Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Exploring a Unique Reactivity of N-Heterocyclic Carbenes (NHC) in Rhodium(III)-Catalyzed Intermolecular C–H Activation/Annulation

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CONTENTS

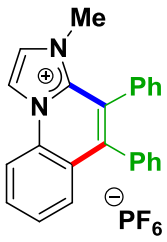
1. General methods and materials

^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR spectra were recorded on Bruker AVANCE III 400, 500 and 700 MHz NMR spectrometers at room temperature unless mentioned otherwise. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H spectra, 77.2 ppm for $^{13}C\{^{1}H\}$ spectra; CH_3CN: δ = 1.94 ppm for ^{1}H spectra, 1.3 ppm for $^{13}C\{^{1}H\}$ spectra). All coupling constants (J) are expressed in hertz (Hz) and only given for ^{1}H-^{1}H couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplets), ddd (doublet of doublet of doublets), m (multiplet). ESI mass spectroscopy was performed on a Bruker microTOF QII spectrometer. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at different low temperatures for each crystal. Dry solvents and reagents were obtained from commercial suppliers and used without further purification. Deuterated solvents and $RhCl_3.xH_2O$ were purchased from Aldrich. $IrCl_3.xH_2O$ and $RuCl_3.xH_2O$ were purchased from Johnson Matthey and used as received without further purification. $[RhCp^*Cl_2]_2$[1], $[IrCp^*Cl_2]_2$[2], $[Ru(p\text{-cym})Cl_2]_2$[3], $[RhCl(COD)]_2$[4], *N*-substituted aryl imidazole[5], 1-nitro-4-(phenylethynyl)benzene[6], 1-methoxy-4-(phenylethynyl)benzene6, 1,4-Diphenylbutadiyne[7] were synthesized according to reported procedures.

2. Stoichiometric silver-transmetalation method of the annulation reaction

In an oven dried Schlenk tube, a mixture of **1a** (14.3 mg, 0.05 mmol) and Ag_2O (6.0 mg, 0.55 mmol) in dry and degassed CH_2Cl_2 (5 mL) was stirred under N_2 atmosphere at room temperature under dark condition. After 4 h, to that solution $[RhCp^*Cl_2]_2$ (15.4 mg, 0.025 mmol) was added and the mixture was again stirred at room temperature for another 4 h. Then KPF_6 (18.4 mg, 0.1 mmol) and **2a** (10.7 mg, 0.06 mmol) were added to this solution and stirred further for 16 h under the same condition. After that the whole reaction mixture was passed through a short celite pad which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a 7:1 (v/v) $CHCl_3$/MeOH solvent mixture affording **3a** as a pale yellow solid (18 mg, 0.037 mmol, 75%).

3-methyl-4,5-diphenylimidazo[1,2-*a*]quinolinium hexafluorophosphate (**3a**): ^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 8.63 (d, *J* = 1.9 Hz, 1H), 8.35 (d, *J* = 8.5 Hz, 1H), 7.97 (t, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 1.8 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.29 (m, 8H), 7.15 – 7.13 (m, 2H), 3.40 (s, 3H). HRMS (ESI, positive ion): M^+ = 335.1560 (calculated 335.1543 for $[C_{24}H_{19}N_2]^+$).



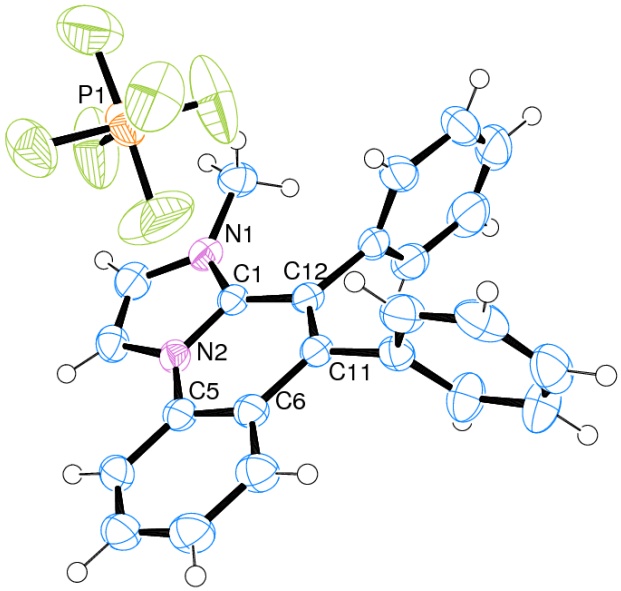
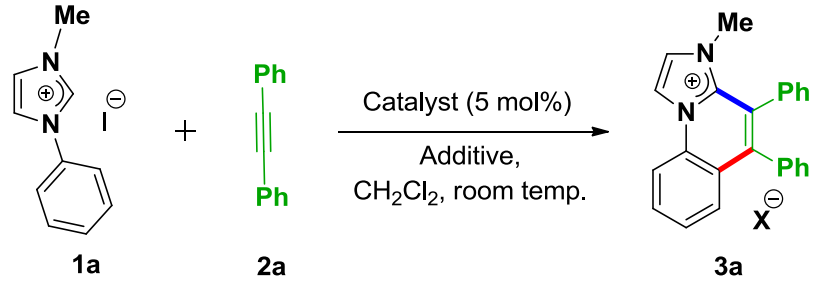


Figure S1. Molecular structure of product **3a** of hexafluorophosphate salt (30% probability level). Selected bond lengths (Å) and bond angles (°): C_1–N_1 = 1.342(4); C_1–N_2 = 1.364(4); C_1–C_{12} = 1.429(4); C_5–N_2 = 1.394(4); C_5–C_6 = 1.400(5); C_6–C_{11} = 1.445(4); C_{11}–C_{12} = 1.363(4); N_1–C_1–N_2 = 106.9(3); N_2–C_1–C_{12} = 121.2(3); N_1–C_1–C_{12}.= 131.8(3); C_1–N_2–C_5 = 122.6(3); N_2–C_5–C_6 = 116.9(3); C_5–C_6–C_{11} = 120.5(3); C_{12}–C_{11}–C_6 = 121.1(3); C_{11}–C_{12}–C_1 = 117.3(3).

3. Optimization of the reaction conditions

To an oven dried Schlenk tube, **1a** (0.1 mmol), Ag_2O / NaOAc (0.055 mmol/ 0.4 mmol), catalyst (0.005 mmol), AgOTf (0.3 mmol) and **2a** (0.12 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N_2 gas. To this mixture, dry and degassed CH_2Cl_2 (3.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at room temperature under dark. After a certain time, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a 7:1 (v/v) $CHCl_3$/MeOH solvent mixture.

Table S1: Optimization studies[a]



1a 2a 3a

Entry	Catalyst	Additives (equiv.)	Time (h)	Yield (%)[b]
1	$[RhCp^*Cl_2]_2$	Ag_2O (0.55) + KPF_6 (2.5)	12	13[c]
2	$[RhCp^*Cl_2]_2$	NaOAc (4) + KPF_6 (2.5)	12	trace[c]
3	$[RhCp^*Cl_2]_2$	Ag_2O (0.55) + AgOTf (2)	12/24	55/66
4	$[RhCp^*Cl_2]_2$	Ag_2O (2) + AgOTf (3)	24	49
5	$[RhCp^*Cl_2]_2$	NaOAc (2.2) + AgOTf (2)	24	45
6	$[RhCp^*Cl_2]_2$	NaOAc (4) + AgOTf (2)	12	56
7	$[RhCp^*Cl_2]_2$	NaOAc (4) + AgOTf (2)	24	66
8	**$[RhCp^*Cl_2]_2$**	**NaOAc (4) + AgOTf (3)**	**24**	**81**
9	$[RhCp^*Cl_2]_2$	NaOAc (4) + AgOTf (3)	4	<15[c]
10	$[RhCp^*Cl_2]_2$	NaOAc (4) + $CuCl_2 \cdot 2H_2O$ (3)	24	trace[c]
11	$[RhCp^*Cl_2]_2$	NaOAc (4) + $Cu(OAc)_2 \cdot H_2O$ (3)	24	Not detected[c]
12	$[RhCp^*Cl_2]_2$	AgOTf (3)	24	Not detected[c]
13	-----	NaOAc (4) + AgOTf (3)	24	Not detected[c]

14	**[RhCp*Cl$_2$]$_2$[d]**	**NaOAc (4) + AgOTf (3)**	**24**	**76**
15	[IrCp*Cl$_2$]$_2$	NaOAc (4) + AgOTf (3)	24	33
16	[Ru(*p*-cym)Cl$_2$]$_2$	NaOAc (4) + AgOTf (3)	24	Not detected[c]
17	[Rh(COD)Cl]$_2$	NaOAc (4) + AgOTf (3)	24	trace[c]
18	RhCl$_3$.xH$_2$O	NaOAc (4) + AgOTf (3)	24	Not detected[c]
19	**[RhCp*Cl$_2$]$_2$[e]**	**NaOAc (4) + AgOTf (3)**	**2**	**86**

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (5 mol%), Additives (as indicated above), degassed CH_2Cl_2 (3.0 mL), N_2 atmosphere, room temp. [b]Isolated yields are shown. [c]By ^{1}H NMR spectroscopy. [d]With 2 mol% of catalyst. [e]Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (0.5 mol%), Additives (as indicated above), degassed $ClCH_2CH_2Cl$ (3.0 mL), N_2 atmosphere, reflux.

Table S2: Comparison of TON and TOF values of reported catalytic annulations methods with this work

Entry	Directing group (DG)	Reaction Conditions	References	TON	TOF (h^{-1})
1	2-substituted Pyridine	1 mol% Cp*Rh(H_2O)$_3$(OTf)$_2$, HOTf, MeOH, O_2 (1 atm), 120 °C, 22 h	*J. Am. Chem. Soc.*, 2013, **135**, 8850	99	4.5
2	2-substituted Pyridine	0.1 mol% Cp*Rh(H_2O)$_3$(OTf)$_2$, HOTf, MeOH, O_2 (1 atm), 120 °C, 8 days	*J. Am. Chem. Soc.*, 2013, **135**, 8850	740	3.85
3	2-substituted Pyridine	1 mol% [(RhCp*Cl$_2$)$_2$], 0.5 equiv. Cu(BF_4)$_2$·6H_2O, DME, O_2, 25 – 30 °C, 24 h	*Chem. Eur. J.*, 2013, **19**, 14181	47	1.95
4	N-substituted pyrazole	1 mol% [(RhCp*Cl$_2$)$_2$], 1 equiv. Cu(OAc)$_2$·H_2O, 1 equiv. Na_2CO_3, *o*-xylene, 150 °C, N_2, 2 h	*J. Org. Chem.*, 2011, **76**, 13	40.5	20.2
5	3-substituted pyrazole	5 mol% [Rh(MeCN)$_3$Cp*][PF_6]$_2$, 2.5 equiv. Cu(OAc)$_2$·H_2O, DCE, 83 °C, 16 h	*J. Org. Chem.*, 2014, **79**, 1954	19.6	1.22
6	3-substituted thiophene	5 mol% [(RhCp*Cl$_2$)$_2$], 2 equiv. Cu(OAc)$_2$·H_2O, 30 mol% Cs_2CO_3, toluene, 125 °C, 10 h	*Chem. Eur. J.*, 2014, **20**, 385	8.6	0.86
7	Sulphonic acid	2 mol% [(RhCp*Cl$_2$)$_2$], 8 mol% $AgSbF_6$, 2 equiv. AgOAc, dioxane, 100 °C, 16 h, Ar	*Chem. Commun.*, 2014, 50, 9776	21.5	1.34
8	Amide	2.5 mol% [(RhCp*Cl$_2$)$_2$], 30 mol% CsOAc, MeOH (0.2M), 60 °C, 16 h	*J. Am. Chem. Soc.*, 2010, **132**, 6908	18	1.12
9	Amide	4 mol% [(RhCp*Cl$_2$)$_2$], 1.1 equiv. Ag_2CO_3, CH_3CN, 120 °C, N_2, 6 h	*J. Org. Chem.*, 2011, **76**, 7583	5.6	0.93

10	Acetanilide	5 mol% $[Cp^*Rh(MeCN)_3][SbF_6]_2$, 20 mol% $Cu(OAc)_2 \cdot H_2O/O_2$ (1 atm), *t*AmOH (0.2 M), 60 °C, 16 h	*J. Am. Chem. Soc.*, 2010, **132**, 18326	18	1.12
11	Carboxylic acids	1 mol% $[(RhCp^*Cl_2)_2]$, 5 mol% $Cu(OAc)_2 \cdot H_2O$, DMF, 120 °C, air, 2 h	*J. Org. Chem.*, 2007, **72**, 5362	48	24
12	Azobenzene	1 mol% $[(RhCp^*Cl_2)_2]$, 0.5 $Cu(BF_4)_2 \cdot 6H_2O$, *t*BuOH, 70 °C, 16 h, air	*Chem. Eur. J.*, 2013, **19**, 6198	45.5	2.84
13	N-substituted benzimidazole	5 mol% $[(RhCp^*Cl_2)_2]$, 1.2 equiv. $Cu(OAc)_2 \cdot H_2O$, toluene, 110 °C, 4 h	*Chem. Eur. J.*, 2012, **18**, 8896	9.8	2.45
14	2-substituted imidazole	5 mol% $[(RhCp^*Cl_2)_2]$, 1.2 equiv. $Cu(OAc)_2 \cdot H_2O$, toluene, 110 °C, 24h	*Org. Lett.*, 2013, **15**, 1878	9.9	0.41
15	**NHC**	**2 mol% $[(RhCp^*Cl_2)_2]$, 4 equiv. NaOAc, 3 equiv. AgOTf, DCE, Room Temp., 24 h, N_2**	**This work**	**19**	**0.79**
16	**NHC**	**0.5 mol% $[(RhCp^*Cl_2)_2]$, 4 equiv. NaOAc, 3 equiv. AgOTf, DCE, Reflux, 2 h, N_2**	**This work**	**86**	**43**

4. General procedure for the synthesis of imidazolium salts

The syntheses of imidazolium salts were performed according to the reported procedure[8], by stirring a mixture of *N*-aryl imidazole or benzimidazole (5 mmol) and iodomethane (0.44 mL, 7 mmol) in dry THF (7 mL) for 24 h at room temperature. The resultant precipitate was collected by filtration and washed with hexane and then dried *in vacuo*.

3-methyl-1-phenyl-1*H*-imidazol-3-ium iodide (1a): ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 9.05 (s, 1H), 7.76 (s, 1H), 7.65 – 7.60 (m, 5H), 7.56 (s, 1H), 3.96 (s, 3H). HRMS (ESI, positive ion): M^+ = 159.0921 (calculated 159.0917 for $[C_{10}H_{11}N_2]^+$).

3-methyl-1-(4-nitrophenyl)-1*H*-imidazol-3-ium iodide (1b)[9]: ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 9.35 (s, 1H), 8.47 – 8.45 (m, 2H), 7.91 (d, *J* = 8.9 Hz, 2H), 7.88 (t, *J* = 1.7 Hz, 1H), 7.62 (s, 1H), 3.99 (s, 3H).

1-(4-methoxyphenyl)-3-methyl-1*H*-imidazol-3-ium iodide (1c)[9]: ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 9.05 (s, 1H), 7.69 – 7.68 (m, 1H), 7.58 – 7.54 (m, 3H), 7.14 – 7.12 (m, 2H), 3.95 (s, 3H), 3.86 (s, 3H).

3-methyl-1-phenyl-1*H*-benzo[*d*]imidazol-3-ium iodide (1d): ^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 11.03 (s, 1H), 7.88 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.64 (m, 6H), 4.47 (s, 3H).

3-butyl-1-phenyl-1*H*-imidazol-3-ium iodide (1e)[10]: A mixture of *N*-phenyl imidazole (0.38 mL, 3 mmol) and iodobutane (0.375 mL, 3.3 mmol) in 1,4-dioxane (~ 10 mL) were refluxed at 100°C for 24h. After cooling, all volatiles were evapourated and the residue was washed several times with diethyl ether. Then resultant brown thicky liquid was dried under reduced pressure which gives **1e** (580 mg, 1.76 mmol, 59%). ^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 10.40 (s, 1H), 7.81 (t, *J* = 1.8 Hz, 1H), 7.78 – 7.77 (m, 1H), 7.77 – 7.74 (m, 2H), 7.52 – 7.43 (m, 3H), 4.51 (t, *J* = 7.4 Hz, 2H), 1.97 – 1.92 (m, 2H), 1.41 – 1.35 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

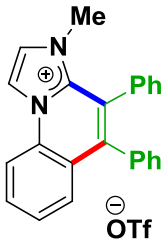
3-benzyl-1-phenyl-1*H*-imidazol-3-ium bromide (1f)[11]: In an oven dried screw cap sealed tube, *N*-phenyl imidazole (253 µL, 2 mmol), CH_2Cl_2 (2 mL) and benzyl bromide (476 µL, 4 mmol) were taken and flushed with N_2. Then the mixture was stirred at 35°C in oil bath for 36 h. After cooling, all volatiles were evaporated and the residue was washed with hexane and diethyl ether. Final product **1f** as pale yellow liquid was obtained after drying under reduced pressure (190 mg, 0.6 mmol, 30%). ^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 10.68 (s, 1H), 7.77 (s, 1H), 7.69 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 3.0 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.19 – 7.17 (m, 3H), 5.66 (s, 2H).

5. General procedure for the annulation reactions

To an oven dried Schlenk tube, **1** (0.1 mmol), NaOAc (0.4 mmol), $[RhCp^*Cl_2]_2$ (0.005 mmol), AgOTf (0.3 mmol) and **2** (0.12 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N_2 gas. To this mixture, dry and degassed CH_2Cl_2 (3.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at room temperature under dark. After 24 h stirring, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a $CHCl_3$/MeOH solvent mixture.

6. Experimental characterization data for the products (3a-3p)

3-methyl-4,5-diphenylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (**3a**): 39.2 mg, 81% yield. ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 8.70 (d, *J* = 2.3 Hz, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 8.03 – 7.99 (m, 1H), 7.82 (d, *J* = 2.3 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.53 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.37 – 7.34 (m, 8H), 7.22 (dd, *J* = 6.6, 3.0 Hz, 2H), 3.28 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN, 300K): δ 147.20, 138.31, 135.62, 133.35, 133.03, 132.18, 131.73, 130.99, 130.18, 130.13, 129.34, 129.19, 129.13, 128.67, 125.44, 124.46, 123.72, 120.54, 117.32, 114.15, 38.69. ^{19}F NMR (376 MHz, $CDCl_3$, 300K): δ -78.34 (s). HRMS (ESI, positive ion): M^+ = 335.1549 (calculated 335.1543 for $[C_{24}H_{19}N_2]^+$).



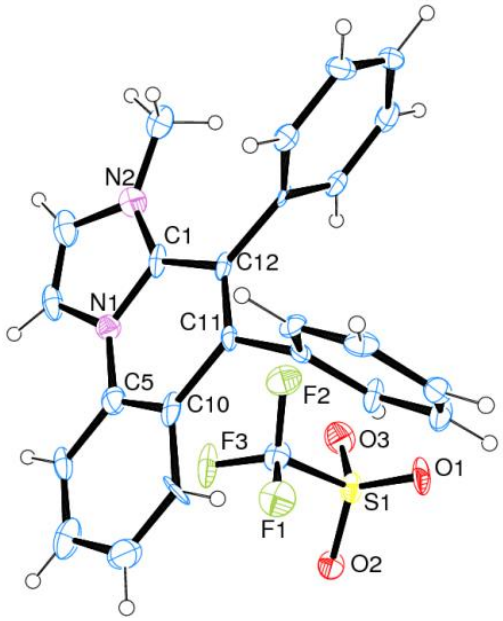
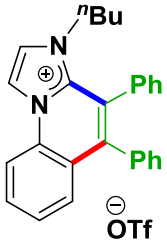
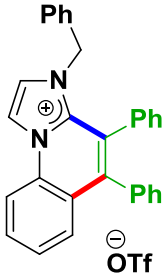


Figure S2. Molecular structure of product **3a** of trifluoromethanesulfonate sulfonate salt (30% probability level). Selected bond lengths (Å) and bond angles (°): C_1-N_1 = 1.396(9), C_1-N_2 = 1.315(8), C_1-C_{12} = 1.428(8), C_{10}-C_{11} = 1.482(9), C_{11}-C_{12} = 1.352(9), N_2-C_1-N_1 = 108.2(6), N_2-C_1-C_{12} = 131.9(7), N_1-C_1-C_{12} = 119.8(6).

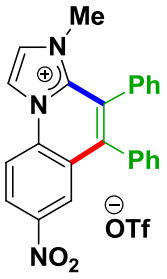


3-butyl-4,5-diphenylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3b): 29 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 9.10 (d, *J* = 2.3 Hz, 1H), 8.61 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 2.3 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.53 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.34 – 7.31 (m, 3H), 7.30 – 7.27 (m, 5H), 7.12 – 7.09 (m, 2H), 3.73 – 3.69 (m, 2H), 1.54 – 1.50 (m, 2H), 0.92 (dd, *J* = 15.2, 7.5 Hz, 2H), 0.70 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN, 300K): δ 147.56, 137.95, 135.71, 133.48, 133.06, 131.82, 130.91, 130.20, 130.08, 129.48, 129.27, 129.09, 127.16, 125.44, 124.21, 117.29, 114.74, 50.42, 33.51, 20.16, 13.56. ^{19}F NMR (376 MHz, CD_3CN, 300K): δ -79.29 (s). HRMS (ESI, positive ion): M^+ = 377.2018 (calculated 377.2012 for $[C_{27}H_{25}N_2]^+$).



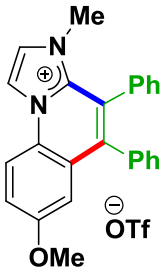
3-benzyl-4,5-diphenylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3c): 36 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 9.09 (d, *J* = 2.4 Hz, 1H), 8.61 (d, *J* = 8.6 Hz, 1H), 7.92 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.70 (d, *J* = 2.3 Hz, 1H), 7.69 – 7.54 (m, 2H), 7.27 – 7.22 (m, 7H), 7.17 – 7.15 (m, 4H), 7.10 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.79 – 6.77 (m, 2H), 4.97 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, 300K): δ 147.62, 136.65, 134.26, 133.81, 132.71, 131.70, 130.99, 129.89, 129.32, 129.30, 129.15, 128.83, 128.64, 128.47, 128.27, 128.23, 127.09, 126.80, 124.41, 122.99, 122.47, 119.28, 117.09, 114.84, 53.40. HRMS (ESI, positive ion): M^+ = 411.1863 (calculated 411.1856 for $[C_{30}H_{23}N_2]^+$).

3-methyl-7-nitro-4,5-diphenylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3d):



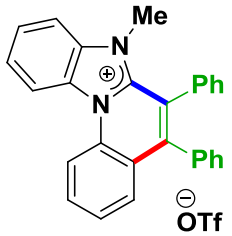
48 mg, 90% yield. ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 8.83 (d, *J* = 2.4 Hz, 1H), 8.72 (t, *J* = 1.4 Hz, 2H), 8.27 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.93 (d, *J* = 2.4 Hz, 1H), 7.42 – 7.38 (m, 8H), 7.27 (ddd, *J* = 5.4, 2.9, 1.5 Hz, 2H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN, 300K): δ 147.44, 146.81, 139.03, 134.66, 134.58, 132.69, 131.93, 131.08, 130.48, 129.92, 129.51, 129.46, 129.39, 126.66, 125.77, 125.63, 123.64, 120.45, 119.64, 115.23, 38.99. ^{19}F NMR (376 MHz, CD_3CN, 300K): δ -79.28 (s). HRMS (ESI, positive ion): M^+ = 380.1404 (calculated 380.1394 for $[C_{24}H_{18}N_3O_2]^+$).

7-methoxy-3-methyl-4,5-diphenylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3e):



15 mg, 29% yield. ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 8.61 (d, *J* = 2.3 Hz, 1H), 8.40 (d, *J* = 9.3 Hz, 1H), 7.78 (d, *J* = 2.3 Hz, 1H), 7.62 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.37 – 7.34 (m, 8H), 7.22 (ddd, *J* = 5.0, 3.3, 2.2 Hz, 2H), 6.83 (d, *J* = 2.8 Hz, 1H), 3.72 (s, 3H), 3.25 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN, 300K): δ 159.76, 146.50, 137.52, 135.61, 133.43, 132.12, 130.93, 130.14, 129.36, 129.30, 129.20, 128.52, 126.91, 126.36, 124.78, 122.16, 120.56, 118.96, 113.86, 110.80, 56.45, 38.58. ^{19}F NMR (376 MHz, CD_3CN, 300K): δ -79.32 (s). HRMS (ESI, positive ion): M^+ = 365.1665 (calculated 365.1648 for $[C_{25}H_{21}N_2O]^+$).

7-methyl-5,6-diphenylbenzo[4,5]imidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3f):



44 mg, 82% yield. ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 9.15 (d, *J* = 8.7 Hz, 1H), 9.00 (dd, *J* = 6.7, 2.6 Hz, 1H), 8.16 (ddd, *J* = 8.7, 7.3, 1.4 Hz, 1H), 8.00 – 7.90 (m, 3H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.65 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.43 – 7.38 (m, 8H), 7.26 (dd, *J* = 6.6, 2.9 Hz, 2H), 3.44 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN, 300K): δ 152.19, 142.94, 135.66, 135.21, 134.39, 134.14, 133.78, 132.31, 130.83, 130.72, 130.29, 129.59, 129.55, 129.49, 129.13, 128.88, 128.65, 127.80, 125.76, 124.38, 123.69, 120.50, 117.82, 114.12, 34.94. ^{19}F NMR (376 MHz, CD_3CN, 300K): δ -79.27 (s). HRMS (ESI, positive ion): M^+ = 385.1705 (calculated 385.1699 for $[C_{28}H_{21}N_2]^+$).

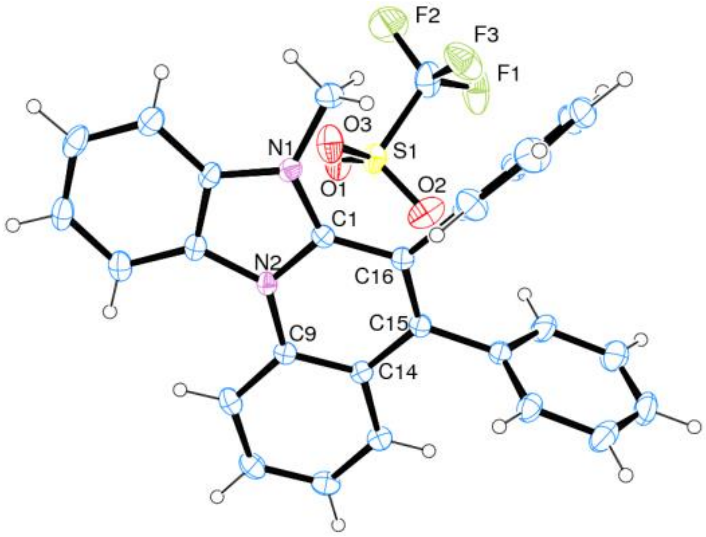
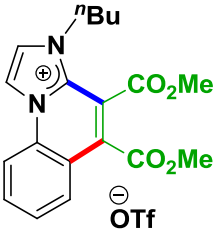


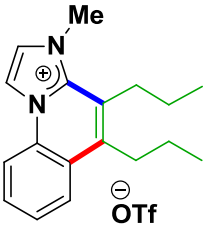
Figure S3. Molecular structure of product **3f** of trifluoromethanesulfonate sulfonate salt (30% probability level). Selected bond lengths (Å) and bond angles (°): C_1-N_1 = 1.346(3), C_1-N_2 = 1.375(3), C_1-C_{16} = 1.428(3), C_{15}-C_{16} = 1.367(3), N_1-C_1-N_2 = 109.07(19), N_1-C_1-C_{16} = 129.3(2), N_2-C_1-C_{16} = 121.6(2).

7-methyl-5,6-dipropylbenzo[4,5]imidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3g): 42 mg, 90% yield. ^{1}H NMR (700 MHz, CD_3CN, 300K): δ 8.92 (d, *J* = 8.6 Hz, 1H), 8.78 (d, *J* = 8.6 Hz, 1H), 8.38 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.05 – 8.02 (m, 2H), 7.87 (ddd, *J* = 8.3, 7.3, 0.8 Hz, 1H), 7.83 (ddd, *J* = 8.1, 7.1, 0.9 Hz, 1H), 7.78 (ddd, *J* = 8.4, 7.3, 1.1 Hz, 1H), 4.40 (s, 3H), 3.29 – 3.25 (m, 4H), 1.81 – 1.80 (m, 2H), 1.75 – 1.73 (m, 2H), 1.19 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (176 MHz, CD_3CN, 300K): δ 151.79, 144.38, 135.19, 133.73, 133.04, 129.23, 128.68, 128.47, 128.04, 127.26, 124.62, 123.22, 121.19, 118.46, 117.63, 113.97, 35.33, 31.51, 30.15, 25.20, 25.06, 14.64, 13.96. ^{19}F NMR (376 MHz, $CDCl_3$, 300K): δ -78.35 (s). HRMS (ESI, positive ion): M^+ = 317.2040 (calculated 317.2012 for $[C_{22}H_{25}N_2]^+$).

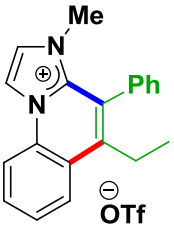
4,5-bis(methoxycarbonyl)-3-methylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3h): 22 mg, 49% yield. ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 8.75 (d, *J* = 2.2 Hz, 1H), 8.47 (d, *J* = 8.6 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.17 – 8.13 (m, 1H), 8.04 (d, *J* = 2.2 Hz, 1H), 7.91 (t, *J* = 7.8 Hz, 1H), 4.08 (s, 3H), 4.07 (s, 3H), 4.02 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN, 300K): δ 165.60, 163.79, 138.28, 135.56, 133.03, 130.27, 129.93, 129.37, 126.74, 123.56, 120.38, 117.20, 116.46, 115.74, 55.37, 55.06, 38.70. ^{19}F NMR (376 MHz, $CDCl_3$, 300K): δ -79.02 (s). HRMS (ESI, positive ion): M^+ = 299.1040 (calculated 299.1026 for $[C_{16}H_{15}N_2O_4]^+$).

3-butyl-4,5-bis(methoxycarbonyl)imidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3i): 

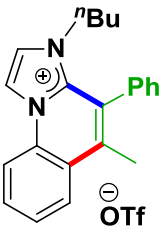
19 mg, 39% yield. ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 8.75 (d, *J* = 2.4 Hz, 1H), 8.46 (d, *J* = 8.6 Hz, 1H), 8.24 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.15 (ddd, *J* = 8.6, 7.3, 1.3 Hz, 1H), 8.08 (d, *J* = 2.4 Hz, 1H), 7.91 (ddd, *J* = 8.3, 7.3, 1.0 Hz, 1H), 4.41 – 4.37 (m, 2H), 4.09 (s, 3H), 4.07 (s, 3H), 1.85 – 1.81 (m, 2H), 1.42 – 1.34 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN, 300K): δ 165.65, 164.14, 138.54, 135.60, 134.52, 133.16, 130.26, 129.36, 128.69, 120.57, 120.40, 117.94, 116.45, 116.08, 55.55, 55.10, 51.52, 32.67, 20.30, 13.76. ^{19}F NMR (376 MHz, CD_3CN, 300K): δ -79.33 (s). HRMS (ESI, positive ion): M^+ = 341.1516 (calculated 341.1496 for $[C_{19}H_{21}N_2O_4]^+$).

3-methyl-4,5-dipropylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3j): 

31 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 8.75 (d, *J* = 2.4 Hz, 1H), 8.38 (d, *J* = 8.1 Hz, 1H), 8.08 (dd, *J* = 10.4, 1.6 Hz, 2H), 7.86 (ddd, *J* = 8.5, 7.2, 1.2 Hz, 1H), 7.74 – 7.70 (m, 1H), 4.41 (s, 3H), 3.16 – 3.08 (m, 4H), 1.72 (ddd, *J* = 14.9, 7.5, 2.2 Hz, 4H), 1.17 (td, *J* = 7.3, 1.6 Hz, 6H). ^{13}C NMR (176 MHz, CD_3CN, 300K): δ 145.83, 139.51, 131.94, 131.19, 128.90, 128.61, 127.54, 124.37, 123.44, 117.47, 113.57, 39.34, 30.77, 29.50, 25.36, 24.96, 14.55, 13.96. ^{19}F NMR (376 MHz, $CDCl_3$, 300K): δ -78.34 (s). HRMS (ESI, positive ion): M^+ = 267.1856 (calculated 267.1856 for $[C_{18}H_{23}N_2]^+$).

5-ethyl-3-methyl-4-phenylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3k): 

34 mg, 78% yield. ^{1}H NMR (700 MHz, CD_3CN, 300K): δ 8.62 (d, *J* = 2.3 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 8.00 (ddd, *J* = 8.5, 7.2, 1.2 Hz, 1H), 7.87 – 7.85 (m, 1H), 7.74 (d, *J* = 2.3 Hz, 1H), 7.65 – 7.62 (m, 3H), 7.50 – 7.49 (m, 2H), 3.22 (s, 3H), 2.90 (q, *J* = 7.6 Hz, 2H), 1.16 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (176 MHz, CD_3CN, 300K): δ 148.26, 138.19, 133.59, 132.75, 131.84, 131.47, 130.77, 130.13, 129.19, 128.16, 128.03, 123.73, 123.62, 117.75, 113.65, 38.33, 23.43, 15.31. ^{19}F NMR (376 MHz, $CDCl_3$, 300K): δ -78.35 (s). HRMS (ESI, positive ion): M^+ = 287.1568 (calculated 287.1543 for $[C_{20}H_{19}N_2]^+$).

3-butyl-5-methyl-4-phenylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3l): 

32 mg, 69% yield. ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 8.66 (d, *J* = 2.4 Hz, 1H), 8.42 (d, *J* = 8.2 Hz, 1H), 8.32 (dd, *J* = 8.3, 1.0 Hz, 1H), 8.01 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.87 – 7.85 (m, 1H), 7.83 (d, *J* = 2.3 Hz, 1H), 7.66 – 7.64 (m, 3H), 7.50 – 7.48 (m, 2H), 3.57 – 3.53 (m, 2H), 2.44 (s, 3H), 1.53 – 1.49 (m, 2H), 0.91 (dt, *J* = 14.1, 7.0 Hz, 2H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN, 300K): δ 143.35, 137.94, 134.19, 132.85, 131.50, 131.15, 130.79, 130.41, 129.10, 128.06, 126.57, 124.91, 123.75, 120.54, 117.50, 114.35, 50.17, 33.48, 20.19, 16.83, 13.59. ^{19}F NMR (376 MHz, CD_3CN, 300K): δ -79.24 (s). HRMS (ESI, positive ion): M^+ = 315.1877 (calculated 315.1856 for $[C_{22}H_{23}N_2]^+$).

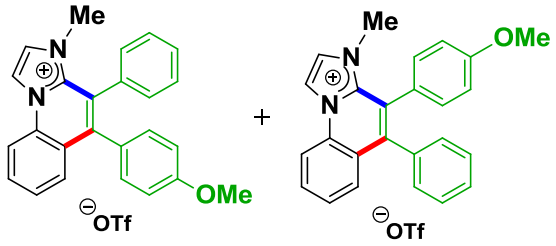
5-ethyl-7-methyl-6-phenylbenzo[4,5]imidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3m): 45 mg, 93% yield. ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 9.09 (d, *J* = 8.4 Hz, 1H), 8.91 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.49 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.17 (ddd, *J* = 8.7, 7.2, 1.4 Hz, 1H), 7.95 – 7.84 (m, 4H), 7.71 – 7.69 (m, 3H), 7.58 – 7.56 (m, 2H), 3.38 (s, 3H), 3.01 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (101 MHz, CD_3CN, 300K): δ 154.01, 142.85, 135.07, 134.50, 134.03, 133.90, 131.64, 131.01, 130.44, 129.33, 128.79, 128.75, 128.62, 127.50, 124.01, 123.74, 123.58, 118.74, 117.71, 113.91, 34.59, 24.12, 15.32. ^{19}F NMR (376 MHz, $CDCl_3$, 300K): δ -78.35 (s). HRMS (ESI, positive ion): M^+ = 337.1710 (calculated 337.1699 for $[C_{24}H_{21}N_2]^+$).

Figure S4. Molecular structure of product **3m** of trifluoromethanesulfonate sulfonate salt (30% probability level). Selected bond lengths (Å) and bond angles (°): C_1-N_1 = 1.348(3), C_1-N_2 = 1.374(3), C_1-C_{16} = 1.419(4), C_{15}-C_{16} = 1.373(3), N_1-C_1-N_2 = 108.9(2), N_1-C_1-C_{16} = 129.1(2), N_2-C_1-C_{16} = 122.0(2).

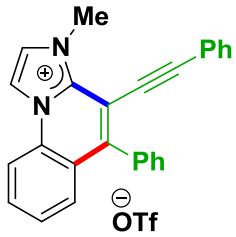
3-methyl-5-(4-nitrophenyl)-4-phenylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate and 3-methyl-4-(4-nitrophenyl)-5-phenylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3n + 3n' (2:1)): 35 mg, 66% yield. ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 8.78 (t, *J* = 2.6 Hz, 1H), 8.53 (dd, *J* = 8.5, 3.7 Hz, 1H), 8.17 – 8.14 (m, 2H), 8.04 (ddt, *J* = 8.7, 7.2, 1.5 Hz, 1H), 7.89 (t, *J* = 2.7 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.64 – 7.54 (m, 2H), 7.49 – 7.47 (m, 1H), 7.38 – 7.35 (m, 4H), 7.23 – 7.21 (m, 1H), 3.32 (s, 1.94H), 3.32 (s, 0.98H).^{13}C NMR (101 MHz, CD_3CN, 300K): δ 149.23, 148.78, 147.43, 144.83, 142.56, 140.26, 137.93, 137.64, 135.02,

133.66, 133.49, 133.29, 132.70, 132.52, 132.03, 131.94, 131.77, 130.88, 130.46, 130.17, 129.60, 129.58, 129.55, 129.36, 129.33, 128.93, 128.78, 125.14, 124.67, 124.62, 124.28, 124.19, 123.61, 122.52, 120.42, 117.56, 117.44, 114.48, 114.40, 39.07, 38.75. ^{19}F NMR (376 MHz, CD_3CN, 300K): δ -79.27 (s), -79.27 (s). HRMS (ESI, positive ion): M^+ = 380.1422 (calculated 380.1394 for $[C_{24}H_{18}N_3O_2]^+$).

5-(4-methoxyphenyl)-3-methyl-4-phenylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate and 4-(4-methoxyphenyl)-3-methyl-5-phenylimidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3o + 3o' (1:1.2)): 18 mg, 35% yield. ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 8.69 (dd, *J* = 6.6, 2.2 Hz, 1H), 8.47 (d, *J* = 8.6 Hz, 1H), 8.05 – 7.97 (m, 1H), 7.81 (dd, *J* = 4.5, 2.3 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.56 (dd, *J* = 30.9, 8.3 Hz, 1H), 7.40 – 7.35 (m, 4H), 7.25 – 7.20 (m, 2H), 7.14 – 7.11 (m, 1H), 6.90 – 6.87 (m, 2H), 3.76 (s, 3H), 3.31 (s, 1.3H), 3.27 (s, 1.7H). ^{13}C NMR (101 MHz, CD_3CN, 300K): δ 161.14, 160.49, 147.49, 147.16, 135.81, 133.56, 133.39, 132.95, 132.91, 132.37, 132.18, 131.72, 131.65, 130.96, 130.20, 130.13, 130.08, 129.35, 129.29, 129.14, 129.12, 128.61, 127.52, 126.03, 125.75, 125.47, 125.12, 124.97, 124.66, 124.35, 117.28, 114.67, 114.47, 114.06, 56.06, 56.00, 38.78, 38.68. ^{19}F NMR (376 MHz, CD_3CN, 300K): δ -79.32 (s), -79.33 (s). HRMS (ESI, positive ion): M^+ = 365.1670 (calculated 365.1648 for $[C_{25}H_{21}N_2O]^+$).



3-methyl-5-phenyl-4-(phenylethynyl)imidazo[1,2-*a*]quinolinium trifluoromethanesulfonate (3p): 20 mg, 40% yield. ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 8.66 (d, *J* = 2.4 Hz, 1H), 8.42 (d, *J* = 8.5 Hz, 1H), 8.01 (ddd, *J* = 8.6, 6.7, 1.9 Hz, 1H), 7.95 (d, *J* = 2.3 Hz, 1H), 7.73 – 7.67 (m, 5H), 7.54 – 7.52 (m, 2H), 7.42 – 7.41 (m, 1H), 7.38 – 7.34 (m, 2H), 7.23 – 7.20 (m, 2H), 4.53 (s, 3H). ^{13}C NMR (101 MHz, CD_3CN, 300K): δ 151.79, 137.48, 135.96, 133.75, 132.07, 131.73, 131.07, 130.76, 130.49, 130.05, 129.80, 129.78, 129.47, 128.39, 126.07, 124.80, 123.73, 121.94, 118.33, 117.54, 114.51, 106.81, 102.85, 38.54. ^{19}F NMR (376 MHz, CD_3CN, 300K): δ -79.30 (s). HRMS (ESI, positive ion): M^+ = 359.1572 (calculated 359.1543 for $[C_{26}H_{19}N_2]^+$).



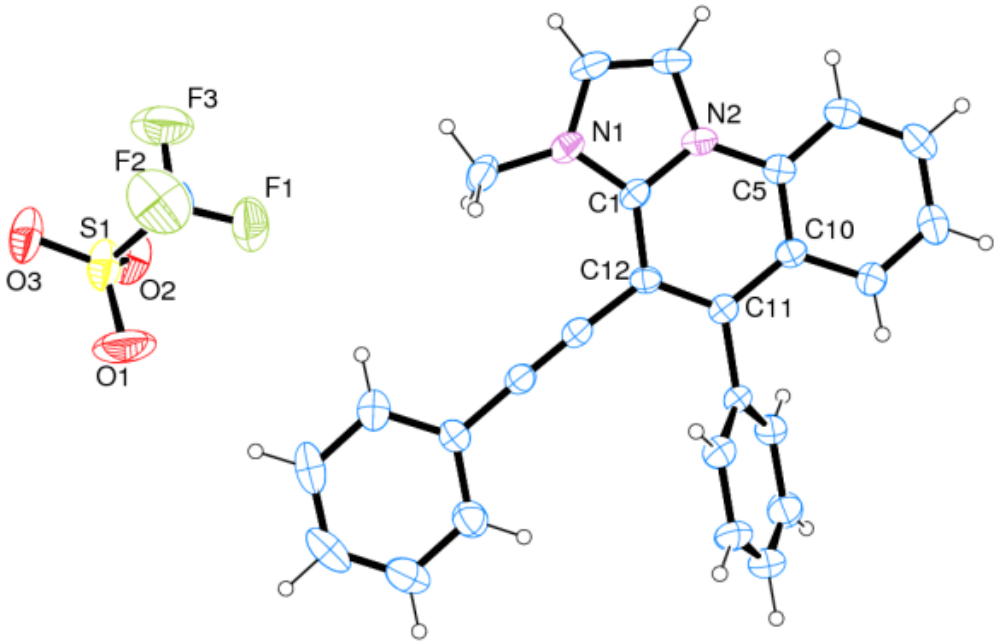
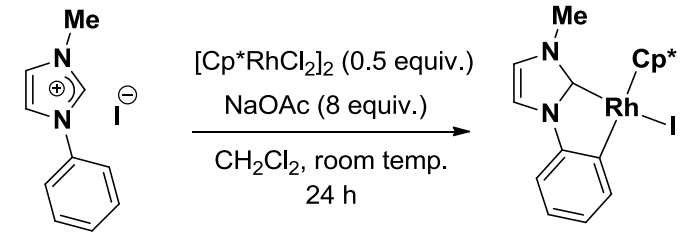


Figure S5. Molecular structure of product **3p** of trifluoromethanesulfonate sulfonate salt (30% probability level). Selected bond lengths (Å) and bond angles (°): C_1-N_1 = 1.358(6), C_1-N_2 = 1.365(6), C_1-C_{12} = 1.418(6), C_{11}-C_{12} = 1.375(6), N_1-C_1-N_2 = 106.6(4), N_1-C_1-C_{12} = 131.6(4), N_2-C_1-C_{12} = 121.8(4).

7. Mechanistic studies

A. Synthesis of the cyclometalated Rh(III) intermediate complex 4:



1a, 0.05 mmol

4, 76%

A mixture of $[RhCp^*Cl_2]_2$ (15.4 mg, 0.025 mmol) and NaOAc (32.8 mg, 0.4 mmol) was stirred in dry and degassed CH_2Cl_2 (5 mL) for 15 minute in dry Schlenk tube. **1a** (14.3 mg, 0.05 mmol) was added to the reaction mixture and stirring continued for further 24 h at room temperature. The resulting solution was filtered through a Celite plug. Solvent was removed under reduced pressure and the solid formed was redissolved in minimum quantity of CH_2Cl_2. This solution was poured into hexane (~20 times) and kept in a refrigerator. Orange crystalline solid was formed and then decantation of liquid portion followed by washing with hexane produces the desired complex **4** (20 mg, 0.038 mmol, 76%) after drying under reduced pressure.

B. Single crystal X-ray structure of 4:

The structure of this complex was characterised by single crystal X-ray diffraction study, which was further confirmed by NMR, HRMS and elemental analysis.

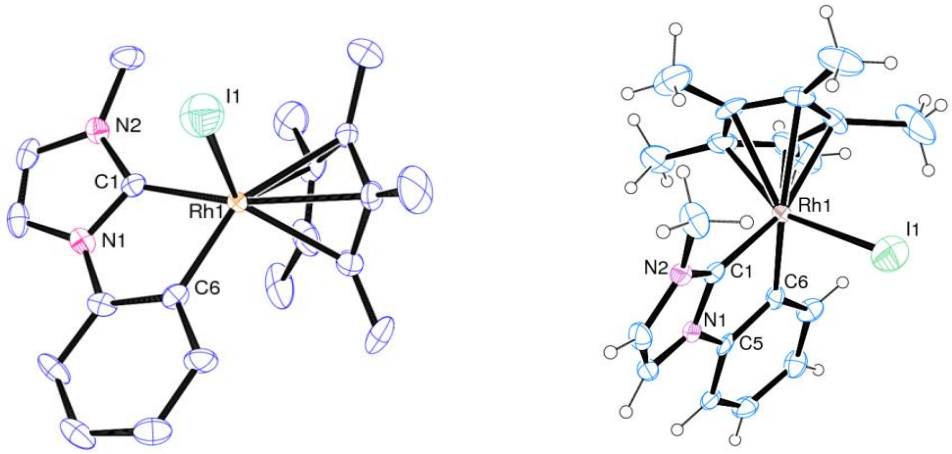


Figure S6: Molecular structure of **4** (30% probability level) (left: shown without H atoms for clarification purpose; right: shown with all the H atoms). Selected bond lengths (Å) and bond angles (°): C_1–Rh_1 = 2.008(11); C_6–Rh_1 = 2.030(11); I_1–Rh_1 = 2.5972(15); C_1–N_1 = 1.362(15); C_1–N_2 = 1.364(15); N_1–C_1–N_2 = 104.7(9); C_1–Rh_1–C_6 = 77.0(4); C_1–Rh_1–I_1 = 92.6(3), C_6–Rh_1–I_1 = 96.2(3).

C. Characterization data of 4:

^{1}H NMR (400 MHz, $CDCl_3$, 300K): δ 7.74 (d, *J* = 7.0 Hz, 1H), 7.39 (d, *J* = 1.7 Hz, 1H), 7.14 – 7.05 (m, 1H), 7.03 – 6.93 (m, 3H), 3.90 (s, 3H), 1.85 (s, 15H). ^{13}C NMR (176 MHz, $CDCl_3$, 300K): δ 182.62 (d, *J* = 55.3 Hz), 156.71 (d, *J* = 34.5 Hz), 145.61, 139.18, 125.00, 122.43, 122.20, 115.11, 110.88, 97.92 (d, *J* = 4.7 Hz), 38.01, 10.69. HRMS (ESI, positive ion): $(M-I)^+$ = 395.1008 (calculated 395.0989 for $[C_{20}H_{24}N_2Rh]^+$). Anal. Calcd for $C_{20}H_{24}N_2IRh(522.2)\cdot 1/4CH_2Cl_2$: C, 44.75; H, 4.54; N, 5.15. Found: C, 45.11; H, 4.63; N, 5.10.

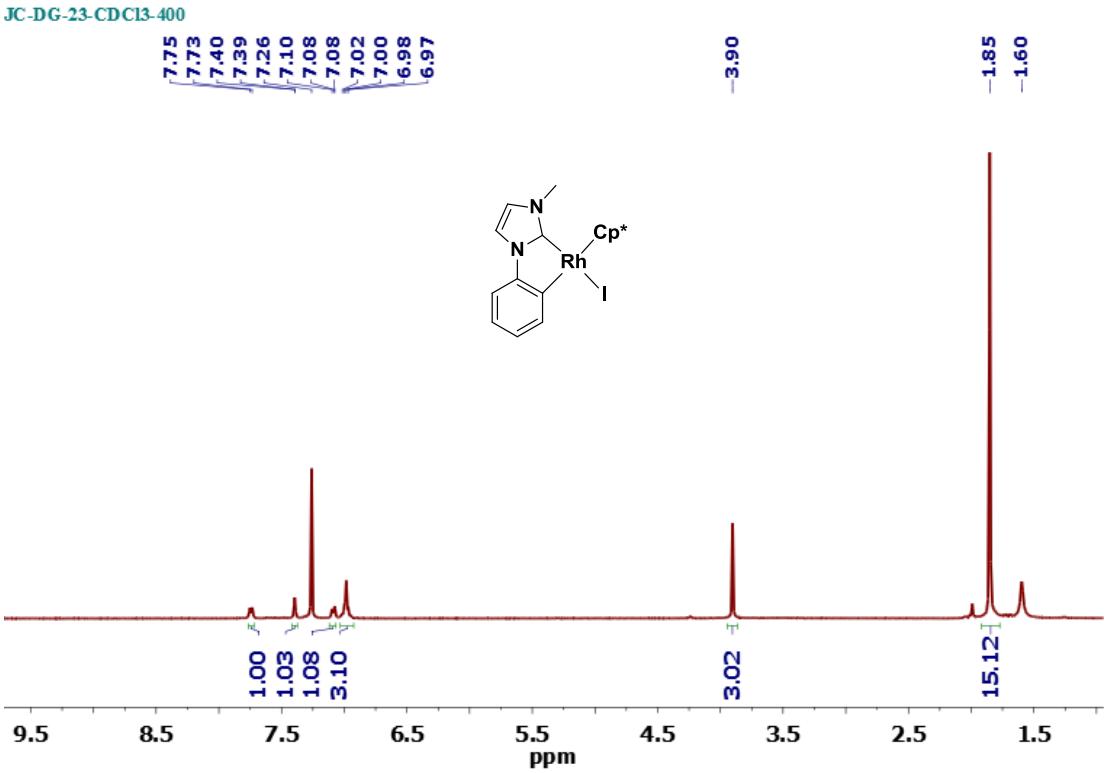


Figure S7. ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$, 300 K).

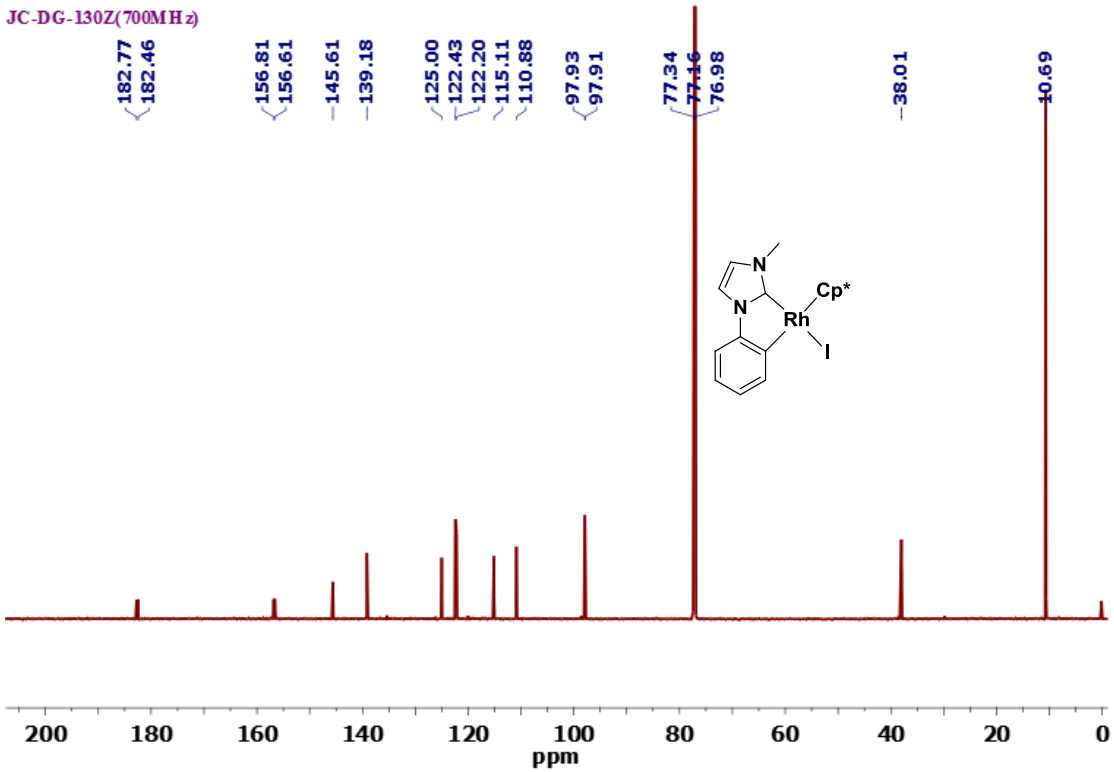


Figure S8. ^{13}C{^{1}H} NMR spectrum of **4** (176 MHz, $CDCl_3$, 300 K).

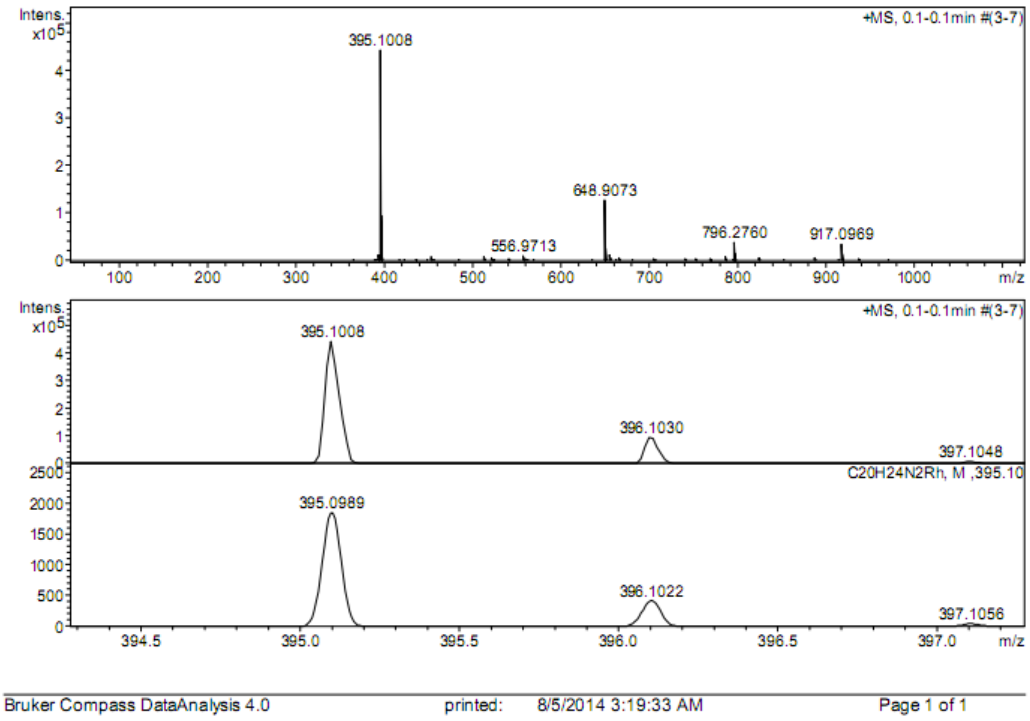
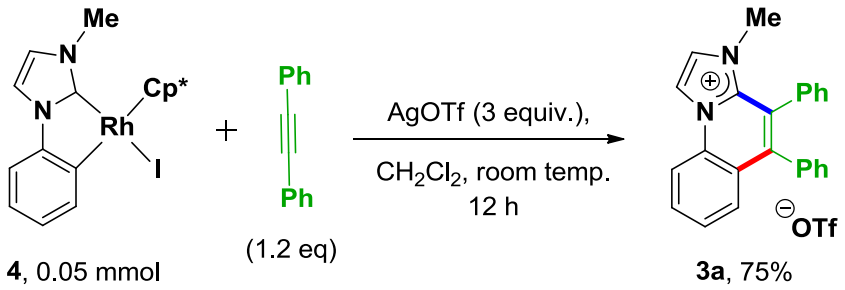


Figure S9. ESI-HRMS of the Rh(III)-complex **4.**

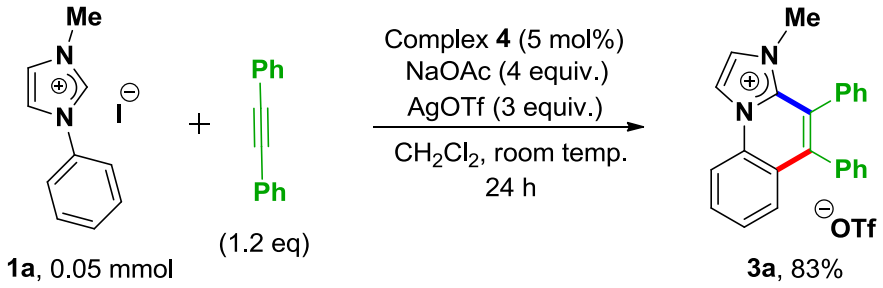
D. Stoichiometric reaction of the Rh(III) complex 4



4, 0.05 mmol (1.2 eq) **3a**, 75%

A mixture of Complex **4** (26.1 mg, 0.05 mmol), AgOTf (38.5 mg, 0.15 mmol) and **2a** (10.7 mg, 0.06 mmol) in dry and degassed CH_2Cl_2 (5.0 mL) were stirred in dry Schlenk tube at room temperature under dark. After 12 h stirring, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a 7:1 (v/v) $CHCl_3$/MeOH solvent mixture **3a** (18.3 mg, 0.0375 mmol, 75%).

E. Catalytic reaction with the Rh(III) complex 4

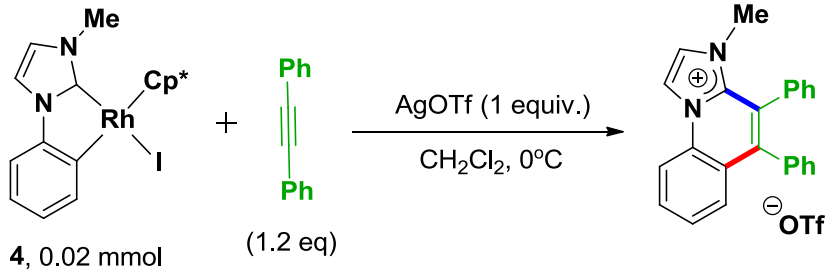


1a, 0.05 mmol

3a, 83%

To an oven dried Schlenk tube, **1a** (14.3 mg, 0.05 mmol), NaOAc (16.4 mg, 0.2 mmol), complex **4** (0.0025 mmol), AgOTf (38.5 mg, 0.15 mmol) and **2a** (10.7 mg, 0.06 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N_2 gas. To this mixture, dry and degassed CH_2Cl_2 (2.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at room temperature under dark. After 24 h, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×3 mL). The combined filtrate was concentrated under reduced pressure. Final product was separated by silica gel column chromatography, eluted with a 7:1 (v/v) $CHCl_3$/MeOH solvent mixture, afforded **3a** (20 mg, 0.041 mmol, 83%).

F. Preliminary combined time dependent ^{1}H NMR spectroscopic and ESI-MS study for the reaction of 4 with 2a:



4, 0.02 mmol

To an oven dried Schlenk tube, complex **4** (10.5 mg, 0.02 mmol), AgOTf (5.17 mg, 0.02 mmol) and **2a** (3.92 mg, 0.022 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N_2 gas. To this mixture, dry and degassed CH_2Cl_2 (2.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at 0°C under dark. The progress of the reaction was monitored by withdrawing aliquots at different time intervals, removing the solvent under vacuum, adding 0.5 mL of $CDCl_3$, and subjecting to ^{1}H NMR spectroscopy as well as ESI-HRMS.

The ^{1}H NMR spectral analysis established the gradual consumption of the cyclometalated intermediate **4** in the reaction with diphenylacetylene **2a** as indicated by the decrease of the characteristic peaks at 1.85 ppm (Cp* protons) and 3.90 ppm (CH_3 protons), along with the evolution of the product **3a** as indicated by the generation of the characteristic new peaks in the aromatic region and also at 3.43 ppm due to CH_3 protons (Figure S10, A). Most interestingly, a new peak due to Cp* protons at 1.61 ppm evolved which was speculated to be due to the Cp*Rh(I) intermediate **I"** (Figure S10, A). An ESI-HRMS analysis of this sample provided evidence in favor of the formation of the postulated **3a**-coordinated, 18-electron, Cp*Rh(I) complex **I"** in this reaction (Figure S10, B). *Further studies are underway to isolate and fully characterize the above-proposed intermediate.*

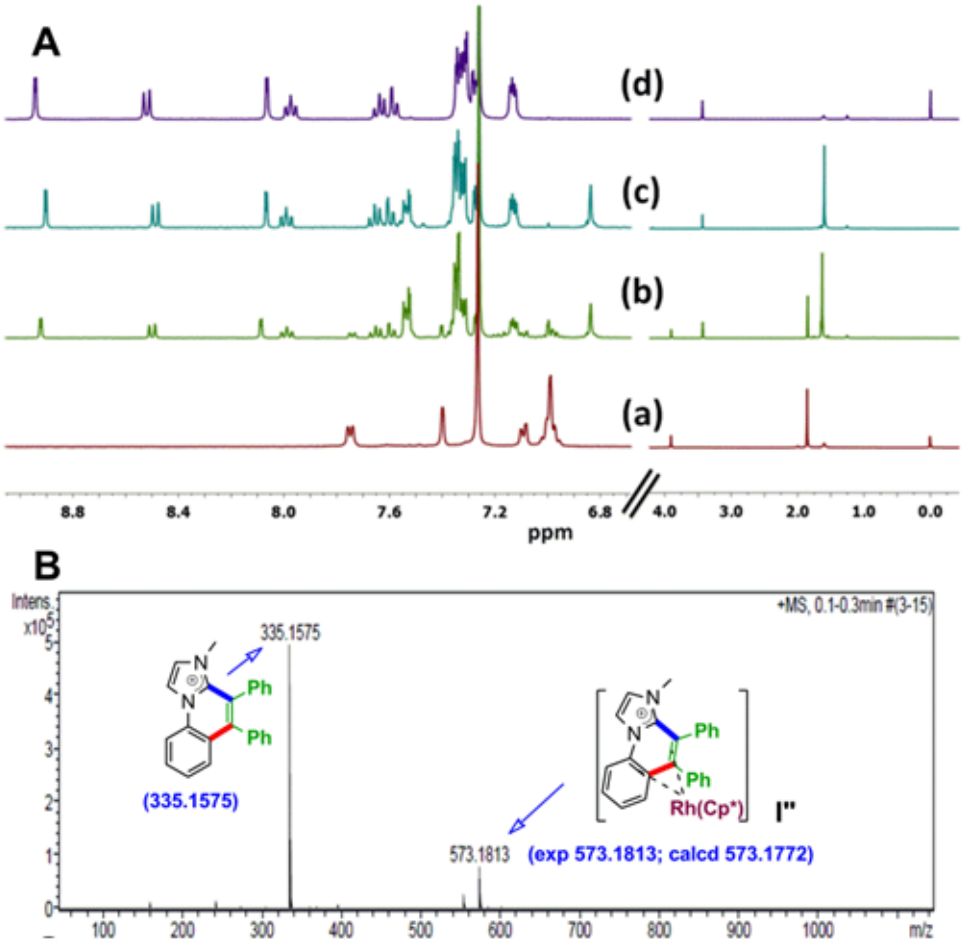
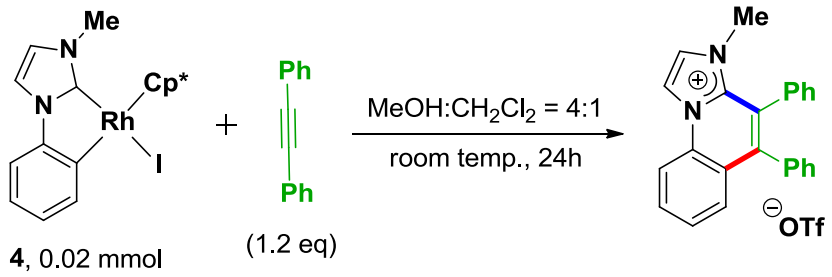


Figure S10. (A) Time-dependent ^{1}H NMR spectral profile for the reaction of the complex **4** (0.02 mmol) with diphenylacetylene **2a** (0.022 mmol) in the presence of AgOTf (0.02 mmol) in CH_2Cl_2 at 0 °C: (a) only **4**; (b) **4** + **2a**, 10 min; (c) **4** + **2a**, 60 min; (d) product **3a** (for reference). (B) ESI-HRMS profile of the same reaction mixture as described in (c) above.

G. Preliminary reaction study of 4 with 2a in the absence of AgOTf

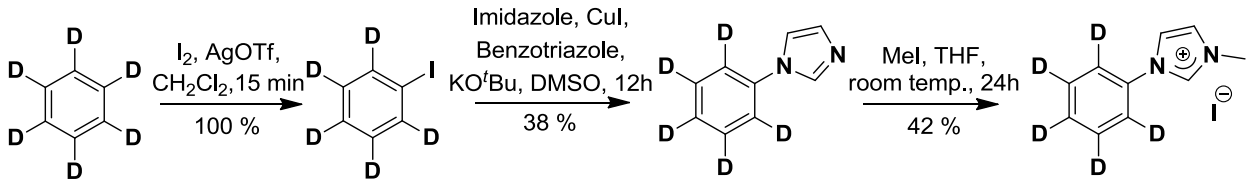


To an oven dried Schlenk tube, complex **4** (10.5 mg, 0.02 mmol) and **2a** (3.92 mg, 0.022 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N_2 gas. To this mixture, dry and degassed CH_2Cl_2:MeOH (1:4, v/v, 5 mL) solvent mixture was added under Schlenk technique and the reaction mixture was left with stirring at room temperature for 24 h.

The ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectral analysis of the above mentioned reaction mixtures indicates that the major compound is **4** which is unaltered along with little formation of products but no intermediate was detected.

H. Determination of kinetic isotope effect (KIE)

Synthesis of *N*-Methyl-*N*-(pentadeuteriophenyl)iimidazolium iodide (D_5-1a):



Synthesis of D_5-iodobenzene

The title compound was synthesized by following a similar procedure reported in the literature for the synthesis of iodobenzene[12], by stirring a mixture of D_6-benzene (0.23 mL, 2.5 mmol), AgOTf (642 mg, 2.5 mmol) and iodine (635 mg, 2.5 mmol) in dry CH_2Cl_2 (10 mL) for 15 min at room temperature in dark condition. Reaction mixture was passed through a short celite plug and washed with CH_2Cl_2. Then combined filtrate was washed with dilute NH_4OH solution, dilute Na_2SO_3 and water, followed by organic solution was dried over anhyd. Na_2SO_4, filtered and evapourated under reduced pressure. The resulting residue was utilized directly for further reaction purpose.

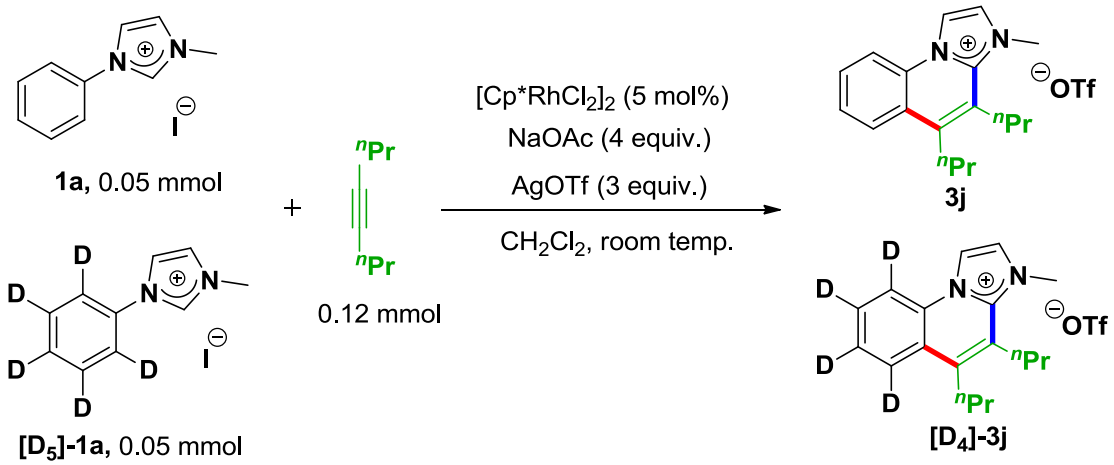
Synthesis of *N*-(pentadeuteriophenyl)imidazole

The title compound was synthesized by following a similar procedure reported in the literature for the synthesis of N-phenyl imidazole5. A mixture of CuI (28.5 mg, 0.15 mmol) and benzotriazole (38.5 mg, 0.3 mmol) in DMSO (~3 mL) was stirred at room temperature for 5 minutes. To that solution D_5-iodobenzene (627 mg, 3 mmol), imidazole (204 mg, 3 mmol) and KO^{t}Bu (471 mg, 4.2 mmol) were added and heating the solution at 120°C for 12 h. After cooling, EtOAc (~30 mL) was added to that solution and washed with water (2× 30 mL). Then the whole organic solution was dried over Na_2SO_4 and filtrate was evapourated under reduced pressure. Final product (170 mg, 1.14 mmol, 38% yield) was separated by silica gel column chromatography using EtOAc and hexane (4:1, v/v) solvent mixture as an eluting solvent. ^{1}H NMR (500 MHz, CD_3CN, 300K): δ 7.97 (s, 1H), 7.47 (t, J = 1.3 Hz, 1H), 7.13 (s, 1H).

Synthesis of *N*-Methyl-*N*-(pentadeuteriophenyl)imidazolium iodide, D_5-1a

The title compound was synthesized by following a similar procedure reported in the literature for the synthesis of *N*-methyl-*N*-phenyl imidazolium iodide8, by stirring a mixture of *N*-(pentadeuteriophenyl) imidazole (300 mg, 2 mmol) and iodomethane (0.19 mL, 3 mmol) in dry THF (4 mL) for 24 h at room temperature. The resultant precipitate was collected by filtration and washed with hexane and then dried *in vacuo* (248 mg, 0.85 mmol, 42% yield). ^{1}H NMR (400 MHz, CD_3CN, 300K): δ 9.14 (br s, 1H), 7.77 (d, J = 1.8 Hz, 1H), 7.57 (s, 1H), 3.97 (d, J = 1.9 Hz, 3H). HRMS (ESI, positive ion): M^+ = 164.1211 (calculated 164.1231 for $[C_{10}H_6D_5N_2]^+$).

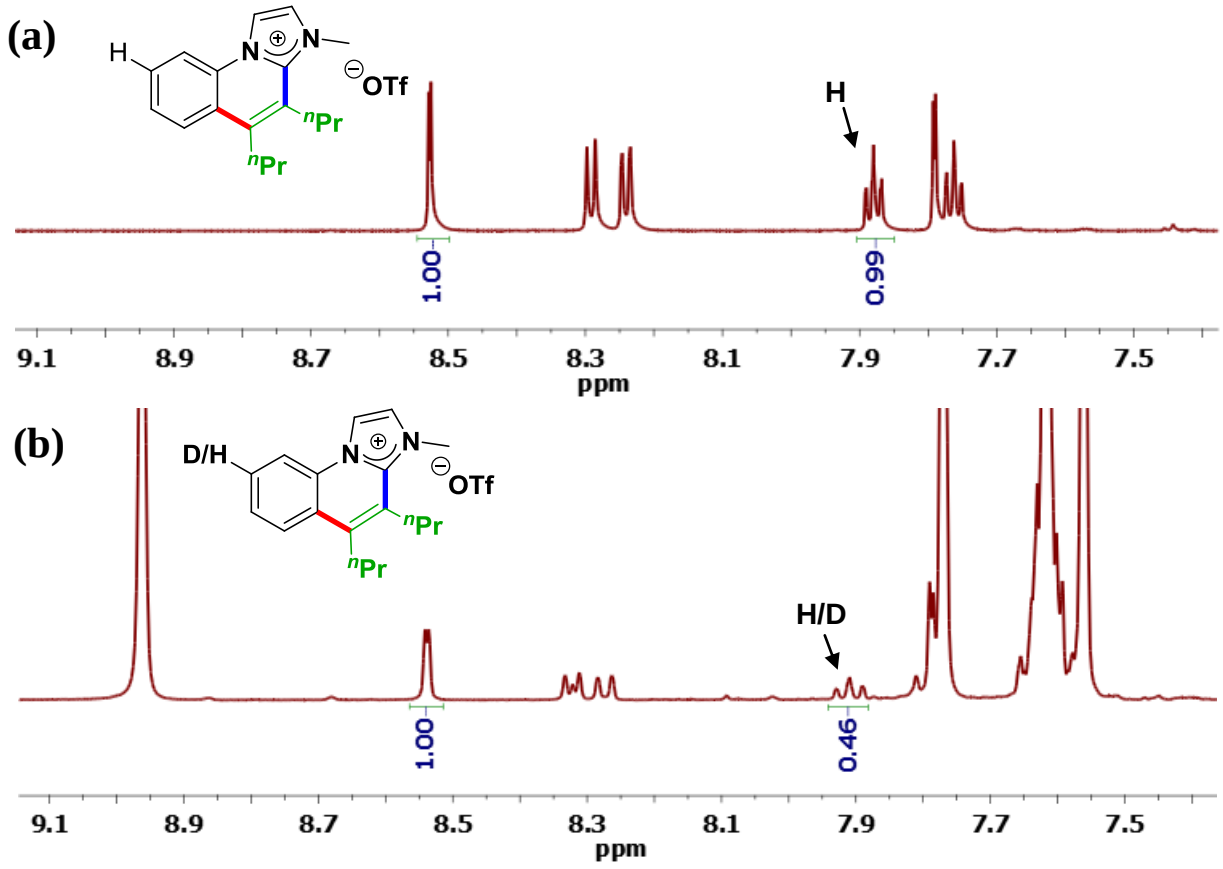
Determination of intermolecular kinetic isotope effect (KIE)



After 4h, **3j + [D$_4$]-3j** = 11% yield, *k*H / *k*D = 0.87
After 4h, **3j + [D$_4$]-3j** = 10% yield, *k*H / *k*D = 0.94
After 11h, **3j + [D$_4$]-3j** = 27% yield, *k*H / *k*D = 0.87

To an oven dried Schlenk tube, **1a** (14.3 mg, 0.05 mmol), **D$_5$-1a** (14.55 mg, 0.05 mmol), NaOAc (32.8 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (3.08 mg, 0.005 mmol), AgOTf (77.1 mg, 0.3 mmol)

and 4-Octyne (18 µL, 0.12 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube was filled with N_2 gas. To this mixture, dry and degassed CH_2Cl_2 (3.0 mL) was added under Schlenk technique and the reaction mixture was left with stirring at room temperature under dark. After different time intervals, the reaction mixture was passed through a short celite pad which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. To the crude residue, mesitylene (0.01 mmol) was added as internal standard and it was subjected to ^{1}H NMR spectroscopy. The ^{1}H NMR spectral analysis indicates the average value of k_H/k_D = 0.87-0.94 as shown in Figure S11.



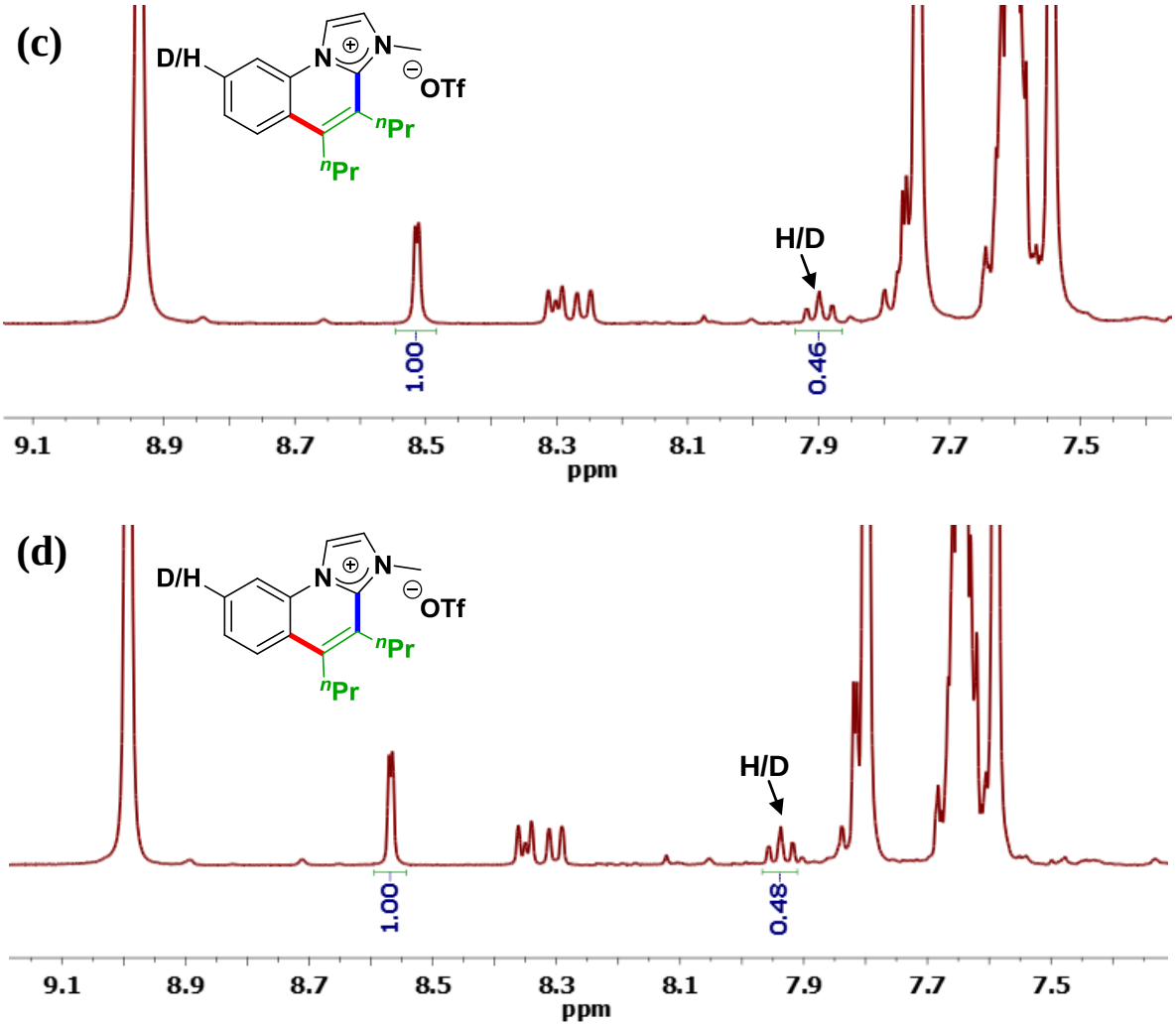
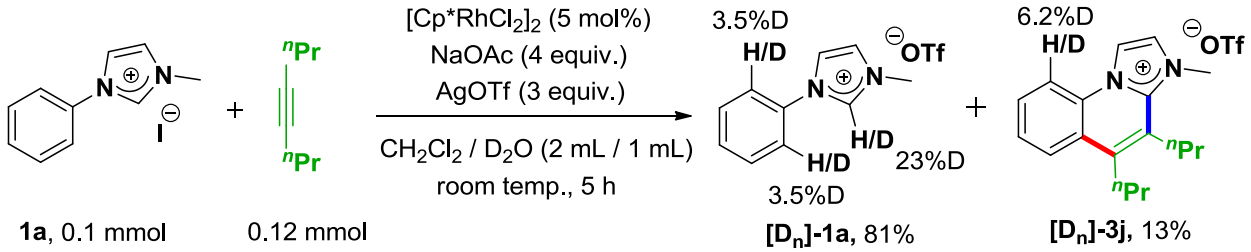


Figure S11. ^{1}H NMR spectra of **3j** and crude reaction mixture using mesitylene as internal standard: (a) **3j**, (b) after 4 h (yield = 11%) and (c) after 11 h (yield = 27%) (d) second expt. after 4 h (yield = 10%).

I. Deuterium Exchange Experiment



To an oven dried Schlenk tube, **1a** (28.6 mg, 0.1 mmol), NaOAc (32.8 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (3.08 mg, 0.005 mmol), AgOTf (77.1 mg, 0.3 mmol) and 4-Octyne (18 µL, 0.12 mmol) were loaded and then the tube was kept under vacuum for 15 minutes. After that the tube

was filled with N_2 gas. To this mixture, dry and degassed CH_2Cl_2 (2 mL) and then D_2O (1 mL) was added under Schlenk technique and the reaction mixture was left with stirring at room temperature under dark. After a certain time, the whole reaction mixture was passed through a short celite pad and which was washed with dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure. To the crude residue, mesitylene (0.01 mmol) was added as internal standard and it was subjected to ^{1}H NMR spectroscopy.

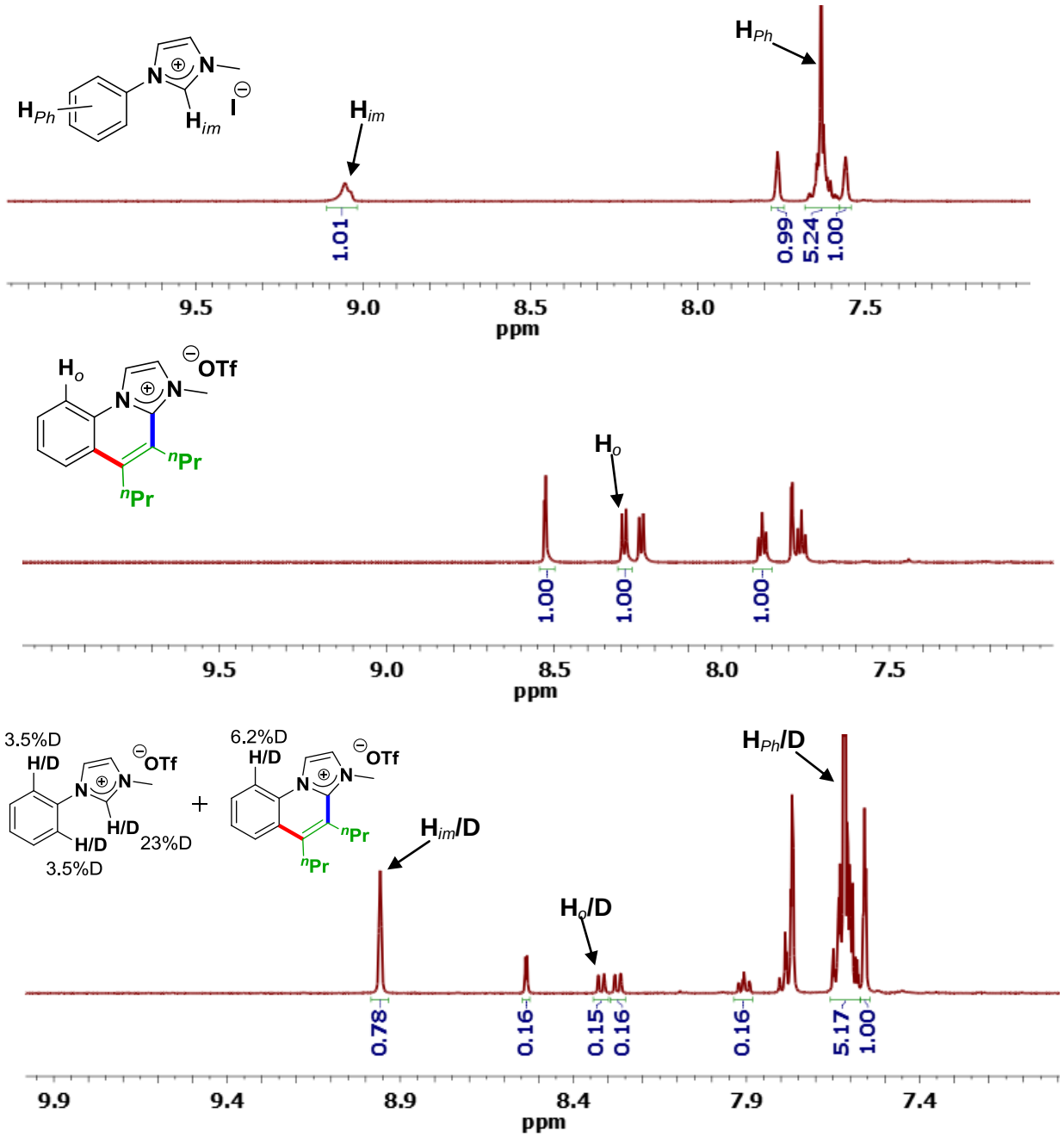


Figure S12. ^{1}H NMR spectra of pure **1a**, **3j** and crude reaction mixture using mesitylene as internal standard.

The ^{1}H NMR spectral analysis showed the incorporation of deuterium into the labeled protons of substrate, **1a** as well as in annulated product, **3j** as shown in Figure S12.

8. Importance of imidazo/benzimidazo-fused poly aromatic compounds

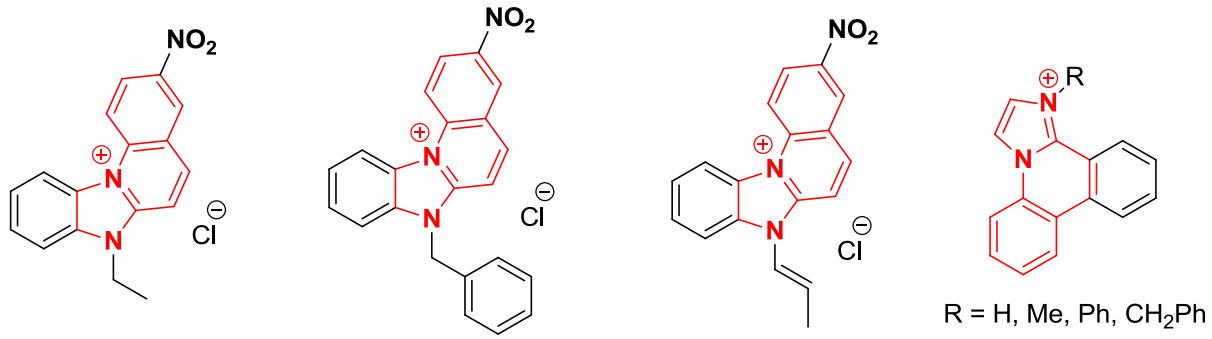


Figure S13: Examples of a few biologically active imidazo/benzimidazo-fused polyaromatic compounds.[13]

Imidazo-fused poly aromatic cationic systems are found to be biologically important molecules. A few selected examples are shown in Figure S13. These types of molecules possess high affinity for DNA because of their planer geometry and charge characteristics which shows an effective antitumor or anticancer activity.[13] Additionally, these molecules display fluorescence property which might be useful in organic light-emitting diode (OLED) applications.[14] Fluorescence spectra of a few imidazo[1,2-*a*]quinolinium salts are shown in Figure S14 which have been synthesized by our protocol.

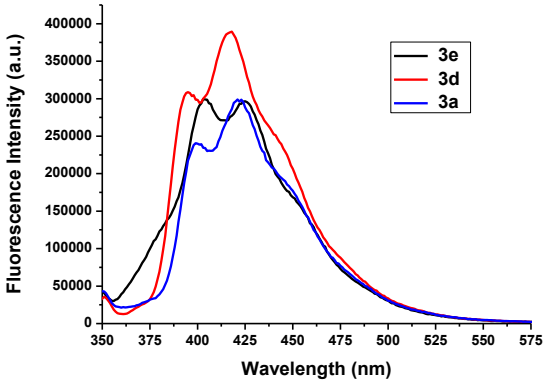


Figure S14: Fluorescence spectra of selected imidazo[1,2-*a*]quinolinium salts at a concentration of 5×10^{-8} M in acetonitrile.

9. ^{1}H, ^{13}C & ^{19}F NMR and HRMS data

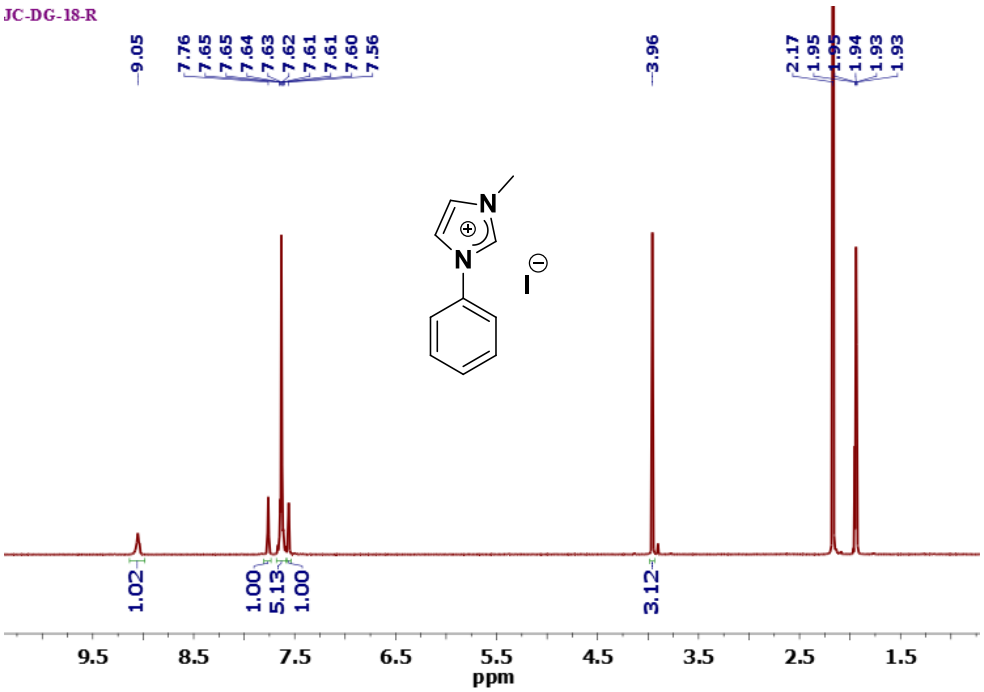


Figure S15. ^{1}H NMR spectrum of **1a** (400 MHz, CD_3CN, 300 K).

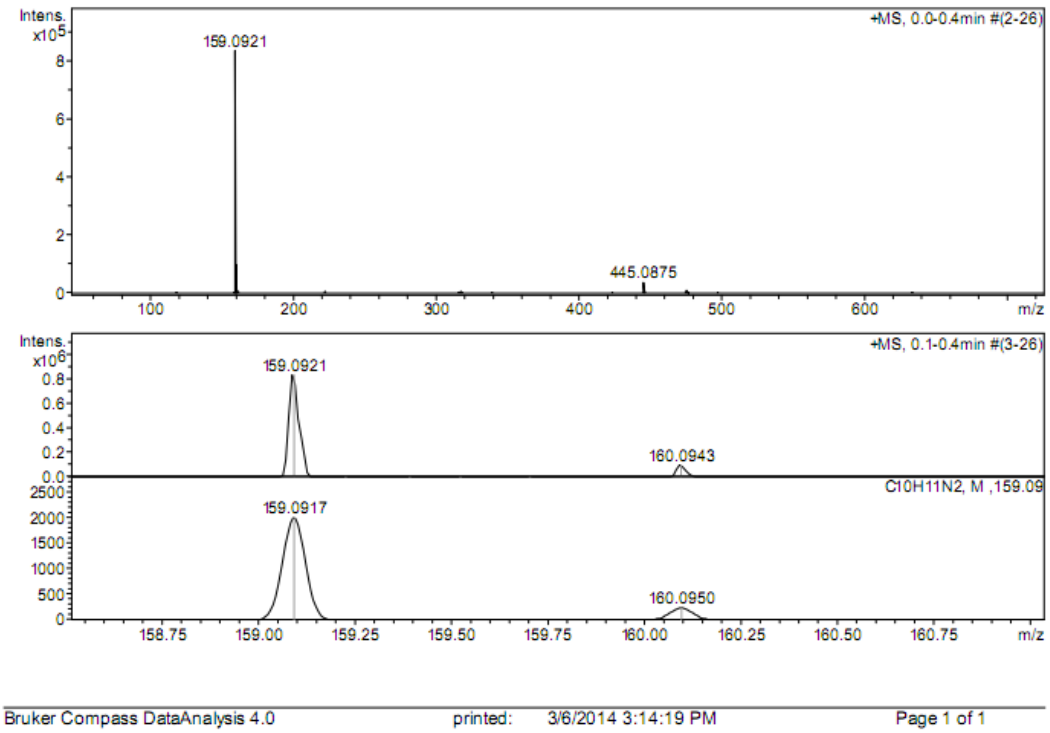


Figure S16. ESI-HRMS (positive ion mode) spectrum of **1a.**

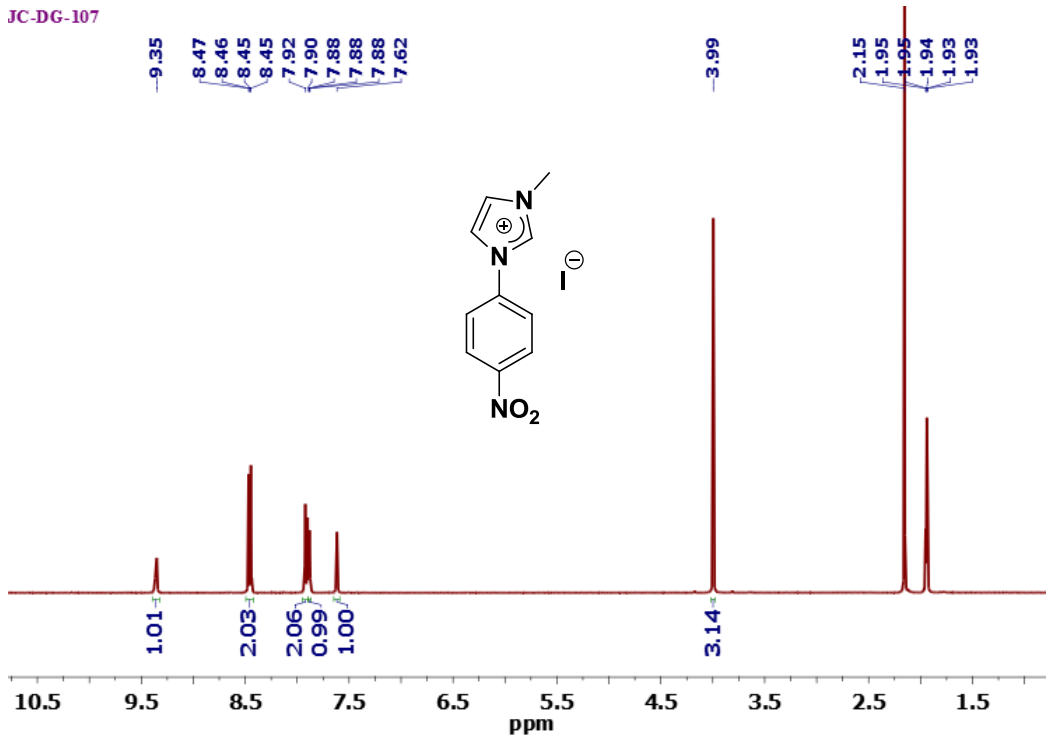


Figure S17. ^{1}H NMR spectrum of **1b** (400 MHz, CD_3CN, 300 K).

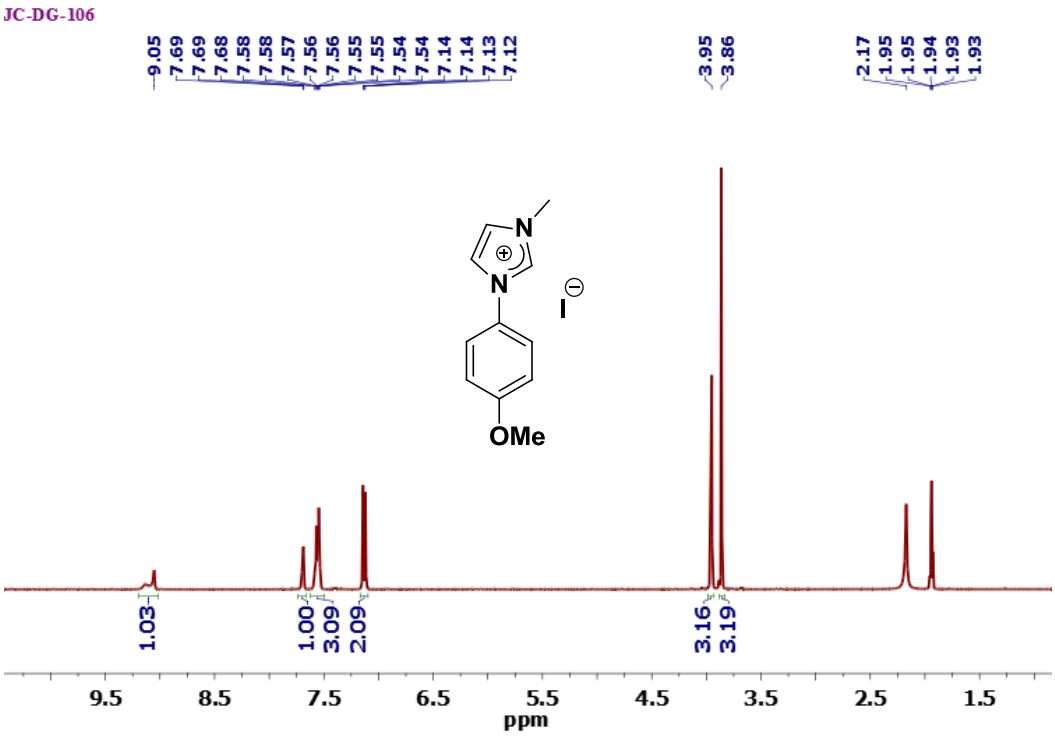


Figure S18. ^{1}H NMR spectrum of **1c** (400 MHz, CD_3CN, 300 K).

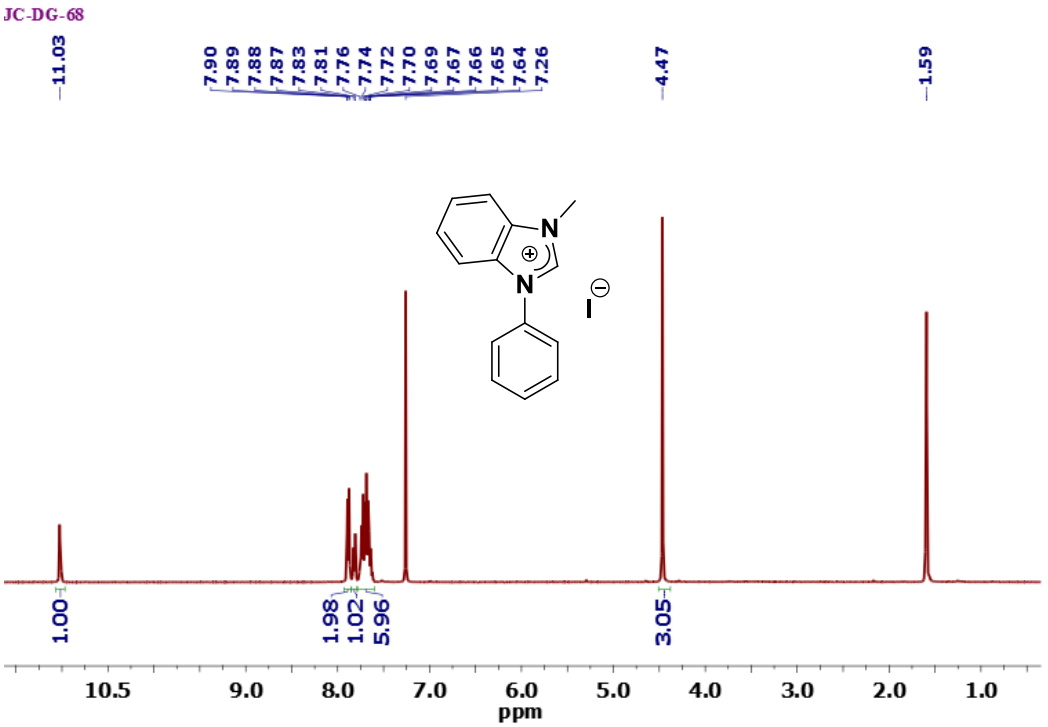


Figure S19. ^{1}H NMR spectrum of **1d** (400 MHz, $CDCl_3$, 300 K).

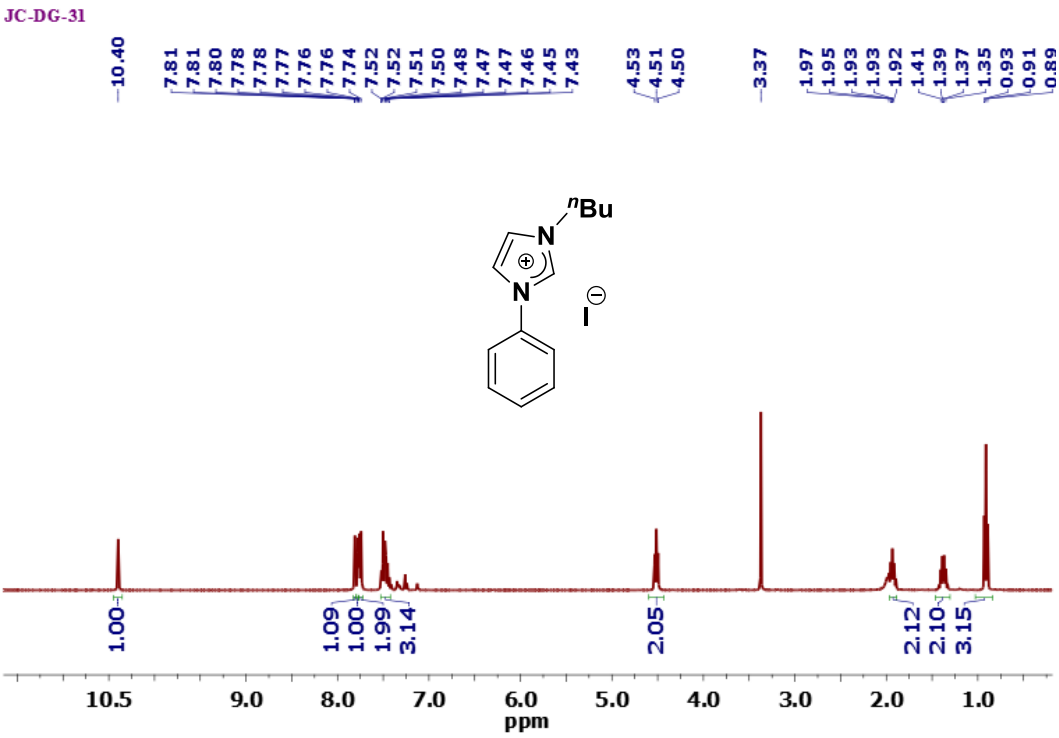


Figure S20. ^{1}H NMR spectrum of **1e** (400 MHz, $CDCl_3$, 300 K).

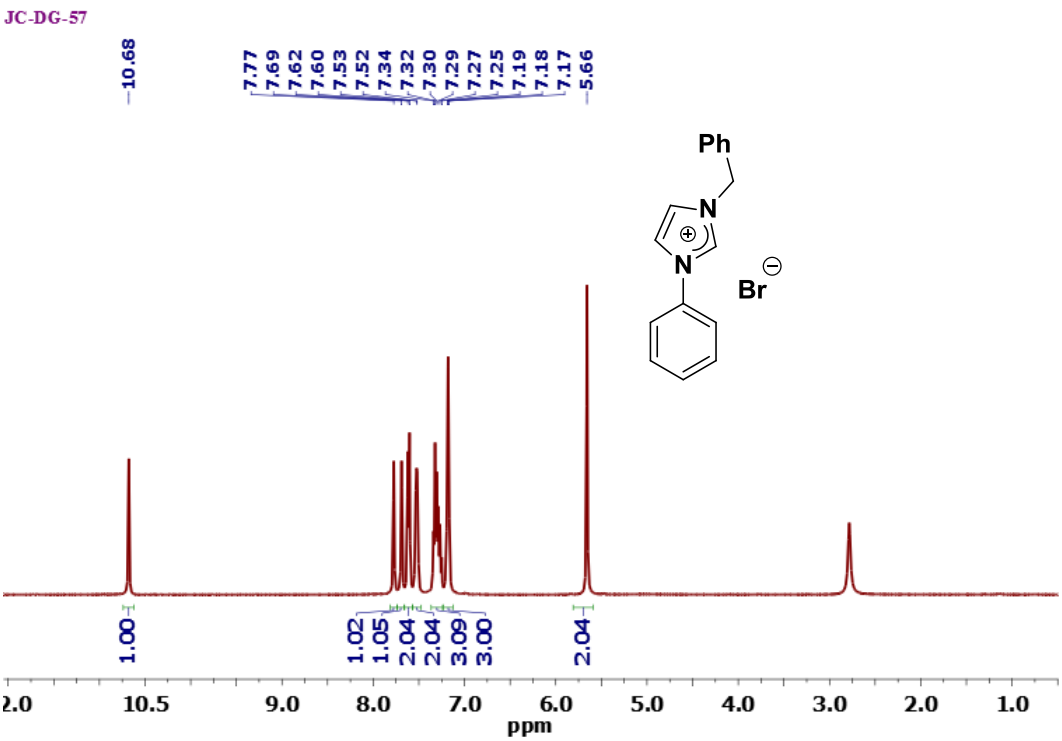


Figure S21. ^{1}H NMR spectrum of **1f** (400 MHz, $CDCl_3$, 300 K).

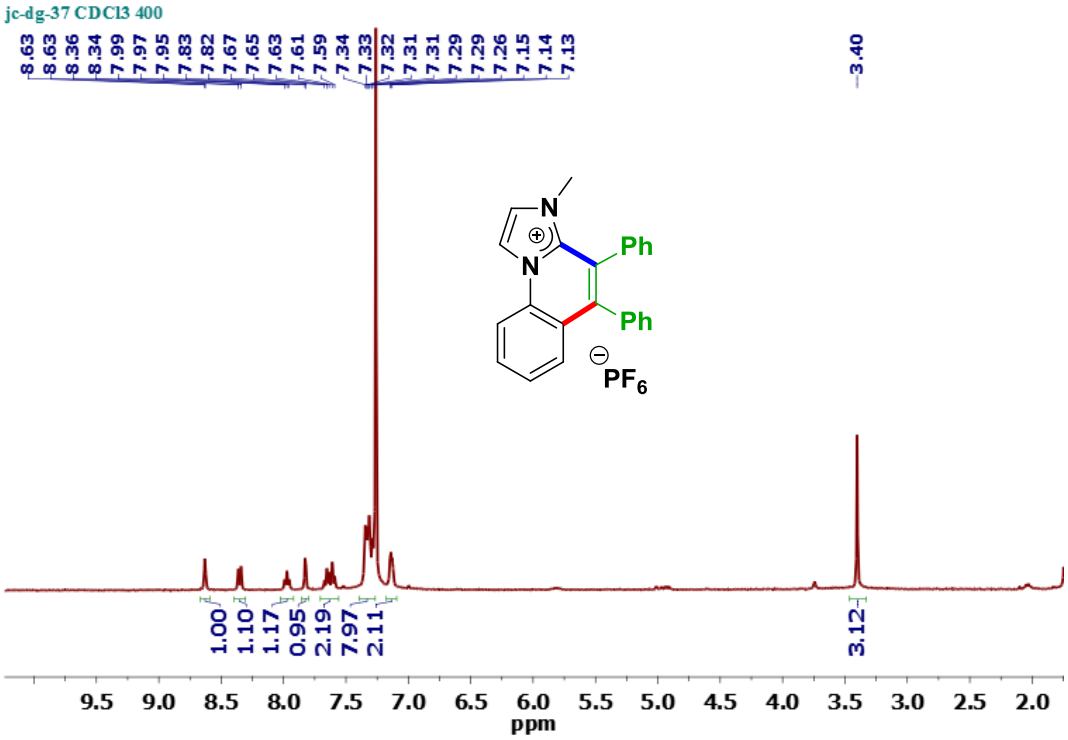


Figure S22. ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$, 300 K).

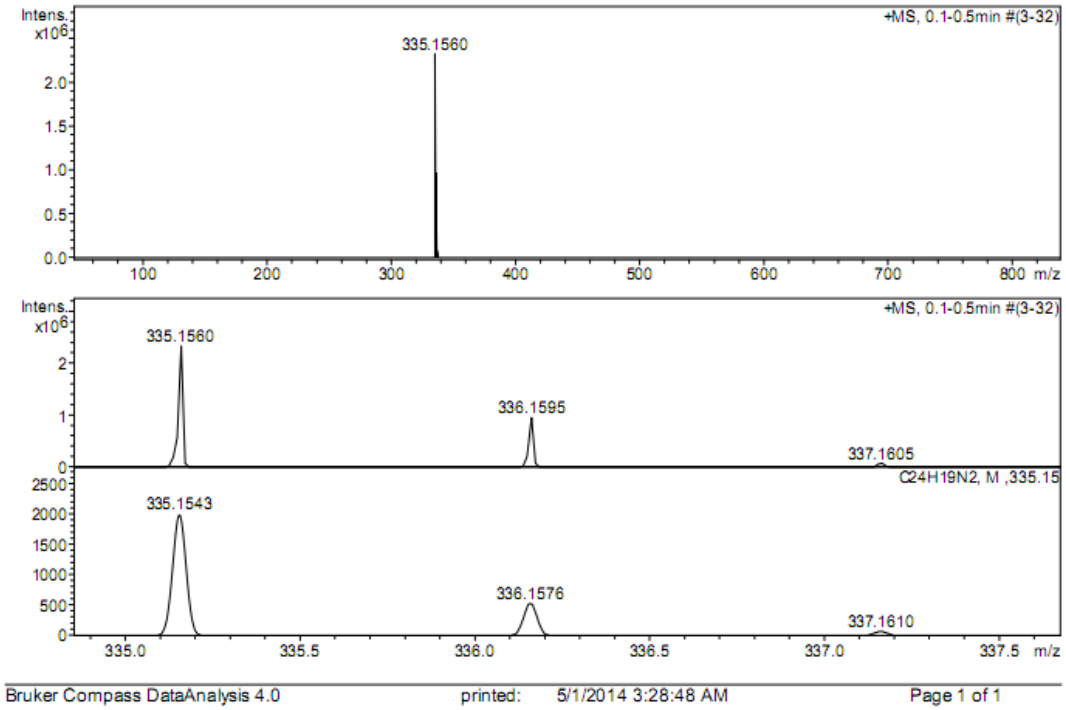


Figure S23. ESI-HRMS (positive ion mode) spectrum of **3a.**

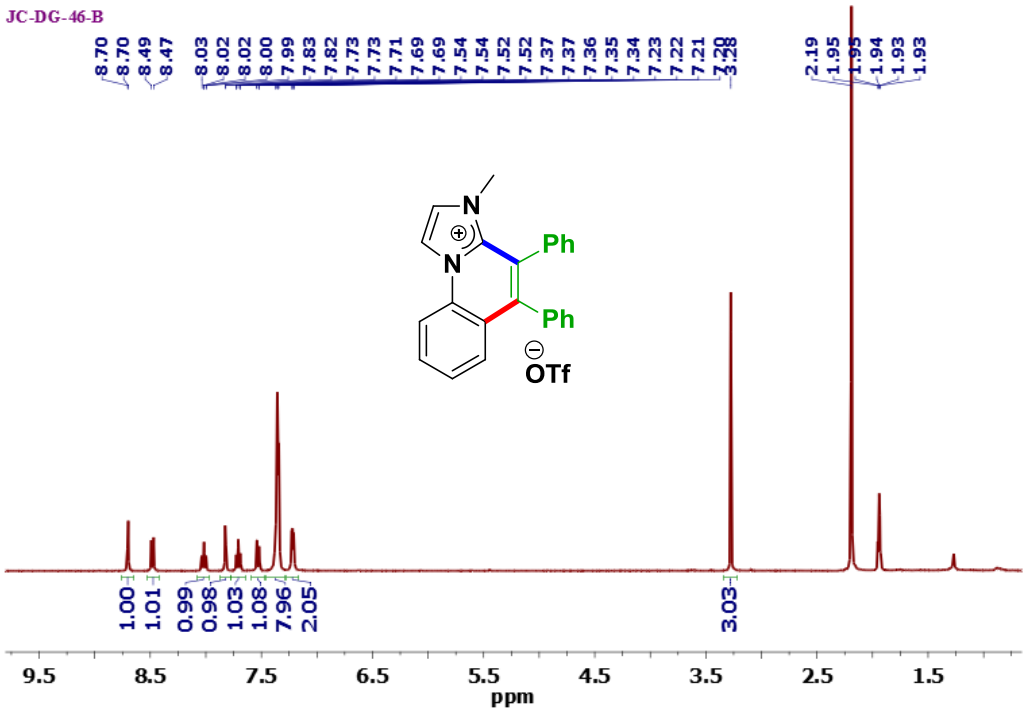


Figure S24. ^{1}H NMR spectrum of **3a** (400 MHz, CD_3CN, 300 K).

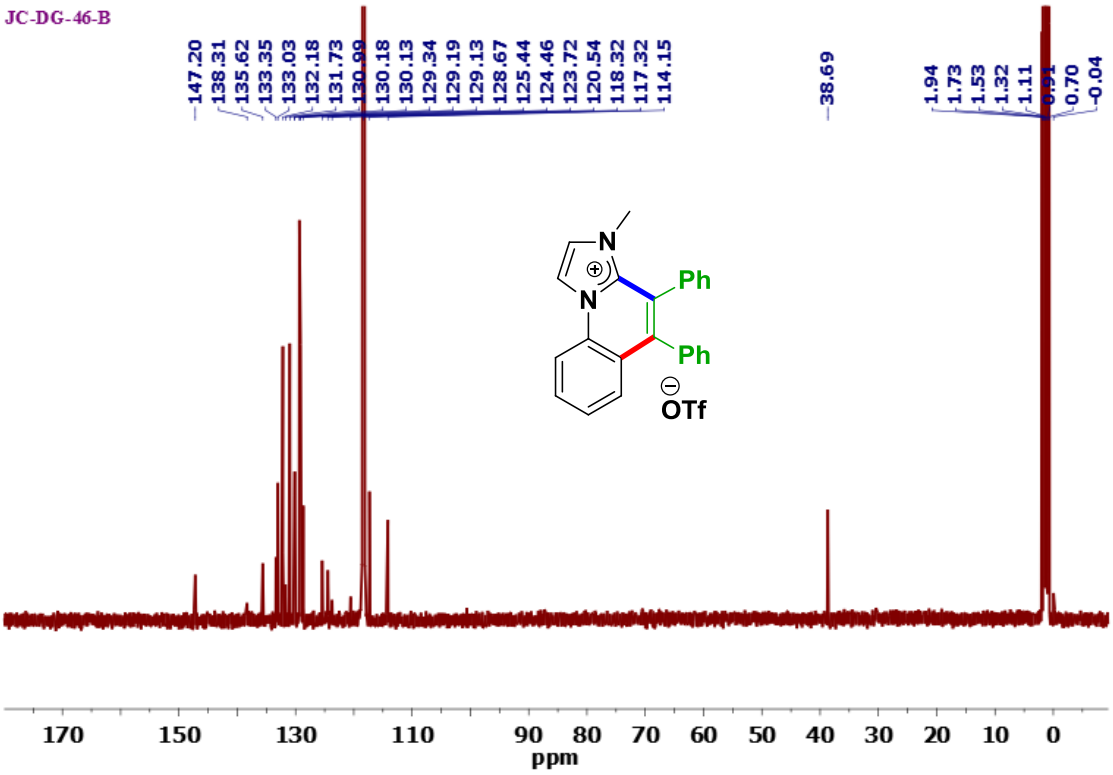


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (101 MHz, CD_3CN, 300 K).

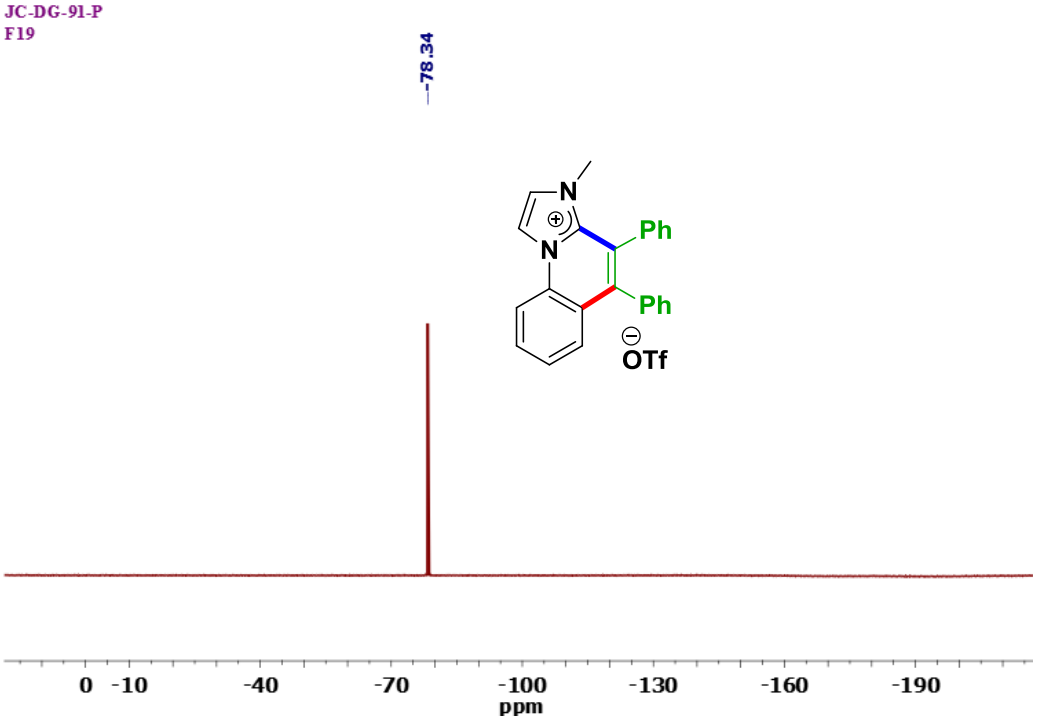


Figure S26. ^{19}F NMR spectrum of **3a** (376 MHz, $CDCl_3$, 300 K).

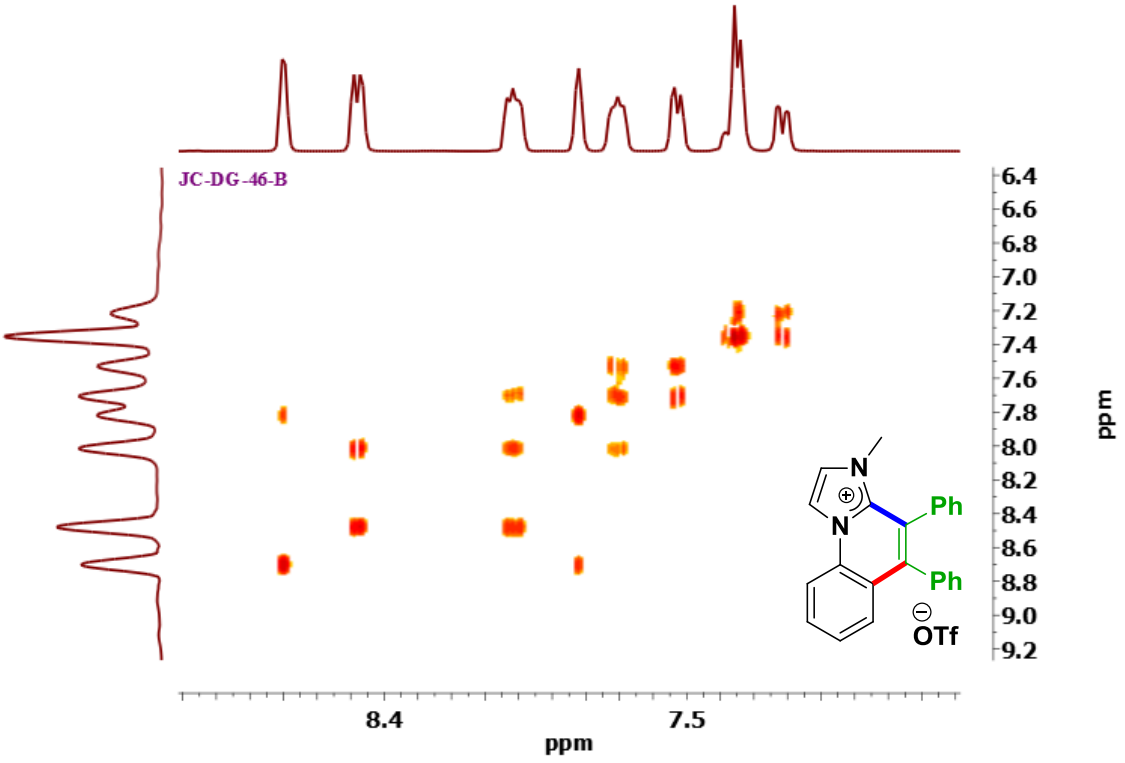


Figure S27. ^{1}H-^{1}H COSY NMR spectrum of **3a** (400 MHz, $CDCl_3$, 300 K).

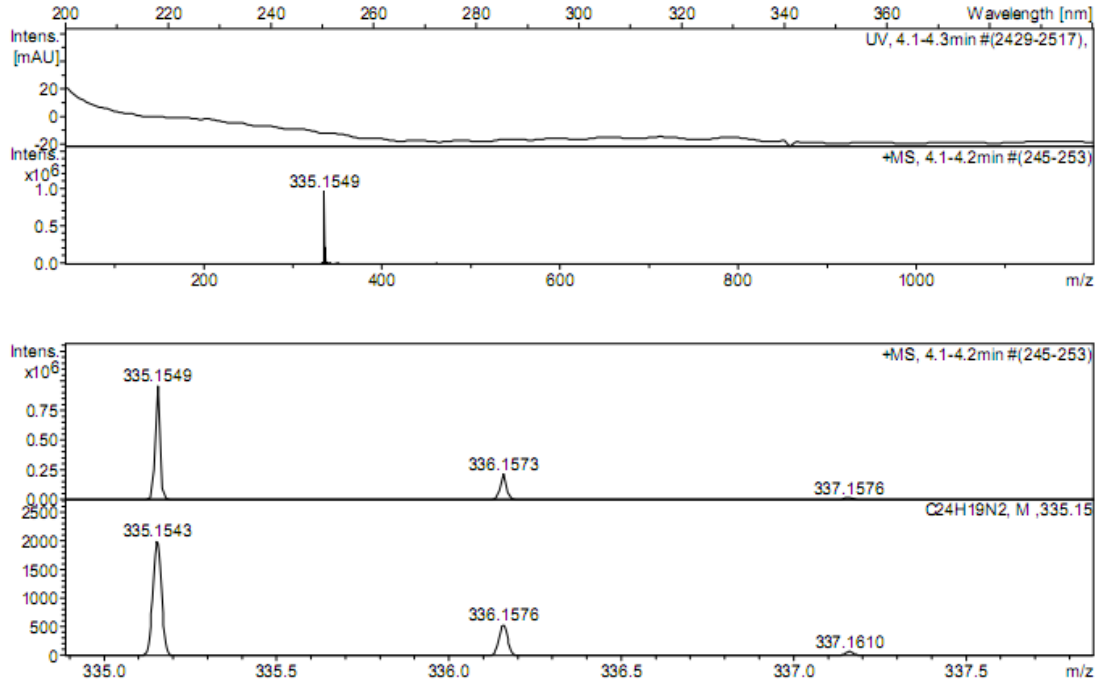


Figure S28. ESI-HRMS (positive ion mode) spectrum of **3a.**

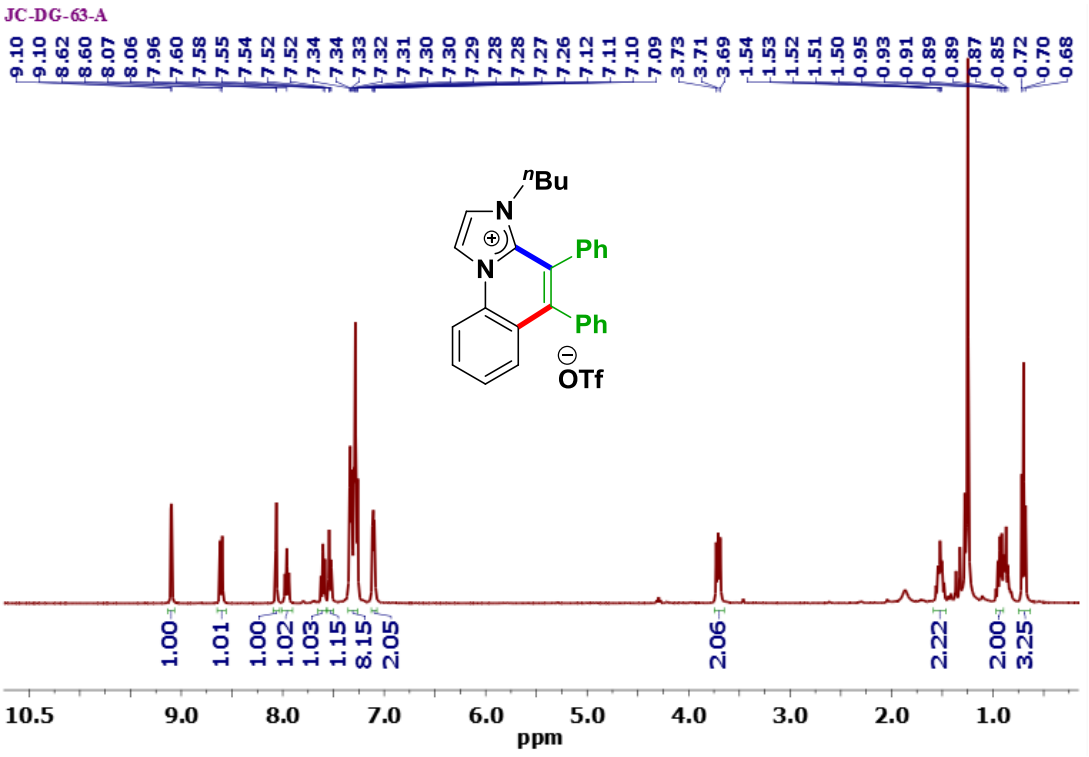


Figure S29. ^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$, 300 K).

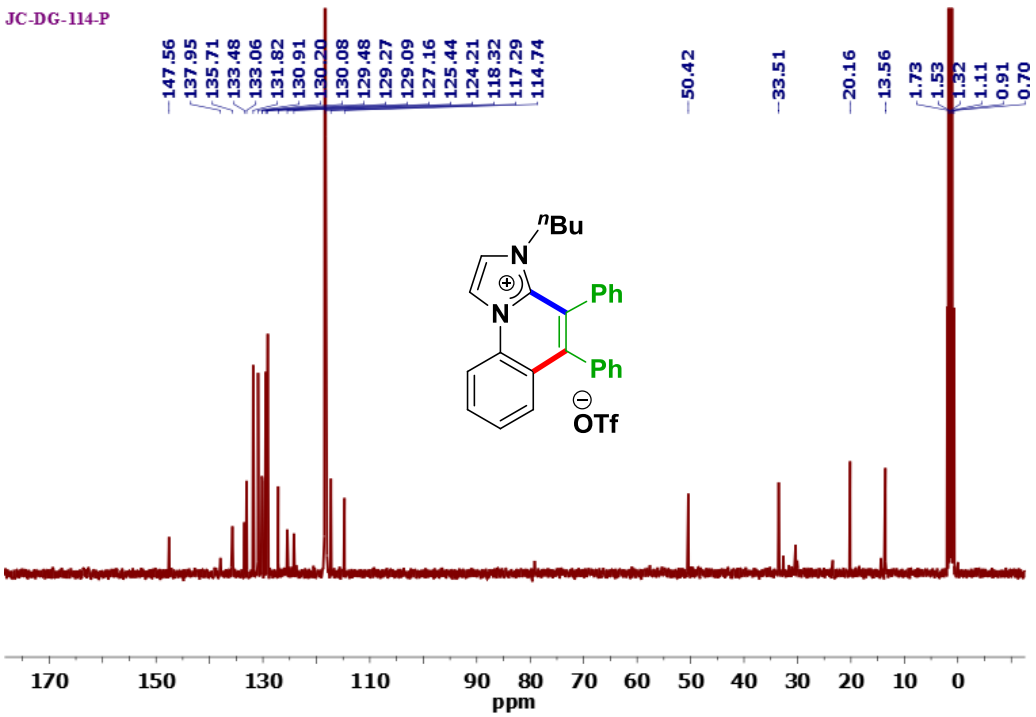


Figure S30. ^{13}C{^{1}H} NMR spectrum of **3b** (101 MHz, CD_3CN, 300 K).

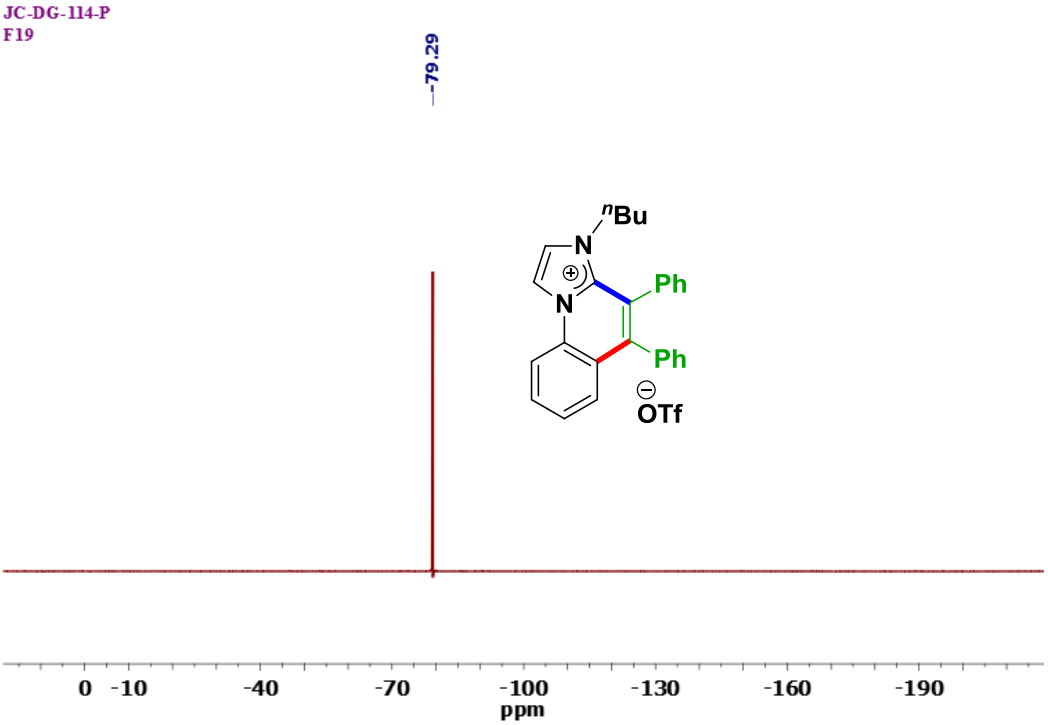


Figure S31. ^{19}F NMR spectrum of **3b** (376 MHz, CD_3CN, 300 K).

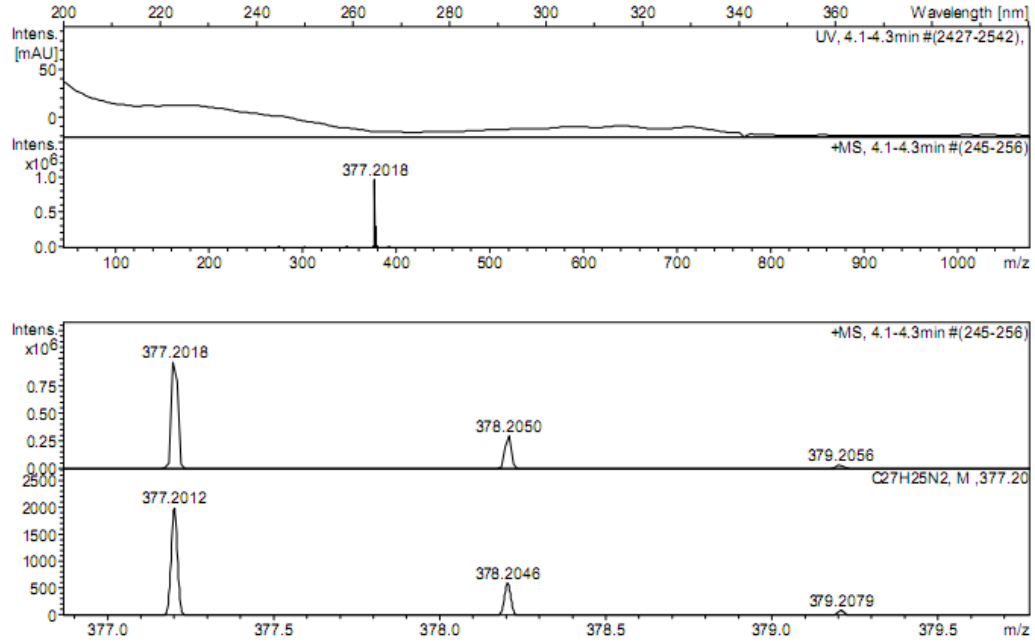


Figure S32. ESI-MS (positive ion mode) spectrum of **3b.**

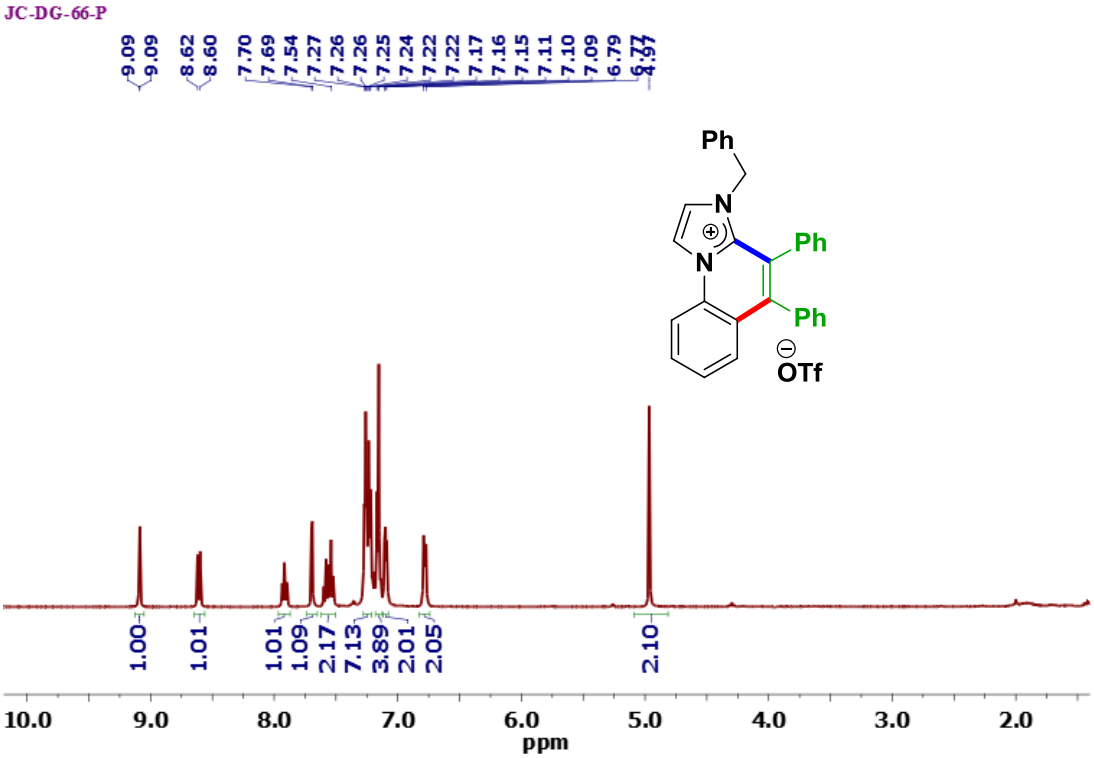


Figure S33. ^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$, 300 K).

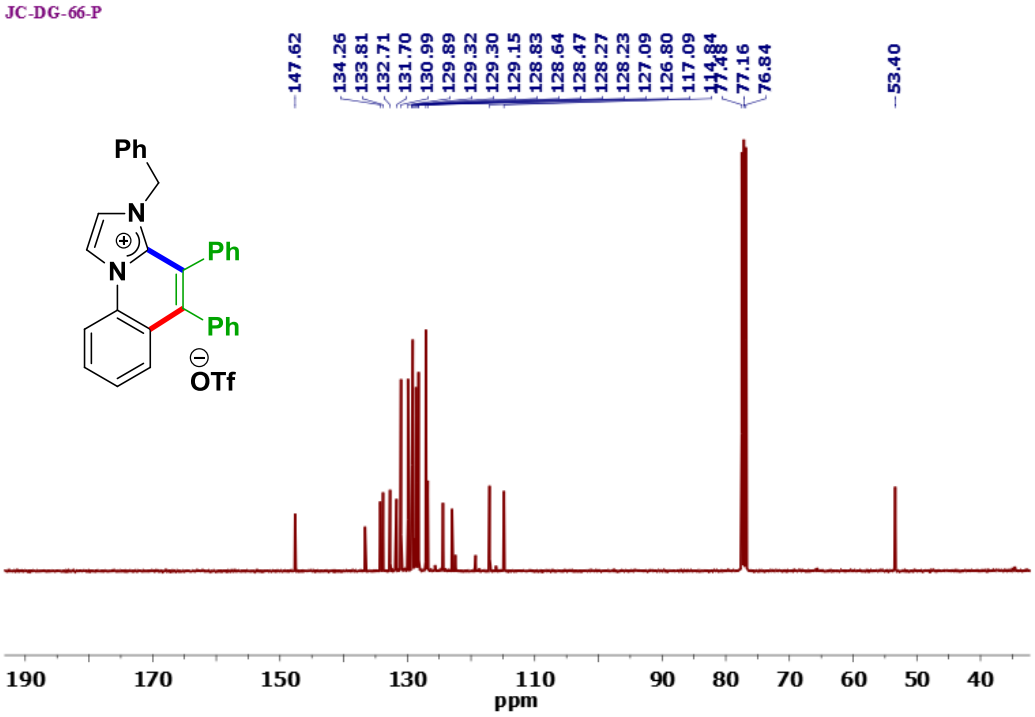


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **3c** (101 MHz, $CDCl_3$, 300 K).

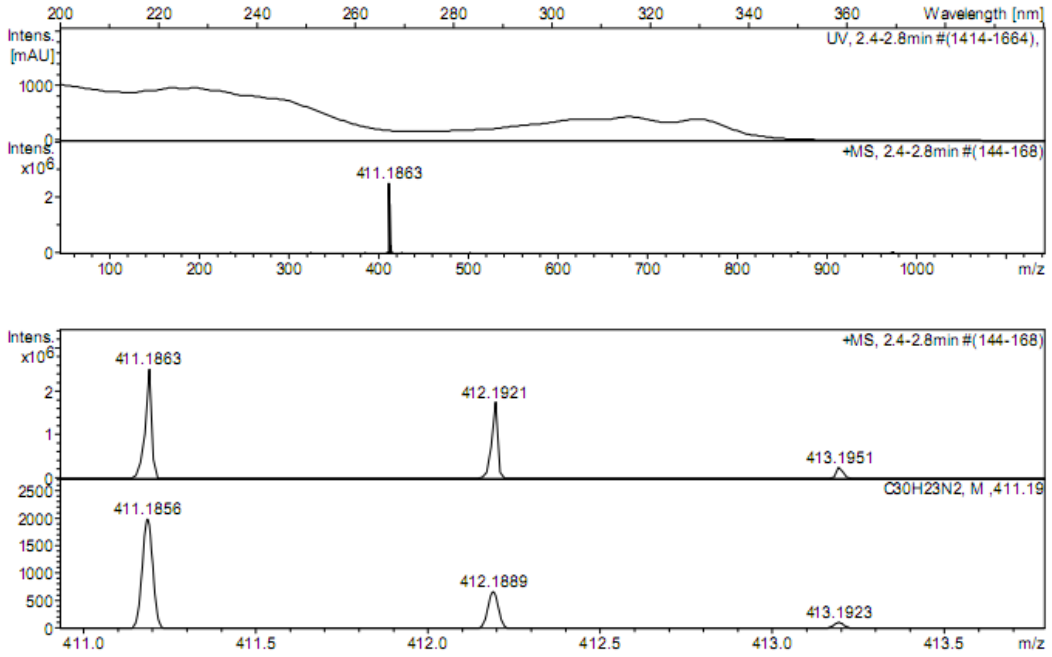


Figure S35. ESI-HRMS (positive ion mode) spectrum of **3c.**

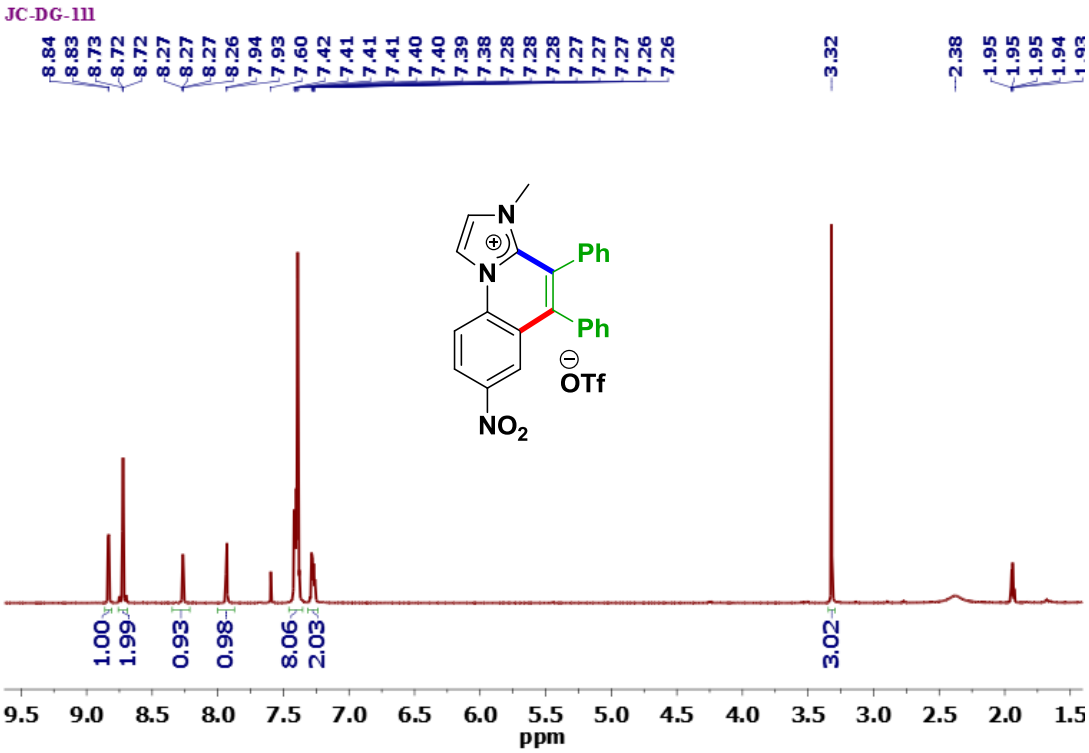


Figure S36. ^{1}H NMR spectrum of **3d** (400 MHz, CD_3CN, 300 K).

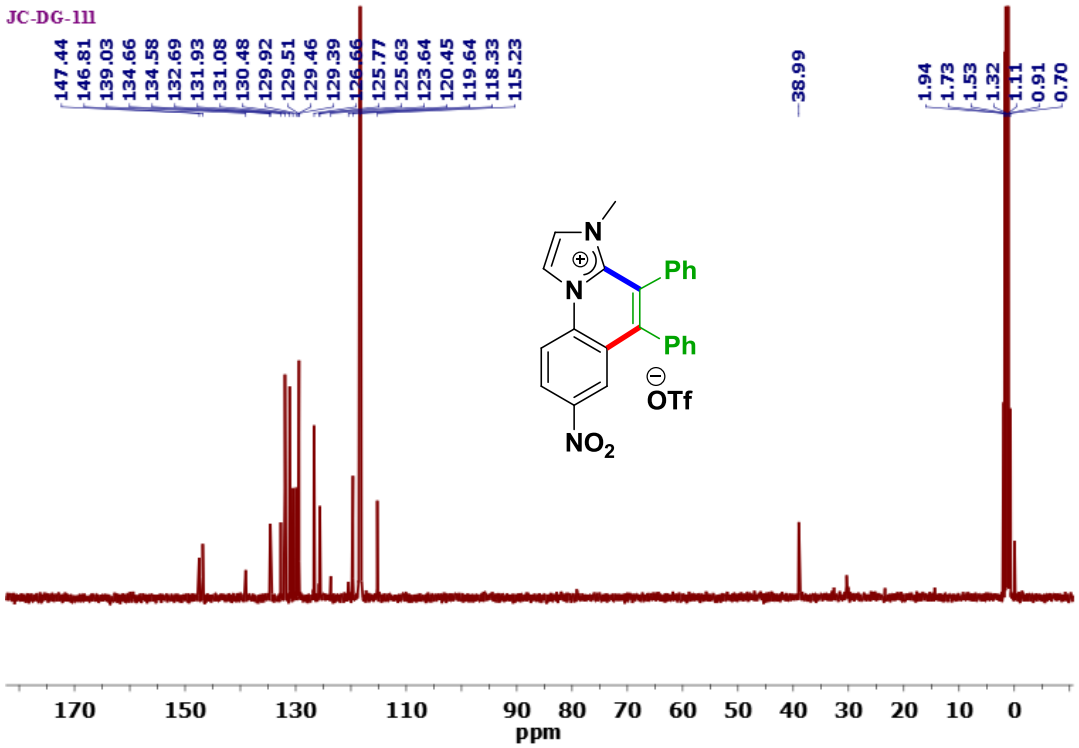


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of **3d** (101 MHz, CD_3CN, 300 K).

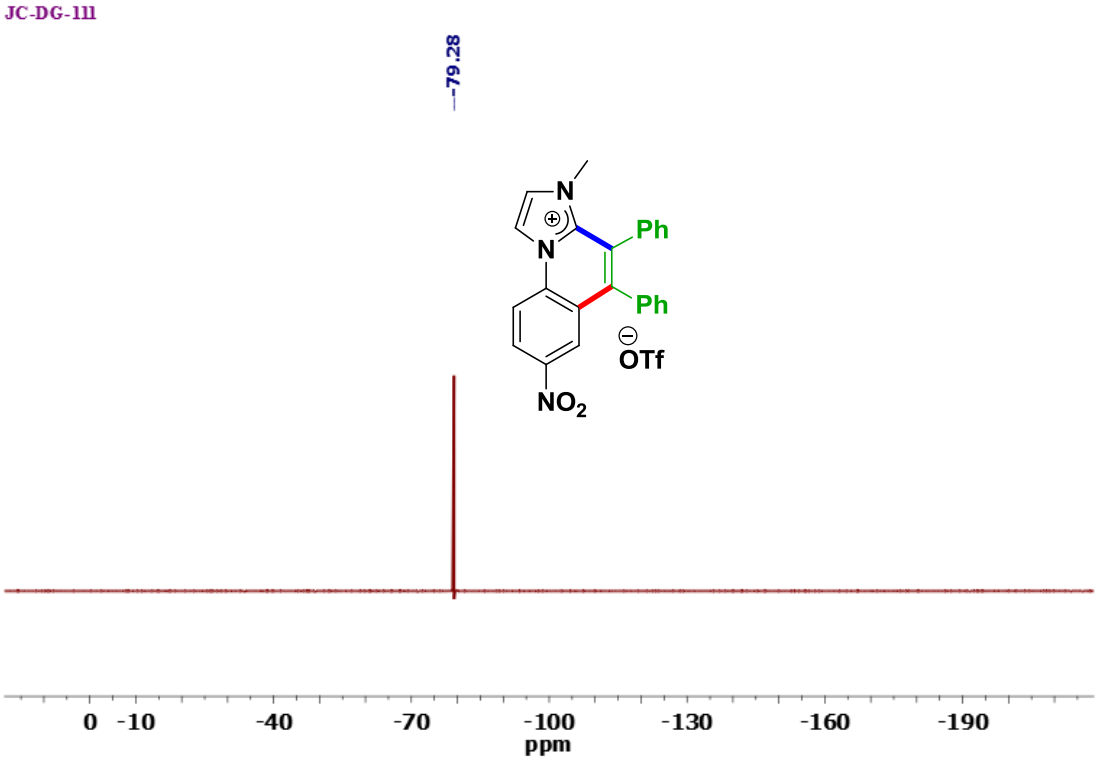


Figure S38. ^{19}F NMR spectrum of **3d** (376 MHz, CD_3CN, 300 K).

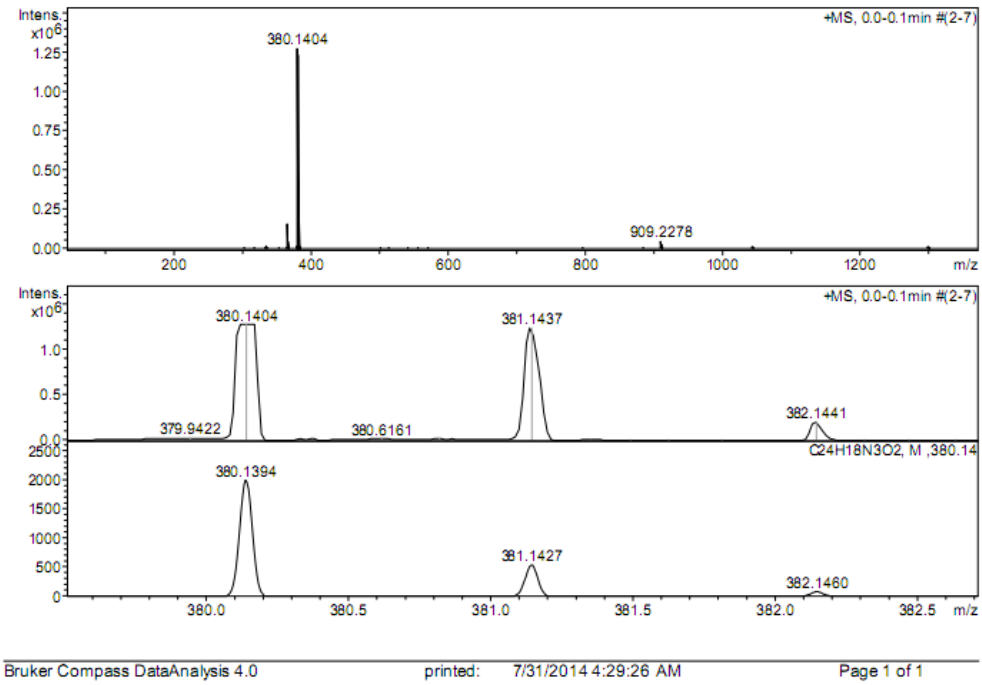


Figure S39. ESI-HRMS (positive ion mode) spectrum of **3d.**

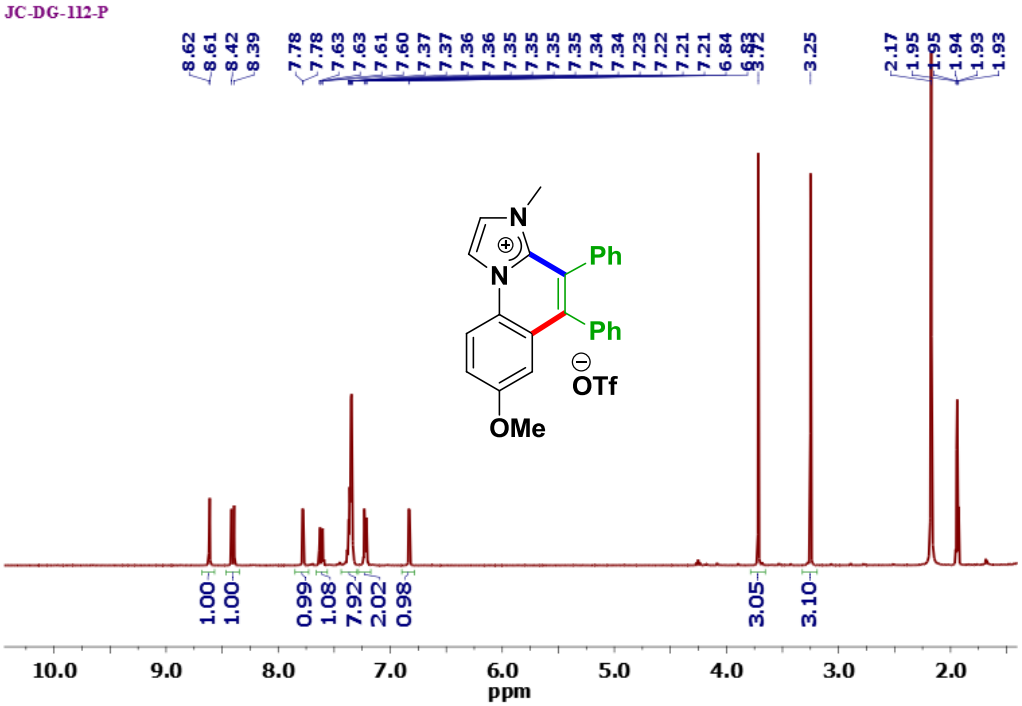


Figure S40. ^{1}H NMR spectrum of **3e** (400 MHz, CD_3CN, 300 K).

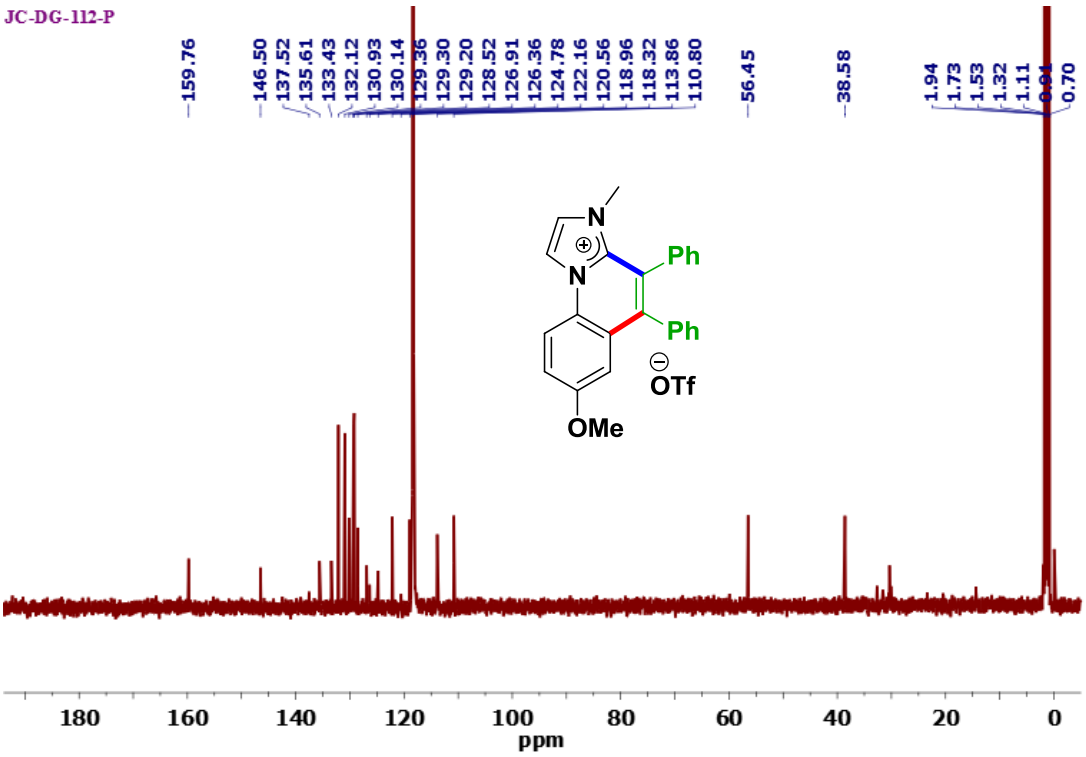


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of **3e** (101 MHz, CD_3CN, 300 K).

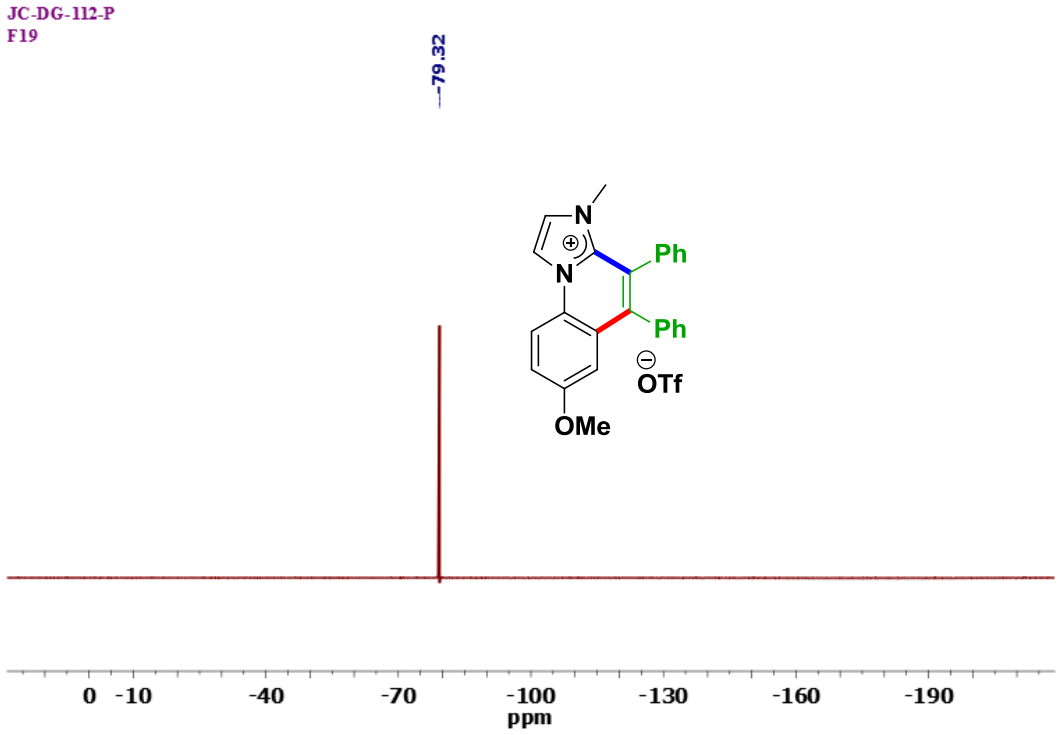


Figure S42. ^{19}F NMR spectrum of **3e** (376 MHz, CD_3CN, 300 K).

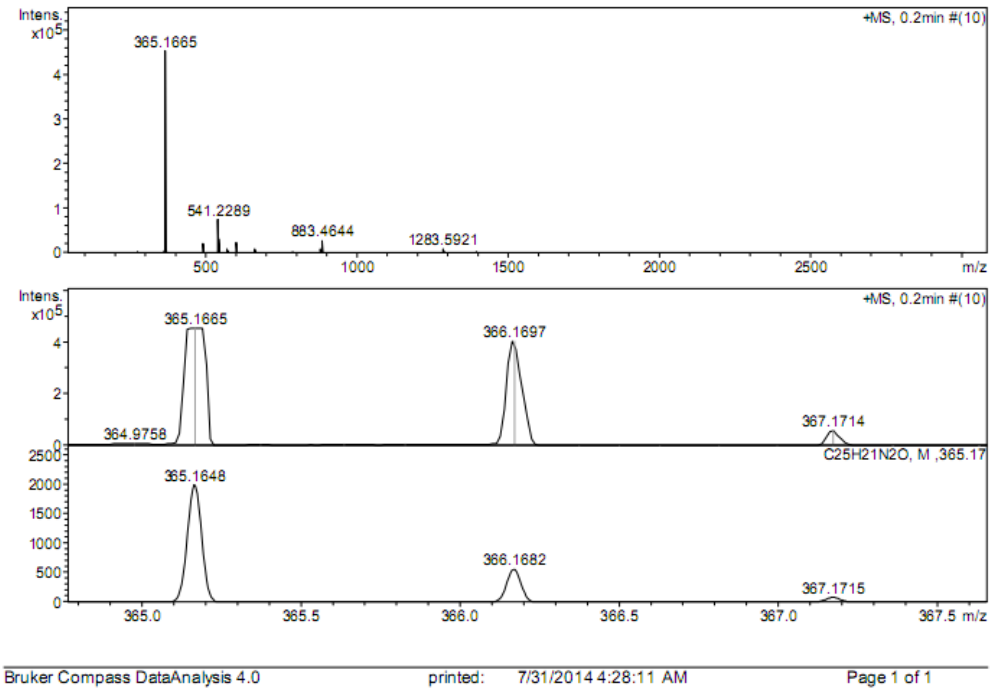


Figure S43. ESI-HRMS (positive ion mode) spectrum of **3e.**

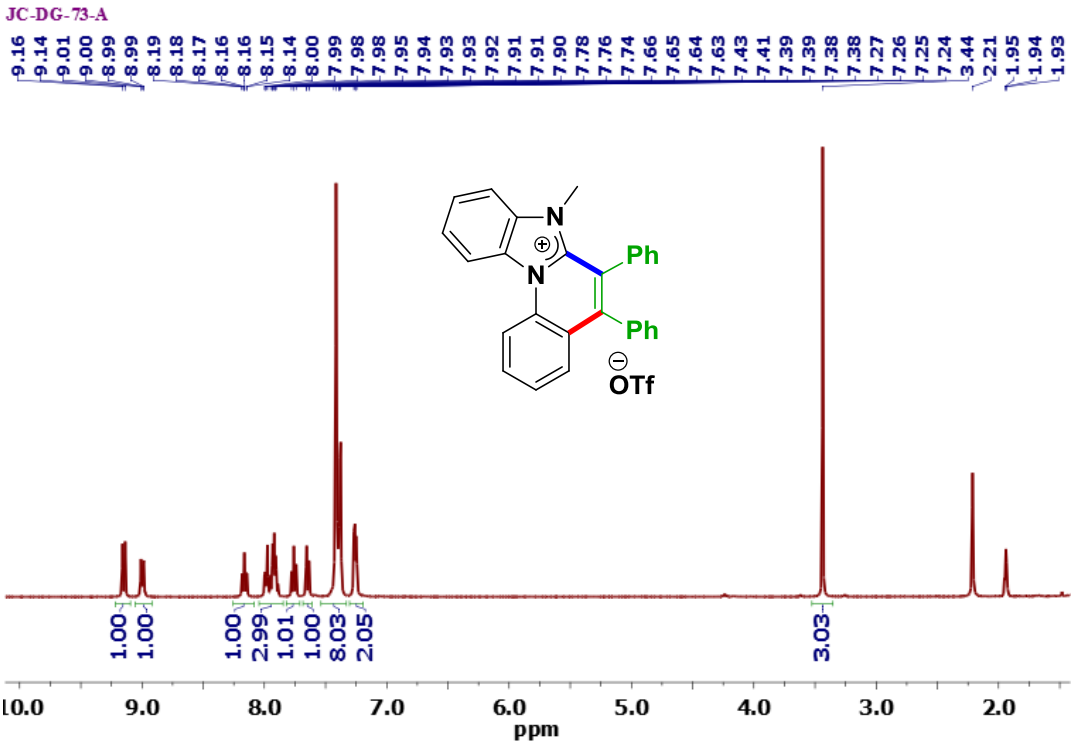


Figure S44. ^{1}H NMR spectrum of **3f** (400 MHz, CD_3CN, 300 K).

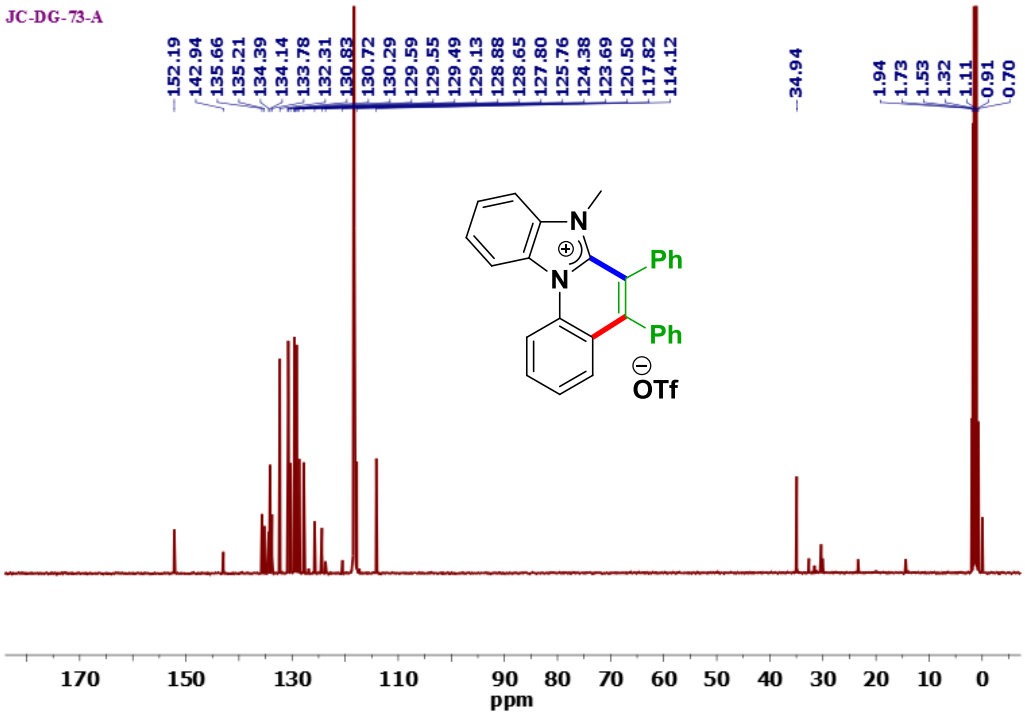


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of **3f** (101 MHz, CD_3CN, 300 K).

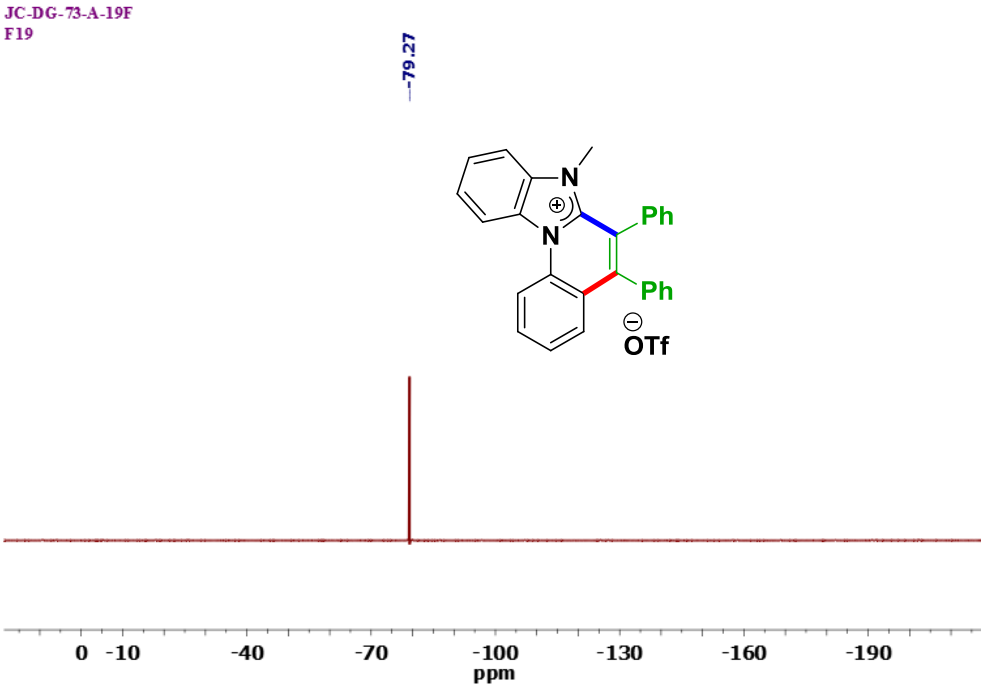


Figure S46. ^{19}F NMR spectrum of **3f** (376 MHz, CD_3CN, 300 K).

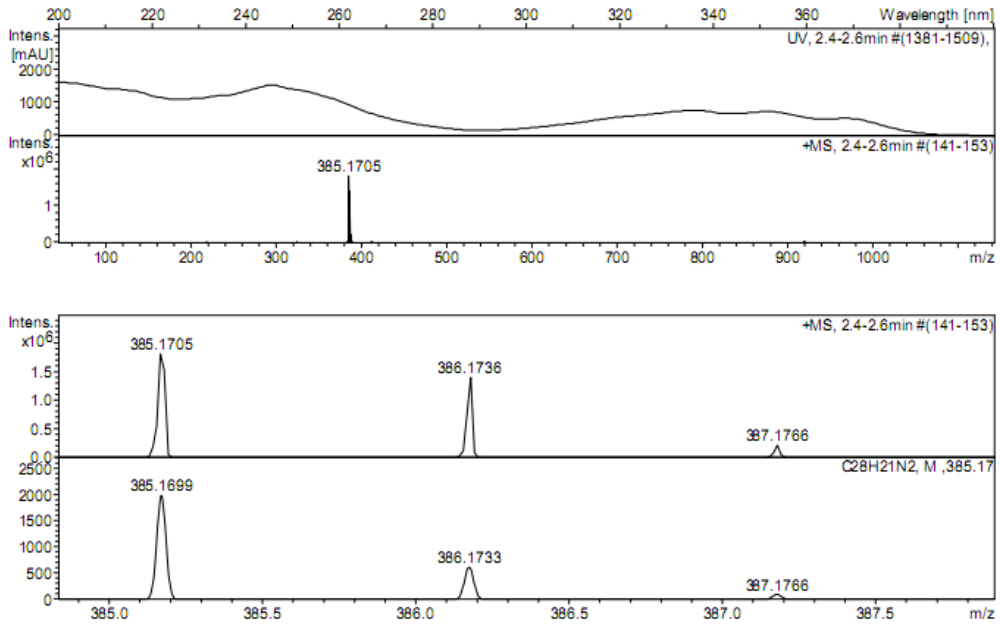


Figure S47. ESI-HRMS (positive ion mode) spectrum of **3f.**

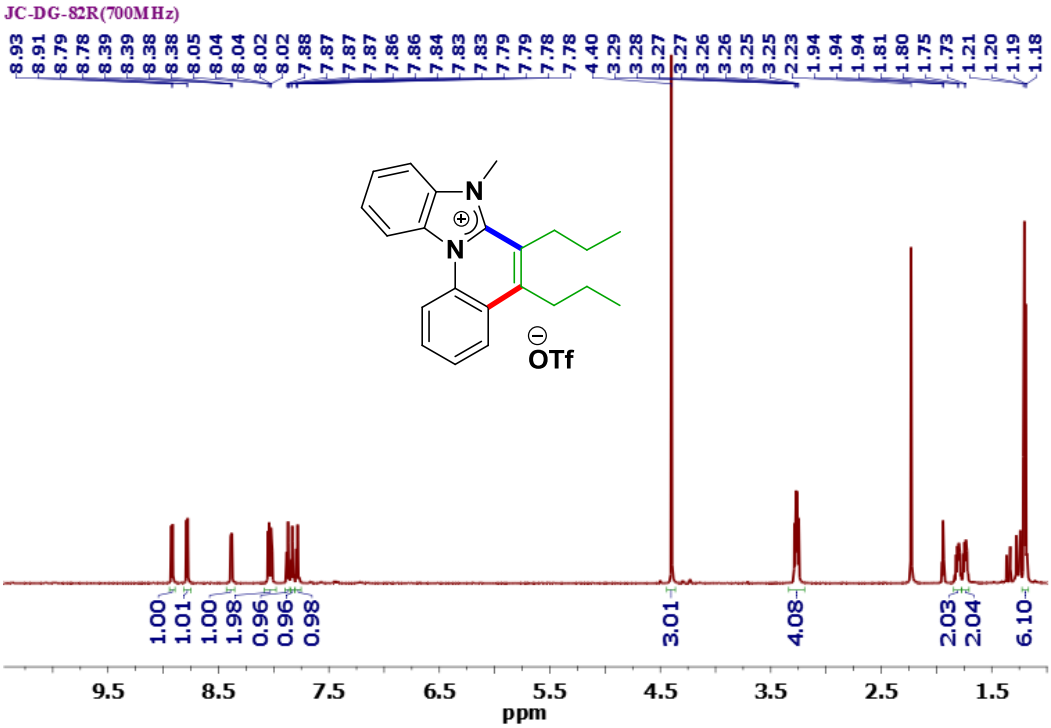


Figure S48. ^{1}H NMR spectrum of **3g** (700 MHz, CD_3CN, 300 K).

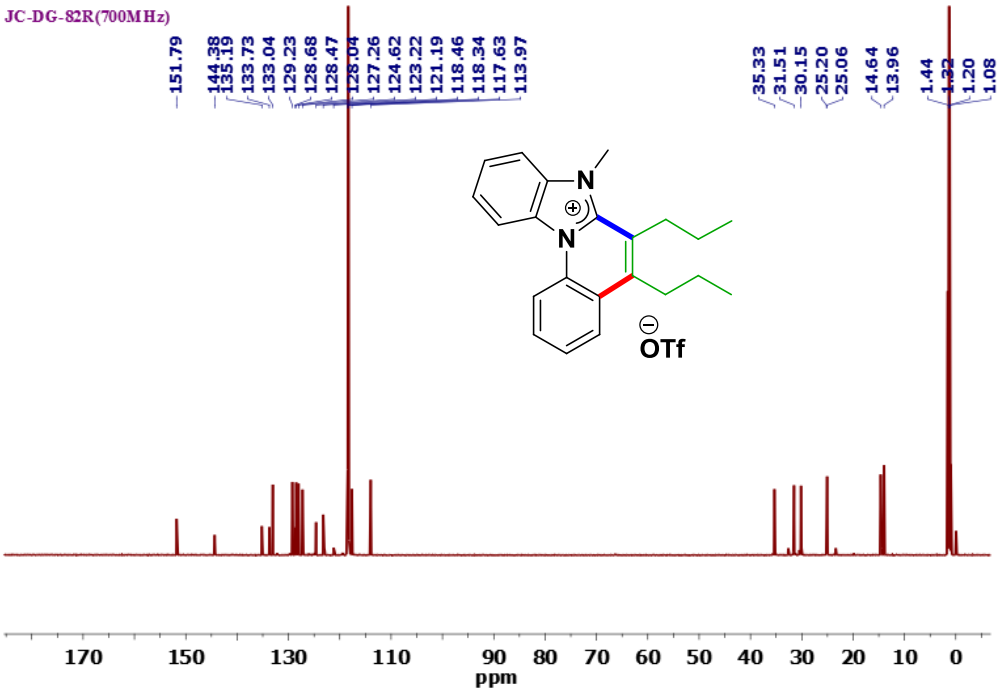


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of **3g** (176 MHz, CD_3CN, 300 K).

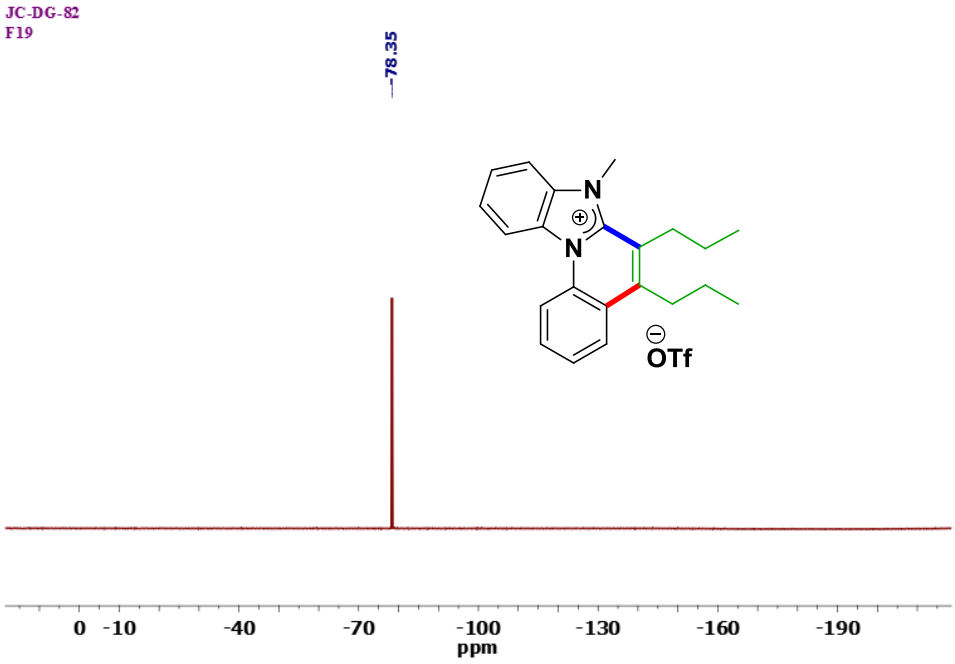


Figure S50. ^{19}F NMR spectrum of **3g** (376 MHz, $CDCl_3$, 300 K).

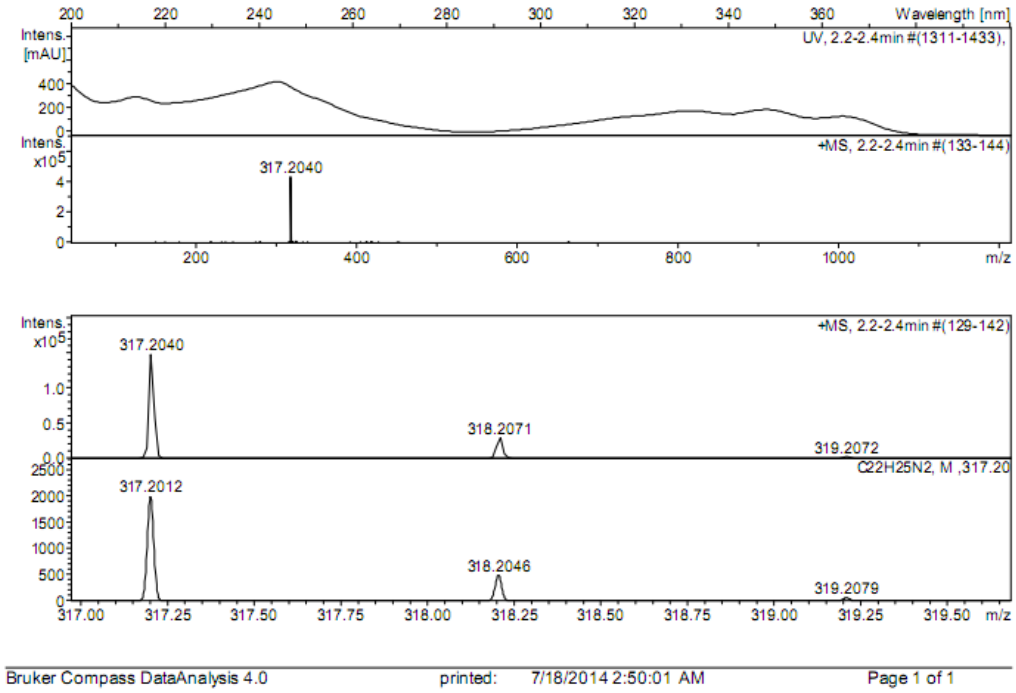


Figure S51. ESI-HRMS (positive ion mode) spectrum of **3g.**

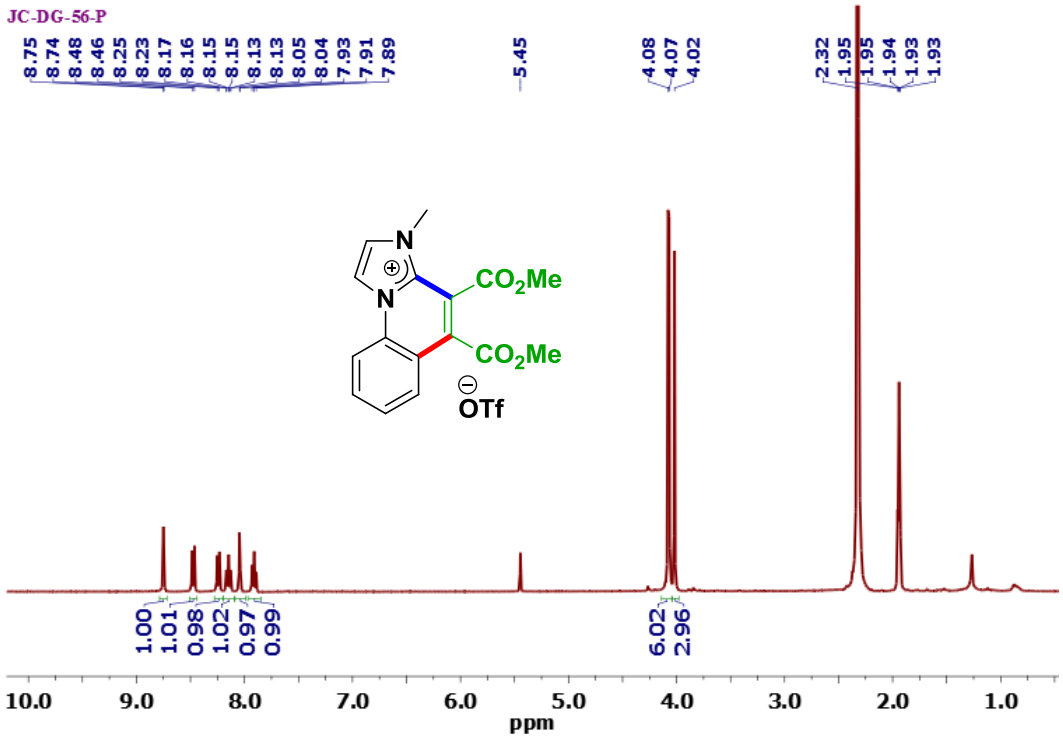


Figure S52. ^{1}H NMR spectrum of **3h** (400 MHz, CD_3CN, 300 K).

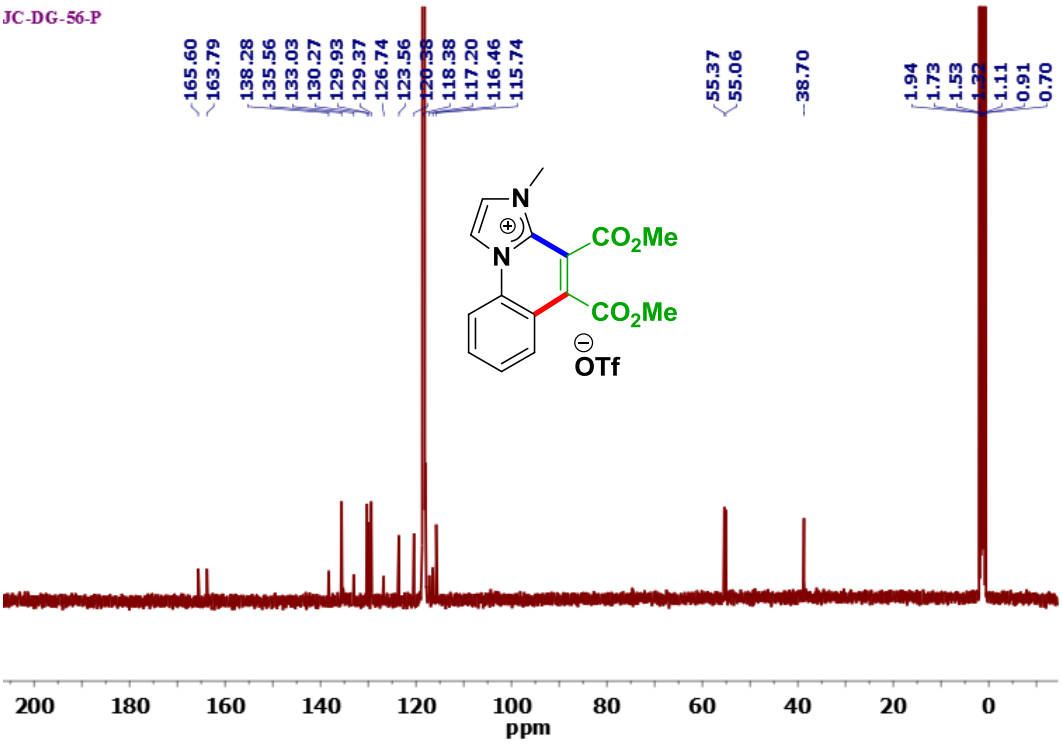


Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of **3h** (101 MHz, CD_3CN, 300 K).

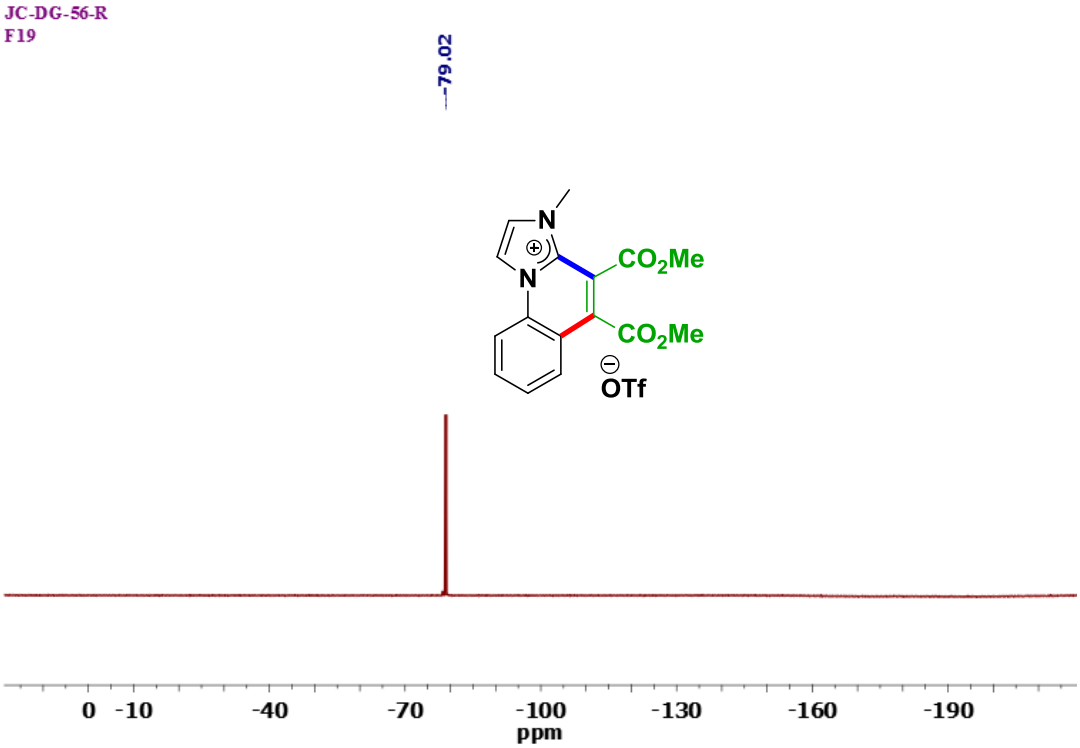


Figure S54. ^{19}F NMR spectrum of **3h** (376 MHz, $CDCl_3$, 300 K).

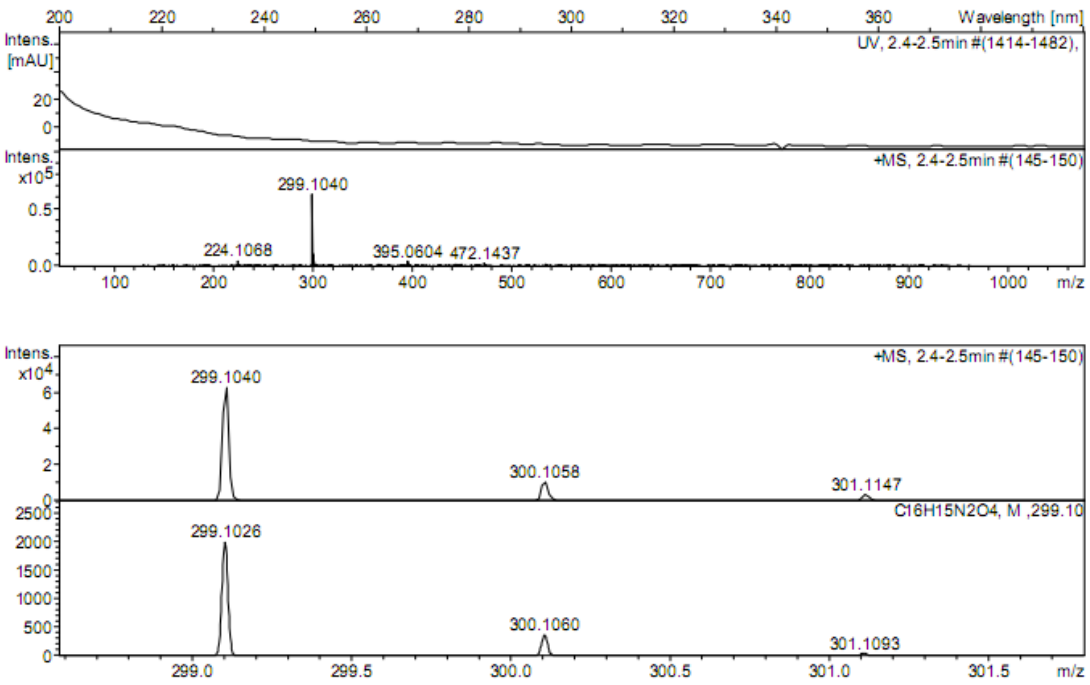


Figure S55. ESI-HRMS (positive ion mode) spectrum of **3h.**

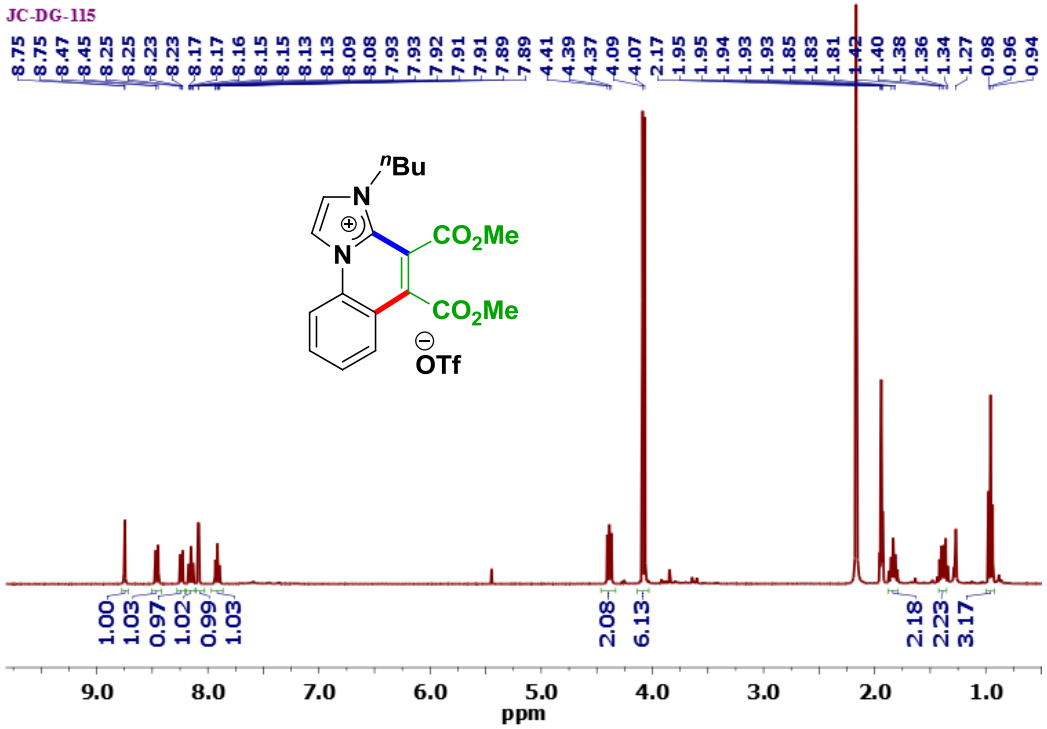


Figure S56. ^{1}H NMR spectrum of **3i** (400 MHz, CD_3CN, 300 K).

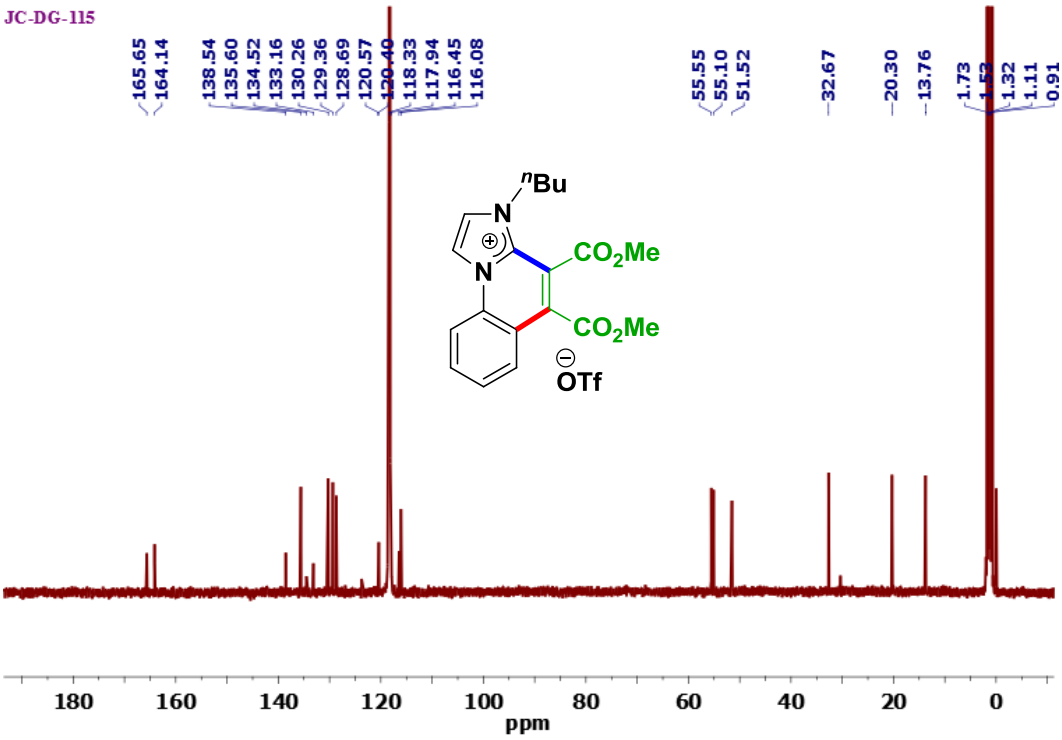


Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum of **3i** (101 MHz, CD_3CN, 300 K).

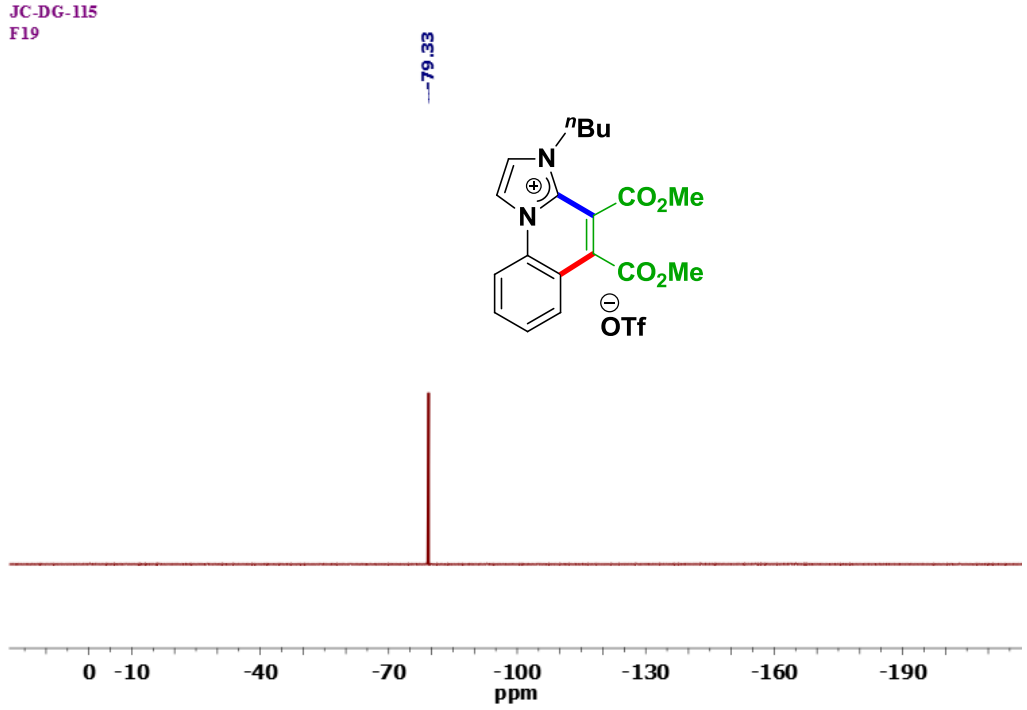


Figure S58. ^{19}F NMR spectrum of **3i** (376 MHz, CD_3CN, 300 K).

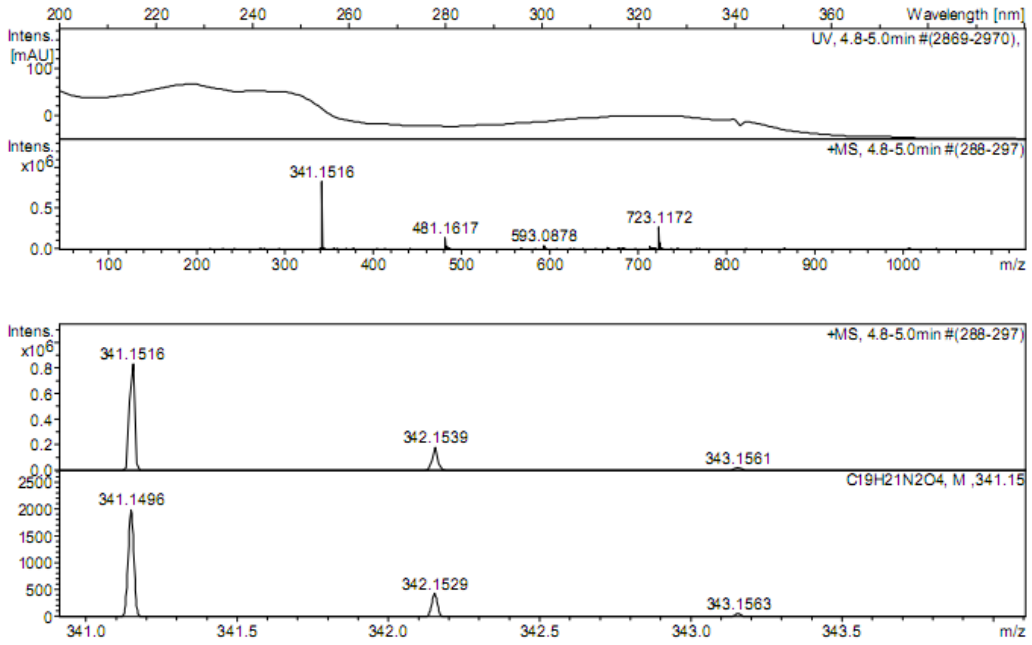


Figure S59. ESI-HRMS (positive ion mode) spectrum of **3i.**

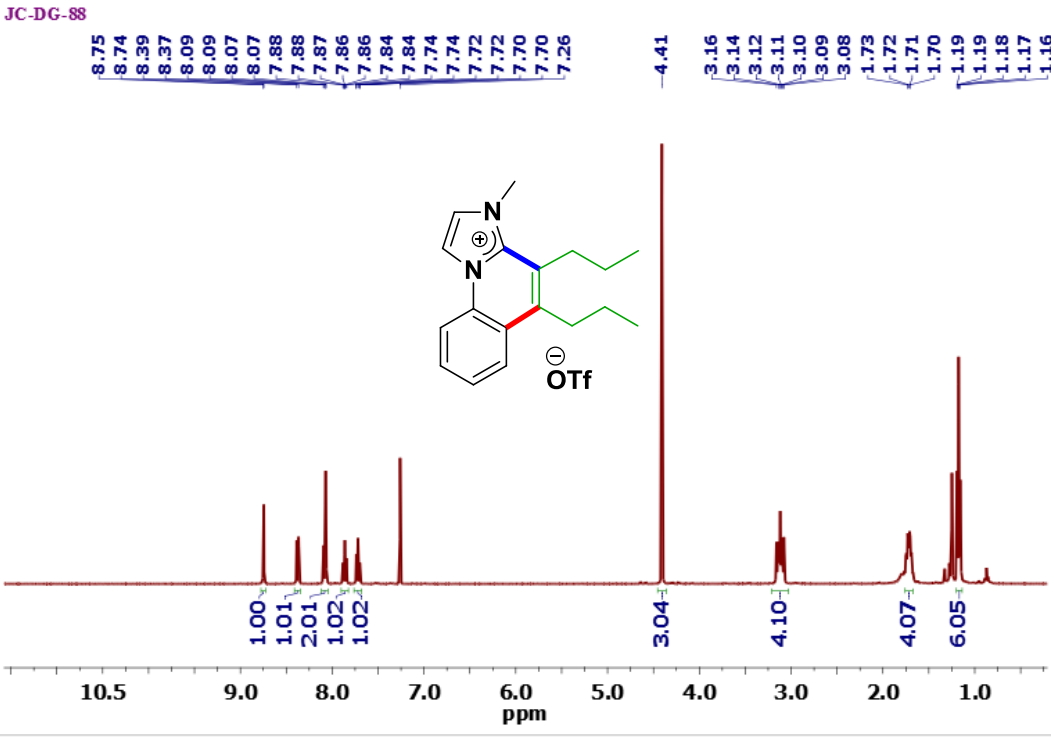


Figure S60. ^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$, 300 K).

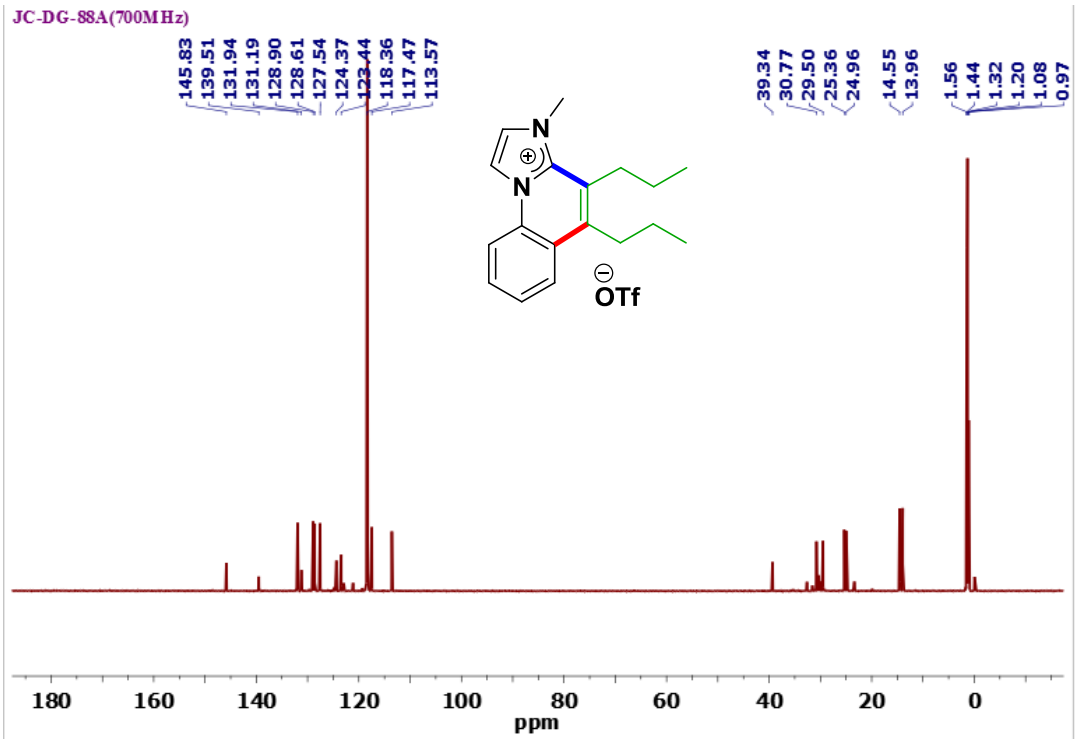


Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of **3j** (176 MHz, CD_3CN, 300 K).

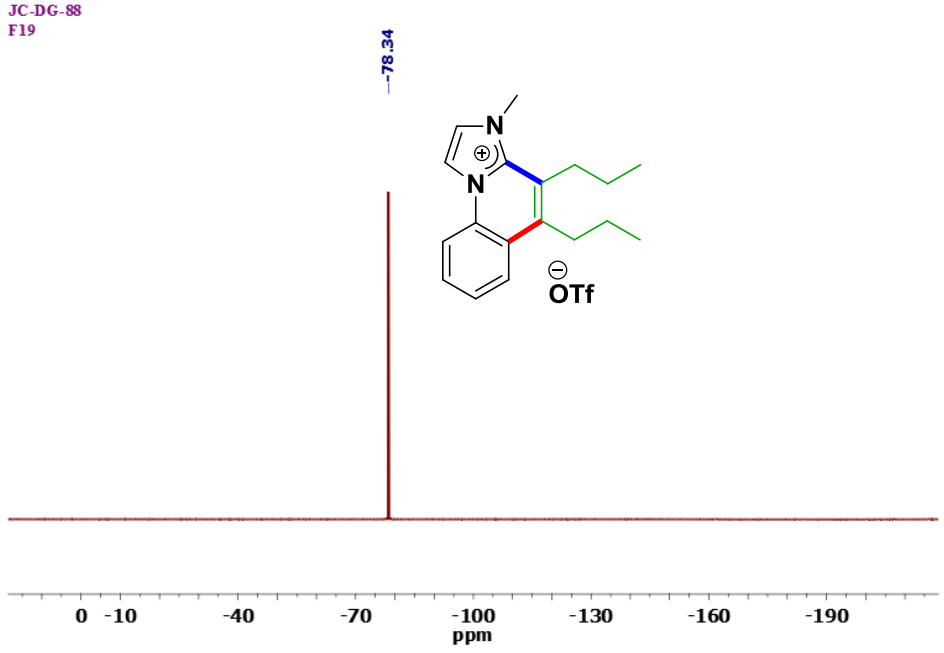


Figure S62. ^{19}F NMR spectrum of **3j** (376 MHz, $CDCl_3$, 300 K).

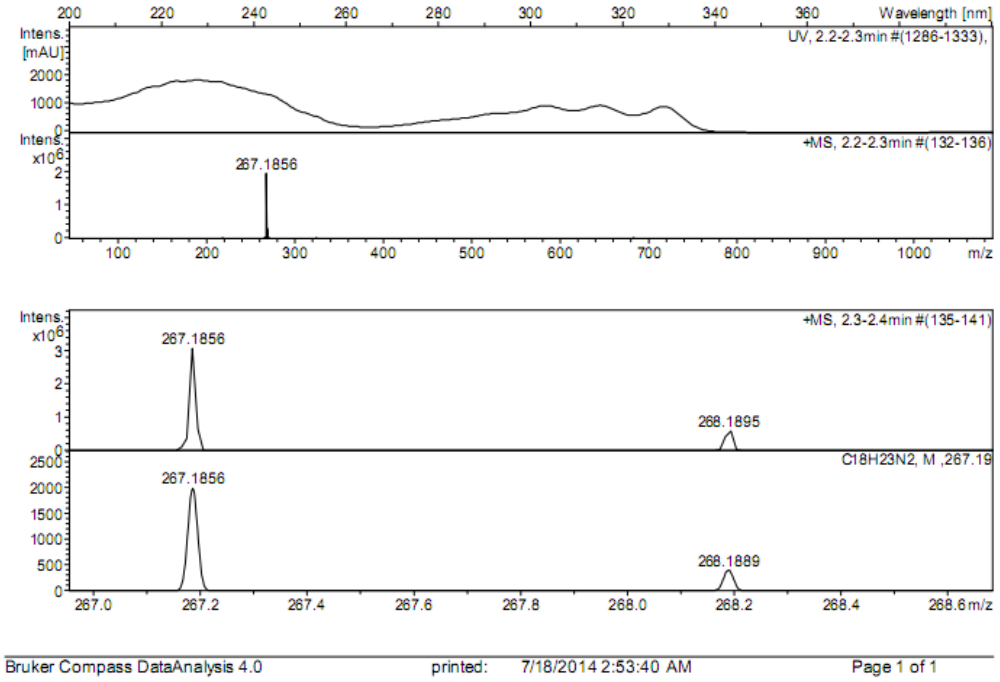


Figure S63. ESI-HRMS (positive ion mode) spectrum of **3j.**

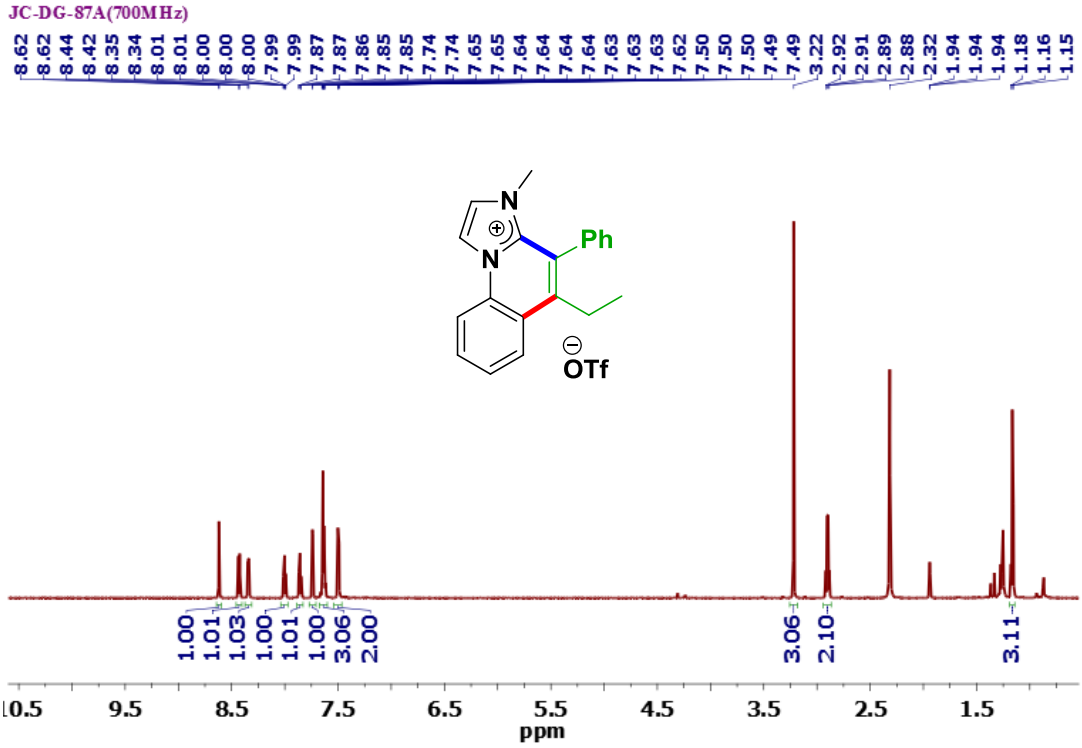


Figure S64. ^{1}H NMR spectrum of **3k** (700 MHz, CD_3CN, 300 K).

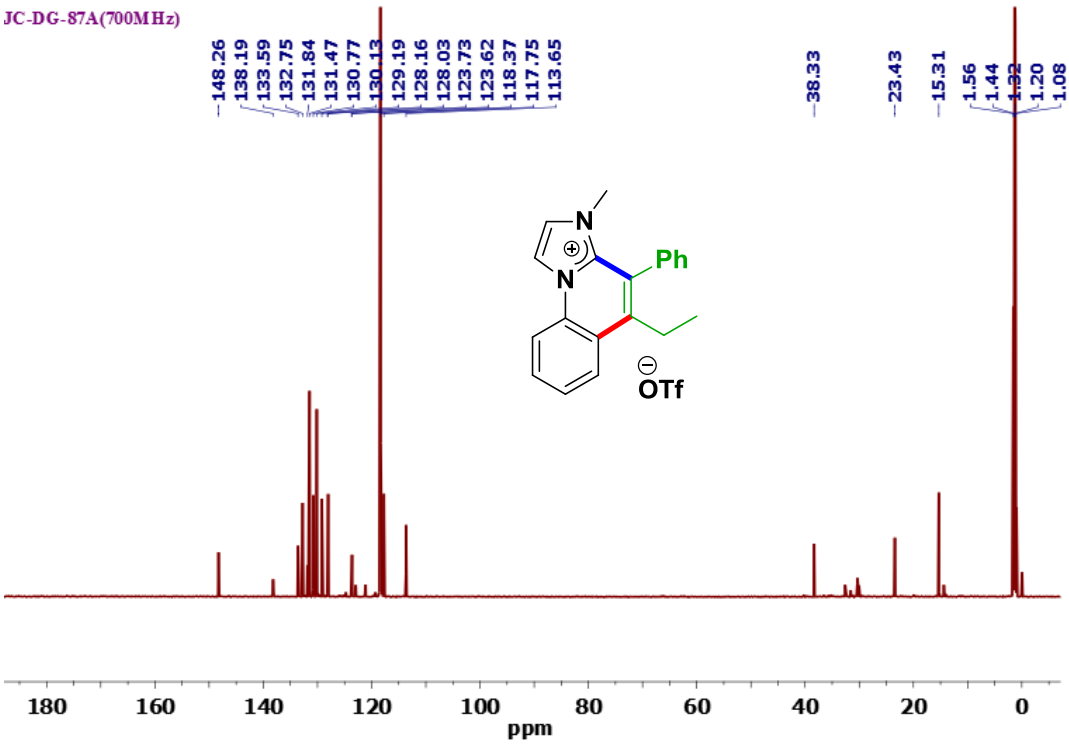


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of **3k** (176 MHz, CD_3CN, 300 K).

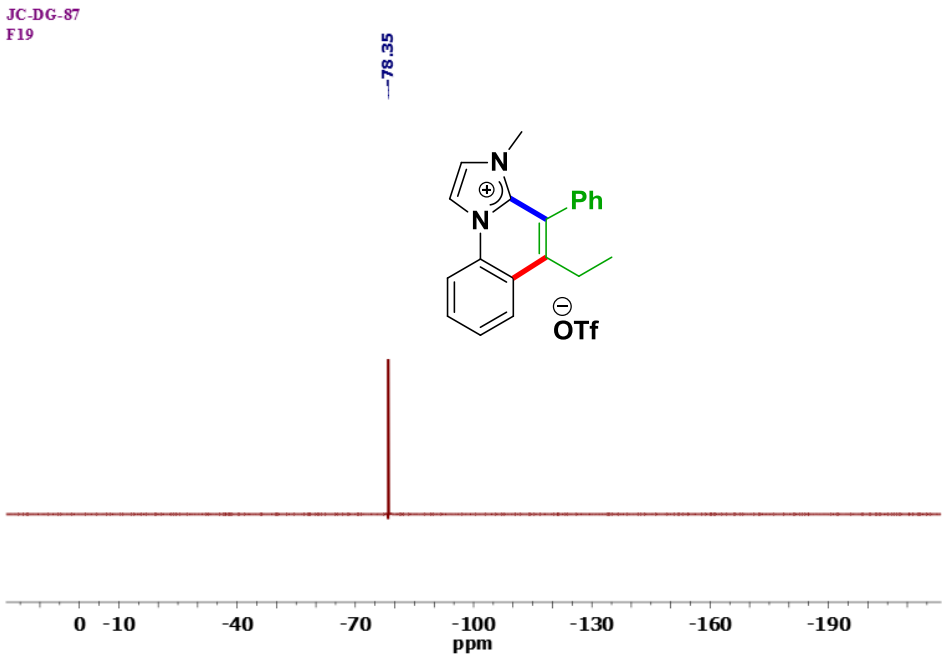


Figure S66. ^{19}F NMR spectrum of **3k** (376 MHz, $CDCl_3$, 300 K).

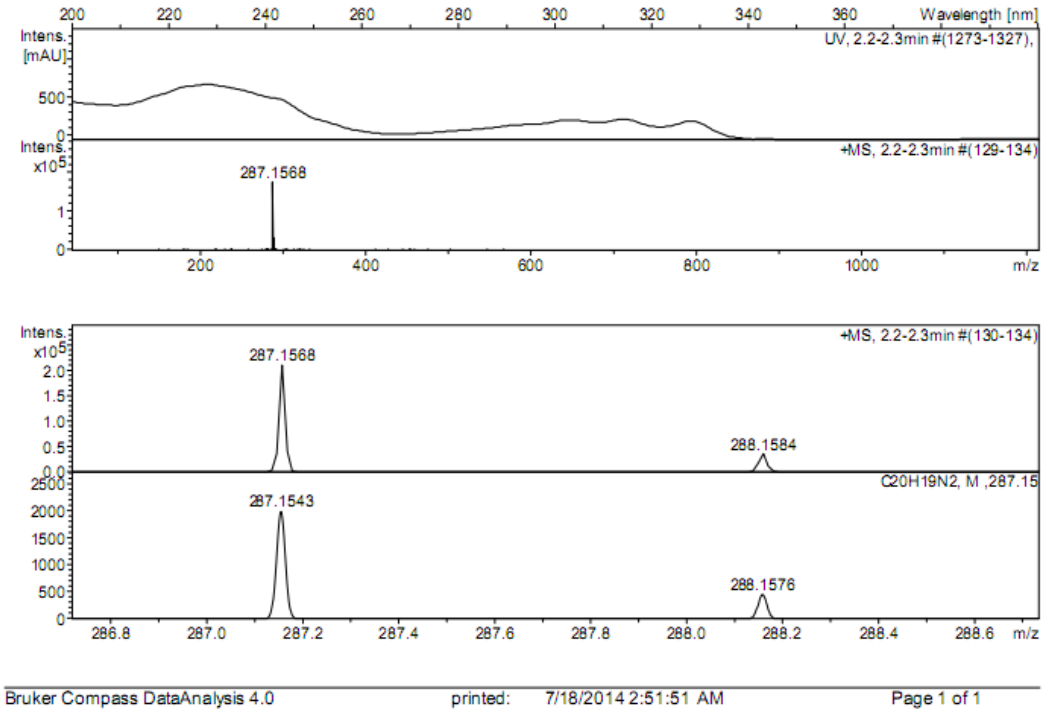


Figure S67. ESI-HRMS (positive ion mode) spectrum of **3k.**

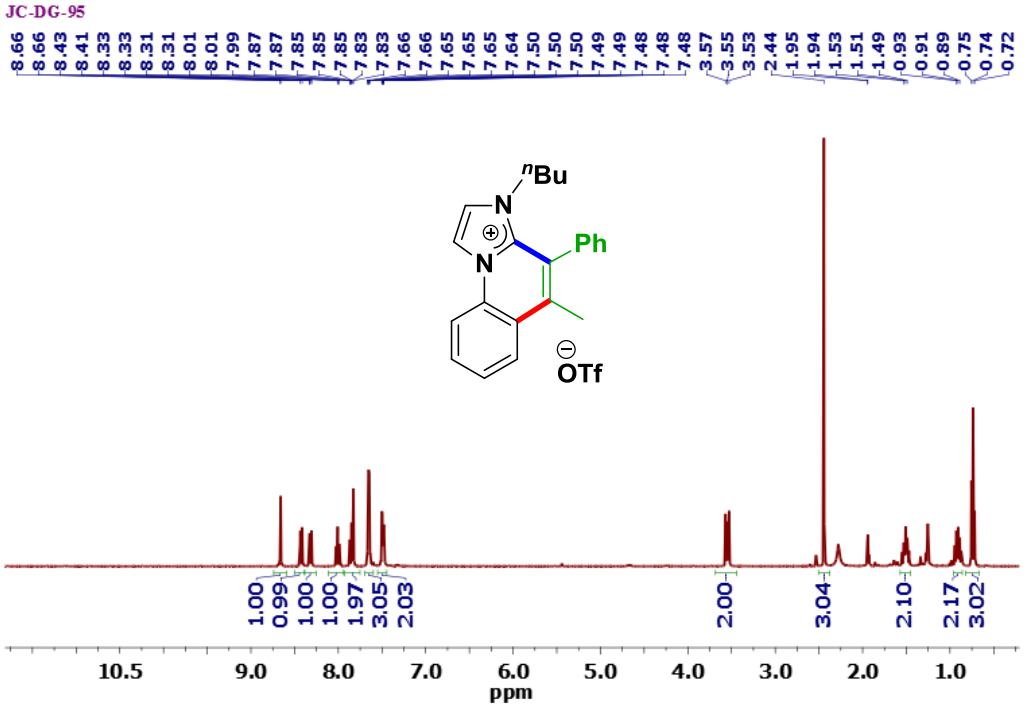


Figure S68. ^{1}H NMR spectrum of **3l** (400 MHz, CD_3CN, 300 K).

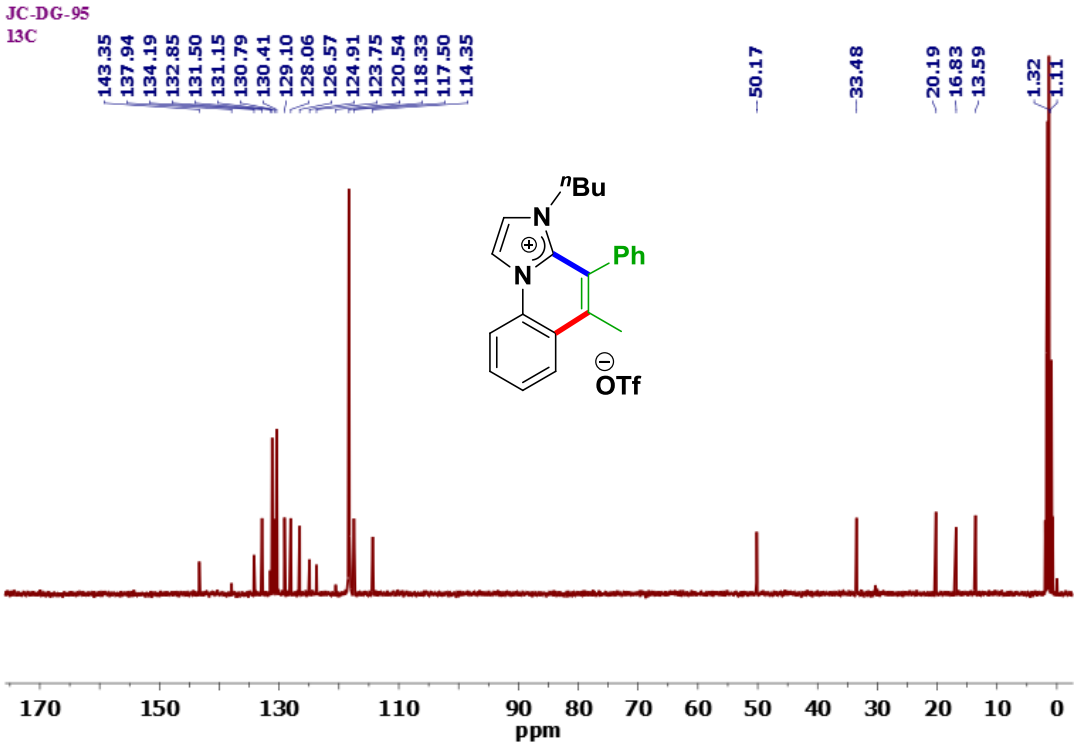


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum of **3l** (101 MHz, CD_3CN, 300 K).

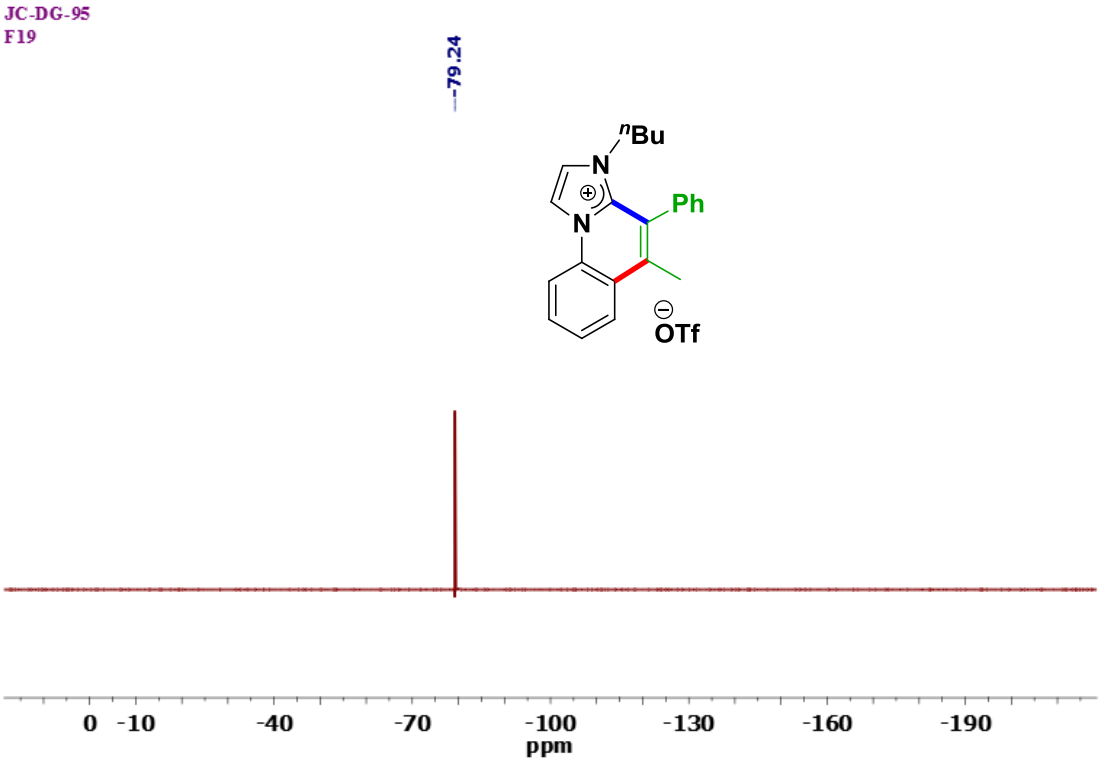


Figure S70. ^{19}F NMR spectrum of **3l** (376 MHz, CD_3CN, 300 K).

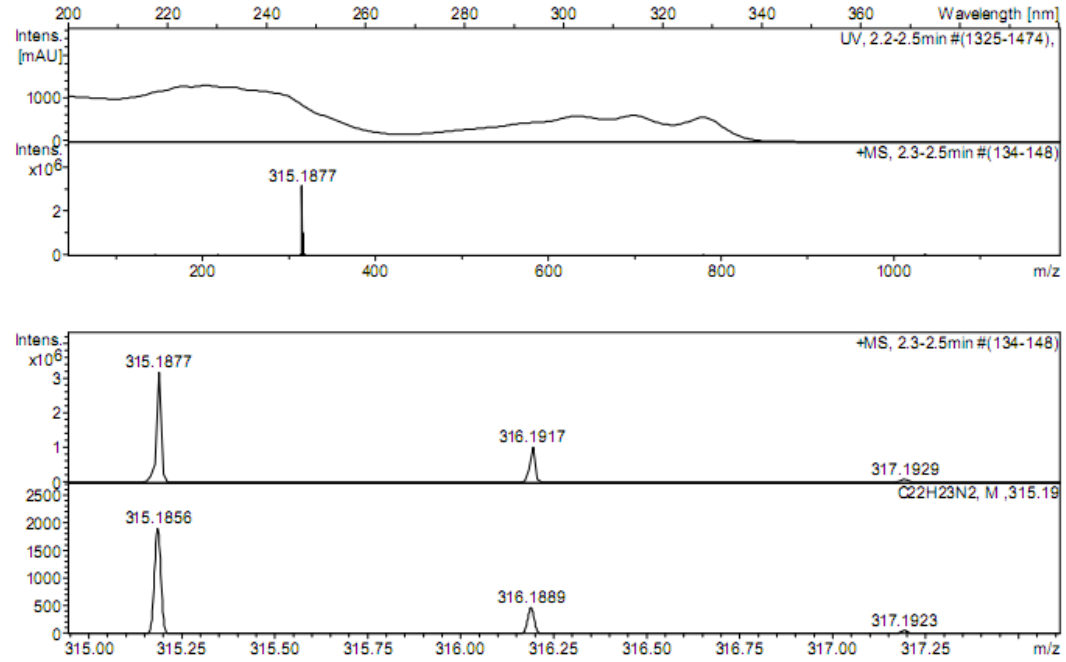


Figure S71. ESI-HRMS (positive ion mode) spectrum of **3l.**

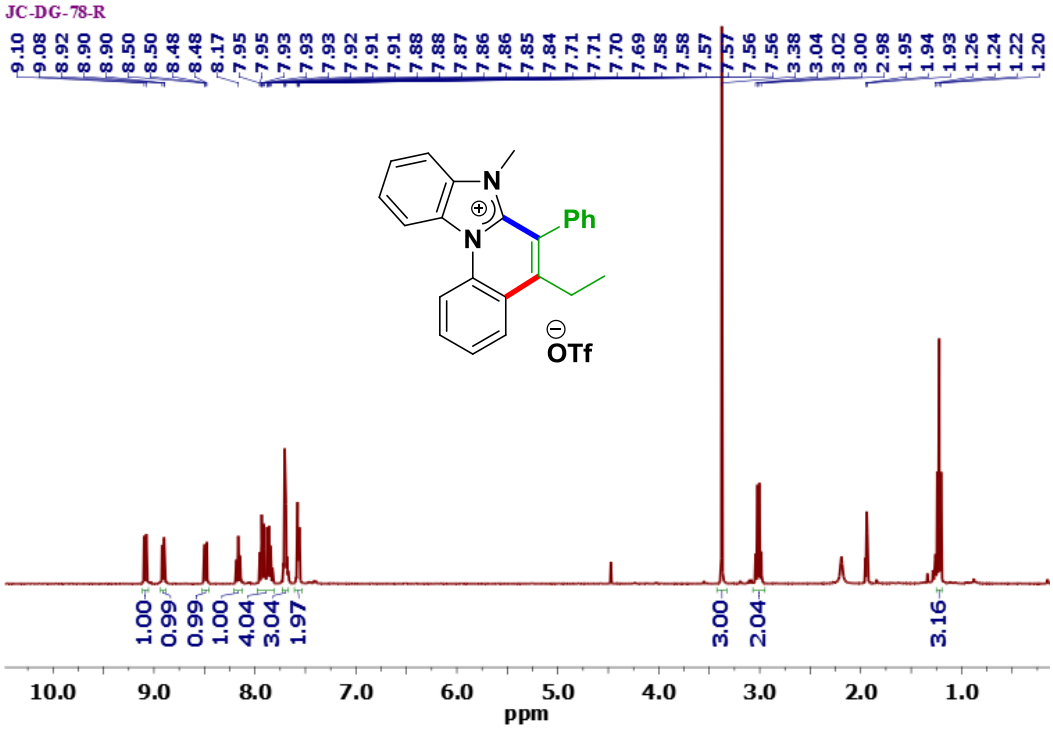


Figure S72. ^{1}H NMR spectrum of **3m** (400 MHz, CD_3CN, 300 K).

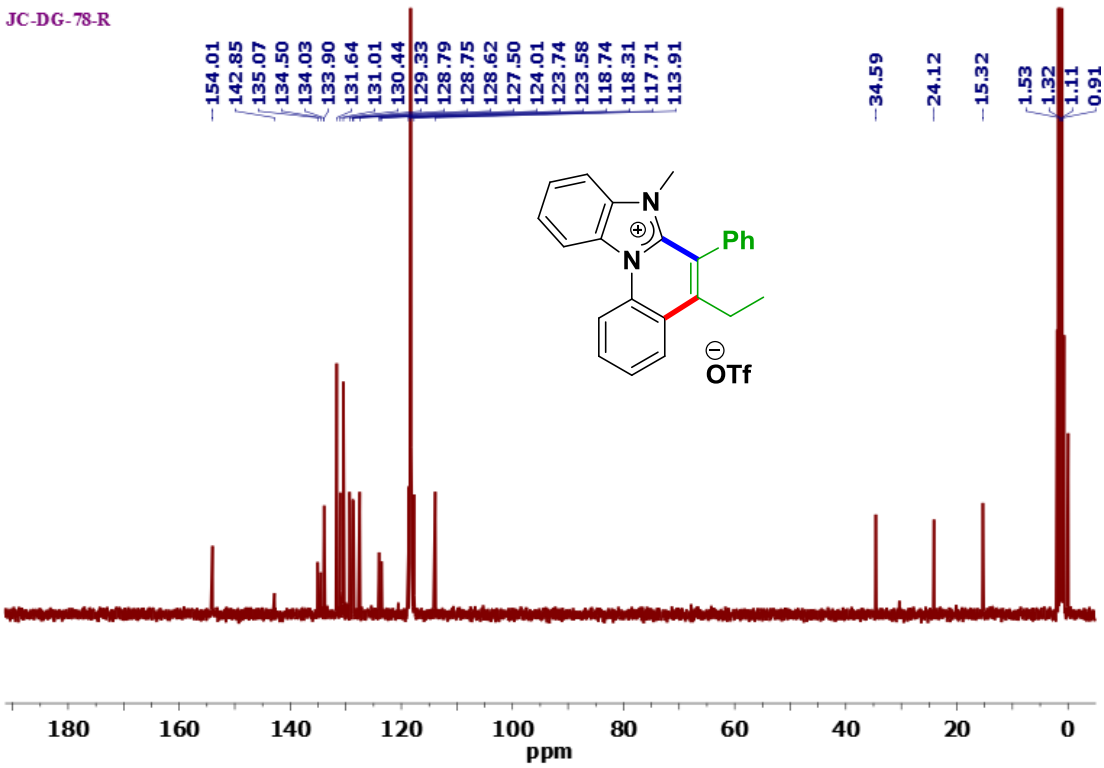


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of **3m** (101 MHz, CD_3CN, 300 K).

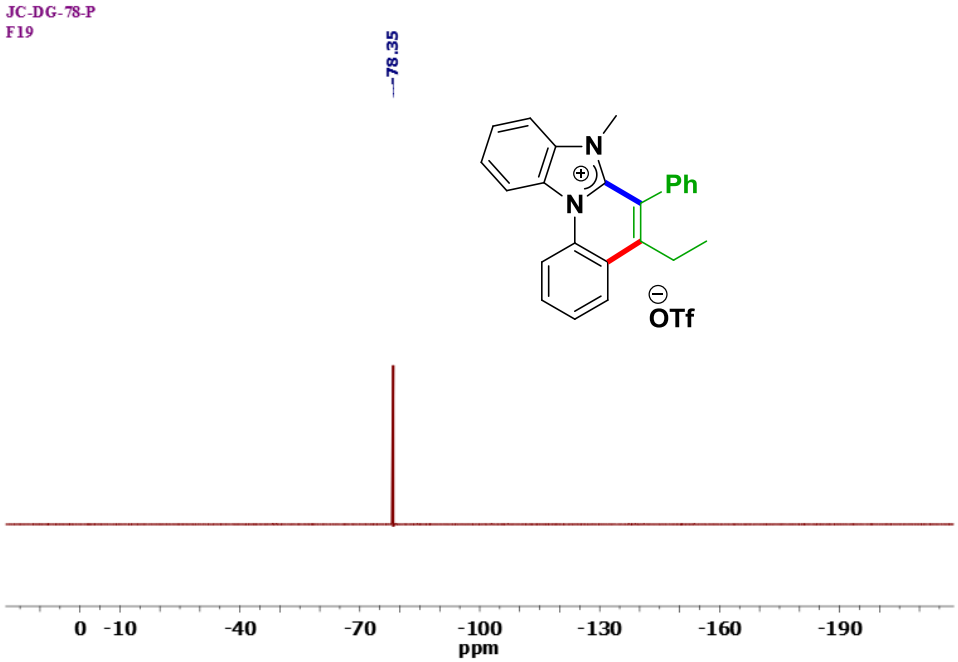


Figure S74. ^{19}F NMR spectrum of **3m** (376 MHz, $CDCl_3$, 300 K).

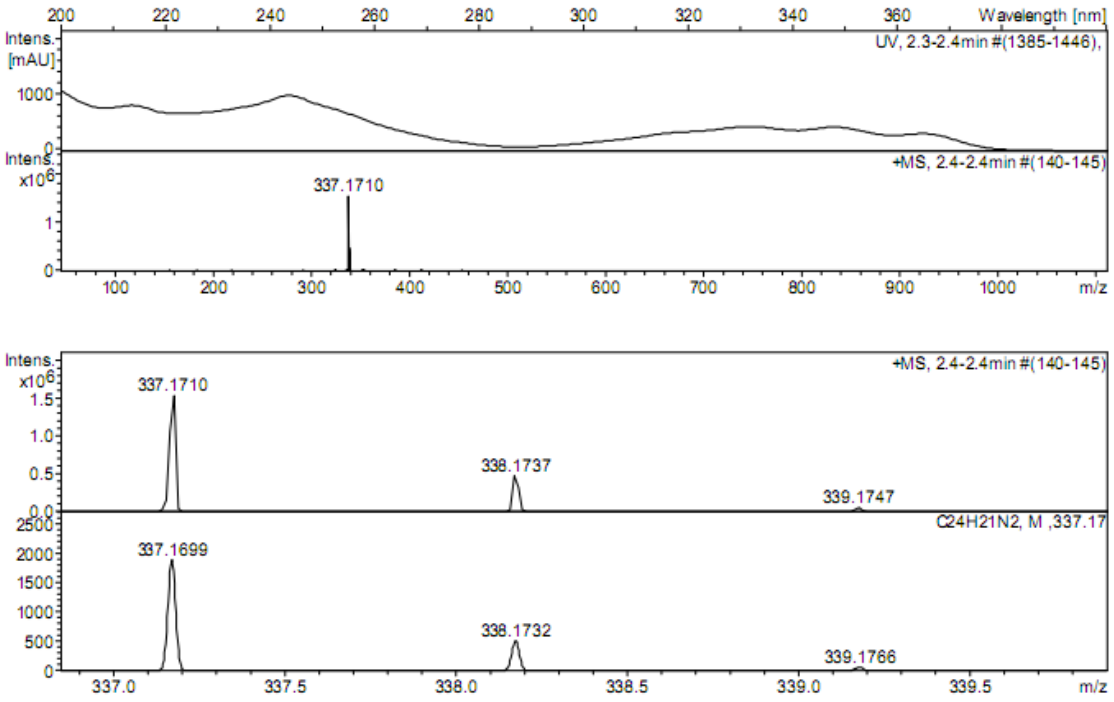


Figure S75. ESI-HRMS (positive ion mode) spectrum of **3m.**

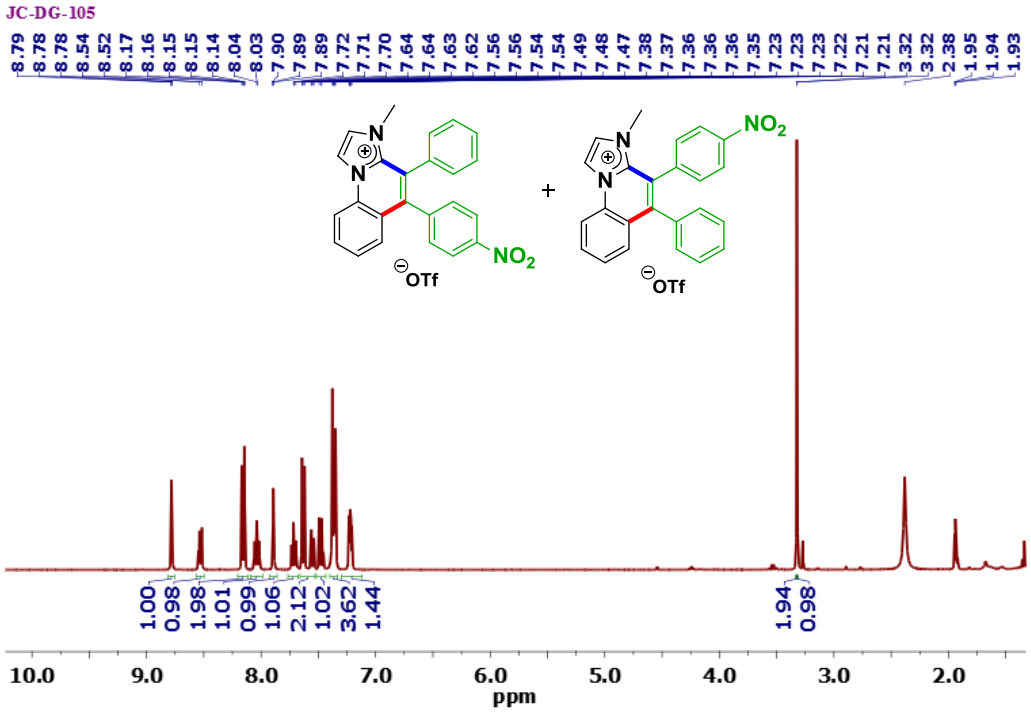


Figure S76. ^{1}H NMR spectrum of **3n** (400 MHz, CD_3CN, 300 K).

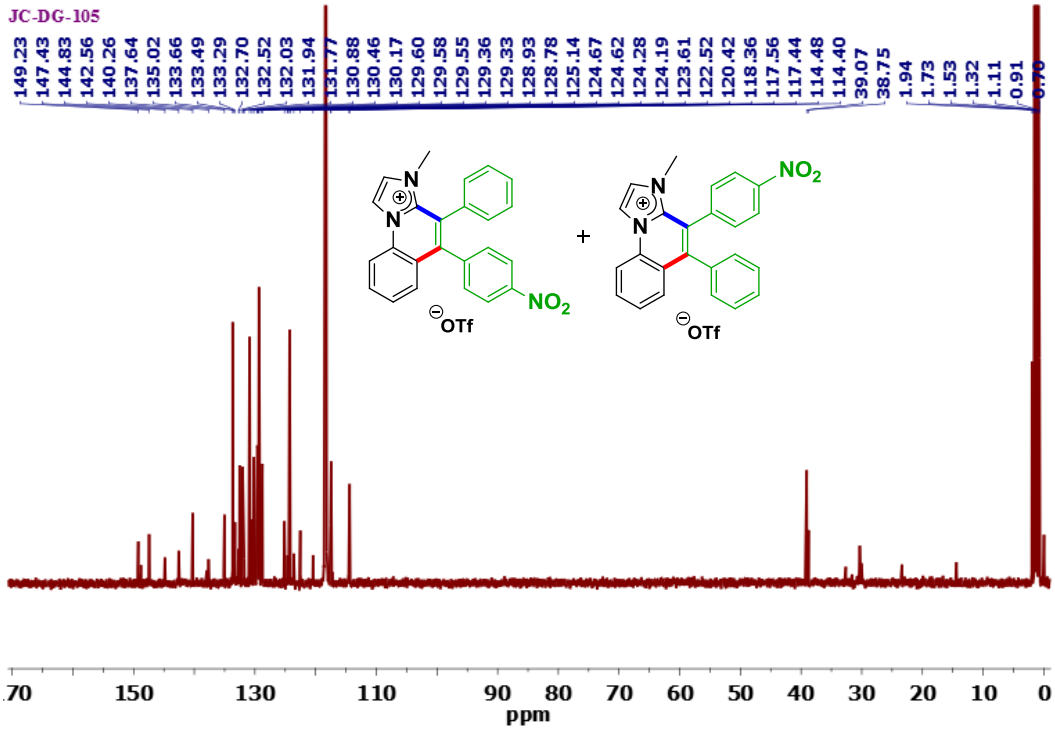


Figure S77. $^{13}C\{^{1}H\}$ NMR spectrum of **3n** (101 MHz, CD_3CN, 300 K).

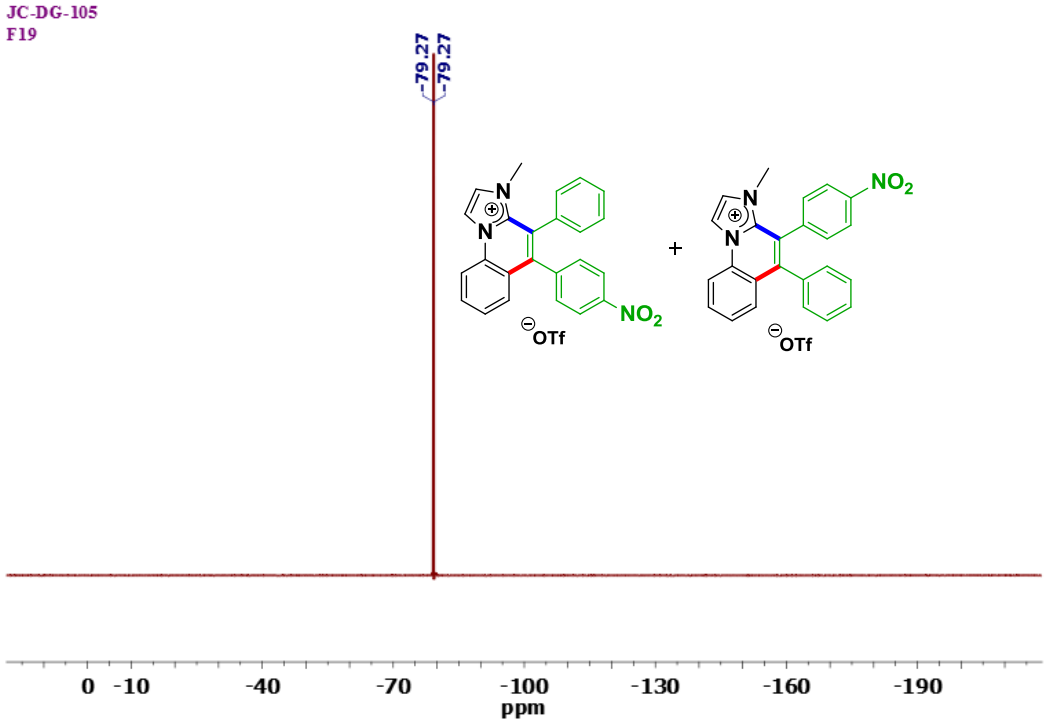


Figure S78. ^{19}F NMR spectrum of **3n** (376 MHz, CD_3CN, 300 K).

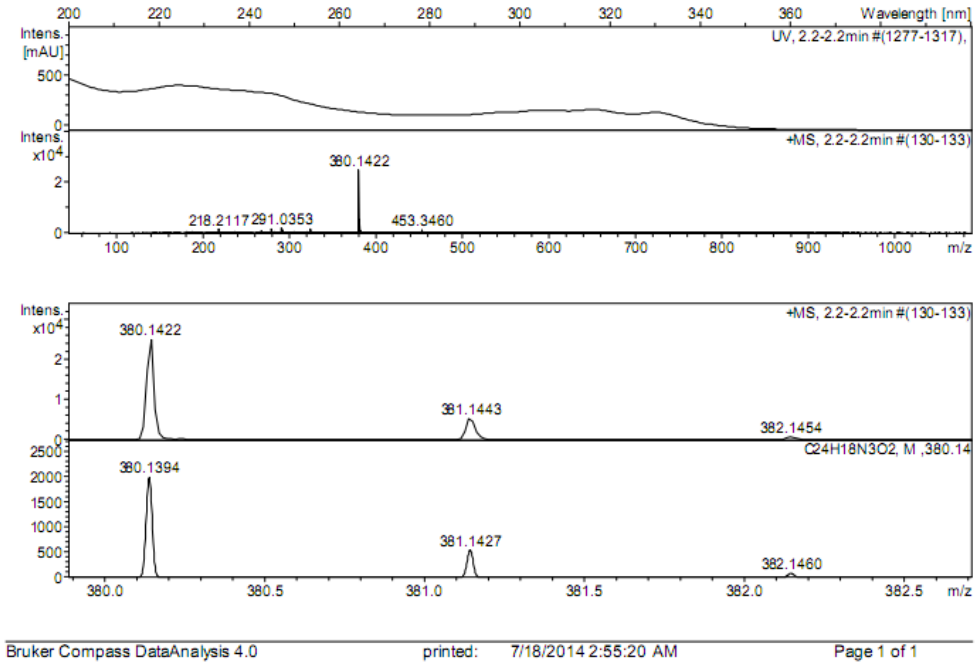


Figure S79. ESI-HRMS (positive ion mode) spectrum of **3n.**

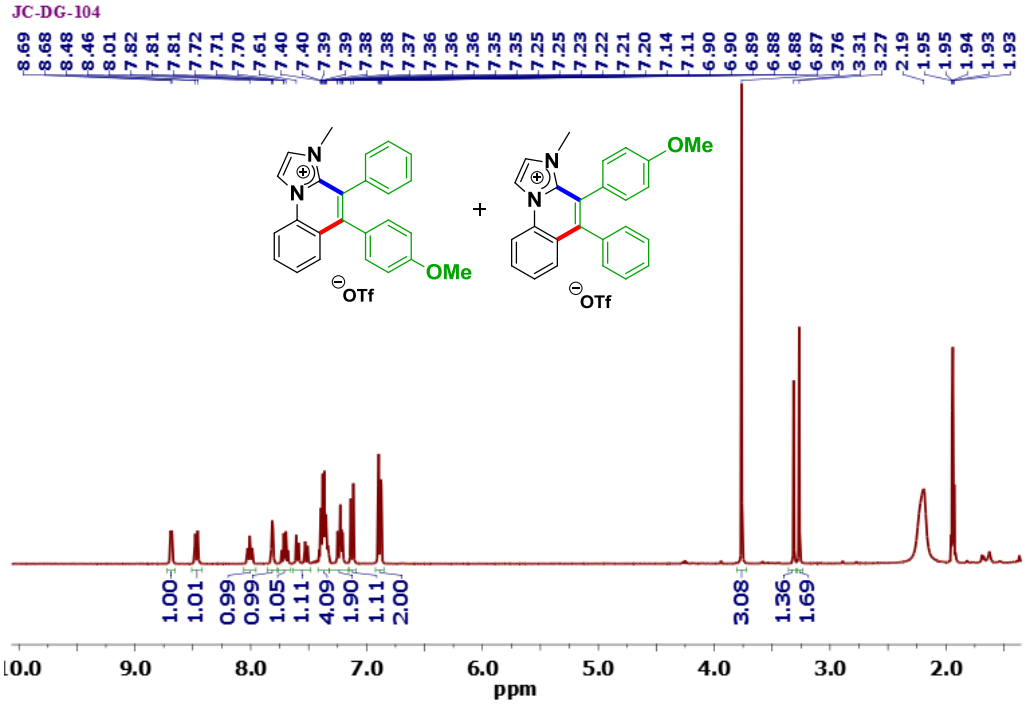


Figure S80. ^{1}H NMR spectrum of **3o** (400 MHz, CD_3CN, 300 K).

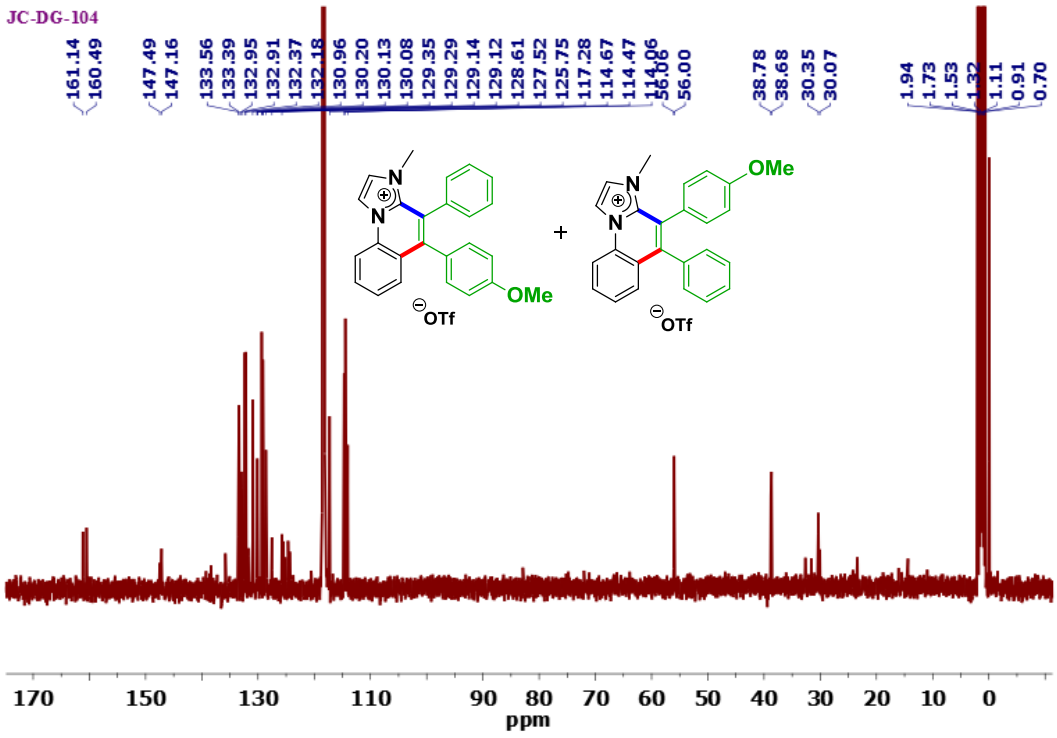


Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum of **3o** (101 MHz, CD_3CN, 300 K).

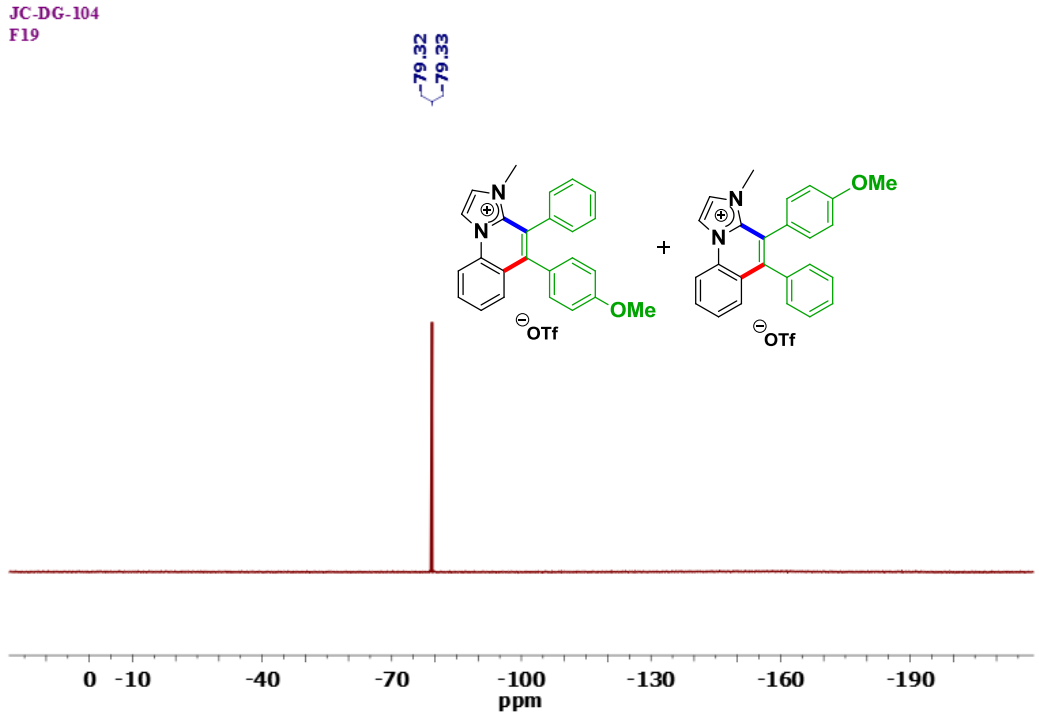


Figure S82. ^{19}F NMR spectrum of **3o** (376 MHz, CD_3CN, 300 K).

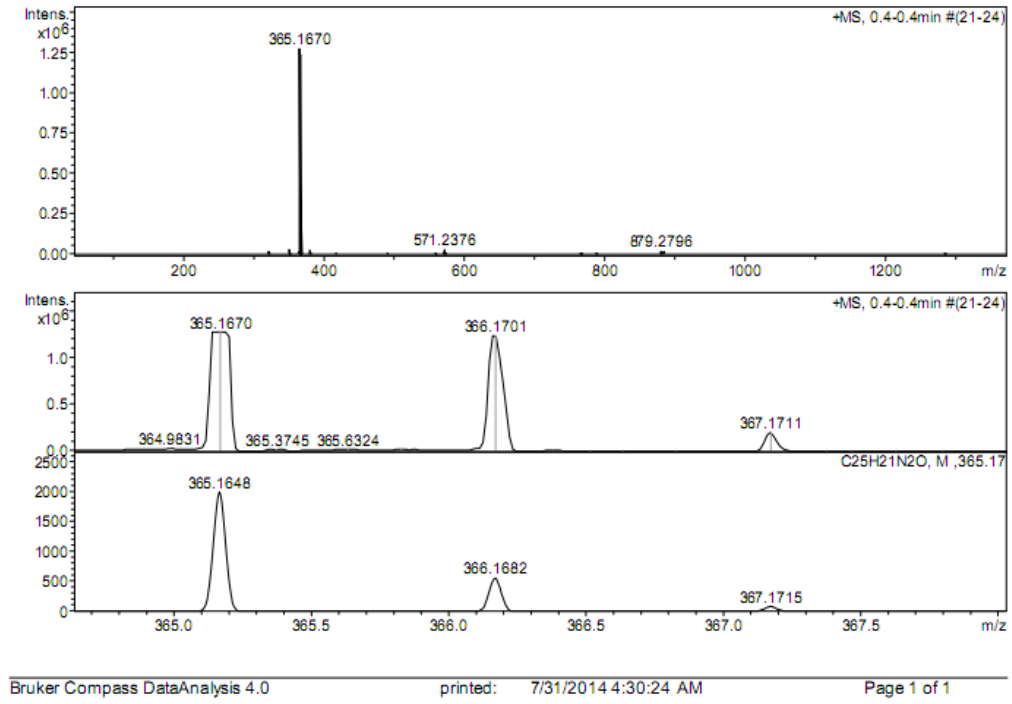


Figure S83. ESI-HRMS (positive ion mode) spectrum of **3o.**

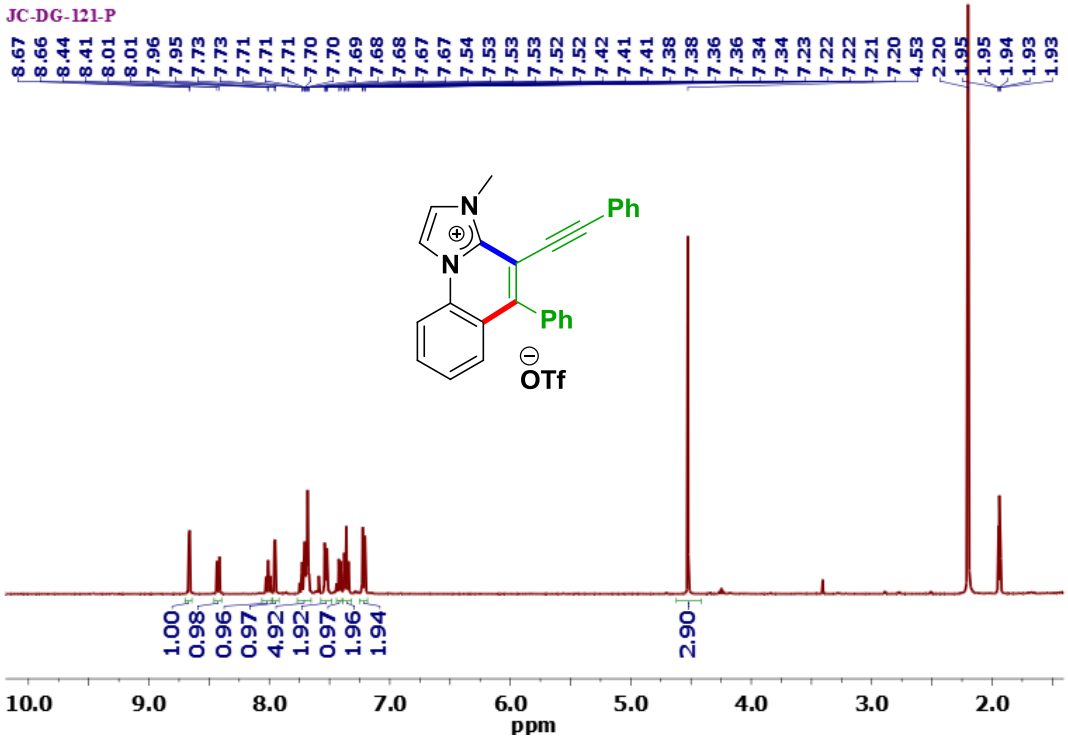


Figure S84. ^{1}H NMR spectrum of **3p** (400 MHz, CD_3CN, 300 K).

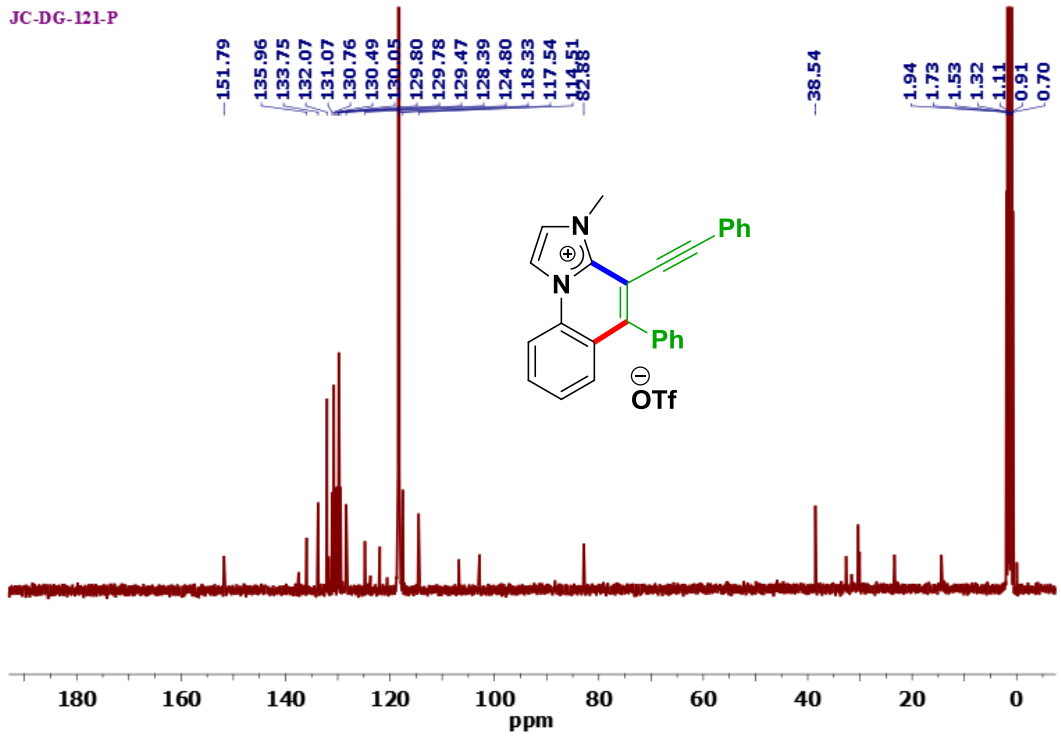


Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum of **3p** (101 MHz, CD_3CN, 300 K).

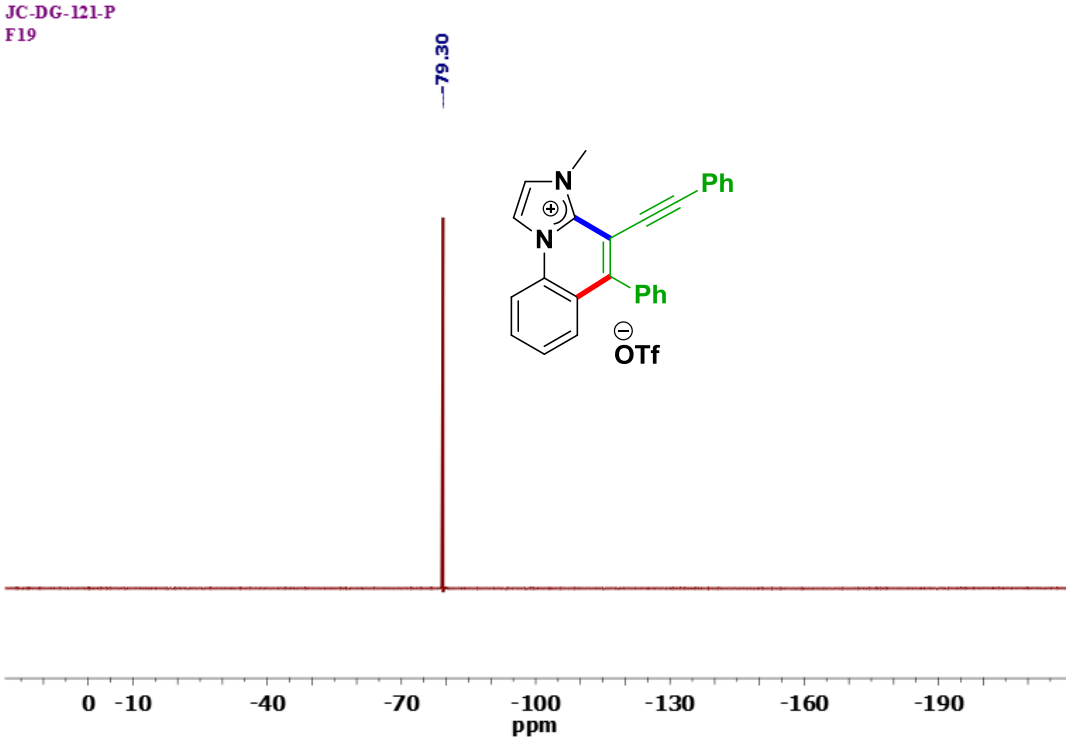


Figure S86. ^{19}F NMR spectrum of **3p** (376 MHz, CD_3CN, 300 K).

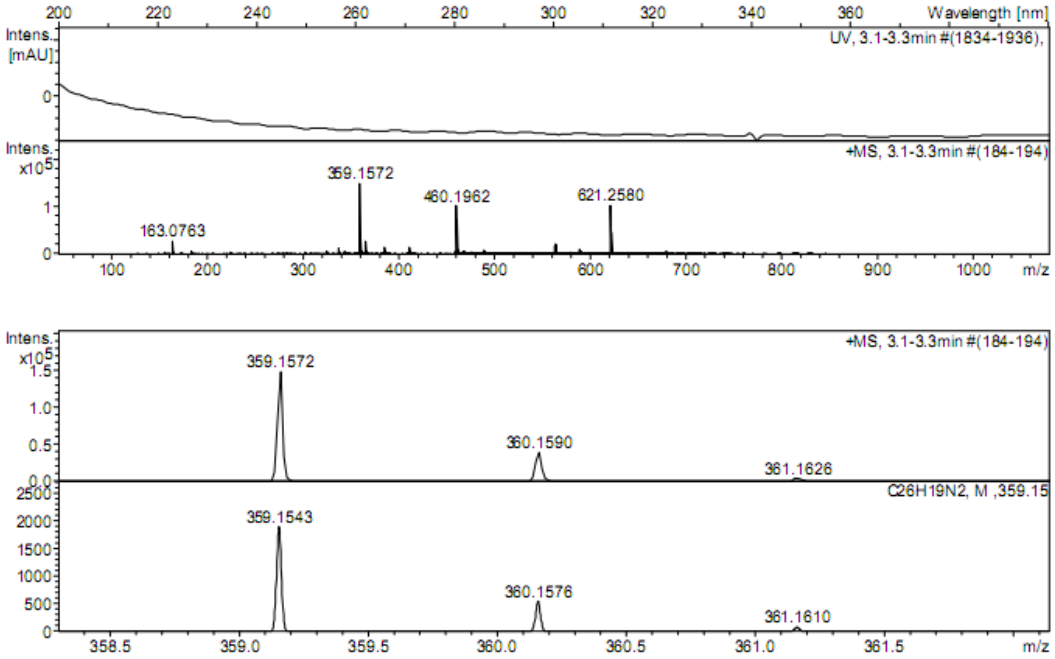


Figure S87. ESI-HRMS (positive ion mode) spectrum of **3p.**

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