Supporting Information for

Small Organic Fluorophores with SWIR Emission Detectable Beyond 1300 nm

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1) General

All reactions, work-up and chromatography were performed under protection from light by wrapping an aluminium foil. The glassware for the reactions was oven dried at 100 °C and cooled under high vacuum (HV) before use and kept under argon. Absolute solvents were prepared by MBRAUN solvent purification system. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator (water bath temp ≤ 37°C) under protection from light. Thin-layer chromatography was carried out using Merck silica gel 60 F254 aluminium plates with F-254 indicator and separated bands were visualized under UV light (254 nm, 320 nm). Column chromatography was performed using Merck silica gel 60 (230-400 mesh) or fine silica gel (70-230 mesh). Technical grade solvents, dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc), hexane, and methanol were distilled before their use in column chromatography. Chemicals were procured from commercial vendors, Chempur, Acors Organics, Merck-Sigma Aldrich and VWR. All chemicals were used as obtained without further purification.

Spectroscopy: (^{1}H- ^{19}F-, and ^{13}C-) NMR spectra were recorded on a Varian AV400 or AV600 spectrometer at 298K (in ^{19}F: 376, 564, in ^{13}C: 100 or 125 MHz). The solvent residual signal was used as internal reference (^{1}H: C*H*Cl_3, δ(H) 7.26, δ(^{13}*C*HCl_3)=77.2 ppm for in $CDCl_3$; ^{1}H: C*H*D2SOCD3, δ(H) 2.50, δ(^{13}*C*D_3SOCD_3)=39.52 ppm). For ^{19}F NMR, $CFCl_3$ was used as external standard in $CDCl_3$ and reported data with set reference δ(C*F*Cl_3)= 0.0. Data were reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (*J*) are in Hertz (Hz), rounded to the nearest 0.1 Hz. UV/Vis spectroscopy: *PerkinElmer Lambda 1050 spectrometer*, in 10 mm quartz cells, reported λ_{max} in nm. Fluorescence spectroscopy: *Homebuilt based on NKT SuperK and Princeton instruments spectrograph with a Pixis and Pylon.* excitation (λ_{exc}) from 400-1600 nm, and (λ_{Em} (intensity)) emission detection upto 1600 nm. Mass Spectrometry: ESI Thermo Fisher LTQ-Orbitrap XL, positive ion mode, *m/z* (rel. intensity %) or a Finnigan SSQ 7000 mass spectrometer (EI or CI).

Fluorescence quantum yield (QY): QY was determined based on a comparative method against well-characterized two standards dyes, IR-26 (QY= 0.048%) and IR-1061 (QY= 0.32%) in dichloroethane (DCE).[1]

Fluorescence QY values were determined based on the gradients from the plot of integrated fluorescence intensity vs absorbance, and η -refractive index of the solvent

$$\Phi_X = \Phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right)$$

Steady-state absorbance was measured on a PerkinElmer LAMBDA 950 UV/Vis/NIR spectrophotometer. Fluorescence spectra were recorded on Princeton Instruments IsoPlane spectrograph equipped with PyLoN 1700 InGaAs camera in the SWIR range using an 880 nm beam of a Ti:sapphire laser (Spectra-Physics, MaiTai). We used 1 cm optical path quartz cells (Hellma) for all measurements.[1]

[1] H. Piwoński, S. Nozue, S. Habuchi, *ACS Nanosci. Au*, **2022**, *2*, 253

2) NIR-II Imaging with an InGaAs camera based system

Kaer Imaging System NIR-II (KIS system; manufactured by Kaer Labs, Nantes, France) eqipped with 808 nm and 980 nm lasers, each with a power density of 40 $mWcm^{-2}$ at the focal plane, was used. For the fluorescence phantom imaging, the dyes solutions in DMSO at 0.1 mg /mL (ca 200 µM, in Eppendorf tubes) were exposed to 980 nm, (for ICG comparison, a 808 nm laser). The fluorescence signal was obtained with longpass filters at 1050 nm, 1200 nm, 1300 nm and 1400 nm collecting photons upto 1700 nm. Exposure times ranged from 100 ms to 2 seconds, using a 512 ×512 pixels InGaAs camera with 16 bit depth. An 1050-nm bandpass filter was used as default unless otherwise stated.

2.1) Image processing of the observed NIR-II emission

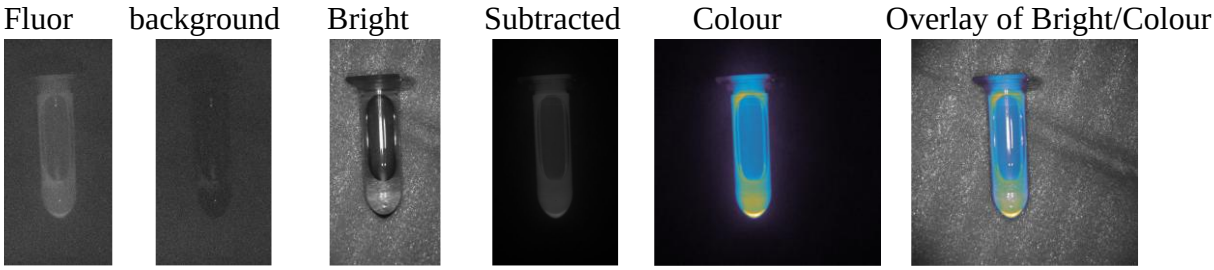


Figure S1: Background subtraction: From the recorded fluoresence signal, the background (signal without excitation) was subtracted, that then could be visualized either in grey or pseudo-colours. For real-time visuation, the pseudo-colour coded signal image is overlaid on the bright LED light image (reflection image). The example here is using compound **1a**, with conc 0.1 mg/mL, using Exc. 980 nm, and 1050 nm longpass filter.

<u>Real-time imaging processing routine used for the data obtained with KIS system</u>

- Fluor: the fluorescent image produced with the laser excitation 980 nm, and collection of all photons emitted from 1050 nm until 1700 nm.
- Background: Image collected without the laser excitation under identical conditions as the fluorescence signal (also with the same exposure time)
- Bright: white light image (reflection), obtained with infrared LED illumination
- Subtracted: the difference between Fluor and Background images (Fluor – Background)
- Colour: Subtracted image with a colour palette (look up table coding to highlight signal)
- Overlay: overlay of the colour image on the bright image

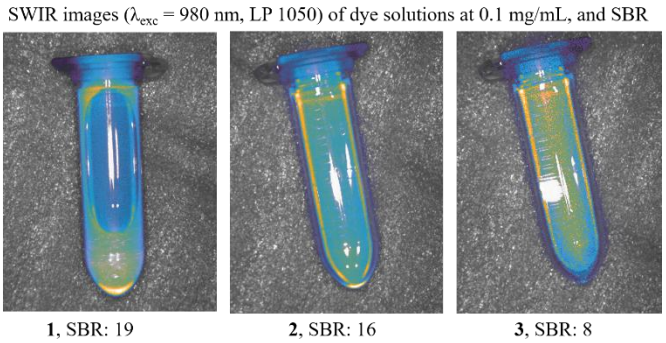
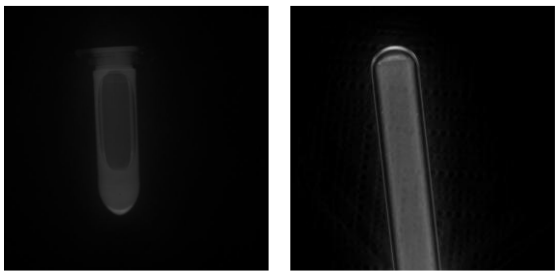


Figure S2: Overlay of bright and fluorescence images of the three dyes (at a conc. 0.1 mg/mL, DMSO) discussed here, with quantified signal-to-background-ratios (SBR, for excitation at 980 nm; 1050 LP filter nm; and 1 sec exposure).

2.2) NIR-II images of 1a and ICG under identical conditions

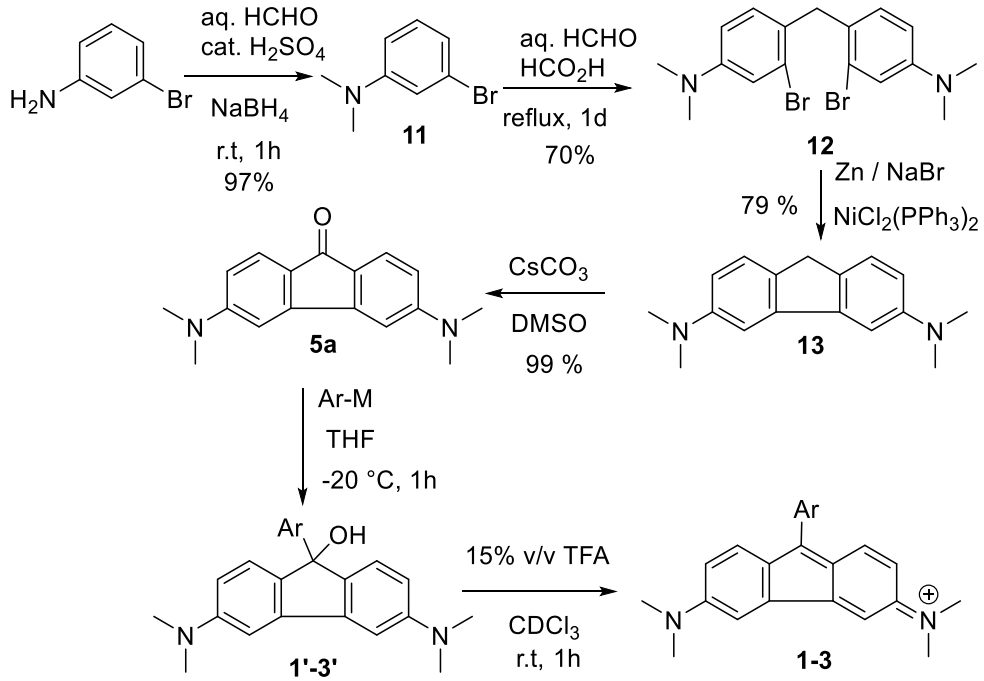


1a **ICG**

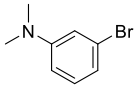
Figure S3. The (background subtracted) NIR-II images of ICG and dye **1a** solutions at conc. 0.1 mg/mL using 808 nm laser excitation and 1050 LP filter. The ICG exhibited about 6,5 better signal-to- background ratio compared to **1a**. (Exposure times 1sec for **1a** and 100 ms for ICG).

3) Experimental Procedures

3.1) Synthesis of 3,6-bis(dimethylamino)-9*H*-fluoren-9-one (5a)



a) 3-bromo-*N*,*N*-dimethylaniline (11)



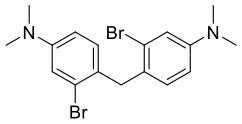
To aqueous formaldehyde (37%, 26 mL, 450 mmol), dissolved in fresh THF (310 mL) and precooled in ice bath, a solution of H_2SO_4 (3 M, 70 mL) was added in one portion, and the mixture was stirred for 10 min. To this, 3-bromoaniline (20 g, 116.26 mmol) was added drop-wise within 10 min, and the reaction mixture was stirred until the resulting precipitate dissolved. Stirring the mixture in 0°C bath, solid $NaBH_4$ (17.6 g, 465.24 mmol) was added in small portions over 1h. After completion of the additions, the reaction mixture was allowed to warm to RT, and stirred continued for additional 1h, and the TLC (EtOAc / pentane 5:95 *v*/*v*) of reaction indicated full consumption of starting material. To this, saturated solution of $NaHCO_3$ (300 mL) was added, and the reaction mixture was extracted

with CH_2Cl_2 (3×150 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and solvents were evaporated. The crude product was filtered through pad of silica gel (300 g) using gradient of EtOAc / pentane, from 0:1 to 5:95 (*v*/*v*) to obtain pure compound **11** as clear light yellow oil (22.75 g, 113.7 mmol, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, *J* = 8.0, 1H), 6.88 – 6.77 (m, 2H), 6.66 – 6.58 (m, 1H), 2.94 (s, 6H).

NMR data matched those reported in the literature.[2]

b) 4,4'-methylenebis(3-bromo-*N*,*N*-dimethylaniline) (12) – To the solution of 3-bromo-*N*,*N*-dimethylaniline (**11**, 3.5 g, 17.5 mmol) in formic acid (60 mL) at room temperature, aqueous formaldehyde (37%, 1.35 mL, 18.0 mmol) was added, over 30 min. The reaction mixture was stirred at 60°C for 24h. Then, toluene (60 mL) was added to the flask and the mixture of solvents was evaporated under reduced pressure. The residual acid was neutralized with saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed with brine (2x50 mL), dried over Na_2SO_4, filtered and solvents were evaporated. The resulting red viscous oil was chromatographed (EtOAc / pentane, from 1:20 to 1:10, *v*/*v*) to obtain pure compound **12** as white crystalline solid (2.5 g, 6.06 mmol, 70%).



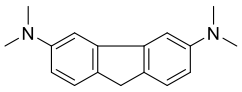
^{1}H NMR (400 MHz, $CDCl_3$) δ (in ppm): 6.95 (d, *J* = 2.7 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.59 (dd, *J* = 8.5, 2.7 Hz, 2H), 4.01 (s, 2H), 2.92 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (in ppm): 150.0, 130.7, 127.0, 125.6, 116.2, 111.8, 40.5, 39.8.

HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{21}Br_2N_2$: 411.9973; found, 411.9961.

NMR data matched those reported in the literature.[1]

c) *N*,*N*,*N*,*N*-tetramethyl-9*H*-fluorene-3,6-diamine (13) – The title compound was synthesized using a modified procedure reported.[3]



To the argon purged flask, Zn dust (25 mg, 0.38 mmol), $NiCl_2(PPh_3)_2$ (40 mg, 0.06 mmol), PPh_3 (94 mg, 0.36 mmol) and NaBr (37 mg, 0.36 mmol) were introduced, the contents purged with argon and flask was sealed with septum, followed by added DMF (0.3 mL). The resulting thick suspension was degassed, filled with argon (4x), to observe colour change (from green to deep red). The mixture was then transferred to preheated oil bath at 80 °C and stirred for 30 min. To hot blood-red mixture, degassed solution of **12** (50 mg, 0.12 mmol) in DMF (0.3 mL) was added dropwise and heating was continued at 80 °C for 18 h. The mixture was diluted with toluene (5 mL), filtered through cotton pad to remove all insolubilities and filtrate was evaporated. The residual was dissolved in EtOAc (25 mL) washed with water (2×25 mL) and brine (25 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated. The resulting off-white residue was chromatographed (EtOAc

[2] T. Pastierik, P. Šebej, J. Medalová, P. Štacko, P. Klán, *J. Org. Chem.* **2014**, *79*, 3374–3382.
[3] V. Sharma, B. Bachand, M. Simard, J. D. Wuest, *J. Org. Chem.* **1994**, *2*, 7785–7792.

/ pentane, from 1:10 to 1:6, *v*/*v*) system to obtain compound **13** as white crystalline solid (24 mg, 0.095 mmol, yield 79%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 2.4 Hz, 2H), 6.74 (dd, *J* = 8.2, 2.4 Hz, 2H), 3.72 (s, 2H), 3.03 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3, 143.0, 133.1, 125.1, 112.3, 104.1, 41.4, 35.1.

HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{21}N_2$: 252.1626; found, 252.1619.

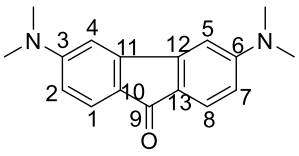
The possibility of reducing the catalyst loading has been checked. The reactions were performed according to the protocol given above. Keeping the number of equivalents unchanged for: Zn (3.2 eq.), PPh_3 (3.0 eq.), NaBr (3.0 eq.) and concentration of the reaction mixture (0.2 M). The scale of the reaction was increased with the reduction of the catalyst loading, as shown in Table 1.

Table S1. Optimization of catalyst loading.

Entry	Scale [mmol]	$NiCl_2(PPh_3)_2$ [mol %]	Isolated yield [%]
1	0.12	50	79
2	0.73	20	96
3	2.36	10	86
4*	5.34	10	85

*In the case of Entry 4 the catalyst was generated *in situ*. Substrate **12** and all reactants were placed in the flask from the beginning.

d) 3,6-bis(dimethylamino)-9*H*-fluoren-9-one (5a) – The title compound was synthesized according to the modified procedure reported in literature.[4]



To the mixture of compound **13** (520 mg, 2.06 mmol) and Cs_2CO_3 (2.0 g, 6.18 mmol), DMSO (20 mL) was added, flask was equipped with septum, next air was evacuated and flask was backfilled with O_2 (2x). Reaction mixture was stirred under an atmosphere of O_2 (balloon) in room temperature for 18h. After this time TLC (EtOAc / pentane 1:1 *v*/*v*) indicated full consumption of starting material. Deep orange mixture was diluted with 200 mL of CH_2Cl_2, and washed with water (3×100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated. The brown orange residual was dissolved in small volume of CH_2Cl_2 (20 mL), followed by EA (70 mL), slow evaporation of the mixture of solvents furnish shiny orange crystals which were filtered and washed with cold EtOAc and dried under vacuum to give product **5a** (542 mg, 2.035 mmol, yield 99%).

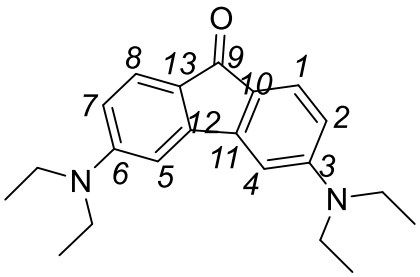
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H, C1-*H*), 6.79 (d, *J* = 2.3 Hz, 2H, C4-*H*), 6.45 (dd, *J* = 8.3, 2.3 Hz, 2H, C2-*H*), 3.12 (s, 12H, N-C*H*$_3$).).

^{13}C NMR (151 MHz, $CDCl_3$) δ 191.5 (C9), 154.4 (C3), 146.0 (C11), 125.2 (C1), 124.3 (C10), 110.2(C2), 103.0 (C4), 40.5 (C3).

HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{17}H_{18}N_2ONa$: 289.1311; found, 289.1310.

[4] K. K. Park, L. K. Tsou, A. D. Hamilton, *Synthesis*, **2006**, *21*, 3617–3620.

e) 3,6-bis(diethylamino)-9*H*-fluoren-9-one (5b)



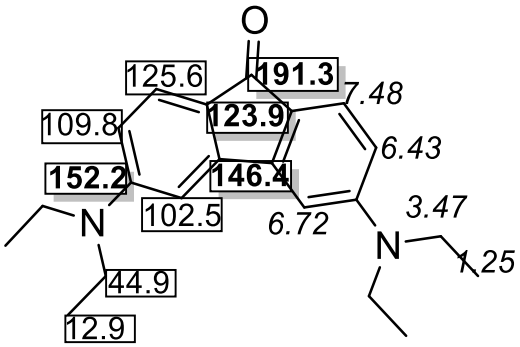
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (*d*, *J*= 8.4 Hz, 2H; C1-*H*) 6.72 (*d*, J= 2.2 Hz, 2H, C4-*H*), 6.43 (*dd*, J= 8.4, 2.4 Hz, 2H, C2-*H*), 3.47 (*q*, *J*= 7.3 Hz, 4H, N-C*H*$_2$), 1.25 (t, *J*= 7.3, 6H, N-CH_2-C*H*$_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.3 (C9), 152.2 (C3), 146.4 (C11), 125.6 (C1), 123.9 (C10), 109.8 (C2), 102.5 (C4), 44.9 (N-$\underline{CH_2}$-CH_3), 12.9 (N-CH_2-$\underline{CH_3}$).

HSQC: ^{1}H (**^{13}C**) in $CDCl_3$): δ 7.48 (**125.6**, C1) 6.72 (**102.5**, C4), 6.43 (**109.8**, C2), 3.47 (**44.9**, N-$\underline{CH_2}$-CH_3), 1.25 (**12.9,** N-CH_2-$\underline{CH_3}$).

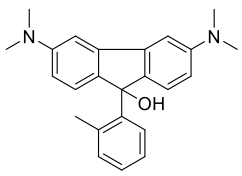
HMBC ^{1}H (**^{13}C**). 7.48 (***102.5, 109.8, 146.4, 152.2*, *191.3***), 6.72 (***146.4, 123.9, 109.8***), 6.43 (***102.5, 123.9***), 3.47 (***152.2***)

HRMS (ESI, m/z): Calcd. for $[C_{21}H_{26}N_2O + H]^+$: 323.2045; found: 323,2086



Signals assignement: 1H (right part of the molecule) based on COSY, and 13C (left part) based on HSQC (rectangle), and with HMBC (bold, shaded rectangle)

3.2a) 3,6-bis(dimethylamino)-9-(o-tolyl)-9*H*-fluoren-9-ol (1a')



To a flame dried 10 mL round bottom flask was charged activated Mg (33 mg, 1.35 mmol) and anhydrous THF (1.5 mL), under Ar atmosphere. To this suspension 1-bromo-2-methylbenzene **6** (192 mg, 0.135 mL, 1.126 mmol) was added dropwise. The reaction was mildly exothermic. After competition of the addition the mixture was transferred to preheated oil bath and stirred at 60 °C for 1h. The Grignard reagent was decanted and titrated (0.7 M), (0.5 mL, 0.3378 mmol) of this reagent was added dropwise to flame dried 25 mL round bottom flask, cooled to -20 °C, charged with ketone **5a** (30 mg, 0.1126 mmol) and 5 mL anhydrous

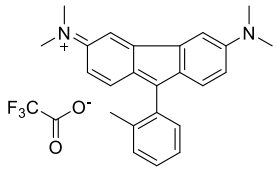
THF, under Ar atmosphere. Disappearance of yellow fluorescence of the substrate was observed after the addition. The flask was then transferred to the ice bath and the reddish solution was stirred for additional 30 min. The reaction mixture was quenched with saturated solution of $NaHCO_3$ (5 mL), diluted with water (50 mL), extracted with ethyl acetate (4×30 mL), the combined yellow organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and evaporated. The resulting pinkish residue was then chromatographed (EtOAc / pentane, from 1:10 to 1:5, *v*/*v*) system to obtain pure compound **1a'** as off-white solid (24 mg, 0.067 mmol, yield 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.17 (td, *J* = 7.4, 1.5 Hz, 1H), 7.02 – 6.97 (m, 4H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.56 (dd, *J* = 8.4, 2.4 Hz, 2H), 3.03 (s, 12H), 2.30 (s, 1H), 1.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 141.6, 141.5, 138.6, 135.5, 131.3, 126.9, 126.5, 125.4, 124.5, 112.3, 103.8, 81.9, 41.0, 19.5.

HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{26}N_2ONa$: 381.1937; found 381.1936.

3.2b) *N*-(6-(dimethylamino)-9-(o-tolyl)-3*H*-fluoren-3-ylidene)-*N*-methylmethanaminium trifluoroacetate (1a.TFA)



Carbinol **1a'** (10 mg, 0.028 mmol) was placed in 5 mL glass vial, dissolved in $CDCl_3$ (0.5 mL), and transferred to NMR tube (the first ^{1}H spectrum was recorded as a starting point). Next (40 µL) of 1M solution of TFA-*d*[1] in $CDCl_3$ was added. Progress of the reaction was monitored by ^{1}H NMR, first spectrum recorded after 5 min., showed full conversion of starting material. After 1h reaction mixture was evaporated and dried on vacuum. Dark green residue was recrystalised from CH_2Cl_2 / Et_2O to obtain pure compound **1a.TFA** as dark green powder (12 mg, 0.026 mmol, yield 94%).

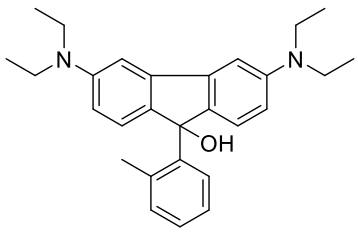
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 2.1 Hz, 2H, C4-*H*,), 7.41 (t, *J* = 7.5 Hz, 1H,), 7.36 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.9 Hz, 2H, C1-*H*), 6.11 (dd, *J* = 8.9, 2.1 Hz, 2H, C2-*H*), 3.37 (s, 12H N-CH_3), 2.33 (s, 3H, -C2'-CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 158.0, 147.7, 135.9, 133.9, 131.4, 131.1, 130.7, 129.8, 128.3, 126.0, 111.9, 111.3, 41.7, 20.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.91.

HRMS (ESI, m/z): $[M]^+$ Calcd. for $C_{24}H_{25}N_2$: 341.2012; found, 341.2011.

3.3a) 3,6-bis(dimethylamino)-9-(o-tolyl)-9*H*-fluoren-9-ol (1b')

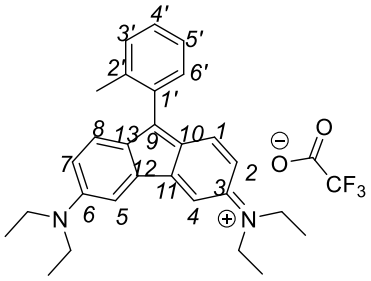


Similar to the procedure described for **1a'**, to the ketone **5b** (20 mg, 0.062 mmol) in absolute THF, the Grignard reagent **6** was added (2 eq. in THF) at low temperature and left to stir for 2h. After the reaction quenched with saturated NH_4Cl, the extracted crude reaction mixture was chromatographed (EtOAc / hexane mixture on Biotage) to obtain the corresponding product **1b'** as light yellow solid (12 mg, 0.06 mmol, yield 49 %). The product was found to be labile, thus used further immediately.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (*d*, *J*= 7.1 Hz, 1H; C6′-*H*), 7.31 (t, *J*= 7.6 Hz, 1H, C5′-*H*),7.32 (t, 2H; C4′-*H*), 6.97 (s, 2H, C4-H), overlapped with 6.95 (C2′-*H, 1H*), and 6.93 (*d*, *J*= 8.7 Hz, 2H; C1-*H*), 6.14 (dd, *J*= 2.4, 8.5 Hz, 2H, C2-*H*), 3.42 (q, *J*= 7.5 Hz, -N-C*H2*-), 1.21 (t, 3H, *J*= 7 Hz, -NCH2-C*H3*).

HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{28}H_{34}N_2ONa$: 437,2568; found, 437.2543.

3.3b) *N*-(6-(dimethylamino)-9-(o-tolyl)-3*H*-fluoren-3-ylidene)-*N*-methylmethanaminium trifluoroacetate (1b.TFA)

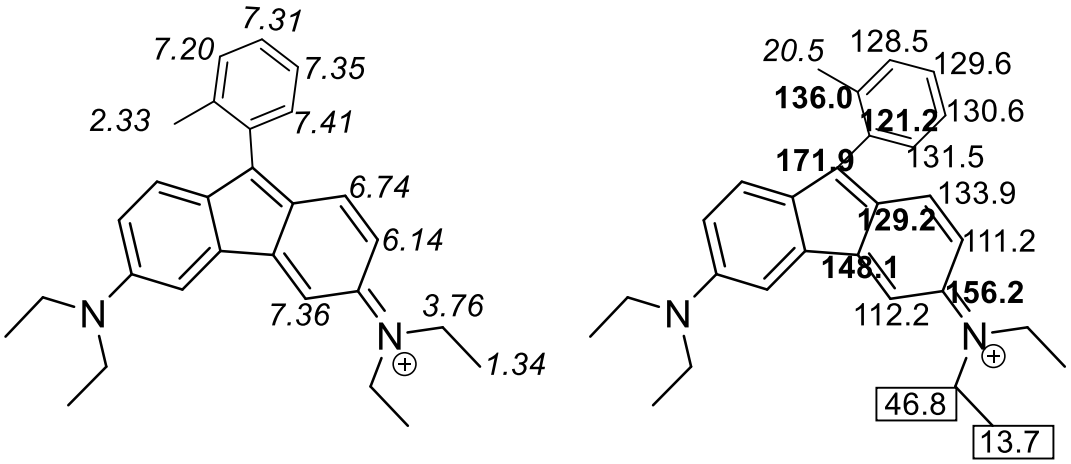


Carbinol **1b'** (21 mg, 0.028 mmol) was placed in 5 mL glass vial, dissolved in $CDCl_3$ (0.5 mL), and transferred to NMR tube (the first ^{1}H spectrum was recorded as a starting point). Next (40 µL) of 1M solution of TFA-*d*[1] in $CDCl_3$ was added. Progress of the reaction was monitored by ^{1}H NMR, first spectrum recorded after 5 min., showed full conversion of starting material. After 1h reaction mixture was evaporated and dried on vacuum. Dark green residue was recrystalised from CH_2Cl_2 / Et_2O to obtain pure compound **1b.TFA** as dark powder.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (*m*, 1H; C5′-*H*), 7.33 (m, 1H, C4′-*H*), 7.33 (br, 1H, C6′-*H*, overlapped with 7.31 (2H, C4-*H*) 7.20 (br *d*, *J*= 7.5, 1H; *C3′-H*), 6.75 (*d*, *J*= 8.7 Hz, 2H; C1-*H*), 6.14 (br *d*, *J*= 9.2 Hz, 2H; C2-*H*), 3.76 (q, *J*= 7.5 Hz, -N-C*H2*-), 1.34 (t, 3H, *J*= 6.8 Hz, -NCH2-C*H3*).

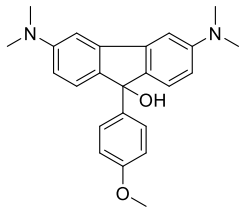
^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 156.2, 148.1, 136.0, 133.9, 131.5, 130.6, 129.6, 128.5, 126.2, 112.2, 111.2, 46.8, 20.5, 13.6.

HRMS (ESI, m/z): $[M]^+$ Calcd. for $C_{28}H_{33}N_2^+$: 397.2638; found: 397.2622



Signals assignement: 1H (right part of the molecule) based on COSY, and 13C (left part) based on HSQC (rectangle), and with HMBC (bold, shaded rectangle)

3.4a) 3,6-bis(dimethylamino)-9-(4-methoxyphenyl)-9*H*-fluoren-9-ol (2')



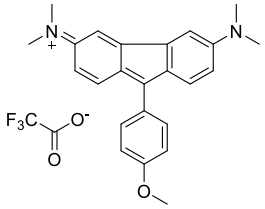
The title compound was synthesized according to the procedure described for **2'** from Mg (146 mg, 6.0 mmol), 1-bromo-4-methoxybenzene **7** (935 mg, 0.625 mL, 5.0 mmol) in THF (5.0 mL), (concentration of Grignard reagent has been determined as (0.6M). Addition to the ketone **5a** (30 mg, 0.1126 mmol) was realised (0.56 mL, 0.336 mmol) at low temperature. The crude reaction mixture was chromatographed (EtOAc / pentane, from 1:10 to 1:5, *v*/*v*) system to give the corresponding product **2'** as reddish solid (41 mg, 0.112 mmol, yield 97%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H, C3'-*H*), 7.15 (d, *J* = 8.4 Hz, 2H, C1-*H*), 6.98 (d, *J* = 2.4 Hz, 2H, C4-*H*), 6.78 (d, *J* = 8.8 Hz, 2H, C2'-*H*), 6.60 (dd, *J* = 8.4, 2.4 Hz, 1H, C2-*H*), 3.76 (s, 3H, C2'-OC*H*$_3$), 3.02 (s, 12H N-C*H3*), 2.42 (s, 1H, C9-O*H*).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 151.4, 140.9, 139.9, 136.8, 126.6, 124.9, 113.4, 112.4, 103.6, 82.5, 55.2, 41.0.

HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{26}N_2O_2Na$: 397.1892; found, 397.1886.

3.4b) *N*-(6-(dimethylamino)-9-(4-methoxyphenyl)-3*H*-fluoren-3-ylidene)-*N*-methylmethanaminium trifluoroacetate (2.TFA)



Carbinol **2'** (10 mg, 0.027 mmol) was placed in 5 mL glass vial, dissolved in $CDCl_3$ (0.5 mL), and transferred to NMR tube (the first ^{1}H spectrum was recorded as a starting point). Next (40 µL) of 1M solution of TFA-*d*^{1} in $CDCl_3$ was added. Progress of the reaction was monitored by ^{1}H NMR, first spectrum recorded after 5 min., showed full conversion of starting material. After 1h reaction mixture was evaporated and dried on vacuum. Dark brownish residue was recrystalised from CH_2Cl_2 / Et_2O to obtain pure compound **2.TFA** as dark green-redish powder (12 mg, 0.025 mmol, yield 95%).

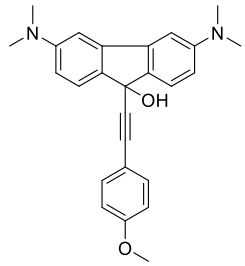
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 (br, C4-*H*) overlapped with 7.55 (m, 4H, C3'-*H*), 7.10 (d, *J* = 9.0 Hz, 2H, C1-*H*), 7.07 (d, *J* = 8.5 Hz, 2H, C2'-*H*), 6.19 (dd, *J* = 9.0, 2.1 Hz, 2H, C2-*H*), 3.92 (s, 3H, C4'-OC*H*$_3$), 3.36 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 163.9, 160.17 (q, *J* = 38.1 Hz), 157.4, 147.9, 133.7, 131.7, 127.8, 124.5, 115.82 (q, *J* = 289.4 Hz), 115.0, 111.3, 111.1, 55.7, 41.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.46.

HRMS (ESI, m/z): $[M]^+$ Calcd. for $C_{24}H_{25}N_2O$: 357.1961; found, 357.1965.

3.5a) 3,6-bis(dimethylamino)-9-((4-methoxyphenyl)ethynyl)-9*H*-fluoren-9-ol (3')



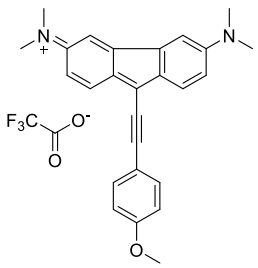
To the degassed and cooled to -78 °C solution of 1-ethynyl-4-methoxybenzene **9** (45 mg, 0.338 mmol) in anhydrous THF (1 mL), under Ar atmosphere, *n*-butyllithium (0.21 mL of 1.6 M solution in hexane, ~0.336 mmol) was carefully introduced through a needle along the wall of the flask. Clear solution quickly turned orange and then light pinkish. Mixture of reagents was stirred at -78 °C for next 20 min, next the degassed, deep orange solution of ketone **5** (30 mg, 0.1126 mmol) in anhydrous THF (1 mL) was injected over 1-2 min along the wall of the flask. Disappearance of yellow fluorescence of the substrate was observed after the addition, the reddish solution was stirred for additional 30 min. The cooling bath was removed and the mixture was allowed to warm up to ~0 °C (~30 min). The reaction mixture was quenched with saturated solution of $NaHCO_3$ (5 mL), diluted with water (50 mL), extracted with ethyl acetate (4×30 mL), the combined yellow organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and evaporated. The resulting pinkish residue was then chromatographed (EtOAc / pentane, from 1:10 to 1:5, *v*/*v*) system to obtain pure compound **3'** as grey solid (38 mg, 0.0953 mmol, yield 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H, C1-*H*), 7.35 (d, *J* = 8.7 Hz, 2H, C5'-*H*), 6.94 (d, *J* = 2.4 Hz, 2H, C4-*H*), 6.77 (d, *J* = 8.7 Hz, 2H, C4'-*H*), 6.69 (dd, *J* = 8.4, 2.4 Hz, 2H, C2-*H*), 3.78 (s, 3H, -O*CH3*), 3.04 (s, 12H, N*CH3*), 2.47 (s, 1H, -O*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 151.9, 140.5, 136.7, 133.4, 124.6, 115.2, 113.6, 112.4, 103.6, 92.8, 88.7, 81.8, 55.2, 41.0.

HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{26}H_{26}N_2O_2Na$: 421.1886; found, 421.1883.

3.5b) *N*-(6-(dimethylamino)-9-((4-methoxyphenyl)ethynyl)-3*H*-fluoren-3-ylidene)-*N*-methylmethanaminium trifluoroacetate (3.TFA)



The procedure was similar to other dehydrations, using the carbinol **3'** in a NMR tube with the addition of 40µL of 1M solution of TFA-*d*[1] in $CDCl_3$. Dark brownish residue was recrystallized from CH_2Cl_2 / Et_2O to obtain pure compound **3.TFA** as dark powder with over 95% yield.

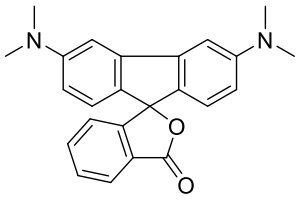
^{1}H NMR (400 MHz, $CDCl_3$): **3** exists as of mixture two isomers

Major: δ 7.43 (d), overlapped with 7.39 (d) (4H), 6.91 (d) overlapped with 6.85 (d) 6H), 3.82 (s, 3H), 3.37 (s, 12H).

Minor: δ 7.65 (d, *J* = 8.2 Hz, 2H, C1-*H*), 7.10 (br, 2H, C4-*H*), 6.99 (d, *J* = 9.1 Hz, 2H,), 6.36 (dd, *J* = 8.4 Hz, 2H, , C4-*H*), 5,48 (d, *J* =2.92, 2H, C4-*H*), 5.12 (d, *J* =2.92, 2H), 3.92 (s, 3H), 3.4 (s, 12H).

HRMS (ESI, m/z): $[M]^+$ Calcd. for $C_{26}H_{25}N_2O$: 381.1961; found, 381.1963.

3.6) 3,6-bis(dimethylamino)-3'*H*-spiro[fluorene-9,1'-isobenzofuran]-3'-one (4')



To the degassed and cooled to -100 °C (bath temperature, diethyl ether – liquid N_2) solution of *tert*-butyl-2-bromobenzoate (87 mg, 0.34 mmol) in anhydrous THF (3 mL), under Ar atmosphere, *tert*-butyllithium (180 µL of 1.9 M solution in pentane, ~0.681 mmol) was carefully introduced through a needle along the wall of the flask. Clear solution quickly turned yellowish. Mixture of reagents was stirred at -100 °C for next 20 min.

To this lithium reagent, cooled to -100 °C, degassed solution of ketone **5** (30 mg, 0.1126 mmol) in anhydrous THF (2 mL) was injected over 1-2 min along the wall of the flask. Disappearance of yellow fluorescence of the substrate was observed after the addition, the yellowish solution was stirred for additional 30 min. The cooling bath was removed and the mixture was allowed to warm up to ~0 °C (~30 min). The reaction mixture was quenched with saturated solution of $NaHCO_3$ (5 mL), diluted with water (50 mL), extracted with ethyl acetate (4×30 mL), the combined yellow organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and evaporated. The resulting yellowish residue was then chromatographed (EA / pentane, from 1:6 to 1:3, *v*/*v*) system to obtain pure compound **4** as off-white solid (32 mg, 0.086 mmol, yield 77%).

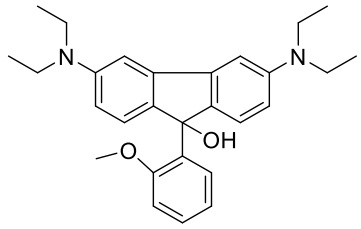
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 1H, C3'-*H*), 7.52 – 7.48 (m, 2H, C4'-*H*, C5'-*H*), 7.01 (d, *J* = 2.4 Hz, 2H, C4-*H*), 6.96 – 6.93 (m, 1H, C6'-*H*), 6.82 (d, *J* = 8.4 Hz, 2H, C1-*H*), 6.51 (dd, *J* = 8.4, 2.4 Hz, 2H, C2-*H*), 3.05 (s, 12H, N-C*H*$_3$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 152.2, 151.7, 142.4, 134.3, 130.8, 128.9, 126.5, 125.1, 124.8, 122.3, 111.8, 103.5, 92.7, 40.8.

HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{22}N_2O_2Na$: 393.1573; found, 393.1573.

Calcd. for $[C24H22N2O2 +H]^+$ 371.1754, found: 371,16813

3.7a) 3,6-bis(dimethylamino)-9-(4-methoxyphenyl)-9*H*-fluoren-9-ol (10')



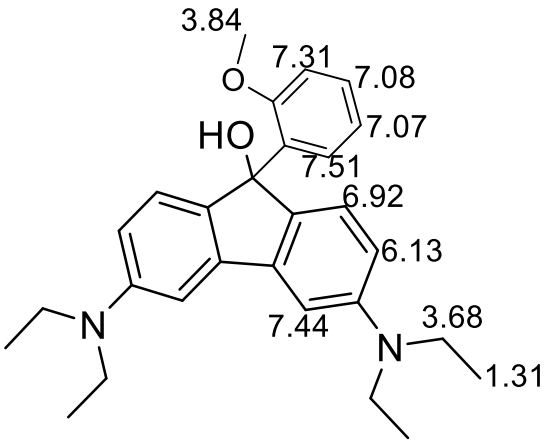
The title compound was synthesized according to the procedure described for **1a'** with a commercially available (2-methoxyphenyl) magnesium **11** (1 M) in THF. Addition to the ketone **5b** (22 mg, 0.1126 mmol) at low temperature. The crude reaction mixture was chromatographed (EtOAc / pentane, from 1:10 to 1:5, *v*/*v*) system to give the corresponding product **10'** as light yellow solid (41 mg, 0.112 mmol, yield 97%).

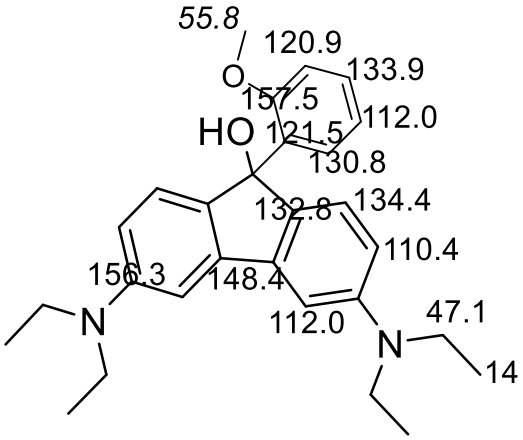
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (*dt*, *J*= 2.3, 7.5 Hz, 2H; C6′-*H*), 7.44 (br s, 2H; C4-*H*), 7.31 (*dd*, *J*= 1.5. 7.7 Hz, 1H; C3′-*H*), 7.08 (*dt*, *J*= 2.3, 7.3 Hz, 1H; *C4′-H*) overlapped with 7.07 (*d*, *J* = ca 8.5 Hz, *C5′-H*), 6.92 (*d*, *J*= 8.8 Hz, 2H; C1-*H*), 6.13 (*dd*, *J*= 2.3, 8.8 Hz, 2H; C2-*H*), 3.84 (s, 3H, -OC*H3*), 3.68 (br, overlapped 3.84, 4H, -N-C*H2*-), 1.31 (t, 3H, *J*= 6 Hz, -NCH2-C*H3*).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 157.5, 156.3, 148.4, 134.4, 133.9, 130.6, 129.2, 121.2, 120.9, 112.1, 110.7, 55.8, 46.8, 13.8.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 157.5, 156.3, 148.4, 133.9, 132.8, 130.6, 129.0, 121.58, 120.9, 114.0, 112.0, 110.4, 55.8, 47.1, 14.0.

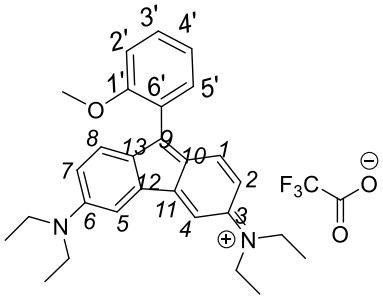
HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{26}N_2O_2Na$: 397.1892; found, 397.1886





Signals assignement for **10'**: 1H (left part of the molecule) based on 1D-, COSY, and 13C (right part based on **10**),

3.7b) *N*-(6-(dimethylamino)-9-(4-methoxyphenyl)-3*H*-fluoren-3-ylidene)-*N*-methylmethanaminium trifluoroacetate (10.TFA)



Carbinol **10'** (12 mg, 0.0223 mmol) was placed in 5 mL glass vial, dissolved in $CDCl_3$ (0.5 mL), and transferred to NMR tube (the first ^{1}H spectrum was recorded as a starting point). Next (40 µL) of 1M solution of TFA-d^1 in $CDCl_3$ was added. Progress of the reaction was monitored by ^{1}H NMR, first spectrum recorded after 5 min., showed full conversion of starting material. After 1h reaction mixture was evaporated and dried on vacuum. Dark brownish residue was recrystalised from CH_2Cl_2 / Et_2O to obtain pure compound **10.TFA** as rose-red powder (11 mg, 0.021 mmol, yield 94%).

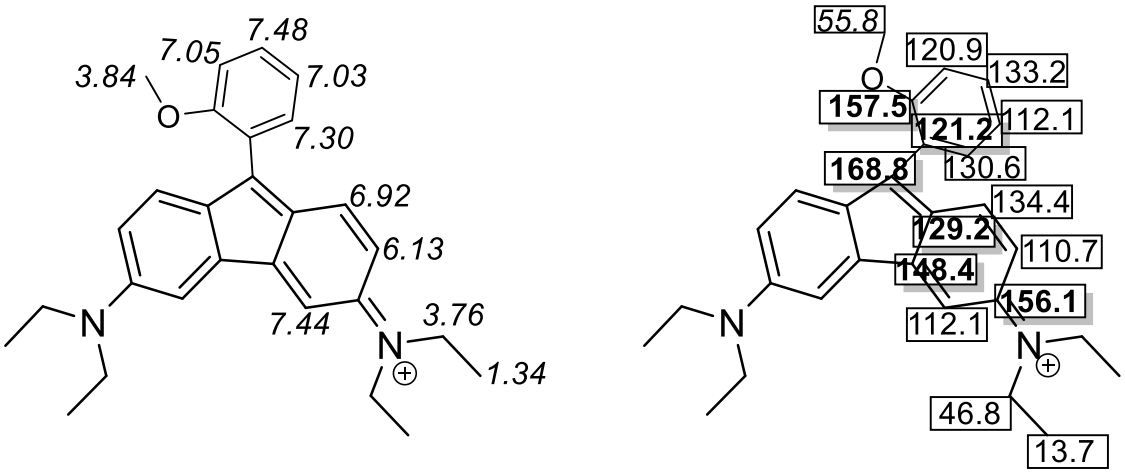
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (*dt*, *J*= 2.3, 7.5 Hz, 2H; C4′-*H*), 7.44 (br m, 2H; C4-*H*), 7.30 (*dd*, *J*= 1.5. 7.7 Hz, 1H; C6′-*H*), 7.05 (overlapped with 7.03 *m*, 1H; *C3′-H*, *C5′-H*), 6.92 (*d*, *J*= 9 Hz, 2H; C1-*H*), 6.13 (br *d*, *J* = 9.1 Hz, 2H; C2-*H*), 3.83 (s, 3H, $C_{2'}$-OC*H3*), 3.76 (br, overlapped with 3.83, 4H, -N-C*H2*-), 1.34 (t, 3H, *J*= 6.8 Hz, -NCH2-C*H3*).

HSQC: ^{1}H(**^{13}C**), 500 MHz, **125** MHz (in CDCl3)
δ 7.48 (**133.2,** C3′-*H*), 7.44 (**112.1**, C4-H), 7.30 (**130.6,** C6′-*H*), 7.05 (**120.9**, *C5′-H*) 7.03 (**112.1**, C4′-*H*), 6.87 (**134.4**, C1-*H*), 6.07 (**110.7**, C2-*H*), 3.83 (**55.8**, -OC*H3*), 3.76 (**46.8**, N-C*H2*-), 1.34 (**13.7,** -N CH2-*CH3*).

HMBC: ^{1}H(**^{13}C**), 500 MHz, **125** MHz (in CDCl3)
6.13 (**112.2**, **129.9**), 6.92 (**110.7, 148.4, 157.0, 168.8),** 7.06-7.07 (**112.2**, **130.6**, **121.2, 120.9, 157.5**, **168.8**), 7.30 (**133.2, 157.5**, **168.8**), 7.48 **(130.6, 157.5**).

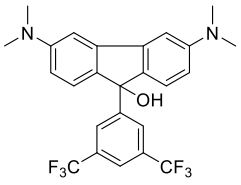
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8 (C9), 157.5 (C2‘), 156.1 (C3), 148.4 (C11), 134.4 (C1), 133.2 (C4‘), 130.6 (C6‘), 129.2 (C10), 121.2 (C1‘), 120.9 (C3’), 112.1 (C4’), 110.7 (C2), 55.8 ($C_{2'}$-O*C*H3), 46.8 (N *C*H2-CH3), 13.7 (N CH2-*C*H3*)*.

HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{28}H_{33}N_2O^+$: 413.2587; found: 413.2543;



Signals assignement for **10**: 1H (left), and 13C (rightt) based on HSQC (rectangle), with HMBC (bold, shaded rectangle), and H,H-COSY.

3.8a) 9-(3,5-bis(trifluoromethyl)phenyl)-3,6-bis(dimethylamino)-9*H*-fluoren-9-ol (12’)



The title compound was synthesized according to the procedure described for **1a’** from Mg (146 mg, 6.0 mmol), 1-bromo-3,5-bis(trifluoromethyl)benzene (1.465 g, 0.86 mL, 5.0 mmol) in THF (5.0 mL), (concentration of Grignard reagent has been determined as (0.59M). Addition to ketone **5a** (40 mg, 0.150 mmol) in THF (7.5 mL), was realised by (0.76 mL, 0.448 mmol) of GR. The crude reaction mixture was chromatographed (EA / pentane, from 1:10 to 1:5, *v*/*v*) system to give the corresponding product **12’** as yellowish solid (67 mg, 0.139 mmol, yield 93%).

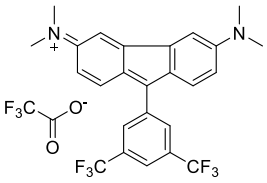
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (*br* s, 1H, C4’-*H*), 7.65 (d, 2H, C2’-*H*, C6’-*H*), 7.06 (d, *J* = 8.3 Hz, 2H, C1-*H*), 6.98 (d, *J* = 2.4 Hz, 2H, C4-*H*), 6.58 (dd, *J* = 8.3, 2.4 Hz, 2H, C2-*H*), 3.04 (s, 12H, N-C*H3*), 2.61 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 147.9, 141.1, 138.1, 131.1 (q, *J* = 33.1 Hz), 126.0 (d, *J* = 3.2 Hz), 124.8, 123.5 (q, *J* = 272.8 Hz), 120.7 (p, *J* = 3.4 Hz), 112.5, 103.7, 82.2, 40.9.

^{19}F NMR (564 MHz, $CDCl_3$) δ -62.63.

HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{23}F_6N_2O$: 480.1636; found 480.1624.

3.8b) *N*-(9-(3,5-bis(trifluoromethyl)phenyl)-6-(dimethylamino)-3*H*-fluoren-3-ylidene)--methylmethanaminium trifluoroacetate (12.TFA)



Carbinol **12'** (10 mg, 0.021 mmol) was placed in 5 mL glass vial, dissolved in $CDCl_3$ (0.5 mL), and transferred to NMR tube (the first ^1H spectrum was recorded as a starting point). Next (30 µL) of 1M solution of TFA-*d*[1] in $CDCl_3$ was added. Progress of the reaction was monitored by ^1H NMR, full conversion of starting material was not accomplished after 48h, additional portion of 1M solution of TFA-*d*[1] was added and NMR tube was placed in preheated oil bath, 40 °C for 1h. NMR analysis showed full conversion of starting material. Reaction mixture was evaporated and dried on vacuum. Dark brownish residue was recrystalised from CH_2Cl_2 / Et_2O to obtain pure compound **12.TFA** as dark reddish powder (12 mg, 0.025 mmol, yield 99%).

^1H NMR (600 MHz, $CDCl_3$) δ 8.06 (*br* s, 1H, C4'-*H*), 7.94 (*br* s, 2H, C2'-*H*, C6'-*H*), 7.69 (*br* s, 2H, C4-*H*), 6.88 (d, *J* = 9.0 Hz, 2H, C1-*H*), 6.22 (dd, *J* = 9.0, 1.8 Hz, 2H, C2-*H*), 3.42 (s, 12H, N-C*H*$_3$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2, 159.6 (q, *J* = 40.5 Hz, (TFA^-)), 157.9, 147.4, 133.5, 133.0 (q, *J* = 33.8 Hz), 132.8, 128.5 (d, *J* = 4.0 Hz), 128.4, 124.9 (p, *J* = 3.5 Hz), 122.73 (q, *J* = 273.2 Hz), 115.0 (q, *J* = 286.2 Hz, (TFA^-)), 112.8, 112.2, 41.9.

^{19}F NMR (564 MHz, $CDCl_3$) δ -63.00 (Ar-CF_3), -75.90.

HRMS (ESI, m/z): $[M]^+$ Calcd. for $C_{25}H_{21}F_6N_2$: 463.1603; found, 463.1603.

4) Supplementary Figures

4.1) Absorption spectra

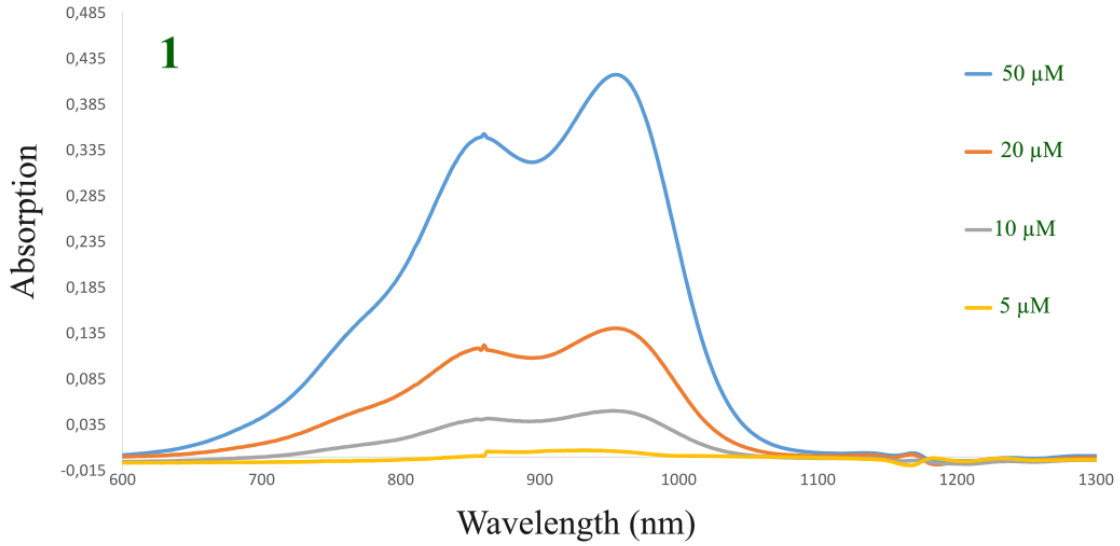


Figure S4. Absorption spectra of **1** at concentrations ranging from 50 µM (blue), 20 nm (orange), 10 nm (grey) and 5 µM yellow.

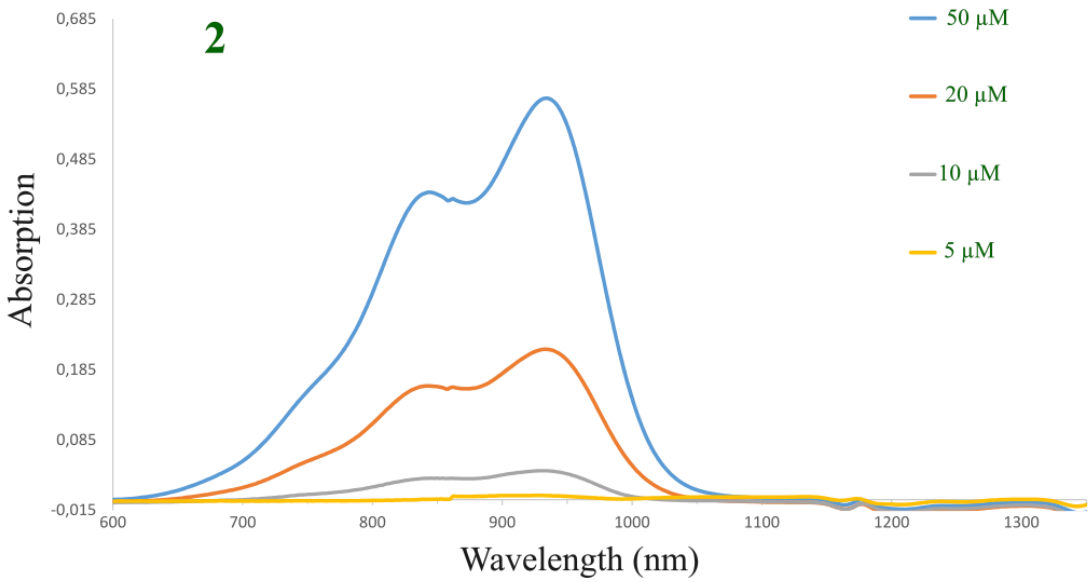


Figure S5. Absorption spectra of **2** at concentrations ranging from 50 µM (blue), 20 nm (orange), 10 nm (grey) and 5 µM (yellow).

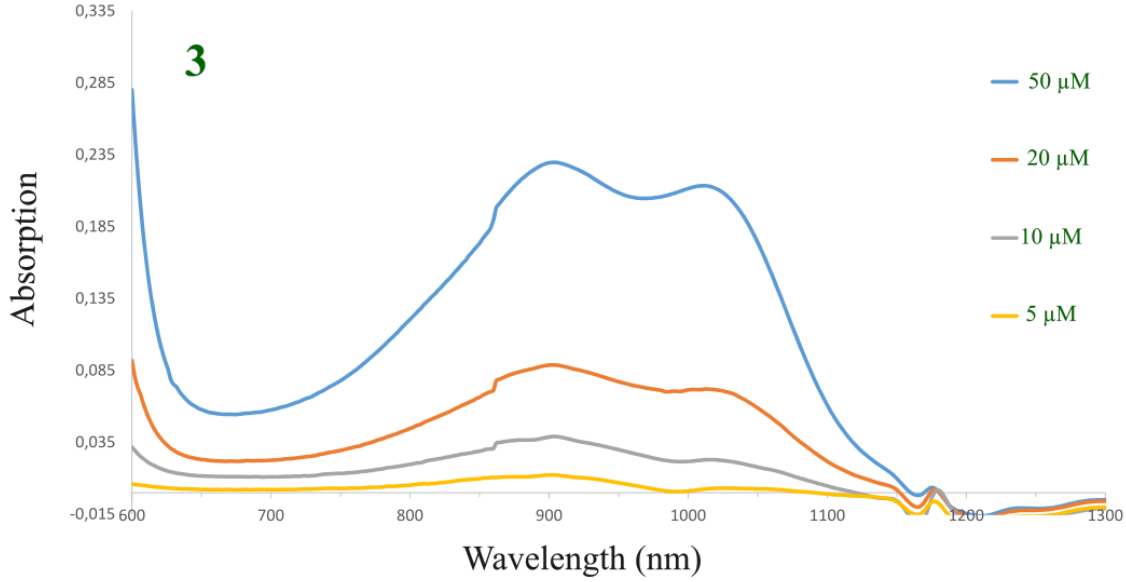


Figure S6. Absorption spectra of **3** at concentrations ranging from 50 µM (blue), 20 nm (orange), 10 nm (grey) and 5 µM yellow

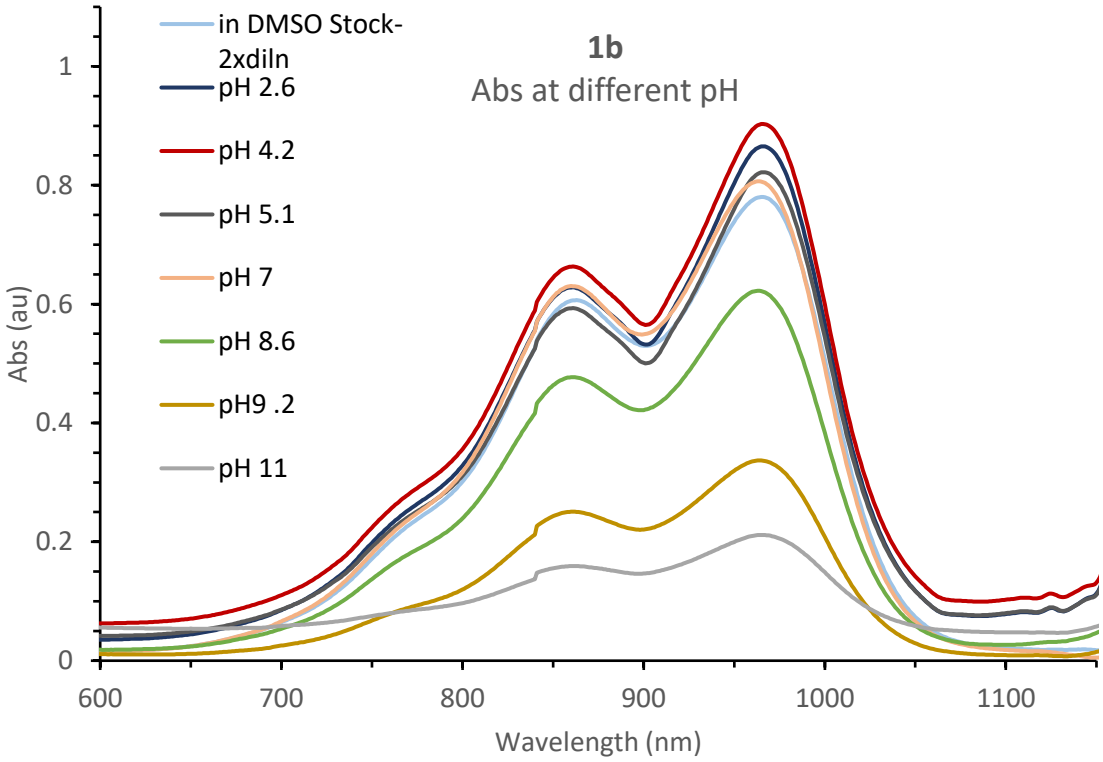


Figure S7. Absorption spectra of **1b** at different pH ranges (Conc. 50µM, prepared by diluting the DMSO stock solution with aqueous buffer in 1:1 ratio)

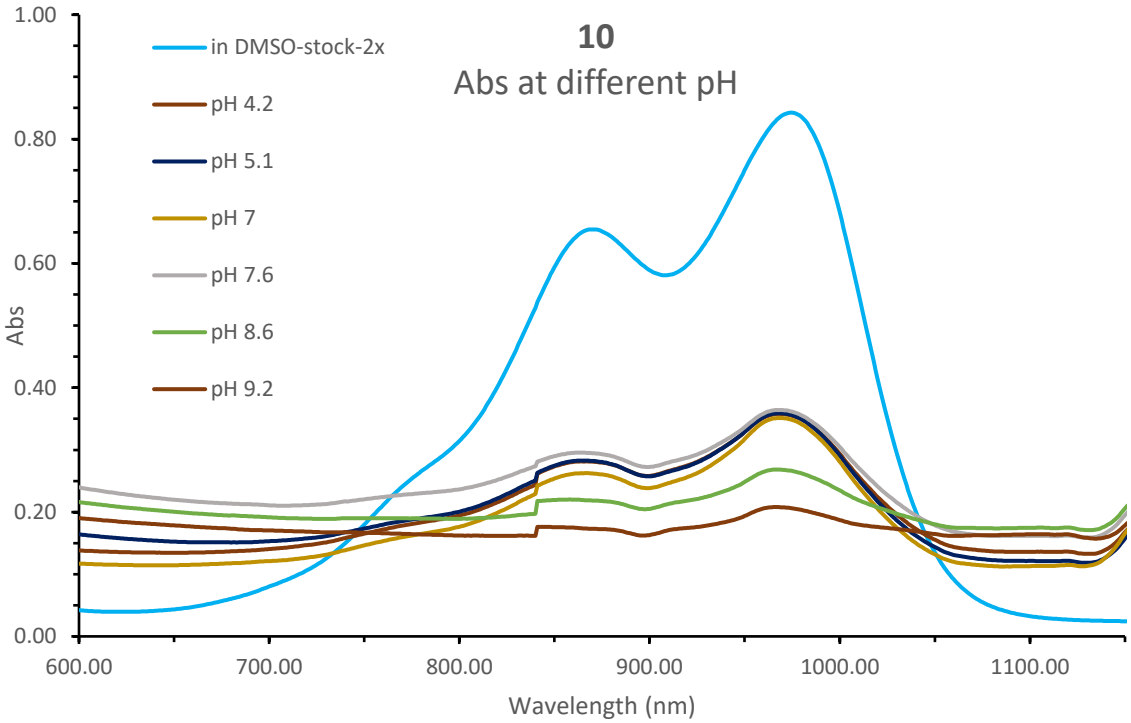


Figure S8. Absorption spectra of **10** at different pH ranges (DMSO stock Conc. 50 µM, and 20 µM prepared by diluting the DMSO stock solution with aqueous buffer in 5:2 ratio)

4.2) Fluorescence emission spectra at different pHs

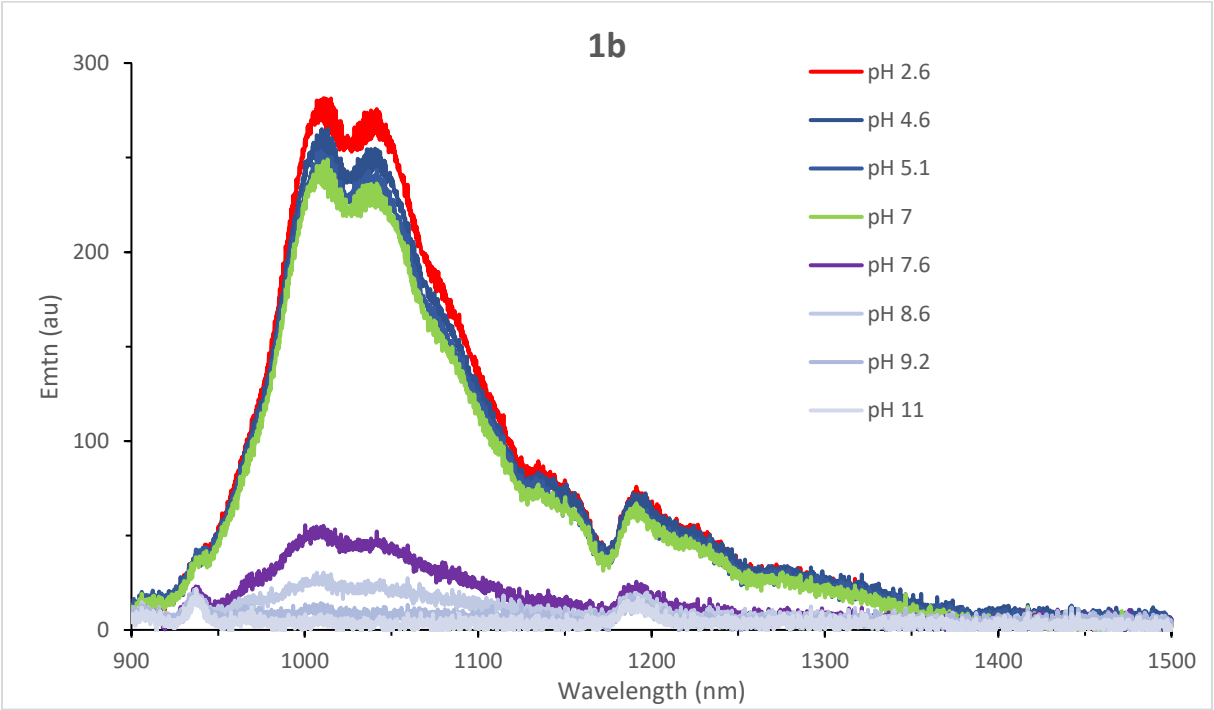


Figure S9. pH dependent fluorescence emission spectra of **1b** (with a 880 nm long pass filter, conc. 25 µM); quenching in basic buffer medium was observed.

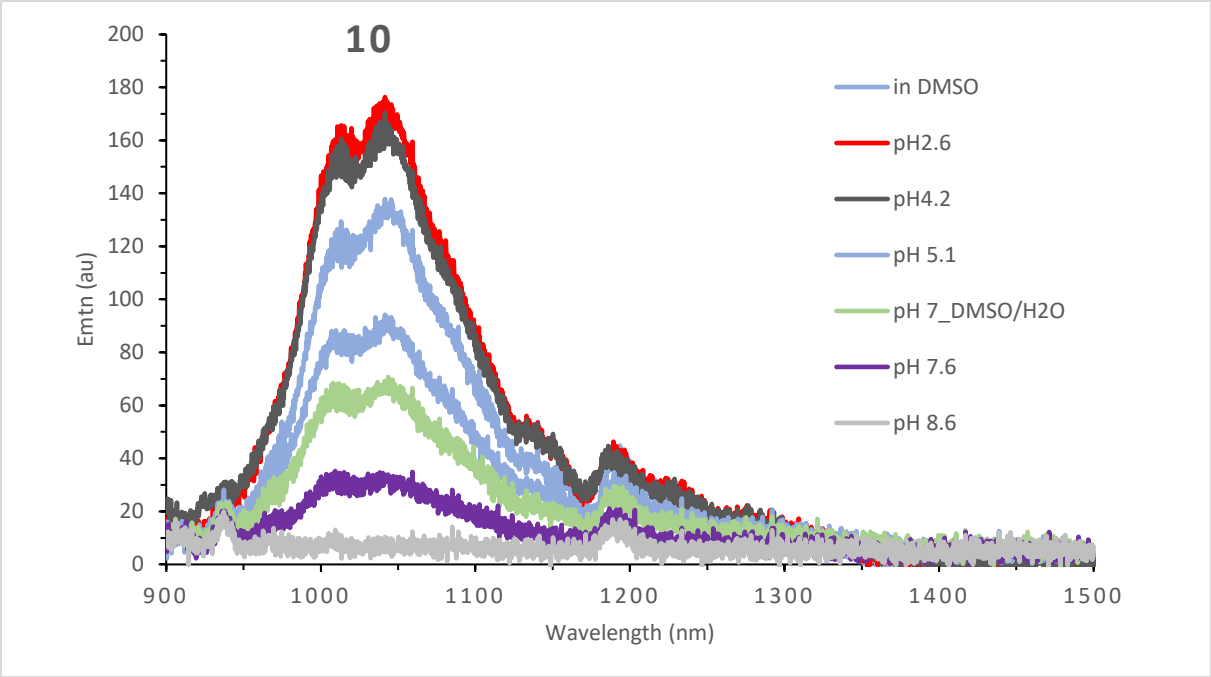


Figure S10. pH dependent emission spectra of **10** (with a 880 nm filter, conc. 20 µM), in 1:1 DMSO/buffer medium.

4.2) Determination of fluorescence quantum yields

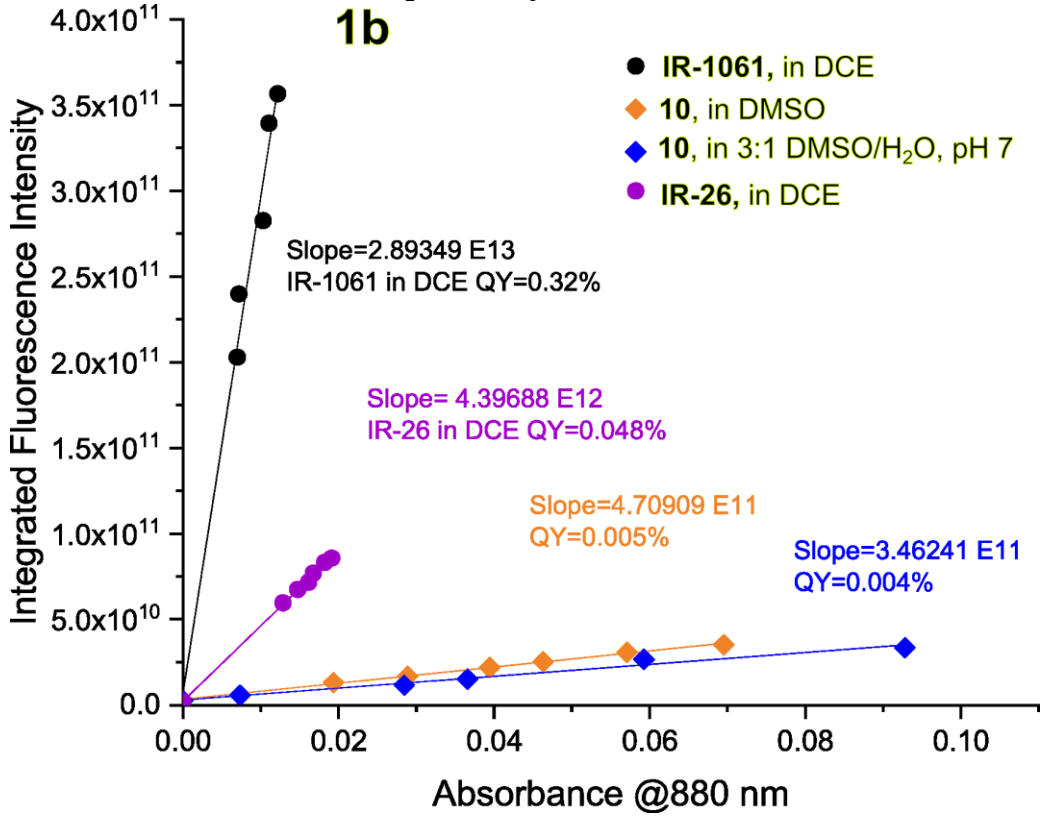


Figure S11. Determination quantum yield (Φ_{fl}) of **1b** with respective to IR-26 and IR-1061 as reference, based on integrated fluorescence intensity vs absorbance (previoulsly determined Φ_{fl} of IR-26 = 0.048%, and IR-1061 = 0.32% in DCE).

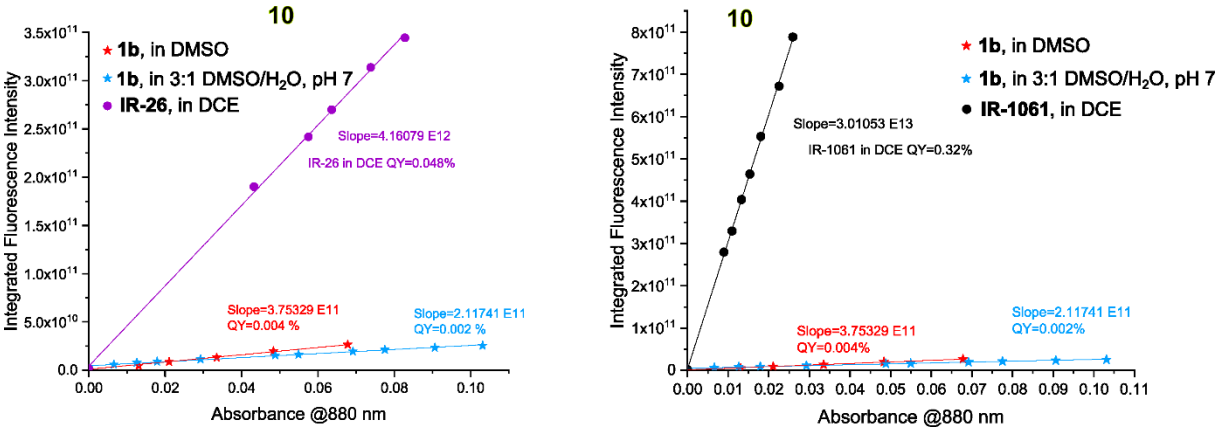


Figure S12. Determination of quantum yield (Φ_{fl}) of **10** with respective to IR-1061, IR-26 references, based on integrated fluorescence intensity vs absorbance (previoulsly determined Φ_{fl} of IR-26 = 0.048%, and IR-1061 = 0.32% in DCE).

4.3) Computational Details

4.3a) TF-DFT predicted spectra with respective maxima

In water:

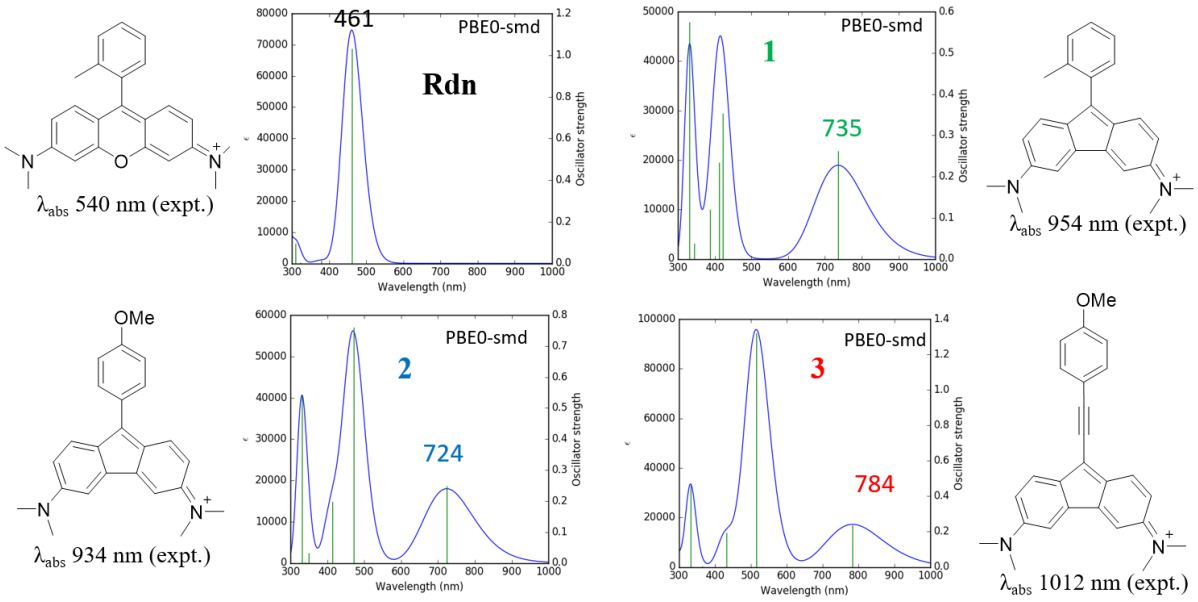


Figure S13a. The TD-DFT (PBE0, in water) predicted optical spectra with oscillator strength (y-axis) of three dyes (**1-3**), along with rhodamine (Rdn) for comparison to estimate the prediction error.

In DMSO:

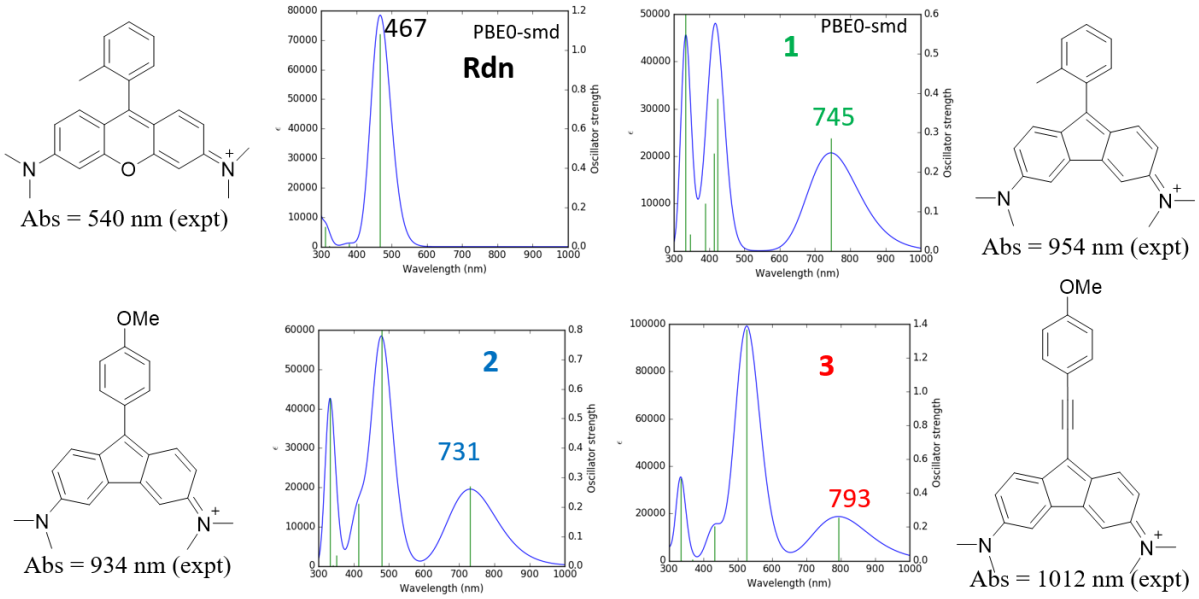


Figure S13b. The TD-DFT (PBE0, in DMSO) predicted optical spectra with oscillator strength (y-axis) of three dyes (**1**-**3**), along with rhodamine (Rdn) for comparison to estimate the prediction error.

Table S2. TD-DFT computed absorption wavelengths (λ_{max}) and HOMO→LUMO energy gap ($\Delta E_{H\text{-}L}$) using two different types of basis sets

Compd.	PBE0(SMD:DMSO)/Def2TZVPP		PBE0(SMD:DMSO)/6-311G(d,p)	
	λ_{max} (nm)	$\Delta E_{H\text{-}L}$ (eV)	λ_{max} (nm)	$\Delta E_{H\text{-}L}$ (eV)
Rdn	467	3.14	566	3.13
1a	745	2.30	741	2.29
2	731	2.34	727	2.33
3	793	2.14	788	2.13

4.3b) Computational methods

All the geometries were optimized with Gaussian 16 program package,[5] using long-range dispersion corrected hybrid density functional, ωB97X-D.[6] All atoms were treated with the Ahlrichs split-valance polarization basis function def2-TZVP.[7] The geometries were optimized without any symmetry constraints. Harmonic force constants were computed at the optimized geometries to characterize the stationary points as minima or saddle points. The solvent effects

[5] M. J. Frisch *et al*, *Gaussian 16, Revision C.02,*, Gaussian, Inc., Wallingford CT, **2019**..
[6] J. D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys*. **2008**, *10*, 6615.
[7] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys*. **1992**, 97, 2571.

(DMSO: ε = 46.826) were evaluated implicitly by a self-consistent reaction field (SCRF) approach using the SMD continuum solvation model for geometry optimization.[8] Time-dependent DFT (TD-DFT) calculations were performed using hybrid exchange and correlation functional of Perdew, Burke, and Ernzerhof, called PBE0[9] which includes Hartree-Fock (HF) exchange in a 3:1 ratio of PBE to HF, and basis function def2-TZVPP. Natural population analysis was conducted using the natural bonding orbital, NBO program, Version 6.[10]

Full Reference for Gaussian 16, Revision C.02,

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2019**.

[9] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J Phys Chem B* **2009**, *113*, 6378.
[10] C. Adamo, V. Barone, *J. Chem. Phys*. **1999**, *110* (13), 6158.
[10] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.

Cartesian coordinates (Å) of the optimized structures at ωB97X-D(SMD-DMSO)/def2-TZVP level of theory.

Rdn

C	3.624236	0.050862	-0.115173
C	2.486509	0.786416	-0.153169
C	1.204078	0.179439	-0.139098
C	1.175207	-1.233590	-0.084196
C	2.311452	-2.001953	-0.045609
C	3.576244	-1.380582	-0.056132
C	0.000002	0.887709	-0.164145
C	-1.175235	-1.233574	-0.084190
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1a

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2

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H	6.991530	0.179174	-1.612440
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3

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H	-6.204330	-4.223931	0.002392
C	-3.916337	-5.267431	-0.001826
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C	-0.130108	-0.042465	-0.004067
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C	6.016590	0.940823	0.002845
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C	6.667962	-0.294748	0.001732
H	6.440246	-2.427524	-0.003436
H	6.574849	1.865730	0.006015
O	7.997433	-0.442590	0.004594
C	8.813274	0.721224	0.010576
H	9.840615	0.364668	0.012763
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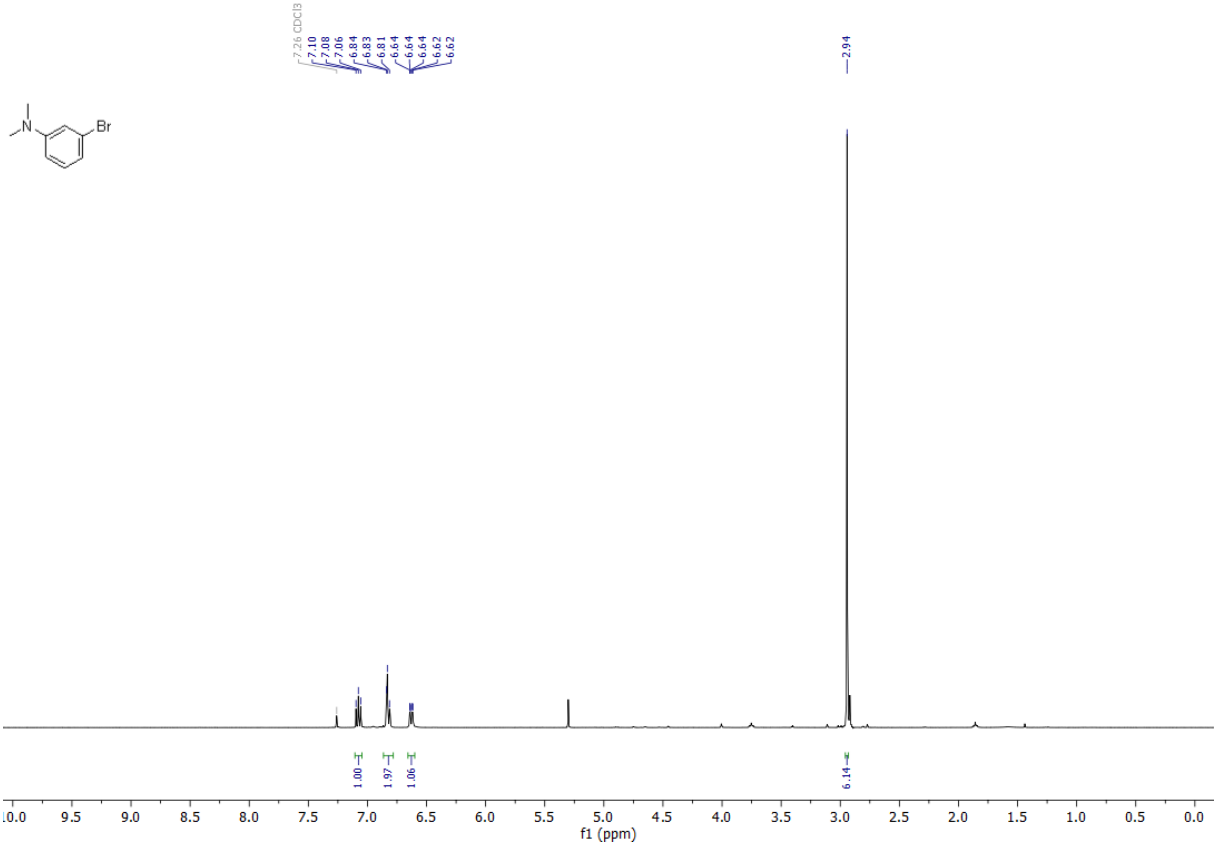
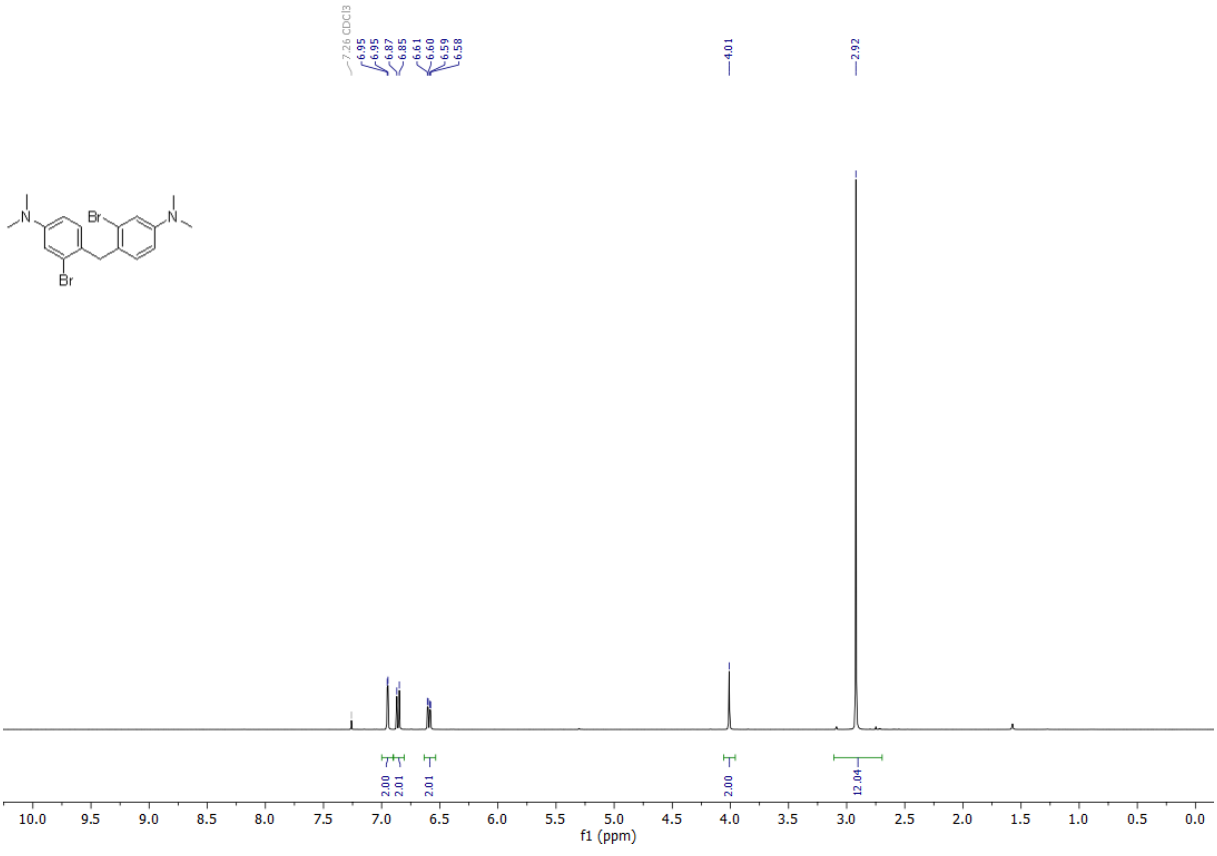
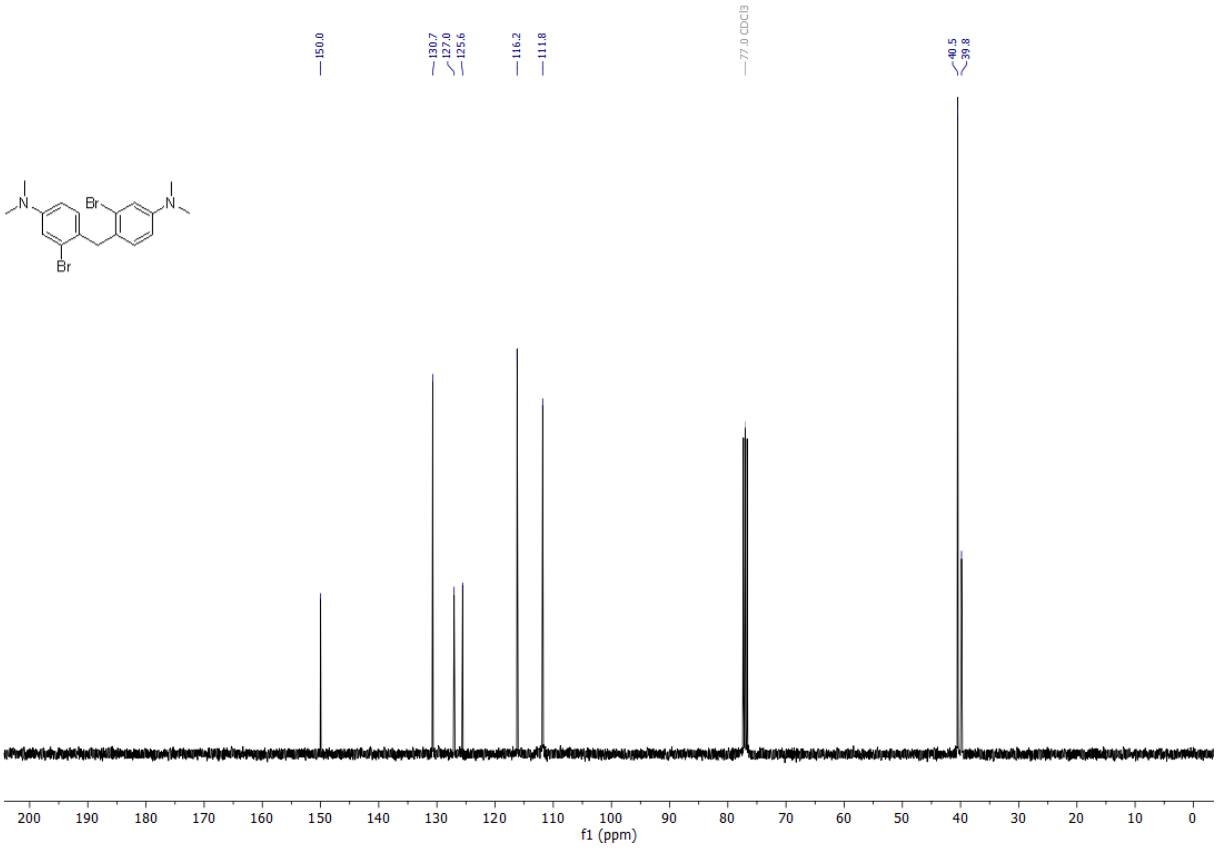
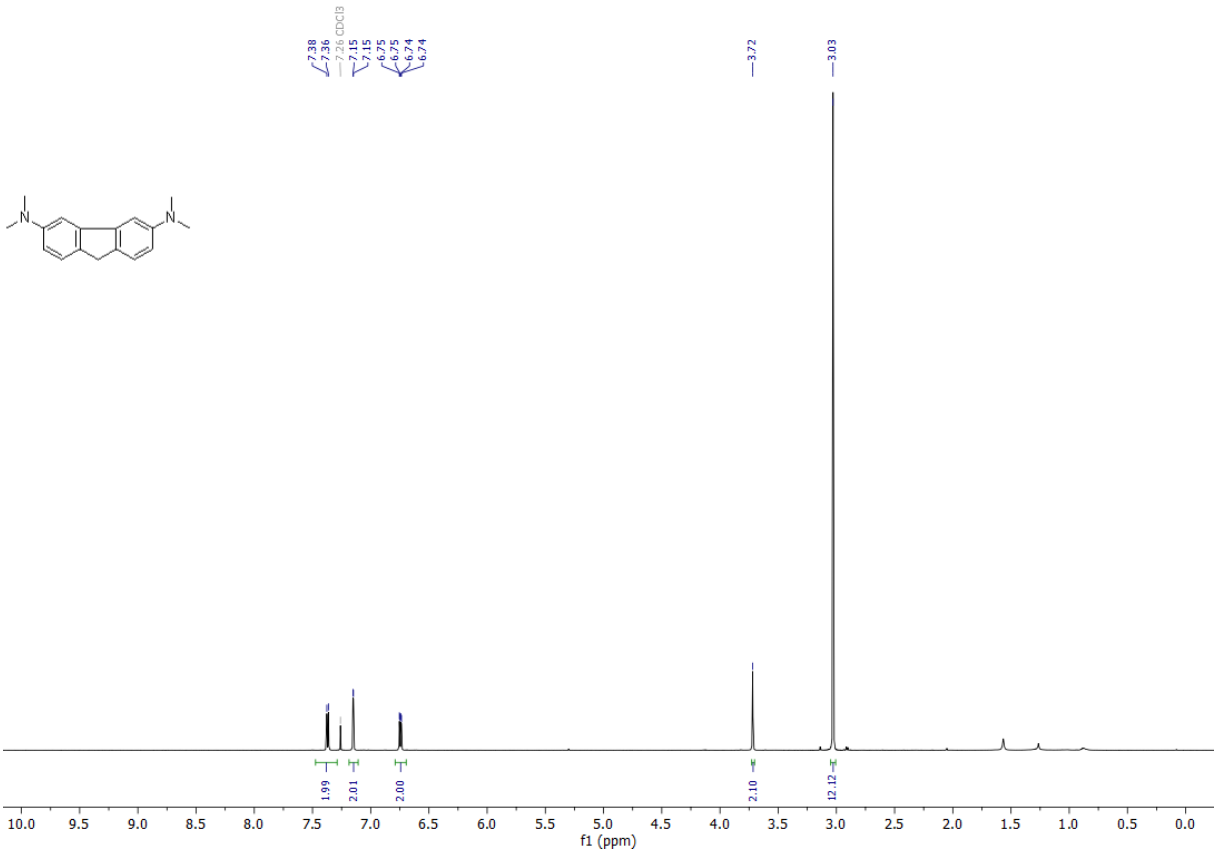
5) NMR spectra

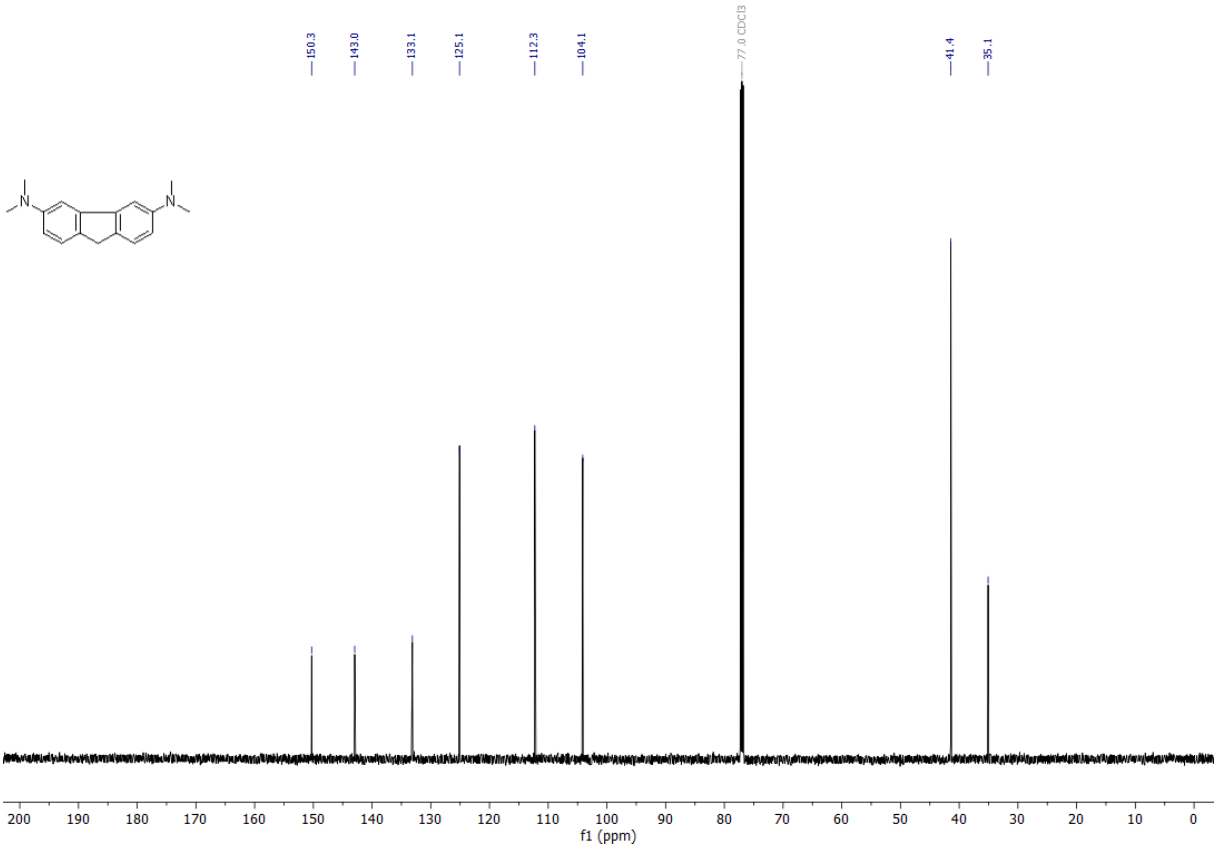
5.1) Precursors towards the compound 5

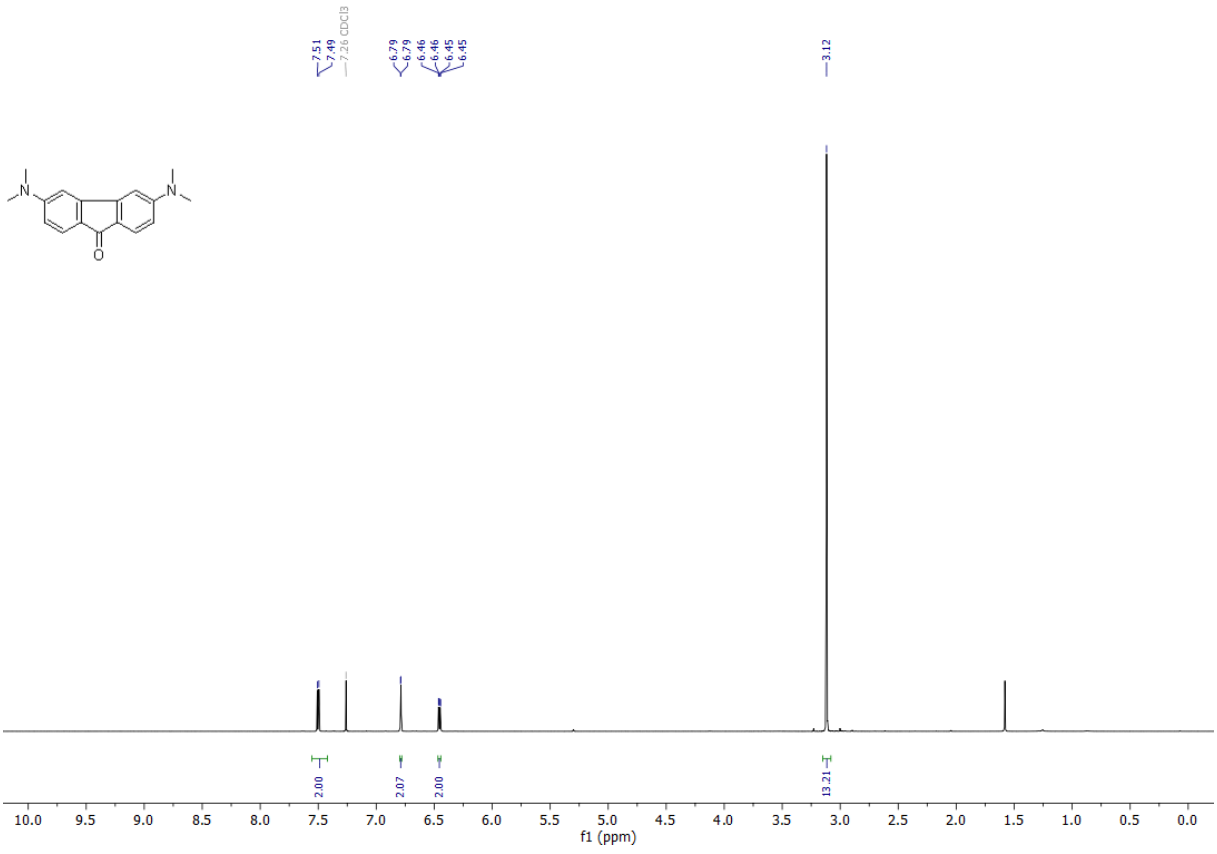


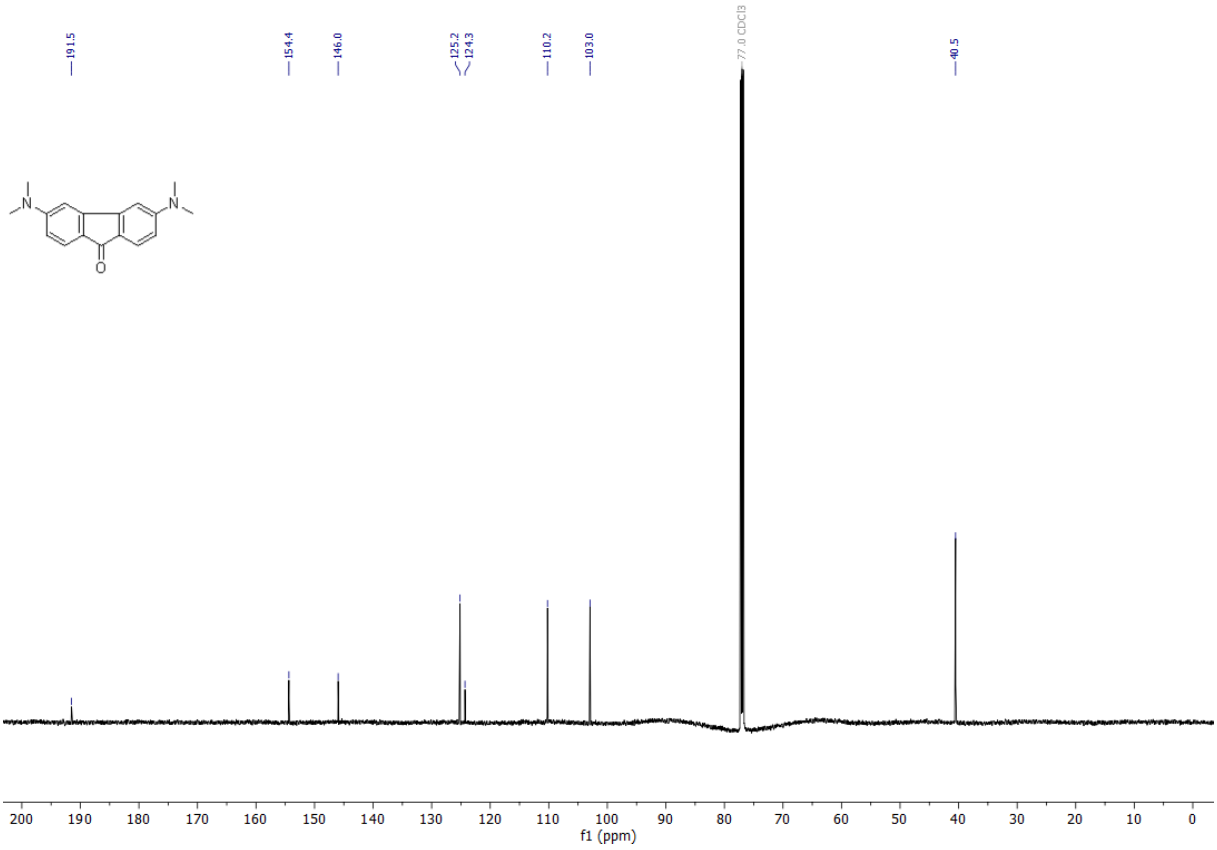



150.0
130.7
127.0
125.6
116.2
111.8
77.0 CDCl3
40.5
39.8
Br
Br
f1 (ppm)

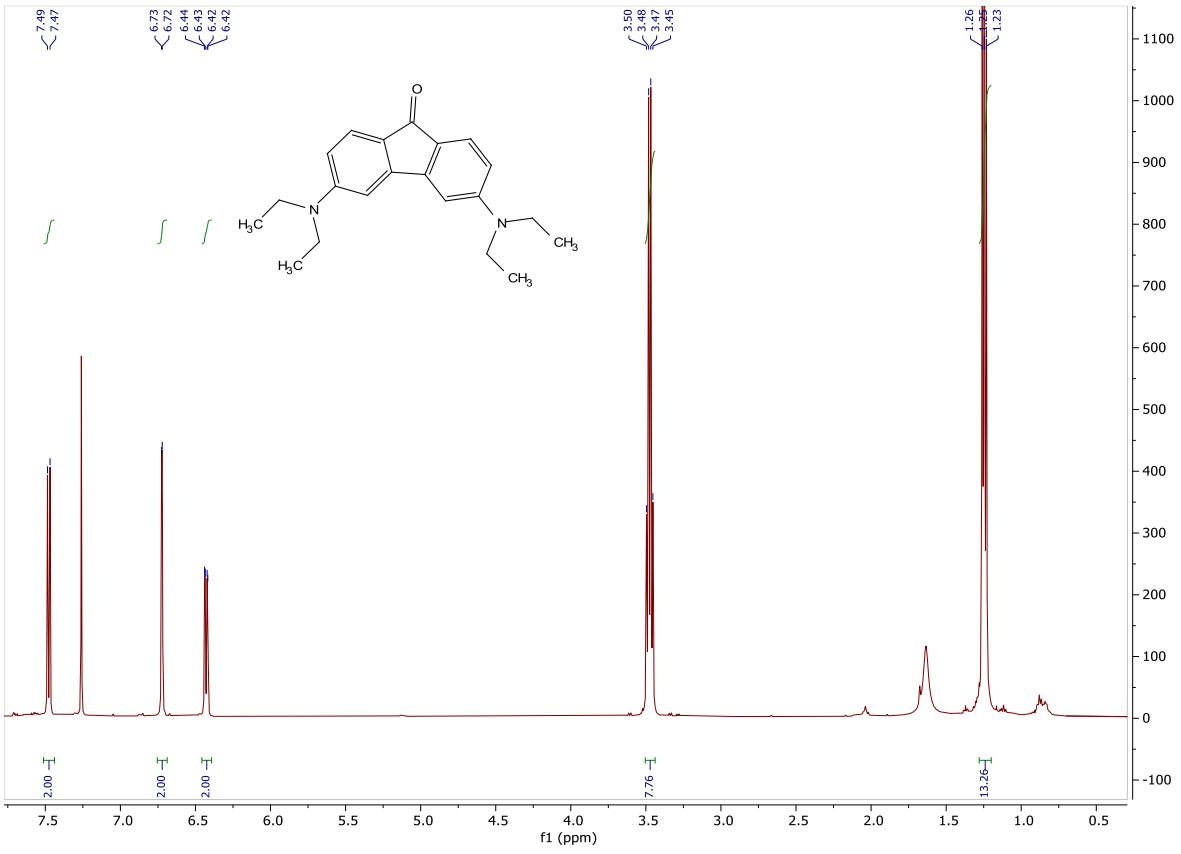

7.38
7.36
7.26 CDCl3
7.15
7.15
6.75
6.75
6.74
6.74
3.72
3.03
1.99
2.01
2.00
2.10
12.12
f1 (ppm)


150.3
143.0
133.1
125.1
112.3
104.1
77.0 CDCl3
41.4
35.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

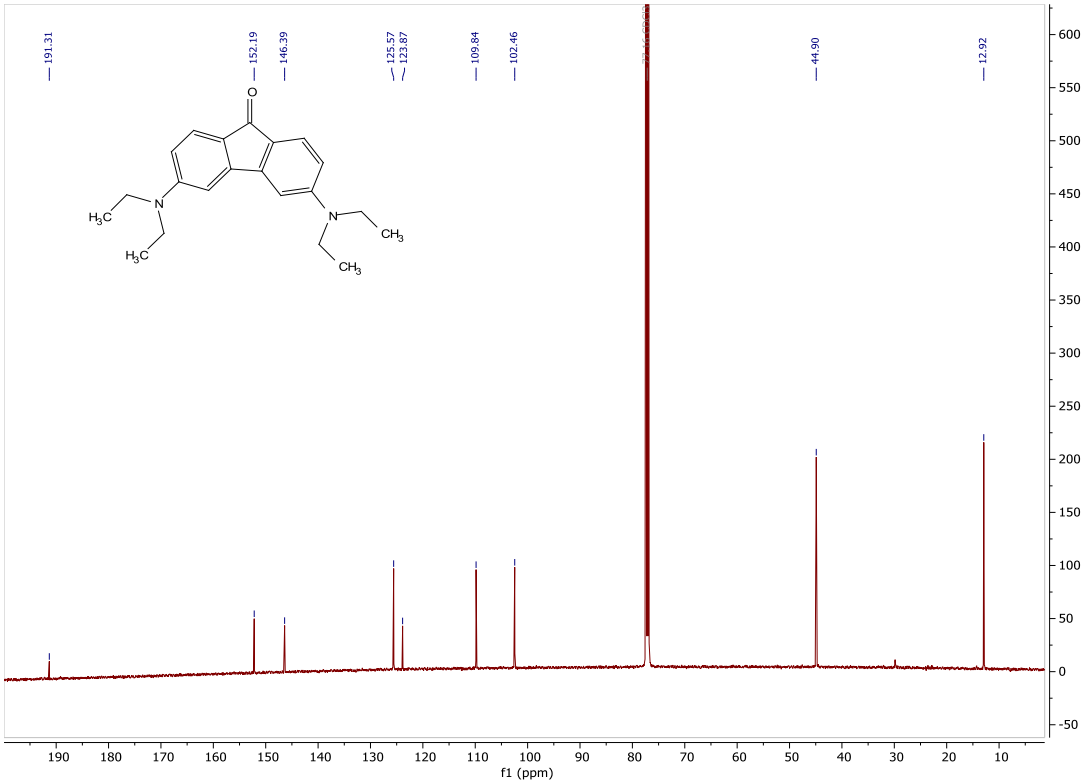

7.51
7.49
7.26 CDCl3
6.79
6.79
6.46
6.46
6.45
6.45
3.12
2.00
2.07
2.00
13.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

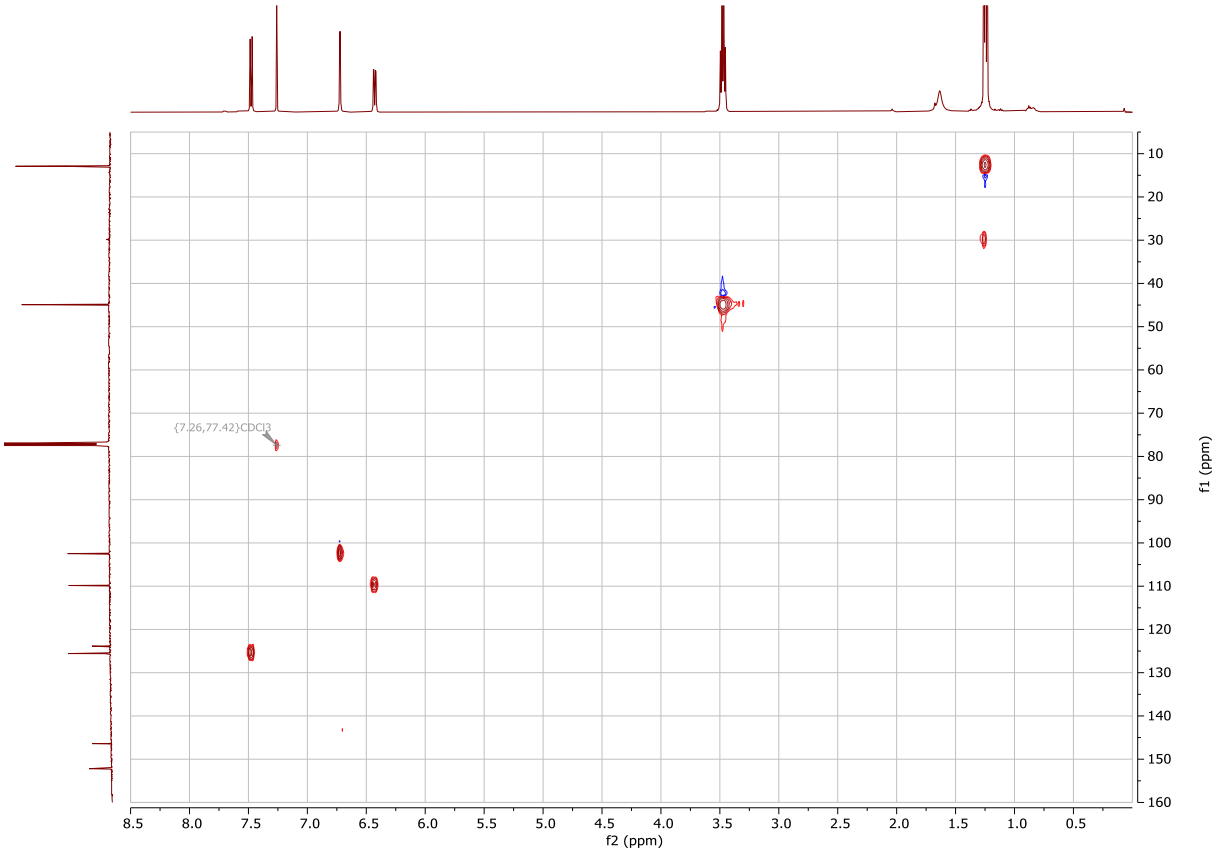


3,6-bis(diethylamino)-9H-fluoren-9-one (5b):

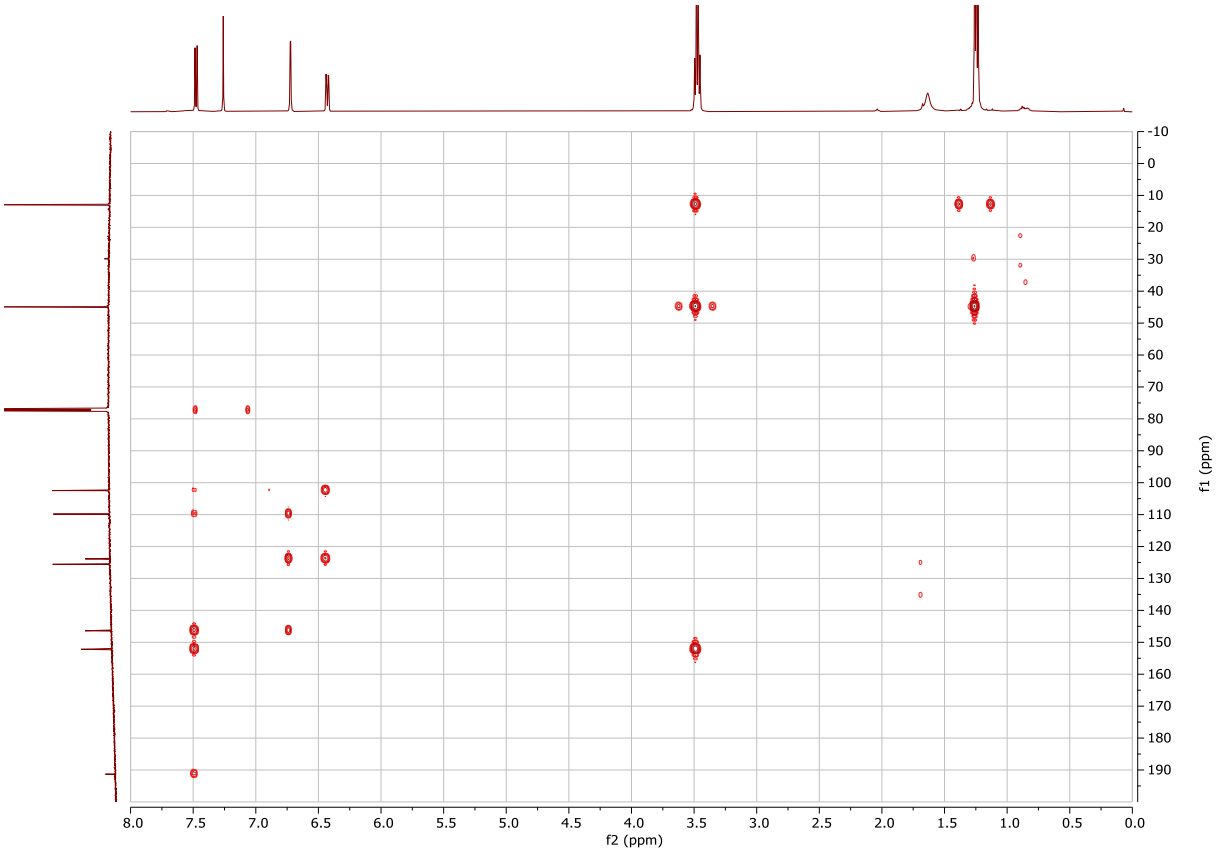


13C NMR

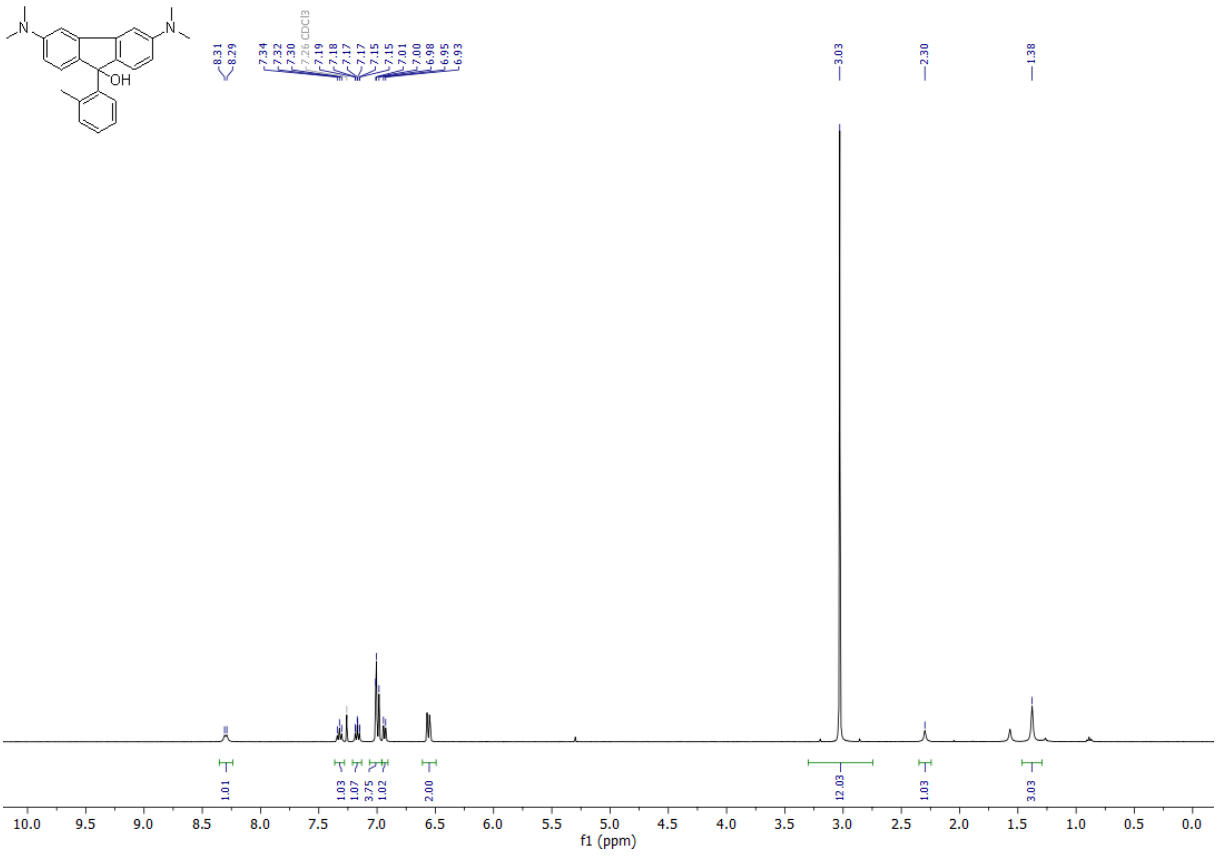


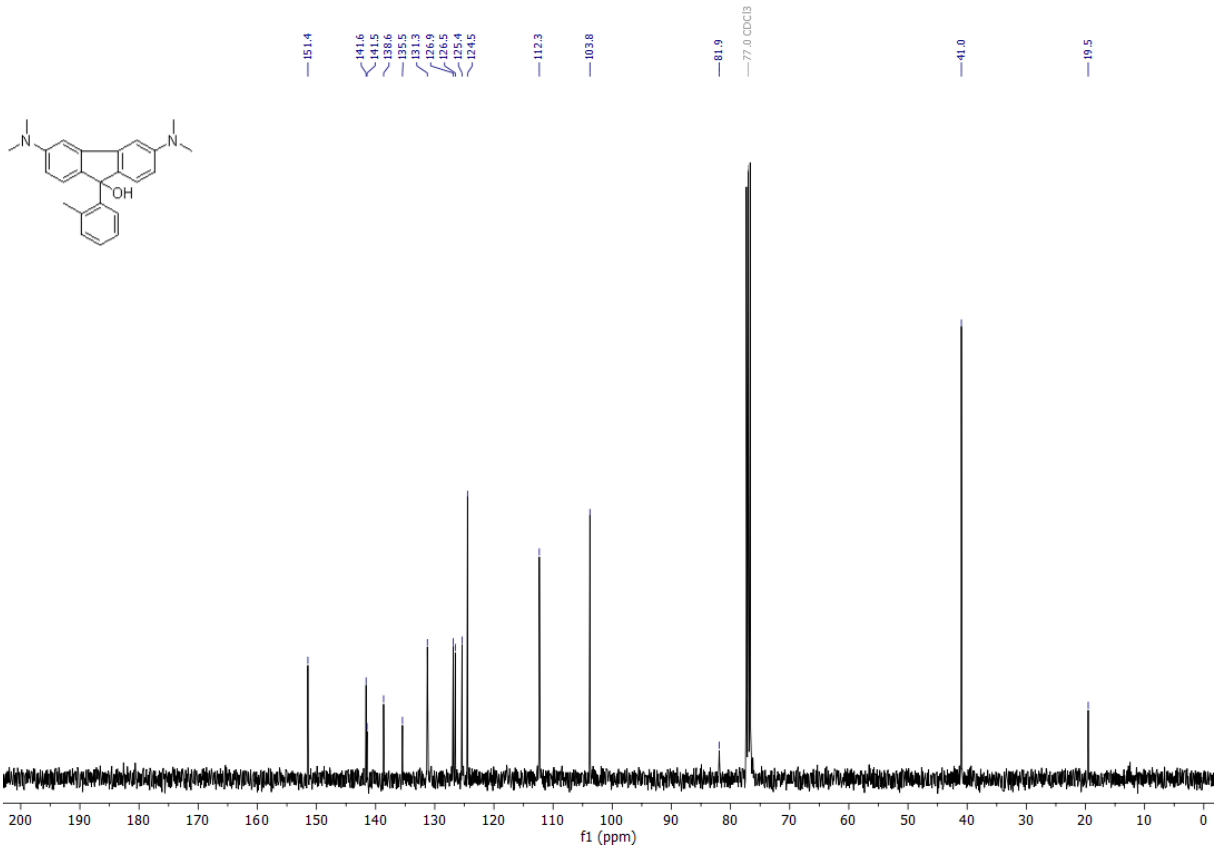


^{1}H, ^{13}C-HSQC

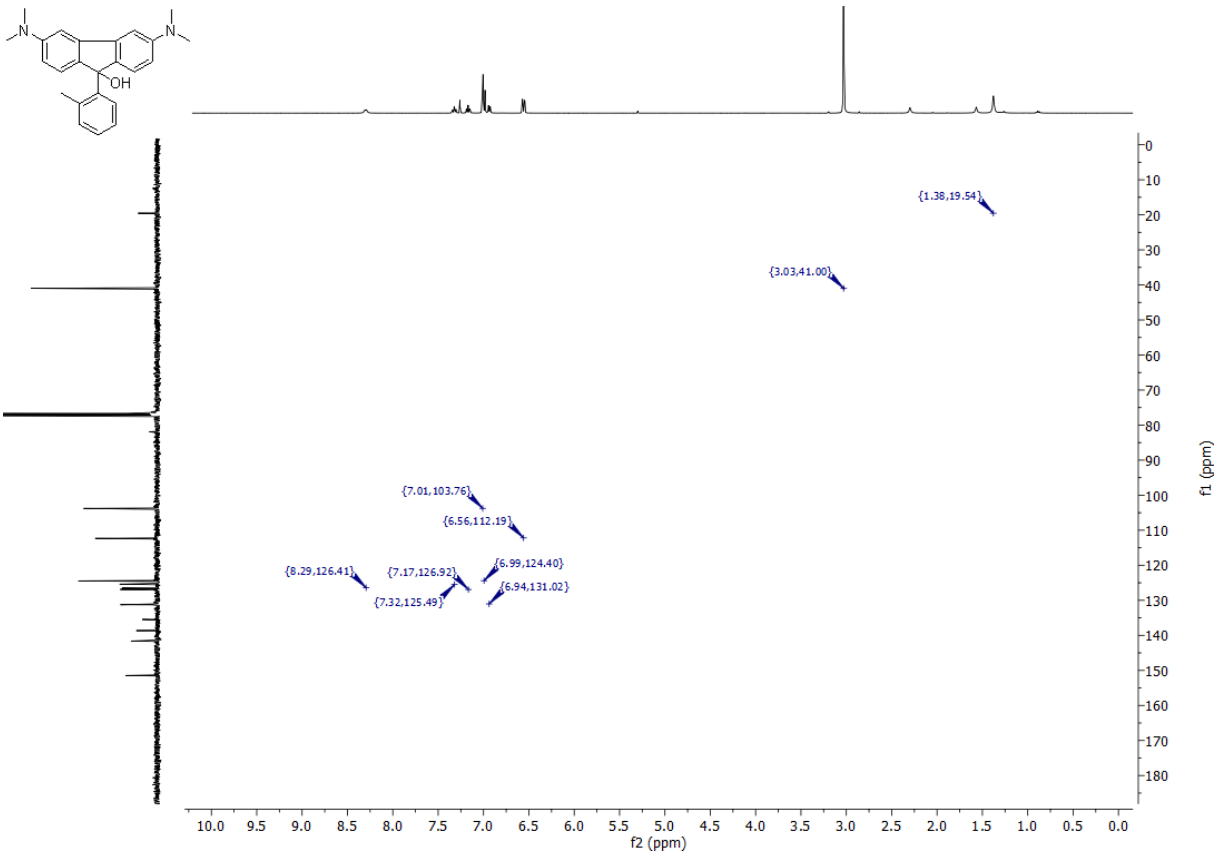

f2 (ppm)
f1 (ppm)

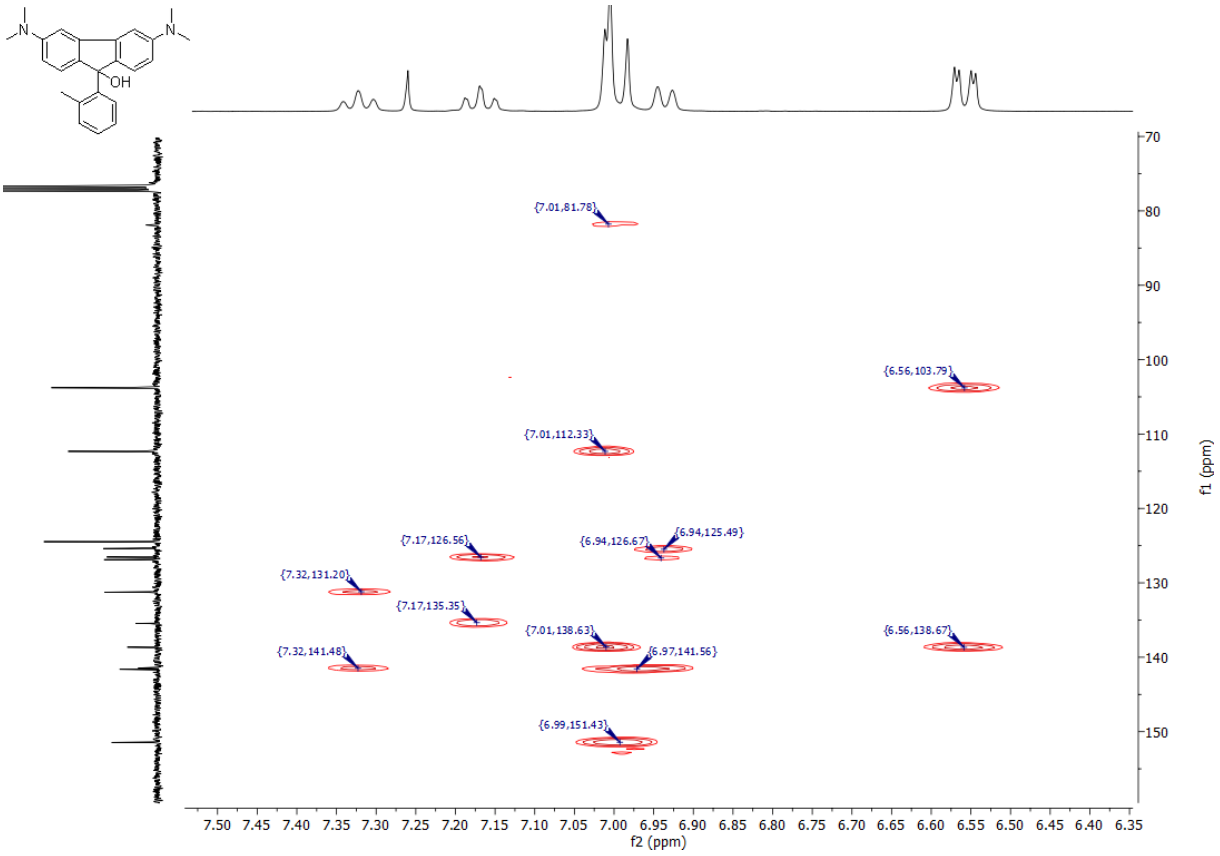
5.2) NMR spectra towards compound 1a

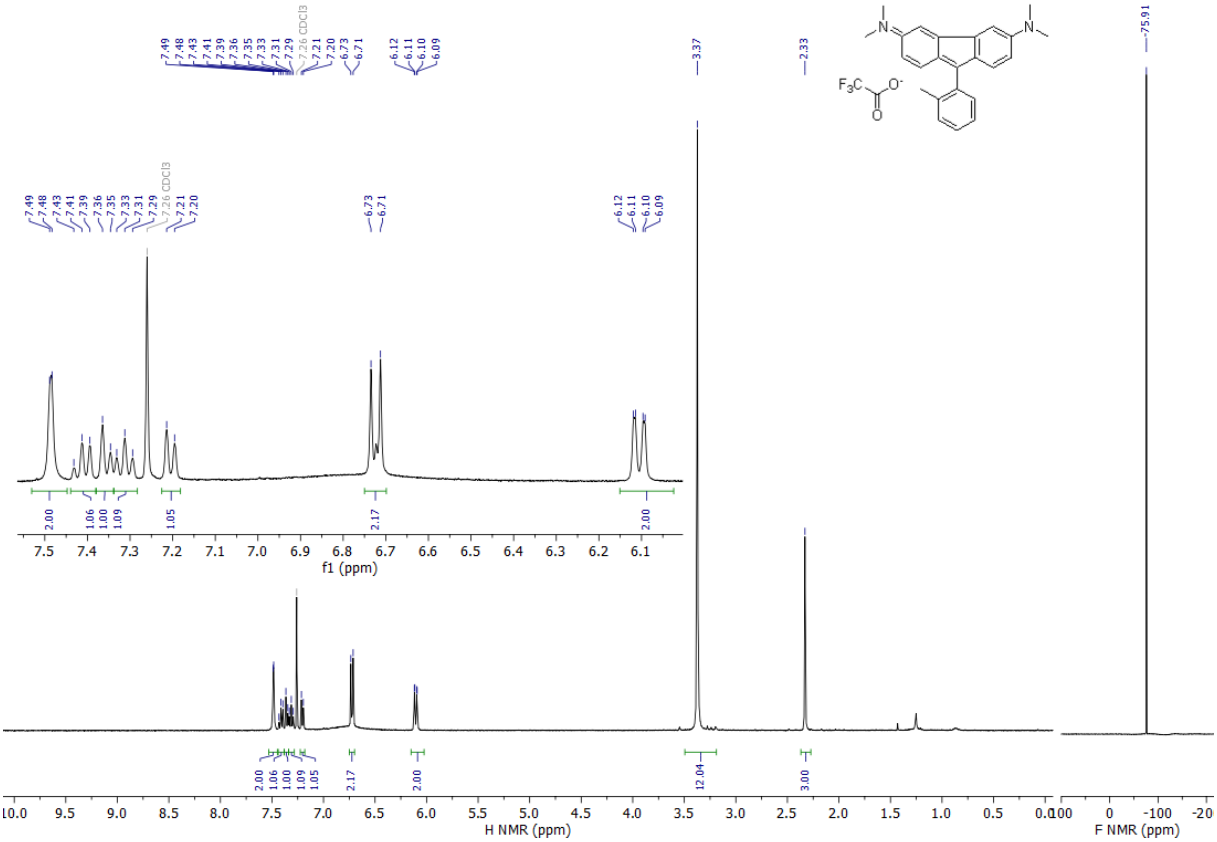


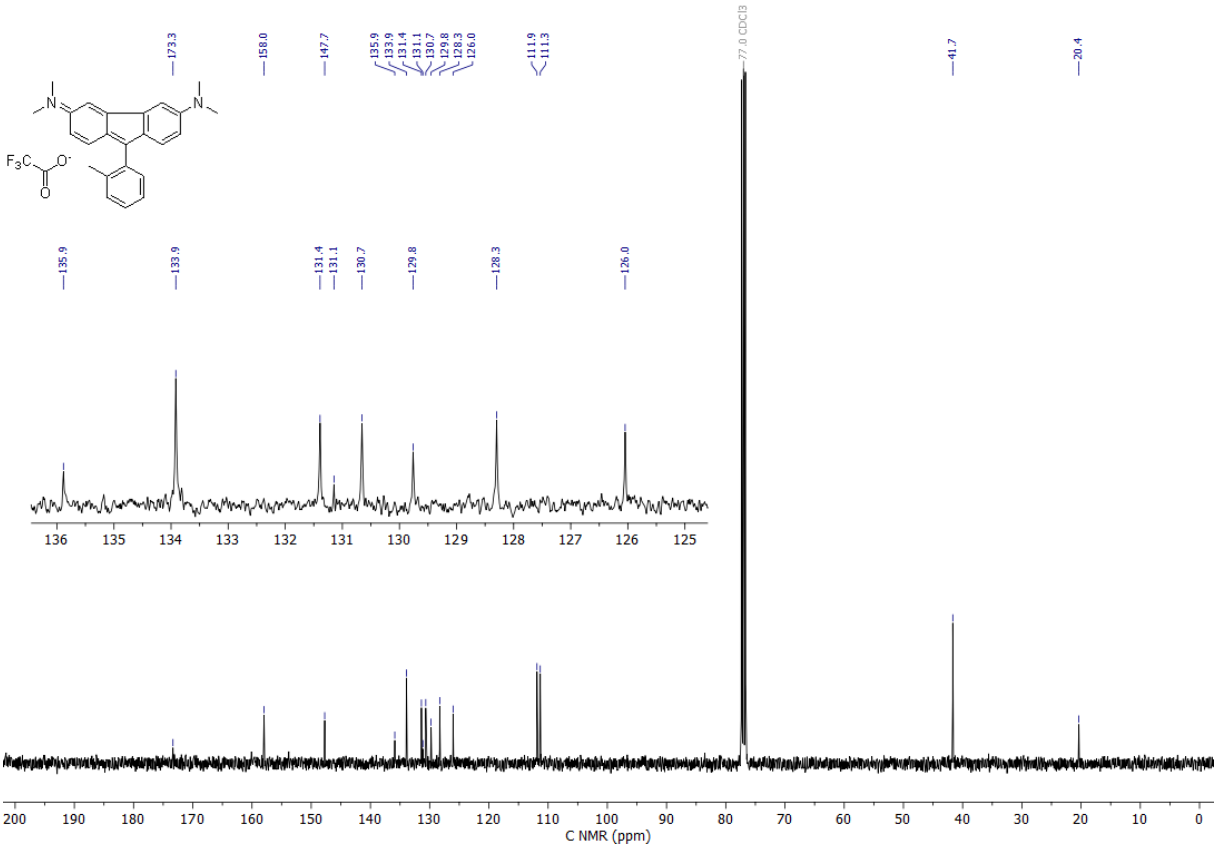


^{1}H, ^{13}C HSQC

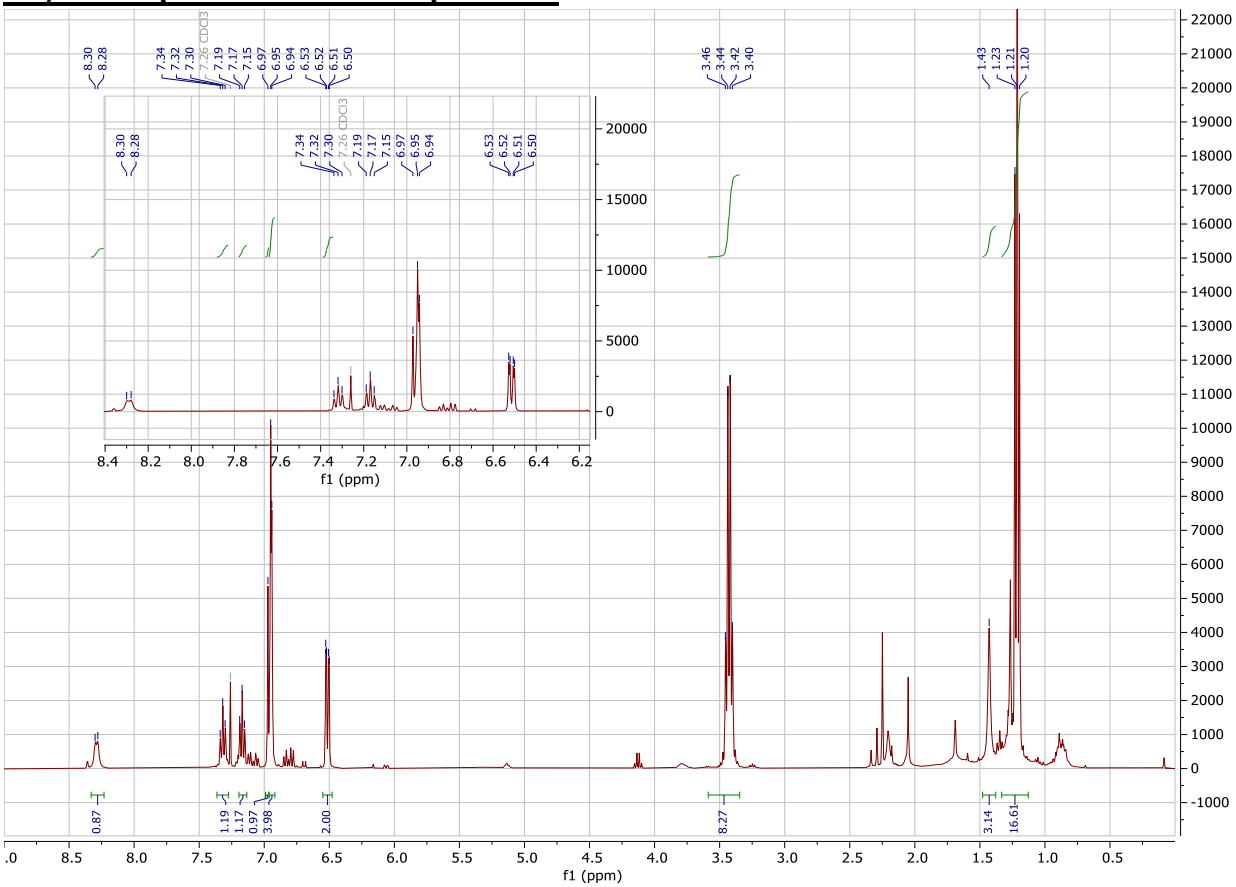

{1.38,19.54}
{3.03,41.00}
{7.01,103.76}
{6.56,112.19}
{8.29,126.41}
{7.17,126.92}
{6.99,124.40}
{6.94,131.02}
{7.32,125.49}
f1 (ppm)
f2 (ppm)

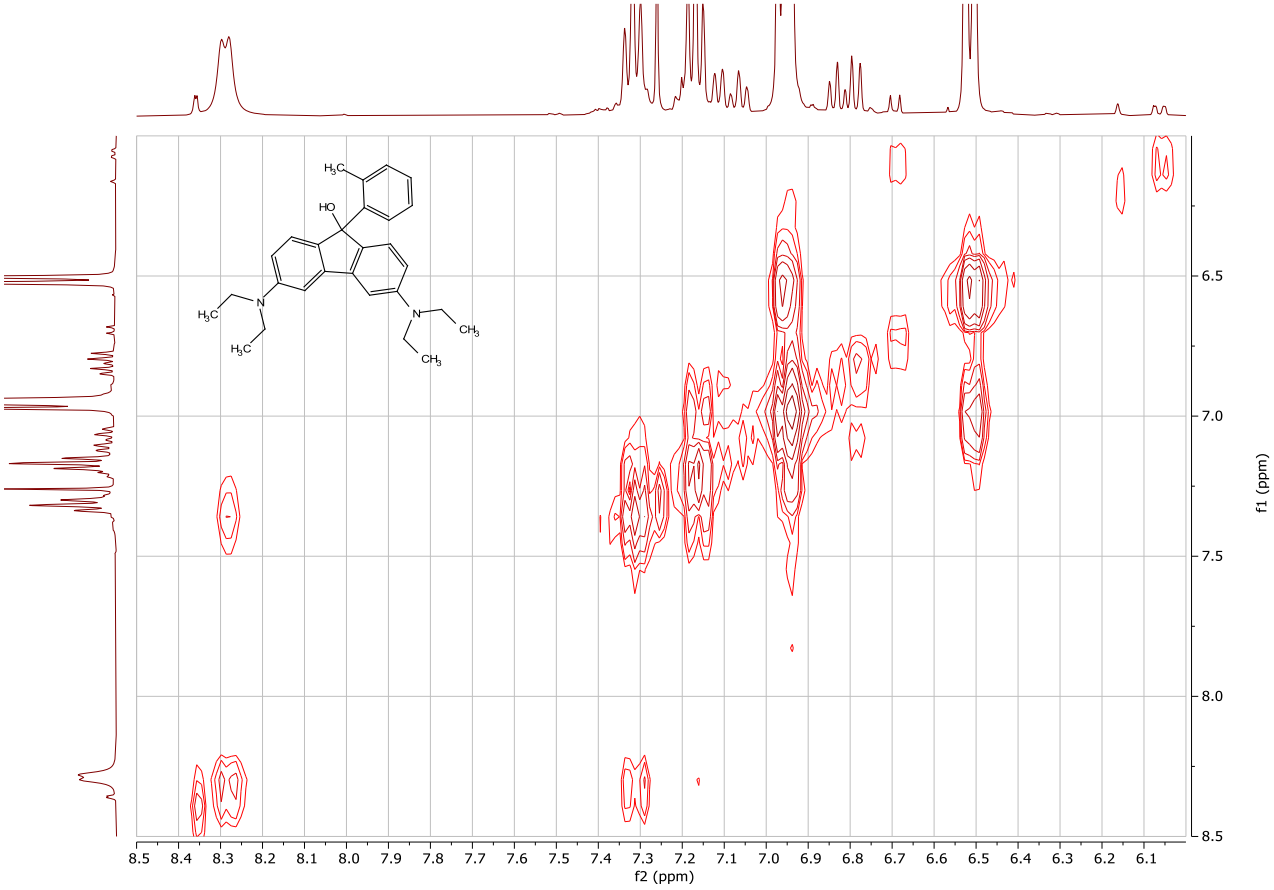

{7.01,81.78}
{6.56,103.79}
{7.01,112.33}
{7.17,126.56}
{6.94,126.67}
{6.94,125.49}
{7.32,131.20}
{7.17,135.35}
{7.01,138.63}
{6.56,138.67}
{7.32,141.48}
{6.97,141.56}
{6.99,151.43}
f1 (ppm)
f2 (ppm)

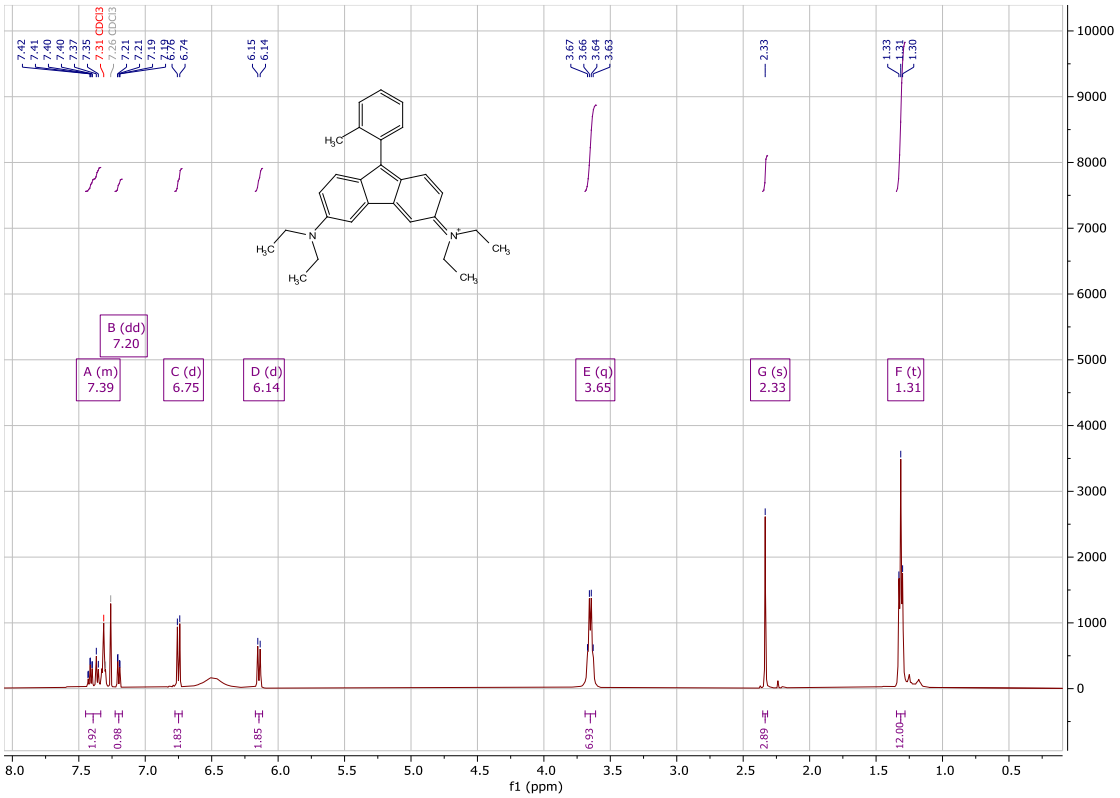

f1 (ppm)
H NMR (ppm)
F NMR (ppm)

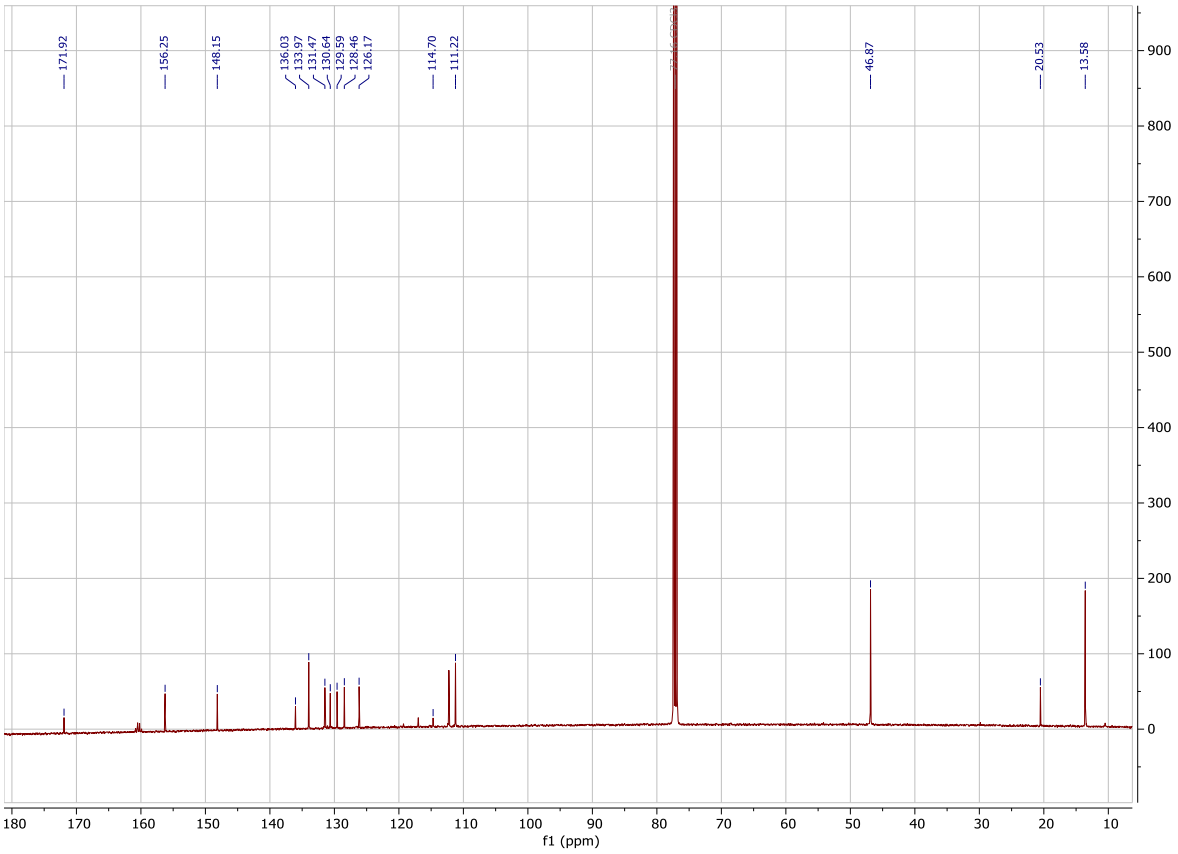

C NMR (ppm)

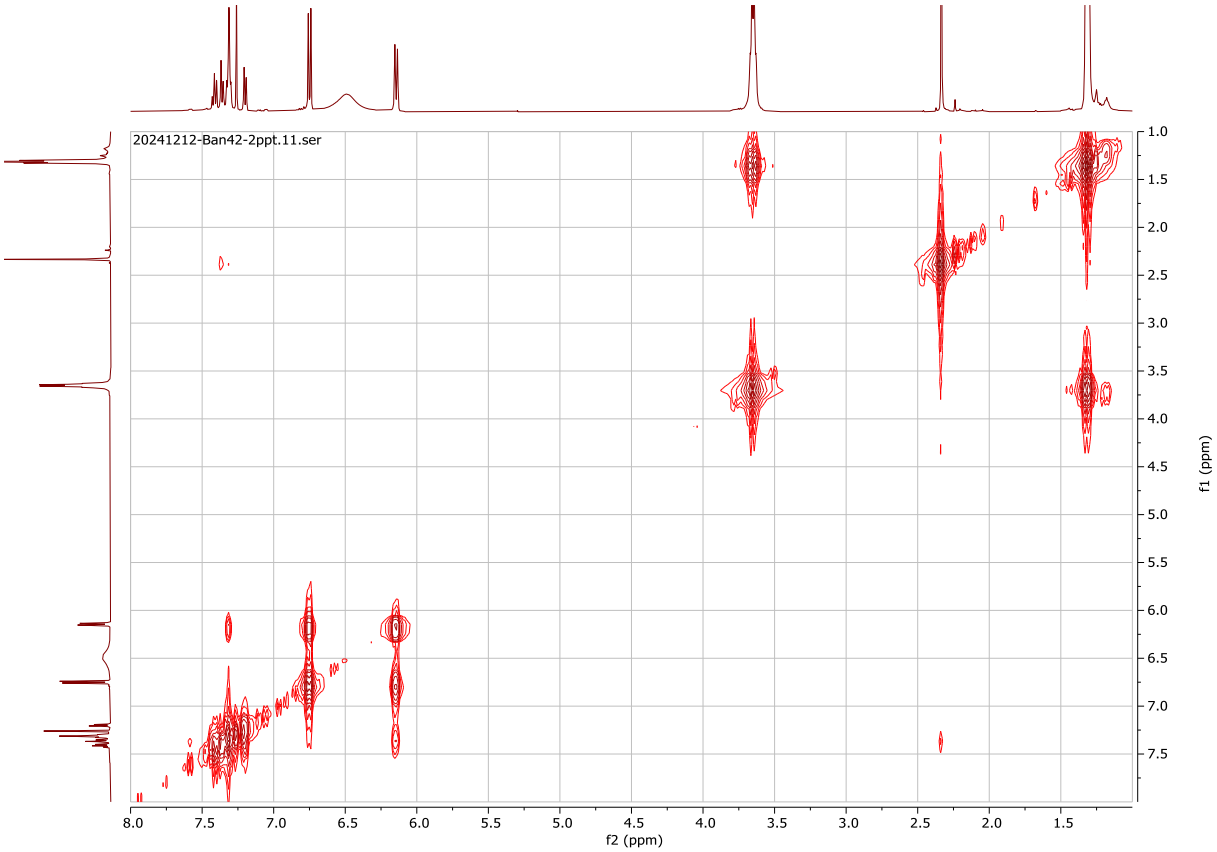
5.3) NMR spectra towards compound 1b





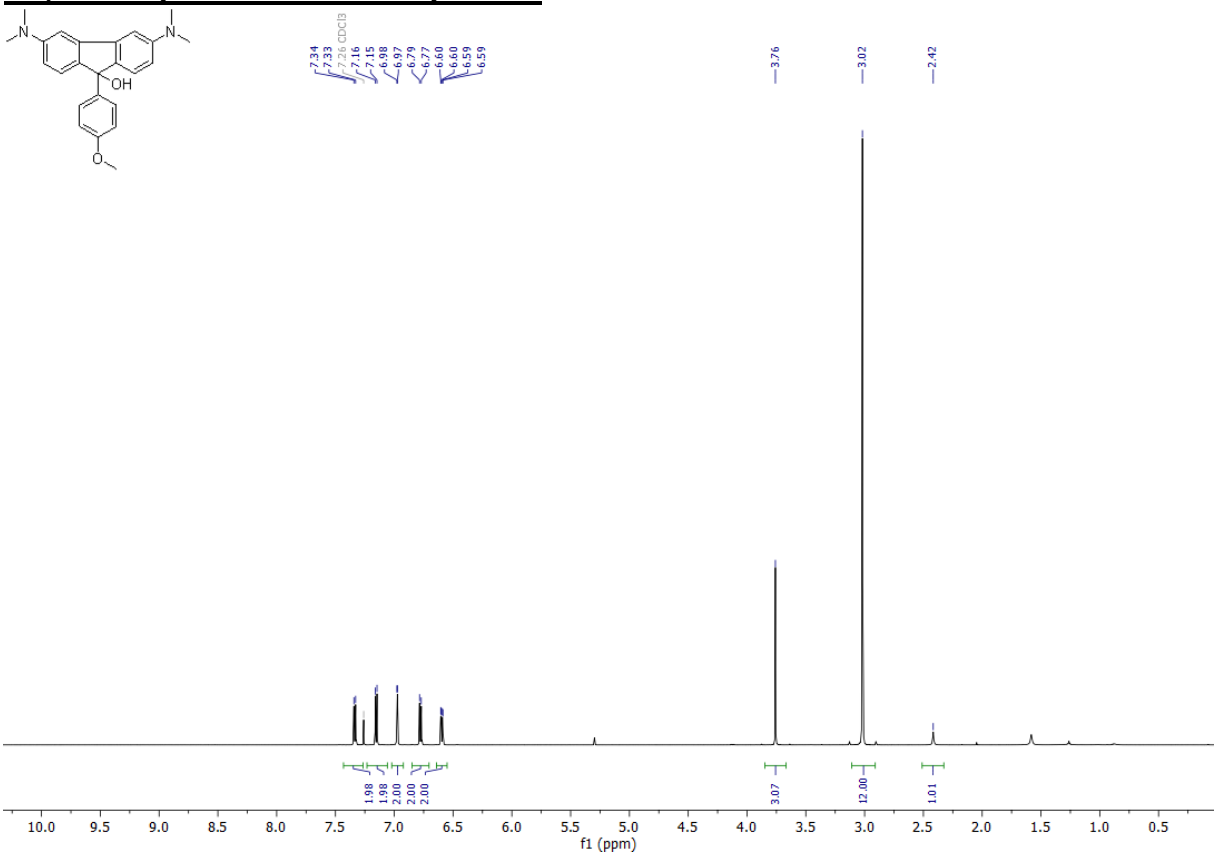

7.42
7.41
7.40
7.40
7.37
7.35
7.31 CDCl3
7.26 CDCl3
7.21
7.21
7.19
6.76
6.74
6.15
6.14
3.67
3.66
3.64
3.63
2.33
1.33
1.31
1.30
B (dd)
7.20
A (m)
7.39
C (d)
6.75
D (d)
6.14
E (q)
3.65
G (s)
2.33
F (t)
1.31
1.92
0.98
1.83
1.85
6.93
2.89
12.00
f1 (ppm)

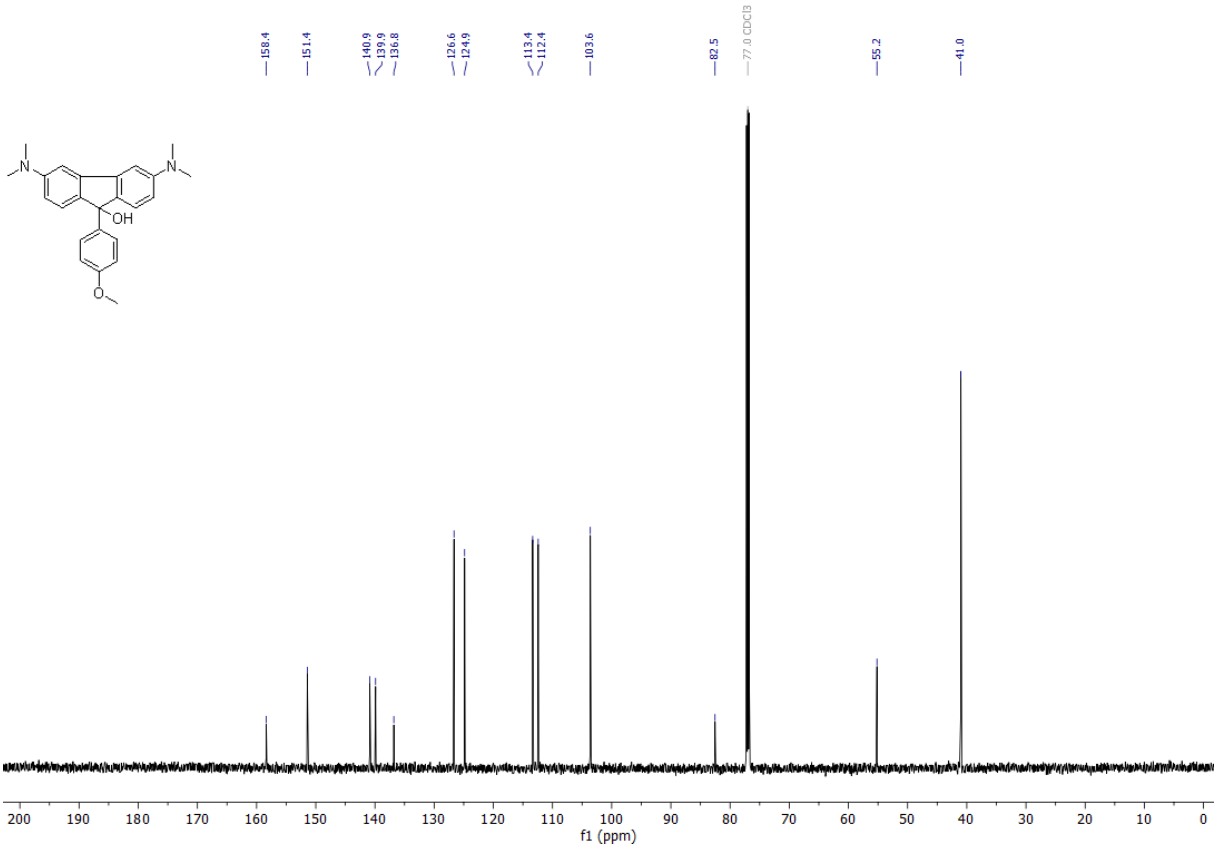

171.92
156.25
148.15
136.03
133.97
131.47
130.64
129.59
128.46
126.17
114.70
111.22
46.87
20.53
13.58
f1 (ppm)

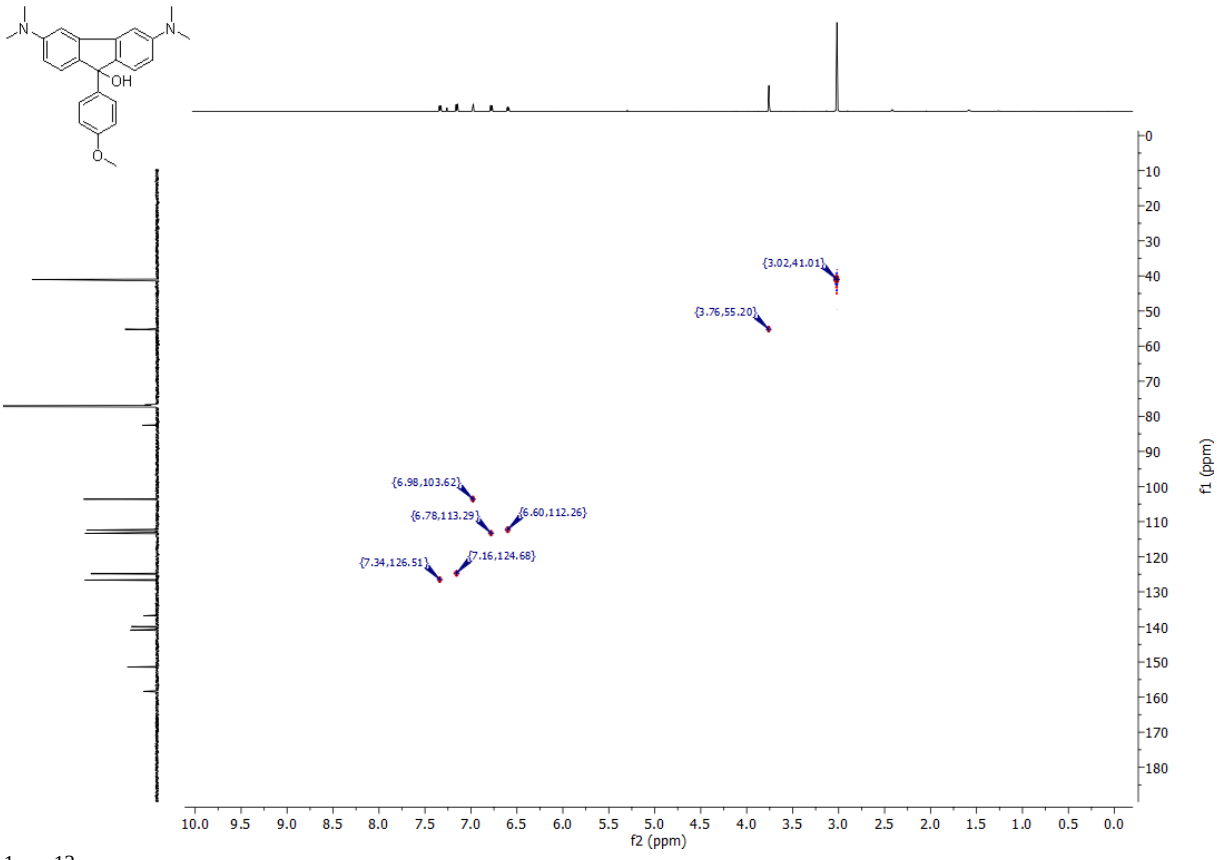


^{1}H, ^{1}H-COSY

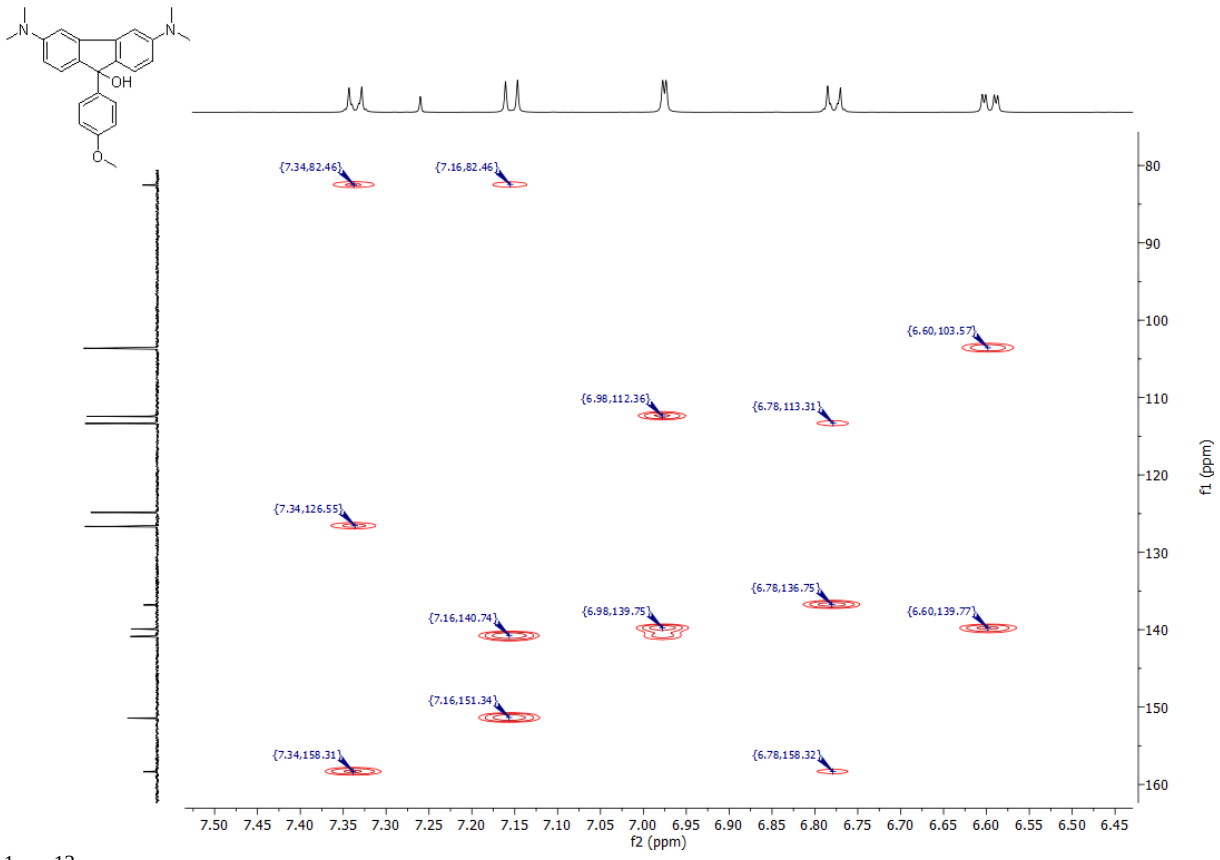
5.4) NMR spectra towards compound 2



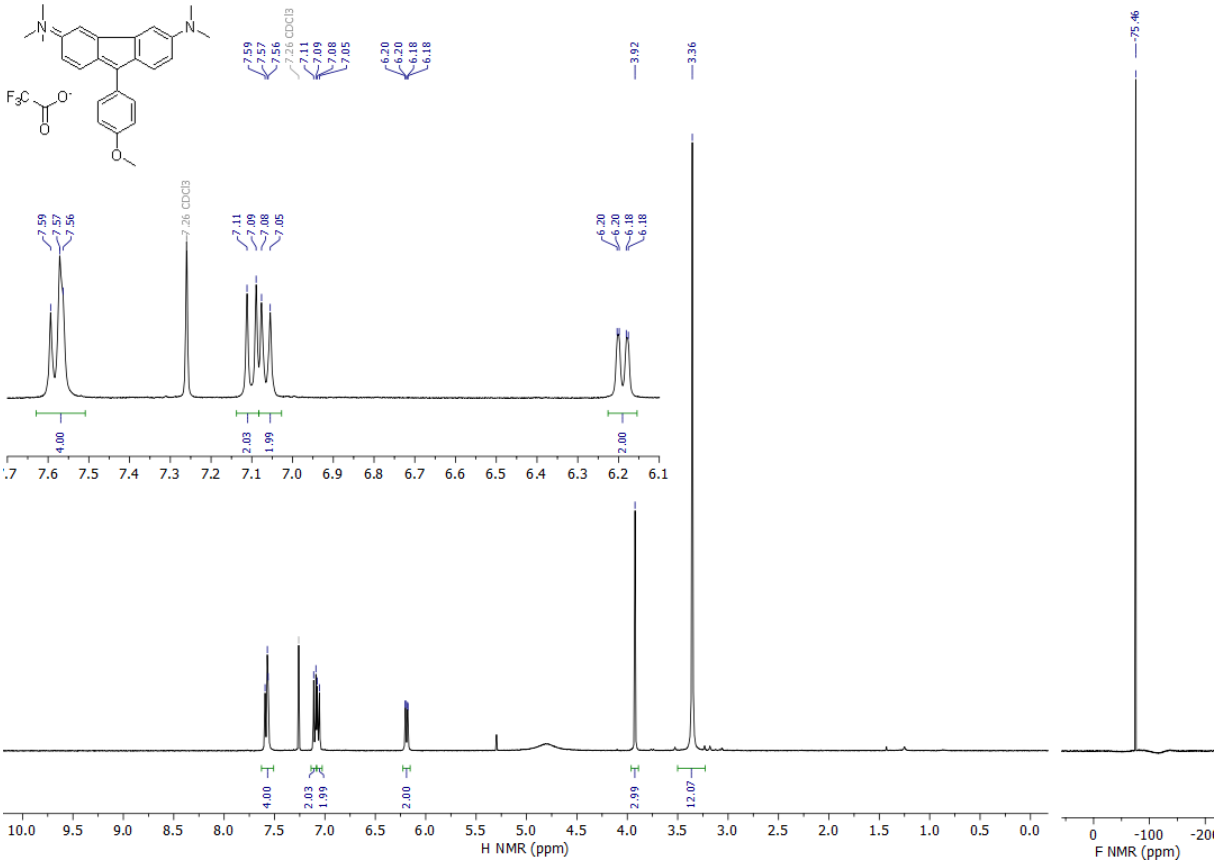

158.4
151.4
140.9
139.9
136.8
126.6
124.9
113.4
112.4
103.6
82.5
77.0 CDCl3
55.2
41.0
OH
f1 (ppm)

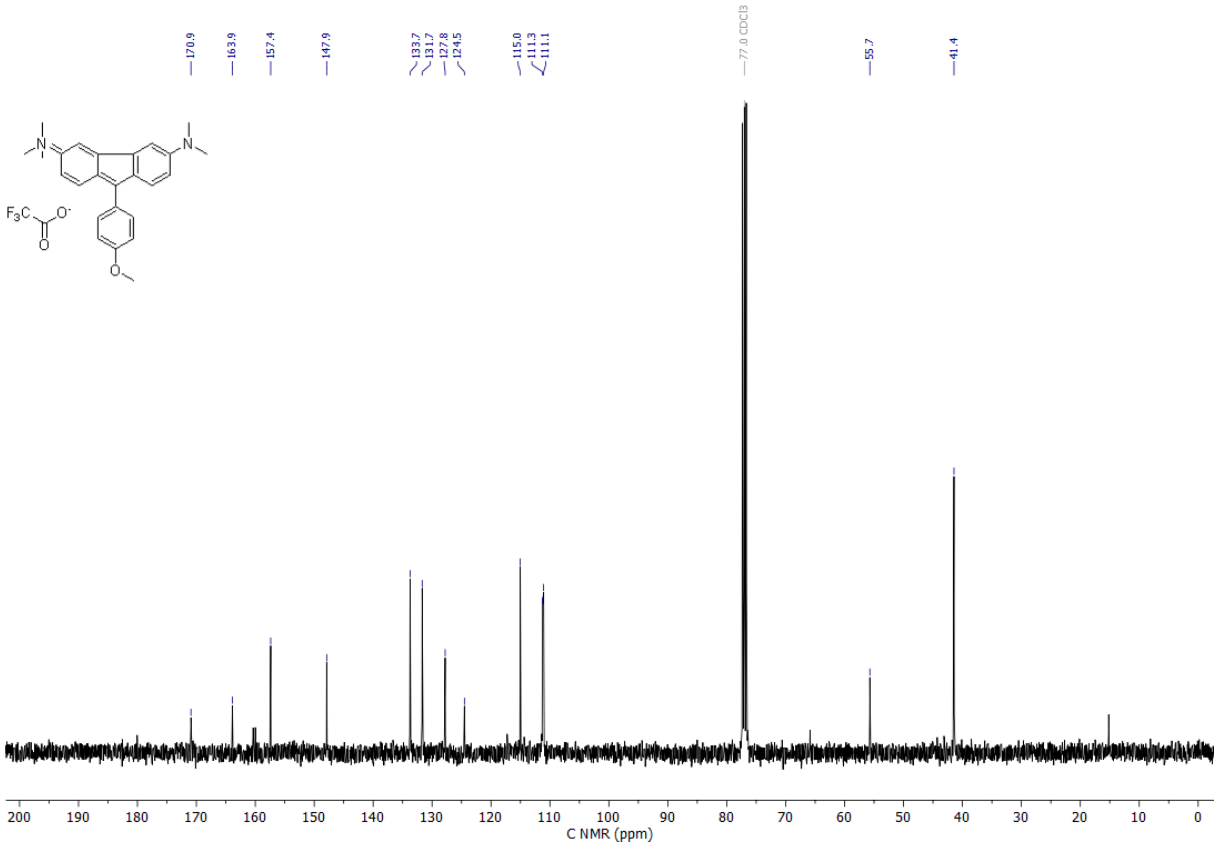

OH
{3.02,41.01}
{3.76,55.20}
{6.98,103.62}
{6.78,113.29}
{6.60,112.26}
{7.34,126.51}
{7.16,124.68}
f2 (ppm)
f1 (ppm)

^{1}H, ^{13}C-HSQC

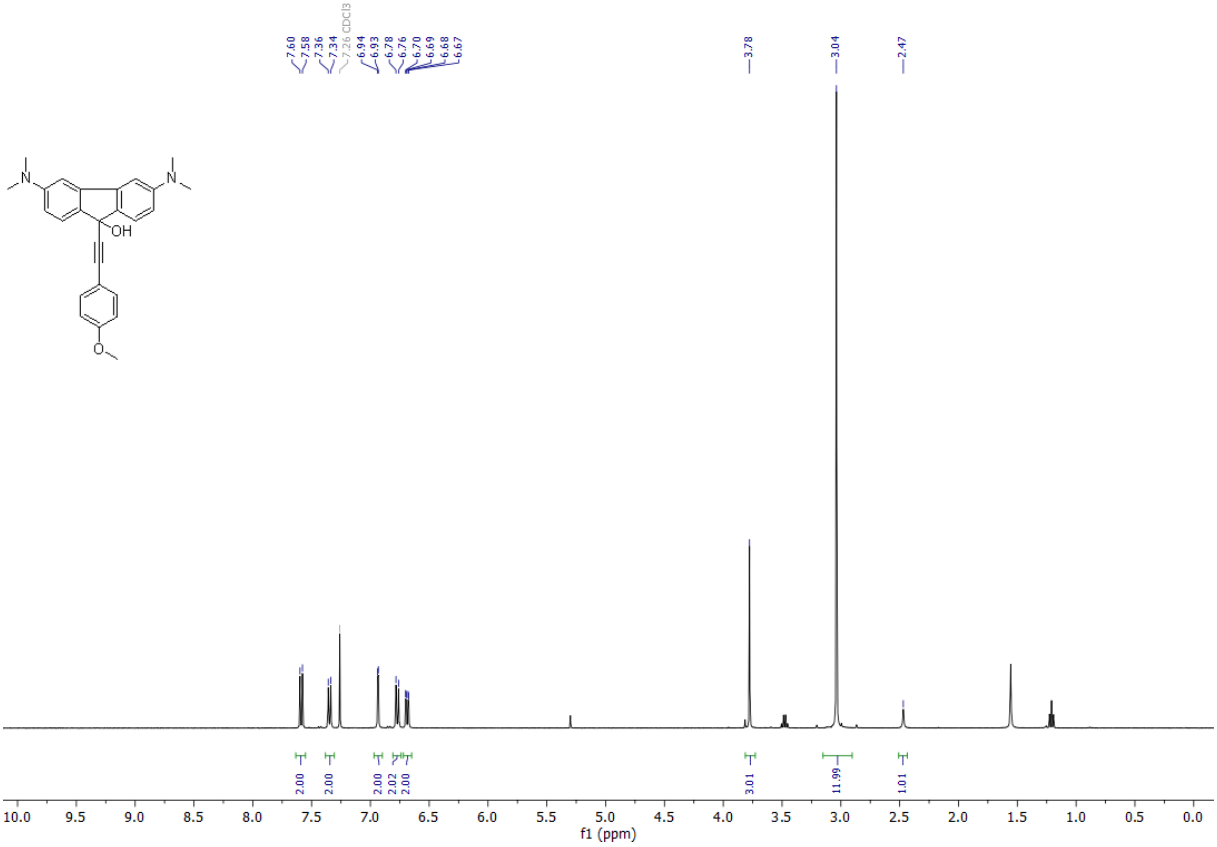

{7.34,82.46}
{7.16,82.46}
{6.60,103.57}
{6.98,112.36}
{6.78,113.31}
{7.34,126.55}
{6.78,136.75}
{7.16,140.74}
{6.98,139.75}
{6.60,139.77}
{7.16,151.34}
{7.34,158.31}
{6.78,158.32}
f1 (ppm)
f2 (ppm)

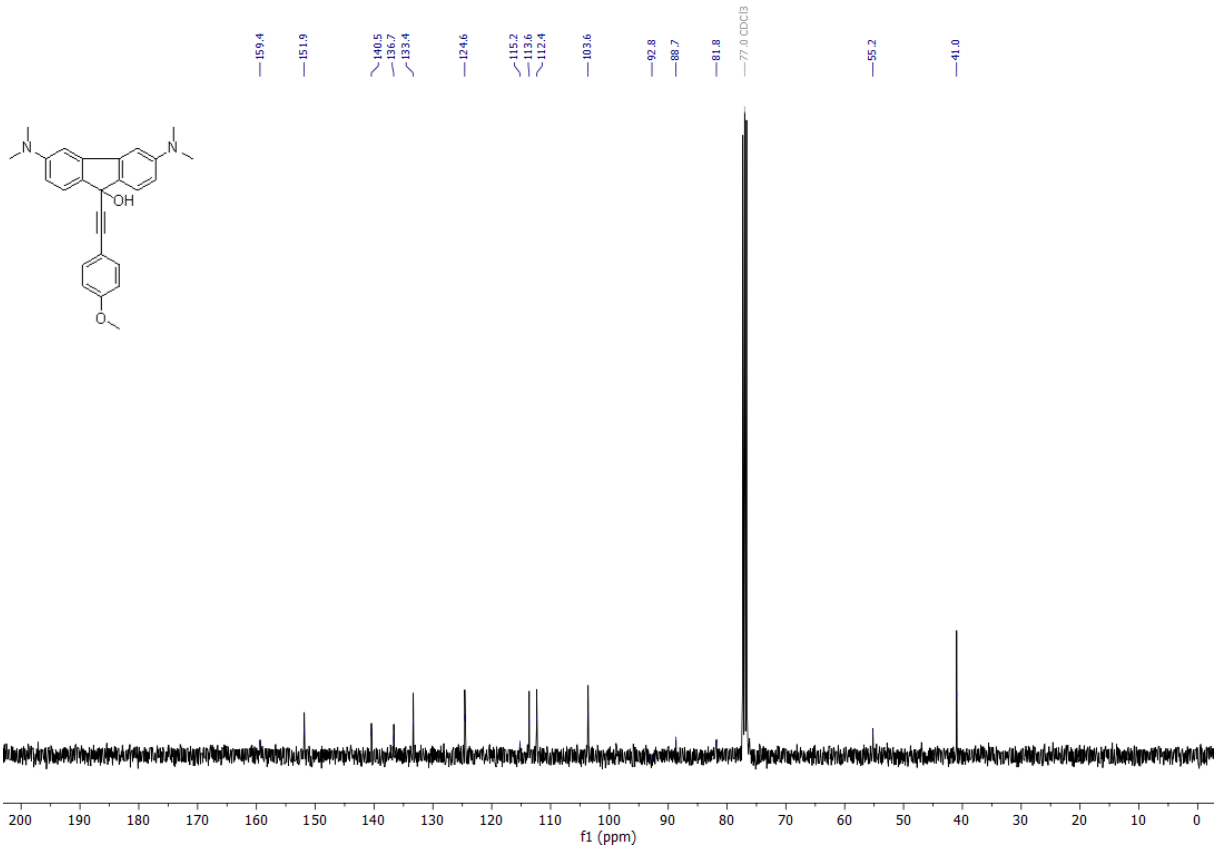
^{1}H, ^{13}C-HSQC


7.59
7.57
7.56
7.26 CDCl3
7.11
7.09
7.08
7.05
6.20
6.18
3.92
3.36
-75.46
4.00
2.03
1.99
2.00
2.99
12.07
H NMR (ppm)
F NMR (ppm)

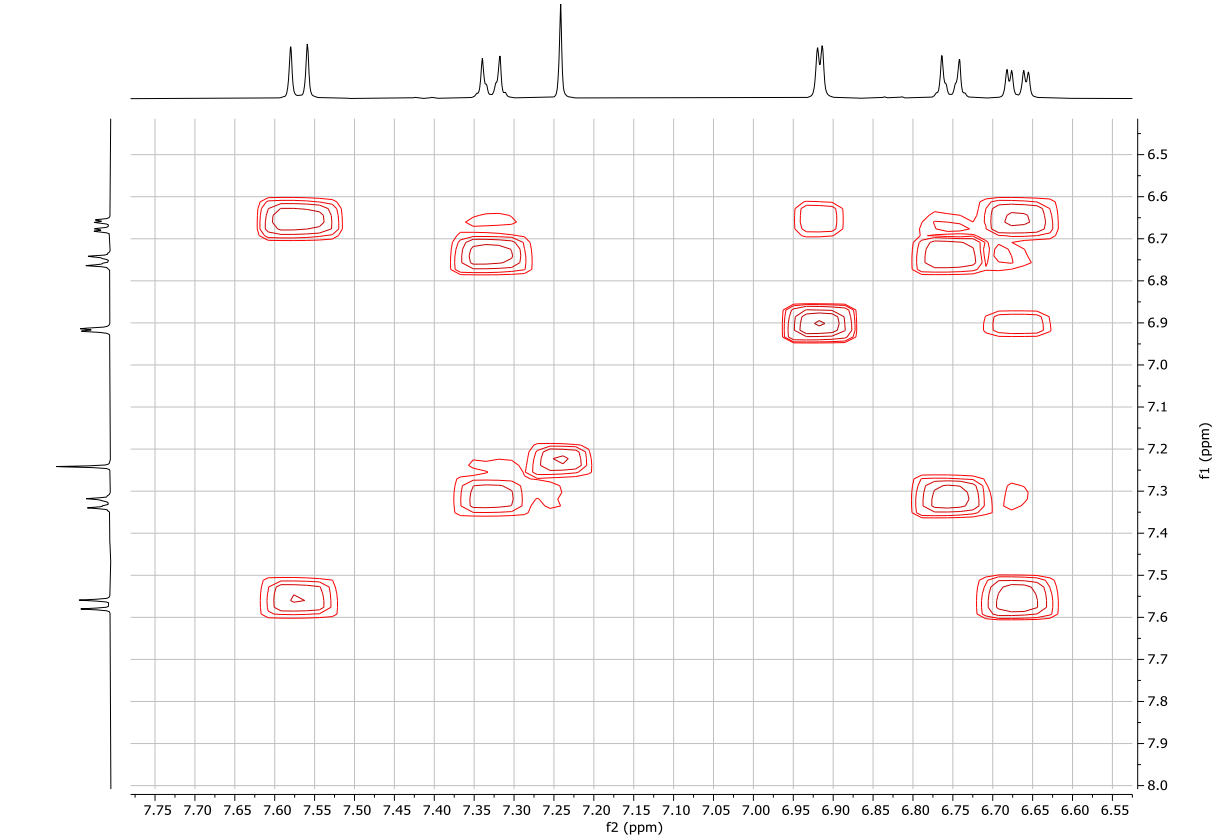

170.9
163.9
157.4
147.9
133.7
131.7
127.8
124.5
115.0
111.3
111.1
77.0 CDCl3
55.7
41.4
F3C
O-
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
C NMR (ppm)

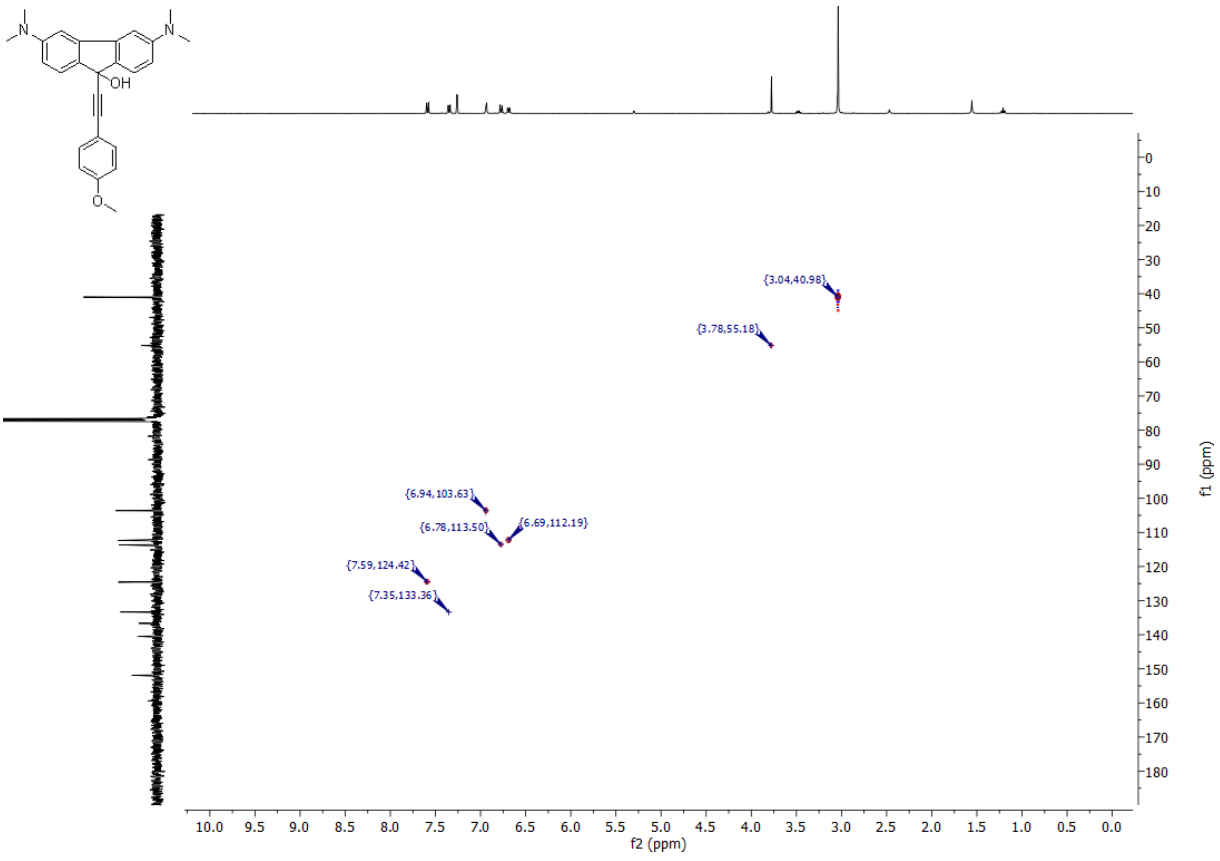
5.5) NMR spectra towards compound 3



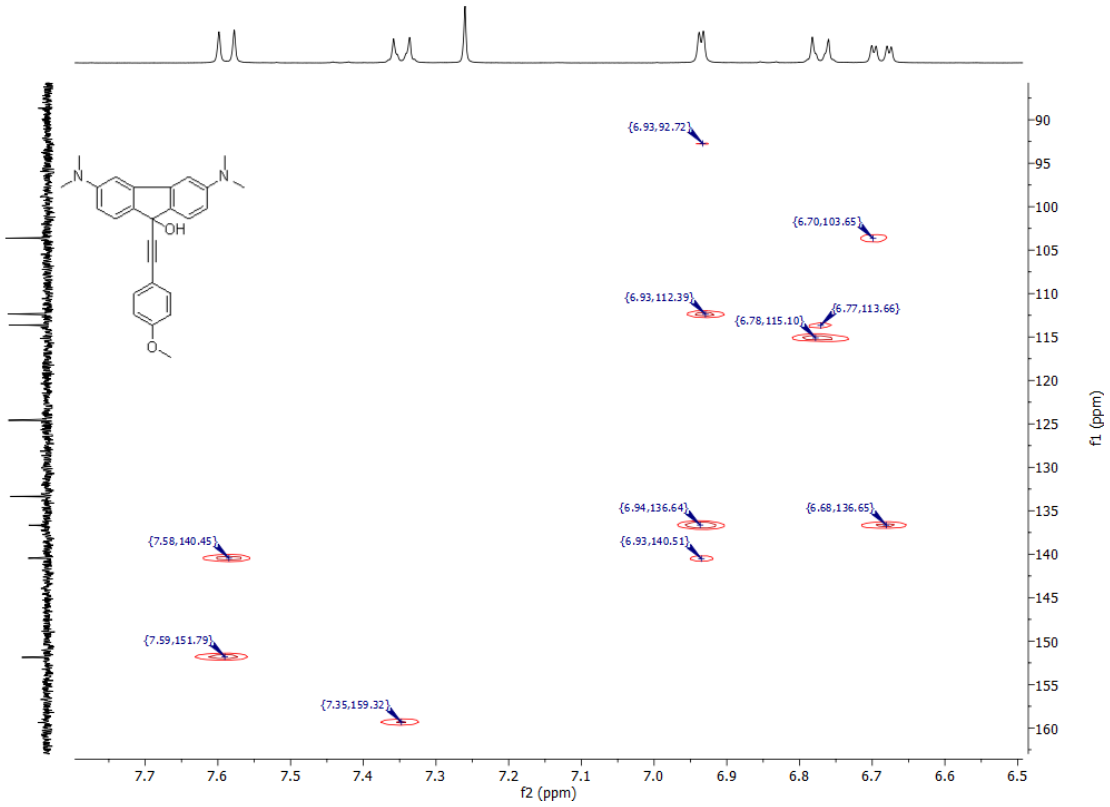


^{1}H, ^{1}H-COSY

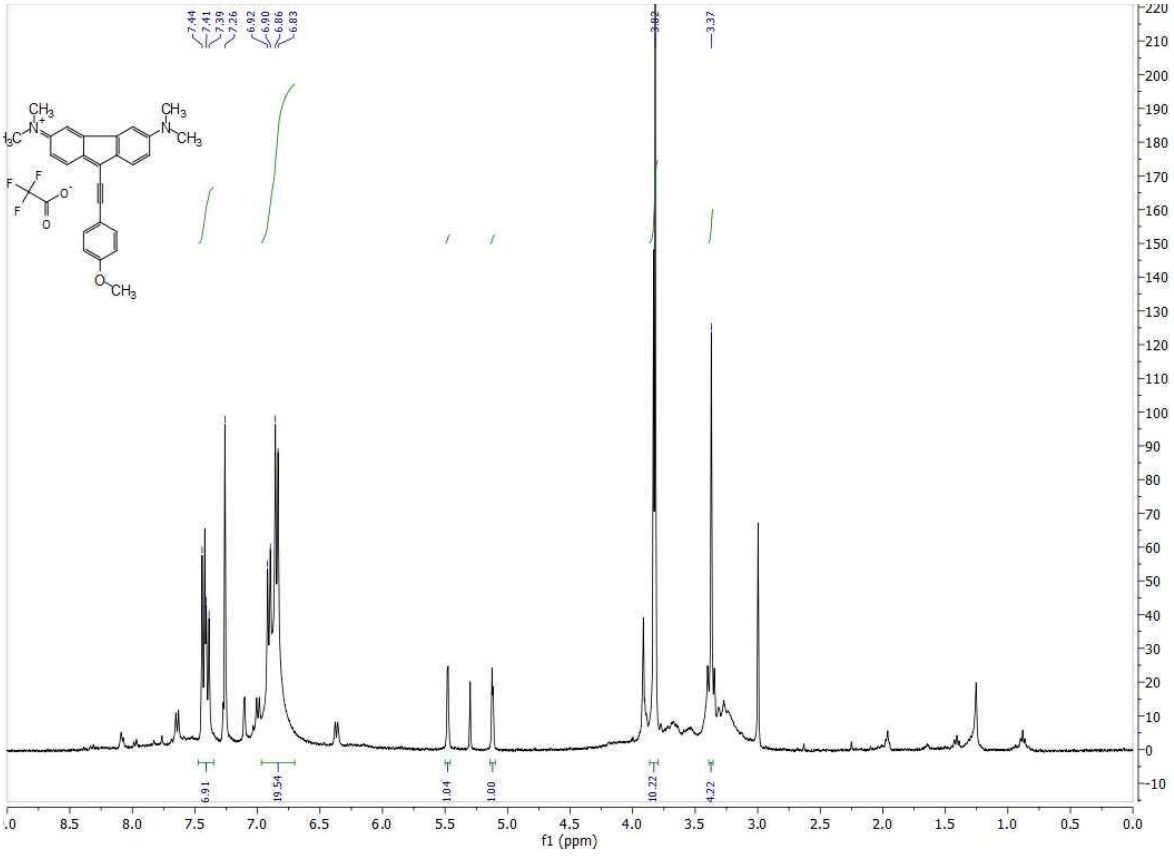


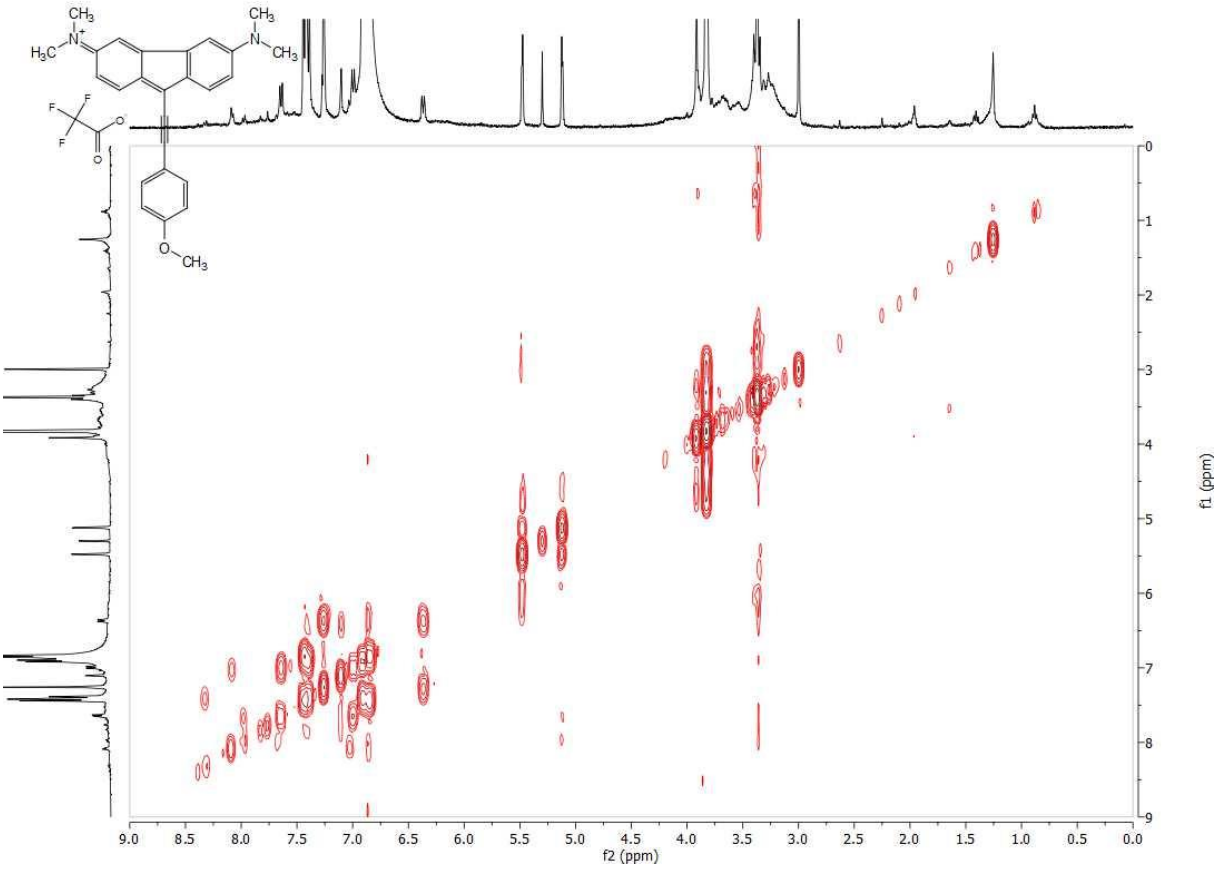


^{1}H, ^{13}C-HSQC

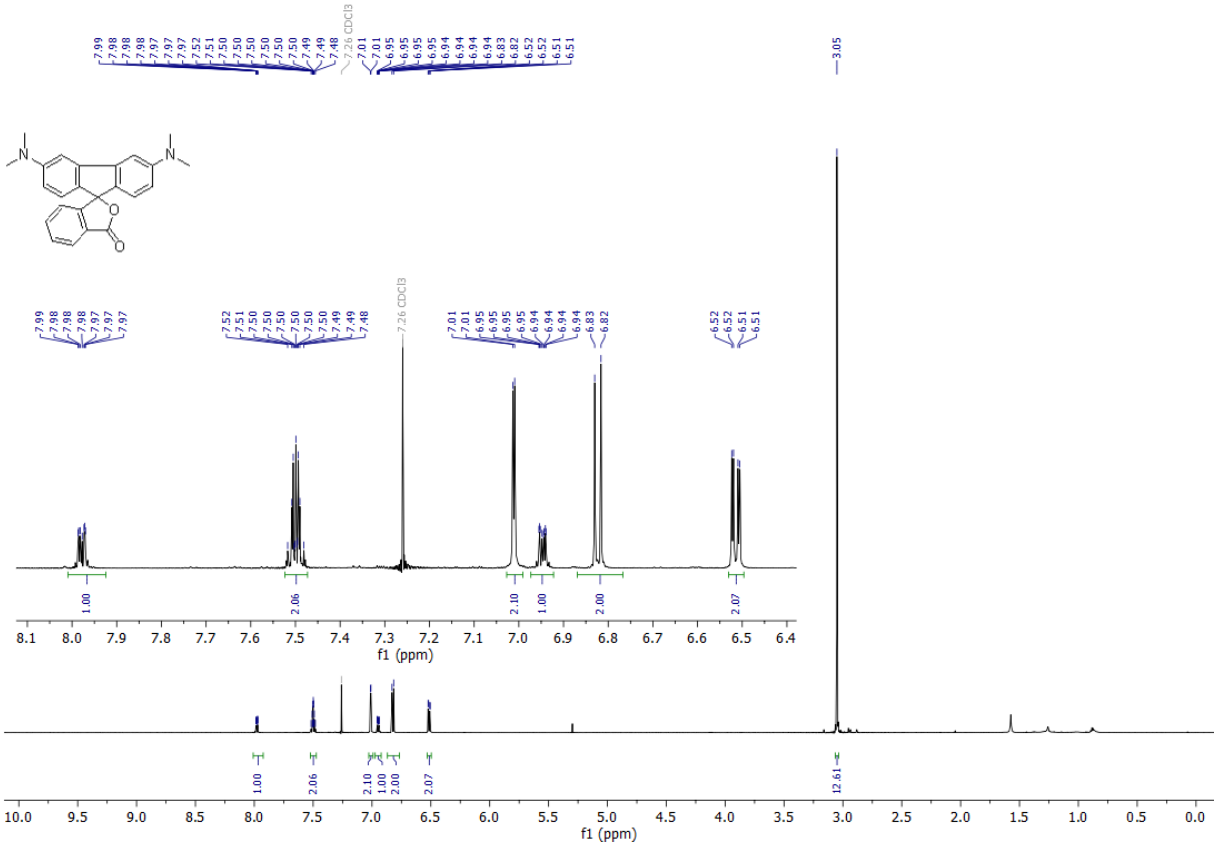

{6.93,92.72}
{6.70,103.65}
{6.93,112.39}
{6.78,115.10}
{6.77,113.66}
{6.94,136.64}
{6.68,136.65}
{7.58,140.45}
{6.93,140.51}
{7.59,151.79}
{7.35,159.32}
OH
f1 (ppm)
f2 (ppm)

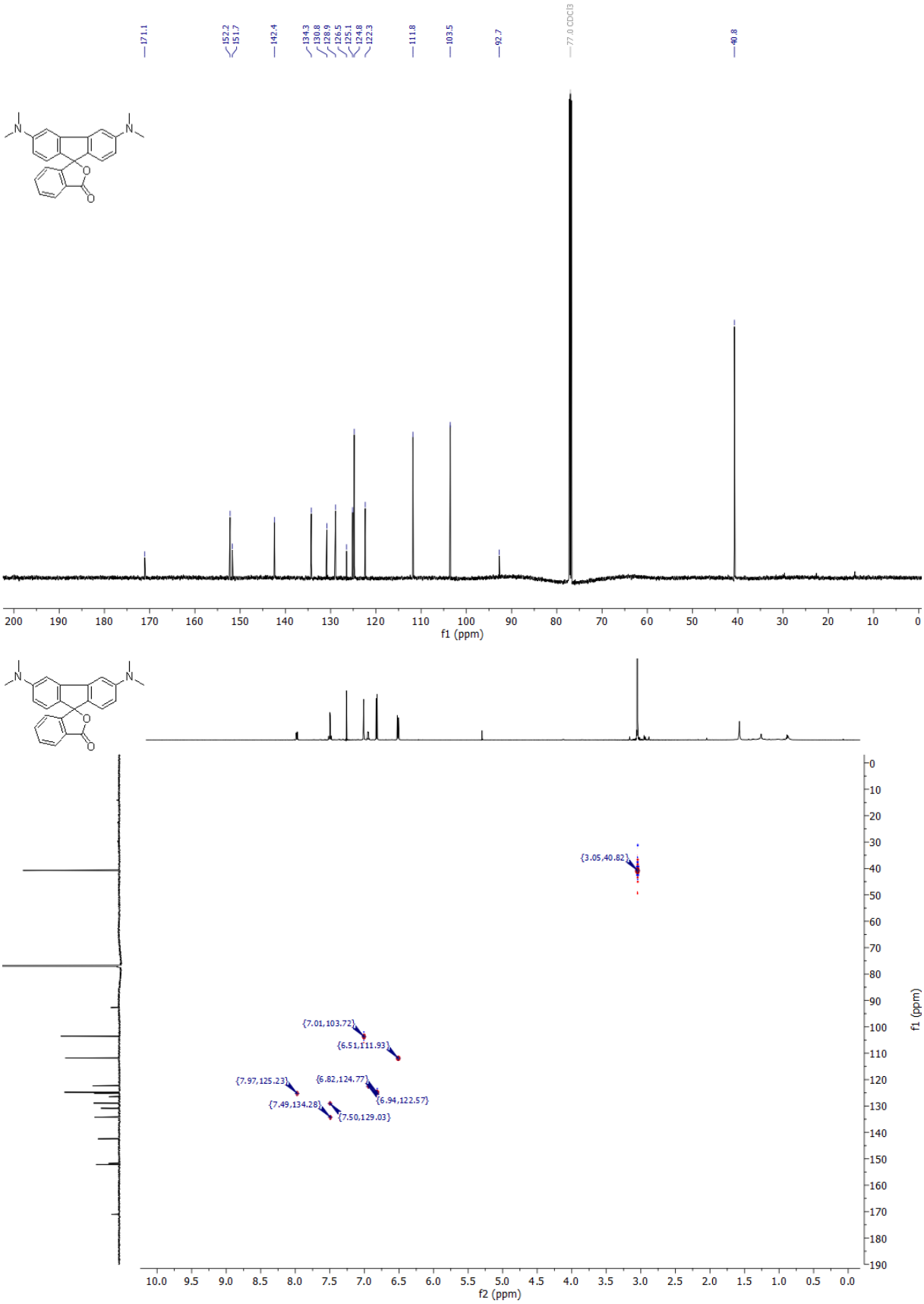
^{1}H, ^{13}C-HMBC


7.44
7.41
7.39
7.26
6.92
6.90
6.86
6.83
3.82
3.37
6.91
19.54
1.04
1.00
10.22
4.22
f1 (ppm)

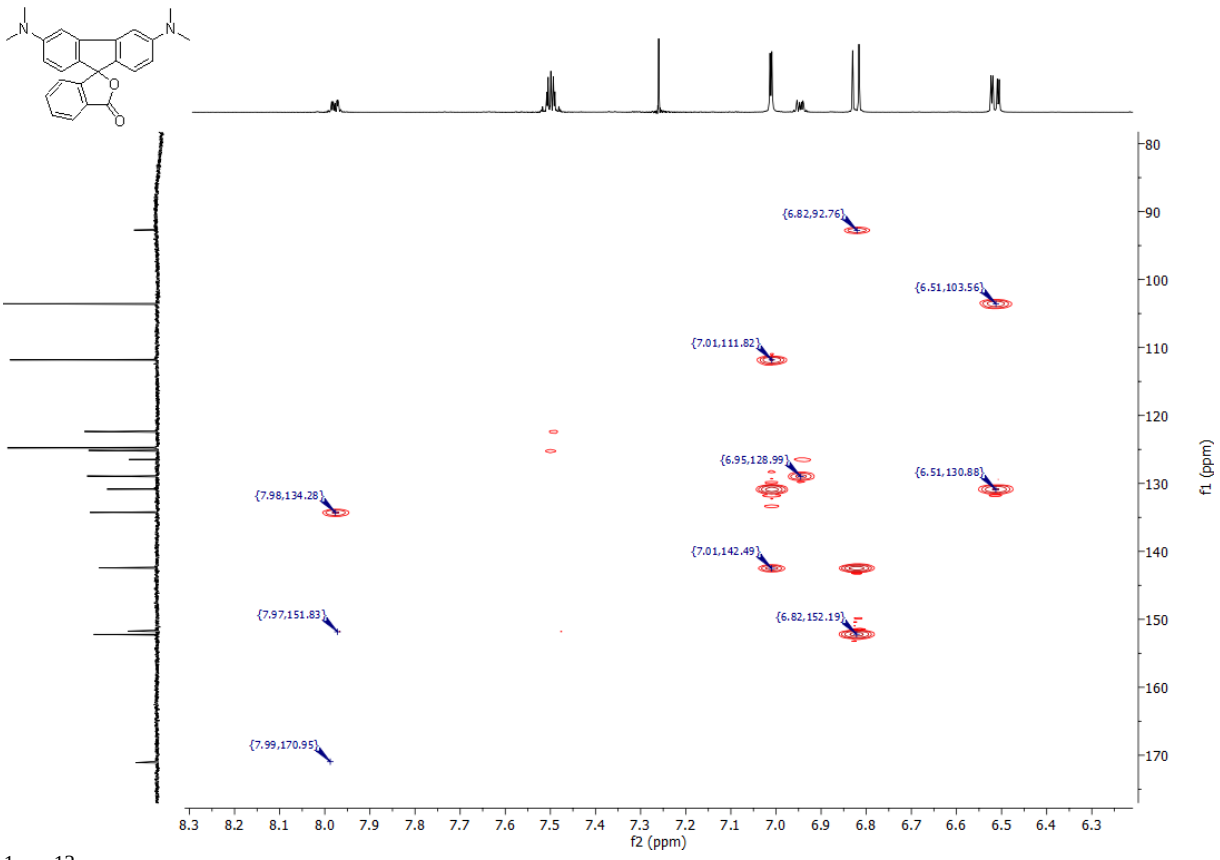


5.6) NMR spectra of compound 4



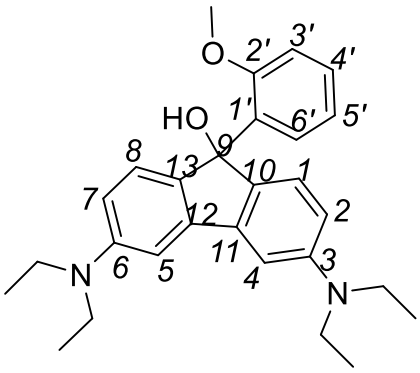

171.1
152.2
151.7
142.4
134.3
130.8
128.9
126.5
125.1
124.8
122.3
111.8
103.5
92.7
77.0 CDCl3
40.8
f1 (ppm)
{3.05,40.82}
{7.01,103.72}
{6.51,111.93}
{7.97,125.23}
{6.82,124.77}
{6.94,122.57}
{7.49,134.28}
{7.50,129.03}
f2 (ppm)
f1 (ppm)

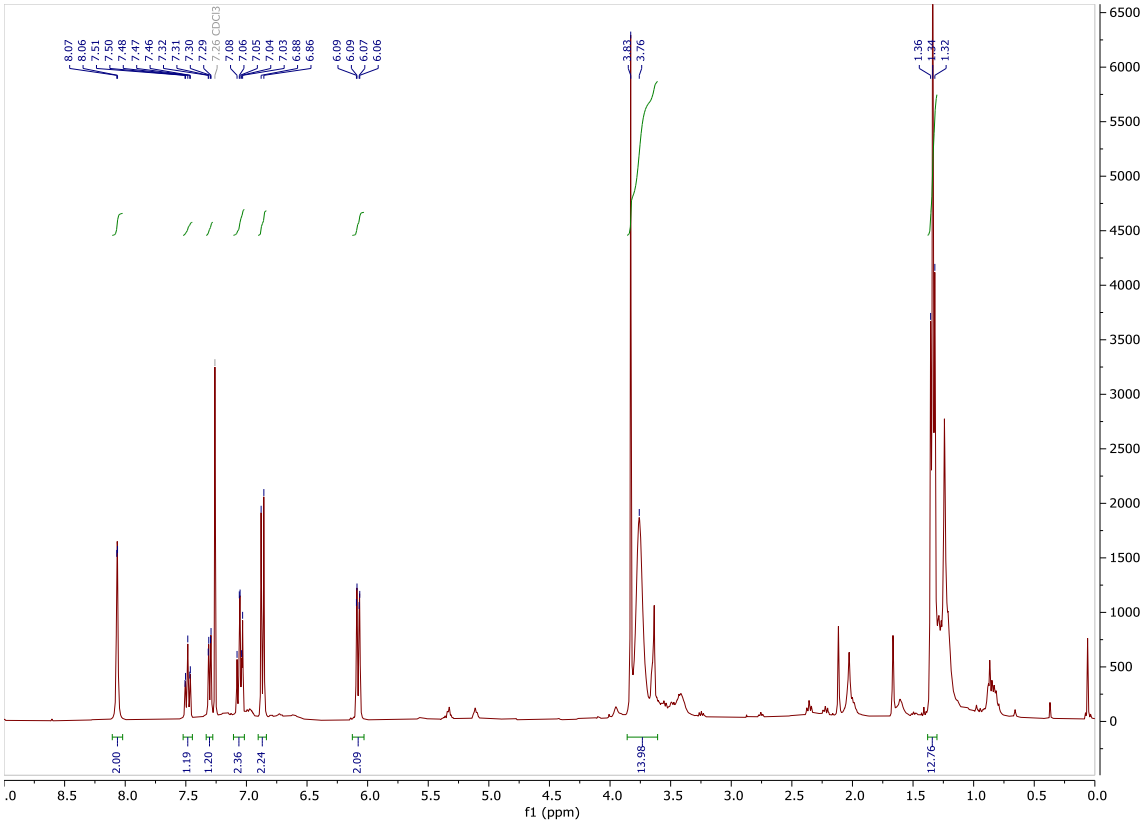
^{1}H, ^{1}H-HSQC

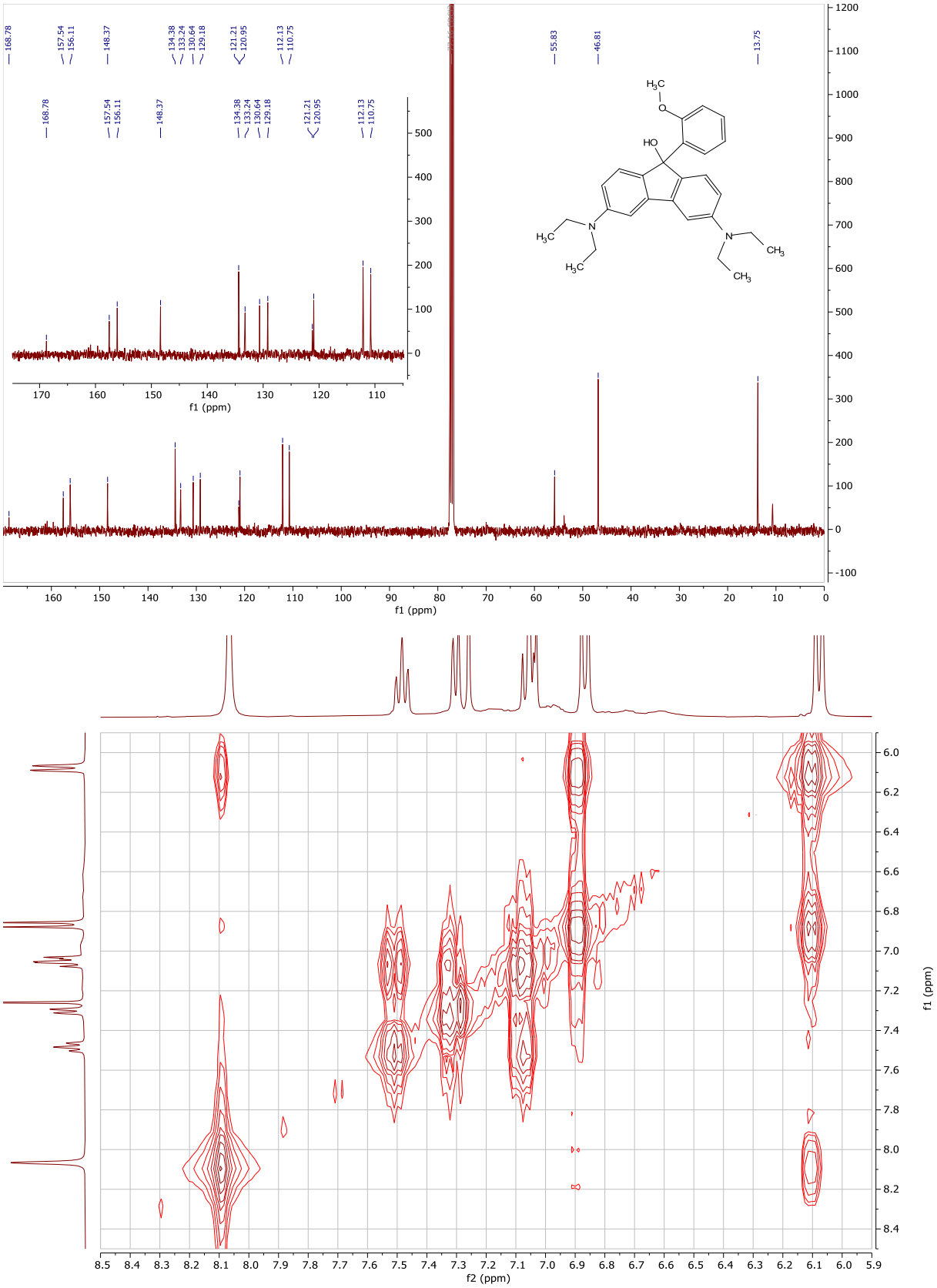

{6.82,92.76}
{6.51,103.56}
{7.01,111.82}
{6.95,128.99}
{6.51,130.88}
{7.98,134.28}
{7.01,142.49}
{7.97,151.83}
{6.82,152.19}
{7.99,170.95}
f2 (ppm)
f1 (ppm)

^{1}H, ^{13}C-HMBC

5.7) NMR spectra towards compound 10

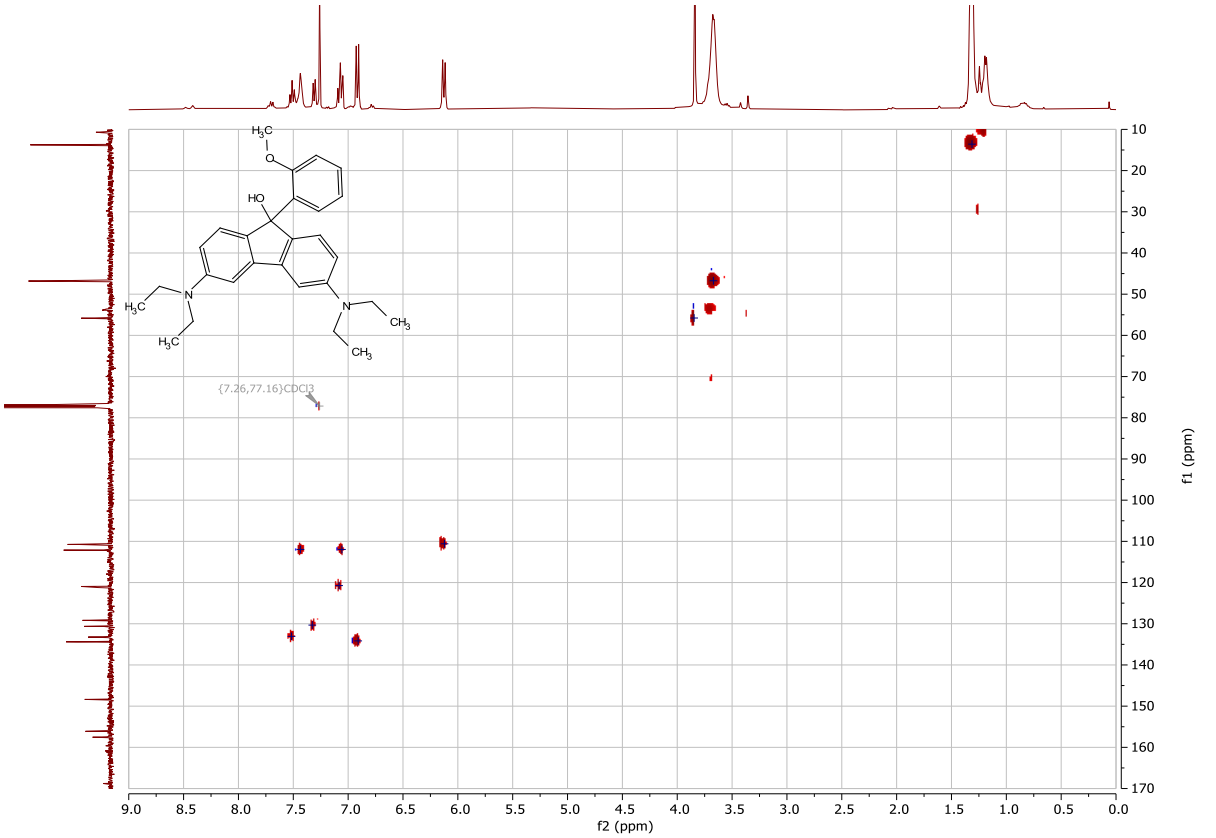


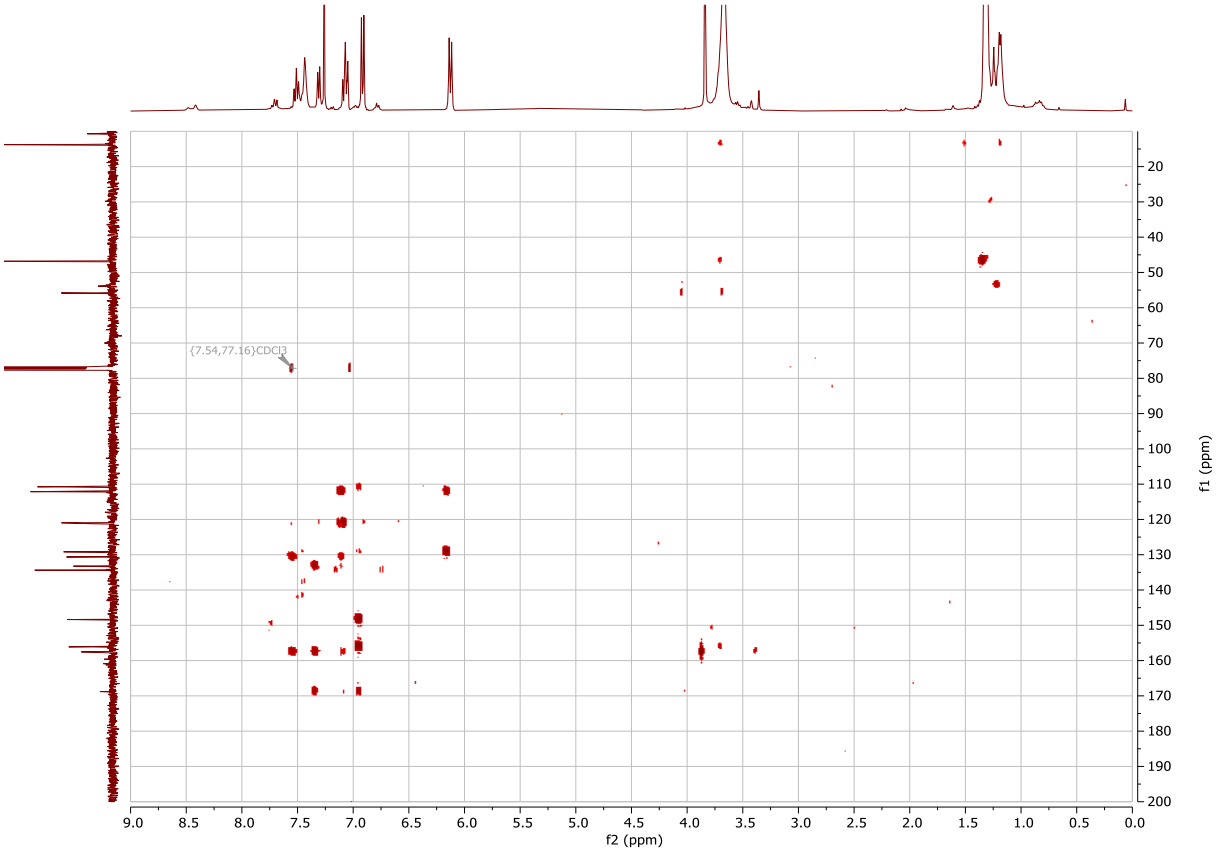



168.78
157.54
156.11
148.37
134.38
133.24
130.64
129.18
121.21
120.95
112.13
110.75
55.83
46.81
13.75
f1 (ppm)
f2 (ppm)

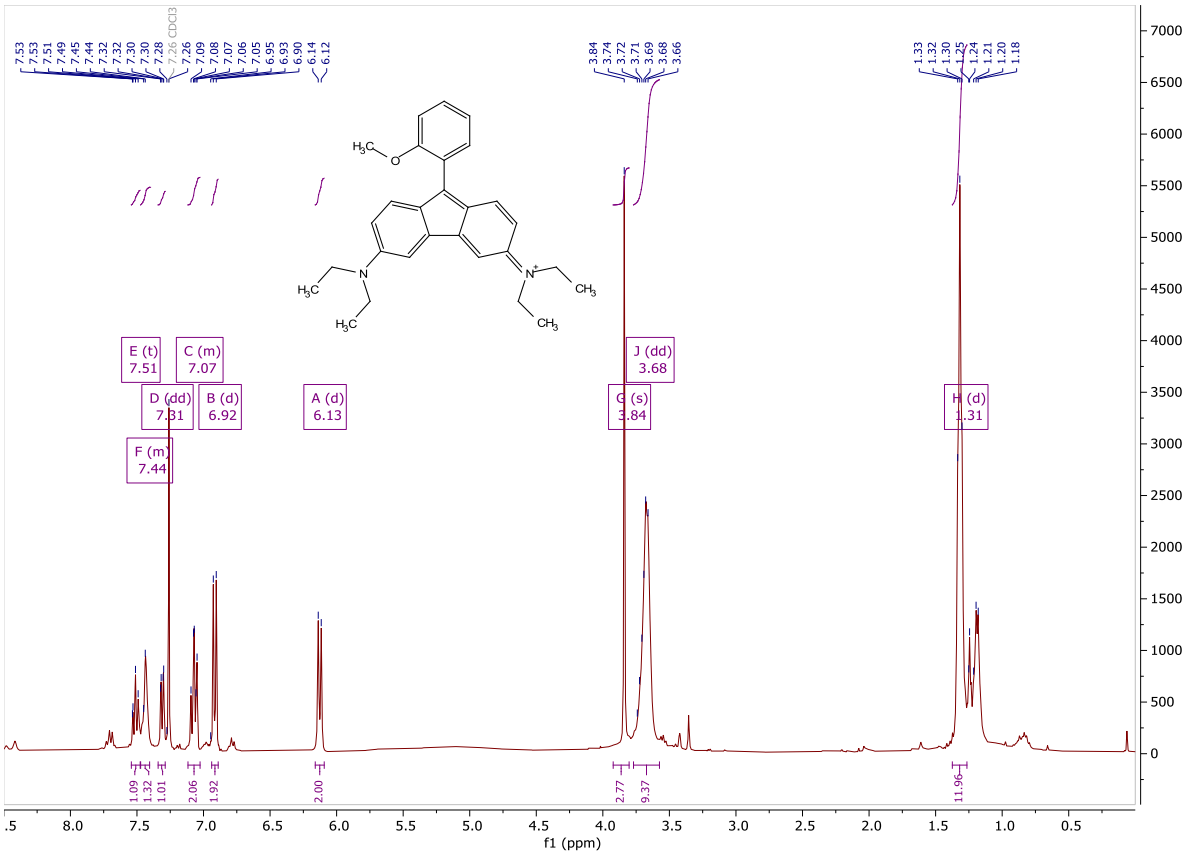
^{1}H, ^{1}H-COSY

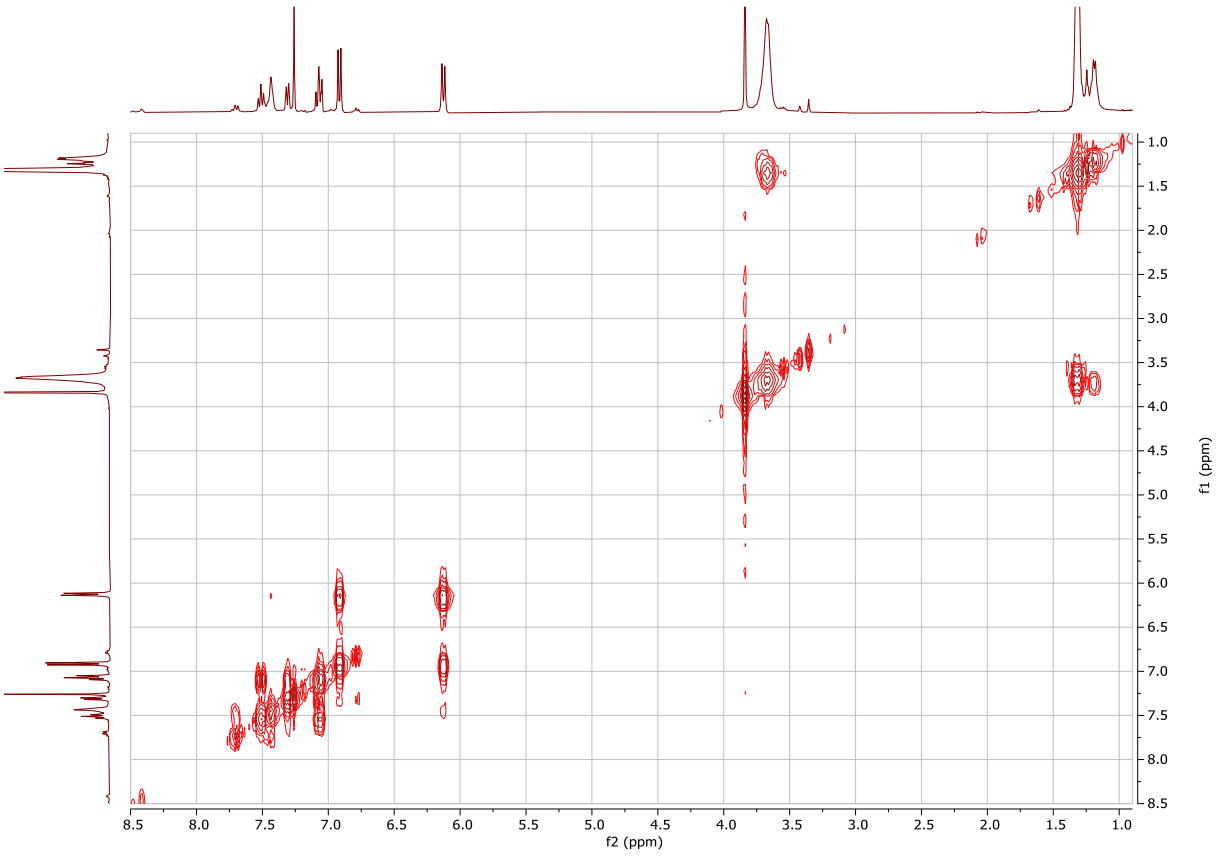
^{1}H, ^{13}C- HSQC:





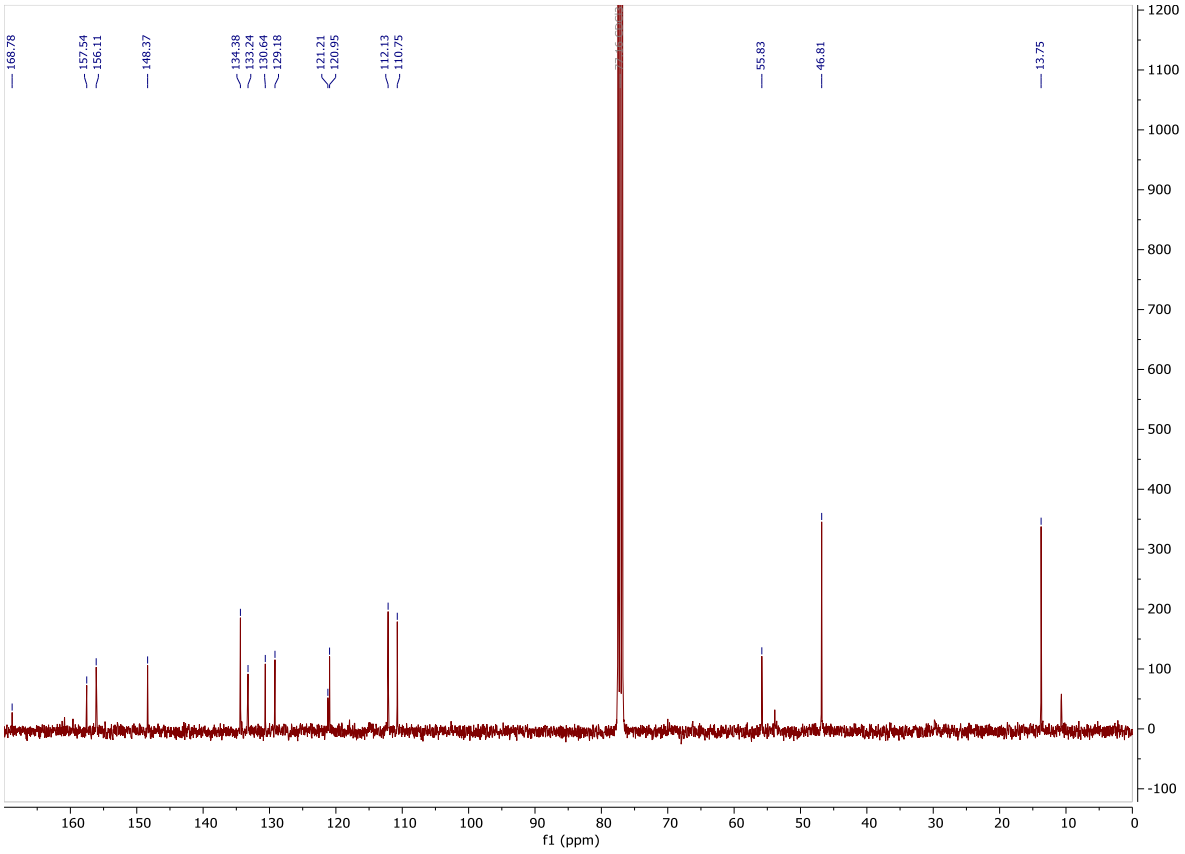
^{1}H, ^{13}C- HMBC

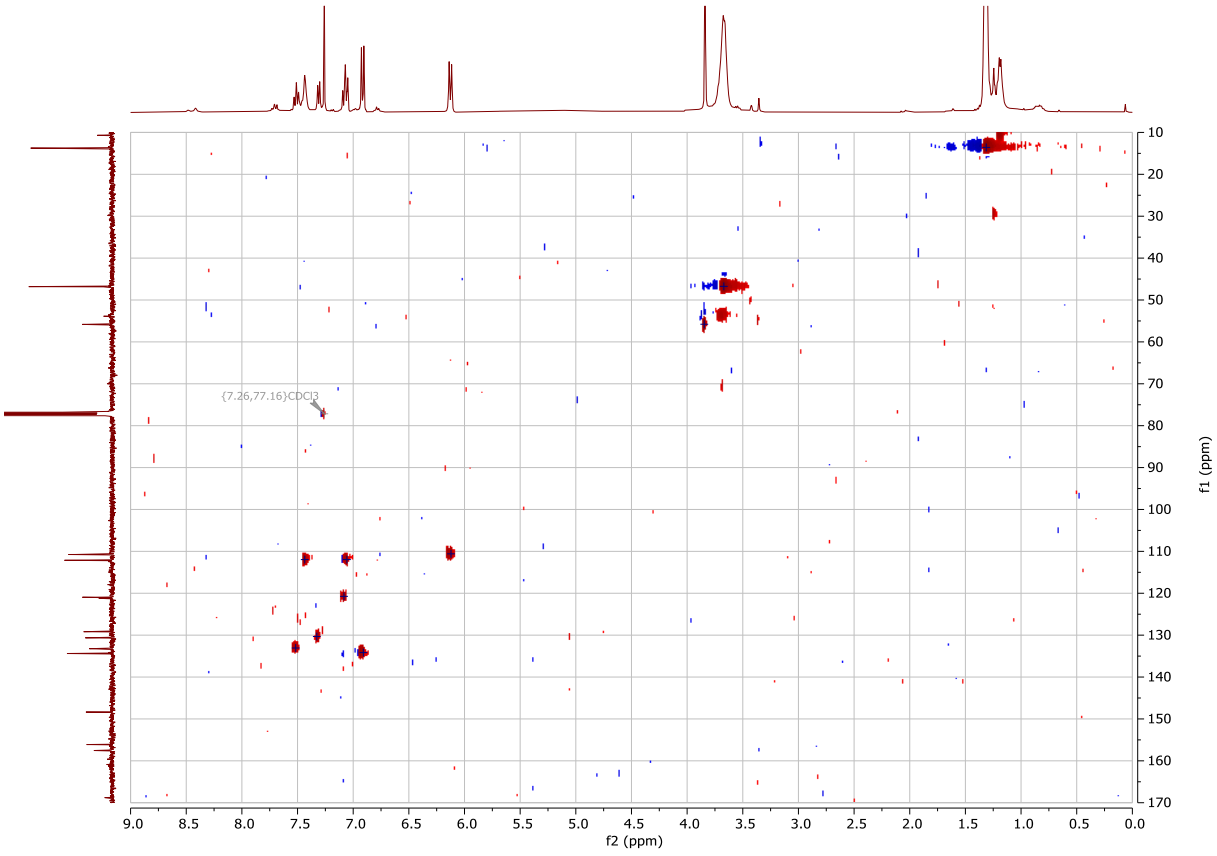

E (t)
7.51
C (m)
7.07
D (dd)
7.31
B (d)
6.92
A (d)
6.13
F (m)
7.44
J (dd)
3.68
G (s)
3.84
H (d)
1.31
f1 (ppm)


f2 (ppm)
f1 (ppm)

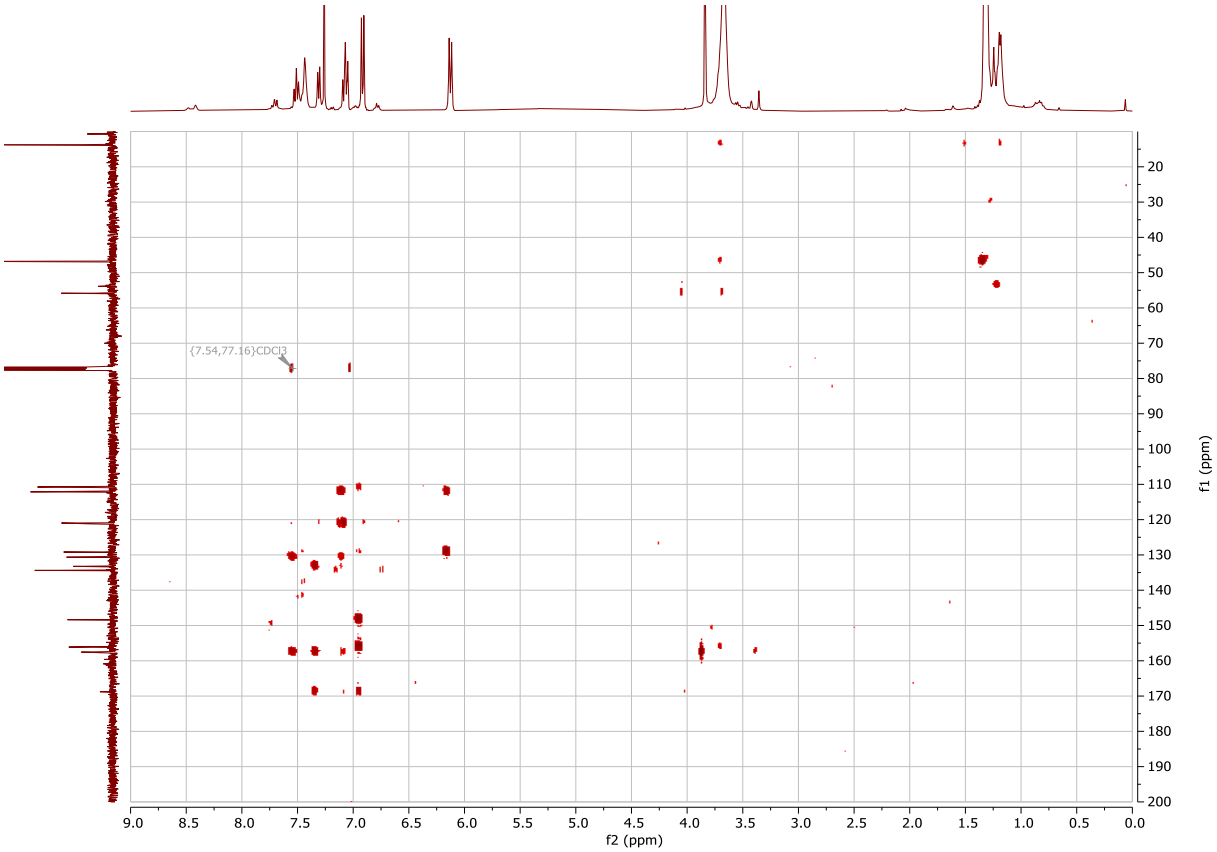
^{1}H, ^{1}H COSY

^{13}C-Spectra



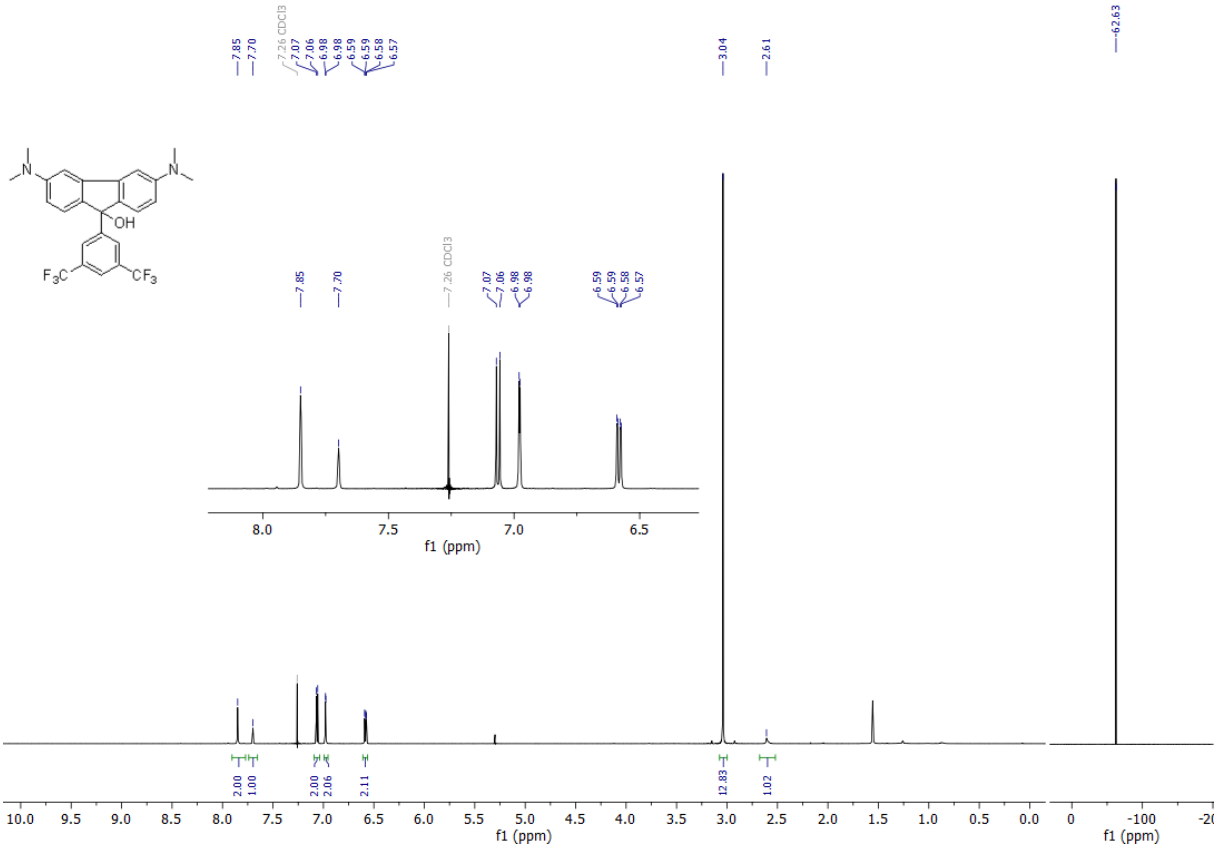


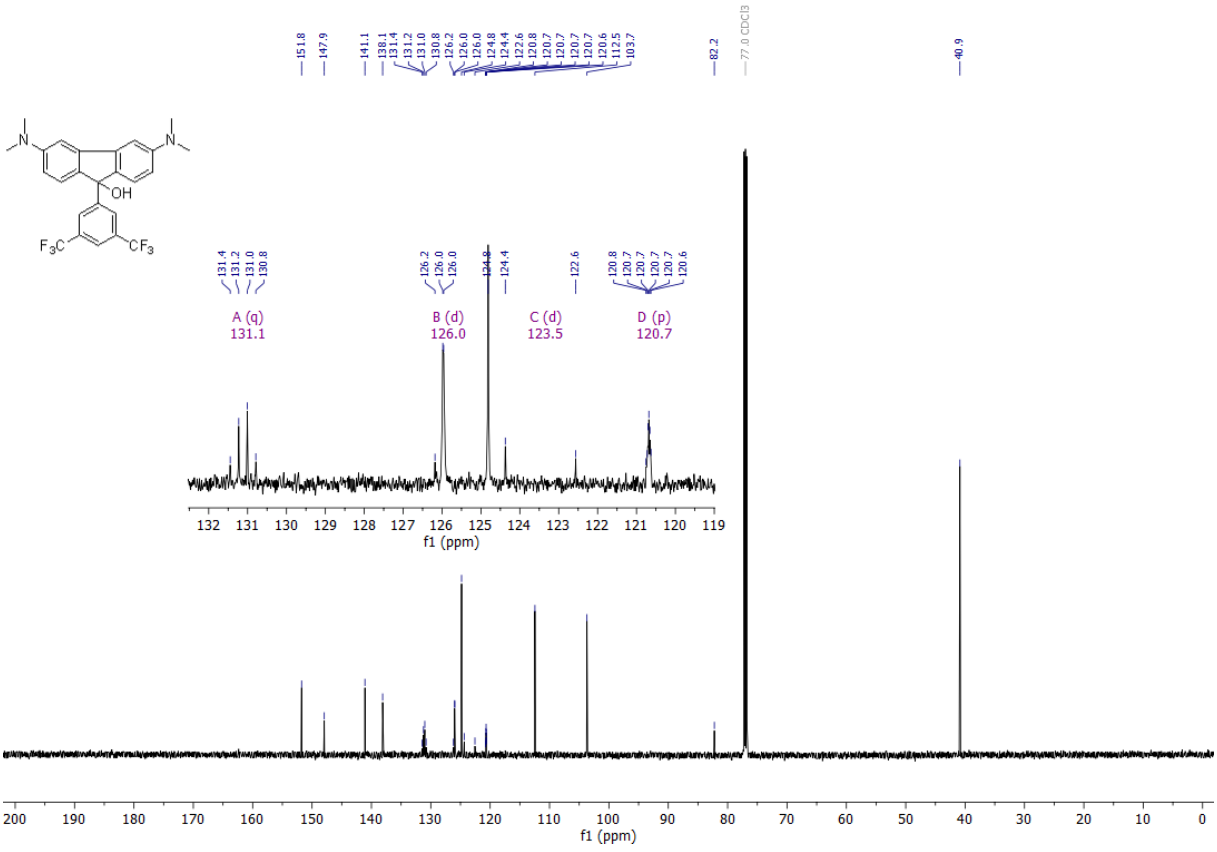
^{1}H, ^{13}C- HSQC:

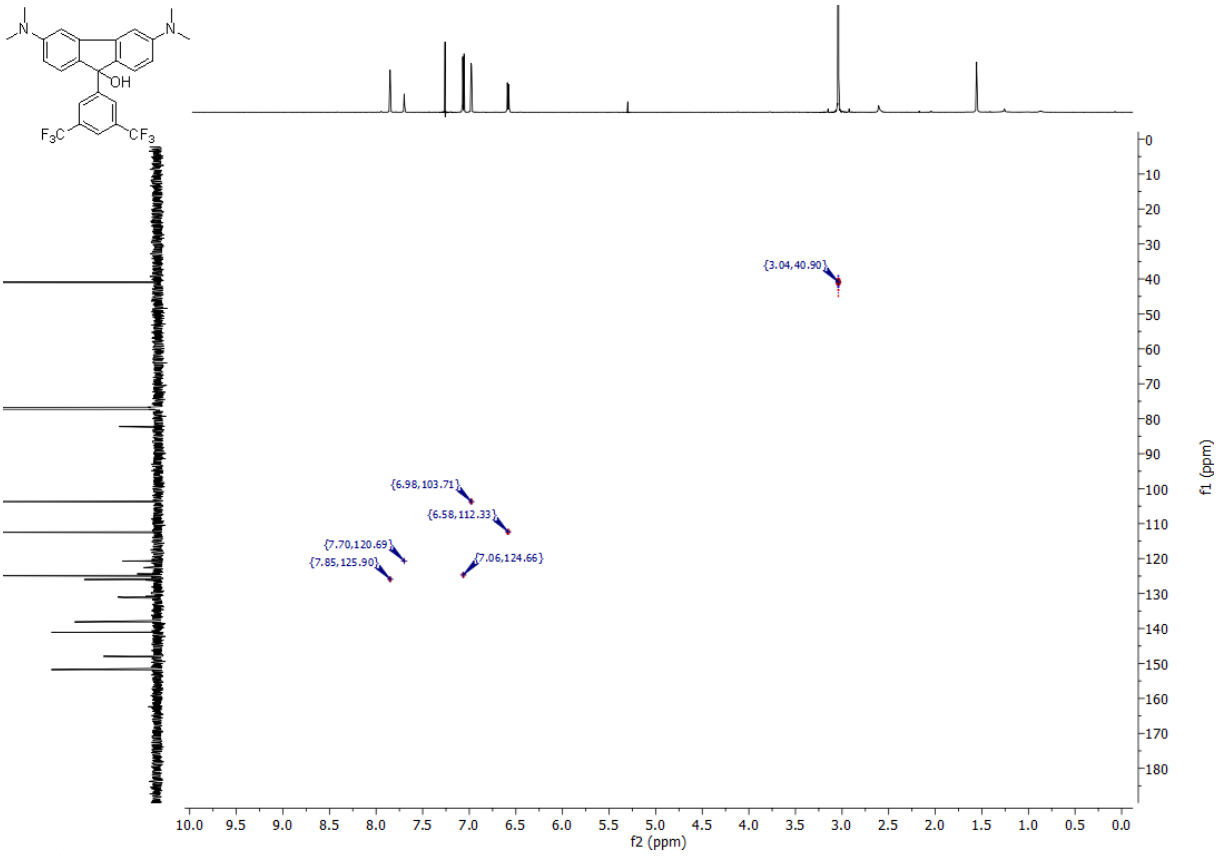


^{1}H, ^{13}C- HMBC

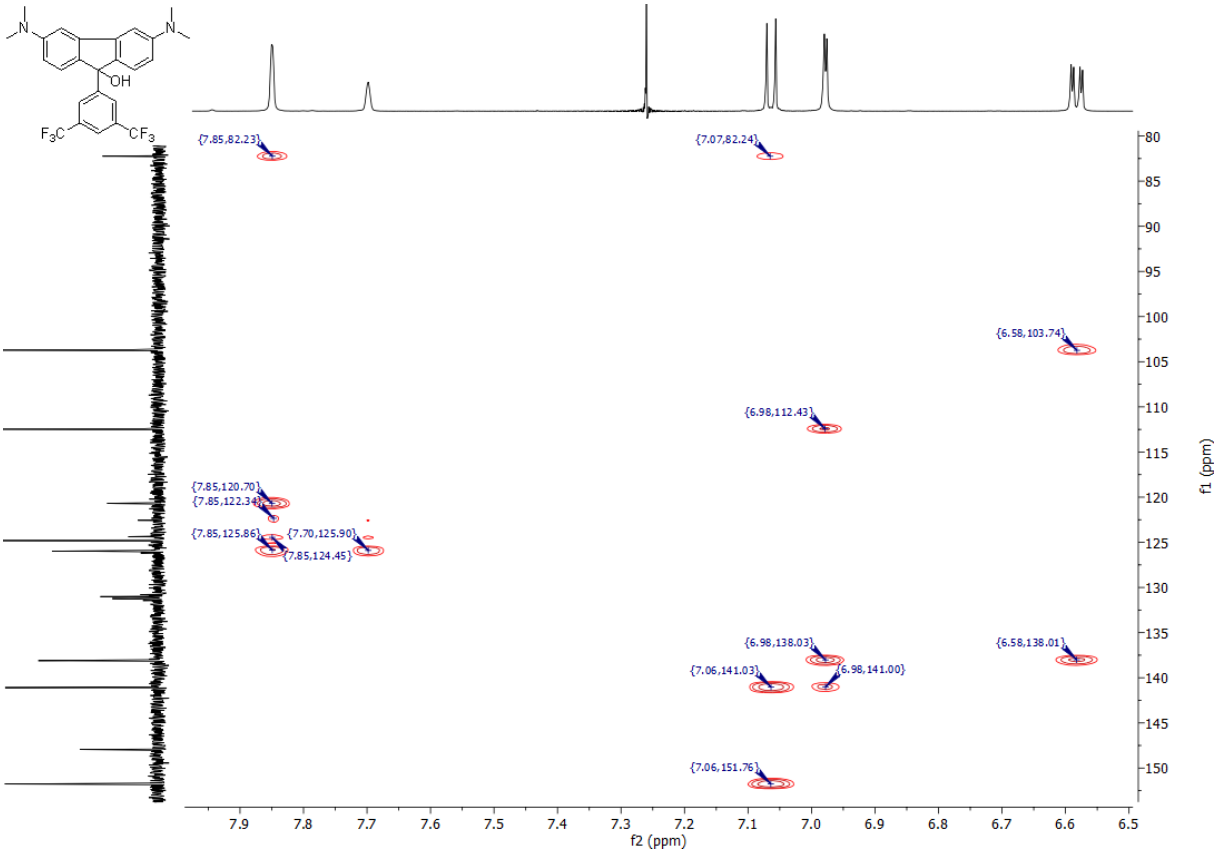
5.8) NMR spectra of towards compound 12



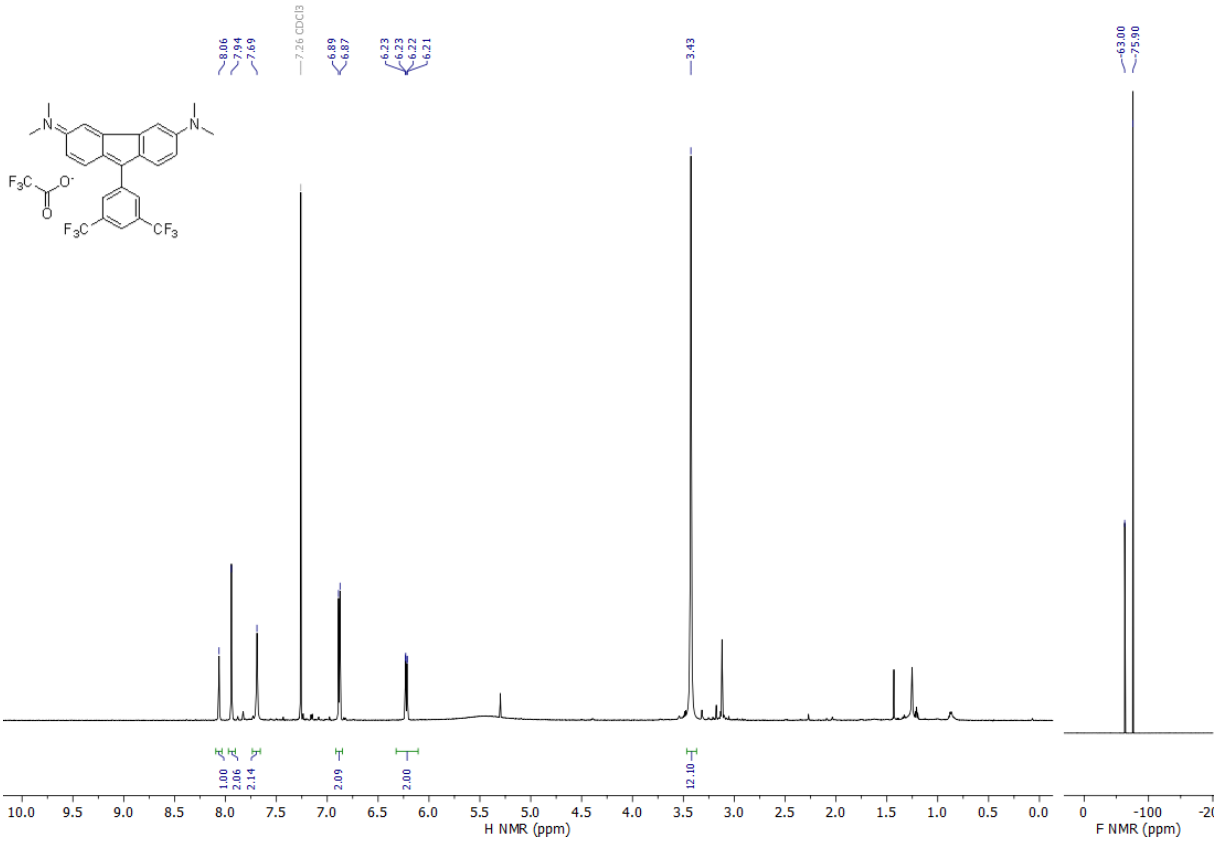


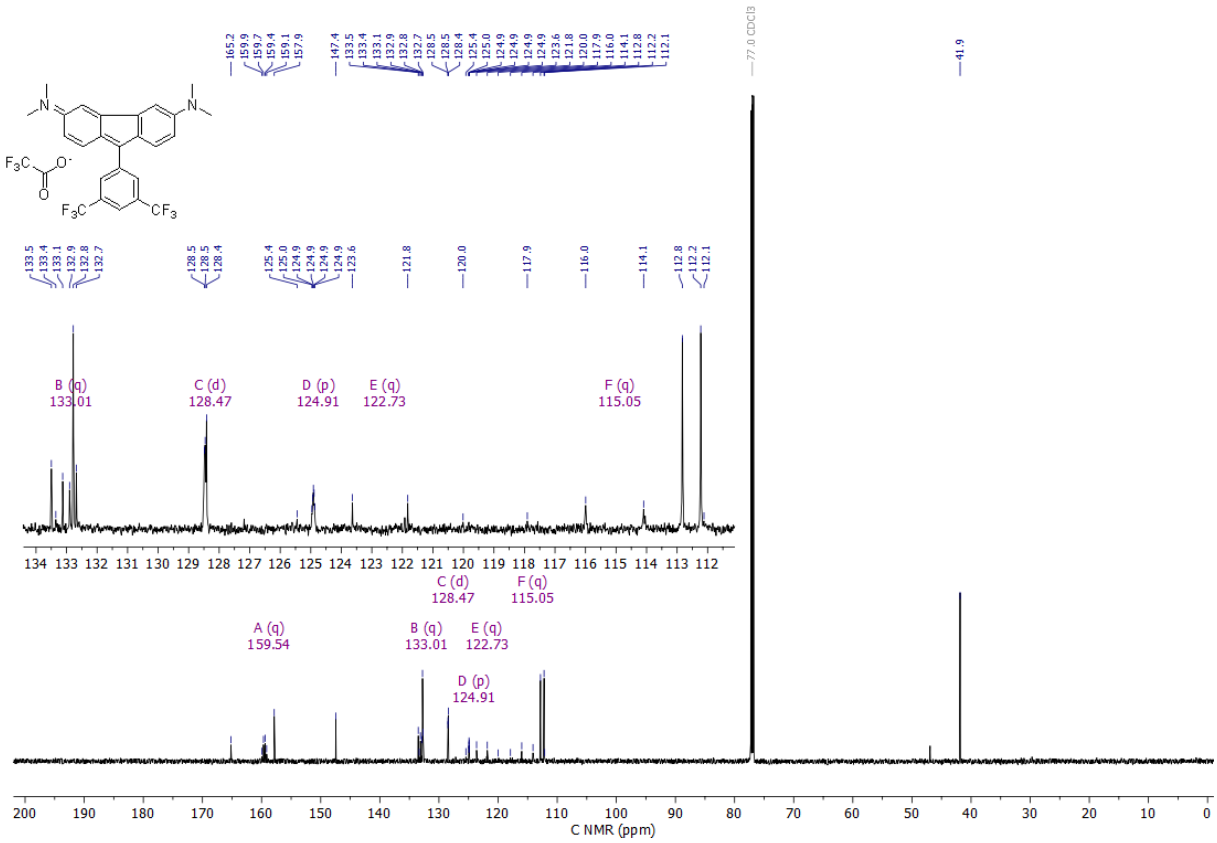


^{1}H, ^{1}H-COSY



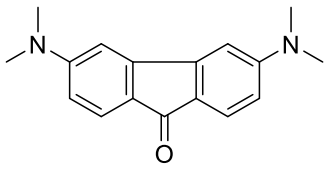
^{1}H, ^{13}C-HSQC


8.06
7.94
7.69
7.26 CDCl3
6.89
6.87
6.23
6.23
6.22
6.21
3.43
-63.00
-75.90
1.00
2.06
2.14
2.09
2.00
12.10
H NMR (ppm)
F NMR (ppm)

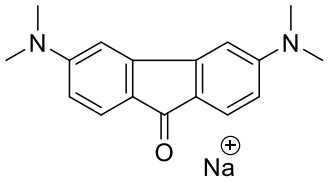

165.2
159.9
159.7
159.4
159.1
157.9
147.4
133.5
133.4
133.1
132.9
132.8
132.7
128.5
128.5
128.4
125.4
125.0
124.9
124.9
124.9
123.6
121.8
120.0
117.9
116.0
114.1
112.8
112.2
112.1
77.0 CDCl3
41.9
B (q)
133.01
C (d)
128.47
D (p)
124.91
E (q)
122.73
F (q)
115.05
A (q)
159.54
C NMR (ppm)

6) Mass spectra

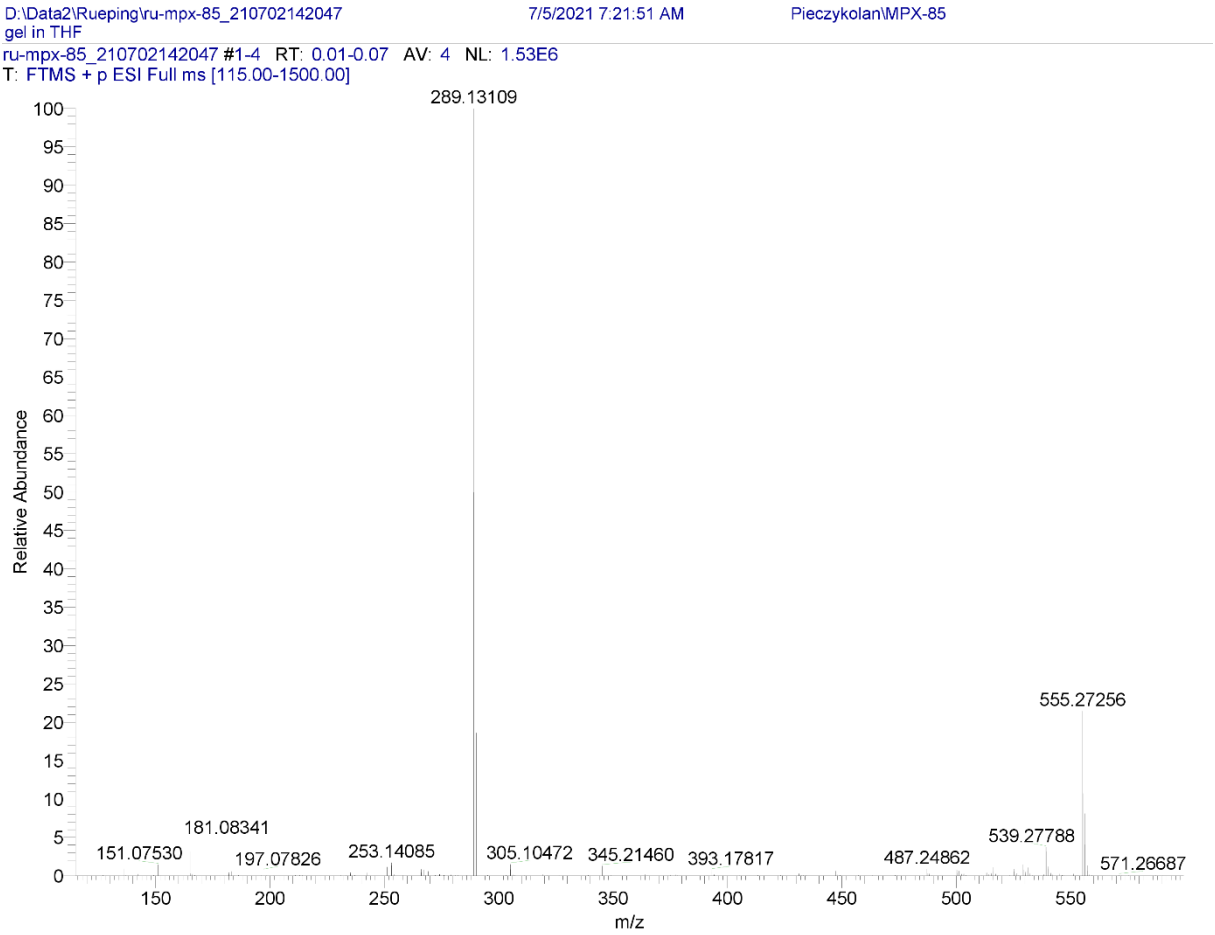
6.1) HRMS of Compound 5a



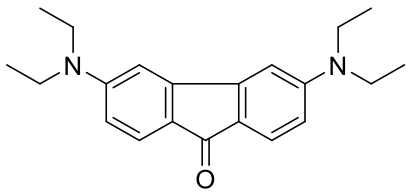
Chemical Formula: $C_{17}H_{18}N_2O$
Molecular Weight: 266,3440



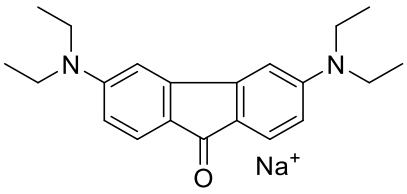
Chemical Formula: $C_{17}H_{18}N_2NaO$
Molecular Weight: 289,1311



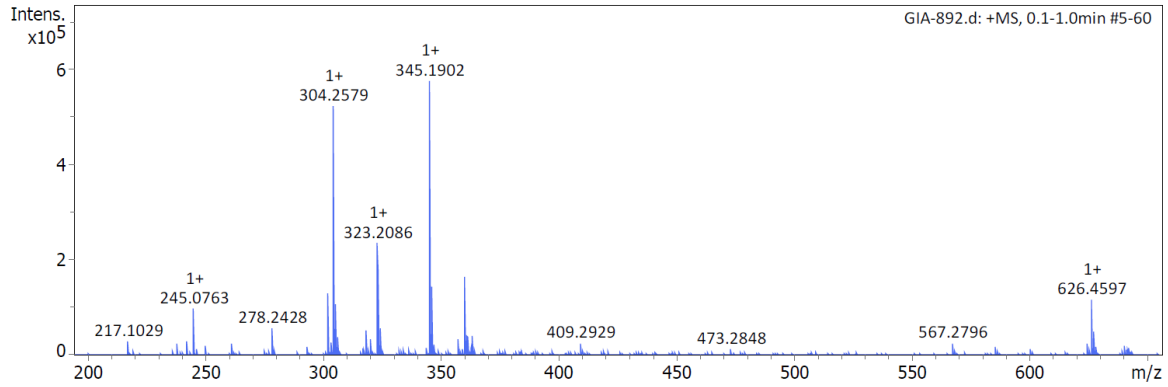
6.2) HRMS of Compound 5b



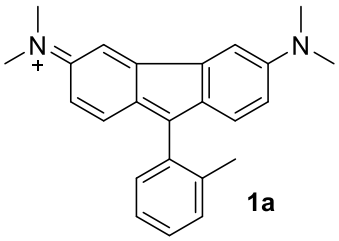
Chemical Formula: $C_{21}H_{26}N_2O$
Molecular Weight: 322,4520



Chemical Formula: $C_{21}H_{26}N_2NaO^+$
Molecular Weight: 345,1937

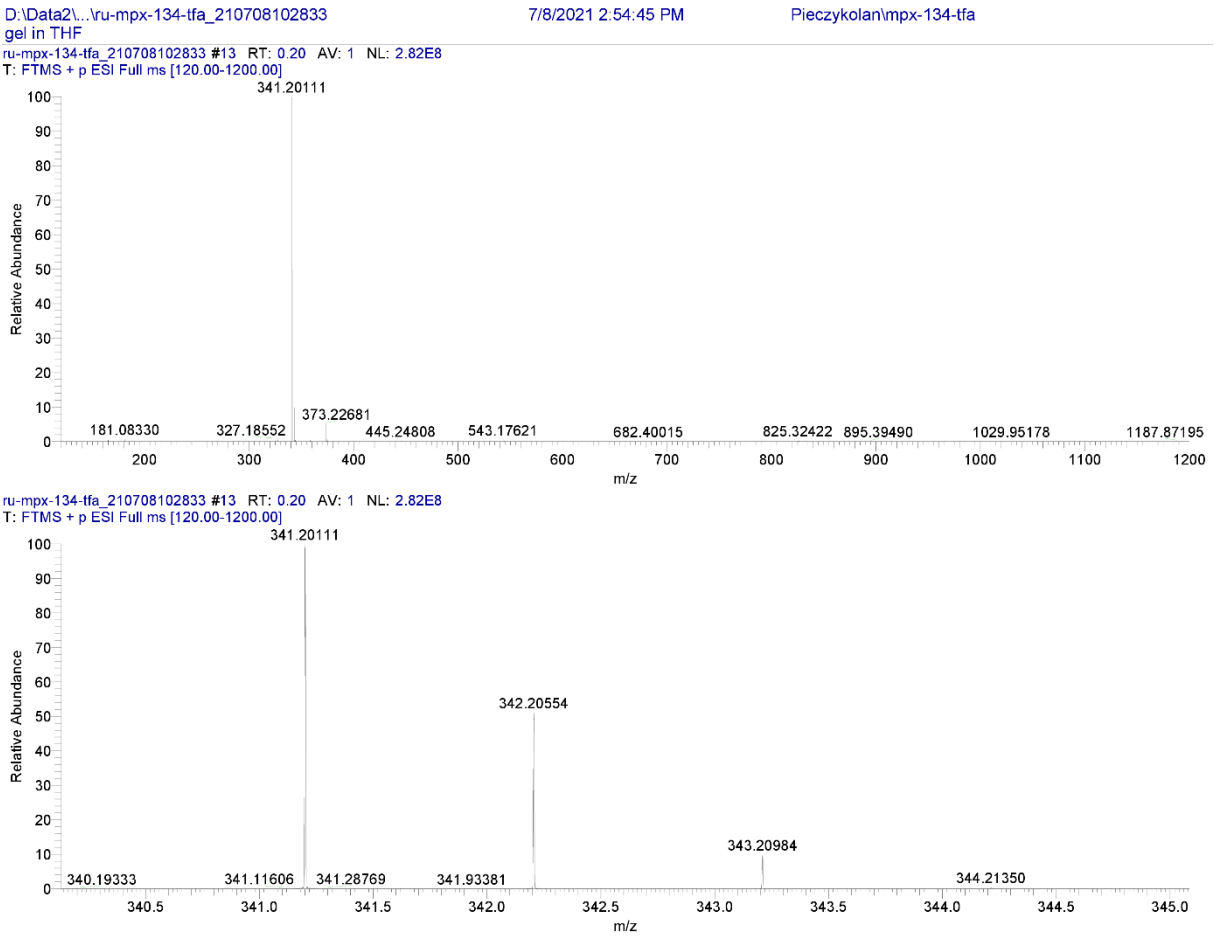


6.3) HRMS of Compound 1a

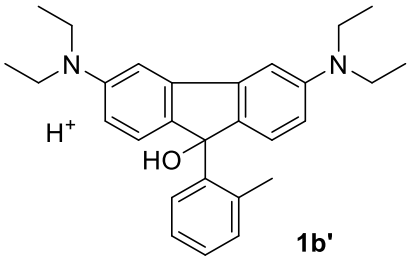


Chemical Formula: $C_{24}H_{25}N_2^+$

Exact Mass: 341,2012



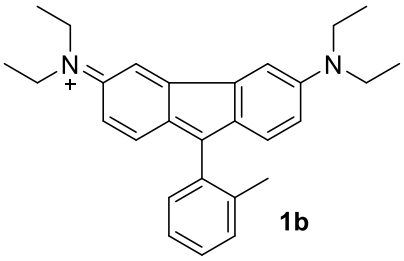
6.4) HRMS of Compound 1b



1b'

Chemical Formula: $C_{28}H_{35}N_2O^+$
Exact Mass: 415.2744

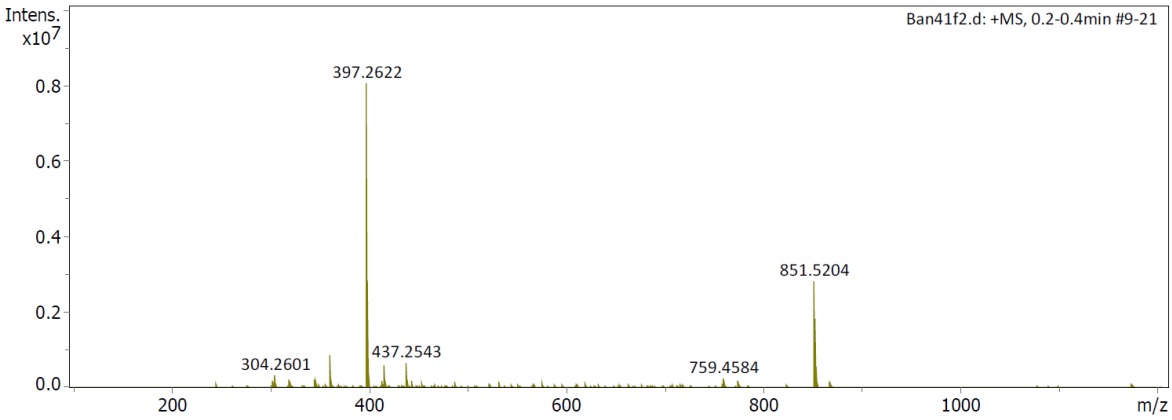
and

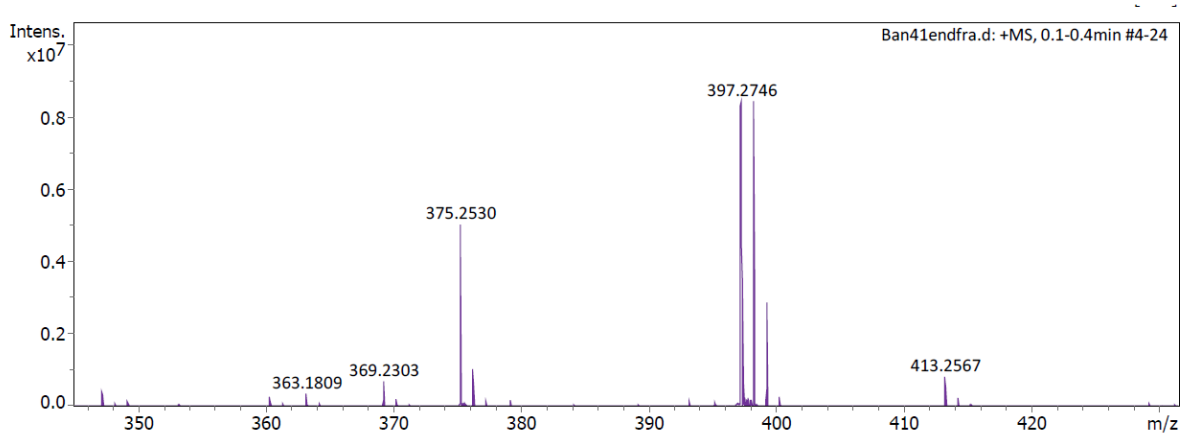


1b

Chemical Formula: $C_{28}H_{33}N_2^+$
Exact Mass: 397,2638

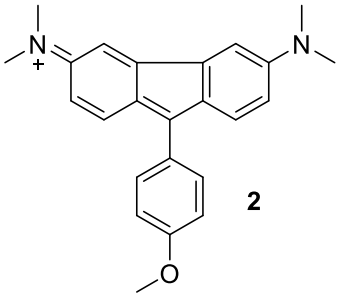
1b'





1b

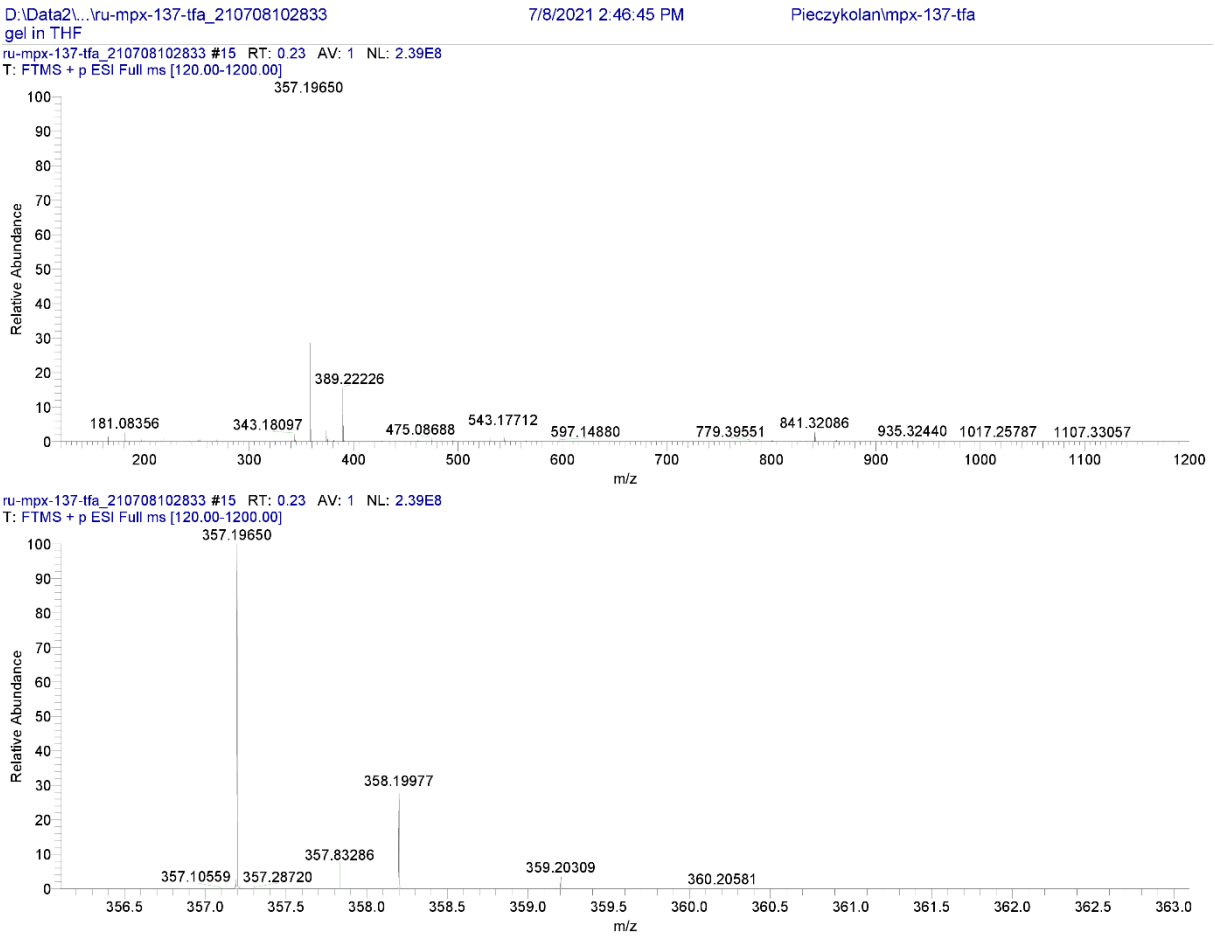
6.5) HRMS of Compound 2



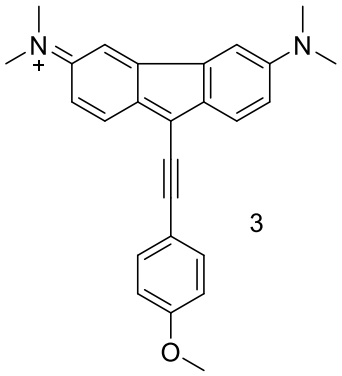
2

Chemical Formula: $C_{24}H_{25}N_2O^+$

Exact Mass: 357,1961



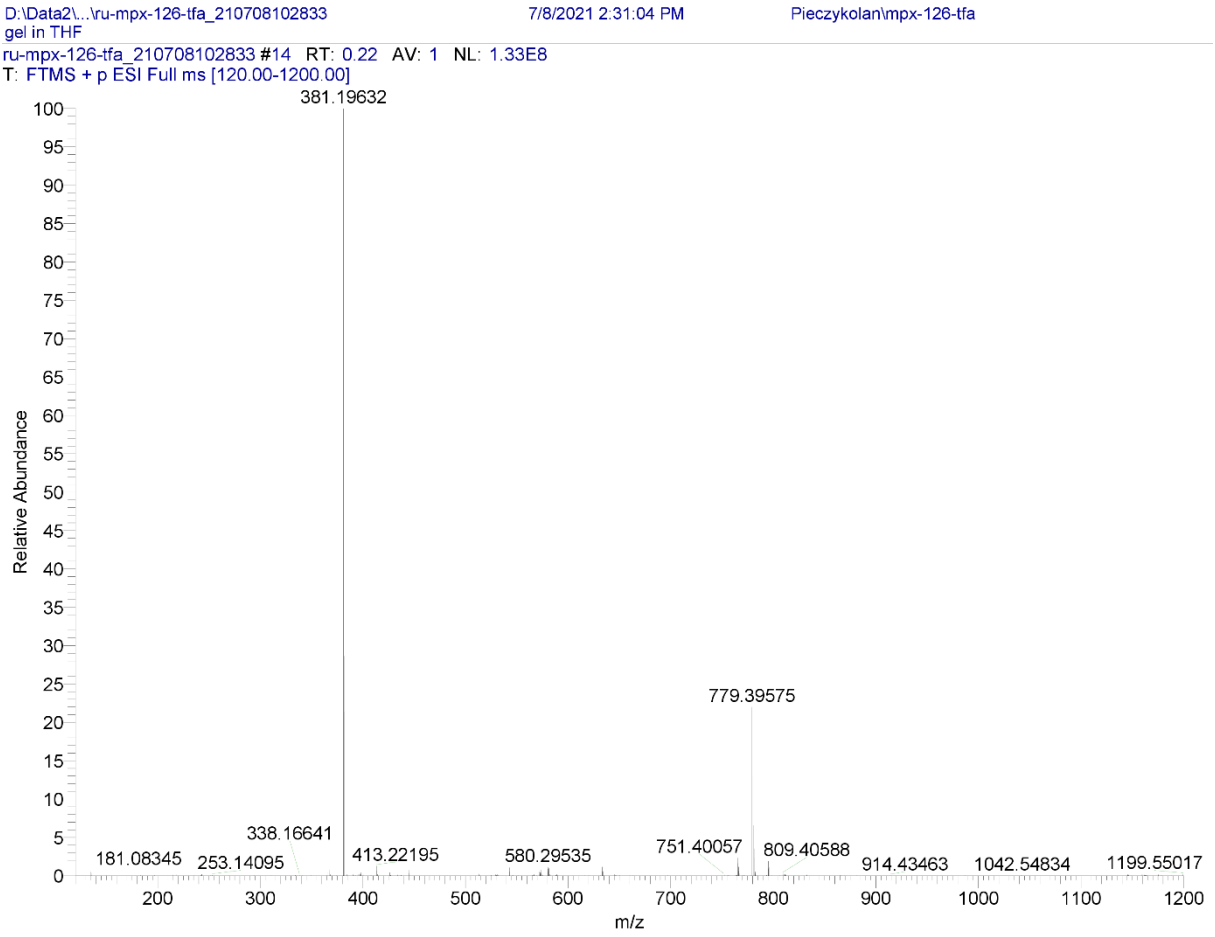
6.6) HRMS of compound 3



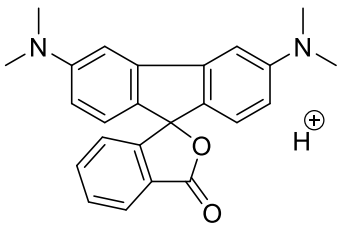
3

Chemical Formula: $C_{26}H_{25}N_2O^+$

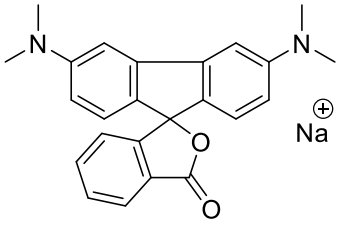
Exact Mass: 381,1961



6.7) HRMS of Compound 4

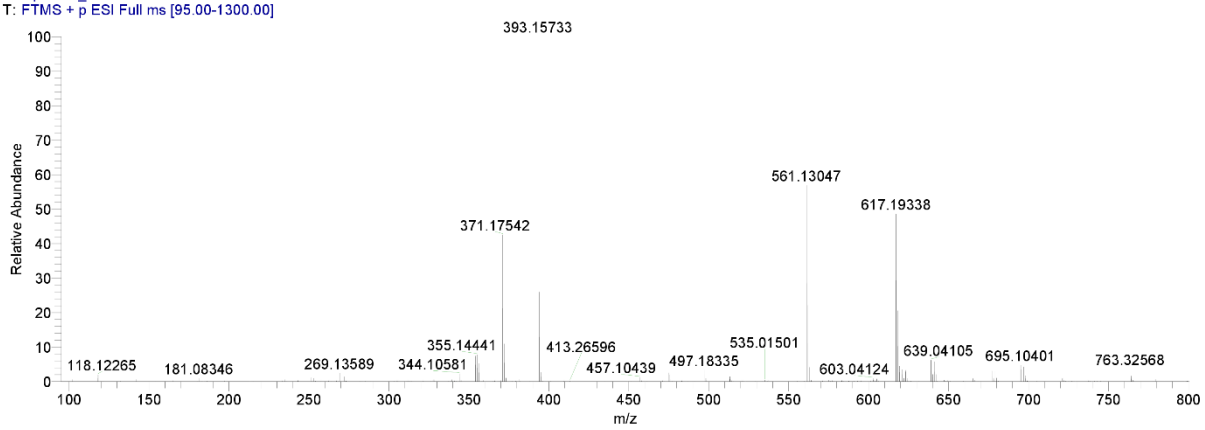


Chemical Formula: $C_{24}H_{23}N_2O_2^+$
Exact Mass: 317,1750

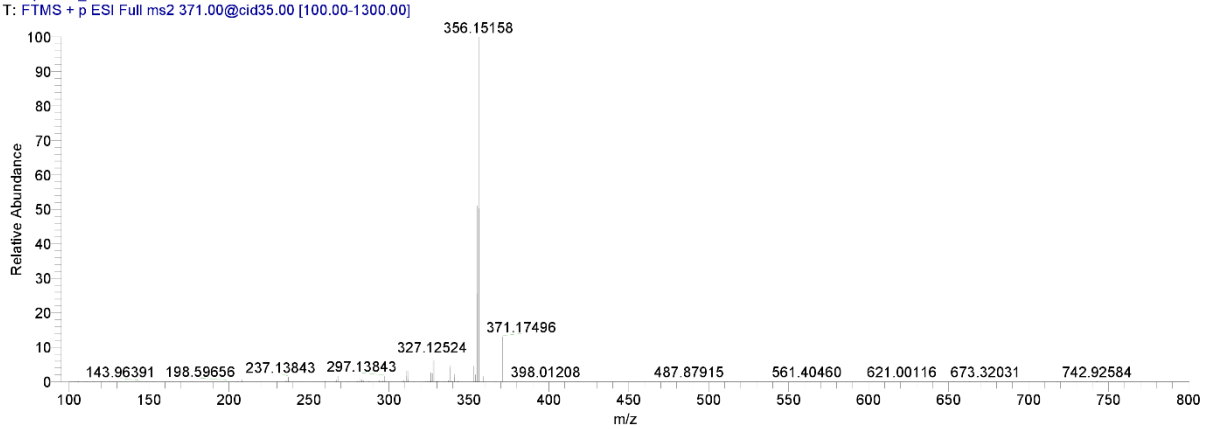


Chemical Formula: $C_{24}H_{22}N_2NaO_2$
Exact Mass: 393,15735

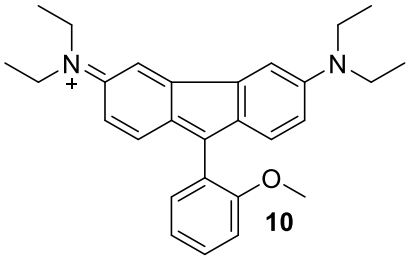
D:\Data2\Rueping\ru-mpx-142_210708081955 7/8/2021 8:49:35 AM Pieczyk/MPX-142
gel in THF
ru-mpx-142_210708081955 #108-114 RT: 2.45-2.57 AV: 7 NL: 1.02E6
T: FTMS + p ESI Full ms [95.00-1300.00]



ru-mpx-142_210708081955 #22 RT: 0.47 AV: 1 NL: 2.89E5
T: FTMS + p ESI Full ms2 371.00@cid35.00 [100.00-1300.00]



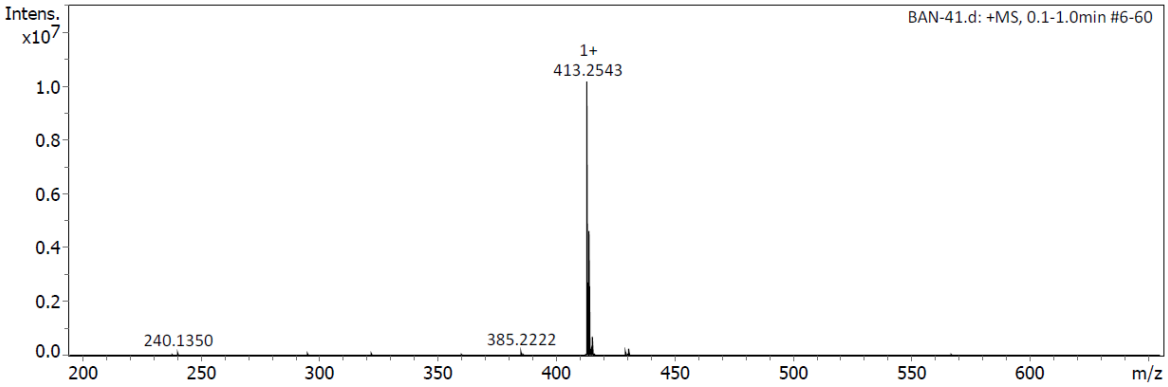
6.8) HRMS of Compound 10



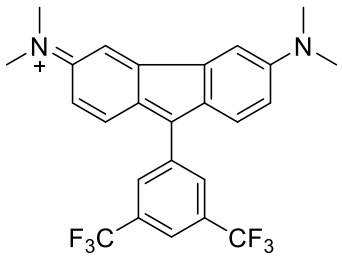
10

Chemical Formula: $C_{28}H_{33}N_2O^+$

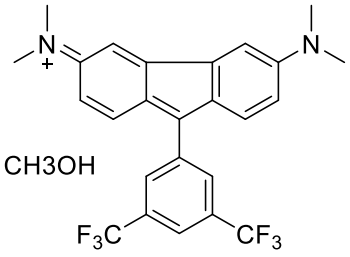
Exact Mass: 413,25874



6.9) HRMS of Compound 12



Chemical Formula: $C_{25}H_{21}F_6N_2^+$
Exact Mass: 463,16034



Chemical Formula: $C_{26}H_{25}F_6N_2O^+$
Exact Mass: 495,18656