Manganese Catalyzed Switchable C- Alkylation/Alkenylation of Fluorenes and Indene with Alcohols

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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. The preparation of catalyst was carried out under argon atmosphere with freshly distilled dry THF. All catalytic reactions were carried out under argon atmosphere using dried glassware and standard syringe/septa techniques. Bruker Advance 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. FTIR were collected on PerkinElmer IR spectrometer. 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.

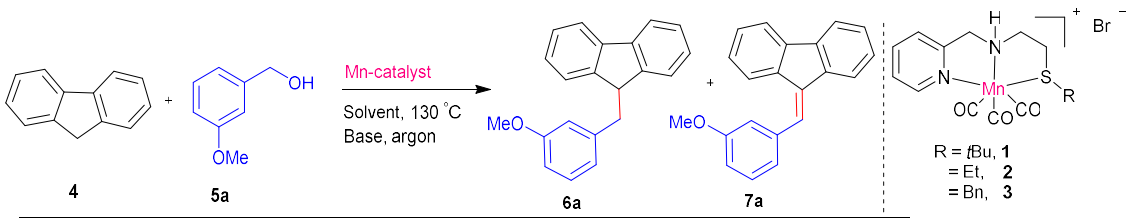
2. Ligands synthesis:

All three ligands were prepared according to previous reported literature methods.[1] Pyridine-2-carboxaldehyde (10 mmol) and amino-thiol compound (10 mmol,) were dissolved in dry CH_2Cl_2 (30 mL) and then Na_2SO_4 (40 mmol) was added to it. The resulting suspension was stirred for 20 h at room temperature. Then, it was filtered and the residue was washed thoroughly with CH_2Cl_2 and the combined solvent was removed under reduced pressure. The residue obtained was directly used for the next step without further purification. The residue was dissolved in methanol (30 ml) and $NaBH_4$ (30 mmol) was added portion wise in stirring condition at 0 °C and the stirring was continued for overnight at room temperature. Then the solvent was evaporated and 30 mL of water was added. After that, it was extracted by CH_2Cl_2 and the organic portion was collected and passed through Na_2SO_4. Then the solvent was evaporated to get the crude product, which was purified further by silica gel (100-200 mess) column chromatography using 20-40 % ethyl acetate in hexane.

3. Complex preparation:

All three complexes were prepared according to previous reported literature methods.[1] Ligand [$(PyCH_2)HN(CH_2CH_2SR)$, R= Et, *t*Bu, Bn] (2.0 mmol) was taken in 5 mL dry THF and was added dropwise to the orange-yellow suspension of $[MnBr(CO)_5]$ (2.0 mmol) in 5 mL degassed dry THF. 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 solvent was evaporated to obtain the residue, which was further washed with hexane and dried under vacuum to get yellow solid of Mn-complex.

4. Optimization table for alkylation and alkenylation of fluorene[a]:

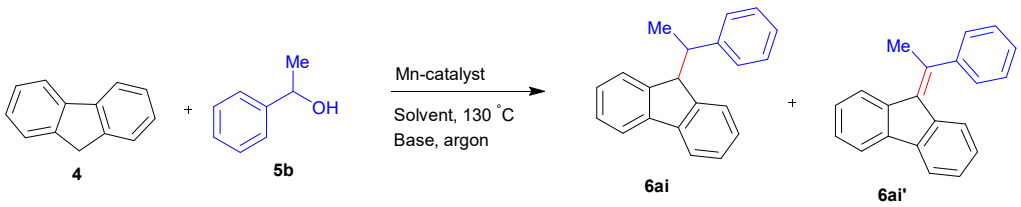


4 5a 6a 7a

Entry	Cat	Base (mmol)	Solvent (ml)	Time (h)	Fluorene : Alcohol (mmol)	% Yield [b] 6a	7a
1	**1**	*t*BuOK (0.5)	Toluene(2)	24	0.5 : 0.5	50	Trace
2	**1**	*t*BuOK(0.5)	Toluene(2)	36	0.5 : 0.5	51	Trace
3	**1**	*t*BuOK(0.5)	Toluene(2)	24	0.5 : 0.75	65	--
4	**1**	*t*BuOK(0.5)	Toluene(2)	24	0.5 : 1.0	98	--
5	**1**	*t*BuOK(0.5)	Xylene(2)	24	0.5 : 1.0	52	Trace
6	**1**	*t*BuOK (0.5)	*t*AmOH(2)	24	0.5 : 1.0	12	--
7	**1**	*t*BuOK (0.5)	Dioxane(2)	24	0.5 : 1.0	Trace	--
8	**1**	Na_2CO_3(0.5)	Toluene(2)	24	0.5 : 1.0	--	--
9	**1**	K_2CO_3(0.5)	Toluene(2)	24	0.5 : 1.0	--	--
10	**1**	NaOH(0.5)	Toluene(2)	24	0.5 : 1.0	10	--
11	**1**	KOH (0.5)	Toluene(2)	24	0.5 : 1.0	10	--
12	**1**	CsOH.H_2O (0.5)	Toluene(2)	24	0.5 : 1.0	15	Trace
13	**1**	*t*BuOK (0.5)	Neat	24	0.5 : 1.0	40	--
14	**1**	*t*BuOK (0.25)	Toluene(2)	24	0.5 : 1.0	8	78
15	**1**	*t*BuOK (0.15)	Toluene(2)	24	0.5 : 1.0	--	48
16	**1**	*t*BuOK (0.25)	Toluene(2)	24	0.5 : 0.55	--	83
17	**1**	*t*BuOK (0.25)	Toluene(2)	24	0.5 : 0.5	--	78
18	--	*t*BuOK (0.25)	Toluene(2)	24	0.5 : 0.55	Trace	Trace
19	**1**	---	Toluene(2)	24	0.5 : 0.55	Trace	--
20	...	*t*BuOK(0.5)	Toluene(2)	24	0.5 : 1.0	22	--
21	**2**	*t*BuOK (0.5)	Toluene(2)	24	0.5 : 1.0	98	--
22	**3**	*t*BuOK (0.5)	Toluene(2)	24	0.5 : 1.0	95	--
23[c]	**1**	*t*BuOK (0.5)	Toluene(2)	24	0.5 : 1.0	60	--
25[d]	**1**	*t*BuOK (0.5)	Toluene(2)	24	0.5 : 1.0	75	--
26	**$MnBr(CO_5)$**	*t*BuOK (0.5)	Toluene(2)	24	0.5 : 1.0	20	Trace

[a]**Conditions**: **4** (0.5 mmol), **5a** (0.5-1.0 mmol), KO*t*Bu (0.15-0.5 mmol), Mn-catalyst (5 mol%), under argon. [b]Isolated yield, nr = no reaction. [c]catalyst loading 2.5 mol%. [d]temperature 110 °C.

5. Optimization table for fluorene alkylation by secondary alcohol[a]:

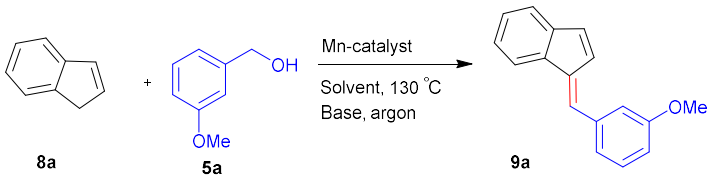


4 **5b** **6ai** **6ai'**

Entry	Cat	Base (mmol)	Solvent (ml)	Time (h)	Fluorene : Alcohol (mmol)	% Yield [b] **6ai**	**6ai'**
1	**1**	*t*BuOK (0.5)	Toluene(2)	24	0.5 : 1.0	35	--
2	**1**	*t*BuOK (0.5)	Toluene(2)	48	0.5 : 1.0	42	--
3	**1**	*t*BuOK (1.0)	Toluene(2)	48	0.5 : 1.0	62	--
4[c]	**1**	*t*BuOK (1.0)	Toluene(2)	48	0.5 : 1.0	63	--
5	**1**	*t*BuOK (1.0)	Toluene(2)	36	0.5 : 1.0	62	--
6	**1**	*t*BuOK (1.0)	Toluene(2)	24	0.5 : 1.0	48	--
7	**1**	$CsOH.H_2O$ (1.0)	Toluene(2)	36	0.5 : 1.0	51	--
8	**2**	*t*BuOK (1.0)	Toluene(2)	24	0.5 : 1.0	61	--
9	**3**	*t*BuOK (1.0)	Toluene(2)	24	0.5 : 1.0	21	--
10[d]	**1**	*t*BuOK (1.0)	Toluene(2)	36	0.5 : 1.0	70	--

[a]**Conditions**: **4** (0.5 mmol), **5b** (0.5-1.0 mmol), *t*BuOK (0.5-1.0 mmol), Mn-catalysts (5-12 mol%), under argon. [b]Isolated yield, [c]Temperature 160 °C. [d]Catalyst loading 12 mol%.

6. Optimization table for the alkenylation of indene[a]:

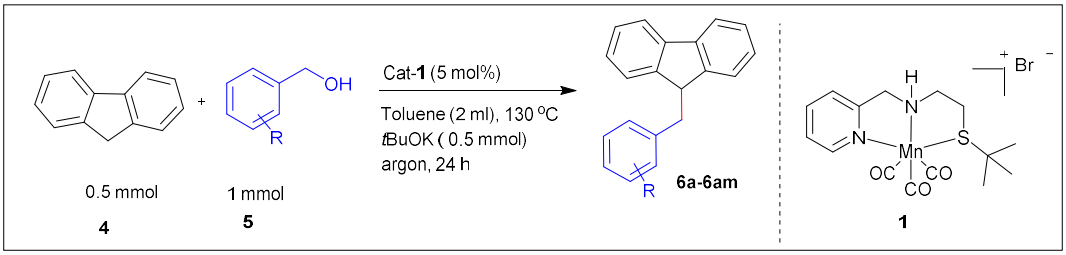


8a **5a** **9a**

Entry	Cat	Base (mmol)	Solvent (ml)	Time (h)	Tempr. (°C)	Indene : Alcohol (mmol)	% Yield [b] **9a**
1	**1**	*t*BuOK (0.5)	Toluene(2)	24	130 °C	0.5 : 1.0	Trace
2	**1**	CsOH.H_2O(0.5)	Toluene(2)	24	130 °C	0.5 : 1.0	Trace
3	**1**	CsOH.H_2O(0.5)	Toluene(2)	24	130 °C	0.5 : 1.0	Trace
4	**1**	CsOH.H_2O(0.5)	^{t}AmOH(2)	24	130 °C	0.5 : 1.0	20
5	**1**	CsOH.H_2O(0.5)	^{t}AmOH(1) + EtOH(1)	24	130 °C	0.5 : 1.0	22
6	**1**	NaOH(0.5)	^{t}AmOH(2)	24	130 °C	0.5 : 1.0	70
7	**1**	NaOH(0.5)	Toluene(2)	24	130 °C	0.5 : 1.0	10
8	**1**	*t*BuOK (0.5)	^{t}AmOH(2)	24	130 °C	0.5 : 1.0	15
9	**1**	NaOH(0.5)	^{t}AmOH(2)	12	130 °C	0.5 : 1.0	46
10	**1**	NaOH(0.5)	Dioxane(2)	24	130 °C	0.5 : 1.0	85
11	**1**	NaOH(0.5)	Dioxane(2)	24	110 °C	0.5 : 1.0	85
12	**1**	NaOH(0.25)	Dioxane(2)	24	110 °C	0.5 : 1.0	32
13	**1**	KOH(0.5)	Dioxane(2)	24	110 °C	0.5 : 1.0	65
14	**1**	NaO^{t}Bu(0.5)	Dioxane(2)	24	110 °C	0.5 : 0.5	65
15	**1**	NaOH(0.5)	Dioxane(2)	24	110 °C	0.5 : 0.55	84
16	.....	NaOH(0.5)	Dioxane(2)	24	110 °C	0.5 : 0.55	Trace
17	**1**	.....	Dioxane(2)	24	110 °C	0.5 : 1.0	Trace
18	**1**	NaOH(0.5)	Dioxane(2)	24	100 °C	0.5 : 1.0	71
19	**2**	NaOH(0.5)	Dioxane(2)	24	110 °C	0.5 : 1.0	81
20	**3**	NaOH(0.5)	Dioxane(2)	24	110 °C	0.5 : 1.0	62

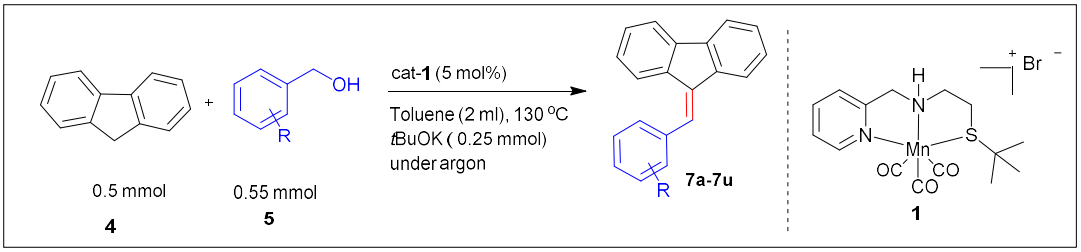
[a]**Conditions**: **8a** (0.5 mmol), **5a** (0.5-1.0 mmol), Base (0.25 - 0.5 mmol), Mn-Catalyst (5 mol%), under argon. [b]Isolated yield, Temperature (130 °C – 100 °C).

7. General experimental procedure for the alkylation of fluorene:



To an oven dried 10 mL round bottomed flask, fluorene **4** (0.5 mmol), alcohols **5** (1.0 mmol), *t*BuOK (0.5 mmol) and cat-**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 2%-5% ethyl acetate in hexane to get pure compound.

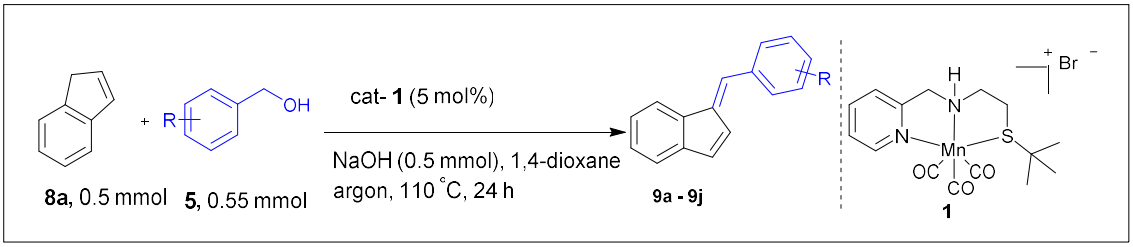
8. General experimental procedure for the alkenylation of fluorene:



A mixture of aromatic primary alcohol **5** (0.55 mmol), fluorene **4** (0.5 mmol), *t*BuOK (0.25 mmol) and cat-**1** (5 mol%) were stirred in toluene (2 ml) under argon atmosphere at 130 °C for 24 h. After the reaction was completed, it 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 2%-5% ethyl acetate in hexane to get pure compound.

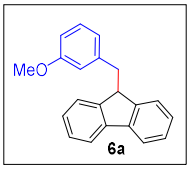
9. General experimental procedure for the alkenylation of indene:

To an oven dried 10 mL round bottom flask, aromatic primary alcohol (0.55 mmol), indene **8a** (0.5 mmol), cat-**1** catalyst (5 mol%), NaOH (0.5 mmol) and dioxane (2 mL) were added under argon atmosphere. The reaction mixture was kept for refluxing in preheated oil bath at 110 °C for 24 h. Then, the reaction was cooled at room temperature and ethyl acetate was added, diluted 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 2%-5% ethyl acetate as an eluting system.



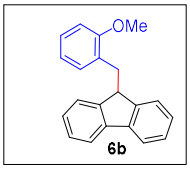
10. Characterization data:

9-(3-methoxybenzyl)-9H-fluorene (6a):[2]



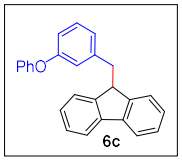
Yellow solid, 98% Yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.24 –7.19 (m, 5H), 6.86 – 6.75 (m, 3H), 4.23 (t, *J* = 7.5 Hz, 1H), 3.75 (s, 3H), 3.09 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 147.0, 141.5, 141.0, 129.3, 127.2, 126.8, 125.0, 122.1, 120.0, 115.0, 112.1, 55.3, 48.7, 40.2.

9-(2-methoxybenzyl)-9H-fluorene (6b):[2]



Yellow solid, 96% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.30 (td, *J* = 8.1, 1.6 Hz, 1H), 7.22 – 7.16 (m, 4H), 7.05 (d, *J* = 7.5Hz, 1H), 6.95-9.89 (m, 2H), 4.36 (t, *J* = 7.5 Hz, 1H), 3.88 (s, 3H), 3.06 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.1, 147.8, 140.8, 131.7, 128.7, 128.0, 127.0, 126.6, 125.1, 120.3, 119.8, 110.4, 55.4, 46.8, 35.7.

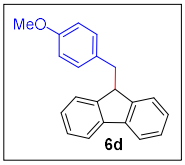
9-(3-phenoxybenzyl)-9H-fluorene (6c):[3]



Yellow solid, 90% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.34 – 7.29 (m, 4H), 7.24 – 7.19 (m, 5H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.93 – 6.87 (m, 4H), 6.81 (s, 1H), 4.19 (t, *J* = 7.4 Hz, 1H), 3.09 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR

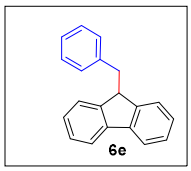
(150 MHz, $CDCl_3$) δ 157.5, 157.0, 146.6, 141.8, 141.0, 130.0, 129.6, 127.3, 126.8, 125.0, 124.7, 123.1, 120.3, 120.0, 118.7, 48.6, 40.0.

9-(4-methoxybenzyl)-9H-fluorene (6d):[3]



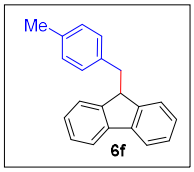
White solid, 98% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.15 (m, 4H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.16 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.03 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 147.0, 140.9, 131.9, 130.5, 127.2, 126.7, 125.0, 119.9, 113.7, 55.3, 49.0, 39.3.

9-benzyl-9H-fluorene (6e):[4]



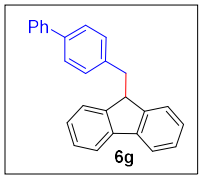
White solid, 93% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.15 (m, 11H), 4.23 (t, *J* = 7.6 Hz, 1H), 3.11 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.0, 141.0, 140.0, 129.7, 128.4, 127.2, 126.8, 126.5, 125.0, 120.0, 48.8, 40.2.

9-(4-methylbenzyl)-9H-fluorene (6f):[3]



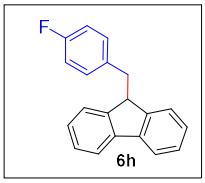
White solid, 94% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.24 – 7.17 (m, 4H), 7.14 – 7.10 (m, 4H), 4.21 (t, *J* = 7.6 Hz, 1H), 3.07 (d, *J* = 7.6 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 141.0, 136.9, 135.9, 129.5, 129.1, 127.2, 126.8, 125.0, 119.9, 48.9, 39.8, 21.3.

9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene(6g):[3]



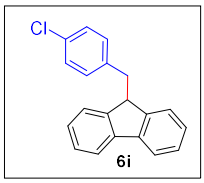
White solid, 78% Yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.32 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.19 (m, 4H), 4.26 (t, *J* = 7.6 Hz, 1H), 3.14 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 141.0, 141.0, 139.3, 139.1, 130.1, 128.9, 127.3, 127.1, 127.1, 126.8, 125.0, 120.0, 48.8, 39.9.

9-(4-fluorobenzyl)-9H-fluorene (6h):[3]



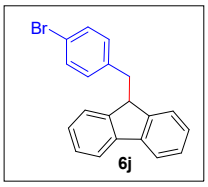
White solid, 65% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.23 –7.18 (m, 4H), 7.11– 7.09 (m, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 4.17 (t, *J* = 7.4 Hz, 1H), 3.09 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7 (d, *J* = 241.5 Hz), 146.6, 141.0, 135.3 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 7.5 Hz), 127.3, 126.8, 124.9, 120.0, 115.1 (d, *J* = 21.0 Hz), 48.8, 39.2.

9-(4-chlorobenzyl)-9H-fluorene (6i):[2]



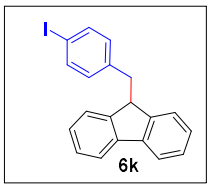
White solid, 64% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.25 – 7.18 (m, 6H), 7.09 (d, *J* = 8.3 Hz, 2H), 4.19 (t, *J* = 7.4 Hz, 1H), 3.10 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.5, 141.0, 138.1, 132.2, 131.0, 128.4, 127.4, 126.8, 124.8, 120.0, 48.6, 39.4.

9-(4-bromobenzyl)-9H-fluorene (6j):[2]



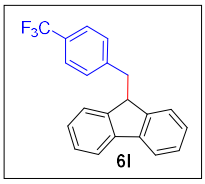
White solid, 86% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.25 – 7.19 (m, 4H), 7.03 (d, *J* = 8.3 Hz, 2H), 4.19 (t, *J* = 7.3 Hz, 1H), 3.09 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 141.0, 138.6, 131.4, 131.4, 127.4, 126.9, 124.8, 120.3, 120.0, 48.5, 39.4.

9-(4-iodobenzyl)-9H-fluorene (6k):[4]



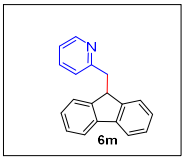
White solid, 72% Yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.19 (m, 4H), 6.92 (d, *J* = 7.9 Hz, 2H), 4.19 (t, *J* = 7.3 Hz, 1H), 3.08 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 141.0, 139.4, 137.4, 131.7, 127.4, 126.9, 124.9, 120.1, 91.7, 48.5, 39.6.

9-(4-(trifluoromethyl)benzyl)-9H-fluorene (6l):[3]



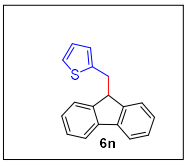
White solid, 63% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.22 – 7.14 (m, 6H), 4.18 (t, *J* = 7.3 Hz, 1H), 3.14 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.3, 143.8, 141.0, 130.0, 128.8 (q, *J* = 31.6 Hz), 127.5, 127.2, 127.0, 125.4, 125.2 (q, *J* = 4.5 Hz), 124.8, 124.6 (q, *J* = 270 Hz), 48.4, 39.8.

2-((9H-fluoren-9-yl)methyl)pyridine (6m):[2]



White solid, 92% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70-8.68 (m, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.62 (td, *J* = 7.6, 1.8 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.18 (m, 3H), 7.07 (d, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 8 Hz, 1H), 4.63 (t, *J* = 7.7 Hz, 1H), 3.23 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 149.7, 147.2, 140.9, 136.4, 127.2, 126.9, 124.8, 124.5, 121.8, 120.0, 47.3, 42.7.

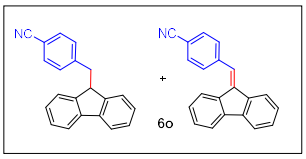
2-((9H-fluoren-9-yl)methyl)thiophene (6n):[2]



Yellow solid, 68% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.29 – 7.23 (m, 4H), 7.12 (d, *J* = 4.0 Hz, 1H), 6.89 – 6.86 (m, 1H), 6.71 (s, 1H), 4.23 (t, *J* = 8.0 Hz, 1H), 3.39 (d, *J* = 8.0 Hz, 2H). ^{13}C

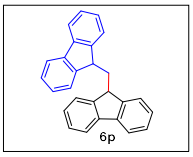
NMR (100 MHz, $CDCl_3$) δ 146.3, 142.2, 141.1, 127.4, 126.9, 126.7, 126.1, 124.8, 123.9, 120.0, 49.1, 34.1.

4-((9H-fluoren-9-yl)methyl)benzonitrile(6o): [5]



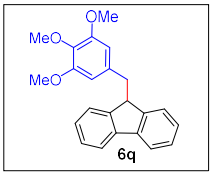
Yellow solid, 35% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 – 7.66 (m, 36H), 7.55 (s, 5H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.32 (m, 22H), 7.25 – 7.19 (m,5 H), 7.17 (d, *J* = 7.4 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 5H), 4.23 (t, *J* = 7.0 Hz, 1H), 3.22 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.9, 145.0, 142.0, 141.8, 141.0, 139.6, 139.0, 138.6, 136.0, 132.4, 132.0, 130.4, 130.2, 129.5, 129.1, 127.6, 127.4, 127.0, 126.9, 124.7, 124.4, 124.4, 120.6, 120.2, 119.9, 119.1, 118.9, 111.6, 110.3, 48.2, 39.9.

Di (9H-fluoren-9-yl)methane (6p):[6]



White solid, 63% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.6 Hz, 4H), 7.55 (d, *J* = 7.5 Hz, 4H), 7.40 (t, *J* = 7.5 Hz, 4H), 7.29 (t, *J* = 7.2 Hz, 4H), 4.40 (t, *J* = 7.6 Hz, 2H), 2.24 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.6, 141.1, 127.4, 127.1, 125.1, 120.2, 46.0, 39.0.

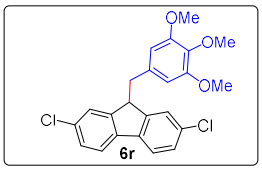
9-(3,4,5-trimethoxybenzyl)-9H-fluorene (6q): [7]



White solid, 63% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.35-7.32 (m, 2H), 7.26 – 7.22 (m, 4H), 6.35 (s, 2H), 4.20 (t, *J* = 7.3 Hz, 1H), 3.84 (s, 3H), 3.74 (s, 6H), 3.07 (d, *J* = 7.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.9, 146.6, 141.0, 136.4, 135.2, 127.2, 126.7, 125.0, 120.0, 106.4, 61.1, 56.1, 48.7, 40.3.

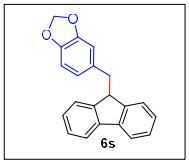
2,7-dichloro-9-(3,4,5-trimethoxybenzyl)-9H-fluorene(6r):

White solid, 72% Yield.^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.32 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.23 (s, 2H), 6.28 (s, 2H), 4.14 (t, *J* = 7.1 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 6H), 3.04 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 148.1, 138.7, 137.1, 133.9, 132.8, 127.7, 125.5, 120.9, 106.8, 61.1, 56.2, 48.9, 40.1. HRMS (ESI) m/z (M+H): 415.0868, found: 415.0869.



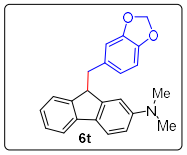
5-((9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole (6s):[8]

White solid, 96% Yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.36-7.32 (m, 2H), 7.25 – 7.19 (m, 4H), 6.74 – 6.72 (m, 2H), 6.62 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.94 (s, 2H), 4.15 (t, *J* = 7.5 Hz, 1H), 3.02 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 146.8, 146.1, 141.0, 133.7, 127.3, 126.8, 125.0, 122.7, 120.0, 109.8, 108.1, 101.0, 49.0, 40.0.



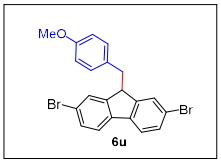
9-(benzo[d][1,3]dioxol-5-ylmethyl)-N,N-dimethyl-9H-fluoren-2-amine (6t):

Brown solid, 89% Yield.[1]H NMR (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 6.9 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.79 (s, 1H), 6.75 (d, *J* = 7.8 Hz, 2H), 6.68 (d, *J* = 7.7 Hz, 1H), 6.54 (s, 1H), 5.94 (s, 1H), 5.93 (s, 1H), 4.07 (t, *J* = 7.5 Hz, 1H), 3.05 (dd, *J* = 13.7, 7.5 Hz, 1H), 2.96 – 2.92 (m, 7H). [13]C NMR (151 MHz, $CDCl_3$) δ 148.4, 147.6, 146.1, 146.0, 141.5, 134.1, 127.2, 125.0, 124.6, 122.8, 120.5, 118.6, 112.1 110.1, 109.7 108.1, 100.9, 49.1, 41.2, 40.4. HRMS (ESI) m/z (M+H): 344.1651, found: 344.1657.



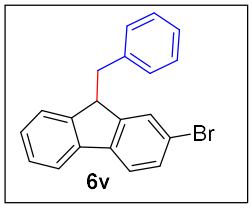
2,7-dibromo-9-(4-methoxybenzyl)-9H-fluorene(6u):

Yellow solid, 82% Yield. [1]H NMR (500 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.29 (s, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.11 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 3.02 (d, *J* = 7.5 Hz, 2H). [13]C NMR (125 Chloroform-*d*) δ 158.6, 148.6, 139.0, 130.7, 130.4, 130.5, 128.4, 121.3, 121.0, 114.0, 55.5, 49.1, 39.0. HRMS (ESI) m/z (M+K): 480.0905, found: 480.0903.



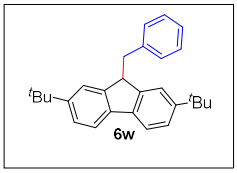
9-benzyl-2-bromo-9H-fluorene (6v):[2]

White solid, 86% Yield.[1]H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.45 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.34 – 7.17 (m, 8H), 7.18 (d, *J* = 7.2 Hz, 1H), 4.18 (t, *J* = 7.6 Hz, 1H), 3.04 – 3.01 (m, 2H). [13]C NMR (150 MHz, $CDCl_3$) δ 148.9, 146.6, 140.0, 139.9, 139.3, 130.3, 129.6, 128.5, 128.3, 127.4, 127.2, 126.7, 125.0, 121.2, 120.5, 120.0, 48.8, 40.0.



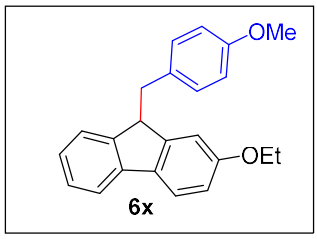
9-benzyl-2,7-di-tert-butyl-9H-fluorene(6w):[9]

White solid, 86% Yield.[1]H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.31 (m, 4H), 7.25 (dd, *J* = 13.2, 5.8 Hz, 3H), 7.11 (s, 2H), 4.14 (t, *J* = 7.8 Hz, 1H), 3.06 (d, *J* = 7.9 Hz, 2H), 1.28 (s, 18H). [13]C NMR (125 MHz, $CDCl_3$) δ 149.5, 147.0, 140.5, 138.3, 129.9, 128.4, 126.4, 124.2, 122.0, 119.1, 49.1, 40.8, 34.9, 31.7.



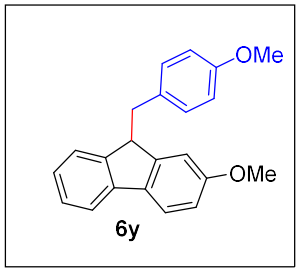
2-ethoxy-9-(4-methoxybenzyl)-9H-fluorene (6x):

White solid, 94% Yield. [1]H NMR (500 MHz, Chloroform-*d*) δ 7.61 (t, *J* = 8.1 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.13 – 7.12 (m, 4H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.70 (s, 1H), 4.11 (t, *J* = 7.6 Hz, 1H), 3.97 (m, 2H), 3.80 (s, 1H), 3.07 – 2.99 (m, 2H), 1.39 (t, *J* = 6.9 Hz, 3H). [13]C NMR (125 MHz, $CDCl_3$) δ 158.5, 158.3, 148.8, 146.6, 141.0, 133.8, 132.0, 130.6, 127.18, 125.6, 124.8, 120.6, 119.1, 114.1, 113.8, 111.2, 63.8, 55.4, 49.1, 39.5, 15.0. HRMS (ESI) m/z (M+H): 331.1698, found: 331.1698



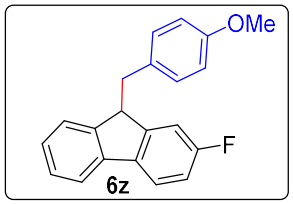
2-methoxy-9-(4-methoxybenzyl)-9H-fluorene (6y):

White solid, 95% Yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 (t, *J* = 8.1 Hz, 2H), 7.31 – 7.28 (m, 1H), 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), 3.08 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.98 (dd, *J* = 13.8, 7.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 158.4, 148.9, 146.6, 140.9, 134.0, 132.0, 130.6, 127.2, 125.6, 124.8, 120.6, 119.1, 113.8, 113.4, 110.6, 55.5, 55.4, 49.1, 39.5. HRMS (ESI) m/z (M+H): 317.1542, found: 317.1549.



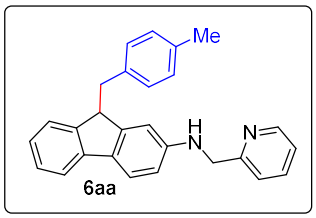
2-fluoro-9-(4-methoxybenzyl)-9H-fluorene (6z):

White solid, 81% Yield.^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 – 7.62 (m, 2H), 7.34 – 7.31 (m, 1H), 7.22 – 7.18 (m, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.03 – 7.00 (m, 1H), 6.83 (d, *J* = 8.5 Hz, 3H), 4.14 (t, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.08 (dd, *J* = 13.8, 7.6 Hz, 1H), 2.98 (dd, *J* = 13.8, 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2 (d, *J* =243.0 Hz), 158.3, 149.0 (d, *J* = 8.2 Hz), 146.7 (d, *J* = 2.1 Hz), 140.0, 136.8 (d, *J* = 2.4 Hz), 131.3, 130.4, 127.2, 126.3, 124.8, 120.6 (d, *J* = 8.1 Hz), 119.5, 114.2 (d, *J* = 22.9 Hz), 113.8, 112.3 (d, *J* = 22.6 Hz), 55.3, 48.9 (d, *J* = 2.3 Hz), 39.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.3. HRMS (ESI) m/z (M+H): 305.1342, found: 305.1346.



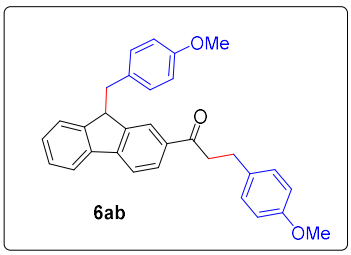
9-(4-methylbenzyl)-N-(pyridin-2-ylmethyl)-9H-fluoren-2-amine (6aa):

Yellow solid, 90% Yield.^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 4.5 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.17 – 7.15 (m, 1H), 7.10 – 7.04 (m, 6H), 6.64 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.47 (s, 1H), 4.40 (s, 2H), 4.08 (t, *J* = 7.5 Hz, 1H), 3.01 (d, *J* = 7.5 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 149.3, 150.0, 147.4, 146.1, 141.6, 137.1, 136.8, 135.7, 131.3, 129.6, 129.0, 127.0, 124.8, 124.6, 122.2, 121.8, 120.7, 118.5, 112.6, 109.6, 49.5, 48.8, 40.0, 21.2. HRMS (ESI) m/z (M+H): 377.2018, found: 377.2019.



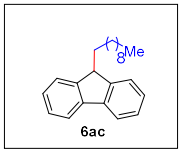
1-(9-(4-methoxybenzyl)-9H-fluoren-2-yl)-3-(4-methoxyphenyl)propan-1-one (6ab):

White solid, 62% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 2H), 7.72 (s, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.20 (t, *J* = 7.5 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.17 (t, *J* = 7.2 Hz, 2H), 3.11 – 3.02 (m, 2H), 3.00 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.4, 158.4, 158.1, 148.3, 147.0, 145.7, 139.7, 135.3, 133.5, 131.5, 130.6, 129.5, 128.0, 127.8, 127.5, 125.2,



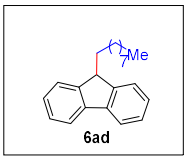
124.9, 120.9, 119.8, 114.1, 113.8, 55.4, 55.3, 49.1, 40.8, 39.1, 29.6. HRMS (ESI) m/z (M+H): 449.2117, found: 449.2118.

9-decyl-9H-fluorene (6ac):[2]



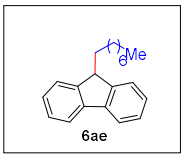
Sticky yellow oil, 96% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.25 (m, 4H), 3.94 (t, *J* = 5.8 Hz, 1H), 1.99 – 1.96 (m, 2H), 1.29 – 1.19 (m, 16H), 0.88 – 0.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 141.2, 126.9, 126.9, 124.5, 119.9, 47.3, 33.2, 32.1, 30.1, 29.8, 29.7, 29.6, 29.5, 25.8, 22.8, 14.3.

9-nonyl-9H-fluorene (6ad):[2]



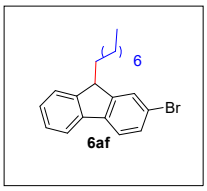
Sticky yellow oil, 83% Yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 2H), 7.38–7.33 (m, 2H), 7.31 –7.28 (m, 2H), 3.96 (t, *J* = 5.9 Hz, 1H), 2.01 – 1.96 (m, 2H), 1.29 – 1.15 (m, 14H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 141.2, 126.9, 126.9, 124.5, 119.9, 47.6, 33.2, 32.0, 30.1, 29.7, 29.6, 29.4, 25.9, 22.8, 14.2.

9-octyl-9H-fluorene (6ae):[3]



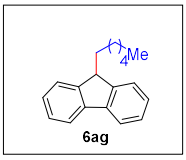
Sticky yellow oil, 81% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.27 (m, 4H), 3.96 (t, *J* = 5.9 Hz, 1H), 2.01 – 1.95 (m, 2H), 1.27 – 1.14 (m, 12H), 0.85 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 141.2, 126.9, 126.9, 124.5, 119.9, 47.6, 33.2, 32.0, 30.1, 29.5, 29.4, 25.8, 22.8, 14.2.

2-bromo-9-octyl-9H-fluorene (6af):[2]



Sticky colourless oil, 87% Yield**.** ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.5 Hz, 1H), 7.62 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.0 Hz, 2H), 7.36 – 7.30 (m, 2H), 3.94 (t, *J* = 5.5 Hz, 1H), 2.02 – 1.92 (m, 2H), 1.26 – 1.12 (m, 13H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 147.5, 140.3, 140.3, 130.1, 127.8, 127.4, 127.2, 124.5, 121.2, 120.8, 120.0, 47.7, 33.0, 32.0, 30.3, 29.5, 29.4, 25.7, 22.8, 14.2.

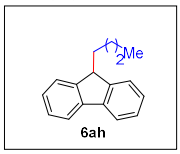
9-hexyl-9H-fluorene (6ag):[3]



Sticky yellow oil, 56% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.33 (m,2H), 7.31 – 7.28 (m, 2H), 3.96 (t, *J* = 5.9 Hz, 1H), 2.01 – 1.96 (m, 2H), 1.27 – 1.15 (m, 8H), 0.83 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 141.2, 126.9, 126.9, 124.5, 119.9, 47.6, 33.2, 31.8, 29.8, 25.8, 22.8, 14.2.

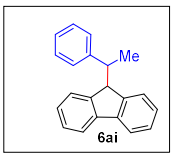
9-butyl-9H-fluorene (6ah):[3]

Sticky yellow oil, 39% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.49 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 3.95 (t, *J* = 5.6 Hz, 1H), 2.01 – 1.97 (m, 2H), 1.28 – 1.23 (m, 2H), 1.17 – 1.12 (m, 2H), 0.81 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.7, 141.2, 126.9, 126.9, 124.4, 119.9, 47.6, 32.9, 27.9, 23.2, 14.1.



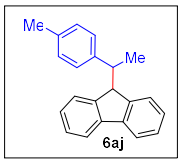
9-(1-phenylethyl)-9H-fluorene (6ai):[2]

Yellow solid, 62% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.68 (m, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.38 – 7.28 (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), 3.70 – 3.64 (m, 1H), 0.91 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 144.7, 144.7, 142.0, 141.5, 128.3, 128.2, 127.2, 127.2, 126.9, 126.4, 126.4, 125.8, 124.4, 119.8, 119.7, 54.3, 42.0, 14.0.



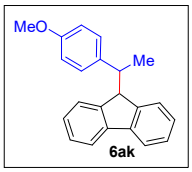
9-(1-(p-tolyl)ethyl)-9H-fluorene (6aj):[2]

Yellow solid, 68% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.68 (m, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.37 – 7.27 (m, 3H), 7. 23 – 7.08 (m, 5H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.26 (d, *J* = 4.3 Hz, 1H), 3.67 – 3.60 (m, 1H), 2.36 (s, 3H), 0.88 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 144.8, 141.2, 141.7, 141.5, 135.9, 129.0, 128.0, 127.1, 127.1, 126.9, 126.3, 125.8, 124.4, 119.8, 119.7, 54.4, 41.6, 21.2, 14.0.



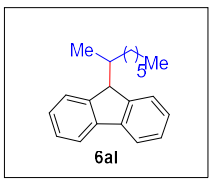
9-(1-(4-methoxyphenyl)ethyl)-9H-fluorene (6ak):[2]

Yellow solid, 71% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.68 (m, 2H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.11 (td, *J* = 7.5 Hz, 0.88 Hz, 1H), 6.89 – 6.83 (m, 3H), 4.25 (d, *J* = 4.5 Hz, 1H), 3.83 (s, 3H), 3.66 – 3.60 (m, 1H), 0.89 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 146.7, 144.8, 141.9, 141.5, 136.8, 129.1, 127.2, 127.1, 126.9, 126.3, 125.8, 124.4, 119.8, 119.7, 113.6, 55.4, 54.5, 41.2, 14.3.

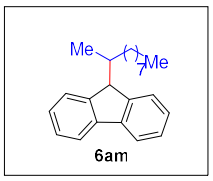


9-(octan-2-yl)-9H-fluorene (6al):[2]

Sticky yellow oil, 64% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.72 (m, 2H), 7.52 – 7.49 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 4H), 7.28 (q, *J* = 7.0 Hz, 1H), 3.99 (brs, 1H), 2.39 – 2.35 (m, 1H), 1.47 – 1.27 (m, 10H), 0.88 (t, *J* = 6.3 Hz, 3H), 0.60 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 145.9, 142.0, 141.6, 126.9, 126.9, 126.9, 126.7, 125.3, 124.5, 119.8, 119.7, 52.6, 37.3, 34.6, 32.0, 29.6, 28.1, 22.8, 15.8, 14.3.

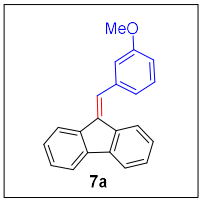


9-(decan-2-yl)-9H-fluorene (6am):



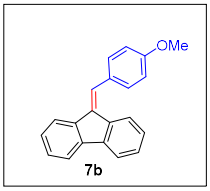
Sticky yellow oil, 69% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.65 (m, 2H), 7.44 – 741 (m, 2H), 7.30 – 7.26 (m, 2H), 7.23 – 7.17 (m, 2H), 3.91 (d, *J* = 2.6 Hz, 1H), 2.32 – 2.25 (m, 1H), 1.40 – 1.19 (m, 14H), 0.82 (t, *J* = 6.6 Hz, 3H), 0.52 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 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. HRMS (ESI) m/z (M+): 306.2348, found: 306.2322.

9-(3-methoxybenzylidene)-9H-fluorene (7a):[10]



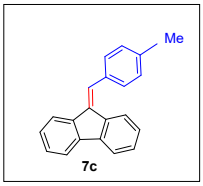
Yellow solid, 83% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.65 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.40 – 7.28 (m, 4H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.11 (s, 1H), 7.08 – 7.04 (m, 1H), 6.94 – 6.92 (m, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 141.4, 139.5, 139.3, 138.3, 136.7, 136.6, 129.7, 128.7, 128.4, 127.2, 127.1, 126.8, 124.7, 121.8, 120.4, 119.8, 119.7, 114.3, 114.2, 55.4.

9-(4-methoxybenzylidene)-9H-fluorene (7b):[5]



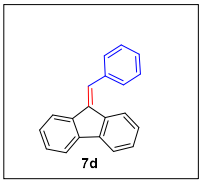
Yellow solid, 75% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.4 Hz, 1H), 7.73 – 7.69 (m, 3H), 7.65 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.28 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 141.1, 139.7, 138.9, 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-methylbenzylidene)-9H-fluorene (7c): [5]



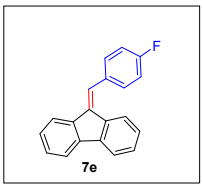
Yellow solid, 82% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.4 Hz, 1H), 7.75 – 7.74 (m, 2H), 7.70 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 2.47 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 141.2, 139.6, 139.1, 138.0, 136.6, 135.9, 133.8, 129.3, 129.2, 128.4, 128.0, 127.6, 126.9, 126.6, 124.4, 120.2, 119.7, 119.6, 21.5.

9-benzylidene-9H-fluorene (7d):[11]



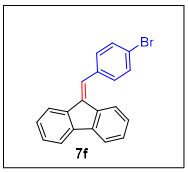
Yellow solid, 52% Yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.28 Hz, 1H), 7.73 – 7.70 (m, 3H), 7.60 – 7.56 (m, 3H), 7.48 – 7.44 (m, 2H), 7.41 – 7.29 (m, 4H), 7.05 (td, *J* = 7.4, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 139.5, 139.2, 136.9, 136.6, 136.5, 129.3, 128.5, 128.2, 128.0, 127.3, 127.0, 126.7, 124.4, 120.2, 119.7, 119.6.

9-(4-fluorobenzylidene)-9H-fluorene (7e): [5]



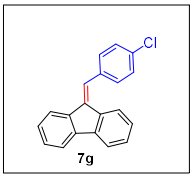
Yellow solid, 59% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.61 (s, 1H), 7.55 – 7.53 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.32 (q, *J* = 6.3 Hz, 2H), 7.14 (t, *J* = 8.6 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.6 (d, *J* = 246 Hz), 141.4, 139.4, 139.3, 136.8, 136.5, 133.0 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 7.5 Hz), 128.8, 128.4, 127.2, 126.8, 126.1, 124.4, 120.3, 119.9, 119.8, 115.7 (d, *J* = 21.0 Hz).

9-(4-bromobenzylidene)-9H-fluorene (7f):[5]



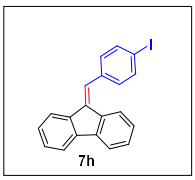
Yellow solid, 75% Yield.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.60 – 7.56 (m, 3H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.45 (m, 2H), 7.38 (td, *J* = 7.4, 1.2 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.08 (td, *J* = 7.5, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 139.3 (2C), 137.1, 136.3, 135.8, 131.8, 131.0, 128.8, 128.5, 127.1, 126.8, 125.6, 124.3, 122.1, 120.1, 119.9, 119.7.

9-(4-chlorobenzylidene)-9H-fluorene (7g):[5]



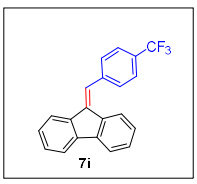
Yellow solid, 60% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.62 (s, 1H), 7.56 – 7.54 (m, 3H), 7.46 – (m, 2H), 7.43 – 7.40 (dt, *J* = 7.74 Hz, *J* = 1.0 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.07 (td, *J* = 7.8 Hz, 1.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.4, 139.3, 139.2, 137.1, 136.3, 135.3, 133.9, 130.7, 128.8, 128.5, 127.1, 126.8, 125.7, 124.3, 120.3, 119.9, 119.7.

9-(4-iodobenzylidene)-9H-fluorene (7h):[12]



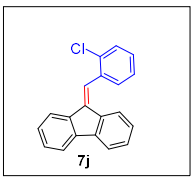
Yellow solid, 61% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.53 (m, 2H), 7.38 (t, J = 7.8 Hz, 1H), 7.33 (t, *J* = 8.1 Hz, 4H), 7.09 –7.06 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.4, 139.3, 139.2, 137.7, 137.0, 136.4, 136.3, 131.2, 128.8, 128.5, 127.1, 126.8, 125.8, 124.4, 120.3, 119.9, 119.7, 93.7.

9-(4-(trifluoromethyl)benzylidene)-9H-fluorene (7i):[5]



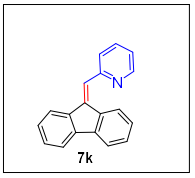
Yellow solid, 59% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.75 – 7.71 (m, 6H), 7.62 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.40 (td, *J* = 7.4, 1.1 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.06 (td, *J* = 7.6, 1.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.5, 140.7, 139.4, 139.1, 137.9, 136.1, 129.9 (d, J = 40.5 Hz), 129.6, 129.1, 128.7, 125.5 (q, *J* = 3.5 Hz), 125.0, 124.4, 124.2 (q, *J* = 269.0 Hz), 120.4, 119.9, 119.7.

9-(2-chlorobenzylidene)-9H-fluorene (7j):[5]



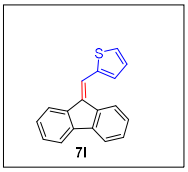
Yellow oil, 55% Yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.71 – 7.65 (m, 3H), 7.60 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.28 (m, 6H), 7.03 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 139.6, 139.3, 137.7, 136.5, 135.6, 134.2, 131.6, 129.9, 129.6, 128.9, 128.7, 127.3, 126.9, 126.7, 124.5, 124.0, 120.8, 119.9, 119.8.

2-((9H-fluoren-9-ylidene)methyl)pyridine (7k):[5]



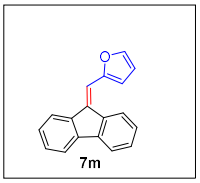
Yellow solid, 36% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 4.8 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 7.82 – 7.79 (m, 1H), 7.77 – 7.75 (m, 1H), 7.71 – 7.69 (m, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.60 (s, 1H), 7.42 – 7.27 (m, 4H), 7.17 (td, *J* = 7.7, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 149.8, 141.9, 140.0, 139.8, 138.9, 136.4, 136.4, 129.4, 128.8, 127.2, 127.2, 126.4, 125.8, 125.8, 122.6, 120.6, 119.7, 119.7.

2-((9H-fluoren-9-ylidene)methyl)thiophene (7l):[5]



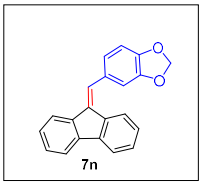
Yellow solid, 70% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.7 Hz, 1H), 7.72 (q, *J* = 7.4 Hz, 3H), 7.61 (s, 1H), 7.47 – 7.44 (m, 2H), 7.38 – 7.29 (m, 3H), 7.21 – 7.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 139.7, 139.2, 139.1, 136.7, 136.3, 129.4, 128.9, 128.4, 127.7, 127.5, 127.1, 127.0, 124.5, 120.3, 120.0, 119.8, 119.1.

2-((9H-fluoren-9-ylidene)methyl)furan (7m):[5]



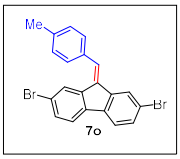
Yellow solid, 68% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 (d, *J* = 7.3 Hz, 1H), 7.74 – 7.67 (m, 4H), 7.40 – 7.28 (m, 5H), 6.75 (d, *J* = 3.4 Hz, 1H), 6.57 (dd, *J* = 3.4, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 143.9, 141.1, 140.3, 139.0, 136.2, 132.7, 128.5, 127.9, 127.1, 126.8, 125.7, 119.9, 119.6, 119.6, 115.6, 112.7, 112.5.

5-((9H-fluoren-9-ylidene)methyl)benzo[d][1,3]dioxole (7n):[5]



Yellow solid, 52% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.72 – 7.70 (m, 3H), 7.58 (s, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.31–7.29 (m, 2H), 7.11 –7.07 (m, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.03 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.9, 147.7, 141.3, 139.7, 139.2, 136.5, 136.0, 130.7, 128.6, 128.2, 127.3, 127.3, 126.8, 124.5, 123.6, 120.2, 119.9, 119.7, 109.7, 108.6, 101.4.

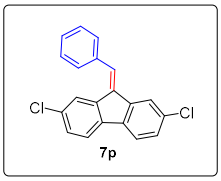
2,7-dibromo-9-(4-methylbenzylidene)-9H-fluorene (7o):[13]



Yellow solid, 77% Yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 – 7.85 (m, 1H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.65 (s, 1H), 7.53 – 7.51 (m, 2H), 7.48 – 7.44 (m, 3H), 7.42 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5, 139.2, 139.2, 138.3, 137.0, 134.0, 132.8, 131.5, 131.2, 130.5, 129.6, 129.4, 127.5, 123.7, 121.3, 121.1, 121.0, 120.9, 21.6.

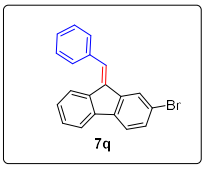
9-benzylidene-2,7-dichloro-9H-fluorene (7p):[14]

Yellow solid , 65% Yield, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 1.5 Hz, 1H), 7.70 (s, 1H), 7.59 – 7.55 (m, 4H), 7.51 – 7.43 (m, 4H), 7.34 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.28 (dd, *J* = 8.1, 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.1, 138.8, 138.0, 136.7, 135.9, 134.8, 133.3, 132.7, 130.0, 129.3, 128.9, 128.9, 128.8, 128.5, 124.7, 120.9, 120.7.



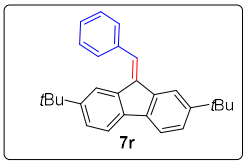
(E)-9-benzylidene-2-bromo-9H-fluorene (7q):[15]

Yellow solid, 80% Yield, ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.8 Hz, 1H), 7.68 – 7.66 (m, 2H), 7.58 – 7.55 (m, 4H), 7.50 – 7.48 (m, 3H), 7.42 – 7.40 (m, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 141.5, 140.4, 138.1, 136.5, 136.4, 135.6, 131.1, 129.3, 128.9, 128.7, 128.7, 128.5, 127.2, 124.5, 123.7, 121.0, 119.9.



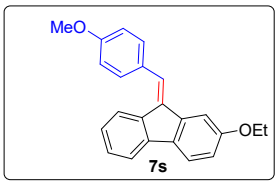
9-benzylidene-2,7-di-tert-butyl-9H-fluorene (7r):[14]

Yellow solid, 81% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.68 (s, 1H), 7.60 – 7.56 (m, 4H), 7.52 (s, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 1.41 (s, 9H), 1.15 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 149.4, 139.6, 138.8, 137.5, 137.5, 137.1, 137.0, 129.4, 128.5, 128.0, 126.1, 125.7, 125.7, 121.9, 119.1, 119.0, 117.1, 35.1, 34.9, 31.7, 31.4.



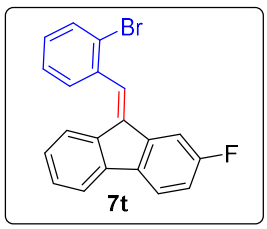
(E)-2-ethoxy-9-(4-methoxybenzylidene)-9H-fluorene (7s):

White solid, 72% Yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.5 Hz, 1H), 7.61 – 7.54 (m, 5H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.22 (m, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.86 (dd, *J* = 8.1, 2.0 Hz, 1H), 3.89 – 3.85 (m, 5H), 1.33 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 158.3, 139.6, 139.3, 138.3, 135.7, 134.4, 130.9, 129.2, 128.1, 127.4, 125.9, 120.5, 120.0, 118.9, 115.5, 114.1, 110.3, 63.6, 55.5, 15.0. HRMS (ESI) m/z (M+H): 329.1542, found: 329.1547.

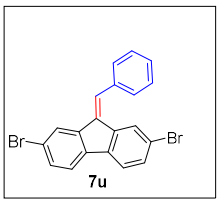


(E)-9-(2-bromobenzylidene)-2-fluoro-9H-fluorene (7t): [16]

Yellow solid, 63% Yield ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.44 (m, 5H), 7.32 – 7.30 (m, 1H), 7.27 – 7.25 (m, 2H), 7.16 (td, *J* = 8.5, 2.3 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.6, 163.6 (d, *J* = 247.5 Hz), 144.0, 140.2 (d, *J* = 3.0 Hz), 136.4 (d, *J* = 7.2 Hz), 135.2, 134.4 (d, *J* = 2.3 Hz), 128.8, 124.7, 121.7 (d, *J* = 8.0 Hz), 120.9 (d, *J* = 23.1 Hz), 120.2, 112.0 (d, *J* = 23.3 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -111.7.

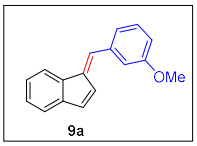


9-benzylidene-2,7-dibromo-9H-fluorene (7u):[14]



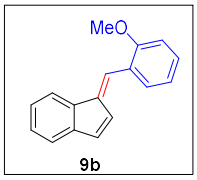
Yellow solid, 70% Yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.87 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.48 (m, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 139.2, 138.1, 137.1, 135.8, 134.6, 131.6, 131.3, 130.1, 129.3, 129.0, 128.9, 127.5, 123.8, 121.4, 121.1, 121.0, 120.9.

(E)-1-(3-methoxybenzylidene)-1H-indene (9a):[17]



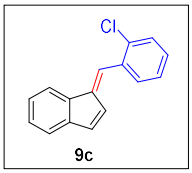
Yellow solid, 84% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.2 Hz, 1H), 7.46 (s, 1H), 7.34 – 7.30 (m, 2H), 7.26 – 7.18 (m, 3H), 7.13 (s, 1H), 7.03 – 7.00 (m, 2H), 6.90 (d, *J* = 8.2 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 142.2, 140.4, 138.4, 137.5, 134.7, 129.8, 128.7, 127.7, 126.2, 125.3, 123.0, 121.1, 119.3, 115.5, 114.2, 55.4.

(E)-1-(2-methoxybenzylidene)-1H-indene (9b):[18]



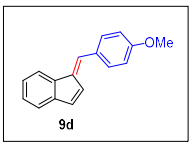
Yellow solid, 82% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.67 (d, *J* = 7.1 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.17 – 7.12 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.91 – 6.87 (m, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 142.3, 140.0, 137.5, 134.0, 132.1, 130.0, 127.4, 126.6, 126.2, 125.1, 124.6, 120.9, 120.7, 119.6, 110.7, 55.7.

(E)-1-(2-chlorobenzylidene)-1H-indene (9c):[19]



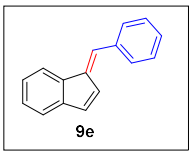
Yellow solid, 65% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.2 Hz, 1H), 7.70 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.28 (d, *J* = 7.32 Hz, 1H), 7.25 –7.22 (m, 2H), 7.01 (d, J = 5.76 Hz, 1H), 6.82 (d, *J* = 5.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.6, 141.8, 137.1, 135.3, 135.3, 134.9, 132.6, 129.8, 129.5, 128.1, 126.9, 126.1, 125.5, 125.3, 121.2, 119.8.

(E)-1-(4-methoxybenzylidene)-1H-indene (9d):[19]



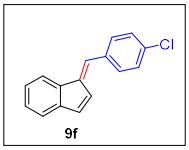
Yellow solid, 85% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.44 (s, 1H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.05 (d, *J* = 5.76 Hz, 1H), 7.00 (d, *J* = 5.76 Hz, 1H), 6.95 (d, *J* = 8.58 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.1, 141.9, 138.3, 137.8, 133.9, 131.9, 129.8, 128.7, 127.2, 126.1, 125.1, 121.0, 119.0, 114.4, 55.5.

(E)-1-benzylidene-1H-indene (9e):[19]



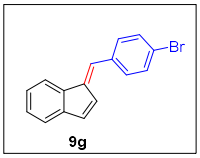
Yellow solid, 78% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 6.6 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.50 (s, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 –7.30 (m, 2H), 7.25 – 7.20 (m, 2H), 7.04 – 7.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 140.3, 137.6, 137.1, 134.7, 130.4, 128.9, 128.8, 128.5, 127.7, 126.3, 125.3, 121.1, 119.3.

(E)-1-(4-chlorobenzylidene)-1H-indene (9f):[19]



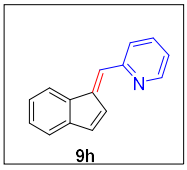
Yellow solid, 66% Yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.37 (m, 3H), 7.30 (d, *J* = 6.7 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.01 (d, *J* = 5.5 Hz, 1H), 6.94 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 140.7, 137.4, 135.5, 135.2, 134.5, 131.5, 129.1, 127.9, 127.3, 125.8, 125.5, 121.2, 119.3.

(E)-1-(4-bromobenzylidene)-1H-indene (9g):[20]



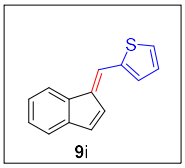
Yellow solid, 61% Yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.60 – 7.56 (m, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.45 (m, 1H), 7.38 (td, *J* = 7.4, 1.2 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.08 (td, *J* = 7.5, 1.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 140.8, 137.4, 136.0, 135.3, 132.0, 131.7, 127.9, 127.3, 125.8, 125.5, 122.8, 121.2, 119.3.

(E)-2-((1H-inden-1-ylidene)methyl)pyridine (9h):[8]



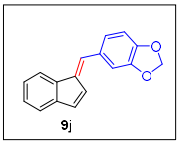
Yellow solid, 75% Yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 4.56 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.64 (d, *J* = 6.4 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.36 (s, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.18 – 7.16 (m, 1H), 7.02 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.9, 150.2, 142.9, 142.7, 137.8, 136.5, 135.9, 128.3, 127.6, 126.2, 126.0, 125.4, 122.5, 121.2, 119.6.

(E)-2-((1H-inden-1-ylidene)methyl)thiophene (9i):[19]



Yellow solid, 68% Yield.^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.0 Hz, 1H), 7.52 (s, 1H), 7.43 (d, *J* = 5.04 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.22 – 7.17 (m, 3H), 7.08 – 7.06 (m, 1H), 6.99 (d, *J* = 5.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.0, 140.8, 137.7, 137.4, 134.2, 131.8, 129.3, 127.8, 127.4, 125.7, 125.3, 121.3, 121.1, 119.1.

(E)-5-((1H-inden-1-ylidene)methyl)benzo[d][1,3]dioxole (9j):[8]



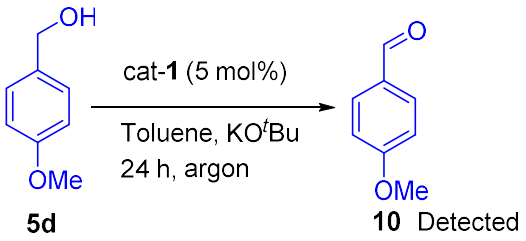
Yellow solid, 63% Yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 6.9 Hz, 1H), 7.39 (s, 1H), 7.31 (d, *J* = 6.8 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.15 (s, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 7.03 – 7.00 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 2H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 148.3, 148.2, 141.9, 138.7, 137.7, 134.2, 131.3, 128.7, 127.4, 125.9, 125.4, 125.2, 121.1, 119.1, 109.9, 108.8, 101.5.

11. Mechanistic investigation:

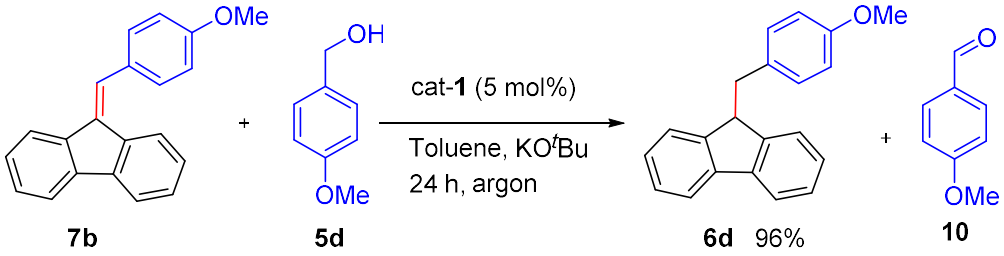
11.1. Manganese catalyzed dehydrogenation of alcohol:

To an oven-dried 10 mL round bottomed flask, cat-**1** (5 mol%), 4-methoxy benzyl alcohol (1.0 mmol), toluene (2 mL) was added under argon. The reaction mixture was kept for heating at 130 °C for 24 h. Then, the reaction mixture was submitted for crude nmr analysis.



5d **10** Detected

11.2. Manganese catalyzed hydrogenation of intermediate (7b) by alcohol (5d):

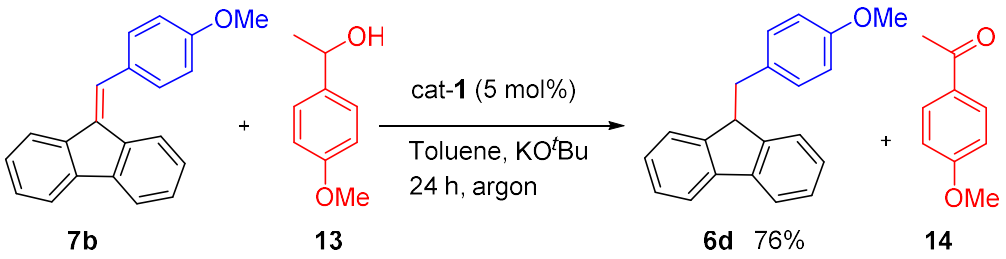


7b **5d** **6d** 96% **10**

To an oven dried round bottomed flask intermediate **7b** (0.5 mmol), 4-methoxy benzyl alcohol **10** (1.0 mmol), KO*t*Bu (0.5 mmol) and cat-**1** (5 mol%) were taken, then toluene was added under argon atmosphere. The resulting mixture was then placed into the preheated oil bath at 130 °C for 24 h. 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 (2-5%) as eluent, and 96% of **6d** was obtained.

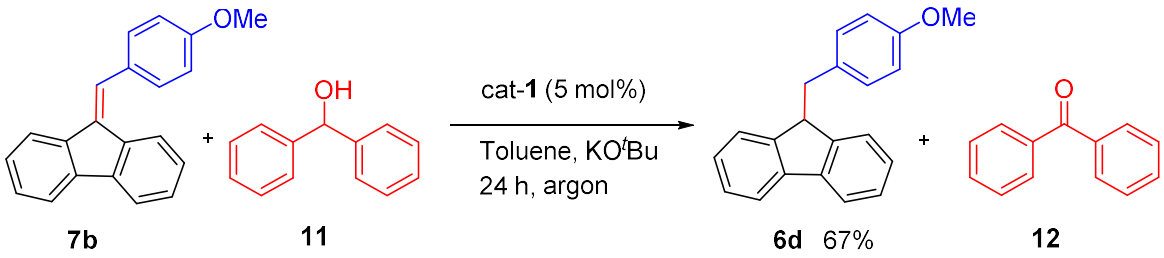
11.3. Manganese catalyzed hydrogenation of intermediate (7b) by secondary alcohol (13):

To an oven dried round bottomed flask intermediate **7b** (0.5 mmol), 4-methoxy alpha methyl benzyl alcohol **13** (1.0 mmol), KO*t*Bu (0.5 mmol) and cat-**1** (5 mol%) were taken, then toluene was added under argon atmosphere. The resulting mixture was then placed into the preheated oil bath at 130 °C for 24 h. After completion the reaction cooled to room temperature, afterthat 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 (2-5%) as eluent, 76% of **6d** was obtained.



7b **13** **6d** 76% **14**

11.4. Manganese catalyzed hydrogenation of intermediate (7b) by diphenyl methanol (11):



7b **11** **6d** 67% **12**

To an oven dried round bottomed flask intermediate **7b** (0.5 mmol), diphenyl methanol **11** (1.0 mmol), KO*t*Bu (0.5 mmol) and cat-**1** (5 mol%) were taken, then toluene was added under argon atmosphere. The resulting mixture was then placed into the preheated oil bath at 130 °C for 24 h. After completion the reaction cooled to room temperature, afterthat ethyl acetate was added to it and filtered through celite. The filtrate was concentrated under vacuum, the residue was used for ^{1}H NMR analysis which indicates 67% of **6d** was formed.

11.5. Preparation of deuterated alcohol:

Deuterated benzyl alcohol was prepared according to previously reported literature method.[21] Alcohol (10 mmol), Ru-MACHO (0.020 mmol), KO^{t}Bu (0.06 mmol) were charged in a 60 mL seal tube The degas D_2O (10 mL) was added using syringe and reaction mixture purged with argon and tube is sealed with cap and heated at 80 °C in an oil bath. The reaction was stopped after 8 h and reaction mixture is extracted with dichloromethane .The removal of solvent under reduced pressure provided pure products for further reaction. The ^{1}H-NMR data reveals 97% deuterium incorporation in 4-methoxy benzyl alcohol.

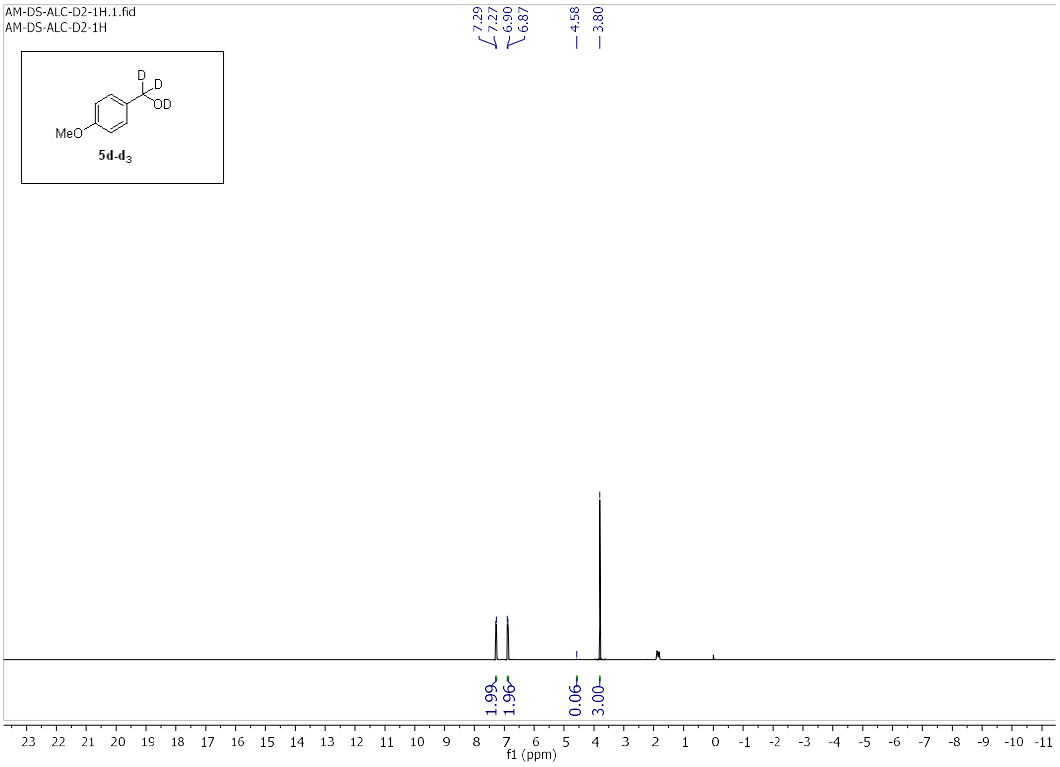
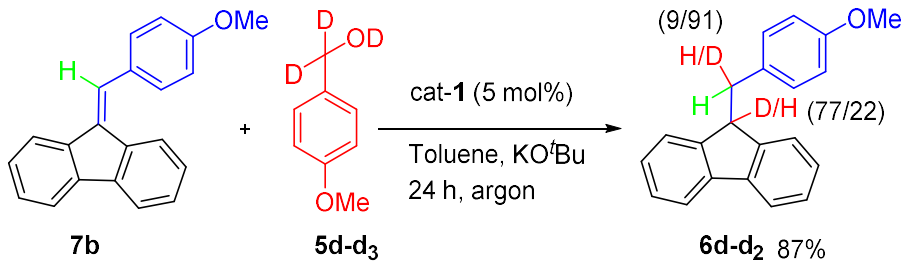


Figure S1. ^{1}H NMR Spectrum of (4-methoxyphenyl) methan-d2-ol-d **(5d-d$_3$)** in $CDCl_3$.

11.6. Manganese catalyzed hydrogenation of intermediate (7b) by deuterated alcohol (5d-d$_3$):



To an oven dried round bottomed flask intermediate **7b** (0.5 mmol), deuterated 4-methoxy benzyl alcohol **5d-d$_3$** (1.0 mmol), KO*t*Bu (0.5 mmol) and cat-**1** (5 mol%) were taken, then toluene was added under argon atmosphere. The resulting mixture was then placed into the preheated oil bath at 130 °C for 24 h. After completion the reaction cooled to room temperature, afterthat 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 (2-5%) as eluent, 87% of **6d-d$_2$** was obtained. The ^{1}H analysis of the product **6d-d$_2$** revealed that 78-89% incorporation occurred.

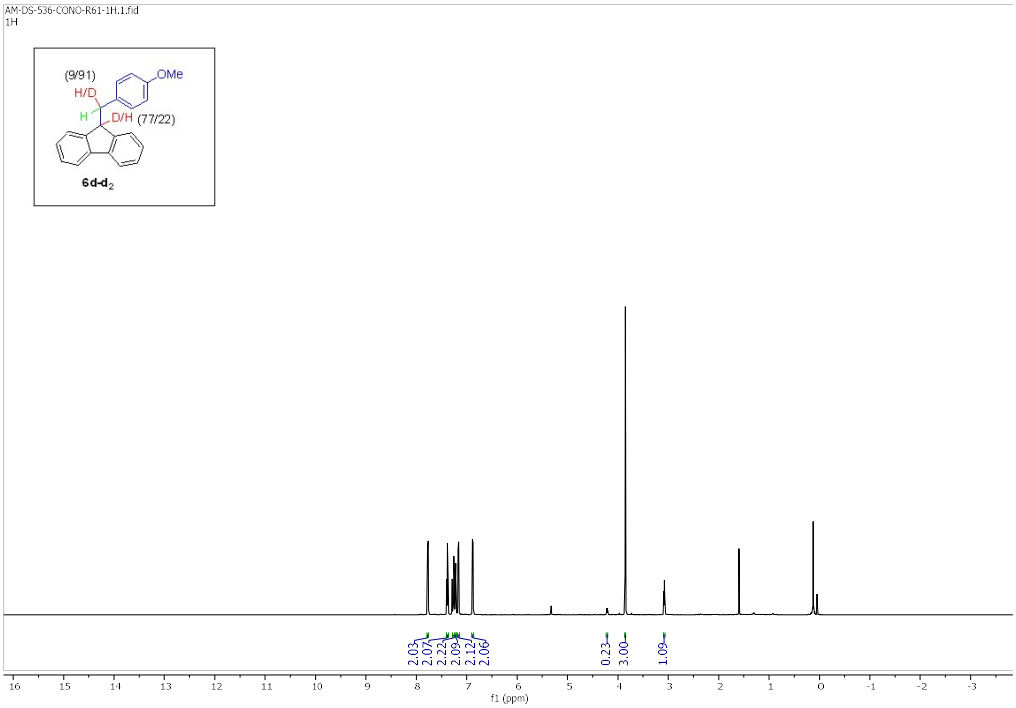


Figure S2. ^{1}H NMR Spectrum of **(6d-d$_2$)** in $CDCl_3$.

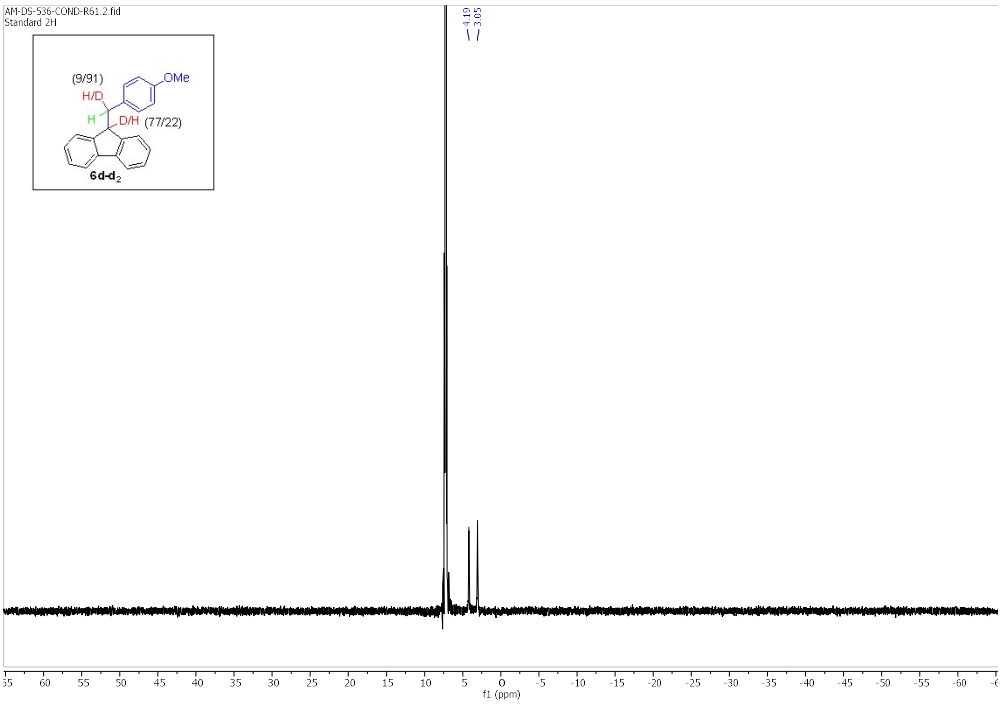
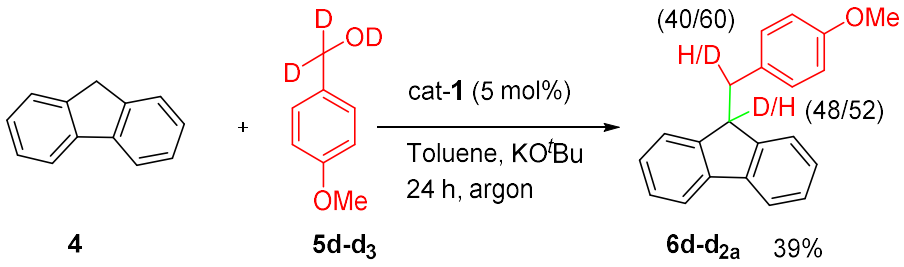


Figure S3. ^{2}D NMR Spectrum of **(6d-d$_2$)** in $CDCl_3$.

11.7. Manganese catalyzed alkylation of fluorene (4) by deuterated labelled alcohol (5d-d$_3$):



To an oven dried round bottomed flask fluorene, **4** (0.5 mmol), deuterated 4-methoxy benzyl alcohol **5d-d$_3$** (1.0 mmol), KO*t*Bu (0.5 mmol) and cat-**1** (5 mol%) were taken, then toluene was added under argon atmosphere. The resulting mixture was then placed into the preheated oil bath at 130 °C for 24 h. 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 (2-5%) as eluent, 39% of **6d-d$_{2a}$** was obtained. The ^{1}H analysis of the product **6d-d$_{2a}$** revealed that 48-60% incorporation occurred.

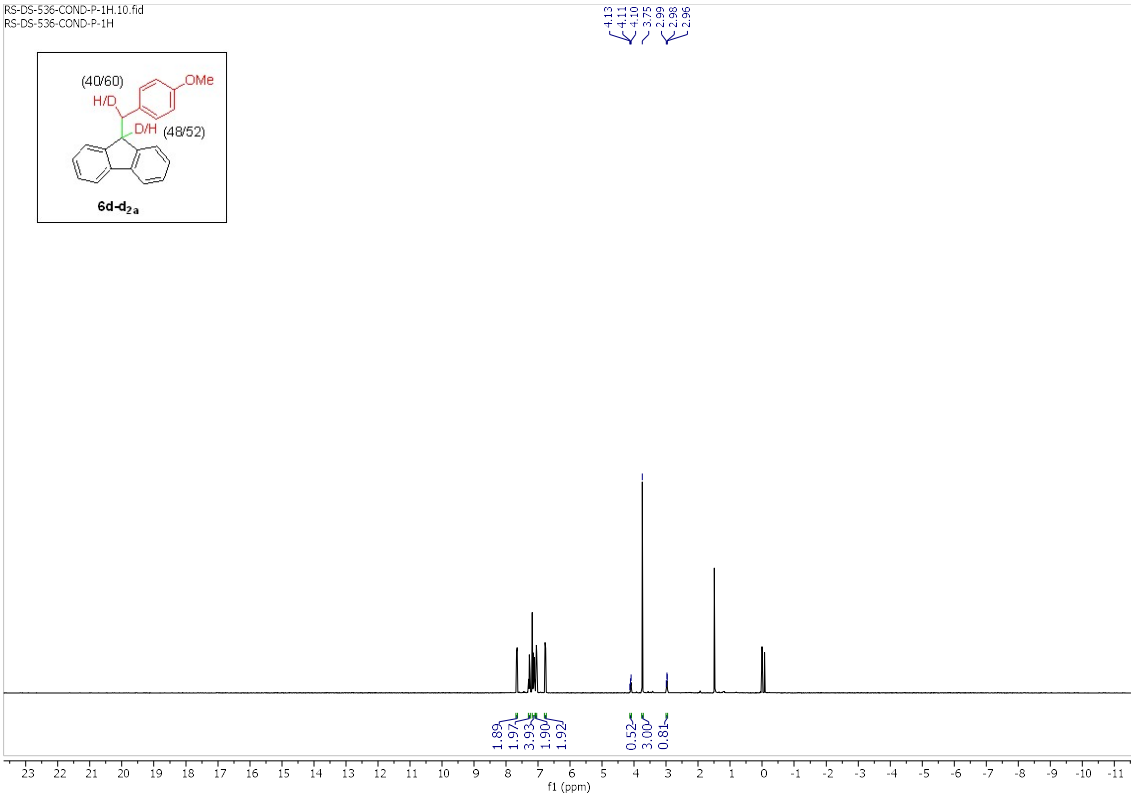
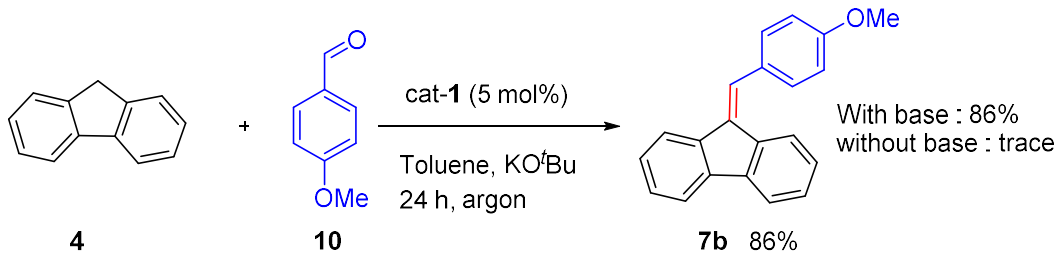


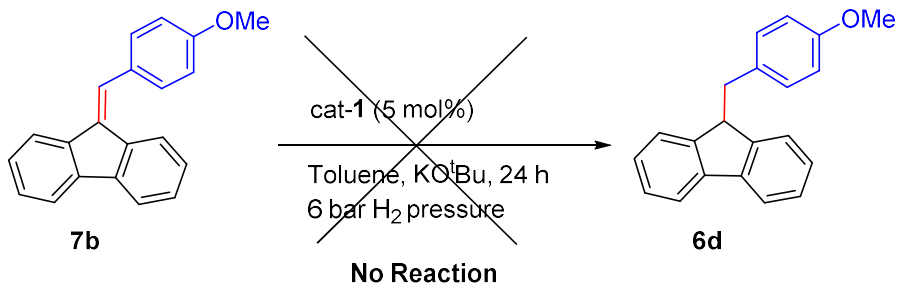
Figure S4. ^{1}H NMR Spectrum of **(6d-d_{2a})** in $CDCl_3$.

11.8. Manganese catalyzed alkenylation of fluorene (4) by 4-methoxy benzaldehyde (10):



Fluorene **4** (0.5 mmol), *t*-BuOK (56 mg, 0.5 mmol) and 4-methoxy benzylaldehyde **10** (1.0 mmol) were charged in an oven dried round bottomed flask in toluene (2 mL) under argon. The flask was then placed in a preheated oil bath at 130 °C. After 24 h, the crude reaction mixture was diluted by ethyl acetate and filter through celite. The filtrate was concentrated under vacuum and resultant residue was purified by column chromatography using 100-200 mesh size silica with hexane / ethyl acetate as an eluent, 86% product (**7b**) was obtained. No product (**7b**) was formed in the absence of *t*-BuOK.

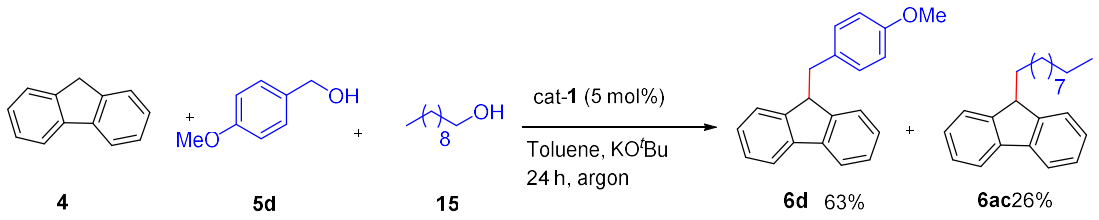
11.9. Manganese catalyzed hydrogenation of intermediate (7b) under hydrogen pressure:



To an oven dried reaction vessel intermediate **7b** (0.25 mmol), KO*t*Bu (0.25 mmol) and cat-**1** (5 mol%) were taken, then toluene was added under 6 bar H_2 pressure. The resulting mixture was then placed into the preheated oil bath at 130 °C for 24 h. After completion the reaction cooled to room temperature, afterthat ethyl acetate was added to it and filtered through celite. Then concentrated the filtrate under vacuum, then the crude residue was analysed by ^{1}H NMR which indicates no hydrogenated product was formed.

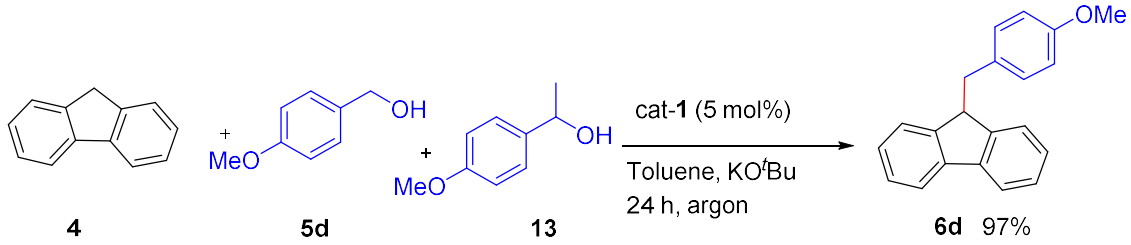
12. Competitive Experiments:

12.1. Manganese catalyzed alkylation of fluorene (4) with primary aromatic (5d) and aliphatic (15) alcohol:



Fluorene **4** (0.5 mmol), 4-methoxy benzylalcohol **5d** (1.0 mmol), 1-decanol **15** (1.0 mmol), cat-**1** (5 mol%) and *t*-BuOK (56 mg, 0.5 mmol) were charged in an oven dried round bottomed flask in toluene (2 mL) under argon. The flask was then placed in a preheated oil bath at 130 °C. After 24 h, the crude reaction mixture was diluted by ethyl acetate and filter through celite. The filtrate was concentrated under vacuum and resultant residue was purified by column chromatography using 100-200 mesh size silica with hexane / ethyl acetate as an eluent, 63% **6d** and 26% **6ac** were isolated

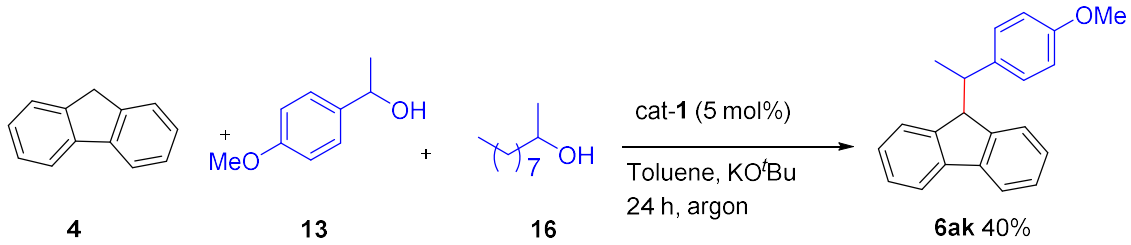
12.2. Alkylation of fluorene with primary and secondary aromatic alcohol:



4 5d 13 **6d** 97%

Fluorene **4** (0.5 mmol), 4-methoxy benzylalcohol **5d** (1.0 mmol), 4-methoxy alpha methyl benzyl alcohol **13** (1.0 mmol), *t*-BuOK (56 mg, 0.5 mmol) and cat-**1** (5 mol%) were charged in an oven dried round bottomed flask in toluene (2 mL) under argon. The flask was then placed in a preheated oil bath at 130 °C. After 24 h, the crude reaction mixture was diluted by ethyl acetate and filter through celite. The filtrate was concentrated under vacuum and resultant residue was purified by column chromatography using 100-200 mesh size silica with hexane / ethyl acetate as an eluent, only 97% **6d** was isolated. The result indicates that primary alcohol is more reactive towards alkylation than seconadary alcohol.

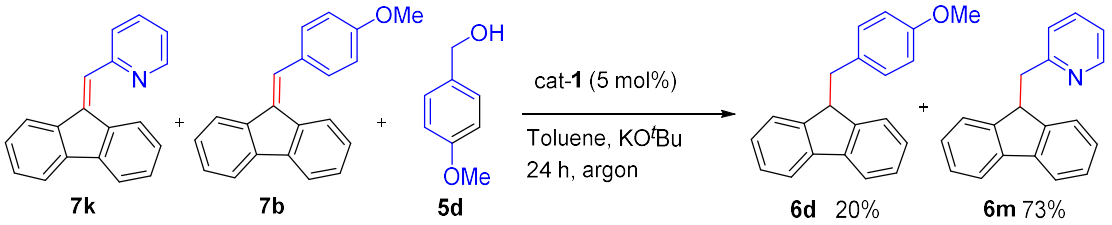
12.3. Alkylation of fluorene with primary and secondary aromatic alcohol:



4 13 16 **6ak** 40%

Fluorene **4** (0.5 mmol), 4-methoxy alpha methyl benzyl alcohol **13** (1.0 mmol), and 2-decanol **16** (1mmol), *t*-BuOK (56 mg, 0.5 mmol) and cat-**1** (5 mol%) were charged in an oven dried round bottomed flask in toluene (2 mL) under argon. The flask was then placed in a preheated oil bath at 130 °C. After 24 h, the crude reaction mixture was diluted by ethyl acetate and filter through celite. The filtrate was concentrated under vacuum and resultant residue was purified by column chromatography using 100-200 mesh size silica with hexane / ethyl acetate as an eluent, only 40% **6ak** was isolated. The result indicates that secondary benzyl alcohol is more reactive towards alkylation than seconadary aliphatic alcohol.

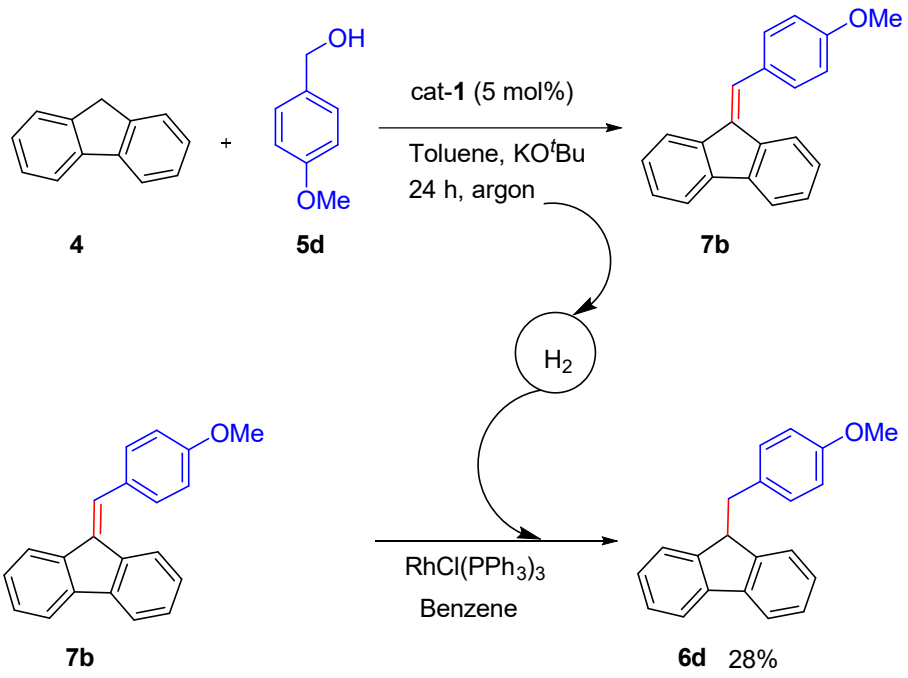
12.4. Manganese catalyzed rate of hydrogenation of (7k) & (7b) in presence of 4-methoxy benzyl alcohol (11):



An equimolar mixture of **7k**, **7b** & 4-methoxy benzylalcohol (**5d)** were taken (0.3 mmol of each) in an oven dried round bottomed flask. Then cat-**1** (5 mol%) and *t*-BuOK (33.6 mg, 0.3 mmol) were charged in toluene (2 mL) under argon. The flask was then placed in a preheated oil bath at 130 °C. After 24 h, the crude reaction mixture was diluted by ethyl acetate and filter through celite. The filtrate was concentrated under vacuum and resultant residue was purified by column chromatography using 100-200 mesh size silica with hexane / ethyl acetate as an eluent, 73% **6m** & only 20% of **6d** was isolated which indicates that the rate of hydrogenation of coordinating substrate is greater than others.

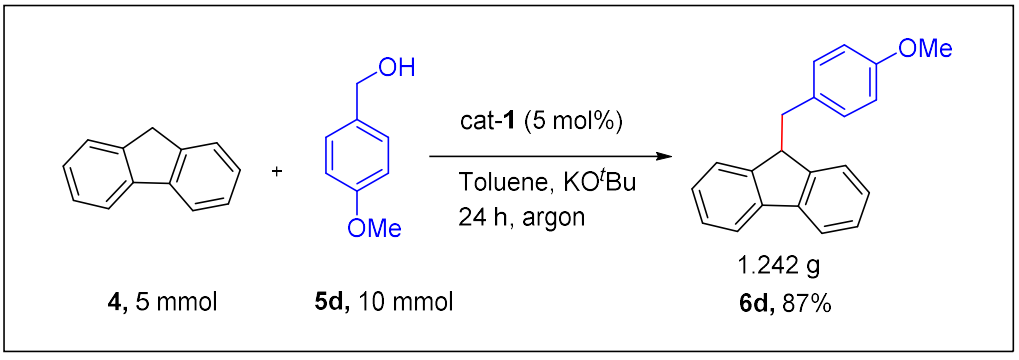
13. Utilization of liberated hydrogen gas:

To an oven dried 10mL round bottomed flask (**A**) fluorene **4** (1.0 mmol), 4-methoxy benzyl alcohol **5d** (1.2 mmol), KO^{t}Bu (0.5 mmol) and cat-**1** (5 mol%) were added, the entire system was degassed and flushed with argon for 5 minutes (three times), then dry toluene (2 mL) was added. To another 10 mL round bottomed flask (**B**) $RhCl(PPh_3)_3$ (6 mol%) catalyst, and intermediate **7b** (0.25 mmol) were dissolved in benzene (2 mL). Both the flask (**A** & **B**) were connected through a double headed syringe and allowed to equilibrate for 5 minutes. The mixture in the flask (**A**) was heated at 130 °C (oil-bath temperature), while the mixture in the flask (**B**) was stirred at 60 °C (oil-bath temperature). After 24 h, the organic entities present in the flask (**B**) were analyzed by GC which showed a clean conversion (28%) of the **7b** to **6d**.



14. Gram scale synthesis:

To an oven dried 50 mL round bottomed flask fluorene **4** (5.0 mmol), 4-methoxy benzyl alcohol (**5d** mmol), KO*t*Bu (5.0 mmol) and cat-**1** (5 mol%) were taken, then toluene was added under argon atmosphere. The resulting mixture was then placed into the preheated oil bath at 130 °C for 24 h. Upon 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 (2-5%) as eluent, and 87% of **6d** was obtained. Yield 87% (1.242 g)



15. Kinetic monitoring:

In a 10 mL 2-neck round bottomed flask, fluorene **4** (1.0 mmol), 4-methoxy benzyl alcohol **5d** (2.0 mmol), cat-**1** (5 mol%) and *t*BuOK (1.0 mmol) were taken under argon atmosphere. After that the final mixture was placed in preheated oil bath at 130 °C. The reaction mixture was analyzed by GC using mesitylene as an internal standard at specified time interval.

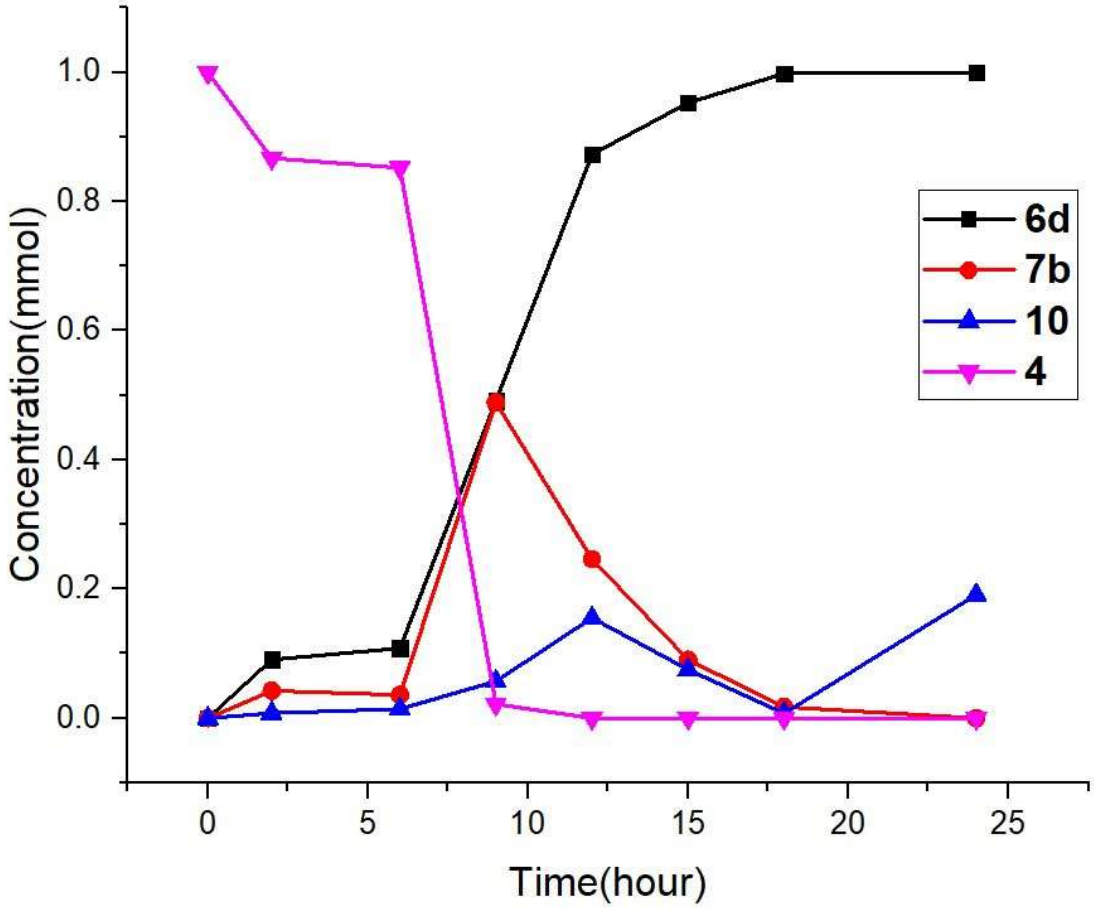


Figure S5. Kinetic profile of manganese catalyzed alkylation of fluorene with 4-methoxy benzyl alcohol.

16. NMR pictures:

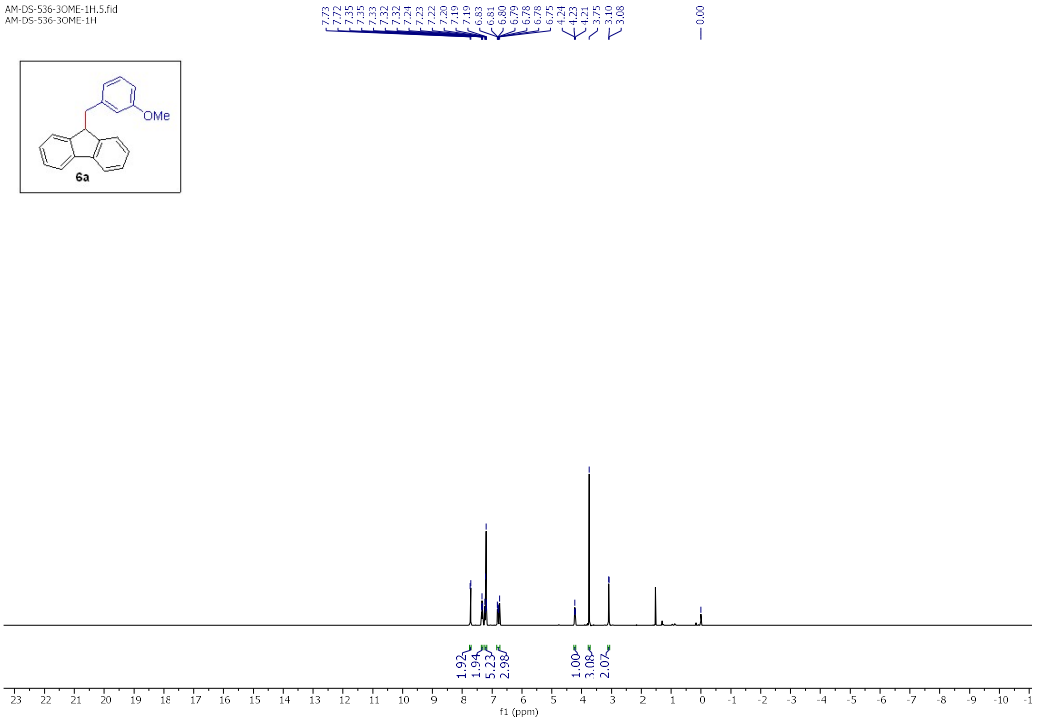


Figure S6. ^{1}H NMR Spectrum of 9-(3-methoxybenzyl)-9H-fluorene **(6a)** in $CDCl_3$.

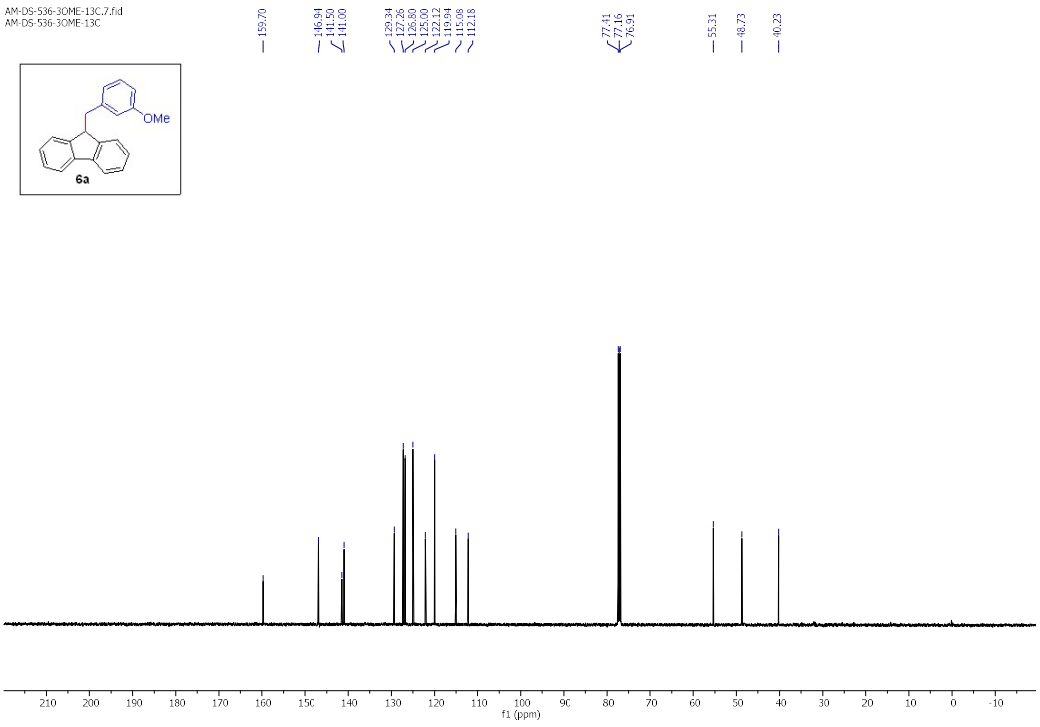


Figure S7. ^{13}C NMR Spectrum of 9-(3-methoxybenzyl)-9H-fluorene **(6a)** in $CDCl_3$.

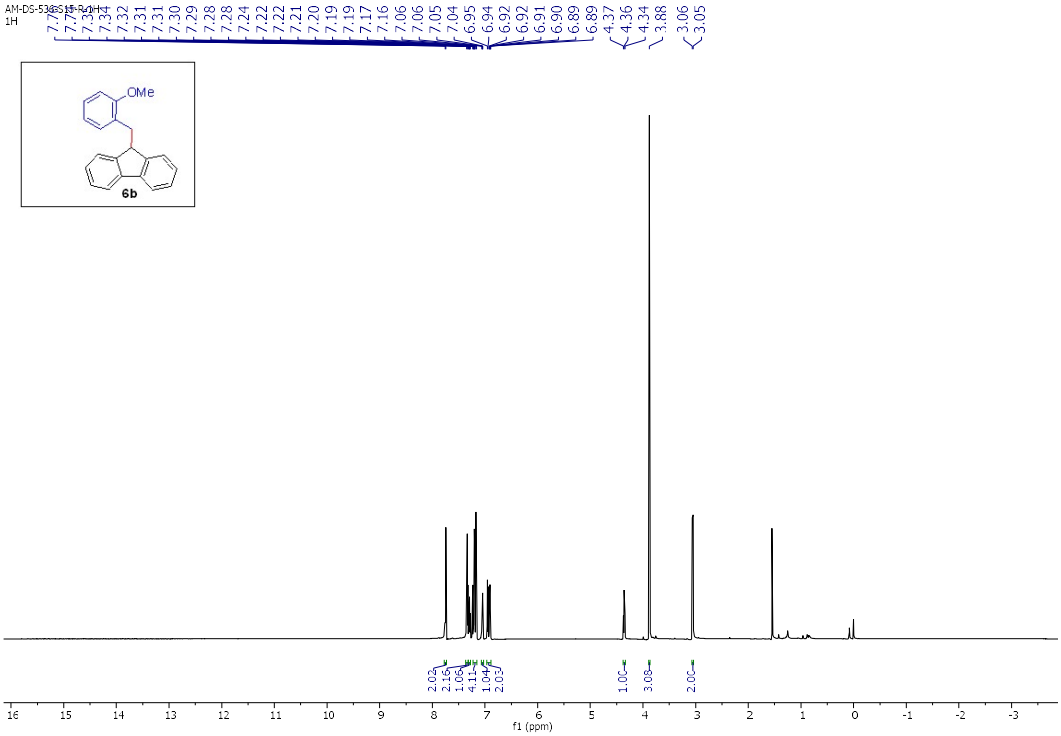


Figure S8. ^{1}H NMR Spectrum of 9-(2-methoxybenzyl)-9H-fluorene **(6b)** in $CDCl_3$.

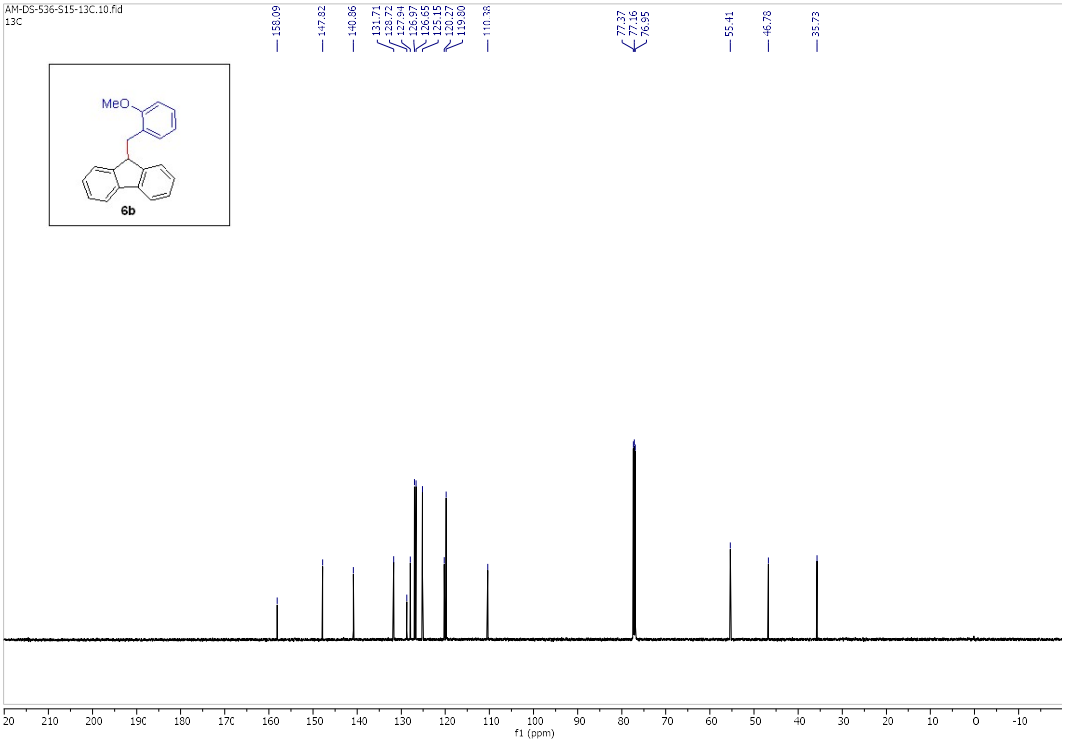


Figure S9. ^{13}C NMR Spectrum of 9-(2-methoxybenzyl)-9H-fluorene **(6b)** in $CDCl_3$.

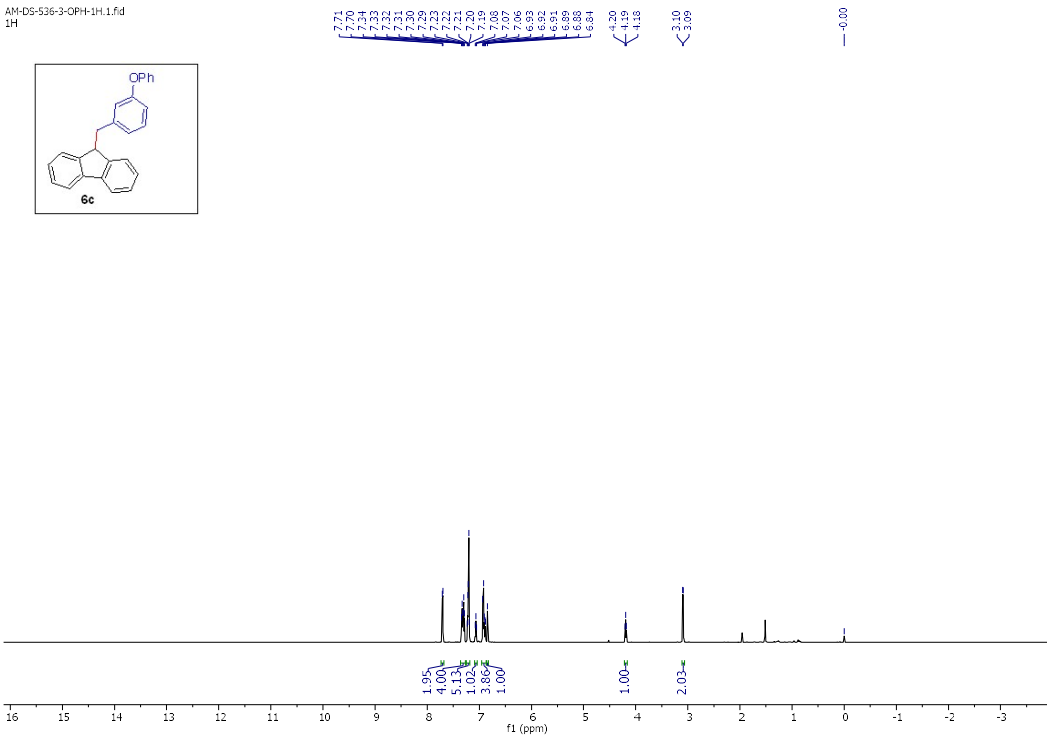


Figure S10. ^{1}H NMR Spectrum of 9-(3-phenoxybenzyl)-9H-fluorene **(6c)** in $CDCl_3$.

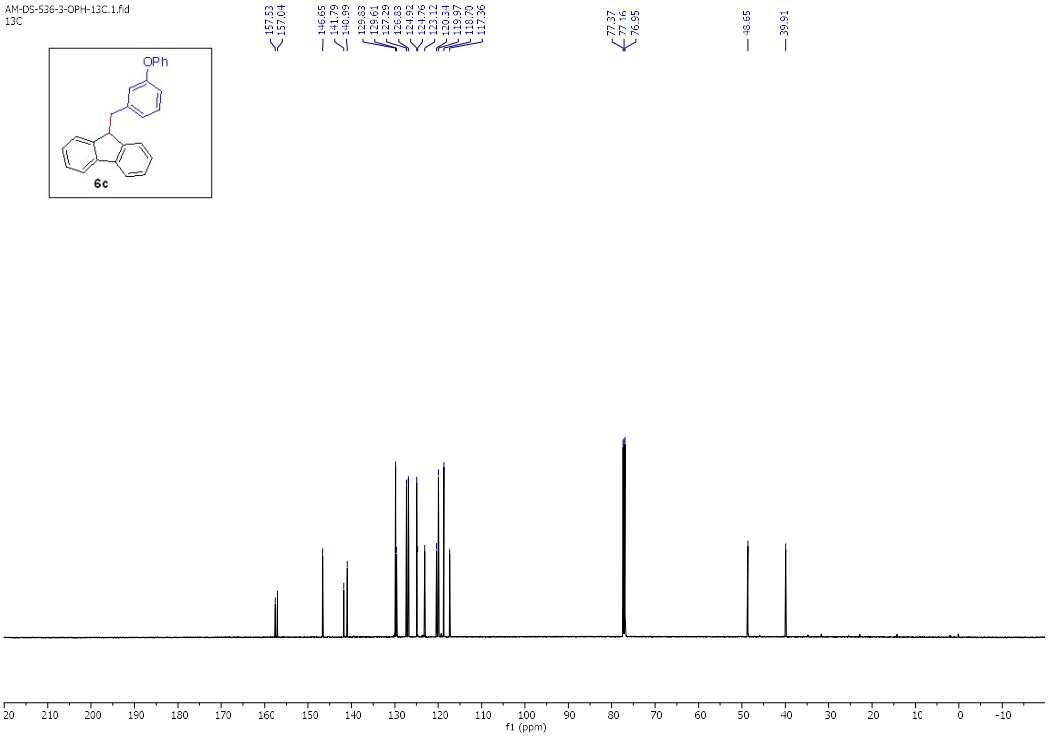


Figure S11. ^{13}C NMR Spectrum of 9-(3-phenoxybenzyl)-9H-fluorene **(6c)** in $CDCl_3$.

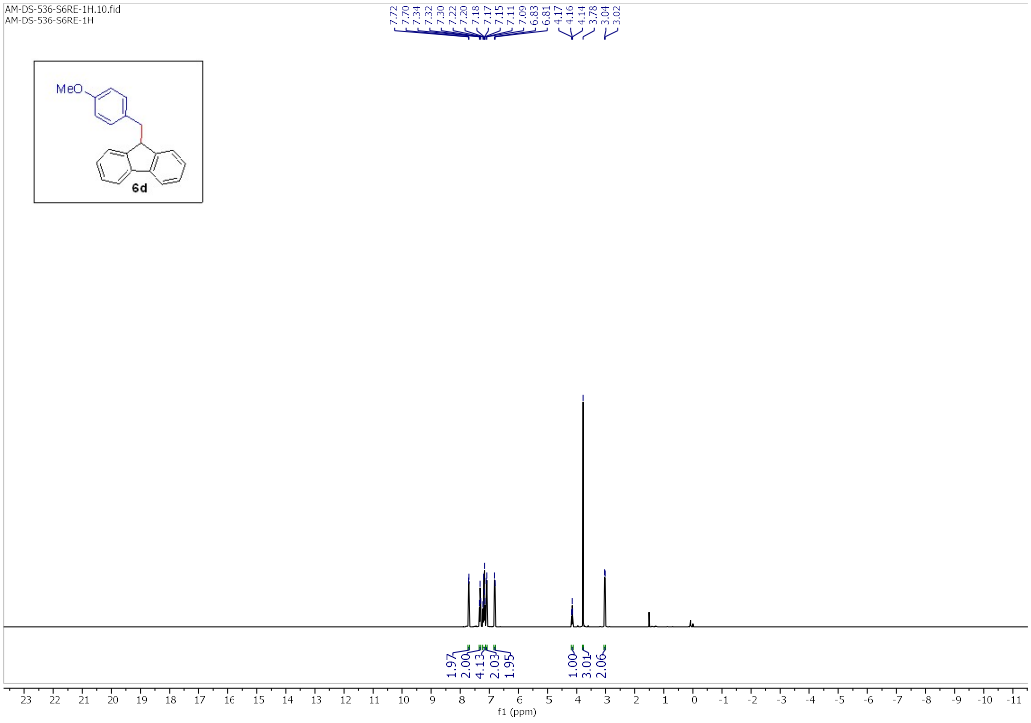


Figure S12. ^{1}H NMR Spectrum of 9-(4-methoxybenzyl)-9H-fluorene **(6d)** in $CDCl_3$.

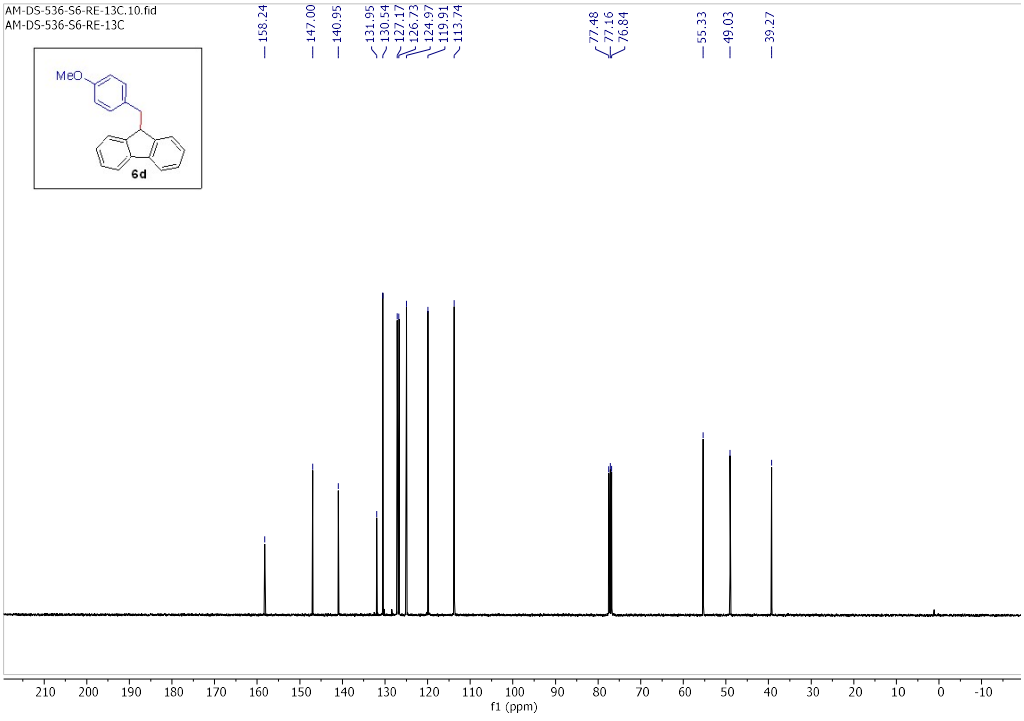


Figure S13. ^{13}C NMR Spectrum of 9-(4-methoxybenzyl)-9H-fluorene **(6d)** in $CDCl_3$.

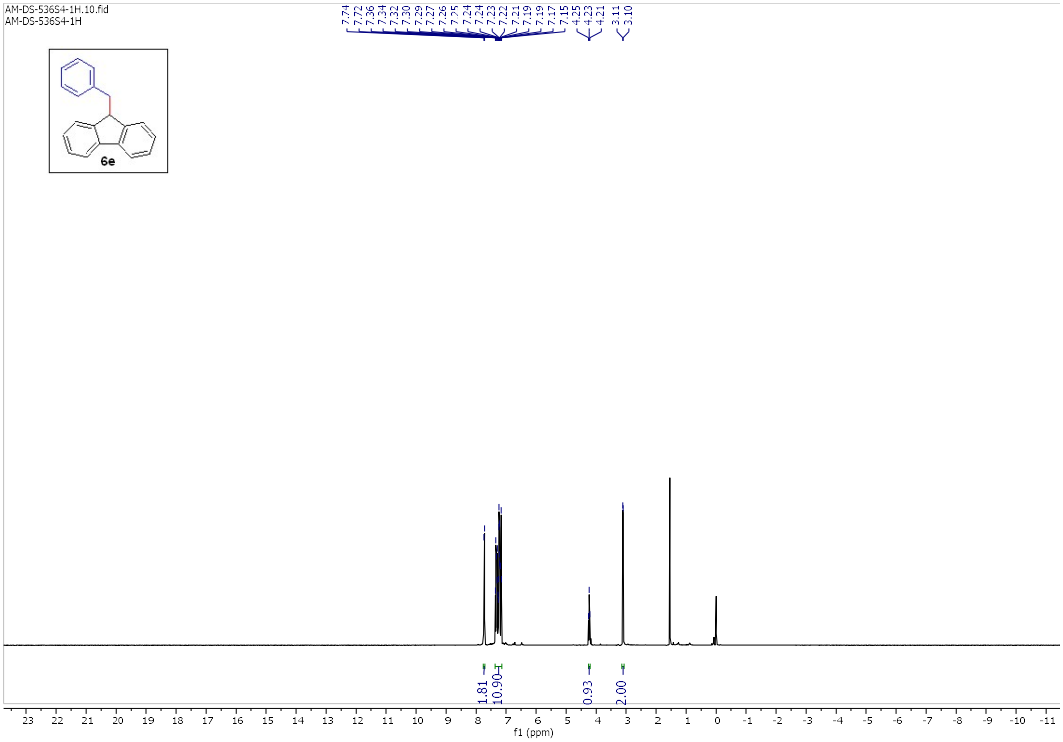


Figure S14. ^{1}H NMR Spectrum of 9-benzyl-9H-fluorene **(6e)** in $CDCl_3$.

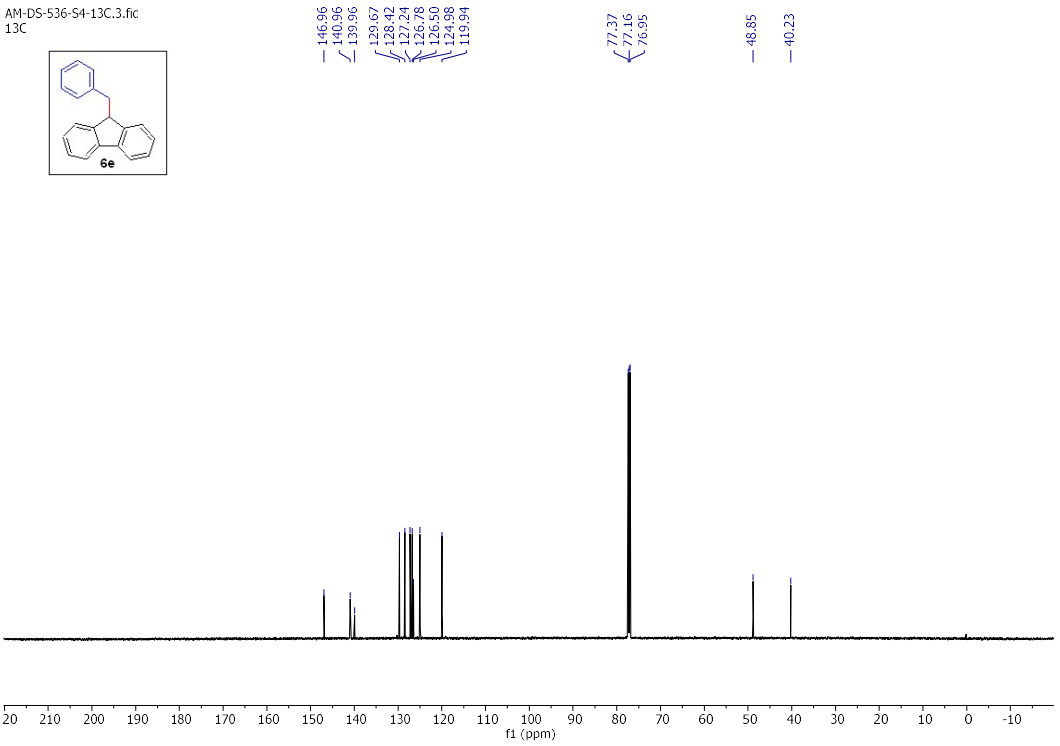


Figure S15. ^{13}C NMR Spectrum of 9-benzyl-9H-fluorene **(6e)** in $CDCl_3$.

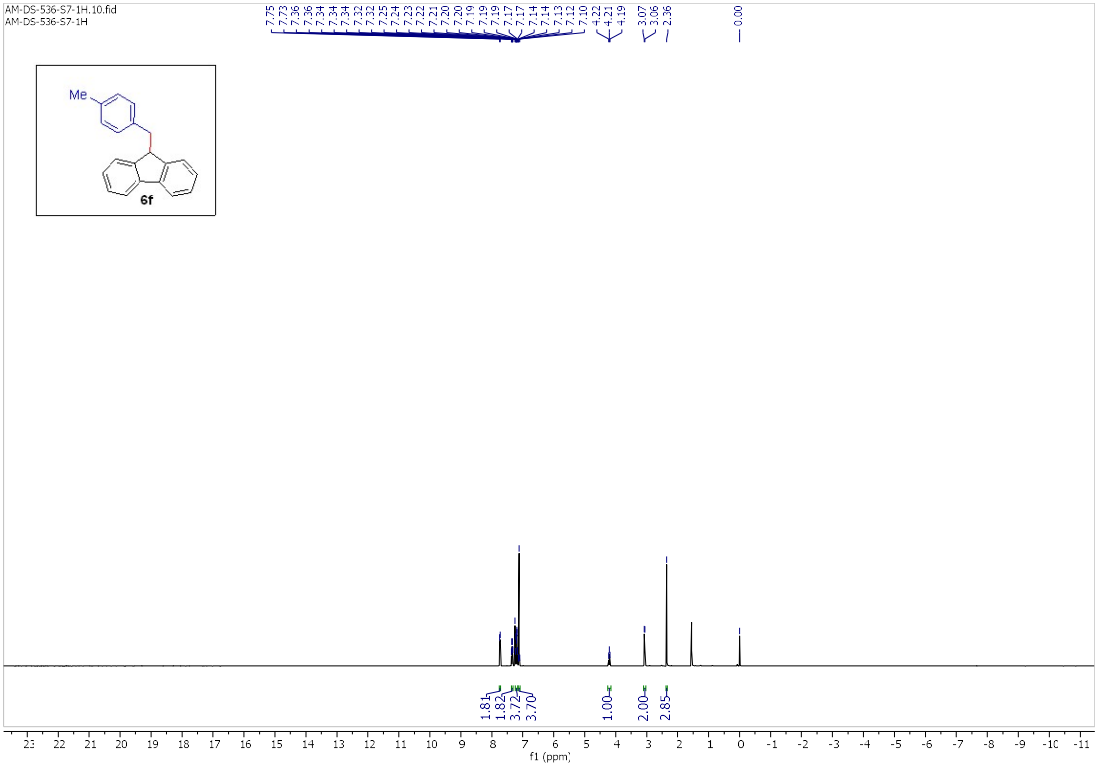


Figure S16. ^{1}H NMR Spectrum of 9-(4-methylbenzyl)-9H-fluorene **(6f)** in $CDCl_3$.

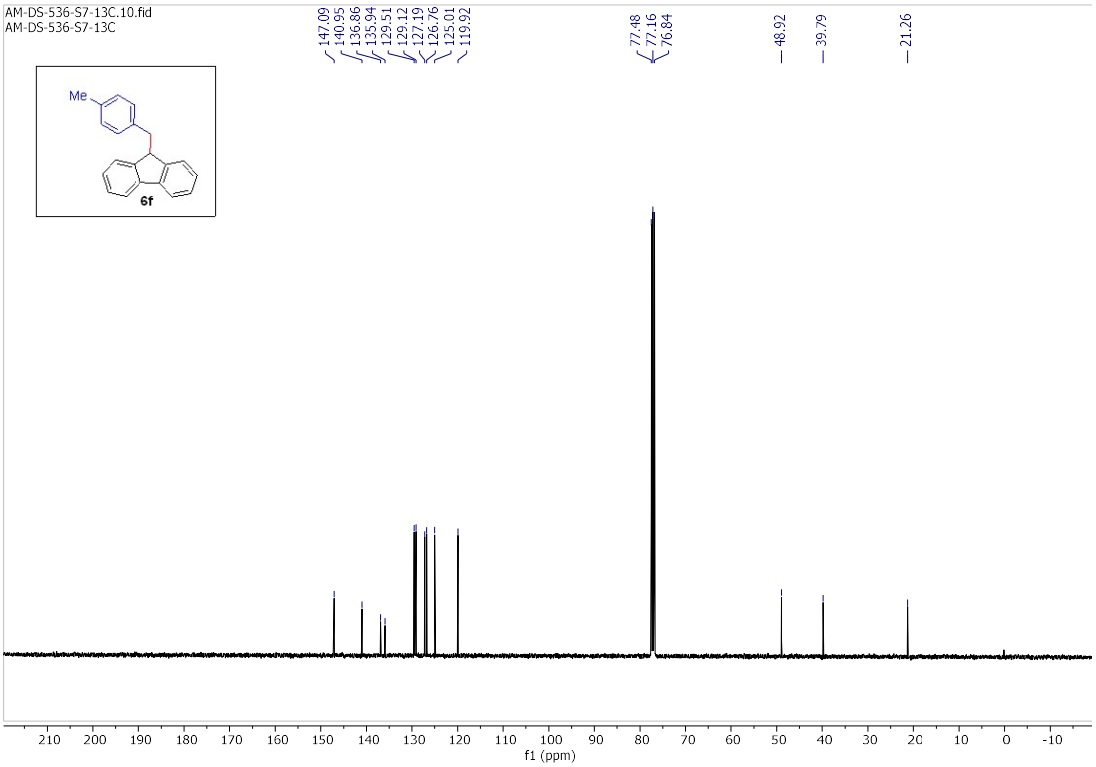


Figure S17. ^{13}C NMR Spectrum of 9-(4-methylbenzyl)-9H-fluorene **(6f)** in $CDCl_3$.

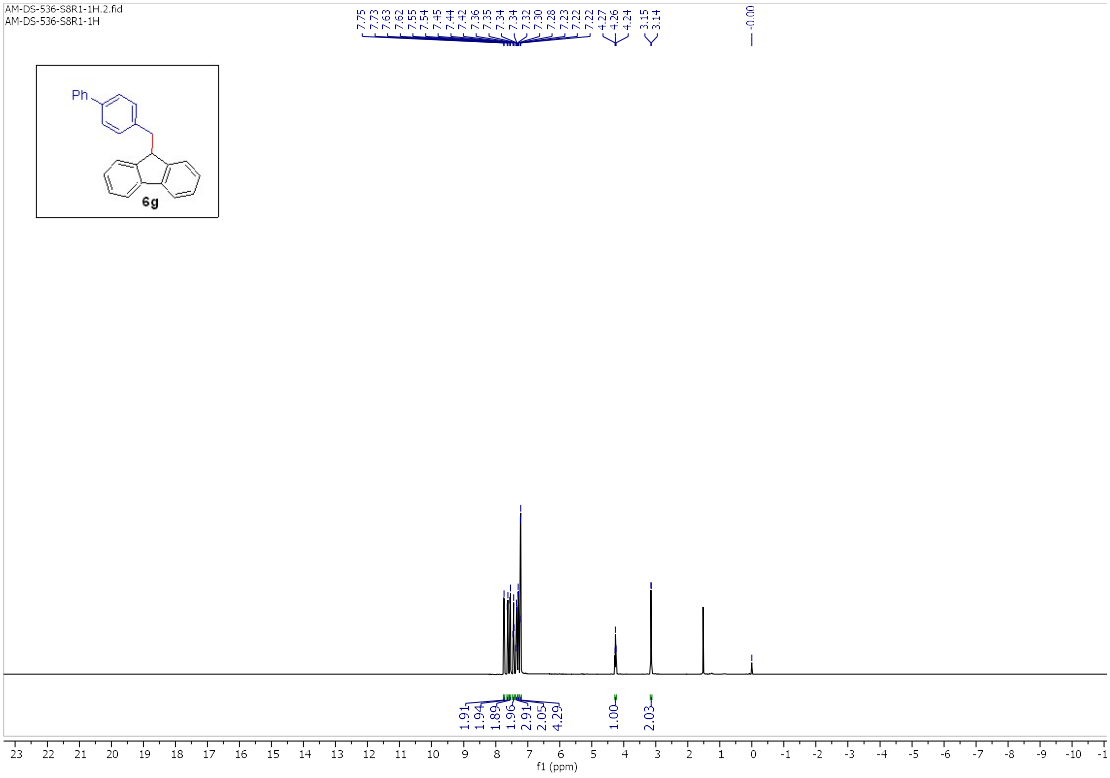


Figure S18. ^{1}H NMR Spectrum of 9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene **(6g)** in $CDCl_3$.

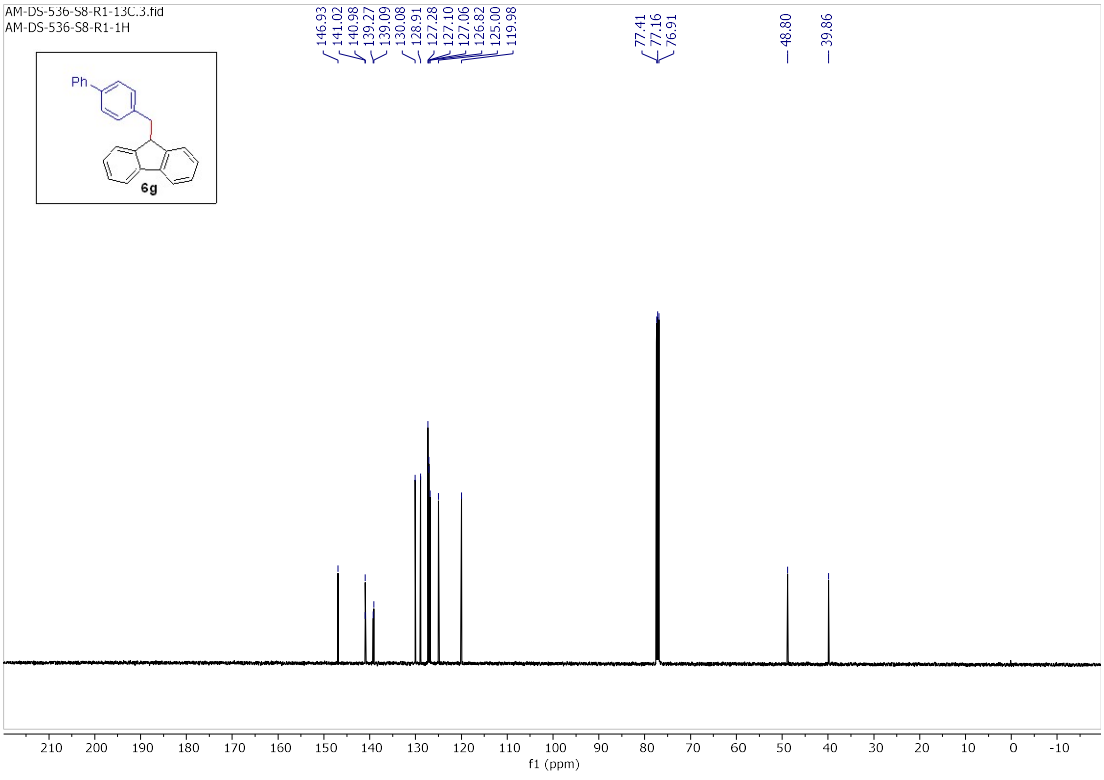


Figure S19. ^{13}C NMR Spectrum of 9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene **(6g)** in $CDCl_3$.

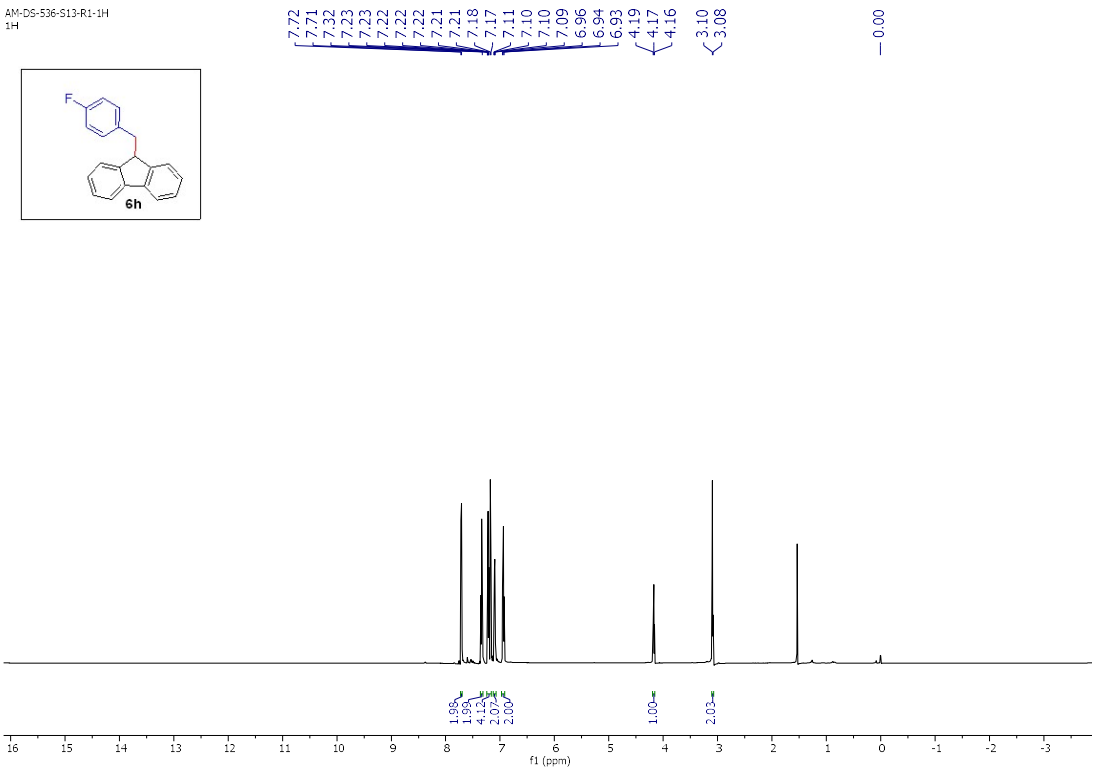


Figure S20. ^{1}H NMR Spectrum of 9-(4-fluorobenzyl)-9H-fluorene **(6h)** in $CDCl_3$.

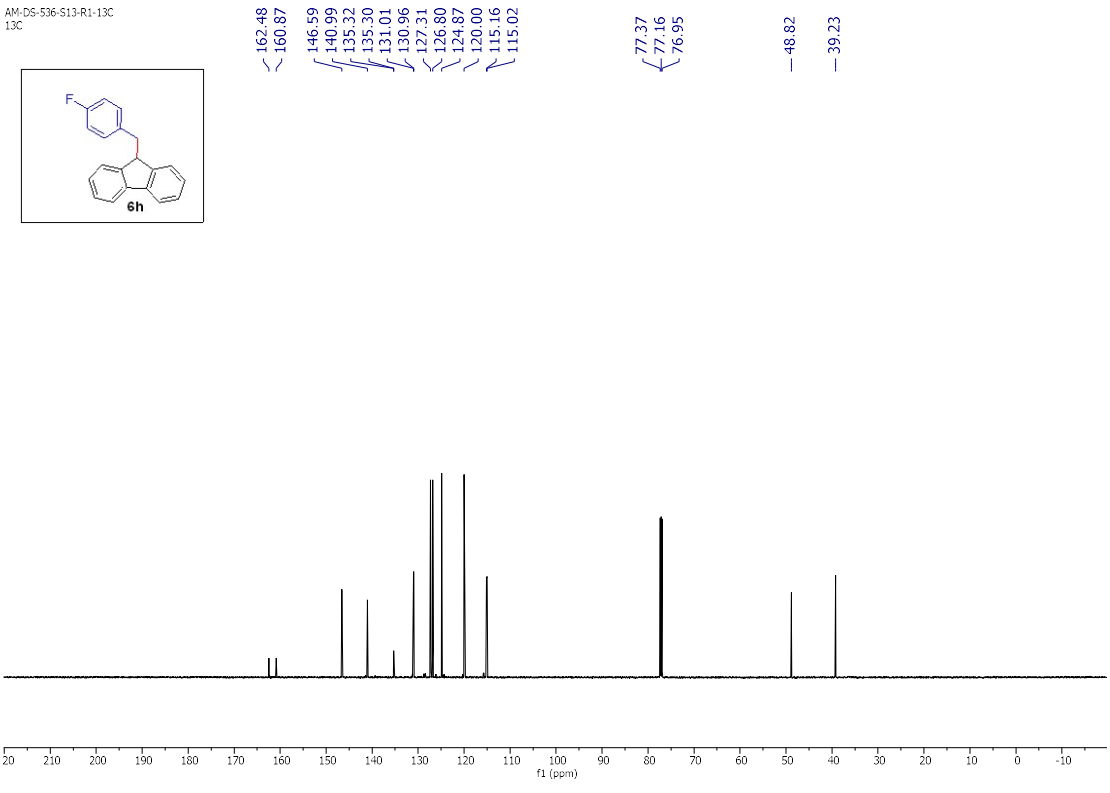


Figure S21. ^{13}C NMR Spectrum of 9-(4-fluorobenzyl)-9H-fluorene **(6h)** in $CDCl_3$.

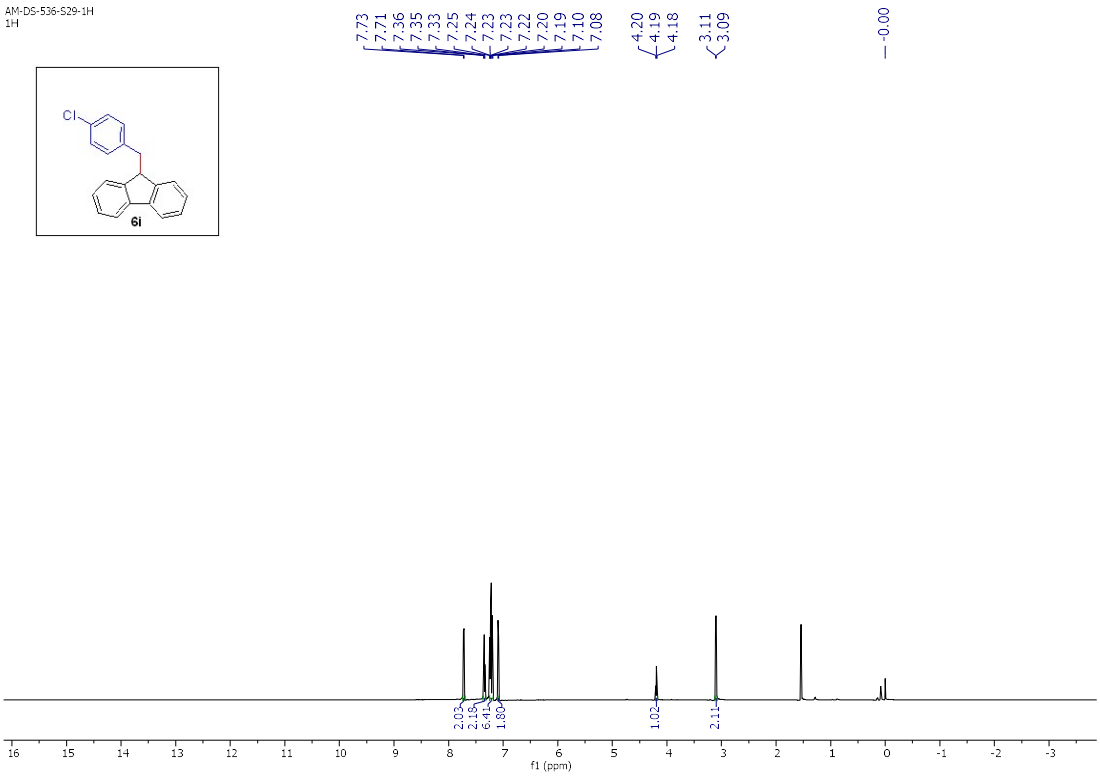


Figure S22. ^{1}H NMR Spectrum of 9-(4-chlorobenzyl)-9H-fluorene **(6I)** in $CDCl_3$.

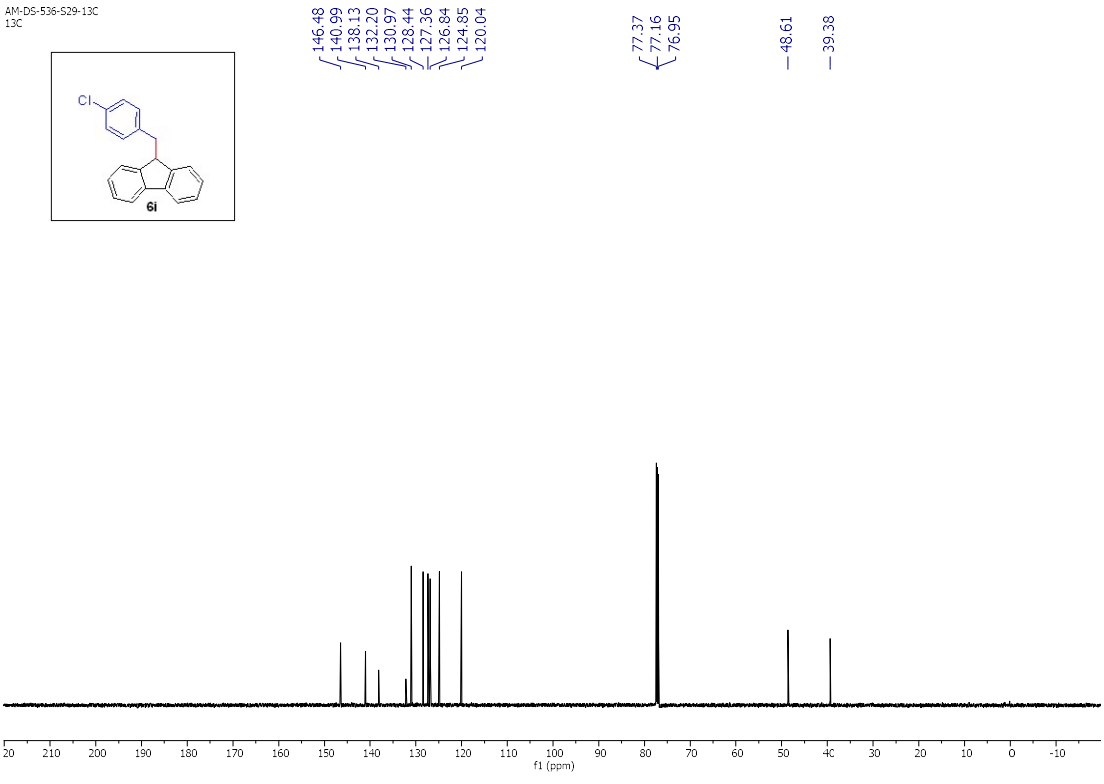


Figure S23. ^{13}C NMR Spectrum of 9-(4-chlorobenzyl)-9H-fluorene **(6I)** in $CDCl_3$.

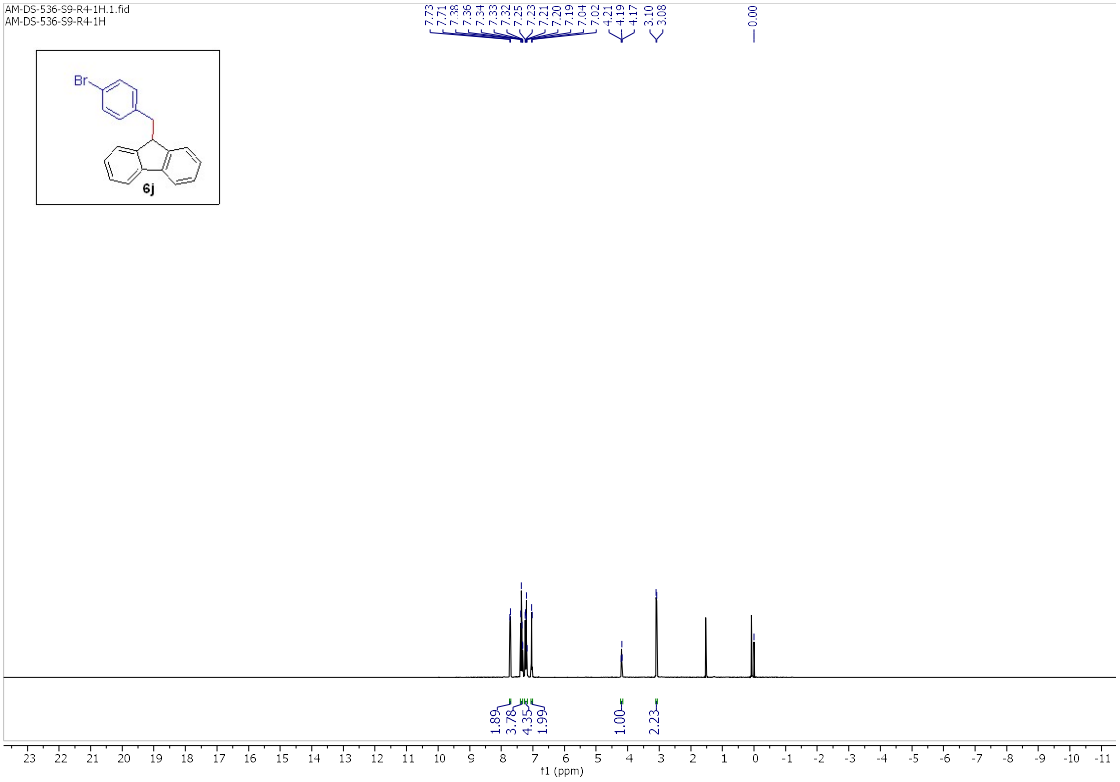


Figure S24. ^{1}H NMR Spectrum of 9-(4-bromobenzyl)-9H-fluorene **(6j)** in $CDCl_3$.

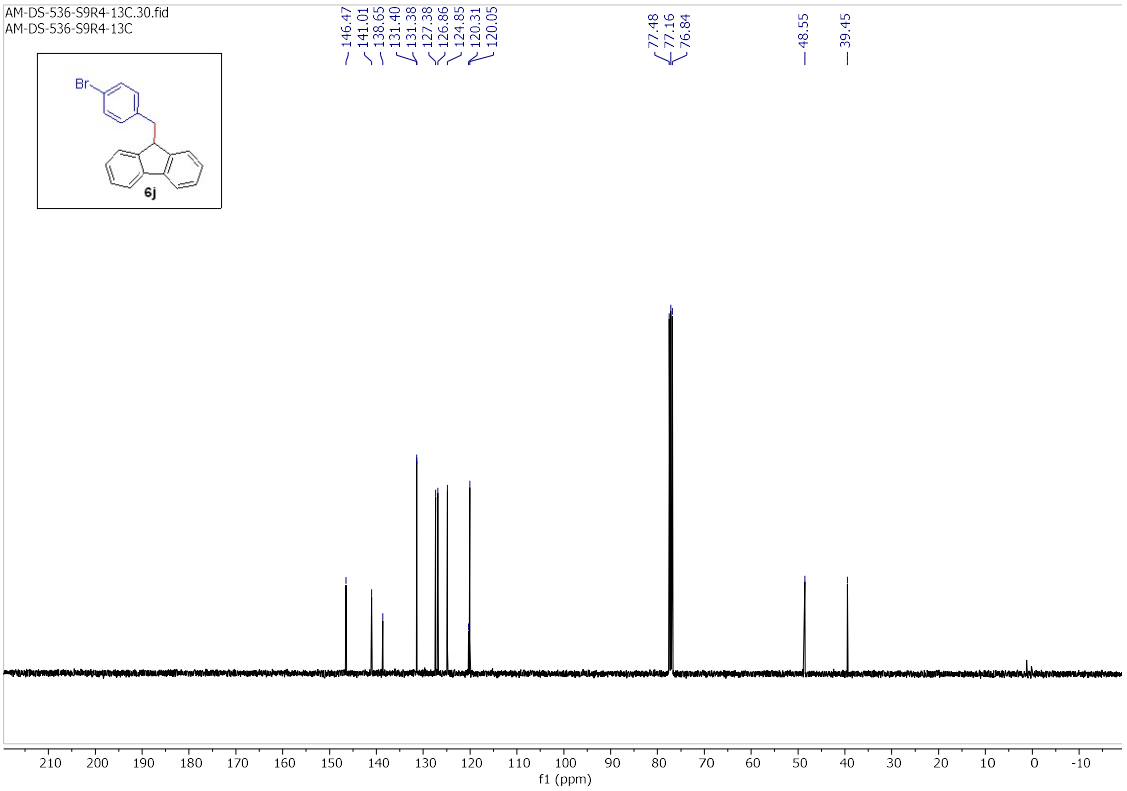


Figure S25. ^{13}C NMR Spectrum of 9-(4-bromobenzyl)-9H-fluorene **(6j)** in $CDCl_3$.

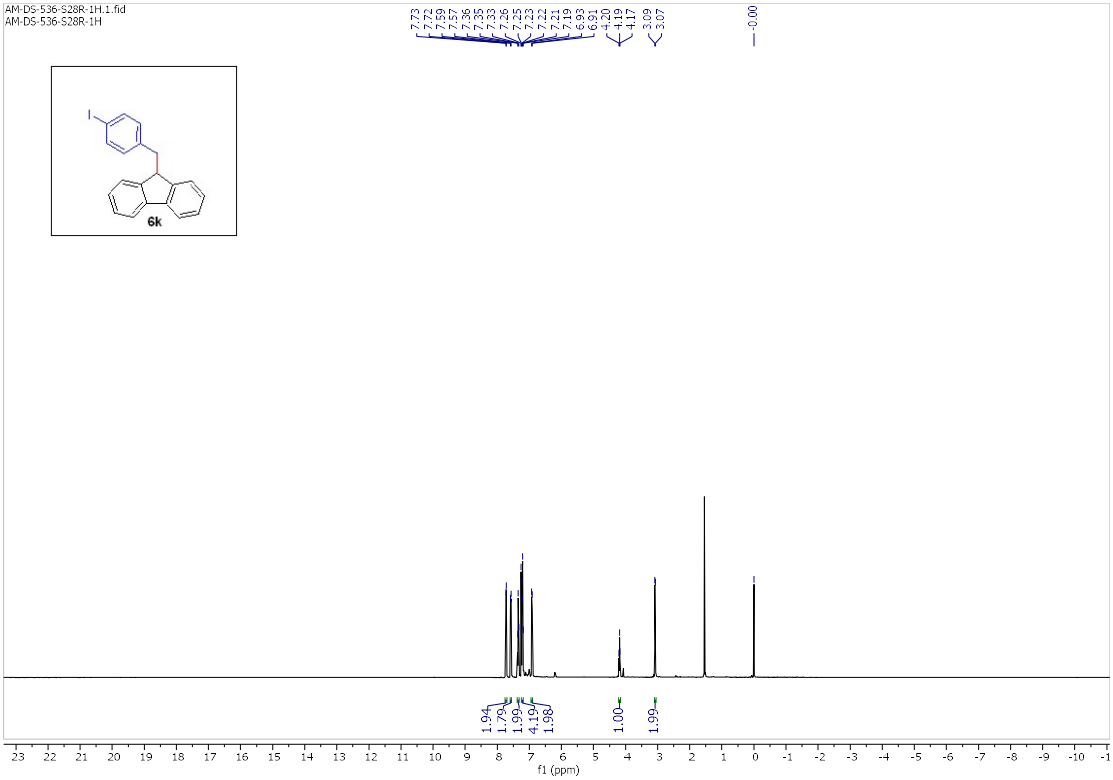


Figure S26. ^{1}H NMR Spectrum of 9-(4-iodobenzyl)-9H-fluorene **(6k)** in $CDCl_3$.

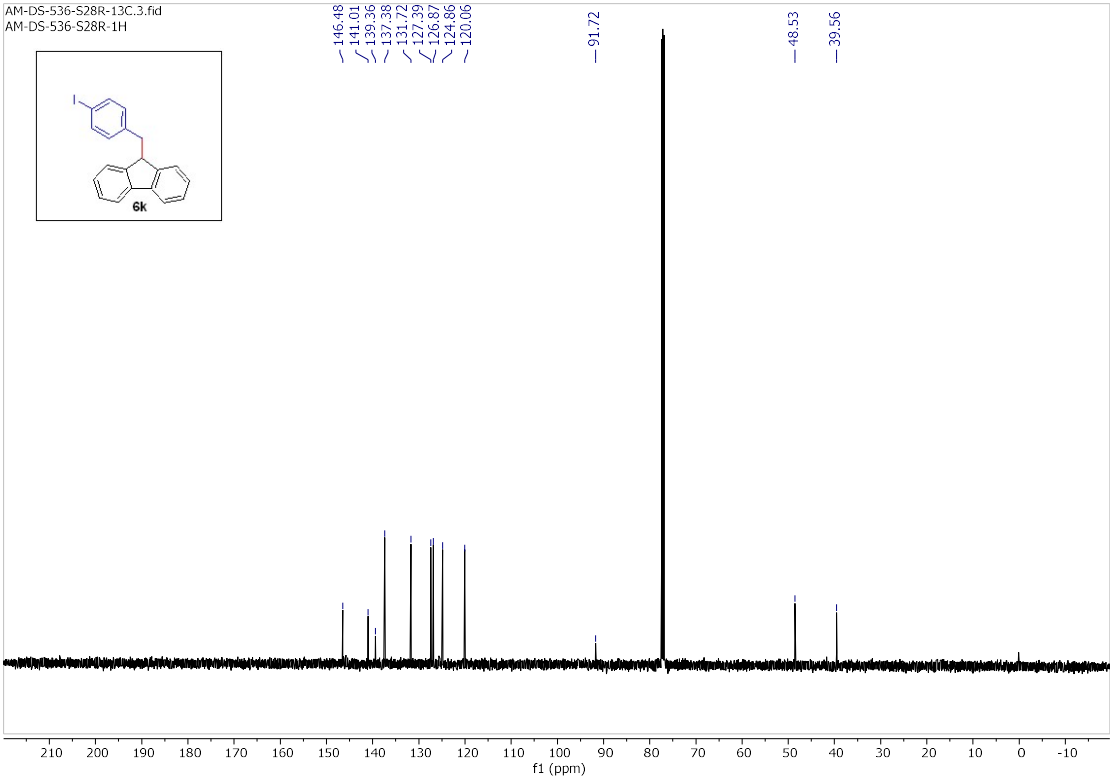


Figure S27. ^{13}C NMR Spectrum of 9-(4-iodobenzyl)-9H-fluorene **(6k)** in $CDCl_3$.

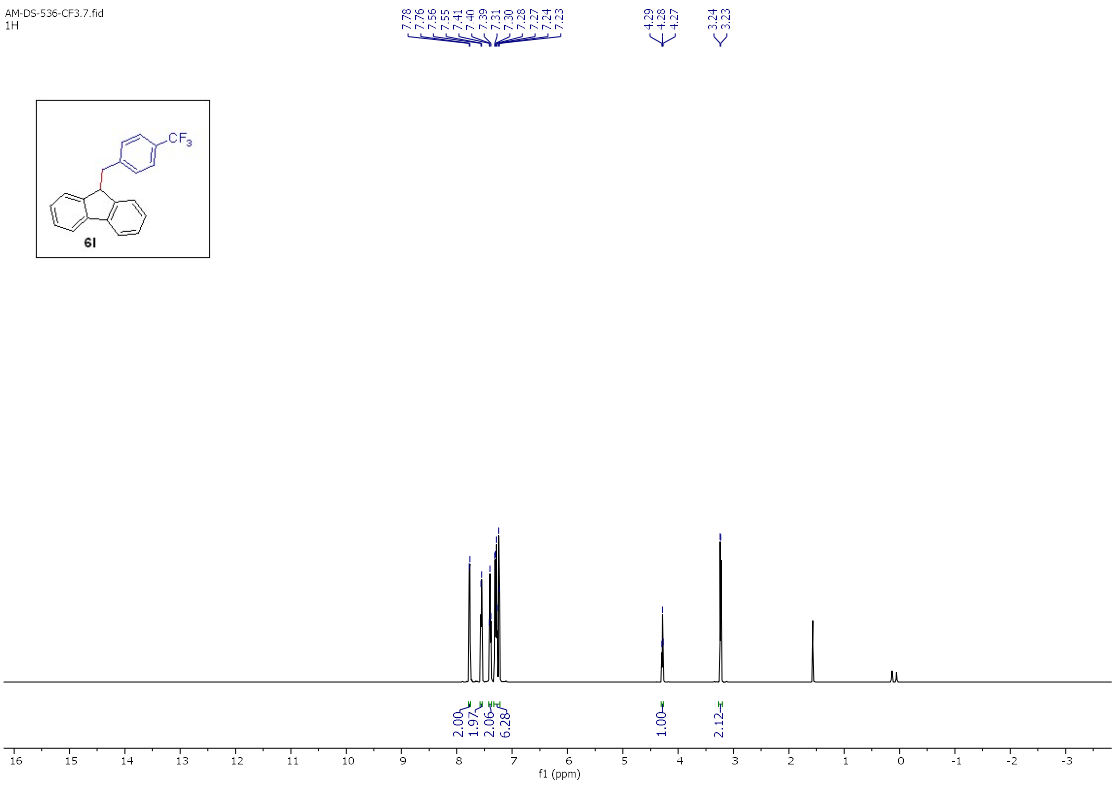


Figure S28. ^{1}H NMR Spectrum of 9-(4-(trifluoromethyl)benzyl)-9H-fluorene **(6l)** in $CDCl_3$.

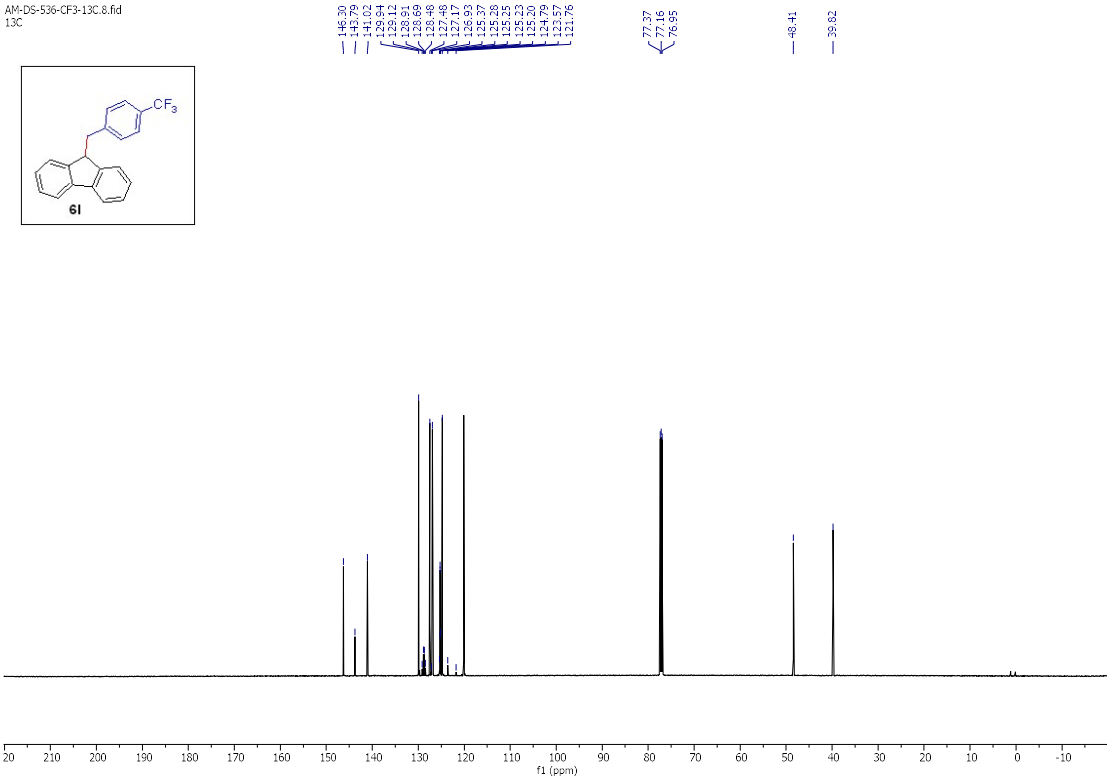


Figure S29. ^{13}C NMR Spectrum of 9-(4-(trifluoromethyl)benzyl)-9H-fluorene **(6l)** in $CDCl_3$.

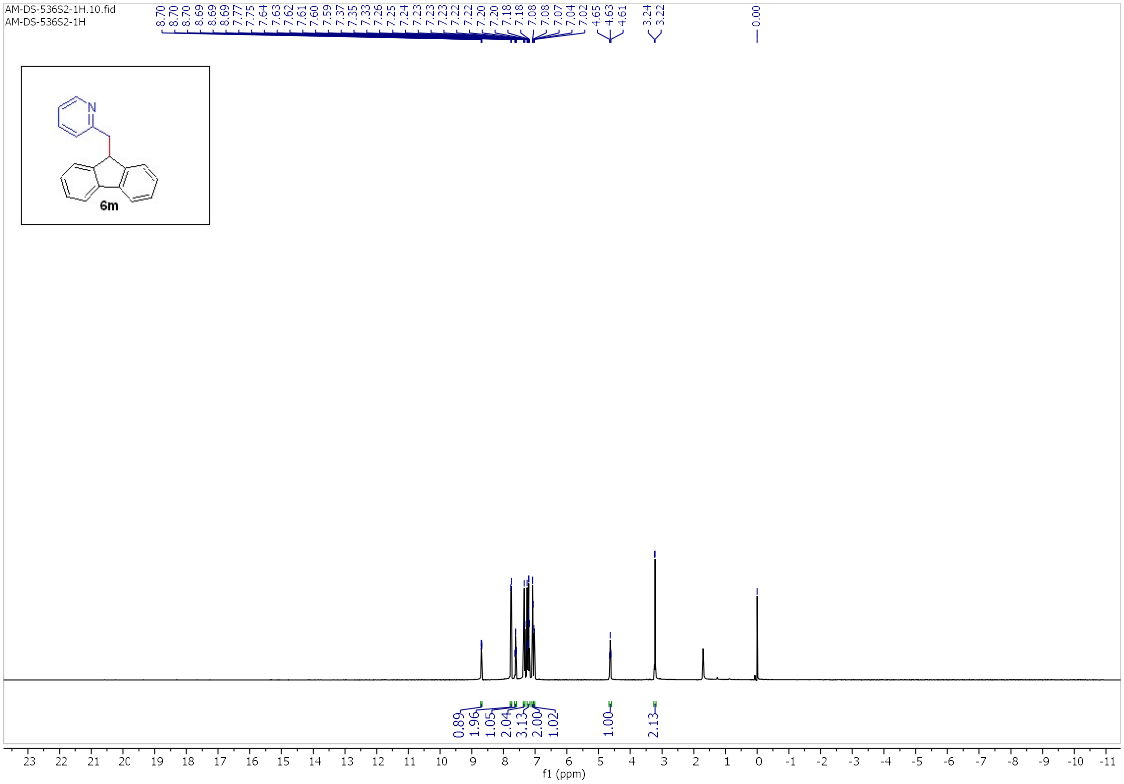


Figure S30. ^{1}H NMR Spectrum of 2-((9H-fluoren-9-yl)methyl)pyridine **(6m)** in $CDCl_3$.

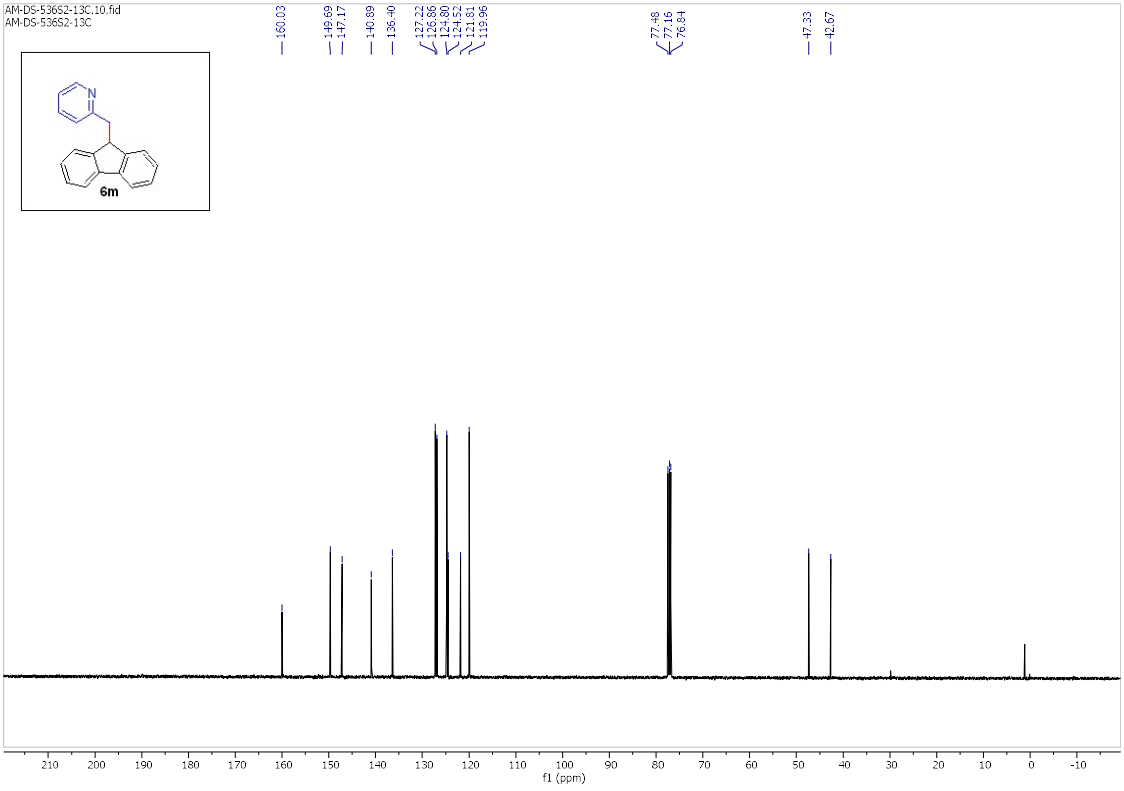


Figure S31. ^{13}C NMR Spectrum of 2-((9H-fluoren-9-yl)methyl)pyridine **(6m)** in $CDCl_3$.

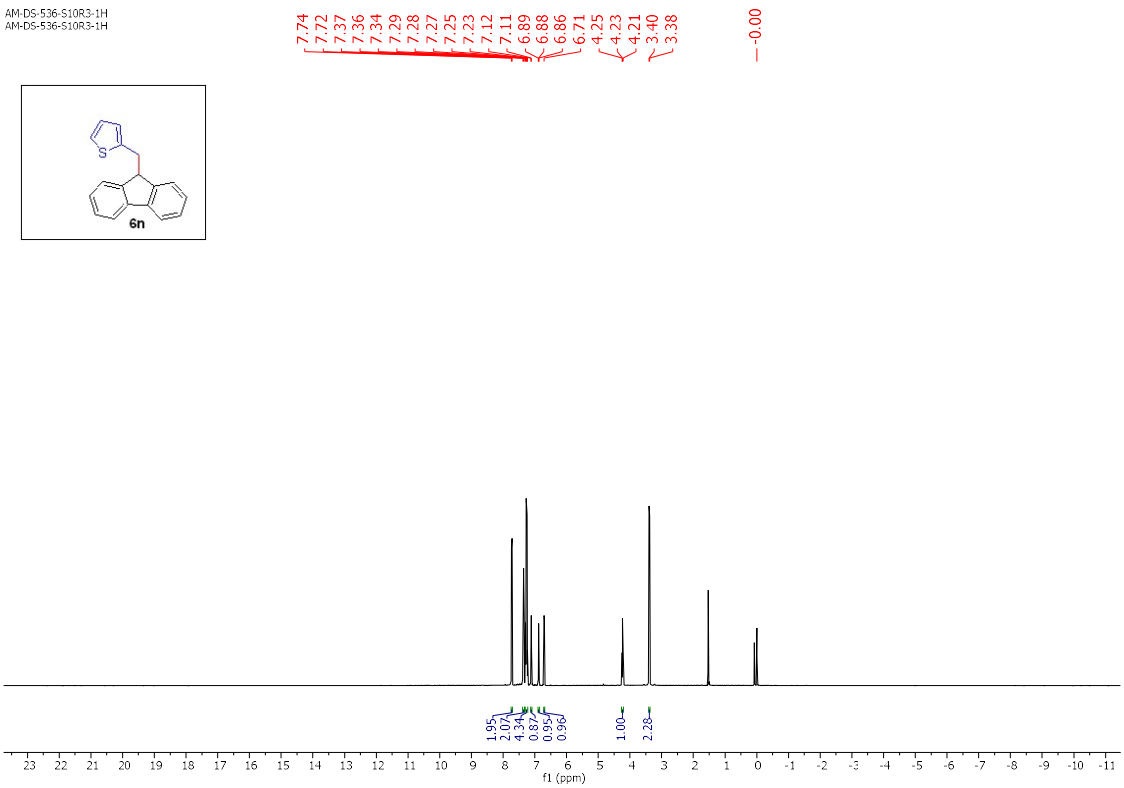


Figure S32. ^{1}H NMR Spectrum of 2-((9H-fluoren-9-yl)methyl)thiophene **(6n)** in $CDCl_3$.

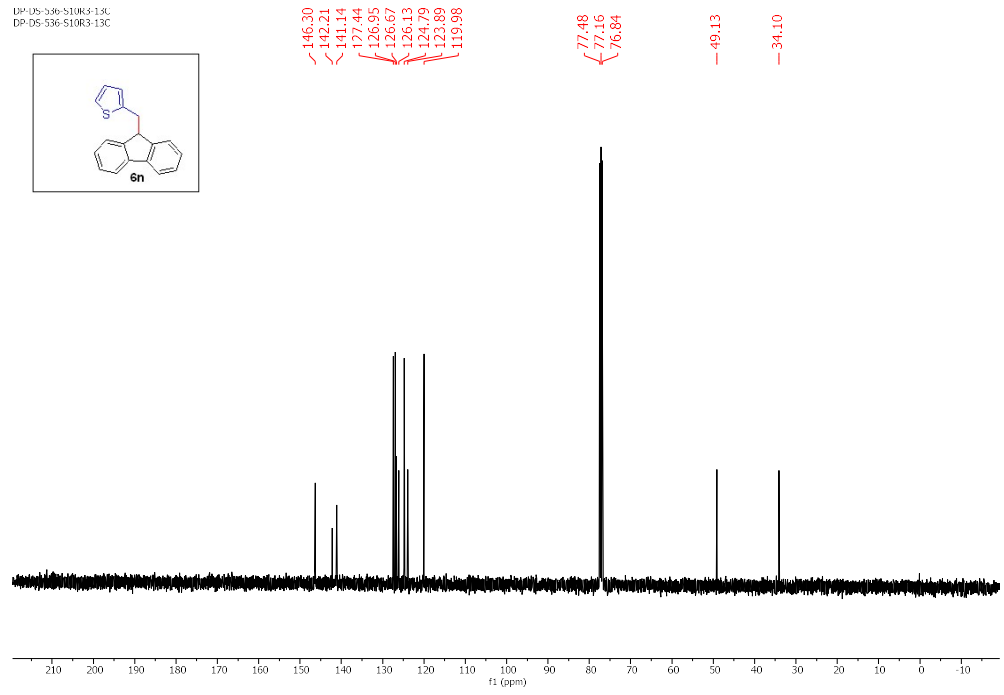


Figure S33. ^{13}C NMR Spectrum of 2-((9H-fluoren-9-yl)methyl)thiophene **(6n)** in $CDCl_3$

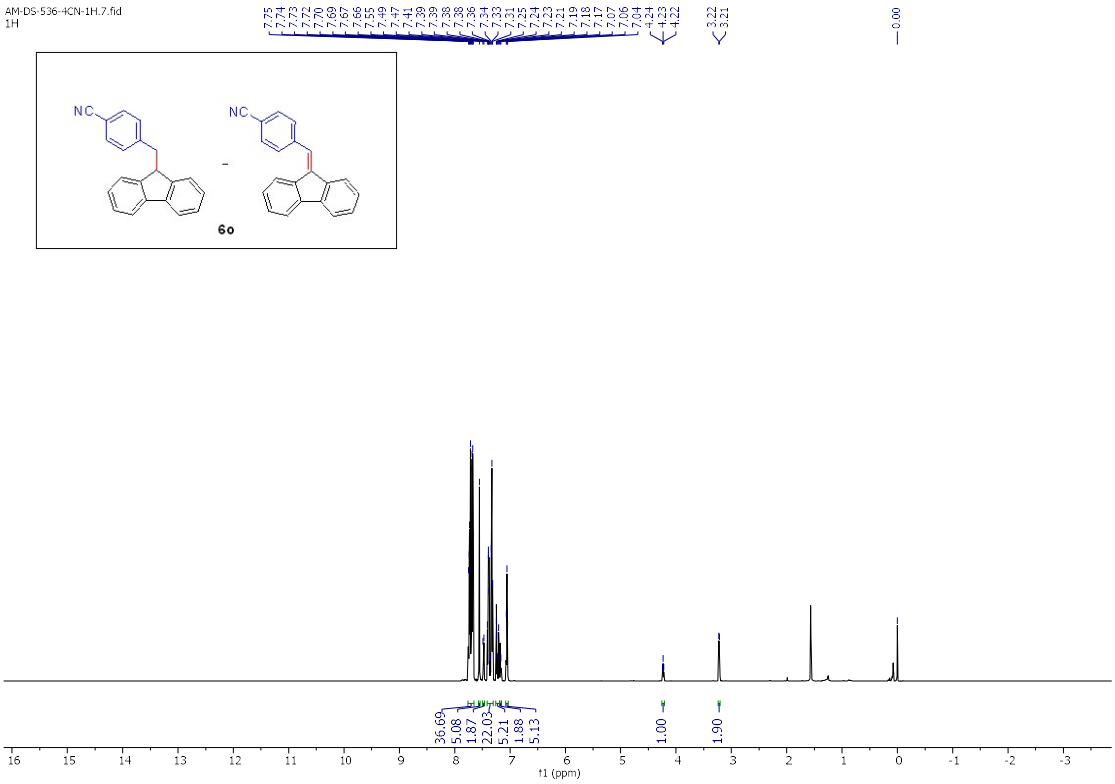


Figure S34. ^{1}H NMR Spectrum of **(6o)** in $CDCl_3$.

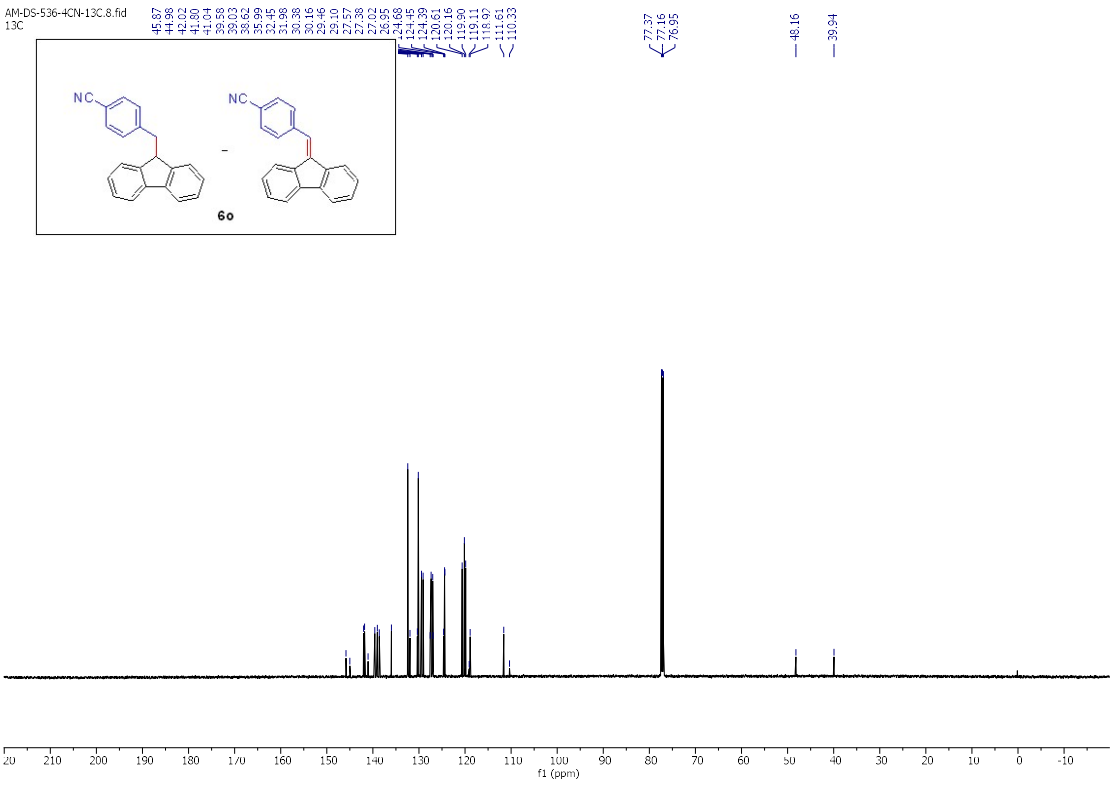


Figure S35. ^{13}C NMR Spectrum of **(6o)** in $CDCl_3$.

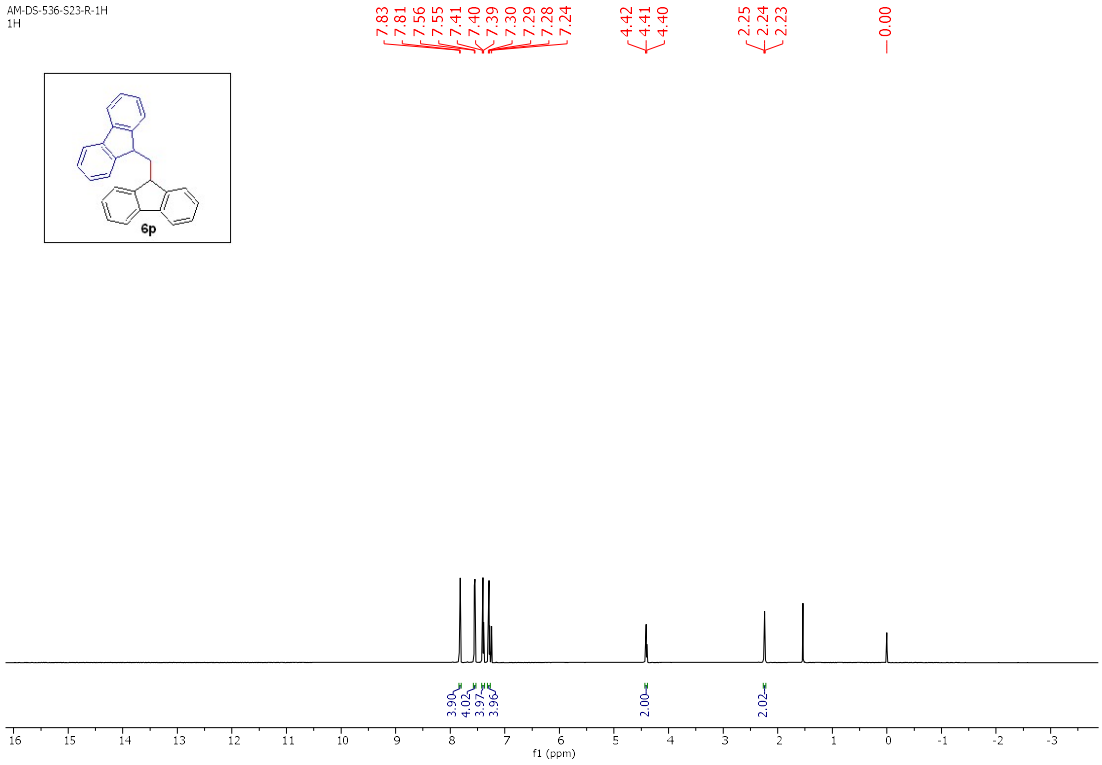


Figure S36. ^{1}H NMR Spectrum of di(9H-fluoren-9-yl)methane **(6p)** in $CDCl_3$.

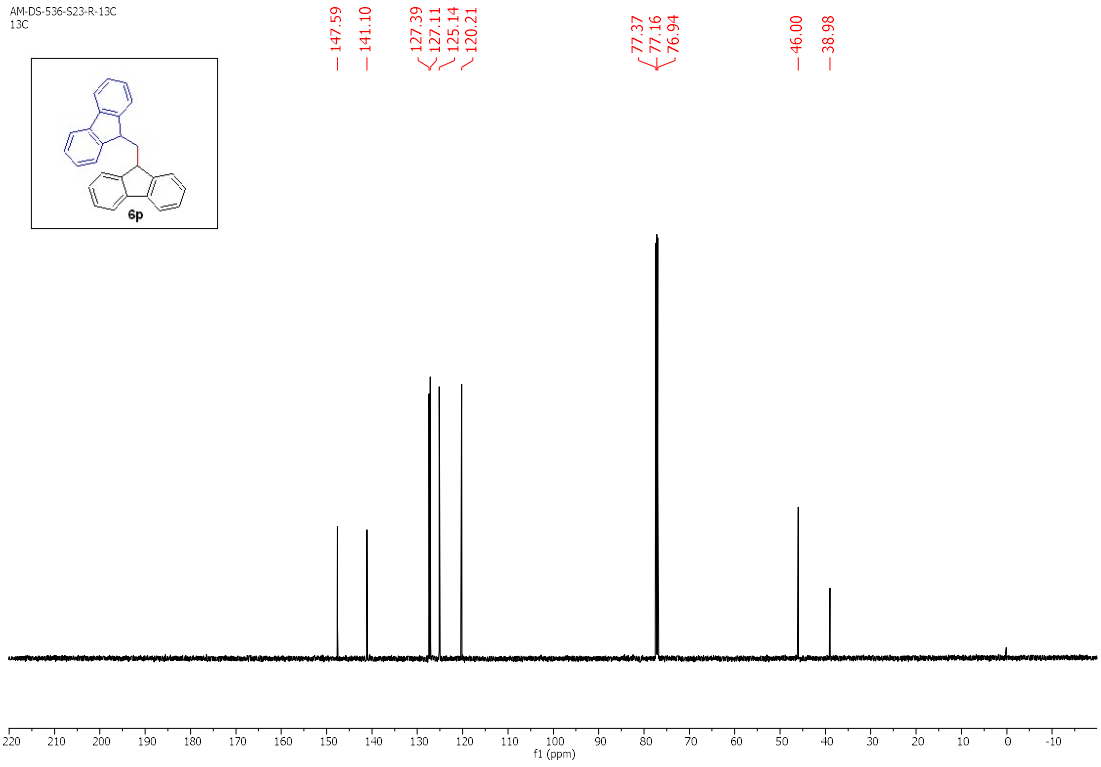


Figure S37. ^{13}C NMR Spectrum of di(9H-fluoren-9-yl)methane **(6p)** in $CDCl_3$.

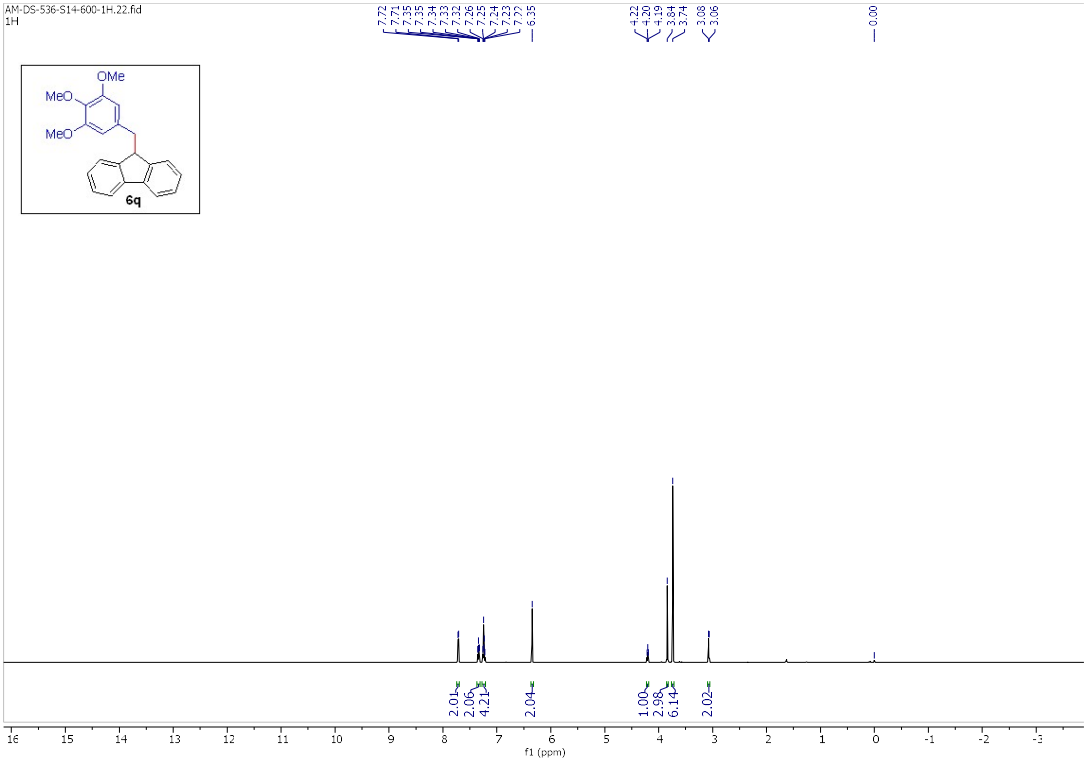


Figure S38. ^{1}H NMR Spectrum of 9-(3,4,5-trimethoxybenzyl)-9H-fluorene **(6q)** in $CDCl_3$.

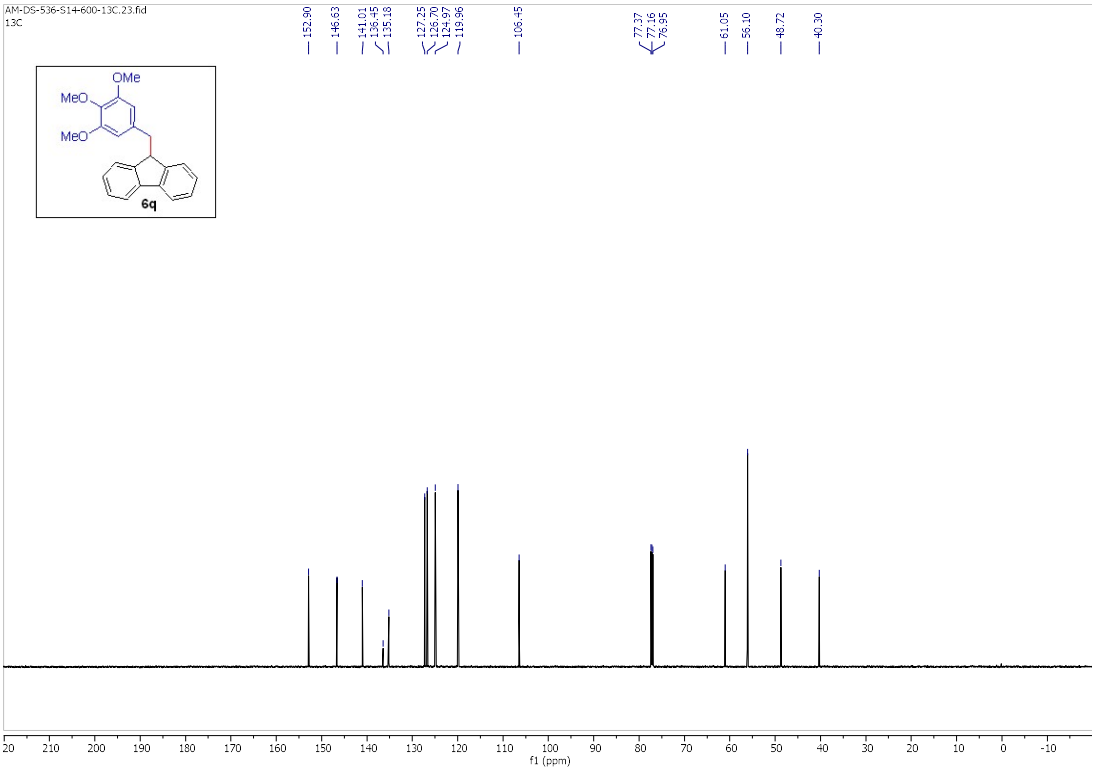


Figure S39. ^{13}C NMR Spectrum of 9-(3,4,5-trimethoxybenzyl)-9H-fluorene **(6q)** in $CDCl_3$.

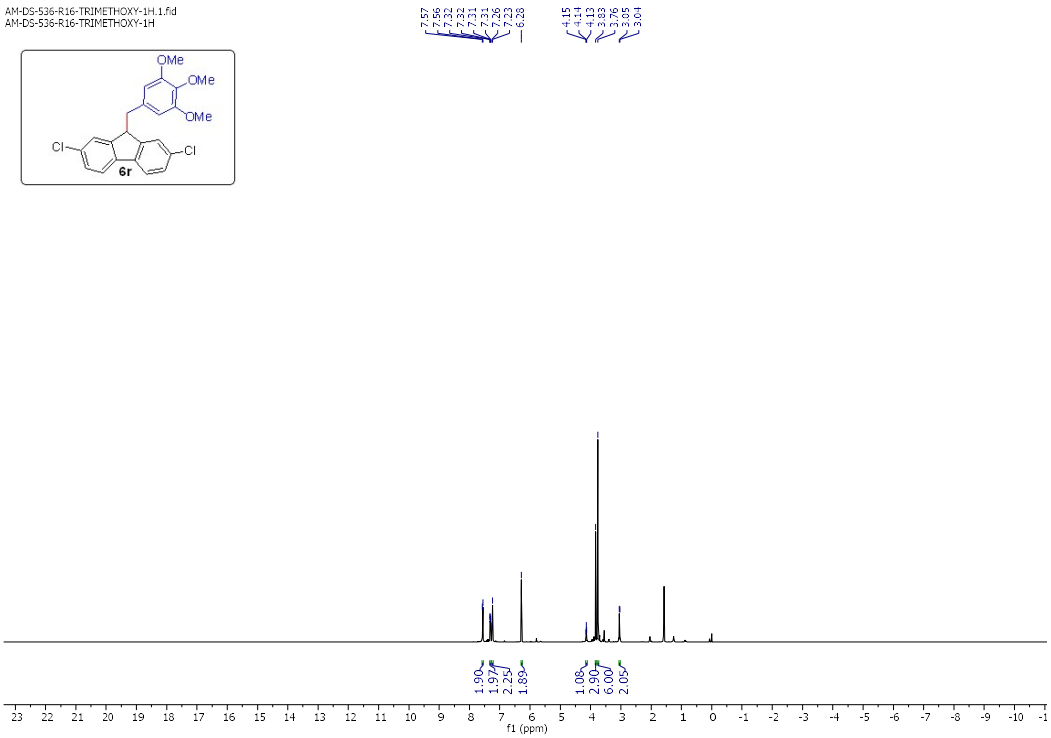


Figure S40. ^{1}H NMR Spectrum of 2,7-dichloro-9-(3,4,5-trimethoxybenzyl)-9H-fluorene **(6r)** in $CDCl_3$.

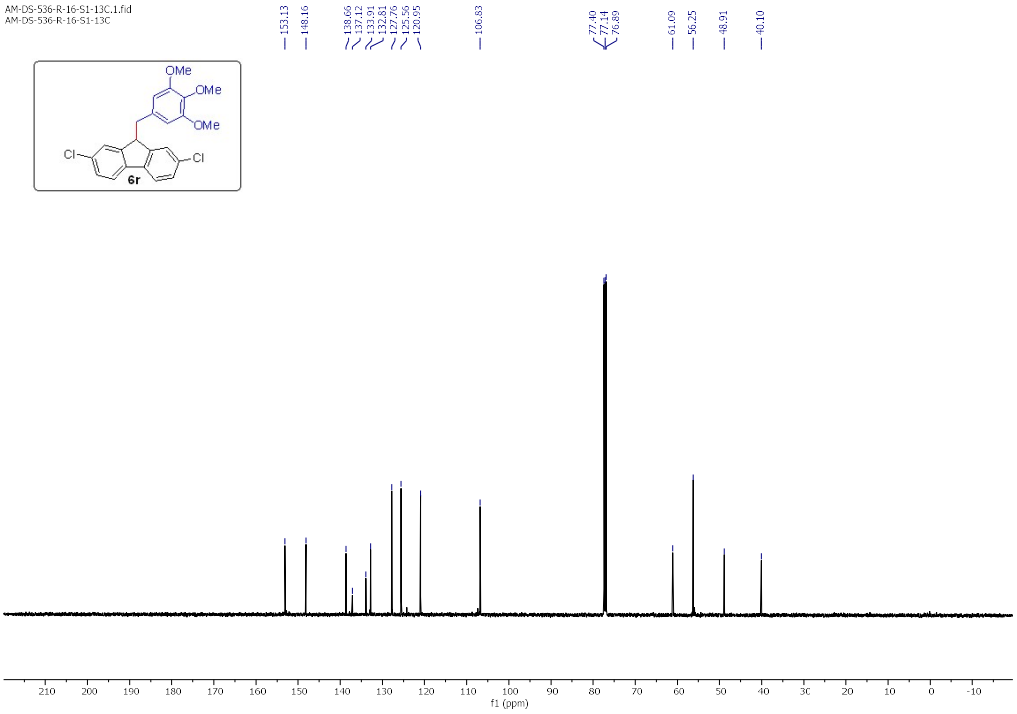


Figure S41. ^{13}C NMR Spectrum of 2,7-dichloro-9-(3,4,5-trimethoxybenzyl)-9H-fluorene **(6r)** in $CDCl_3$.

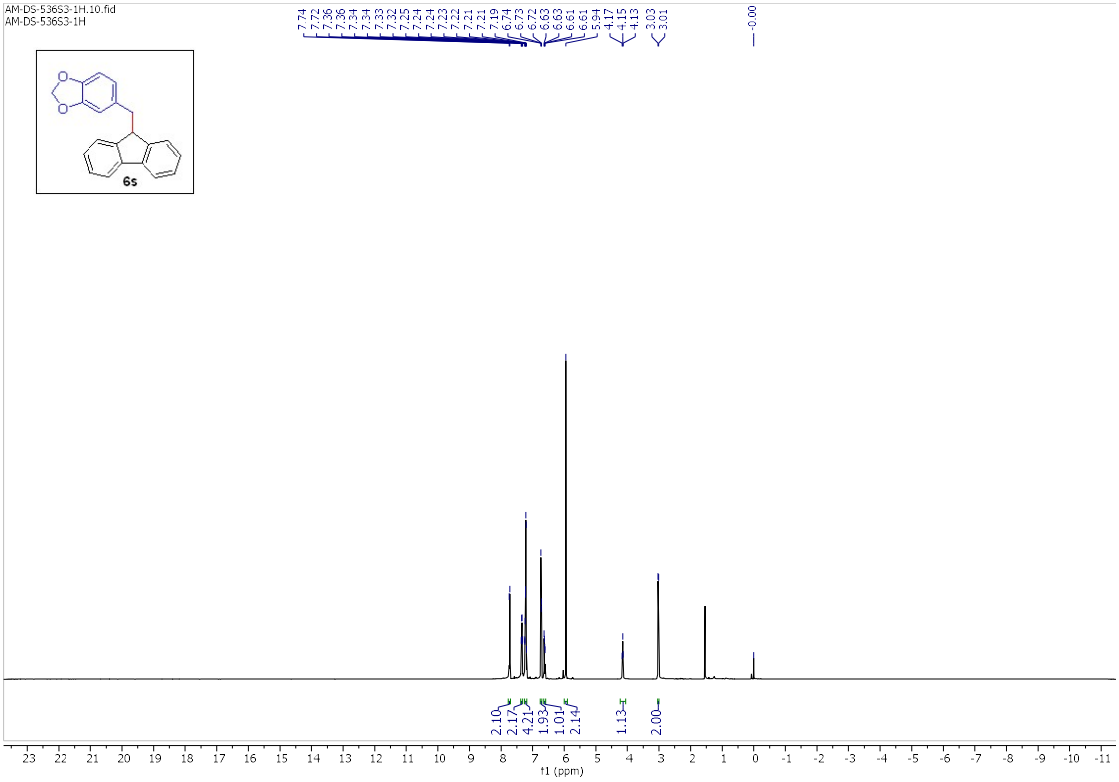


Figure S42. ^{1}H NMR Spectrum of 5-((9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole **(6s)** in $CDCl_3$.

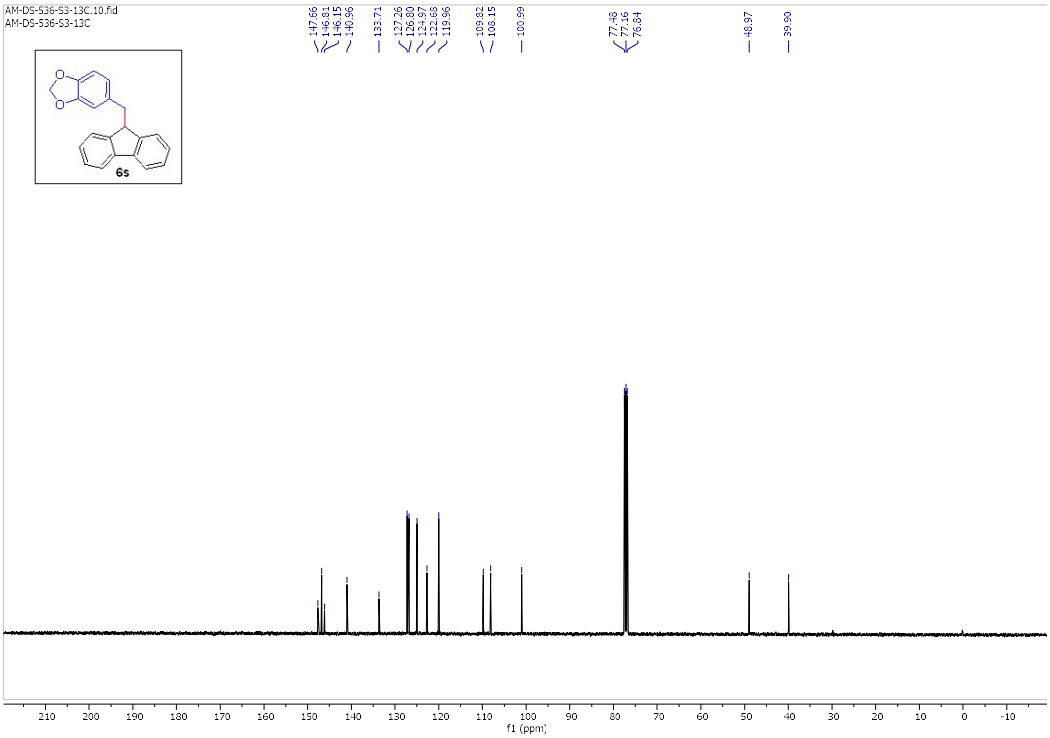


Figure S43. ^{13}C NMR Spectrum of 5-((9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole **(6s)** in $CDCl_3$.

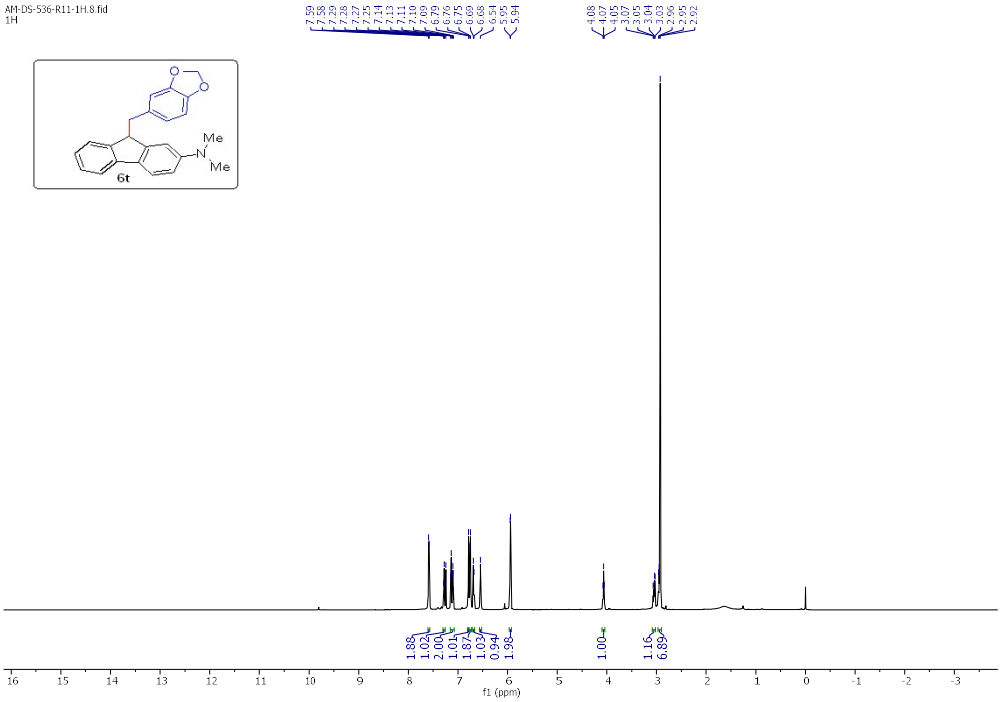


Figure S44. ^{1}H NMR Spectrum of 9-(benzo[d][1,3]dioxol-5-ylmethyl)-N,N-dimethyl-9H-fluoren-2-amine **(6t)** in $CDCl_3$.

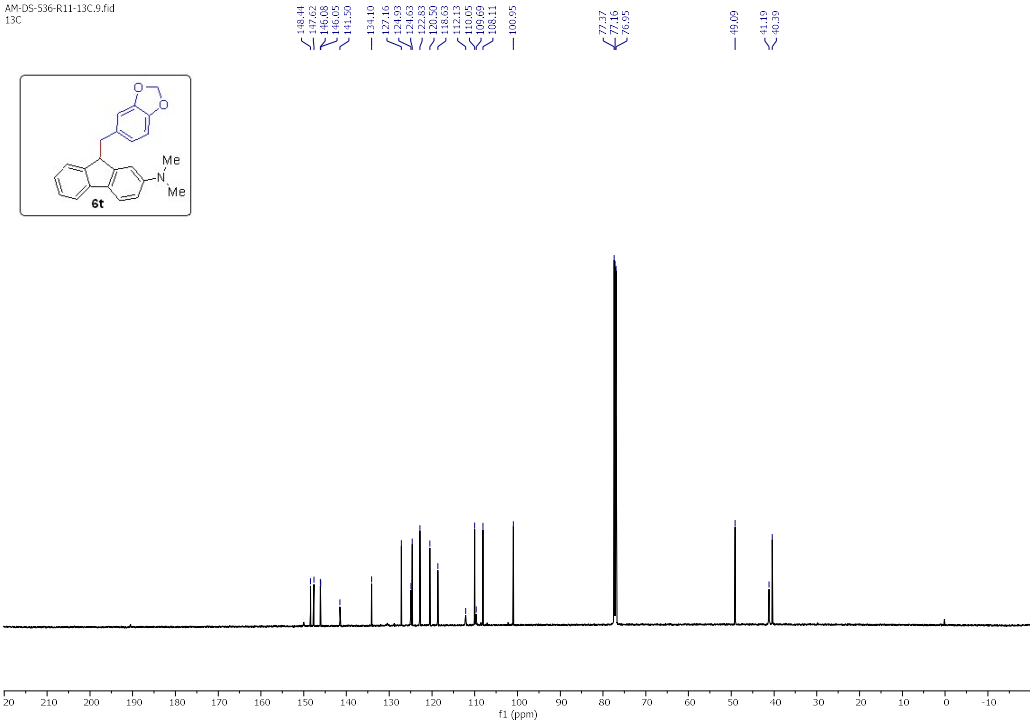


Figure S45. ^{13}C NMR Spectrum of 9-(benzo[d][1,3]dioxol-5-ylmethyl)-N,N-dimethyl-9H-fluoren-2-amine **(6t)** in $CDCl_3$.

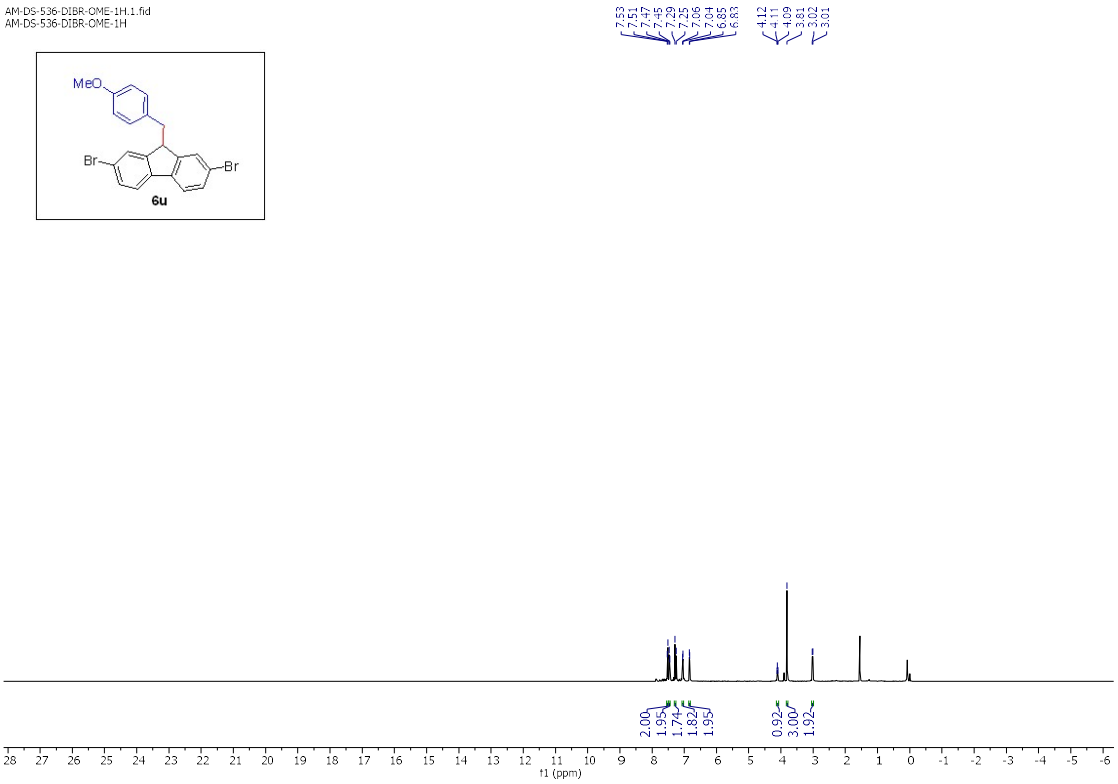


Figure S46. ^{1}H NMR Spectrum of 2,7-dibromo-9-(4-methoxybenzyl)-9H-fluorene **(6u)** in $CDCl_3$.

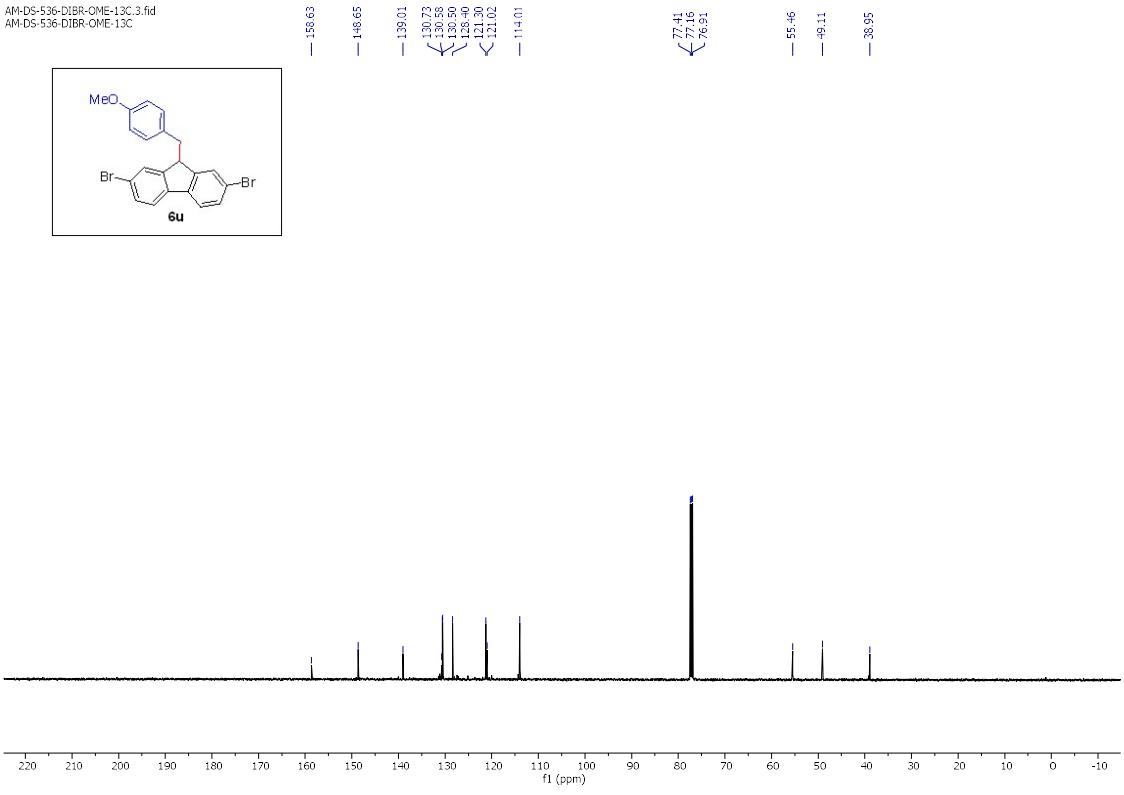


Figure 47. ^{13}C NMR Spectrum of 2,7-dibromo-9-(4-methoxybenzyl)-9H-fluorene **(6u)** in $CDCl_3$.

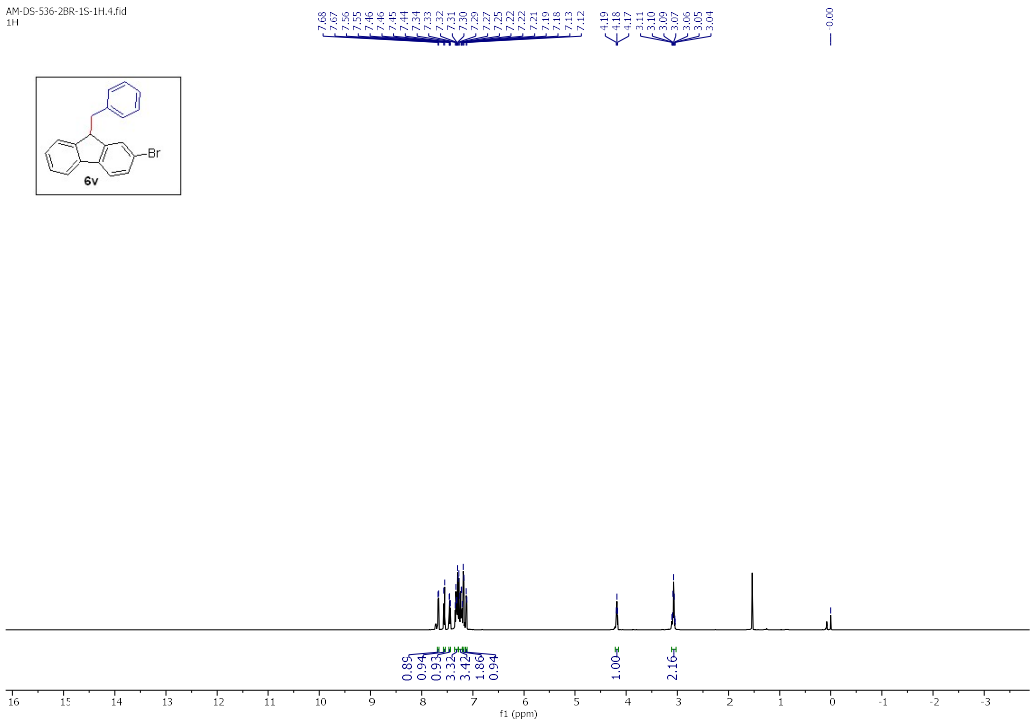


Figure 48. ^{1}H NMR Spectrum of 9-benzyl-2-bromo-9H-fluorene **(6v)** in $CDCl_3$.

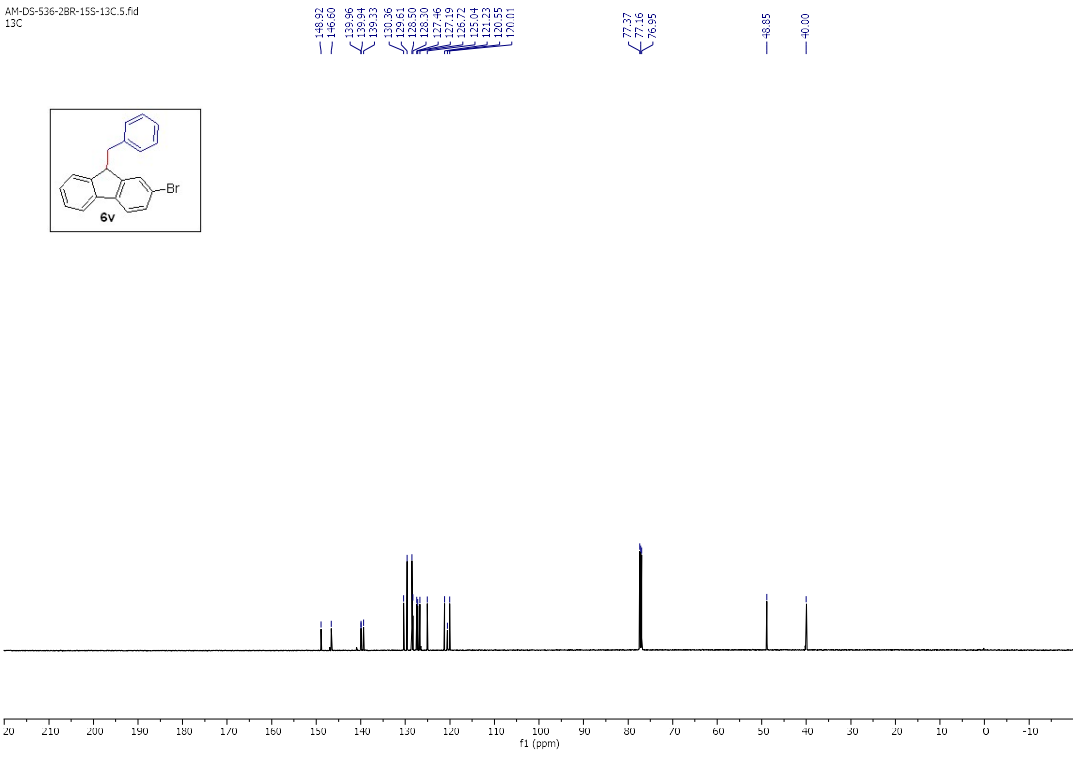


Figure 49. ^{13}C NMR Spectrum of 9-benzyl-2-bromo-9H-fluorene **(6v)** in $CDCl_3$.

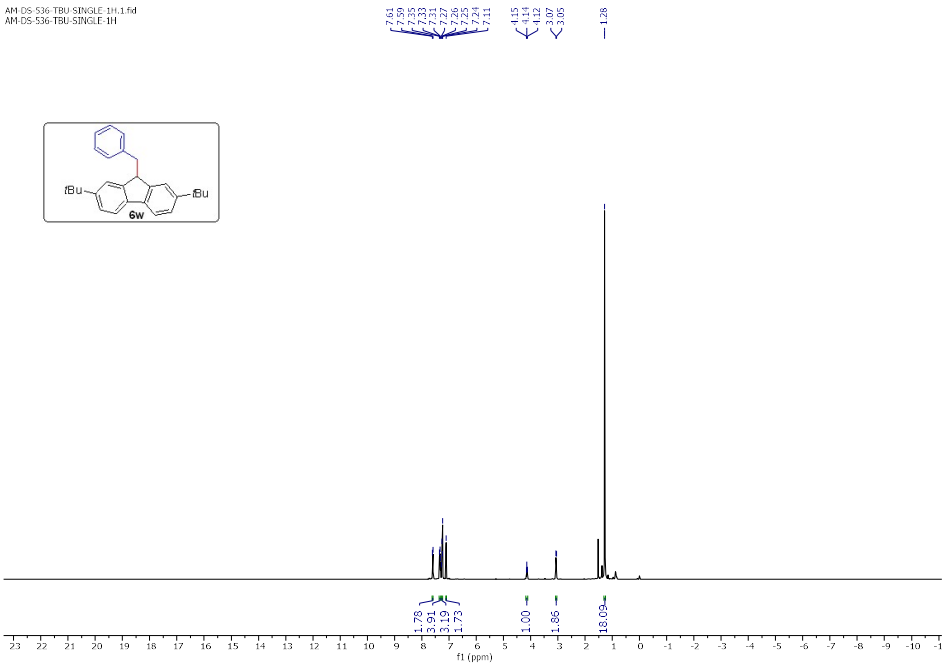


Figure 50. ^{1}H NMR Spectrum of 9-benzyl-2,7-di-tert-butyl-9H-fluorene **(6w)** in $CDCl_3$.

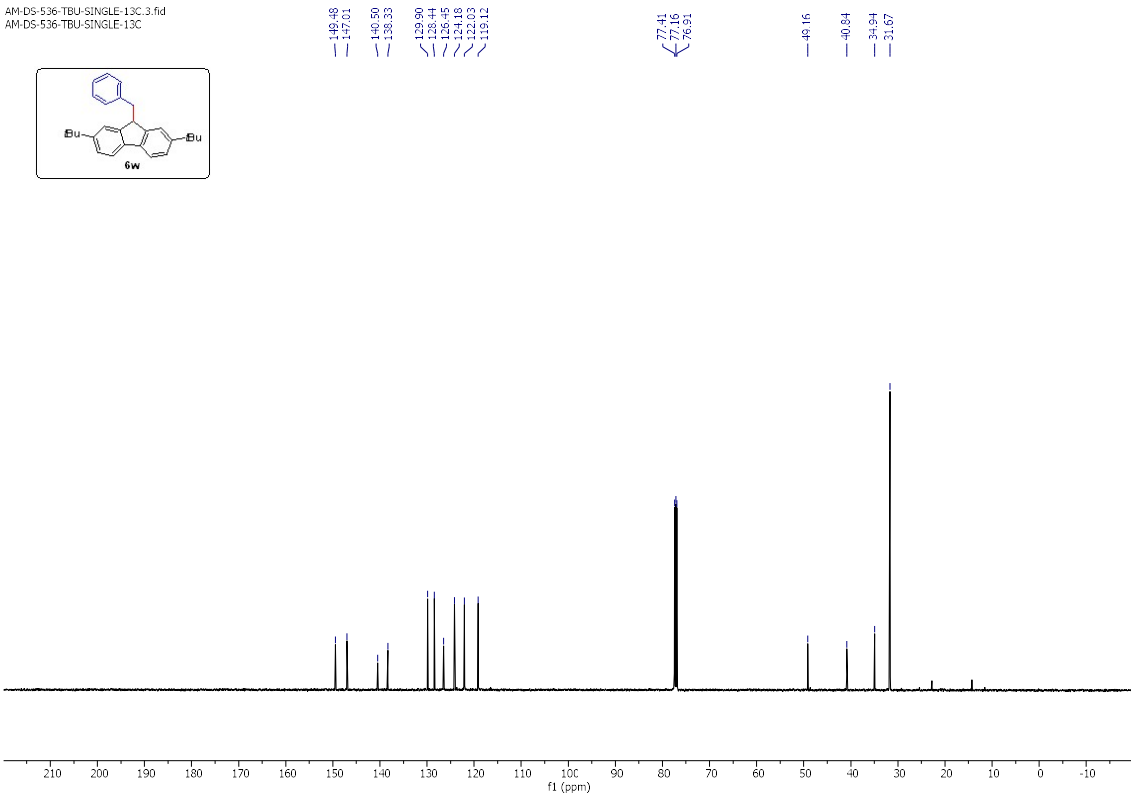


Figure 52. ^{13}C NMR Spectrum of 9-benzyl-2,7-di-tert-butyl-9H-fluorene **(6w)** in $CDCl_3$.

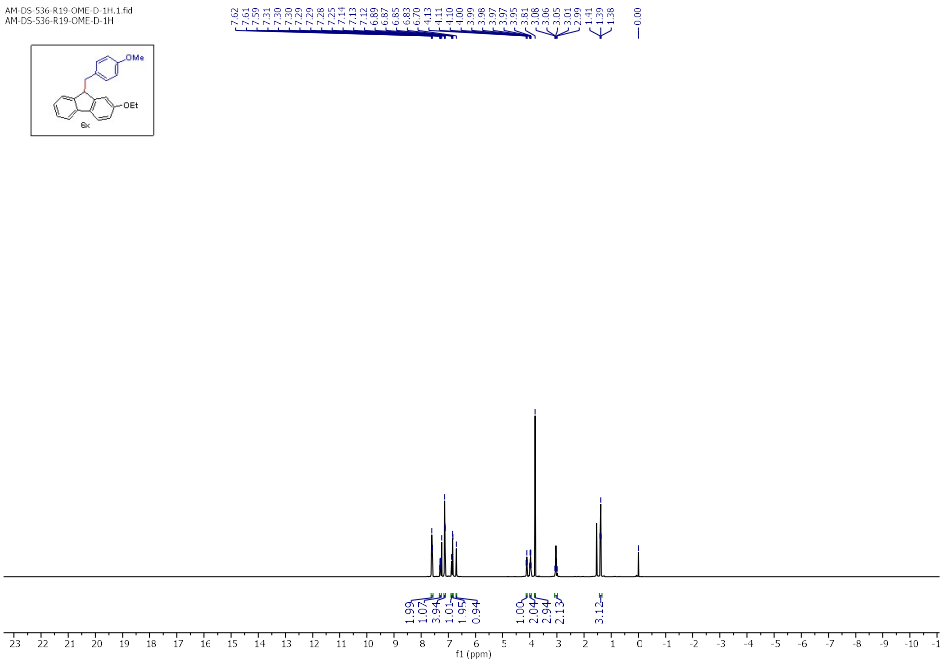


Figure 53. ^{1}H NMR Spectrum of 2-ethoxy-9-(4-methoxybenzyl)-9H-fluorene **(6x)** in $CDCl_3$.

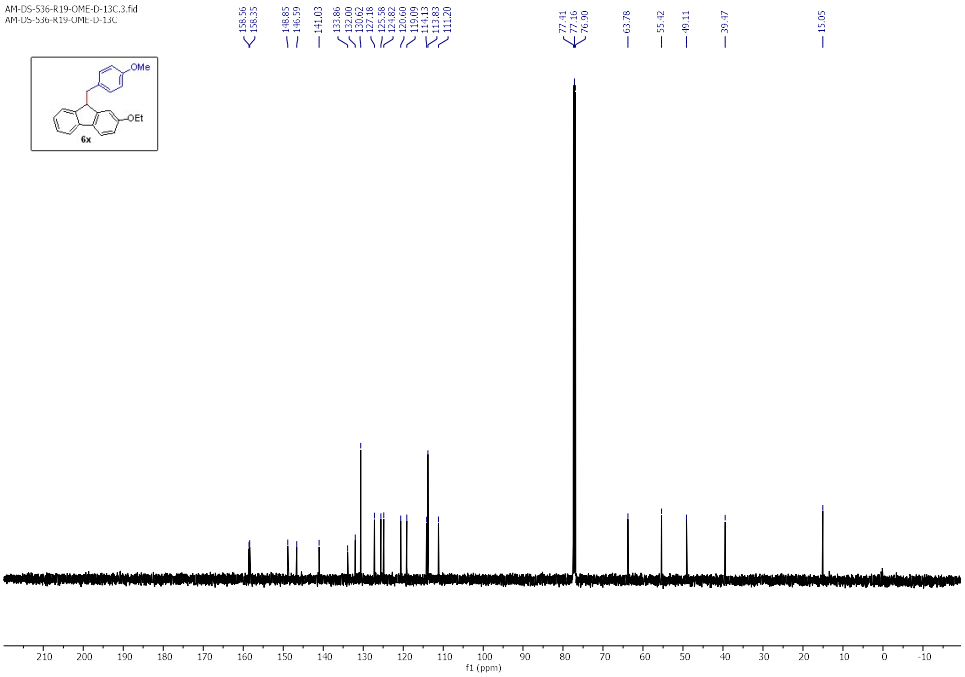


Figure 54. ^{13}C NMR Spectrum of 2-ethoxy-9-(4-methoxybenzyl)-9H-fluorene **(6x)** in $CDCl_3$.

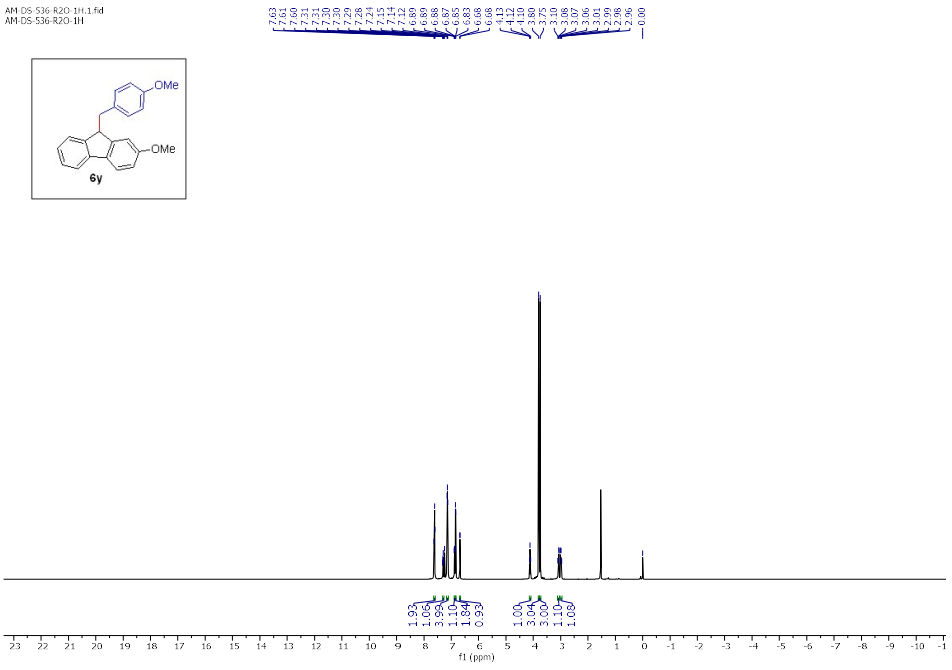


Figure 55. ^{1}H NMR Spectrum of 2-methoxy-9-(4-methoxybenzyl)-9H-fluorene **(6y)** in $CDCl_3$.

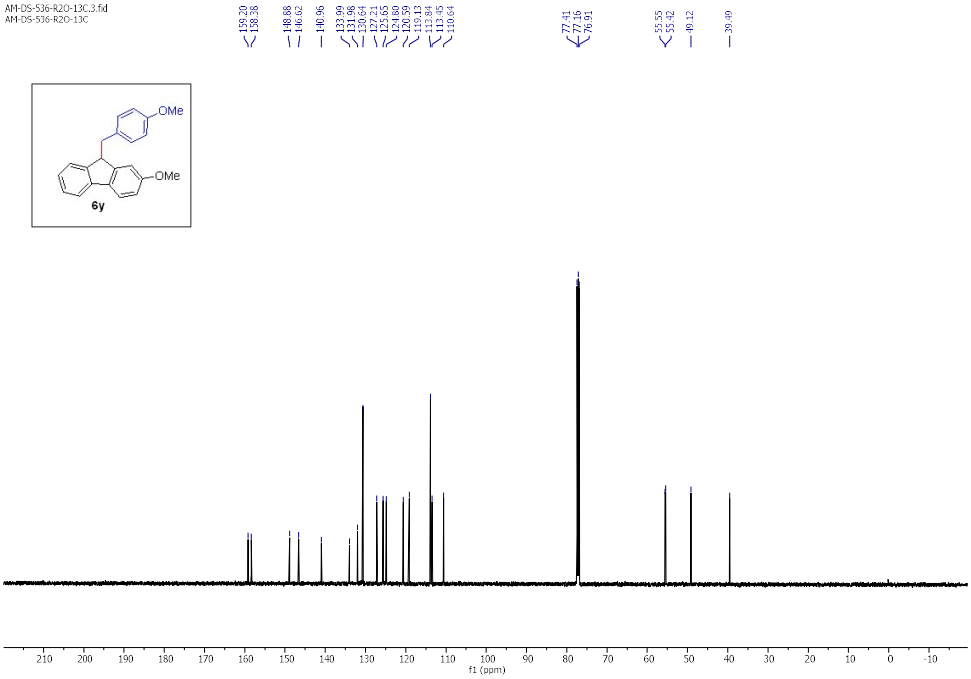


Figure 56. ^{13}C NMR Spectrum of 2-methoxy-9-(4-methoxybenzyl)-9H-fluorene **(6y)** in $CDCl_3$.

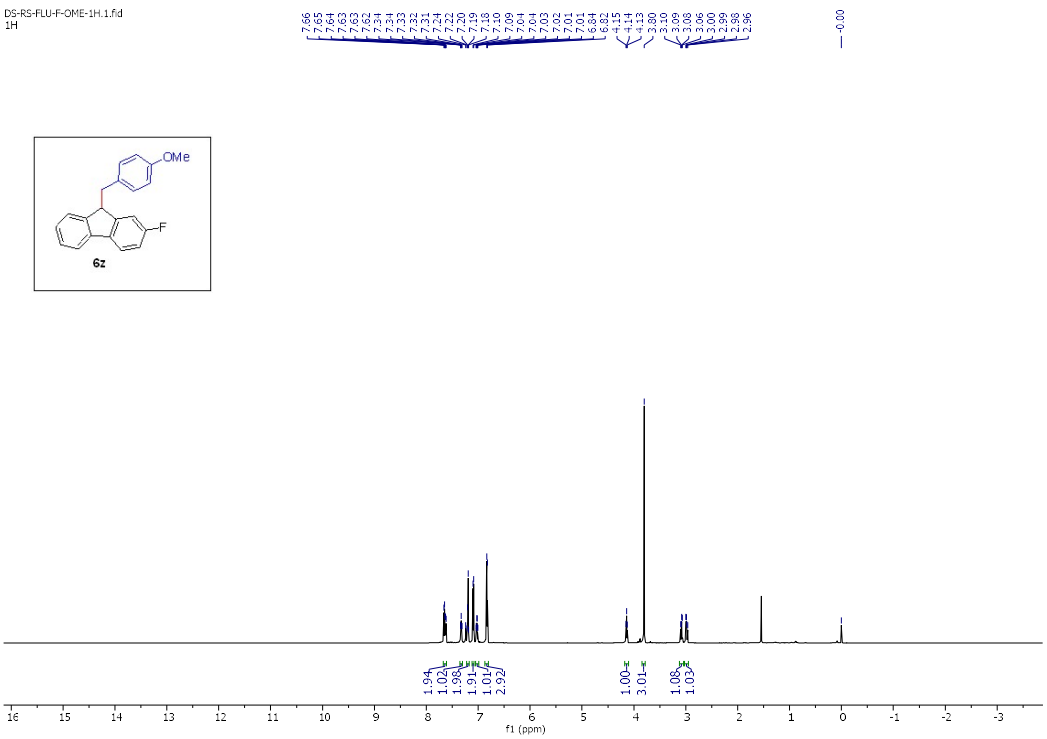


Figure 57. ^{1}H NMR Spectrum of 2-fluoro-9-(4-methoxybenzyl)-9H-fluorene **(6z)** in $CDCl_3$.

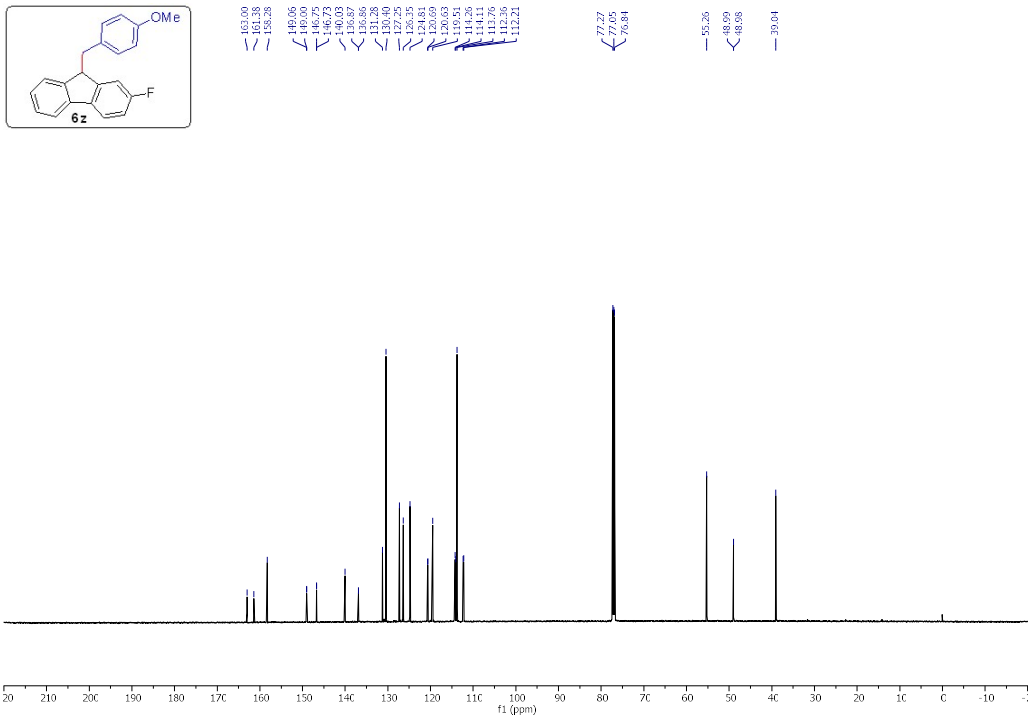


Figure 58. ^{13}C NMR Spectrum of 2-fluoro-9-(4-methoxybenzyl)-9H-fluorene **(6z)** in $CDCl_3$.

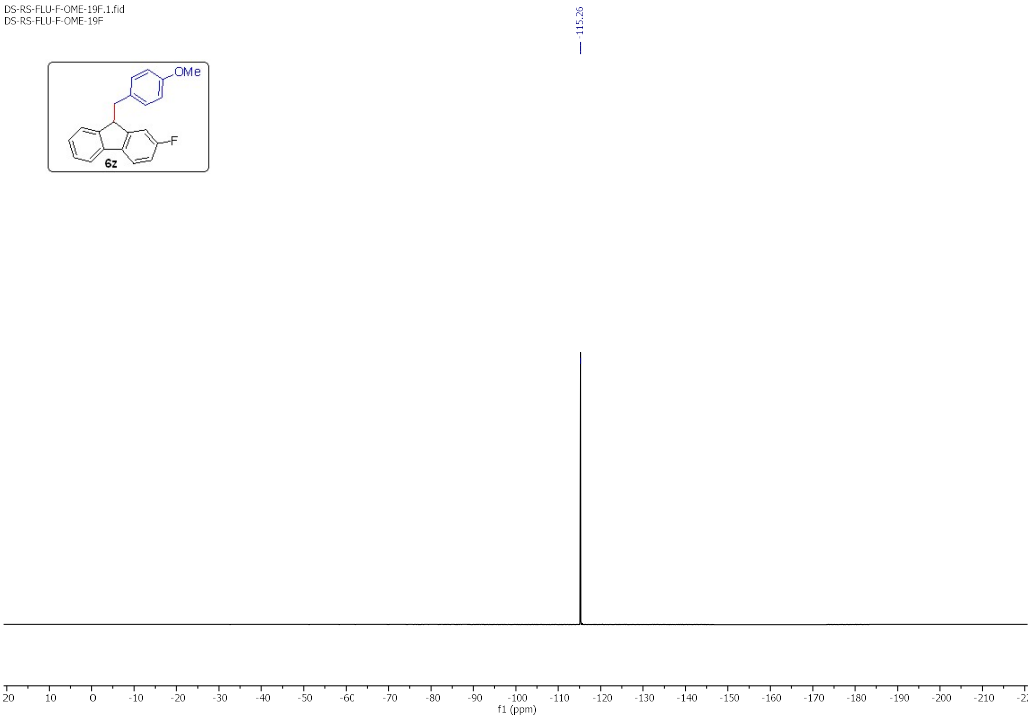


Figure 58. ^{19}F NMR Spectrum of 2-fluoro-9-(4-methoxybenzyl)-9H-fluorene **(6z)** in $CDCl_3$.

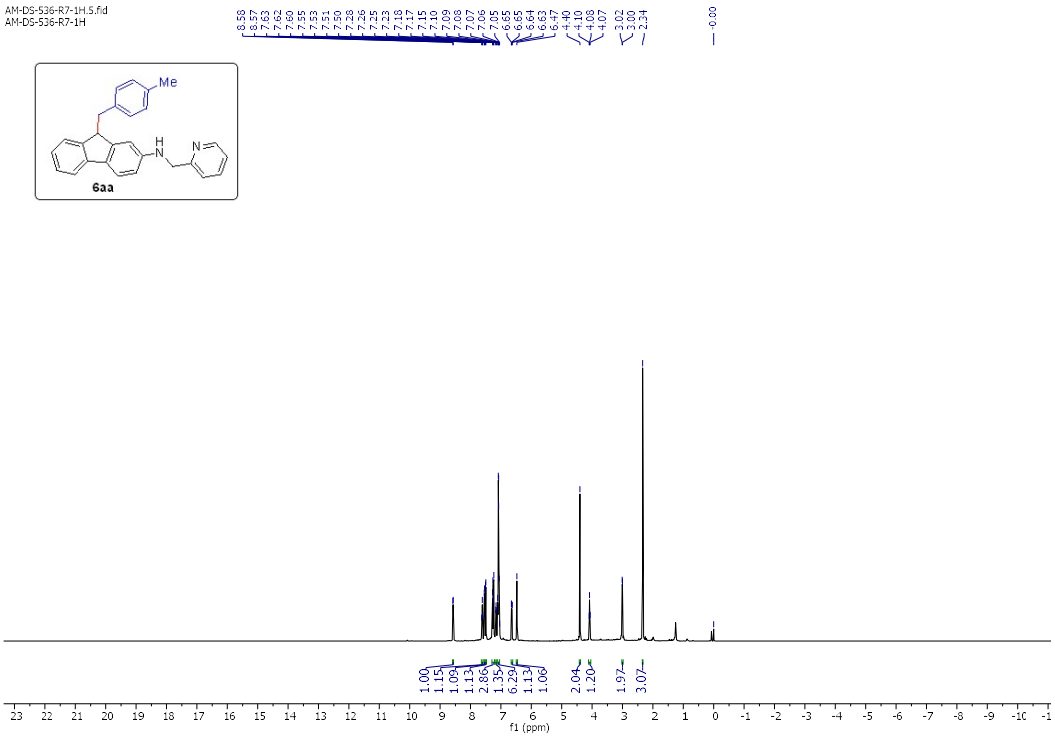


Figure 59. ^{1}H NMR Spectrum of 9-(4-methylbenzyl)-N-(pyridin-2-ylmethyl)-9H-fluoren-2-amine **(6aa)** in $CDCl_3$.

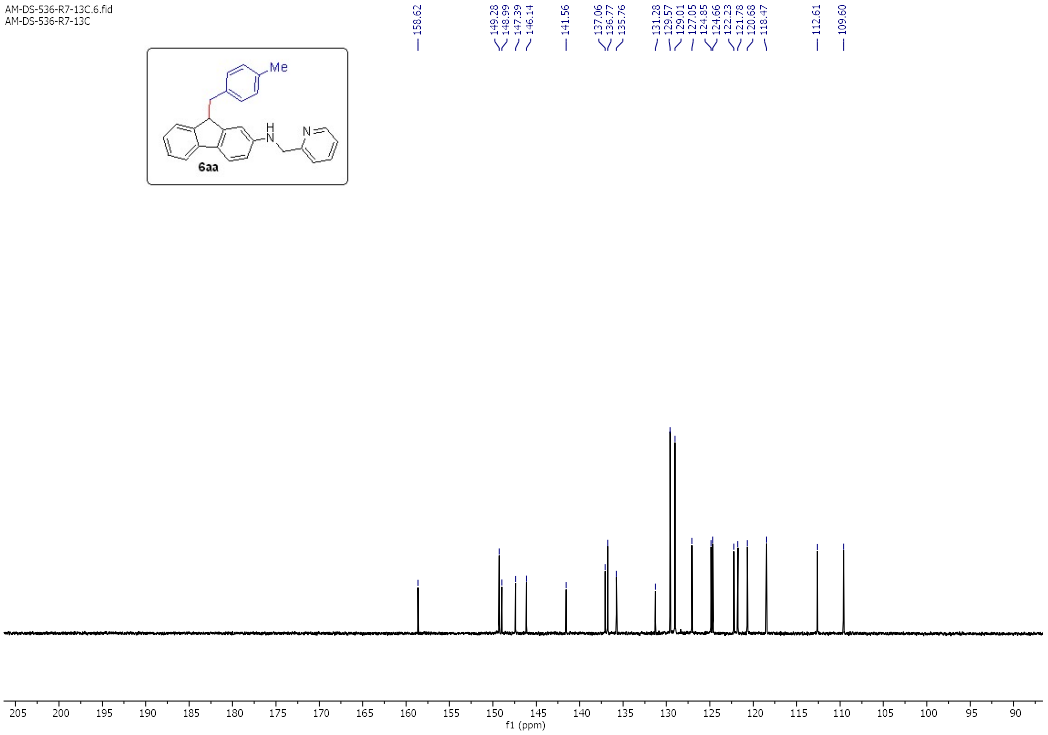


Figure 60. ^{13}C NMR Spectrum of 9-(4-methylbenzyl)-N-(pyridin-2-ylmethyl)-9H-fluoren-2-amine **(6aa)** in $CDCl_3$.

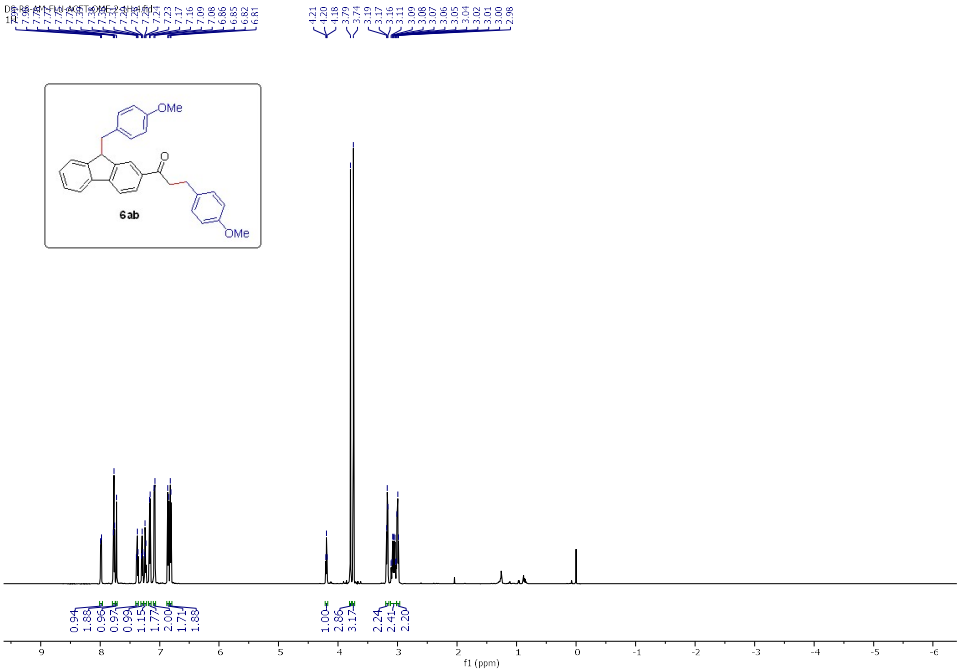


Figure 61. ^{1}H NMR Spectrum of 1-(9-(4-methoxybenzyl)-9H-fluoren-2-yl)-3-(4-methoxyphenyl)propan-1-one **(6ab)** in $CDCl_3$.

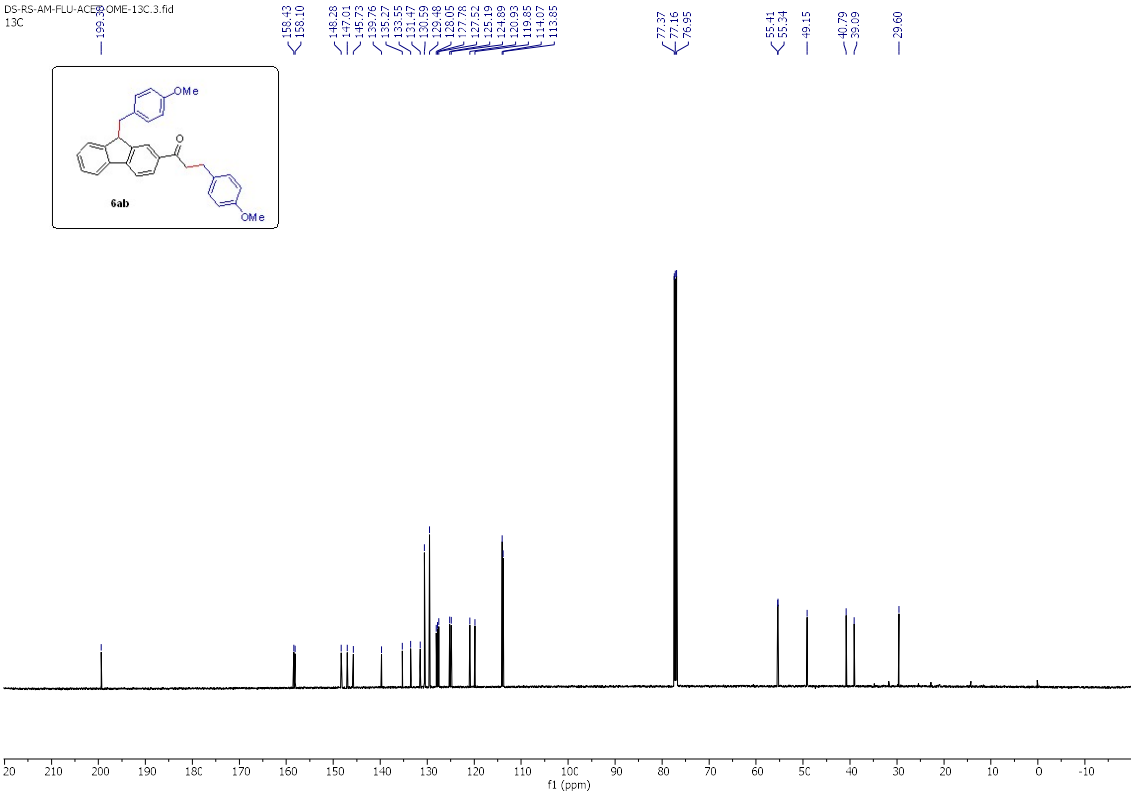


Figure 62. ^{13}C NMR Spectrum of 1-(9-(4-methoxybenzyl)-9H-fluoren-2-yl)-3-(4-methoxyphenyl)propan-1-one **(6ab)** in $CDCl_3$.

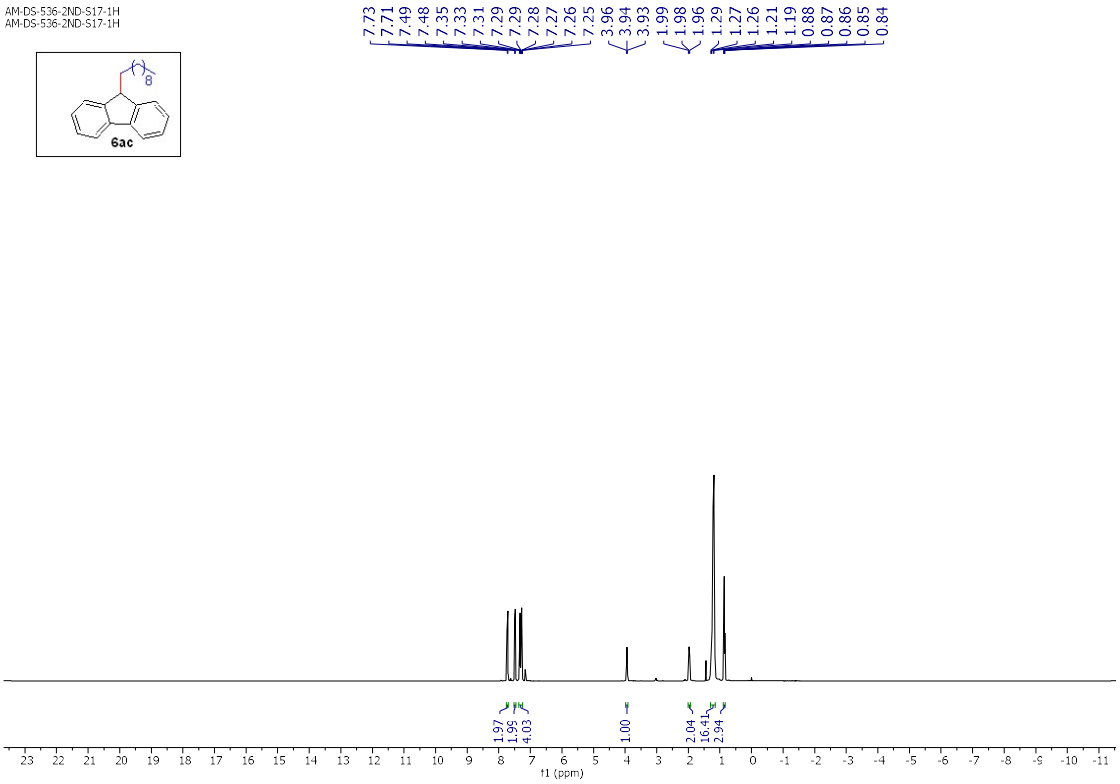


Figure S63. ^{1}H NMR Spectrum of 9-decyl-9H-fluorene **(6ac)** in $CDCl_3$.

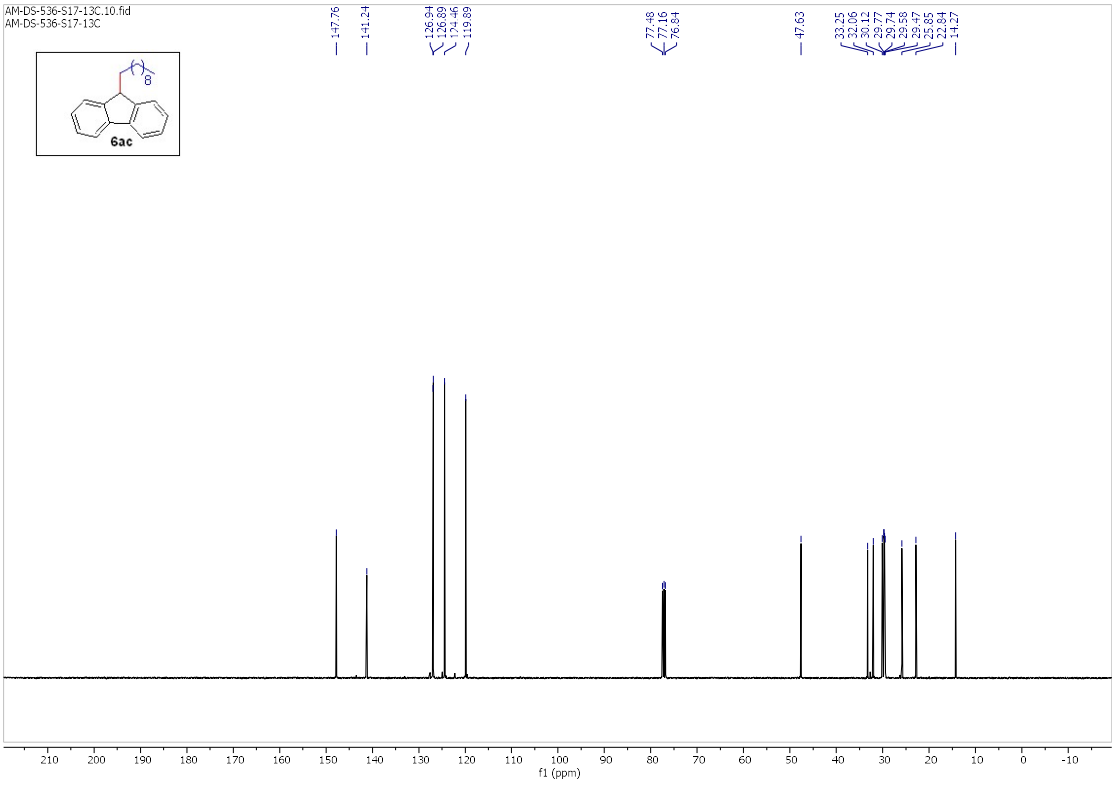


Figure S64. ^{13}C NMR Spectrum of 9-decyl-9H-fluorene **(6ac)** in $CDCl_3$.

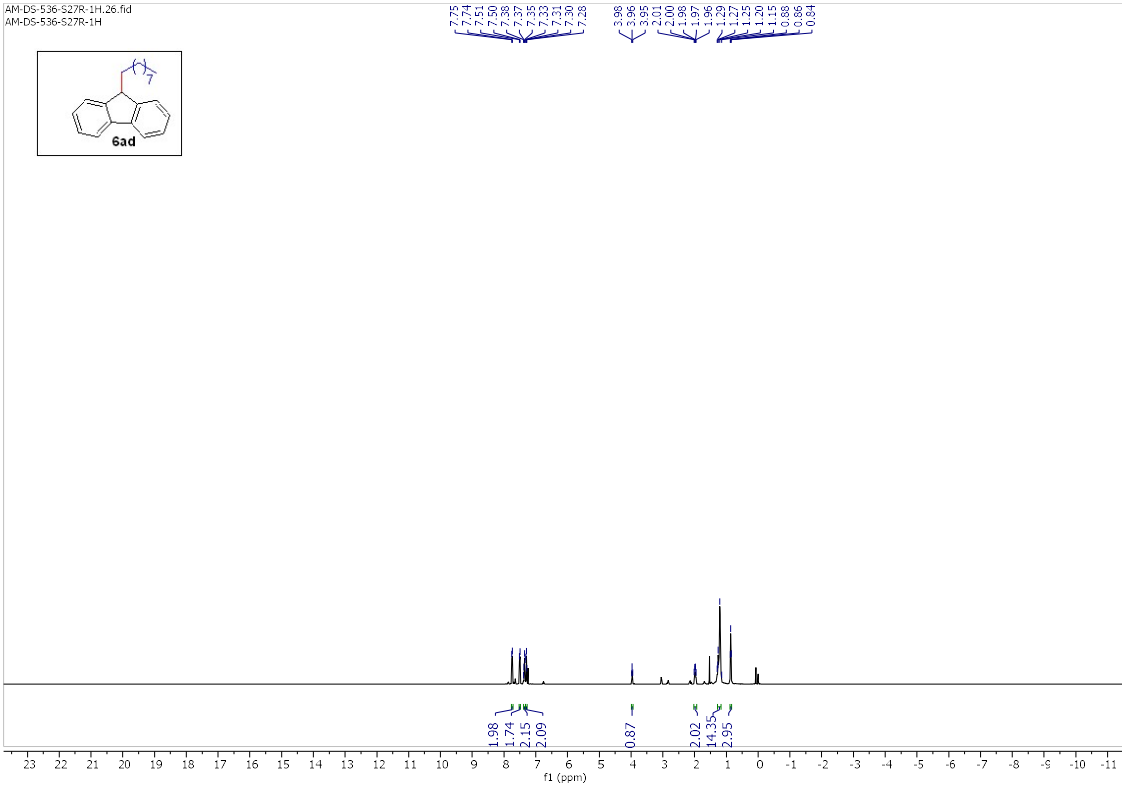


Figure S65. ^{1}H NMR Spectrum of 9-nonyl-9H-fluorene **(6ad)** in $CDCl_3$.

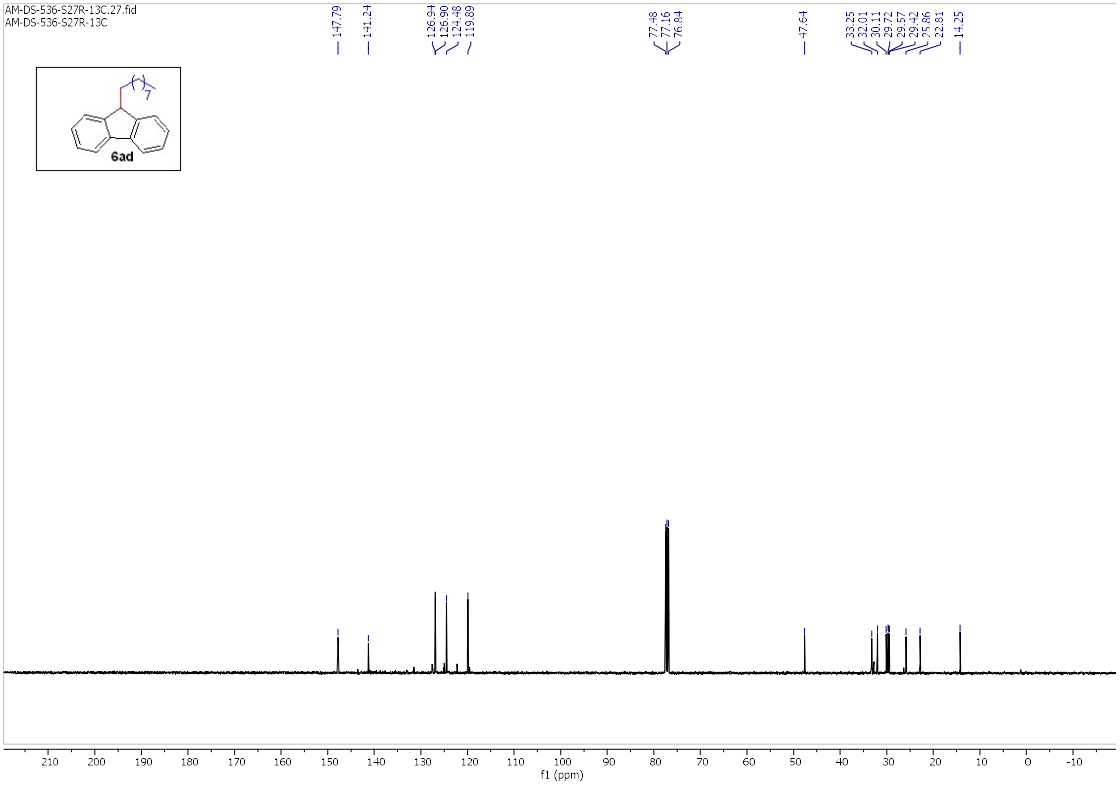


Figure S66. ^{13}C NMR Spectrum of 9-nonyl-9H-fluorene **(6ad)** in $CDCl_3$.

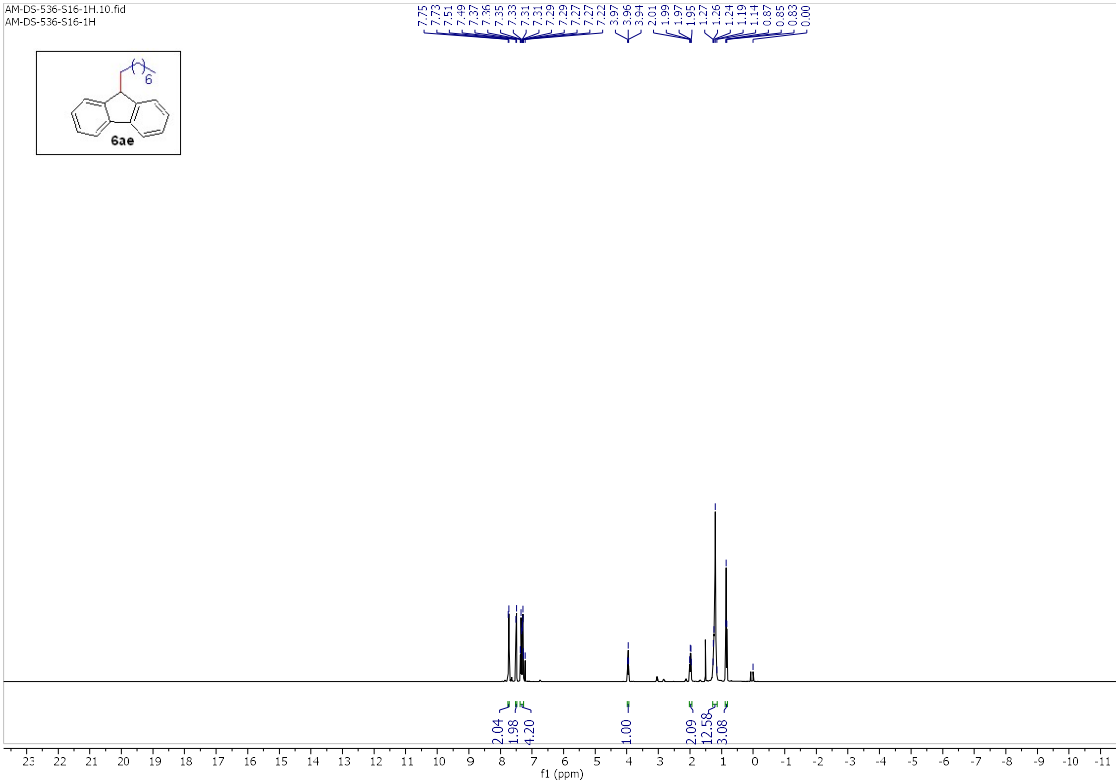


Figure S67. ^{1}H NMR Spectrum of 9-octyl-9H-fluorene **(6ae)** in $CDCl_3$.

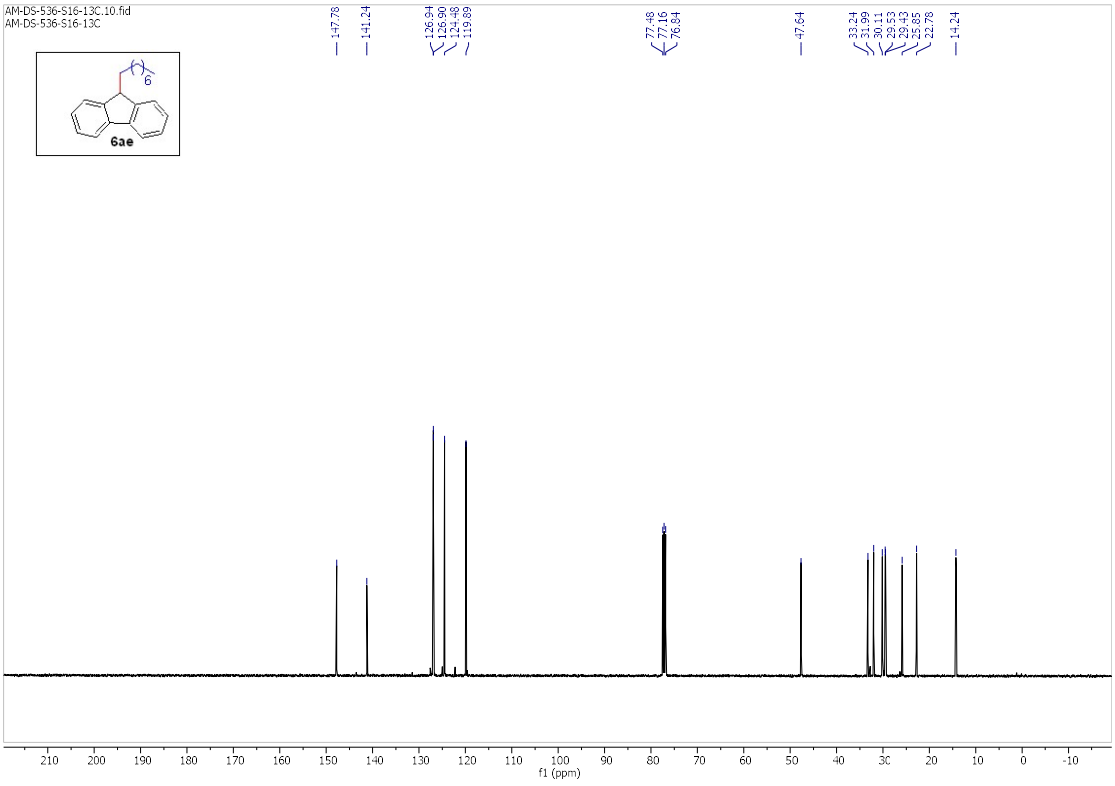


Figure S68. ^{13}C NMR Spectrum of 9-octyl-9H-fluorene **(6ae)** in $CDCl_3$.

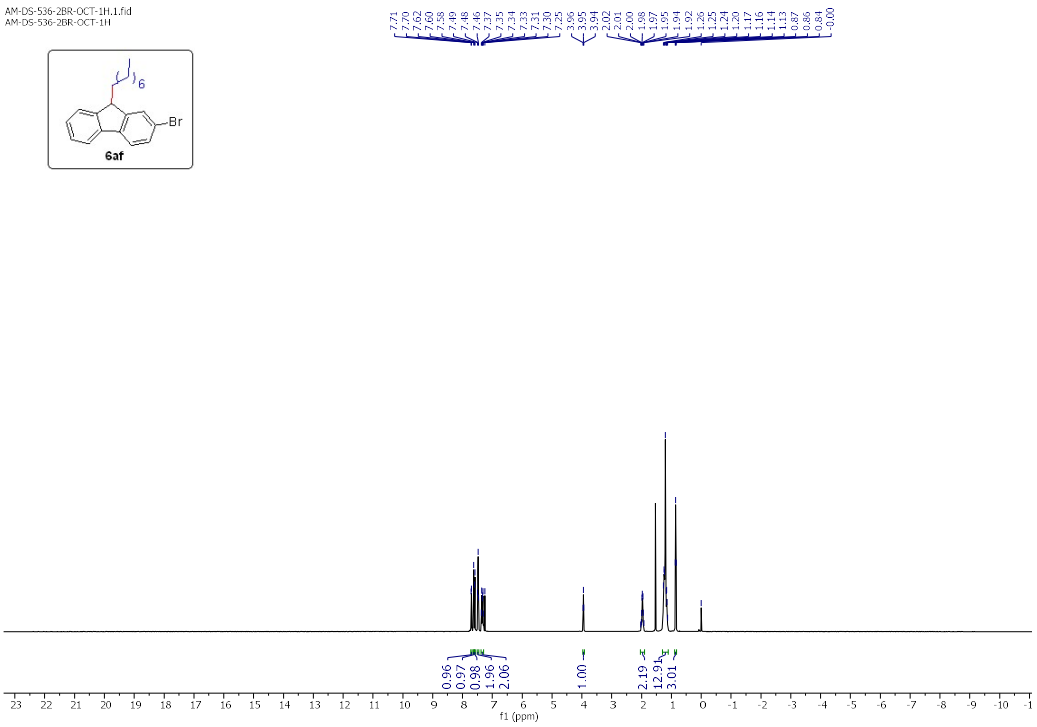


Figure S69. ^{1}H NMR Spectrum of 2-bromo-9-octyl-9H-fluorene **(6af)** in $CDCl_3$.

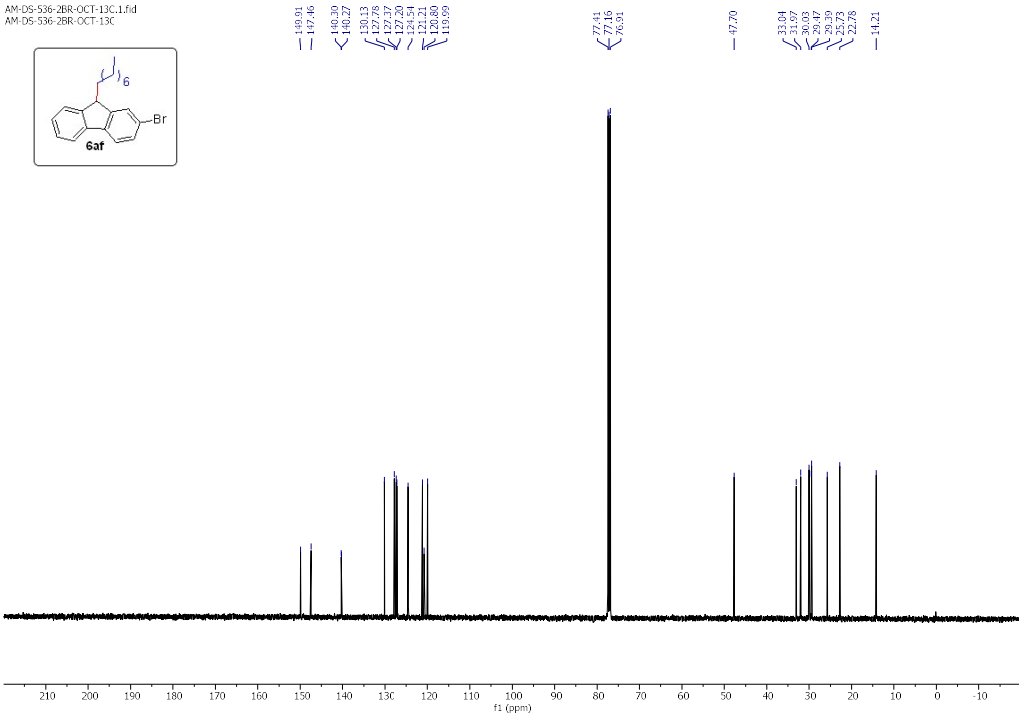


Figure S70. ^{13}C NMR Spectrum of 2-bromo-9-octyl-9H-fluorene **(6af)** in $CDCl_3$.

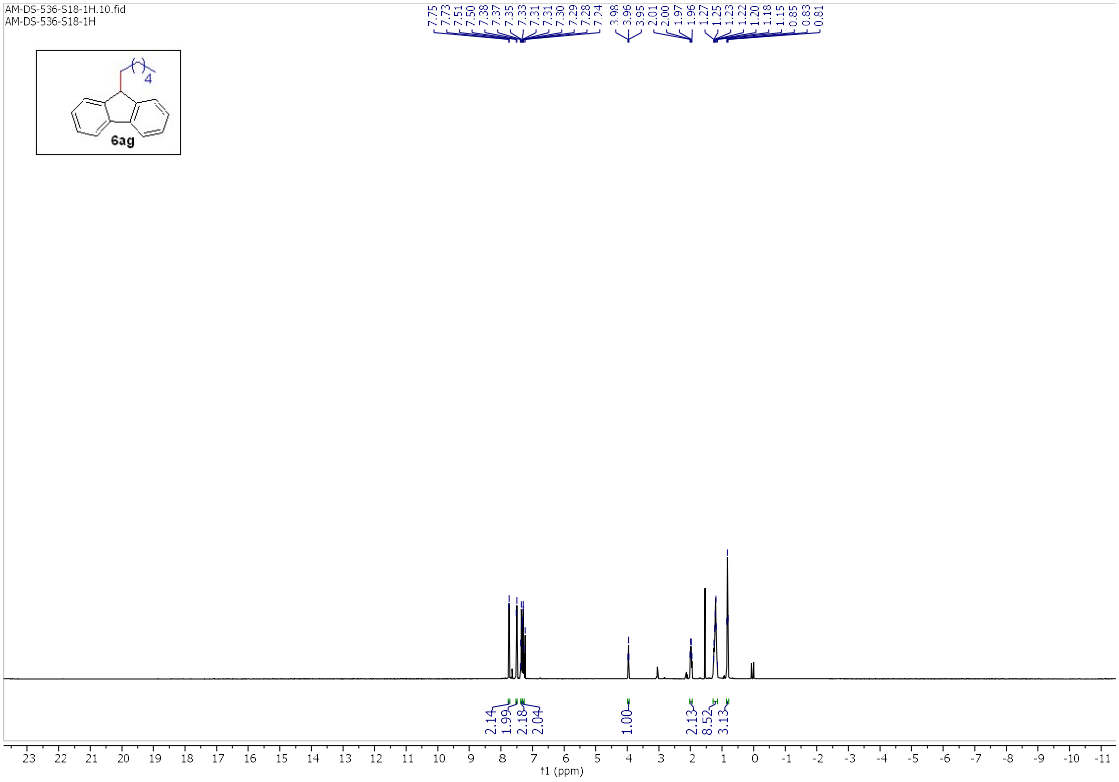


Figure S71. [1] H NMR Spectrum of 9-hexyl-9H-fluorene **(6ag)** in $CDCl_3$.

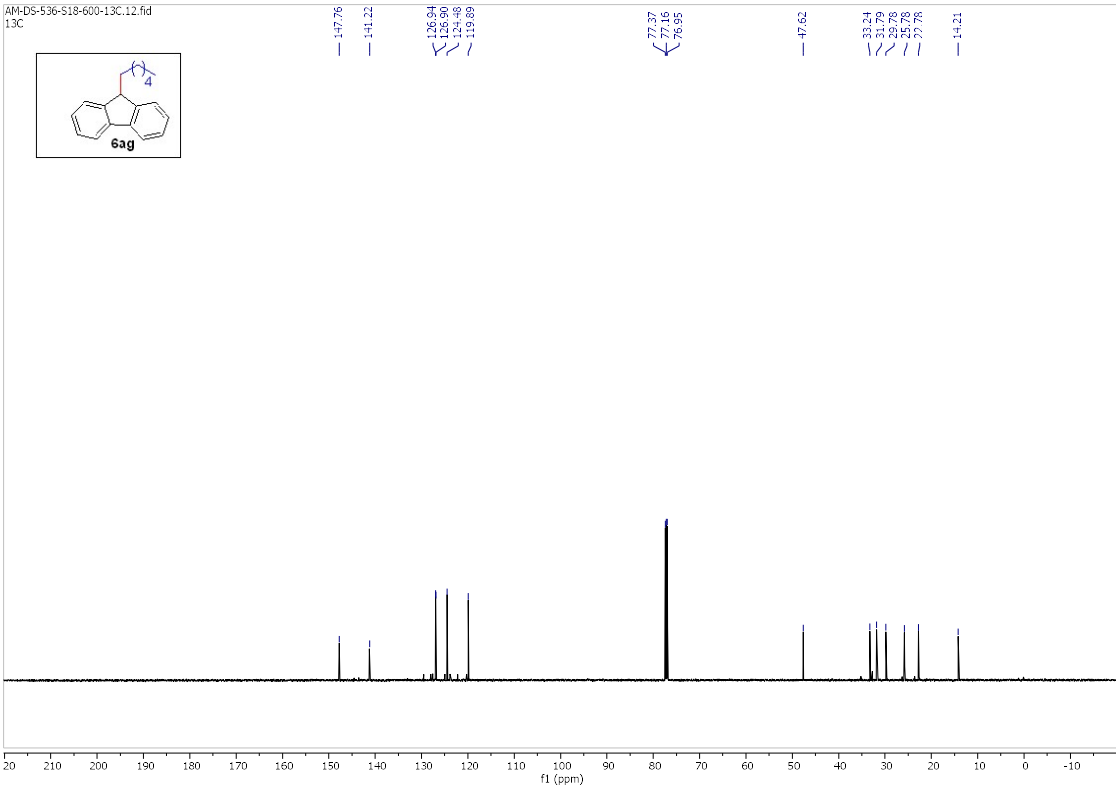


Figure S72. [13]C NMR Spectrum of 9-hexyl-9H-fluorene **(6ag)** in $CDCl_3$.

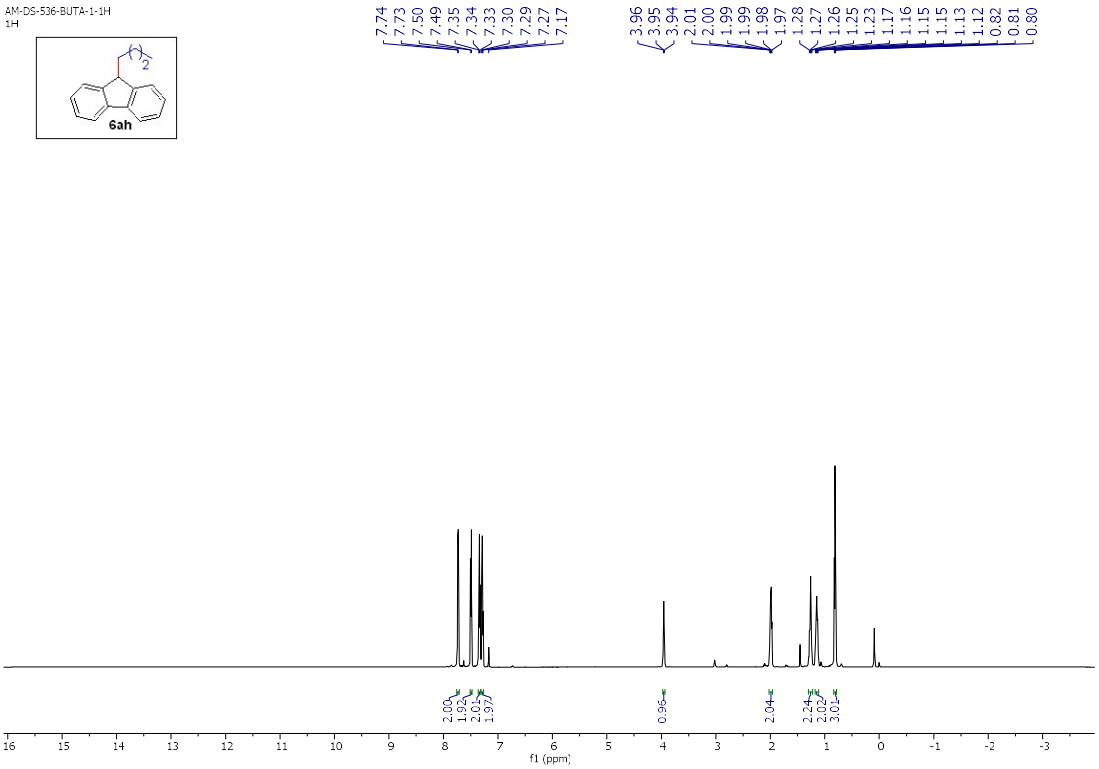


Figure S73. ^{1}H NMR Spectrum of 9-butyl-9H-fluorene **(6ah)** in $CDCl_3$.

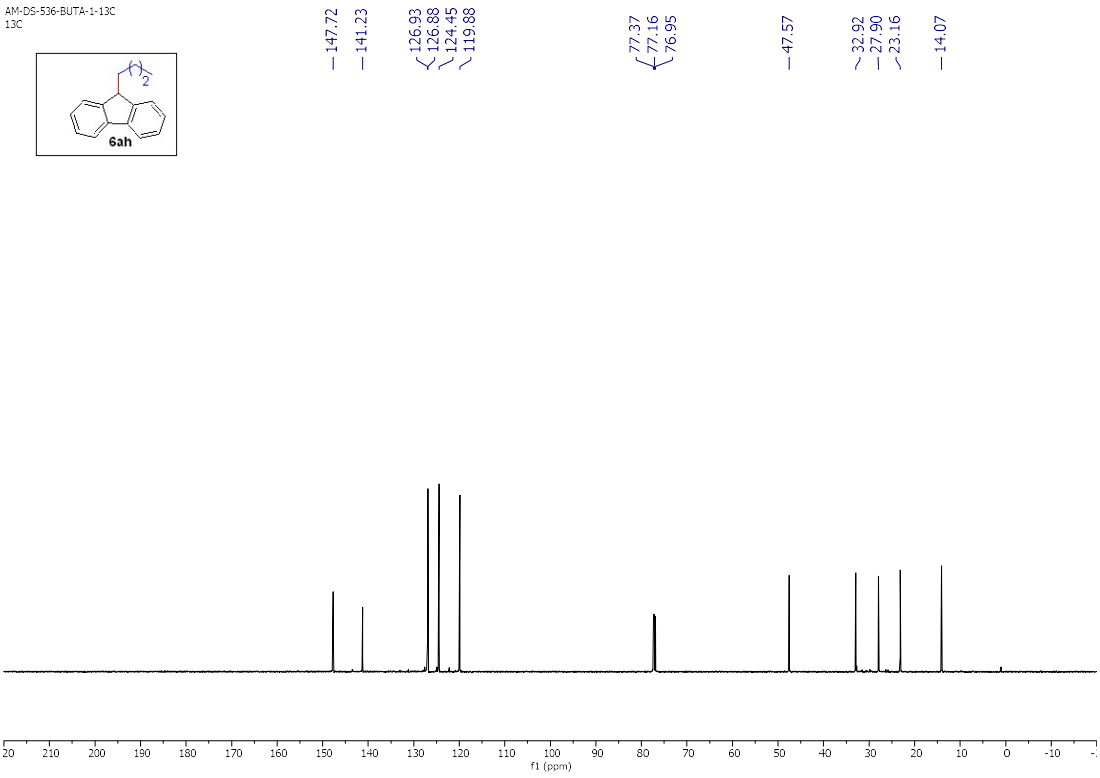


Figure S74. ^{13}C NMR Spectrum of 9-butyl-9H-fluorene **(6ah)** in $CDCl_3$.

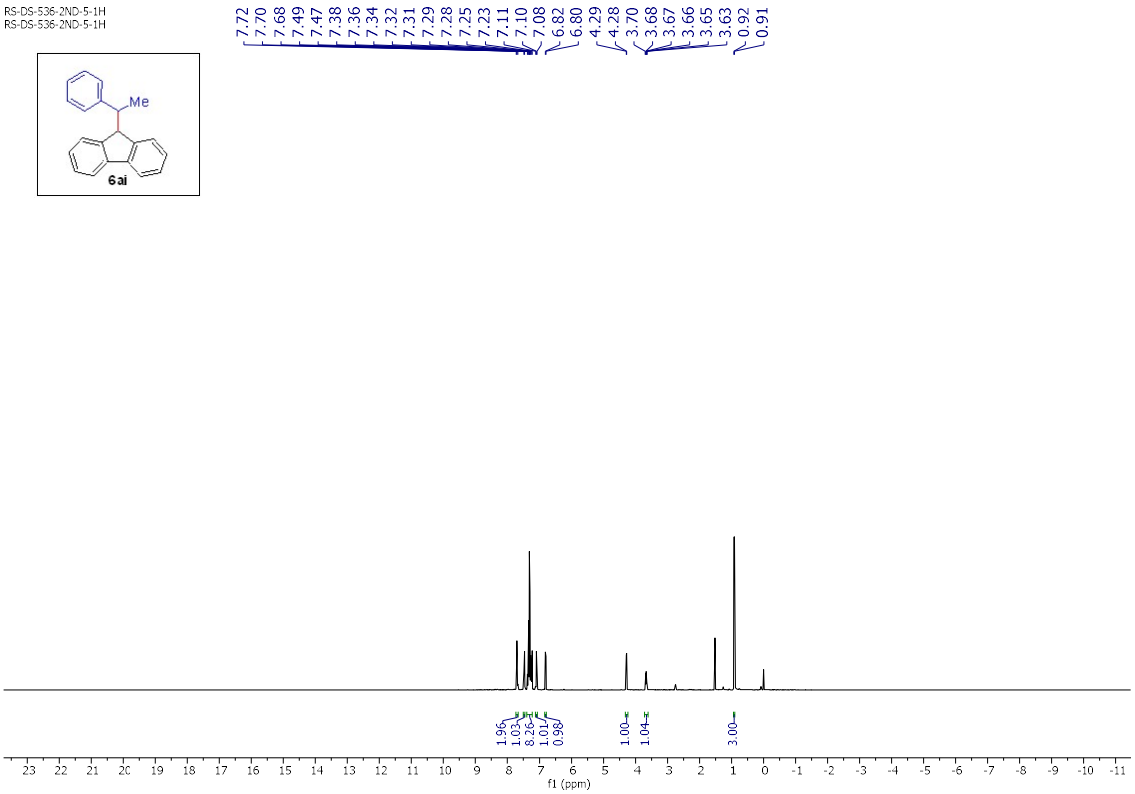


Figure S75. ^{1}H NMR Spectrum of 9-(1-phenylethyl)-9H-fluorene **(6ai)** in $CDCl_3$.

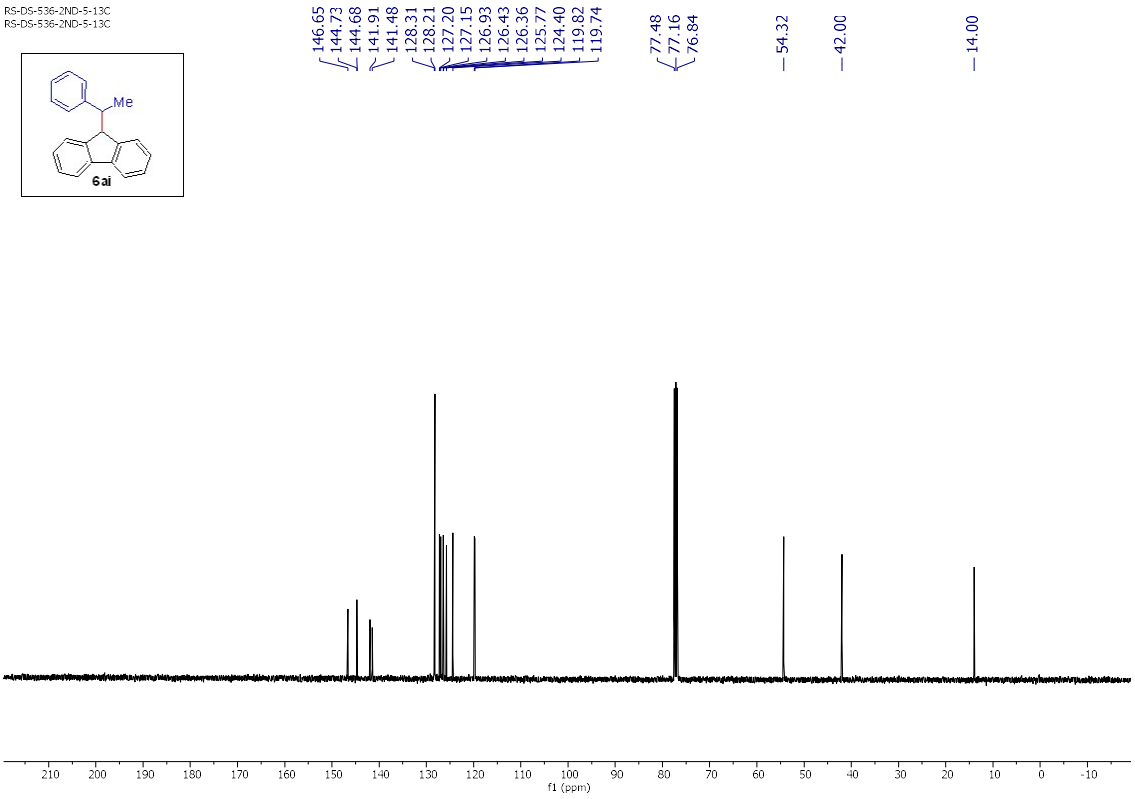


Figure S76. ^{13}C NMR Spectrum of 9-(1-phenylethyl)-9H-fluorene **(6ai)** in $CDCl_3$.

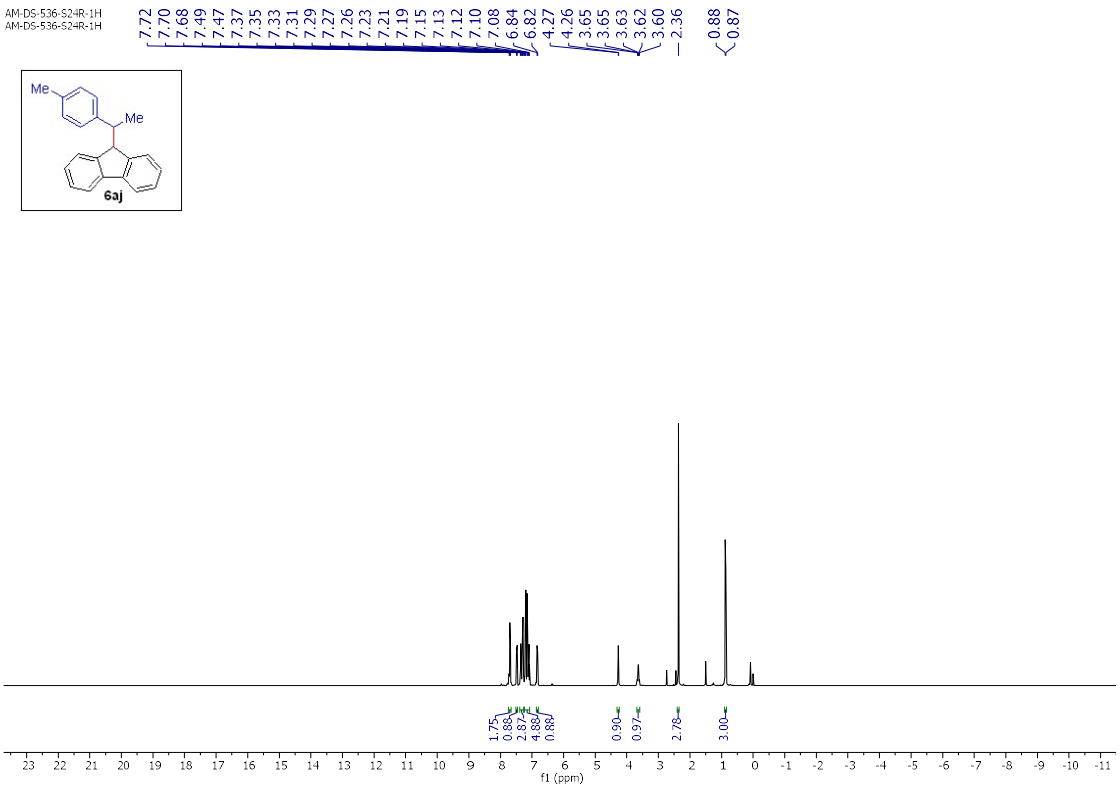


Figure S77. ^{1}H NMR Spectrum of 9-(1-(p-tolyl)ethyl)-9H-fluorene **(6aj)** in $CDCl_3$.

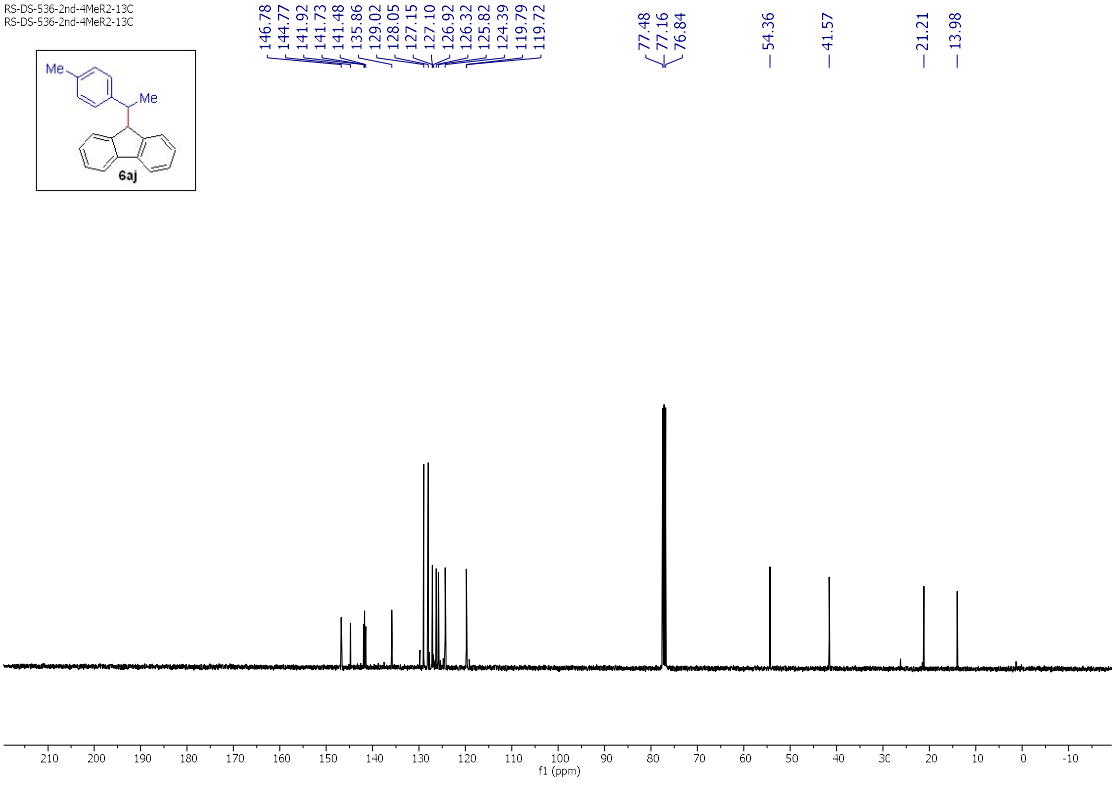


Figure S78. ^{13}C NMR Spectrum of 9-(1-(p-tolyl)ethyl)-9H-fluorene **(6aj)** in $CDCl_3$.

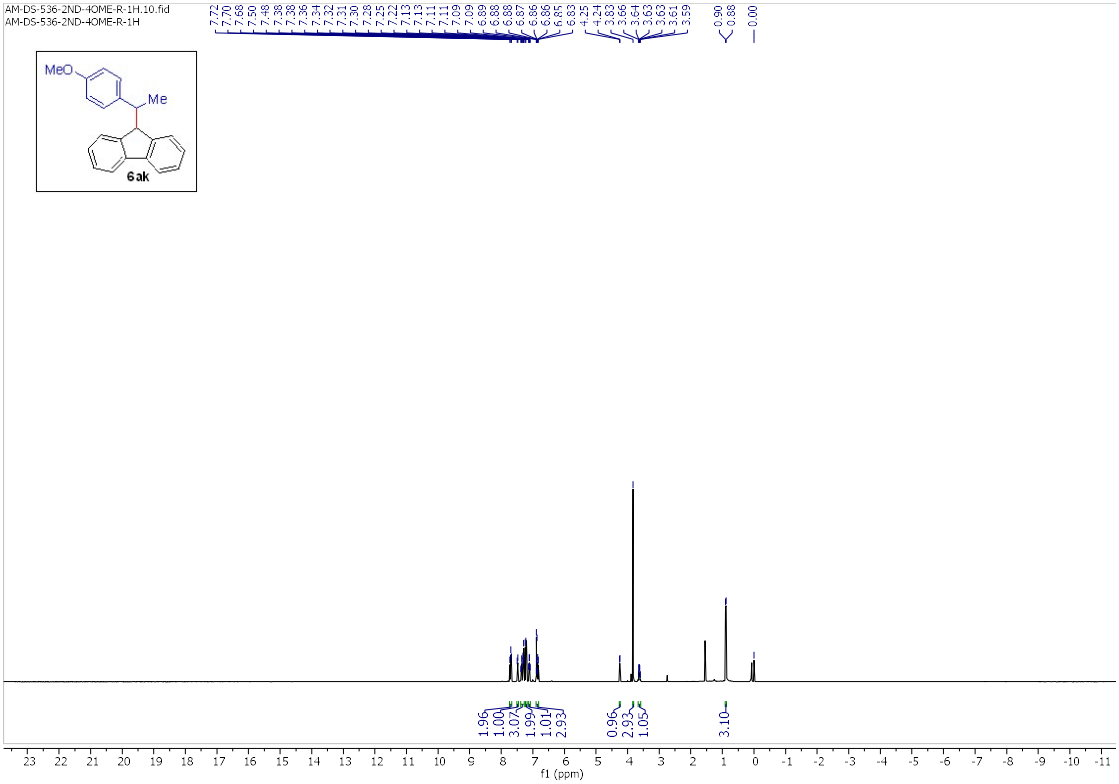


Figure S79. ^{1}H NMR Spectrum of 9-(1-(4-methoxyphenyl)ethyl)-9H-fluorene **(6ak)** in $CDCl_3$.

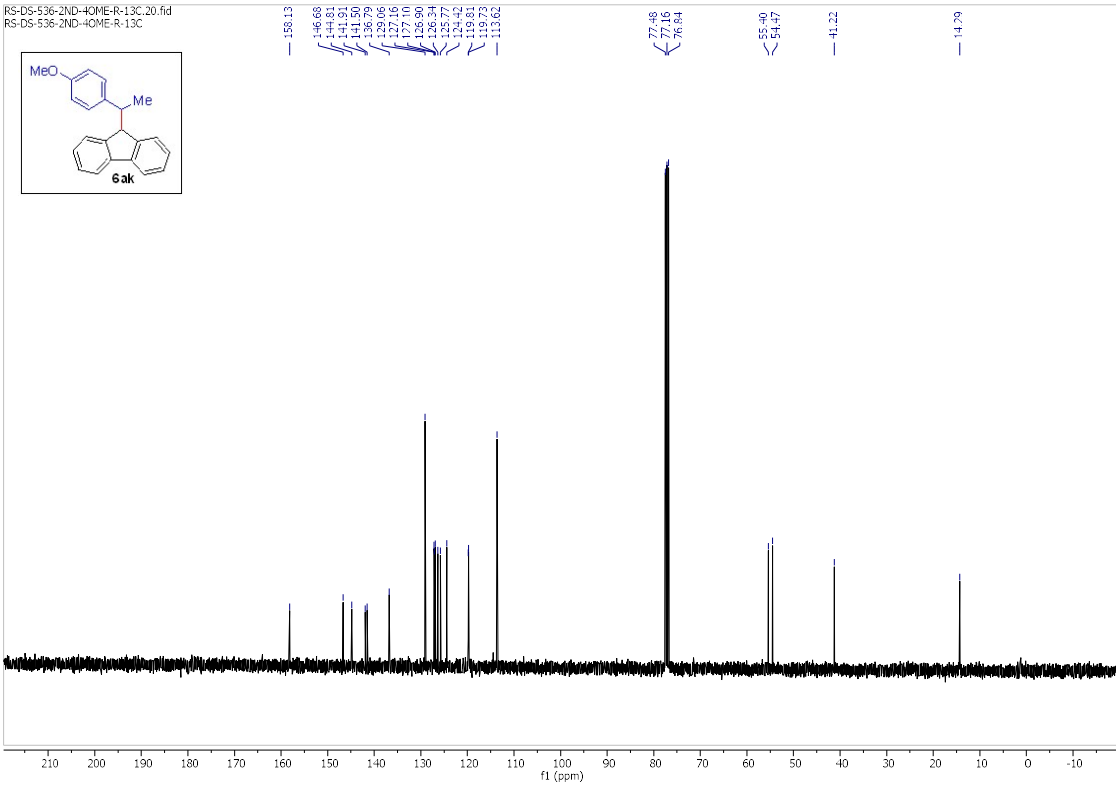


Figure S80. ^{13}C NMR Spectrum of 9-(1-(4-methoxyphenyl)ethyl)-9H-fluorene **(6ak)** in $CDCl_3$.

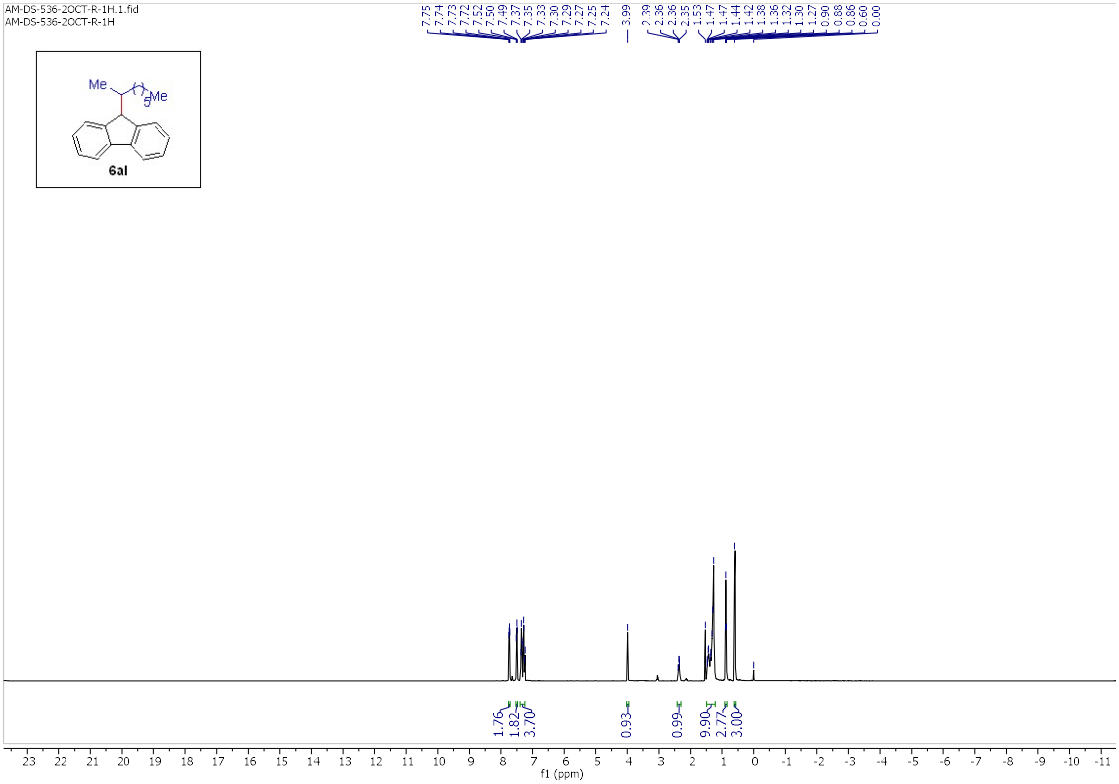


Figure S81. ^{1}H NMR Spectrum of 9-(octan-2-yl)-9H-fluorene **(6al)** in $CDCl_3$.

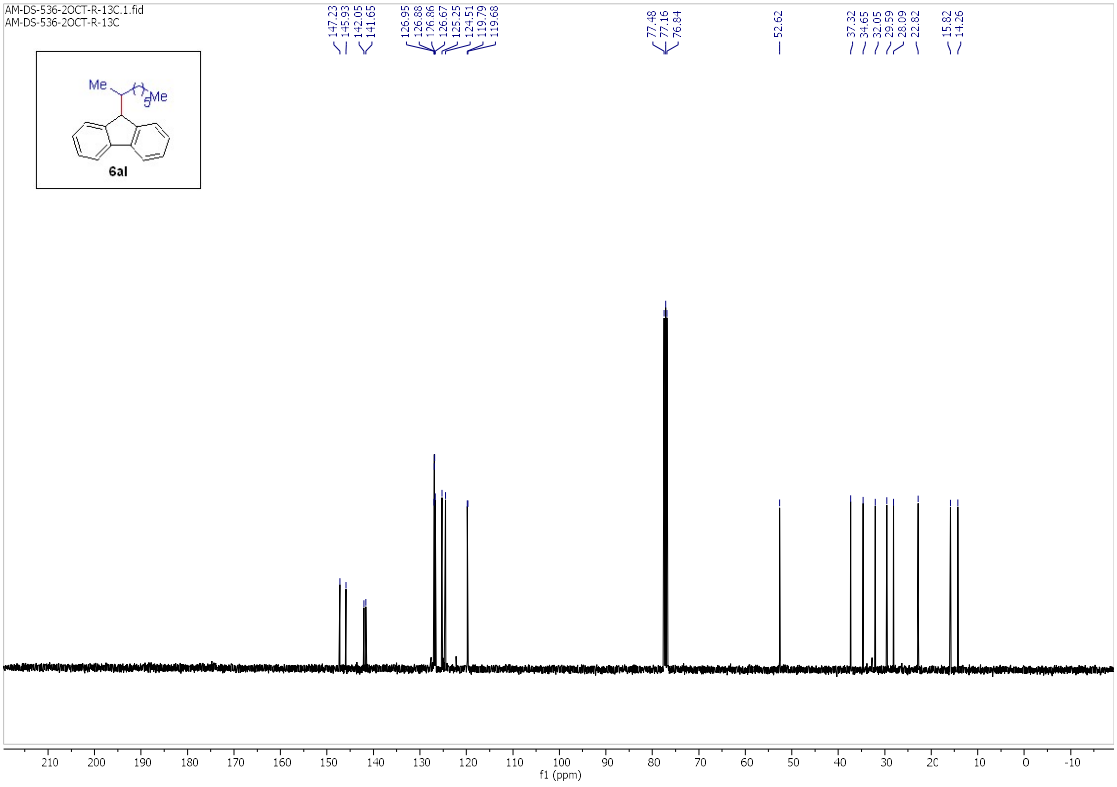


Figure S82. ^{13}C NMR Spectrum of 9-(octan-2-yl)-9H-fluorene **(6al)** in $CDCl_3$.

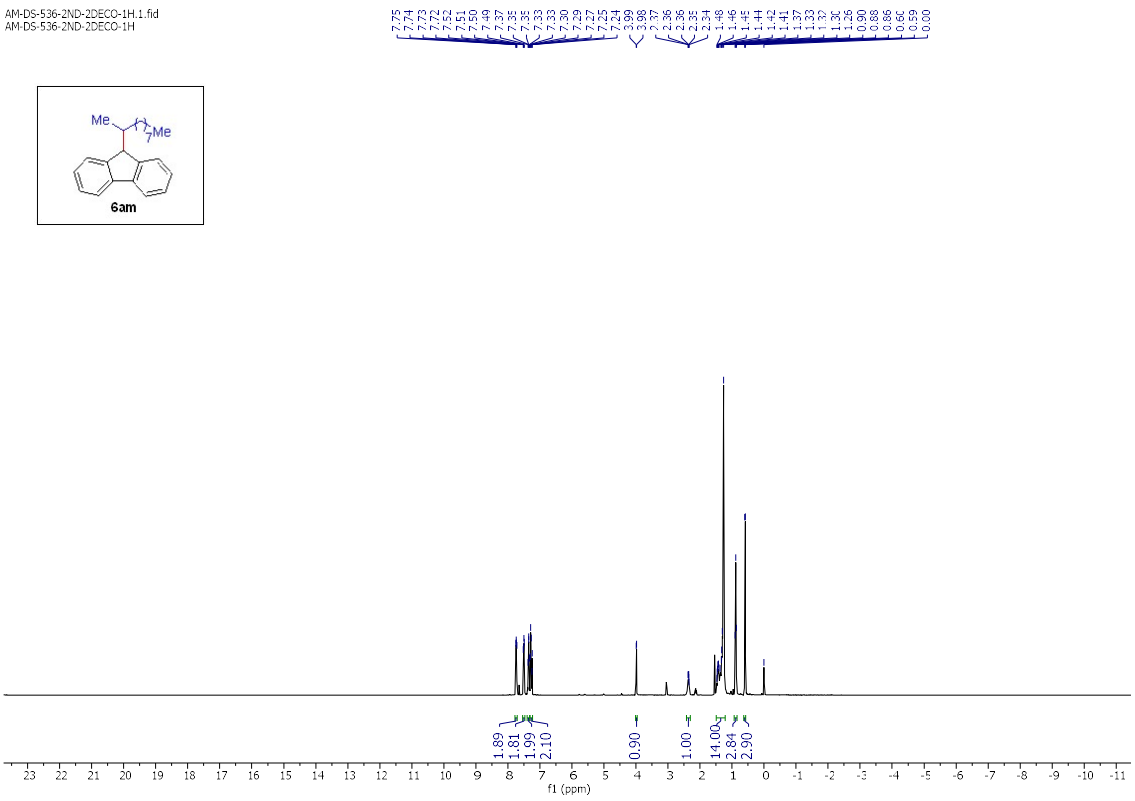


Figure S83. ^{1}H NMR Spectrum of 9-(decan-2-yl)-9H-fluorene **(6am)** in $CDCl_3$.

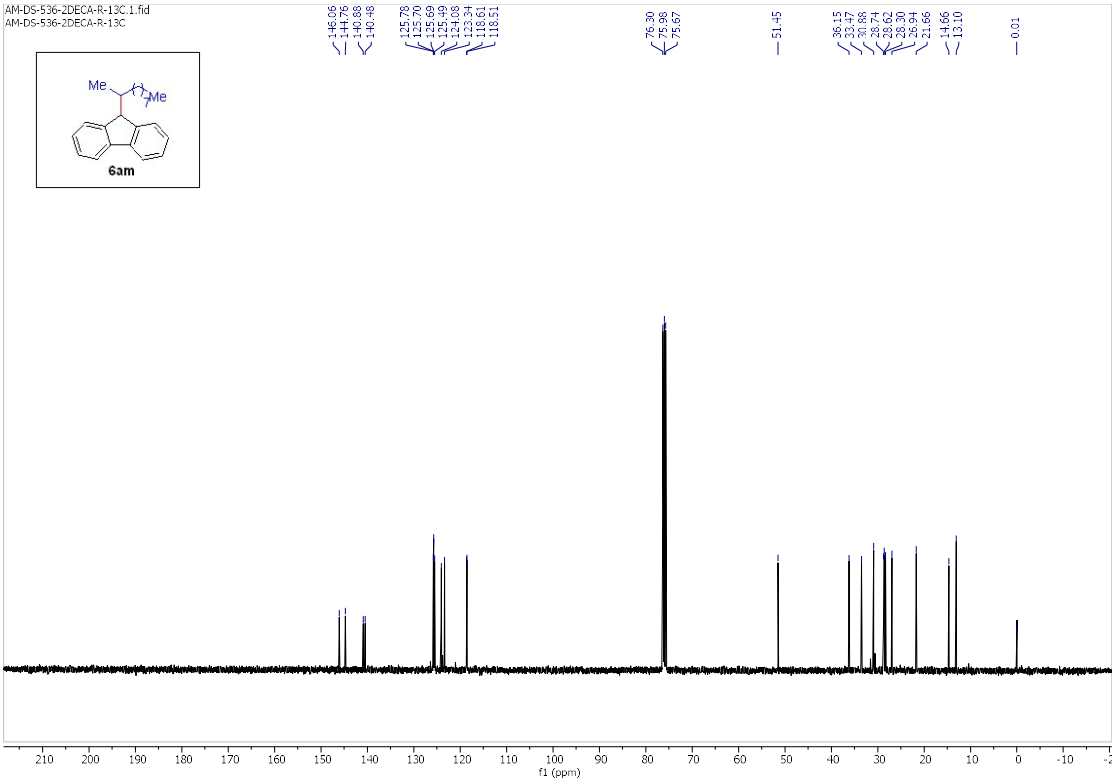


Figure S84. ^{13}C NMR Spectrum of 9-(decan-2-yl)-9H-fluorene **(6am)** in $CDCl_3$.

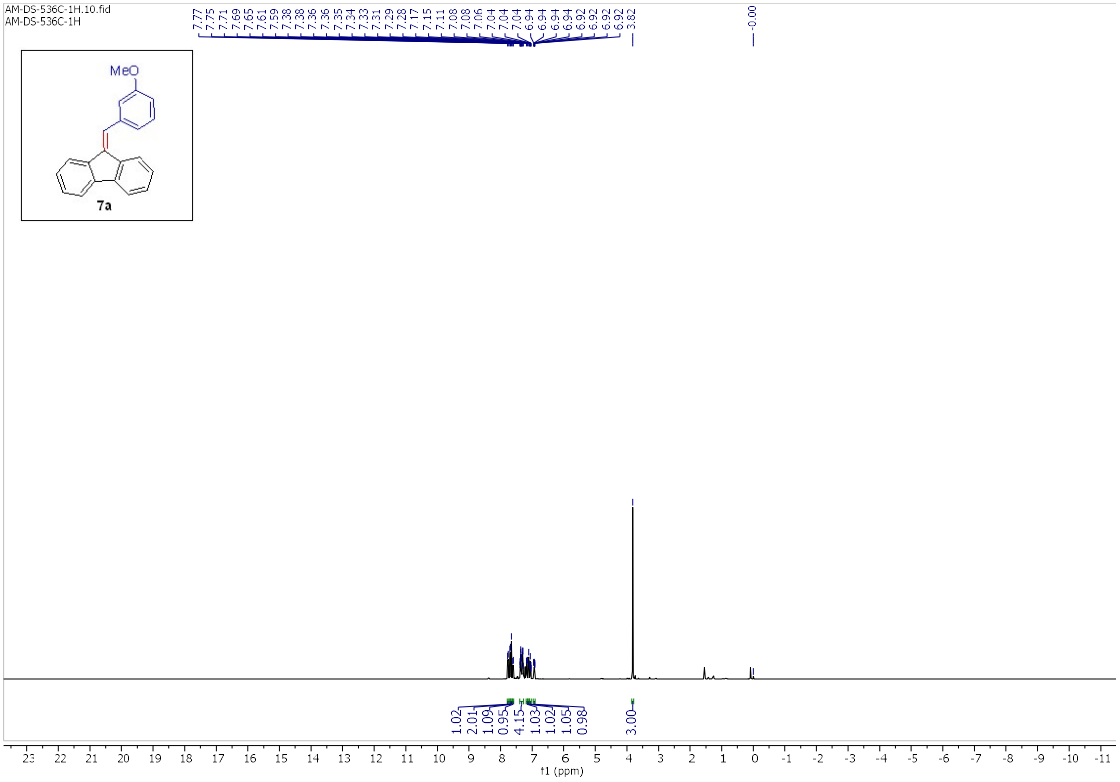


Figure S85. ^{1}H NMR Spectrum of 9-(3-methoxybenzylidene)-9H-fluorene **(7a)** in $CDCl_3$.

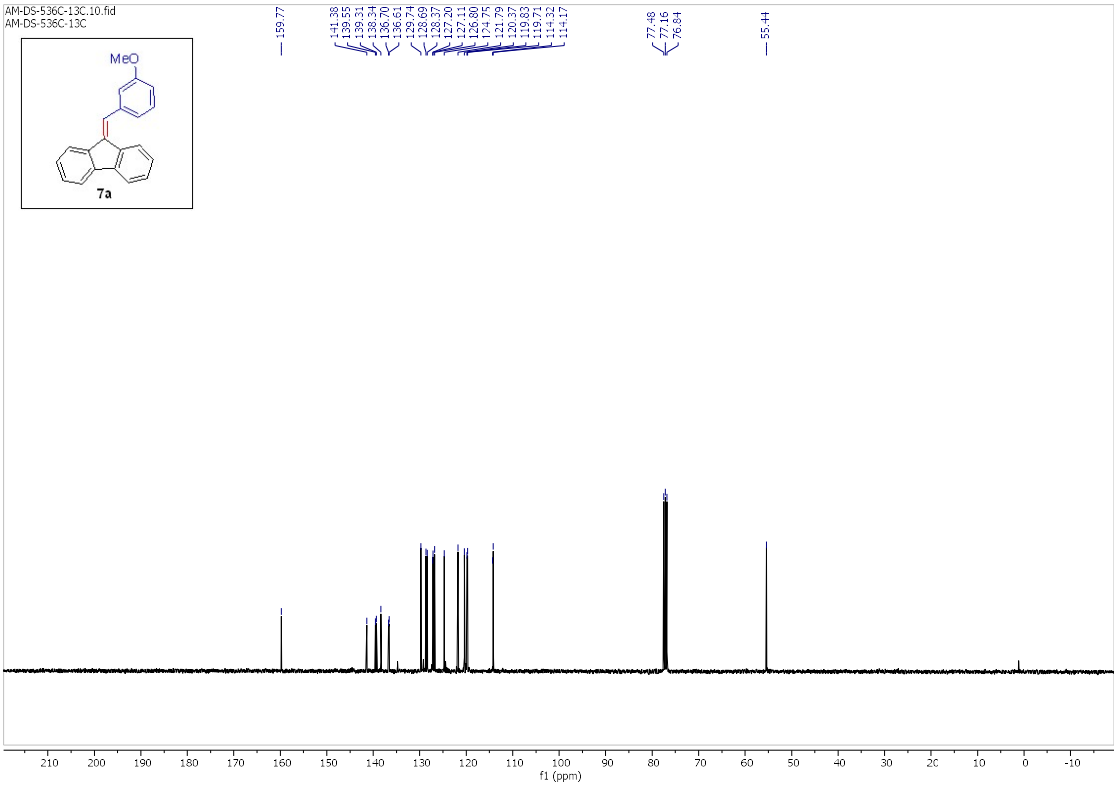


Figure S86. ^{13}C NMR Spectrum of 9-(3-methoxybenzylidene)-9H-fluorene **(7a)** in $CDCl_3$.

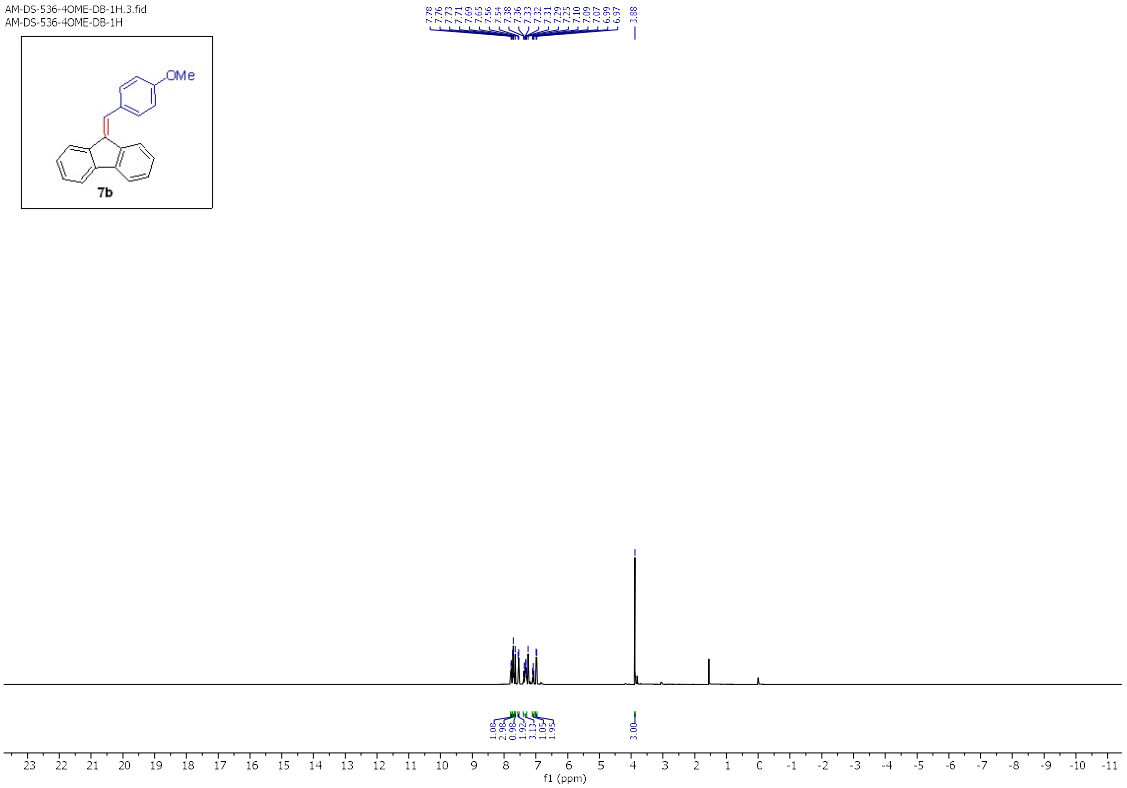


Figure S87. ^{1}H NMR Spectrum of 9-(4-methoxybenzylidene)-9H-fluorene **(7b)** in $CDCl_3$.

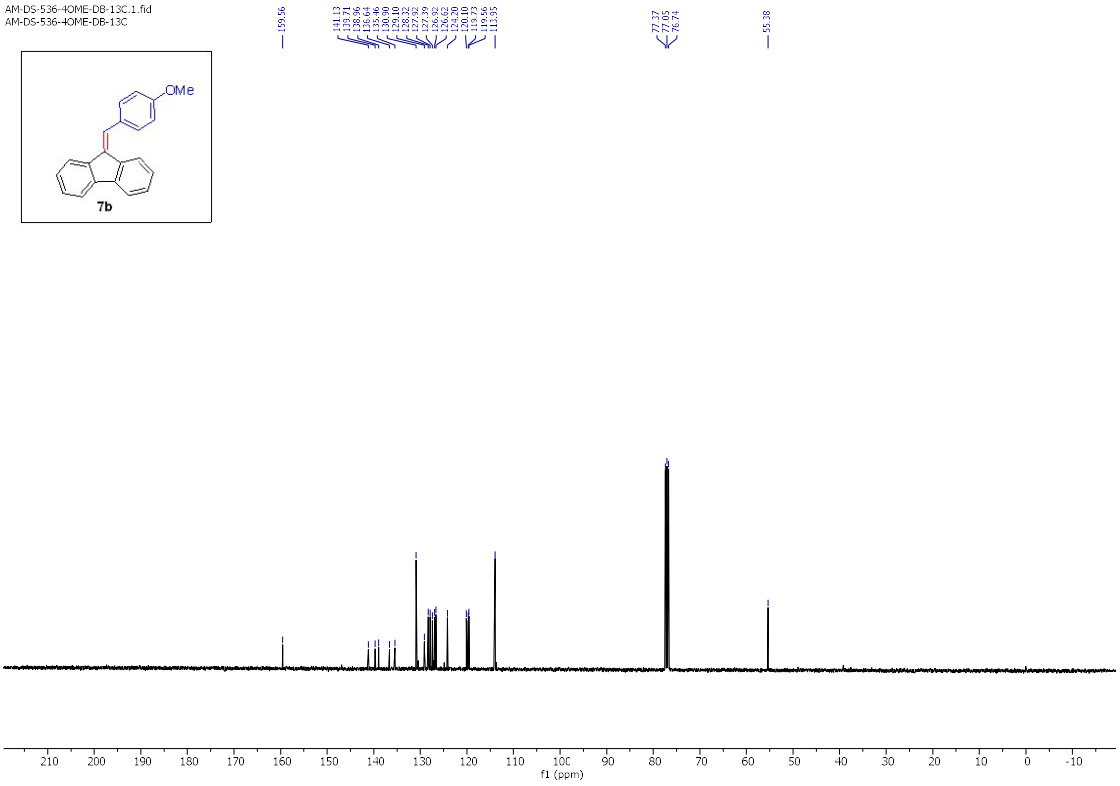


Figure S88. ^{13}C NMR Spectrum of 9-(4-methoxybenzylidene)-9H-fluorene **(7b)** in $CDCl_3$.

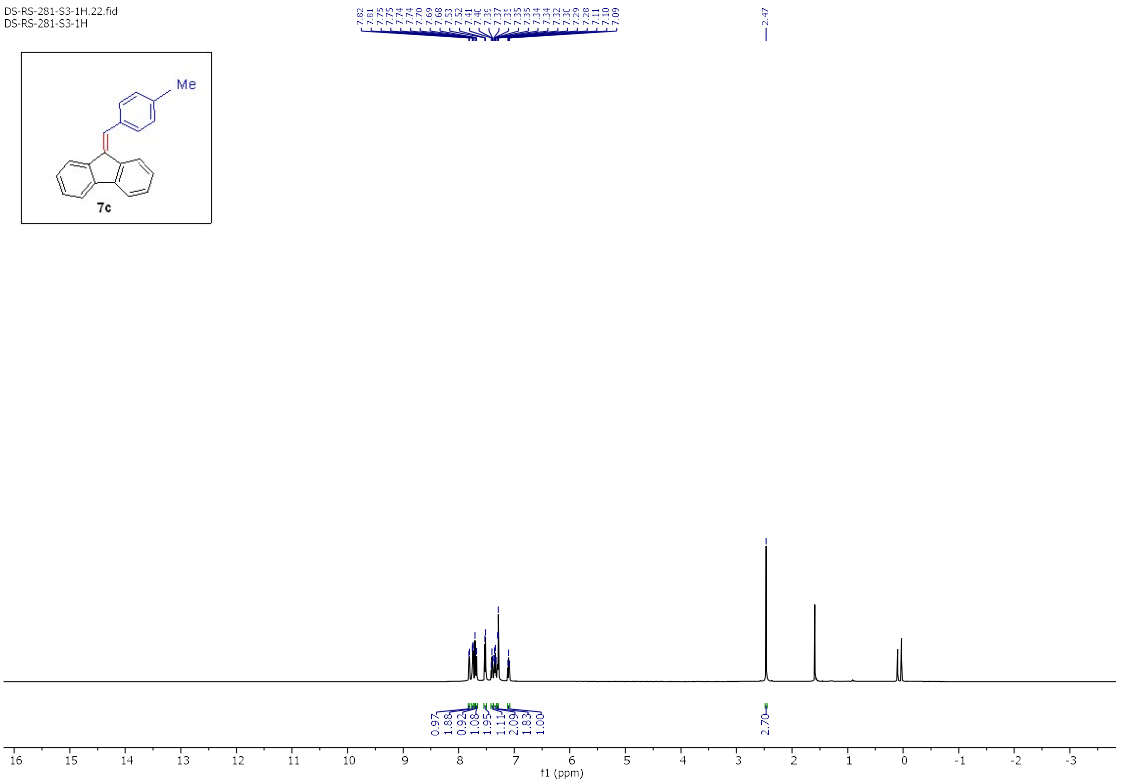


Figure S89. ^{1}H NMR Spectrum of 9-(4-methylbenzylidene)-9H-fluorene **(7c)** in $CDCl_3$.

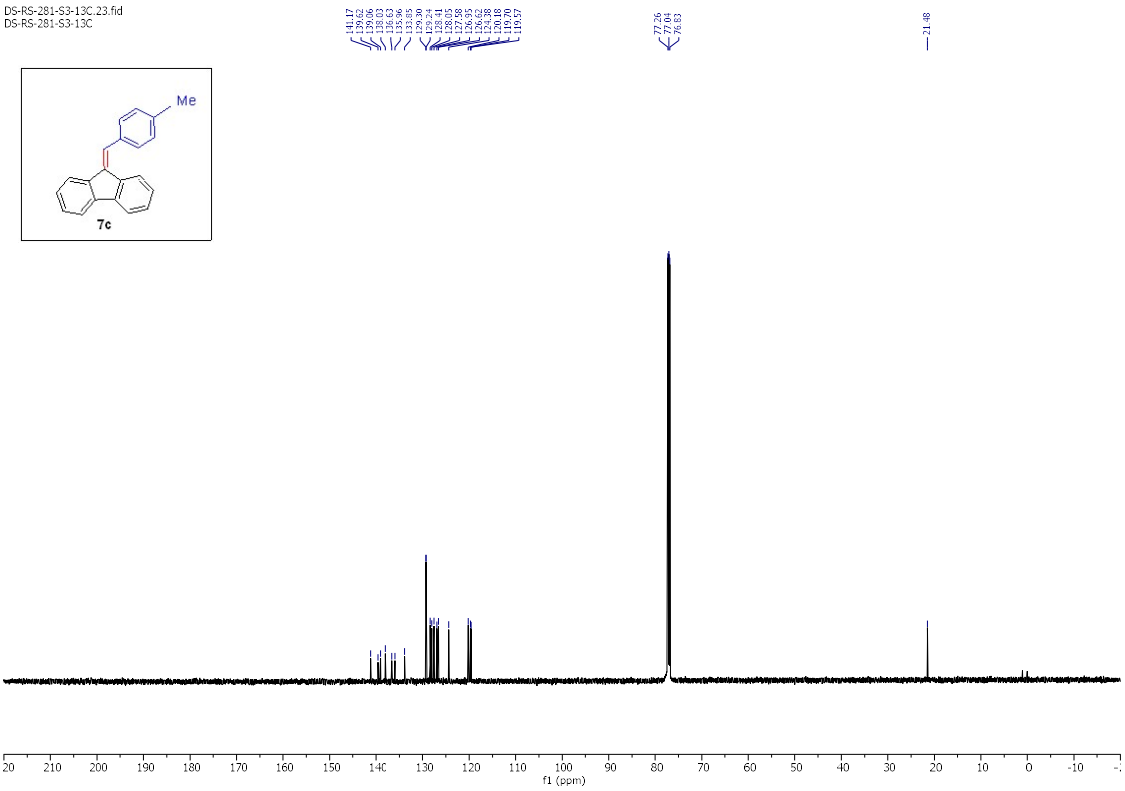


Figure 90. ^{13}C NMR Spectrum of 9-(4-methylbenzylidene)-9H-fluorene **(7c)** in $CDCl_3$.

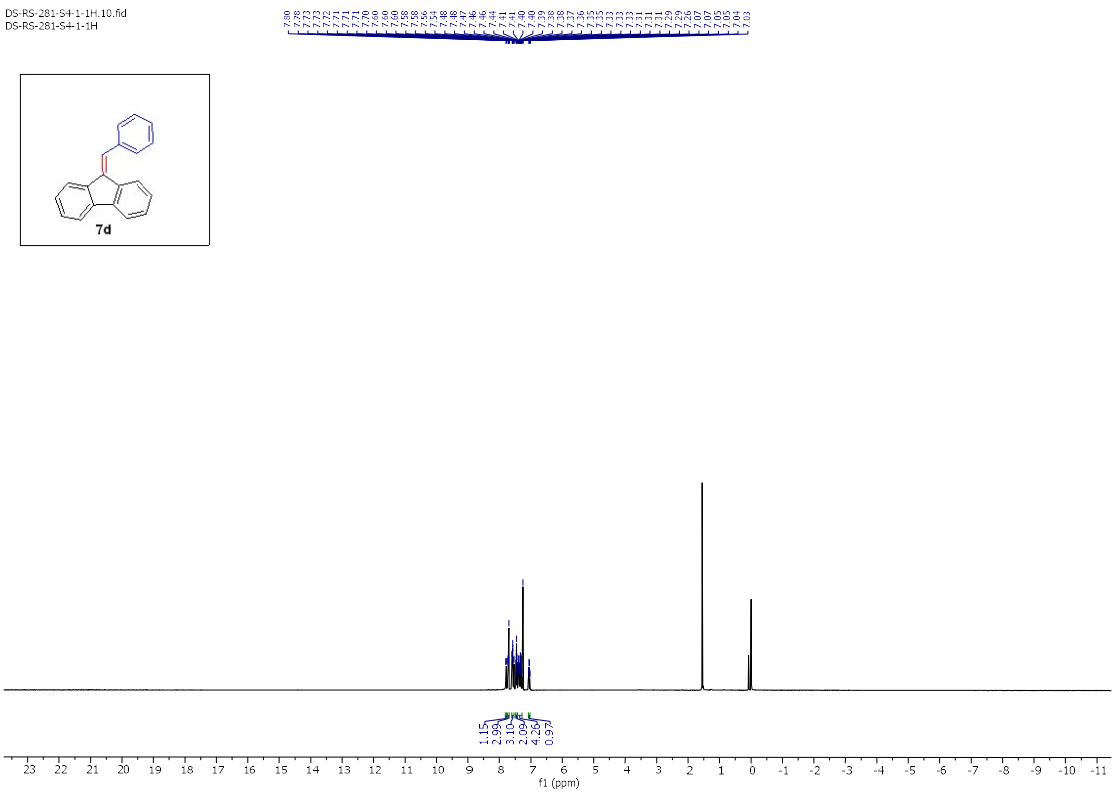


Figure S91. ^{1}H NMR Spectrum of 9-benzylidene-9H-fluorene **(7d)** in $CDCl_3$.

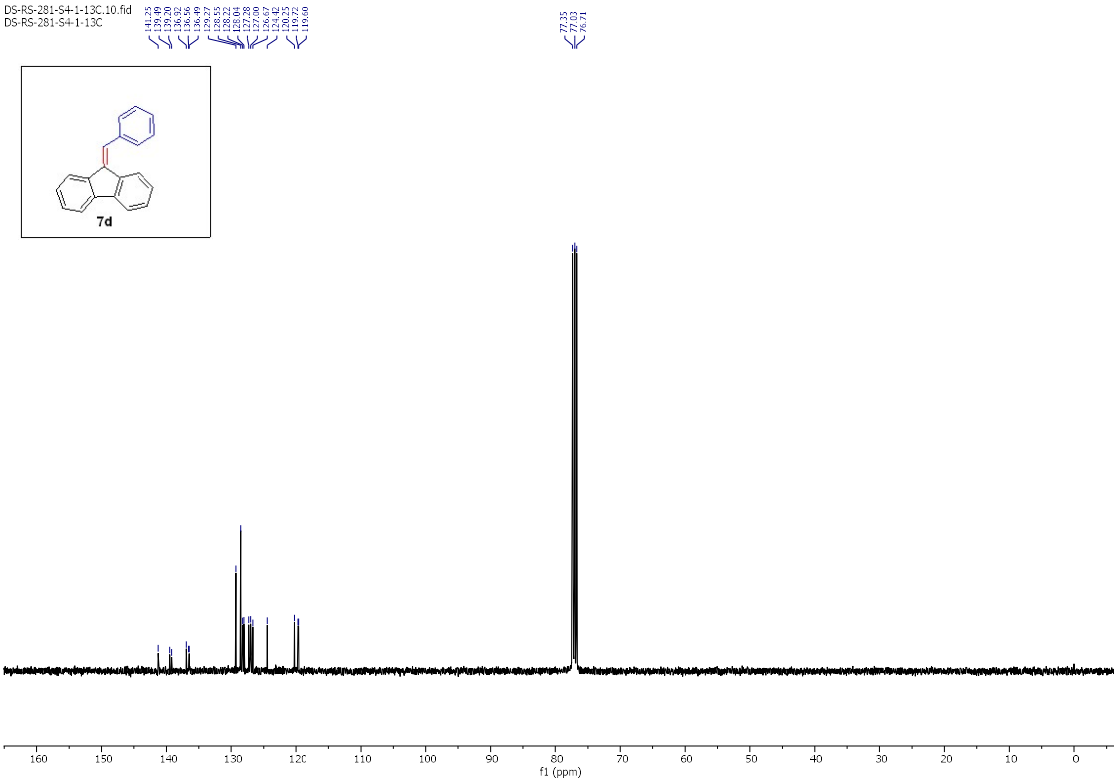


Figure S92. ^{13}C NMR Spectrum of 9-benzylidene-9H-fluorene **(7d)** in $CDCl_3$.

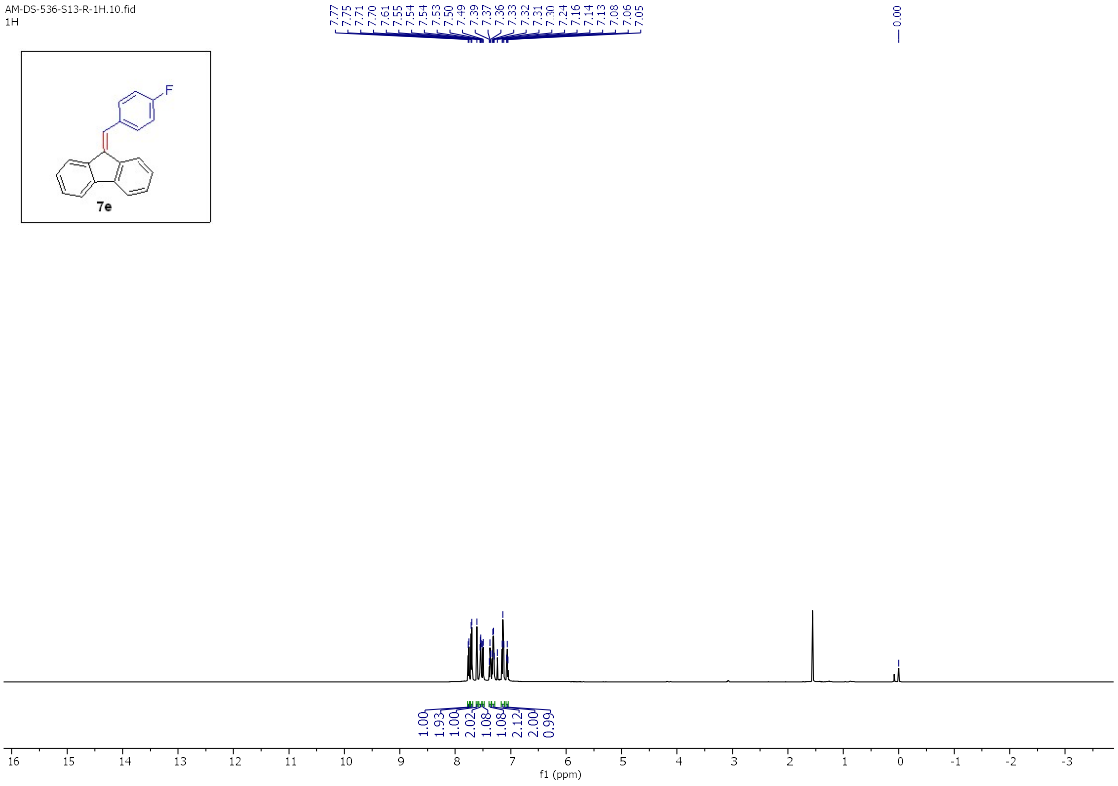


Figure S93. ^{1}H NMR Spectrum of 9-(4-fluorobenzylidene)-9H-fluorene **(7e)** in $CDCl_3$.

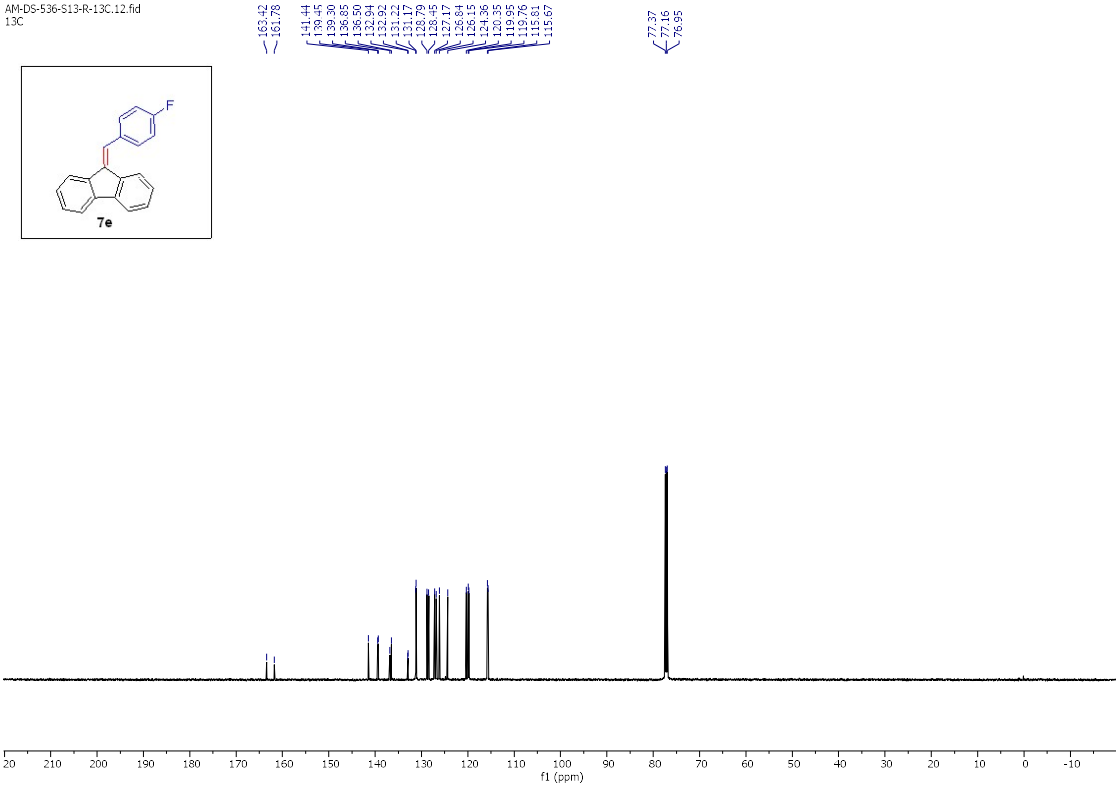


Figure S94. ^{13}C NMR Spectrum of 9-(4-fluorobenzylidene)-9H-fluorene **(7e)** in $CDCl_3$.

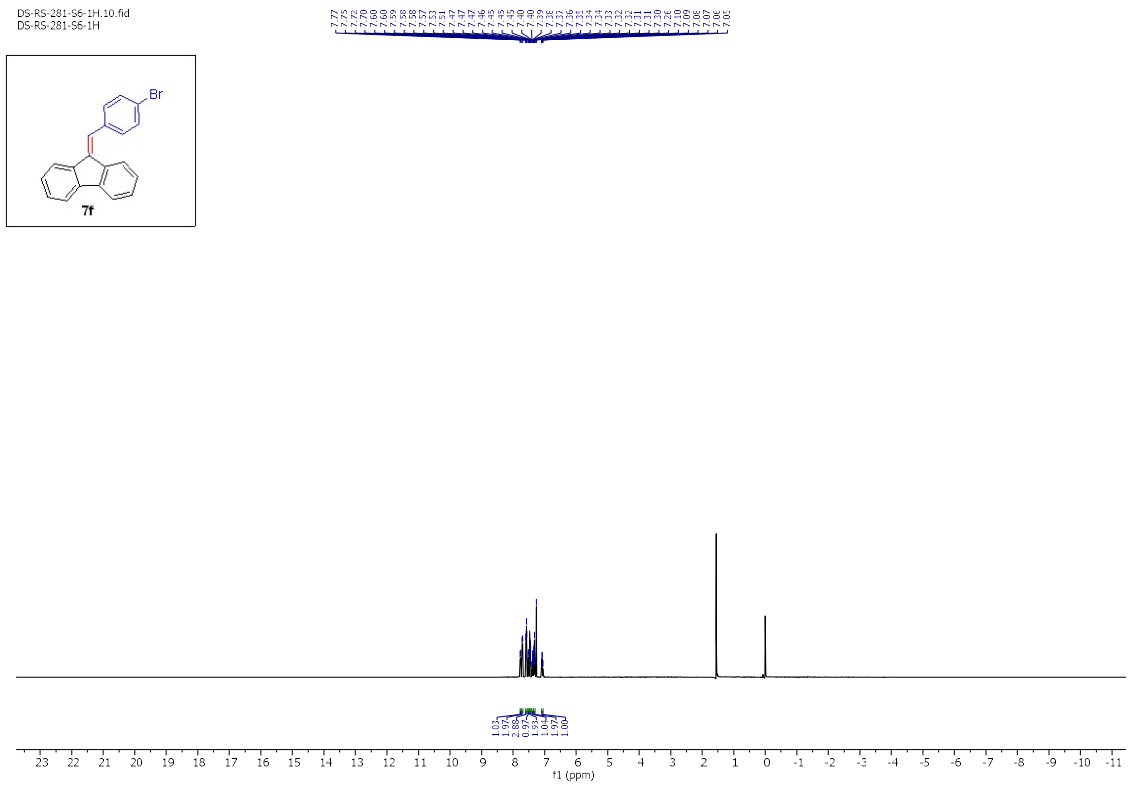


Figure S95. ^{13}C NMR Spectrum of 9-(4-bromobenzylidene)-9H-fluorene **(7f)** in $CDCl_3$.

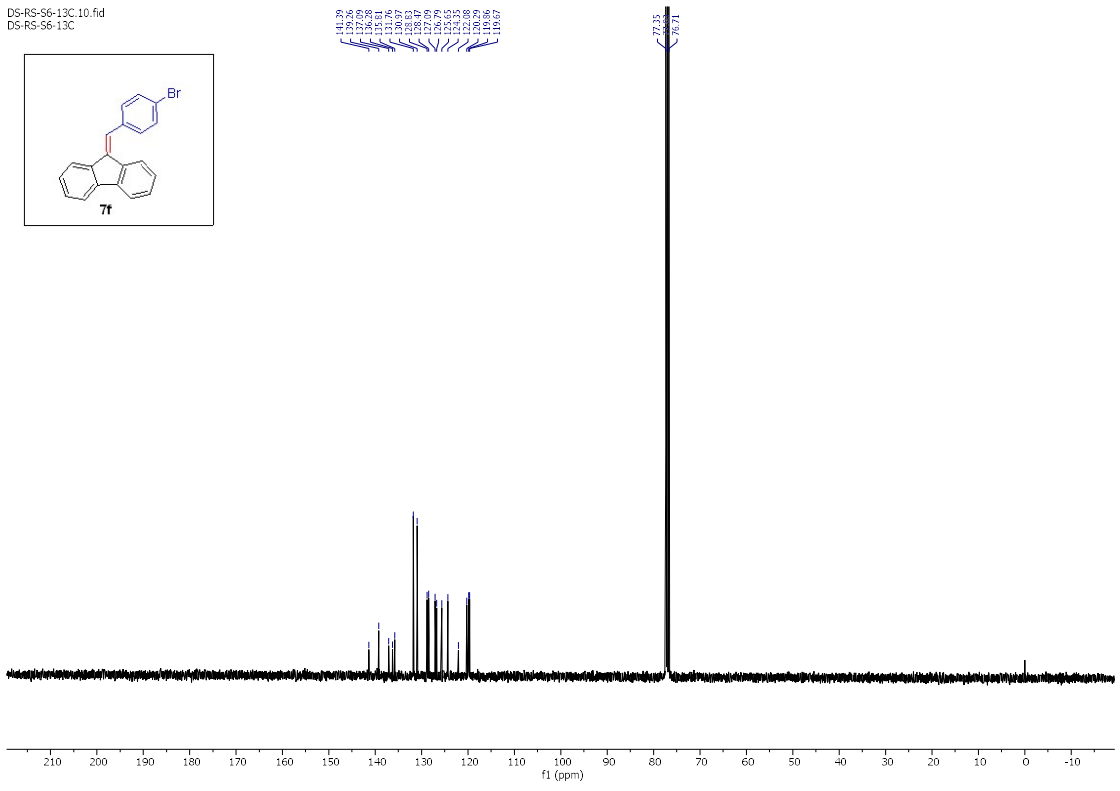


Figure S96. ^{13}C NMR Spectrum of 9-(4-bromobenzylidene)-9H-fluorene **(7f)** in $CDCl_3$.

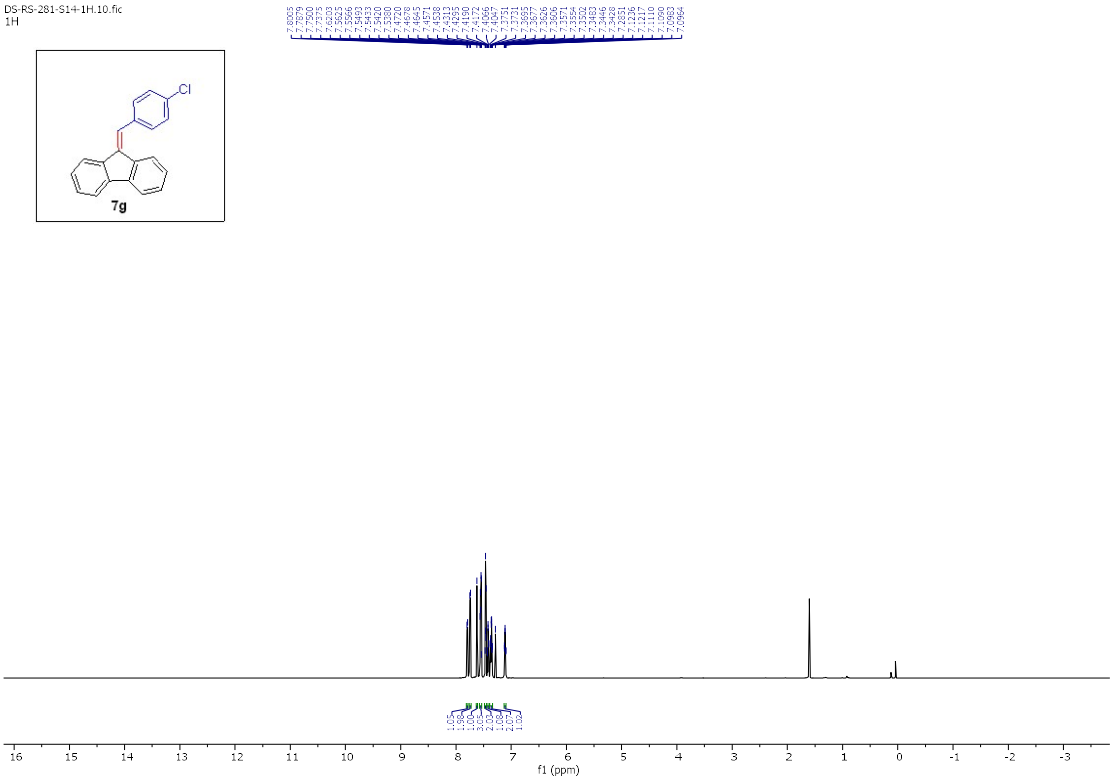


Figure S97. ^{1}H NMR Spectrum of 9-(4-chlorobenzylidene)-9H-fluorene **(7g)** in $CDCl_3$.

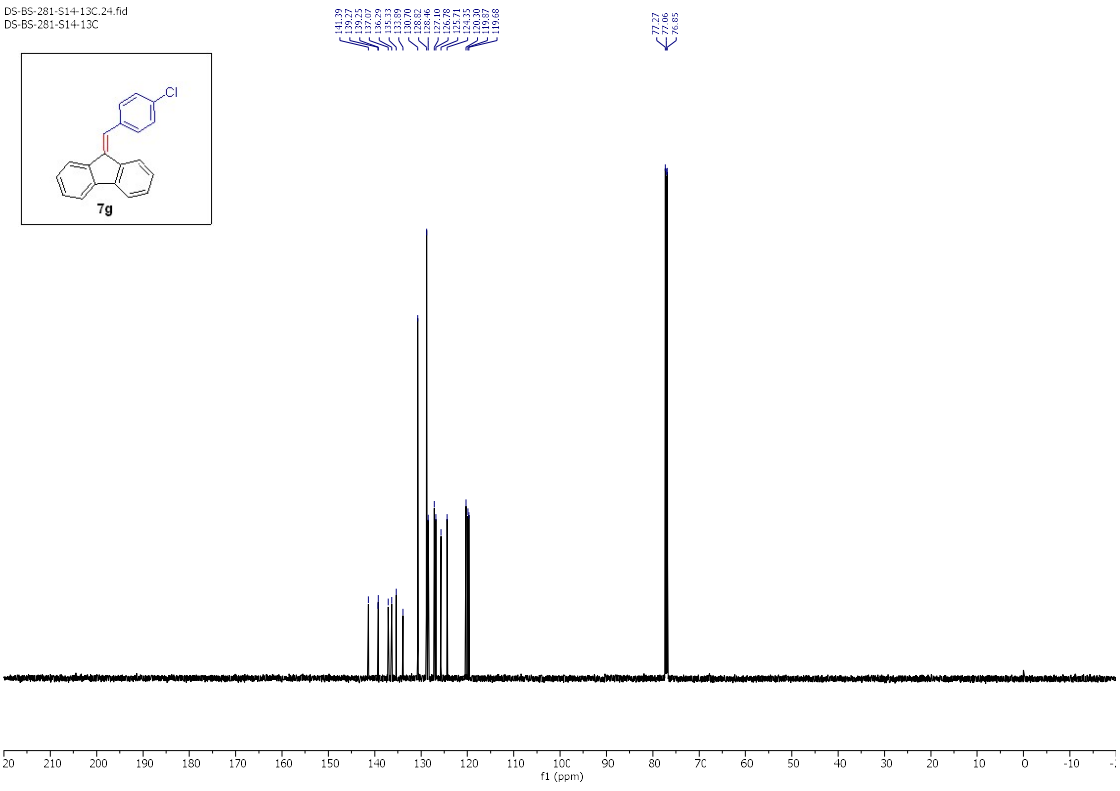


Figure S98. ^{13}C NMR Spectrum of 9-(4-chlorobenzylidene)-9H-fluorene **(7g)** in $CDCl_3$.

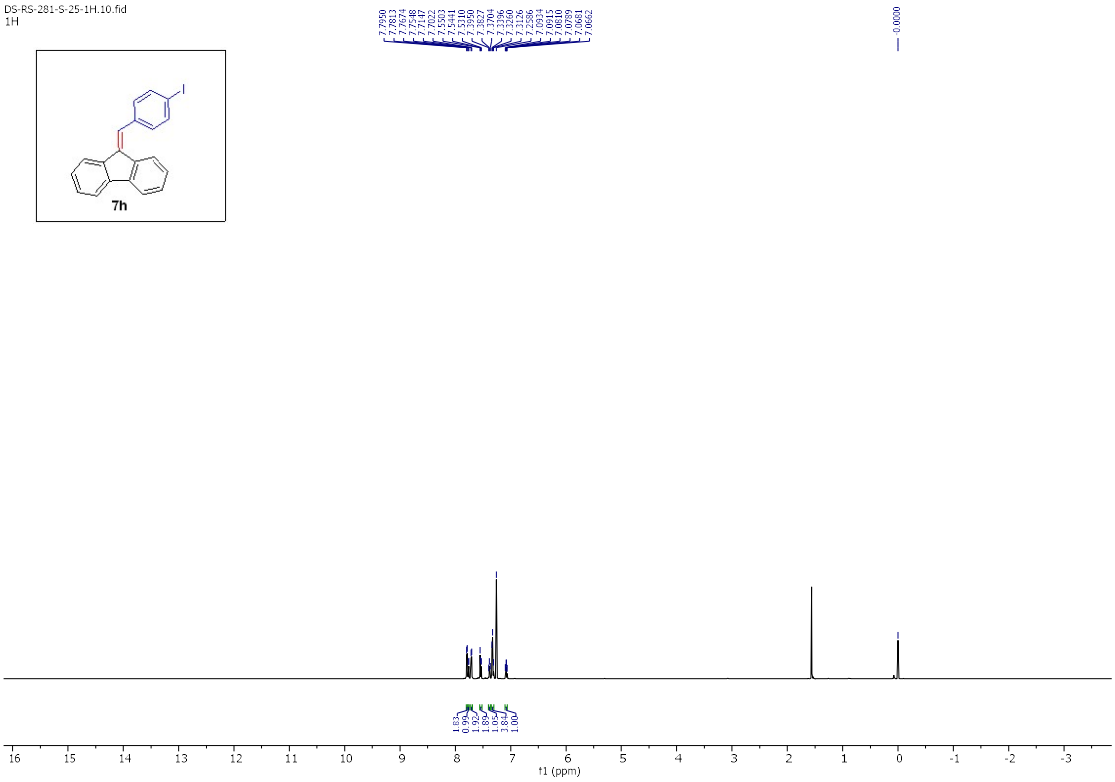


Figure S99. ^{13}C NMR Spectrum of 9-(4-iodobenzylidene)-9H-fluorene **(7h)** in $CDCl_3$.

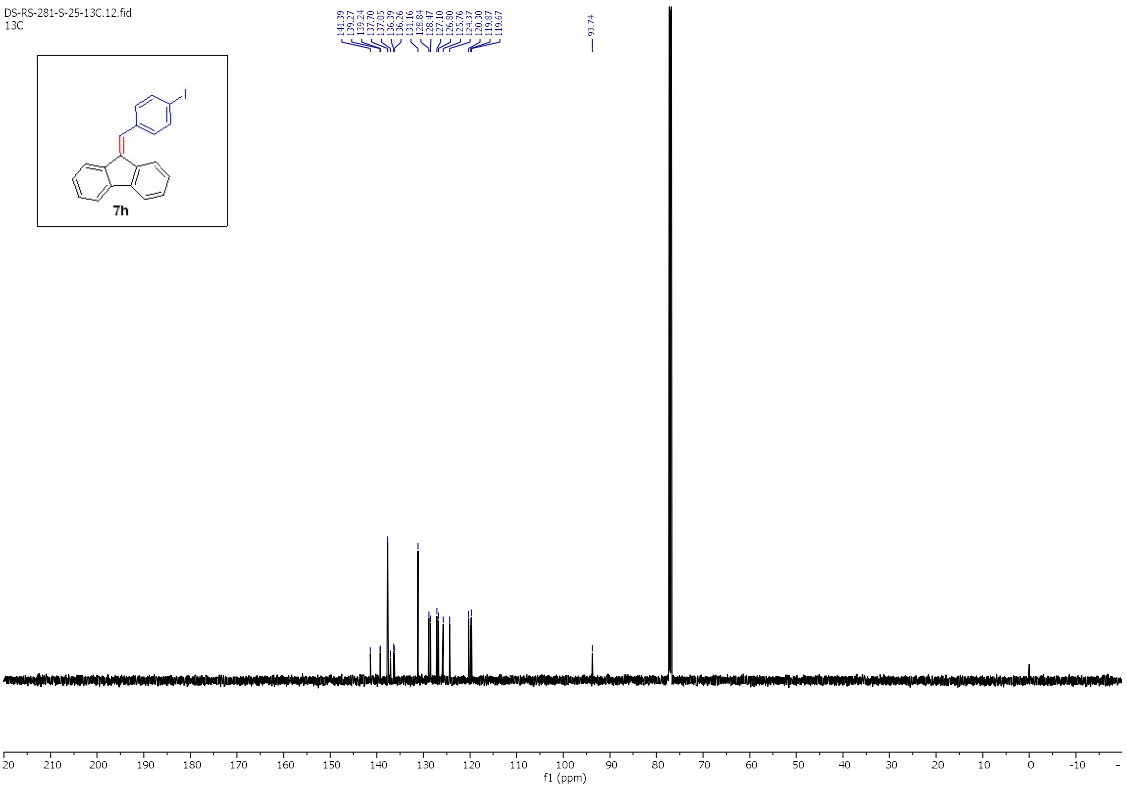


Figure S100. ^{13}C NMR Spectrum of 9-(4-iodobenzylidene)-9H-fluorene **(7h)** in $CDCl_3$.

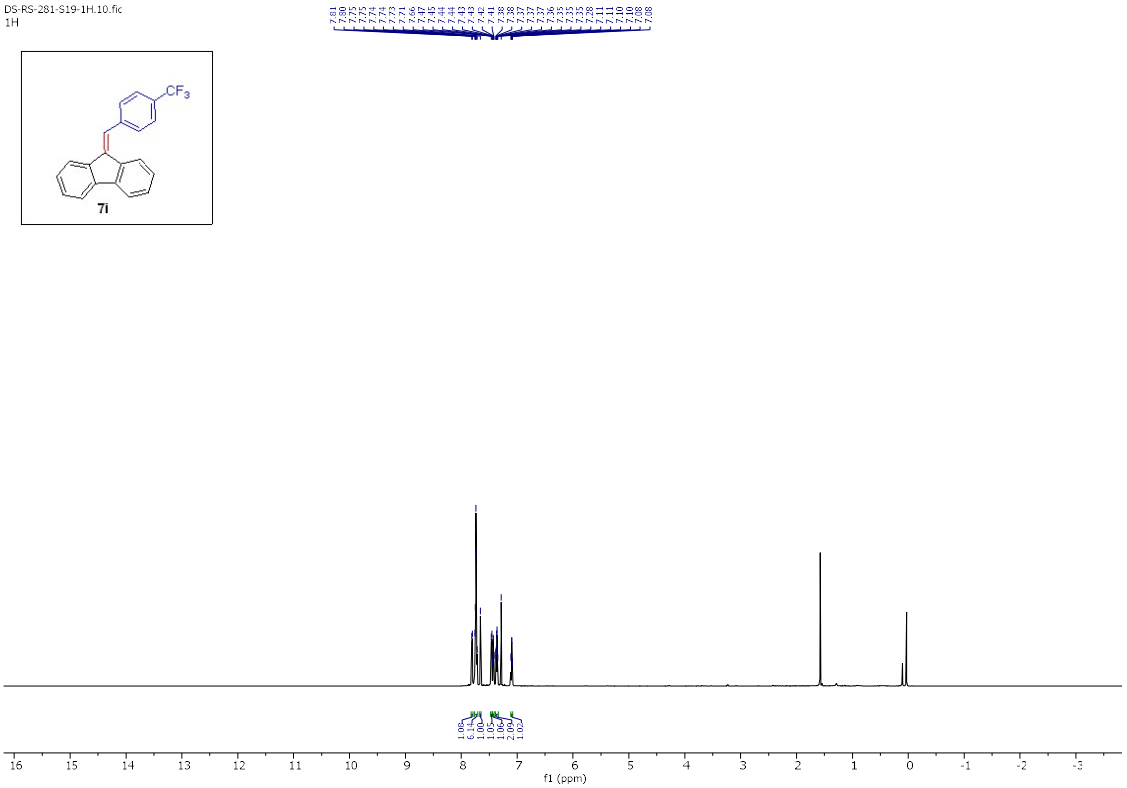


Figure S101. ^{1}H NMR Spectrum of 9-(4-(trifluoromethyl)benzylidene)-9H-fluorene **(7i)** in $CDCl_3$.

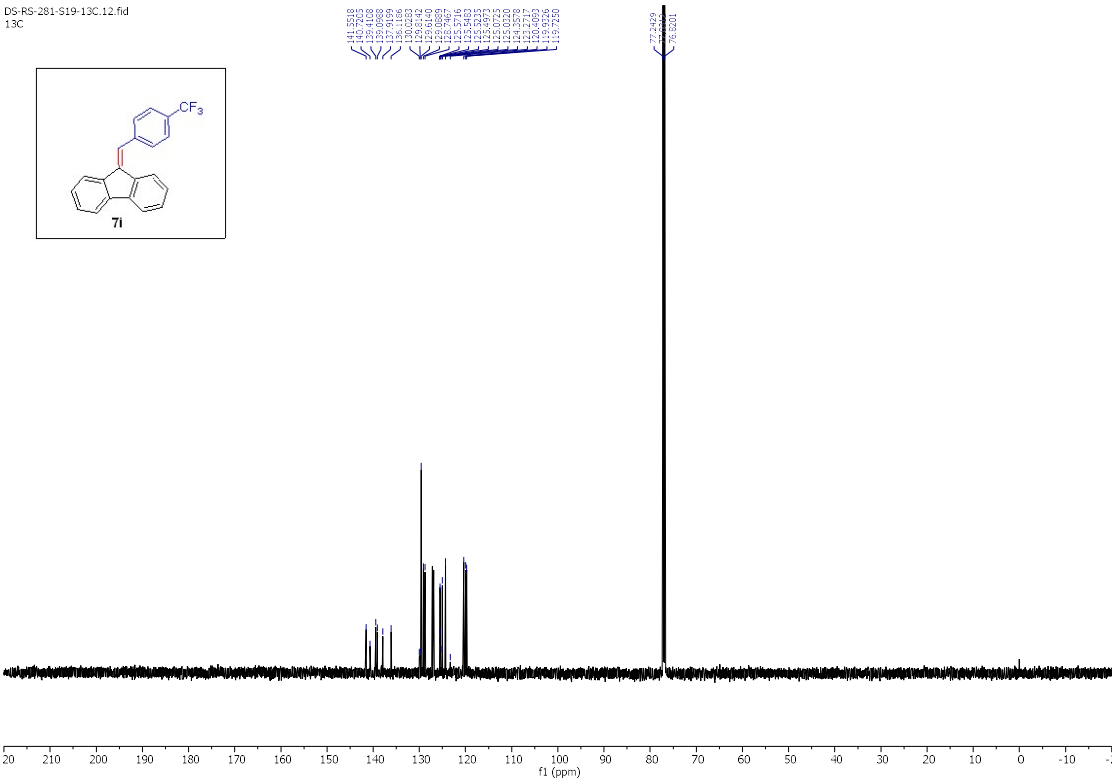


Figure S102. ^{13}C NMR Spectrum of 9-(4-(trifluoromethyl)benzylidene)-9H-fluorene **(7i)** in $CDCl_3$.

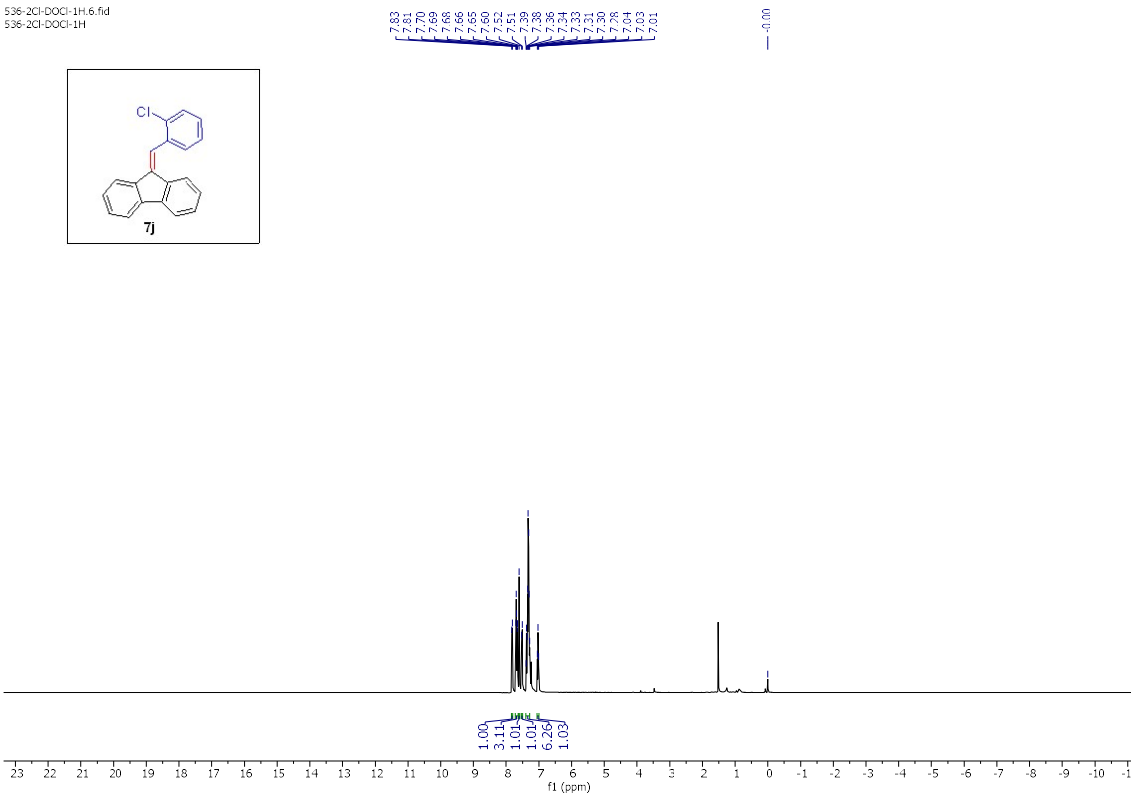


Figure S103. ^{1}H NMR Spectrum of 9-(2-chlorobenzylidene)-9H-fluorene **(7j)** in $CDCl_3$.

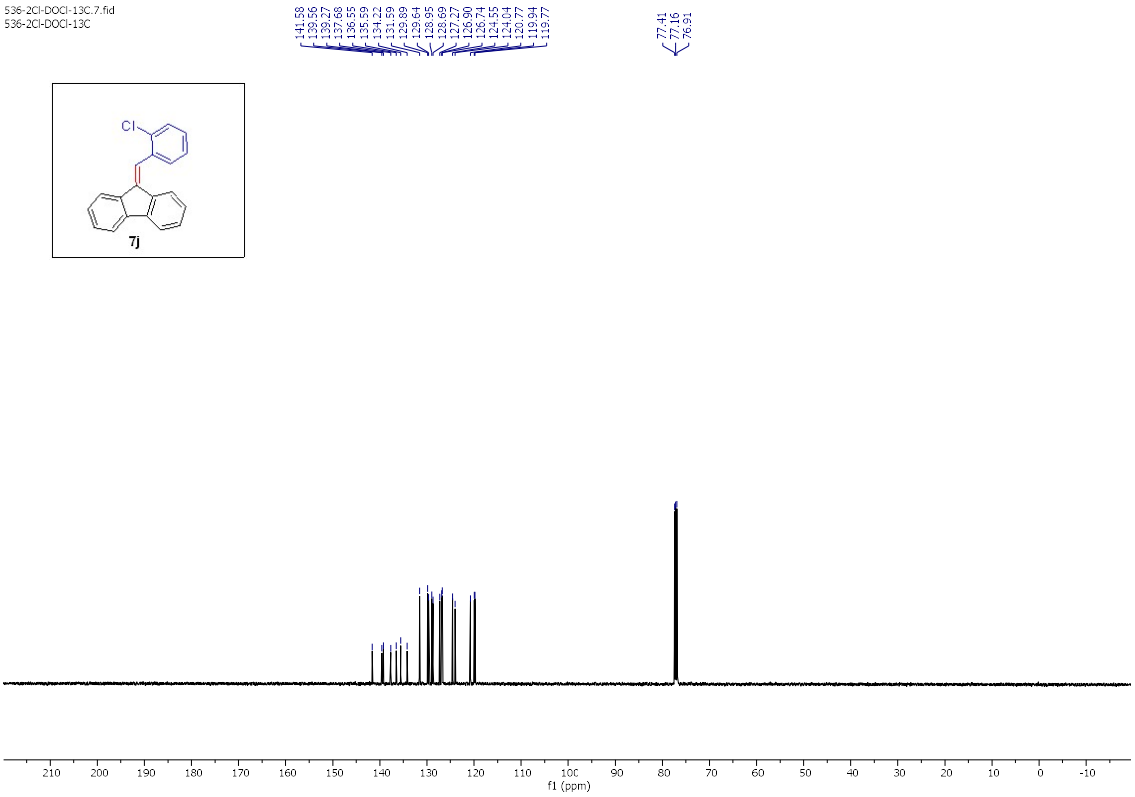


Figure S104. ^{13}C NMR Spectrum of 9-(2-chlorobenzylidene)-9H-fluorene **(7j)** in $CDCl_3$.

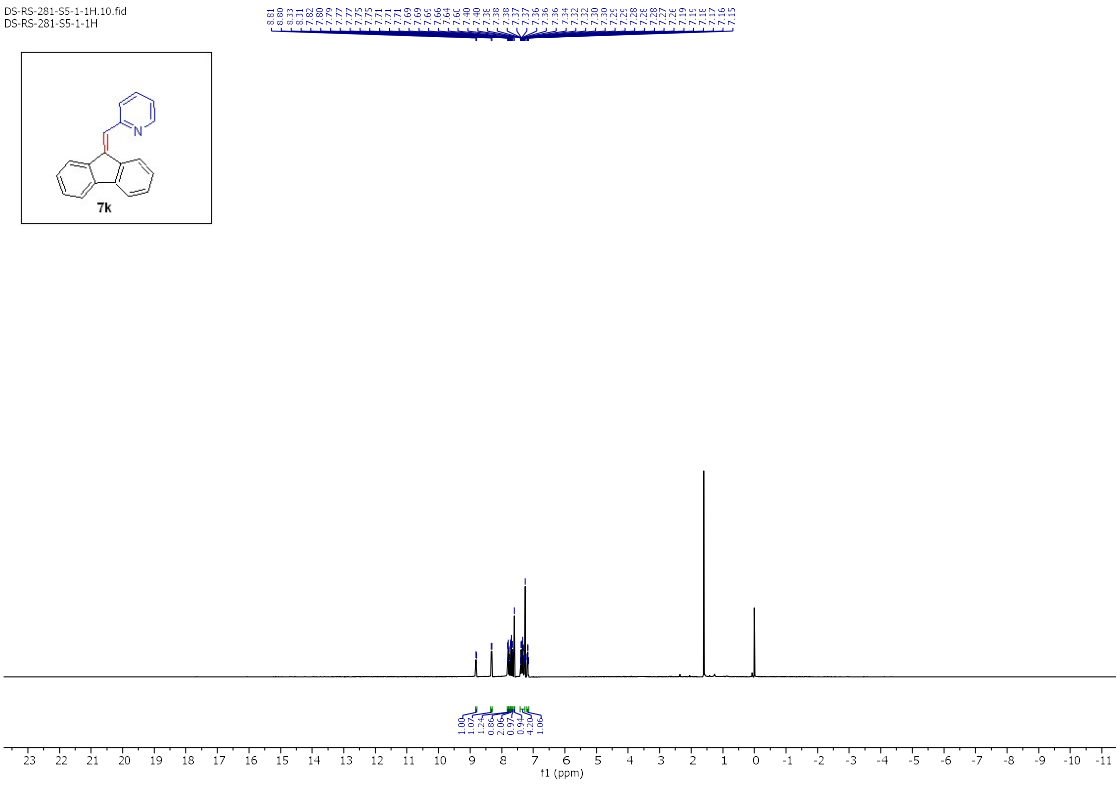


Figure S105. ^{1}H NMR Spectrum of 2-((9H-fluoren-9-ylidene)methyl)pyridine **(7k)** in $CDCl_3$.

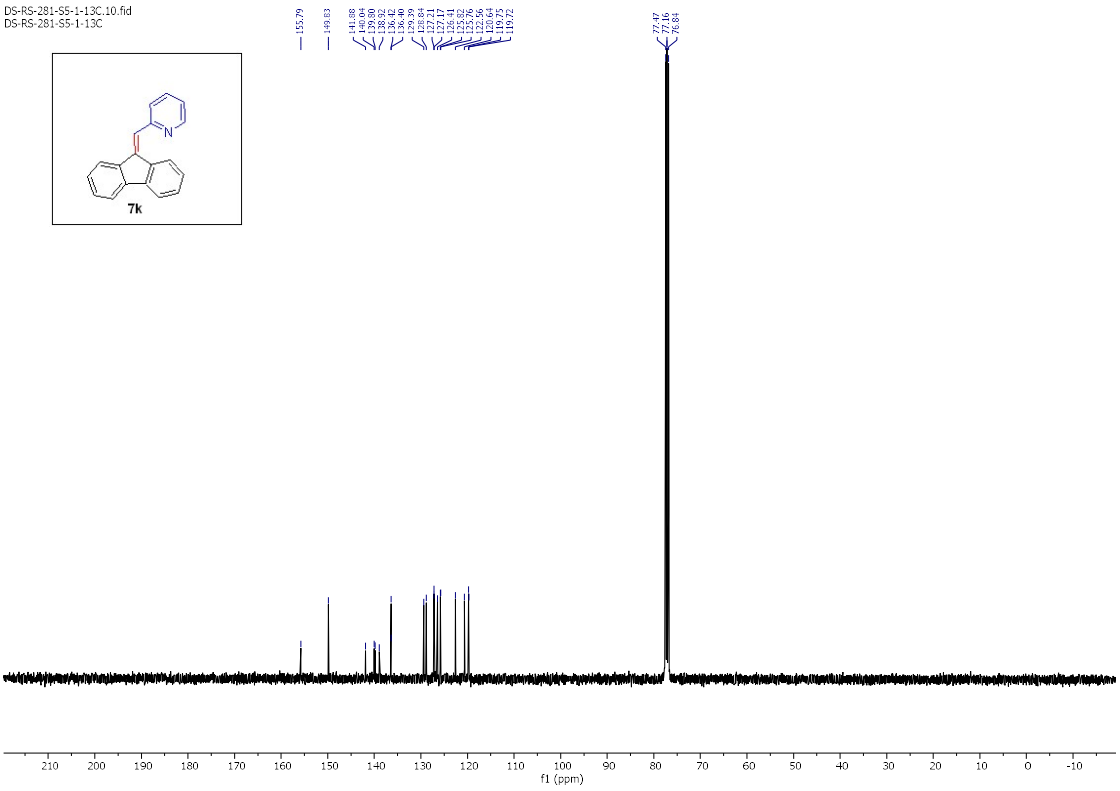


Figure S106. ^{13}C NMR Spectrum of 2-((9H-fluoren-9-ylidene)methyl)pyridine **(7k)** in $CDCl_3$.

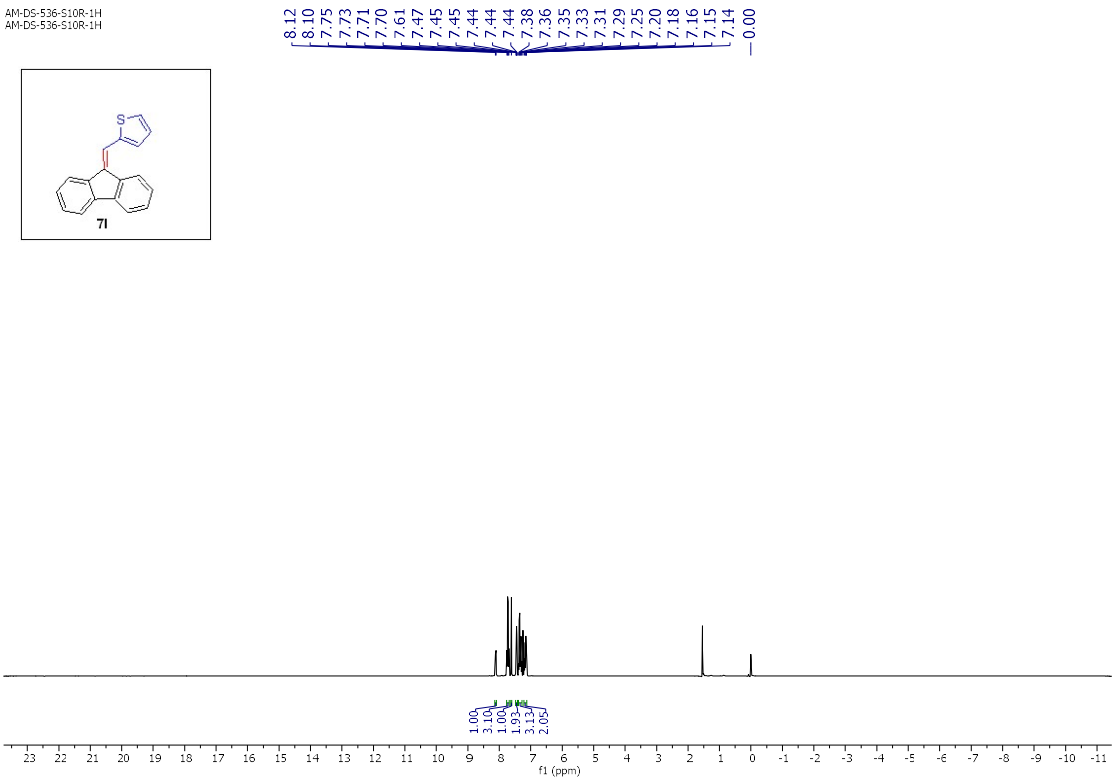


Figure S107. ^{1}H NMR Spectrum of 2-((9H-fluoren-9-ylidene)methyl)thiophene **(7l)** in $CDCl_3$.

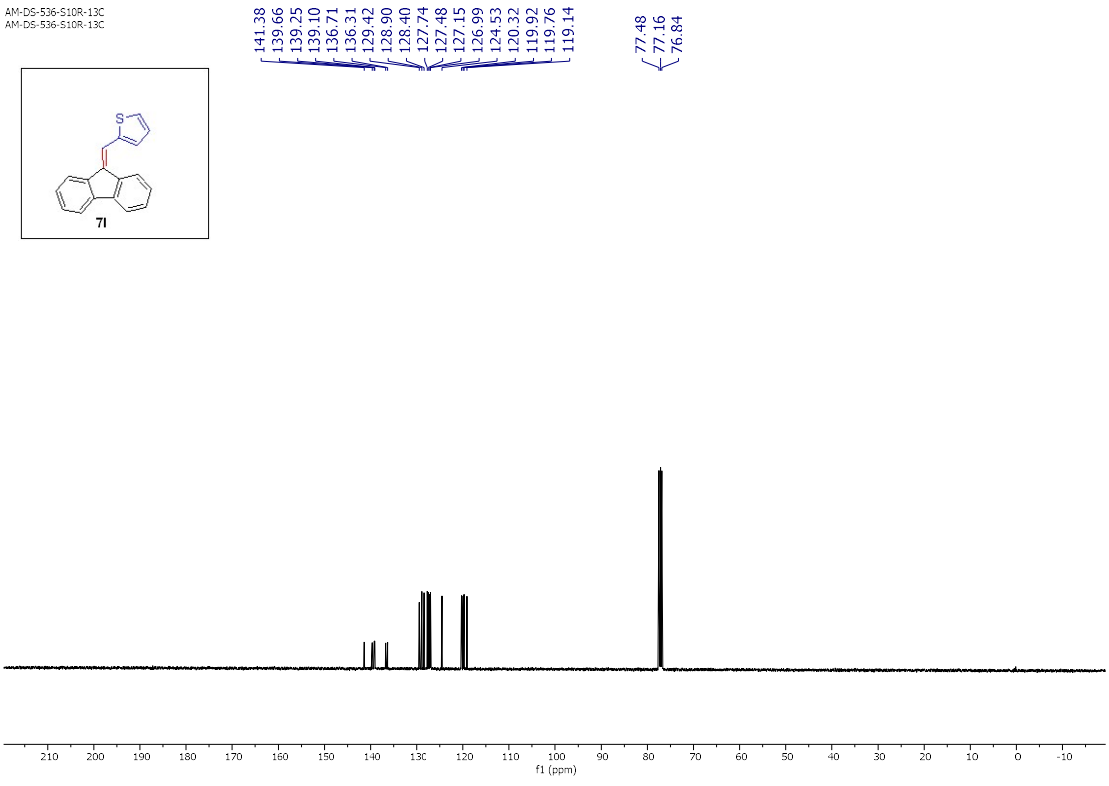


Figure S108. ^{13}C NMR Spectrum of 2-((9H-fluoren-9-ylidene)methyl)thiophene **(7l)** in $CDCl_3$.

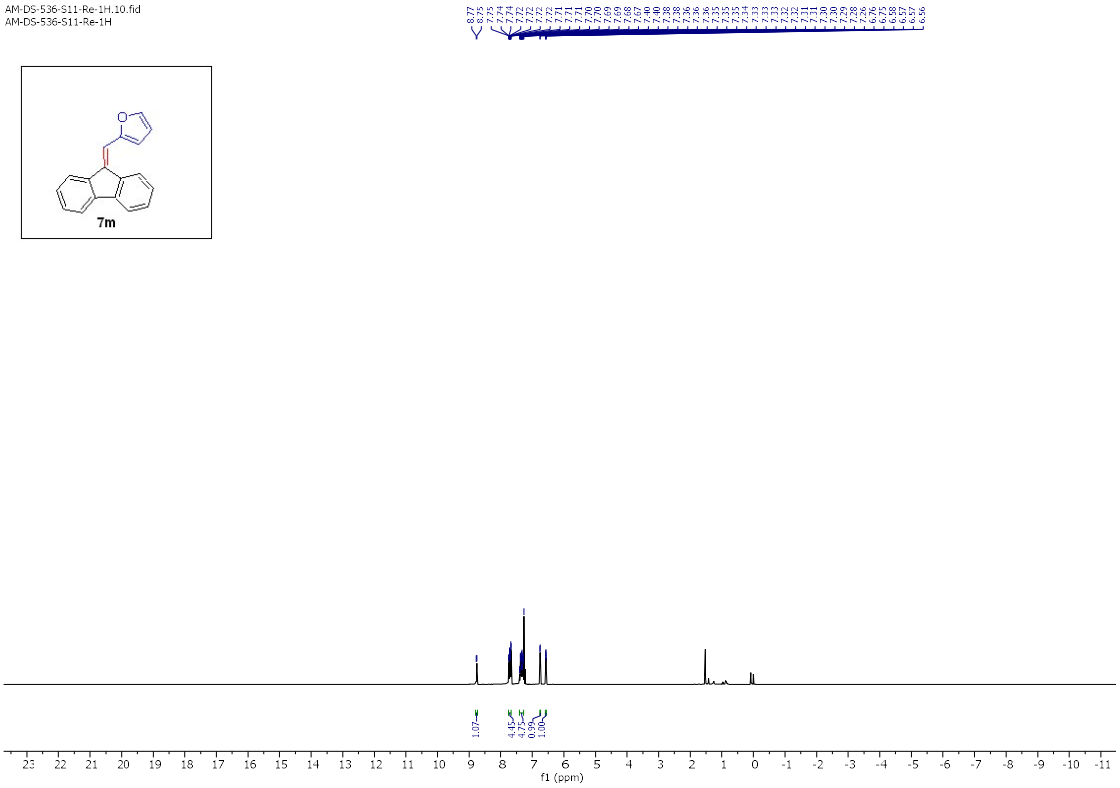


Figure S109. ^{13}C NMR Spectrum of 2-((9H-fluoren-9-ylidene)methyl)furan **(7m)** in $CDCl_3$.

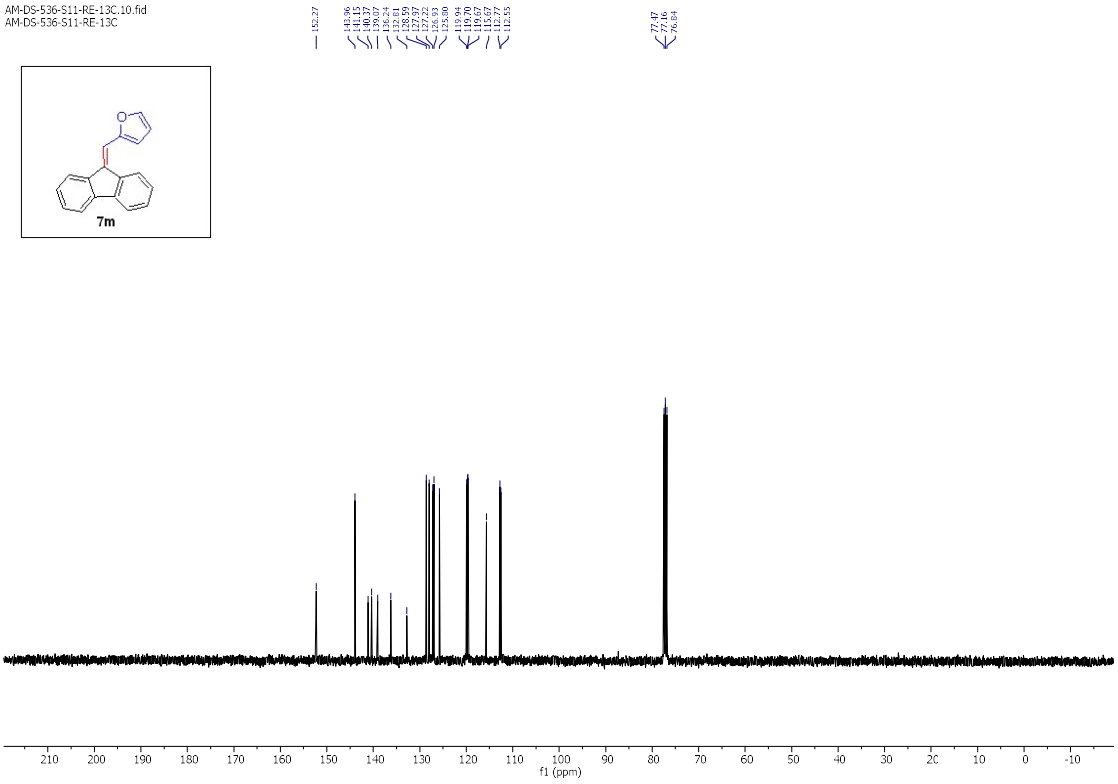


Figure S110. ^{13}C NMR Spectrum of 2-((9H-fluoren-9-ylidene)methyl)furan **(7m)** in $CDCl_3$.

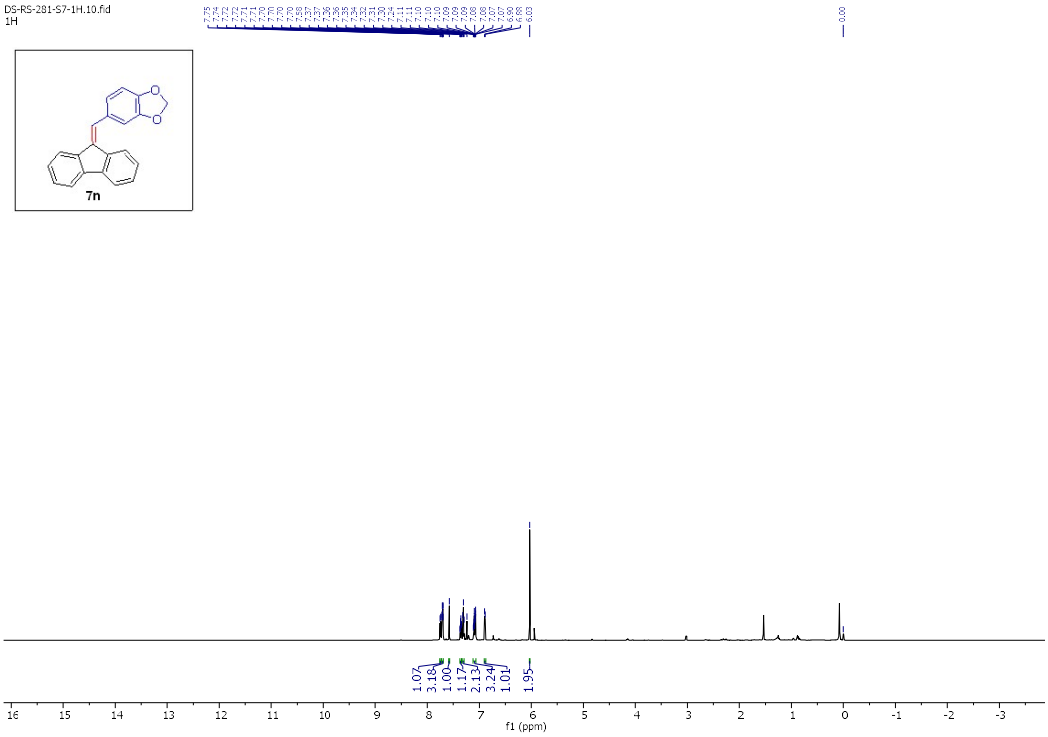


Figure S111. [1]H NMR Spectrum of 5-((9H-fluoren-9-ylidene)methyl)benzo[d][1,3]dioxole **(7n)** in $CDCl_3$.

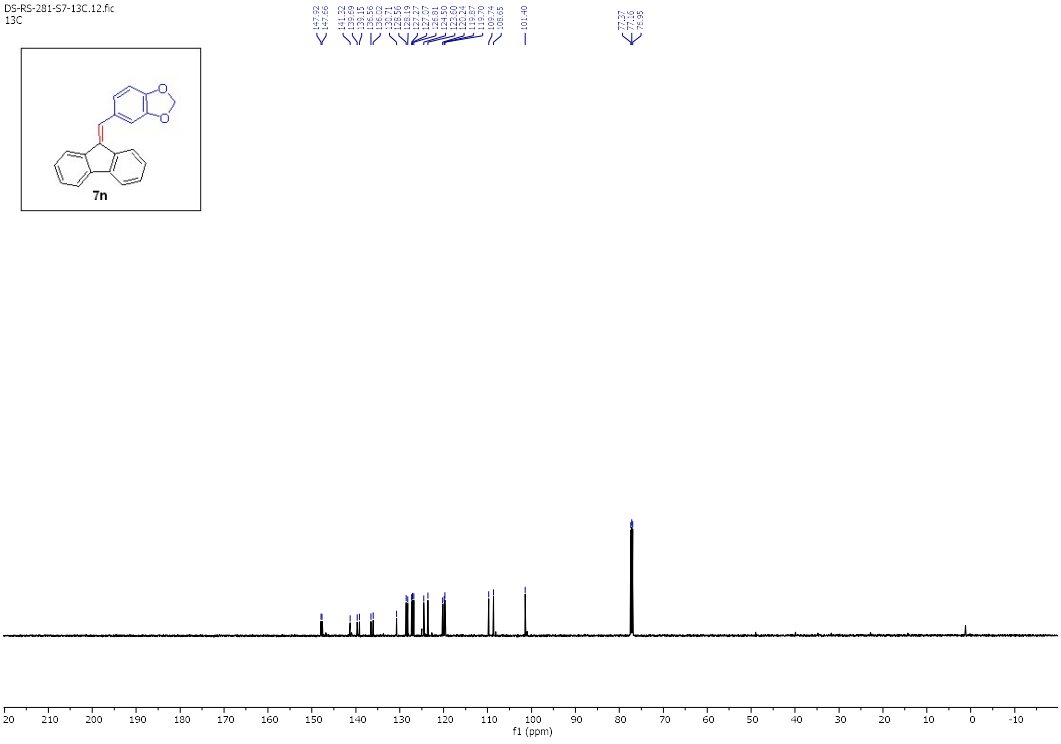


Figure S112. [13]C NMR Spectrum of 5-((9H-fluoren-9-ylidene)methyl)benzo[d][1,3]dioxole **(7n)** in $CDCl_3$.

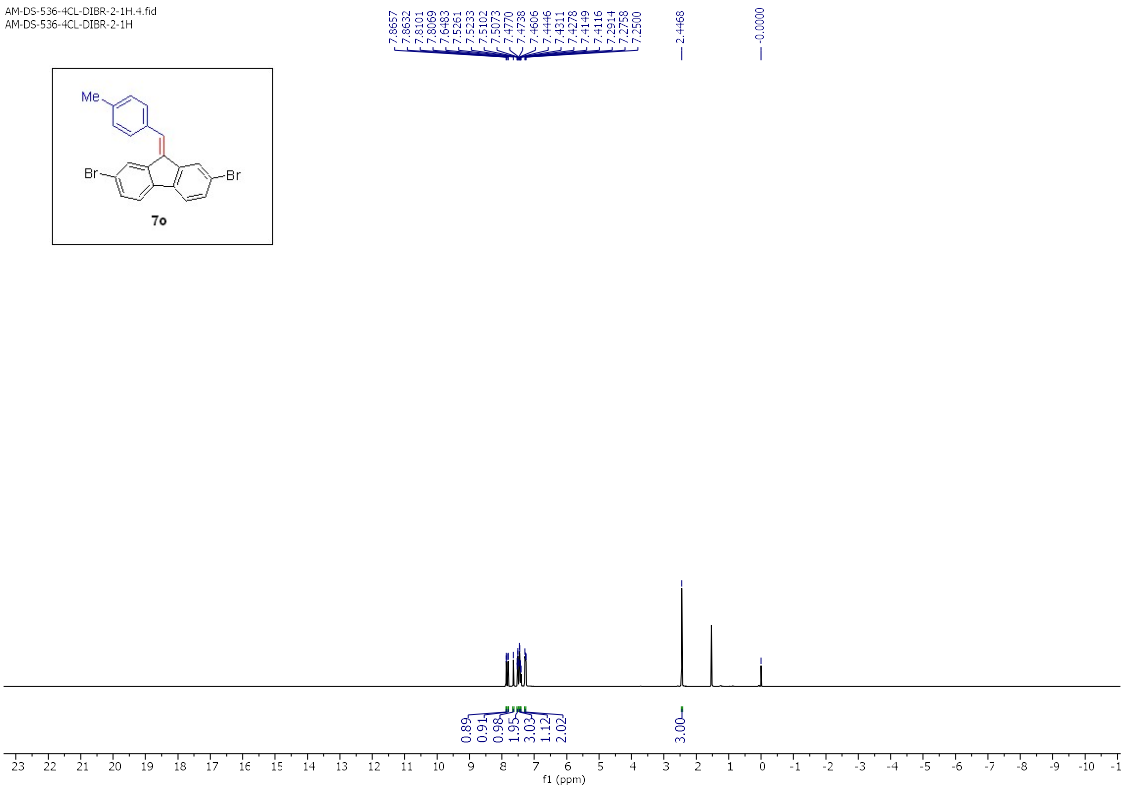


Figure S113. ^{1}H NMR Spectrum of 2,7-dibromo-9-(4-methylbenzylidene)-9H-fluorene **(7o)** in $CDCl_3$.

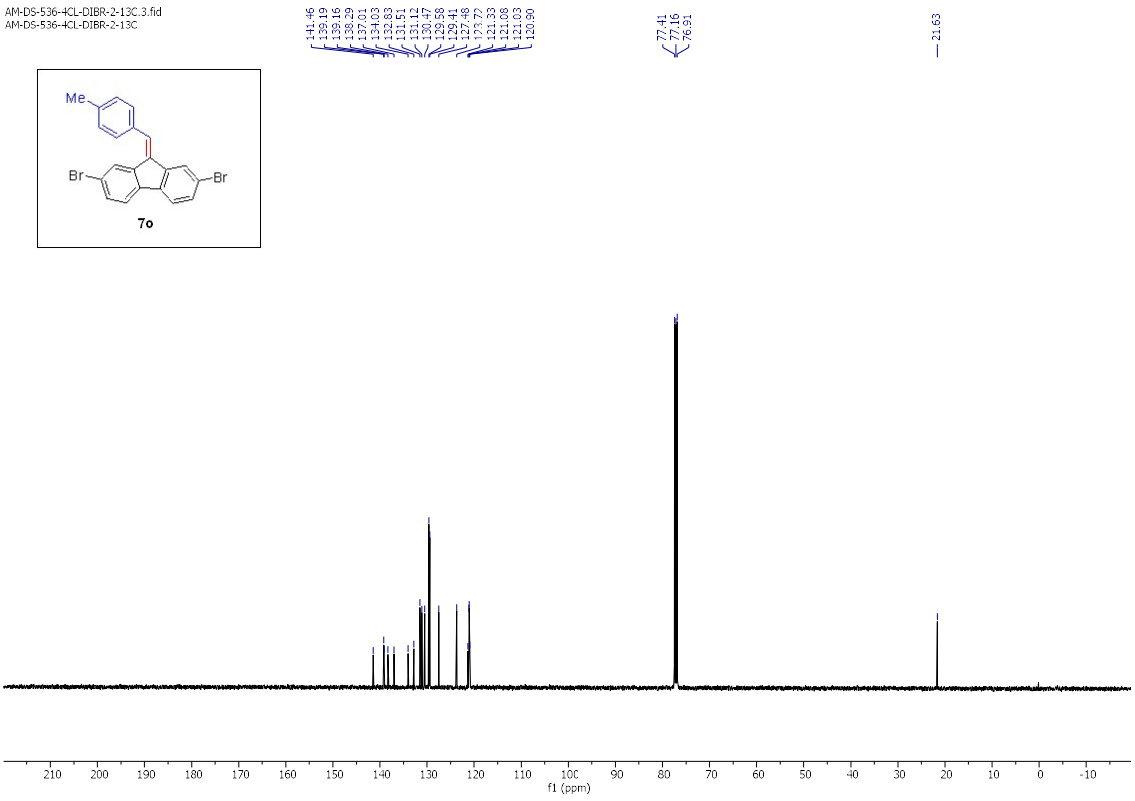


Figure S114. ^{13}C NMR Spectrum of 2,7-dibromo-9-(4-methylbenzylidene)-9H-fluorene **(7o)** in $CDCl_3$.

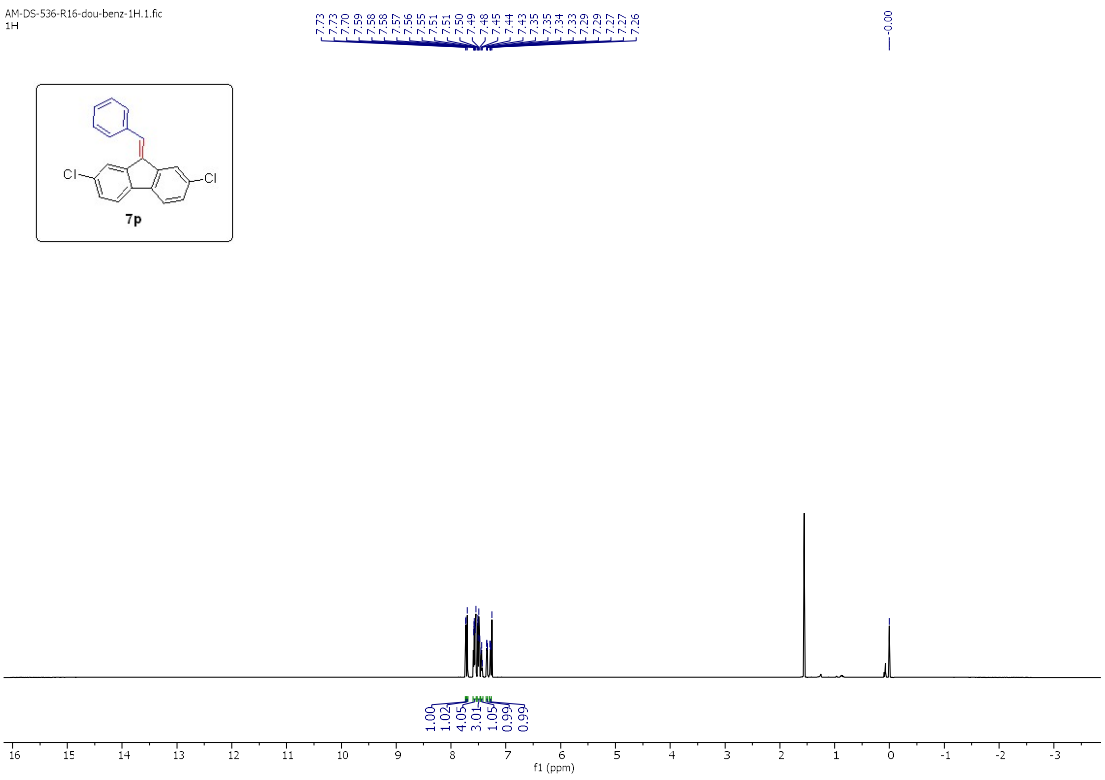


Figure S115. ^{1}H NMR Spectrum of 9-benzylidene-2,7-dichloro-9H-fluorene **(7p)** in $CDCl_3$.

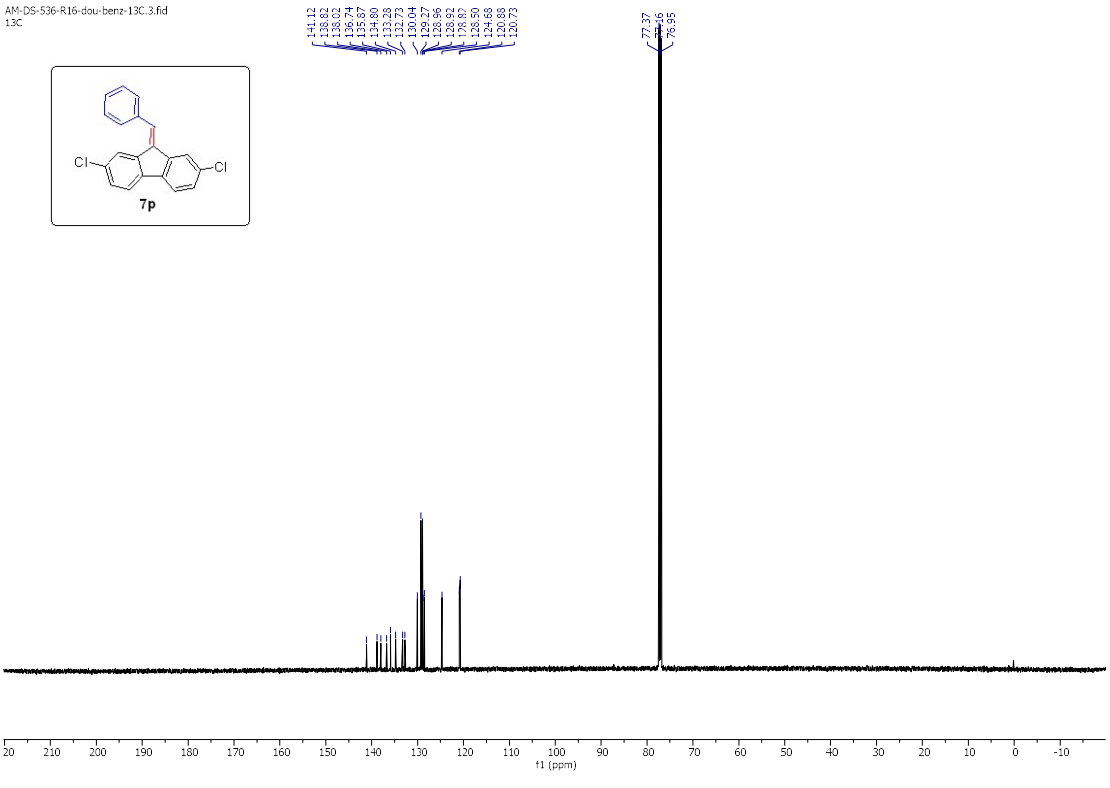


Figure S116. ^{13}C NMR Spectrum of 9-benzylidene-2,7-dichloro-9H-fluorene **(7p)** in $CDCl_3$.

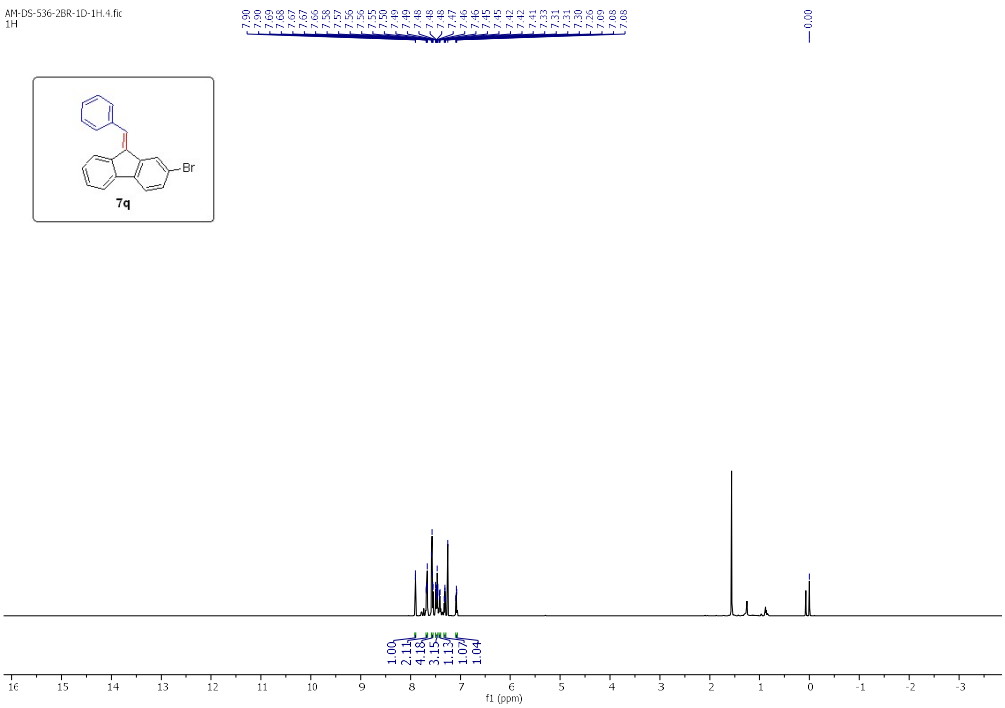


Figure S117. ^{1}H NMR Spectrum of (E)-9-benzylidene-2-bromo-9H-fluorene **(7q)** in $CDCl_3$.

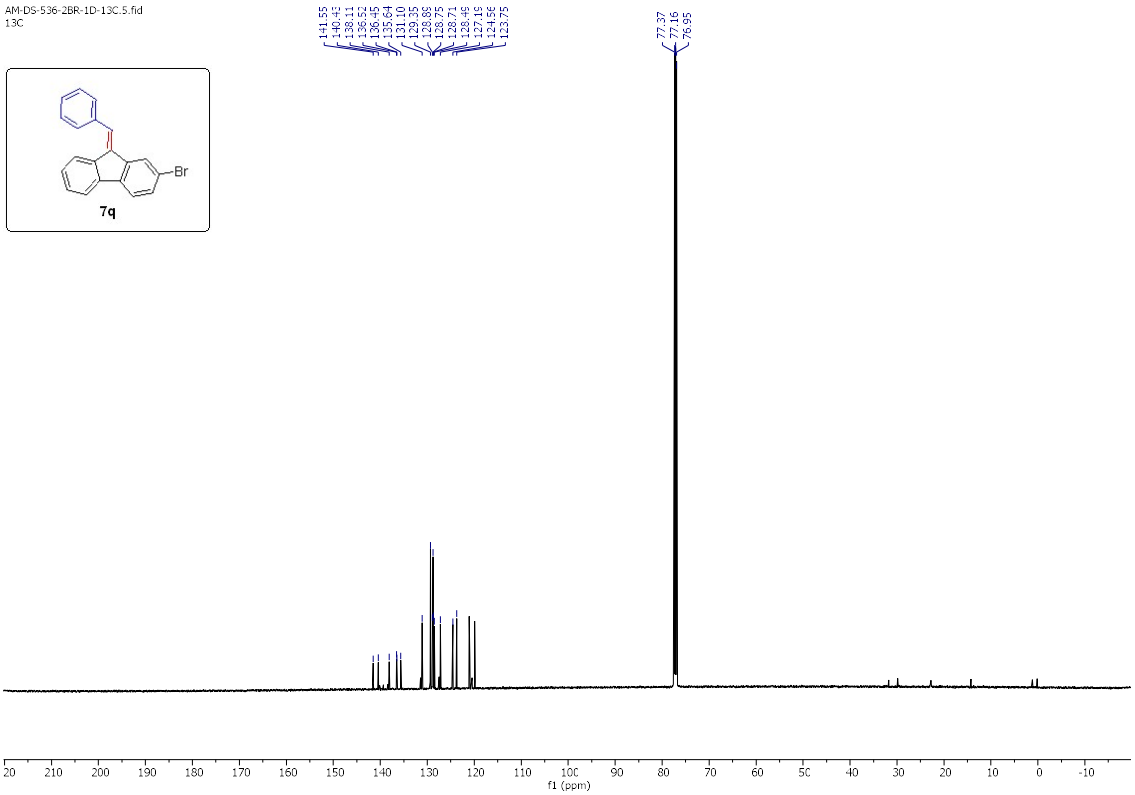


Figure S118. ^{13}C NMR Spectrum of (E)-9-benzylidene-2-bromo-9H-fluorene **(7q)** in $CDCl_3$.

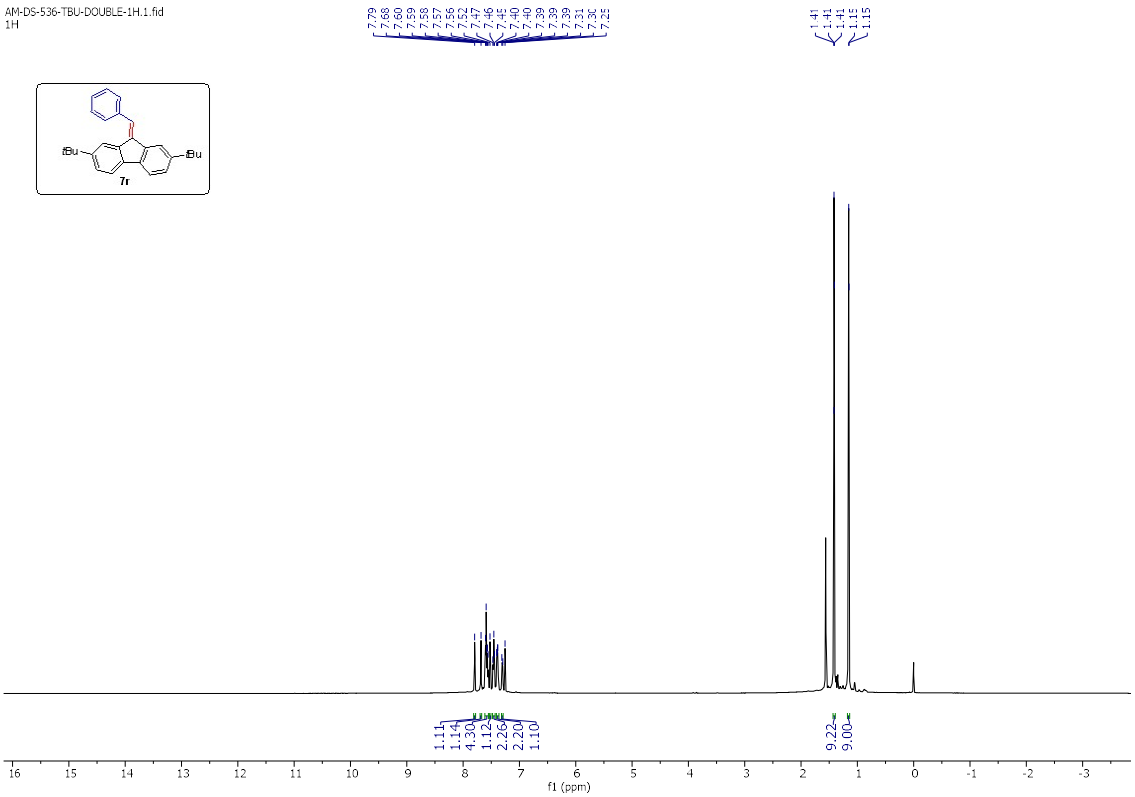


Figure S119. ^{1}H NMR Spectrum of 9-benzylidene-2,7-di-tert-butyl-9H-fluorene **(7r)** in $CDCl_3$.

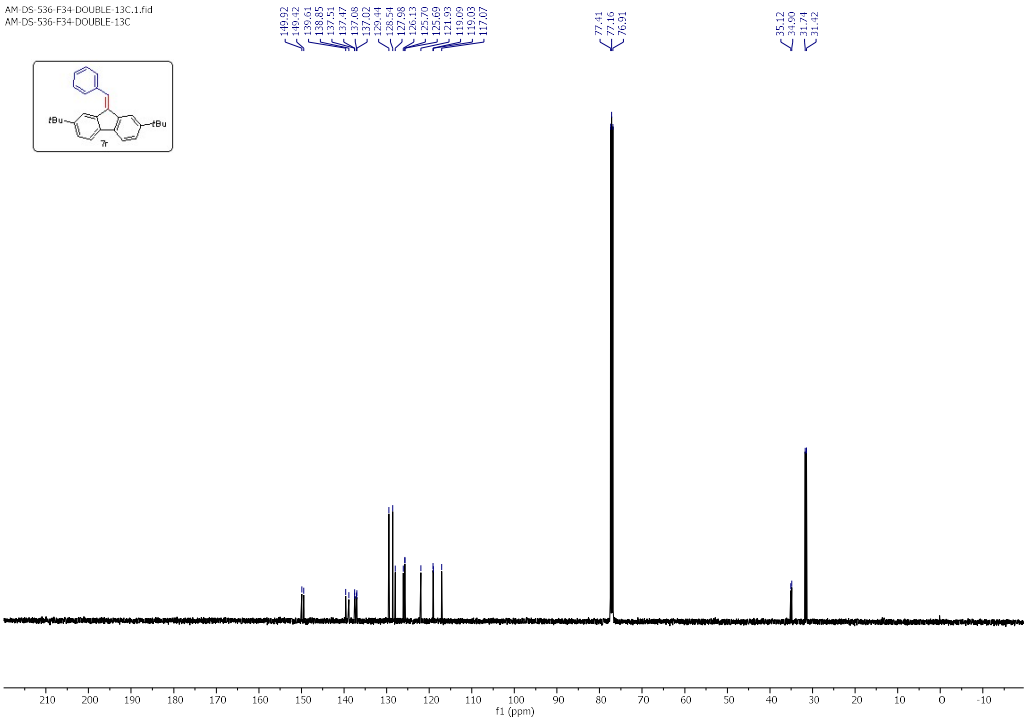


Figure S120. ^{13}C NMR Spectrum of 9-benzylidene-2,7-di-tert-butyl-9H-fluorene **(7r)** in $CDCl_3$.

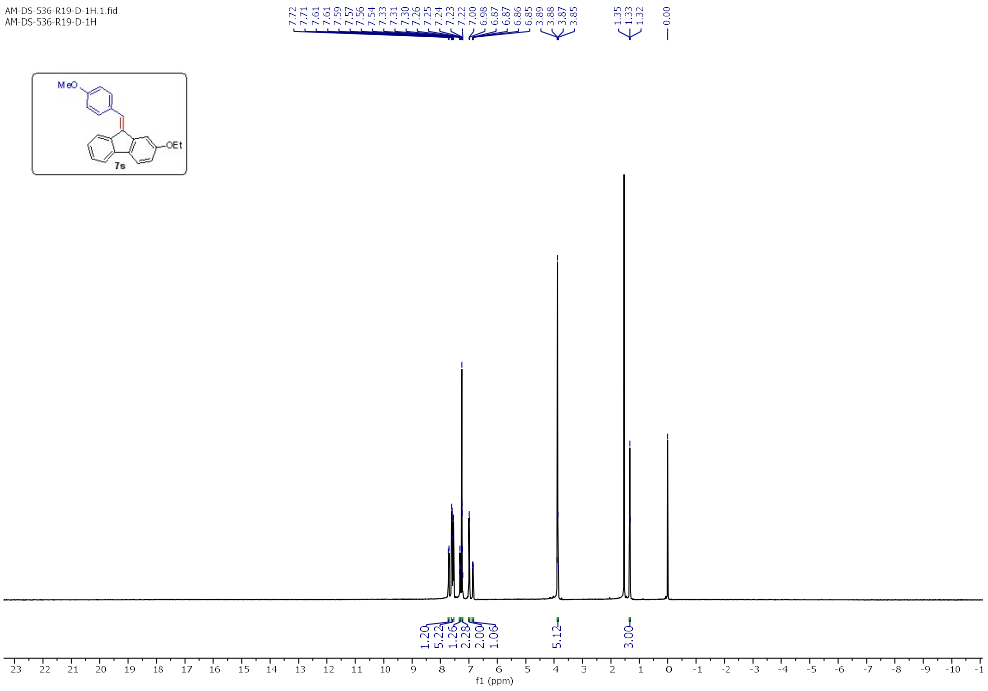


Figure S121. ^{1}H NMR Spectrum of (E)-2-ethoxy-9-(4-methoxybenzylidene)-9H-fluorene **(7s)** in $CDCl_3$.

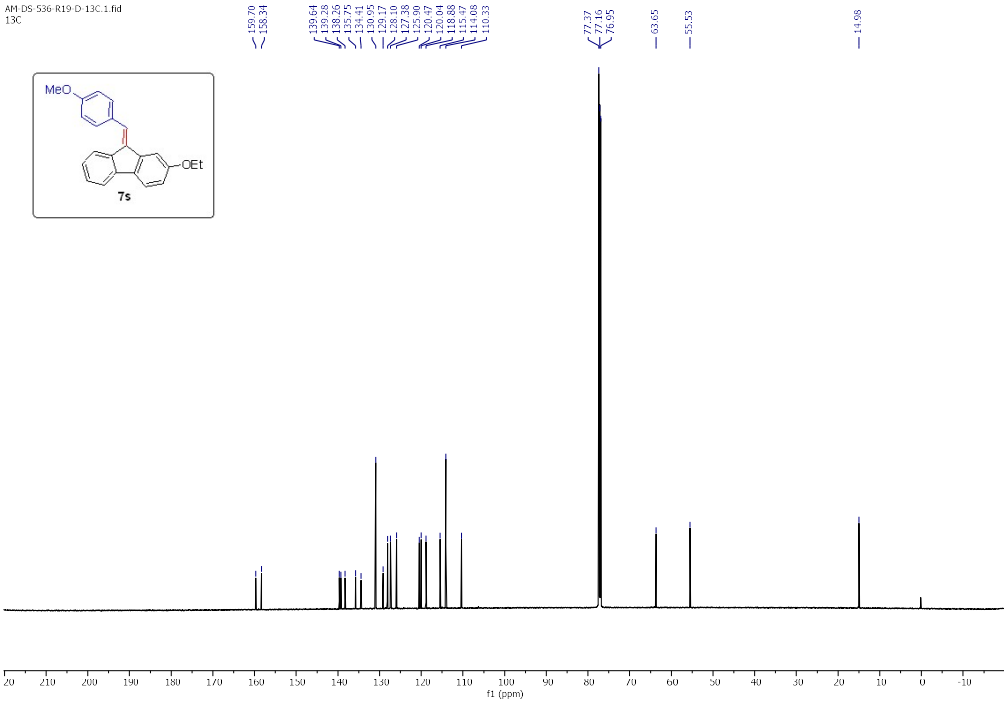


Figure S122. ^{13}C NMR Spectrum of (E)-2-ethoxy-9-(4-methoxybenzylidene)-9H-fluorene **(7s)** in $CDCl_3$.

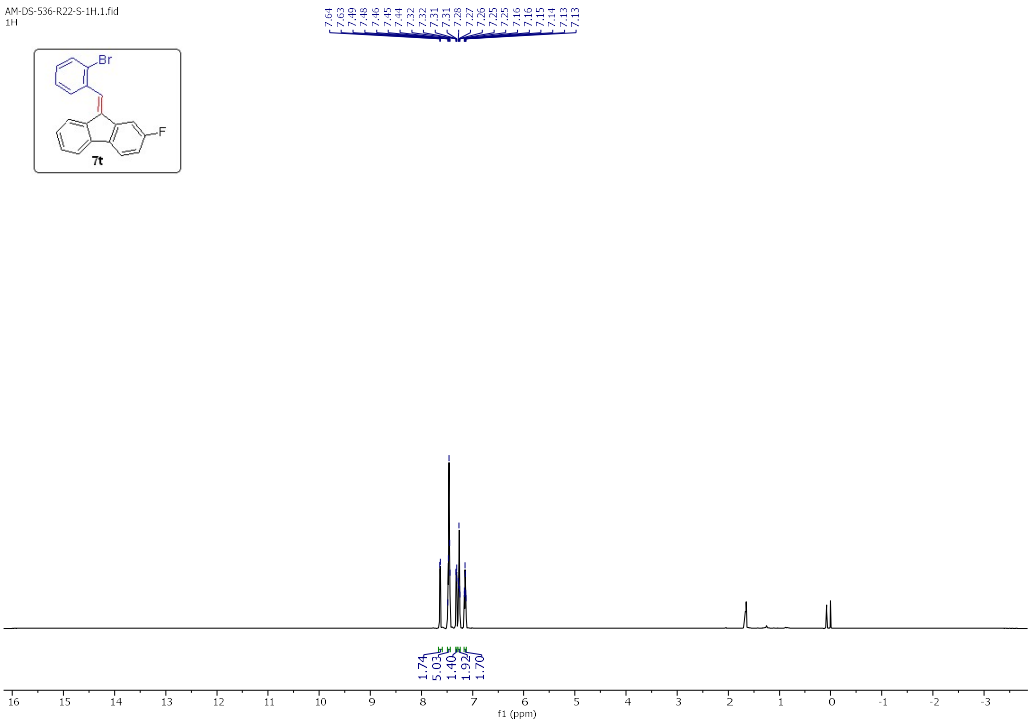


Figure S123. ^{1}H NMR Spectrum of (E)-9-(2-bromobenzylidene)-2-fluoro-9H-fluorene **(7t)** in $CDCl_3$.

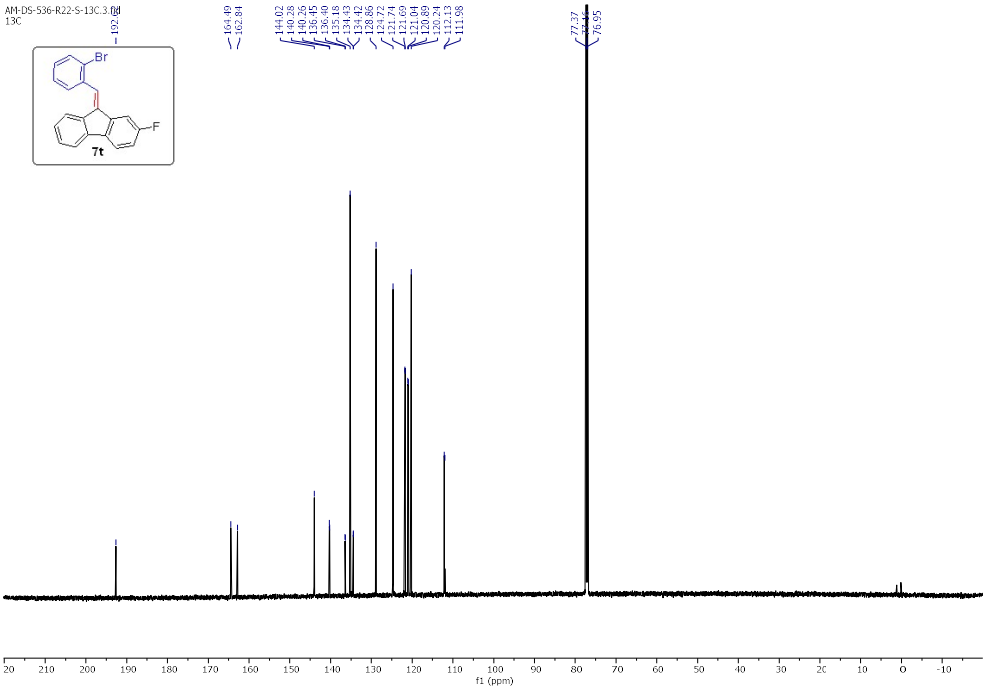


Figure S124. ^{13}C NMR Spectrum of (E)-9-(2-bromobenzylidene)-2-fluoro-9H-fluorene **(7t)** in $CDCl_3$.

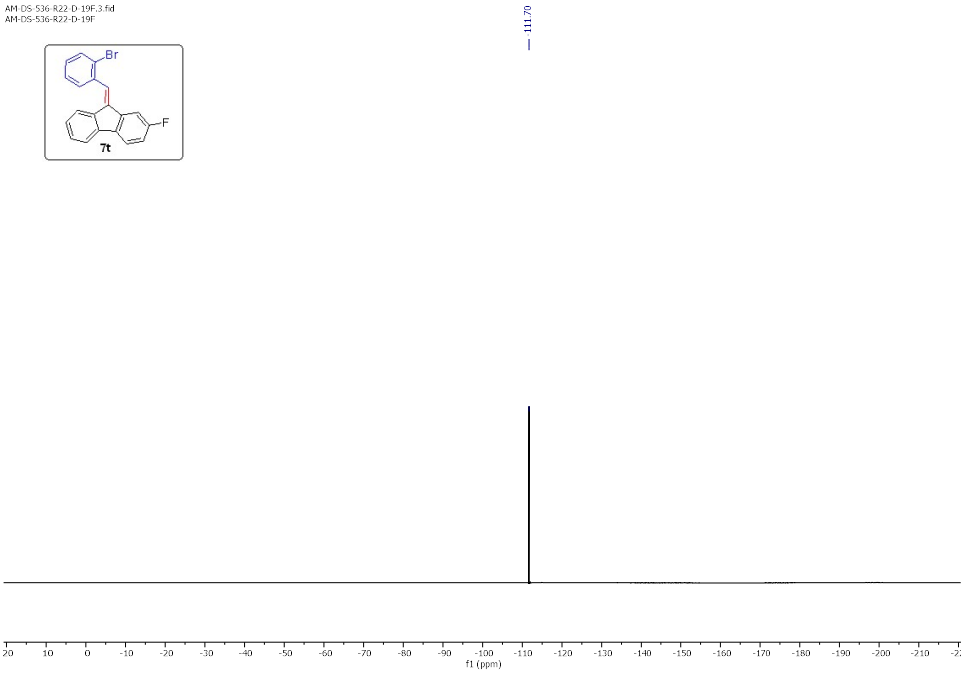


Figure S125. ^{19}F NMR Spectrum of (E)-9-(2-bromobenzylidene)-2-fluoro-9H-fluorene **(7t)** in $CDCl_3$.

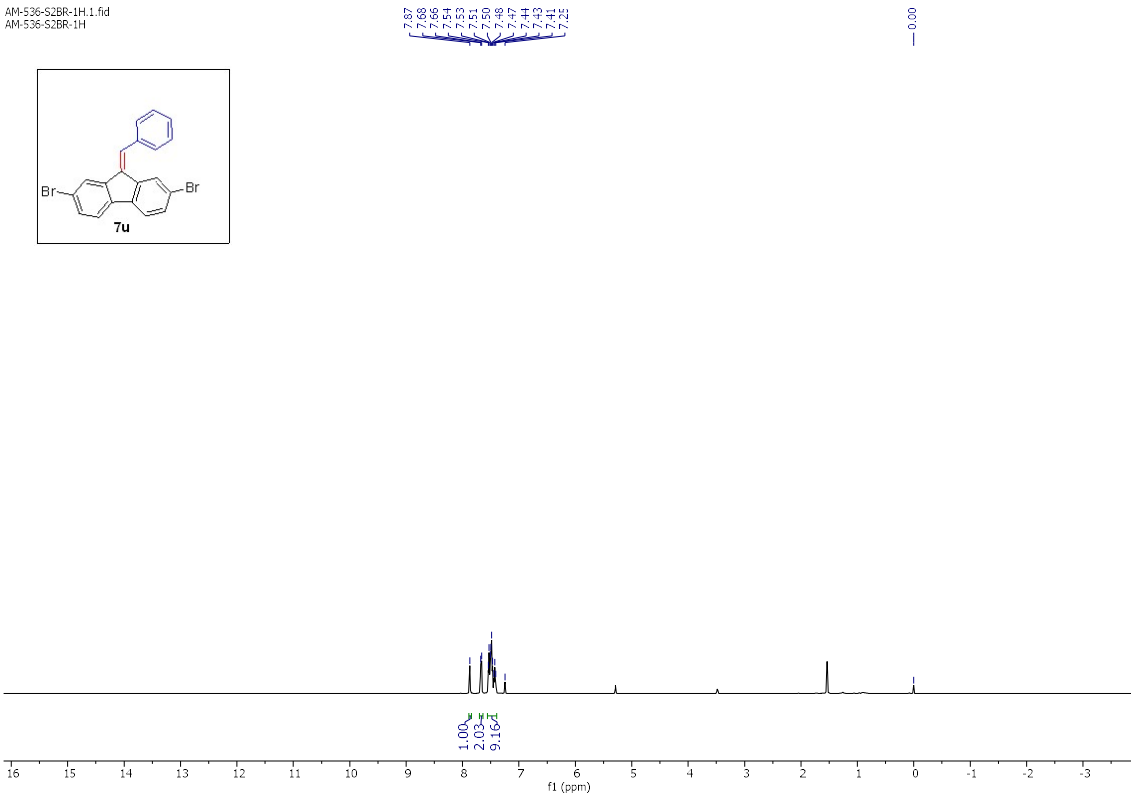


Figure S126. ^{1}H NMR Spectrum of 9-benzylidene-2,7-dibromo-9H-fluorene **(7u)** in $CDCl_3$.

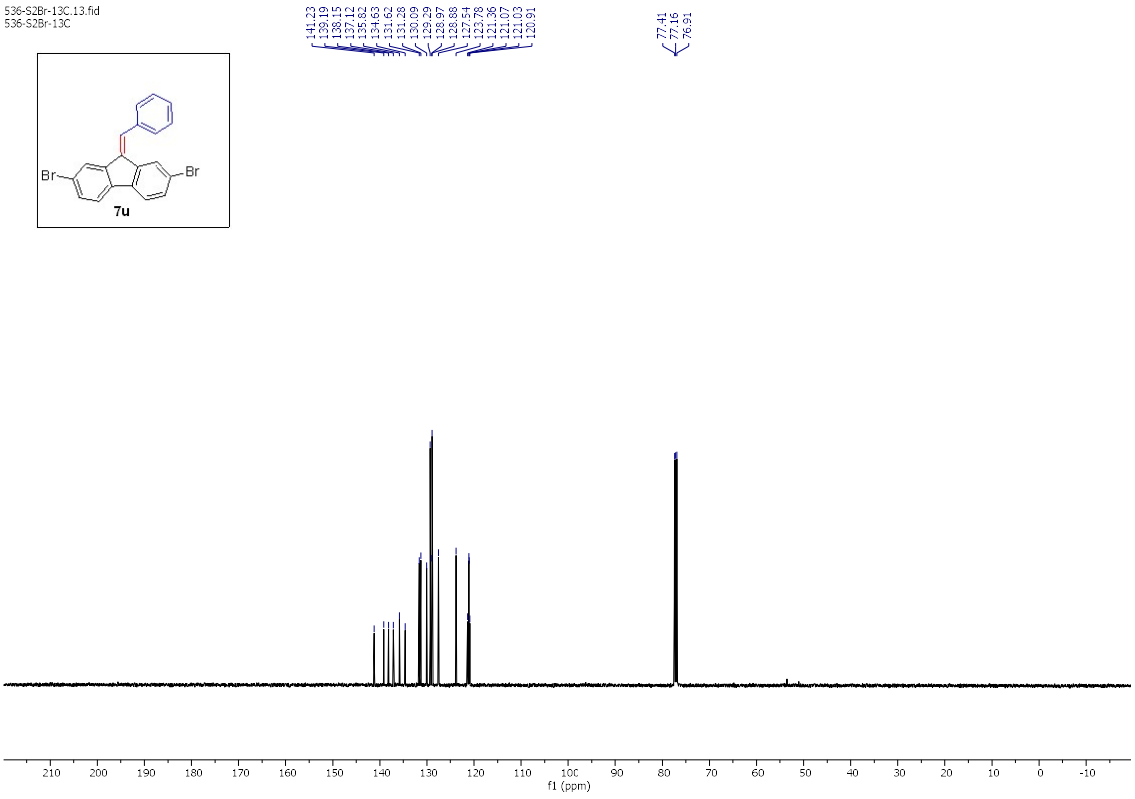


Figure S127. ^{13}C NMR Spectrum of 9-benzylidene-2,7-dibromo-9H-fluorene **(7u** in $CDCl_3$.

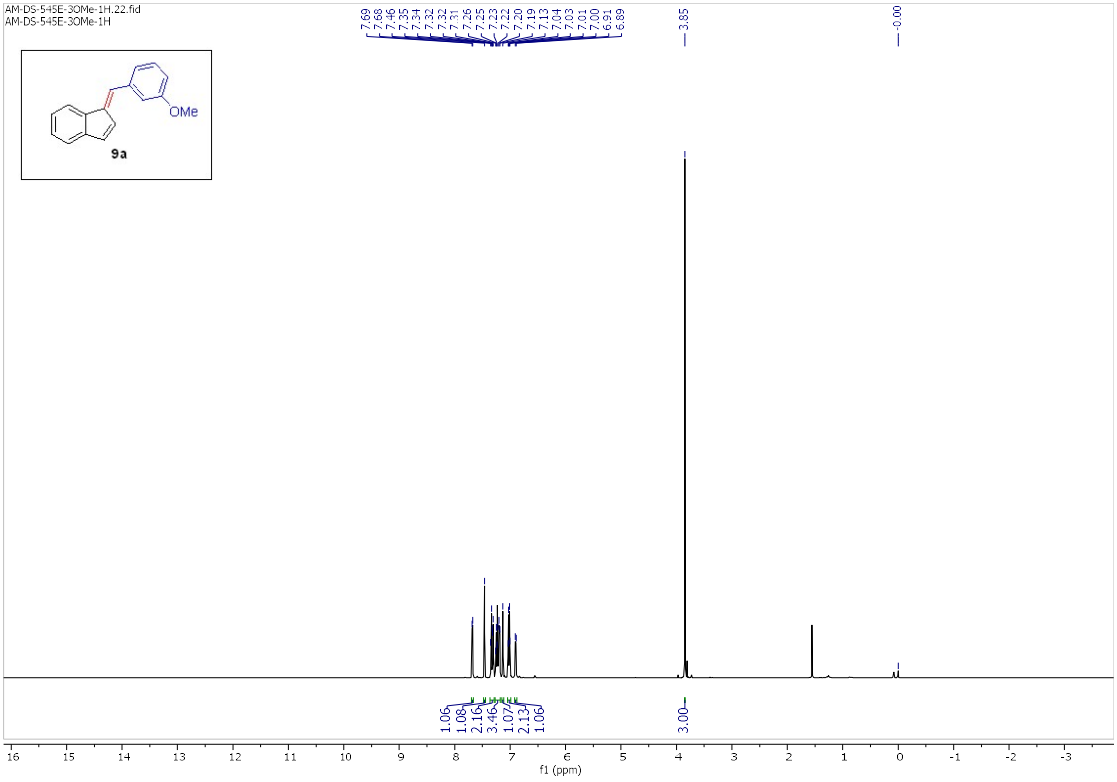


Figure S128. ^{1}H NMR Spectrum of (E)-1-(3-methoxybenzylidene)-1H-indene **(9a)** in $CDCl_3$.

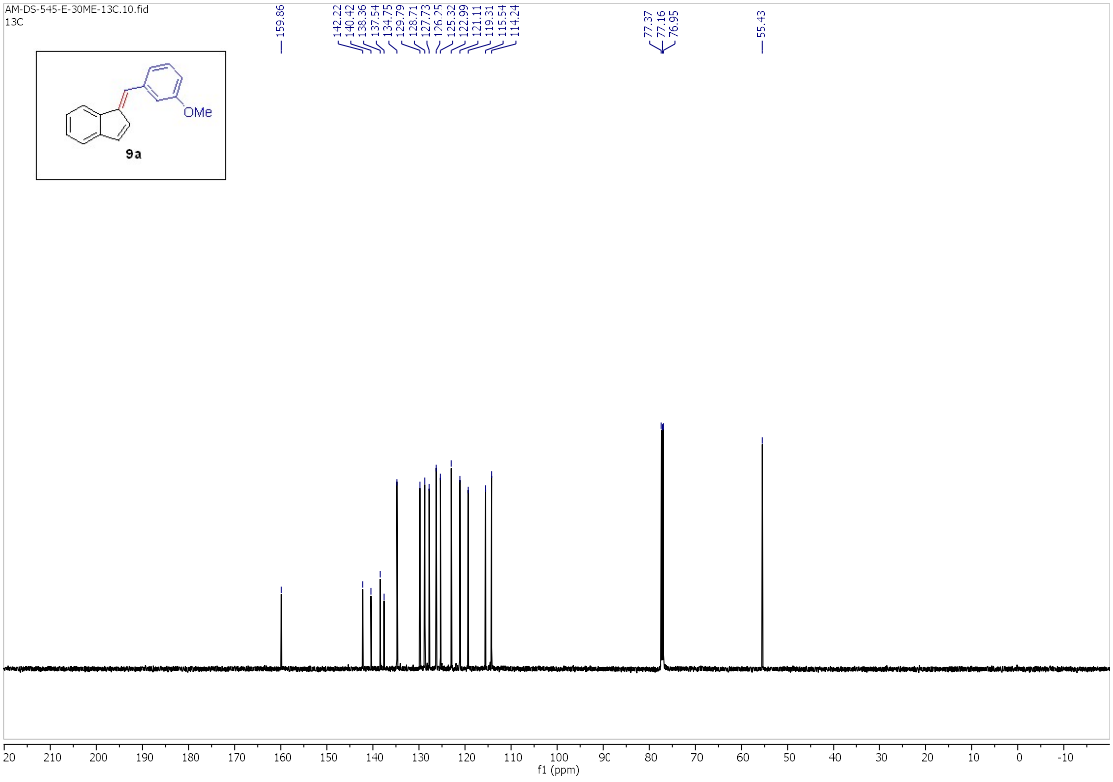


Figure S129. ^{13}C NMR Spectrum of (E)-1-(3-methoxybenzylidene)-1H-indene **(9a)** in $CDCl_3$.

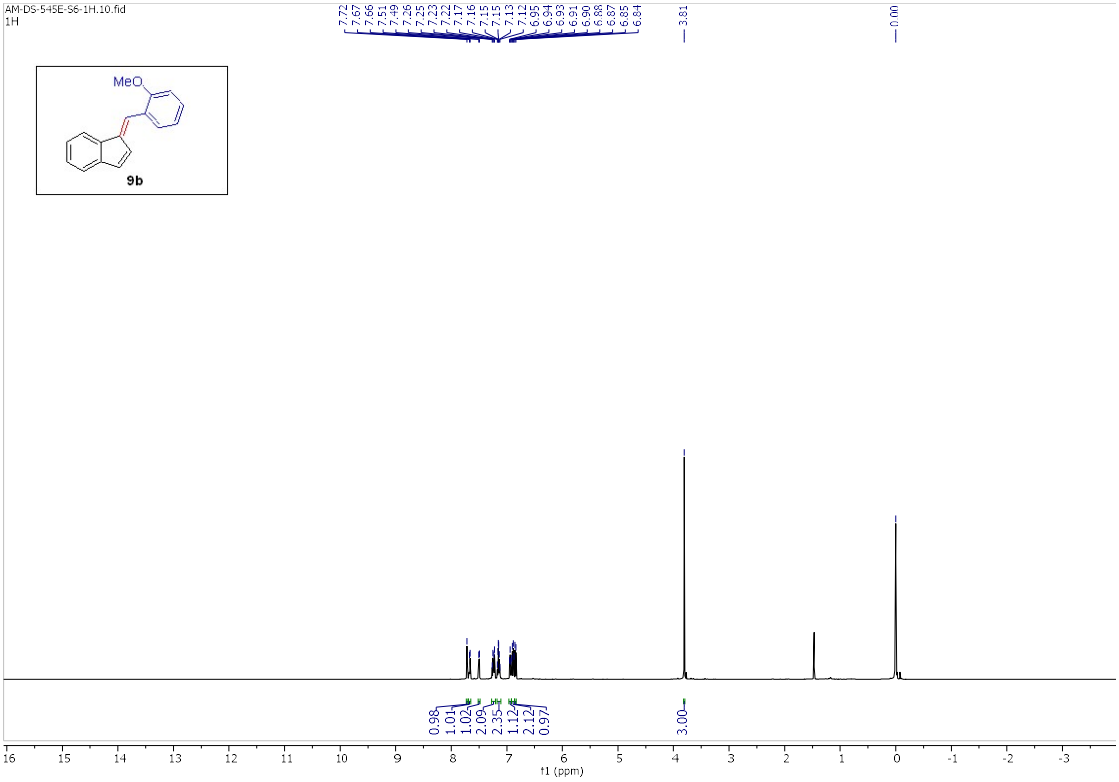


Figure S130. ^{1}H NMR Spectrum of (E)-1-(2-methoxybenzylidene)-1H-indene **(9b)** in $CDCl_3$.

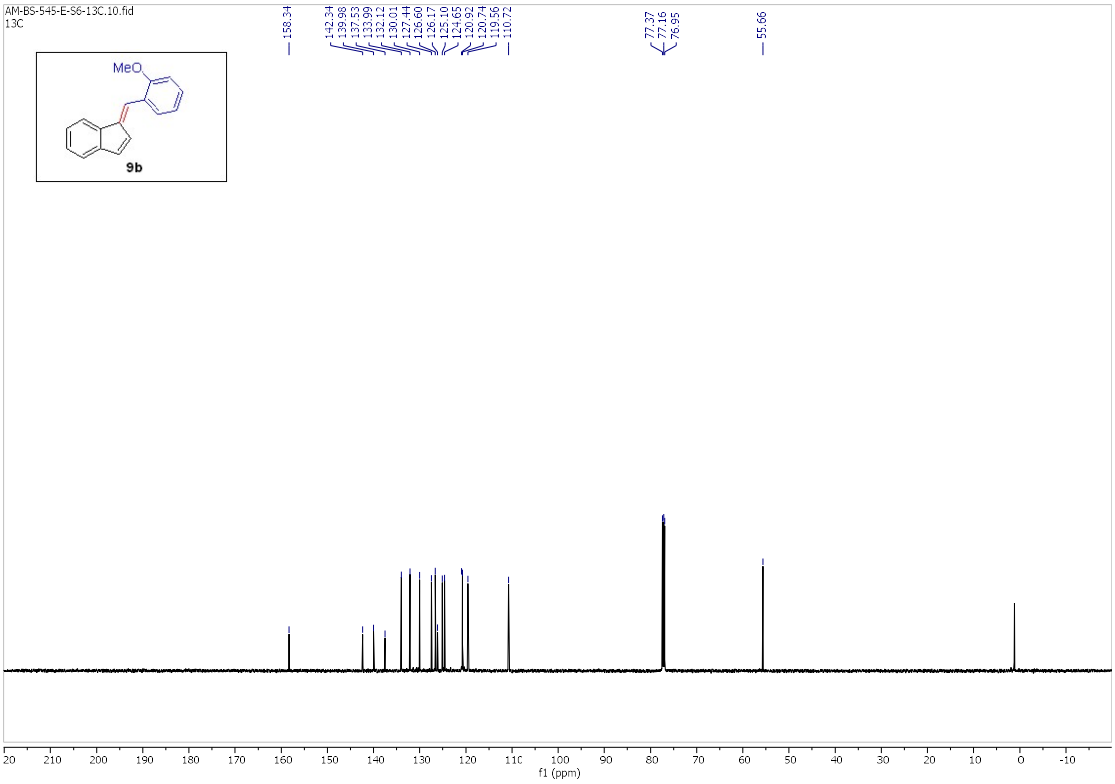


Figure S130. ^{13}C NMR Spectrum of (E)-1-(2-methoxybenzylidene)-1H-indene **(9b)** in $CDCl_3$.

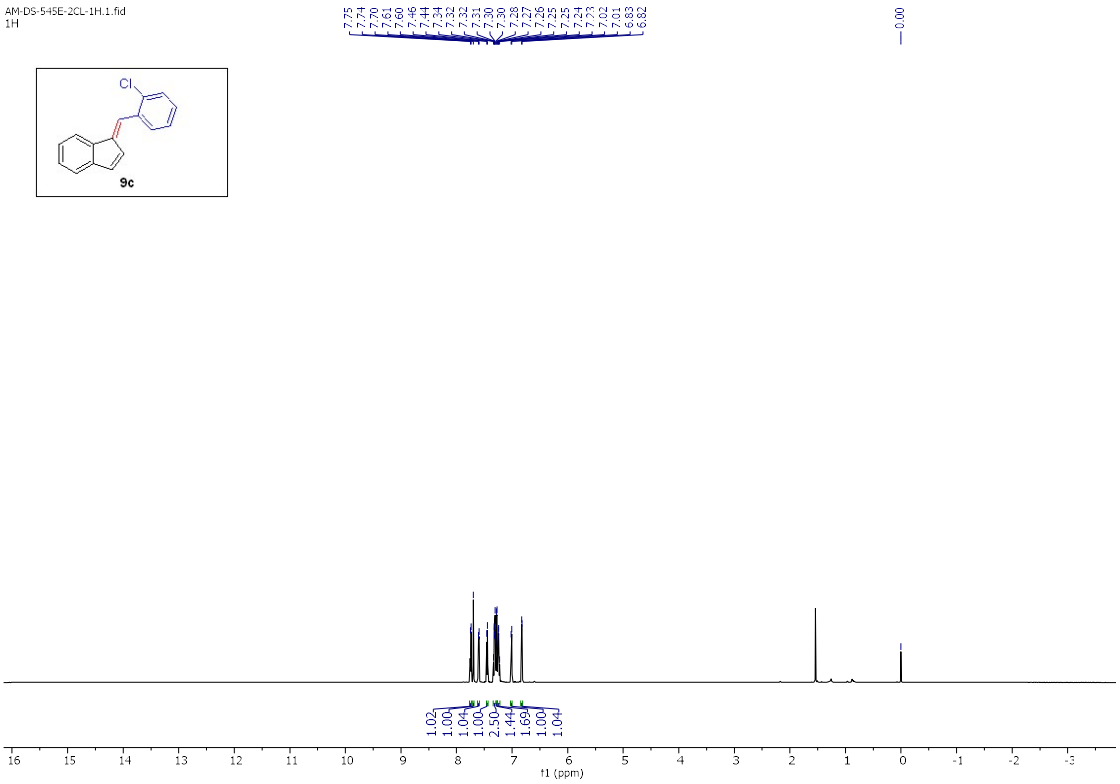


Figure S132. ^{1}H NMR Spectrum of (E)-1-(2-chlorobenzylidene)-1H-indene **(9c)** in $CDCl_3$.

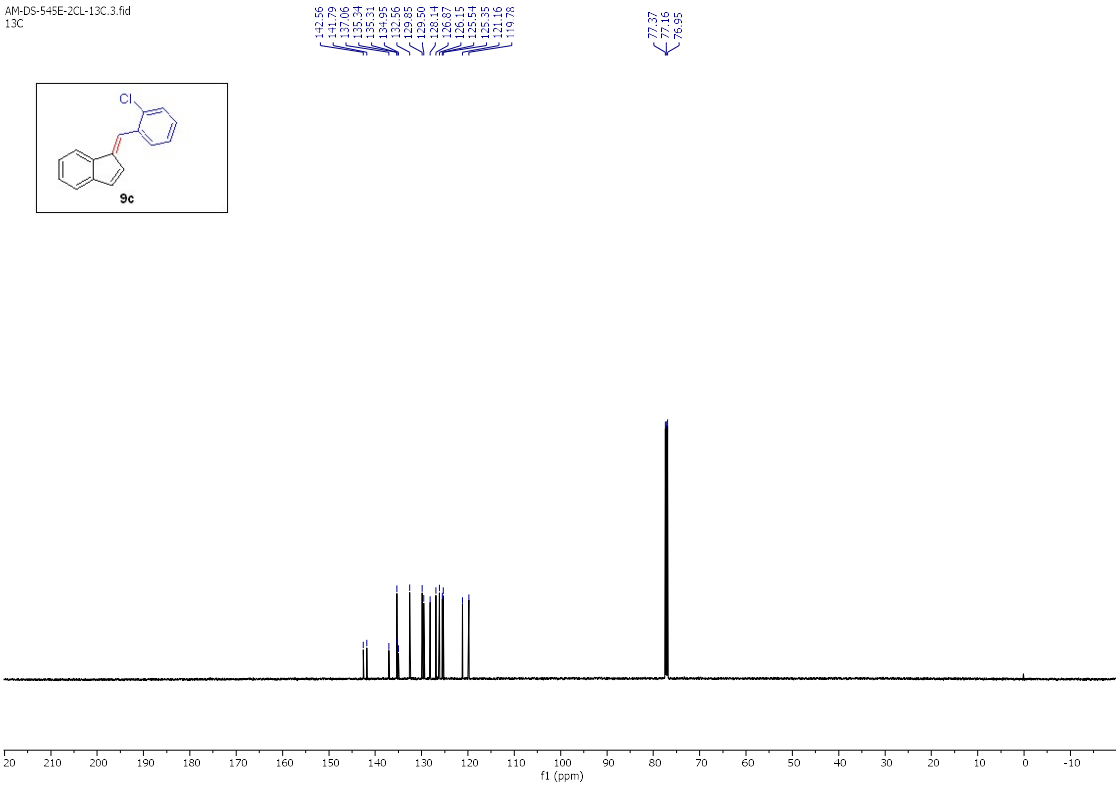


Figure S133. ^{13}C NMR Spectrum of (E)-1-(2-chlorobenzylidene)-1H-indene **(9c)** in $CDCl_3$.

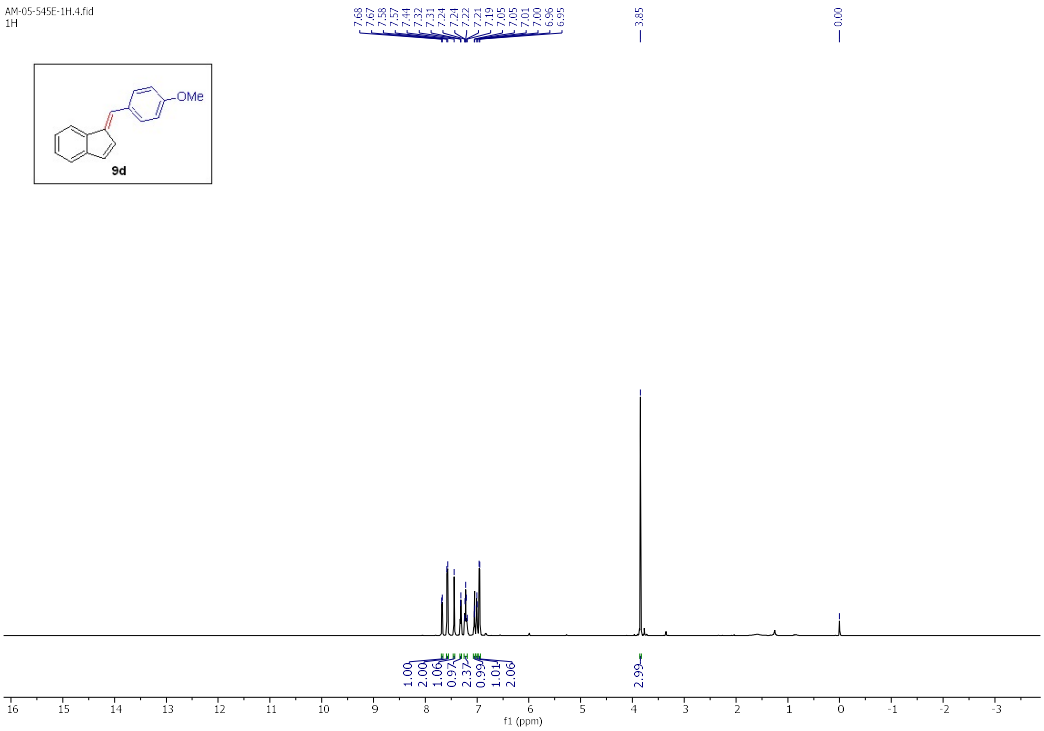


Figure S134. ^{1}H NMR Spectrum of (E)-1-(4-methoxybenzylidene)-1H-indene **(9d)** in $CDCl_3$.

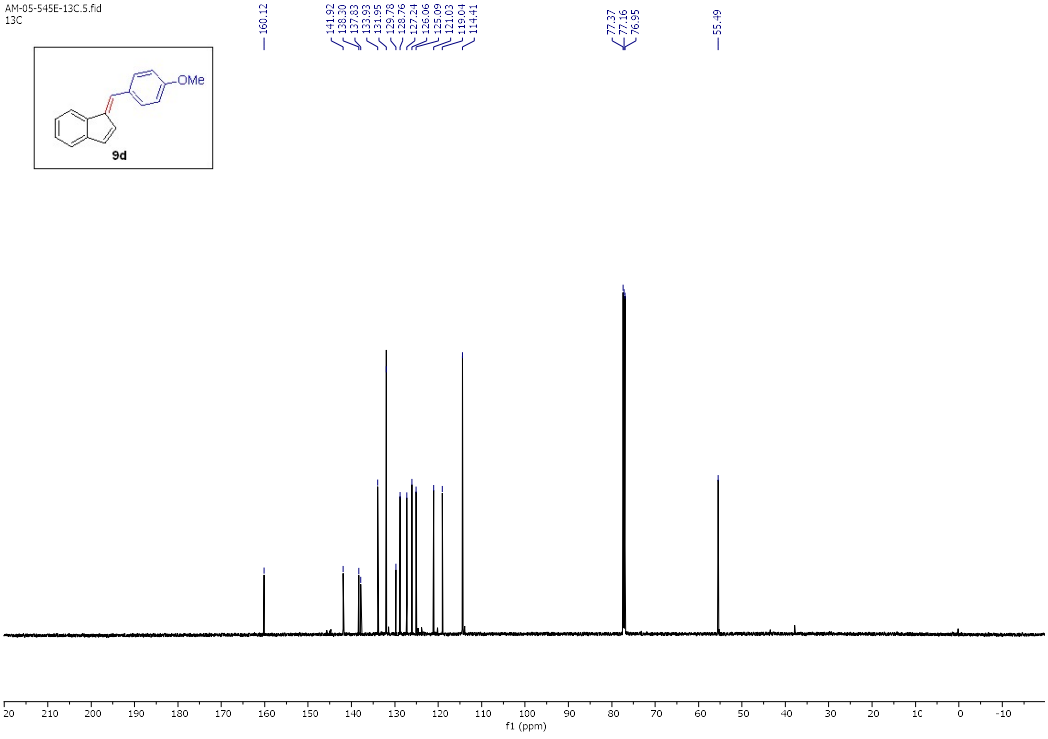


Figure S135. ^{13}C NMR Spectrum of (E)-1-(4-methoxybenzylidene)-1H-indene **(9d)** in $CDCl_3$.

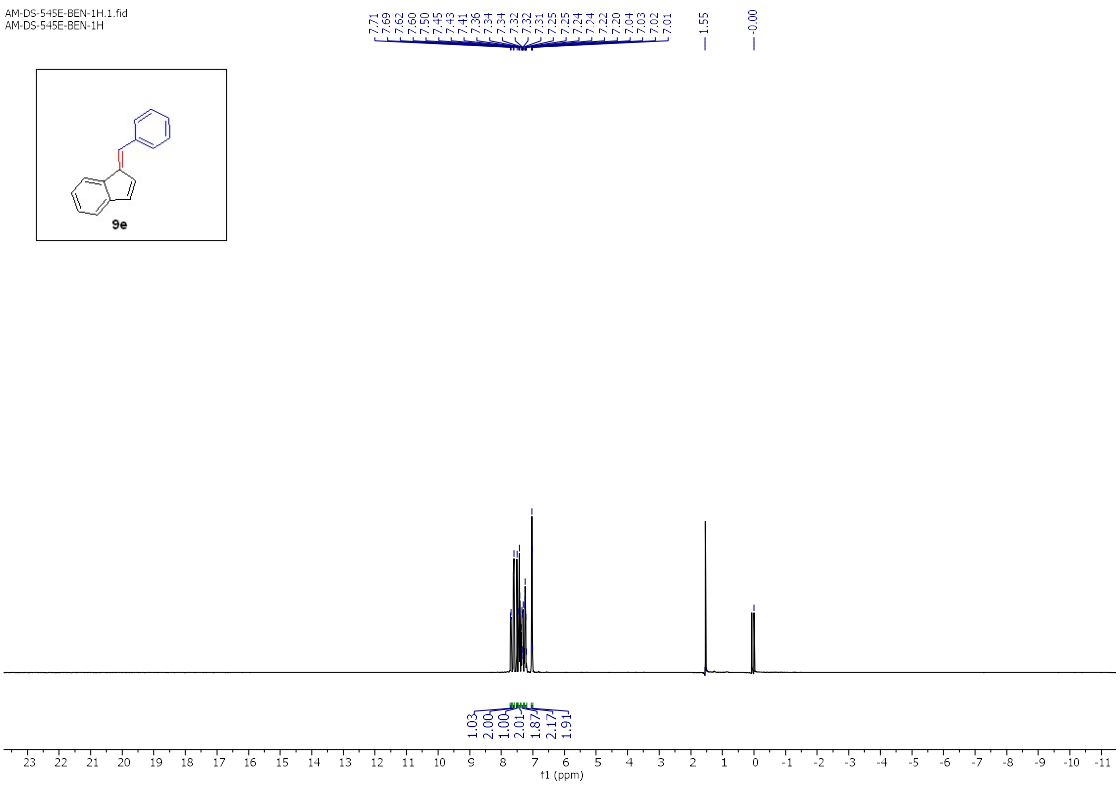


Figure S136. ^{1}H NMR Spectrum of (E)-1-benzylidene-1H-indene **(9e)** in $CDCl_3$.

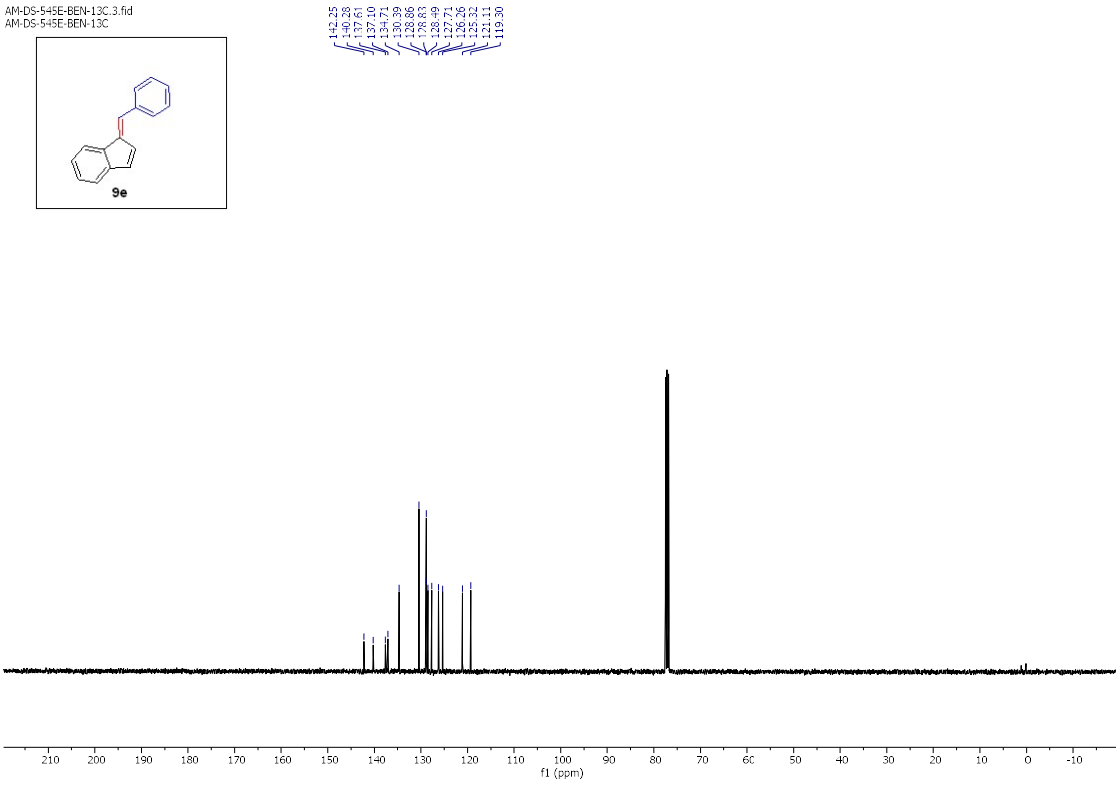


Figure S137. ^{13}C NMR Spectrum of (E)-1-benzylidene-1H-indene **(9e)** in $CDCl_3$.

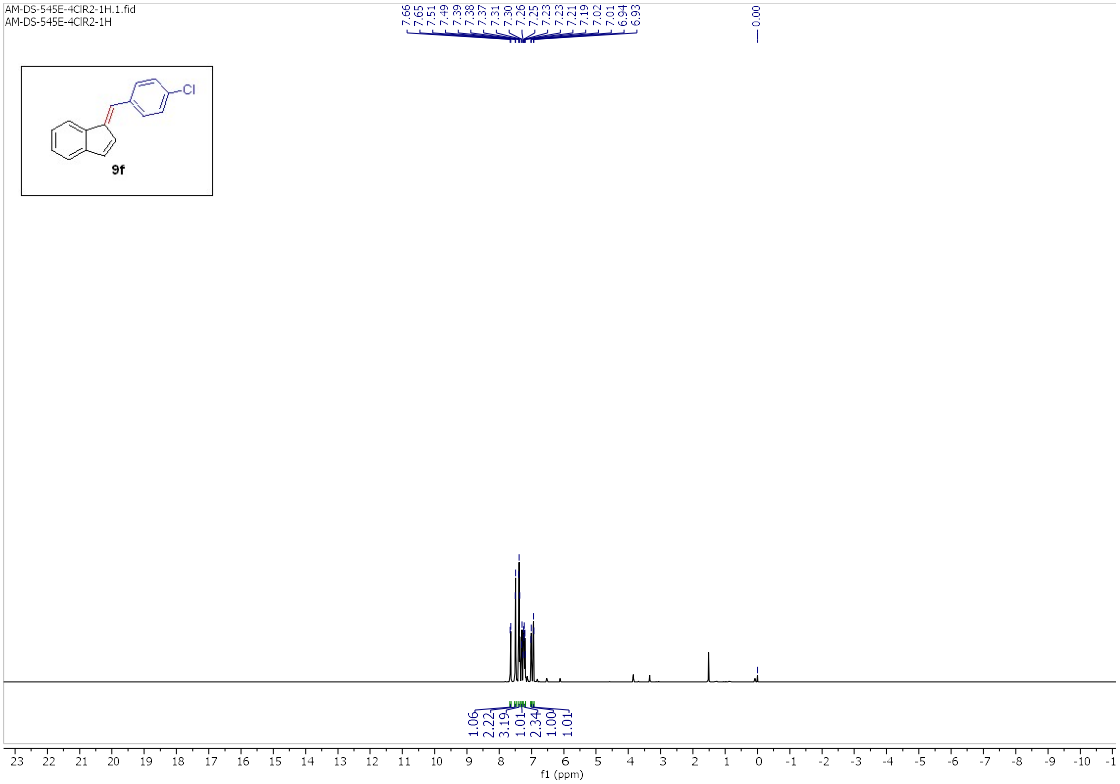


Figure S138. ^{1}H NMR Spectrum of (E)-1-(4-chlorobenzylidene)-1H-indene **(9f)** in $CDCl_3$.

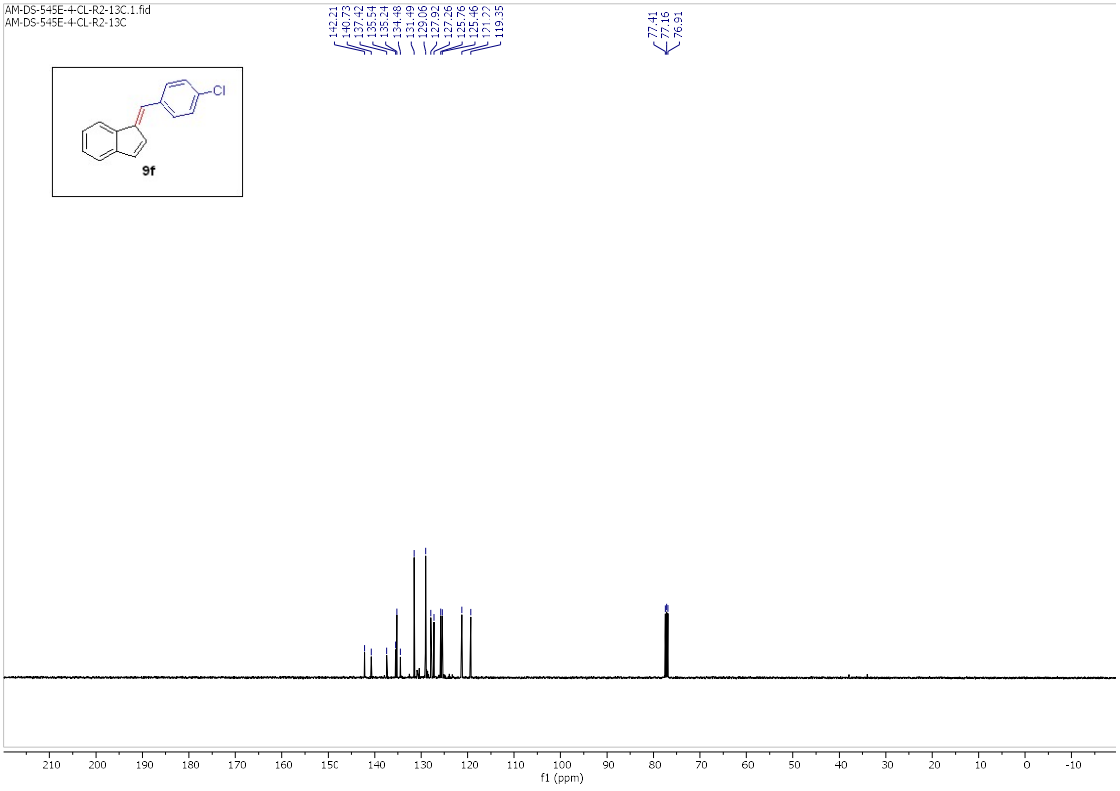


Figure S139. ^{13}C NMR Spectrum of (E)-1-(4-chlorobenzylidene)-1H-indene **(9f)** in $CDCl_3$.

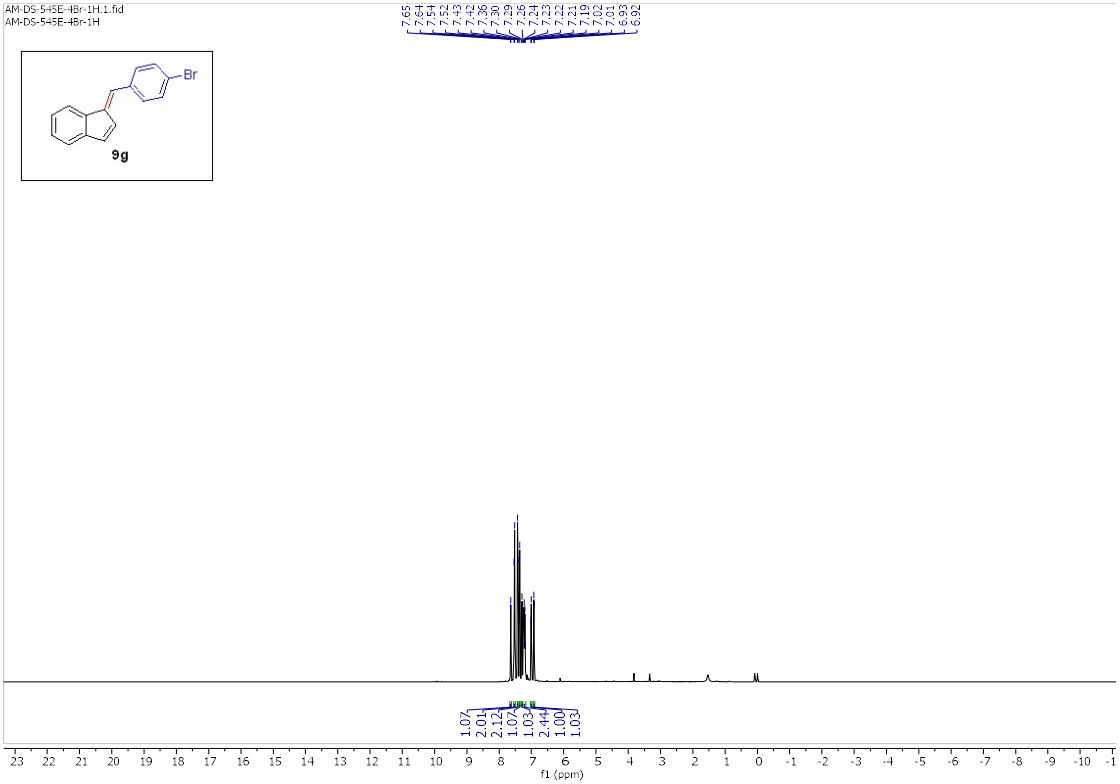


Figure S140. ^{1}H NMR Spectrum of (E)-1-(4-bromobenzylidene)-1H-indene **(9g)** in $CDCl_3$.

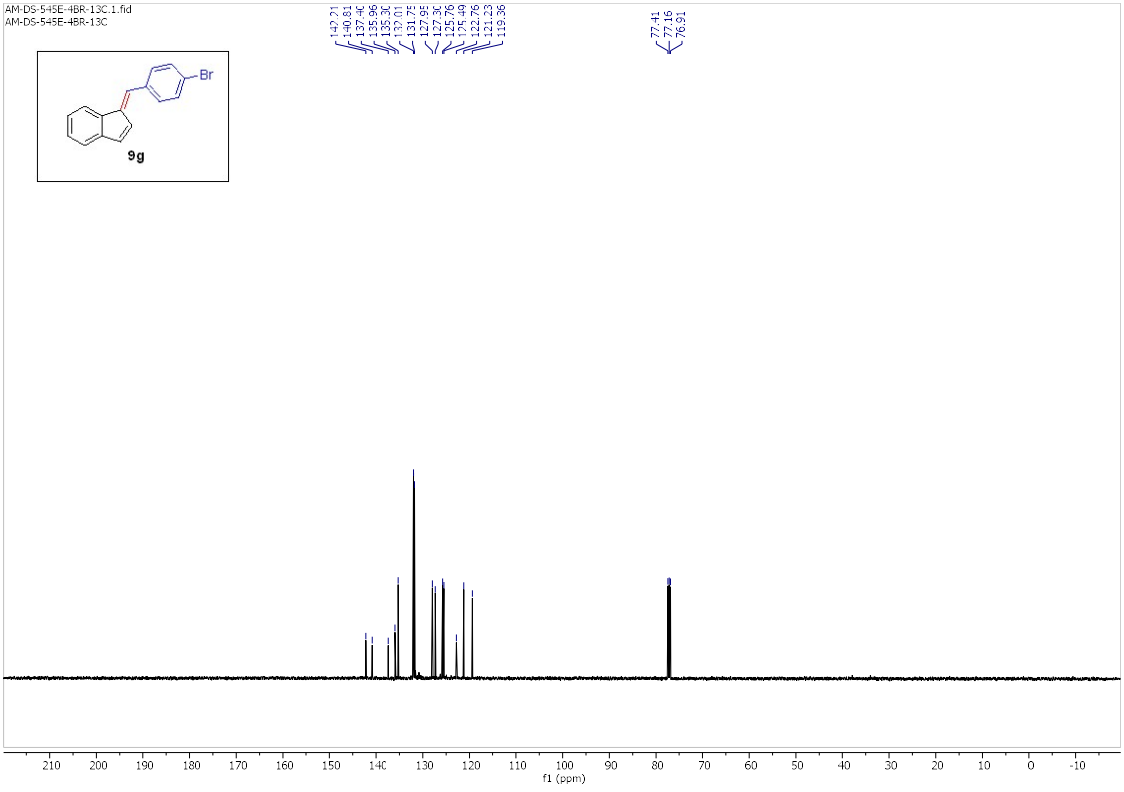


Figure S141. ^{13}C NMR Spectrum of (E)-1-(4-bromobenzylidene)-1H-indene **(9g)** in $CDCl_3$.

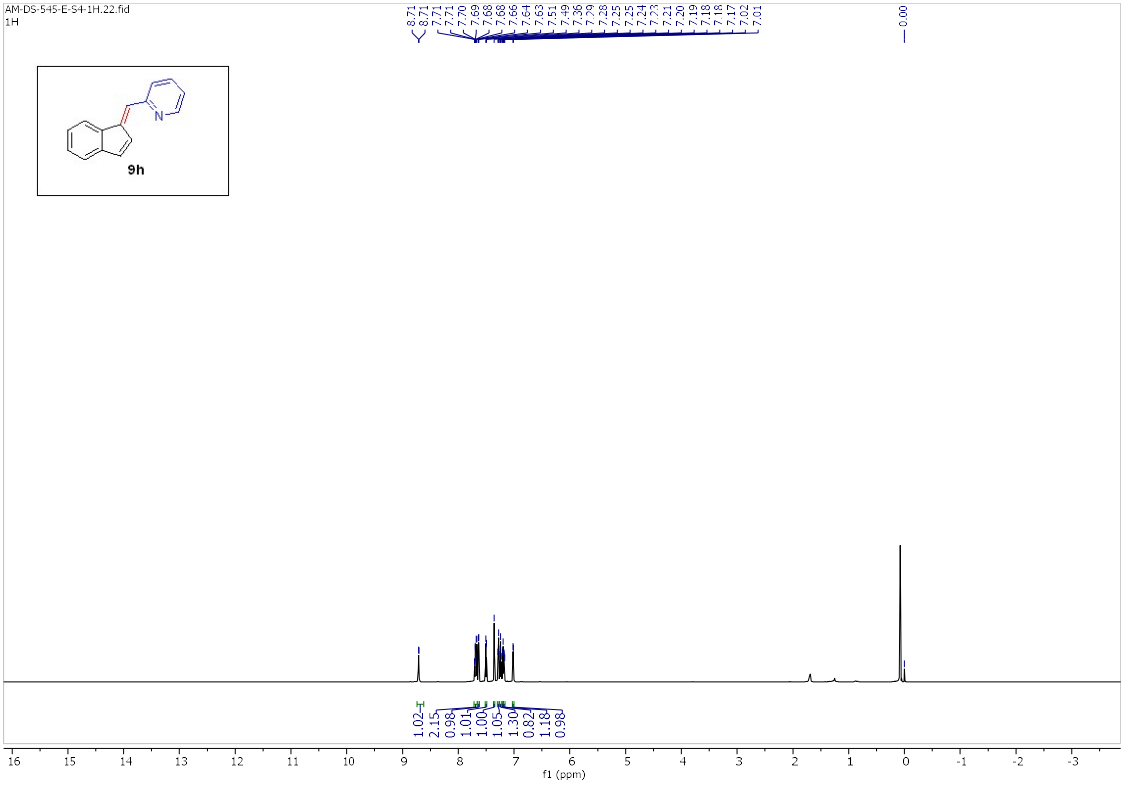


Figure S142. ^{1}H NMR Spectrum of (E)-2-((1H-inden-1-ylidene)methyl)pyridine **(9h)** in $CDCl_3$.

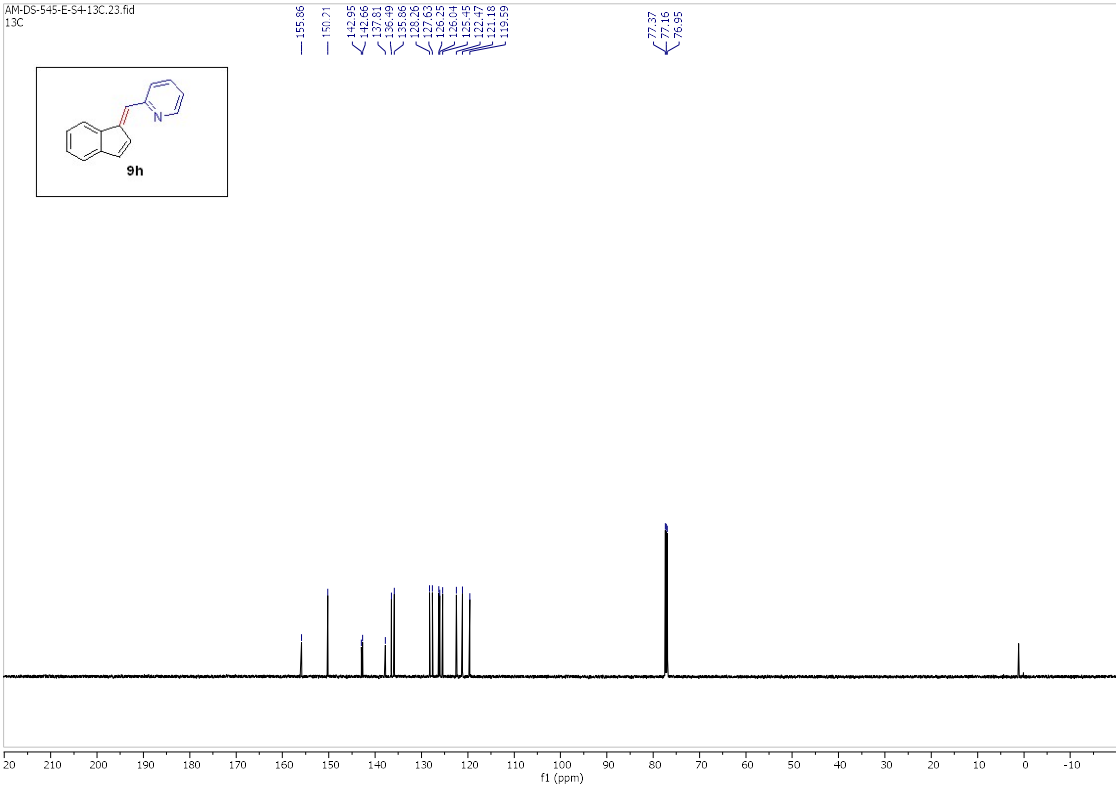


Figure S143. ^{13}C NMR Spectrum of (E)-2-((1H-inden-1-ylidene)methyl)pyridine **(9h)** in $CDCl_3$.

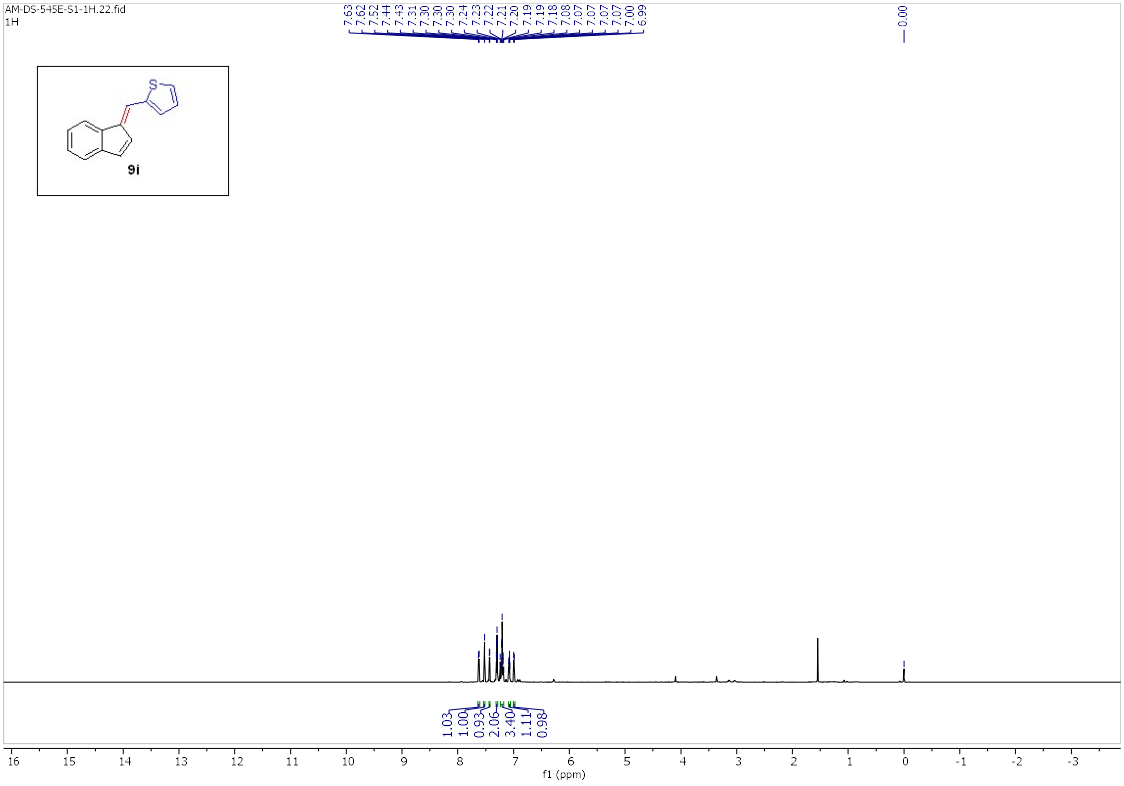


Figure S144. ^{1}H NMR Spectrum of (E)-2-((1H-inden-1-ylidene)methyl)thiophene **(9i)** in $CDCl_3$.

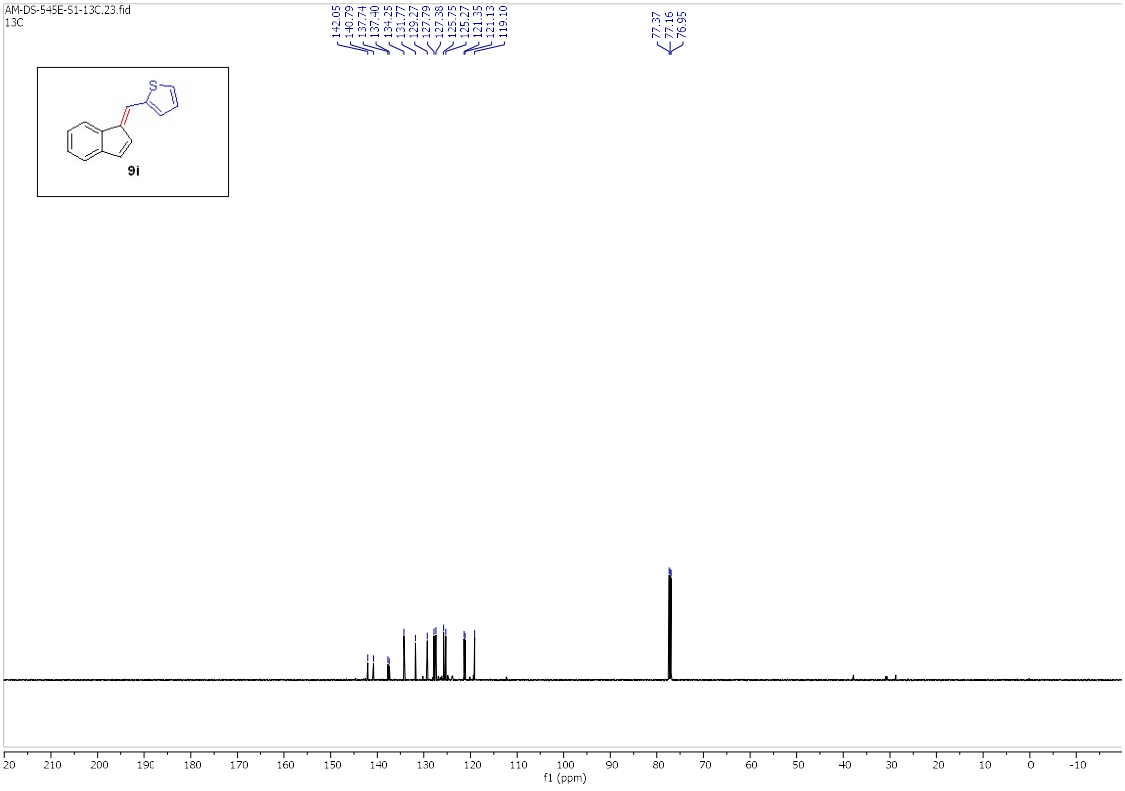


Figure S145. ^{13}C NMR Spectrum of (E)-2-((1H-inden-1-ylidene)methyl)thiophene **(9i)** in $CDCl_3$.

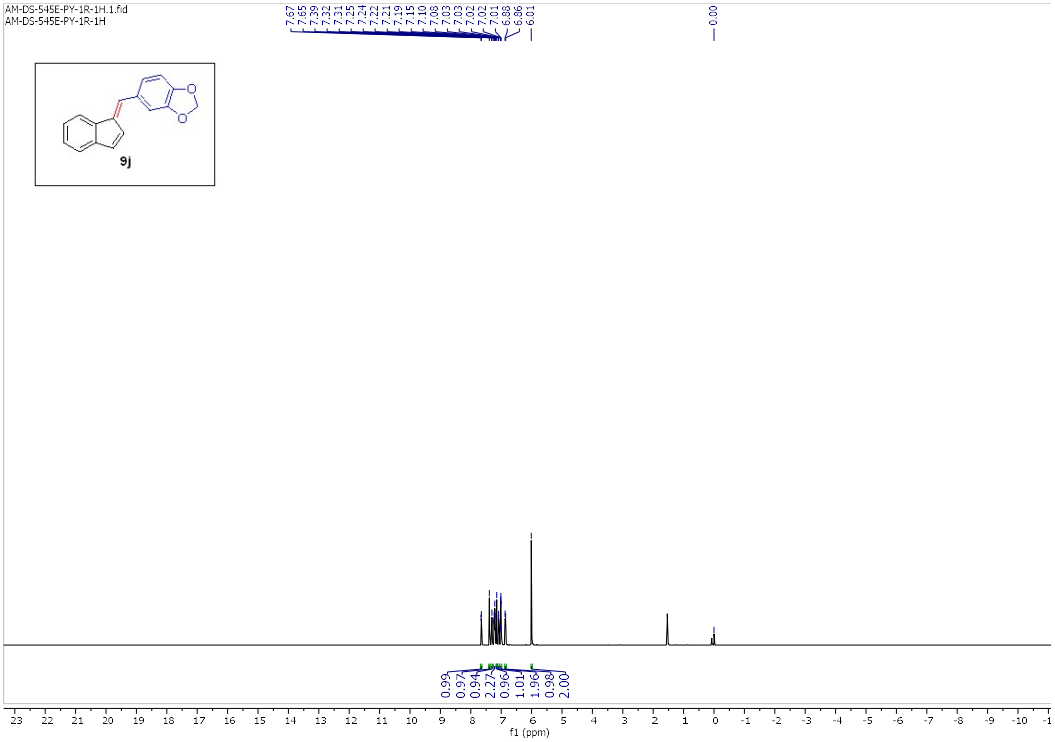


Figure S146. ^{1}H NMR Spectrum of (E)-5-((1H-inden-1-ylidene)methyl)benzo[d][1,3]dioxole **(9j)** in $CDCl_3$.

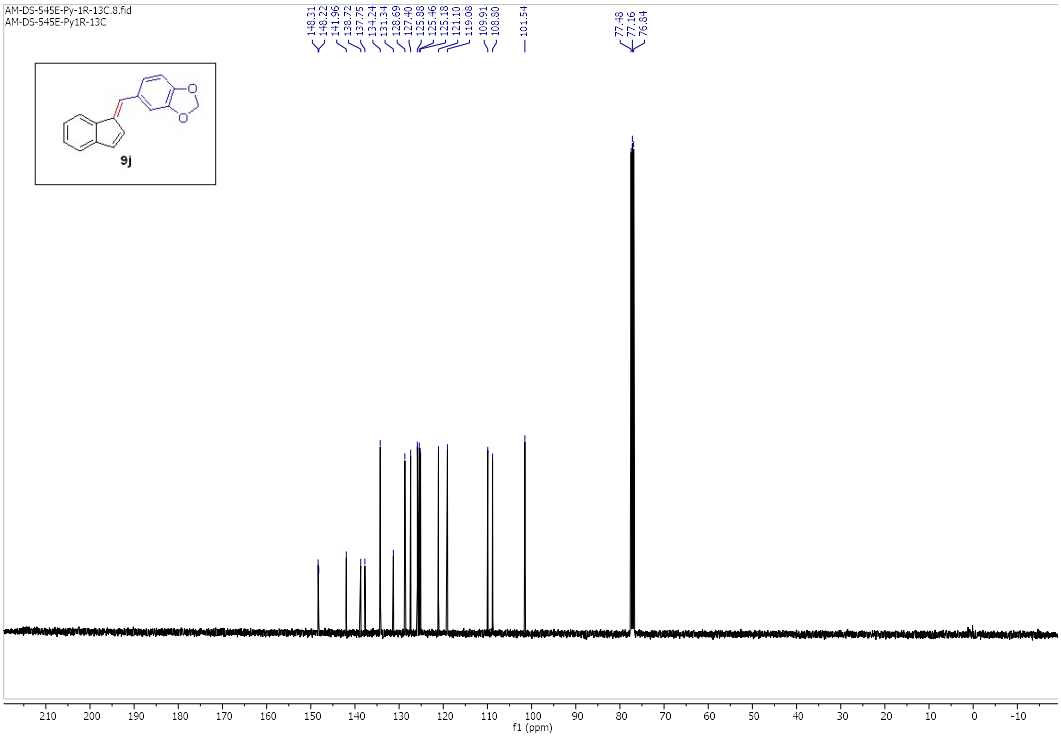


Figure S147. ^{13}C NMR Spectrum of (E)-5-((1H-inden-1-ylidene)methyl)benzo[d][1,3]dioxole **(9j)** in $CDCl_3$.

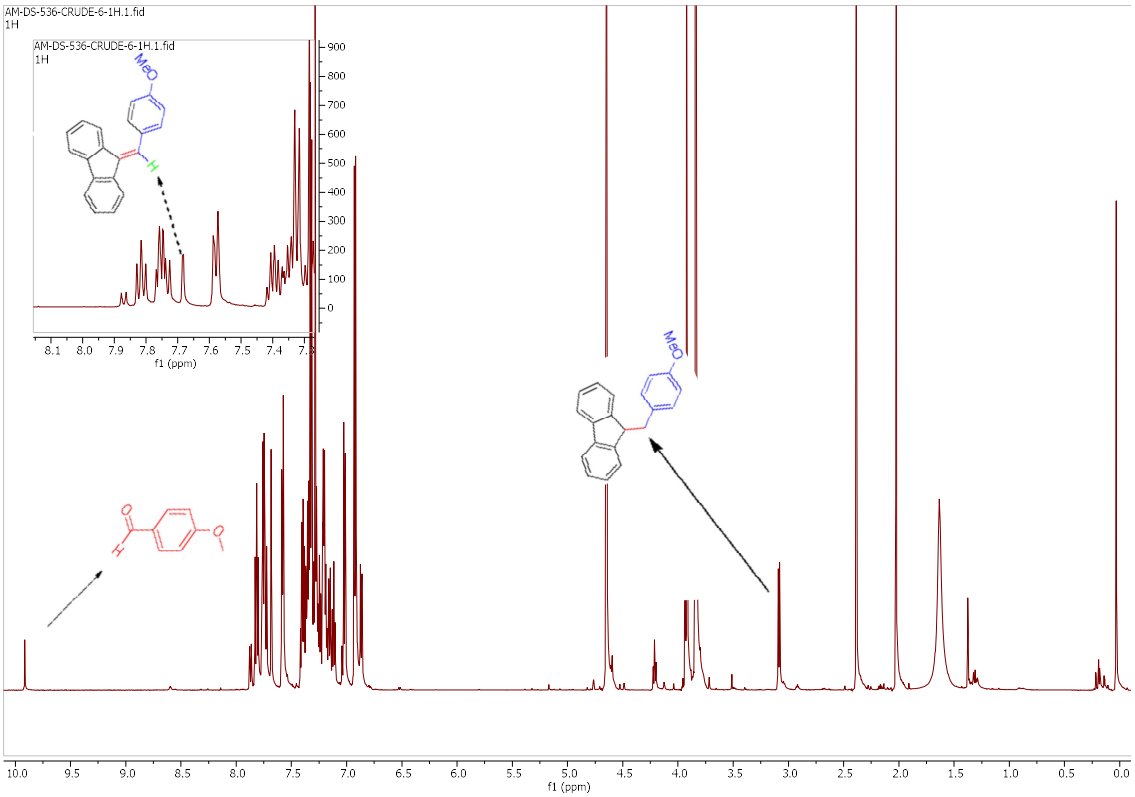


Figure S148. ^{1}H NMR Spectrum of Crude reaction mixture in $CDCl_3$.

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