Electronic Supporting Information

Ligand-assisted nickel catalysis enabling sp^3 C−H alkylation of 9*H*-fluorene with alcohols

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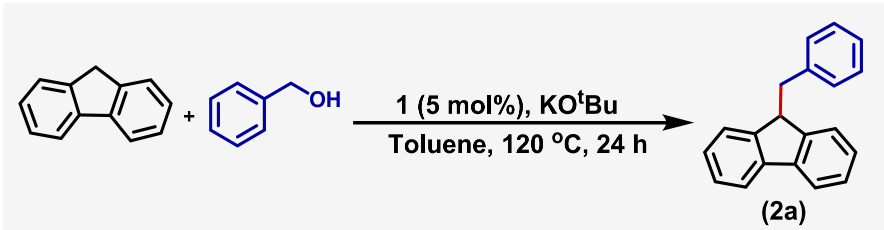
1. General information

Reagent information: All starting materials utilized in this study were procured from commercial suppliers. Potassium *tert*-butoxide, potassium hydroxide, potassium carbonate, sodium hydroxide were purchased from Avra Synthesis Pvt. Ltd., India. Primary and secondary alcohols were purchased from TCI (India) and BLD Pharma. Fluorene was purchased from BLD Pharma. All these chemicals were used without further purification. Glassware was dried overnight at 160 °C. Solvents such as acetonitrile, ethanol, and dichloromethane were used as received (Finar Chemicals). Toluene was dried by heating over sodium with benzophenone as an indicator. For thin layer chromatography (TLC), aluminum foil coated with silica and fluorescent indicator @254 nm (from Merck) was used. Column chromatography was performed using SD Fine silica gel (100-200 mesh) using a gradient of hexane and diethyl ether as mobile phase.

Analytical information: All synthesized products were isolated and characterized by ^{1}H and ^{13}C NMR spectroscopies and High-Resolution Mass spectrometry. IR spectra were recorded on a Perkin–Elmer FTIR spectrometer as a KBr pellet. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Biospin Advance III FT-NMR spectrometer. NMR shifts have been reported as delta (δ) units in parts per million (ppm) and coupling constants (*J*) have been reported in hertz (Hz). Chemical shifts (δ) have been quoted to the nearest 0.01 ppm relative to the residual protons in $CDCl_3$ (δ 7.26 ppm). Carbon chemical shifts have been internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm). High-resolution mass spectra (HRMS) were recorded on a Waters QTOF mass spectrometer.

2. Reaction optimization

Table S1: Optimization table

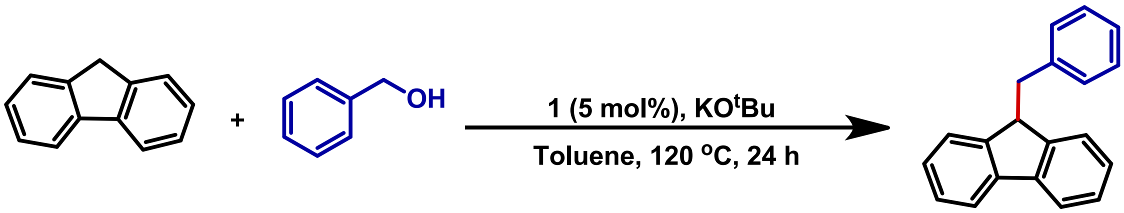


entry	catalyst Loading	base (mmol)	Yield % (2a)
1	$NiCl_2$	KO^{t}Bu	n.r
2	$NiBr_2$	KO^{t}Bu	n.r
3	1 (5 mol%)	KO^{t}Bu (0.25)	28
4	1 (5 mol%)	KO^{t}Bu (0.5)	41
5	1 (2.5 mol%)	KO^{t}Bu (0.75)	38
6	1 (5 mol%)	KOH	n.r
7	1 (5 mol%)	K_2CO_3	n.r
8	1 (5 mol%)	NaOH	n.r
10	1 (5 mol%)	KO^{t}Bu (0.75)	91
11[a]	1 (5 mol%)	KO^{t}Bu (0.75)	62
12	-	KO^{t}Bu (0.5)	14
13	1 (5 mol%)	-	n.r

Reaction conditions: 1 (x mol %, with respect to fluorene), fluorene (1 mmol), alcohol (2 mmol), KO^{t}Bu (x mmol), toluene (2 mL), 120 °C, 24 h (isolated yield), [a]1:1 ratio of fluorene and alcohol was taken.

3. Mechanistic studies

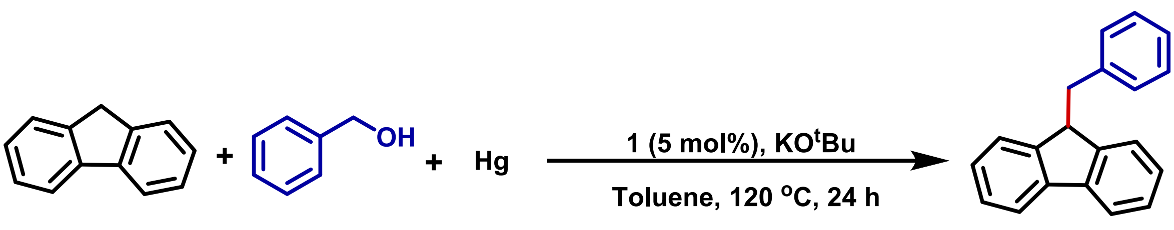
3a. Synthetic application: gram-scale synthesis



(2a, 87%)

In a typical reaction, a 30 mL pressure tube was charged with **1**[1] (5 mol%), KO^{t}Bu (505 mg, 4.5 mmol), benzyl alcohol (1.3 g, 12 mmol), fluorene (1 g, 6.01 mmol), dissolved in 15 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 120 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane as an eluent to afford pure product (1.351 g, 87% yield).

3b. Mercury drop test

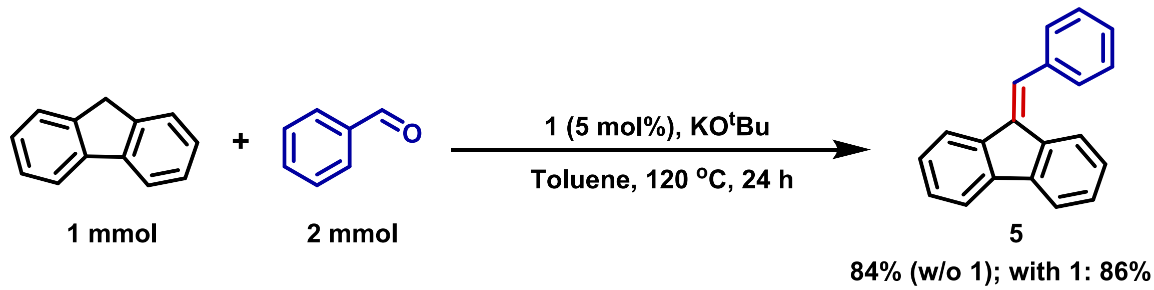


2a, 87%

In order to establish the homogeneity of **1** in C-alkylation of fluorene reaction, we carried out mercury drop experiment.

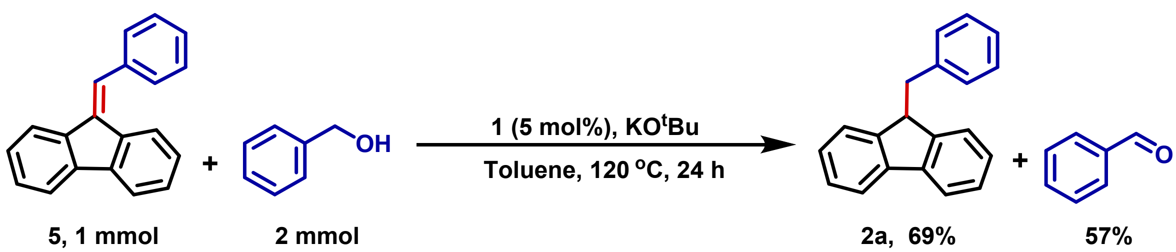
In a typical reaction, a 15 mL pressure tube was charged with **1** (5 mol%), KO^{t}Bu (0.75 mmol), benzyl alcohol (2 mmol), fluorene (1 mmol), dissolved in 2 mL toluene. To this reaction mixture, a drop of mercury was added. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 120 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The isolation of the product (87% yield) after 24 h confirmed the homogeneous behaviour of the catalyst.

3c. Alkenylation of fluorene

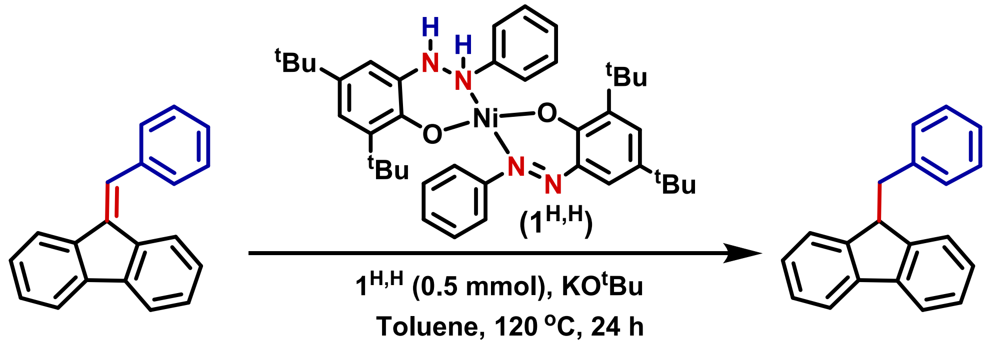


In a typical reaction, a 15 mL pressure tube was charged with KO^{t}Bu (0.75 mmol), benzaldehyde (2 mmol), fluorene (1 mmol), dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 120 ^{o}C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane as an eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies. Interestingly, product **5** was formed in the absence of **1**.

3d. Hydrogenation of 5



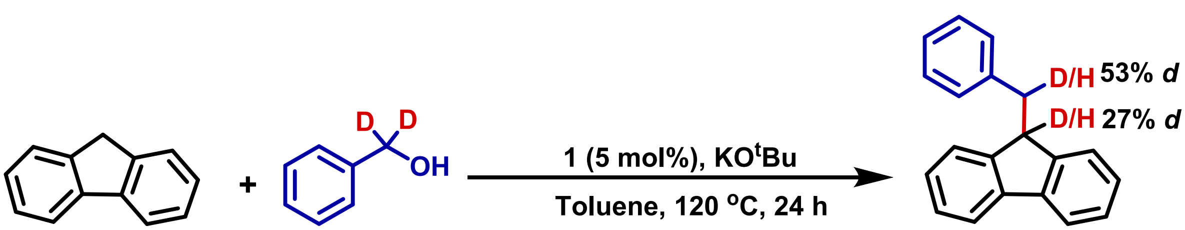
In a typical reaction, a 15 mL pressure tube was charged with **1** (5 mol%), KO^{t}Bu (0.75 mmol), benzyl alcohol (2 mmol), **5** (1 mmol), dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 120 ^{o}C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane as an eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies. The C-alkylated product formation was isolated in 69% yield in the presence of catalyst.



5, 1 mmol 2a, 68%

In a typical reaction, a 15 mL pressure tube was charged with **1**^{H,H} (0.5 mmol), KO^{t}Bu (0.75 mmol), **5** (0.5 mmol), dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 120 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane as an eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies. The hydrogenated product was isolated in 68% yield.

3e. Deuterium incorporation studies



1 mmol 2 mmol 88%

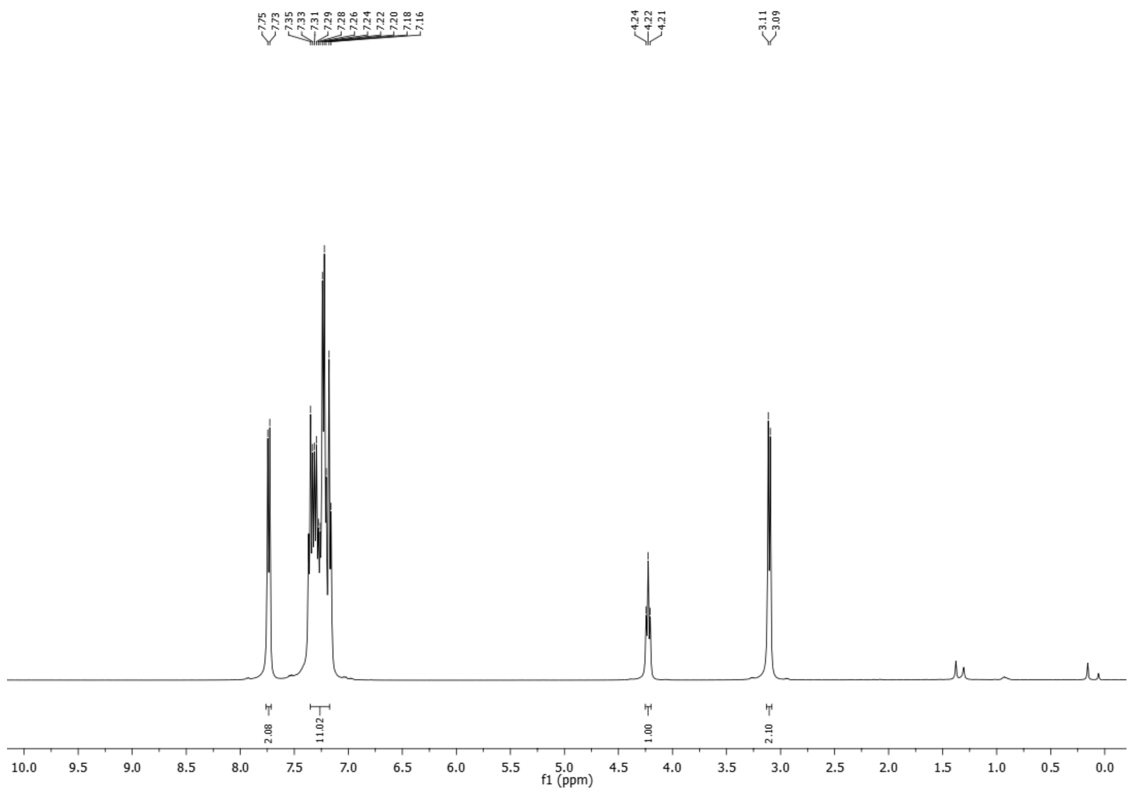


Figure S1. ^1H NMR spectrum (400 MHz) of 2a in $CDCl_3$.

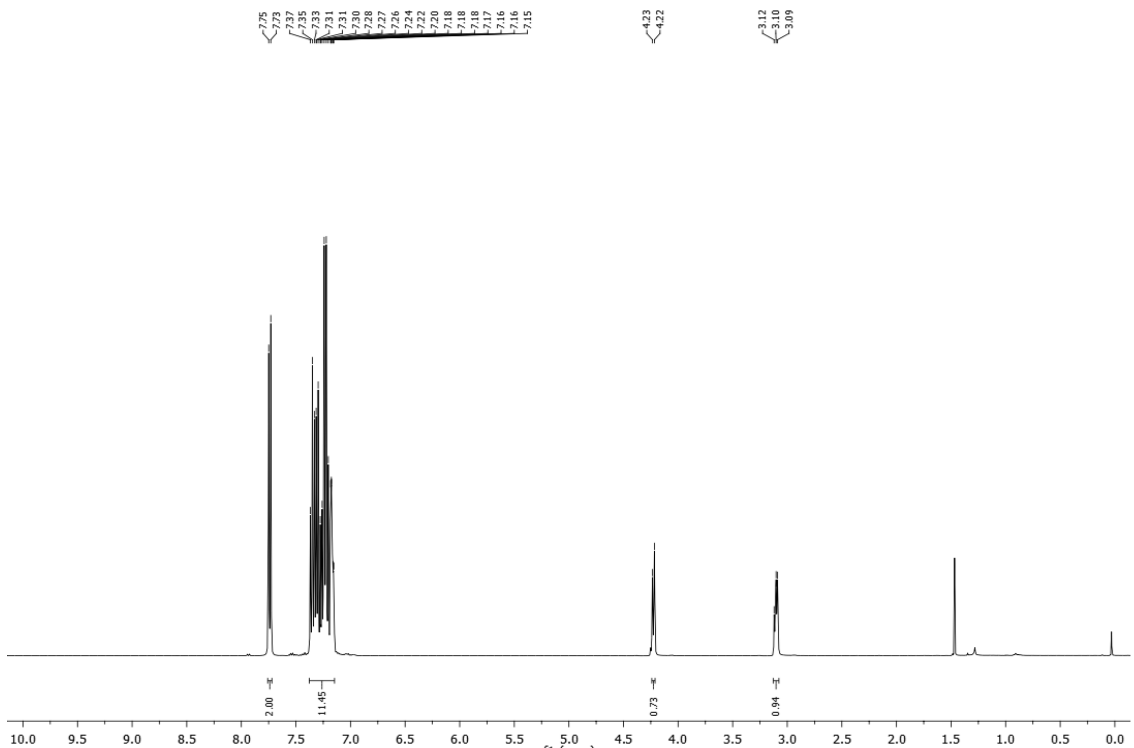
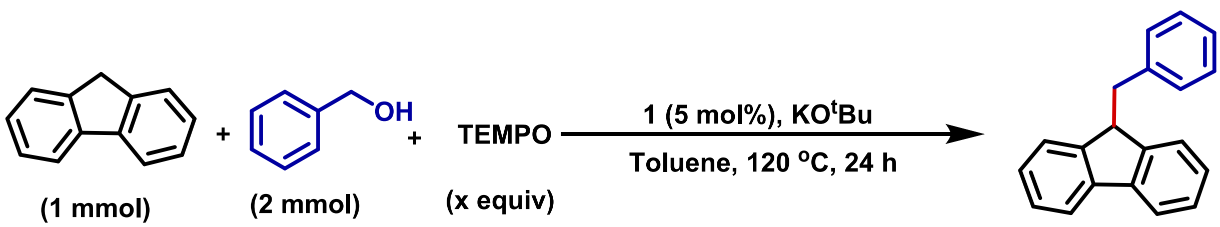


Figure S2. ^1H NMR spectrum (400 MHz) of deuterated 2a in $CDCl_3$.

Table S2: The conversion of D-labelled alcohol as monitored by ^{1}H NMR spectroscopy:

	2a	D-incorporation calculation	D-incorporation calculation
Signal δ (ppm)	7.75-7.73	4.23-4.22 (1H)	3.12-3.09 (2H)
Integral value	2.00	0.73	0.94
Calculated ratio		(1-0.73) *100 = 27%	[(2-0.94)/2]*100 = 53%

3f. Radical quenching experiment



In a typical reaction, a 15 mL pressure tube was charged with **1** (5 mol%), KO^{t}Bu (0.75 mmol), alcohols (2 mmol), substituted fluorene (1 mmol), and TEMPO (x equiv) dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 120 ^{o}C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The yield of the reaction decreased drastically with the addition of TEMPO, and complete quenching of reaction was observed when it was administered in 1 equivalent.

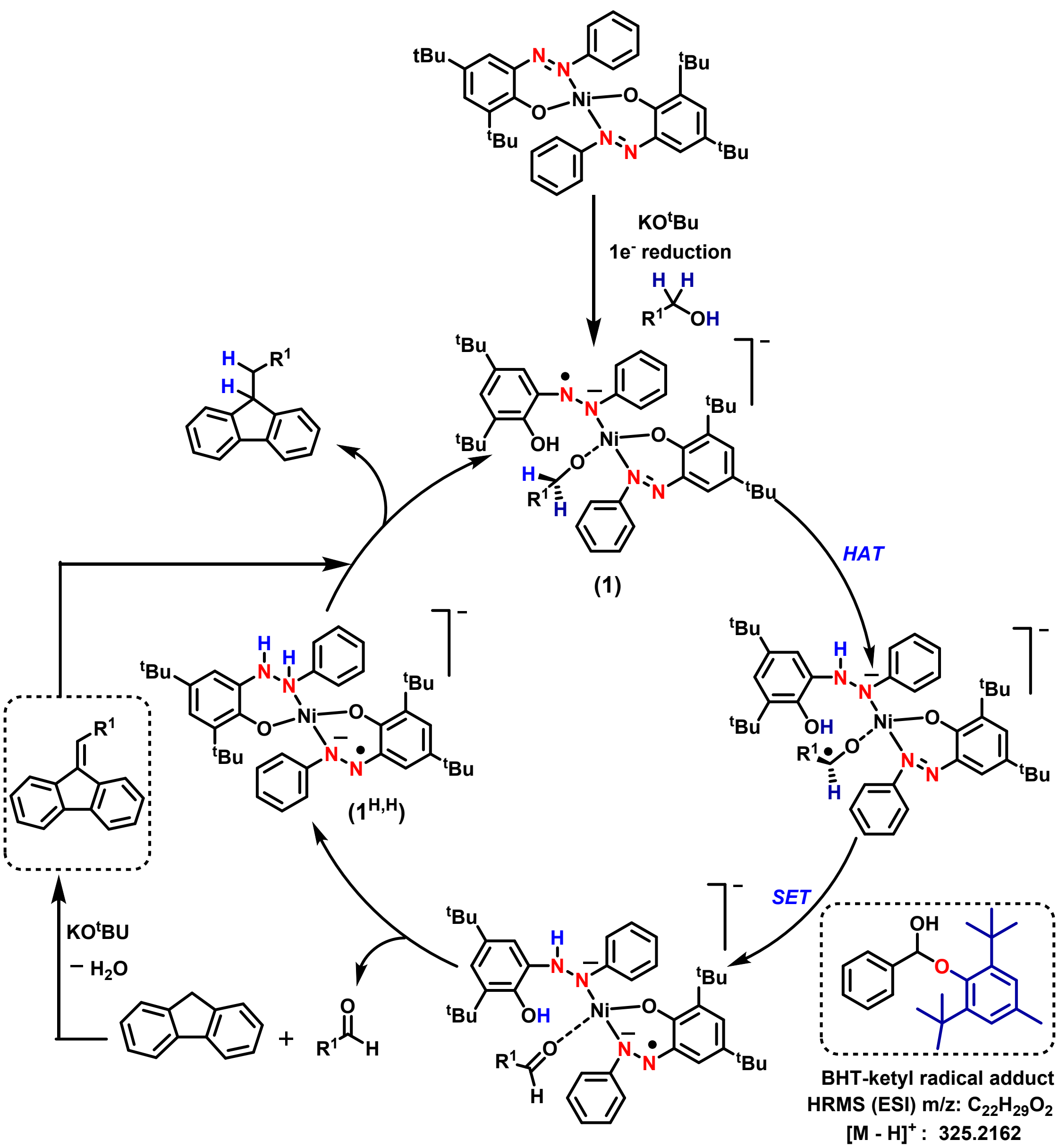
Table S3: Product yield upon varying equivalence of radical quencher

Entry	TEMPO equivalence	Yield (%)
1.	0.5 equiv.	14%
2.	1 equiv.	n.r.

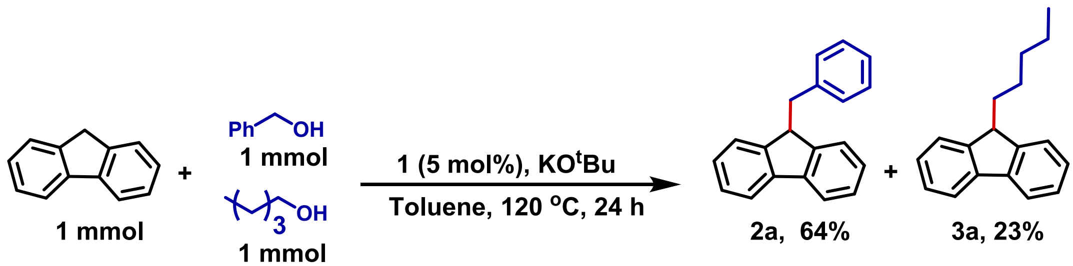
3g. BHT-ketyl adduct detection

In a typical reaction, a 15 mL pressure tube was charged with **1** (5 mol%), KO^{t}Bu (0.75 mmol), benzyl alcohol (2 mmol), substituted fluorene (1 mmol), and BHT (0.6 equiv) dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 120 °C for 24 h. The crude reaction mixture was filtered through a silica plug and sent for ESI-MS analysis. The ketyl-BHT adduct was identified by mass spectrometry. HRMS for $[M-H]^+$ $C_{22}H_{29}O_2$, calcd. 325.2168, observed 325.2162.

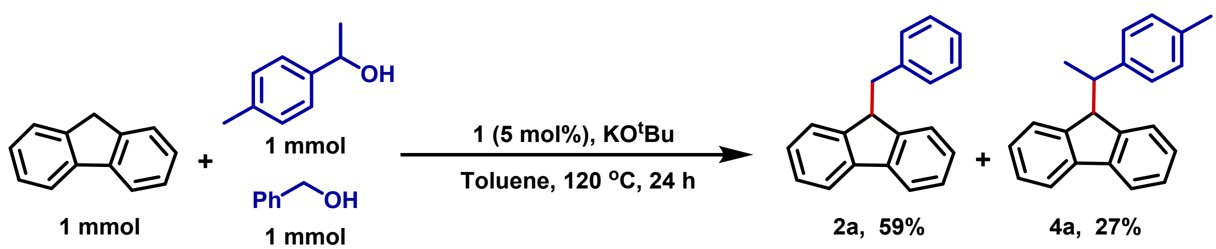
3h. Plausible mechanistic pathway



4. Competitive experiment:



In a typical reaction, a 15 mL pressure tube was charged with **1** (5 mol%), KO^{t}Bu (0.75 mmol), benzyl alcohols (1 mmol), 1-pentanol (1 mmol), fluorene (1 mmol), dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 120 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane as an eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies. It resulted in 9-benzyl-9*H*-fluorene (**2a**, 64%) and 9-pentyl-9*H*-fluorene (**3a**, 23%), proving that aromatic alcohols are more reactive and selective than aliphatic alcohols for this transformation.



In a typical reaction, a 15 mL pressure tube was charged with **1** (5 mol%), KO^{t}Bu (0.75 mmol), benzyl alcohols (1 mmol), α-methyl benzyl alcohol (1 mmol), fluorene (1 mmol), dissolved in 2 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 120 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane as an eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies. It resulted in 9-benzyl-9*H*-fluorene (**2a**, 59%) and 9-(1-(*p*-tolyl)ethyl)-9*H*-fluorene (**3a**, 27%), proving that aromatic alcohols are more reactive and selective than aliphatic alcohols for this transformation.

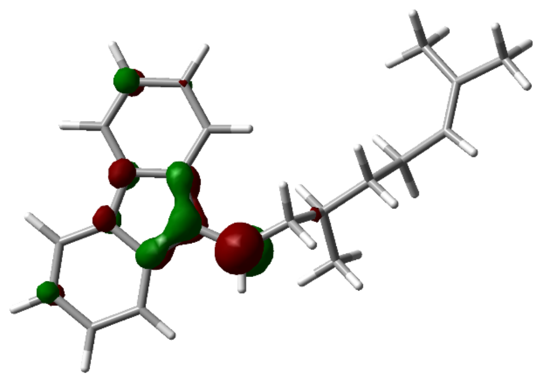
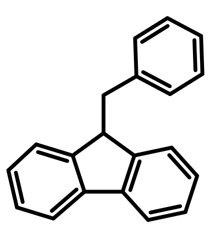


Figure S3. LUMO of the unsaturated intermediate *en route* to **3m**. The LUMO largely resides on the exocyclic double bond (B3LYP/6-31G* level of theory).

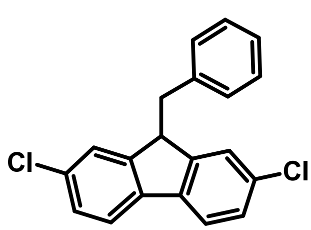
5. Analytical data:

9-Benzyl-9H-fluorene (2a): White solid (yield: 233 mg, 91%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[2].



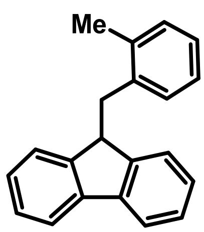
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.73 (d, J = 7.9 Hz, 2H), 7.35-7.16 (m, 11 H), 4.22 (t, J = 6 Hz, 1H), 3.10 (d, J = 7.9 Hz, 2H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 146.9, 140.9, 139.9, 129.6, 128.3, 127.2, 126.7, 126.4, 124.9, 119.9, 48.8, 40.1 ppm.

2,7-Dichloro-9-Benzyl-9H-fluorene (2b): White solid (yield: 267 mg, 82%), eluent: hexane.



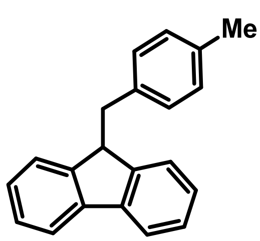
^1H NMR (400 MHz, $CDCl_3$): δ 7.58-7.56 (d, *J* = 7.9 Hz, 2H), 7.34-7.29 (m, 5H), 7.19-7.17 (d, *J* = 7.9 Hz, 2H), 7.11 (s, 2H), 4.14 (t, *J* = 7.5 Hz, 1H), 3.07 (d, *J* = 8 Hz, 2H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 148.3, 138.7, 138.4, 132.7, 129.5, 128.5, 127.7, 126.9, 125.4, 120.8, 48.7, 39.7 ppm. HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{20}H_{13}Cl_2$ 323.0394; Found 325.0385. Molecular Formula: $C_{20}H_{14}Cl_2$.

9-(2-Methylbenzyl)-9H-fluorene (2c): White solid (yield: 230 mg, 85%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[2].



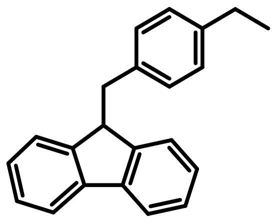
^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.45 (t, *J* = 6 Hz, 2H), 7.36-7.28 (m, 6H), 7.21-7.19 (d, *J* = 7.5 Hz, 2H), 4.28 (t, *J* = 7.9 Hz, 1H), 3.13 (d, *J* = 8 Hz, 2H), 2.36 (s, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 147.1, 140.8, 138.4, 136.8, 130.5, 130.4, 127.2, 126.7, 124.9, 119.9, 47.7, 37.8, 19.8 ppm.

9-(4-Methylbenzyl)-9H-fluorene (2d): White solid (yield: 243 mg, 90%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[3].



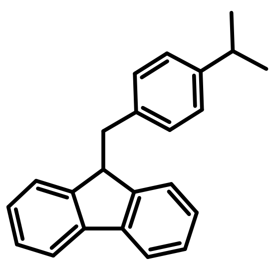
^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.38-7.36 (t, *J* = 7.5 Hz, 2H), 7.26-7.20 (m, 4H), 7.14 (m, 4H), 4.22 (t, *J* = 7.5 Hz, 1H), 3.08 (d, *J* = 7.8 Hz, 2H), 2.38 (s, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 147.0, 140.8, 136.8, 135.8, 129.4, 129.0, 127.1, 126.7, 124.9, 119.8, 48.8, 39.6, 21.2 ppm.

9-(4-Ethylbenzyl)-9H-fluorene (2e): White solid (yield: 229 mg, 81%), eluent: hexane.



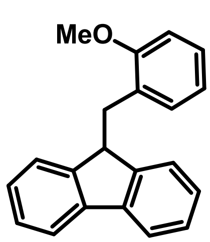
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 7.9 Hz, 2H), 7.39-7.35 (t, J = 8.1 Hz, 2H), 7.24 -7.18 (m, 8H), 4.23(t, J = 7.5 Hz, 1H), 3.09 (d, J = 7.6 Hz, 2H), 2.72-2.66 (m, 2H), 1.29 (t, J = 8 Hz, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 147.0, 140.8, 137.3, 129.4, 127.14, 126.7, 126.4, 124.9, 119.8, 48.8, 39.77, 33.81, 24.2 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}$ 285.1643; Found 285.1672. Molecular Formula: $C_{22}H_{20}$.

9-(4-Isopropylbenzyl)-9H-fluorene (2f): White solid (yield: 233 mg, 78%), eluent: hexane.



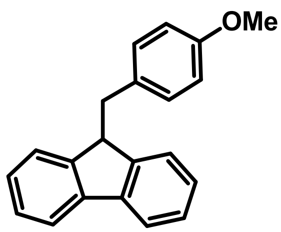
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.6 Hz, 2H), 7.56-7.53 (t, J = 6 Hz, 2H), 7.44 -7.37 (m, 8H), 4.40 (t, J = 8 Hz, 1H), 3.27 (d, J = 7.9 Hz, 2H), 3.20-3.11 (m, 1H), 1.51 (d, J = 7.5 Hz, 6H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 147.0, 140.8, 137.3, 129.4, 127.1, 126.7, 126.4, 124.9, 119.8, 48.8, 39.7, 33.8, 24.2 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}$ 299.1800 ; Found 299.1809. Molecular Formula: $C_{23}H_{22}$.

9-(2-Methoxybenzyl)-9H-fluorene (2g): Yellow solid (yield: 226 mg, 79%), eluent: hexane/ ethyl acetate (98:2). The NMR spectroscopic data is in agreement with the literature[3].



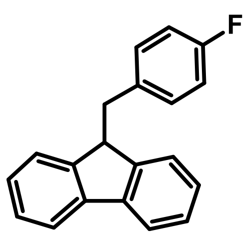
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 7.9 Hz, 2H), 7.48-7.39 (m, 3H), 7.35-7.30 (m, 4H), 7.18 (d, J = 7.5 Hz, 1H), 7.05-7.01 (m, 2H), 4.5 (t, J = 8.1 Hz, 1H), 3.96 (s, 3H), 3.2 (d, J = 7.6 Hz, 2H). ^{13}C{H} NMR (100MHz, $CDCl_3$): δ 158.0, 147.7, 140.8, 131.6, 128.6, 127.9, 126.9, 126.6, 125.1, 120.2, 119.7, 110.3, 55.3, 46.7, 35.7 ppm.

9-(4-Methoxybenzyl)-9H-fluorene (2h): Yellow solid (yield: 268 mg, 94%), eluent: hexane/ ethyl acetate (98:2). The NMR spectroscopic data is in agreement with the literature[3].



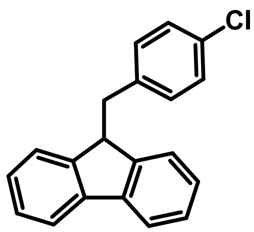
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.3 Hz, 2H), 7.29-7.28 (m, 2H), 7.22 (m, 4H), 7.19 (d, J = 7.9 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 4.26 (t, J = 7.5 Hz, 1H), 3.88 (s, 3H), 3.13 (d, J = 8.0 Hz, 2H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 158.1, 146.9, 140.9, 131.9, 130.5, 127.1, 126.7, 124.9, 119.8, 113.7, 55.2, 49.0, 39.2 ppm.

9-(4-Fluorobenzyl)-9H-fluorene (2i): White solid (yield: 252 mg, 92%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[3].



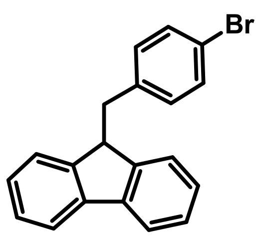
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 7.6 Hz, 2H), 7.41-7.37 (m, 2H), 7.30-7.28 (m, 4H), 7.24-7.14 (m, 2H), 7.02-6.98 (m, 2H), 4.23 (t, J = 7.9 Hz, 1H), 3.15 (d, J = 8.1 Hz, 2H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 162.9 (d, $J_{C\text{-}F}$ = 243.5 Hz), 160.4, 146.6, 141.0, 135.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.3, 126.8, 124.8, 120.0, 115.2 (d, $J_{C\text{-}F}$ = 20.9 Hz), 114.9, 48.8, 39.2 ppm.

9-(4-Chlorobenzyl)-9H-fluorene (2j): White solid (yield: 252 mg, 87%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[3].



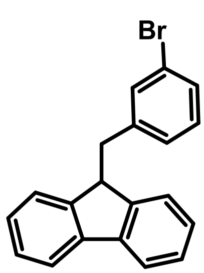
[1]H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.38-7.34 (t, *J* = 7.3 Hz, 2H), 7.25-7.19 (m, 6H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.19 (t, *J* = 7.5 Hz, 1H), 3.10 (d, *J* = 7.0 Hz, 2H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 146.4, 140.9, 138.1, 132.1, 130.9, 128.4, 127.3, 126.8, 124.8, 120.0, 48.5, 39.3 ppm.

9-(4-Bromobenzyl)-9H-fluorene (2k): White solid (yield: 274 mg, 82%**),** eluent: hexane. The NMR spectroscopic data is in agreement with the literature[3].



[1]H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.42-7.36 (m, 4H), 7.27-7.22 (m, 4H), 7.06 (d, *J* = 7.3 Hz, 2H), 4.21 (t, *J* = 7.5 Hz, 1H), 3.11 (d, *J* = 7.0 Hz, 2H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 146.4, 140.9, 138.6, 131.4, 131.3, 127.3, 126.8, 124.8, 120.0, 48.5, 39.4 ppm.

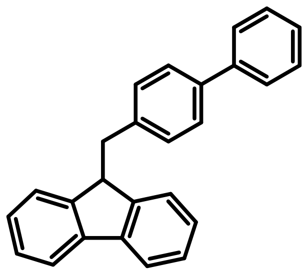
9-(3-Bromobenzyl)-9H-fluorene (2l): White solid (yield: 293 mg, 88%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[4].



[1]H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.7 Hz, 2H), 7.39-7.34 (m, 4H), 7.25-7.22 (t, *J* = 7.3 Hz, 2H), 7.19-7.10 (m, 4H), 4.20 (t, *J* = 7.4 Hz, 1H), 3.08 (d, *J* = 7.0 Hz, 2H). $^{13}C\{H\}$ NMR (100

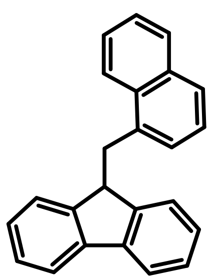
MHz, $CDCl_3$): δ 146.4, 142.1, 140.9, 132.6, 129.8, 129.6, 128.3, 127.4, 126.8, 124.8, 122.4, 120.0, 48.5, 39.7 ppm.

9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene (2m): Pinkish white solid (yield: 264 mg, 80%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[3].



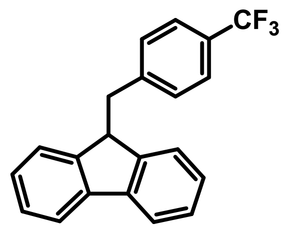
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 7.8 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.38 – 7.31 (m, 5H), 7.29 – 7.23 (m, 4H), 4.27 (t, J = 7.6 Hz, 1H), 3.15 (d, J = 7.6 Hz, 2H). ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ: 146.9, 141.0, 140.9, 139.2, 139.0, 130.0, 128.9, 127.2, 127.1, 127.0, 119.9, 48.7, 39.8 ppm.

9-(Naphthalen-1-ylmethyl)-9H-fluorene (2n): White solid with a greenish tinge (yield: 272 mg, 89%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[4].



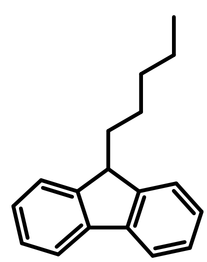
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 7.5 Hz, 2H), 7.58-7.53 (m, 2H), 7.47-7.43 (m, 1H), 7.38-7.34 (m, 2H), 7.28 (d, J = 7.0 Hz, 1H), 7.22-7.18 (m, 2H), 7.08 (d, J = 7.5 Hz, 2H), 4.42 (t, J = 8.0 Hz, 1H), 3.47 (d, J = 8.0 Hz, 2H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 147.1, 140.8, 136.0, 134.1, 132.0, 129.1, 128.3, 127.5, 127.2, 126.7, 126.1, 125.7, 125.3, 125.2, 123.8, 119.9, 47.6, 38.0 ppm.

9-(4-(trifluoromethyl)benzyl)-9H-fluorene (2o): White solid (yield: 263 mg, 81%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[3].



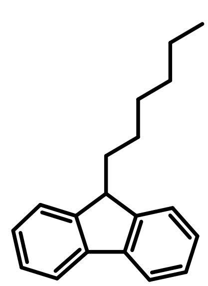
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 7.5 Hz, 2H), 7.52 (d, J = 7.7 Hz, 2H), 7.36 (t, J = 7.3 Hz, 2H), 7.29 – 7.19 (m, 6H), 4.18 (t, J = 7.3 Hz, 1H), 3.14 (d, J = 7.3 Hz, 2H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 146.3, 143.8, 141.0, 130.0, 129.3 (q, J = 32.1 Hz), 128.9 (q, J = 32.1 Hz), 128.6 (q, J = 32.1 Hz), 128.3 (q, J = 32.1 Hz), 127.5, 126.9, 125.8, 125.3 (q, J = 3 Hz), 125.2 (q, J = 3 Hz), 125.2 (q, J = 3 Hz), 125.1 (q, J = 3 Hz), 124.8, 123.1, 120.1, 48.4, 39.8.

9-Pentyl-9H-fluorene (3a): Yellow sticky oil (yield: 178 mg, 71%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[4].



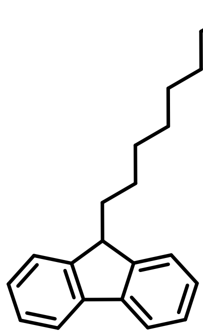
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 7.9 Hz, 2H), 7.35-7.28 (m, 4H), 3.94 (t, J = 6.0 Hz, 1H), 2.00-1.95 (m, 2H), 1.24-1.22 (m, 6H), 0.83 (t, J = 6.5 Hz, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 147.7, 141.2, 126.9, 126.8, 124.4, 119.8, 47.5, 33.1, 32.2, 25.4, 22.5, 14.2 ppm.

9-Hexyl-9H-fluorene (3b): Yellow sticky oil (yield: 190 mg, 76%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[4].



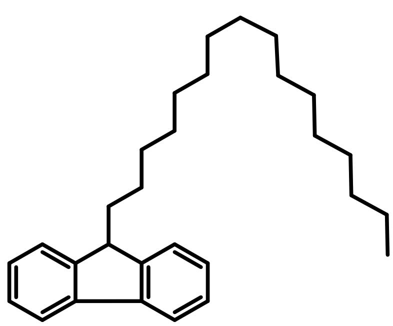
^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.35-7.28 (m, 4H), 3.95 (t, *J* = 6.0 Hz, 1H), 2.00-1.94 (m, 2H), 1.22-1.16 (m, 8H), 0.81 (t, *J* = 7.0 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 147.7, 141.2, 127.0, 126.9, 124.4, 119.8, 47.6, 33.2, 31.7, 29.7, 25.7, 22.7, 14.2 ppm.

9-Octyl-9H-fluorene (3c): Colorless oil (yield: 247 mg, 89%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[4].



^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.35-7.28 (m, 4H), 3.94 (t, *J* = 6.0 Hz, 1H), 1.99-1.98 (m, 2H), 1.21 (m, 12H), 0.85 (t, *J* = 7.0 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 147.7, 141.2, 126.9, 126.8, 124.4, 119.8, 47.6, 33.2, 32.0, 30.1, 29.5, 29.4, 25.8, 22.8, 14.2 ppm.

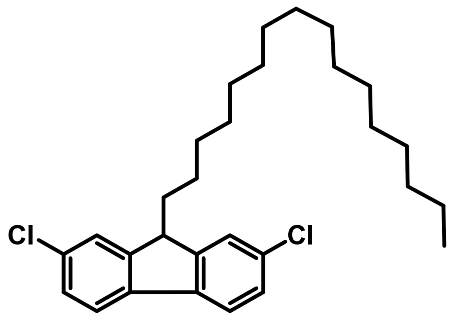
9-hexadecyl-9H-fluorene (3d): White solid (yield: 332 mg, 85%), eluent: hexane.



^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.48-7.45 (t, *J* = 6.0 Hz, 2H), 7.43-7.40 (t, *J* = 5.9 Hz, 2H), 4.08 (t, J = 6.0 Hz, 1H), 2.14-2.10 (m, 2H), 1.41-1.35 (m, 28H), 1.05-1.02 (t, J = 5.9 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 147.7, 141.2, 126.9, 126.8, 124.4, 119.8, 47.6, 33.2, 32.1, 30.1, 29.9, 29.8, 29.6, 29.5, 25.8, 22.8, 14.3 ppm.

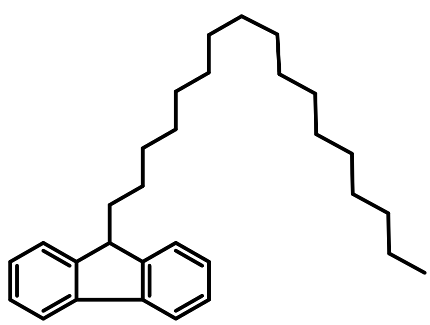
HRMS (ESI) m/z: [M - H]$^+$ Calcd for $C_{29}H_{41}$ 389.3208 ; Found 389.3221. Molecular Formula: $C_{29}H_{42}$.

2,7-dichloro-9-hexadecyl-9H-fluorene (3e): White solid (yield: 412 mg, 90%), eluent: hexane.



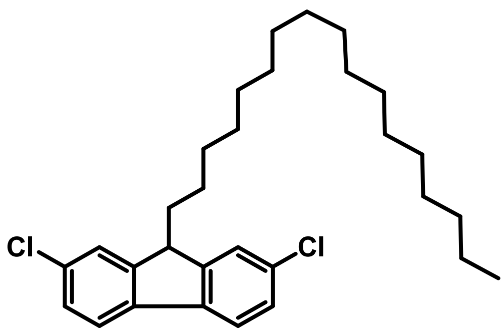
[1]H NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (d, *J* = 8.1 Hz, 2H), 7.47 (s, 2H), 7.34-7.33 (dd, *J* = 4.0, *J* = 4.1, Hz, 2H), 3.93 (t, *J* = 6.0 Hz, 1H), 1.99-1.95 (m, 2H), 1.30-1.22 (m, 28H), 0.92-0.89 (t, *J* = 6.2 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 149.2, 138.7, 133.0, 127.4, 124.8, 120.8, 47.6, 32.8, 32.0, 29.9, 29.8, 29.7, 29.53, 29.51, 25.5, 22.8, 14.2 ppm; HRMS (ESI) m/z: [M - H]$^+$ Calcd for $C_{29}H_{39}Cl_2$ 457.2429 ; Found 457.2432. Molecular Formula: $C_{29}H_{40}Cl_2$.

9-heptadecyl-9H-fluorene (3f): White solid (yield: 372 mg, 92%), eluent: hexane.



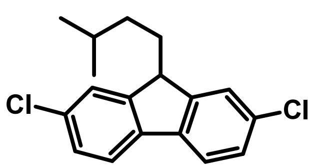
[1]H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.45-7.42 (t, *J* = 6.1 Hz, 2H),7.40-7.36 (t, *J* = 5.9 Hz, 2H), 4.05 (t, *J* = 6.0 Hz, 1H), 2.10-2.06 (m, 2H), 1.39-1.30 (m, 30H), 1.01-0.98 (t, *J* = 6.1 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 147.7, 141.2, 126.9, 126.8, 124.4, 119.8, 47.6, 33.2, 32.1, 30.1, 29.9, 29.8, 29.6, 29.5, 25.8, 22.8, 14.3 ppm; HRMS (ESI) m/z: [M - H]$^+$ Calcd for $C_{30}H_{43}$ 403.3365 ; Found 403.3317. Molecular Formula: $C_{30}H_{44}$.

2,7-dichloro-9-heptadecyl-9H-fluorene (3g): White solid (yield: 415 mg, 88%), eluent: hexane.



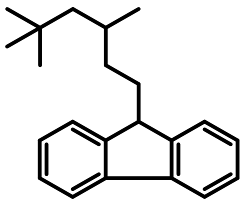
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (d, *J* = 8.1 Hz, 2H), 7.47 (s, 2H), 7.34-7.32 (dd, *J* = 4.0, *J* = 4.0 Hz, 2H), 3.92 (t, *J* = 6.1 Hz, 1H), 1.99-1.95 (m, 2H), 1.29-1.23 (m, 30H), 0.93-0.90 (t, *J* = 6.0 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 149.2, 138.7, 133.0, 127.4, 124.8, 120.8, 47.6, 32.8, 32.1, 29.9, 29.8, 29.7, 29.54, 29.51, 25.5, 22.8, 14.2 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{43}Cl_2$ 473.2742 ; Found 473.2767. Molecular Formula: $C_{30}H_{42}Cl_2$.

2,7-dichloro-9-isopentyl-9H-fluorene (3h): Yellow sticky oil (yield: 222 mg, 73%), eluent: hexane.



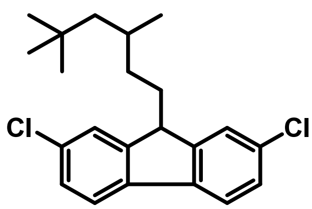
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.60 (d, *J* = 7.5 Hz, 2H), 7.46 (s, 2H), 7.35-7.33 (dd, *J* = 4.1, *J* = 4.0, Hz, 2H), 3.94 (t, *J* = 4.1 Hz, 1H), 2.02-1.96 (m, 2H), 1.53-1.44 (m, 1H), 1.02-0.97 (m, 2H), 0.85-0.83 (d, *J* = 4.0 Hz, 6H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 148.2, 138.8, 133.0, 127.5, 124.8, 120.9, 47.7, 34.3, 30.6, 28.4, 22.6 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}Cl_2$ 305.0864 ; Found 305.0875. Molecular Formula: $C_{18}H_{18}Cl_2$.

9-(3,5,5-trimethylhexyl)-9H-fluorene (3i): White solid (yield: 254 mg, 87%), eluent: hexane.



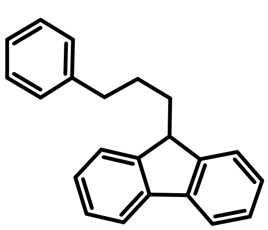
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.44-7.40 (dd, *J* = 7.4 Hz, *J* = 7.5 Hz, 2H), 7.38-7.35 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 2H), 4.03 (t, *J* = 4.1 Hz, 1H), 2.12-2.05 (m, 2H), 1.49-1.44 (m, 1H),1.23-1.17 (m, 2H), 1.10-1.01 (m, 2H), 0.94-0.92 (d, *J*= 7.4 Hz, 3H), 0.90 (s, 9H), $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 147.6, 144.5, 141.29, 141.21, 129.5, 127.9, 126.95, 126.91, 124.4, 123.8, 120.2, 119.8, 94.0, 51.1, 47.7, 35.1, 31.1, 30.6, 30.1, 30.0, 29.6, 22.7 ppm. HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{21}H_{27}$ 291.2113; Found 291.2139. Molecular Formula: $C_{22}H_{28}$.

2,7-dichloro-9-(3,5,5-trimethylhexyl)-9H-fluorene (3j): White solid (yield: 303 mg, 84%), eluent: hexane.



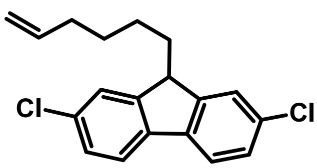
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.57 (d, *J* = 7.9 Hz, 2H), 7.49 (s, 2H), 7.35-7.33 (dd, *J* = 3.9, *J* = 4.0 Hz, 2H), 3.91 (t, *J* = 4.2 Hz, 1H), 2.03-1.98 (m, 2H), 1.46-1.40 (m, 1H), 1.18-1.09 (m, 2H), 1.03-0.99 (m, 2H), 0.91-0.89 (d, *J* = 7.5 Hz, 3H), 0.88(s, 9H), $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 149.1, 138.7, 133.0, 127.4, 124.8, 120.8, 50.9, 47.6, 34.8, 31.0, 30.3, 30.1, 29.6, 22.5. HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{22}H_{25}Cl_2$ 359.1333; Found 359.1368. Molecular Formula: $C_{22}H_{26}Cl_2$.

9-(3-phenylpropyl)-9H-fluorene (3k): Colorless oil (yield: 255 mg, 90%), eluent: hexane.



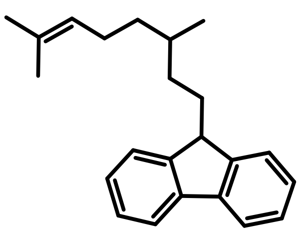
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.66–7.62 (d, *J* = 16.1 Hz, 2H), 7.38–7.35 (d, *J* = 12.2 Hz, 2H), 7.25–7.11 (m, 6H), 7.07–7.04 (d, *J* = 11.8 Hz, 1H), 6.99–6.96 (d, *J* = 12.1 Hz, 2H), 3.90–3.86 (t, *J* = 7.9 Hz, 1H), 2.47–2.43 (m, 2H), 1.98–1.93 (m, 2H), 1.43–1.35 (m, 2H). ^{13}C{H} NMR (100 MHz, CDCl$_3$): δ 147.4, 147.3, 142.2, 141.3, 141.2, 128.5, 128.4, 128.4, 128.3, 127.0, 127.0, 126.9, 126.9, 125.8, 124.4, 124.4, 119.9, 119.9, 47.4, 36.2, 32.6, 27.3 ppm; HRMS (ESI) m/z: [M - H]$^+$ Calcd for $C_{22}H_{19}$ 283.1487 ; Found 283.1505. Molecular Formula: $C_{22}H_{20}$.

2,7-dichloro-9-(hex-5-en-1-yl)-9H-fluorene (3l): Colorless oil (yield: 295 mg, 93%), eluent: hexane.



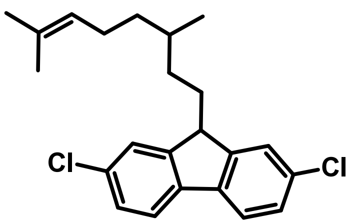
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.59-7.57 (d, *J* = 8.1 Hz, 2H), 7.47 (s, 2H), 7.35-7.33 (dd, *J* = 4.1, *J* = 4.2, Hz, 2H), 5.82-5.72 (m, 1H), 5.01-4.94 (dd, *J* = 16.2 Hz, *J* = 12.1 Hz, 2H), 3.91 (t, J = 4.3 Hz, 1H), 2.01-1.97 (m, 4H), 1.41-1.34 (m, 2H), 1.21-1.13 (m, 2H). ^{13}C{H} NMR (100 MHz, CDCl$_3$): δ 149.0, 138.7, 132.9, 127.4, 124.7, 120.8, 114.5, 47.4, 33.5, 32.5, 29.1, 24.8 ppm; HRMS (ESI) m/z: [M - H]$^+$ Calcd for $C_{19}H_{17}Cl_2$ 315.0707 ; Found 315.0708. Molecular Formula: $C_{19}H_{18}Cl_2$.

9-(3,7-dimethyloct-6-en-1-yl)-9H-fluorene (3m): Colorless oil (yield: 240 mg, 79%), eluent: hexane.



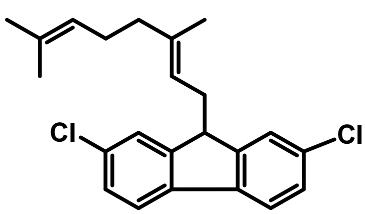
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 4.5 Hz, 2H), 7.44-7.41 (t, *J* = 6.1 Hz, 2H), 7.39-7.36 (t, *J* = 6.2 Hz, 2H), 5.15-5.13 (t, *J* = 4.5 Hz, 1H), 4.04 (t, *J* = 6.3 Hz, 1H), 2.13-2.07 (m, 2H), 2.02-1.94 (m, 2H), 1.75 (s, 3H), 1.65 (s, 3H), 1.46-1.44 (m, 1H),1.37-1.34 (m, 1H), 1.30-1.25 (m, 1H), 1.19-1.14 (m, 1H), 1.13-1.08 (m, 1H), 0.92-0.90 (d, *J* = 6.0 Hz, 3H). ^{13}C{H} NMR (100 MHz, CDCl$_3$): δ 147.4, 147.4, 141.0, 130.8, 126.7, 126.6, 124.8, 124.2, 124.1, 119.6, 47.4, 36.6, 32.4, 32.2, 30.1, 25.5, 25.3, 19.3, 17.5 ppm; HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{23}H_{27}$ 303.2113 ; Found 303.2128. Molecular Formula: $C_{23}H_{28}$.

2,7-dichloro-9-(3,7-dimethyloct-6-en-1-yl)-9H-fluorene (3n): Colorless oil (yield: 306 mg, 82%), eluent: hexane.



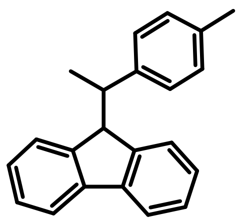
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.59 (d, *J* = 4.5 Hz, 2H), 7.47 (s, 2H), 7.35-7.33 (dd, *J* = 4.1, *J* = 3.9, Hz, 2H), 5.09-5.06 (t, *J* = 6.3 Hz, 1H), 3.93 (t, *J* = 6.0 Hz, 1H), 2.02-1.96 (m, 2H), 1.94-1.88 (m, 2H), 1.69 (s, 3H), 1.59 (s, 3H), 1.40-1.34 (m, 1H), 1.25-1.24 (m, 1H), 1.14-1.12 (m, 1H), 1.12-1.10 (m, 1H), 0.98-0.96 (m, 1H), 0.86-0.85 (d, *J* = 6.0 Hz, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 148.9, 148.8, 138.5, 131.0, 127.2, 124.6, 124.5, 124.5, 120.5, 47.4, 36.5, 32.3, 32.0, 29.8, 25.5, 25.2, 19.2, 17.4 ppm. HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{23}H_{25}Cl_2$ 371.1333; Found 371.1365. Molecular Formula: $C_{23}H_{26}Cl_2$.

(E)-2,7-dichloro-9-(3,7-dimethylocta-2,6-dien-1-yl)-9H-fluorene (3o): Colorless oil (yield: 282 mg, 76%), eluent: hexane.



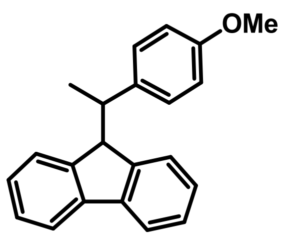
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (d, *J* = 7.9 Hz, 2H), 7.50-7.48 (dd, *J* = 4.5 Hz, *J* = 4.1 Hz, 2H), 7.34-7.32 (d, *J* = 8.1, *J* = 4.6 Hz, 2H), 5.18-5.15 (t, *J* = 6.6 Hz, 1H), 5.07-5.04 (t, *J* = 6.2 Hz, 1H), 3.89 (t, *J* = 16.3 Hz, 1H), 2.57 (t, *J* = 6.5 Hz, 2H), 2.07-1.97 (m, 4H), 1.73-1.69 (d, *J* = 16.1 Hz, 3H), 1.65-1.61 (d, *J* = 16.3 Hz, 3H), 1.56-1.54 (d, *J* = 16.1 Hz, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 149.1, 138.6, 138.2, 132.9, 131.7, 127.5, 125.1, 124.8, 124.2, 121.6, 120.8, 47.6, 39.9, 32.2, 31.9, 31.7, 26.7, 25.8, 23.5,17.8, 17.7, 16.4 ppm; HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{23}H_{23}Cl_2$ 369.1177; Found 369.1174. Molecular Formula: $C_{23}H_{24}Cl_2$.

9-(1-(p-Tolyl)ethyl)-9H-fluorene (4a): White solid (yield: 213 mg, 75%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[4].



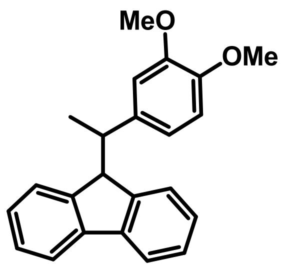
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.78 (m, 2H), 7.59-7.57 (d, *J* = 7.2 Hz, 1H), 7.47-7.41 (m, 3H), 7.40-7.32 (m, 2H), 7.30-7.23 (m, 3H), 7.21-7.19 (d, *J* = 7.5 Hz, 1H), 4.37 (d, *J* = 4.5 Hz, 1H), 3.77-3.72 (m, 1H), 2.47 (s, 3H), 0.99 (d, *J* = 7.2 Hz, 3H). ^{13}C{H} NMR (100MHz, $CDCl_3$): δ 146.4, 144.4, 141.5, 141.3, 141.1, 135.4, 128.7, 128.6, 127.7, 126.8, 126.7, 126.5, 125.9, 125.4, 124.0, 119.4, 119.3, 54.0, 41.2, 20.8, 13.7 ppm.

9-(1-(4-methoxyphenyl)ethyl)-9H-fluorene (4b): Yellow oil (yield: 268 mg, 77%), eluent: hexane/ ethyl acetate (98:2). The NMR spectroscopic data is in agreement with the literature[4].



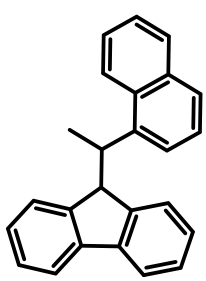
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.70 (m, 2H), 7.51-7.50 (d, *J* = 4.5 Hz, 1H), 7.40-7.38 (d, *J* = 8.7 Hz,, 1H), 7.36-7.30 (m, 2H), 7.23-7.21 (d, *J* = 8.7 Hz, 2H), 7.15-7.11 (m, 1H), 6.90-6.86 (m, 3H), 4.27 (d, *J* = 4.5 Hz, 1H), 3.84 (s, 3H), 3.68-3.61 (m, 1H), 0.93-0.91 (d, *J* = 6.9 Hz, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 158.0, 146.5, 144.7, 141.8, 141.4, 136.7, 128.9, 127.1, 127.0, 126.8, 124.3, 119.7, 119.6, 113.5, 55.2, 54.3, 41.1, 14.2 ppm.

9-(1-(3,4-dimethoxyphenyl)ethyl)-9H-fluorene (4c): Yellow solid (yield: 201 mg, 61%), eluent: hexane/ ethyl acetate (98:2).



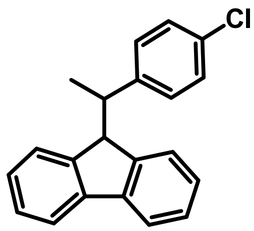
[1]H NMR (400 MHz, $CDCl_3$): δ 7.71–7.66 (dd, *J* = 8.7 Hz, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.36–7.32 (m, *J* = 8.7 Hz, 1H), 7.30-7.26 (m, 2H), 7.13 (t, *J* = 8.7 Hz, 1H), 6.96 (d, *J* =7.5 Hz, 1H), 6.78-6.76 (m, 2H), 6.70 (s, 1H), 4.25 (d, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 3.64-3.61 (m, 1H), 1.03-1.01 (d, *J* = 6.9 Hz, 3H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 148.5, 147.4, 146.4, 144.9, 141.8, 141.6, 136.8, 127.19, 127.12, 126.8, 126.3, 125.7, 124.5, 120.0, 119.8, 119.7, 111.3, 110.7, 55.9, 54.4, 41.8, 15.2 ppm. HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{23}H_{21}O_2$ 329.1541; Found 329.1585. Molecular Formula: $C_{23}H_{22}O_2$.

9-(1-(naphthalen-1-yl)ethyl)-9H-fluorene (4d): Brown solid (yield: 205 mg, 64%), eluent: hexane/ ethyl acetate (99:1).



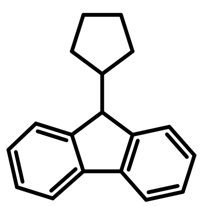
[1]H NMR (400 MHz, $CDCl_3$): δ 8.56–8.53 (d, *J* = 12 Hz, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 1H), 7.84–7.79 (m, 2H), 7.76–7.75 (d, *J* = 7.2 Hz, 2H), 7.69–7.65 (m, 1H), 7.59–7.55 (m, 2H), 7.44–7.40 (m, 3H), 7.32 (t, *J* = 8.2 Hz, 1H), 7.09–7.05 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 4.58–4.52 (m, 1H), 4.49–4.48 (d, *J* = 4.5 Hz, 1H), 0.84 (d, *J* = 7.2 Hz, 3H) $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 147.1, 144.2, 142.1, 141.5, 140.3, 134.2, 131.6, 129.5,127.5,127.3, 127.2, 127.0,126.3, 126.2, 125.6, 125.3, 124.8, 123.7, 123.0, 119.9, 119.7, 52.2, 37.2, 12.6 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}$ 321.1643; Found 321.1618. Molecular Formula: $C_{25}H_{20}$.

9-(1-(4-chlorophenyl)ethyl)-9H-fluorene (4e): White solid (yield: 249 mg, 82%), eluent: hexane.



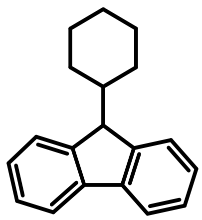
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.63 (m, 2H), 7.45–7.43 (d, *J* = 7.5 Hz, 1H), 7.34–7.20 (m, 6H), 7.12–7.07 (m, 2H), 6.85–6.83 (d, *J* = 7.5 Hz, 1H), 4.18 (d, *J* = 4.5 Hz, 1H), 3.61–3.55 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 146.1, 144.4, 142.9, 141.8, 141.5, 132.0, 129.5, 128.2, 127.3, 127.2, 126.9, 126.4, 125.4, 124.3, 119.9, 119.8, 54.0, 41.6, 14.6 ppm. HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{21}H_{16}Cl$ 303.0941; Found 303.0960. Molecular Formula: $C_{21}H_{17}Cl$.

9-cyclopentyl-9H-fluorene (4f): Colorless oil (yield: 189 mg, 81%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[4].



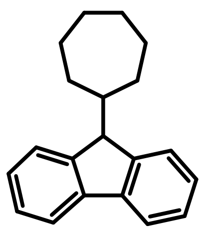
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.72 (d, *J* = 8.0 Hz, 2H), 7.56-7.55 (d, *J* = 7.5 Hz, 2H), 7.34 (m, 2H), 7.28 (m, 2H), 4.00 (d, *J* = 5.5 Hz, 1H), 2.38-2.36 (m, 1H), 1.77-1.75 (m, 2H), 1.57-1.55 (m, 2H), 1.49-1.45 (m, 2H), 1.37-1.35 (m, 2H). ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 147.2, 141.4, 126.9, 126.6, 125.2, 119.7, 51.3, 44.4, 30.1, 25.3 ppm.

9-cyclohexyl-9H-fluorene (4g): Colorless oil (yield: 186 mg, 75%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[4].



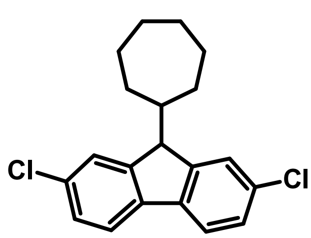
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7,70 (d, *J* = 7.5 Hz, 2H), 7.52-7.51 (d, *J* = 6.9 Hz, 2H), 7.34-7.33 (m, 2H), 7.31-7.28 (m, 2H), 3.86 (m, 1H), 2.17-2.09 (m, 1H), 1.65-1.57 (m, 3H), 1.45-1.42 (d, *J* = 11.1 Hz, 2H), 1.24-1.04 (m, 5H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 146.5, 141.6, 126.8, 126.6, 124.9, 119.6, 53.6, 43.1, 29.7, 26.9, 26.5 ppm.

9-cycloheptyl-9H-fluorene (4h): Colorless oil (yield: 220 mg, 84%), eluent: hexane.



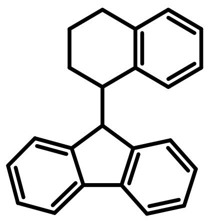
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.71 (d, *J* = 7.2 Hz, 2H), 7.55-7.53 (d, *J* = 6.8 Hz, 2H), 7.35-7.31 (m, 2H), 7.28-7.24 (m, 2H), 3.94-3.93 (m, 1H), 2.36-2.30 (m, 1H), 1.62-1.25 (m, 12H). $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 146.7, 141.8, 126.9, 126.7, 124.8, 119.6, 54.9, 54.8, 44.1, 31.8, 27.8, 27.7 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}$ 263.1800; Found 263.1799. Molecular Formula: $C_{20}H_{22}$.

2,7-dichloro-9-cycloheptyl-9H-fluorene(4i): White solid (yield: 261 mg, 79%), eluent: hexane.



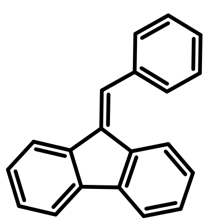
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (d, *J* = 7.9 Hz, 2H), 7.52 (s, 2H), 7.34-7.32 (dd, *J* = 6.5 Hz, 2H), 3.91-3.90 (m, 1H), 2.32-2.26 (m, 1H), 1.67-1.64 (m, 2H), 1.59-1.57 (m, 2H), 1.51-1.41 (m, 4H), 1.39-1.31 (m, 2H), 1.30-1.25 (m, 2H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ 148.2, 139.3, 132.8, 127.4, 125.1, 120.6, 54.9, 43.9, 31.6, 27.7, 27.6, 27.5 ppm. HRMS (ESI) m/z: [M - H]$^+$ Calcd for $C_{20}H_{19}Cl_2$ 329.0864; Found 329.0848. Molecular Formula: $C_{20}H_{20}Cl_2$.

9-(1,2,3,4-tetrahydronaphthalen-1-yl)-9H-fluorene (4j): Colorless oil (yield: 183 mg, 62%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[4].



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.87 (m, 2H),7.84-7.82 (m, 1H), 7.73-7.71 (d, J = 7.5 Hz, 1H), 7.52-7.32 (m, 5H), 7.24 (d, J = 6.9 Hz, 1H), 7.11-7.07 (m, 1H), 6.49-6.47 (d, J = 7.9 Hz, 1H), 4.79-4.78 (d, J = 3.9 Hz, 1H), 4.02-3.98 (m, 1H), 2.73-2.68 (m, 1H), 2.61-2.53 (m, 1H), 1.51-1.47 (m, 3H), 0.84-0.78 (m, 1H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 146.5, 145.3, 141.9, 141.5, 139.3, 138.8, 129.4, 128.2, 127.07, 127.04, 126.9, 126.6, 126.1, 125.9, 125.3, 123.7, 119.8, 119.5, 52.5, 40.6, 30.3, 23.3, 21.9 ppm.

9-benzylidene-9H-fluorene (5): White solid (yield: 218 mg, 78%), eluent: hexane. The NMR spectroscopic data is in agreement with the literature[3].



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.83 (d, J = 7.9 Hz, 1H), 7.79-7.75 (m, 3H), 7.66-7.64 (d, J = 7.5 Hz, 3H), 7.54-7.50 (t, J = 6 Hz, 2H), 7.47-7.35 (m, 4H), δ 7.15-7.11 (dt, J = 7.5 Hz, J = 7.6 Hz, 1H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ 141.3, 139.5, 139.2, 136.9, 136.6, 136.5, 129.3, 128.7, 128.6, 128.3, 128.1, 127.3, 127.0, 126.7, 124.4, 120.3, 119.8, 119.6 ppm.

6. ^{1}H and ^{13}C NMR spectra of synthesized compounds:

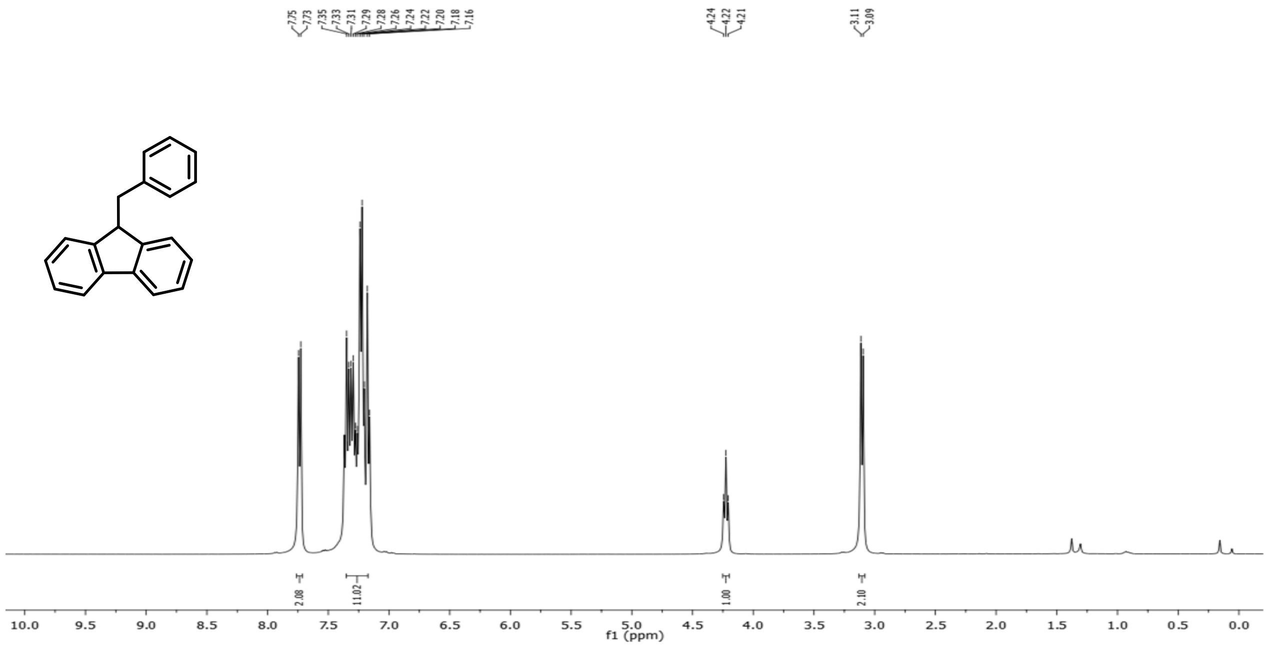


Figure S4. ^{1}H **NMR spectrum (400 MHz) of 2a in** $CDCl_3$

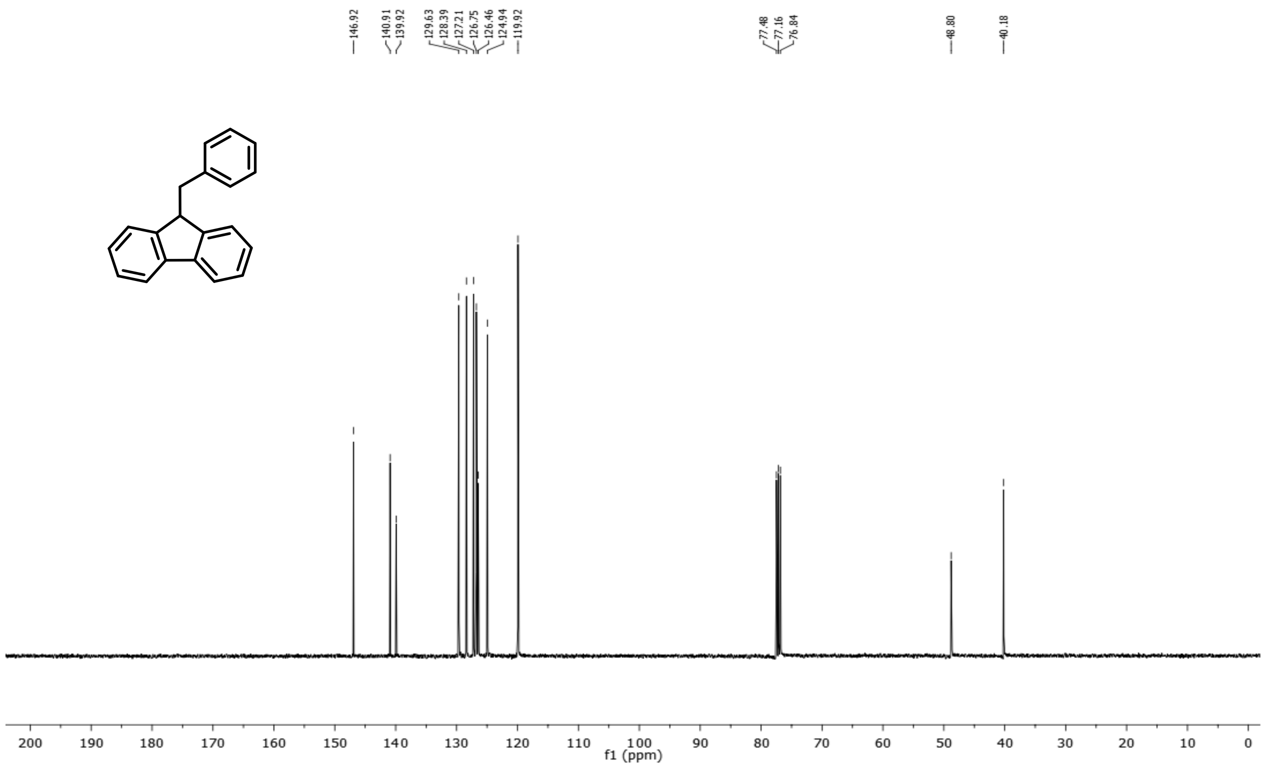


Figure S5. ^{13}C **NMR spectrum (100 MHz) of 2a in** $CDCl_3$

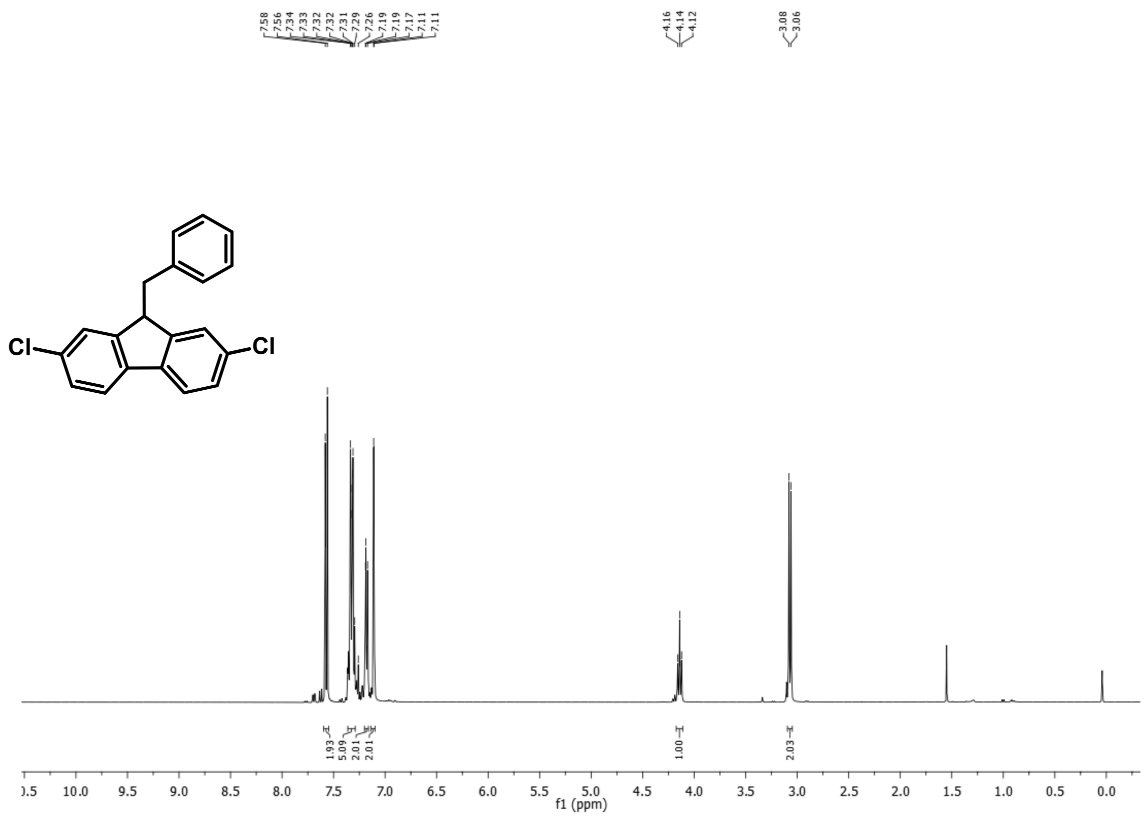


Figure S6. ^{1}H NMR spectrum (400 MHz) of 2b in $CDCl_3$

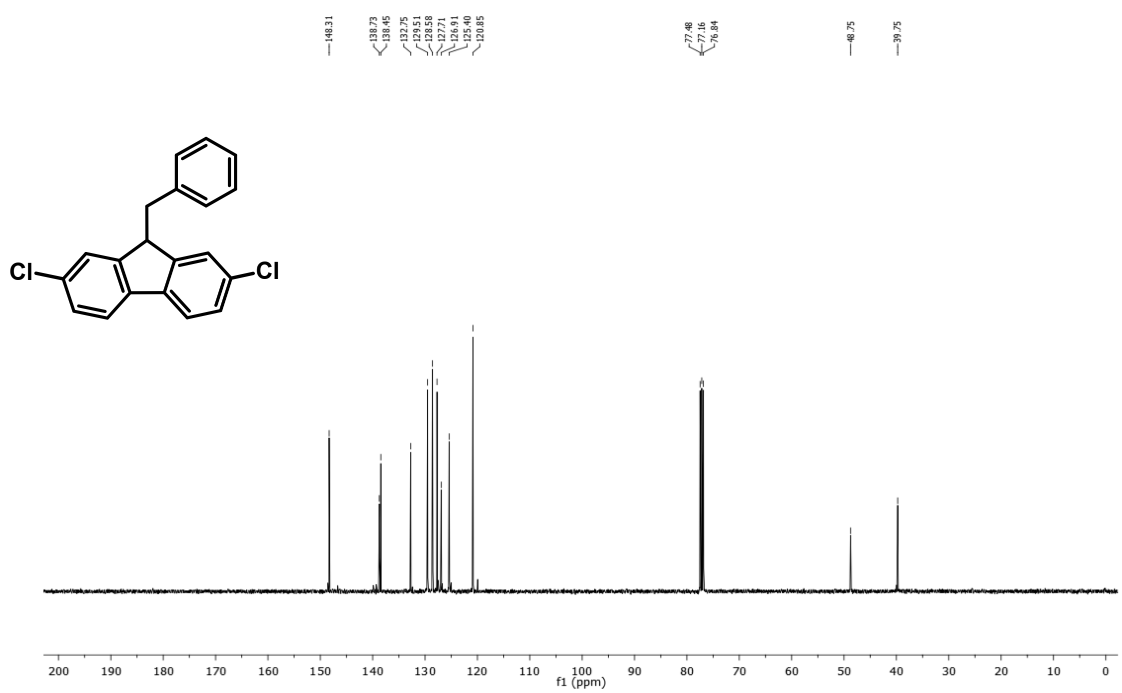


Figure S7. ^{13}C NMR spectrum (100 MHz) of 2b in $CDCl_3$

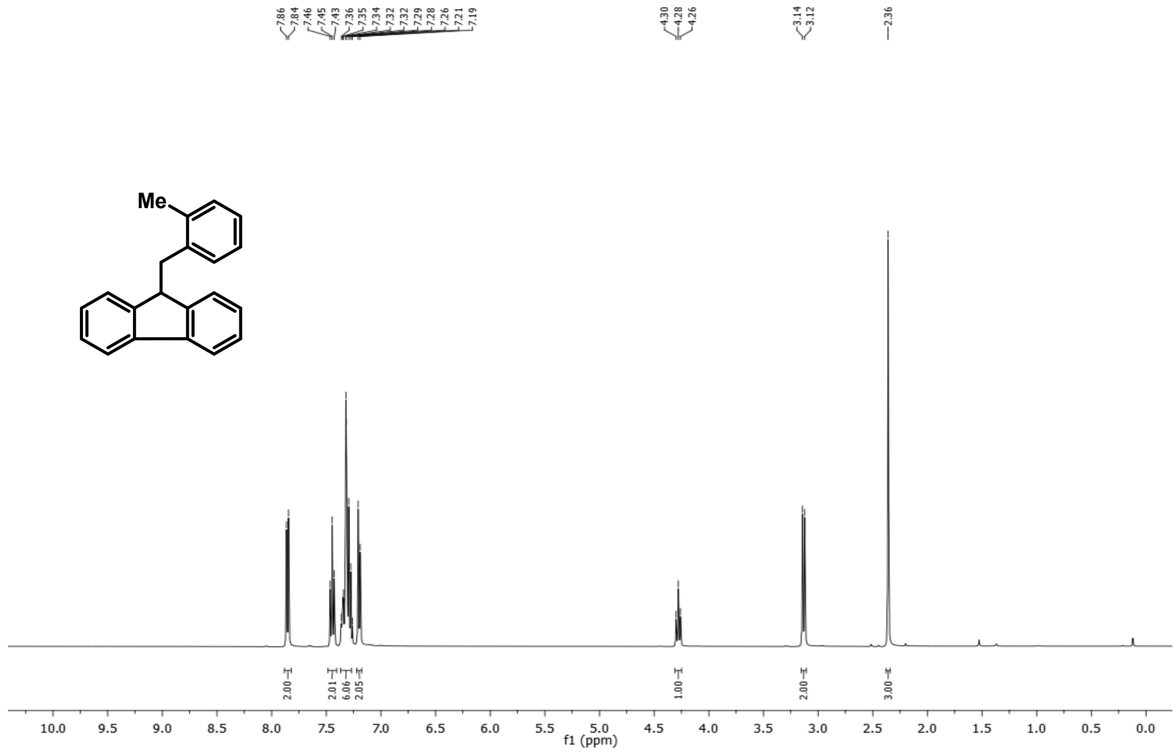


Figure S8. ^{1}H NMR spectrum (400 MHz) of 2c in $CDCl_3$

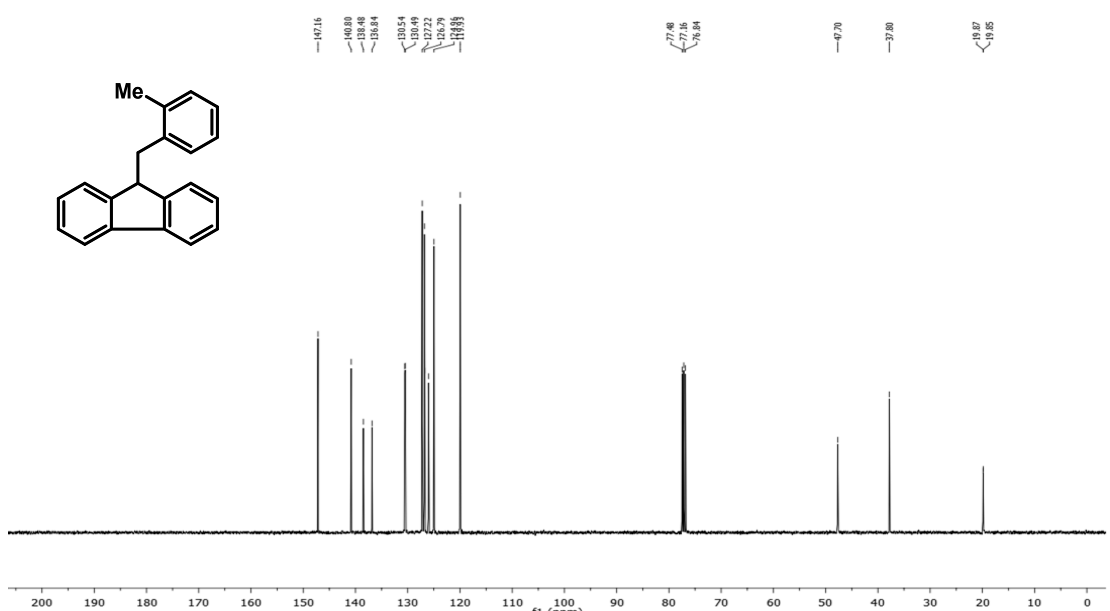


Figure S9. ^{13}C NMR spectrum (100 MHz) of 2c in $CDCl_3$

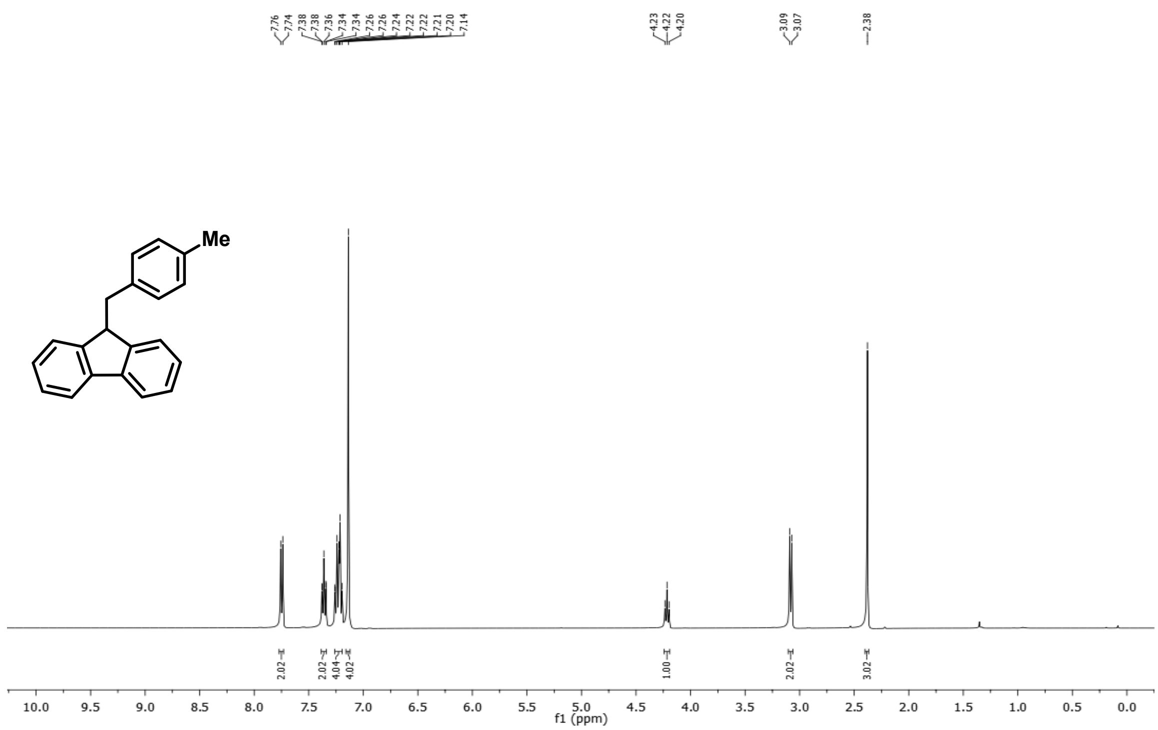


Figure S10. ^1H NMR spectrum (400 MHz) of 2d in $CDCl_3$

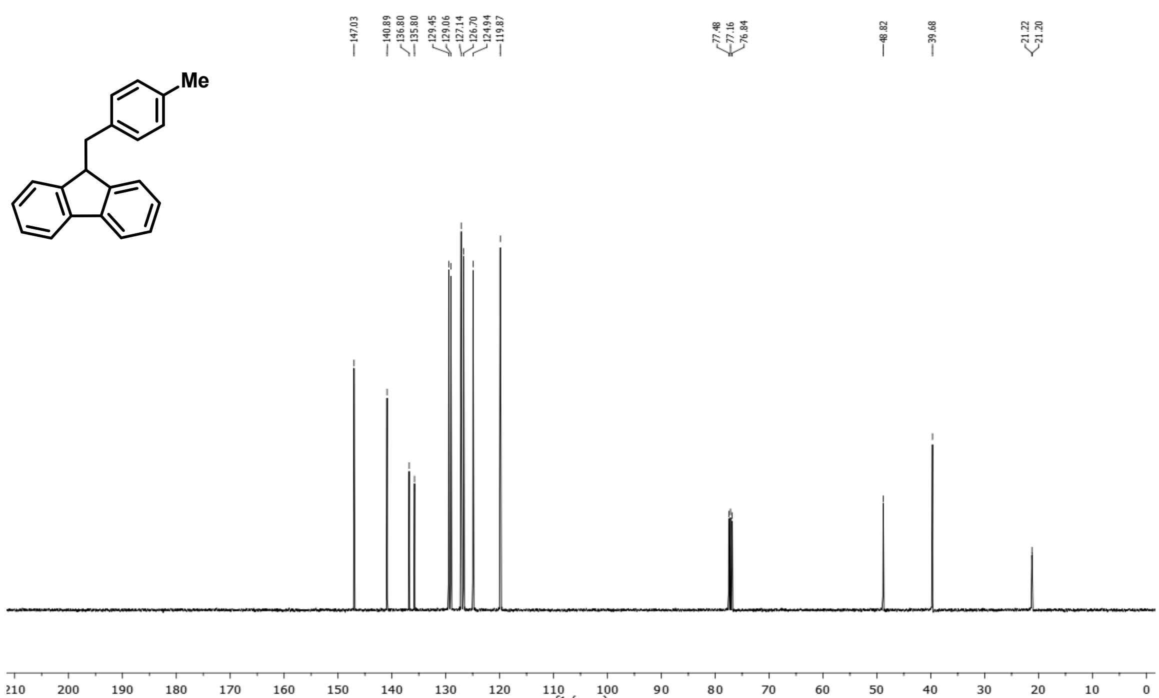


Figure S11. ^{13}C NMR spectrum (100 MHz) of 2d in $CDCl_3$

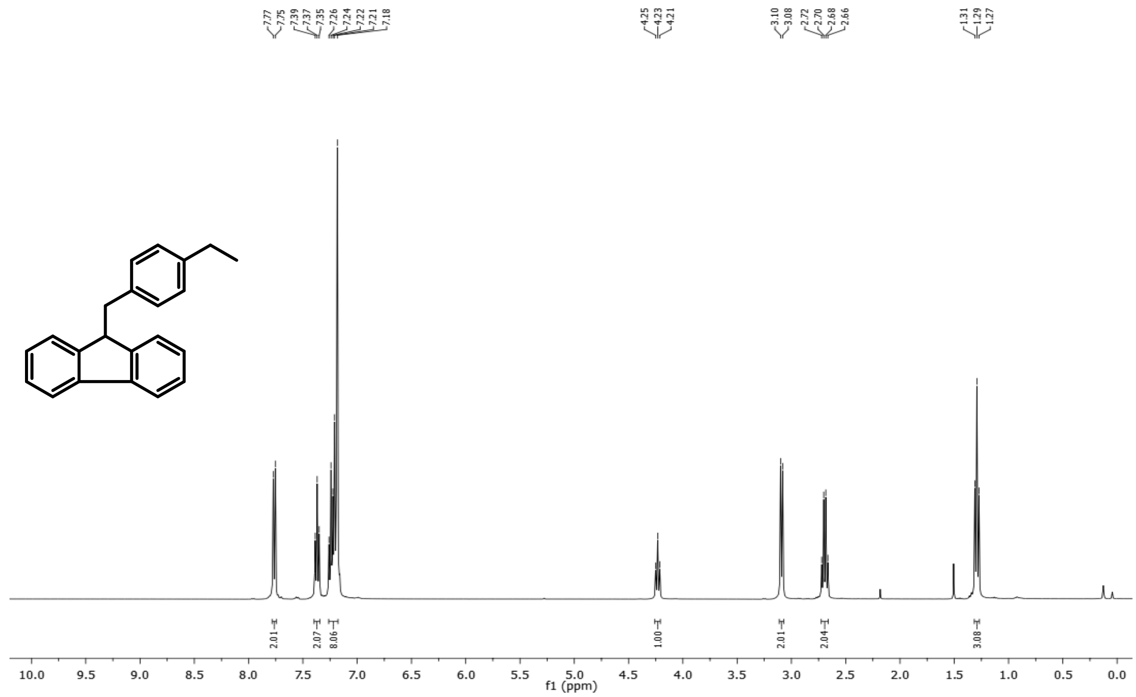


Figure S12. **[1]H NMR spectrum (400 MHz) of 2e in $CDCl_3$**

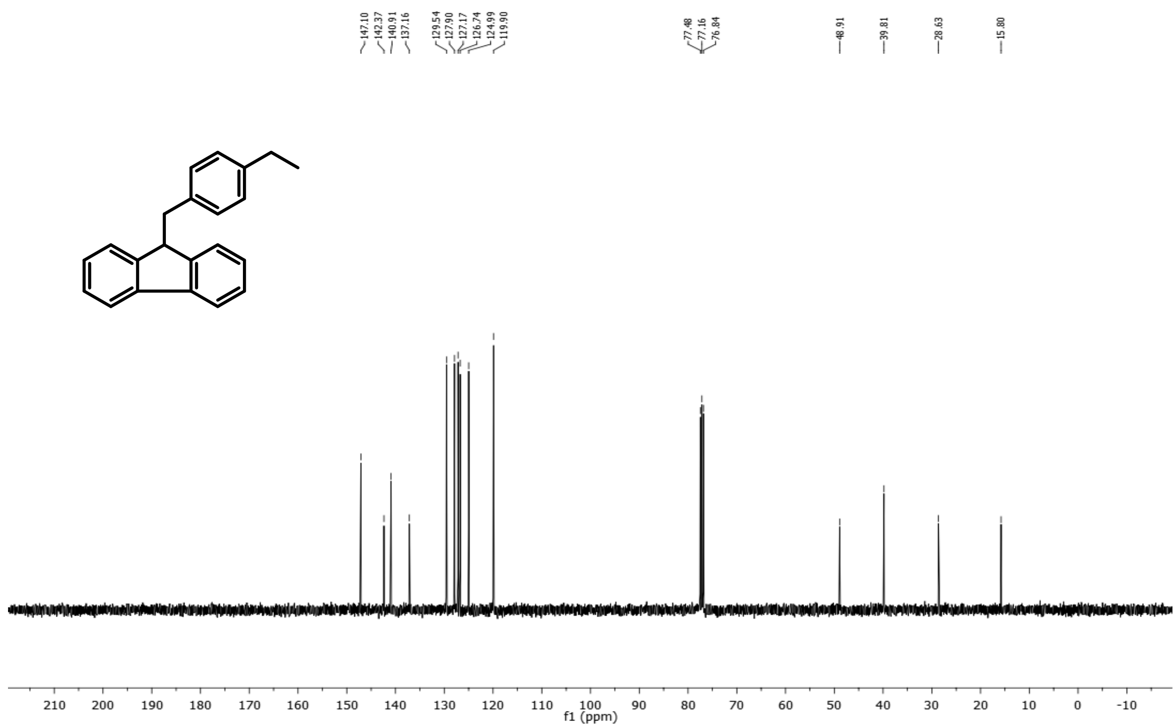


Figure S13. **[13]C NMR spectrum (100 MHz) of 2e in $CDCl_3$**

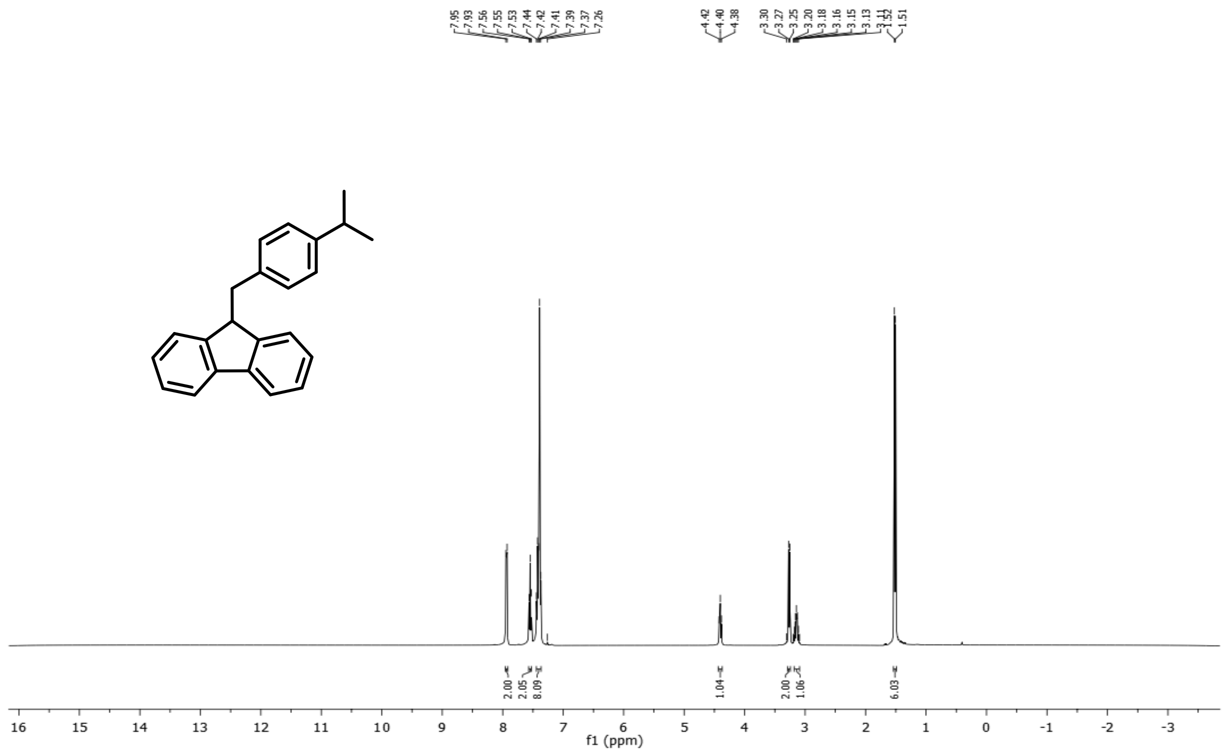


Figure S14. ^{1}H NMR spectrum (400 MHz) of 2f in $CDCl_3$

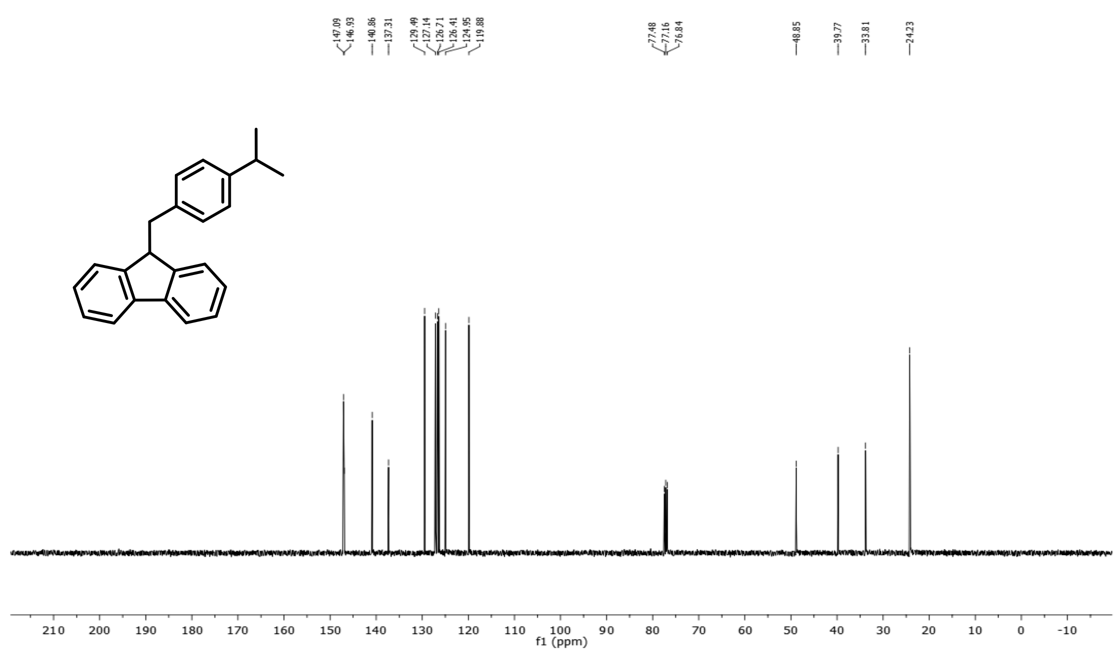


Figure S15. ^{13}C NMR spectrum (100 MHz) of 2f in $CDCl_3$

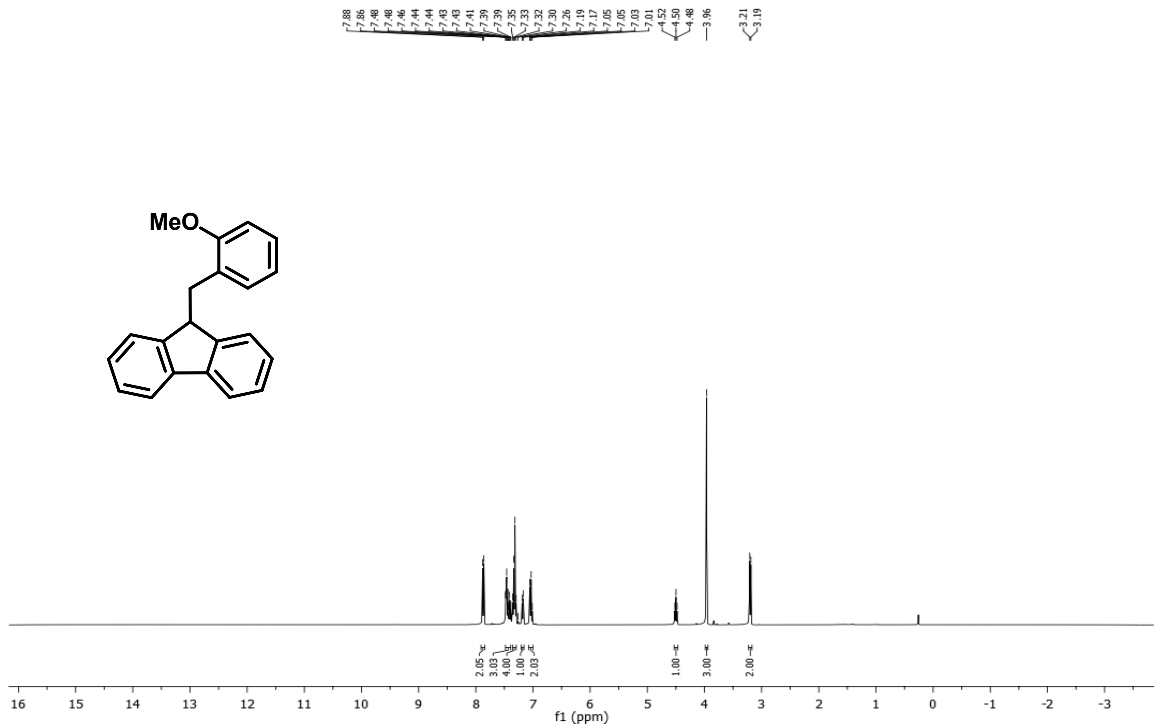


Figure S16. ^{1}H NMR spectrum (400 MHz) of 2g in $CDCl_3$

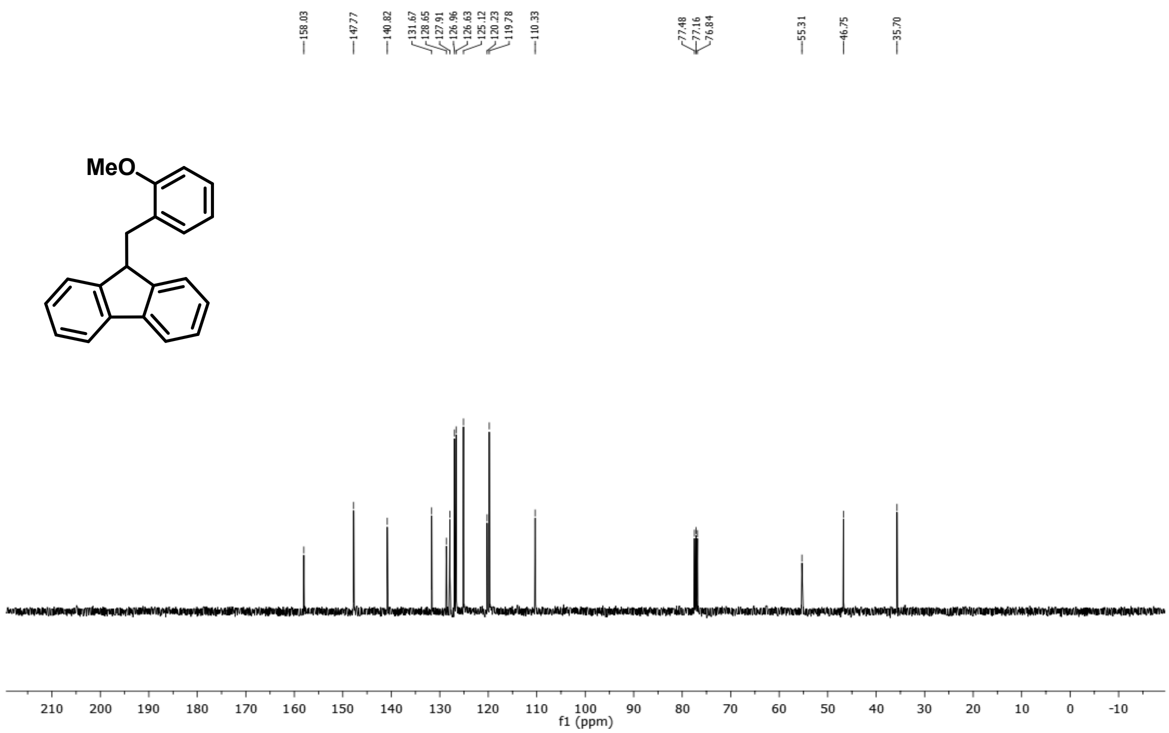


Figure S17. ^{13}C NMR spectrum (100 MHz) of 2g in $CDCl_3$

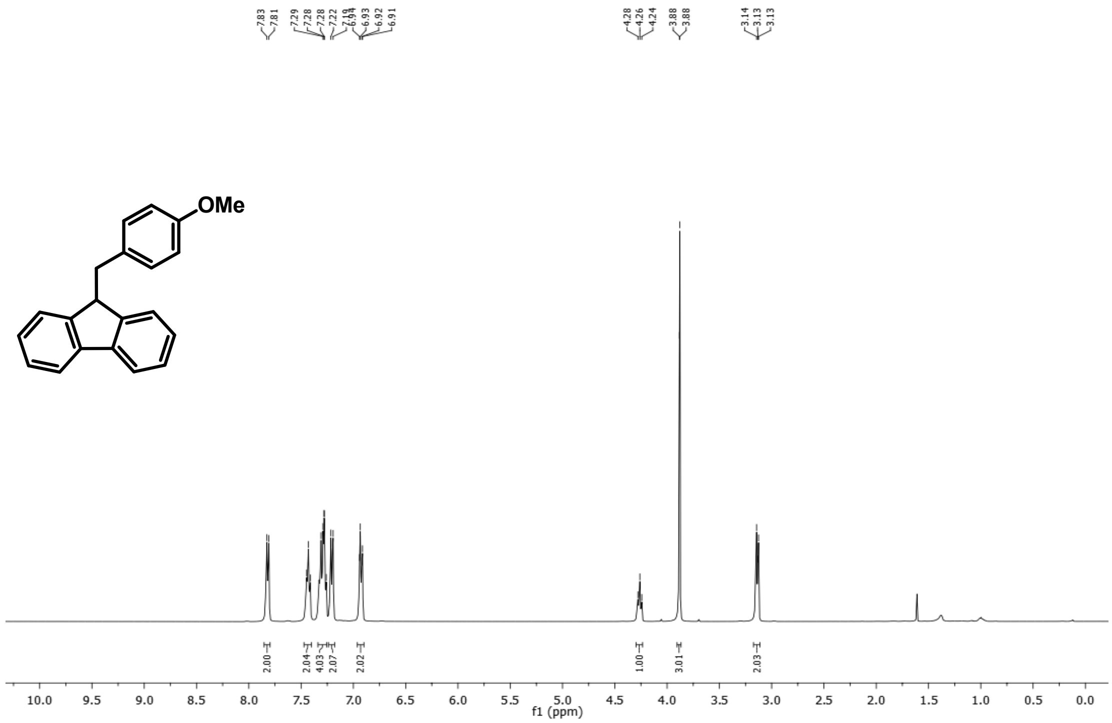


Figure S18. ^{1}H NMR spectrum (400 MHz) of 2h in $CDCl_3$

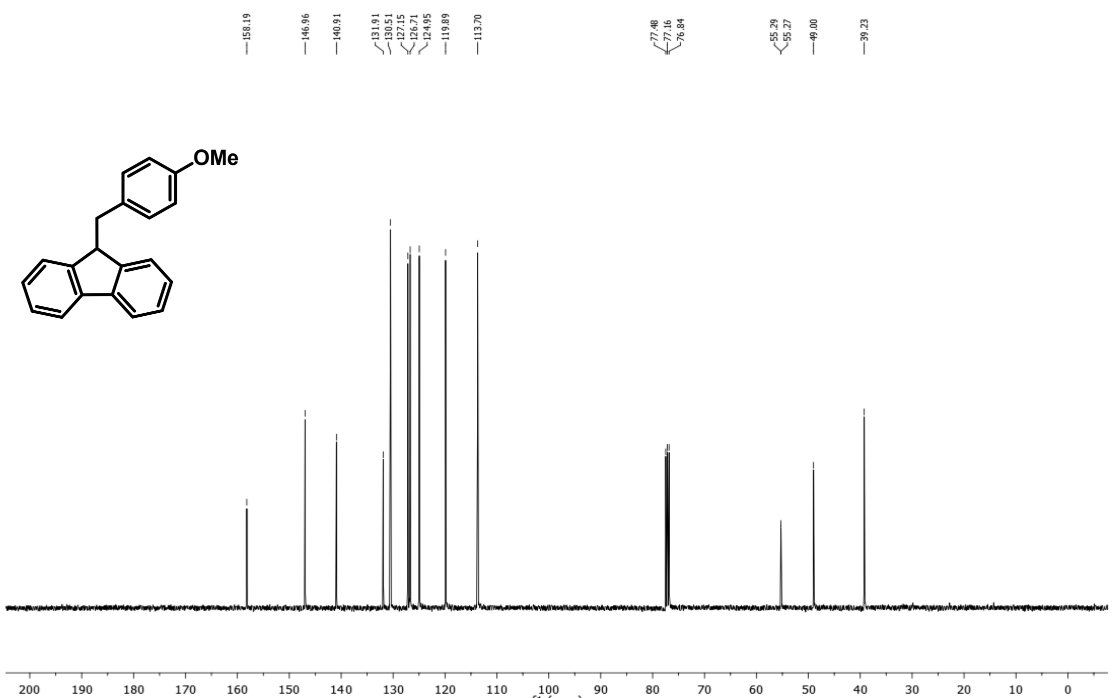


Figure S19. ^{13}C NMR spectrum (100 MHz) of 2h in $CDCl_3$

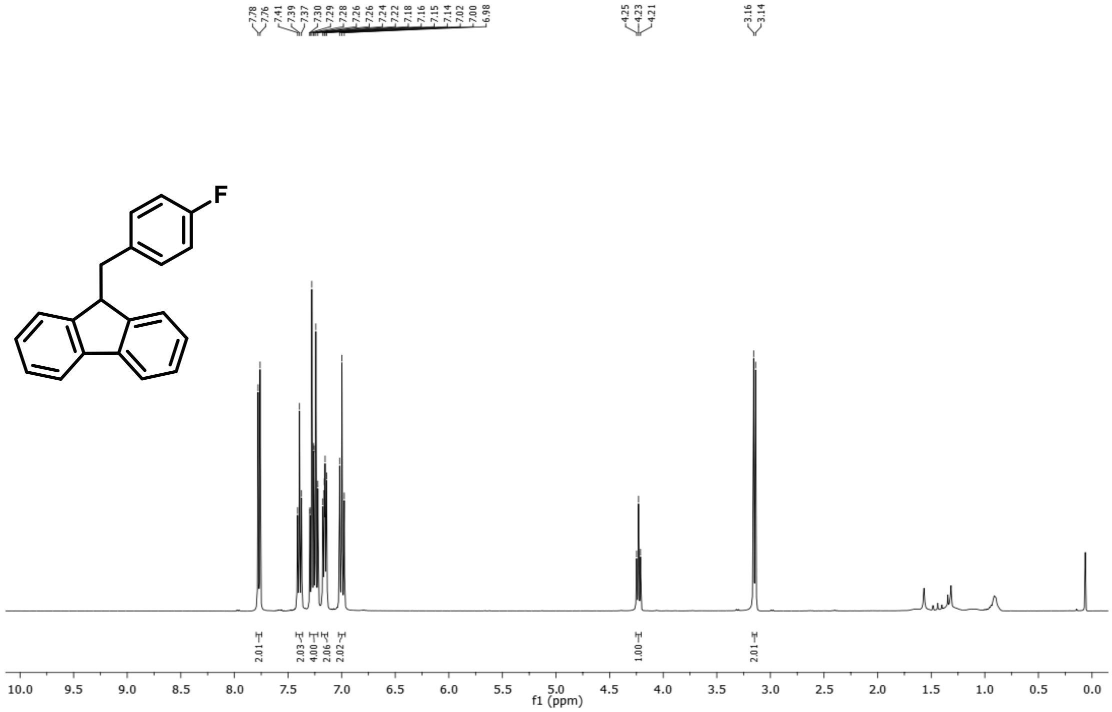


Figure S20. ^{1}H NMR spectrum (400 MHz) of 2i in $CDCl_3$

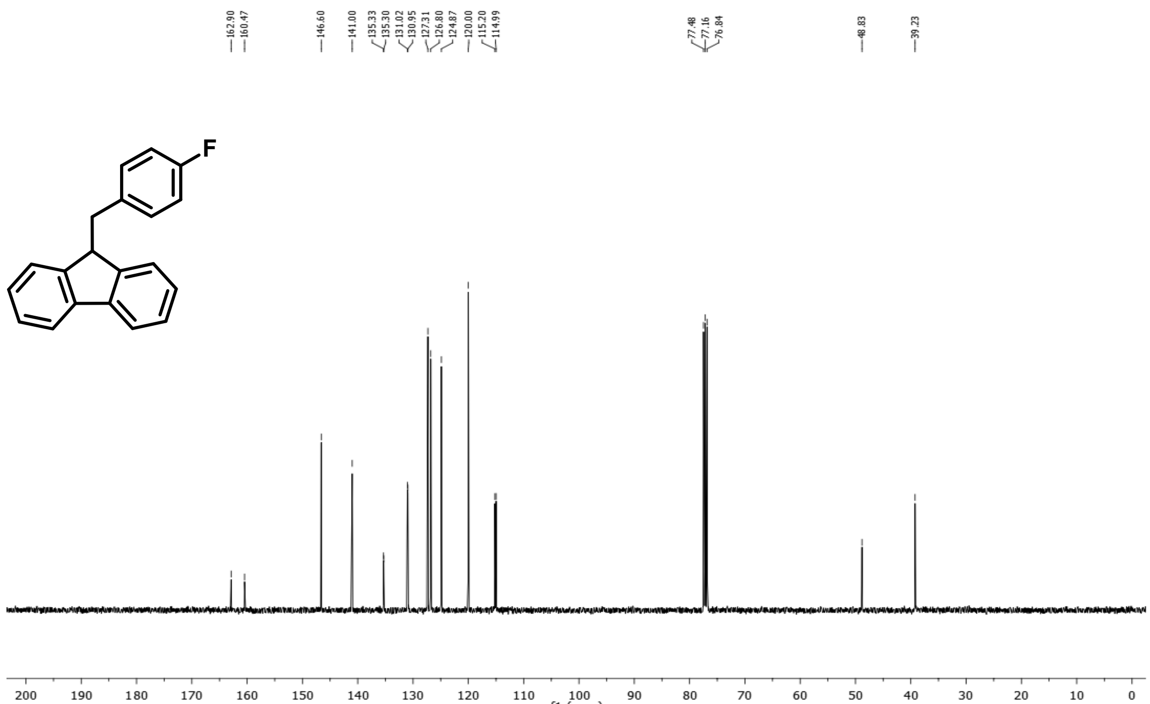


Figure S21. ^{13}C NMR spectrum (100 MHz) of 2i in $CDCl_3$

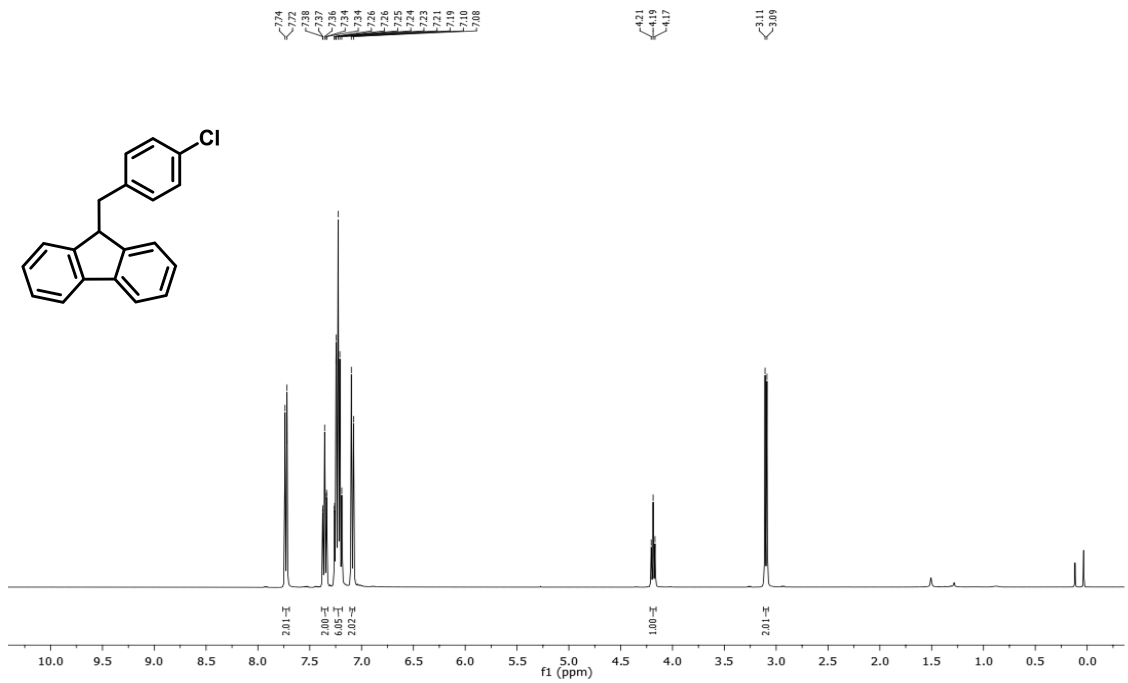


Figure S22. ^{1}H NMR spectrum (400 MHz) of 2j in $CDCl_3$

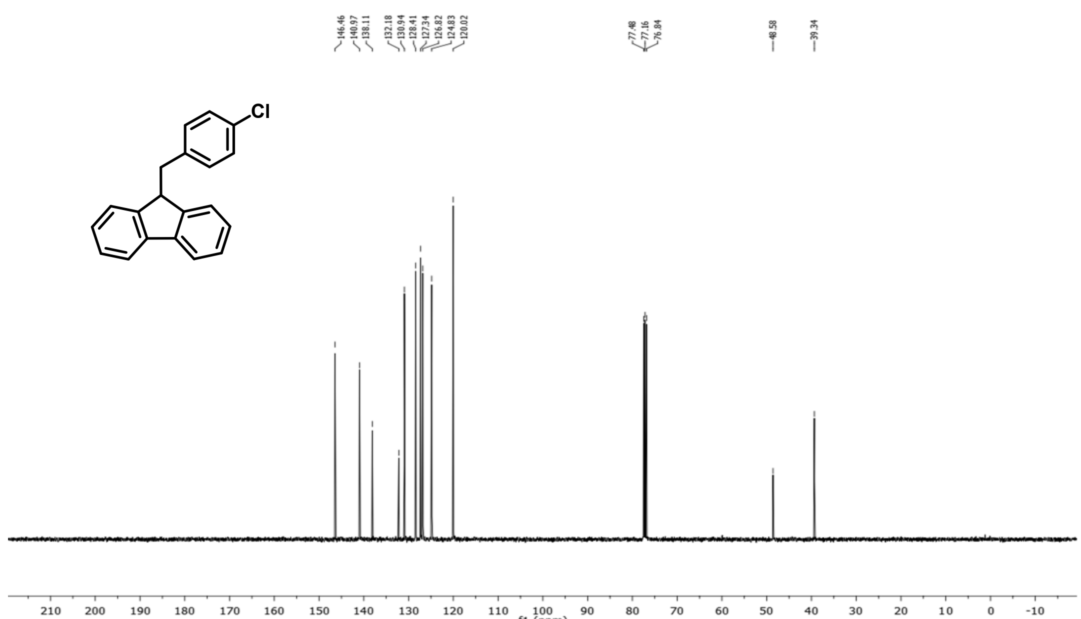


Figure S23. ^{13}C NMR spectrum (100 MHz) of 2j in $CDCl_3$

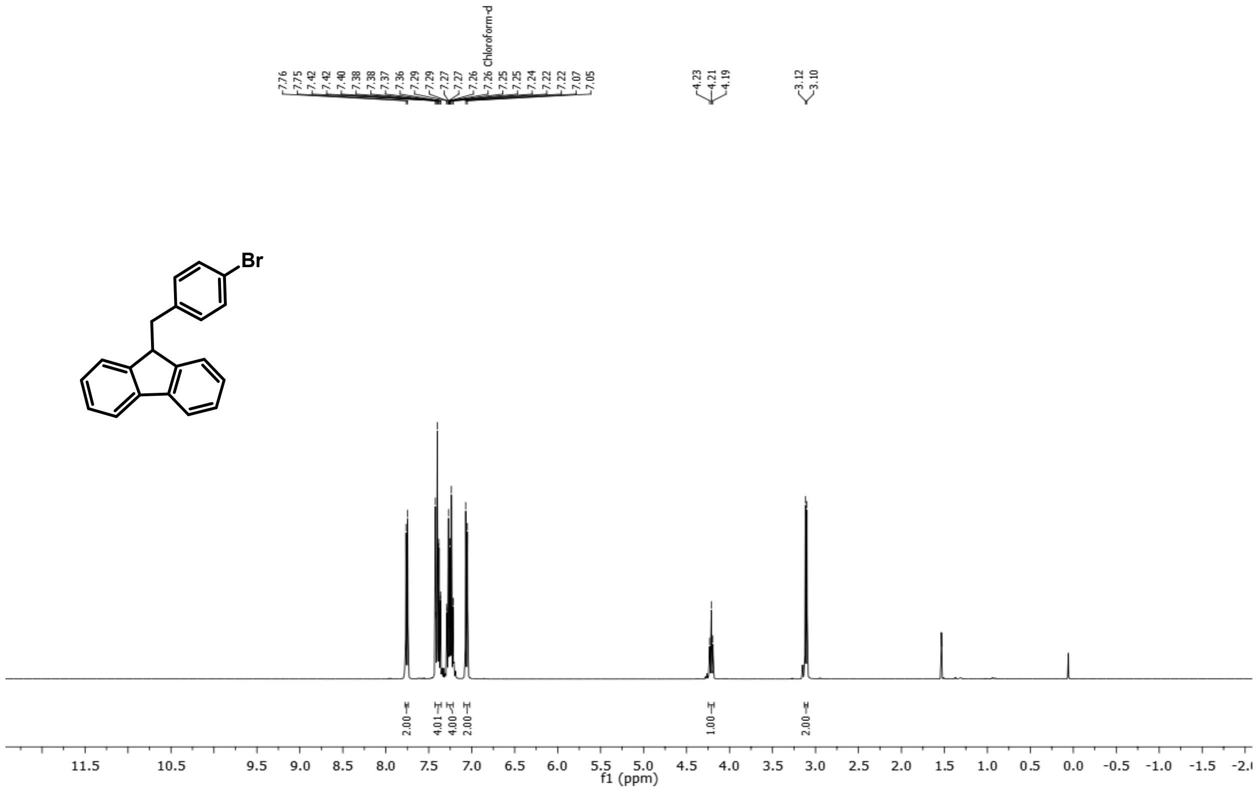


Figure S24. [1]H NMR spectrum (400 MHz) of 2k in $CDCl_3$

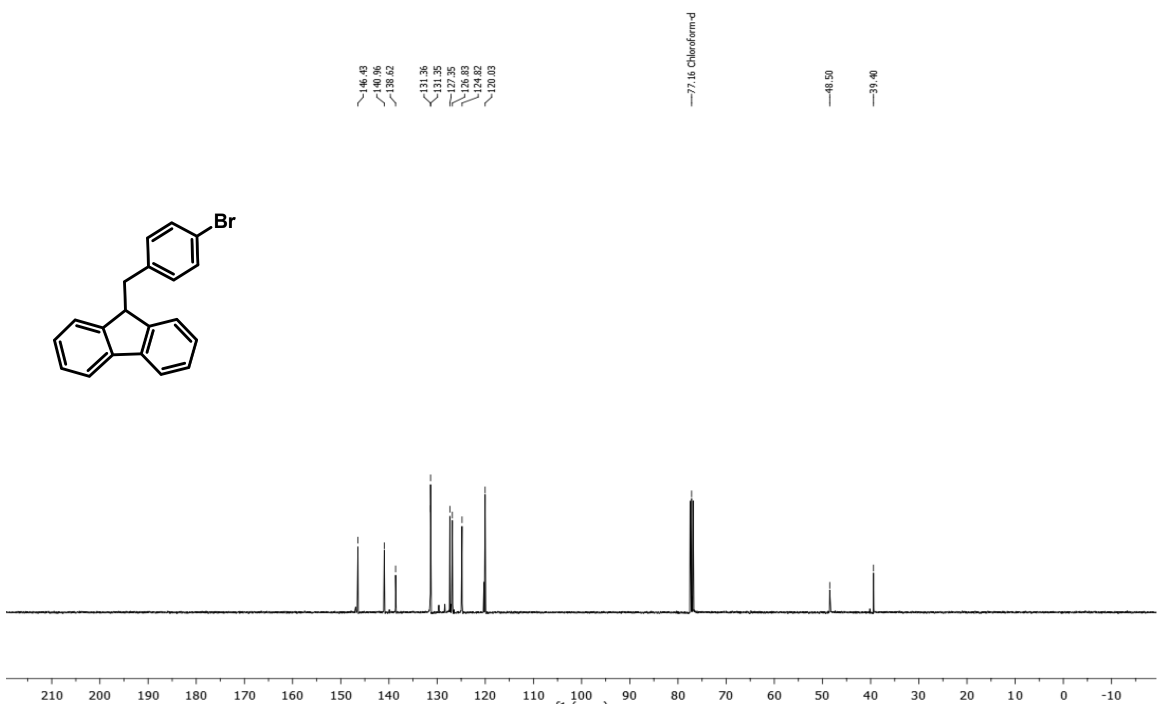


Figure S25. [13]C NMR spectrum (100 MHz) of 2k in $CDCl_3$

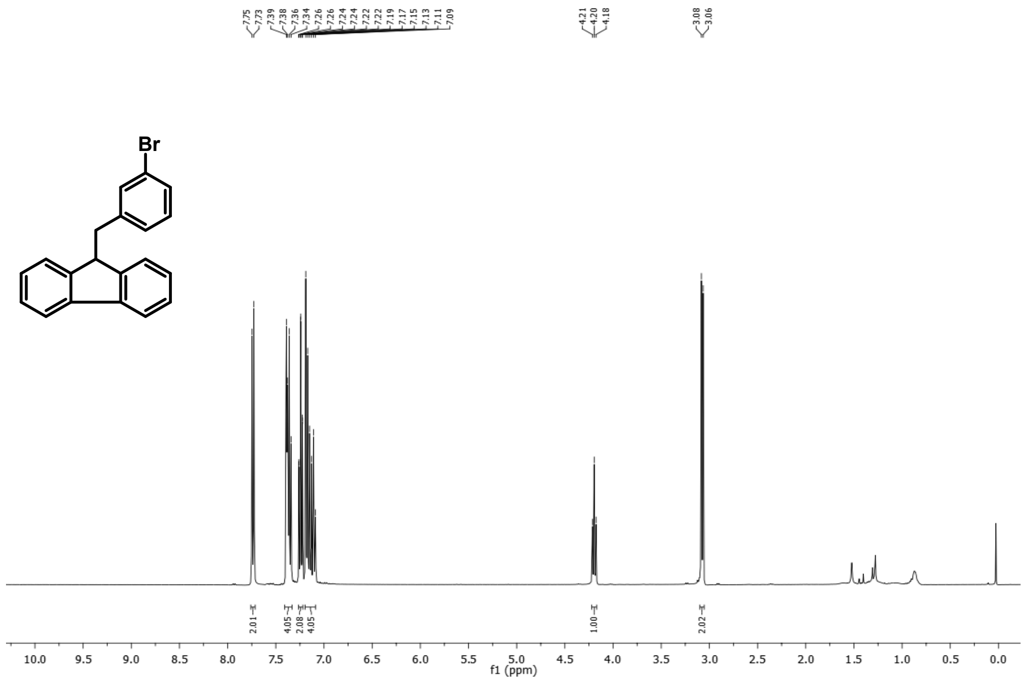


Figure S26. ^{1}H NMR spectrum (400 MHz) of 2l in $CDCl_3$

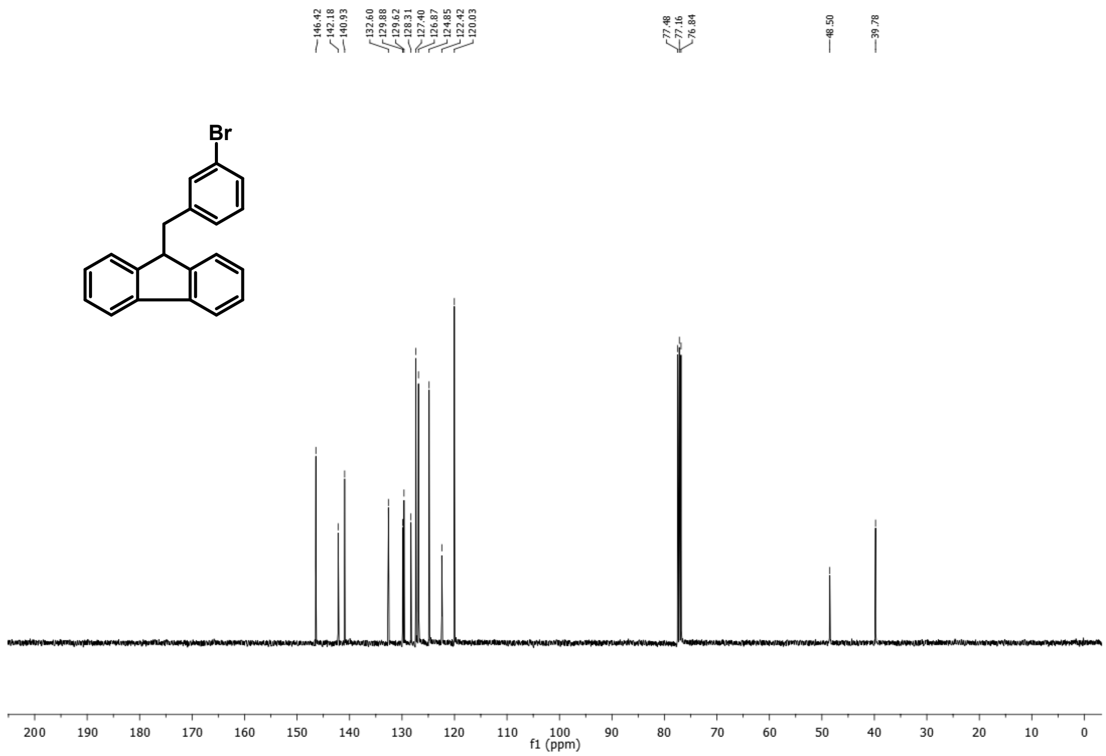


Figure S27. ^{13}C NMR spectrum (100 MHz) of 2l in $CDCl_3$

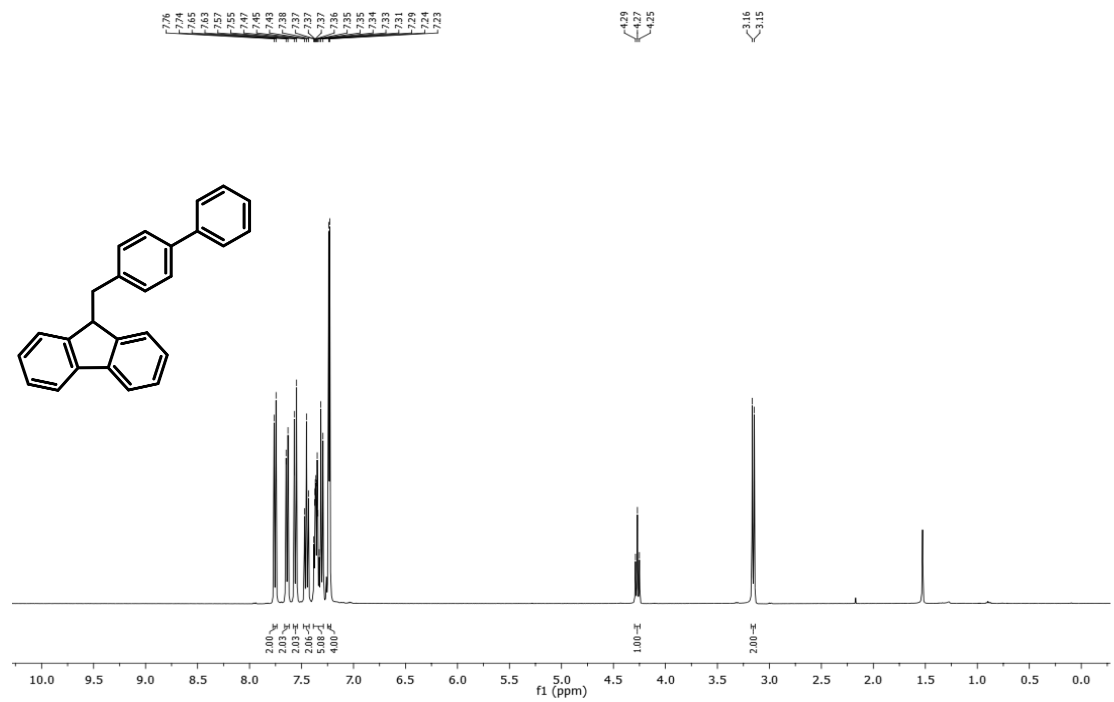


Figure S28. ^{1}H NMR spectrum (400 MHz) of 2m in $CDCl_3$

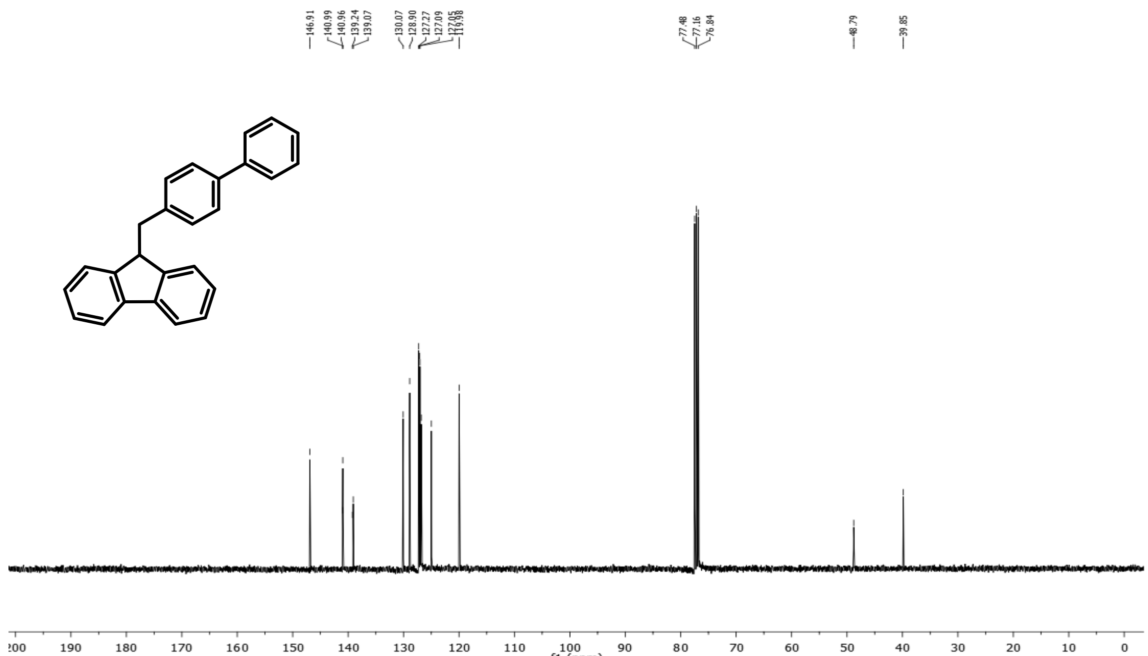


Figure S29. ^{13}C NMR spectrum (100 MHz) of 2m in $CDCl_3$

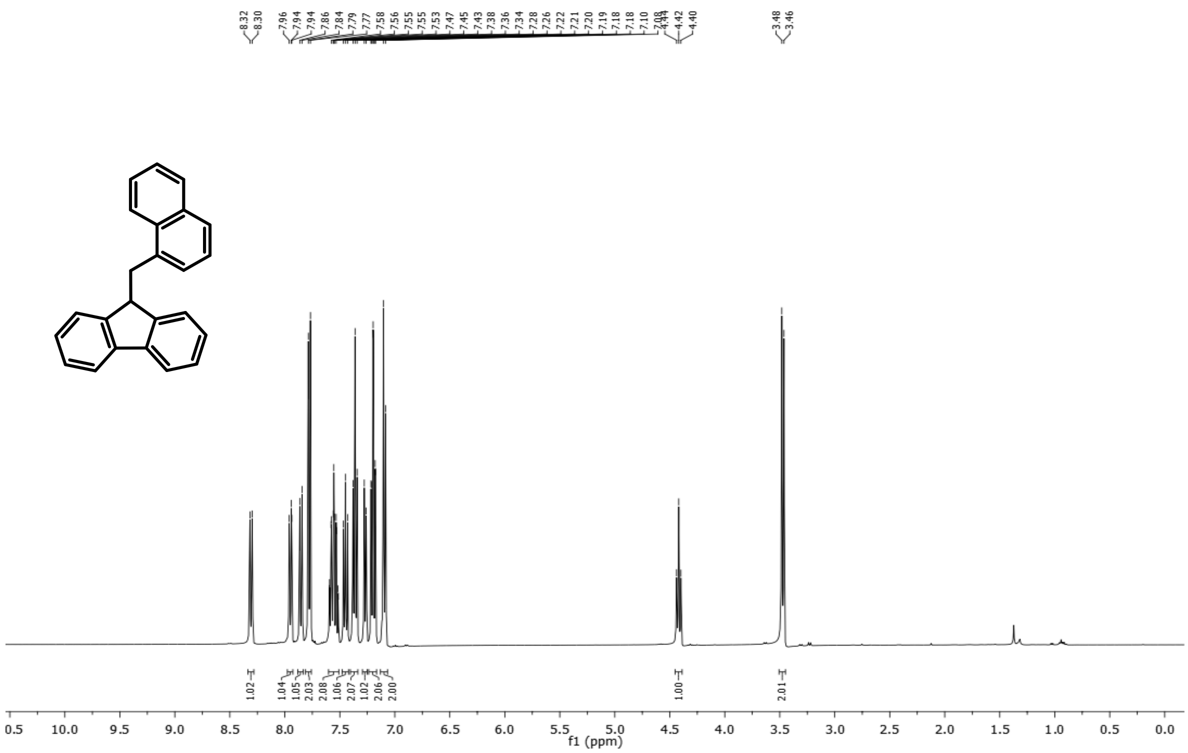


Figure S30. ^{1}H NMR spectrum (400 MHz) of 2n in $CDCl_3$

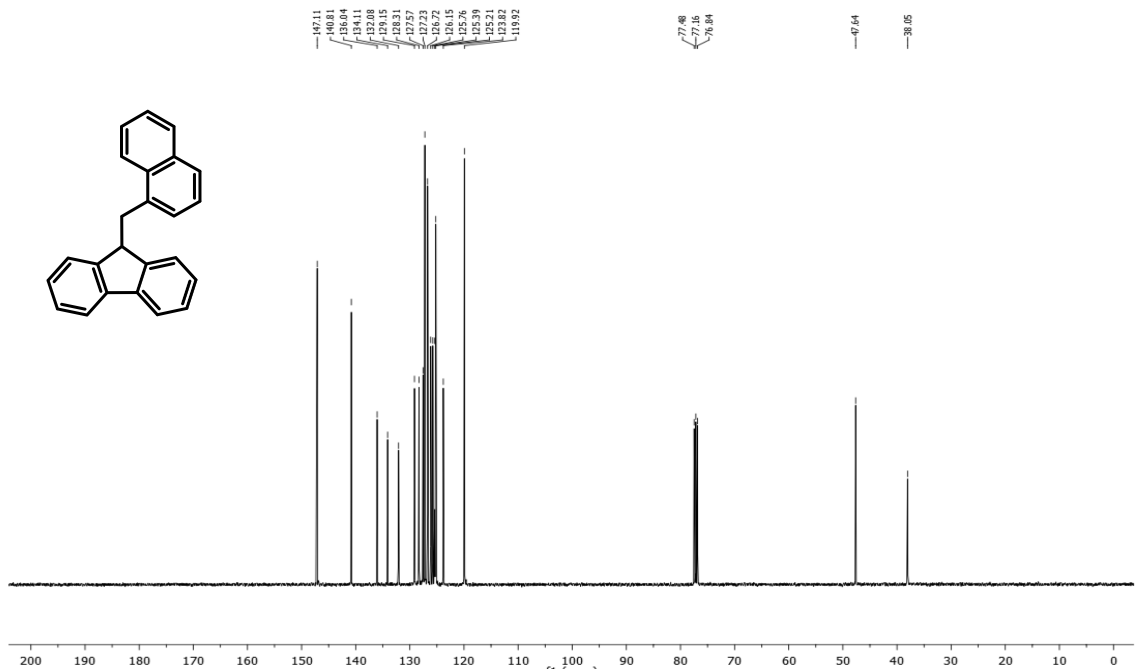


Figure S31. ^{13}C NMR spectrum (100 MHz) of 2n in $CDCl_3$

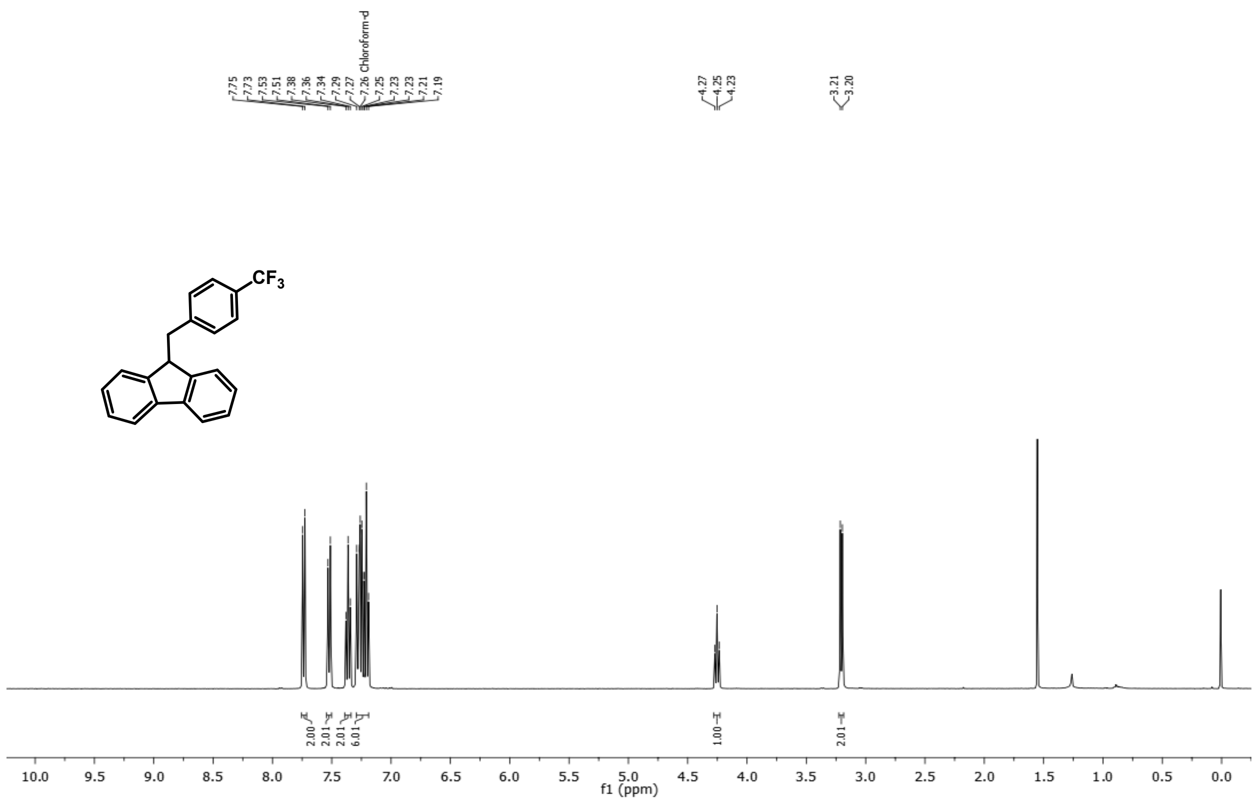


Figure S32. ^{1}H NMR spectrum (400 MHz) of 2o in $CDCl_3$

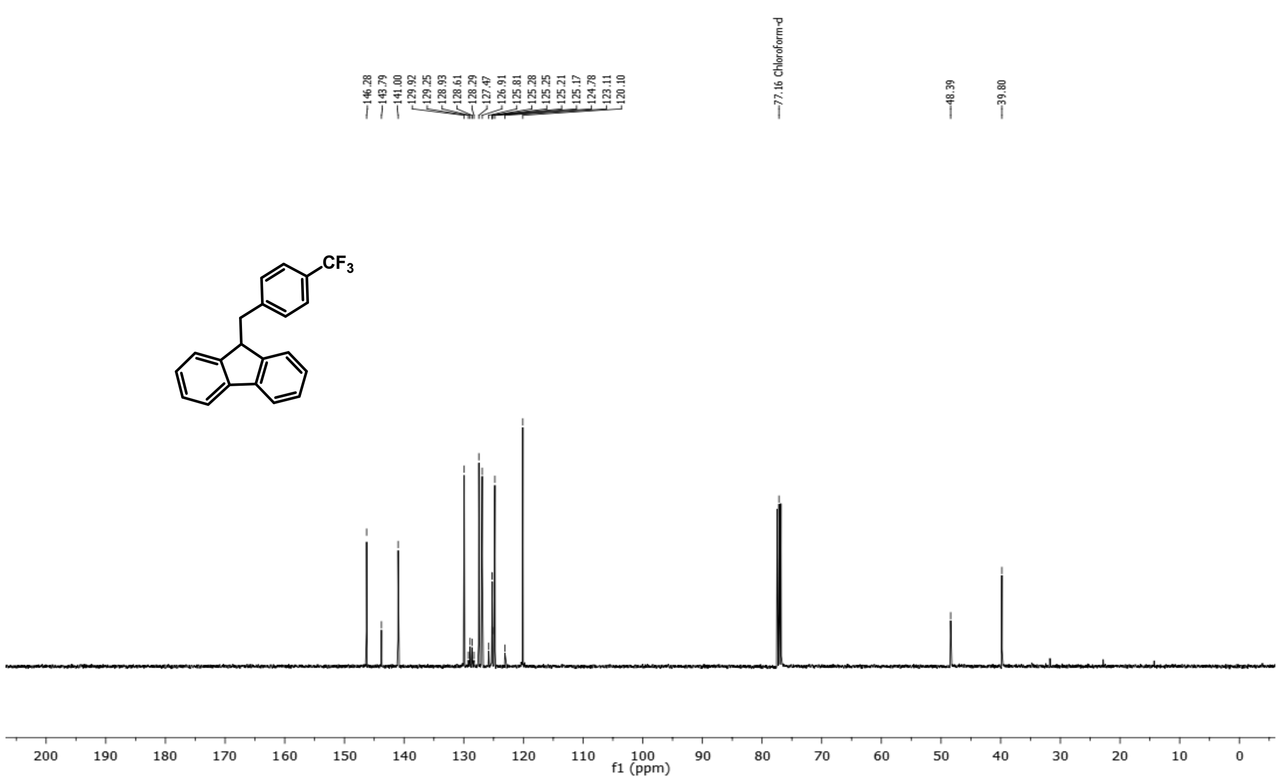


Figure S33. ^{13}C NMR spectrum (100 MHz) of 2o in $CDCl_3$

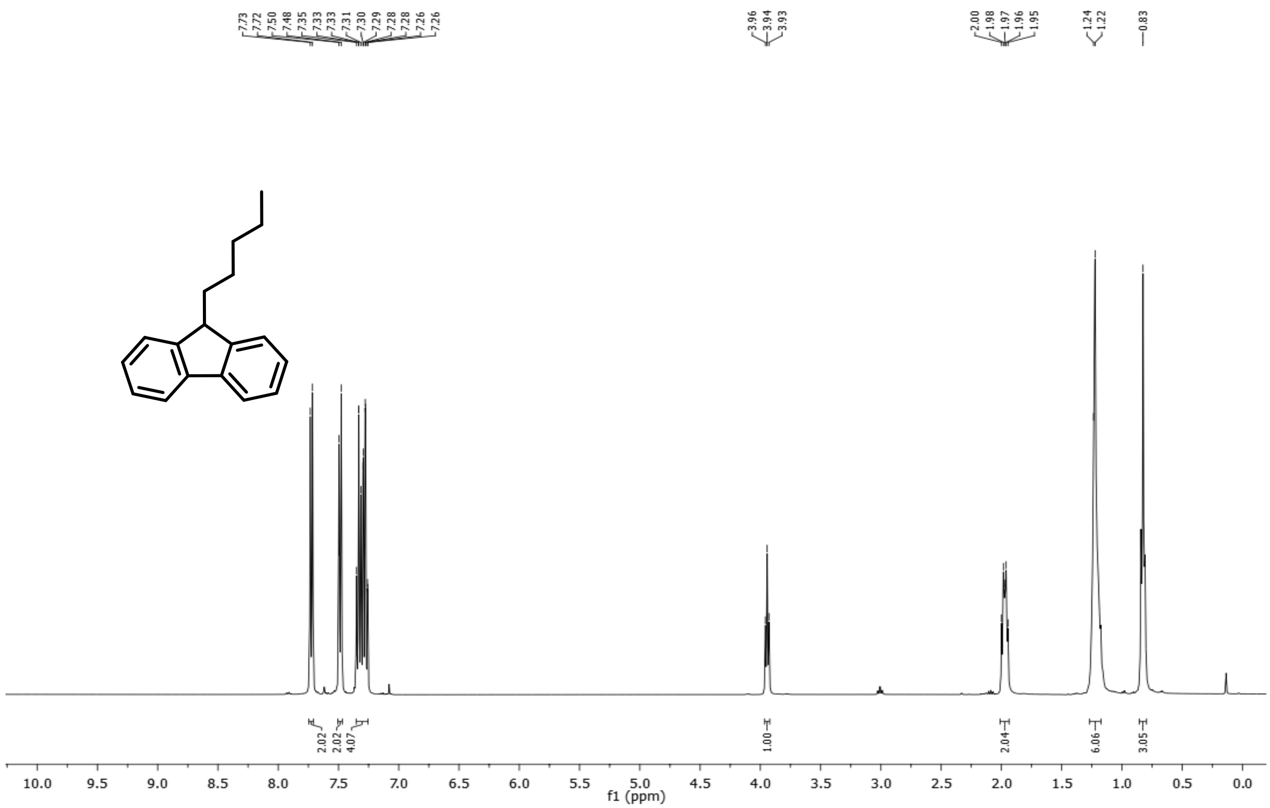


Figure S34. ^{1}H NMR spectrum (400 MHz) of 3a in $CDCl_3$

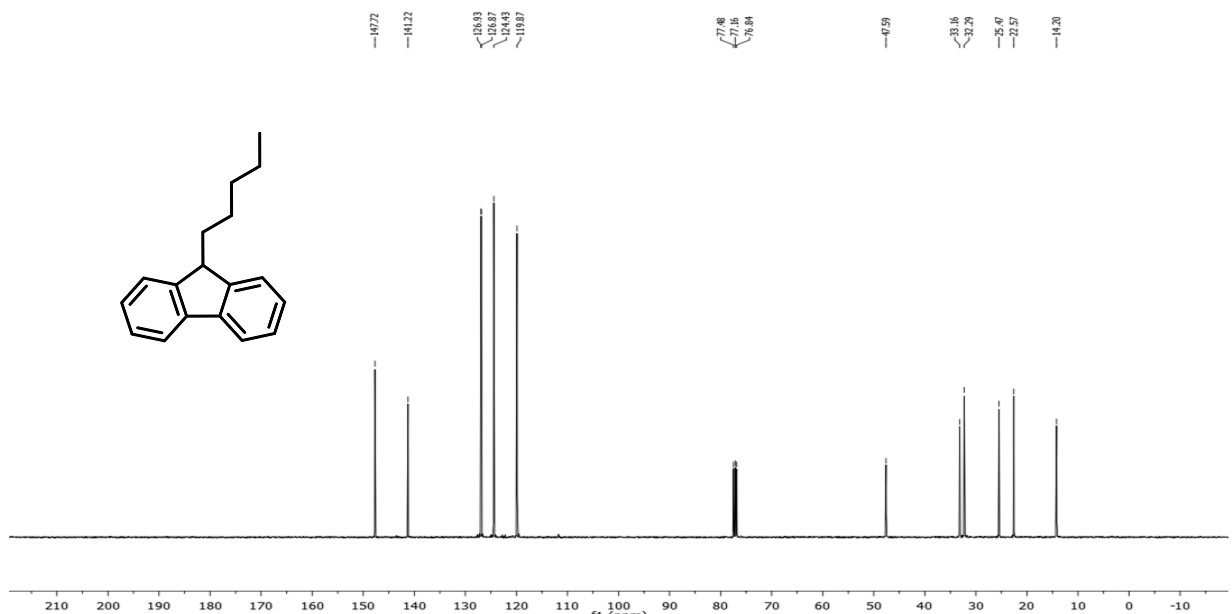


Figure S35. ^{13}C NMR spectrum (100 MHz) of 3a in $CDCl_3$

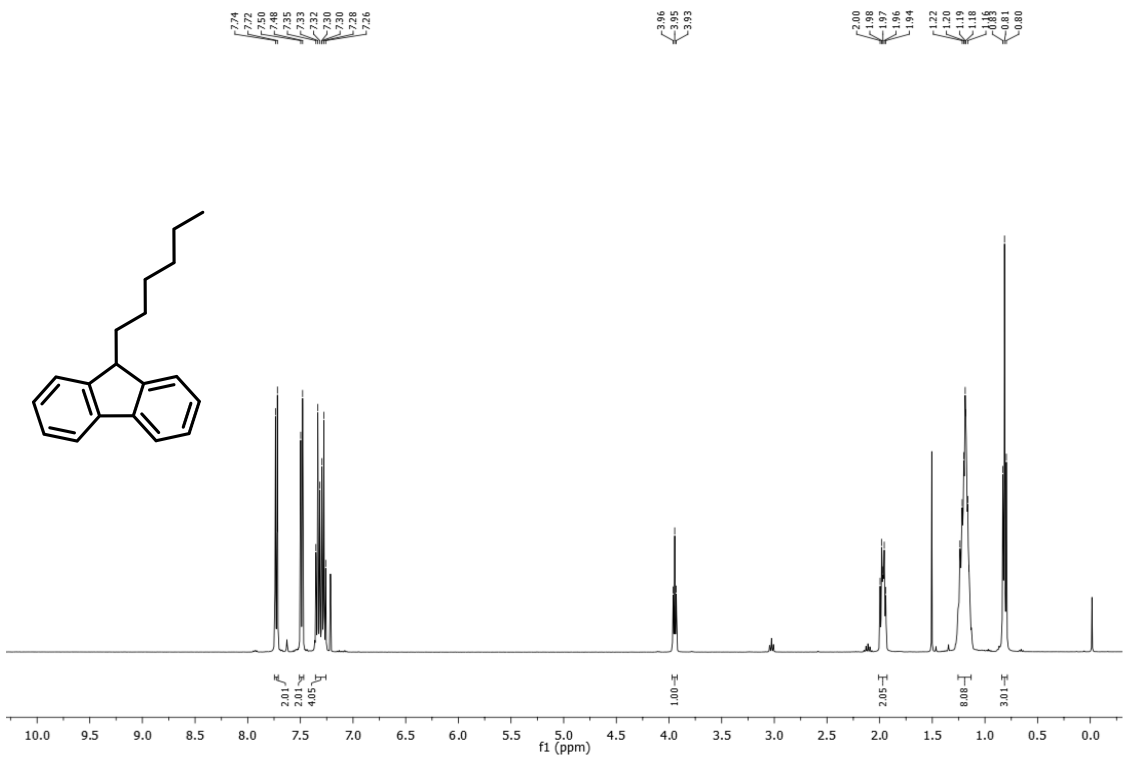


Figure S36. **^{1}H NMR spectrum (400 MHz) of 3b in $CDCl_3$**

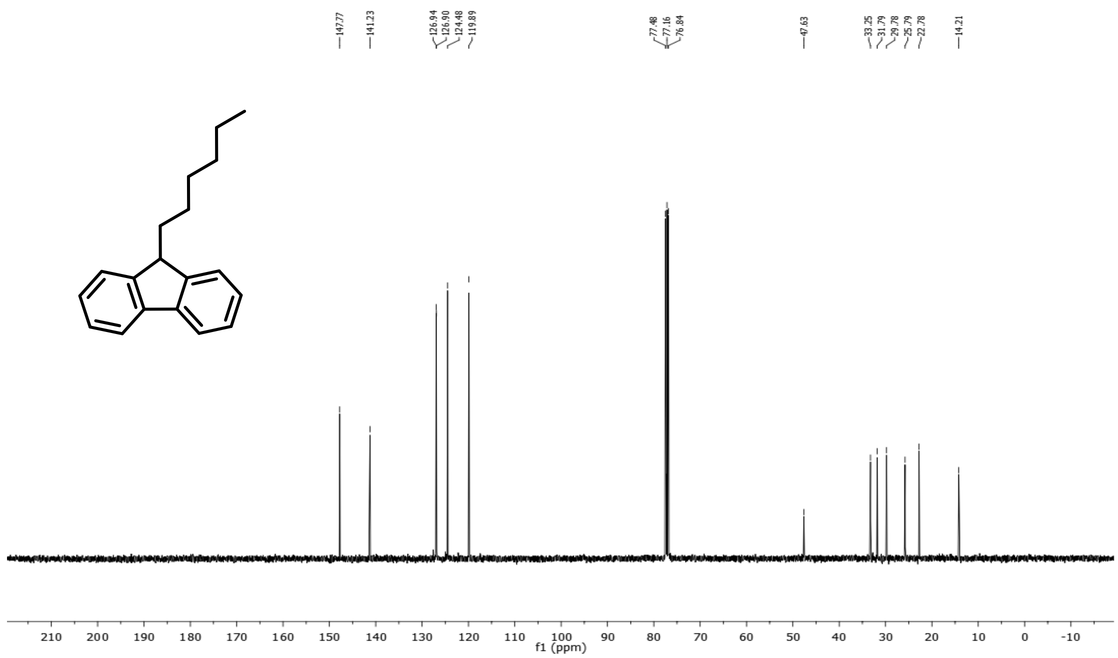


Figure S37. **^{13}C NMR spectrum (100 MHz) of 3b in $CDCl_3$**

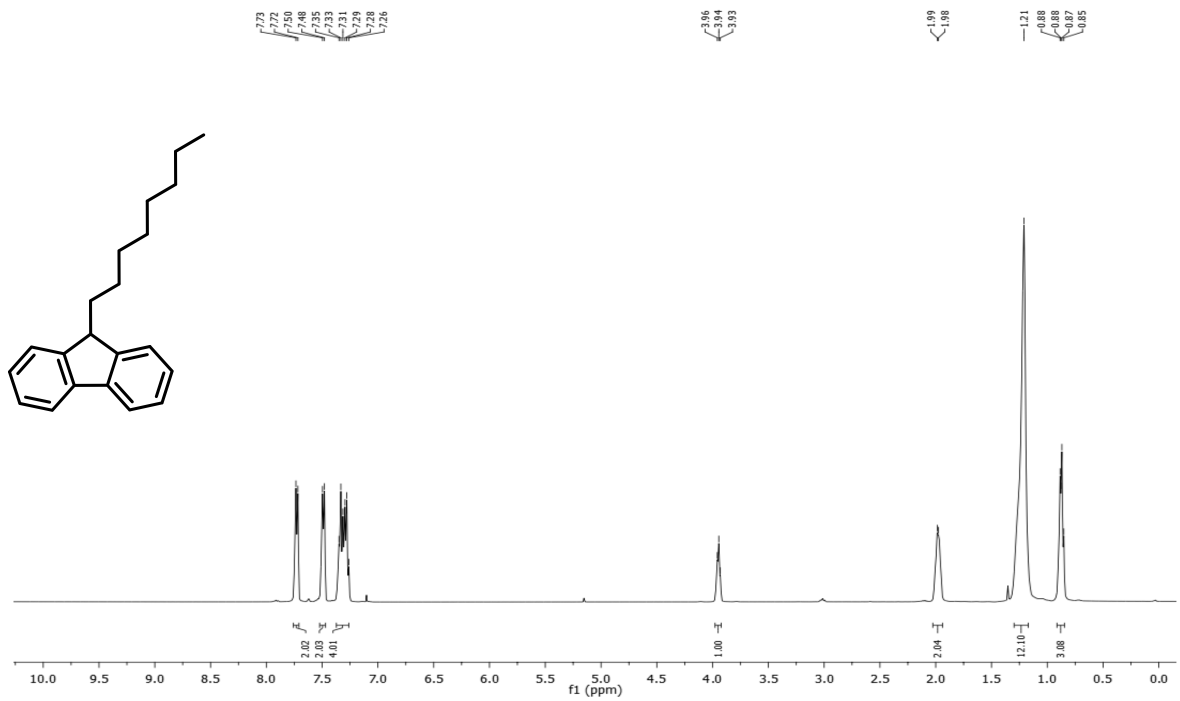


Figure S38. **^{1}H NMR spectrum (400 MHz) of 3c in $CDCl_3$**

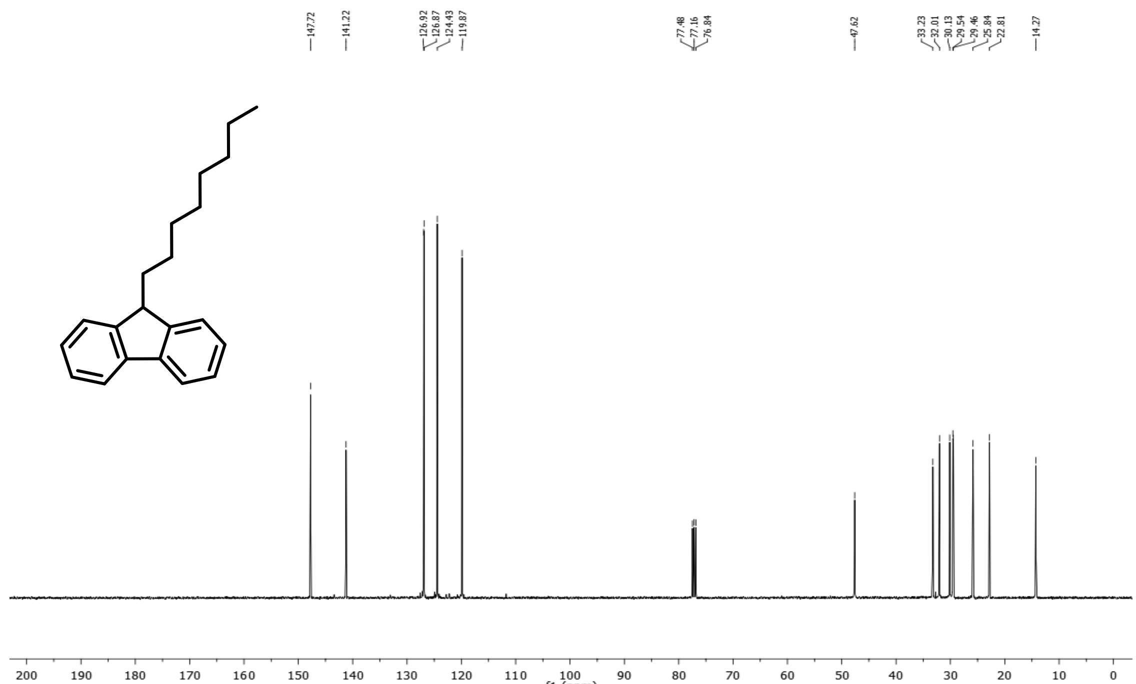


Figure S39. **^{13}C NMR spectrum (100 MHz) of 3c in $CDCl_3$**

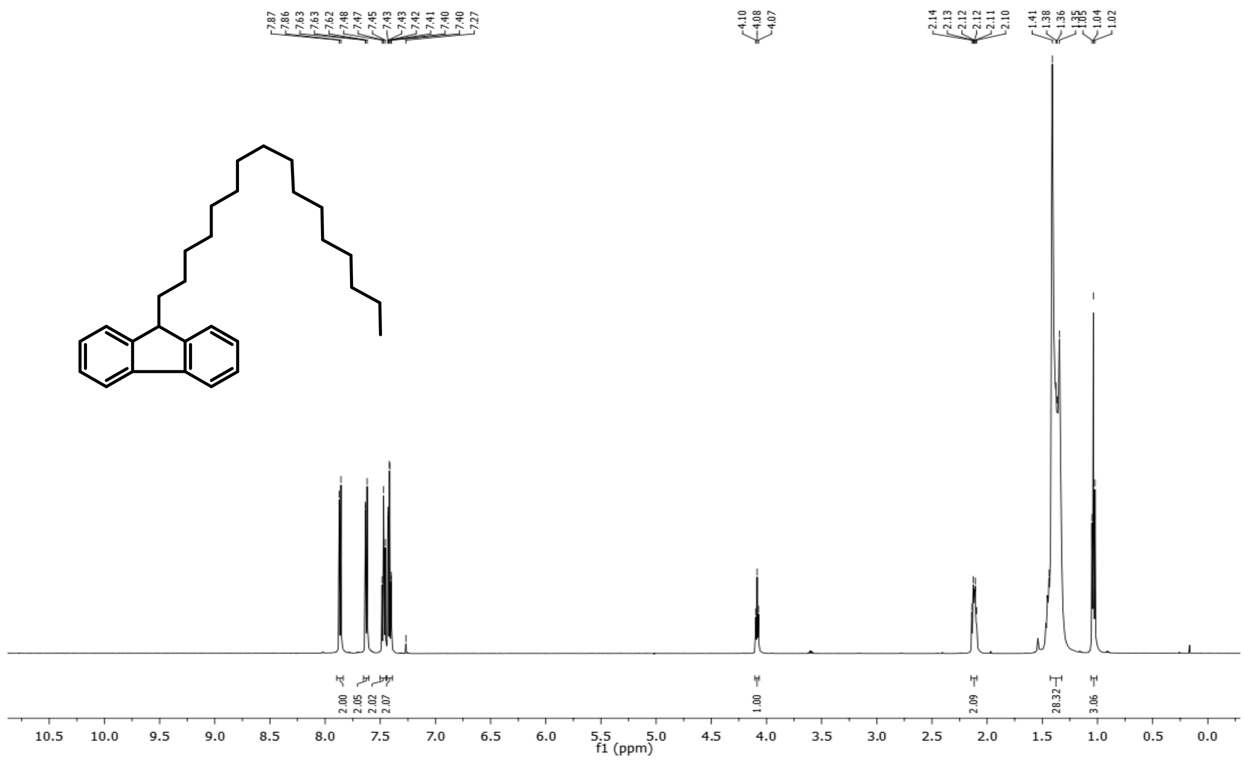


Figure S40. ^{1}H NMR spectrum (400 MHz) of 3d in $CDCl_3$

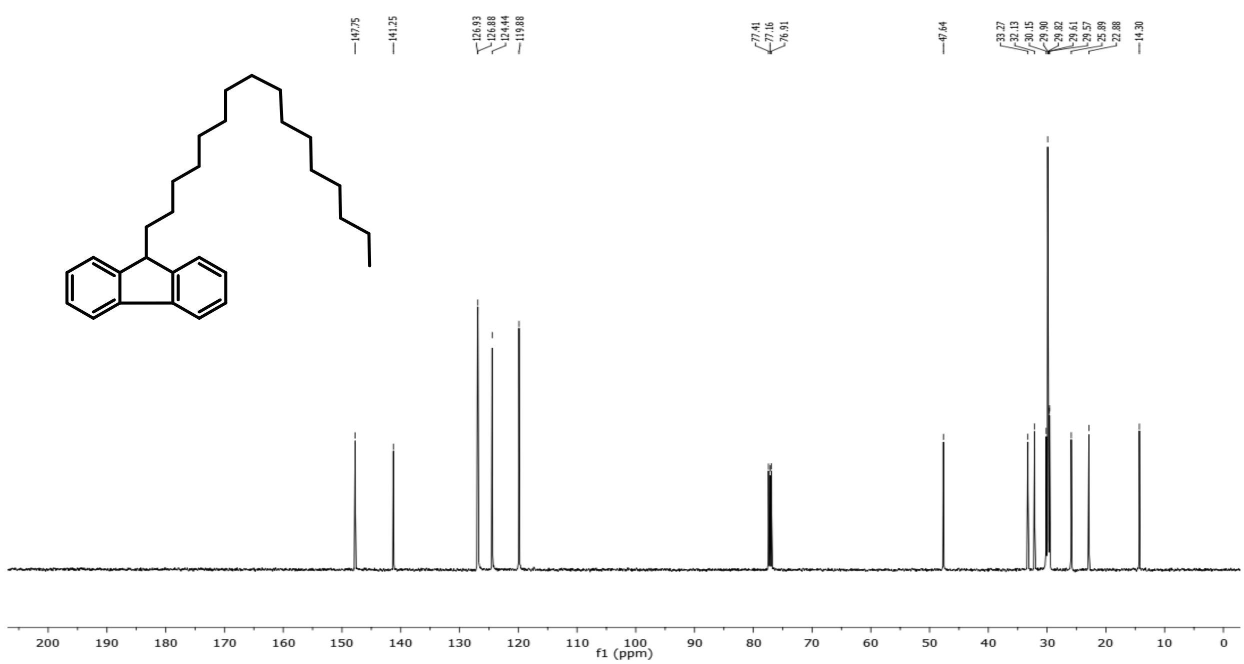


Figure S41. ^{13}C NMR spectrum (100 MHz) of 3d in $CDCl_3$

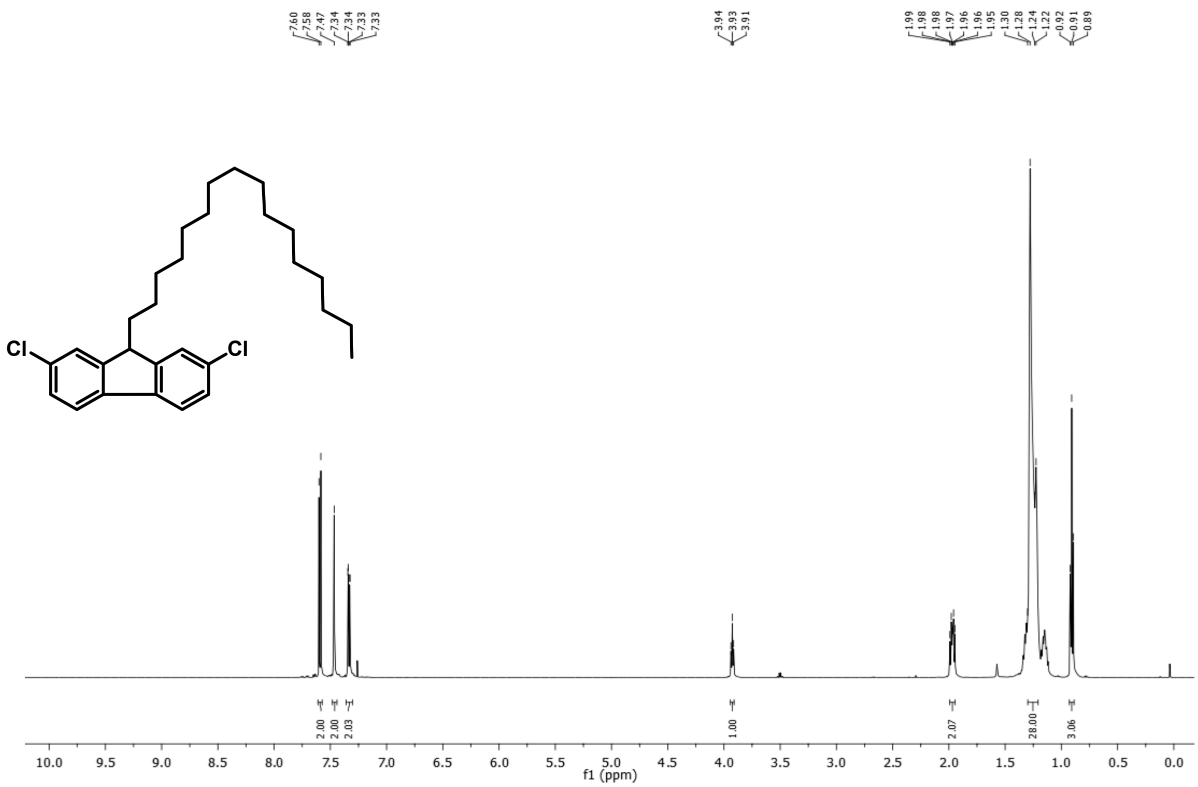


Figure S42. ^{1}H **NMR spectrum (400 MHz) of 3e in** $CDCl_3$

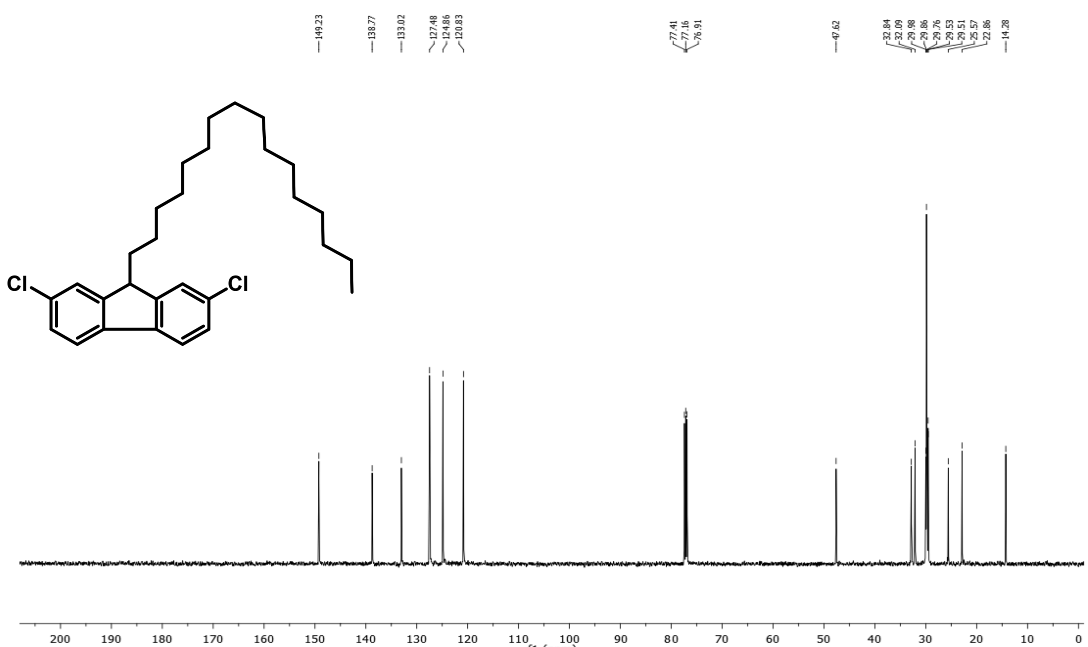


Figure S43. ^{13}C **NMR spectrum (100 MHz) of 3e in** $CDCl_3$

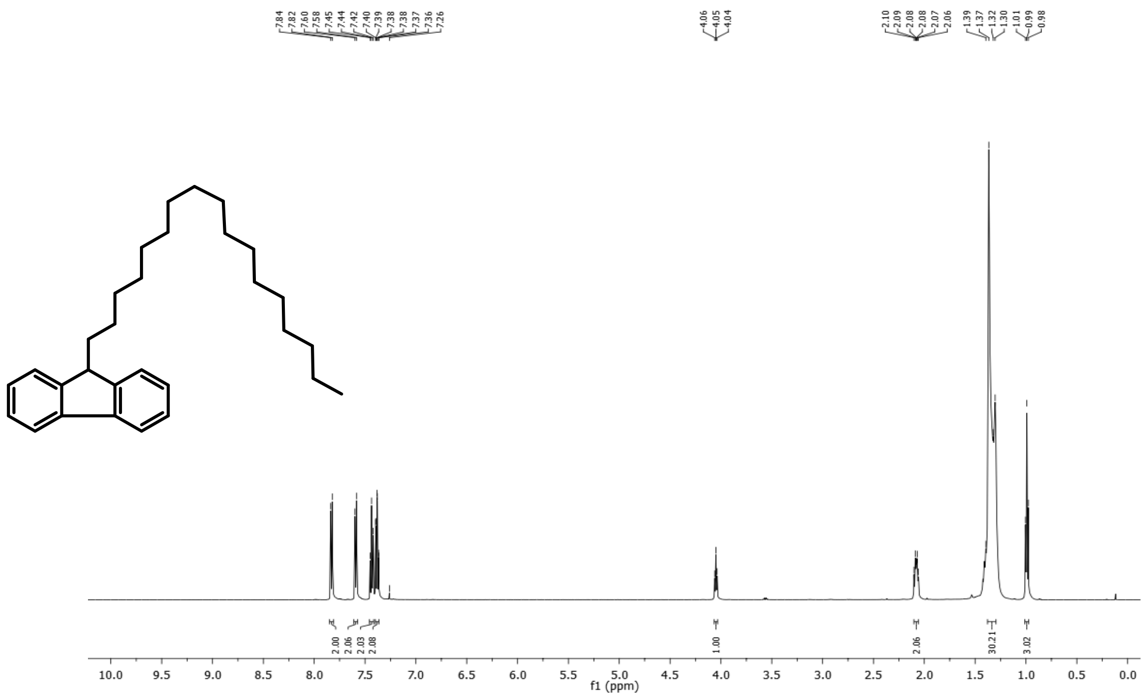


Figure S44. ^{1}H NMR spectrum (400 MHz) of 3f in $CDCl_3$

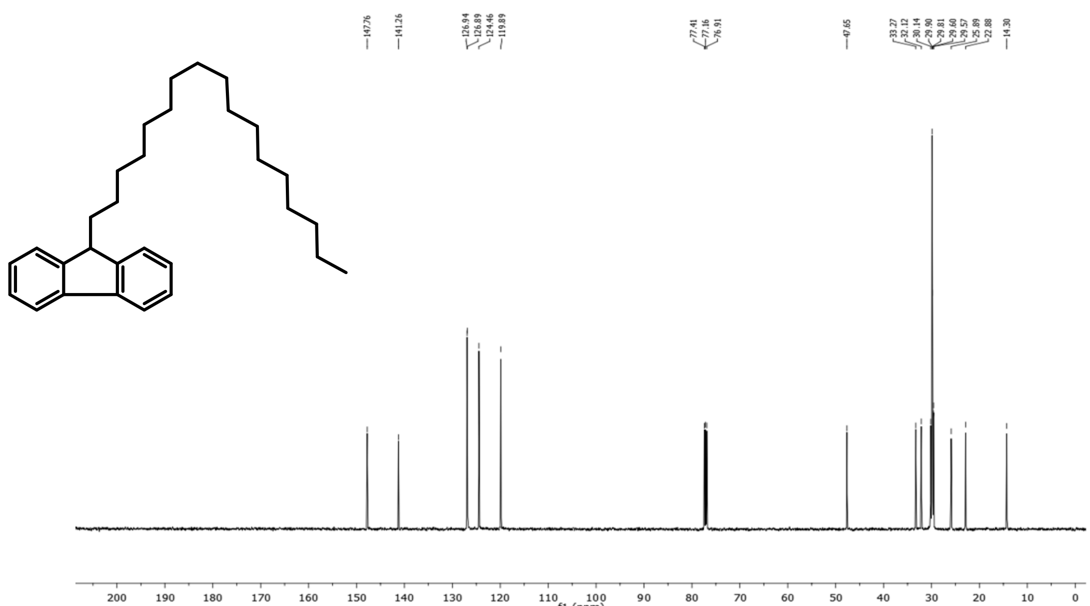


Figure S45. ^{13}C NMR spectrum (100 MHz) of 3f in $CDCl_3$

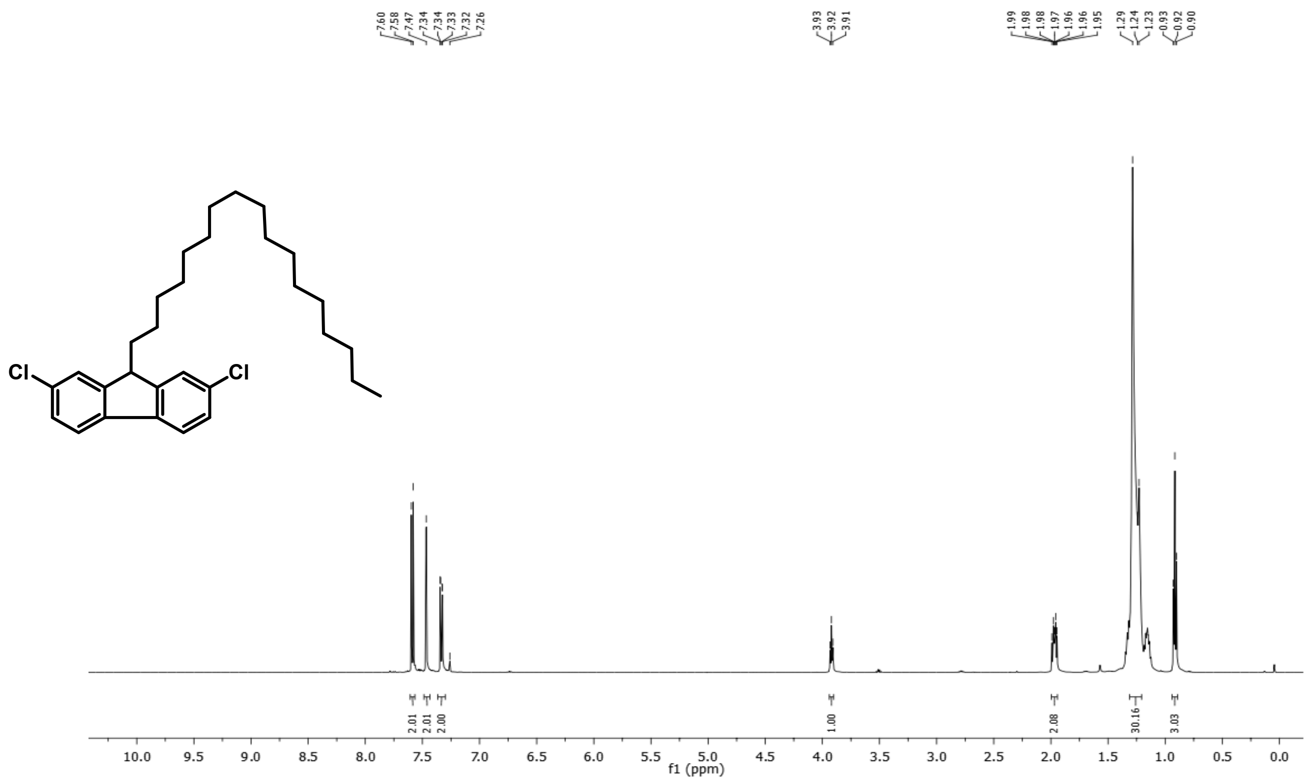


Figure S46. ^{1}H NMR spectrum (400 MHz) of 3g in $CDCl_3$

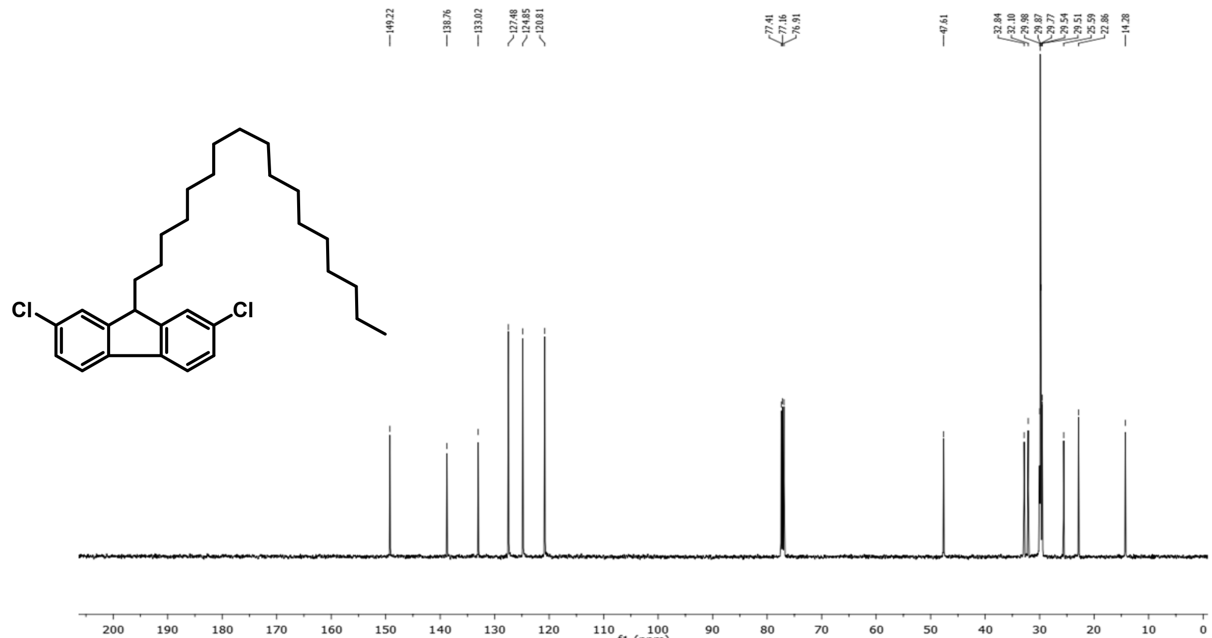


Figure S47. ^{13}C NMR spectrum (100 MHz) of 3g in $CDCl_3$

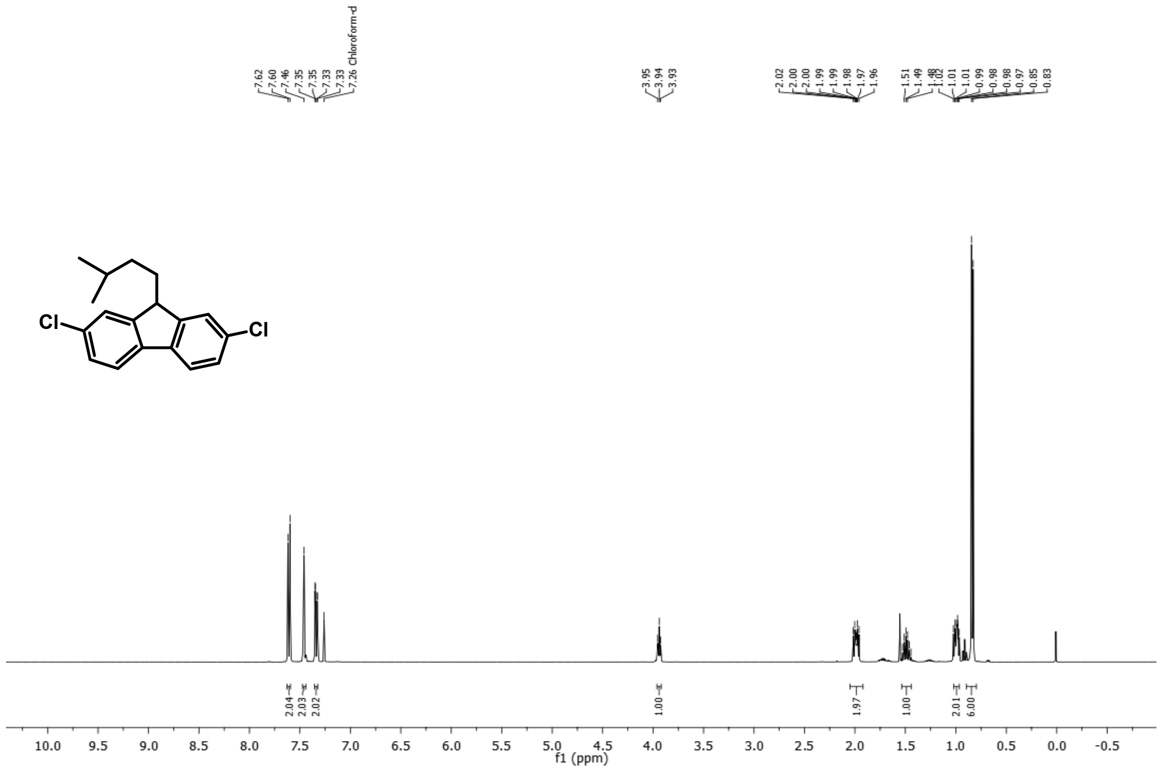


Figure S48. ^{1}H NMR spectrum (400 MHz) of 3h in $CDCl_3$

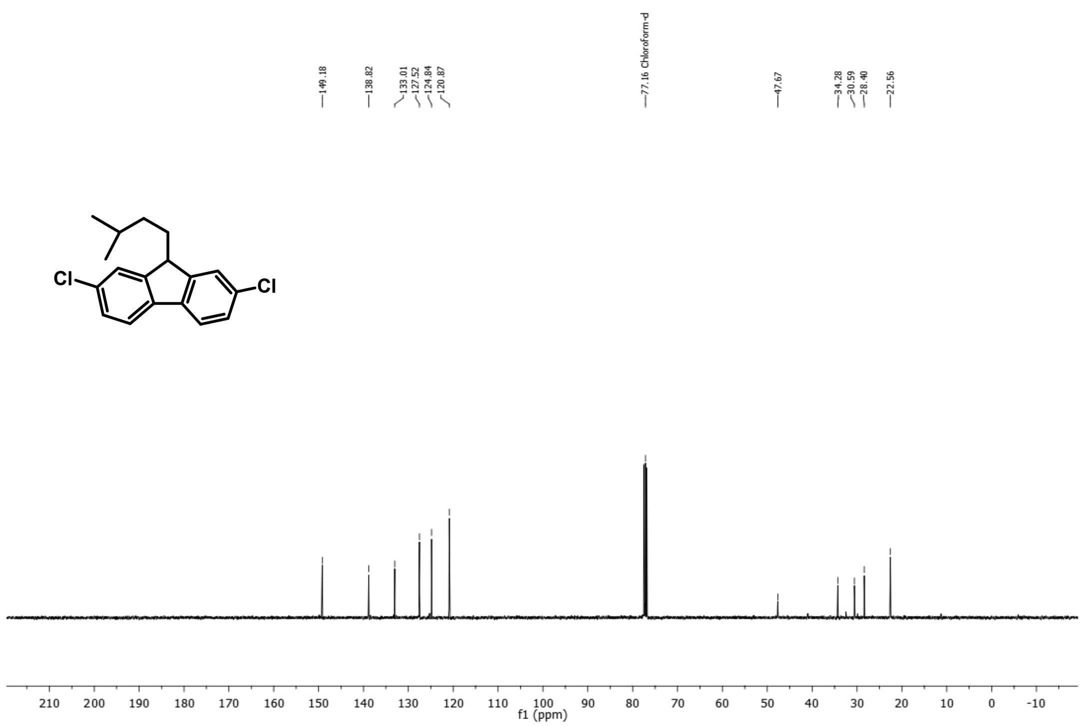


Figure S49. ^{13}C NMR spectrum (100 MHz) of 3h in $CDCl_3$

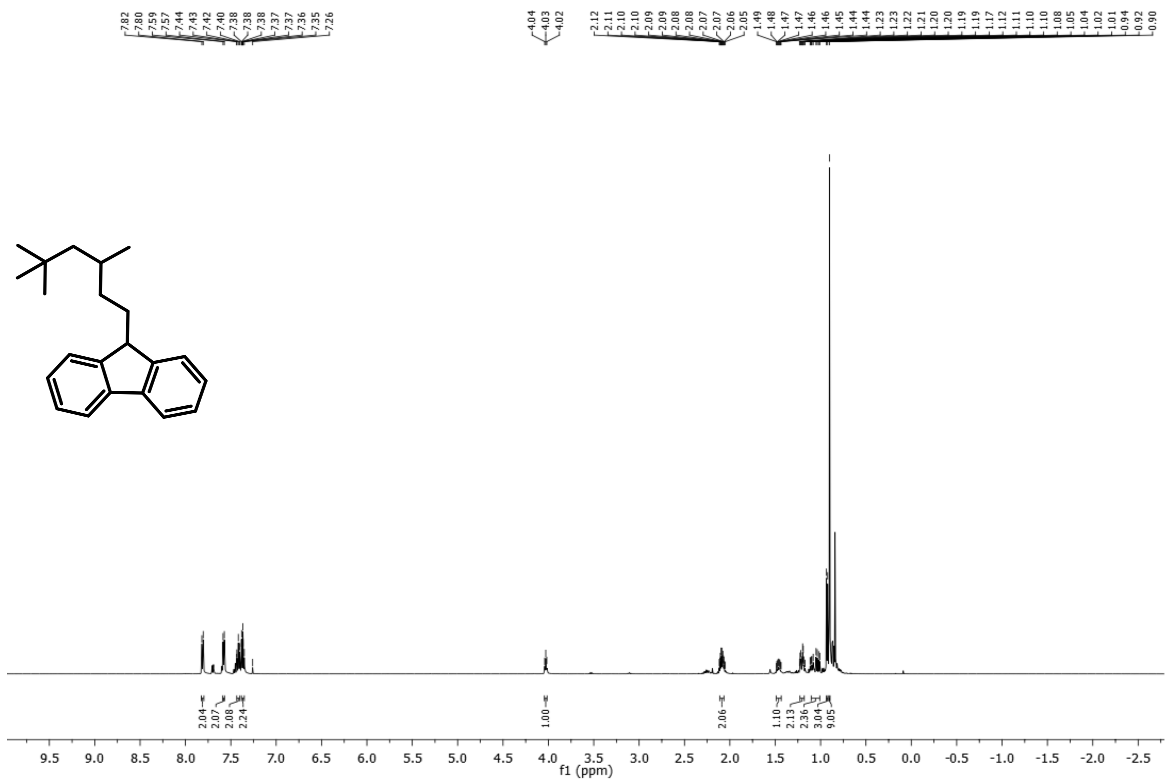


Figure S50. [1]H NMR spectrum (400 MHz) of 3i in $CDCl_3$

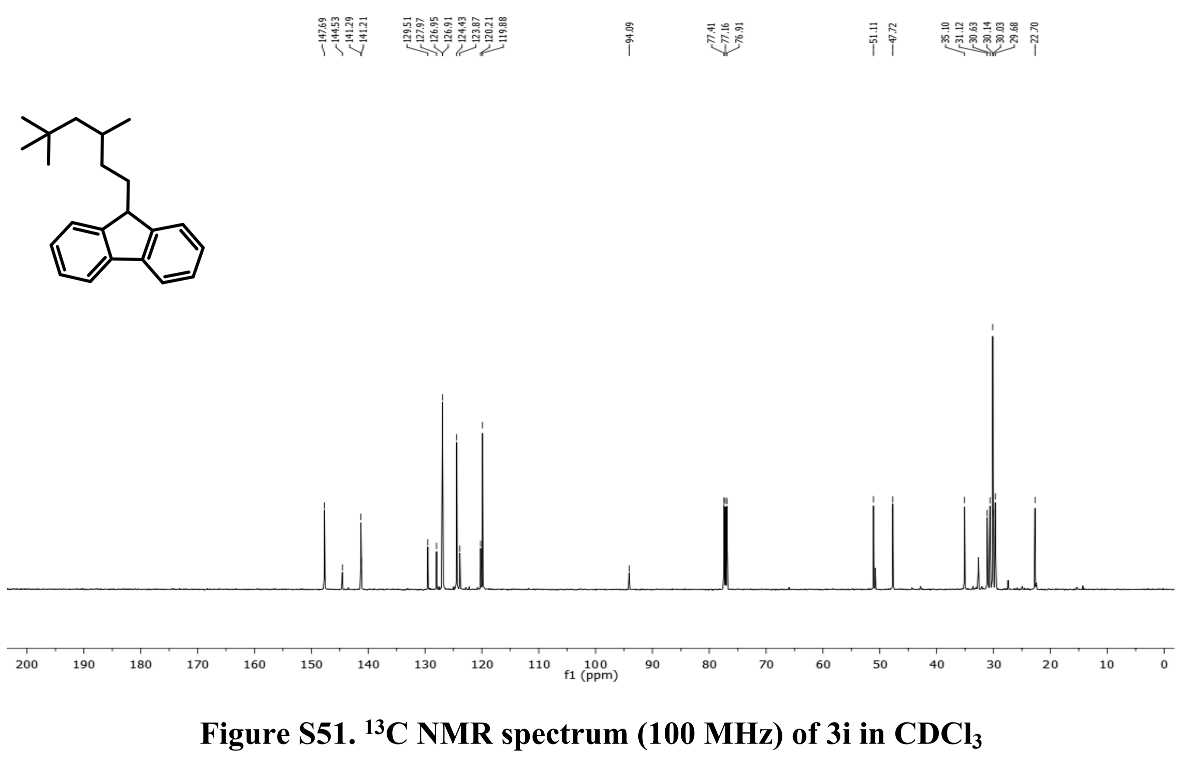


Figure S51. [13]C NMR spectrum (100 MHz) of 3i in $CDCl_3$

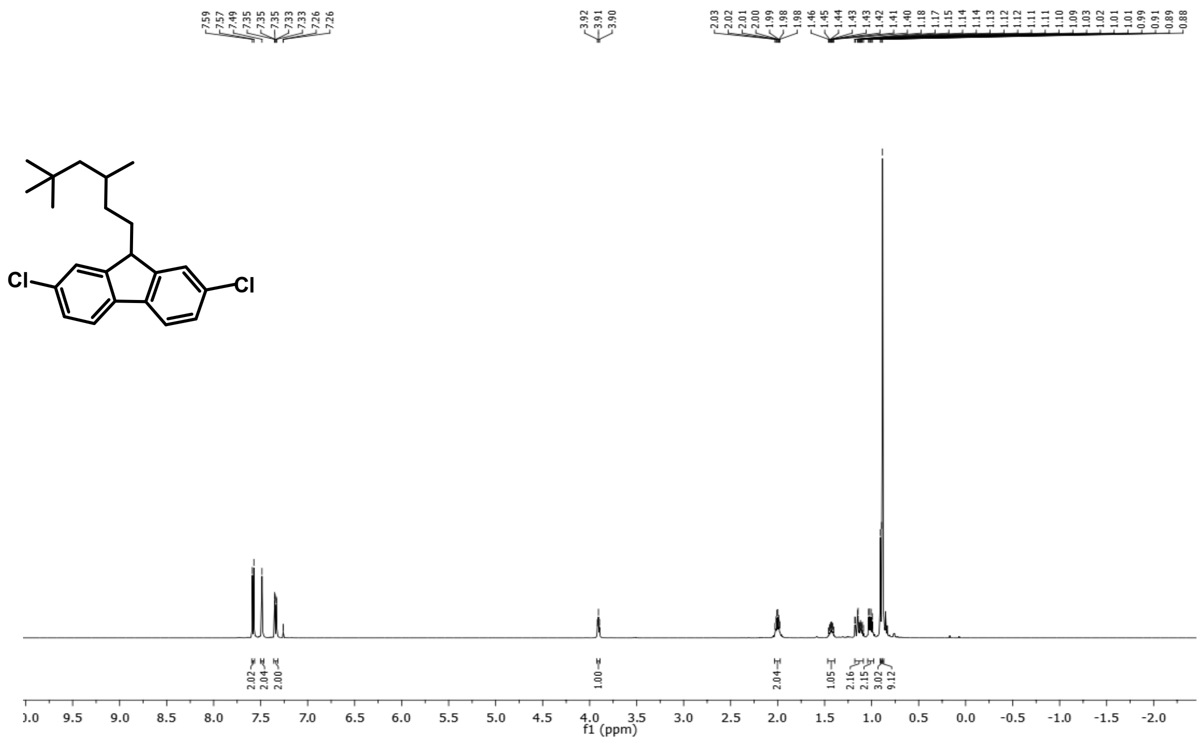


Figure S52. ^{1}H NMR spectrum (400 MHz) of 3j in $CDCl_3$

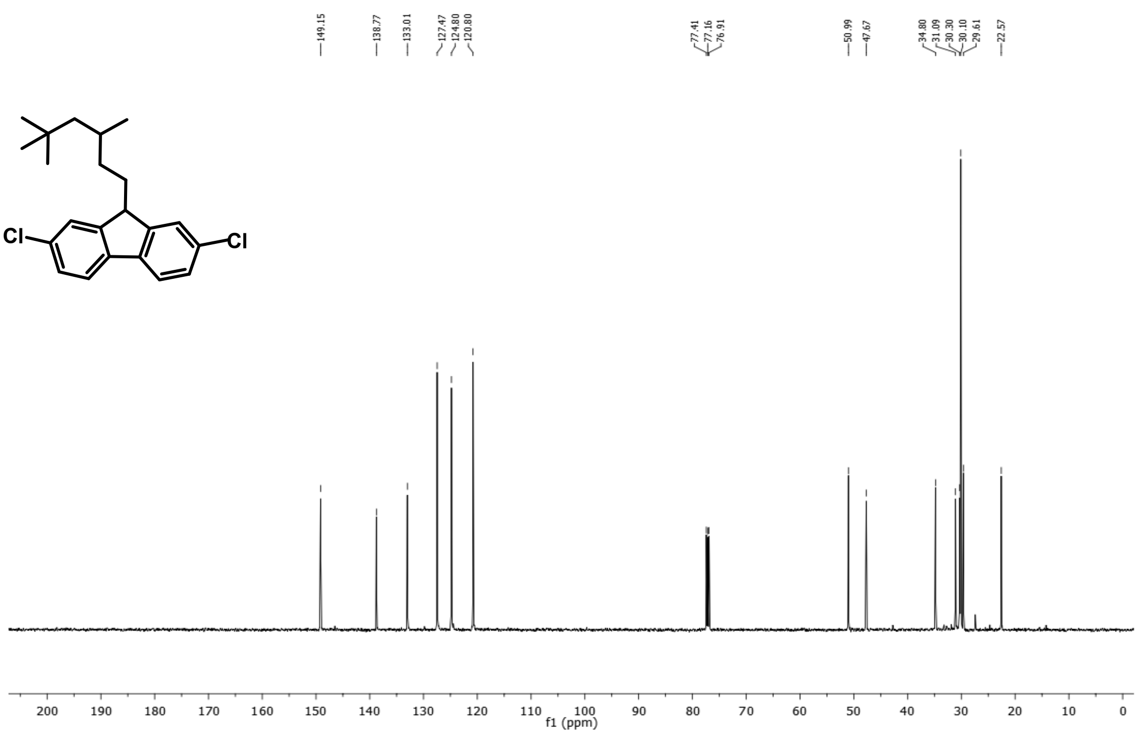


Figure S53. ^{13}C NMR spectrum (100 MHz) of 3j in $CDCl_3$

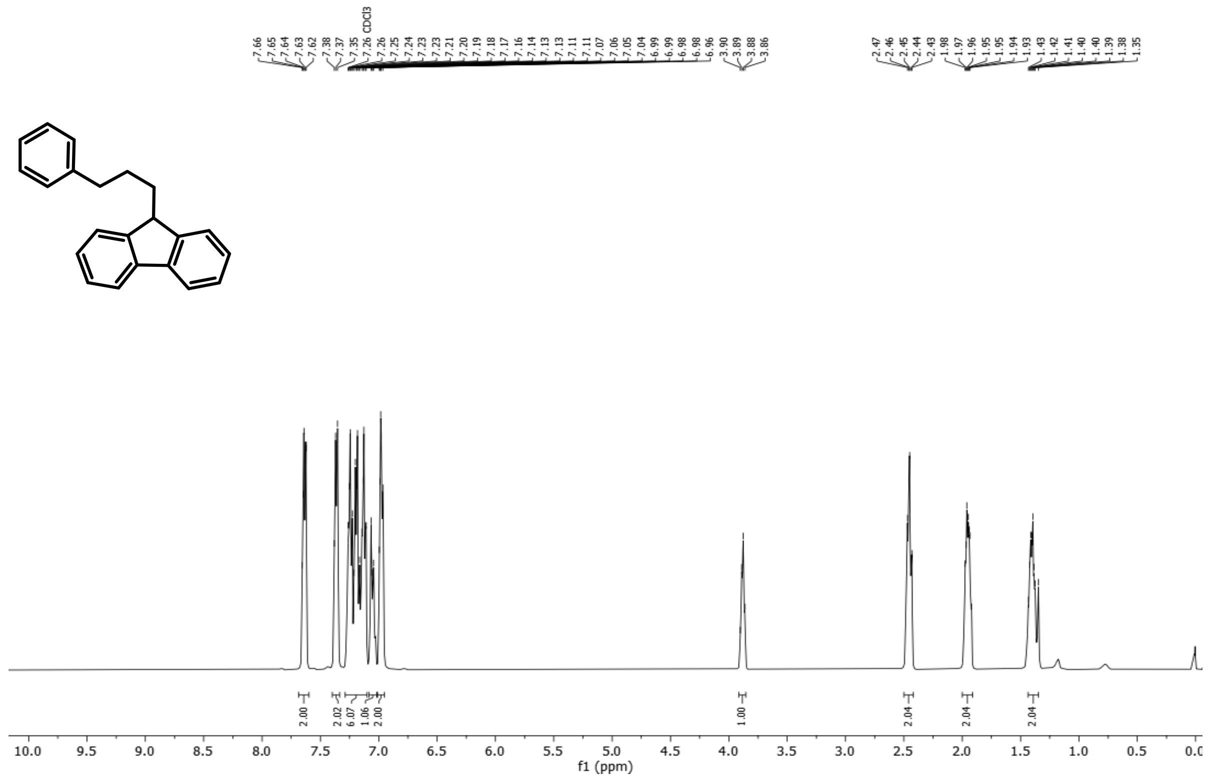


Figure S54. ^{1}H NMR spectrum (400 MHz) of 3k in $CDCl_3$

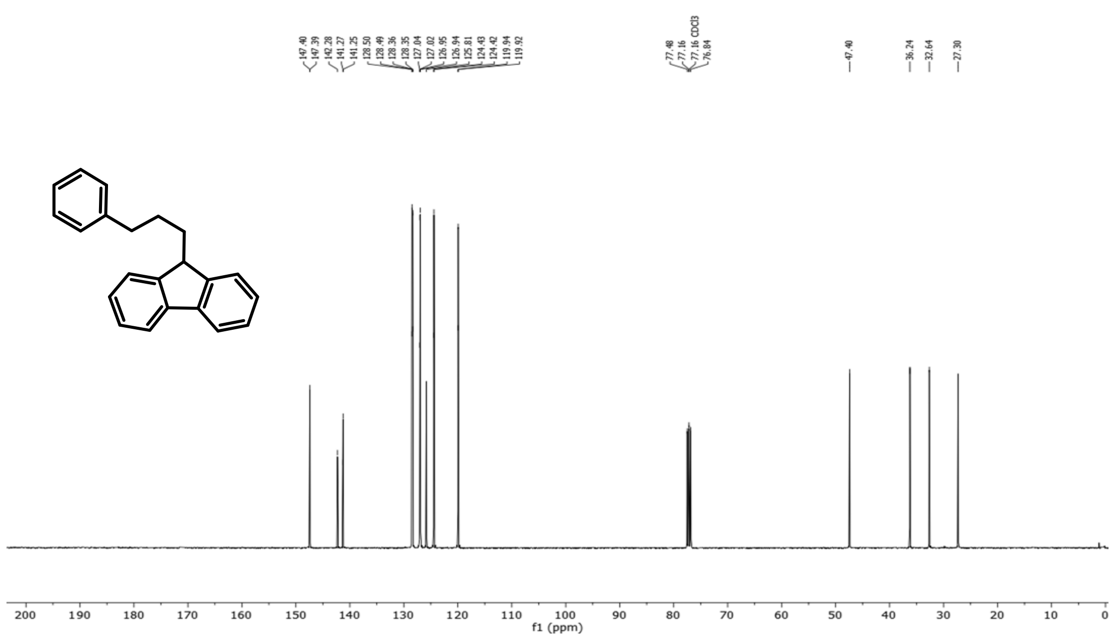


Figure S55. ^{13}C NMR spectrum (100 MHz) of 3k in $CDCl_3$

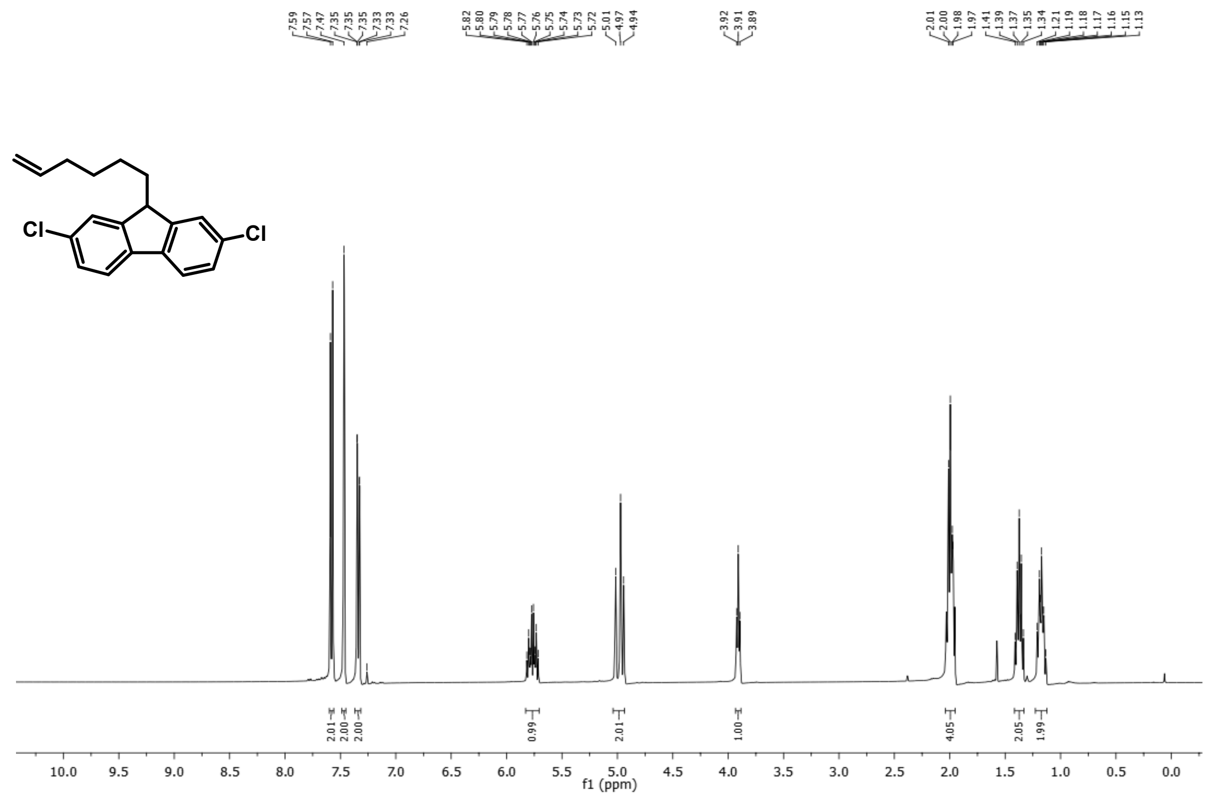


Figure S56. ^{1}H NMR spectrum (400 MHz) of 3l in $CDCl_3$

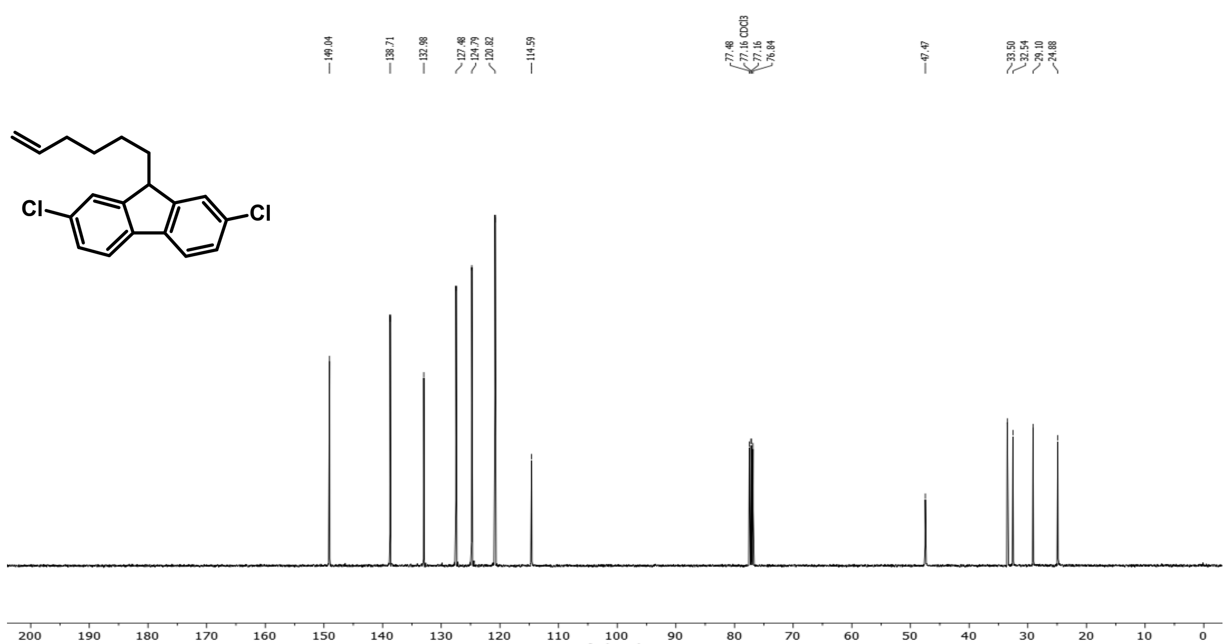


Figure S57. ^{13}C NMR spectrum (100 MHz) of 3l in $CDCl_3$

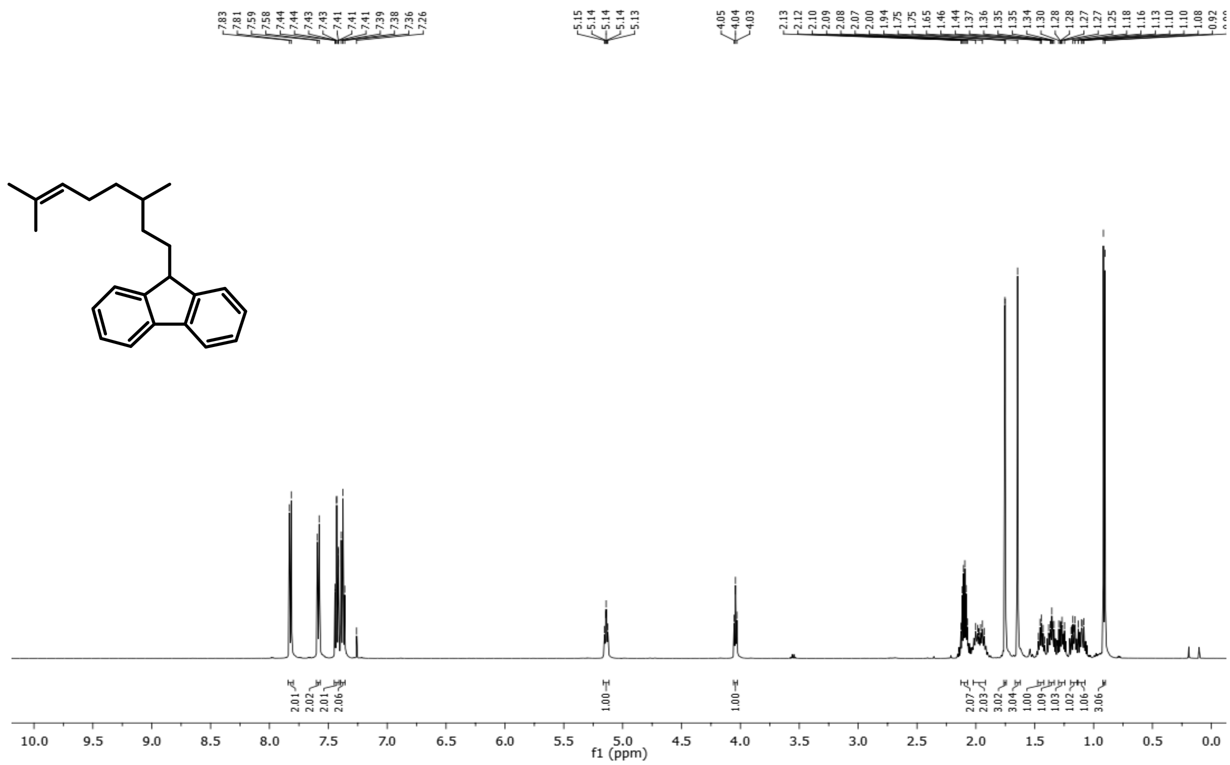


Figure S58. ^{1}H NMR spectrum (400 MHz) of 3m in $CDCl_3$

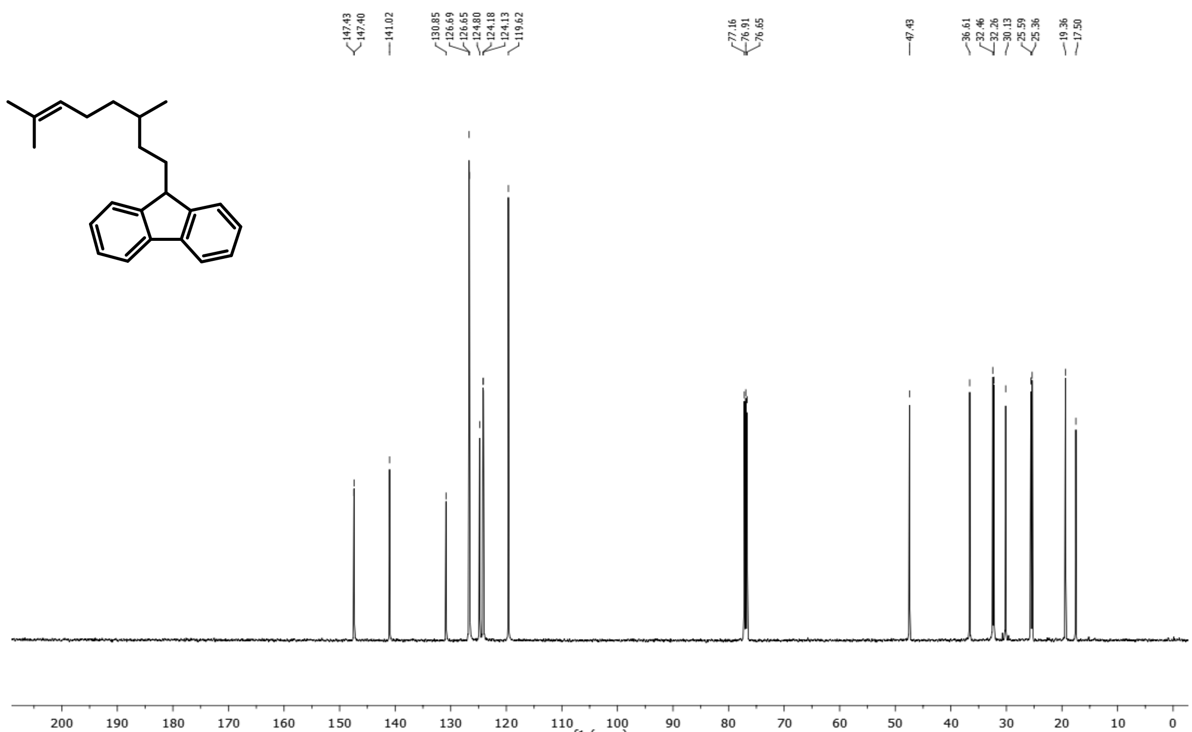


Figure S59. ^{13}C NMR spectrum (100 MHz) of 3m in $CDCl_3$

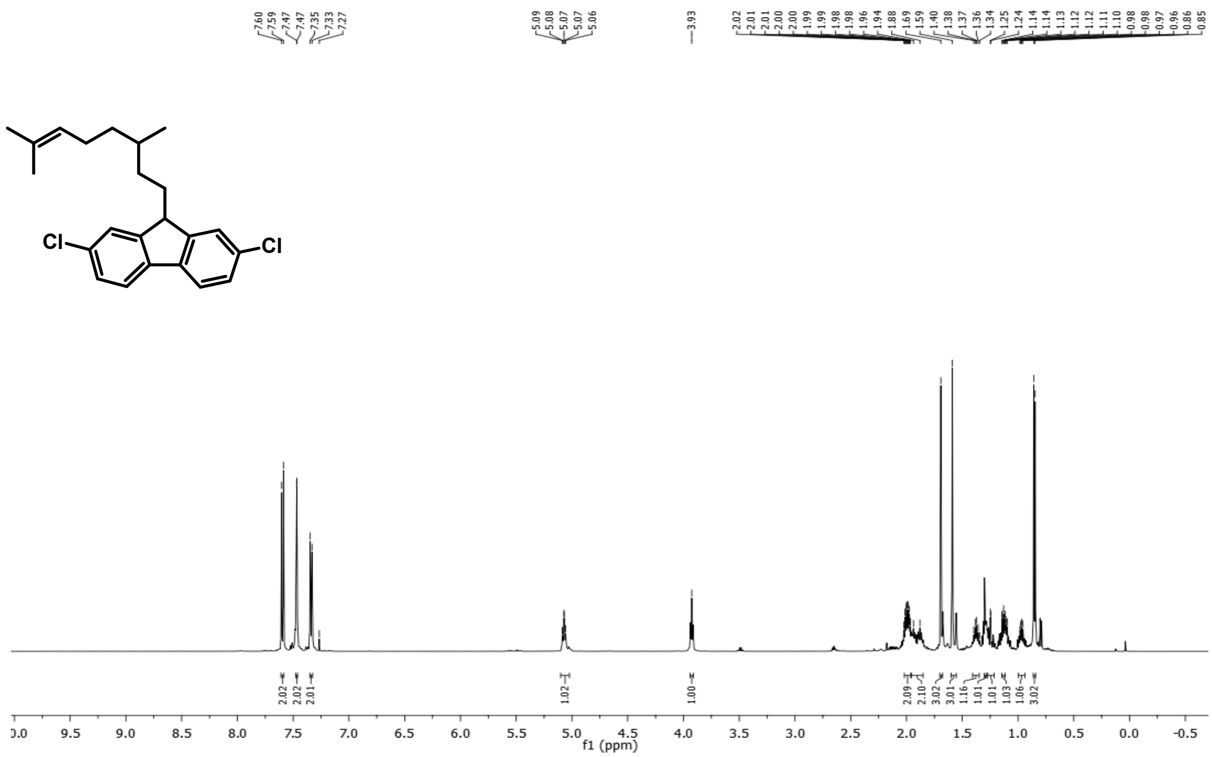


Figure S60. ^{1}H NMR spectrum (400 MHz) of 3n in $CDCl_3$

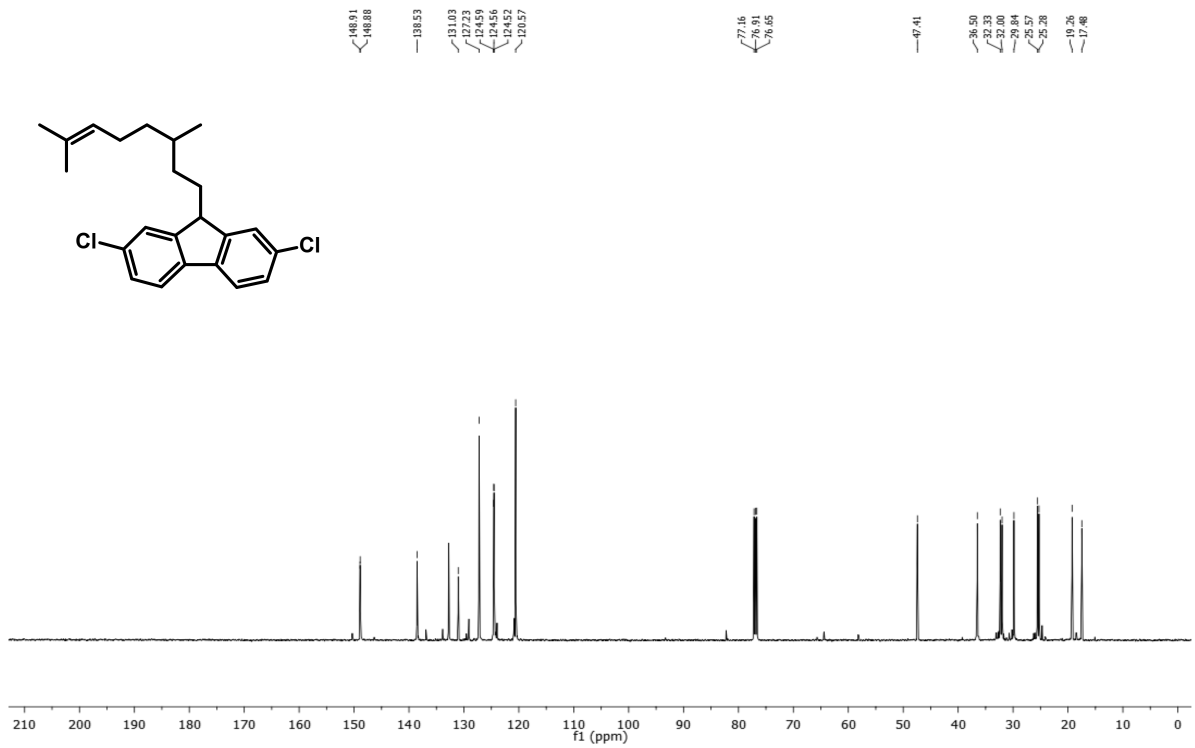


Figure S61. ^{13}C NMR spectrum (100 MHz) of 3n in $CDCl_3$

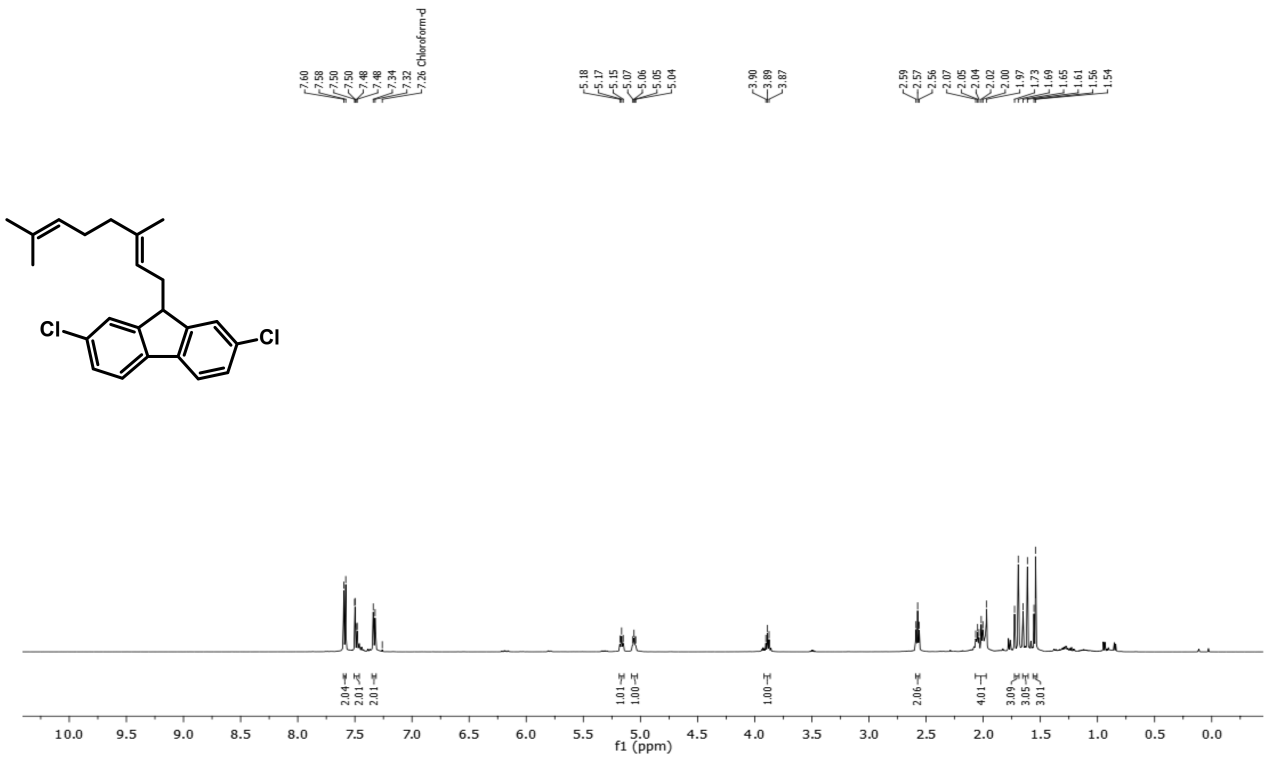


Figure S62. ^{1}H NMR spectrum (400 MHz) of 3o in $CDCl_3$

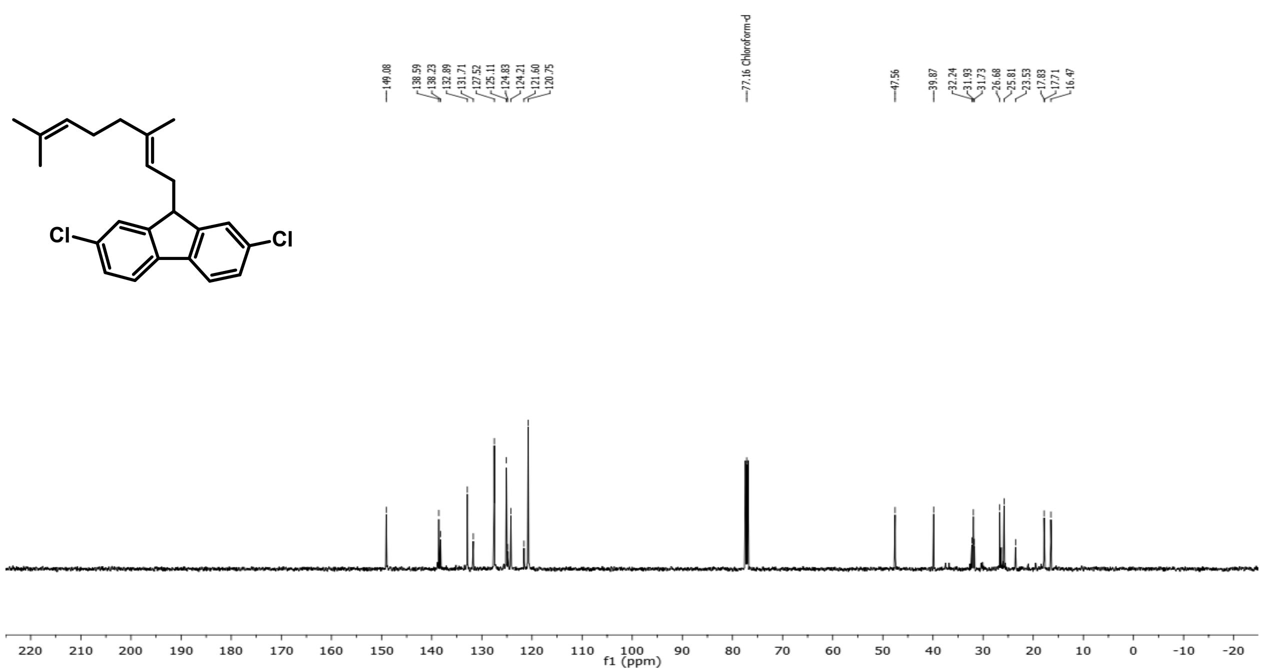


Figure S63. ^{13}C NMR spectrum (100 MHz) of 3o in $CDCl_3$

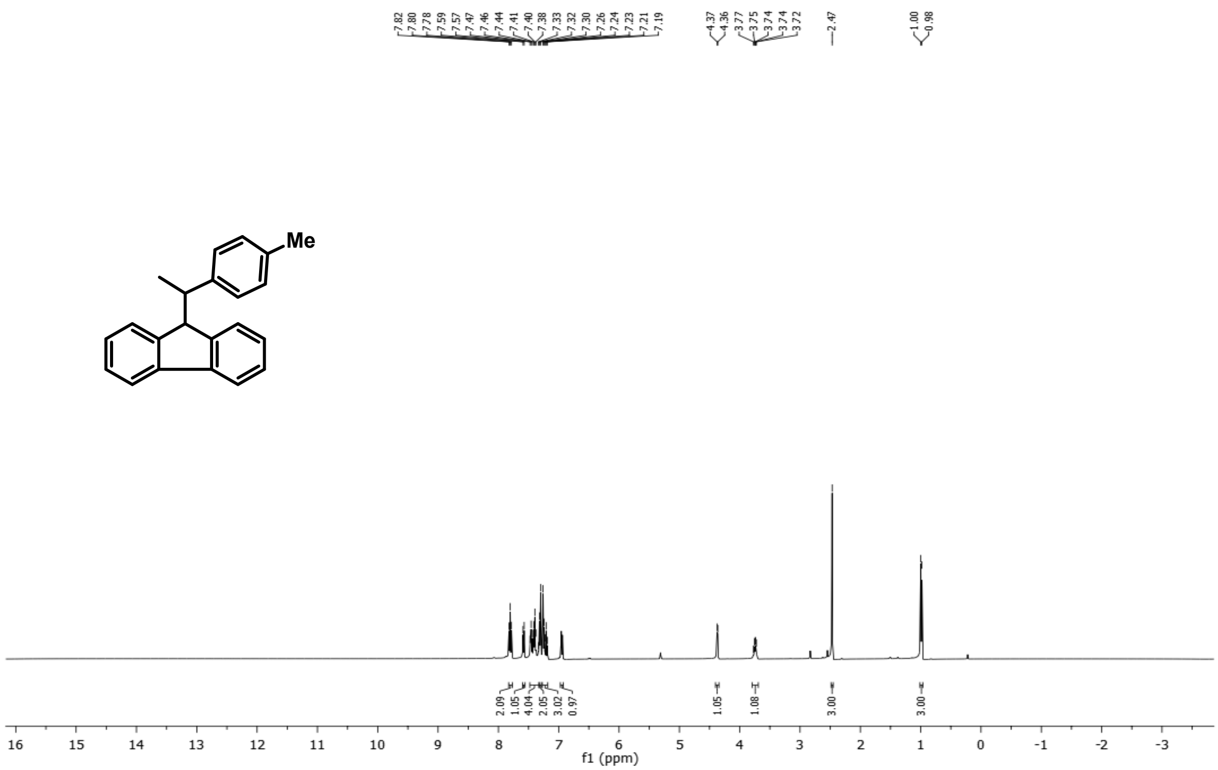


Figure S64. ^{1}H NMR spectrum (400 MHz) of 4a in $CDCl_3$

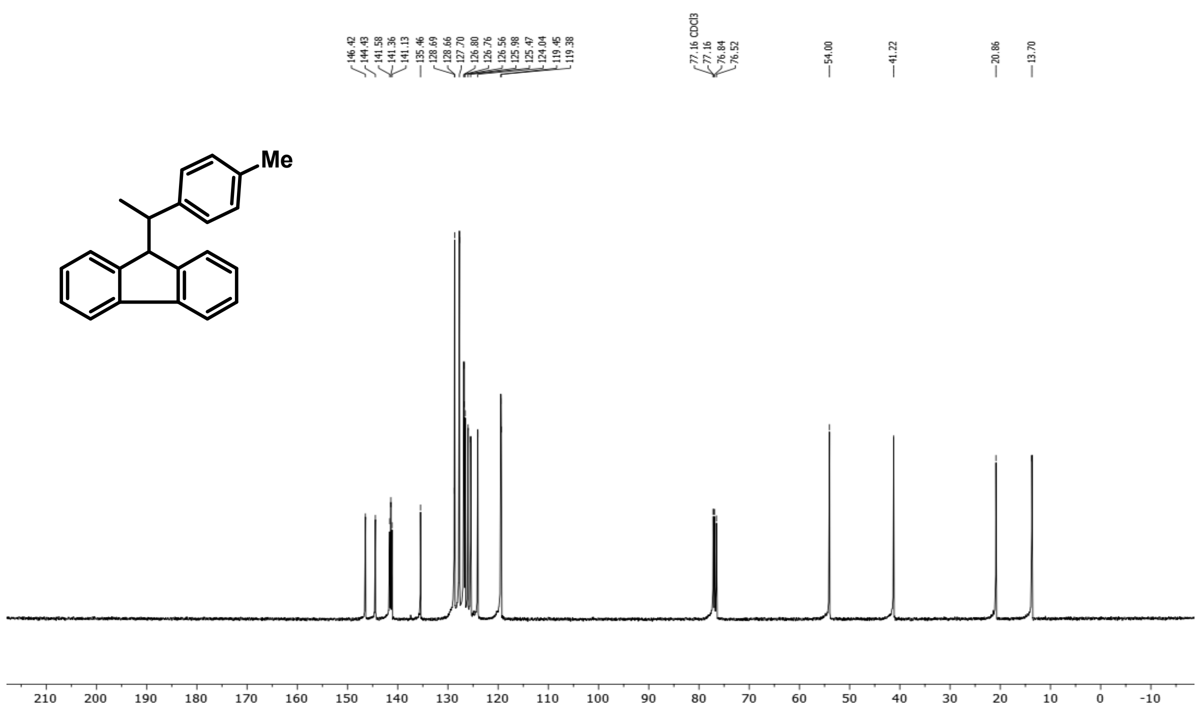


Figure S65. ^{13}C NMR spectrum (100 MHz) of 4a in $CDCl_3$

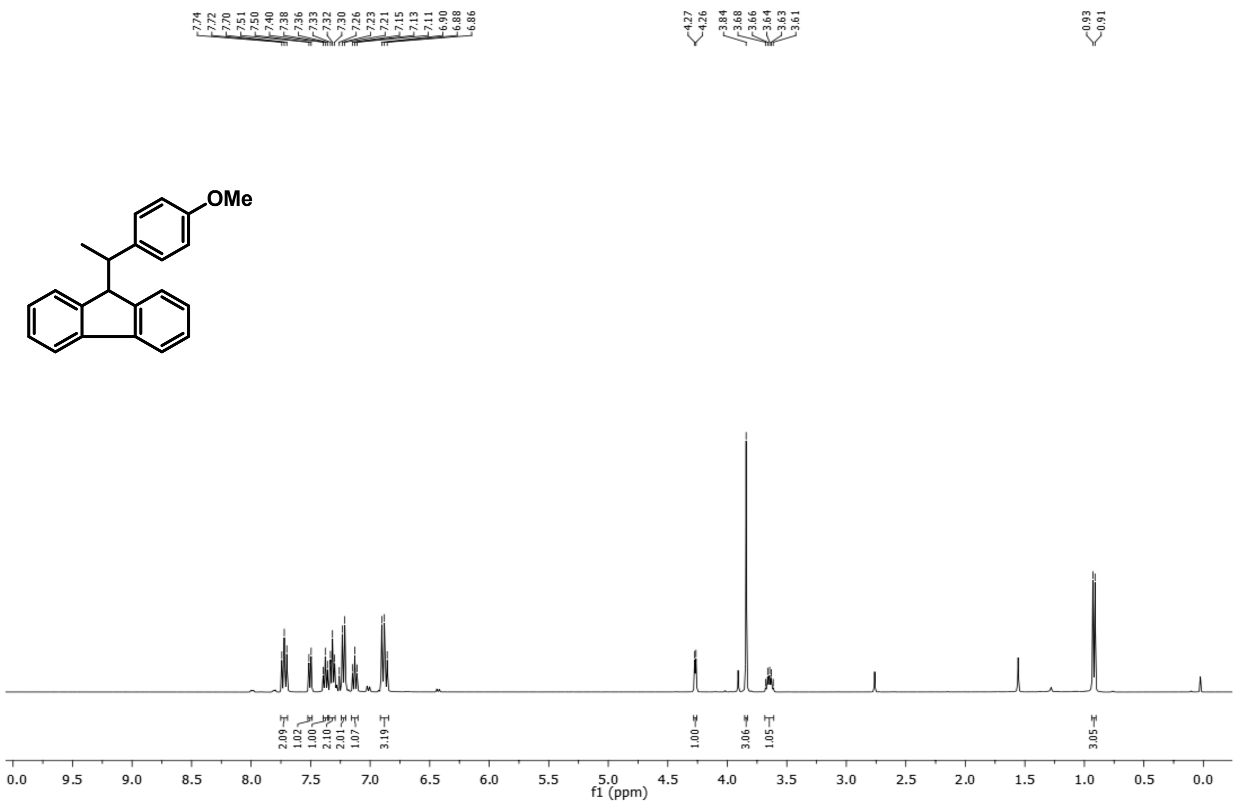


Figure S66. ^{1}H NMR spectrum (400 MHz) of 4b in $CDCl_3$

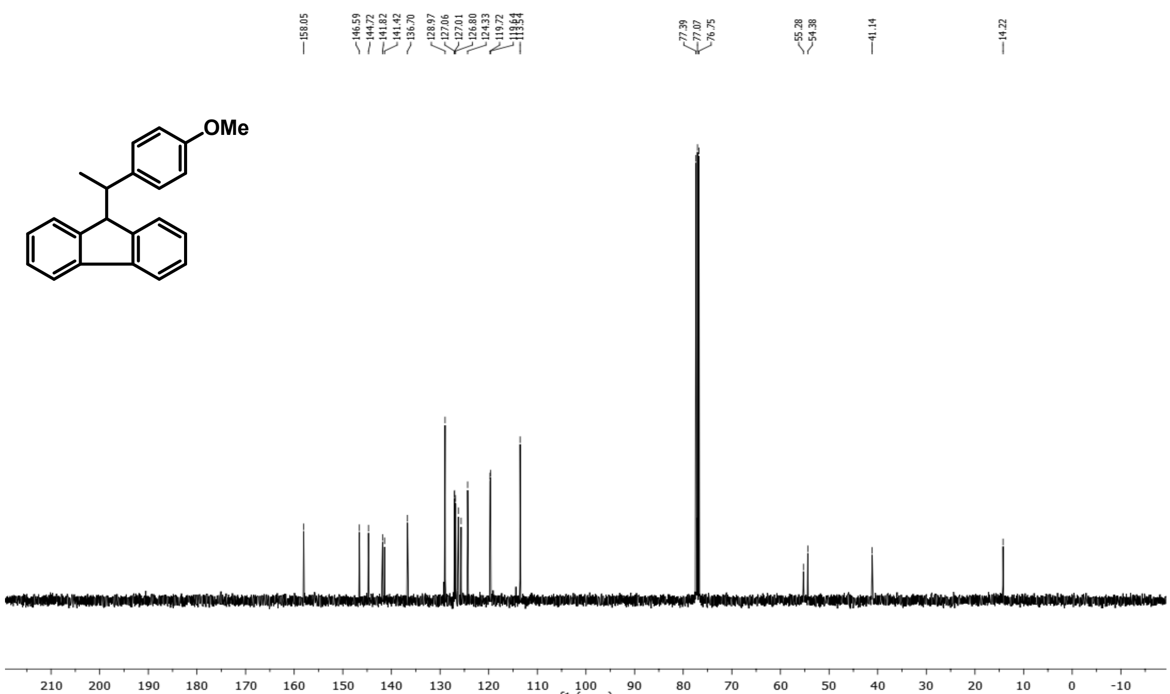


Figure S67. ^{13}C NMR spectrum (100 MHz) of 4b in $CDCl_3$

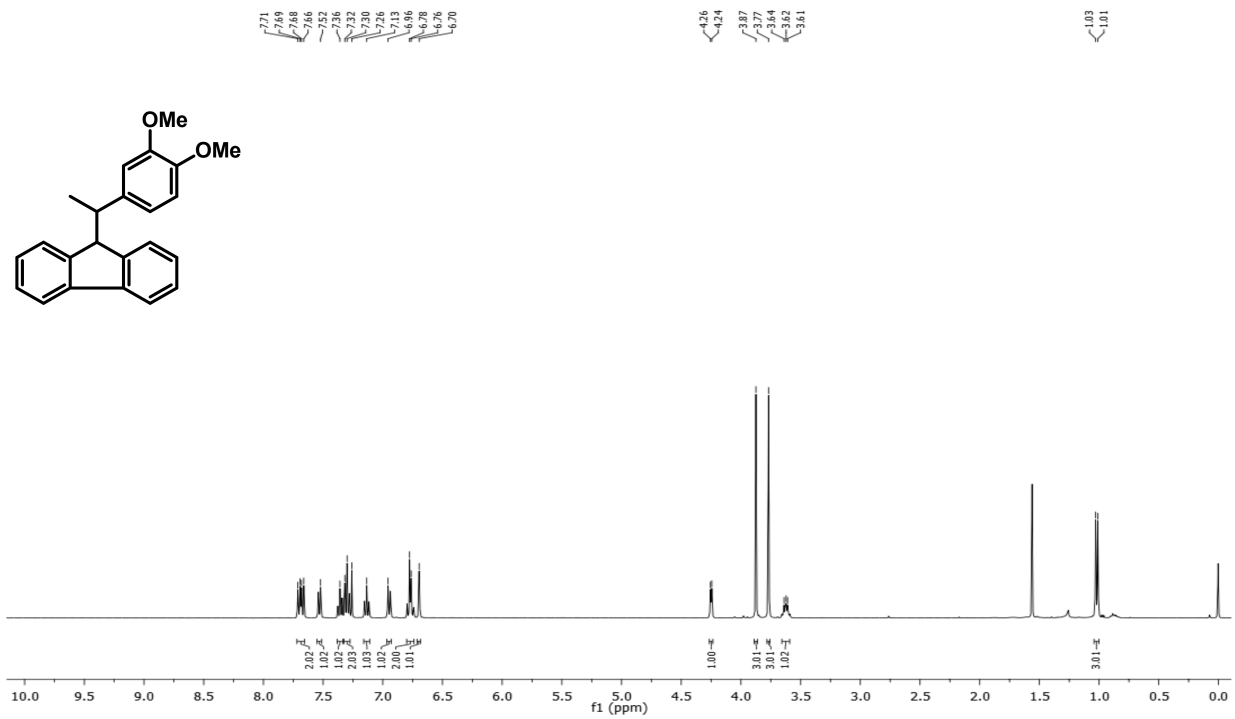


Figure S68. ^{1}H NMR spectrum (400 MHz) of 4c in $CDCl_3$

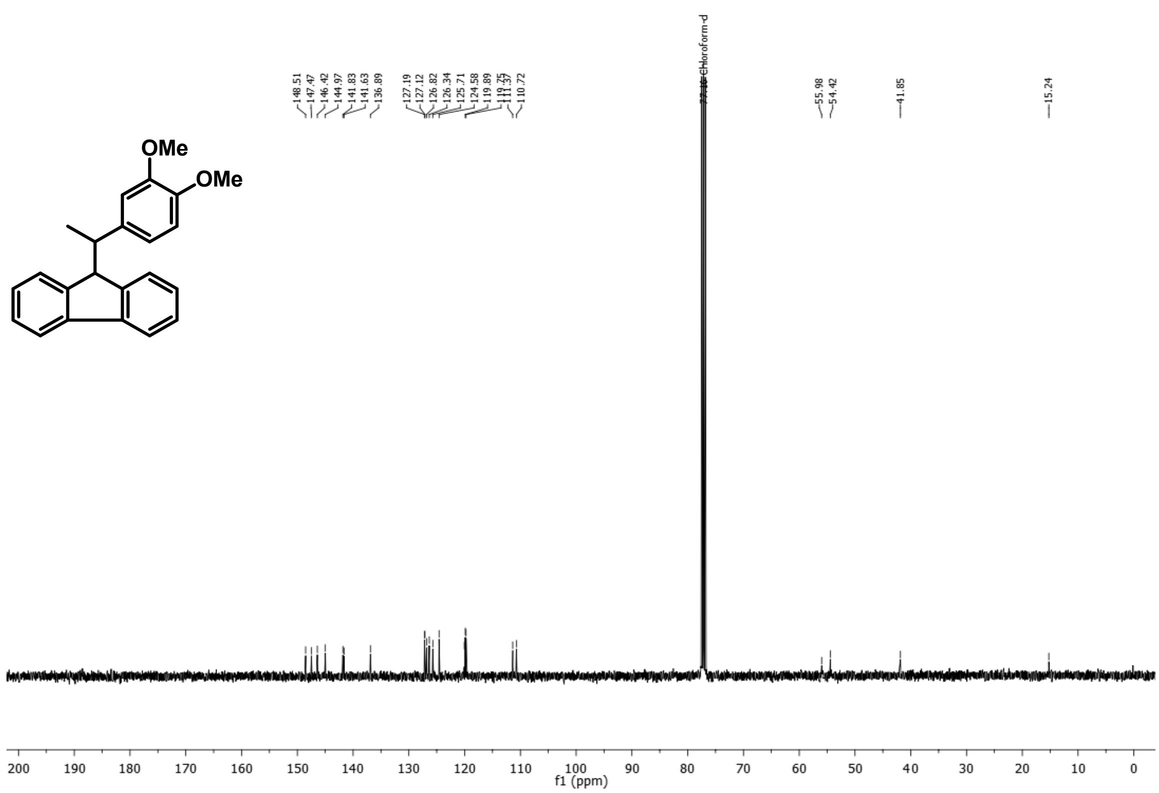


Figure S69. ^{13}C NMR spectrum (100 MHz) of 4c in $CDCl_3$

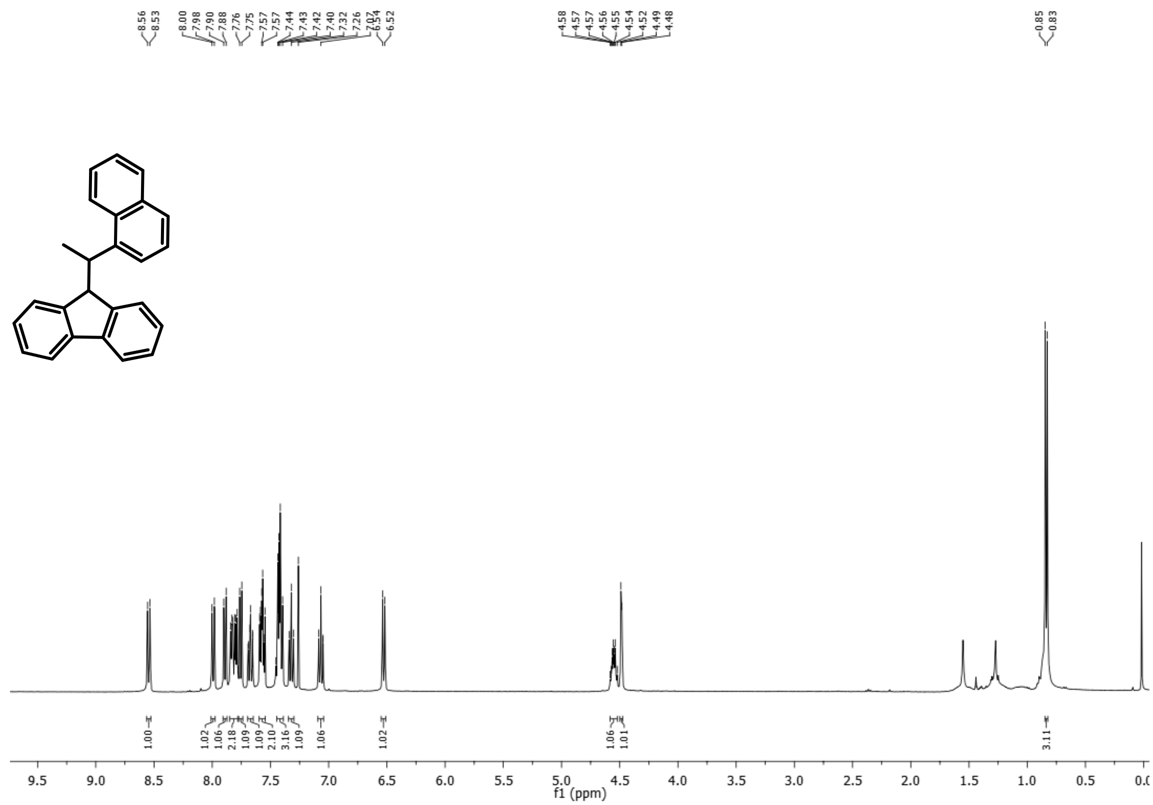


Figure S70. ^{1}H NMR spectrum (400 MHz) of 4d in $CDCl_3$

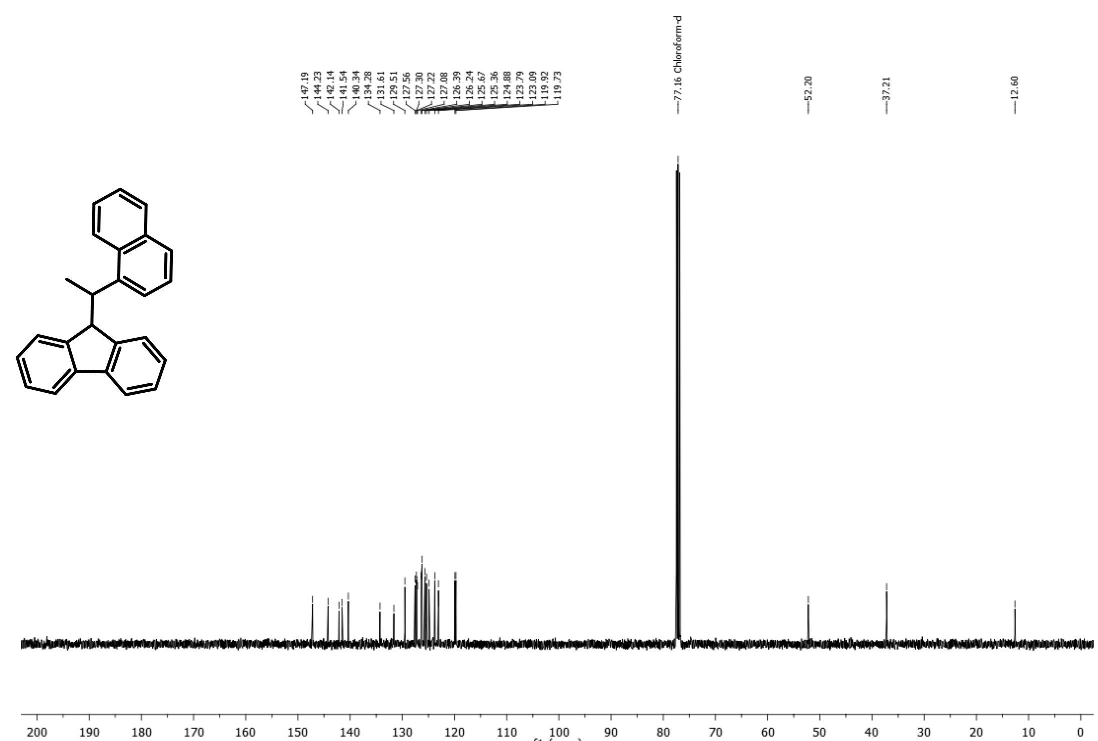


Figure S71. ^{13}C NMR spectrum (100 MHz) of 4d in $CDCl_3$

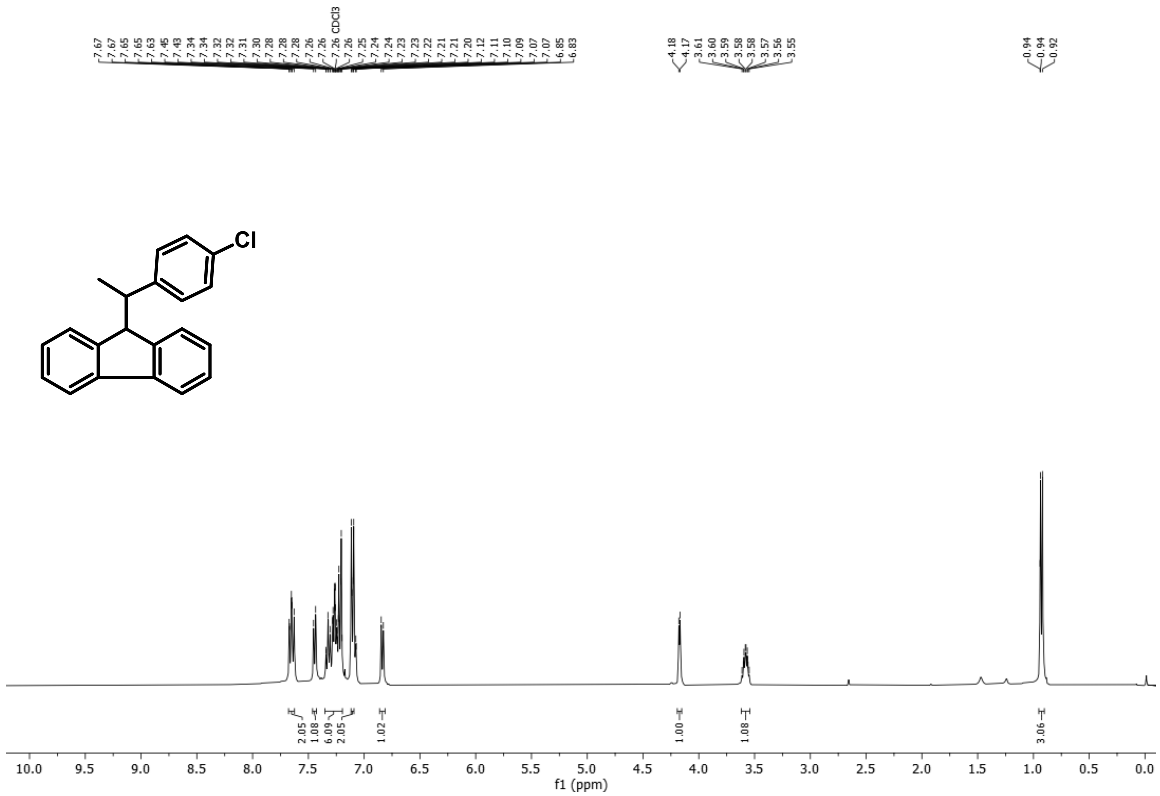


Figure S72. ^{1}H NMR spectrum (400 MHz) of 4e in $CDCl_3$

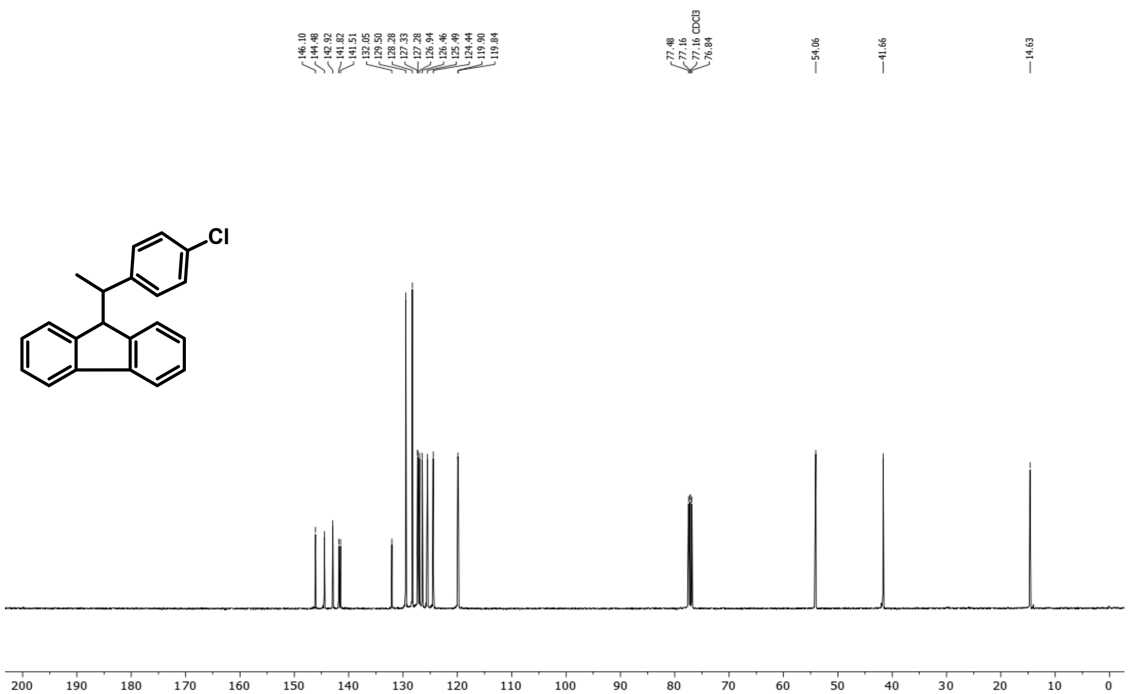


Figure S73. ^{13}C NMR spectrum (100 MHz) of 4e in $CDCl_3$

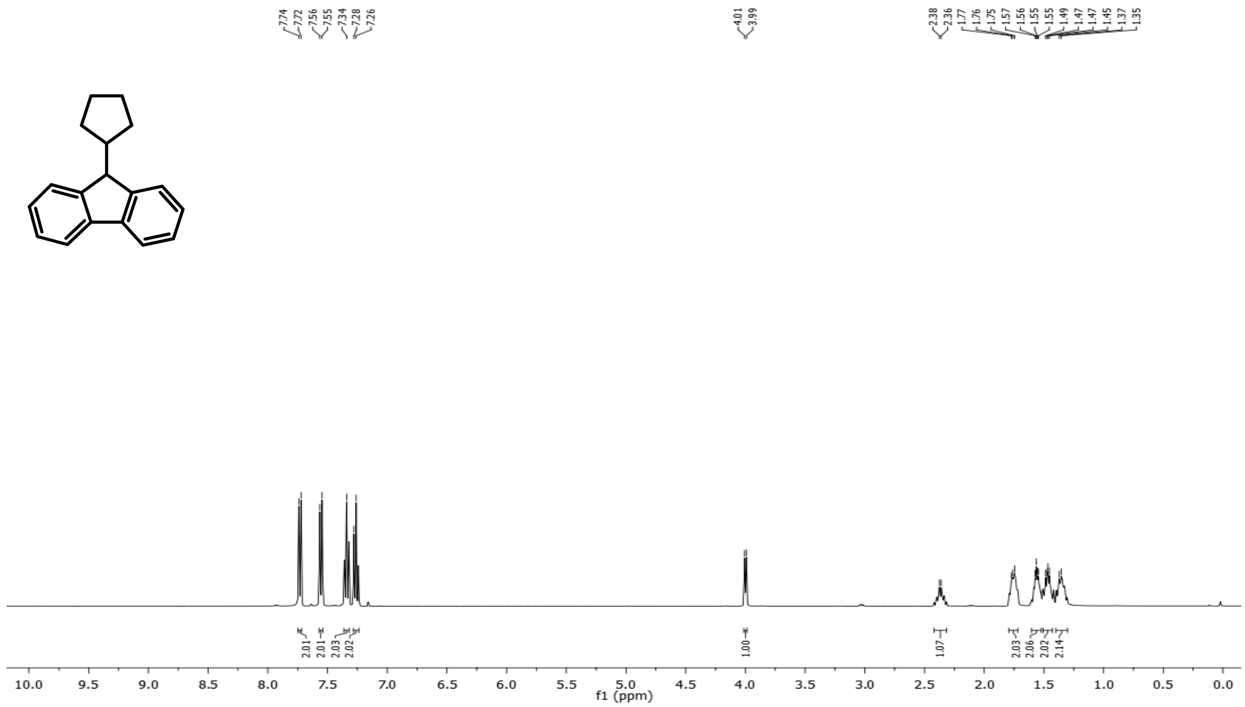


Figure S74. ^{1}H NMR spectrum (400 MHz) of 4f in $CDCl_3$

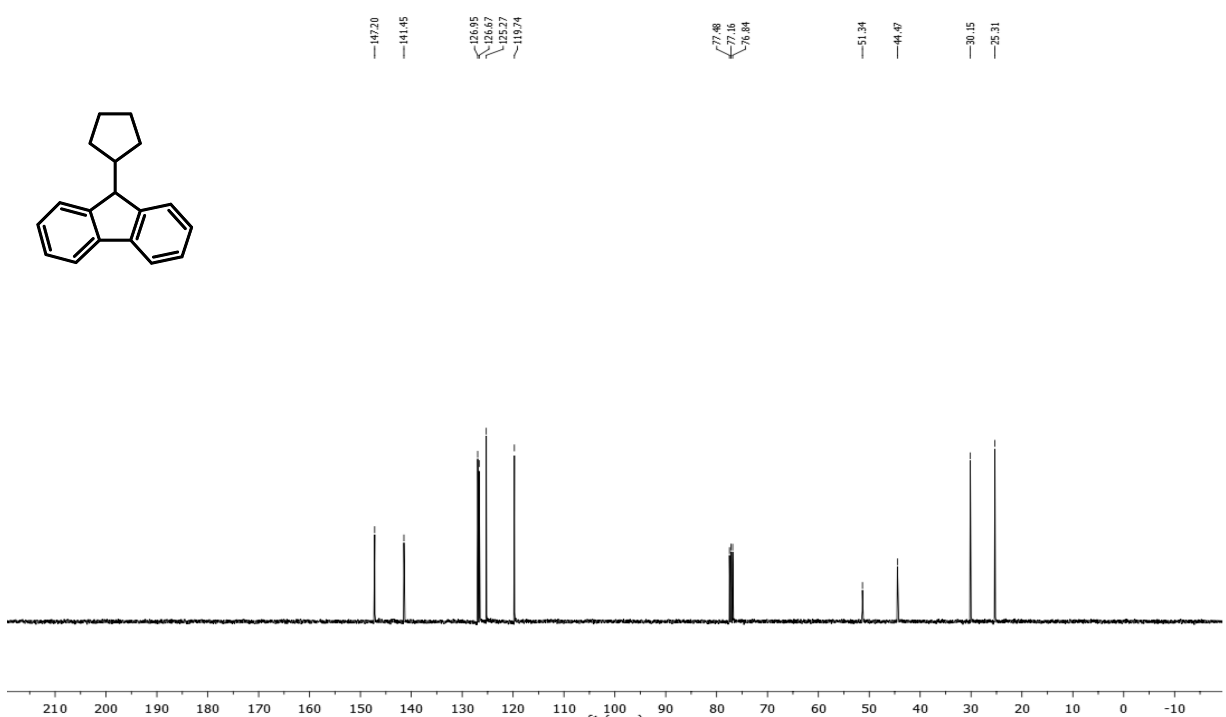


Figure S75. ^{13}C NMR spectrum (100 MHz) of 4f in $CDCl_3$

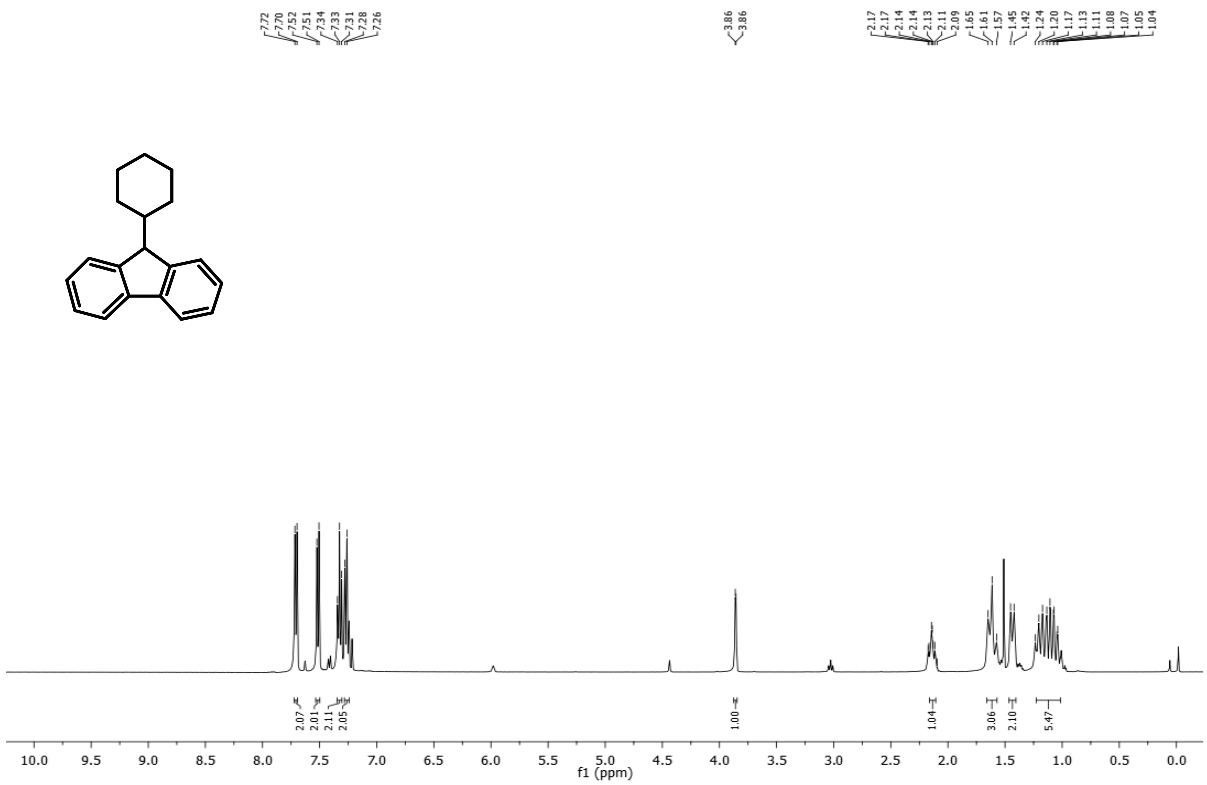


Figure S76. ^{1}H NMR spectrum (400 MHz) of 4g in $CDCl_3$

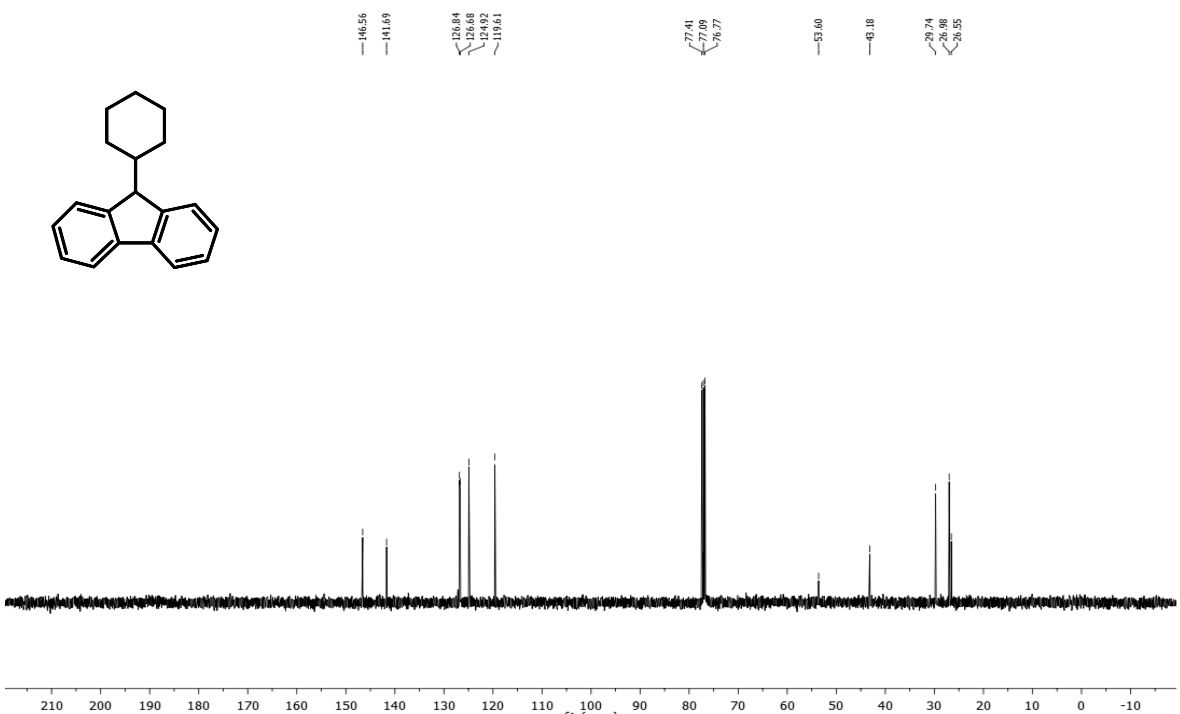


Figure S77. ^{13}C NMR spectrum (100 MHz) of 4g in $CDCl_3$

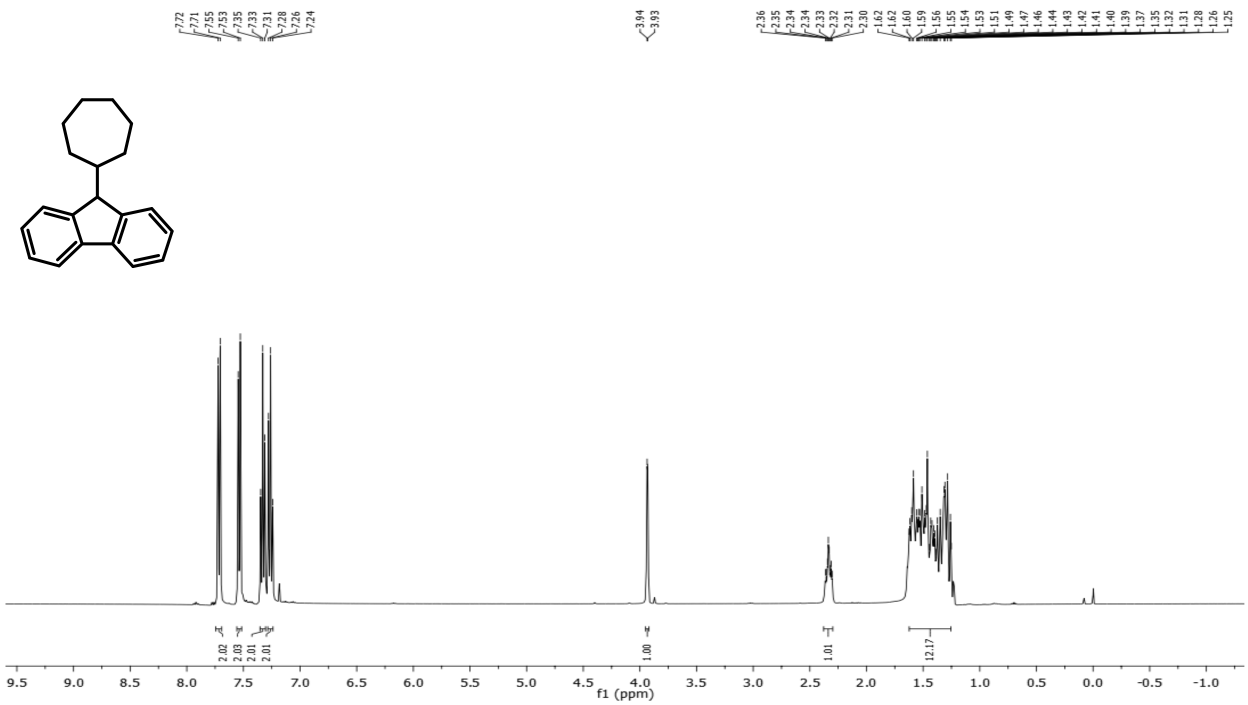


Figure S78. ^{1}H NMR spectrum (400 MHz) of 4h in $CDCl_3$

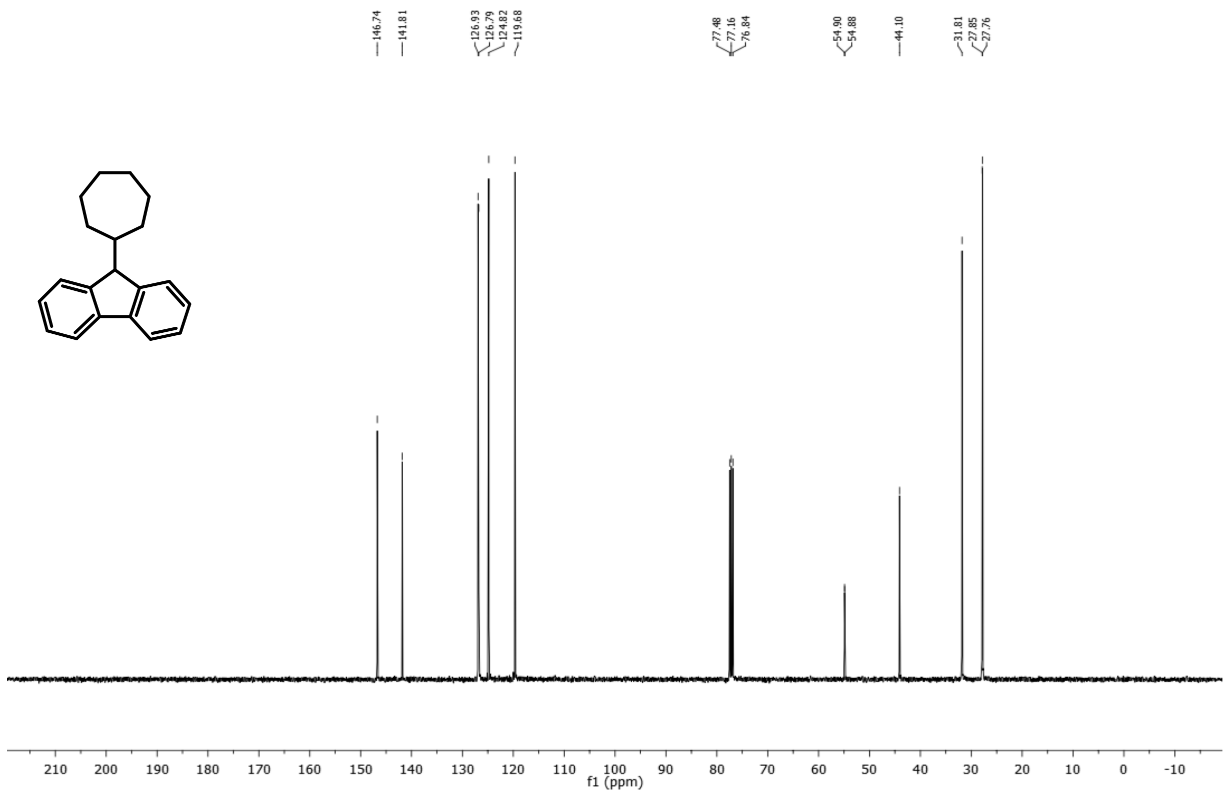


Figure S79. ^{13}C NMR spectrum (100 MHz) of 4h in $CDCl_3$

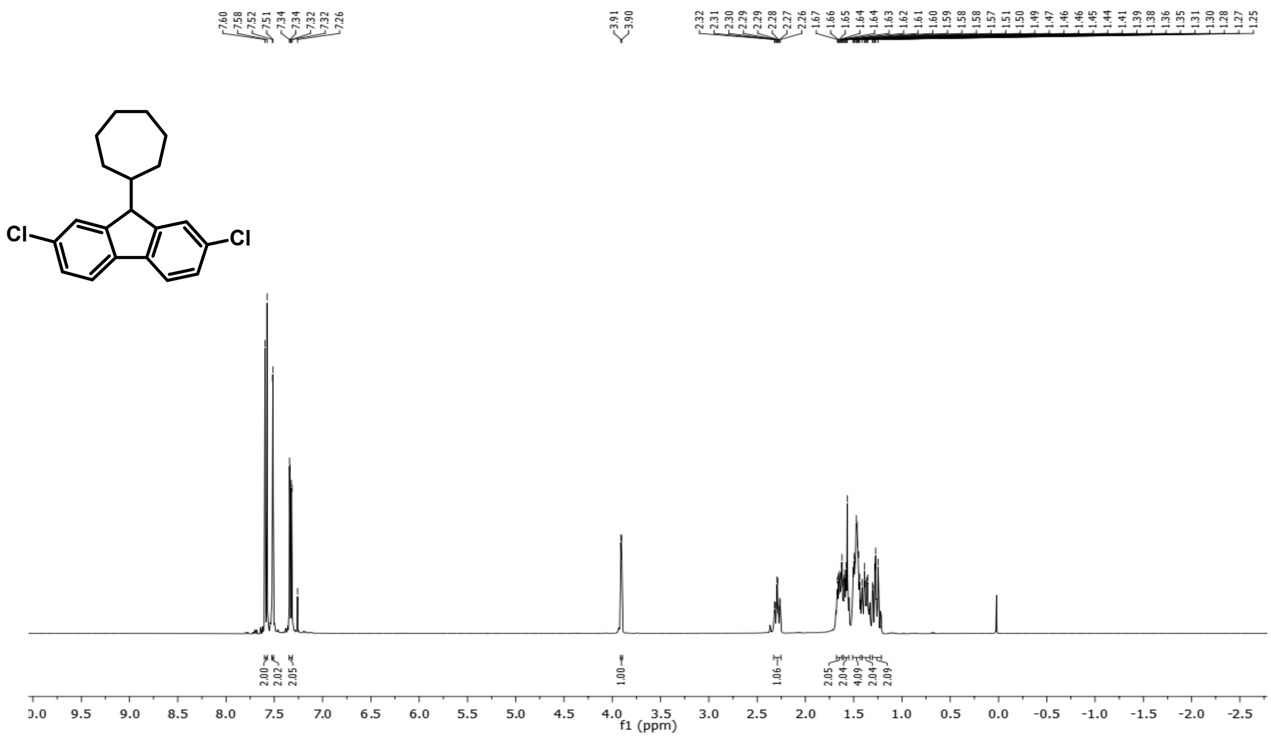


Figure S80. ^{1}H NMR spectrum (400 MHz) of 4i in $CDCl_3$

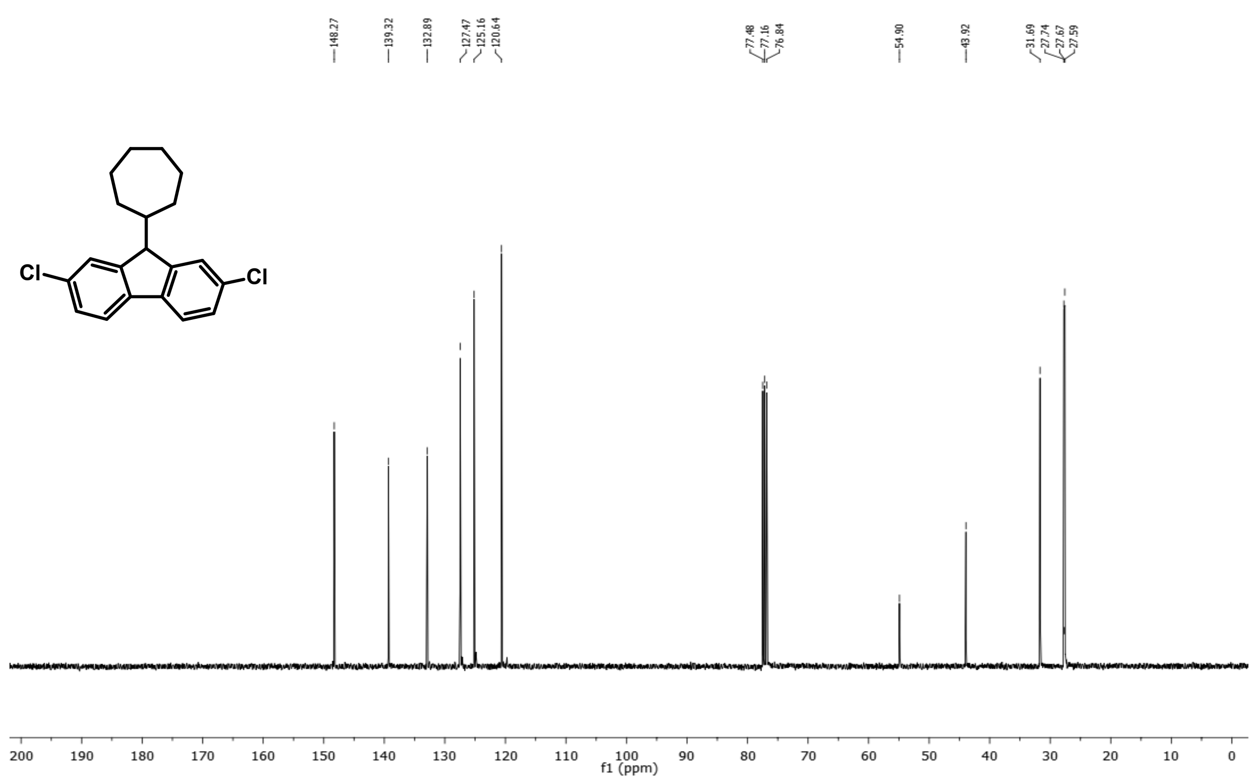


Figure S81. ^{13}C NMR spectrum (100 MHz) of 4i in $CDCl_3$

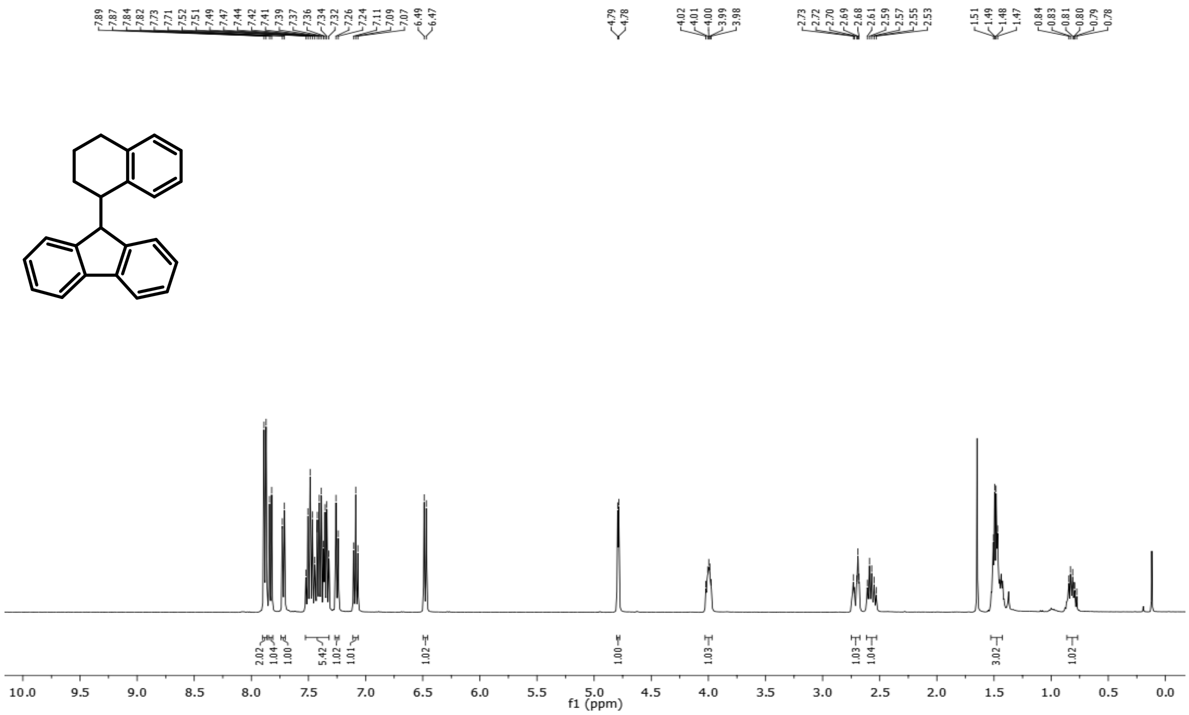


Figure S82. ^{1}H NMR spectrum (400 MHz) of 4j in $CDCl_3$

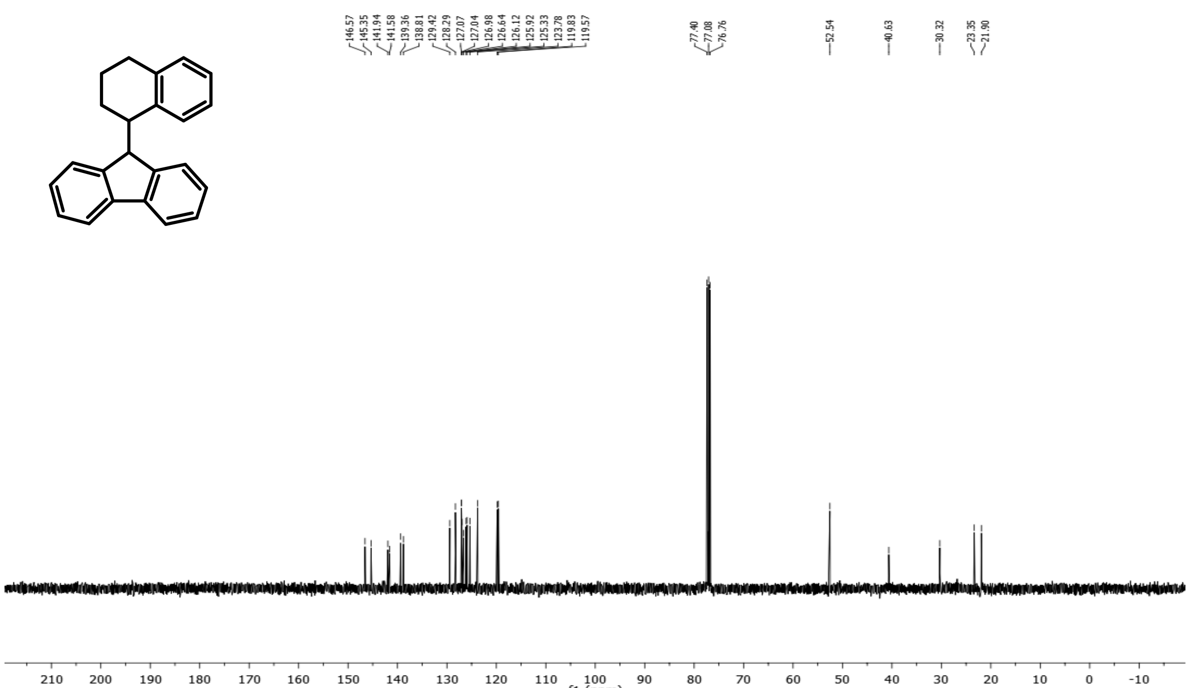


Figure S83. ^{13}C NMR spectrum (100 MHz) of 4j in $CDCl_3$

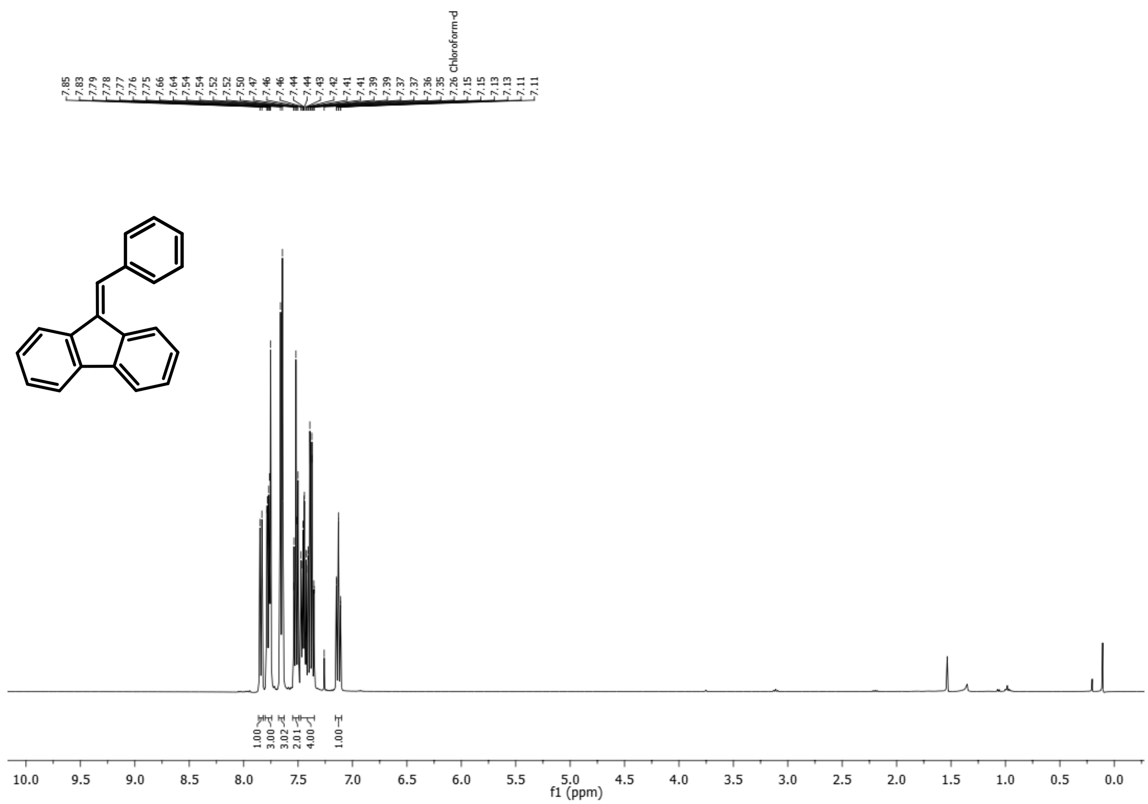


Figure S84. ^{1}H NMR spectrum (400 MHz) of 5 in $CDCl_3$

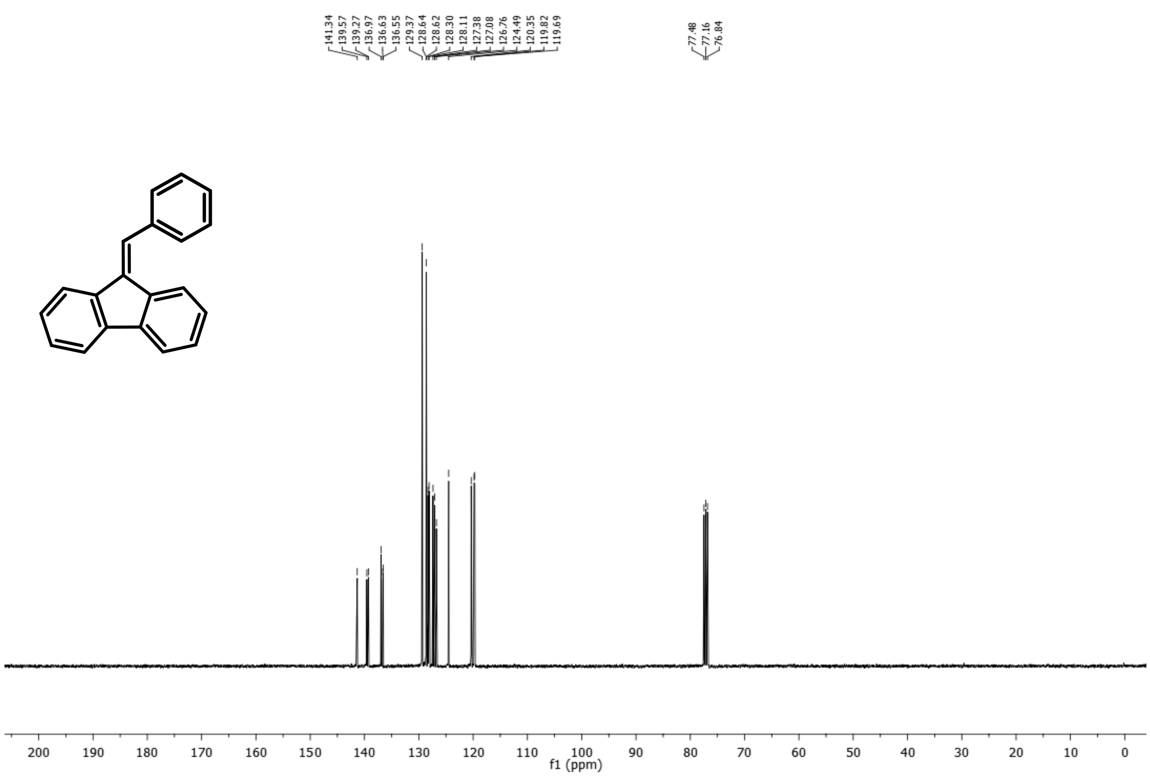


Figure S85. ^{13}C NMR spectrum (100 MHz) of 5 in $CDCl_3$

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