Supporting Information

Diastereoselective Strategy for Dihydrophenanthrene-Fused Spirooxindoles *via* [1,2]-phospha-Brook Rearrangement

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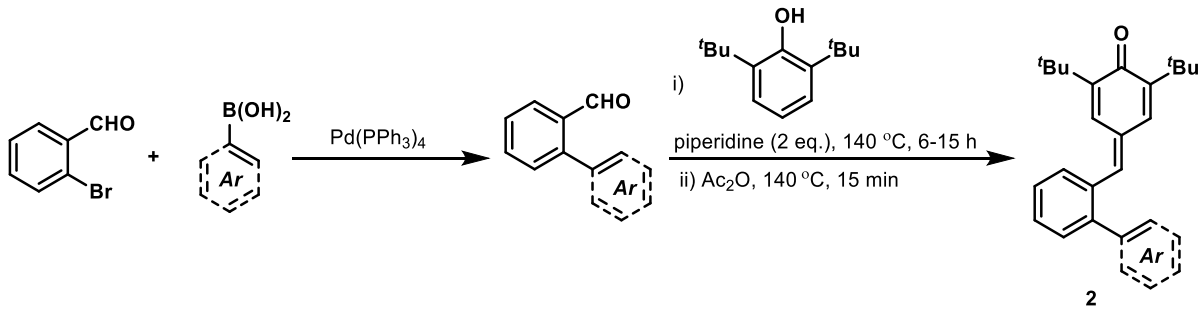
1. General Information:

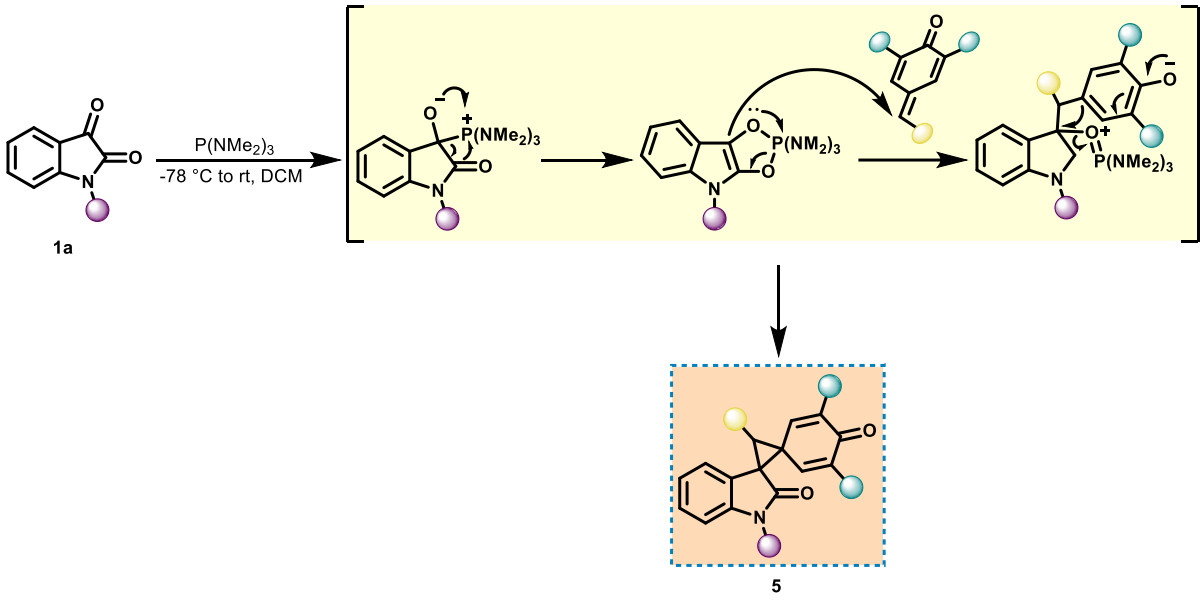
1.1 Materials and Instruments. Unless otherwise noted, all the reactions were performed in flame or oven-dried glassware under a dry nitrogen atmosphere using dry solvents. The Bruker AV-500 MHz NMR spectrometer was used to record NMR spectra in deuterated solvents using their residual solvent proton signal as an internal reference. ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), integration, coupling constant (Hz). ^{13}C NMR data are recorded in terms of chemical shift (δ, ppm). ^{19}F NMR data are recorded in terms of chemical shift (δ, ppm). The mass spectrum of compounds was recorded using a micrOTOF-Q mass spectrometer. Compounds were purified by column chromatography using silica gel (100–200 mesh) and EtOAc:hexane as eluent. The diastereomeric ratio was determined using ^{1}H NMR of the crude reaction mixture.

2. Preparation of Substrates: Isatins used are commercially available that are purchased from Sigma Aldrich and used as it is. 2-phenyl-*para*-Quinone methides were synthesized according to the following procedure.[1,2]

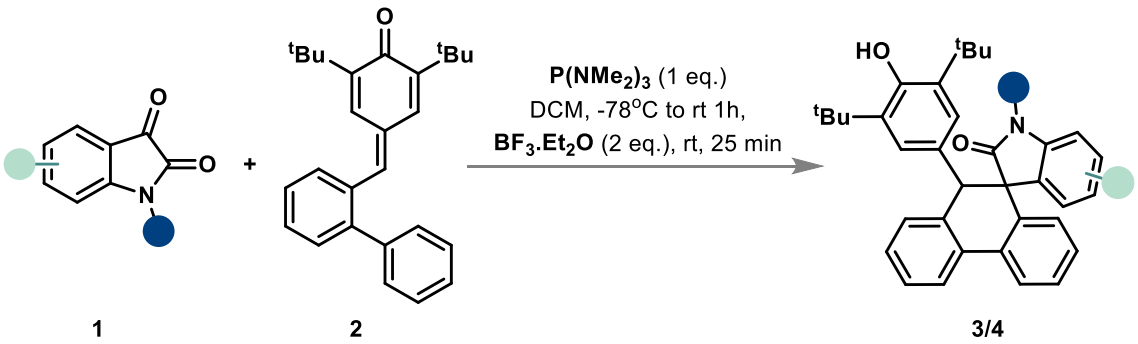


Scheme 1: Synthesis of 2-vinyl and 2-aryl-*p*-QMs

3. Synthesis of Dispirocyclopropane intermediate (5) *via* [1,2]-phospha-Brook Rearrangement:



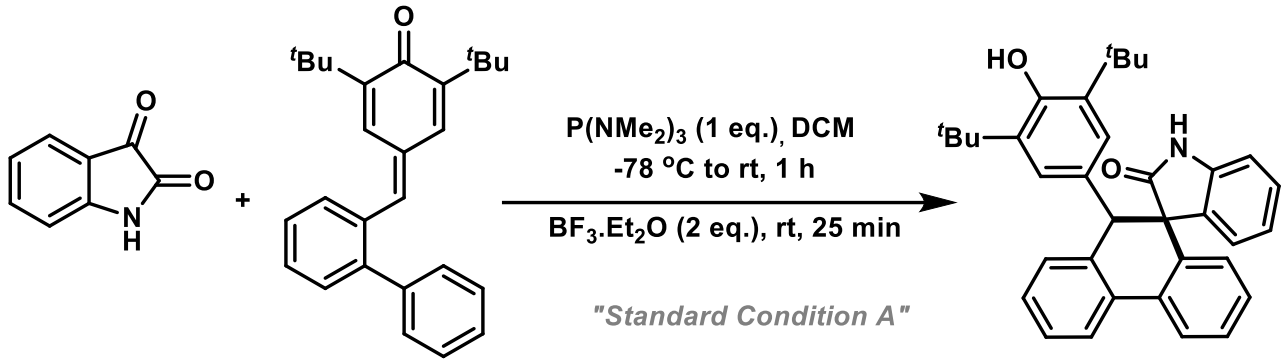
4. General procedure for the synthesis of spirooxindole-dihydrophenanthrene scaffolds:



Under an inert atmosphere, a 5 ml long neck round bottom flask charged with isatin derivative **1**(0.1 mmol, 1 eq.) and 2-phenyl-*p*-QMs **2** (0.11 mmol, 1.1 eq.) in dry DCM (1 mL) was cooled to -78 °C, followed by the addition of $P(NMe_2)_3$ (0.1 mmol, 18.2 µl) dropwise by a syringe over a period of 5 min, after complete addition of $P(NMe_2)_3$, the resulting reaction mixture was brought to room temperature gradually and further allowed to react which is monitored by thin-layer chromatography (TLC). The consumption of isatin and formation of cyclopropane intermediate usually takes 1 h indicating completion of the first step, afterward $BF_3.Et_2O$ (14 µl, 0.2 mmol, 2 eq.) was added slowly over a period of 5 min and further allowed to react which is monitored by TLC. After the complete consumption of the cyclopropane intermediate adduct, the reaction mixture was concentrated under reduced pressure. The crude mixture was

immediately purified by flash column chromatography on silica gel (100–200 meshes) to furnish the corresponding spirooxindole products **3/4**.

5. Optimization of reaction conditions for Lewis acids and solvents



1a **2a** **3a**

Entry	Deviation from standard condition A	Yield (%)
1	None	84
2	Without $P(NMe_2)_3$	n.d
3	Without $BF_3.Et_2O$	n.d
4	$In(OTf)_3$ (0.2 eq.) instead $BF_3.Et_2O$	25
5	$In(OTf)_3$ (0.3 eq.) instead $BF_3.Et_2O$	33
6	$BF_3.Et_2O$ (0.2 eq.) instead of 2 eq.	28
7	$BF_3.Et_2O$ (0.5 eq.) instead of 2 eq.	47
8	$BF_3.Et_2O$ (1.0 eq.) instead of 2 eq.	60
9	TFA (1.0 eq.) instead of 2 eq.	42
10	$P(OEt)_3$,PPh_3 instead of $P(NMe_2)_3$	n.d

All reactions were performed under argon atmosphere, **1a** (0.1 mmol) and **2a** (0.11 mmol) were dissolved in solvent (1 ml) and cooled to -78 °C followed by the addition of $P(NMe_2)_3$ (0.1 mmol) afterward Lewis acid was added at rt.

6. Single Crystal X-ray of compound

Crystallization of compound **4h** was carried out at room temperature by Solvent Evaporation Method using ethyl acetate and heptane (3:7) as a solvent system.

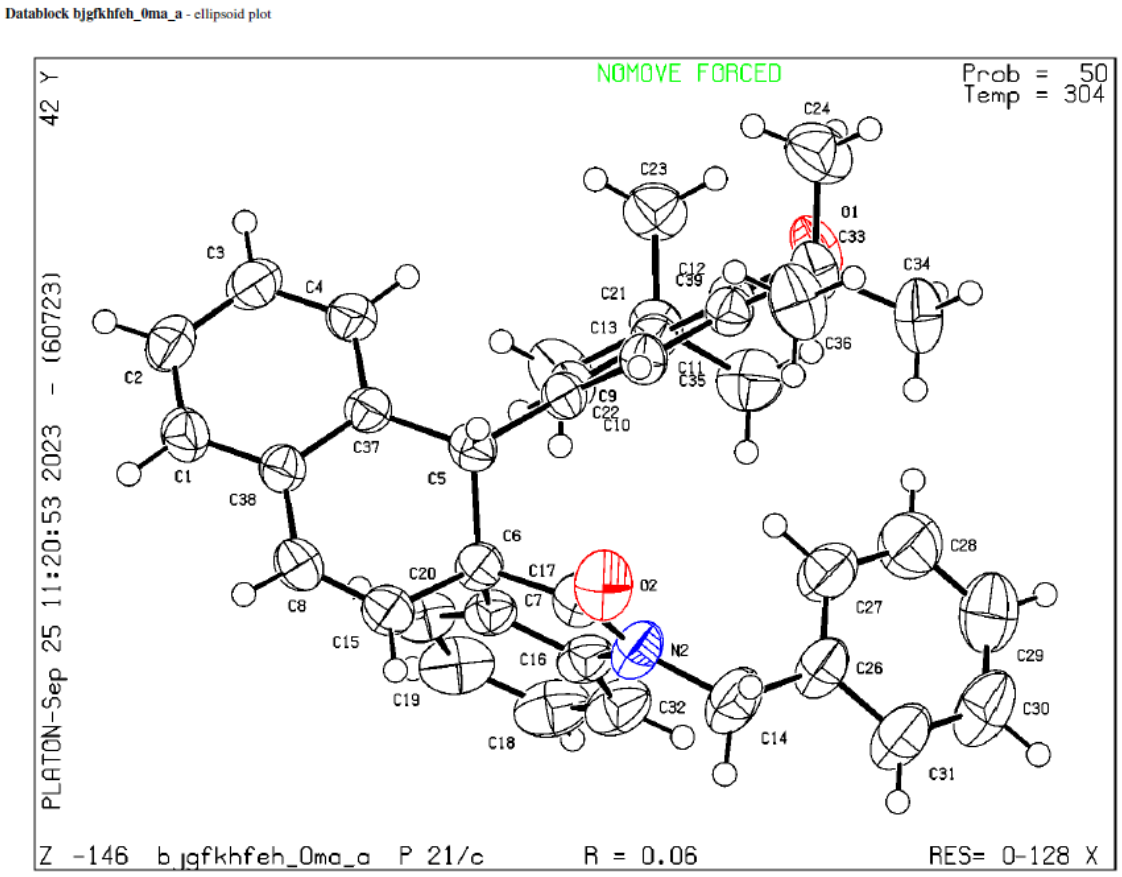


Table 1.1: Crystal data and structure refinement for **4h**

Bond precision:	C-C = 0.0023 A		Wavelength=0.71073
Cell:	a=18.2704(6)	b=10.4138(4)	c=18.7490(5)
	alpha=90	beta=118.769(1)	gamma=90
Temperature:	304 K		

	Calculated	Reported
Volume	3126.95(18)	3126.95(18)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C38 H38 N O2	C38 H38 N O2
Sum formula	C38 H38 N O2	C38 H38 N O2
Mr	540.69	540.69
Dx,g cm-3	1.148	1.148
Z	4	4
Mu (mm-1)	0.070	0.070

F000	1156.0	1156.0
F000'	1156.46	
h,k,lmax	24,13,25	24,13,25
Nref	7785	7784
Tmin,Tmax		
Tmin'		

Correction method= Not given

Data completeness= 1.000 Theta(max)= 28.322

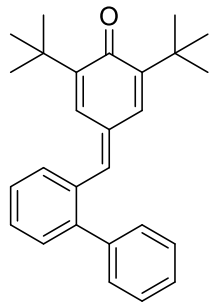
R(reflections)= 0.0603(4067) wR2(reflections)= 0.1515(7751)

S = 0.762 Npar= 377

7. Characterization data of the compounds:

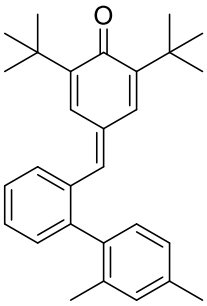
7.1 The spectral and analytical data of the compounds:

4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one(2a): The general procedure 2 was followed and the product **2a** was isolated as yellow solid (89 % yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.3 Hz, 1H), 7.40 (d, *J* = 3.6 Hz, 3H), 7.36 (d, *J* = 7.4 Hz, 3H), 7.33 (d, *J* = 6.8 Hz, 1H), 7.31 – 7.27 (m, 2H), 6.93 (s, 1H), 6.81 (s, 1H), 1.25 (s, 9H), 1.23 (s, 9H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.6, 149.3, 147.5, 143.0, 142.9, 140.3, 134.9, 133.9, 132.0, 131.7, 130.4, 129.9, 129.3, 128.4, 127.7, 127.3, 35.5, 35.0, 29.6, 29.5.



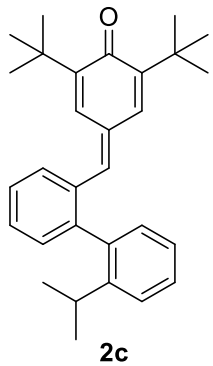
2a

2,6-di-tert-butyl-4-((2',4'-dimethyl-[1,1'-biphenyl]-2-yl)-methylene)-cyclohexa-2,5-dien-1-one (2b): The general procedure 2 was followed and the product **2b** was isolated as yellow solid (87 % yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 2.4 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.54 – 7.46 (m, 2H), 7.39 – 7.33 (m, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.97 – 6.85 (m, 2H), 2.41 (s, 3H), 2.06 (s, 3H), 1.42 (s, 9H), 1.37 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 186.7, 149.3, 147.5, 143.7, 142.5, 140.2, 137.3, 135.0, 134.8, 134.7, 131.8, 131.3, 130.7, 129.6, 129.1, 128.3, 127.9, 127.1, 125.3, 35.5, 35.1, 29.7, 29.6, 20.7, 16.9.



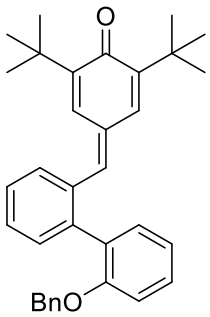
2b

2,6-di-tert-butyl-4-((2'-isopropyl-[1,1'-biphenyl]-2-yl)-methylene)-cyclohexa-2,5-dien-1-one (2c): The general procedure 2 was followed and the product **2c** was isolated as yellow solid (89 % yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.53 – 7.43 (m, 4H), 7.40 – 7.36 (m, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 6.87 (d, *J* = 2.3 Hz, 1H), 2.88 – 2.75 (m, 1H), 1.42 (s, 9H), 1.36 (s, 9H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 186.6, 149.4, 147.6, 146.9, 142.9, 142.4, 138.9, 135.0, 134.8, 132.0, 131.1, 130.7, 130.0, 129.0, 128.5, 128.3, 127.2, 125.7, 125.6, 35.5, 35.1, 29.9, 29.8, 29.6, 24.8, 23.3.



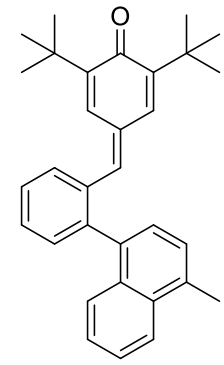
2c

4-((2'-(benzyloxy)-[1,1'-biphenyl]-2-yl)-methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (2d): The general procedure 2 was followed and the product **2d** was isolated as yellow solid (85 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.40 (m, 5H), 7.35 (ddd, *J* = 8.3, 7.5, 1.8 Hz, 1H), 7.22 (m, *J* = 7.5, 4.8, 1.6 Hz, 5H), 7.14 (dt, *J* = 5.2, 2.1 Hz, 1H), 7.08 – 6.99 (m, 2H), 6.95 (d, *J* = 0.8 Hz, 1H), 6.82 (dd, *J* = 2.5, 0.7 Hz, 1H), 5.01 (d, *J* = 10.5 Hz, 2H), 1.31 (s, 9H), 1.28 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 186.8, 155.9, 149.0, 147.4, 143.3, 140.1, 137.1, 135.2, 135.1, 132.0, 131.7, 131.6, 131.3, 131.2, 130.0, 129.5, 128.9, 128.6, 128.6, 128.5, 128.4, 127.8, 127.4, 127.3, 126.8, 126.7, 121.1, 120.8, 113.3, 113.1, 70.5, 70.3, 35.5, 35.1, 29.7, 29.6.



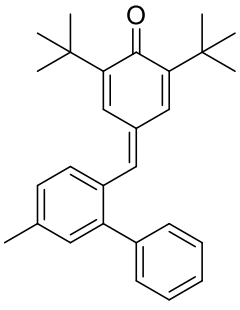
2d

2,6-di-tert-butyl-4-(2-(4-methylnaphthalen-1-yl)-benzylidene)-cyclohexa-2,5-dien-1-one (2e): The general procedure 2 was followed and the product **2e** was isolated as pale yellow solid (84 % yield). .**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.75 – 7.66 (m, 3H), 7.60 (t, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.1 Hz, 1H), 6.90 (s, 1H), 6.75 (d, *J* = 2.3 Hz, 1H), 2.84 (s, 3H), 1.46 (s, 9H), 1.31 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 186.7, 149.3, 147.3, 142.6, 141.9, 136.3, 135.6, 135.0, 134.6, 132.9, 131.9, 131.9, 131.9, 131.6, 128.9, 128.4, 128.1, 127.5, 126.7, 126.2, 126.0, 126.0, 124.6, 35.6, 35.0, 29.8, 29.6,19.7.



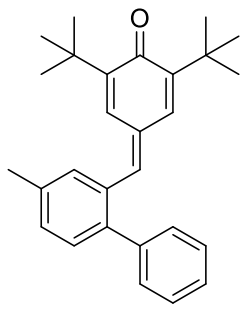
2e

2,6-di-tert-butyl-4-((5-methyl-[1,1'-biphenyl]-2-yl)methylene)cyclohexa-2,5-dien-1-one (2f): The general procedure 2 was followed and the product **2f** was isolated as yellow solid (89 % yield). .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 2.5, 0.8 Hz, 1H), 7.43 (d, *J* = 1.9 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.35 (t, *J* = 1.6 Hz, 1H), 7.29 (dt, *J* = 1.9, 0.7 Hz, 1H), 7.27 (dt, *J* = 1.8, 0.6 Hz, 1H), 6.98 (s, 1H), 6.88 (d, *J* = 1.7 Hz, 1H), 2.45 (s, 3H), 1.32 (s, 9H), 1.29 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 186.7, 149.1, 147.3, 143.4, 143.0, 140.4, 139.8, 135.1, 132.1, 131.3, 131.3, 130.0, 128.6, 128.4, 128.2, 127.7, 35.6, 35.1, 29.7, 29.6, 21.5.



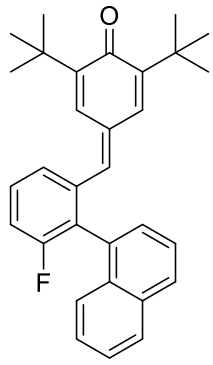
2f

2,6-di-tert-butyl-4-((4-methyl-[1,1'-biphenyl]-2-yl)-methylene)-cyclohexa-2,5-dien-1-one(2g): The general procedure 2 was followed and the product **2g** was isolated as yellow solid (86 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 2.4, 0.9 Hz, 1H), 7.42 (d, *J* = 2.1 Hz, 1H), 7.41 (d, *J* = 1.5 Hz, 1H), 7.38 (t, *J* = 2.6 Hz, 1H), 7.37 – 7.30 (m, 4H), 7.30 – 7.25 (m, 1H), 7.00 (s, 1H), 6.88 (d, *J* = 2.5 Hz, 1H), 2.44 (s, 3H), 1.32 (s, 9H), 1.29 (s, 9H).**^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 186.7, 149.1, 147.5, 143.4, 140.3, 137.1, 135.0, 133.8, 131.7, 130.4, 130.2, 130.0, 128.6, 128.4, 127.6, 35.6, 35.1, 29.7, 29.6, 21.2.



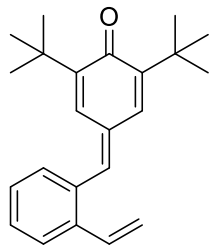
2g

2,6-di-tert-butyl-4-(3-fluoro-2-(naphthalen-1-yl)-benzylidene)-cyclohexa-2,5-dien-1-one (2h): The general procedure 2 was followed and the product **2h** was isolated as yellow solid (83 % yield). .**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 12.0 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.53 – 7.40 (m, 5H), 7.37 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.33 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.28 – 7.24 (m, 1H), 6.64 – 6.53 (m, 2H), 1.31 (s, 9H), 1.19 (s, 9H).**^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 186.7, 149.7, 147.8, 140.4, 140.4, 138.0, 137.9, 134.7, 133.7, 132.7, 129.2, 129.1, 128.5, 127.9, 127.3, 127.3, 126.7, 126.3, 125.5, 116.3, 35.6, 35.1, 29.7, 29.5.**^{19}F{^{1}H} NMR** (376 MHz, DMSO-d_6) δ -111.6.



2h

2,6-di-tert-butyl-4-(2-vinylbenzylidene)-cyclohexa-2,5-dien-1-one (2i): The general procedure 2 was followed and the product **2i** was isolated as yellow solid (81 % yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.34 – 7.25 (m, 4H), 7.08 – 6.98 (m, 1H), 6.88 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.69 (dd, *J* = 17.4, 1.1 Hz, 1H), 5.38 (dd, *J* = 11.0, 1.1 Hz, 1H), 1.33 (s, 9H), 1.24 (s, 9H).**^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 186.7, 149.3, 147.9, 141.4, 137.9, 134.8, 134.7, 133.9, 132.6, 131.3, 129.3, 128.5, 127.6, 126.6, 117.5, 35.5, 35.1, 29.6, 29.6.

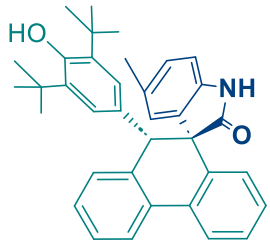


2i

(±)**3'-([1,1'-biphenyl]-2-yl)-3,5-di-tert-butyldispiro[cyclohexane-1,1'-cyclopropane-2',3''-indoline]-2,5-diene-2'',4-dione** (**5**): The first step of general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and isatin **1a** (14.7 mg, 0.1 mmol). The product **5** was isolated as pale-yellow solid in 45.6 mg (91% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-25:75 v/v). (*major/minor* >20:1)**^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.53 – 7.42 (m, 2H), 7.40 – 7.31 (m, 2H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.18 – 7.05 (m, 4H), 7.03 – 6.93 (m, 2H), 6.83 – 6.72 (m, 2H), 6.60 (s, 1H), 6.19 (d, *J* = 7.8 Hz, 1H), 4.38 (s, 1H), 1.27 (s, 9H), 1.13 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 185.5, 175.4, 149.4, 149.1, 143.9, 141.6, 140.0, 138.2, 134.9, 131.6, 130.5, 129.2, 128.7, 128.7, 127.9, 127.6, 127.1, 126.9, 124.6, 124.5, 121.4, 110.2, 48.5, 45.8, 43.7, 35.8, 35.5, 29.5, 29.3. **IR** (cm^{-1}) 3437, 2950, 1695, 1620, 1228, 745. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{36}NO_2$ 502.2746, found 502.2736.

(±)-*anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (**3a**): The general procedure 4 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and isatin **1a** (14.7 mg, 0.1 mmol). The product **3a** was isolated as off-white solid in 42.1 mg (84% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-25:75 v/v), (For crude reaction mixture, *anti/syn* >20:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.97 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.42 (td, *J* = 7.6, 1.3 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.14 – 7.10 (m, 2H), 7.10 – 7.05 (m, 1H), 6.98 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.80 – 6.70 (m, 2H), 6.48 (d, *J* = 7.5 Hz, 1H), 6.24 (d, *J* = 2.2 Hz, 1H), 5.10 (s, 1H), 4.86 (s, 1H), 1.37 (s, 9H), 1.07 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 181.6, 153.1, 140.3, 137.3, 136.7, 135.1, 134.8, 134.1, 131.4, 129.3, 129.0, 128.6, 128.4, 128.4, 127.9, 127.6, 126.5, 126.3, 125.0, 124.8, 124.8, 123.8, 122.5, 110.1, 59.9, 53.2, 34.2, 34.2, 30.5, 30.1. **IR** (cm^{-1}) 3630, 3434, 2956, 1705, 1616, 1471, 1436, 1233, 746. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{35}NNaO_2$ 524.2565, found 524.2559.

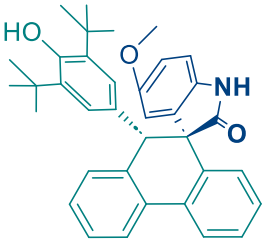
(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methyl-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3b):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 5-methylindoline-2,3-dione **1b** (16.1 mg, 0.1 mmol). The product **3b** was isolated as an off-white solid in 44.9 mg (87 % yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-25:75 v/v), (For crude reaction mixture, *anti/syn* >20:1).



3b

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.10 (s, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 6.27 (s, 2H), 5.08 (s, 1H), 4.83 (s, 1H), 2.04 (s, 3H), 1.35 (s, 9H), 1.07 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 181.8, 153.0, 137.9, 137.4, 136.8, 135.1, 134.8, 134.7, 134.1, 131.7, 131.5, 129.2, 129.0, 128.7, 128.6, 128.4, 127.9, 127.5, 126.6, 126.5, 125.4, 125.1, 124.7, 123.7, 109.9, 60.0, 52.9, 34.2, 34.1, 30.5, 30.0, 21.1. **IR** (cm^{-1}) 3409, 2927, 1723, 1442, 1264, 667. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{37}NNaO_2$ 538.2722, found 538.2716.

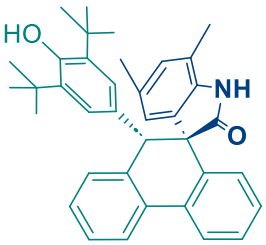
(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methoxy-10'H-spiro[indoline-3,9'-phenanthren]-2-one** (**3c**)**:** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 5-methoxyindoline-2,3-dione **1c** (17.7 mg, 0.1 mmol). The product **3c** was isolated as off-white solid in 47.3 mg (89 % yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-30:70 v/v), (For crude reaction mixture, *anti/syn* >20:1).



3c

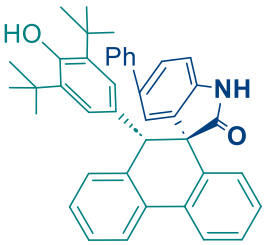
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.97 – 7.91 (m, 2H), 7.45 – 7.36 (m, 2H), 7.26 – 7.15 (m, 2H), 7.09 – 7.03 (m, 2H), 6.96 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.68 – 6.60 (m, 2H), 6.29 (d, *J* = 2.2 Hz, 1H), 6.05 (d, *J* = 2.2 Hz, 1H), 5.08 (s, 1H), 4.80 (s, 1H), 3.46 (s, 3H), 1.34 (s, 9H), 1.08 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 181.4, 155.5, 153.1, 137.2, 136.7, 135.1, 134.9, 134.7, 134.1, 134.0, 132.6, 129.2, 129.1, 128.6, 128.5, 127.9, 127.6, 126.6, 125.0, 124.8, 123.8, 113.3, 111.7, 110.4, 60.2, 55.6, 53.0, 34.2, 30.5, 30.1. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{37}NNaO_3$ 554.2671, found 554.2665.

(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-5,7-dimethyl-10'H-spiro[indoline-3,9'-phenanthren]-2-one** (**3d**): The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 5,7-dimethylindoline-2,3-dione **1d** (17.5 mg, 0.1 mmol). The product **3d** was isolated as off-white solid in 39.2 mg (74% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-25:75 v/v), (For crude reaction mixture, *anti/syn* >20:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.88 – 7.80 (m, 2H), 7.35 – 7.25 (m, 2H), 7.16 – 7.07 (m, 2H), 6.96 (s, 1H), 6.93 – 6.89 (m, 2H), 6.87 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.62 (s, 1H), 6.16 (s, 1H), 5.94 (s, 1H), 4.95 (s, 1H), 4.68 (s, 1H), 1.96 (s, 3H), 1.90 (s, 3H), 1.27 (s, 9H), 0.97 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 181.5, 153.0, 137.5, 137.1, 136.8, 135.0, 134.8, 134.8, 134.2, 131.5, 131.1, 130.2, 129.1, 129.0, 128.5, 128.2, 127.8, 127.4, 127.0, 126.8, 125.1, 124.6, 123.6, 122.9, 118.9, 60.0, 53.0, 34.2, 30.5, 30.0, 21.1, 16.6. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{37}H_{39}NNaO_2$ 552.2878, found 552.2872.



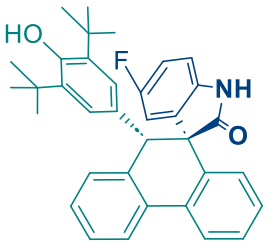
3d

(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-phenyl-10'H-spiro[indoline-3,9'-phenanthren]-2-one** (**3e**): The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2** (40.8 mg, 0.11 mmol) and 5-phenylindoline-2,3-dione **1e** (22.3 mg, 0.1 mmol). The product **3e** was isolated as off-white solid in 45.1 mg (78% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-25:75 v/v), (For crude reaction mixture, *anti/syn* >20:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.95 (dd, *J* = 8.0, 4.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.64 (s, 1H), 6.36 (s, 1H), 5.08 (s, 1H), 4.80 (s, 1H), 1.35 (s, 9H), 1.04 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 180.8, 153.2, 141.0, 139.6, 136.8, 135.7, 135.2, 135.0, 134.8, 134.4, 132.0, 129.6, 129.1, 128.8, 128.6, 128.5, 128.0, 127.7, 127.3, 126.8, 126.7, 126.7, 125.0, 124.9, 124.0, 123.9, 110.0, 59.7, 53.2, 34.3, 34.2, 30.5, 30.1. **IR** (cm^{-1}) 3636, 2957, 1710, 1614, 1232, 749. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{39}NNaO_2$ 600.2878, found 600.2872.



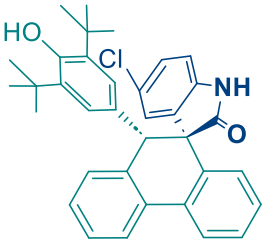
3e

(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-fluoro-10'H-spiro[indoline-3,9'-phenanthren]-2-one** (**3f**): The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 5-fluoroindoline-2,3-dione **1f** (16.5 mg, 0.1 mmol). The product **3f** was isolated as an off-white solid in 36.4 mg (70% yield), (For crude reaction mixture, *anti/syn* >20:1). **Eluent**: ethyl acetate/ petroleum ether (10:90-25:75 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.95 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.43 (dt, *J* = 15.6, 7.6 Hz, 2H), 7.29 – 7.19 (m, 1H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.81 (td, *J* = 8.9, 2.7 Hz, 1H), 6.66 (dd, *J* = 8.5, 4.2 Hz, 1H), 6.27 (s, 1H), 6.17 (d, *J* = 8.4 Hz, 1H), 5.10 (s, 1H), 4.80 (s, 1H), 1.35 (s, 9H), 1.08 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 181.3, 159.8, 157.9, 153.2, 136.5, 136.4, 136.2, 135.3, 135.0, 134.5, 134.1, 133.1, 133.1, 129.3, 129.1, 128.8, 128.7, 128.2, 127.9, 126.5, 126.3, 125.0, 124.8, 123.9, 114.9, 114.7, 113.0, 112.8, 110.5, 60.3, 53.1, 34.2, 34.2, 30.5, 30.1. **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) δ -120.71. **IR** (cm^{-1}) 3635, 2958, 1711, 1628, 1483, 1240, 744. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{34}FNNaO_2$ 542.2471, found 542.2465.



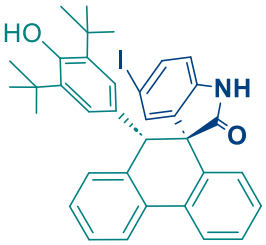
3f

(±)-***anti*-5-chloro-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one** (**3g**): The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 5-chloroindoline-2,3-dione **1g** (18.2 mg, 0.1 mmol). The product **3g** was isolated as an off-white solid in 39.7 mg (74% yield), (For crude reaction mixture, *anti/syn* >20:1). **Eluent**: ethyl acetate/ petroleum ether (10:90-25:75 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.97 (dd, *J* = 7.8, 4.2 Hz, 2H), 7.49 – 7.38 (m, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.12 – 7.03 (m, 3H), 6.93 – 6.88 (m, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 6.38 (d, *J* = 2.2 Hz, 1H), 6.31 (d, *J* = 2.2 Hz, 1H), 5.11 (s, 1H), 4.78 (s, 1H), 1.35 (s, 9H), 1.10 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 181.6, 153.2, 139.0, 136.1, 136.1, 135.3, 135.1, 134.3, 134.1, 133.2, 129.1, 129.0, 128.8, 128.6, 128.3, 128.2, 127.9, 127.6, 126.5, 126.3, 125.3, 124.9, 123.9, 111.2, 60.2, 53.0, 34.2, 34.2, 30.5, 30.1. **IR** (cm^{-1}) 3632, 2955, 1715, 1612, 1235, 741. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{34}ClNNaO_2$ 558.2176, found 558.2170.



3g

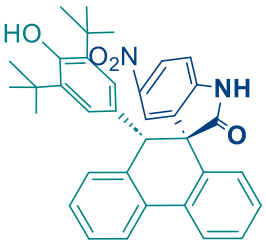
(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-iodo-10'H-spiro[indoline-3,9'-phenanthren]-2-one** (**3h**): The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 5-iodoindoline-2,3-dione **1h** (27.3 mg, 0.1 mmol). The product **3h** was isolated as an off-white solid in 49.6 mg (79% yield), (For crude reaction mixture, *anti/syn* >20:1).



3h

Eluent: ethyl acetate/ petroleum ether (10:90-25:75 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.98 – 7.92 (m, 2H), 7.48 – 7.38 (m, 3H), 7.29 – 7.27 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.07 – 7.01 (m, 2H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.67 (s, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 6.29 (s, 1H), 5.09 (s, 1H), 4.75 (s, 1H), 1.35 (s, 9H), 1.09 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 180.8, 153.2, 140.0, 137.2, 136.2, 136.1, 135.3, 135.1, 134.3, 134.2, 134.0, 133.8, 129.1, 129.0, 128.8, 128.6, 128.2, 127.9, 126.6, 126.4, 125.0, 125.0, 123.9, 112.1, 85.1, 59.9, 53.0, 34.3, 34.2, 30.5, 30.1. **IR** (cm^{-1}) 3631, 2924, 1714, 1608, 1234, 742. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{34}INNaO_2$ 650.1532, found 650.1526.

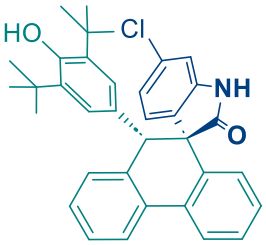
(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-nitro-10'H-spiro[indoline-3,9'-phenanthren]-2-one** (**3i**): The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2**a (40.8 mg, 0.11 mmol) and 5-nitroindoline-2,3-dione **1i** (19.2 mg, 0.1 mmol). The product **3i** was isolated as off-white solid in 38.3 mg (70% yield), (For crude reaction mixture, *anti/syn* >20:1).



3i

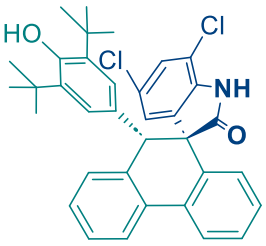
Eluent: ethyl acetate/ petroleum ether (10:90-25:75 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.54 – 7.44 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.17 (s, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.96 (s, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 6.29 (s, 1H), 5.13 (s, 1H), 4.74 (s, 1H), 1.34 (s, 9H), 1.06 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 181.1, 153.5, 146.3, 143.2, 135.6, 135.5, 135.0, 134.5, 134.1, 132.3, 129.2, 129.2, 128.9, 128.7, 128.5, 128.3, 126.5, 125.4, 125.2, 124.5, 124.1, 121.2, 109.6, 59.7, 53.2, 34.2, 34.2, 30.4, 30.0. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{34}N_2NaO_4$ 569.2416, found 569.2410.

(±)-***anti*-6-chloro-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3j):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 6-chloroindoline-2,3-dione **1j** (19.2 mg, 0.1 mmol). The product **3j** was isolated as off-white solid in 41.2 mg (77% yield), (For crude reaction mixture, *anti/syn* >20:1). **Eluent**: ethyl acetate/ petroleum ether (10:90-25:75 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.93 (m, *J* = 7.9, 2.8, 1.3 Hz, 2H), 7.47 – 7.34 (m, 2H), 7.28 – 7.17 (m, 2H), 7.08 – 6.99 (m, 2H), 6.90 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.74 (d, *J* = 1.9 Hz, 1H), 6.68 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.35 (d, *J* = 8.1 Hz, 1H), 6.18 (d, *J* = 2.1 Hz, 1H), 5.10 (s, 1H), 4.79 (s, 1H), 1.33 (s, 9H), 1.09 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 181.7, 153.3, 141.5, 136.5, 136.2, 135.3, 135.0, 134.6, 134.2, 134.0, 129.8, 129.2, 129.0, 128.7, 128.0, 127.7, 126.4, 126.0, 125.8, 124.9, 124.9, 123.8, 122.3, 110.6, 59.7, 53.2, 34.2, 30.4, 29.9. **IR** (cm^{-1}) 3635, 2957, 1715, 1612, 1235, 745. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{34}ClNNaO_2$ 558.2176, found 558.2170.



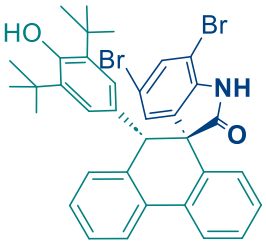
3j

(±)-***anti*-5,7-dichloro-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3k):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 5,7-dichloroindoline-2,3-dione **1k** (21.6 mg, 0.1 mmol). The product **3k** was isolated as off-white solid in 43.9 mg (77% yield). (For crude reaction mixture, *anti/syn* >20:1). **Eluent**: ethyl acetate/ petroleum ether (10:90-25:75 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.9 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.32 (dt, J = 23.5, 7.6 Hz, 2H), 7.16 – 7.02 (m, 4H), 6.94 (d, J = 8.7 Hz, 1H), 6.86 (d, J = 8.7 Hz, 1H), 6.76 – 6.64 (m, 2H), 5.38 (s, 1H), 4.97 (d, J = 7.2 Hz, 1H), 1.26 (s, 9H), 1.18 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 175.6, 153.1, 140.6, 135.5, 135.2,135.1,134.9,132.7,130.0,129.7,129.1,129.0,128.6,128.1,127.9,127.7,127.5,127.1,126.6, 125.4,124.2,124.1,123.4,113.1,61.3,50.4,34.5,34.2,30.4,30.2.**HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{33}Cl_2NNaO_2$ 592.1786, found 592.1780.



3k

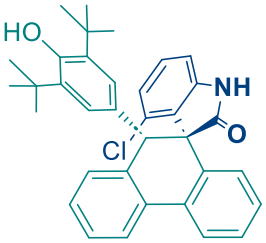
(±)-***anti*-5,7-dibromo-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one** (**3l**): The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2**a(40.8 mg, 0.11 mmol) and 5,7-dibromoindoline-2,3-dione **1l** (30.5 mg, 0.1 mmol). The product **3l** was isolated as off-white solid in 49.3 mg (75% yield), (For crude reaction mixture, *anti/syn* >20:1). **Eluent**: ethyl acetate/ petroleum ether (10:90-25:75 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.94 (t, *J* = 7.4 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.26 (d, *J* = 9.5 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.06 – 6.92 (m, 3H), 6.37 (d, *J* = 1.7 Hz, 1H), 6.27 (d, *J* = 2.2 Hz, 1H), 5.12 (s, 1H), 4.74 (s, 1H), 1.41 (s, 9H), 1.10 (s, 9H).**^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 178.8, 153.4, 139.1, 135.9, 135.6, 135.6, 135.3, 134.3, 134.2, 134.1, 133.1, 129.2, 129.1, 129.0, 128.7, 128.3, 128.0, 127.1, 126.8, 126.3, 125.0, 124.6, 123.9, 115.0, 103.2, 61.2, 53.3, 34.3, 34.2, 30.6, 30.4, 30.1, 29.8.



3l

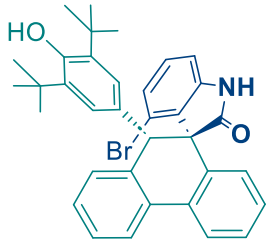
. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{33}Br_2NNaO_2$ 682.0755, found 682.0749.

(±)-***anti*-4-chloro-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3m):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 4-chloroindoline-2,3-dione **1m** (23.7 mg, 0.1 mmol) to give an inseparable mixture of diastereomers of **3m**. The product **3m** was isolated as off-white solid in 40.7 mg (76% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* =76:24). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.01 (d, *J* = 6.9 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.18 – 7.13 (m, 3H), 6.99 (d, *J* = 1.5 Hz, 1H), 6.77 – 6.70 (m, 2H), 6.26 (d, *J* = 8.7 Hz, 1H), 5.51 (s, 1H), 4.96 (s, 1H), 1.23 (s, 9H), 1.19 (s, 9H).**^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 177.3, 152.3, 143.2, 135.6, 135.0, 134.8, 134.6, 133.1, 130.9, 130.5, 129.4, 128.6, 128.2, 127.7, 127.4, 127.3, 127.1, 126.7, 124.9, 124.6, 123.3, 123.1, 107.9, 59.9, 49.6, 34.2, 34.0, 30.2, 30.1.. **IR** (cm^{-1}) 3632, 2956, 1709, 1616, 1228, 742. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{34}ClNNaO_2$ 558.2176, found 558.2165.



3m

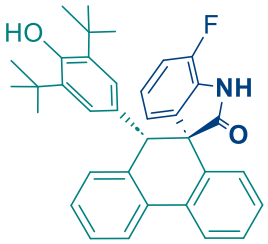
(±)-***anti*-4-bromo-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3n):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 4-bromoindoline-2,3-dione **1n** (23.7 mg, 0.1 mmol). The product **3n** was isolated as off-white solid in 45.7 mg (79 % yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* >20:1).



3n

^{1}H NMR (500 MHz, $CDCl_3$)δ 8.01 (d, *J* = 9.5 Hz, 1H), 7.93 (d, *J* = 9.3 Hz, 1H), 7.87 (s, 1H), 7.44 – 7.35 (m, 2H), 7.23 – 7.12 (m, 5H), 6.94 (t, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 2.2 Hz, 1H), 6.75 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.36 (dd, *J* = 7.8, 0.9 Hz, 1H), 5.62 (s, 1H), 4.97 (s, 1H), 1.24 (s, 18H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 177.0, 152.7, 143.4, 135.5, 135.1, 135.0, 134.8, 134.6, 133.0, 130.5, 129.6, 128.6, 128.5, 128.3, 127.7, 127.4, 127.3, 127.1, 127.0, 126.6, 124.9, 124.7, 123.2, 120.1, 108.3, 60.5, 49.3, 34.3, 34.0, 30.3, 30.1. **IR** (cm^{-1}) 3636, 3439, 2956, 1709, 1615, 1226, 743. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{35}BrNO_2$ 580.1851, found 580.1859.

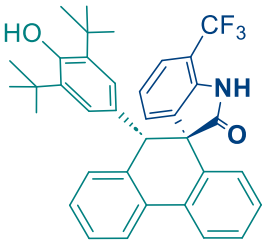
(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-7-fluoro-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3o):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 7-flouroindoline-2,3-dione **1o** (23.7 mg, 0.1 mmol). The product **3o** was isolated as off-white solid in 37.4 mg (72% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* >20:1).



3o

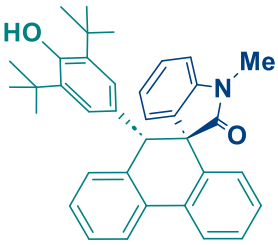
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 2H), 7.45 (dt, *J* = 18.9, 7.7 Hz, 2H), 7.31 – 7.21 (m, 2H), 7.15 (d, *J* = 2.2 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 9.0 Hz, 1H), 6.70 (td, *J* = 8.0, 4.7 Hz, 1H), 6.30 (d, *J* = 7.6 Hz, 1H), 6.24 (d, *J* = 2.1 Hz, 1H), 5.17 (s, 1H), 4.91 (s, 1H), 1.42 (s, 9H), 1.12 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 180.2, 153.2, 148.0, 146.1, 136.7, 136.4, 135.3, 134.9, 134.6, 134.2, 133.9, 129.3, 128.9, 128.6, 128.5, 127.9, 127.7, 127.6, 127.6, 126.5, 126.1, 124.8, 124.6, 123.7, 122.9, 122.9, 120.5, 115.2, 115.1, 60.2, 53.2, 34.2, 34.1, 30.4, 30.1. **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) δ -133.5. **IR** (cm^{-1}) 3638, 2956, 1718, 1640, 1229, 733. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{34}FNNaO_2$ 542.2471, found 542.2479.

(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-7-(trifluoromethyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3p):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 7-(trifluoromethyl)-2,3-dione **1p** (23.7 mg, 0.1 mmol) to give an inseparable mixture of diastereomers of **3p**. The product **3p** was isolated as off-white solid in 43.2 mg (76% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* =87:13) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.9, 4.5 Hz, 2H), 7.54 – 7.39 (m, 3H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.10 – 7.01 (m, 3H), 6.83 (t, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.16 (d, *J* = 2.2 Hz, 1H), 5.12 (s, 1H), 4.88 (s, 1H), 1.44 (s, 9H), 1.05 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 179.5, 153.3, 136.4, 136.1, 135.5, 135.1, 134.6, 134.0, 133.1, 129.3, 129.1, 128.8, 128.7, 128.4, 128.1, 127.8, 126.6, 125.9, 124.9, 124.5, 123.8, 122.2, 58.7, 53.2, 34.2, 34.1, 30.4, 30.2, 29.9. **^{19}F{^{1}H} NMR** (471 MHz, $CDCl_3$) δ -60.82. **IR** (cm^{-1})3645, 3446, 2956, 1721, 1621, 1118, 744. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{34}F_3NNaO_2$ 592.2439 , found 592.2461.



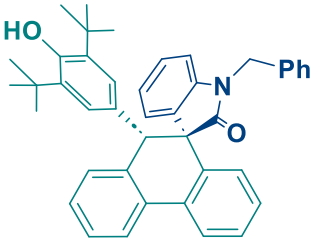
3p

(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-methyl-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3q):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 1-benzylindoline-2,3-dione **1q** (23.7 mg, 0.1 mmol). The product **3q** was isolated as off-white solid in 37.1 mg (72% yield), (For crude reaction mixture, *anti/syn* >20:1). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (t, *J* = 7.9 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.19 (m, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 7.12 – 7.09 (m, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 7.4 Hz, 1H), 6.16 – 6.12 (m, 1H), 5.08 (s, 1H), 4.87 (s, 1H), 2.86 (s, 3H), 1.47 (s, 9H), 1.07 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 180.7, 153.1, 139.9, 137.1, 136.1, 136.0, 135.2, 135.0, 134.2, 134.0, 133.9, 133.7, 129.0, 128.9, 128.7, 128.5, 128.1, 127.7, 126.5, 126.3, 124.9, 124.8, 123.8, 112.0, 85.0, 52.9, 34.1, 34.1, 30.4, 30.0. **IR** (cm^{-1})3628, 3445, 2920, 1713, 1607, 1437, 748. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{37}NNaO_2$ 538.2722 , found 538.2718.



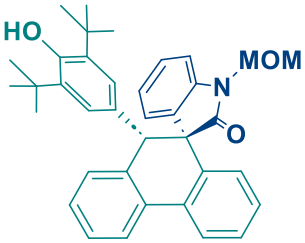
3q

(±)-***anti*-1-benzyl-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one** (**3r**): The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 1-benzylindoline-2,3-dione **1r** (23.7 mg, 0.1 mmol). The product **3r** was isolated as off-white solid in 47.3 mg (80% yield), (For crude reaction mixture, *anti/syn* >20:1). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.39 (td, *J* = 7.6, 1.3 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.21 – 7.18 (m, 3H), 7.18 – 7.13 (m, 1H), 7.02 – 6.90 (m, 3H), 6.70 (td, *J* = 7.6, 1.0 Hz, 1H), 6.62 – 6.56 (m, 3H), 6.41 (d, *J* = 7.8 Hz, 1H), 6.23 (d, *J* = 2.2 Hz, 1H), 5.21 (s, 1H), 5.11 (d, *J* = 15.8 Hz, 1H), 4.99 (s, 1H), 4.45 (d, *J* = 15.8 Hz, 1H), 1.43 (s, 9H), 0.97 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 178.8, 153.4, 142.1, 138.1, 137.2, 135.5, 135.4, 134.9, 134.8, 133.9, 131.2, 129.7, 129.0, 129.0, 128.7, 128.3, 128.2, 127.9, 127.5, 127.1, 126.9, 126.5, 126.4, 125.7, 124.7, 124.3, 123.7, 122.6, 109.4, 59.3, 52.6, 44.1, 34.4, 34.3, 30.6, 30.3. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{42}H_{41}NNaO_2$ 614.3035, found 614.3030.



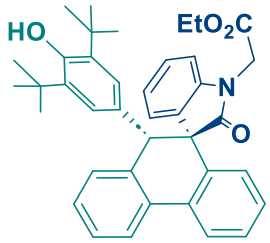
3r

(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(methoxymethyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3s):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 1-(methoxymethyl)-indoline-2,3-dione **1s** (19.1 mg, 0.1 mmol). The product **3s** was isolated as off-white solid in 43 mg (79% yield), (For crude reaction mixture, *anti/syn* >20:1). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.36 (m, 2H), 7.24 – 7.08 (m, 3H), 6.96 – 6.88 (m, 1H), 6.78 (td, *J* = 7.6, 1.1 Hz, 3H), 6.54 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.18 (d, *J* = 2.2 Hz, 1H), 5.09 (s, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 4.90 – 4.86 (m, 2H), 2.60 (s, 3H), 1.38 (s, 9H), 1.03 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 179.1, 153.4, 141.2, 138.0, 136.9, 135.4, 135.0, 134.8, 133.9, 130.6, 129.6, 128.9, 128.6, 128.6, 128.4, 128.0, 127.6, 126.6, 126.2, 125.0, 124.8, 124.5, 123.8, 123.1, 109.8, 71.3, 59.6, 55.3, 53.0, 34.2, 34.1, 30.4, 30.0. **IR** (cm^{-1})3612, 2953, 1715, 1606, 1437, 1346, 1236, 1078, 750. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{37}H_{39}NNaO_3$ 568.2828, found 568.2805.



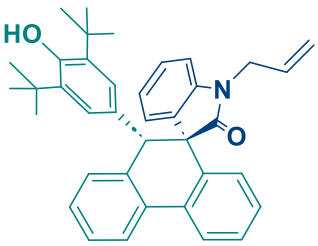
3s

(±)-***anti*-ethyl 2-(10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-oxo-10'H-spiro[indoline-3,9'-phenanthren]-1-yl)acetate (3t):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and ethyl 2-(2,3-dioxoindolin-1-yl)acetate **1t** (23.3 mg, 0.1 mmol). The product **3t** was isolated as off-white solid in 41.7 mg (81% yield), (For crude reaction mixture, *anti/syn* >20:1). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (ddd, *J* = 7.7, 6.2, 1.3 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.22 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.14 – 7.04 (m, 4H), 6.74 (td, *J* = 7.6, 1.0 Hz, 1H), 6.52 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 6.19 (d, *J* = 2.2 Hz, 1H), 5.08 (s, 1H), 4.86 (s, 1H), 4.50 (d, *J* = 17.4 Hz, 1H), 4.20 (qd, *J* = 7.1, 2.8 Hz, 2H), 3.58 (d, *J* = 17.5 Hz, 1H), 1.43 (s, 9H), 1.27 – 1.24 (m, 5H), 1.03 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 178.6, 167.7, 153.1, 141.6, 137.1, 136.3, 135.1, 134.9, 134.6, 134.0, 130.7, 129.2, 129.0, 128.7, 128.4, 128.4, 127.8, 127.6, 127.1, 126.2, 125.0, 124.9, 124.6, 123.8, 122.8, 107.8, 61.8, 59.5, 53.2, 41.1, 34.3, 34.1, 30.6, 30.1, 14.2. **IR**(cm^{-1})3576, 2957, 1759, 1727, 1438, 1208, 747. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{39}H_{41}NNaO_4$ 610.2933, found 610.2932.



3t,

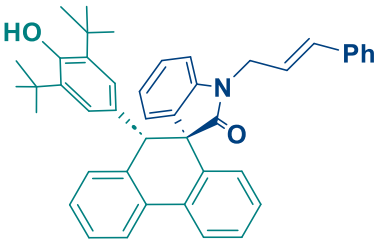
(±)-***anti*-1-allyl-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one** (**3u**): The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 1-allylindoline-2,3-dione **1u** (18.7 mg, 0.1 mmol). The product **3u** was isolated as off-white solid in 44.4 mg (82% yield), (For crude reaction mixture, *anti/syn* >20:1). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.24 – 7.20 (m, 2H), 7.15 – 7.05 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.97 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.59 (t, *J* = 6.7 Hz, 2H), 6.14 (d, *J* = 2.2 Hz, 1H), 5.11 (s, 1H), 5.05 – 5.00 (m, 1H), 4.93 – 4.90 (m, 2H), 4.62 (d, *J* = 1.9 Hz, 1H), 4.62 – 4.45 (m, 1H), 3.82 (dd, *J* = 16.3, 6.5 Hz, 1H), 1.44 (s,9H), 1.04 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 178.1, 153.3, 142.1, 137.7, 136.8, 135.2, 134.9, 134.6, 134.0, 131.7, 130.9, 129.6, 128.9, 128.6, 128.3, 128.2, 127.8, 127.5, 126.6, 126.3, 125.3, 124.7, 124.4, 123.7,



3u

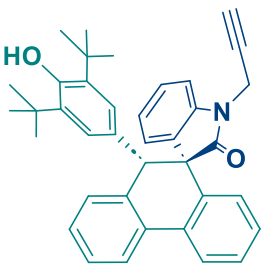
122.4, 117.1, 109.1, 59.4, 53.1, 42.2, 34.2, 34.1, 30.5, 30.0. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{40}NO_2$ 564.2878, found 564.2876.

(±)-***anti*-1-cinnamyl-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3v):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 1-cinnamylindoline-2,3-dione **1v** (26.3 mg, 0.1 mmol). The product **3v** was isolated as off-white solid in 48.8 mg (79% yield), (For crude reaction mixture, *anti/syn* >20:1). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (ddd, *J* = 8.0, 3.5, 1.3 Hz, 2H), 7.47 – 7.38 (m, 2H), 7.33 – 7.28 (m, 4H), 7.27 (dt, *J* = 4.1, 2.0 Hz, 2H), 7.23 (dd, *J* = 3.5, 1.2 Hz, 1H), 7.18 (d, *J* = 2.2 Hz, 1H), 7.11 – 7.09 (m, 2H), 7.01 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.75 – 6.68 (m, 2H), 6.60 – 6.52 (m, 1H), 6.16 (d, *J* = 2.2 Hz, 1H), 5.36 (ddd, *J* = 15.9, 7.8, 4.7 Hz, 1H), 5.13 (s, 1H), 4.95 (s, 1H), 4.57 (ddd, *J* = 15.8, 4.7, 2.0 Hz, 1H), 4.07 (ddd, *J* = 15.8, 7.8, 1.3 Hz, 1H), 1.48 (s, 9H), 0.96 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 178.1, 153.1, 142.3, 137.5, 136.7, 136.2, 135.3, 135.0, 134.5, 134.1, 133.2, 130.9, 129.7, 129.0, 128.7, 128.6, 128.6, 128.4, 128.3, 128.0, 127.9, 127.6, 126.8, 126.7, 126.6, 126.4, 125.3, 124.8, 124.6, 124.1, 123.8, 122.5, 109.1, 59.4, 53.3, 42.3, 34.5, 34.1, 30.6, 30.2. **IR** (cm^{-1})3628, 3431, 2953, 1718, 1435, 1353, 746. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{43}NNaO_2$ 640.3191, found 640.3217.



3v

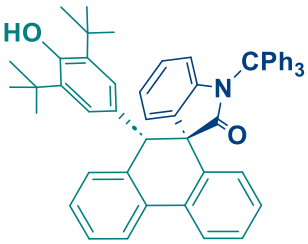
(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(prop-2-yn-1-yl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3w) :** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 1-(prop-2-yn-1-yl)indoline-2,3-dione **1w** (18.5 mg, 0.1 mmol). The product **3w** was isolated as off-white solid in 40.4 mg (73% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* >20:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 – 7.96 (m, 2H), 7.48 – 7.39 (m, 2H), 7.29 – 7.21 (m, 1H), 7.13 (ddd, *J* = 15.5, 7.5, 1.8 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.99 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.61 (dd, *J* = 7.6, 5.8 Hz, 2H), 6.17 (d, *J* = 2.2 Hz, 1H), 5.13 (s, 1H), 4.95 – 4.92 (m, 2H), 4.63 (dd, *J* = 17.1, 2.0 Hz, 1H), 4.50 (ddt, *J* = 16.2, 4.0, 2.1 Hz,



3w

1H), 3.84 (dd, *J* = 16.2, 6.5 Hz, 1H), 1.47 (s, 9H), 1.06 (s, 9H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 177.4, 153.2, 141.1, 137.1, 136.4, 134.9, 134.8, 134.4, 133.9, 130.6, 129.2, 128.9, 128.5, 128.3, 128.2, 127.8, 127.5, 126.6, 125.8, 125.0, 124.6, 124.6, 124.5, 123.7, 122.7, 108.9, 71.9, 59.6, 53.3, 34.2, 34.1, 30.6, 30.4, 30.0, 28.8. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{37}NNaO_2$ 562.2722, found 562.2719.

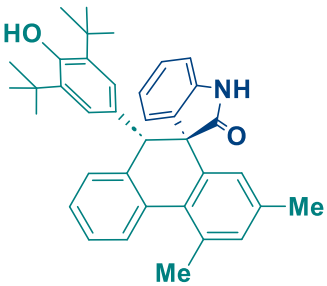
(±)-*anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-trityl-10'H-spiro[indoline-3,9'-phenanthren]-2-one (3x): The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (40.8 mg, 0.11 mmol) and 1-tritylindoline-2,3-dione **1x** (38.9 mg, 0.1 mmol). The product **3x** was isolated as off-white solid in 55.75mg (75% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* >20:1).



3x

^{1}H NMR δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.14 – 7.02 (m, 18H), 7.00 – 6.92 (m, 2H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.57 (dd, *J* = 8.3, 4.4 Hz, 1H), 6.51 – 6.31 (m, 4H), 5.97 (d, *J* = 8.2 Hz, 1H), 5.21 (s, 1H), 4.80 (s, 1H), 1.37 (s, 9H), 1.04 (s, 9H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 180.0, 153.4, 142.5, 142.2, 139.1, 137.7, 135.2, 134.6, 133.3, 132.0, 129.8, 129.5, 129.2, 128.3, 127.9, 127.8, 127.6, 127.5, 127.3, 127.3, 127.0, 126.8, 126.6, 124.2, 123.8, 123.4, 122.1, 116.2, 75.5, 58.5, 52.5, 34.3, 30.4. **IR** (cm^{-1})3630, 3441, 2955, 1725, 1598, 1438, 745, 703. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{54}H_{49}NNaO_2$ 766.3661, found 766.3670.

(±)-*anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-5',7'-dimethyl-10'H-spiro[indoline-3,9'-phenanthren]-2-one (4a): The general procedure 3 was followed using 2,6-di-tert-butyl-4-((2',4'-dimethyl-[1,1'-biphenyl]-2-yl)-methylene)-cyclohexa-2,5-dien-1-one **2b** (43.8 mg, 0.11 mmol) and indoline-2,3-dione **1a** (14.7 mg, 0.1 mmol). The product **4a** was isolated as off-white solid in 40.7 mg (77% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* >20:1).

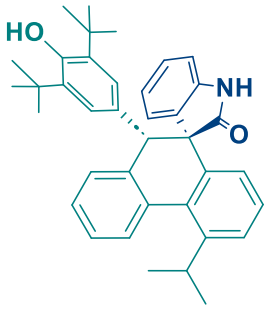


4a

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.75 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.25(m, 1H), 7.24 – 7.04 (m, 5H), 6.74 – 6.53 (m, 3H), 6.13 (s, 1H), 6.07 – 6.00 (m, 1H), 5.07 (s, 1H), 4.79 (s, 1H), 2.59 (s, 3H), 2.35 (s, 3H), 1.33 (s, 9H), 1.06 (s, 9H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 181.4, 153.1, 140.8, 138.3, 138.2, 135.4, 135.2, 134.6, 134.0, 129.5, 129.4, 129.0, 128.5, 128.2, 127.0, 126.3, 124.8, 122.5,

110.2, 53.3, 34.2, 34.2, 30.4, 30.1, 21.1, 19.7. **IR** (cm^{-1})3641, 3443, 2954, 1709, 1616, 1467, 1437, 1232, 750. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{37}H_{39}NNaO_2$ 552.2878, found 552.2896.

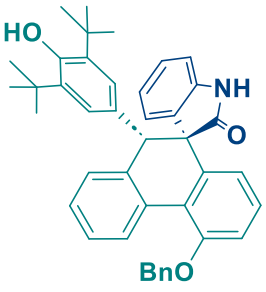
(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-5'-isopropyl-10'H-spiro[indoline-3,9'-phenanthren]-2-one (4b):** The general procedure 3 was followed using 2,6-di-tert-butyl-4-((2'-isopropyl-[1,1'-biphenyl]-2-yl) methylene)-cyclohexa-2,5-dien-1-one **2c** (45.3 mg, 0.11 mmol) and indoline-2,3-dione **1a** (14.7 mg, 0.1 mmol). The product **4b** was isolated as off-white solid in 37.5 mg (69% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* >20:1).



4b

^{1}H NMR (500 MHz, DMSO) δ 10.39 (s, 1H), 7.55 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.19 (td, *J* = 7.6, 1.2 Hz, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.99 (td, *J* = 7.6, 1.3 Hz, 1H), 6.92 (s, 1H), 6.68 (q, *J* = 7.4 Hz, 3H), 6.53 – 6.45 (m, 1H), 6.04 – 6.00 (m, 1H), 5.66 (d, *J* = 7.6 Hz, 1H), 4.53 (s, 1H), 1.49 (d, *J* = 6.7 Hz, 3H), 1.29 (s, 9H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.92 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO) δ 179.4, 153.3, 146.4, 142.2, 141.6, 139.1, 138.9, 138.3, 134.5, 132.8, 131.7, 129.1, 128.6, 128.5, 128.4, 127.6, 127.5, 127.1, 127.0, 124.2, 123.6, 123.4, 121.7, 110.2, 79.7, 59.8, 52.2, 34.8, 34.7, 30.8, 26.1, 24.9. **IR** (cm^{-1})3414, 2957, 1705, 1653, 1468, 1001, 751. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{41}NNaO_2$ 566.3035, found 566.3030.

(±)-***anti*-5'-(benzyloxy)-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (4c):** The general procedure 3 was followed using 4-((2'-(benzyloxy)-[1,1'-biphenyl]-2-yl)-methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **2d** (52.4 mg, 0.11 mmol) and indoline-2,3-dione **1a** (14.7 mg, 0.1 mmol). The product **4c** was isolated as off-white solid in 44.9 mg (74% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* >20:1).

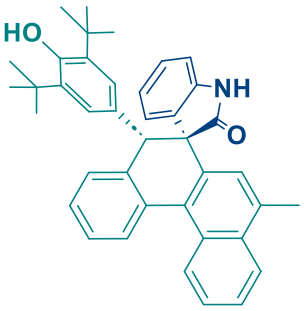


4c

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.37 (dt, *J* = 7.7, 4.0 Hz, 2H), 7.28 (s, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 9.4, 5.7 Hz, 2H), 7.04 (t, *J* = 8.5 Hz, 2H), 6.70 (dt, *J* = 21.9, 8.2 Hz, 3H), 6.34 (d, *J* = 7.6 Hz, 1H), 6.18 (s, 1H), 5.25 (d, *J* = 12.0 Hz, 1H), 5.18 (d, *J* = 12.1 Hz, 1H), 5.08 (s, 1H), 4.83 (s, 1H), 1.39 (s, 9H), 1.06 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 181.2, 156.7, 153.1, 140.4, 137.2, 137.1, 135.1, 134.7, 132.9, 131.2, 129.5,

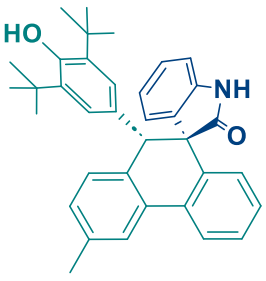
129.1, 128.8, 128.7, 128.7, 128.4, 127.9, 127.3, 127.3, 127.2, 126.7, 124.8, 122.6, 119.4, 113.8, 109.9, 71.3, 60.3, 53.1, 34.2, 34.2, 30.5, 30.1. **IR** (cm^{-1}) 3644, 3431, 2954, 1712, 1614, 1439, 1237, 749. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{42}H_{41}NNaO_3$ 630.2984, found 630.3011.

(±)-***anti*-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-8-methyl-5H-spiro[benzo[c]phenanthrene-6,3'-indolin]-2'-one (4d):** The general procedure 3 was followed using 2,6-di-tert-butyl-4-(2-(4-methylnaphthalen-1-yl)-benzylidene)-cyclohexa-2,5-dien-1-one **2e** (47.8 mg, 0.11 mmol) and indoline-2,3-dione **1a** (14.7 mg, 0.1 mmol). The product **4d** was isolated as off-white solid in 45.3 mg (80% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* >20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.3 Hz, 1H), 8.62 (dt, *J* = 7.0, 3.4 Hz, 2H), 8.12 – 7.83 (m, 3H), 7.67 – 7.37 (m, 5H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.06 (dt, *J* = 15.2, 7.8 Hz, 2H), 6.92 (s, 1H), 6.78 – 6.45 (m, 3H), 6.31 – 5.96 (m, 2H), 5.11 (s, 1H), 4.94 (d, *J* = 21.9 Hz, 1H), 2.60 (d, *J* = 6.1 Hz, 3H), 1.37 (d, *J* = 4.9 Hz, 9H), 1.05 (d, *J* = 5.7 Hz, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 181.6, 153.0, 140.5, 137.9, 135.3, 135.2, 134.6, 134.5, 133.6, 130.9, 130.4, 129.4, 129.1, 129.0, 128.7, 128.4, 127.9, 126.9, 126.8, 126.5, 126.0, 125.8, 125.7, 125.6, 124.8, 124.6, 124.5, 124.4, 122.5, 122.1, 110.0, 60.8, 53.2, 34.2, 34.1, 30.5, 30.1, 19.7. **IR** (cm^{-1})3642, 3418, 2959, 1707, 1615, 1469, 1439, 1233, 751. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{40}H_{39}NNaO_2$ 588.2878, found 588.2877.



4d

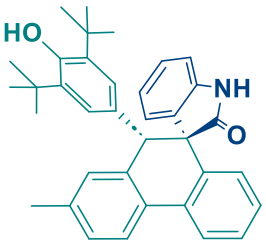
(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-3'-methyl-10'H-spiro[indoline-3,9'-phenanthren]-2-one (4e):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2f** (42.3 mg, 0.11 mmol) and indoline-2,3-dione **1a** (23.7 mg, 0.1 mmol). The product **4e** was isolated as off-white solid in 41.73mg (81% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* >20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 1.7 Hz, 1H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.12 – 6.99 (m, 3H), 6.93 (t, *J* = 6.6 Hz, 2H), 6.77 – 6.64 (m, 2H), 6.49 (d, *J* = 7.4 Hz, 1H), 6.19 (d, *J* = 2.2 Hz, 1H), 5.05 (s, 1H), 4.79 (s, 1H), 2.48 (s, 3H), 1.33 (s, 9H), 1.04 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 181.7, 153.1, 140.3, 137.4, 137.0, 135.0, 134.7, 134.6, 134.1, 133.7, 131.5, 129.3, 128.9, 128.6, 128.5, 128.3, 128.3,



4e

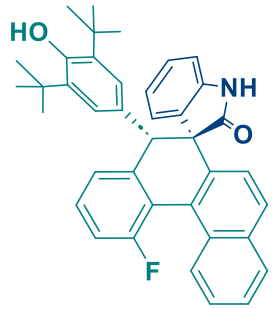
126.5, 125.0, 124.9, 124.7, 124.5, 122.4, 110.1, 60.0, 52.9, 34.2, 30.4, 30.1, 21.6. **IR** (cm^{-1})3637, 3431, 2924, 1710, 1616, 1469, 1439, 1234, 746. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{37}NNaO_2$ 538.2722, found 538.2721.

(±)-***anti*-10'-(3,5-di-tert-butyl-4-hydroxyphenyl)-2'-methyl-10'H-spiro[indoline-3,9'-phenanthren]-2-one (4f):** The general procedure 3 was followed using 2,6-di-tert-butyl-4-((4-methyl-[1,1'-biphenyl]-2-yl)-methylene)-cyclohexa-2,5-dien-1-one **2g** (42.3 mg, 0.11 mmol) and indoline-2,3-dione **1a** (14.7 mg, 0.1 mmol). The product **4f** was isolated as off-white solid in 41.25mg (80% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* >20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.91 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.36 (td, *J* = 7.6, 1.3 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.17 (td, *J* = 7.5, 1.3 Hz, 1H), 7.11 – 7.01 (m, 2H), 6.95 – 6.84 (m, 2H), 6.76 – 6.65 (m, 2H), 6.44 (d, *J* = 7.5 Hz, 1H), 6.22 (d, *J* = 2.1 Hz, 1H), 5.08 (s, 1H), 4.77 (s, 1H), 3.70 (s, 1H), 2.28 (s, 3H), 1.33 (s, 9H), 1.05 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 181.9, 153.1, 140.4, 137.7, 136.8, 136.5, 135.0, 134.7, 134.3, 132.1, 131.4, 129.8, 129.2, 128.9, 128.4, 128.3, 128.3, 128.1, 127.2, 126.5, 126.4, 125.2, 125.0, 124.5, 123.7, 122.4, 115.9, 115.0, 110.1, 67.2, 60.0, 53.1, 34.2, 30.4, 30.1, 21.6. **IR** (cm^{-1})3635, 3444, 2958, 2924, 1711, 1616, 1472, 1438, 1209, 746. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{36}H_{37}NNaO_2$ 538.2722, found 538.2716.



4f

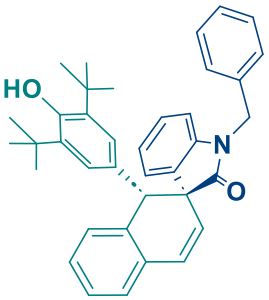
(±)-***anti*-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-fluoro-5H-spiro[benzo[c]phenanthrene-6,3'-indolin]-2'-one (4g):** The general procedure 3 was followed using 4-([1,1'-biphenyl]-2-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2h** (48.3mg, 0.11mmol) indoline-2,3-dione **1a** (14.7 mg, 0.1 mmol) to give an inseparable mixture of diastereomers of **4g**. The product **4g** was isolated as off-white solid in 46.7 mg (82% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* = 75:25) **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.60 (s, 1H), 7.95 – 7.81 (m, 4H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.60 – 7.44 (m, 3H), 7.41 – 7.32 (m, 2H), 7.14 – 7.03 (m, 3H), 6.99 (d, *J* = 2.4 Hz, 2H), 6.88 – 6.73 (m, 3H), 6.72 – 6.58 (m, 4H), 6.52 (d, *J* = 7.7 Hz, 1H), 6.12 (d, *J* = 2.1 Hz, 1H), 5.92 (dd, *J* = 7.5, 1.1 Hz, 1H), 4.66 (s, 1H), 1.33 (s, 9H), 1.27 (s, 4H), 1.16 (s, 4H), 0.99 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ 179.0, 177.0, 157.3, 153.7, 152.9, 142.4, 140.5, 139.1, 138.5,



4g

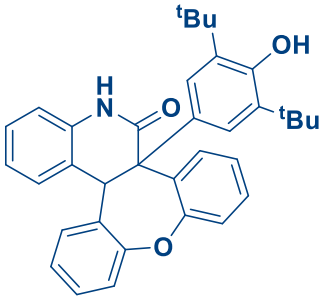
133.4, 130.6, 130.1, 129.9, 129.2, 128.3, 127.0, 127.0, 126.6, 126.4, 124.7, 124.3, 124.2, 123.6, 122.1, 121.9, 121.8, 110.6, 79.7, 59.8, 58.5, 53.0, 35.2, 34.9, 34.8, 34.7, 31.0, 30.9, 30.8, 30.6. **IR** (cm^{-1})3440, 2924, 1705, 1646, 1615, 1465, 748. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{39}H_{36}FNNaO_2$ 592.2628, found 592.2635.

(±)-***anti*-1-benzyl-1'-(3,5-di-tert-butyl-4-hydroxyphenyl)-1'H-spiro[indoline-3,2'-naphthalen]-2-one (4h):** The general procedure 3 was followed using 2,6-di-tert-butyl-4-(2-vinylbenzylidene)-cyclohexa-2,5-dien-1-one **2i** (35.3 mg, 0.11 mmol) and 1-benzylindoline-2,3-dione **1r** (23.7 mg, 0.1 mmol). The product **4h** was isolated as off-white solid in 38.4 mg (71% yield). **Eluent**: ethyl acetate/ petroleum ether (10:90-20:80 v/v), (For crude reaction mixture, *anti/syn* >20:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 3H), 7.17 (tq, *J* = 9.7, 6.4, 4.6 Hz, 5H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.88 – 6.75 (m, 3H), 6.46 (d, *J* = 7.2 Hz, 2H), 6.32 (t, *J* = 5.4 Hz, 2H), 6.01 (d, *J* = 9.5 Hz, 1H), 5.22 (s, 1H), 5.15 (d, *J* = 16.1 Hz, 1H), 5.03 (s, 1H), 4.30 (d, *J* = 16.1 Hz, 1H), 1.42 (s, 9H), 1.00 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 179.4, 153.2, 142.1, 136.8, 135.3, 135.1, 134.8, 133.7, 129.2, 129.2, 128.9, 128.8, 128.5, 127.8, 127.8, 126.9, 126.5, 126.4, 126.2, 125.8, 124.3, 122.5, 109.3, 56.2, 52.4, 43.8, 34.2, 34.2, 30.5, 30.2. **IR** (cm^{-1}) 3565, 2962, 1705, 1605, 1434, 1362, 1106, 751, 693. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{39}NNaO_2$ 564.2678, found 564.2671.



4h

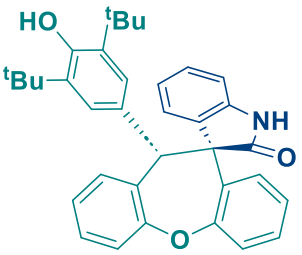
(±)**13b-(3,5-di-tert-butyl-4-hydroxyphenyl)-4b,15-dihydrodibenzo[2,3:6,7]oxepino[4,5-c]quinolin-14(13bH)-one (8):** An oven-dried 5ml round bottom flask was charged with a magnetic bar and compound **7** (103.4 mg, 0.2 mmol) and dissolved in dry DCM (2 ml) and $BF_3.Et_2O$(1eq.) was added at RT and monitored with TLC, after complete consumption of **7** the reaction mixture was quenched with saturated aq. NH_4Cl solution (2 mL) and diluted with Ethyl acetate. Afterwards, the reaction mixture was transferred to a separating funnel. The organic layer was separated, and the aqueous layer was washed with Ethyl acetate (3 x 5 mL), the organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash chromatography (silica gel, eluent: ethyl acetate/petroleum ether = 10:90-35:65 v/v) to afford **8** (white solid, 71.43 mg, 69 %) **^{1}H**



8

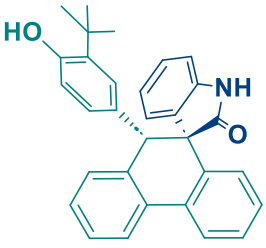
NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.09 (m, 5H), 6.96 (q, *J* = 6.9, 6.2 Hz, 3H), 6.88 – 6.67 (m, 3H), 6.48 (d, *J* = 7.4 Hz, 1H), 4.99 (s, 1H), 4.64 (s, 1H), 1.23 (s, 18H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 172.4, 156.3, 154.6, 152.1, 135.8, 134.9, 133.9, 132.4, 131.1, 129.9, 129.1, 128.4, 127.8, 127.2, 125.7, 124.4, 123.6, 123.1, 121.4, 120.7, 58.7, 54.2, 34.2, 30.2. **IR** (cm^{-1}) 3615, 2923, 1675, 1593, 1484, 1438, 1235, 750. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{39}NNaO_2$ 540.2515, found 540.2529.

(±)-*anti*-11-(3,5-di-tert-butyl-4-hydroxyphenyl)-11H-spiro[dibenzo[b,f]oxepine-10,3'-indolin]-2'-one (10): An oven-dried 5ml round bottom flask was charged with a magnetic bar and compound **7** (103.4 mg, 0.2 mmol) and dissolved in dry DCM (2 ml) and $Cu(OTf)_2$ (0.3 eq.) was added at RT and monitored with TLC, after complete consumption of **9** solvent was concentrated under reduced pressure. Then the crude mixture was purified by flash chromatography (silica gel, eluent: ethyl acetate/petroleum ether = 10:90-35:65 v/v) to afford **10** (white solid, 80.75 mg, 78 %); (For crude reaction mixture, *anti/syn* =1:1) **^1H NMR** (500 MHz, DMSO-D_6) δ 10.50 (s, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.20 (m, 4H), 7.10 (t, *J* = 8.2 Hz, 1H), 7.04 (s, 2H), 6.93 (t, *J* = 8.2 Hz, 3H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.61 (s, 2H), 6.51 (d, *J* = 8.1 Hz, 1H), 5.39 (s, 1H), 1.28 (s, 18H). **$^{13}C\{^1H\}$ NMR** (126 MHz, DMSO-D_6) δ 179.1, 158.1, 155.6, 152.7, 141.5, 138.3, 137.3, 133.6, 131.2, 130.6, 130.4, 128.8, 128.0, 127.9, 126.8, 124.8, 124.7, 122.5, 121.8, 120.4, 109.4, 59.2, 50.6, 34.9, 30.8. **IR** (cm^{-1})3639, 3389, 2957, 1718, 1616, 1474, 1436, 1233, 754. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{35}NNaO_3$ 540.2515, found 540.2525.



10,

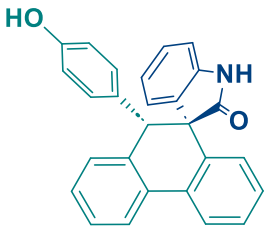
(±)-*anti*-10'-(3-(tert-butyl)-4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (11): An oven-dried 5ml round bottom flask was charged with magnetic bar and compound **3a** (92 mg, 0.2 mmol) and dissolved in dry toluene (2 ml) at rt followed by $AlCl_3$ (133mg, 5 eqv.) in argon environment and allowed to react at the same temperature. The reaction mixture was monitored by TLC, after complete consumption of **3a** the reaction mixture was quenched with saturated aq. NH_4Cl solution (2 mL) and diluted with Ethyl acetate. Afterwards, the reaction mixture was transferred to a separating funnel. The organic layer was separated, and the aqueous layer was washed with Ethyl acetate (3 x 5 mL), the organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash chromatography (silica gel, eluent: ethyl acetate/petroleum ether = 10:90-35:65 v/v) to afford **11** (white solid,



11

64.08 mg, 72 %), (For crude reaction mixture, *anti/syn* >20:1).**^{1}H NMR** (500 MHz, DMSO-D_6) δ 10.42 (s, 1H), 9.24 (s, 1H), 8.05 (dd, *J* = 8.3, 5.2 Hz, 2H), 7.41 (ddd, *J* = 8.9, 6.1, 2.3 Hz, 2H), 7.24 (t, *J* = 7.0 Hz, 2H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.95 – 6.86 (m, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.67 (dd, *J* = 28.7, 7.8 Hz, 3H), 6.32 (d, *J* = 7.5 Hz, 1H), 6.26 – 6.22 (m, 1H), 5.76 (s, 1H), 4.64 (s, 1H), 0.95 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-D_6) δ 179.4, 155.6, 141.8, 138.5, 137.2, 134.5, 134.4, 133.6, 131.7, 130.9, 128.9, 128.7, 128.6, 128.3, 128.0, 126.7, 126.6, 126.3, 125.0, 124.2, 124.1, 121.7, 116.0, 110.1, 58.9, 55.4, 51.9, 34.4, 29.5. **IR** (cm^{-1}) 3431, 2952, 1653, 1002, 764. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{27}NNaO_2$ 468.1939, found 468.1924.

(±)-*anti*-10'-(4-hydroxyphenyl)-10'H-spiro[indoline-3,9'-phenanthren]-2-one (12): An

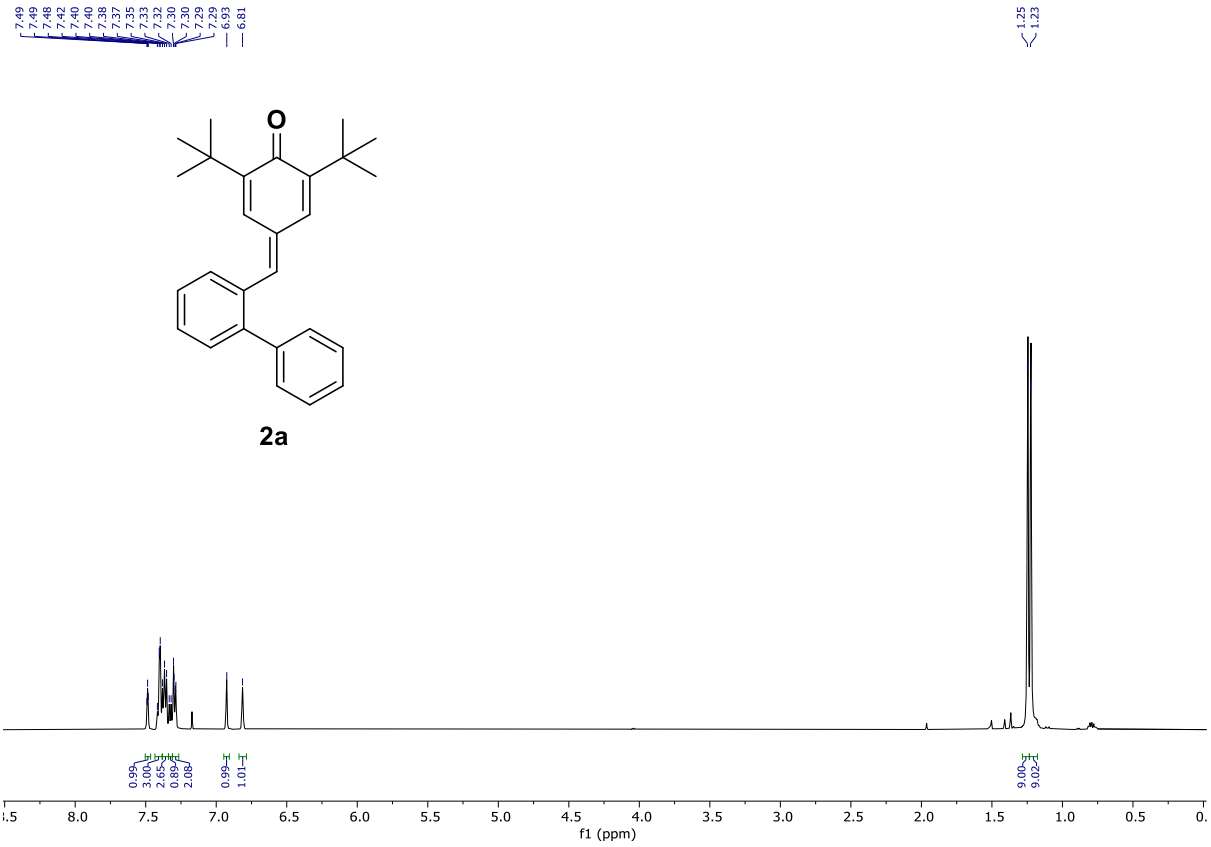


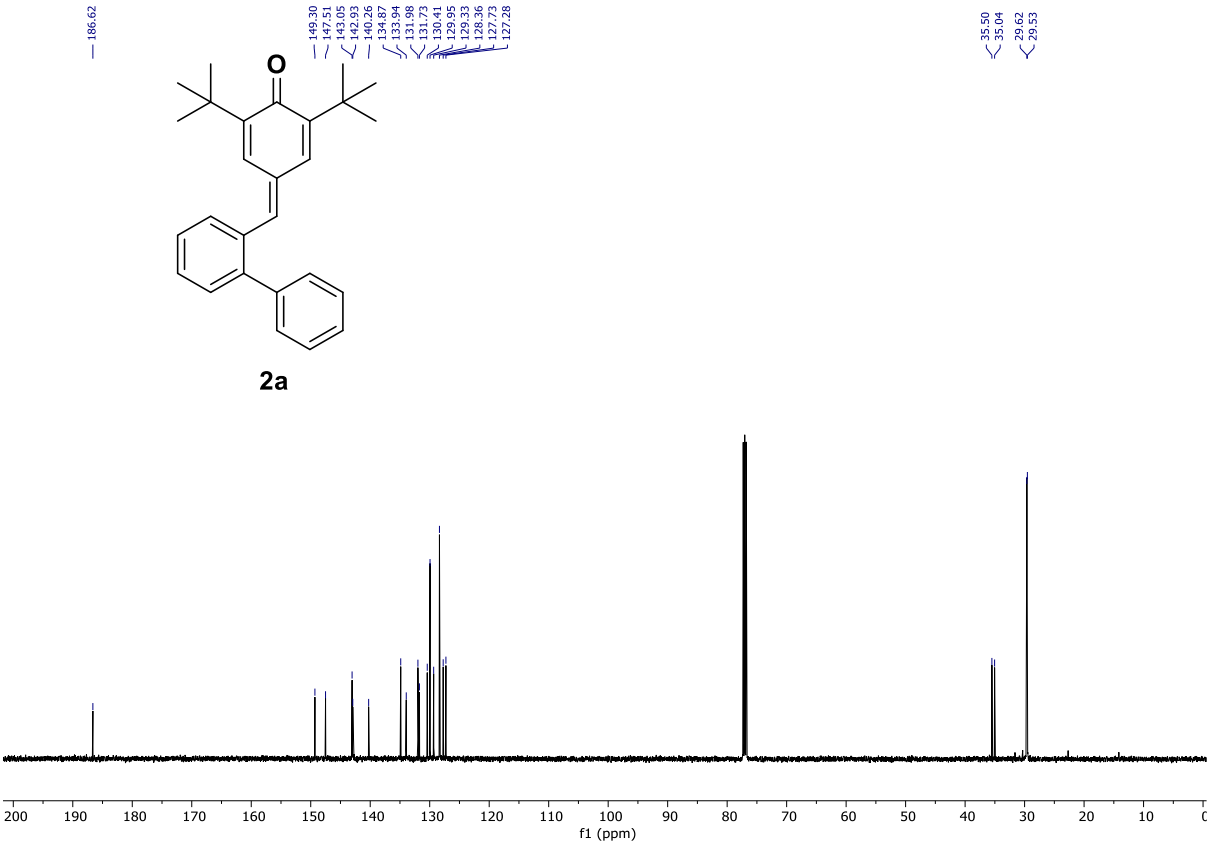
12

oven-dried 5ml round bottom flask was charged with magnetic bar and compound **3a** (92 mg, 0.2 mmol) and dissolved in dry toluene (2 ml) at rt followed by $AlCl_3$ (266 mg, 10 eqv.) in argon environment and allowed to react at the same temperature. The reaction mixture was monitored by TLC, after complete consumption of **3a** the reaction mixture was quenched with saturated aq. NH_4Cl solution (2 mL) and diluted with Ethyl acetate. Afterwards, the reaction mixture was transferred to a separating funnel. The organic layer was separated and the aqueous layer was washed with Ethyl acetate (3 x 5 mL), the organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash chromatography (silica gel, eluent: ethyl acetate/petroleum ether = 10:90-35:65 v/v) to afford **12** (white solid, 53.70 mg, 69 %). (For crude reaction mixture, *anti/syn* >20:1). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.42 (s, 1H), 9.30 (s, 1H), 8.12 – 7.94 (m, 2H), 7.42 (q, *J* = 7.5 Hz, 2H), 7.24 (q, *J* = 7.4 Hz, 2H), 7.10 (td, *J* = 7.6, 1.3 Hz, 1H), 6.95 – 6.87 (m, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.27 (d, *J* = 7.5 Hz, 1H), 4.65 (s, 1H).**^{13}C NMR** (101 MHz, DMSO-d_6) δ 180.4, 158.2, 141.9, 138.3, 137.3, 134.4, 134.0, 133.7, 131.5, 129.0, 128.7, 128.5, 128.1, 127.4, 126.7, 125.1, 124.3, 121.7, 115.1, 110.3, 79.7, 58.7, 53.0. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{19}NNaO_2$ 412.1313, found 412.1310.

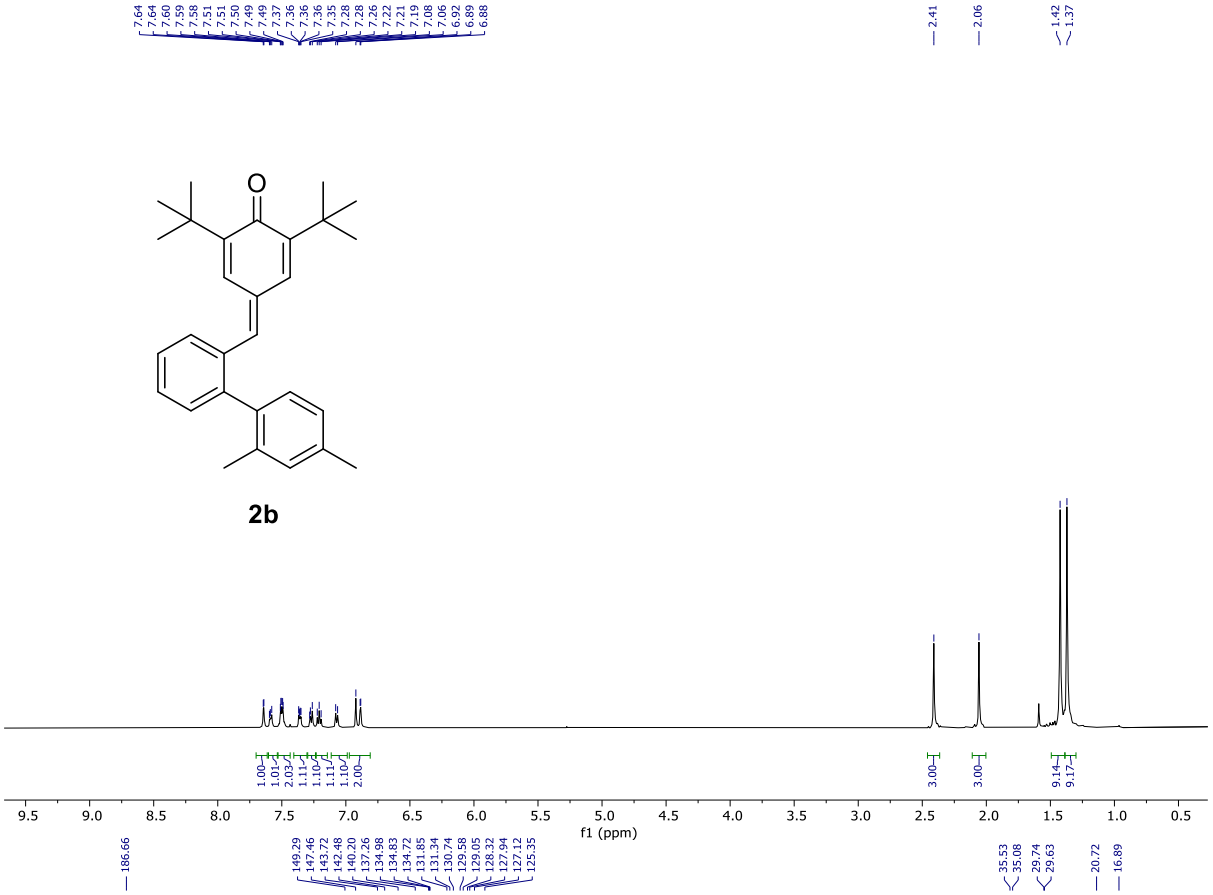
^{1}H, ^{13}C and ^{19}F Spectra of the Compounds:

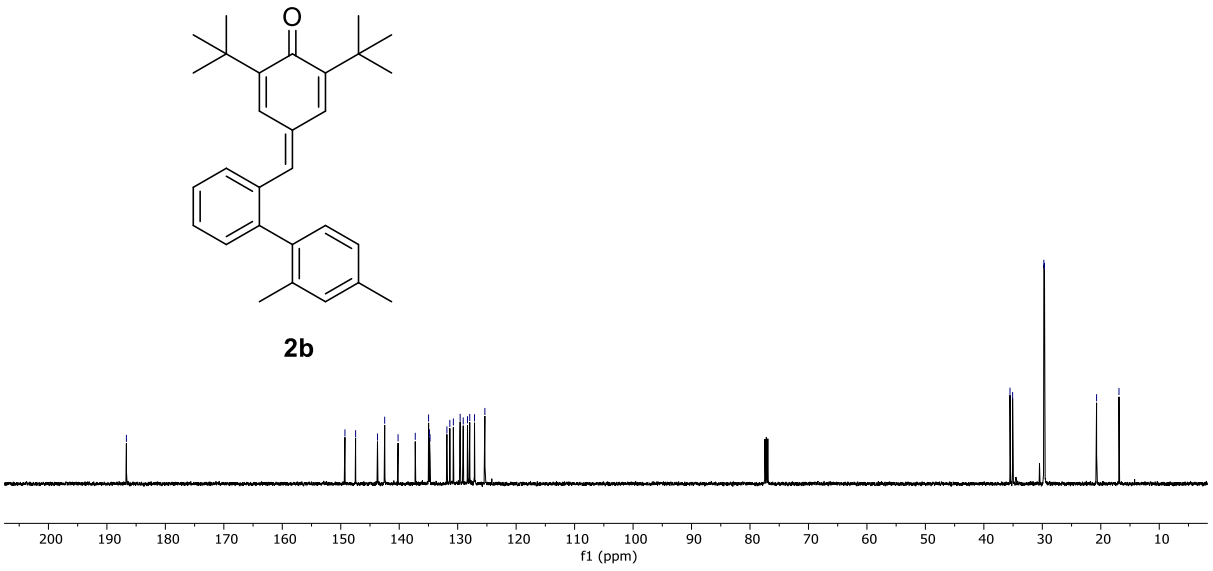
^{1}H and ^{13}C Spectra of 2a (500 MHz, $CDCl_3$) :



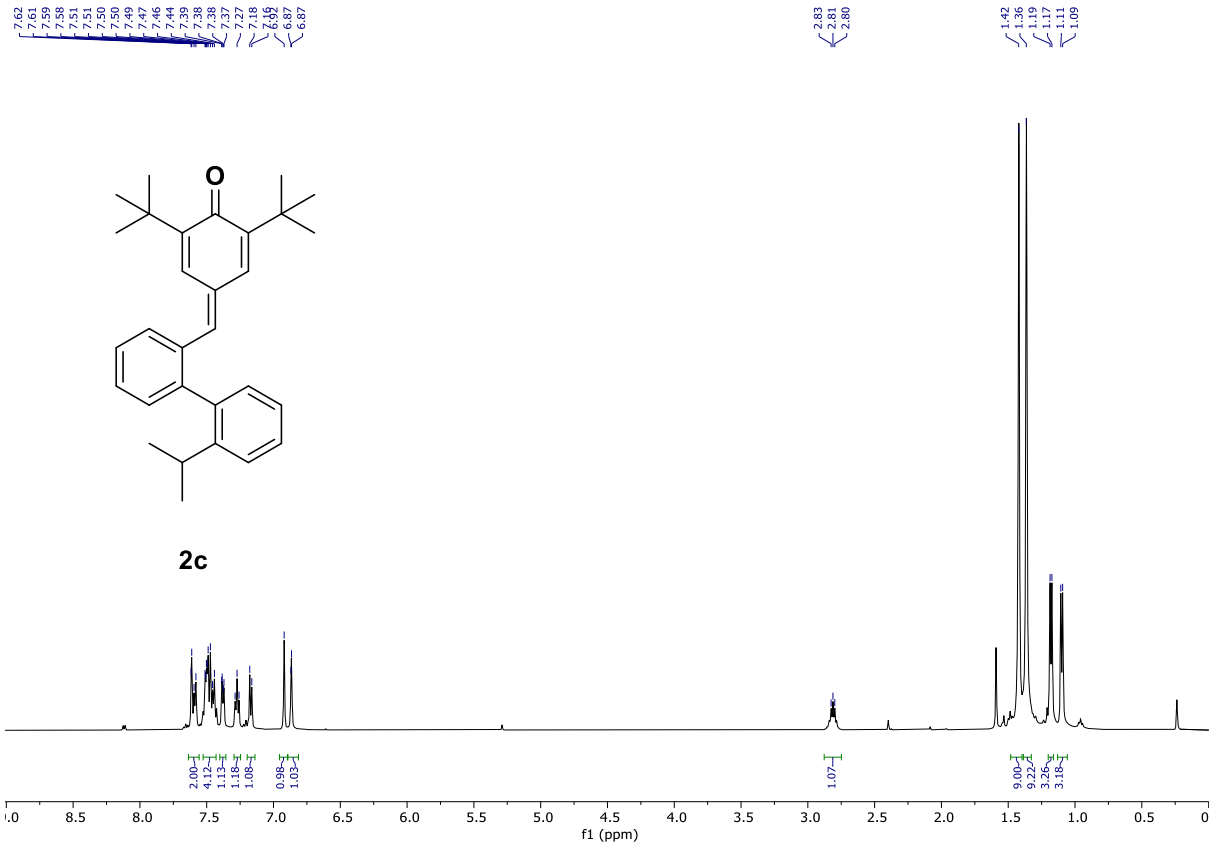


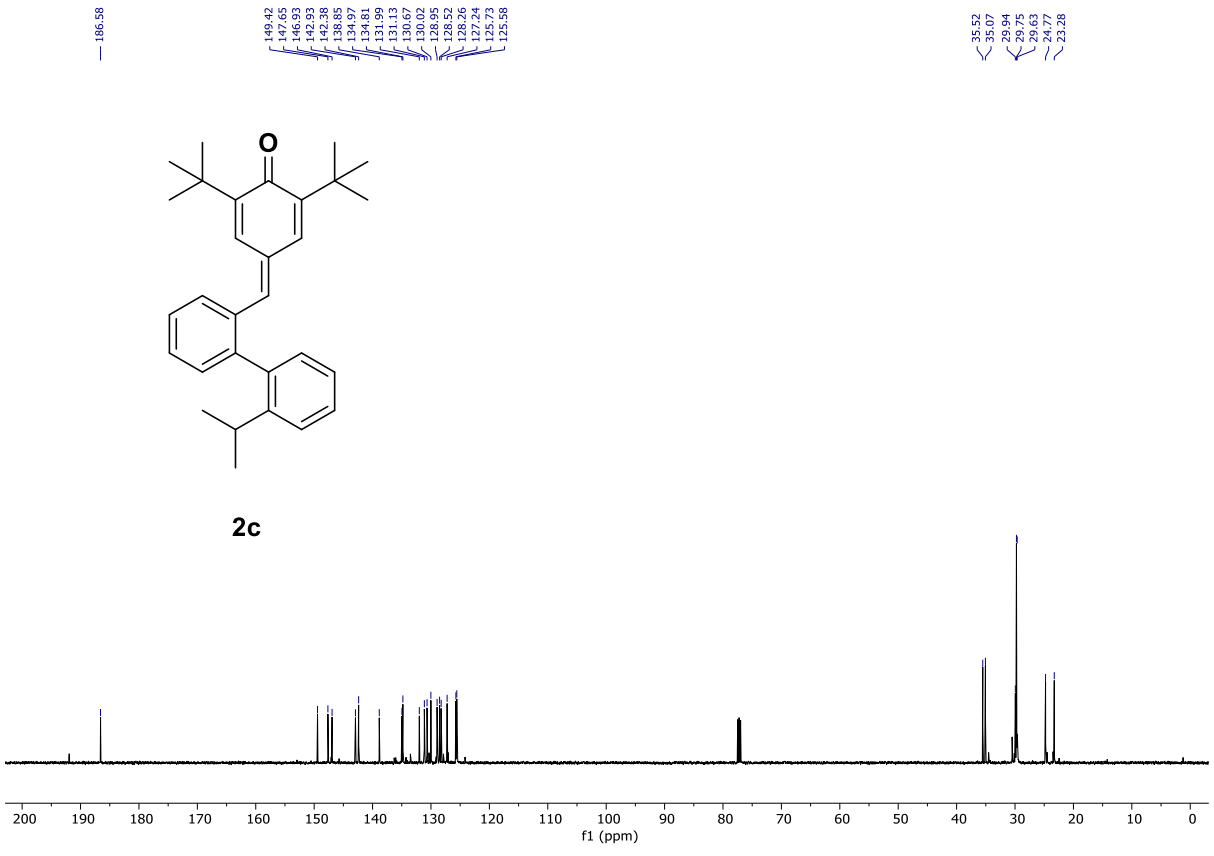
^{1}H and ^{13}C Spectra of 2b (500MHz, $CDCl_3$) :



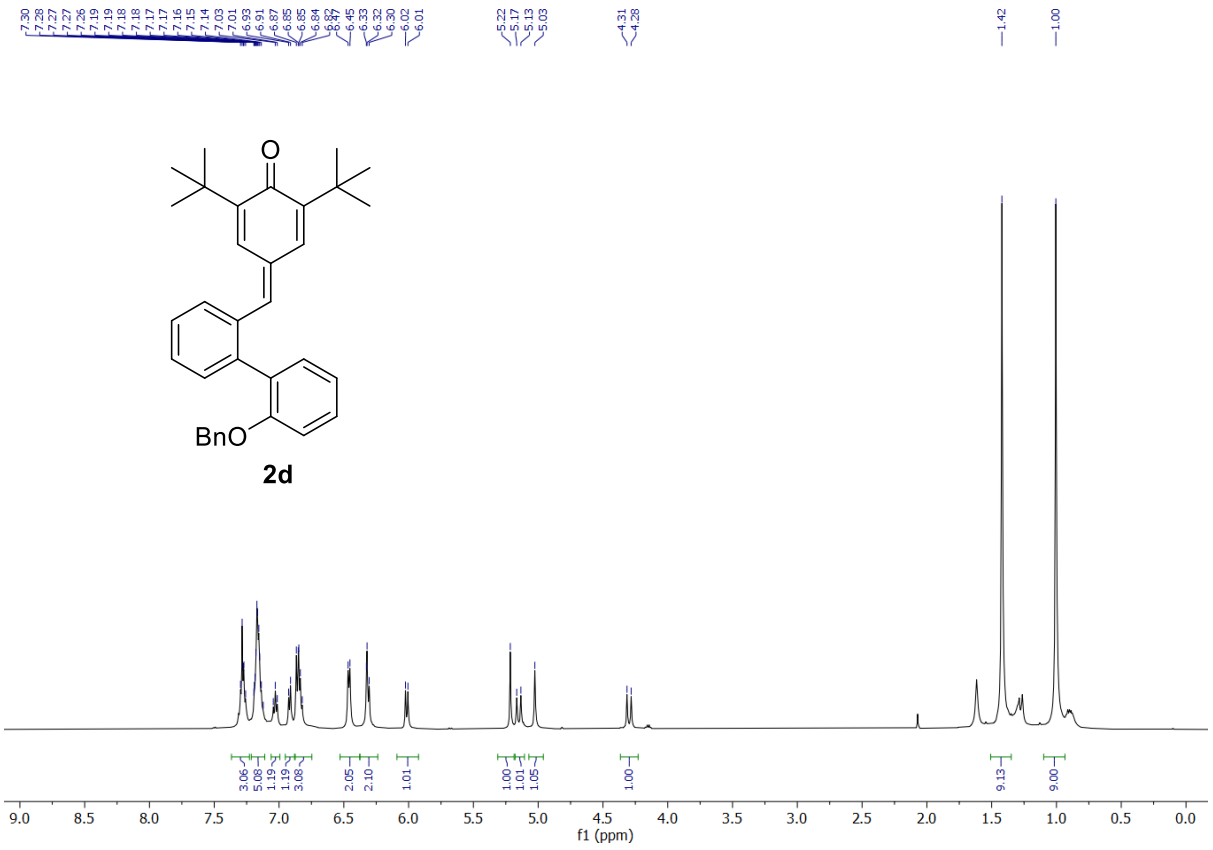


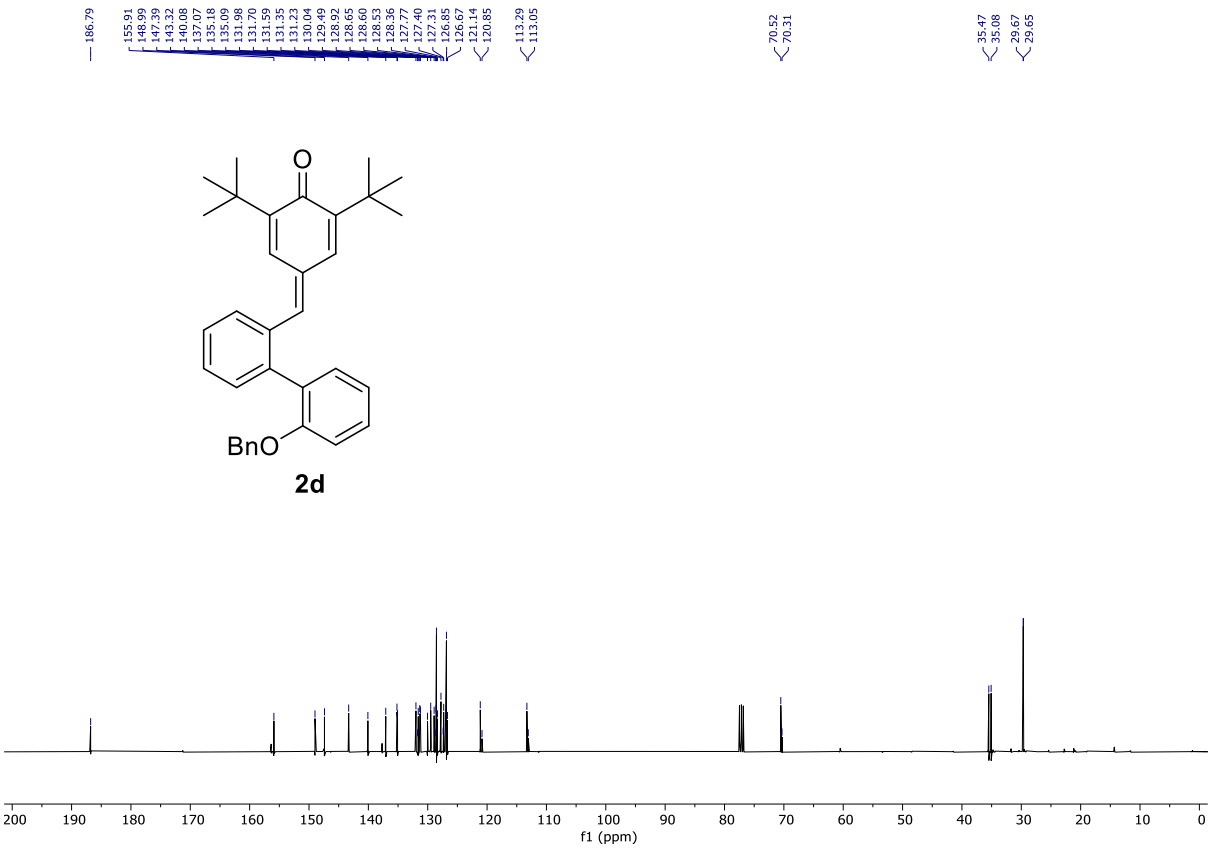
^{1}H and ^{13}C Spectra of 2c (500MHz, $CDCl_3$) :



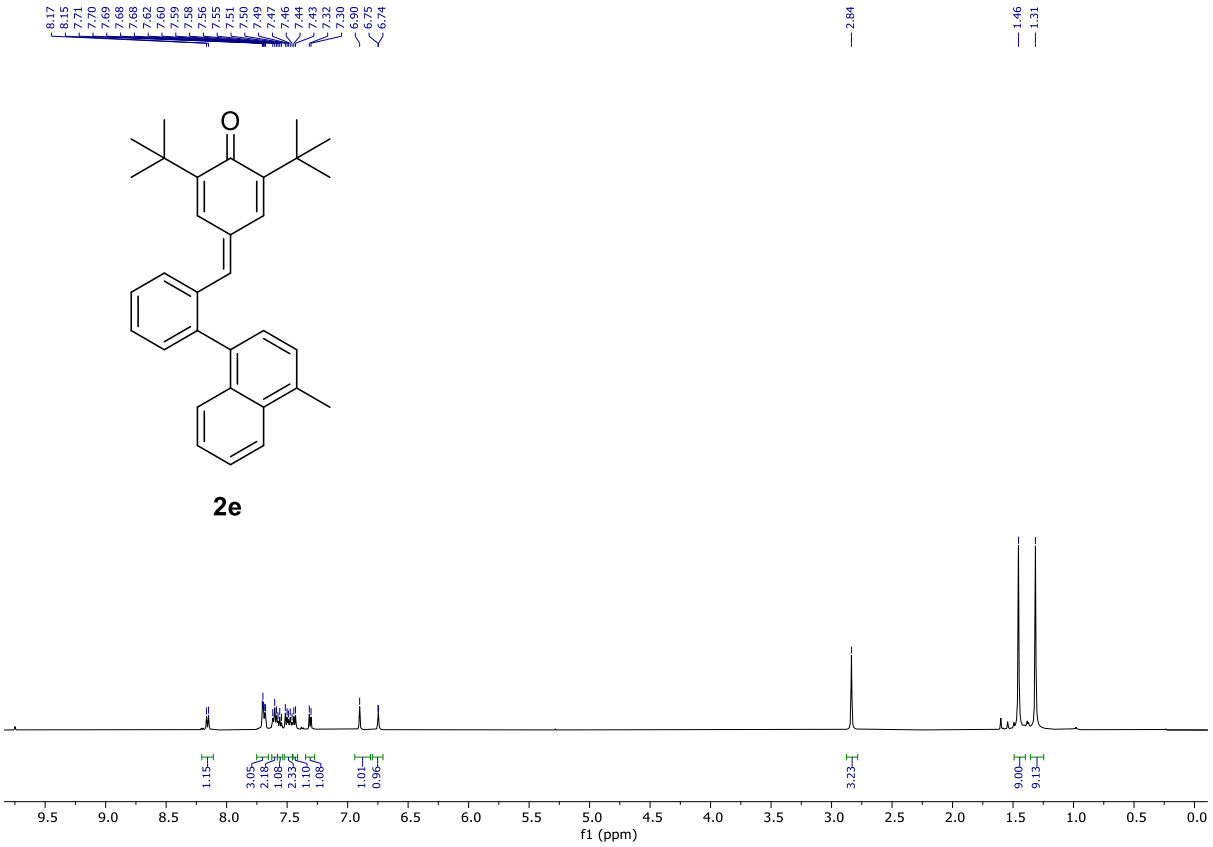


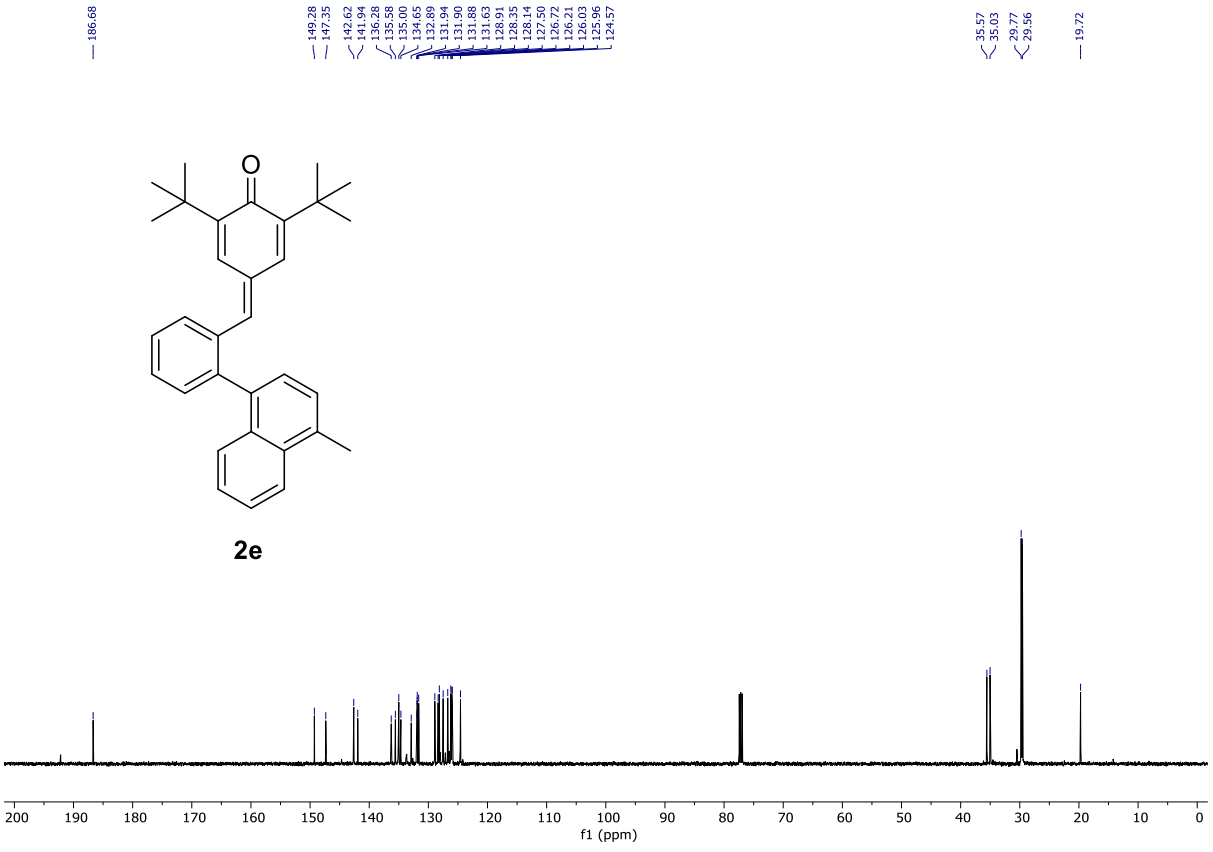
^{1}H and ^{13}C Spectra of 2d (400MHz, $CDCl_3$) :



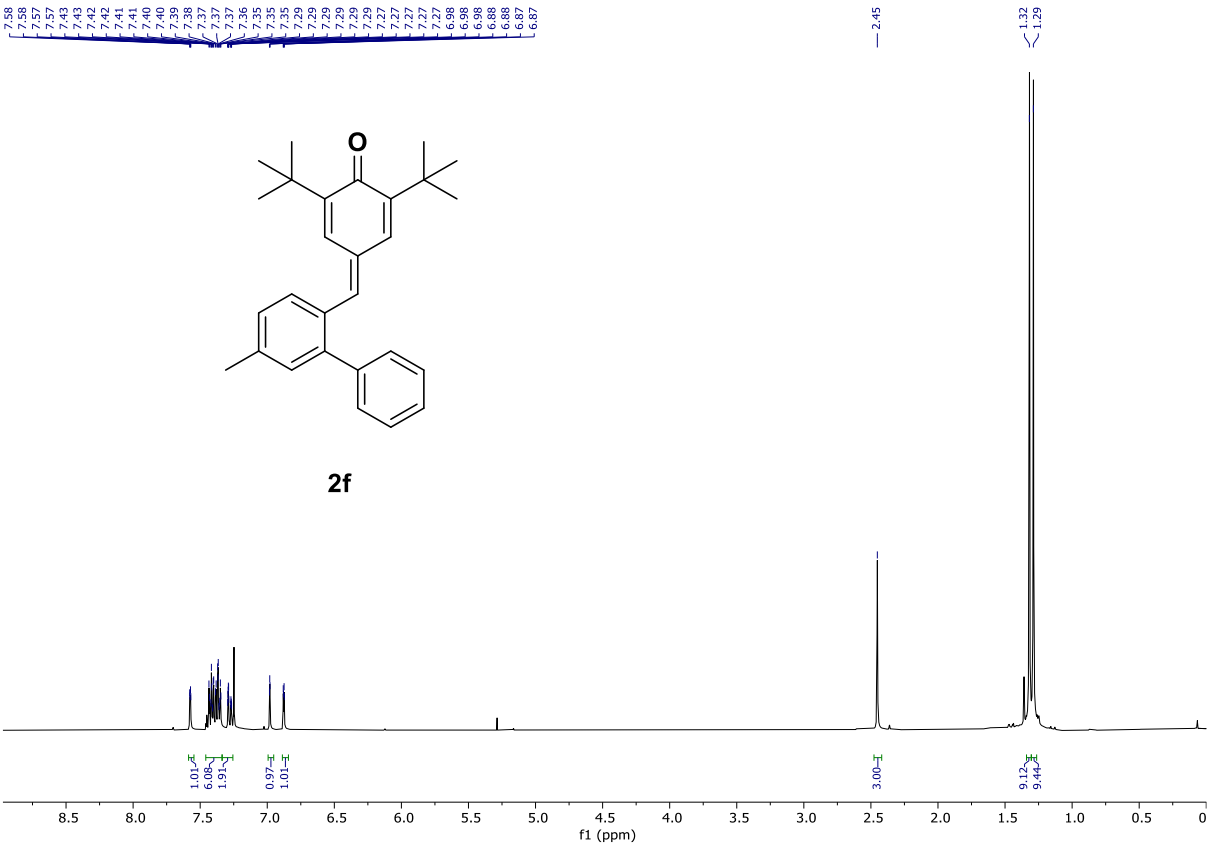


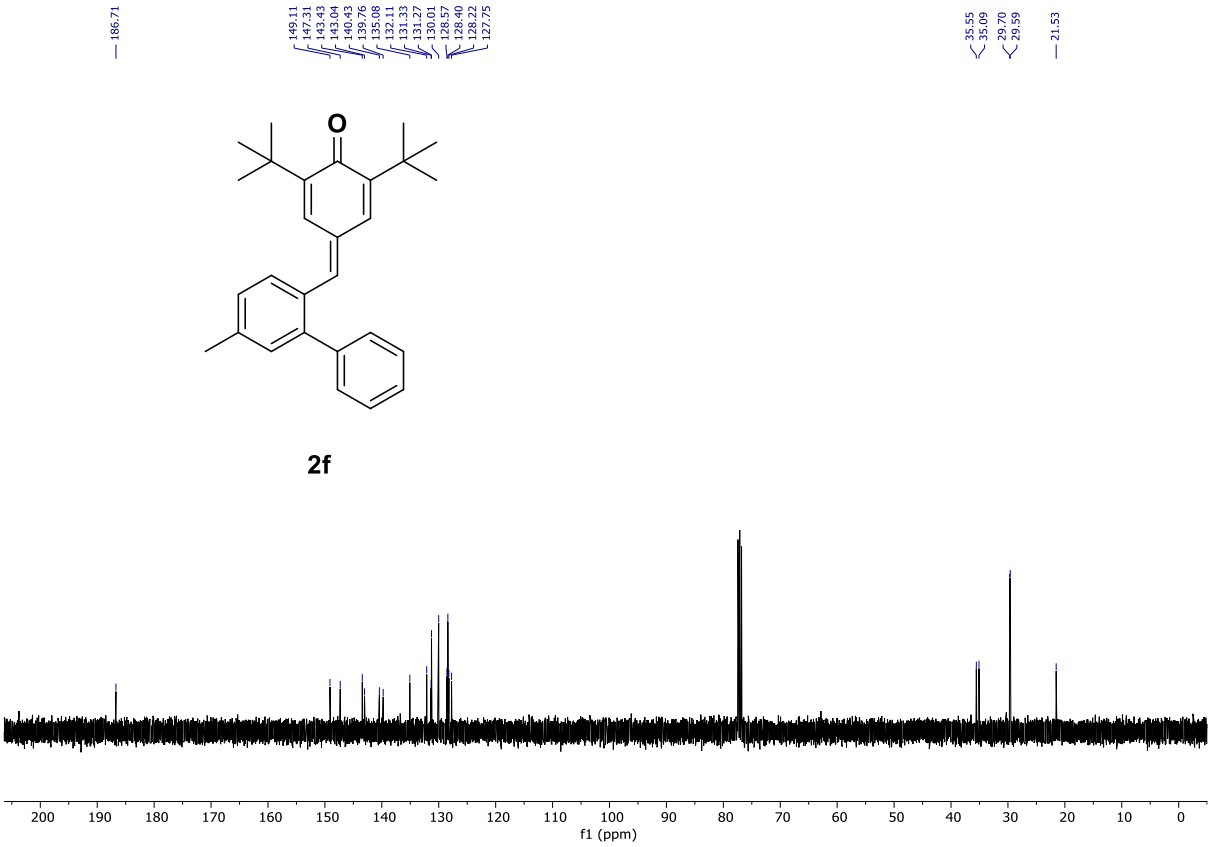
^{1}H and ^{13}C Spectra of 2e (500MHz, $CDCl_3$) :



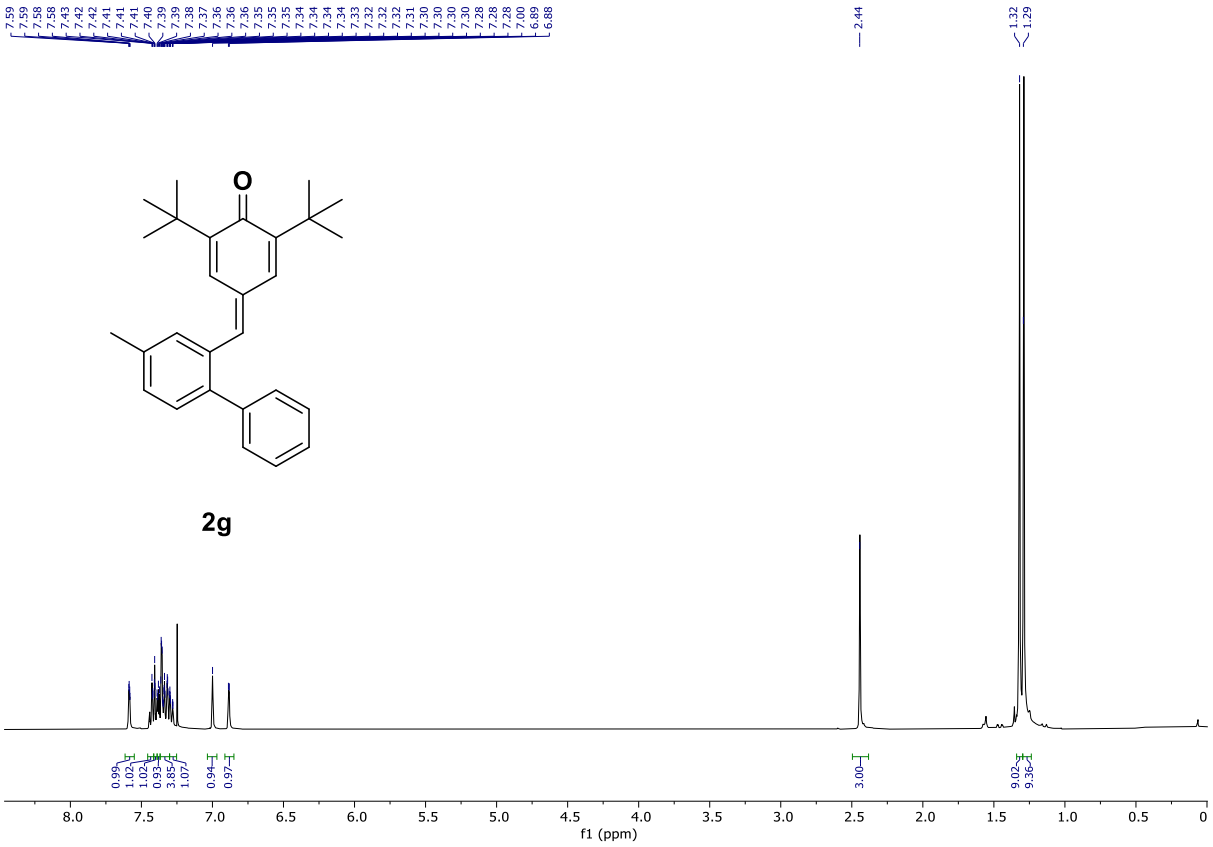


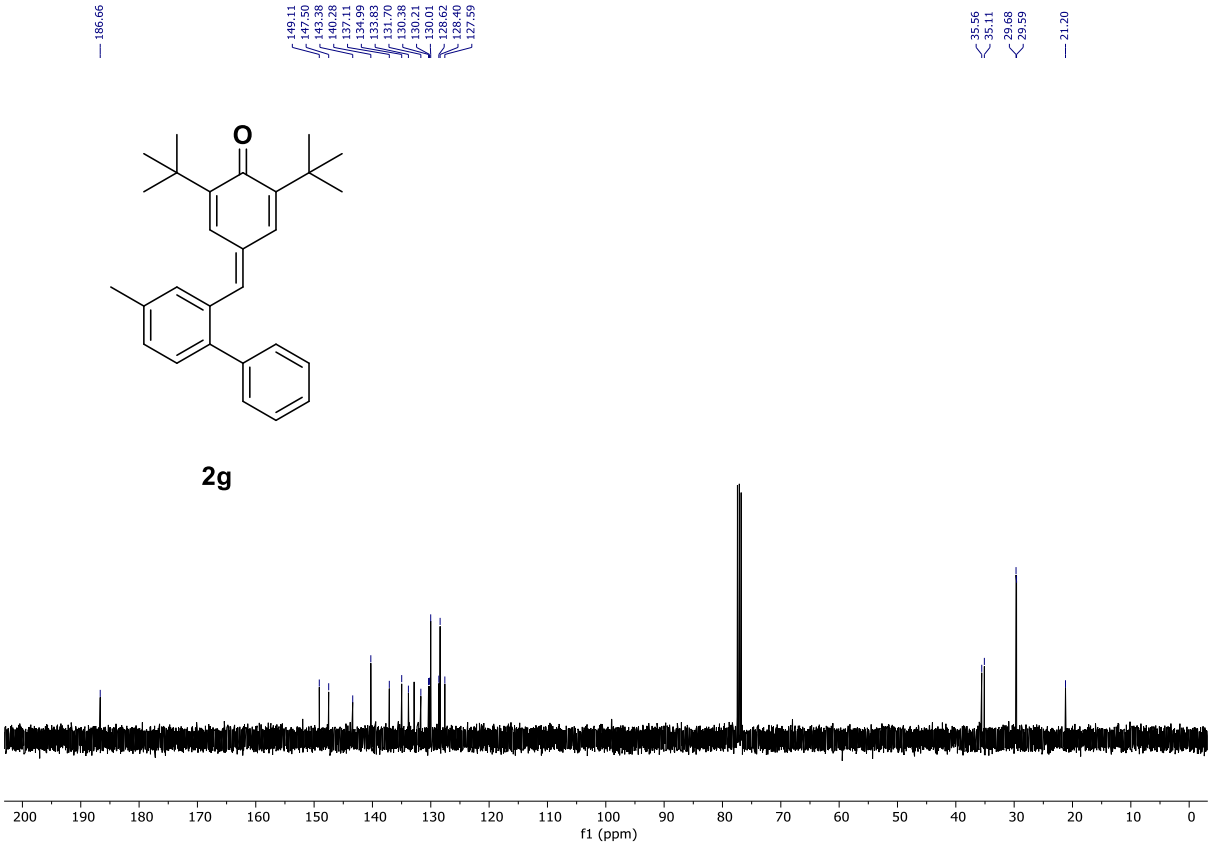
^{1}H and ^{13}C Spectra of 2f (400MHz, $CDCl_3$) :



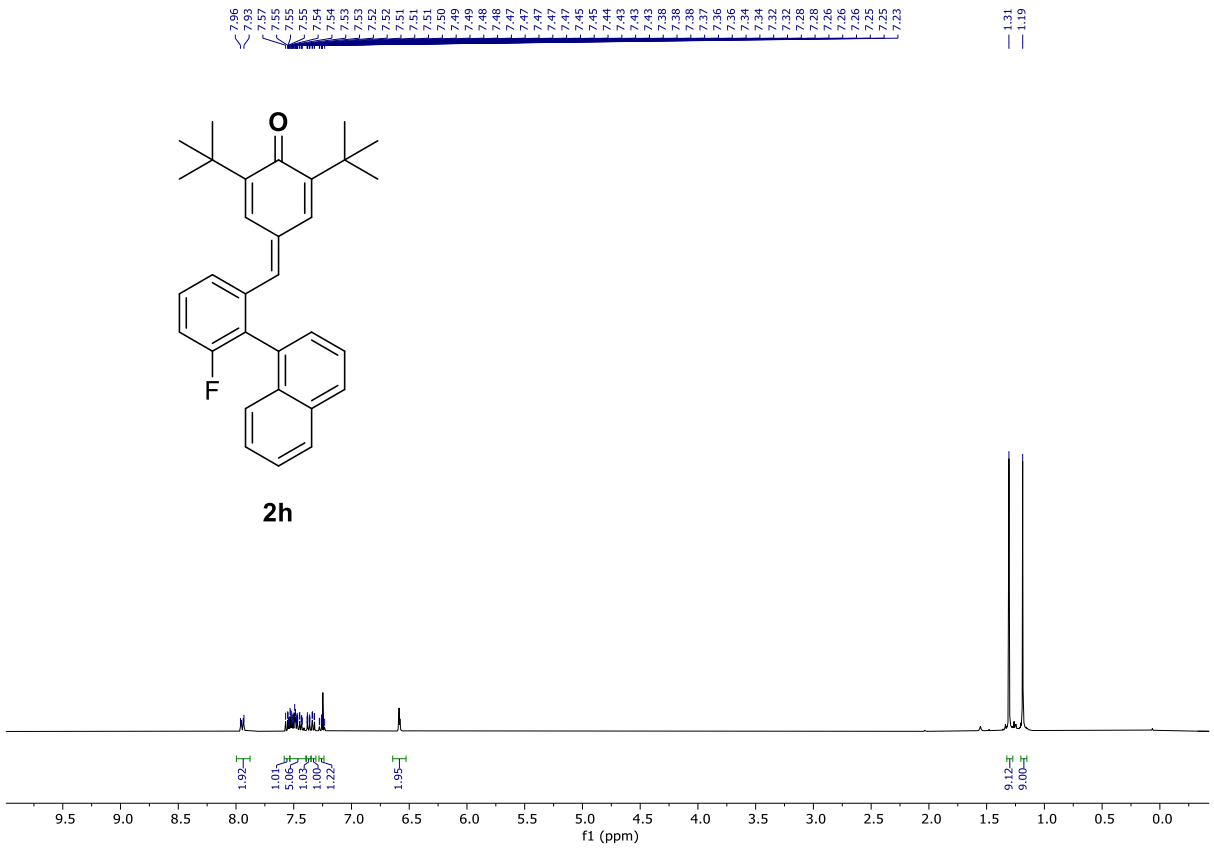


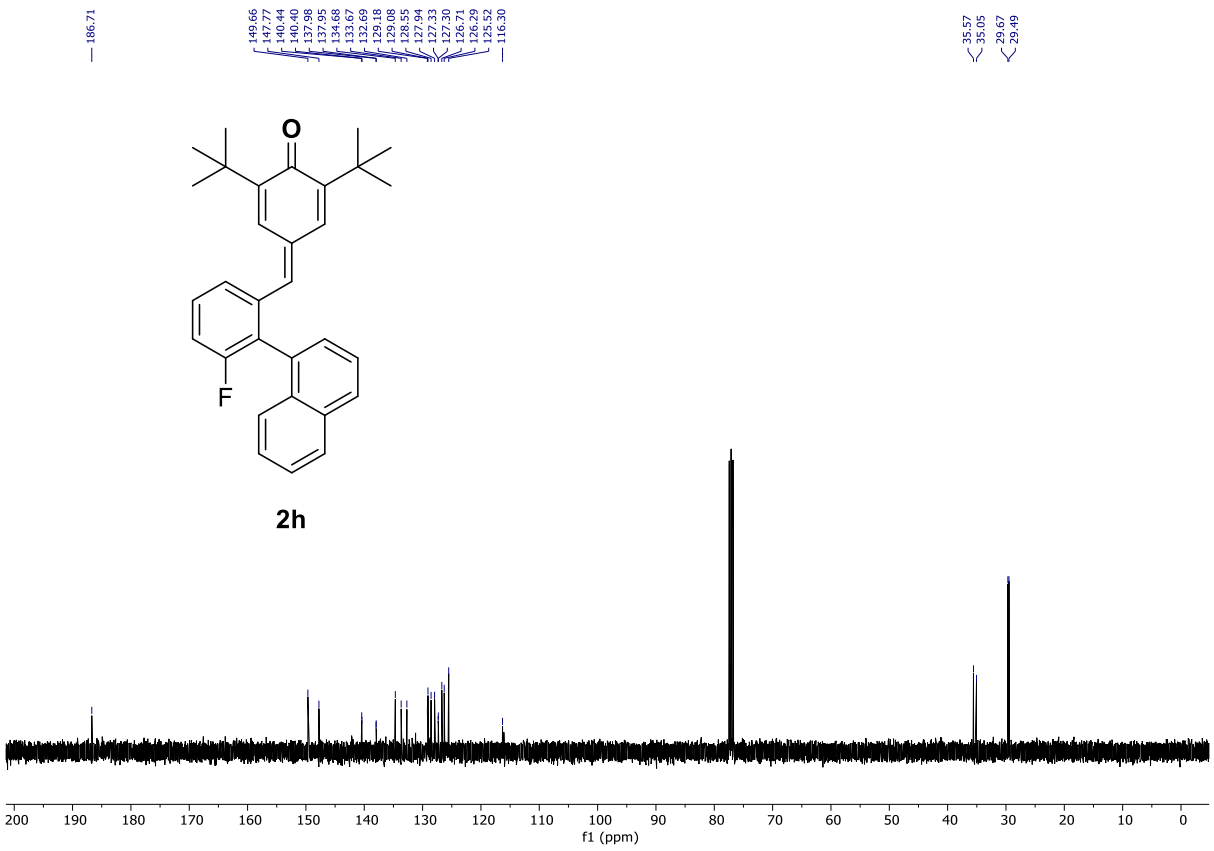
^{1}H and ^{13}C Spectra of 2g (400MHz, $CDCl_3$) :

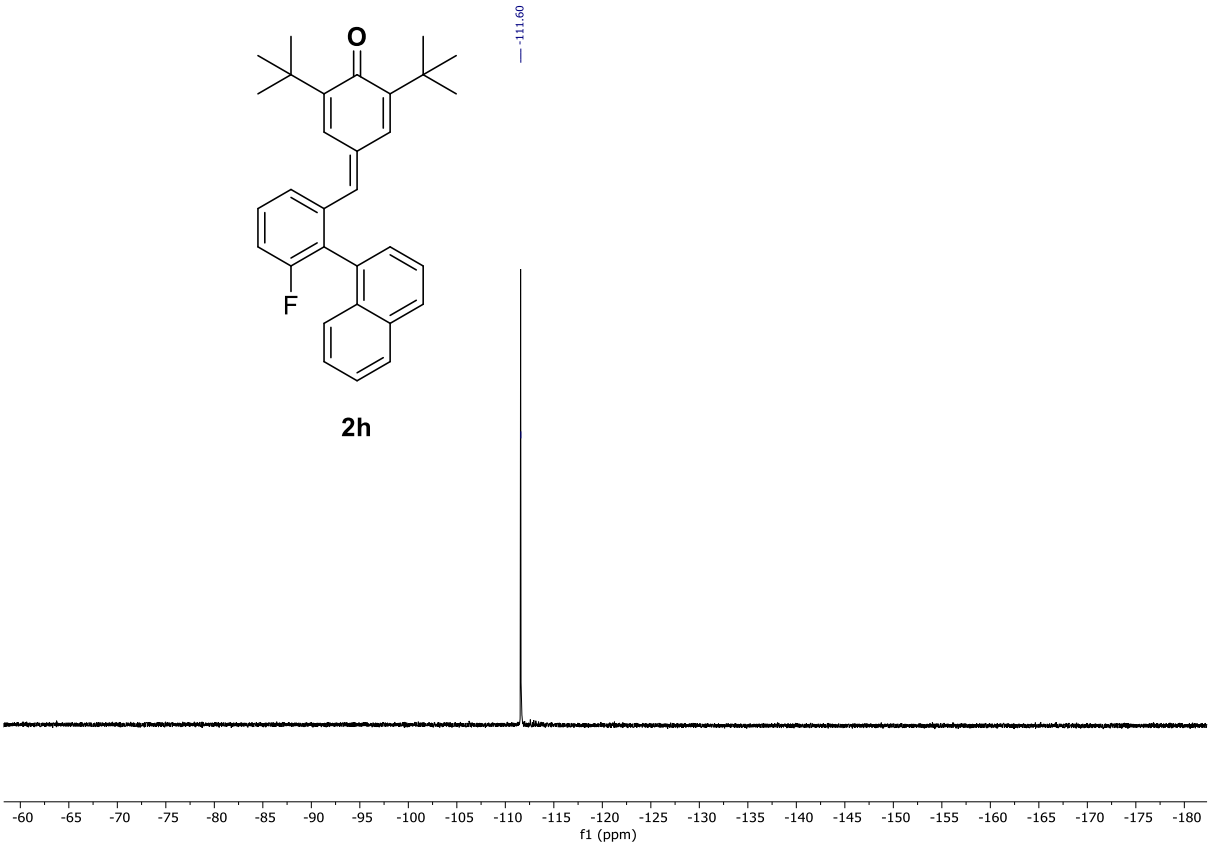




^{1}H ,^{13}C and ^{19}F Spectra of 2h (400MHz, $CDCl_3$) :

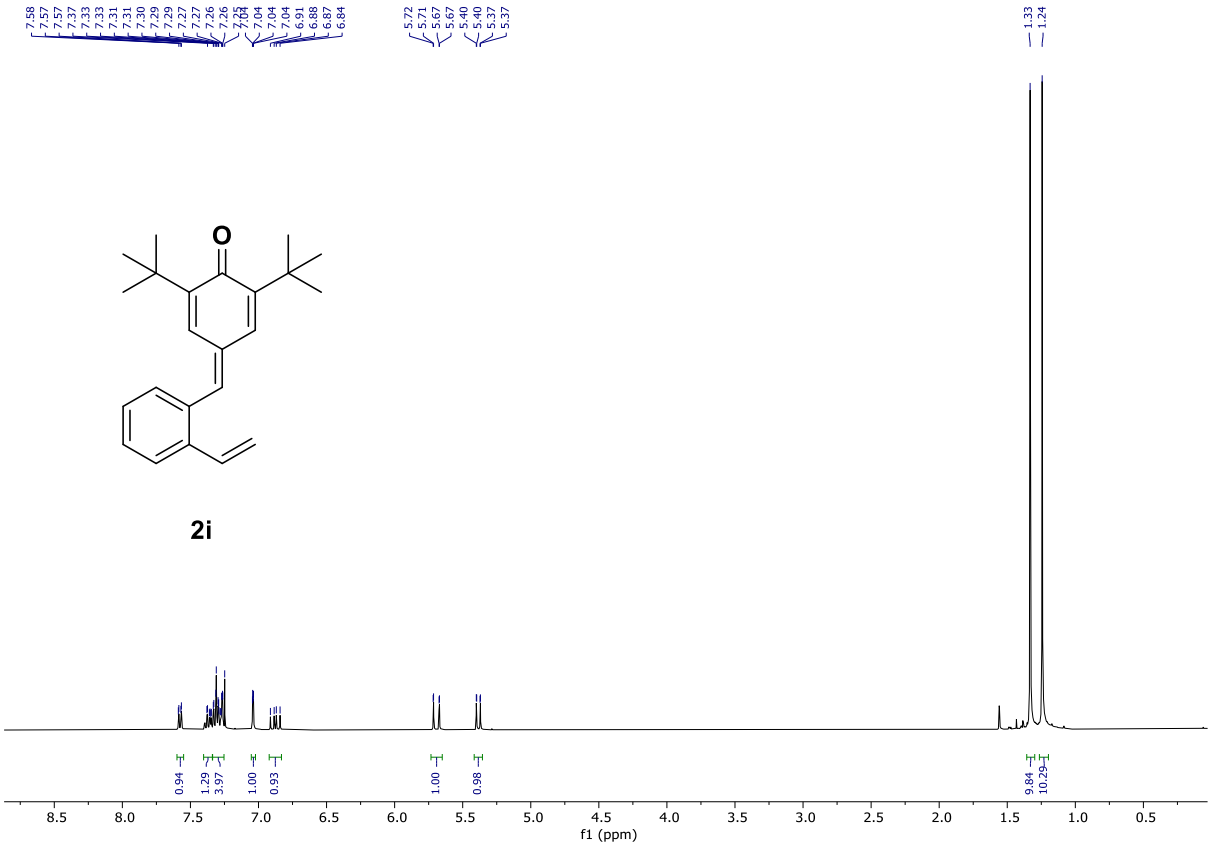


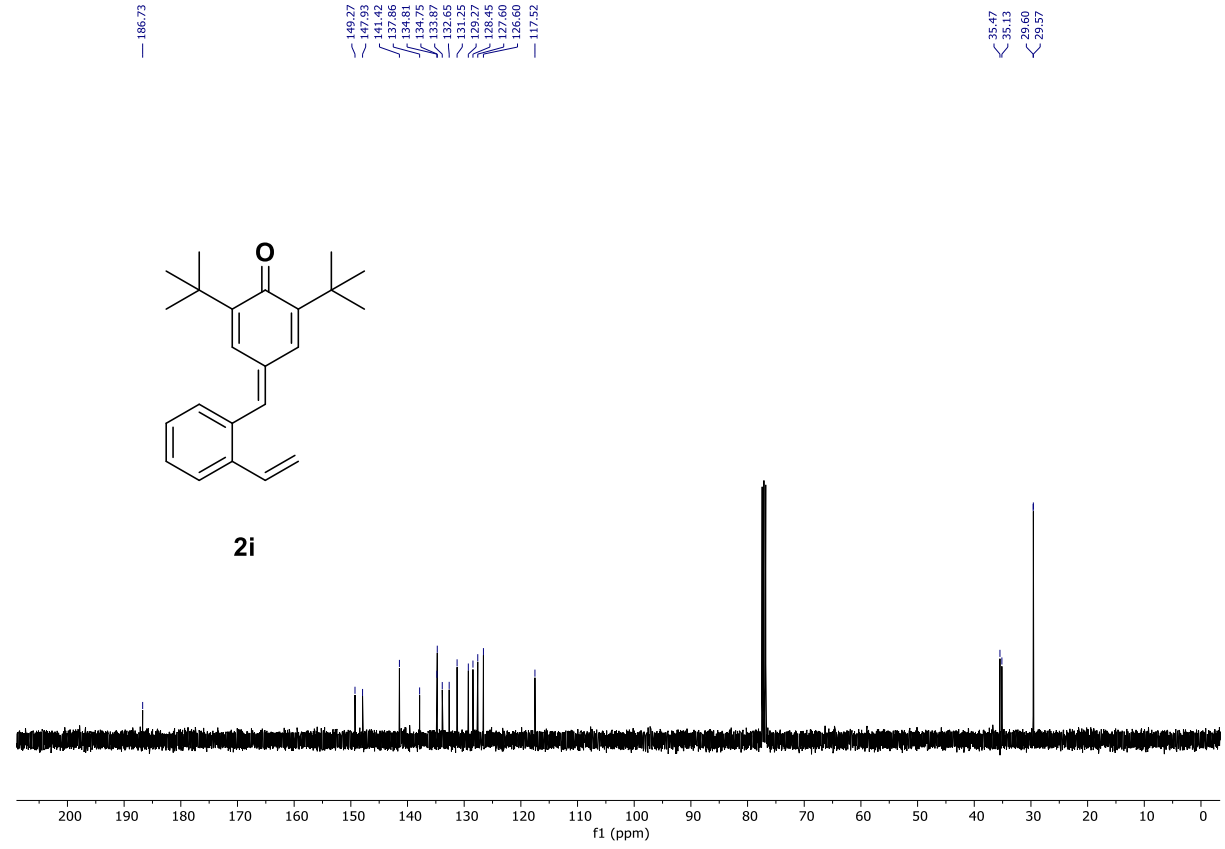



O
F
-111.60
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
f1 (ppm)

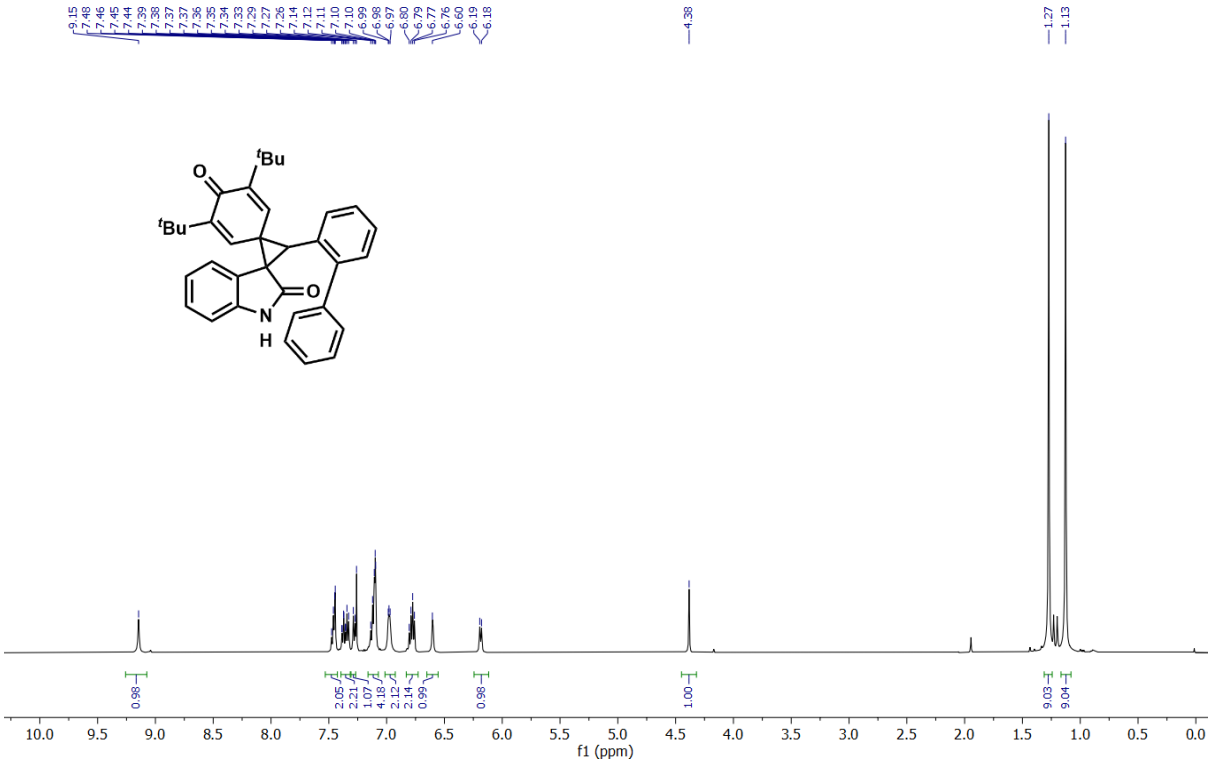
2h

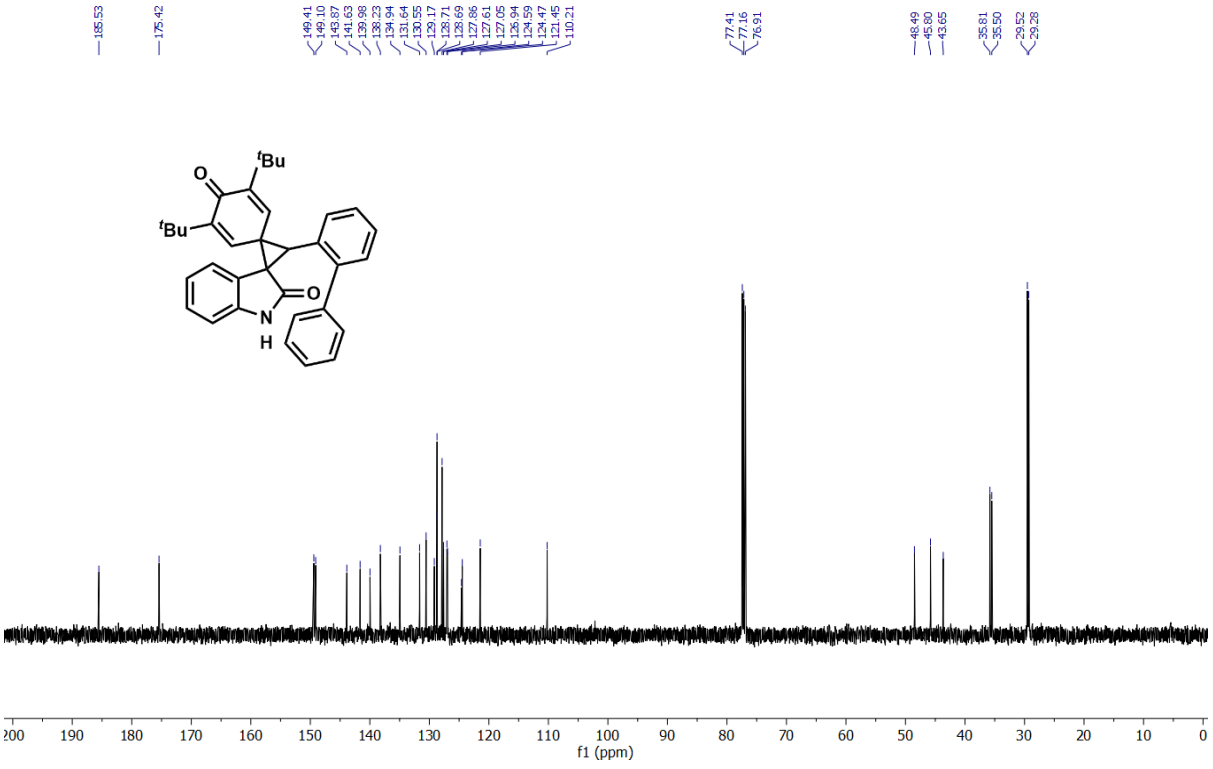
^{1}H and ^{13}C Spectra of 2i (400MHz, $CDCl_3$) :



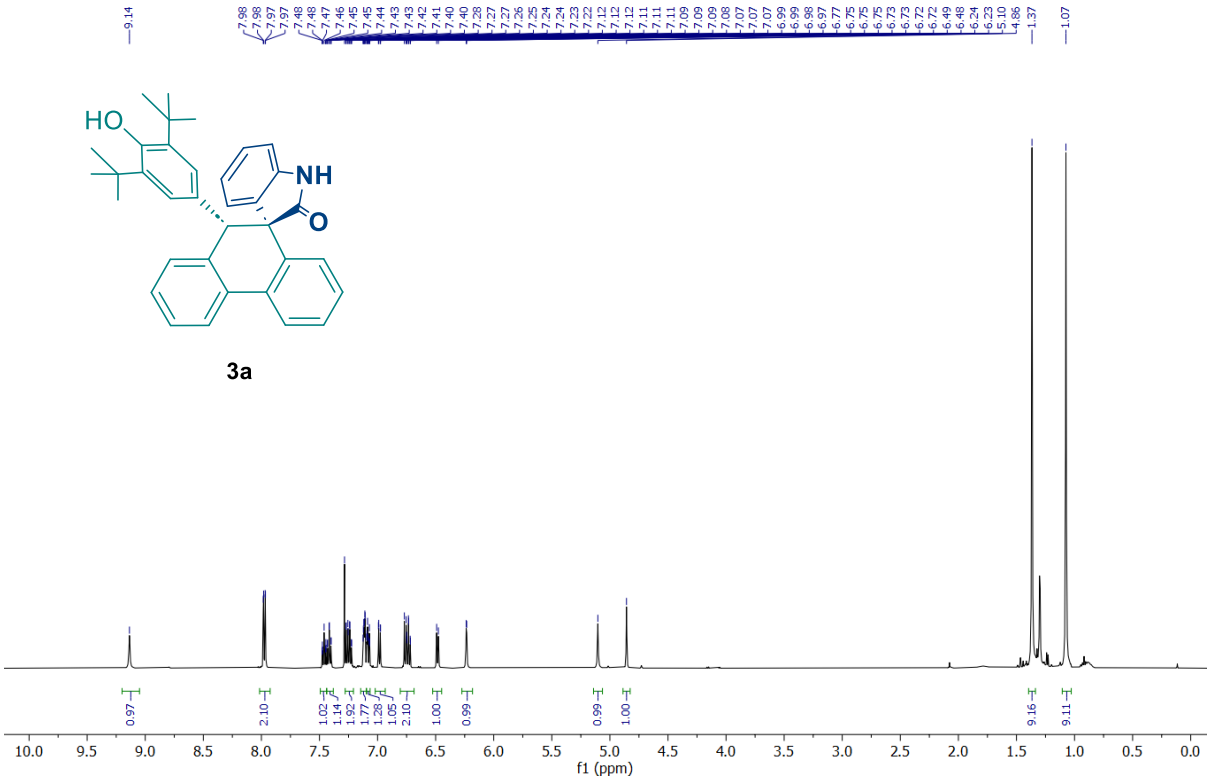


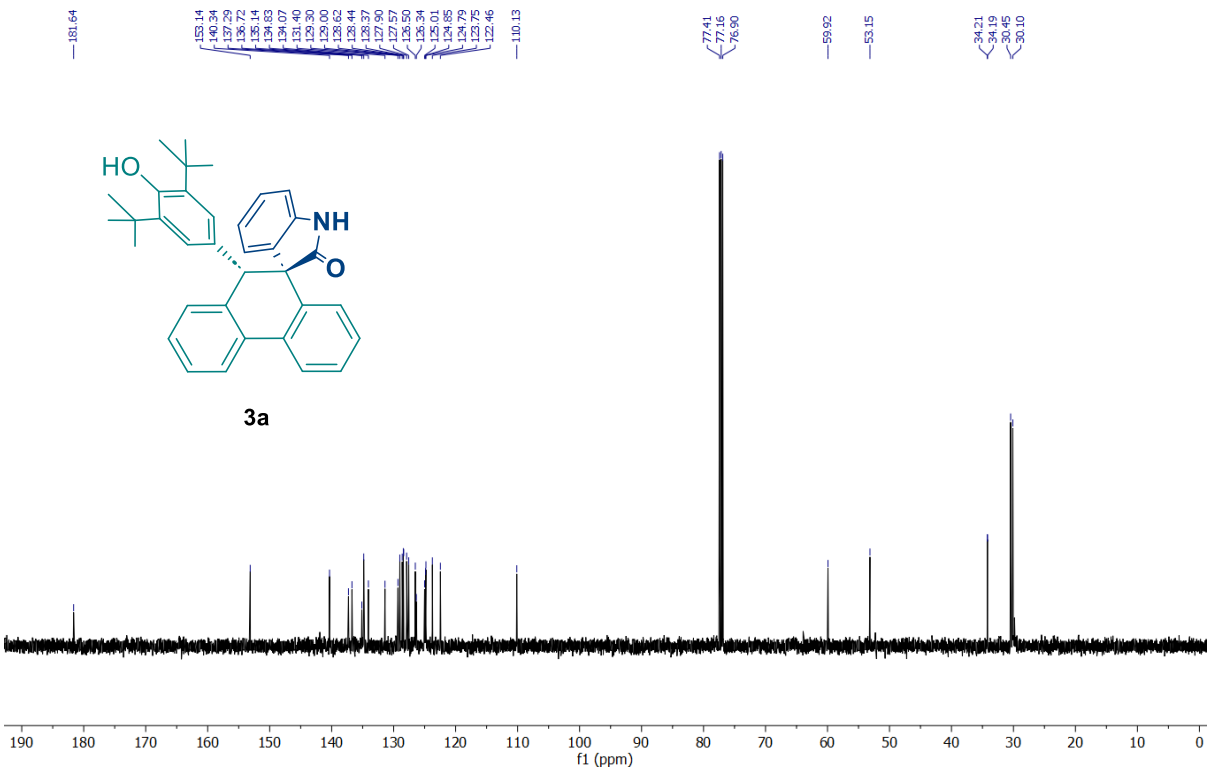
^{1}H and ^{13}C Spectra of 5 (500MHz, $CDCl_3$) :



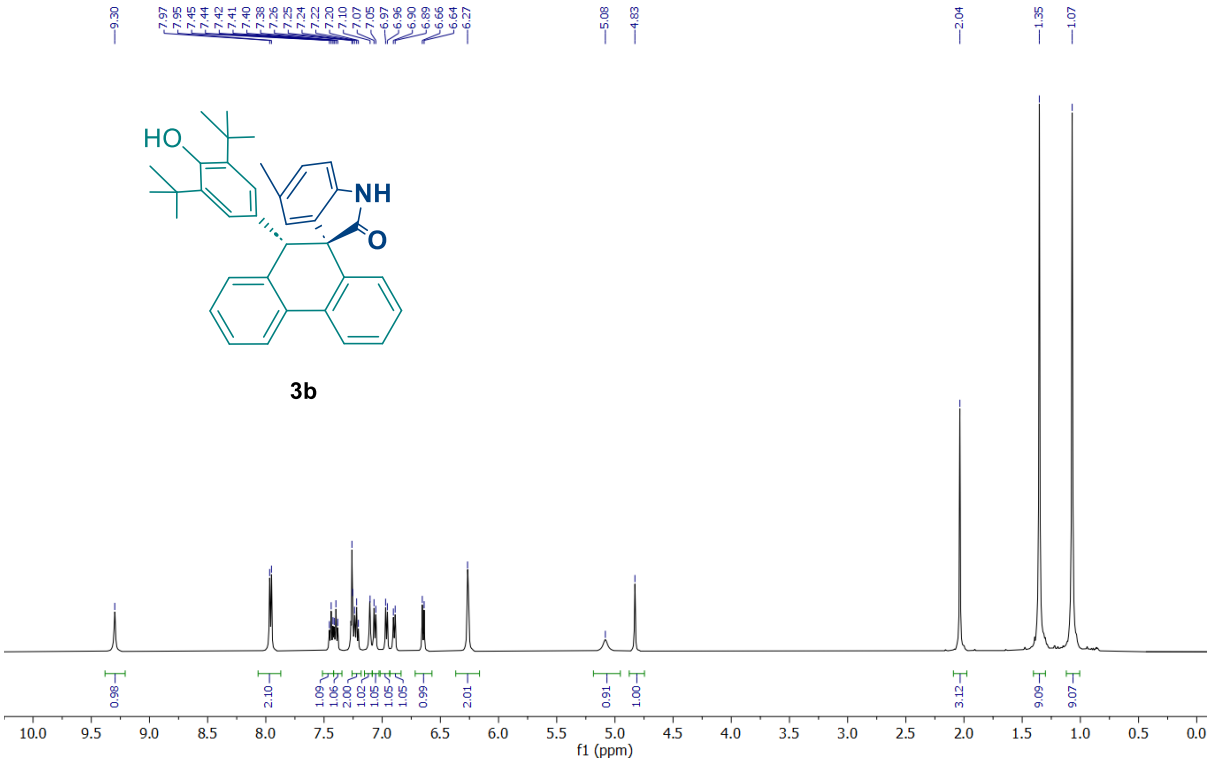


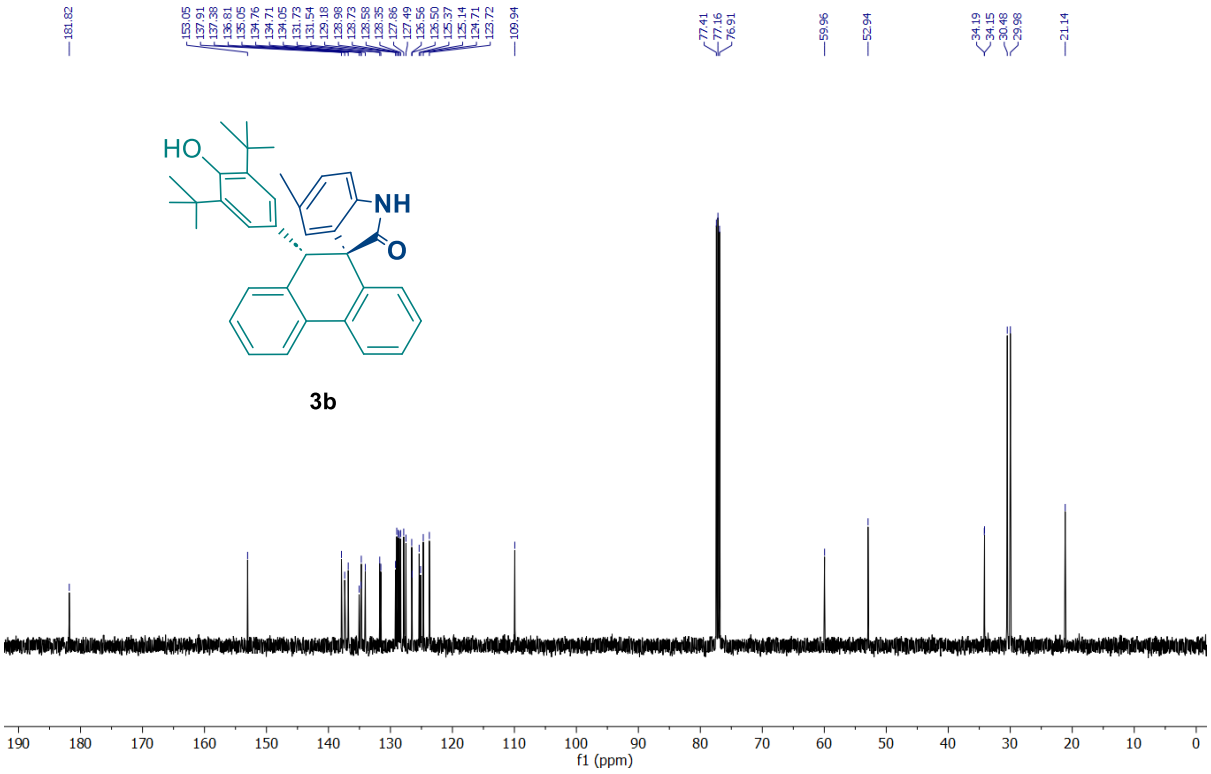
^{1}H and ^{13}C Spectra of 3a (500MHz, $CDCl_3$) :



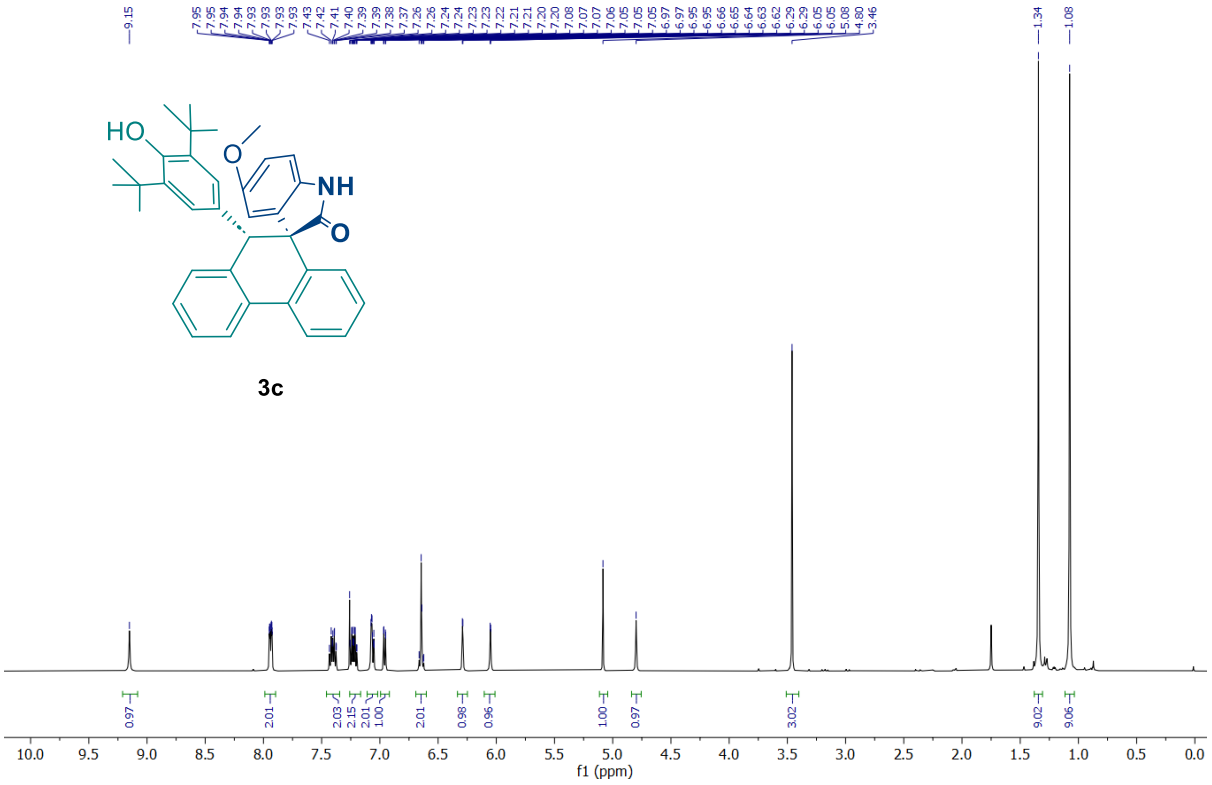


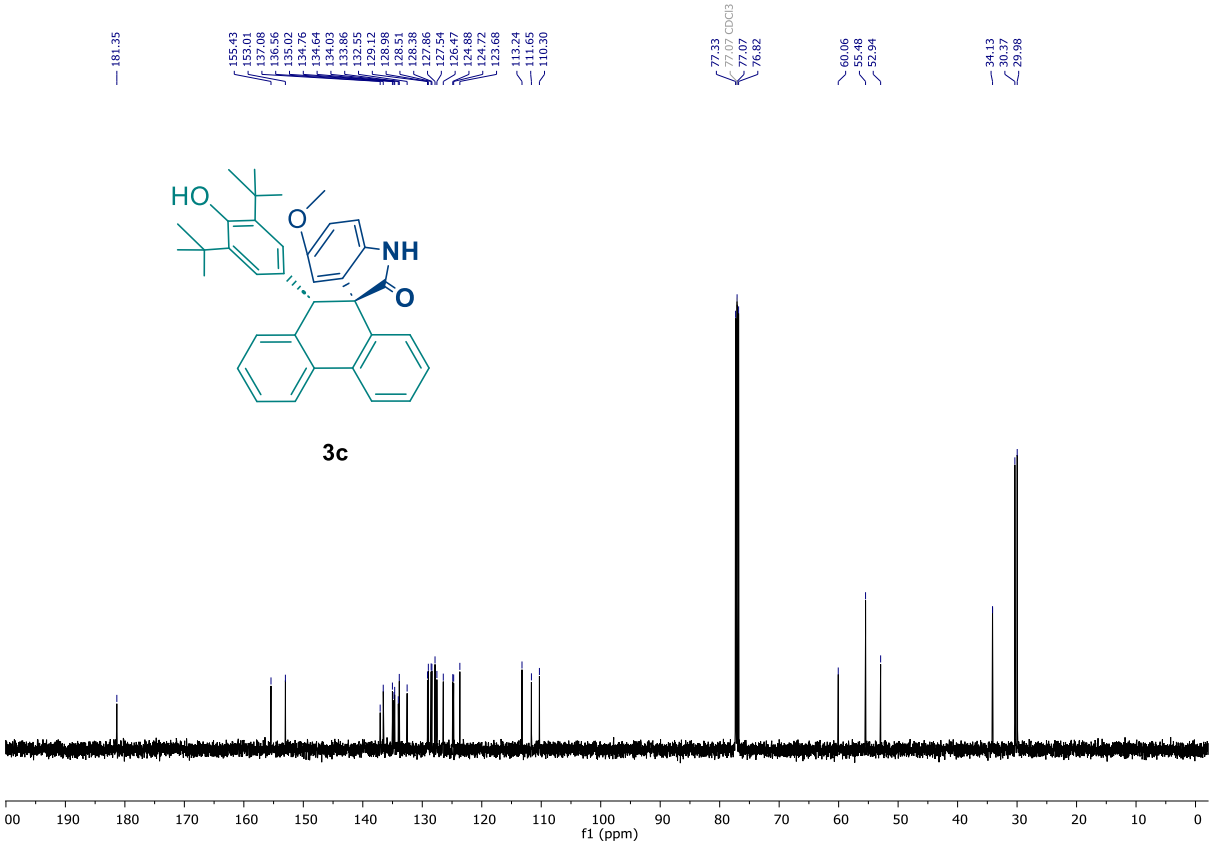
^{1}H and ^{13}C Spectra of 3b (500MHz, $CDCl_3$) :



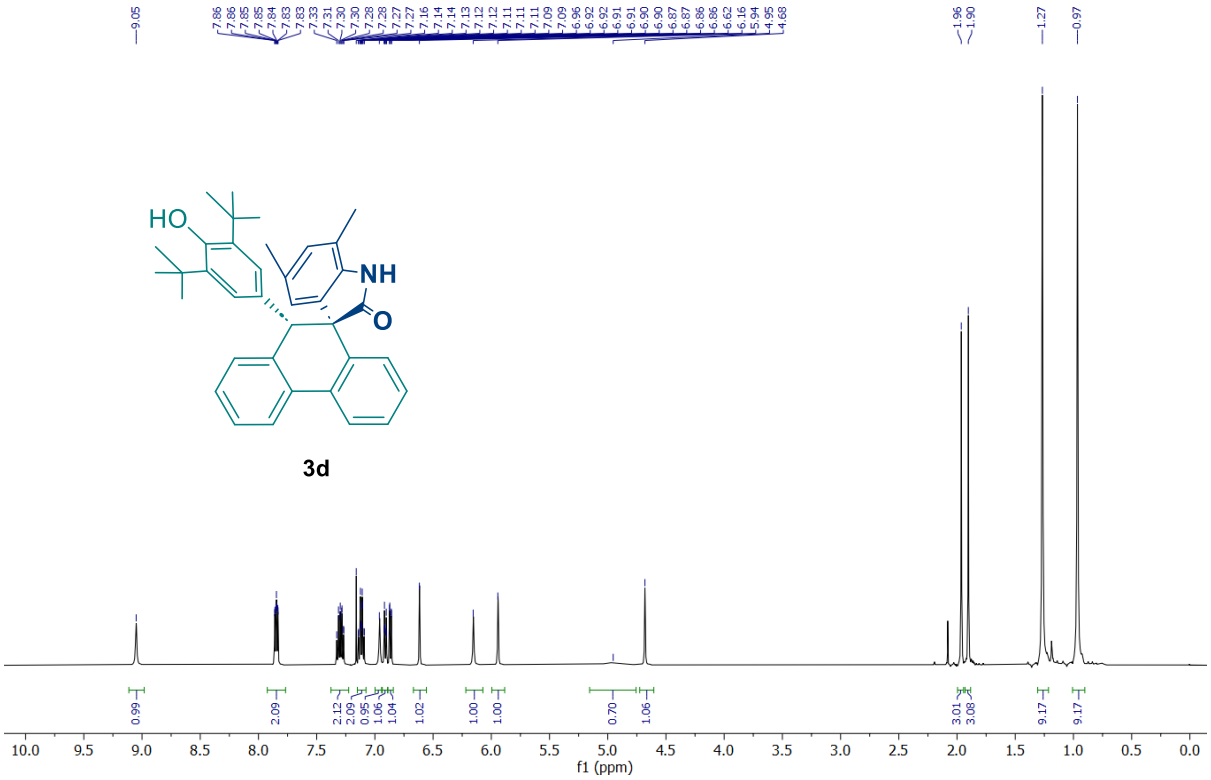


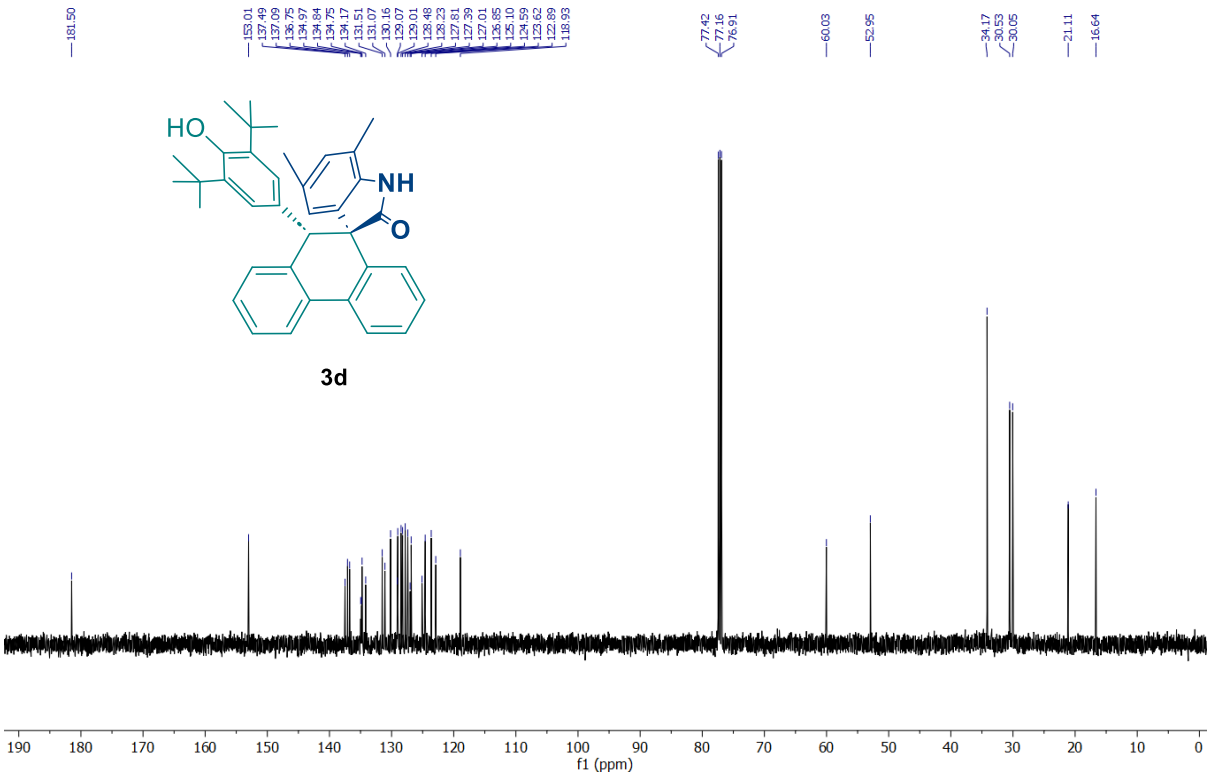
^{1}H and ^{13}C Spectra of 3c (500MHz, $CDCl_3$) :



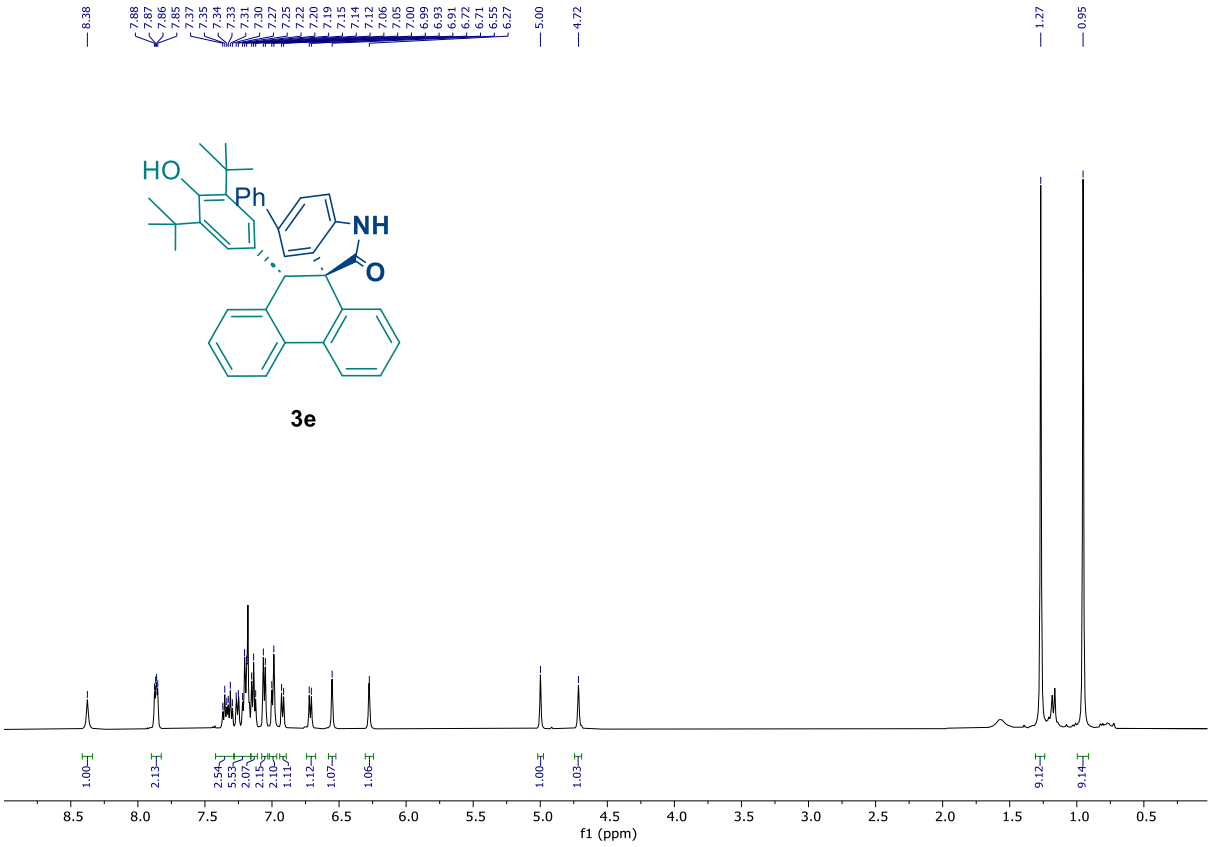


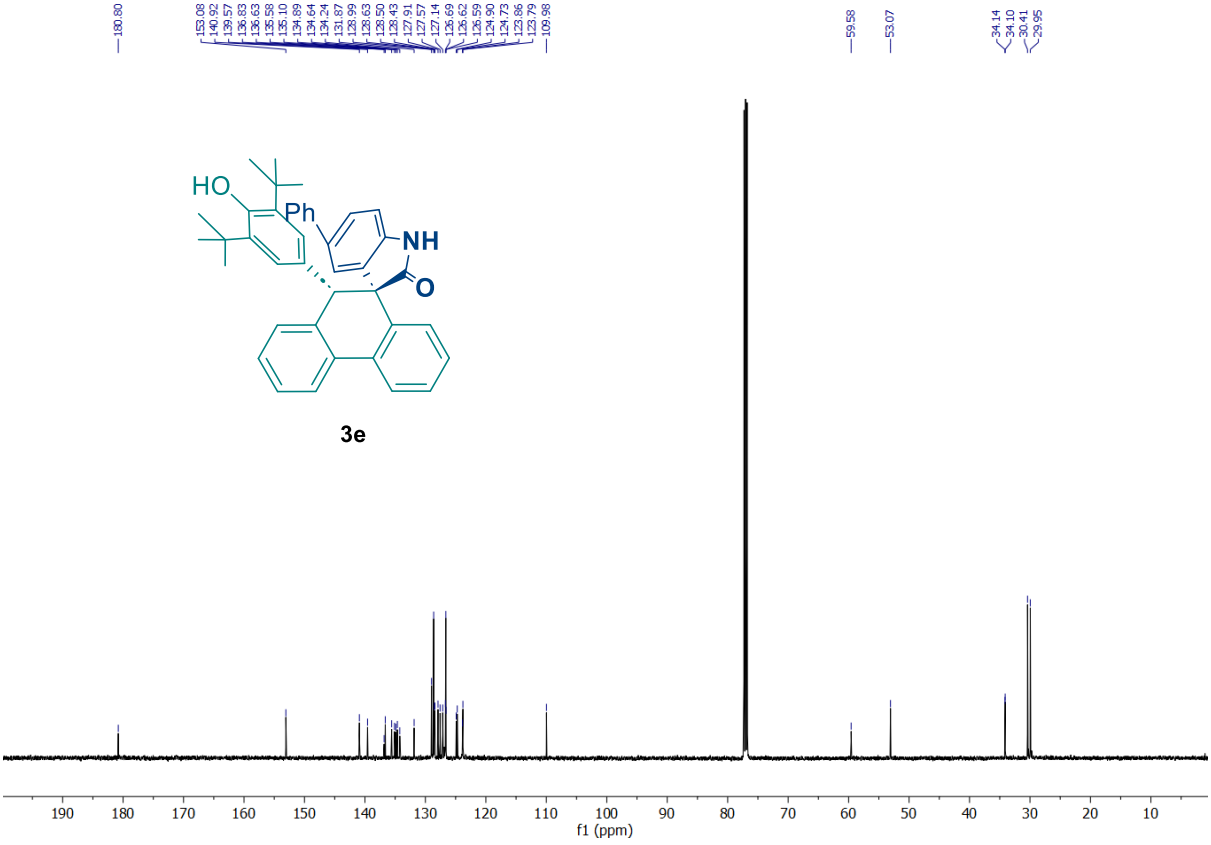
^{1}H and ^{13}C Spectra of 3d (500MHz, $CDCl_3$) :



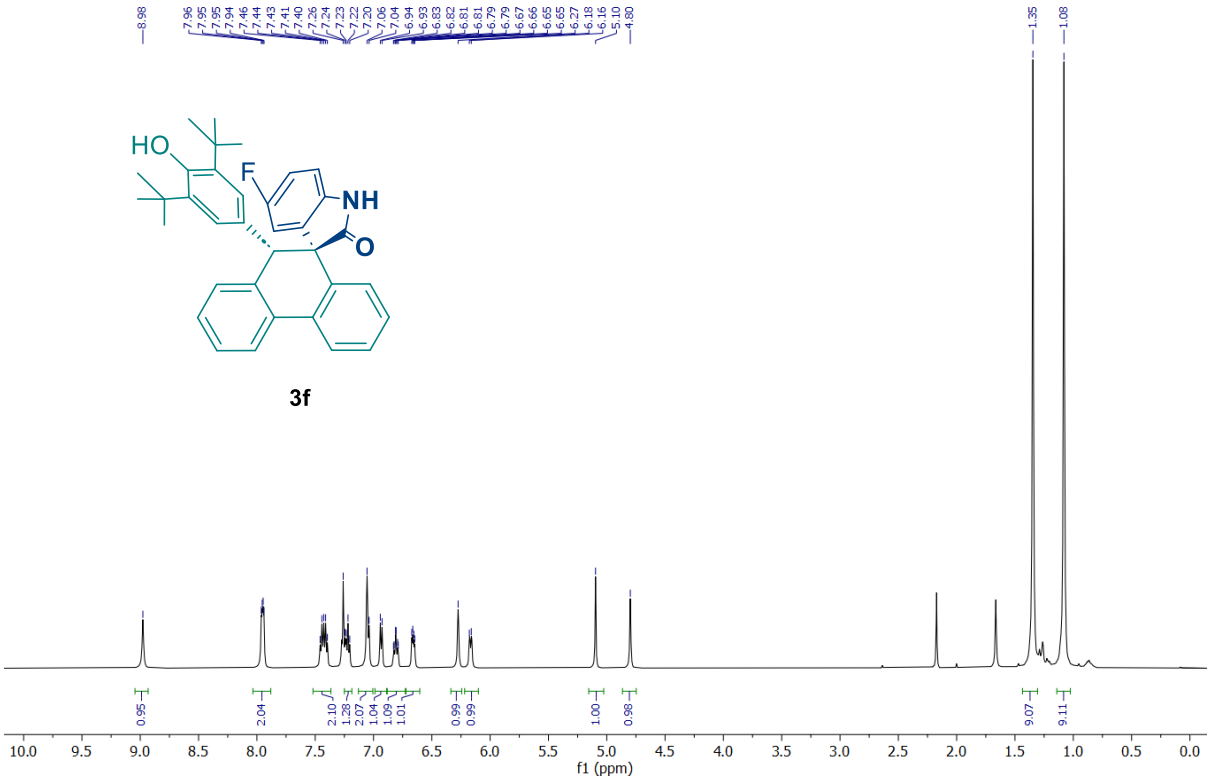


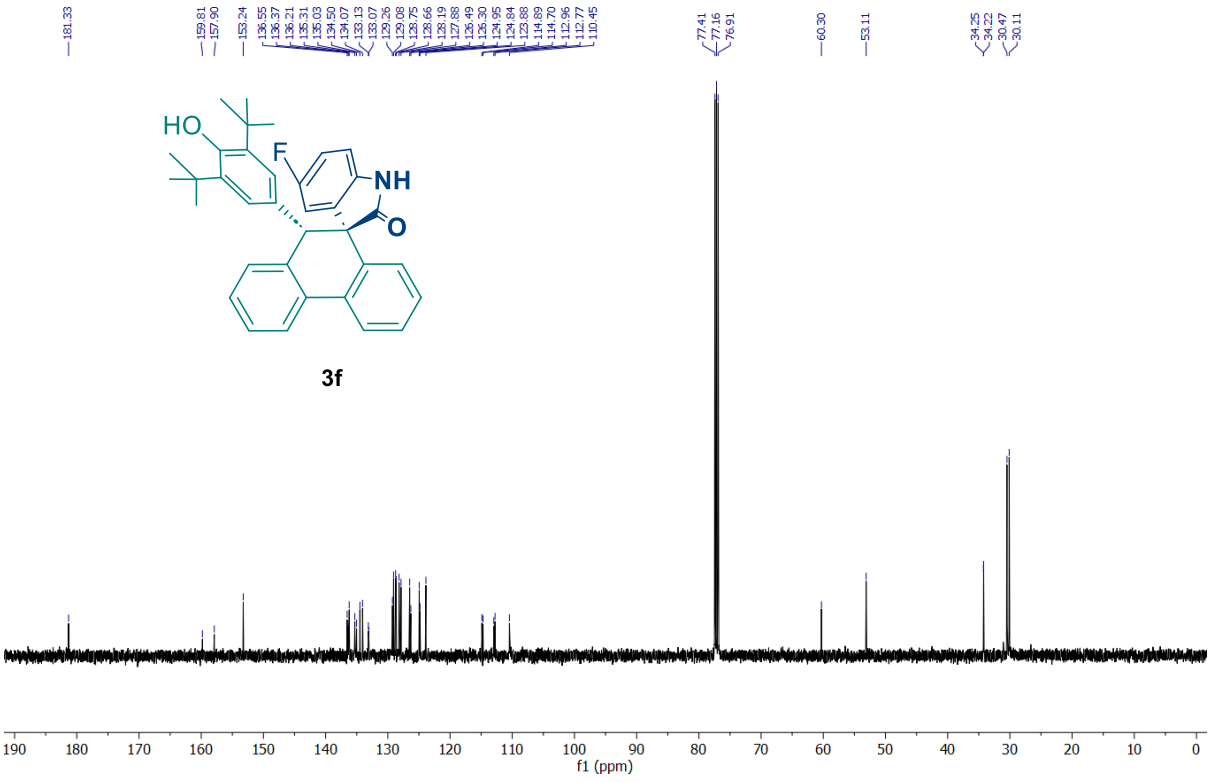
^{1}H and ^{13}C Spectra of 3e (500MHz, $CDCl_3$) :

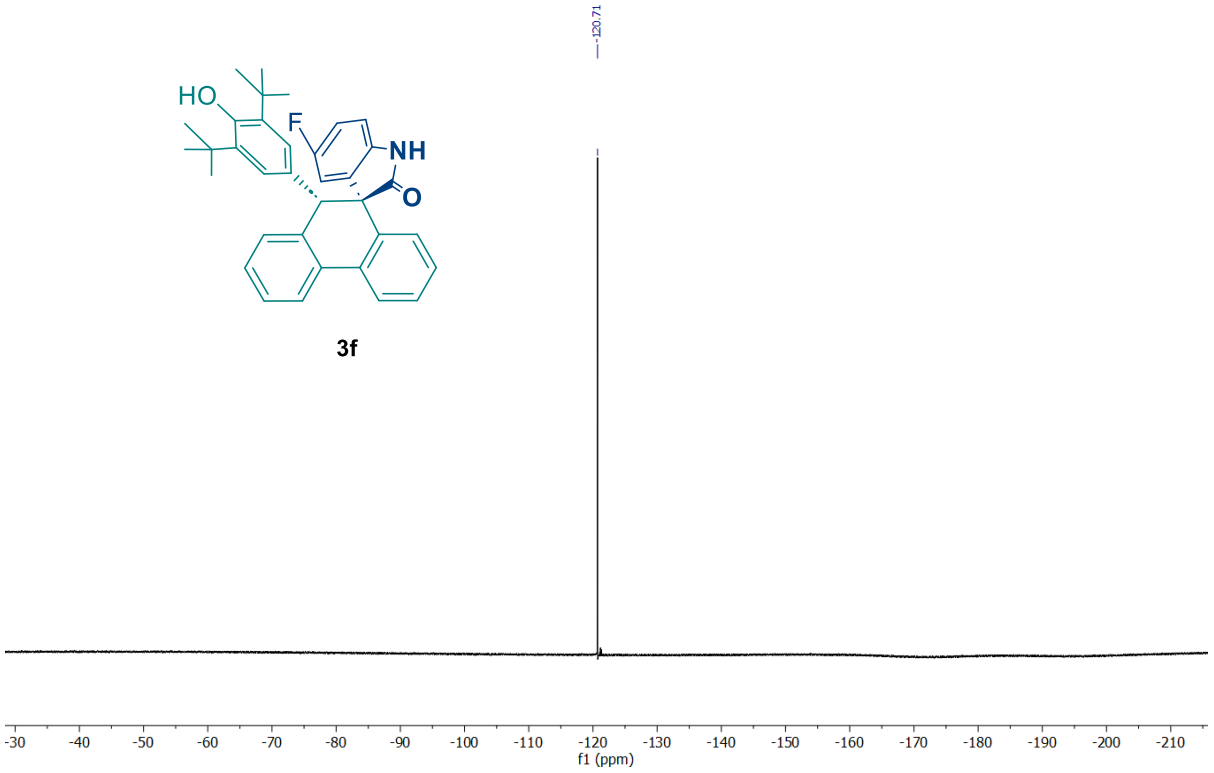




^{1}H, ^{13}C and ^{19}F Spectra of 2b (500MHz, $CDCl_3$) :

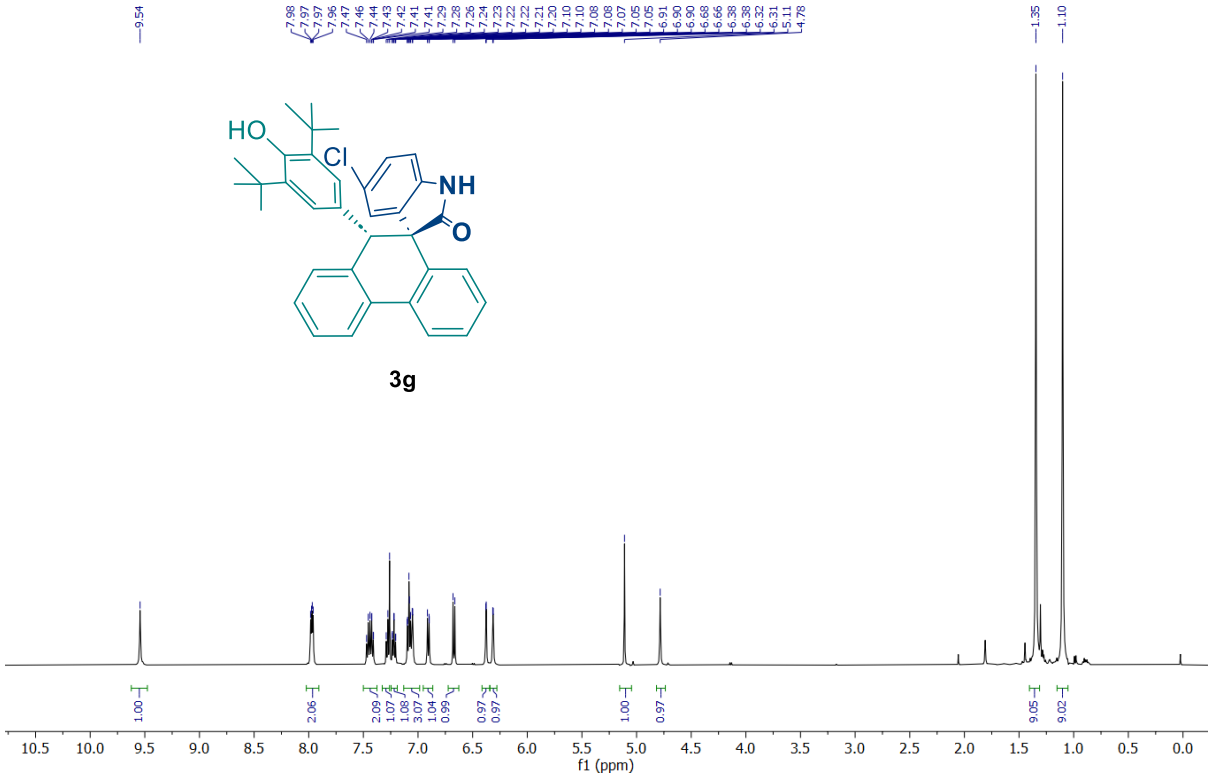


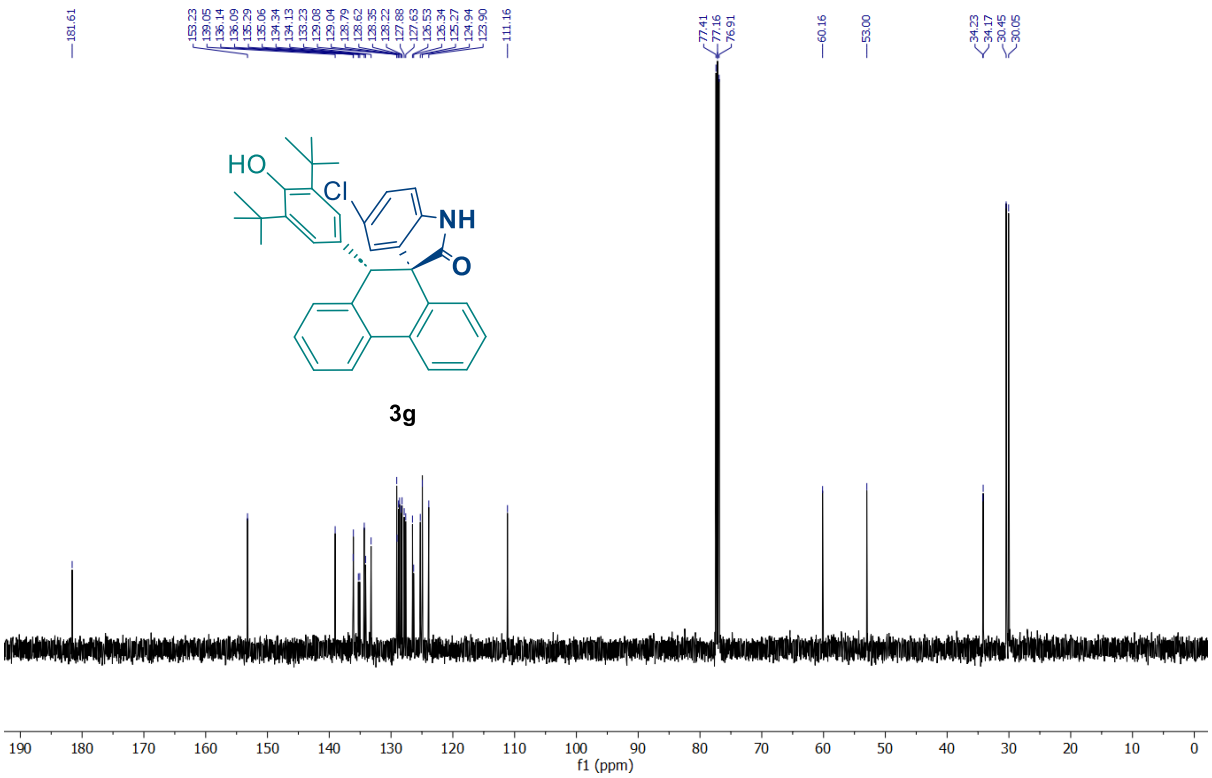



HO
F
NH
O
-120.71
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

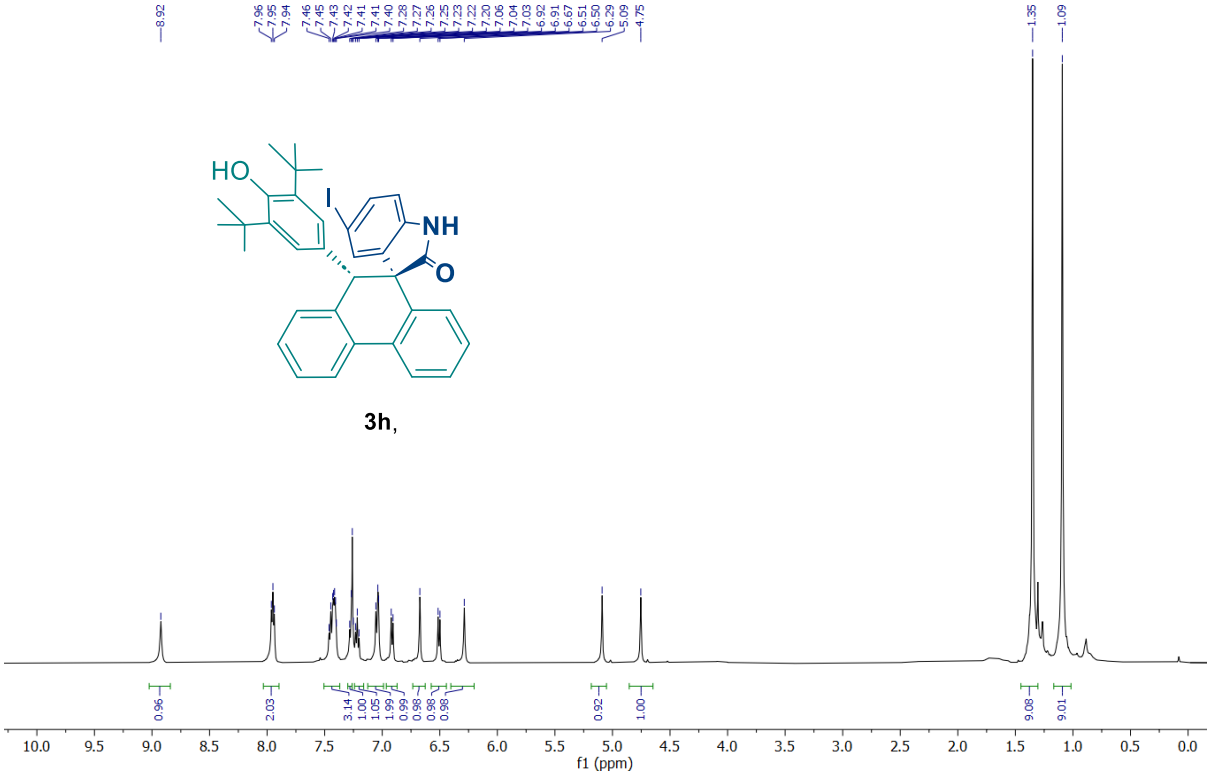
3f

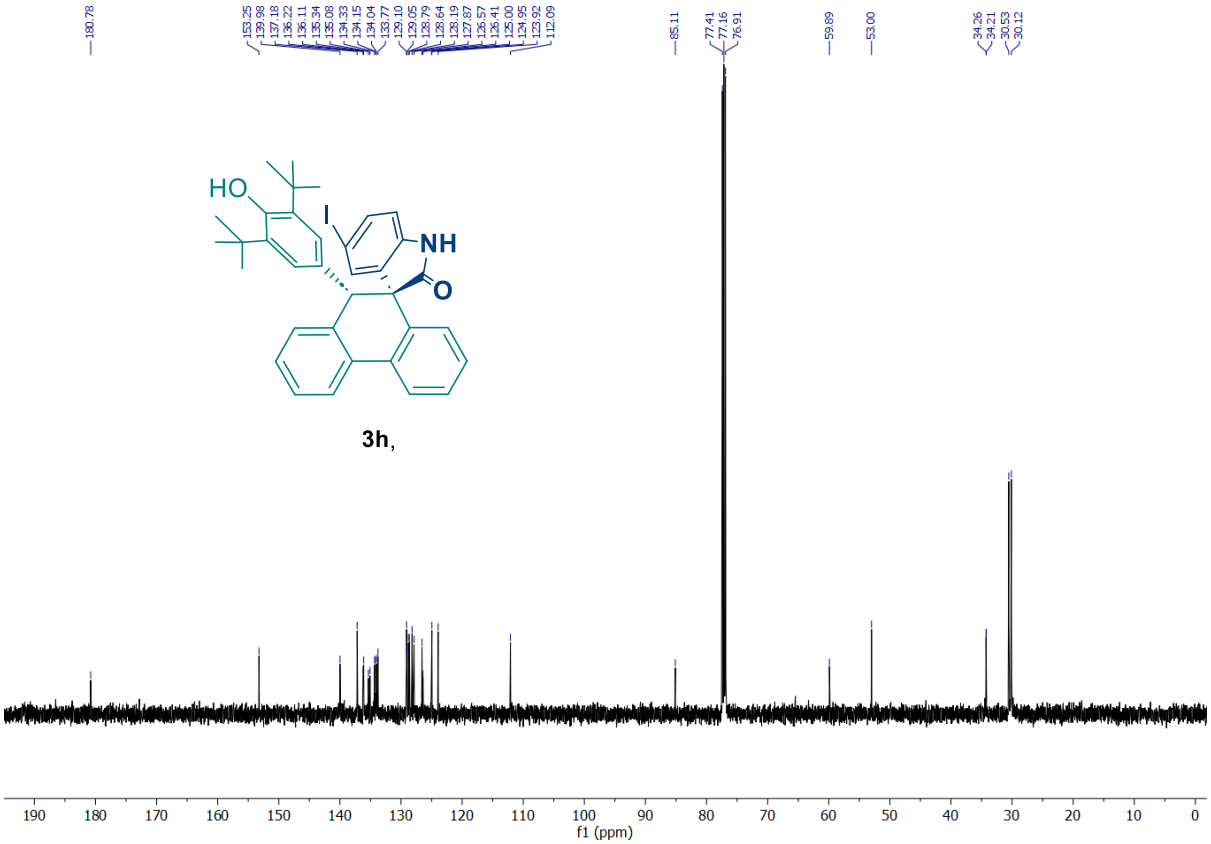
^{1}H and ^{13}C Spectra of 3g (500MHz, $CDCl_3$) :



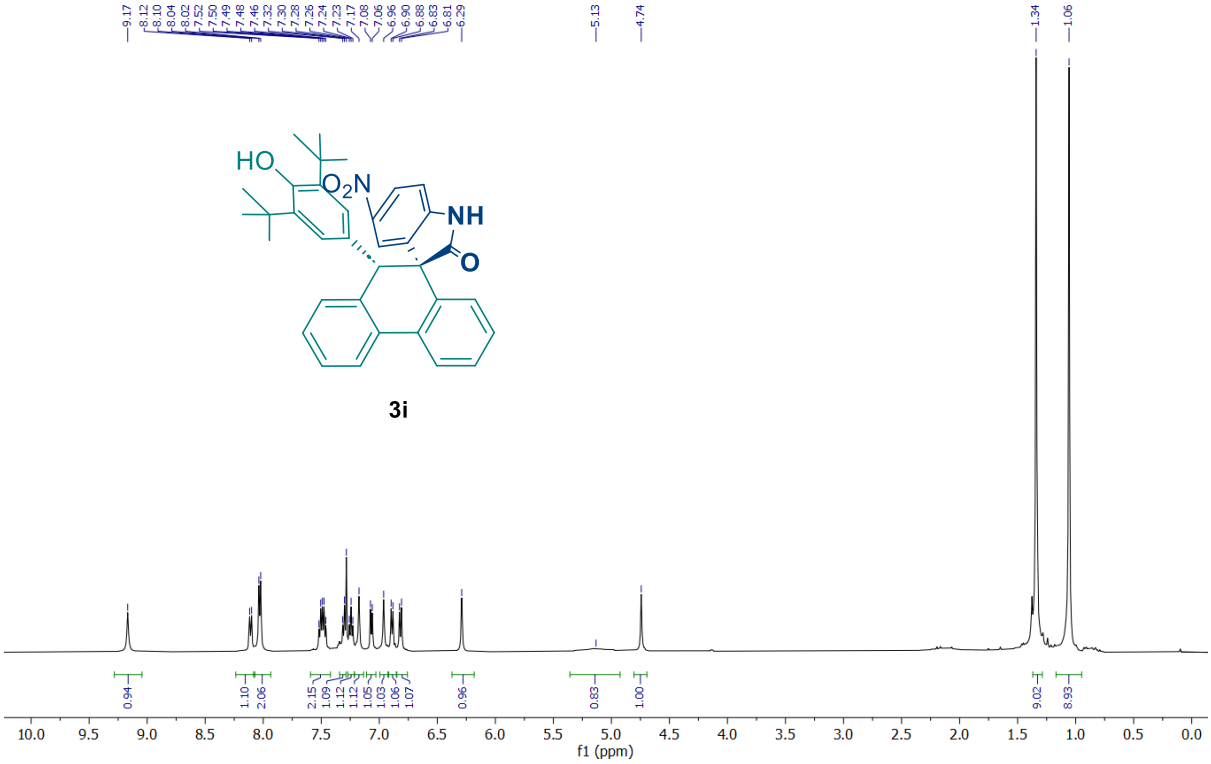


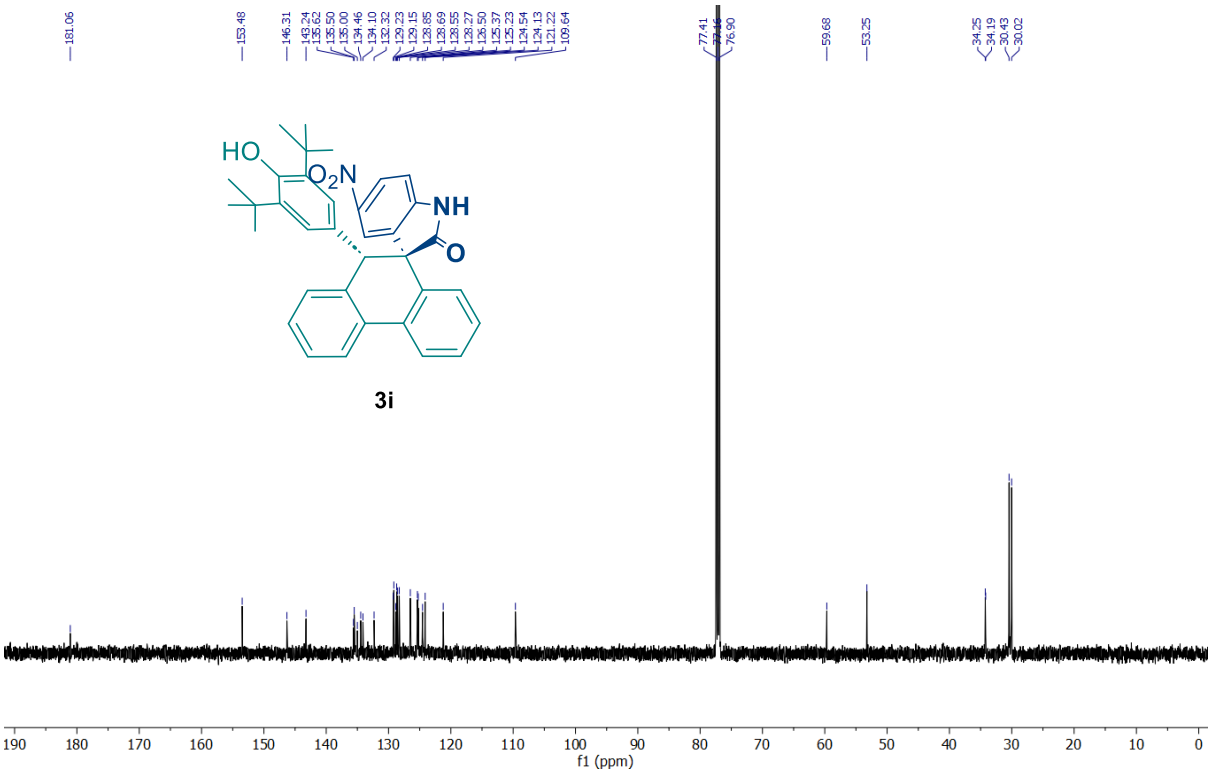
^{1}H and ^{13}C Spectra of 3h (500MHz, $CDCl_3$) :



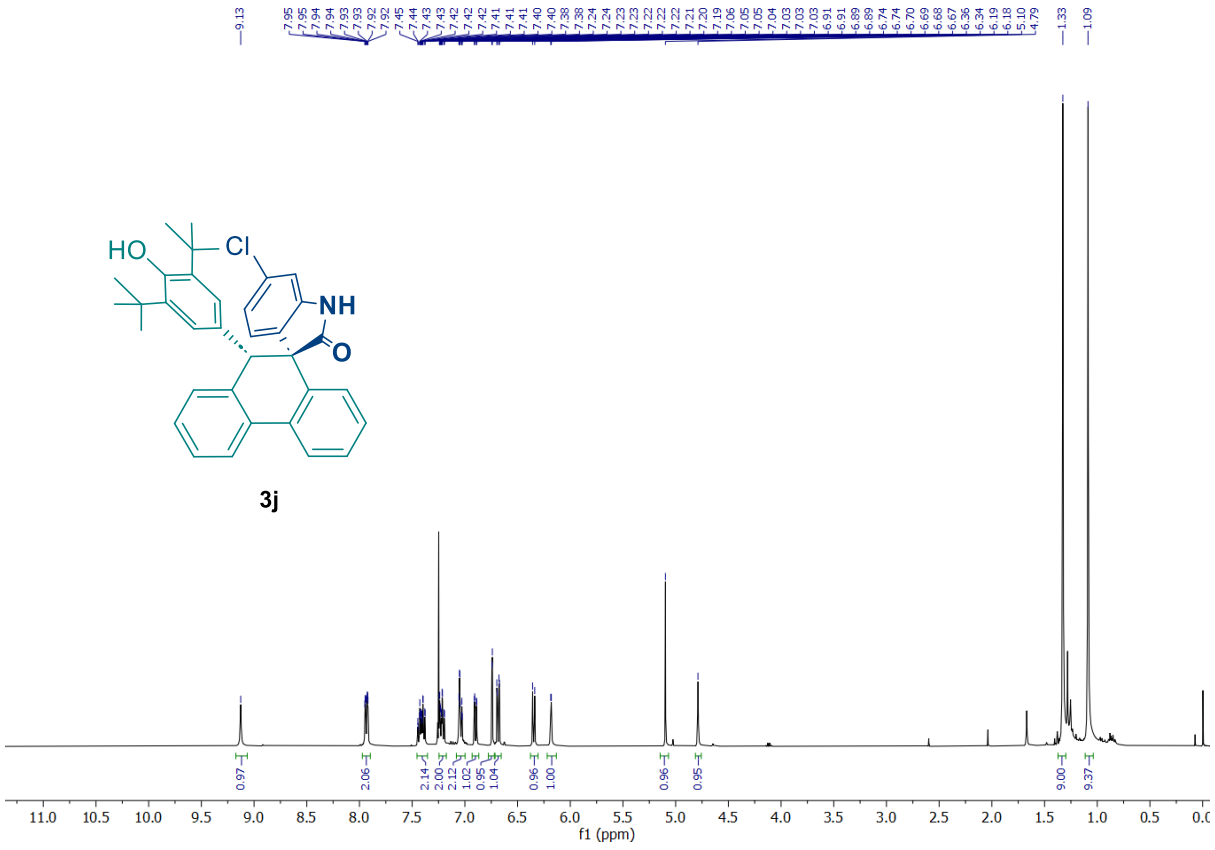


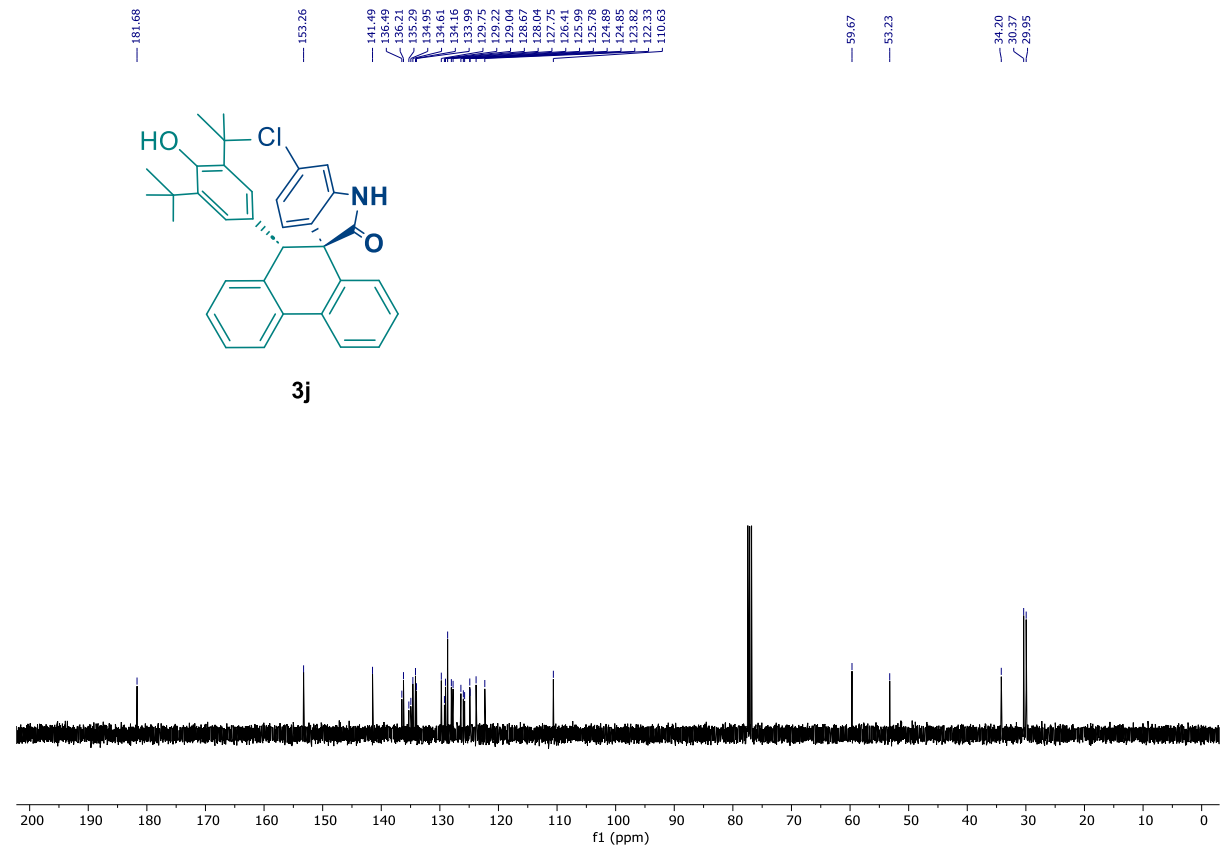
^{1}H and ^{13}C Spectra of 3i (500MHz, $CDCl_3$) :



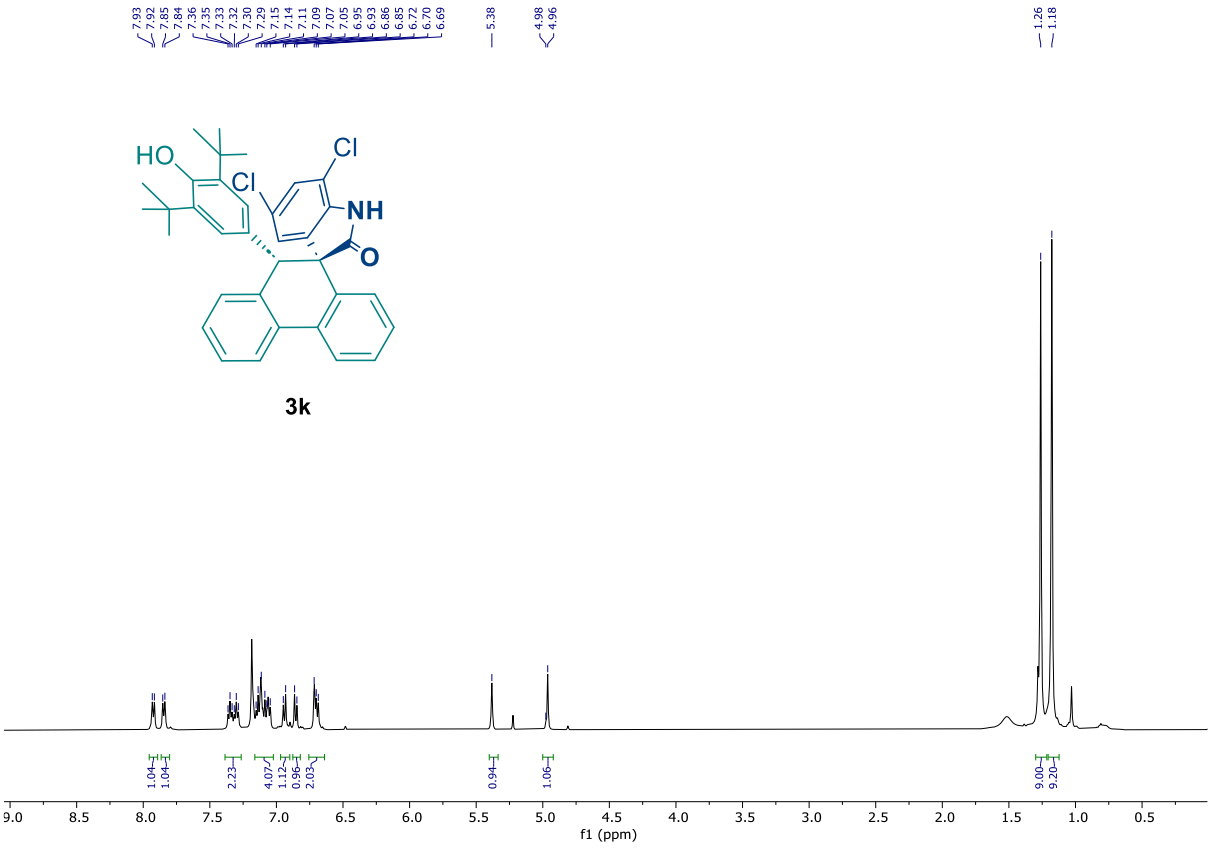


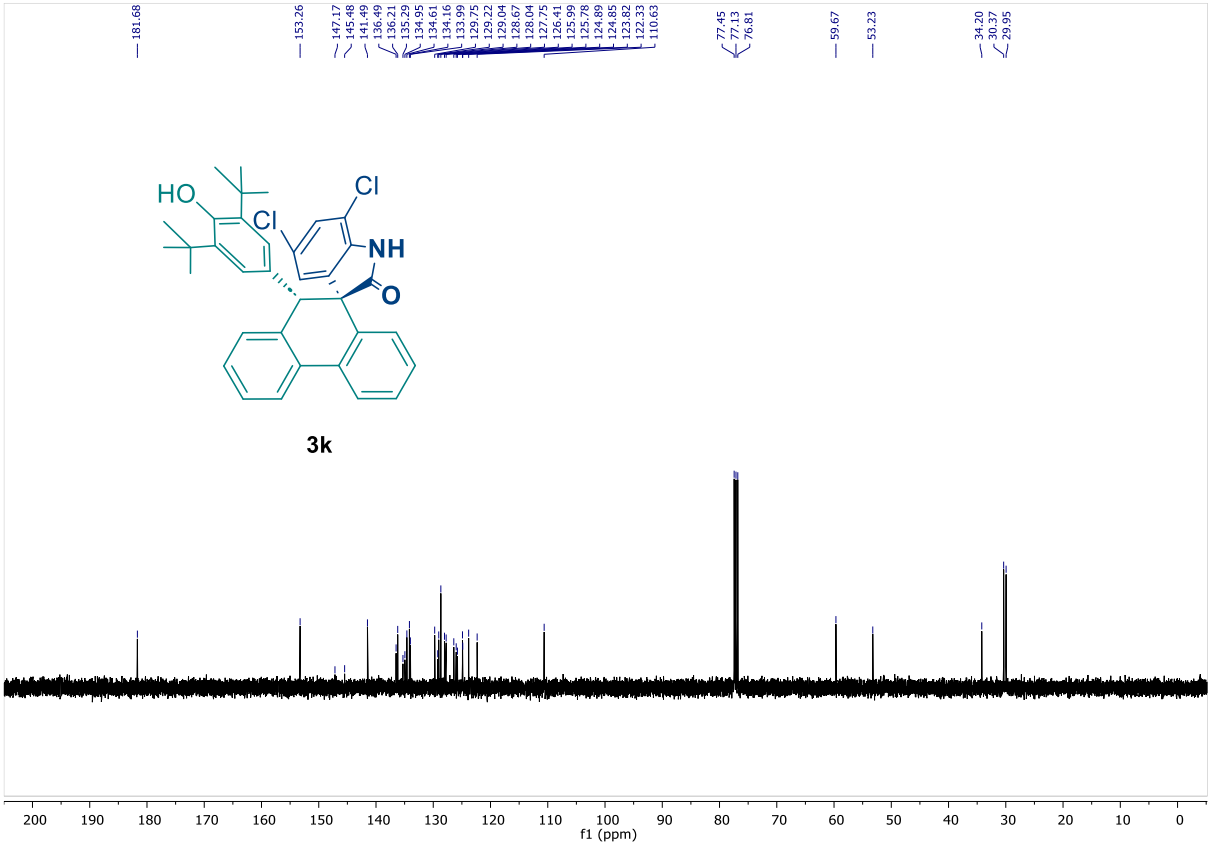
^{1}H and ^{13}C Spectra of 3j (500MHz, $CDCl_3$) :



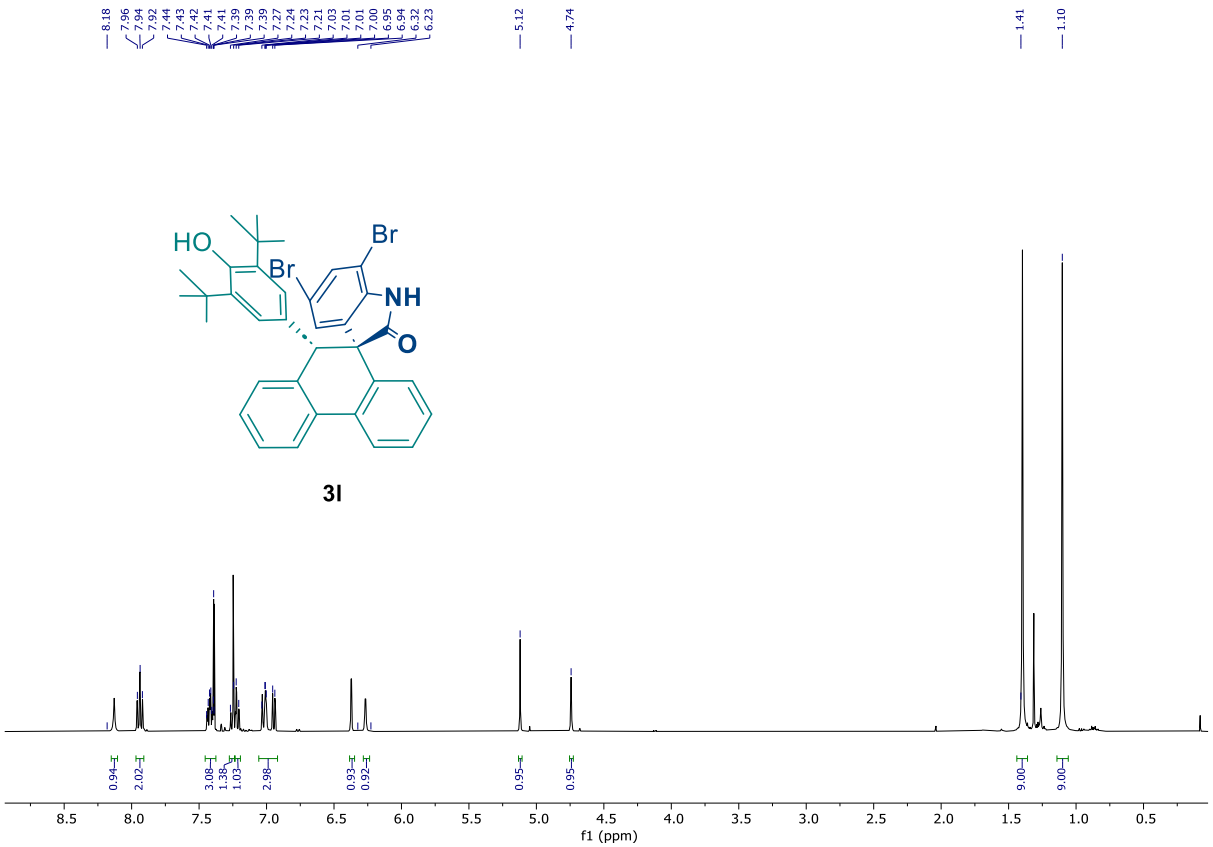


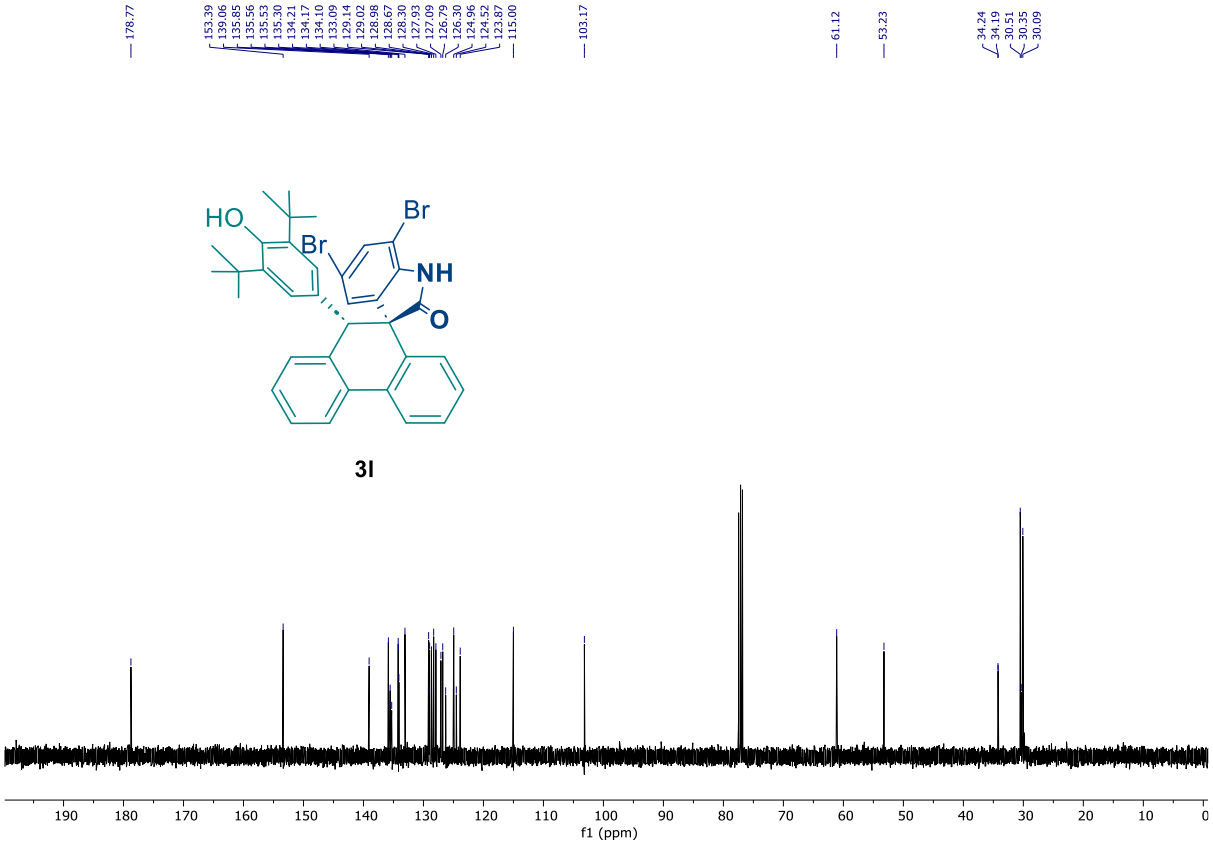
^{1}H and ^{13}C Spectra of 3k (500MHz, $CDCl_3$) :



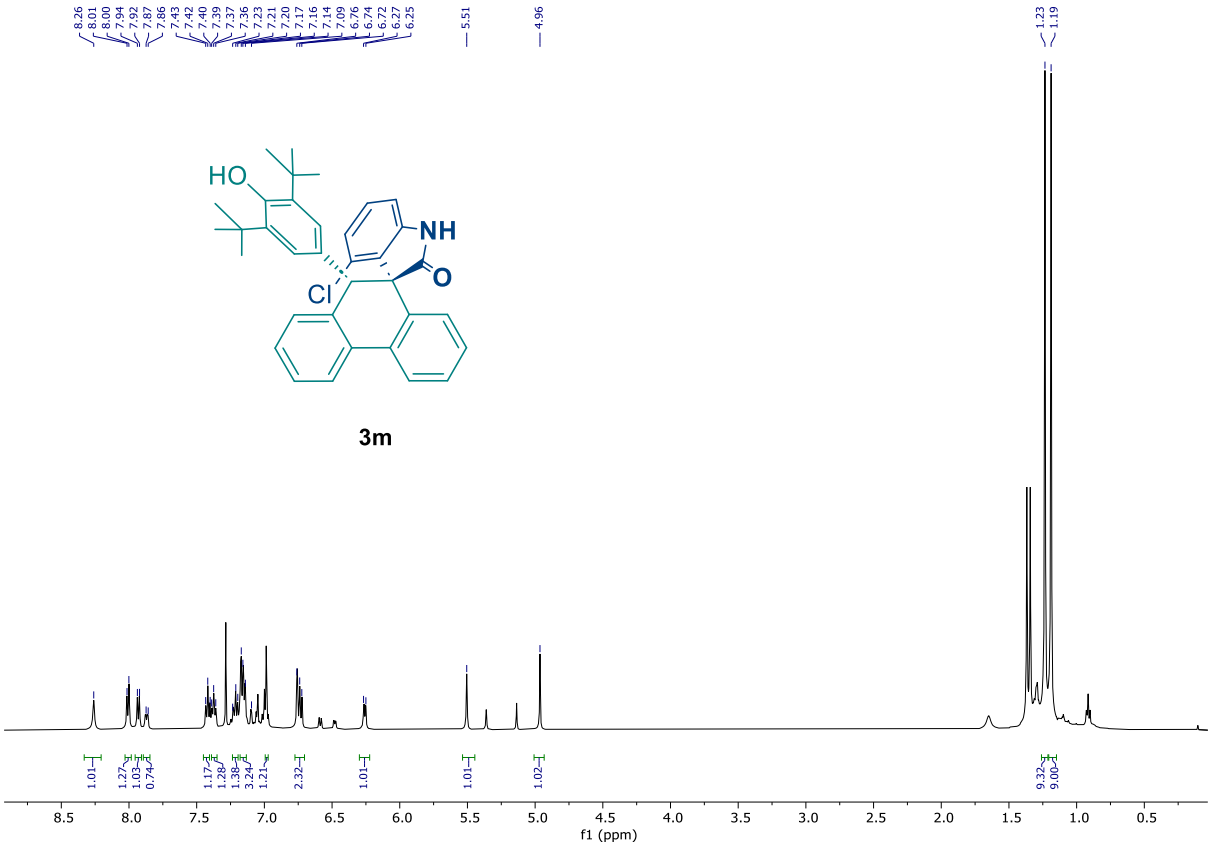


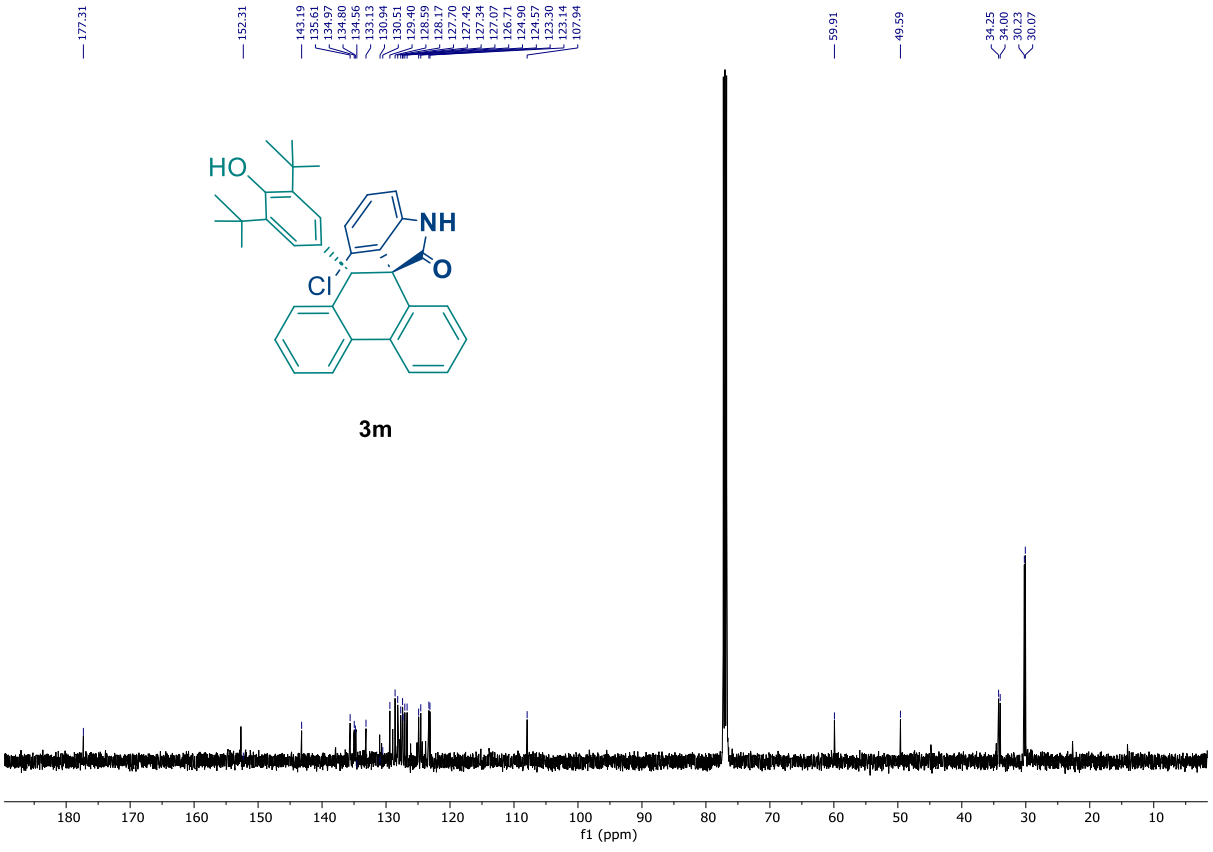
^{1}H and ^{13}C Spectra of 3l (400MHz, $CDCl_3$) :



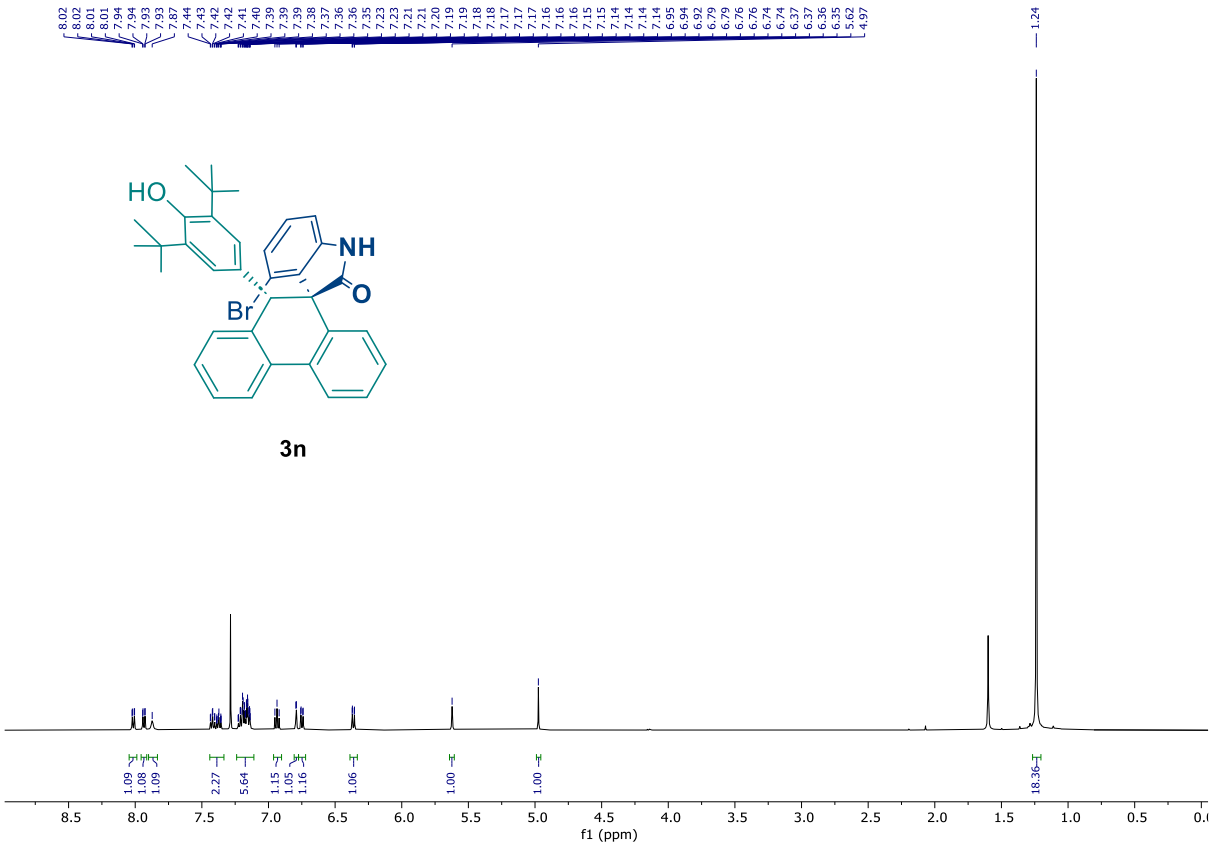


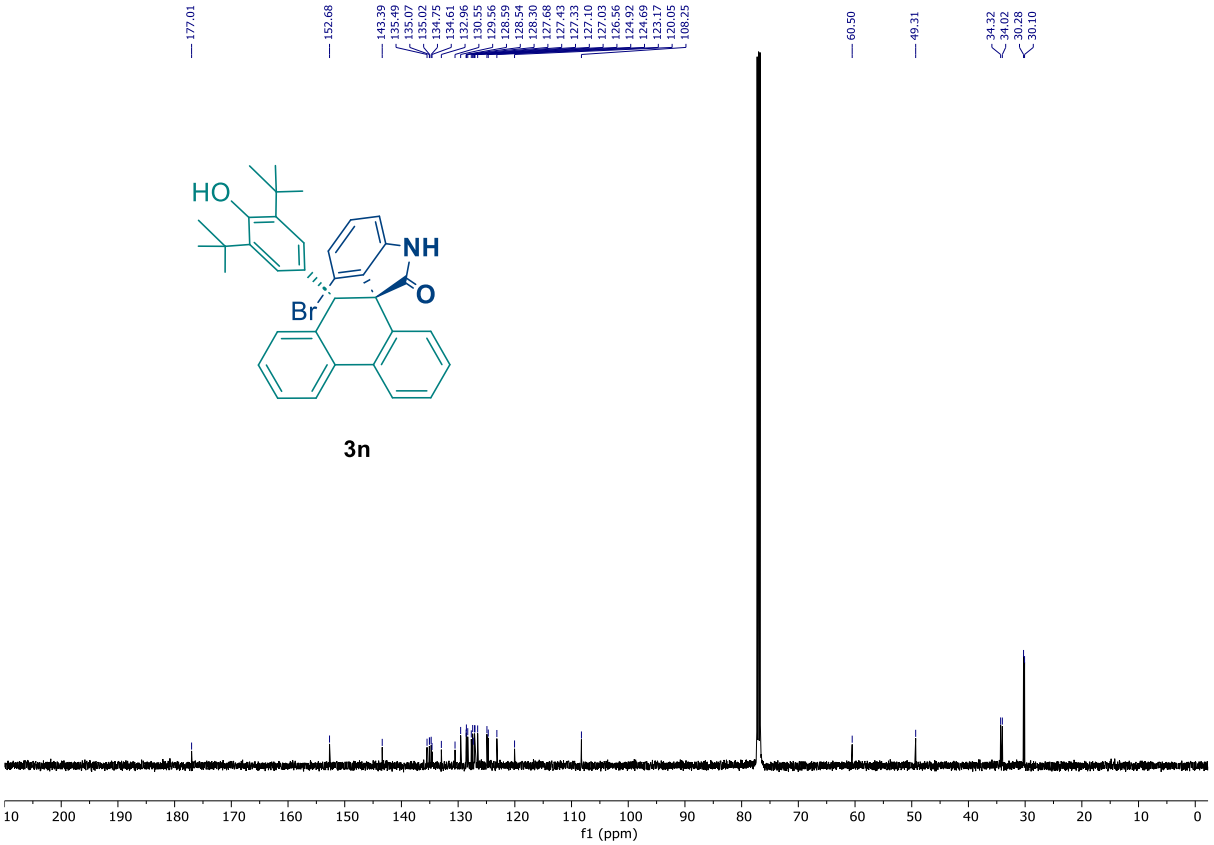
^{1}H and ^{13}C Spectra of 3m (500MHz, $CDCl_3$) :



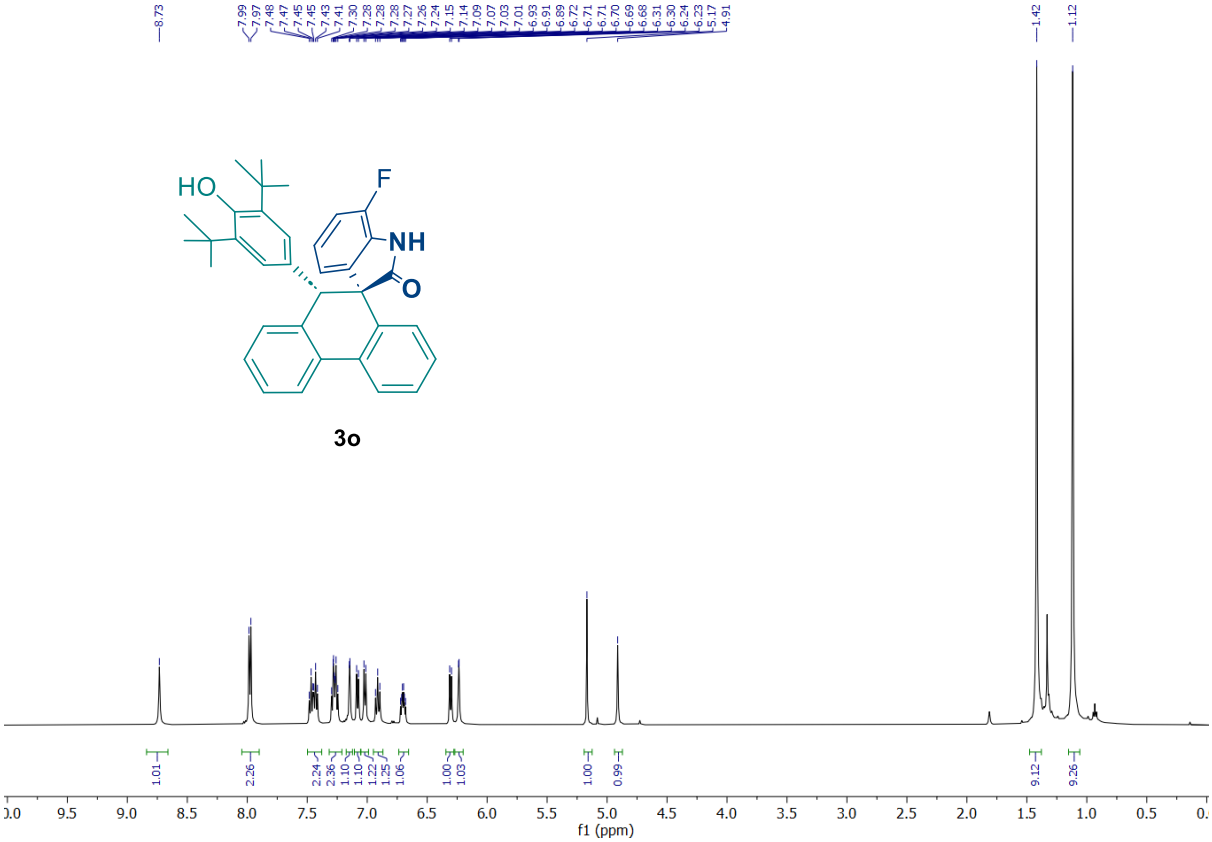


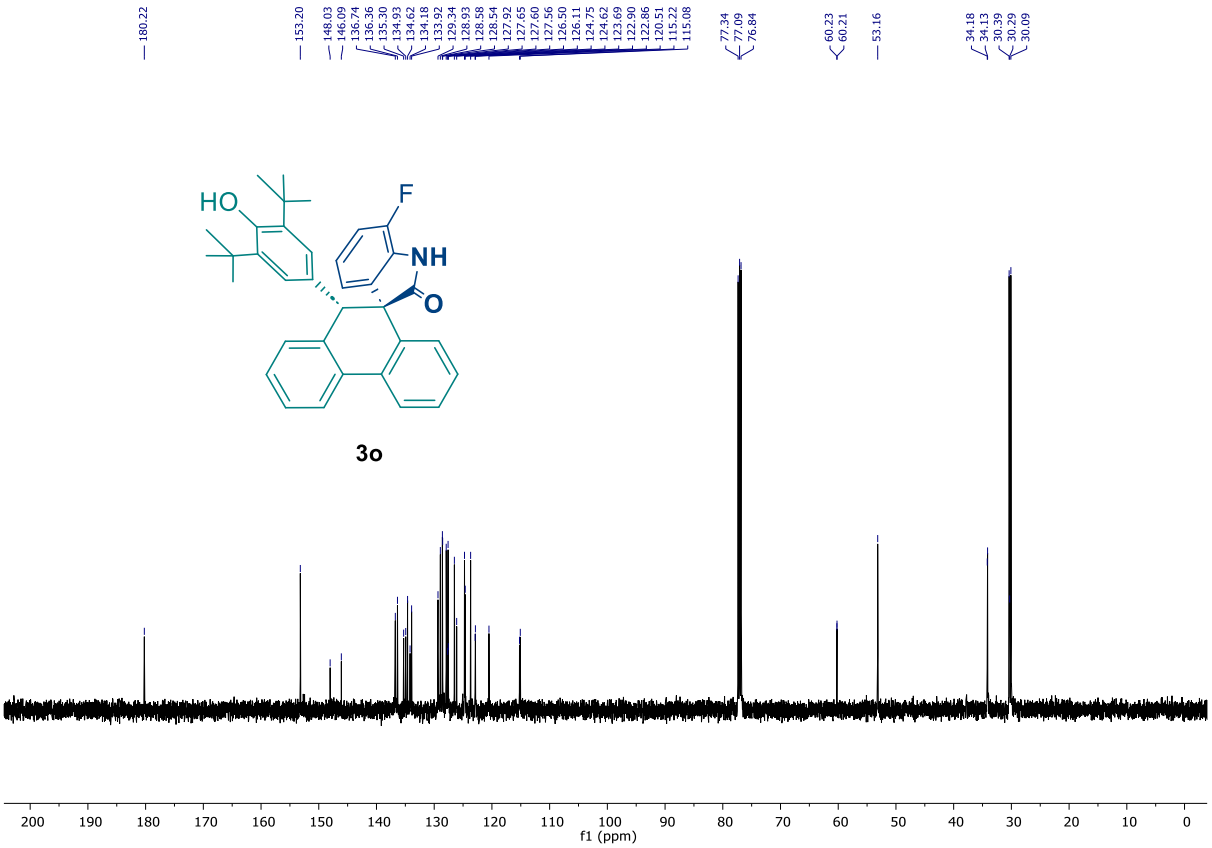
^{1}H and ^{13}C Spectra of 3n (500MHz, $CDCl_3$) :

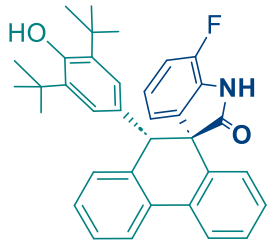




^{1}H ,^{13}C and ^{19}F Spectra of 3o (500MHz, $CDCl_3$) :



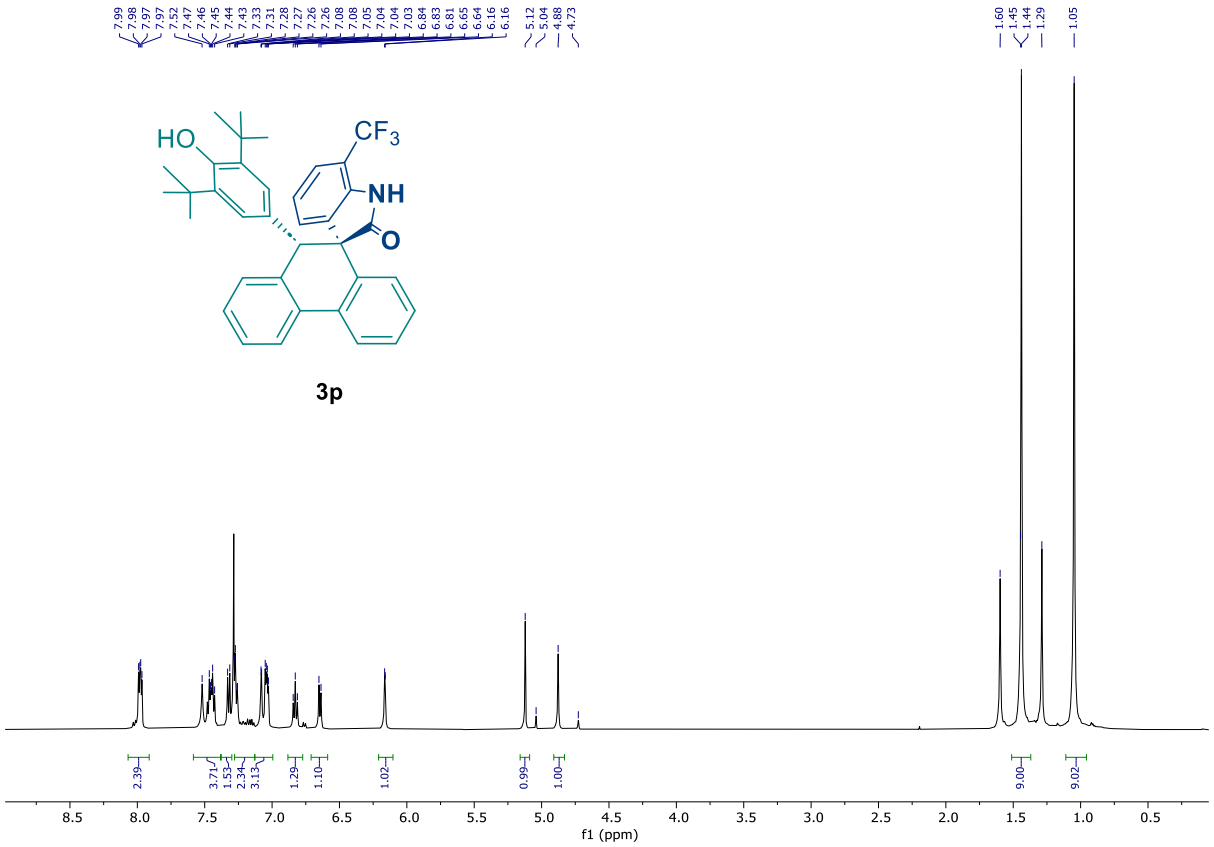


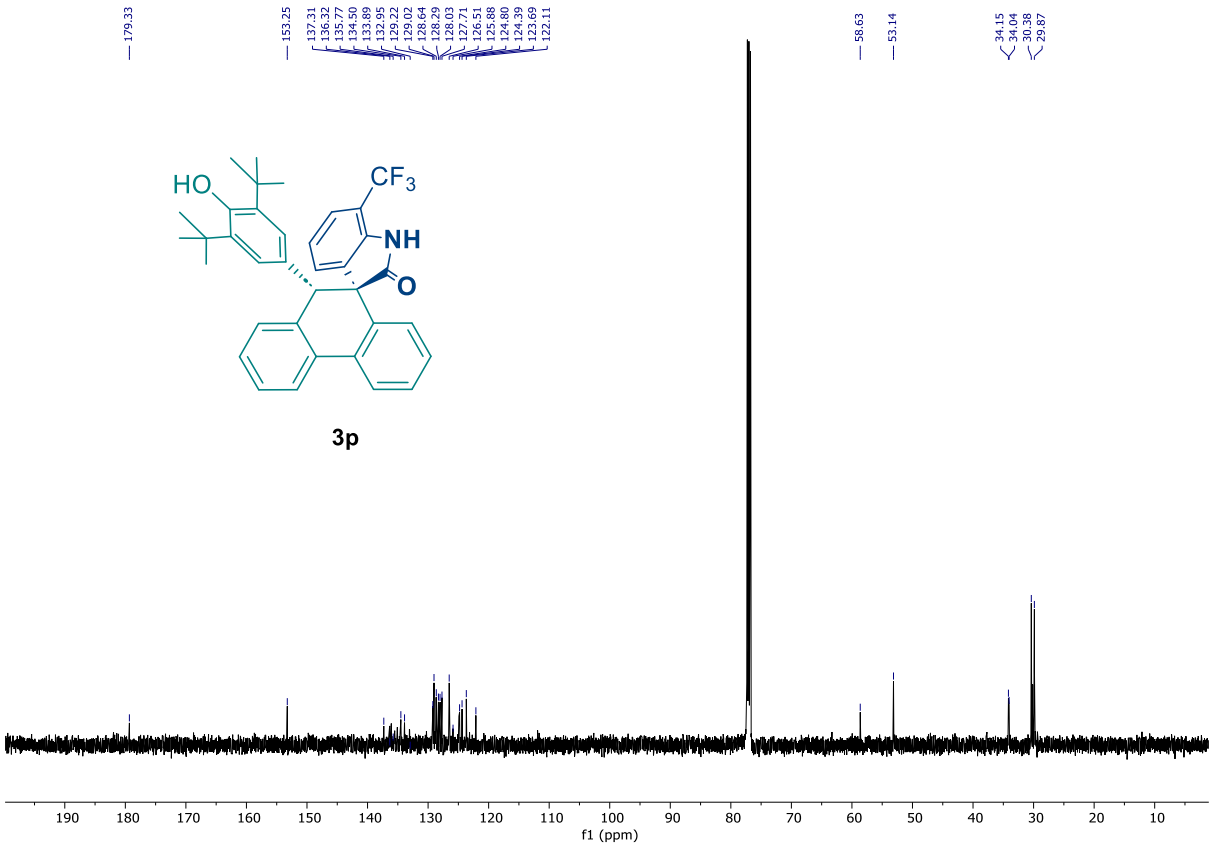

HO
F
NH
O

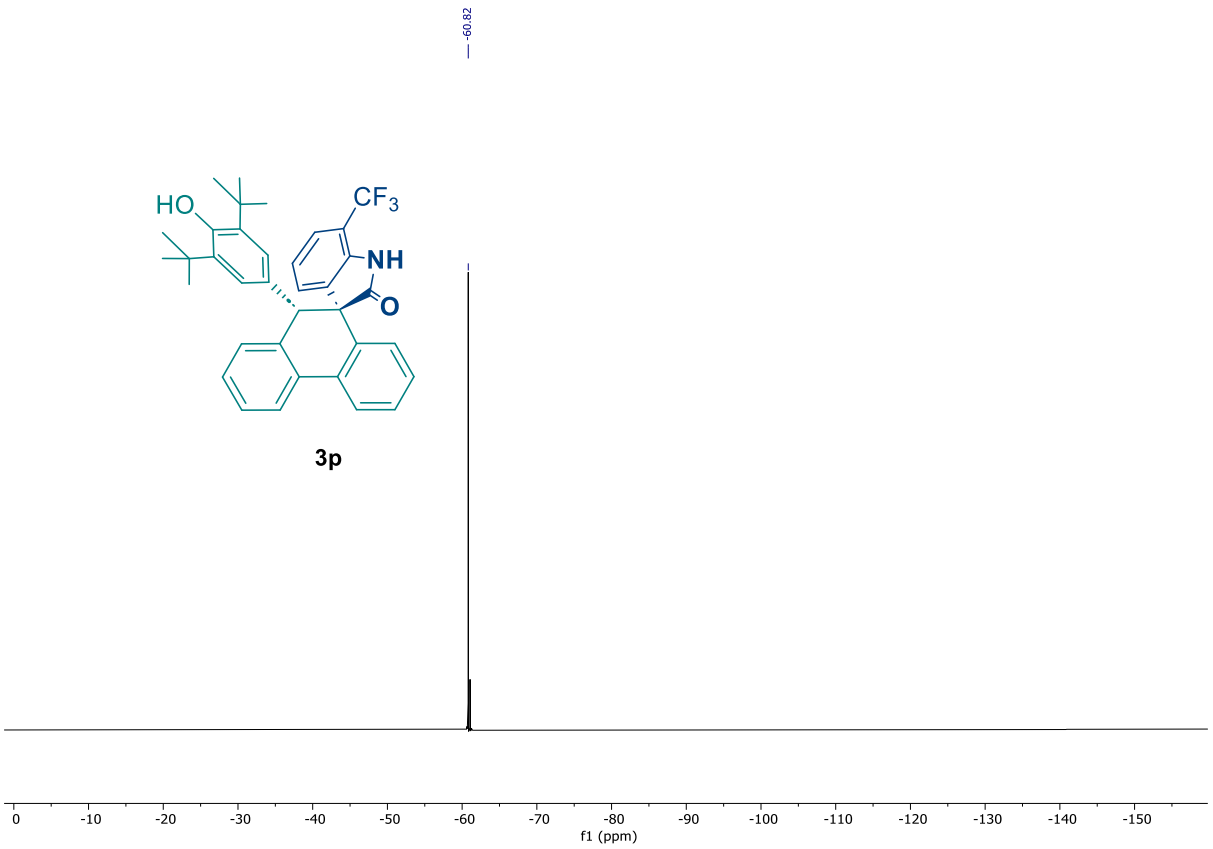
3o

-133.52
-55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185
f1 (ppm)

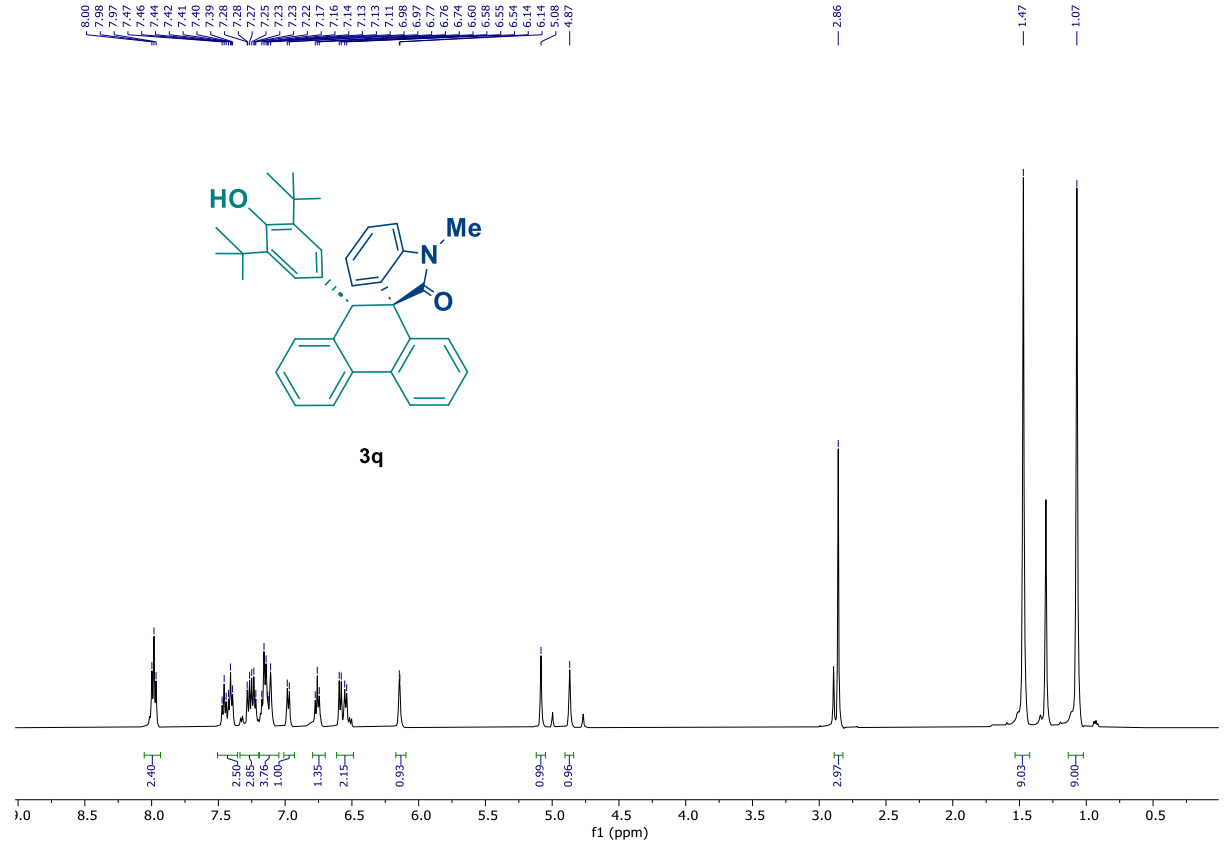
^{1}H, ^{13}C and ^{19}F Spectra of 3p (500MHz, $CDCl_3$) :

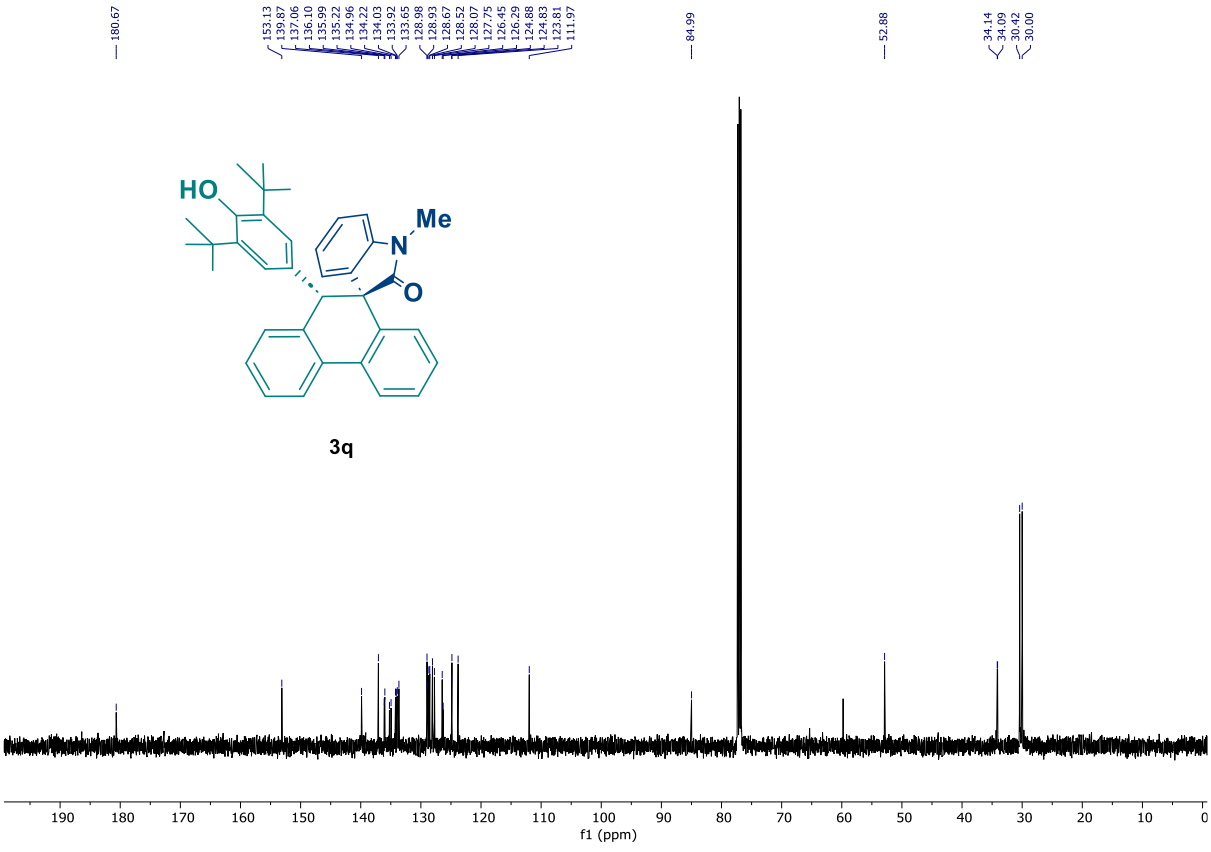




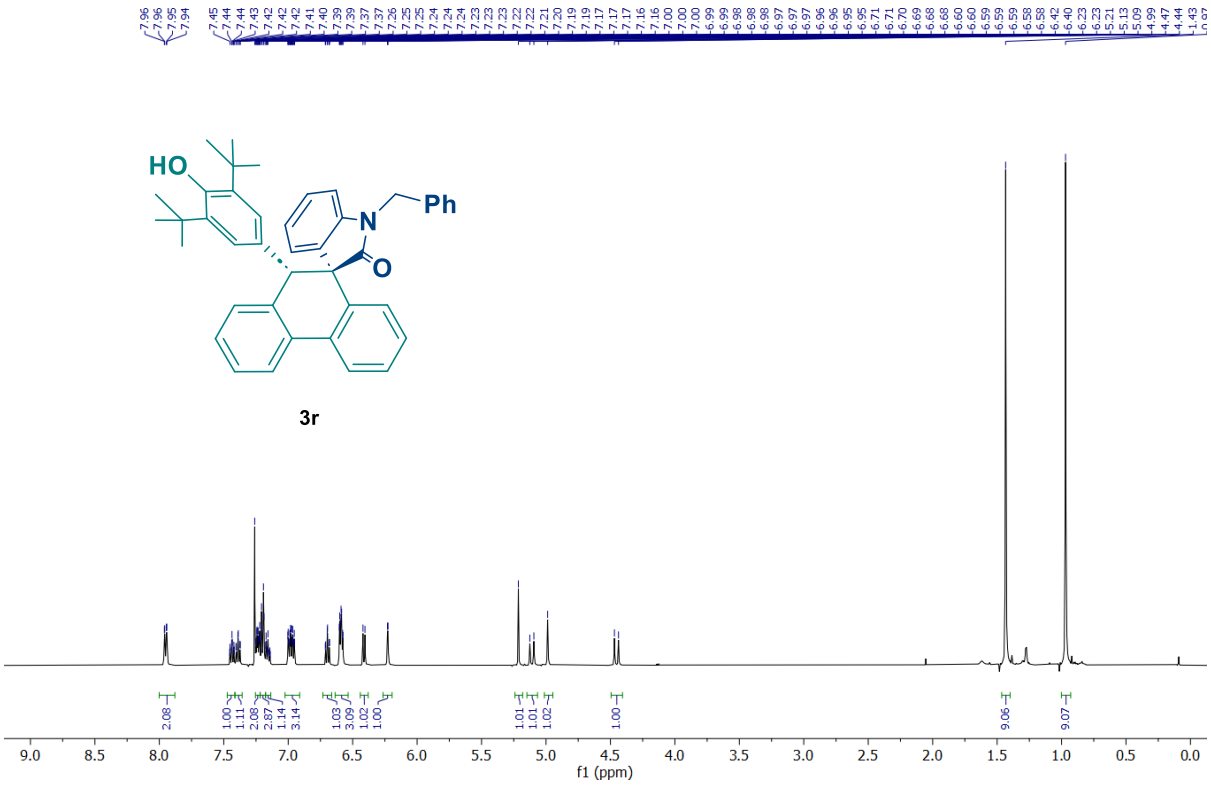

-60.82
HO
CF3
NH
O
3p
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

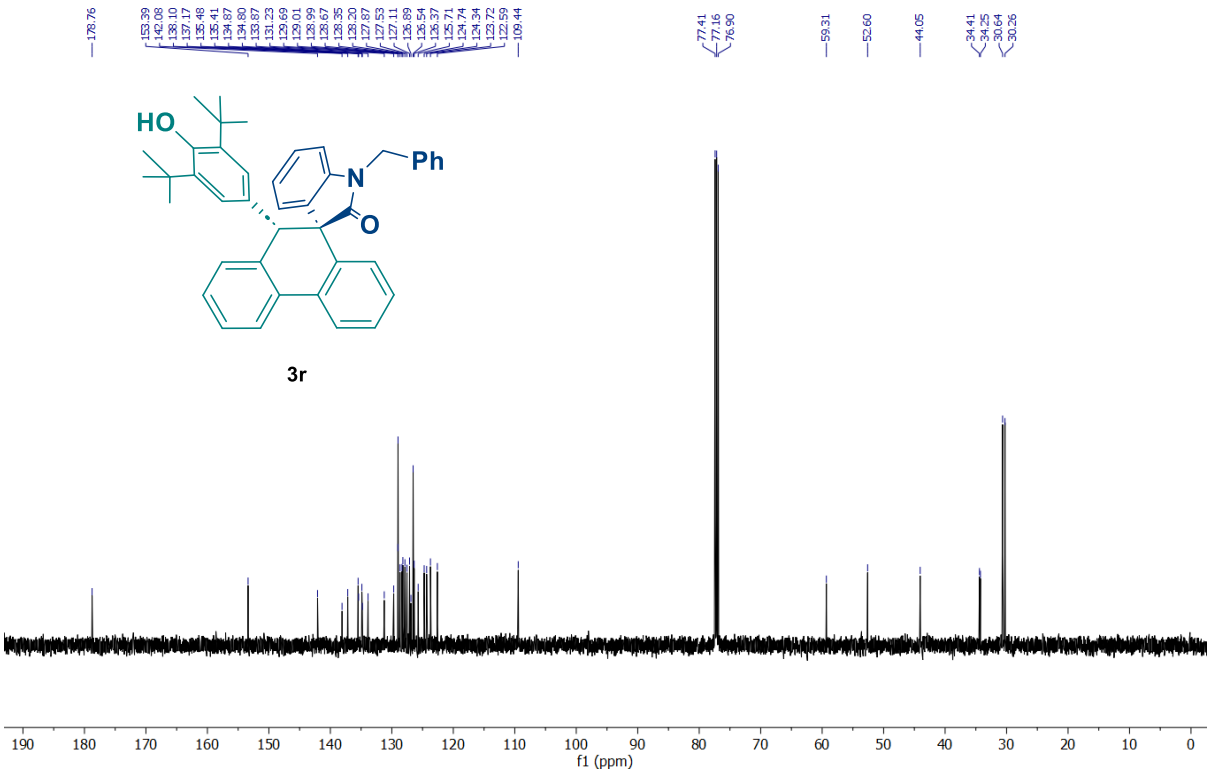
^{1}H and ^{13}C Spectra of 3q (500MHz, $CDCl_3$) :



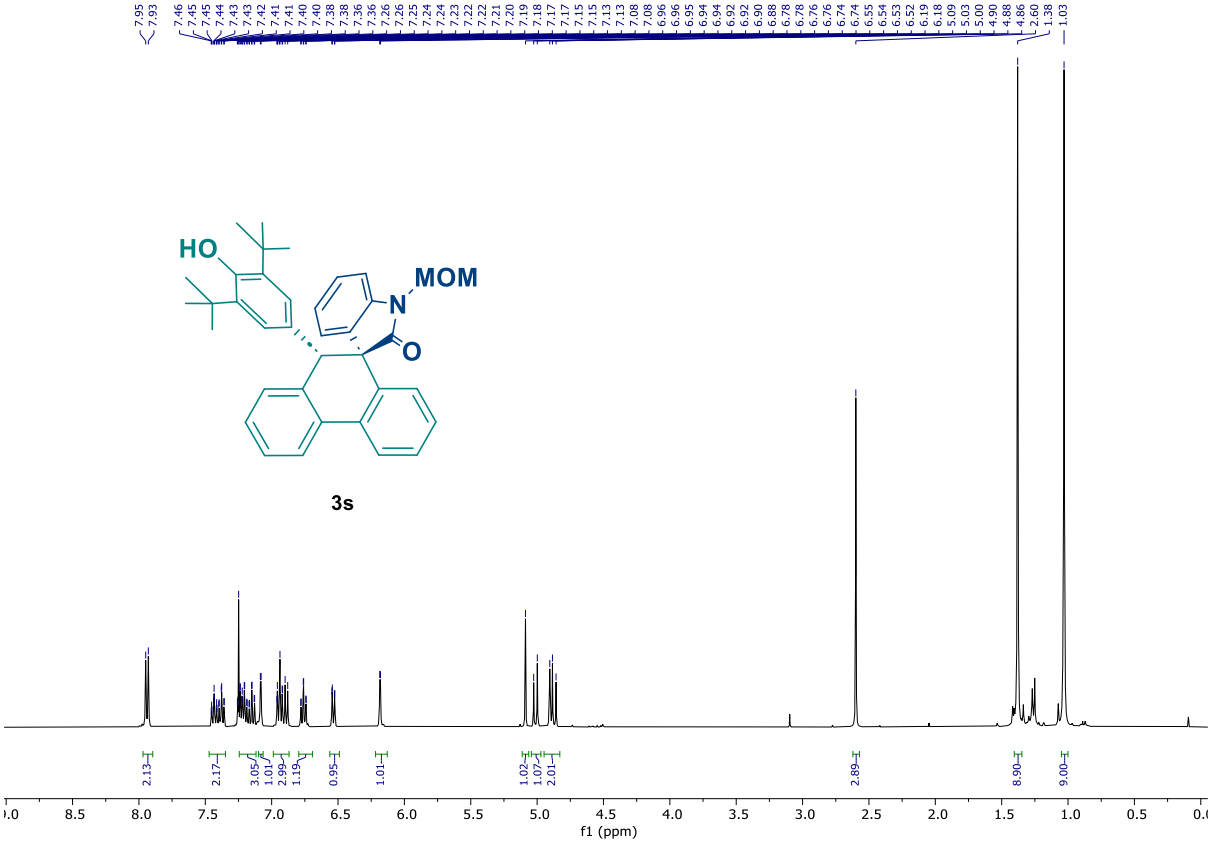


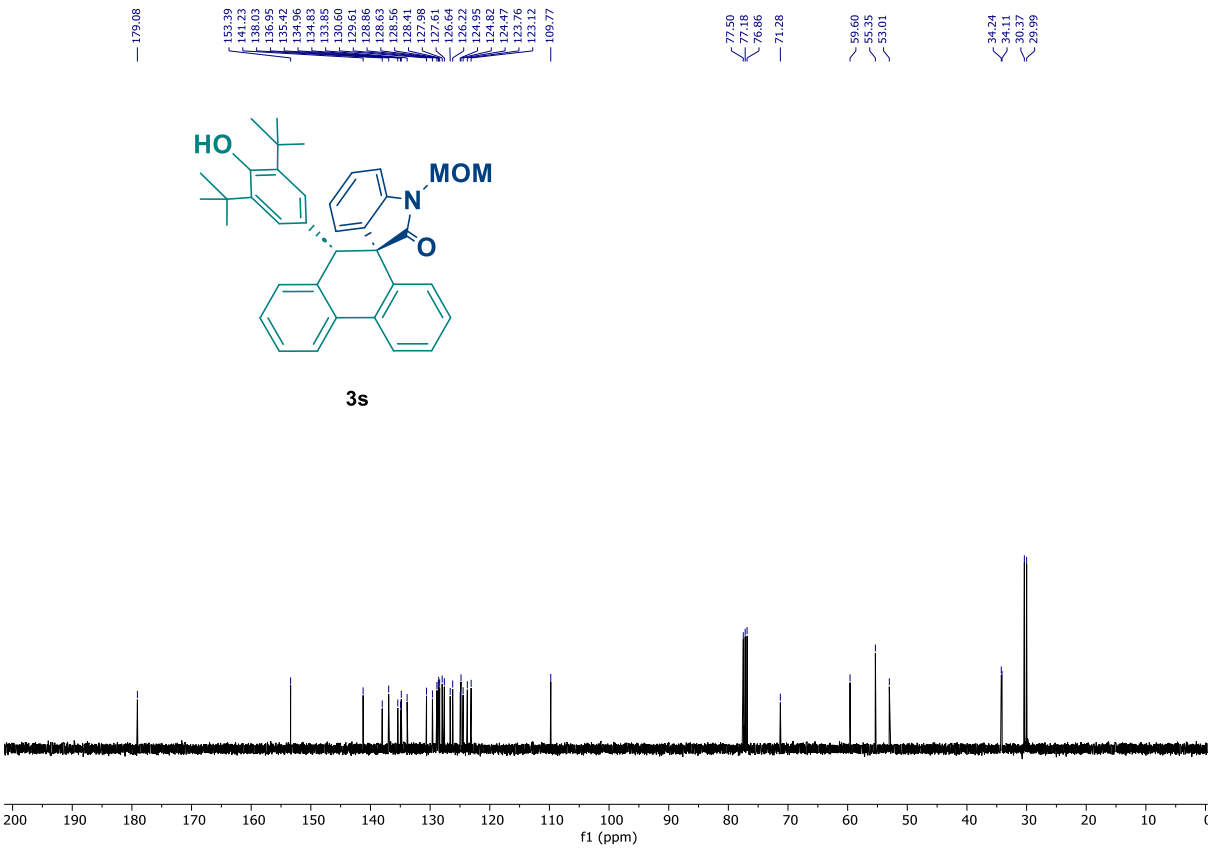
^{1}H and ^{13}C Spectra of 3r (500MHz, $CDCl_3$) :



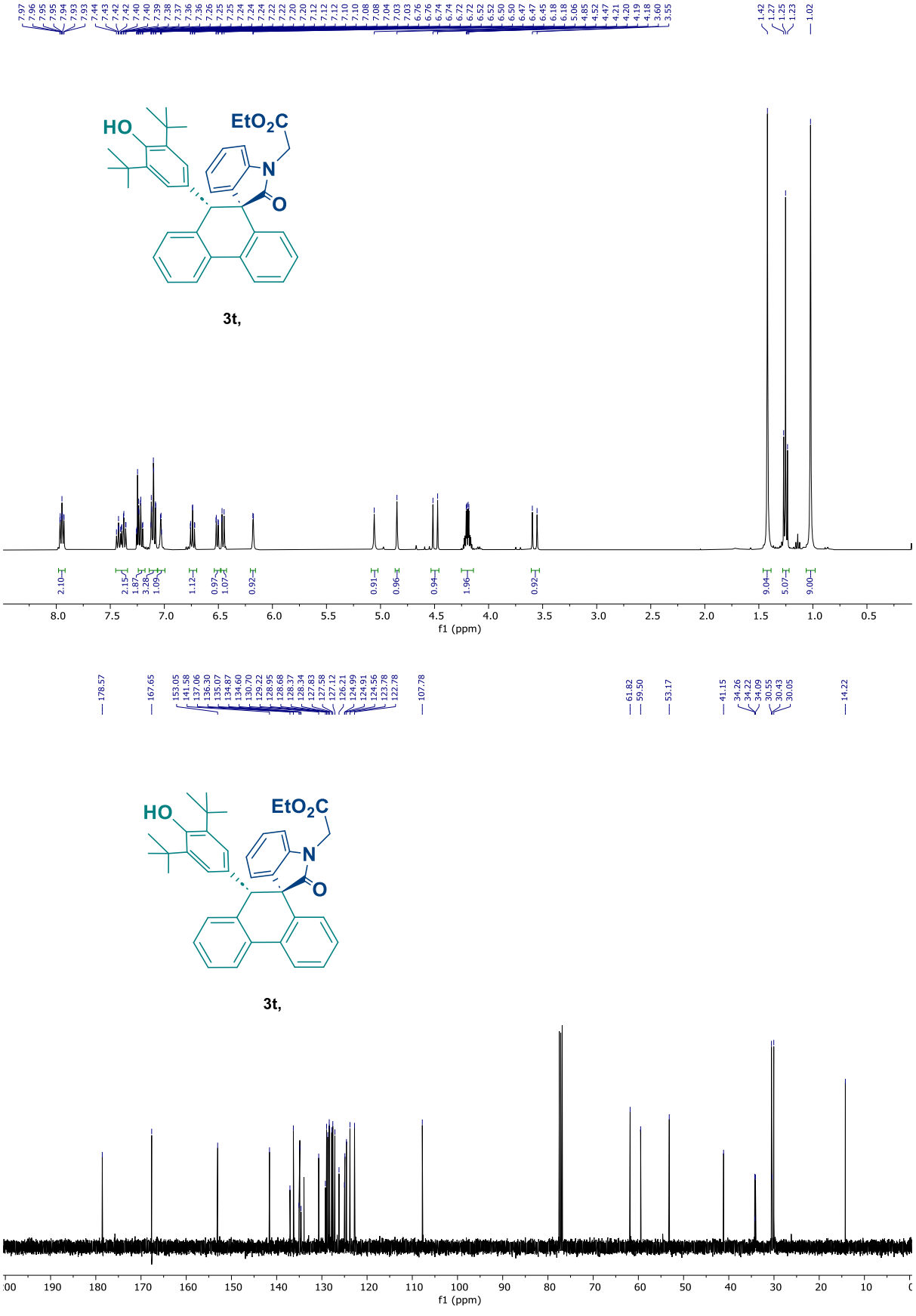


^{1}H and ^{13}C Spectra of 3s (400MHz, $CDCl_3$) :

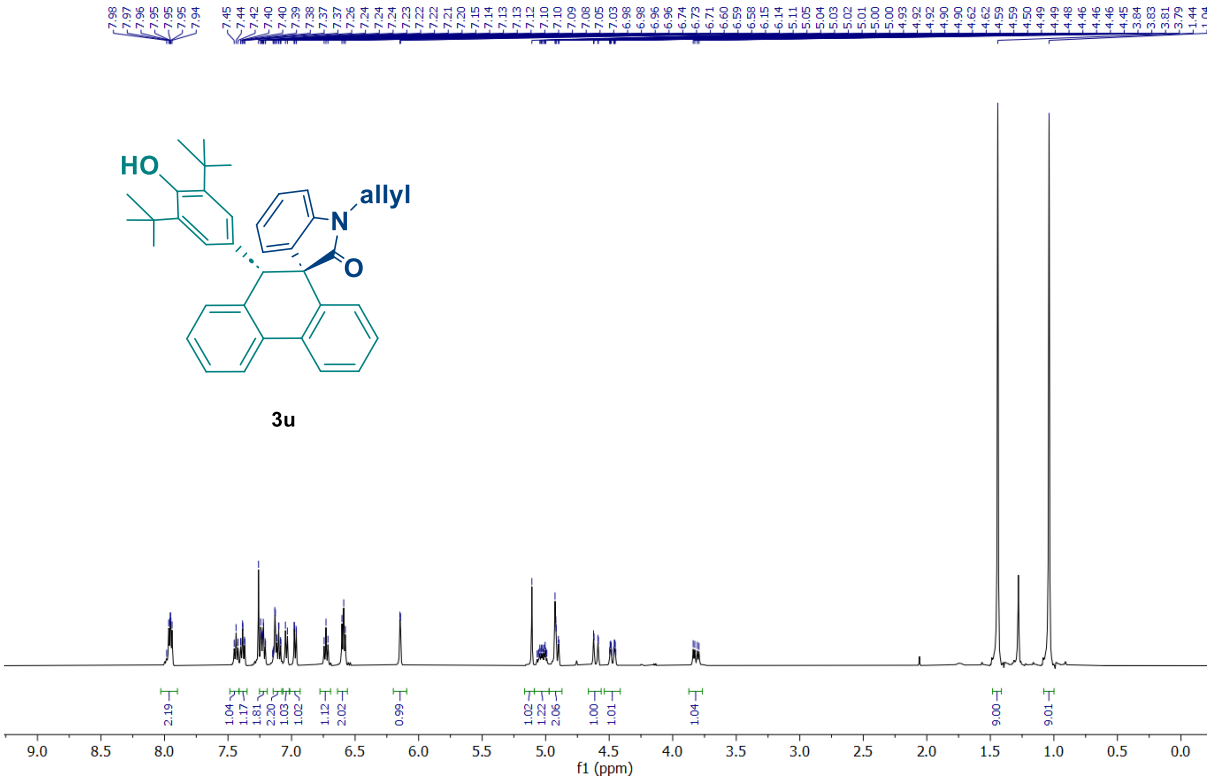


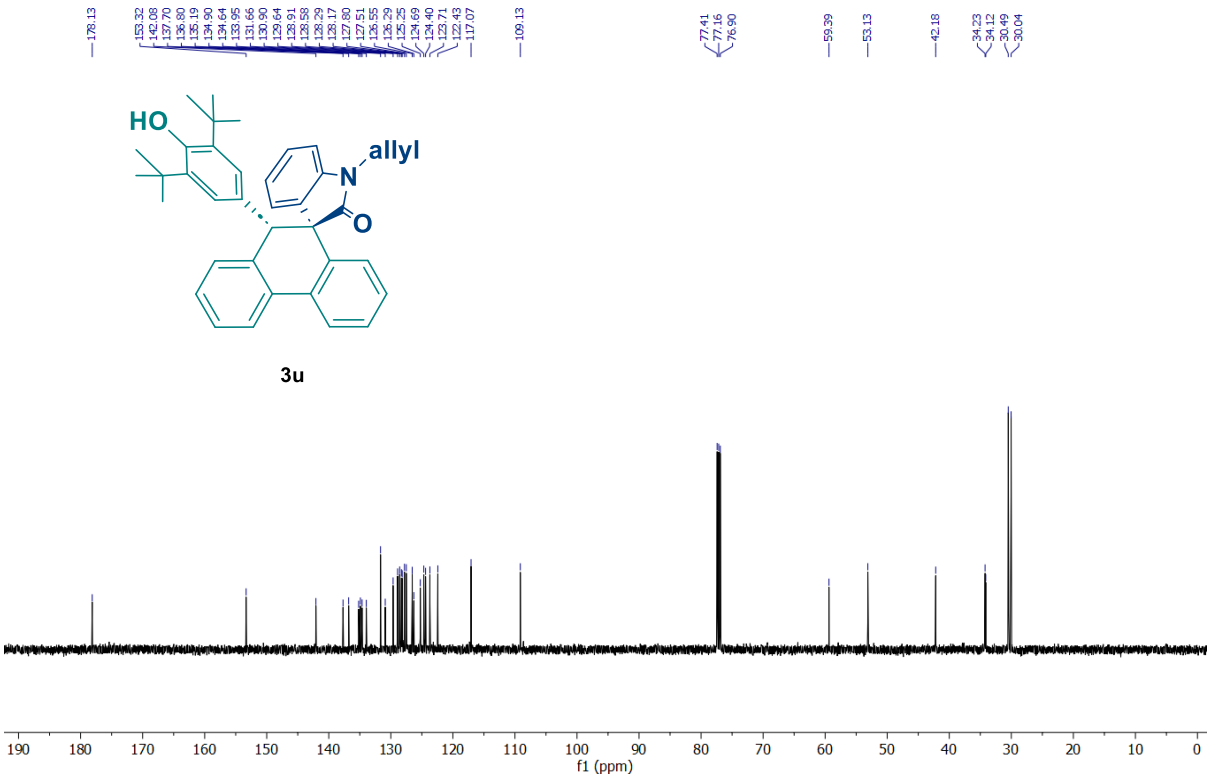


^{1}H and ^{13}C Spectra of 3t (400MHz, $CDCl_3$) :

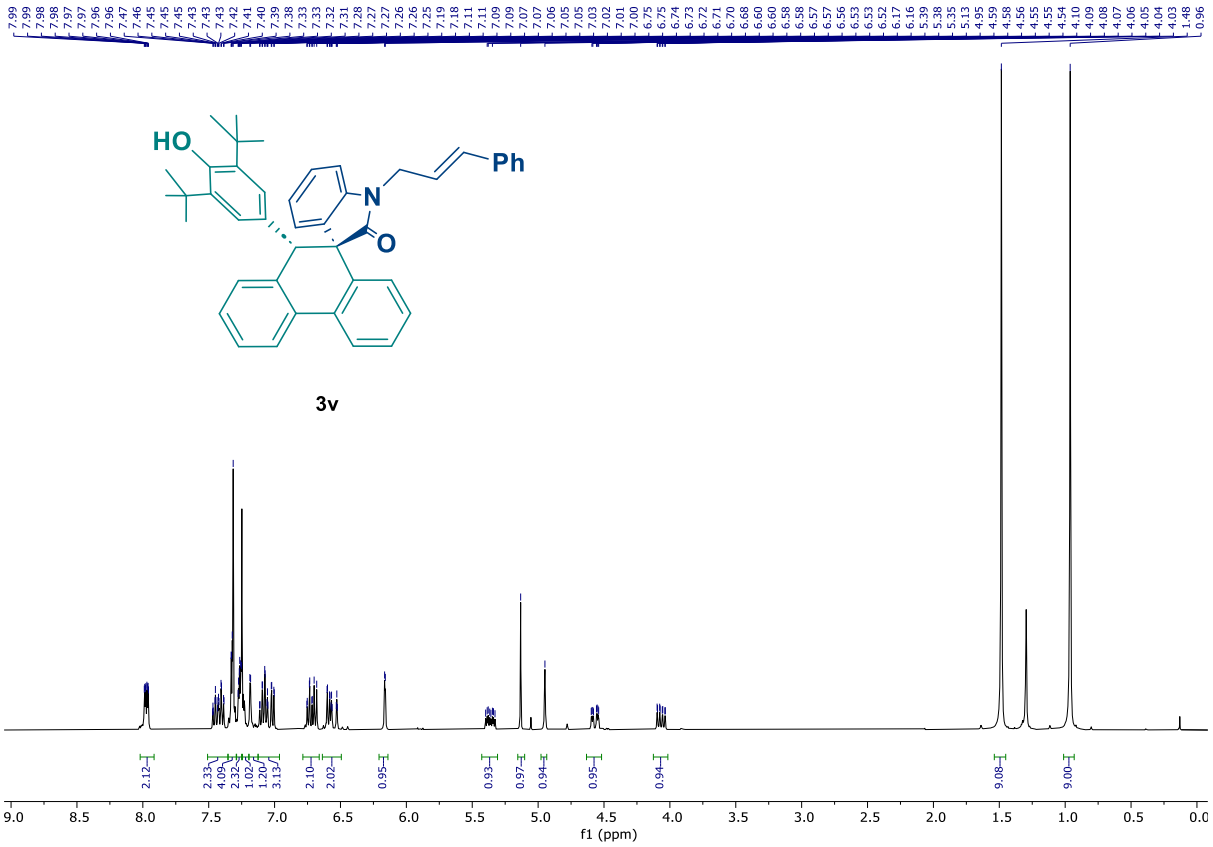


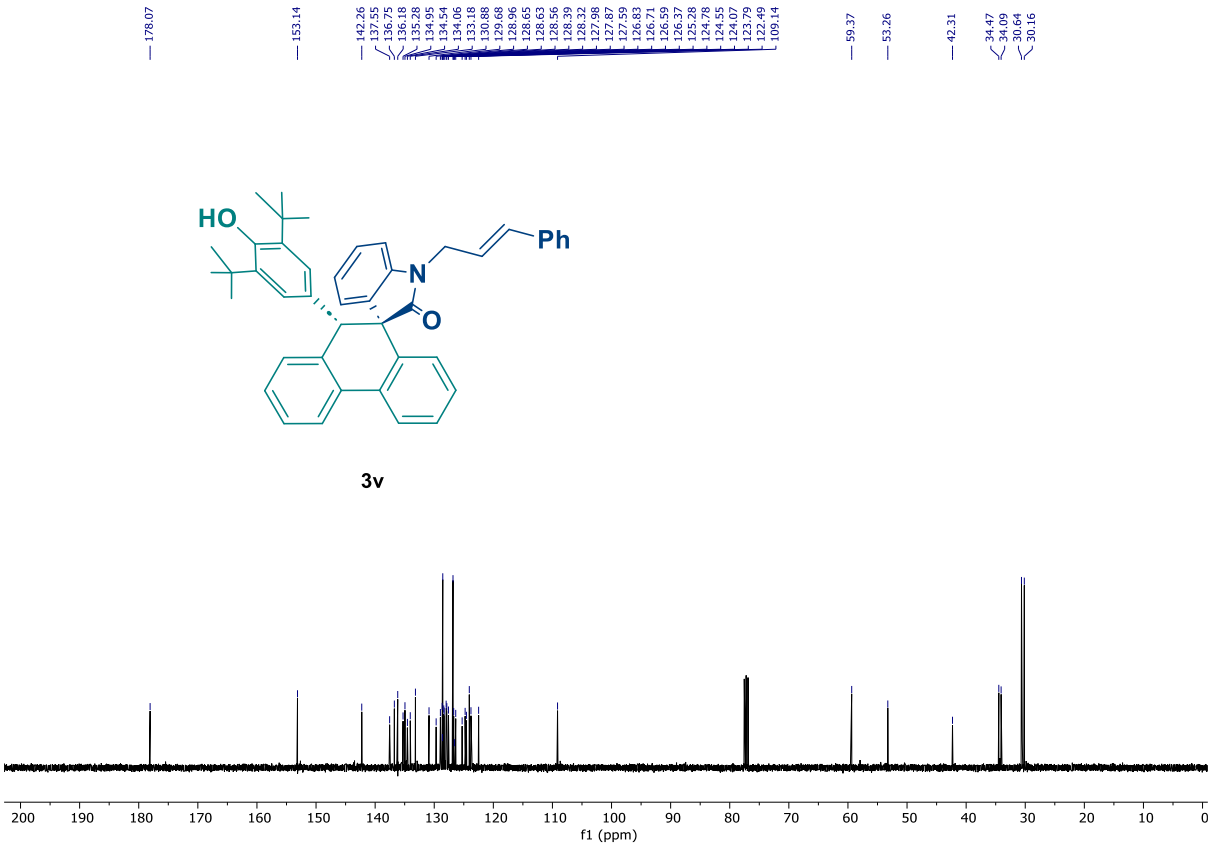
^{1}H and ^{13}C Spectra of 3u (500MHz, $CDCl_3$) :



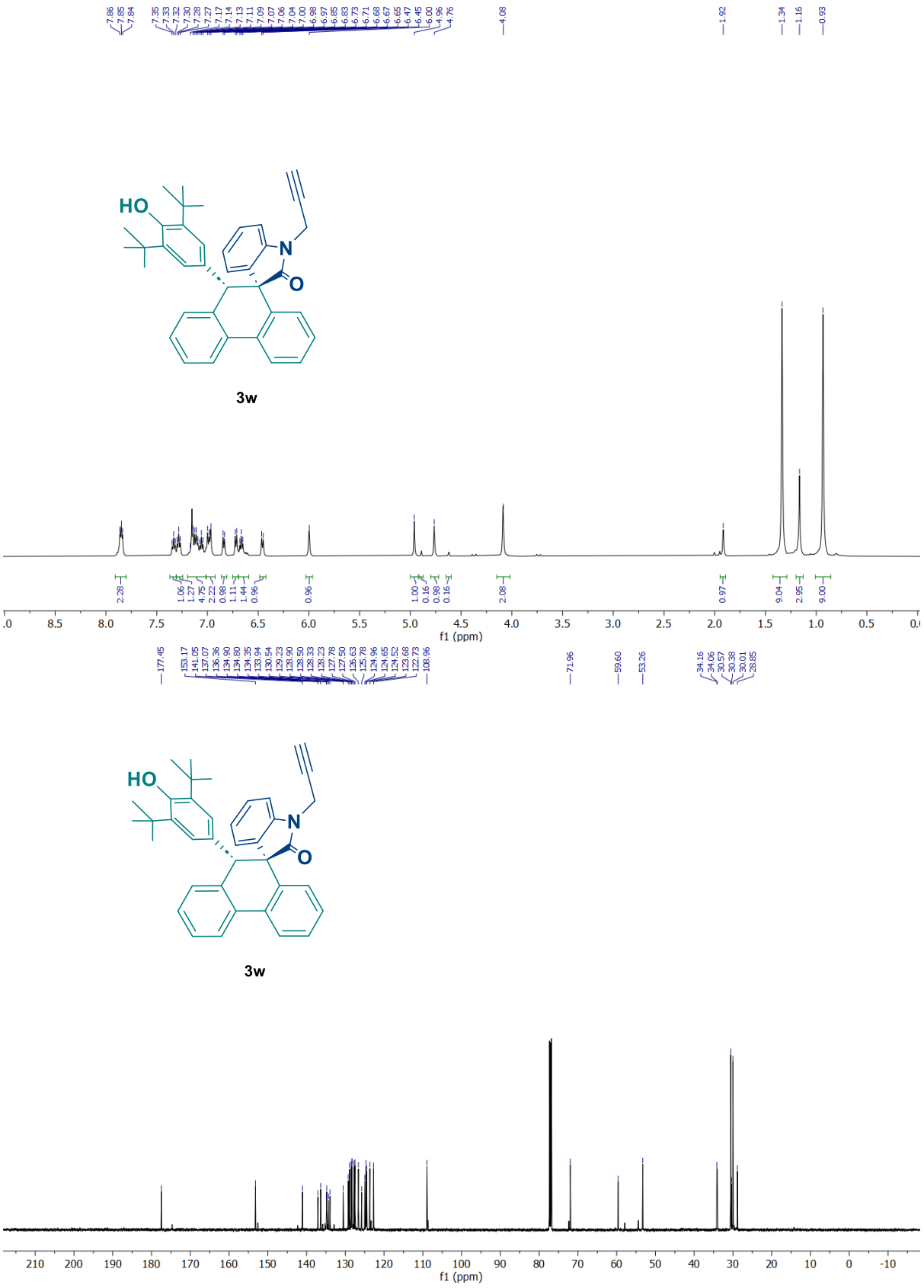


^{1}H and ^{13}C Spectra of 3v (400MHz, $CDCl_3$) :

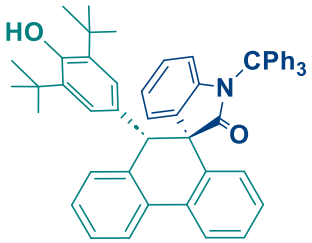




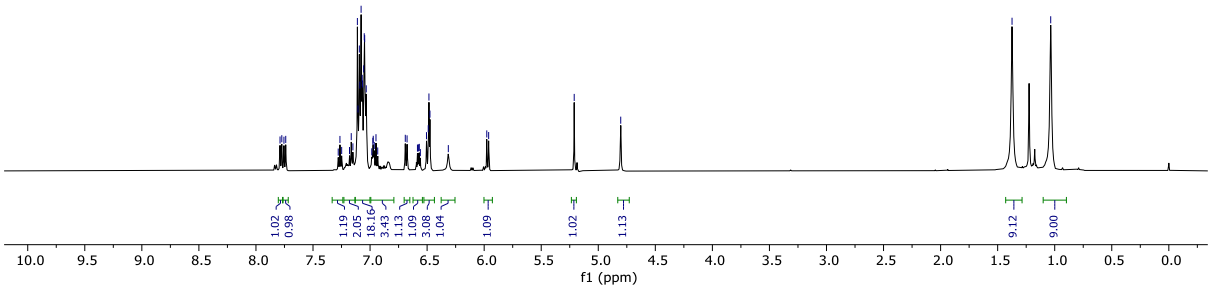
^{1}H and ^{13}C Spectra of 3w (500MHz, $CDCl_3$) :

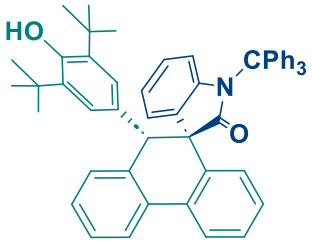


^{1}H and ^{13}C Spectra of 3x (500MHz, $CDCl_3$) :

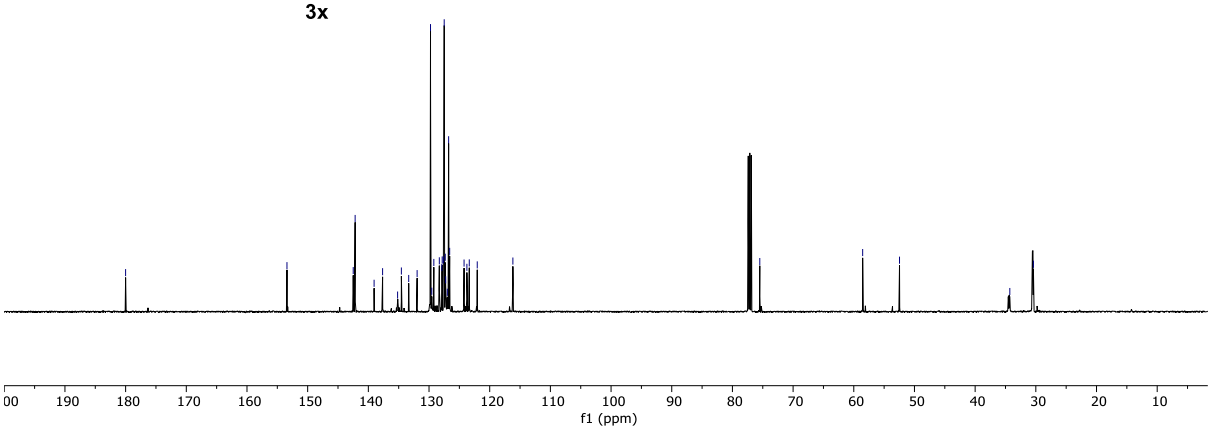


3x

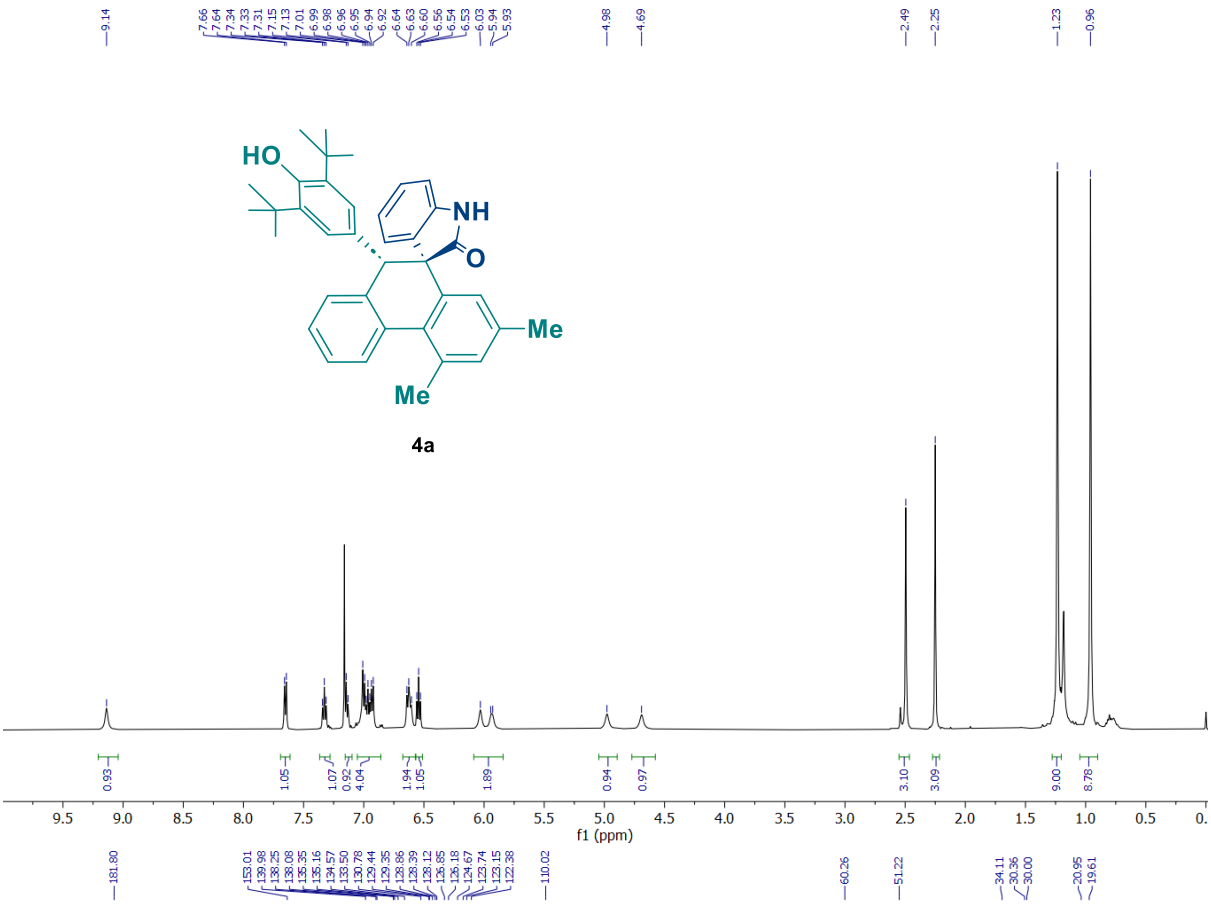


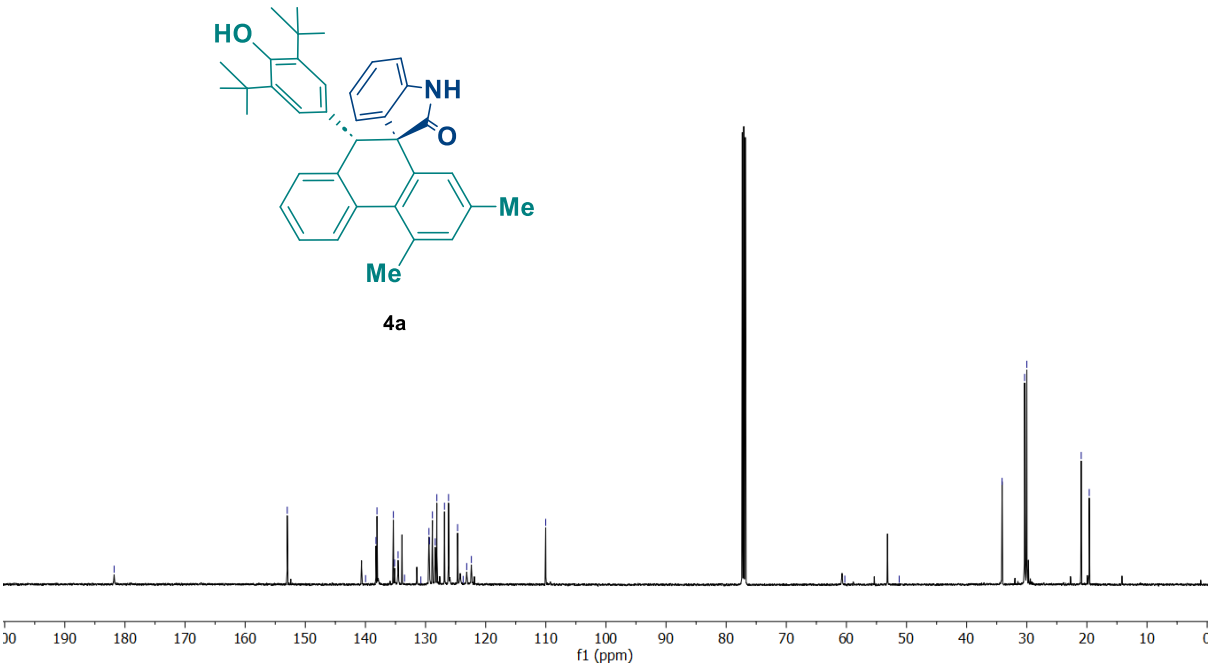


3x

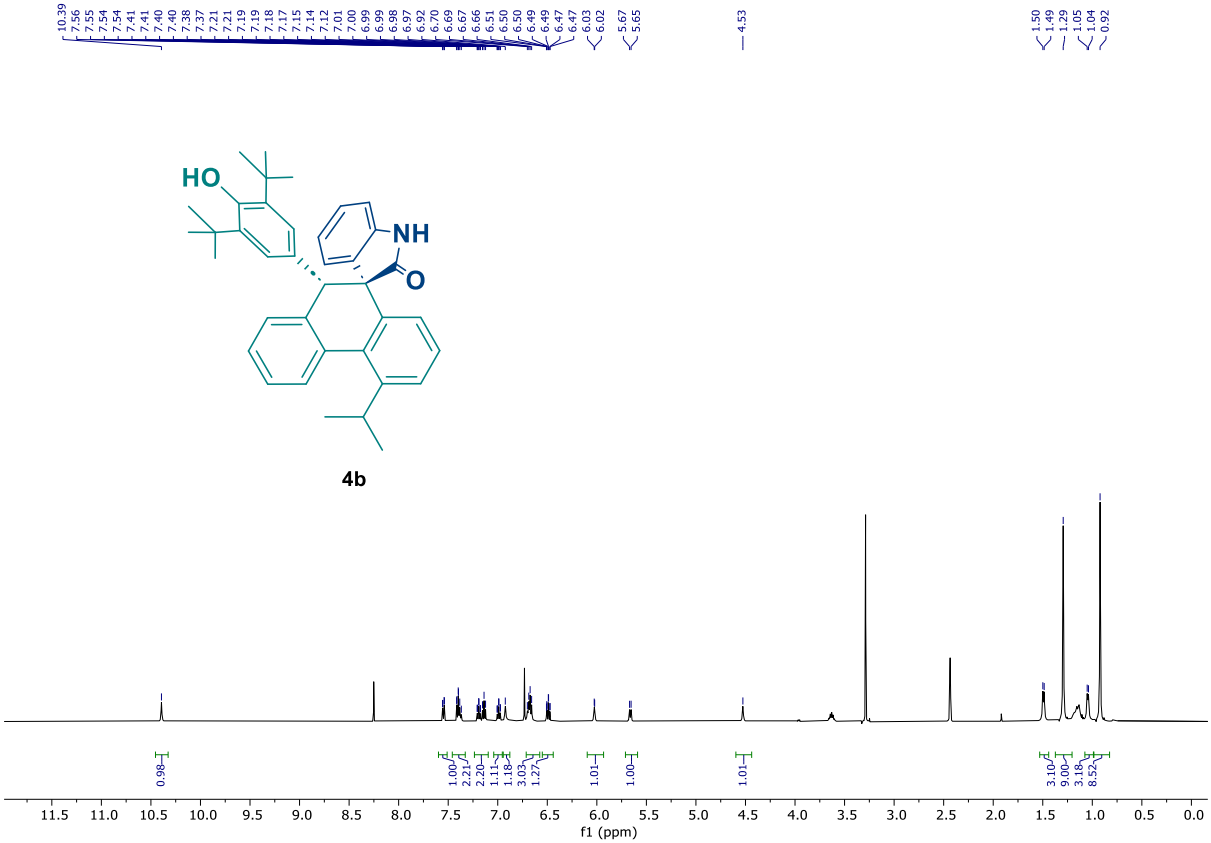


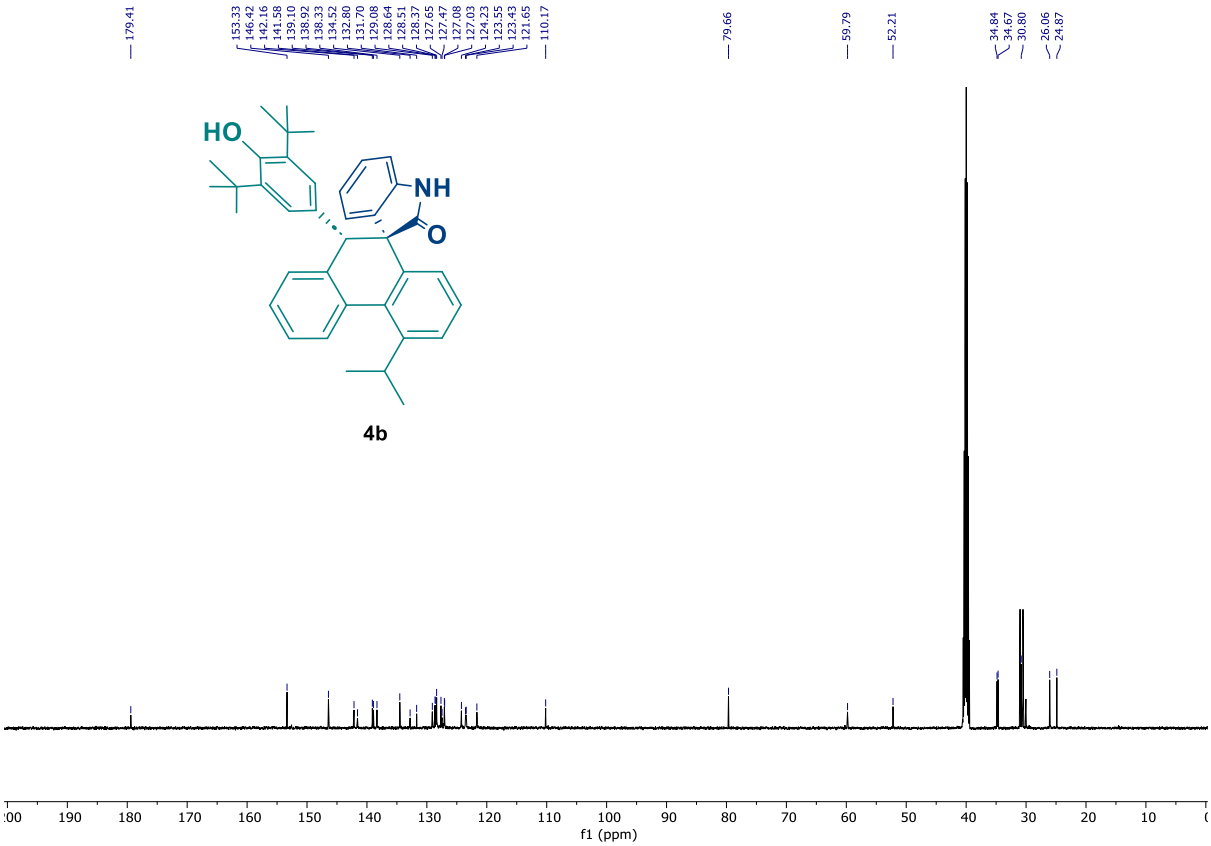
^{1}H and ^{13}C Spectra of 4a (400MHz, $CDCl_3$) :



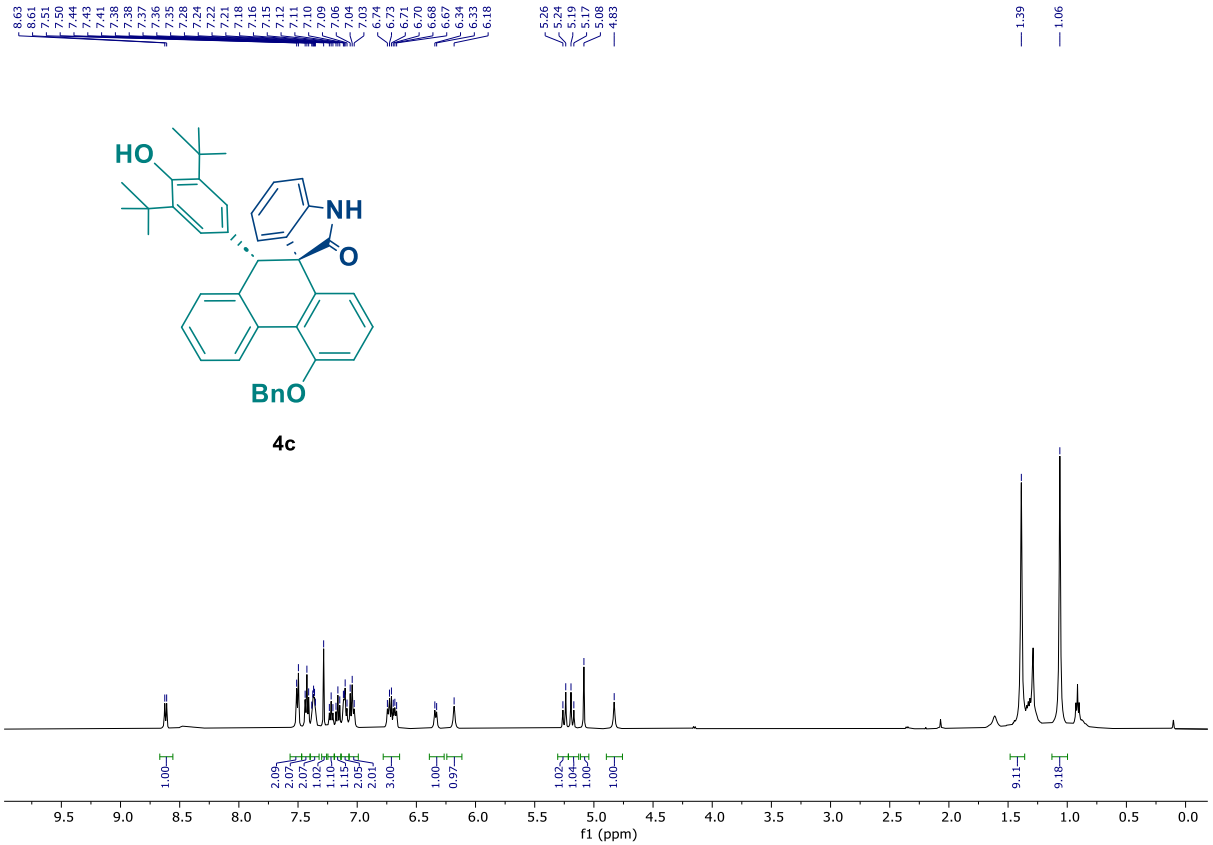


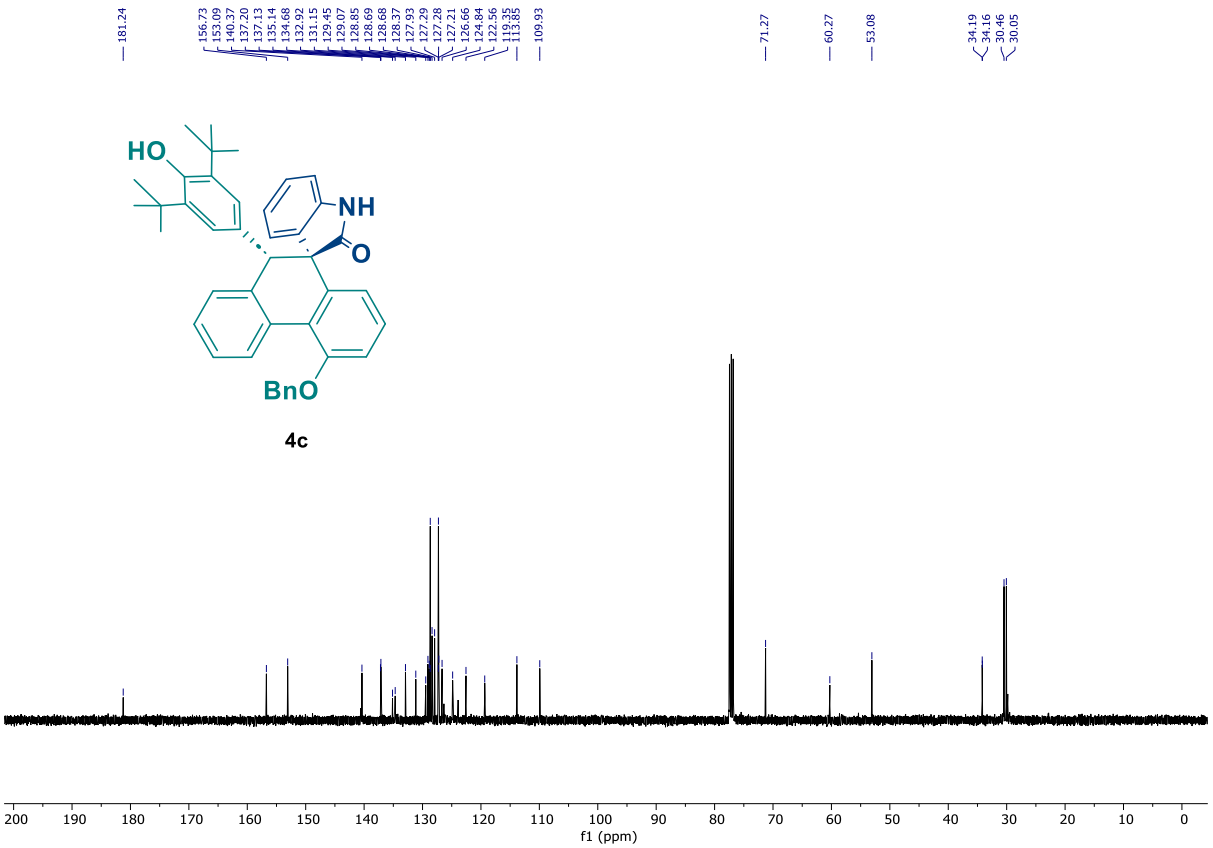
^{1}H and ^{13}C Spectra of 4b (500MHz, DMSO-d_6) :



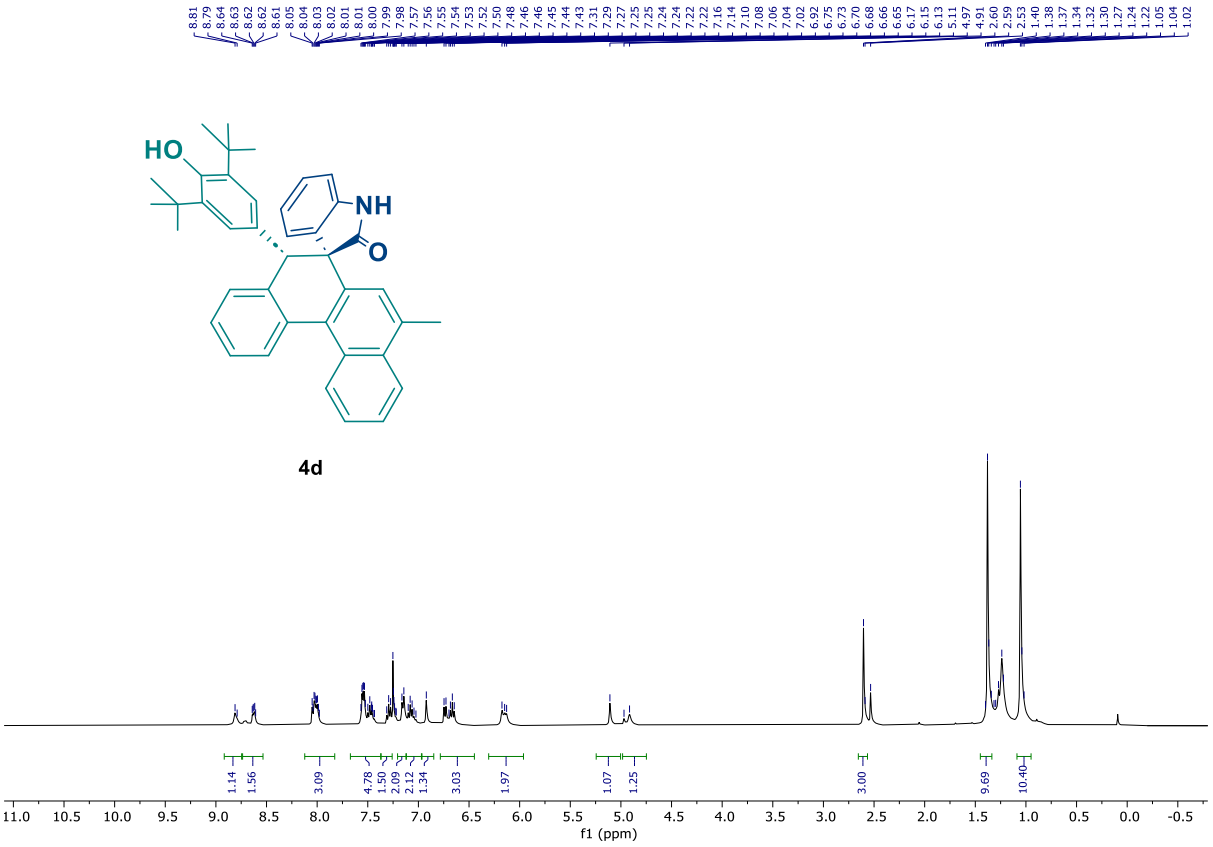


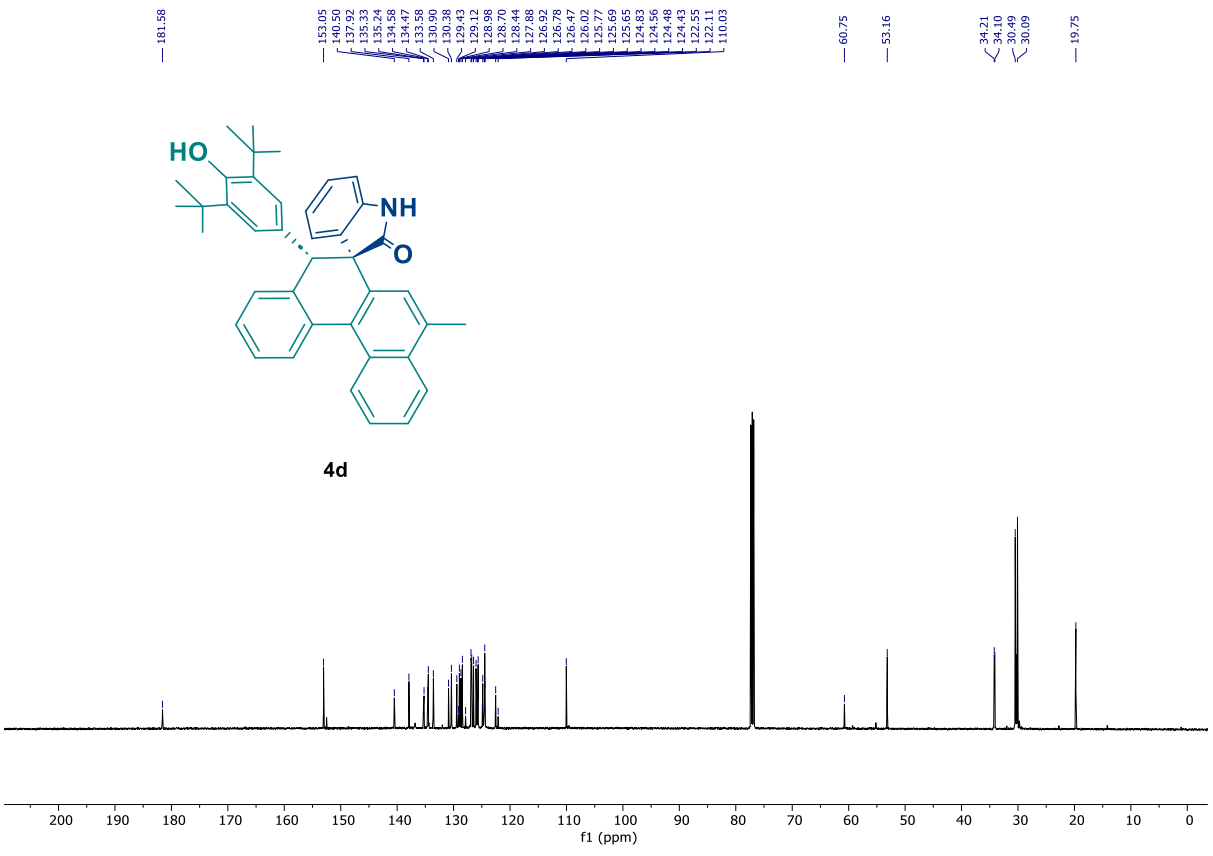
^{1}H and ^{13}C Spectra of 4c (500MHz, $CDCl_3$) :



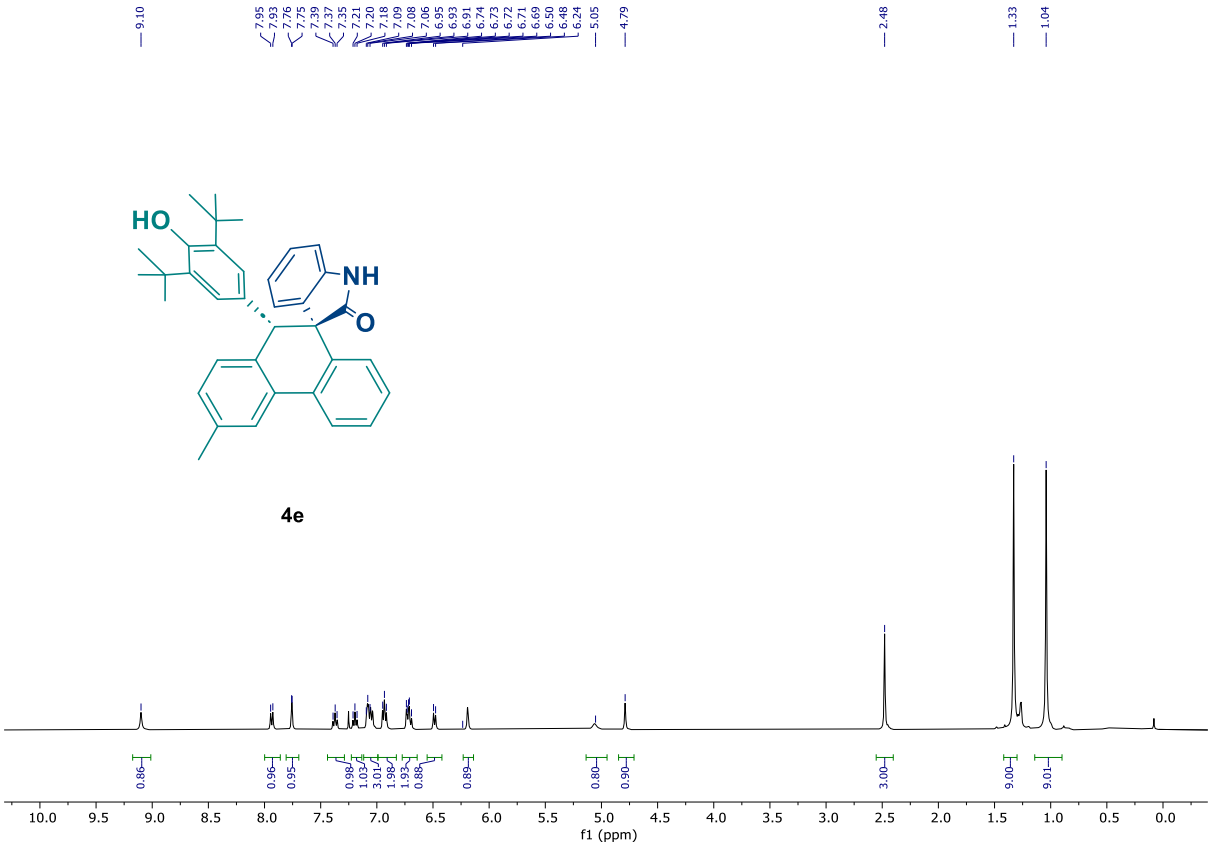


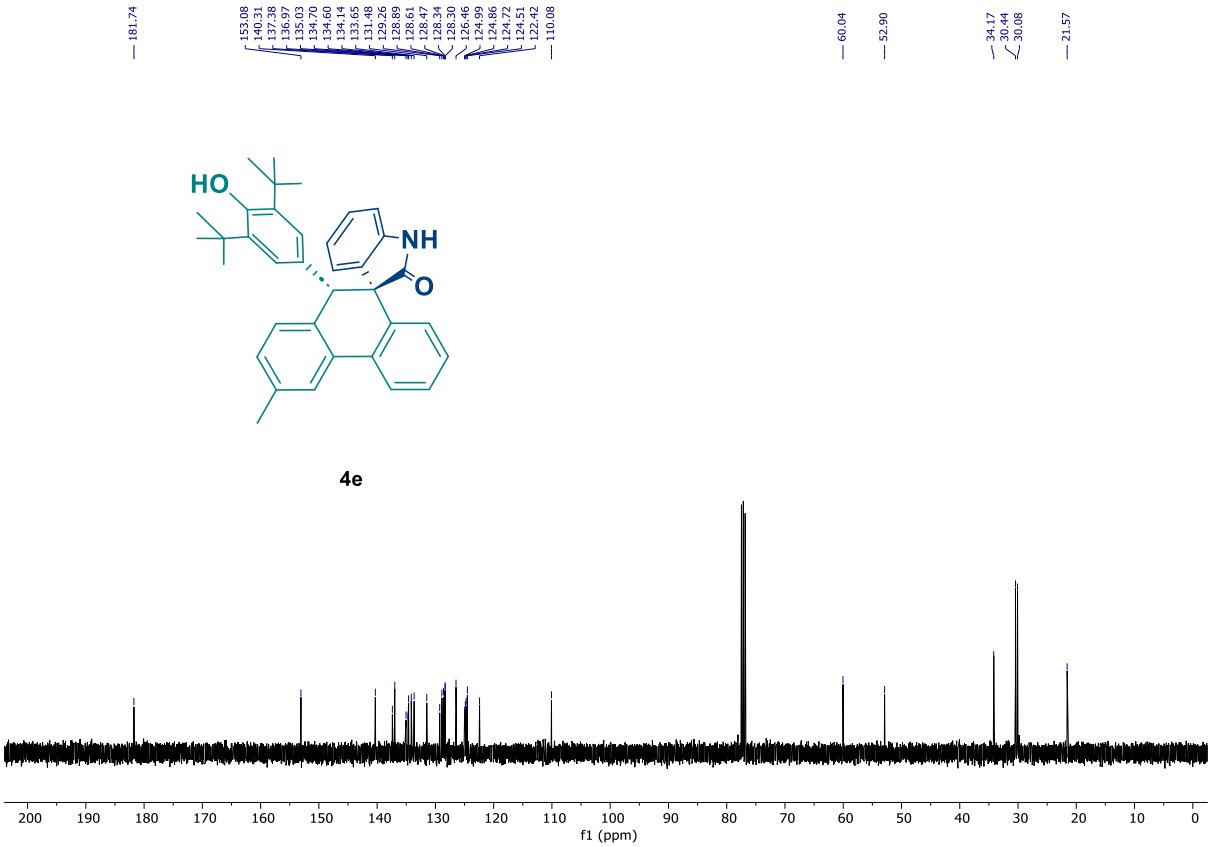
^{1}H and ^{13}C Spectra of 4d (400MHz, $CDCl_3$) :



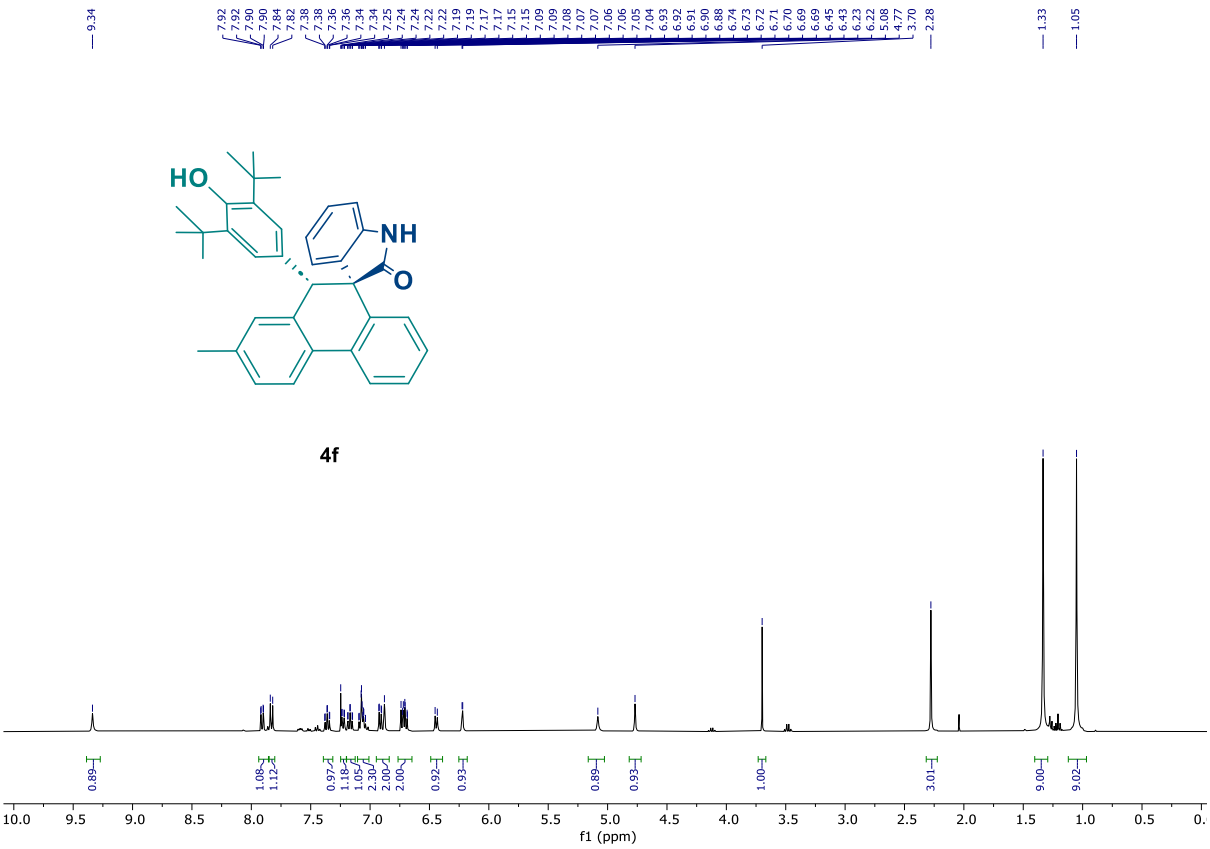


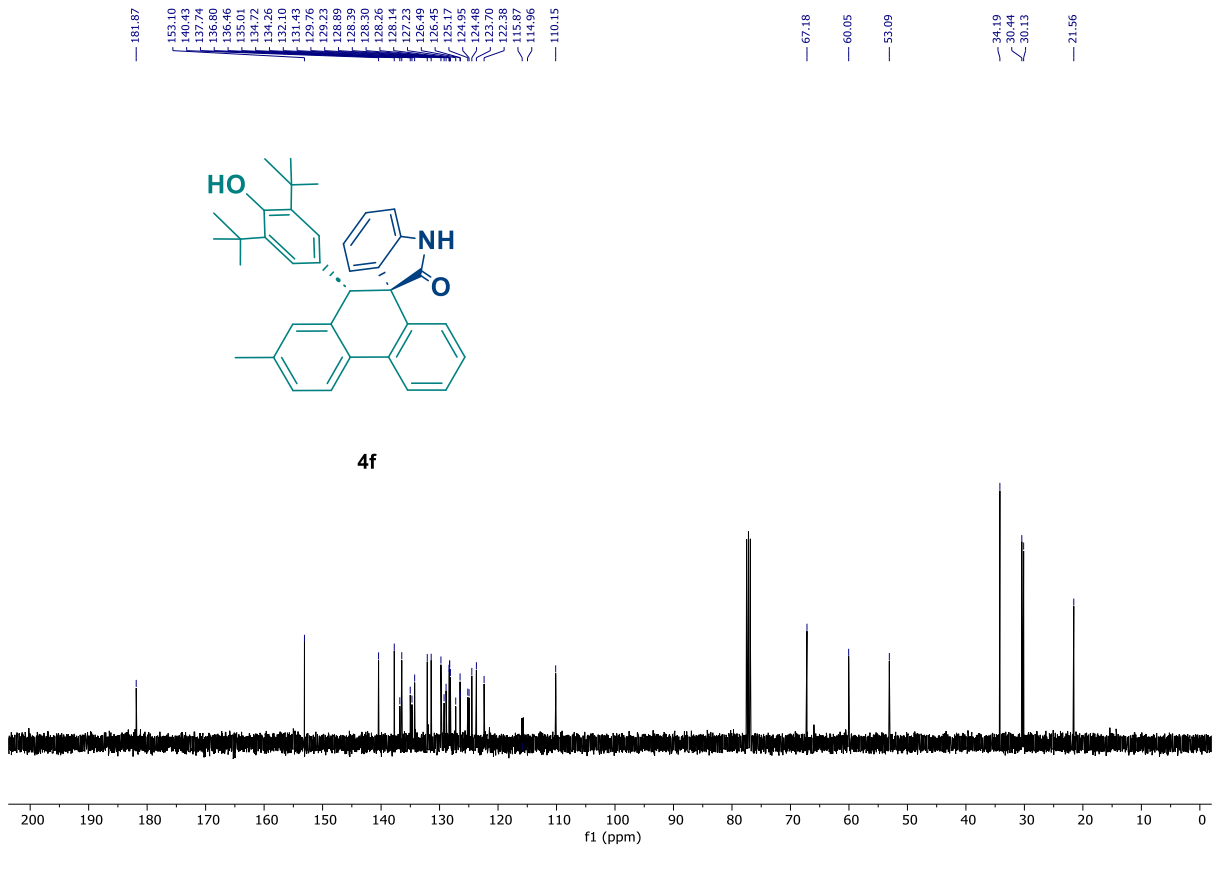
^{1}H and ^{13}C Spectra of 4e (500MHz, $CDCl_3$) :



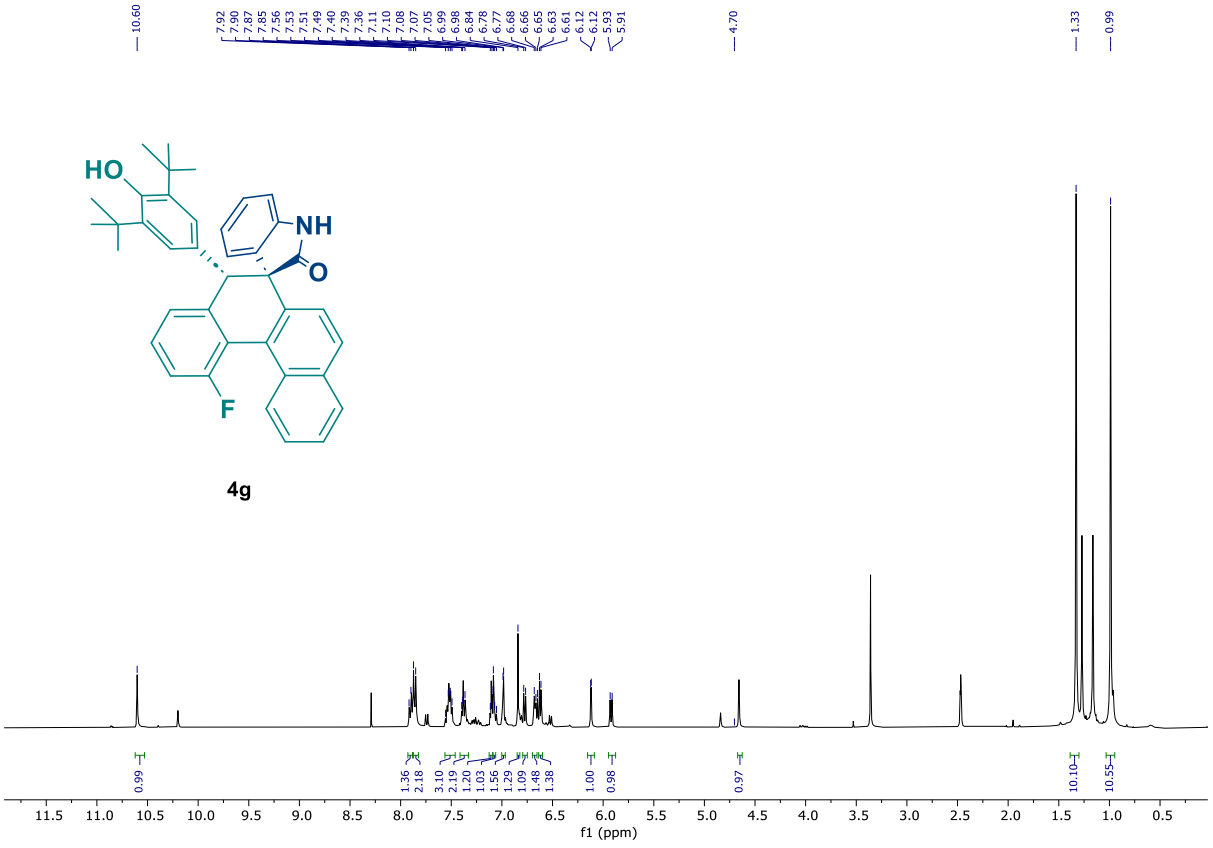


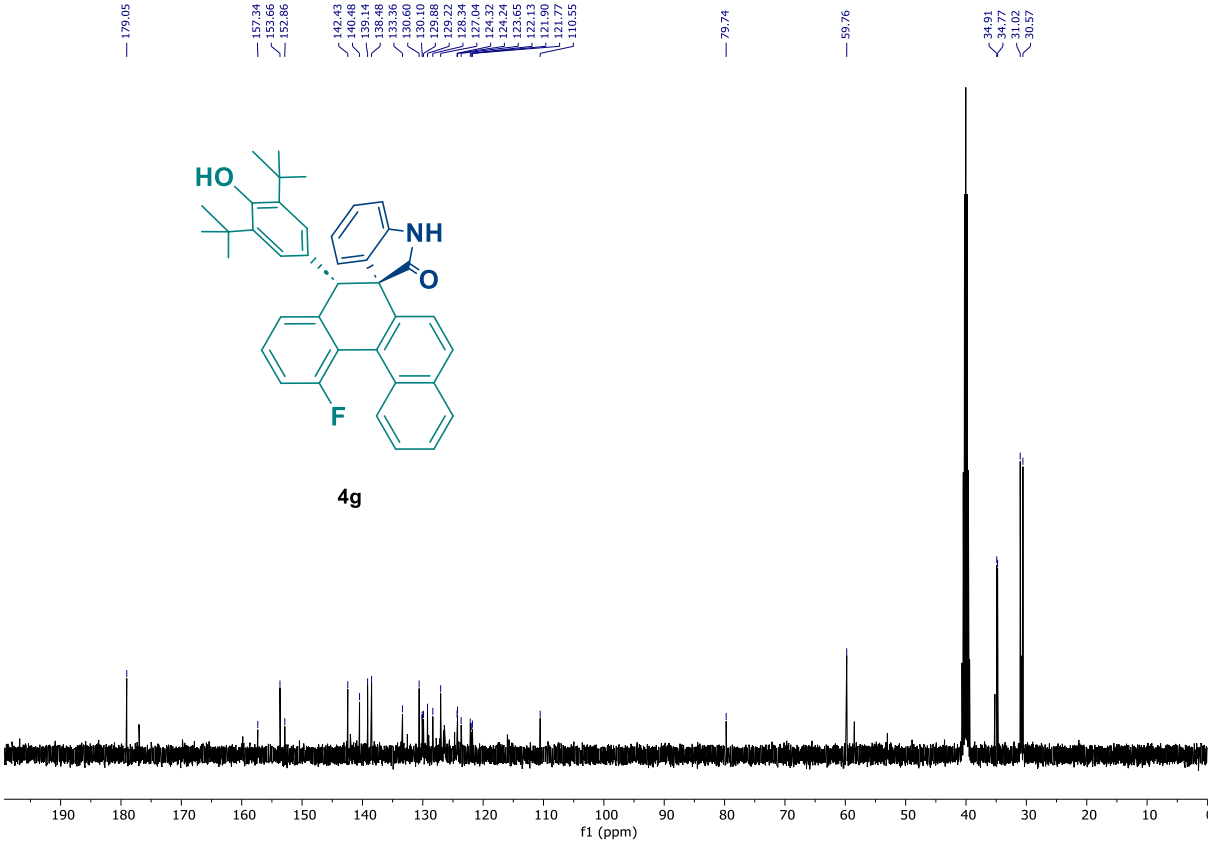
^{1}H and ^{13}C Spectra of 4f (400MHz, $CDCl_3$) :

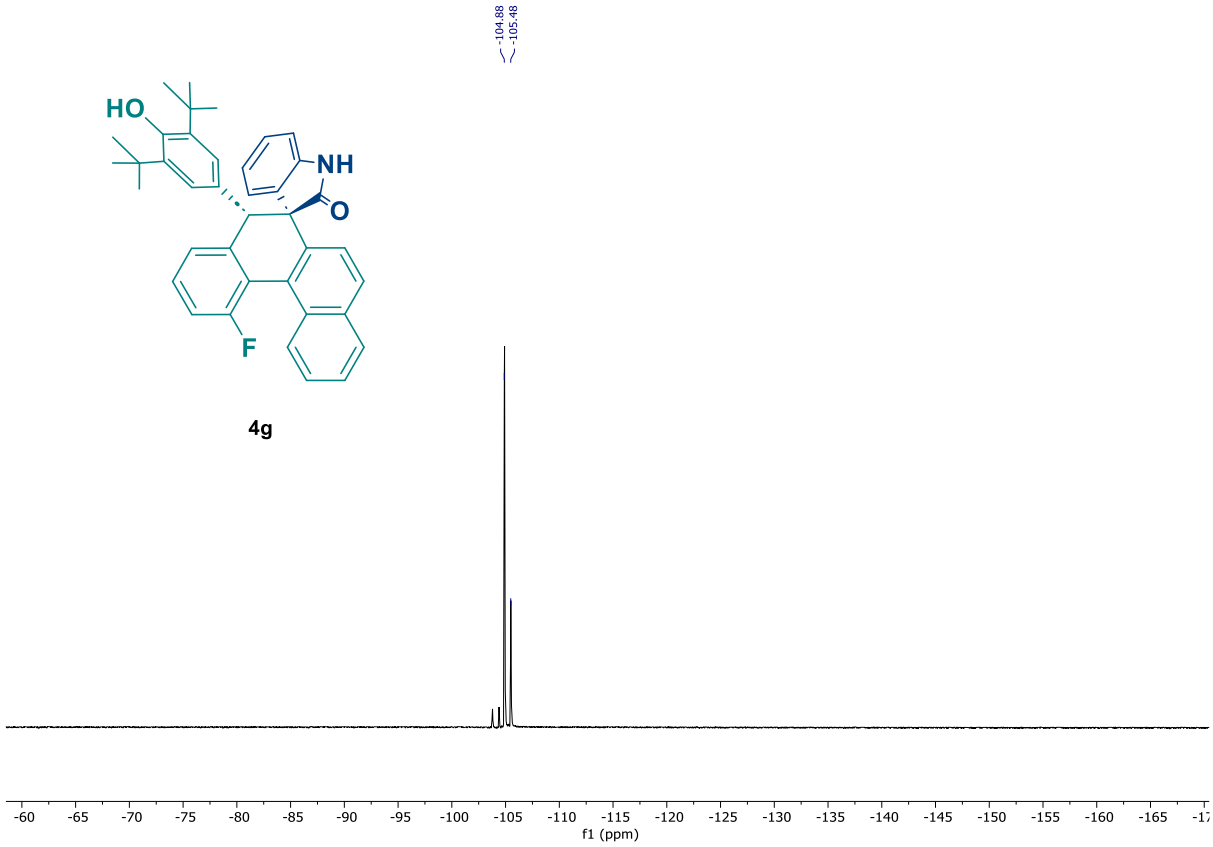




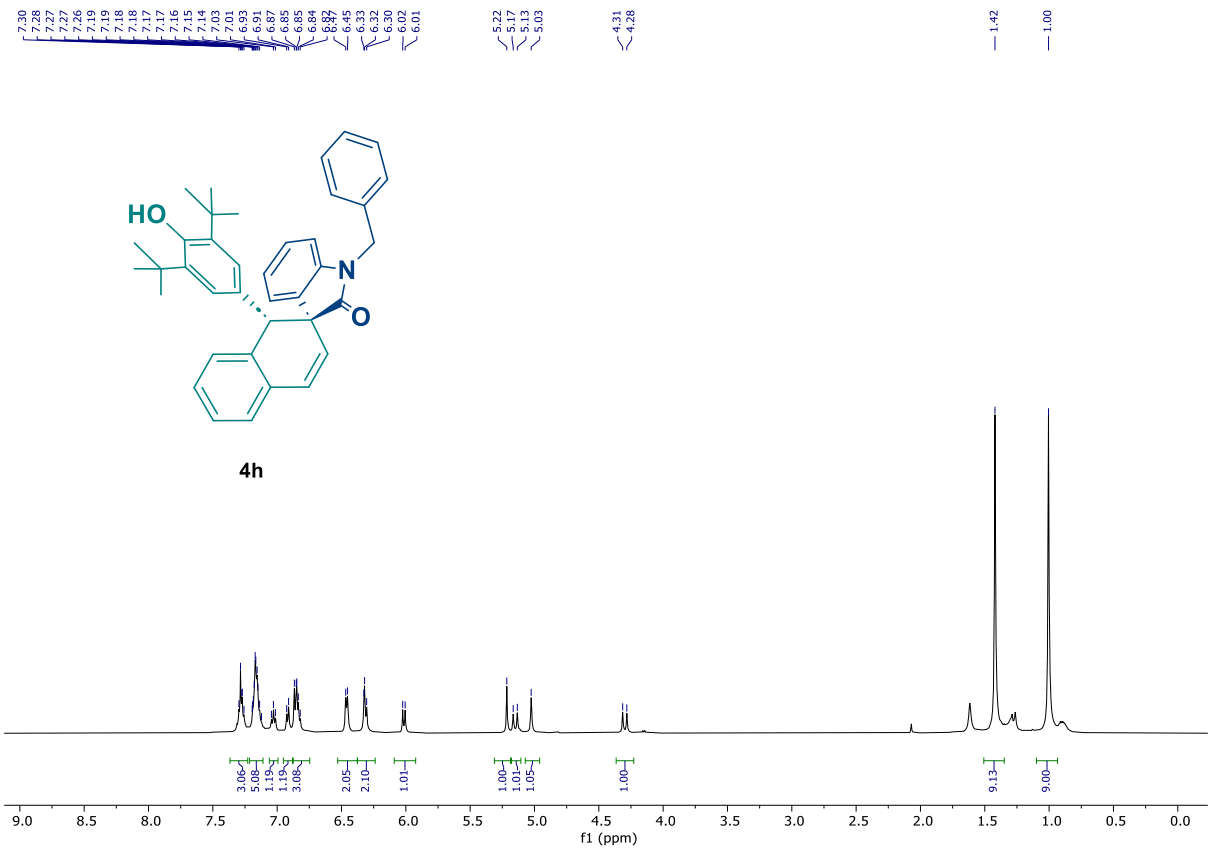
^{1}H, ^{13}C and ^{19}F Spectra of 4g (400MHz, DMSO-d_6) :

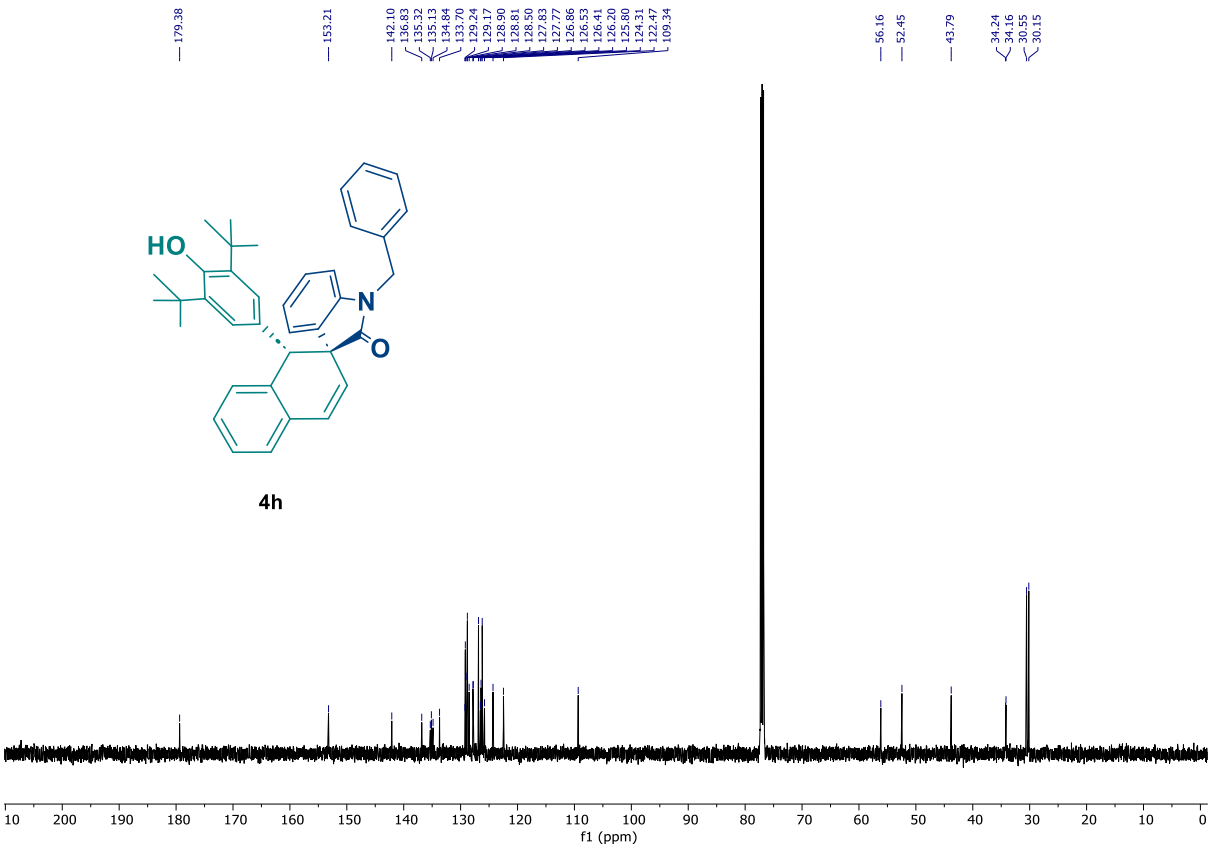




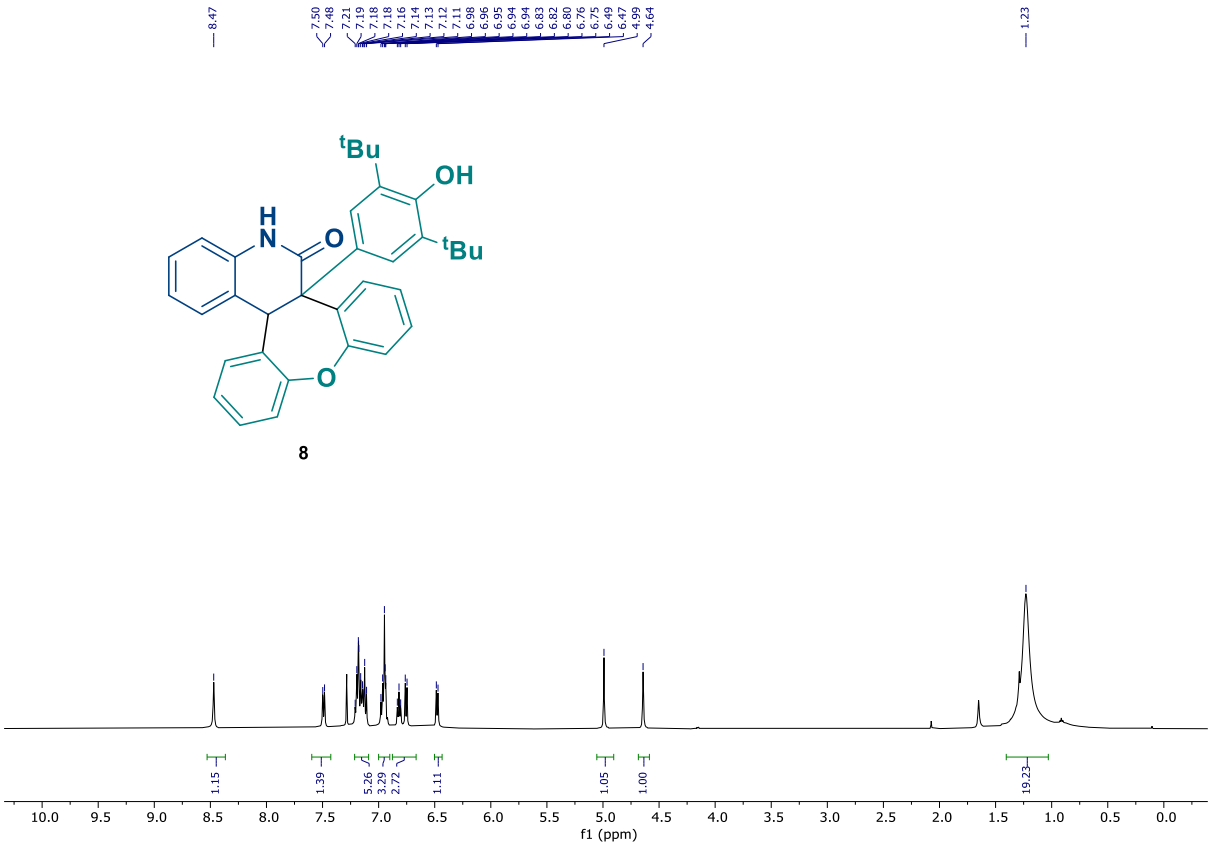

-104.88
-105.48
HO
NH
O
F
4g
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
f1 (ppm)

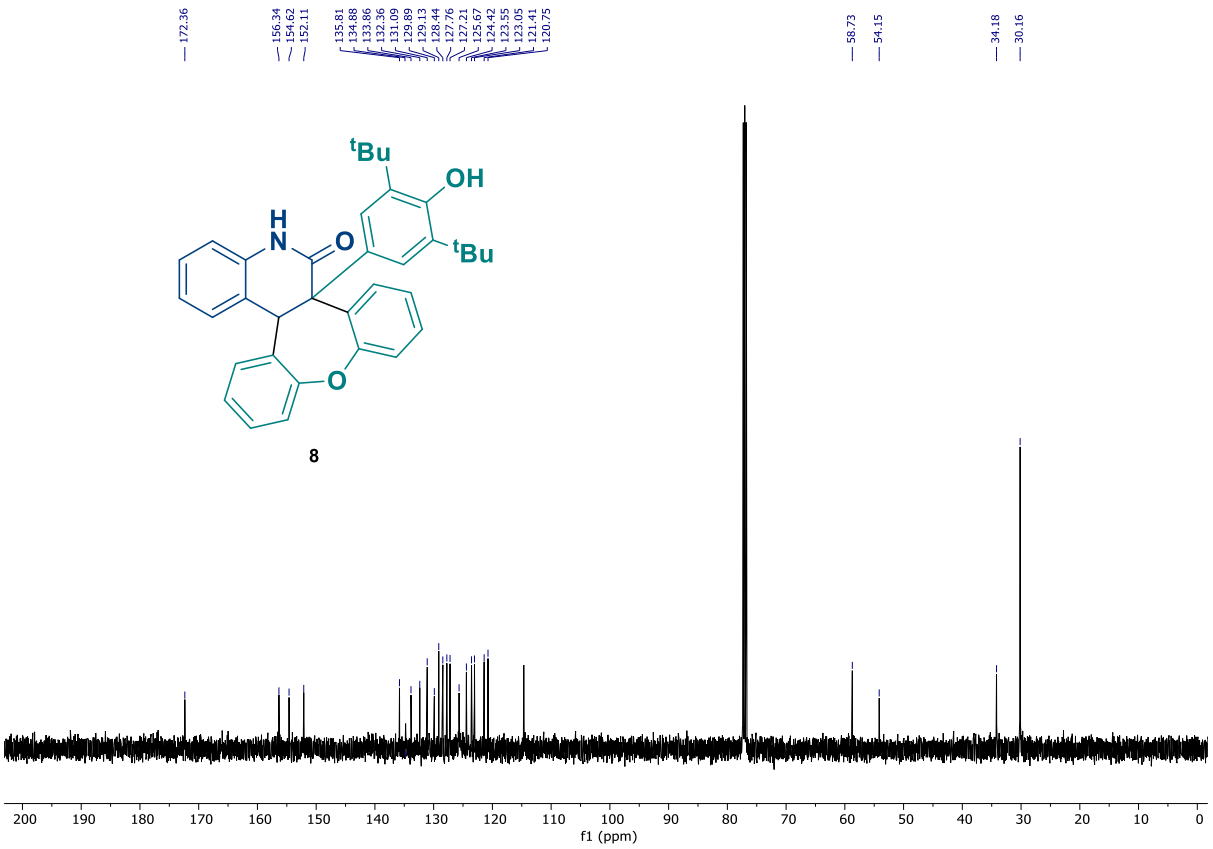
^{1}H and ^{13}C Spectra of 4h (500MHz, $CDCl_3$) :



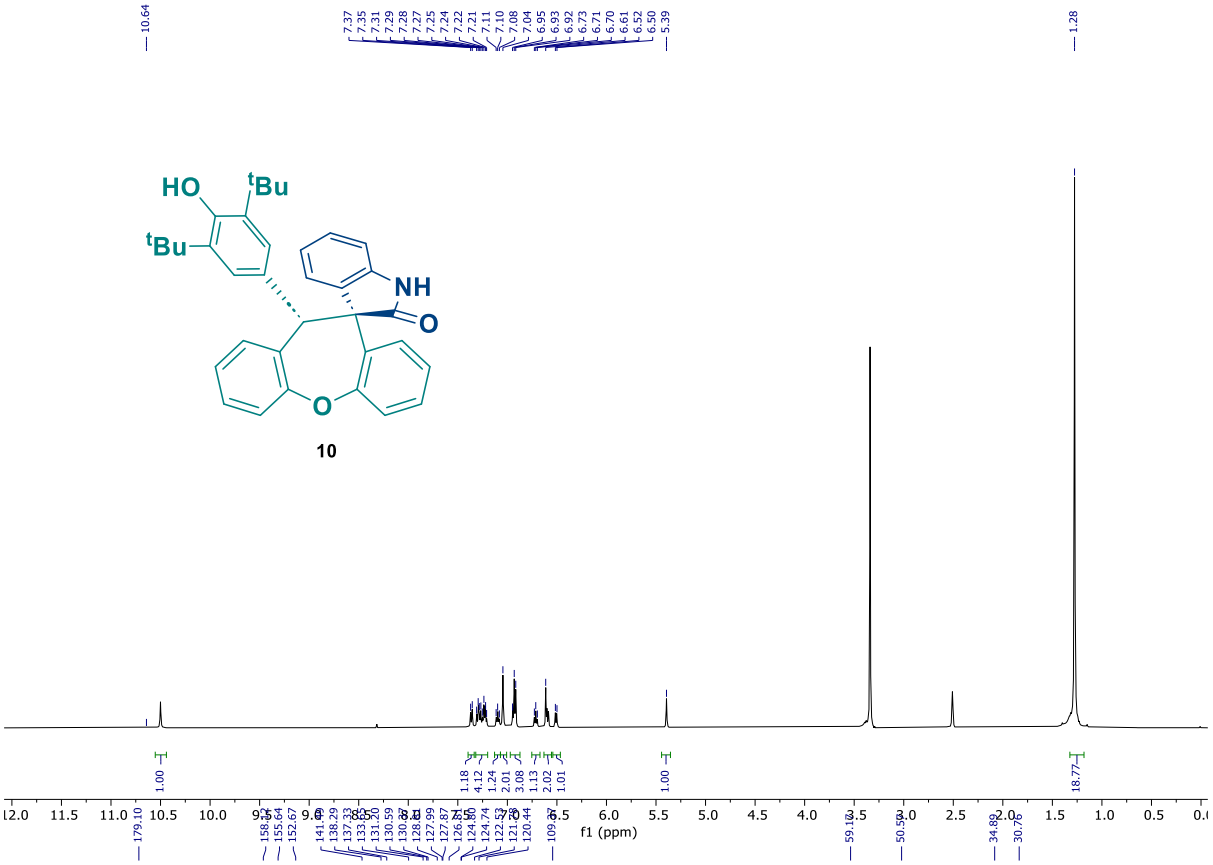


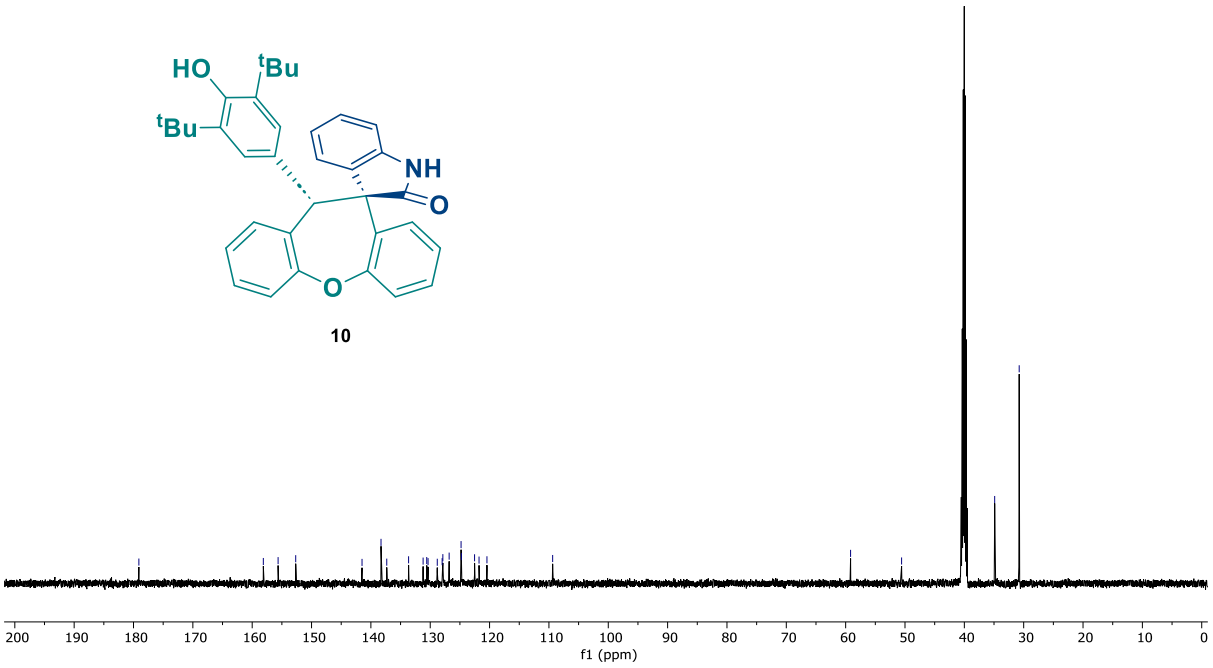
^{1}H and ^{13}C Spectra of 8 (500MHz, $CDCl_3$) :



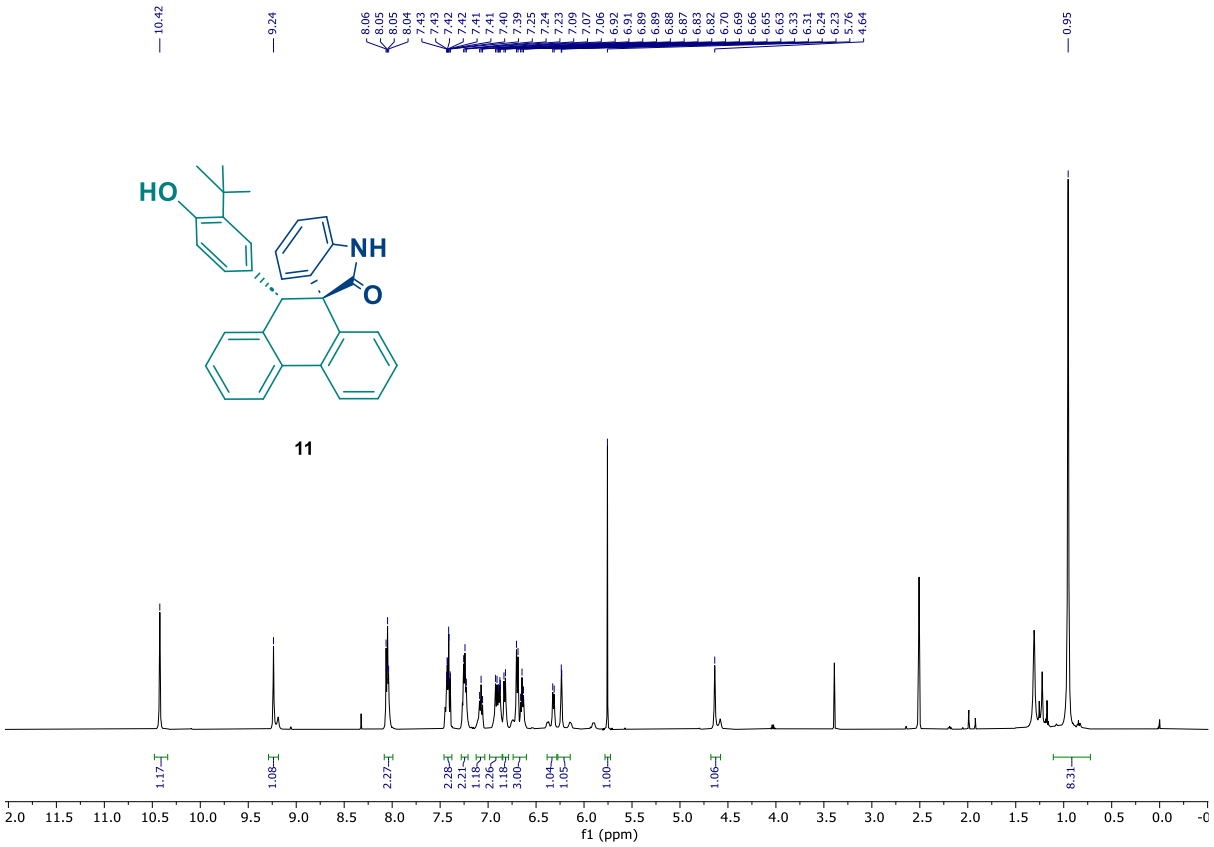


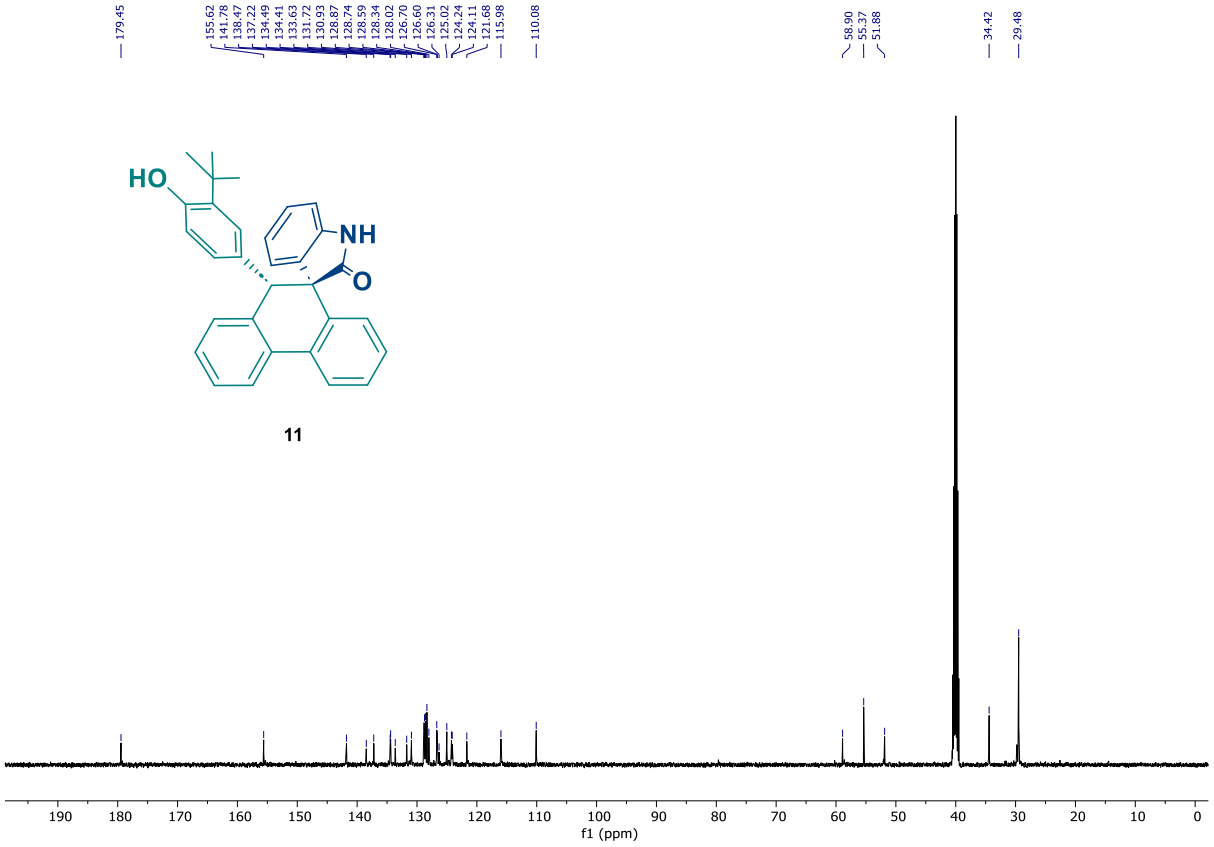
^{1}H and ^{13}C Spectra of 10 (500MHz, DMSO-*d*$_6$) :



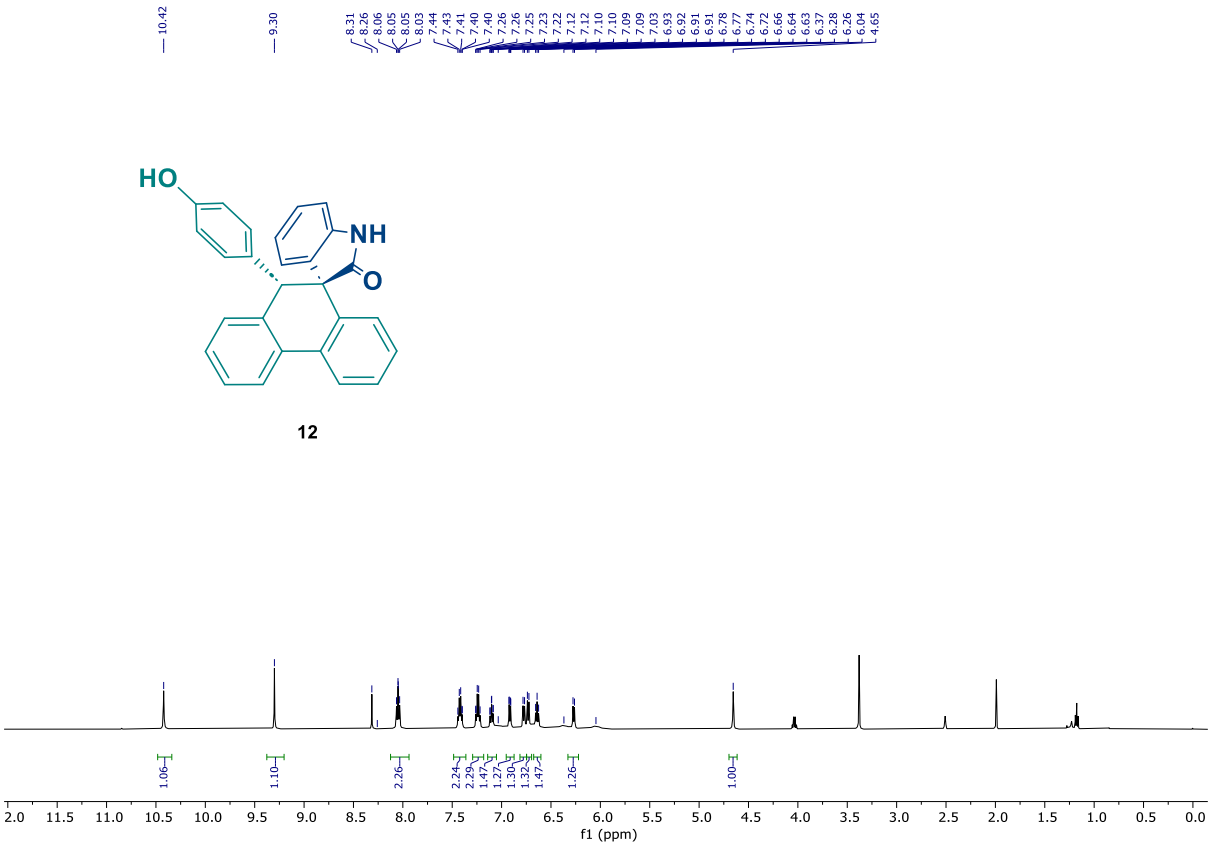


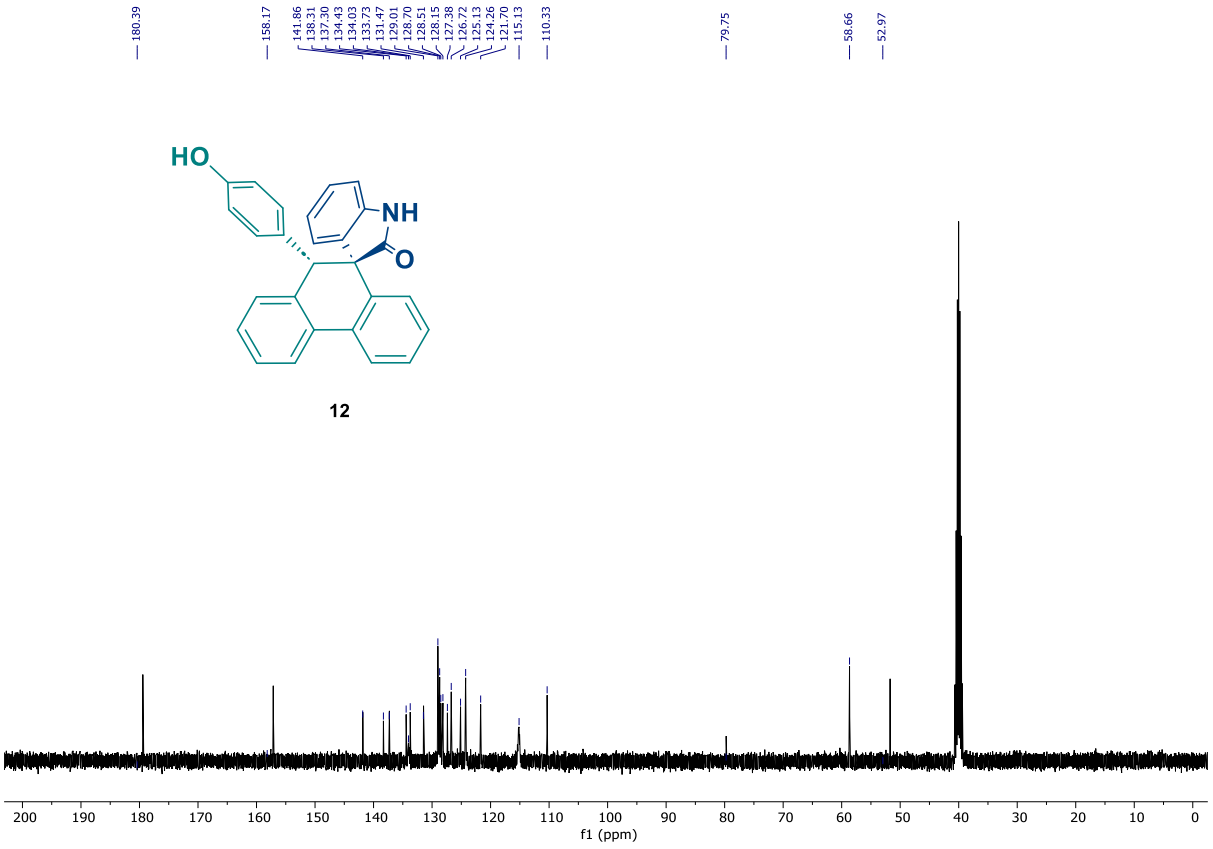
^{1}H and ^{13}C Spectra of 11 (500MHz, DMSO-d_6) :





^{1}H and ^{13}C Spectra of 12 (500MHz, DMSO-d_6) :





8. References:

1. B. C. Raju, A. K. Tiwari, J. A. Kumar, A. Z. Ali, S. B. Agawane, G. Saidachary and K. Madhusudana, *Bioorganic & Medicinal Chemistry*, 2010, **18**, 358–365.(b) A. Ali, H. K. Harit, M. Devi, D. Ghosh and R. P. Singh, *J. Org. Chem.*, 2022, **87**, 16313–16327.
2. J.-Y. Wang, W.-J. Hao, S.-J. Tu and B. Jiang, *Org. Chem. Front.*, 2020, **7**, 1743–1778.