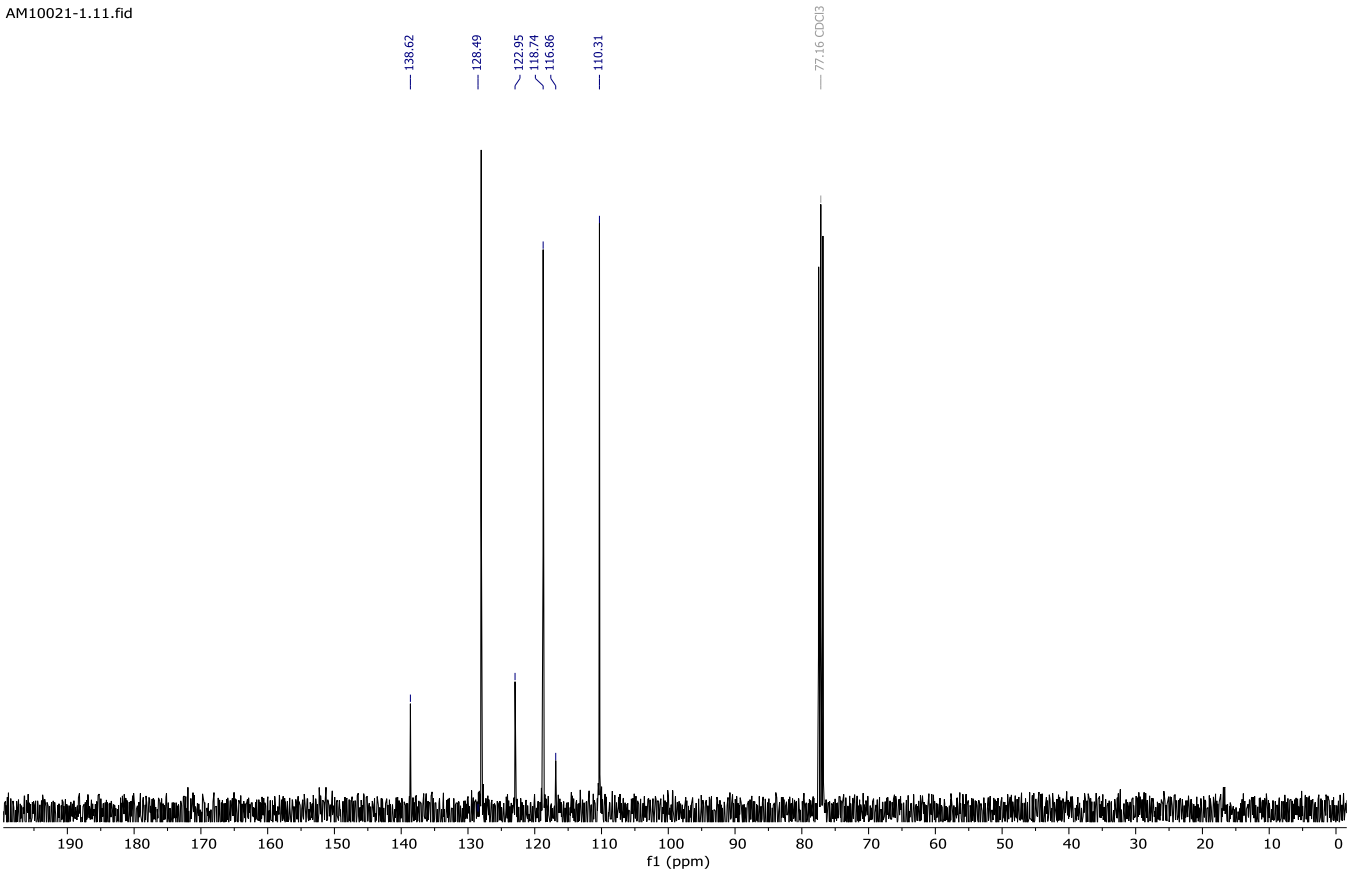
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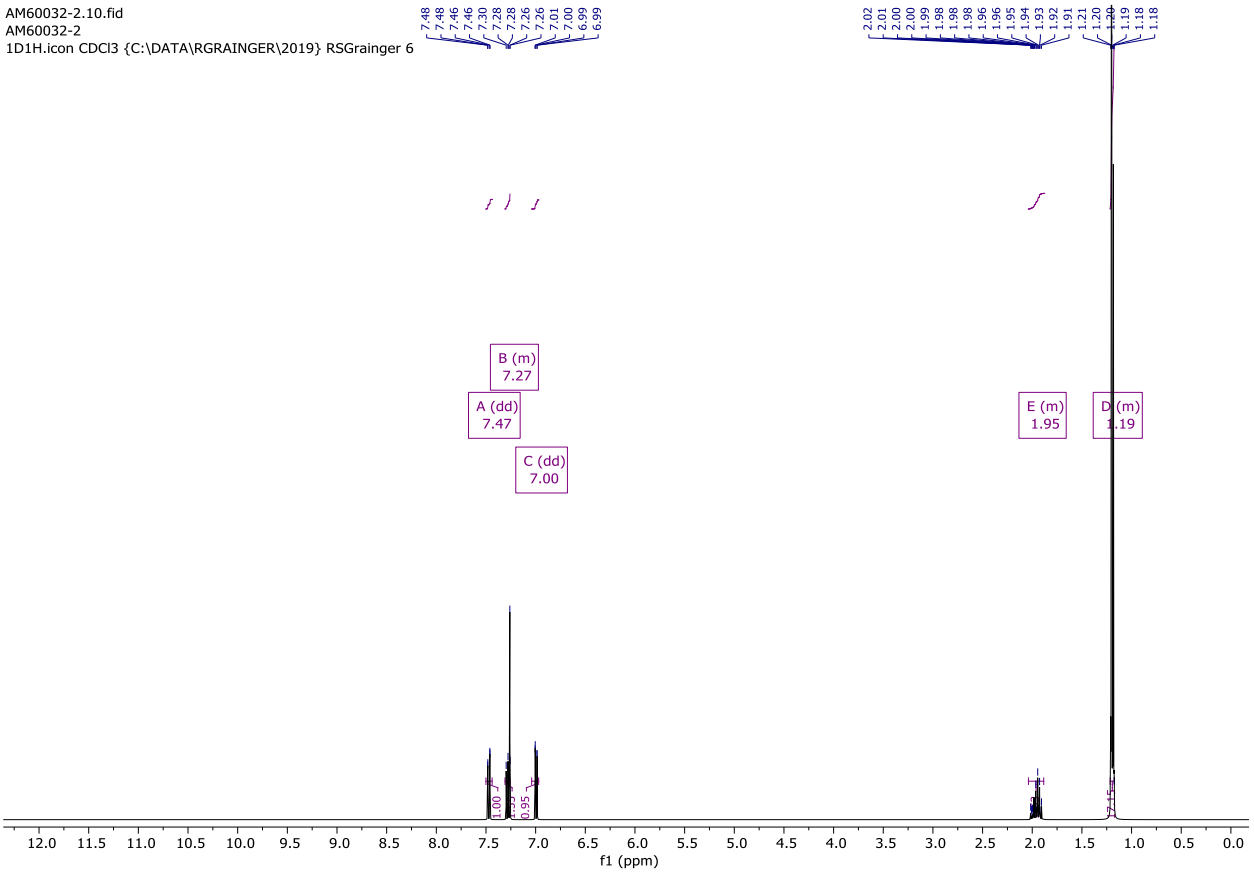
^{1}H-NMR data for 9H-[1,2]diselenino[3,4,5,6-def]carbazole 133



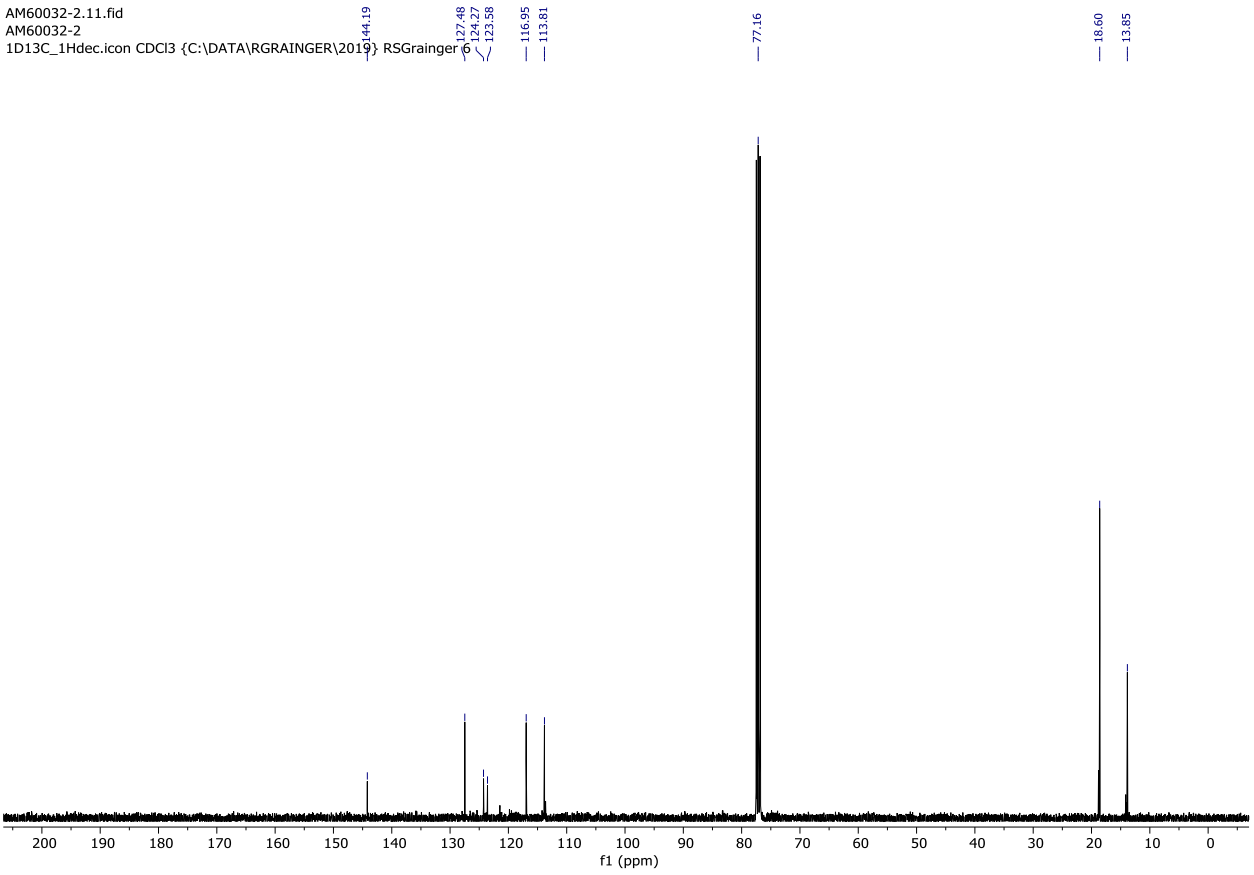
^{13}C-NMR data for 9H-[1,2]diselenino[3,4,5,6-def]carbazole 133



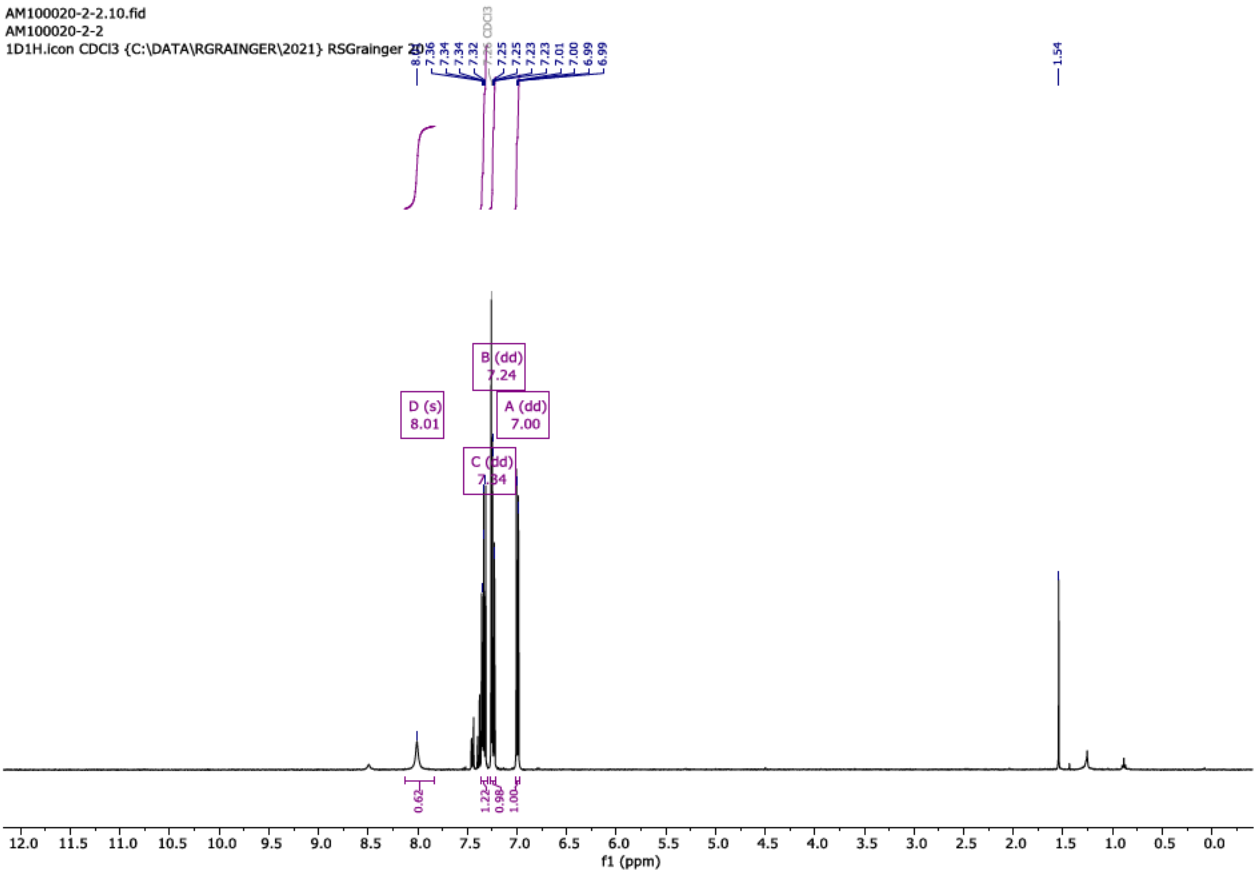
^{1}H-NMR data for 9-(triisopropylsilyl)-9H-[1,2]dithiino[3,4,5,6-def]carbazole 86



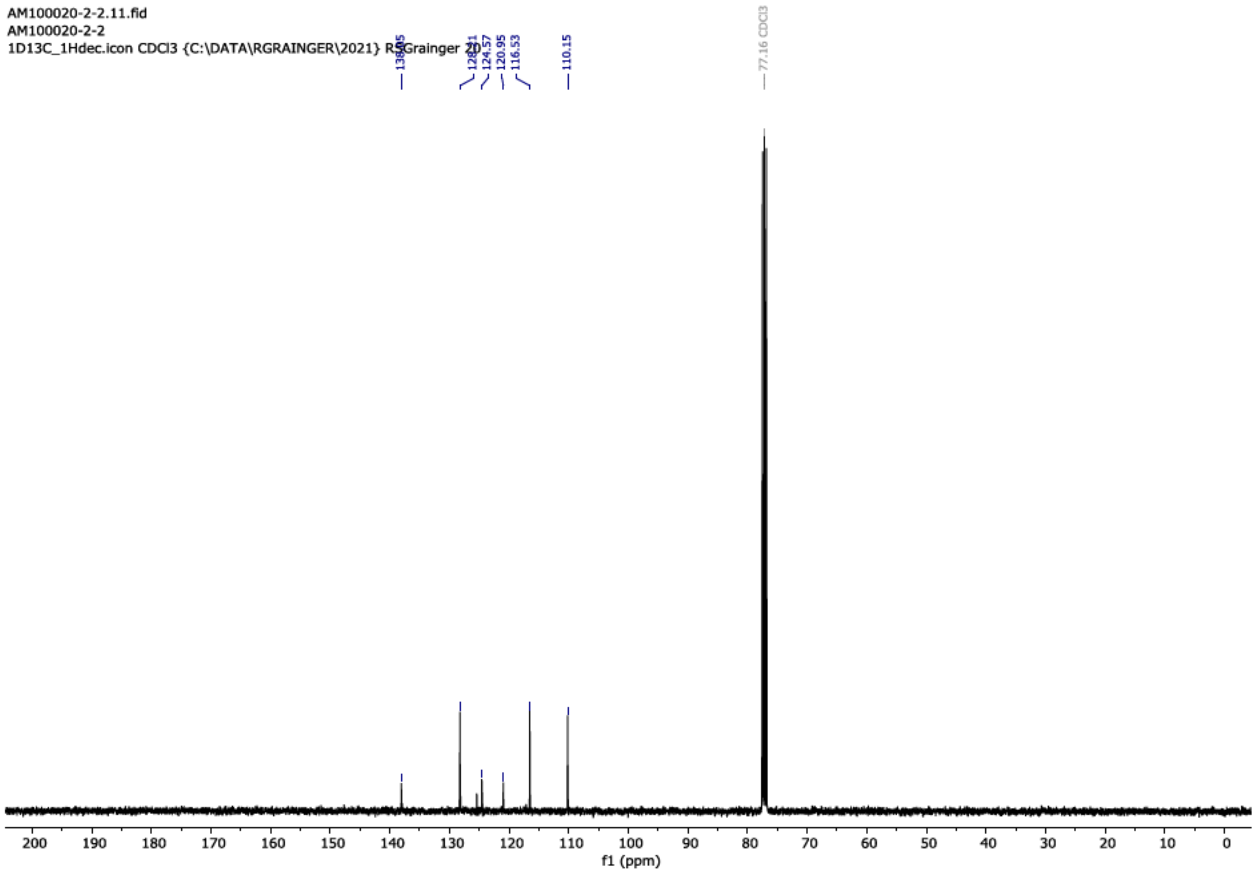
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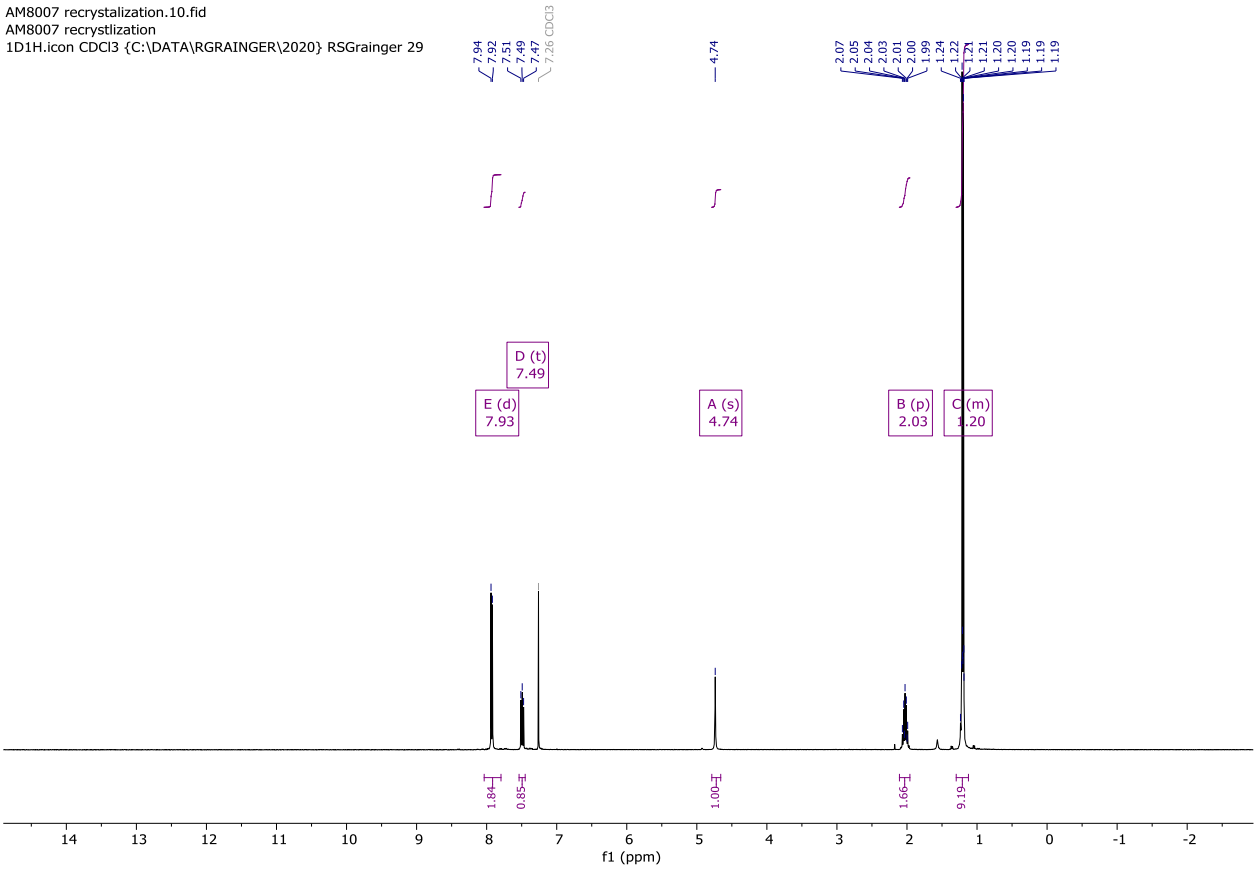
^{1}H-NMR data for 9H-[1,2]dithiino[3,4,5,6-def]carbazole 134



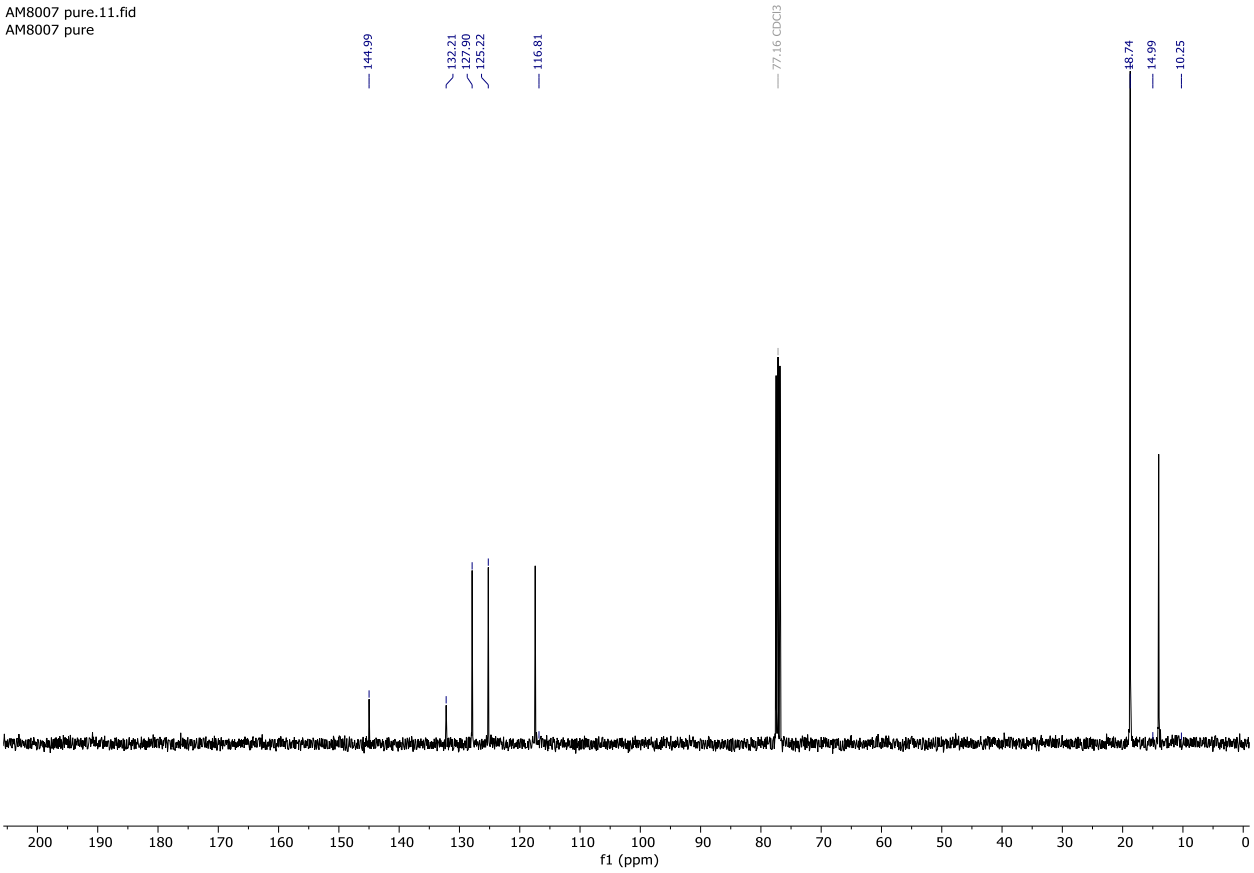
^{13}C-NMR data for 9H-[1,2]dithiino[3,4,5,6-def]carbazole 134



^{1}H-NMR data for 4-(triisopropylsilyl)-4H-[1,2,7]oxadiborepino[3,4,5,6-def]carbazole-8,10-diol 121

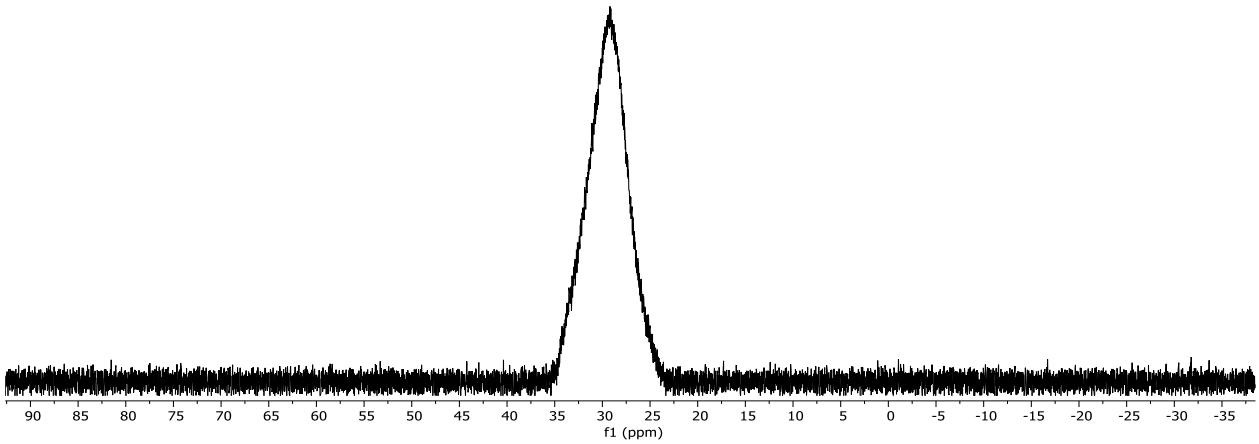


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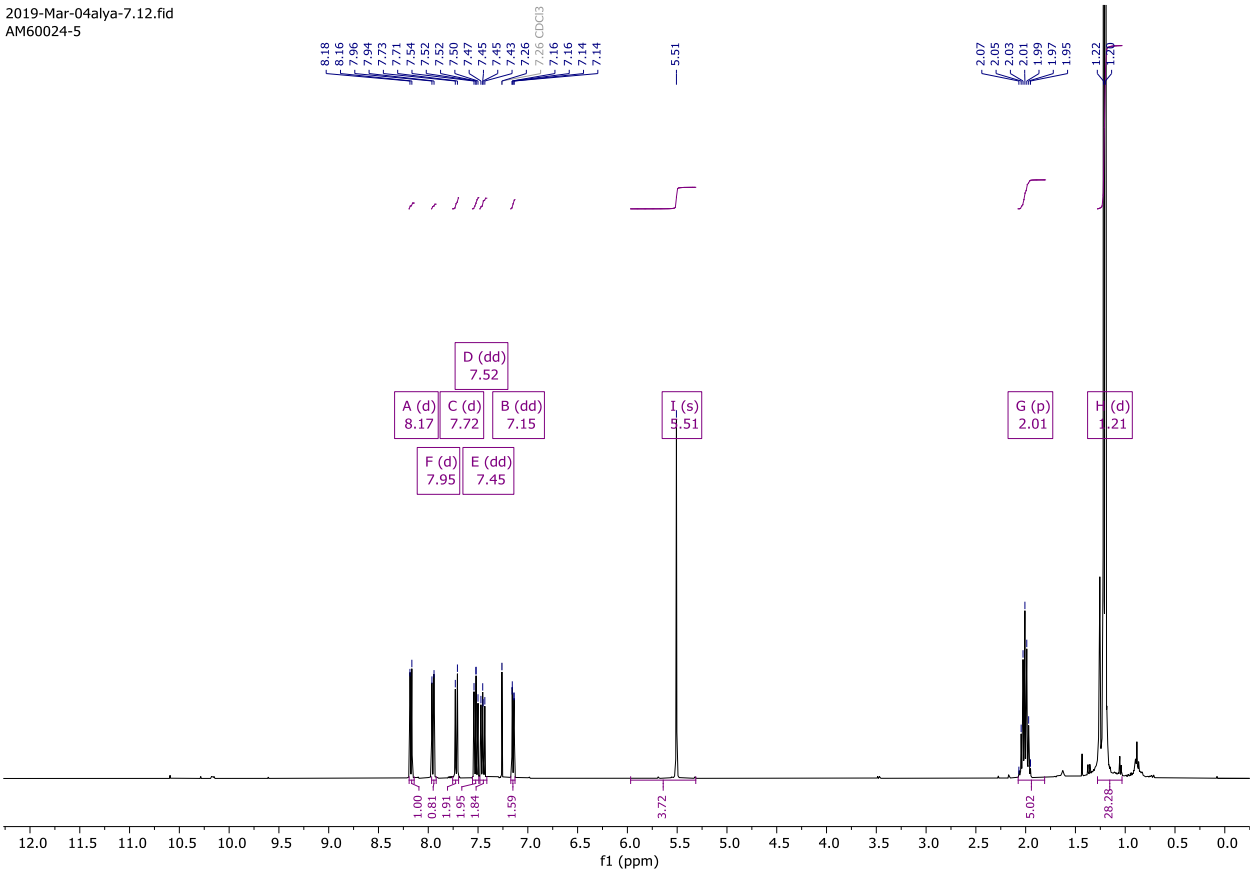


^{19}B-NMR data for 4-(triisopropylsilyl)-4H-[1,2,7]oxadiborepino[3,4,5,6-def]carbazole-8,10-diol 121

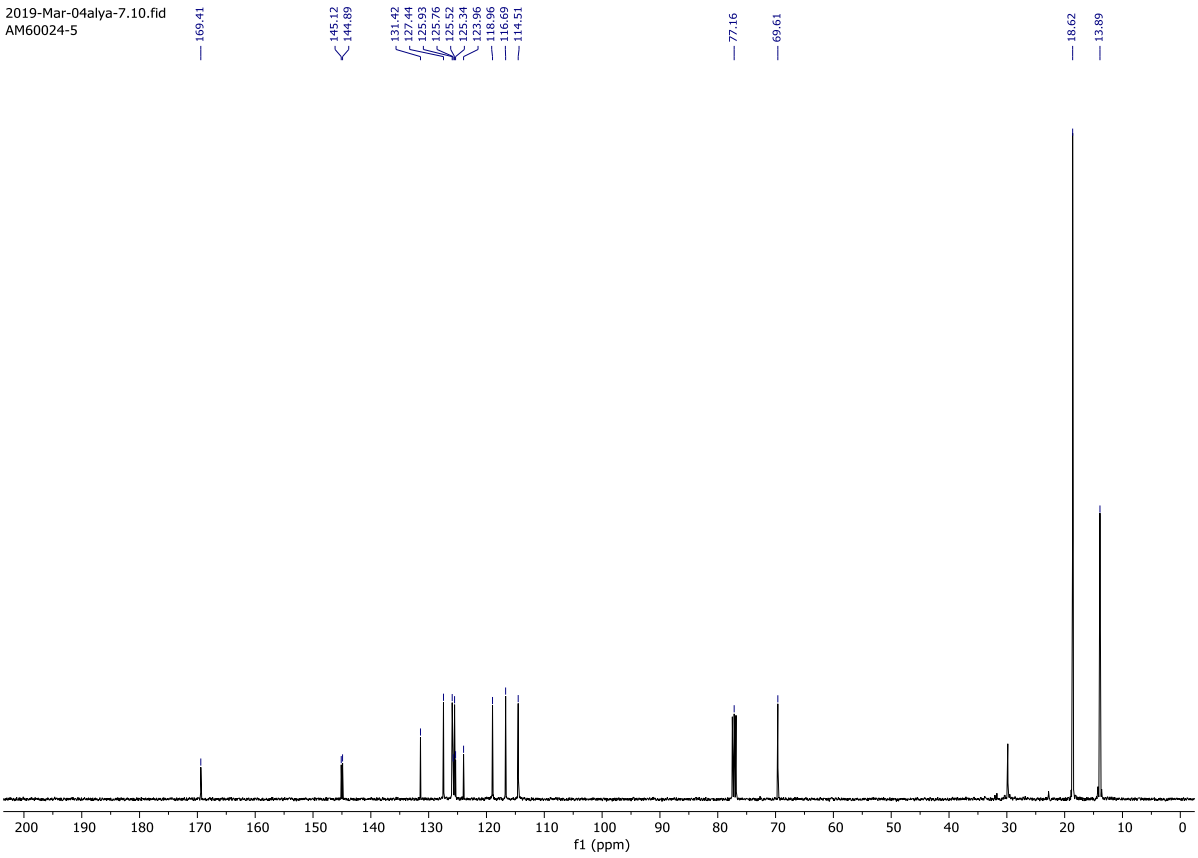
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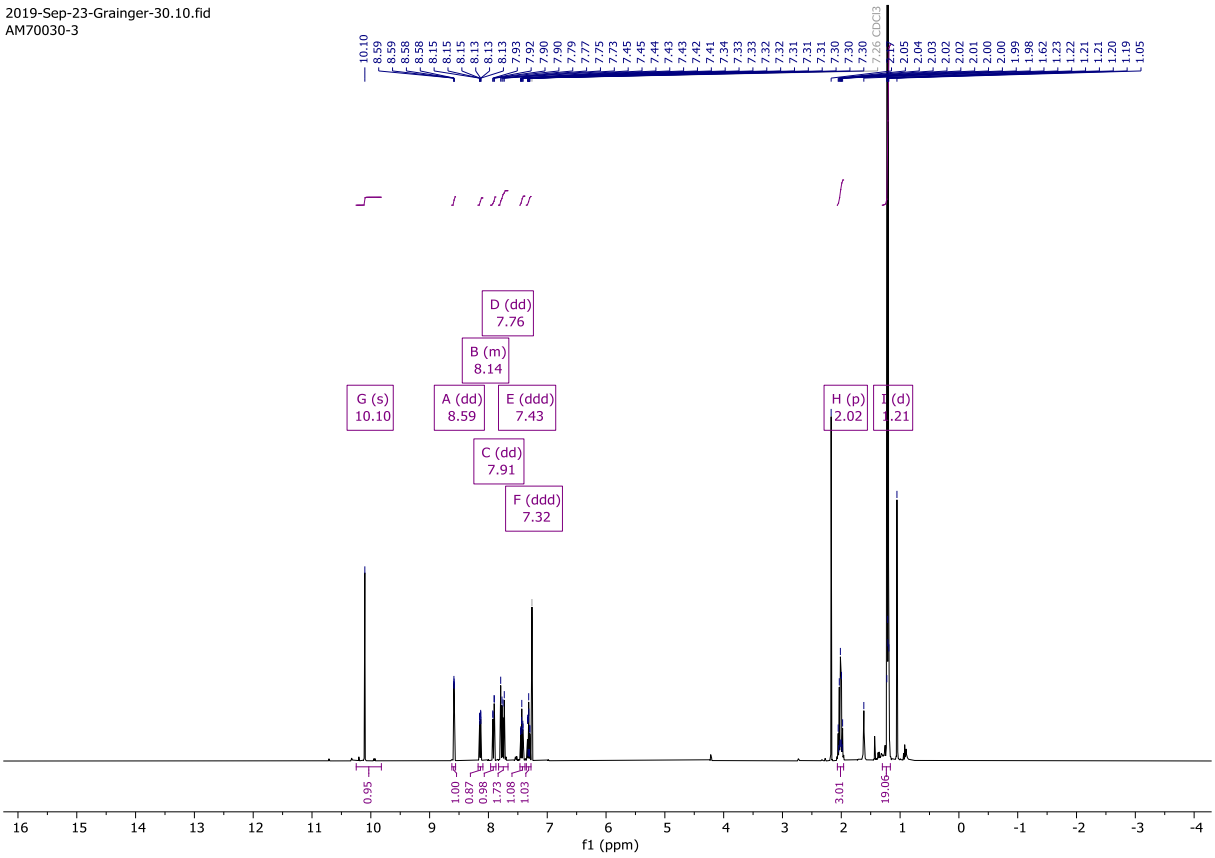
^{1}H-NMR data for4-(triisopropylsilyl)-4,10-dihydro-8H-oxepino[3,4,5,6-def]carbazol-8-one 126



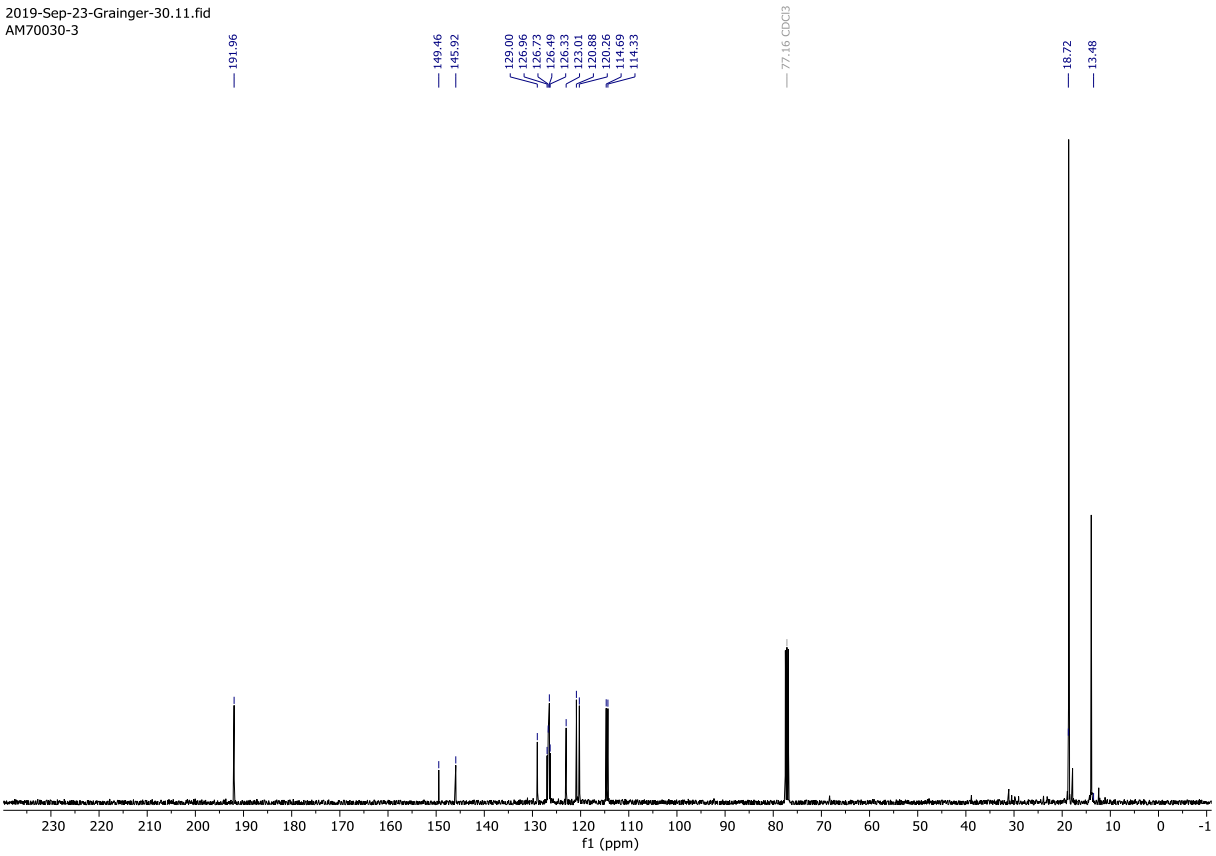
^{13}C-NMR data for4-(triisopropylsilyl)-4,10-dihydro-8H-oxepino[3,4,5,6-def]carbazol-8-one 126



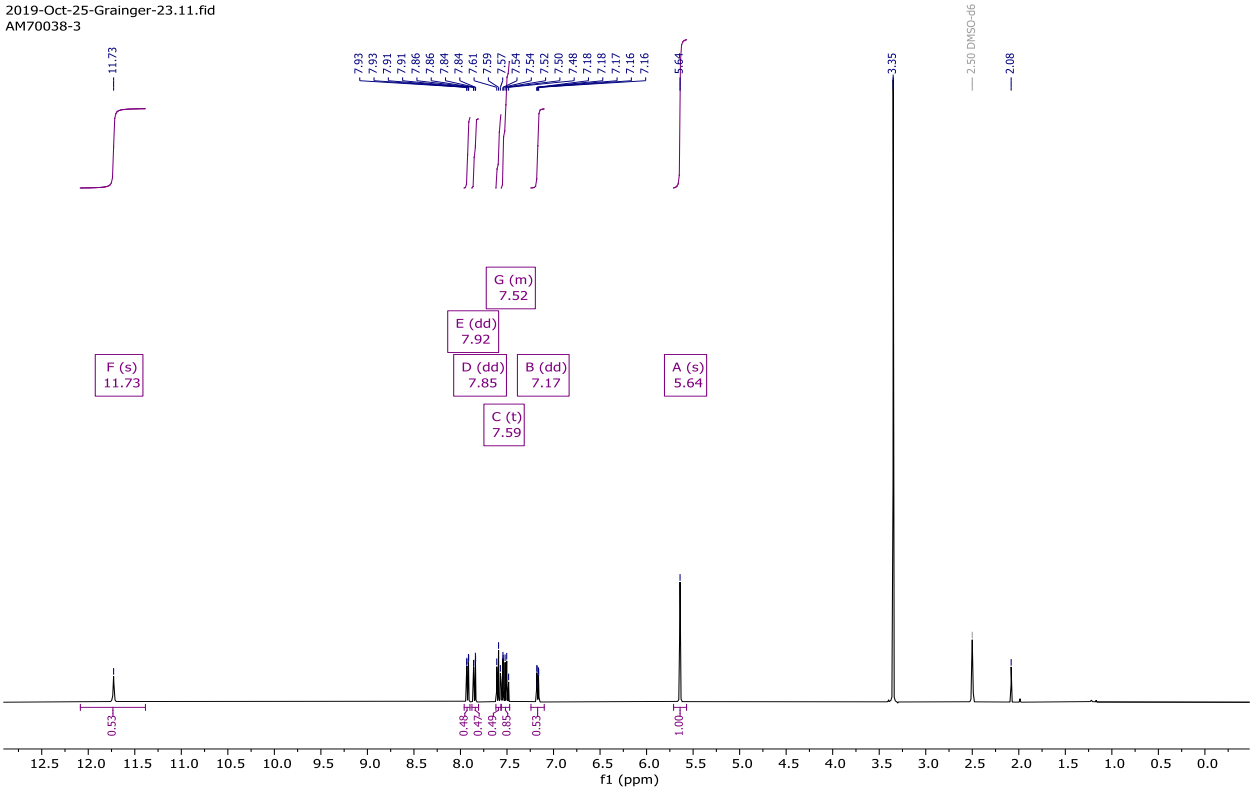
^{1}H-NMR data for 9-(triisopropylsilyl)-9H-carbazole-4-carbaldehyde 127



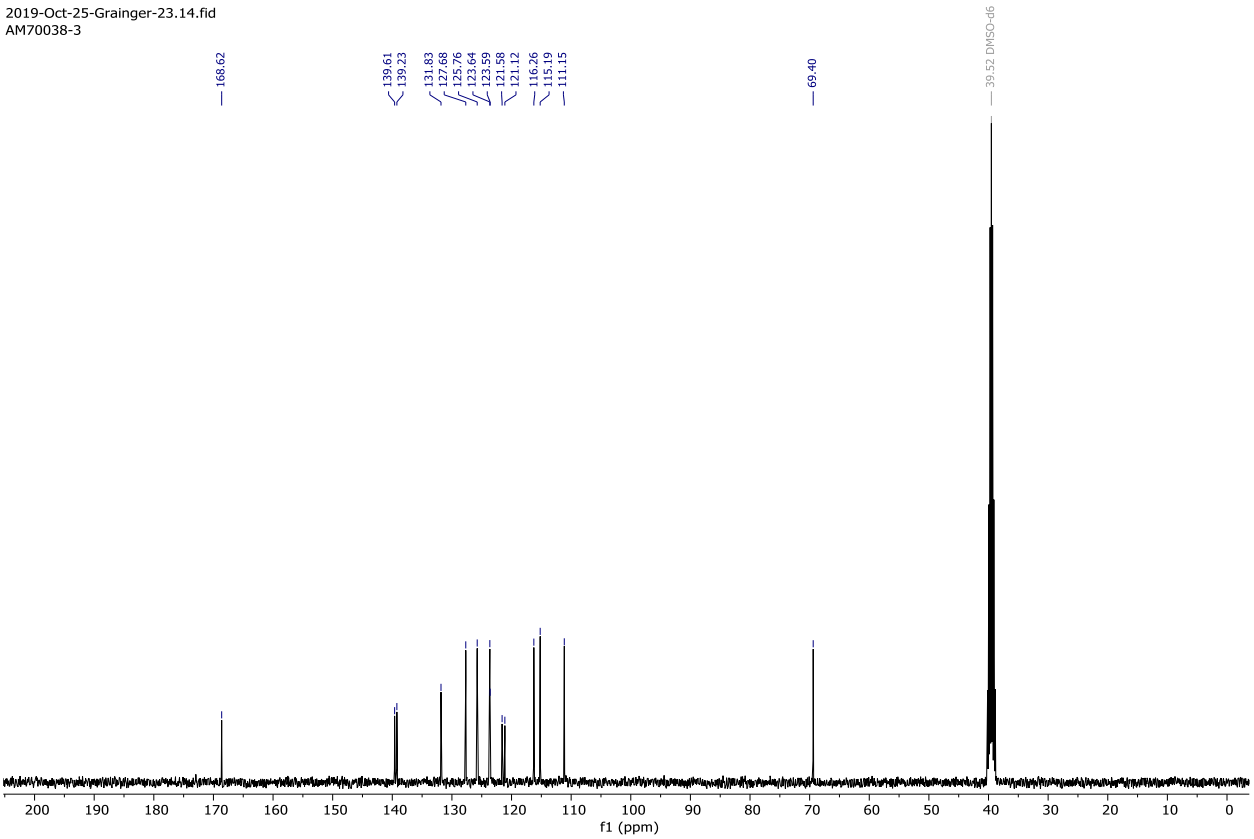
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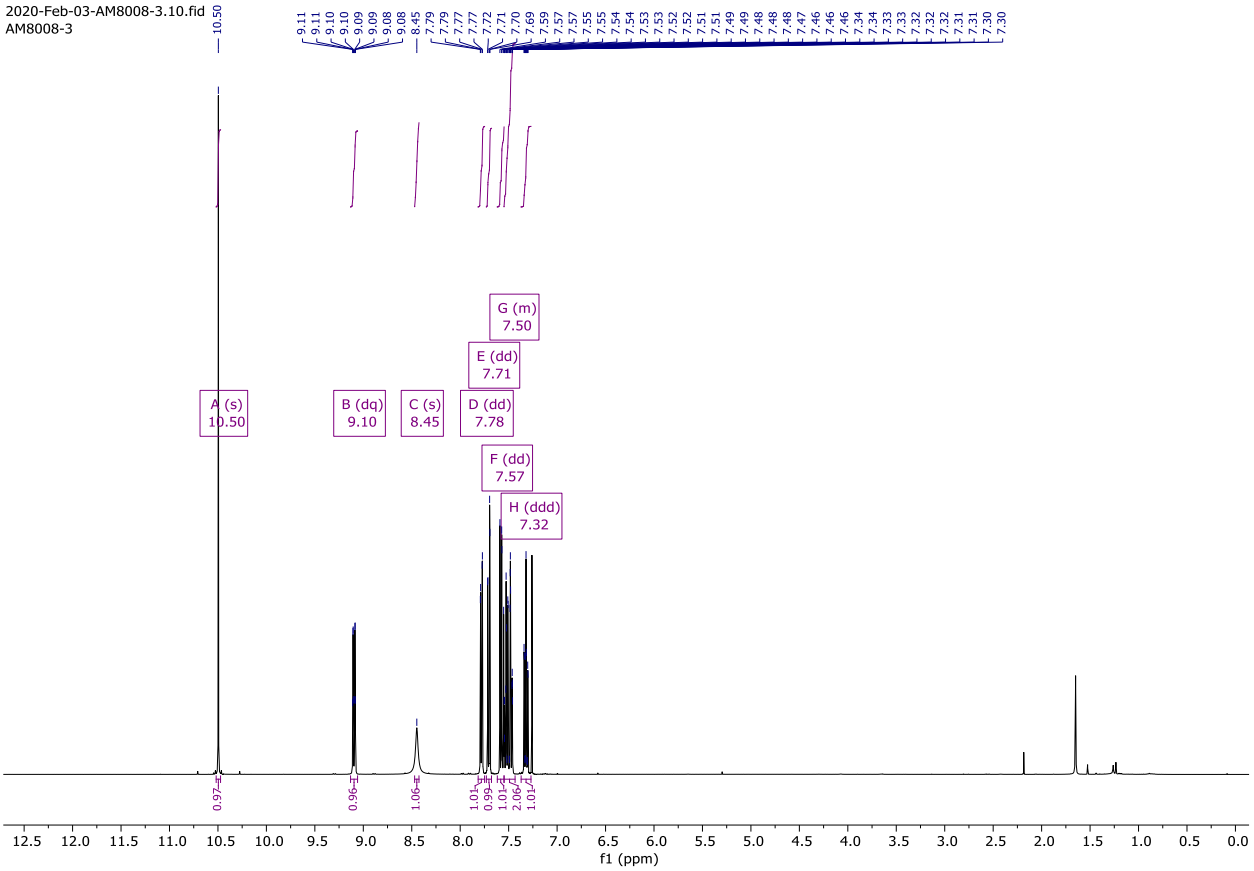
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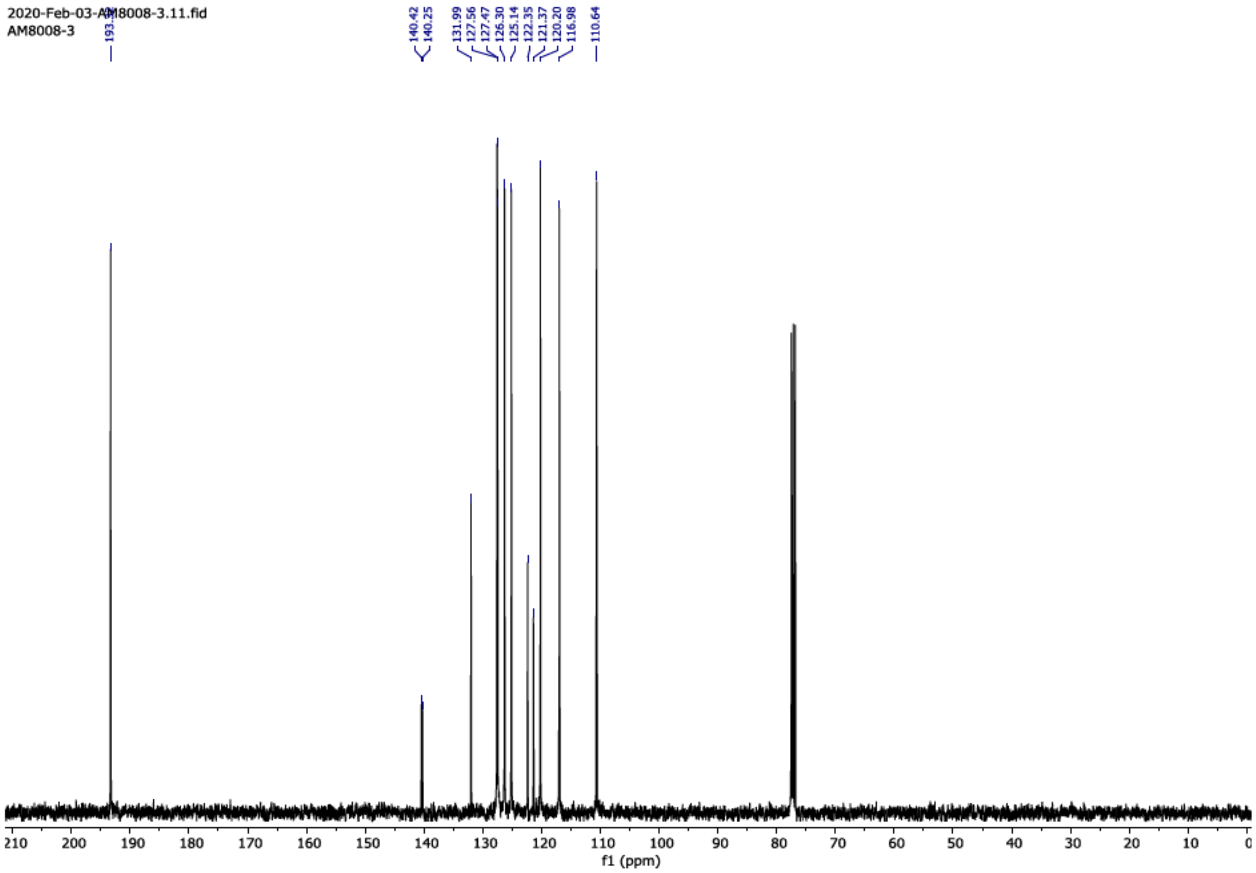
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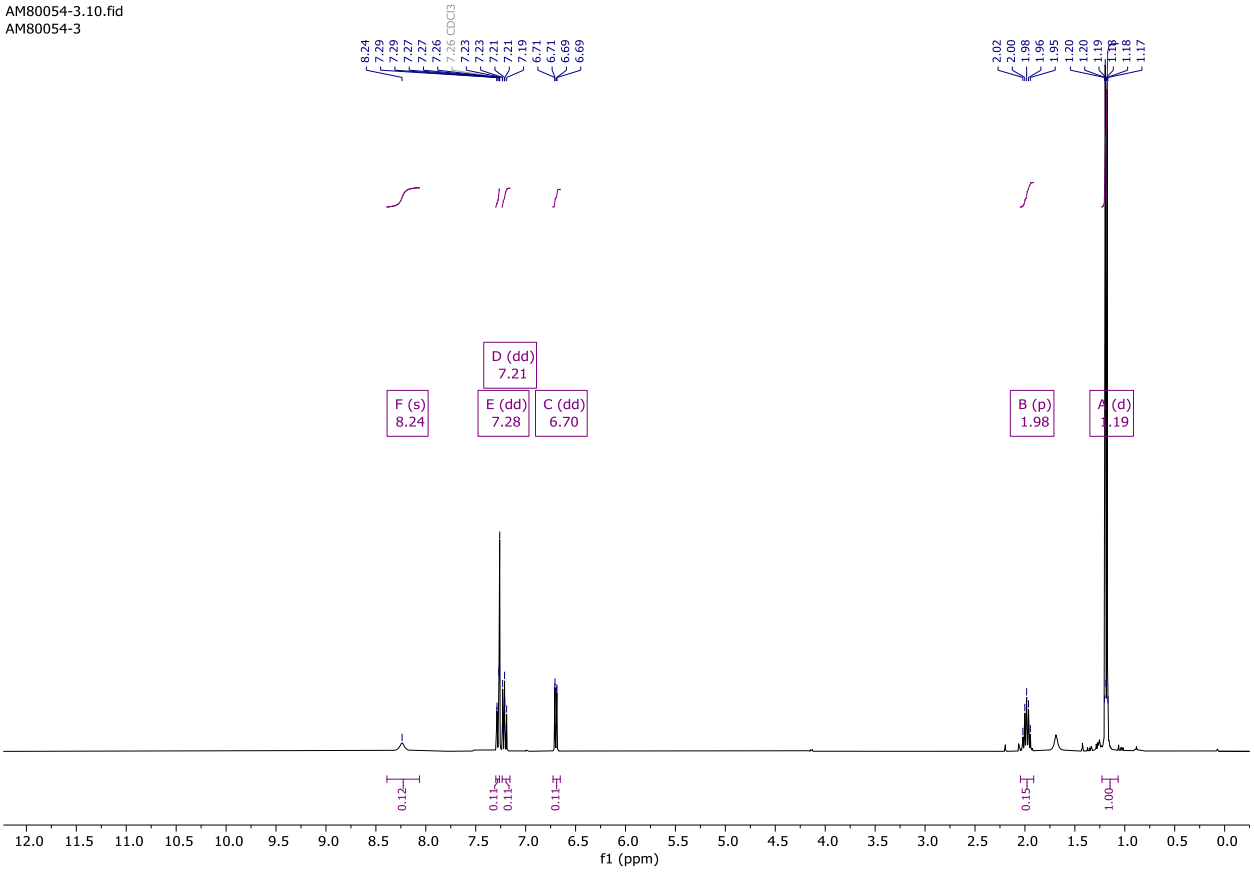
^{1}H-NMR data for 9H-carbazole-4-carbaldehyde 130



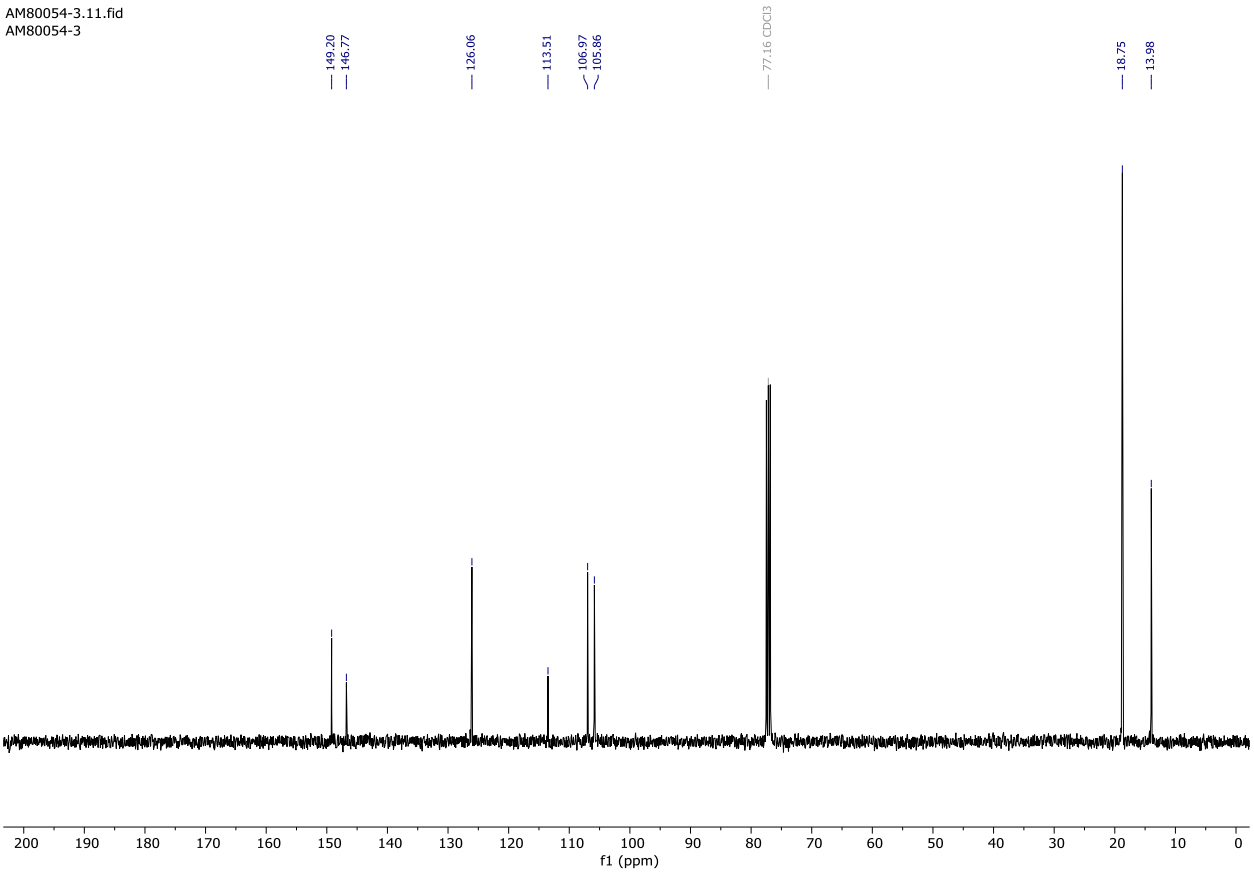
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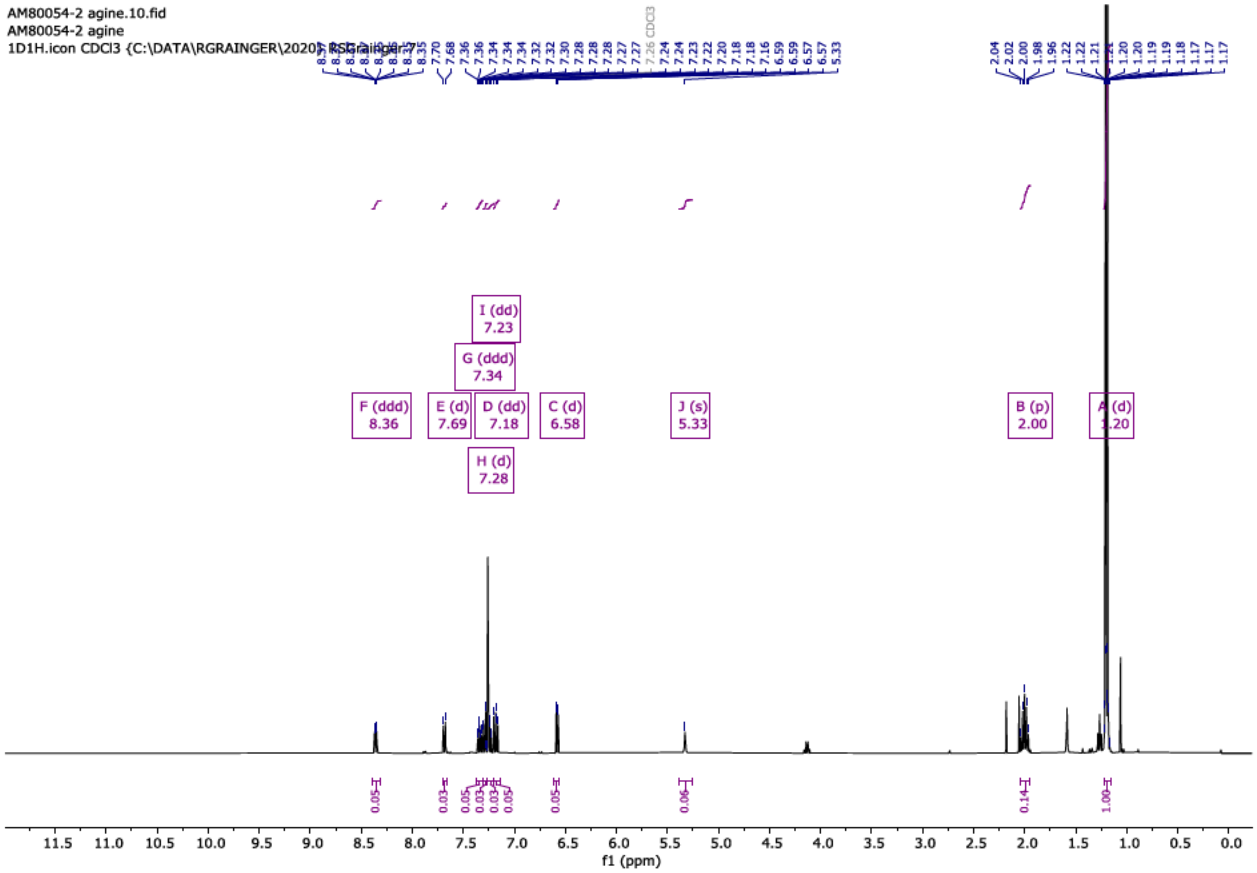
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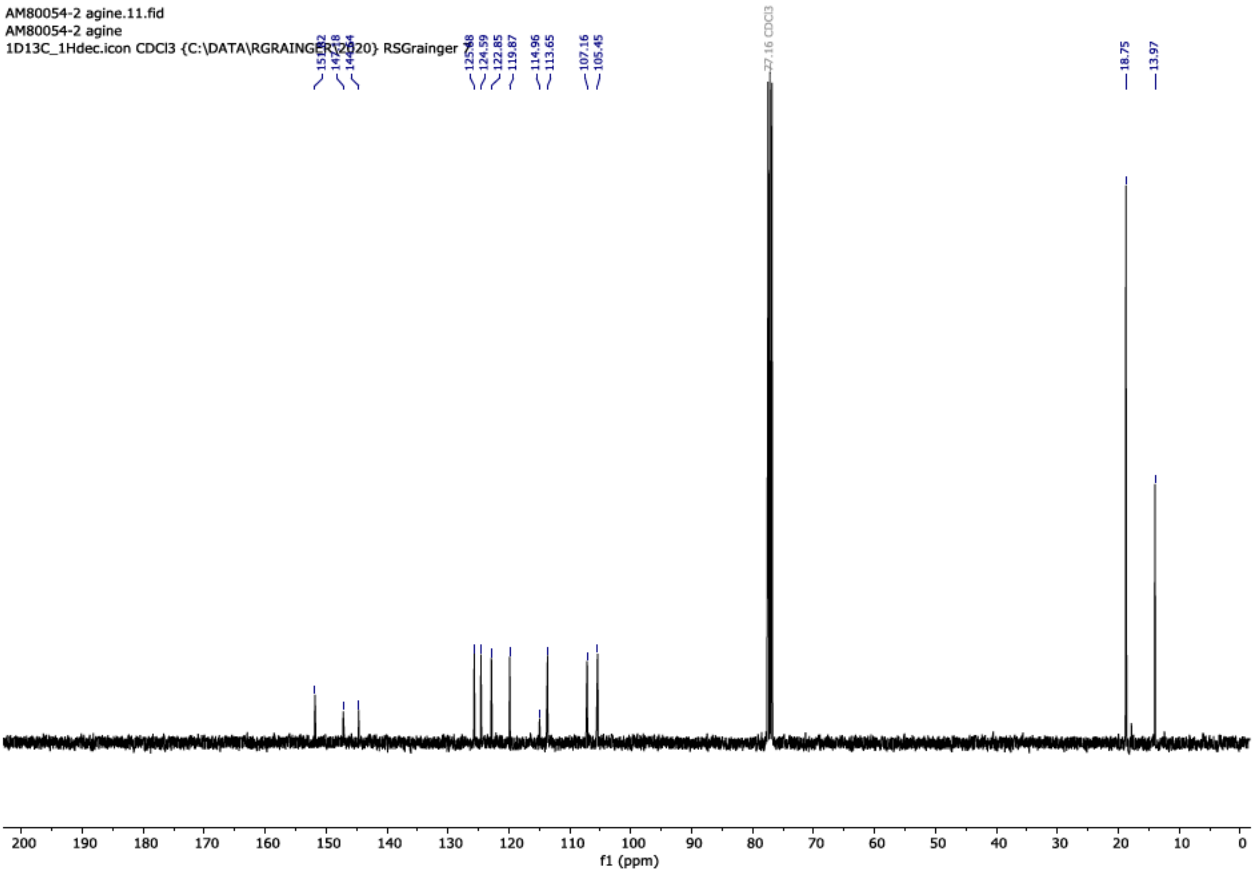
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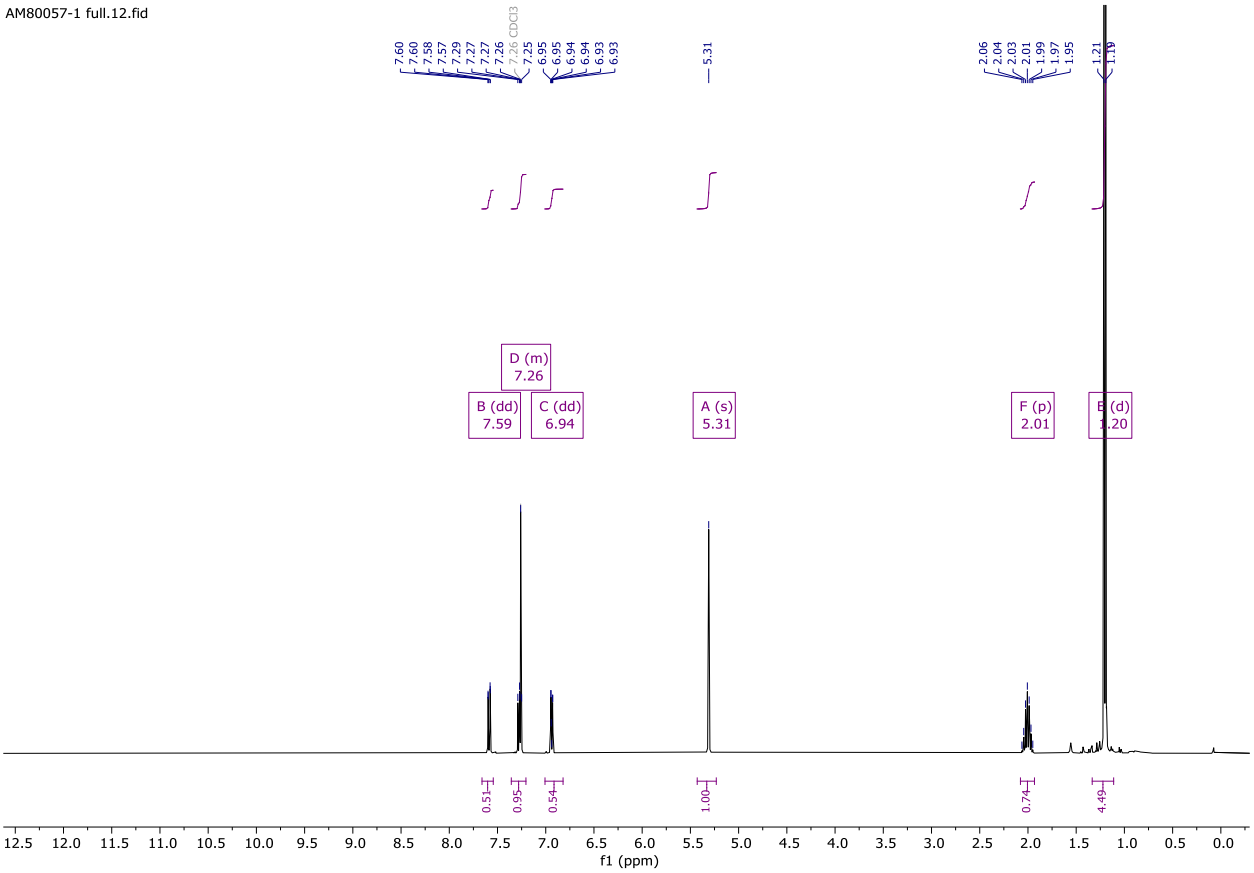
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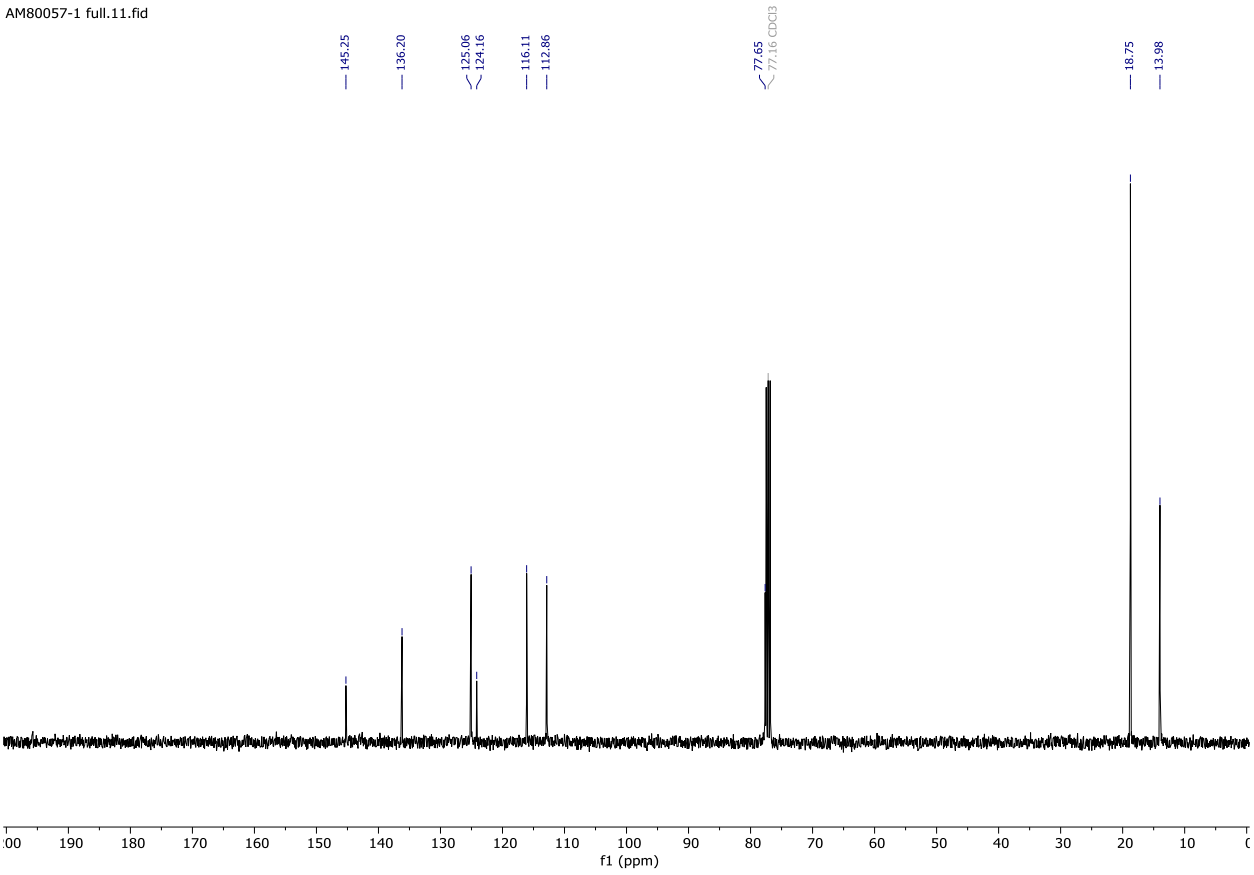
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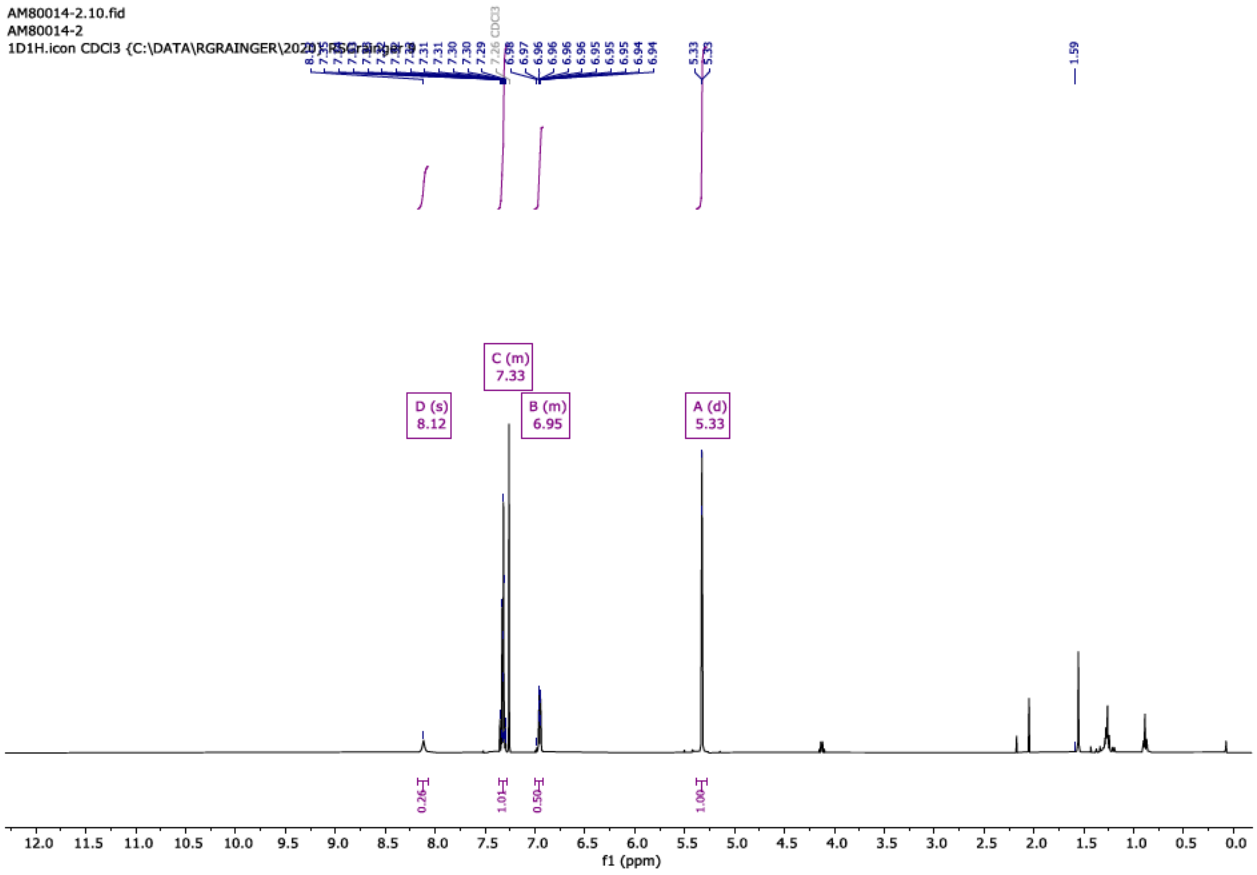
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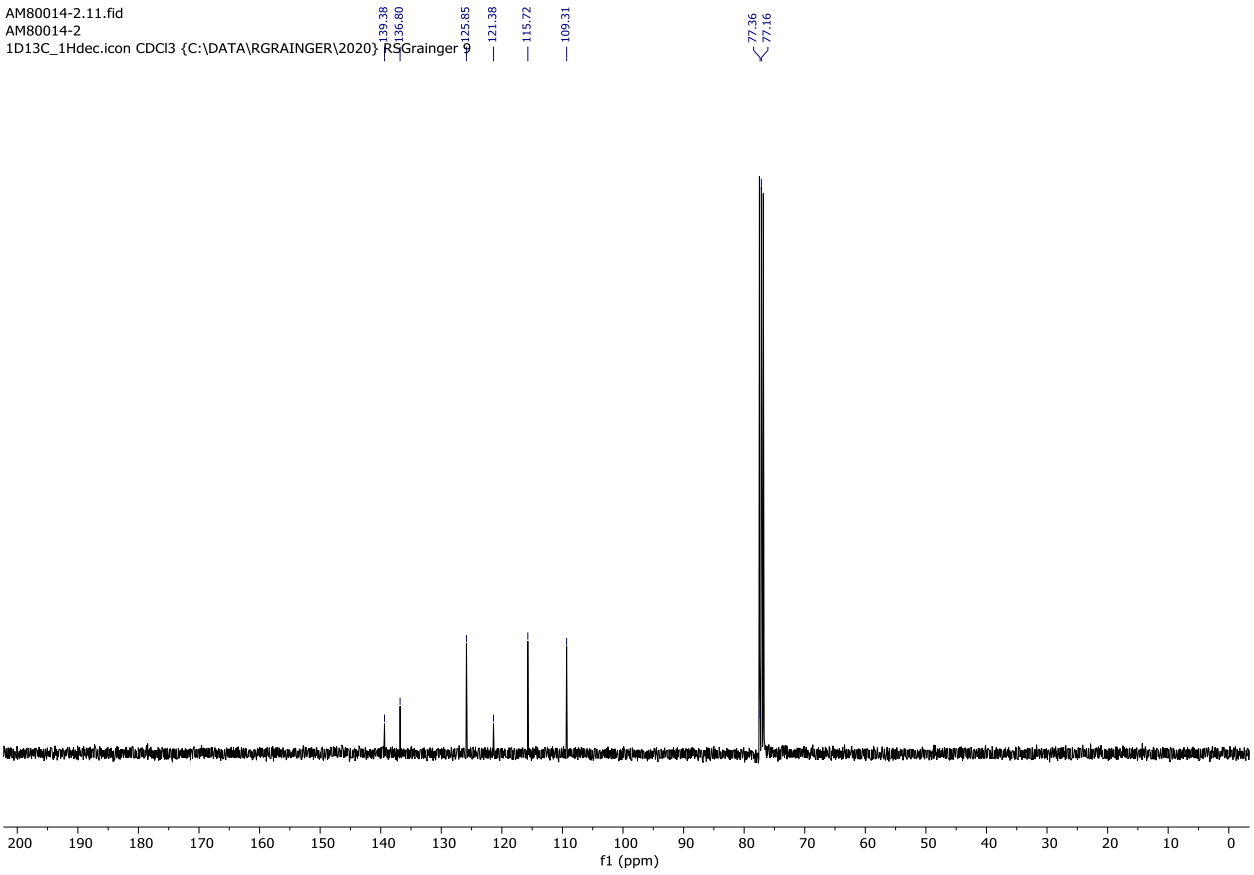
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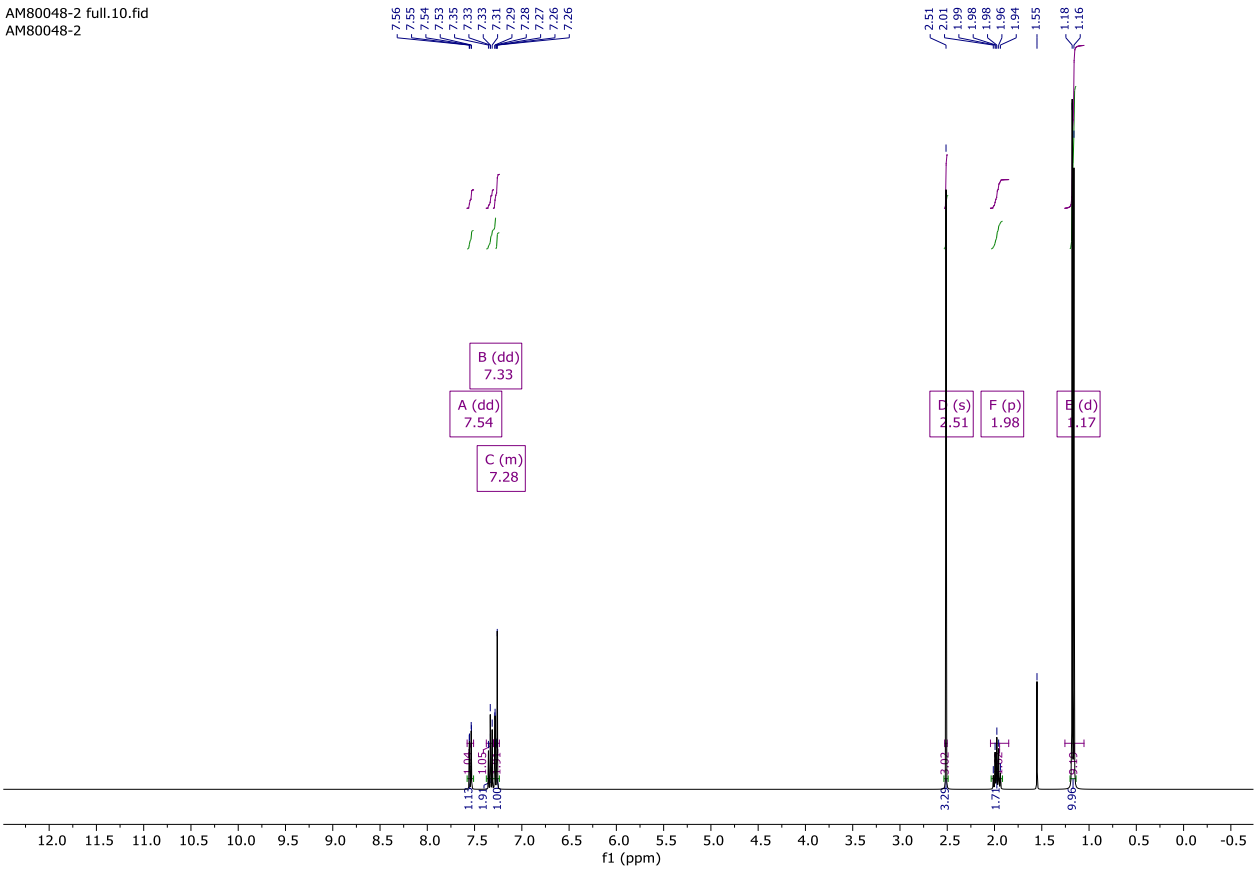
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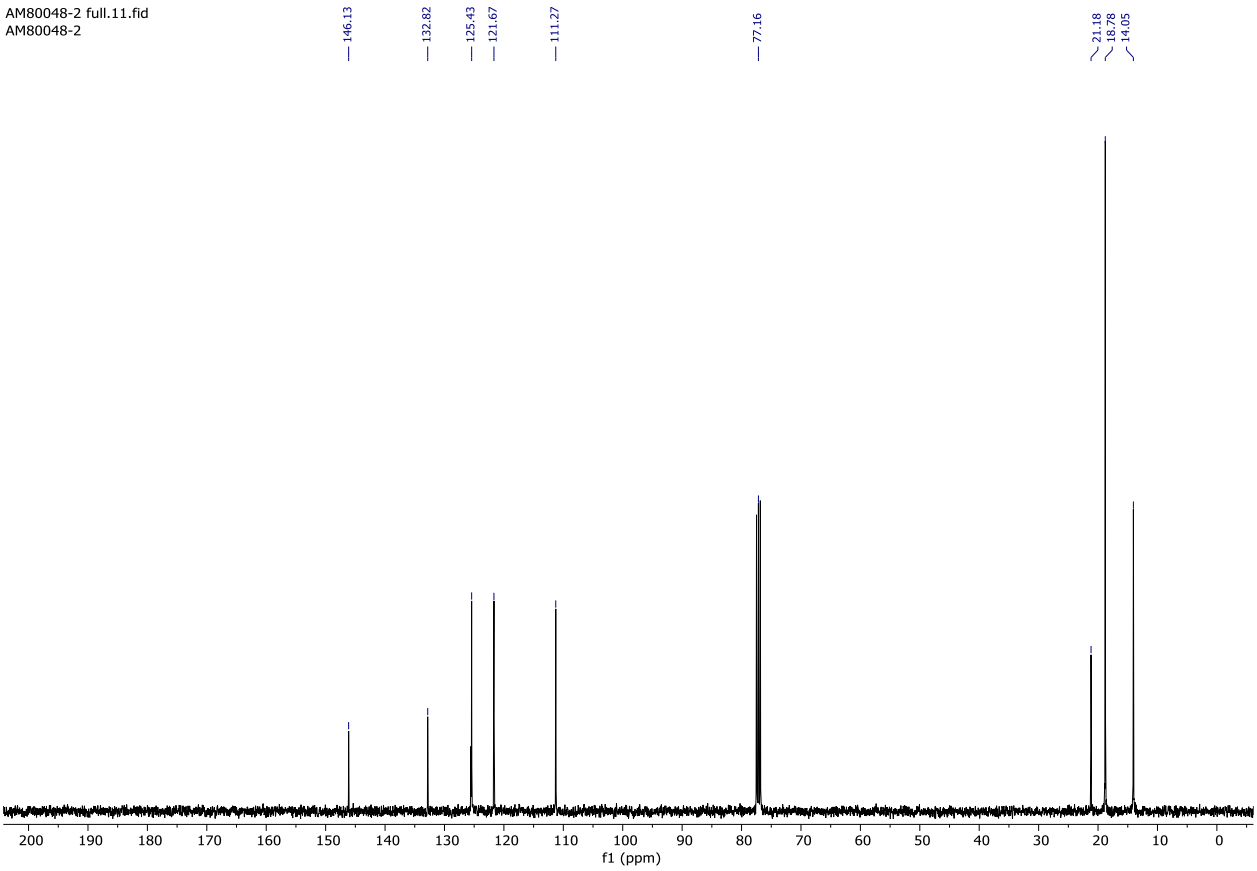
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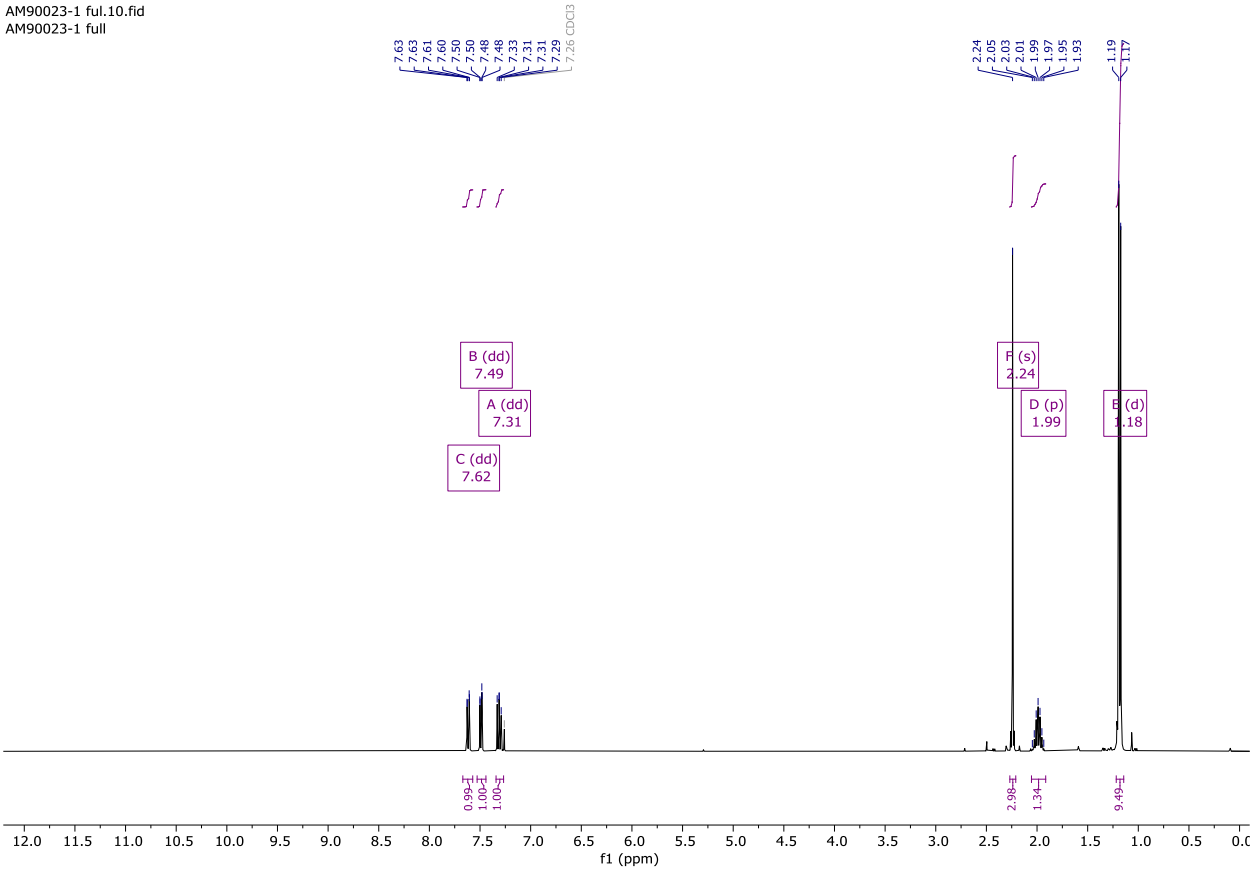
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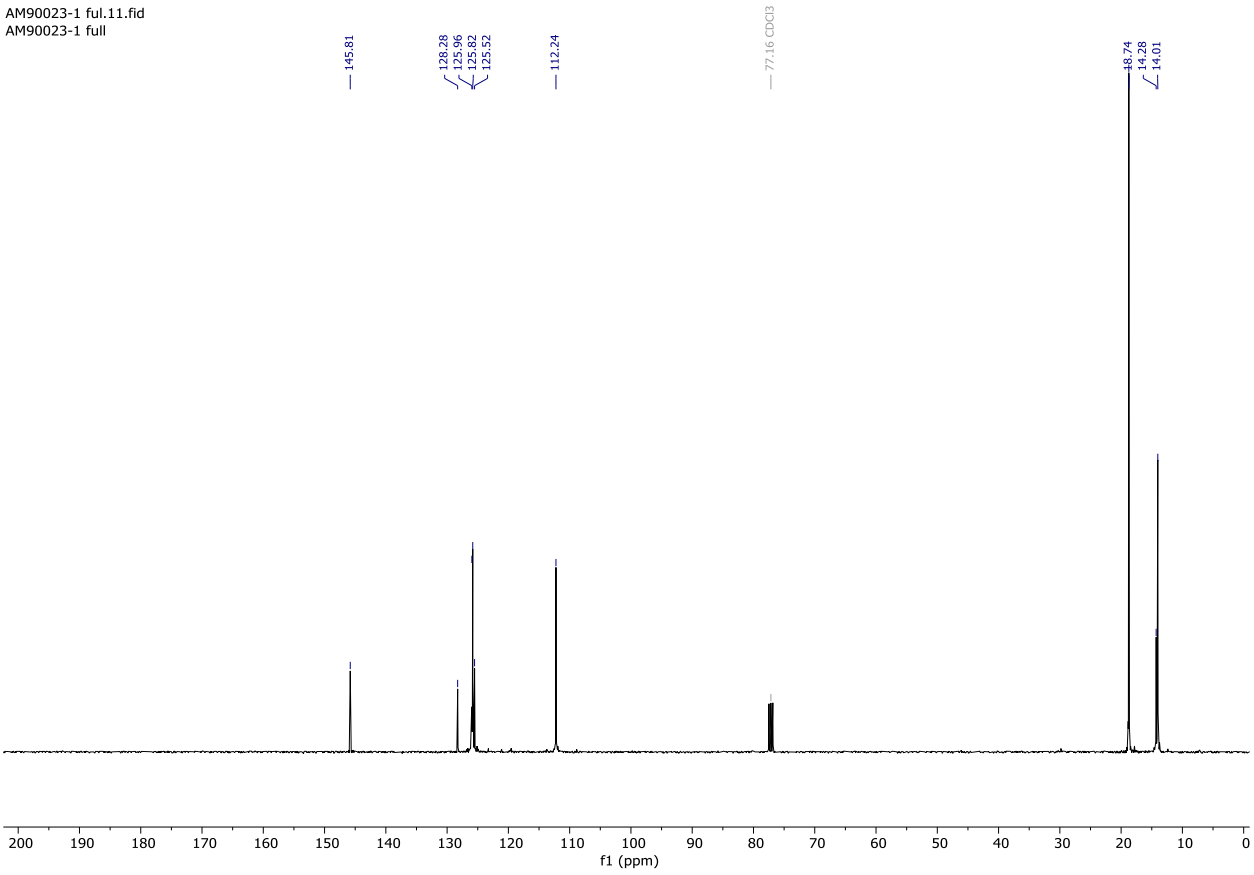
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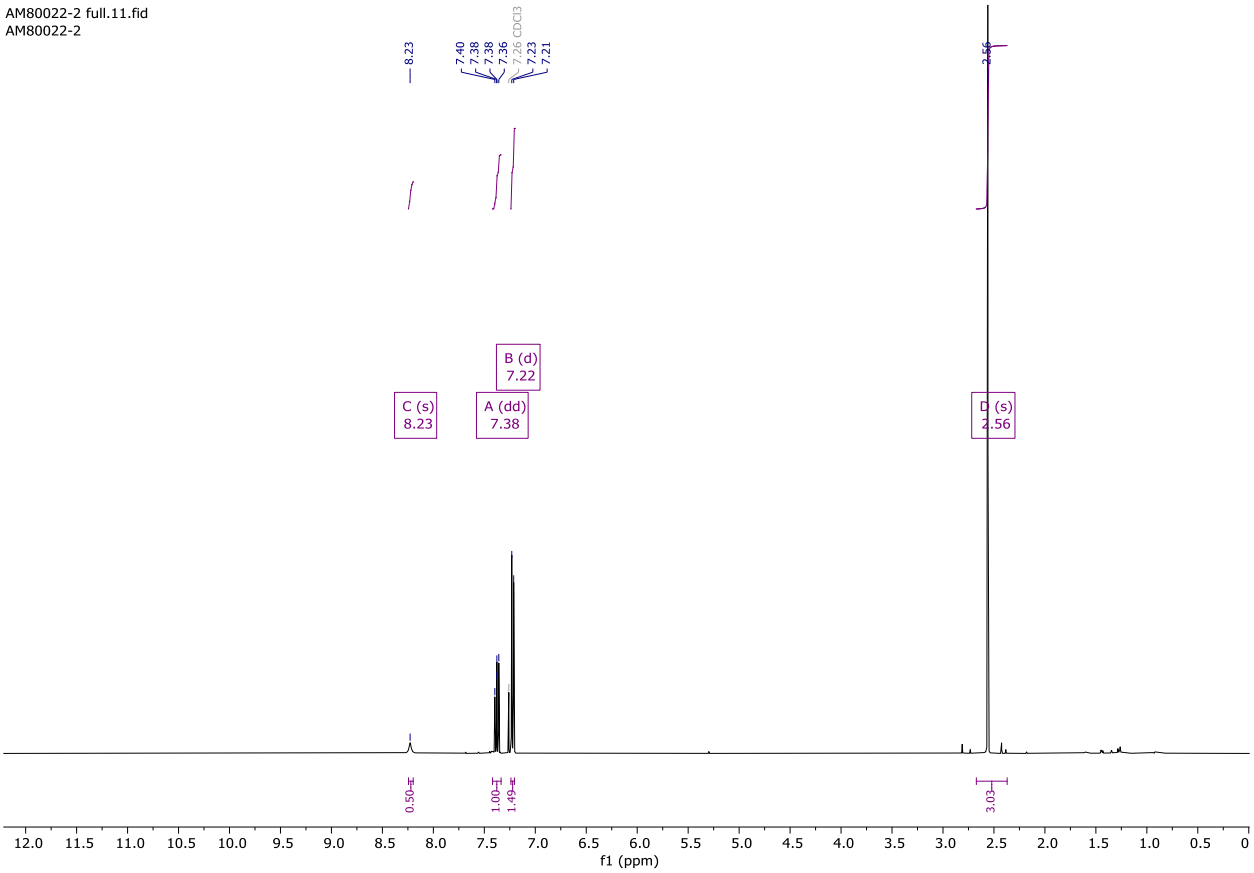
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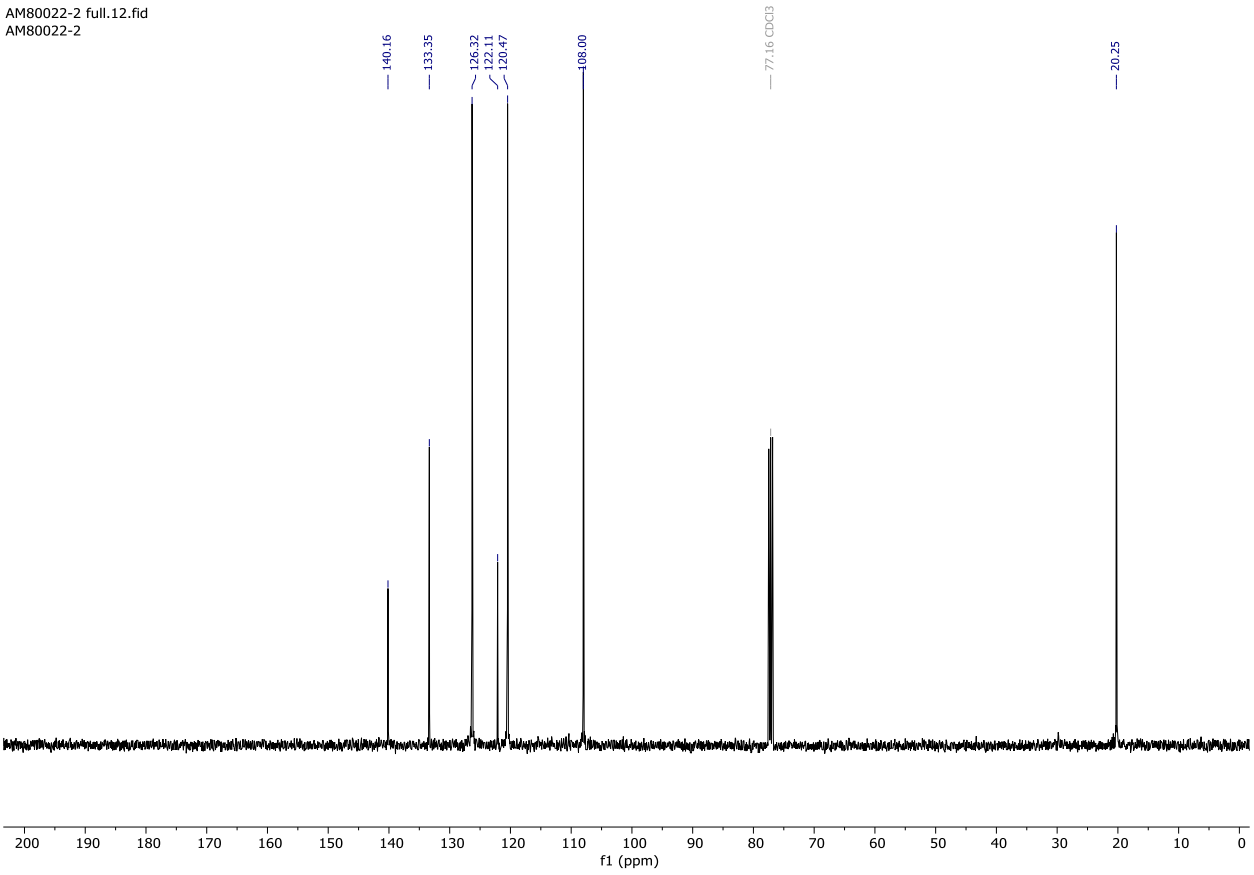
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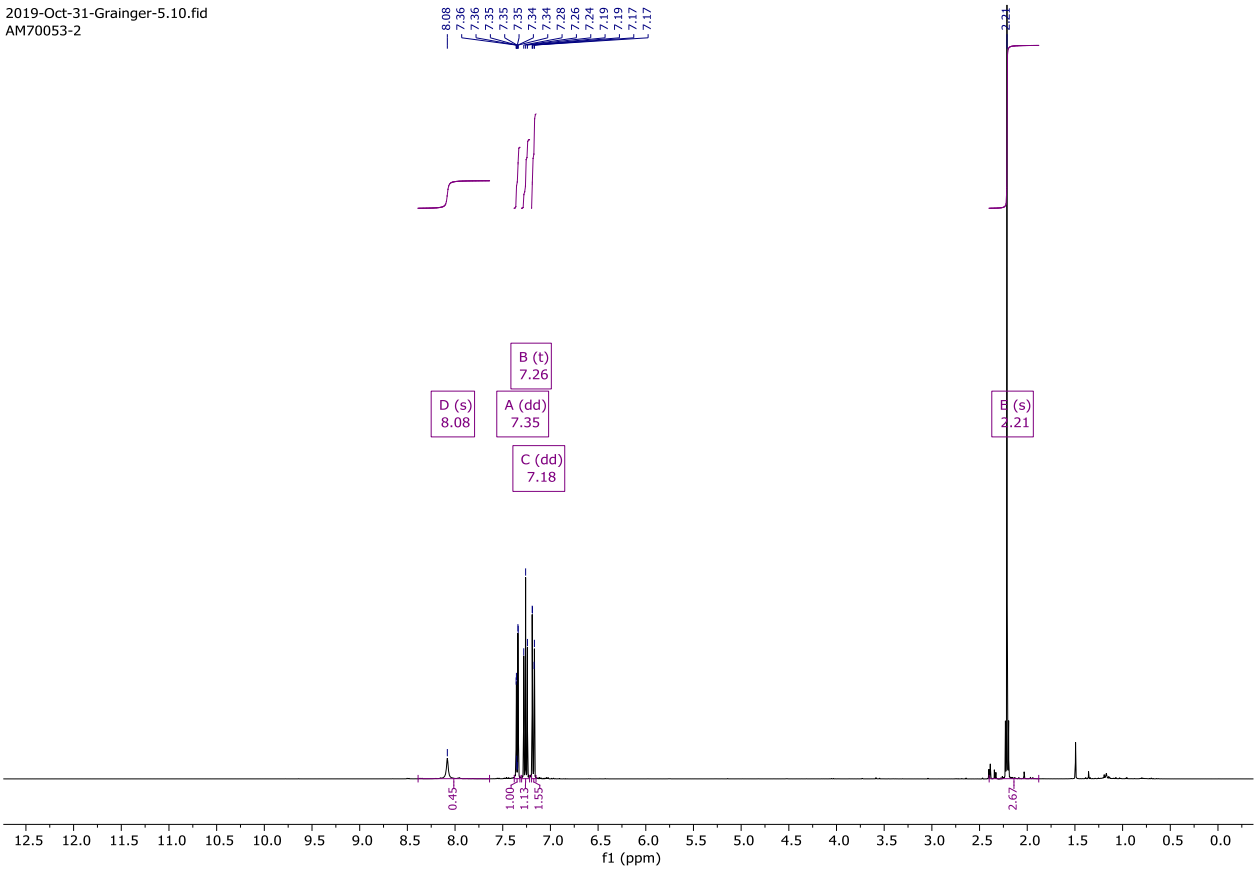
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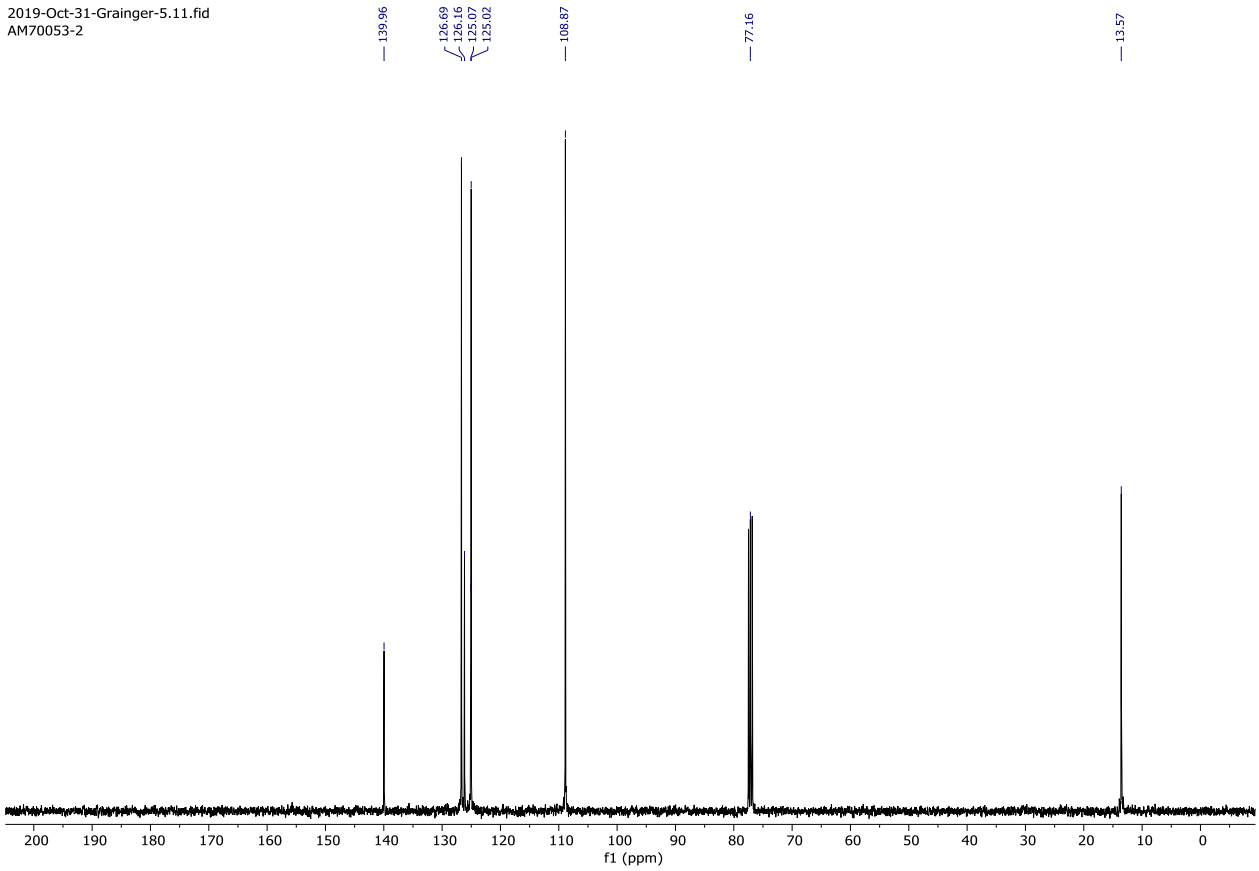
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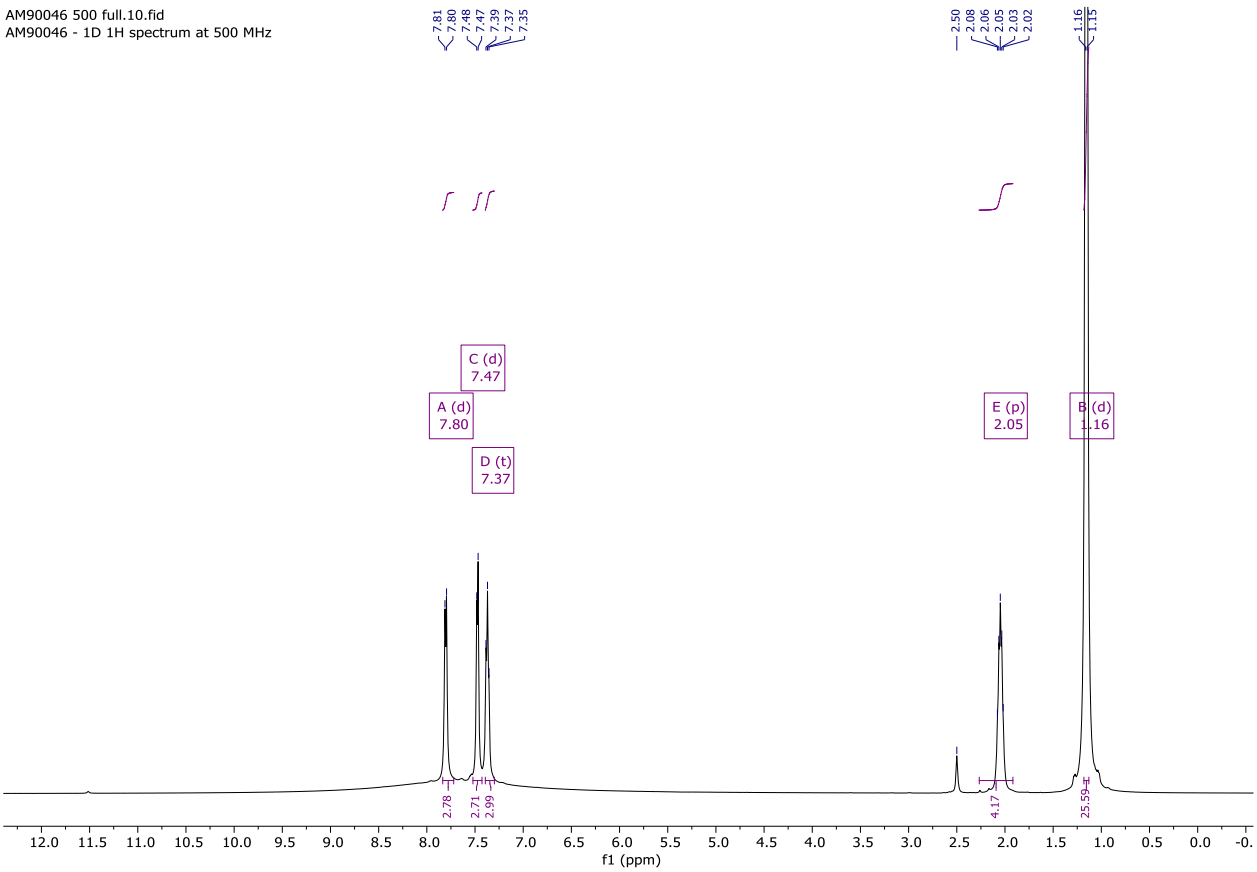
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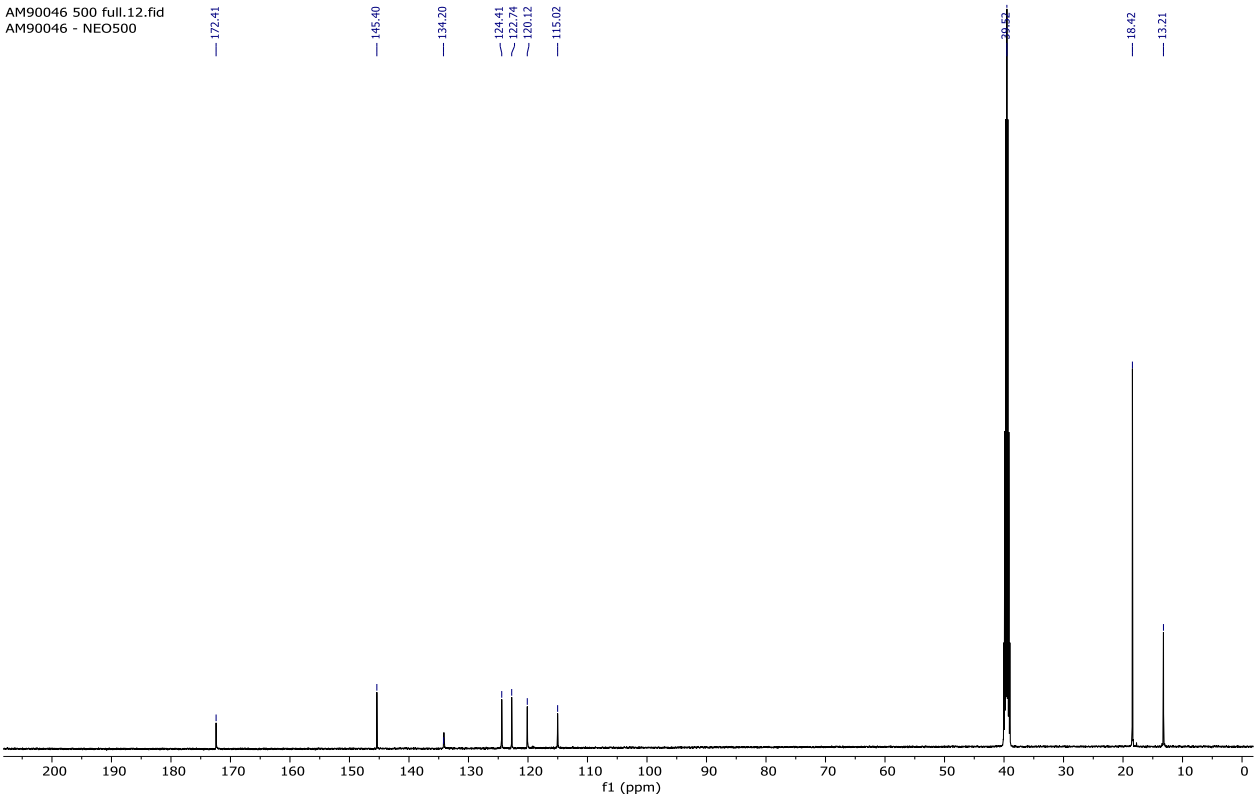
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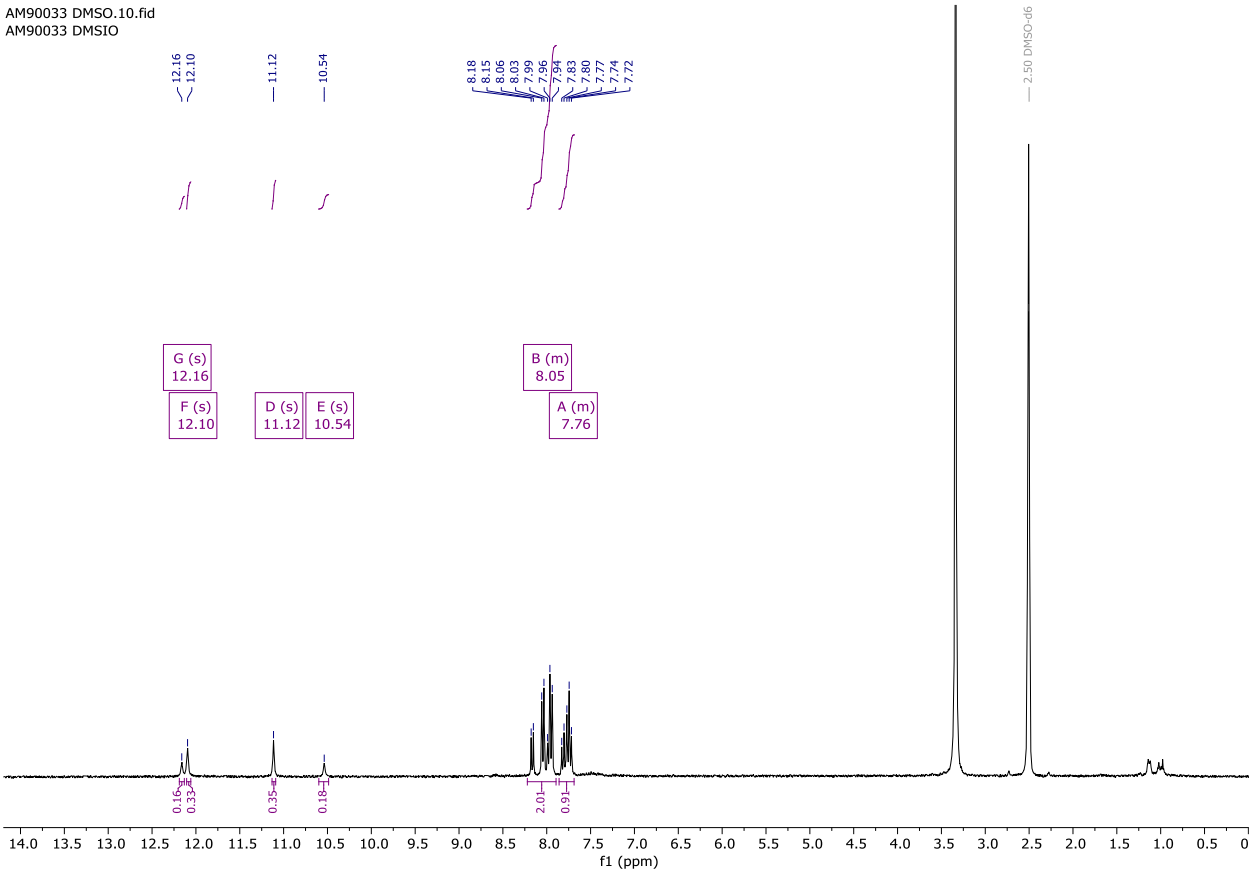
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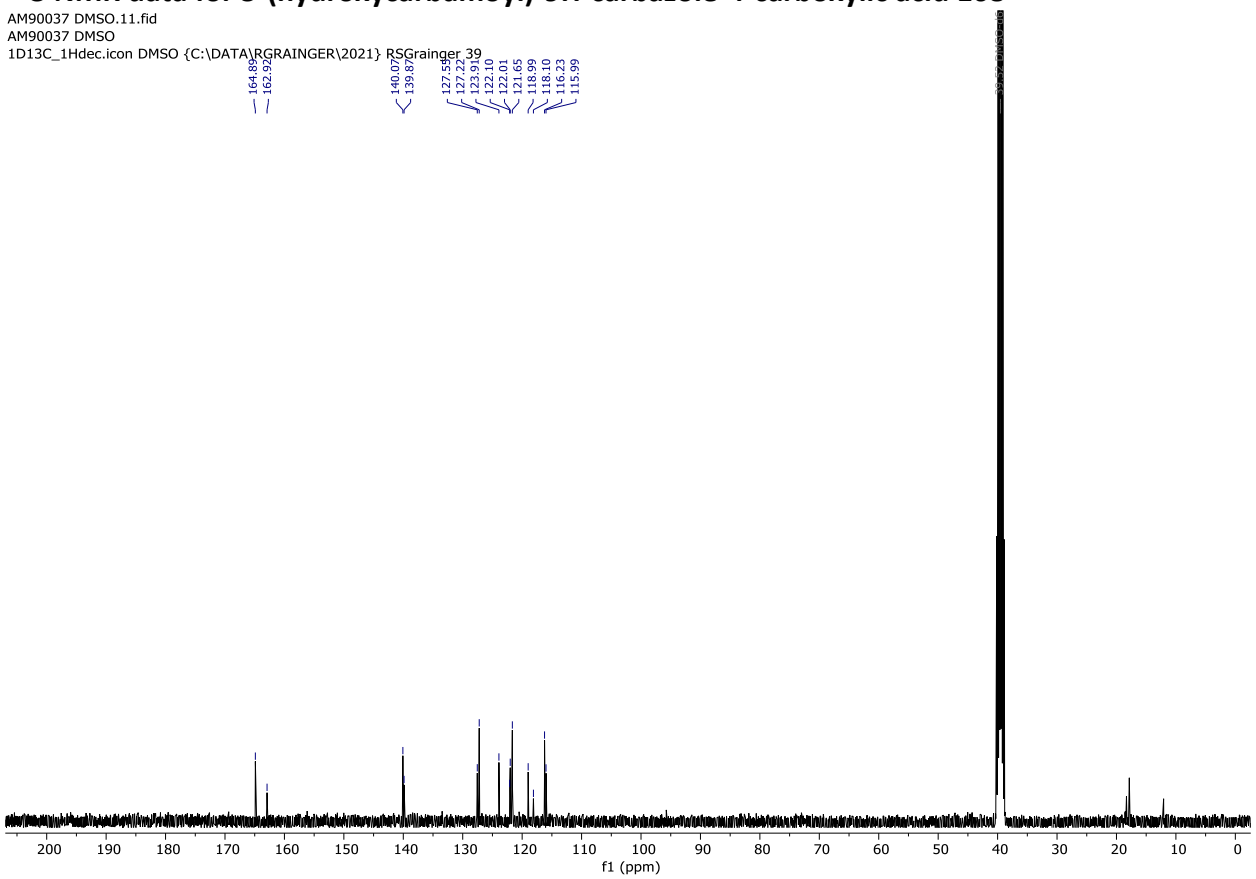
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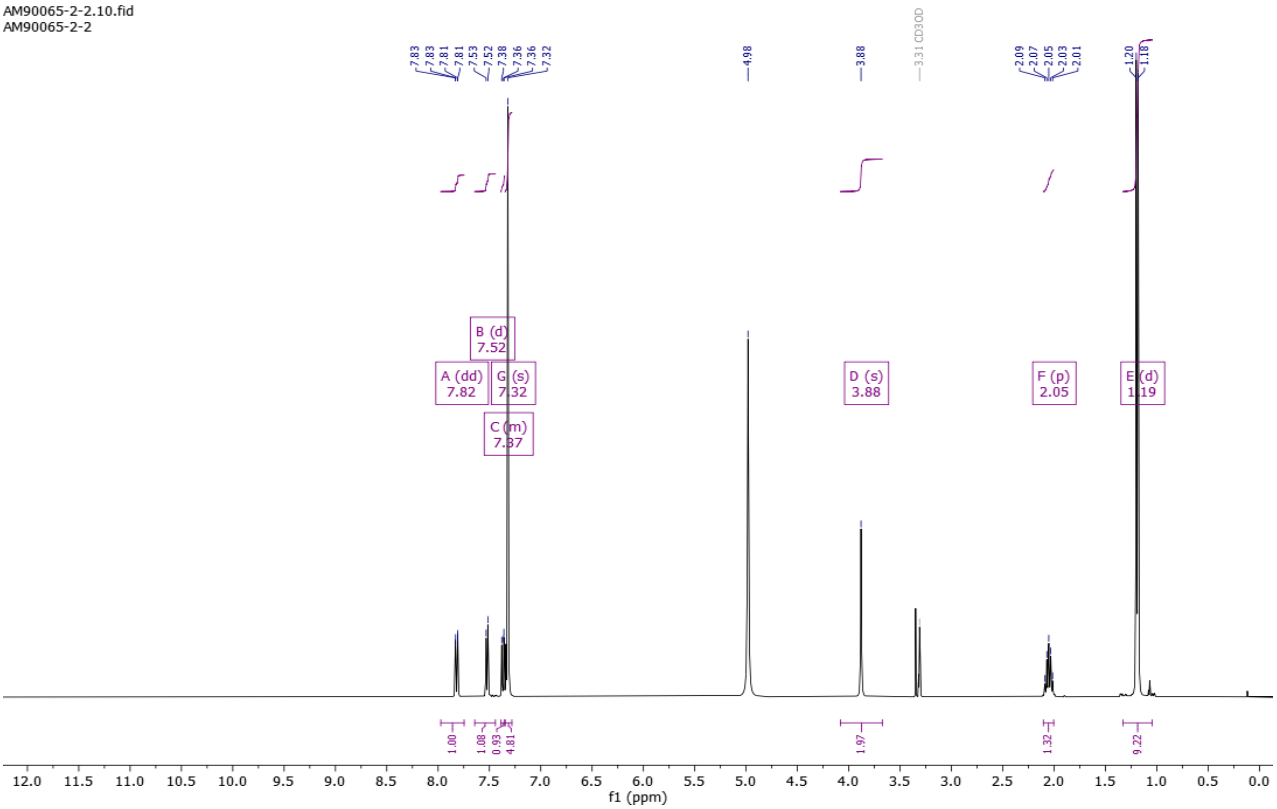
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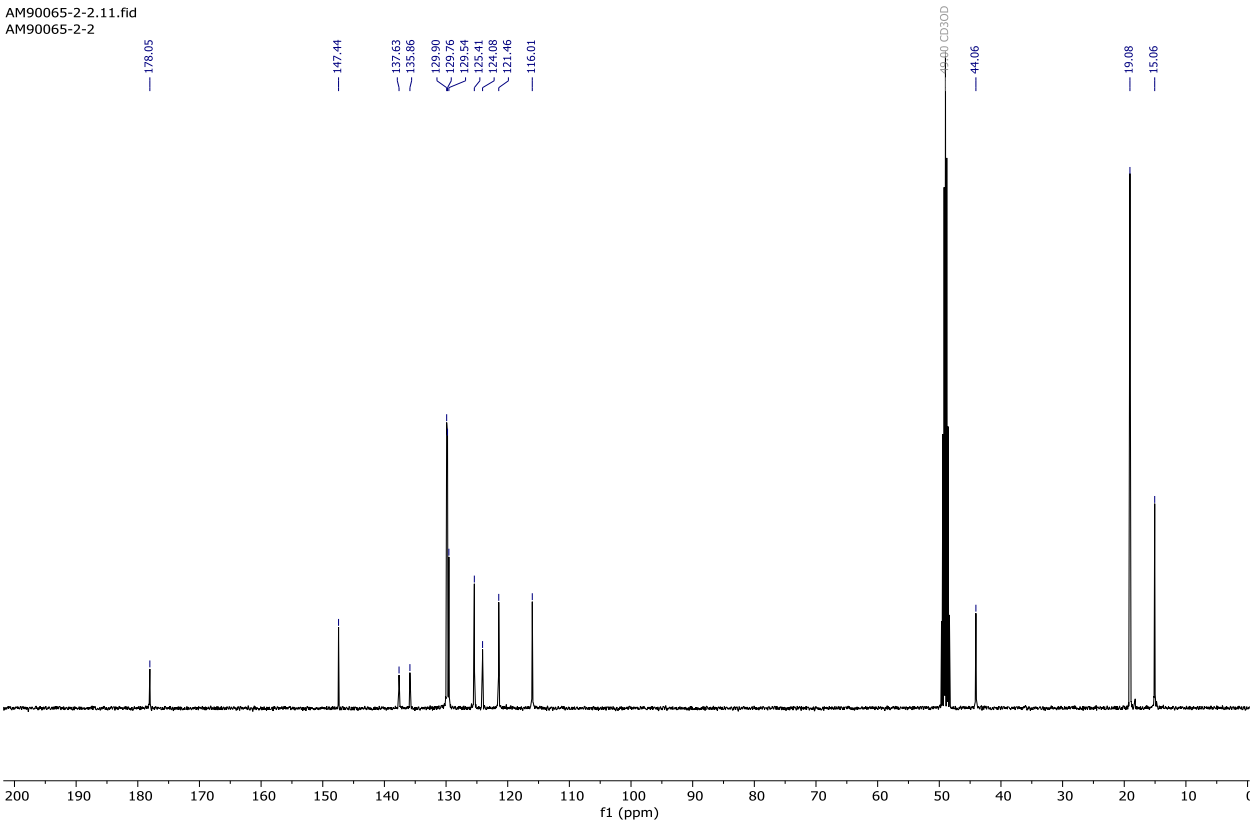
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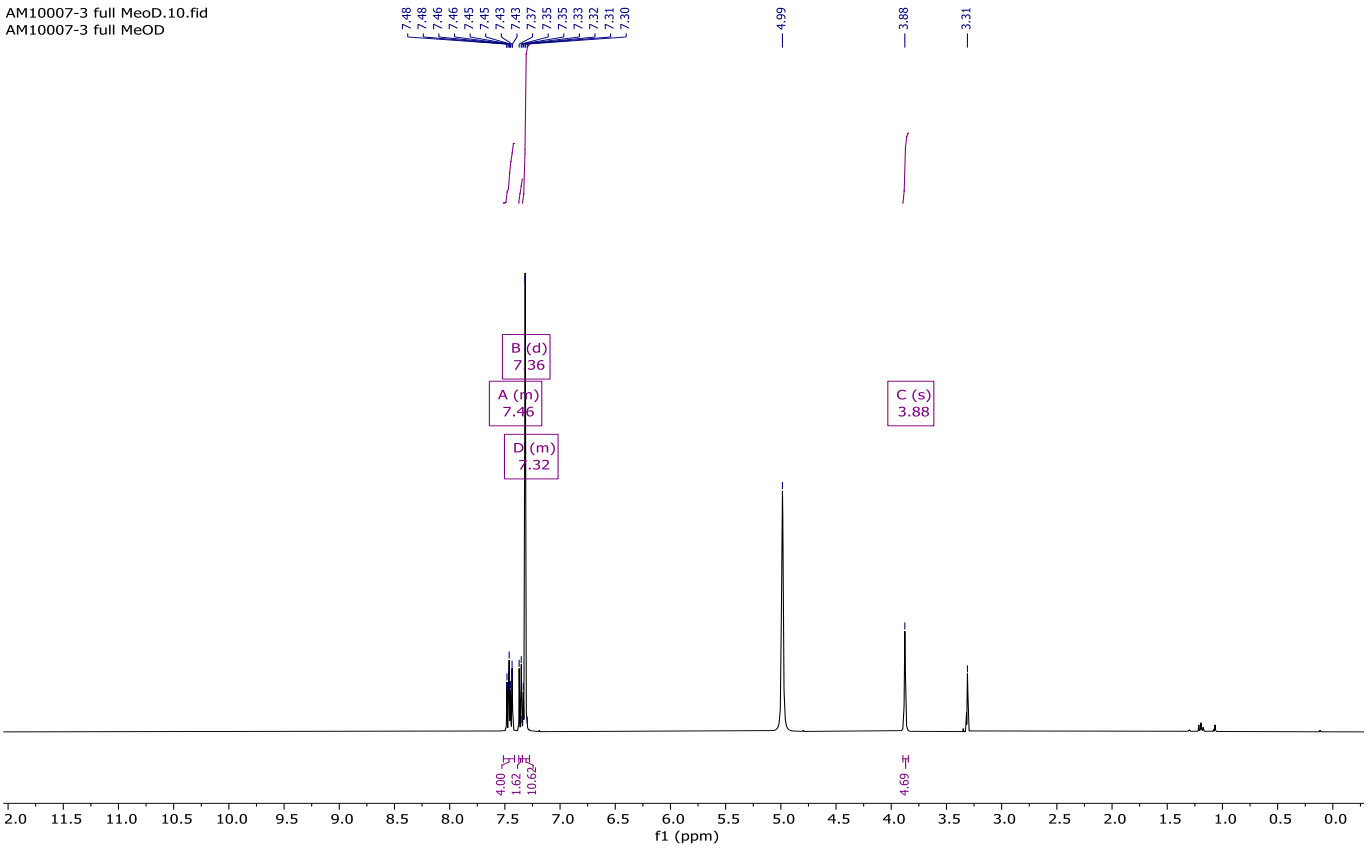
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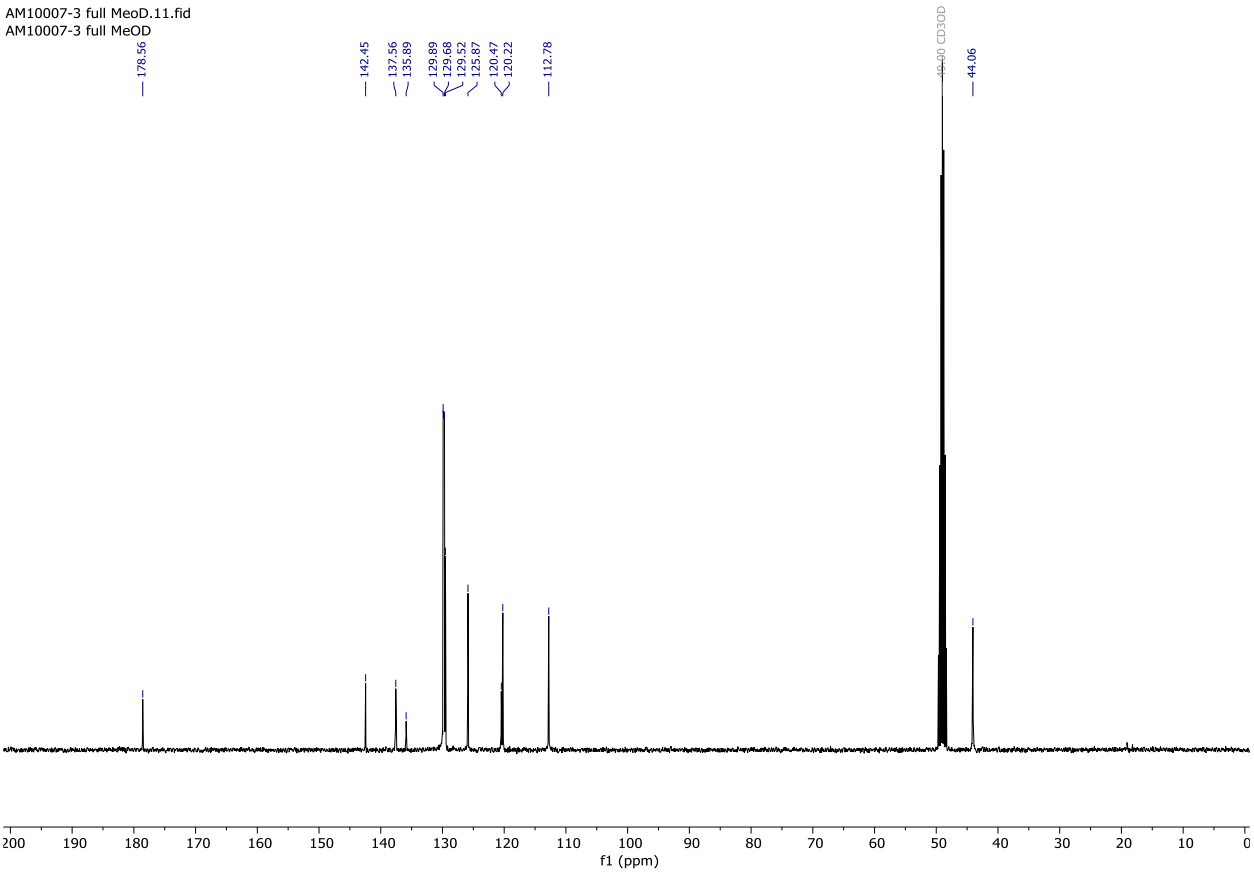
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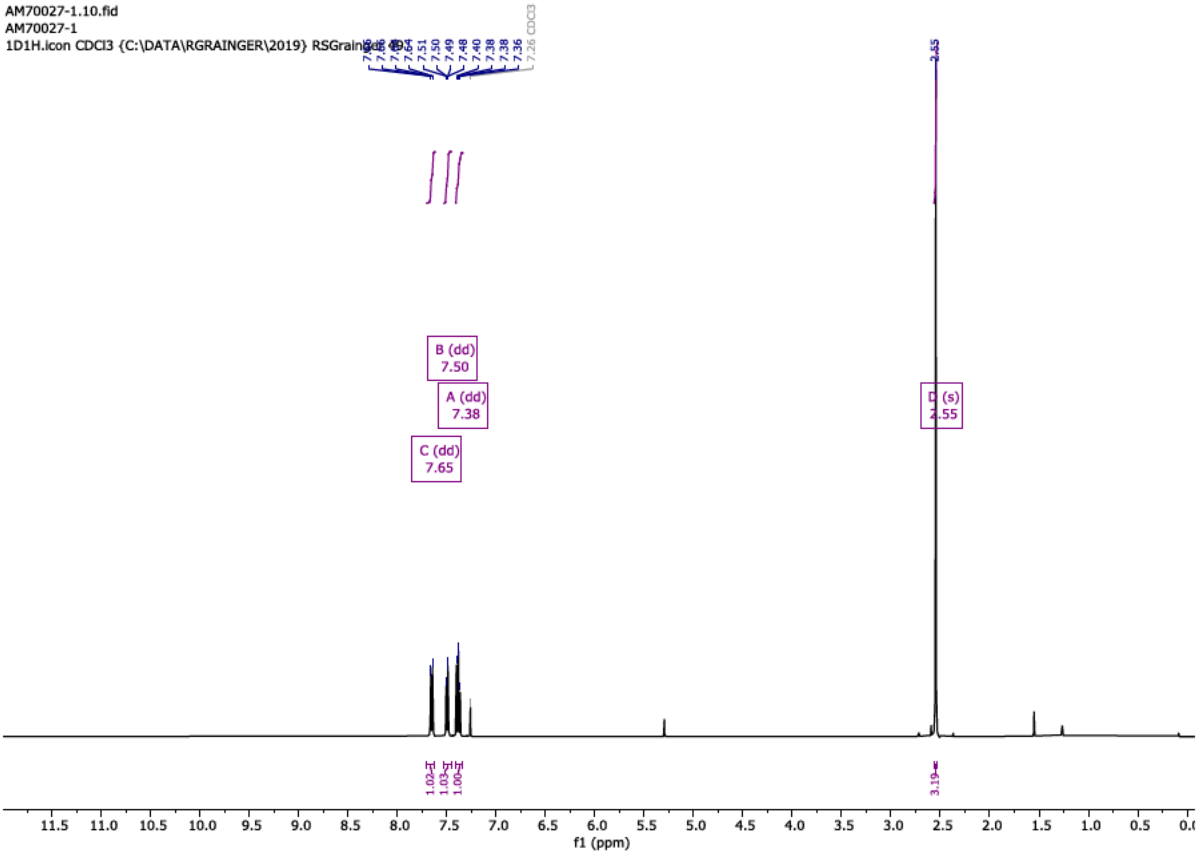
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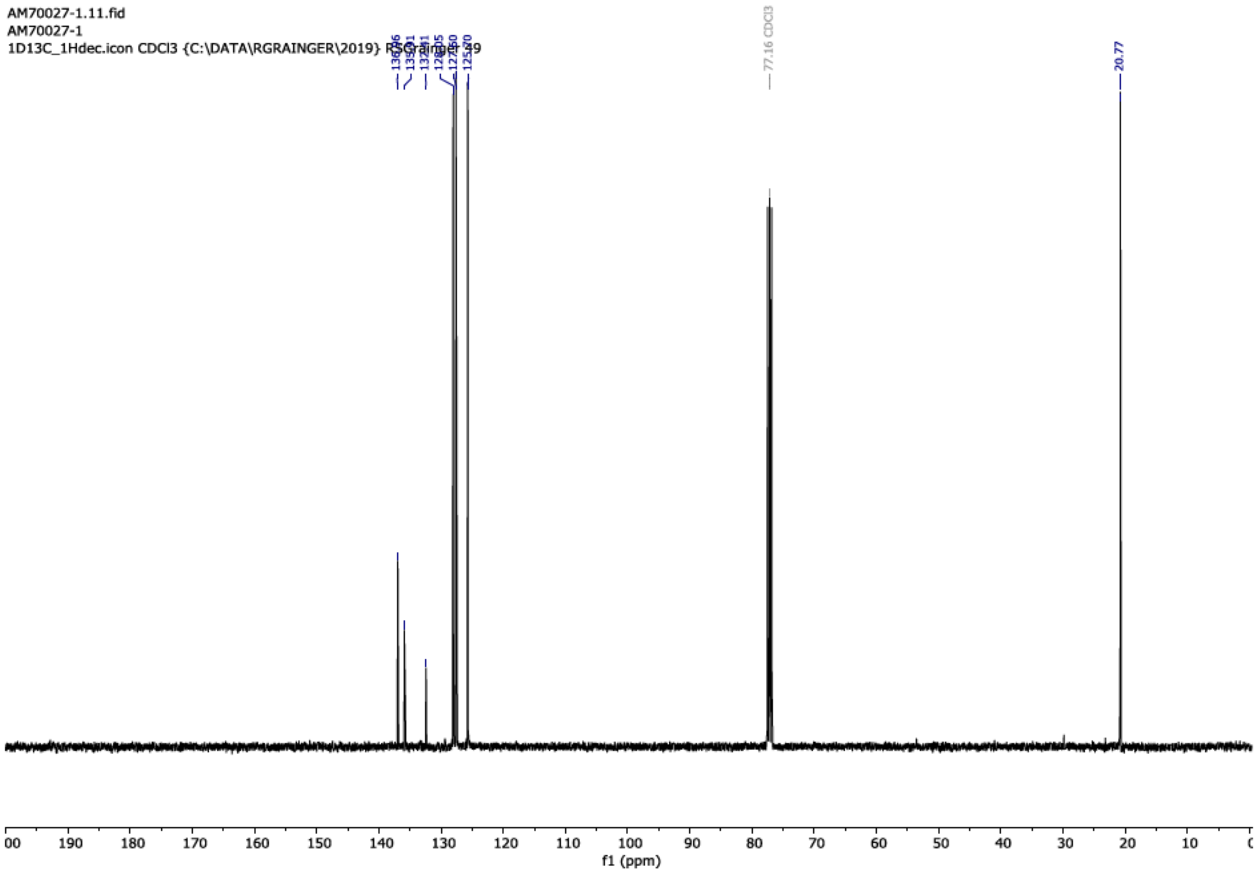
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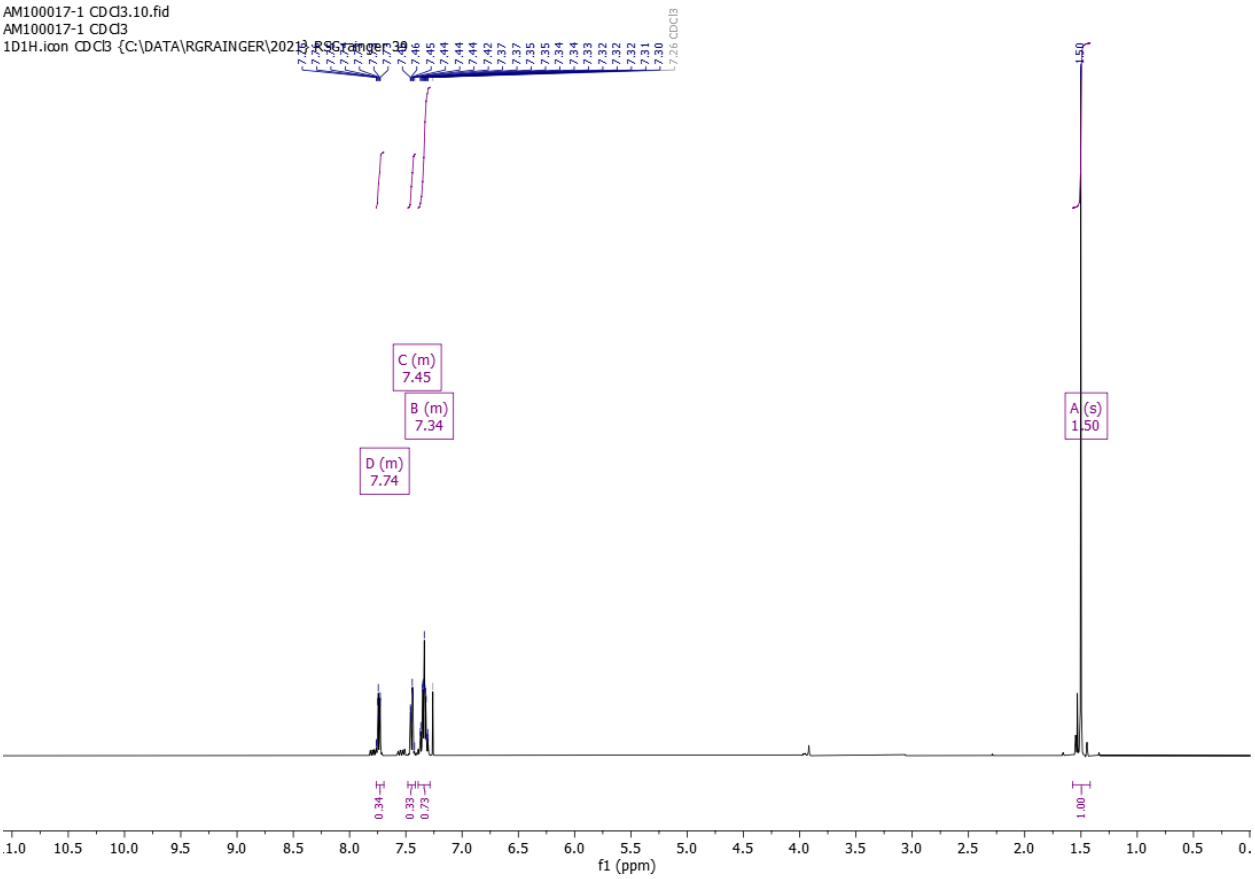
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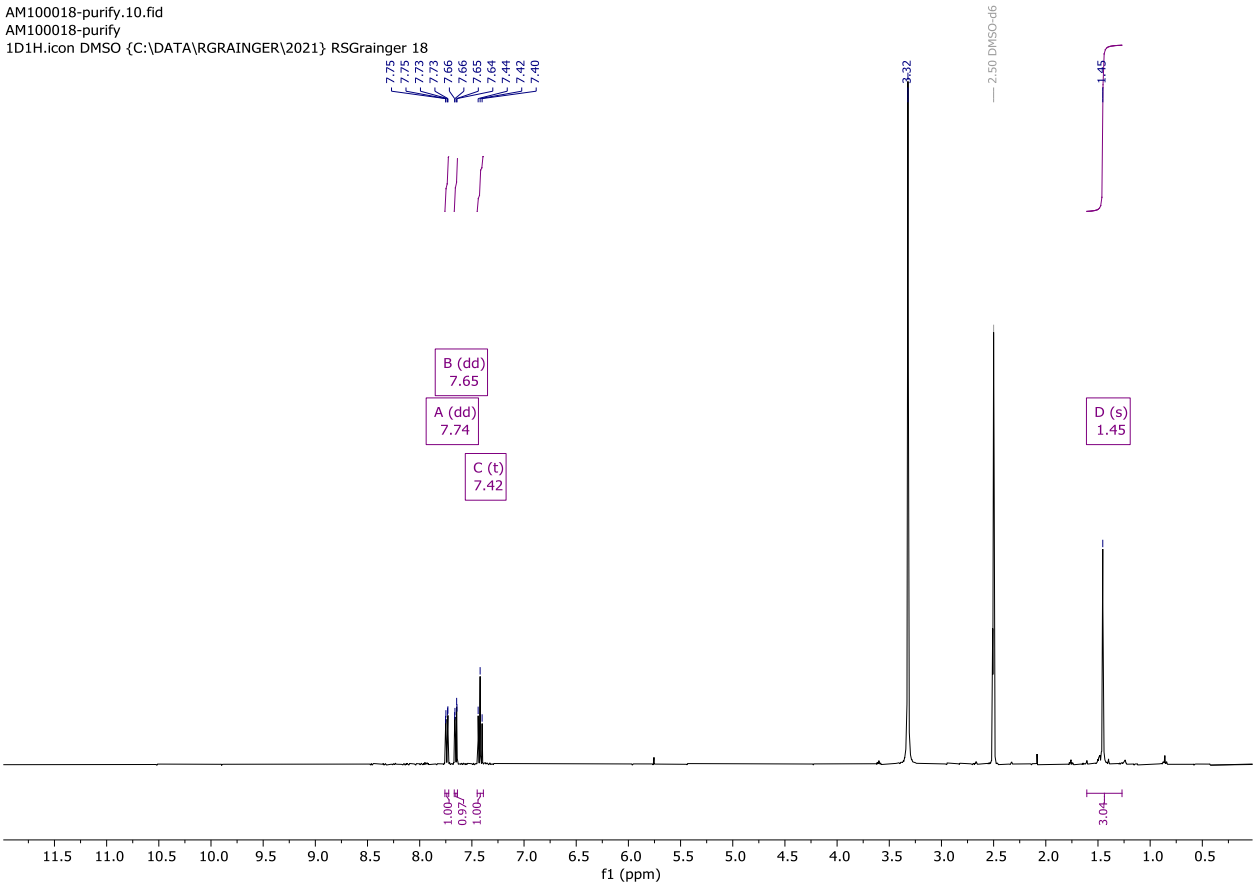
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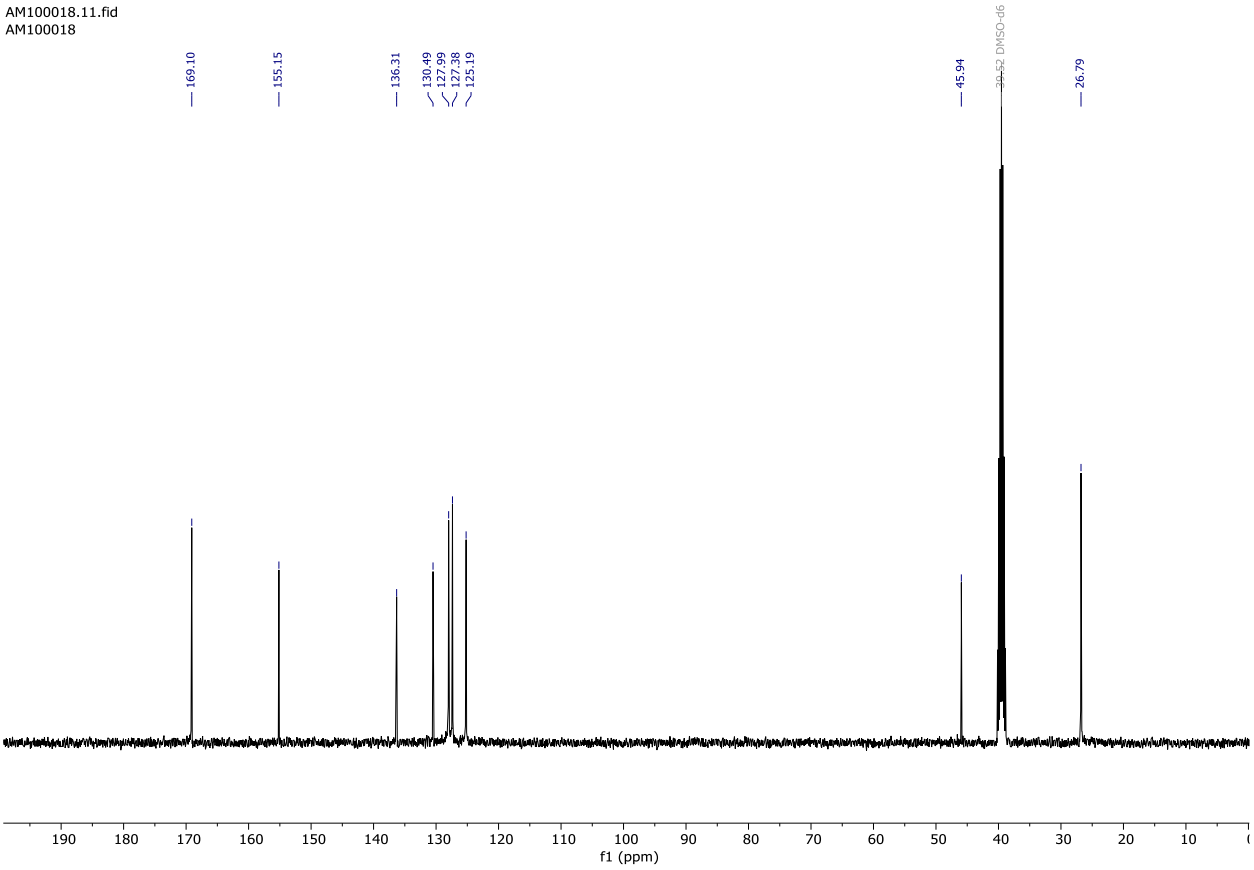
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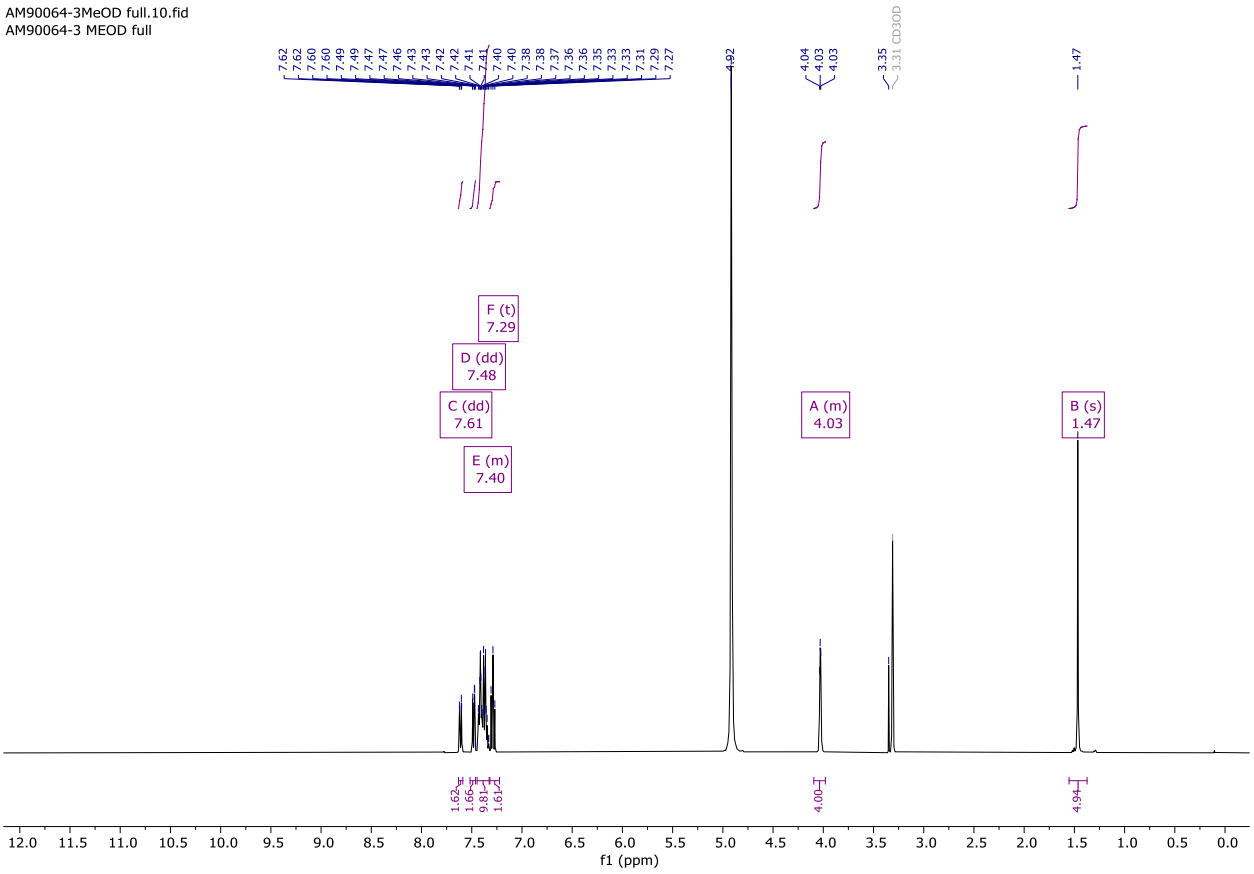
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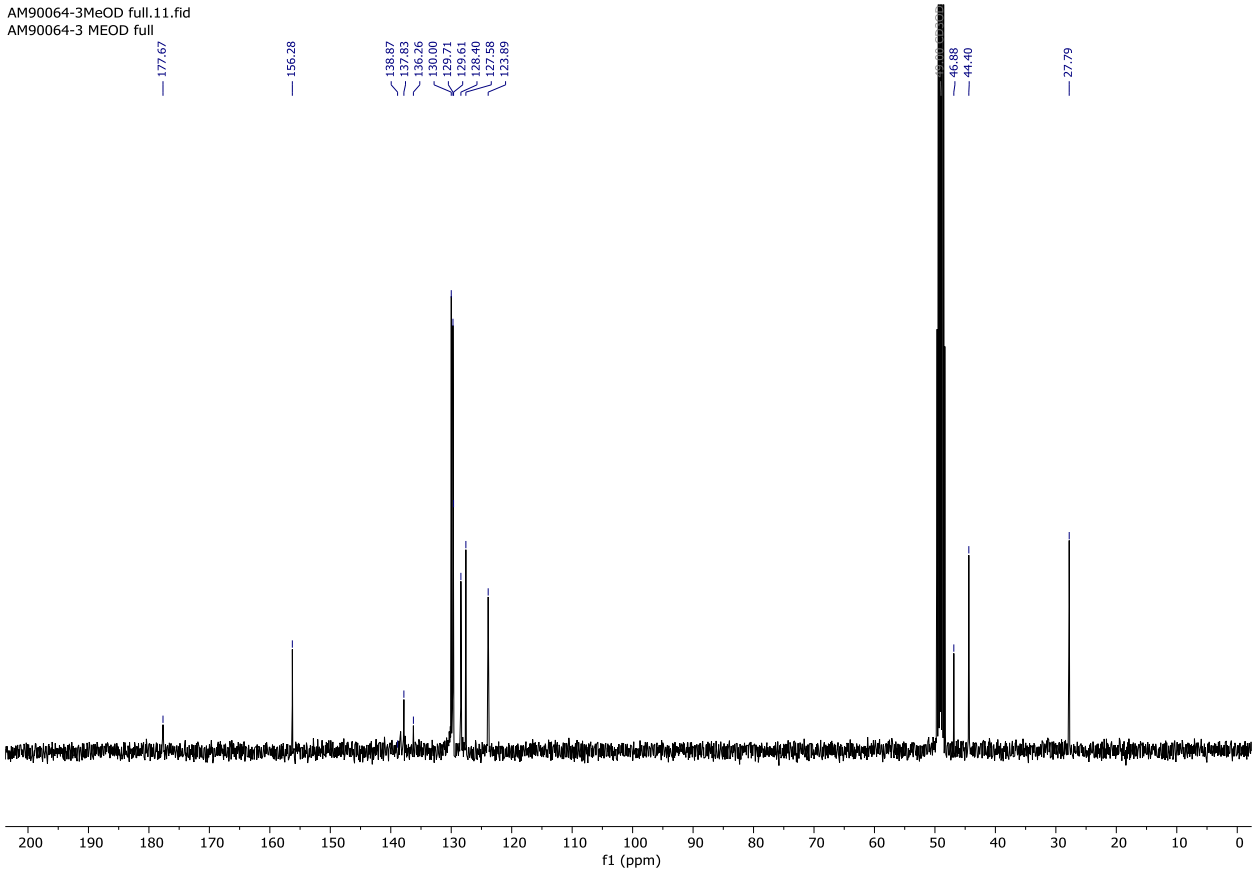
^{13}C-NMR data for 9,9- dimethylfluorene anhydried 177



^{1}H-NMR data for 9,9-dimethyl-9H-fluorene-4,5- dicarboxylatedibezylammonium 183



^{13}C-NMR data for 9,9-dimethyl-9H-fluorene-4,5- dicarboxylatedibezylammonium 183



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