A Passage from Pincer Complexes to Rationally Designed Phosphine-Free Co(III) Catalysts Supported by Pentadentate Ligand for Activation of Alcohols: Studies on sp^3 C–H Alkylation of 9H-Fluorene and Quinoline Synthesis

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1. Experimental

1.1 Materials used

All the chemicals and solvents were purchased from commercially available sources such as Aldrich, Merck, TCI, SRL, and ACROS organics and used as received. Analytical grade reagents and solvents were used for whole activities and spectroscopic studies. 2,6-Bis(1-phenylhydrazinyl) pyridine was synthesized according to literature.[1] UV-Vis. Spectra were recorded using a UV-Vis Spectrophotometer (UV-2600 from Shimadzu). IR spectra were recorded on an ALPHA II compact FT-IR spectrometer with the use of KBr pellets (16 scans in cm^{-1}). NMR spectra were recorded using Bruker Avance III 500 MHz (AV 500) and Jeol 500MHz spectrometers in deuterated solvents. Chemical shift values in NMR are recorded in δ (ppm) values against TMS as internal standard. NMR coupling constants (J) are represented in hertz (Hz) values. Multiplets in the chemical shift are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triples), td (triplet of doublets).

1.2 X-ray crystallography

The X-ray data collection and processing of complex 1 and complex 2 were performed on a Bruker Kappa (D8 QUEST) Apex-IV CMOS diffractometer by using graphite monochromated Mo-Kα radiation (λ = 0.71070 Å) at 119 K and 105 K, respectively. The crystal structures were solved by SIR-92 GUI control methods. The Olex[2] software was used to solve the crystal structures and refine them using ShelXT and ShelXL, respectively.[3] The bond lengths and bond angles were computed with the help of MERCURY software. Additionally, ORTEP[4] images was generated using the same MERCURY program. The hydrogen atoms were placed in geometrically determined positions and refined using the riding model. The accompanying supplementary information (SI) files contains pertinent crystallographic parameters.

2. Synthesis

2.1 Synthesis of Ligand BPAPA-H = (2-(bis(pyridin-2-ylmethyl)amino)-*N*'-phenyl-*N*'-(pyridin-2-yl)acetohydrazide)

Bis(pyridin-2-ylmethyl)glycine (1.29 g, 3.6 mmol) was dissolved in 15–20 mL dimethylformamide solution and then cooled on an ice bath. To this solution, 1070.23 mg (7.92 mmol) of 1-hydroxybenzotriazole (HOBT) and 817 mg (3.96 mmol) of dicyclohexylcarbodiimide (DCC) were added directly and the mixture was stirred for 5-10 min at 0 °C. Subsequently, a batch of 2-(1-phenylhydrazineyl)pyridine (666 mg, 3.6 mmol) was added to the reaction mixture with stirring for an additional 3 hours on the same ice bath. Afterward, the ice bath was removed and the stirring was continued for 24 hours at room temperature. The white precipitate of *N*,*N*'-dicyclohexylurea was removed by filtration, and the product was extracted with ethyl acetate and water. The ethyl acetate layer was dried using a rotatory evaporator, yielding an orange-red oil which was purified by column chromatography (using hexane and ethyl acetate as eluents) to give a red oil product. Yield - 998 mg (65%). Selected IR data (KBr, ν_{max}/cm^{-1}): 1663 $\nu_{C=O\ amide,}$ 1391. UV–visible [ACN, λ_{max}/nm ($\varepsilon/M^{-1}cm^{-1}$)]: 303.8 (6961.05), 269.45 (15498.94). **^{1}H** NMR (500 MHz, $CDCl_3$) δ 11.33 (s, 1H), 8.49 (d, *J* = 4.1 Hz, 2H), 8.10 (d, *J* = 4.1 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.15 – 7.12 (m, 3H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.72 – 6.70 (m, 1H), 3.98 (s, 4H), 3.52 (s, 2H). **^{13}C{^{1}H}** NMR (126 MHz, $CDCl_3$) δ 171.14, 158.20, 157.18, 149.26, 147.74, 144.28, 137.40, 136.69, 129.00, 125.26, 124.22, 123.33, 122.46, 115.82, 109.33, 60.34, 57.66.

2.2 Synthesis of Co(III) complexes C1 & C2.

To a methanolic solution of ligand BPAPA-H (213 mg, 0.5 mmol in 5 mL methanol), triethylamine (101 mg, 1 mmol) was added and stirred for 20 minutes. To this mixture, a solution of $CoCl_2.6H_2O$ (119 mg, 0.5 mmol) or $CoBr_2$ (109 mg, 0.5 mmol) in 1 ml methanol was added dropwise. The solution turned greenish and was stirred for 4 hours under air. Subsequently, anhydrous $NaClO_4$ (98 mg, 0.7 mmol) dissolved in 1 mL methanol was added slowly dropwise and stirred for 1 hour. A brown precipitate formed, which was filtered and washed several times with diethyl ether. Yield: C1= 219mg (71%), C2 = 245 mg (74%), **Co2** = 231 mg (70%). Solubility – DMSO, methanol, ACN. Selected IR data (KBr, ν_{max}/cm^{-1}): **Co1** = 1648 $\nu_{C=O\ amide,}$ 1474, 1096 ν_{ClO4}, 768, 623 ν_{ClO4}, **Co2** = 1647 $\nu_{C=O\ amide,}$ 1474, 1090 ν_{ClO4}, 767, 627 ν_{ClO4}. UV–visible [ACN, λ_{max}/nm ($\varepsilon/M^{-1}cm^{-1}$)]: **Co1** = 345 (3369.22), 451 (642.29), **Co2** = 345 (4926.6), 258 (22427.13). **^{1}H** NMR (500 MHz, DMSO) of **Co1** = δ 9.12 (d, *J* = 6.0 Hz, 1H), 8.15 (t, *J* = 7.7 Hz, 2H), 8.06 (t, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 6.6 Hz, 2H), 7.41 (t, *J* = 6.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 5.7 Hz, 2H), 6.99 (d, *J* = 7.7 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 1H), 5.45 (d, *J* = 15.6 Hz, 2H), 4.94 (d, *J* = 15.6 Hz, 2H), 4.27 (s, 2H). **^{13}C{^{1}H}** NMR (126 MHz, DMSO) of **Co1** = *δ* 169.55, 163.52, 162.80, 149.84, 149.70 143.01, 142.33, 140.97, 129.86, 128.48, 127.19, 126.99, 124.83, 119.34, 111.19, 69.38, 69.20.

^{1}H NMR (500 MHz, DMSO) of **Co2** = *δ* 9.12 (d, *J* = 5.6 Hz, 1H), 8.16 (t, *J* = 7.5 Hz, 2H), 8.09 – 8.06 (m, 1H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 6.6 Hz, 2H), 7.42 (t, *J* = 6.3 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 5.6 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 1H), 5.45 (d, *J* = 15.4 Hz, 2H), 5.00 (d, *J* = 15.6 Hz, 2H), 4.29 (s, 2H). **^{13}C{^{1}H}** NMR (126 MHz, DMSO) of **Co2** = *δ* 169.56, 163.56, 162.80, 149.86, 149.71, 143.03, 142.41, 141.03, 129.91, 128.49, 127.21, 127.03, 124.96, 119.39, 111.23, 69.46, 69.37.

3. Characterization

3.1 Characterization of Ligand (BPAPA-H)

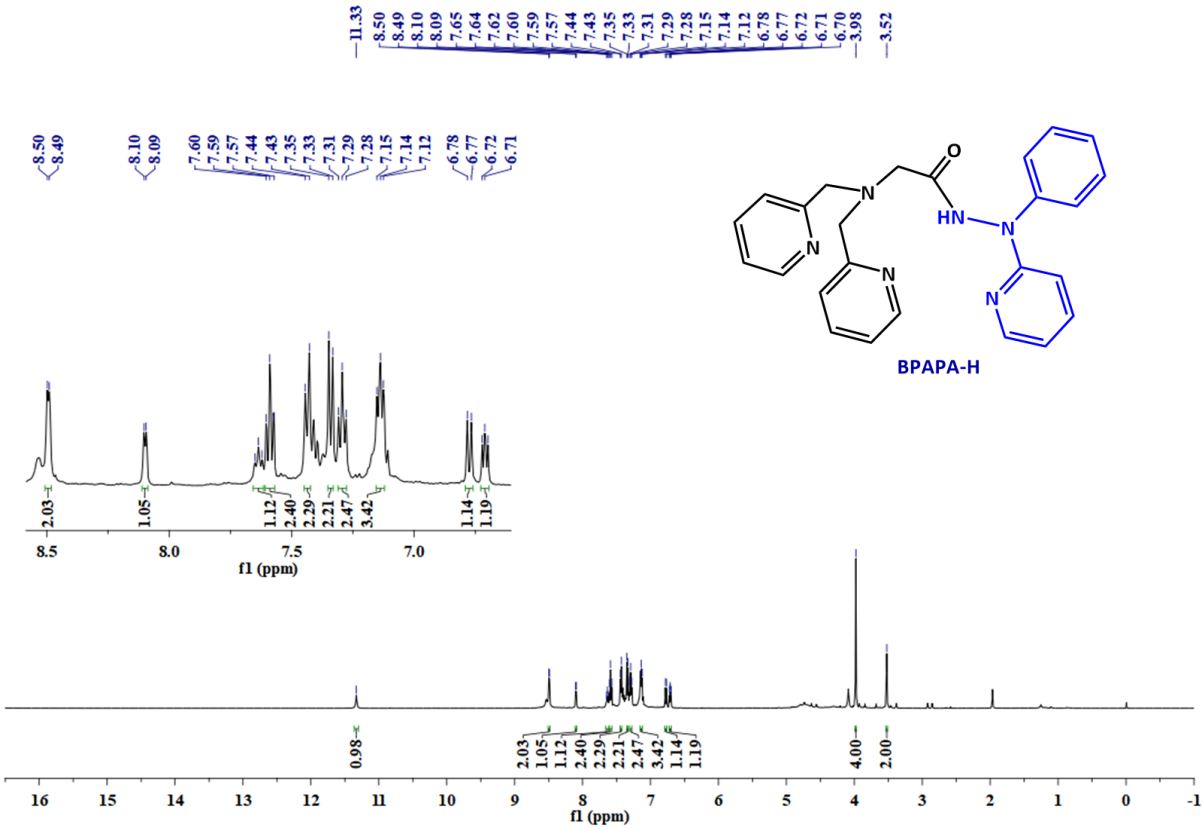


Figure S1- **^{1}H** NMR spectrum of BPAPA-H

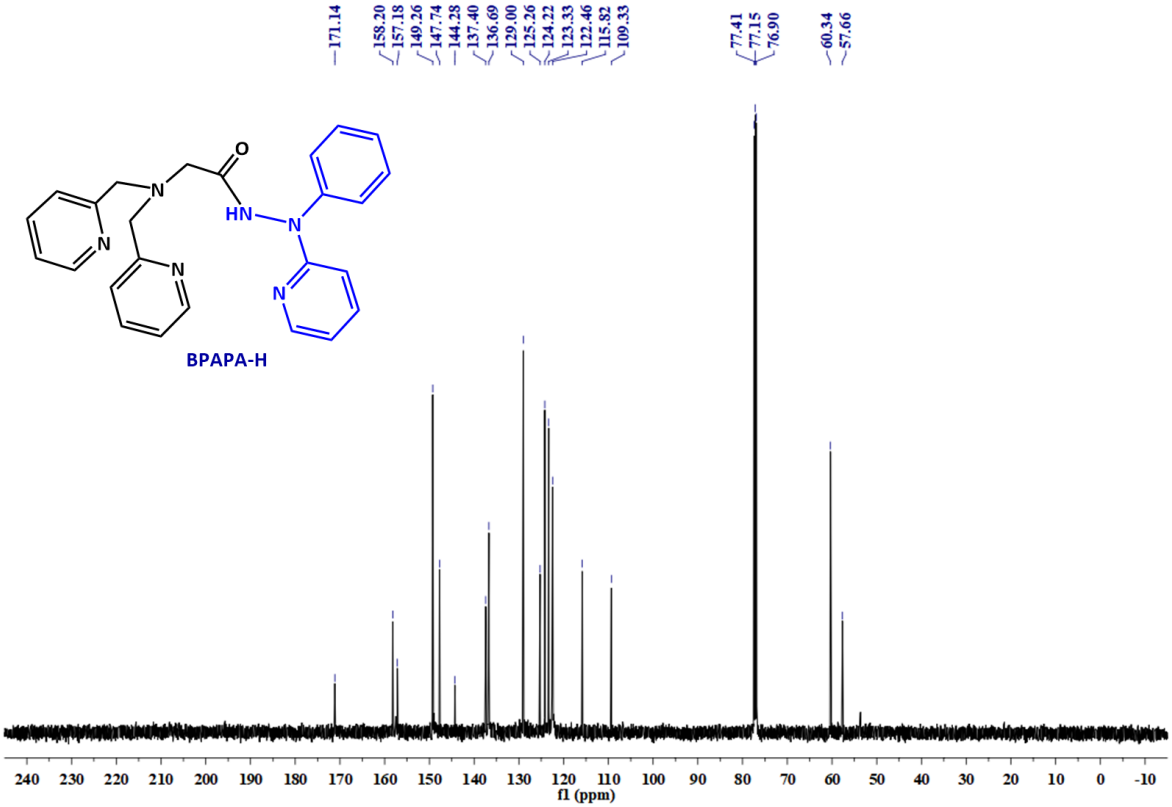


Figure S2 - $^{13}C\{^{1}H\}$ NMR spectrum of BPAPA-H

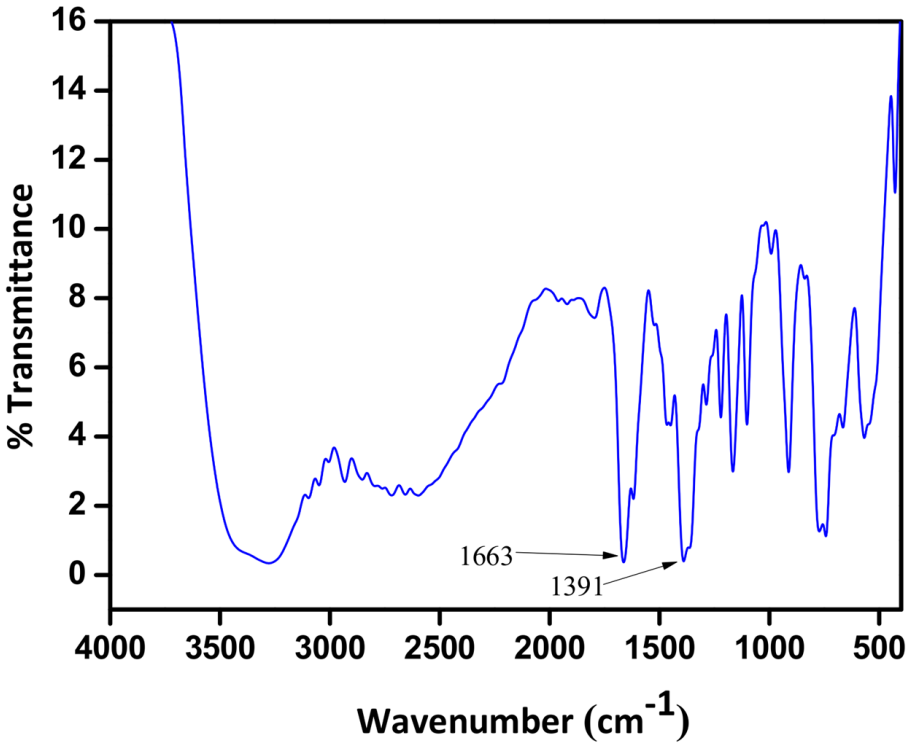


Figure S3 - IR spectrum of BPAPA-H

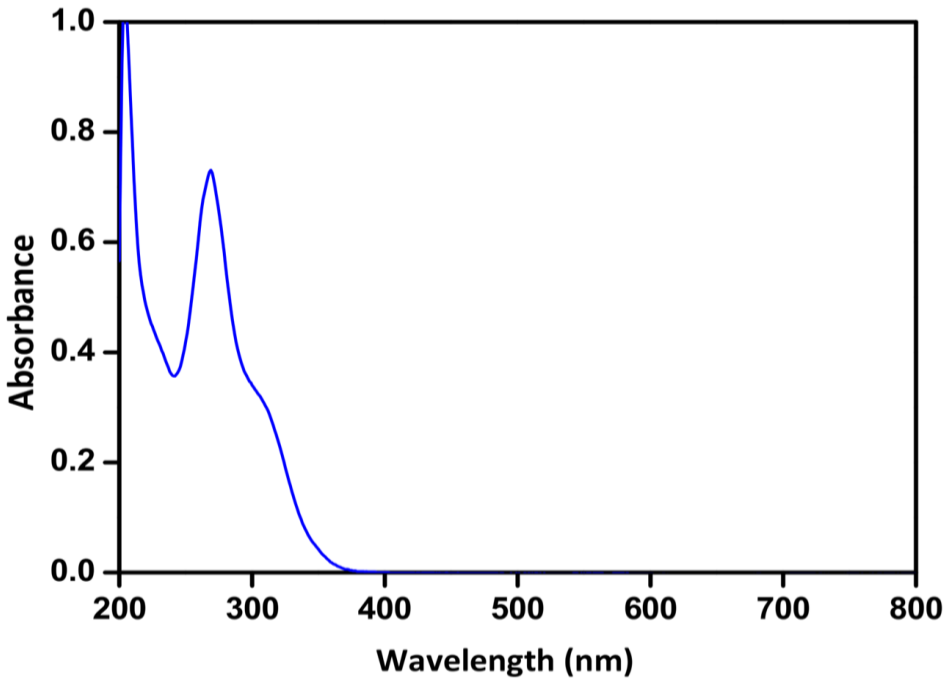


Figure S4 -UV visible spectrum of BPAPA-H

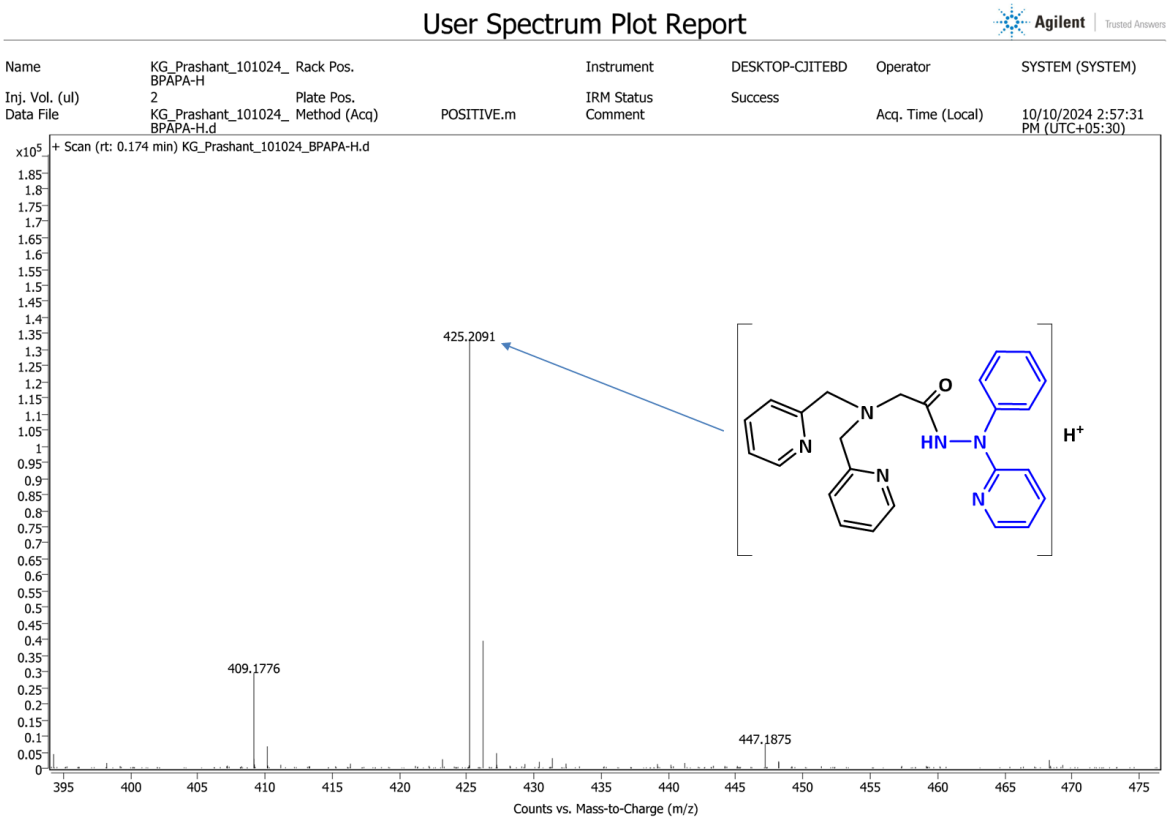


Figure S5 -HRMS spectrum of **BPAPA-H**

3.2 Characterization of complexes [Co(III)(BPAPA)Cl]ClO_4 and [Co(III)(BPAPA)Br]ClO_4

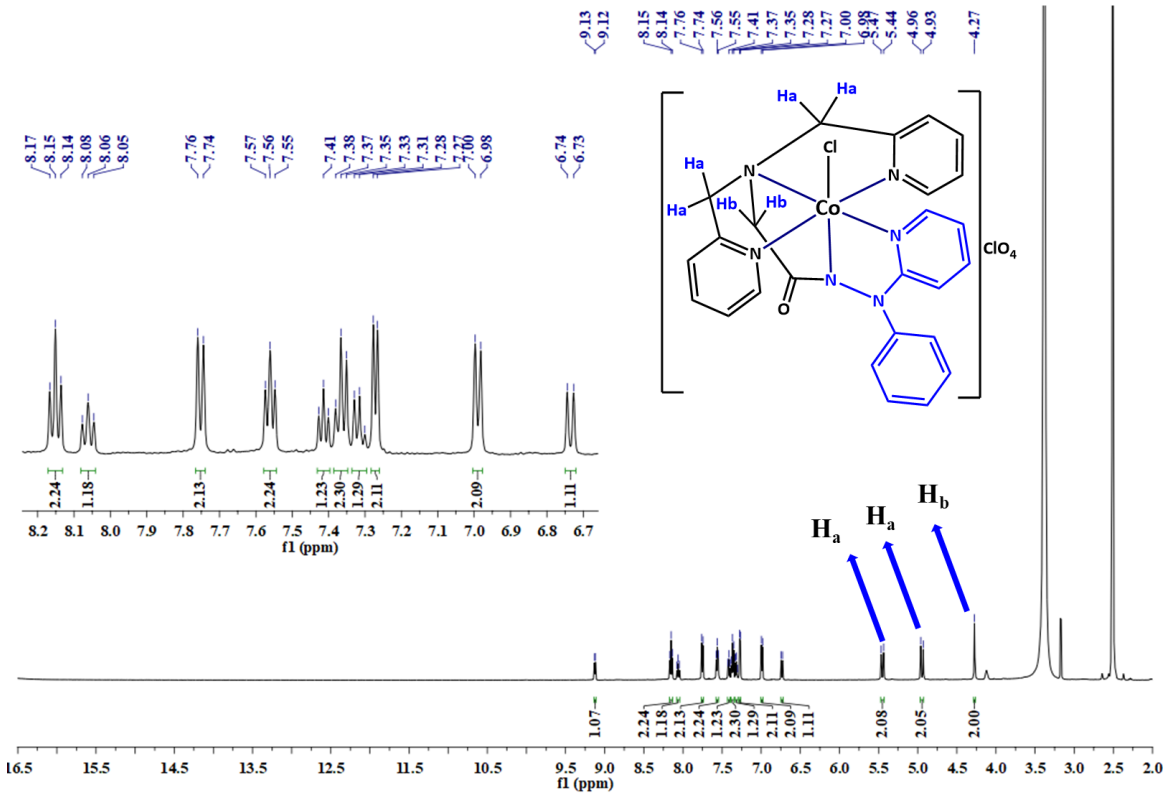


Figure S6 - ^{1}H NMR spectrum of **C1**

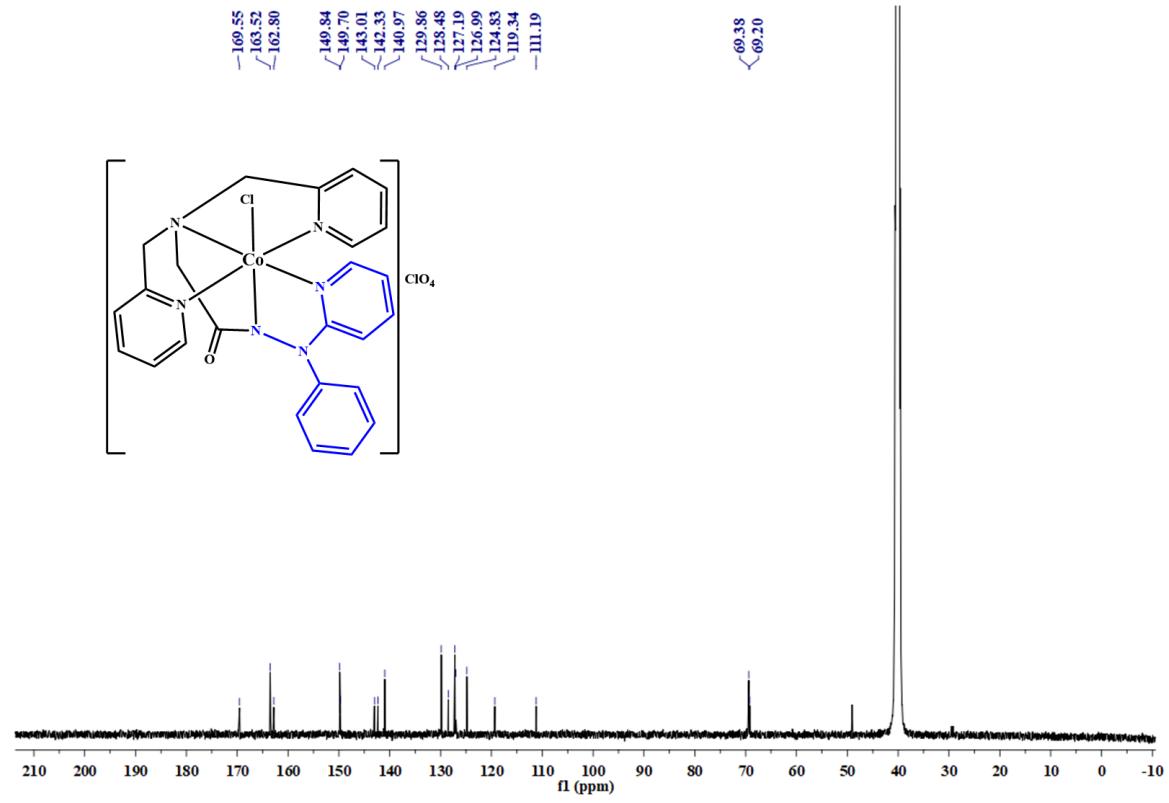


Figure S7 - ^{13}C{^{1}H} NMR spectrum of **C1**

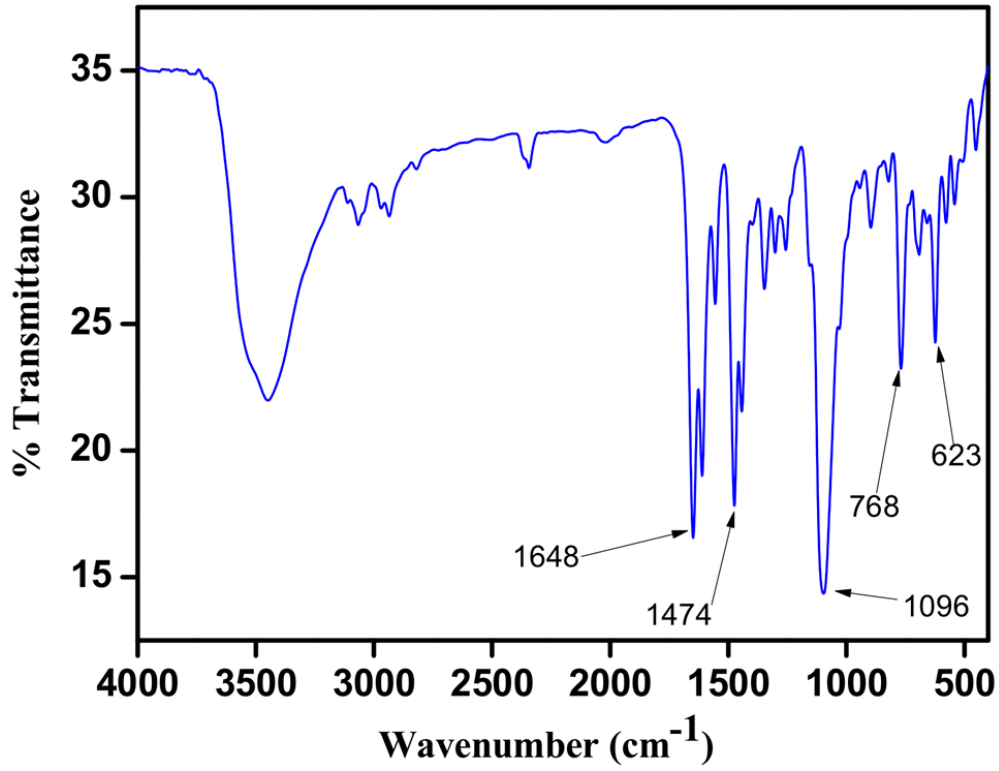


Figure S8 - IR spectrum of **C1**

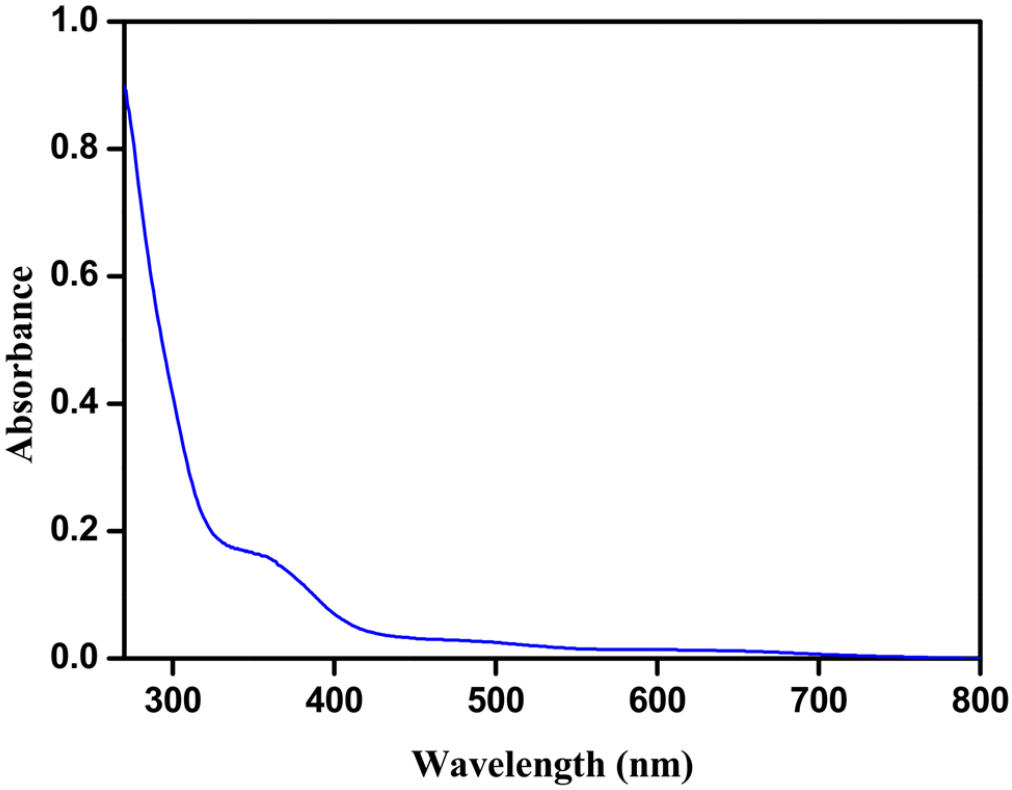


Figure S9 - UV visible spectrum of **C1**

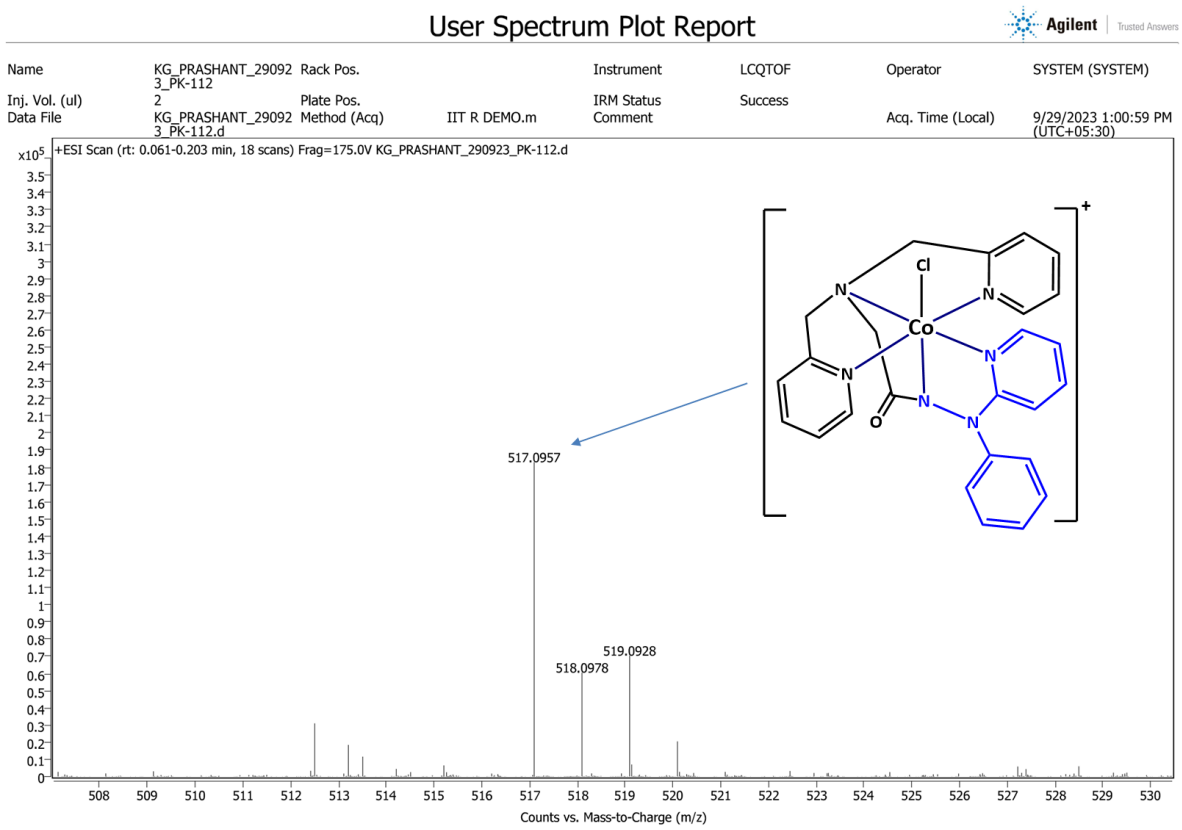


Figure S10 – HRMS spectrum of **C1**

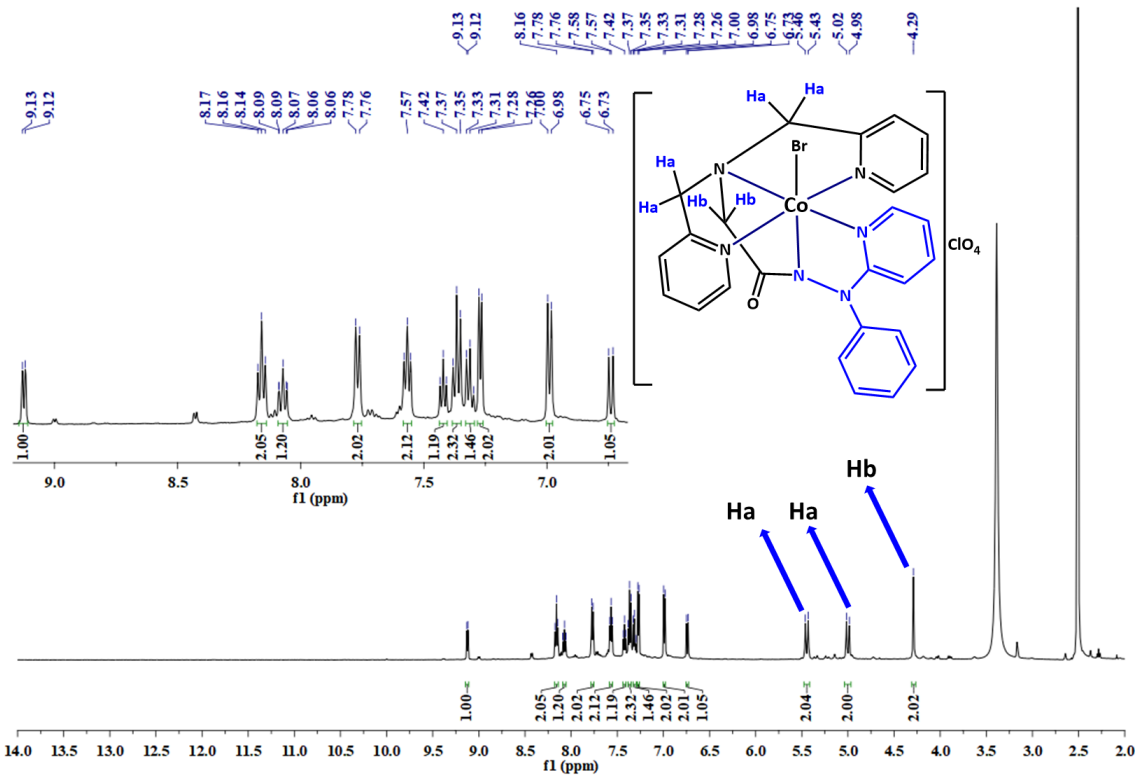


Figure S11 - ^{1}H NMR spectrum of **C2**

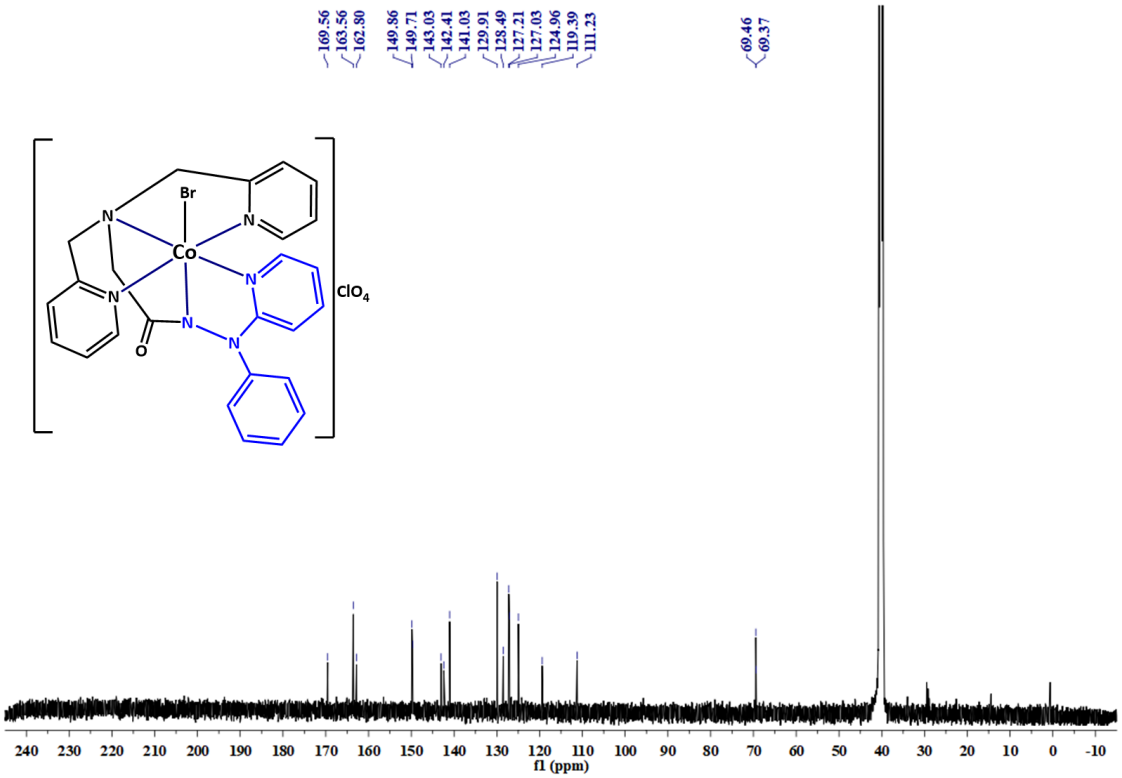


Figure S12 - $^{13}C\{^{1}H\}$ NMR spectrum of **C2**

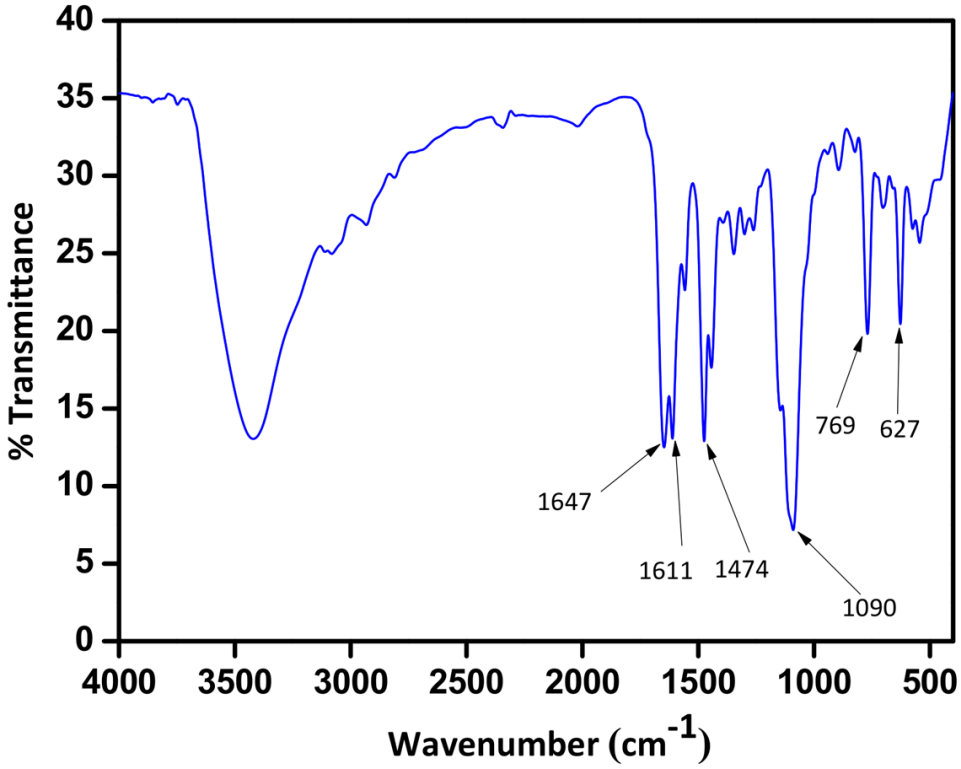


Figure S13 - IR spectrum of **C2**

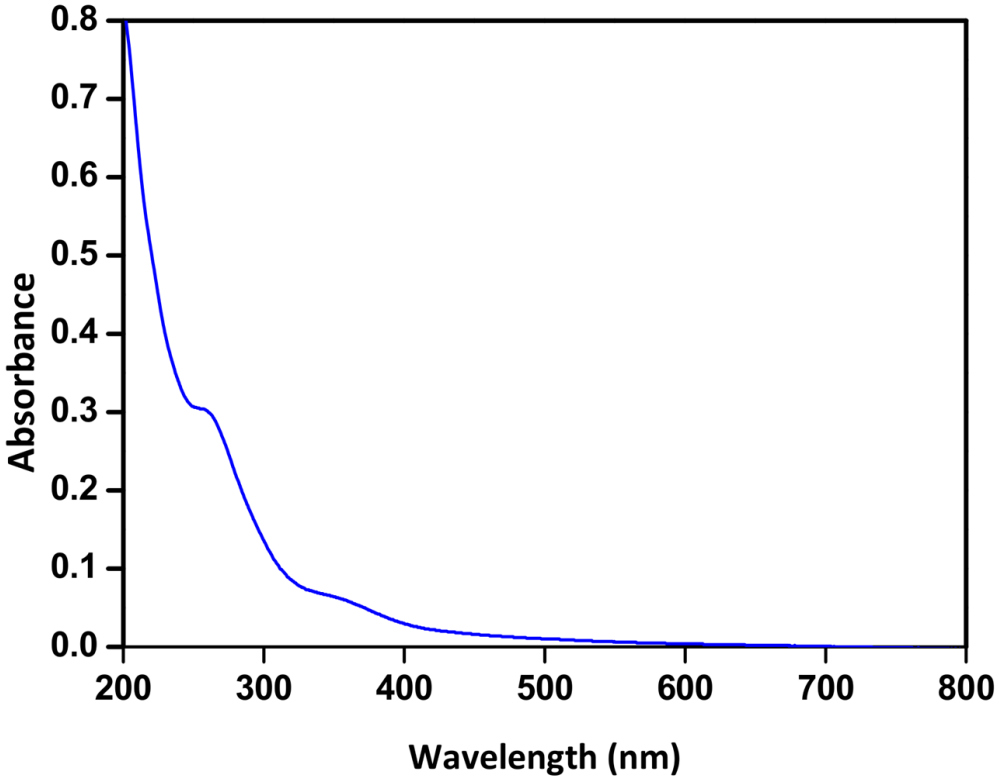


Figure S14 - UV visible spectrum of **C2**

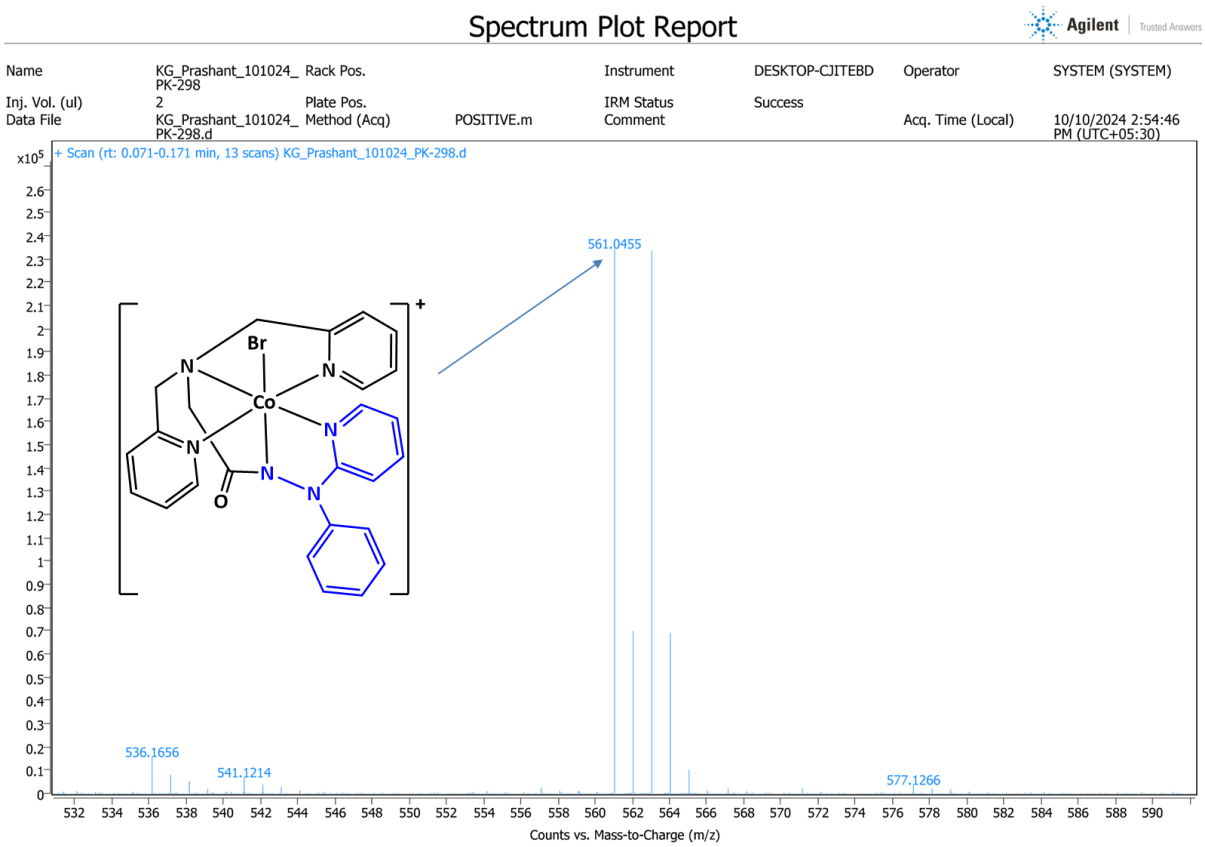


Figure S15 – HRMS spectrum of **C2**

4. Single crystal XRD characterization

4.1 Crystal data collections and refinement parameters

Identification code	[Co(III)BPAPA(Cl)]ClO_4	[Co(III)BPAPA(Br)]ClO_4
Empirical formula	$C_{50}H_{46}Cl_4Co_2N_{12}O_{10}$	$C_{27}BrClCoN_7O_5H_{26}$
Formula weight	1234.65	702.84
Temperature/K	104.00	109.0
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	8.6873(4)	9.1862(4)
b/Å	16.7926(8)	12.1495(5)
c/Å	18.9662(10)	14.5113(7)
α/°	85.258(2)	111.807(2)
β/°	76.904(2)	96.893(2)
γ/°	86.461(2)	100.568(2)
Volume/Å^3	2683.0(2)	1446.42(11)
Z	2	2
ρ_{calc}g/cm^3	1.528	1.614
μ/mm^{-1}	0.887	2.118
F(000)	1264.0	712.0
Crystal size/mm^3	0.202 × 0.114 × 0.04	0.138 × 0.03 × 0.013
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.42 to 56.714	4.61 to 56.738
Index ranges	-11 ≤ h ≤ 11, -22 ≤ k ≤ 22, -25 ≤ l ≤ 25	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19
Reflections collected	102746	54627
Independent reflections	13389 [R_{int} = 0.0497, R_{sigma} = 0.0321]	7216 [R_{int} = 0.0561, R_{sigma} = 0.0360]
Data/restraints/parameters	13389/0/703	7216/0/380
Goodness-of-fit on F^2	1.027	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0480, wR_2 = 0.1254	R_1 = 0.0373, wR_2 = 0.0909
Final R indexes [all data]	R_1 = 0.0559, wR_2 = 0.1310	R_1 = 0.0496, wR_2 = 0.0978
Largest diff. peak/hole / e Å^{-3}	3.68/-1.81	0.96/-0.45

Table S1 – Crystal data collections and refinement parameters for **C1** and **C2**

4.2 Single crystal structure of [Co(III)BPAPA(Cl)]ClO_4

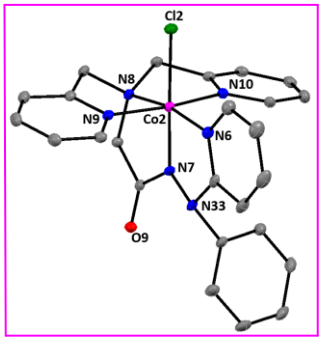


Figure S16 - ORTEP diagram (25% probability level) of [Co(III)BPAPA(Cl)]ClO_4 (**C1**). Hydrogen atoms connected to C atoms, anion and solvent molecule are omitted for clarity.

Bond	Bond Length/Å	Bond	Bond Length/Å
Co2Cl2	2.2486(7)	Co2N10	1.932(2)
Co2N6	1.927(2)	O9C45	1.238(3)
Co2N7	1.858(2)	N7N33	1.430(3)
Co2N8	1.951(2)	N7C45	1.334(3)

Table S2 – Selected bond lengths of [Co(III)BPAPA(Cl)]ClO_4 (**C1**)

Bond	Bond Angle (°)	Bond	Bond Angle (°)
N6Co2Cl2	97.45(7)	N7Co2N10	89.75(9)
N6Co2N8	168.16(9)	N8Co2Cl2	94.34(6)
N6Co2N9	95.05(9)	N9Co2Cl2	89.78(6)
N6Co2N10	95.80(9)	N9Co2N8	83.90(9)
N7Co2Cl2	178.58(7)	N10Co2Cl2	88.88(6)
N7Co2N6	82.32(9)	N10Co2N8	85.47(9)
N7Co2N8	85.92(9)	N10Co2N9	169.15(9)
N7Co2N9	91.63(9)		

Table S3 – Selected bond angles of [Co(III)BPAPA(Cl)]ClO_4 (**C1**)

4.3 Single crystal structure of [Co(III)BPAPA(Br)]ClO_4

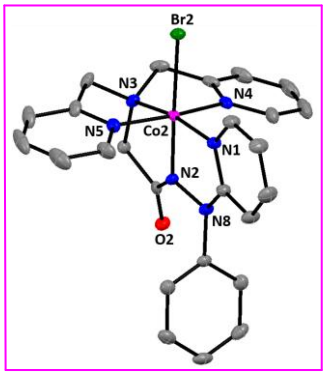


Figure S17 - ORTEP diagram (25% probability level) of [Co(III)BPAPA(Br)]ClO_4 (**C2**). Hydrogen atoms connected to C atoms, anion and solvent molecule are omitted for clarity.

Bond	Bond length (Å)	Bond	Bond length (Å)
Br2 Co2	2.4096(4)	Co2 N4	1.949(2)
Co2 N1	1.945(2)	N2 N8	1.416(3)
Co2 N2	1.8716(19)	O2 C17	1.228(3)
Co2 N3	1.9534(19)	N2 C17	1.334(3)

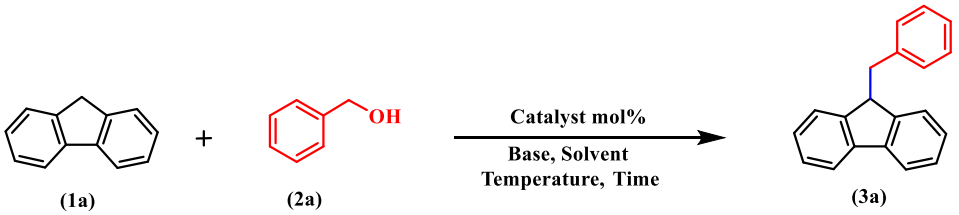
Table S4 – Selected bond lengths of [Co(III)BPAPA(Br)]ClO_4 (**C2**)

Bond	Bond angles (°)	Bond	Bond angles (°)
N1 Co2 Br2	96.09(6)	N3 Co2 Br2	95.26(6)
N1 Co2 N3	168.65(8)	N4 Co2 Br2	90.11(6)
N1 Co2 N4	95.50(9)	N4 Co2 N3	84.13(9)
N2 Co2 Br2	178.44(6)	N5 Co2 Br2	91.11(6)
N2 Co2 N1	82.56(8)	N5 Co2 N1	96.13(9)
N2 Co2 N3	86.08(8)	N5 Co2 N3	83.98(9)
N2 Co2 N4	89.23(9)	N5 Co2 N4	168.11(9)
N2 Co2 N5	89.82(9)		

Table S5 – Selected bond angles of [Co(III)BPAPA(Br)]ClO_4 (**C2**)

5. Optimization of reaction conditions for sp^3-H alkylation of fluorene

5.1. Optimization of base



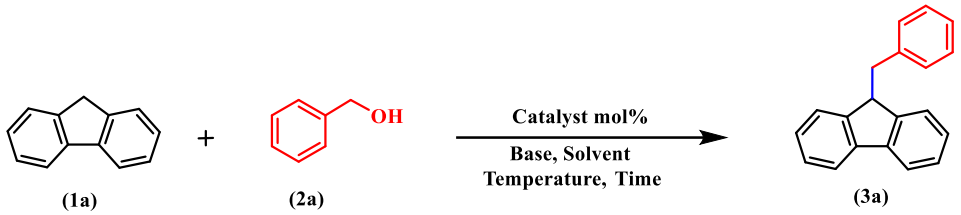
(1a) (2a) (3a)

Entry	Catalyst mol%	Base	Temp. (°C)	Solvent	Time (hrs)	Yield (%)
1	$CoCl_2.6H_2O$ 1 mol%	^{t}BuOK 0.75eq	100	Toluene	12	NR
2	$CoBr_2$ 1 mol%	^{t}BuOK 0.75eq	100	Toluene	12	NR
3	BPAPA-H 1 mol%	^{t}BuOK 0.75eq	100	Toluene	12	NR
4	C1, 1mol%	^{t}BuOK 0.75eq	100	Toluene	12	88
5	C2, 1mol%	^{t}BuOK 0.75eq	100	Toluene	12	94
6	C1, 1mol%	-	100	Toluene	12	NR
7	C2, 1mol%	-	100	Toluene	12	NR
8	-	^{t}BuOK 0.75eq	100	Toluene	12	NR
9	C2, 1mol%	^{t}BuOK 0.5eq	100	Toluene	12	71
10	C2, 1mol%	^{t}BuOK 0.75eq	100	Toluene	12	94
11	C2, 1mol%	^{t}BuOK 1.0eq	100	Toluene	12	94

12	C2, 1mol%	^{t}BuOK 1.5eq	100	Toluene	12	94

Table S6: Fluorene (1a, 0.5 mmol), benzyl alcohol (2a, 0.75 mmol), temperature 100 °C; base: 0.75 equivalent, solvent: Toluene 2ml, catalyst 1mol% and time 12 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

5.2. Optimization of solvent

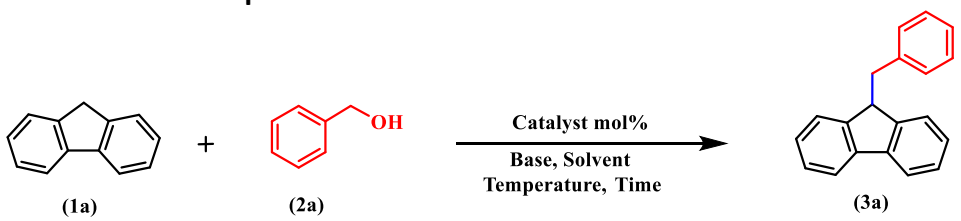


(1a) (2a) (3a)

Entry	Catalyst mol%	Base	Temp. (°C)	Solvent	Time (hrs)	Yield (%)
1	C2, 1mol%	^{t}BuOK 0.75eq	100	Toluene	12	94
2	C2, 1mol%	^{t}BuOK 0.75eq	100	Xylene	12	76
3	C2, 1mol%	^{t}BuOK 0.75eq	100	Benzene	12	67
4	C2, 1mol%	^{t}BuOK 0.75eq	100	DMF	12	NR
5	C2, 1mol%	^{t}BuOK 0.75eq	100	DMSO	12	NR
6	C2, 1mol%	^{t}BuOK 0.75eq	100	t-amyl alcohol	12	NR
7	C2, 1mol%	^{t}BuOK 0.75eq	100	1,4-dioxane	12	32%

Table S7: Fluorene (1a, 0.5 mmol), benzyl alcohol (2a, 0.75 mmol), temperature 100 °C; ^{t}BuOK: 0.75 equivalent, solvent: 2ml, catalyst 1mol% and time 12 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

5.3. Optimization of base equivalent

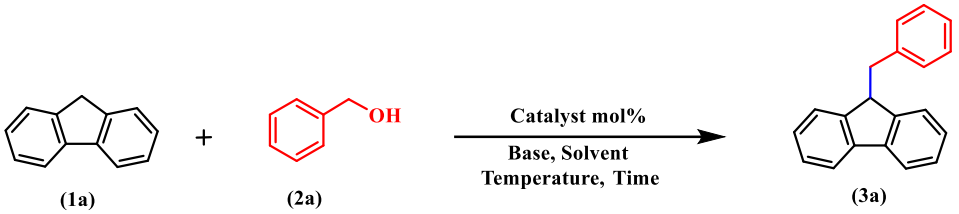


(1a) (2a) (3a)

Entry	Catalyst (Co1) mol%	Base	Temp. (°C)	Solvent	Time (hours)	Yield (%)
1	C2, 1mol%	KOH 0.75eq	100	Toluene	12	81
2	C2, 1mol%	NaOH 0.75eq	100	Toluene	12	74
3	C2, 1mol%	Cs_2CO_3 0.75eq	100	Toluene	12	62
4	C2, 1mol%	Na_2CO_3 0.75eq	100	Toluene	12	NR
5	C2, 1mol%	K_2CO_3 0.75eq	100	Toluene	12	NR
6	C2, 1mol%	$NaHCO_3$ 0.75eq	100	Toluene	12	NR

Table S8: Fluorene (1a, 0.5 mmol), benzyl alcohol (2a, 0.75 mmol), temperature 100 °C; ^{t}BuOK: 0.5 – 1.5 equivalent, solvent: Toluene 2ml, catalyst 1mol% and time 12 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

5.4. Optimization of catalyst mol%

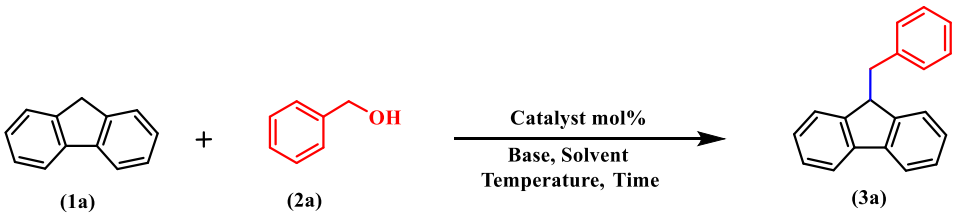


(1a) (2a) (3a)

Entry	Catalyst (C2) mol%	Base	Temp. (°C)	Solvent	Time (hrs)	Yield (%)
1	0.5 mol%	^{t}BuOK 0.75eq	100	Toluene	12	53
1	0.75 mol%	^{t}BuOK 0.75eq	100	Toluene	12	72
3	1.0 mol%	^{t}BuOK 0.75eq	100	Toluene	12	94
4	1.25 mol%	^{t}BuOK 0.75eq	100	Toluene	12	94

Table S9: Fluorene (1a, 0.5 mmol), benzyl alcohol (2a, 0.75 mmol), temperature 100 °C; ^{t}BuOK: 0.75 equivalent, solvent: Toluene 2ml, catalyst 0.5-1.5 mol% and time 12 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

5.5. Optimization of time

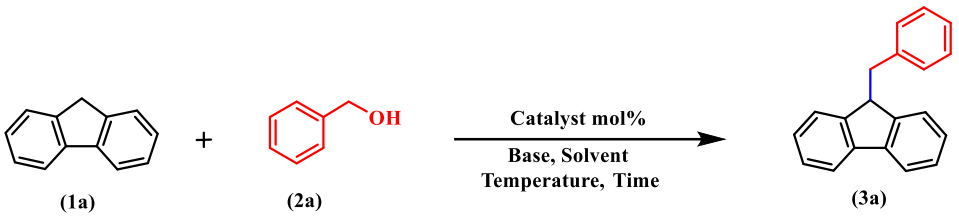


(1a) (2a) (3a)

Entry	Catalyst mol%	Base	Temp. (°C)	Solvent	Time (hrs)	Yield (%)
1	C2, 1mol%	^{t}BuOK 0.75eq	100	Toluene	10	77
2	C2, 1mol%	^{t}BuOK 0.75eq	100	Toluene	11	86
3	C2, 1mol%	^{t}BuOK 0.75eq	100	Toluene	12	94
4	C2, 1mol%	^{t}BuOK 0.75eq	100	Toluene	13	94
5	C2, 1mol%	^{t}BuOK 0.75eq	100	Toluene	14	94

Table S10: Fluorene (1a, 0.5 mmol), benzyl alcohol (2a, 0.75 mmol), temperature 100 °C; ^{t}BuOK: 0.75 equivalent, solvent: Toluene 2ml, catalyst 1.0 mol% and time 10-14 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

5.6. Optimization of temperature



(1a) (2a) (3a)

Entry	Catalyst (C2) mol%	Base	Temp. (°C)	Solvent	Time (hrs)	Yield (%)
1	C2, 1 mol%	^{t}BuOK 0.75eq	80	Toluene	12	64
2	C2, 1 mol%	^{t}BuOK 0.75eq	90	Toluene	12	78
3	C2, 1 mol%	^{t}BuOK 0.75eq	100	Toluene	12	94
4	C2, 1 mol%	^{t}BuOK 0.75eq	110	Toluene	12	94
5	C2, 1 mol%	^{t}BuOK 0.75eq	120	Toluene	12	94

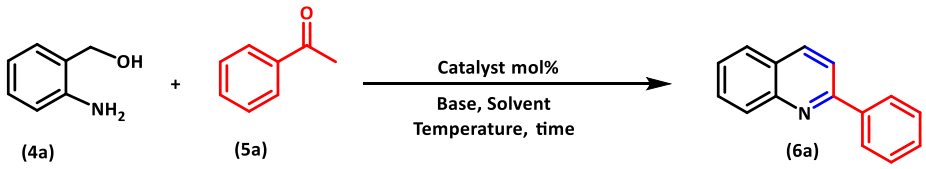
Table S11: Fluorene (1a, 0.5 mmol), benzyl alcohol (2a, 0.75 mmol), temperature 80-120 °C; ^{t}BuOK: 0.75 equivalent, solvent: Toluene 2ml, catalyst 1.0 mol% and time 12 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

5.7. General procedure for sp^3-H alkylation of fluorene

In a clean and dried 20 ml pressure tube filled with Fluorene derivatives (0.5 mmol), benzyl alcohol derivatives (0.75 mmol), ^{t}BuOK (0.75 equivalent), and catalyst (C2 1.0 mol%). The vial was filled with 2.0 mL of toluene and an inert atmosphere was created by purging N_2 to the reaction tube. The reaction mixture was heated in an oil bath at 100 °C for the next 10 hours. TLC was used to track the reaction's completion and ethyl acetate (4 × 5 mL) was used to extract the reaction mixture. After being dried over anhydrous Na_2SO_4, the resultant organic layer of ethyl acetate was concentrated under reduced pressure. Hexane/ethyl acetate was used as an eluent in column chromatography on silica (100–200 mesh size) to purify the resultant organic mixture. **^{1}H** and **^{13}C{^{1}H}** NMR spectroscopy was used to characterize the isolated products.

6. Optimization of reaction conditions for quinoline synthesis

6.1. Optimization of base

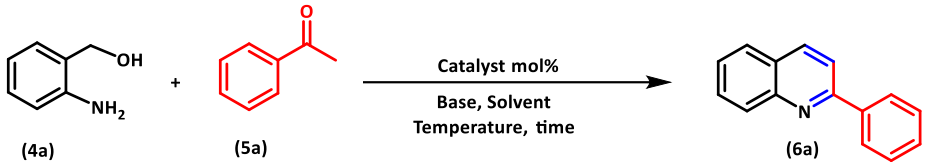


(4a) (5a) (6a)

Entry	Catalyst mol%	Base	Temp. (°C)	Solvent	Time (hrs)	Yield (%)
1	$CoCl_2.6H_2O$ 1 mol%	^{t}BuOK 0.75eq	100	Toluene	12	NR
2	$CoBr_2$ 1 mol%	^{t}BuOK 0.75eq	100	Toluene	12	NR
3	BPAPA-H 1 mol%	^{t}BuOK 0.75eq	100	Toluene	12	NR
4	C1, 1mol%	^{t}BuOK 0.75eq	100	Toluene	12	91
5	C2, 1 mol%	^{t}BuOK 0.75eq	100	Toluene	12	95
6	-	^{t}BuOK 0.75eq	100	Toluene	12	NR
7	C1, 1mol%	-	100	Toluene	12	NR
8	C2, 1mol%	-	100	Toluene	12	NR
9	C2, 1 mol%	^{t}BuOK 0.5eq	100	Toluene	12	74
10	C2, 1 mol%	^{t}BuOK 0.75eq	100	Toluene	12	95
11	C2, 1 mol%	^{t}BuOK 1.0eq	100	Toluene	12	95
12	C2, 1 mol%	^{t}BuOK 1.5eq	100	Toluene	12	95

Table S12: 2-amino benzyl alcohol (4a, 0.5 mmol), acetophenone (5a, 0.5 mmol), temperature 100 °C; base: 1.0 equivalent, solvent: Toluene 2ml, catalyst 1mol% and time 12 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

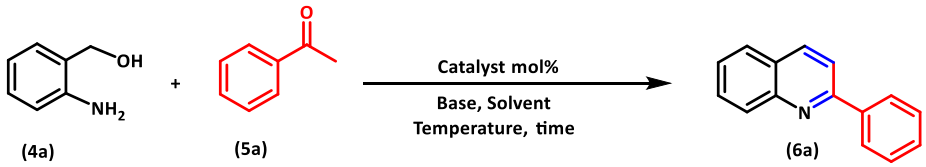
6.2. Optimization of base equivalent



Entry	Catalyst mol%	Base	Temp. (°C)	Solvent	Time (hrs)	Yield (%)
3	**C2, 1 mol%**	^{t}BuOK 0.75eq	100	Toluene	12	95
4	C2, 1 mol%	KOH 0.75eq	100	Toluene	12	86
5	C2, 1 mol%	NaOH 0.75eq	100	Toluene	12	78
6	C2, 1 mol%	Cs_2CO_3 0.75eq	100	Toluene	12	66
7	C2, 1 mol%	Na_2CO_3 0.75eq	100	Toluene	12	NR
8	C2, 1 mol%	K_2CO_3 0.75eq	100	Toluene	12	NR
9	C2, 1 mol%	$NaHCO_3$ 0.75eq	100	Toluene	12	NR

Table S13: 2-amino benzyl alcohol (4a, 0.5 mmol), acetophenone (5a, 0.5 mmol), temperature 100 °C; base: 1.0 equivalent, solvent: Toluene 2ml, catalyst 1mol% and time 12 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

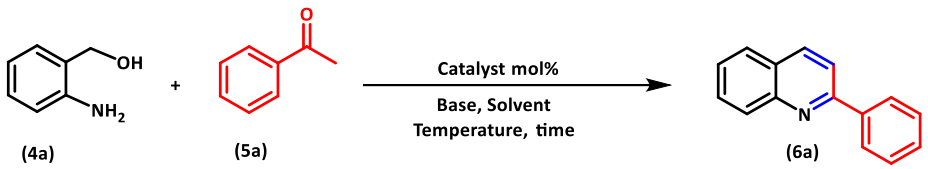
6.3. Optimization of solvent



Entry	Catalyst mol%	Base	Temp. (°C)	Solvent	Time (hrs)	Yield (%)
1	C2, 1 mol%	^{t}BuOK 0.75eq	100	Toluene	12	95
2	C2, 1 mol%	^{t}BuOK 0.75eq	100	Xylene	12	70
3	C2, 1 mol%	^{t}BuOK 0.75eq	100	Benzene	12	62
4	C2, 1 mol%	^{t}BuOK 0.75eq	100	DMF	12	NR
5	C2, 1 mol%	^{t}BuOK 0.75eq	100	DMSO	12	NR
6	C2, 1 mol%	^{t}BuOK 0.75eq	100	t-amyl alcohol	12	NR
7	C2, 1 mol%	^{t}BuOK 0.75eq	100	1,4-dioxane	12	25

Table S14: 2-amino benzyl alcohol (4a, 0.5 mmol), acetophenone (5a, 0.5 mmol), temperature 100 °C; ^{t}BuOK: 1.0 equivalent, solvent: Toluene 2ml, catalyst 1mol% and time 12 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

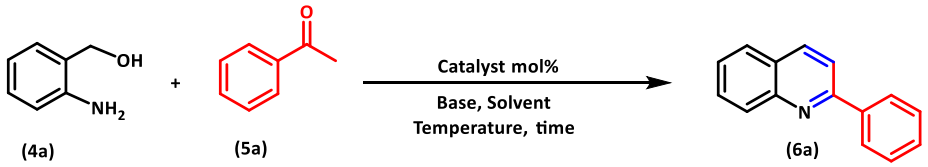
6.4. Optimization of catalyst mol%



Entry	Catalyst mol%	Base	Temp. (°c)	Solvent	Time (hrs)	Yield (%)
1	0.5 mol%	^{t}BuOK 0.75eq	100	Toluene	12	59
1	0.75 mol%	^{t}BuOK 0.75eq	100	Toluene	12	75
3	1.0 mol%	^{t}BuOK 0.75eq	100	Toluene	12	95
4	1.5 mol%	^{t}BuOK 0.75eq	100	Toluene	12	95

Table S15: 2-amino benzyl alcohol (4a, 0.5 mmol), acetophenone (5a, 0.5 mmol), temperature 100 °C; ^{t}BuOK: 1.0 equivalent, solvent: Toluene 2ml, catalyst 1mol% and time 12 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

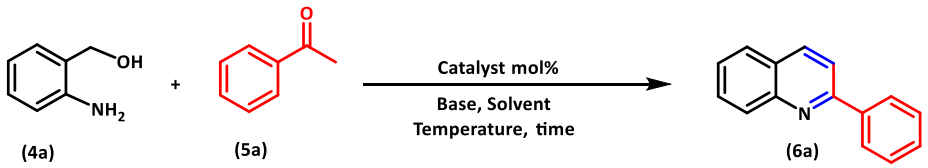
6.5. Optimization of time



Entry	Catalyst mol%	Base	Temp. (°c)	Solvent	Time (hrs)	Yield (%)
1	1 mol%	^{t}BuOK 0.75eq	100	Toluene	10	72
2	1 mol%	^{t}BuOK 0.75eq	100	Toluene	11	83
3	1 mol%	^{t}BuOK 0.75eq	100	Toluene	12	95
4	1 mol%	^{t}BuOK 0.75eq	100	Toluene	13	95

Table S16: 2-amino benzyl alcohol (4a, 0.5 mmol), acetophenone (5a, 0.5 mmol), temperature 100 °C; base: 1.0 equivalent, solvent: Toluene 2ml, catalyst 1mol% and time 12 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

6.6. Optimization of temperature



Entry	Catalyst mol%	Base	Temp. (°c)	Solvent	Time (hrs)	Yield (%)
1	1 mol%	^{t}BuOK 0.75eq	80	Toluene	10	63
2	1 mol%	^{t}BuOK 0.75eq	90	Toluene	10	80
3	1 mol%	^{t}BuOK 0.75eq	100	Toluene	10	95

4	1 mol%	^{t}BuOK 0.75eq	110	Toluene	10	95
5	1 mol%	^{t}BuOK 0.75eq	120	Toluene	10	95

Table S17: 2-amino benzyl alcohol (4a, 0.5 mmol), acetophenone (5a, 0.5 mmol), temperature 100-120 °C; base: 1.0 equivalent, solvent: Toluene 2ml, catalyst 1mol% and time 12 hours (under inert atmosphere of N_2). Isolated yields after column chromatography.

6.7. General procedure for quinoline synthesis

In a clean and dried 20 ml pressure tube filled with 2- amino benzyl alcohol derivative (0.5 mmol), acetophenone derivative (0.5 mmol), ^{t}BuOK (0.75 equivalent) and catalyst (C2 1.0 mol%). The charged vial was filled with 2.0 mL of toluene and an inert atmosphere was created by purging N_2 to the reaction tube. The reaction mixture was heated in an oil bath at 100 °C for the next 12 hours. TLC was used to track the reaction's completion and ethyl acetate (4 × 5 mL) was used to extract the reaction mixture. After being dried over anhydrous Na_2SO_4, the resultant organic layer of ethyl acetate was concentrated under reduced pressure. Hexane/ethyl acetate was used as an eluent in column chromatography on silica (100–200 mesh size) to purify the resultant organic mixture. **^{1}H** and **^{13}C{^{1}H}** NMR spectroscopy were used to characterize the isolated products.

7. Characterization of intermediates and side product (H_2) by GC-MS

7.1 Detection of in-situ formed 9-benzylidene-9H-fluorene during sp³ C–H alkylation of fluorene

In a 10 ml pressure tube Fluorene (0.5 mmol), 4-methoxy benzyl alcohol (0.75 mmol), ^{t}BuOK (0.75 equivalent) and catalyst (C2 1mol%) were taken in 2 ml toluene under inert atmosphere of N_2. Tube was sealed, heated at 100 ^{o}C for the next 4 hours, after that the reaction mixture was cooled at room temperature extracted with ethyl acetate and water. Formation of α,β unsaturated carbonyl compound (E)-1,3-bis(4-methoxyphenyl)prop-2-en-1-one and 3,5-bis(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole were then detected by GC-MS analysis.

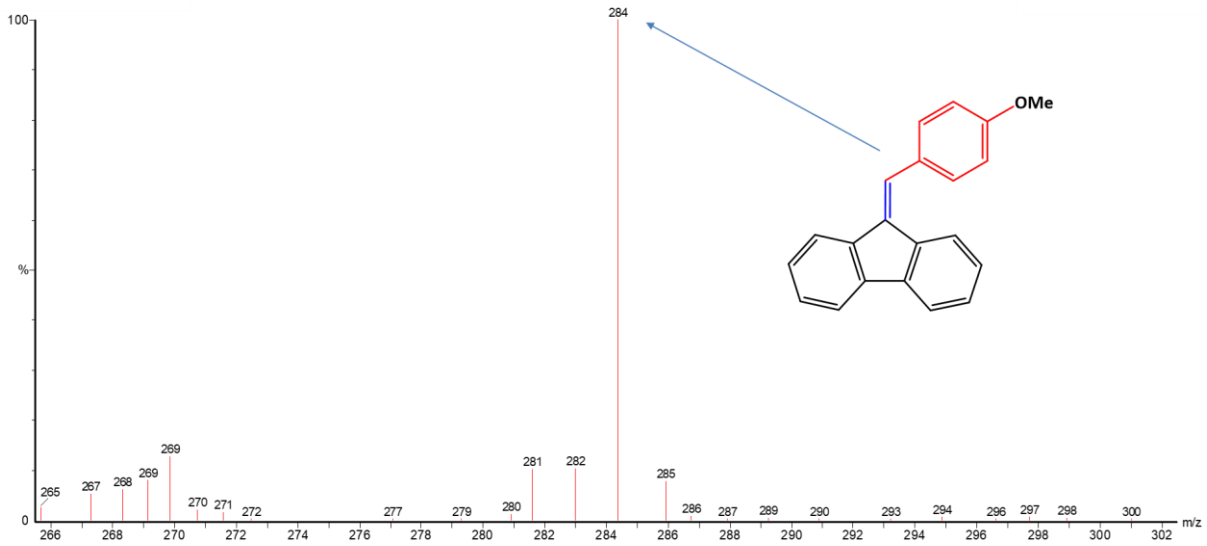
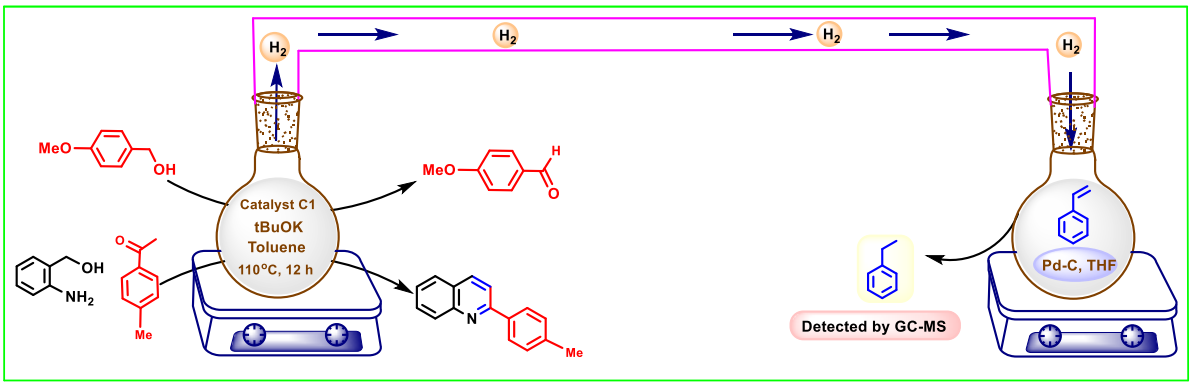


Figure S18 - GC–MS spectrum of 9-(4-methoxybenzylidene)-9H-fluorene

7.2 Detection of H_2 via styrene reduction in presence of 10% Pd-C and in-situ formed α–β unsaturated carbonyl compound



The two 20 ml round bottom flask was connected through a U-shaped tube. The first flask was charged with catalyst base and substrates, and the second flask was charged with styrene, Pd-C in THF at room temperature. The in situ-produced H_2 travelled from the first flask to the second flask and styrene was reduced to ethylbenzene by H_2 in the presence of Pd-C which was detected by GC-MS analysis.

Stoichiometry of reaction for dehydrogenation of 4-methoxy benzyl alcohol: In the first-round bottom flask, 4-methoxy benzyl alcohol (1.0 mmol), ^{t}BuOK (0.75 equivalent) and catalyst (C2, 1.0 mol%). The vial was filled with 2.0 mL of toluene and an inert atmosphere was created by purging N_2 to the reaction tube. The reaction mixture was heated in an oil bath at 100 °C for the next 12 hours. In the second-round bottom flask, styrene 0.5 mmol, Pd-C 10 mol% in THF 10 ml.

Stoichiometry of reaction for quinoline synthesis: In the first-round bottom flask 2-aminobenzyl alcohol (1.0 mmol), 4-methyl acetophenone (1.0 mmol), ^{t}BuOK (0.75 equivalent) and catalyst (C2, 1.0 mol%). The vial was filled with 2.0 mL of toluene and an inert atmosphere was created by purging N_2 to the reaction tube. The reaction mixture was heated in an oil bath at 100 °C for the next 12 hours. In the second-round bottom flask, styrene 0.5 mmol, Pd-C 10 mol% in THF 10 ml.

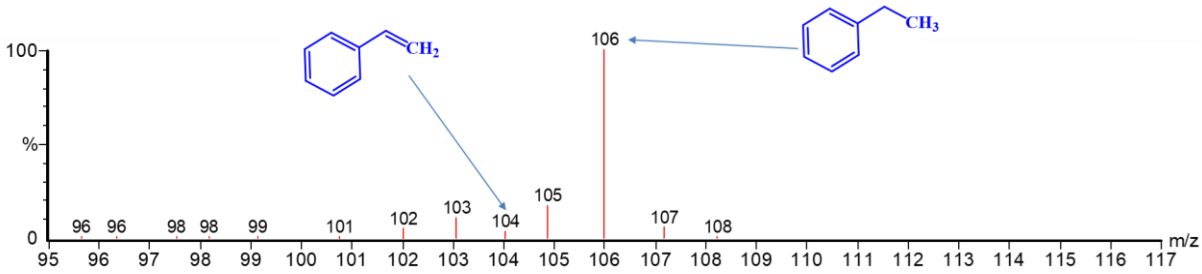


Figure S19- GC–MS characterization of styrene and ethyl benzene

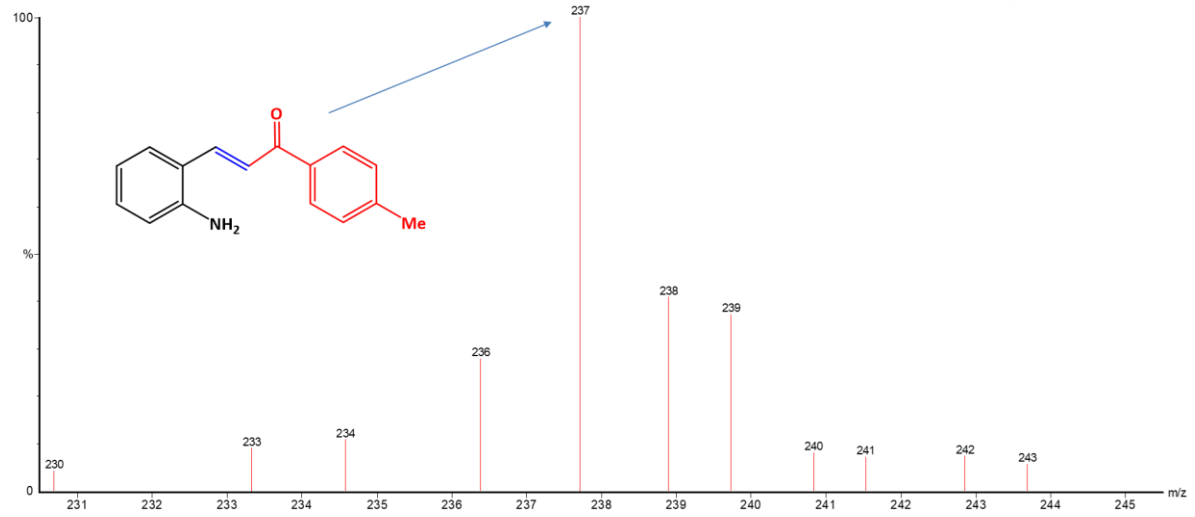


Figure S20 - GC–MS spectrum of (*E*)-3-(2-aminophenyl)-1-(p-tolyl)prop-2-en-1-one

7.3 Detection of Co-H and Co-alkoxy intermediates during catalysis

In a 10 ml pressure tube, benzyl alcohol (1.0 mmol), ^{t}BuOK (0.5 equivalent), C2 (1 mol%) was taken in 2 ml dry toluene. The pressure tube was then heated at 100 ^{o}C for the next 3 hours. Cool the reaction mixture at room temperature, and the reaction mixture was analysed by HRMS study. All the nickel-hydride and nickel-alkoxy intermediates formed by the reaction of catalysts C1 and C2 with benzyl alcohol are detected by HRMS. All experimental and calculated *m/z* values are shown in the table below.

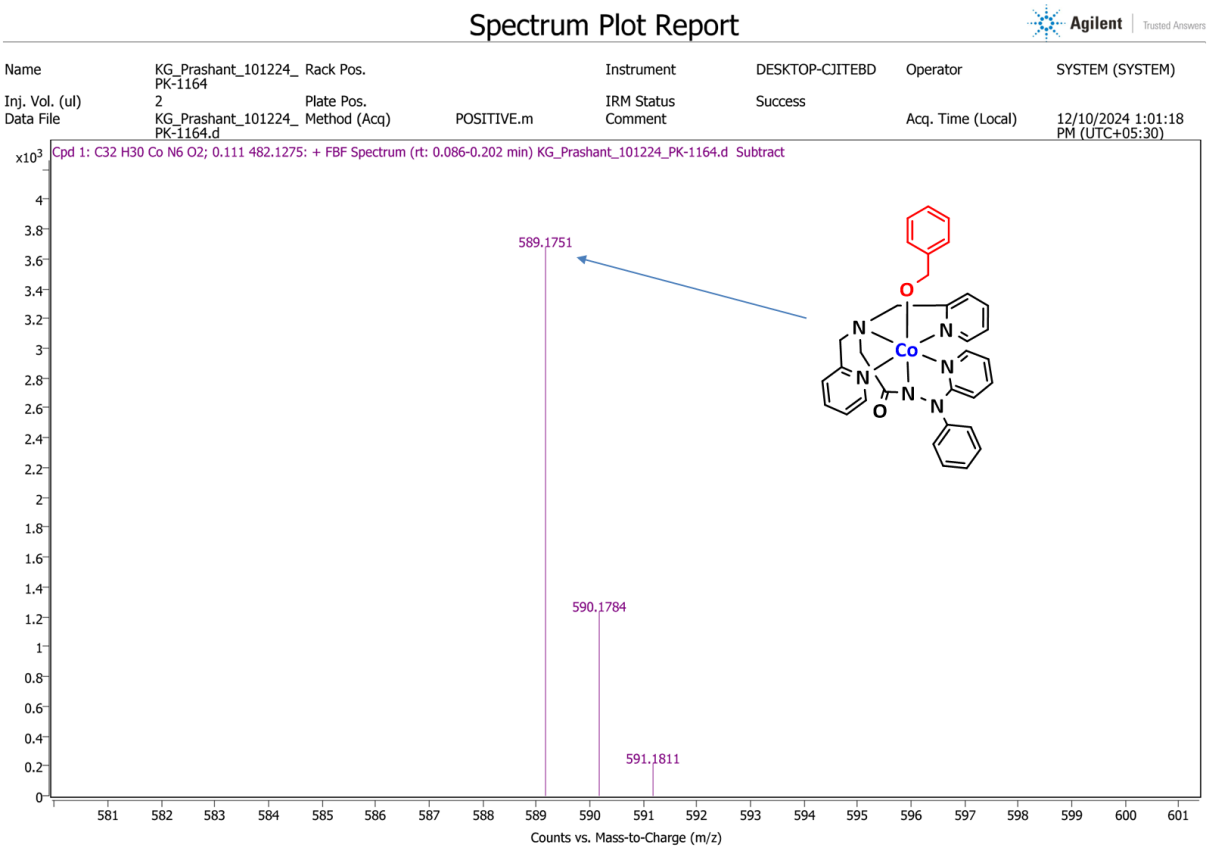


Figure S21 - HRMS spectrum of [Co(BPAPA)(O-CH_2Ph)]$^{+}$

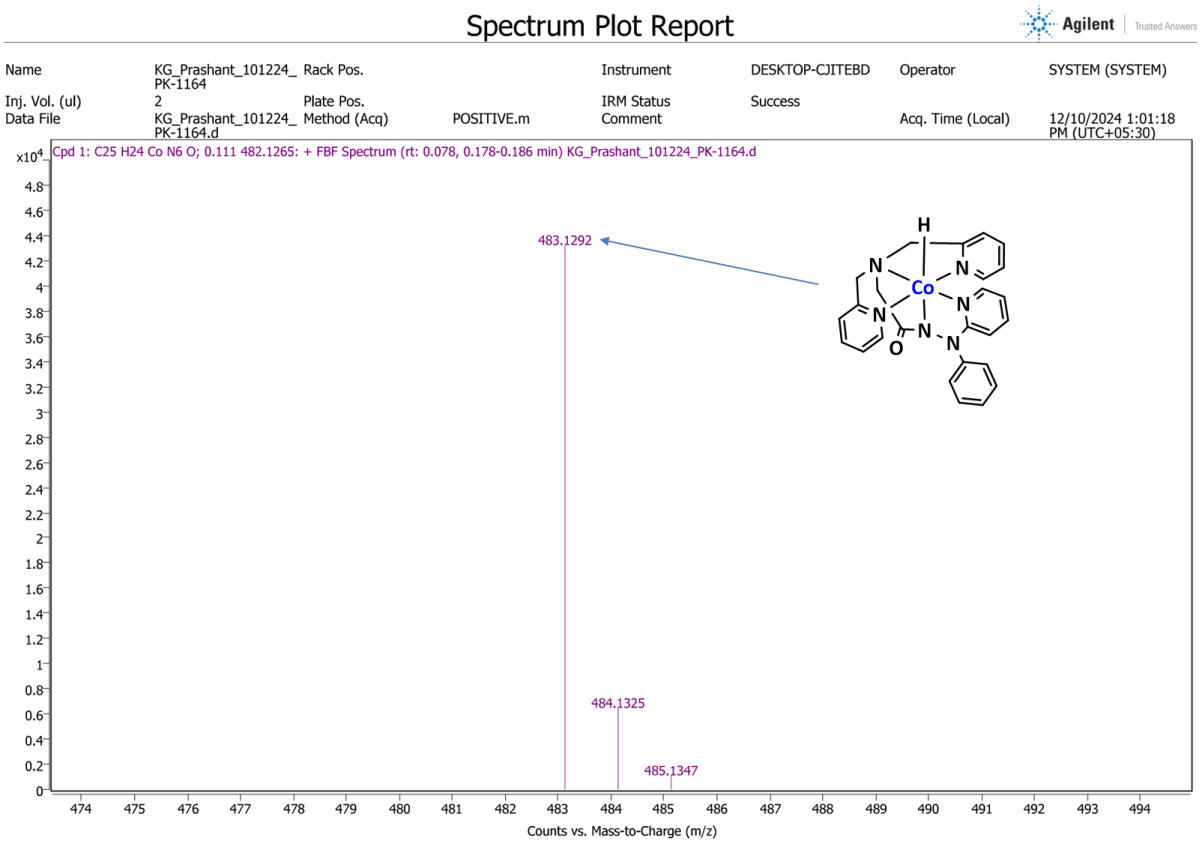
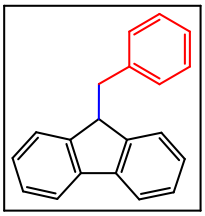


Figure S22 - HRMS spectrum of $[Co(BPAPA)(H)]^+$

8. ^1H and $^{13}C\{^1H\}$ NMR characterization of sp^3 C–H alkylated fluorene derivatives

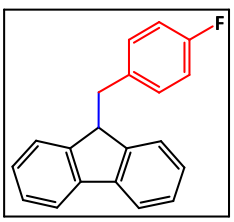
The NMR spectroscopic data for all the reported monoalkylated fluorene derivatives are in agreement with the previously reported literatures.[5–14]

9-benzyl-9H-fluorene (3a)



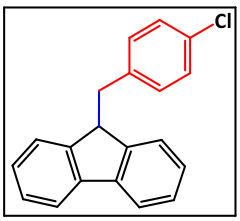
Yield: 94%, 120 mg. **^1H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.31 (m, 11H), 4.37 (t, *J* = 7.5 Hz, 1H), 3.25 (d, *J* = 7.6 Hz, 2H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 146.99, 140.99, 139.98, 129.69, 128.44, 127.28, 126.81, 126.52, 125.00, 119.99, 48.85, 40.23.

9-(4-fluorobenzyl)-9H-fluorene (3b)



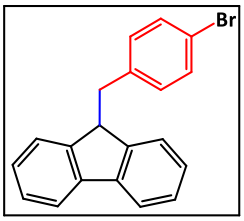
Yield: 85%, 117 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.18 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 4.26 (t, *J* = 7.3 Hz, 1H), 3.18 (d, *J* = 7.4 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.63, 160.69, 146.58, 140.98, 135.28 (d, *J* = 3.2 Hz), 130.94 (d, *J* = 7.8 Hz), 127.27, 126.76, 124.83, 119.96, 115.12, 114.95 48.77, 39.17. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.35 – -116.69 (m).

9-(4-chlorobenzyl)-9H-fluorene (3c)



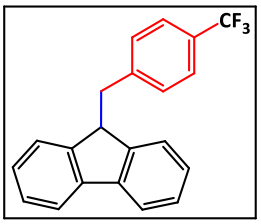
Yield: 89%, 129 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.32 – 7.25 (m, 6H), 7.15 (d, *J* = 8.3 Hz, 2H), 4.24 (t, *J* = 7.3 Hz, 1H), 3.15 (d, *J* = 7.4 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 146.42, 140.93, 138.07, 132.14, 130.90, 128.37, 127.30, 126.78, 124.79, 119.98, 48.52, 39.29.

9-(4-bromobenzyl)-9H-fluorene (3d)



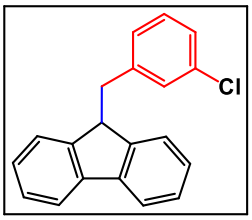
Yield: 91%, 153 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.44 (dd, *J* = 17.0, 8.0 Hz, 4H), 7.32 (td, *J* = 7.4, 1.0 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 4.25 (t, *J* = 7.3 Hz, 1H), 3.15 (d, *J* = 7.4 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.44, 140.96, 138.61, 131.35, 131.33, 127.35, 126.82, 124.81, 120.27, 120.02, 48.47, 39.37.

9-(4-(trifluoromethyl)benzyl)-9H-fluorene (3e)



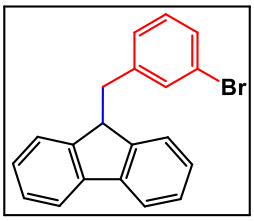
Yield: 88%, 143 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.33 (ddd, *J* = 7.3, 3.9, 1.0 Hz, 4H), 7.27 (d, *J* = 7.5 Hz, 2H), 4.30 (t, *J* = 7.3 Hz, 1H), 3.25 (d, *J* = 7.3 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 146.25, 143.74, 140.96, 129.87, 128.86, 128.61, 127.42, 126.87, 125.52, 125.16 (q, *J* = 3.7 Hz), 124.73, 123.36, 120.04, 48.33, 39.73. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -61.97 (s).

9-(3-chlorobenzyl)-9H-fluorene (3f)



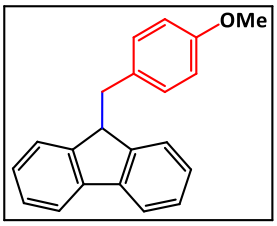
Yield: 93%, 135 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.28 (m, 4H), 7.25 (t, *J* = 7.9 Hz, 3H), 7.12 (d, *J* = 7.2 Hz, 1H), 4.26 (t, *J* = 7.5 Hz, 1H), 3.14 (d, *J* = 7.5 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 146.40, 141.83, 140.89, 134.09, 129.63, 129.53, 127.80, 127.35, 126.83, 126.66, 124.80, 119.98, 48.42, 39.73.

9-(3-bromobenzyl)-9H-fluorene (3g)



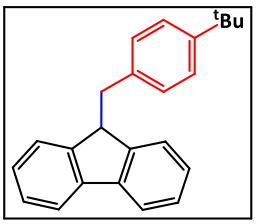
Yield: 92%, 154 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.47 – 7.41 (m, 4H), 7.32 (td, *J* = 7.4, 1.0 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 4.25 (t, *J* = 7.5 Hz, 1H), 3.13 (d, *J* = 7.5 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 146.40, 142.16, 140.91, 132.57, 129.85, 129.60, 128.28, 127.38, 126.85, 124.82, 122.40, 120.01, 48.45, 39.72.

9-(4-methoxybenzyl)-9H-fluorene (3h)



Yield: 96%, 138 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.35 (td, *J* = 7.4, 0.9 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 4.29 (t, *J* = 7.6 Hz, 1H), 3.90 (s, 3H), 3.17 (d, *J* = 7.6 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 158.27, 147.03, 140.98, 131.95, 130.56, 127.20, 126.76, 125.00, 119.95, 113.77, 55.29, 49.04, 39.27.

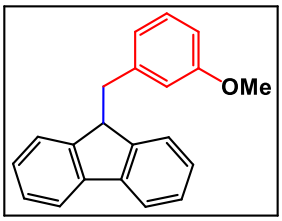
9-(4-(tert-butyl)benzyl)-9H-fluorene (3i)



Yield: 94%, 147 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.50 (dd, *J* = 11.9, 5.6 Hz, 4H), 7.39 – 7.32 (m, 6H), 4.36 (t, *J* = 7.6 Hz, 1H), 3.22 (d, *J* = 7.7 Hz, 2H), 1.53 (s, 9H).

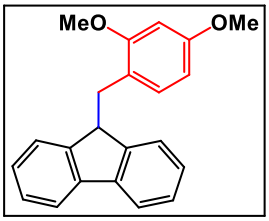
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 149.38, 147.23, 140.96, 137.05, 129.31, 127.22, 126.81, 125.35, 125.03, 119.95, 48.91, 39.78, 34.61, 31.65.

9-(3-methoxybenzyl)-9H-fluorene (3j)



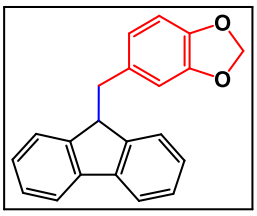
Yield: 97%, 139 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.45 – 7.42 (m, 2H), 7.34 – 7.29 (m, 5H), 6.93 – 6.89 (m, 2H), 6.86 (s, 1H), 4.32 (t, *J* = 7.5 Hz, 1H), 3.83 (s, 3H), 3.18 (d, *J* = 7.6 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 159.61, 146.87, 141.45, 140.93, 129.31, 127.22, 126.77, 124.96, 122.06, 119.91, 112.08, 55.22, 48.65, 40.14.

9-(2,4-dimethoxybenzyl)-9H-fluorene (3k)



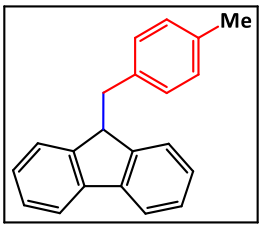
Yield: 89%, 141 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.26 (m, 4H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.63 (d, *J* = 2.1 Hz, 1H), 6.51 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.40 (t, *J* = 7.6 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.08 (d, *J* = 7.7 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 159.80, 158.90, 147.82, 140.82, 131.82, 126.88, 126.57, 125.12, 121.08, 119.73, 103.62, 98.54, 55.42, 55.37, 46.98, 35.00.

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



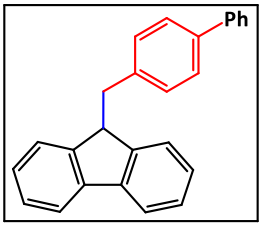
Yield: 91%, 137 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.42 (td, *J* = 7.5, 1.5 Hz, 2H), 7.33 – 7.27 (m, 4H), 6.83 – 6.79 (m, 2H), 6.69 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.00 (s, 2H), 4.22 (t, *J* = 7.5 Hz, 1H), 3.10 (d, *J* = 7.6 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 147.60, 146.76, 146.10, 140.91, 133.63, 127.19, 126.73, 124.90, 122.61, 119.90, 109.76, 108.07, 100.90, 48.89, 39.81.

9-(4-methylbenzyl)-9H-fluorene (3m)



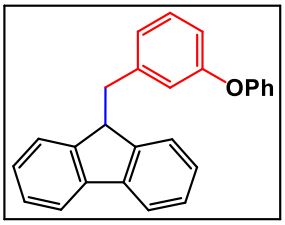
Yield: 94%, 127 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.32 (ddd, *J* = 13.1, 9.8, 4.3 Hz, 4H), 7.24 – 7.20 (m, 4H), 4.31 (t, *J* = 7.6 Hz, 1H), 3.18 (d, *J* = 7.6 Hz, 2H), 2.47 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 147.07, 140.93, 136.83, 135.87, 129.48, 129.08, 127.16, 126.72, 124.97, 119.89, 48.88, 39.73, 21.22.

9-([1,1'-biphenyl]-4-ylmethyl)-9H-fluorene (3n)



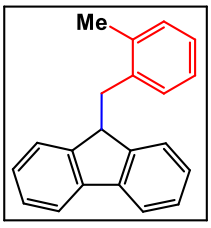
Yield: 86%, 143 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 4.0 Hz, 4H), 4.33 (t, *J* = 7.5 Hz, 1H), 3.22 (d, *J* = 7.6 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 146.86, 140.93, 140.91, 139.18, 138.99, 129.99, 128.81, 127.20, 127.01, 126.96, 126.74, 124.91, 119.90, 48.72, 39.77.

9-(3-phenoxybenzyl)-9H-fluorene (3o)



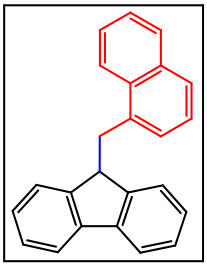
Yield: 84%, 146 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.33 (m, 4H), 7.29 – 7.23 (m, 5H), 7.12 (td, *J* = 7.4, 1.1 Hz, 1H), 7.00 – 6.88 (m, 5H), 4.23 (t, *J* = 7.4 Hz, 1H), 3.13 (d, *J* = 7.4 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 157.54, 157.02, 146.65, 141.80, 140.98, 129.85, 129.63, 127.30, 126.84, 124.93, 124.78, 123.13, 120.36, 119.98, 118.70, 117.37, 48.64, 39.90.

9-(2-methylbenzyl)-9H-fluorene (3p)



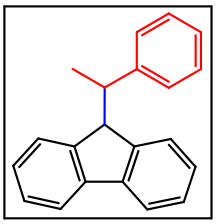
Yield: 92%, 124 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.30 (m, 6H), 7.23 (d, *J* = 7.1 Hz, 2H), 4.30 (t, *J* = 8.0 Hz, 1H), 3.16 (d, *J* = 8.1 Hz, 2H), 2.38 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 147.30, 140.94, 138.61, 136.95, 130.67, 130.61, 127.35, 126.92, 126.84, 126.15, 125.09, 120.06, 47.83, 37.92, 19.96.

9-(naphthalen-1-ylmethyl)-9H-fluorene (3q)



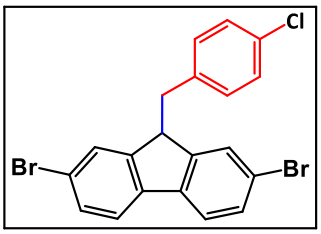
Yield: 95%, 146 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 2H), 7.71 (dt, *J* = 14.7, 6.9 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 6.9 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 2H), 4.57 (t, *J* = 7.9 Hz, 1H), 3.62 (d, *J* = 7.9 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 147.21, 140.91, 136.14, 134.21, 132.19, 129.25, 128.41, 127.67, 127.32, 126.82, 126.25, 125.85, 125.49, 125.31, 123.92, 120.02, 47.74, 38.15.

9-(1-phenylethyl)-9H-fluorene (3r)



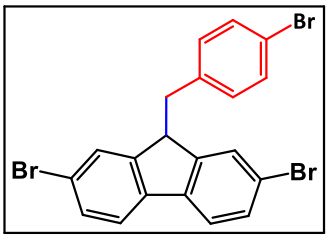
Yield: 88%, 119 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 11.8, 7.5 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.45 – 7.31 (m, 8H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 4.36 (d, *J* = 4.5 Hz, 1H), 3.78 – 3.70 (m, 1H), 1.00 (d, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 146.58, 144.66, 144.61, 141.85, 141.41, 128.23, 128.14, 127.13, 127.08, 126.86, 126.36, 126.29, 125.70, 124.34, 119.75, 119.67, 54.25, 41.93, 13.95.

2,7-dibromo-9-(4-chlorobenzyl)-9H-fluorene (3s)



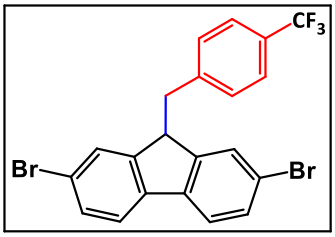
Yield: 87%, 195 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 4H), 7.33 (s, 2H), 7.26 (dd, *J* = 8.6, 2.0 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 4.08 (t, *J* = 7.2 Hz, 1H), 3.06 (d, *J* = 7.2 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 147.99, 138.88, 136.78, 132.59, 130.72, 130.65, 128.53, 128.09, 121.30, 121.00, 48.39, 38.79.

2,7-dibromo-9-(4-bromobenzyl)-9H-fluorene (3t)



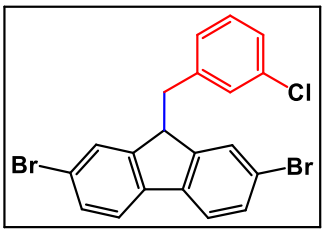
Yield: 90%, 222 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.46 (ddd, *J* = 8.1, 1.8, 0.5 Hz, 2H), 7.39 – 7.36 (m, 2H), 7.33 – 7.31 (m, 2H), 6.97 – 6.93 (m, 2H), 4.12 (t, *J* = 7.1 Hz, 1H), 3.05 (d, *J* = 7.1 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 148.01, 138.98, 137.31, 131.52, 131.17, 130.72, 128.16, 121.39, 121.04, 120.71, 48.40, 38.92.

2,7-dibromo-9-(4-(trifluoromethyl)benzyl)-9H-fluorene (3u)



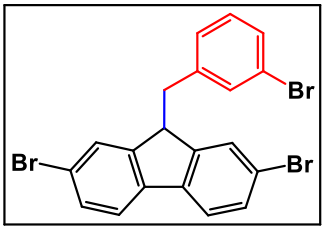
Yield: 86%, 207 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 6H), 7.29 (s, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 4.17 – 4.10 (m, 1H), 3.14 (t, *J* = 5.8 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 147.81, 142.47, 138.96, 130.81, 129.81, 129.30, 129.04, 128.78, 128.12, 125.37 (q, *J* = 3.78 Hz), 123.20, 121.43, 121.09, 48.23, 39.25. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.19 (s).

2,7-dibromo-9-(3-chlorobenzyl)-9H-fluorene (3v)



Yield: 89%, 200 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 4H), 7.30 – 7.24 (m, 4H), 7.19 (s, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 4.06 (s, 1H), 3.02 (d, *J* = 7.4 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 147.96, 140.63, 138.80, 134.33, 130.69, 129.71, 129.50, 128.16, 127.66, 127.09, 121.29, 121.02, 48.34, 39.29.

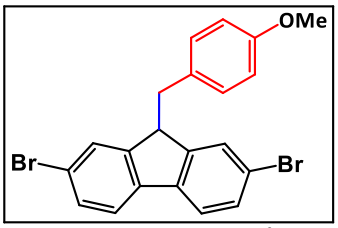
2,7-dibromo-9-(3-bromobenzyl)-9H-fluorene (3w)



Yield: 92%, 227 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.45 (ddd, *J* = 8.1, 1.8, 0.5 Hz, 2H), 7.40 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.32 (t, *J* = 1.7 Hz, 1H), 7.24 (dd, *J* = 1.7, 0.8 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.02 (ddd, *J* = 7.6, 1.5, 1.0 Hz, 1H), 4.05 (t, *J* = 7.5 Hz, 1H),

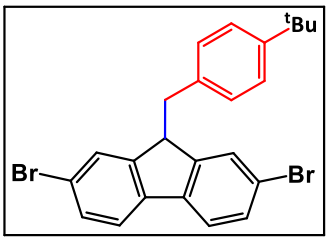
2.98 (d, *J* = 7.5 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 147.99, 140.99, 138.87, 132.53, 130.76, 130.08, 128.25, 128.19, 122.62, 121.38, 121.07, 48.45, 39.36.

2,7-dibromo-9-(4-methoxybenzyl)-9H-fluorene (3x)



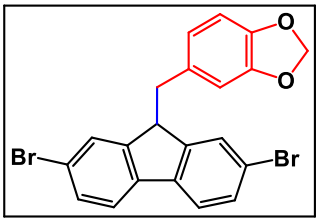
Yield: 95%, 211 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.9 Hz, 4H), 7.31 (s, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 4.03 (t, *J* = 7.1 Hz, 1H), 3.84 (s, 3H), 3.00 (d, *J* = 6.9 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 158.49, 148.55, 138.84, 130.61, 130.46, 130.40, 128.25, 121.21, 120.94, 113.90, 55.34, 48.93, 38.74.

2,7-dibromo-9-(4-(tert-butyl)benzyl)-9H-fluorene (3y)



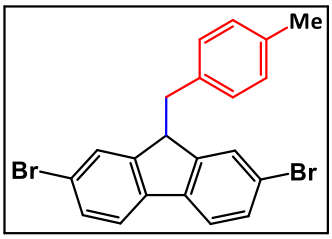
Yield: 93%, 219 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.49 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.19 (s, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 4.11 (t, *J* = 7.9 Hz, 1H), 3.03 (d, *J* = 7.9 Hz, 2H), 1.42 (s, 9H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 149.92, 148.56, 138.78, 135.80, 130.42, 129.17, 128.38, 125.42, 121.14, 120.89, 48.87, 39.23, 34.56, 31.49.

5-((2,7-dibromo-9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole (3z)



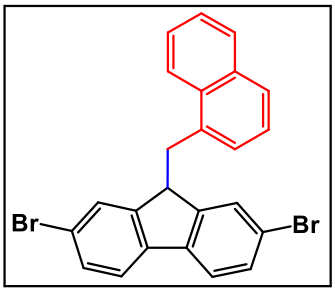
Yield: 92%, 211 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.1, 3.9 Hz, 2H), 7.44 (ddd, *J* = 8.1, 1.8, 0.5 Hz, 2H), 7.28 – 7.26 (m, 2H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 1.6 Hz, 1H), 6.54 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.95 (s, 2H), 4.04 – 3.98 (m, 1H), 2.94 (d, *J* = 7.5 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 148.38, 147.83, 146.46, 138.88, 132.42, 130.58, 128.29, 122.64, 121.28, 121.00, 109.54, 108.23, 101.08, 48.85, 39.42.

2,7-dibromo-9-(4-methylbenzyl)-9H-fluorene (3aa)



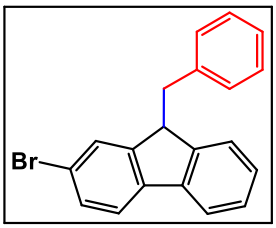
Yield: 93%, 198 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 4H), 7.27 (s, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 4.10 – 4.02 (m, 1H), 3.00 (d, *J* = 7.5 Hz, 2H), 2.37 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 148.64, 138.89, 136.41, 135.60, 130.52, 129.37, 129.26, 128.33, 121.26, 120.98, 48.87, 39.28, 21.28.

2,7-dibromo-9-(naphthalen-1-ylmethyl)-9H-fluorene (3ab)



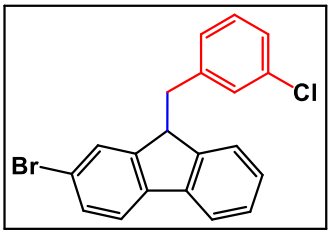
Yield: 90%, 209 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.56 (m, 4H), 7.53 – 7.49 (m, 3H), 7.23 (d, *J* = 6.8 Hz, 1H), 7.17 (s, 2H), 4.31 (t, *J* = 7.9 Hz, 1H), 3.42 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.61, 138.73, 134.78, 134.13, 131.77, 130.51, 129.29, 128.05, 126.35, 125.91, 125.26, 123.40, 121.18, 120.90, 47.50, 37.68.

9-benzyl-2-bromo-9H-fluorene (3ac)



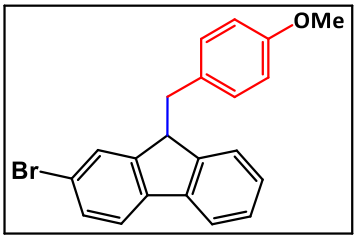
Yield: 89%, 149 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 2H), 7.38 – 7.34 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 (dt, *J* = 5.1, 2.1 Hz, 1H), 7.24 (dt, *J* = 4.6, 1.6 Hz, 2H), 7.22 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.18 (ddd, *J* = 7.5, 1.9, 0.8 Hz, 2H), 4.24 (t, *J* = 7.6 Hz, 1H), 3.12 (d, *J* = 7.6 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 146.92, 140.92, 139.93, 139.31, 130.33, 129.64, 128.39, 127.21, 126.75, 126.47, 124.94, 121.21, 119.91, 48.81, 40.19.

2-bromo-9-(3-chlorobenzyl)-9H-fluorene (3ad)



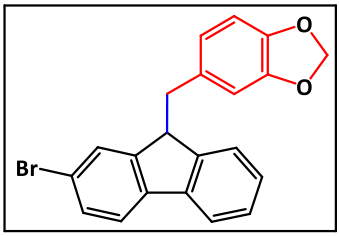
Yield: 87%, 161 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.47 (ddd, *J* = 8.1, 1.8, 0.6 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.32 – 7.30 (m, 1H), 7.24 (ddd, *J* = 10.6, 8.3, 4.0 Hz, 3H), 7.19 (dd, *J* = 3.9, 2.9 Hz, 1H), 7.13 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.02 (dt, *J* = 6.8, 1.7 Hz, 1H), 4.15 (t, *J* = 7.5 Hz, 1H), 3.05 (ddd, *J* = 35.6, 13.8, 7.5 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 148.42, 146.07, 141.25, 139.92, 134.24, 130.51, 129.66, 129.61, 128.15, 127.78, 127.61, 127.27, 126.91, 124.92, 121.30, 120.60, 120.09, 48.46, 39.57.

2-bromo-9-(4-methoxybenzyl)-9H-fluorene (3ae)



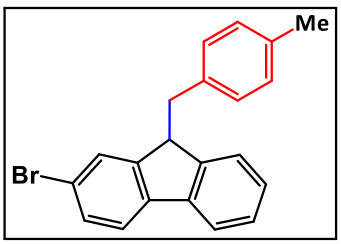
Yield: 92%, 168 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.46 (ddd, *J* = 8.1, 1.8, 0.6 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.24 (td, *J* = 7.5, 1.1 Hz, 1H), 7.15 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.10 – 7.07 (m, 2H), 6.86 – 6.83 (m, 2H), 4.14 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 3.03 (ddd, *J* = 32.5, 13.8, 7.5 Hz, 2H) **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 158.36, 148.98, 146.62, 139.93, 131.30, 130.49, 130.27, 128.24, 127.38, 127.13, 126.72, 125.05, 121.20, 120.51, 119.97, 113.82, 55.36, 49.03, 39.04.

5-((2-bromo-9H-fluoren-9-yl)methyl)benzo[d][1,3]dioxole (3af)



Yield: 89%, 169 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.46 (ddd, *J* = 8.1, 1.8, 0.6 Hz, 1H), 7.34 (tddd, *J* = 4.1, 3.7, 1.0, 0.6 Hz, 2H), 7.25 (td, *J* = 7.4, 1.1 Hz, 1H), 7.17 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.70 (d, *J* = 1.7 Hz, 1H), 6.59 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.95 (dd, *J* = 4.5, 1.5 Hz, 2H), 4.11 (t, *J* = 7.5 Hz, 1H), 3.00 (ddd, *J* = 32.2, 13.9, 7.6 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 148.78, 147.72, 146.42, 146.28, 139.92, 139.91, 133.04, 130.34, 128.22, 127.44, 127.18, 125.02, 122.64, 121.22, 120.54, 120.00, 109.67, 108.17, 101.00, 48.92, 39.64.

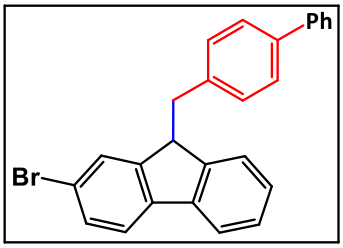
2-bromo-9-(4-methylbenzyl)-9H-fluorene (3ag)



Yield: 90%, 157 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.47 (ddd, *J* = 8.1, 1.8, 0.6 Hz, 1H), 7.34 (ddd, *J* = 9.0, 1.7, 1.1 Hz, 2H), 7.24 (td, *J* = 7.5, 1.1 Hz, 1H), 7.16 – 7.08 (m, 5H), 4.17 (t, *J* = 7.6 Hz, 1H), 3.05 (ddd, *J* = 32.8, 13.8, 7.6 Hz, 2H),

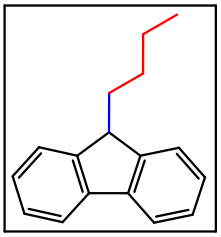
2.36 (s, 3H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 149.05, 146.69, 139.92, 139.90, 136.20, 136.14, 130.28, 129.41, 129.15, 128.25, 127.37, 127.13, 125.06, 121.18, 120.52, 119.95, 48.90, 39.51, 21.22.

9-([1,1'-biphenyl]-4-ylmethyl)-2-bromo-9H-fluorene (3ah)



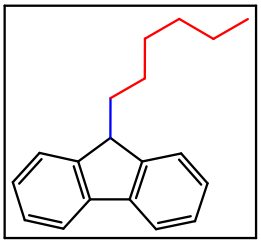
Yield: 85%, 175 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.63 (dt, *J* = 6.2, 2.3 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.49 – 7.43 (m, 3H), 7.38 – 7.33 (m, 3H), 7.27 – 7.23 (m, 3H), 7.20 (d, *J* = 7.4 Hz, 1H), 4.23 (t, *J* = 7.5 Hz, 1H), 3.13 (ddd, *J* = 30.8, 13.7, 7.6 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 148.87, 146.53, 140.93, 139.95, 139.48, 138.40, 130.37, 130.00, 128.88, 128.27, 127.73, 127.20, 127.10, 125.05, 121.25, 120.57, 120.03, 48.78, 39.58.

9-butyl-9H-fluorene (3ai)



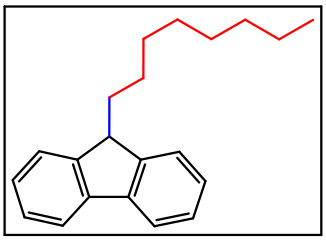
Yield: 85%, 94.65 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.45 (tdd, *J* = 7.4, 1.1, 0.6 Hz, 2H), 7.40 (td, *J* = 7.4, 1.2 Hz, 2H), 4.07 (t, *J* = 5.8 Hz, 1H), 2.10 (ddd, *J* = 10.0, 8.0, 5.9 Hz, 2H), 1.42 – 1.34 (m, 2H), 1.31 – 1.24 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 147.81, 141.32, 127.02, 126.97, 124.53, 119.97, 47.66, 33.00, 27.99, 23.23, 14.14.

9-hexyl-9H-fluorene (3aj)



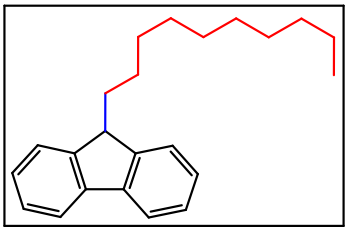
Yield: 87%, 109 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.42 (td, *J* = 7.4, 1.1 Hz, 2H), 4.09 (t, *J* = 5.9 Hz, 1H), 2.15 – 2.09 (m, 2H), 1.42 – 1.29 (m, 8H), 0.98 (t, *J* = 7.0 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 147.75, 141.23, 126.93, 126.89, 124.45, 119.88, 47.62, 33.25, 31.79, 29.79, 25.80, 22.78, 14.21.

9-octyl-9H-fluorene (3ak)



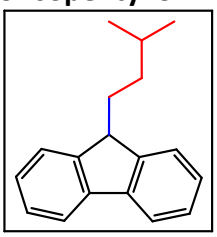
Yield: 89%, 124 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.42 (td, *J* = 7.4, 0.9 Hz, 2H), 4.09 (t, *J* = 5.9 Hz, 1H), 2.15 – 2.09 (m, 2H), 1.42 – 1.31 (m, 12H), 1.00 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 147.75, 141.23, 126.93, 126.88, 124.45, 119.88, 47.62, 33.23, 31.99, 30.12, 129.53, 29.44, 25.84, 22.79, 14.25.

9-decyl-9H-fluorene (3al)



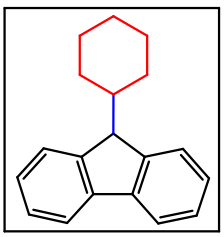
Yield: 92%, 141 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.44 (td, *J* = 7.4, 1.1 Hz, 2H), 4.11 (t, *J* = 5.9 Hz, 1H), 2.18 – 2.11 (m, 2H), 1.49 – 1.35 (m, 16), 1.06 (t, *J* = 7.0 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 147.87, 141.38, 127.07, 127.02, 124.58, 120.02, 47.76, 33.38, 32.22, 30.29, 29.95, 29.91, 29.74, 29.64, 25.99, 23.01, 14.44.

9-isopentyl-9H-fluorene (3am)



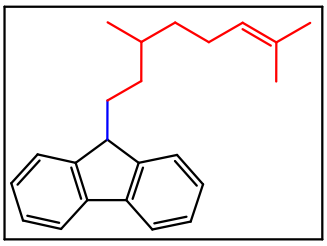
Yield: 90%, 106 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.42 (td, *J* = 7.4, 1.2 Hz, 2H), 4.08 (t, *J* = 5.8 Hz, 1H), 2.13 (ddd, *J* = 10.5, 8.1, 5.8 Hz, 2H), 1.61 (dp, *J* = 13.3, 6.6 Hz, 1H), 1.18 (ddd, *J* = 15.3, 6.8, 4.7 Hz, 2H), 0.94 (d, *J* = 6.6 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 147.67, 141.25, 126.993, 129.89, 124.42, 119.87, 47.64, 34.58, 30.87, 28.43, 22.60.

9-cyclohexyl-9H-fluorene (3an)



Yield: 89%, 110.60 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 7.0 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.42 (td, *J* = 7.4, 1.1 Hz, 2H), 4.02 (d, *J* = 3.0 Hz, 1H), 2.30 (tq, *J* = 11.8, 3.1 Hz, 1H), 1.83 – 1.73 (m, 3H), 1.60 (d, *J* = 12.7 Hz, 2H), 1.40 – 1.14 (m, 5H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 146.62, 141.77, 126.92, 126.76, 124.98, 119.69, 53.68, 43.25, 29.81, 27.06, 26.63.

9-(3,7-dimethyloct-6-en-1-yl)-9H-fluorene (3ao)

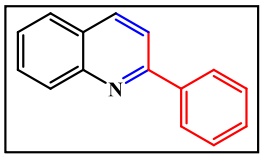


Yield: 86%, 131 mg. **^{1}H NMR** (500 MHz, $CDCl_3$) δ δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 5.06 (t, *J* = 7.1 Hz, 1H), 3.98 (t, *J* = 5.8 Hz, 1H), 2.03 (qd, *J* = 5.8, 3.1 Hz, 2H), 1.88 (ddt, *J* = 21.8, 14.5, 7.3 Hz, 2H), 1.68 (s, 3H), 1.57 (s, 3H), 1.41 – 1.33 (m, 1H), 1.31 – 1.25 (m, 1H), 1.24 – 1.15 (m, 1H), 1.10 (ddd, *J* = 14.3, 9.5, 5.7 Hz, 1H), 1.05 – 0.97 (m, 1H), 0.84 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 147.74, 147.70, 141.31, 141.29, 131.21, 126.98, 126.95, 125.07, 124.49, 124.44, 119.92, 47.72, 36.89, 32.75, 32.55, 30.43, 25.89, 25.64, 19.65, 17.80.

9. ^{1}H and ^{13}C{^{1}H} NMR characterization of quinoline derivatives

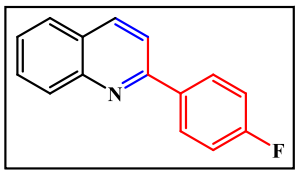
The NMR spectroscopic data for all the reported quinoline derivatives are in agreement with the previously reported literatures.[15–24]

2-phenylquinoline (6a)



Yield: 94%, 96 mg. **^{1}H NMR (500 MHz)** δ 8.27 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 7.7 Hz, 2H), 8.19 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.87 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.77 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.54 – 7.50 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz) δ 157.45, 148.41, 139.80, 136.87, 129.86, 129.77, 129.44, 128.96, 127.70, 127.58, 127.30, 126.39, 119.10.

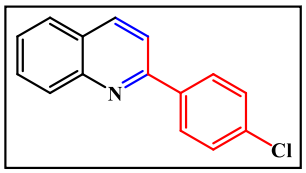
2-(4-fluorophenyl)quinoline (6b)



Yield: 85%, 95mg. **^{1}H NMR (500 MHz)** δ 8.25 (d, *J* = 8.6 Hz, 1H), 8.21 – 8.16 (m, 3H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.76 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.56 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.26 – 7.21 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz) δ 164.87, 162.89, 156.35, 148.29, 137.03, 135.89 (d, *J*

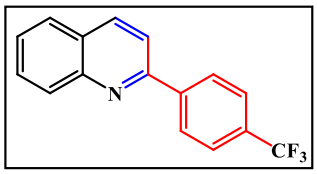
= 3.1 Hz), 129.90, 129.70, 129.54, 129.47, 127.57, 127.16, 126.45, 118.75, 115.86 (d, *J* = 21.4 Hz). **^{19}F NMR** (471 MHz) δ -112.27 – -112.42 (m).

2-(4-chlorophenyl)quinoline (6c)



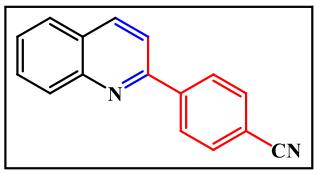
Yield: 90%, 108mg. **^{1}H NMR (500 MHz)** δ 8.19 (d, *J* = 8.4 Hz, 2H), 8.14 – 8.11 (m, 2H), 7.82 (t, *J* = 8.0 Hz, 2H), 7.76 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.53 – 7.49 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz) δ 156.06, 148.30, 138.11, 137.05, 135.63, 129.94, 129.76, 129.10, 128.91, 127.59, 127.30, 126.59, 118.64.

2-(4-(trifluoromethyl)phenyl)quinoline (6d)



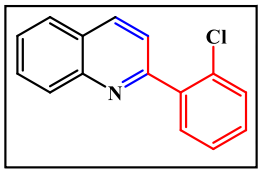
Yield: 89% 122 mg. **^{1}H NMR (500 MHz)** δ 8.26 (dd, *J* = 8.7, 0.7 Hz, 2H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.18 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.83 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.79 – 7.73 (m, 3H), 7.55 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz) δ 155.75, 148.34, 143.02, 137.23, 131.27, 131.01, 130.09, 129.92, 127.92, 127.62, 127.51, 126.94, 125.83 (q, 3.78 Hz), 125.38, 123.22, 118.87. **^{19}F NMR** (471 MHz) δ -62.39 (s).

4-(quinolin-2-yl)benzonitrile (6e)



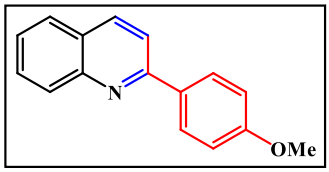
Yield: 86%, 99 mg. **^{1}H NMR (500 MHz)** δ 8.33 – 8.30 (m, 3H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.86 – 7.82 (m, 2H), 7.80 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.63 – 7.59 (m, 1H). **^{13}C{^{1}H} NMR** (126 MHz) δ 154.89, 148.25, 143.68, 137.30, 132.60, 130.18, 129.89, 128.07, 127.58, 127.54, 127.17, 118.86, 118.61, 112.70.

2-(2-chlorophenyl)quinoline (6f)



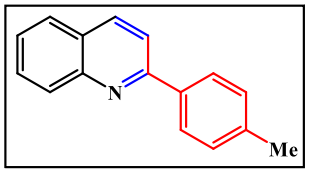
Yield: 84%, 101 mg. **^{1}H NMR (500 MHz)** δ 8.23 (dd, *J* = 12.5, 8.7 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.78 (dd, *J* = 7.6, 4.4 Hz, 2H), 7.73 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.38 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz) δ 157.44, 148.09, 139.67, 135.71, 132.38, 131.72, 130.12, 129.91, 129.72, 129.69, 127.59, 127.20, 127.15, 126.81, 122.80.

2-(4-methoxyphenyl)quinoline (6g)



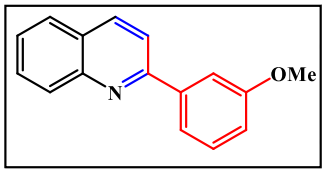
Yield: 96%, 113 mg. **^{1}H NMR (500 MHz)** δ 8.20 – 8.15 (m, 4H), 7.83 (dd, *J* = 11.4, 8.4 Hz, 2H), 7.74 (dd, *J* = 11.8, 4.7 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz) δ 160.83, 156.93, 148.30, 136.67, 132.26, 129.61, 129.52, 128.92, 127.48, 126.93, 125.94, 118.59, 114.25, 55.41.

2-(p-tolyl)quinoline (6h)



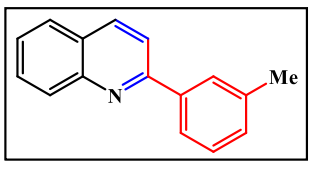
Yield: 95%, 104mg. **^{1}H NMR (500 MHz)** δ 8.24 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.76 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 2H), 2.48 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz) δ 157.42, 148.42, 139.49, 136.99, 136.75, 129.77, 129.69, 127.57, 127.22, 126.18, 118.94, 21.45.

2-(3-methoxyphenyl)quinoline (6i)



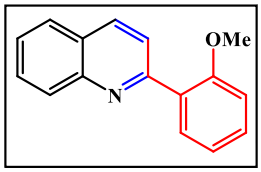
Yield: 88%, 104mg. **^{1}H NMR (500 MHz)** δ 8.24 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.78 – 7.73 (m, 2H), 7.55 (t, *J* = 7.1 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.06 (ddd, *J* = 8.2, 2.5, 0.6 Hz, 1H), 3.95 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz) δ 160.23, 157.23, 148.29, 141.24, 136.89, 129.92, 129.81, 129.78, 127.57, 127.37, 126.44, 120.13, 119.22, 115.48, 112.83, 77.45, 77.19, 76.94, 55.51.

2-(m-tolyl)quinoline (6j)



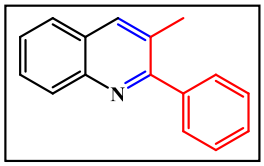
Yield: 92%, 101mg. **^{1}H NMR (500 MHz)** δ 8.23 (t, *J* = 9.3 Hz, 2H), 8.06 (s, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.77 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.55 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 2.52 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz) δ 157.62, 148.30, 139.69, 138.55, 136.75, 130.16, 129.72, 129.67, 128.78, 128.32, 127.50, 127.21, 126.25, 124.76, 119.20, 21.64.

2-(2-methoxyphenyl)quinoline (6k)



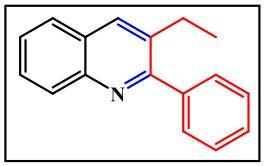
Yield: 86%, 101mg. **^{1}H NMR (500 MHz)** δ 8.22 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.89 (ddd, *J* = 18.8, 15.8, 8.3 Hz, 3H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 8.5 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz) δ 157.23, 157.17, 148.34, 135.13, 131.52, 130.37, 129.75, 129.64, 129.26, 127.44, 127.08, 126.22, 123.50, 121.30, 111.47, 55.67.

3-methyl-2-phenylquinoline (6l)



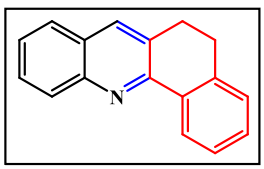
Yield: 92%, 101mg. **^{1}H NMR (500 MHz)** δ 8.17 (d, *J* = 8.5 Hz, 1H), 8.04 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.69 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.63 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.56 – 7.50 (m, 3H), 7.49 – 7.45 (m, 1H), 2.49 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz) δ 160.56, 146.65, 140.90, 136.77, 129.32, 129.24, 128.88, 128.78, 128.34, 128.22, 127.63, 126.74, 126.44, 20.66.

3-ethyl-2-phenylquinoline (6m)



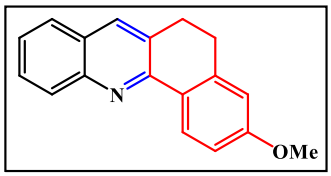
Yield: 94%, 110mg. **^{1}H NMR (500 MHz)** δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.91 (s, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.53 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.43 – 7.39 (m, 3H), 7.40 – 7.32 (m, 3H), 7.32 – 7.28 (m, 1H), 2.66 (q, *J* = 7.1 Hz, 2H), 1.06 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz) δ 160.67, 146.35, 140.92, 135.33, 134.97, 129.27, 128.84, 128.75, 128.32, 128.12, 127.77, 126.96, 126.41, 26.04, 14.75.

5,6-dihydrobenzo[c]acridine (6n)



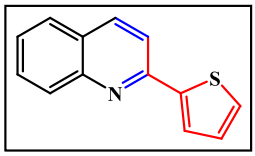
Yield: 90%, 104mg. **^{1}H NMR (500 MHz)** δ 8.64 (d, *J* = 7.6 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.92 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.49 (dt, *J* = 12.7, 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 7.3 Hz, 1H), 3.16 – 3.11 (m, 2H), 3.06 – 3.01 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz) δ 153.43, 147.67, 139.47, 134.76, 133.75, 130.63, 129.73, 129.44, 128.70, 128.01, 127.91, 127.38, 126.99, 126.11, 28.85, 28.43.

3-methoxy-5,6-dihydrobenzo[c]acridine (6o)



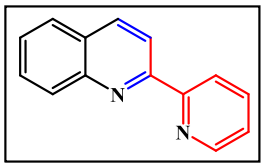
Yield: 91%, 119 mg. **^{1}H NMR (500 MHz)** δ 8.56 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.87 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.82 (d, *J* = 2.5 Hz, 1H), 3.89 (s, 3H), 3.12 – 3.09 (m, 2H), 3.01 – 2.97 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz) δ 160.94, 153.43, 147.68, 141.30, 133.52, 130.04, 129.15, 128.59, 127.83, 127.81, 127.58, 126.96, 125.64, 113.06, 112.97, 55.36, 28.90, 28.78.

2-(thiophen-2-yl)quinoline (6p)



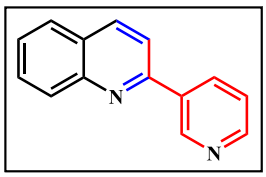
Yield: 87%, 92 mg. **^{1}H NMR (500 MHz)** δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.79 (t, *J* = 9.1 Hz, 2H), 7.76 – 7.70 (m, 2H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.18 (dd, *J* = 4.9, 3.7 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz) δ 152.36, 148.13, 145.41, 136.65, 129.85, 129.27, 128.62, 128.12, 127.52, 127.21, 126.13, 125.90, 117.67.

2-(pyridin-2-yl)quinoline (6q)



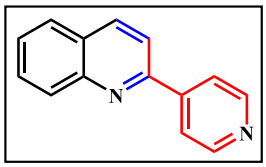
Yield: 89%, 92 mg. **^{1}H NMR (500 MHz)** δ 8.76 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 8.67 (dt, *J* = 8.0, 0.9 Hz, 1H), 8.58 (d, *J* = 8.6 Hz, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.75 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.57 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.37 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz) δ 156.34, 156.17, 149.19, 147.93, 136.99, 136.85, 129.82, 129.59, 128.26, 127.65, 126.79, 124.06, 121.87, 118.98.

2-(pyridin-3-yl)quinoline (6r)



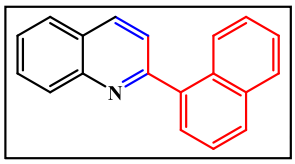
Yield: 88%, 91 mg. **^{1}H NMR (500 MHz)** δ 9.36 (d, *J* = 1.8 Hz, 1H), 8.70 (dd, *J* = 4.7, 1.3 Hz, 1H), 8.52 – 8.48 (m, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.84 (dd, *J* = 11.7, 8.4 Hz, 2H), 7.77 – 7.73 (m, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 7.9, 4.8 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz) δ 154.57, 150.18, 148.78, 148.35, 137.17, 135.10, 134.95, 130.00, 129.74, 127.57, 127.36, 126.79, 123.69, 118.49.

2-(pyridin-4-yl)quinoline (6s)



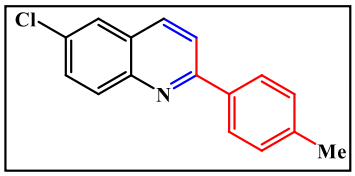
Yield: 90%, 93 mg. **^{1}H NMR (500 MHz)** δ 8.76 (dd, *J* = 4.0, 2.1 Hz, 2H), 8.23 (dd, *J* = 7.6, 5.0 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 8.06 – 8.02 (m, 2H), 7.84 (ddd, *J* = 12.0, 7.4, 2.4 Hz, 2H), 7.78 – 7.72 (m, 1H), 7.56 (ddd, *J* = 9.8, 3.0, 1.5 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz) δ 154.34, 150.40, 148.23, 146.64, 137.28, 130.13, 129.95, 127.81, 127.57, 127.23, 121.63, 118.40.

2-(naphthalen-1-yl)quinoline (6t)



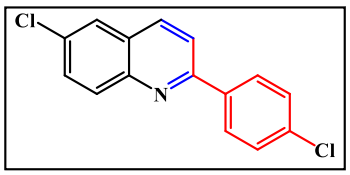
Yield: 94%, 120 mg. **^{1}H NMR (500 MHz)** δ 8.37 (d, *J* = 8.4 Hz, 1H), 8.25 (dd, *J* = 12.7, 8.4 Hz, 2H), 8.00 (t, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.83 (ddd, *J* = 14.8, 8.1, 4.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.66 (dd, *J* = 8.1, 7.1 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.56 (dddd, *J* = 16.6, 8.1, 6.8, 1.3 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz) δ 159.50, 148.23, 138.84, 136.38, 134.13, 131.39, 129.90, 129.80, 129.27, 128.55, 127.93, 127.73, 127.09, 126.74, 126.69, 126.11, 125.84, 125.53, 123.34.

6-chloro-2-(p-tolyl)quinoline (6u)



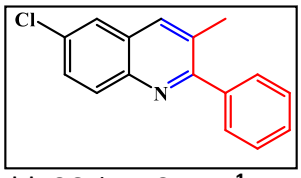
Yield: 83%, 105 mg. **^{1}H NMR (500 MHz)** δ 8.08 – 8.03 (m, 4H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 2.3 Hz, 1H), 7.63 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.32 (dd, *J* = 8.5, 0.6 Hz, 2H), 2.43 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz) δ 157.58, 146.72, 139.82, 136.45, 135.81, 131.73, 131.31, 130.55, 129.74, 127.70, 127.47, 126.21, 119.71, 21.48.

6-chloro-2-(4-chlorophenyl)quinoline (6v)



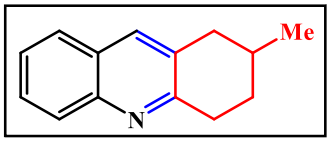
Yield: 87%, 119 mg. **^{1}H NMR (500 MHz)** δ 8.09 (ddd, *J* = 14.3, 12.7, 8.9 Hz, 4 H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 2.2 Hz, 1H), 7.65 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.51 – 7.46 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz) δ 156.28, 146.67, 137.64, 136.12, 135.90, 132.23, 131.35, 130.86, 129.18, 128.83, 127.82, 126.25, 119.45.

6-chloro-2-(4-chlorophenyl)quinoline (6w)



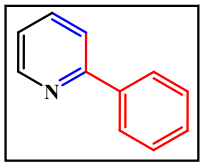
Yield: 86%, 118 mg. **^{1}H NMR (500 MHz)** δ 8.04 (d, *J* = 9.0 Hz, 1H), 7.90 (s, 1H), 7.73 (d, *J* = 2.3 Hz, 1H), 7.60 – 7.54 (m, 3H), 7.52 – 7.41 (m, 3H), 2.45 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz) δ 160.88, 145.05, 140.53, 135.85, 132.11, 131.02, 130.44, 129.76, 128.88, 128.49, 128.46, 128.24, 125.45, 20.78.

2-methyl-1,2,3,4-tetrahydroacridine (6x)



Yield: 81%, 80 mg. **^{1}H NMR (500 MHz)** δ 7.96 (d, *J* = 8.5 Hz, 1H), 7.76 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.58 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.44 – 7.37 (m, 1H), 3.21 (ddd, *J* = 17.9, 5.7, 3.4 Hz, 1H), 3.08 (ddd, *J* = 17.8, 11.5, 6.2 Hz, 1H), 3.03 – 2.97 (m, 1H), 2.57 (dd, *J* = 16.3, 10.8 Hz, 1H), 2.05 (tdd, *J* = 8.5, 5.9, 3.2 Hz, 1H), 2.01 – 1.91 (m, 1H), 1.59 (dtd, *J* = 13.1, 11.2, 5.7 Hz, 1H), 1.11 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz) δ 159.11, 146.72, 135.05, 130.68, 128.59, 128.32, 127.22, 126.97, 125.61, 37.88, 33.17, 31.50, 29.18, 21.76.

2-phenylpyridine (6y)



Yield: 52%, 40mg. **^{1}H NMR (500 MHz)** δ 8.70 – 8.67 (m, 1H), 8.00 – 7.97 (m, 2H), 7.72 – 7.70 (m, 2H), 7.49 – 7.45 (m, 2H), 7.42 – 7.39 (m, 1H), 7.20 (ddd, *J* = 5.8, 4.8, 2.7 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz) δ 157.54, 149.75, 139.48, 136.88, 129.07, 128.86, 127.02, 122.21, 120.70.

10. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectrum of sp^3 C–H alkylated fluorene derivatives

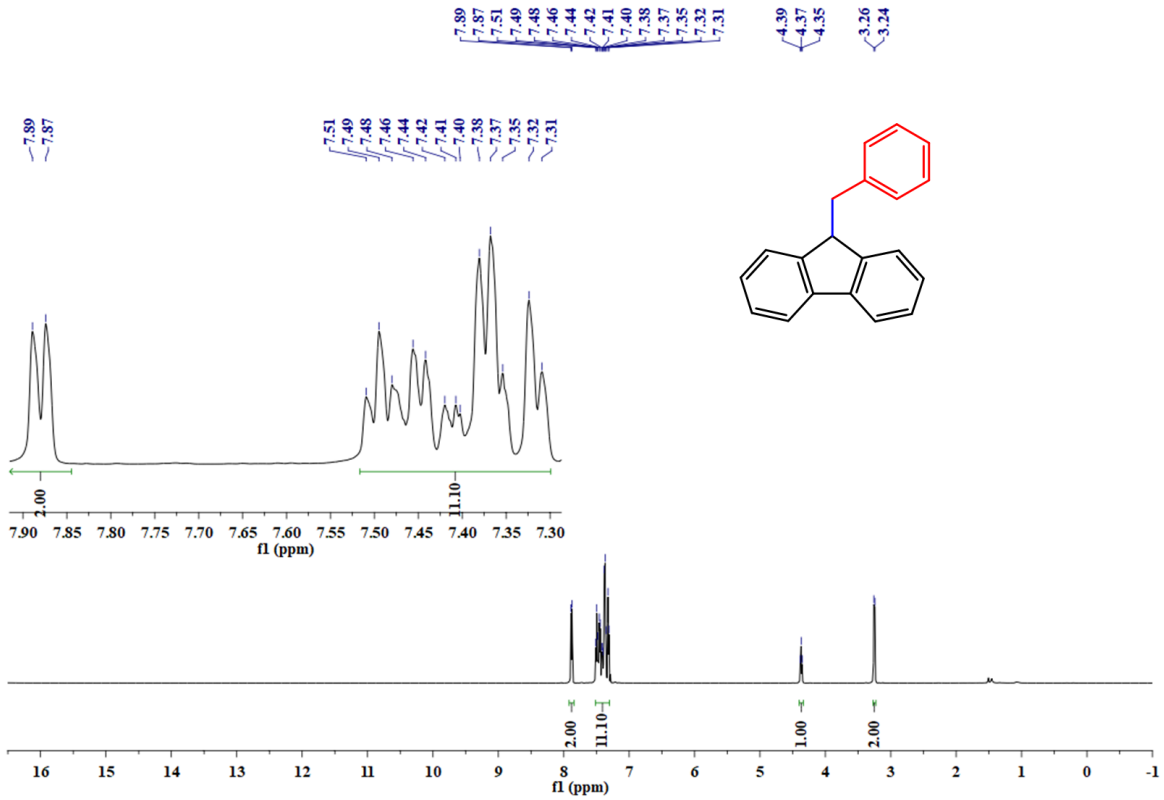


Figure S23: ^{1}H NMR spectrum of 3a in $CDCl_3$ at 500 MHz.

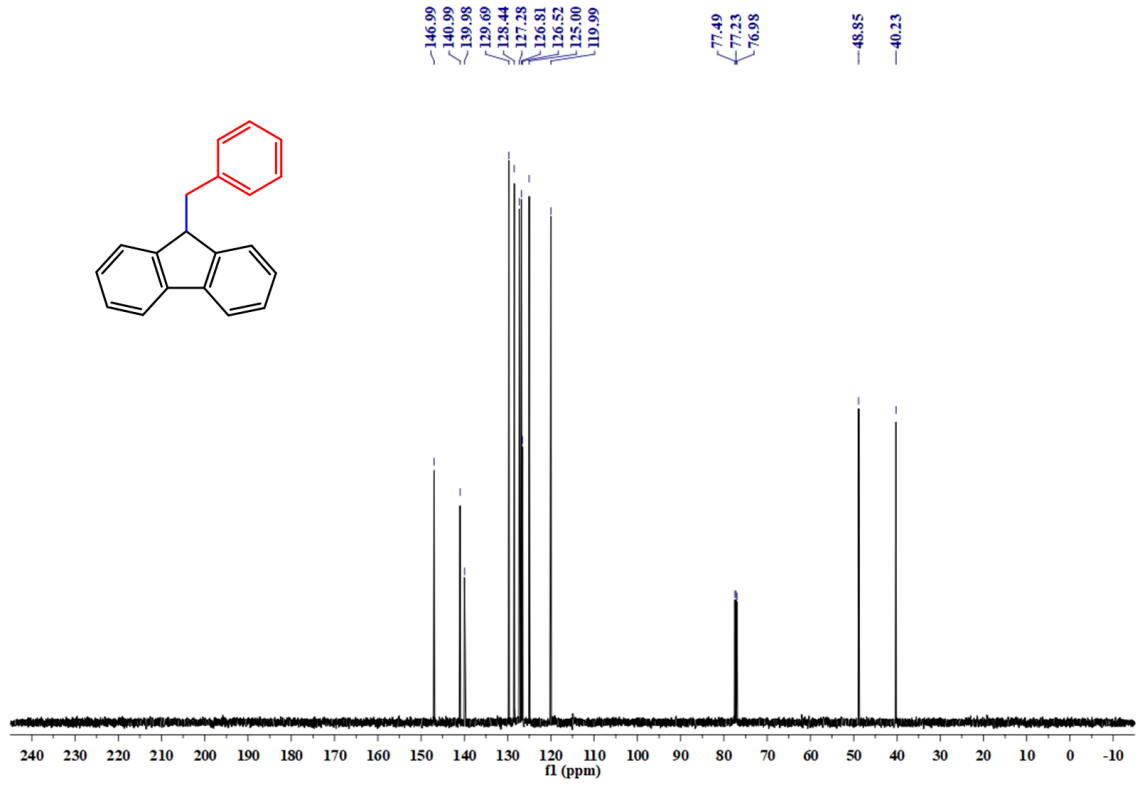


Figure S24: $^{13}C\{^{1}H\}$ NMR spectrum of 3a in $CDCl_3$ at 126 MHz.

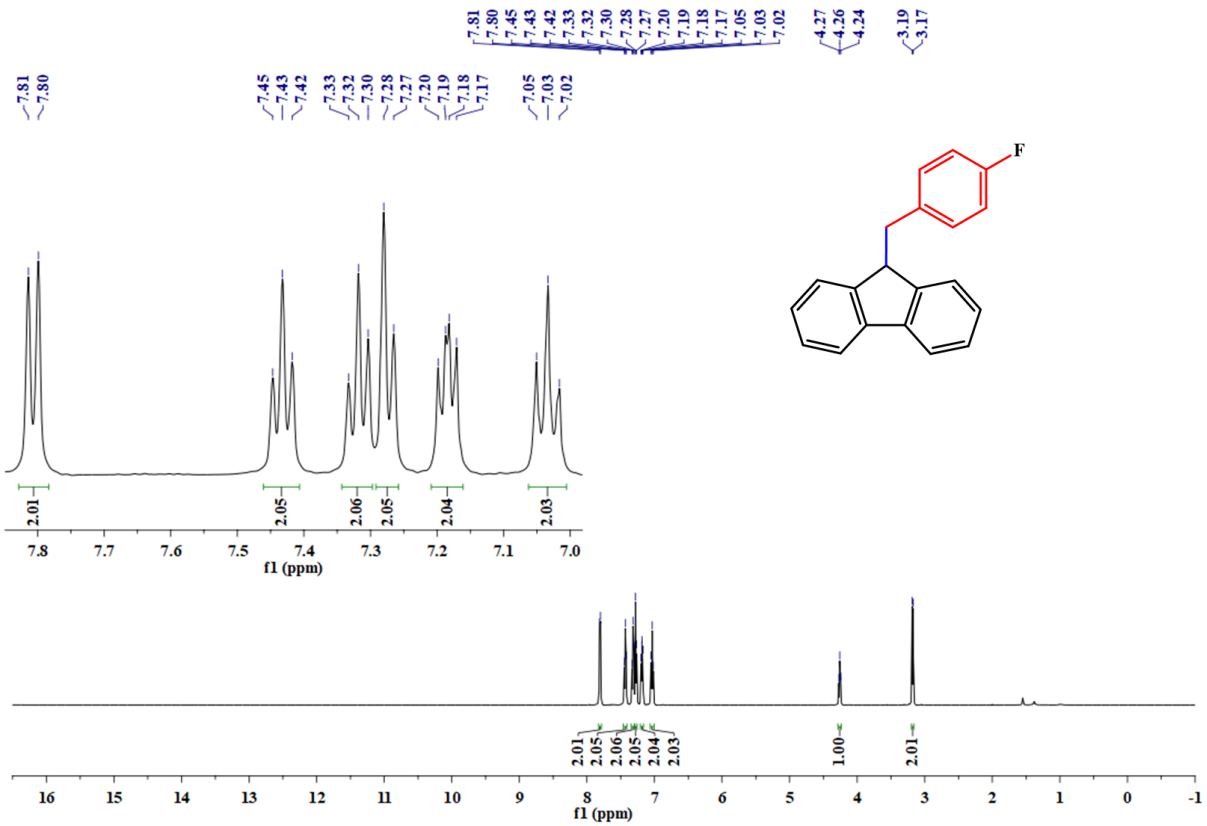


Figure S25: ^{1}**H** NMR spectrum of 3b in $CDCl_3$ at 500 MHz.

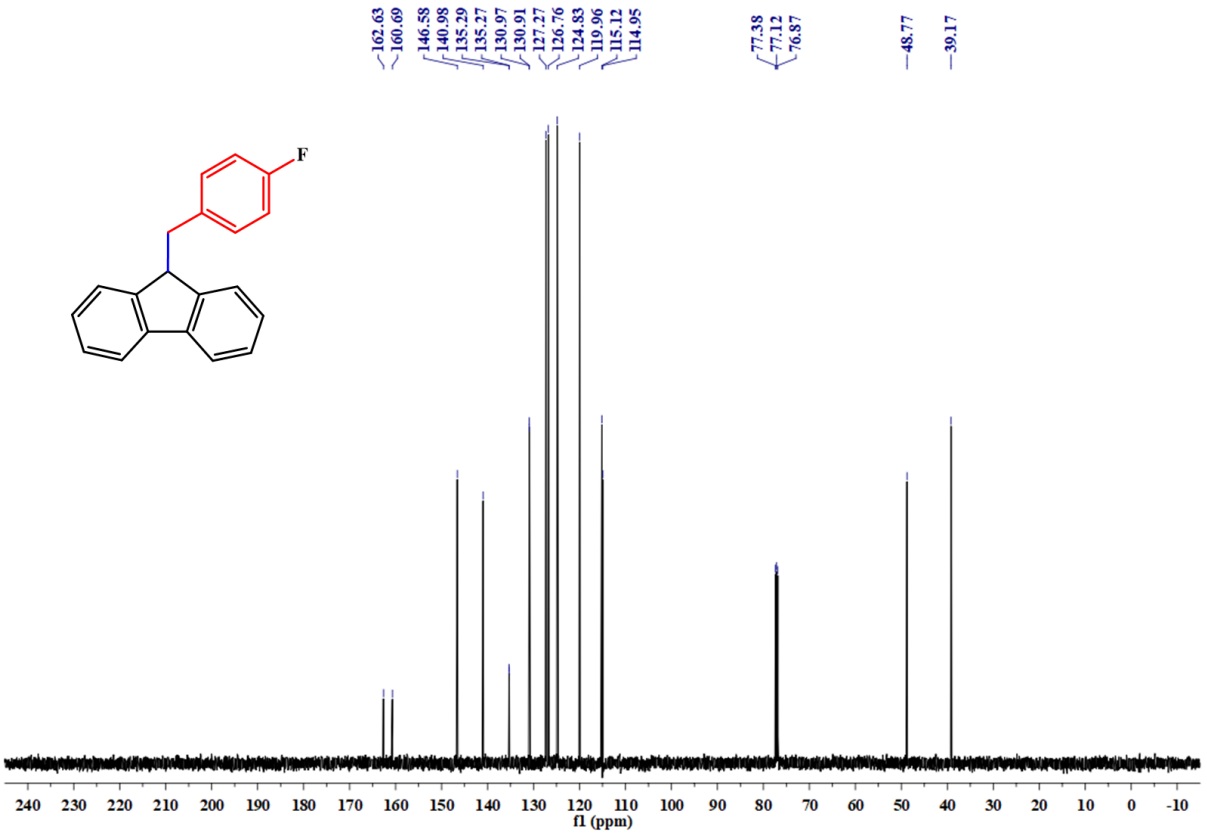


Figure S26: ^{13}**C{**^{1}**H}** NMR spectrum of 3b in $CDCl_3$ at 126 MHz.

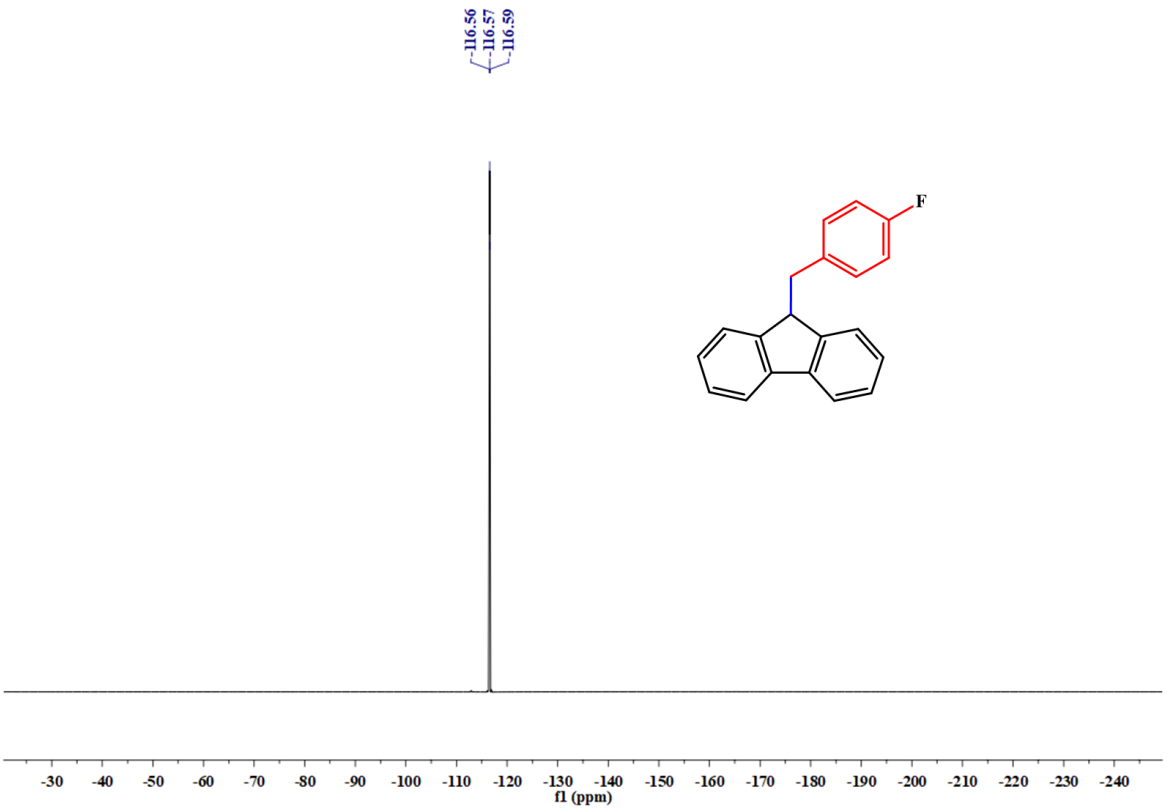


Figure S27: ^{19}**F** NMR spectrum of 3b in $CDCl_3$ at 471 MHz.

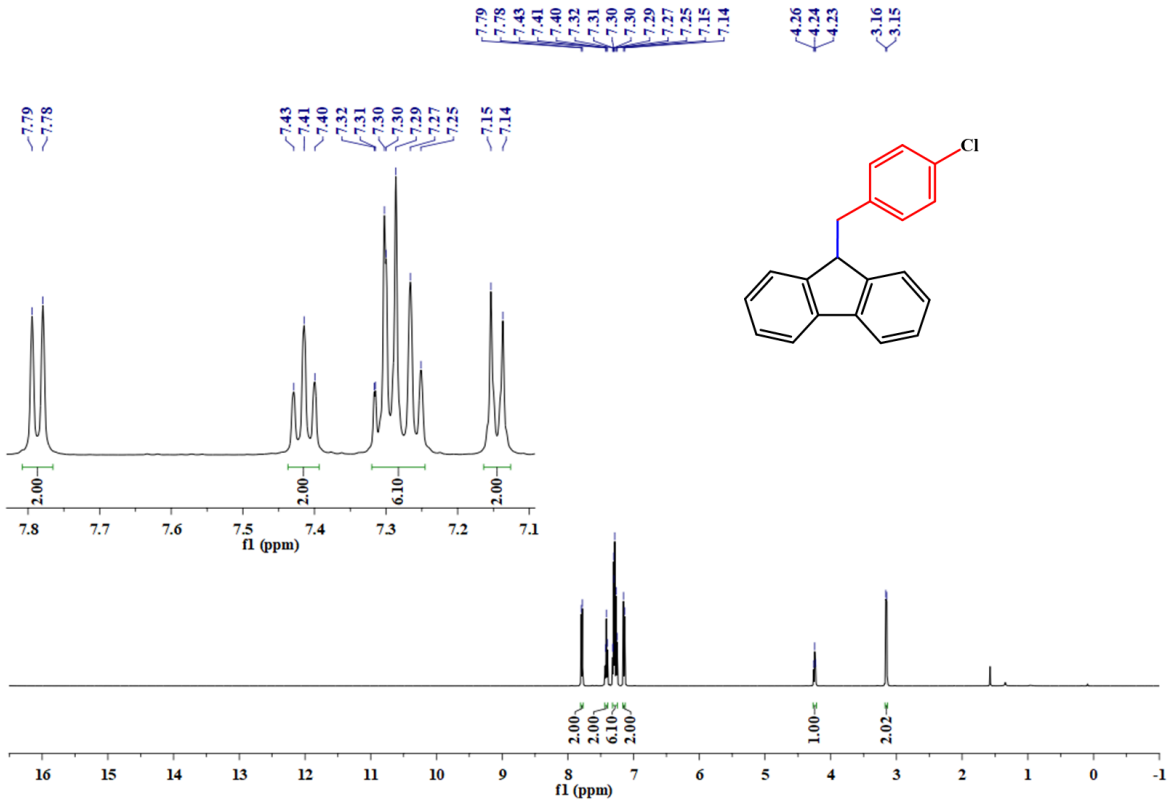


Figure S28: ^{1}**H** NMR spectrum of 3c in $CDCl_3$ at 500 MHz.

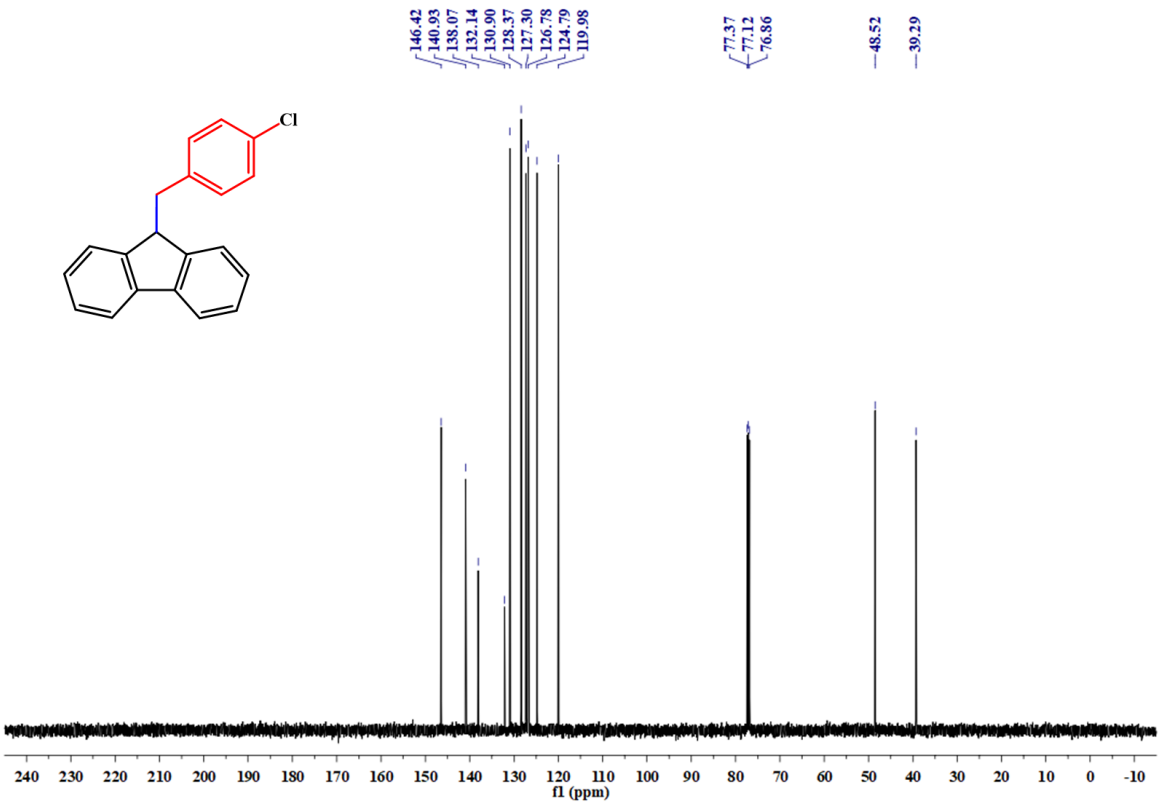


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum of 3c in $CDCl_3$ at 126 MHz.

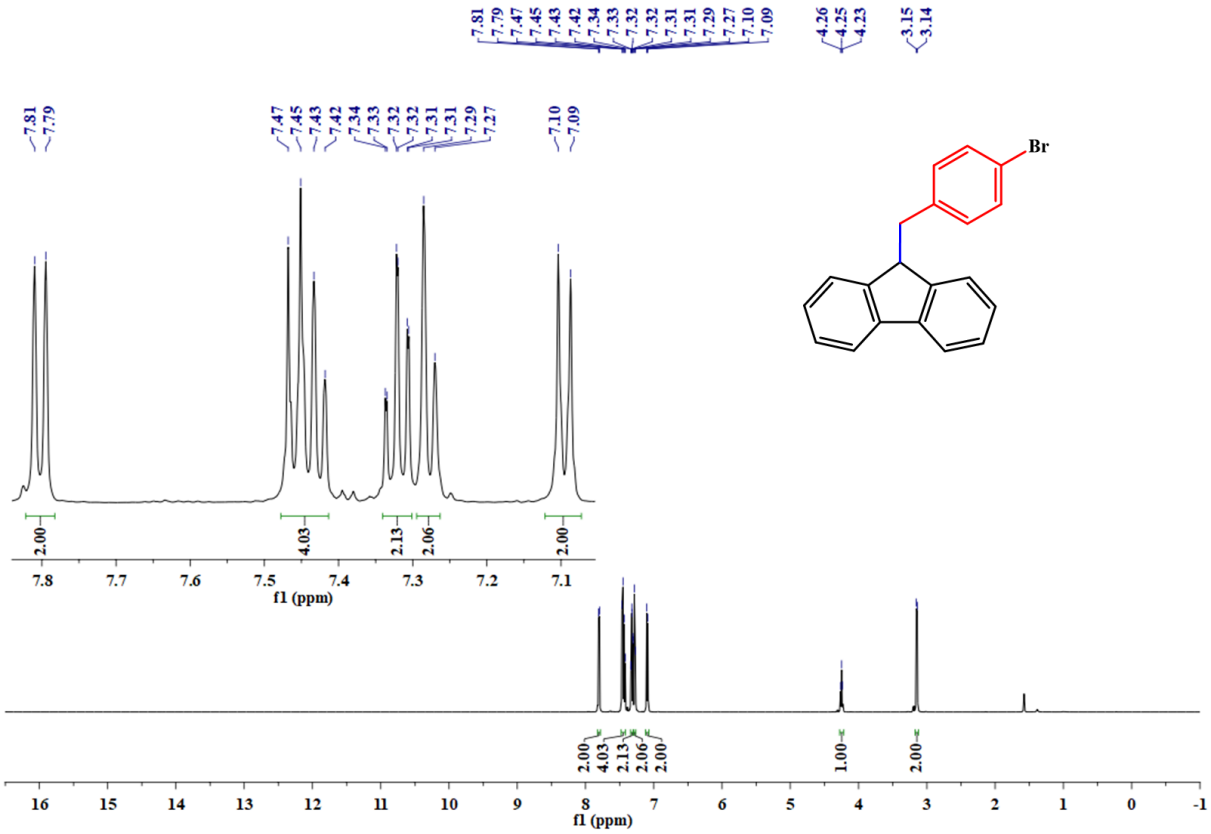


Figure S30: ^{1}H NMR spectrum of 3d in $CDCl_3$ at 500 MHz.

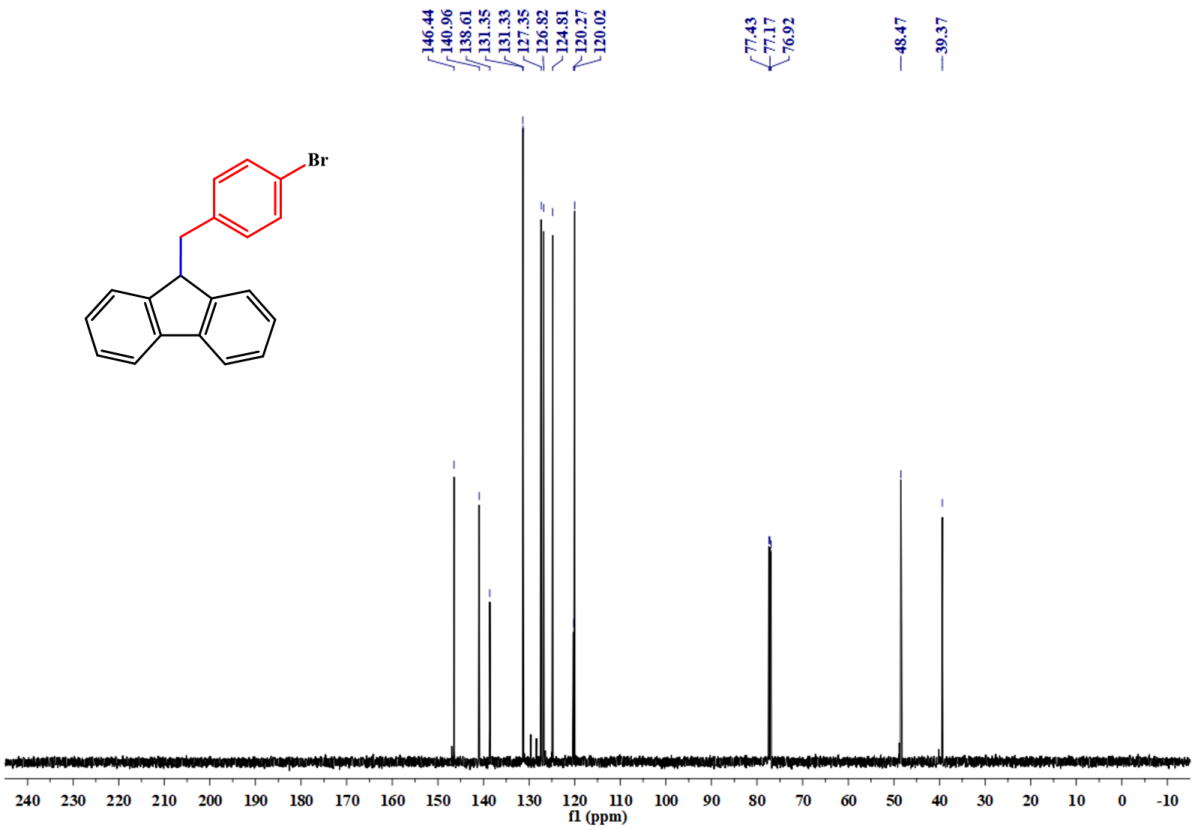


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum of 3d in $CDCl_3$ at 126 MHz.

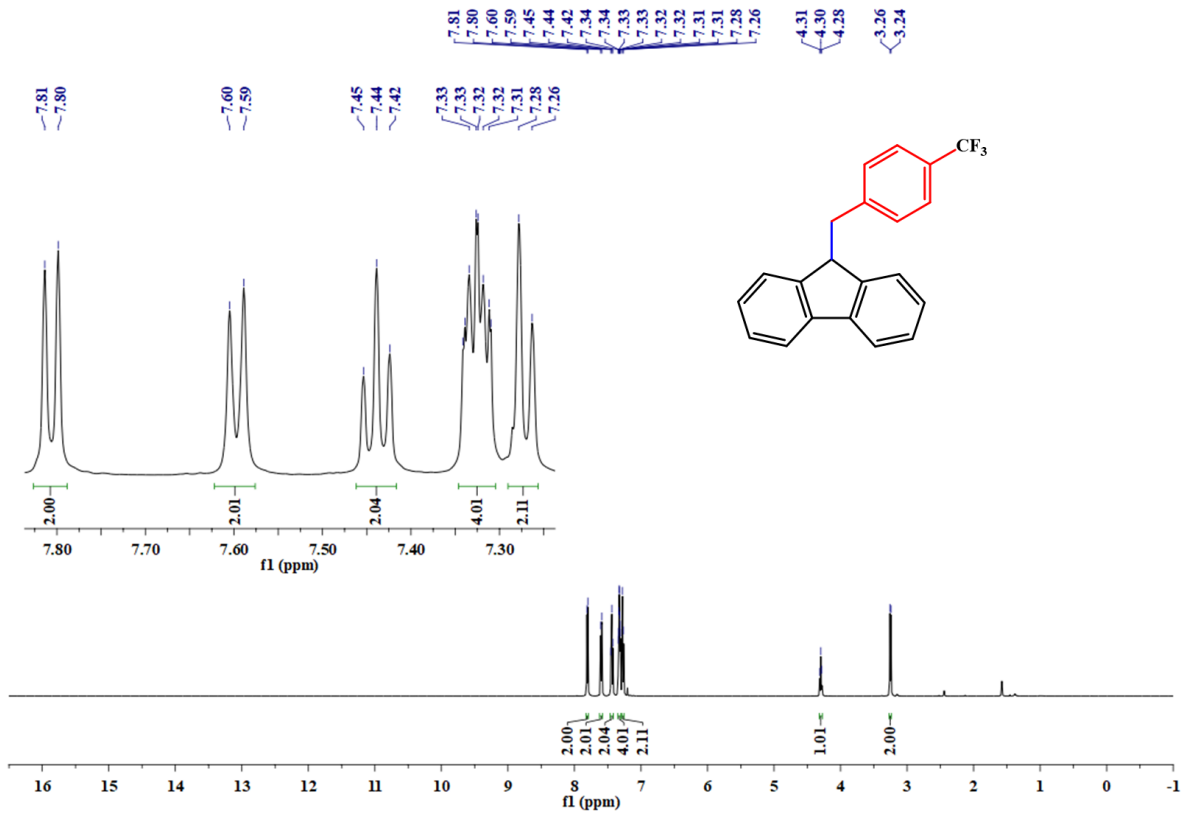


Figure S32: ^{1}H NMR spectrum of 3e in $CDCl_3$ at 500 MHz.

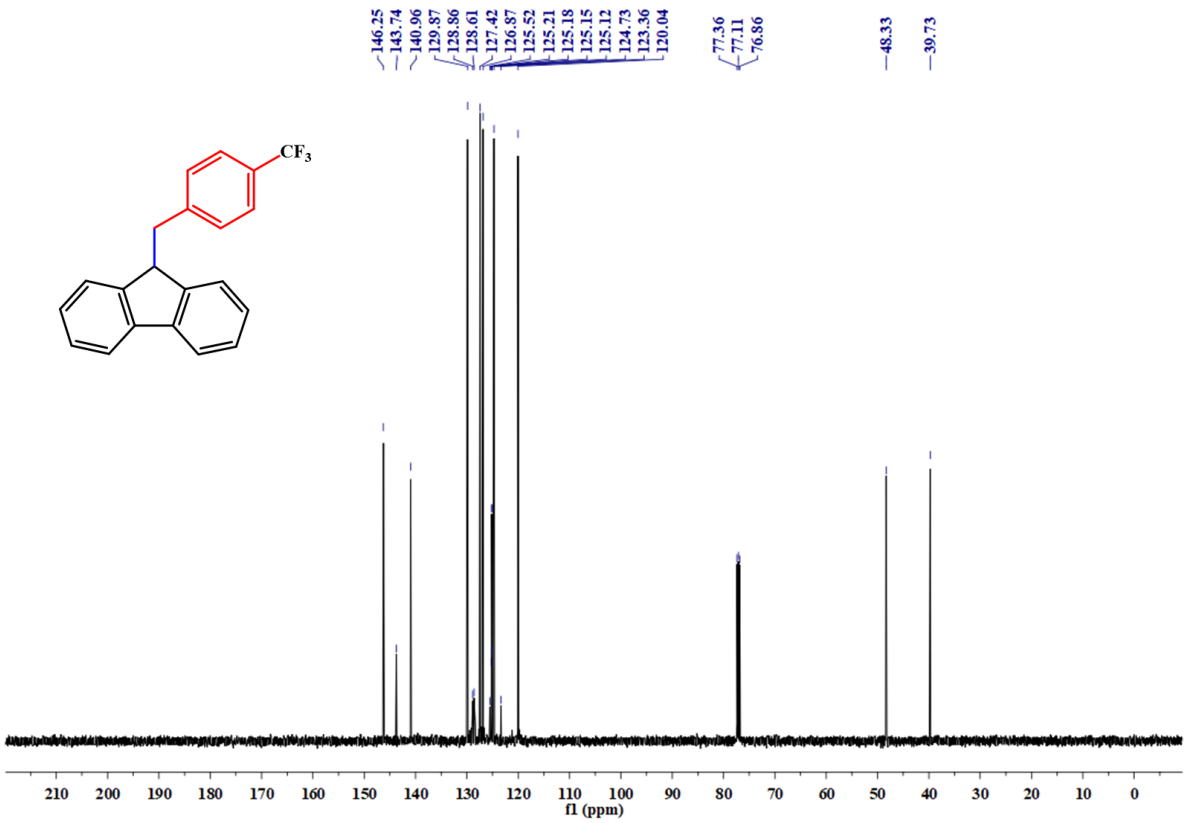


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum of 3e in $CDCl_3$ at 126 MHz.

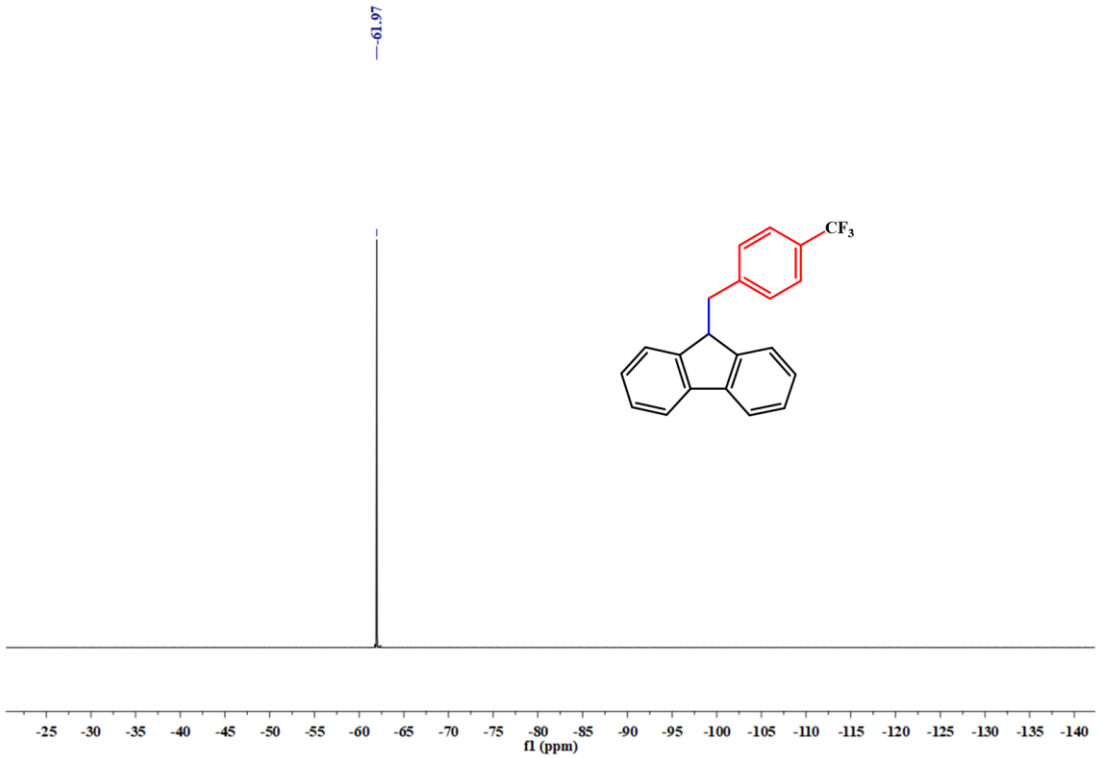


Figure S34: ^{19}F NMR spectrum of 3e in $CDCl_3$ at 471 MHz.

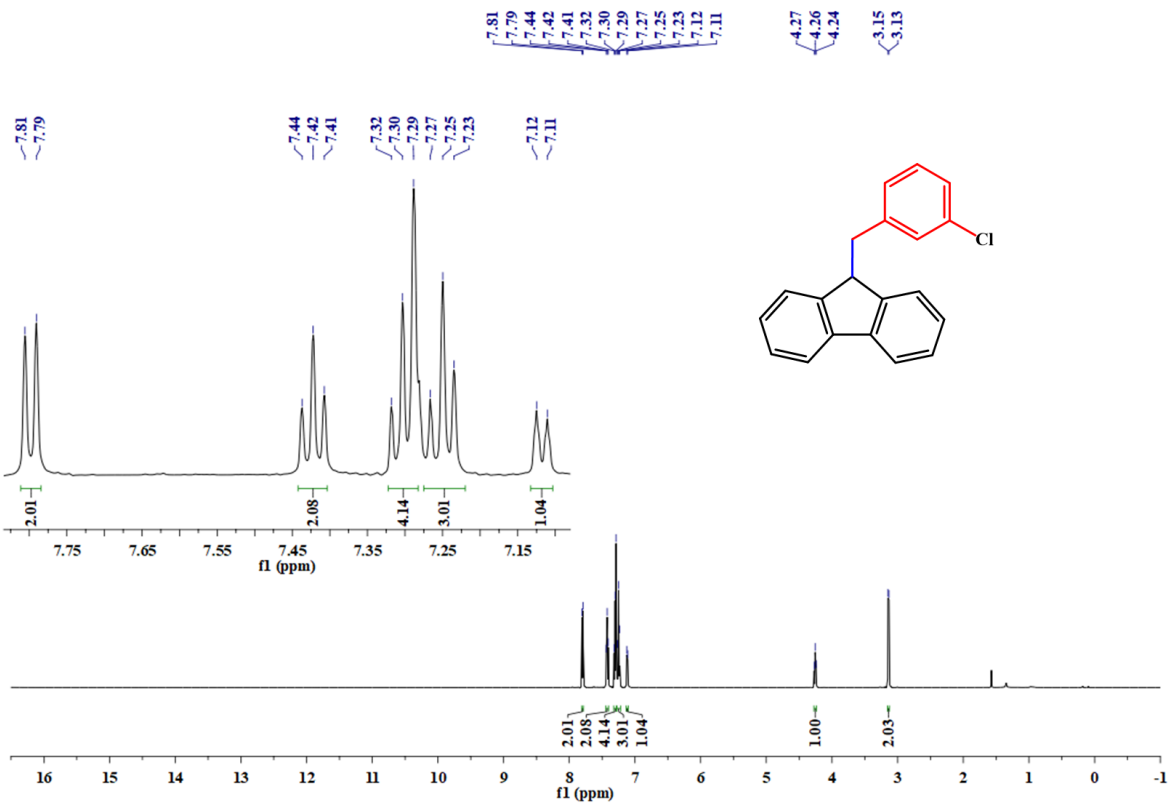


Figure S35: ^{1}**H** NMR spectrum of 3f in $CDCl_3$ at 500 MHz.

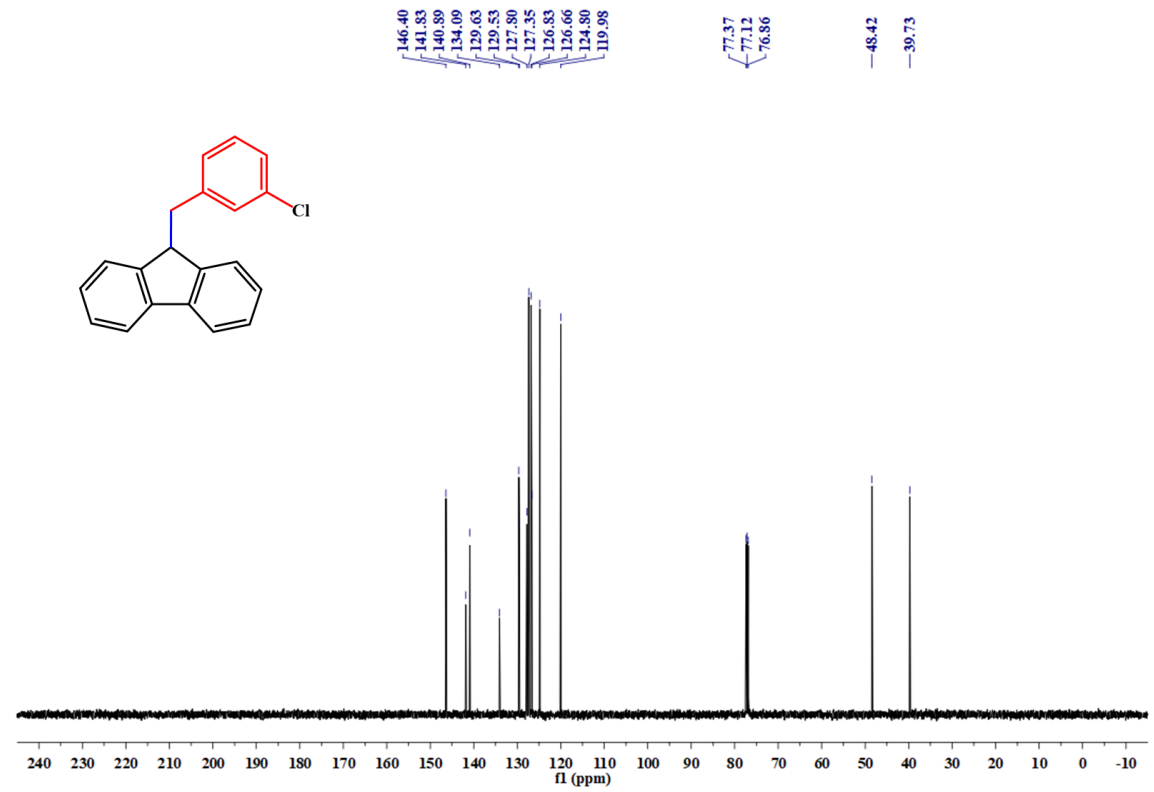


Figure S36: ^{13}**C{**^{1}**H}** NMR spectrum of 3f in $CDCl_3$ at 126 MHz.

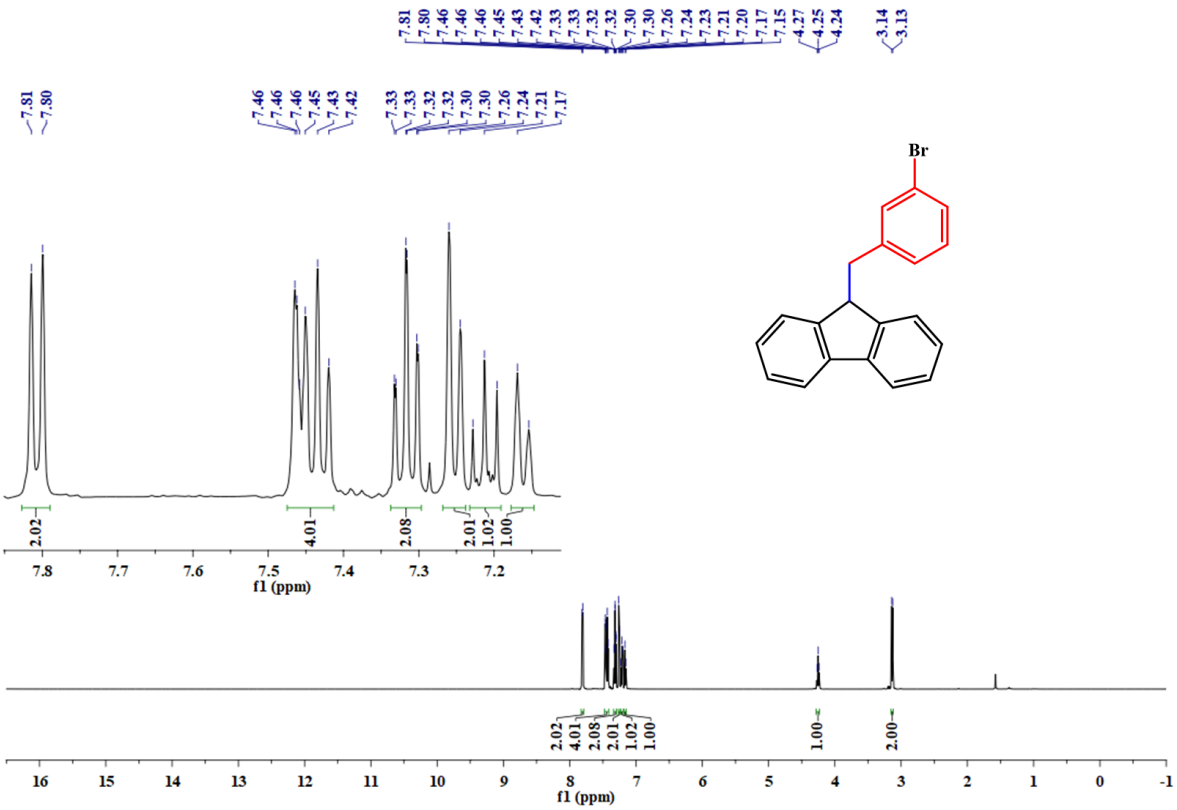


Figure S37: ^{1}**H** NMR spectrum of 3g in $CDCl_3$ at 500 MHz.

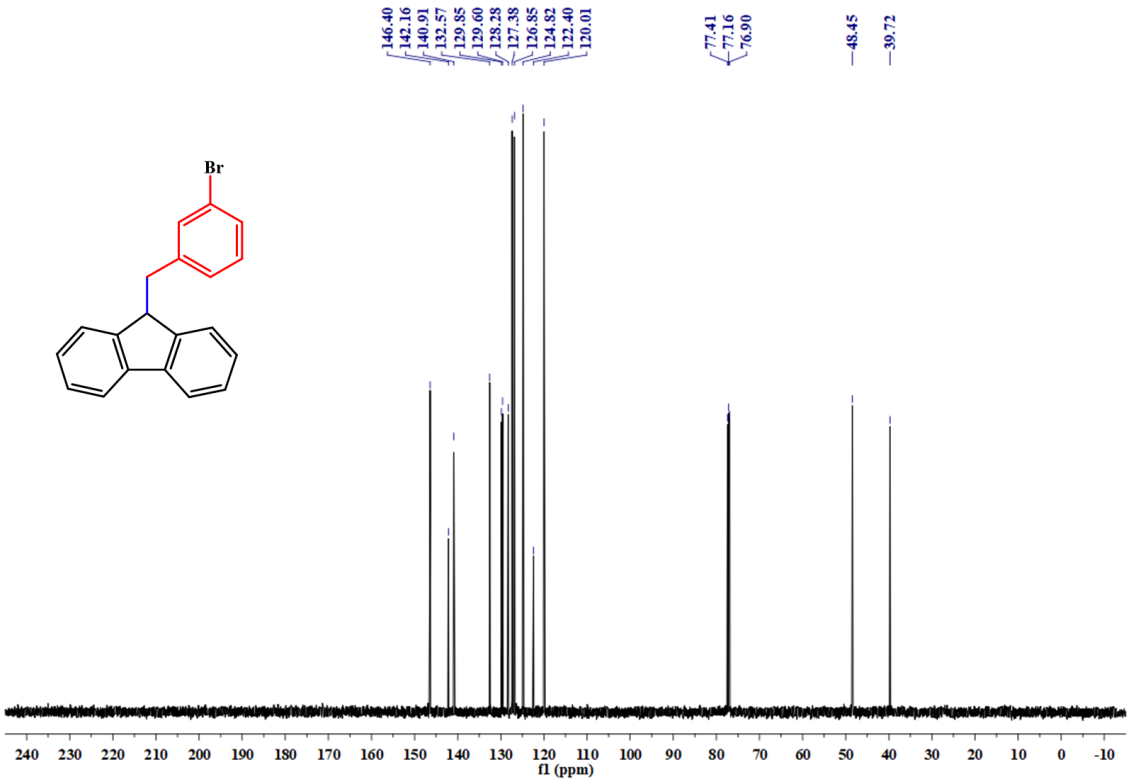


Figure S38: ^{13}**C{**^{1}**H}** NMR spectrum of 3g in $CDCl_3$ at 126 MHz.

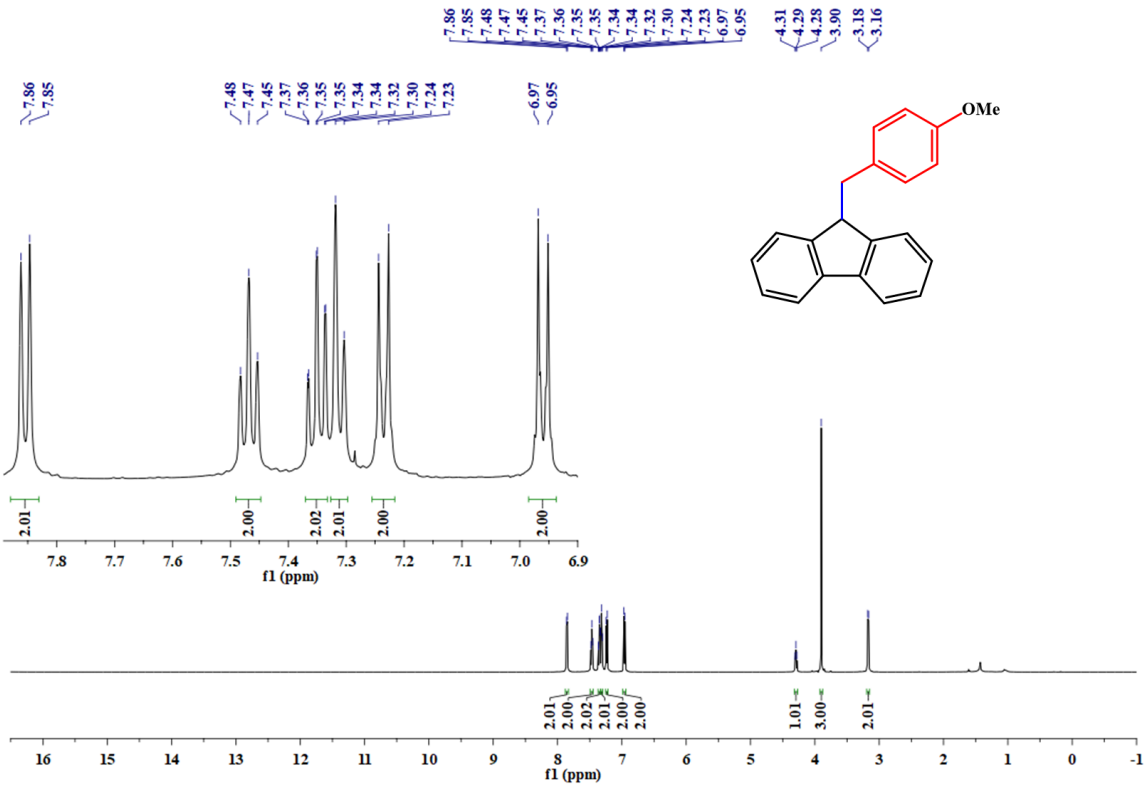


Figure S39: ^{1}**H** NMR spectrum of 3h in $CDCl_3$ at 500 MHz.

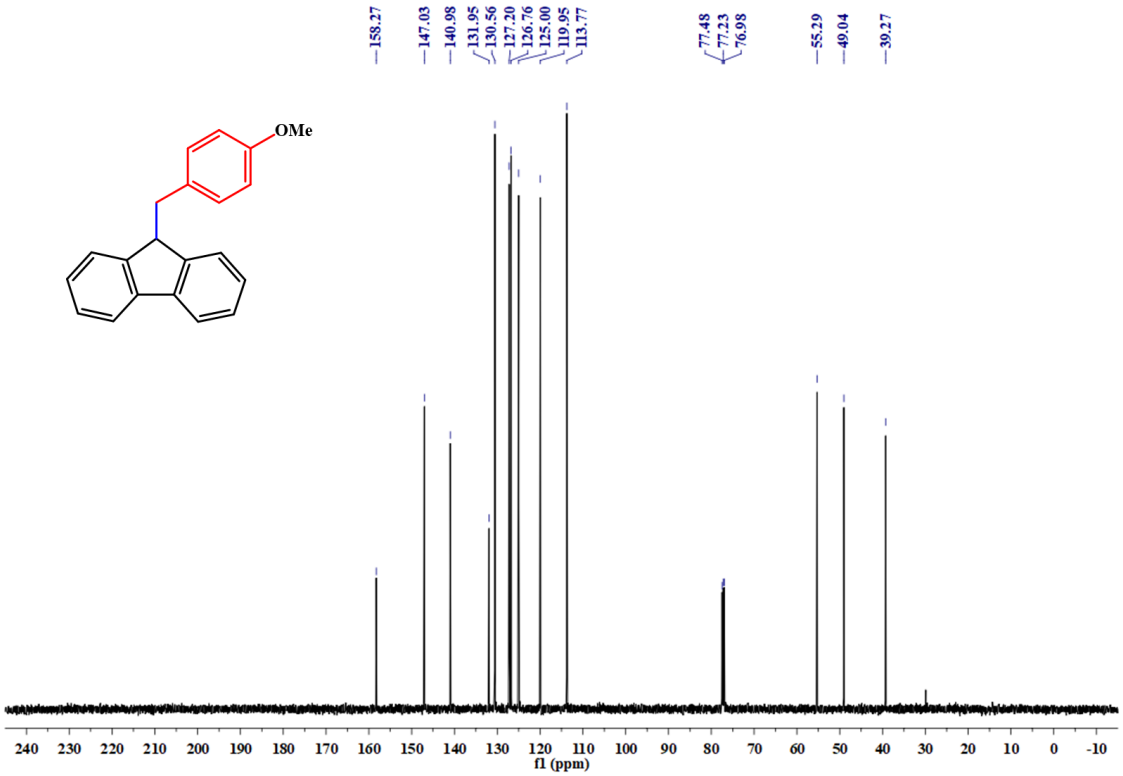


Figure S40: ^{13}**C{**^{1}**H}** NMR spectrum of 3h in $CDCl_3$ at 126 MHz.

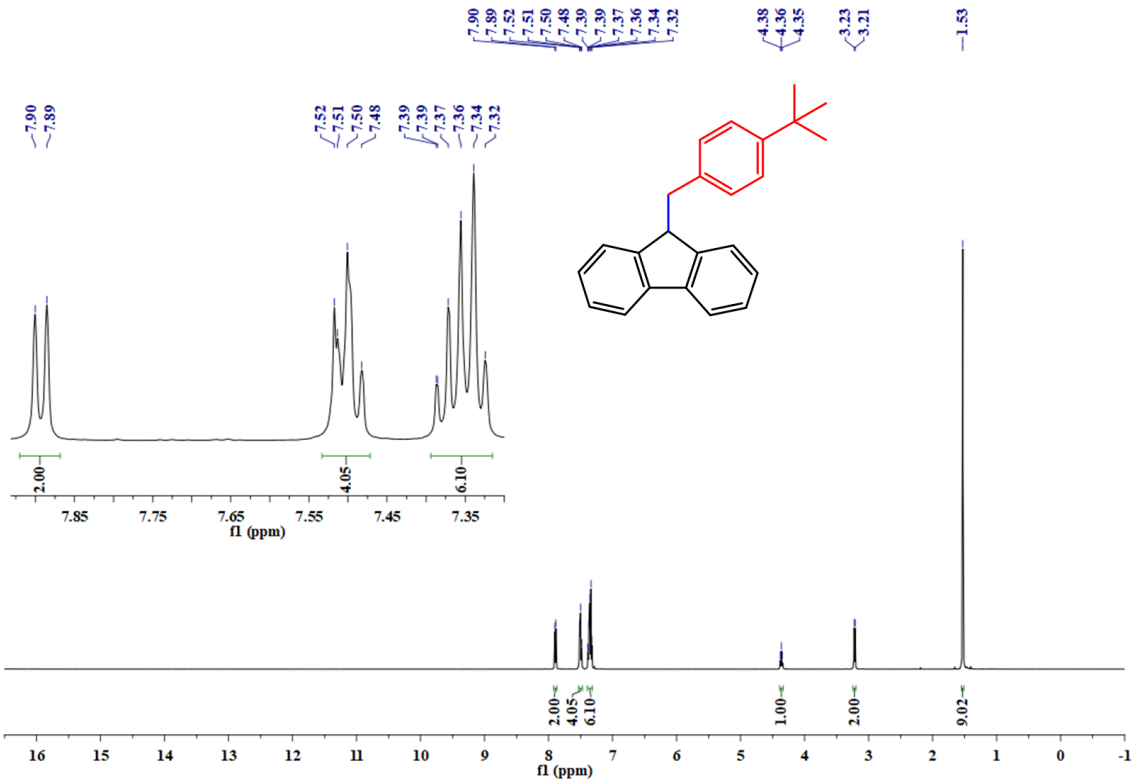


Figure S41: ^{1}**H** NMR spectrum of 3i in $CDCl_3$ at 500 MHz.

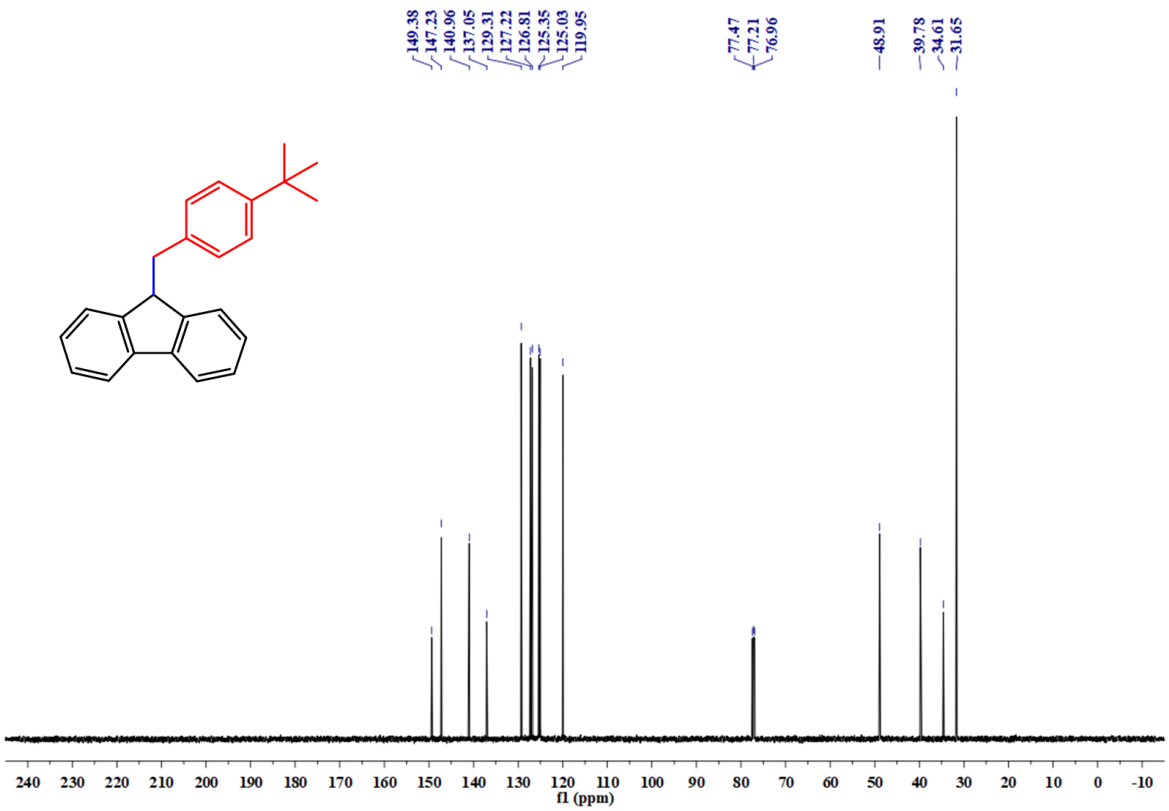


Figure S42: ^{13}**C{**^{1}**H}** NMR spectrum of 3i in $CDCl_3$ at 126 MHz.

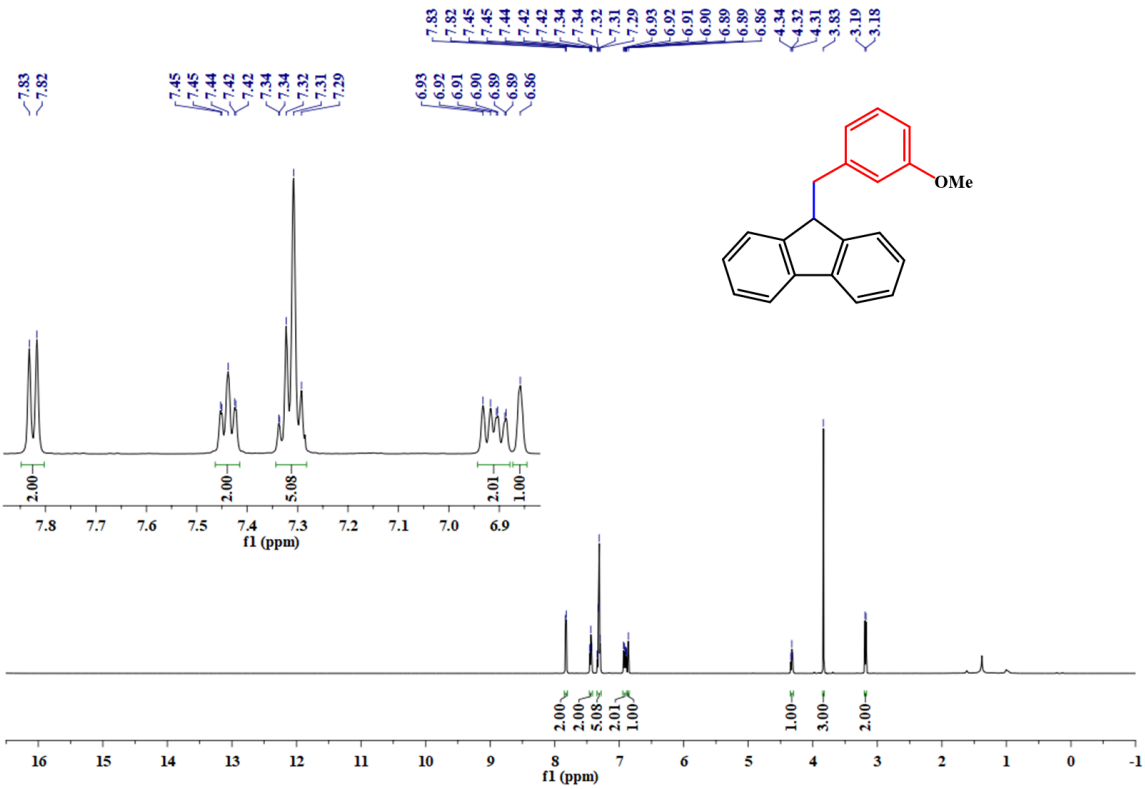


Figure S43: ^{1}**H** NMR spectrum of 3j in $CDCl_3$ at 500 MHz.

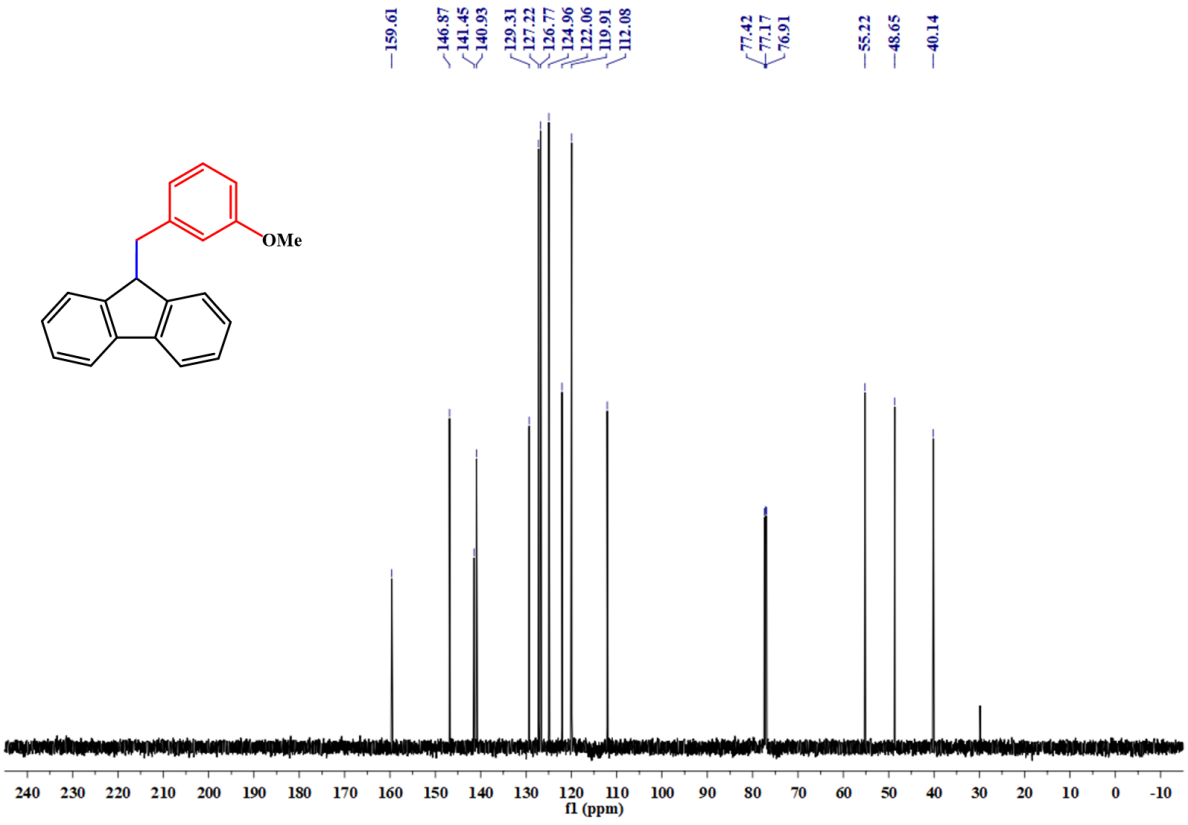


Figure S44: ^{13}**C{**^{1}**H}** NMR spectrum of 3j in $CDCl_3$ at 126 MHz.

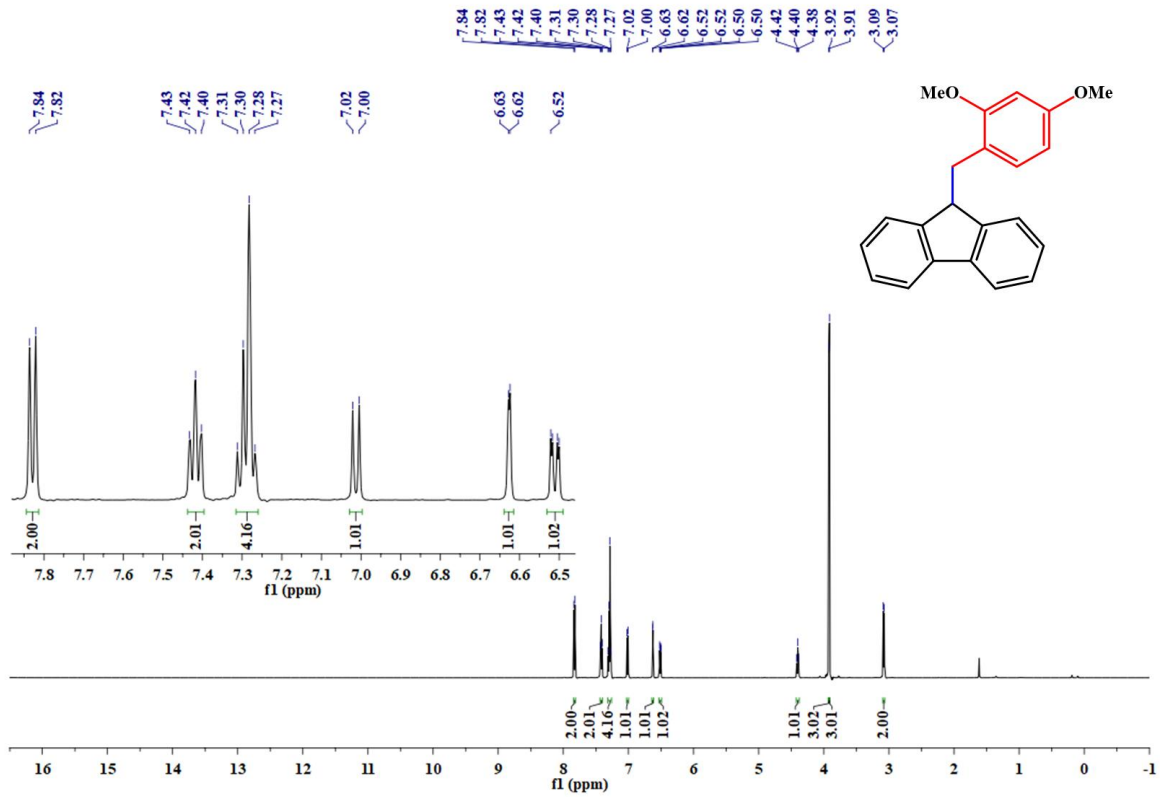


Figure S45: ^{1}**H** NMR spectrum of 3k in $CDCl_3$ at 500 MHz.

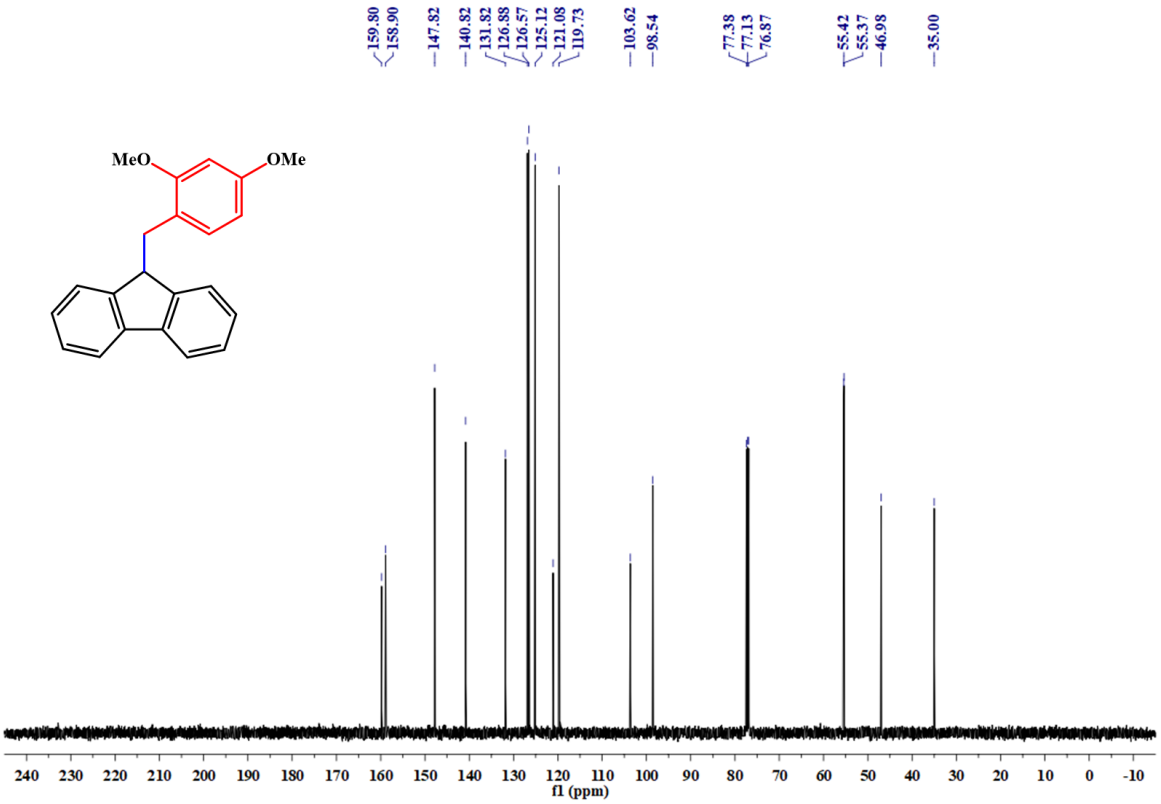


Figure S46: ^{13}**C{**^{1}**H}** NMR spectrum of 3k in $CDCl_3$ at 126 MHz.

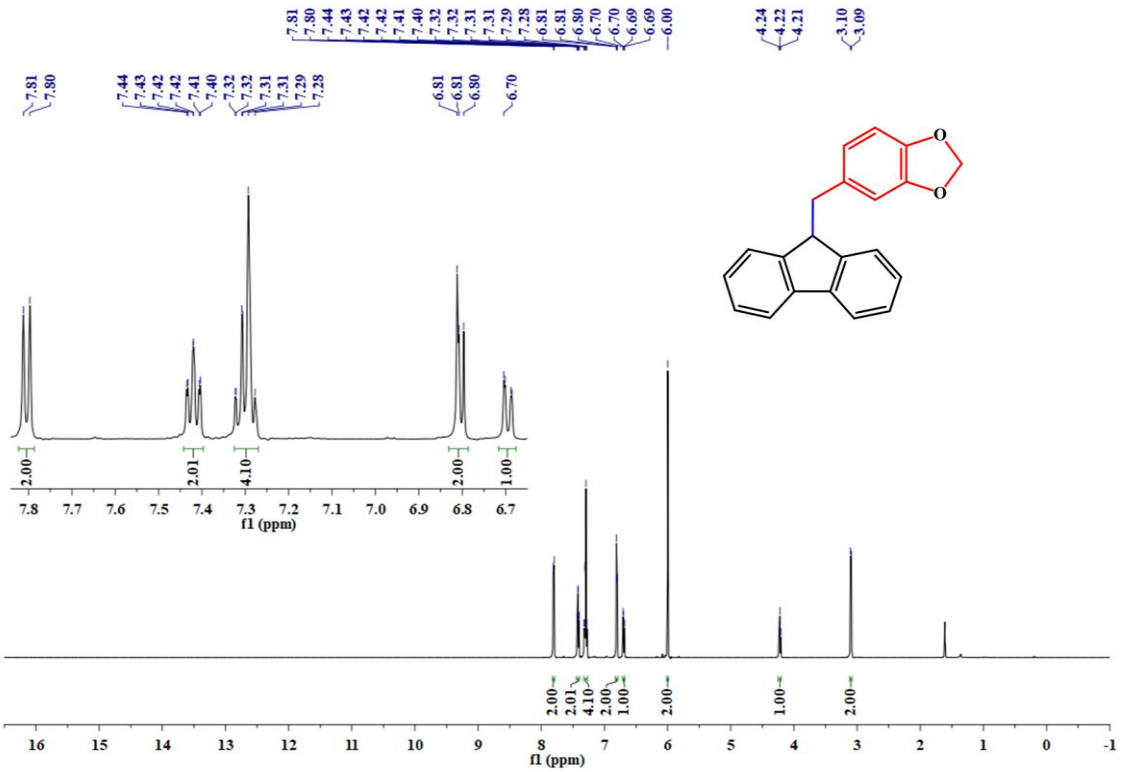


Figure S47: ^{1}H NMR spectrum of 3l in $CDCl_3$ at 500 MHz.

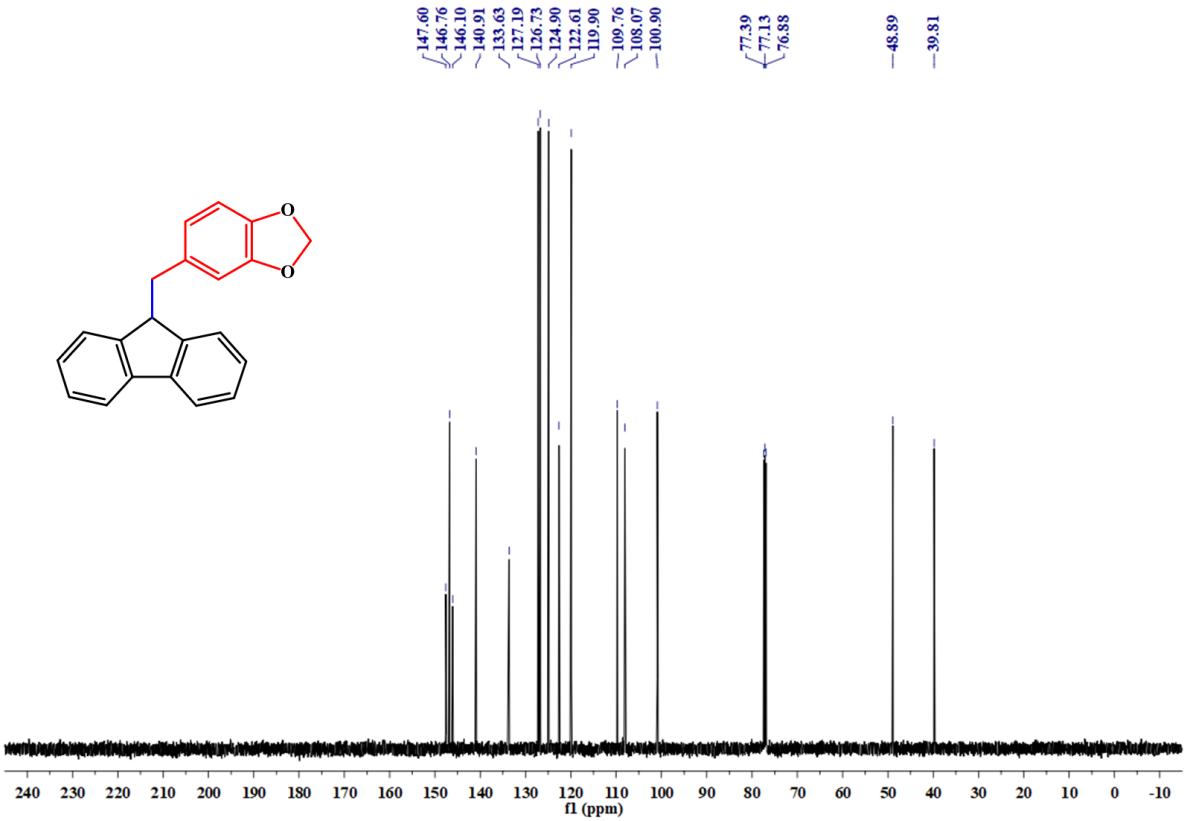


Figure S48: $^{13}C\{^{1}H\}$ NMR spectrum of 3l in $CDCl_3$ at 126 MHz.

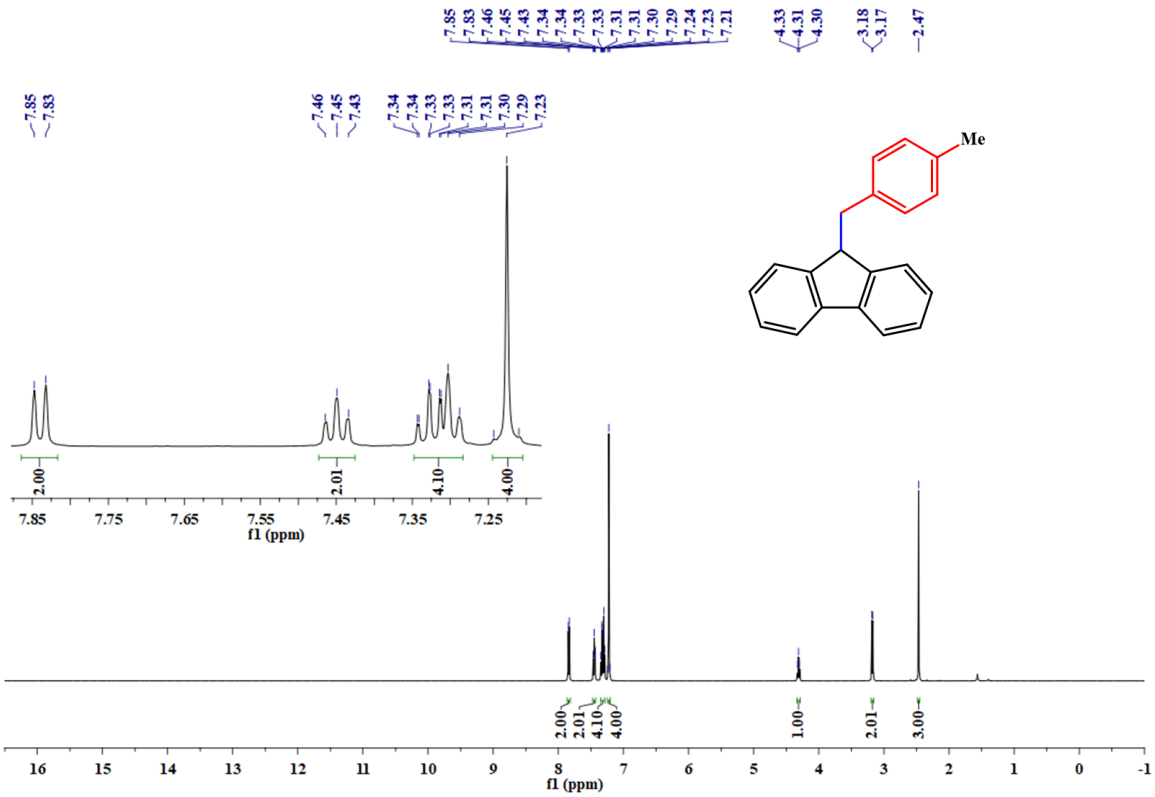


Figure S49: ^{1}**H** NMR spectrum of 3m in $CDCl_3$ at 500 MHz.

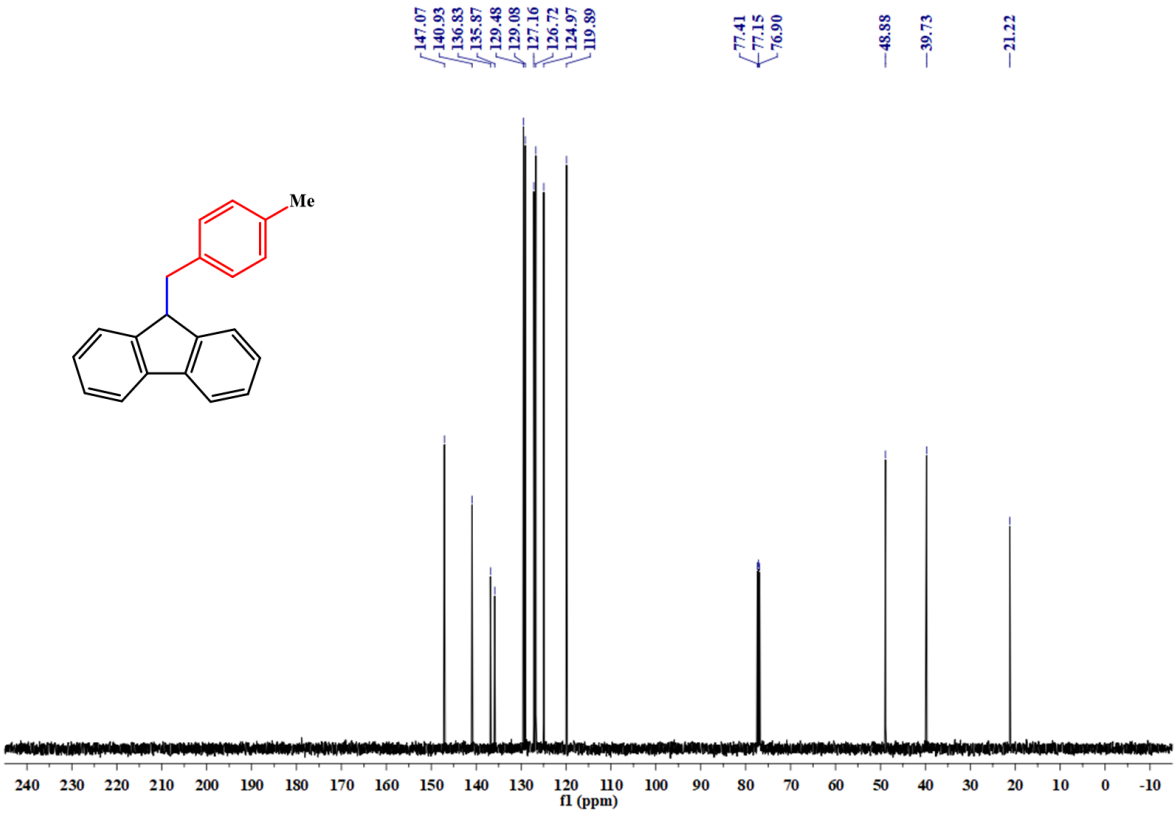


Figure S50: ^{13}**C{**^{1}**H}** NMR spectrum of 3m in $CDCl_3$ at 126 MHz.

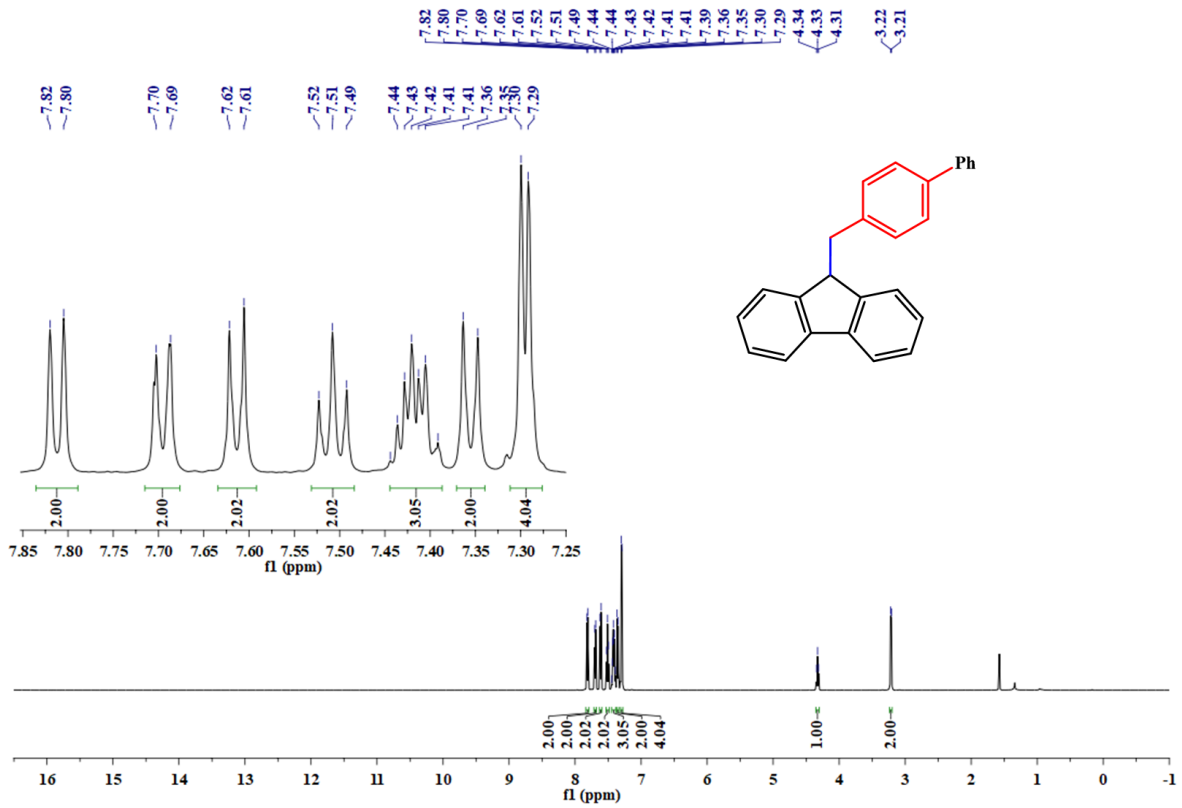


Figure S51: ^{1}**H** NMR spectrum of 3n in $CDCl_3$ at 500 MHz.

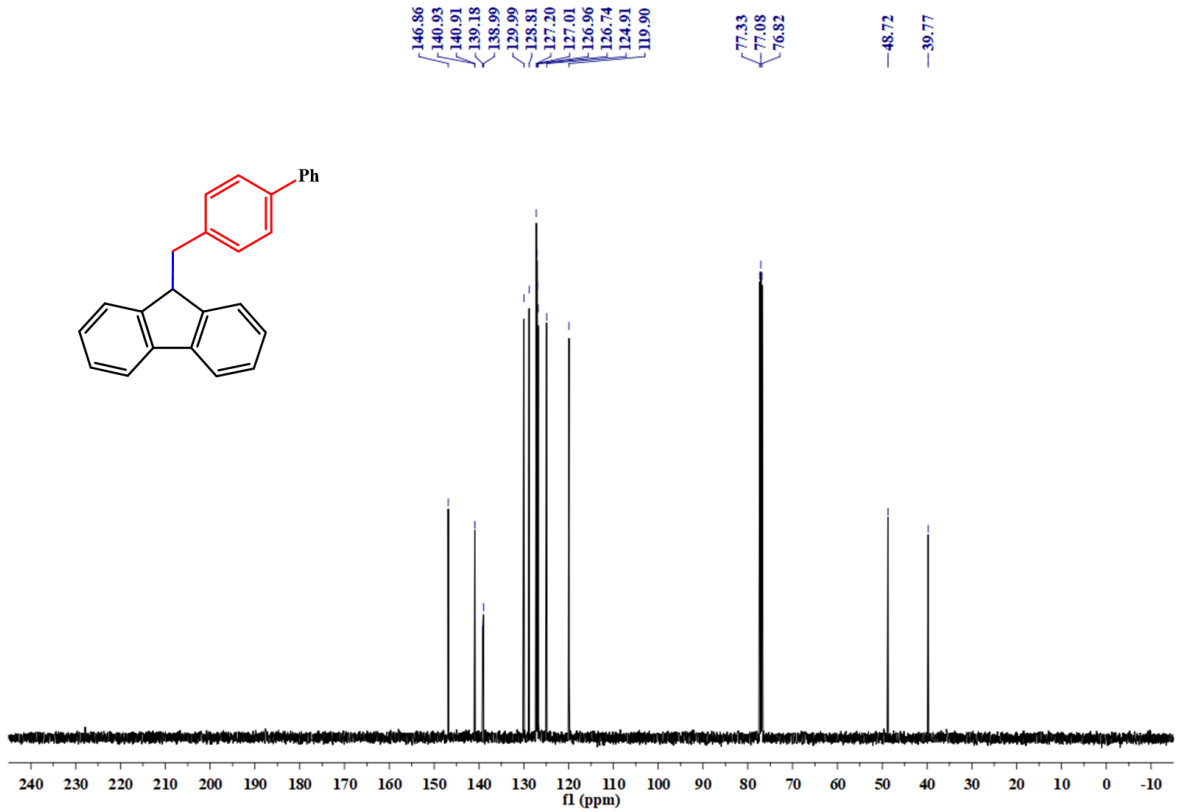


Figure S52: ^{13}**C{**^{1}**H}** NMR spectrum of 3n in $CDCl_3$ at 126 MHz.

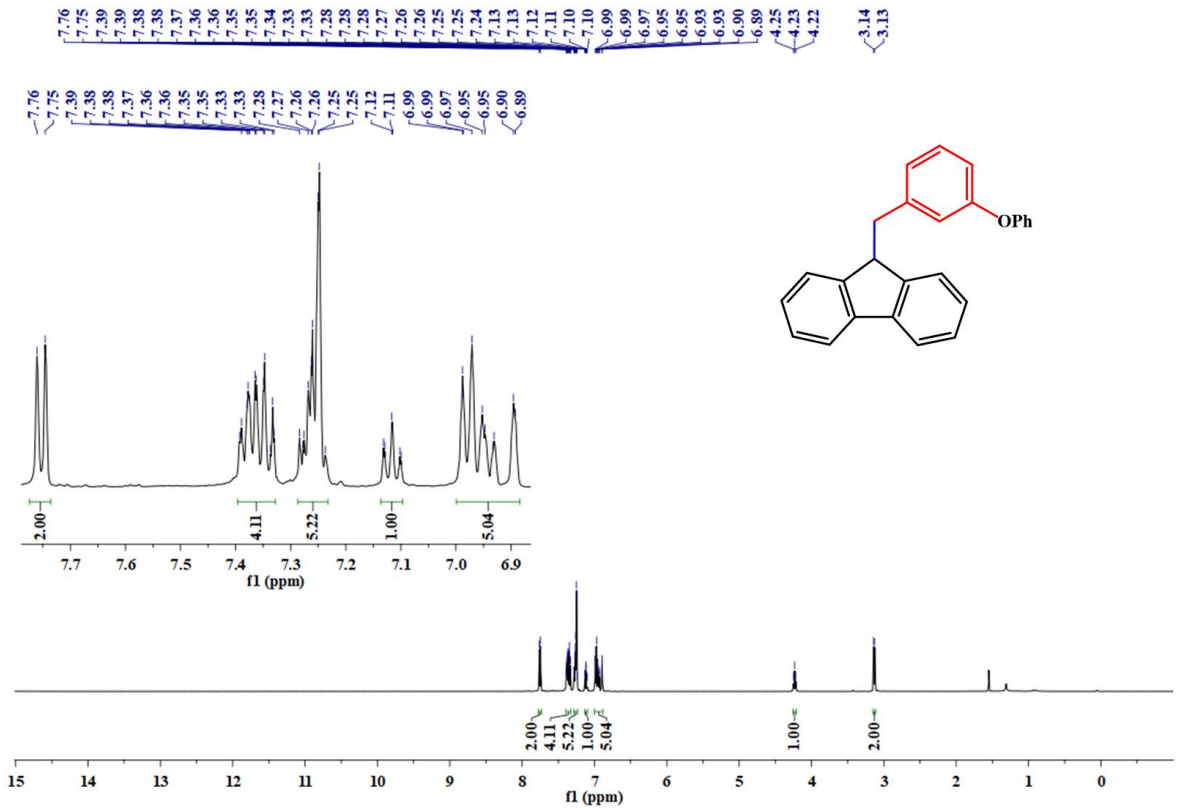


Figure S53: ^{1}**H** NMR spectrum of 3o in $CDCl_3$ at 500 MHz.

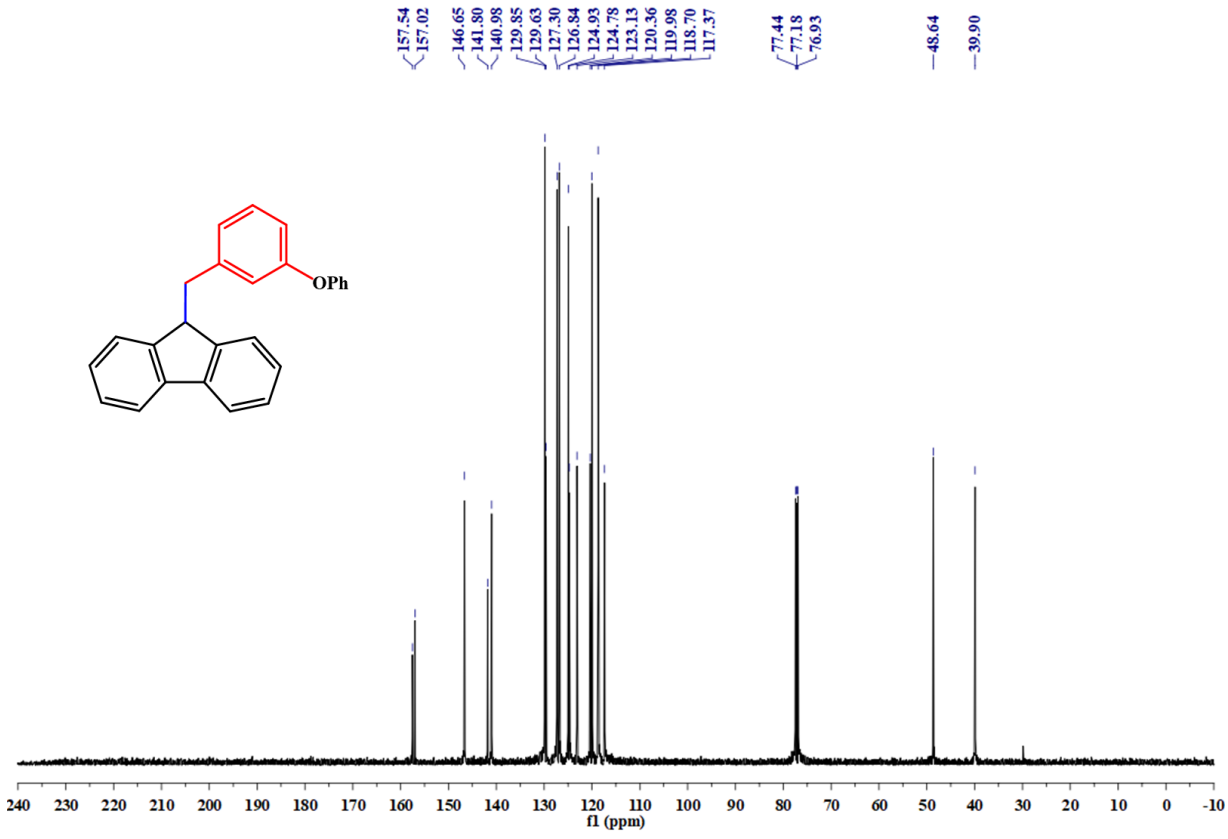


Figure S54: ^{13}**C{**^{1}**H}** NMR spectrum of 3o in $CDCl_3$ at 126 MHz.

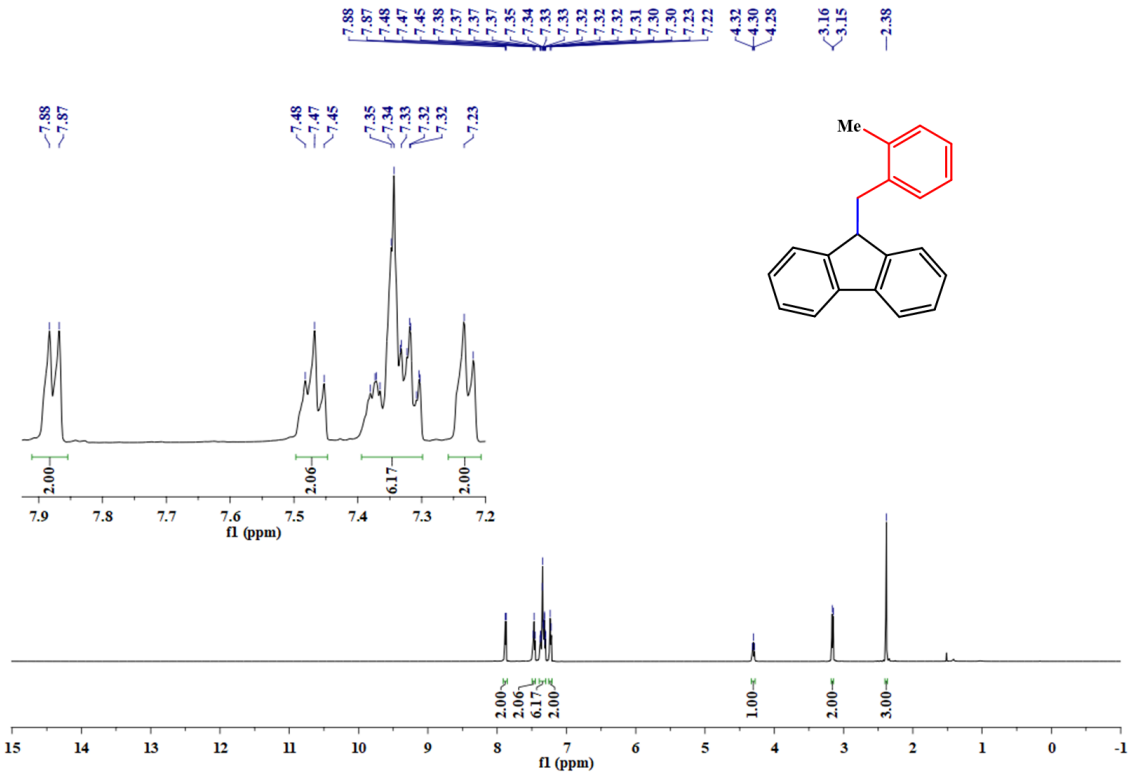


Figure S55: ^{1}**H** NMR spectrum of 3p in $CDCl_3$ at 500 MHz.

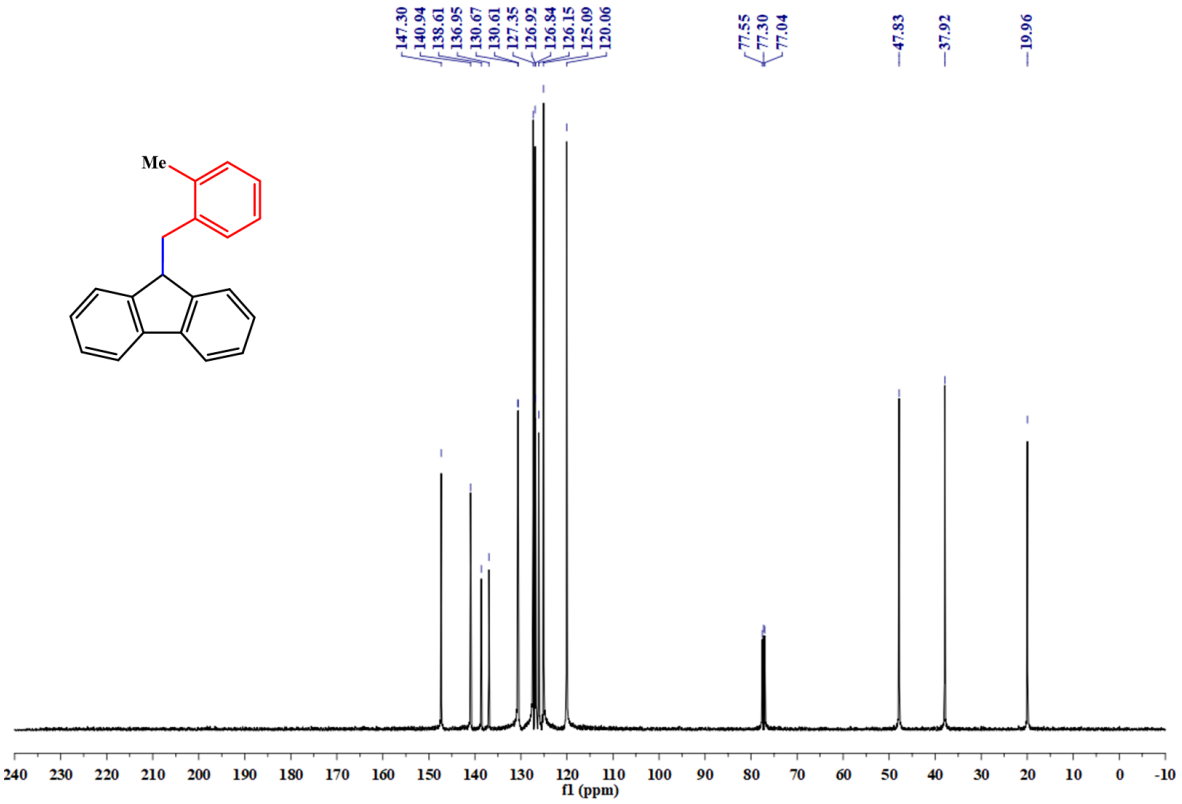


Figure S56: ^{13}**C{**^{1}**H}** NMR spectrum of 3p in $CDCl_3$ at 126 MHz.

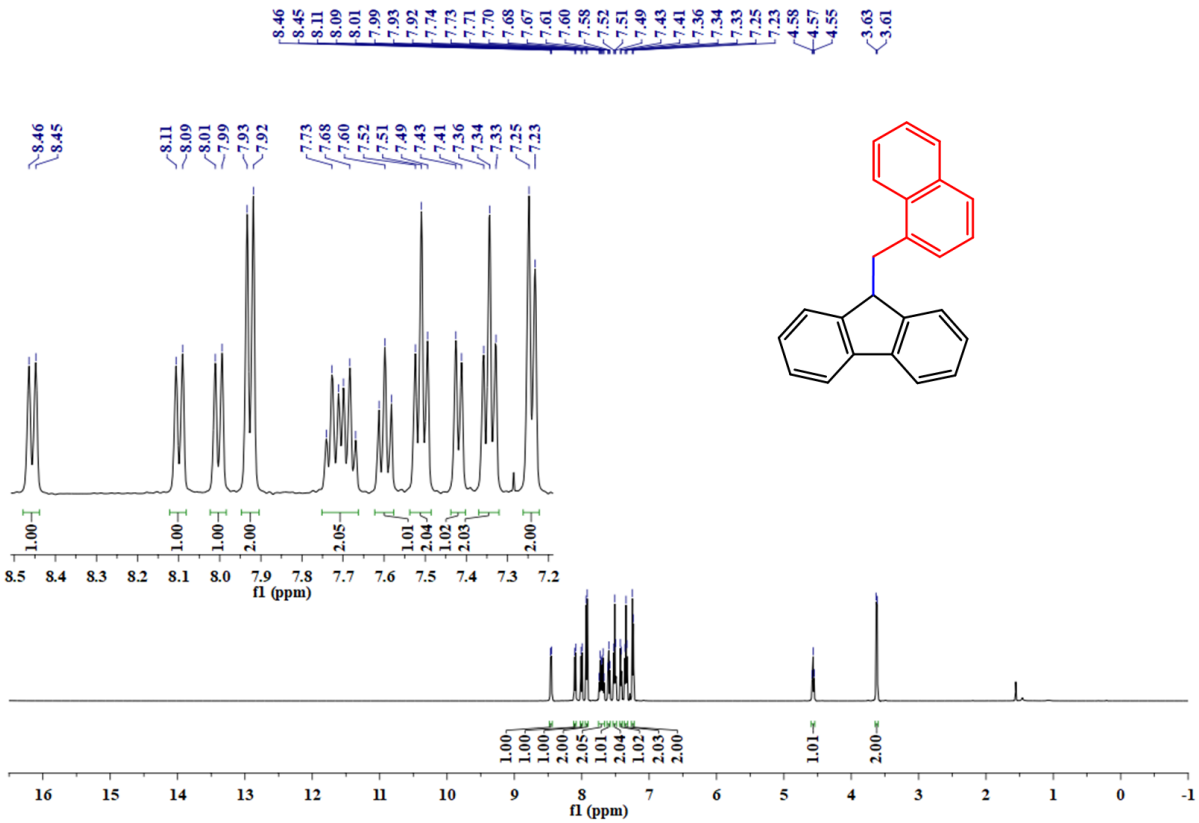


Figure S57: **^{1}H** NMR spectrum of 3q in $CDCl_3$ at 500 MHz.

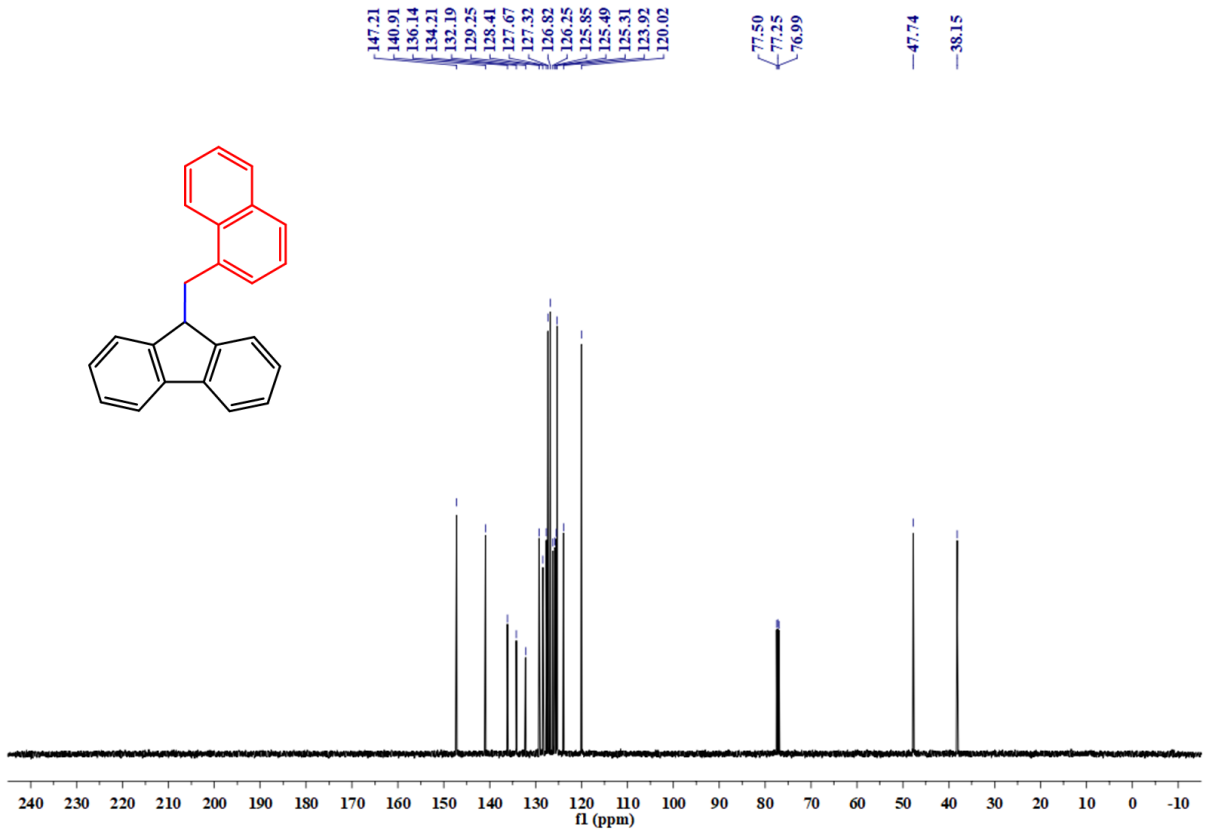


Figure S58: **^{13}C{^{1}H}** NMR spectrum of 3q in $CDCl_3$ at 126 MHz.

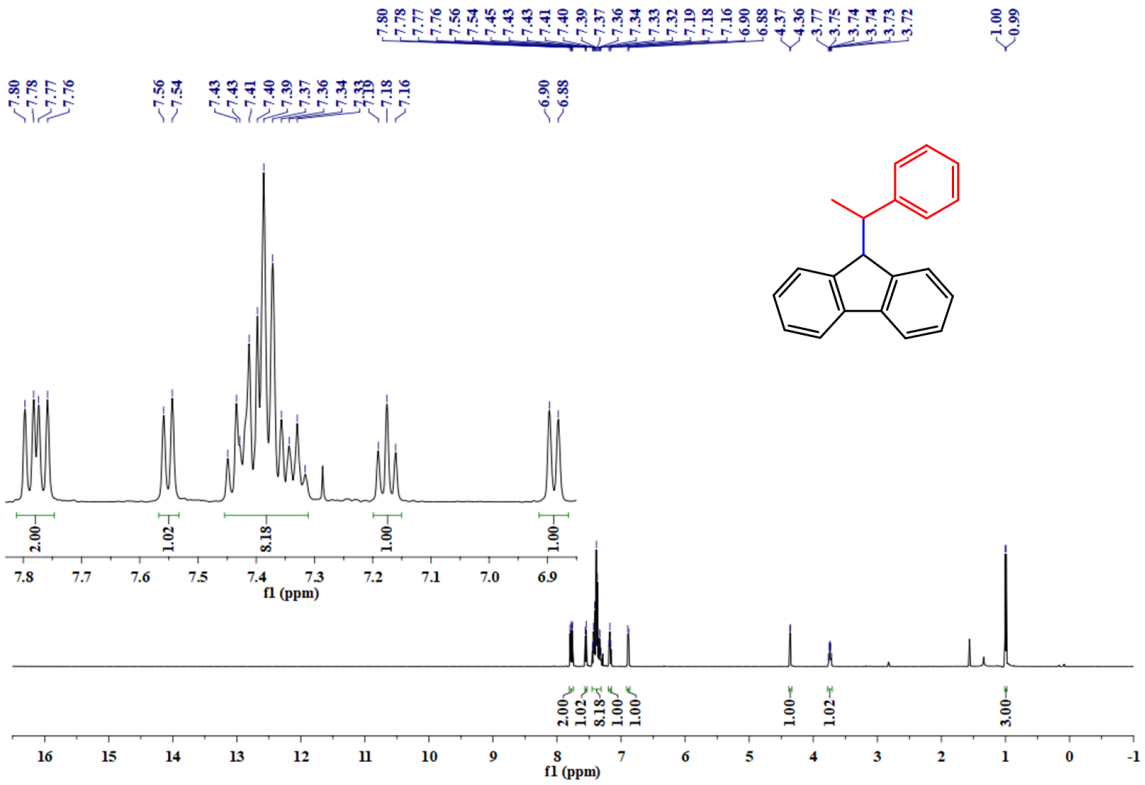


Figure S59: ^{1}H NMR spectrum of 3r in $CDCl_3$ at 500 MHz.

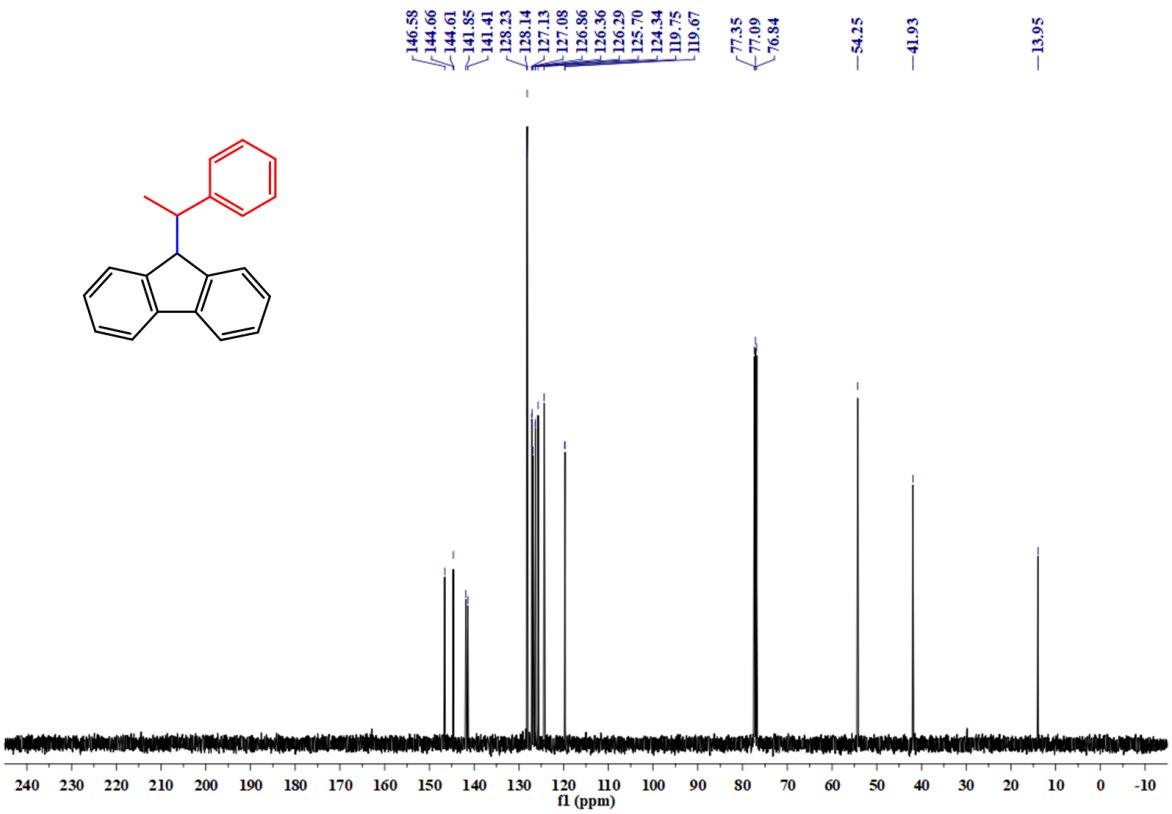


Figure S60: $^{13}C\{^{1}H\}$ NMR spectrum of 3r in $CDCl_3$ at 126 MHz.

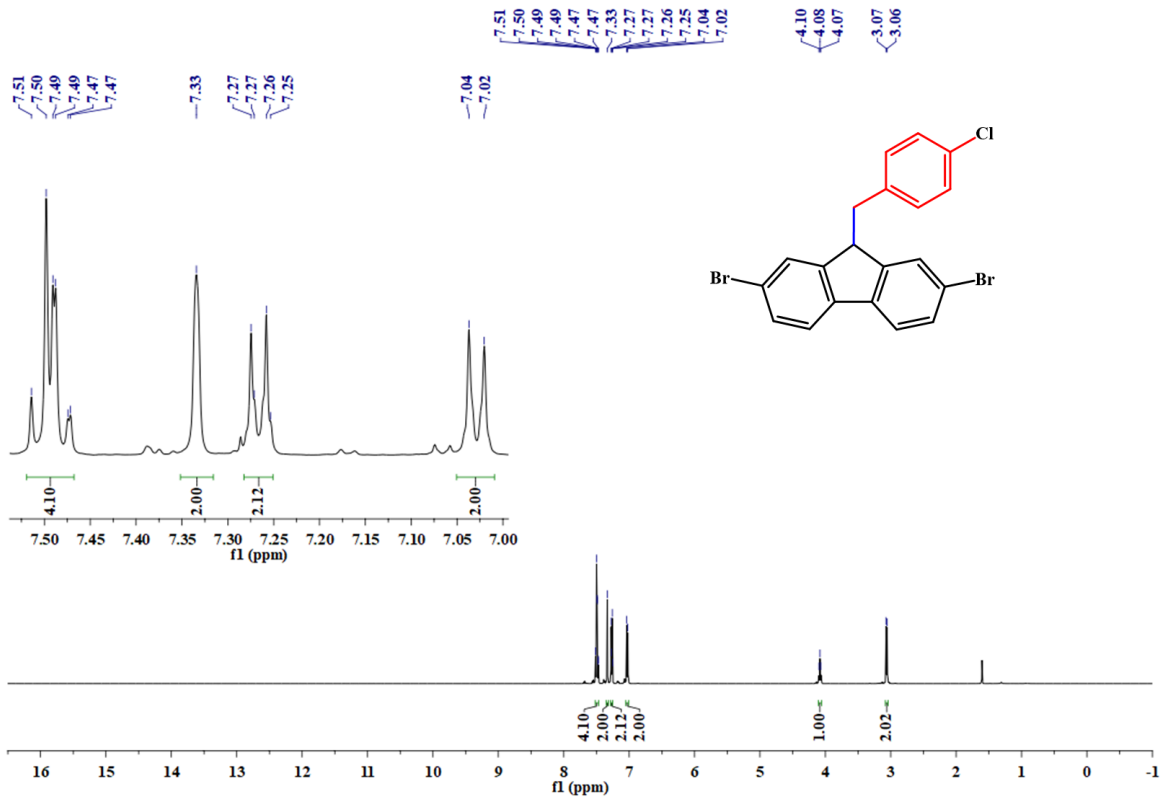


Figure S61: ^{1}**H** NMR spectrum of 3s in $CDCl_3$ at 500 MHz.

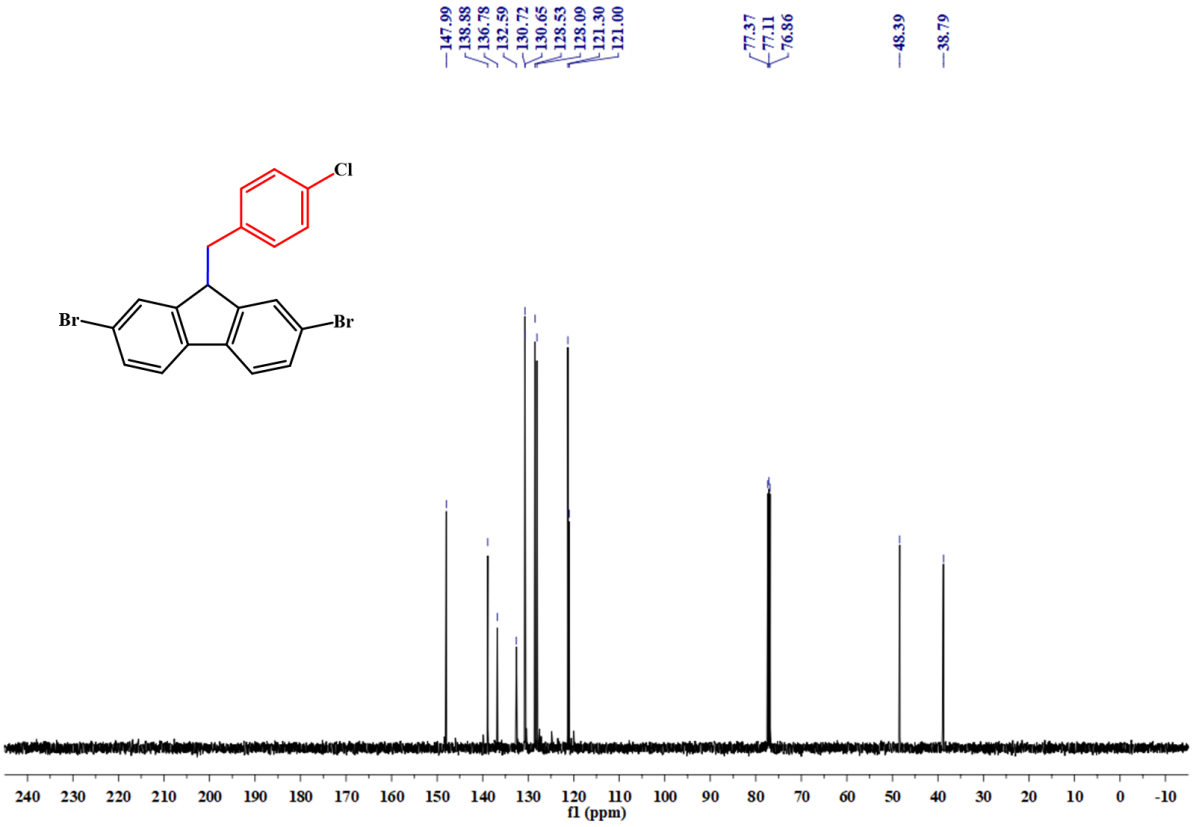


Figure S62: ^{13}**C{**^{1}**H}** NMR spectrum of 3s in $CDCl_3$ at 126 MHz.

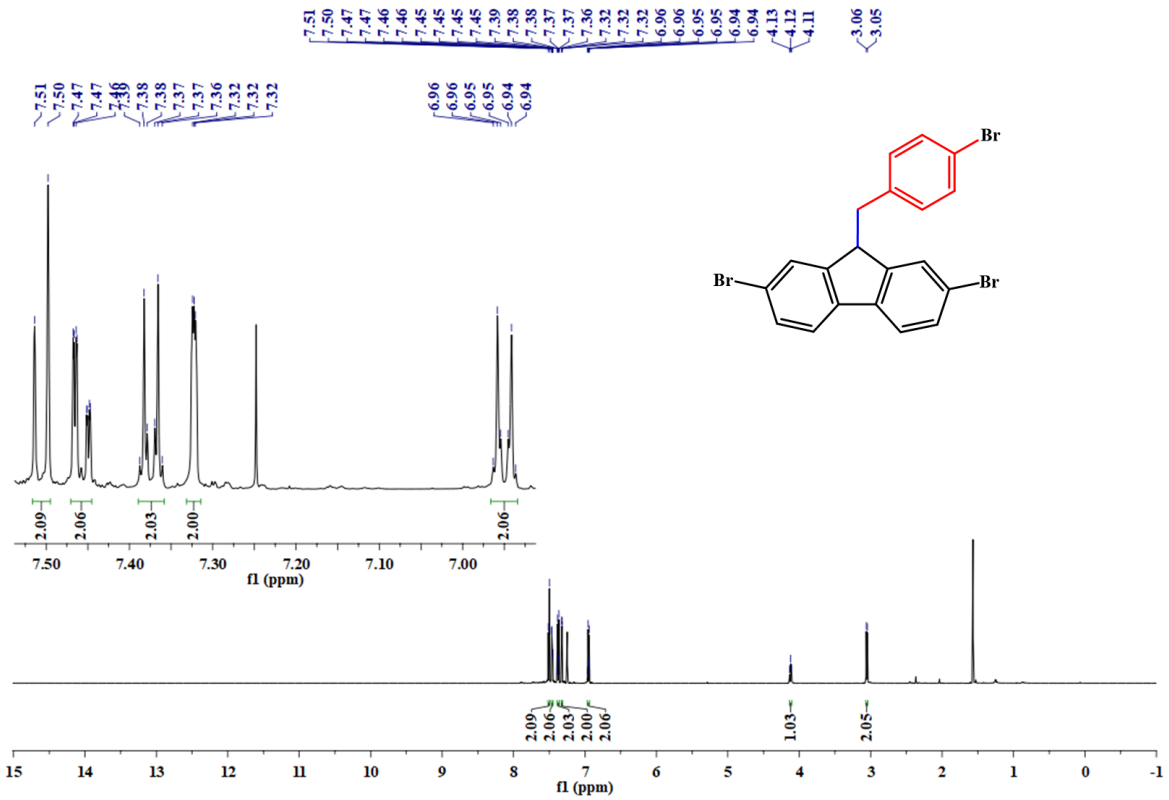


Figure S63: ^{1}H NMR spectrum of 3t in $CDCl_3$ at 500 MHz.

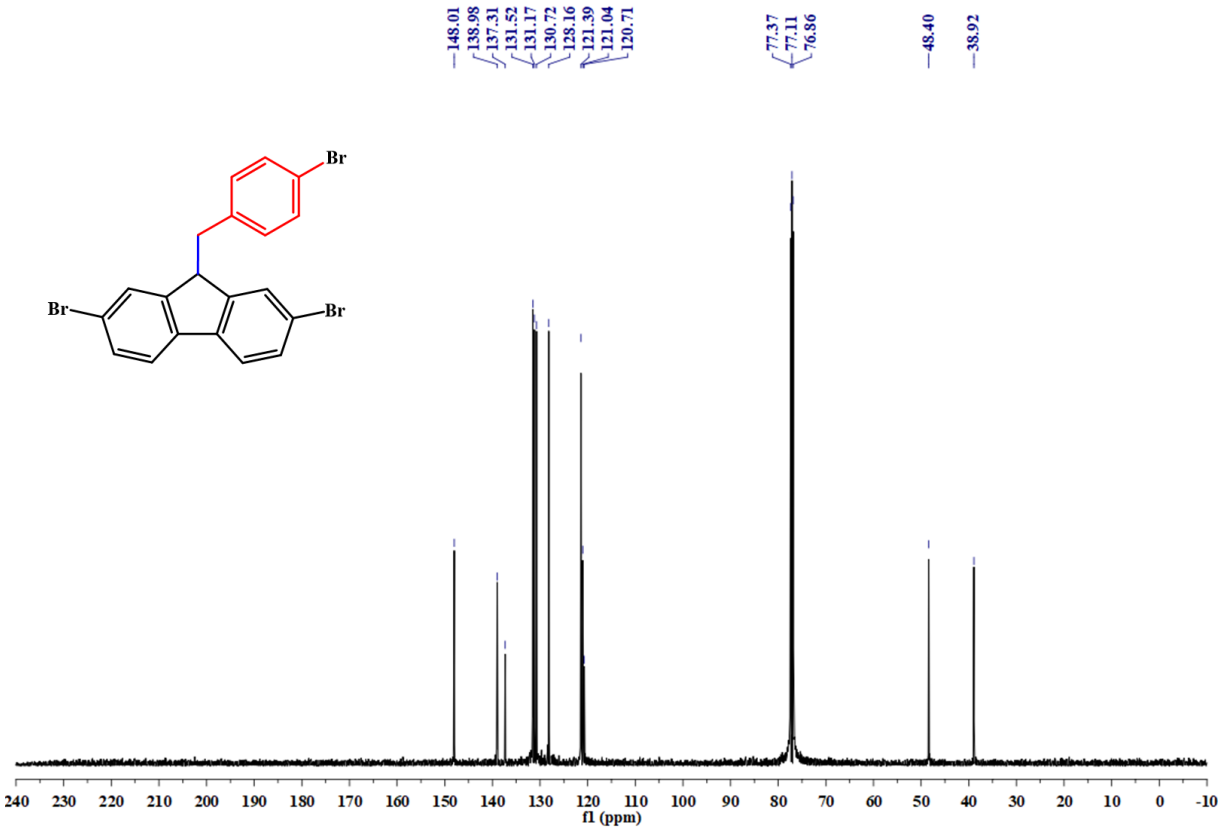


Figure S64: $^{13}C\{^{1}H\}$ NMR spectrum of 3t in $CDCl_3$ at 126 MHz.

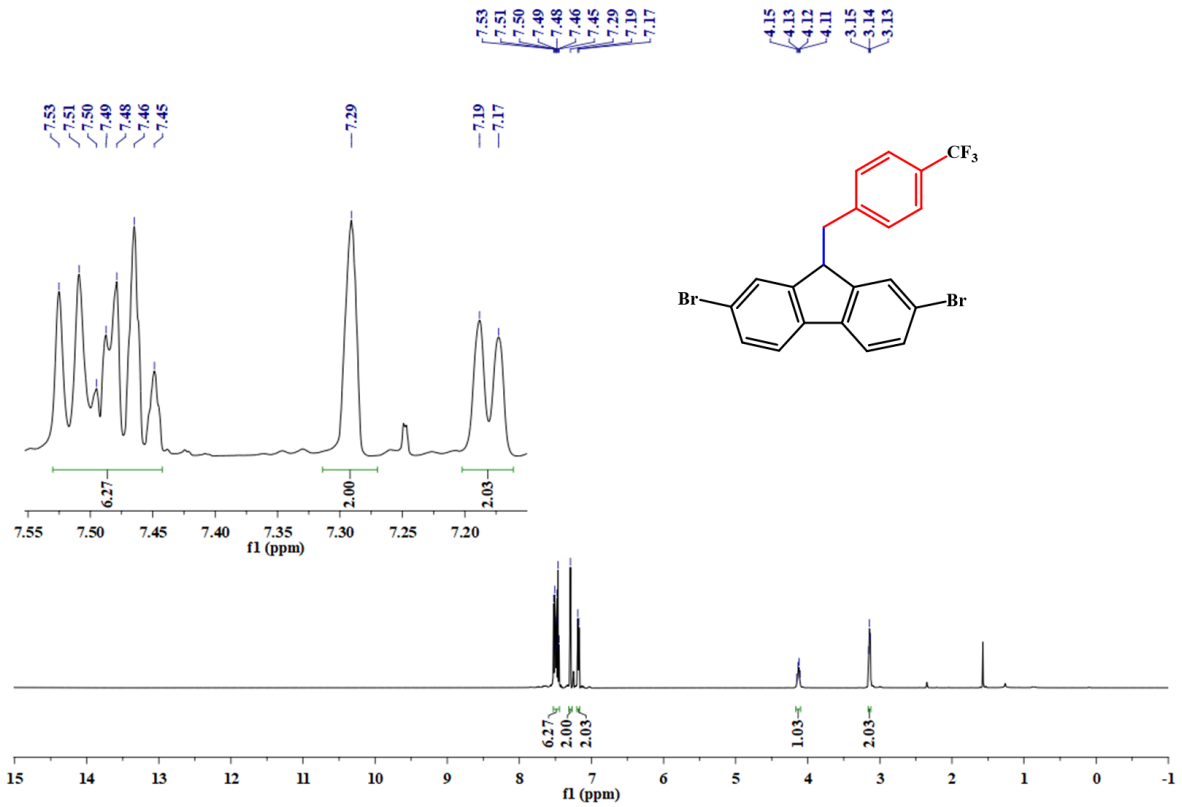


Figure S65: ^{1}**H** NMR spectrum of 3u in $CDCl_3$ at 500 MHz.

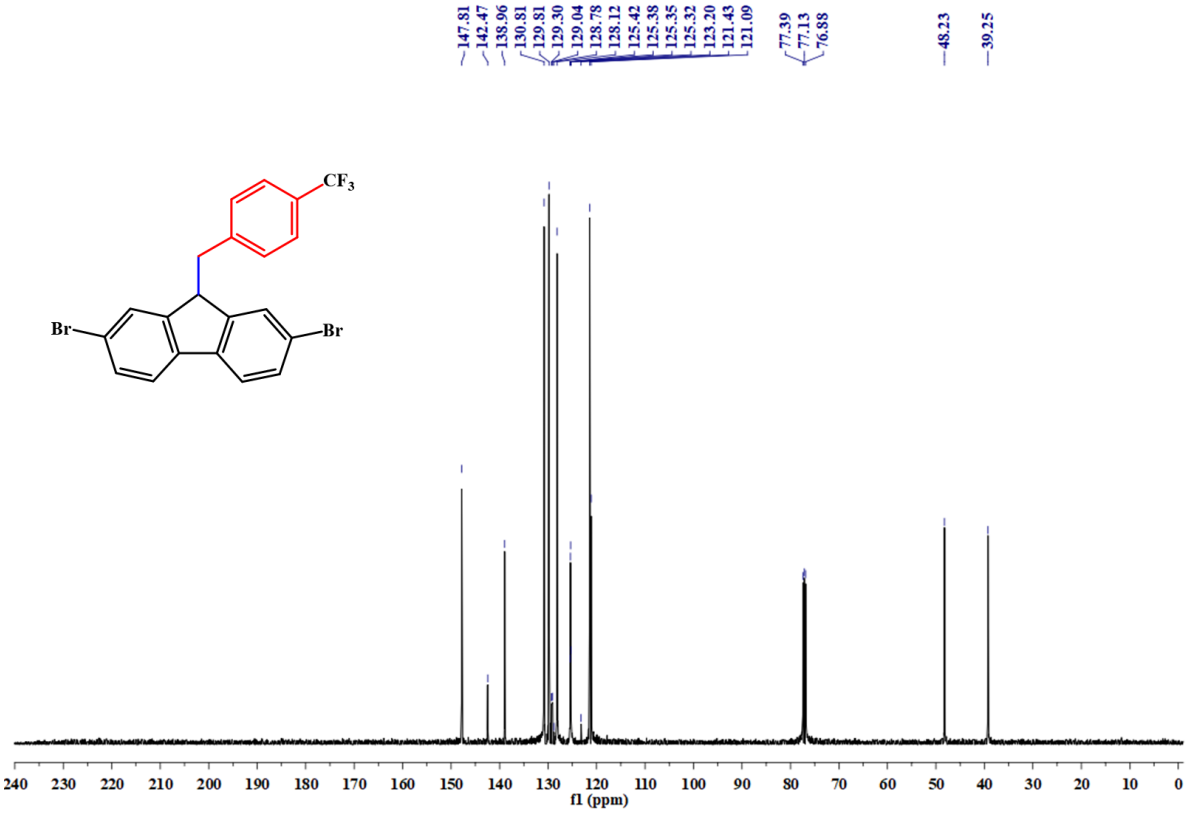


Figure S66: ^{13}**C{**^{1}**H}** NMR spectrum of 3u in $CDCl_3$ at 126 MHz.

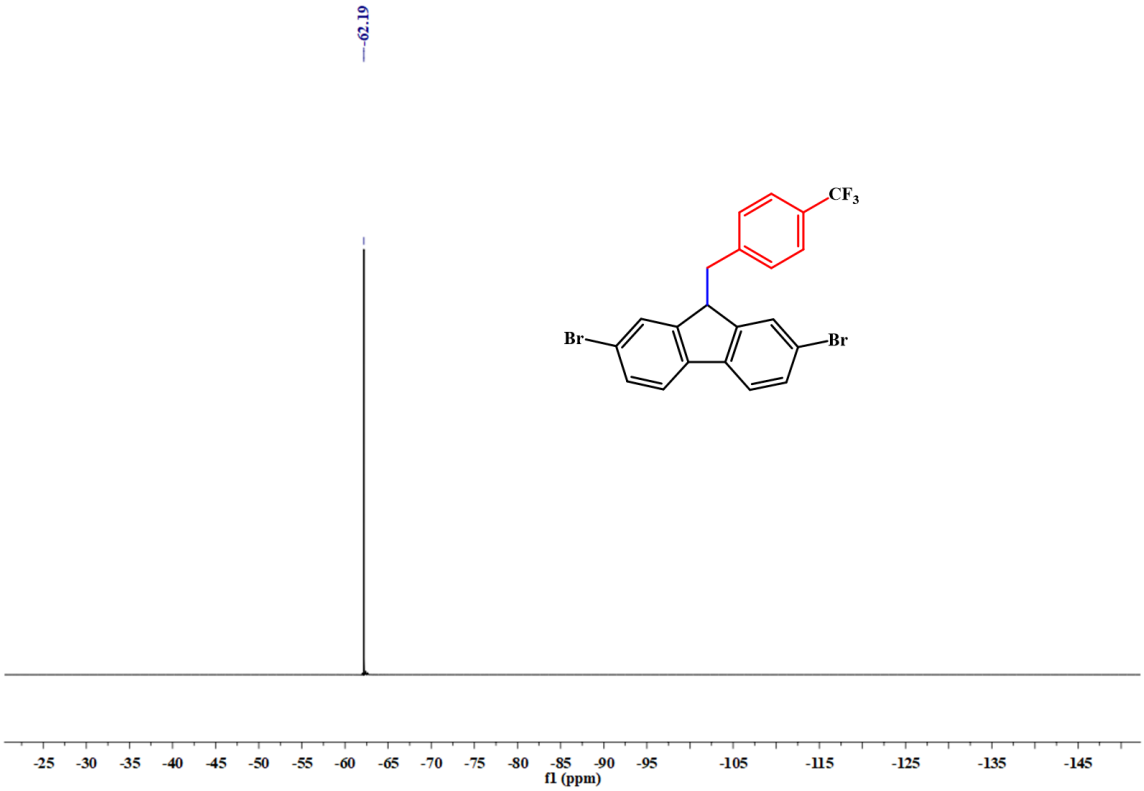


Figure S67: ^{19}**F** NMR spectrum of 3u in $CDCl_3$ at 471 MHz.

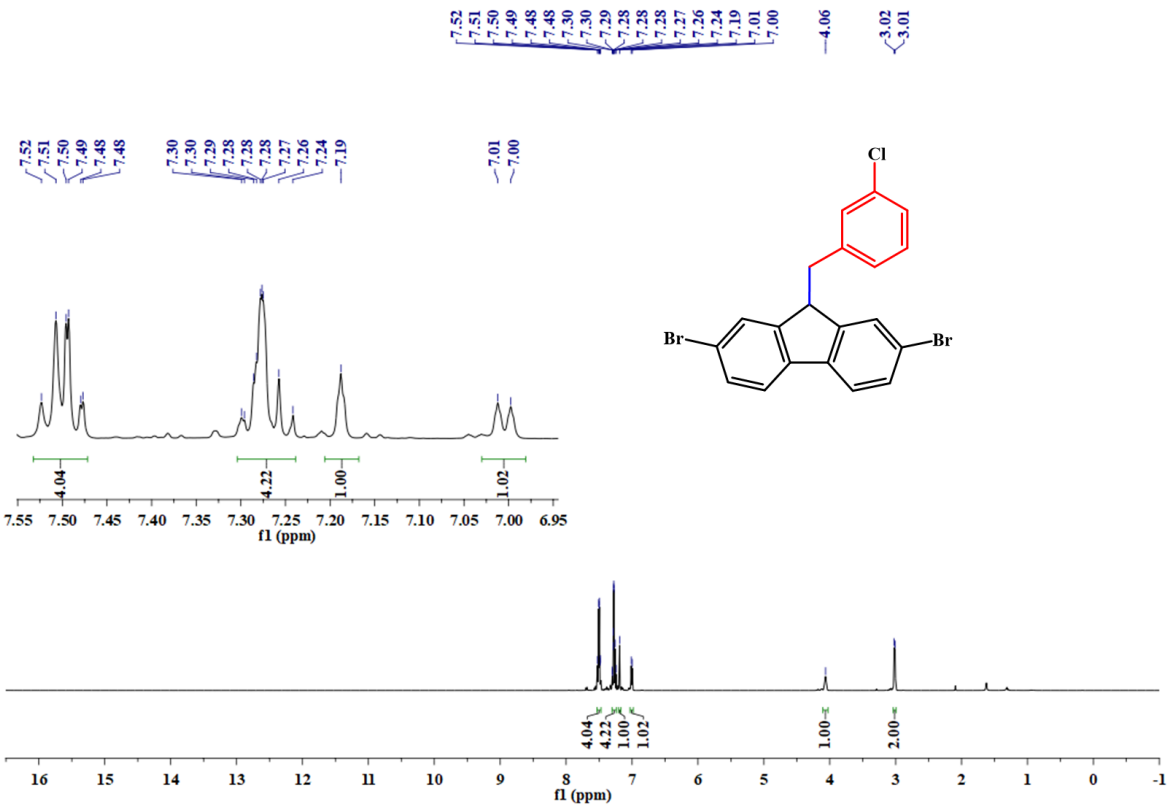


Figure S68: ^{1}**H** NMR spectrum of 3v in $CDCl_3$ at 500 MHz.

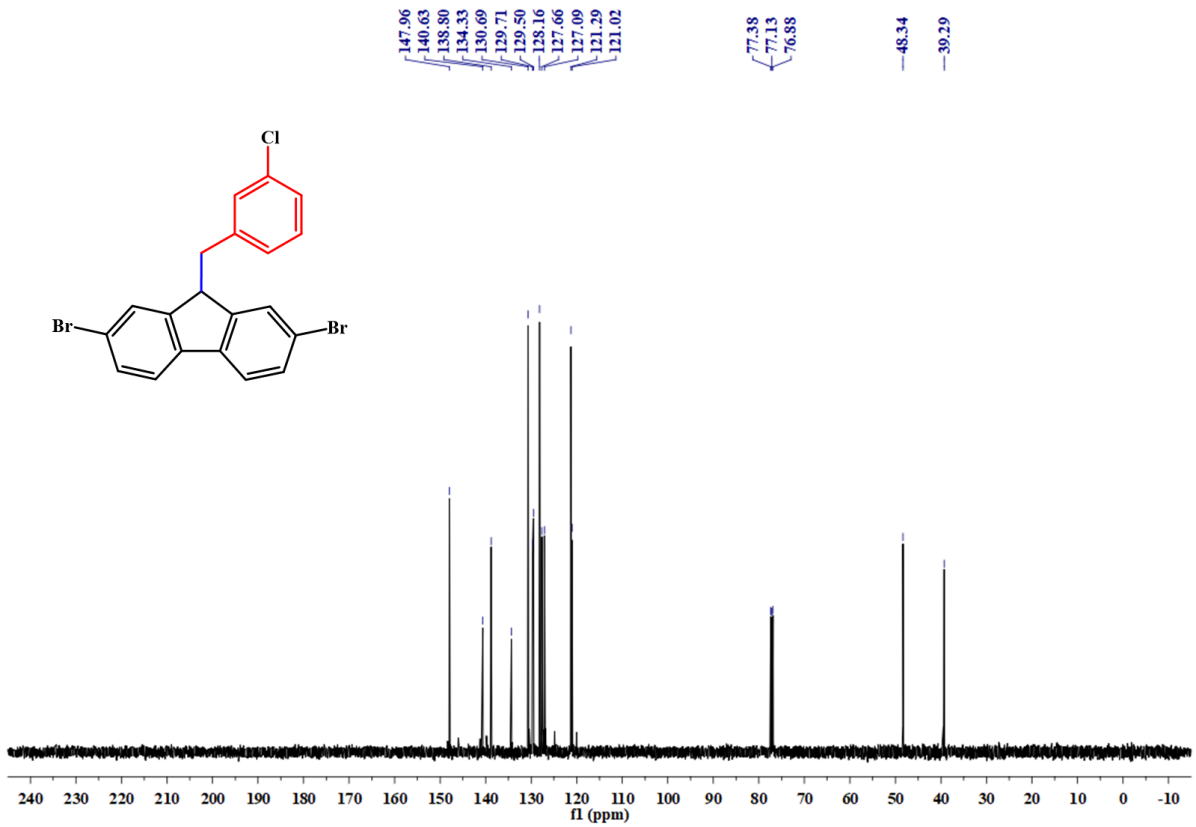


Figure S69: $^{13}C\{^{1}H\}$ NMR spectrum of 3v in $CDCl_3$ at 126 MHz.

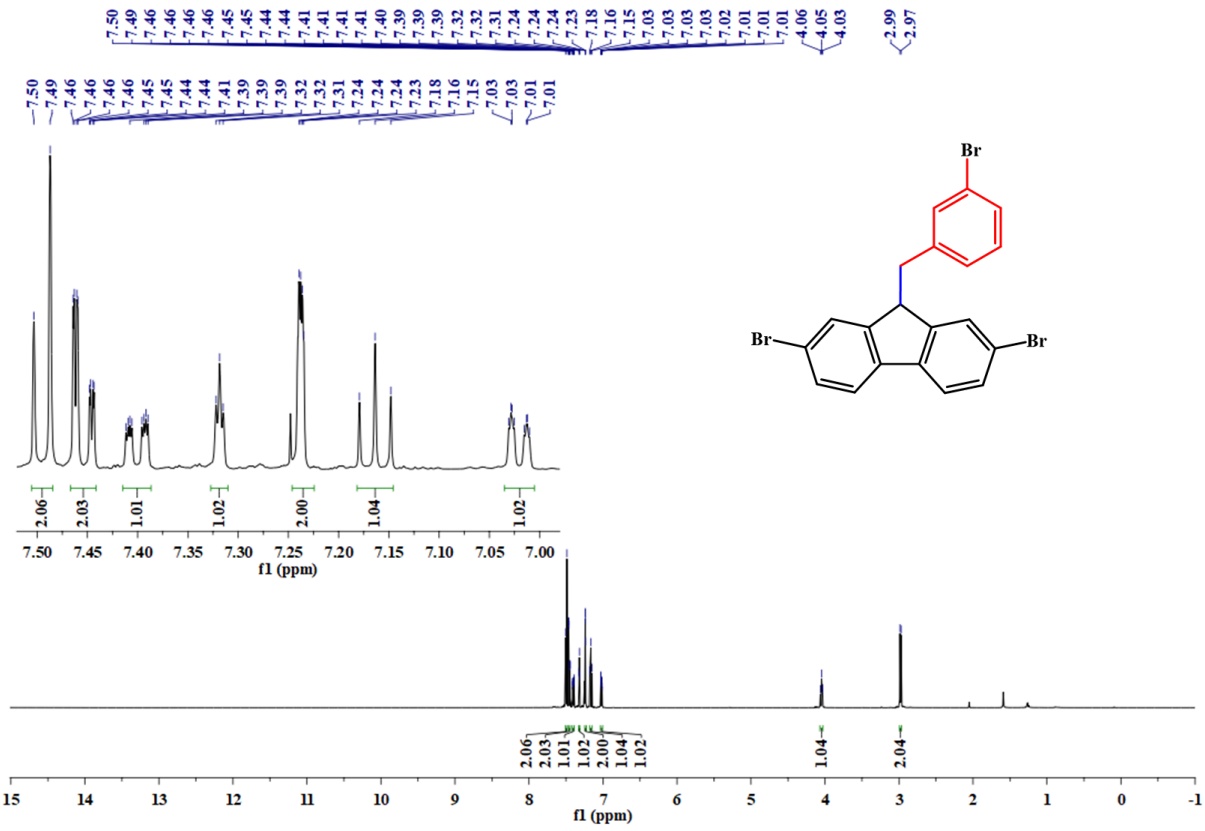


Figure S70: ^{1}H NMR spectrum of 3w in $CDCl_3$ at 500 MHz.

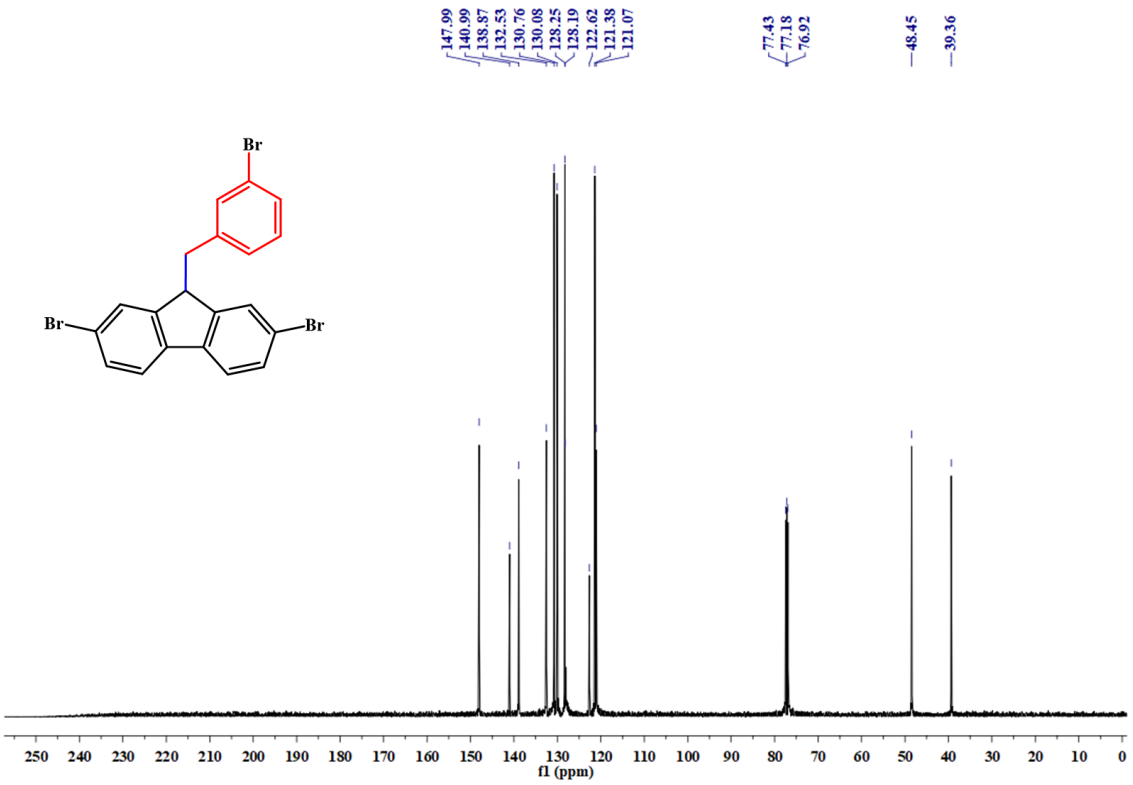


Figure S71: $^{13}C\{^{1}H\}$ NMR spectrum of 3w in $CDCl_3$ at 126 MHz.

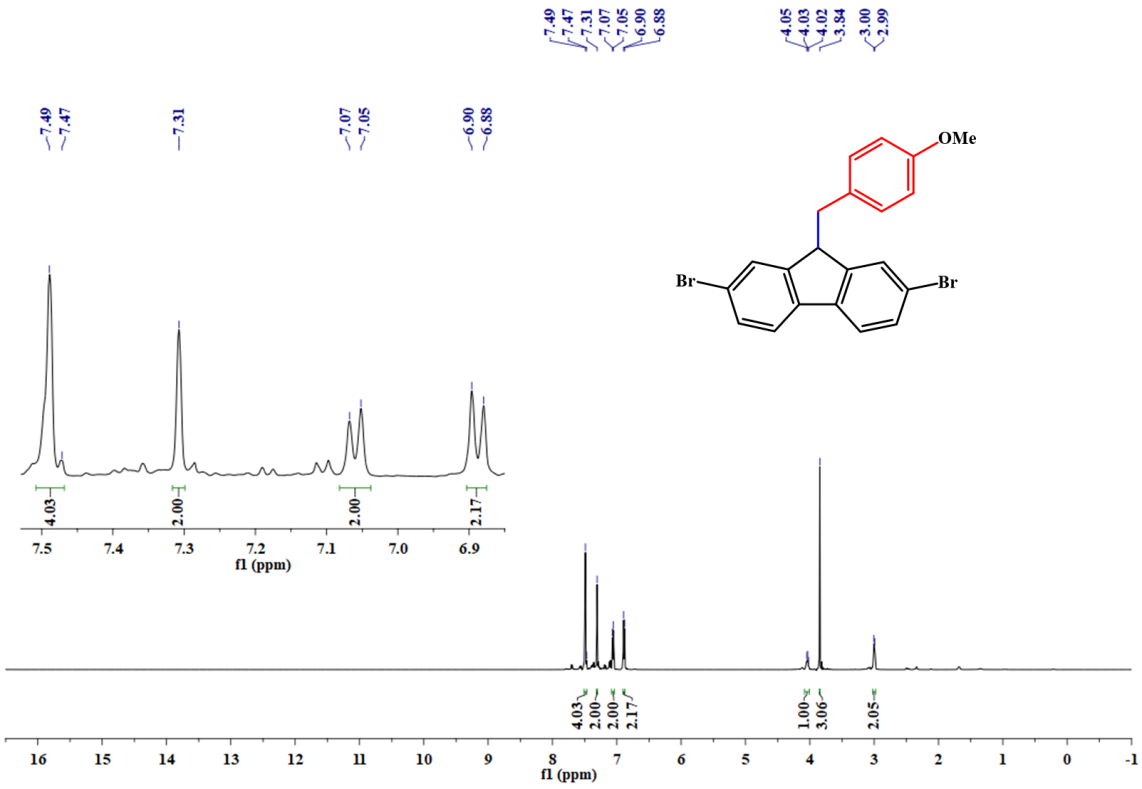


Figure S72: ^{1}H NMR spectrum of 3x in $CDCl_3$ at 500 MHz.

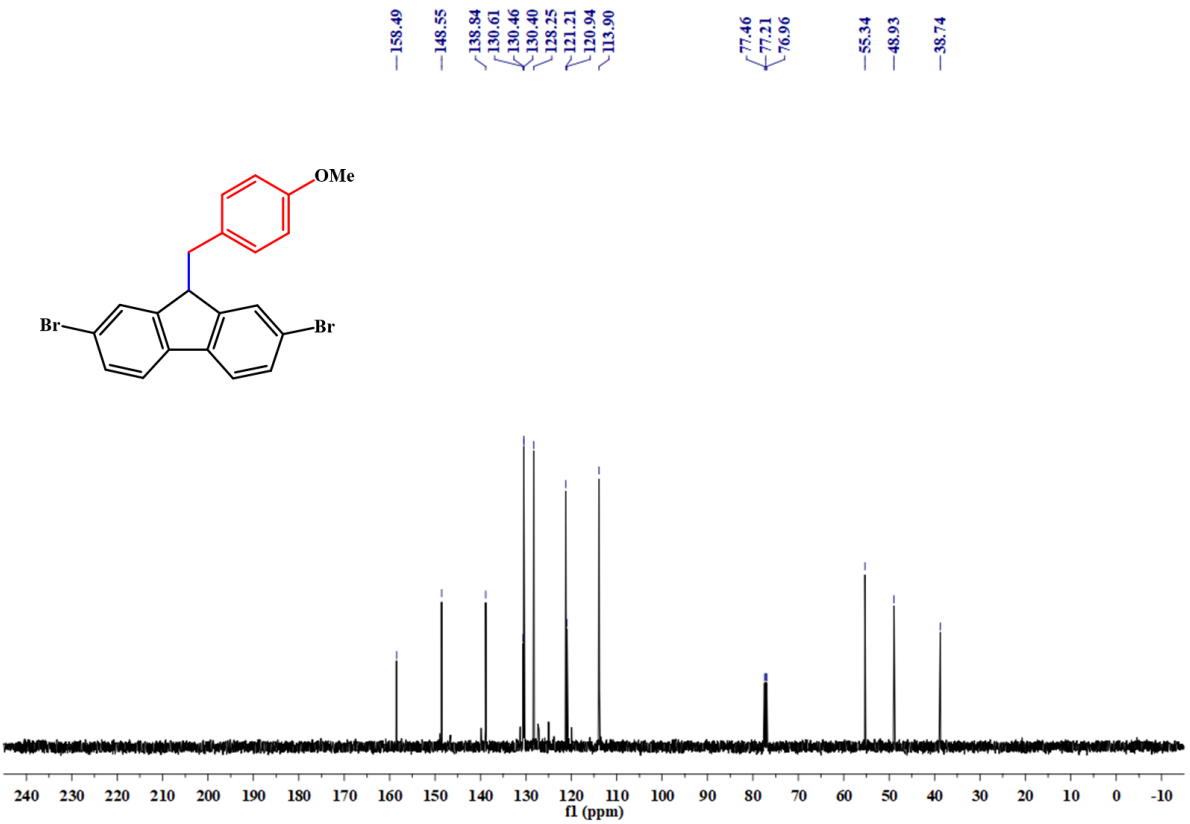


Figure S73: $^{13}C\{^{1}H\}$ NMR spectrum of 3x in $CDCl_3$ at 126 MHz.

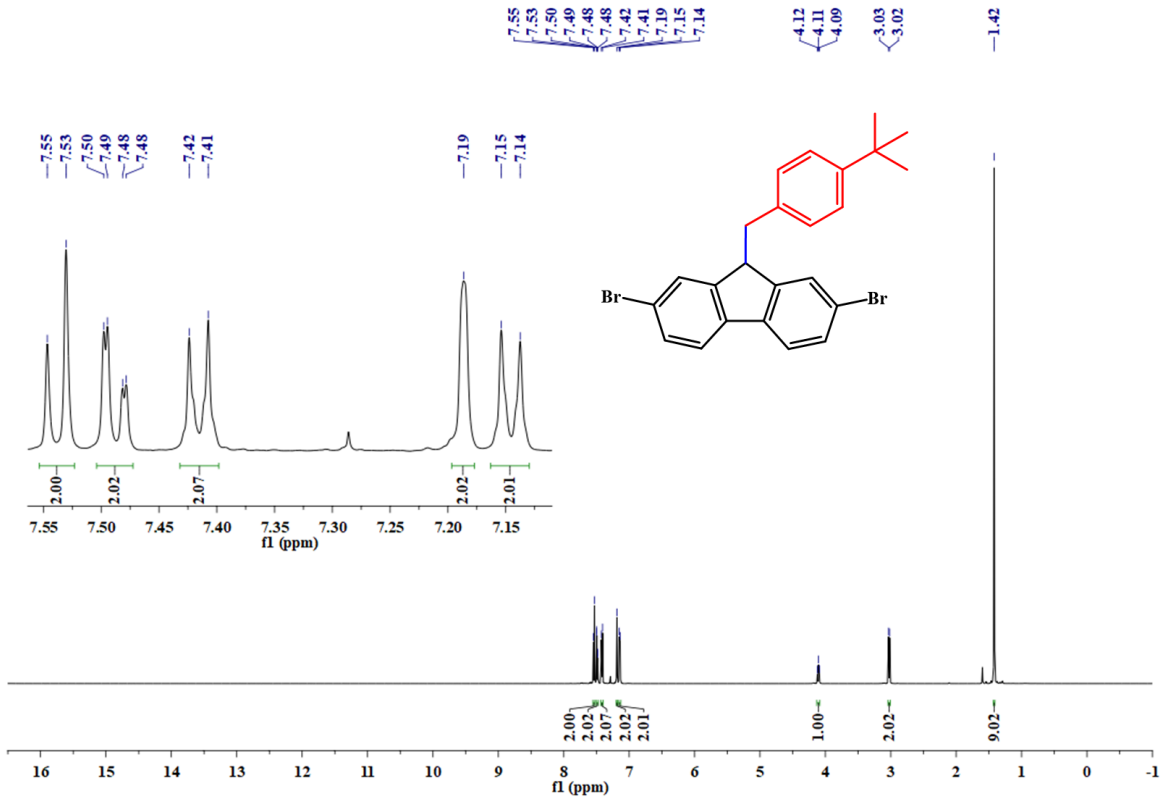


Figure S74: ^{1}H NMR spectrum of 3y in $CDCl_3$ at 500 MHz.

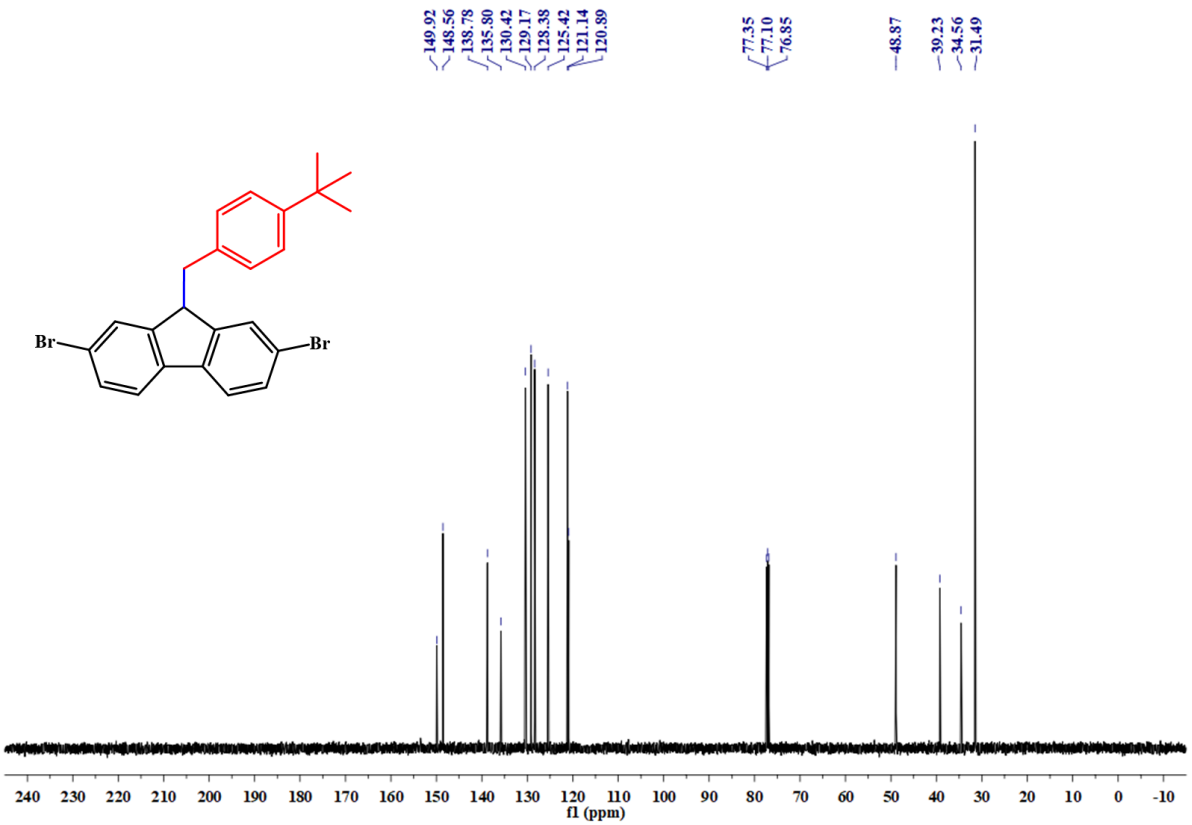


Figure S75: $^{13}C\{^{1}H\}$ NMR spectrum of 3y in $CDCl_3$ at 126 MHz.

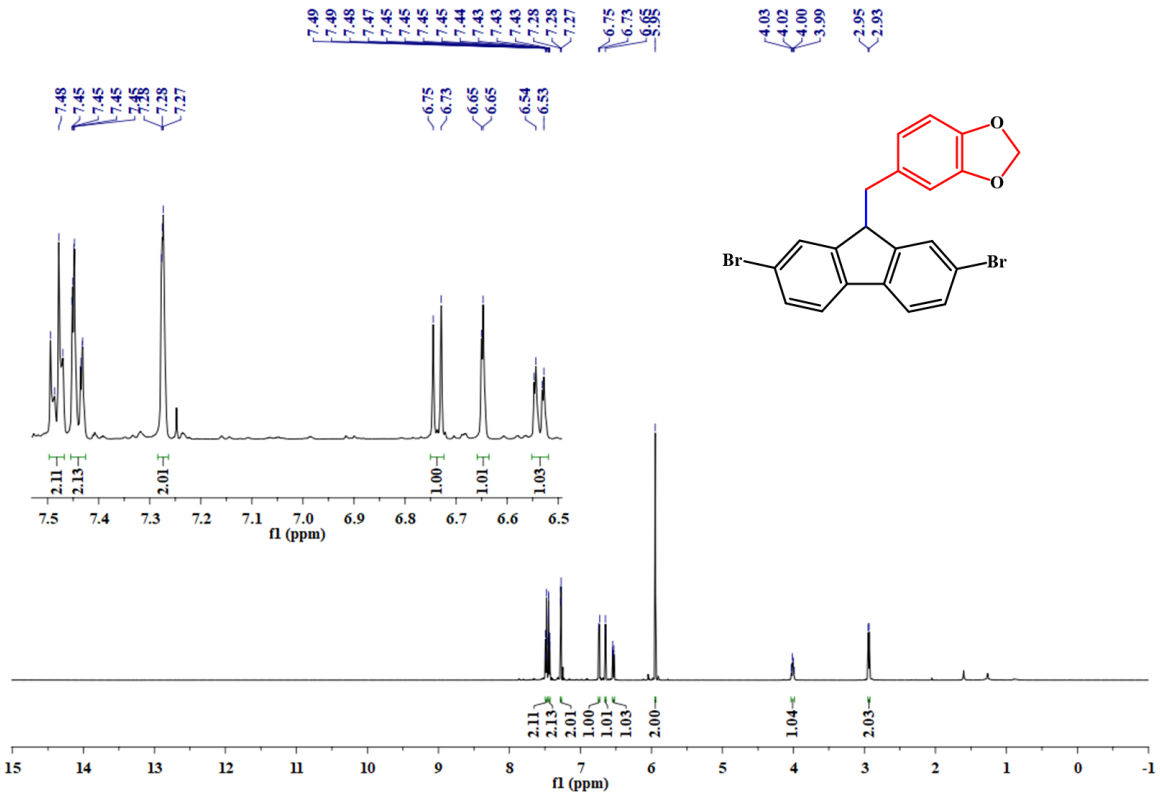


Figure S76: ^{1}H NMR spectrum of 3z in $CDCl_3$ at 500 MHz.

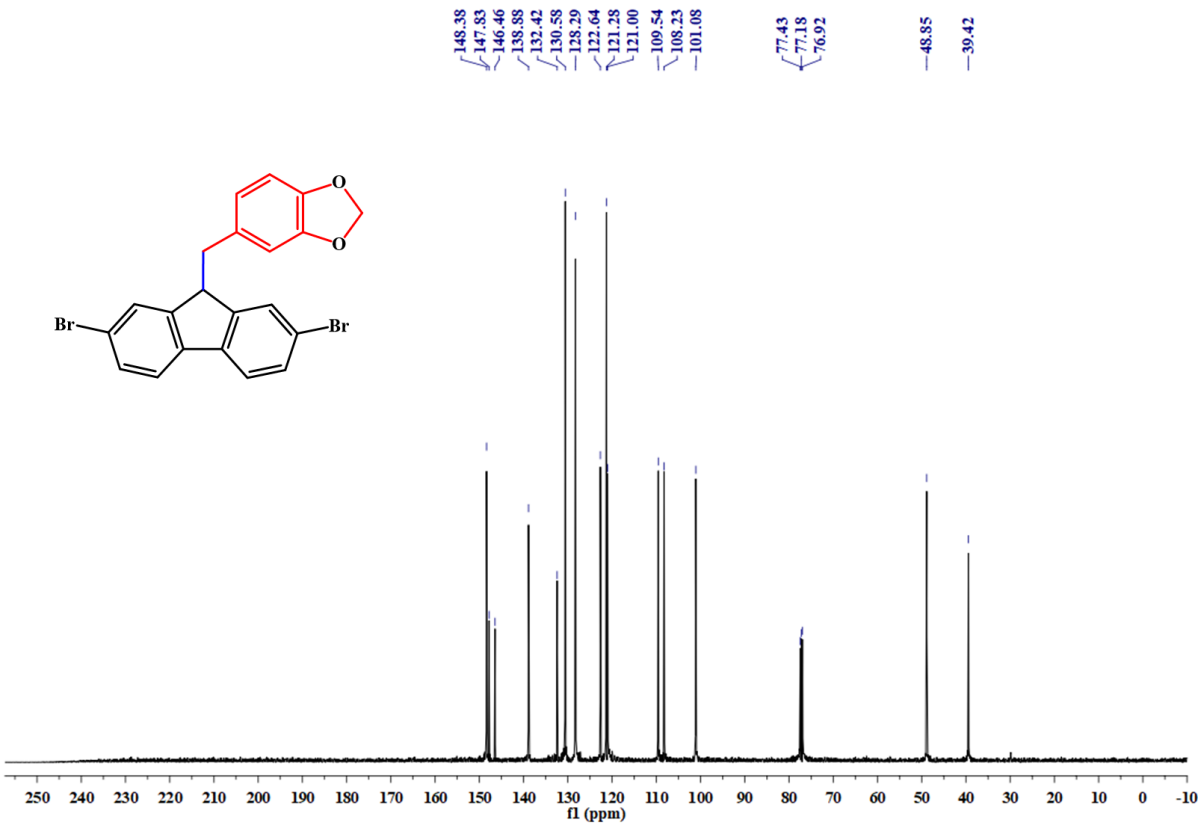


Figure S77: $^{13}C\{^{1}H\}$ NMR spectrum of 3z in $CDCl_3$ at 126 MHz.

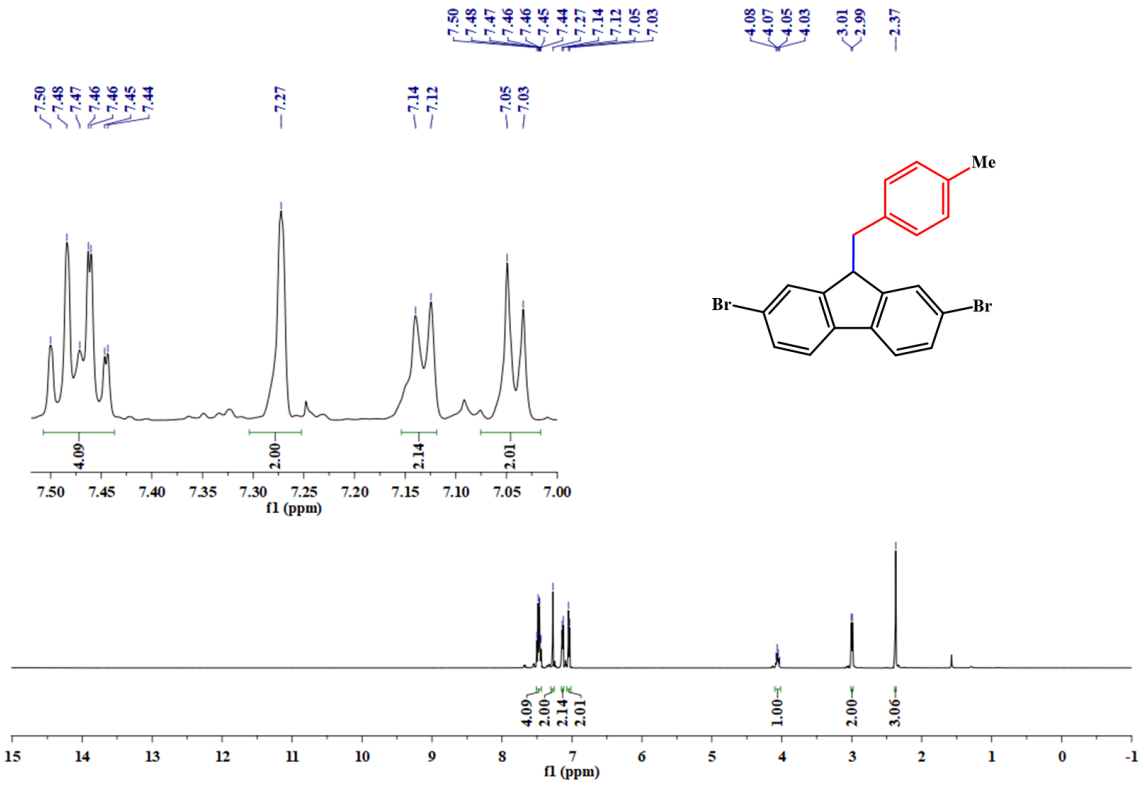


Figure S78: ^{1}H NMR spectrum of 3aa in $CDCl_3$ at 500 MHz.

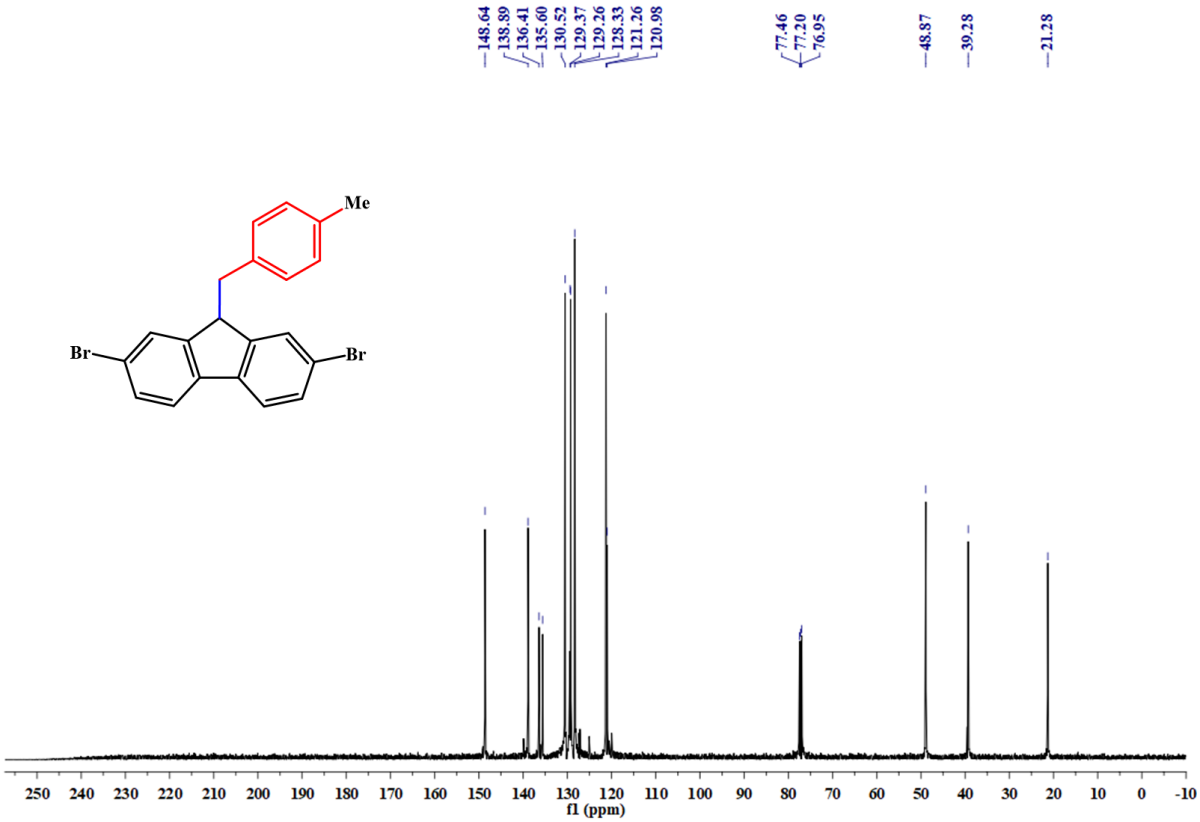


Figure S79: $^{13}C\{^{1}H\}$ NMR spectrum of 3aa in $CDCl_3$ at 126 MHz.

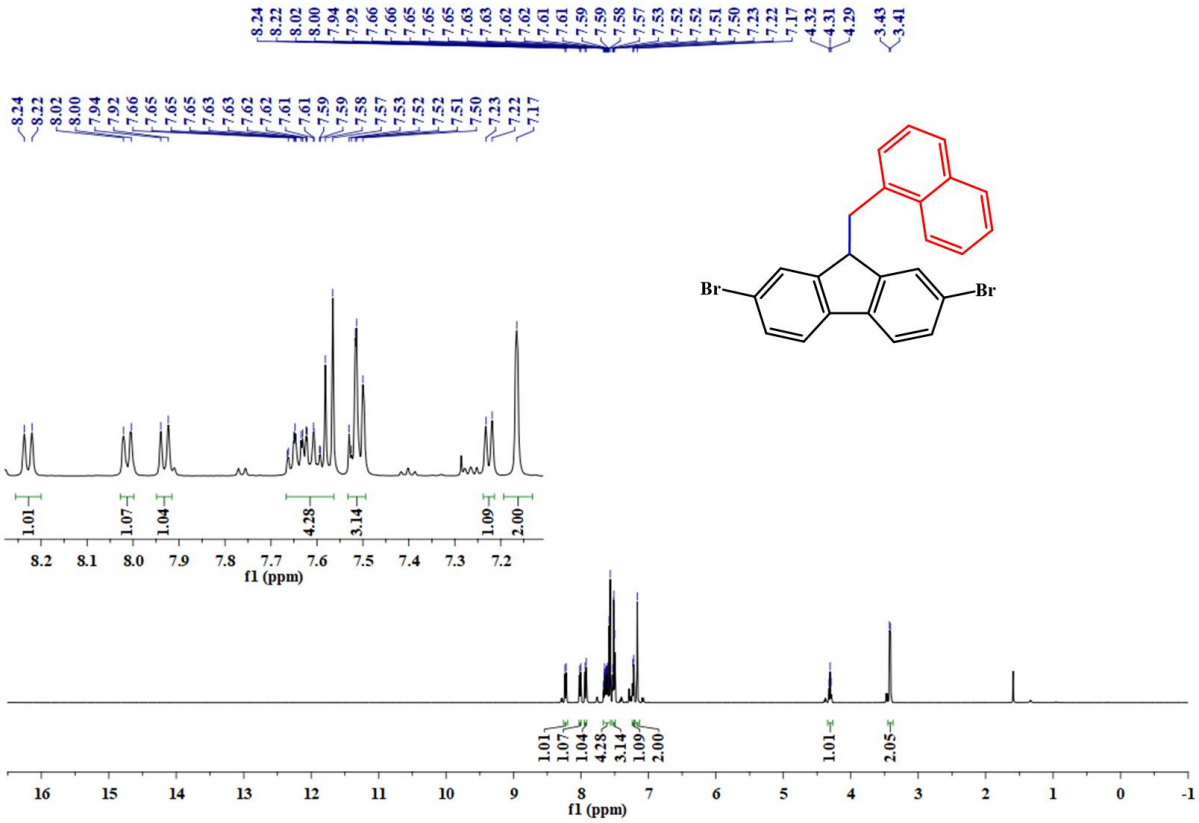


Figure S80: ^{1}H NMR spectrum of 3ab in $CDCl_3$ at 500 MHz.

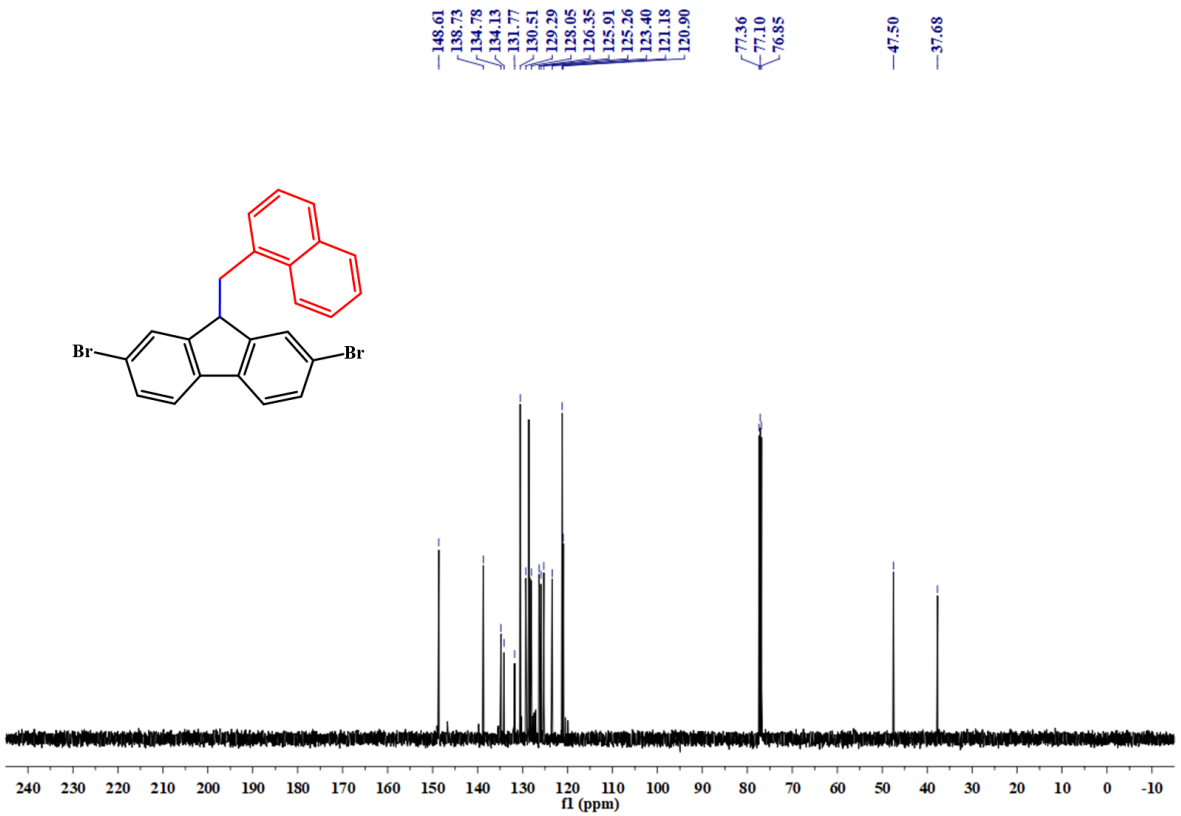


Figure S81: $^{13}C\{^{1}H\}$ NMR spectrum of 3ab in $CDCl_3$ at 126 MHz.

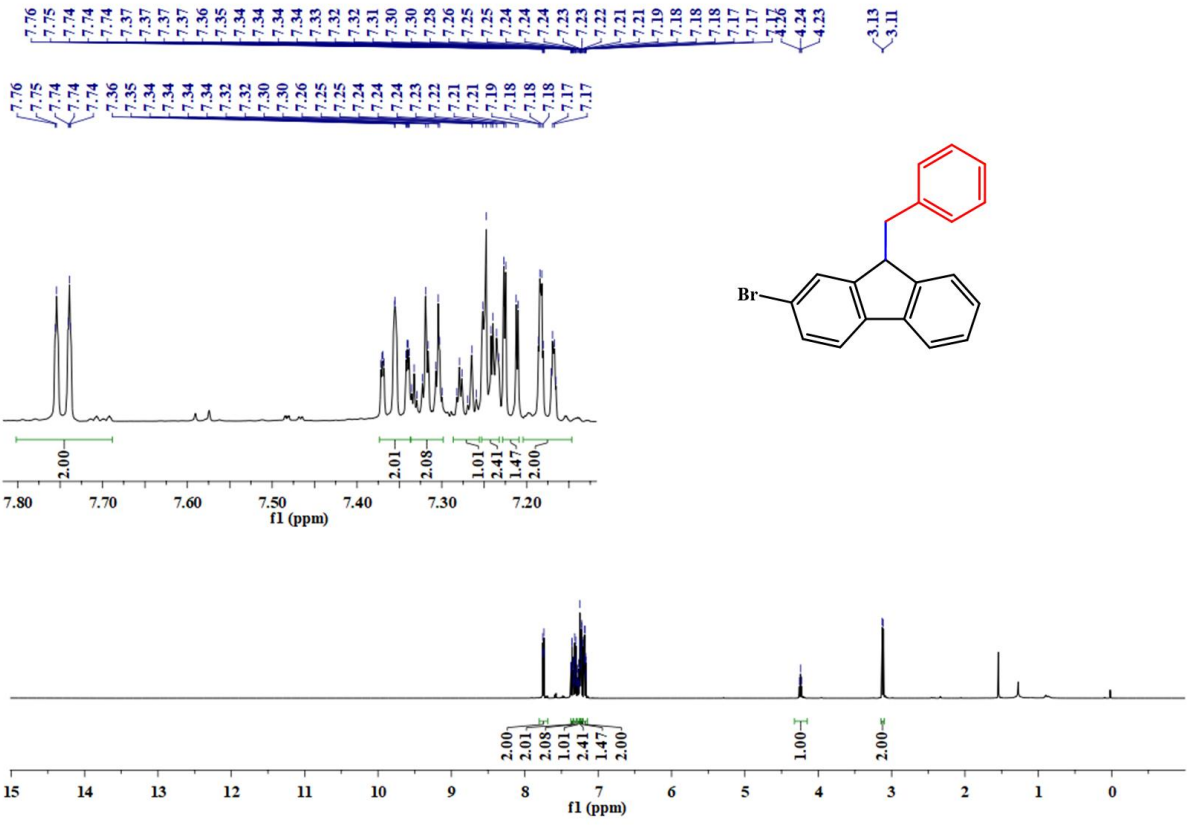


Figure S82: ^{1}H NMR spectrum of 3ac in $CDCl_3$ at 500 MHz.

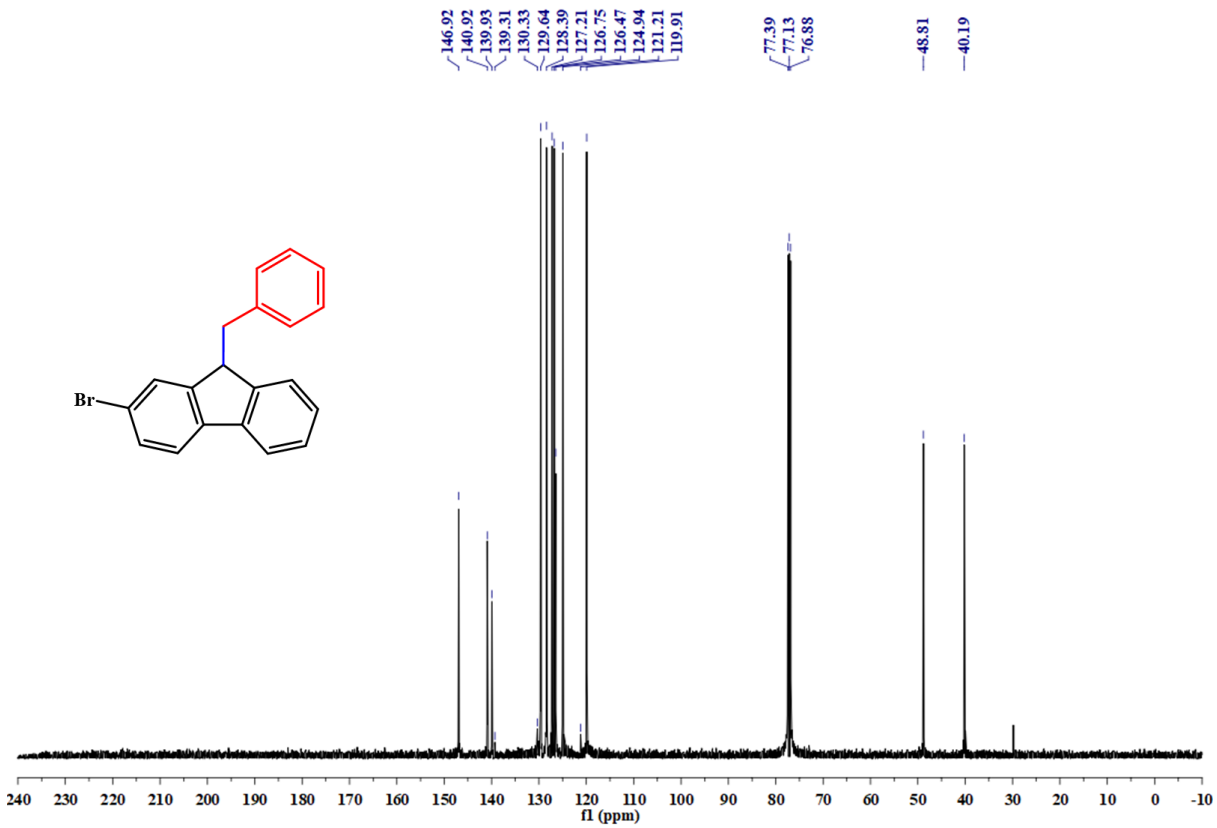


Figure S83: $^{13}C\{^{1}H\}$ NMR spectrum of 3ac in $CDCl_3$ at 126 MHz.

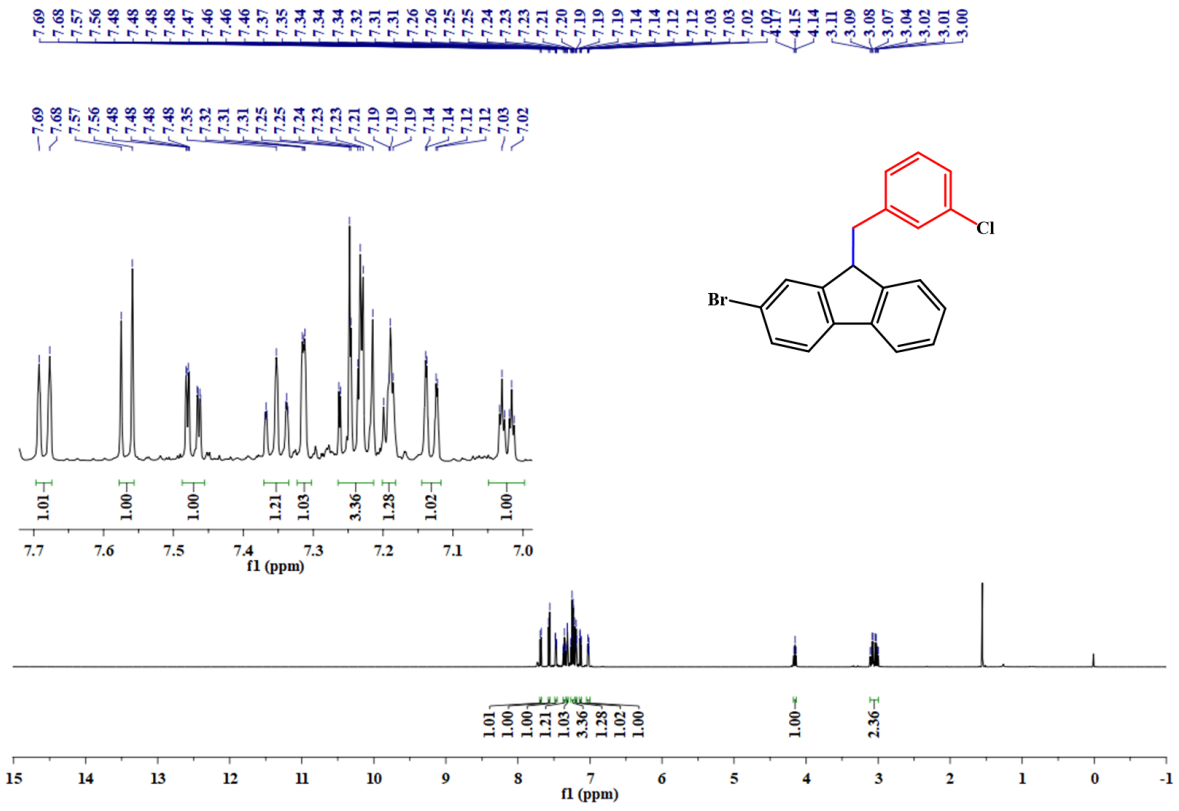


Figure S84: ^{1}H NMR spectrum of 3ad in $CDCl_3$ at 500 MHz.

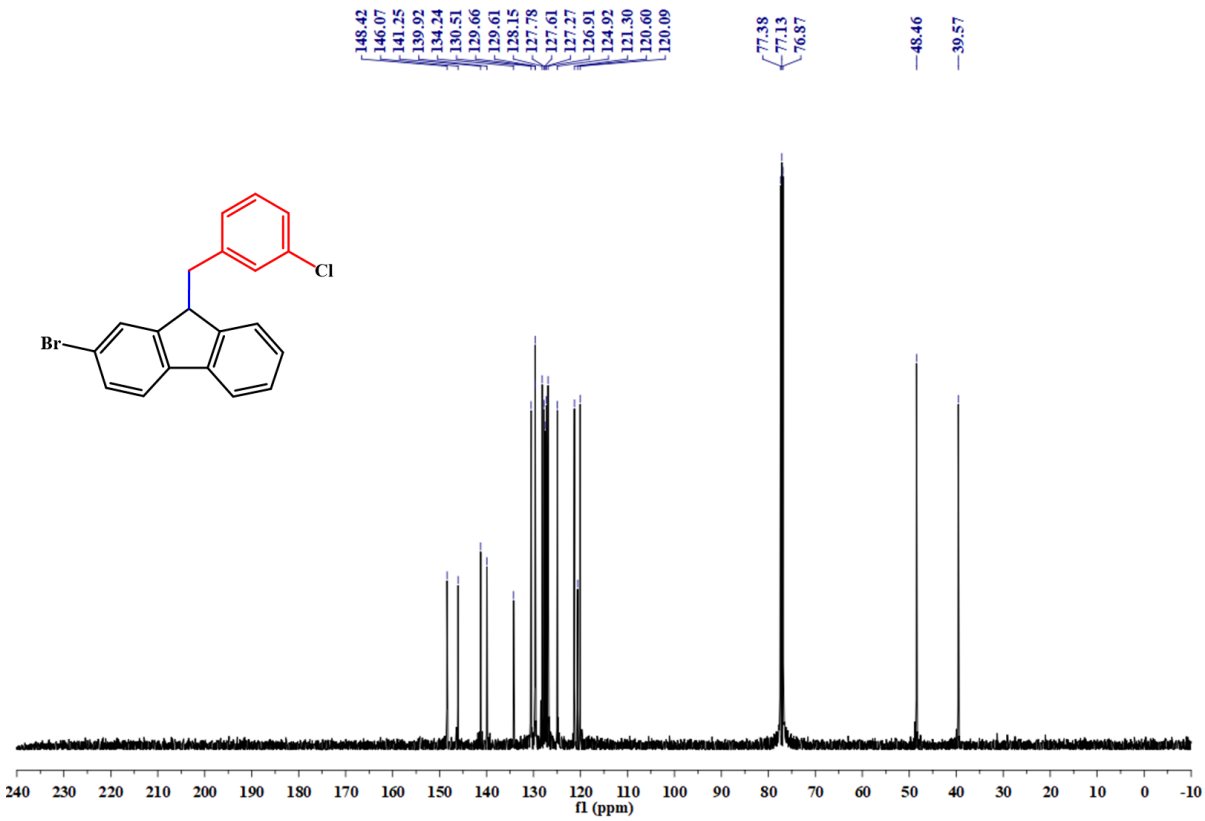


Figure S85: $^{13}C\{^{1}H\}$ NMR spectrum of 3ad in $CDCl_3$ at 126 MHz.

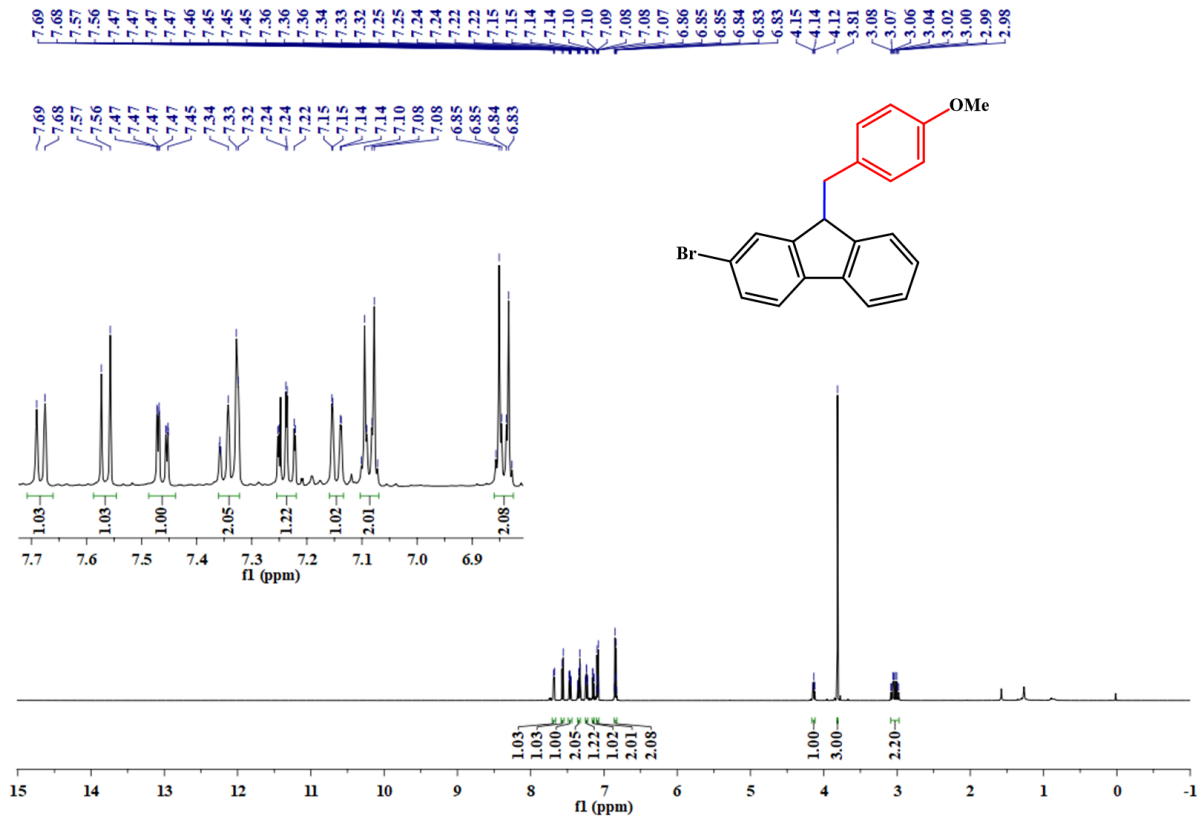


Figure S86: ^{1}H NMR spectrum of 3ae in $CDCl_3$ at 500 MHz.

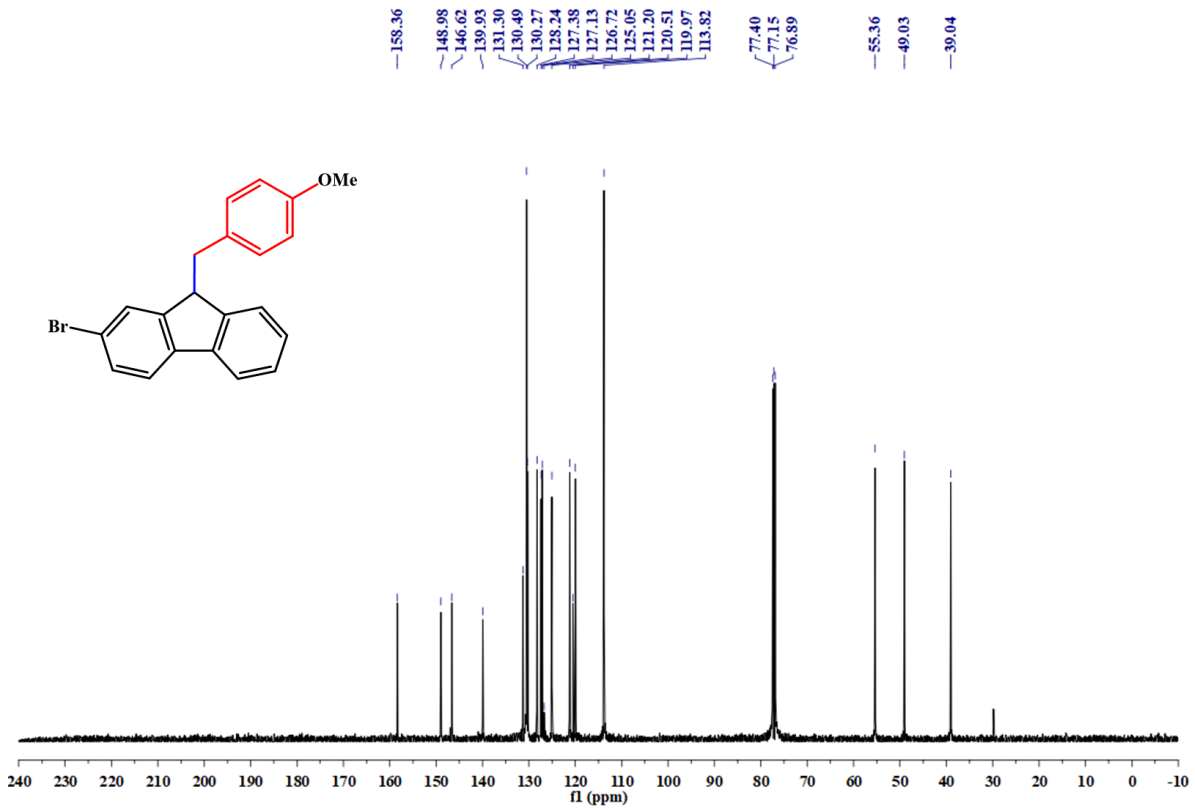


Figure S87: $^{13}C\{^{1}H\}$ NMR spectrum of 3ae in $CDCl_3$ at 126 MHz.

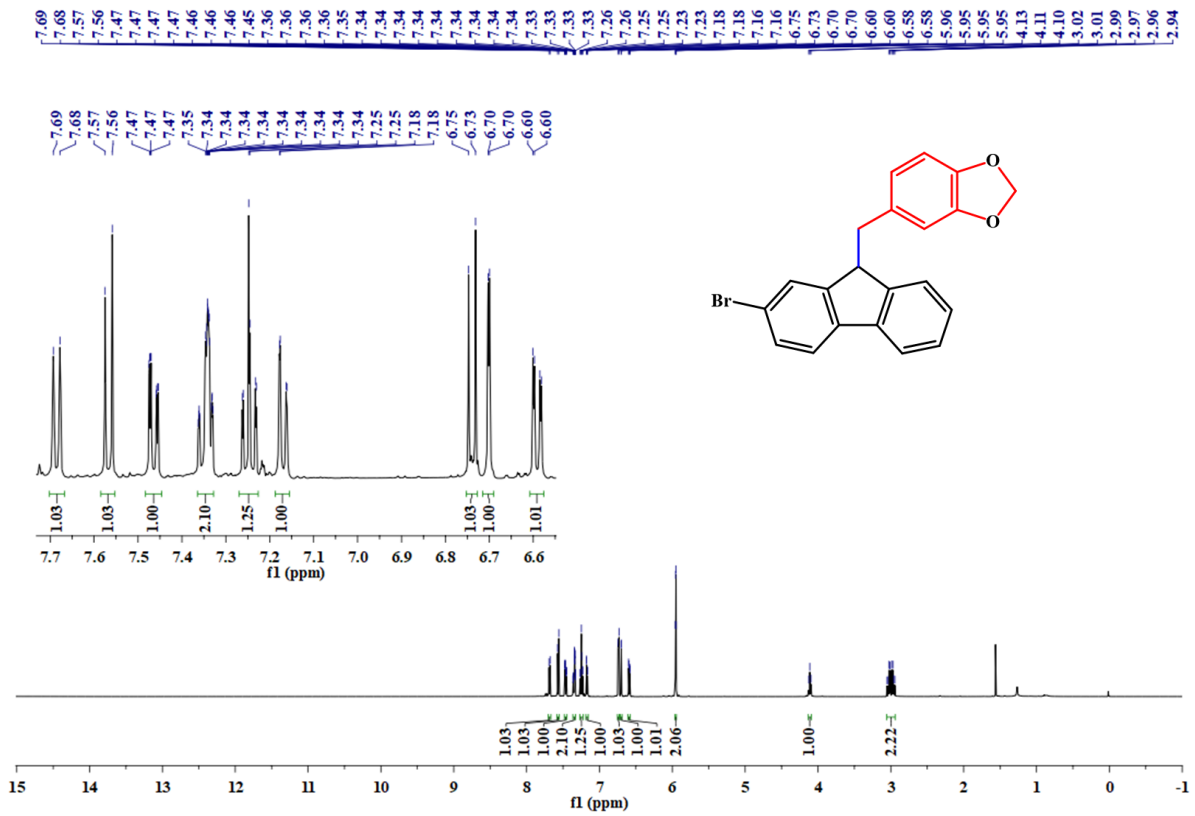


Figure S88: ^{1}H NMR spectrum of 3af in $CDCl_3$ at 500 MHz.

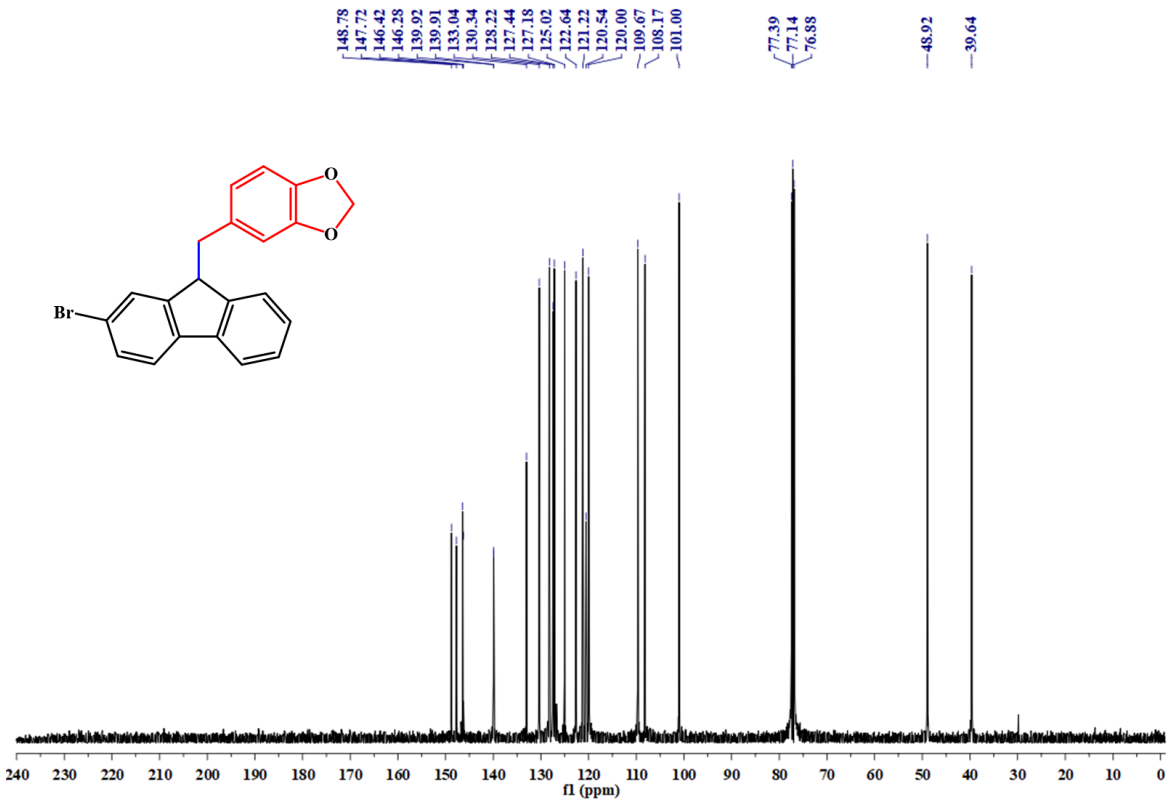


Figure S89: $^{13}C\{^{1}H\}$ NMR spectrum of 3af in $CDCl_3$ at 126 MHz.

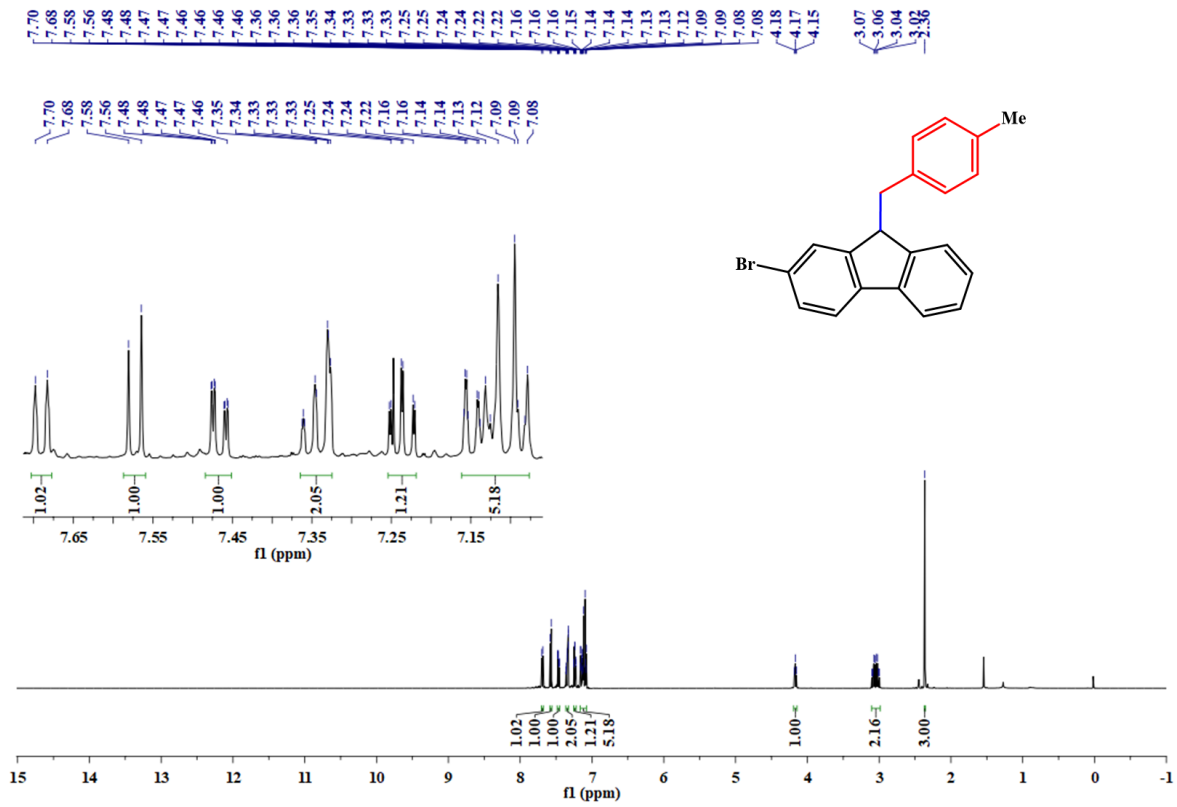


Figure S90: ^{1}H NMR spectrum of 3ag in $CDCl_3$ at 500 MHz.

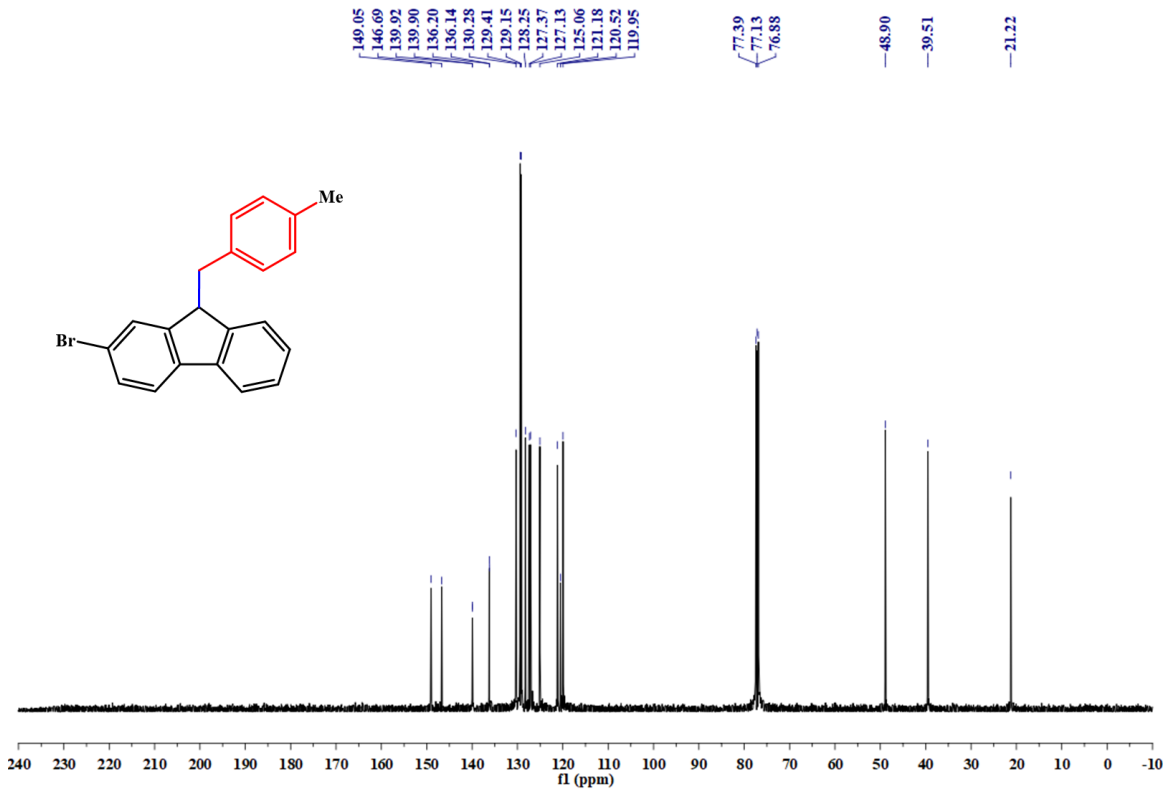


Figure S91: $^{13}C\{^{1}H\}$ NMR spectrum of 3ag in $CDCl_3$ at 126 MHz.

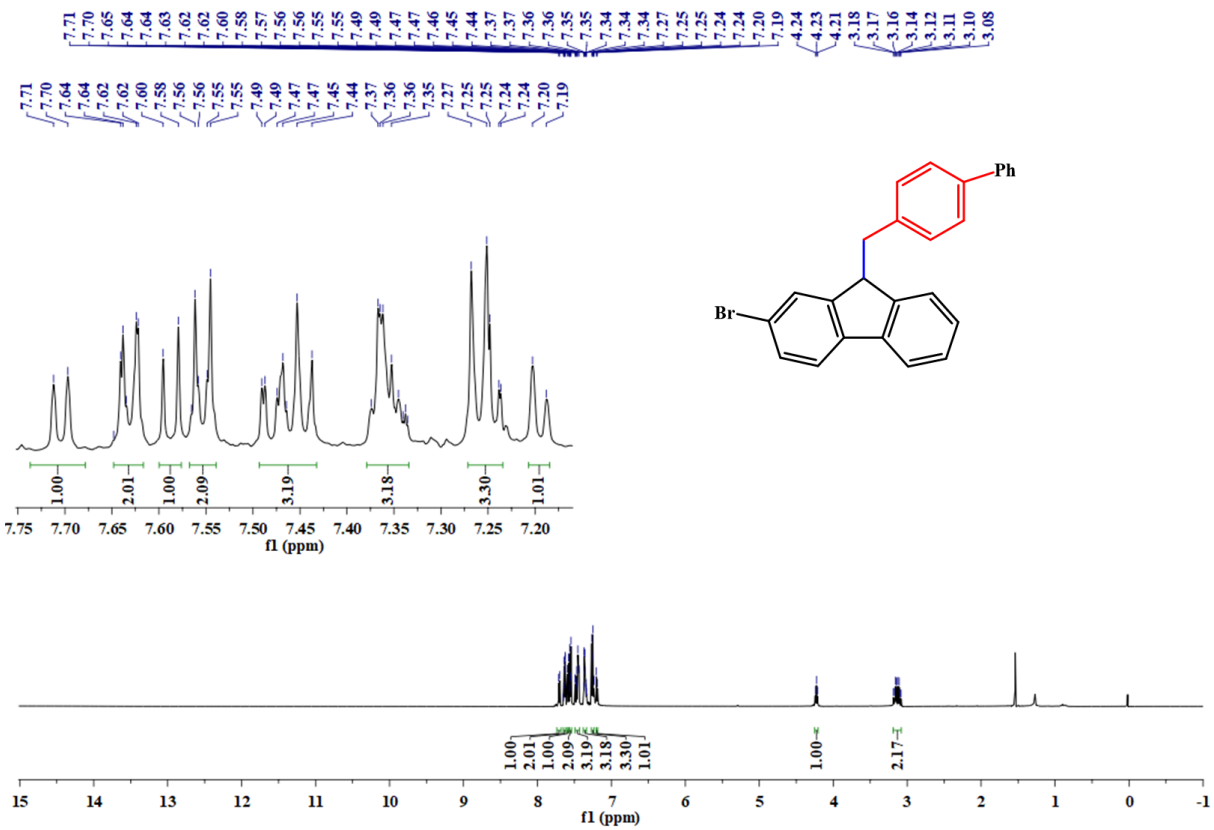


Figure S92: ^{1}H NMR spectrum of 3ah in $CDCl_3$ at 500 MHz.

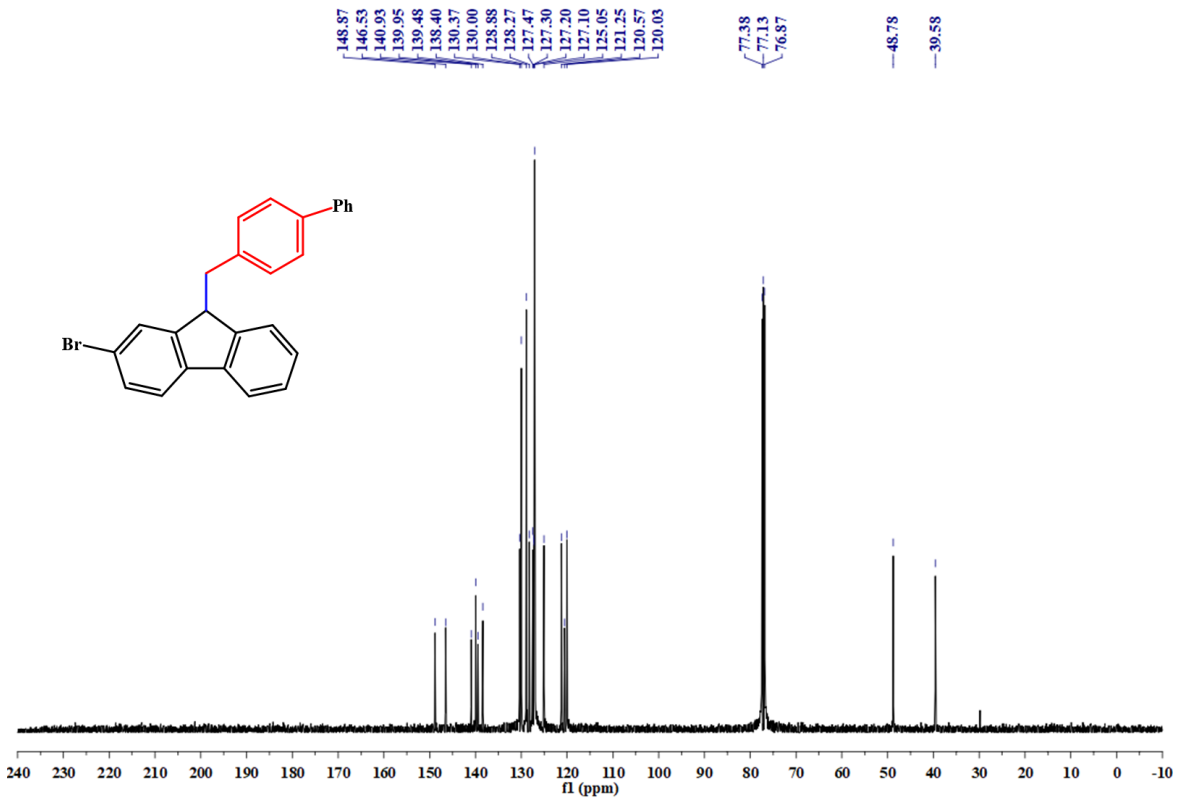


Figure S93: $^{13}C\{^{1}H\}$ NMR spectrum of 3ah in $CDCl_3$ at 126 MHz.

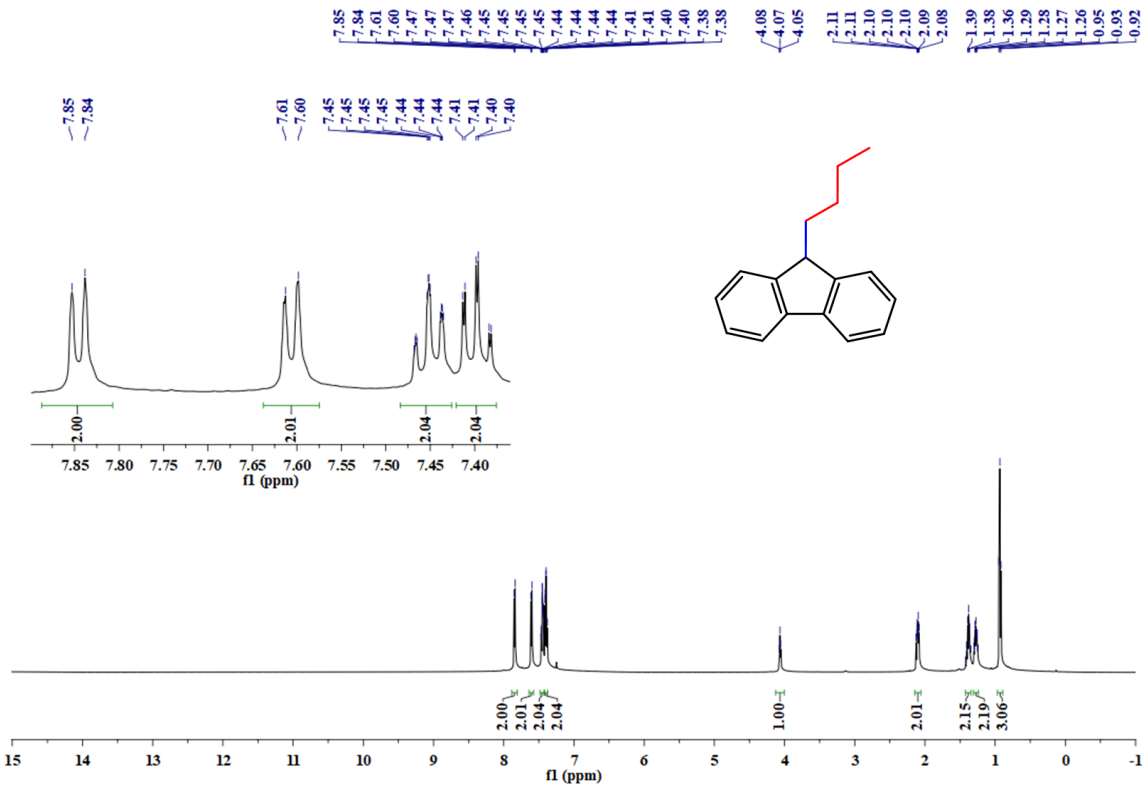


Figure S94: ^{1}H NMR spectrum of 3ai in $CDCl_3$ at 500 MHz.

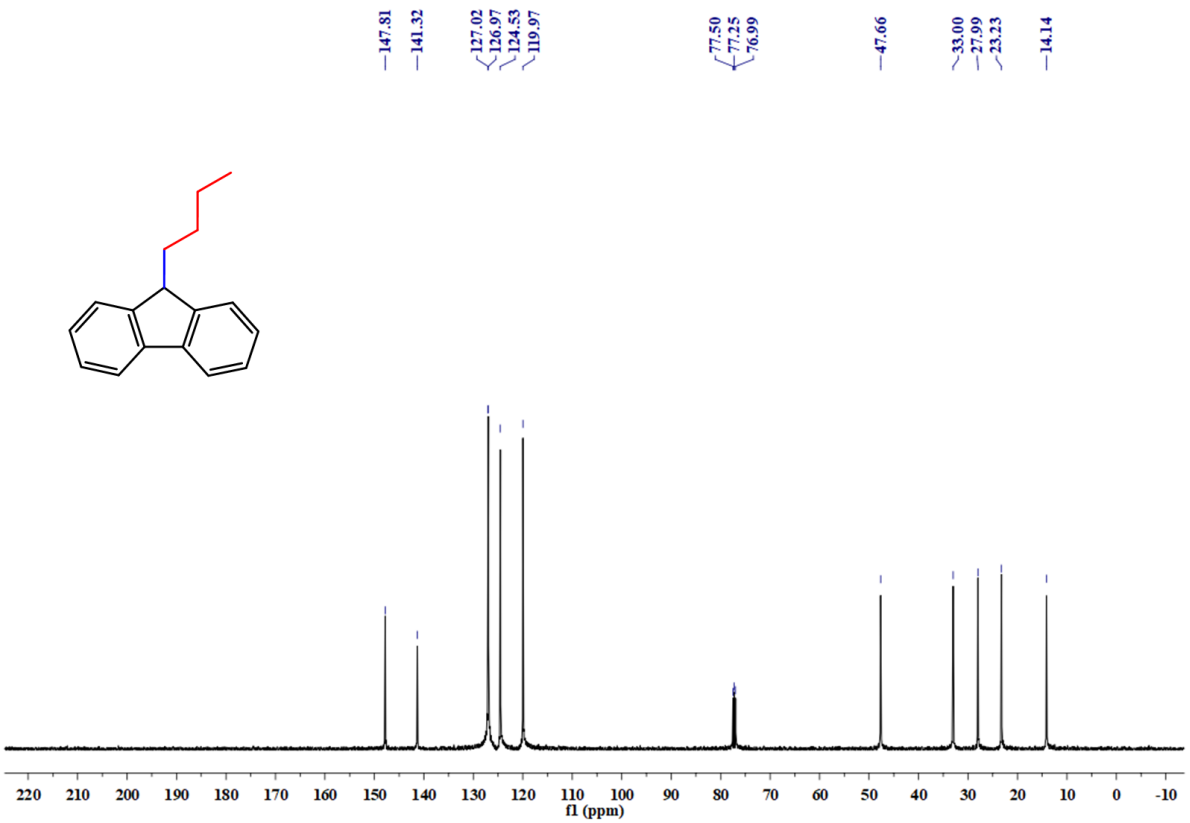


Figure S95: $^{13}C\{^{1}H\}$ NMR spectrum of 3ai in $CDCl_3$ at 126 MHz.

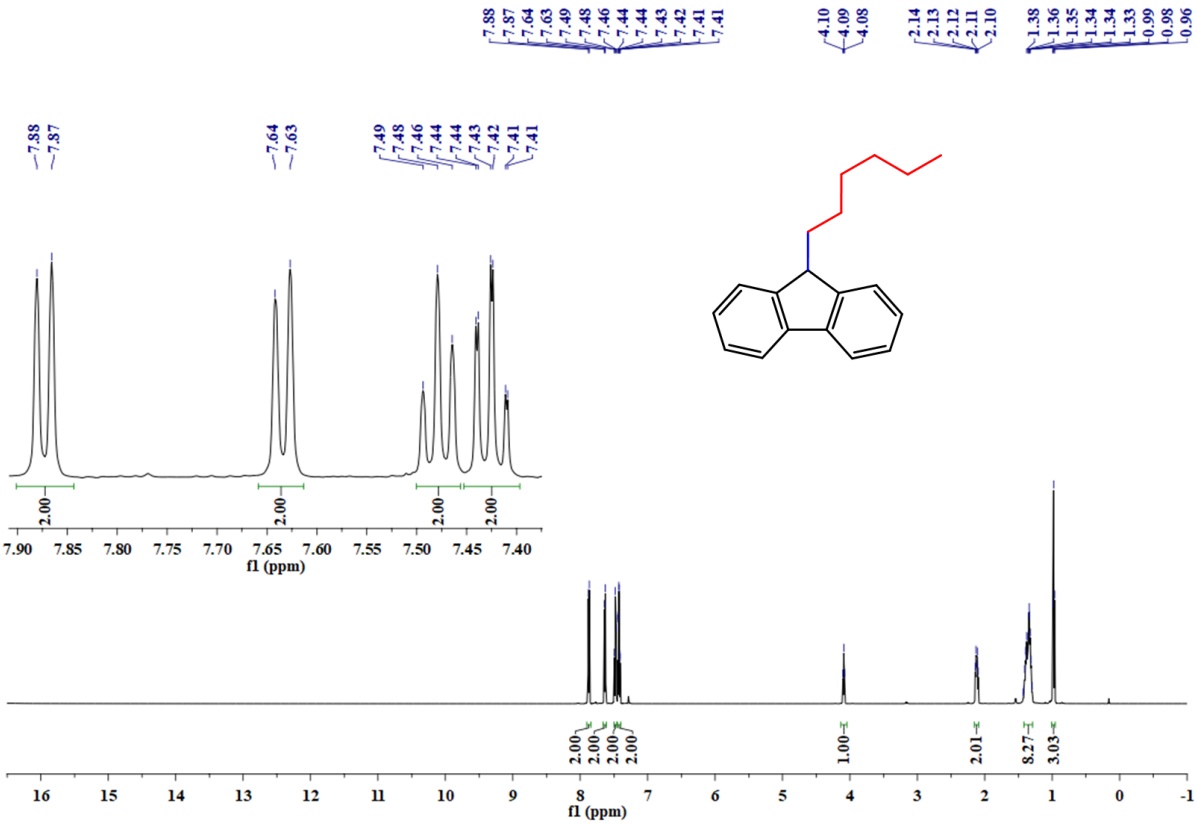


Figure S96: ^{1}H NMR spectrum of 3aj in $CDCl_3$ at 500 MHz.

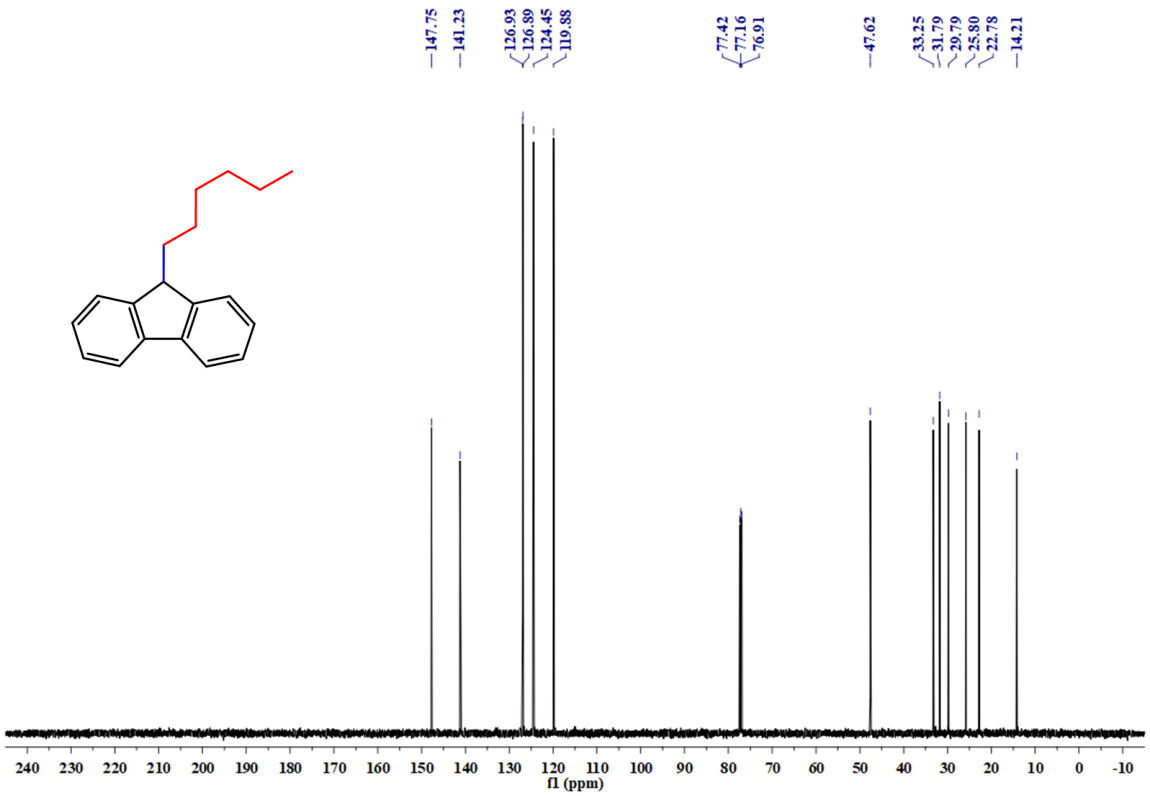


Figure S97: $^{13}C\{^{1}H\}$ NMR spectrum of 3aj in $CDCl_3$ at 126 MHz.

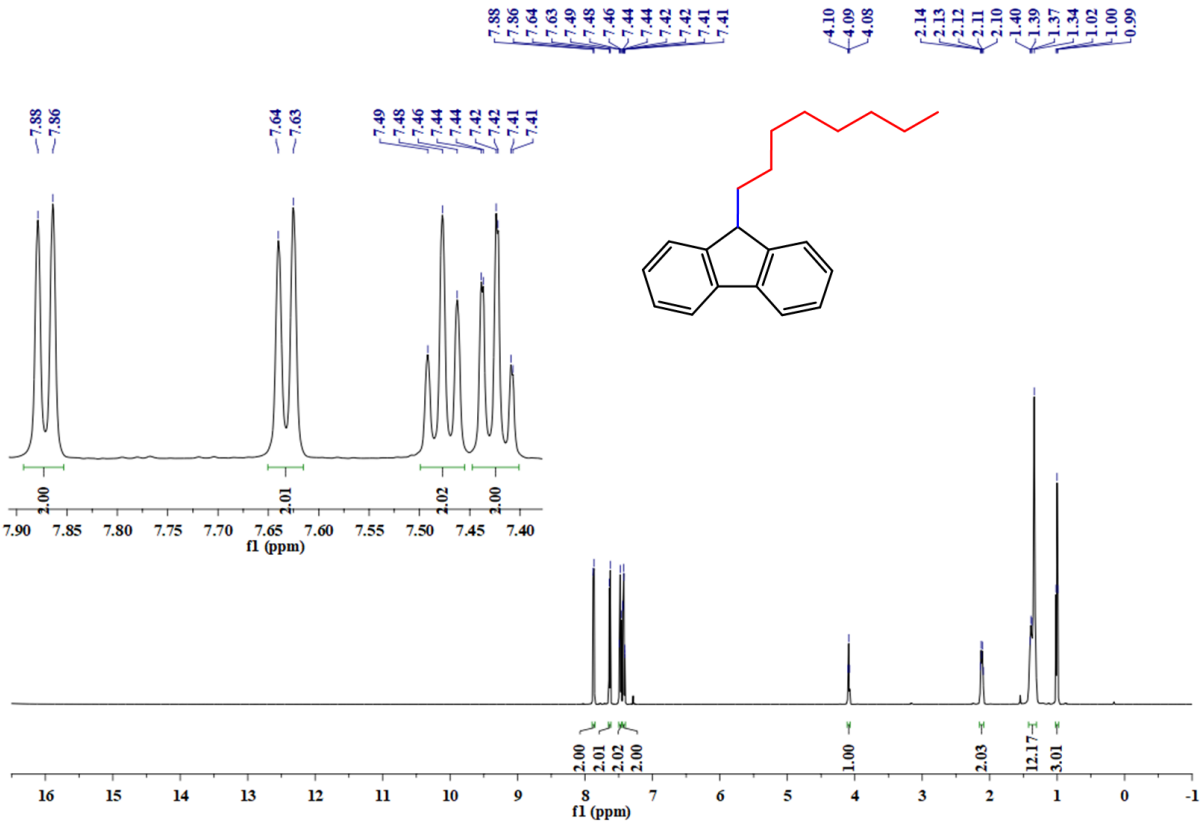


Figure S98: ^{1}H NMR spectrum of 3ak in $CDCl_3$ at 500 MHz.

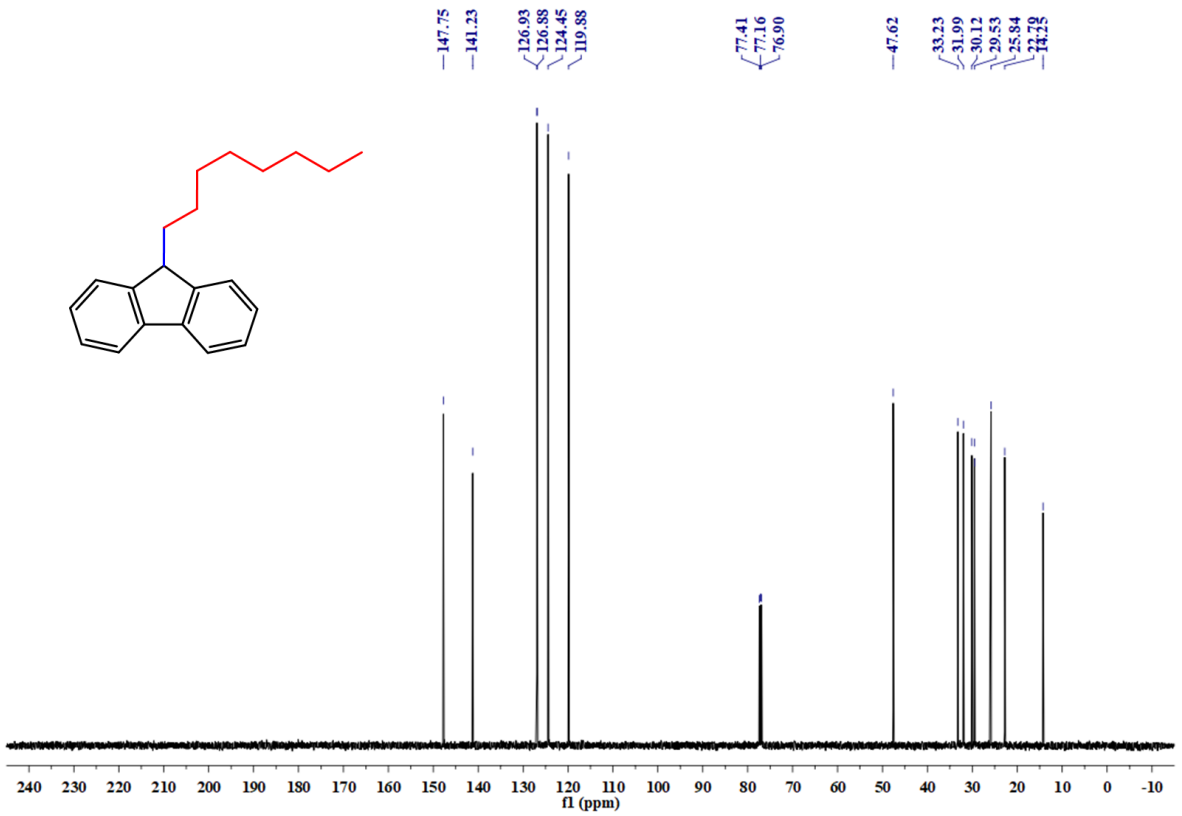


Figure S99: $^{13}C\{^{1}H\}$ NMR spectrum of 3ak in $CDCl_3$ at 126 MHz.

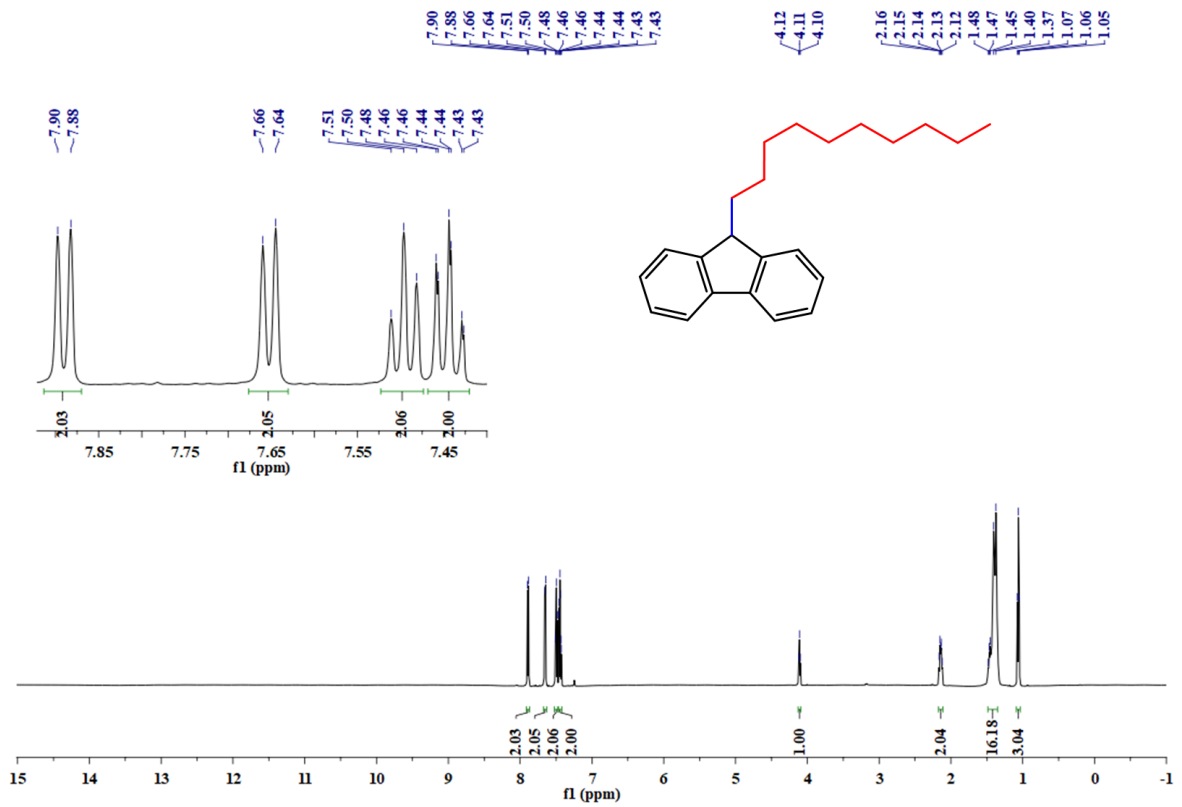


Figure S100: ^{1}H NMR spectrum of 3al in $CDCl_3$ at 500 MHz.

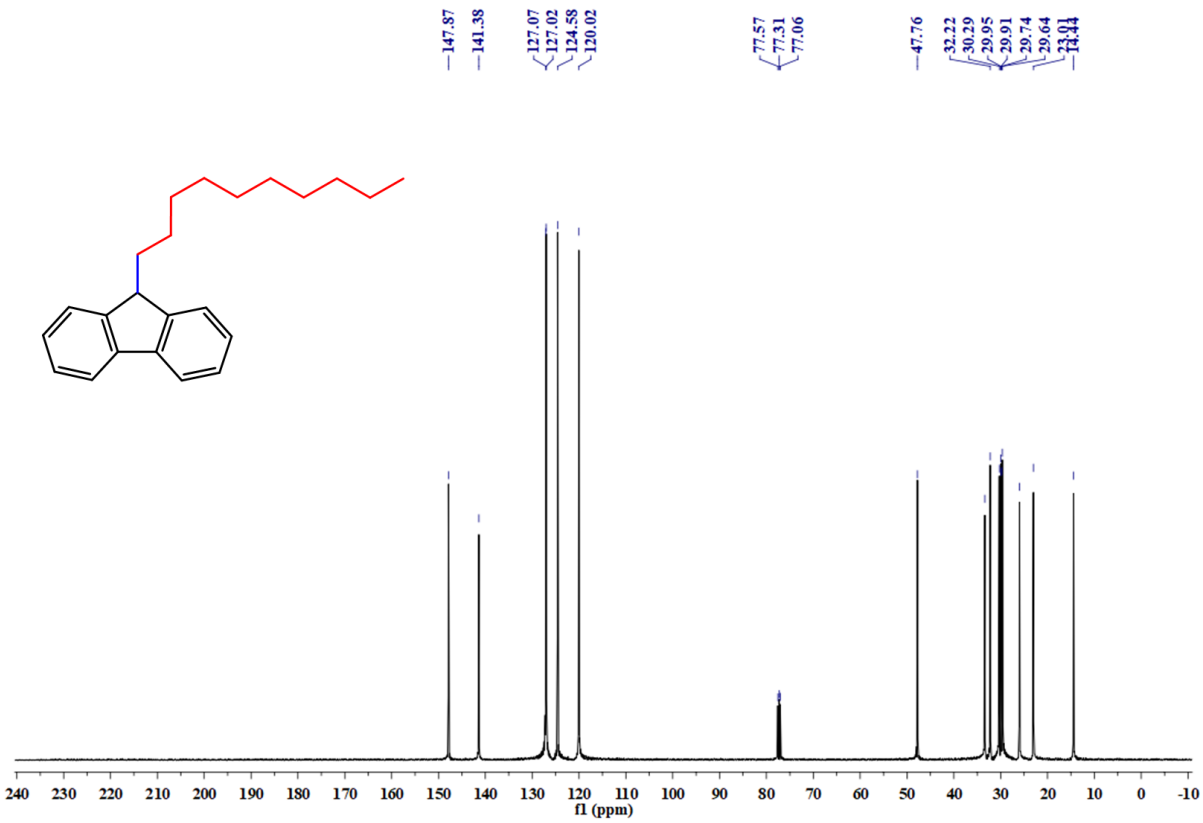


Figure S101: $^{13}C\{^{1}H\}$ NMR spectrum of 3al in $CDCl_3$ at 126 MHz.

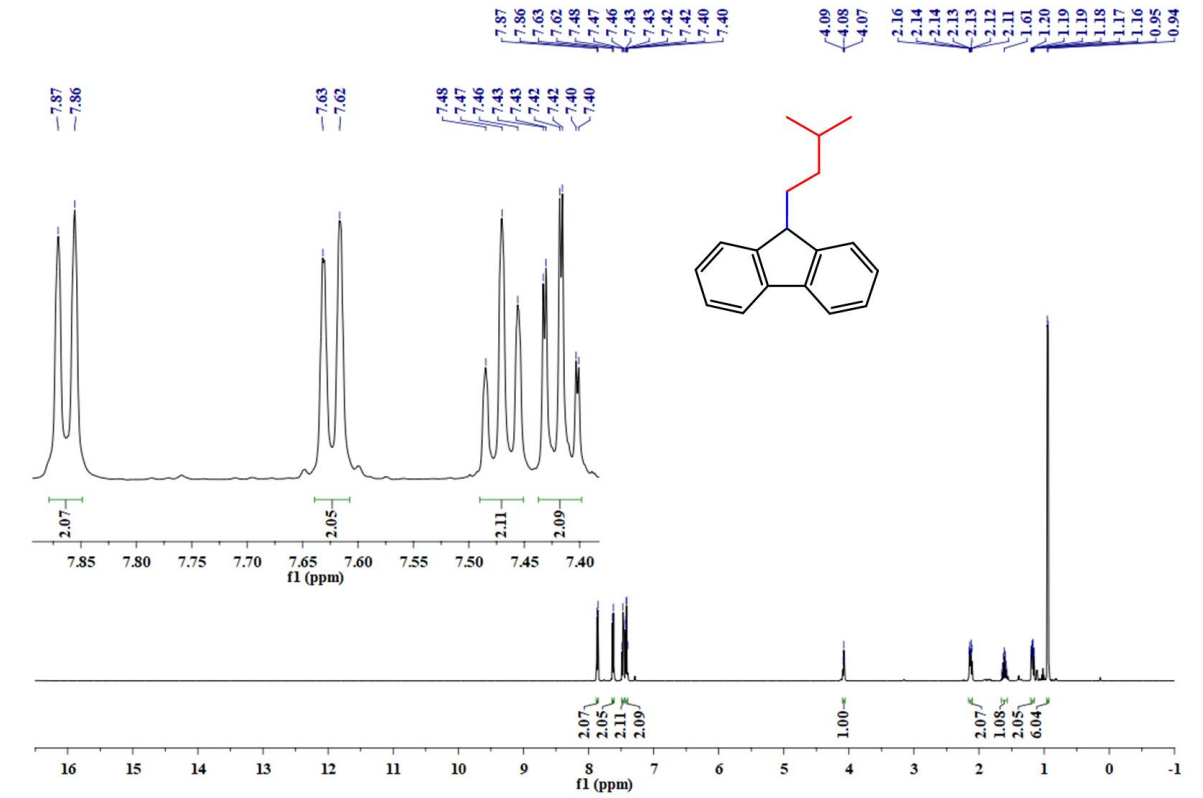


Figure S102: ^{1}H NMR spectrum of 3am in $CDCl_3$ at 500 MHz.

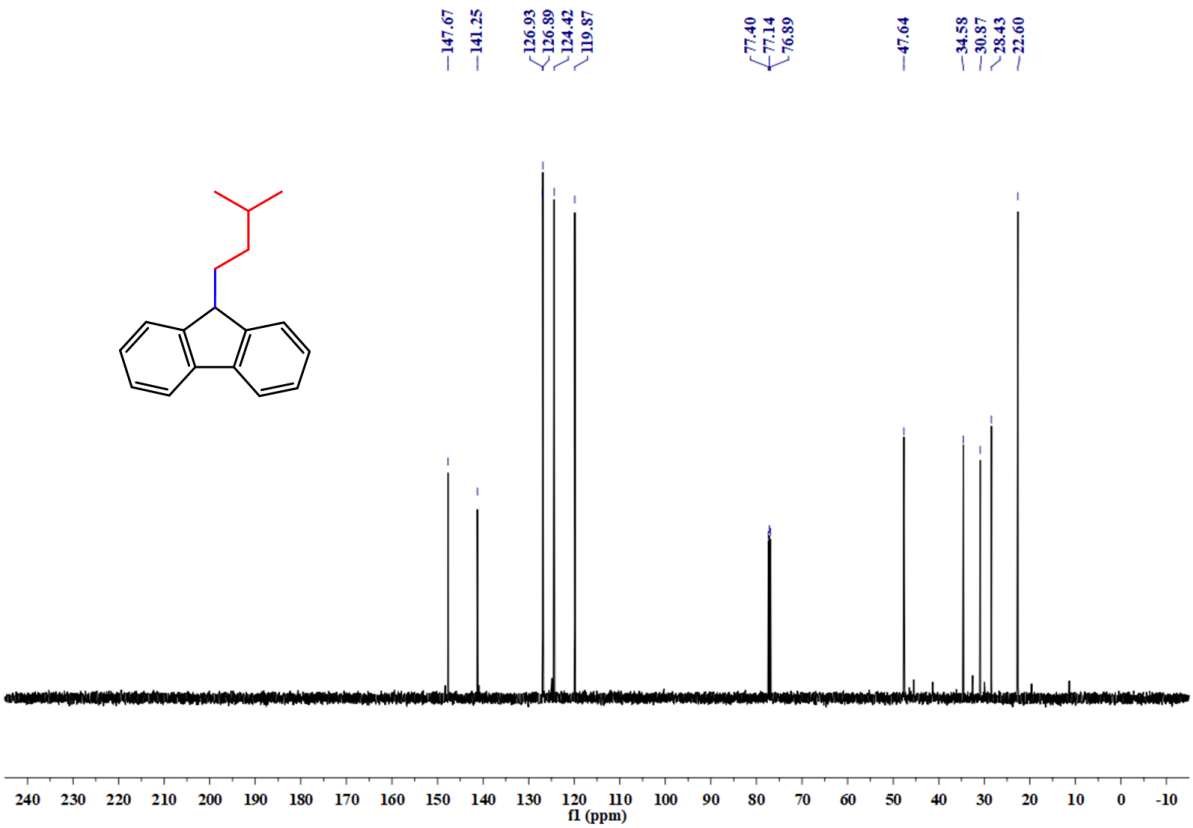


Figure S103: $^{13}C\{^{1}H\}$ NMR spectrum of 3am in $CDCl_3$ at 126 MHz.

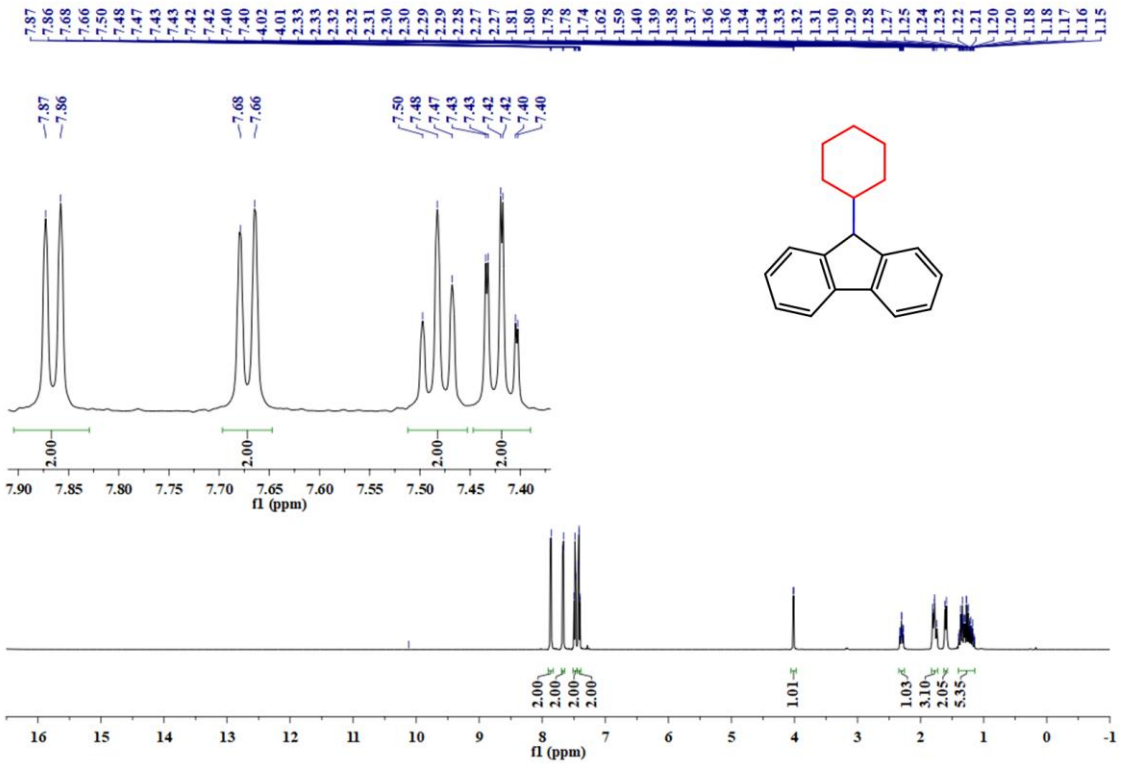


Figure S104: ^{1}H NMR spectrum of 3an in $CDCl_3$ at 500 MHz.

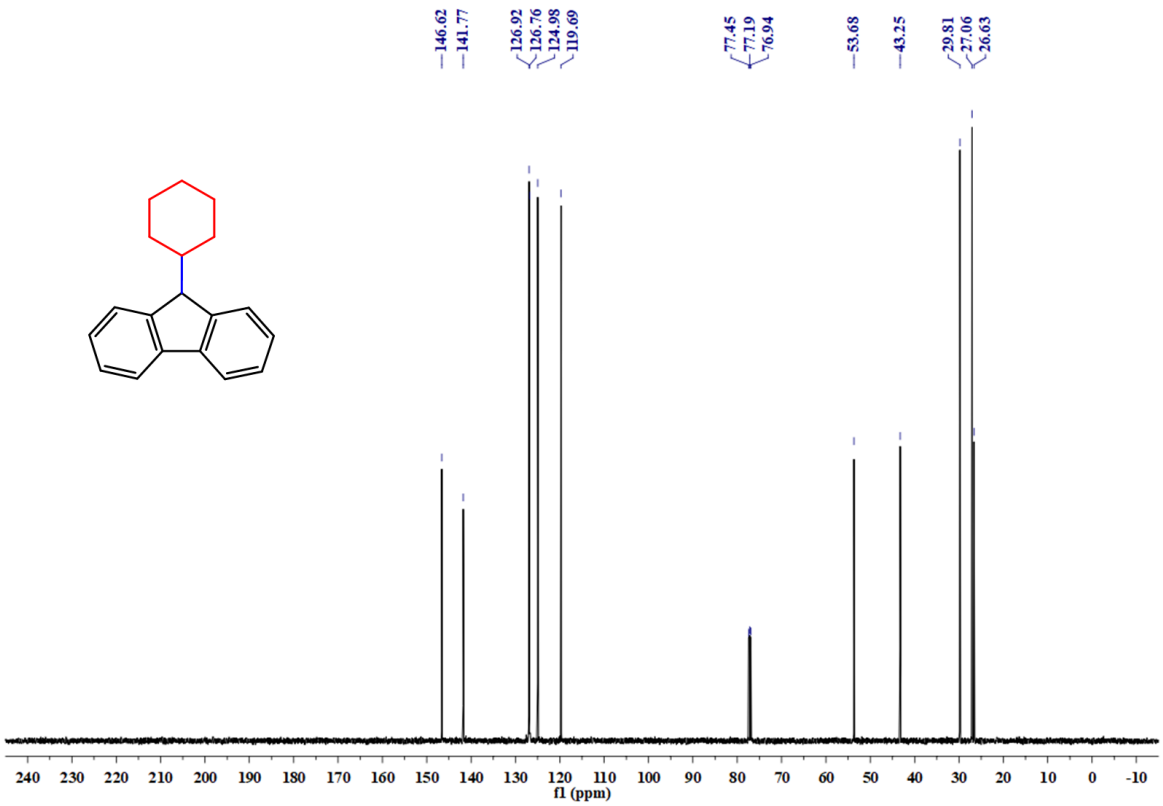


Figure S105: $^{13}C\{^{1}H\}$ NMR spectrum of 3an in $CDCl_3$ at 126 MHz.

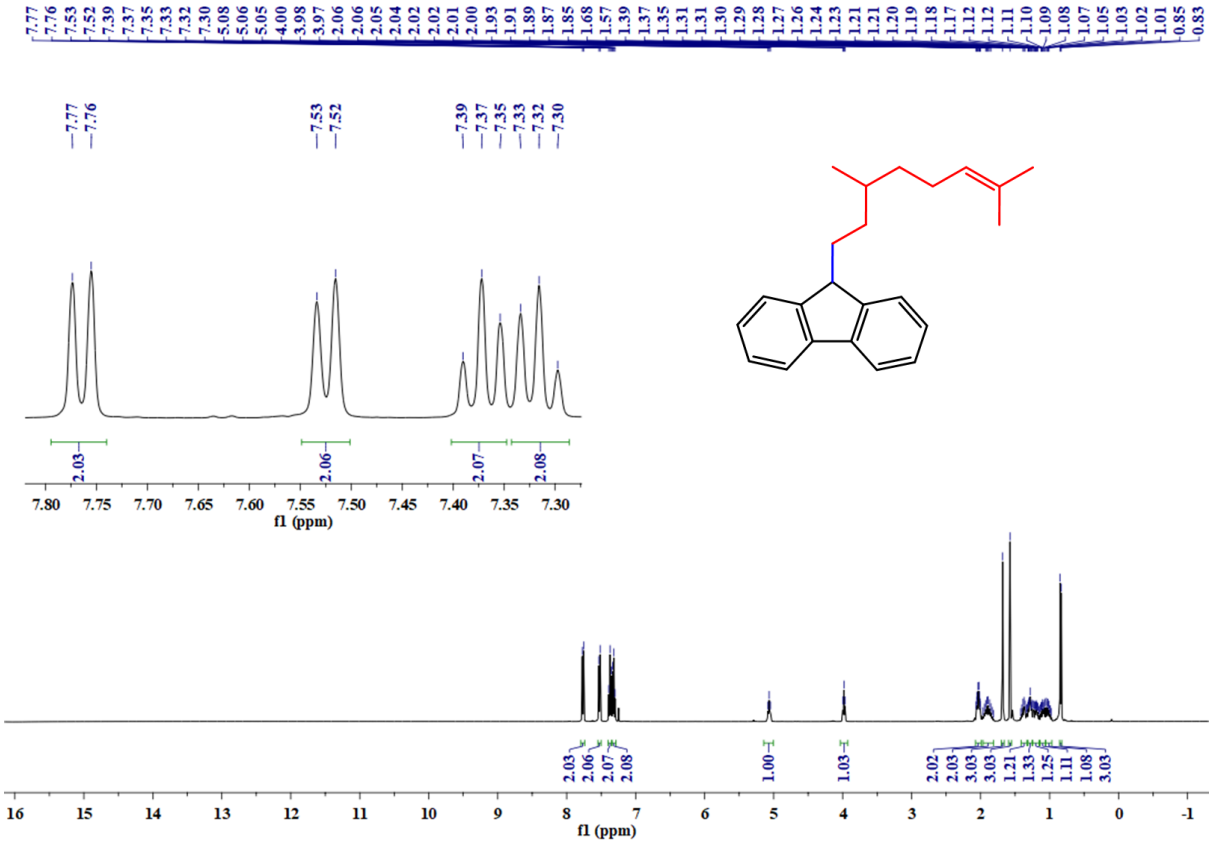


Figure S106: ^{1}H NMR spectrum of 3ao in $CDCl_3$ at 500 MHz.

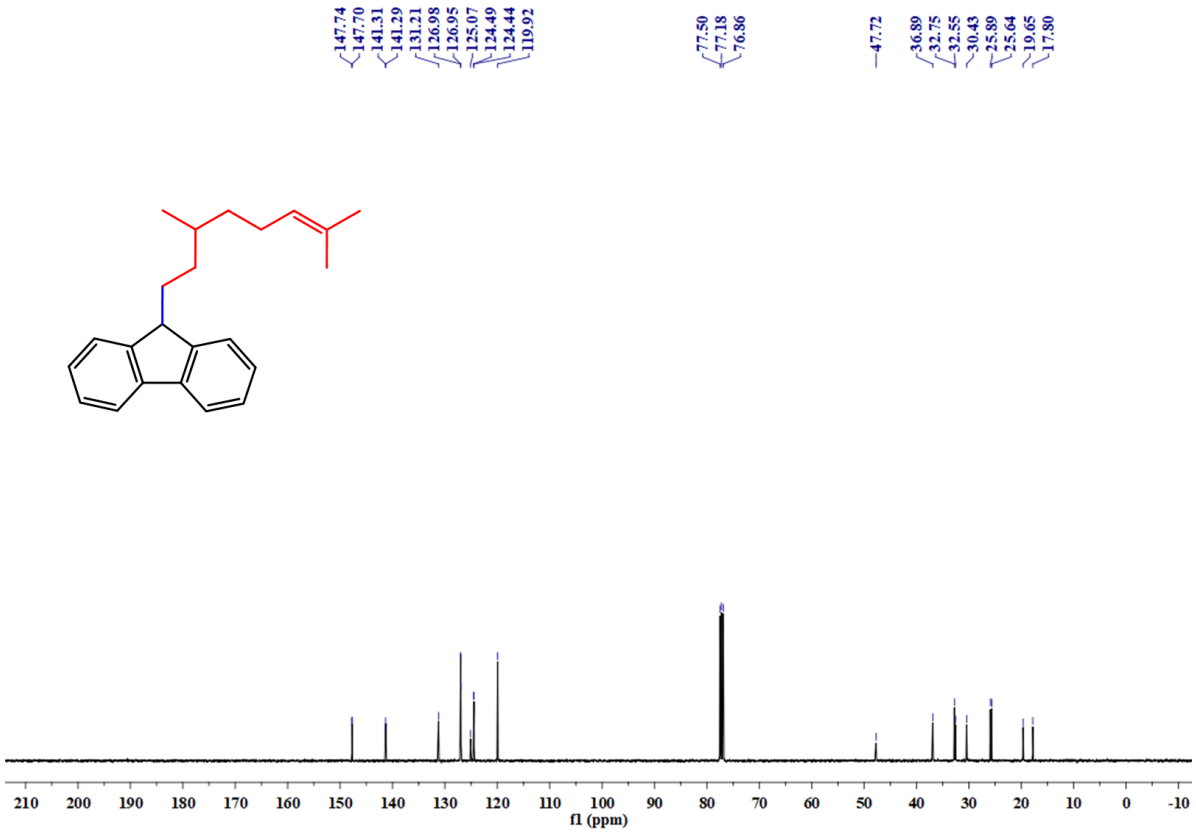


Figure S107: $^{13}C\{^{1}H\}$ NMR spectrum of 3ao in $CDCl_3$ at 126 MHz.

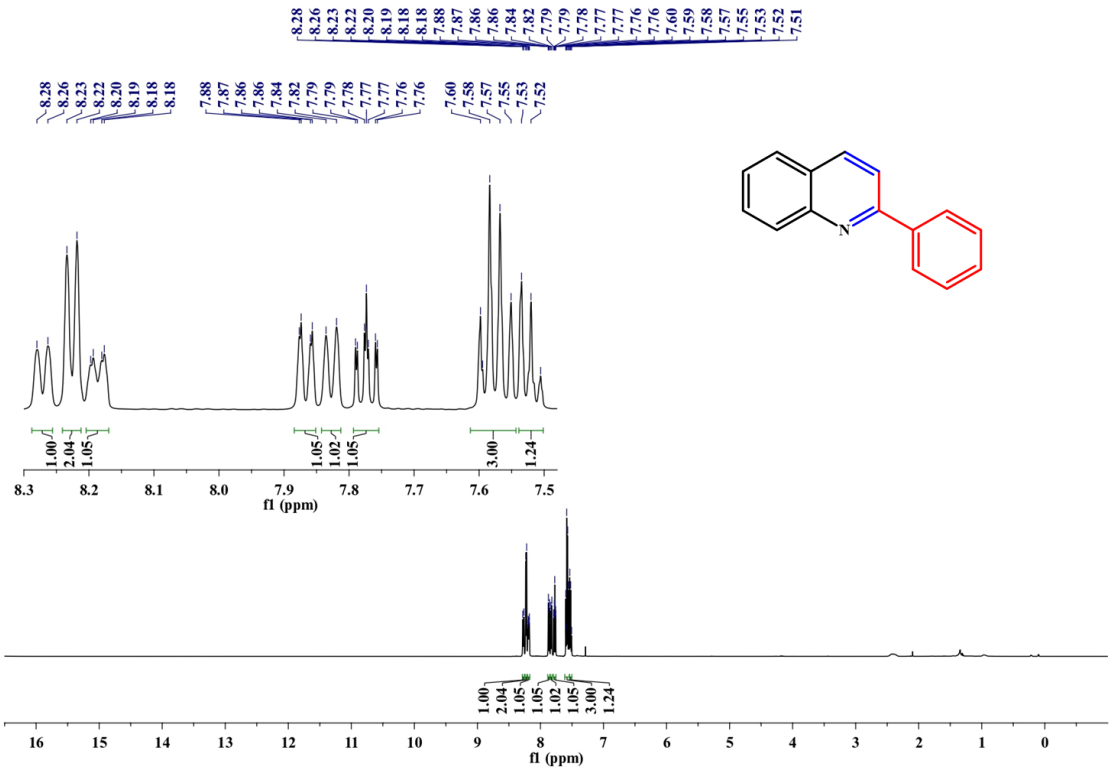


Figure S108: ^{1}H NMR spectrum of 6a in $CDCl_3$ at 500 MHz.

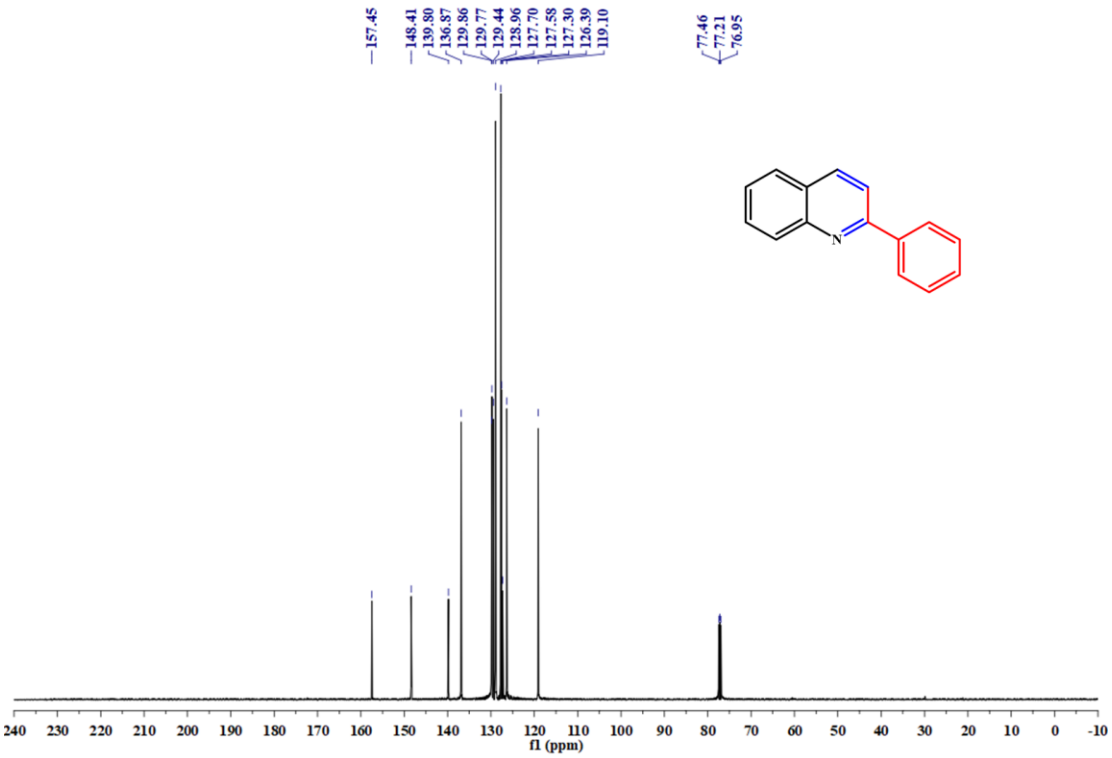


Figure S109: $^{13}C\{^{1}H\}$ NMR spectrum of 6a in $CDCl_3$ at 126 MHz.

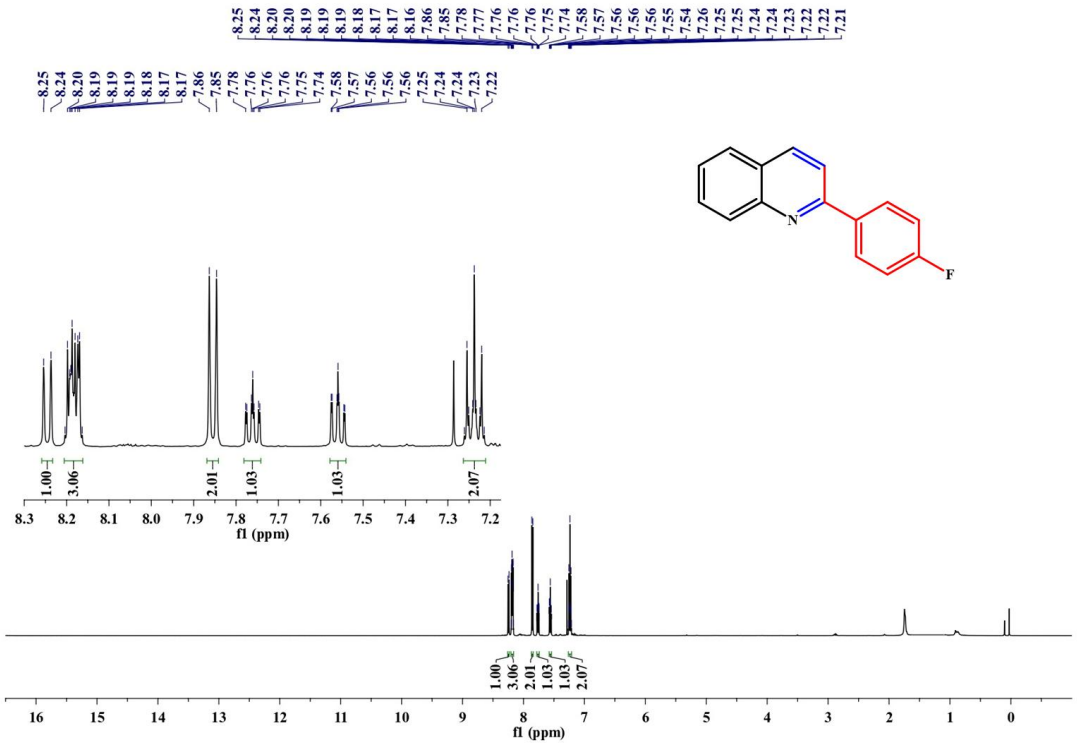


Figure S110: ^{1}H NMR spectrum of 6b in $CDCl_3$ at 500 MHz.

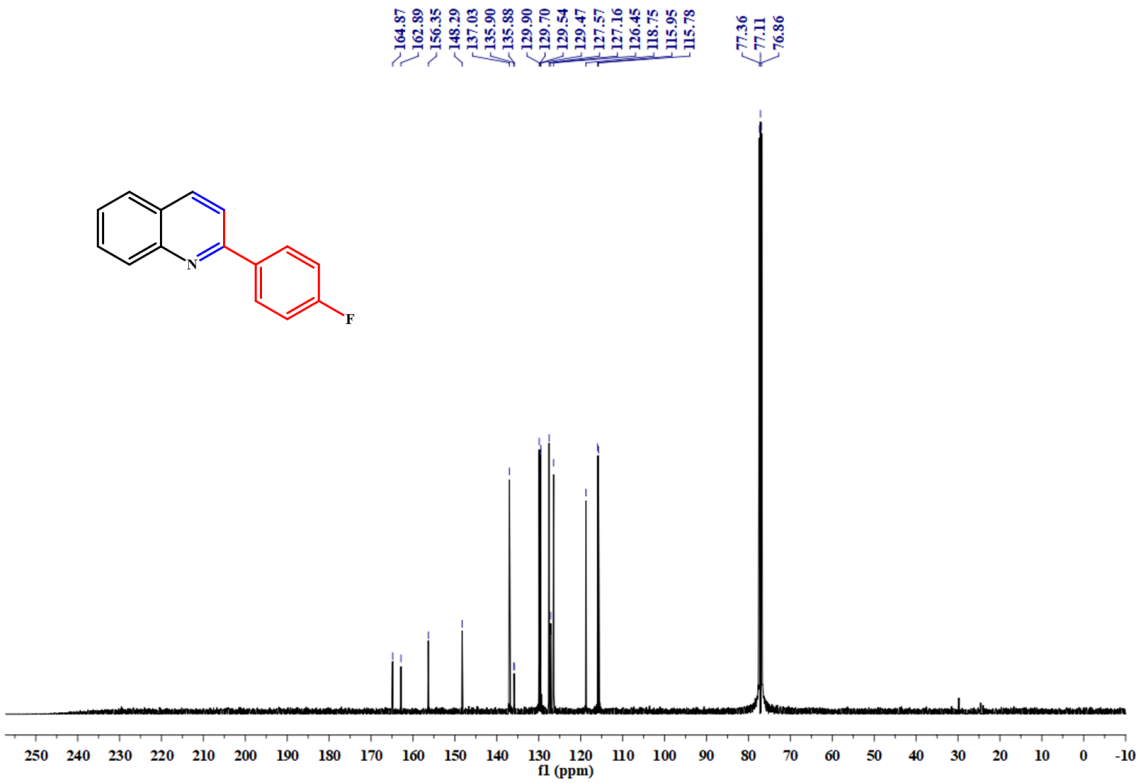


Figure S111: $^{13}C\{^{1}H\}$ NMR spectrum of 6b in $CDCl_3$ at 126 MHz.

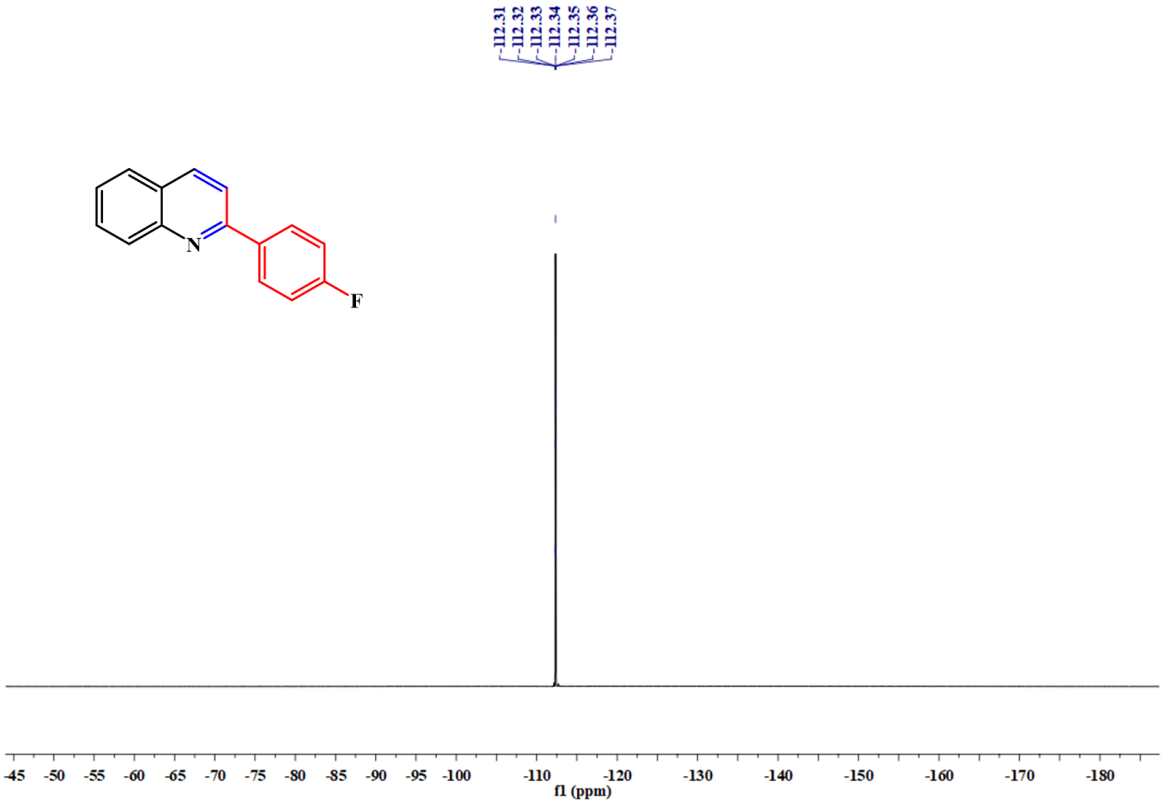


Figure S112: ^{19}F NMR spectrum of 6b in $CDCl_3$ at 471 MHz.

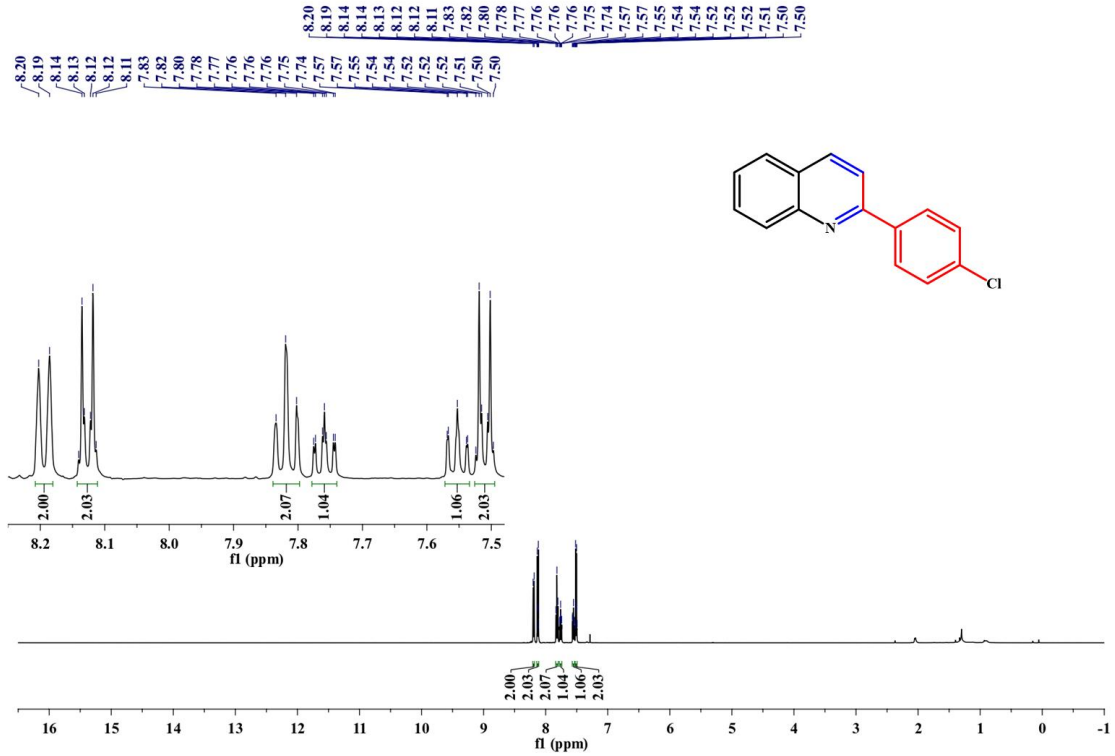


Figure S113: ^{1}**H** NMR spectrum of 6c in $CDCl_3$ at 500 MHz.

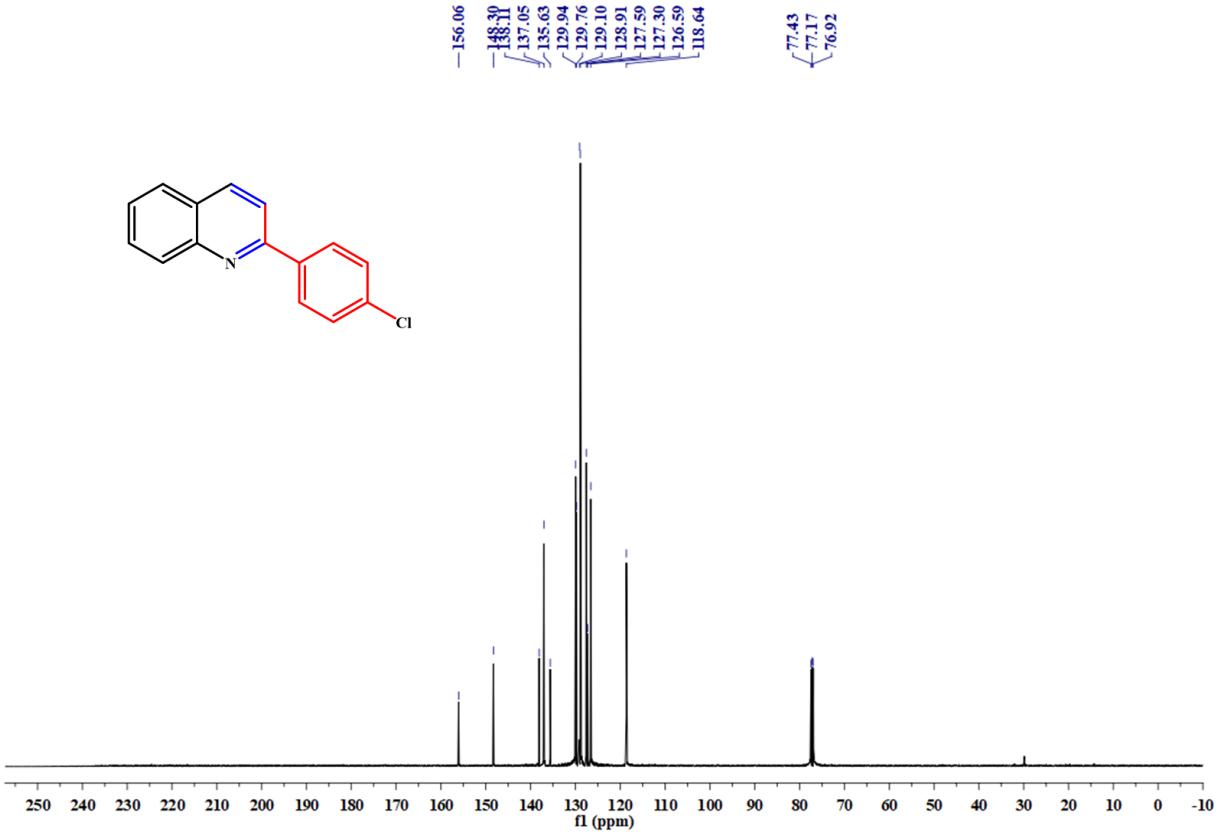


Figure S114: ^{13}**C{^{1}H}** NMR spectrum of 6c in $CDCl_3$ at 126 MHz.

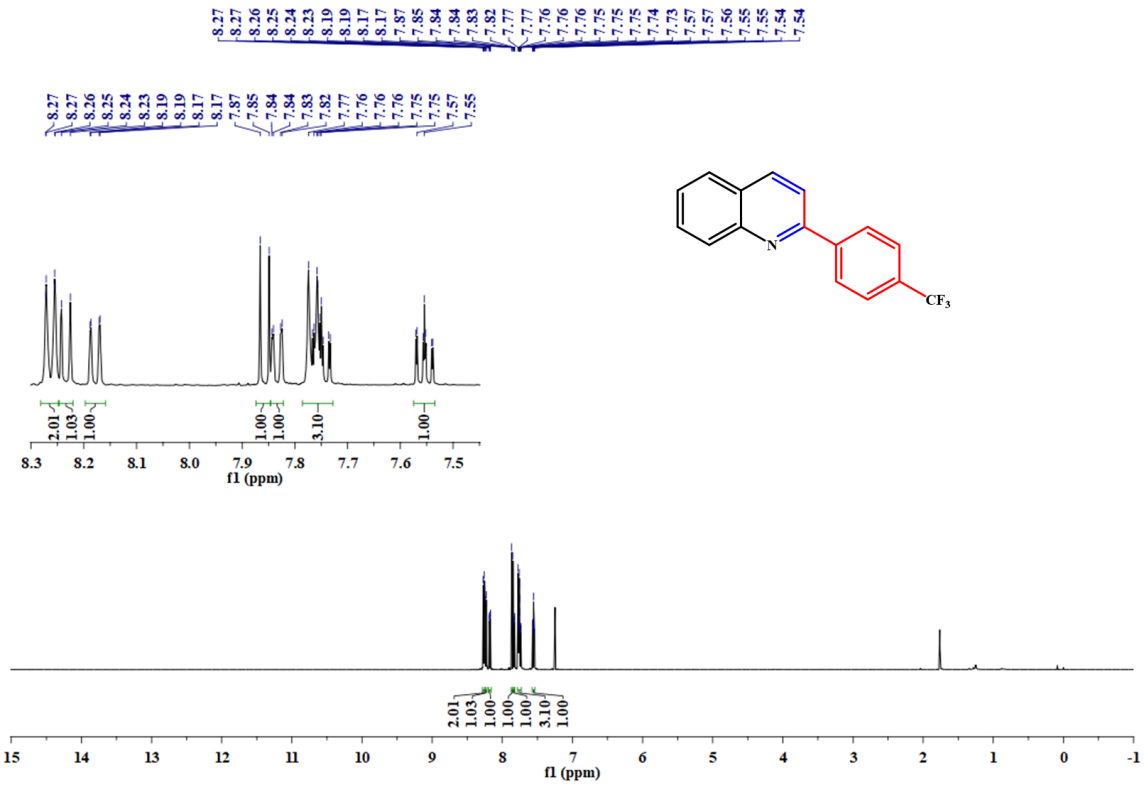


Figure S115: ^{1}**H** NMR spectrum of 6d in $CDCl_3$ at 500 MHz.

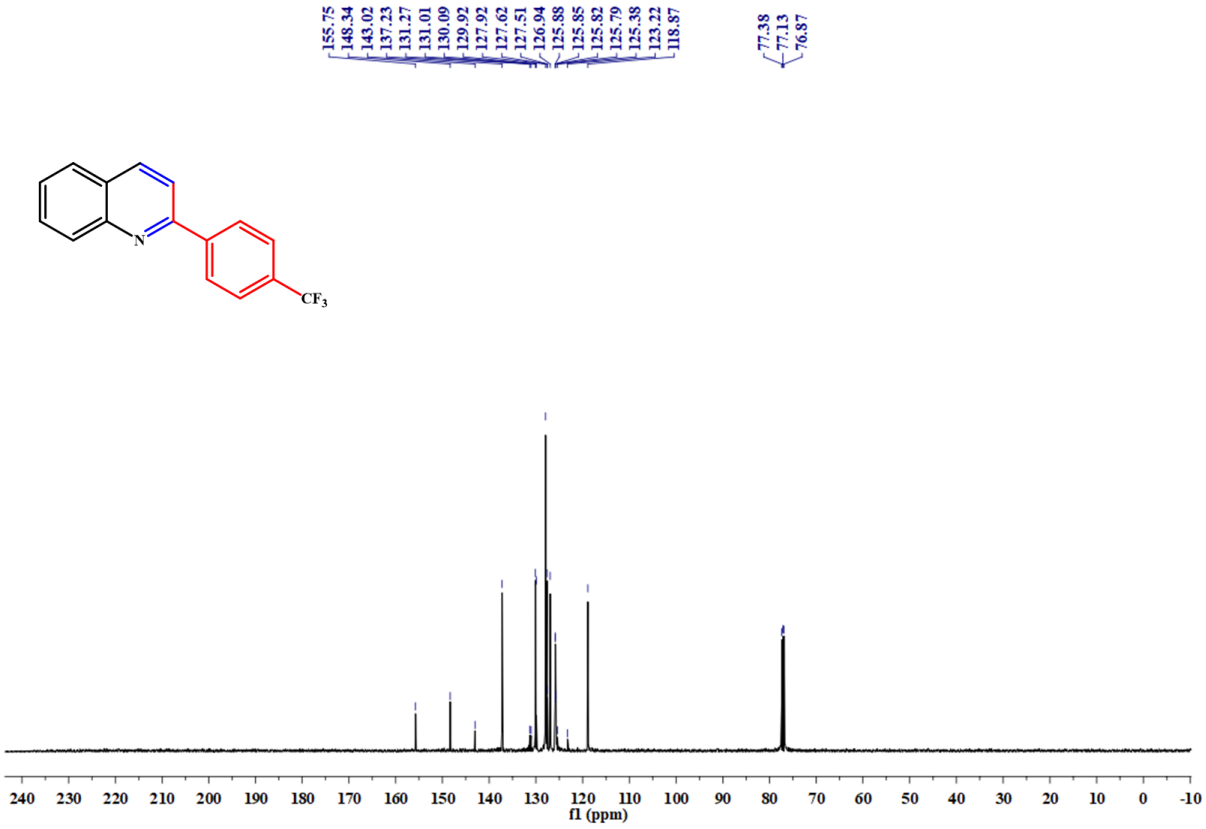


Figure S116: ^{13}**C{**^{1}**H}** NMR spectrum of 6d in $CDCl_3$ at 126 MHz.

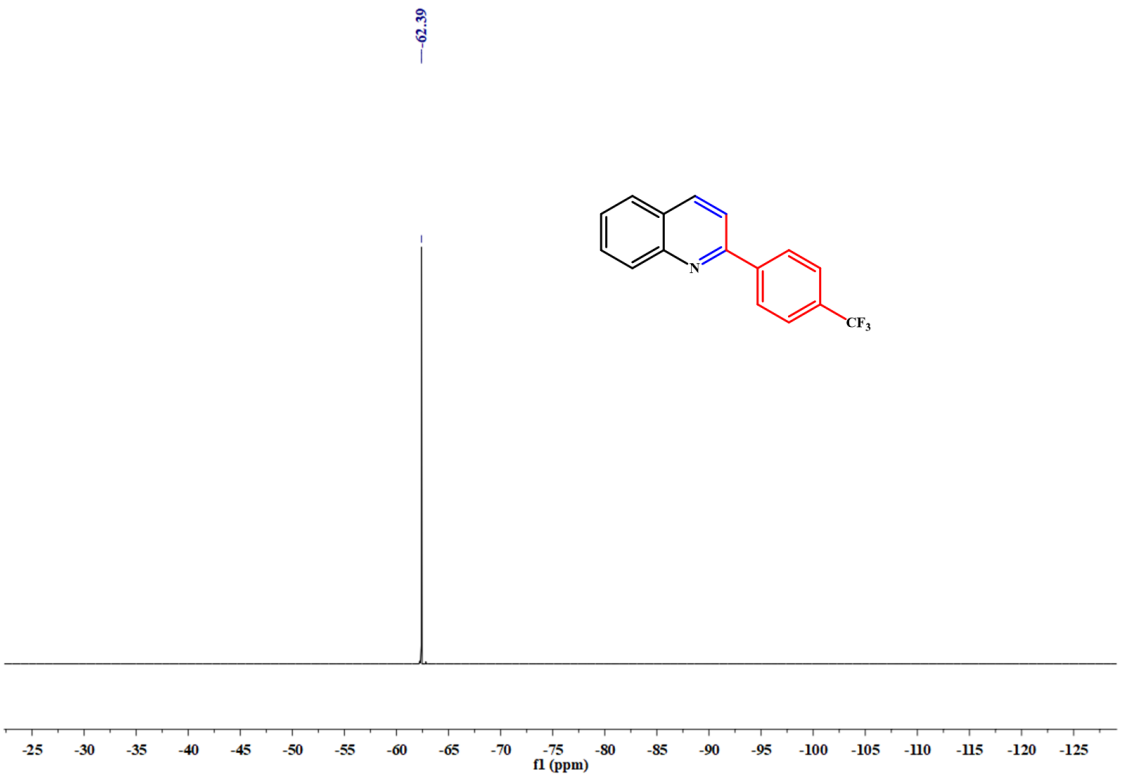


Figure S117: ^{19}**F** NMR spectrum of 6d in $CDCl_3$ at 471 MHz.

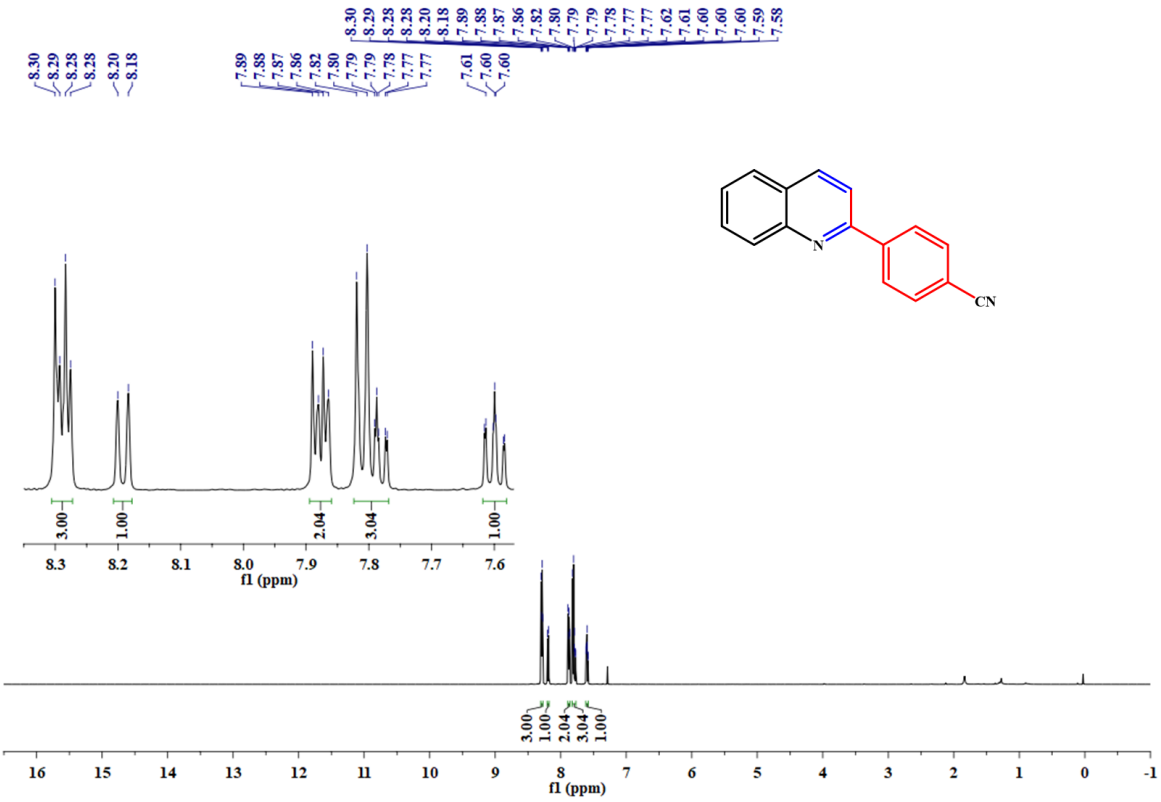


Figure S118: ^{1}**H** NMR spectrum of 6e in $CDCl_3$ at 500 MHz.

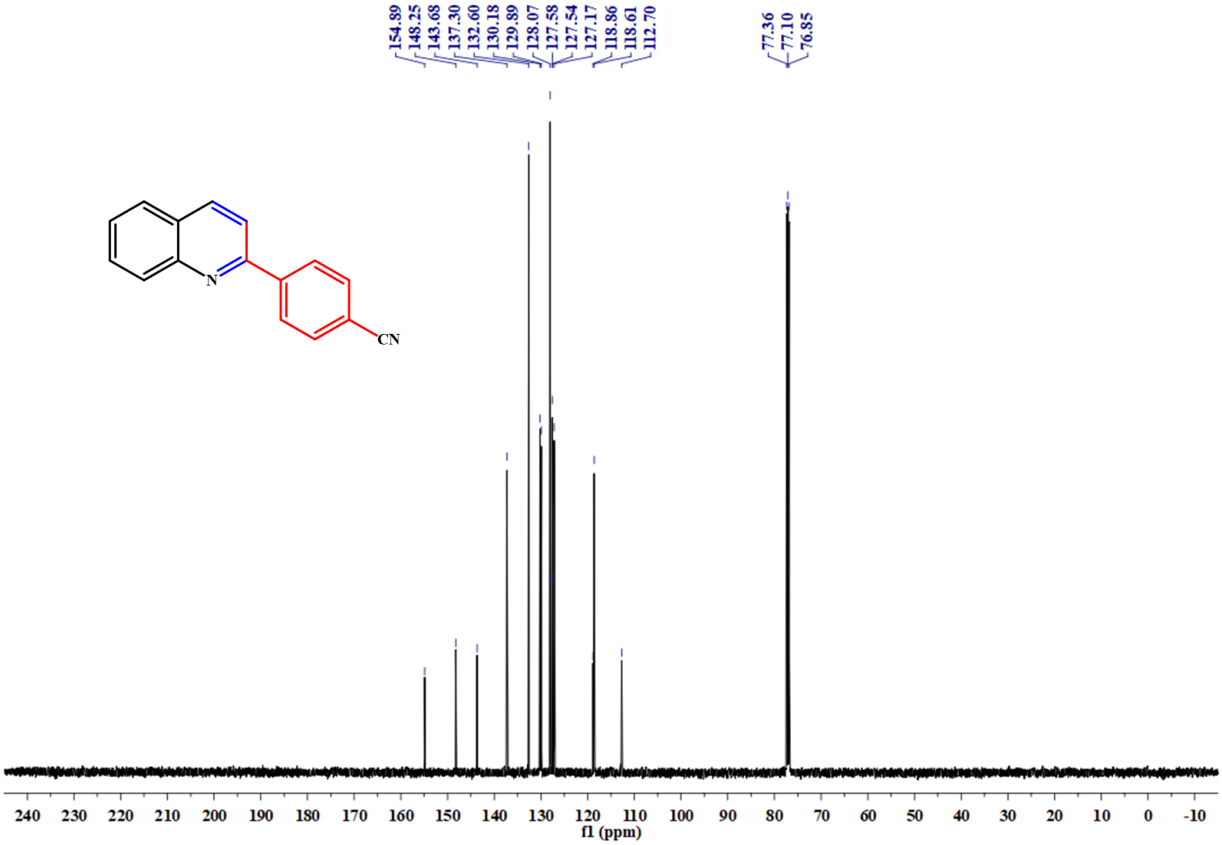


Figure S119: $^{13}C\{^{1}H\}$ NMR spectrum of 6e in $CDCl_3$ at 126 MHz.

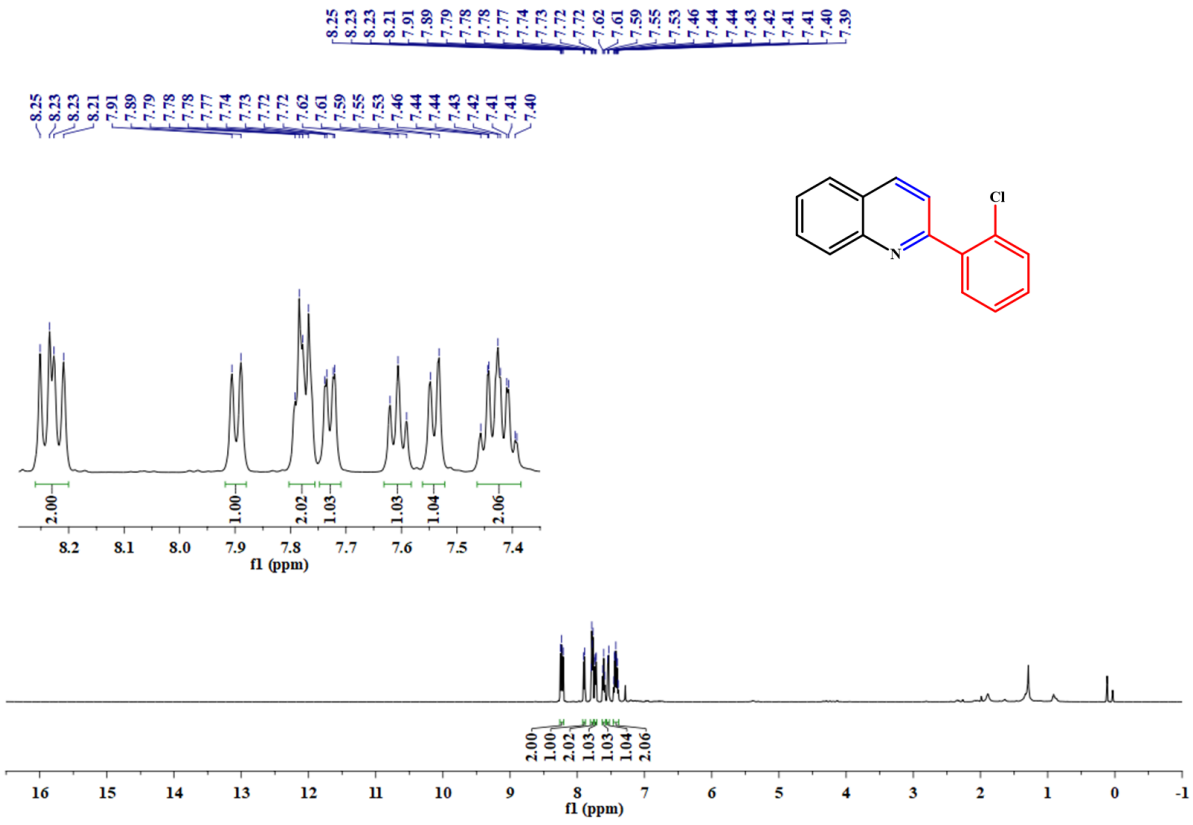


Figure S120: ^{1}H NMR spectrum of 6f in $CDCl_3$ at 500 MHz.

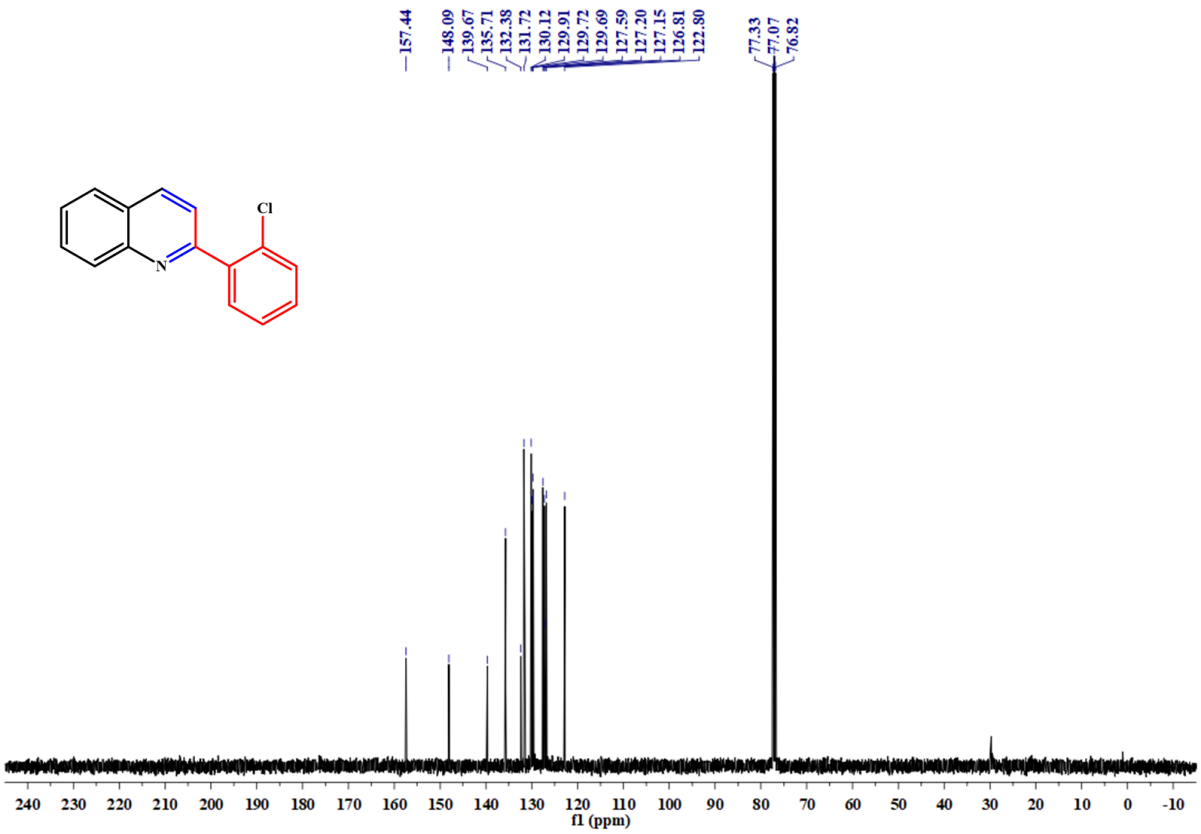


Figure S121: $^{13}C\{^{1}H\}$ NMR spectrum of 6f in $CDCl_3$ at 126 MHz.

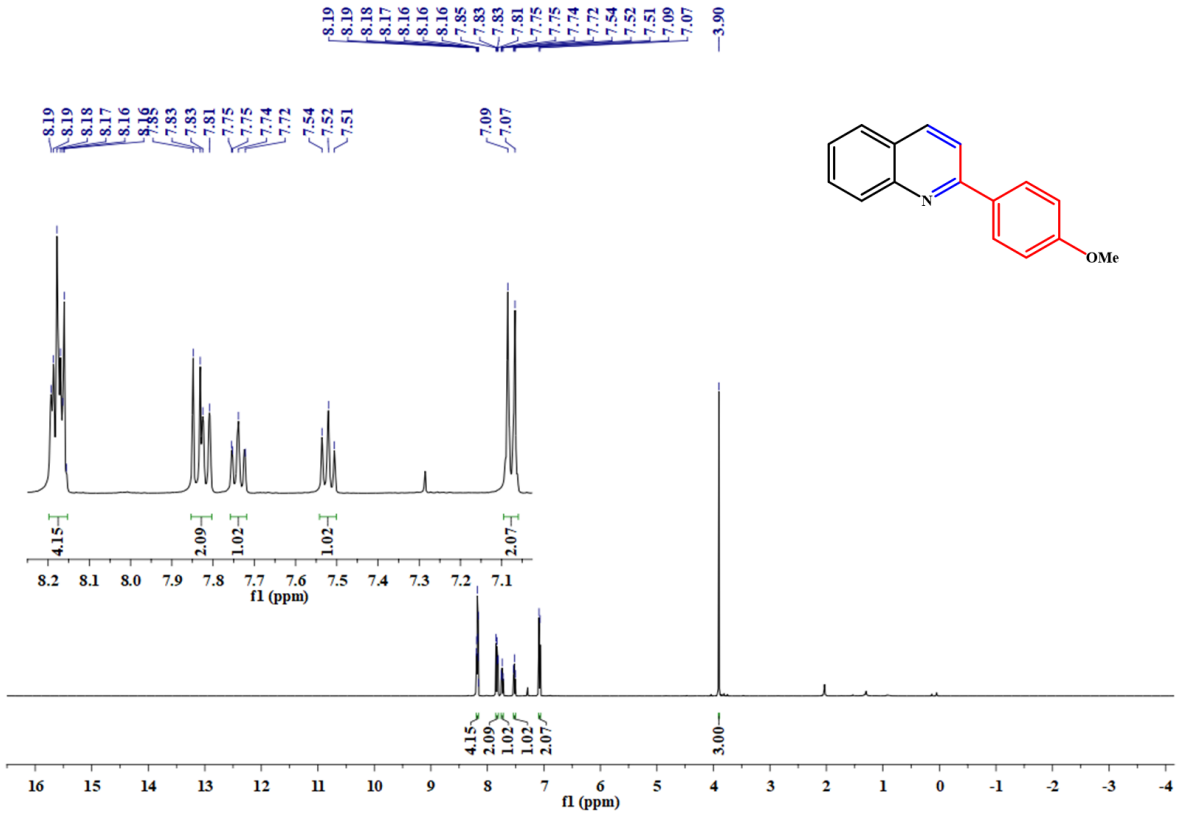


Figure S122: ^{1}H NMR spectrum of 6g in $CDCl_3$ at 500 MHz.

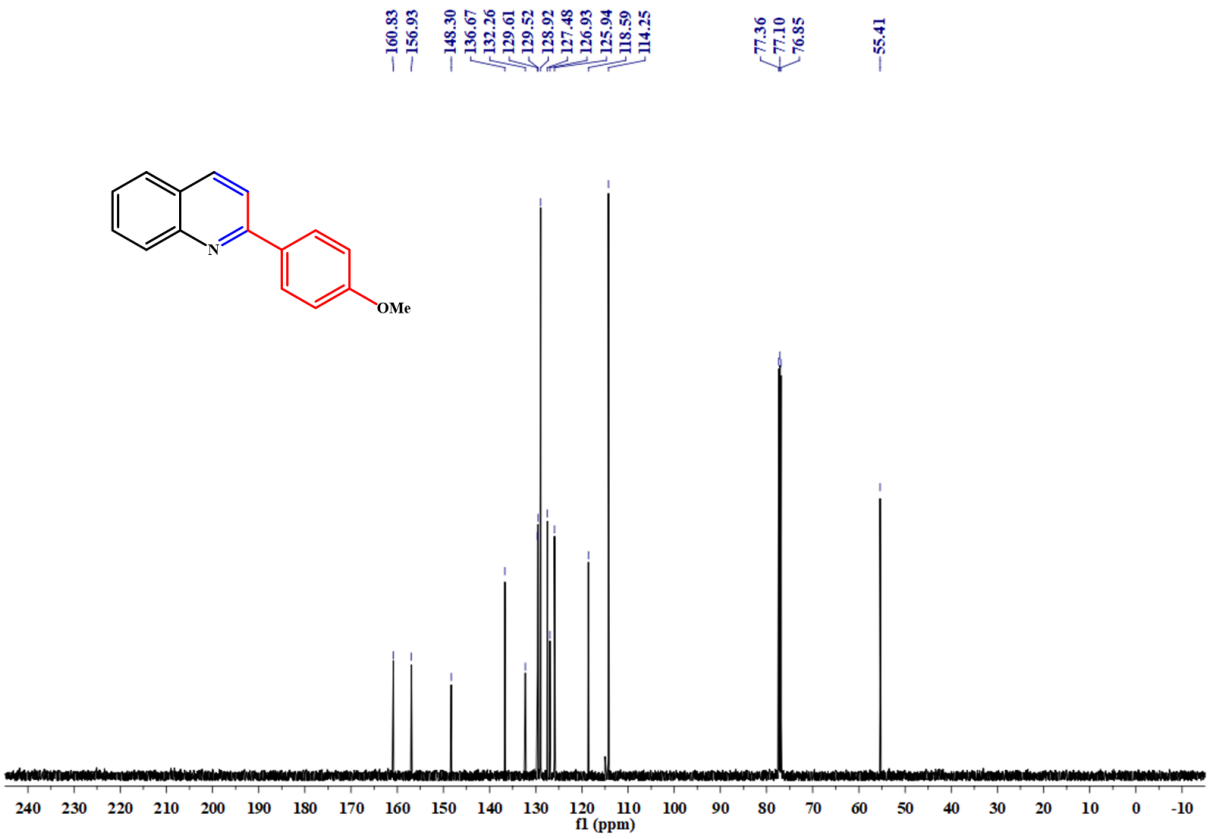


Figure S123: $^{13}C\{^{1}H\}$ NMR spectrum of 6g in $CDCl_3$ at 126 MHz.

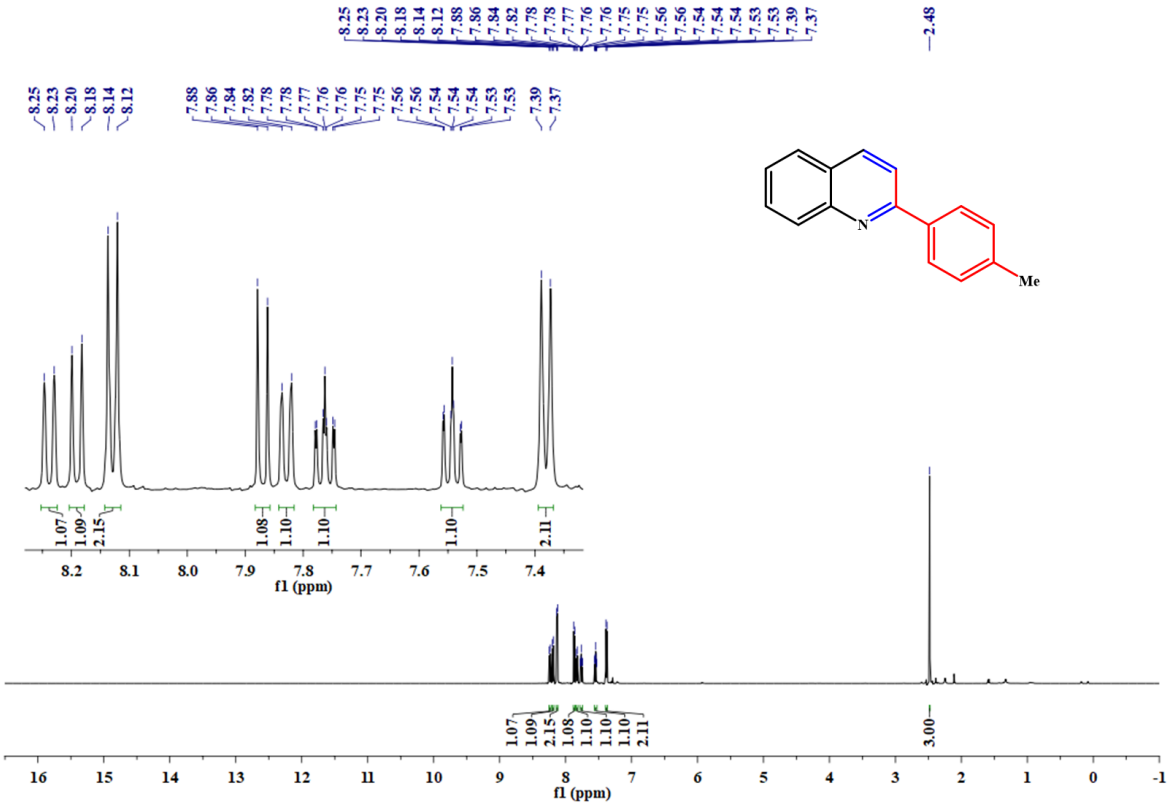


Figure S124: ^{1}H NMR spectrum of 6h in $CDCl_3$ at 500 MHz.

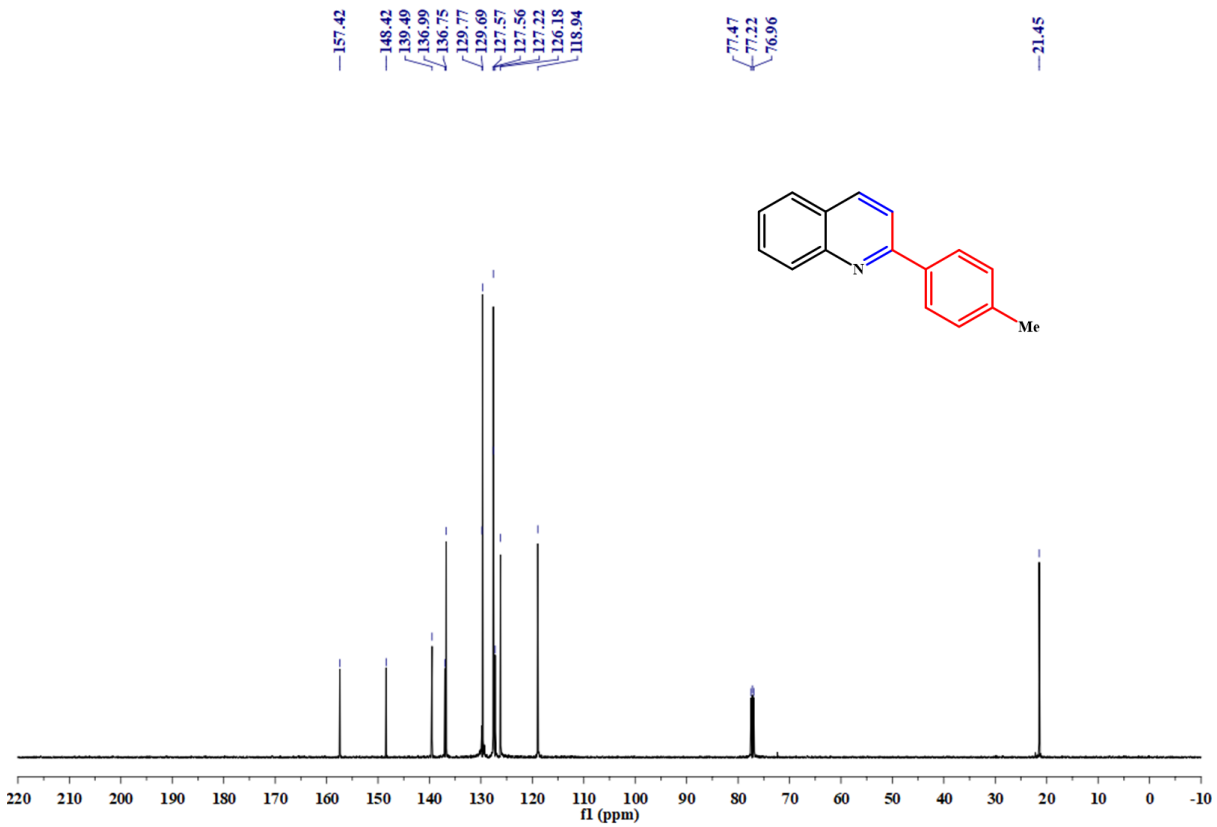


Figure S125: $^{13}C\{^{1}H\}$ NMR spectrum of 6h in $CDCl_3$ at 126 MHz.

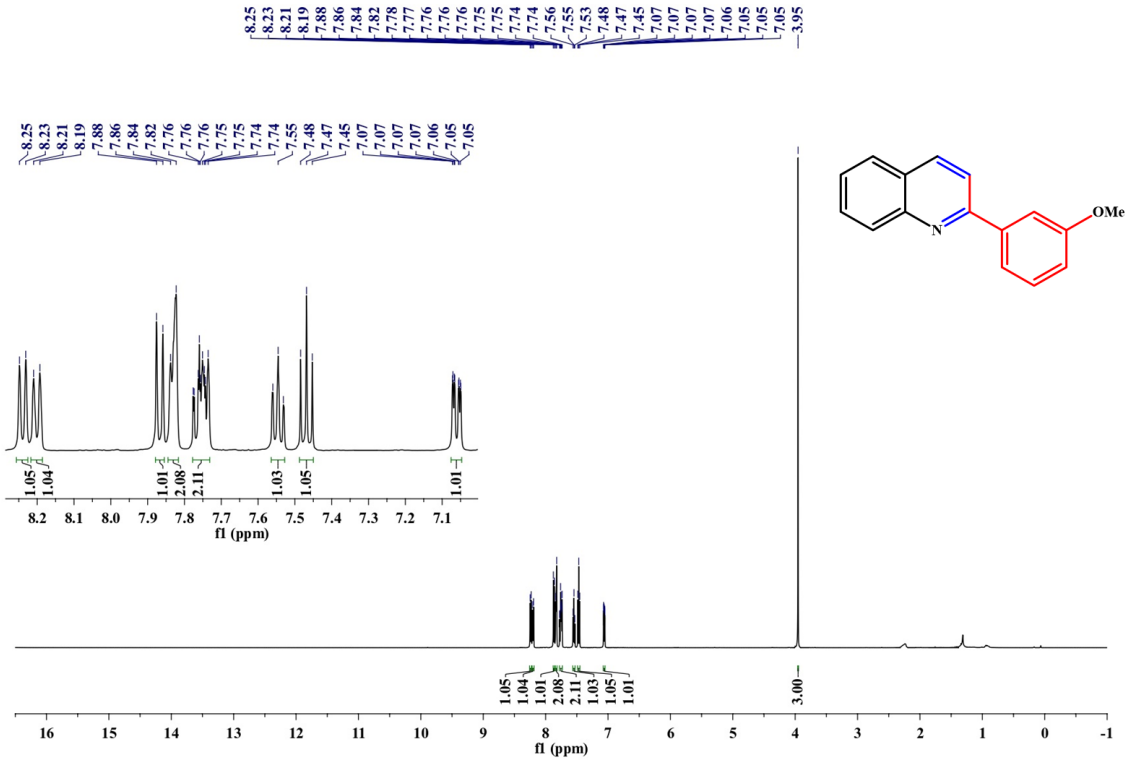


Figure S126: ^{1}H NMR spectrum of 6i in $CDCl_3$ at 500 MHz.

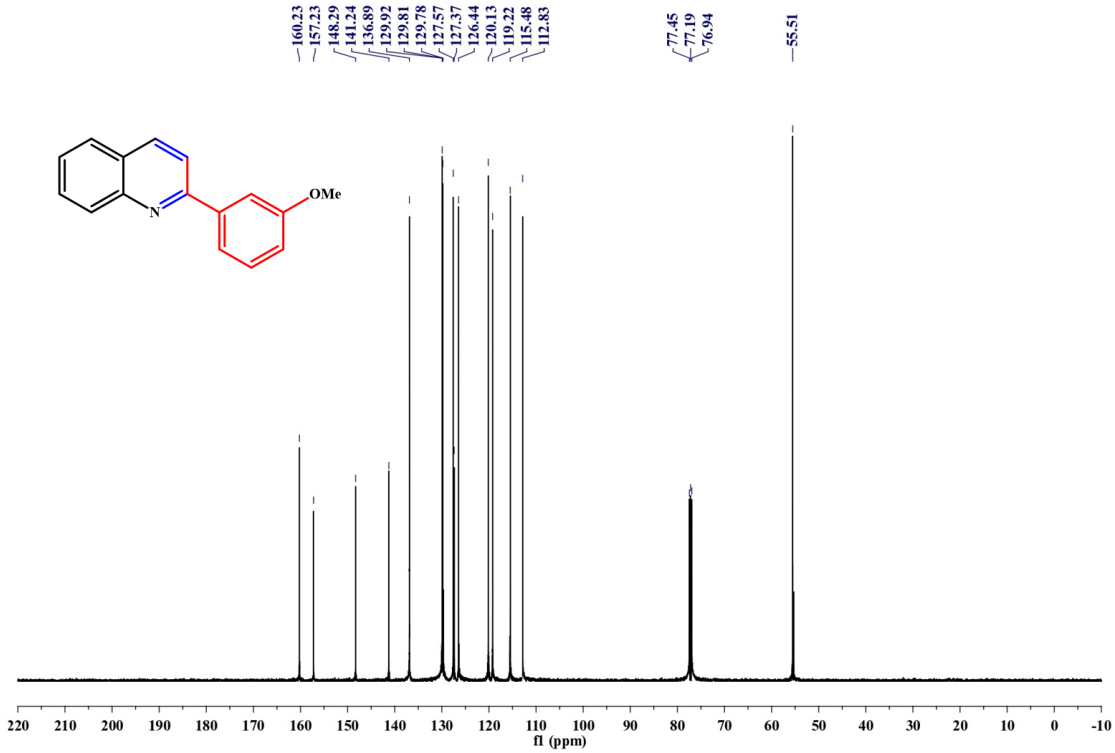


Figure S127: $^{13}C\{^{1}H\}$ NMR spectrum of 6i in $CDCl_3$ at 126 MHz.

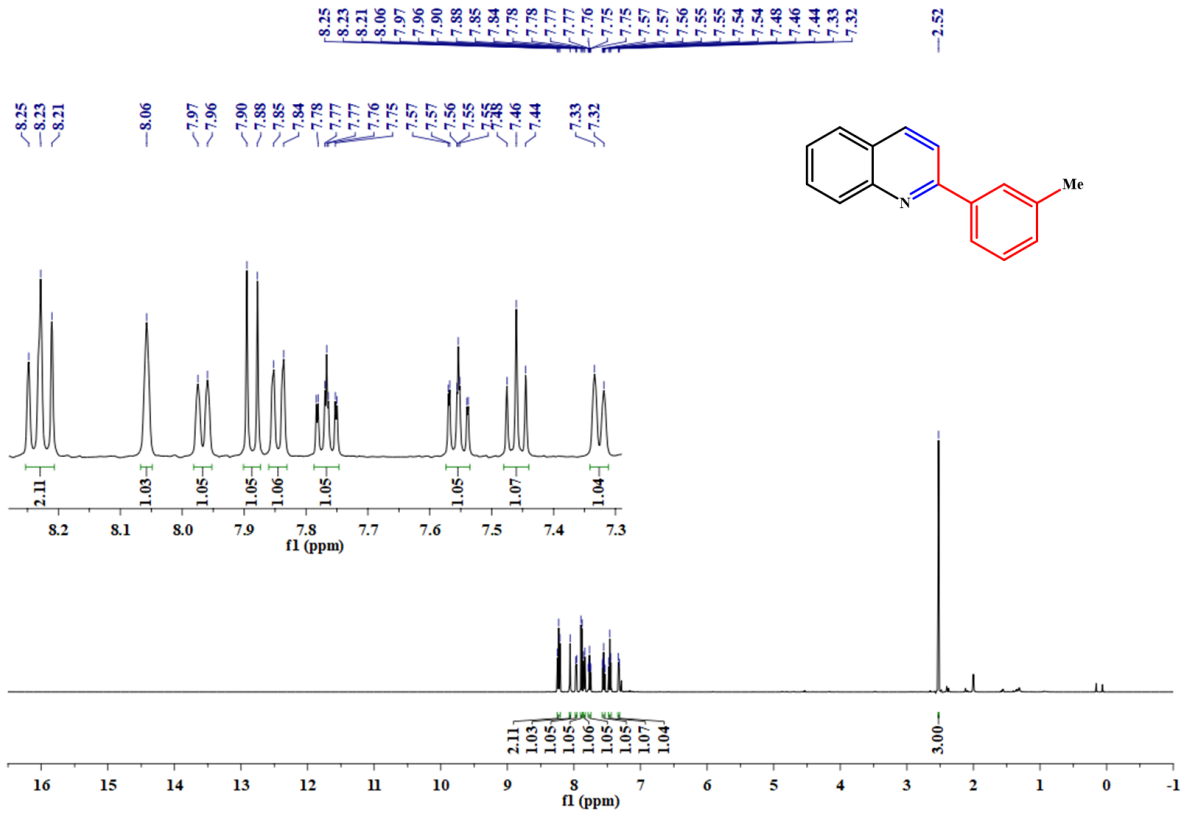


Figure S128: ^{1}H NMR spectrum of 6j in $CDCl_3$ at 500 MHz.

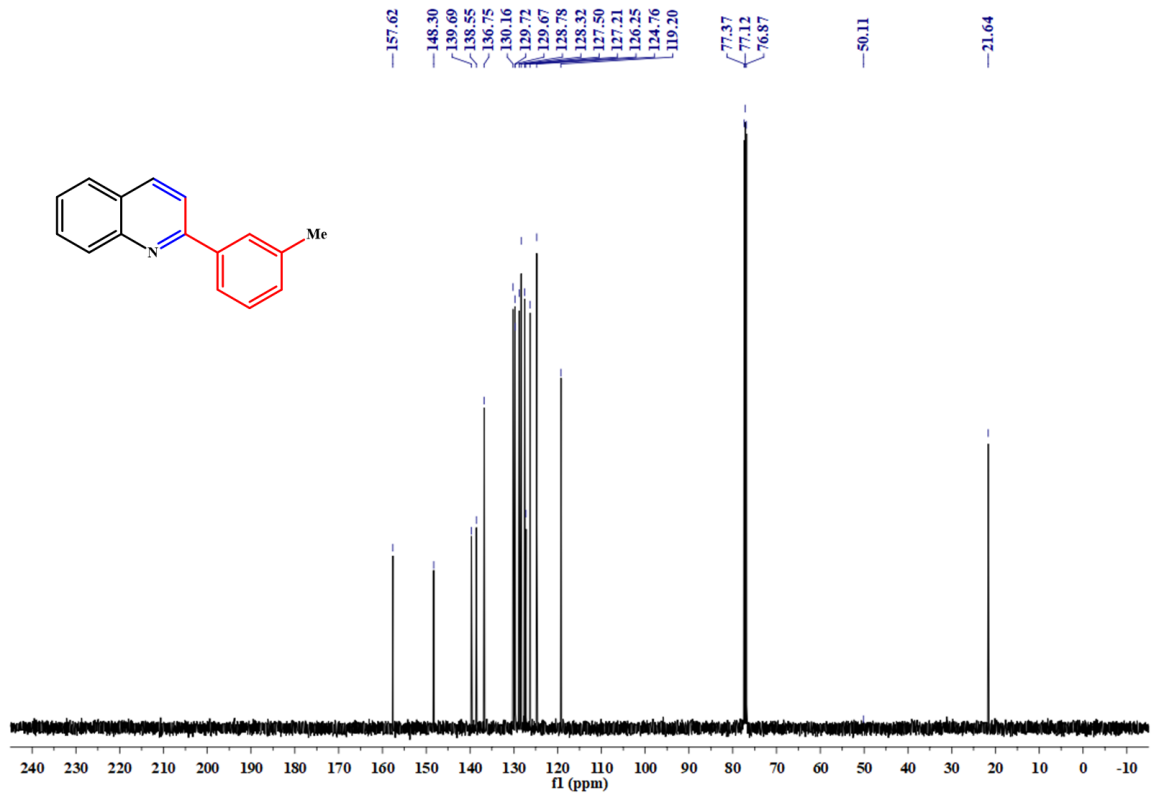


Figure S129: $^{13}C\{^{1}H\}$ NMR spectrum of 6j in $CDCl_3$ at 126 MHz.

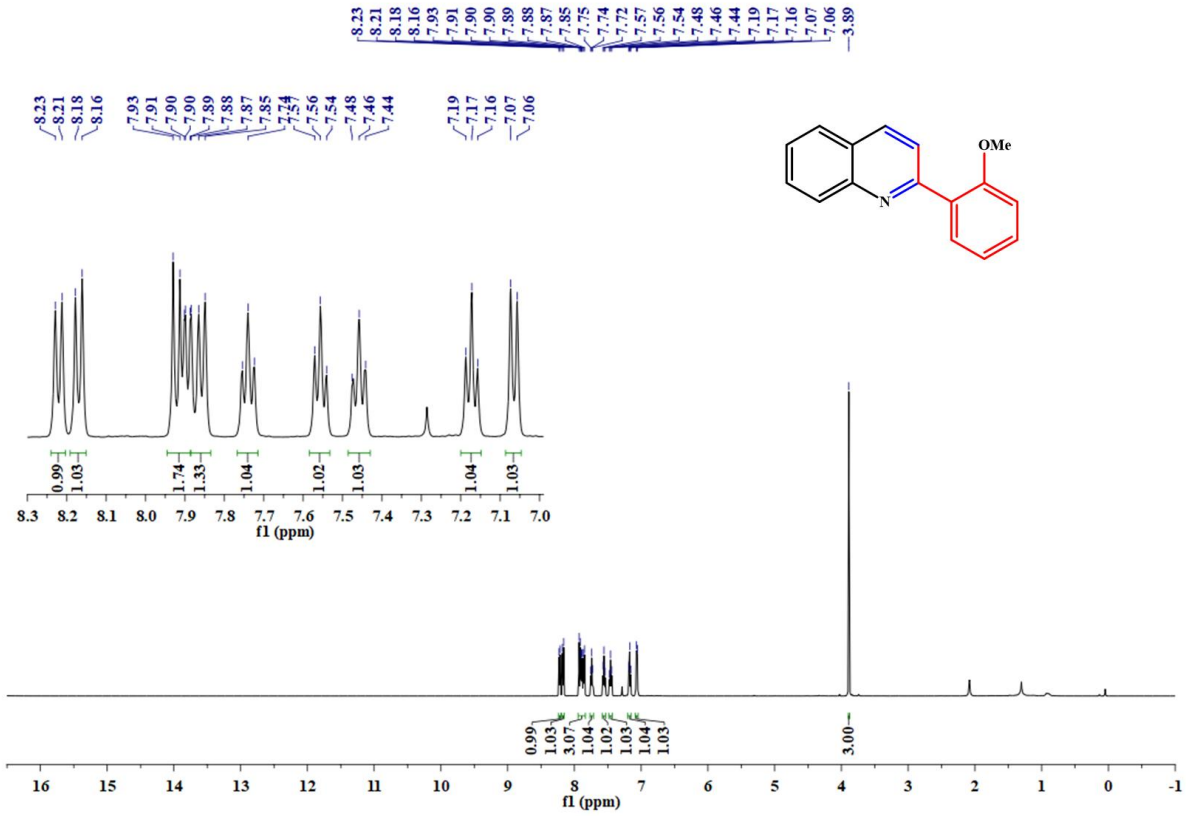


Figure S130: ^{1}H NMR spectrum of 6k in $CDCl_3$ at 500 MHz.

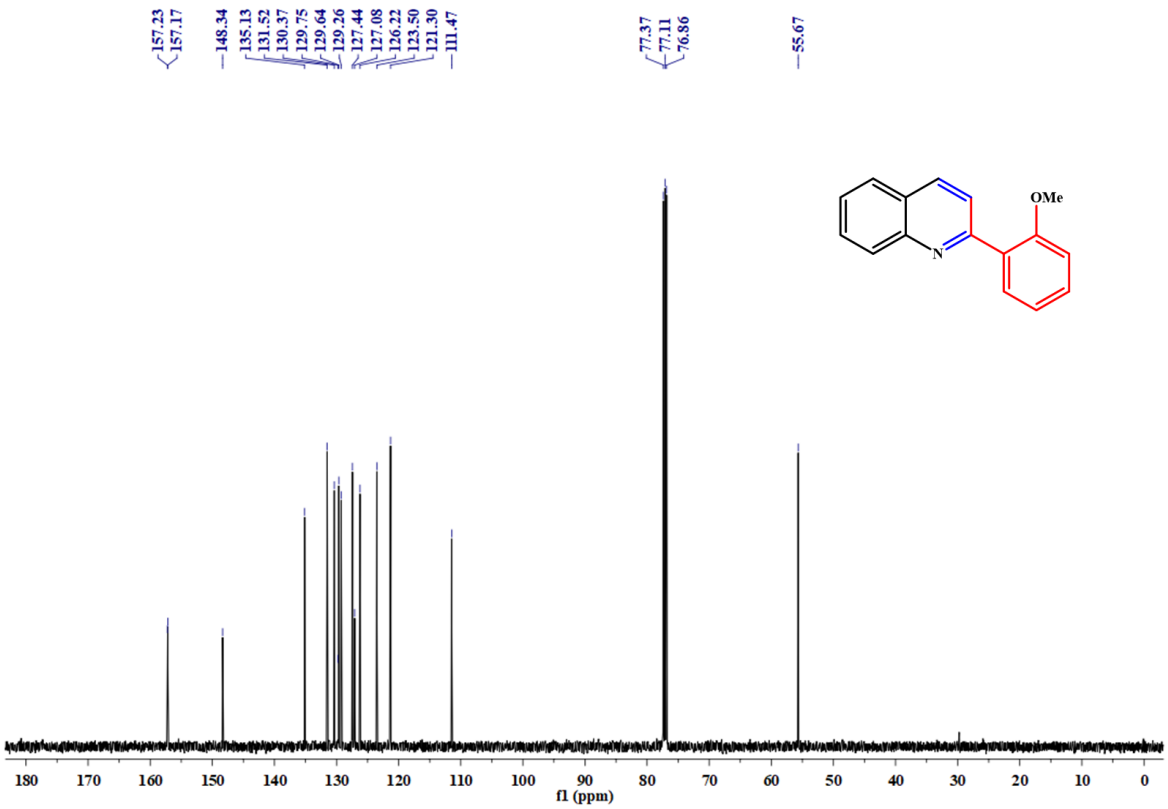


Figure S131: $^{13}C\{^{1}H\}$ NMR spectrum of 6k in $CDCl_3$ at 126 MHz.

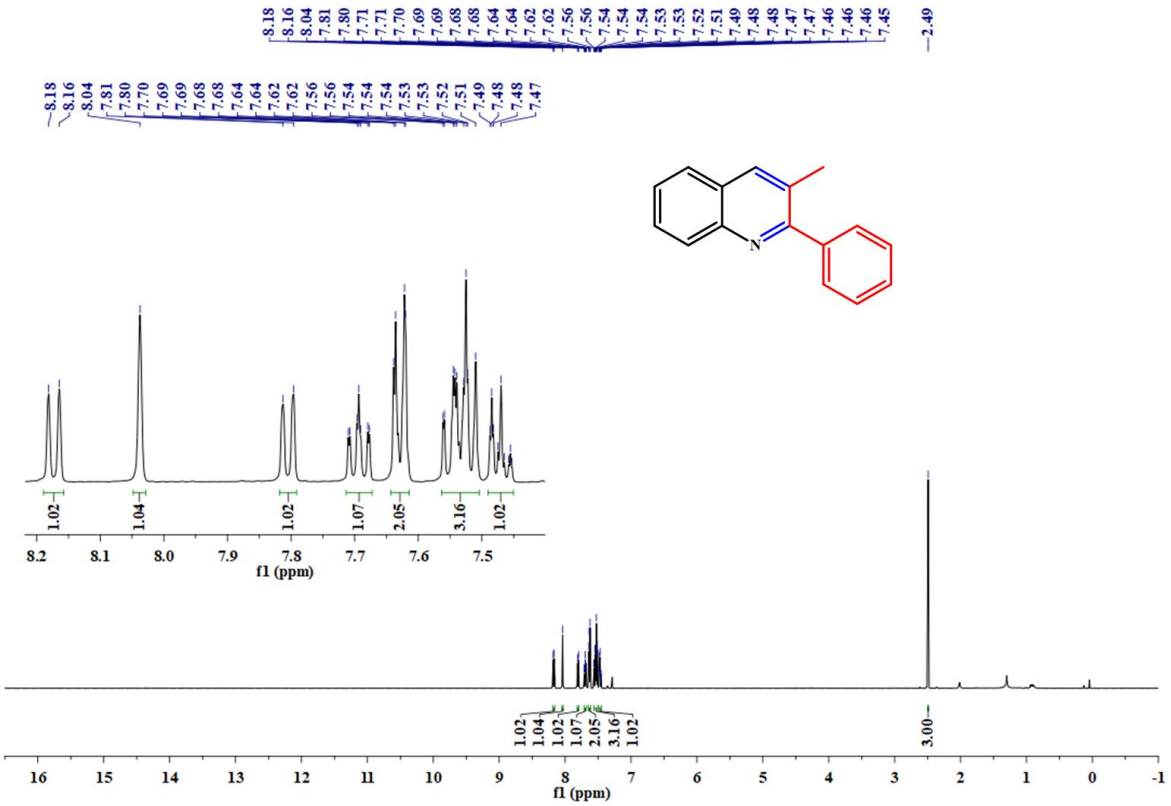


Figure S132: ^{1}H NMR spectrum of 6l in $CDCl_3$ at 500 MHz.

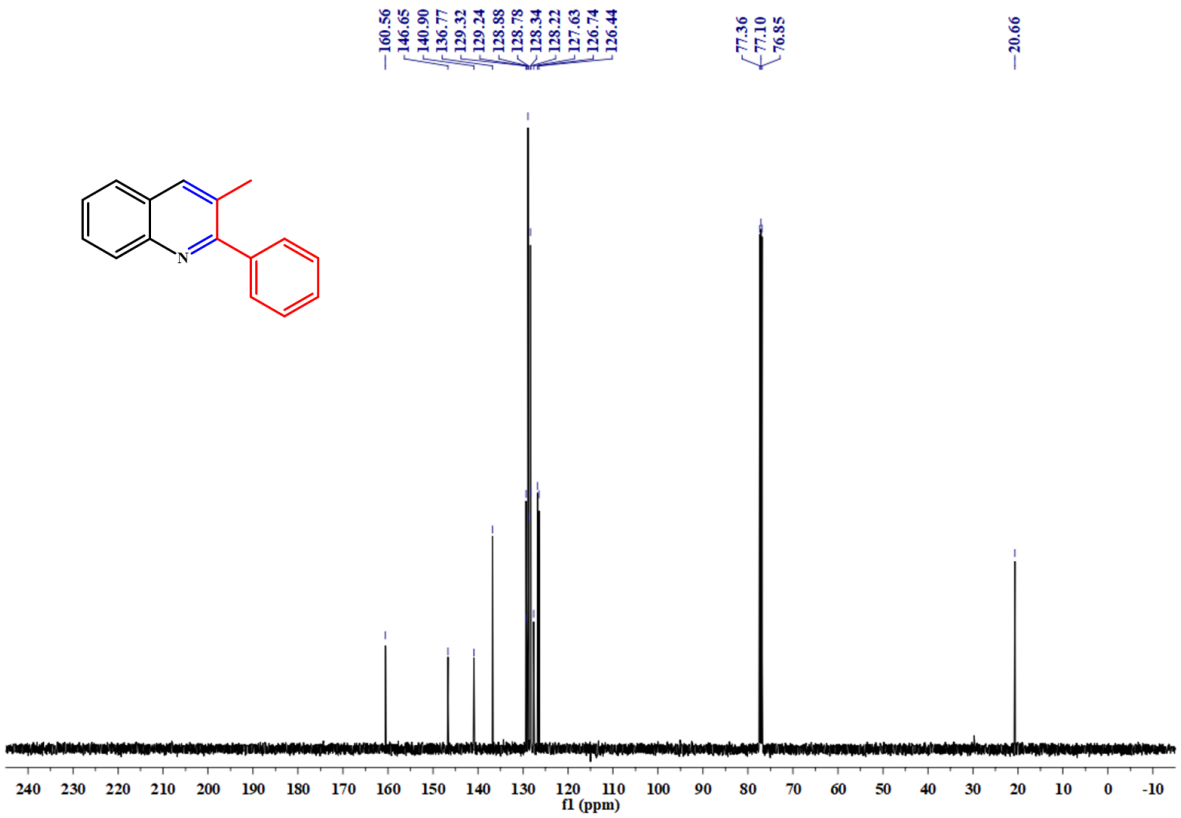


Figure S133: $^{13}C\{^{1}H\}$ NMR spectrum of 6l in $CDCl_3$ at 126 MHz.

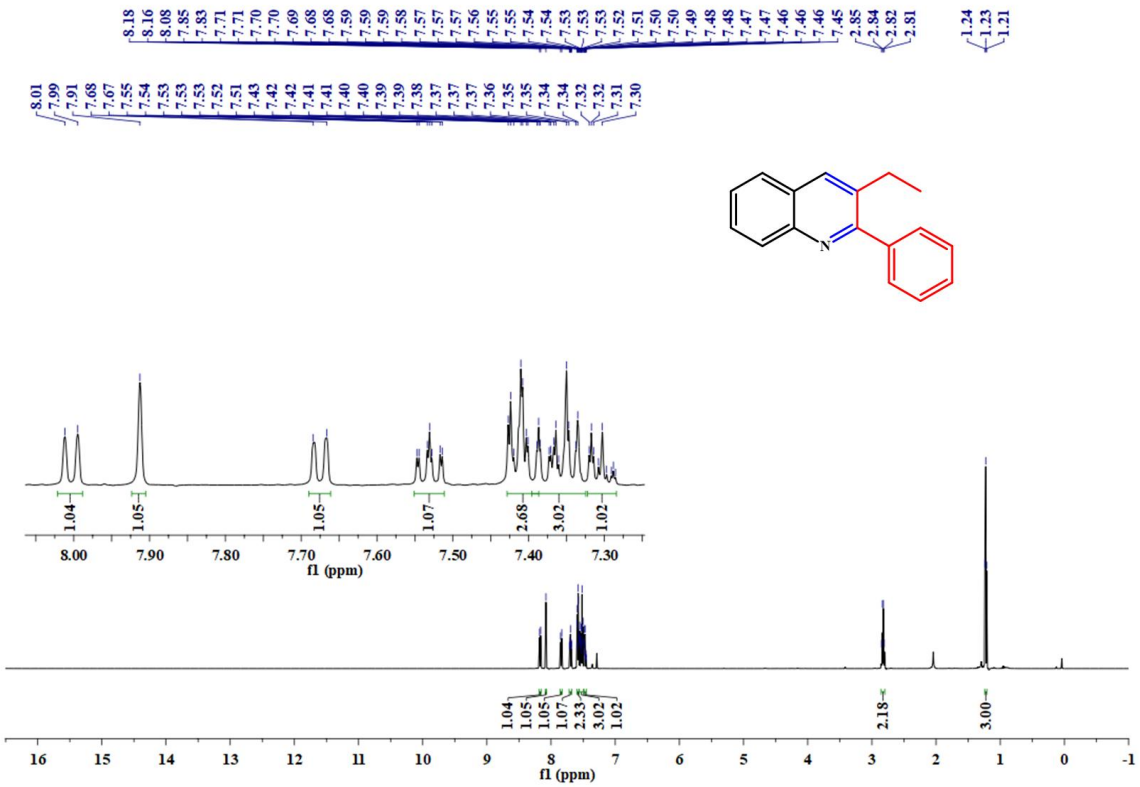


Figure S134: ^{1}H NMR spectrum of 6m in $CDCl_3$ at 500 MHz.

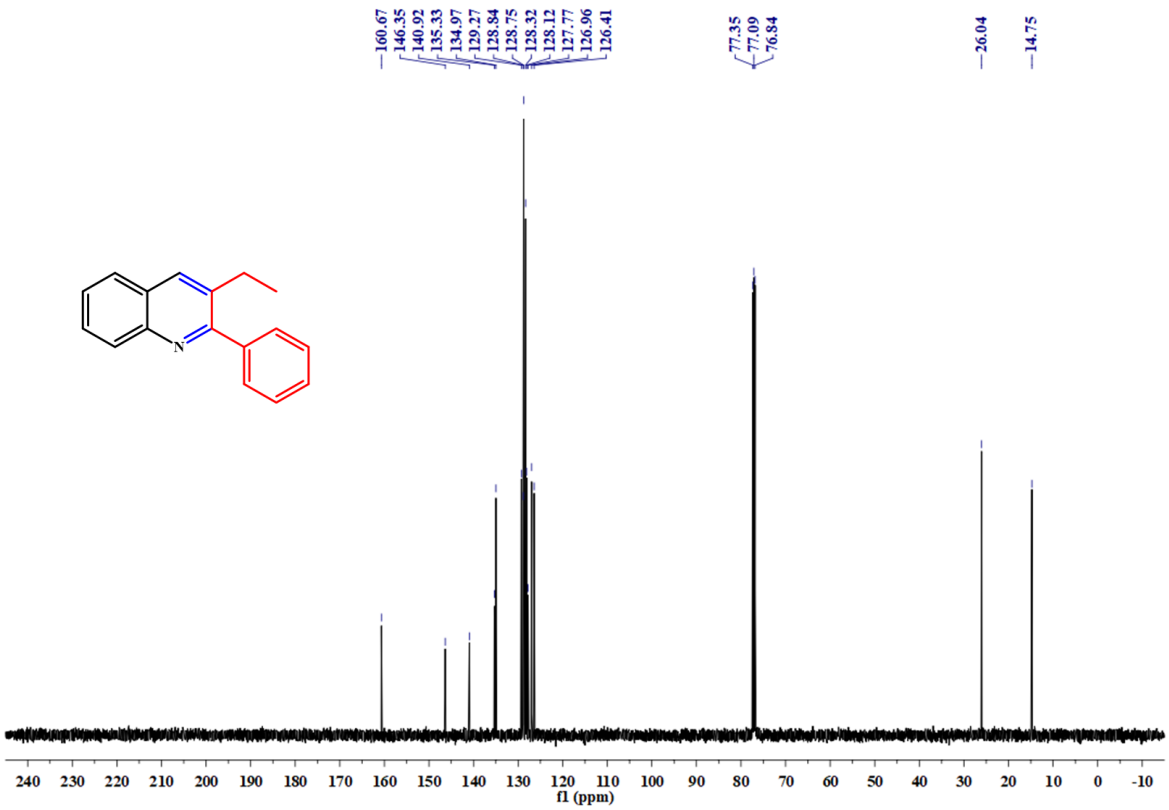


Figure S135: $^{13}C\{^{1}H\}$ NMR spectrum of 6m in $CDCl_3$ at 126 MHz.

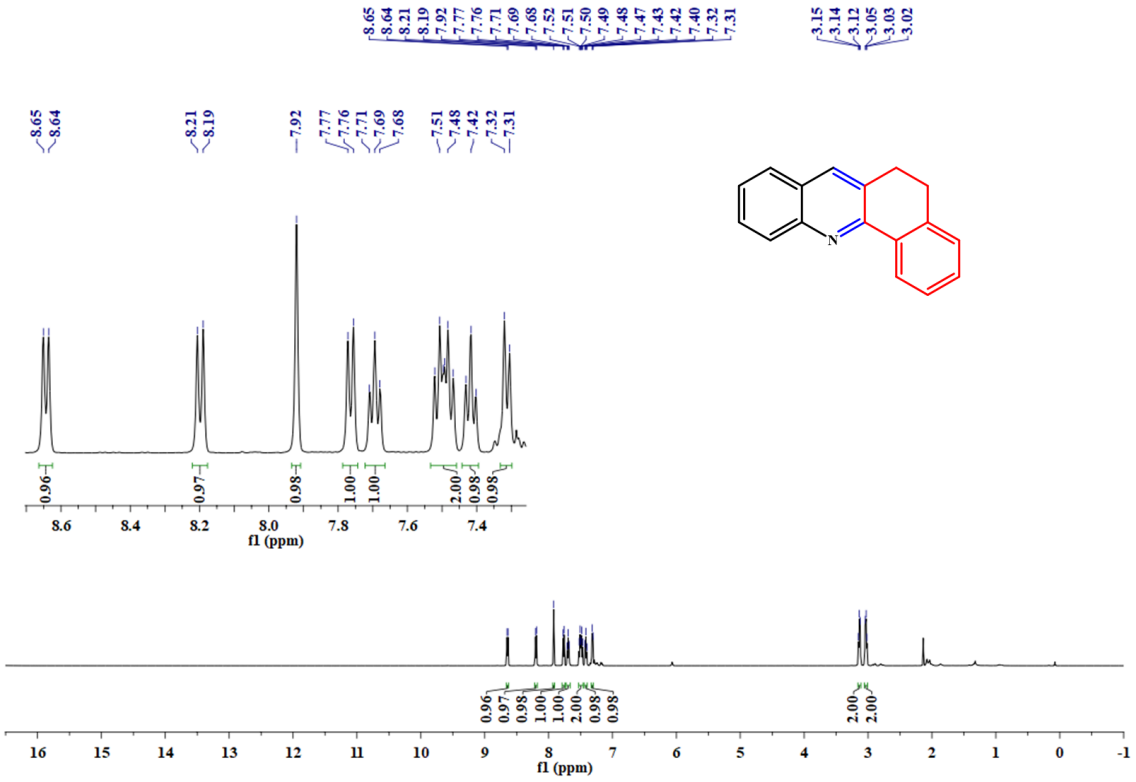


Figure S136: ^{1}H NMR spectrum of 6n in $CDCl_3$ at 500 MHz.

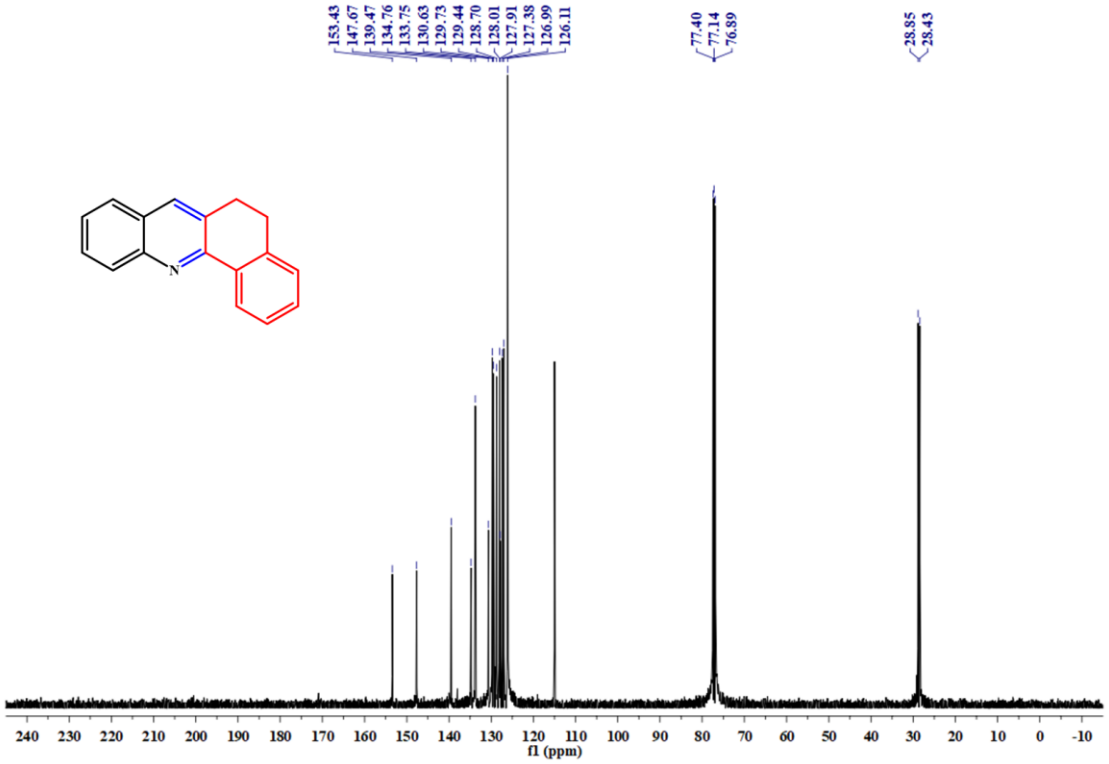


Figure S137: $^{13}C\{^{1}H\}$ NMR spectrum of 6n in $CDCl_3$ at 126 MHz.

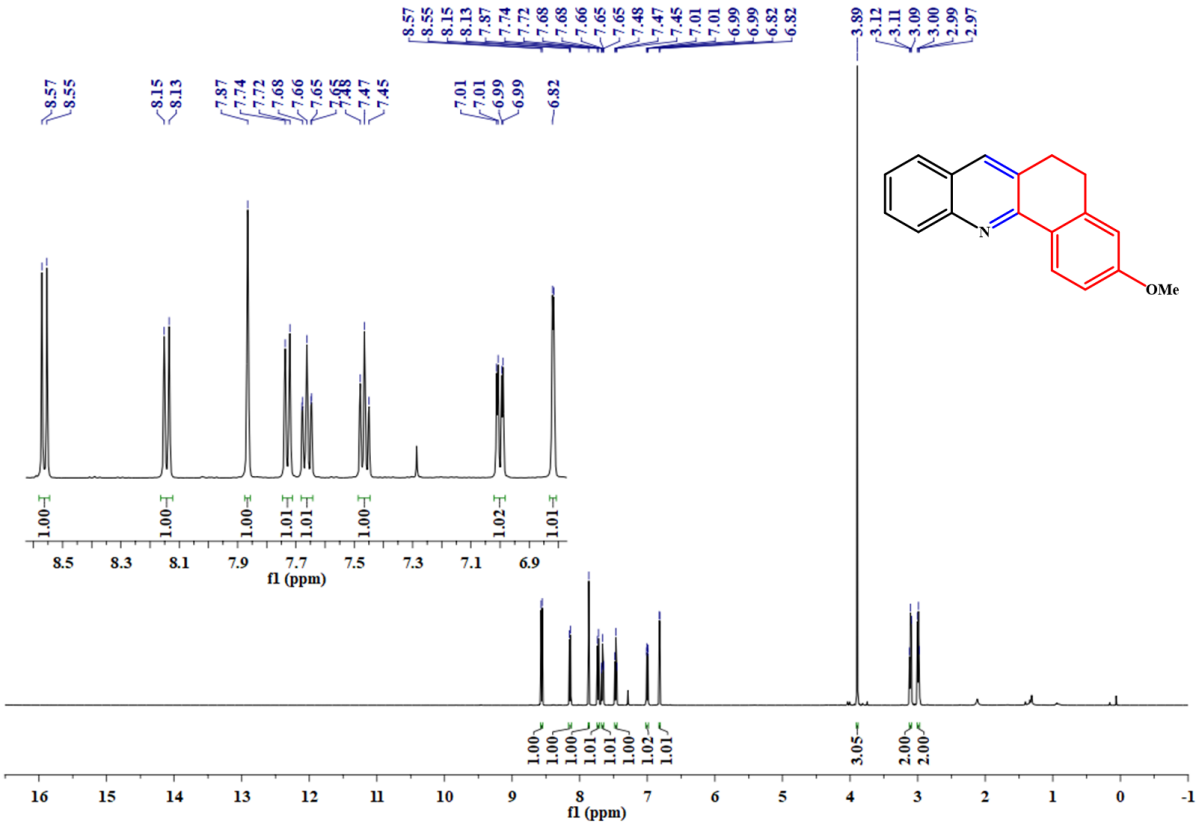


Figure S138: ^{1}H NMR spectrum of 6o in $CDCl_3$ at 500 MHz.

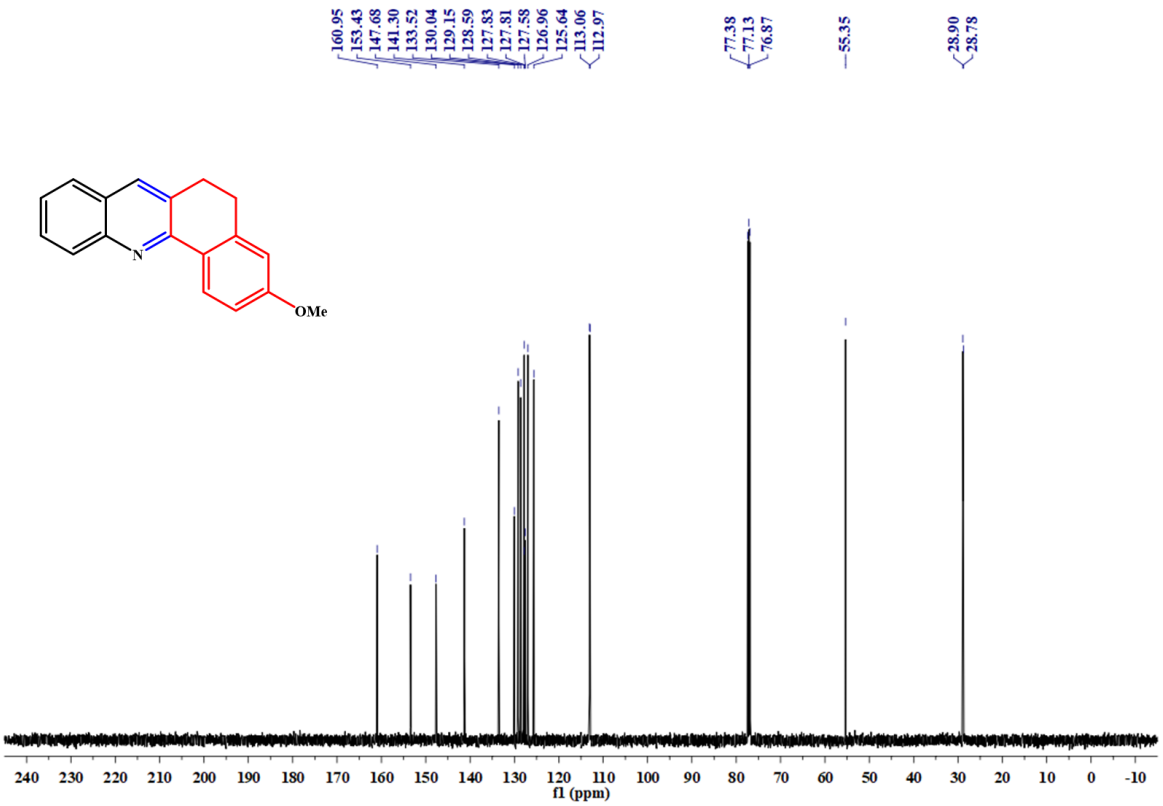


Figure S139: $^{13}C\{^{1}H\}$ NMR spectrum of 6o in $CDCl_3$ at 126 MHz.

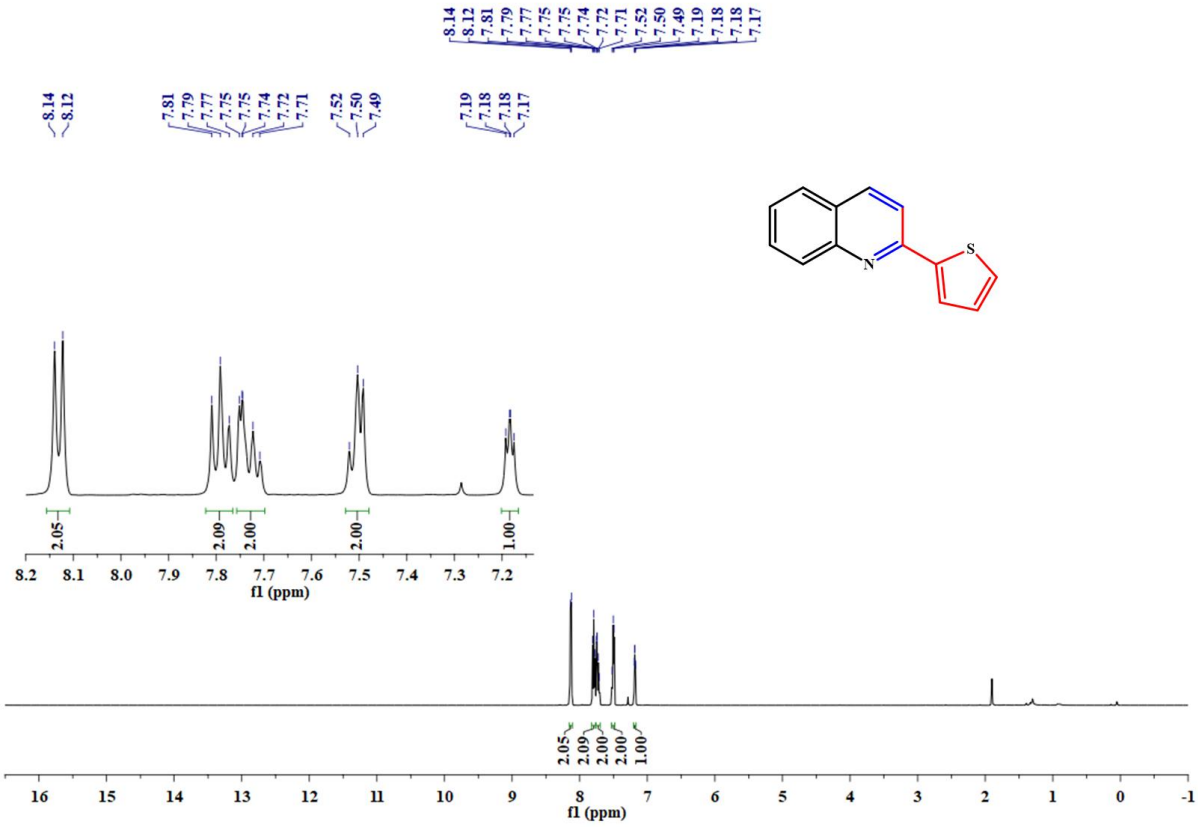


Figure S140: ^{1}H NMR spectrum of 6p in $CDCl_3$ at 500 MHz.

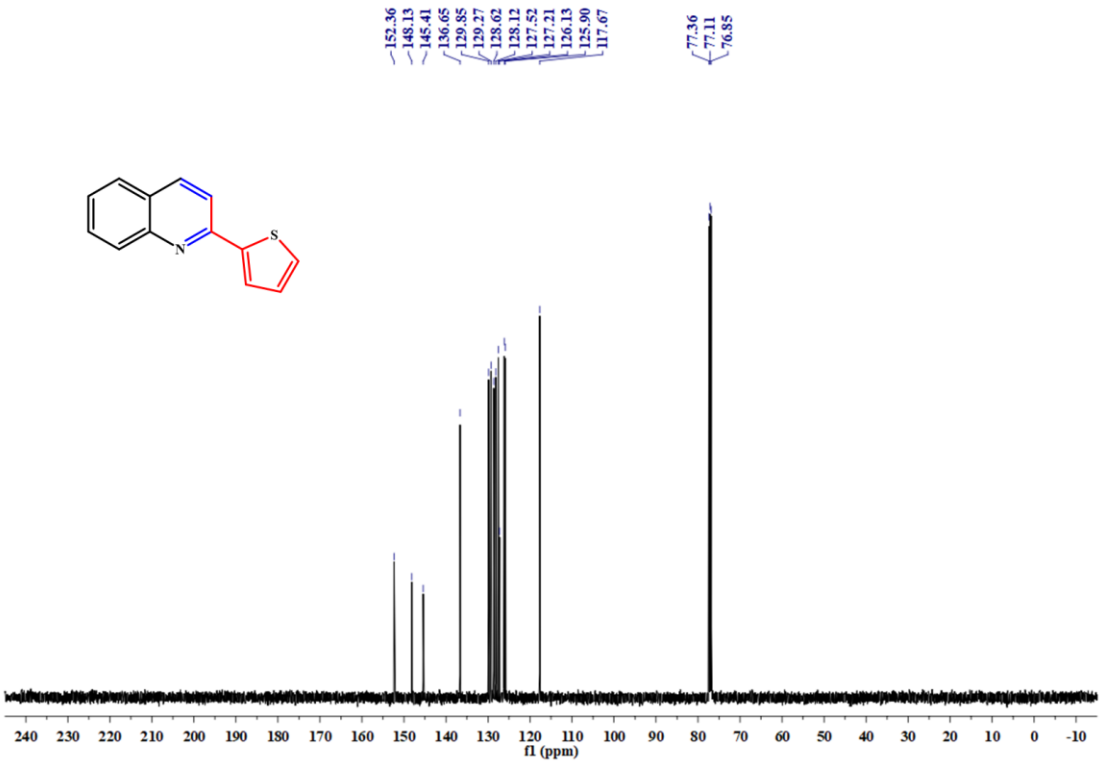


Figure S141: $^{13}C\{^{1}H\}$ NMR spectrum of 6p in $CDCl_3$ at 126 MHz.

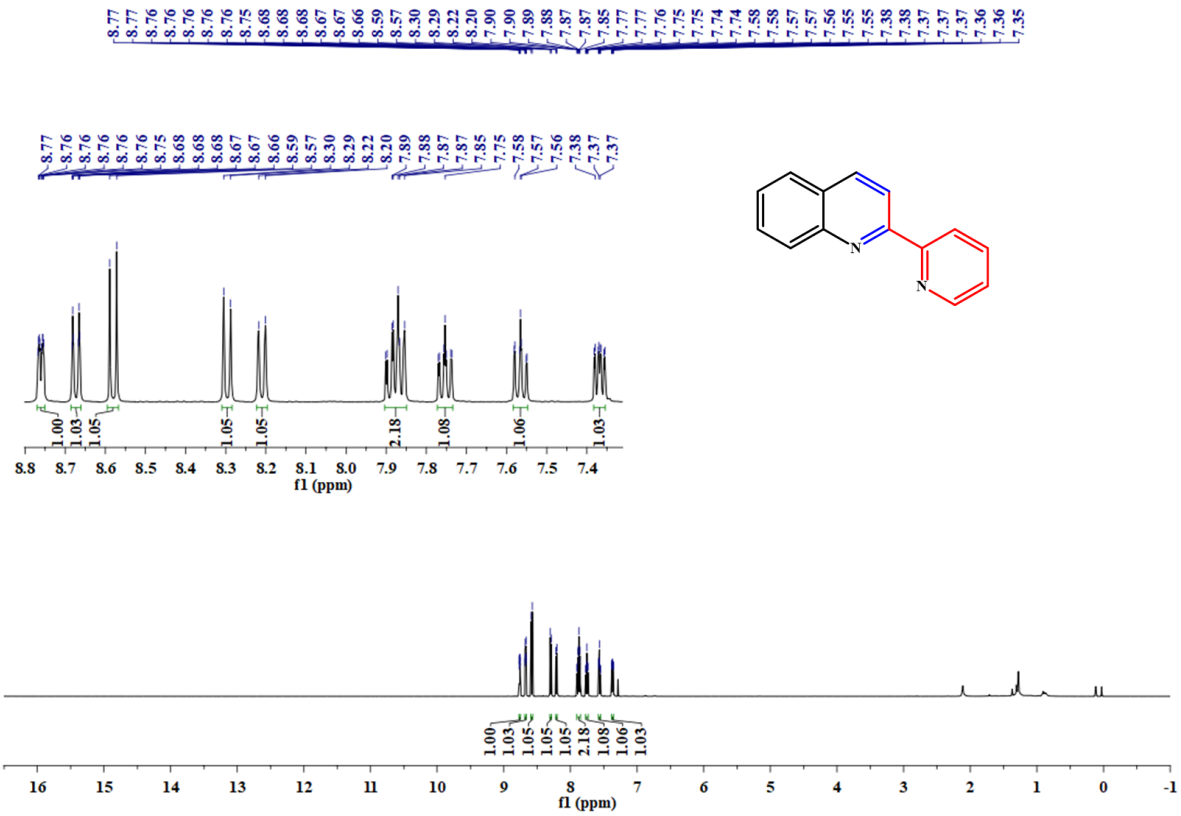


Figure S142: ^{1}H NMR spectrum of 6q in $CDCl_3$ at 500 MHz.

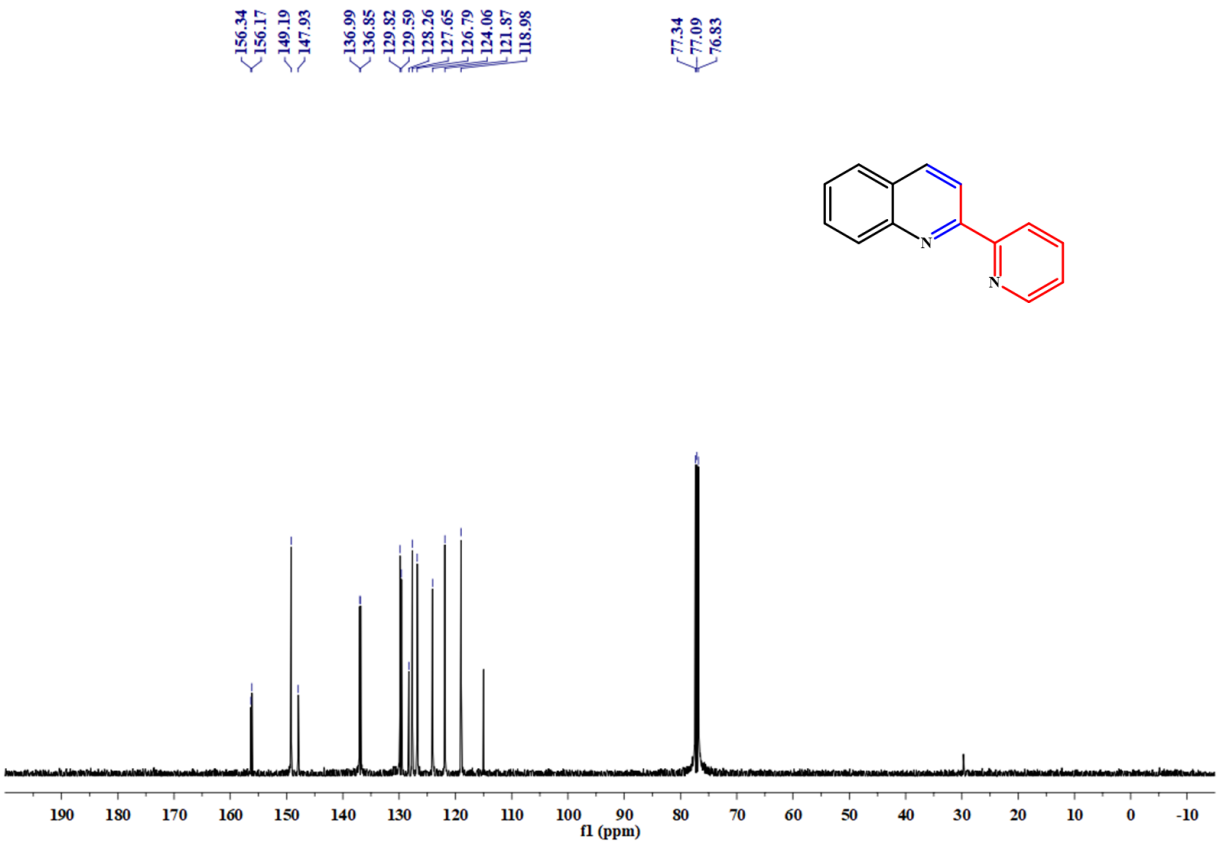


Figure S143: $^{13}C\{^{1}H\}$ NMR spectrum of 6q in $CDCl_3$ at 126 MHz.

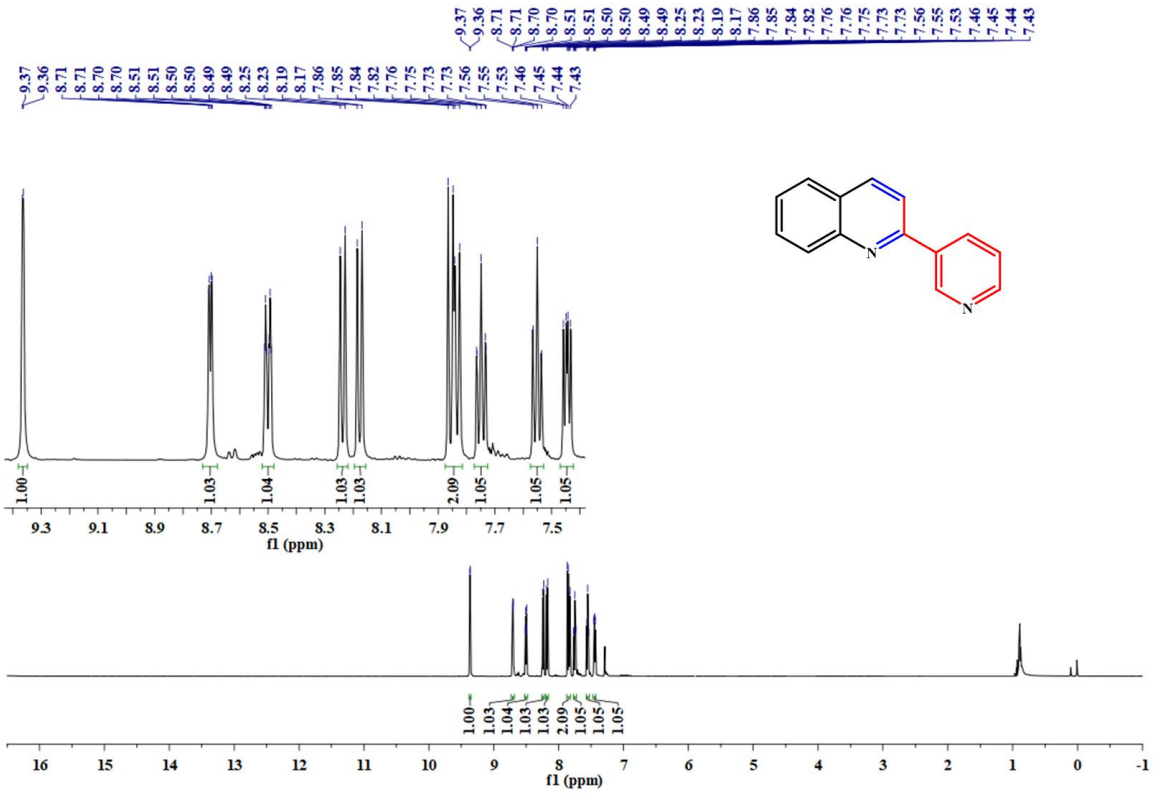


Figure S144: ^{1}H NMR spectrum of 6r in $CDCl_3$ at 500 MHz.

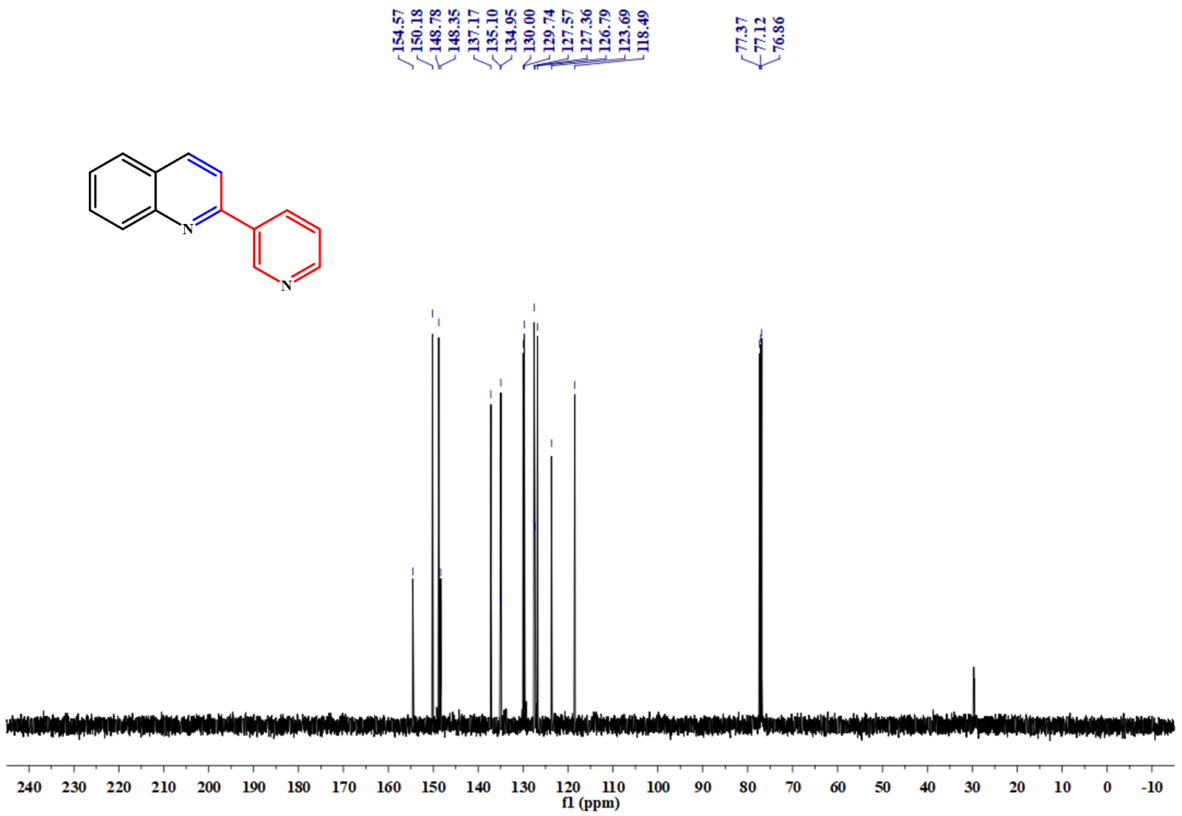


Figure S145: $^{13}C\{^{1}H\}$ NMR spectrum of 6r in $CDCl_3$ at 126 MHz.

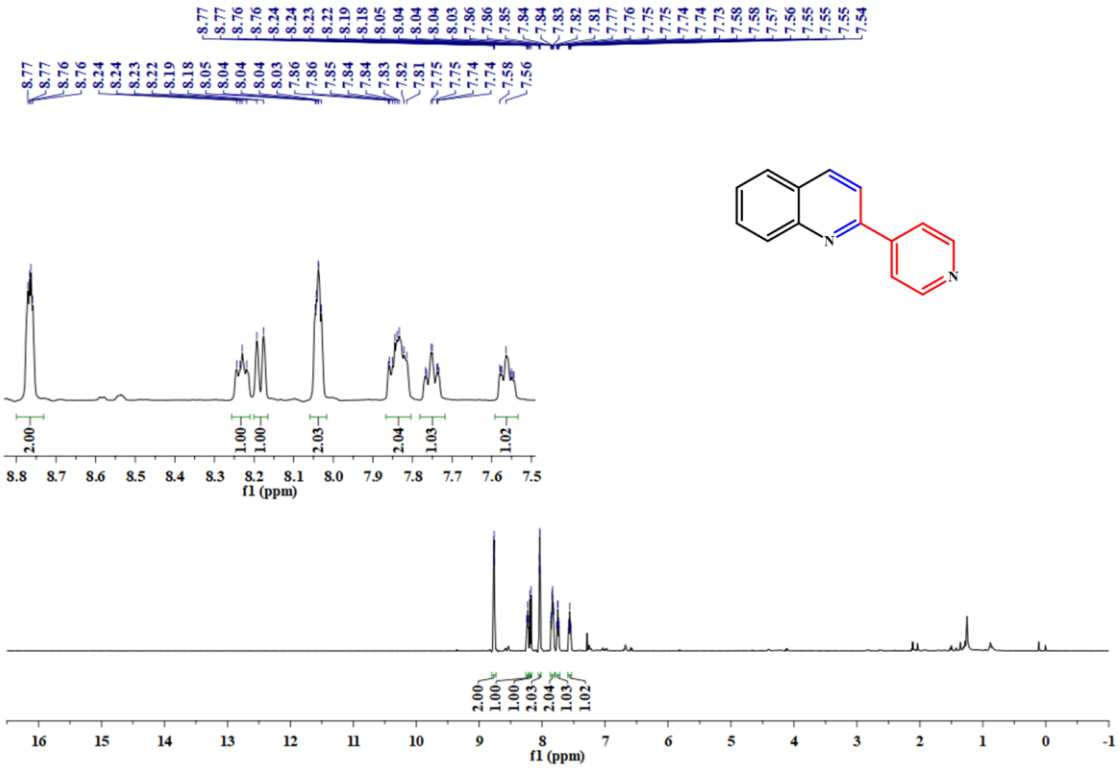


Figure S146: ^{1}H NMR spectrum of 6s in $CDCl_3$ at 500 MHz.

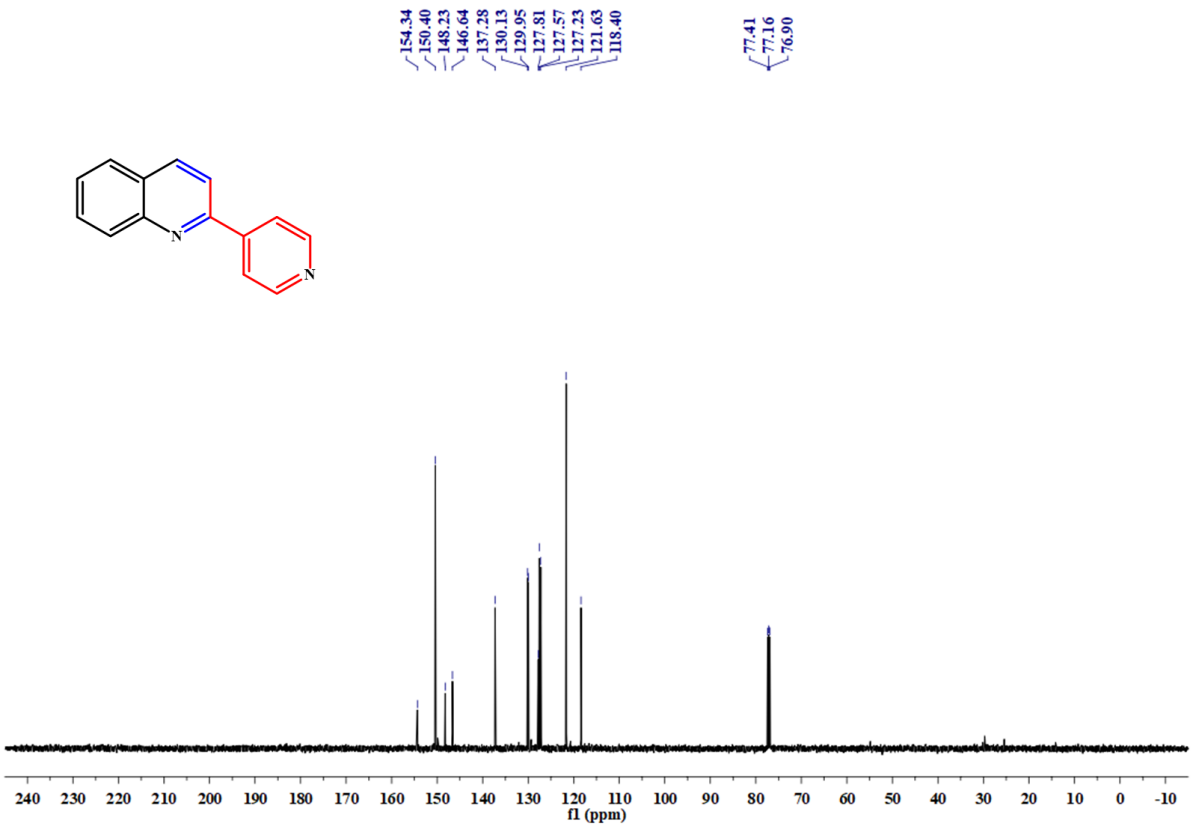


Figure S147: $^{13}C\{^{1}H\}$ NMR spectrum of 6s in $CDCl_3$ at 126 MHz.

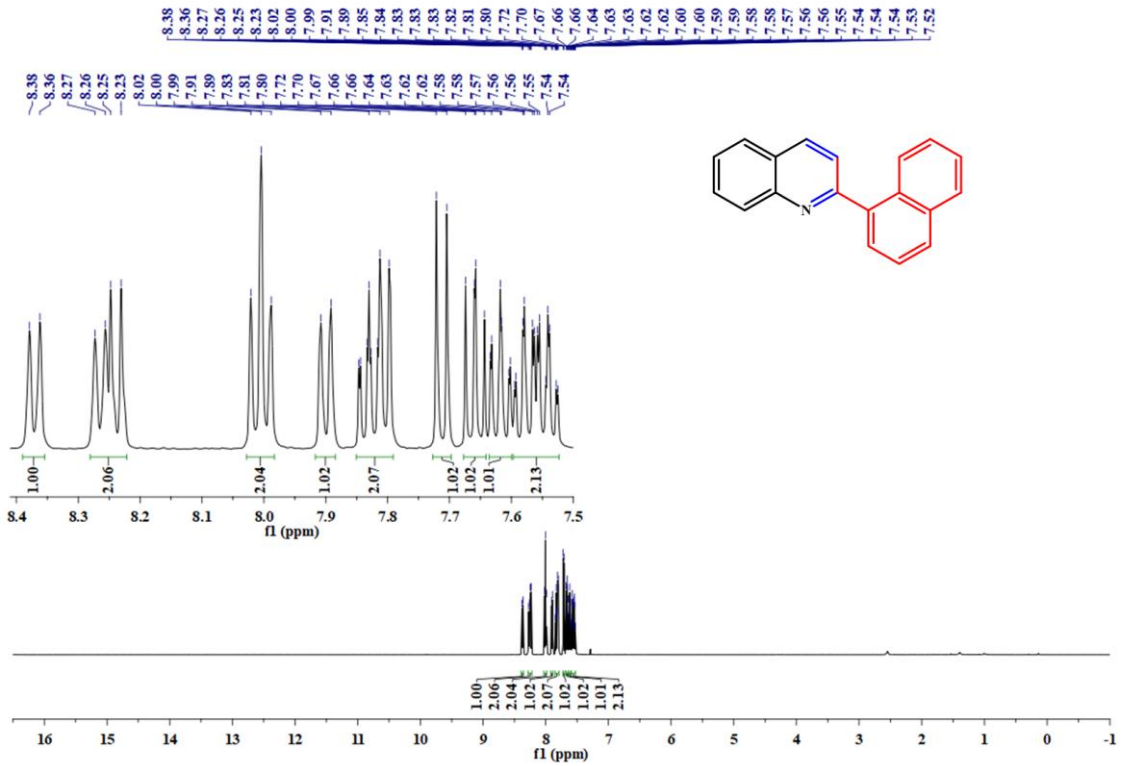


Figure S148: ^{1}H NMR spectrum of 6t in $CDCl_3$ at 500 MHz.

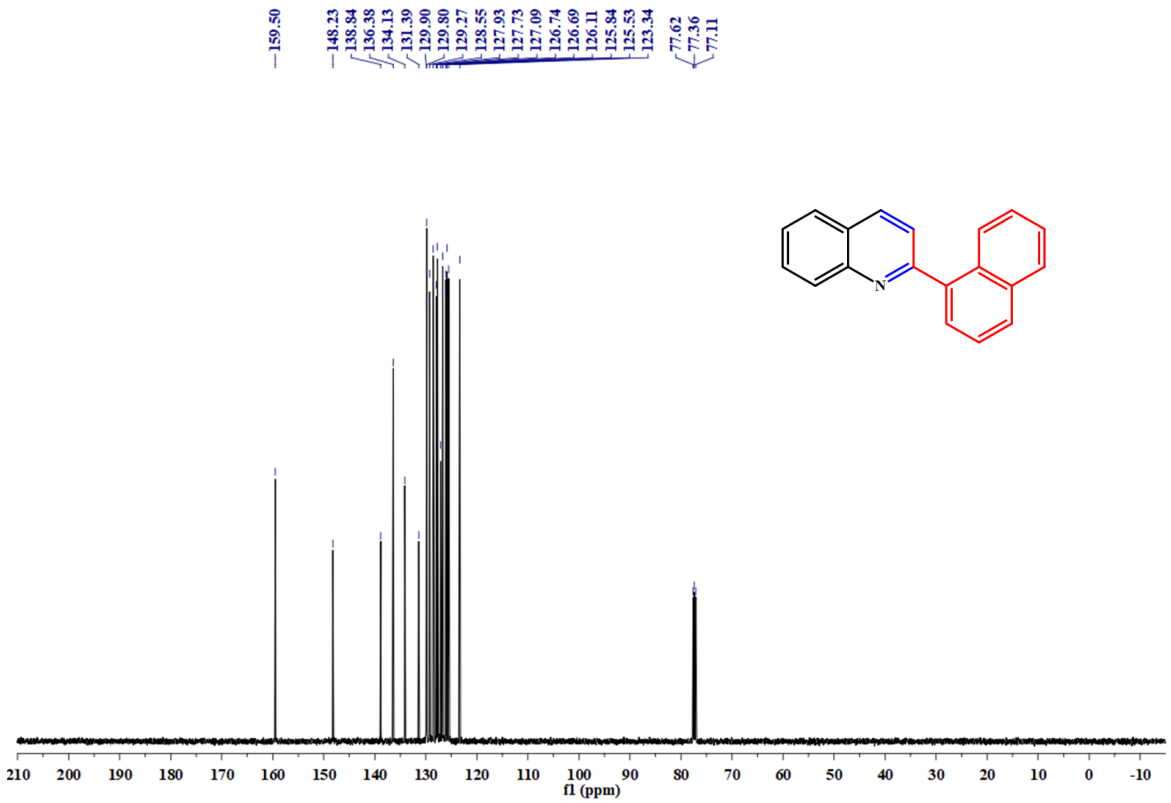


Figure S149: $^{13}C\{^{1}H\}$ NMR spectrum of 6t in $CDCl_3$ at 126 MHz.

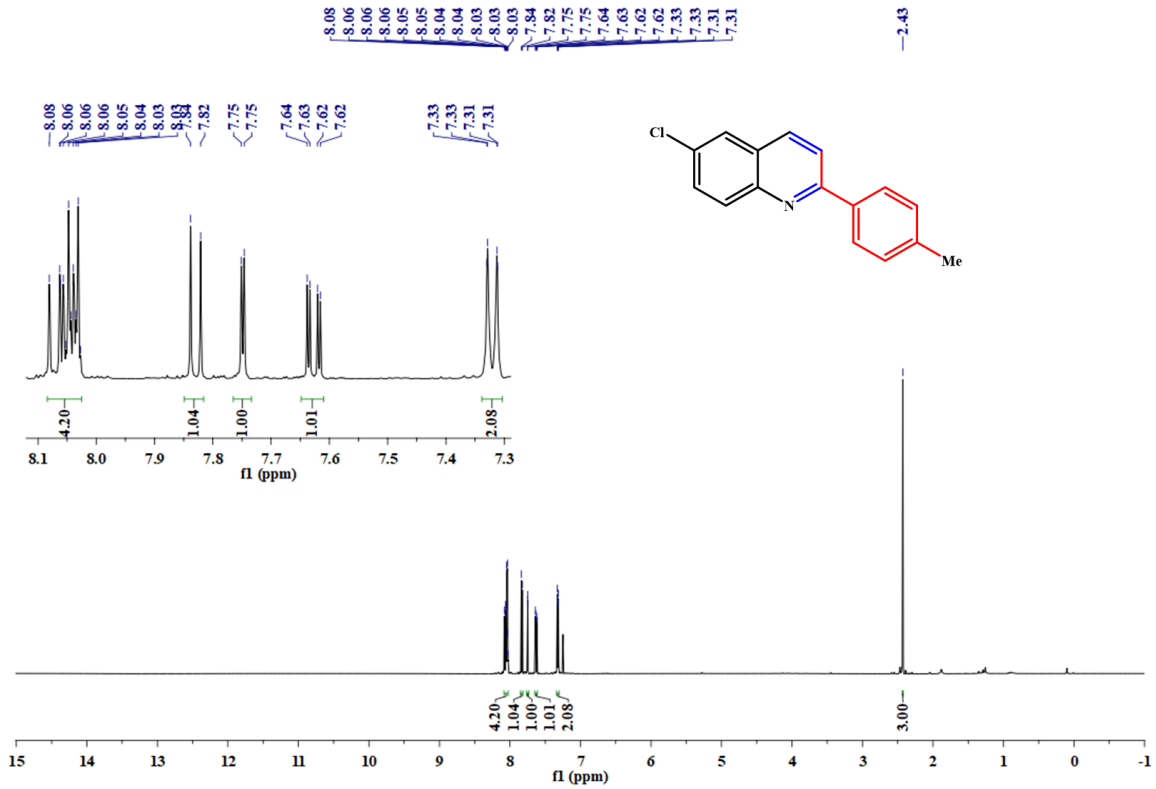


Figure S150: ^{1}H NMR spectrum of 6u in $CDCl_3$ at 500 MHz.

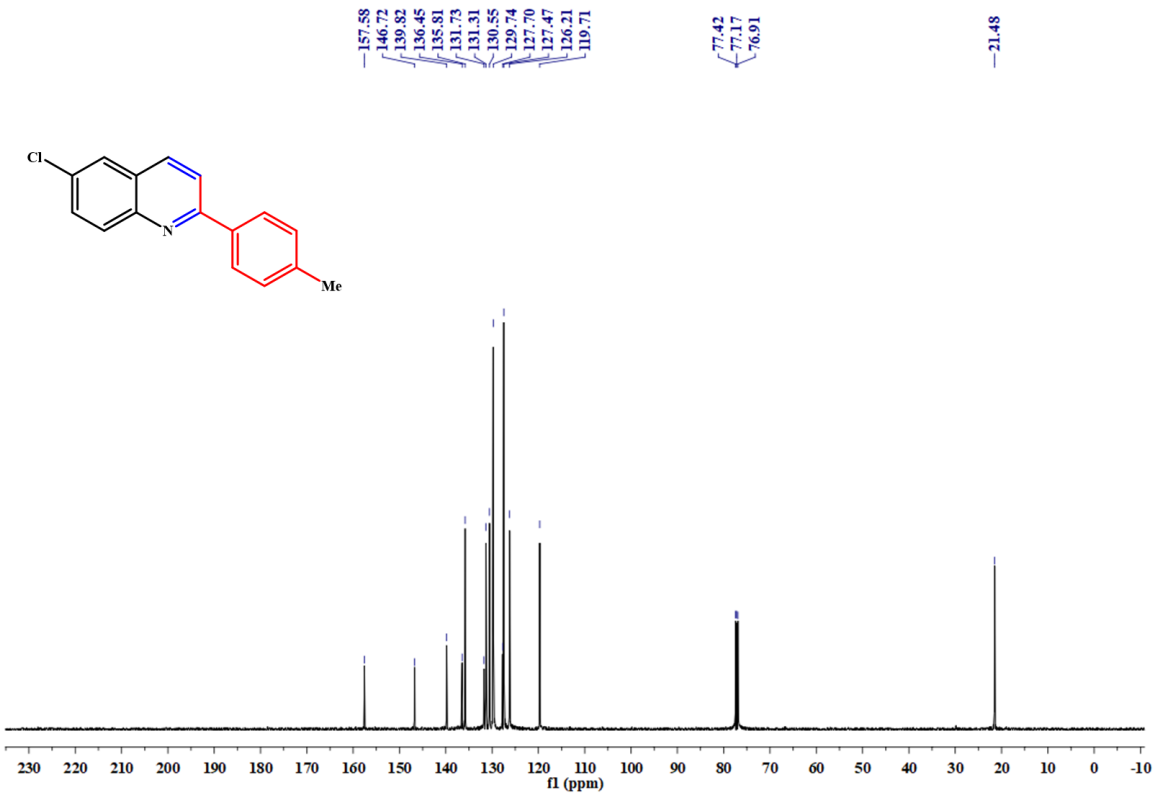


Figure S151: $^{13}C\{^{1}H\}$ NMR spectrum of 6u in $CDCl_3$ at 126 MHz.

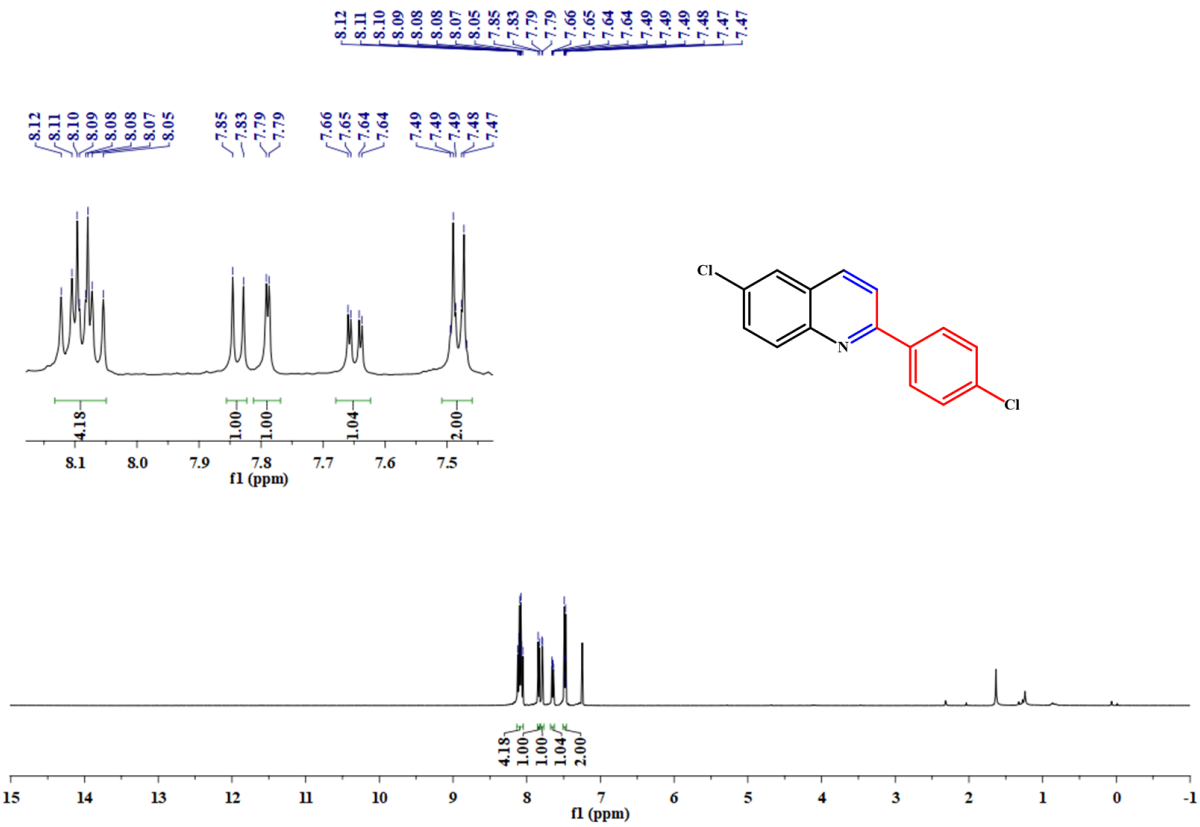


Figure S152: ^{1}H NMR spectrum of 6v in $CDCl_3$ at 500 MHz.

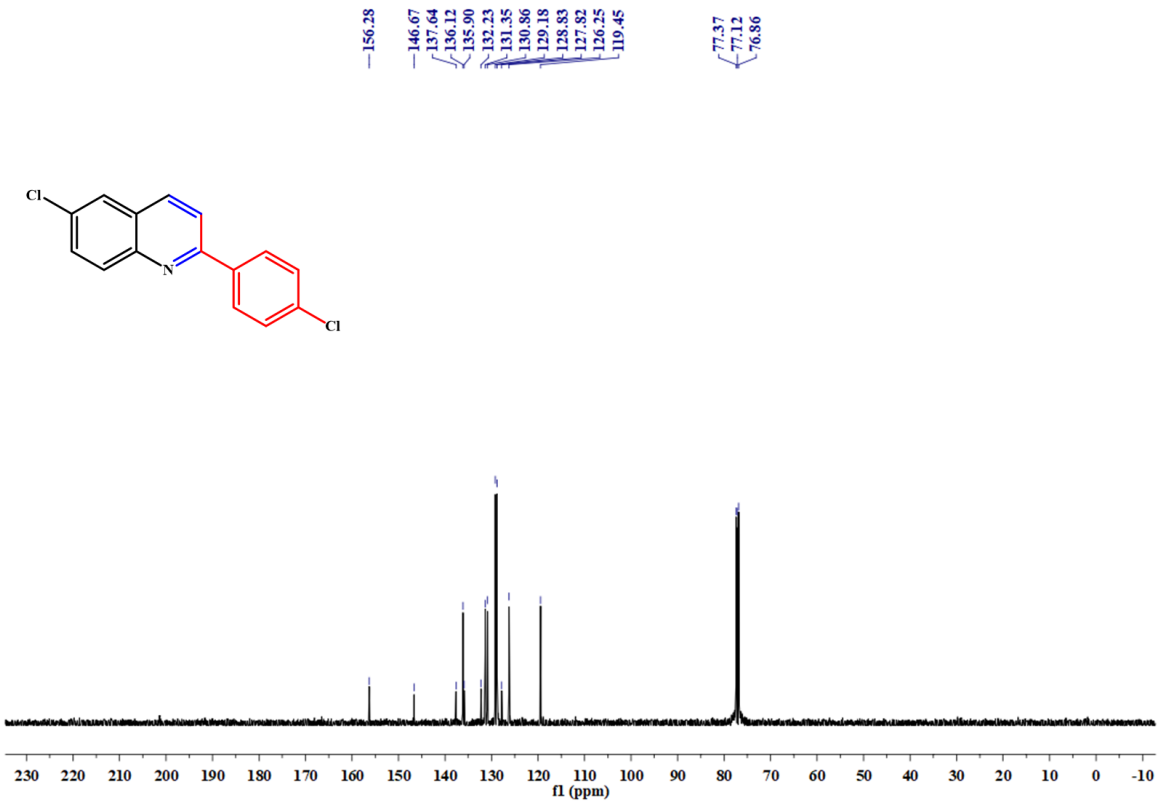


Figure S153: $^{13}C\{^{1}H\}$ NMR spectrum of 6v in $CDCl_3$ at 126 MHz.

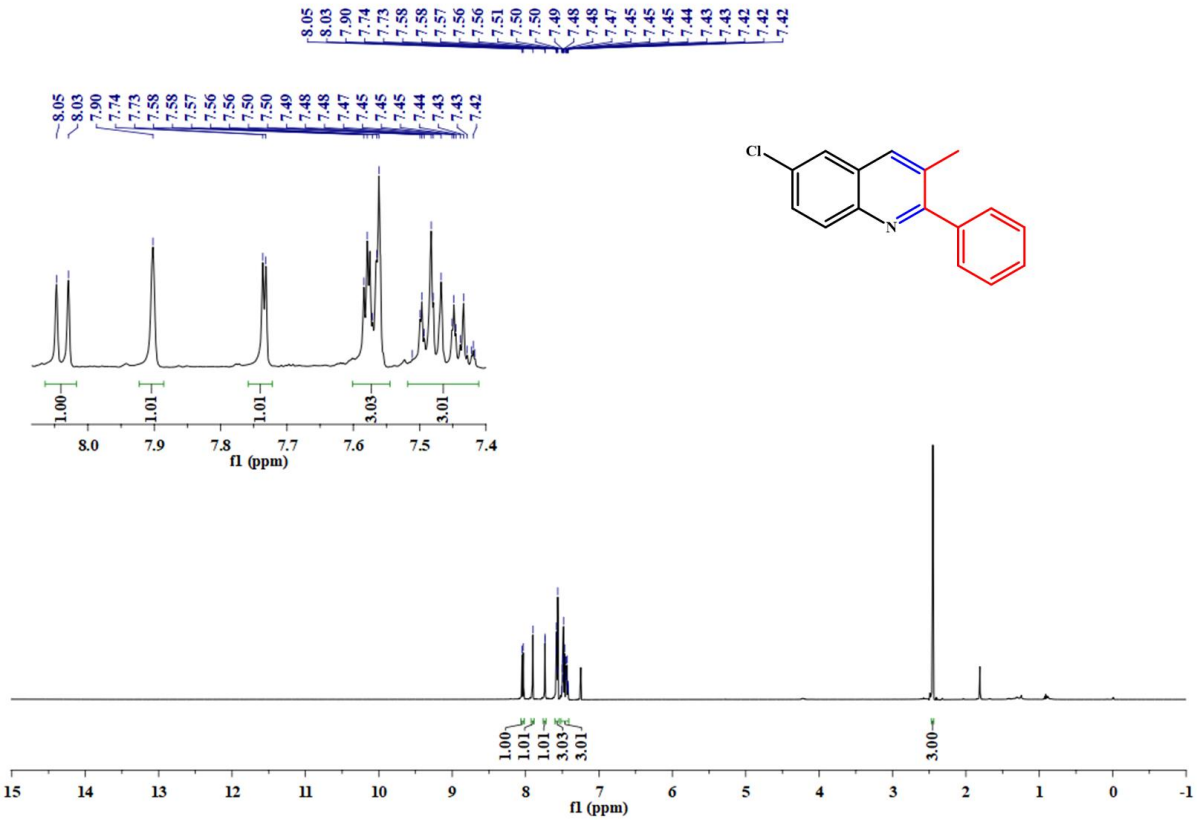


Figure S154: ^{1}H NMR spectrum of 6w in $CDCl_3$ at 500 MHz.

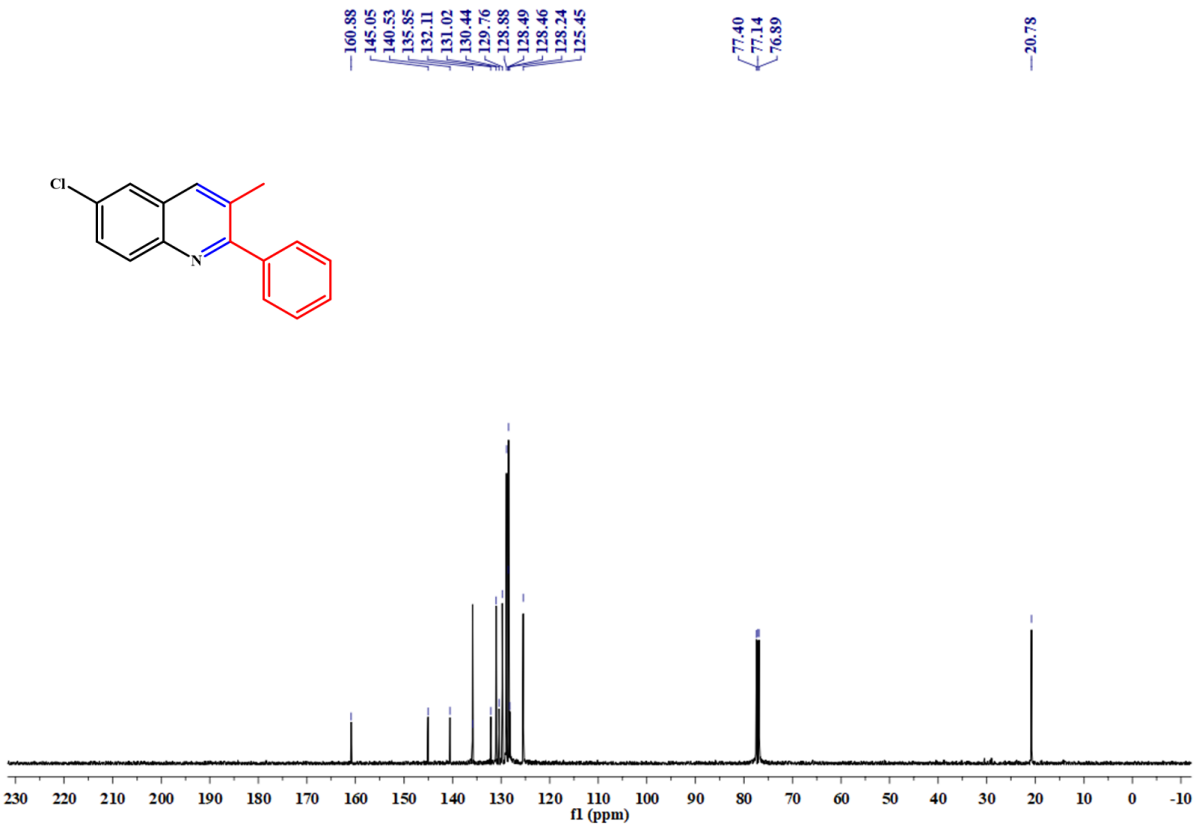


Figure S155: $^{13}C\{^{1}H\}$ NMR spectrum of 6w in $CDCl_3$ at 126 MHz.

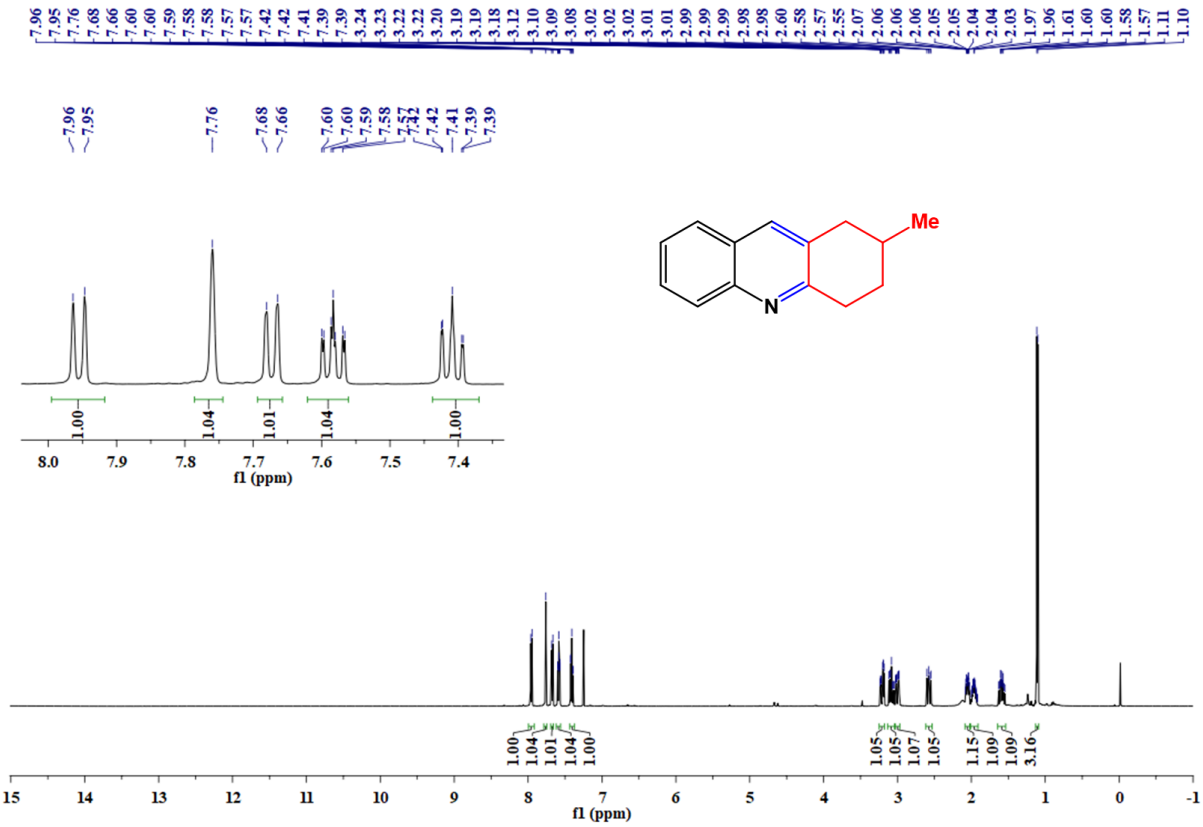


Figure S156: ^{1}H NMR spectrum of 6x in $CDCl_3$ at 500 MHz.

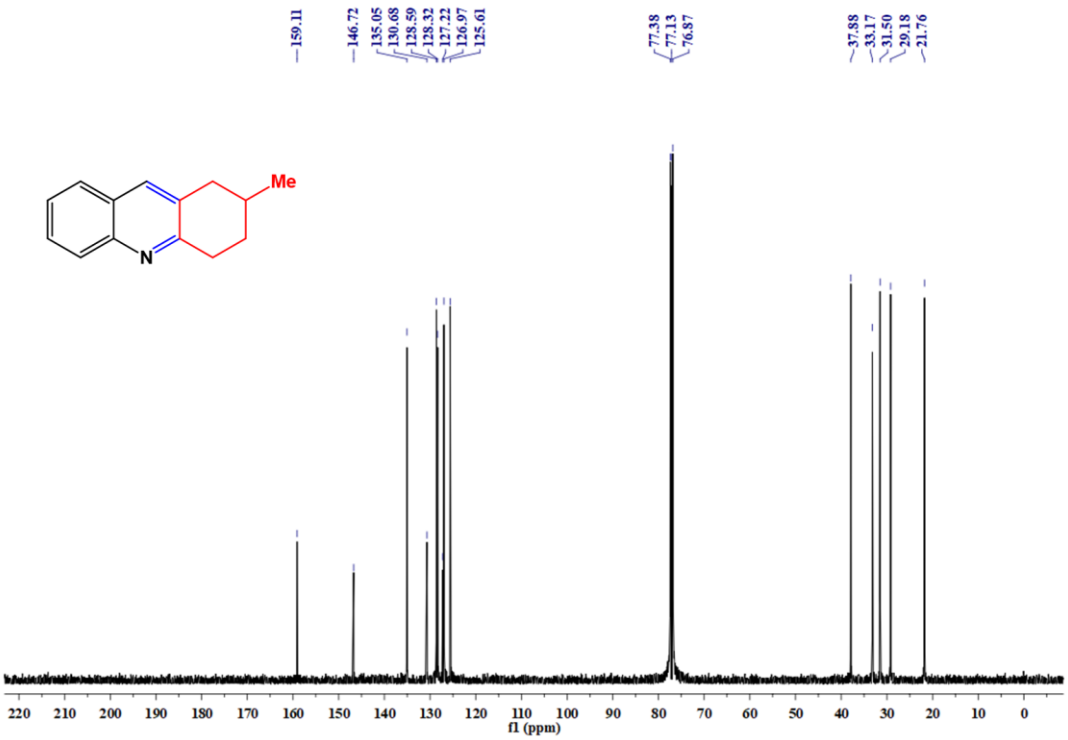


Figure S157: $^{13}C\{^{1}H\}$ NMR spectrum of 6x in $CDCl_3$ at 126 MHz.

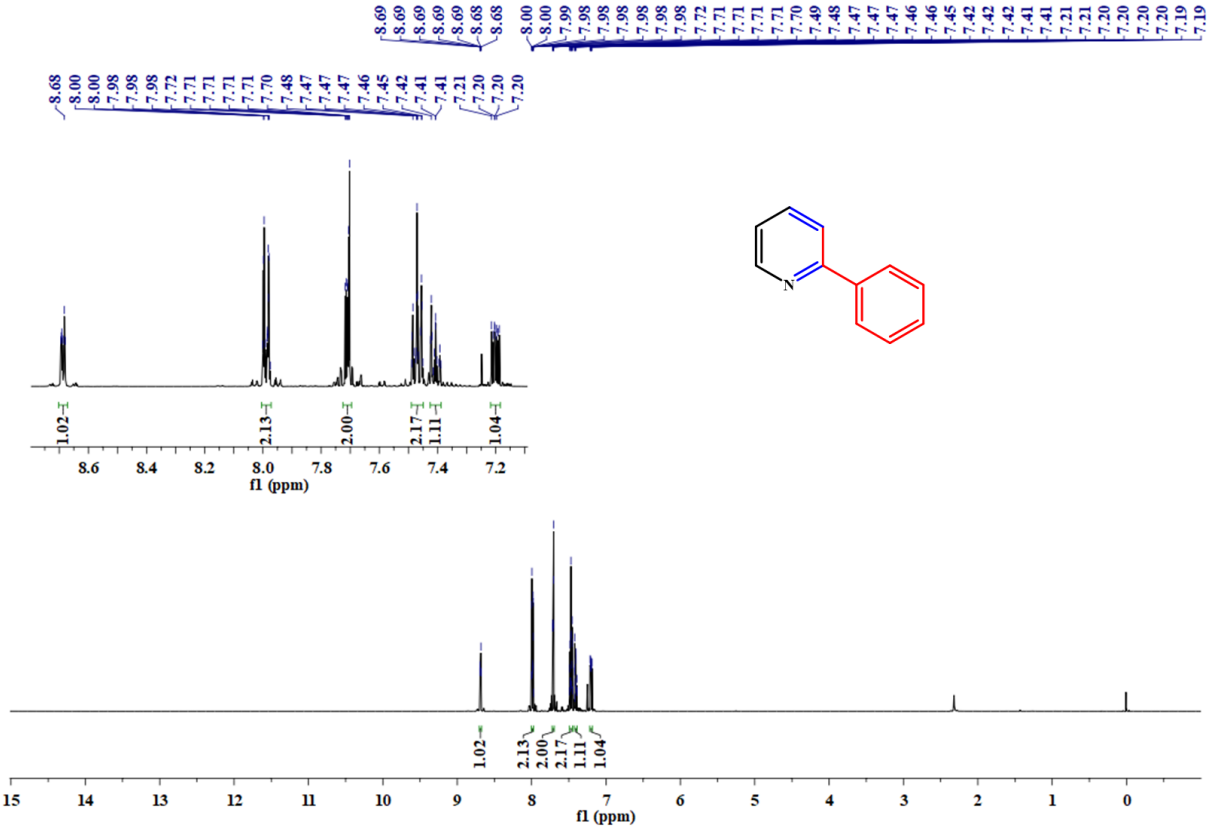


Figure S158: ^{1}H NMR spectrum of 6y in $CDCl_3$ at 500 MHz.

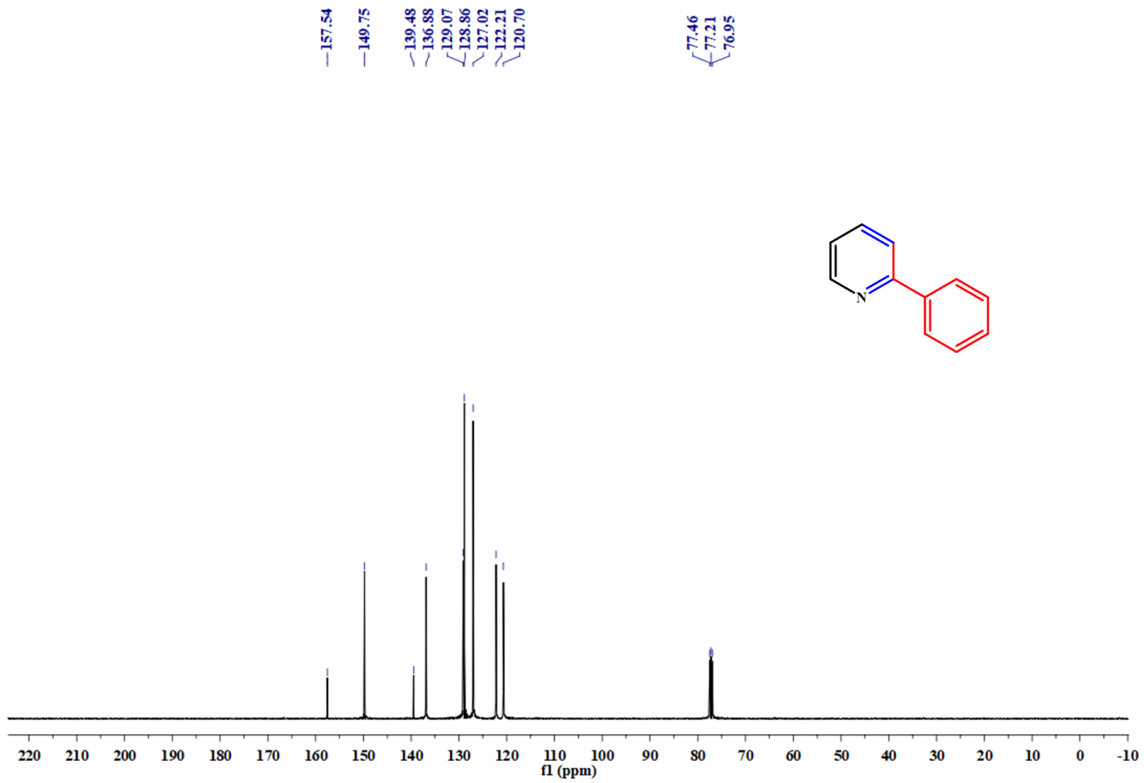


Figure S159: $^{13}C\{^{1}H\}$ NMR spectrum of 6y in $CDCl_3$ at 126 MHz.

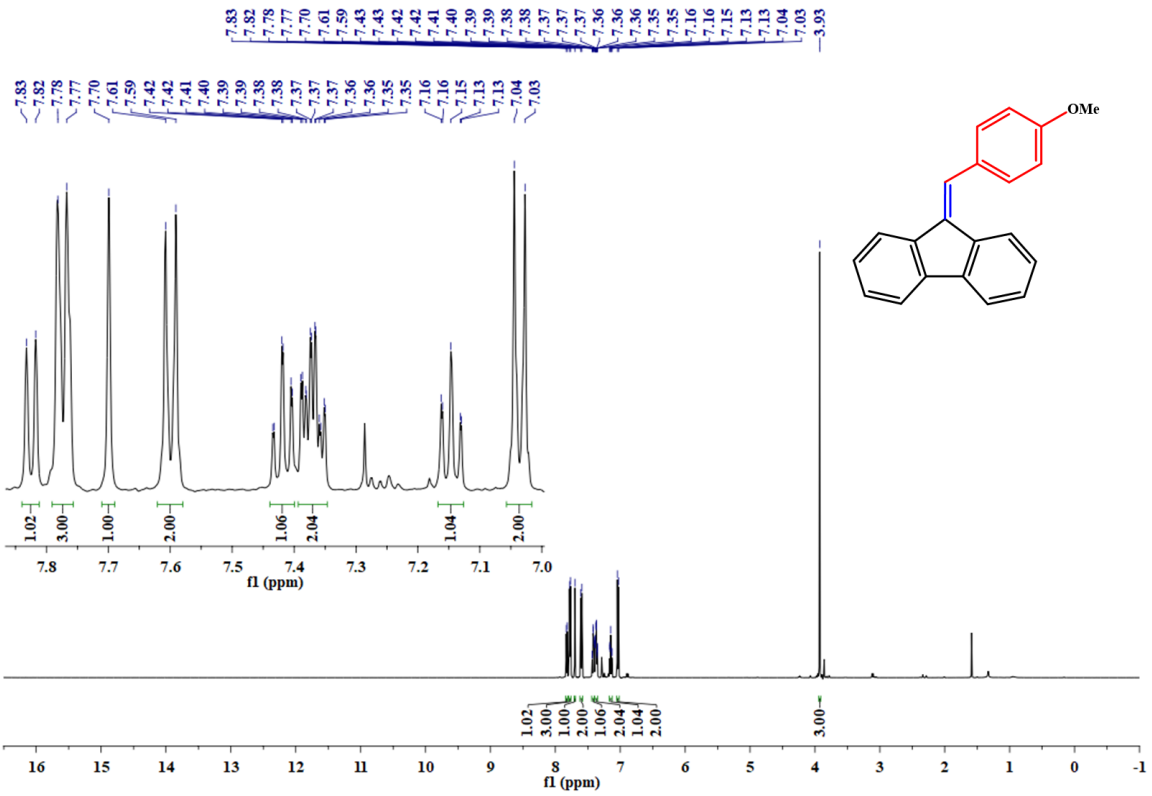


Figure S160: ^{1}H NMR spectrum of 4b in $CDCl_3$ at 500 MHz.

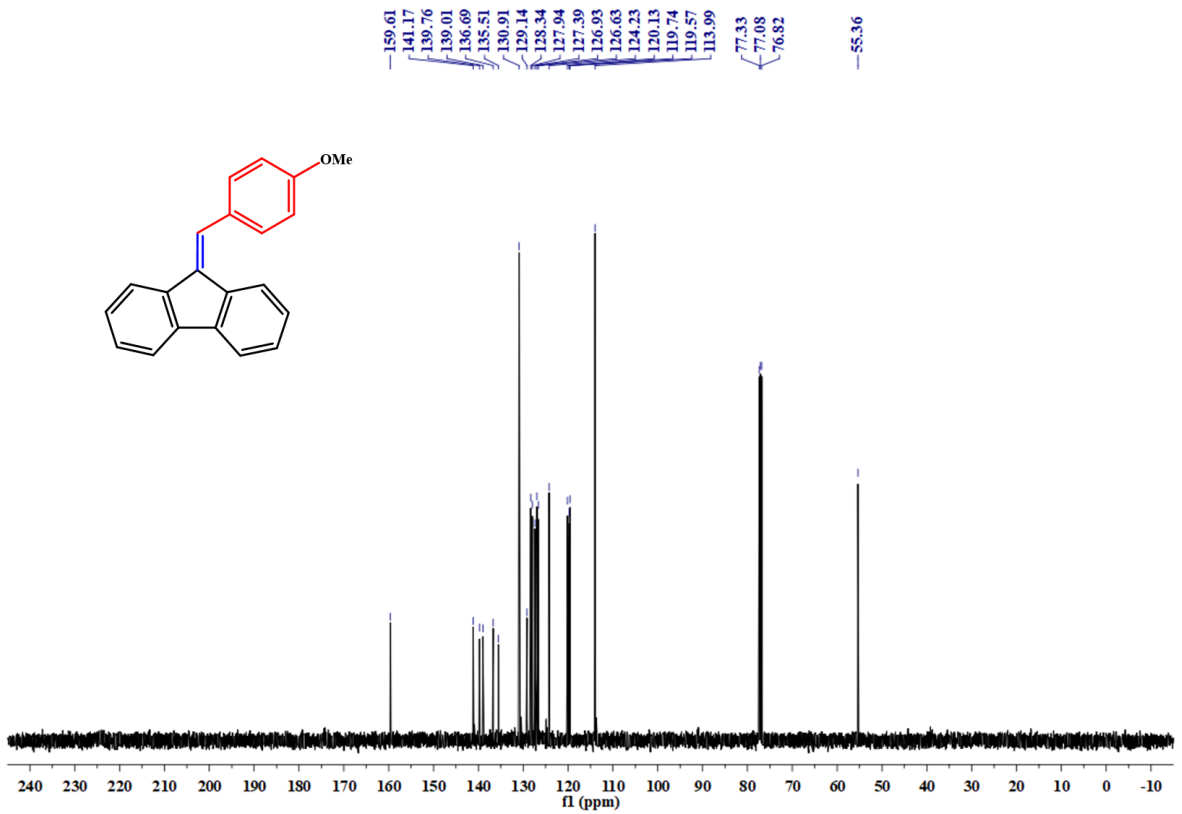


Figure S161: $^{13}C\{^{1}H\}$ NMR spectrum of 4b in $CDCl_3$ at 126 MHz.

11. References

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