Electronic Supplementary Information for

A Magnetic Nanoparticle-Supported *N*-heterocyclic Carbene-Palladacycle: An Efficient and Recyclable Solid Molecular Catalyst for Suzuki-Miyaura Cross-Coupling of 9-Chloroacridine

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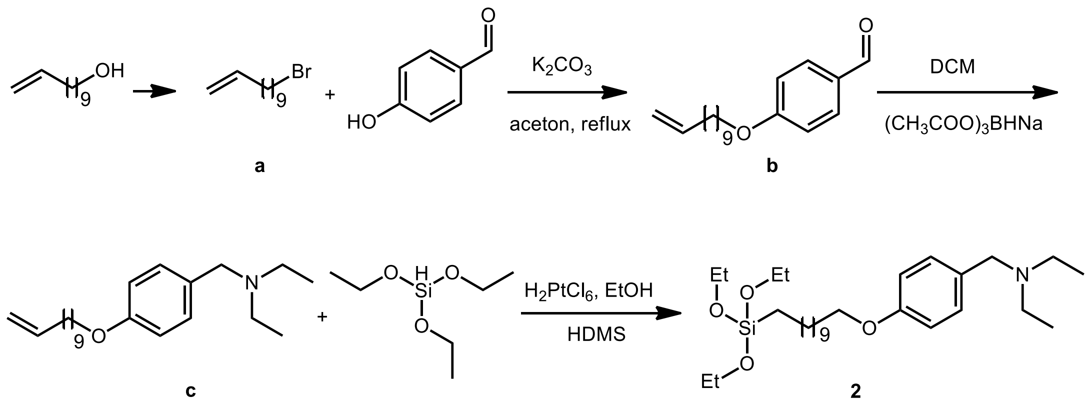
1. General.

All commercial reagents were used directly without further purification, unless othervise stated. 1, 4-dioxane, methanol (MeOH) and *tert*-butanol (*t*-BuOH) were distilled from anhydrous calcium chloride prior to use. Xylene,toluene and benzene were distilled from sodium/benzophenone prior to use. *t*-BuOK was purchased from Acros. All reaction vials (50 mL) were purchased from Beijing Synthware Glass. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. ^1H, ^{13}C NMR were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. The chemical shifts (δ) for ^1H are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent ($CHCl_3$ at δ 7.26 ppm); coupling constants are expressed in hertz (Hz). ^{13}C NMR spectra were referenced to the carbon signal of $CDCl_3$ (77.0 ppm). The following abbreviations are used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = mulitplet, dd = doublet of doublets, q = quartet, quint = quintet. ESI-MS spectra were recorded on a Bruker micrOTOF II instrument. IR spectra were recorded on AVATAR FT-IR 360 instrument. Powder XRD studies were performed on a Bruker AXS D8. SEM experiments were carried out on a Philips XL30 microscope operatwd at 20kV. TEM experiments were carried out on a JEOL JEM-2010 transmission electron microscope. Analysis of Pd content was measured by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) using OPTIMA 4300 DV (Perkin–Elmer).

2. Experimental sections

2.1 Synthesis of $SiO_2@Fe_3O_4$–support Pd complexes.



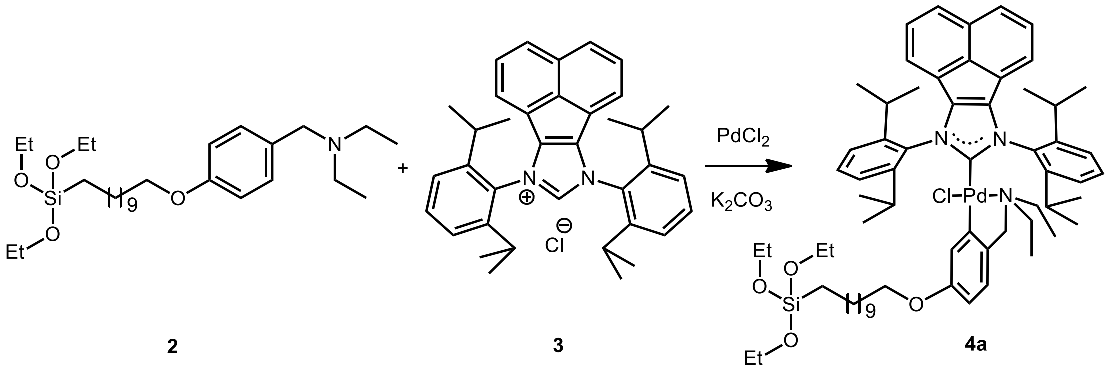
Scheme S1. Synthesis of linker compound **2**.

11-bromoundec-1-ene a:[S1] To a mixture of undec-10-en-1-ol (5.1 g, 30 mmol) and carbon tetrabromide (13.3 g, 40 mmol) in dichloromethane (100 mL) was added portionwise triphenylphosphine (10.5 g, 40 mmol), and the solution was stirred for 3 h at room temperature. Filtration followed by concentration in vacuo left an oil, which was then chromatographed on SiO_2 (eluent, hexane) to afford **a** as clear colorless oil (6.6 g, 95 %): ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 5.86-5.76 (m, 1H), 5.02-4.91 (m, 2H), 3.40 (t, J = 6.8 Hz, 2H), 2.04 (q, J = 7.1 Hz, 2H), 1.85 (quint, J = 7.2 Hz, 2H), 1.44-1.34 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 138.9, 114.0, 33.7, 33.6, 32.8, 29.3, 29.0, 28.8, 28.7, 28.1.

4-(undec-10-en-1-yloxy)benzaldehyde b:[S2] A stirred suspension of p-hydroxybenzaldehyde (16.6 g, 136 mmol), 11-bromoundec-1-ene **a** (15.0 g, 65 mmol), and K_2CO_3 (18.0 g, 130 mmol) in dry acetone 75mL was refluxed for 24 h. The reaction was monitored by TLC. The hot reaction mixture was filtered and evaporated to dryness. The mixture was ready for purification by flash chromatography to afford **b** as light yellow solid (14.2 g, 80 %): ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 9.88 (s, 1H), 7.83 (dt, J = 8.8 Hz , J = 2.2 Hz, 2H), 6.99 (dt, J = 8.8 Hz , J = 2.4 Hz, 2H), 5.86-5.76 (m, 1H), 5.02-4.91 (m, 2H), 4.04 (t, J = 6.6 Hz, 2H), 2.04 (q, J = 7.1 Hz, 2H), 1.81 (quint, J = 7.0 Hz, 2H), 1.50-1.30 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 189.7, 163.7, 138.4, 131.3, 129.4, 114.2, 113.7, 67.8, 33.3, 29.1, 29.0, 28.9, 28.7, 28.6, 28.5, 25.5.

N-ethyl-N-(4-(undec-10-en-1-yloxy)benzyl)ethanamine c:[S3] To a solution of **b** (1 g, 8.2 mmol) in 90 mL of dry CH_2Cl_2 were added diethylamine (2.54 mL, 24.6 mmol), after 2h, $NaHB(OAc)_3$ (5.22 g, 32.8 mmol). After stirring the mixture at room temperature for 18 h, 10 mL of a solution of $NaHCO_3$ 1 M was added. The solvent was then evaporated and the residue was taken up in AcOEt. The reactive medium was then filtrated, the filtrate was concentrated and the residue purified by column chromatography to yield compound **c** (2.58 g, 95% yield); ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.21 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 5.86-5.76 (m, 1H), 5.02-4.91 (m, 2H),3.94 (t, J = 6.4 Hz, 2H), 3.50 (s, 2H), 2.50 (q, J = 7.1 Hz, 4H), 2.04 (q, J = 7.1 Hz, 4H), 1.77 (quint, J = 7.0 Hz, 2H), 1.46-1.24 (m, 12H), 1.03 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 158.0, 139.0, 131.2, 130.0, 114.04, 113.98, 67.8, 56.7, 46.3, 33.7, 29.4, 29.34, 29.31, 29.2, 29.0, 28.8, 26.0, 11.5. HR-MS (ESI): m/z 331.2875 (calcd, $[M]^+$); 332.2964 (found, $[M+H]^+$).

N-ethyl-N-(4-((11-(triethoxysilyl)undecyl)oxy)benzyl)ethanamine 2:[S4] **c** (0.07 g, 0.21 mmol) and triethoxysilane (1.8 g, 10.8 mmol) were placed into a previously HMDS-passivated dry, round-bottomed flask and heated under an argon atmosphere to about 80 ℃. After the addition of EtOH H_2PtCl_6 solution (50 µL, 0.027 mg/µL), the mixture was allowed to react for 4 h at 80 ℃ and then to cool. Excess triethoxysilane was removed in vacuum, the residue purified by column chromatography to yield compound **2** (0.10g, 96% yield); ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.21 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 3.94 (t, J = 6.6 Hz, 2H), 3.81 (q, J = 7.1 Hz, 6H), 3.5 (s, 2H), 2.50 (q, J = 7.2 Hz, 4H), 1.76 (quint, J = 7.0 Hz, 2H), 1.56-1.37 (m, 4H), 1.36-1.33 (m, 12H), 1.23 (t, J = 7.0 Hz, 9H), 1.04 (t, J = 7.2 Hz, 6H), 0.72-0.54 (m, 2H).

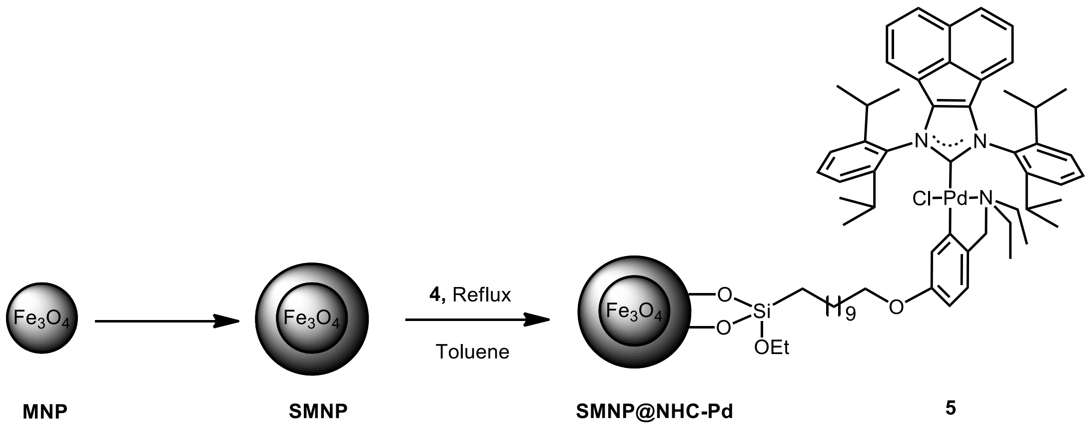


2 3 4a

Scheme S2. Synthesis of **Pd complexes 4.**

Acenaphthoimidazolium chloride 3 was prepared according to literature procedure.[S5] Yield: 1.28 g, 78%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 11.82 (s, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 8.0 Hz, 2H), 7.57 (t, J = 7.6 Hz, 2H), 7.46 (d, J = 7.6 Hz, 4H), 7.23 (d, J = 6.8 Hz 2H), 2.77-2.66 (m, 4H), 1.39 (d, J = 6.8 Hz, 12H), 1.16 (d, J = 6.8 Hz, 12H); HR-MS (ESI): *m/z* 513.3264 (calcd, $[M-Cl]^+$); 513.3264 (found, $[M-Cl]^+$).

Pd complexes 4a was prepared according to literature procedure.[S6] A Schlenk tube (50 mL) was charged with $PdCl_2$ (177 mg, 1.0 mmol), CH_3CN (20 mL, HPLC grade) and N, N-diethylbenzylamine (209 mg, 1.05 mmol). The stirred mixture was heated until a clear, dark orange solution was formed and $PdCl_2$ had dissolved completely. Then powdered K_2CO_3 (345 mg, 2.5 mmol) was added and stirred until the solution changed to canary yellow. Afterward, **3** (445 mg, 1.05 mmol) was added in one portion and refluxed for another 30 min. After cooling down, the mixture was diluted with CH_2Cl_2, filtered, and dried under vacuum. Yield: 0.48 g, 41%. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.71 (d, J = 8.4 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.42-7.30 (m, 6H), 6.90 (d, J = 6.8 Hz, 2H), 6.67 (d, J = 8.4 Hz, 1H), 6.35 (dd, J = 2.2 Hz, J = 8.0 Hz, 1H), 6.29 (d, J = 2.0 Hz, 1H), 3.81 (q, J = 6.9 Hz, 6H), 3.71 (t, J = 6.6 Hz, 2H), 3.61 (s, 2H), 3.58 (q, J = 6.4 Hz, 2H), 3.30-3.00 (m, 4H), 2.30 (m, 2H), 1.59 (m, 2H), 1.47 (d, J = 6.4 Hz, 6H), 1.34-1.24 (m, 8H), 1.23 (t, J = 7.0 Hz, 9H), 1.15 (d, J = 6.8 Hz, 6H), 1.11 (m, 6H), 1.00 (t, J = 7.0 Hz, 6H), 0.63 (d, J = 6.8 Hz, 6H), 0.60 (m, *2*H), 0.57 (d, J = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 186.3, 154.9, 149.6, 148.1, 146.0, 143.2, 140.8, 135.0, 130.0, 129.5, 127.7, 127.3, 126.5, 125.4, 124.5, 124.3, 121.8, 119.9, 107.4, 67.2, 64.2, 58.2, 54.8, 33.1, 29.43, 29.39, 29.36, 29.17, 29.13, 29.0, 28.8, 26.0, 25.7, 25.6, 23.9, 23.1, 22.7, 18.3, 12.3, 10.3. HR-MS (ESI): *m/z* 1161.5737 (calcd, $[M-Cl]^+$); 942.4230 (found, $[M-3EtO,-2Et,-Cl,+Na]^+$)



Scheme S3. Synthesis of $SiO_2@Fe_3O_4$–supported **Pd complexes 5**

Silica-coated Fe_3O_4 SMNP: Iron (II, III) oxide nanopowder Fe_3O_4/MNP was used as a Fe_3O_4 source for silica-coated Fe_3O_4/SMNP. The MNP and SMNP were prepared according to a literature procedure.[S7]

$SiO_2@Fe_3O_4$–supported Pd complexes 5 (**SMNP@NHC-Pd)** was prepared according to literature procedure.[S8] The silica-coated Fe_3O_4 (1.0 g) was added to a solution of complex **2** (0.15 g, 0.23 mmol) in toluene (10 mL) and the mixture was refluxed for 12 h. After cooling, the silica-coated Fe_3O_4 was magnetically separated from reaction mixture. Modified Fe_3O_4 was washed with methylene chloride several times and dried at 60 ℃ under vacuum. The Pd content of 0.01 mmol/g Pd as show in Table S1.

Table S1: inductively coupled plasma of different batches of **SMNP@NHC-Pd.**

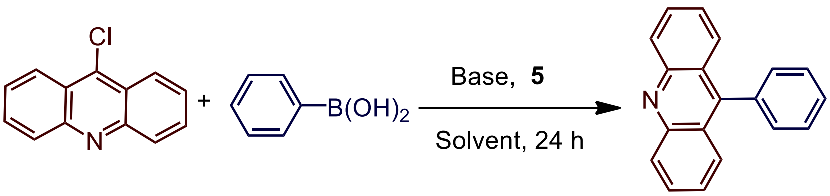
SMNP@NHC-Pd	Pd (mg/kg)	Loading (mmol/g):
A	1210	0.01137
B	1140	0.01071
C	1178	0.01107

D	1259	0.01183

2.2. General Procedure for the Suzuki coupling reaction

To a 50 mL schlenk tube containing base (0.45 mmol) 9-chloroacridine (0.15 mmol), arylboronic acid (0.3 mmol) and catalyst **5** (70 mg, 0.11 mmol/g, 0.5 mol%) were mixed in toluene (4 mL). The mixture was stirred at 100 ℃ in an nitrogen atmosphere for 36 h, Then cooling to the room temperature. After magnetic separation of the catalyst, The solvent was evaporated under reduced pressure. The mixture was ready for purification by flash chromatography to yield the products. The separated catalyst was successively reused for the next reaction without any pre-treatment.

Table S2. Optimization of reaction conditions of Pd-catalyzed Suzuki-Miyaura Coupling of 9-Chloroacridine with phenylboronic acid[a]



	Solvent	Volume (mL)	5/ (mol%)	Base/equiv.	Temp. (°C)	Yield(%)[b]
1.	Xylene	2	0.5	K_3PO_4	90	75
2.	Xylene	2	0.5	K_3PO_4	100	80
3.	Xylene	2	0.5	K_3PO_4	110	74
4.	Xylene	2	0.5	K_3PO_4	120	76
5.	DMF	2	0.5	K_3PO_4	100	42
6.	DMSO	2	0.5	K_3PO_4	100	Complex
7.	Dioxane	2	0.5	K_3PO_4	100	64
8.	Toluene	2	0.5	K_3PO_4	100	89
9.	ACN	2	0.5	K_3PO_4	100	NR
10.	DCE	2	0.5	K_3PO_4	100	Trace
11.	*t*-BuOH	2	0.5	K_3PO_4	100	67
12.	Toluene	2	0.5	KH_2PO_4	100	NR

13.	Toluene	2	0.5	K_2HPO_4	100	NR
14.	Toluene	2	0.5	KOH	100	72
15.	Toluene	2	0.5	K_2CO_3	100	Trace
16.	Toluene	2	0.5	*t*-BuOK	100	79
17.	Toluene	2	0.5	KOAc	100	Trace
18.	Toluene	2	0.5	KF	100	NR
19.	Toluene	1	0.5	K_3PO_4	100	66
20.	Toluene	3	0.5	K_3PO_4	100	94
21.	Toluene	4	0.5	K_3PO_4	100	>99
22.	Toluene	6	0.5	K_3PO_4	100	91
23.	Toluene	4	1.0	K_3PO_4	80	89
24.	Toluene	4	1.0	K_3PO_4	90	98
25.	Toluene	4	1.0	K_3PO_4	100	>99
26.	Toluene	4	0.75	K_3PO_4	100	>99
27.	Toluene	4	0.5	K_3PO_4	100	>99
28.	Toluene	4	0.5	K_3PO_4	100	95 [f]
29.	Toluene	4	0.5	K_3PO_4	100	90 [e]
30.	Toluene	4	0.5	K_3PO_4	100	72 [d]
31.	Toluene	4	0.4	K_3PO_4	100	94
32.	Toluene	4	0.2	K_3PO_4	100	87
33.	Toluene	4	0.5(4b)	K_3PO_4	100	95
34.	Toluene	4	0.5(4c)	K_3PO_4	100	99
35.	Toluene	4	0.5(4d)	K_3PO_4	100	99
36.	Toluene	4	**$PdCl_2$** (0.5)/**Dppf** (0.75)	K_3PO_4	100	Trace [c]
37.	Toluene	4	**$Pd(OAc)_2$** (0.5)/**Binap** (0.75)	K_3PO_4	100	NR [c]
38.	Toluene	4	**$Pd(OAc)_2$** (0.5)/**PPh_3** (1.0)	K_3PO_4	100	23 [c]

39.	Toluene	4	**$Pd_2(dba)_3$** (0.5)/**PPh_3** (1.0)	K_3PO_4	100	17 [c]

[a] Reaction was carried out with 0.15 mmol 9-chloroacridine under N_2 for 24 h;

[b] Isolated yield;

[c] Reaction was carried out with 1.5 mmol scale;

[d] Reaction was carried out with 0.15 mmol 9-chloroacridine under N_2 for 12 h;

[e] Reaction was carried out with 0.15 mmol 9-chloroacridine under N_2 for 18 h;

[f] Reaction was carried out with 0.15 mmol 9-chloroacridine under N_2 for 21 h.

2. Data for the Pd complexes

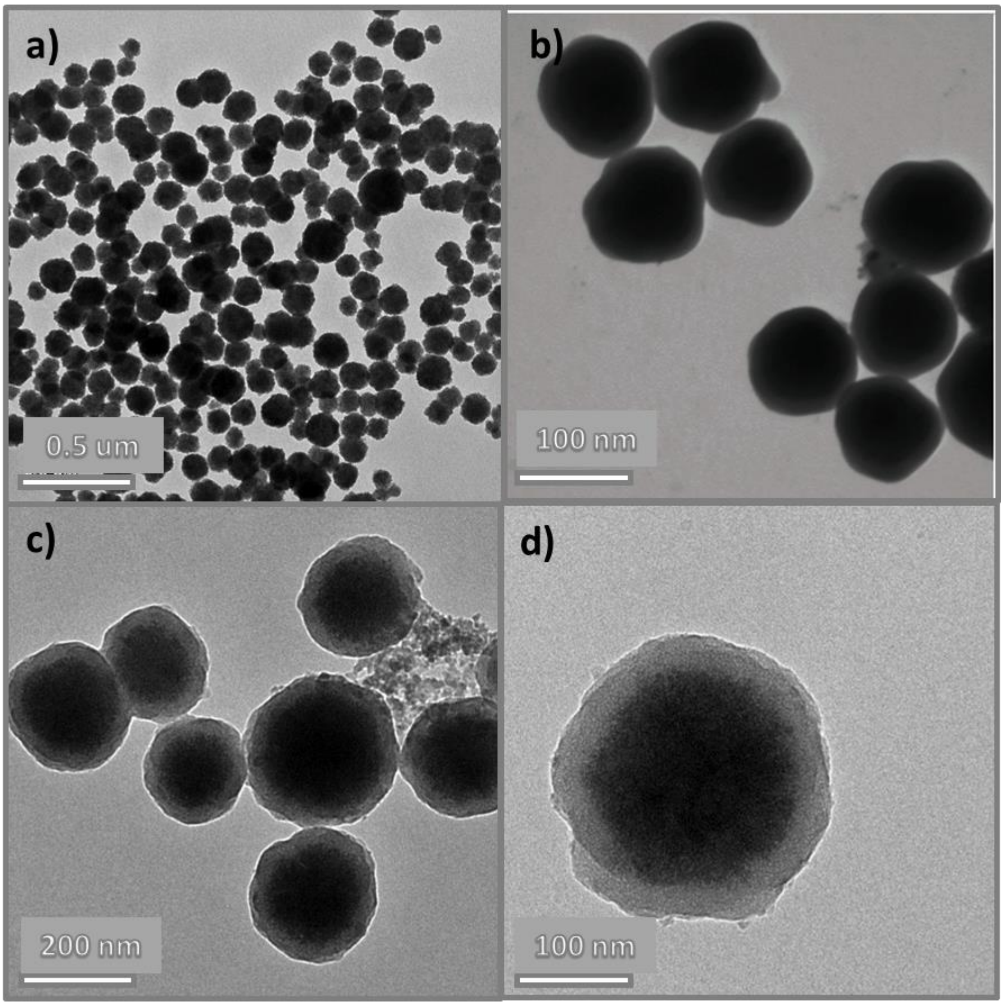


Fig. S1: a) TEM of Fe_3O_4/**MNP**, b) TEM of $Fe_3O_4@SiO_2$/**SMNP**, c) TEM of

SMNP@NHC-Pd, d) TEM of recycled **SMNP@NHC-Pd**.

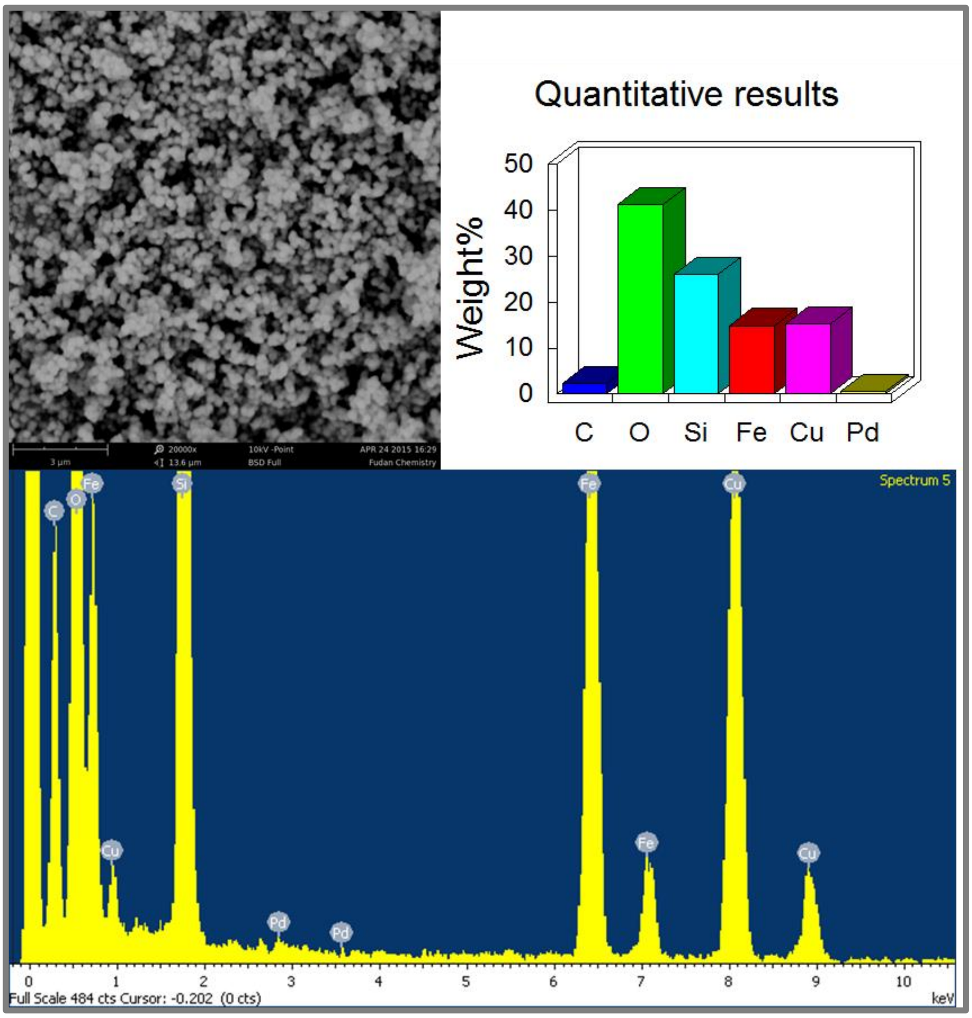


Fig. S2: SEM and EDX of **SMNP@NHC-Pd**.

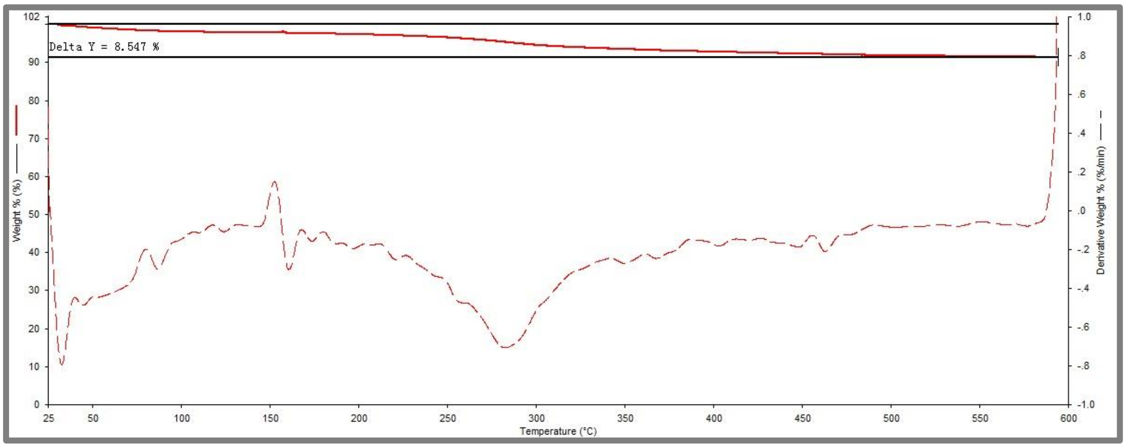


Fig. S3: The differential scanning calorimetry-thermogravimetric analysis (DSC-TGA) of **SMNP@NHC-Pd**.

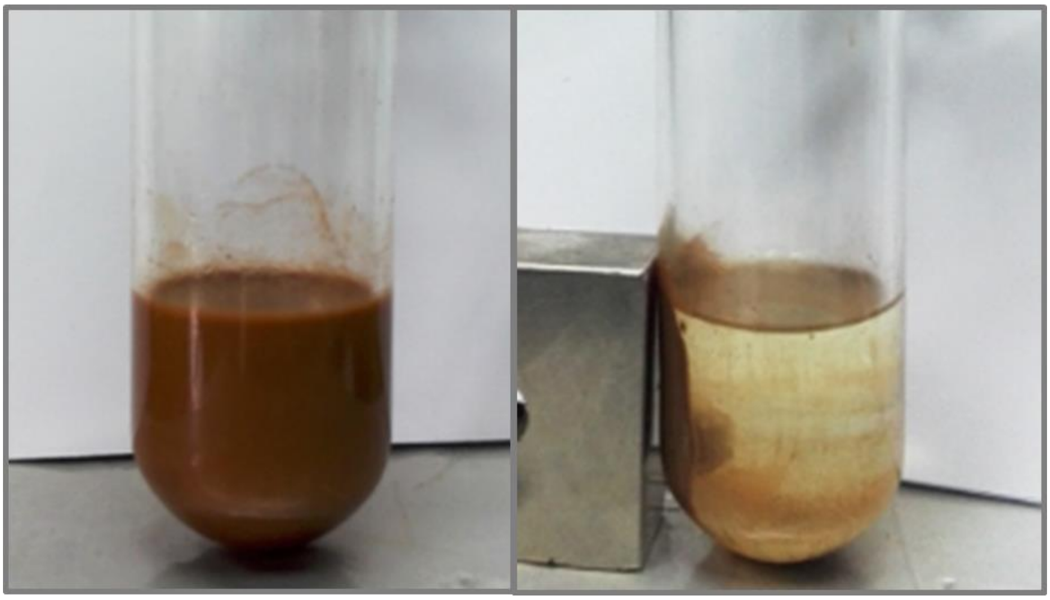


Fig. S4: Recovery effect contrast of reaction post-processing.

Table S3: ICP of every run of the recovered reaction systems.

Runs	Analyte Name	Elem	Reported Conc (Samp)	Samp Units
1	Pd 363.470	Pd	ND	mg/L
2	Pd 324.270	Pd	ND	mg/L
3	Pd 324.270	Pd	ND	mg/L
4	Pd 324.270	Pd	ND	mg/L
5	Pd 363.470	Pd	ND	mg/L

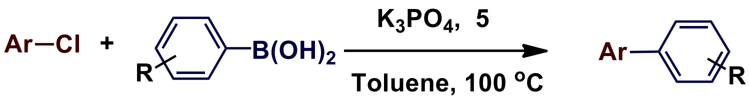
Table S4: ICP of every run of the Pd residue in the isolated products.

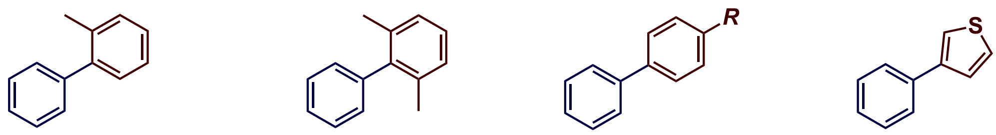
Runs	Analyte Name	Elem	Reported Conc (Samp)	Samp Units
1	Pd 363.470	Pd	ND	mg/L
2	Pd 324.270	Pd	ND	mg/L
3	Pd 324.270	Pd	ND	mg/L
4	Pd 324.270	Pd	ND	mg/L
5	Pd 363.470	Pd	ND	mg/L

Table S5: mercury tests.

Entry	[Cat.] (mol%)	Additive or Note	Time (h)	Yield (%)
1	1	Hg (1 drop after 0 h)	24	81
2	1	Hg (1 drop after 2 h)	24	88
3	1	Hg (1 drop after 4 h)	24	97

Table S6: Substrate scope



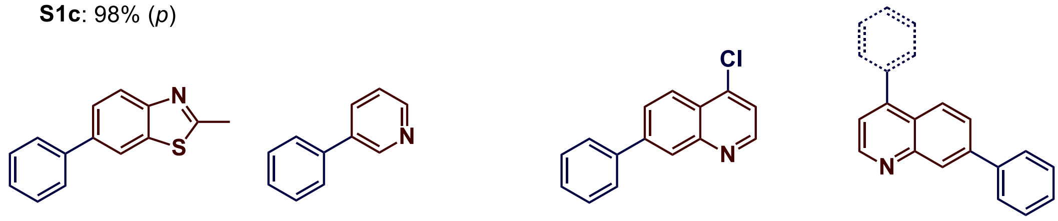


S1a: >98% (*o*)
S1b: 97% (*m*)
S1c: 98% (*p*)

S2: 97%

S3: 95% R=*t*-Bu
S4: 98% R=F

S5: 82%



S6: 72%

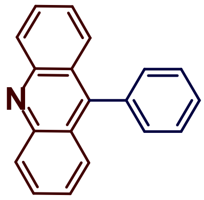
S7: 92%

S8: 96%

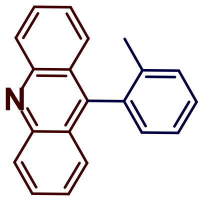
S8: 79%+**S9**: 19%

[a] Reaction was carried out with 0.5 mmol aryl chloride, 0.5 mol% **5** (SMNP@NHC-Pd), 3.0 equiv. K_3PO_4 in 4 mL toluene under N_2 at 100 °C for 24 h; [b] Isolated yield. [c] for 30 h.

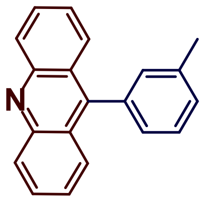
4. Data for the products of carbonylative aminations.

6: 

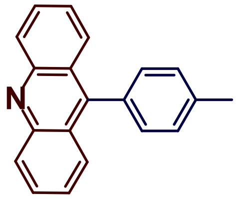
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.38 (d, *J* = 8.4 Hz, 2H), 7.78-7.73 (m, 4H), 7.44-7.40 (m, 2H), 7.20 (s, 1H), 7.05 (s, 2H), 2.44 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.9, 147.2, 136.0, 130.5, 130.0, 129.7, 128.5, 128.4, 126.9, 125.7, 125.2.

7a: 

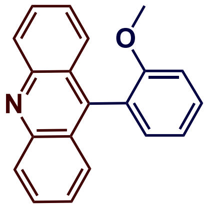
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.29 (d, *J* = 8.8 Hz, 2H), 7.80-7.76 (m, 2H), 7.55-7.39 (m, 7H), 7.24 (d, *J* = 7.6 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 149.0, 147.1, 137.0, 135.6, 130.3, 130.2, 129.8, 128.9, 128.7, 126.7, 126.0, 125.8, 125.2, 19.8.

7b: 

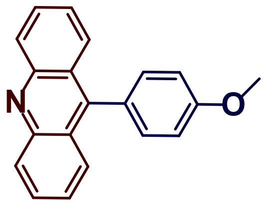
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.27 (d, *J* = 8.8 Hz, 2H), 7.79-7.71 (m, 4H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.44-7.38 (m, 3H), 7.25 (s, 1H), 2.48 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 149.0, 147.3, 138.3, 136.1, 131.2, 130.1, 129.8, 129.2, 128.5, 127.7, 127.1, 125.6, 125.3, 21.7.

7c: 

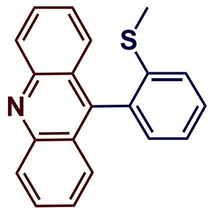
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.28 (d, *J* = 9.2 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 4H), 7.42-7.39 (m, 4H), 7.05 (t, *J* = 7.4 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.9, 147.5, 138.3, 133.0, 130.5, 130.0, 129.7, 129.2, 127.1, 125.6, 125.4, 21.5.

8a: 

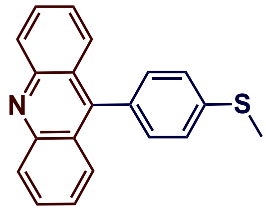
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.27 (d, *J* = 8.8 Hz, 2H), 7.81-7.68 (m, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.59-7.51 (m, 1H), 7.45-7.34 (m, 2H), 7.24 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.16 (dd, *J* = 15.5, 7.9 Hz, 2H), 3.60 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 157.35, 148.80, 144.61, 131.87, 130.12, 129.79, 129.59, 126.83, 125.49, 125.34, 124.59, 120.62, 111.23, 55.54.

8b: 

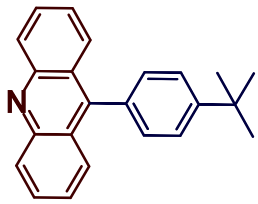
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.27 (d, *J* = 8.8 Hz, 2H), 7.77-7.73 (m, 4H), 7.43-7.34 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 159.6, 148.8, 147.1, 131.7, 129.9, 129.5, 127.8, 126.9, 125.4, 113.9, 55.3.

9a: 

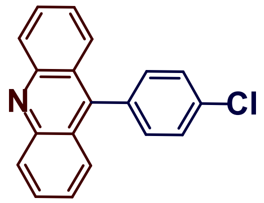
[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.29 (d, J = 8.7 Hz, 2H), 7.77 (t, J = 7.5 Hz, 2H), 7.56 (t, J = 8.7 Hz, 3H), 7.49-7.31 (m, 4H), 7.24 (t, J = 6.5 Hz, 1H), 2.27 (s, 3H). [13]C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.86, 145.20, 138.82, 134.32, 130.65, 130.02, 129.73, 129.23, 126.42, 125.79, 125.17, 125.09, 124.75, 15.56. HR-MS (ESI): m/z 301.0925 (calcd, $[M]^+$); 302.1008 (found, $[M+H]^+$).

9b: 

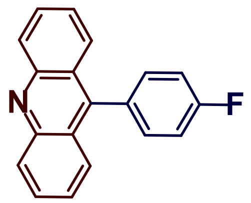
[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.27 (d, J = 8.7 Hz, 2H), 7.76 (dd, J = 15.3, 7.8 Hz, 4H), 7.53-7.39 (m, 4H), 7.37 (d, J = 8.1 Hz, 2H), 2.61 (s, 4H). [13]C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.78, 146.63, 139.18, 132.32, 130.89, 129.95, 129.61, 126.73, 126.06, 125.62, 125.16, 15.51.

10: 

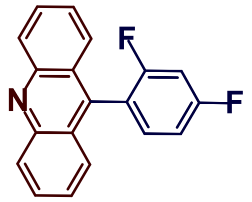
[1]H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.27 (d, J = 9.2 Hz, 2H), 7.78-7.75 (m, 4H), 7.61 (d, J = 8.4 Hz, 2H), 7.44-7.37 (m, 4H), 1.47 (s, 3H). [13]C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 151.3, 148.8, 148.5, 132.8, 130.2, 129.9, 127.1, 125.4, 125.3, 34.8, 31.4.

11: 

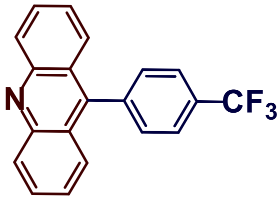
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.28 (d, J = 8.8 Hz, 2H), 7.80-7.76 (m, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.61-7.59 (m, 2H), 7.47-7.38 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.9, 145.7, 134.7, 134.5, 131.9, 130.1, 129.8, 128.9, 126.5, 126.0, 125.1.

12a: 

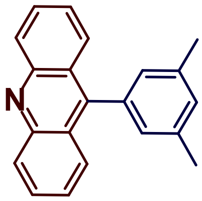
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.28 (d, J = 8.8 Hz, 2H), 7.77-7.74 (m, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.44-7.38 (m, 4H), 7.32-7.28 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 164.0, 161.6, 148.7, 145.9, 132.2, 132.1, 130.0, 129.7, 126.5, 125.8, 115.6 (d, J = 8.0 Hz, 1C). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ = -113.15, -113.19, -113.20. HR-MS (ESI): *m/z* 273.0954 (calcd, $[M]^+$); 274.1046 (found, $[M+H]^+$).

12b: 

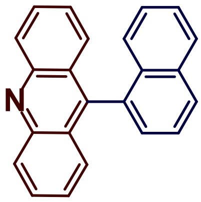
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.30 (d, J = 8.8 Hz, 2H), 7.87-7.72 (m, 2H), 7.63 (d, J = 8.7 Hz, 2H), 7.52-7.44 (m, 2H), 7.43-7.32 (m, 1H), 7.21-7.05 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 164.69 (d, J = 4.0 Hz, 1C), 162.20 (d, J = 4.0 Hz, 1C), 161.53 (d, J = 4.8 Hz, 1C), 159.09, 148.74, 139.71, 133.25 (q, J = 2.0 Hz, 1C), 129.98 (d, J = 7.2 Hz, 1C) 126.08 (d, J = 12 Hz, 1C), 125.36, 119.43 (t, J = 5.6 Hz, 1C), 111.81 (q, J = 2.5 Hz, 1C). 104.60 (t, J = 10.2 Hz, 1C). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ = -108.18, -108.20, -108.22, -108.24, -108.48, -108.51, -108.53, -108.55, -108.57.

13: 

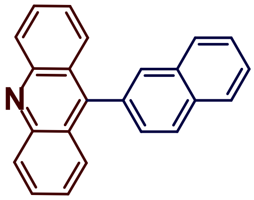
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.30 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.81-7.77 (m, 2H), 7.60 (t, J = 7.4 Hz, 4H), 7.45 (t, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 147.9, 144.3, 139.1, 130.0, 129.2, 129.0, 125.3, 124.7, 124.7(q, J = 14.7 Hz, 1C), 123.9. ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ = -62.51. HR-MS (ESI): m/z 323.0922 (calcd, $[M]^+$); 324.0989 (found, $[M+H]^+$).

14: 

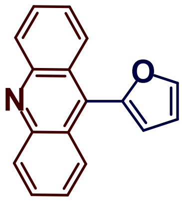
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.38 (d, J = 8.4 Hz, 2H), 7.78-7.73 (m, 4H), 7.44-7.40 (m, 2H), 7.20 (s, 1H), 7.05 (s, 2H), 2.44 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.9, 147.9, 138.1, 135.9, 130.0, 129.6, 128.3, 127.2, 125.5, 125.3, 21.5.

15: 

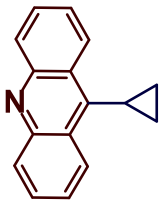
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.34 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.79-7.75 (m, 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.51-7.43 (m, 4H), 7.34-7.30 (m, 2H), 7.25-7.21 (m, 1H), 7.03 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 149.0, 145.9, 133.8, 133.6, 132.7, 130.2, 129.8, 129.0, 128.6, 128.5, 128.4, 127.1, 126.8, 126.4, 126.2, 126.1, 125.9, 125.4.

16: 

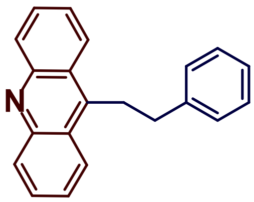
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.31 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.95-7.92 (m, 2H), 7.81-7.73 (m, 4H), 7.66-7.55 (m, 3H), 7.45-7.40 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.0, 146.3, 132.6, 132.2, 129.1, 128.9, 128.8, 127.4, 127.32, 127.27, 127.1, 126.1, 126.0, 125.9, 124.8, 124.5.

17: 

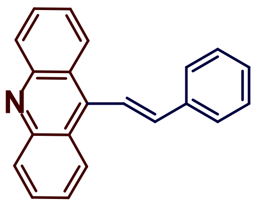
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.27 (d, J = 8.8 Hz, 2H), 8.09 (d, J = 8.8 Hz, 2H), 7.82-7.77 (m, 3H), 7.52 (t, J = 7.2 Hz, 2H), 6.85 (d, J = 2.0 Hz, 1H), 6.76 (d, J = 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.9, 148.2, 144.0, 130.0, 129.8, 126.4, 126.3, 125.2, 114.1, 111.4. HR-MS (ESI): *m/z* 245.0841 (calcd, $[M]^+$); 246.0906 (found, $[M+H]^+$).

18: 

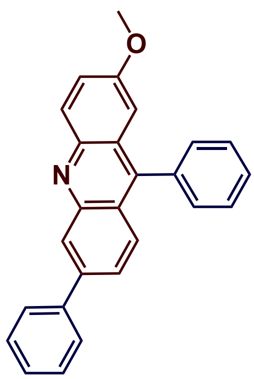
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.67 (d, J = 8.8 Hz, 2H), 8.21 (d, J = 8.8 Hz, 2H), 7.73 (t, J = 7.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 2H), 2.49-2.45 (m, 1H), 1.48-1.45 (m, 2H), 0.86-0.85 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.5, 146.0, 129.9, 129.6, 126.7, 125.7, 125.0, 10.0, 8.4. HR-MS (ESI): *m/z* 219.1048 (calcd, $[M]^+$); 220.1105 (found, $[M+H]^+$).

19: 

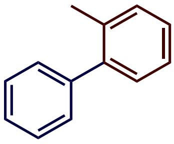
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.25 (d, J = 9.2 Hz, 4H), 7.80-7.76 (m, 2H), 7.58-7.54 (m, 2H), 7.36-7.30 (m, 4H), 7.28-7.24 (m, 1H), 3.95-3.91 (m, 2H), 3.14-3.09 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.7, 145.5, 141.1, 130.4, 129.8, 128.7, 128.3, 126.5, 125.7, 124.8, 124.1, 37.1, 29.7.

20: 

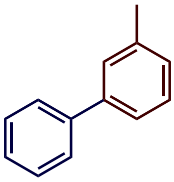
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.34 (d, J = 8.8 Hz, 2H), 8.25 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 16.8 Hz, 1H), 7.81-7.77 (m, 2H), 7.70 (d, J = 7.2 Hz, 2H), 7.56-7.47 (m, 4H), 7.43-7.39 (m, 1H), 7.06 (d, J = 16.4 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 148.9, 143.1, 139.6, 136.6, 130.1, 130.0, 129.1, 128.9, 127.0, 126.0, 125.7, 124.6, 122.2.

21: 

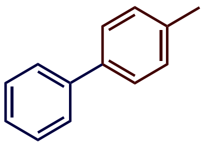
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.47 (s, 1H), 8.17 (d, J = 9.4 Hz, 1H), 7.79 (d, J = 7.3 Hz, 2H), 7.69 (s, 2H), 7.65-7.54 (m, 3H), 7.53-7.42 (m, 5H), 7.39 (t, J = 7.2 Hz, 1H), 6.83 (s, 1H), 3.72 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 156.91, 147.42, 146.40, 144.43, 141.11, 140.16, 136.26, 131.10, 130.28, 128.96, 128.62, 128.29, 127.86, 127.34, 126.81, 126.70, 125.92, 125.67, 125.00, 124.52, 102.09, 55.25. HR-MS (ESI): *m/z* 361.1467 (calcd, $[M]^+$); 362.1542 (found, $[M+H]^+$).

S1a: 

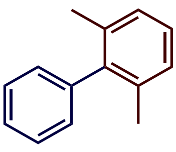
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.66-7.59 (m, 2H), 7.55 (d, *J* = 7.2 Hz, 3H), 7.51-7.43 (m, 4H), 2.51 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 141.92, 141.89, 135.22, 130.25, 129.74, 129.13, 128.01, 127.20, 126.69, 125.72, 20.40.

S1b: 

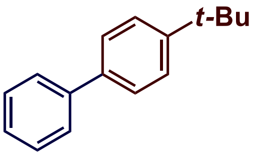
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.55 (d, *J* = 7.5 Hz, 2H), 7.37 (dd, *J* = 12.4, 5.0 Hz, 4H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.3 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 141.48, 141.36, 138.41,128.81, 128.12, 128.09, 127.29, 124.40, 21.65.

S1c: 

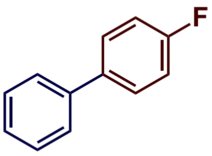
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.56 (d, *J* = 7.3 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 141.23, 138.42,137.06, 129.55, 128.78, 127.04, 21.16.

S2: 

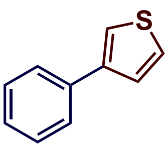
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.36 (t, J = 7.4 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H), 7.19-7.02 (m, 5H), 2.01 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 141.80, 141.06, 135.92, 128.94, 128.36, 127.24, 126.99, 126.54, 20.79.

S3: 

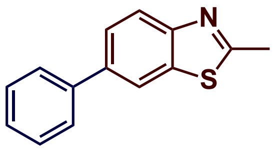
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.58 (d, J = 7.4 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 150.21, 141.04, 138.30, 128.67, 127.00, 126.96, 126.77, 125.69, 34.50, 31.36.

S4: 

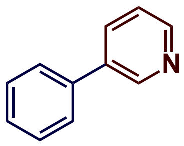
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.64 – 7.55 (m, 4H), 7.49 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 7.18 (t, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 163.67, 161.22, 140.21, 137.31, 137.29, 128.69 (t, J = 3.6 Hz, 1C). 127.10 (d, J = 9.8 Hz, 1C)., 115.57 (d, J = 8.5 Hz, 1C). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ = -115.67, -115.68, -115.69, -115.72.

S5: 

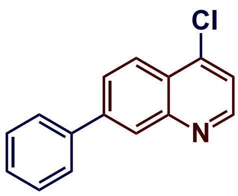
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.59 (d, J = 7.7 Hz, 2H), 7.44 (d, J = 1.7 Hz, 1H), 7.42 – 7.35 (m, 4H), 7.28 (t, J = 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 142.36, 135.85, 128.78, 127.11, 126.44, 126.33,126.17,120.25. (t, J = 3.6 Hz, 1C). 127.10 (d, J = 9.8 Hz, 1C)., 115.57 (d, J = 8.5 Hz, 1C).

S6: 

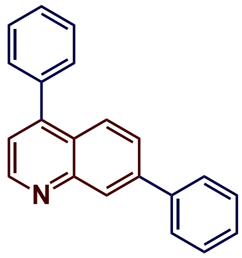
^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.16 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.55 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 2.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 167.49, 153.96, 140.62, 139.36, 134.48, 128.77, 127.28, 127.20, 124.02, 121.38, 120.56, 20.04. (t, *J* = 3.6 Hz, 1C). 127.10 (d, *J* = 9.8 Hz, 1C)., 115.57 (d, *J* = 8.5 Hz, 1C).

S7: 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.85 (s, 1H), 8.57 (d, *J* = 4.2 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.26 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 147.82, 147.68, 137.37, 136.59, 134.48, 133.04, 128.92, 128.02, 127.30, 126.94, 123.48. ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ = -115.67, -115.68, -115.69,115.72. HR-MS (ESI): *m/z* 273.0954 (calcd, $[M]^+$); 274.1046 (found, $[M+H]^+$).

S8: 

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.89 (d, *J* = 4.4 Hz, 1H), 8.15 (d, *J* = 1.9 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.49 (t, *J* = 6.2 Hz, 3H), 7.46-7.34 (m, 3H), 7.28 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 150.79, 148.90, 148.36, 137.25, 135.06, 134.66, 130.31, 129.27, 128.54, 127.40, 127.15, 124.99, 121.29.



S9:

^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.93 (d, J = 4.4 Hz, 1H), 8.40 (d, J = 1.5 Hz, 1H), 7.98 (d, J = 8.7 Hz, 1H), 7.82-7.68 (m, 3H), 7.62-7.44 (m, 7H), 7.41 (dd, J = 7.4, 3.2 Hz, 1H), 7.31 (d, J = 4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 150.33, 148.89, 148.33, 141.94, 140.02, 137.85, 130.62, 129.46, 128.95, 128.57, 128.45, 127.89, 127.41, 127.27, 126.32, 126.18, 121.15.

5. ^{1}H, ^{13}C NMR and MS spectra for important compounds.

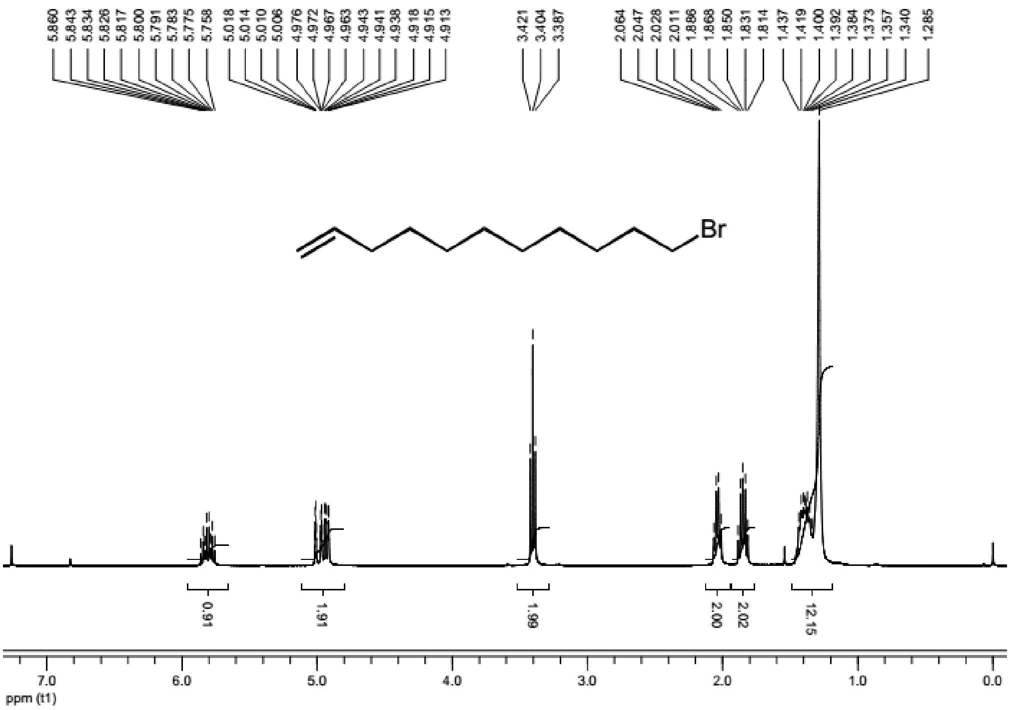


Figure S1. ^{1}H NMR spectrum of compound **a**.

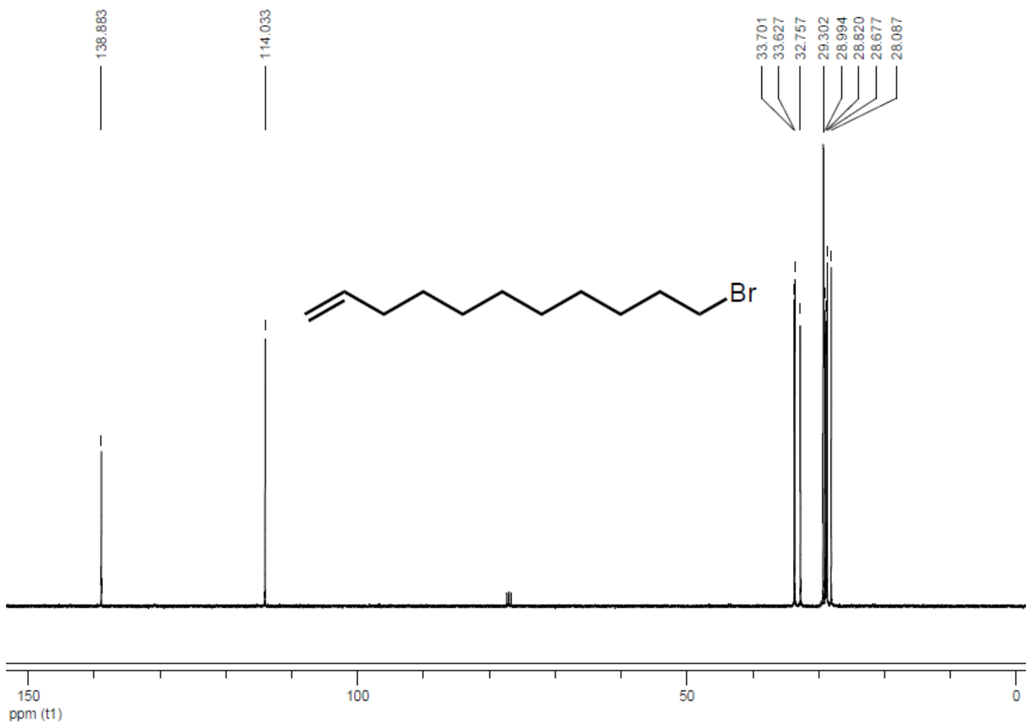


Figure S2. ^{13}C NMR spectrum of compound **a**.

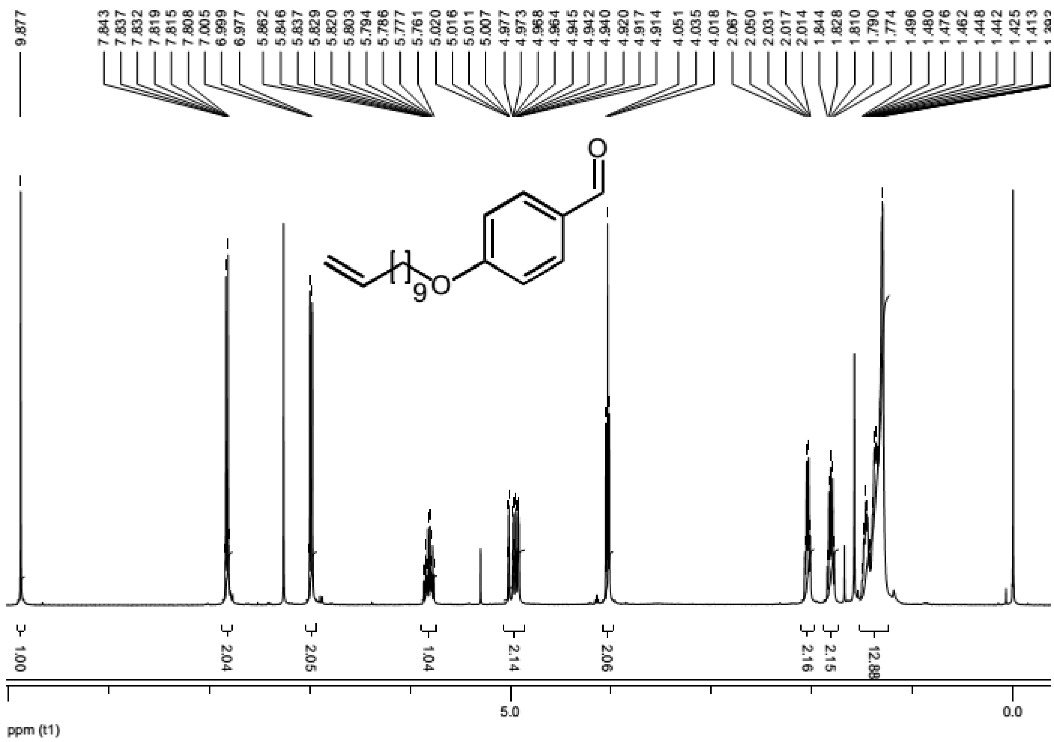


Figure S3. ^{1}H NMR spectrum of compound **b**.

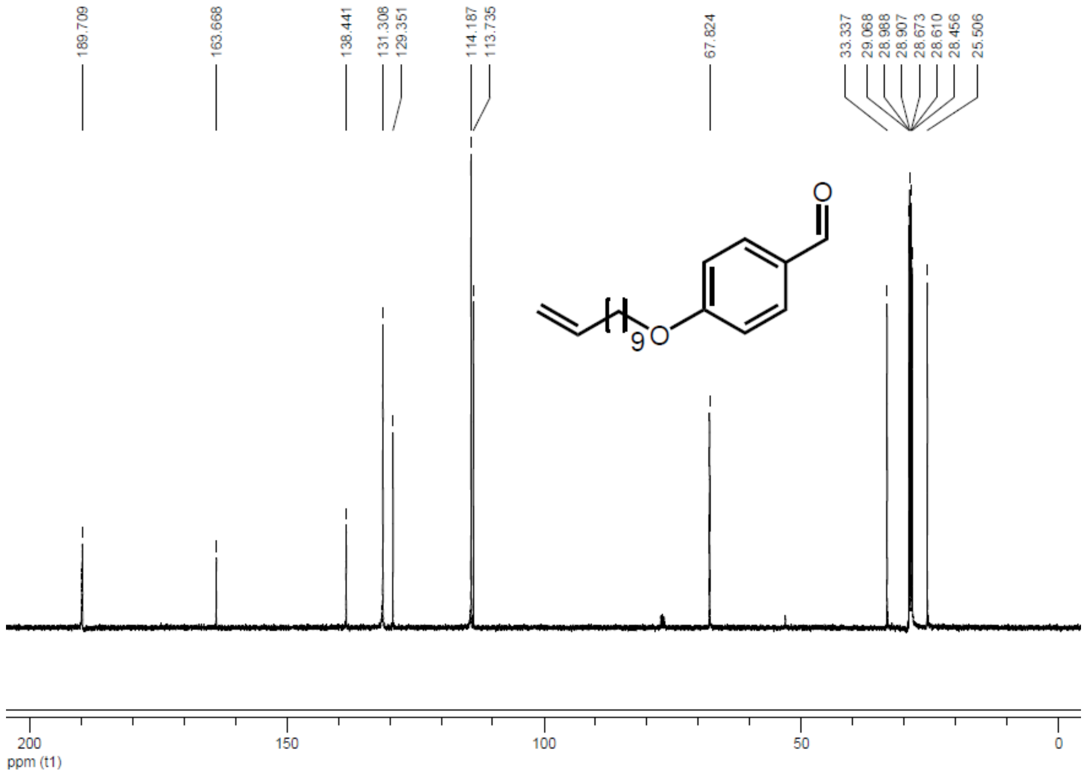


Figure S4. ^{13}C NMR spectrum of compound **b**

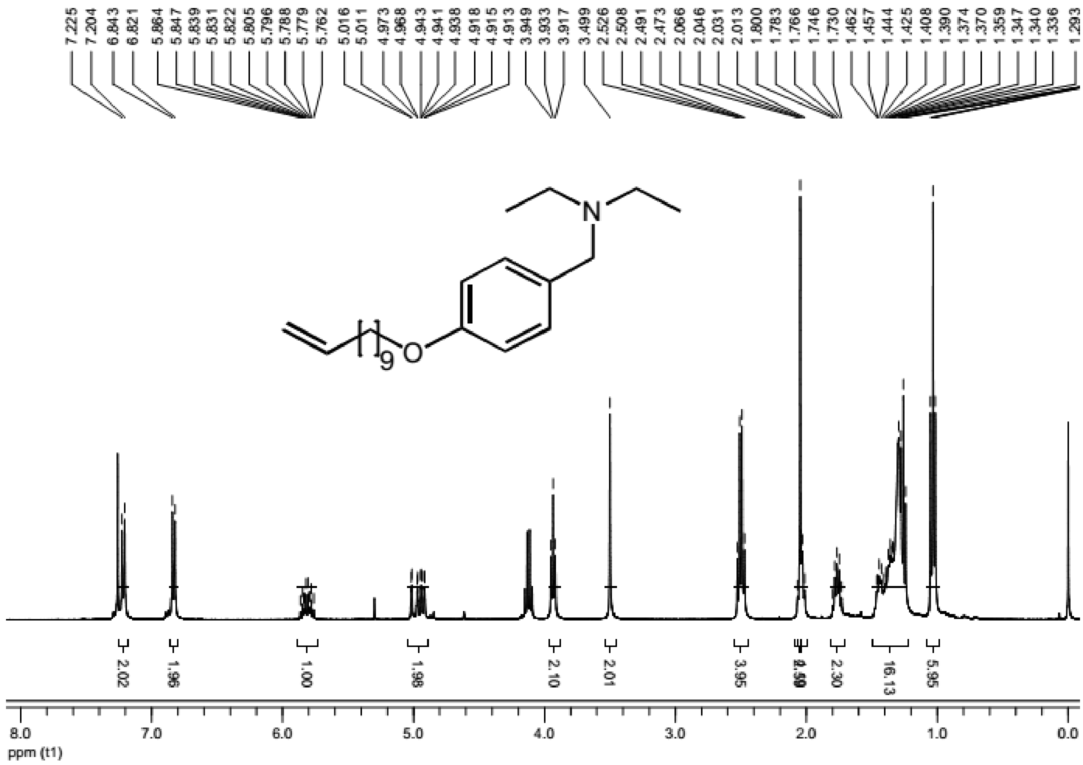


Figure S5. ^{1}H NMR spectrum of compound **c**.

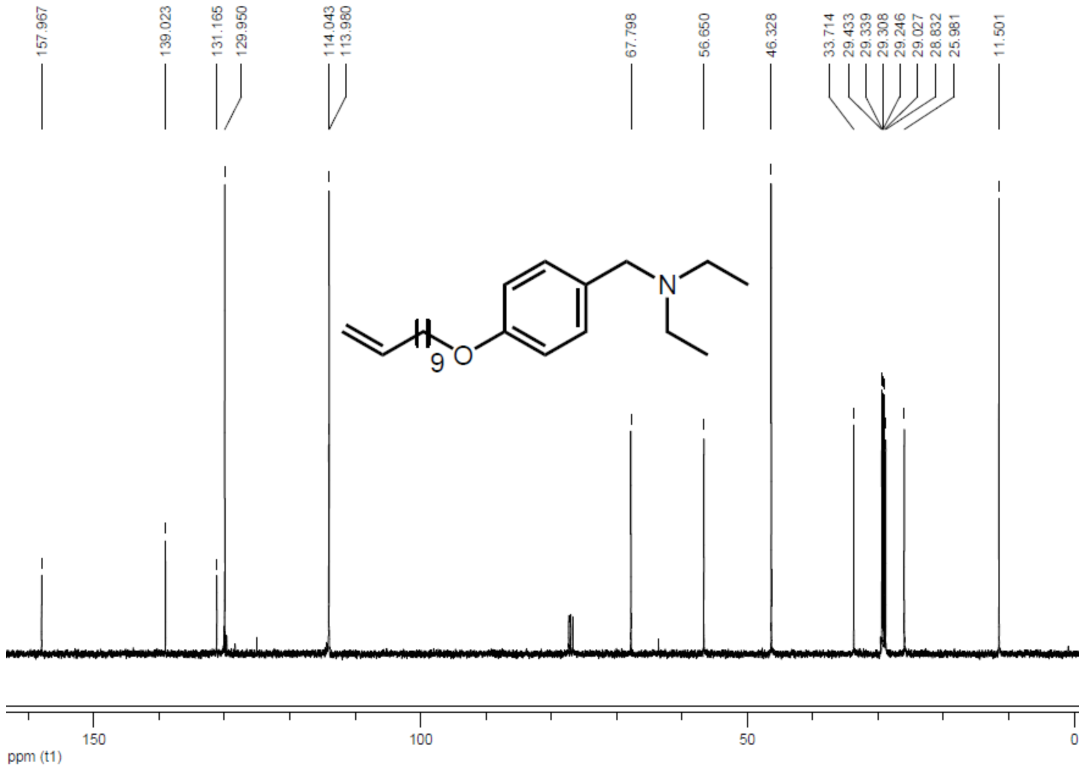


Figure S6. ^{13}C NMR spectrum of compound **c**.

Display Report

Analysis Info

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Method	tune_200-800_hcoona-pos-10min.m	Operator	gftang
Sample Name	DQ-1604191	Instrument / Ser#	micrOTOF II 10257
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
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Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

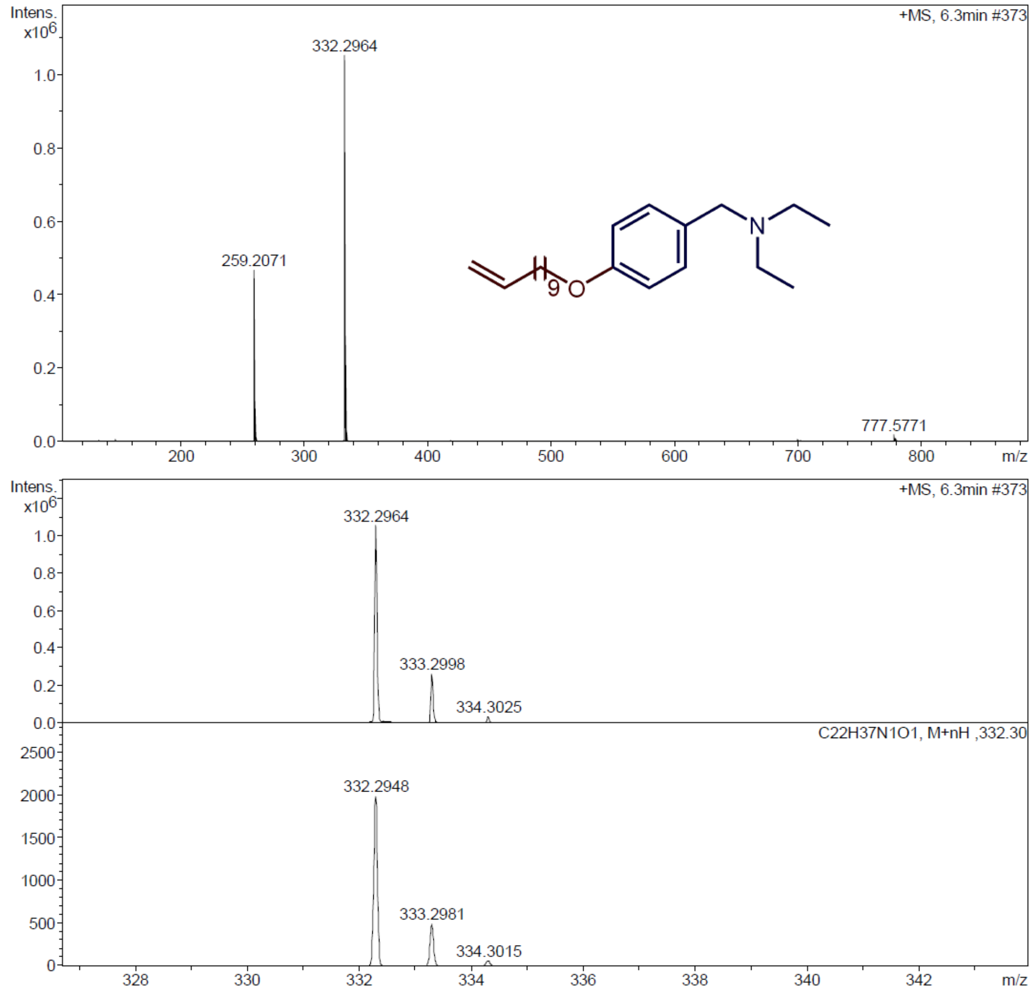

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Figure S7. ESI-MS spectrum of compound **c.**

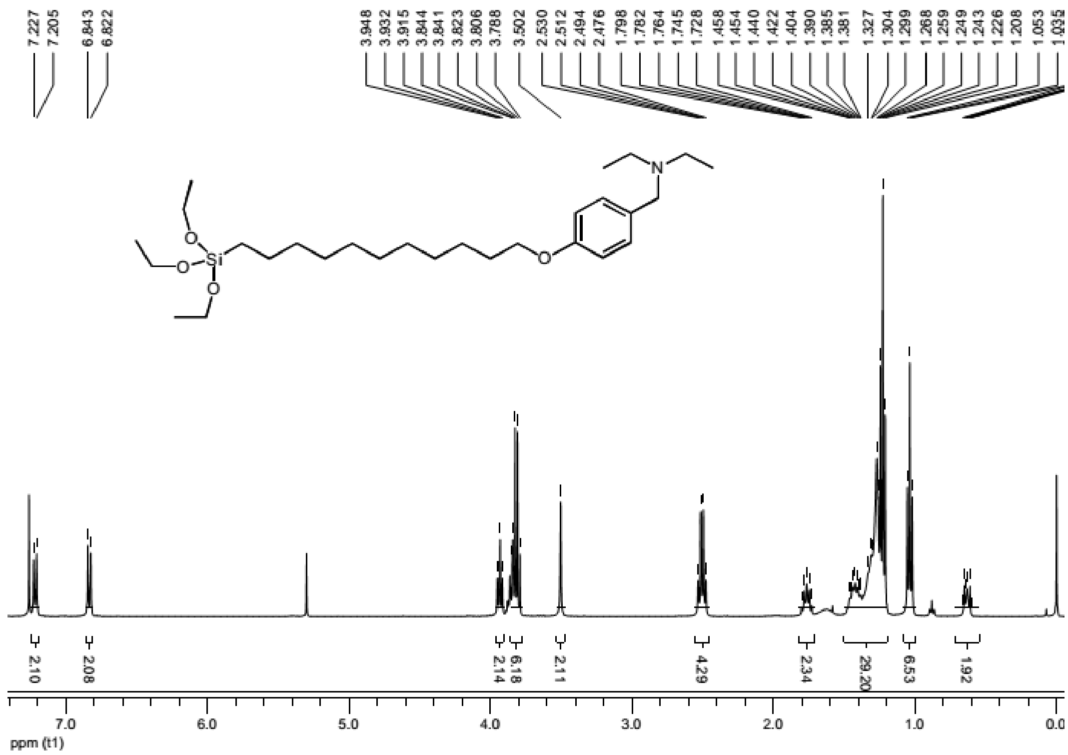

Figure S8. ^{1}H NMR spectrum of compound **2**.

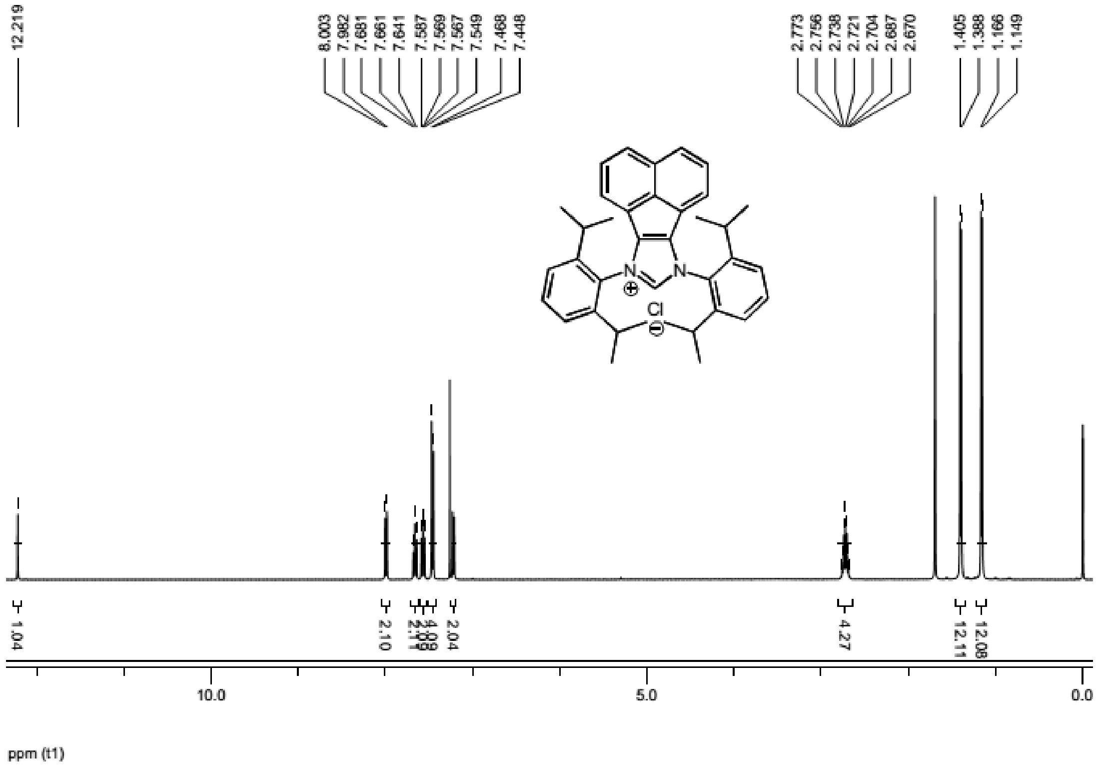

Figure S9. ^{1}H NMR spectrum of compound **2**.

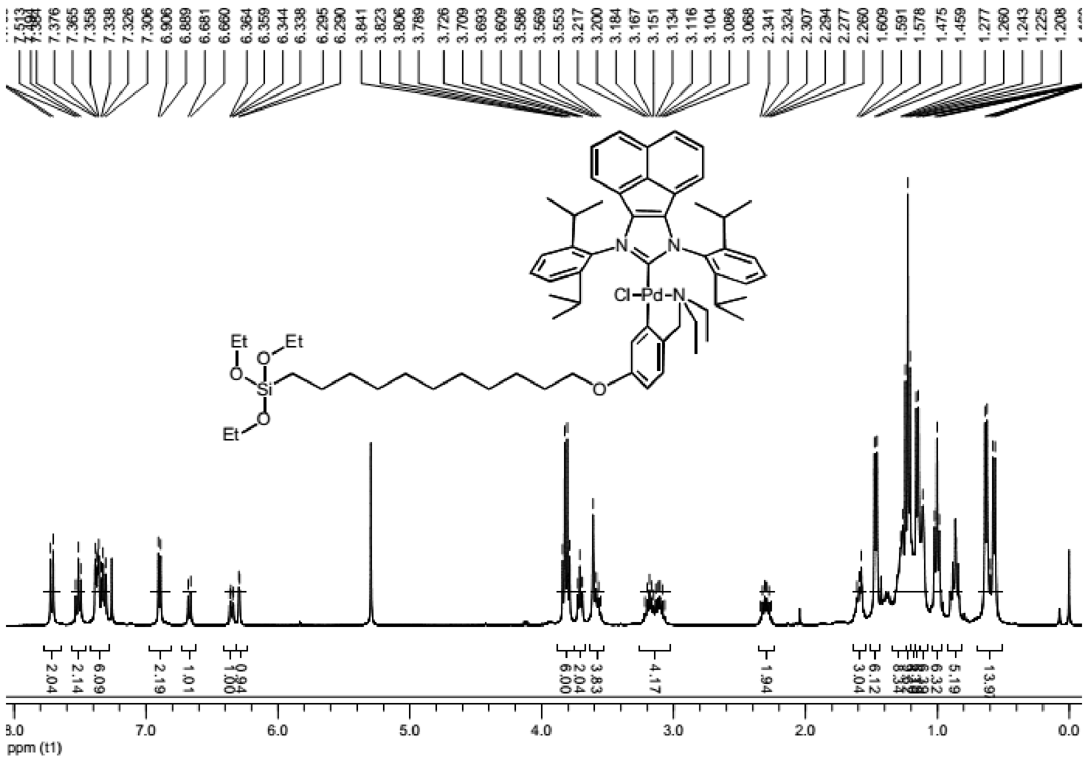

Figure S10. ^{1}H NMR spectrum of compound **4a**.

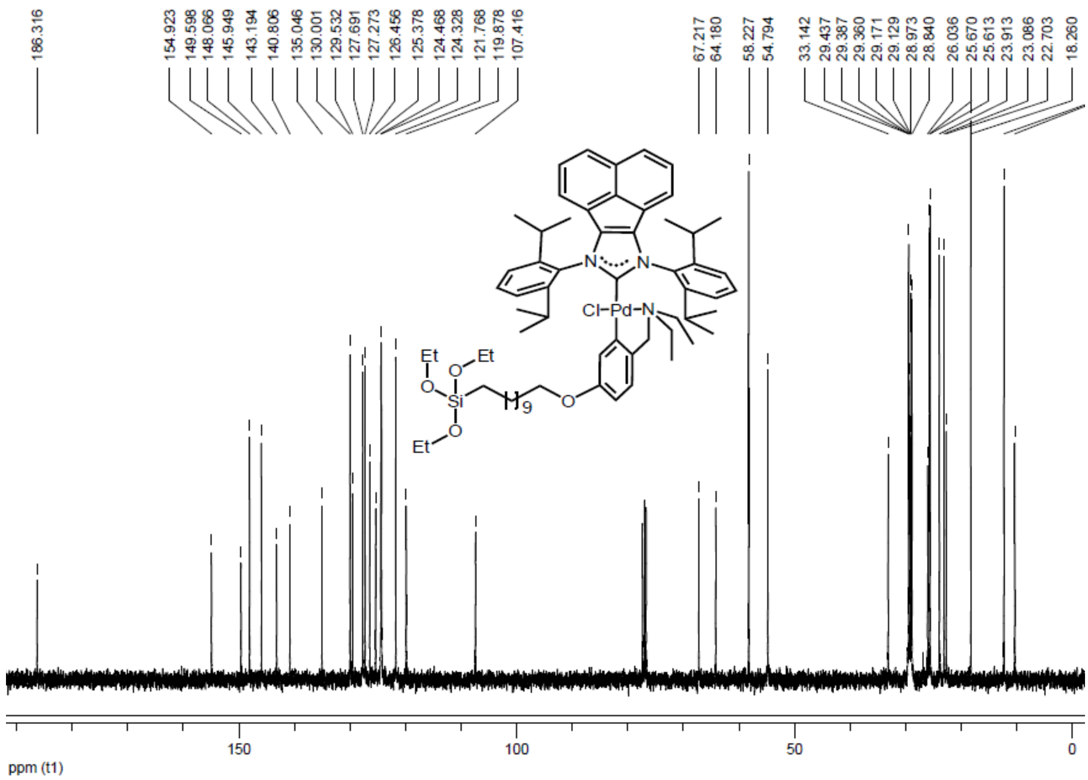

Figure S11. ^{13}C NMR spectrum of compound **4a**.

Display Report

Analysis Info

Analysis Name	D:\Data\2016MS\TT\0419\DQ-1604192_RC6_01_8810.d	Acquisition Date	4/20/2016 4:37:18 AM
Method	tune_200-800_hcoona-pos-10min.m	Operator	gftang
Sample Name	DQ-1604192	Instrument / Ser#	micrOTOF II 10257
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 ℃
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Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

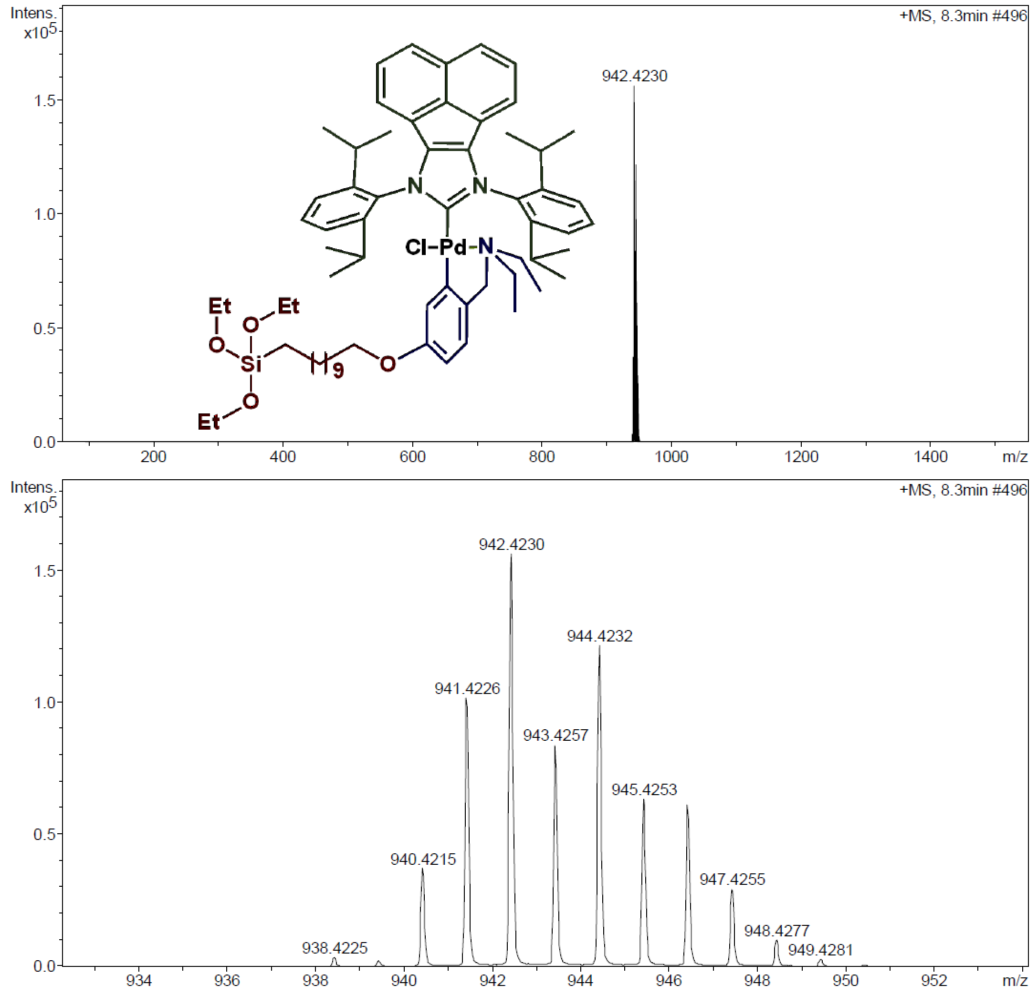

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Figure S12. ESI-MS spectrum of compound **4a.**

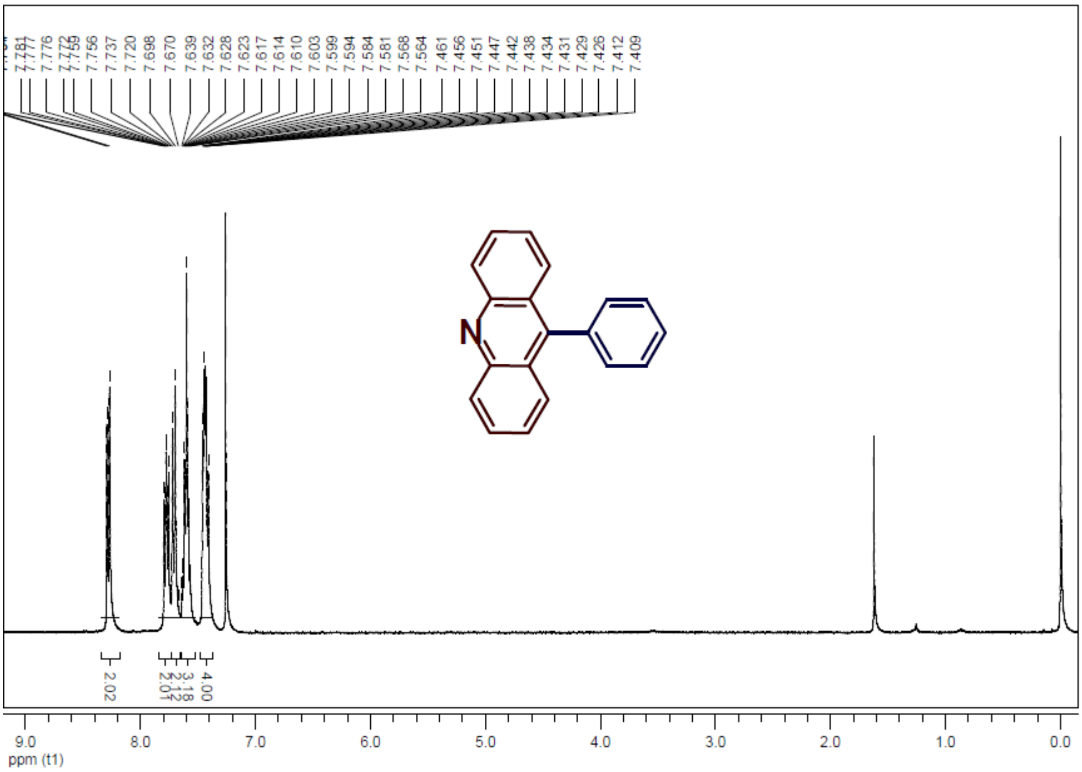

Figure S13. ^{1}H NMR spectrum of compound **6.**

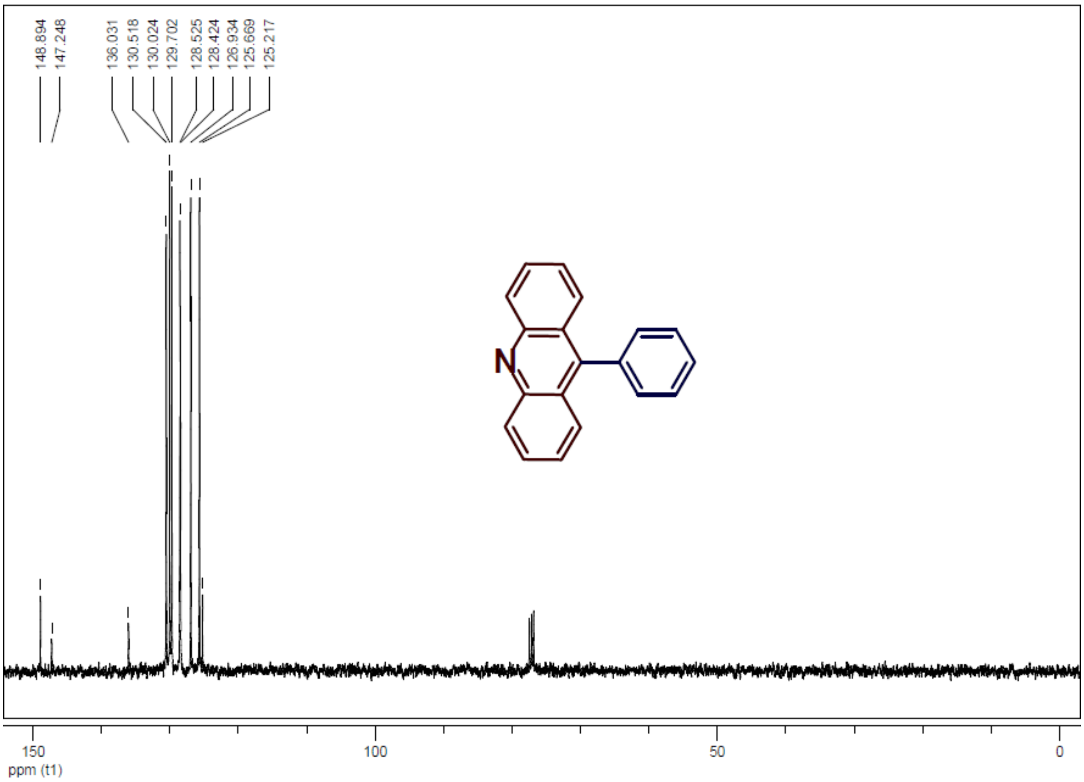

Figure S14. ^{13}C NMR spectrum of compound **6**.

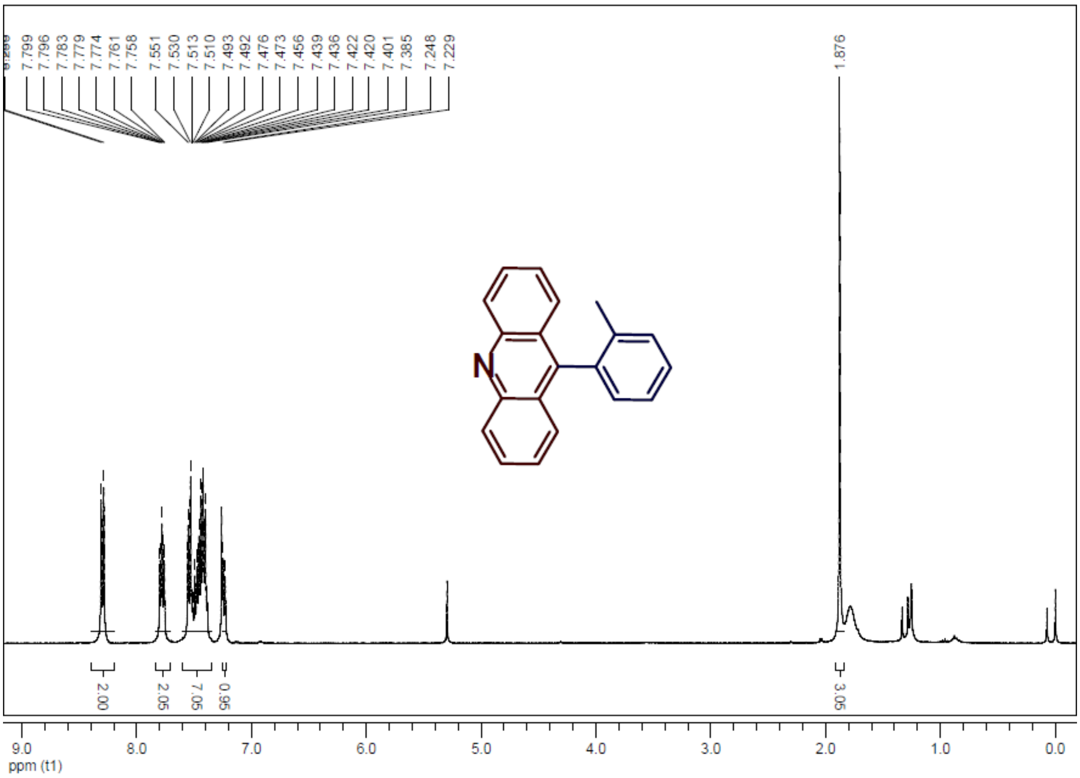

Figure S15. ^{1}H NMR spectrum of compound **7a.**

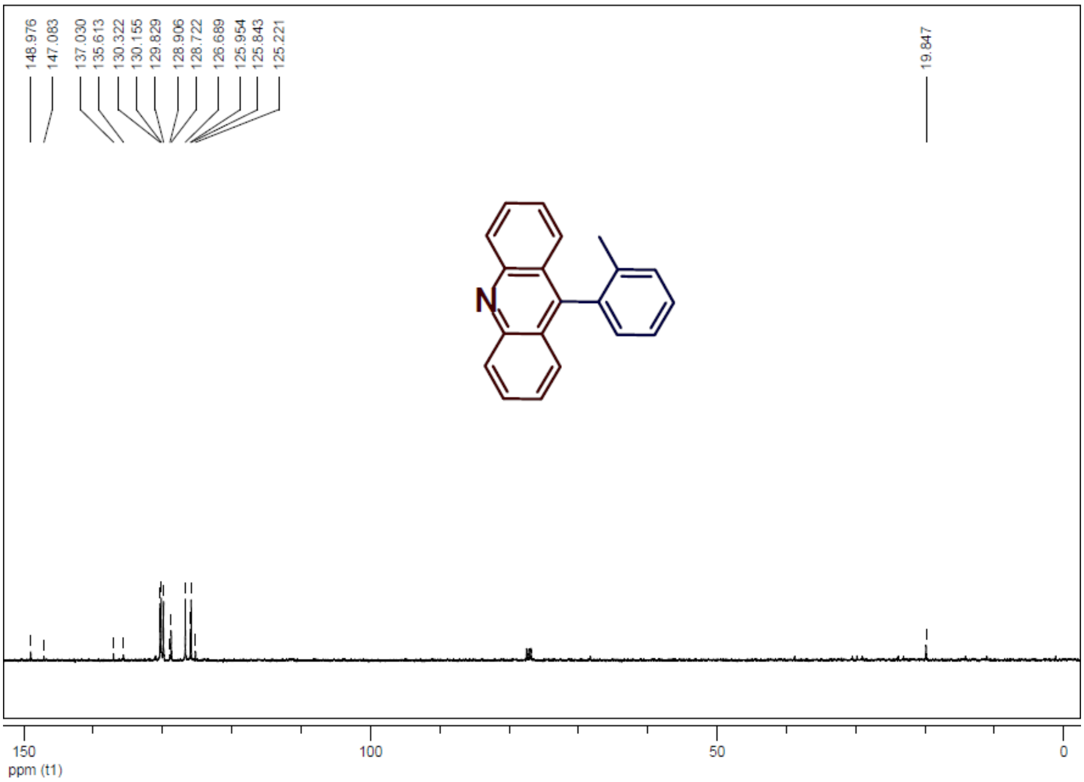

Figure S16. ^{13}C NMR spectrum of compound **7a**.

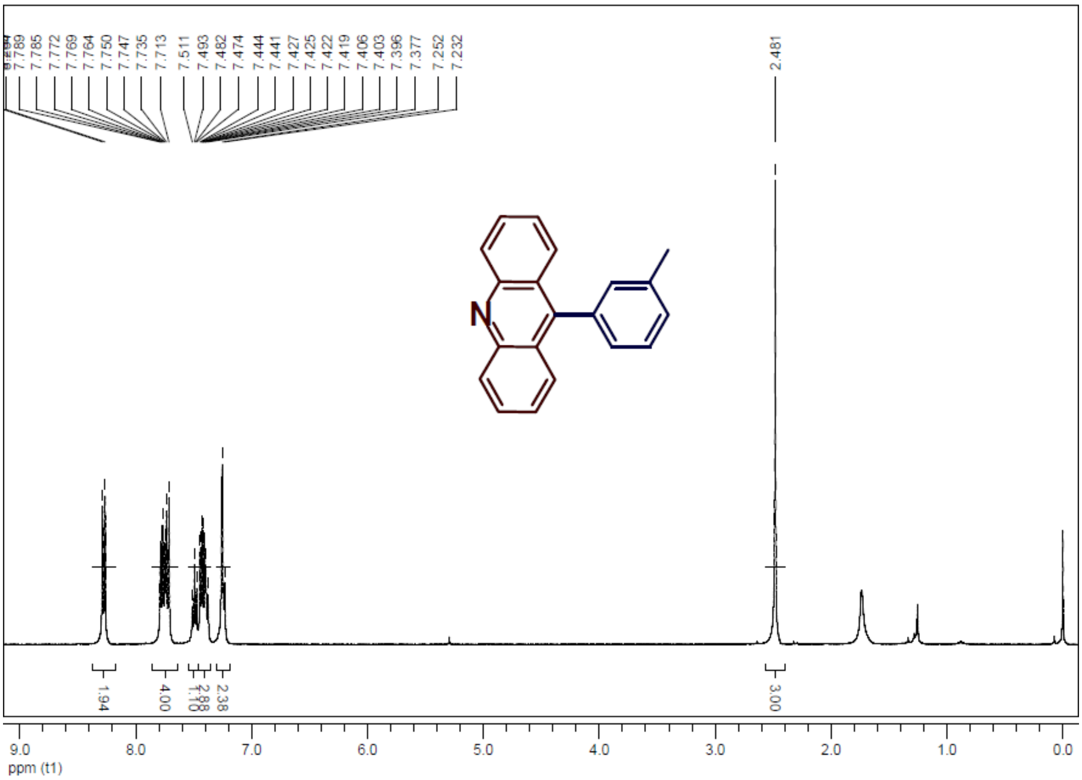

Figure S17. ^{1}H NMR spectrum of compound **7b.**

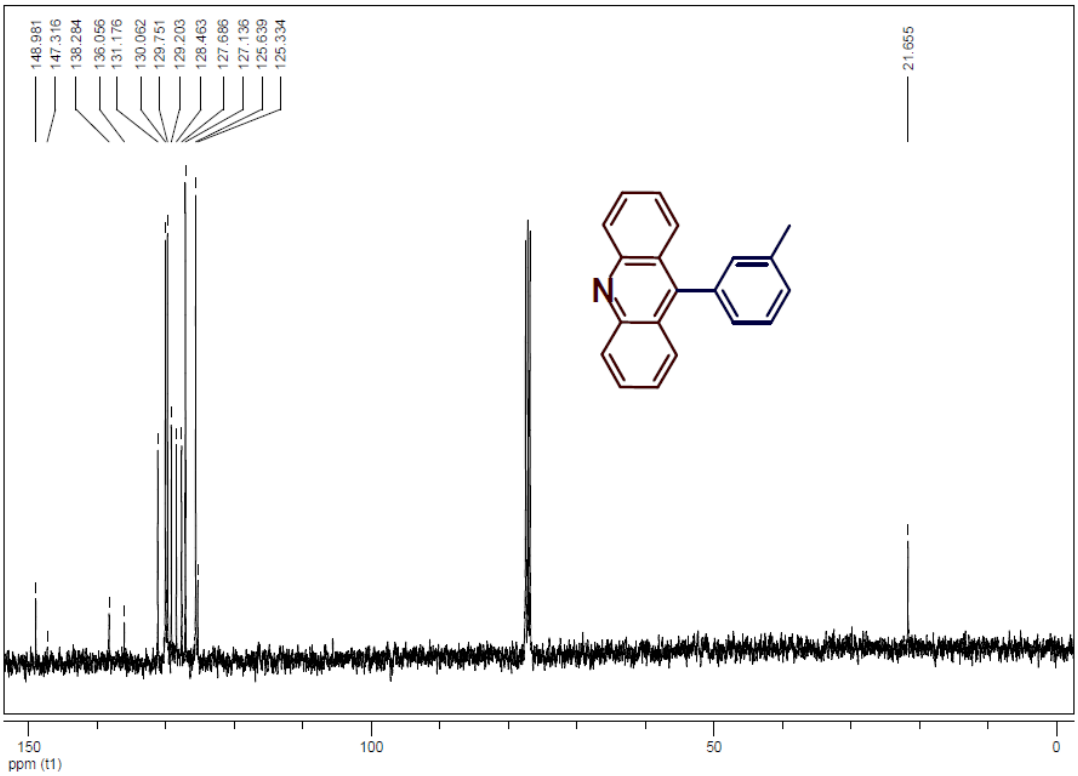

Figure S18. ^{13}C NMR spectrum of compound **7b**.

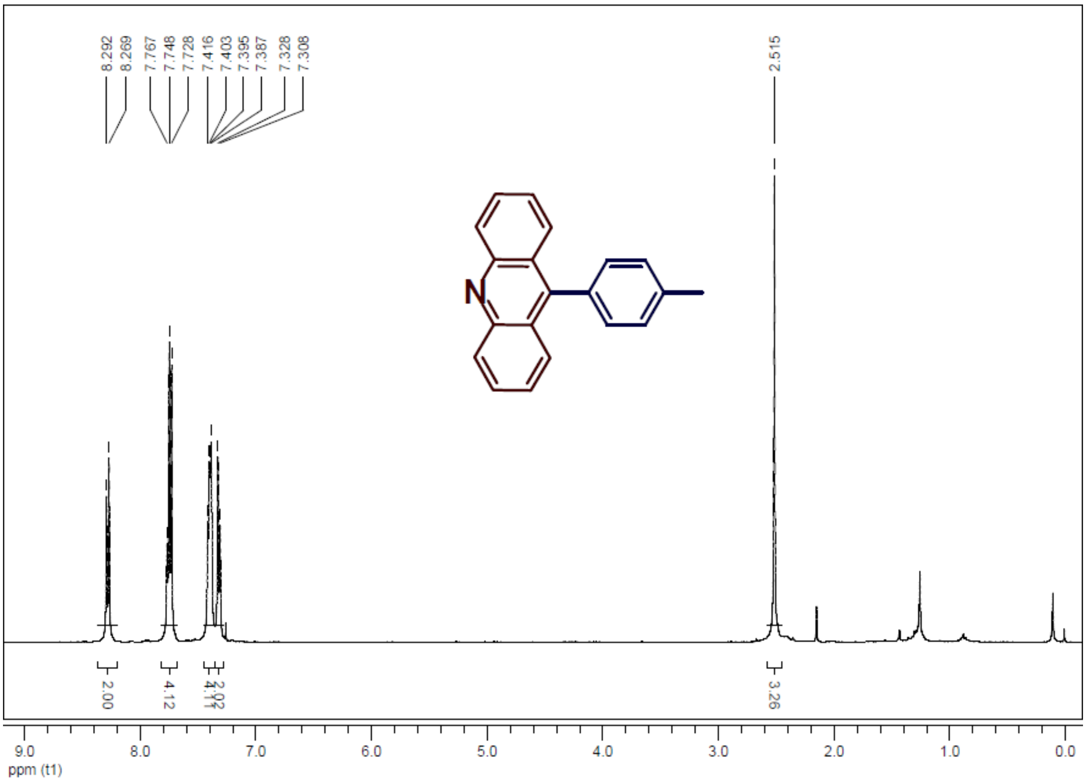

Figure S19. ^{1}H NMR spectrum of compound **7c.**

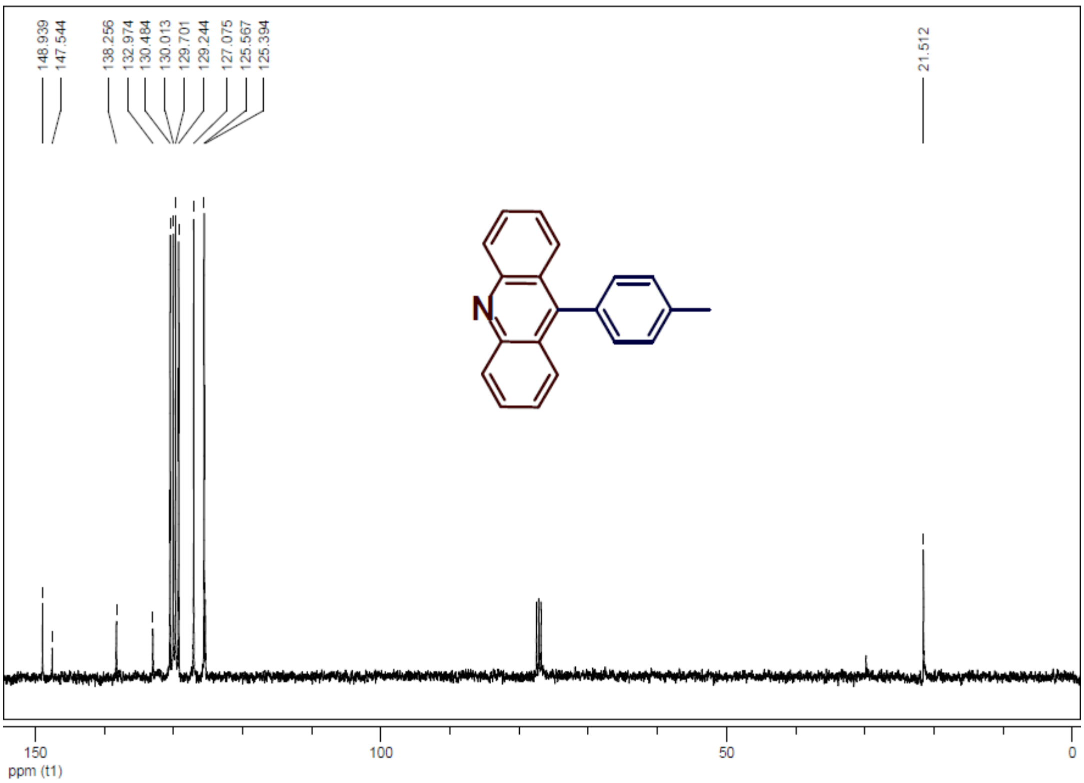

Figure S20. ^{13}C NMR spectrum of compound **7c**.

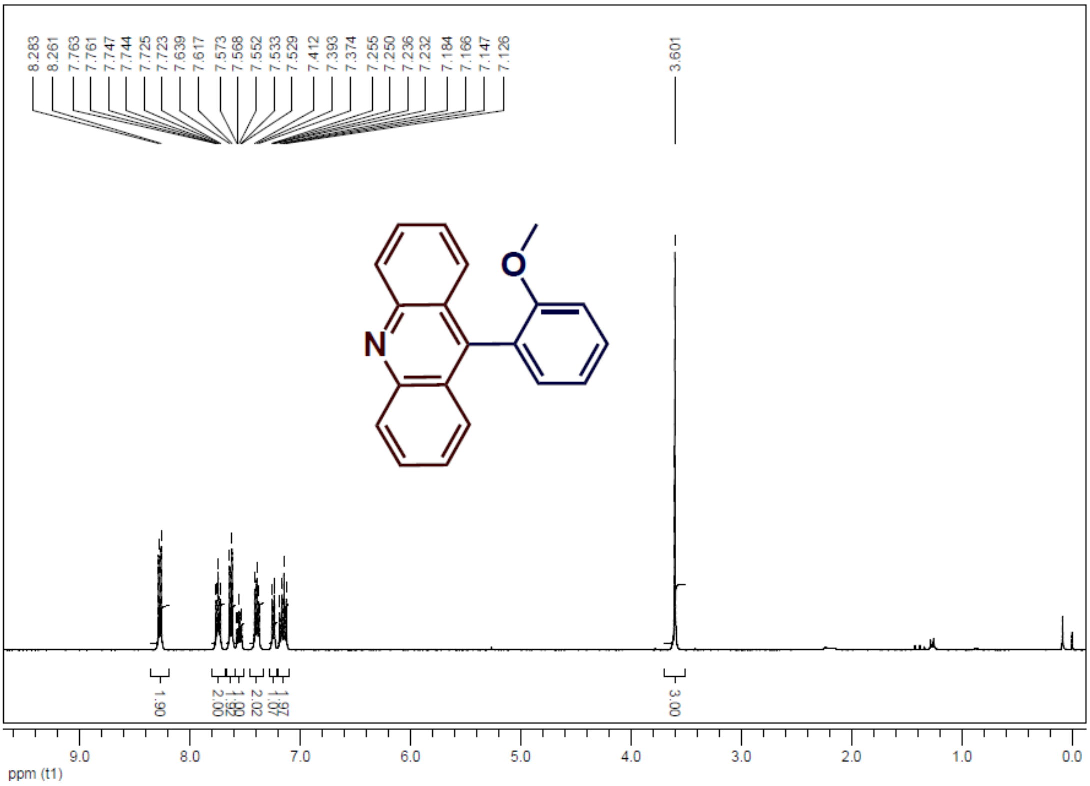

Figure S21. ^{1}H NMR spectrum of compound **8a.**

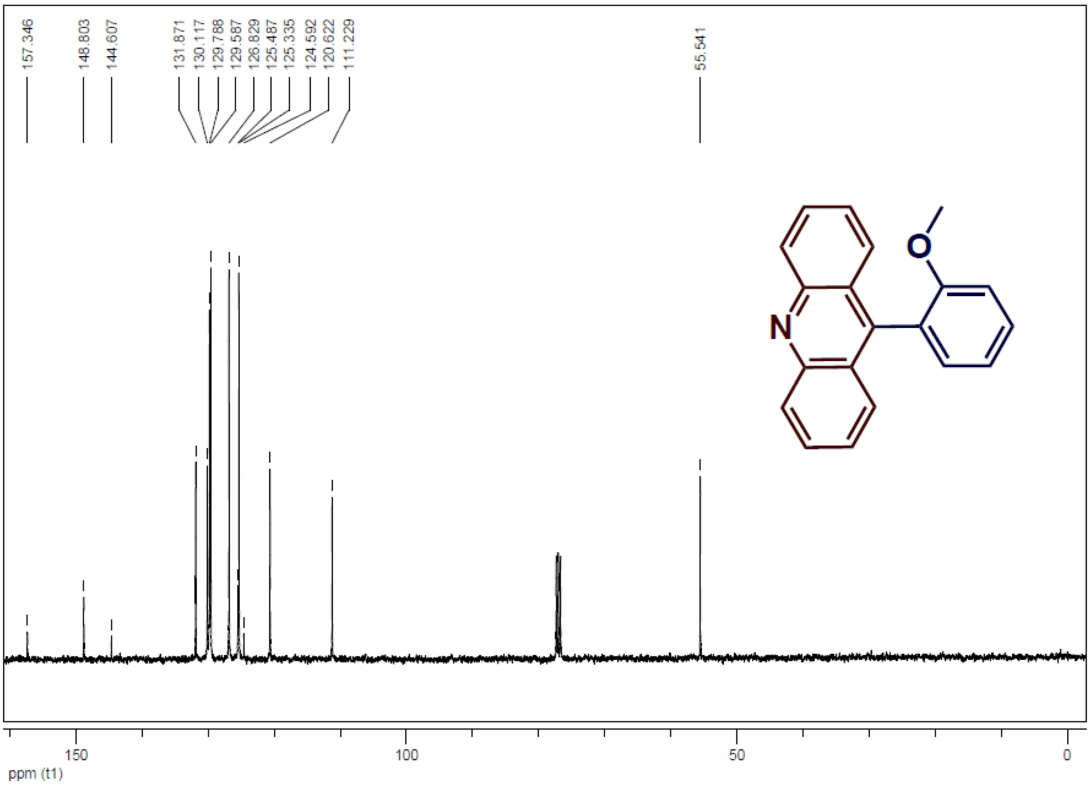

Figure S22. ^{13}C NMR spectrum of compound **8a**.

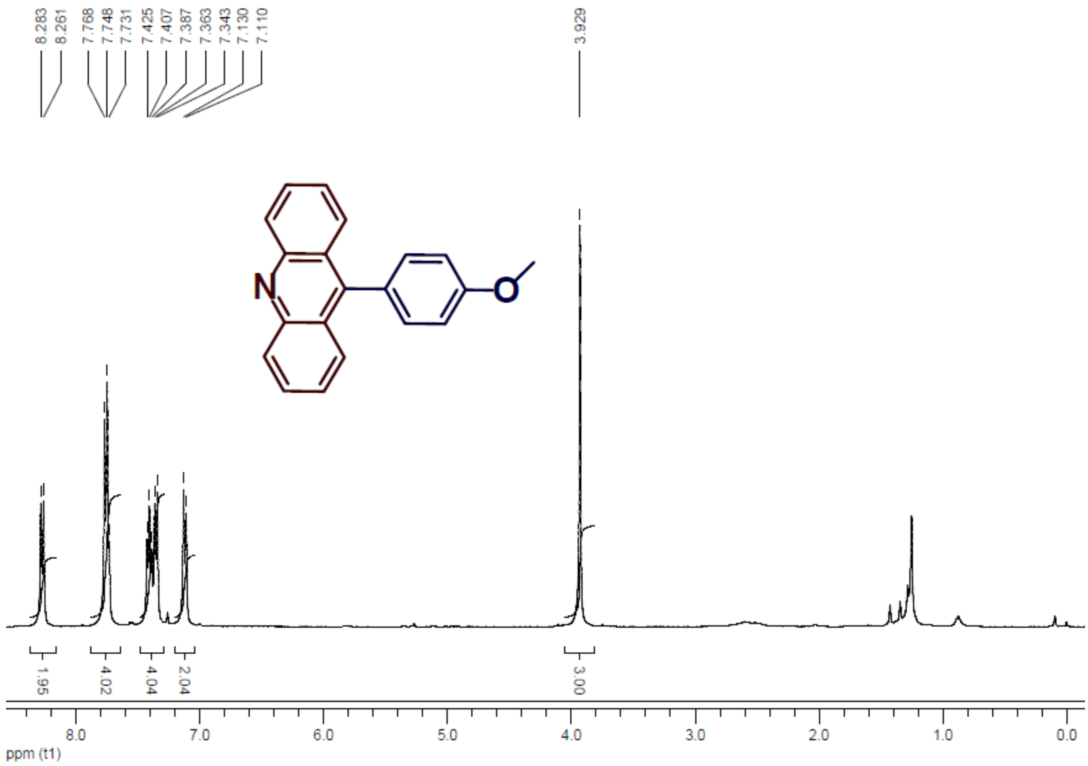

Figure S23. ^{1}H NMR spectrum of compound **8b.**

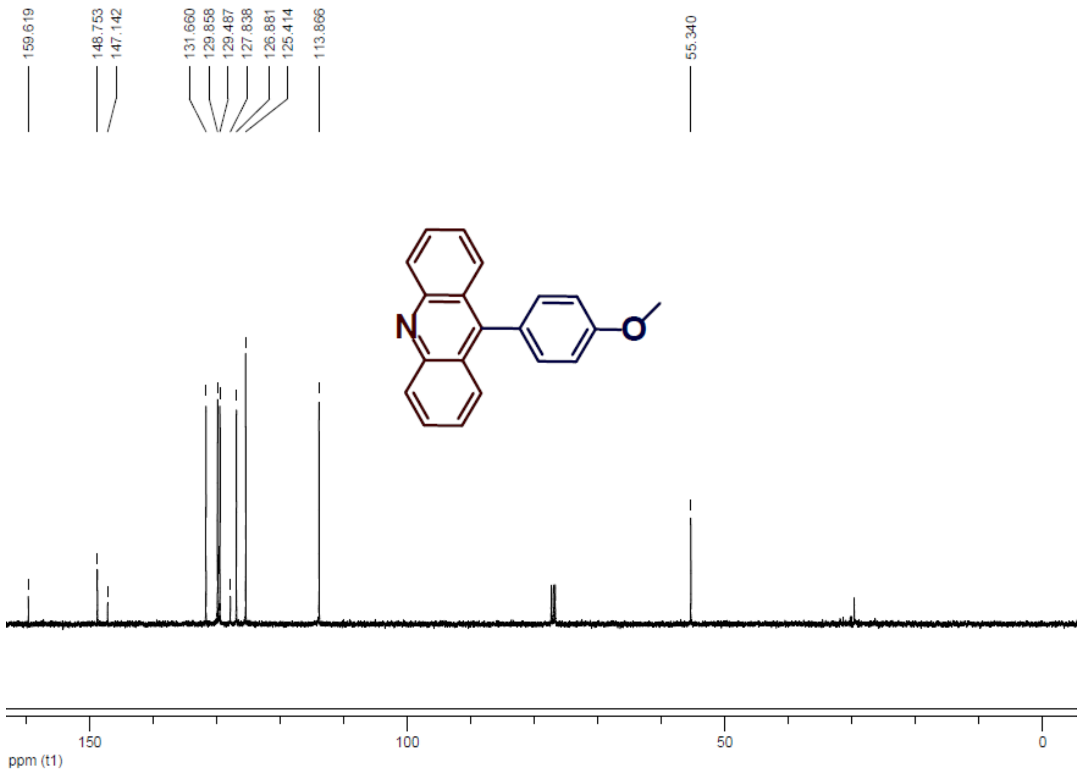

Figure S24. ^{13}C NMR spectrum of compound **8b**.

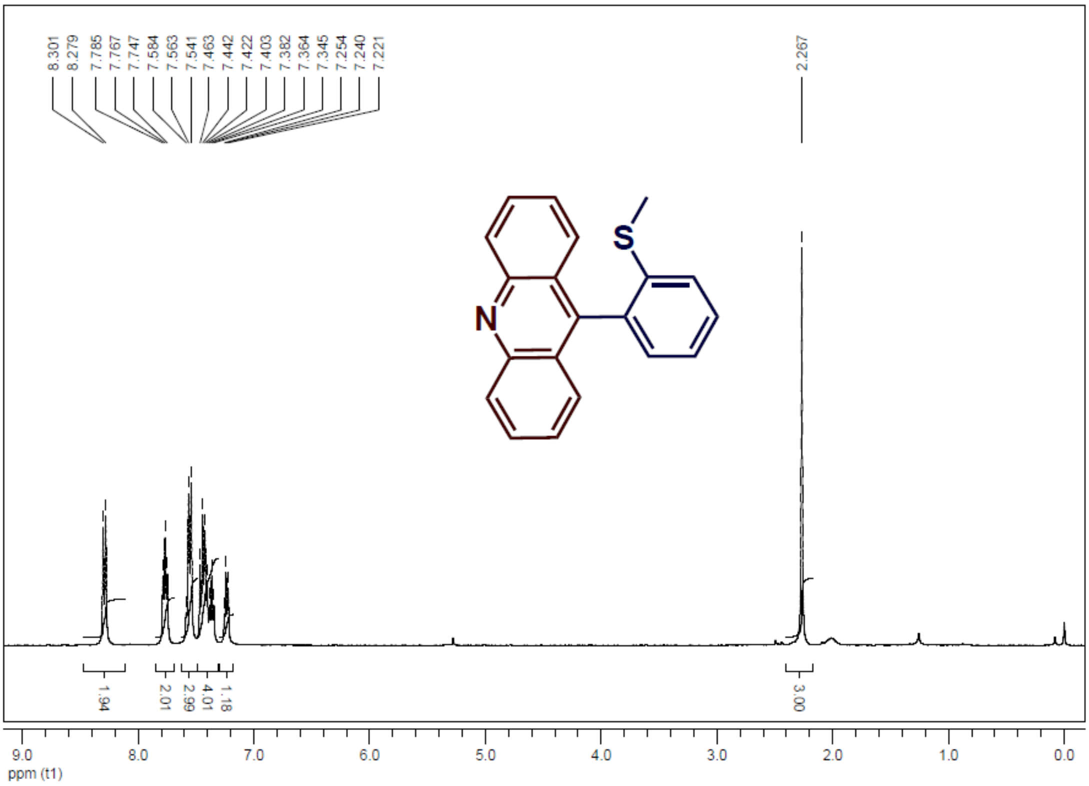

Figure S25. ^{1}H NMR spectrum of compound **9a.**

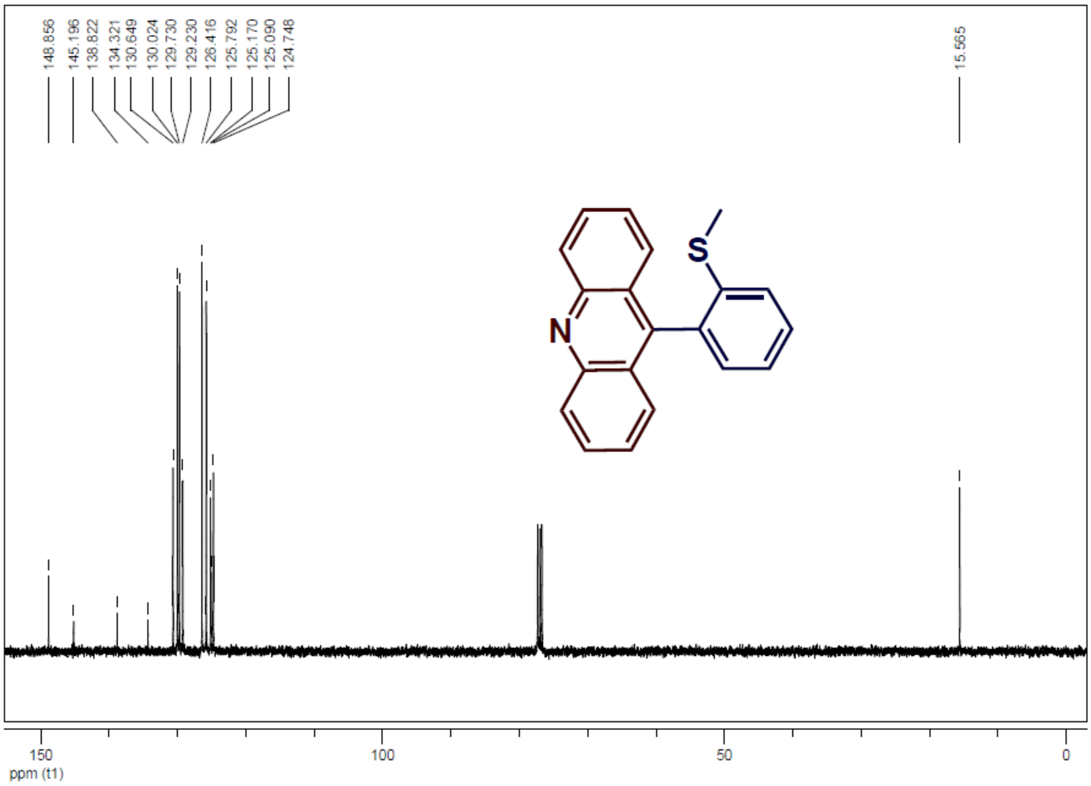

Figure S26. ^{13}C NMR spectrum of compound **9a**.

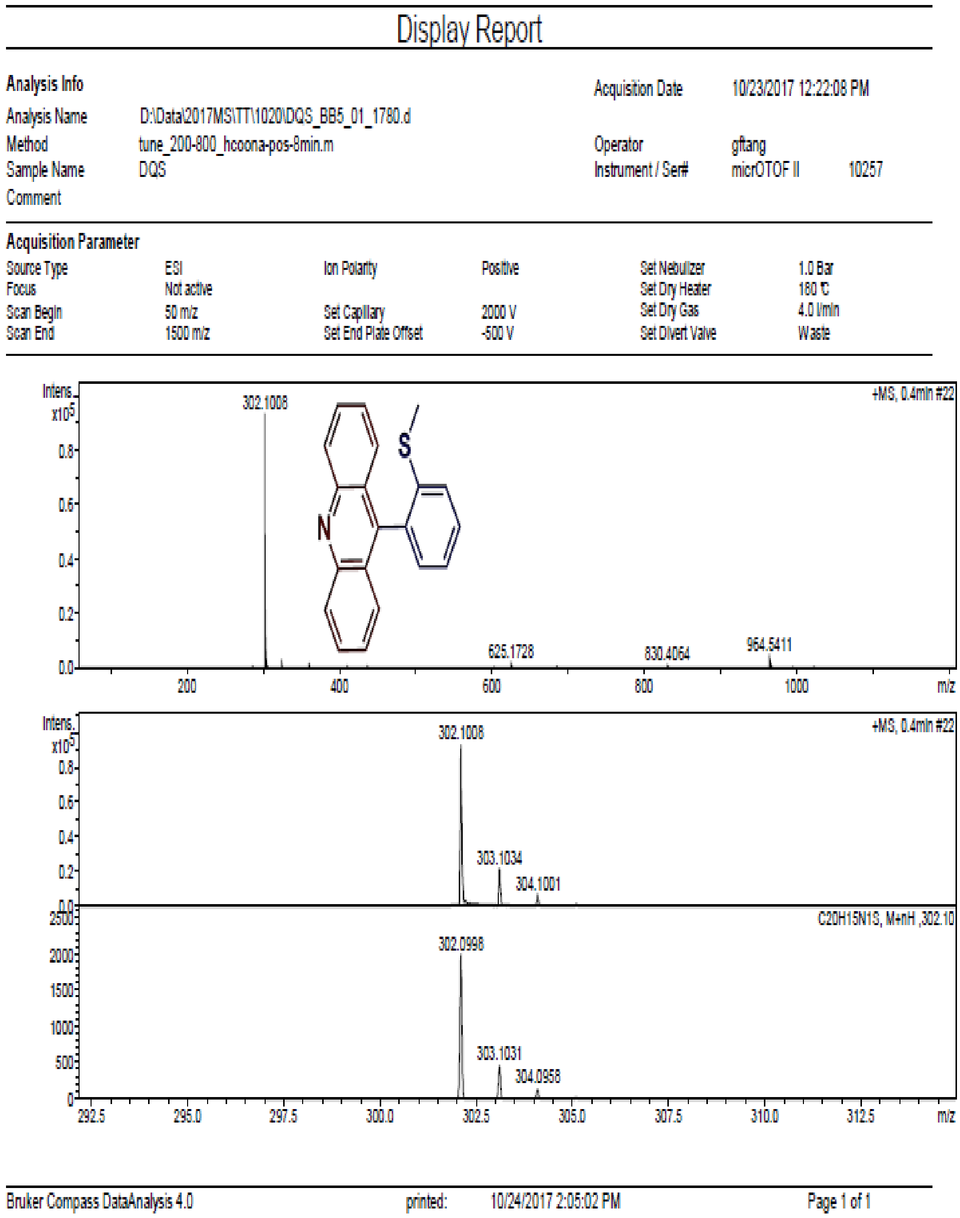

Figure S27. ESI-MS spectrum of compound **9a**

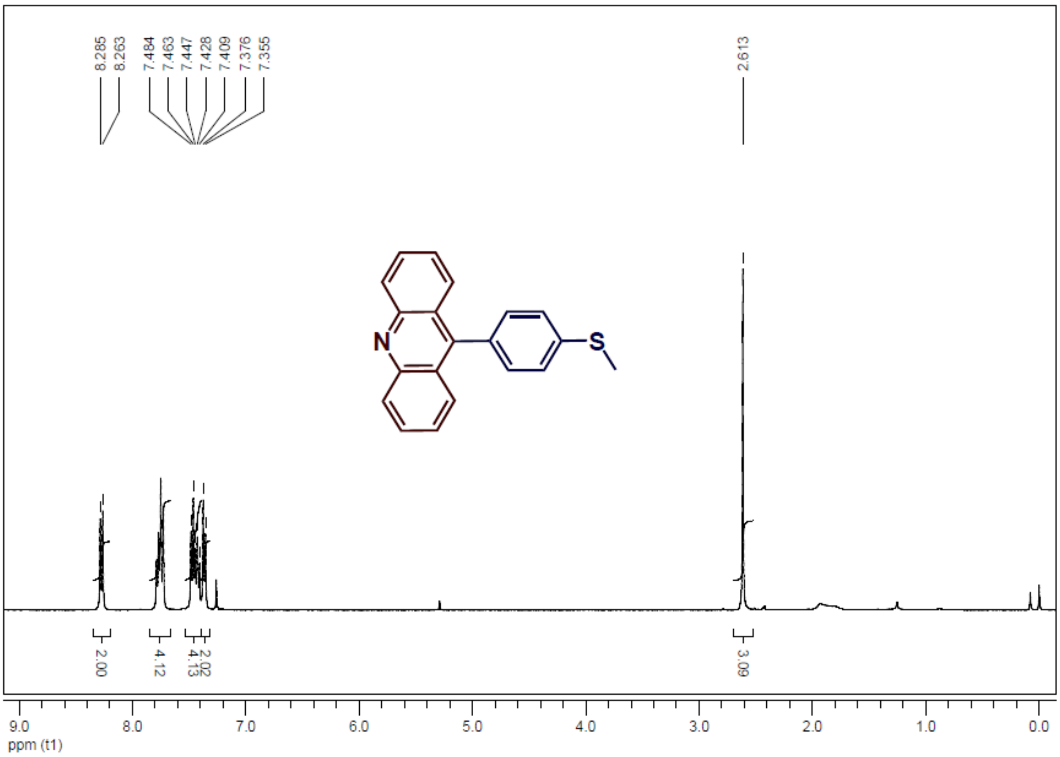

Figure S28. ^{1}H NMR spectrum of compound **9b.**

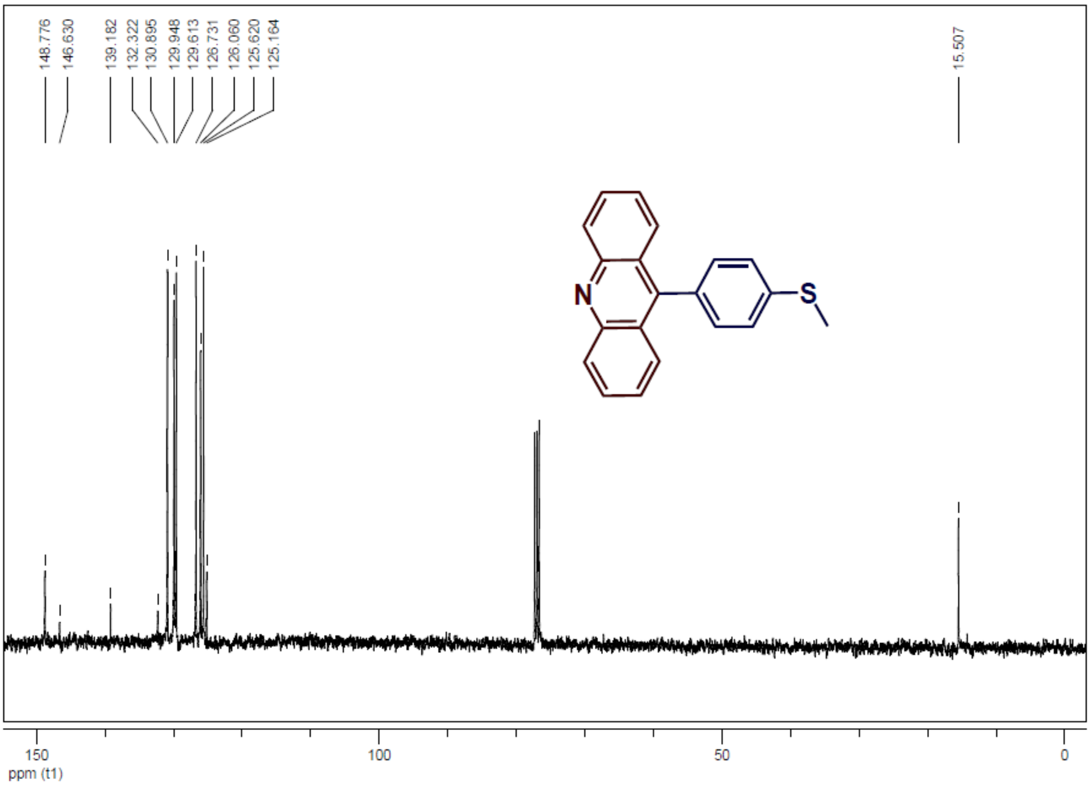

Figure S29. ^{13}C NMR spectrum of compound **9b**.

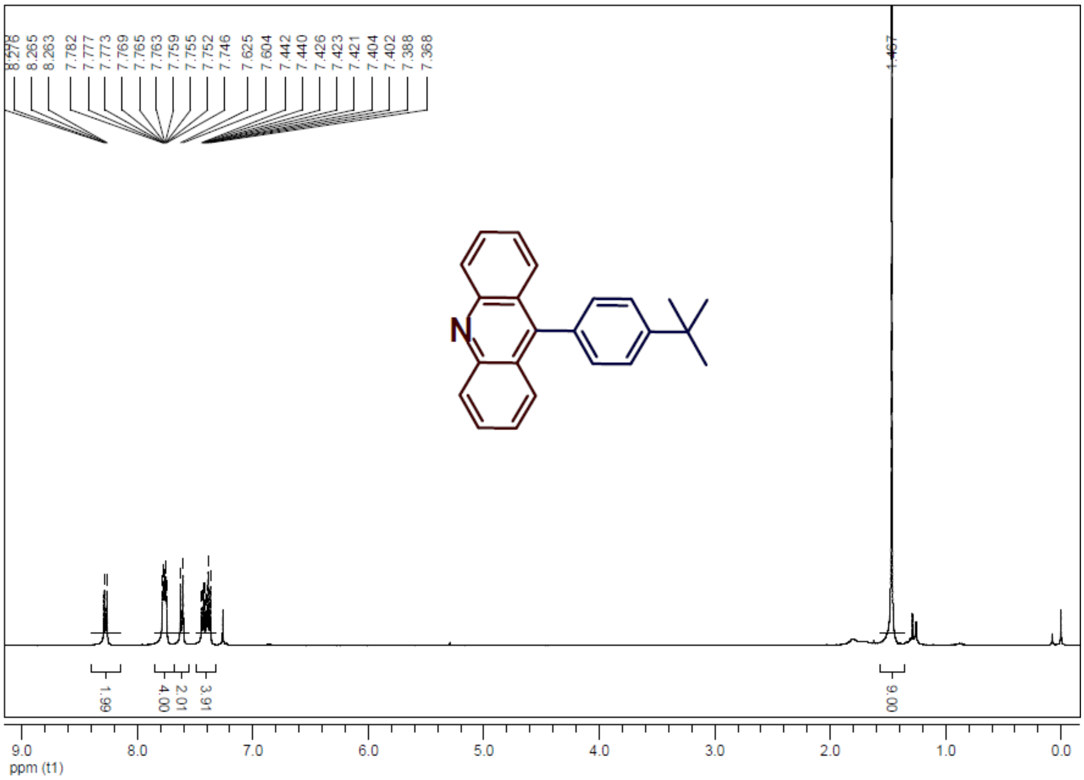

Figure S30. ^{1}H NMR spectrum of compound **10.**

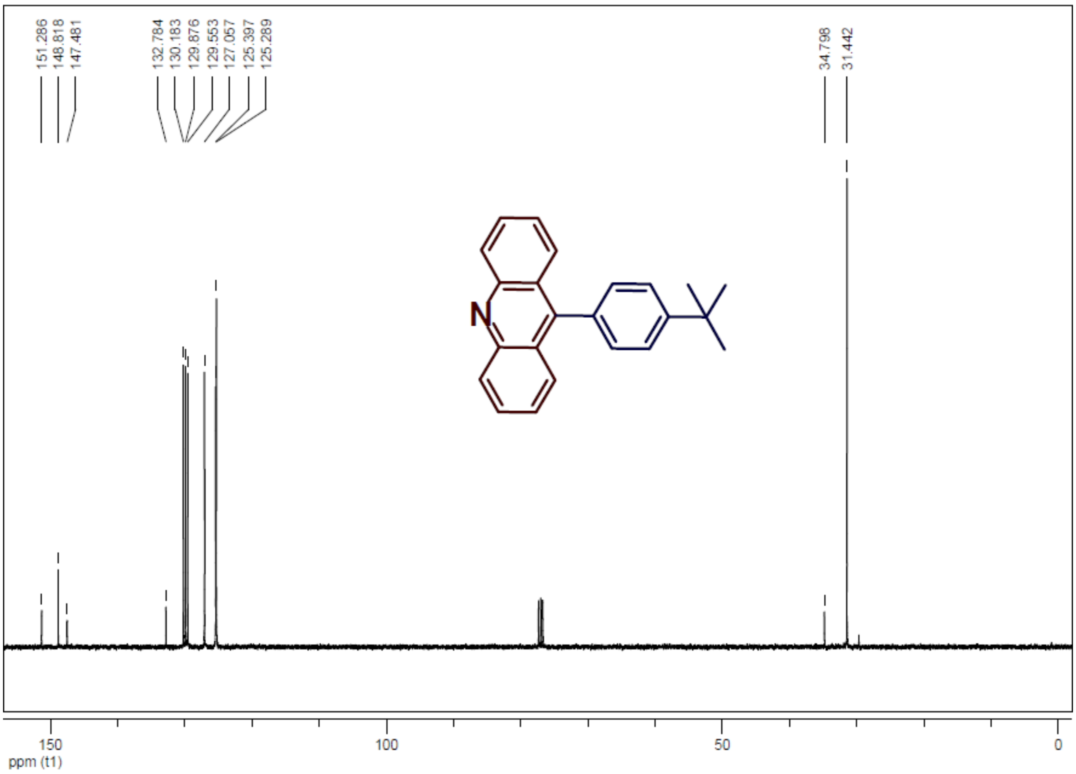

Figure S31. ^{13}C NMR spectrum of compound **10**.

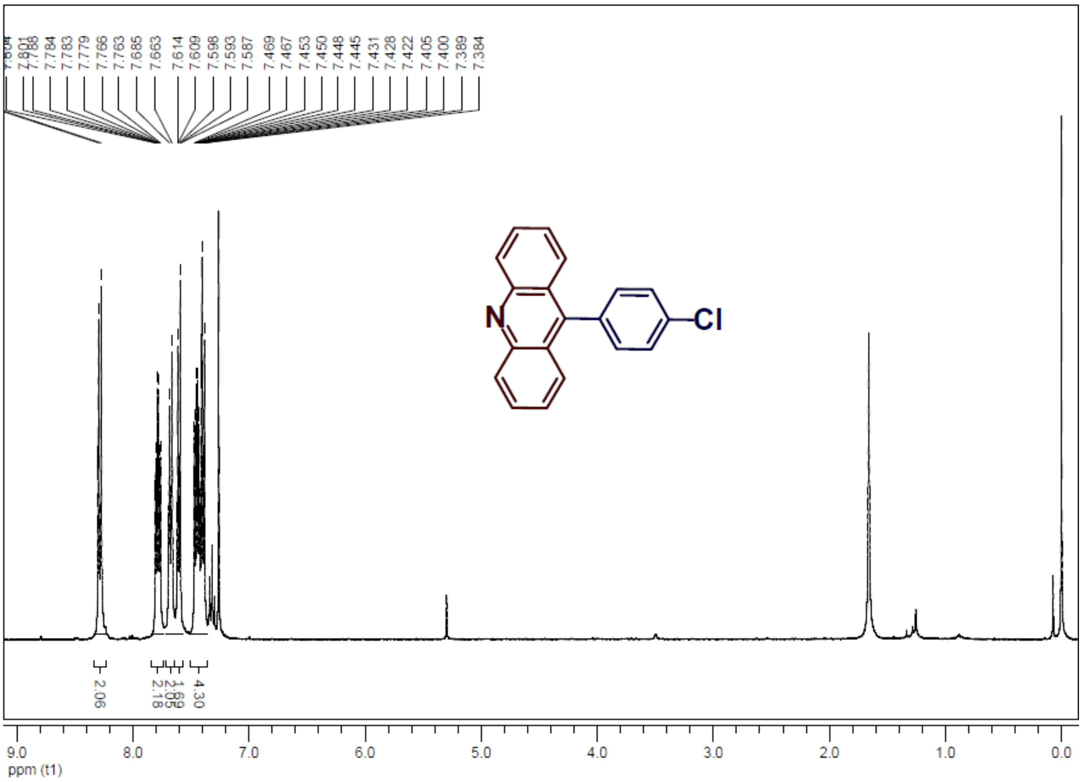

Figure S32. [1]H NMR spectrum of compound **11.**

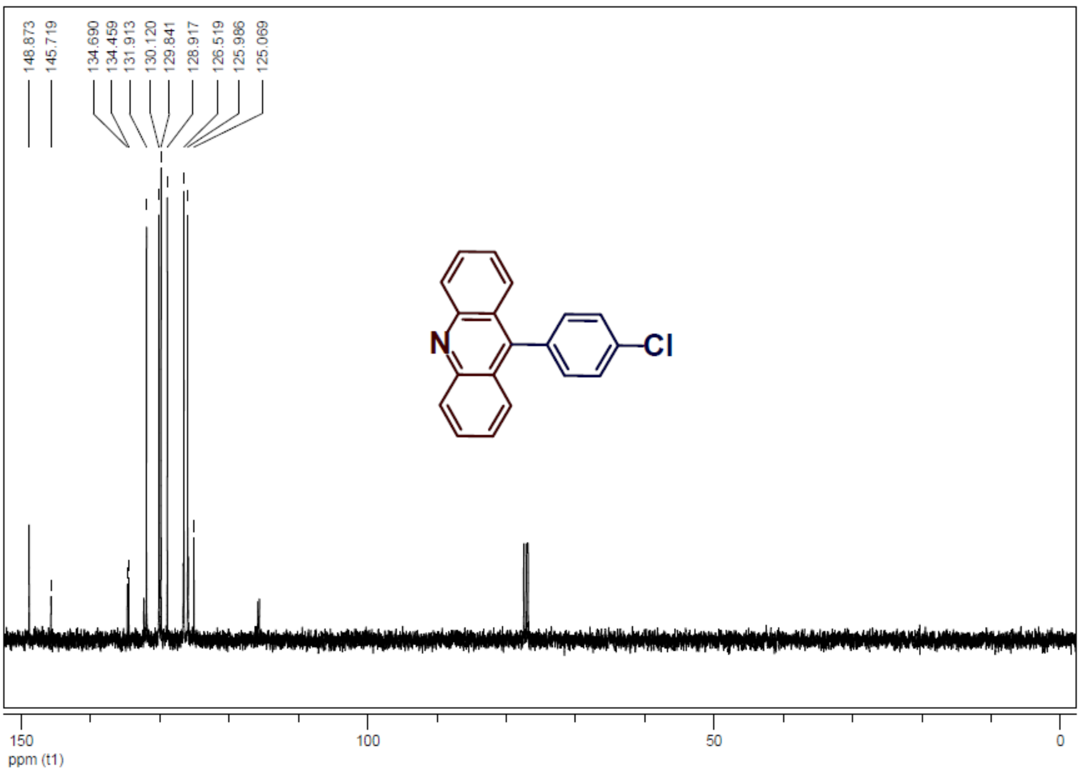

Figure S33. [13]C NMR spectrum of compound **11**.

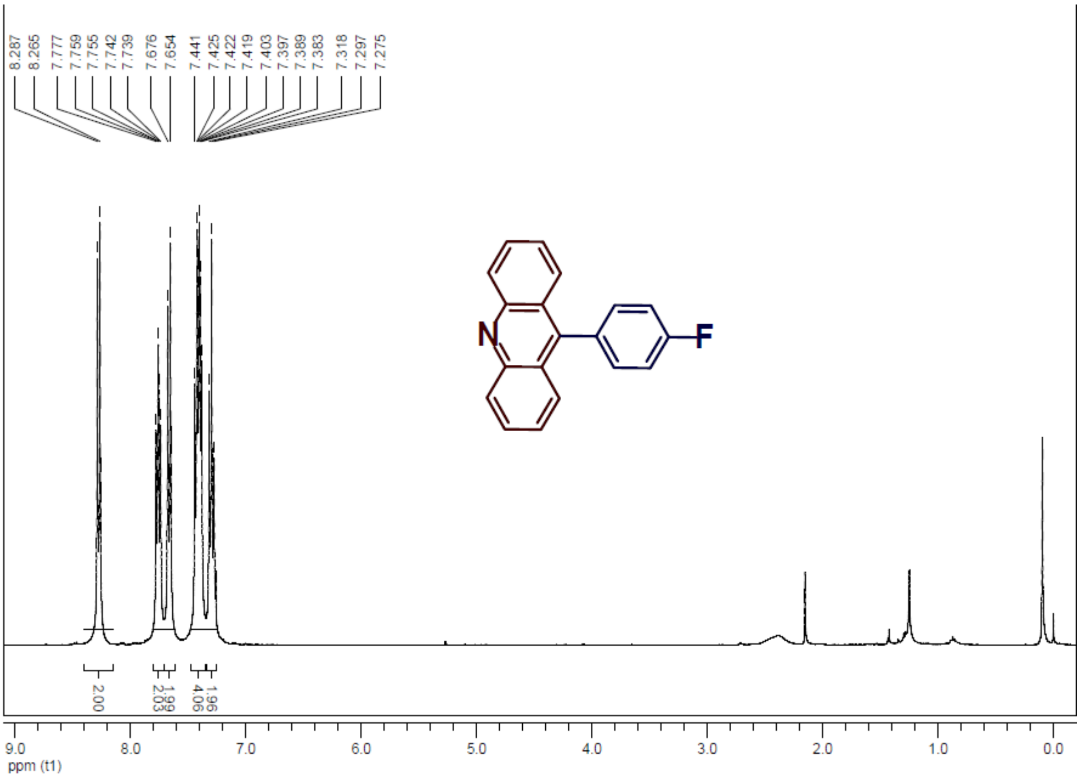

Figure S34. ¹H NMR spectrum of compound **12a.**

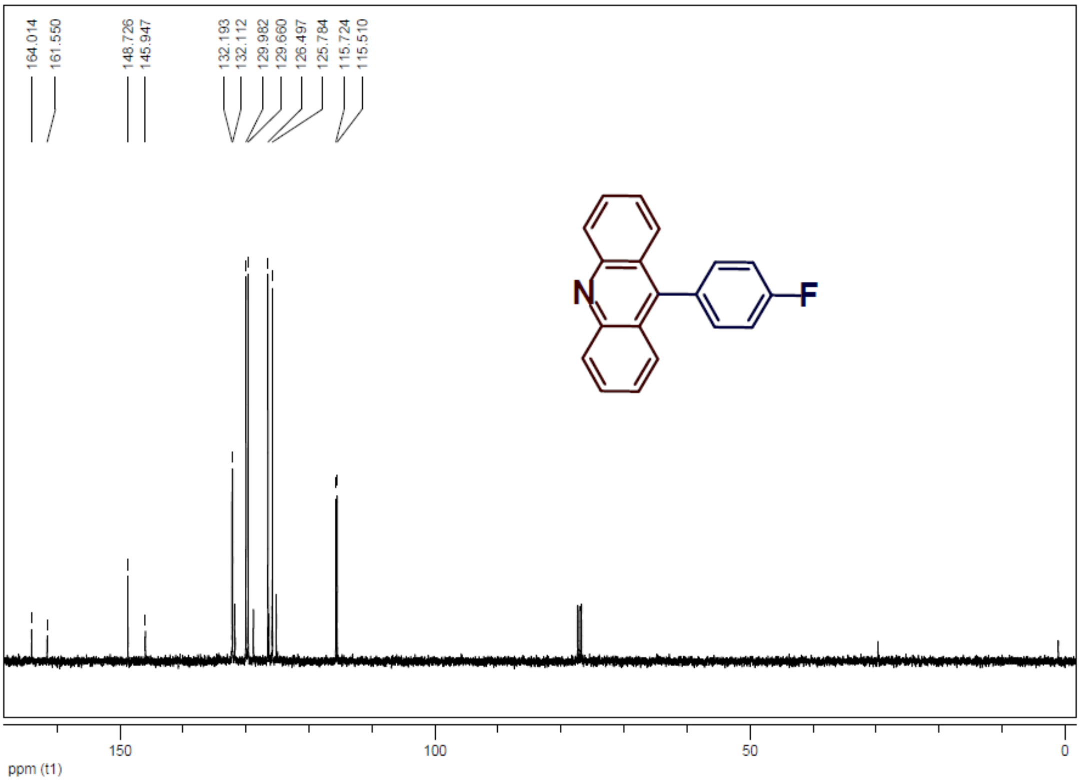

Figure S35. ¹³C NMR spectrum of compound **12a**.

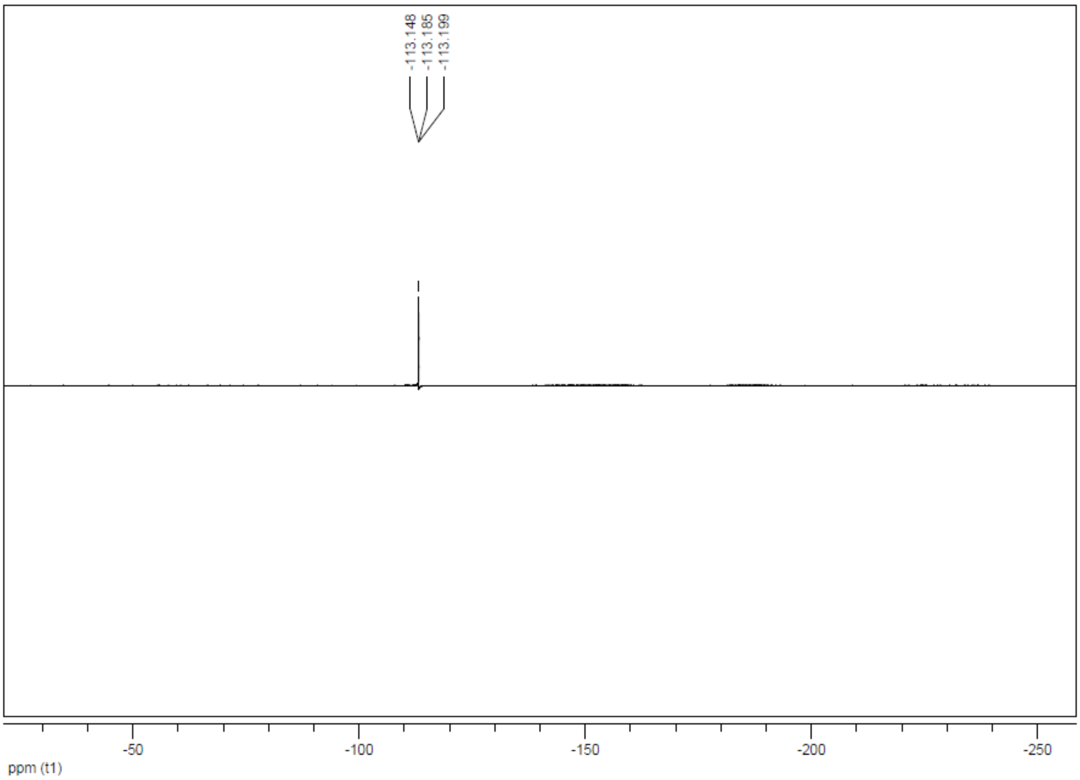

Figure S36. ^{19}F NMR spectrum of compound **12a**.

Display Report

Analysis Info

Analysis Name	D:\Data\2016MS\TT\0419\DQ-1604193_RD7_01_8844.d	Acquisition Date	4/21/2016 4:26:30 PM
Method	tune_200-800_hcoona-pos-10min.m	Operator	gftang
Sample Name	DQ-1604193	Instrument / Ser#	micrOTOF II 10257
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
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Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

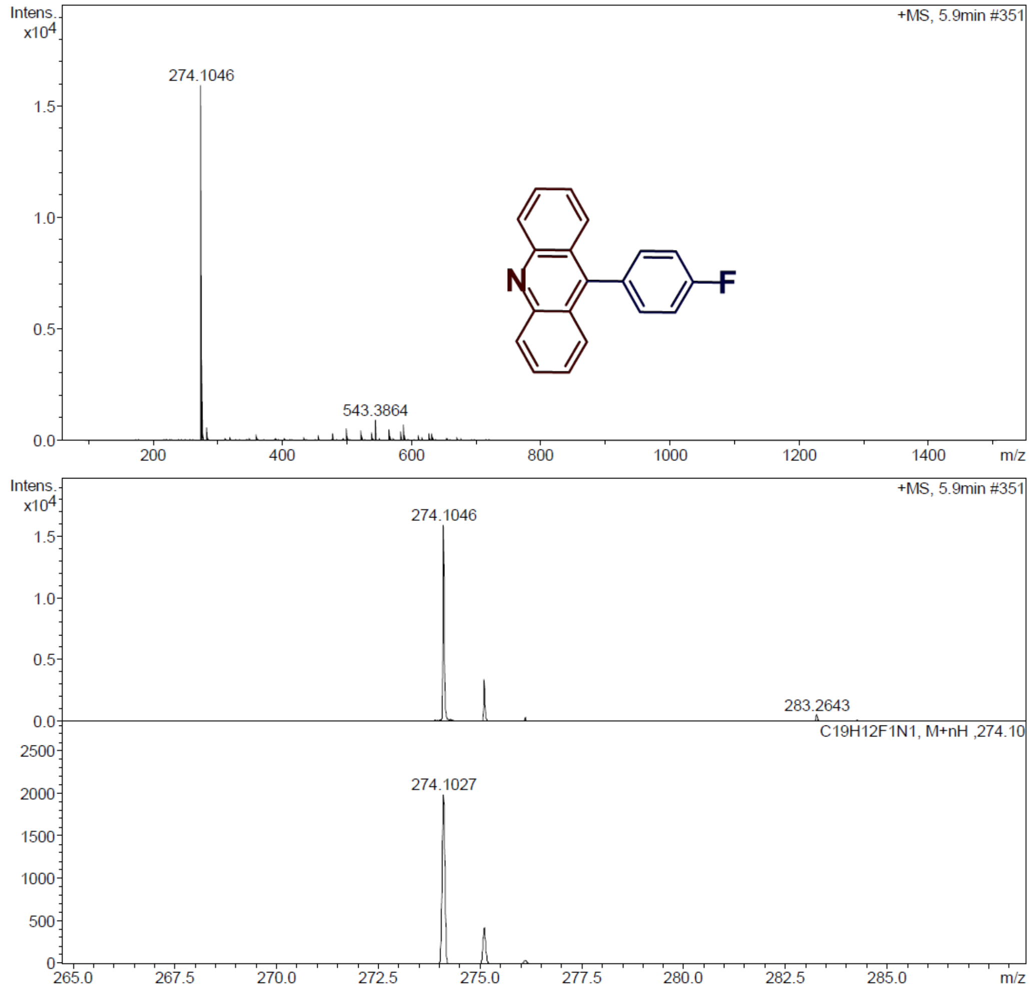

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Figure S37. ESI-MS spectrum of compound **12a**

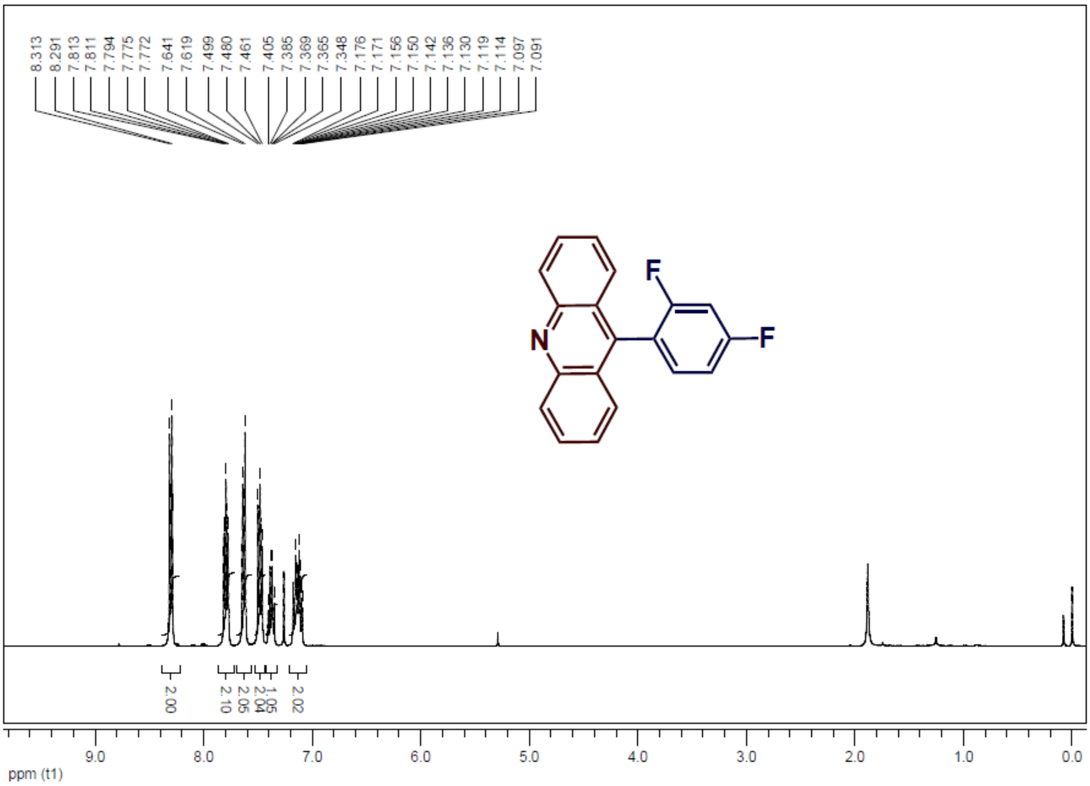

Figure S38. ^{1}H NMR spectrum of compound **12b**

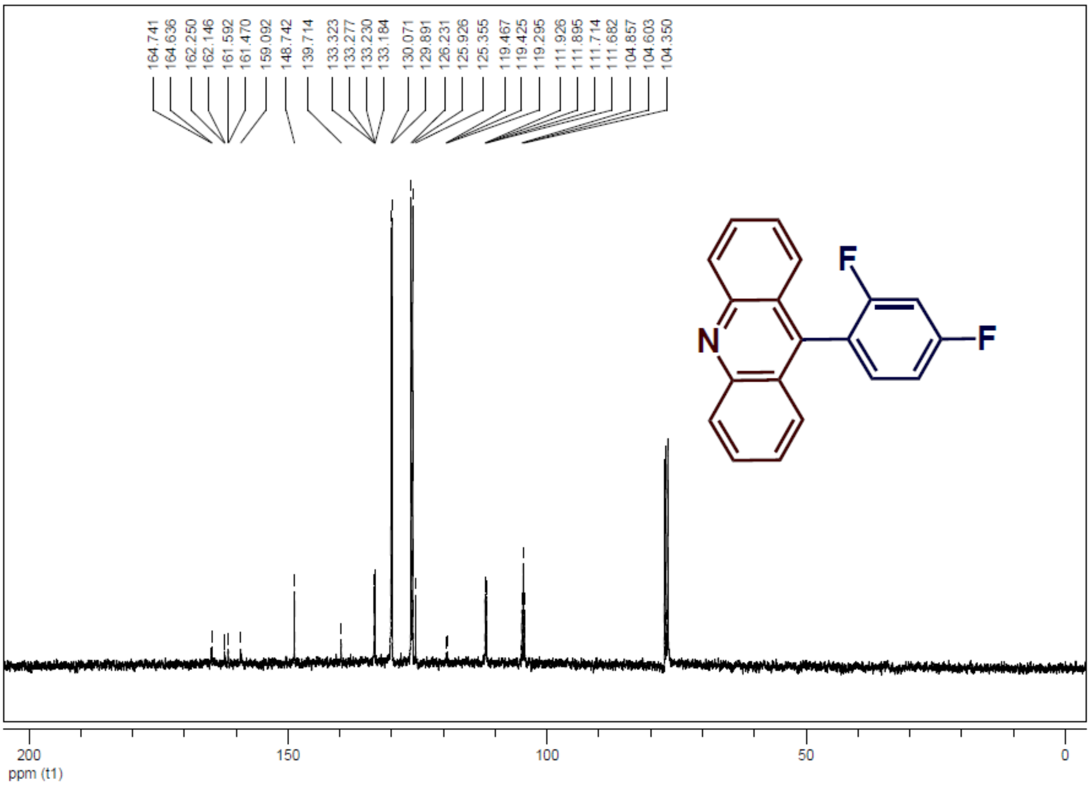

Figure S39. ^{13}C NMR spectrum of compound **12b**.

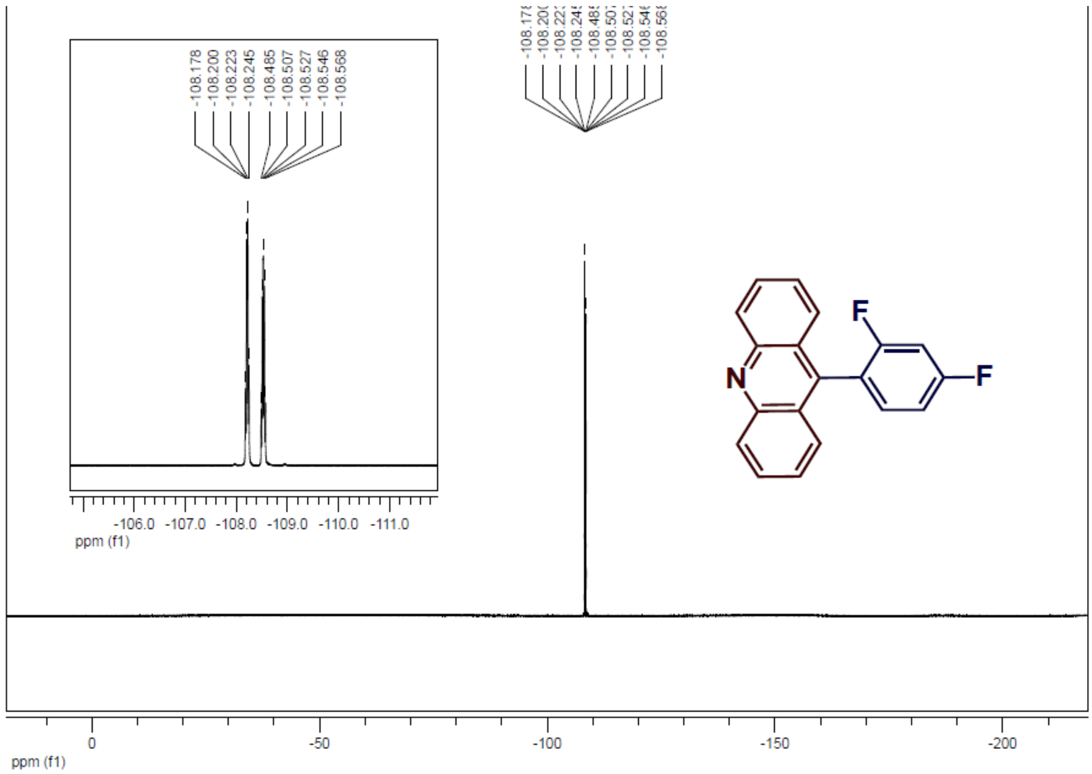

Figure S40. ^{19}F NMR spectrum of compound **12b**.

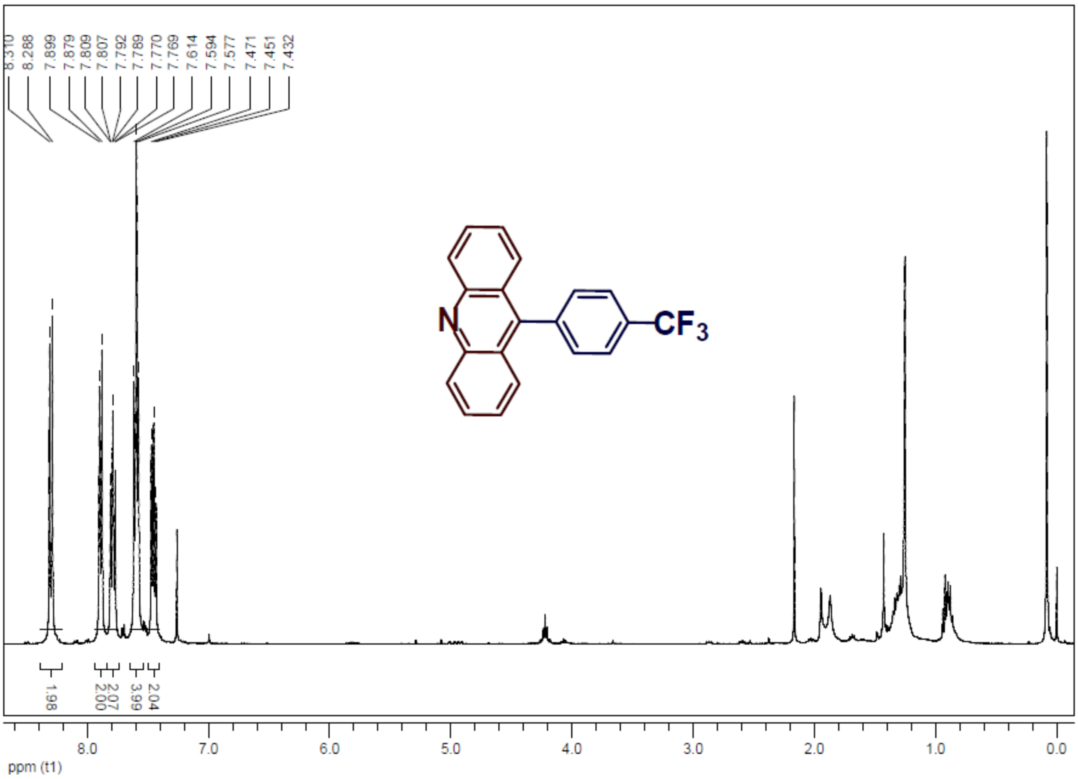

Figure S41. ^{1}H NMR spectrum of compound **13.**

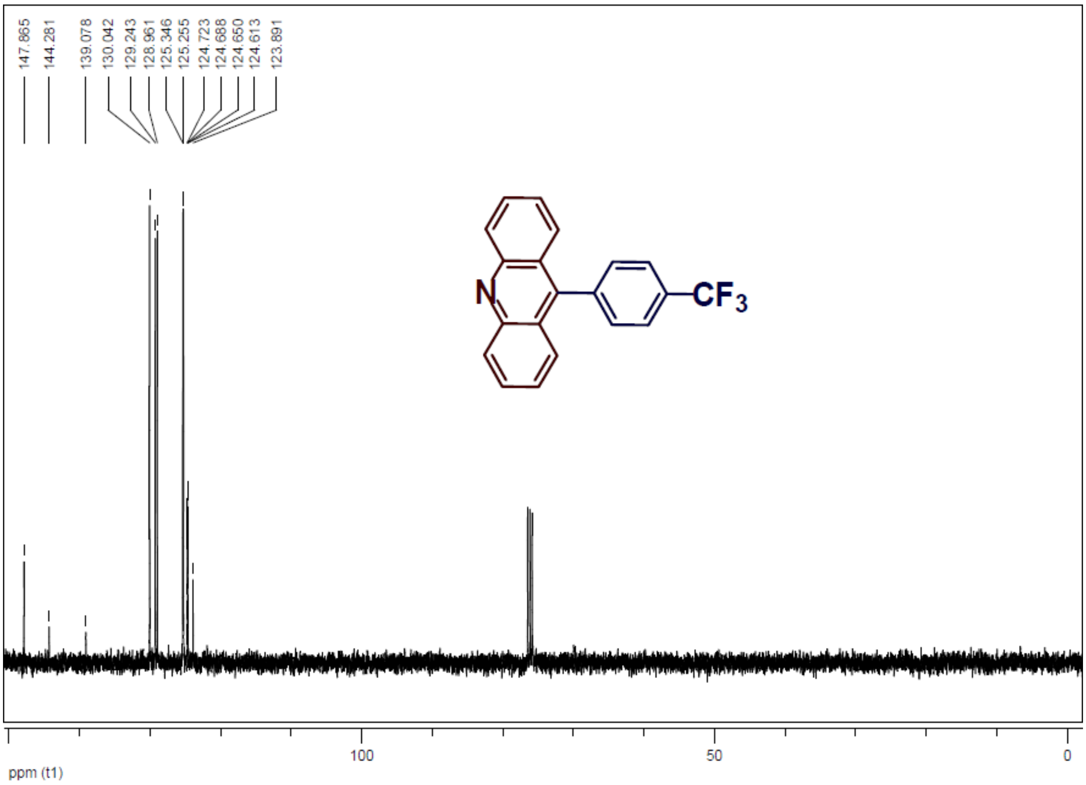

Figure S42. ^{13}C NMR spectrum of compound **13**.

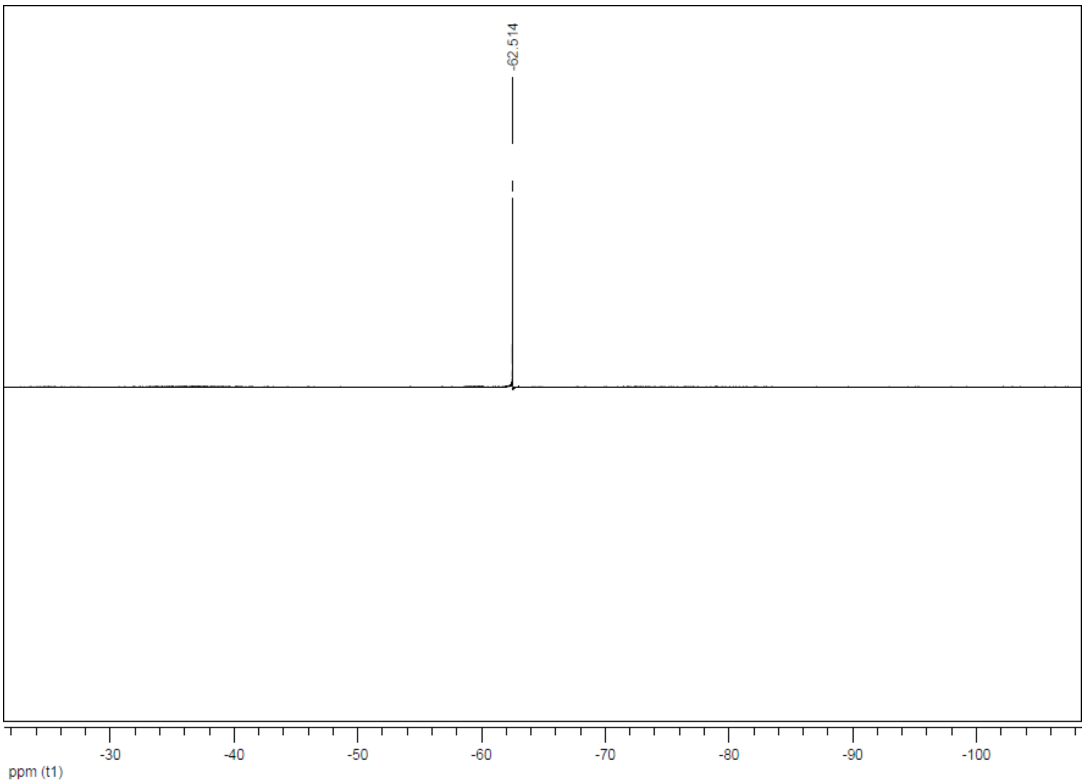

Figure S43. ^{19}F NMR spectrum of compound **13**.

Display Report

Analysis Info

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Sample Name	DQ-1604194	Instrument / Ser#	micrOTOF II 10257
Comment			

Acquisition Parameter

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Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

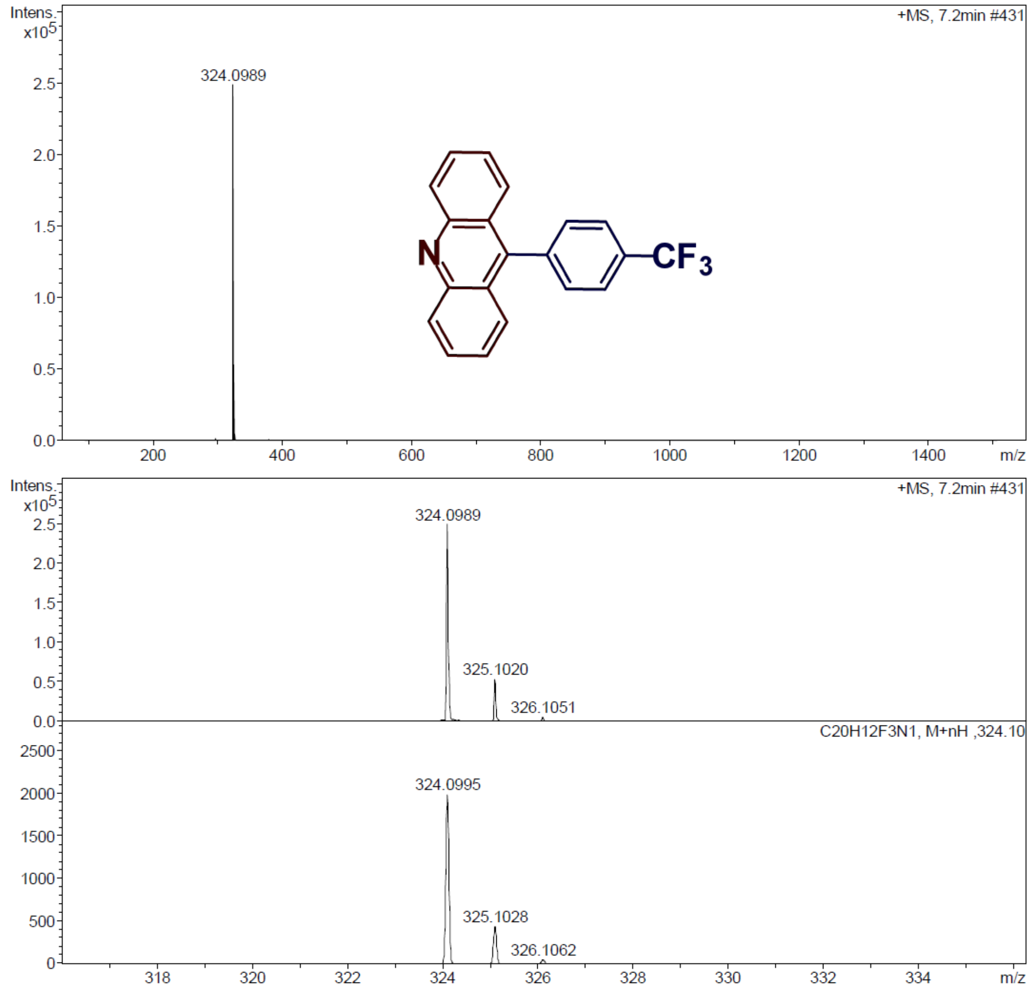

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Figure S44. ESI-MS spectrum of compound **13.**

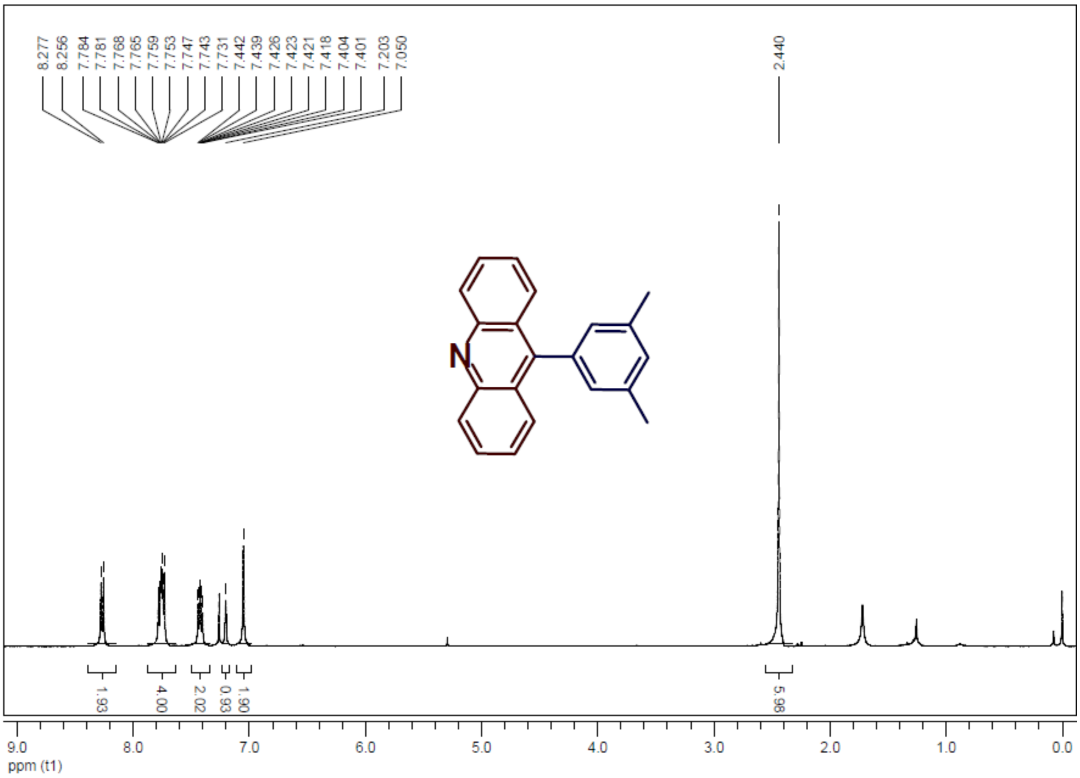

Figure S45. ^{1}H NMR spectrum of compound **9.**

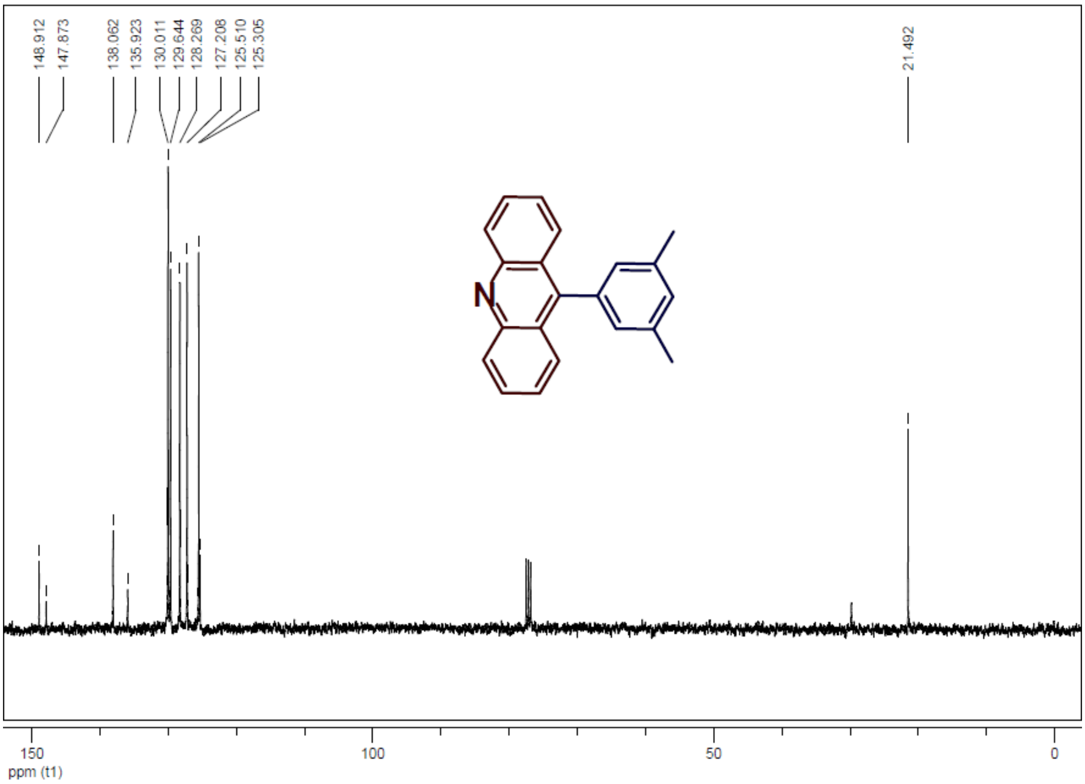

Figure S46. ^{13}C NMR spectrum of compound **9**.

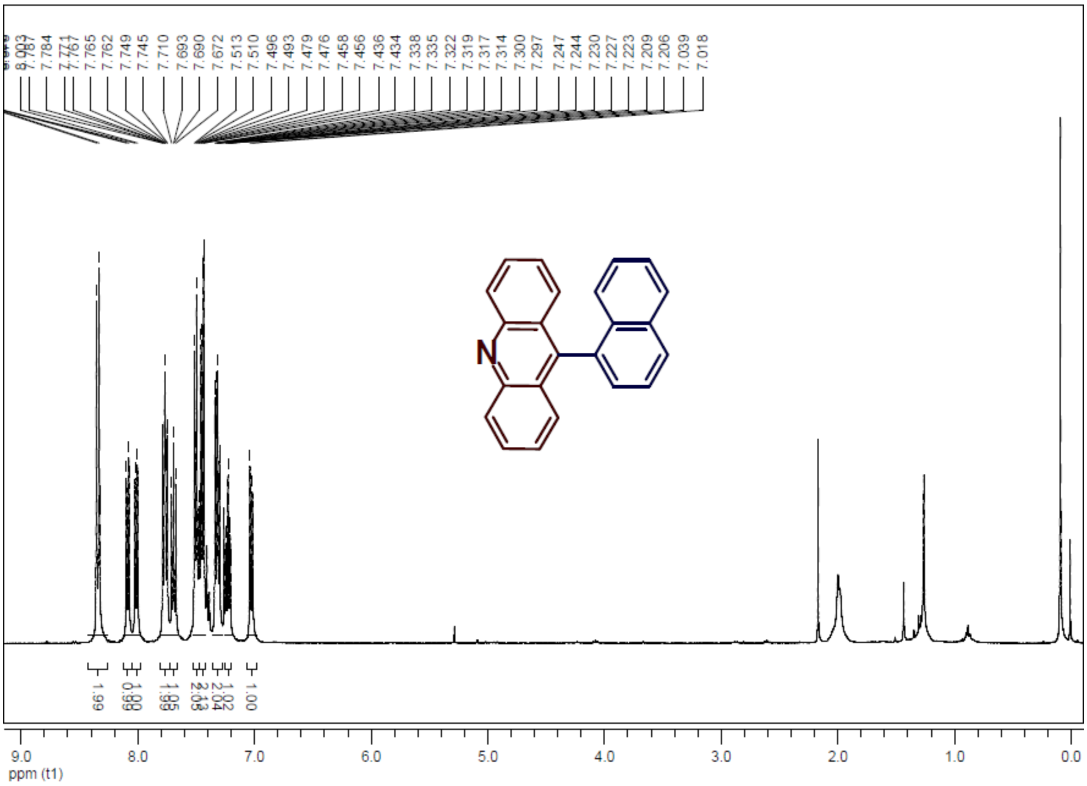

Figure S47. ^{1}H NMR spectrum of compound **15.**

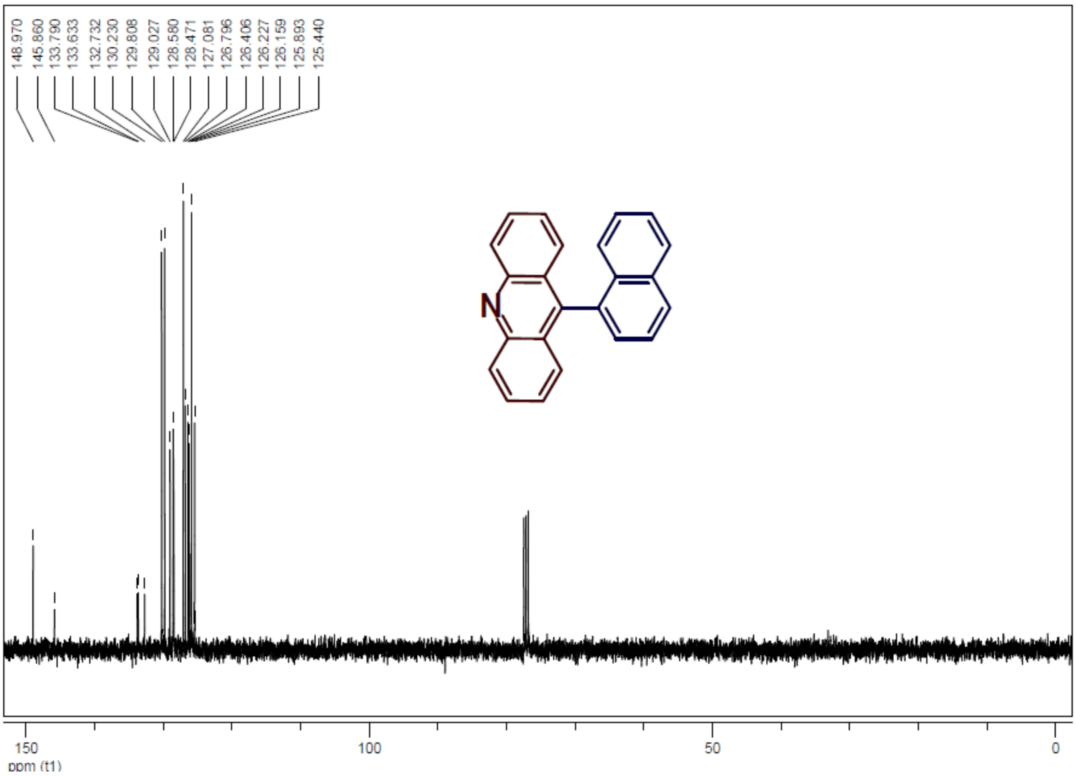

Figure S48. ^{13}C NMR spectrum of compound **15**.

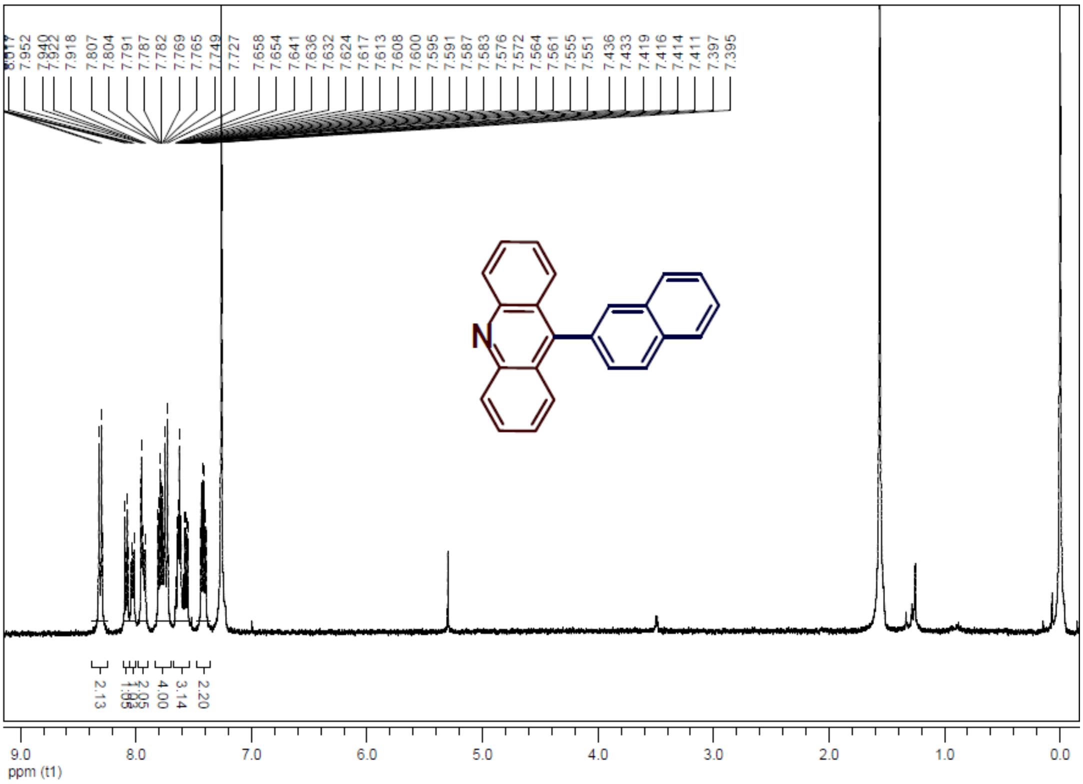

Figure S49. ^{1}H NMR spectrum of compound **16.**

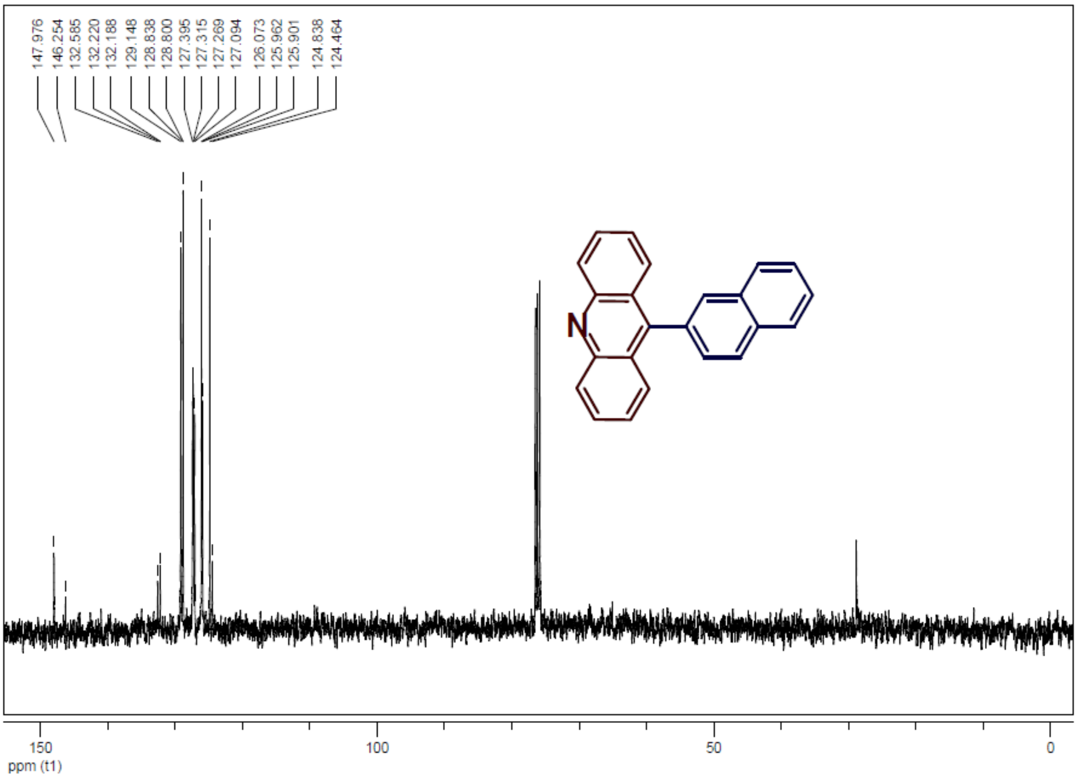

Figure S50. ^{13}C NMR spectrum of compound **16**.

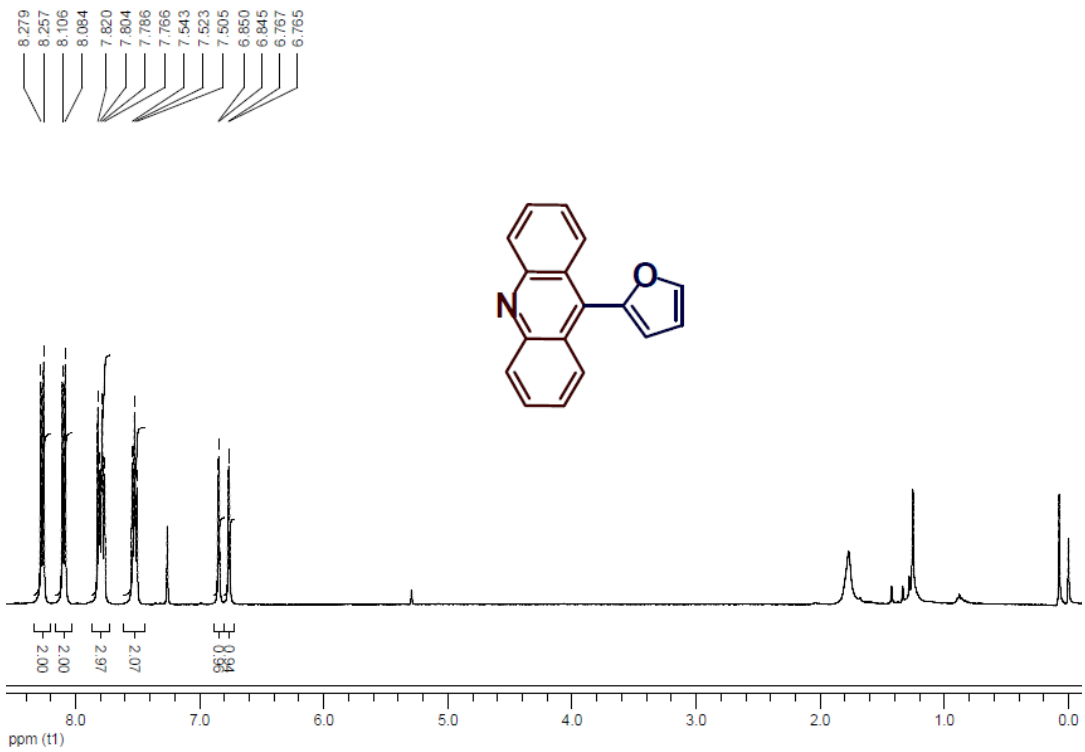

Figure S51. ^{1}H NMR spectrum of compound **17.**

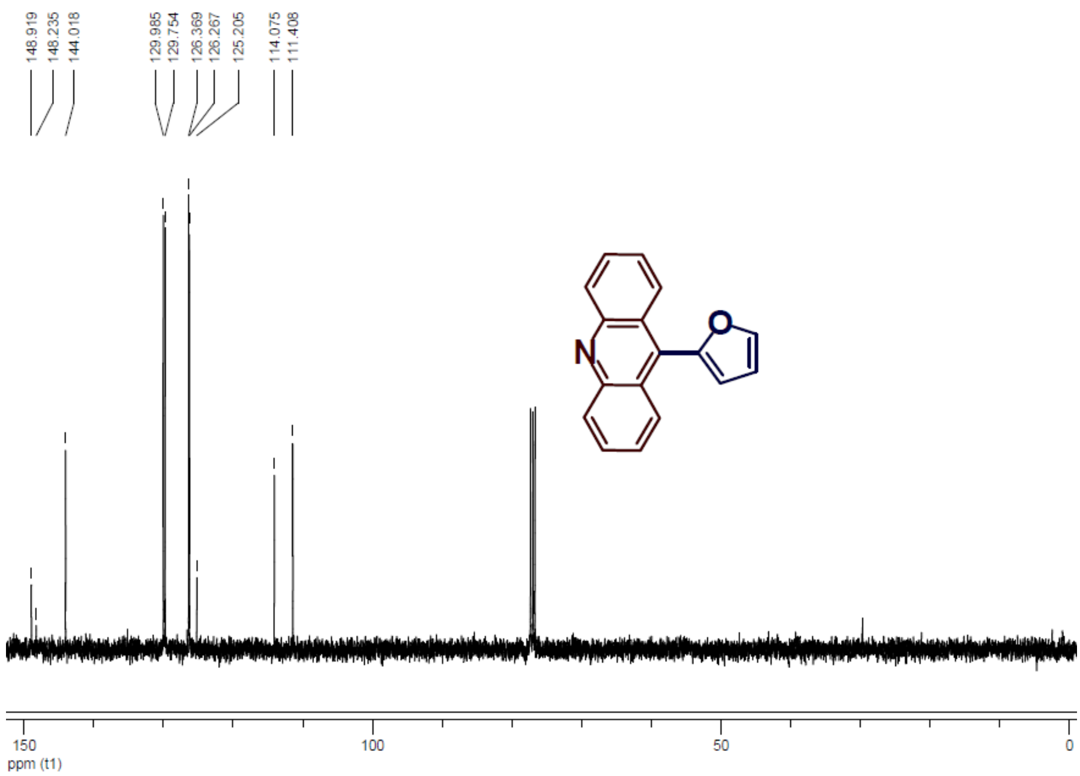

Figure S52. ^{13}C NMR spectrum of compound **17**.

Display Report

Analysis Info		Acquisition Date	4/20/2016 5:19:00 AM
Analysis Name	D:\Data\2016MS\TT\0419\DQ-1604195_RC8_01_8812.d		
Method	tune_200-800_hcoona-pos-10min.m	Operator	gftang
Sample Name	DQ-1604195	Instrument / Ser#	micrOTOF II 10257
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 ℃
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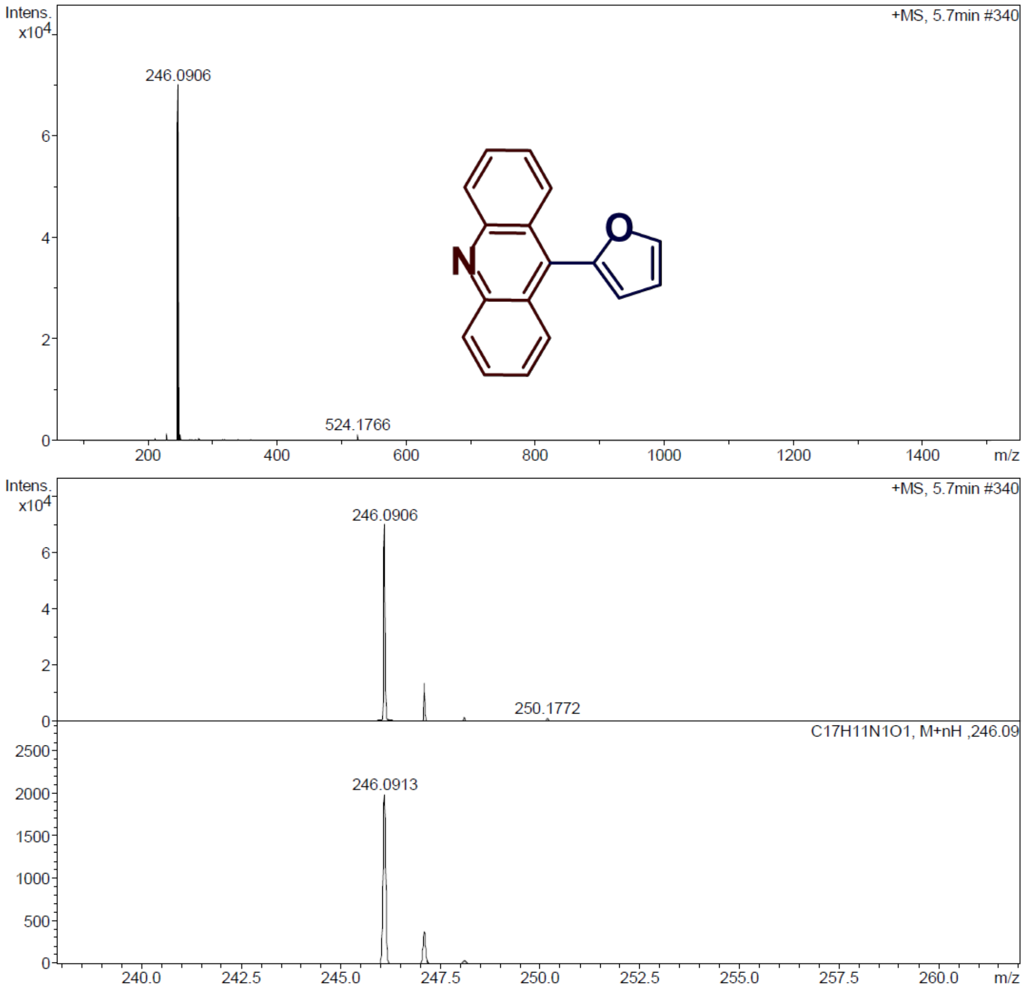

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Figure S53. ESI-MS spectrum of compound **17**

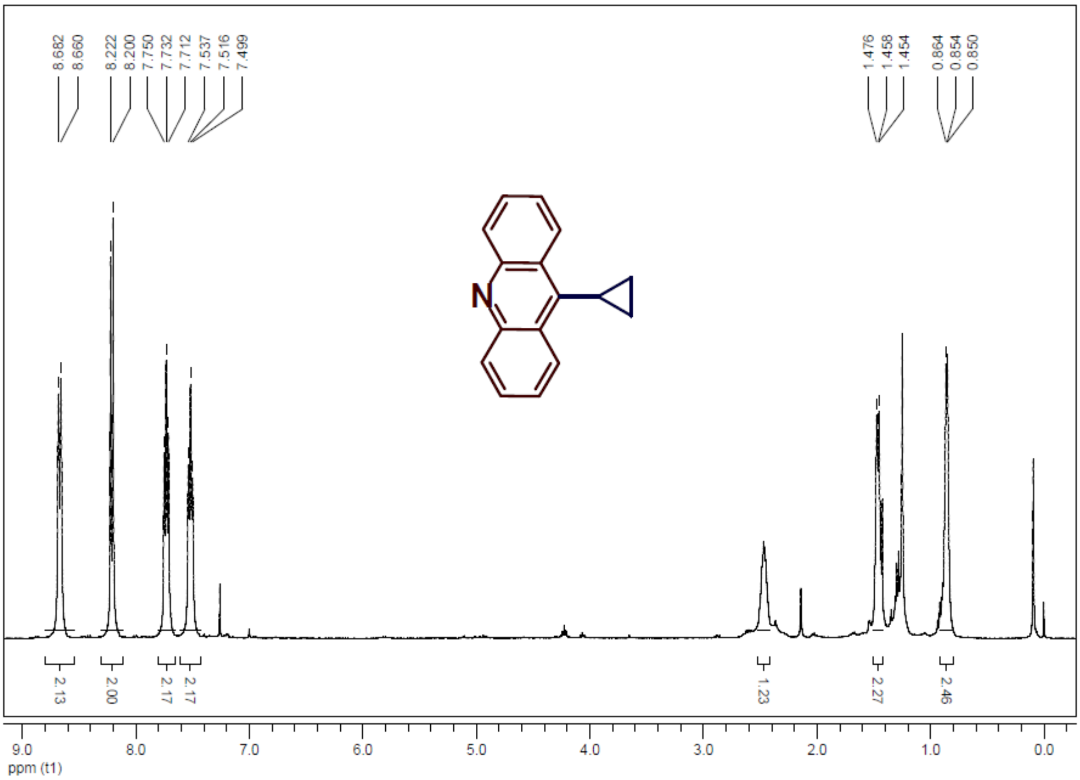

Figure S54. ^{1}H NMR spectrum of compound 1**8.**

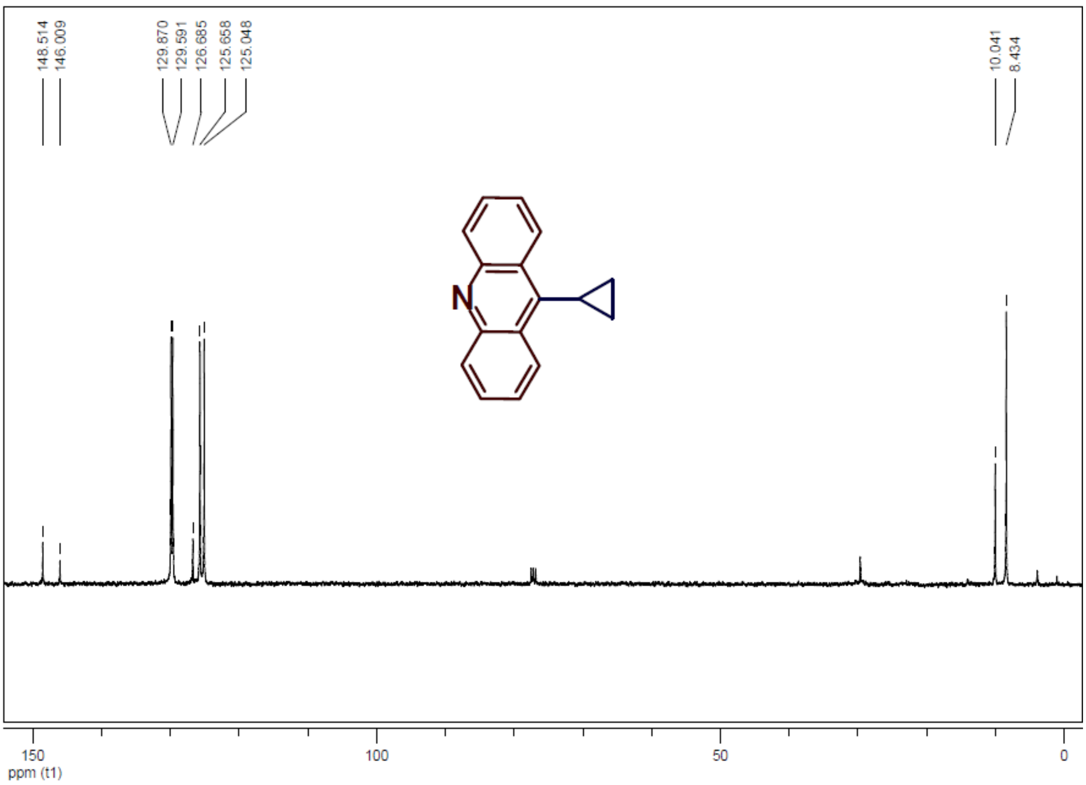

Figure S55. ^{13}C NMR spectrum of compound 1**8**.

Display Report

Analysis Info

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Sample Name	DQ-1604197	Instrument / Ser#	micrOTOF II 10257
Comment			

Acquisition Parameter

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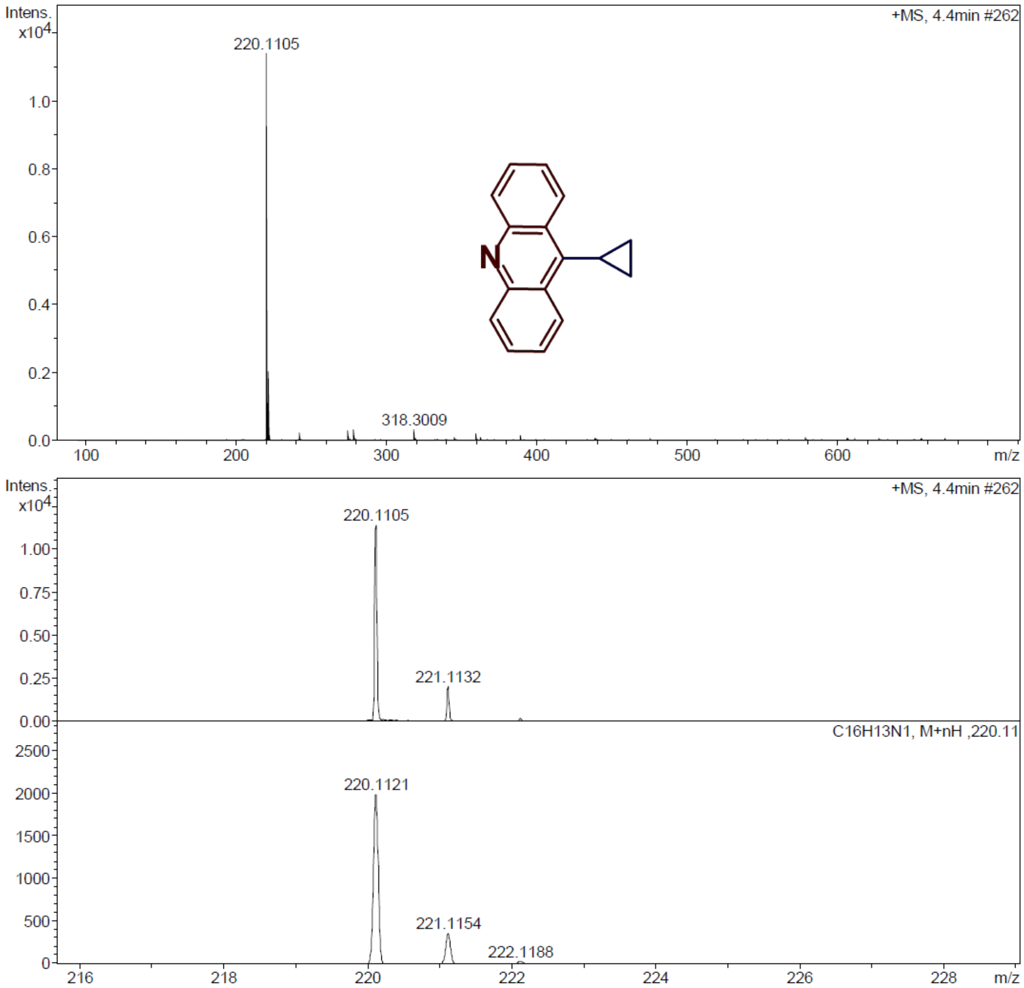

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Figure S56. ESI-MS spectrum of compound 1**8**

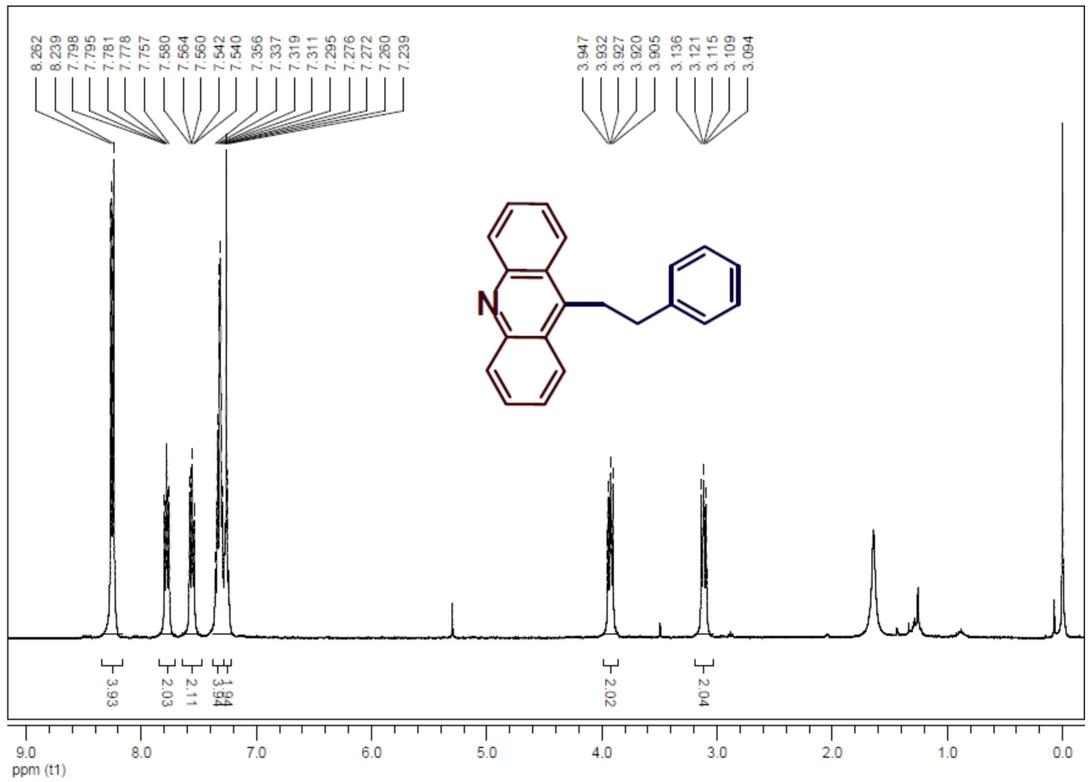

Figure S57. ^{1}H NMR spectrum of compound 1**9.**

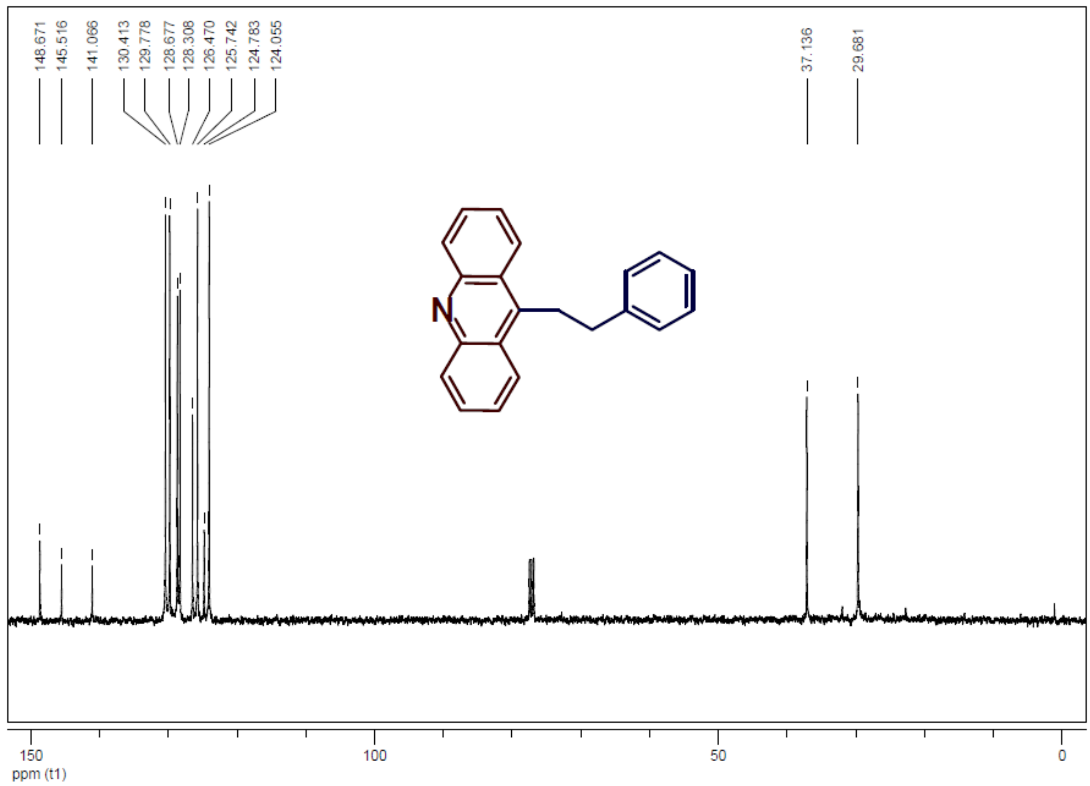

Figure S58. ^{13}C NMR spectrum of compound **19**.

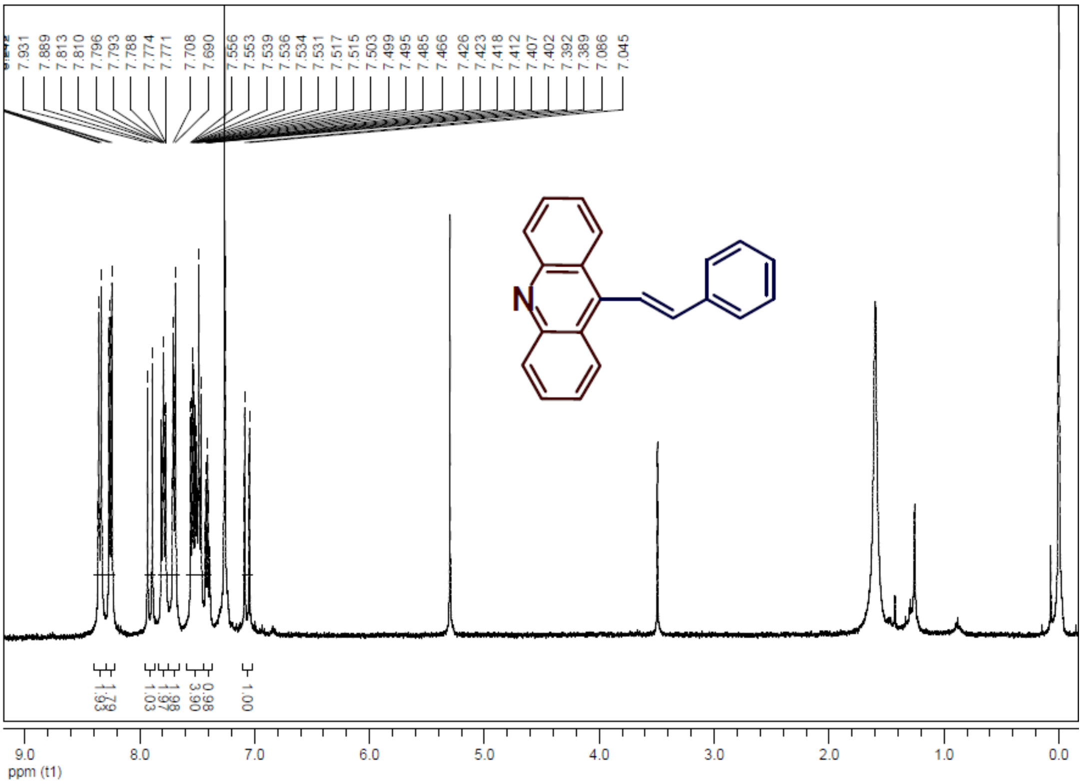

Figure S59. ^{1}H NMR spectrum of compound **20.**

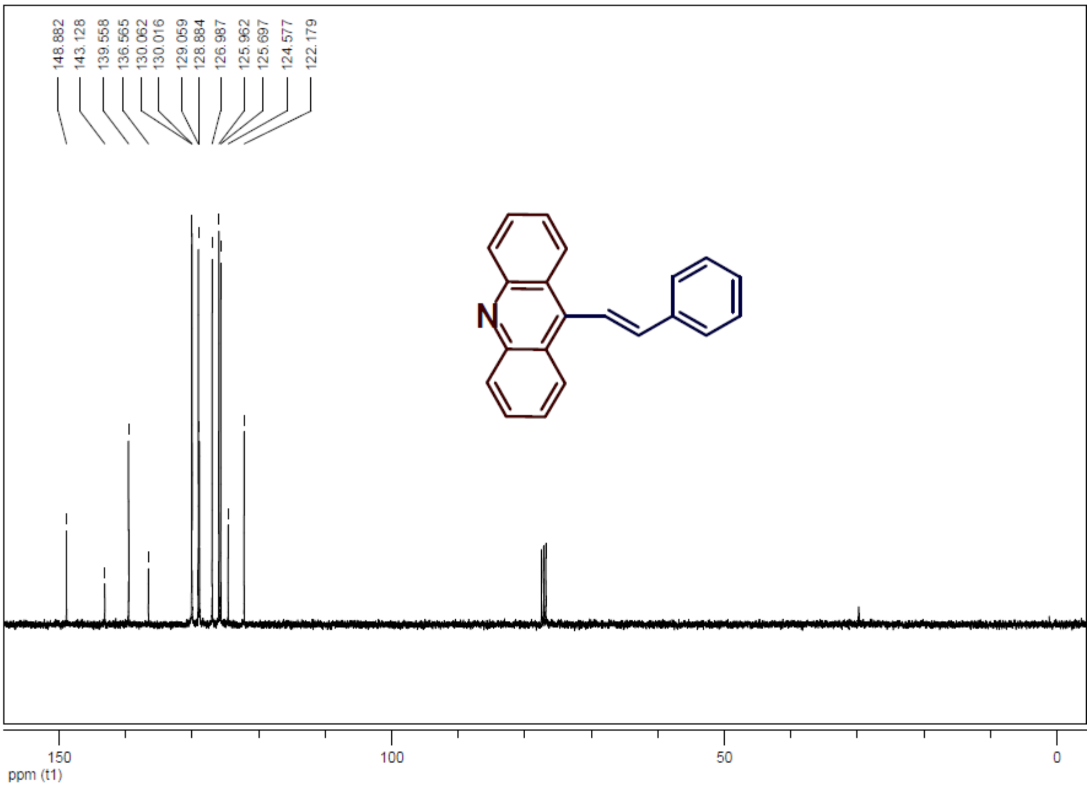

Figure S60. ^{13}C NMR spectrum of compound **20**.

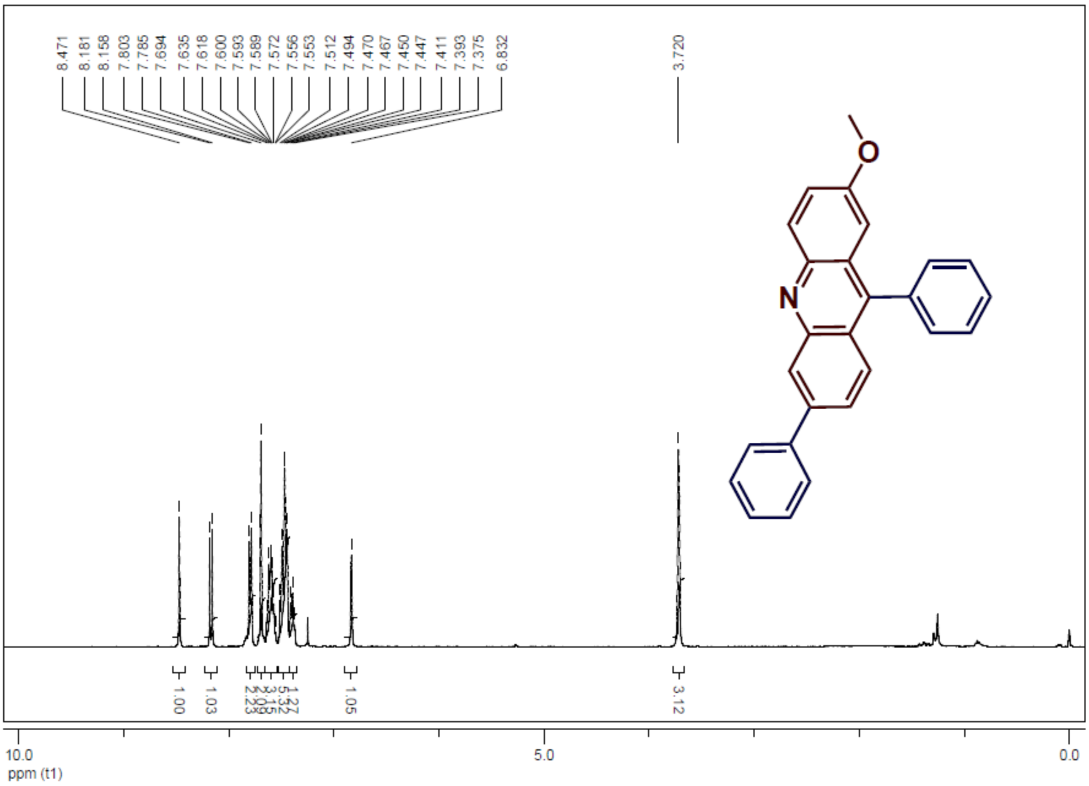

Figure S61. ^{1}H NMR spectrum of compound **21.**

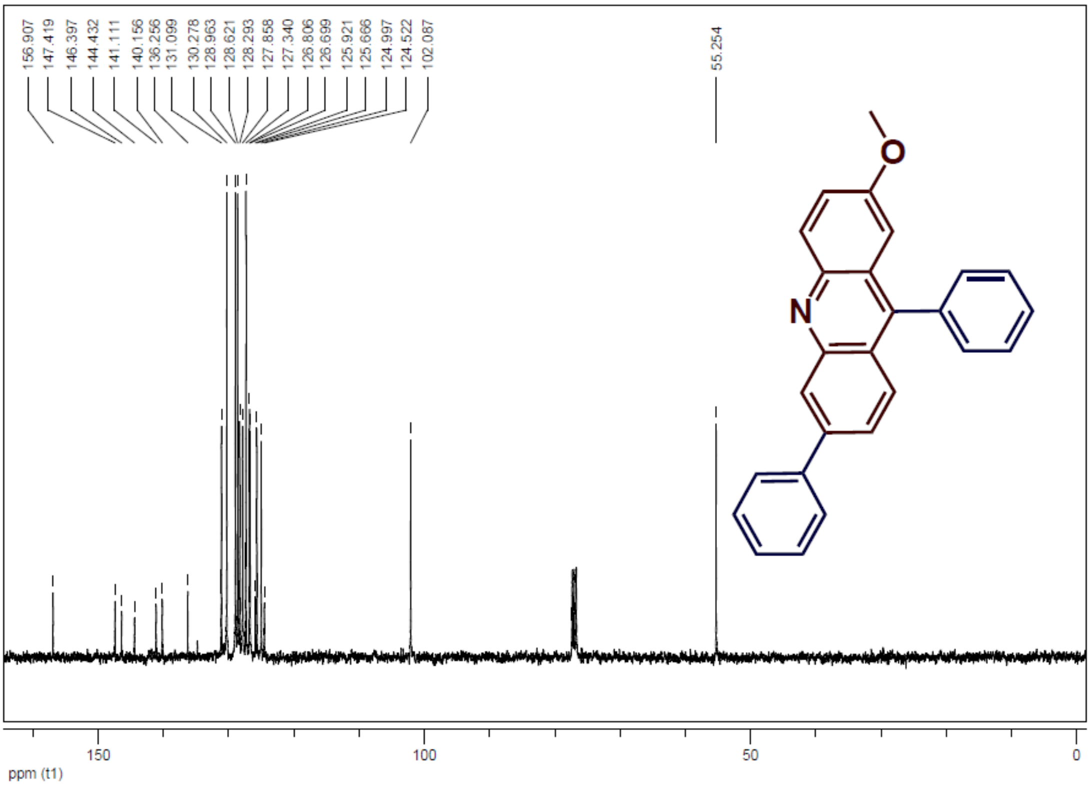

Figure S62. ^{13}C NMR spectrum of compound **S21**.

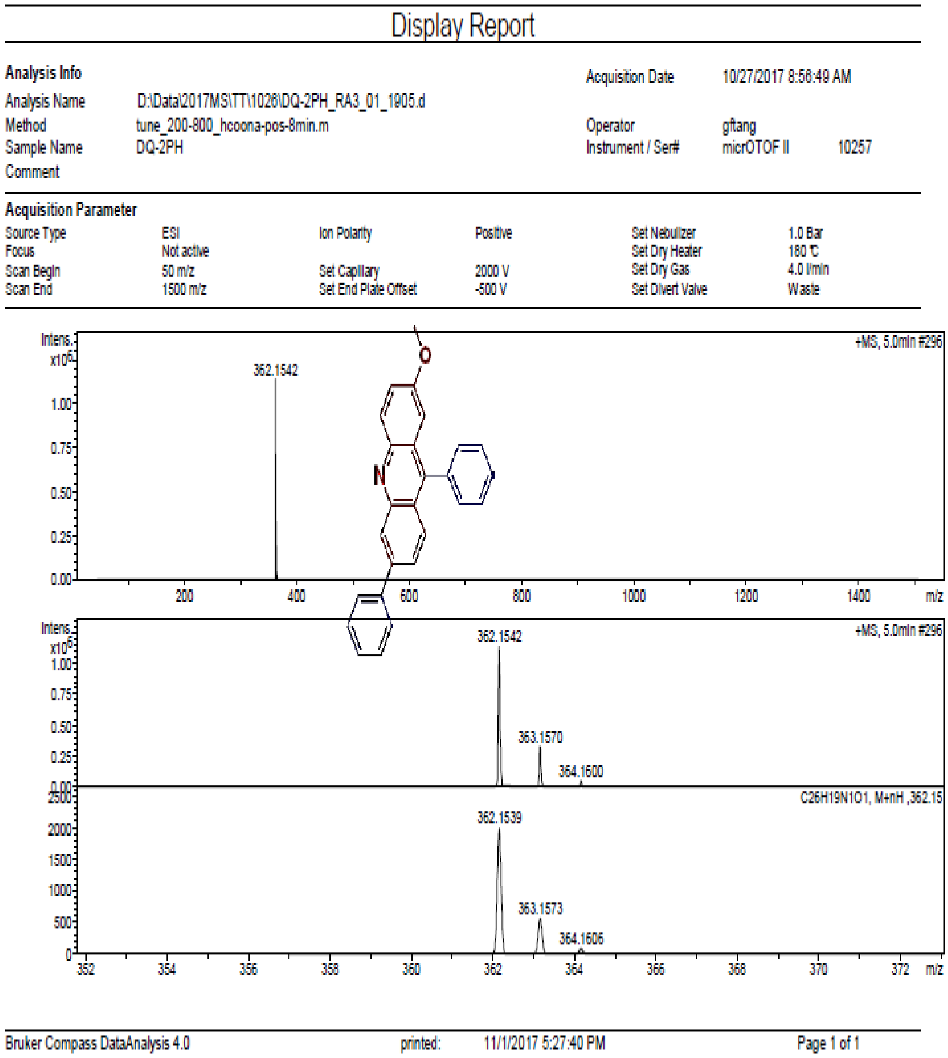

Figure S63. ESI-MS spectrum of compound **21**

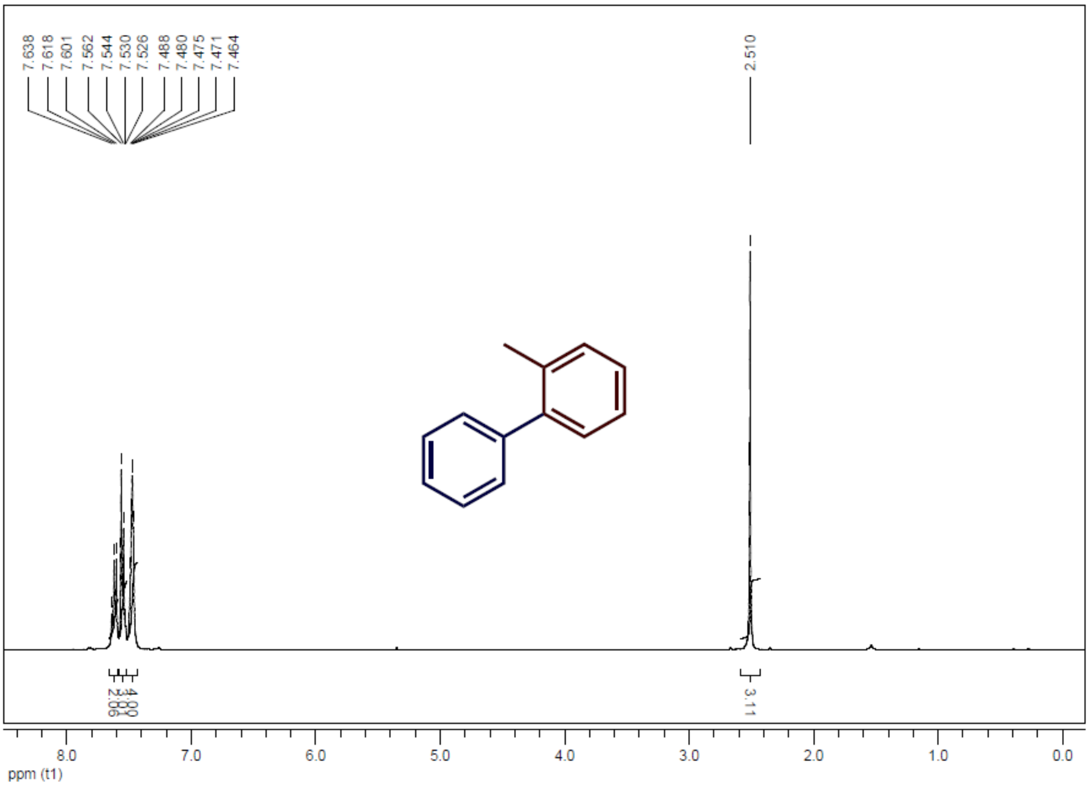

Figure S64. ^{1}H NMR spectrum of compound **S1a.**

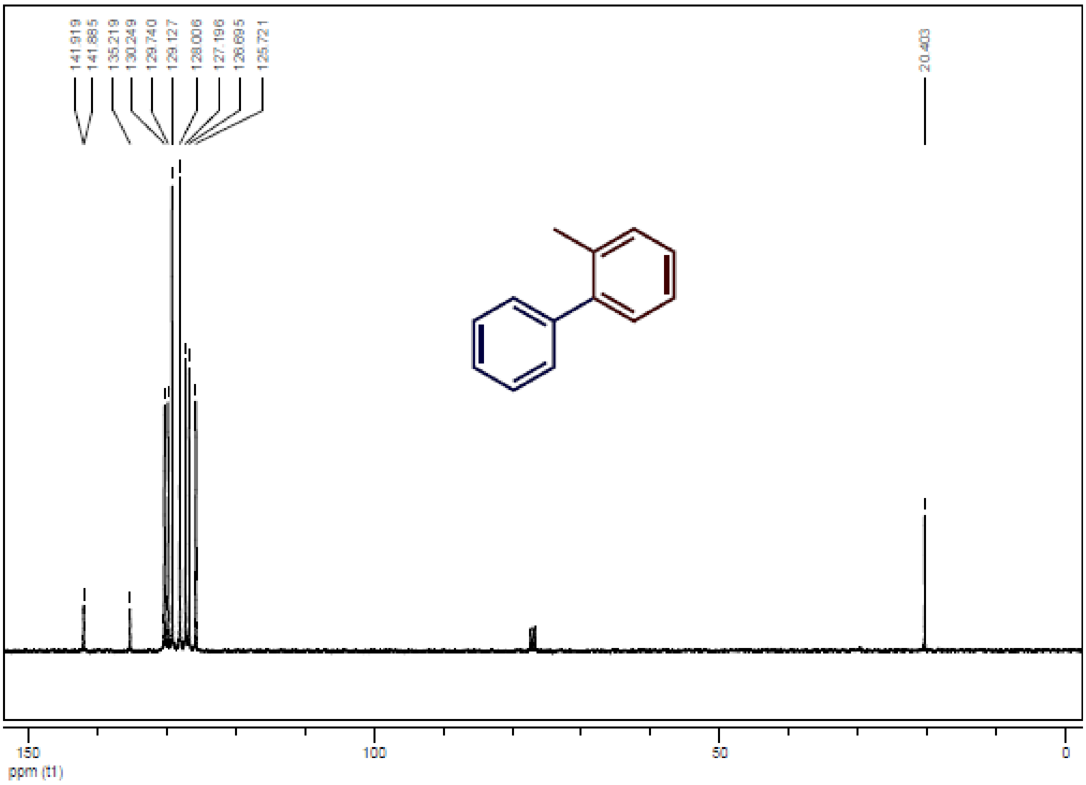

Figure S65. ^{13}C NMR spectrum of compound **S1a**.

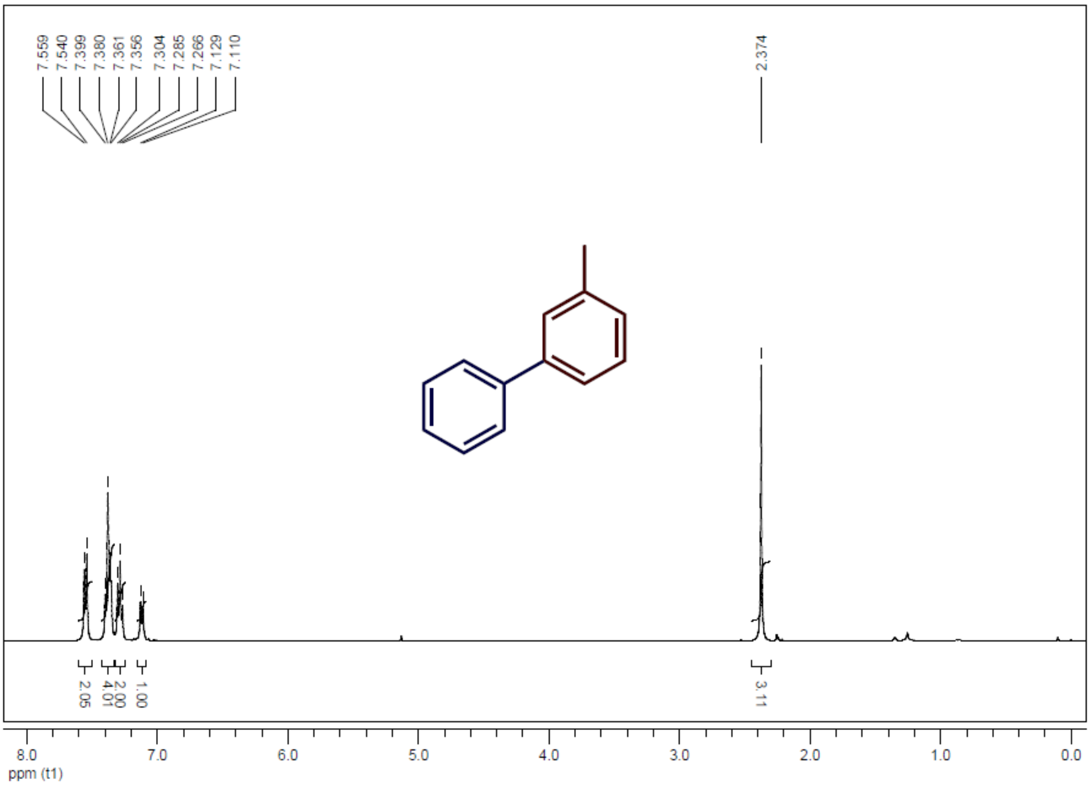

Figure S66. [1]H NMR spectrum of compound **S1b.**

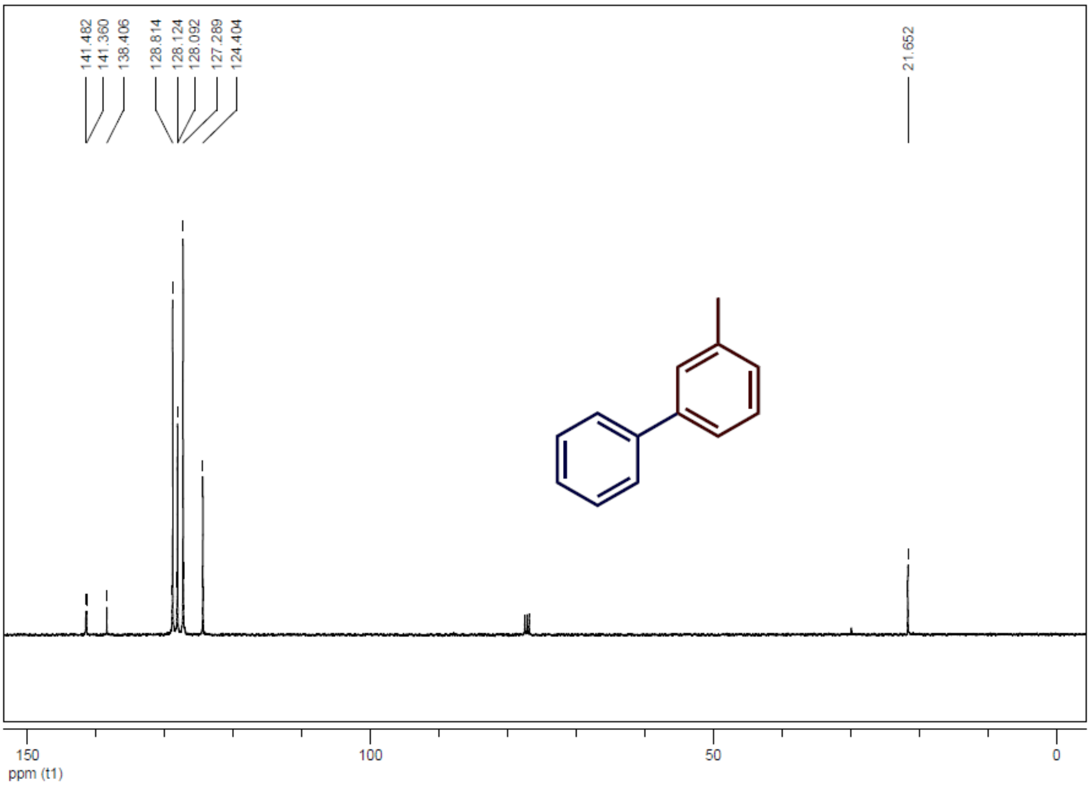

Figure S67. [13]C NMR spectrum of compound **S1b**.

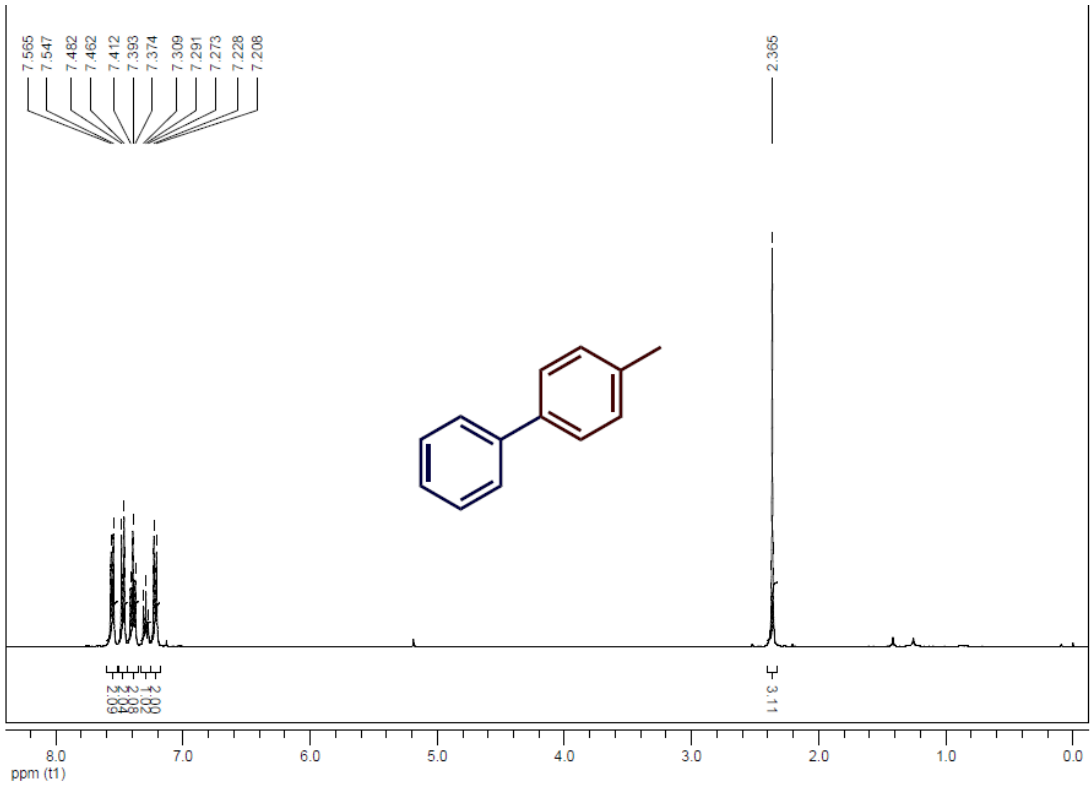

Figure S68. ^{1}H NMR spectrum of compound **S1c.**

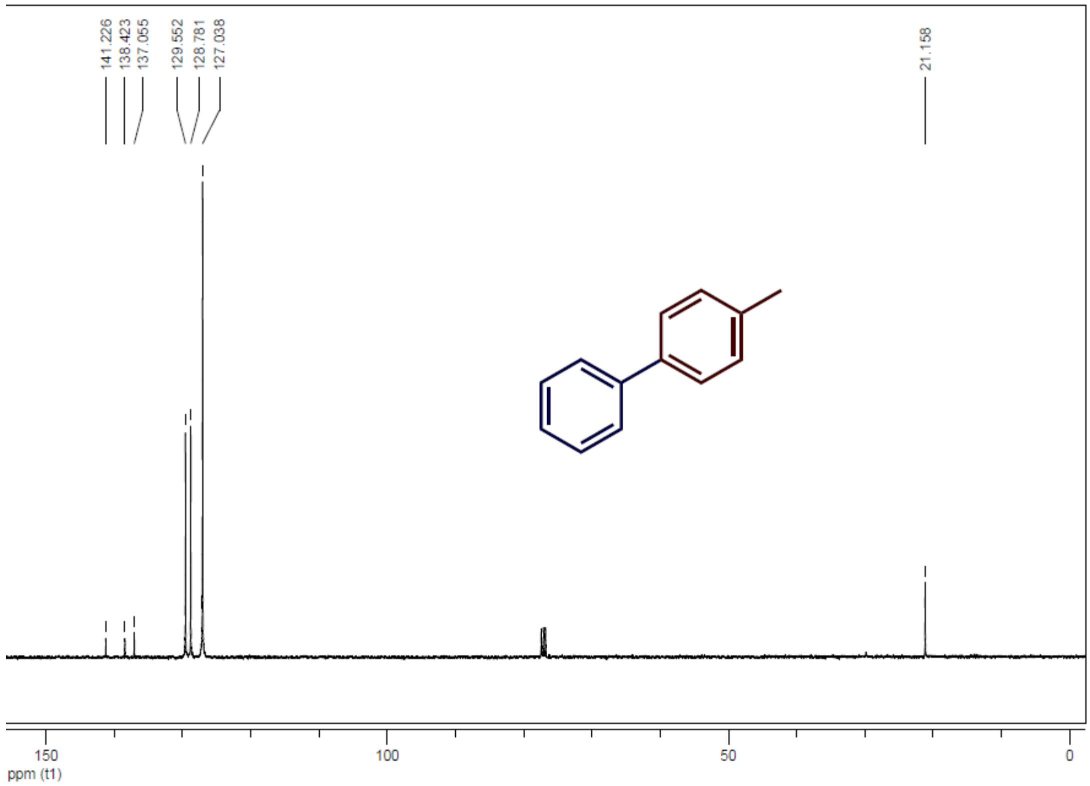

Figure S69. ^{13}C NMR spectrum of compound **S1c**.

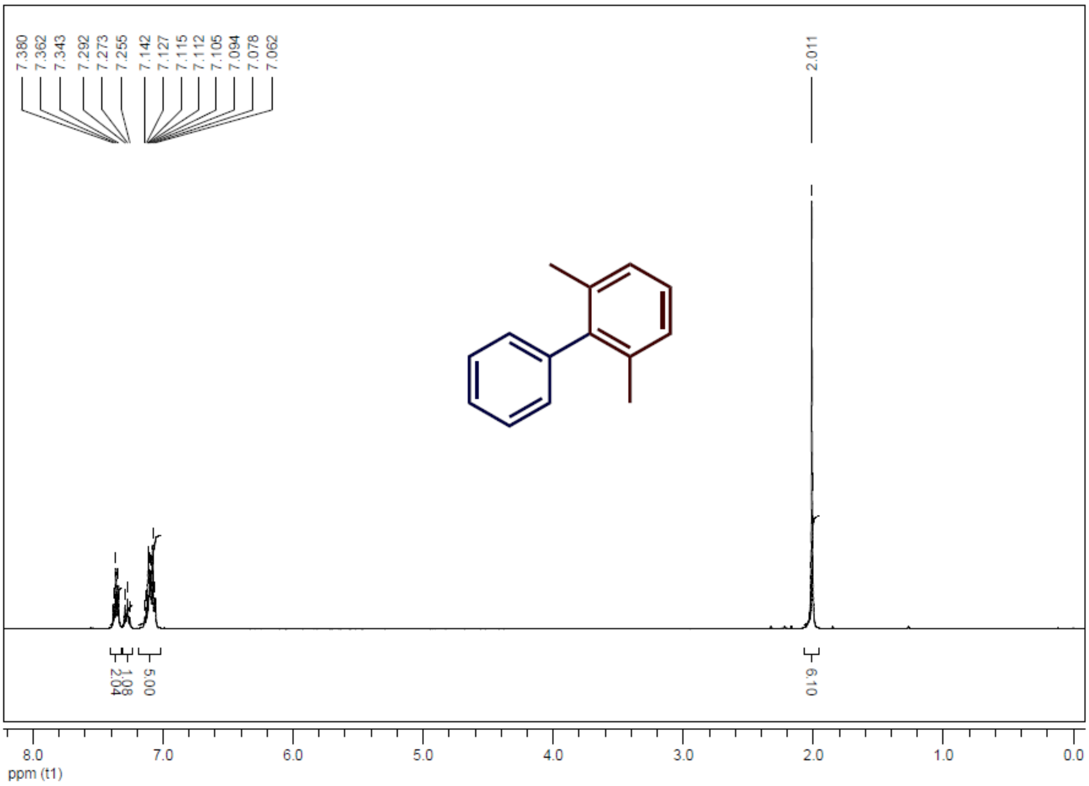

Figure S70. ^{1}H NMR spectrum of compound **S2.**

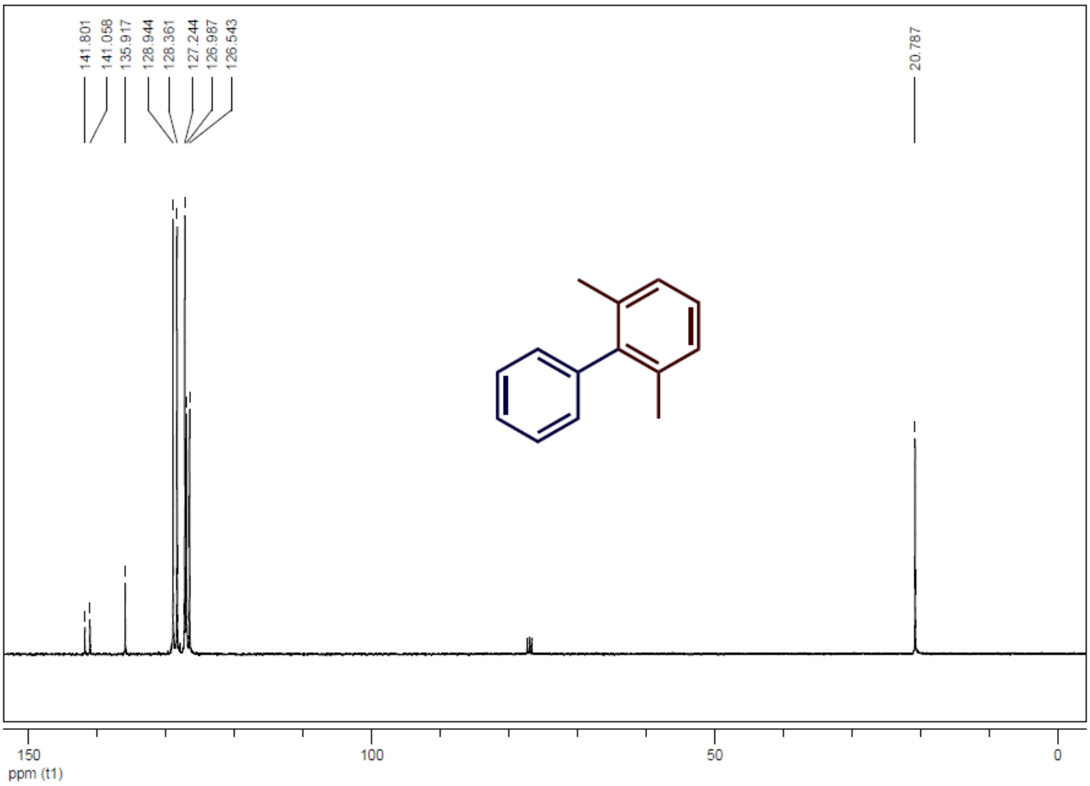

Figure S71. ^{13}C NMR spectrum of compound **S2**.

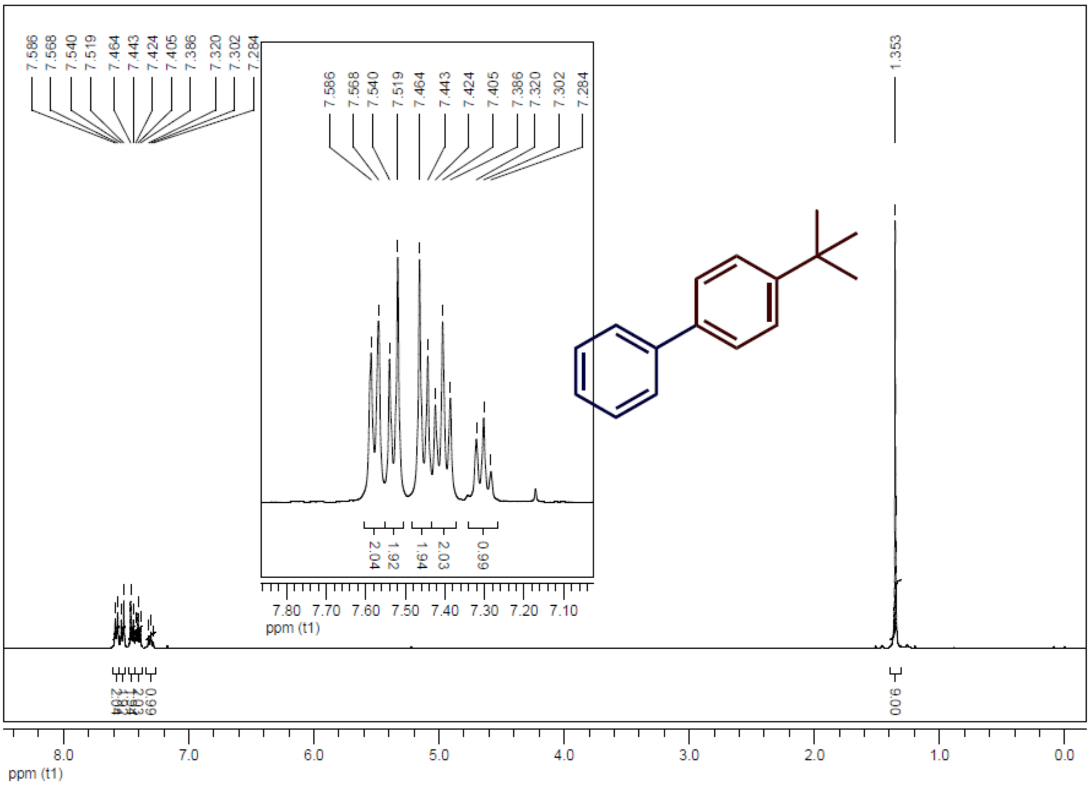

Figure S72. ^{1}H NMR spectrum of compound **S3.**

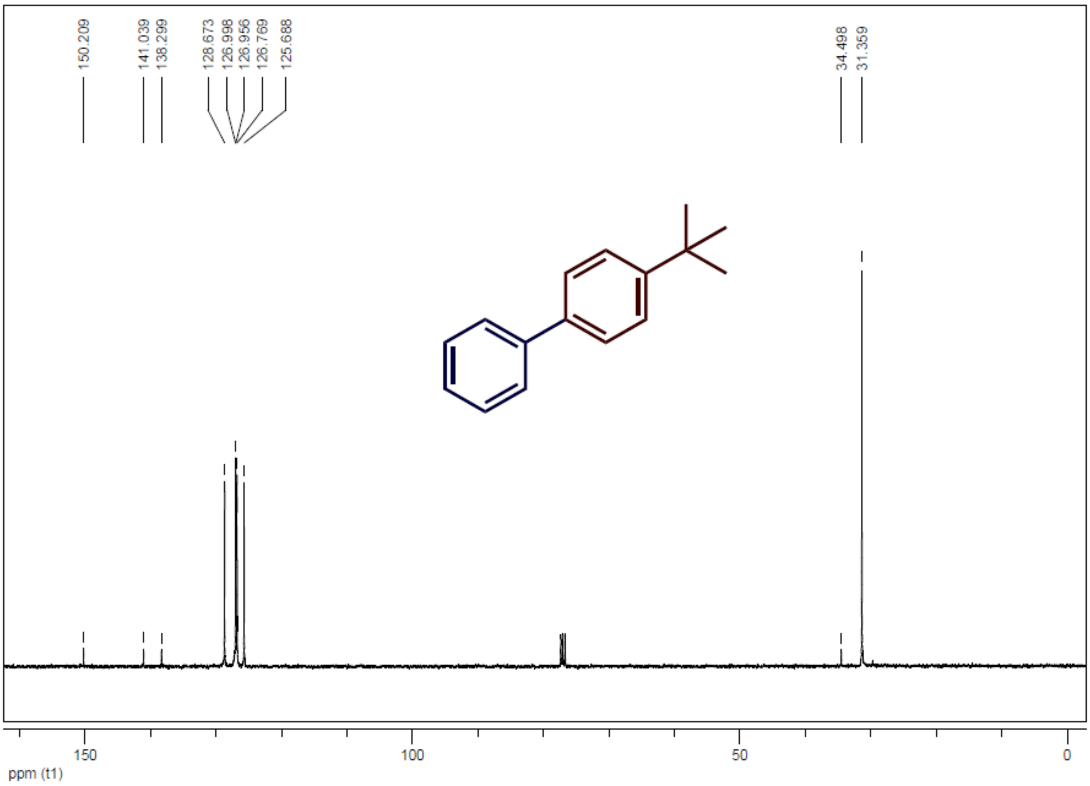

Figure S73. ^{13}C NMR spectrum of compound **S3**.

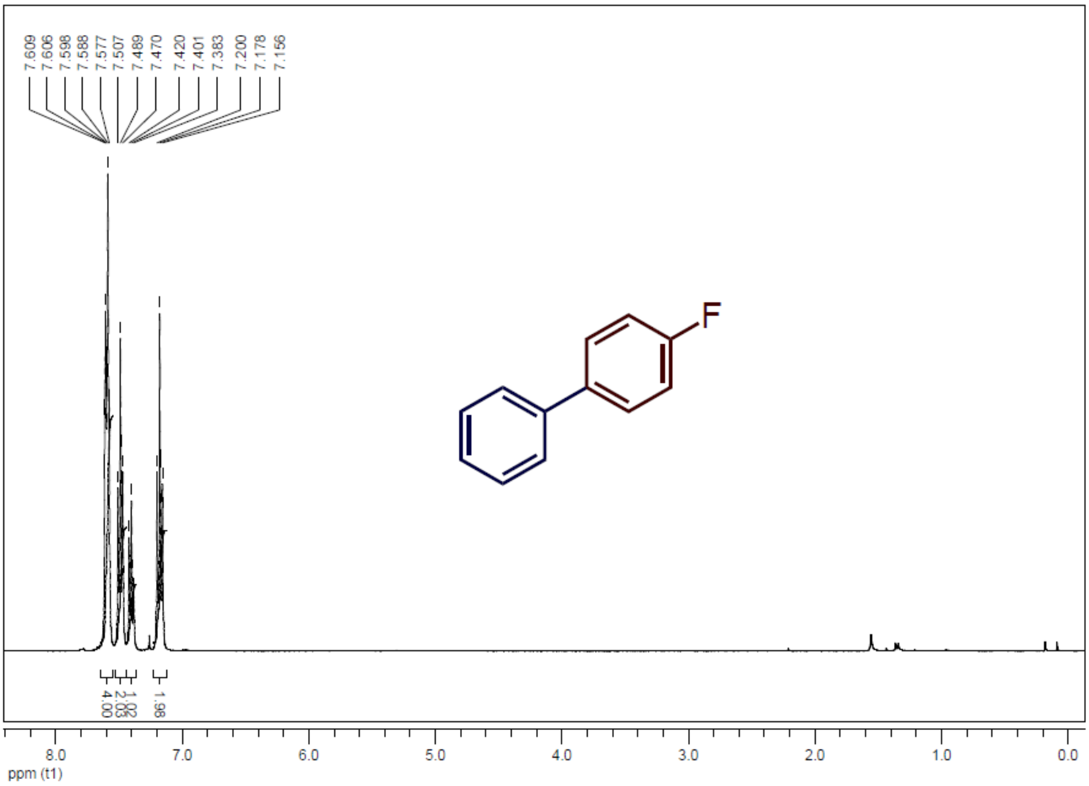

Figure S74. [1]H NMR spectrum of compound **S4.**

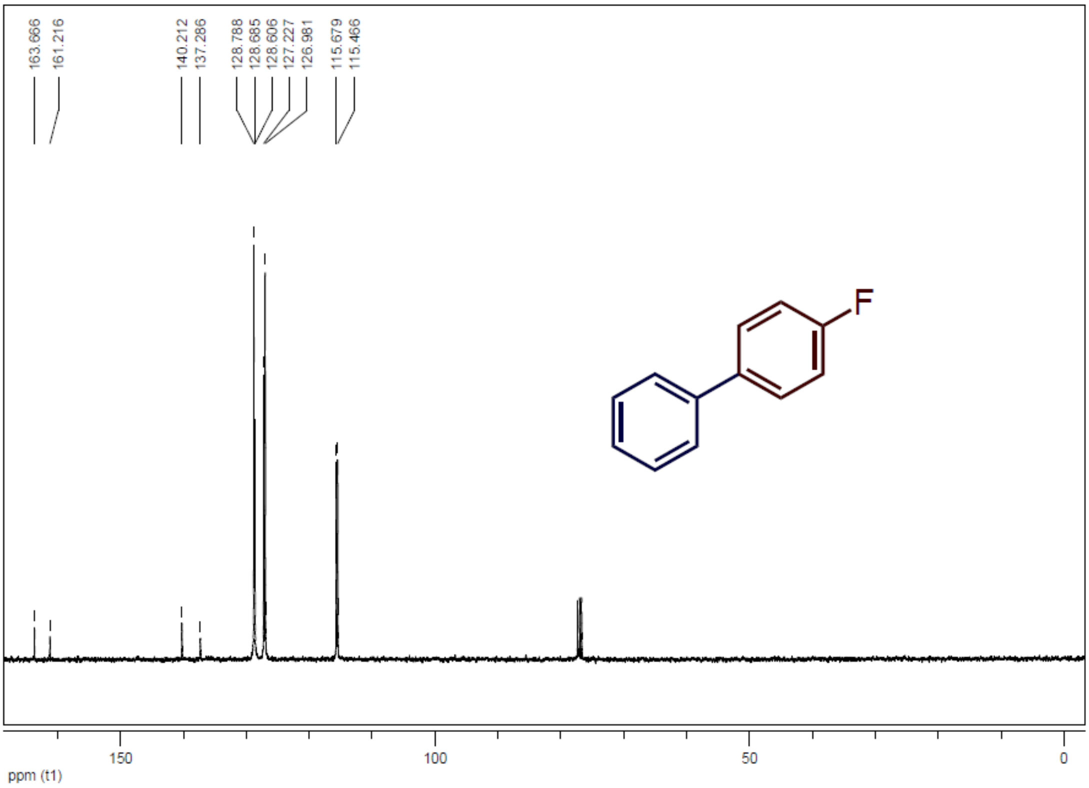

Figure S75. [13]C NMR spectrum of compound **S4**.

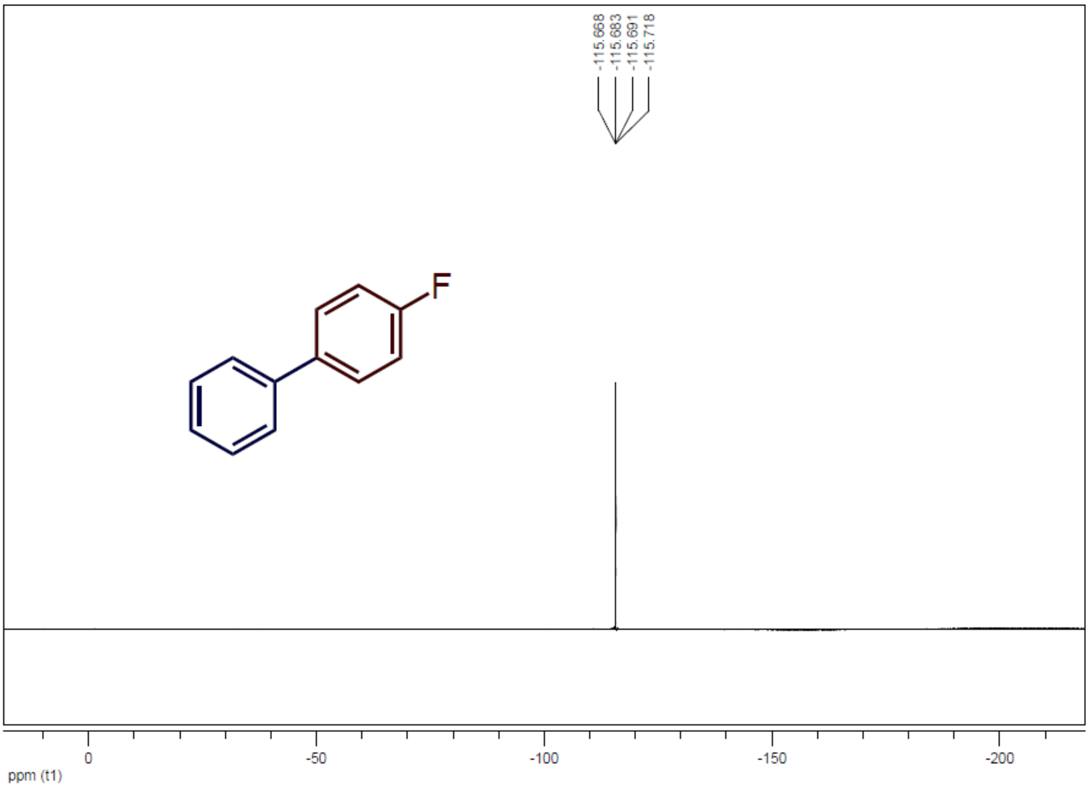

Figure S76. [19]F NMR spectrum of compound **S4**.

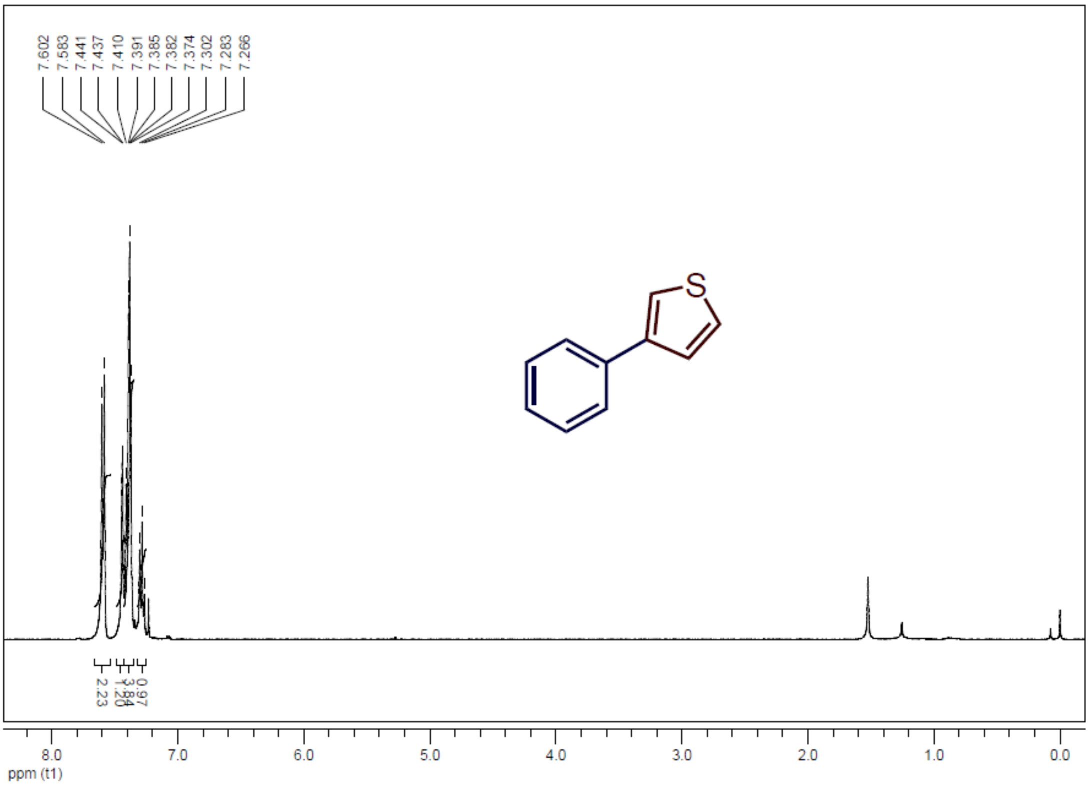

Figure S77. [1]H NMR spectrum of compound **S5.**

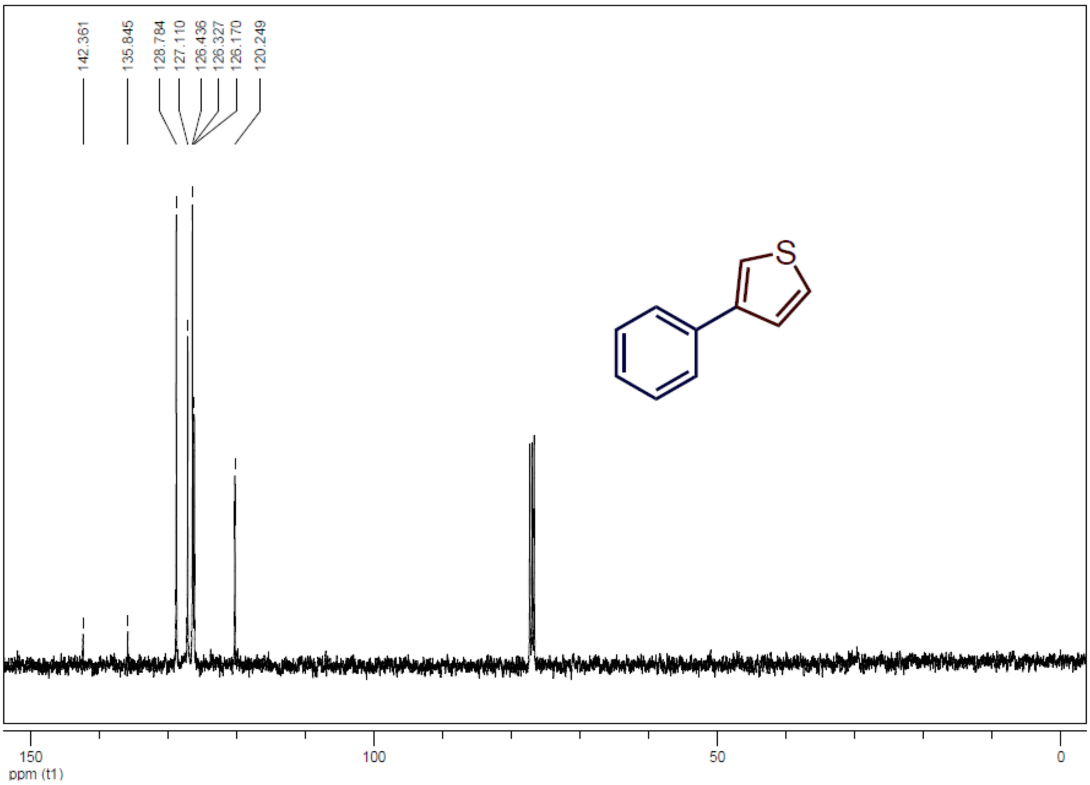

Figure S78. ^{13}C NMR spectrum of compound **S5**.

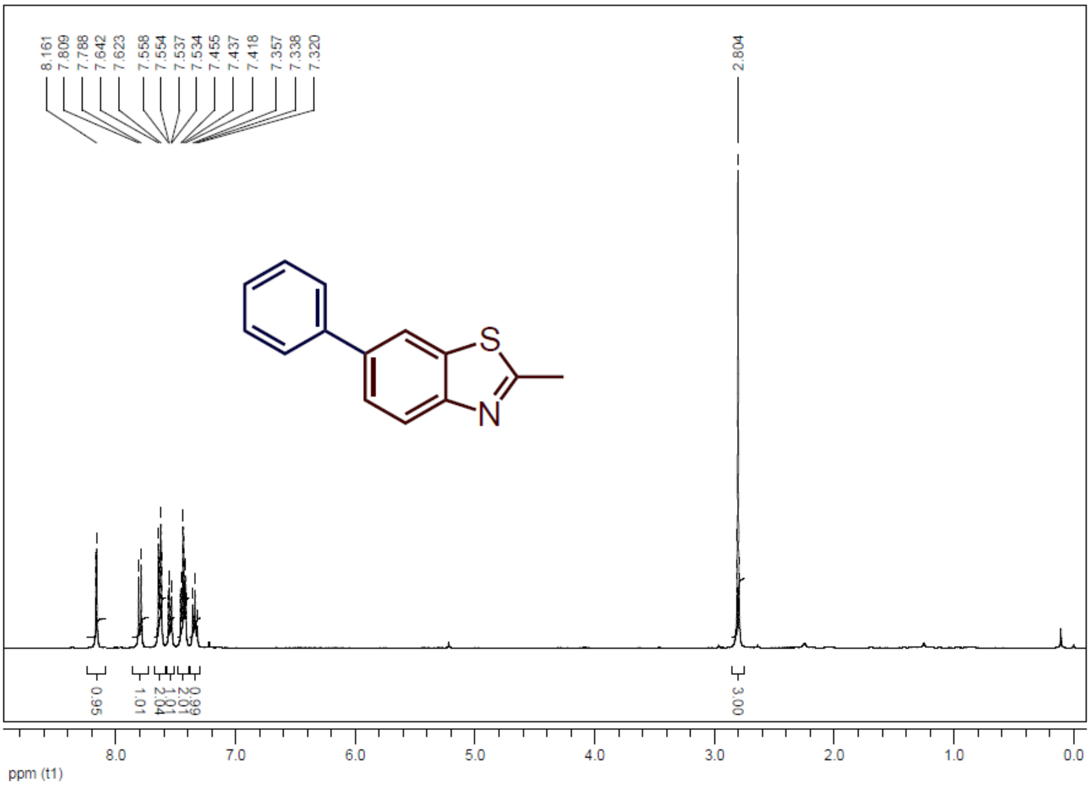

Figure S79. ^{1}H NMR spectrum of compound **S6.**

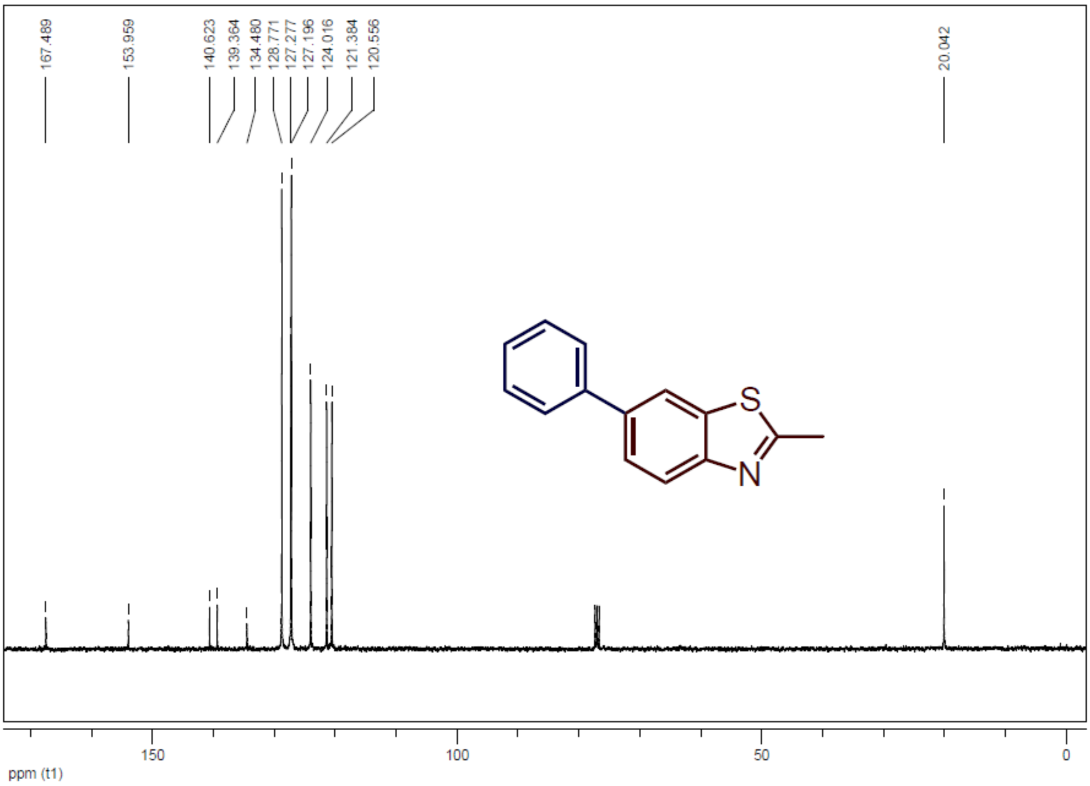

Figure S80. ^{13}C NMR spectrum of compound **S6**.

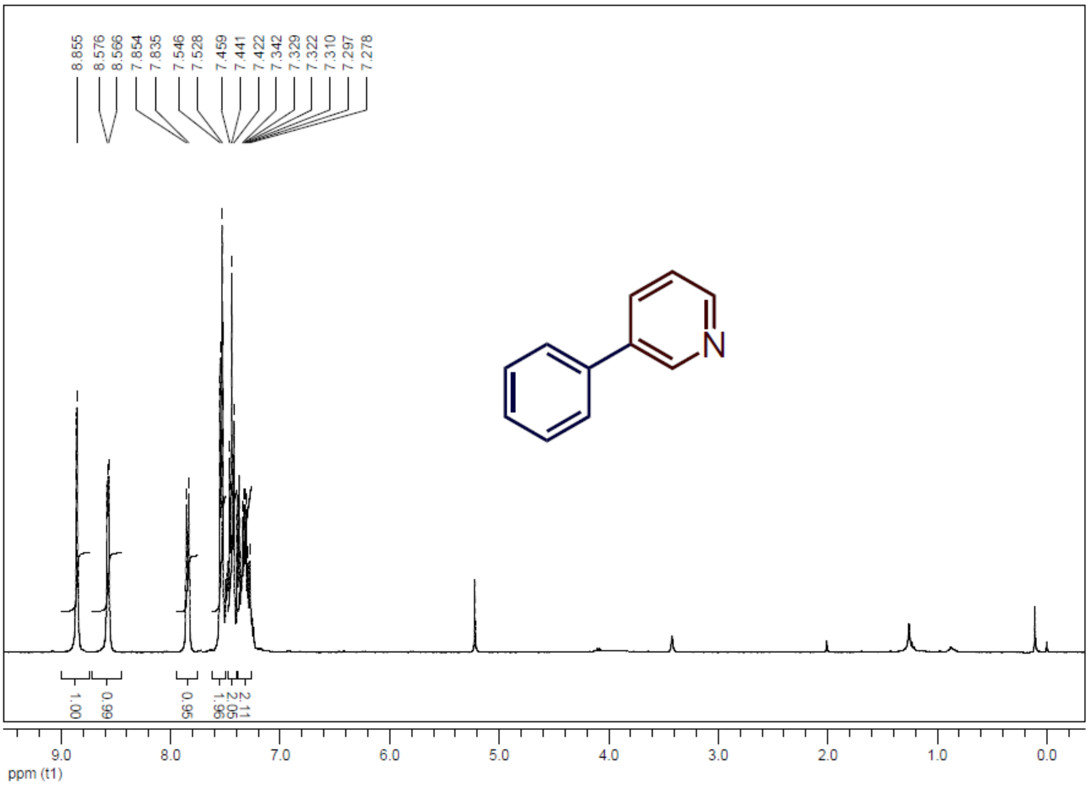

Figure S81. ^{1}H NMR spectrum of compound **S7.**

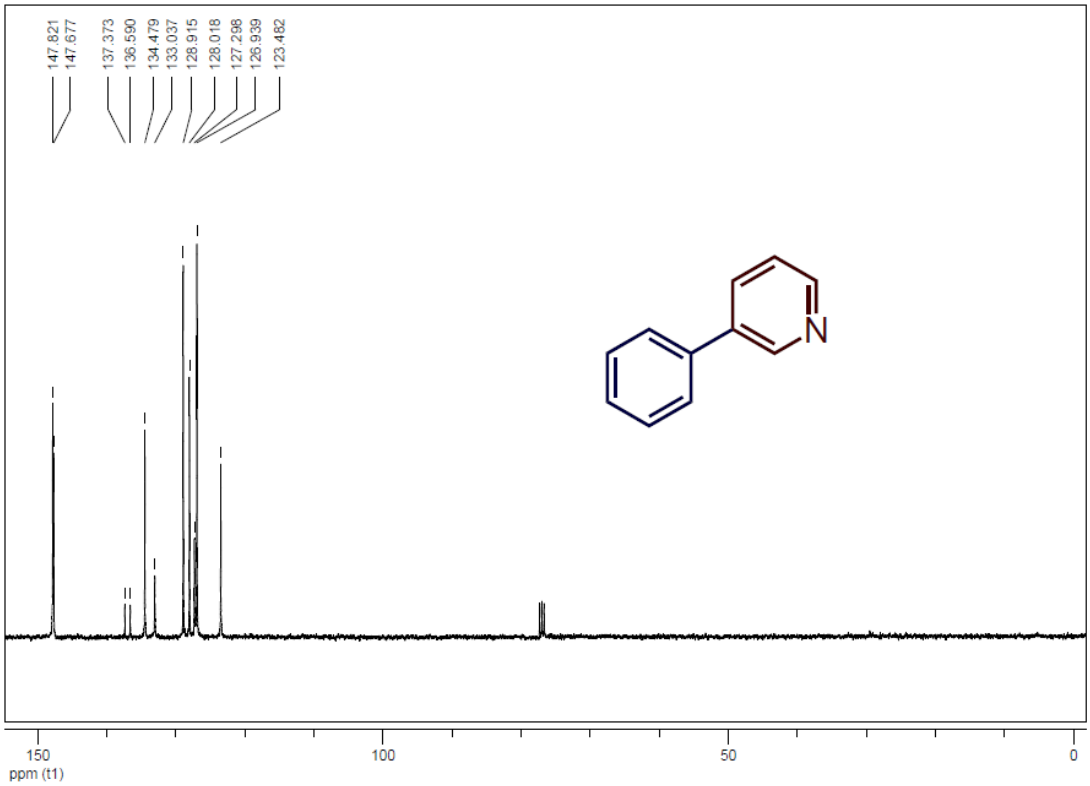

Figure S82. ^{13}C NMR spectrum of compound **S7**.

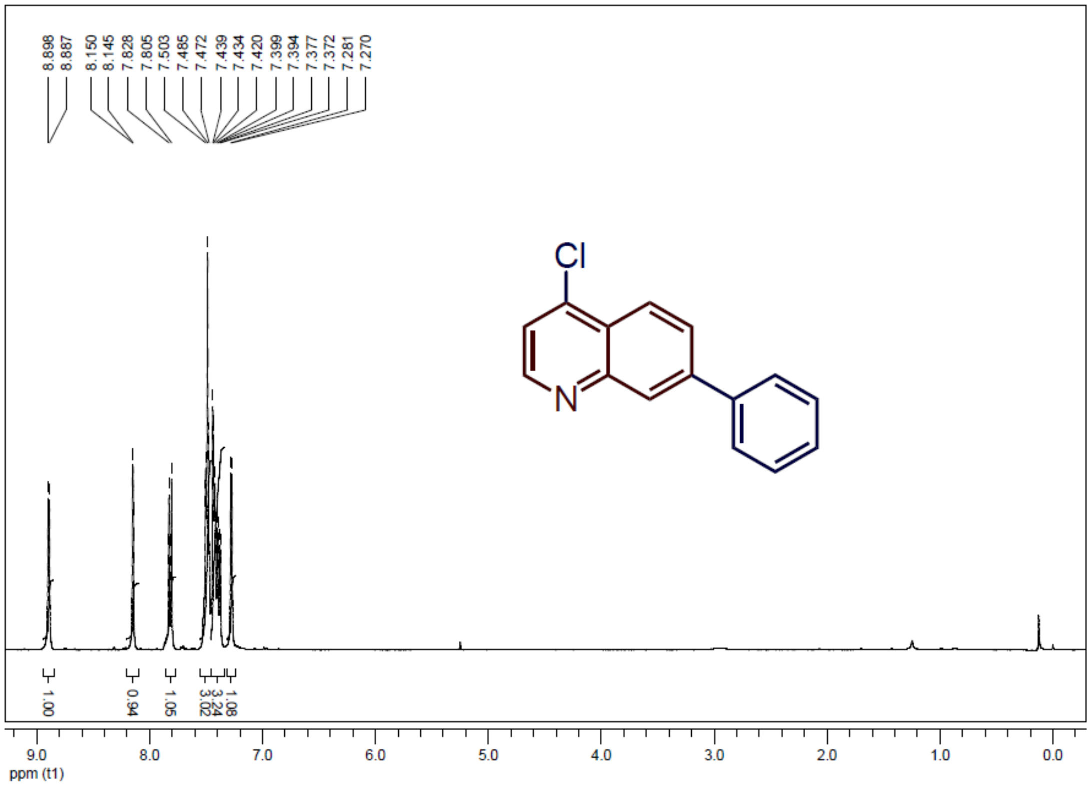

Figure S83. ^{1}H NMR spectrum of compound **S8.**

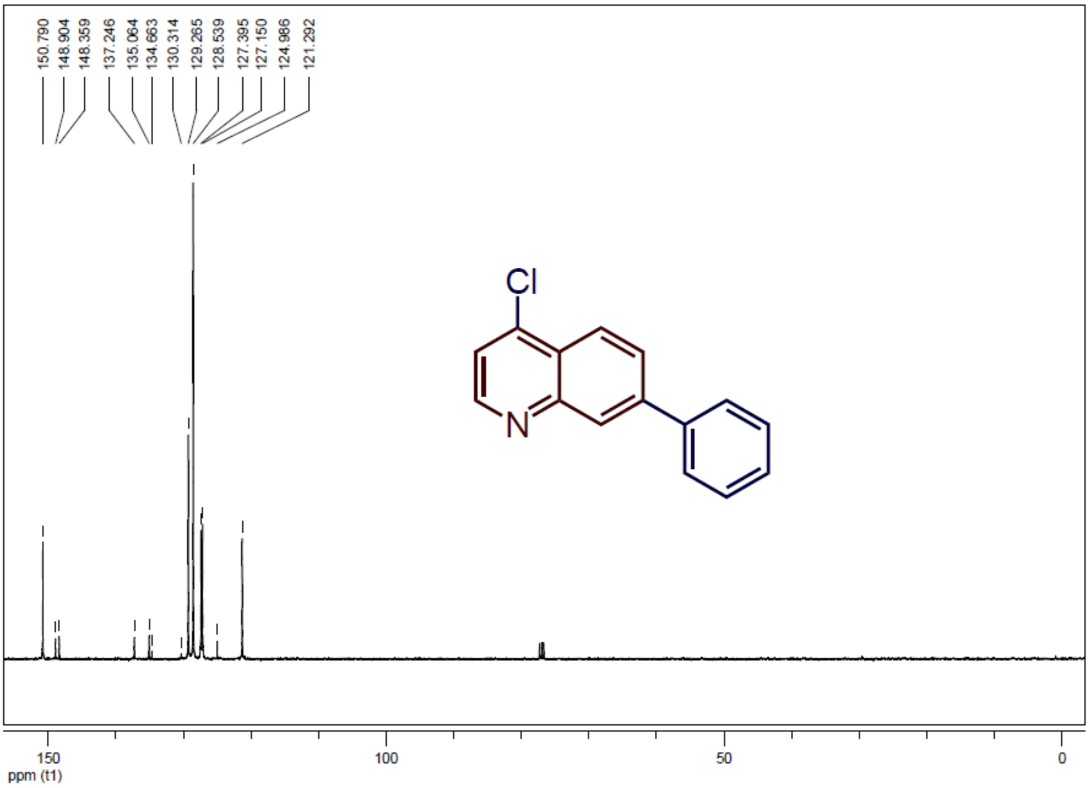

Figure S84. ^{13}C NMR spectrum of compound **S8**.

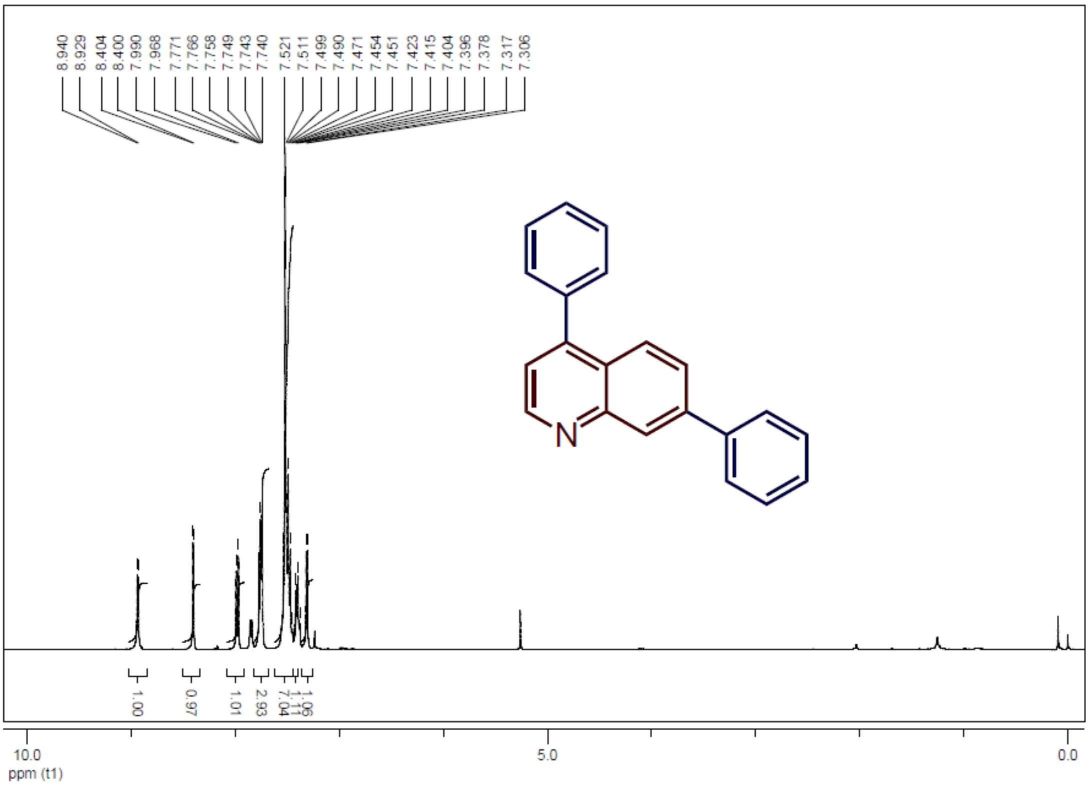

Figure S85. ^{1}H NMR spectrum of compound **S9.**

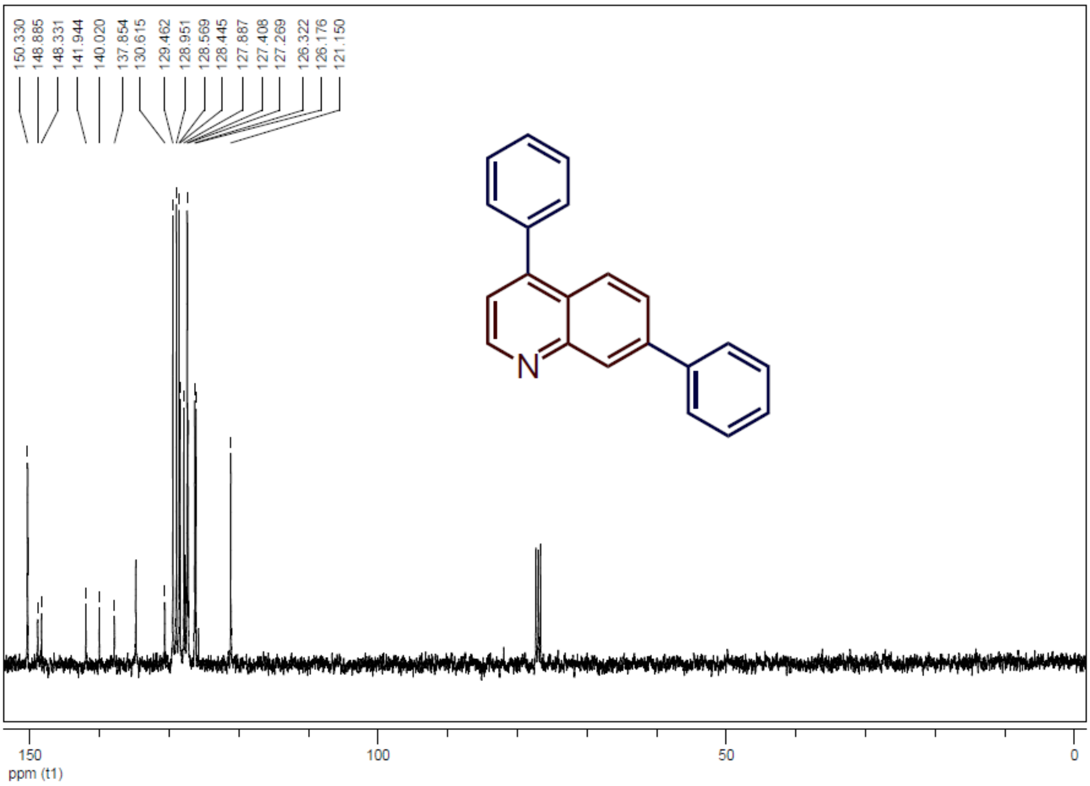

Figure S86. ^{13}C NMR spectrum of compound **S9**.

6. References.

S1. S. Kato, F.-Q. Chen and C. Pac, *J. Phys. Chem. B*, 2004, **108**, 320.

S2. L. Yu, R. Cao, W. Yi, Q. Yan, Z. Chen, L. Ma, W. Peng and H. Song, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 3254.

S3. S. Delarue-Cochin, E. Paunescu, L. Maes, E. Mouray, C. Sergheraert, P. Grellier and P. Melnyk, *Eur. J. Med. Chem.*, 2008**, 43,** 252.

S4. P. Stegmaier, J. M. Alonso and A. Campo, *Langmuir*, 2008, **24**, 11872.

S5. T. Tu, W. Fang and J. Jiang, *Chem. Commun.*, 2011**, 47**, 12358.

S6. Y. Wang, X. Yang, C. Zhang, J. Yu, J. Liu and C. Xia, *Adv. Synth. Catal.*, 2014, **356**, 2539.

S7. Q. Yue, Y. Zhang, C. Wang, X. Wang, Z. Sun, X.-F. Hou, D. Zhao and Y. Deng, *J. Mater. Chem. A*, 2015, **3**, 4586.

S8. M.-J. Jin and D.-H. Lee, *Angew. Chem. Int. Ed.*, 2010, **49**, 1119.