Supporting Information

A Concise Synthesis of Quinolinium, and Biquinolinium Salts and Biquinolines from Benzylic Azides and Alkenes Promoted by Copper(II) Species

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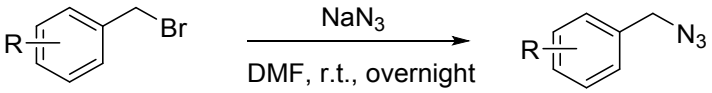
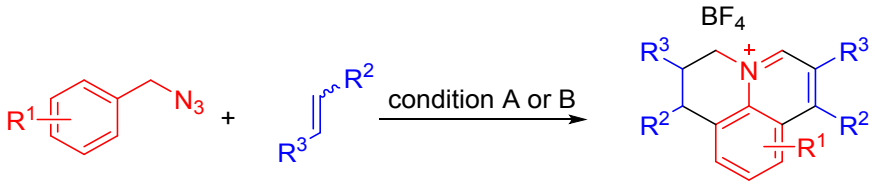
General. All reactions were conducted under nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. Benzyl azides were synthesized according to the literature procedures. Other reagents were commercially available and used as purchased.

General Procedure for the Synthesis of Benzylic Azides 1[1]



Substituted benzyl bromide (1.0 equiv.) and sodium azide (1.5 equiv.) were dissolved in DMF (2.0 mL/mmol) and stirred at room temperature for overnight. At the end of the reaction, the mixture was diluted with water and extracted with diethyl ether. The combined organic solution was concentrated in vacuo and the mixture was purified by a silica gel column (*n*-hexane/EtOAc, 90:10) to afford the substituted benzyl azide.

General Procedure for the Synthesis of Quinolinium Salts 3



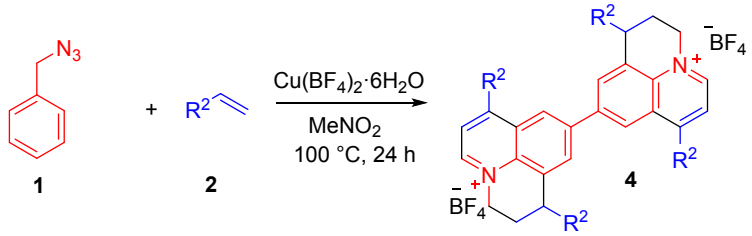
1a **2** **3**

***Condition A**:* A sealed tube that contained $CuSO_4$ (178 mg, 1.12 mmol) and $NaBF_4$ (24 mg, 0.2 mmol) was evacuated and purged with nitrogen gas three times. $MeNO_2$ (2.0 mL) was then added to the tube, and the suspension was stirred for 2 min at ambient temperature. Then, benzylic azide **1** (0.64 mmol), alkene **2** (0.32 mmol), H_2O (40 μL, 2.22 mmol), and additional $MeNO_2$ (1 mL) were added to the system via syringe sequentially. The reaction was stirred at 100°C for 24 h. At the end of the reaction, the mixture was diluted with CH_2Cl_2 (10 mL), filtered through a Celite pad, and washed three times with CH_2Cl_2 (3 × 20 mL). The combined filtrate was concentrated in vacuo and the mixture was purified by a silica gel column using DCM/MeOH (95:5) as eluent to afford the desired pure product **3**.

***Condition B**:* A sealed tube that contained $CuSO_4$ (13 mg, 0.080 mmol), $NaBF_4$ (24 mg, 0.20 mmol) and $(NH_4)_2S_2O_8$ (92 mg, 0.40 mmol) was evacuated and purged with nitrogen gas three times. $MeNO_2$ (2.0 mL) was then added to the tube, and the suspension was stirred for 2 min at ambient temperature. Then, benzylic azide **1** (0.64 mmol), alkene **2** (0.32 mmol), H_2O (40 μL, 2.22 mmol) and additional $MeNO_2$ (1 mL)

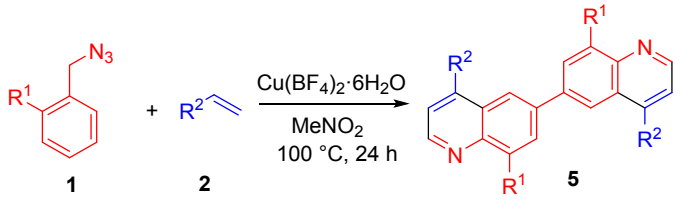
were added to the system via syringe sequentially. The reaction was stirred at 100°C for 24 h. At the end of the reaction, the mixture was diluted with CH_2Cl_2 (10 mL), filtered through a Celite pad, and washed three times with CH_2Cl_2 (3 × 20 mL). The combined filtrate was concentrated in vacuo and the mixture was purified by a silica gel column using DCM/MeOH (95:5) as eluent to afford the desired pure product **3**.

General Procedure for the Synthesis of Biquinolinium Salts 4



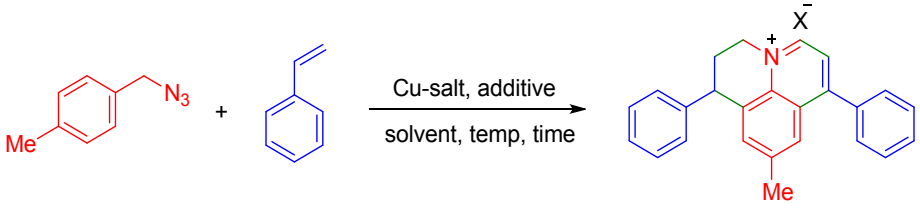
A sealed tube containing $Cu(BF_4)_2.6H_2O$ (276 mg, 0.80 mmol) was dissolved in $MeNO_2$ (2 mL) under nitrogen gas. Then, benzylic azide **1** (0.64 mmol), alkene **2** (0.32 mmol) and additional $MeNO_2$ (1 mL) were added to the system via syringe sequentially. The reaction was allowed to stir at 100 °C for 24 h. When the reaction was completed, the mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a Celite pad and washed several times with CH_2Cl_2 (50 mL). The combined filtrate was concentrated in vacuo and the residue was purified by column chromatography on a silica gel column using DCM/MeOH (95:5) as eluent to afford the desired pure product **4**.

General Procedure for the Synthesis of Substituted Biquinolines 5



A sealed tube containing $Cu(BF_4)_2.6H_2O$ (276 mg, 0.80 mmol) was dissolved in $MeNO_2$ (2 mL) under nitrogen gas. Then, benzyl azide **1** (0.64 mmol), alkene **2** (0.32 mmol) and additional $MeNO_2$ (1 mL) were added to the system via syringe sequentially. The reaction was allowed to stir at 100 °C for 24 h. When the reaction was completed, the mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a Celite pad and washed several times with CH_2Cl_2 (50 mL). The combined filtrate was concentrated in vacuo and the residue was purified by column chromatography on a silica gel column using *n*-hexane /Ethyl acetate (95:5) as eluent to afford the desired pure product **5**.

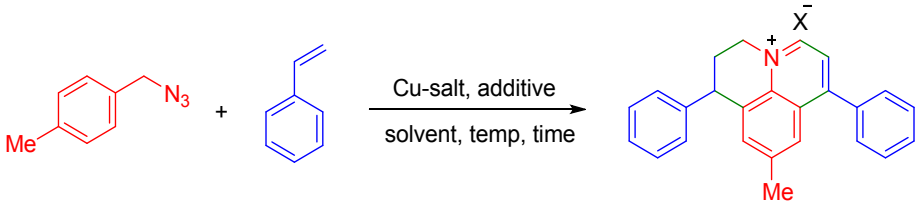
Table S1. Reaction Optimization Studies for the Synthesis of Quinolinium Salt **3aa**[a]



1a **2a** **3aa**

Entry	Cu Salt (mmol)	Additive (mmol)	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	$Cu(BF_4)_2{\cdot}6H_2O$ (0.64)	--	$MeNO_2$	100	24	57
2	$Cu(OAc)_2{\cdot}H_2O$ (0.64)	$NaBF_4$ (0.35)	$MeNO_2$	100	24	--
3	$Cu(OPiv)_2$ (0.64)	$NaBF_4$ (0.35)	$MeNO_2$	100	24	--
4	$Cu(OTf)_2$ (0.64)	$NaBF_4$ (0.35)	$MeNO_2$	100	24	--
5	$Cu(OH)_2$ (0.64)	$NaBF_4$ (0.35)	$MeNO_2$	100	24	--
6	$Cu(OCOCF_3)_2{\cdot}H_2O$(0.64)	$NaBF_4$ (0.35)	$MeNO_2$	100	24	34
7	$CuSO_4$ (0.64)	$NaBF_4$ (0.35)	$MeNO_2$	100	24	73
8	$CuSO_4$ (0.64)	NaI	$MeNO_2$	100	24	16
9	$CuSO_4$ (0.64)	$NaSbF_6$ (0.35)	$MeNO_2$	100	24	39
10	$CuSO_4$ (0.64)	$NaClO_4$ (0.35)	$MeNO_2$	100	24	78
11	$CuSO_4$ (0.64)	--	$MeNO_2$	100	24	--
12	--	$NaBF_4$ (0.35)	$MeNO_2$	100	24	--
13	$CuSO_4$ (0.80)	$NaBF_4$ (0.35)	$MeNO_2$	100	24	80
14	$CuSO_4$ (0.96)	$NaBF_4$ (0.35)	$MeNO_2$	100	24	88
15	$CuSO_4$ (1.12)	$NaBF_4$ (0.35)	$MeNO_2$	100	24	93
16	$CuSO_4$ (1.28)	$NaBF_4$ (0.35)	$MeNO_2$	100	24	92
17	$CuSO_4$ (1.12)	$NaBF_4$ (0.35)	$MeNO_2$	90	24	57
18	$CuSO_4$ (1.12)	$NaBF_4$ (0.35)	$MeNO_2$	80	24	32
19	$CuSO_4$ (1.12)	$NaBF_4$ (0.35)	$MeNO_2$	100	20	80
20	$CuSO_4$ (1.12)	$NaBF_4$ (0.35)	$MeNO_2$	100	12	70
21	$CuSO_4$ (1.12)	$NaBF_4$ (0.35)	$MeNO_2$	100	8	55
22	$CuSO_4$ (1.12)	$NaBF_4$ (0.35)	$MeNO_2$	100	24	85[c]
23	$CuSO_4$ (1.12)	$NaBF_4$ (0.35)	AcOH	100	24	8
24	$CuSO_4$ (1.12)	$NaBF_4$ (0.35)	EtOH	100	24	trace
25	$CuSO_4$ (1.12)	$NaBF_4$ (0.35)	dioxane	100	24	trace
26	$CuSO_4$ (1.12)	$NaBF_4$ (0.2) H2O (1.92)	$MeNO_2$	100	24	88
27	$CuSO_4$ (1.12)	$NaBF_4$ (0.2) H2O (2.22)	$MeNO_2$	100	24	95

Table S1. (Continued)

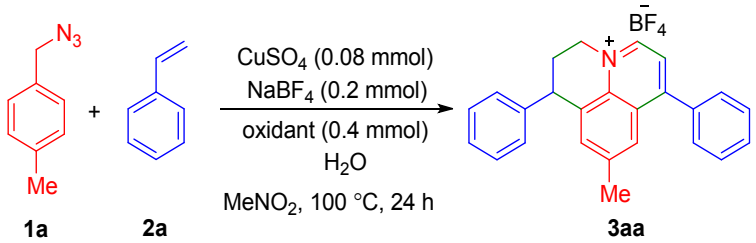


1a **2a** **3aa**

Entry	Cu Salt (mmol)	Additive (mmol)	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
28	$CuSO_4$ (1.12)	$NaBF_4$ (0.2) H2O (2.56)	$MeNO_2$	100	24	80

[a]All reactions were performed using **1a** (0.64 mmol), **2a** (0.32 mmol), Cu-salt, H2O (2.22 mmol) and additive in $MeNO_2$ (3 mL) at 80-100 °C for 8-24 h. [b]Yields were calculated based on **2a** (0.16 mmol) as the limiting reagent; Yields were determined by ^{1}H NMR integration method using mesitylene as the internal standard. [c]Reaction was conducted using **1a** (0.48 mmol) and **2a** (0.32 mmol).

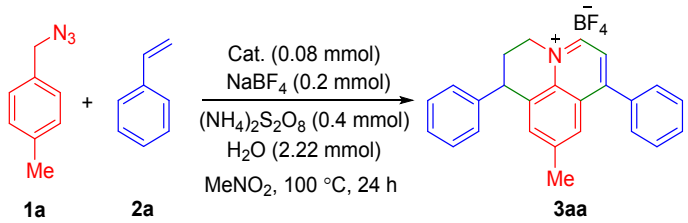
Table S2. Optimization studies for the Suitable Oxidant for the Synthesis of Quinolinium Salt **3aa**[a]



Entry	Oxidant (mmol)	H_2O (mmol)	**3aa** Yield (%)[b]
1	$(NH_4)_2S_2O_8$	--	47
2	$(NH_4)_2S_2O_8$	1.67	60
3	$(NH_4)_2S_2O_8$	2.22	82 (77)
4	$(NH_4)_2S_2O_8$	2.78	51
5	$K_2S_2O_8$	2.22	22
6	$Na_2S_2O_8$	2.22	36
7	oxone	2.22	10
8	DTBP		--
9	$PhI(OAc)_2$		--
10	1 atm O_2		40

[a]All reactions were conducted using **1a** (0.64 mmol), **2a** (0.32 mmol), $CuSO_4$ (0.8 mmol), $NaBF_4$ (0.2 mmol), oxidant (0.4 mmol), and H_2O (used as shown in the Table) in $MeNO_2$ (3 mL) at 100 °C for 24 h. [b]Yields were determined by ^1H NMR integration methods using mesitylene as the internal standard. DTBP - di-*tert*-butyl peroxide. Yield given in the parenthesis was isolated yield.

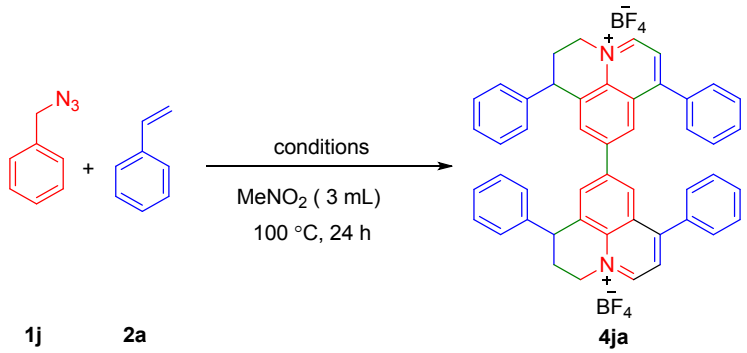
Table S3. Optimization of Lewis Acid Metal-Catalyst for the Quinolinium salt **3aa** Formation[a]



Entry	Metal Catalyst	**3aa** Yield (%)[b]
1	$CuSO_4$	82
2	$FeCl_3$	61
3	$FeBr_3$	73
4	$Fe_2(SO_4)_3$	40
5	$Fe(acac)_3$	19
6	$Fe(ClO_4)_3$	56
7	$FeCl_2$	47
8	$InCl_3$	49
9	$In(OTf)_3$	22

[a]Reaction conditions: **1a** (0.64 mmol), **2a** (0.32 mmol), metal catalyst (0.08 mmol), $(NH_4)_2S_2O_8$ (0.4 mmol), $NaBF_4$ (0.2 mmol), and H_2O (2.22 mmol) in $MeNO_2$ (3 mL) at 100 °C for 24 h. [b]Yields were determined by ^1H NMR method using mesitylene as the internal standard.

Table S4. Optimization Studies for the Synthesis of Biquinolinium Salt **4ja**[a]



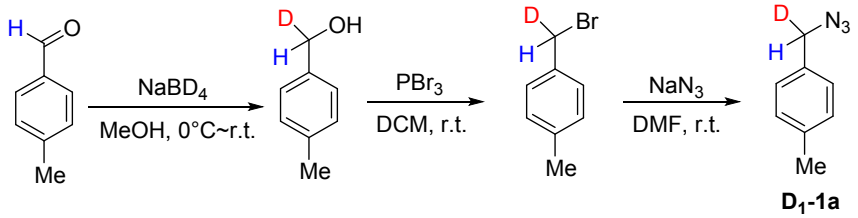
1j **2a** **4ja**

Entry	Condition	Yield (%)[b]
1	$CuSO_4$ (1.12 mmol), $NaBF_4$ (0.2 mmol)	5
2	$Cu(BF_4)_2.6H_2O$ (0.64 mmol)	68
3	$Cu(BF_4)_2.6H_2O$ (0.80 mmol)	73 (70)[c]
4	$Cu(BF_4)_2.6H_2O$ (0.64 mmol), $CuSO_4$ (0.16 mmol)	66
5	$Cu(BF_4)_2.6H_2O$ (0.64 mmol), $CuSO_4$ (0.32 mmol)	63
6	$Cu(BF_4)_2.6H_2O$ (0.96 mmol)	70

[a]All the reactions were conducted using **1j** (0.64 mmol), **2a** (0.32 mmol) with the conditions shown in the table. [b]Isolated yields are given based on **2a** (0.08 mmol) as the limiting reagent. [c]Yield given in the parenthesis was isolated yield.

Deuterium Labeling Experiments

Synthesis of 1-(azidomethyl-*d*)-4-methylbenzene (**D_1-1a)**

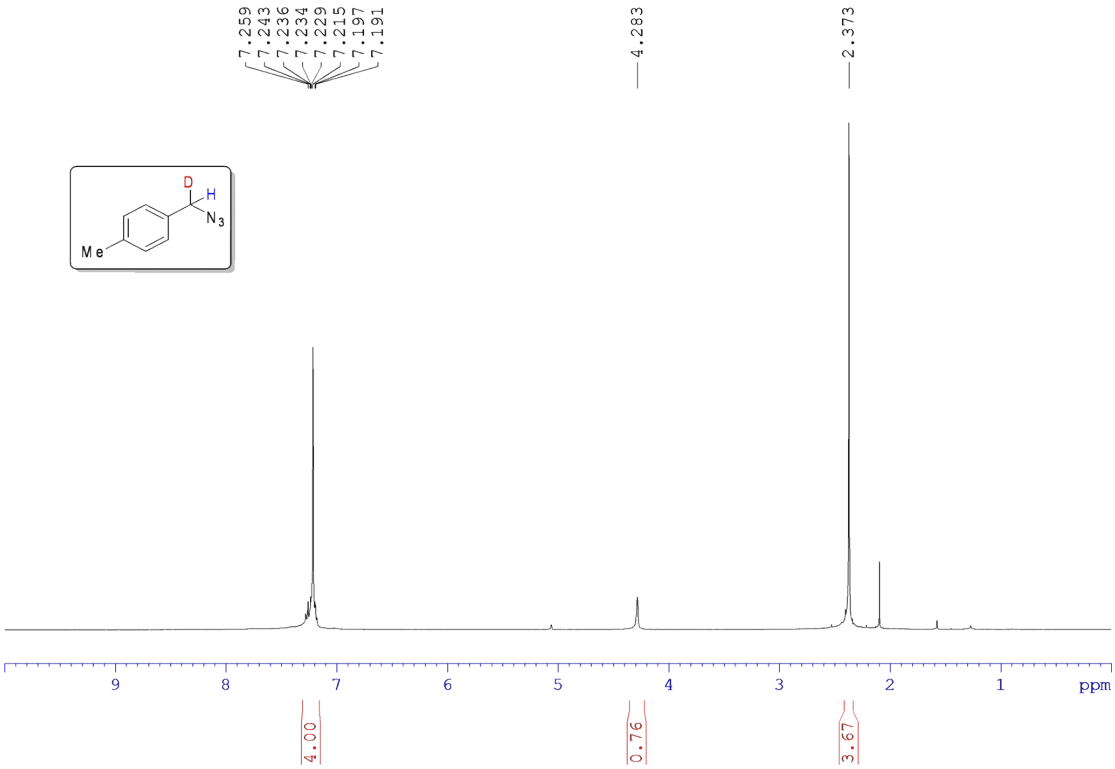


To a solution of 4-Methylbenzaldehyde (1.2 g, 10 mmol) in methanol (50 mL), $NaBD_4$ (630 mg, 20 mmol) was added slowly at 0 °C and stirred at room temperature for 3 h. Then, water (30 mL) was slowly added to the reaction mixture. The reaction mixture was extracted with diethyl ether (20 × 3) and the combined organic solution was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was directly used for next the step without purification.

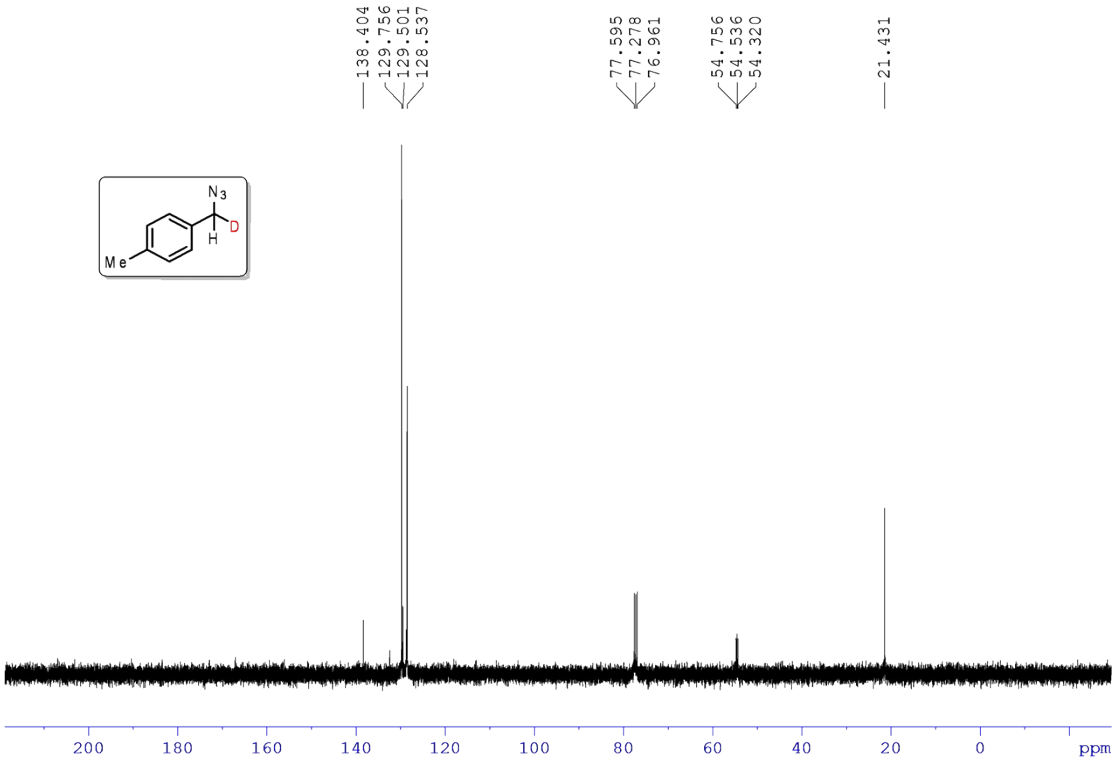
To a solution of *p*-tolylmethan-d_1-ol (1.23 g, 10 mmol) in DCM (100 mL) was added PBr_3 (5.4 g, 1.9 mL, 20 mmol) dropwise at room temperature. The mixture was stirred at room temperature for 15 h. The mixture was washed with ice water, dried over $MgSO_4$ and concentrated under reduced pressure to give 1-(bromomethyl-*d*)-4-methylbenzene in 90% yield.

1-(Bromomethyl-d_1)-4-methylbenzene (9 mmol) and sodium azide (13.5 mmol) were dissolved in DMF (20 mL) and stirred at room temperature for overnight. At the end of the reaction, the mixture was diluted with water and extracted with diethyl ether. The combined organic solution was concentrated in vacuo and the mixture was purified by a silica gel column (*n*-hexane/EtOAc, 90:10) to afford the 1-(azidomethyl-d_1)-4-methylbenzene (1.3 g, 98%). **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 7.24-7.19 (m, 4 H), 4.28 (s, 1 H), 2.37 (s, 3 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 138.4 (C), 129.8 (2 *C*H), 129.5 (C), 128.5 (2 *C*H), 54.5 (t, J = 22 Hz, *C*D), 21.4 (CH_3).

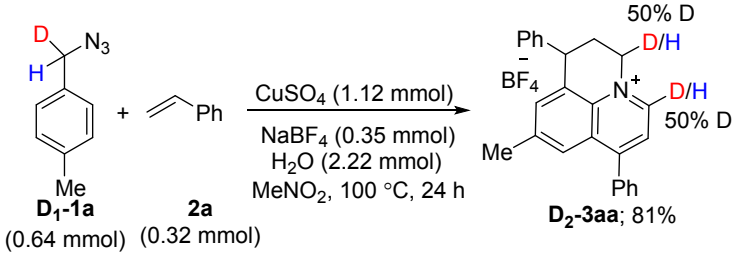
^{1}H NMR spectra of 1-(azidomethyl-d_1)-4-methylbenzene (**D_1-1a**)



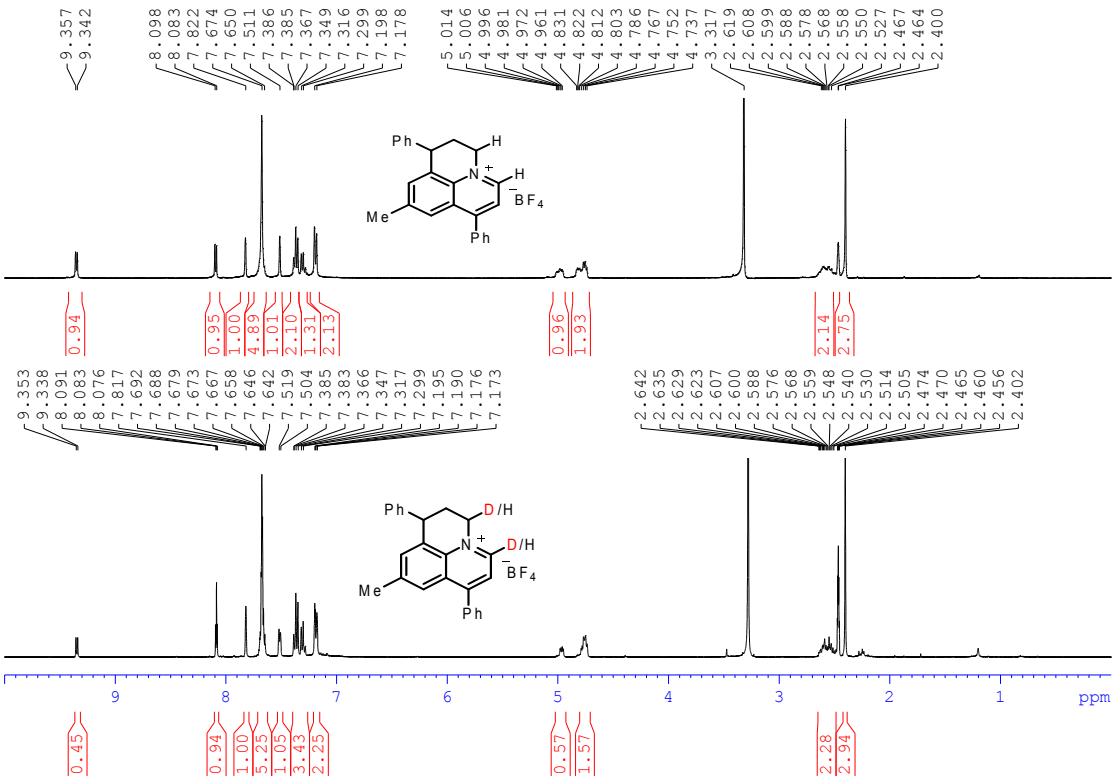
^{13}C NMR spectra of 1-(azidomethyl-d_1)-4-methylbenzene (**D_1-1a**)



Typical Procedure for the Synthesis of Quinolinium Salts D_2-3aa



A sealed tube that contained $CuSO_4$ (178 mg, 1.12 mmol) and $NaBF_4$ (24 mg, 0.2 mmol) was evacuated and purged with nitrogen gas three times. $MeNO_2$ (2.0 mL) was then added to the tube, and the suspension was stirred for 2 min at ambient temperature. Then, 1-(azidomethyl-*d*)-4-methylbenzene **D_1-1a** (94.8 mg, 0.64 mmol), styrene **2a** (33.3 mg, 0.32 mmol), H_2O (40 μL, 2.22 mmol), and additional $MeNO_2$ (1 mL) were added to the system via syringe sequentially. The reaction was stirred at 100°C for 24 h. At the end of the reaction, the mixture was diluted with CH_2Cl_2 (10 mL), filtered through a Celite pad, and washed three times with CH_2Cl_2 (3 × 20 mL). The combined filtrate was concentrated in vacuo and the mixture was purified by a silica gel column using DCM/MeOH (95:5) as eluent to afford the desired pure product **D_2-3aa** (55mg, 81%).

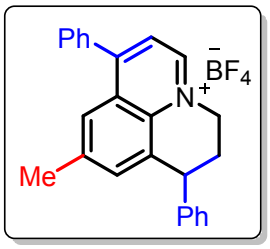


Reference

(1) C.-Z. Luo, P. Gandeepan, Y.-C. Wu, W.-C. Chen, C.-H. Cheng, *RSC Adv.* **2015**, *5*, 106012.

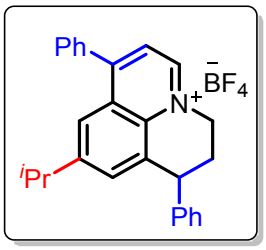
^{1}H and ^{13}C NMR and HRMS Data

9-Methyl-1,7-diphenyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3aa)



Brown solid; m.p. 141-144 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.35 (d, *J* = 6.0 Hz, 1H), 8.09 (d, *J* = 6.0 Hz, 1 H), 7.82 (s, 1 H), 7.67 (s, 5 H), 7.51 (s, 1 H),7.39-7.35 (m, 2 H), 7.32-7.30 (m, 1 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 5.01-4.96 (m, 1 H), 4.83-4.74 (m, 2 H), 2.62-2.53 (m, 2 H), 2.40 (s, 3 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 156.8 (C), 146.6 (*C*H), 143.1 (C), 139.9 (C), 136.4 (*C*H), 135.3 (C), 134.8 (C), 132.7 (C), 130.4 (*C*H), 129.6 (2 *C*H), 129.2 (2 *C*H), 128.8 (2 *C*H), 128.6 (2 *C*H), 127.8 (C), 127.2 (*C*H), 125.1 (*C*H), 121.9 (*C*H), 53.8 (CH_2), 41.7 (*C*H), 28.3 (CH_2), 21.2 (CH_3); **^{11}B NMR** (160 MHz, $(CD_3)_2SO$) : δ −1.231; **^{19}F NMR** (470 MHz, $(CD_3)_2SO$): δ −148.58, −148.64; **HRMS (FAB)** calcd for: $C_{25}H_{22}N^+$ 336.1747, found: 336.1751; **IR (KBr,** cm^{-1}): 1612, 1057 ($\nu_{B\text{-}F}$), 764, 702.

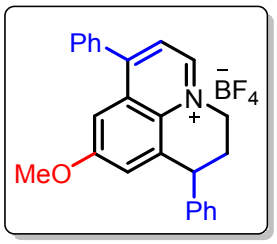
9-Isopropyl-1,7-diphenyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3ba)



Brown solid; m.p. 120-122 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.39 (d, *J* = 6.0 Hz, 1 H), 8.14 (d, *J* = 6.0 Hz, 1 H), 7.88 (s, 1 H), 7.72 (s, 5 H), 7.65 (s, 1 H),7.42-7.39 (m, 2 H), 7.35 (d, *J* = 7.2 Hz, 1 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 5.04-4.99 (m, 1 H), 4.82-4.79 (m, 2 H), 3.05 (quin, *J* = 7.2 Hz, 1 H), 2.67-2.57 (m, 2 H), 1.13 (t, *J* = 7.2 Hz, 6 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 157.0 (C), 149.7 (C), 146.7 (*C*H), 143.1 (C), 135.3 (C), 135.1 (C), 134.1 (*C*H), 133.0 (C), 130.5 (*C*H), 129.7 (2 *C*H), 129.2 (2 *C*H), 128.8 (2 *C*H), 128.5 (2 *C*H), 127.7 (C), 127.1 (*C*H), 122.4 (*C*H), 121.9 (*C*H), 53.7 (CH_2), 41.8 (*C*H), 33.2 (*C*H), 28.3 (CH_2), 23.1 (CH_3), 23.0 (CH_3); **HRMS (FAB)** calcd for: $C_{27}H_{26}N^+$ 364.2060, found: 364.2065; **IR (KBr,** cm^{-1}): 2962, 1612, 1458, 1065 (ν

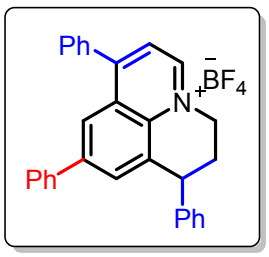
$_{B\text{-}F}$), 764, 702.

9-Methoxy-1,7-diphenyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3ca)



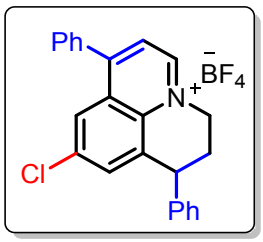
Brown solid; m.p. 161-163 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.29 (d, *J* = 6.0 Hz, 1 H), 8.11 (d, *J* = 6.0 Hz, 1 H), 7.77-7.70 (m, 5 H), 7.43-7.39 (m, 2 H), 7.36-7.35 (m, 2 H), 7.25-7.23 (m, 3 H), 5.04-4.98 (m, 1 H), 4.88-4.82 (m, 1 H), 4.79-4.76 (m, 1 H), 3.78 (s, 3 H), 2.65-2.59 (m, 2 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 158.6 (C), 155.6 (C), 144.8 (*C*H), 142.6 (C), 135.4 (C), 135.3 (C), 132.2 (C), 130.5 (*C*H), 129.5 (C), 129.4 (2 *C*H), 129.3 (2 *C*H), 128.9 (2 *C*H), 128.5 (2 *C*H), 127.3 (*C*H), 125.9 (*C*H), 122.3 (*C*H), 104.5 (*C*H), 55.7 (CH_3), 54.1. (CH_2), 41.9 (*C*H), 28.0 (CH_2); **HRMS (FAB)** calcd for: $C_{25}H_{22}NO^+$ 352.1696, found: 352.1699; **IR (KBr,** cm^{-1}): 1612, 1450, 1041 (ν $_{B\text{-}F}$), 764, 702.

1,7,9-Triphenyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3da)



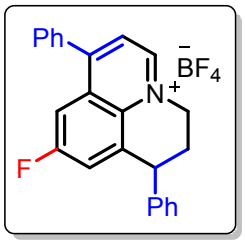
Yellow solid; m.p. 175-177 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.48 (d, *J* = 6.0 Hz, 1 H), 8.22-8.21 (m, 2 H), 8.00 (s, 1 H), 7.82-7.79 (m, 2 H), 7.77-7.73 (m, 3 H), 7.59-7.57 (m, 2 H), 7.50-7.39 (m, 5 H), 7.35-7.33 (m, 1 H), 7.28-7.26 (m, 2 H), 5.09-5.05 (m, 1 H), 4.94-4.85 (m, 2 H), 2.73-2.63 (m, 2 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 157.6 (C), 147.5 (*C*H), 143.1 (C), 140.7 (C), 137.7 (C), 135.7 (C), 135.2 (C), 133.9 (C), 133.5 (*C*H), 130.7 (*C*H), 129.8 (2 *C*H), 129.4 (2 *C*H), 129.3 (2 *C*H), 129.0 (*C*H), 128.9 (2 *C*H), 128.6 (2 *C*H), 128.1 (C), 127.2 (3 *C*H), 123.3 (*C*H), 122.3 (*C*H), 53.8 (CH_2), 41.9 (*C*H), 28.2 (CH_2); **HRMS (FAB)** calcd for: $C_{30}H_{24}N^+$ 398.1903, found: 398.1909; **IR (KBr,** cm^{-1}): 1604, 1057 (ν $_{B\text{-}F}$), 764, 702.

9-Chloro-1,7-diphenyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3ea)



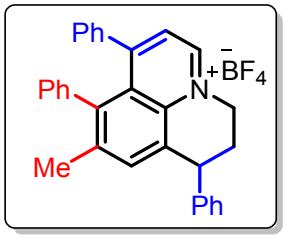
Yellow solid; m.p. 124-126 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.56 (d, *J* = 6.0 Hz, 1 H), 8.25 (d, *J* = 6.0 Hz, 1 H), 7.99 (d, *J* = 2.0 Hz, 1 H), 7.73 (s, 5 H), 7.66-7.65 (m, 1 H), 7.43-7.40 (m, 2 H), 7.37-7.33 (m, 1 H), 7.26-7.23 (m, 2 H), 5.09-5.03 (m, 1 H), 4.92-4.83 (m, 2 H), 2.66-2.59 (m, 2 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 156.8 (C), 148.2 (*C*H), 142.5 (C), 136.0 (C), 135.1 (C), 134.7 (C), 134.2 (C), 134.1 (*C*H), 130.8 (*C*H), 129.7 (2 *C*H), 129.4 (2 *C*H), 128.9 (2 *C*H), 128.7 (C), 128.6 (2 *C*H), 127.4 (*C*H), 124.9 (*C*H), 123.0 (*C*H), 54.1 (CH_2), 41.8 (*C*H), 28.0 (CH_2); **HRMS (FAB)** calcd for: $C_{24}H_{19}ClN^+$ 356.1201, found: 356.1203; **IR (KBr,** cm^{-1}): 1604, 1450, 1057 (ν_{B-F}), 764, 702.

9-Fluoro-1,7-diphenyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3fa)



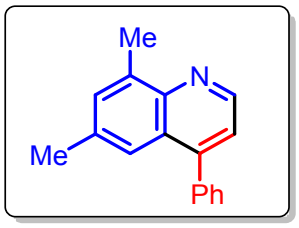
Brown solid; m.p. 76-78 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.47 (d, *J* = 6.0 Hz, 1 H), 8.24 (d, *J* = 6.0 Hz, 1 H), 7.79-7.76 (m, 1 H), 7.73 (s, 5 H), 7.61-7.58 (m, 1 H), 7.44-7.40 (m, 2 H), 7.37-7.34 (m, 1 H), 7.26-7.24 (m, 2 H), 5.09-5.02 (m, 1 H), 4.91-4.84 (m, 2 H), 2.71-2.59 (m, 2 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 160.5 (d, *J* = 250.0 Hz , C), 157.0 (d, *J* = 5.0 Hz , C), 147.5 (*C*H), 142.4 (C), 137.3 (d, *J* = 8.0 Hz , C), 134.8 (C), 133.6 (C), 130.7 (*C*H), 129.6 (2 *C*H), 129.4 (d, *J* = 12.5 Hz , C), 129.3 (2 *C*H) , 128.9 (2 *C*H), 128.6 (2 *C*H), 127.4 (*C*H), 123.8 (d, *J* = 26.0 Hz , *C*H), 122.7 (*C*H), 110.4 (d, *J* = 24.0 Hz , *C*H), 54.1 (CH_2), 42.0 (*C*H), 28.0 (CH_2); **HRMS (FAB)** calcd for: $C_{24}H_{19}FN^+$ 340.1496, found: 340.1501; **IR (KBr,** cm^{-1}): 1619, 1450, 1049 (ν_{B-F}), 764, 702.

9-Methyl-1,7,8-triphenyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3ga)



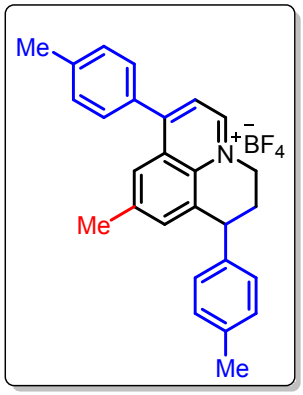
Brown solid; m.p. 156-158 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.41 (d, *J* = 6.0 Hz, 1 H), 8.17 (d, *J* = 6.0 Hz, 1 H), 8.08 (s, 1 H), 7.76-7.73 (m, 5 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 7.29 (d, *J* = 7.2 Hz, 1 H), 7.19-7.17 (m, 3 H), 7.04 (t, *J* = 7.6 Hz, 1 H), 6.74-6.72 (m, 2 H), 6.34 (d, *J* = 7.6 Hz, 1 H), 4.97(d, *J* = 14 Hz, 1 H), 4.50-4.46 (m, 2 H), 2.69-2.62 (m, 1 H), 2.32 (d, *J* = 14 Hz, 1 H), 2.10 (s, 3 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 157.5 (C), 148.9 (C), 148.0 (*C*H), 143.4 (C), 140.0 (C), 137.3 (C), 135.8 (C), 135.7 (C), 130.9 (*C*H), 130.2 (2 *C*H), 129.7 (2 *C*H), 129.4 (C), 129.2 (*C*H) , 128.7 (2 *C*H), 128.6 (3 *C*H), 128.4 (*C*H), 128.3 (*C*H), 128.0 (*C*H), 127.5 (C), 127.1 (*C*H), 126.8 (*C*H), 122.3 (*C*H), 51.8 (CH_2), 40.1 (*C*H), 28.4 (CH_2), 21.9 (CH_3); **HRMS (FAB)** calcd for: $C_{31}H_{26}N^+$ 412.2060, found: 412.2067; **IR (KBr,** cm^{-1}): 1597, 1049 (ν_{B-F}), 764, 702.

6,8-Dimethyl-4-phenylquinoline (3ha')



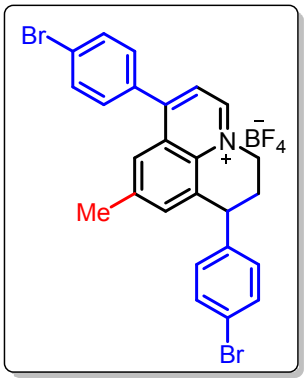
Pale yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.88 (d, *J* = 4.4 Hz, 1 H), 7.51-7.45 (m, 6 H), 7.41 (s, 1 H), 7.26 (d, *J* = 4.4 Hz, 1 H), 2.82 (s, 3 H), 2.40 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ148.0 (C), 147.7 (*C*H), 146.3 (C), 138.6 (C), 136.9 (C), 136.0 (C), 131.9 (*C*H), 129.5 (2 *C*H), 128.4 (2 *C*H), 128.1 (*C*H), 126.7 (C), 122.6 (*C*H), 121.2 (*C*H), 21.7 (CH_3), 18.5 (CH_3); **HRMS (EI)** calcd for: $C_{17}H_{15}N$ 233.1204, found: 233.1211; **IR (KBr,** cm^{-1}): 2924, 2854, 1489, 1450, 864, 764, 702.

9-Methyl-1,7-di-*p*-tolyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3ab)



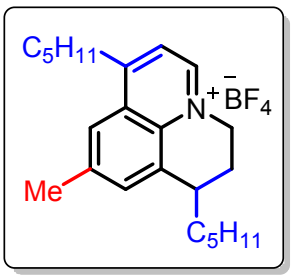
Brown solid; m.p. 99-101 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.36 (d, *J* = 6.0 Hz, 1 H), 8.07 (d, *J* = 6.0 Hz, 1 H), 7.88 (s, 1 H), 7.60 (d, *J* = 8.0 Hz, 2 H), 7.53-7.51 (m, 3 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 5.02-4.96 (m, 1 H), 4.84-4.79 (m, 1 H), 4.73-4.70 (m, 1 H), 2.60-2.54 (m, 2 H), 2.48 (s, 3 H), 2.43 (s, 3 H), 2.31 (s, 3 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 156.9 (C), 146.4 (*C*H), 140.4 (C), 140.1 (C), 139.8 (C), 136.3 (*C*H), 136.3 (C), 134.8 (C), 132.9 (C), 132.5 (C), 129.8 (2 *C*H), 129.7 (2 *C*H), 129.4 (2 *C*H), 128.5 (2 *C*H), 127.7 (C), 125.2 (*C*H), 121.7 (*C*H), 53.8 (CH_2), 41.4 (*C*H), 28.4 (CH_2), 21.2 (CH_3), 21.0 (CH_3), 20.6 (CH_3); **HRMS (FAB)** calcd for: $C_{27}H_{26}N^+$ 364.2080, found: 364.2066; **IR (KBr,** cm^{-1}): 2923, 1612, 1442, 1057 (ν_{B-F}), 825, 733.

1,7-Bis(4-bromophenyl)-9-methyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3ac)



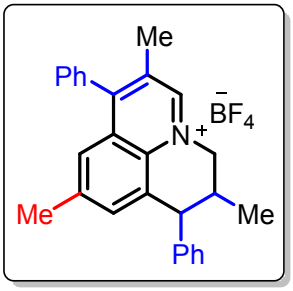
Brown solid; m.p. 64-66 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.40 (d, *J* = 6.0 Hz, 1 H), 8.14 (d, *J* = 6.0 Hz, 1 H), 7.91 (d, *J* = 8.4 Hz, 2 H), 7.85 (s, 1 H), 7.64 (d, *J* = 8.4 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.55 (s, 1 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 5.04-4.99 (m, 1 H), 4.86-4.78 (m, 2 H), 2.62-2.56 (m, 2 H), 2.45 (s, 3 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 155.6 (C), 146.7 (*C*H), 142.5 (C), 140.2 (C), 136.5 (*C*H), 134.7 (C), 134.4 (C), 132.2 (C), 132.2 (2 *C*H), 131.7 (4 *C*H), 130.9 (2 *C*H), 127.7 (C), 125.1 (*C*H), 124.2 (C), 121.9 (*C*H), 120.4 (C), 53.8 (CH_2), 41.2 (*C*H), 28.1 (CH_2), 21.1 (CH_3); **HRMS (FAB)** calcd for: $C_{25}H_{20}Br_2N^+$ 491.9957, found: 491.9965; **IR (KBr,** cm^{-1}): 2962, 1612, 1489, 1057 (ν_{B-F}), 825, 733.

9-Methyl-1,7-dipentyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3ad)



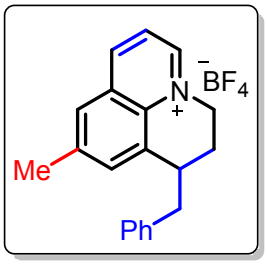
Brown oil; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.16 (d, *J* = 6.0 Hz, 1 H), 8.21 (s, 1 H), 7.96 (d, *J* = 6.0 Hz, 1 H), 7.93 (s, 1 H), 4.86-4.83 (m, 2 H), 3.31-3.29 (m, 2 H), 3.27-3.23 (m, 1 H), 2.62 (s, 3 H), 2.35-2.32 (m, 1 H), 2.25-2.19 (m, 1 H), 1.80-1.66 (m, 4 H), 1.43-1.33 (m, 10 H), 0.91-0.87 (m, 6 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 160.3 (C), 146.0 (*C*H), 139.4 (C), 135.2 (*C*H), 134.0 (C), 133.3 (C), 128.4 (C), 122.9 (*C*H), 121.0 (*C*H), 52.5 (CH_2), 34.9 (*C*H), 34.3 (CH_2), 32.2 (CH_2), 31.2 (CH_2), 31.0 (CH_2), 29.3 (CH_2), 25.7 (CH_2), 23.9 (CH_2), 22.0 (CH_2), 21.9 (CH_2), 21.2 (CH_3), 13.9 (CH_3), 13.8 (CH_3); **HRMS (FAB)** calcd for: $C_{23}H_{34}N^+$ 324.2686, found: 324.2690; **IR (KBr,** cm^{-1}): 2931, 2861, 1612, 1458, 1057 (ν_{B-F}), 764, 732.

2,6,9-Trimethyl-1,7-diphenyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3ae)



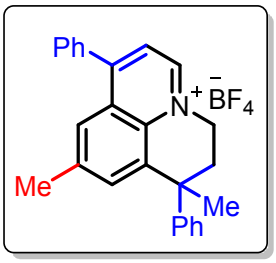
Yellow solid; m.p. 78-80 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.45 (s, 1 H), 7.72-7.66 (m, 3 H), 7.45-7.41 (m, 4 H), 7.38-7.36 (m, 1 H), 7.29 (s, 1 H), 7.23-7.22 (m, 3 H), 4.97-4.93 (m, 1 H), 4.80-4.74 (m, 1 H), 4.36 (d, *J* = 9.2 Hz, 1 H), 2.80-2.76 (m, 1 H), 2.35 (s, 3 H), 2.30 (s, 3 H), 1.01 (d, *J* =6.8 Hz, 3 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 155.5 (C), 148.0 (*C*H), 141.8 (C), 139.8 (C), 135.4 (*C*H), 134.0 (C), 132.9 (C), 132.9 (C), 130.1 (C), 129.5 (*C*H), 129.2 (2 *C*H), 129.0 (2 *C*H), 129.0 (2 *C*H), 128.8 (C), 128.4 (2 *C*H), 127.4 (*C*H), 124.5 (*C*H), 59.6 (CH_2), 49.3 (*C*H), 32.6 (*C*H), 21.3 (CH_3), 17.5 (CH_3), 16.3 (CH_3); **HRMS (FAB)** calcd for: $C_{27}H_{26}N^+$ 364.2080, found: 364.2068 ; **IR (KBr,** cm^{-1}): 2970, 1620, 1450, 1057 (ν_{B-F}), 756, 702.

1-Benzyl-9-methyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium (3af')



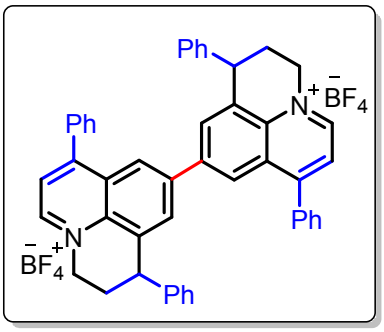
Brown solid; m.p. 163-165 °C; **^{1}H NMR** (600 MHz, $(CD_3)_2SO$): δ 9.34 (d, *J* = 5.4 Hz, 1 H), 9.12 (d, *J* = 8.4 Hz, 1 H), 8.11-8.09 (m, 2 H), 7.88 (s, 1 H), 7.37-7.34 (m, 2 H), 7.32-7.31 (m, 2 H), 7.28-7.26 (m, 1 H), 5.05-5.00 (m, 1 H), 4.93-4.90 (m, 1 H), 3.58-3.55 (m, 1 H), 3.28-3.24 (m, 1 H), 2.94-2.90 (m, 1 H), 2.54 (s, 3 H), 2.26-2.21 (m, 1 H), 2.07-2.03 (m, 1 H); **^{13}C NMR** (150 MHz, $(CD_3)_2SO$): δ 147.2 (*C*H), 145.9 (*C*H), 139.5 (C), 138.9 (C), 136.0 (*C*H), 133.7 (C), 132.4 (C), 129.8 (C), 129.4 (2 *C*H), 128.4 (2 *C*H), 126.9 (*C*H), 126.5 (*C*H), 121.5 (*C*H), 52.5 (CH_2), 40.3 (CH_2), 36.4 (*C*H), 23.6 (CH_2), 21.0 (CH_3); **HRMS (FAB)** calcd for: $C_{20}H_{20}N^+$ 274.1590, found: 274.1595; **IR (KBr,** cm^{-1}): 2924, 2854, 1597, 1450, 1041 (ν_{B-F}), 748, 702.

1,9-Dimethyl-1,7-diphenyl-2,3-dihydro-1*H*-pyrido[3,2,1-*ij*]quinolin-4-ium tetrafluoroborate (3ag')



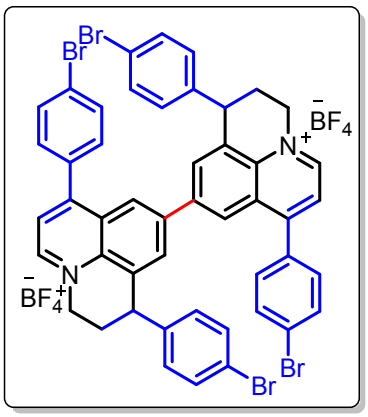
Brown solid; m.p. 146-148 °C; **^{1}H NMR** (600 MHz, $(CD_3)_2SO$): δ 9.30 (d, *J* = 6.0 Hz, 1 H), 8.09 (d, *J* = 6.0 Hz, 1 H), 7.94-7.94 (m, 1 H), 7.88-7.88 (m, 1 H), 7.71-7.68 (m, 5 H), 7.33 (t, *J* = 7.2 Hz, 2 H), 7.27-7.25 (m, 1 H), 7.14-7.13 (m, 2 H), 4.99-4.95 (m, 1 H), 4.47-4.42 (m, 1 H), 2.77-2.73 (m, 1 H), 2.51 (s, 3 H), 2.48-2.45 (m, 1 H), 1.94 (s, 3 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 157.4 (C), 147.4 (C), 147.1 (*C*H), 140.6 (C), 137.3 (C), 136.3 (*C*H), 135.9 (C), 134.8 (C), 130.9 (*C*H), 130.1 (2 *C*H), 129.7 (2 *C*H), 129.0 (2 *C*H), 128.4 (C), 127.6 (2 *C*H), 127.2 (*C*H), 125.8 (*C*H), 122.3 (*C*H), 53.1 (CH_2), 41.9 (C), 35.9 (CH_2), 29.3 (CH_3), 21.8(CH_3); **HRMS (FAB)** calcd for: $C_{26}H_{24}N^+$ 350.1903, found: 351.1986 ; **IR (KBr,** cm^{-1}): 2924, 2854, 1604, 1527, 1442, 1049 (ν_{B-F}), 764, 702.

1,1',7,8'-Tetraphenyl-2,2',3,3'-tetrahydro-1*H*,1'*H*-[9,10'-bipyrido[3,2,1-*ij*]quinoline]-4,4'-diium tetrafluoroborate (4ja)



Yellow solid; m.p. 202-204 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.43 (d, *J* = 6.0 Hz, 2 H), 8.18 (d, *J* = 6.0 Hz, 2 H), 8.09-8.07 (m, 2 H), 7.91 (s, 1H), 7.77-7.73 (m, 3 H), 7.65-7.61 (m, 8 H), 7.31-7.30 (m, 6 H), 7.15-7.12 (m, 4 H), 5.01-4.96 (m, 2 H), 4.85-4.76 (m, 4 H), 2.61-2.56 (m, 4 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ158.3 (C), 158.3 (C), 148.7 (2 *C*H), 143.1 (C), 143.0 (C), 138.4 (C), 138.3 (C), 136.7 (2 C), 135.3 (2 C), 135.2 (C), 135.0 (C), 133.3 (*C*H), 133.3 (*C*H), 131.2 (2 *C*H), 130.1 (4 *C*H), 129.8 (4 *C*H), 129.4 (2 *C*H), 129.3 (2 *C*H), 128.9 (2 *C*H), 128.9 (2 *C*H), 128.5 (2 C), 127.8 (*C*H), 127.8 (*C*H), 125.0 (2 *C*H), 123.0 (*C*H), 123.0 (*C*H), 54.7 (CH_2), 54.4 (CH_2), 42.5 (*C*H), 42.3 (*C*H), 28.6 (2 CH_2); **HRMS (FAB)** calcd for: $C_{48}H_{38}N_2^{2+}$ 642.3024, found: 642.3028; **IR (KBr,** cm^{-1}): 1604, 1442, 1373, 1304, 1242, 1049 (ν_{B-F}), 856, 764, 702.

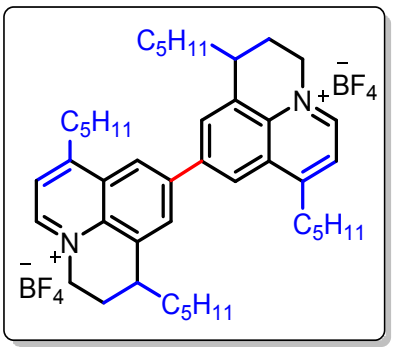
1,1',7,8'-Tetrakis(4-bromophenyl)-2,2',3,3'-tetrahydro-1*H*,1'*H*-[9,10'-bipyrido[3,2,1-*ij*]quinoline]-4,4'-diium tetrafluoroborate (4jc)



Yellow solid; m.p. 216-218 °C; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.49 (d, *J* = 4.8 Hz, 2 H), 8.24 (d, *J* = 6.0 Hz, 2 H), 8.20 (s, 1 H), 8.16 (s, 1 H), 8.07 (s, 1 H), 7.88-7.86 (m, 5 H), 7.70-7.67 (m, 4 H), 7.55-7.53 (m, 4 H), 7.17-7.13 (m, 4 H), 5.03-5.01 (m, 2 H), 4.90-4.80 (m, 4 H), 2.65-2.58 (m, 4 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 156.6 (C), 156.5 (C) 148.4 (2 *C*H), 142.3 (C), 142.1 (C), 138.1 (C), 137.9 (C), 136.2 (C), 136.1 (C), 134.1 (C), 134.0 (C), 133.9 (C), 133.5 (C), 133.3 (*C*H), 133.1 (*C*H), 132.2 (4 *C*H), 131.9 (4 *C*H), 131.6 (2 *C*H), 131.6 (2 *C*H), 130.8 (2 *C*H), 130.8 (2 *C*H), 127.8 (C), 127.8 (C), 124.9 (2 *C*H), 124.7 (C), 124.7 (C), 122.6 (*C*H),

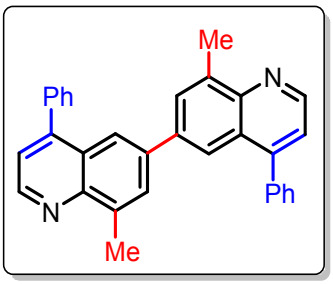
122.5 (*C*H), 120.5 (C), 120.4 (C), 54.0 (*C*H_2), 53.5 (*C*H_2), 41.3 (*C*H), 41.1 (*C*H), 28.0 (*C*H_2), 28.0 (*C*H_2); **HRMS (FAB)** calcd for: $C_{48}H_{34}Br_4N_2^{2+}$ 953.9445, found: 953.9449; **IR (KBr,** cm^{-1}): 2931, 2867, 1589, 1458, 1065 (ν_{B-F}), 825, 733.

1,1',7,8'-tetrapentyl-2,2',3,3'-tetrahydro-1H,1'H-[9,10'-bipyrido[3,2,1-ij]quinoline]-4,4'-diium tetrafluoroborate (4jd)



Brown oil; **^{1}H NMR** (400 MHz, $(CD_3)_2SO$): δ 9.31 (d, *J* = 6.0 Hz, 2 H), 8.74 (s, 2 H), 8.59 (s, 2 H), 8.11 (d, *J* = 6.0 Hz, 2 H), 4.95 (s, 4 H), 3.55-3.51 (m, 4 H), 3.28-3.22 (m, 2 H), 2.45-2.32 (m, 4 H), 1.90-1.77 (m, 8 H), 1.47-1.35 (m, 20 H), 0.91-0.87 (m, 12 H); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$): δ 161.9 (2 C), 147.6 (2 *C*H), 138.2 (C), 138.1 (C), 135.7 (C), 135.6 (C), 134.8 (C), 134.8 (C), 132.6 (*C*H), 132.6 (*C*H), 128.7 (C), 128.7 (C), 122.8 (2 *C*H), 121.9 (2 *C*H), 52.5 (2 *C*H_2), 35.3 (2 *C*H), 34.4 (*C*H_2), 34.3 (*C*H_2), 32.3 (2 *C*H_2), 31.3 (2 *C*H_2), 31.1 (*C*H_2), 31.0 (*C*H_2), 29.6 (2 *C*H_2), 25.9 (*C*H_2), 25.8 (*C*H_2), 23.8 (*C*H_2), 23.8 (*C*H_2), 22.1 (*C*H_2), 22.1 (*C*H_2), 21.9 (2 *C*H_2), 14.0 (2 *C*H_3), 13.9 (2 *C*H_3); **HRMS (FAB)** calcd for: $C_{44}H_{62}N_2^{2+}$ 618.4902, found: 618.4920; **IR (KBr,** cm^{-1}): 3070, 2931, 2862, 1581, 1458, 1041 (ν_{B-F}), 733.

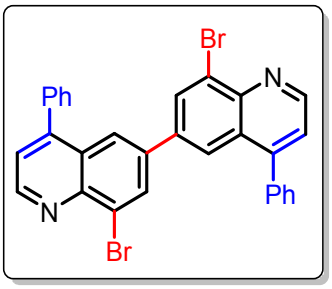
8,8'-Dimethyl-4,4'-diphenyl-6,6'-biquinoline (5ka)



Yellow solid; m.p. 182-184 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.94 (d, *J* = 4.4 Hz, 2 H), 7.95-7.95 (m, 2 H), 7.84-7.83 (m, 2 H), 7.50-7.47 (m, 10 H), 7.33 (d, *J* = 4.4 Hz, 2 H), 2.90 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ148.8 (2 *C*H), 147.3 (2 C), 138.4 (4 C), 138.0 (4 C), 129.6 (4 *C*H), 129.2 (2 *C*H), 128.6 (4 *C*H), 128.3 (2 *C*H), 126.9 (2 C), 122.3 (2 *C*H), 121.7 (2 *C*H), 18.8 (2 *C*H_3); **HRMS (EI)** calcd for: $C_{32}H_{24}N_2$ 436.1939, found: 436.1924; **IR**

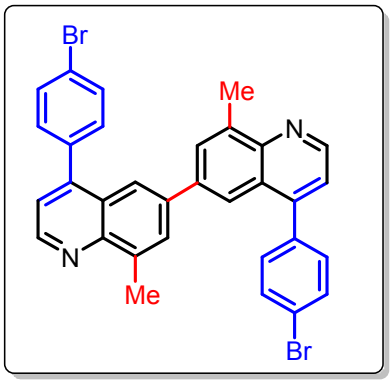
(KBr, cm^{-1}): 2924, 2854, 1489, 1458, 872, 764, 702.

8,8'-Dibromo-4,4'-diphenyl-6,6'-biquinoline (5la)



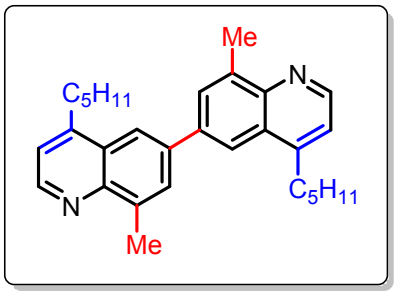
Yellow solid; m.p. 262-264 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.05 (d, *J* = 4.4 Hz, 2 H), 8.29 (d, *J* = 2.0 Hz, 2 H), 8.04 (d, *J* = 2.0 Hz, 2 H), 7.54-7.48 (m, 6 H), 7.47-7.44 (m, 4 H), 7.41 (d, *J* = 4.4 Hz, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ151.0 (2 *C*H), 149.4 (2 C), 145.2 (2 C), 137.8 (2 C), 137.3 (2 C), 132.2 (2 *C*H), 129.5 (4 *C*H), 128.8 (6 *C*H), 128.1 (2 C), 126.2 (2 C), 124.3 (2 *C*H), 122.8 (2 *C*H); **HRMS (EI)** calcd for: $C_{30}H_{18}N_2Br_2$ 563.9831, found: 563.9831; **IR** (KBr, cm^{-1}): 2924, 2854, 1489, 1450, 864, 764, 702.

4,4'-Bis(4-bromophenyl)-8,8'-dimethyl-6,6'-biquinoline (5kc)



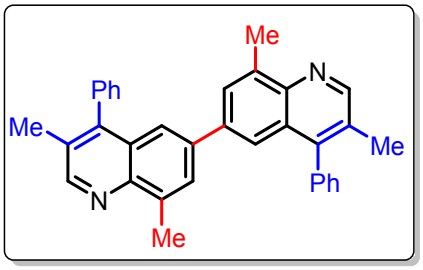
Yellow solid; m.p. 223-225°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.94 (d, *J* = 4.4 Hz, 2 H), 7.85 (s, 2 H), 7.82 (s, 2 H), 7.65 (d, *J* = 8.0 Hz, 4 H), 7.35 (d, *J* = 8.4 Hz, 4 H), 7.31 (d, *J* = 4.0 Hz, 2 H), 2.91 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ148.8 (2 *C*H), 147.6 (C), 147.3 (C), 138.4 (2 C), 138.3 (2 C), 137.2 (2 C), 131.8 (4 *C*H), 131.2 (4 *C*H), 129.2 (2 *C*H), 126.6 (2 C), 122.8 (2 C), 121.9 (2 *C*H), 121.5 (2 *C*H), 18.8 (2 *C*H_3); **HRMS (EI)** calcd for: $C_{32}H_{22}Br_2N_2$ 592.0150, found:592.0162; **IR** (KBr, cm^{-1}): 2916, 2854, 1589, 1481, 864, 818, 725.

8,8'-Dimethyl-4,4'-dipentyl-6,6'-biquinoline (5kd)



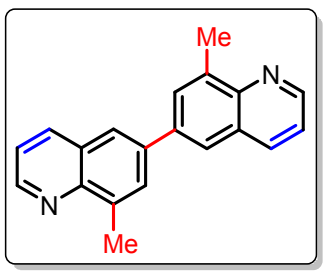
Brown oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.83 (d, *J* = 4.4 Hz, 2 H), 8.14-8.13 (m, 2 H), 7.90-7.89 (m, 2 H), 7.27 (d, *J* = 4.4 Hz, 2 H), 3.13 (t, *J* = 7.6 Hz, 4 H), 2.91 (s, 6 H), 1.86-1.78 (m, 4 H), 1.46-1.36 (m, 8 H),0.93-0.89 (m, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.1 (2 C), 149.0 (2 CH), 146.9 (2 C), 138.4 (2 C), 138.3 (2 C), 129.2 (2 *C*H), 127.7 (2 C), 121.1 (2 *C*H), 120.1 (2 *C*H), 34.4 (2 *C*H_2), 31.8 (2 *C*H_2), 29.9 (2 *C*H_2), 22.5 (2 *C*H_2), 18.9 (2 *C*H_3), 14.0 (2 *C*H_3); **HRMS (EI)** calcd for: $C_{30}H_{36}N_2$ 424.2878, found: 424.2869; **IR** (KBr, cm^{-1}): 3024, 2924, 2852, 1589, 1504, 1458, 864, 732.

3,8,8'-Trimethyl-4-phenyl-4'-(*o*-tolyl)-6,6'-biquinoline (5ke)



Yellow solid; m.p. 185-187 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): 8.82 (s, 2 H), δ 7.68 (s, 2 H), 7.48-7.46 (m, 6 H), 7.35 (d, *J* = 1.6 Hz, 2 H), 7.19-7.17 (m, 4 H), 2.85 (s, 6 H), 2.23 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ151.4 (2 *C*H), 146.7 (2 C), 145.4 (2 C), 138.4 (2 C), 137.3 (2 C), 137.0 (2 C), 129.2 (4 *C*H), 128.6 (4 *C*H), 128.2 (2 *C*H), 128.2 (2 C), 127.7 (2 *C*H), 127.6 (2 C), 122.3 (2 *C*H), 18.5 (2 *C*H_3), 17.6 (2 *C*H_3); **HRMS (EI)** calcd for: $C_{34}H_{28}N_2$ 464.2252, found: 464.2229; **IR** (KBr, cm^{-1}): 2924, 2854, 1489, 1442, 864, 702.

3,8,8'-Trimethyl-4-phenyl-4'-(*o*-tolyl)-6,6'-biquinoline (5kf')

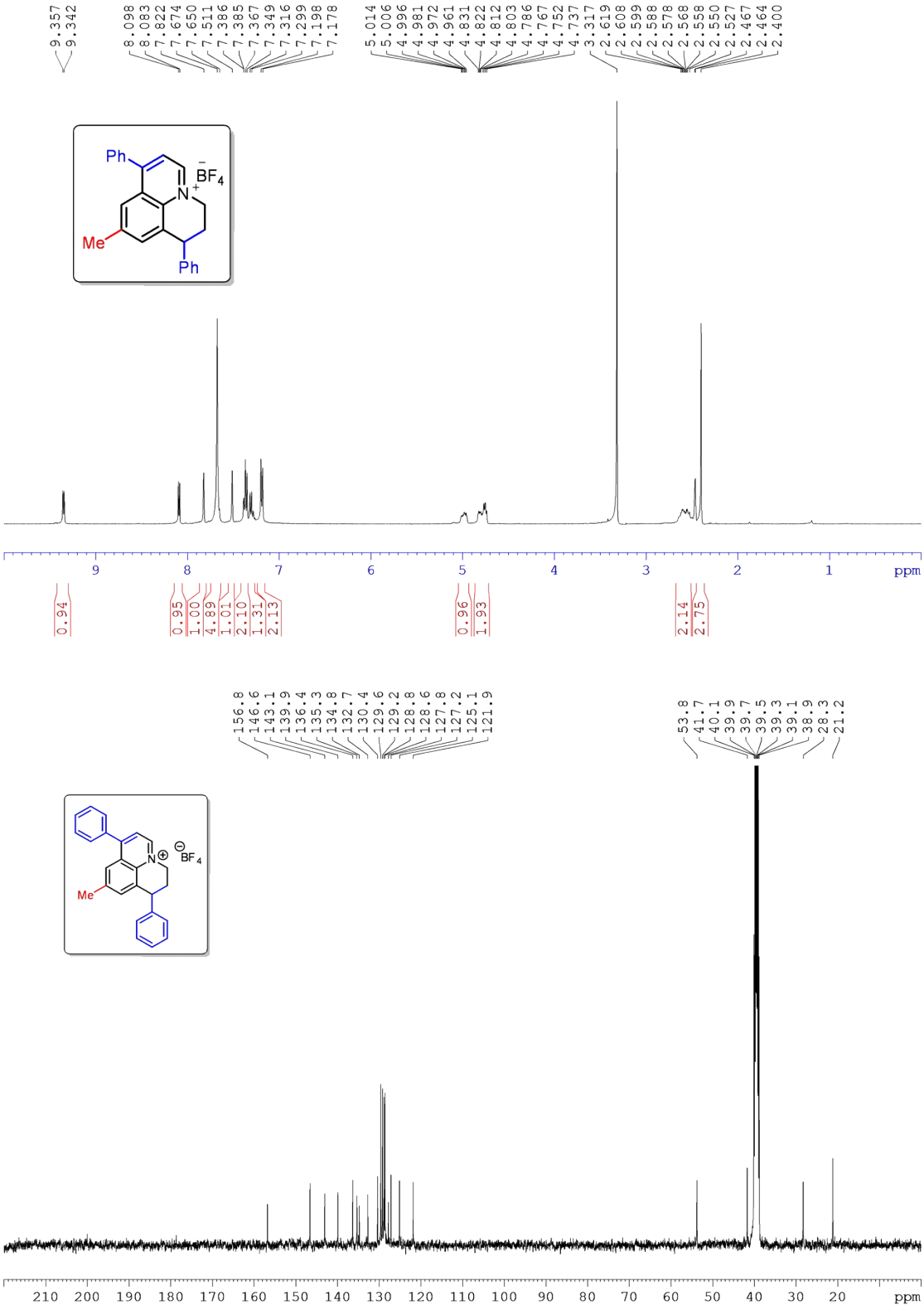


Brown solid; m.p. 186-188 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.96 (dd, *J* = 4.4, 2.0 Hz, 2 H), 8.22 (dd, *J* = 8.4, 2.0 Hz, 2 H), 7.96-7.95 (m, 4 H), 7.44 (dd, *J* = 8.4, 4.4 Hz, 2 H), 2.91 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ149.4 (2 *C*H), 146.9 (2 C), 138.2 (2 C), 137.7 (2 C), 136.7 (2 *C*H), 129.4 (2 *C*H), 128.5 (2 C),

124.0 (2 *C*H), 121.4 (2 *C*H), 18.4 (2 *C*H_3); **HRMS (EI)** calcd for: $C_{20}H_{16}N_2$ 284.1308, found: 284.1308 ; **IR (**KBr, cm^{-1}): 2924, 2854, 1496, 1373, 864, 779, 702.

1H and 13C NMR Spectra

^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra of compound **3aa**



667-i1-B

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Current Data Parameters
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EXPNO                4
PROCNO               1

F2 - Processing parameters
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WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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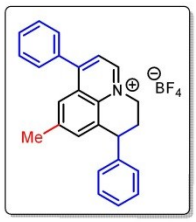

667-i2

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Current Data Parameters
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EXPNO                5
PROCNO               1

F2 - Processing parameters
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GB        0
PC                1.00
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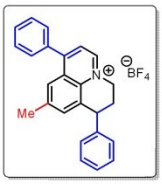
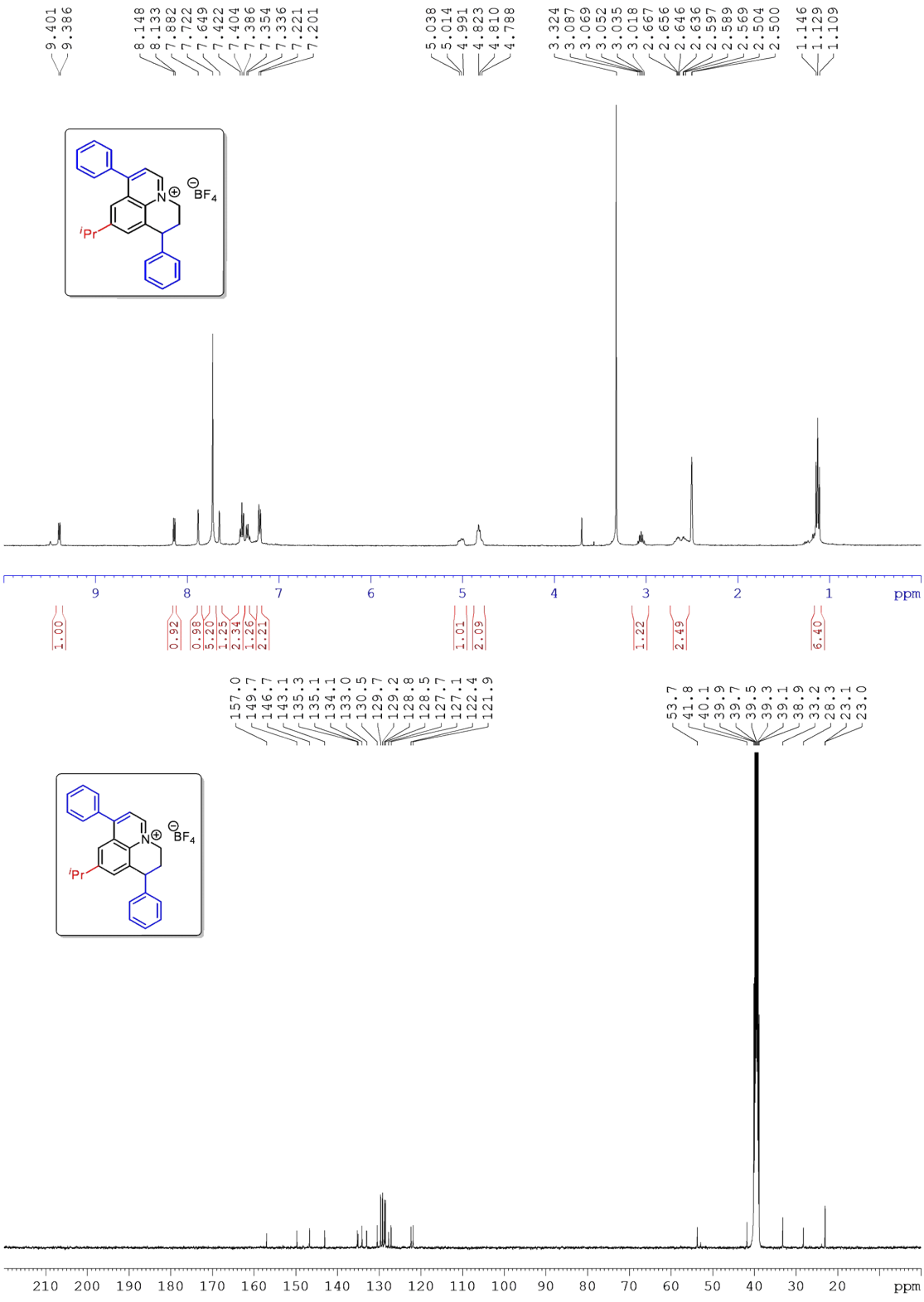
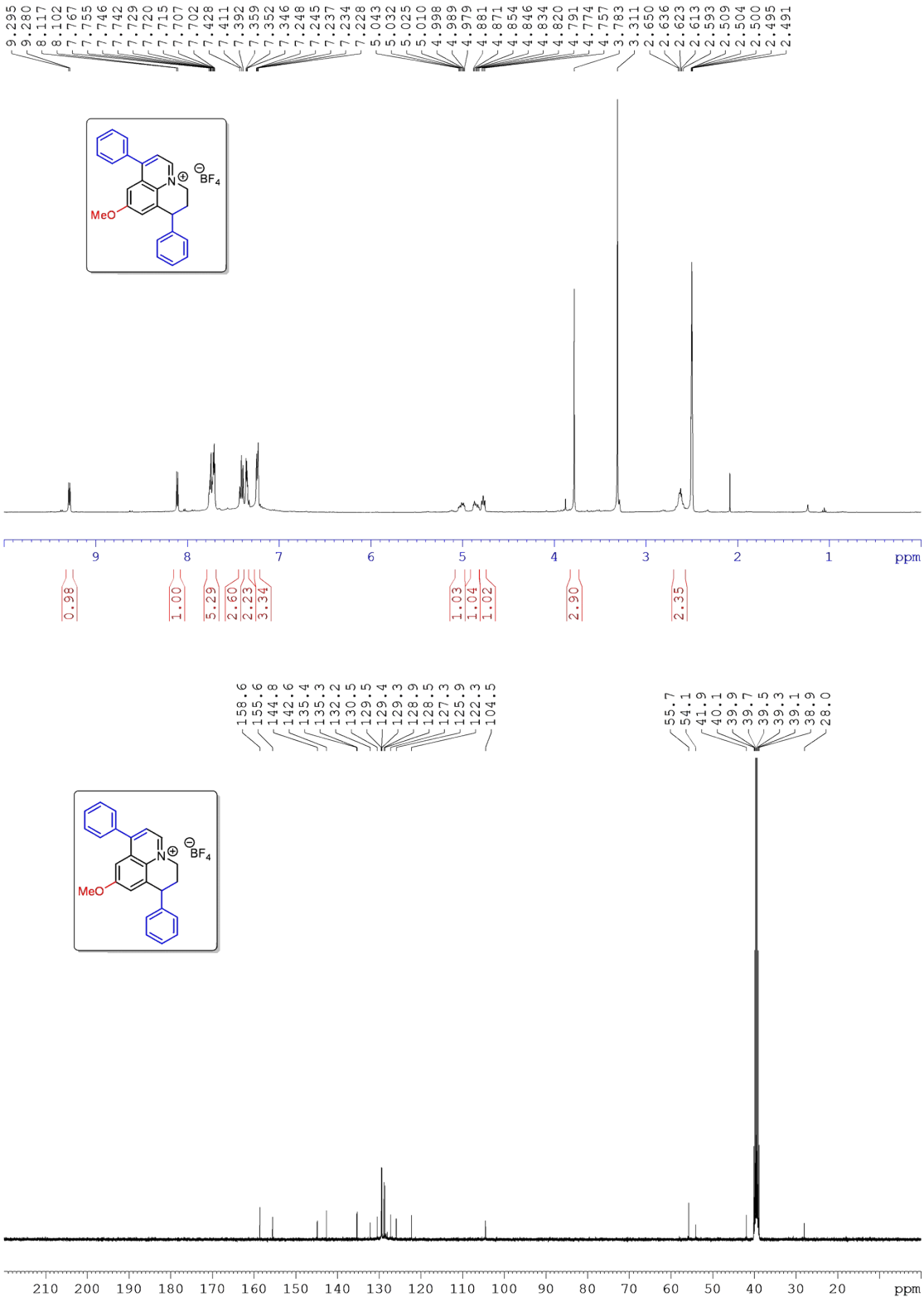


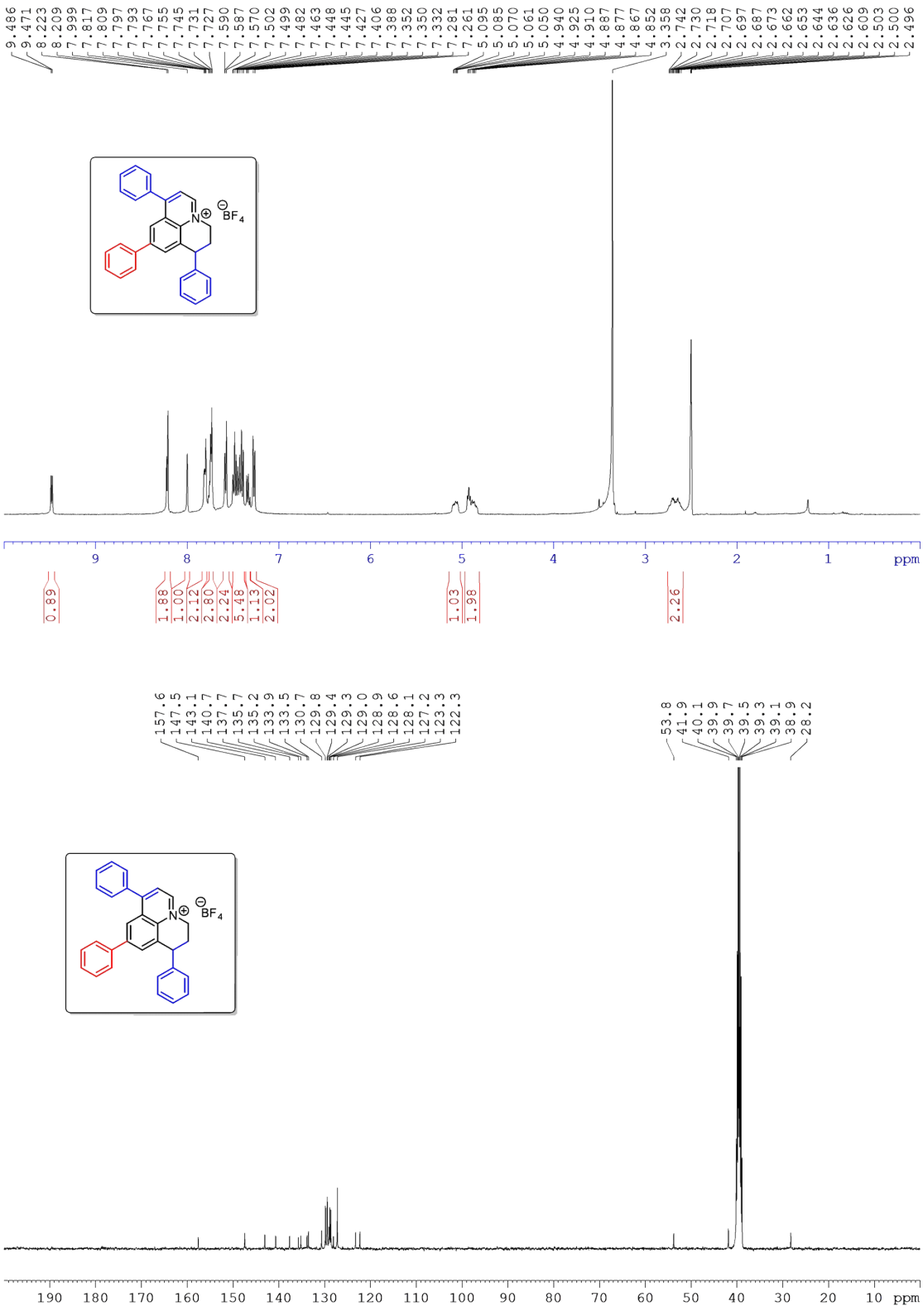
^{1}H and ^{13}C NMR spectra of compound **3ba**



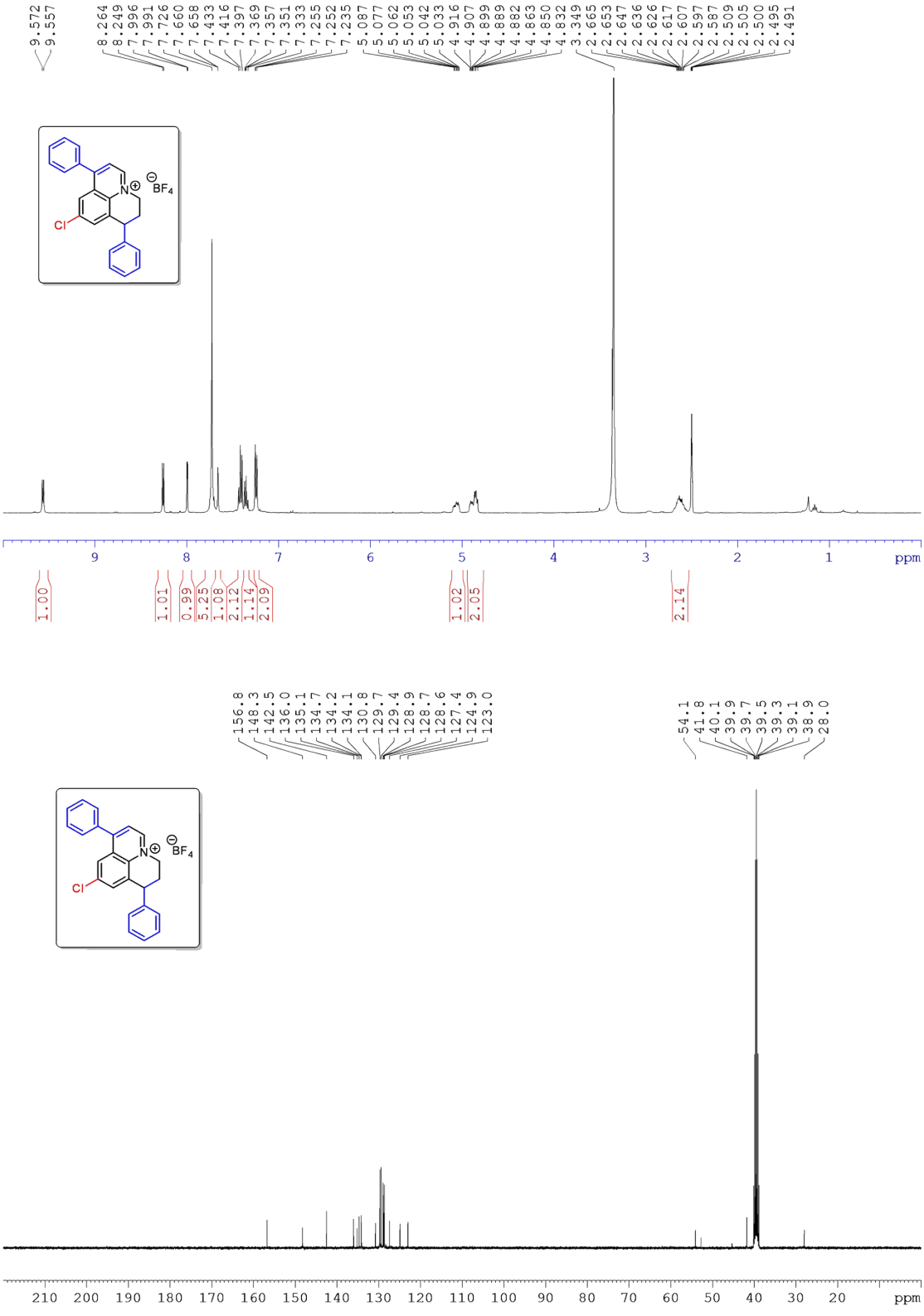
^{1}H and ^{13}C NMR spectra of compound **3ca**



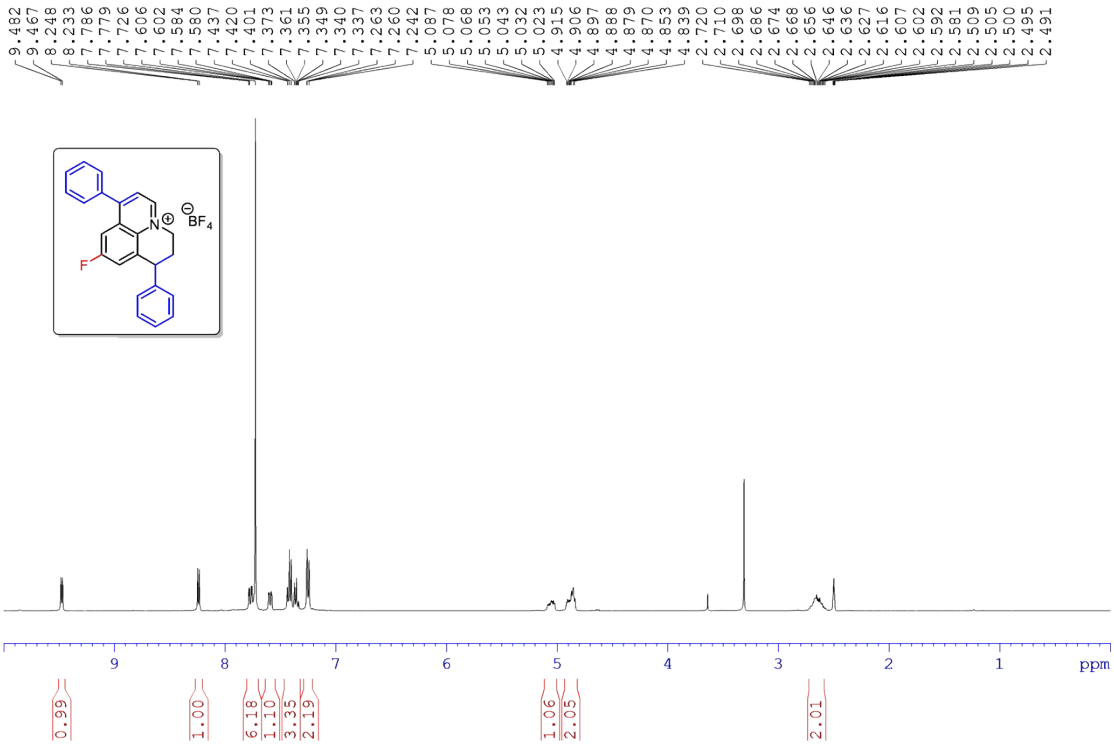
^{1}H and ^{13}C NMR spectra of compound **3da**

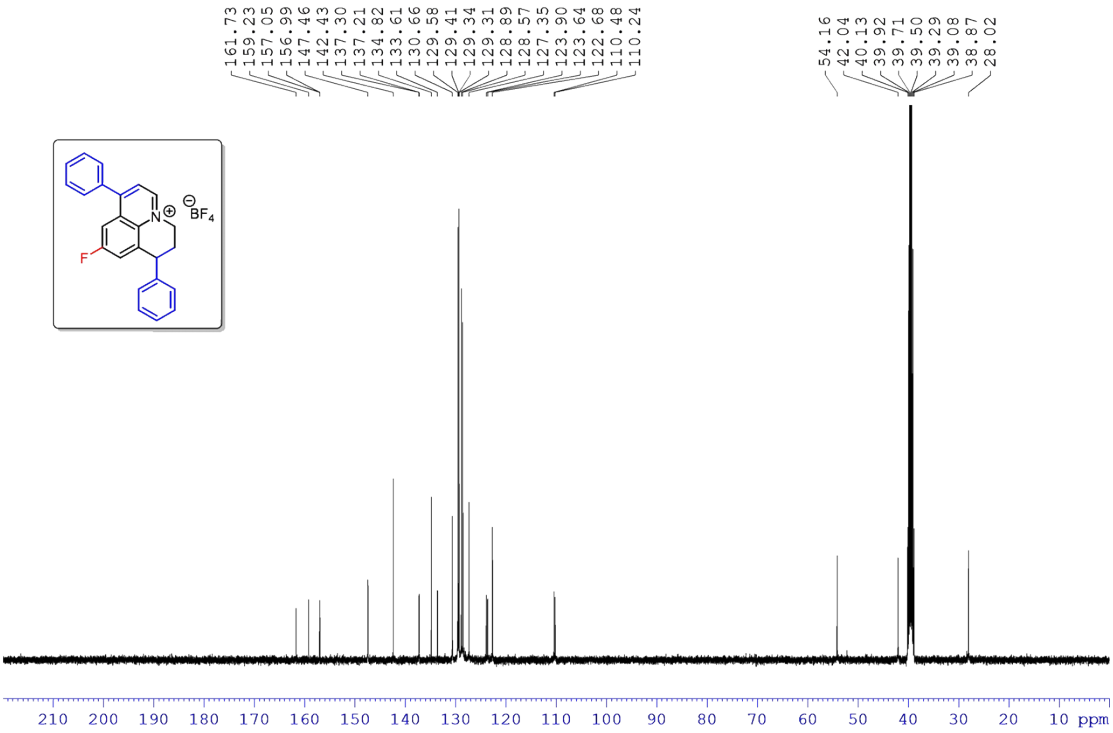


^{1}H and ^{13}C NMR spectra of compound **3ea**

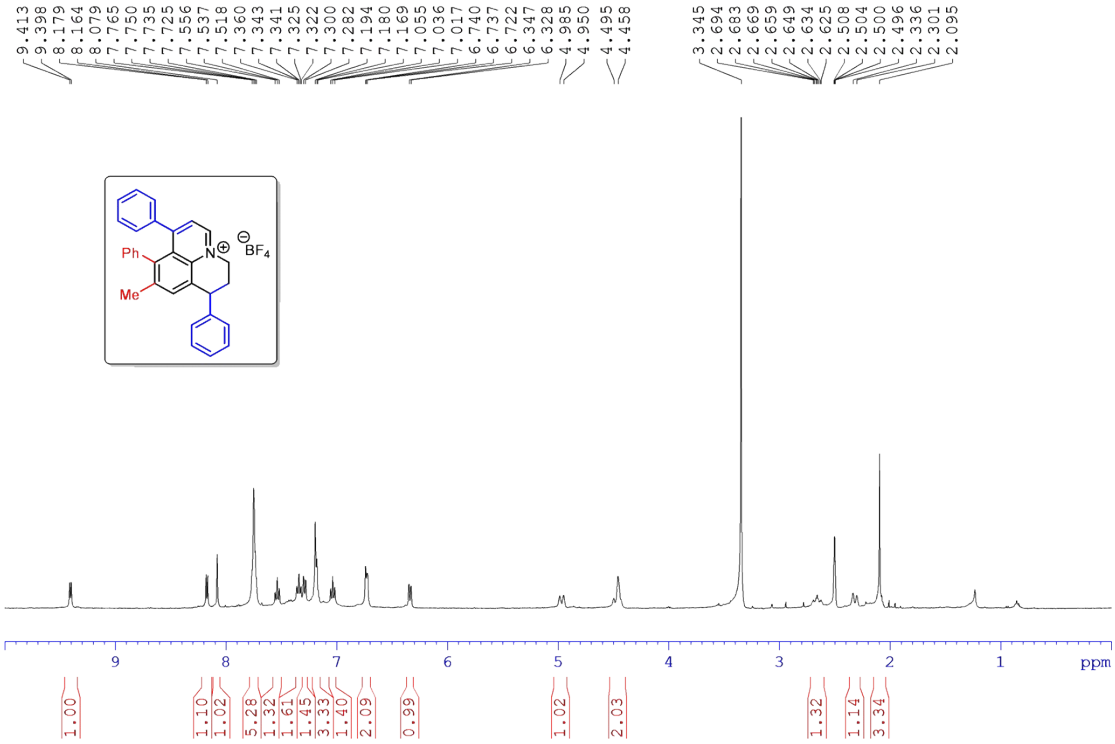


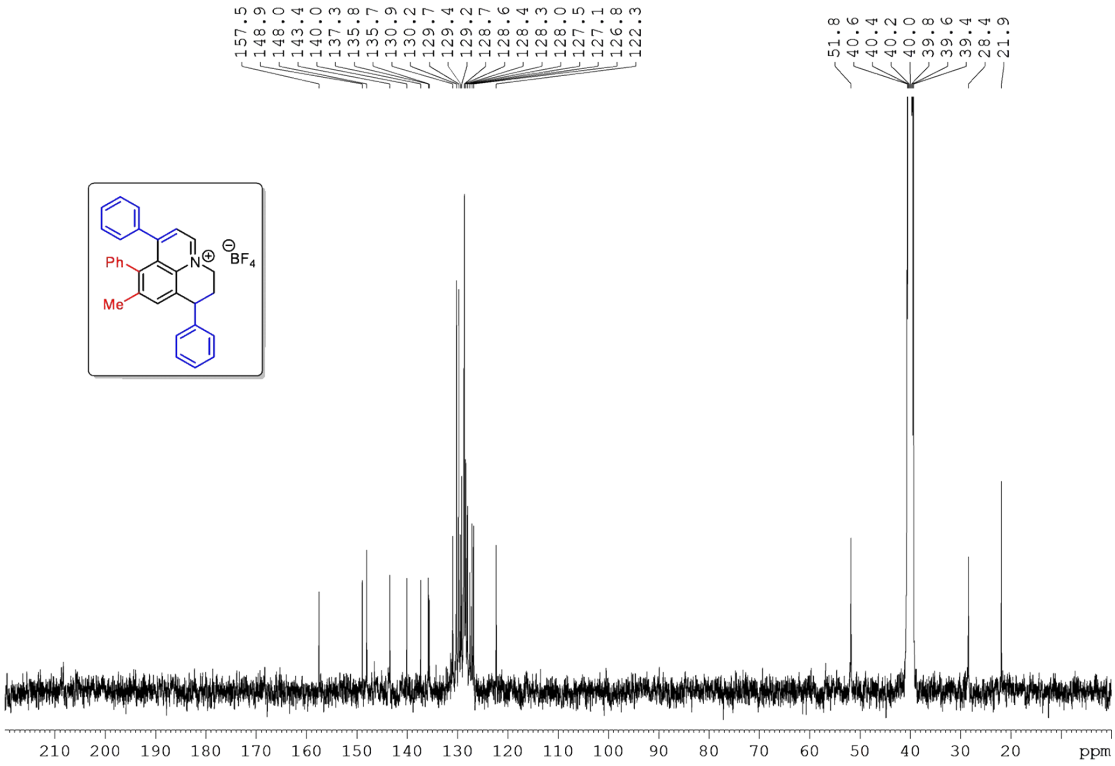
^{1}H and ^{13}C NMR spectra of compound **3fa**



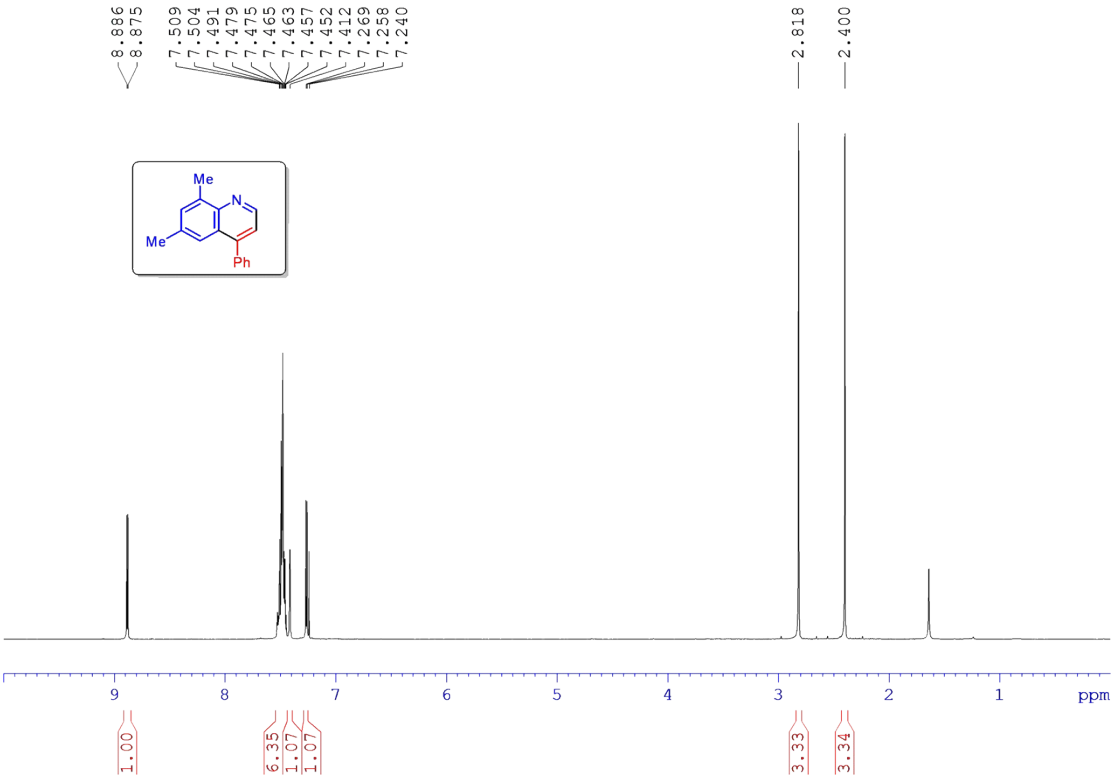


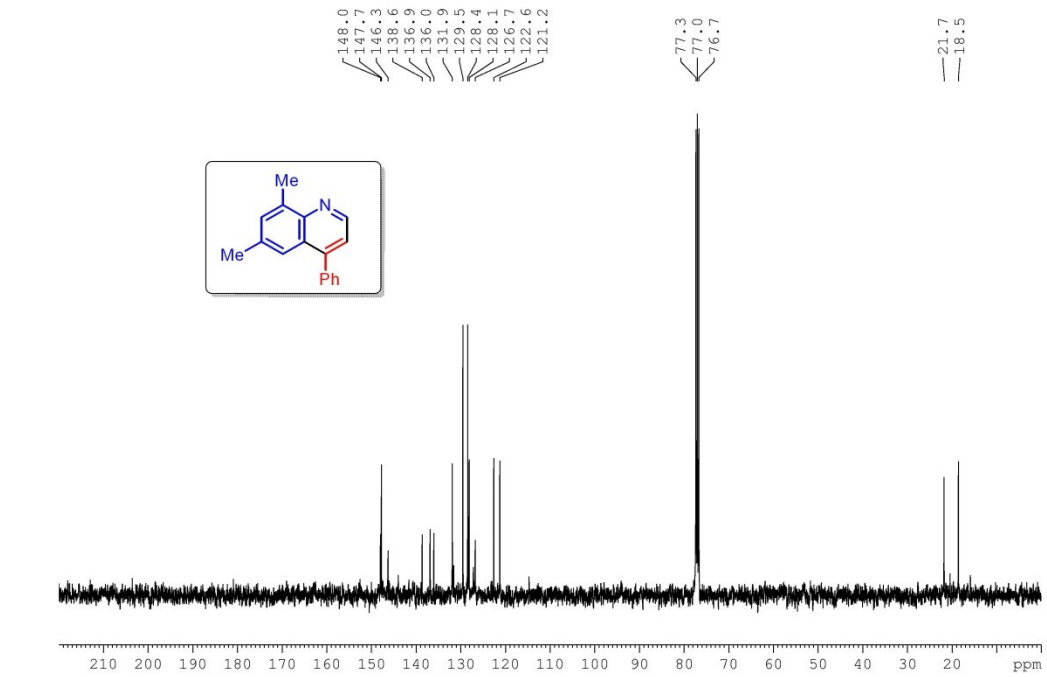
^{1}H and ^{13}C NMR spectra of compound **3ga**



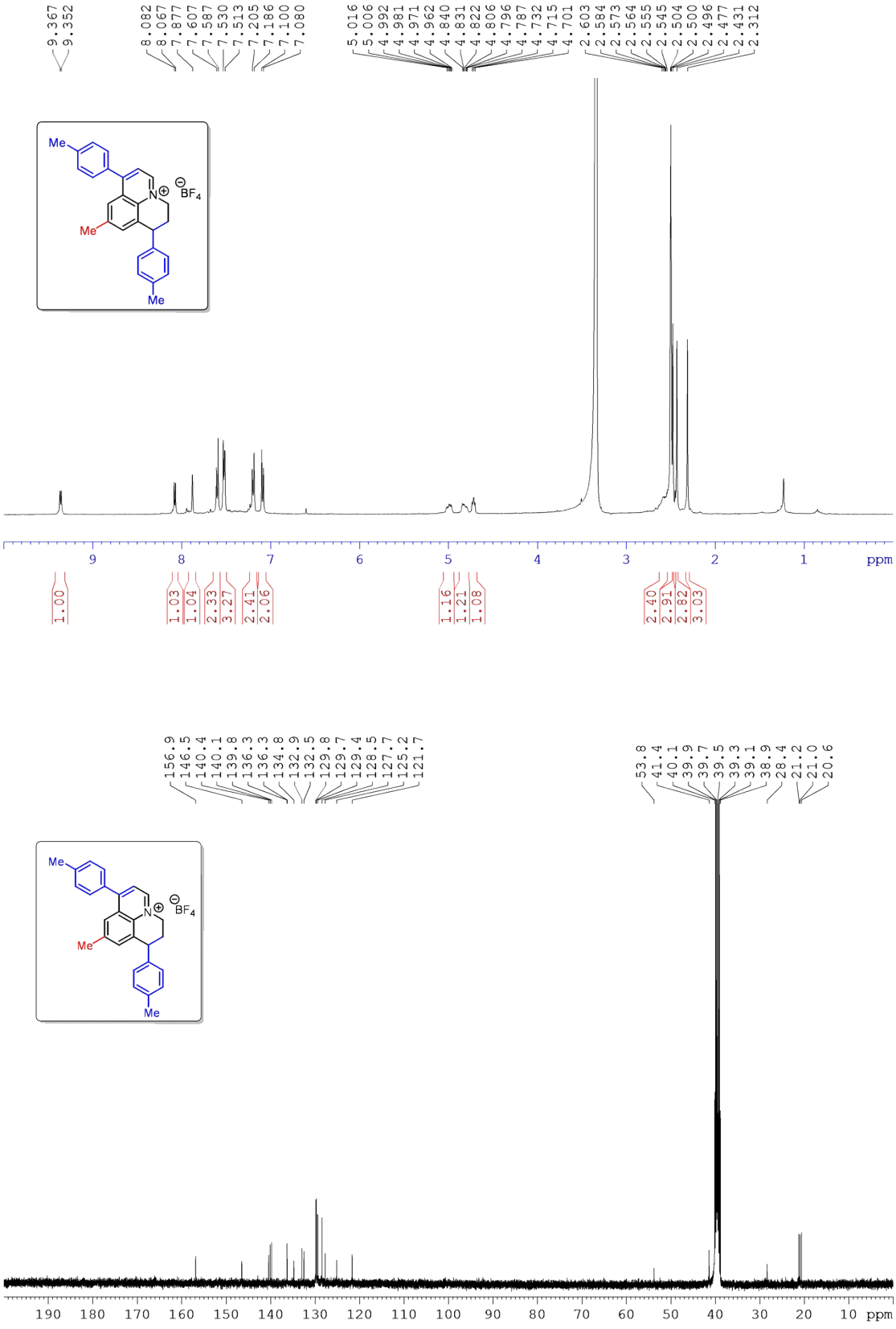


^{1}H and ^{13}C NMR spectra of compound **3ha'**

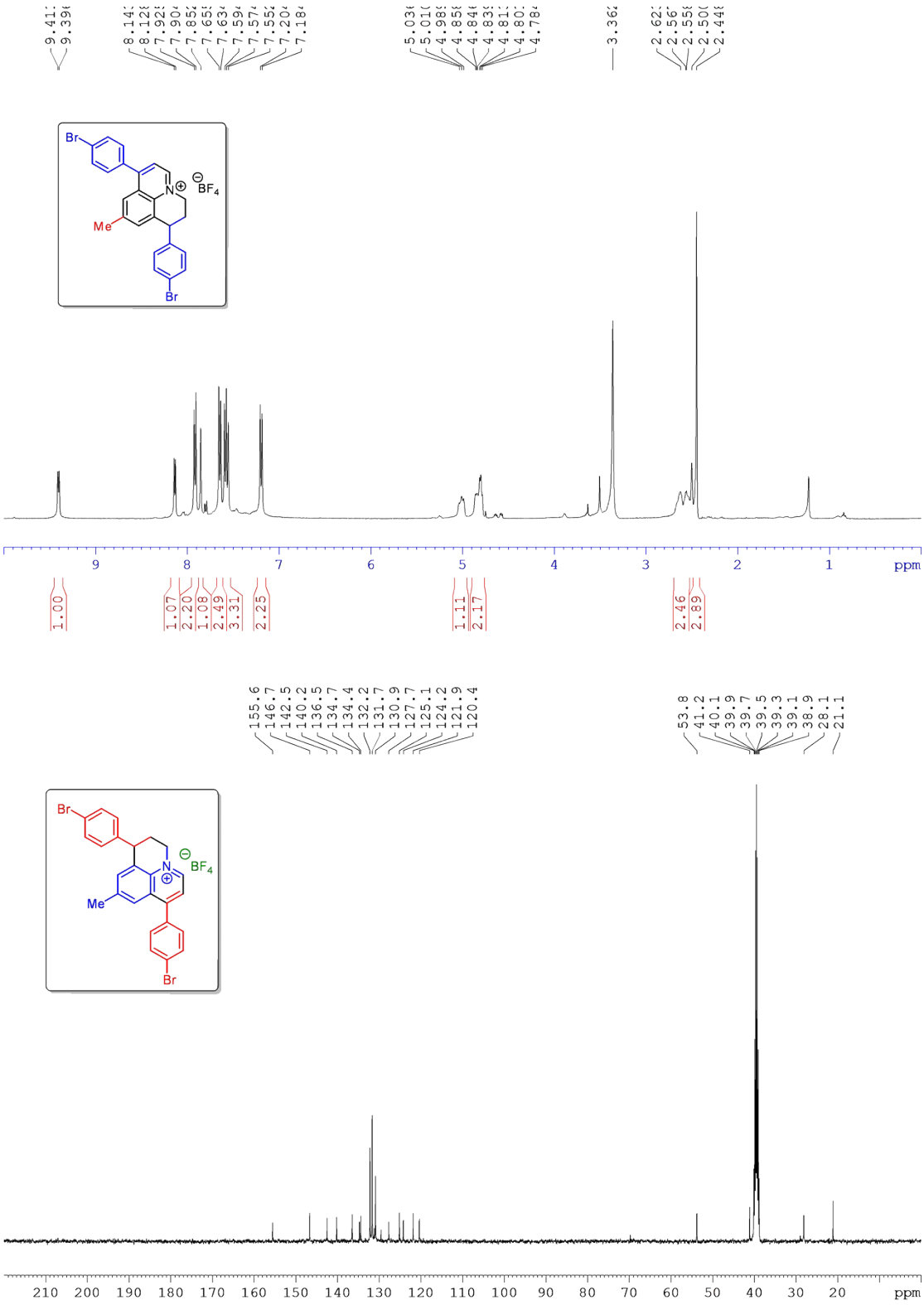




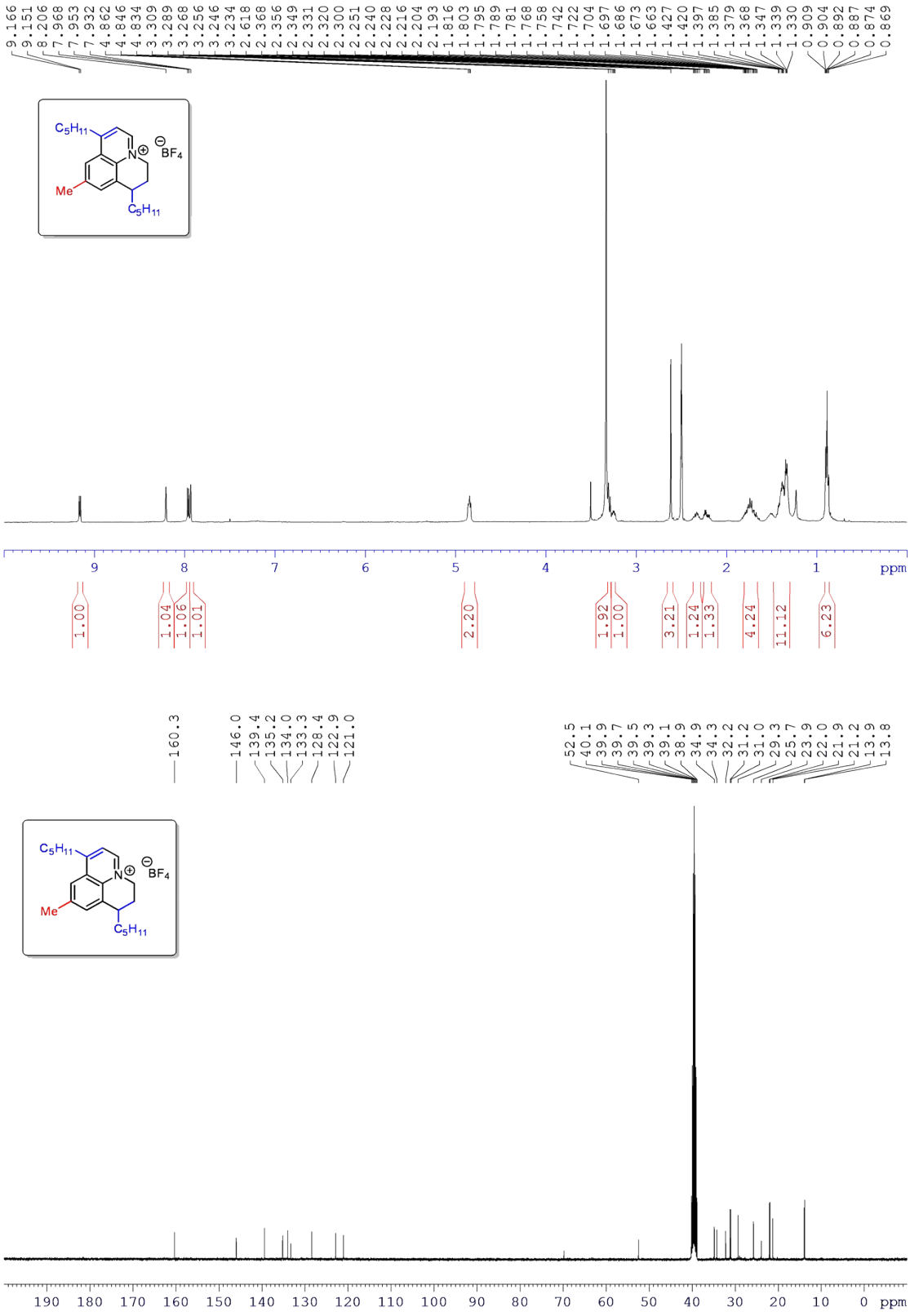
^{1}H and ^{13}C NMR spectra of compound **3ab**



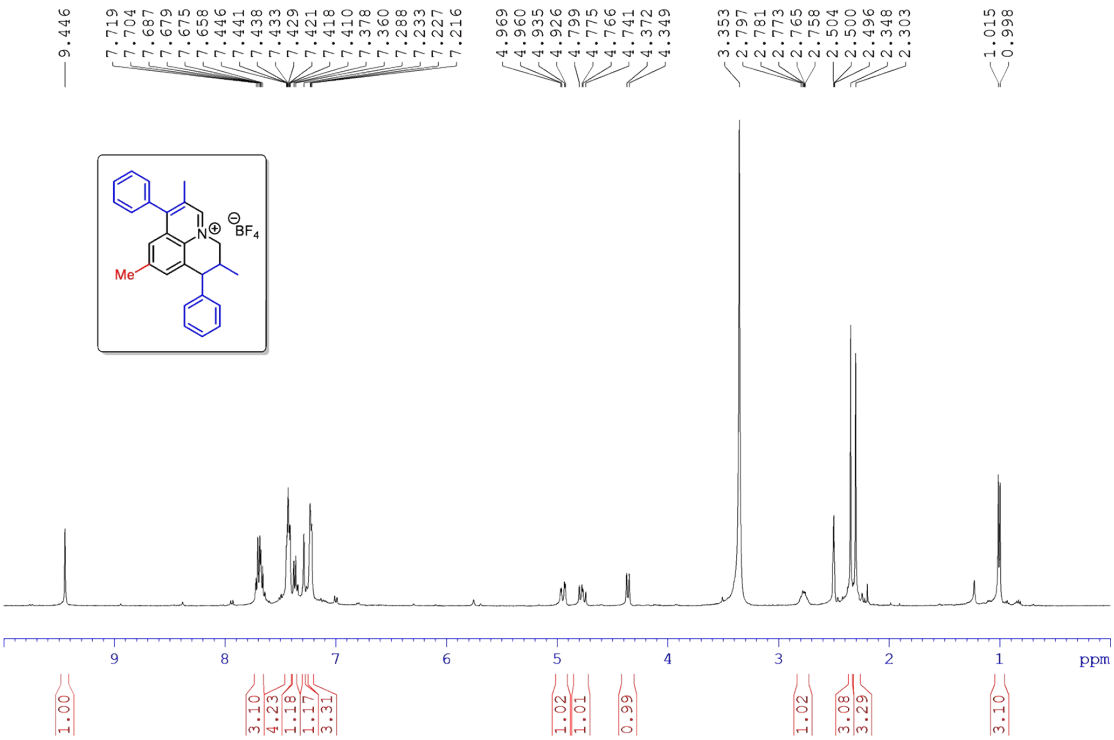
^{1}H and ^{13}C NMR spectra of compound **3ac**

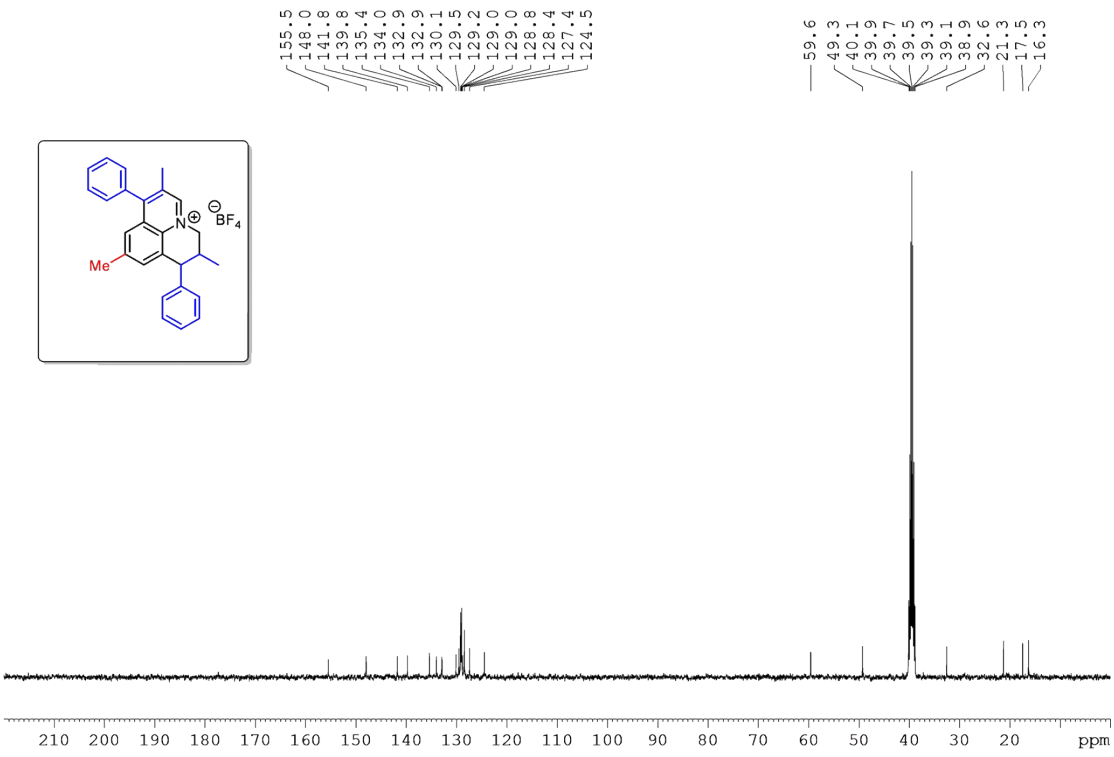


^{1}H and ^{13}C NMR spectra of compound **3ad**

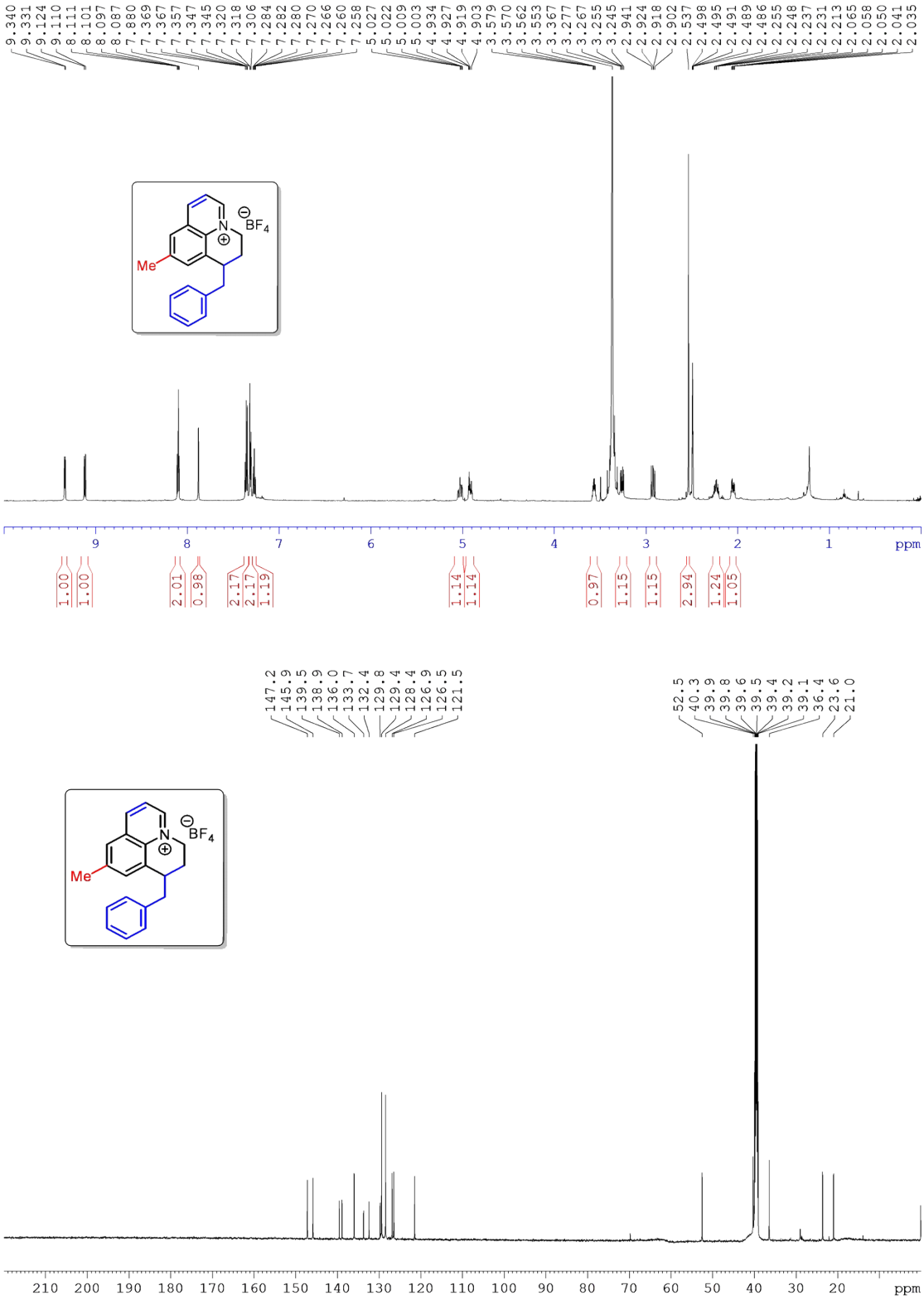


^{1}H and ^{13}C NMR spectra of compound **3ae**

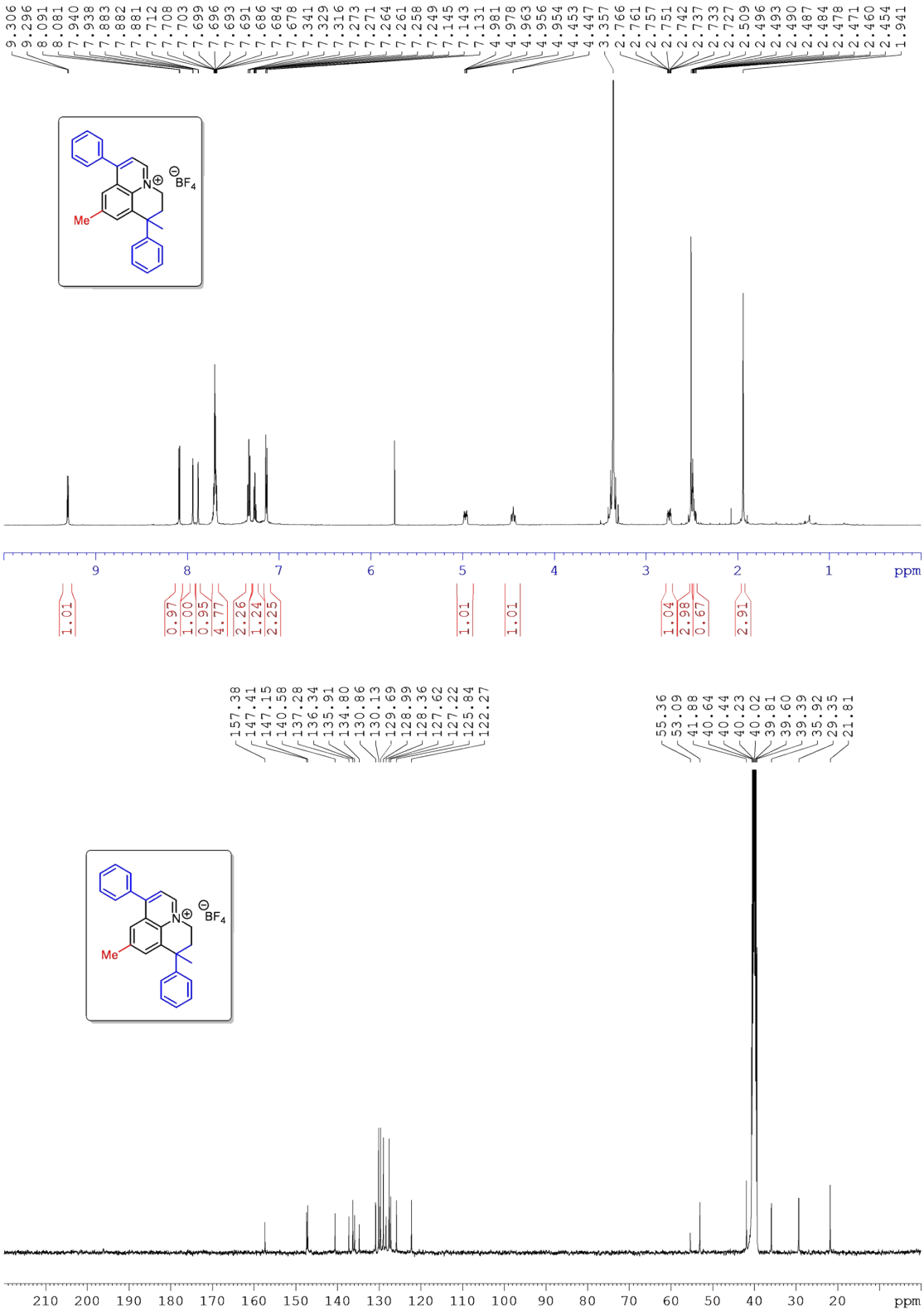




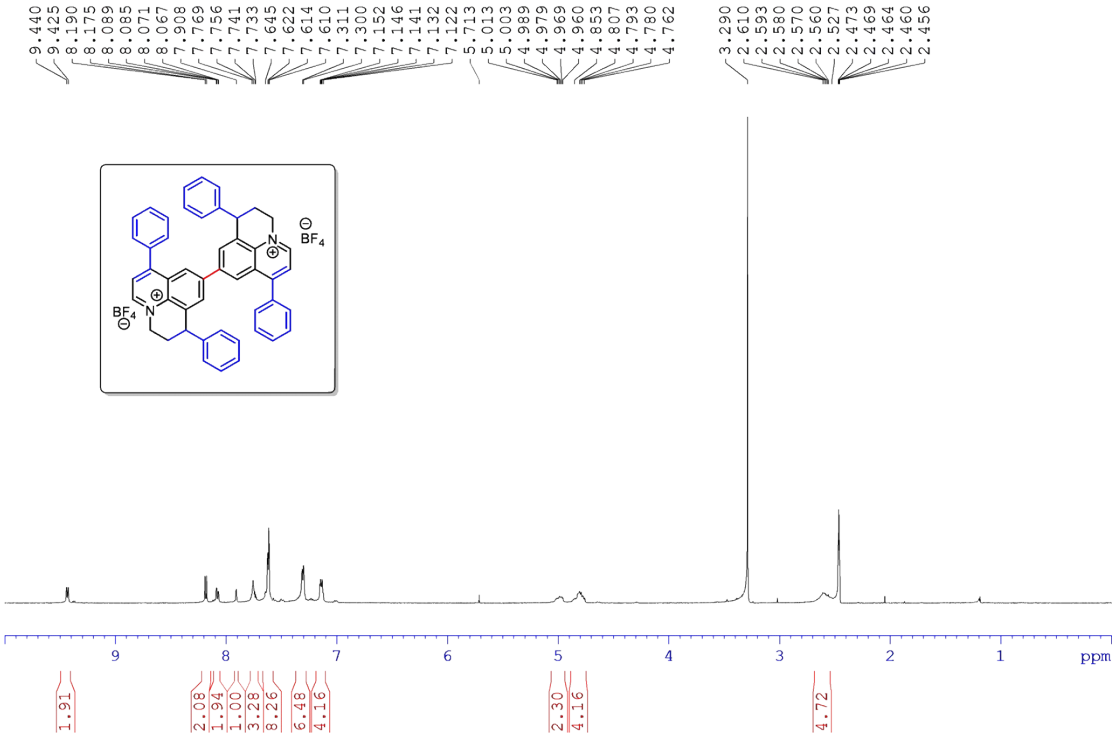
^{1}H and ^{13}C NMR spectra of compound **3af'**

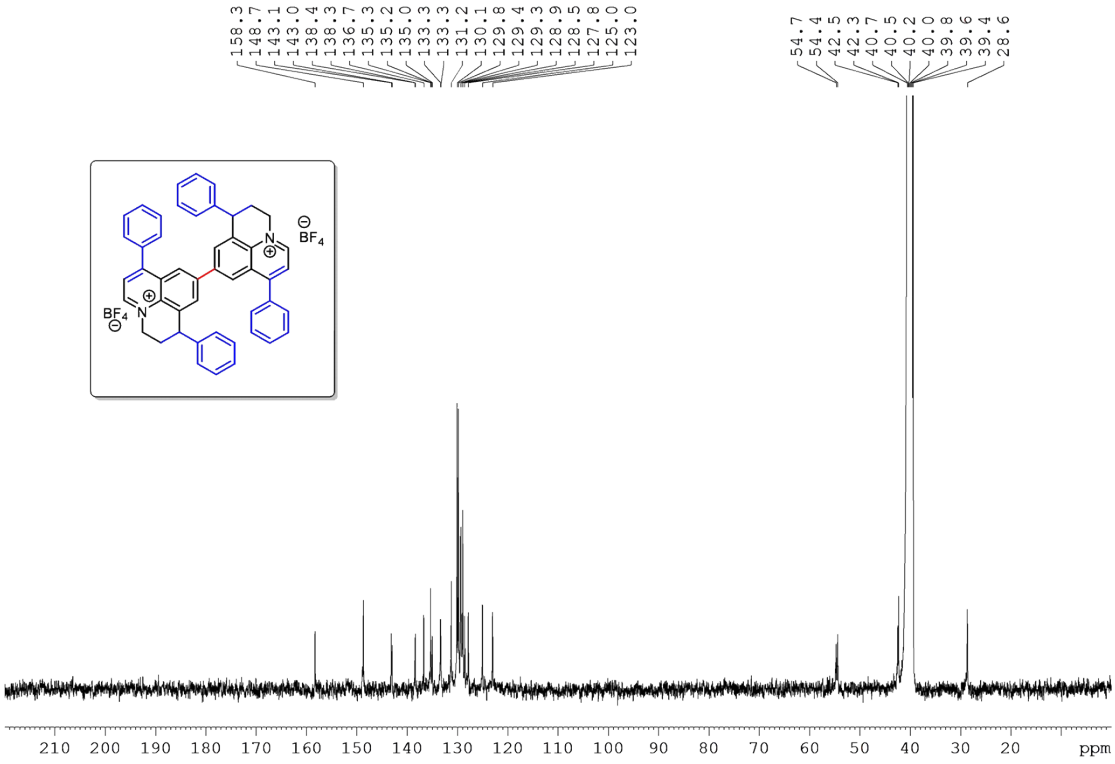


^{1}H and ^{13}C NMR spectra of compound **3ag'**

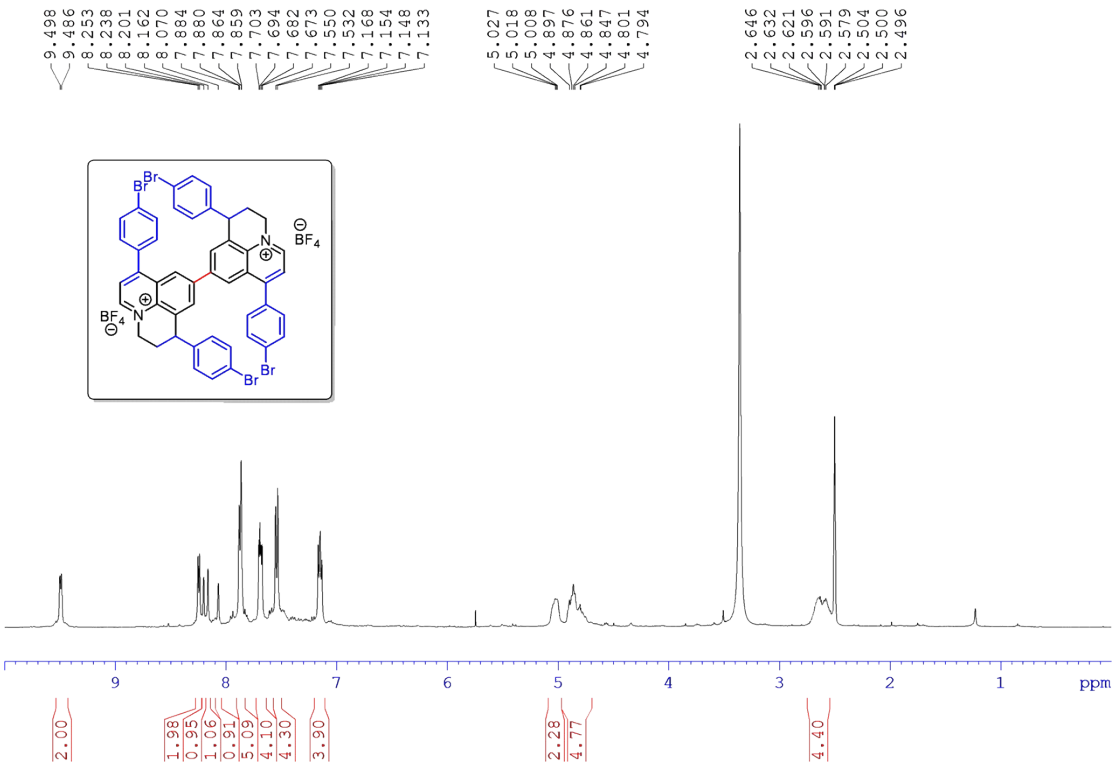


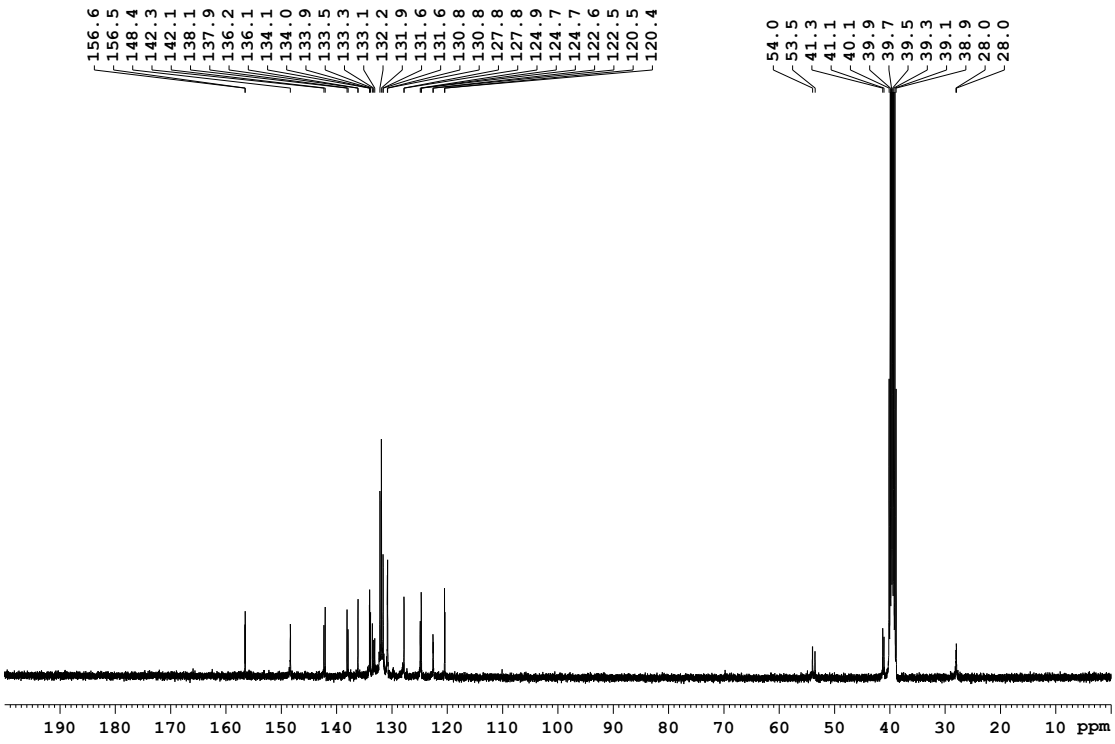
^{1}H and ^{13}C NMR spectra of compound **4ja**



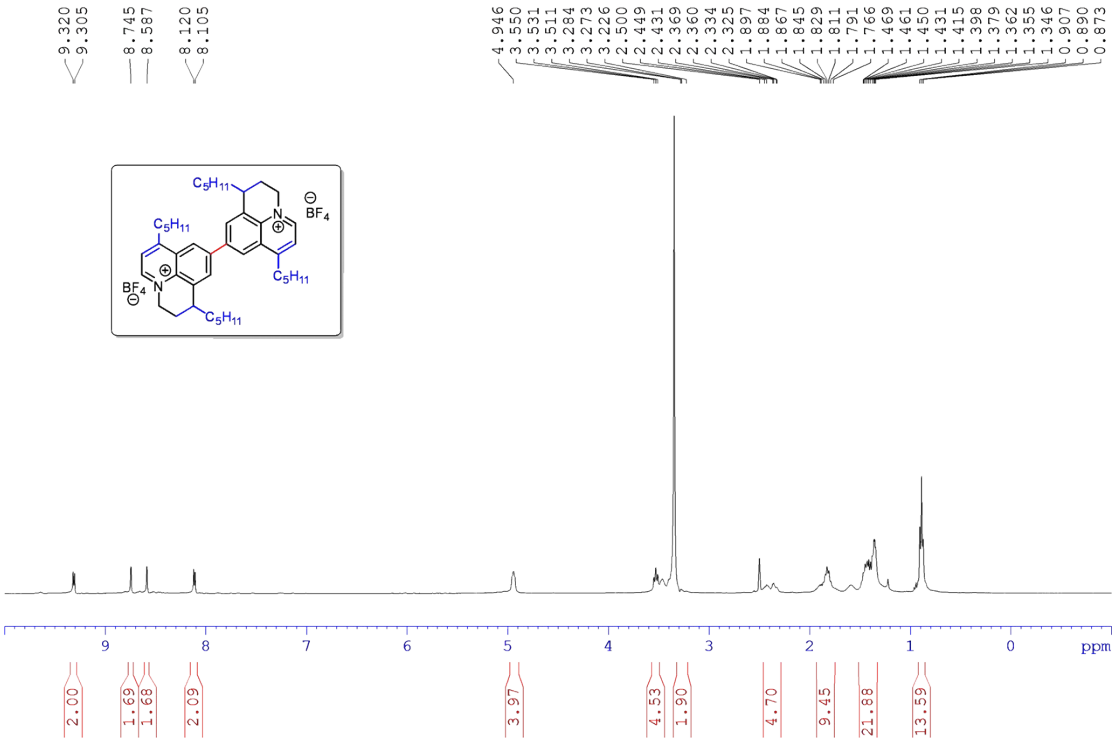


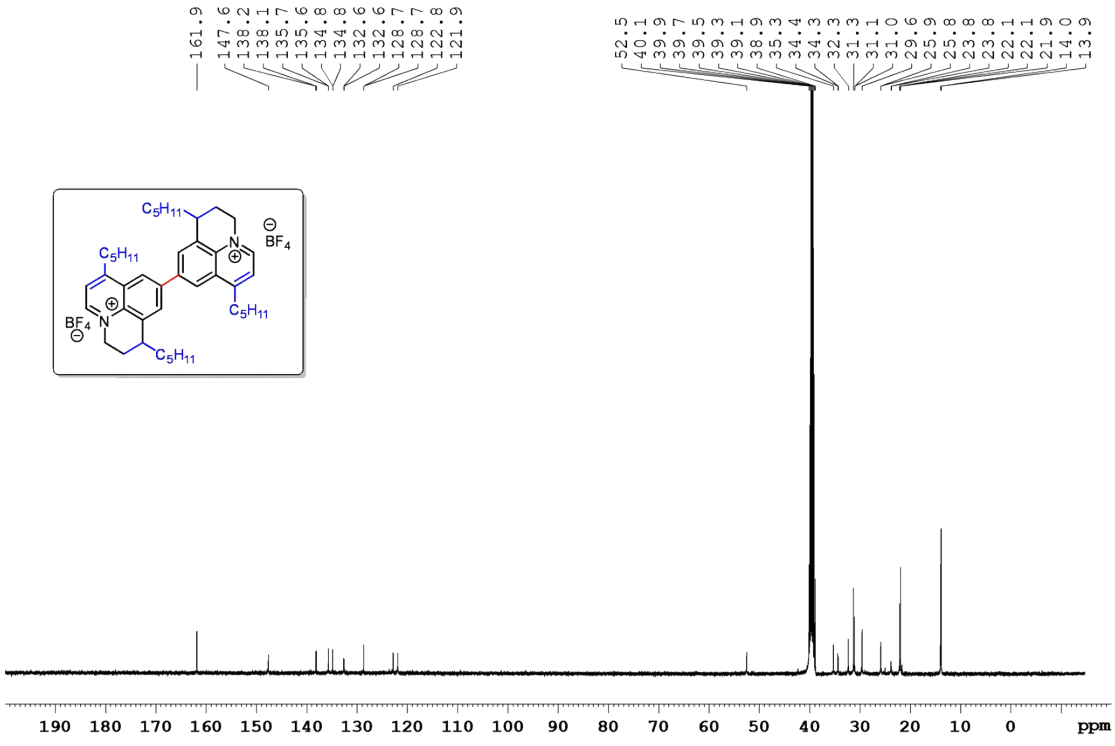
^{1}H and ^{13}C NMR spectra of compound **4jc**



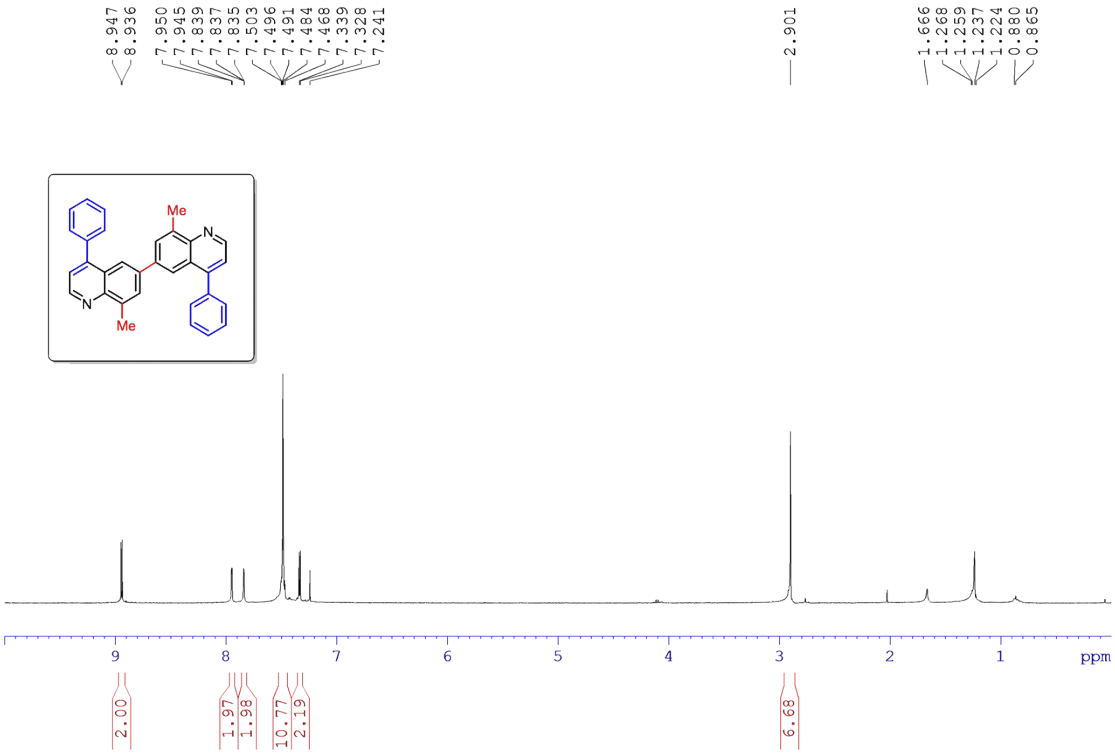


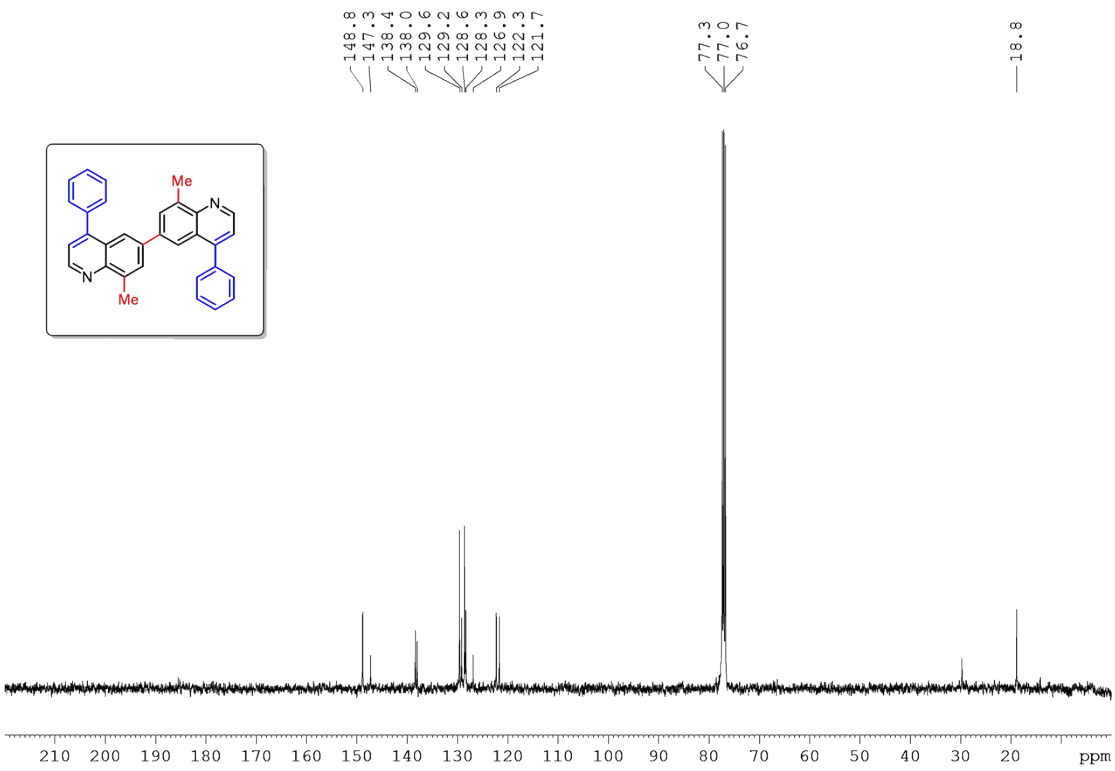
^{1}H and ^{13}C NMR spectra of compound **4jd**



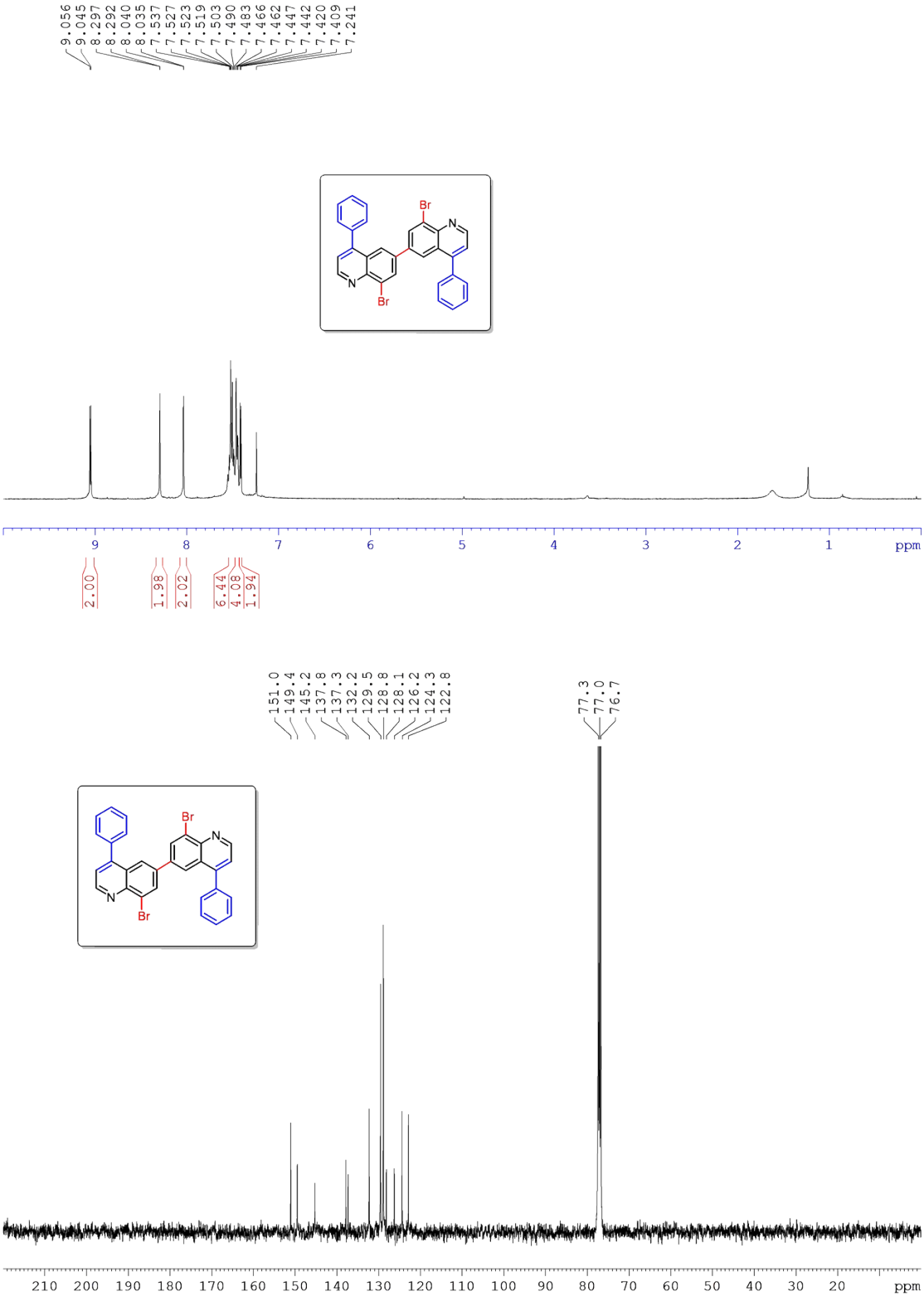


^{1}H and ^{13}C NMR spectra of compound **5ka**

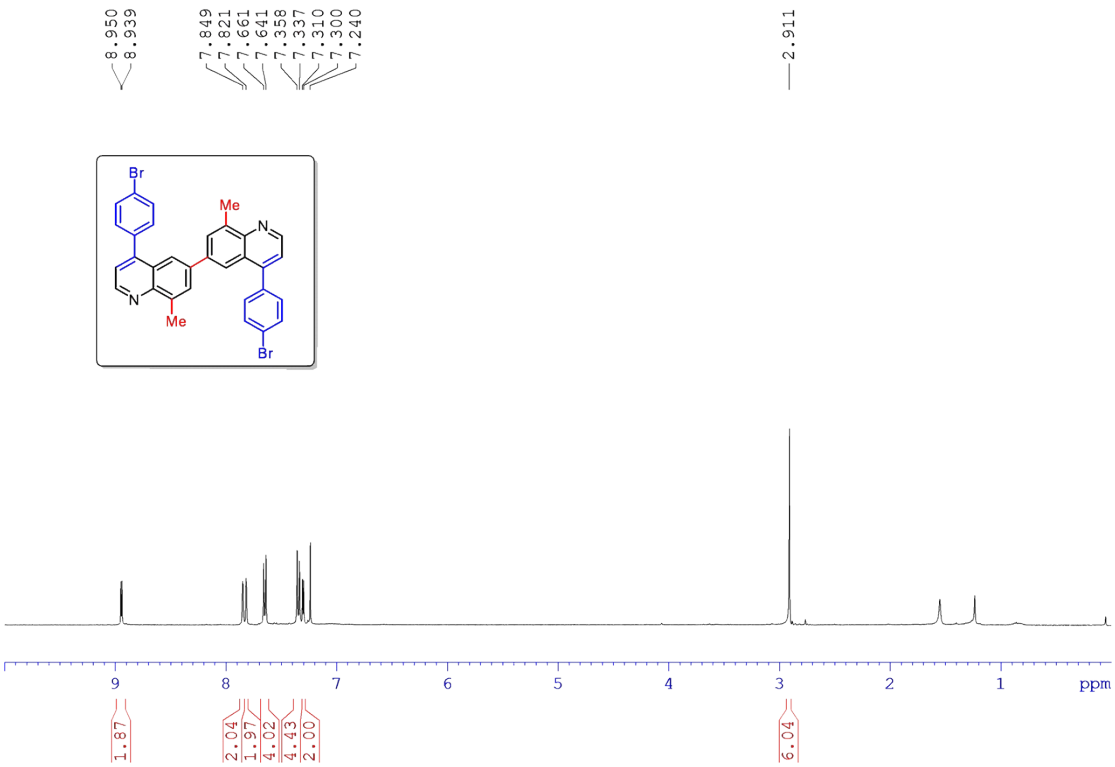


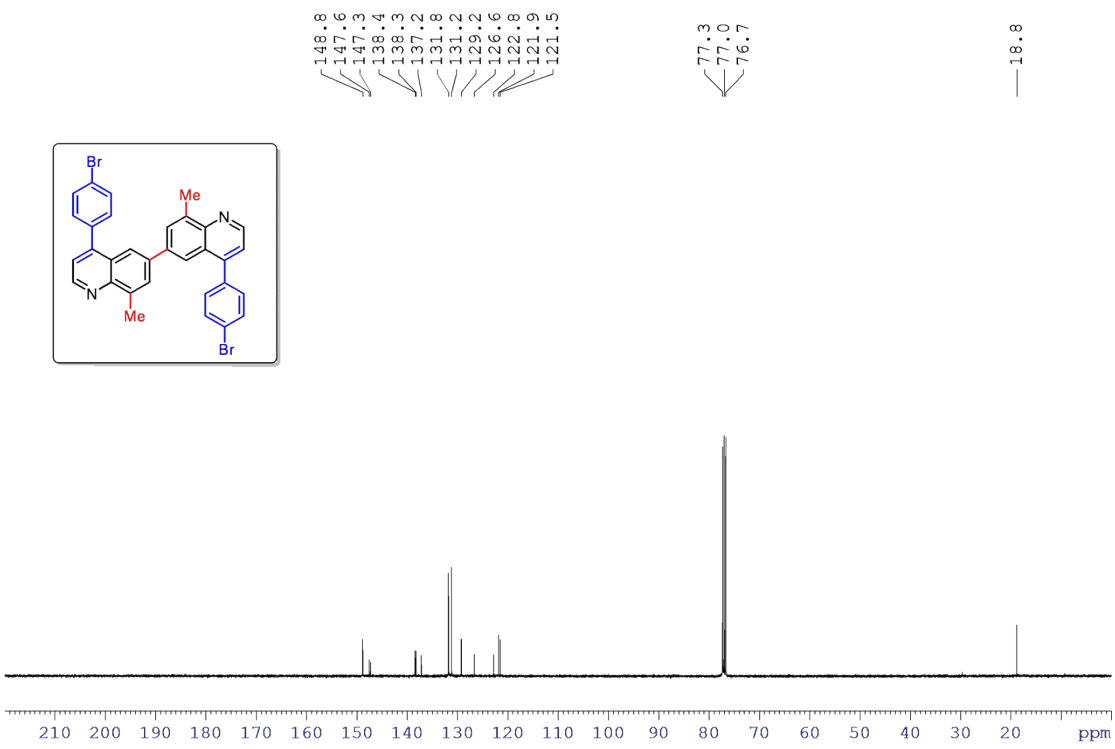


^{1}H and ^{13}C NMR spectra of compound **5la**

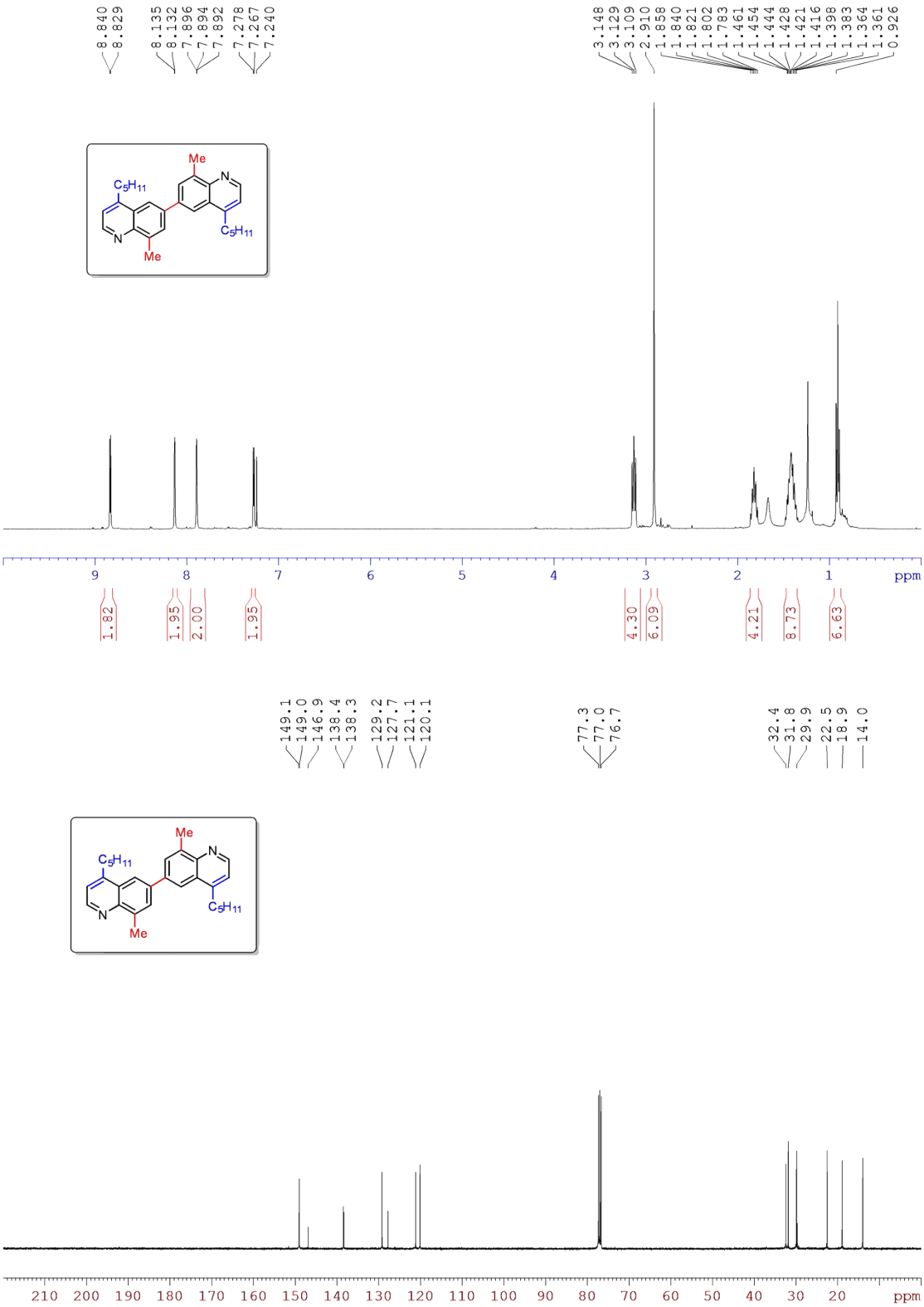


^{1}H and ^{13}C NMR spectra of compound **5kc**

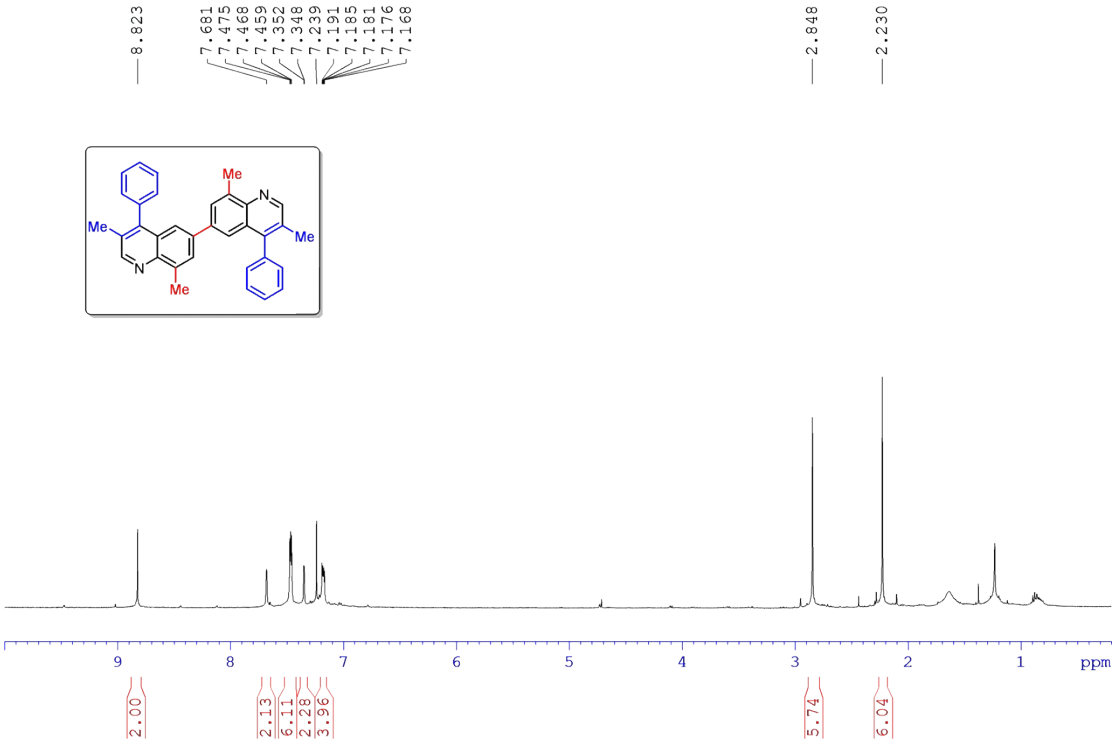


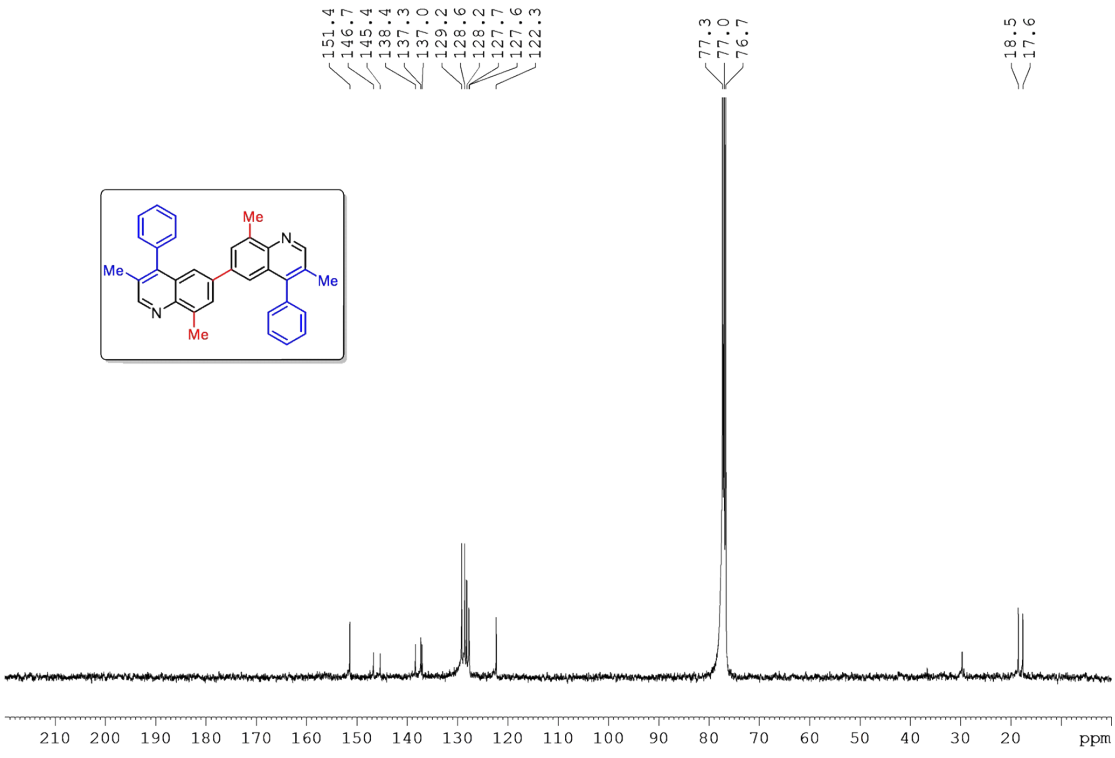


^{1}H and ^{13}C NMR spectra of compound **5kd**

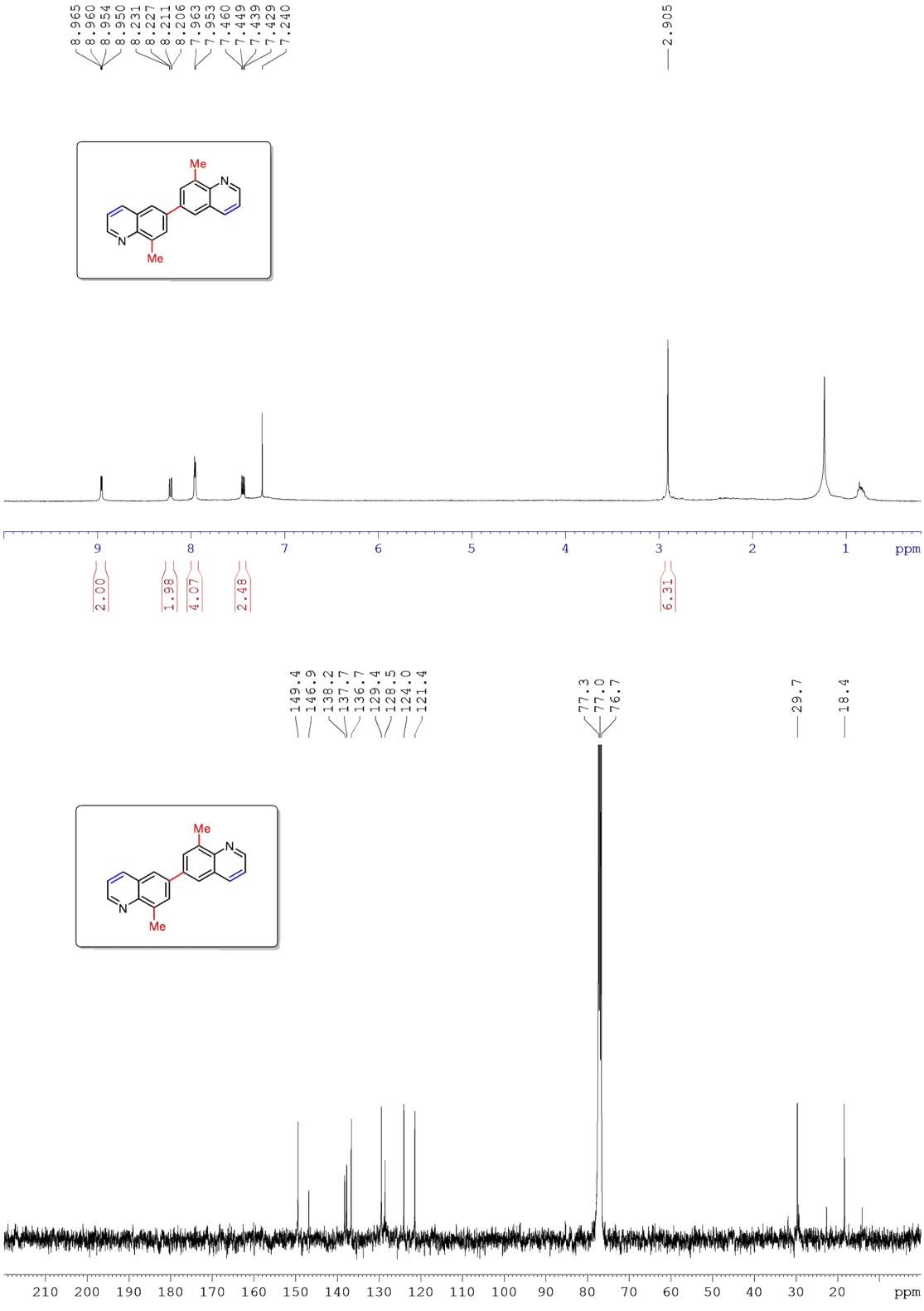


^{1}H and ^{13}C NMR spectra of compound **5ke**



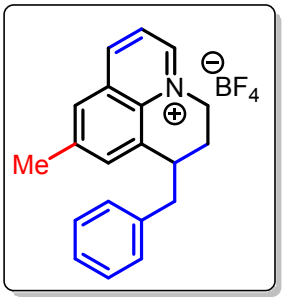


^{1}H and ^{13}C NMR spectra of compound **5kf'**



X-ray Crystallographic Analysis:

ORTEP diagram of compound **3af'**.



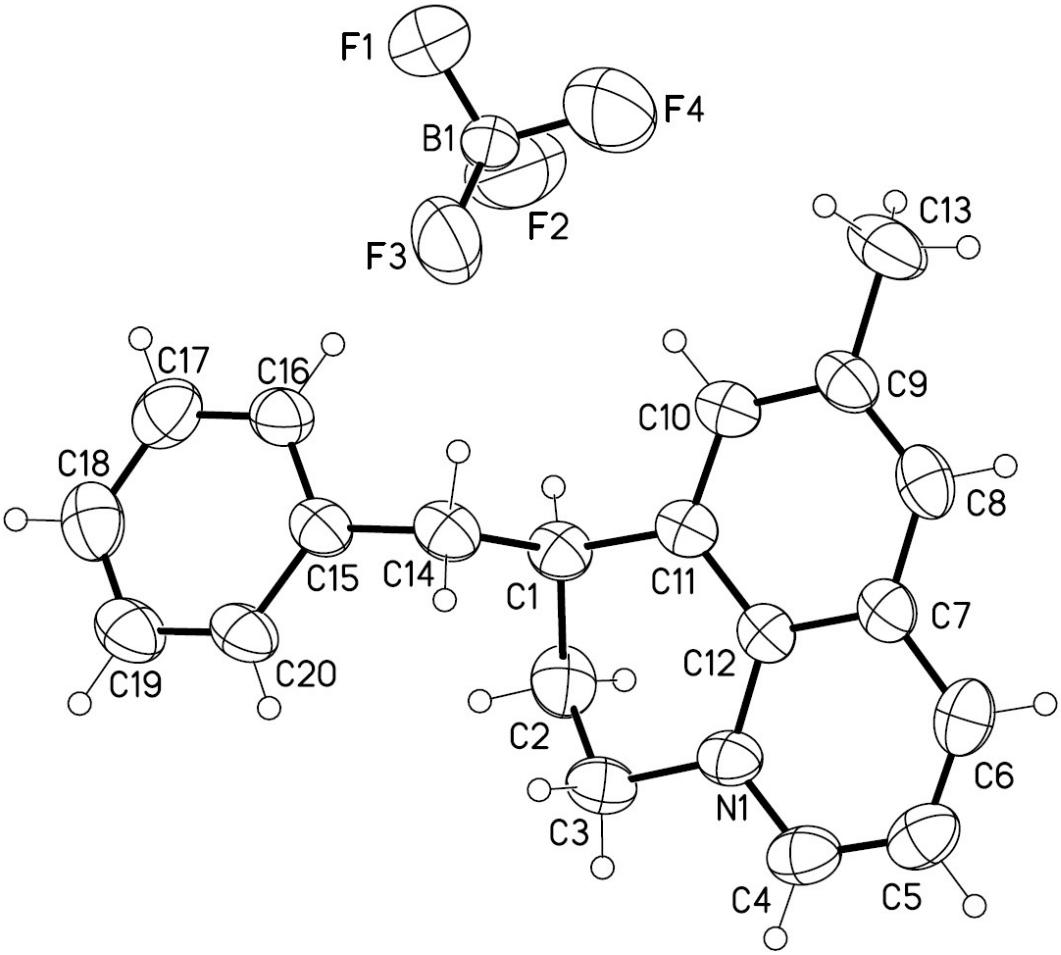
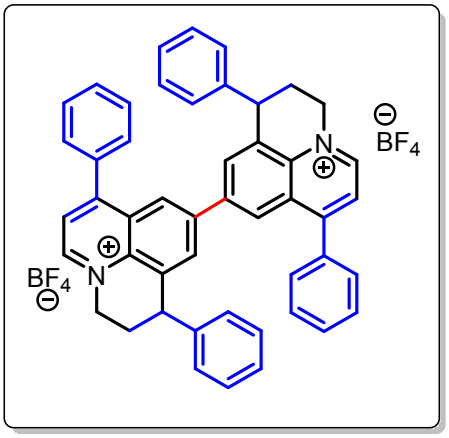


Table S5. Crystal data and structure refinement for MO_150929_0M, **3af'**.

Identification code	mo_150929_0m	
Empirical formula	C20 H20 B F4 N	
Formula weight	361.18	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.0489(7) Å	α = 78.224(2)°.
	b = 10.2453(9) Å	β = 65.746(2)°.
	c = 10.8052(9) Å	γ = 73.570(2)°.
Volume	871.59(13) $Å^3$	
Z	2	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	0.109 mm^{-1}	
F(000)	376	
Crystal size	0.12 x 0.10 x 0.04 mm^3	
Theta range for data collection	2.078 to 26.448°.	
Index ranges	-11<=h<=10, -6<=k<=12, -13<=l<=13	
Reflections collected	12209	
Independent reflections	3512 [R(int) = 0.0339]	
Completeness to theta = 25.242°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9485 and 0.9064	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3512 / 255 / 283	
Goodness-of-fit on F^2	0.907	
Final R indices [I>2sigma(I)]	R1 = 0.0830, wR2 = 0.2507	
R indices (all data)	R1 = 0.1773, wR2 = 0.2990	
Extinction coefficient	0.012(9)	
Largest diff. peak and hole	0.365 and -0.542 $e.Å^{-3}$	

ORTEP diagram of compound **4ja**.



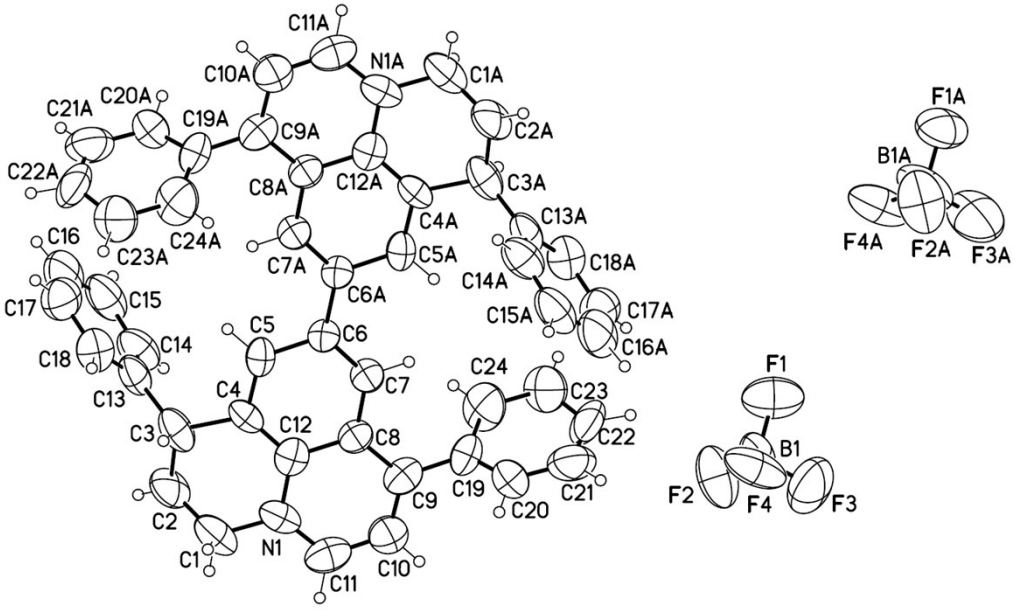
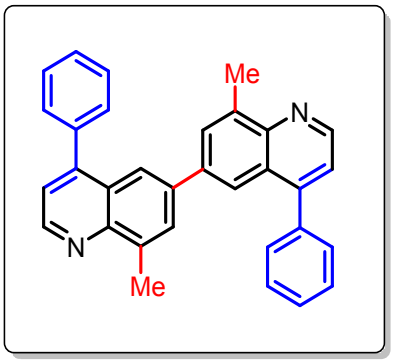


Table S6. Crystal data and structure refinement for 140445LT_a, **4ja**.

Identification code	140445LT_a	
Empirical formula	C48 H36 B2 F8 N2	
Formula weight	814.41	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.2275(13) Å	α= 90°.
	b = 12.9049(11) Å	β= 110.482(6)°.
	c = 12.2015(11) Å	γ = 90°.
Volume	1951.1(3) $Å^3$	
Z	2	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	0.897 mm^{-1}	
F(000)	840	
Crystal size	0.17 x 0.15 x 0.15 mm^3	
Theta range for data collection	3.567 to 66.746°.	
Index ranges	-15<=h<=15, -15<=k<=13, -14<=l<=14	
Reflections collected	13094	
Independent reflections	3356 [R(int) = 0.1157]	
Completeness to theta = 67.679°	95.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9492 and 0.6817	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3356 / 0 / 271	
Goodness-of-fit on F^2	0.670	
Final R indices [I>2sigma(I)]	R1 = 0.0857, wR2 = 0.2190	
R indices (all data)	R1 = 0.2009, wR2 = 0.2861	

Extinction coefficient	n/a
Largest diff. peak and hole	0.270 and -0.166 e.Å^{-3}

ORTEP diagram of compound **5ka**



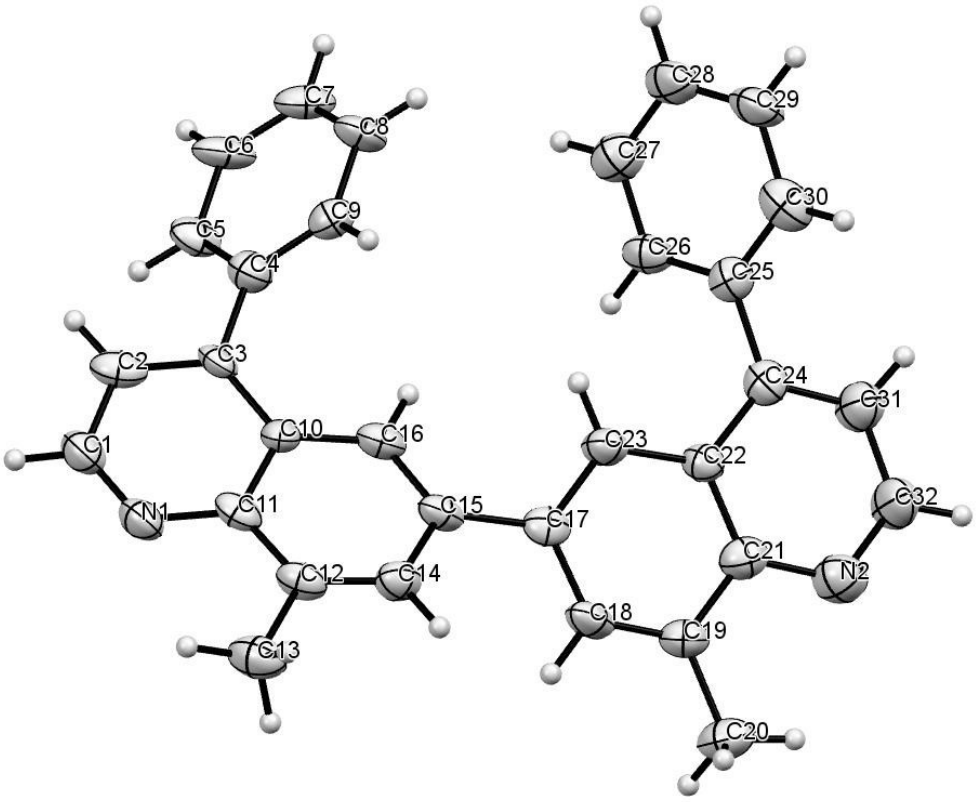


Table S7. Crystal data and structure refinement for a16581a, **5ka**.

Identification code	a16581a	
Empirical formula	C32 H24 N2	
Formula weight	436.53	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 7.917(6) Å	α = 90°.
	b = 22.675(14) Å	β = 90°.
	c = 25.49(2) Å	γ = 90°.
Volume	4577(6) $Å^3$	
Z	8	
Density (calculated)	1.267 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	1840	
Crystal size	0.25 x 0.23 x 0.02 mm^3	
Theta range for data collection	1.97 to 25.05°.	
Index ranges	-8<=h<=9, -26<=k<=17, -30<=l<=26	
Reflections collected	19221	
Independent reflections	4006 [R(int) = 0.1883]	
Completeness to theta = 25.05°	98.6 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9985 and 0.9818	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4006 / 0 / 307	
Goodness-of-fit on F^2	0.915	
Final R indices [I>2sigma(I)]	R1 = 0.0946, wR2 = 0.1475	
R indices (all data)	R1 = 0.3434, wR2 = 0.2222	
Largest diff. peak and hole	0.261 and -0.249 $e.Å^{-3}$	