A Strategic Approach For Csp^3-H Functionalization of 9H-Fluorene: A Acceptorless Dehydrogenation and Borrowing Hydrogen Approach

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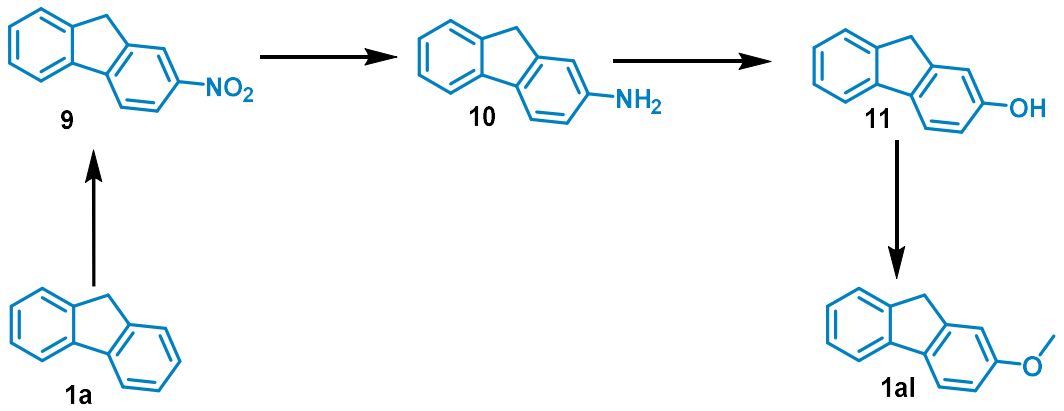
1. General Considerations.

Unless otherwise mentioned, all chemicals were purchased from common commercial sources and used as received. All solvents were dried by using standard procedure. All catalytic reactions were carried out under argon atmosphere using dried glassware and standard syringe/septa techniques. DRX-400 Varian spectrometer and Bruker Avance III 600, 500 and 400 spectrometers were used to record ^{1}H and ^{13}C NMR spectra using $CDCl_3$ as solvent and TMS as an internal standard. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (J) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dt = doublet of triplet, td = triplet of doublet and brs = broad singlet. Q-TOF ESI-MS instrument (model HAB 273) was used for recording mass spectra. SRL silica gel (100-200 mesh) was used for column chromatography.

2. Experimental Procedure for the Synthesis of 2-Methoxy fluorene: [1,2]



2a. Preparation of 2-nitrofluorene:

The 2-nitro-9H-fluorene **(9)** was prepared based on the procedure reported in the literature. 9H-fluorene (2.15 g, 15 mmol) was dissolved in 22 mL of glacial acetic acid at 60 °C and subsequently, nitric acid 65 % (3.5 mL) was added in a dropwise manner over 15 min with vigorous stirring. During the addition, the colour of the solution slightly turns yellow, along with a little precipitation. The resulting mixture was allowed to stir at 80 °C. The progress of the reaction was screened via TLC (ethyl acetate: hexane 1:9 v/v). After completion of the reaction, the mixture was poured into 100 mL of water and then, the crude product was filtered off, washed with water and 80 mL cold ethanol to afford the pure product **9** 90 % (2.848 g) as slightly-yellow solid.

2b. Preparation 2-aminofluorene:

2-nitro-9H-fluorene[1] **9** (2.11 g, 10 mmol) was added dropwise to a flask containing calcium chloride (8 mmol) and zinc powder (9.807 g, 150 mmol) in hot water (25 mL). The mixture was heated under reflux for 30 min. The zinc was filtered and washed and sodium carbonate (0.848 g, 8 mmol) was added to the filtrate. The salt was filtered and washed. The crude product was extracted with ether. The salt was filtered and the solvent was removed under vacuum. The title compound was obtained 84% (1.527g) as a brown solid **10**.

2c. Preparation of 2-hydroxyfluorene:

2- Amino fluorene, **10** (1.81 g, 10 mmol) was boiled in 25 mL of water containing 2.64 mL of concentrated hydrochloric acid until a clear solution resulted. This was cooled to 40 °C and a solution of 1.00 g of sodium nitrite in 10 mL of water was added with stirring. The resulting diazonium solution

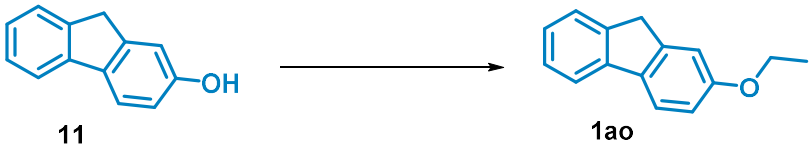
was slowly added (1 h) to 50 mL of boiling water containing 3.3 mL of concentrated sulphuric acid. On cooling, a mixture of white and dark-coloured crystals separated. This was dissolved in 100 mL of warm 10% potassium hydroxide, filtered and acidified which gave a light cream coloured solid **11**.

2d. Preparation of 2-Methoxy fluorene:

To a stirred solution of 2-hydroxyfluorene (0.182 g, 1 mmol) in ACN (1.5 mL) was added K_2CO_3 (0.414 g, 3 mmol) followed by MeI (0.284 g, 2 mmol) and the reaction was stirred at 40 °C for 5 h. Water was added and the resulting beige precipitate was collected by filtration. The filtrate was columned using hexane to 5% EtOAc and hexane to give the title compound (**1al**) as white solid 63% (0.125 g).[3]

White solid, Yield: 63%, 0.125 g, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.14 (s, 1H), 6.97 (d, *J* = 10.2 Hz, 1H), 3.90 (s, 5H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 145.1, 142.7, 141.7, 134.8, 126.8, 125.6, 124.9, 120.5, 119.1, 112.9, 110.6, 55.5, 37.0.

3. Experimental Procedure for Synthesis of 2-Ethoxy fluorene:[3]

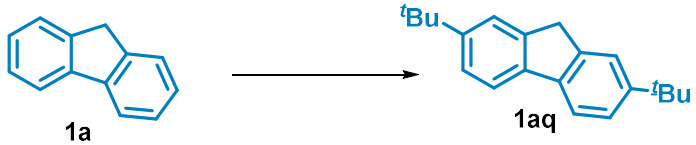


11 **1ao**

To a stirred solution of 2- hydroxyfluorene, **11** (0.182 g, 1 mmol) in ACN (1.5 mL) was added K_2CO_3 (3 mmol) followed by Ethyl Iodide (0.312 g, 2 mmol) and the reaction was stirred at 40 °C for 5 h. Water was added and the resulting beige precipitate was collected by filtration. The filtrate was columned using 5% ethyl acetate and hexane to give the pure product as a white solid **1ao** (0.149 g**)** in 71% yield.

White solid, Yield: 71%, 0.155 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (t, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.08 (s, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.85 (s, 2H), 1.44 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 145.0, 142.7, 141.7, 134.7, 126.7, 125.5, 124.8, 120.5, 119.0, 113.6, 111.2, 63.7, 37.0, 14.9.

4. Experimental Procedure for Synthesis of 2,7-di(tertbutyl) fluorene:[6]

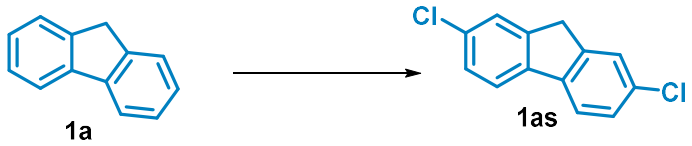


1a **1aq**

To a solution of 0.166 g of fluorene and 1 mL of tert-butyl chloride in 10 mL of CH_2C1_2 under an atmosphere of N_2 was added in small portions anhydrous $FeCl_3$ at a rate to maintain steady evolution of HCl. Over a period of 2.5 h a total of 0.6 g of $FeCl_3$ was used. When the reaction was finished addition of the catalyst no longer caused HC1 evolution. The reaction mixture was washed with five 20-mL portions of 10% hydrochloric acid and two 20-mL portions of water and dried over Na_2SO_4. Removal of solvent and passage of the crude product through a column of basic alumina with elution by hexane served to remove residual $FeCl_3$. There was obtained 0.175 g (72%) of the hydrocarbon **1aq** as white crystals.

White crystal, Yield: 72%, 0.175 g, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.61 (s, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 3.91 (s, 2H), 1.43 (s, 18H).

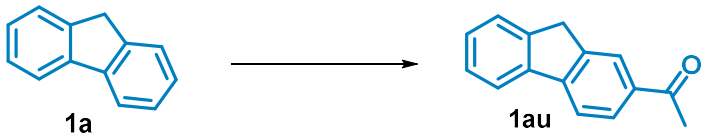
5. Experimental Procedure for Synthesis of 2,7-Dichloro fluorene: [5]



A 100 mL round bottomed flask was charged with fluorene, **1a** (1.99 g, 12 mmol), NCS (3.338 g, 25 mmol), and acetonitrile (7 mL). To the mixture, concentrated hydrochloric acid (0.4 mL) was added dropwise carefully to keep the temperature below the boiling point of acetonitrile. After the completion of the addition, the product was slowly precipitated from the homogeneous mixture while cooling the temperature down to r.t. The suspension was stirred for 24 h and the solid was collected by filtration. The crude product was washed with methanol (25 mL) three times and water (50 mL) twice, respectively. The product was dried under vacuum to obtain 1.825 g of **1as** as white solid in 65% yield.

White solid, Yield: 65%, 1.825 g, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.1 Hz, 1H), 7.49 (s, 1H), 7.34 (d, *J* = 9.1 Hz, 1H), 3.86 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 139.3, 132.8, 127.3, 125.4, 120.8, 36.6.

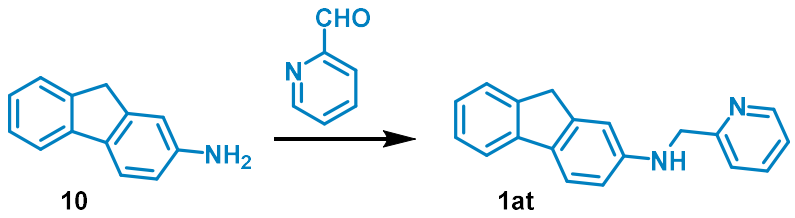
6. Experimental Procedure for Synthesis of 2-Acetyl fluorene:[4]



To a stirred solution of AcCl (0.92 mL; 13 mmol) and $AlCl_3$ (1.99 g; 15 mmol) in DCE (20 mL), 9H-fluorene **1a** (1.66 g, 10 mmol) in the same solvent (20 mL) was added drop wise over 5 min and the mixture was stirred at room temperature for 1 h and then refluxed for another 23 h. At the end of the reaction time, the resulting mixture was cooled and added to a mixture of conc. HCl and ice. The dark brown-yellow solid obtained was chromatographed over a short column of a silica gel and eluted first with petroleum ether to remove any unreacted hydrocarbon and then with benzene which upon concentration gave the white needle-like crystals of 2-acetyl-9H-fluorene **1au** (85% yield).

Pale yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). 85% Yield, 1.78 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.87 (t, *J* = 8.2 Hz, 3H), 7.61 (d, *J* = 7.1 Hz, 1H), 7.43 (dt, *J* = 23.6, 7.2 Hz, 4H), 3.98 (s, 2H), 2.68 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.1, 146.5, 144.5, 143.3, 140.5, 135.6, 128.1, 127.8, 127.1, 125.3, 125.0, 120.9, 119.7, 36.9, 26.8.

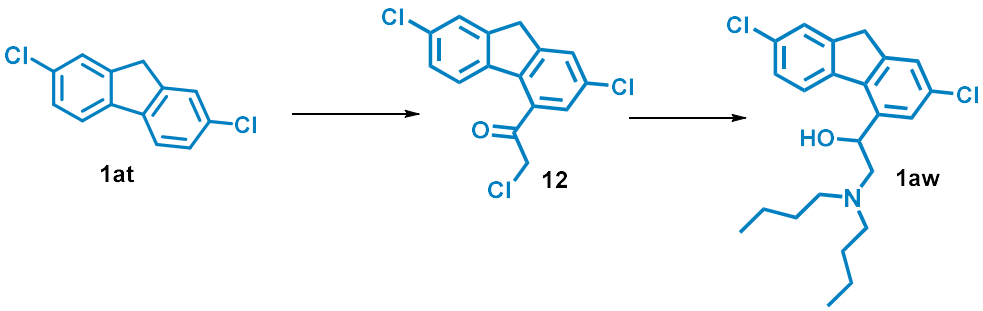
7. Experimental Procedure for Synthesis of N-(pyridin-2-ylmethyl)-9H-fluoren-2-amine:[7]



In a 25 mL RB was charged with magnetic stir, 2-aminofluorene (0.181 g, 1 mmol), **10**, pyridine-2-carboxaldehyde (0.107 g, 1 mmol), and 2.5 mmol of Na_2SO_4 was stirred in DCM overnight. After the complete conversion, the DCM was evaporated to dryness and afterward the imine thus formed (intermediate) was then treated with 4 equiv. $NaBH_4$ in methanol (5 mL) resulting in the title product **1at** yellow solid (0.26 g) in 95% yield.

Yellow solid, Yield: 95%, 0.26 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.60 (d, *J* = 4.3 Hz, 1H), 7.74 – 7.52 (m, 3H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.20 – 7.14 (m, 2H), 6.86 (s, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 4.52 (s, 1H), 3.80 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 149.2, 147.5, 145.2, 142.3, 142.2, 136.6, 132.2, 126.6, 124.8, 124.7, 122.1, 121.6, 120.6, 118.4, 112.3, 109.5, 49.6, 37.0.

8. Experimental Procedure for the Synthesis of 2-(dibutylamino)-1-(2,7-dichloro-9H-fluoren-4-yl)ethan-1-ol:[8]

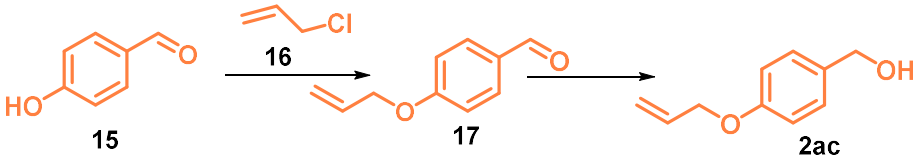


A mixture of chloroacetyl chloride (1.47 g, 13 mmol), $AlCl_3$ (1.99 g, 15 mmol), and dichloromethane (15 mL) was cooled to 0 °C. A solution of **1at** (2.34 g, 10 mmol) dissolved in dichloromethane (10 mL) was added. After 3-10 h, the deep-red reaction mixture was transferred to 15% aqueous hydrochloric acid (75 mL). After phase separation, the organic phase was washed twice with water. Dichloromethane was distilled off, while ethanol was added at the same rate. The crude mixture was purified through column chromatography (5% ethyl acetate in hexane) and isolated **12** in 65% (2.0 g) yield.

To a slurry of **12** (1.54 g, 5 mmol) in ethanol (25 mL) was added sodium borohydride (0.55 g, 15 mmol) portionwise at -5 to 5 °C within 1 h. As the viscosity increased, good mixing was necessary to reach complete conversion. After agitating for 1 h, dibutylamine (2.6 g, 20 mmol) was added, and the mixture was heated up to distill off the ethanol. The mixture was heated to 140 °C for 3 h, cooled down to below 90 °C, and quenched with 10% aqueous sodium hydroxide (50 mL). After phase separation, the organic phase was washed with brine (2 × 50 mL). The organic layer was concentrated under reduced pressure and purified under column chromatography (30% ethyl acetate in hexane) and isolated **1aw** 75% (1.95 g) yield.

Yellow gummy liquid, Yield: 75%, 1.95 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.43 (s, 1H), 7.32 (s, 1H), 7.25 (dd, *J* = 8.3, 1.6 Hz, 1H), 5.31 (dd, *J* = 10.1, 3.3 Hz, 1H), 3.78 (s, 2H), 2.80 (dd, *J* = 13.0, 3.5 Hz, 1H), 2.69 – 2.55 (m, 2H), 2.47 – 2.36 (m, 3H), 1.46 – 1.36 (m, 4H), 1.34 – 1.23 (m, 4H), 0.89 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.5, 145.3, 139.8, 139.2, 135.6, 133.3, 132.4, 127.1, 125.4, 124.5, 123.9, 65.6, 60.0, 53.4, 36.9, 29.1, 20.6, 14.1.

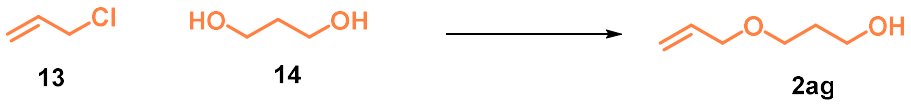
9. General Experimental Procedure for the Synthesis of (4-(allyloxy)phenyl)methanol.[10]



To a 50 mL of round bottom flask, 4-hydroxy benzaldehyde, **15** (0.366 g, 3 mmol), allyl chloride, **16** (1.3 mL, 15 mmol) and K_2CO_3 (0.83 g, 6 mmol) was stirred in acetonitrile (10 mL) overnight. It was followed by evaporation of solvent and then extracted in DCM. The crude mixture was then purified through column chromatography isolating **17** in 90% yield. The obtained product was then treated with $NaBH_4$ (3 equiv.) in methanol (15 mL) at 0 °C (for 30 min) and then continued the reaction in room temperature for 4 h. The solvent was evaporated and the reaction mixture was extracted in DCM which was directly used in catalysis without further purification.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.09 – 6.01 (m, 1H), 5.41 (d, *J* = 17.3 Hz, 1H), 5.29 (d, *J* = 10.5 Hz, 1H), 4.59 (s, 2H), 4.53 (d, *J* = 5.3 Hz, 2H).

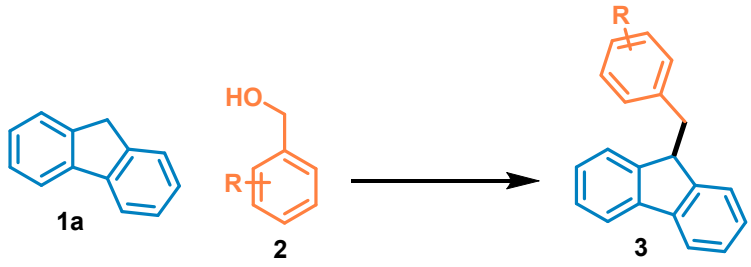
10. General Experimental Procedure for the Synthesis of 3-(allyloxy)propan-1-ol.[9]



A 100 mL oven dried RB flask was charged with NaH (0.4 g, 10 mmol, 1.5 equiv, 60%), DMF (15 mL), and cooled to 0 °C. 1,4-Butanediol, **14** (0.9 g, 10 mmol, 1.5 equiv.) was added into stirred suspension of NaH, stirred for 20 min at room temperature, then allyl chloride, **13** (0.6 mL, 6.7 mmol, 1 equiv.) was added, and reaction mixture was stirred at room temperature for 4 h. The reaction was quenched with ice-cold water (40 mL), and extracted with EtOAc (50 mL x 3). The combined organic layer was concentrated in vacuo, and the residue **2ag** was used for the next step without purification.

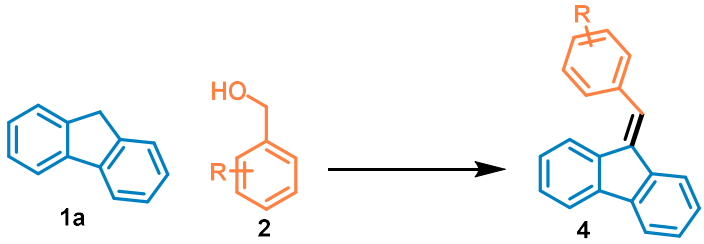
White liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.95 – 5.86 (m, 1H), 5.28 (d, *J* = 17.2 Hz, 1H), 5.19 (d, *J* = 11.6 Hz, 1H), 3.99 (d, *J* = 5.6 Hz, 2H), 3.65 (t, *J* = 5.7 Hz, 2H), 3.49 (t, *J* = 5.8 Hz, 2H), 2.30 (s, 1H), 1.672 – 1.66 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.6, 117.2, 71.9, 70.3, 62.8, 30.2, 26.8.

11. General Experimental Procedure for The Alkylation of Fluorene Derivatives.



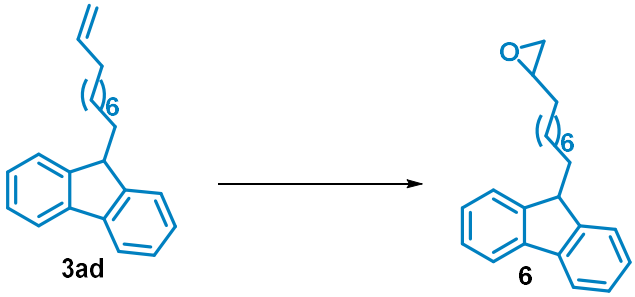
To an oven dried 10 mL round bottom flask, Fluorene **1a** (0.083 g, 0.5 mmol), alcohols **2** (0.75 mmol), KOH (0.023, 80 mol%) and **Cat. 1** (0.009 g, 2 mol%) were taken under argon atmosphere, after that 2 ml of toluene was added to the reaction mixture. The resulting mixture was heated in an oil bath at 130 °C for 24 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using hexane or 1%-10% ethyl acetate in hexane to get pure C-alkylated compound **3**.

12. General Experimental Procedure for The Alkenylation of Fluorene Derivatives.



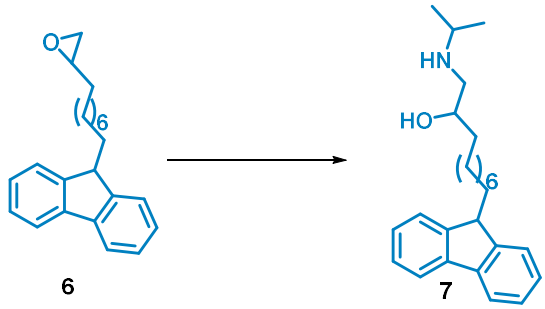
To an oven dried 10 mL round bottom flask, 9H-fluorene **1a** (0.083 g, 0.5 mmol), alcohols **2** (0.55 mmol), KOH (0.011 g, 40 mol%) and **Cat. 1** (0.007 g, 1.5 mol%) were taken under argon atmosphere, after that 2 mL of toluene was added to the reaction mixture. The resulting mixture was heated in an oil bath at 130 °C for 24 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using hexane or 0%-5% ethyl acetate in hexane to get pure C-alkenylated compound **4**.

13. Experimental Procedure for the Epoxidation of 3ad:



To a 10 mL RB equipped with a stir bar was added **3ad** (0.152 g, 0.5 mmol, 1.0 equiv.), $NaHCO_3$ (0.063 g, 0.75 mmol, 1.5 equiv.) and DCM (2 mL). The mixture was cooled to 0 °C before m-CPBA (0.129 g, 0.75 mmol, 1.5 equiv.) was added. After being stirred at 0 °C for 2 h, the reaction was further stirred overnight. The mixture was then diluted with DCM (10 mL) and quenched with saturated Na_2SO_3 (5 mL). The mixture was further stirred for 10 min and the organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude mixture was purified by silica flash chromatography to afford the desired product **6** as a yellow oil (0.136 g, 85% yield).

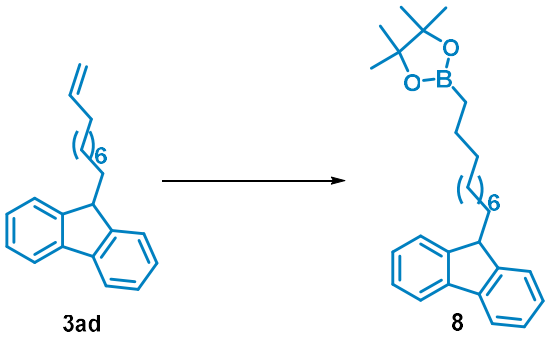
14. Experimental Procedure for the Ring Opening of 6 using Isopropylamine:



6 7

To a 10 ml RB, was equipped with a stir bar was added **7** (0.08 g, 0.25 mmol), and isopropyl amine (10 equiv.) in methanol was heated to reflux overnight. After completion of the reaction, the methanol and excess of isopropyl amine was evaporated and the organic compound was extracted with DCM in the presence of brine. The compound **7** thus isolated in 88% (0.083 g) was directly analysed through NMR.

15. Experimental Procedure for the Borylation of 3ad:



3ad 8

The synthesis of **8** was carried out according to the literature procedure. To a screw cap scintillation vial **3ad** (0.152 g, 0.5 mmol), $RuCl_2$(p-cymene) (1 mol%), and pinacolborane (0.064 g, 0.5 mmol) were charged in the argon filled glove box.[11] The reaction mixture was allowed to stir at room temperature for 12 h. Reaction progress was monitor by GC. Upon completion, the resulted boronate ester product was separated by silica-gel column chromatography using Ethyl acetate in hexane (5:90) as an eluent to give colorless oil as a title compound. The compound was further analysed via ^1H, ^{13}C NMR and HRMS spectrometry.

16. Experiment Investigating Radical Possibility in the Reaction Mechanism:

To an oven dried 10 mL round bottom flask, 9H-fluorene **1a** (0.083 g, 0.5 mmol), 4-methoxybenzyl alcohol **2a** (0.103 g, 0.75 mmol), **Cat. 1** (2 mol%, 0.009 g), KOH (80 mol%, 0.023 g), TEMPO (1

equiv., 0.075 g) and 2 mL toluene were taken under argon atmosphere. Then the reaction mixture was kept for stirring at 130 °C in preheated oil bath. After 24 h, mixture was cooled to room temperature and ethyl acetate was added to dilute the mixture and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography using 2-5% ethyl acetate in hexane as an eluting system to give the desired 9-alkylated fluorene product **3a** in 85% isolated yield.

17. Nickel Catalysed Alkylation of 9H-fluorene by Deuterated Labelled Alcohol:

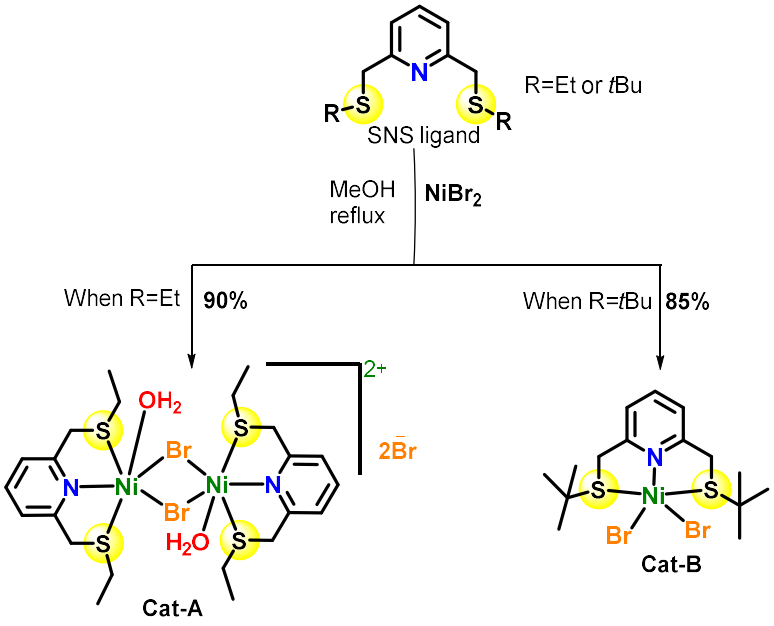
To an oven dried 10 mL round bottom flask, Fluorene **1a** (0.083 g, 0.5 mmol), deuterated 4-methoxybenzyl alcohol **2l-d** (0.105 g, 0.75 mmol), KOH (0.023 g, 80 mol%) and **Cat. 1** (0.009 g, 2 mol%) were taken, then 2 mL toluene was added under argon atmosphere. The resulting mixture was then placed into the preheated oil bath at 130 °C for 24 h under argon atmosphere. After completion the reaction cooled to room temperature, after that ethyl acetate was added to it and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture (0-2%) as eluent, 75% of **3l-d** was obtained with 37% and 29% of deuterium incorporation. The percentage of deuterium incorporation was analysed using ^{1}H-NMR spectroscopy as shown in figure S10.

18. Nickel Catalysed Hydrogenation of Intermediate with Deuterated Labelled Alcohol (2l-d).

To an oven dried 10 mL round bottom flask, alkenylated fluorene **4b** (0.142 g, 0.5 mmol), deuterated 4-methoxybenzyl alcohol **2l-d** (0.105 g, 0.75 mmol), KOH (0.023 g, 80 mol%) and **Cat. 1** (0.009 g, 2 mol%) were taken, then 2 mL toluene was added under argon atmosphere. The resulting mixture was then placed into the preheated oil bath at 130 °C for 24 h under argon atmosphere. After completion the reaction cooled to room temperature, after that ethyl acetate was added to it and filtered through celite. The filtrate was concentrated under vacuum, the residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture (0-2%) as eluent, 80% of **3l-d´** was obtained with 84% and 15% of deuterium incorporation. The percentage of deuterium incorporation was analysed using ^{1}H-NMR spectroscopy as shown in figure S11.

19. Preparation of Ligand and Complexes:[10]

The ligands and complexes were prepared according to the literature suggested which are described below.[10]



Ligand Synthesis.

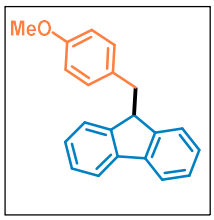
The corresponding thiols (2.1 equiv.) was mixed with MeOH containing 2.2 equiv. of NaOH. Then 2,6-bis(bromomethyl)pyridine (1 equiv.) was added in one portion under stirring at room temperature. The mixture was then heated to reflux and stirred overnight. After evaporation of the solvent, the resulting slurry was taken up in diethylether and washed twice with a saturated aqueous solution of $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent gave the ligands as colorless or slightly yellow oils in typical yields of about 90% and used without further purification. The prepared ligands were characterised using ^1H and ^{13}C NMR technique.

Complex Preparation.

Ligand [$(Py(CH_2CH_2SR)_2$, R= Et, *t*Bu,] (1.2 mmol) was taken in 5 mL MeOH and was added dropwise to the orange suspension of [$NiBr_2$] (1.0 mmol) in 10 mL MeOH. Afterward, the suspension was refluxed for overnight under argon atmosphere. After the completion of the reaction, the reaction mixture was cooled down to the room temperature, then the sol-vent was evaporated to obtain the residue, which was further washed with diethyl ether and dried under vacuum to get beautiful green solid of Ni-complexes. The complex was characterised using HRMS and Single crystal XRD technique.

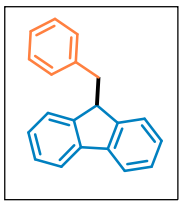
20. Characterisation Data for the Compounds:

9-(4-methoxybenzyl)-9H-fluorene (**3a**)[7]



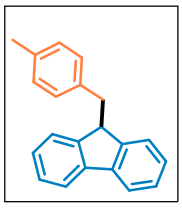
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 90% Yield, 0.128 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.24 – 7.17 (m, 4H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.17 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 3.05 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 146.9, 140.9, 131.9, 130.4, 127.1, 126.6, 124.9, 119.8, 113.7, 55.3, 48.9, 39.2.

9-benzyl-9H-fluorene (**3b**)[7]



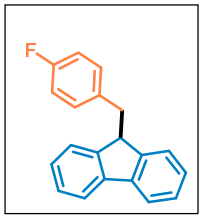
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 88% Yield, 0.112 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 6.2 Hz, 2H), 7.35 – 7.33 (m, 2H), 7.30 – 7.24 (m, 5H), 7.20 (d, *J* = 7.4 Hz, 2H), 4.27 (t, *J* = 7.6 Hz, 1H), 3.15 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.8, 140.8, 139.8, 129. 6, 128.3, 127.1, 126. 7, 126.4, 124.9, 119.8, 48.7, 40.1.

9-(4-methylbenzyl)-9H-fluorene (**3c**) [7]



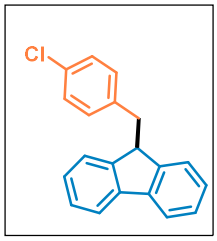
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 89% Yield, 0.120 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.14 (m, 4H), 7.13 – 7.09 (m, 4H), 4.20 (t, *J* = 7.6 Hz, 1H), 3.07 (d, *J* = 7.6 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.0, 140.8, 136.7, 135.8, 129.4, 129.0, 127.1, 126.6, 124. 9, 119.8, 48.8, 39.7, 21.1.

9-(4-fluorobenzyl)-9H-fluorene (**3d**) [7]



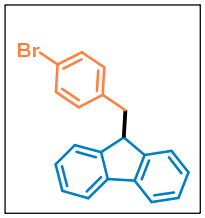
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 87% Yield, 0.119 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.17 – 7.15 (m, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 4.23 (t, *J* = 7.4 Hz, 1H), 3.15 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6 (d, *J* = 243 Hz), 146.5, 140.9, 135.2, 130.9 (d, *J* = 7.5 Hz), 127.2, 126.7, 124.8, 119.9, 115.0 (d, *J* = 21 Hz), 48.7, 39.1.

9-(4-chlorobenzyl)-9H-fluorene (**3e**) [7]



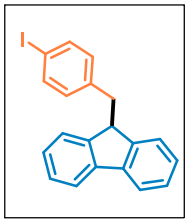
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 86% Yield, 0.125 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.21 (m, 6H), 7.12 (d, *J* = 8.2 Hz, 2H), 4.23 (t, *J* = 7.3 Hz, 1H), 3.14 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 140.9, 138.0, 132.1, 130.9, 128.3, 127.3, 126.7, 124.7, 119.9, 48.5, 39.3.

9-(4-bromobenzyl)-9H-fluorene (**3f**) [7]



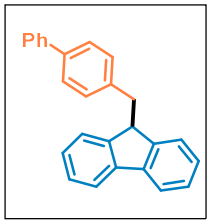
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 88% Yield, 0.147 g. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.18 – 7.11 (m, 4H), 6.95 (d, *J* = 8.3 Hz, 2H), 4.11 (t, *J* = 7.3 Hz, 1H), 3.01 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 140. 9, 138.5, 131.3, 131.3, 127.3, 126.7, 124.7, 120.2, 119.9, 48.4, 39.3.

9-(4-iodobenzyl)-9H-fluorene (**3g**) [7]



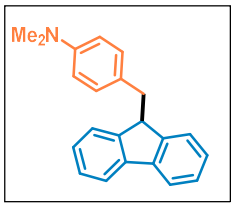
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 89% Yield, 0.170 g. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.21 – 7.08 (m, 4H), 6.85 (d, *J* = 8.2 Hz, 2H), 4.11 (t, *J* = 7.3 Hz, 1H), 3.00 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 140. 9, 139.2, 137.7, 131.3, 127.3, 126.7, 124.7, 119.9, 91.6, 48.4, 39.3.

9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene (**3h**) [7]



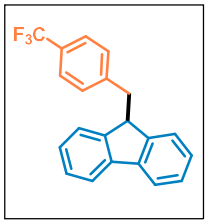
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 76% Yield, 0.127 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.32 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.22 (m, 4H), 4.26 (t, *J* = 7.5 Hz, 1H), 3.15 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 140.9, 140.9, 139.2, 138.9, 129.9, 128.8, 127.2, 127.0, 126.9, 126.7, 124.9, 119.9, 48.7, 39.8.

4-((9H-fluoren-9-yl)methyl)-N,N-dimethylaniline (**3i**)



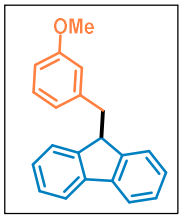
yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:4). 67% Yield, 0.099 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 6.3 Hz, 2H), 7.25 – 7.22 (m, 4H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.67 (d, *J* = 6.2 Hz, 2H), 4.11 (t, *J* = 7.7 Hz, 1H), 2.94 (d, *J* = 7.7 Hz, 2H), 2.89 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.2, 140.8, 135.0, 130.1, 129.1, 127.0, 126.6, 125.0, 120.3, 119.7, 49.1, 41.0, 39.2. HRMS (ESI) m/z: $[M + H]^+$ $C_{22}H_{21}N$: 300.1752; found 300.1752.

9-(4-(trifluoromethyl)benzyl)-9H-fluorene (**3j**) [7]



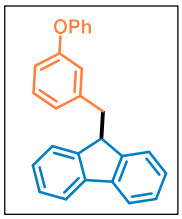
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 68% Yield, 0.110 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.20 – 7.16 (m, 4H), 7.13 (t, *J* = 7.4 Hz, 2H) 4.17 (t, *J* = 7.2 Hz, 1H), 3.13 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.2, 143.7, 140.9, 129.8, 128.7 (q, *J* = 33 Hz), 127.4, 126.8, 125.1 (q, *J* = 4.5 Hz), 124.7, 124.3 (q, *J* = 270 Hz) 120.0, 48.3, 39.7.

9-(3-methoxybenzyl)-9H-fluorene (**3l**) [7]



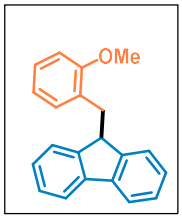
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 90% Yield, 0.128 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.16 (m, 4H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 4.18 (t, *J* = 7.5 Hz, 1H), 3.80 (s, 3H), 3.05 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 146.8, 141.4, 140.9, 129.2, 127.1, 126.7, 124.7, 121.9, 119.8, 114.9, 112.0, 55.2, 48.6, 40.1.

9-(3-phenoxybenzyl)-9H-fluorene (**3m**) [7]



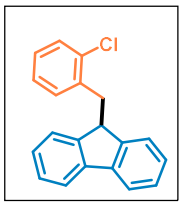
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 80% Yield, 0.128 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.34 (m, 4H), 7.29 – 7.26 (m, 5H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.96 – 6.87 (m, 4H), 6.84 (s, 1H), 4.19 (t, *J* = 7.3 Hz, 1H), 3.10 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.4, 156.9, 146.6, 141.7, 140.9, 129.7, 129.5, 127.2, 126.7, 124.8, 124.7, 123.0, 120.2, 119.9, 118.6, 117.3, 48.5, 39.8.

9-(2-methoxybenzyl)-9H-fluorene (**3n**)[7]



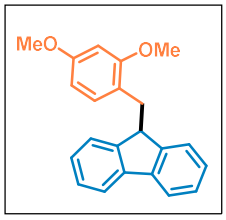
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 83% Yield, 0.118 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.26 – 7.24 (m, 2H), 7.21 (d, *J* = 7.4 Hz, 2H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 4.41 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 3H), 3.10 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 147.7, 140.8, 131.6, 128.6, 127.9, 126.9, 126.6, 125.1, 120.2, 119.7, 110.3, 55.3, 46.7, 35.6.

9-(2-chlorobenzyl)-9H-fluorene (**3o**)[7]



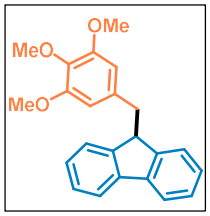
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 85% Yield, 0.123 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.18 – 7.11 (m, 4H), 7.07 – 7.04 (m, 3H), 4.29 (t, *J* = 7.7 Hz, 1H), 3.07 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 140.8, 137.8, 134.7, 132.3, 129.8, 128.1, 127.2, 126.8, 126.6, 125.0, 119.9, 46.5, 38.6.

9-(2,4-dimethoxybenzyl)-9H-fluorene (**3p**)[7]



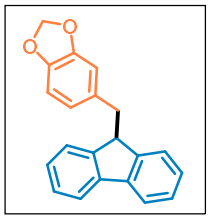
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 81% Yield, 0.128 g. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.20 (m, 4H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.58 (d, *J* = 2.2 Hz, 1H), 6.47 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.35 (t, *J* = 7.7 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.03 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 158.9, 147.8, 140.8, 131.8, 126.8, 126.5, 125.1, 121.1, 119.7, 103.6, 98.5, 55.4, 55.3, 46.9, 34.9.

9-(3,4,5-trimethoxybenzyl)-9H-fluorene (**3q**) [7]



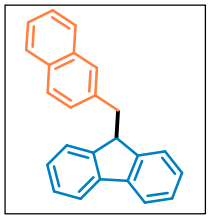
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:5). 81% Yield, 0.140 g. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.29 – 7.20 (m, 4H), 6.34 (s, 2H), 4.21 (t, *J* = 7.2 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 6H), 3.08 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.9, 146.6, 141.0, 136.6, 135.0, 127.2, 126.6, 124.9, 119.9, 106.6, 60.94, 56.1, 48.7, 40.2.

5-((9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole (**3r**) [7]



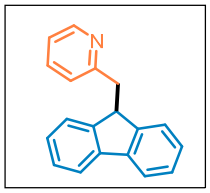
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 86% Yield, 0.129 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.24 (m, 4H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.98 (s, 2H), 4.19 (t, *J* = 7.6 Hz, 1H), 3.06 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.5, 146.7, 146.0, 140.8, 133.6, 127.1, 126.7, 124.9, 122.6, 119.8, 109.7, 108.0, 100.9, 48.9, 39.8.

9-(naphthalen-2-ylmethyl)-9H-fluorene (**3s**) [7]



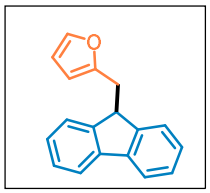
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 88% Yield, 0.135 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.78 (m, 2H), 7.77 – 7.73 (m, 3H), 7.63 (s, 1H), 7.49 – 7.40 (m, 3H), 7.35 – 7.32 (m, 2H), 7.20 – 7.16 (m, 4H), 4.34 (t, *J* = 7.6 Hz, 1H), 3.27 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 140.8, 137.4, 133.5, 132.3, 128.0, 127.9, 127.9, 127.7, 127. 7, 127.2, 126.7, 126.0, 125.4, 124.9, 119.9, 48. 6, 40.4.

2-((9H-fluoren-9-yl)methyl)pyridine (**3t**) [7]



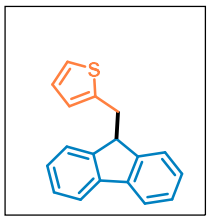
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 78% Yield, 0.100 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.68 (d, *J* = 4.2 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.60 (td, *J* = 7.6, 1.8 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 1H), 4.63 (t, *J* = 7.7 Hz, 1H), 3.23 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 149.6, 147.1, 140.8, 136.3, 127.1, 126.8, 124.7, 124.4, 121.7, 119.9, 47.2, 42.5.

2-((9H-fluoren-9-yl)methyl)furan (**3u**) [7]



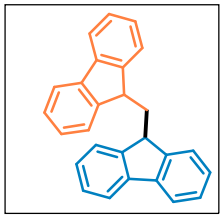
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 82% Yield, 0.101 g. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.12 (d, *J* = 5.0 Hz, 1H), 6.89 – 6.86 (m, 1H), 6.70 (d, *J* = 3.4 Hz, 1H), 4.23 (t, *J* = 7.0 Hz, 1H), 3.39 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 142.1, 141.0, 127.3, 126.8, 126.6, 126.0, 124.7, 123.8, 119.9, 49.0, 34.0.

2-((9H-fluoren-9-yl)methyl)thiophene (**3v**) [7]



White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 85% Yield, 0.111 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.37 – 7.26 (m, 4H), 7.17 (d, *J* = 5.1 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.76 (s, 1H), 4.29 (t, *J* = 7.0 Hz, 1H), 3.45 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.2, 142.1, 141.1, 127.4, 126.9, 126.6, 126.0, 124.7, 123.8, 119.9, 49.0, 34.0.

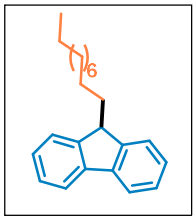
di(9H-fluoren-9-yl)methane (**3w**) [7]



White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 65% Yield, 0.112 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.6 Hz, 4H), 7.60 (d, *J* = 7.5 Hz, 4H),

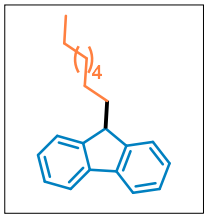
7.44 (t, J = 7.5 Hz, 4H), 7.33 (t, J = 7.4 Hz, 4H), 4.46 (t, J = 7.7 Hz, 2H), 2.26 (t, J = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.4, 141.0, 127.3, 127.0, 125.1, 120.1, 45.8, 38.9.

9-decyl-9H-fluorene (**3x**) [7]



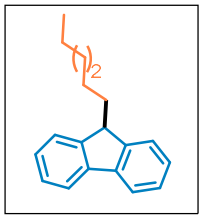
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 72% Yield, 0.110 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, J = 7.4 Hz, 2H), 7.49 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.28 (t, J = 7.8 Hz, 2H), 3.95 (t, J = 5.8 Hz, 1H), 2.00 – 1.95 (m, 2H), 1.27 – 1.16 (m, 16H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 144.8, 140.9, 140.5, 125.8, 125.7, 125.7, 125.5, 124.1, 123.3, 118.6, 118.5, 51.4, 36.1, 33.5, 30.9, 28.7, 28.6, 28.3, 26.9, 21.7, 14.7, 13.1.

9-octyl-9H-fluorene (**3y**) [7]



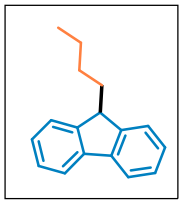
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 75% Yield, 0.104 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 7.4 Hz, 2H), 7.42 (t, J = 7.4 Hz, 2H), 7.36 (t, J = 7.3 Hz, 2H), 4.03 (t, J = 5.9 Hz, 1H), 2.07 – 2.03 (m, 2H), 1.35 – 1.23 (m, 12H), 0.92 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.7, 141.1, 126.9, 126.8, 124.4, 119.8, 47.5, 33.2, 31.9, 30.0, 29.4, 29.3, 25.8, 22.7, 14.2.

9-hexyl-9H-fluorene (**3z**) [7]



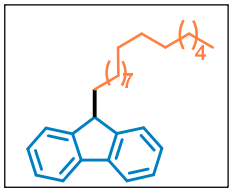
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 75% Yield, 0.094 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, J = 7.4 Hz, 2H), 7.56 (d, J = 7.4 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 4.02 (t, J = 5.9 Hz, 1H), 2.08 – 2.01 (m, 2H), 1.36 – 1.20 (m, 8H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.7, 141.1, 126.8, 126.8, 124.4, 119.8, 47.5, 33.2, 31.7, 29.7, 25.7, 22.7, 14.1.

9-butyl-9H-fluorene (**3aa**) [7]



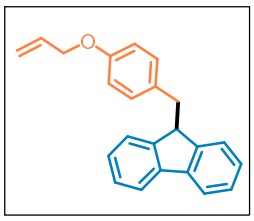
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 70% Yield, 0.078 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 6.9 Hz, 2H), 4.00 (t, *J* = 5.8 Hz, 1H), 2.05 – 2.01 (m, 2H), 1.33 – 1.27 (m, 2H), 1.23 – 1.12 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 141.1, 126.8, 126.8, 124.4, 119.8, 47.5, 32.8, 27.8, 23.1, 14.0.

9-hexadecyl-9H-fluorene (**3ab**)[12]



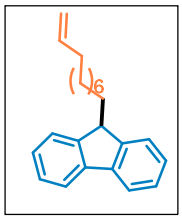
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 60% Yield, 0.117 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 4.00 (t, *J* = 5.3 Hz, 1H), 2.04 – 2.00 (m, 2H), 1.28 – 1.23 (m, 28H), 0.91 (t, *J* = 5.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.7, 141.1, 126.8, 126.8, 124.4, 119.8, 47.5, 33.1, 31.9, 30.0, 29.7, 29.6, 29.4, 29.4, 25.7, 22.7, 14.1.

9-(4-(allyloxy)benzyl)-9H-fluorene (**3ac**)



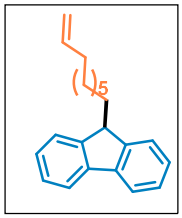
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 85% Yield, 0.133 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.14 – 6.08 (m, 1H), 5.46 (dd, *J* = 17.3, 1.56 Hz, 1H), 5.33 (dd, *J* = 11.8, 1.32 Hz, 1H), 4.58 – 4.56 (m, 2H), 4.21 (t, *J* = 7.6 Hz, 1H), 3.08 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.2, 146.9, 140.8, 133.4, 132.1, 130.4, 127.1, 126.6, 124.9, 119.8, 117.6, 114.5, 68.9, 48.9, 39.2. HRMS (ESI) m/z: $[M + Na]^+$ $C_{23}H_{20}O$: 335.1412; found 335.1412.

9-(dec-9-en-1-yl)-9H-fluorene (**3ad**)



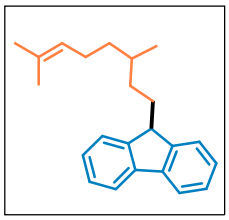
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 80% Yield, 0.122 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 5.85 – 5.78 (m, 1H), 5.03 – 4.97 (m, 1H), 4.94 (d, J = 10.6 Hz, 1H), 4.00 (t, *J* = 5.9 Hz, 1H), 2.05 – 1.98 (m, 4H), 1.39 – 1.31 (m, 2H), 1.27 – 1.17 (m, 10H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 141.1, 139.3, 126.8, 126.8, 124.4, 119.8, 114.1, 47.5, 33.8, 33.1, 30.0, 29.5, 29.4, 29.1, 28.9, 25.6. HRMS (ESI) m/z: $[M - H]^+$ $C_{23}H_{28}$: 303.2111; found 303.2098.

9-(non-8-en-1-yl)-9H-fluorene (**3ae**)



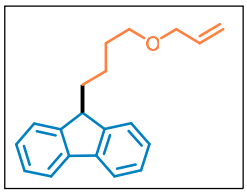
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 79% Yield, 0.114 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 5.85 – 5.78 (m, 1H), 5.00 (d, J = 17.1 Hz, 1H), 4.94 (d, J = 10.1 Hz, 1H)., 4.00 (t, *J* = 5.9 Hz, 1H), 2.04 – 2.00 (m, 4H), 1.37 – 1.32 (m, 2H), 1.29 – 1.18 (m, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 141.1, 139.2, 126.8, 126.8, 124.3, 119.8, 114.1, 47.5, 33.8, 33.1, 29.9, 29.2, 29.1, 28.9, 25.7. HRMS (ESI) m/z: $[M - H]^+$ $C_{22}H_{26}$: 289.1955; found 289.1944.

9-(3,7-dimethyloct-6-en-1-yl)-9H-fluorene (**3af**)[11]



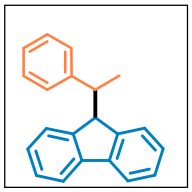
Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 82% Yield, 0.125 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 2H), 4.97 (t, *J* = 7.0 Hz, 1H), 3.89 (t, *J* = 5.8 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.88 – 1.73 (m, 2H), 1.47 (d, *J* = 8.4 Hz, 5H), 1.32 – 0.89 (m, 6H), 0.75 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 147.6, 141.1, 131.0, 126.8, 126.7, 124.9, 124.3, 124.3, 119.8, 47.6, 36.7, 32.6, 32.4, 30.3, 25.7, 25.5, 19.5, 17.6.

9-(4-(allyloxy)butyl)-9H-fluorene (**3ag**)



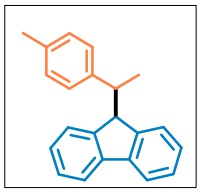
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 60% Yield, 0.083 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 5.94 – 5.87 (m, 1H), 5.26 (d, *J* = 17.2 Hz, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 4.01 (t, *J* = 5.7 Hz, 1H), 3.93 (d, *J* = 5.6 Hz, 2H), 3.37 (t, *J* = 6.7 Hz, 2H), 2.08 – 2.04 (m, 2H), 1.62 – 1.57 (m, 2H), 1.32 – 1.27 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.4, 141.1, 135.0, 126.9, 126.8, 124.4, 119.8, 116.7, 71.8, 70.2, 47.4, 33.0, 30.1, 22.4. HRMS (ESI) m/z: $[M + Na]^+$ $C_{20}H_{22}O$: 279.1749; found 279.1749.

(S)-9-(1-phenylethyl)-9H-fluorene (**3ah**) [7]



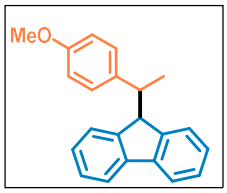
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 58% Yield, 0.078 g. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.65 (m, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.22 (m, 8H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 4.28 (d, *J* = 4.5 Hz, 1H), 3.73 – 3.61 (m, 1H), 0.91 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 144.6, 144.6, 141.8, 141.4, 128.2, 128.1, 127.1, 127.1, 126.8, 126.3, 126.3, 125.7, 124.3, 119.7, 119.6, 54.2, 41.9, 13.9.

(S)-9-(1-(p-tolyl)ethyl)-9H-fluorene (**3ai**) [7]



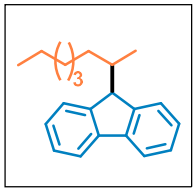
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 53% Yield, 0.075 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 – 7.68 (m, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.0 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 4.27 (d, *J* = 4.3 Hz, 1H), 3.66 – 3.60 (m, 1H), 2.36 (s, 3H), 0.89 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 144.7, 141.8, 141.6, 141.4, 135.7, 128.8, 127.9, 127.0, 126.9, 126.8, 126.2, 125.7, 124.3, 119.7, 119.6, 54.3, 41.5, 21.1, 13.9.

(S)-9-(1-(4-methoxyphenyl)ethyl)-9H-fluorene (**3aj**) [7]



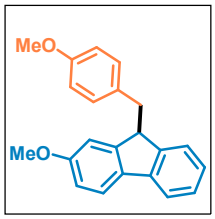
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 55% Yield, 0.083 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.72 (m, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.92 – 6.88 (m, 3H), 4.29 (d, *J* = 4.5 Hz, 1H), 3.86 (s, 3H), 3.70 – 3.62 (m, 1H), 0.94 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 146.6, 144.7, 141.8, 141.4, 136.7, 128.9, 127.0, 127.0, 126.8, 126.2, 125.7, 124.3, 119.7, 119.6, 113.5, 55.3, 54.4, 41.1, 14.2.

9-(octan-2-yl)-9H-fluorene (**3ak**) [7]



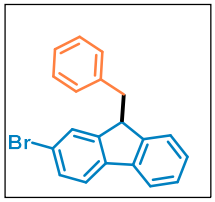
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 48% Yield, 0.067 g.^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 – 7.71 (m, 2H), 7.53 – 7.47 (m, 2H), 7.35 (td, *J* = 7.3, 3.3 Hz, 2H), 7.30 – 7.27 (m, 2H), 3.99 (d, *J* = 3.1 Hz, 1H), 2.43 – 2.33 (m, 1H), 1.49 – 1.27 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.60 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 145.8, 141.9, 141.5, 126.8, 126.7, 126.7, 126.5, 125.1, 124.4, 119.6, 119.5, 52.5, 37.2, 34.5, 31.9, 29.4, 27.9, 22.7, 15.7, 14.1.

(S)-2-methoxy-9-(4-methoxybenzyl)-9H-fluorene (**3al**) [7]



White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:4). 78% Yield, 0.123 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.15 – 7.12 (m, 4H), 6.88 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 2.1 Hz, 1H), 4.12 (t, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.10 – 2.96 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 158.2, 148.7, 146.5, 140.8, 133.8, 131.8, 130.5, 127.1, 125.5, 124. 7, 120.5, 119.0, 113.7, 113.3, 110.5, 55.4, 55.3, 49.0, 39.3.

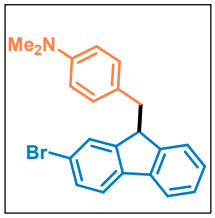
(S)-9-benzyl-2-bromo-9H-fluorene (**3am**) [7]



White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 86% Yield, 0.145 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 9.1 Hz, 1H), 7.39 – 7.25 (m, 6H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 1H), 4.23

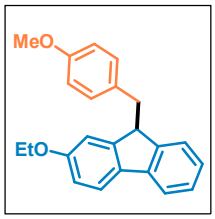
(t, J = 7.6 Hz, 1H), 3.16 – 3.09 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.8, 146.5, 139.8, 139.8, 139.2, 130.2, 129.5, 128.4, 128.2, 127.3, 127.1, 126.6, 124.9, 121.1, 120.4, 119.9, 48.7, 39.9.

(S)-4-((2-bromo-9H-fluoren-9-yl)methyl)-N,N-dimethylaniline (**3an**) [7]



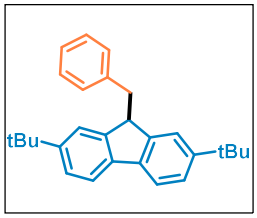
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:4). 88% Yield, 0.188 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.26 (t, J = 7.5 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 7.7 Hz, 2H), 4.18 (t, J = 7.6 Hz, 1H), 3.10 – 3.00 (m, 2H), 2.98 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.2, 146.9, 139.8, 139.8, 137.1, 130.1, 130.0, 128.2, 127.2, 127.0, 125.1, 121.0, 120.5 120.4, 119.8, 112.9, 49.2, 40.9, 39.0. HRMS (ESI) m/z: $[M + H]^+$ $C_{22}H_{20}BrN$: 378.0857; found 378.0851.

(S)-2-ethoxy-9-(4-methoxybenzyl)-9H-fluorene (**3ao**) [7]



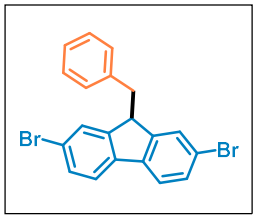
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:4). 80% Yield, 0.132 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 (t, J = 8.3 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.14 – 7.12 (m, 4H), 6.88 (d, J = 8.3 Hz, 1H), 6.84 (d, J = 8.5 Hz, 2H), 6.70 (s, 1H), 4.11 (t, J = 7.5 Hz, 1H), 4.00 – 3.95 (m, 2H), 3.81 (s, 3H), 3.08 – 2.99 (m, 2H), 1.39 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 158.2, 148.7, 146.4, 140. 9, 133.7, 131.9, 130.5, 127.0, 125.4, 124.7, 120.4, 118.9, 113.9, 113.7, 111.0, 63.6, 55.3, 48.9, 39.3, 14.9.

9-benzyl-2,7-di-tert-butyl-9H-fluorene (**3aq**) [7]



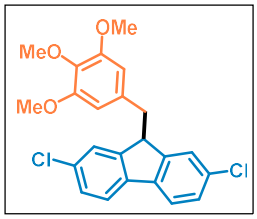
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 79% Yield, 0.145 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, J = 8.0 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.27 – 7.24 (m, 4H), 7.11 (s, 2H), 4.14 (t, J = 7.8 Hz, 1H), 3.06 (d, J = 7.8 Hz, 2H), 1.28 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 146.9, 140.4, 138.2, 129.7, 128.3, 126.3, 124.0, 121. 9, 118.9, 49.0, 40.7, 34.8, 31.5.

9-benzyl-2,7-dibromo-9H-fluorene (**3ar**) [7]



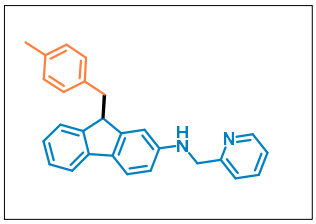
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 70% Yield, 0.144 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 4.20 (t, *J* = 7.6 Hz, 1H), 3.11 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.4, 138.8, 138.6, 130.5, 129.4, 128.5, 128.3, 126.8, 121.2, 120.9, 48.7, 39.7.

2,7-dichloro-9-(3,4,5-trimethoxybenzyl)-9H-fluorene (**3as**) [7]



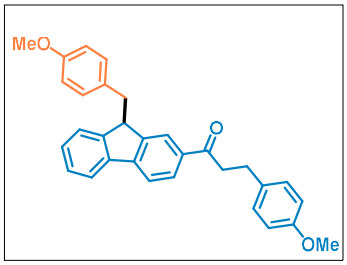
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:5). 75% Yield, 0.155 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.27 (s, 2H), 6.32 (s, 2H), 4.18 (t, *J* = 7.1 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 6H), 3.08 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.0, 148.0, 138.5, 136.8, 133.8, 132.7, 127.6, 125.4, 120.9, 106.6, 61.0, 56.1, 48.8, 40.0.

(R)-9-benzyl-N-(pyridin-2-ylmethyl)-9H-fluoren-2-amine (**3at**) [7]



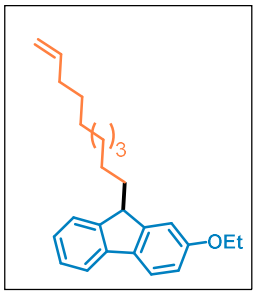
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). 58% Yield, 0.105 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 4.5 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.18 – 7.15 (m, 1H), 7.10 – 7.03 (m, 6H), 6.64 (d, *J* = 8.1 Hz, 1H), 6.47 (s, 1H), 4.40 (s, 2H), 4.08 (t, *J* = 7.6 Hz, 1H), 3.01 (d, *J* = 7.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 149.2, 148.9, 147.3, 146.0, 141.5, 136.9, 136.7, 135.7, 131.2, 129.5, 128.9, 126.9, 124.7, 124.6, 122.1, 121.7, 120.6, 118.4, 112.5, 109.5, 49.4, 48.7, 39.9, 21.1.

(R)-1-(9-(4-methoxybenzyl)-9H-fluoren-2-yl)-3-(4-methoxyphenyl)propan-1-one (**3au**) [7]



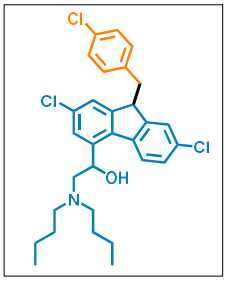
White solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:5). 65% Yield, 0.145 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 2H), 7.76 (s, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 6.12 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.23 (t, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.21 (t, *J* = 7.6 Hz, 2H), 3.14 – 3.06 (m, 2H), 3.03 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.3, 158.3, 158.0, 148.2, 146.9, 145.6, 139.6, 135.2, 133.4, 131.3, 130.5, 129.4, 127.9, 127.7, 127.4, 125.1, 124.8, 120.8, 119.7, 113.9, 113.7, 55.3, 55.2, 49.0, 40.7, 39.0, 29.5.

(R)-2-ethoxy-9-(non-8-en-1-yl)-9H-fluorene (**3av**)



Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 58% Yield, 0.097 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.97 (s, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 5.75 – 5.67 (m, 1H), 4.89 (d, *J* = 17.1 Hz, 1H), 4.83 (d, *J* = 10.0 Hz, 1H), 4.02 (q, *J* = 6.9 Hz, 2H), 3.83 (t, *J* = 5.7 Hz, 1H), 1.95 – 1.86 (m, 4H), 1.37 (t, *J* = 6.9 Hz, 3H), 1.29 – 1.23 (m, 2H), 1.16 – 1.13 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 149.5, 147.1, 141.2, 139.2, 134.1, 126.8, 125.6, 124.1, 120.4, 118.9, 114.1, 113.1, 110.9, 63.7, 47.5, 33.8, 33.2, 29.9, 29.4, 29.3, 29.1, 28.9, 25.5, 14.9. HRMS (ESI) m/z: $[M + H]^+$ $C_{25}H_{32}O$: 349.2531; found 349.2531.

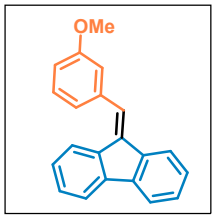
2-(dibutylamino)-1-((S)-2,7-dichloro-9-(4-chlorobenzyl)-9H-fluoren-4-yl)ethan-1-ol (**3aw**)



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.62 – 7.57 (m, 1H), 7.30 (d, *J* = 7.1 Hz, 1H), 7.22 – 7.14 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.35 – 5.31 (m, 1H), 4.22 – 4.05 (m,

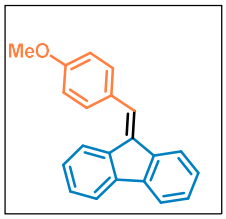
1H), 3.12 – 3.08 (m, 2H), 2.84 – 2.73 (m, 1H), 2.70 – 2.63 (m, 2H), 2.54 – 2.43 (m, 3H), 1.49 – 1.47 (m, 4H), 1.41 – 1.30 (m, 4H), 1.26 – 1.21 (m, 1H), 0.98 – 0.94 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 136.6, 136.4, 134.7, 133.4, 132.6, 132.4, 130.70, 128.45, 128.3, 127.6, 125.2, 124.9, 124.1, 123.9, 123.6, 121.0, 65.6, 60.0, 53.5, 48.2, 39.4, 39.2, 29.1, 20.6, 14.0. HRMS (ESI) m/z: $[M + H]^+$ $C_{30}H_{34}ONCl_2$: 530.1784; found 530.1772.

9-(3-methoxybenzylidene)-9H-fluorene (**4a**) [7]



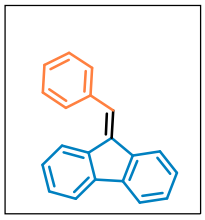
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 65% Yield, 0.092 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.71 (dd, *J* = 7.5, 3.2 Hz, 2H), 7.66 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.28 (m, 4H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.12 (s, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.94 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 141.1, 139.7, 138.9, 136.6, 135.5, 130.9, 129.1, 128.3, 127.9, 127.4, 126.9, 126.6, 124.2, 120.1, 119.7, 119.6, 113.9, 55.4.

9-(4-methoxybenzylidene)-9H-fluorene (**4b**) [7]



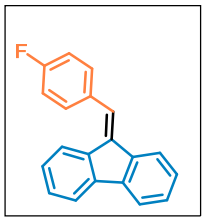
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 65% Yield, 0.092 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.76 – 7.73 (m, 3H), 7.68 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 141.1, 139.7, 139.0, 136.6, 135.5, 130.9, 129.1, 128.3, 127.9, 127.4, 126.9, 126.6, 124.2, 120.1, 119.7, 119.6, 114.0, 55.4.

9-benzylidene-9H-fluorene (**4c**) [7]



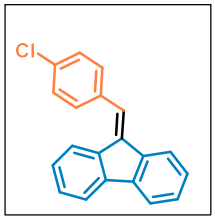
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:2). 63% Yield, 0.080 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.72 – 7.69 (m, 4H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.30 (m, 4H), 7.04 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 139.5, 139.2, 136.9, 136.6, 136.5, 129.3, 128.5, 128.2, 128.0, 127.3, 127.0, 126.7, 124.4, 120.2, 119.7, 119.6.

9-(4-fluorobenzylidene)-9H-fluorene (**4d**) [7]



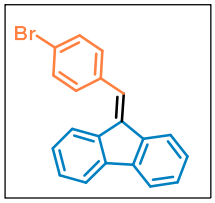
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 55% Yield, 0.075 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.65 (s, 1H), 7.61 – 7.56 (m, 3H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.18 (t, *J* = 8.5 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5 (d, *J* = 247.5 Hz), 141.3, 139.3 (d, *J* = 21.5 Hz), 136.7, 136.4, 132.8 (d, *J* = 3.6 Hz), 131.1, 131.1, 128.7, 128.3, 127.0, 126.7, 126.0, 124.2, 120.2, 119.8, 119.6, 115.7, 115.6.

9-(4-chlorobenzylidene)-9H-fluorene (**4e**) [7]



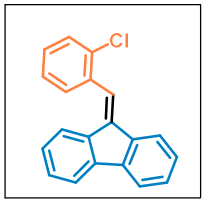
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 63% Yield, 0.091 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.62 (s, 1H), 7.56 – 7.54 (m, 3H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.4, 139.3, 139.2, 137.1, 136.3, 135.3, 133.9, 130.7, 128.8, 128.8, 128.4, 127.1, 126.8, 125.7, 124.3, 120.3, 119.8, 119.7.

9-(4-bromobenzylidene)-9H-fluorene (**4f**) [7]



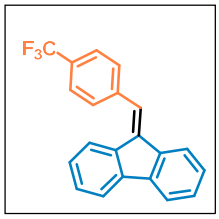
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 66% Yield, 0.109 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.64 – 7.57 (m, 3H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.10 (t, *J* = 8.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.4, 139.3, 137.1, 136.3, 135.8, 131.8 131.0, 128.8, 128.5, 127.1, 126.8, 125.7, 124.3, 122.1, 120.3, 119.9, 119.7.

9-(2-chlorobenzylidene)-9H-fluorene (**4g**) [7]



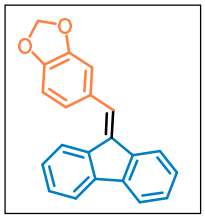
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 60% Yield, 0.086 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.65 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.34 (m, 6H), 7.08 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.4, 139.4, 139.1, 137.5, 136.4, 135.4, 134.1, 131.5, 129.8, 129.5, 128.8, 128.6, 127.1, 126.8, 126.6, 124.4, 124.0, 120.6, 119.8, 119.7.

9-(4-(trifluoromethyl)benzylidene)-9H-fluorene (**4h**) [7]



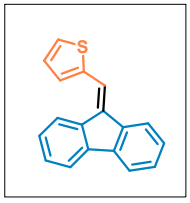
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 60% Yield, 0.097 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.75 – 7.72 (m, 6H), 7.66 (s, 1H), 7.49 – 7.41 (m, 2H), 7.38 – 7.35 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.5, 140.7, 139.4, 139.1, 137.9, 136.1, 129.9 (q, *J* = 32.5 Hz), 129.6, 129.1, 128.7, 127.4, 127.2, 126.9, 125.5 (q, *J* = 3.7 Hz), 125.0, 124.2 (q, *J* = 270 Hz), 120.4, 119.9, 119.7.

5-((9H-fluoren-9-ylidene)methyl)benzo[d][1,3]dioxole (**4i**) [7]



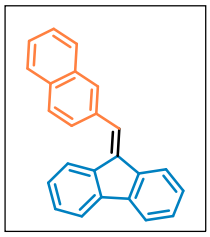
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 50% Yield, 0.074 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 3H), 7.62 (s, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.17 – 7.09 (m, 3H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.07 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.8, 147.5, 141.2, 139.6, 139.0, 136.4, 135.9, 130.6, 128.4, 128.1, 127.1, 126.9, 126.7, 124.4, 123.5, 120.1, 119.7, 119.6, 109.6, 108.5, 101.3.

2-((9H-fluoren-9-ylidene)methyl)thiophene (**4j**) [7]



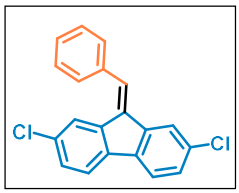
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 46% Yield, 0.060 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.72 (m, 2H), 7.64 – 7.55 (m, 4H), 7.54 – 7.51 (m, 3H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.0, 138.7, 137.9, 136.6, 135.7, 134.7, 133.1, 132.6, 129.9, 129.1, 128.8, 128.8, 128.7, 128.4, 124.5, 120.7, 120.6.

9-(naphthalen-2-ylmethylene)-9H-fluorene (**4k**)[13]



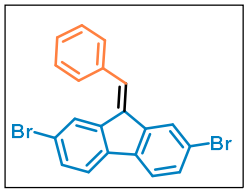
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 55% Yield, 0.084 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.96 – 7.93 (m, 2H), 7.92 – 7.85 (m, 3H), 7.80 – 7.74 (m, 3H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.3, 139.6, 139.2, 136.7, 136.6, 134.4, 133.4, 133.0, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 127.3, 127.2, 127.0, 126.7, 126.7, 126.5, 126.4, 124.4, 120.3, 119.8, 119.6.

9-benzylidene-2,7-dichloro-9H-fluorene (**4l**)[7]



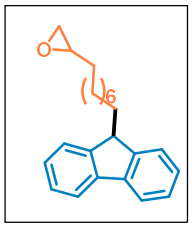
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 49% Yield, 0.079 g. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 1.8 Hz, 1H), 7.70 (s, 1H), 7.60 – 7.53 (m, 4H), 7.53 – 7.43 (m, 4H), 7.34 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.28 (dd, *J* = 8.1, 1.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.7, 137.9, 136.6, 135.7, 134.7, 133.2, 132.6, 129.9, 129.4, 129.1, 128.8, 128.8, 128.7, 128.4, 124.6, 120.7, 120.6.

9-benzylidene-2,7-dibromo-9H-fluorene (**4m**)[7]



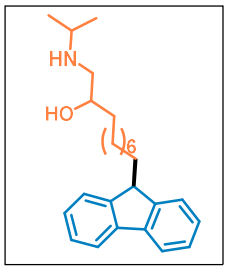
Yellow solid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:1). 70% Yield, 0.143 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.73 – 7.71 (m, 2H), 7.62 – 7.55 (m, 4H), 7.55 – 7.50 (m, 3H), 7.47 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.1, 139.1, 138.0, 137.0, 135.7, 134.5, 131.5, 131.2, 130.0, 129.2, 128.9, 128.8, 127.4, 123.7, 121.2, 121.0, 120.9, 120.8.

2-(8-(9H-fluoren-9-yl)octyl)oxirane (**6**)



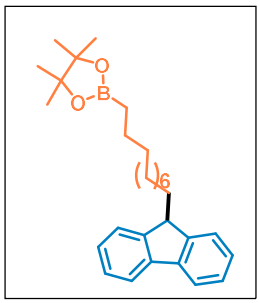
Gummy yellow liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:3). 85% Yield, 0.136 g. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 4.00 (t, *J* = 5.8 Hz, 1H), 2.93 – 2.90 (m, 1H), 2.77 (t, *J* = 4.4 Hz, 1H), 2.48 (dd, *J* = 4.9, 2.7 Hz, 1H), 2.04 – 2.01 (m, 2H), 1.55 – 1.51 (m, 2H), 1.48 – 1.37 (m, 3H), 1.32 – 1.16 (m, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 141.1, 126.8, 126.8, 124.3, 119.8, 52.4, 47.5, 47.2, 33.1, 32.5, 29.9, 29.5, 29.4, 29.3, 25.9, 25.6. HRMS (ESI) m/z: $[M + H]^+$ $C_{25}H_{32}O$: 321.2218; found 321.2247.

10-(9H-fluoren-9-yl)-1-(isopropylamino)decan-2-ol (**7**)



Gummy brown liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:10). 88% Yield, 0.083 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 3.96 (t, *J* = 5.7 Hz, 1H), 3.57 – 3.44 (m, 1H), 2.83 – 2.68 (m, 2H), 2.45 – 2.26 (m, 1H), 2.07 – 1.90 (m, 2H), 1.72 (bs, 2H) 1.48 – 1.30 (m, 4H), 1.25 – 1.13 (m, 10H), 1.16 – 1.05 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 141.1, 126.8, 126.8, 124.4, 119.8, 70.0, 52.8, 48.7, 47.5, 35.2, 33.1, 29.9, 29.7, 29.5, 29.3, 25.7, 25.7, 23.4, 23.0. HRMS (ESI) m/z: $[M + H]^+$ $C_{26}H_{37}NO$: 380.2953; found 380.2953.

2-(10-(9H-fluoren-9-yl)decyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8**)



Colourless liquid. Column chromatography (Silica gel, 100-200 mesh, hexane/ethyl acetate = 90:5). 70% Yield, 0.151 g. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 3.96 (t, *J* = 5.8 Hz, 1H), 2.07 – 1.89 (m, 2H), 1.39 – 1.34 (m, 2H), 1.28 – 1.16 (m, 25H), 0.89 – 0.84 (m, 1H), 0.75 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 141.1, 126.8, 126.7, 124.3, 119.7, 82.8, 47.5, 33.1, 32.4, 30.0, 29.6, 29.5, 29.4, 29.4, 25.7, 24.8, 24.0. HRMS (ESI) m/z: $[M + H]^+$ $C_{26}H_{41}BO_2$: 433.3278; found 433.3238.

21. NMR of Starting Materials:

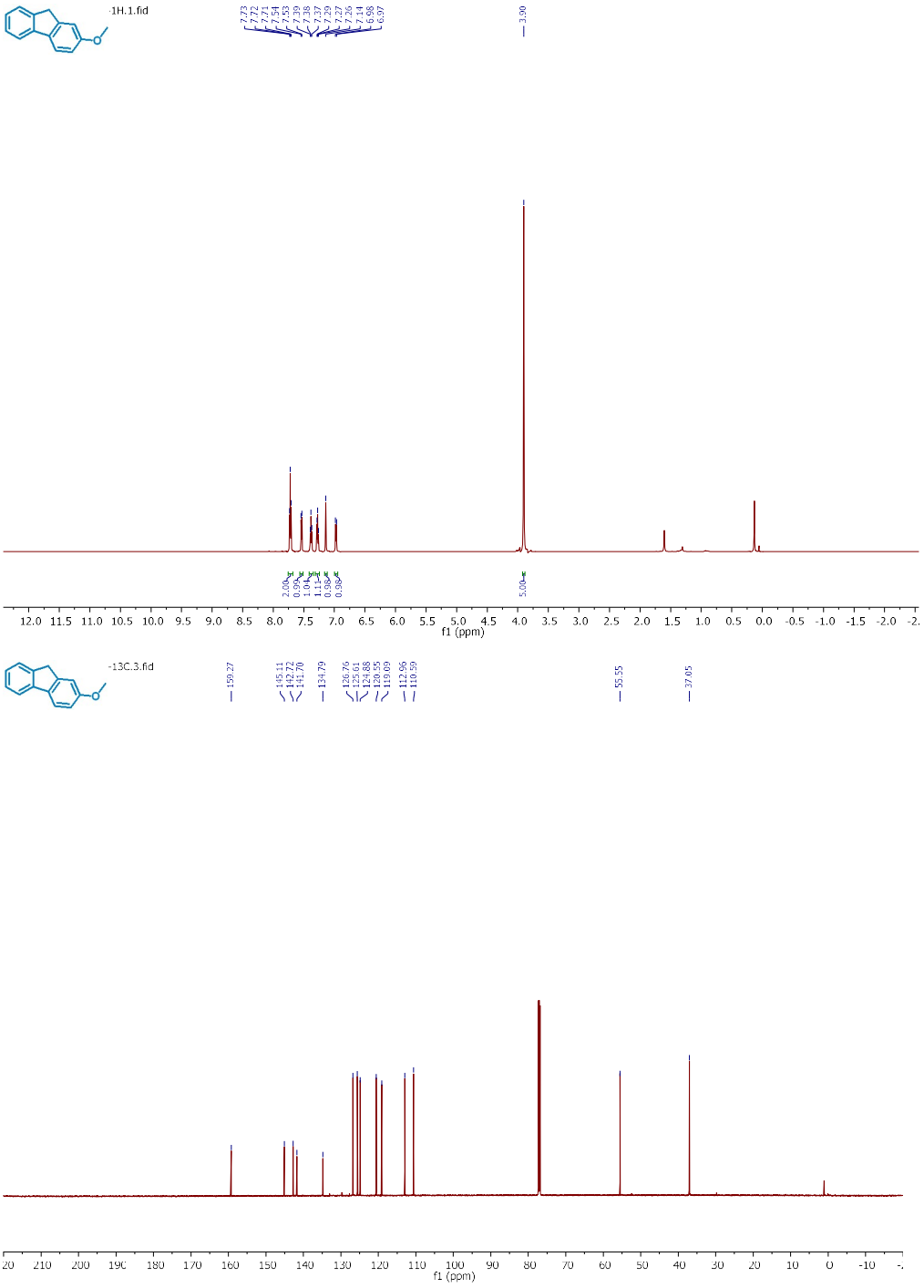


Fig S1: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 2-methoxyfluorene (**1al**) in $CDCl_3$.

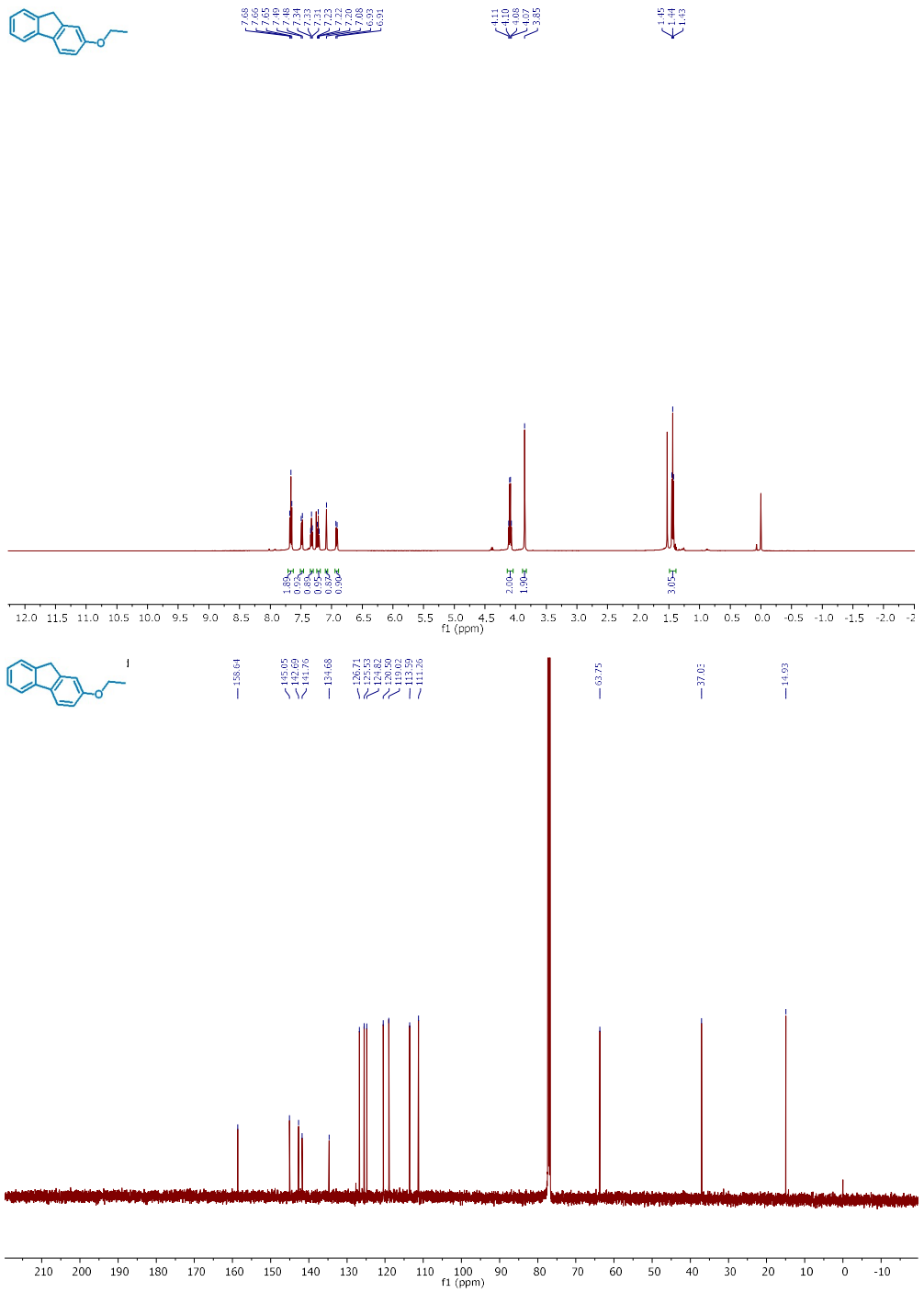


Fig S2: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 2-ethoxyfluorene (**1ao**) in $CDCl_3$.

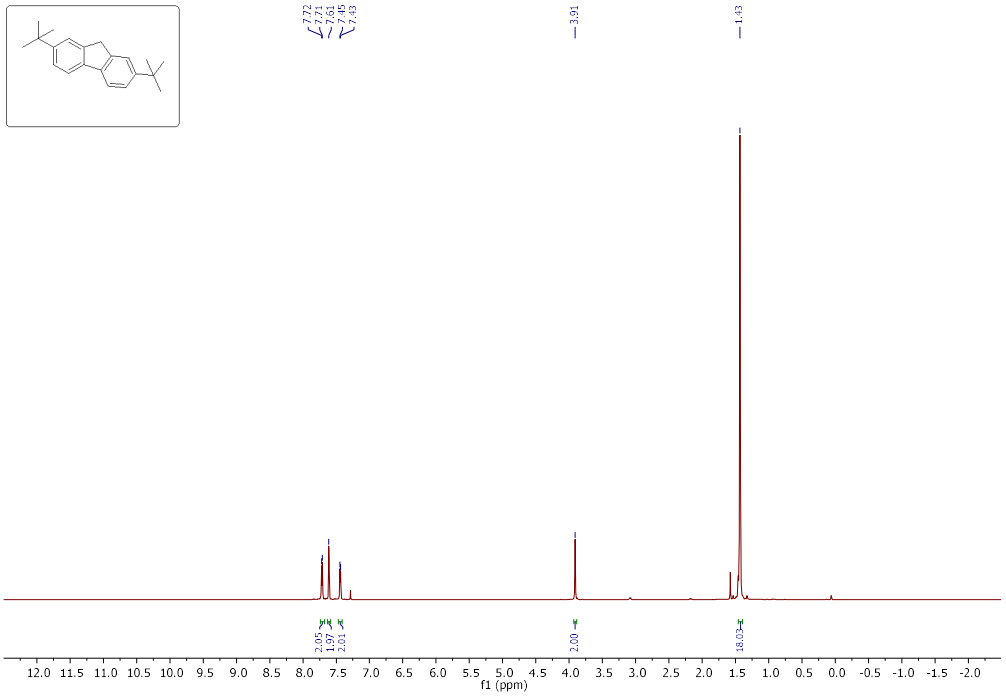
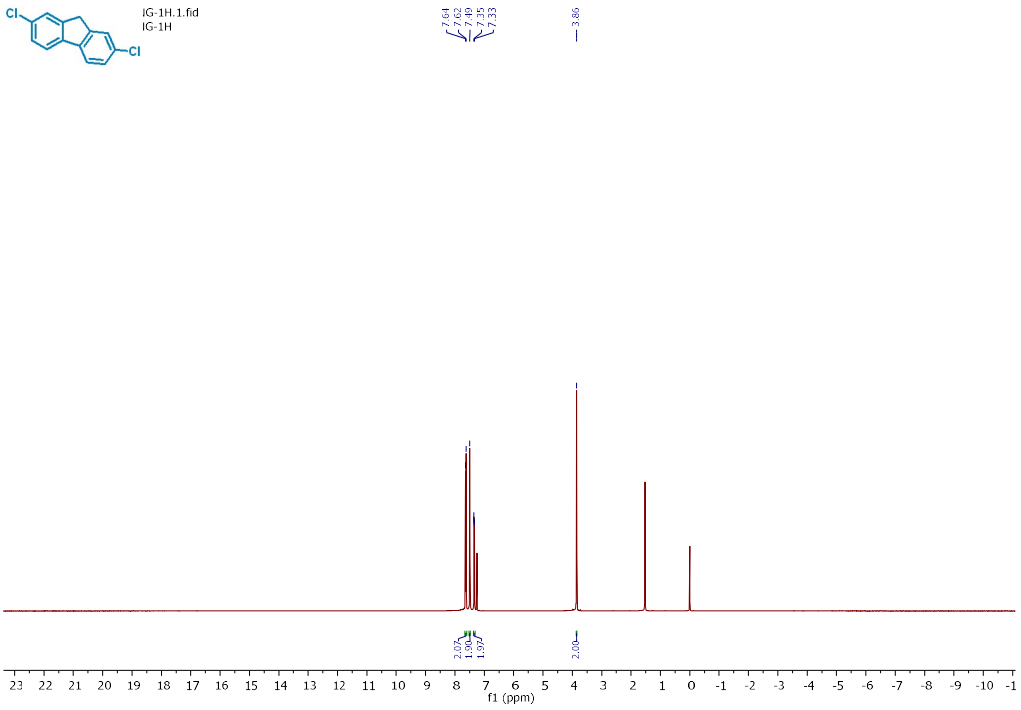


Fig S3: ^{1}H (600 MHz) NMR of 2,7-tertbutylfluorene (**1aq**) in $CDCl_3$.



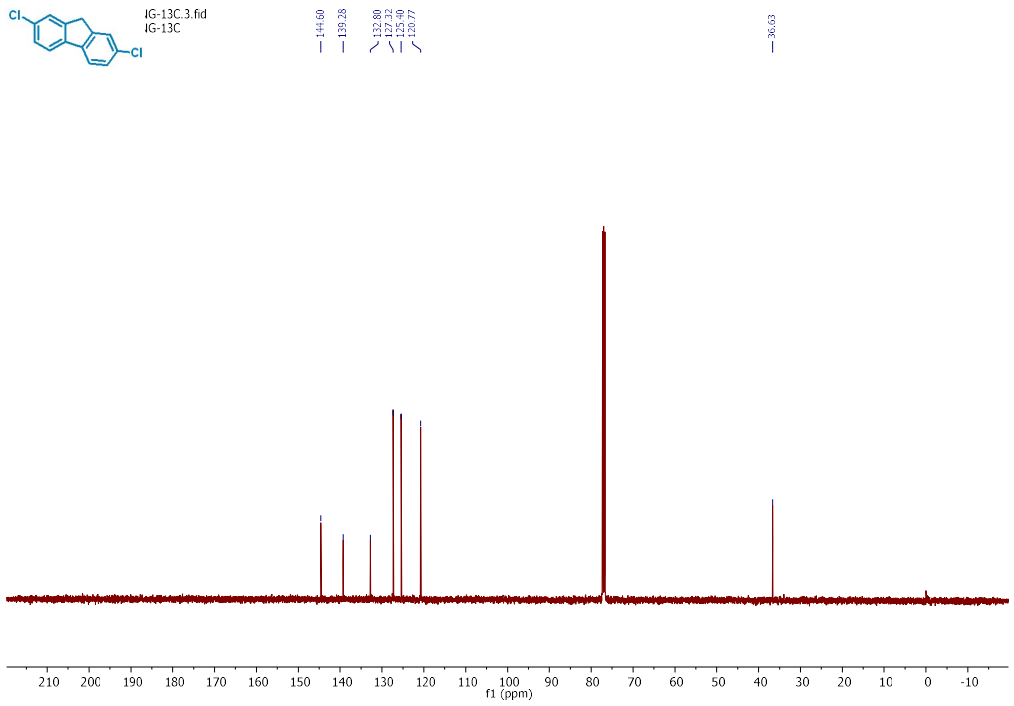
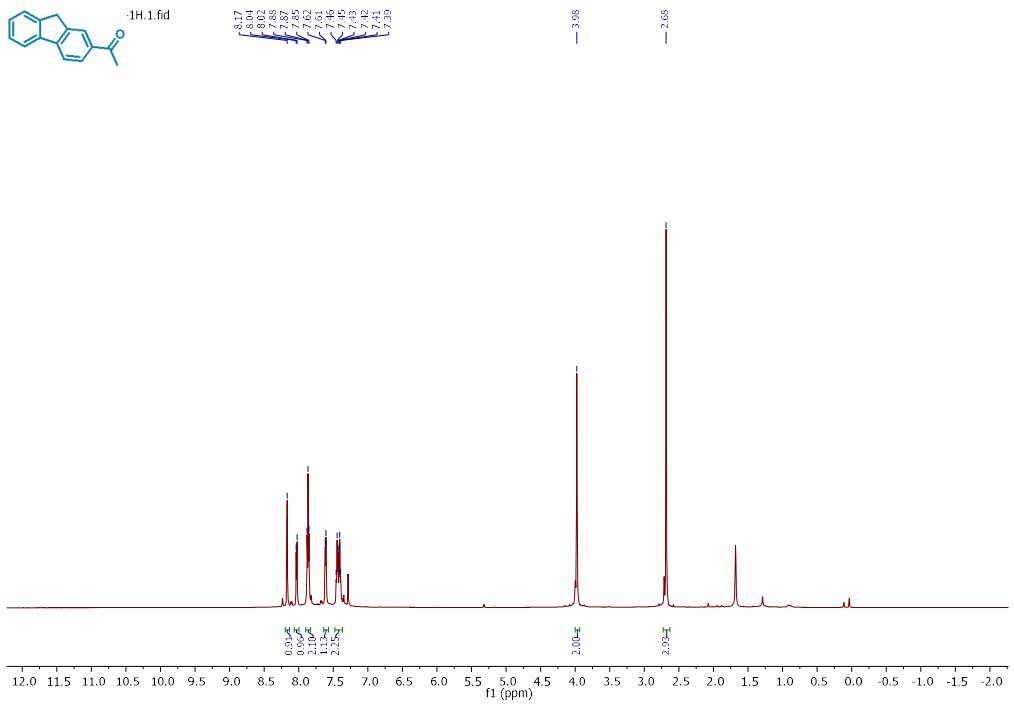


Fig S4: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 2,7-dichlorofluorene (**1as**) in $CDCl_3$.



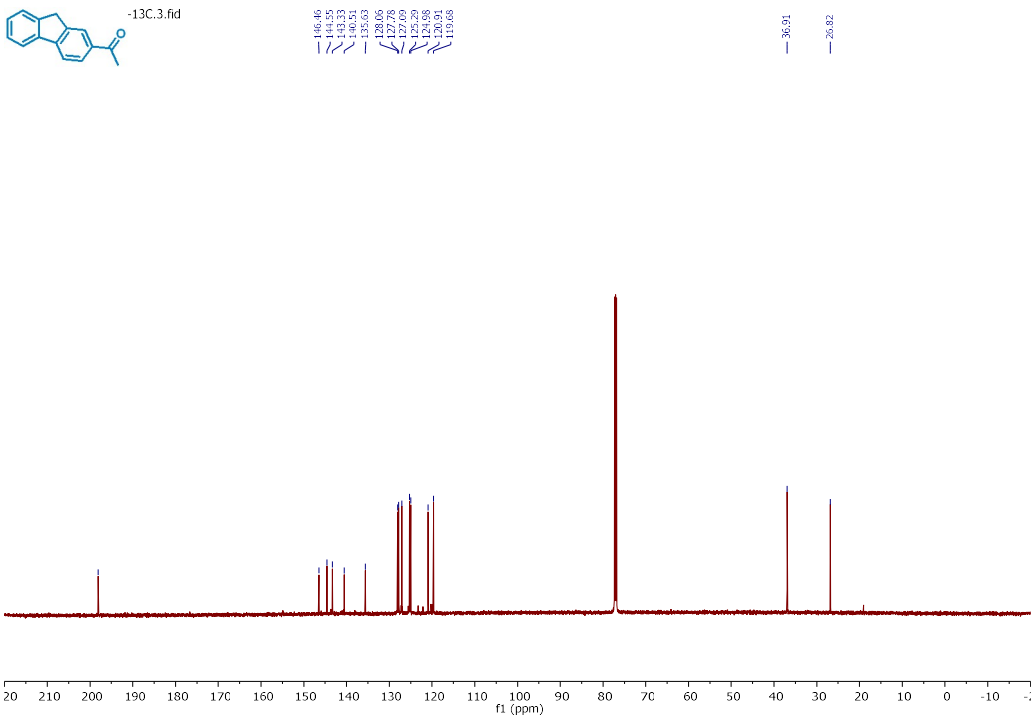
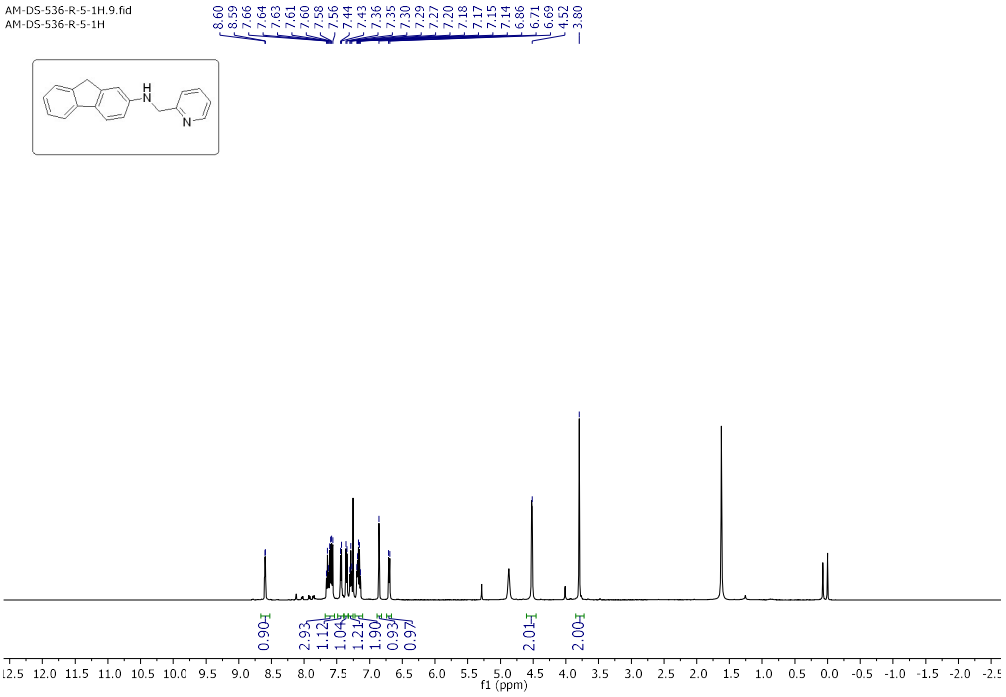


Fig S5: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 2-acetylfluorene (**1au**) in $CDCl_3$.



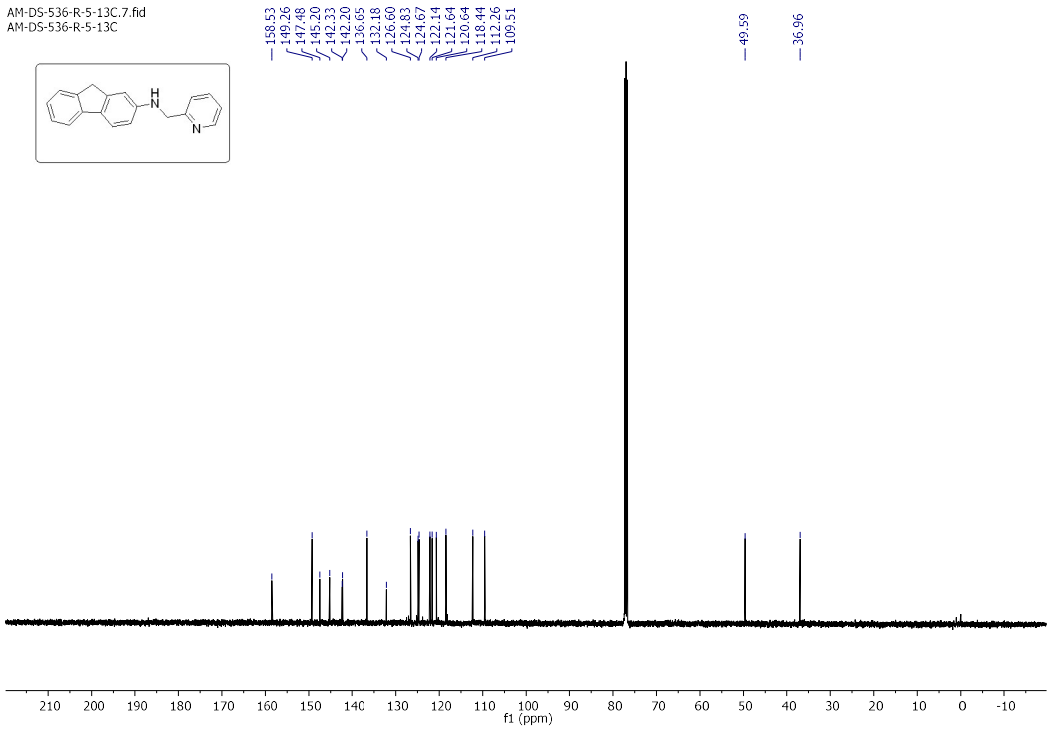


Fig S6: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of N-(pyridin-2-ylmethyl)-9H-fluoren-2-amine (**1aq**) in $CDCl_3$.

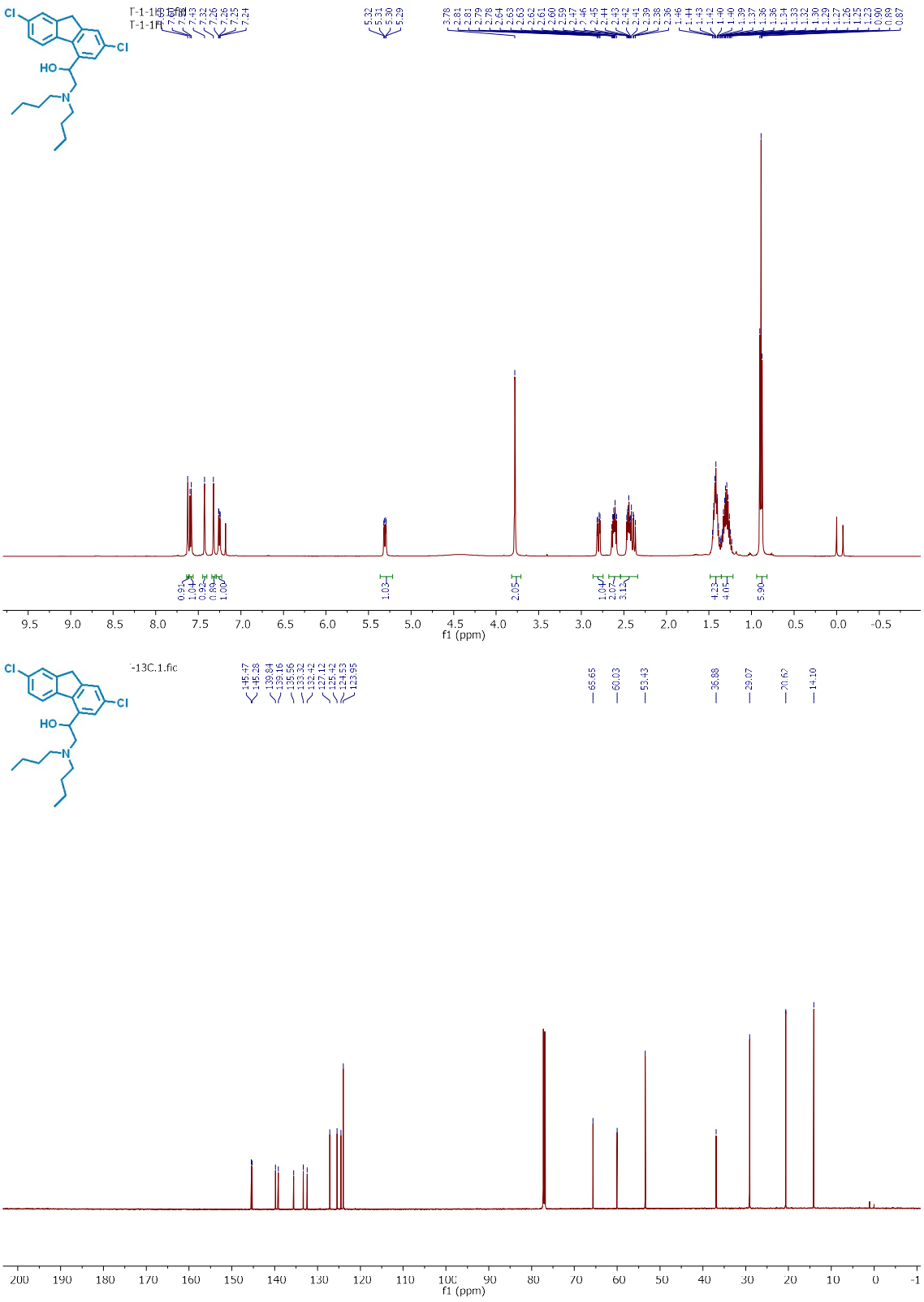


Fig S7: ^{1}H (500 MHz) and ^{13}C (150 MHz) NMR of N-(pyridin-2-ylmethyl)-9H-fluoren-2-amine (**1aw**) in $CDCl_3$.

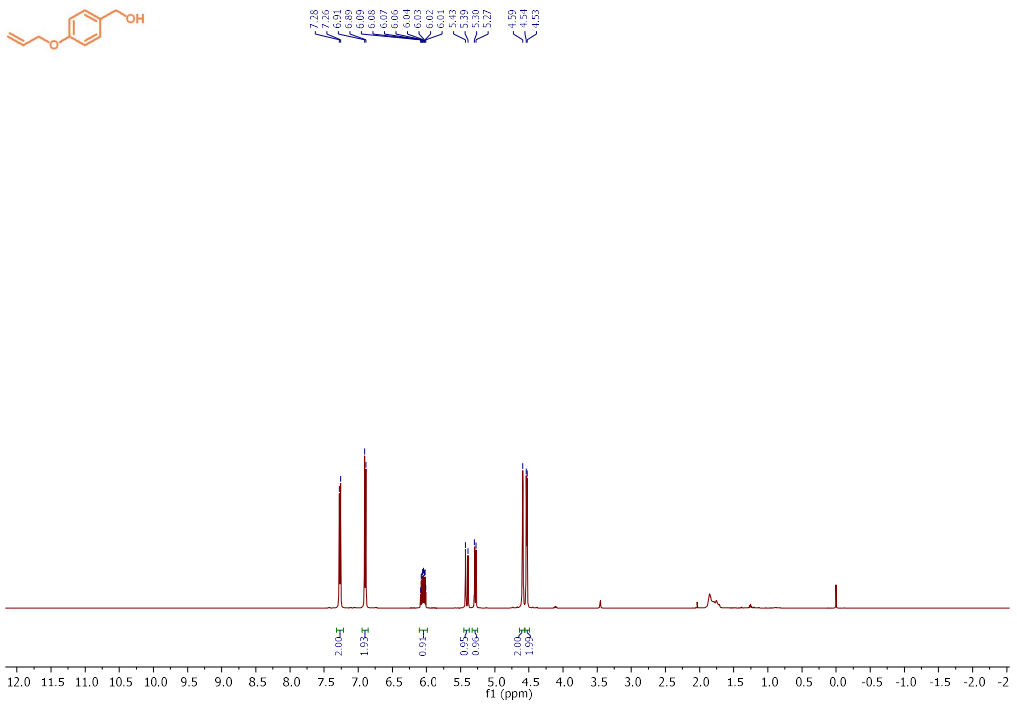
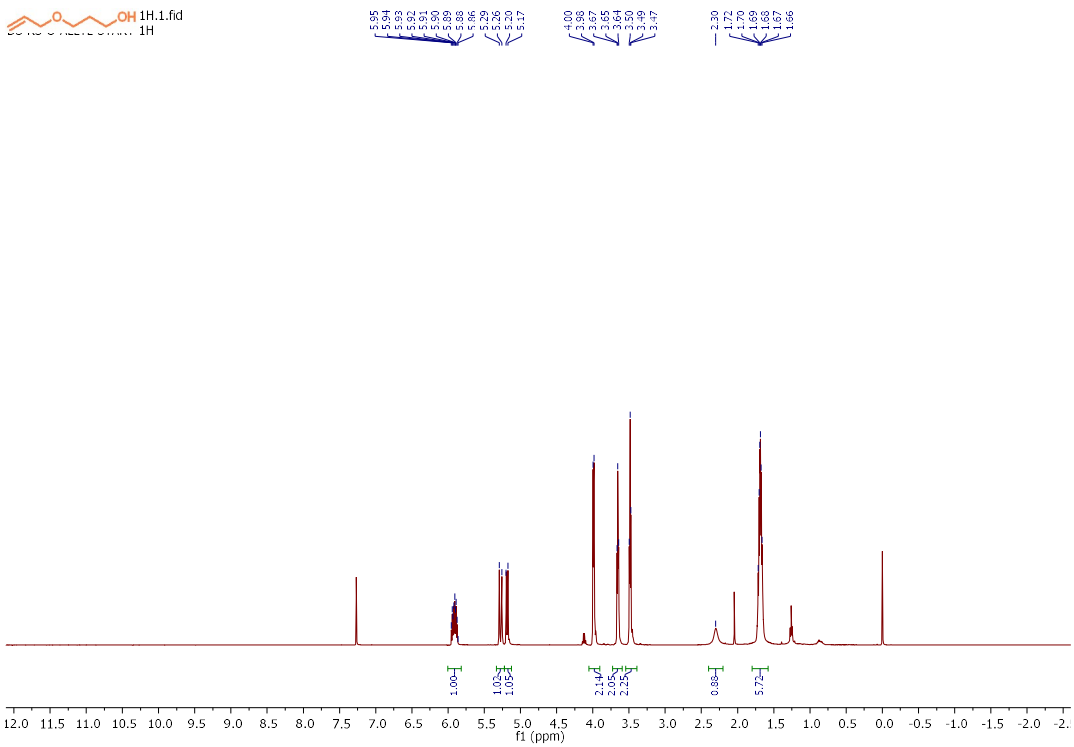


Fig S8: ^{1}H (500 MHz) NMR of N-(pyridin-2-ylmethyl)-9H-fluoren-2-amine (**1aq**) in $CDCl_3$.



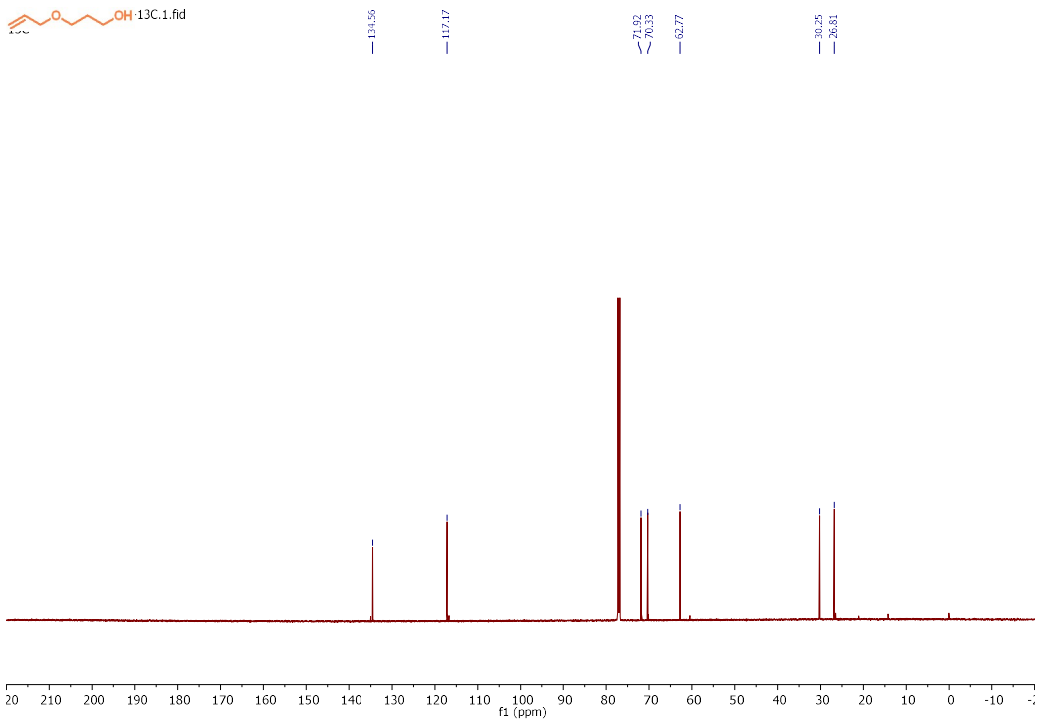


Fig S9: ^{1}H (500 MHz) and ^{13}C (150 MHz) NMR of N-(pyridin-2-ylmethyl)-9H-fluoren-2-amine (**1aq**) in $CDCl_3$.

22. NMR of deuterium labelled experiment:

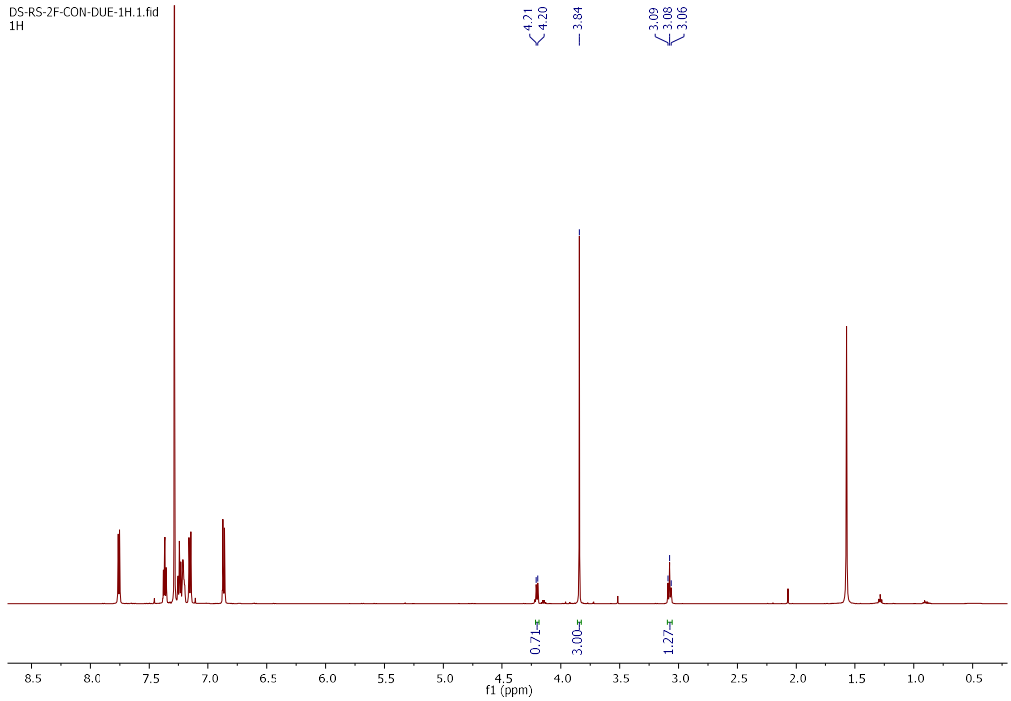


Fig S10: ^{1}H (600 MHz) NMR Spectra of **3l-d**.

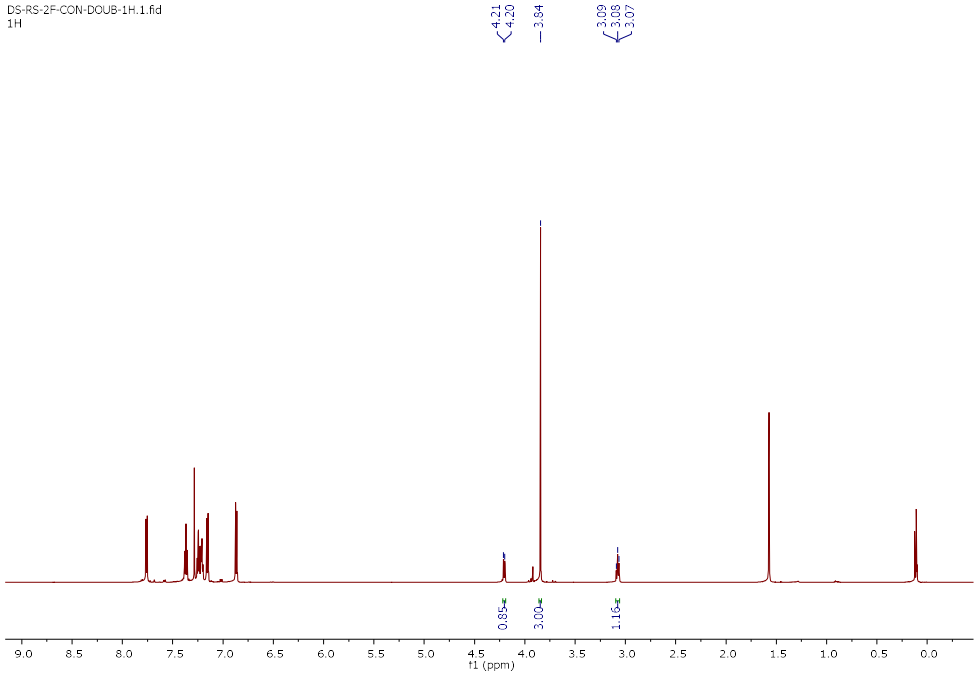


Fig S11: ^{1}H (600 MHz) NMR Spectra of **3l-d'**.

23. NMR Data of Substrates:

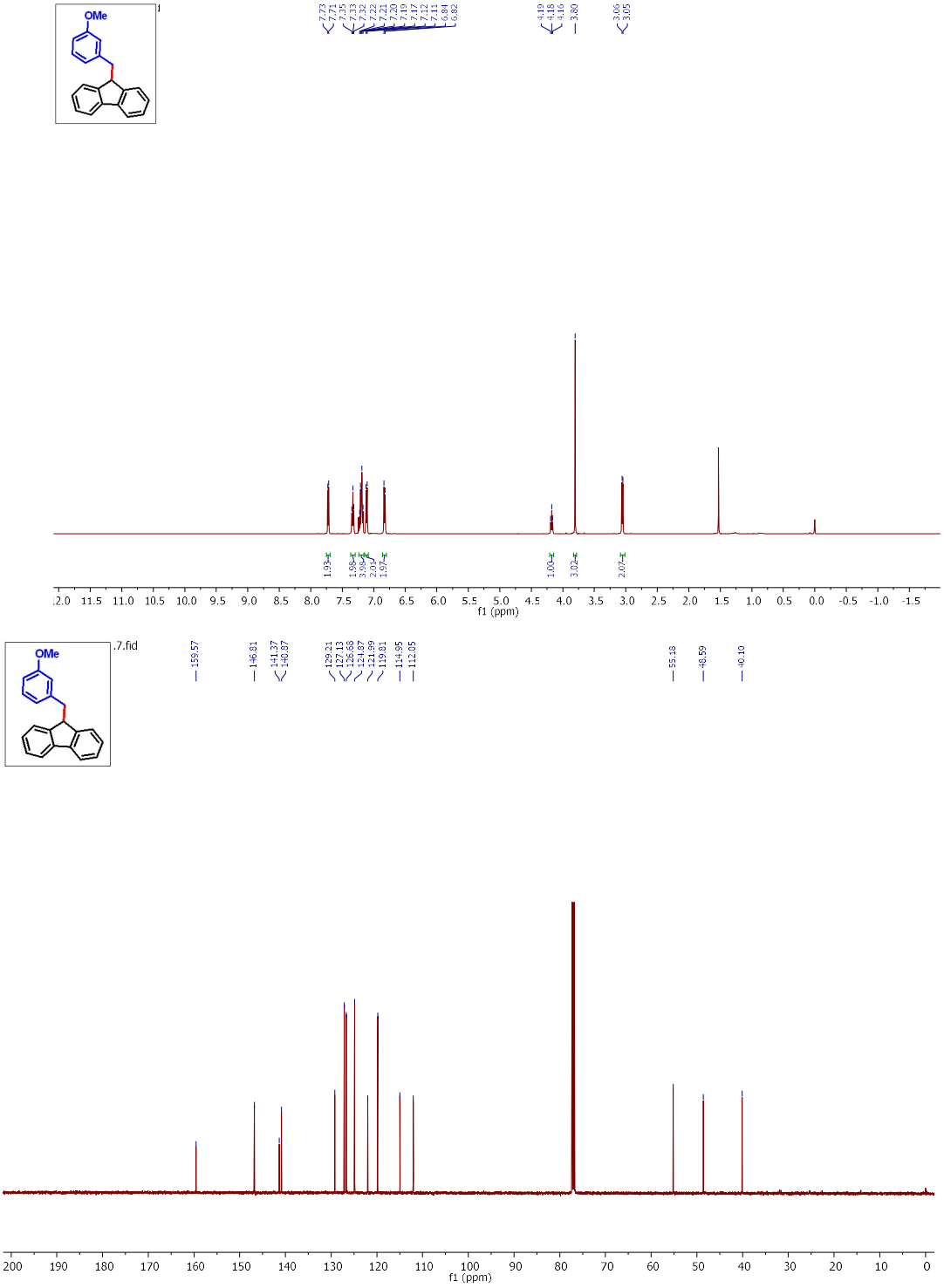


Fig S12: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 9-(3-methoxybenzyl)-9H-fluorene (**3a**) in $CDCl_3$.

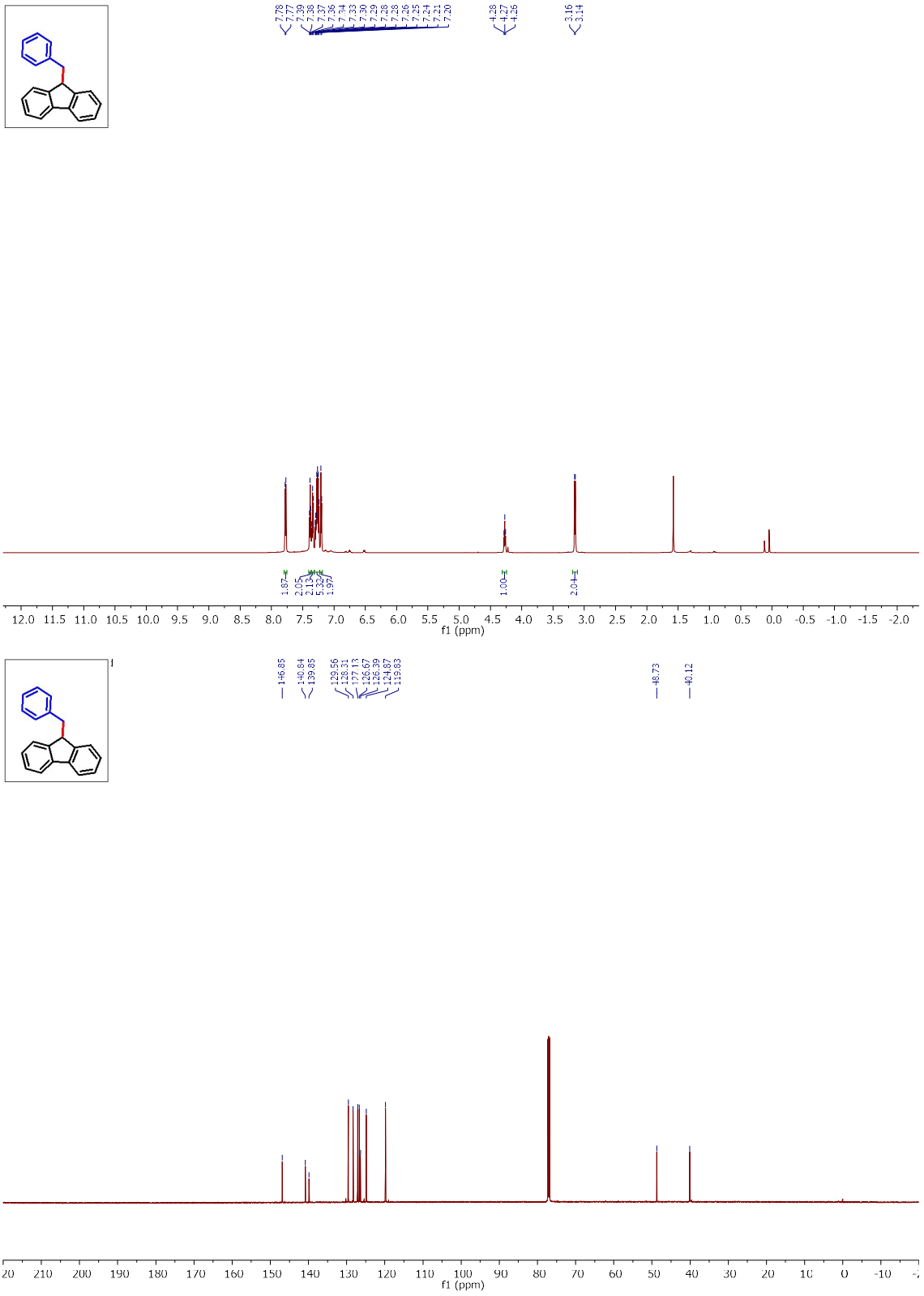


Fig S13: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-benzyl-9H-fluorene (**3b**) in $CDCl_3$.

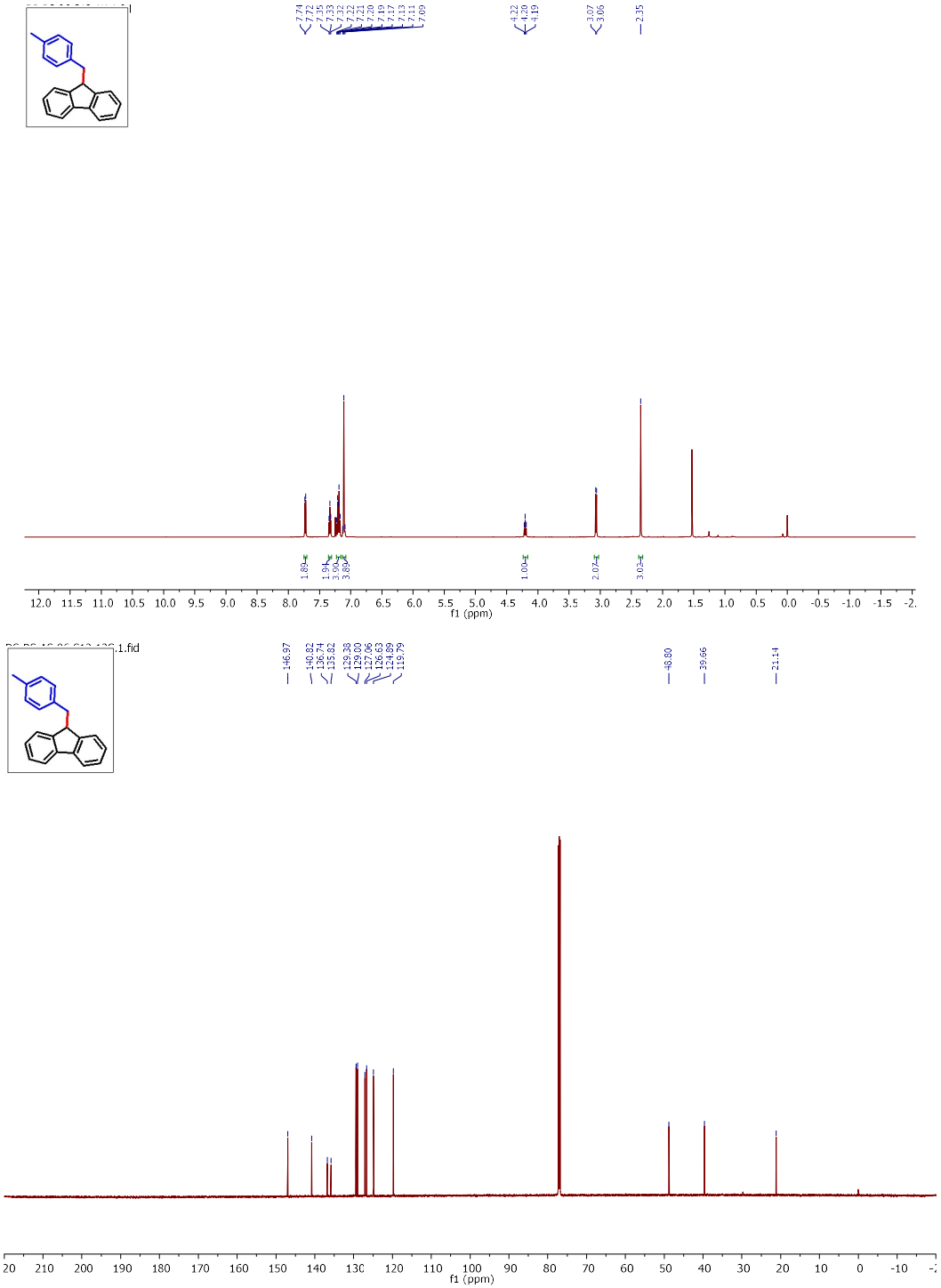


Fig S14: ^{1}H (500 MHz) and ^{13}C (150 MHz) NMR of 9-(4-methylbenzyl)-9H-fluorene (**3c**) in $CDCl_3$.

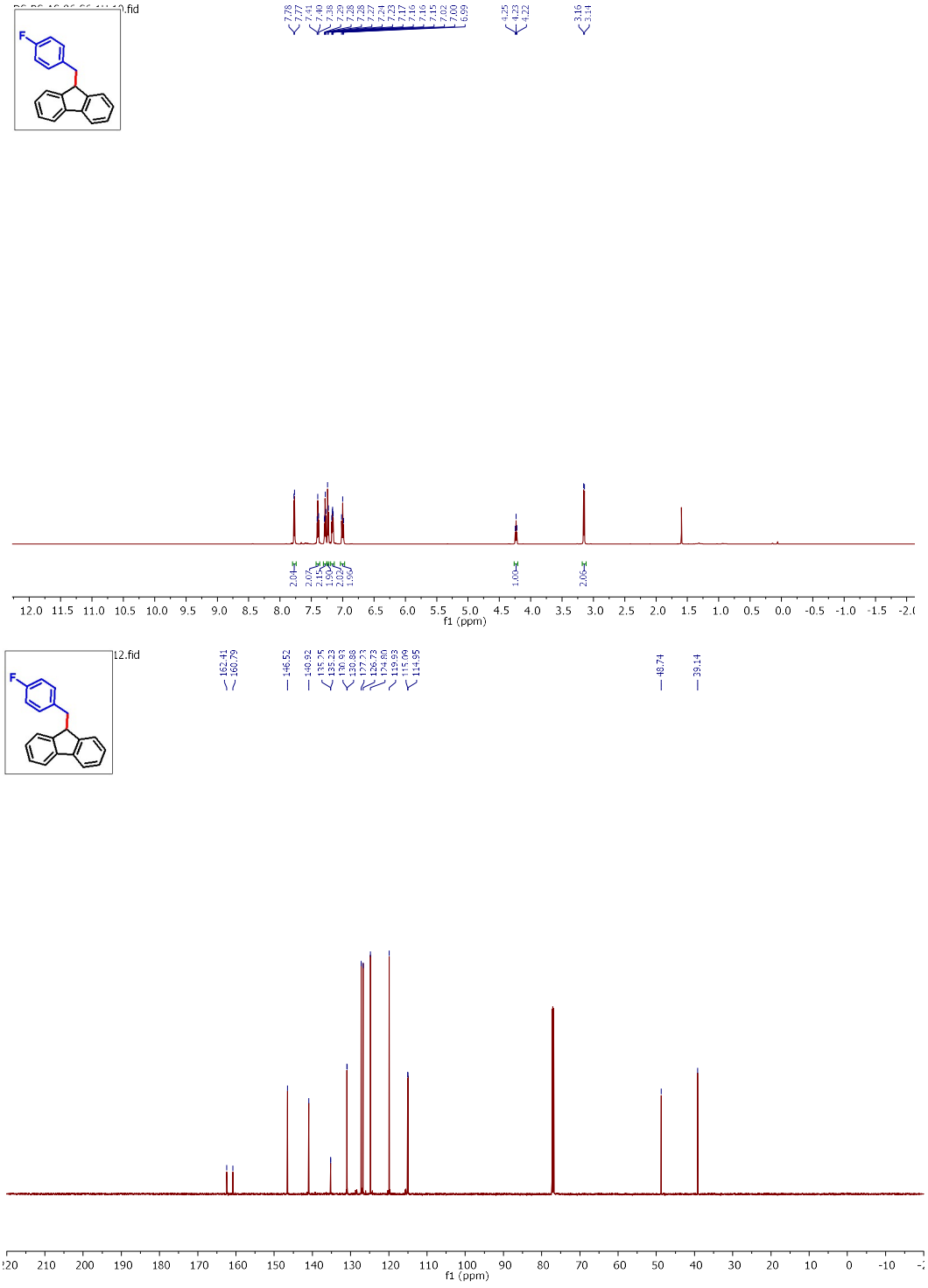


Fig S15: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(4-fluorobenzyl)-9H-fluorene (**3d**) in $CDCl_3$.

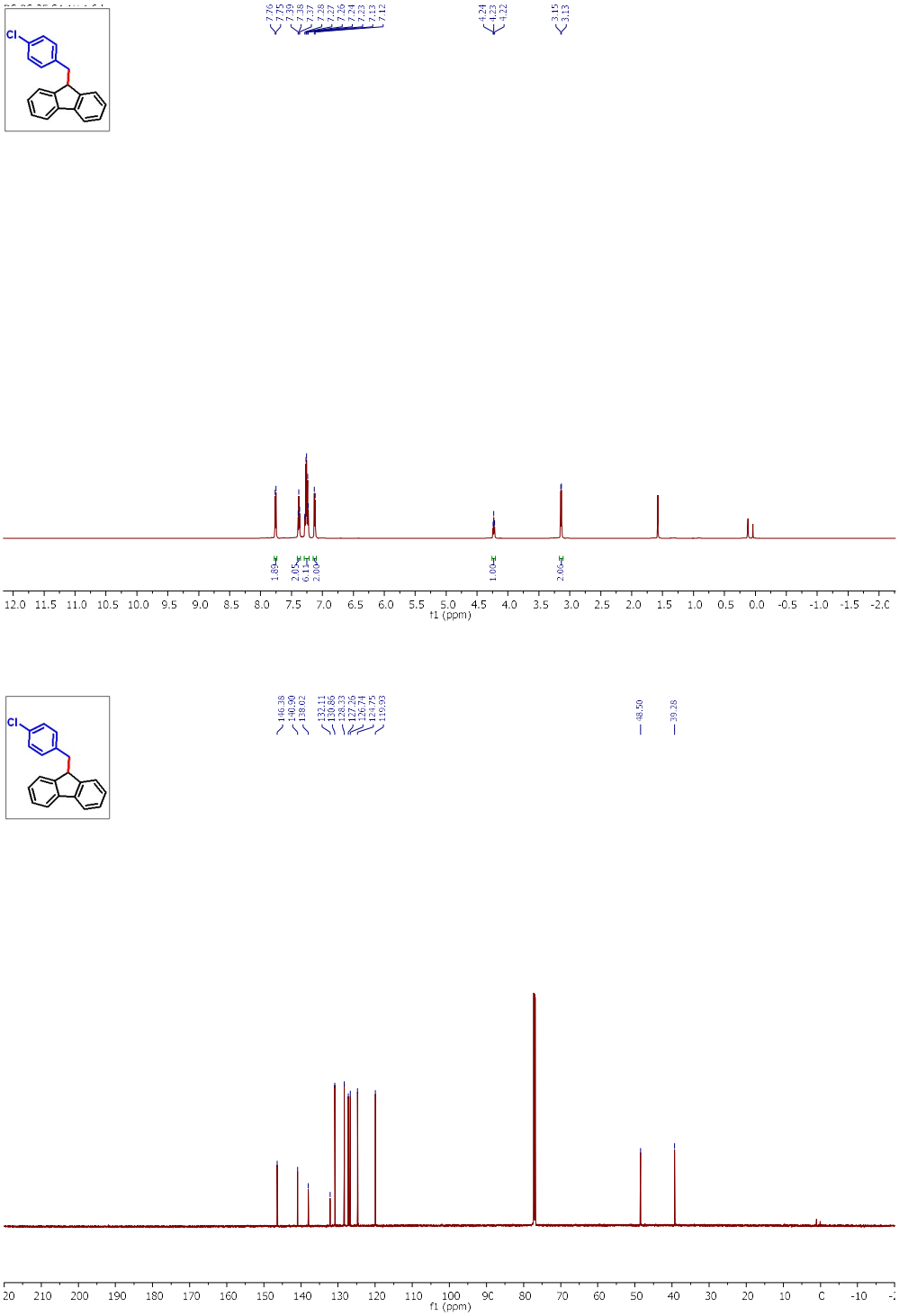


Fig S16: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(4-chlorobenzyl)-9H-fluorene (**3e**) in $CDCl_3$.

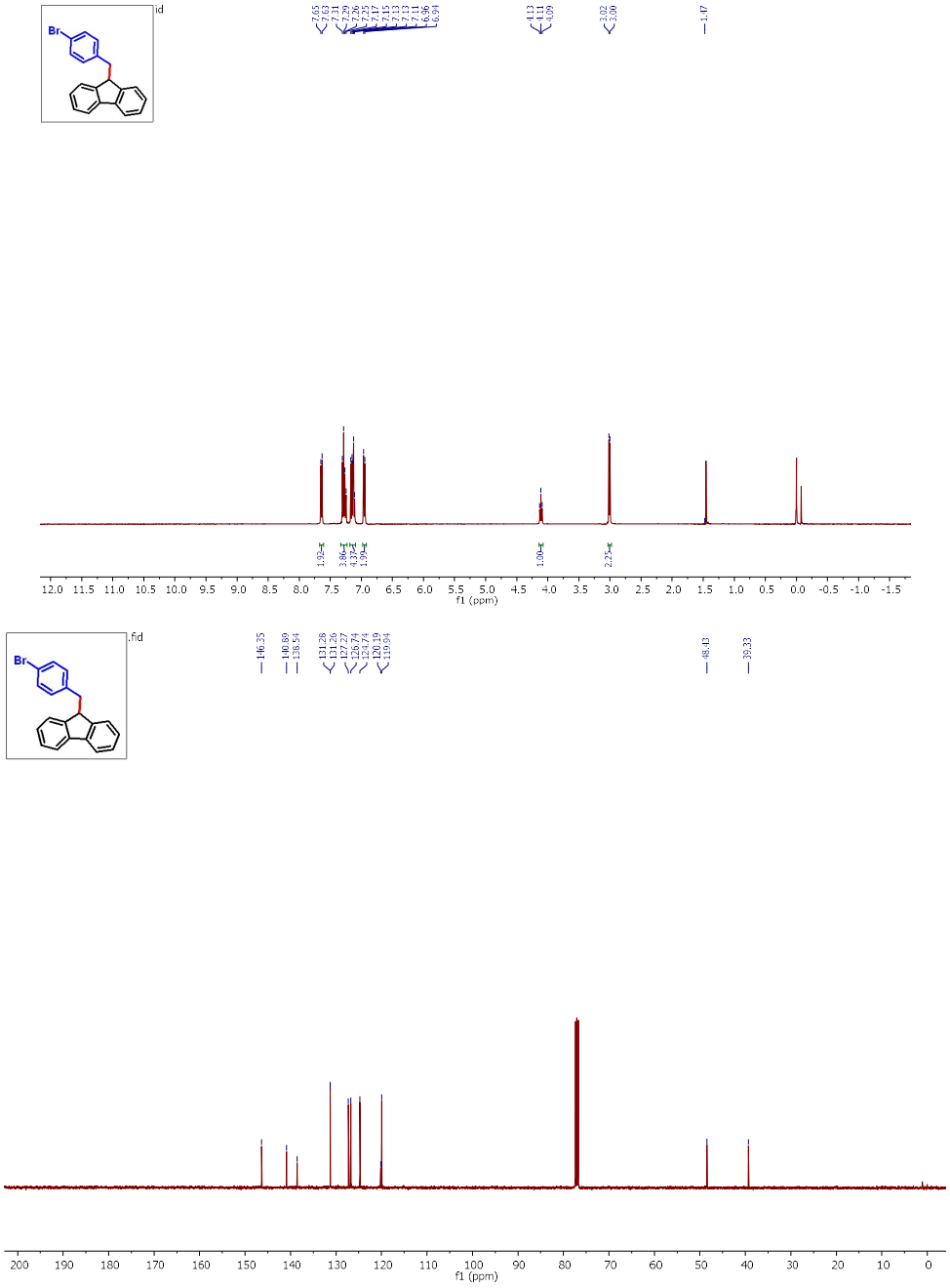


Fig S17: ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR of 9-(4-bromobenzyl)-9H-fluorene (**3f**) in $CDCl_3$.

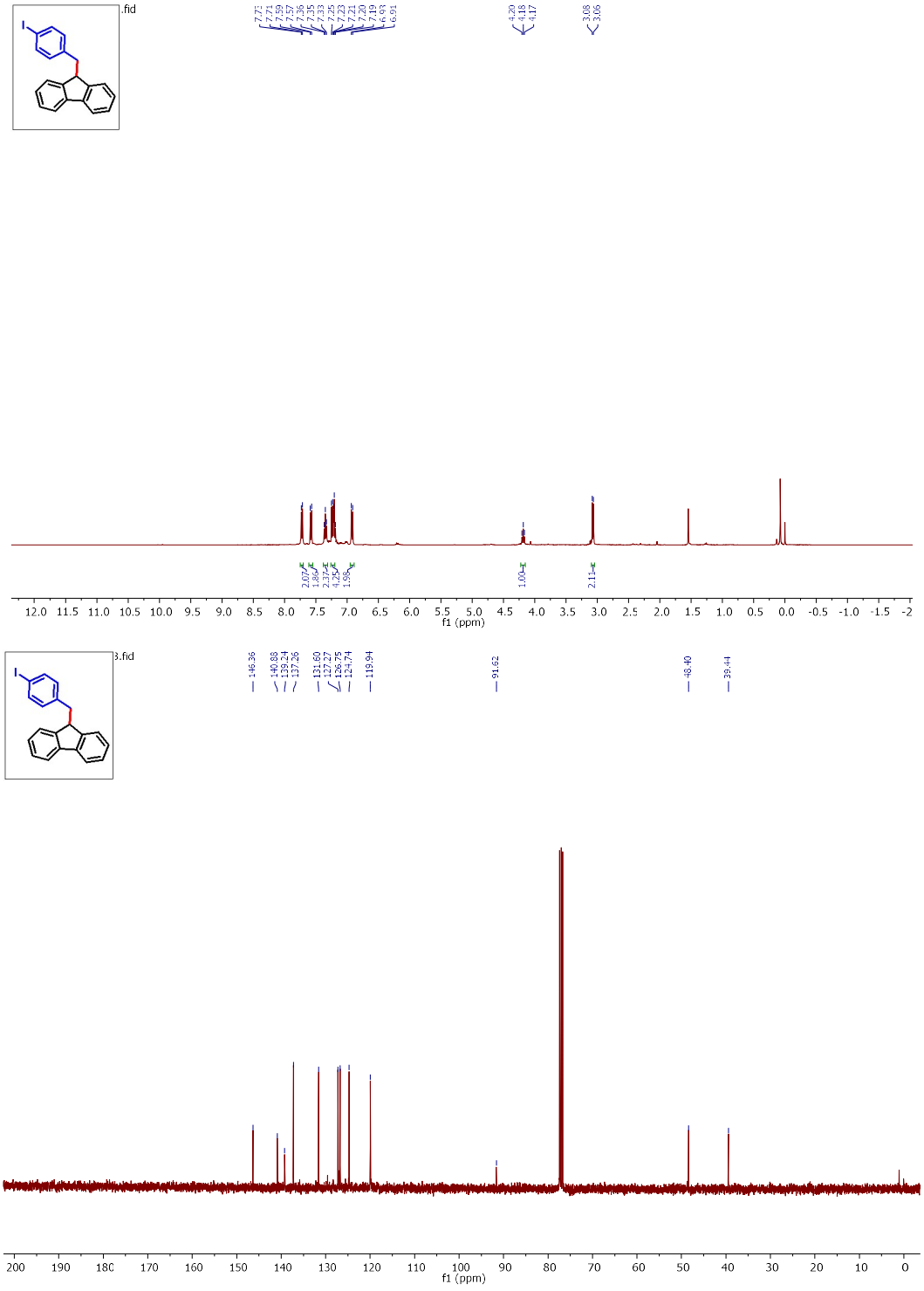


Fig S18: ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR of 9-(4-iodobenzyl)-9H-fluorene (**3g**) in $CDCl_3$.

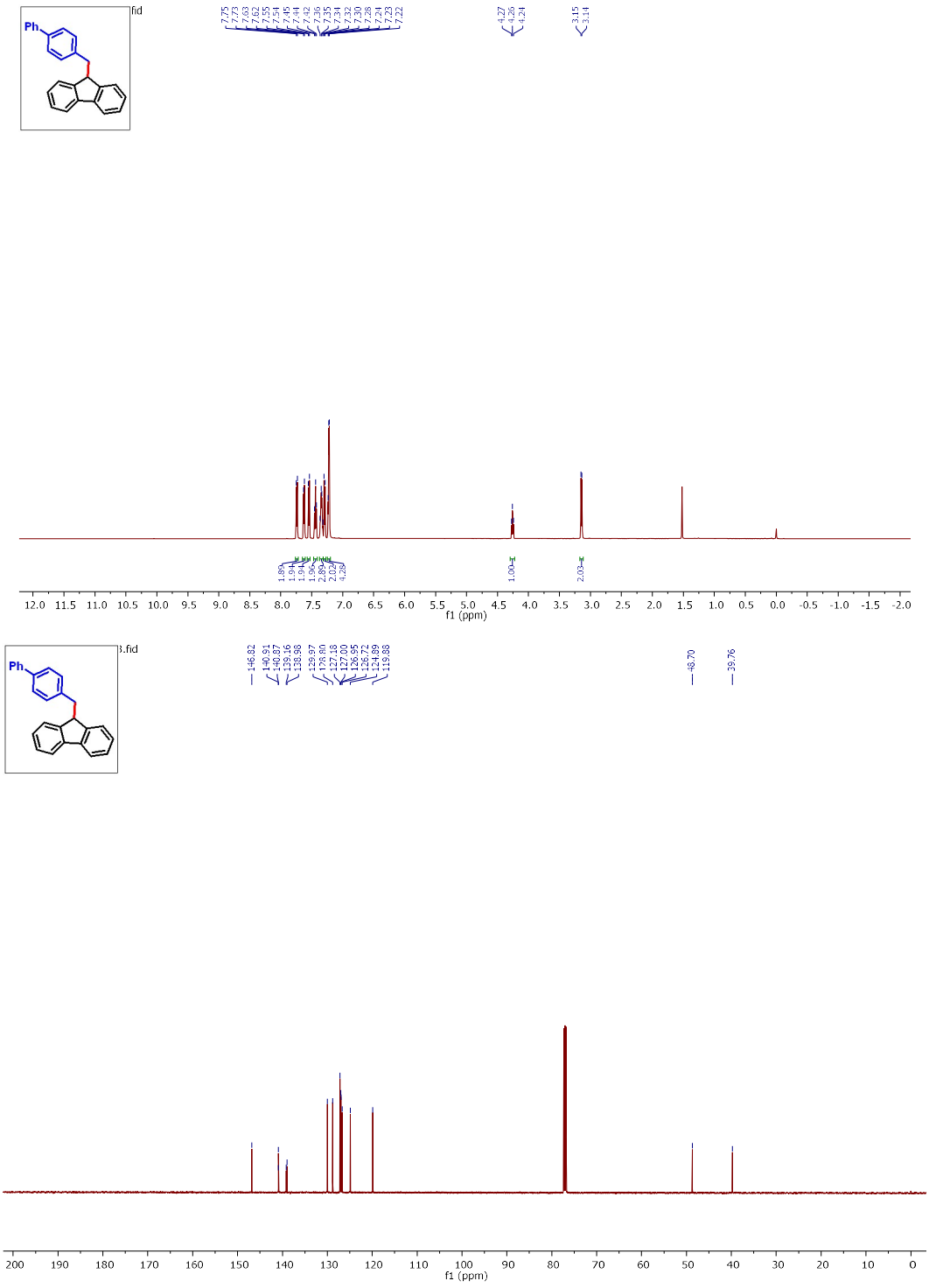


Fig S19: ^{1}H (500 MHz) and ^{13}C (150 MHz) NMR of 9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene (**3h**) in $CDCl_3$.

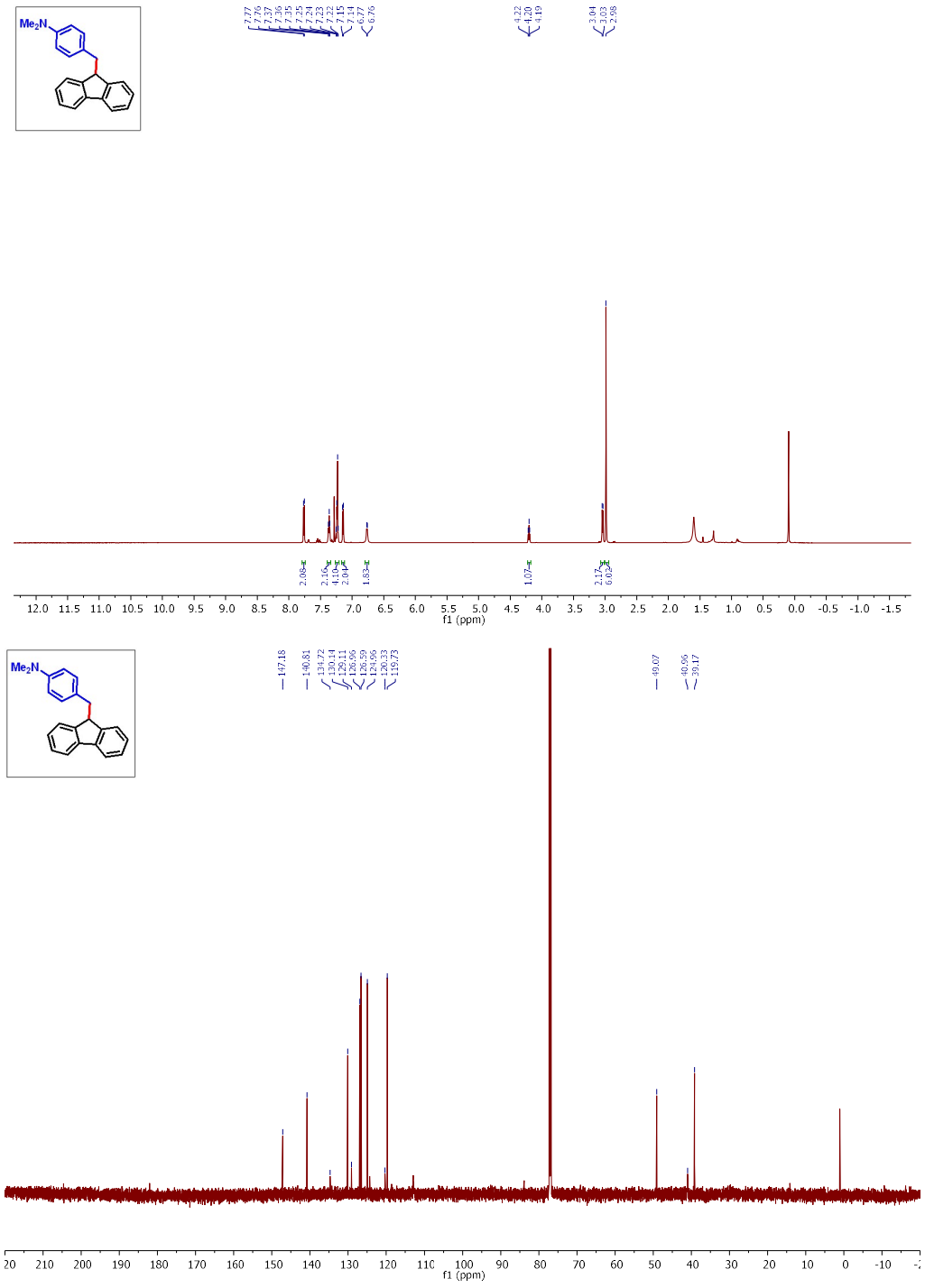


Fig S20: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 4-((9H-fluoren-9-yl)methyl)-N,N-dimethylaniline (**3i**) in $CDCl_3$.

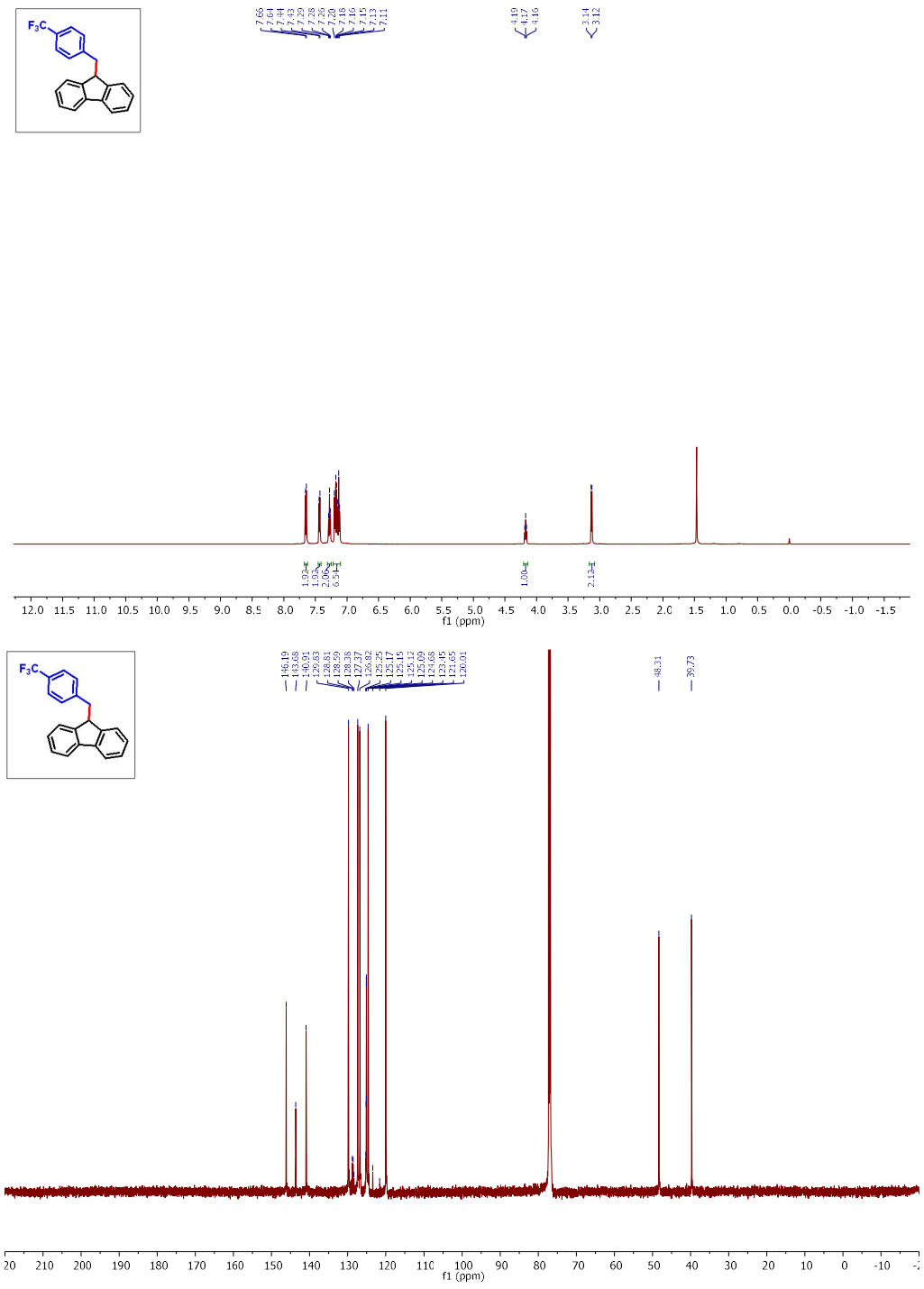


Fig S21: ^{1}H (500 MHz) and ^{13}C (150 MHz) NMR of 9-(4-(trifluoromethyl)benzyl)-9H-fluorene (**3j**) in $CDCl_3$.

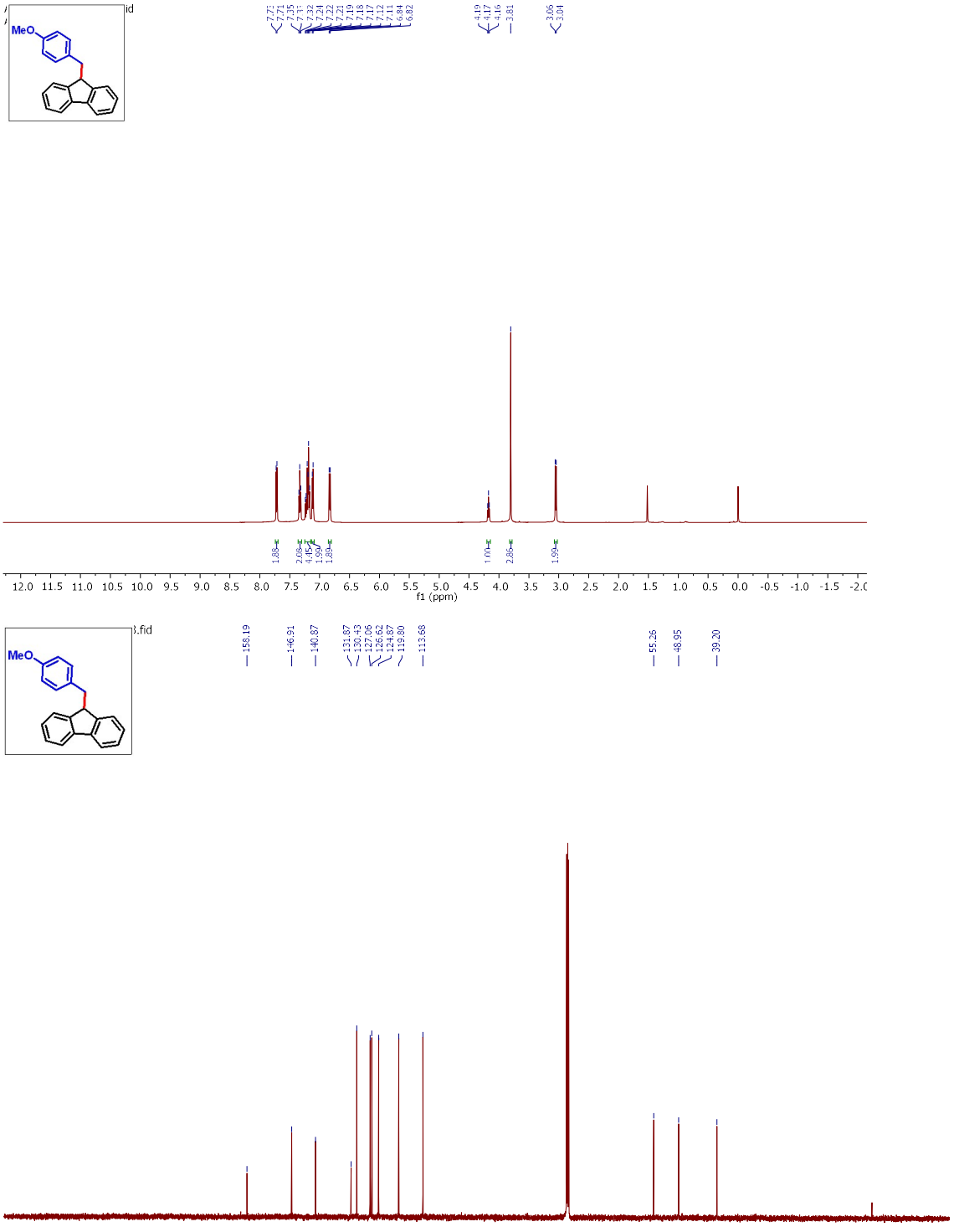


Fig S22: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 9-(4-methoxybenzyl)-9H-fluorene (**3l**) in $CDCl_3$.

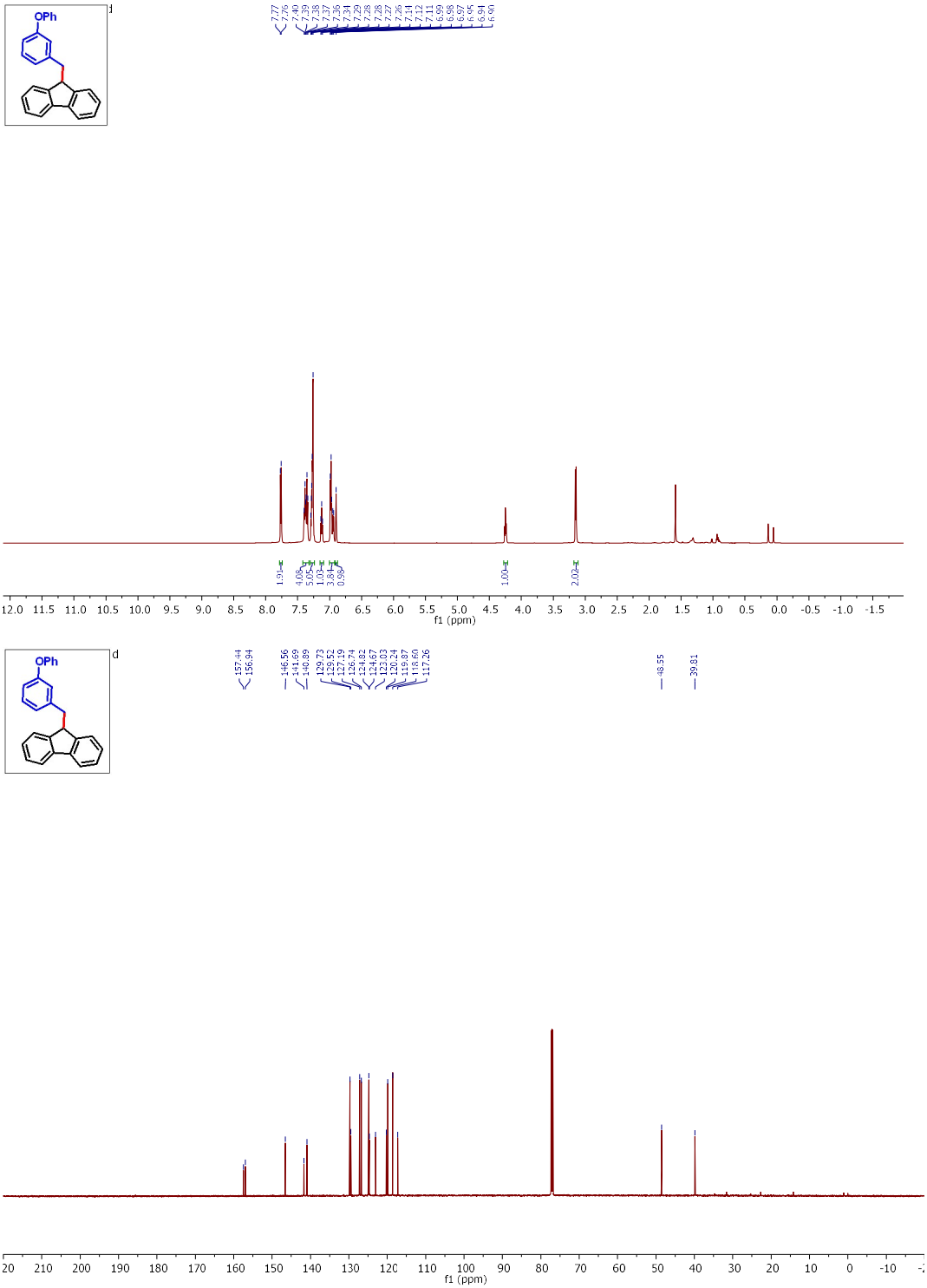


Fig S23: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(3-phenoxybenzyl)-9H-fluorene (**3m**) in $CDCl_3$.

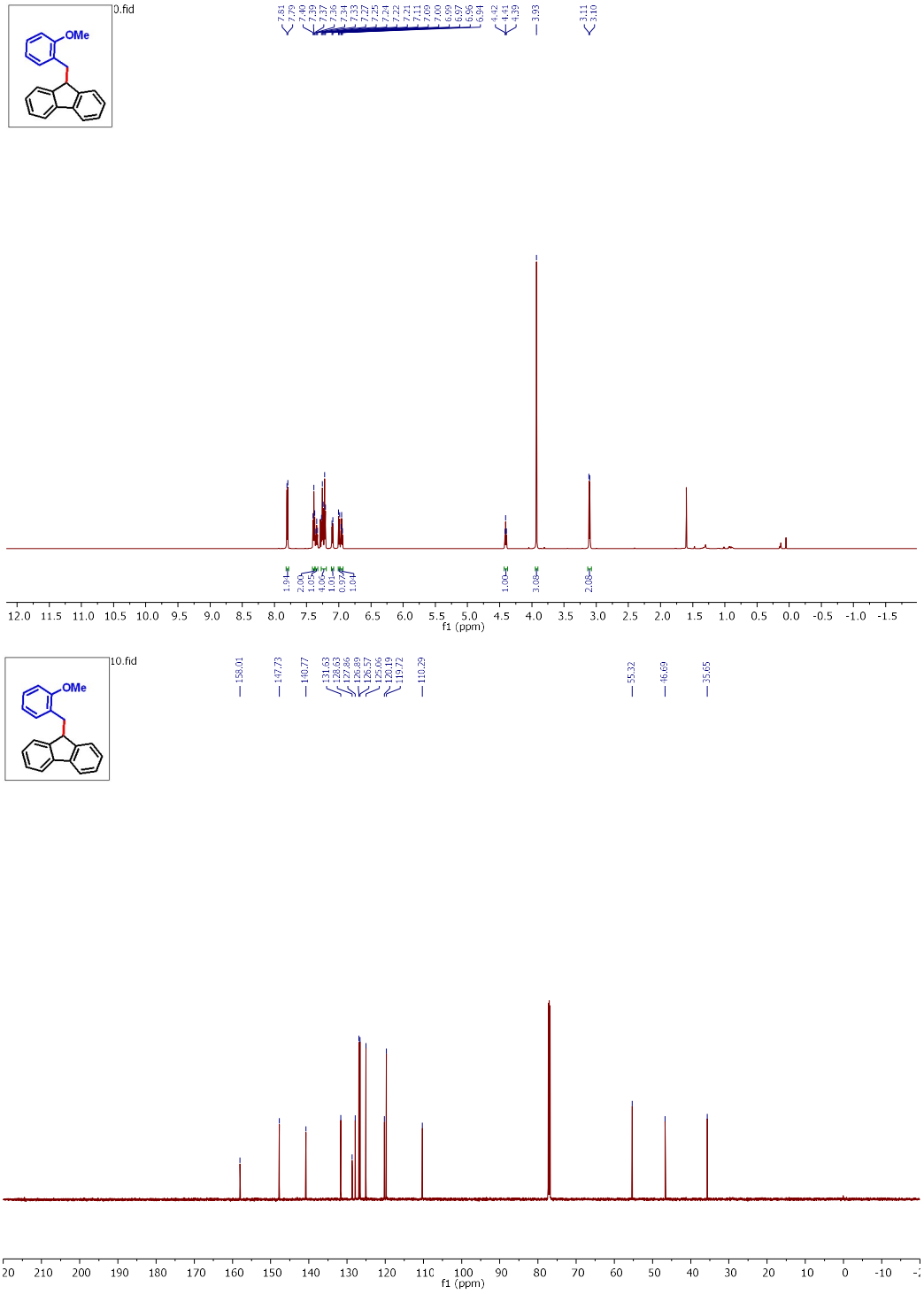


Fig S24: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(2-methoxybenzyl)-9H-fluorene (**3n**) in $CDCl_3$.

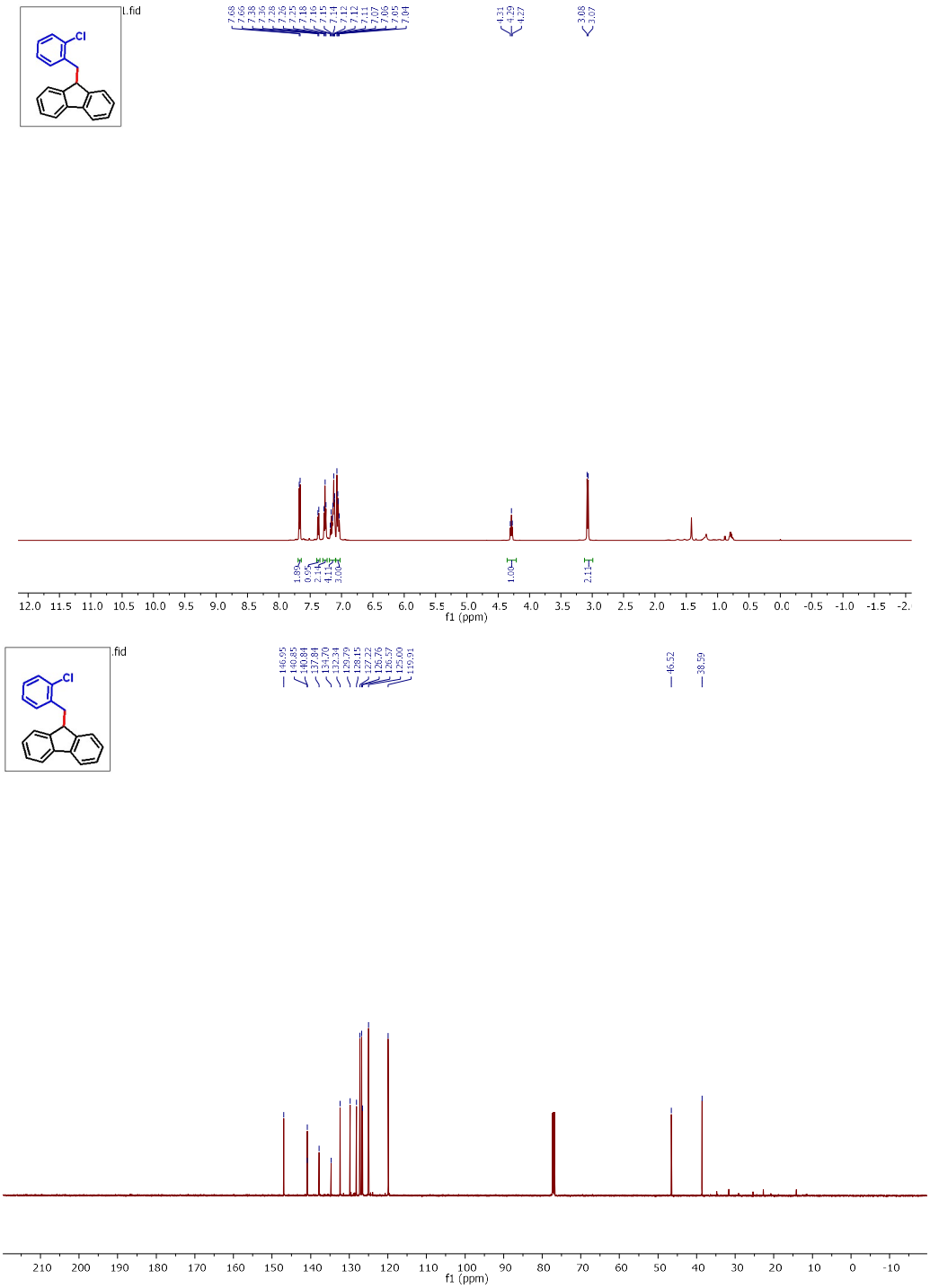


Fig S25: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 9-(2-chlorobenzyl)-9H-fluorene (**3o**) in $CDCl_3$.

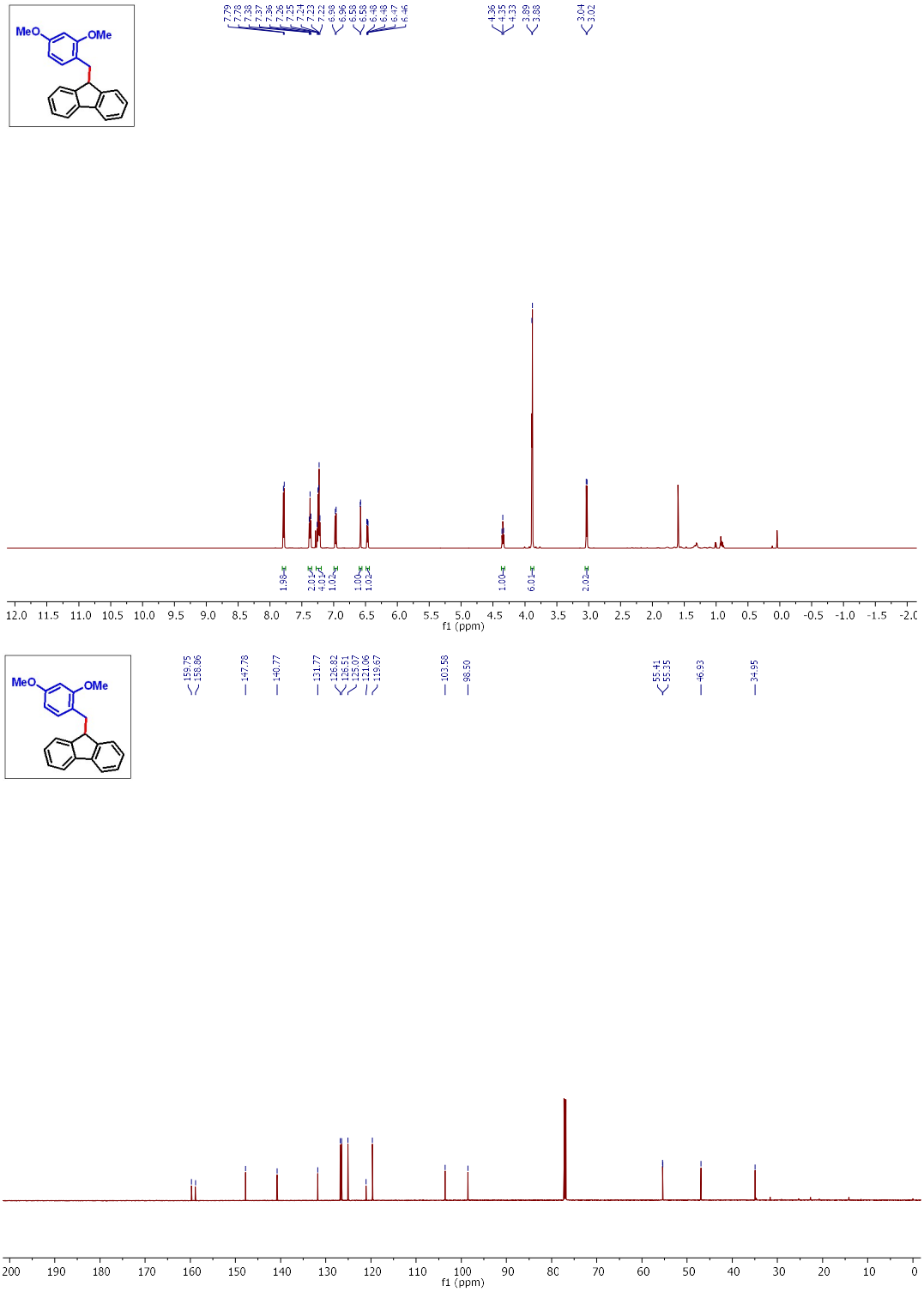


Fig S26: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(2,4-dimethoxybenzyl)-9H-fluorene (**3p**) in $CDCl_3$.

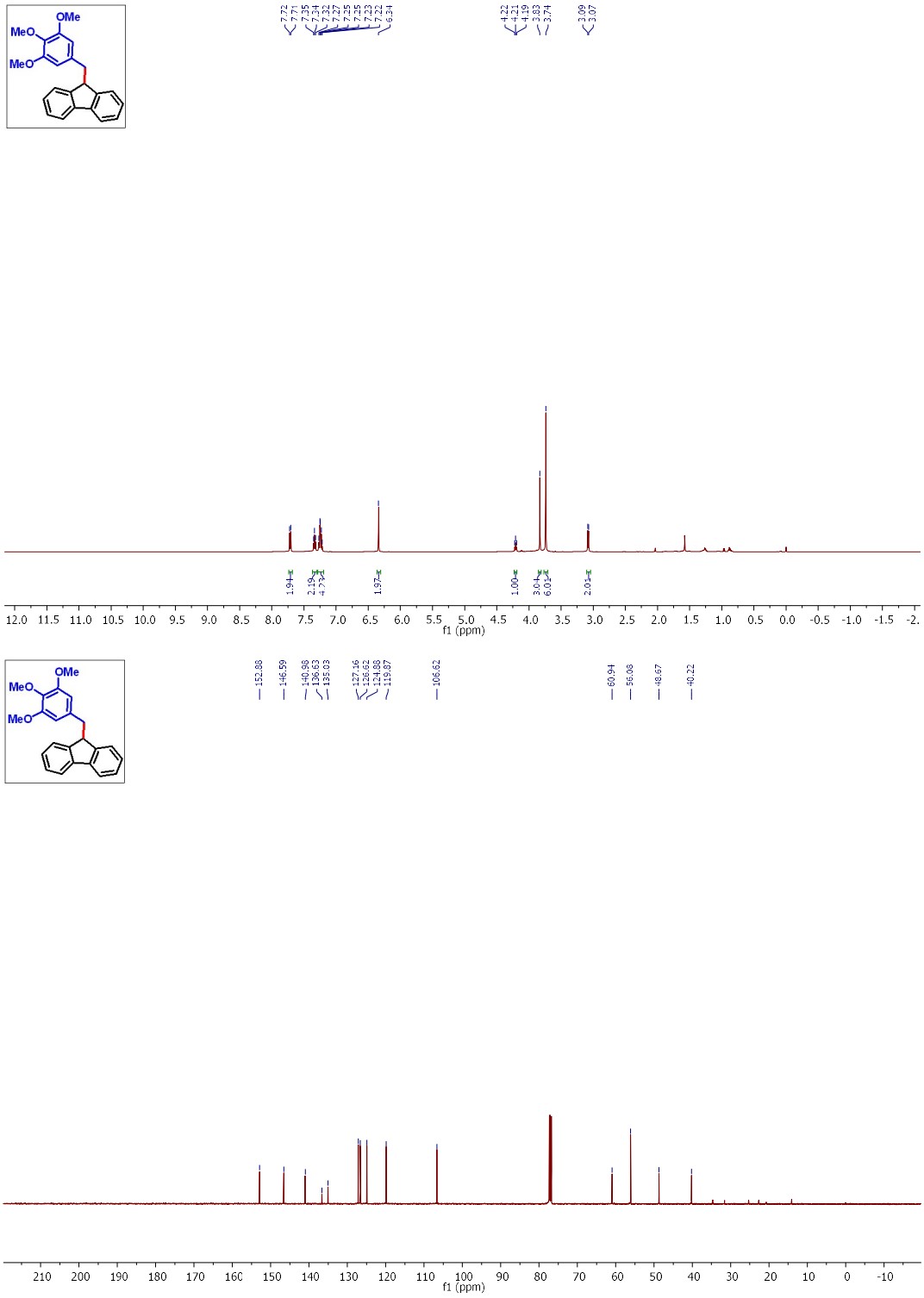


Fig S27: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 9-(3,4,5-trimethoxybenzyl)-9H-fluorene (**3q**) in $CDCl_3$.

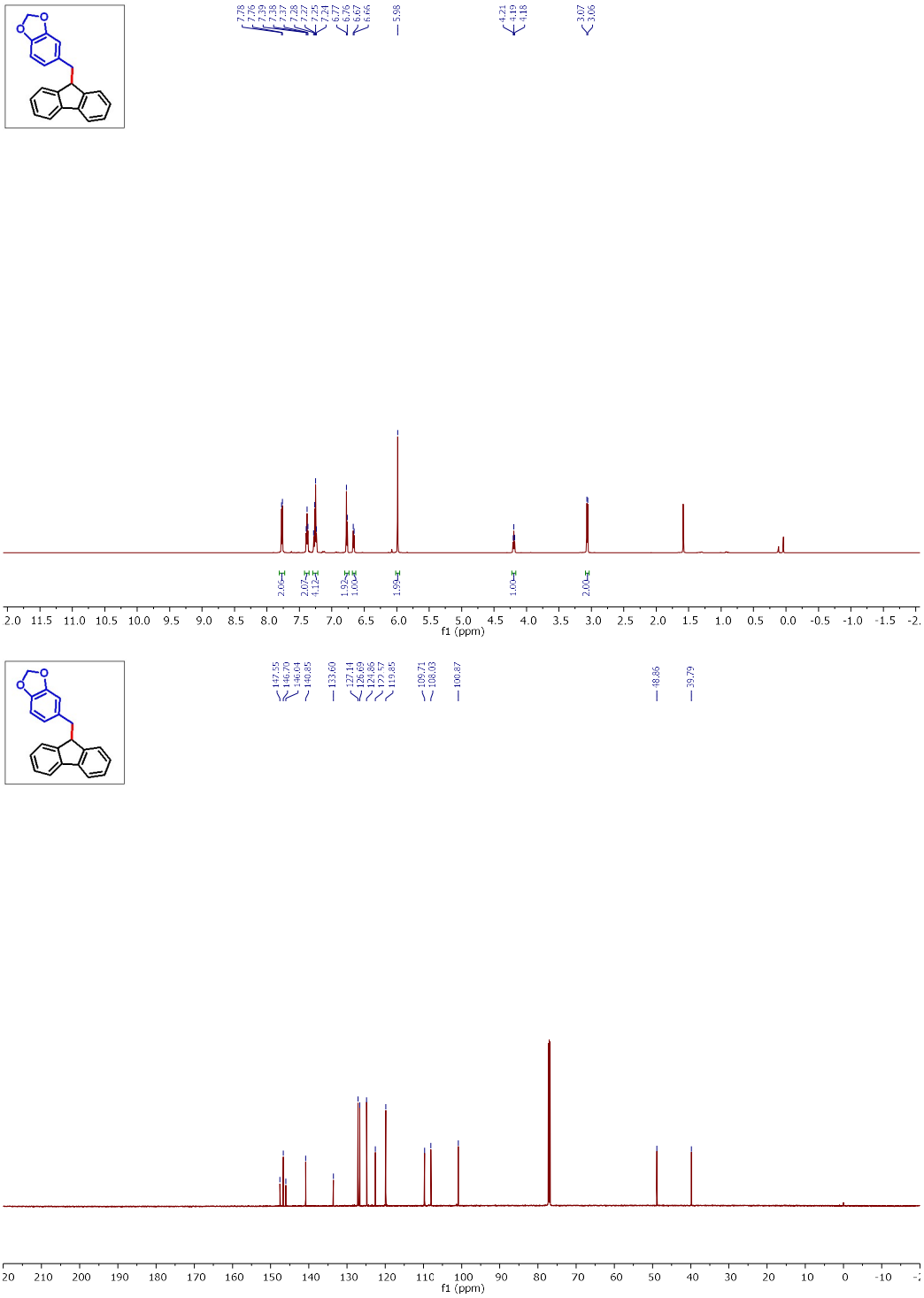


Fig S28: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 5-((9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole (**3r**) in $CDCl_3$.

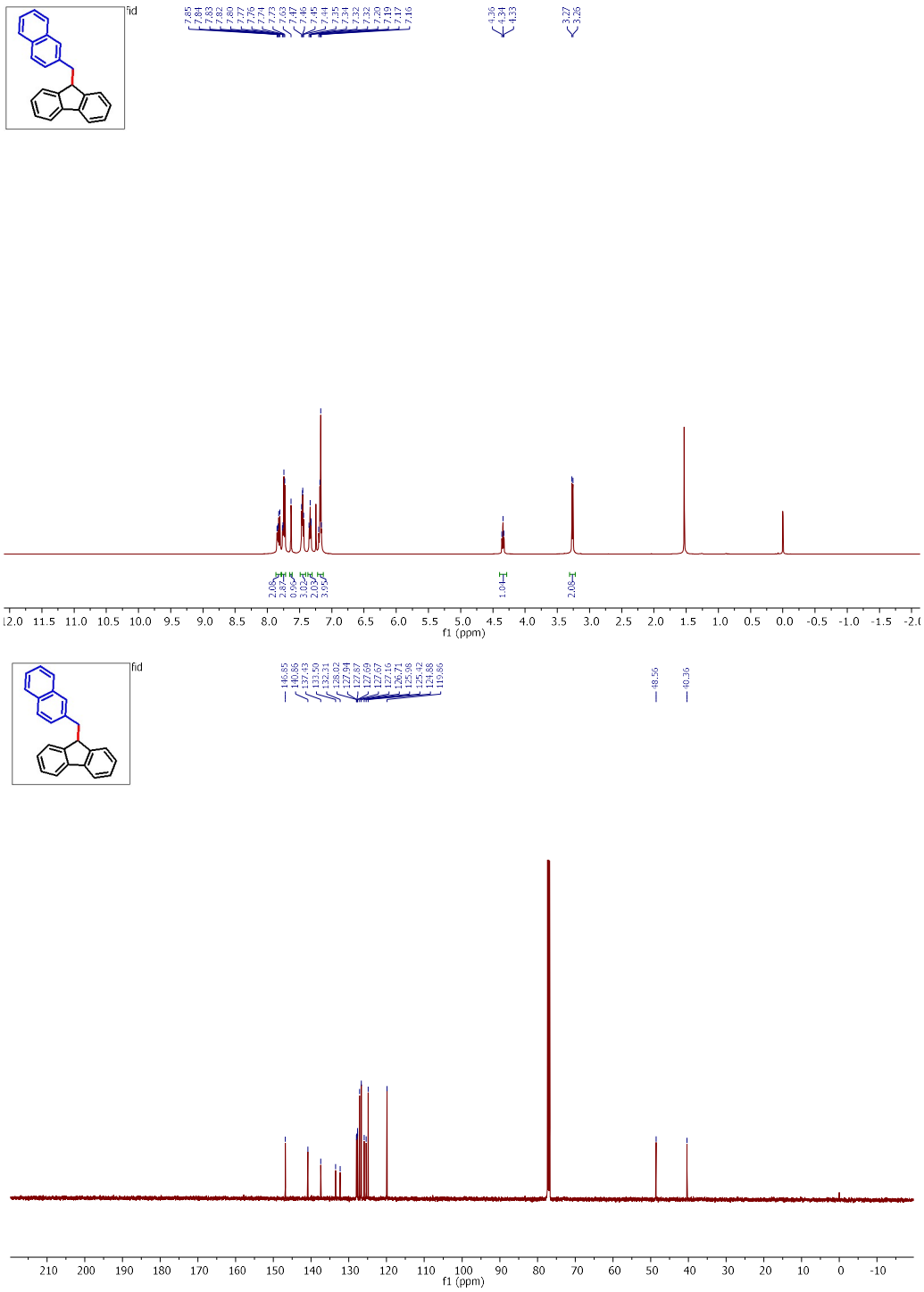


Fig S29: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 9-(naphthalen-2-ylmethyl)-9H-fluorene (**3s**) in $CDCl_3$.

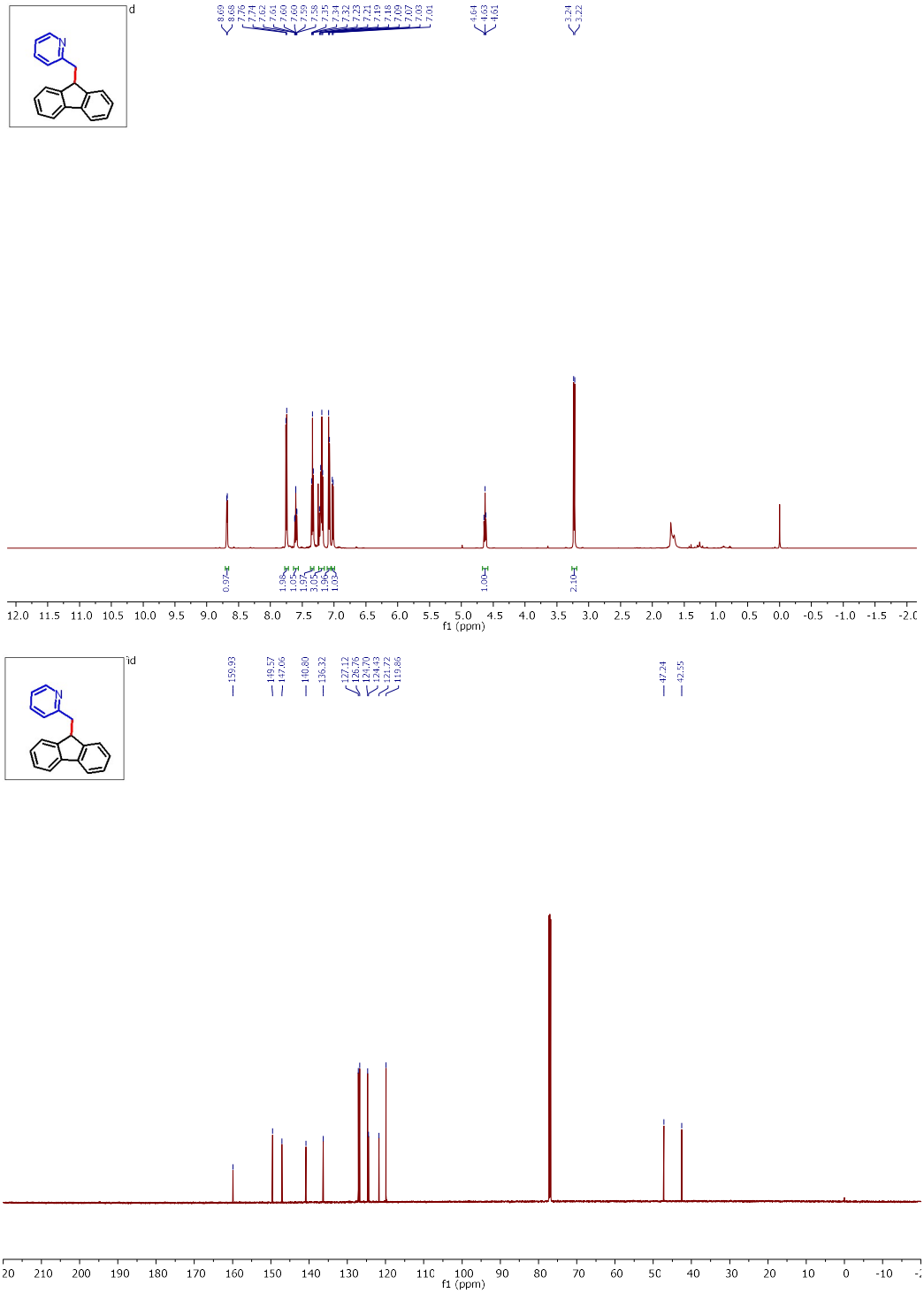


Fig S30: ^{1}H (500 MHz) and ^{13}C (150 MHz) NMR of 2-((9H-fluoren-9-yl)methyl)pyridine (**3t**) in $CDCl_3$.

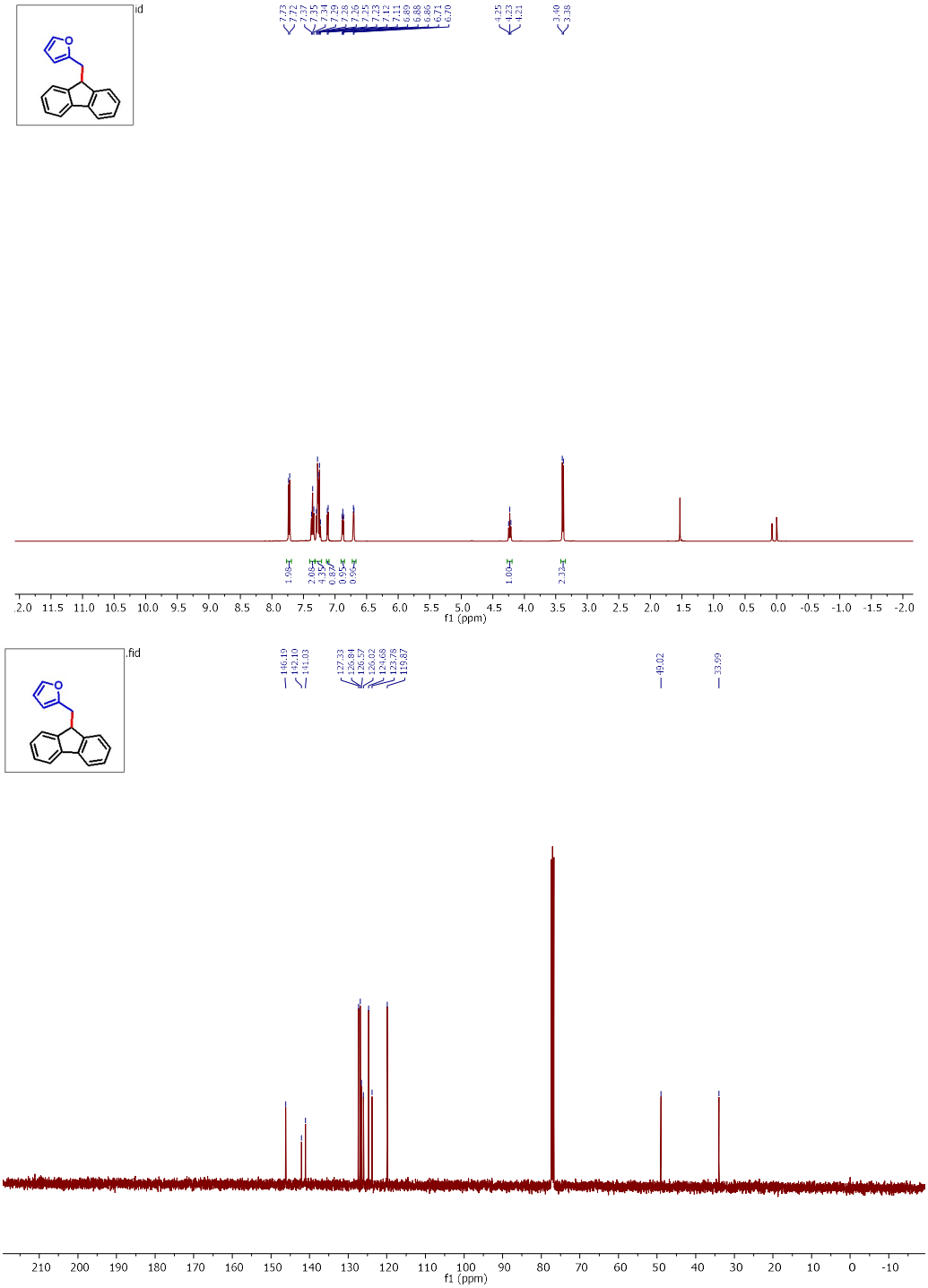


Fig S31: ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR of 2-((9H-fluoren-9-yl)methyl)furan (**3u**) in $CDCl_3$.

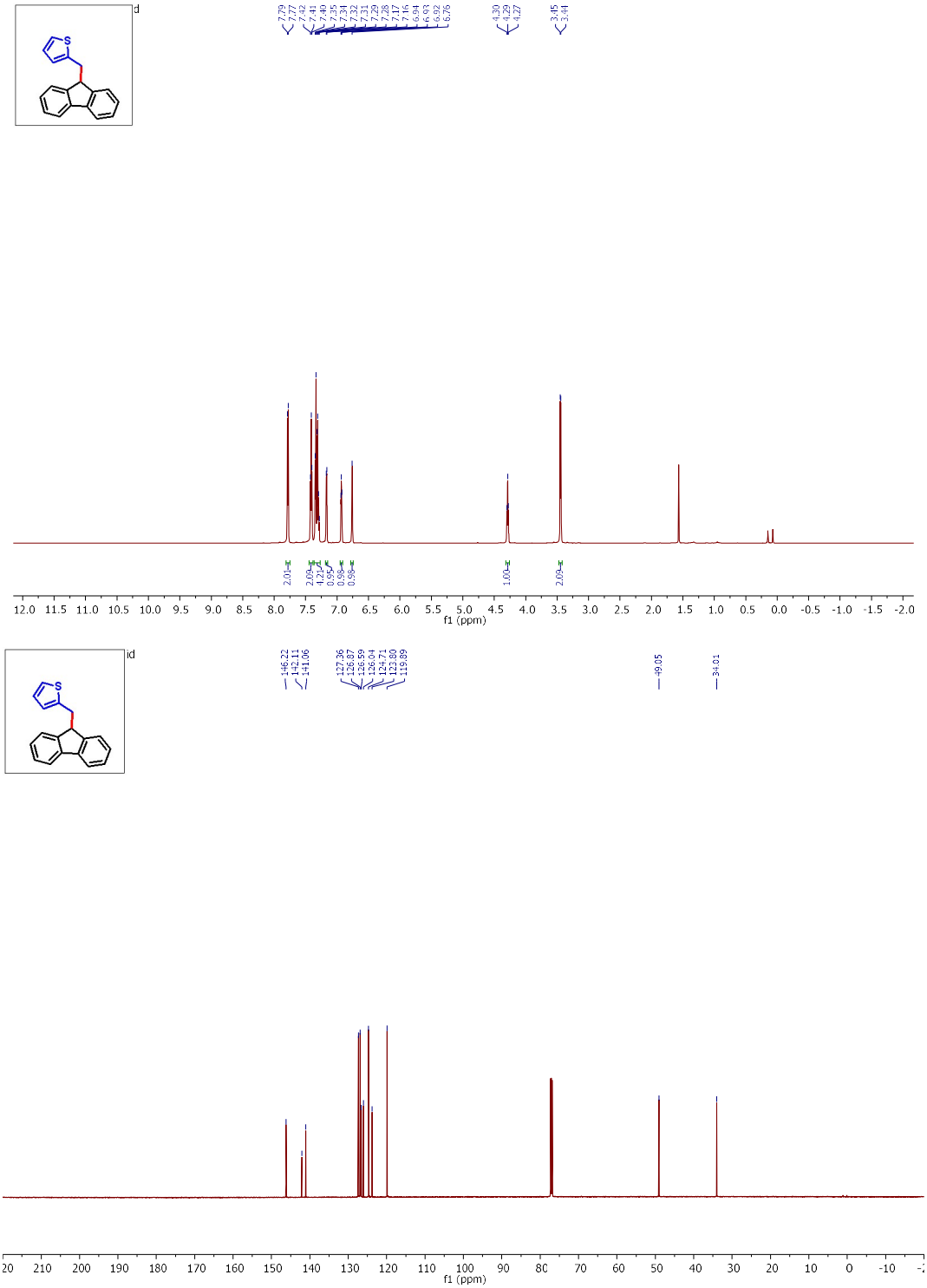


Fig S32: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 2-((9H-fluoren-9-yl)methyl)thiophene (**3v**) in $CDCl_3$.

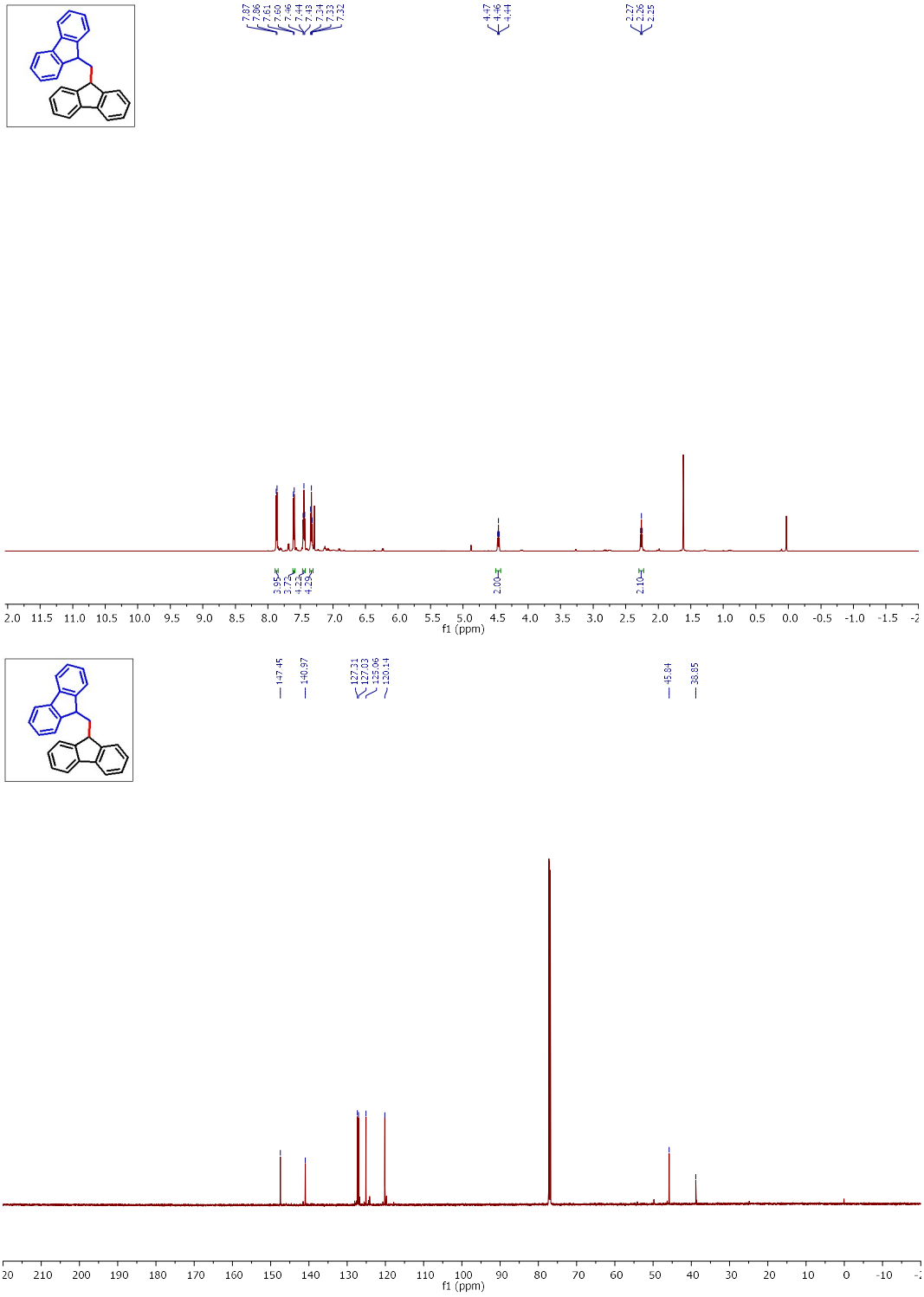


Fig S33: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of di(9H-fluoren-9-yl)methane (**3w**) in $CDCl_3$.

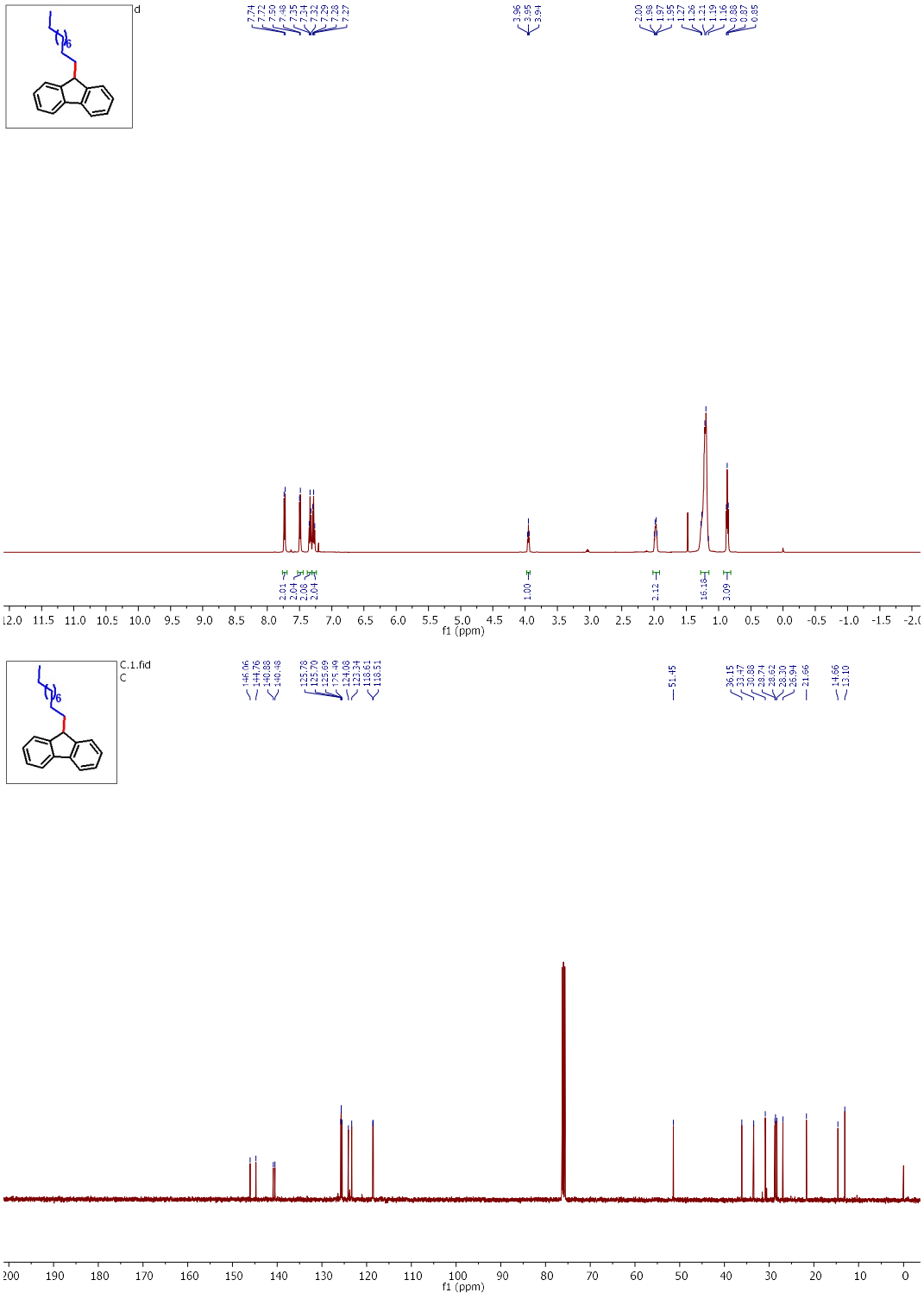


Fig S34: ^{1}H (500 MHz) and ^{13}C (100 MHz) NMR of 9-decyl-9H-fluorene (**3x**) in $CDCl_3$.

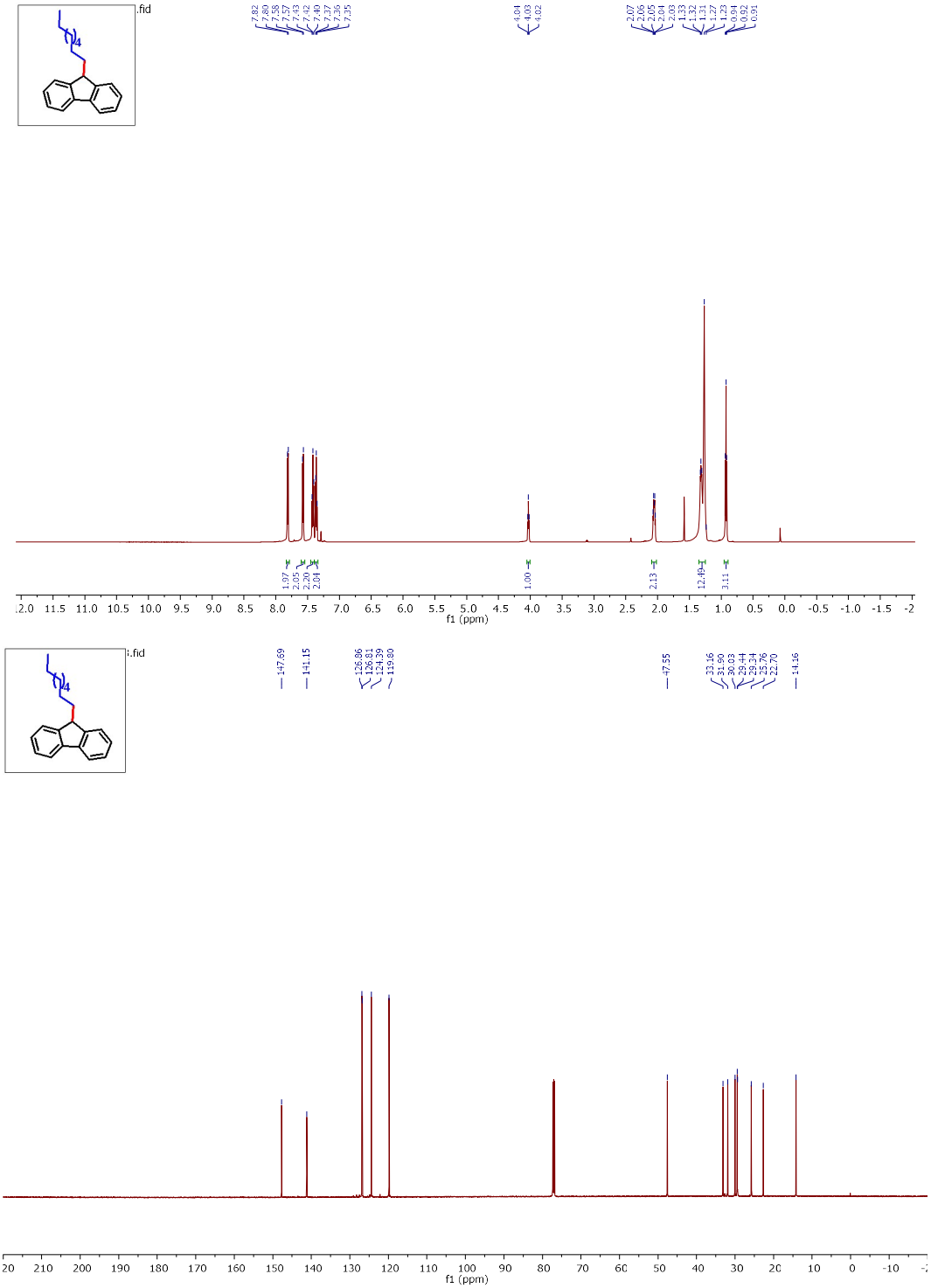


Fig S35: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-octyl-9H-fluorene (**3y**) in $CDCl_3$.

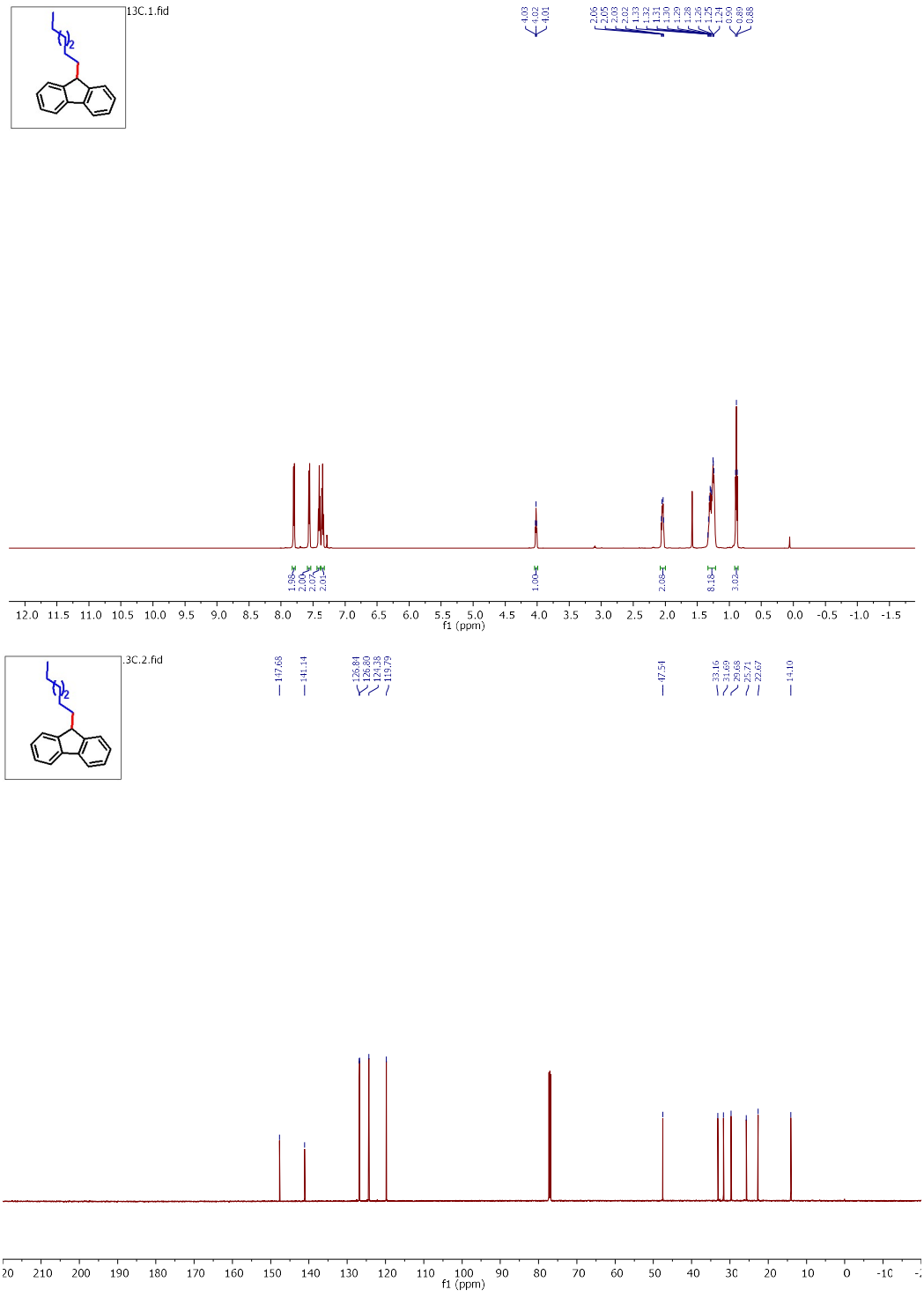


Fig S36: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-hexyl-9H-fluorene (**3z**) in $CDCl_3$.

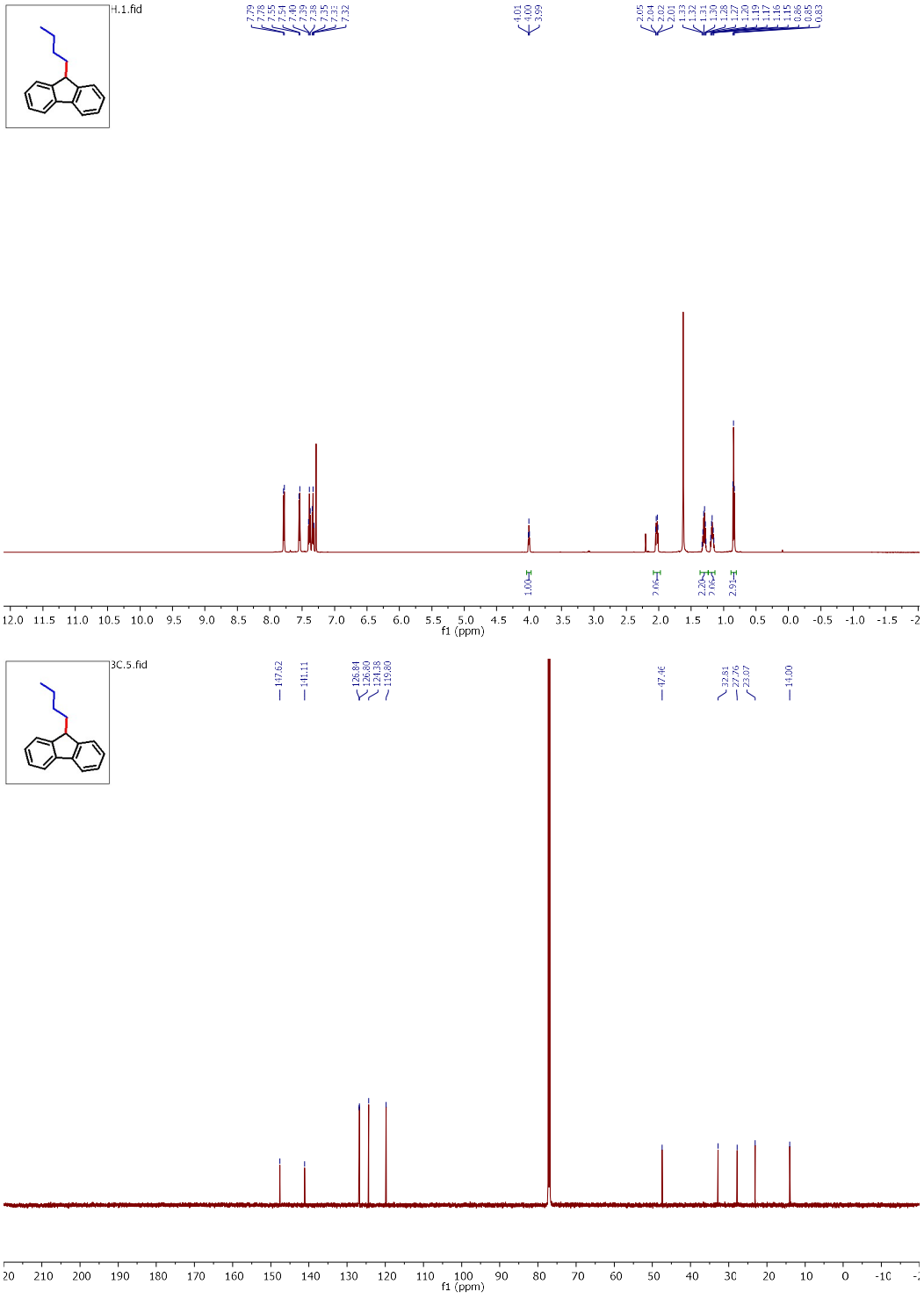


Fig S37: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-butyl-9H-fluorene (**3aa**) in $CDCl_3$.

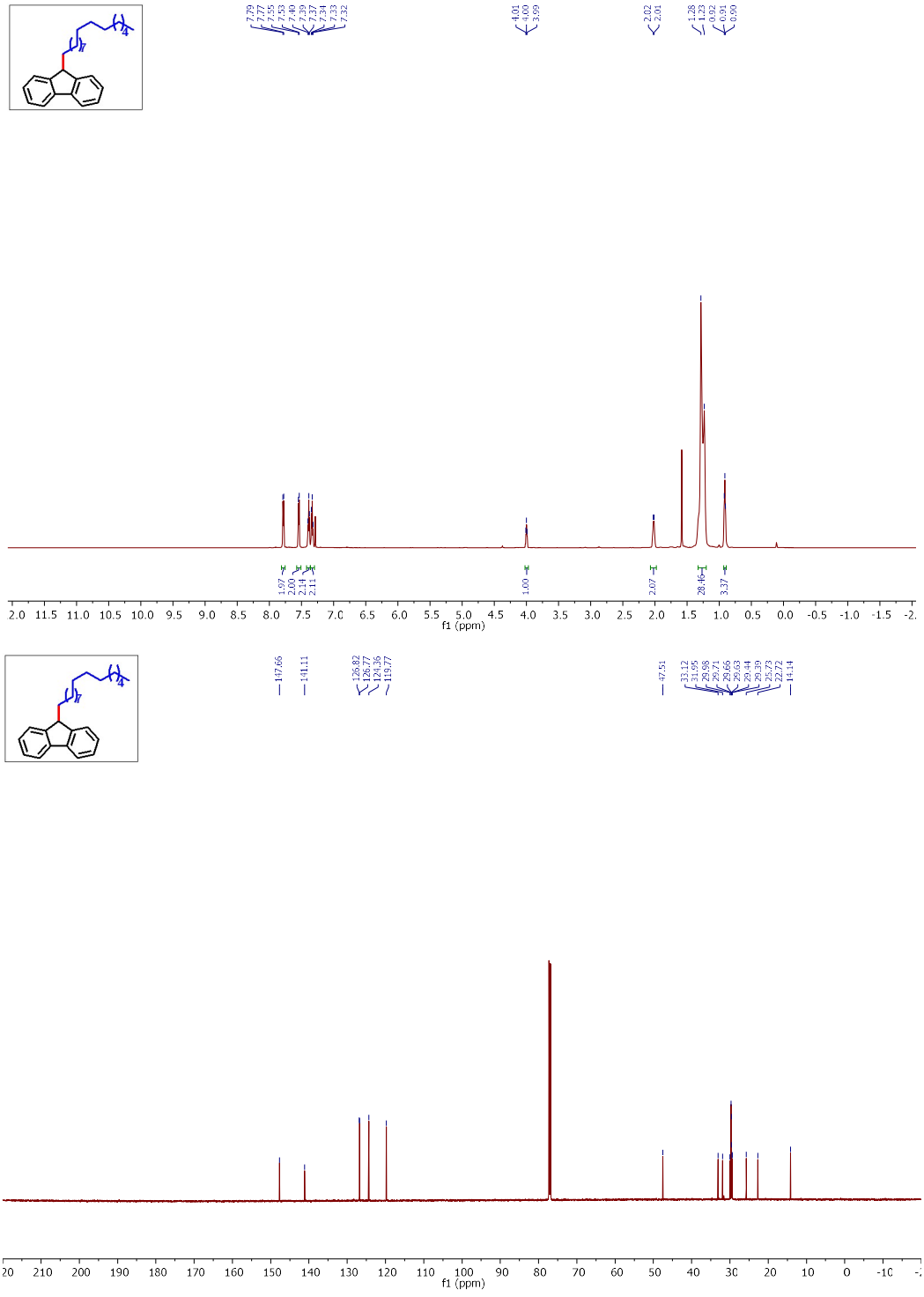


Fig S38: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-hexadecyl-9H-fluorene (**3ab**) in $CDCl_3$.

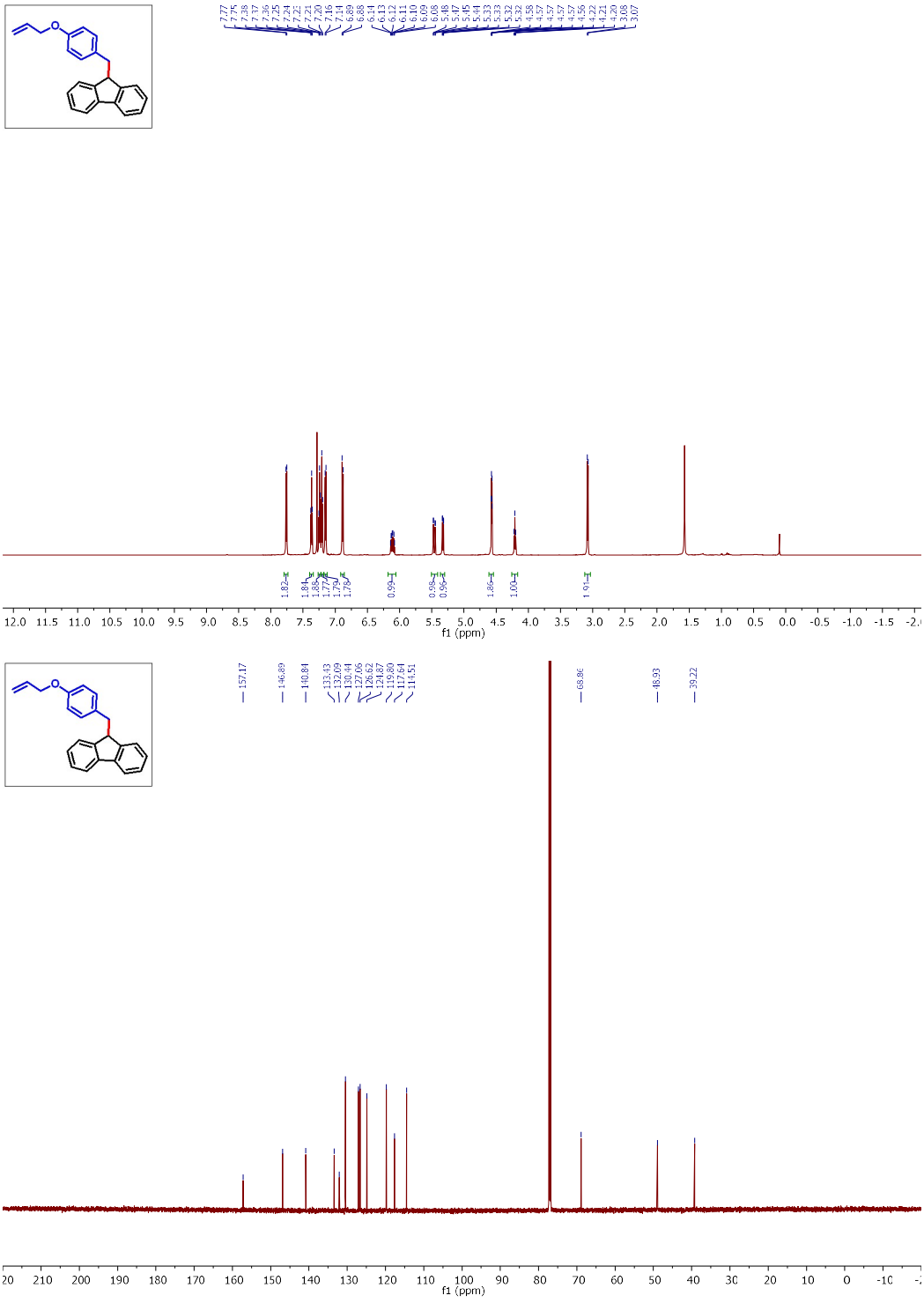


Fig S39: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(4-(allyloxy)benzyl)-9H-fluorene (**3ac**) in $CDCl_3$.

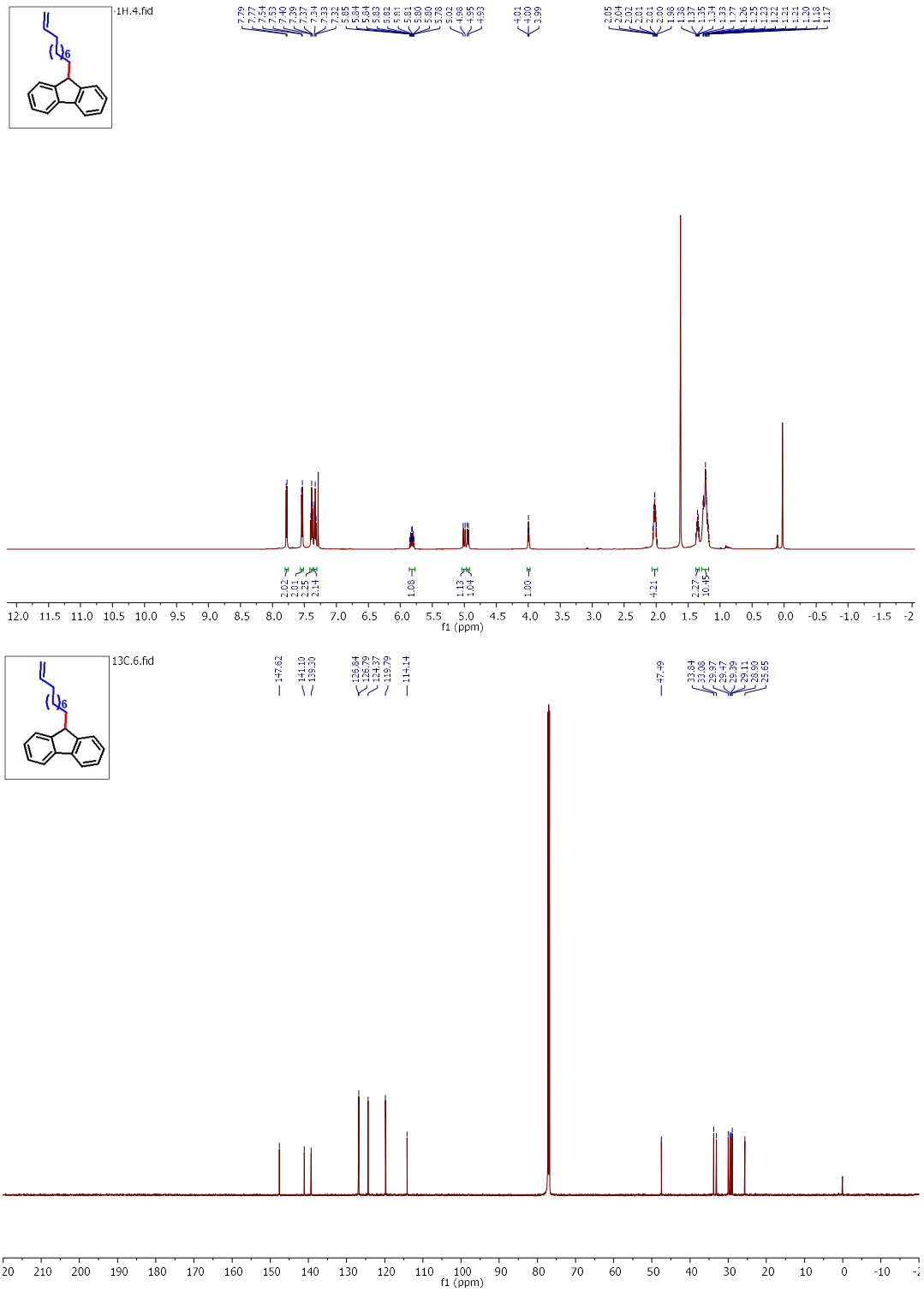


Fig S40: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(dec-9-en-1-yl)-9H-fluorene (**3ad**) in $CDCl_3$.

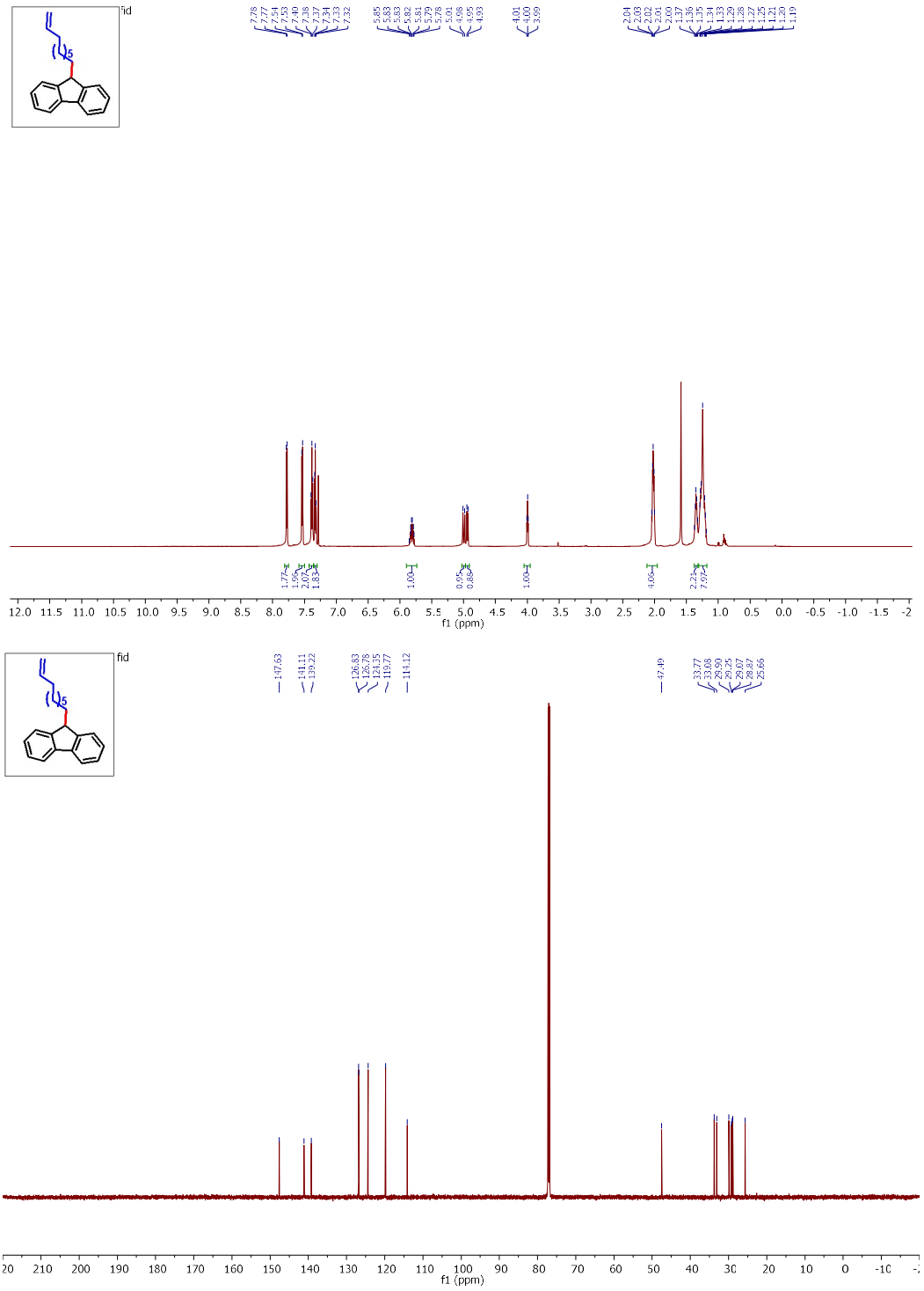


Fig S41: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(non-8-en-1-yl)-9H-fluorene (**3ae**) in $CDCl_3$.

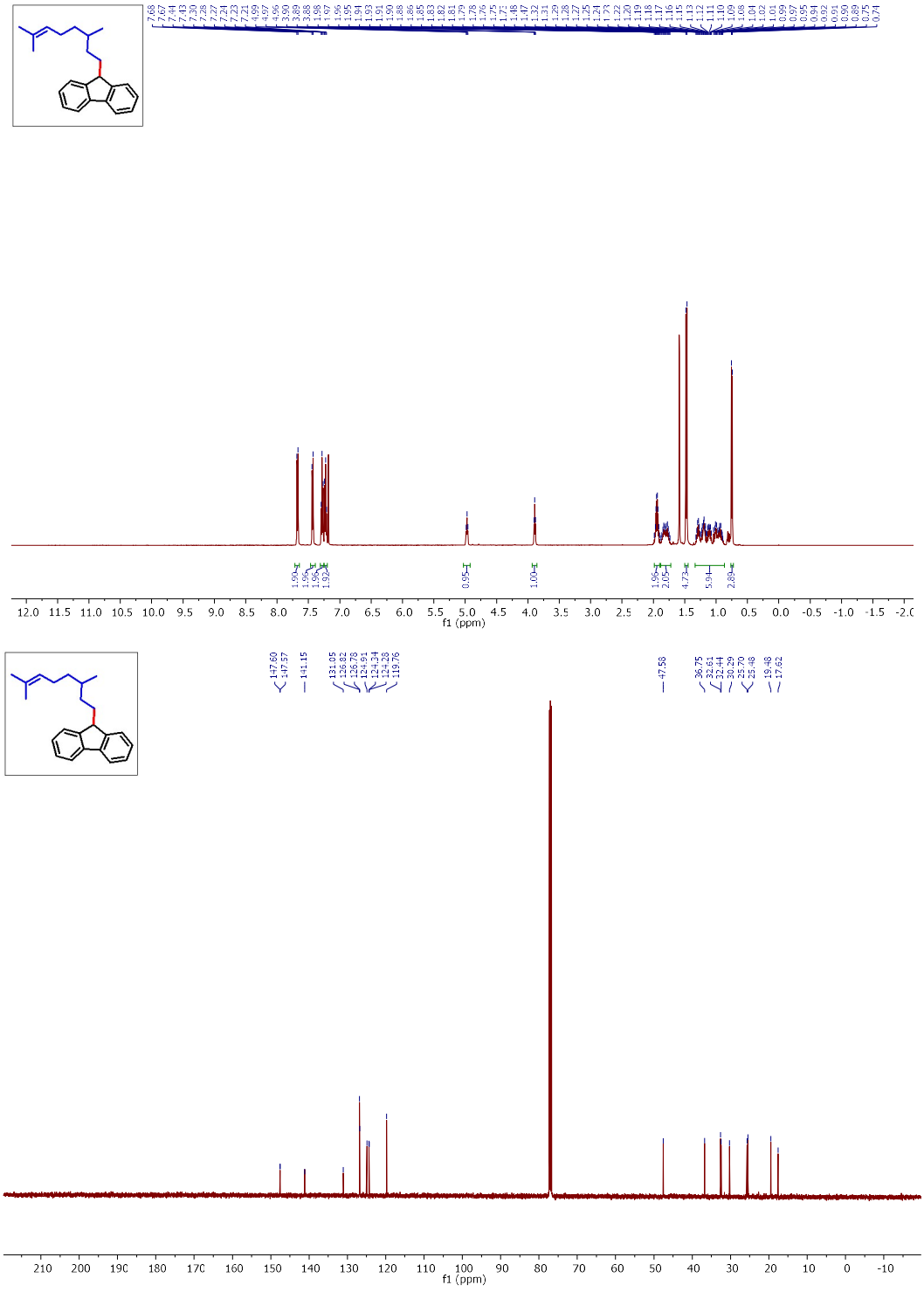


Fig S42: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 9-(3,7-dimethyloct-6-en-1-yl)-9H-fluorene (**3af**) in $CDCl_3$.

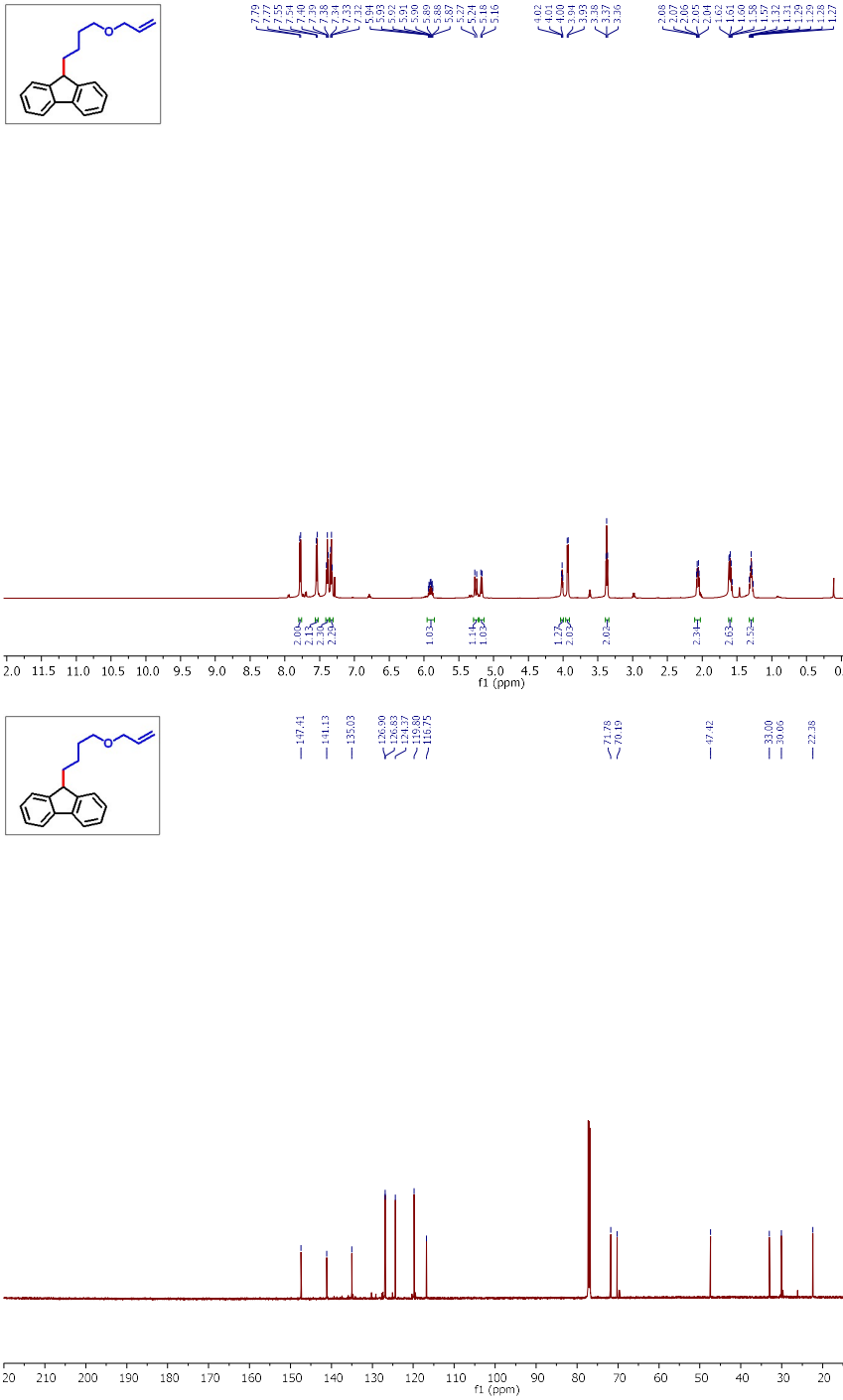


Fig S43: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(4-(allyloxy)butyl)-9H-fluorene (**3ag**) in $CDCl_3$.

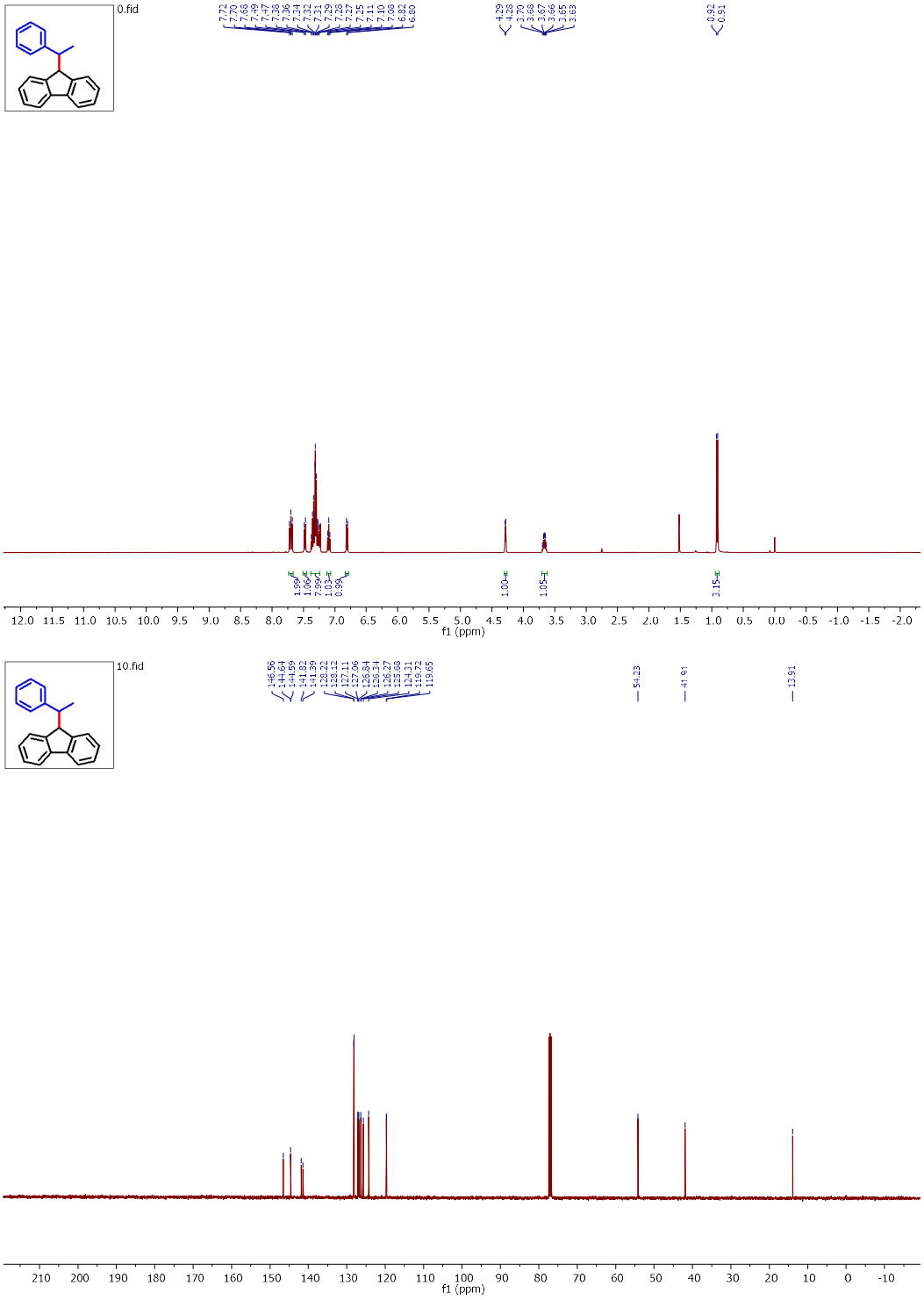


Fig S44: ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR of (S)-9-(1-phenylethyl)-9H-fluorene (**3ah**) in $CDCl_3$.

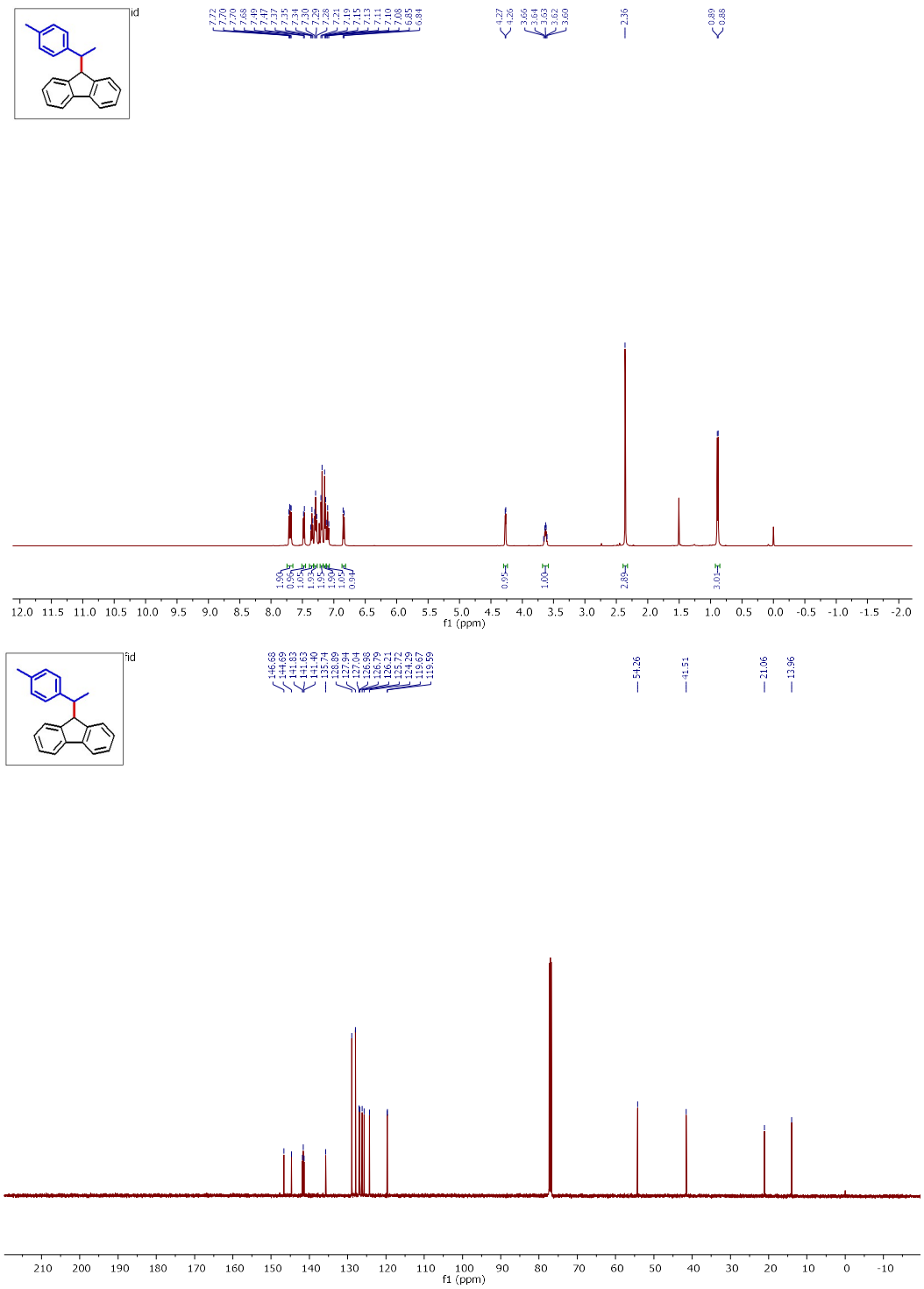


Fig S45: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of (S)-9-(1-(p-tolyl)ethyl)-9H-fluorene (**3ai**) in $CDCl_3$.

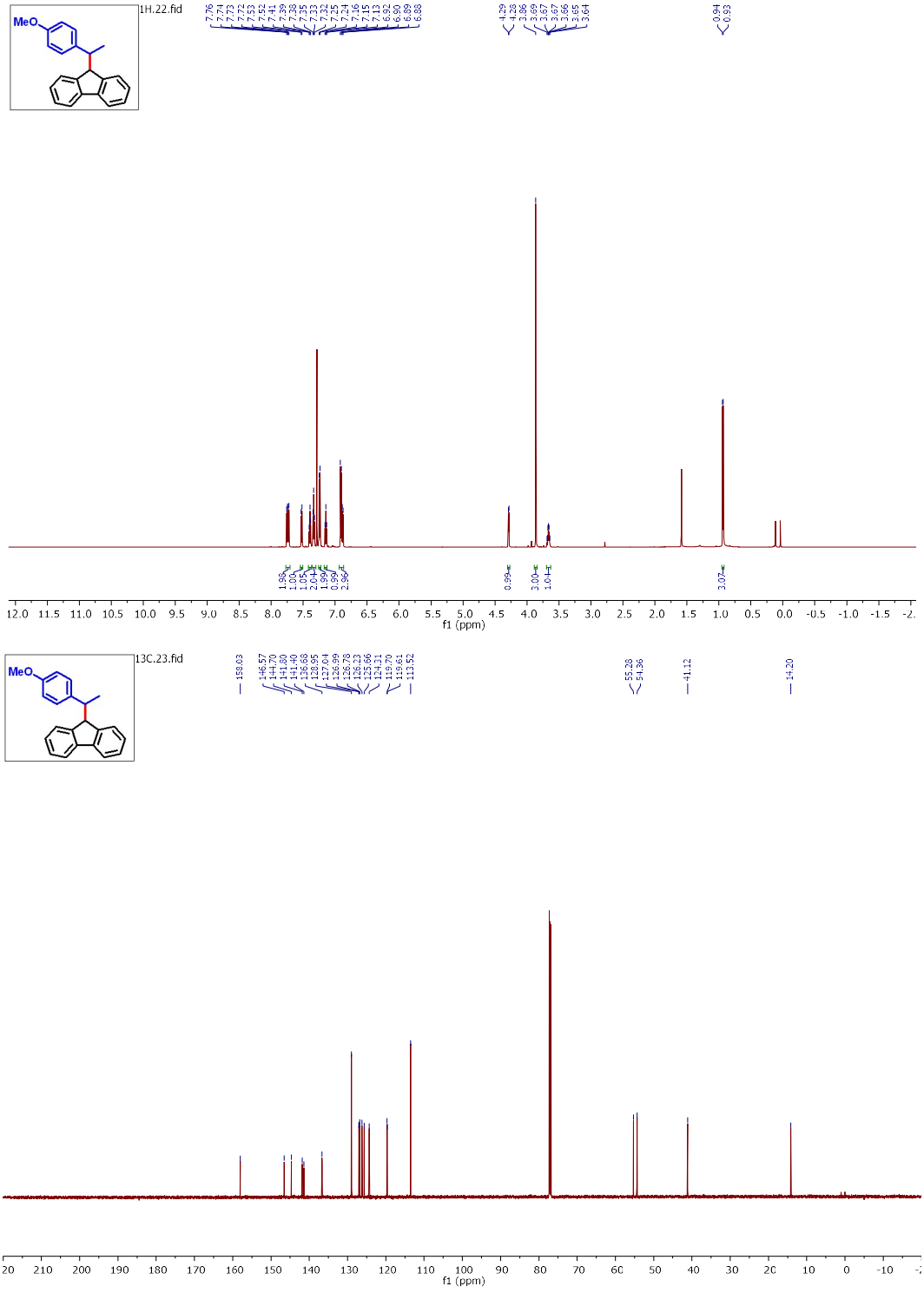


Fig S46: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of (S)-9-(1-(4-methoxyphenyl)ethyl)-9H-fluorene (**3aj**) in $CDCl_3$.

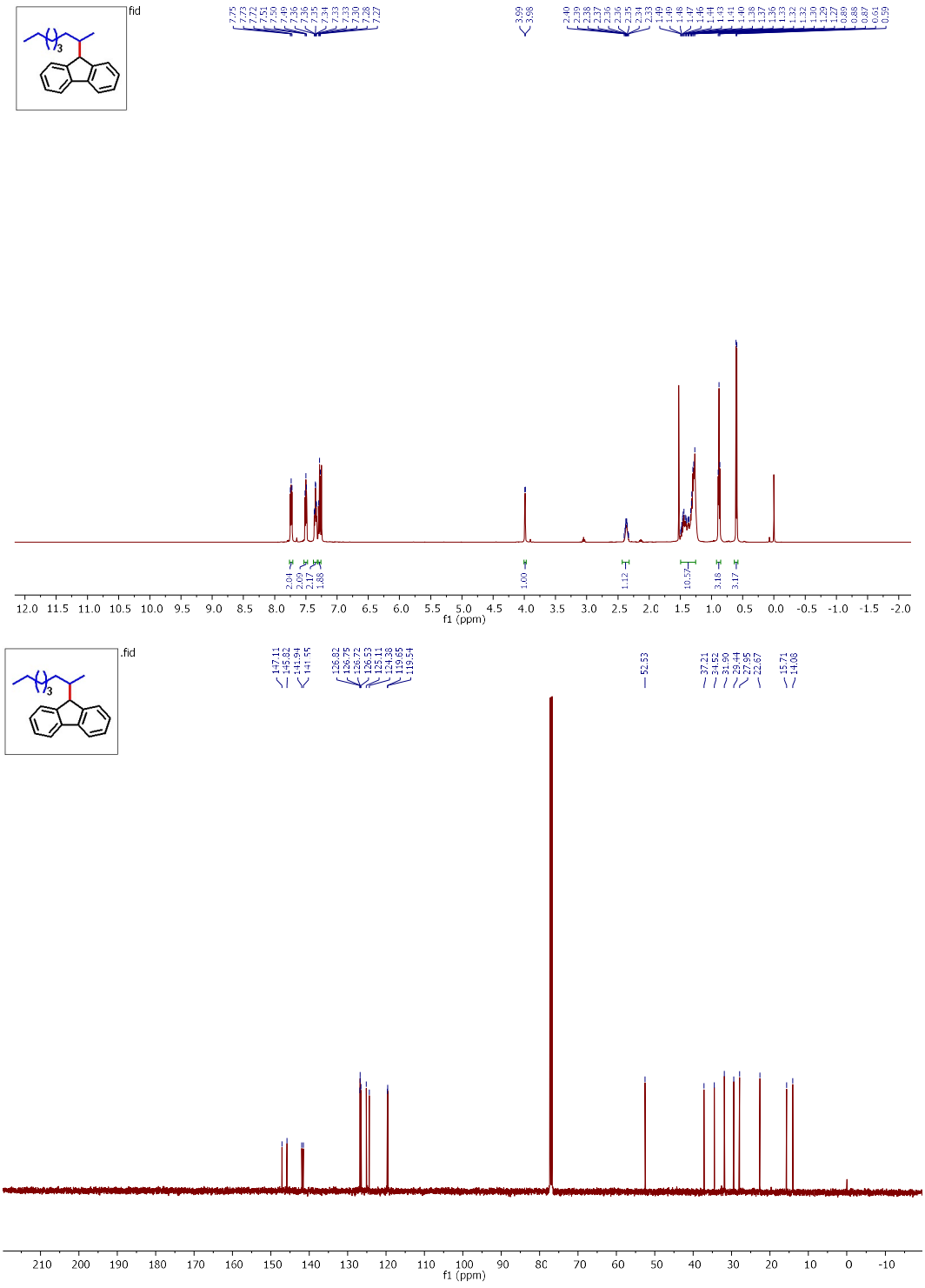


Fig S47: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 9-(octan-2-yl)-9H-fluorene (**3ak**) in $CDCl_3$.

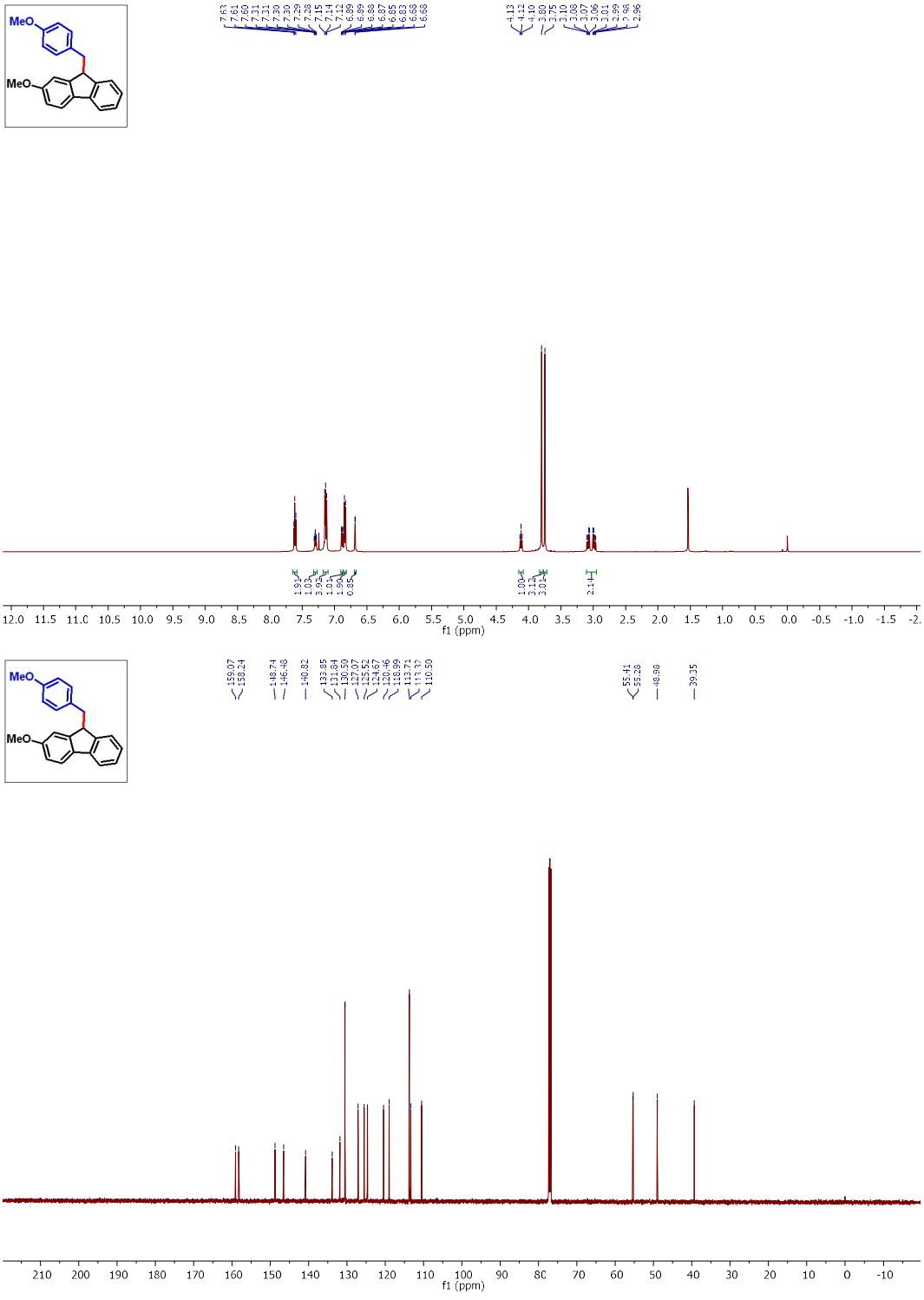


Fig S48: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of (S)-2-methoxy-9-(4-methoxybenzyl)-9H-fluorene (**3al**) in $CDCl_3$.

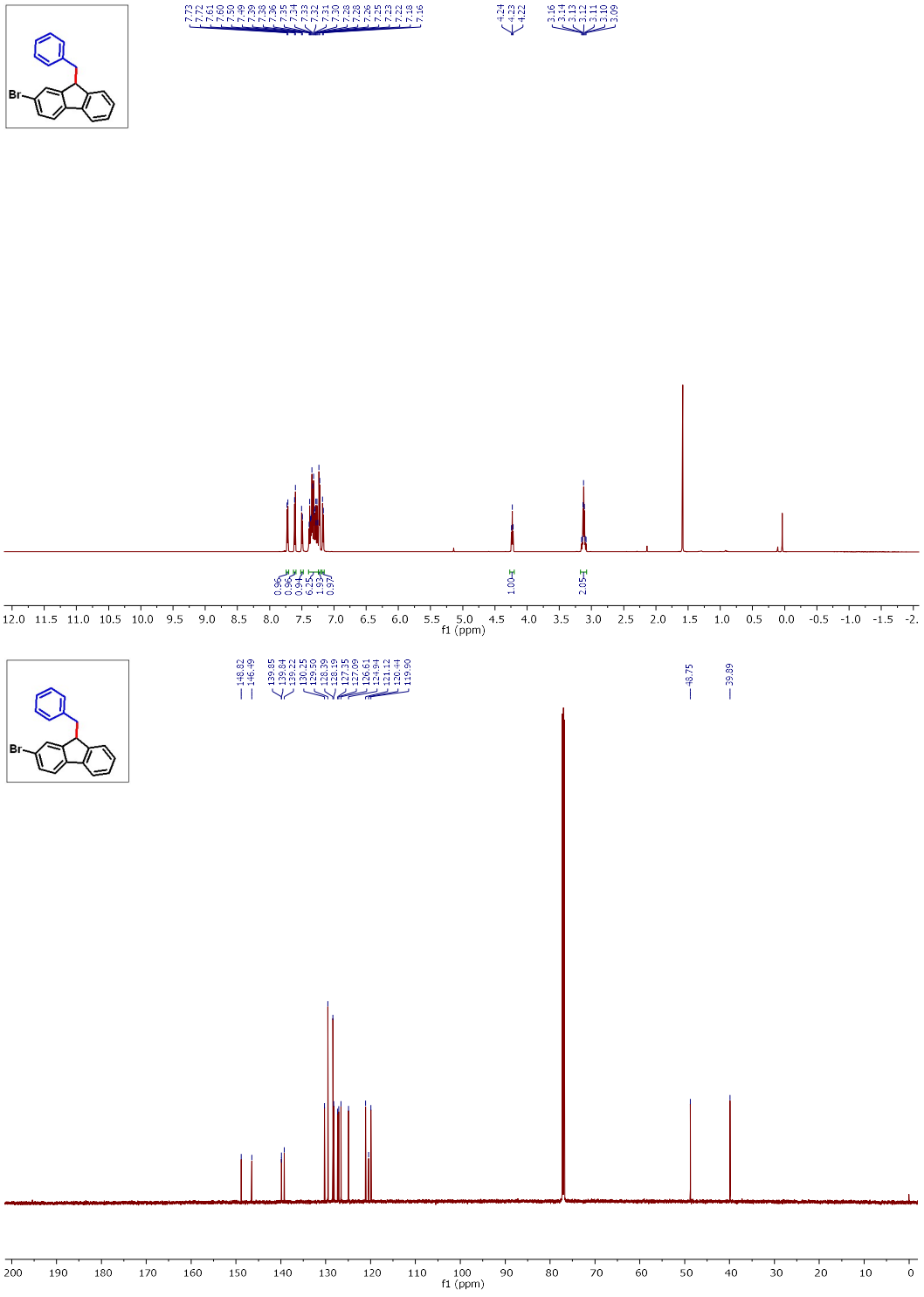


Fig S49: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of (S)-9-benzyl-2-bromo-9H-fluorene (**3am**) in $CDCl_3$.

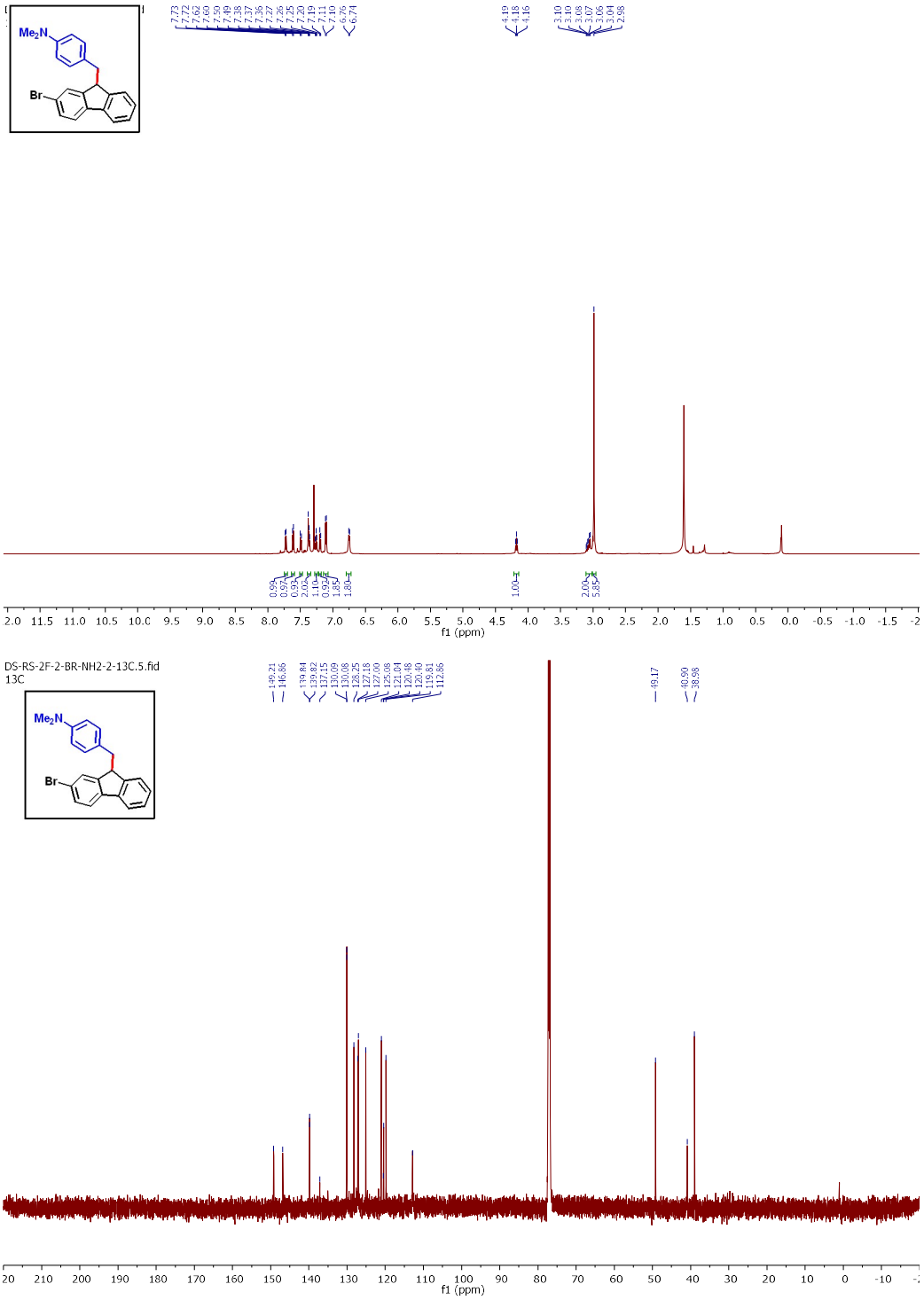


Fig S50: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of (S)-4-((2-bromo-9H-fluoren-9-yl)methyl)-N,N-dimethylaniline (**3an**) in $CDCl_3$.

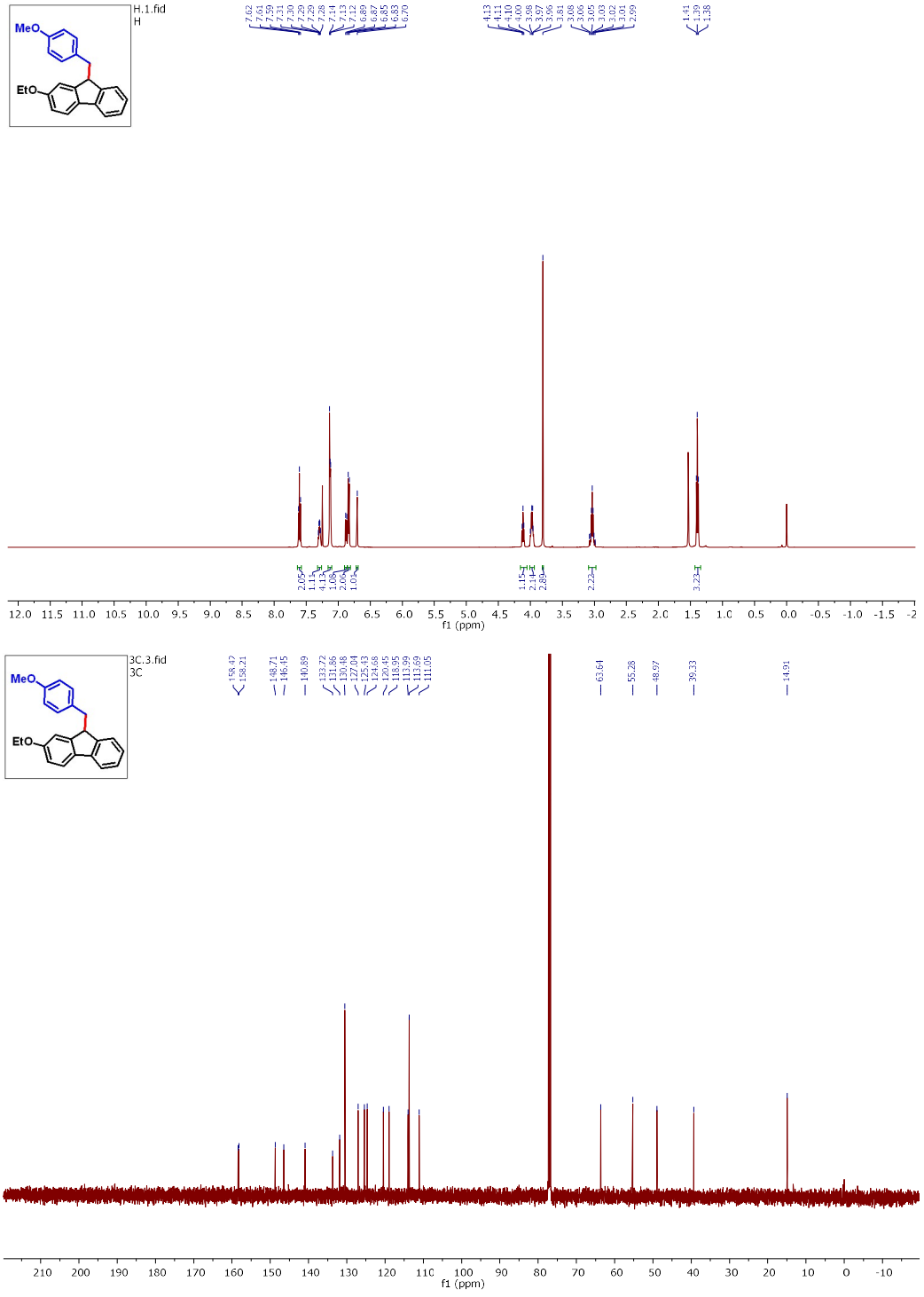


Fig S51: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of (S)-2-ethoxy-9-(4-methoxybenzyl)-9H-fluorene (**3ao**) in $CDCl_3$.

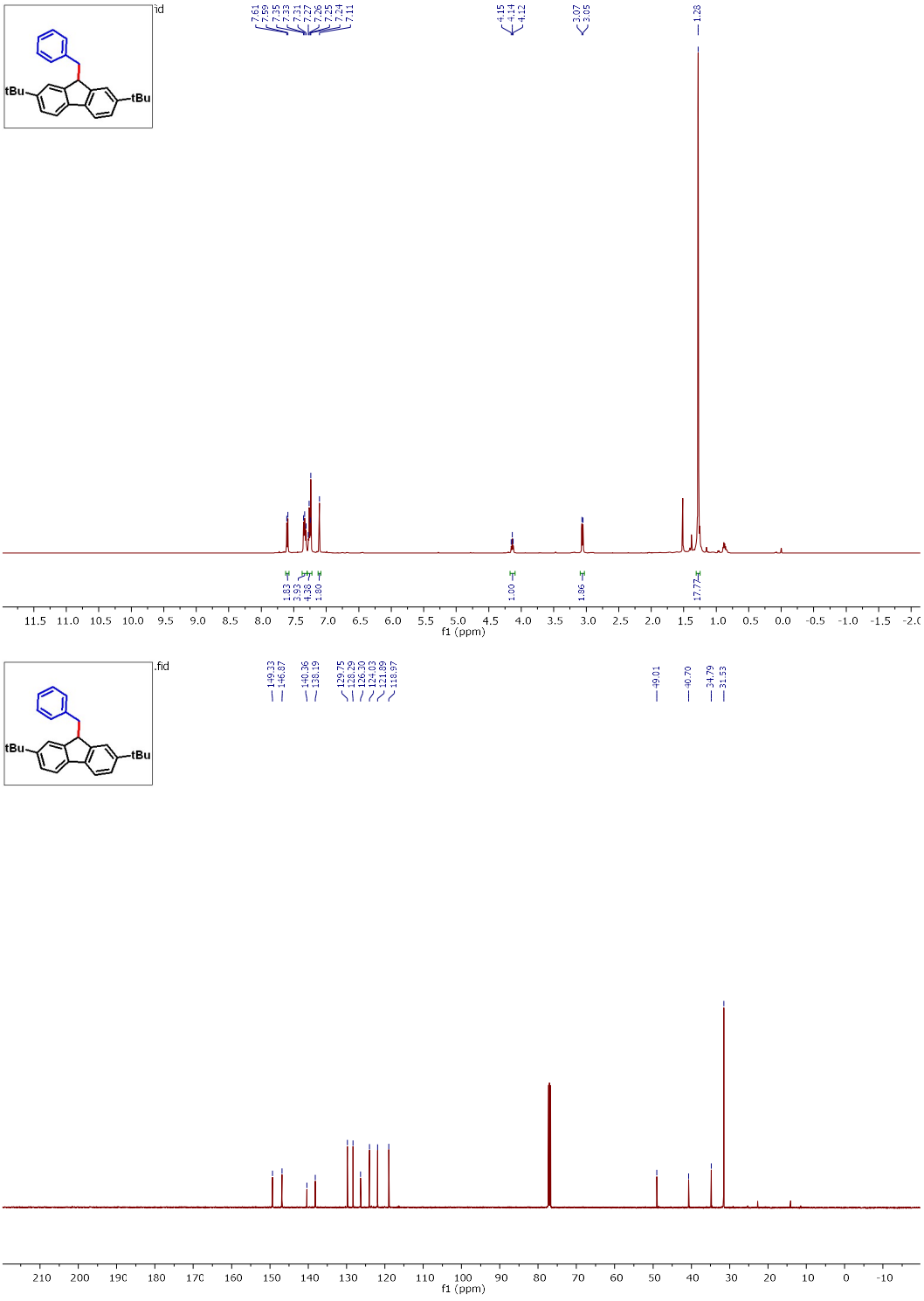


Fig S52: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 9-benzyl-2,7-di-tert-butyl-9H-fluorene (**3aq**) in $CDCl_3$.

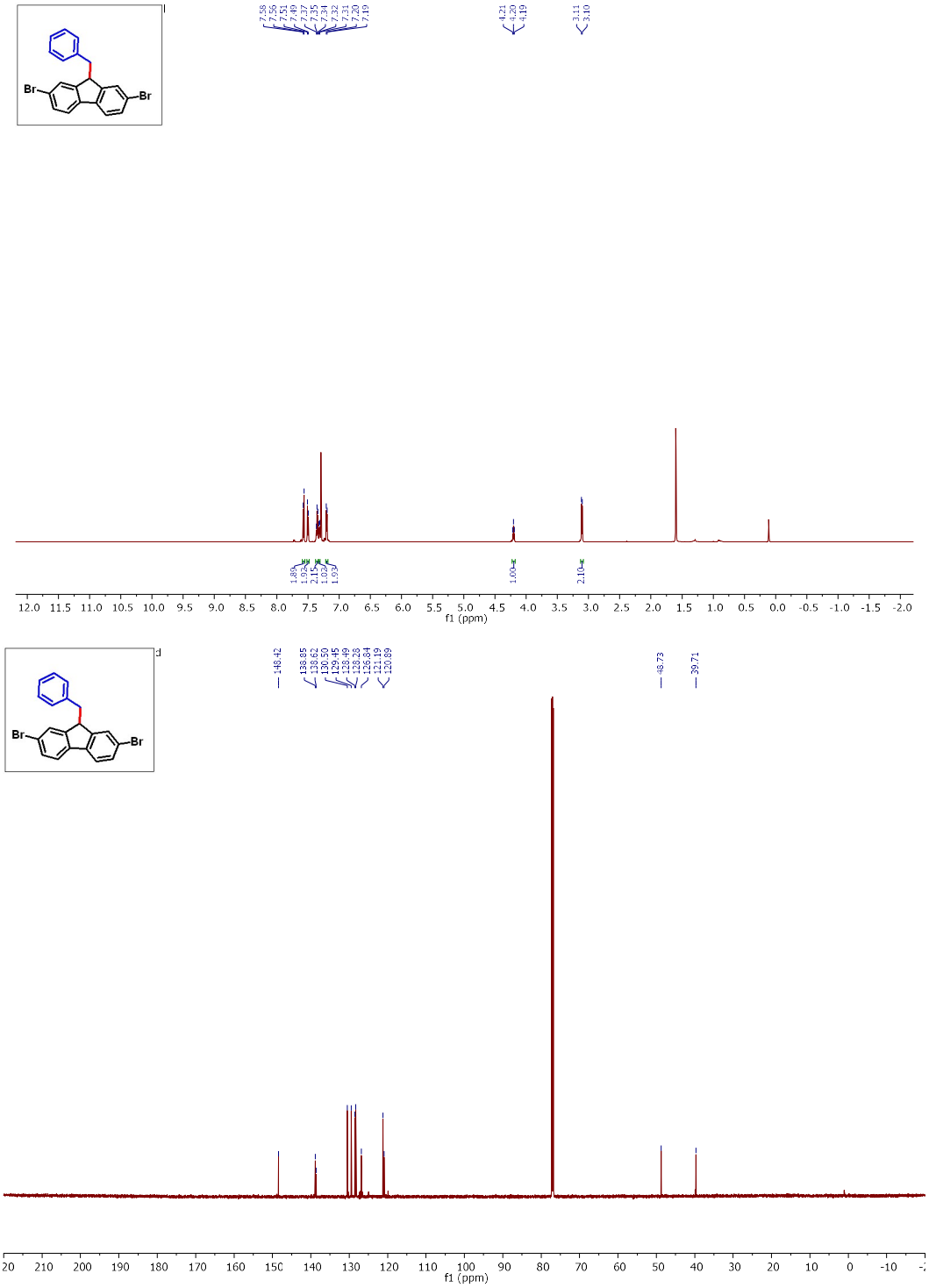


Fig S53: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-benzyl-2,7-dibromo-9H-fluorene (**3ar**) in $CDCl_3$.

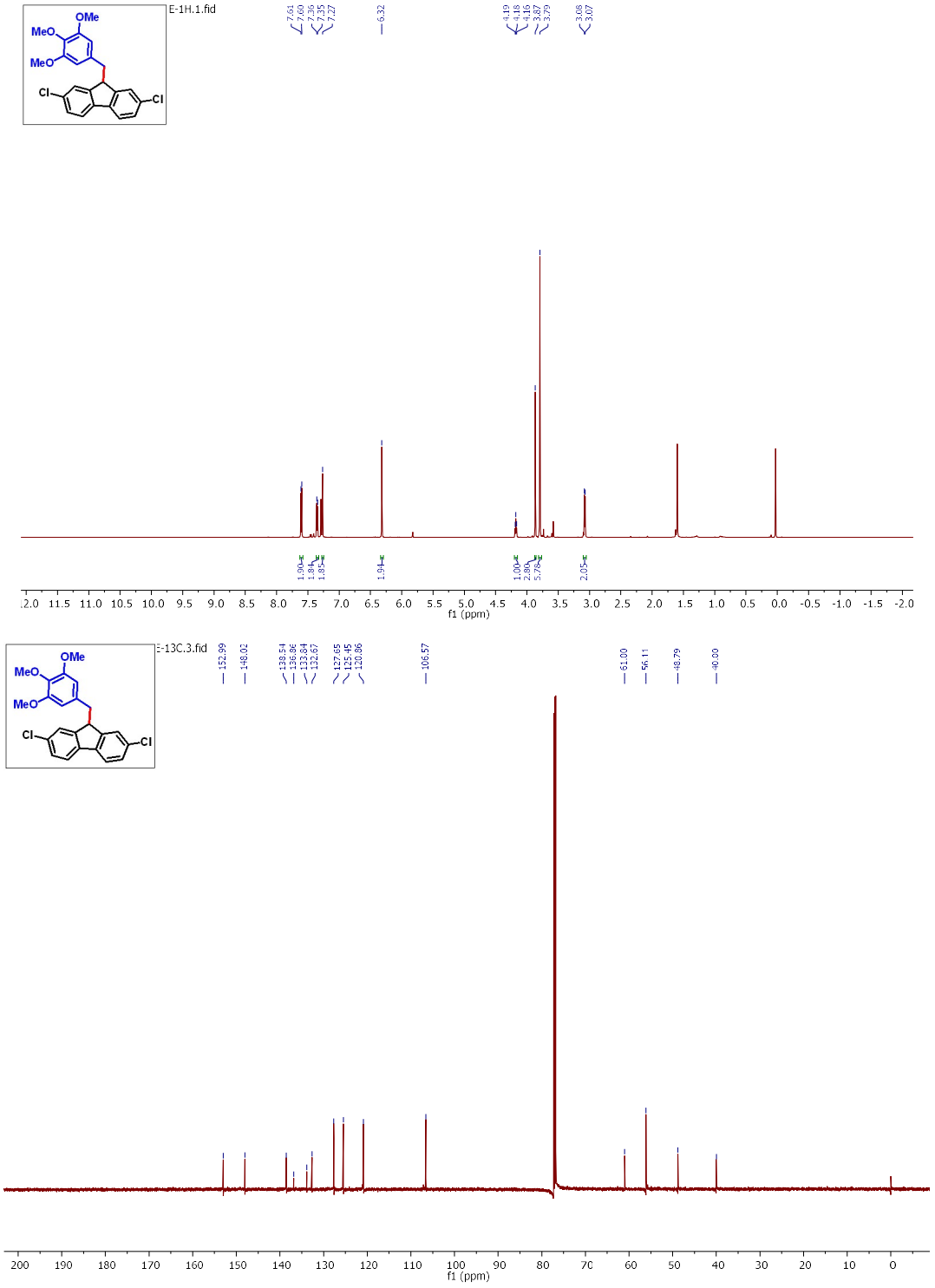


Fig S54: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 2,7-dichloro-9-(3,4,5-trimethoxybenzyl)-9H-fluorene (**3as**) in $CDCl_3$.

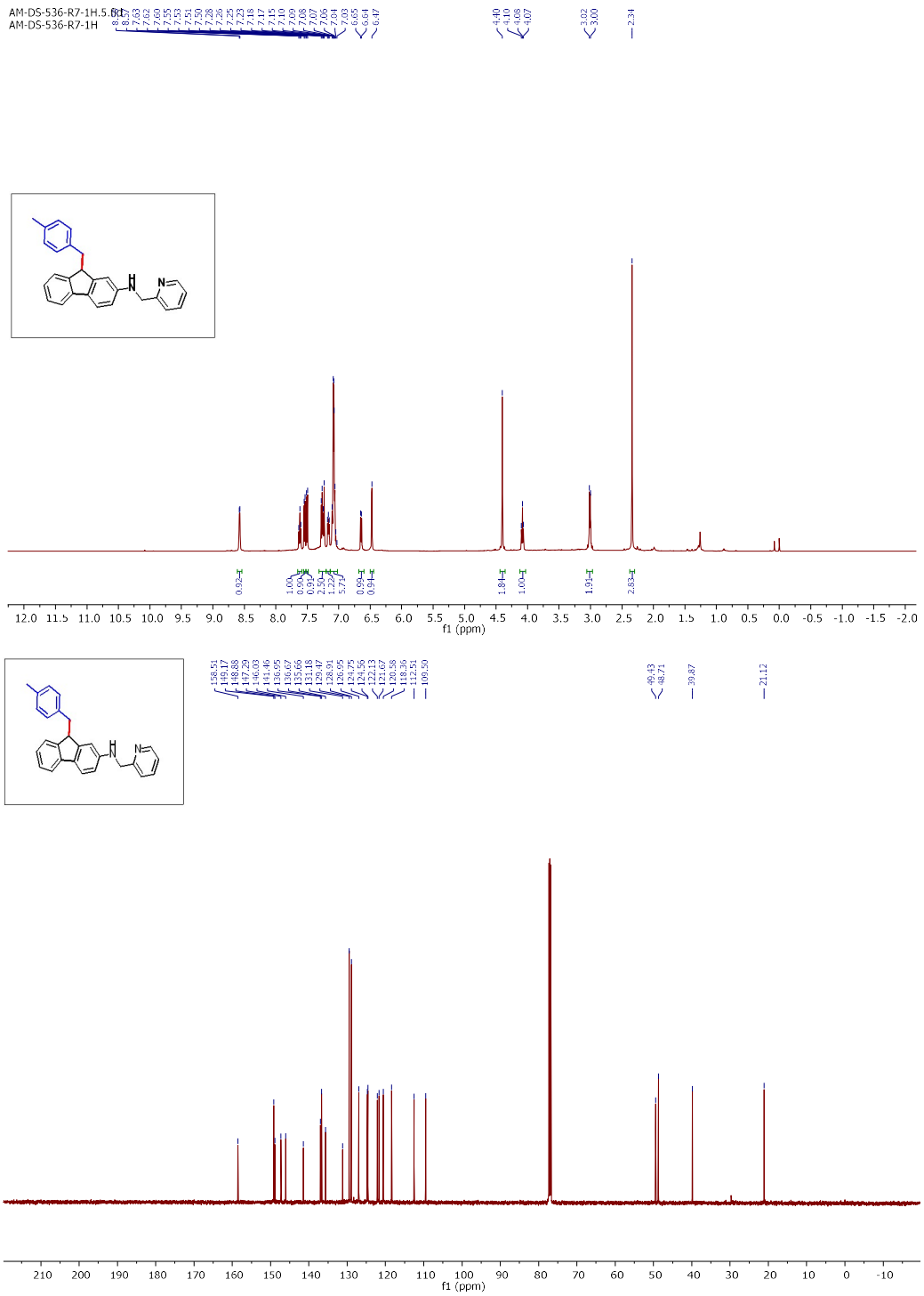


Fig S55: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of (R)-9-benzyl-N-(pyridin-2-ylmethyl)-9H-fluoren-2-amine (**3at**) in $CDCl_3$.

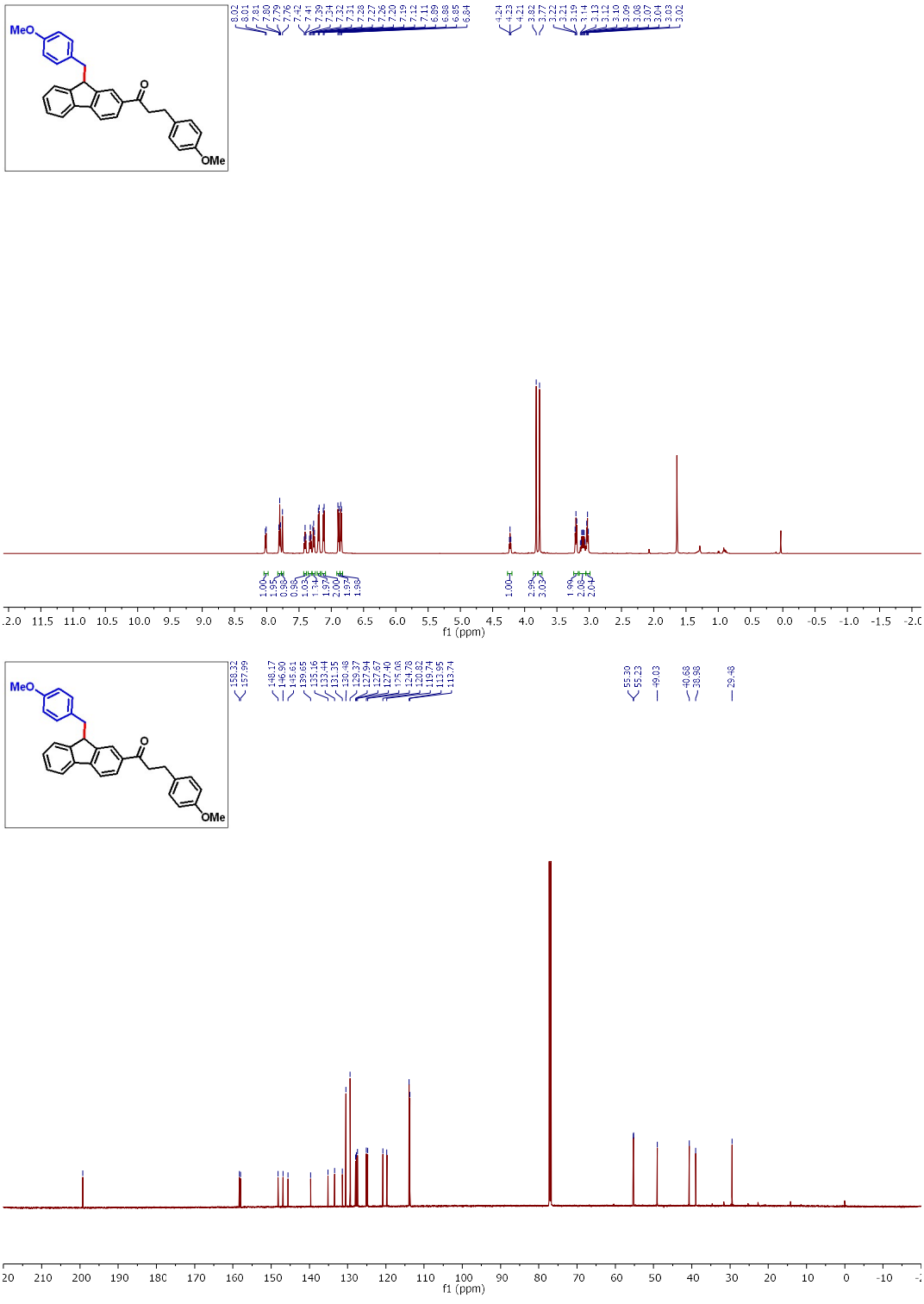


Fig S56: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of (R)-1-(9-(4-methoxybenzyl)-9H-fluoren-2-yl)-3-(4-methoxyphenyl)propan-1-one (**3au**) in $CDCl_3$.

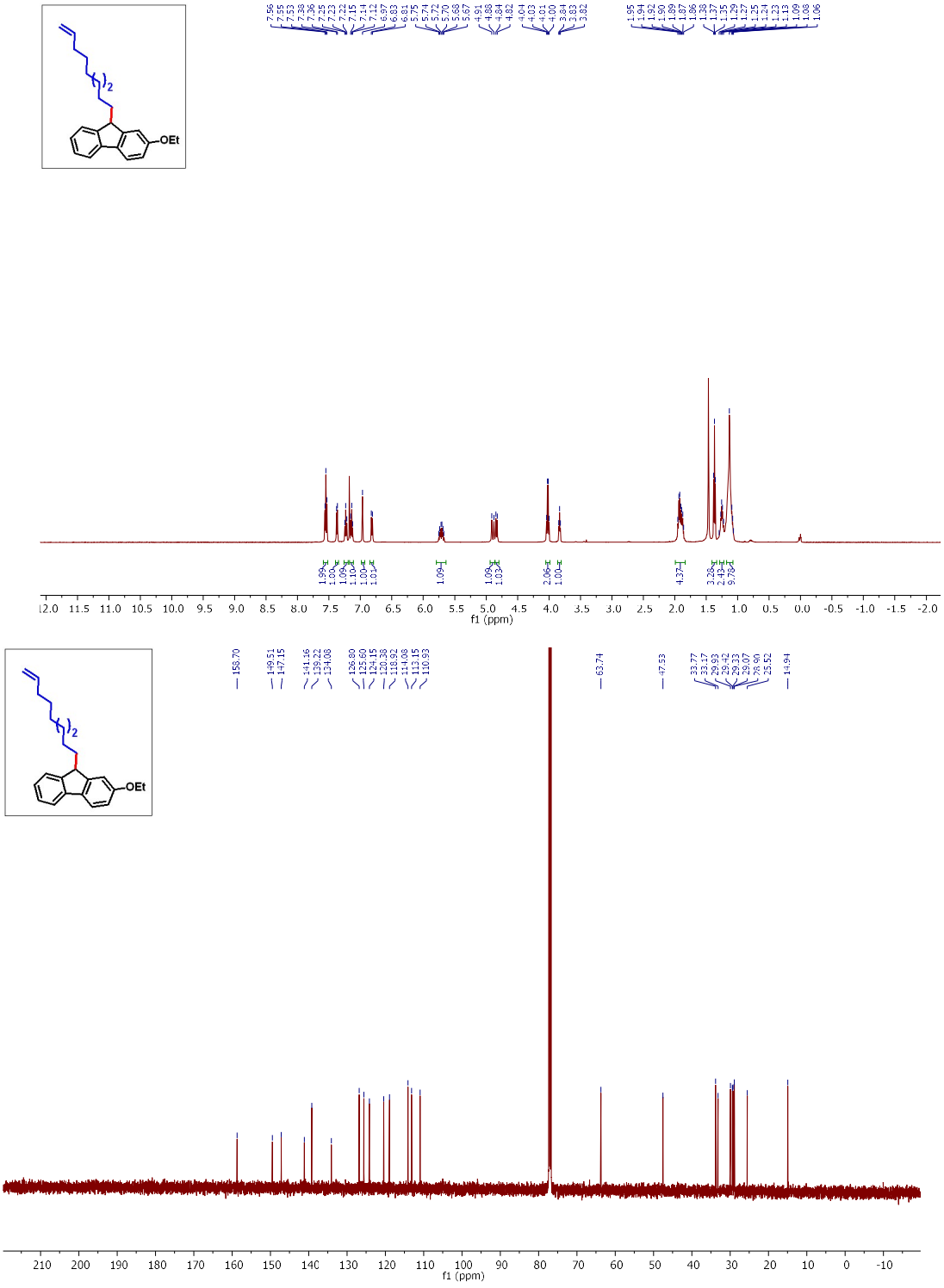


Fig S57: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of (R)-2-ethoxy-9-(non-8-en-1-yl)-9H-fluorene (**3av**) in $CDCl_3$.

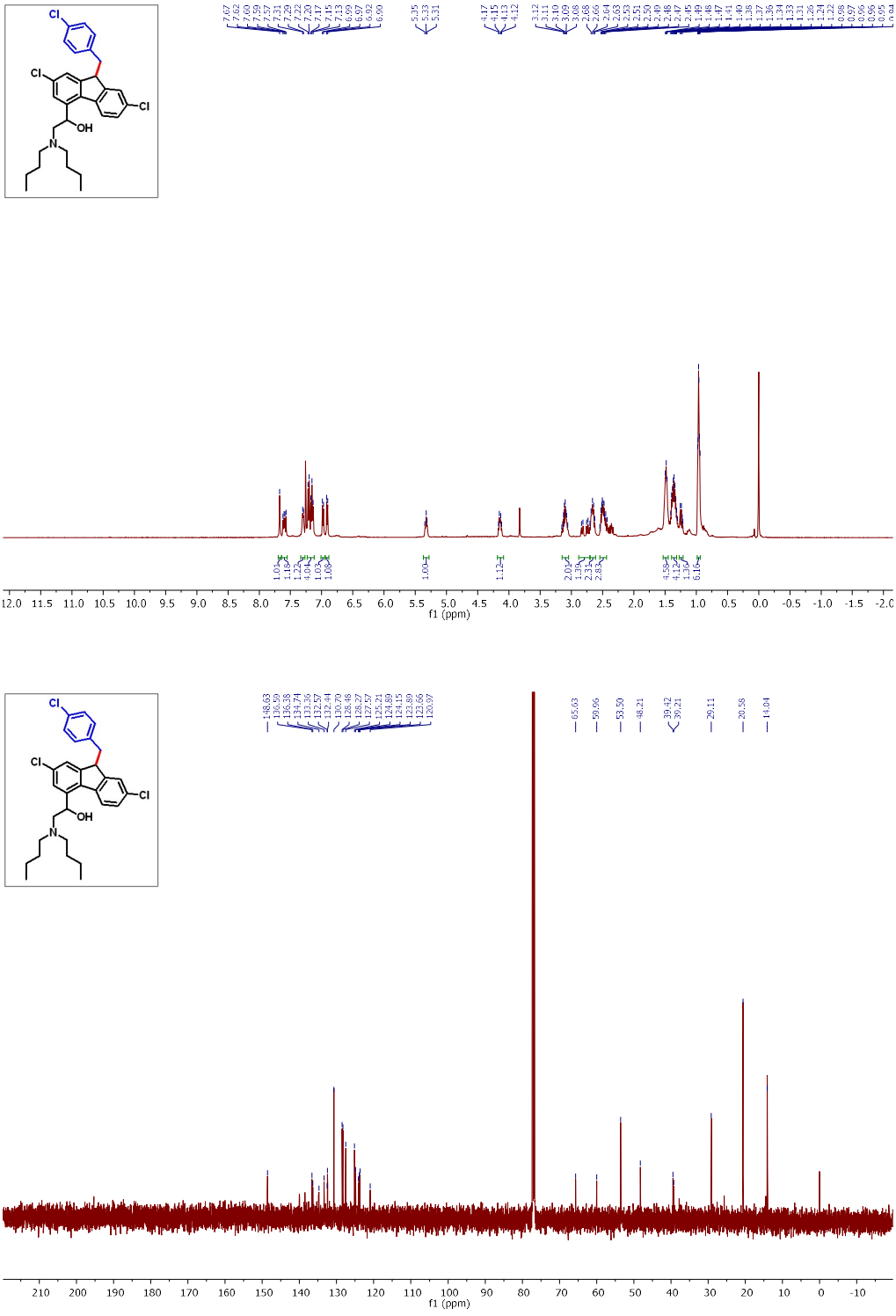


Fig S58: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 2-(dibutylamino)-1-((S)-2,7-dichloro-9-(4-chlorobenzyl)-9H-fluoren-4-yl)ethan-1-ol (**3aw**) in $CDCl_3$.

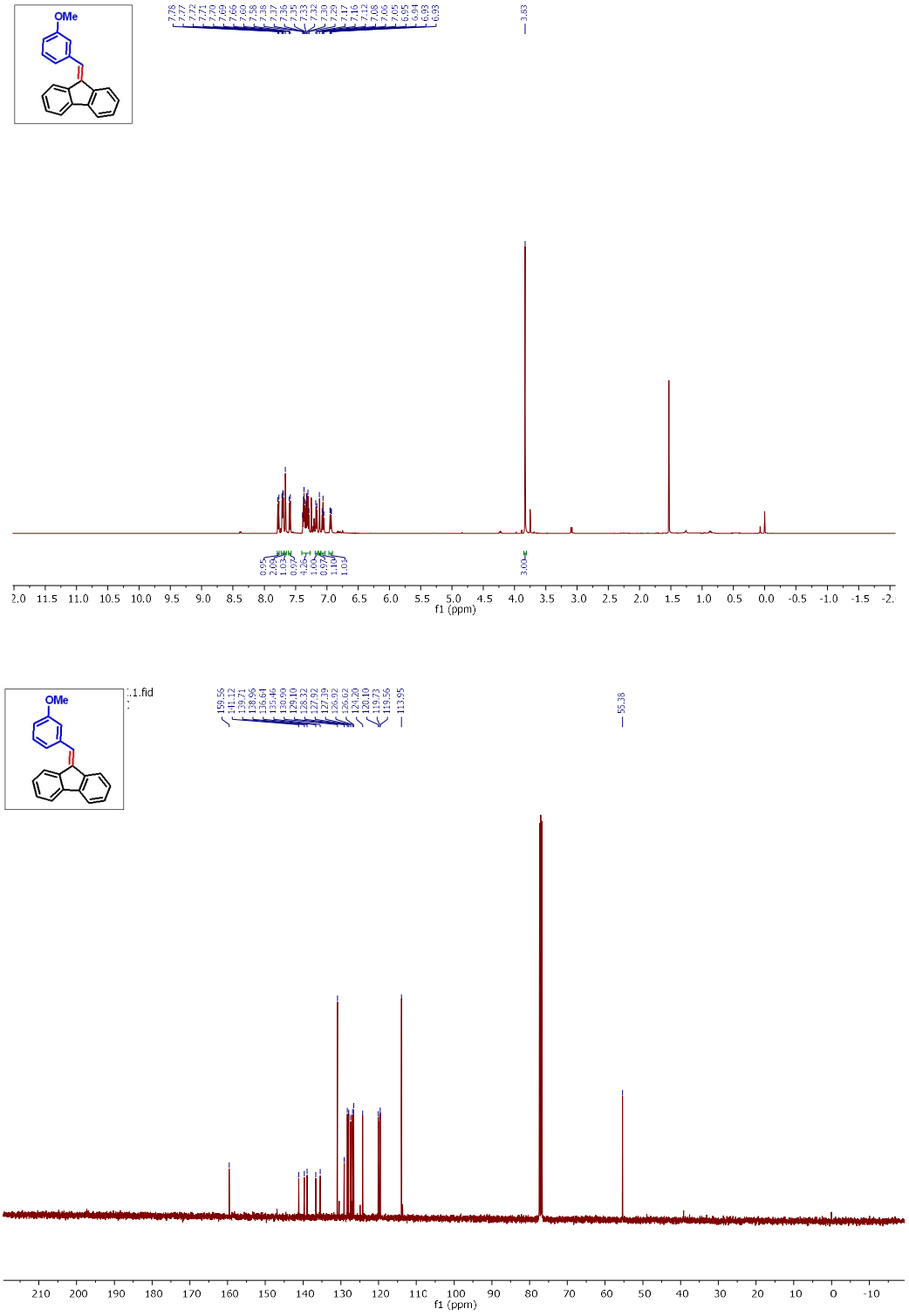


Fig S59: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 9-(3-methoxybenzylidene)-9H-fluorene (**4a**) in $CDCl_3$.

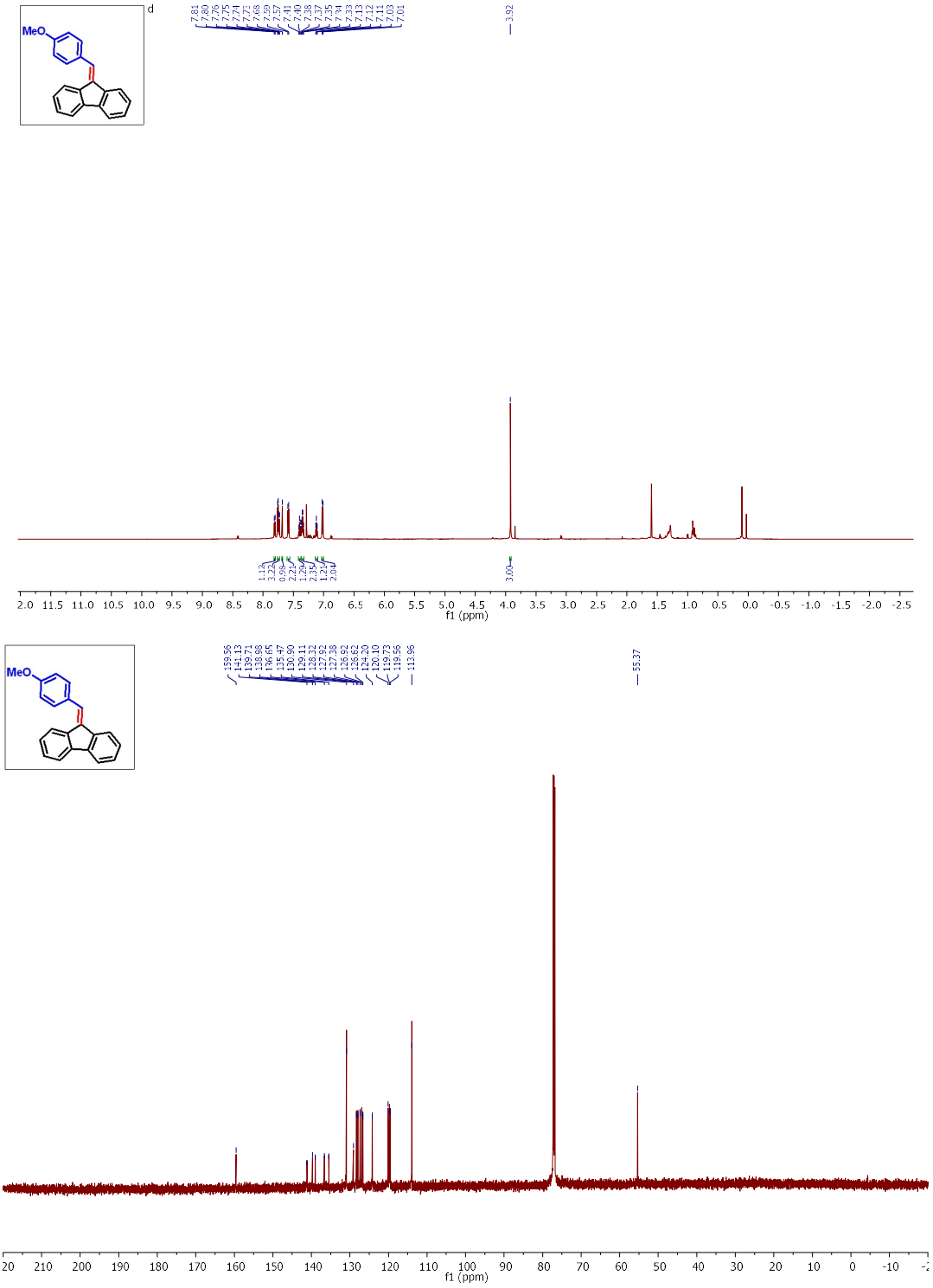


Fig S60: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(4-methoxybenzylidene)-9H-fluorene (**4b**) in $CDCl_3$.

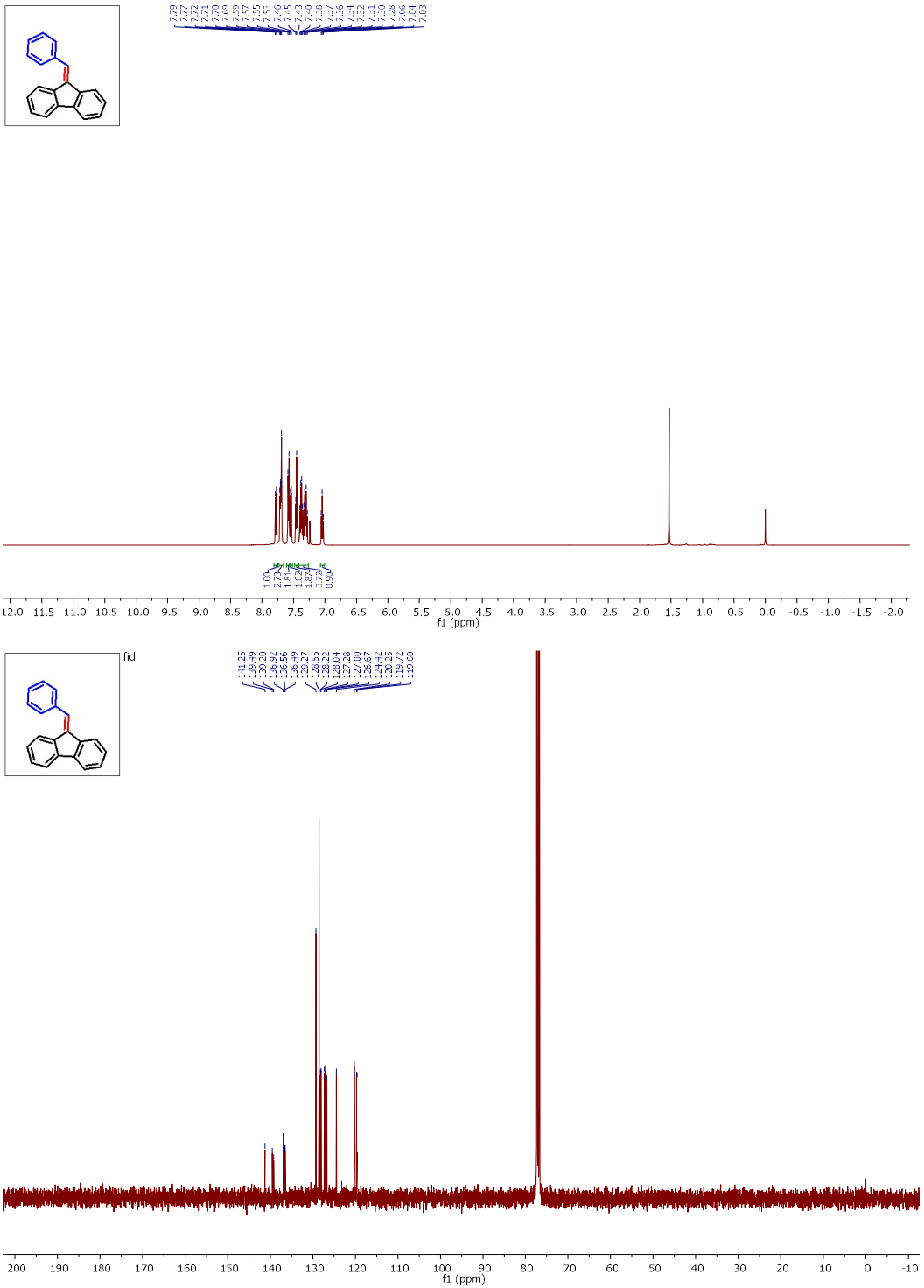


Fig S61: ^{1}H (500 MHz) and ^{13}C (100 MHz) NMR of 9-benzylidene-9H-fluorene (**4c**) in $CDCl_3$.

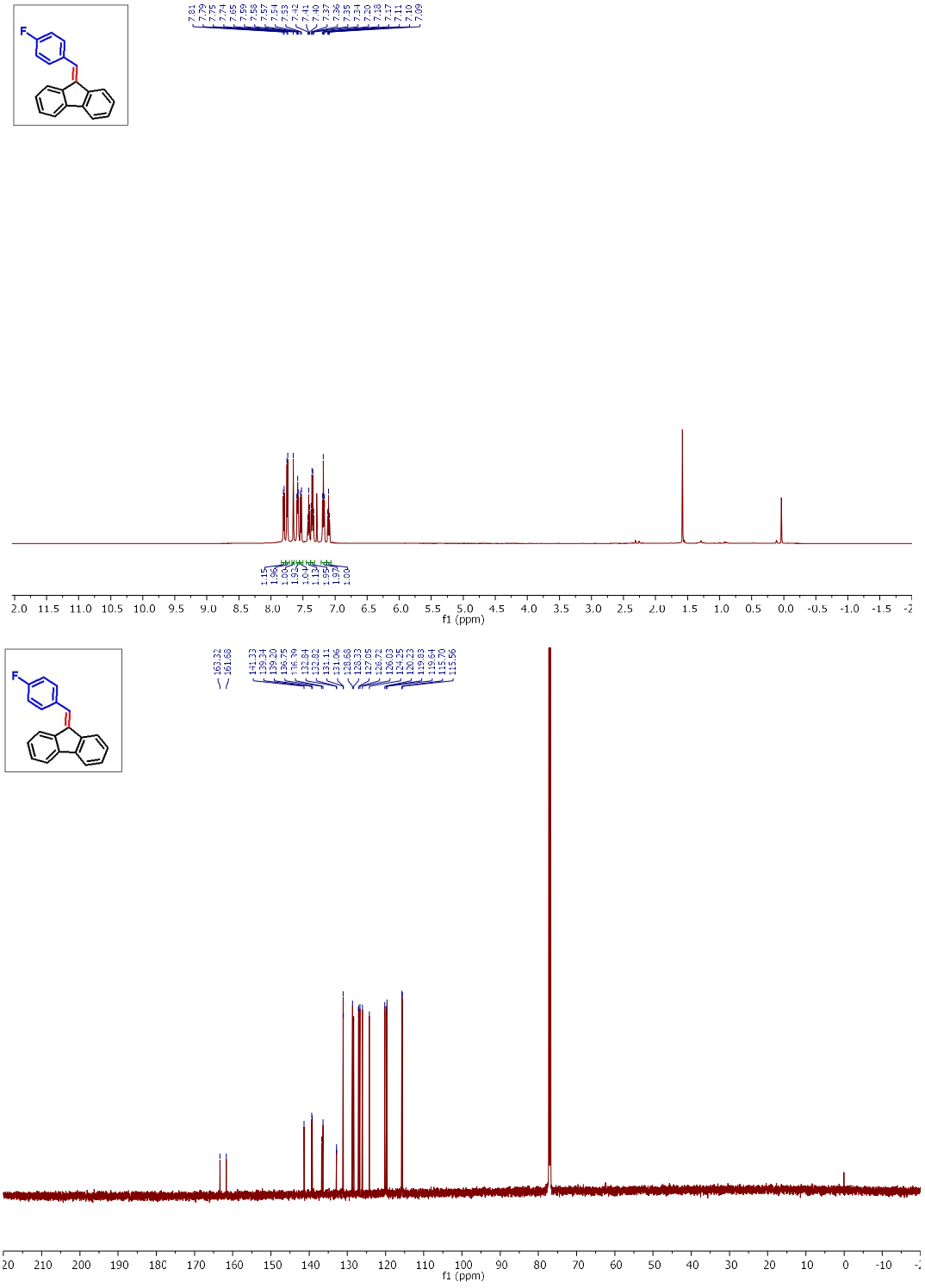


Fig S62: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(4-fluorobenzylidene)-9H-fluorene (**4d**) in $CDCl_3$.

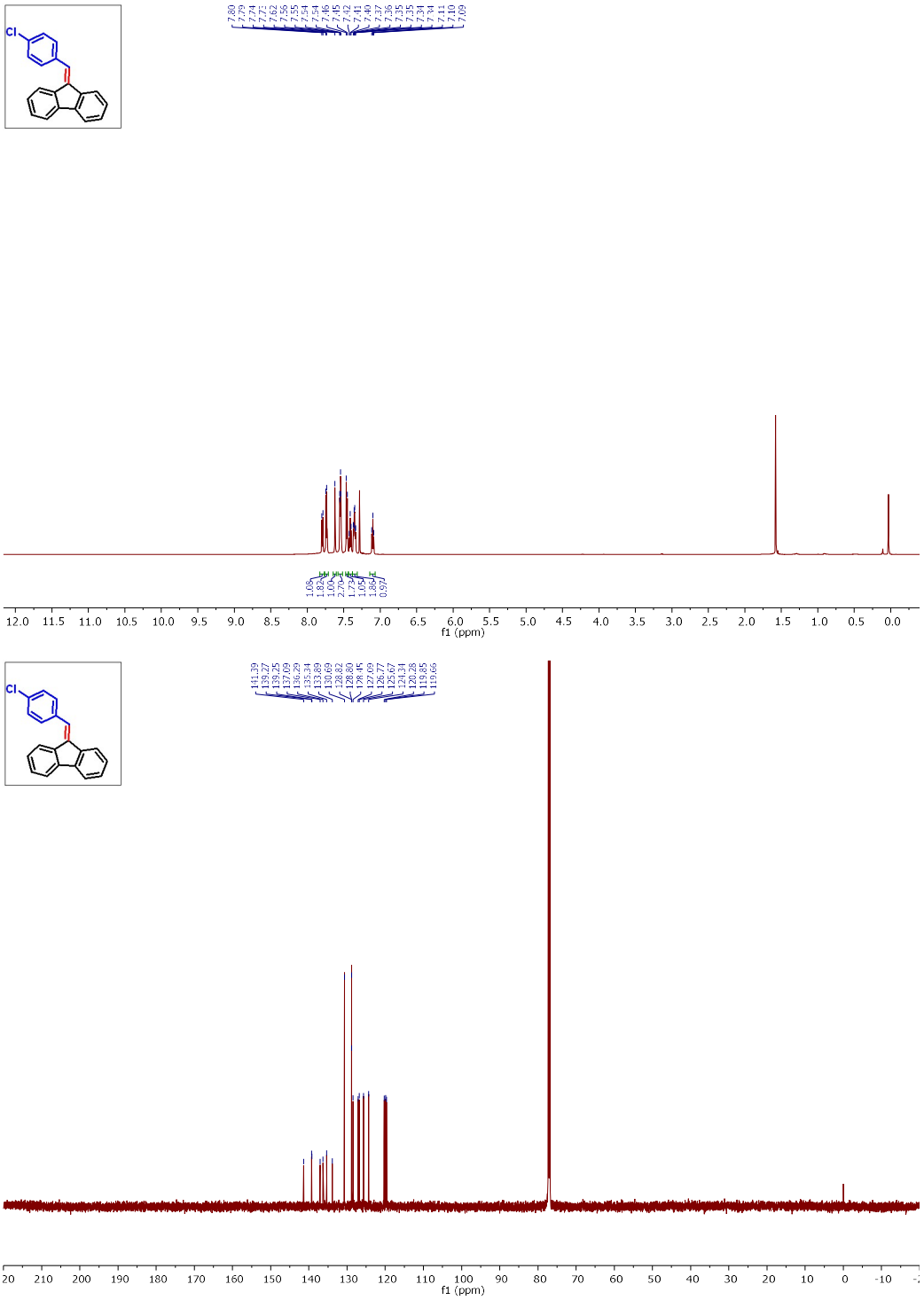


Fig S63: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(4-chlorobenzylidene)-9H-fluorene (**4e**) in $CDCl_3$.

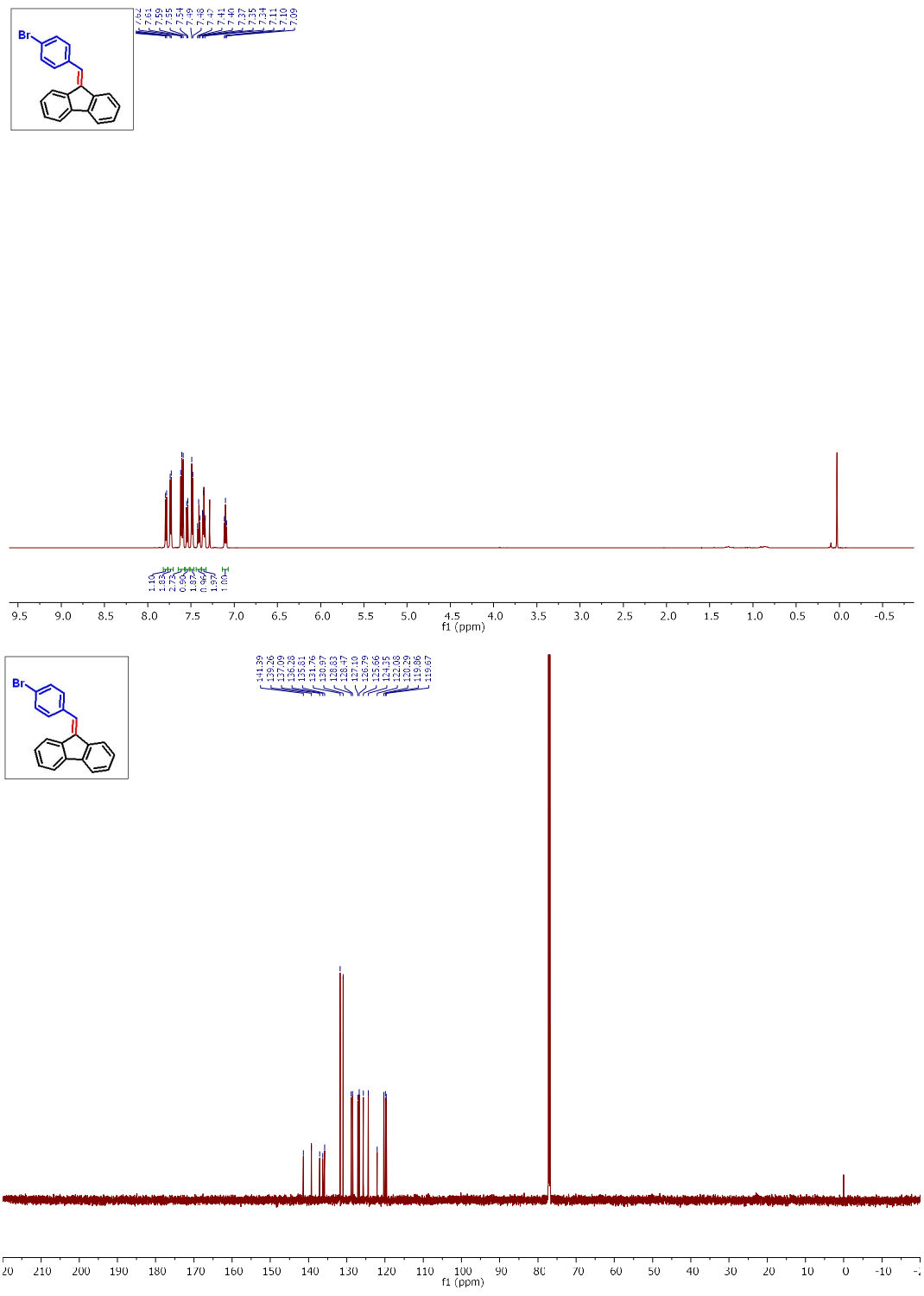


Fig S64: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(4-bromobenzylidene)-9H-fluorene (**4f**) in $CDCl_3$.

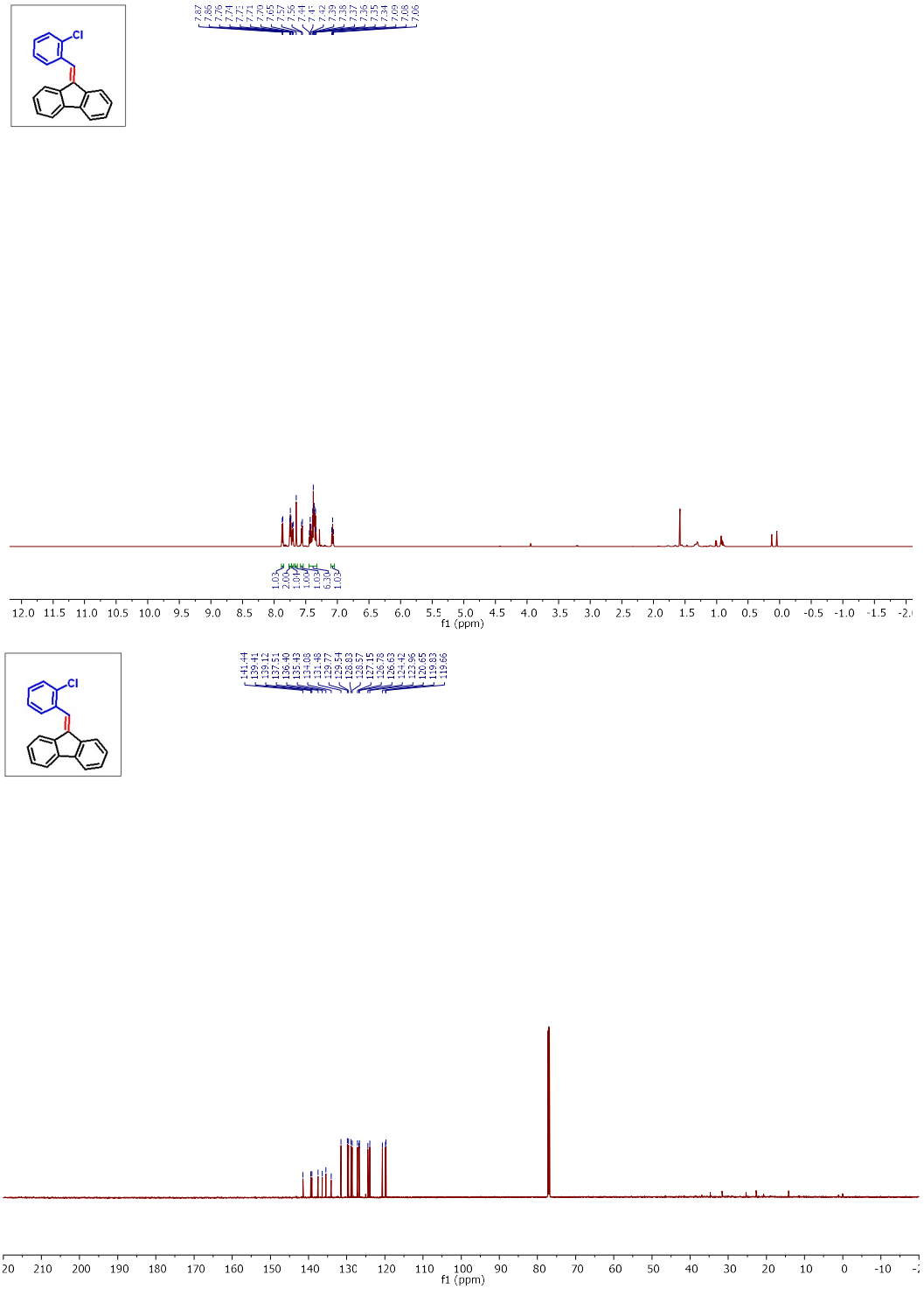


Fig S65: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(2-chlorobenzylidene)-9H-fluorene (**4g**) in $CDCl_3$.

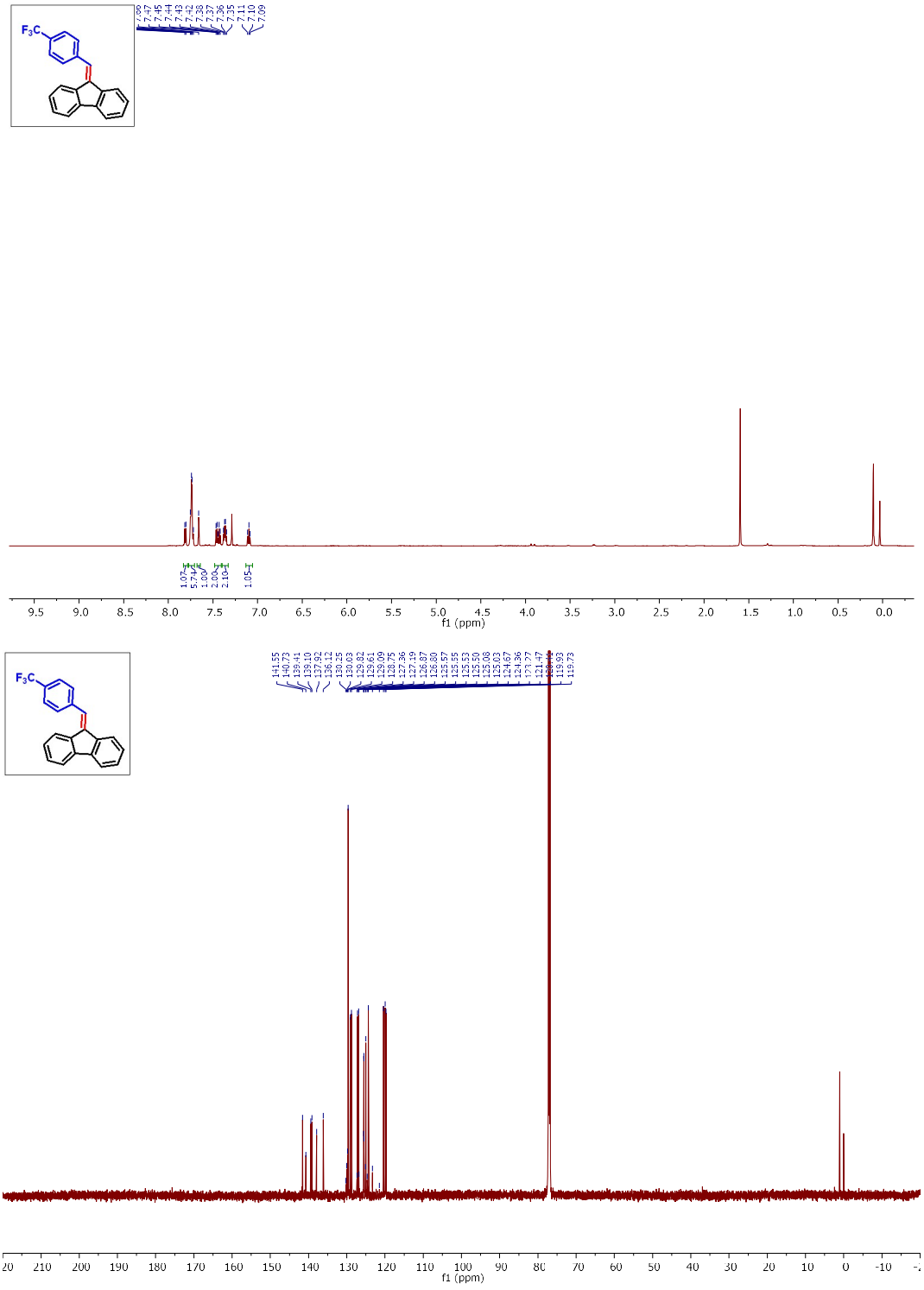


Fig S66: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(4-(trifluoromethyl)benzylidene)-9H-fluorene (**4h**) in $CDCl_3$.

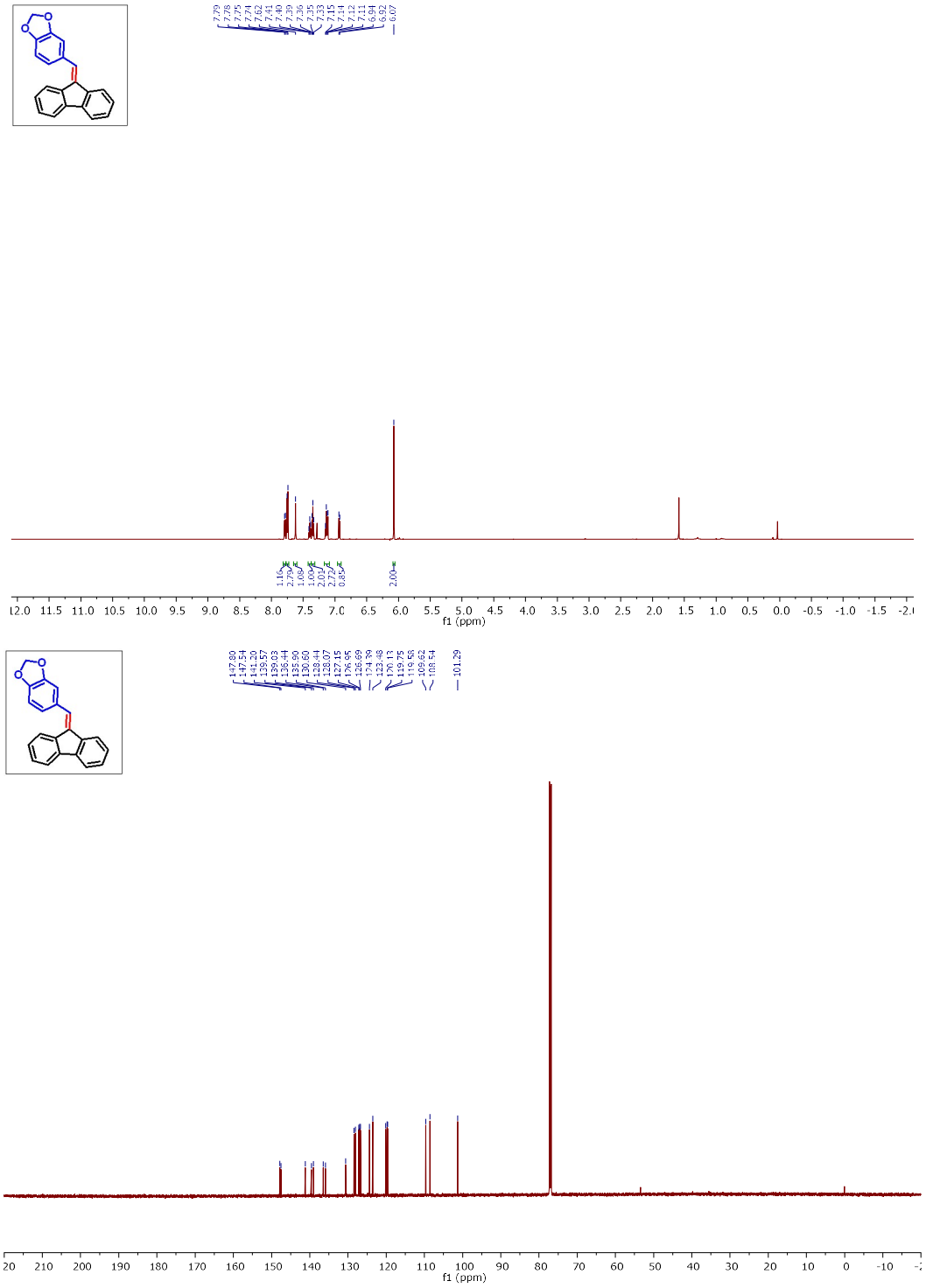


Fig S67: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 5-((9H-fluoren-9 ylidene)methyl)benzo[d][1,3]dioxole (**4i**) in $CDCl_3$.

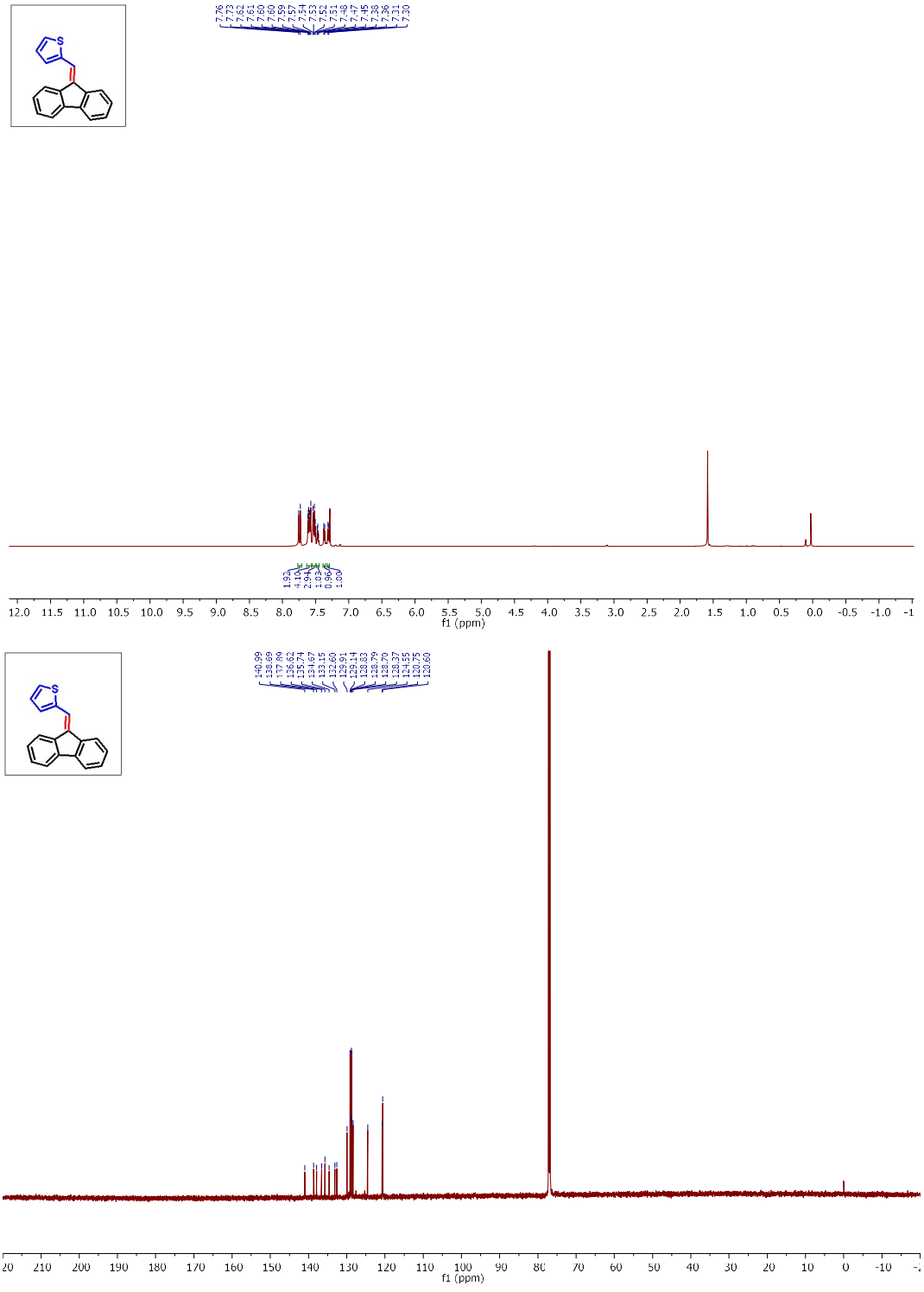


Fig S68: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 2-((9H-fluoren-9-ylidene)methyl)thiophene (**4j**) in $CDCl_3$.

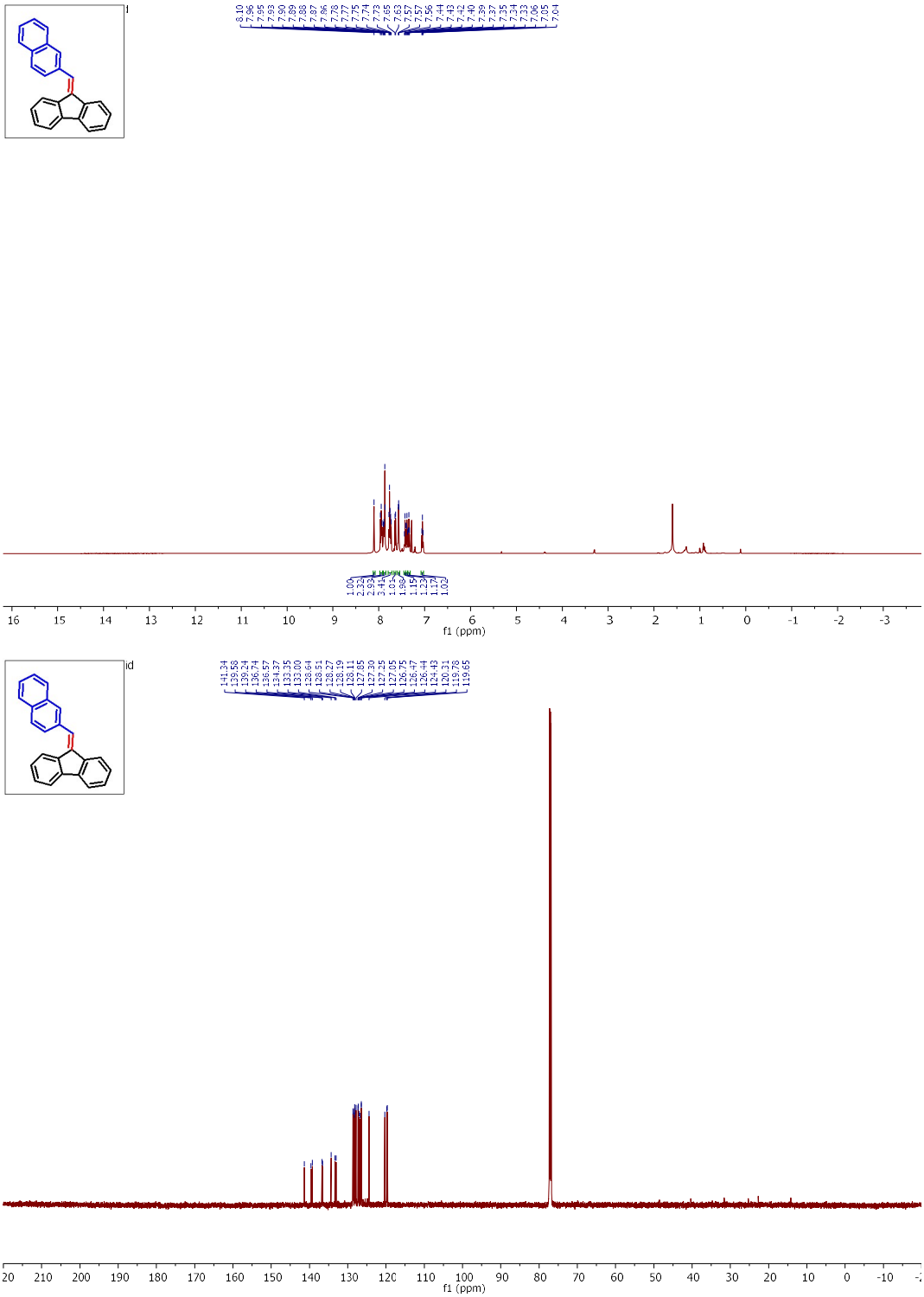


Fig S69: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-(naphthalen-2-ylmethylene)-9H-fluorene (**4k**) in $CDCl_3$.

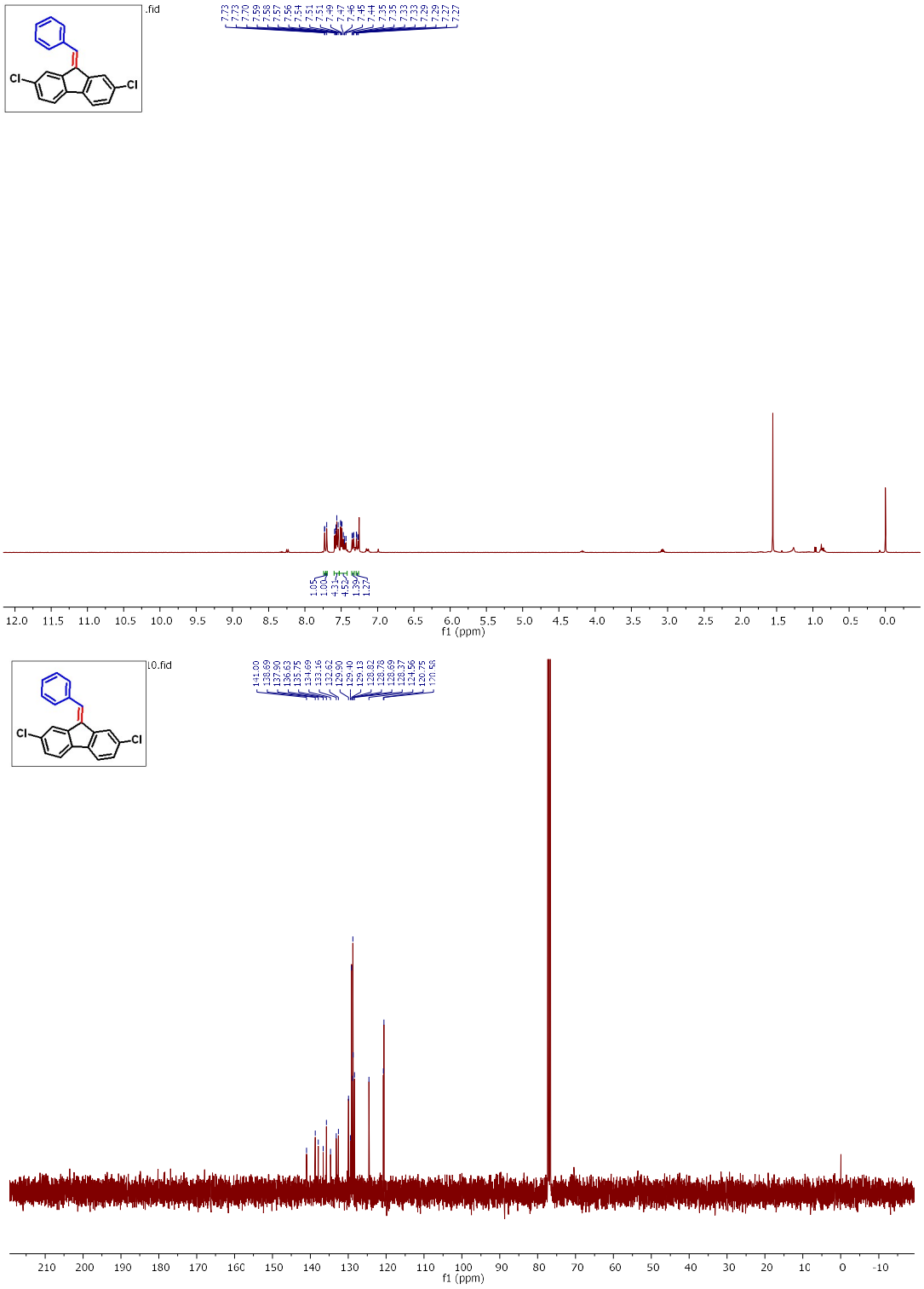


Fig S70: ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR of 9-benzylidene-2,7-dichloro-9H-fluorene (**4l**) in $CDCl_3$.

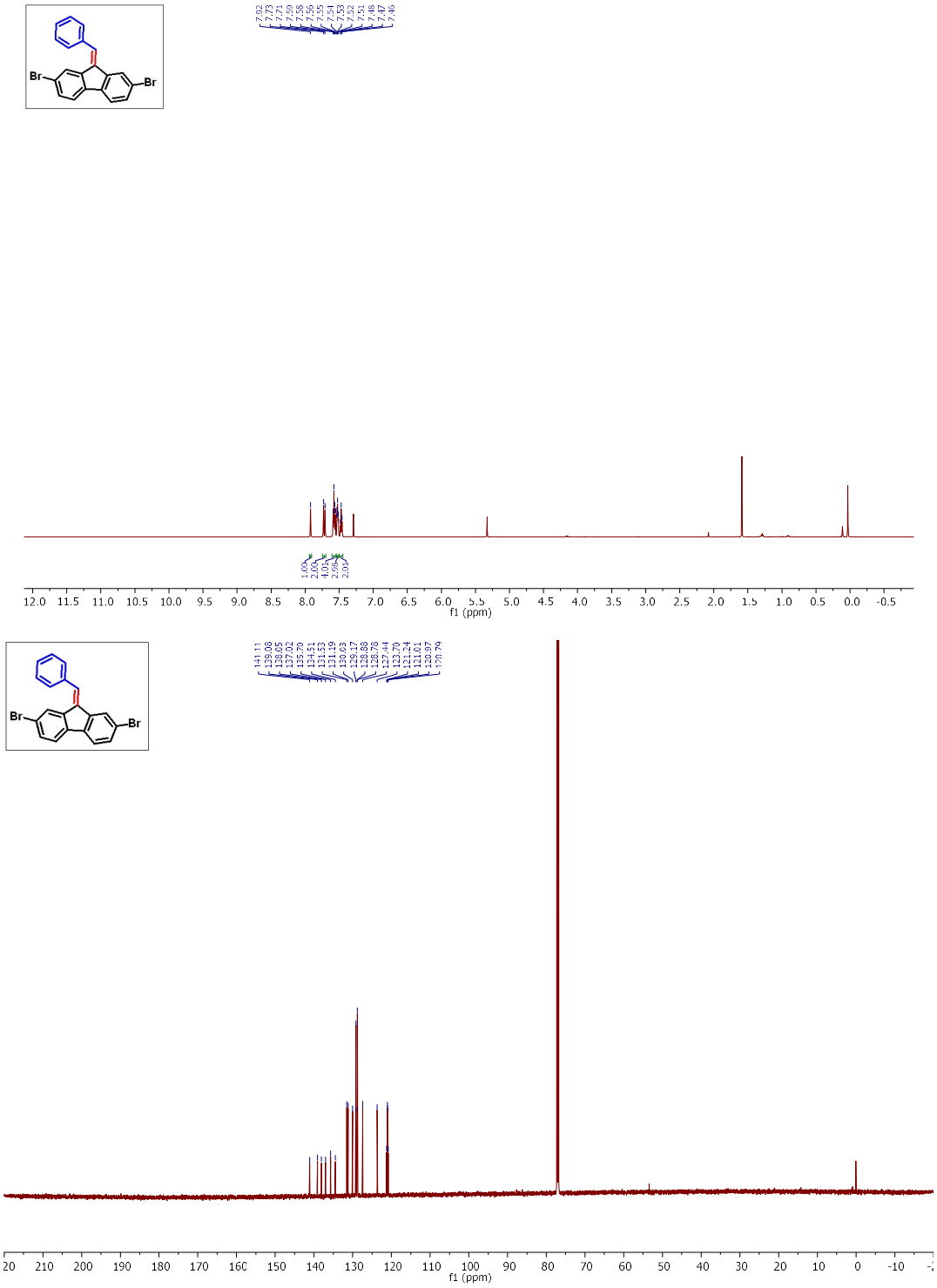


Fig S71: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 9-benzylidene-2,7-dibromo-9H-fluorene (**4m**) in $CDCl_3$.

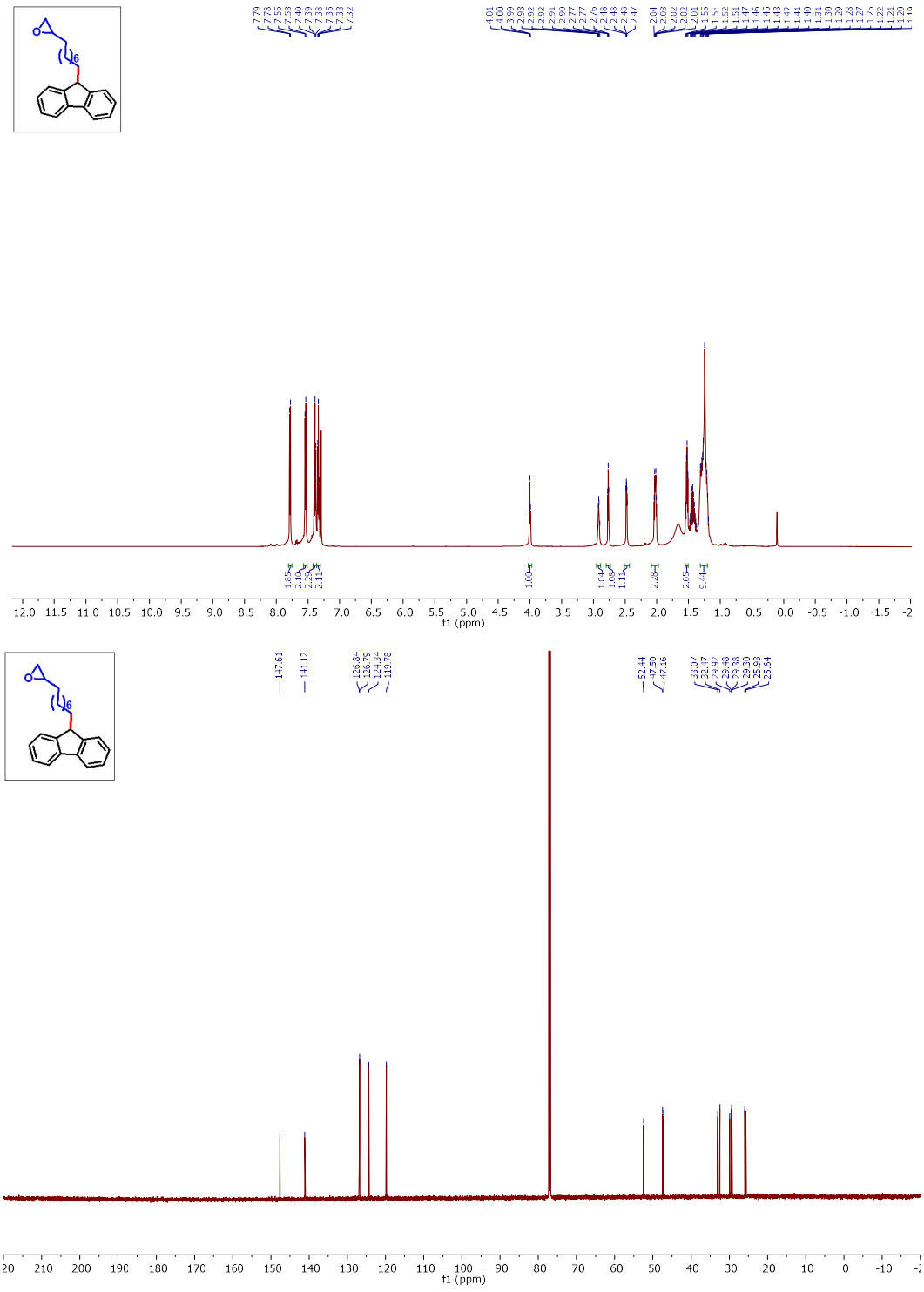


Fig S72: ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR of 2-(8-(9H-fluoren-9-yl)octyl)oxirane (**6**) in $CDCl_3$.

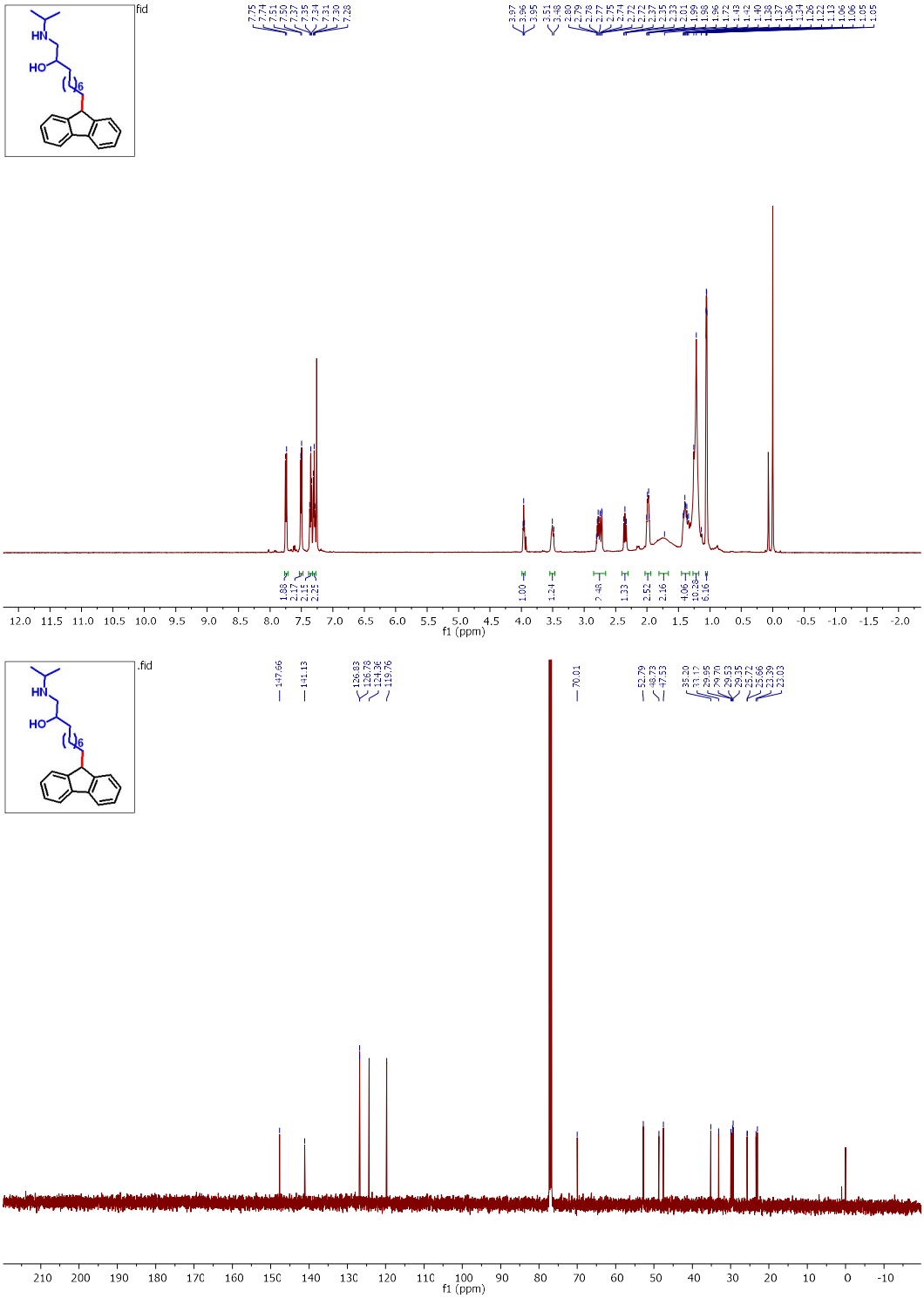


Fig S73: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 10-(9H-fluoren-9-yl)-1-(isopropylamino)decan-2-ol (**7**) in $CDCl_3$.

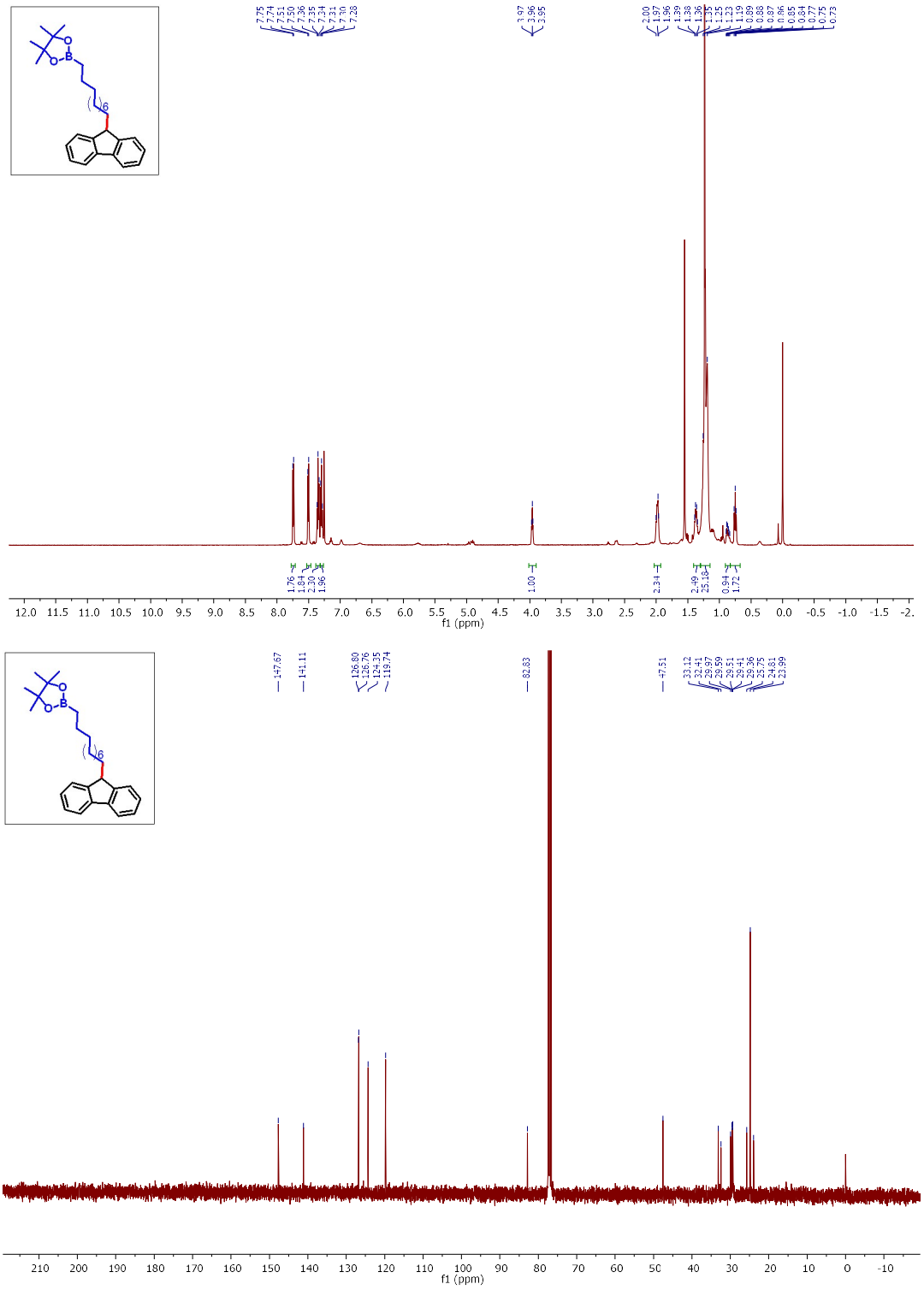


Fig S74: ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR of 2-(10-(9H-fluoren-9-yl)decyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8**) in $CDCl_3$.

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