Electronic Supplementary Material (ESI) for Chemical Communications.

Synthesis of symmetrical and unsymmetrical triarylpyrylium ions by inverse electron demand Diels-Alder reaction

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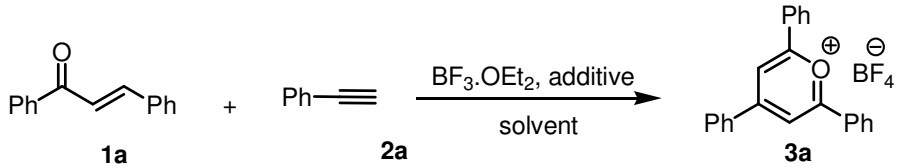
General Methods

All the reactions are performed with commercially available best grade chemicals without further purification. All the solvents used were reagent grade. Column chromatography was performed using 100-200 mesh silica gel and mixtures of hexane-ethyl acetate were used for elution of the starting materials. Melting points were determined on a Buchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker AMX 500 spectrophotometer (DMSO-d_6, CD_3CN as solvents). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of DMSO-d_6 (δ 2.50, quintet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublet); m (multiplet); st (sextet). Coupling constants are reported as *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of DMSO-d_6 (δ 39.51, septet). Mass spectra were recorded under EI/HRMS at 60,000 resolution using Thermo Scientific Exactive mass spectrometer. IR spectra were recorded on Bruker FT-IR spectrometer. All the substituted chalcones were synthesized following the literature reports.

Table S1 Optimisation of IEDDA reaction



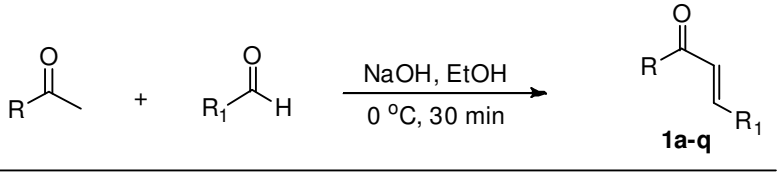
1a **2a** **3a**

Solvent	Lewis acid	Additive	Temperature	Yield(%)[a]
Toluene	$BF_3.OEt_2$	-	rt	trace
DCM	$BF_3.OEt_2$	-	rt	23
DMF	$BF_3.OEt_2$	-	rt	0
1,4-Dioxane	$BF_3.OEt_2$	-	rt	0
EtOAc	$BF_3.OEt_2$	-	rt	0
n-hexane	$BF_3.OEt_2$	-	rt	25
CCl_4	$BF_3.OEt_2$	-	rt	35
CCl_4	$BF_3.OEt_2$(0.2 equiv)	-	rt	trace
CCl_4	$BF_3.OEt_2$(5 equiv)	-	rt	26
Cyclohexane	$BF_3.OEt_2$	-	rt	34
Cyclohexane	$BF_3.OEt_2$	$In(OTf)_3$(0.2 equiv)	rt	30
Cyclohexane	$BF_3.OEt_2$	CF_3COOH(1 equiv)	rt	25
Cyclohexane	$BF_3.OEt_2$	$AuCl_3.3H_2O$(0.2 equiv)	rt	25
Cyclohexane	$BF_3.OEt_2$	$AuClPPh_3$(0.2 equiv)	rt	23
Cyclohexane	$BF_3.OEt_2$	$Cu(OAc)_2$	rt	25
Cyclohexane	$BF_3.OEt_2$	O_2	rt	44
Cyclohexane	$BF_3.OEt_2$	O_2	60-70^o	65
Cyclohexane	$BF_3.OEt_2$	O_2	reflux	35
Cyclohexane[b]	$BF_3.OEt_2$	O_2	60-70^o	49

[a]Reaction conditions: 1a (0.11 mmol), 2a (0.33 mmol), $BF_3.OEt_2$ (0.33 mmol) in 3 ml of cyclohexane. [b]2 equiv. of phenylacetylene is added.

Experimental Procedures

General Procedure for the synthesis of (*E*)-chalcone (1).[1]

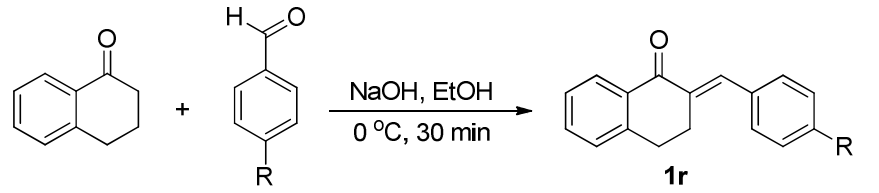


R, R_1 = Aryl or Heteroaryl

Scheme S1

One equivalent of arylaldehyde or heteroarylaldehyde is added to the solution of one equivalent of acetophenone in ethanol. 10% aqueous solution of NaOH was added drop wise to the mixture at 0 °C, which resulted in precipitation. The mixture was then stirred for 30 min, filtered, washed with cold methanol, and dried to yield 60 - 90% solid compound. Product was confirmed from ^{1}H NMR.

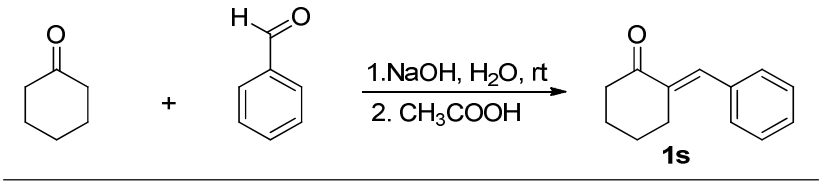
General procedure for the synthesis of (*E*)-2-arylidene-3,4-dihydronaphthalen-1(2*H*)-one (1r).[1]



Scheme S2

One equivalent of arylaldehyde or heteroarylaldehyde is added to the solution of one equivalent of 3,4-dihydronaphthalen-1(2*H*)-one in ethanol. The 5% aqueous solution of NaOH was added drop wise to the mixture at 0 °C which resulted in precipitation. The mixture was then stirred for 30 min, filtered, washed with cold methanol, and dried to yield 60 - 90% solid compound. Product was confirmed from ^{1}H NMR.

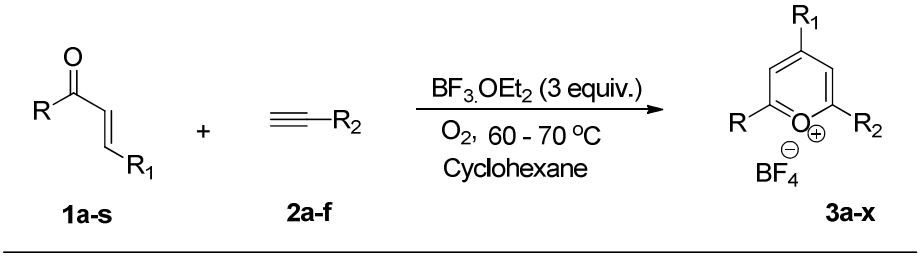
General Procedure for the synthesis of (*E*)-2-arylidenecyclohexanone (1s).[2]



Scheme S3

Cycloalkanone (500 mg, 5.09 mmol) was added to a solution of NaOH (101.5 mg, 2.54 mmol) in water (1mL) and stirred under ambient conditions for 5 min, followed by the addition of benzaldehyde (180.19 mg, 1.69 mmol). After 3 days of stirring, the reaction mixture was neutralized with glacial acetic acid. The product was extracted with toluene (3 x 200 mL) and purified by vacuum distillation, affording the unsaturated ketone as yellow solid. Product was confirmed from ^{1}H NMR.

General procedure for the $BF_3.OEt_2$ mediated synthesis of 2,4,6-Triarypyrylium tetrafluoroborate (3a-3ae)

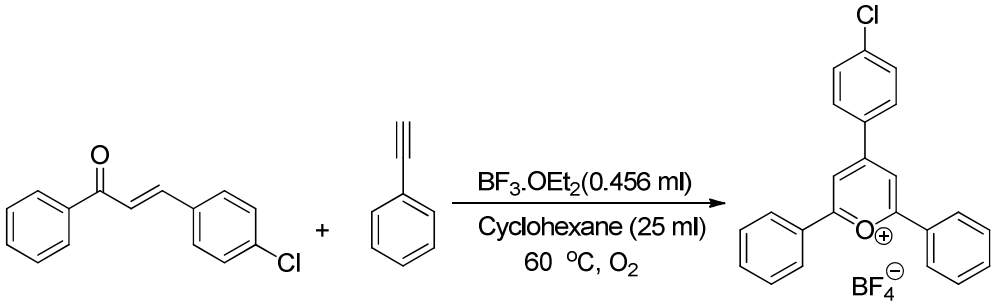


R, R_1, R_2 = Aryl, heteroaryl

Scheme S4

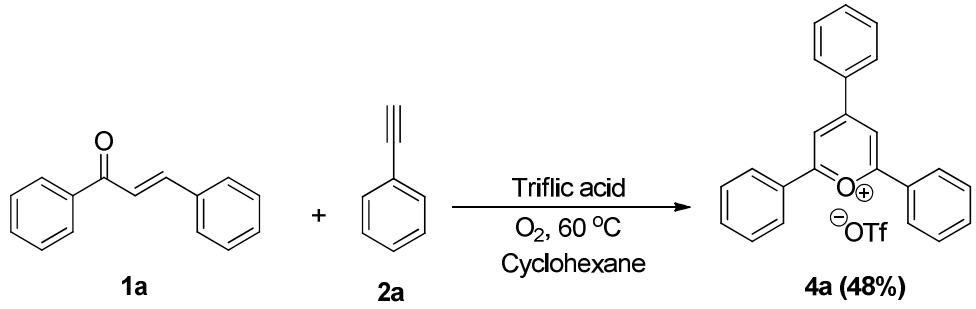
3 equiv. of $BF_3.OEt_2$, is added to the mixture of phenylacetylene (2a-f) (3 equiv, 0.72 mmol), and substituted (*E*)-chalcone (1a-s) (50 mg, 0.24 mmol,1 equiv) in cyclohexane (2 mL) at 60 ^{o}C under oxygen atmosphere and it is stirred for 3 - 6 hours by monitoring the TLC. After completion of the reaction, the reaction mixture was poured in to 10 ml of diethyl ether dissolving the residue in very little amount of DCM, to precipitate the product. The product is filtered and washed with diethyl ether and dried in air.

Gram scale synthesis of 4-(4- chlorophenyl)-2,6- diphenylpyrylium tetrafluoroborate (3f).

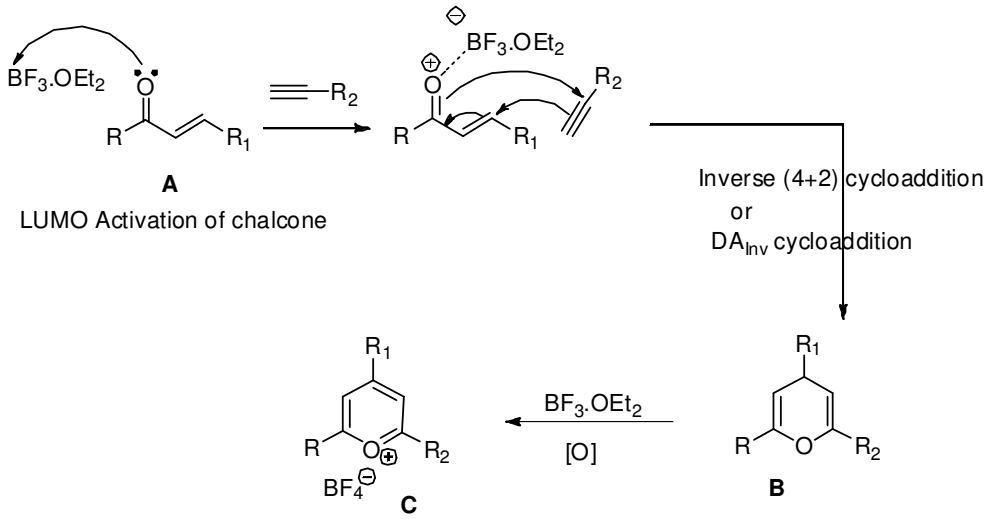


Scheme S5

Synthesis of 2,4,6-triphenylpyrylium triflate (4a)



Scheme S6

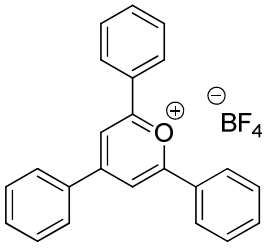


Scheme S7: Plausible mechanistic pathway

The mechanism can be explained as Inverse Electron Demand hetero-Diels-Alder (IEDDA) reaction. The Lewis acid $BF_3.OEt_2$ coordinates to the oxygen of *α,β*-unsaturated ketone, making the LUMO activation of chalcone. 1,4-addition of aryl acetylene to the LUMO activated chalcone, followed by cyclisation of oxygen to phenylacetylene in (4+2) manner leads to the unstable product 4*H*-pyran, which on air-oxidation leads to the product C.

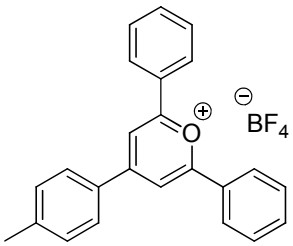
Characterisation of the products

2,4,6-triphenylpyrylium tetrafluoroborate (3a)



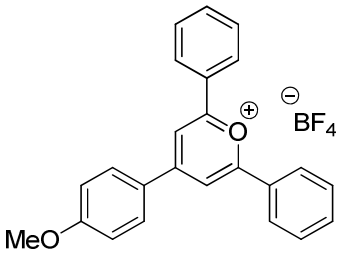
Yield: 62 mg, 65% yield as yellow solid; mp = 225 - 227 °C (232 – 233.5 °C)[3]; **IR (neat, cm^{-1}):** 3069, 2923, 1621, 1592, 1468, 1272, 1194, 1049, 986, 763; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 7.84 - 7.88 (m, 6H), 7.94 (t, *J* = 7.5 Hz, 3H), 8.67 (d, *J* = 7.5 Hz, 6H), 9.24 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d_6):** δ 115.1, 128.8, 129.1, 129.8, 129.9, 130.0, 132.4, 135.0, 135.2, 165.1, 170.0; **HRMS** Calcd. for $C_{23}H_{17}O^+$ ([M^+]): 309.1273, Found: 309.1284.

2,6-diphenyl-4-(*p*-tolyl)pyrylium tetrafluoroborate (3b)



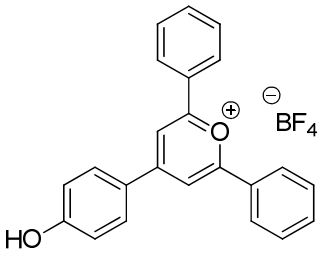
Yield: 69 mg, 70% yield as yellow solid; mp = 257 - 259 °C (263 – 264 °C)[3]; **IR (neat, cm^{-1}):** 2920, 2851, 1624, 1599, 1491, 1254, 1195, 1060, 1027, 822; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 2.53 (s, 3H), 6.63 (d, *J* = 8.0 Hz, 2H), 7.81 (t, *J* = 8.0 Hz, 4H), 7.89 (t, *J* = 7.5 Hz, 2H), 8.59 (t, *J* = 8.5 Hz, 6H), 9.41 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d_6):** δ 21.4, 114.3, 128.7, 129.1, 129.5, 129.8, 130.2, 130.6, 134.9, 147.0, 164.6, 169.7; **^{19}F NMR (471 MHz, DMSO-d_6):** δ -148.21, -148.26; **HRMS** Calcd. for $C_{24}H_{19}O^+$ ([$M]^+$): 323.1430. Found: 323.1437.

4-(4-methoxyphenyl)-2,6-diphenylpyrylium tetrafluoroborate (3c)



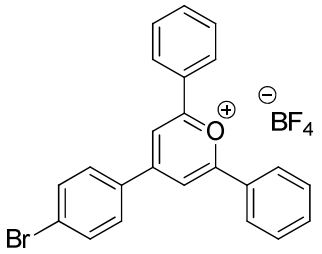
Yield: 57 mg, 56% yield as red orange solid; mp = 218 – 220 °C (238 – 240 °C)[4]; **IR (neat, cm^{-1}):** 3063, 2924, 2850, 1629, 1576, 1442, 1246, 1186, 1055, 836; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 4.01(s, 3H), 7.34 (d, *J* = 9.0 Hz, 2H), 7.79 (t, *J* = 8.0 Hz, 4H), 7.86 (t, *J* = 7.5 Hz, 2H), 8.57 (d, *J* = 7.5 Hz, 4H), 8.72 (d, *J* = 9.0 Hz, 2H) 9.06 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d_6):** δ 61.5, 120.9, 129.6, 133.7, 134.5, 135.0, 139.9, 168.8, 171.1, 174.1 ; **^{19}F NMR (471 MHz, DMSO-d_6):** δ -148.20, -148.26; **HRMS** Calcd. for $C_{24}H_{19}O_2^+$ ([M]$^+$): 339.1380. Found: 339.1390.

4-(4-hydroxyphenyl)-2,6-diphenylpyrylium tetrafluoroborate (3d)



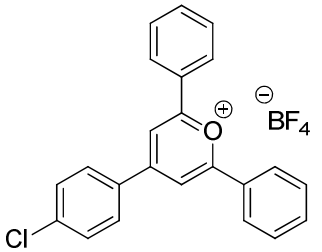
Yield: 66 mg, 67% yield as red-orange solid; mp = 282 - 285 °C; **IR (neat, cm^{-1}):** 3343, 2972, 1633, 1596, 1491, 1277, 1188, 1120, 1069, 844; **^{1}H NMR (500 MHz, DMSo-d_6):** δ 7.13 (d, *J* = 9.0 Hz, 2H), 7.79 (t, *J* = 7.5 Hz, 4H), 7.85 (t, *J* = 7.5 Hz, 2H), 8.55 (d, *J* = 7.0 Hz, 4H), 8.65 (d, *J* = 9.0 Hz, 2H) 8.99 (s, 2H), 11.41 (brs, 1H); **^{13}C NMR (125 MHz, DMSO-d_6):** δ 112.5, 117.1, 122.8, 128.3, 129.3, 129.7, 133.6, 134.5, 163.4, 165.7, 168.3; **^{19}F NMR (471 MHz, DMSO-d_6):** δ -148.20, -148.26; **HRMS** Calcd. for $C_{23}H_{17}O_2^+$ ([M]$^+$): 325.1223. Found: 325.1239.

4-(4-bromophenyl)-2,6-diphenylpyrylium tetrafluoroborate (3e)



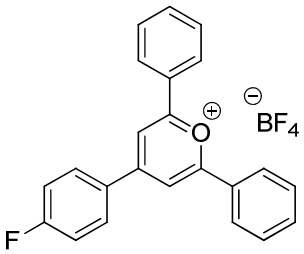
Yield: 55 mg, 48% yield as yellow solid; Mp = 260 - 262 °C (284 – 286 °C)[5]; **IR (neat, cm^{-1}):** 3057, 2920, 1617, 1578, 1490, 1275, 1193, 1065, 777, 683; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.82 (t, *J* = 8.0 Hz, 4H), 7.89 (t, *J* = 7.5 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 8.57 (d, *J* = 8.5 Hz, 2H), 8.61 (d, *J* = 7.5 Hz, 4H), 9.19 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 115.1, 128.8, 129.1, 129.9, 131.6, 131.8, 132.9, 135.1, 163.9, 170.2; **^{19}F NMR (471 MHz, DMSO-d$_6$):** δ -148.21, -148.26; **HRMS** Calcd. for $C_{23}H_{16}BrO^+$ ([M(^{79}Br)]$^+$): 387.0379. Found: 387.0384; ([M(^{81}Br)]$^+$): 389.0364. Found: 389.0363.

4-(4-chlorophenyl)-2,6-diphenylpyrylium tetrafluoroborate (3f)



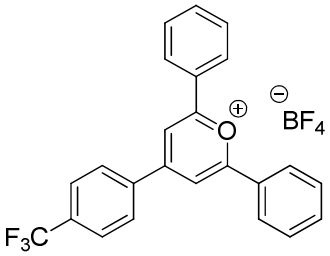
Yield: 45 mg, 51% yield as yellow solid; mp = 253 - 255 °C **IR (neat, cm^{-1}):** 2921, 1622, 1587, 1492, 1248, 1093, 1047, 825, 778, 731; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.82 (t, *J* = 8.0 Hz, 4H), 7.88 - 7.92 (m, 4H), 8.61 (d, *J* = 7.5 Hz, 4H), 8.66 (d, *J* = 9.0 Hz, 2H), 9.19 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 115.2, 128.8, 129.1, 129.8, 129.9, 131.8, 135.2, 163.7, 170.2; **HRMS** Calcd. for $C_{23}H_{16}ClO^+$ ([M(^{35}Cl)]$^+$): 343. 0884. Found: 343.0893; ([M(^{37}Cl)]$^+$): 345.0860. Found: 345.0864.

4-(4-fluorophenyl)-2,6-diphenylpyrylium tetrafluoroborate (3g)



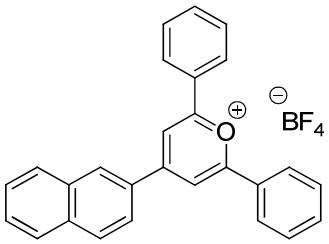
Yield: 64 mg, 64% yield as yellow solid; mp = 208 - 210 °C; **IR (neat, cm^{-1}):** 3062, 2972, 1624, 1493, 1269, 1166, 1120, 1036, 830, 777; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.68 (t, *J* = 8.5 Hz, 2H), 7.81 (t, *J* = 7.5 Hz, 4H), 7.88 (t, *J* = 7.5 Hz, 2H), 8.59 (d, *J* = 7.5 Hz, 4H), 8.72 - 8.75 (m, 2H), 9.16 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 114.9, 117.1, 117.2, 128.8, 129.1, 129.9, 133.2, 133.3, 135.1, 163.8, 166.5 (d, *J* = 255.0 Hz), 169.9; **^{19}F NMR (471 MHz, DMSO-d$_6$):** δ -102.40, -112.07, -148.20, -148.26; **HRMS** Calcd. for $C_{23}H_{16}FO^+$ ([M]$^+$): 327.1180. Found: 327.1189.

2,6-diphenyl-4-(4-(trifluoromethyl)phenyl)pyrylium tetrafluoroborate (3h)



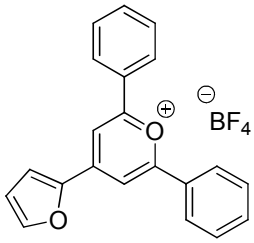
Yield: 52 mg, 47% yield as yellow solid; mp = 245 – 247 °C; **IR (neat, cm^{-1}):** 3109, 3077, 1622, 1495, 1322, 1270, 1171, 1065, 1034, 836; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.59 (t, *J* = 8.0 Hz, 4H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 8.39 (d, *J* = 7.5 Hz, 4H), 8.52 (d, *J* = 8.5 Hz, 2H) 9.03 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 116.3, 126.5, 128.9, 129.9, 130.7, 135.3, 136.5, 163.7, 170.7; **^{19}F NMR (471 MHz, DMSO-d$_6$):** δ -61.09, -61.55, -148.21, -148.26; **HRMS** Calcd. for $C_{24}H_{16}F_3O^+$ ([M]$^+$): 377.1148. Found: 377.1159.

4-(naphthalen-2-yl)-2,6-diphenylpyrylium tetrafluroborate (3i)



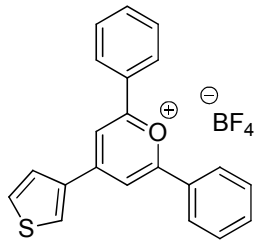
Yield: 62 mg, 58% yield as pale red solid; mp = 190 – 193 ^{o}C; **IR (neat, cm^{-1}):** 3061, 3029, 1611, 1579, 1492, 1273, 1223, 1158, 777; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.76 (t, *J* = 7.5 Hz, 1H), 7.79 - 7.84 (m, 5H), 7.89 (t, *J* = 7.5 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 8.62 (d, *J* = 8.0 Hz, 5H), 9.27 (s, 2H), 9.35 (s, 1H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 115.0, 124.8, 127.8, 127.9, 128.8, 129.2, 129.5, 129.8, 129.9, 130.3, 132.5, 132.6, 135.0, 135.8, 164.7, 169.8; **^{19}F NMR (471 MHz, DMSO-d$_6$):** δ -148.20, -148.25; **HRMS** Calcd. for $C_{27}H_{19}O^{+}$ ([M]$^{+}$): 359.1430 Found: 359.1443.

4-(furan-2-yl)-2,6-diphenylpyrylium tetrafluoroborate (3j)



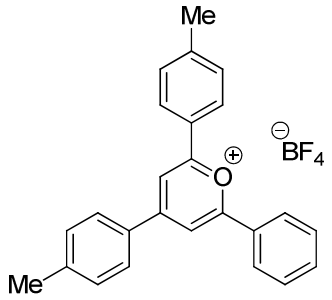
Yield: 65 mg, 71% yield as greenish black solid; mp = 202 - 204 ^{o}C; **IR (neat, cm^{-1}):** 3120, 3061, 1626, 1581, 1495, 1377, 1266, 1063, 946, 766; **^{1}H NMR (500 MHz, CD$_3$CN):** δ 7.06 (dd, *J* = 4.0 Hz, 2.0 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 4H), 7.86 (t, *J* = 7.5 Hz, 2H), 8.18 (d, *J* = 4.0 Hz, 1H), 8.26 (d, *J* = 1.0 Hz, 1H), 8.36 - 8.38 (m, 4H), 8.49 (s, 2H); **^{13}C NMR (125 MHz, CD$_3$CN):** δ 111.6, 117.5, 126.6, 129.3, 130.1, 130.9, 136.1, 149.6, 154.7, 170.9; **^{19}F NMR (471 MHz, DMSO-d$_6$):** δ -148.20, -148.26; **HRMS** Calcd. for $C_{21}H_{15}O_2^{+}$ ([M]$^{+}$): 299.1067. Found: 299.1077.

2,6-diphenyl-4-(thiophen-3-yl)pyrylium tetrafluroborate (3k)



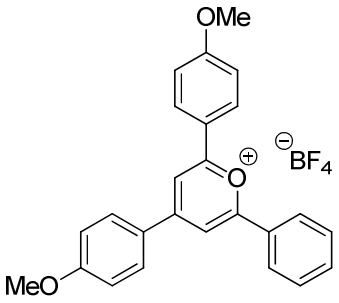
Yield: 65 mg, 67% yield as black solid; mp = 205 - 207 ^{o}C; **IR (neat, cm^{-1}):** 3104, 3062, 1622, 1579, 1492, 1270, 1221, 1055, 775, 700; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.82 (t, *J* = 8.0 Hz, 4H), 7.87 (t, *J* = 7.5 Hz, 2H), 8.04 (dd, *J* = 5.0 Hz, 2 Hz, 1H), 8.43 (dd, *J* = 5.0 Hz, 1.0 Hz, 1H), 8.56 (d, *J* = 7.5 Hz, 4H), 9.06 (s, 2H), 9.49 - 9.51 (m, 1H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 113.9, 127.6, 128.5, 129.2, 129.9, 134.9, 136.1, 138.2, 158.2, 169.7; **HRMS** Calcd. for $C_{21}H_{15}OS^{+}$ ([M]$^{+}$): 315.0838. Found: 315.0849.

2-phenyl-4,6-di-*p*-tolylpyrylium tetrafluoroborate (3l)



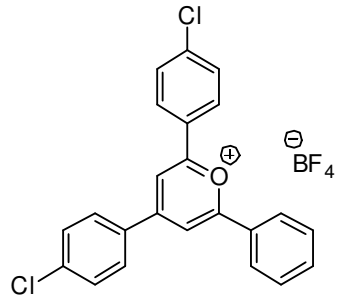
Yield: 49 mg, 48% yield as orange solid; mp = 214 - 216 ^{o}C; **IR (neat, cm^{-1}):** 3124, 2923, 2855, 1624, 1599, 1491, 1228, 1192, 1055, 818; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 2.49 (s, 6H), 7.56 (t, *J* = 7.0 Hz, 4H), 7.77 (t, *J* = 7.5 Hz, 2H), 7.85 (t, *J* = 7.5 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 2H), 8.49 - 8.53 (m, 4H), 8.99 (d, *J* = 3.5 Hz, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 21.3, 21.4, 113.7, 113.8, 126.3, 128.5, 128.7, 129.1, 129.5, 129.8, 130.0, 130.5, 130.5, 134.7, 146.3, 146.9, 164.2, 169.1, 169.8; **HRMS** Calcd. for $C_{25}H_{21}O^{+}$ ([M]$^{+}$): 337.1587. Found: 337.1597.

2,4-bis(4-methoxyphenyl)-6-phenylpyrylium tetrafluoroborate (3m)



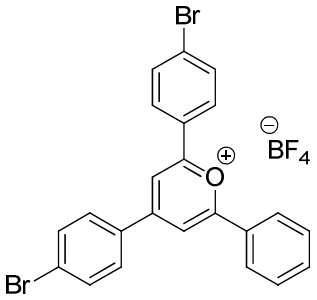
Yield: 56 mg, 51% yield as pale red solid; mp = 245 - 247 °C; **IR (neat, cm^{-1}):** 3161, 3073, 2923, 1629, 1589, 1467, 1246, 1056, 951, 836; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 3.98 - 3.99 (m, 6H), 7.31 - 7.33 (m, 4H), 7.77 (t, *J* = 8.0 Hz, 2H), 7.83 (t, *J* = 7.0 Hz, 1H), 8.52 (d, *J* = 7.5 Hz, 2H), 8.56 (d, *J* = 8.5 Hz, 2H), 8.67 (d, *J* = 9.0 Hz, 2H), 8.93 (d, *J* = 7.5 Hz, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 56.0, 56.1, 111.9, 115.4, 121.3, 124.3, 128.1, 129.3, 129.7, 131.0, 132.7, 134.3, 162.5, 164.8, 165.5, 167.5, 168.9; **^{19}F NMR (471 MHz, DMSO-d$_6$):** δ -148.20, -148.26; **HRMS** Calcd. for $C_{25}H_{21}O_3^+$ ([M]$^+$): 369.1485. Found: 369.1496.

2,4-bis(4-chlorophenyl)-6-phenylpyrylium tetrafluoroborate (3n)



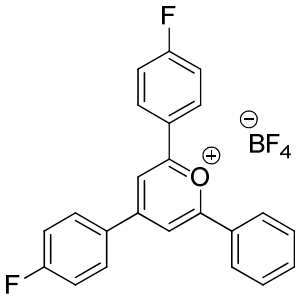
Yield: 56 mg, 50% yield as yellow solid; mp = 243 - 245 °C; **IR (neat, cm^{-1}):** 3070, 2922, 1621, 1586, 1490, 1226, 1121, 1051, 829, 723; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.81 (t, *J* = 8.0 Hz, 2H), 7.87 - 7.89 (m, 5H), 8.59 (t, *J* = 9.0 Hz, 4H), 8.64 (d, *J* = 8.5 Hz, 2H), 9.18 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 115.3, 127.9, 128.8, 128.9, 129.8, 130.0, 130.5, 131.1, 131.8, 135.3, 140.3, 140.6, 163.7, 169.0, 170.3; **HRMS** Calcd. for $C_{23}H_{15}Cl_2O^+$ ([M(^{35}Cl)]$^+$): 377.0494. Found: 377.0509; ([M(^{37}Cl)]$^+$): 379.0470. Found: 379.0480.

2,4-bis(4-bromophenyl)-6-phenylpyrylium tetrafluoroborate (3o)



Yield: 48 mg, 36% yield as yellow solid; mp = 255 - 257 °C; **IR (neat, cm^{-1}):** 3063, 2922, 1622, 1581, 1493, 1266, 1244, 1055, 821, 722; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.82 (t, *J* = 7.5 Hz, 2H), 7.89 (t, *J* = 7.5 Hz, 1H), 8.04 (dd, *J* = 8.5 Hz, 4.0 Hz, 4H), 8.52 - 8.61 (m, 6H), 9.20 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 115.2, 115.3, 128.3, 128.9, 129.0, 129.5, 129.9, 130.1, 130.5, 131.5, 131.8, 132.9, 133.0, 135.3, 163.9, 169.2, 170.4; **HRMS** Calcd. for $C_{23}H_{15}Br_2O^+$ ([M(^{79}Br]$^+$): 464.9484. Found: 464.9489; ([M(^{81}Br)]$^+$): 466.9469. Found: 466.9468.

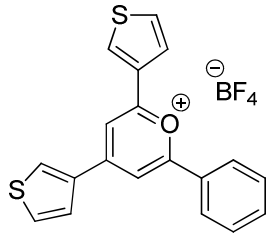
2,4-bis(4-fluorophenyl)-6-phenylpyrylium tetrafluoroborate (3p)



Yield: 59 mg, 57% yield as yellow solid; mp = 190 – 192 °C; **IR (neat, cm^{-1}**): 3068, 2923, 1626, 1595, 1496, 1271, 1165, 1051, 834, 774; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.66 - 7.71 (m, 4H), 7.81 (t, *J* = 8.0 Hz, 2H), 7.89 (t, *J* = 7.5 Hz, 1H), 8.59 (d, *J* = 7.0 Hz, 2H), 8.68 - 8.71 (m, 2H), 8.72 - 8.75 (m, 2H), 9.15 (d, *J* = 2.0 Hz, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 114.7, 114.8, 117.1, 117.1, 117.2, 117.3, 125.8, 128.8, 128.9, 129.0, 129.8, 131.9, 132.0, 133.2, 133.3, 135.1, 163.7, 166.1 (d, *J* =

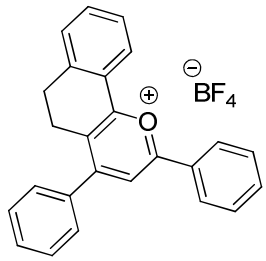
258.8 Hz), 166.5 (d, *J* = 255.0 Hz), 169.0, 169.9; **HRMS** Calcd. for $C_{23}H_{15}F_2O^+$ ($[M]^+$): 345.1085. Found: 345.1092.

2-phenyl-4,6-di(thiophen-3-yl)pyrylium tetrafluoroborate (3q)



Yield: 74 mg, 76% yield as black solid; mp = 219 – 221 °C; **IR (neat, cm^{-1}):** 3106, 2964, 1622, 1513, 1445, 1264, 1224, 1059, 889, 765; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.67 (t, *J* = 8.0 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.90 - 7.93 (m, 2H), 8.11 (dd, *J* = 5.0 Hz, 1.0 Hz, 1H), 8.26 (d, *J* = 5.0 Hz, 1H), 8.43 (d, *J* = 7.5 Hz, 2H), 8.79 (d, j = 1.0 Hz, 1H), 8.85 (s, 1H), 9.11 (d, *J* = 1.5 Hz, 1H), 9.30 (d, *J* = 1.5 Hz, 1H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 113.1, 113.8, 126.4, 127.5, 128.3, 129.0, 129.7, 129.9, 132.0, 134.6, 135.3, 136.1, 137.7, 157.9, 165.6, 168.5; **HRMS** Calcd. for $C_{19}H_{13}OS_2^+$ ($[M]^+$): 321.0402. Found: 321.0412.

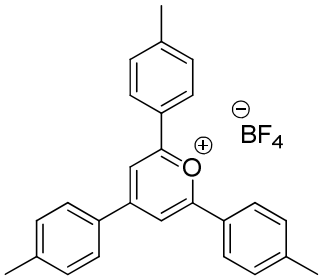
2,4-diphenyl-5,6-dihydrobenzo[*h*]chromen-1-ium tetrafluoroborate (3r)



Yield: 48 mg, 48% yield as yellow solid; mp = 248 - 250 °C; **IR (neat, cm^{-1}):** 3066, 2851, 1612, 1596, 1493, 1386, 1243, 1053, 881, 728; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 3.09 (t, *J* = 7.0 Hz, 2H), 3.25 (t, *J* = 6.5 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.73 - 7.82 (m, 6H), 7.83 - 7.87 (m, 3H), 8.44 (d, *J* = 7.0 Hz, 1H), 8.55 (dd, *J* = 7.5 Hz, 1.5 Hz, 2H), 8.84 (s, 1H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 24.2, 25.7, 119.1, 125.9, 126.8, 128.4, 128.4, 128.8, 128.9, 129.2, 129.3, 129.4,

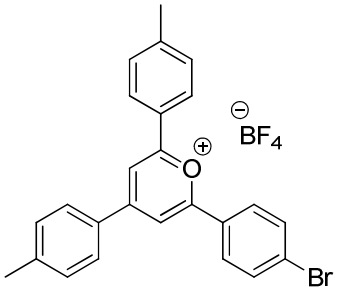
129.9, 132.1, 134.0, 134.7, 135.6, 142.0, 165.8, 166.6, 167.4; **HRMS** Calcd. for $C_{25}H_{19}O^+$ ([M]$^+$): 335.1430. Found: 335.1435.

2,4,6-tri-*p*-tolylpyrylium tetrafluoroborate (3t)



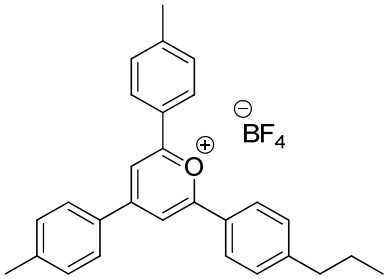
Yield: 67 mg, 64% yield as orange colour solid; mp = 275 – 280 °C (312 °C)[6,7]; **IR (neat, cm^{-1})**: 3129, 3039, 2921, 1624, 1599, 1494, 1256, 1191, 1055, 817; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.54 - 7.57 (m, 6H), 8.42 (d, *J* = 8.5 Hz, 4H), 8.48 (d, *J* = 8.5 Hz, 2H), 8.94 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 21.4, 21.4, 113.3, 126.4, 128.5, 129.9, 130.4, 146.1, 146.7, 163.9, 169.3; **HRMS** Calcd. for $C_{26}H_{23}O^+$ ([M]$^+$): 351.1743. Found: 351.1749.

2-(4-bromophenyl)-4,6-di-*p*-tolylpyrylium tetrafluoroborate (3u)



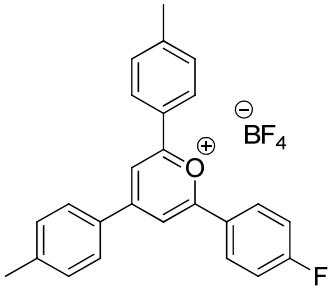
Yield: 62 mg, 52% yield as orange colour solid; mp = 270 – 272 °C; **IR (neat, cm^{-1})**: 3109, 3030, 2854, 1624, 1598, 1498, 1230, 1192, 1055, 1004; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.61 (d, *J* = 8.5 Hz, 4H), 8.02 (d, *J* = 9.0 Hz, 2H), 8.49 (dd, *J* = 9.0 Hz, 3.5 Hz, 4H), 8.55 (d, *J* = 8.5 Hz, 2H), 9.09 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 21.4, 21.5, 113.9, 126.2, 128.3, 128.7, 129.1, 129.4, 130.1, 130.2, 130.5, 130.5, 132.8, 146.5, 147.1, 164.2, 168.0, 169.9; **HRMS** Calcd. for $C_{25}H_{20}BrO^+$ ([M(^{79}Br)]$^+$): 415.0692. Found: 415.0645; ([M(^{81}Br)]$^+$): 417.0677. Found: 417.0692.

2-(4-n-propylphenyl)-4,6-di-*p*-tolylpyrylium tetrafluoroborate (3v)



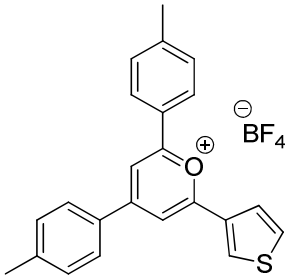
Yield: 66 mg, 59% yield as orange colour solid; mp = 252 – 254 °C; **IR (neat, cm^{-1})**: 3114, 3039, 2928, 2869, 1625, 1600, 1496, 1273, 1055, 818; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 0.95 (t, *J* = 7.5 Hz, 3H), 1.69 (st, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 8.0 Hz, 2H), 7.58 - 7.62 (m, 6H), 8.45 - 8.48 (m, 4H), 8.52 (d, *J* = 8.0 Hz, 2H), 9.00 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 13.6, 21.4, 21.4, 23.6, 37.2, 113.2, 113.3, 126.3, 126.6, 128.5, 128.6, 129.4, 129.8, 129.9, 130.4, 146.1, 146.7, 150.4, 163.8, 169.3; **^{19}F NMR (471 MHz, DMSO-d$_6$):** δ -148.21, -148.26; **HRMS** Calcd. for $C_{28}H_{27}O^+$ ([M]$^+$): 379.2056. Found: 379.2055.

2-(4-fluorophenyl)-4,6-di-*p*-tolylpyrylium tetrafluoroborate (3w)



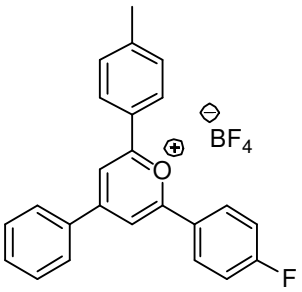
Yield: 47 mg, 44% yield as orange colour solid; mp = 242 – 244 °C; **IR (neat, cm^{-1})**: 2968, 2922, 1626, 1599, 1492, 1348, 1194, 1165, 1055, 845; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.61 (d, *J* = 8.0 Hz, 4H), 7.66 (t, *J* = 8.5 Hz, 2H), 8.48 (d, *J* = 8.5 Hz, 2H), 8.54 (d, *J* = 8.5 Hz, 2H), 8.66 (d, *J* = 9.0 Hz, 5.5 Hz, 2H), 9.05 (d, *J* = 2.0 Hz, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 21.4, 21.4, 113.5, 113.6, 117.0, 117.2, 125.8, 126.3, 128.7, 129.4, 130.0, 130.4, 130.5, 131.6, 131.7, 146.3, 146.9, 164.2, 165.9 (d, *J* = 257.5 Hz), 168.1, 169.7; **HRMS** Calcd. for $C_{25}H_{20}FO^+$ ([M]$^+$): 355.1493. Found: 355.1501.

2-(thiophen-3-yl)-4,6-di-*p*-tolylpyrylium tetrafluoroborate (3x)



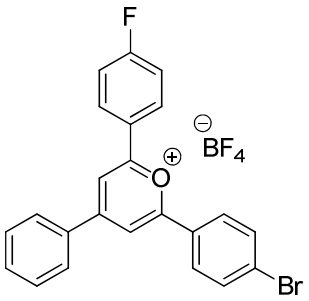
Yield: 101.16 mg, 98% yield as black solid; mp = 232 – 234 °C; **IR (neat, cm^{-1})**: 3108, 2920, 2851, 1625, 1599, 1495, 1266, 1193, 1057, 817; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.60 (t, *J* = 8.5 Hz, 5H), 8.02 (dd, *J* = 5.0 Hz, 3.0 Hz, 1H), 8.23 (d, *J* = 4.0 Hz, 1H), 8.50 (d, *J* = 7.5 Hz, 3H), 8.94 (s, 1H), 8.98 (s, 1H), 9.26 (d, *J* = 1.5 Hz, 1H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 21.4, 21.4, 112.9, 113.6, 126.3, 128.6, 129.5, 129.8, 130.4, 130.5, 132.1, 146.0, 146.6, 164.1, 165.2, 168.8; **HRMS** Calcd. for $C_{23}H_{19}OS^+$ ([M]$^+$): 343.1151. Found: 343.1164.

2-(4-fluorophenyl)-4-phenyl-6-(*p*-tolyl)pyrylium tetrafluoroborate (3y)



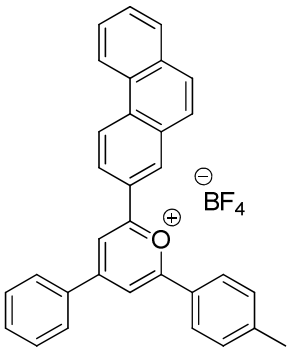
Yield: 52 mg, 51% yield as yellow solid; mp = 220 – 222 °C; **IR (neat, cm^{-1})**: 3106, 2970, 2853, 1633, 1525, 1494, 1274, 1163, 1048, 876; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 8.5 Hz, 2H), 7.78 (t, *J* = 8.0 Hz, 2H), 7.87 (t, *J* = 7.5 Hz, 1H), 8.49 (d, *J* = 8.5 Hz, 2H), 8.57 (d, *J* = 7.5 Hz, 2H), 8.65 – 8.68 (m, 2H), 9.09 (d, *J* = 3.5 Hz, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 21.9, 115.0, 115.1, 117.6, 117.8, 126.4, 126.8, 129.4, 130.3, 130.4, 131.0, 132.3, 132.4, 132.9, 135.6, 146.9, 165.2, 166.5 (d, *J* = 253.8 Hz), 169.1, 170.7; **^{19}F NMR (471 MHz, DMSO-d$_6$):** δ -102.59, -148.21, -148.26; **HRMS** Calcd. for $C_{24}H_{18}FO^+$ ([M]$^+$): 341.1336. Found: 341.1345.

2-(4-bromophenyl)-6-(4-fluorophenyl)-4-phenylpyryliumtetrafluoroborate (3z)



Yield: 67 mg, 57% yield as yellow solid; mp = 244 – 246 °C; **IR (neat, cm^{-1})**: 3072, 2980, 2924, 2852, 1620, 1588, 1494, 1275, 1164, 1051, 840; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.66 (t, *J* = 9.0 Hz, 2H), 7.79 (t, *J* = 8.0 Hz, 2H), 7.88 (t, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 8.51 (d, *J* = 8.5 Hz, 2H), 8.58 (d, *J* = 7.5 Hz, 2H), 8.66 – 8.69 (m, 2H), 9.16 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 115.6, 115.8, 117.6, 117.8, 126.2, 127.5, 128.8, 129.1, 129.9, 130.3, 130.6, 131.0, 132.3, 132.5, 132.6, 132.8, 133.4, 135.8, 165.7, 166.7 (d, *J* = 253.8 Hz), 169.5, 169.8; **^{19}F NMR (471 MHz, DMSO-d$_6$):** δ -102.03, -148.20, -148.26; **HRMS** Calcd. for $C_{23}H_{15}BrFO^+$ ([M(^{79}Br)]$^+$): 405.0284. Found: 405.0304; ([M(^{81}Br)]$^+$): 407.0270. Found: 407.0283.

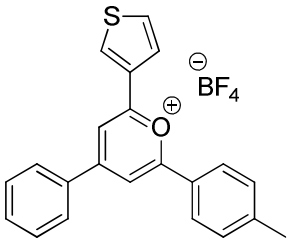
2-(phenanthren-2-yl)-4-phenyl-6-(*p*-tolyl)pyrylium tetrafluoroborate (3aa)



Yield: 80 mg, 65% yield as brick red solid; mp = 196 – 198 °C; **IR (neat, cm^{-1}):** 2923, 2855, 1620, 1496, 1458, 1243, 1193, 1057, 817, 768; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 2.50 (s, 3H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 4.0 Hz, 2H), 7.78 (t, *J* = 7.5 Hz, 2H), 7.87 (t, *J* = 7.0 Hz,1H), 7.96 (d, *J* = 9.0 Hz, 1H), 7.99 – 8.01 (m, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 8.48 (d, *J* = 8.5 Hz, 2H), 8.56 (d, *J* = 7.5 Hz, 2H), 8.61 (d, *J* = 9.0 Hz, 1H), 8.87 – 8.89 (m, 1H), 8.99 (s, 1H), 9.04 (d, *J* = 9.0 Hz, 1H), 9.10 (d, *J* =12.0

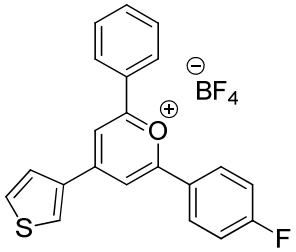
Hz, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** δ 21.9, 114.9, 115.2, 124.5, 125.2, 125.2, 126.7, 127.2, 127.5, 128.1, 129.1, 129.2, 129.3, 130.3, 130.4, 131.0, 131.9, 132.9, 133.3, 134.1, 135.6, 146.9, 164.7, 169.5, 170.4; **HRMS** Calcd. for $C_{23}H_{23}O^+$ ([M]$^+$): 423.1743. Found: 423.1763.

4-phenyl-2-(thiophen-3-yl)-6-(*p*-tolyl)pyrylium tetrafluoroborate (3ab)



Yield: 46 mg, 46% yield as brown yellow solid; mp = 163 – 165 °C; **IR (neat, cm^{-1}):** 2978, 2923, 2857, 1629, 1529, 1496, 1375, 1269, 1194, 1055, 889; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 2.50 (s, 3H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.78 (t, *J* = 8.0 Hz, 2H), 7.86 (t, *J* = 7.5 Hz, 1H), 8.00 – 8.02, (m, 1H), 8.25 (d, *J* = 5.0 Hz, 1H), 8.49 (d, 8.0 Hz, 2H), 8.52 (d, *J* = 7.5 Hz, 2H), 8.96 (d, *J* = 1.0 Hz, 1H), 8.99 (d, *J* = 1.5 Hz, 1H), 9.27 (d, *J* = 1.5 Hz, 1H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** 21.9, 114.9.1, 114.9, 126.8, 127.0, 129.2, 130.2, 130.3, 130.5, 130.9, 132.6, 132.9, 135.4, 136.1, 146.7.9, 164.0, 169.6; **^{19}F NMR (471 MHz, DMSO-d$_6$):** δ -148.19, -148.25; **HRMS** Calcd. for $C_{22}H_{17}OS^+$ ([M]$^+$): 329.0995. Found: 329.1009.

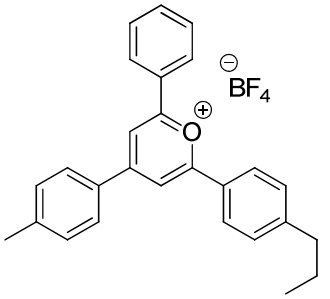
2-(4-fluorophenyl)-6-phenyl-4-(thiophen-3-yl)pyrylium tetrafluoroborate (3ac)



Yield: 60 mg, 59% yield as brown yellow solid; mp = 232 – 234 °C; **IR (neat, cm^{-1}):** 3119, 2976, 2857, 1621, 1600, 1487, 1370, 1273, 1196, 1047, 951; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 7.65 (t, *J* = 9.0 Hz, 2H), 7.78 (t, *J* = 8.0 Hz, 2H), 7.86 (t, *J* = 7.5 Hz, 1H), 8.01 – 8.03 (m, 1H), 8.39 (dd, *J* = 5.5 Hz, 0.5 Hz, 1H), 8.52 (d, *J* = 7.5 Hz,

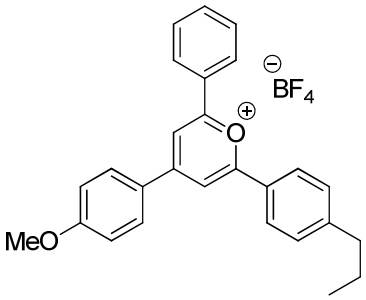
2H), 8.60 – 8.63 (m, 2H), 9.01 (d, *J* = 4.5 Hz, 2H), 9.46 (d, *J* = 1.5 Hz, 1H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** 114.3, 114.4, 117.56, 117.8, 126.3, 126.3, 128.1, 128.9, 129.6, 130.3, 130.6, 132.0, 132.1, 135.3, 136.6, 138.7, 158.6, 166.4 (d, *J* = 253.8 Hz), 169.2, 170.0; **HRMS** Calcd. for $C_{21}H_{14}FOS^+$ ([M]$^+$): 333.0744. Found: 333.0758.

2-phenyl-6-(4-propylphenyl)-4-(*p*-tolyl)pyrylium tetrafluoroborate (3ad)



Yield: 64 mg, 59% yield as orange solid; mp = 208 – 210 °C; **IR (neat, cm^{-1}):** 3045, 2962, 2872, 1626, 1600, 1496, 1343, 1227, 1191, 1056, 880; **^{1}H NMR (500 MHz, DMSO-d$_6$):** δ 0.95 (t, *J* = 7.5 Hz, 3H), 1.69 (st, 7.0 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 7.58 – 7.62 (m, 4H), 7.78 (t, 8.0 Hz, 2H), 7.85 (t, *J* = 7.0 Hz, 1H), 8.49 (d, *J* = 8.5 Hz, 2H), 8.54 (t, *J* = 9.5 Hz, 4H), 9.05 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d$_6$):** 14.0, 21.9, 24.2, 37.8, 114.3, 127.2, 129.1, 129.3, 129.7, 130.0, 130.3, 130.4, 130.6, 131.0, 135.2, 147.3, 151.1, 164.8, 169.7, 170.4; **^{19}F NMR (471 MHz, DMSO-d$_6$):** δ -148.21, -148.26; **HRMS** Calcd. for $C_{27}H_{25}O^+$ ([M]$^+$): 365.1900. Found: 365.1904.

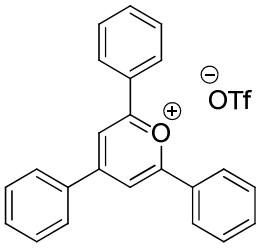
4-(4-methoxyphenyl)-2-phenyl-6-(4-propylphenyl)pyrylium tetrafluoroborate (3ae)



Yield: 63 mg, 56% yield as orange solid; mp = 220 – 222 °C; **IR (neat, cm^{-1}):** 3072, 2961, 2872, 1630, 1592, 1496, 1307, 1246, 1186, 1056, 836; **^{1}H NMR (500 MHz,**

DMSO-d_6): δ 0.93 (t, *J* = 7.5 Hz, 3H), 1.69 (st, 7.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 3.98 (s, 3H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.77 (t, *J* = 8.0 Hz, 2H), 7.84 (t, *J* = 7.0 Hz, 1H), 8.45 (d, *J* = 8.5 Hz, 2H), 8.51 ((d, *J* = 7.5 Hz, 2H), 8.66 (d, *J* = 9.0 Hz, 2H), 8.96 (d, *J* = 1.5 Hz, 2H); **^{13}C NMR (125 MHz, DMSO-d_6):** 14.0, 24.2, 37.7, 56.7, 113.2, 113.3, 116.0, 124.8, 127.3, 128.9, 129.1, 129.8, 130.2, 130.3, 133.4, 134.9, 150.8, 163.7, 166.3, 168.9, 169.6; **^{19}F NMR (471 MHz, DMSO-d_6):** δ -148.20, -148.26; **HRMS** Calcd. for $C_{27}H_{25}O_2^+$ ([M]$^+$): 381.1849. Found: 381.1858.

2,4,6-triphenylpyrylium trifluoromethanesulfonate (4a)



Yield: 56 mg, 48% yield as yellow solid; mp = 252 – 254 °C; **IR (neat, cm^{-1})**: 2920, 2851, 1622, 1594, 1499, 1471, 1254, 1144, 1031, 770, 641; **^{1}H NMR (500 MHz, DMSO-d_6):** δ 7.79 - 7.83 (m, 6H), 7.89 (t, *J* = 7.5 Hz, 3H), 8.62 (d, *J* = 8.0 Hz, 6H), 9.19 (s, 2H); **^{13}C NMR (125 MHz, DMSO-d_6):** δ 115.7, 129.3, 129.6, 130.3, 130.4, 130.5, 132.9, 135.5, 135.7, 165.6, 170.6; **HRMS** Calcd. for $C_{23}H_{17}O^+$ ([M]$^+$): 309.1274. Found: 309.1278.

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Spectra of the products

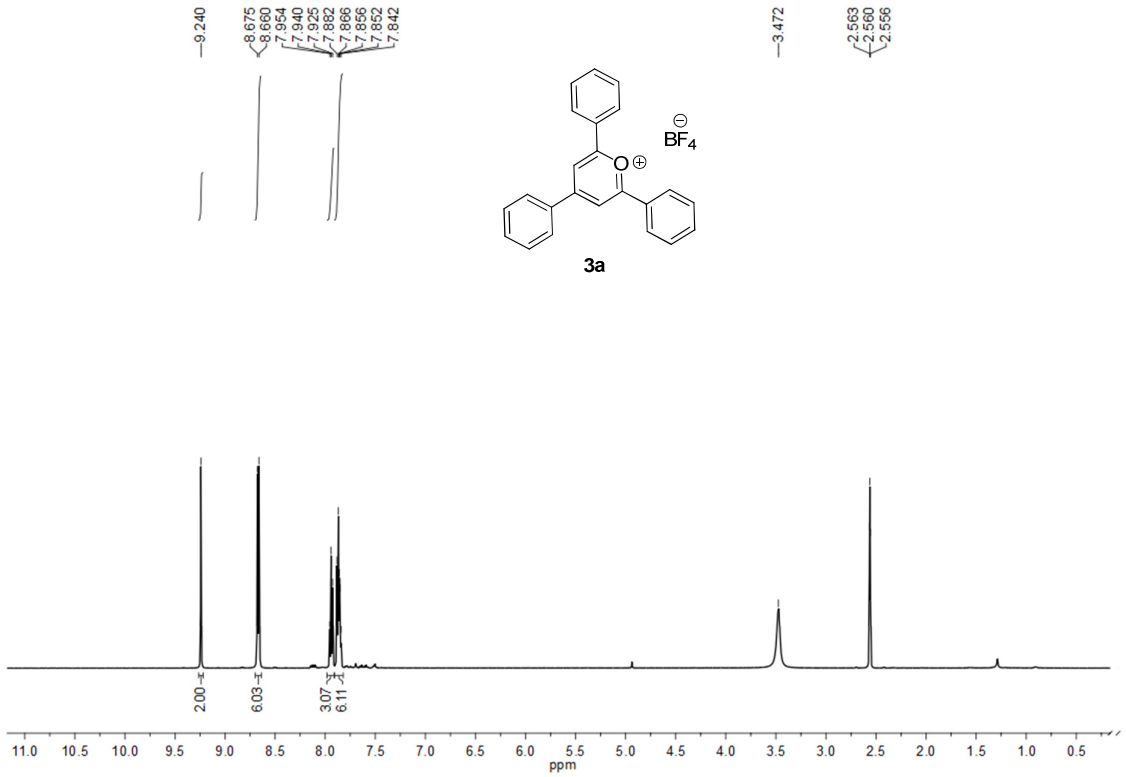

Fig S1. ^{1}H NMR of 3a

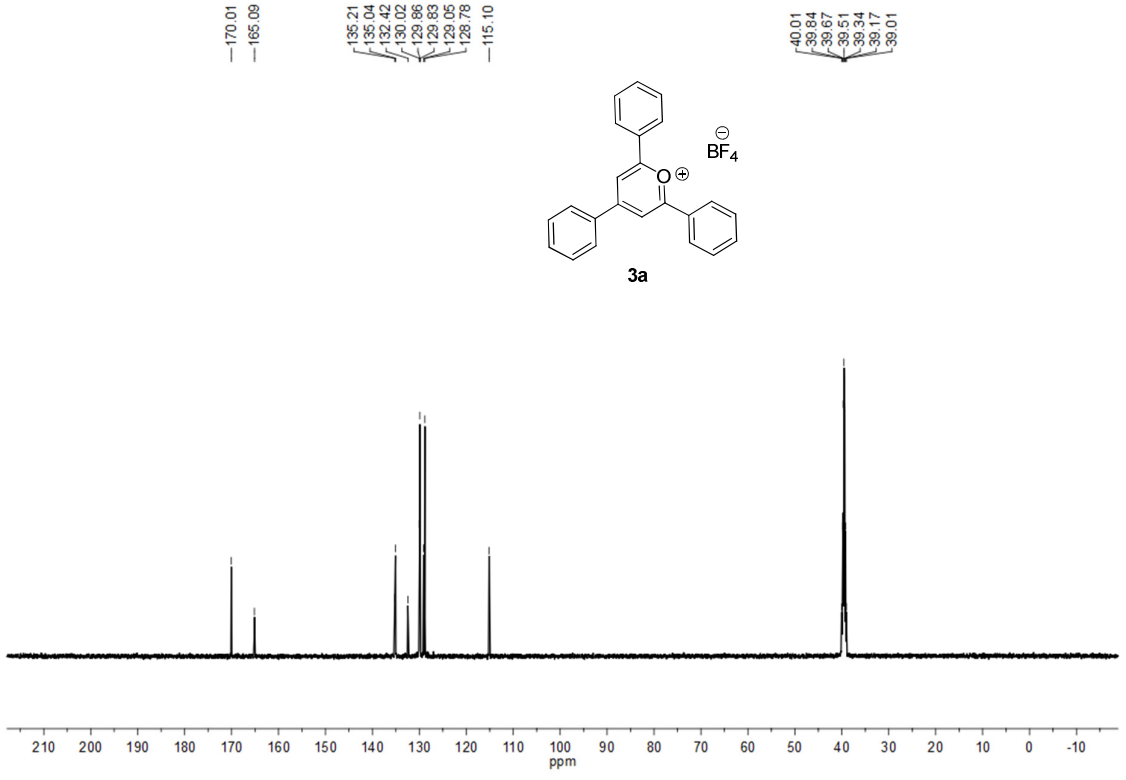

Fig S2. ^{13}C NMR of 3a

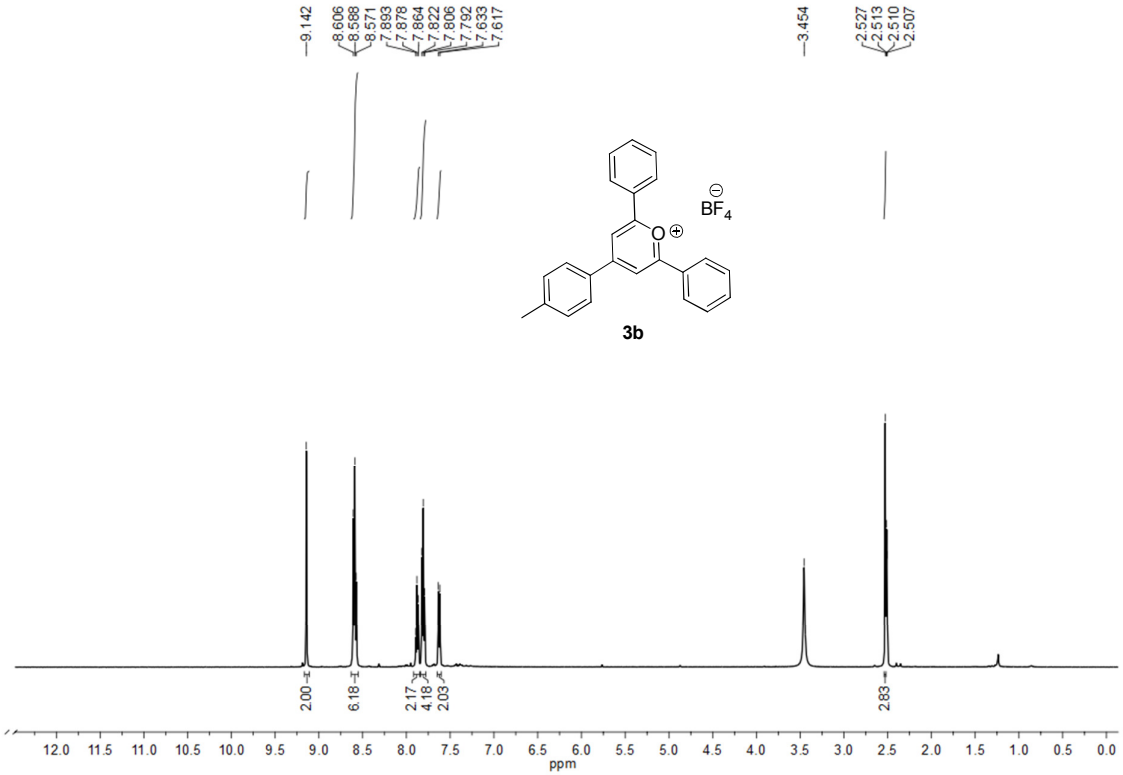

Fig S3. ^{1}H NMR of 3b

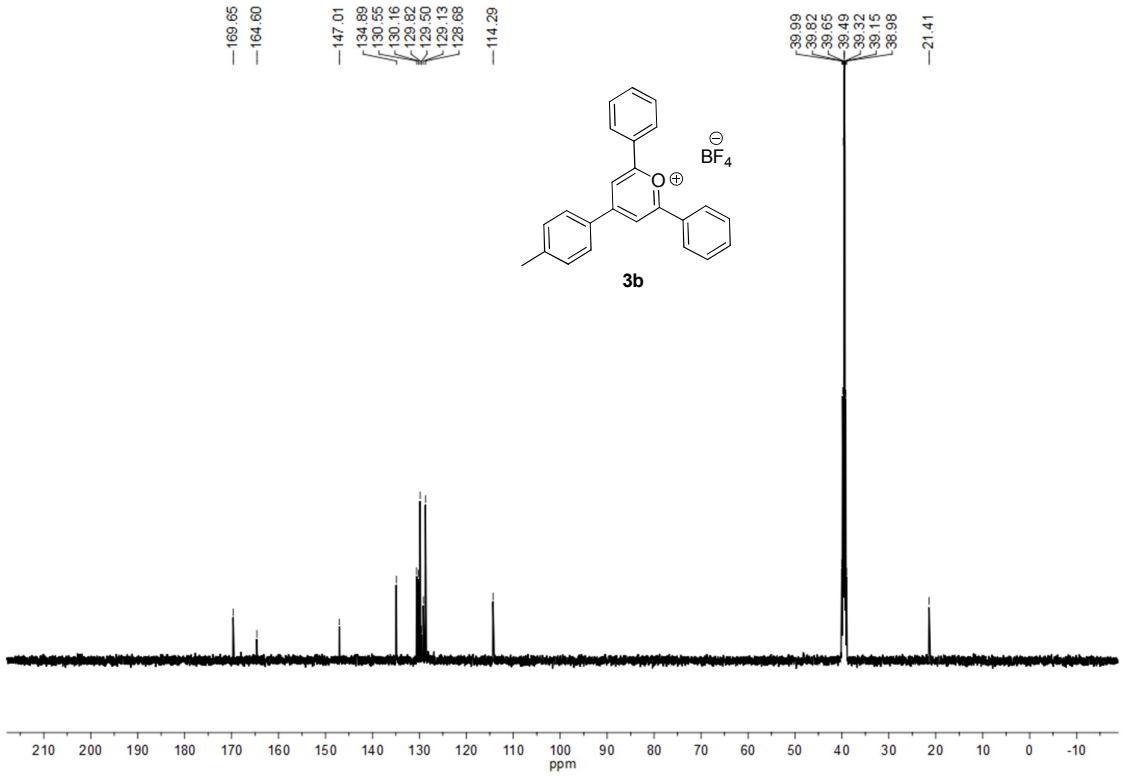

Fig S4. ^{13}C NMR of 3b

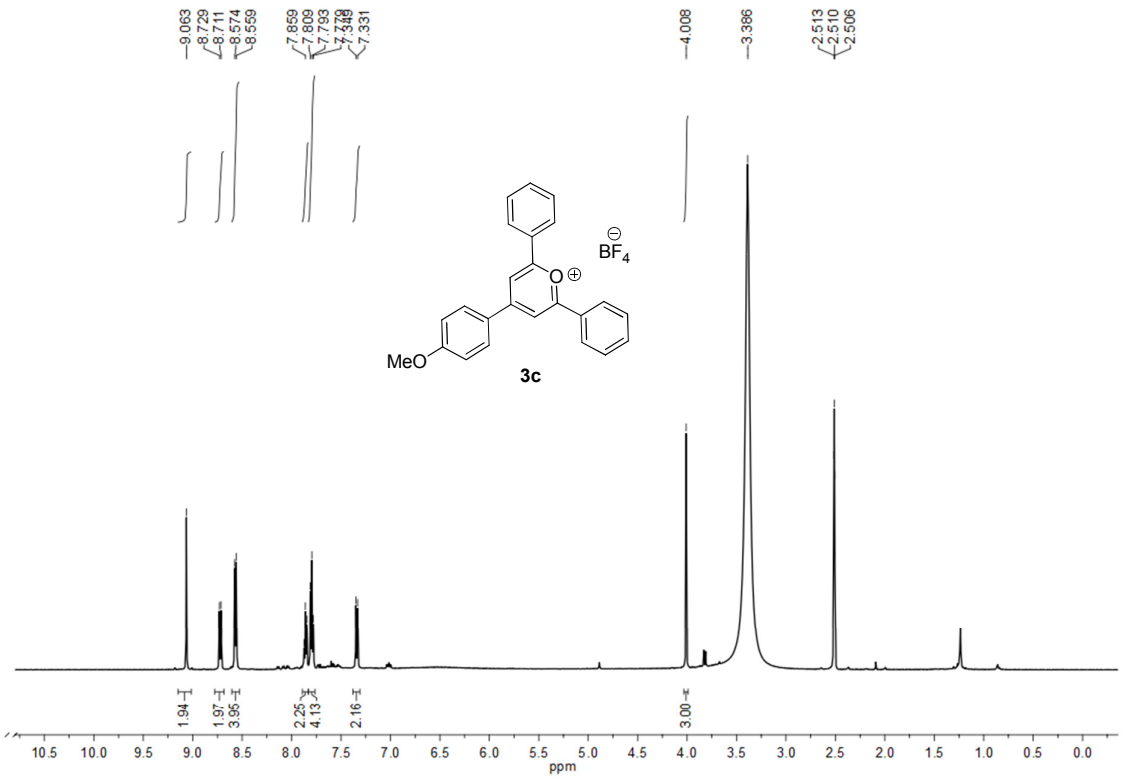

Fig S5. ^{1}H NMR of 3c

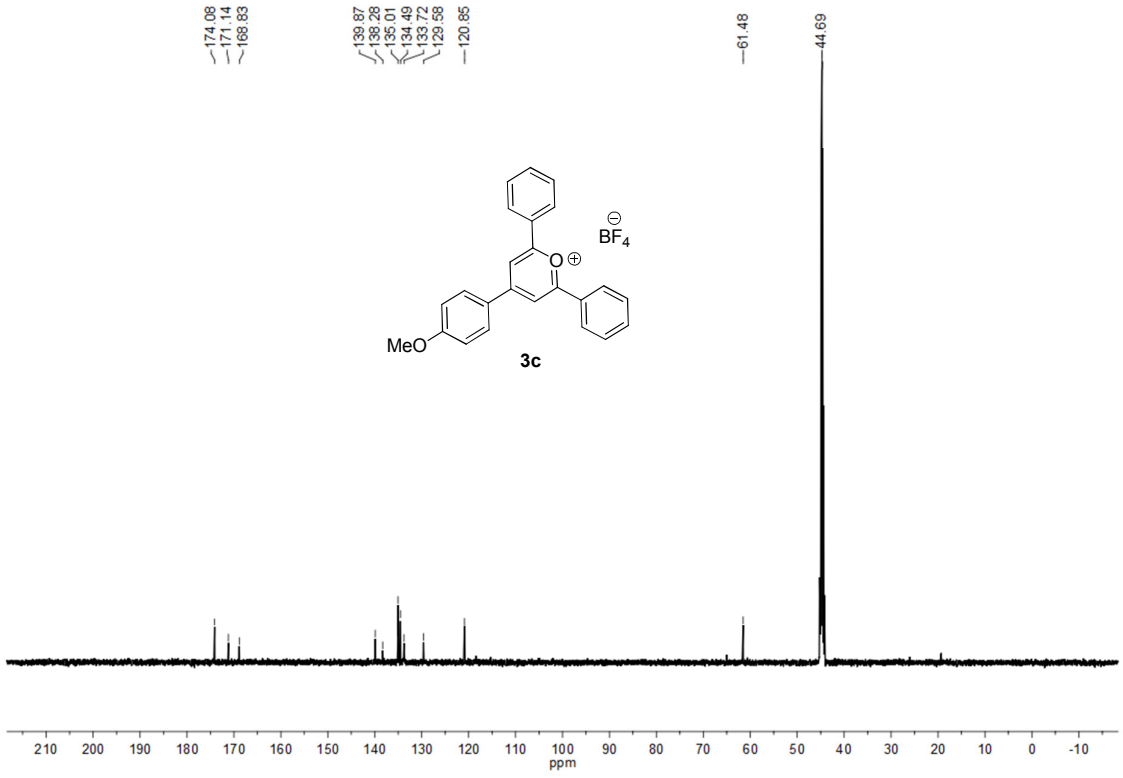

Fig S6. ^{13}C NMR of 3c

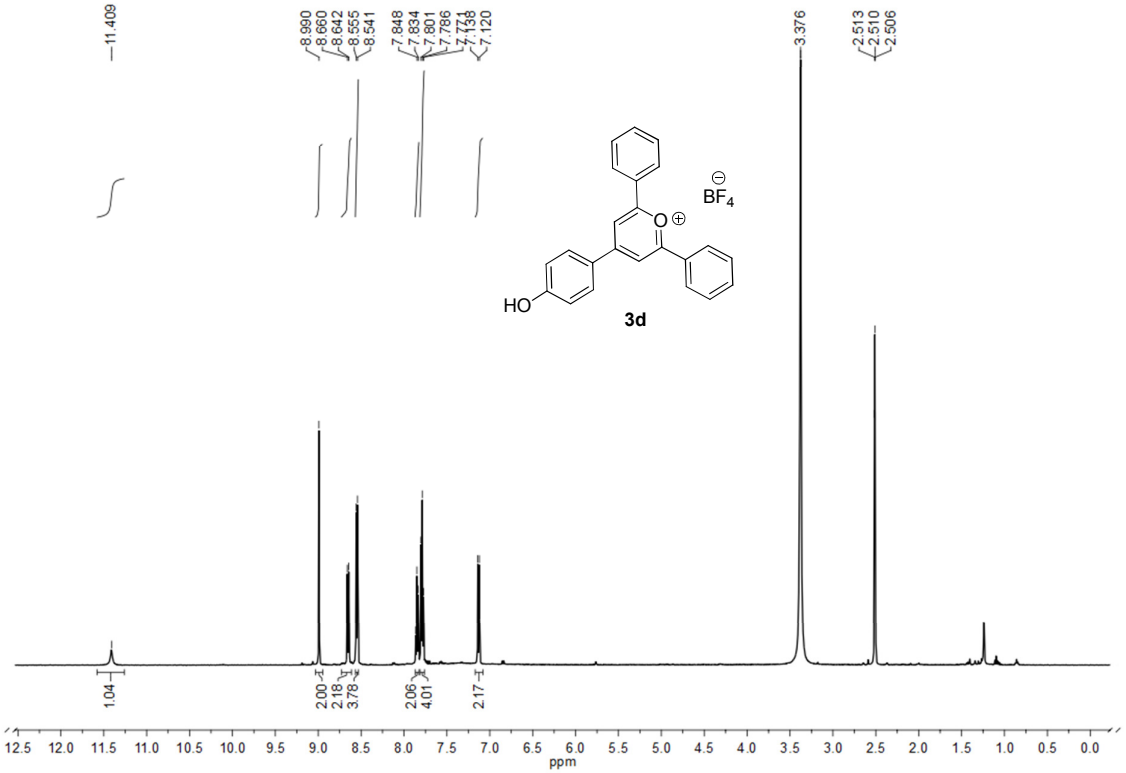

Fig S7. ^{1}H NMR of 3d

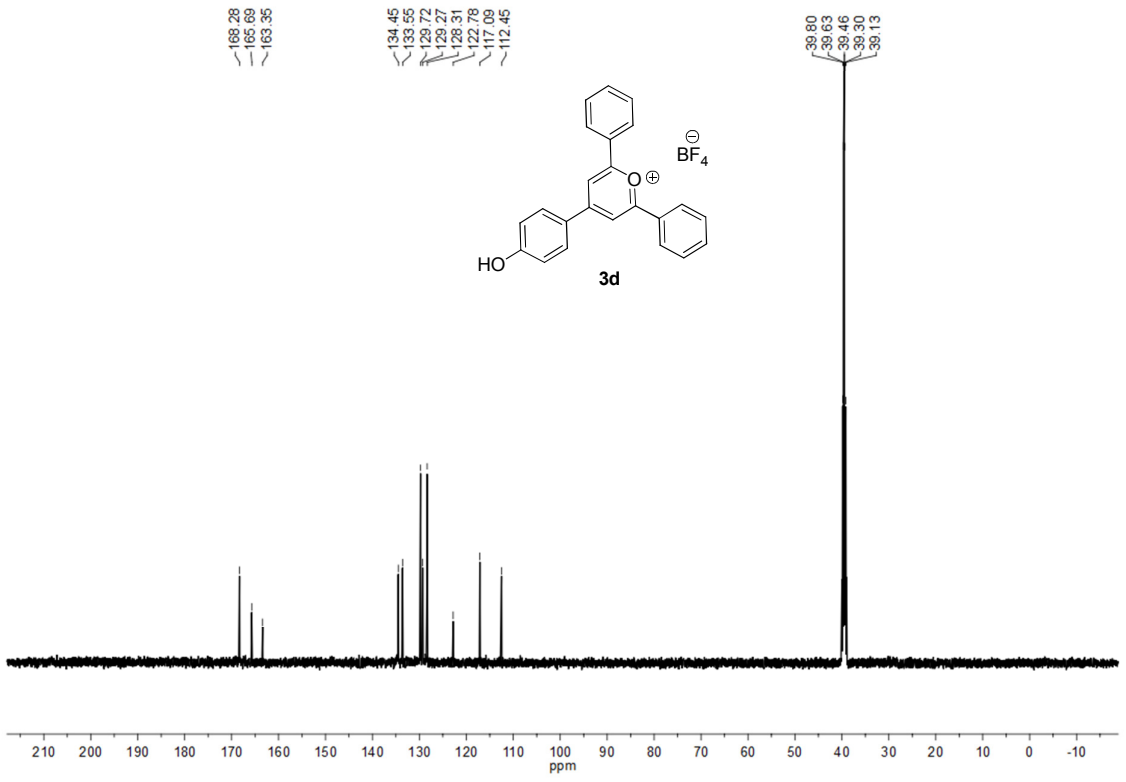

Fig S8. ^{13}C NMR of 3d

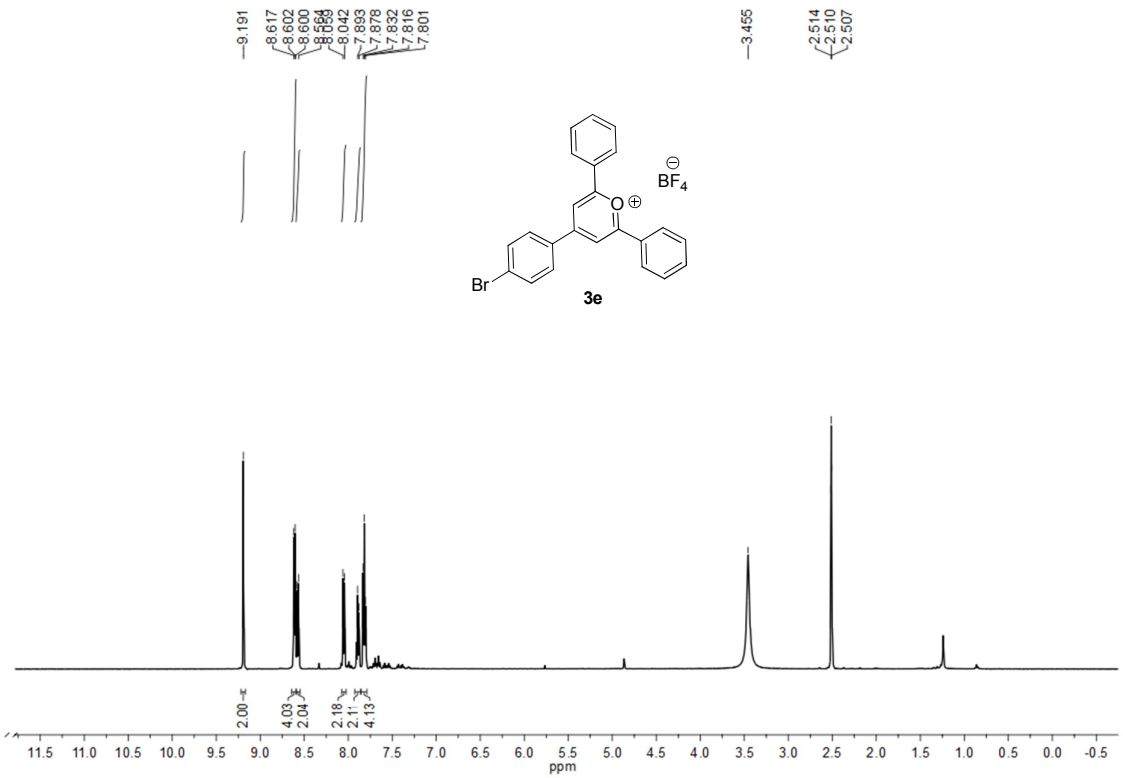

Fig S9. ^{1}H NMR of 3e

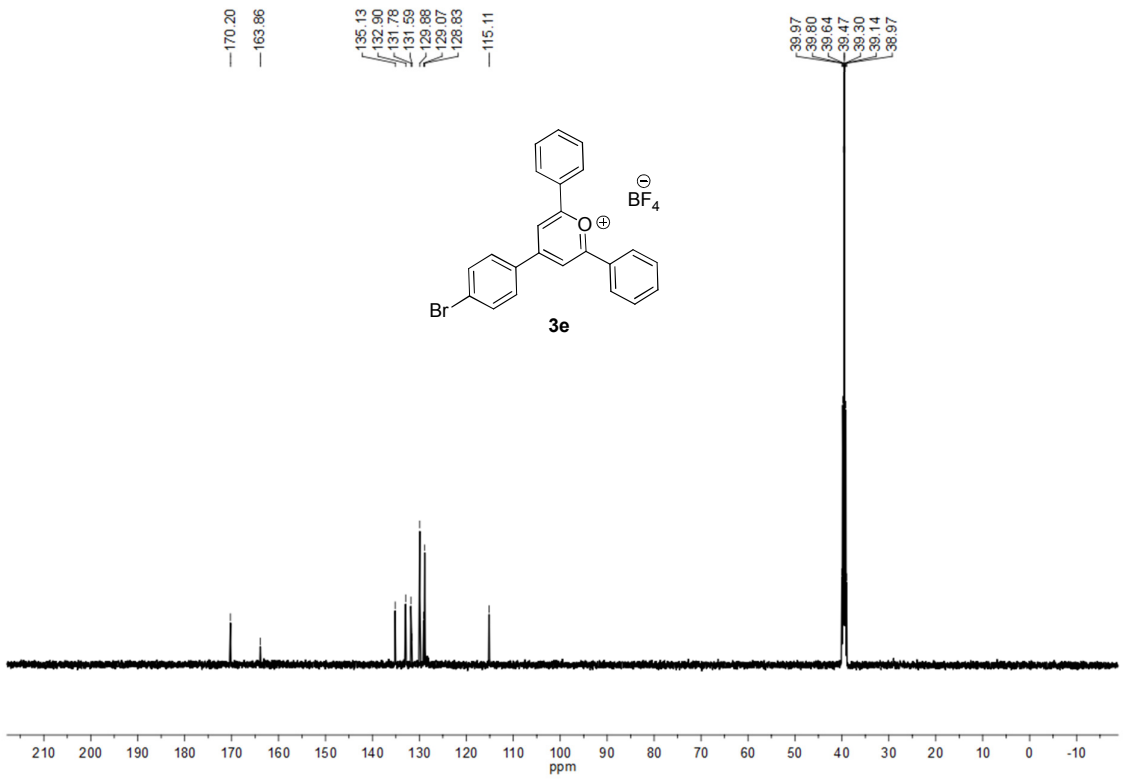

Fig S10. ^{13}C NMR of 3e

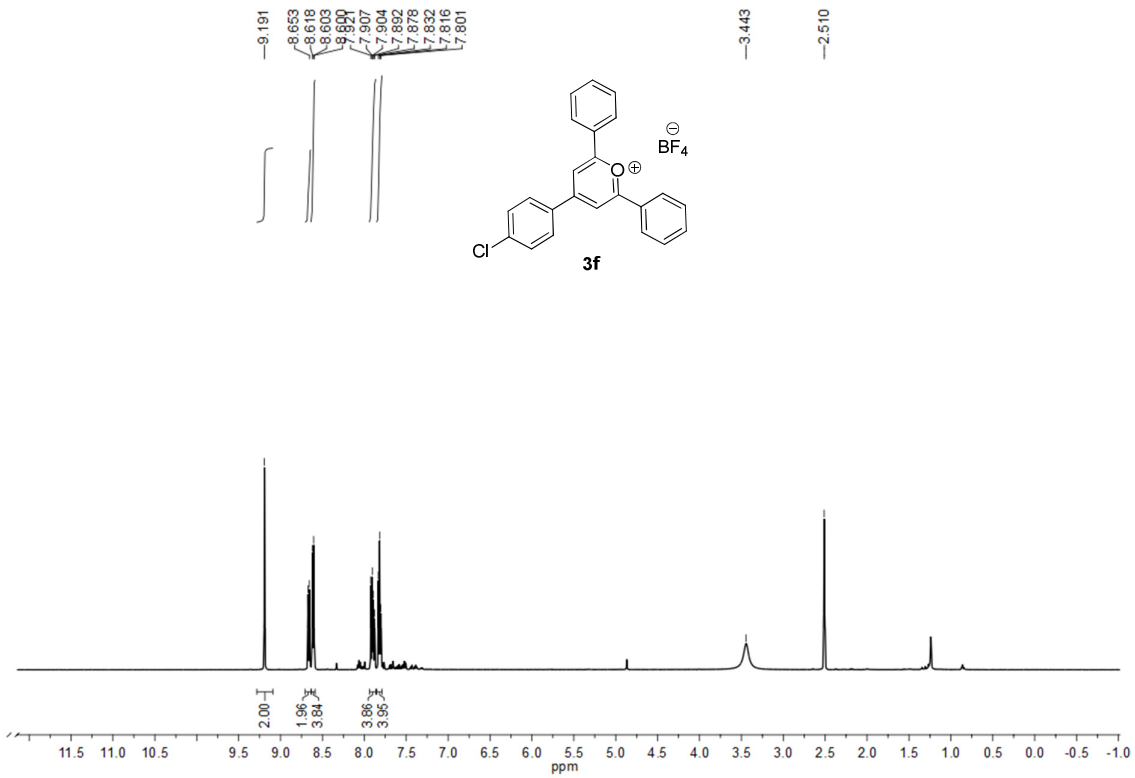

Fig S11. ^{1}H NMR of 3f

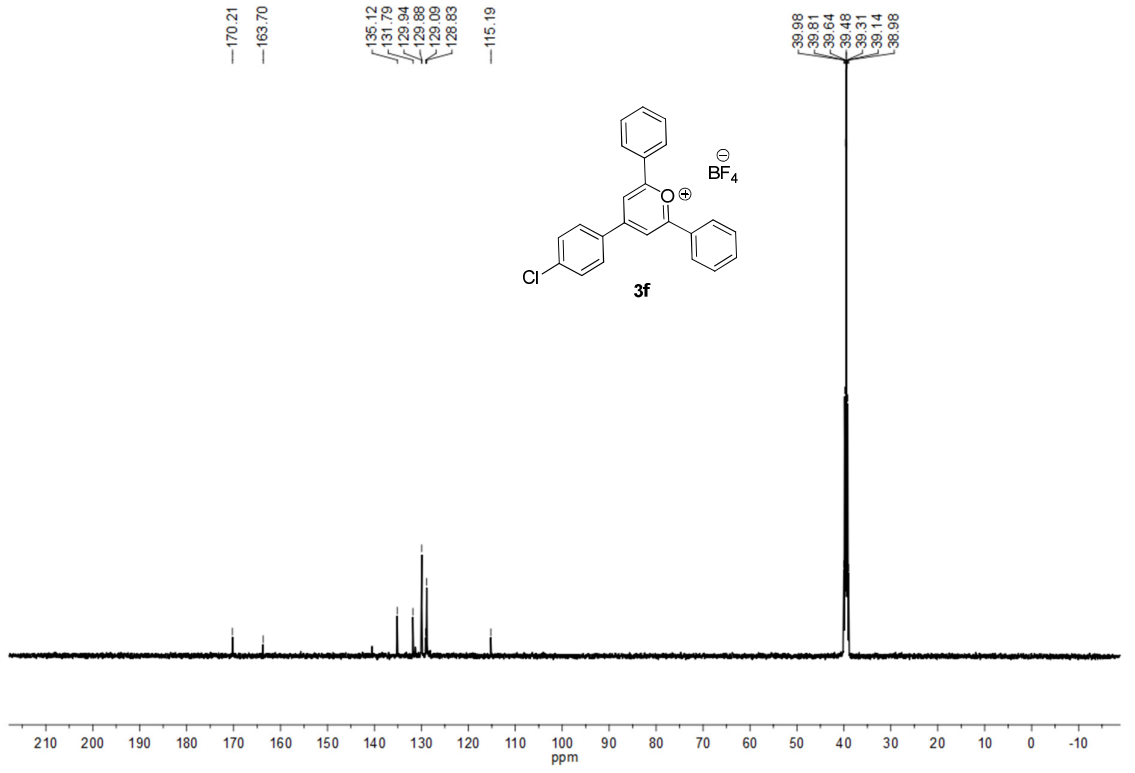

Fig S12. ^{13}C NMR of 3f

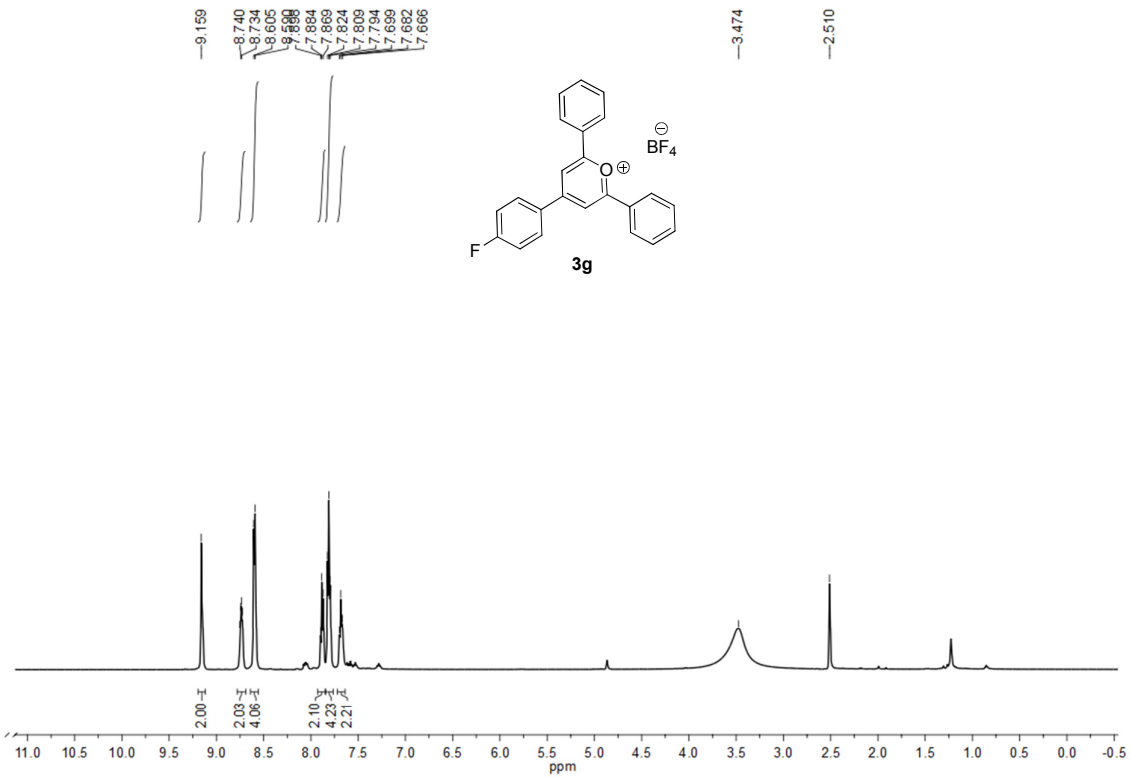

Fig S13. ^{1}H NMR of 3g

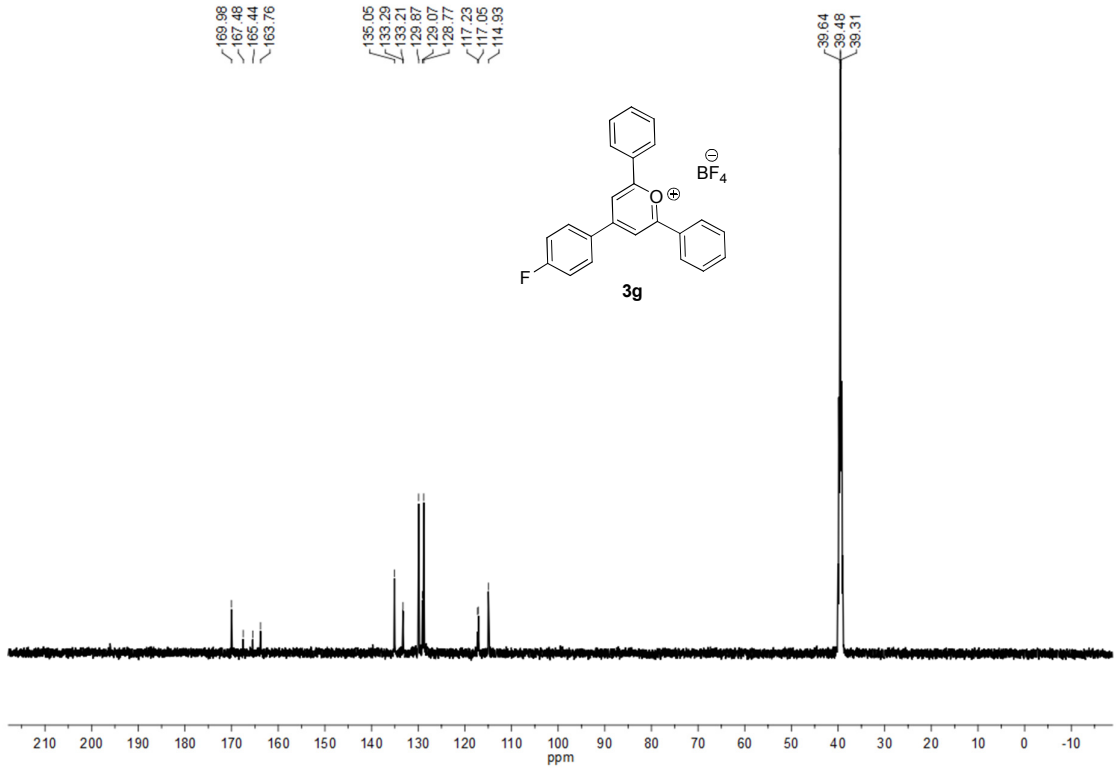

Fig S14. ^{13}C NMR of 3g

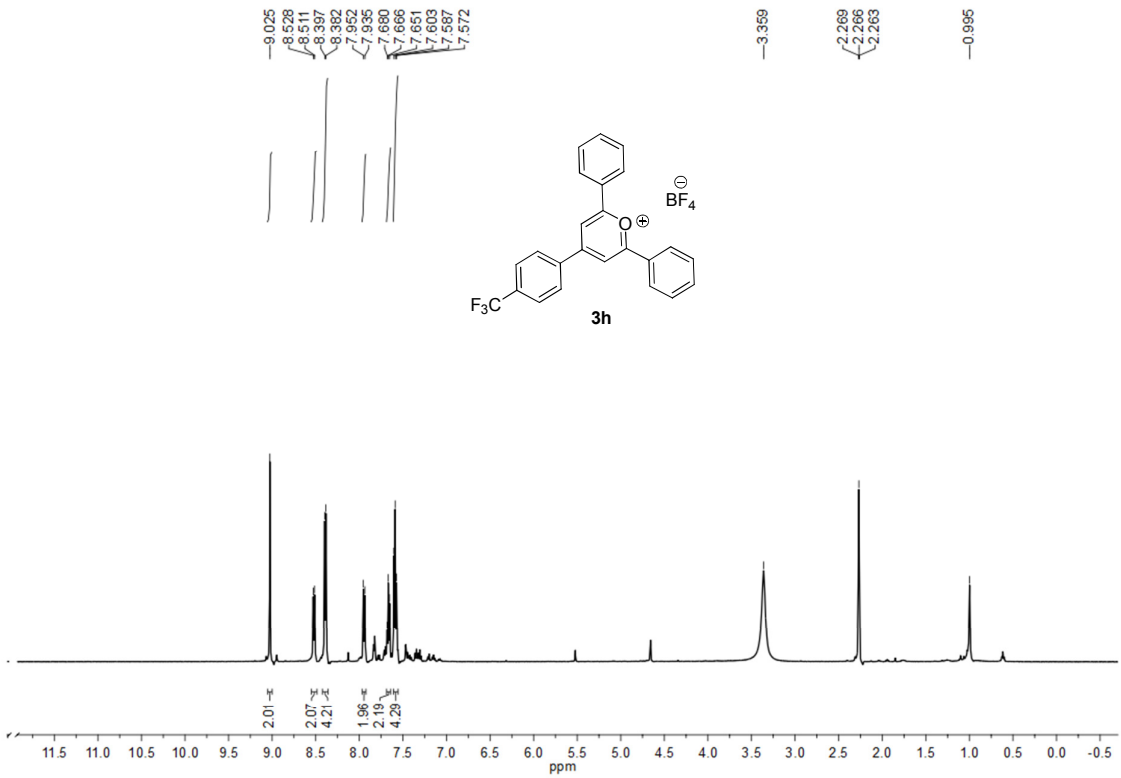

Fig S15. ^{1}H NMR of 3h

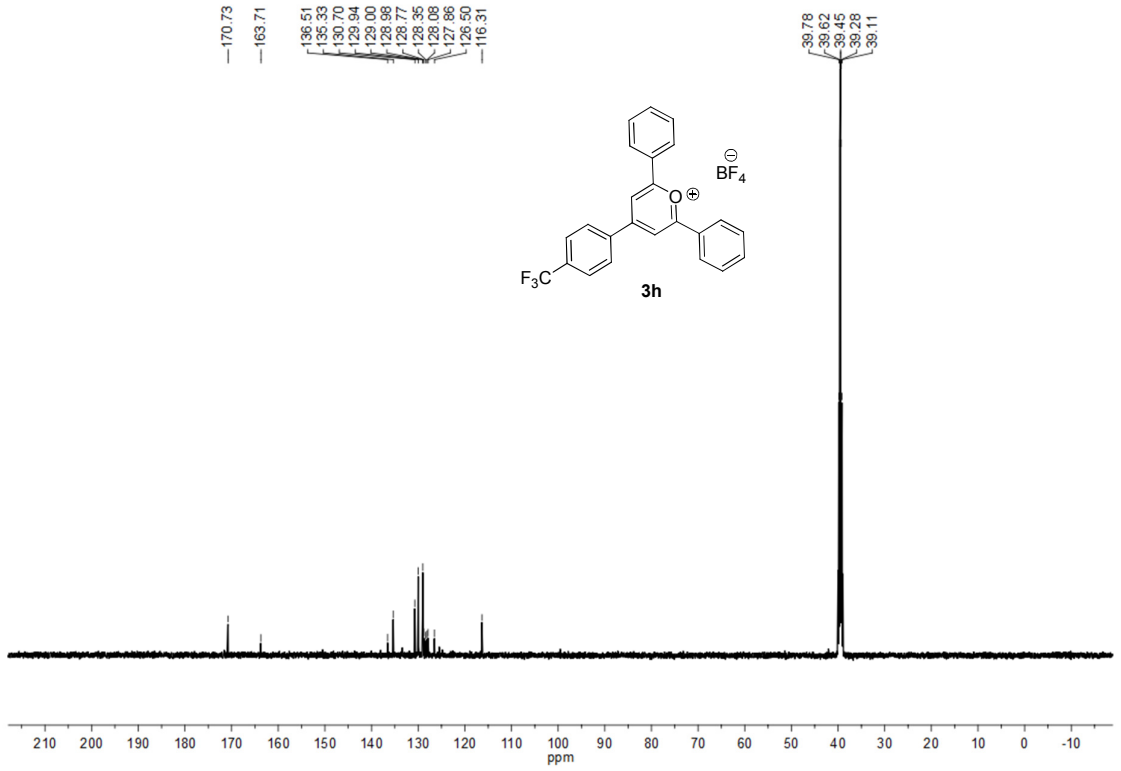

Fig S16. ^{13}C NMR of 3h

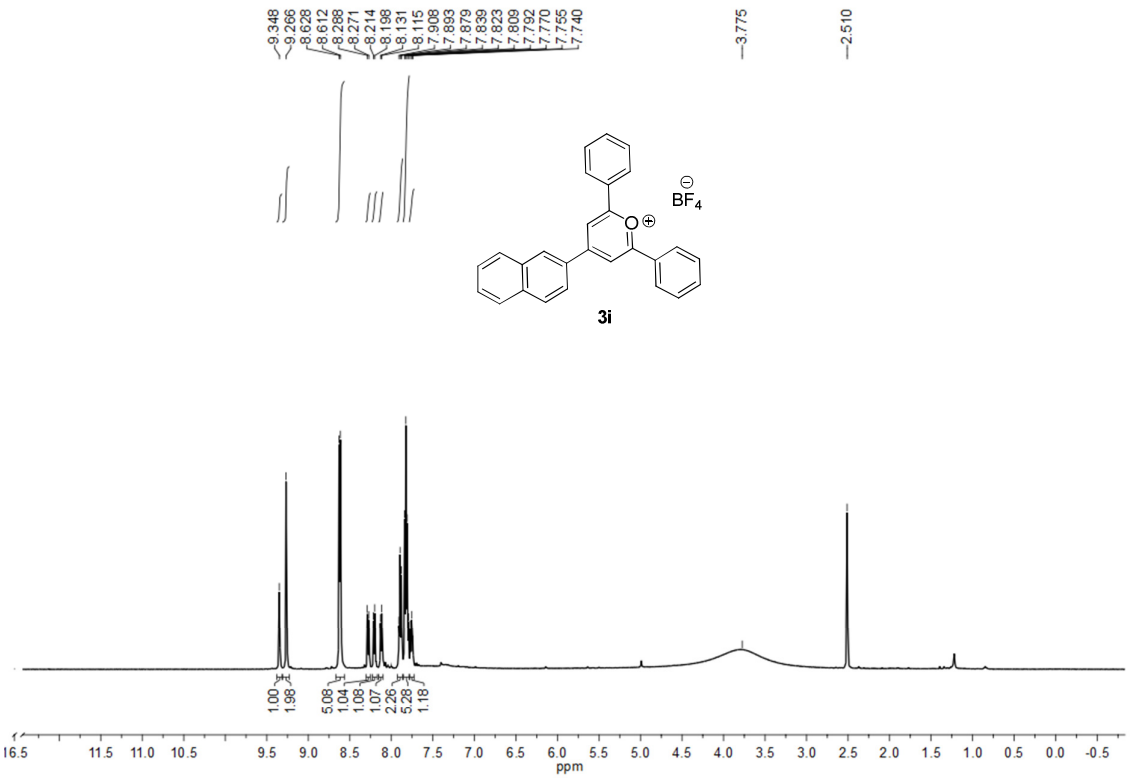

Fig S17. ^{1}H NMR of 3i

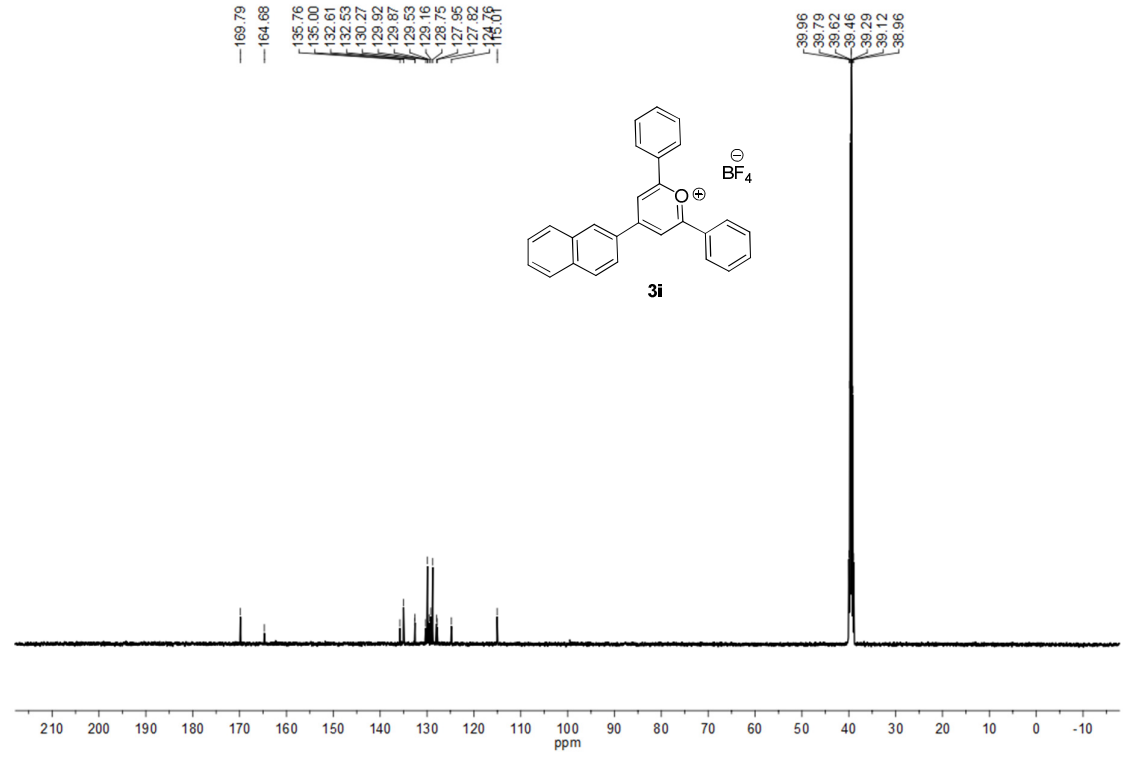

Fig S18. ^{13}C NMR of 3i

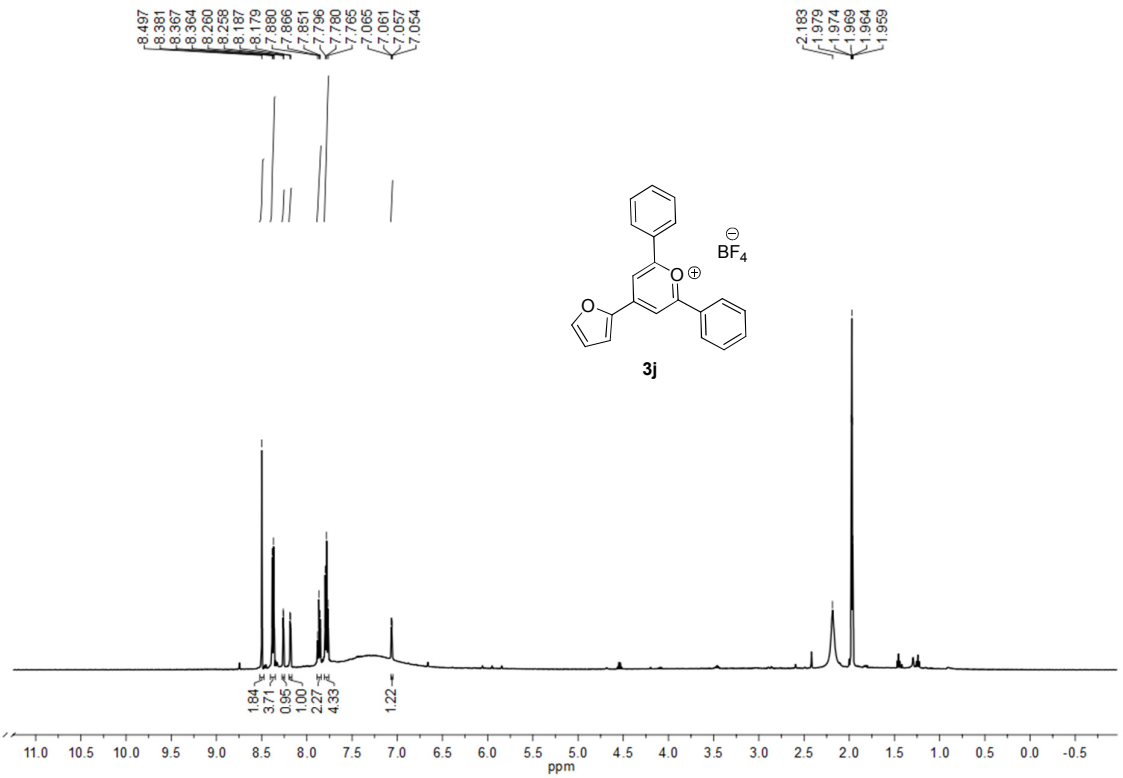

Fig S19. ^{1}H NMR of 3j

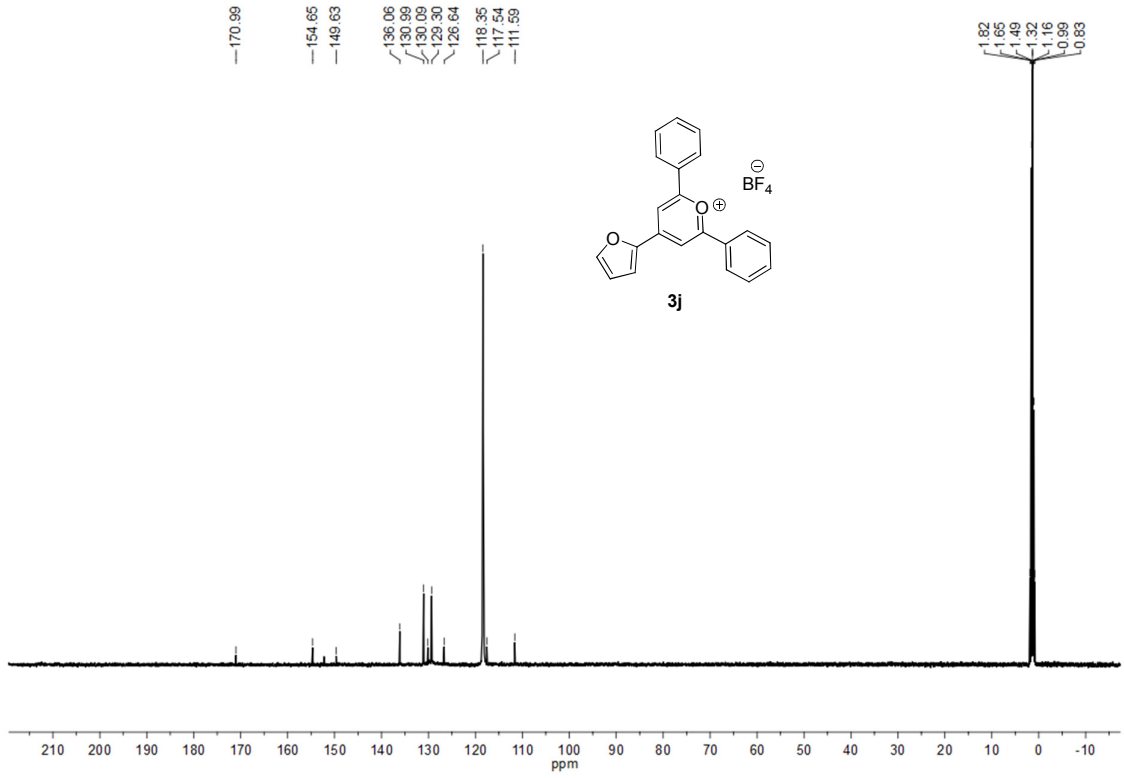

Fig S20. ^{13}C NMR of 3j

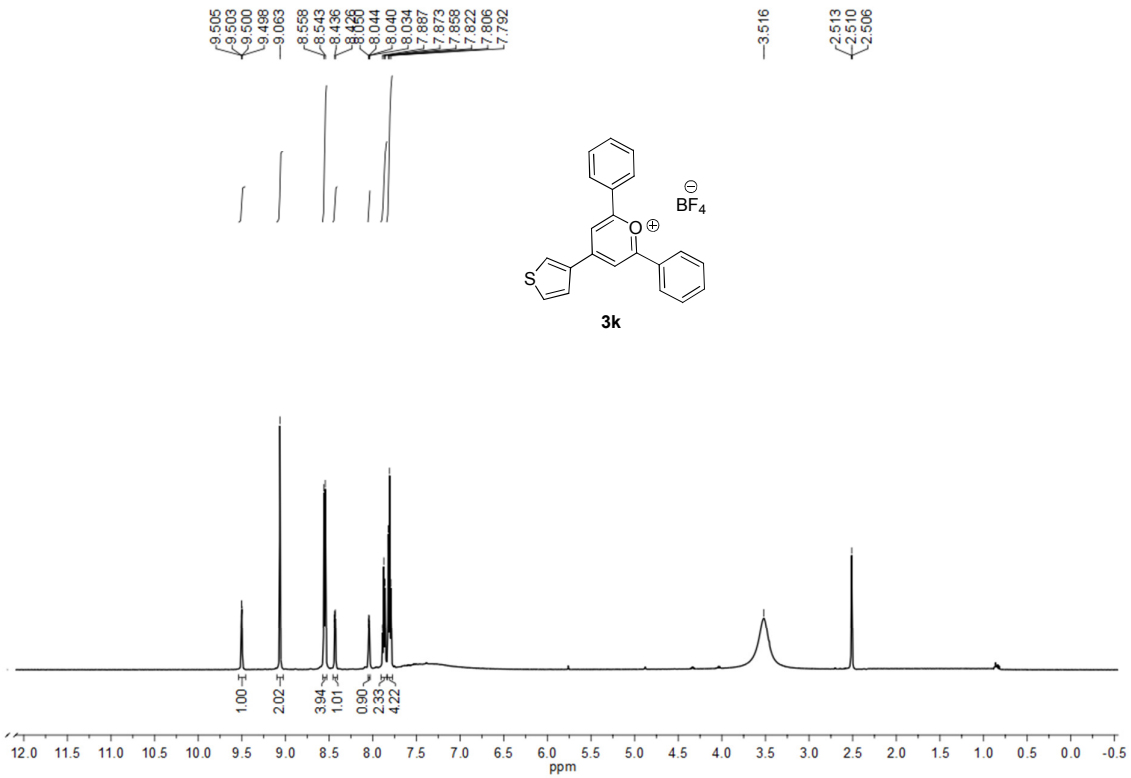

Fig S21. ^{1}H NMR of 3k

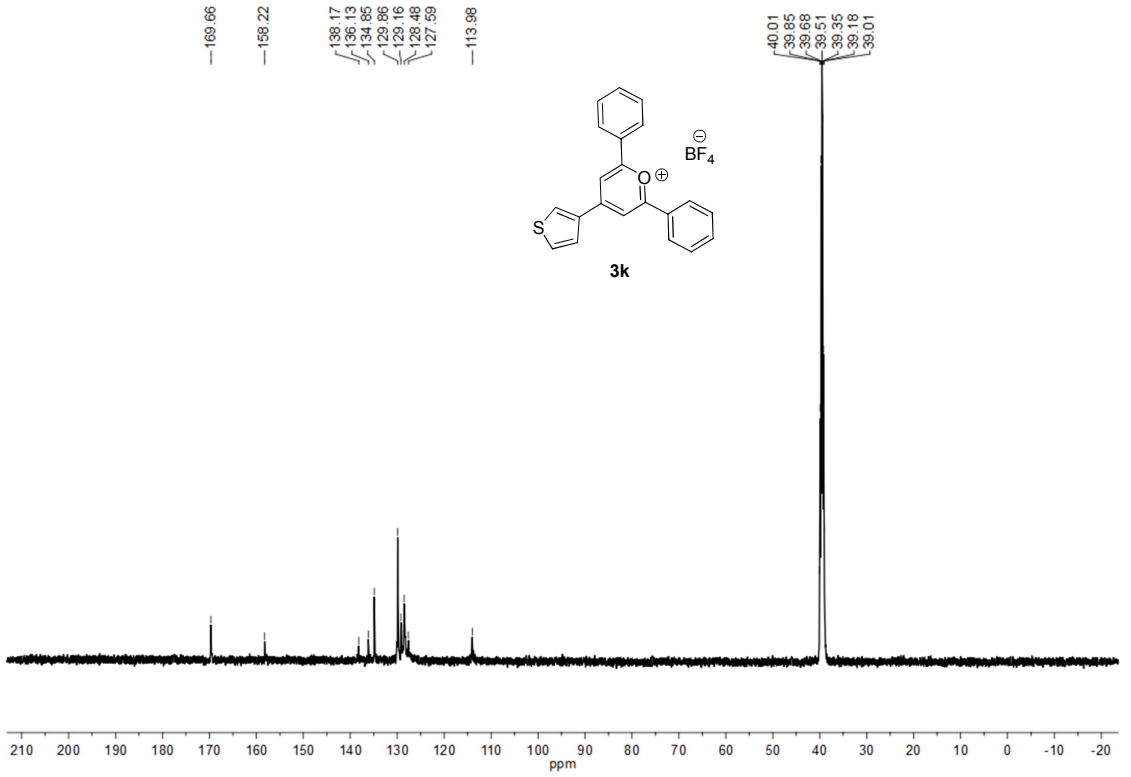

Fig S22. ^{13}C NMR of 3k

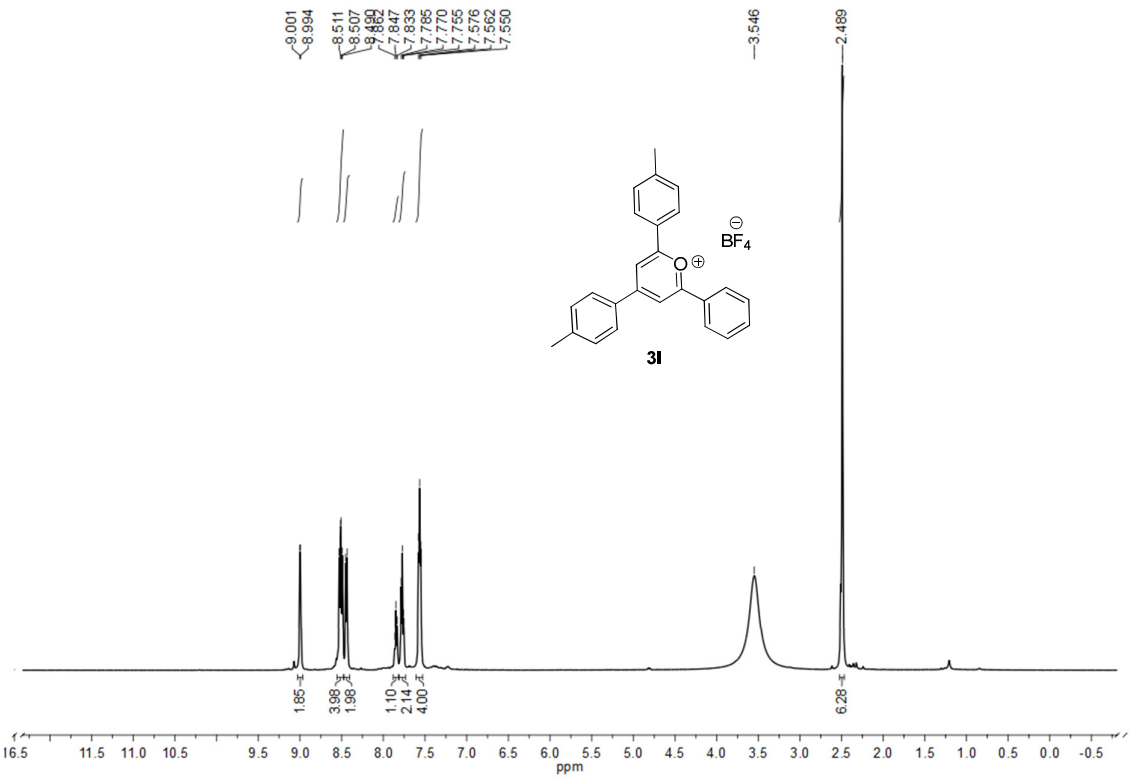

Fig S23. ^{1}H NMR of 3l

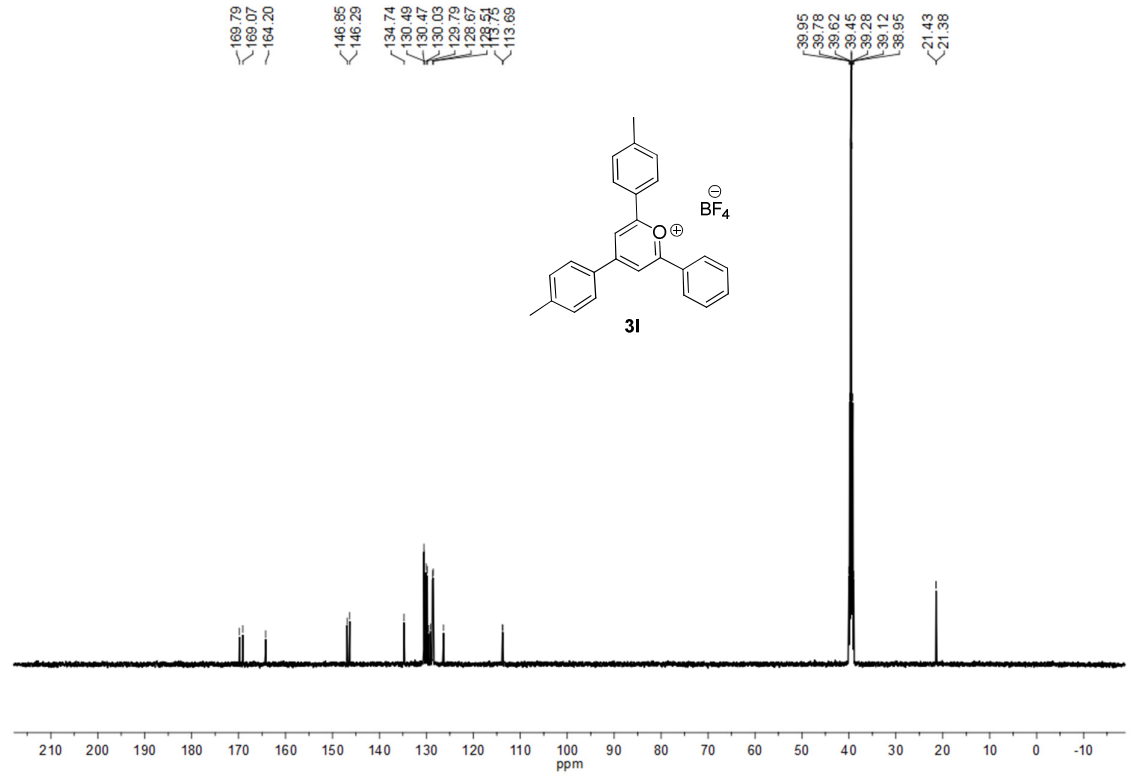

Fig S24. ^{13}C NMR of 3l

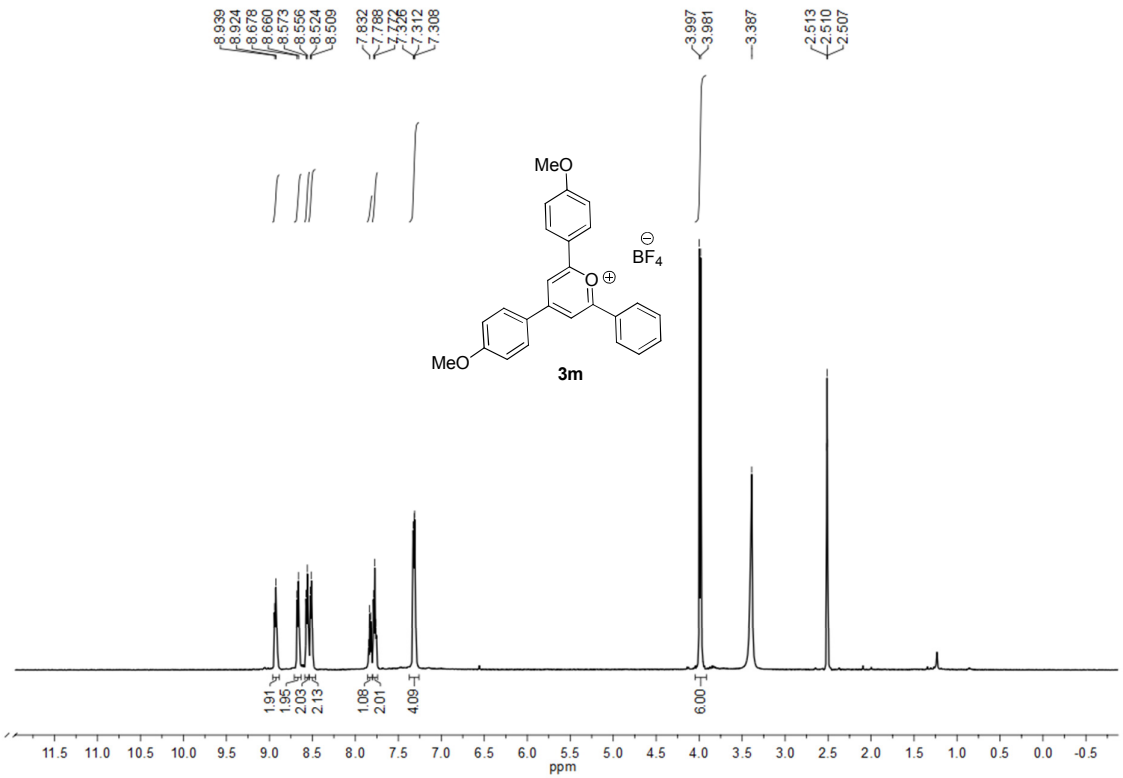

Fig S25. ^{1}H NMR of 3m

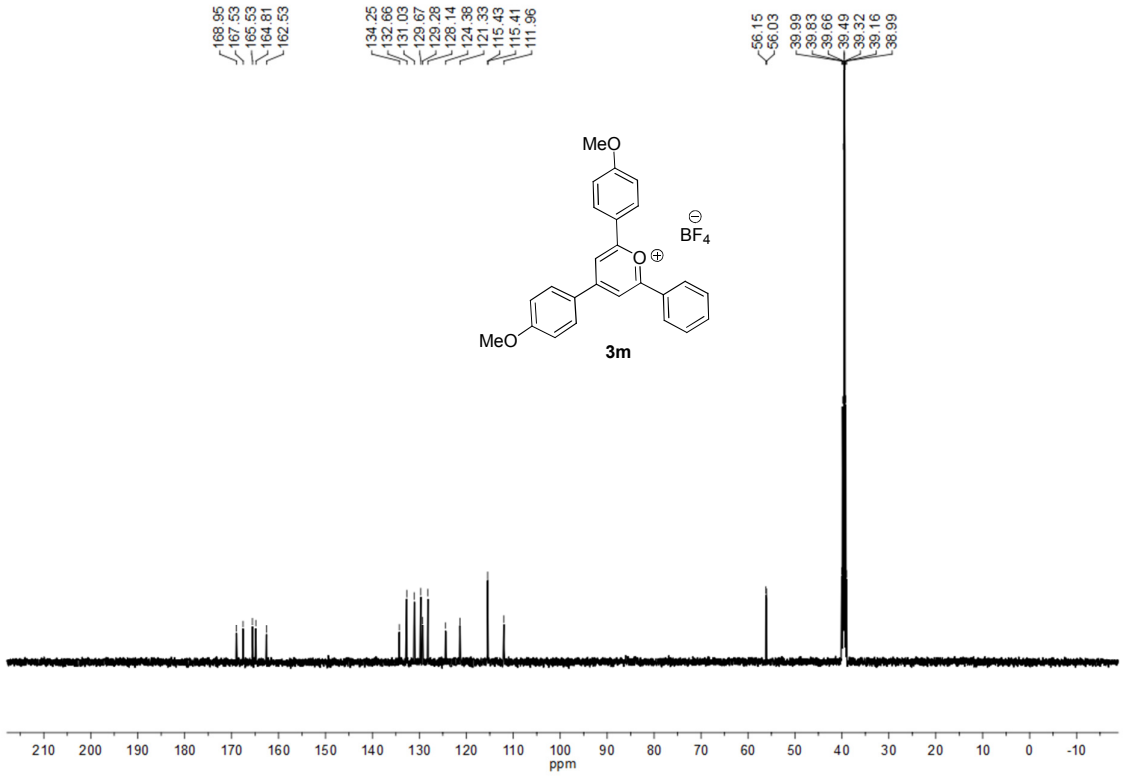

Fig S26. ^{13}C NMR of 3m

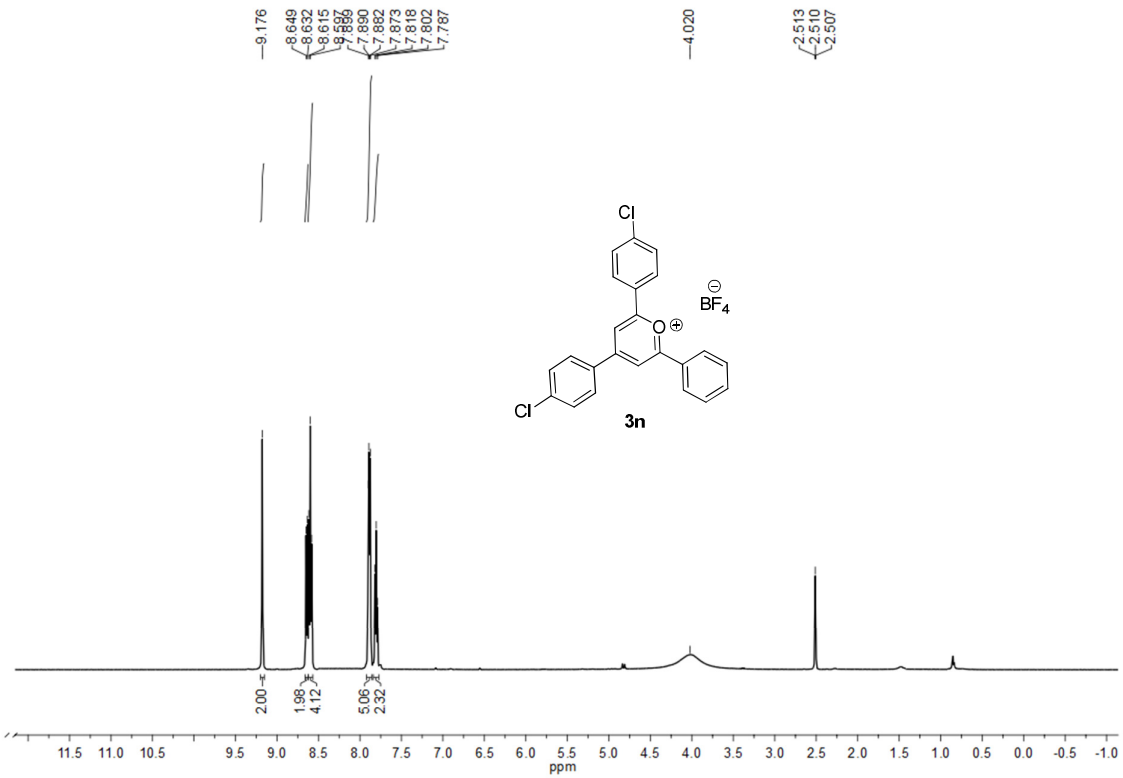

Fig S27. ^{1}H NMR of 3n

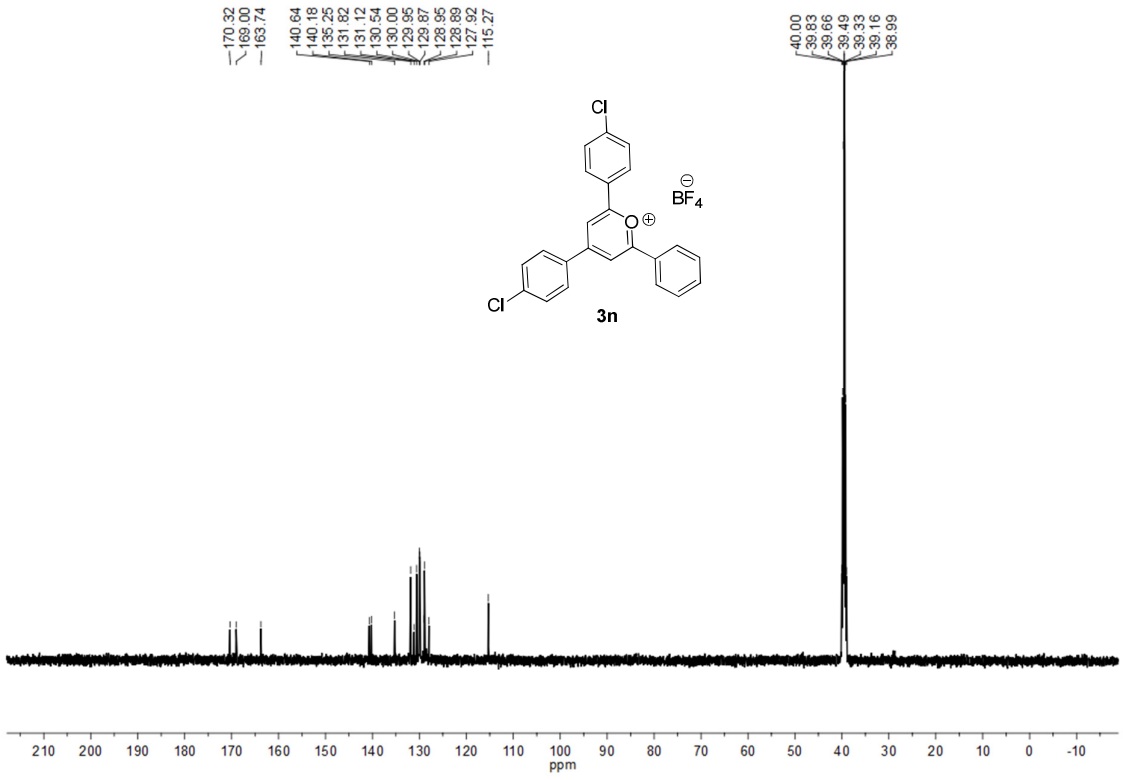

Fig S28. ^{13}C NMR of 3n

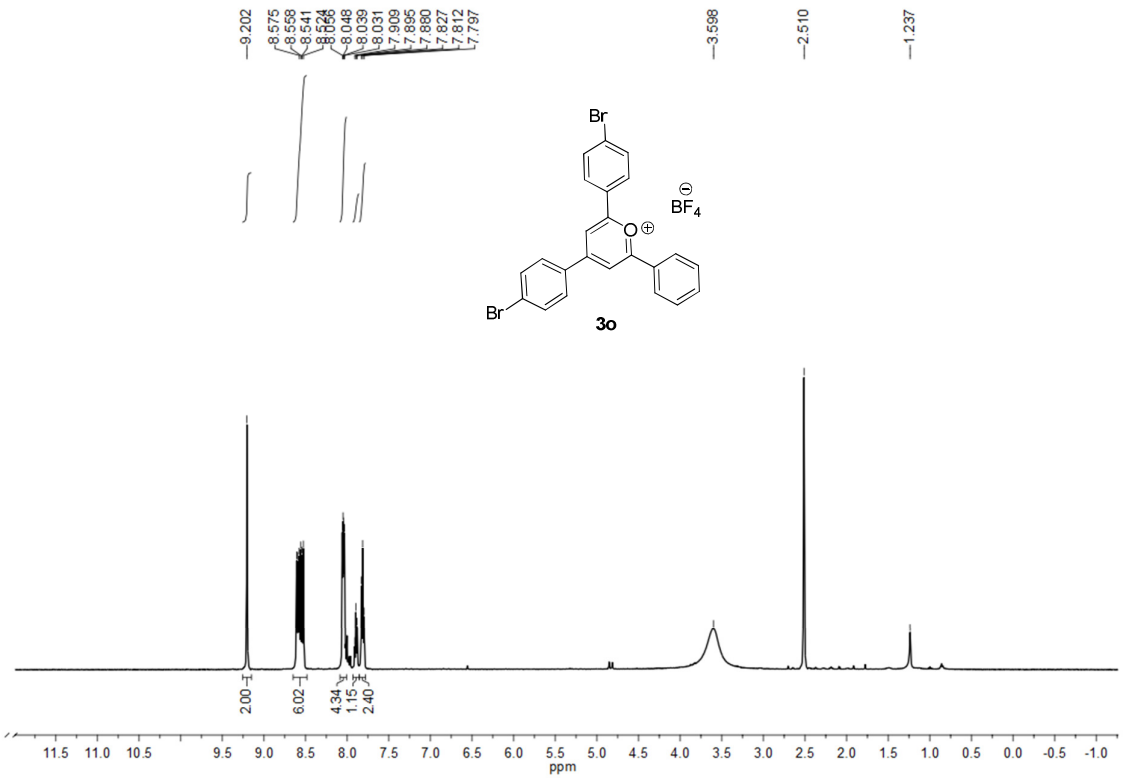

Fig S29. ^{1}H NMR of 3o

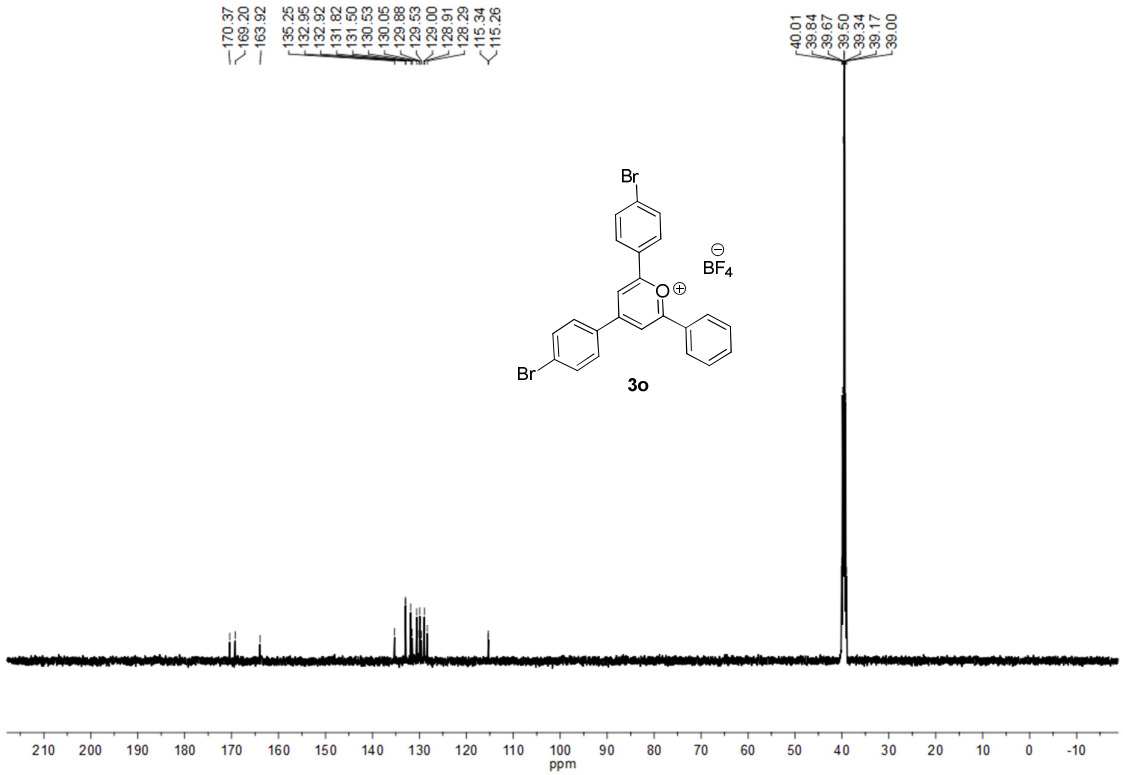

Fig S30. ^{13}C NMR of 3o

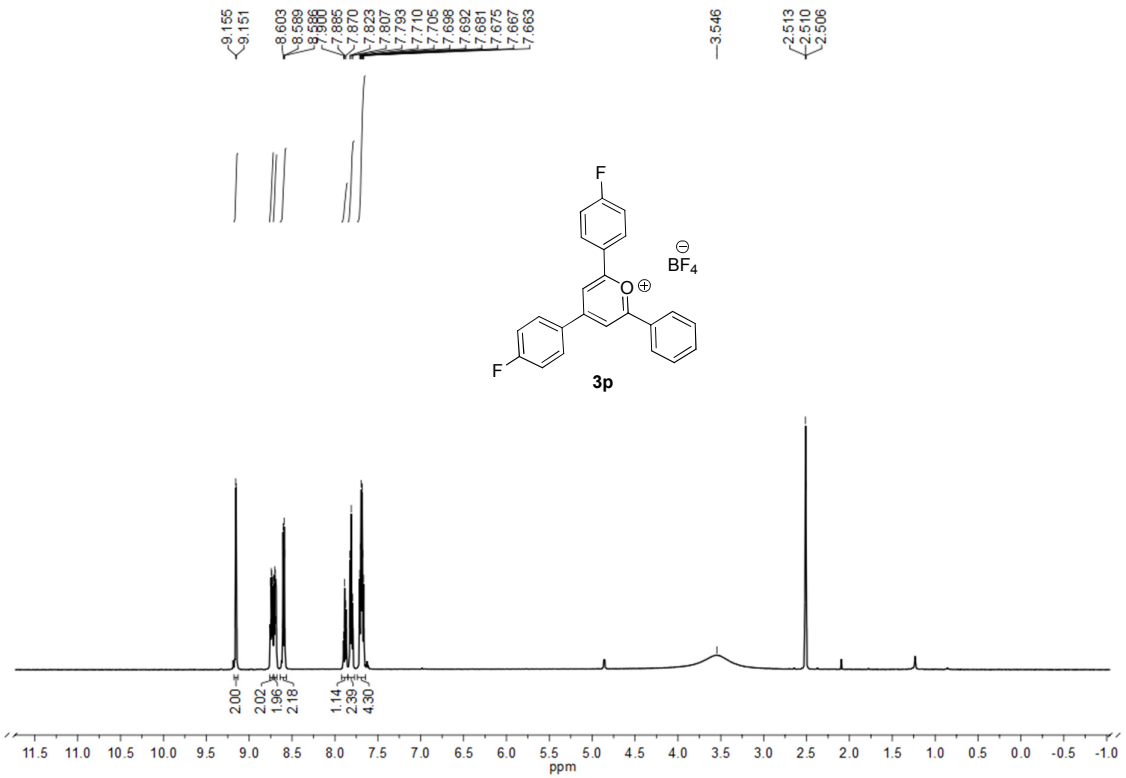

Fig S31. ^{1}H NMR of 3p

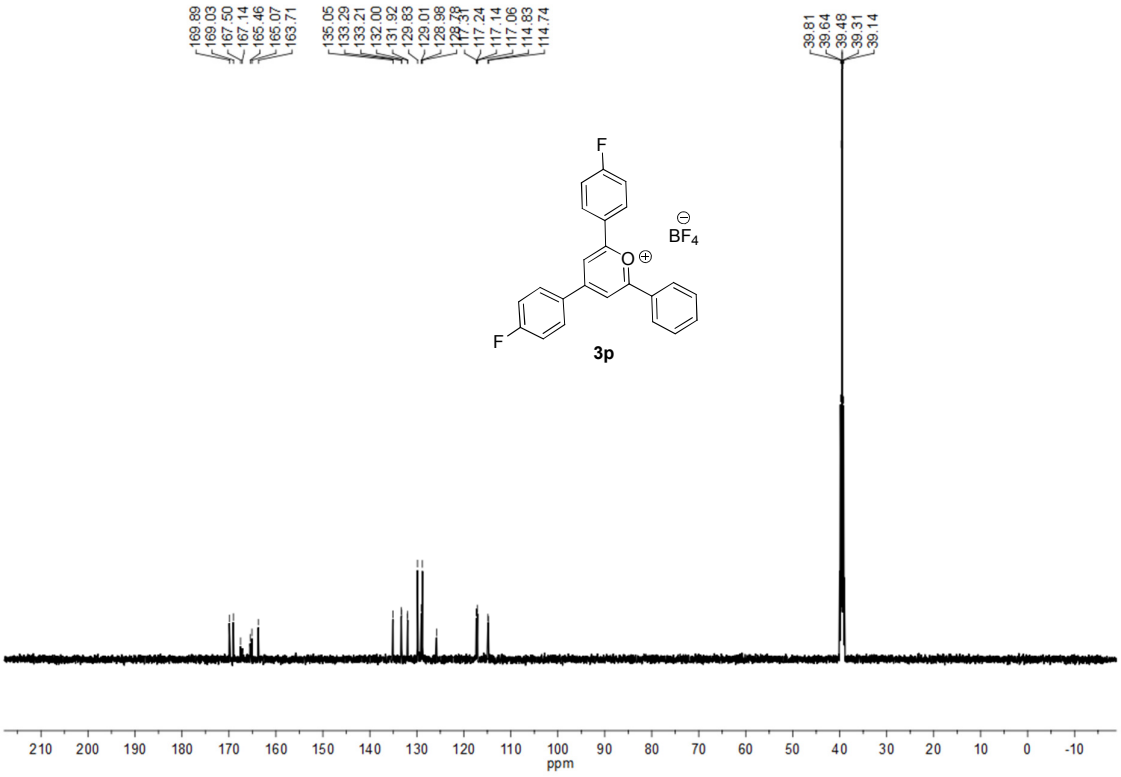

Fig S32. ^{13}C NMR of 3p

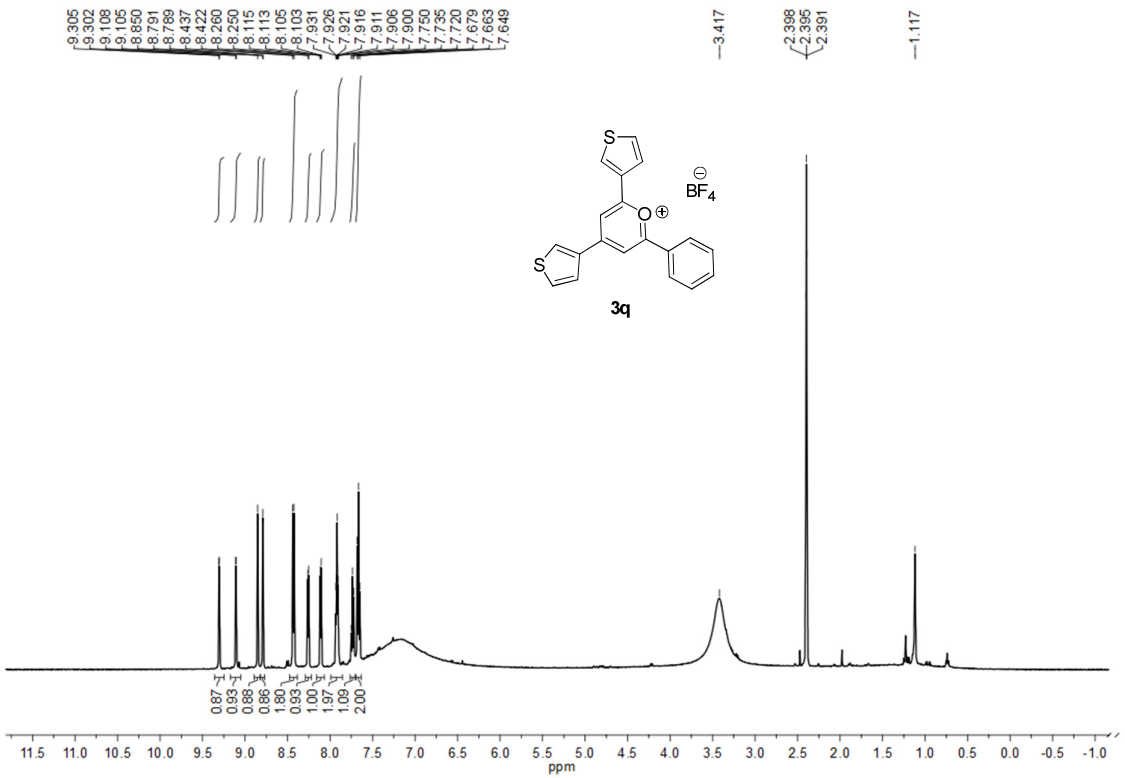

Fig S33. ^{1}H NMR of 3q

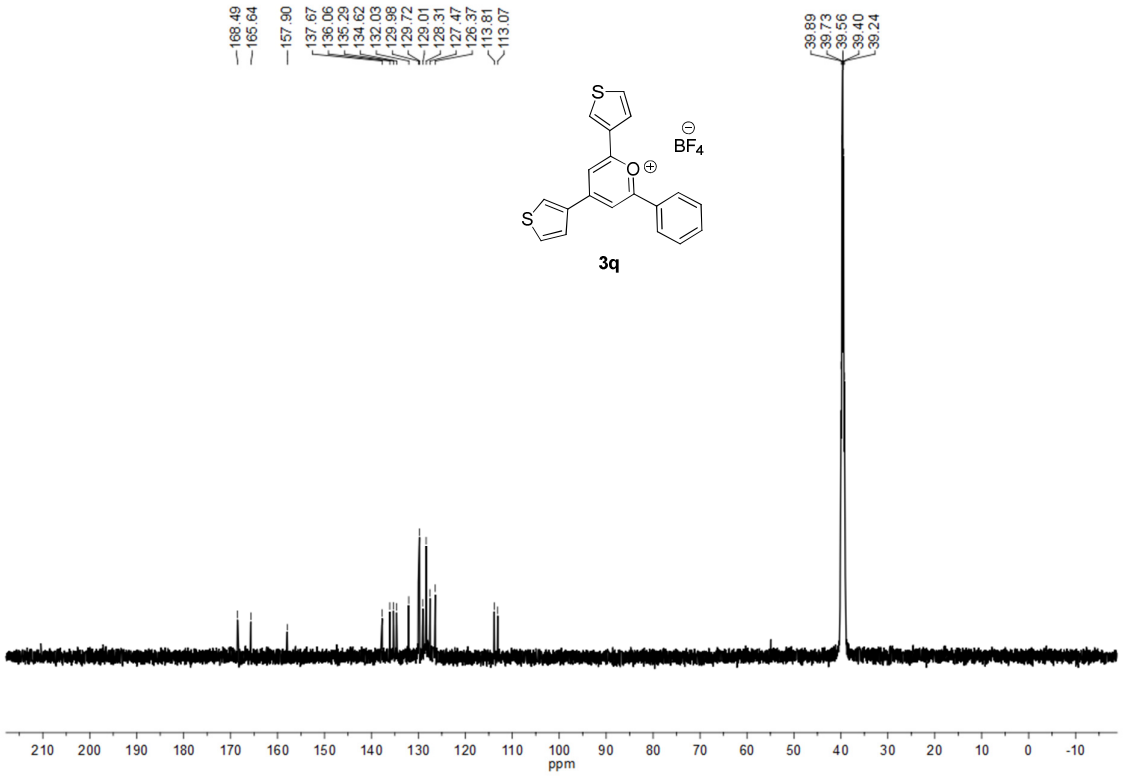

Fig S34. ^{13}C NMR of 3q

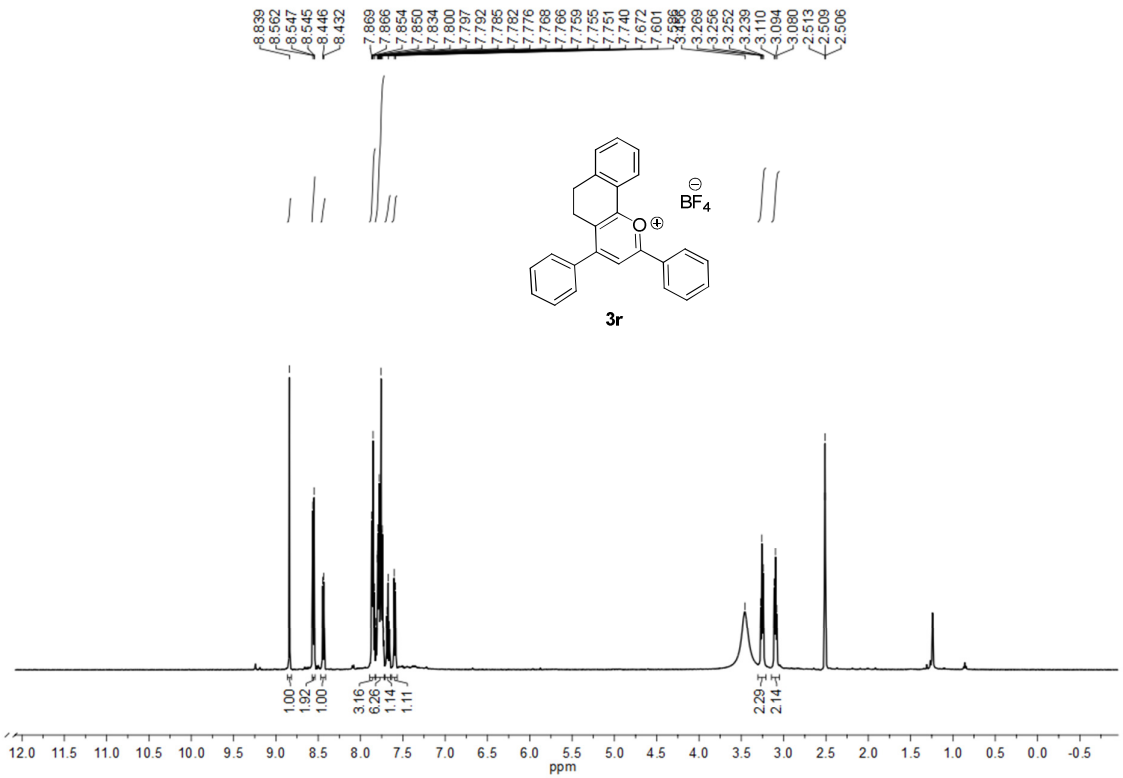

Fig S35. ^{1}H NMR of 3r

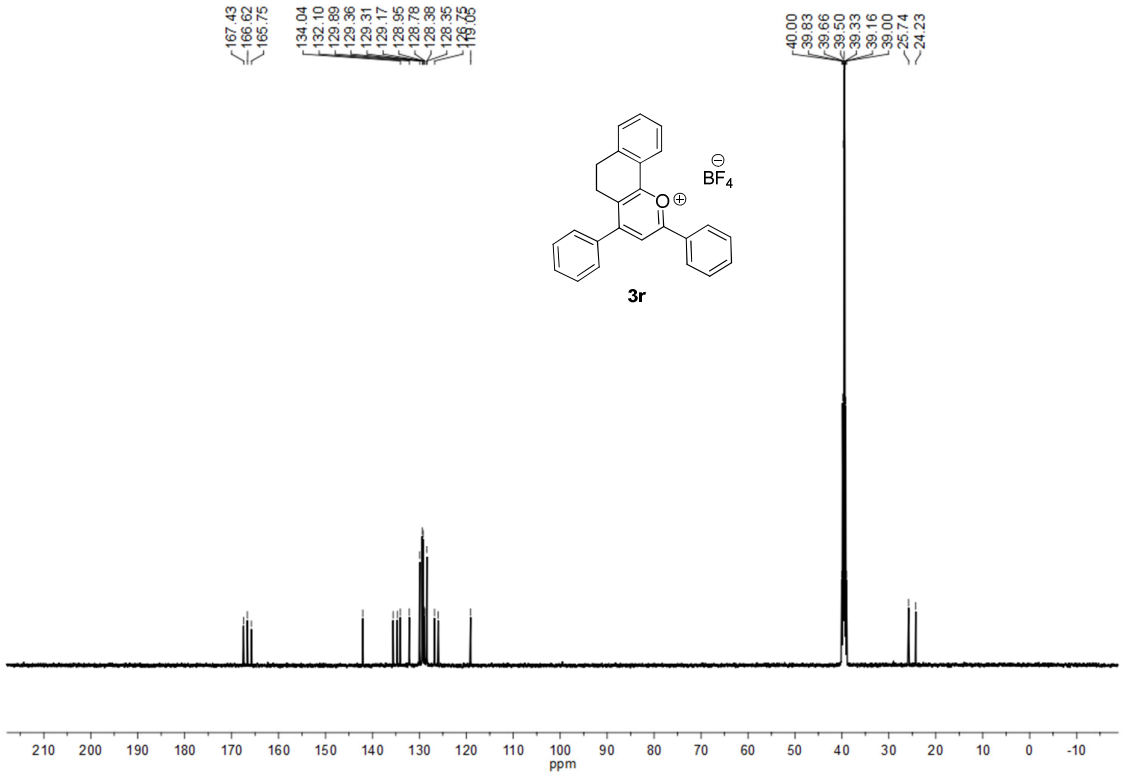

Fig S36. ^{13}C NMR of 3r

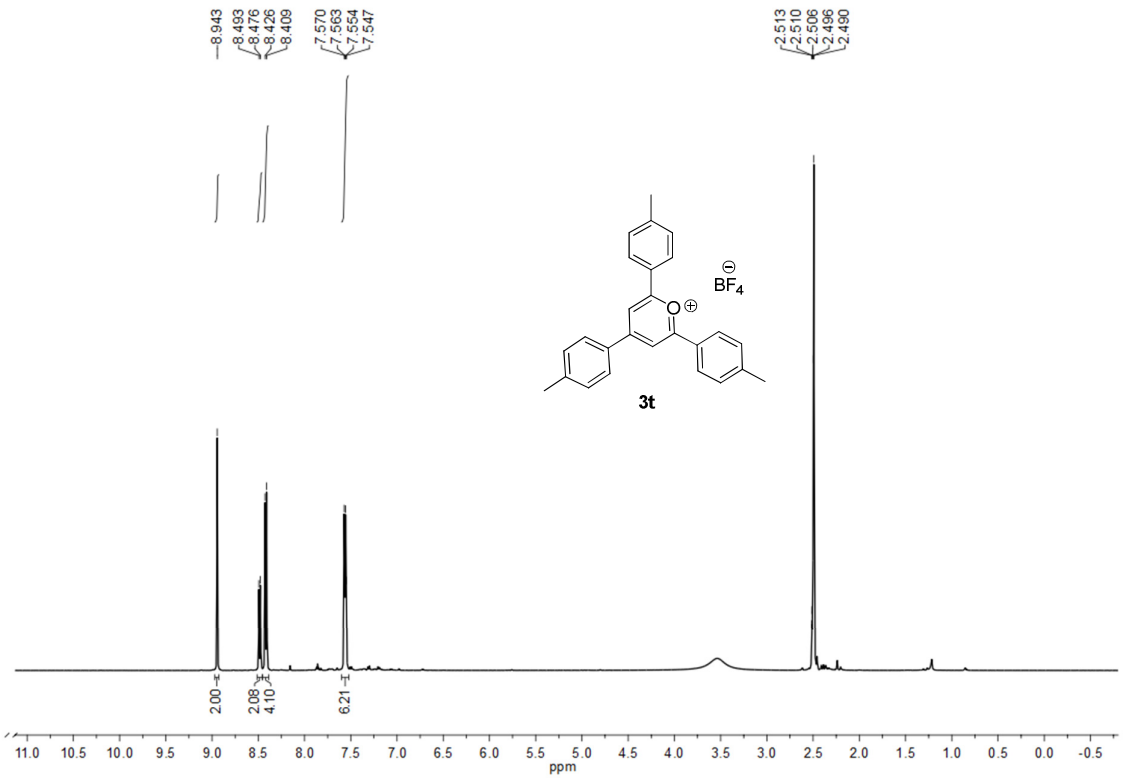

Fig S37. ^{1}H NMR of 3t

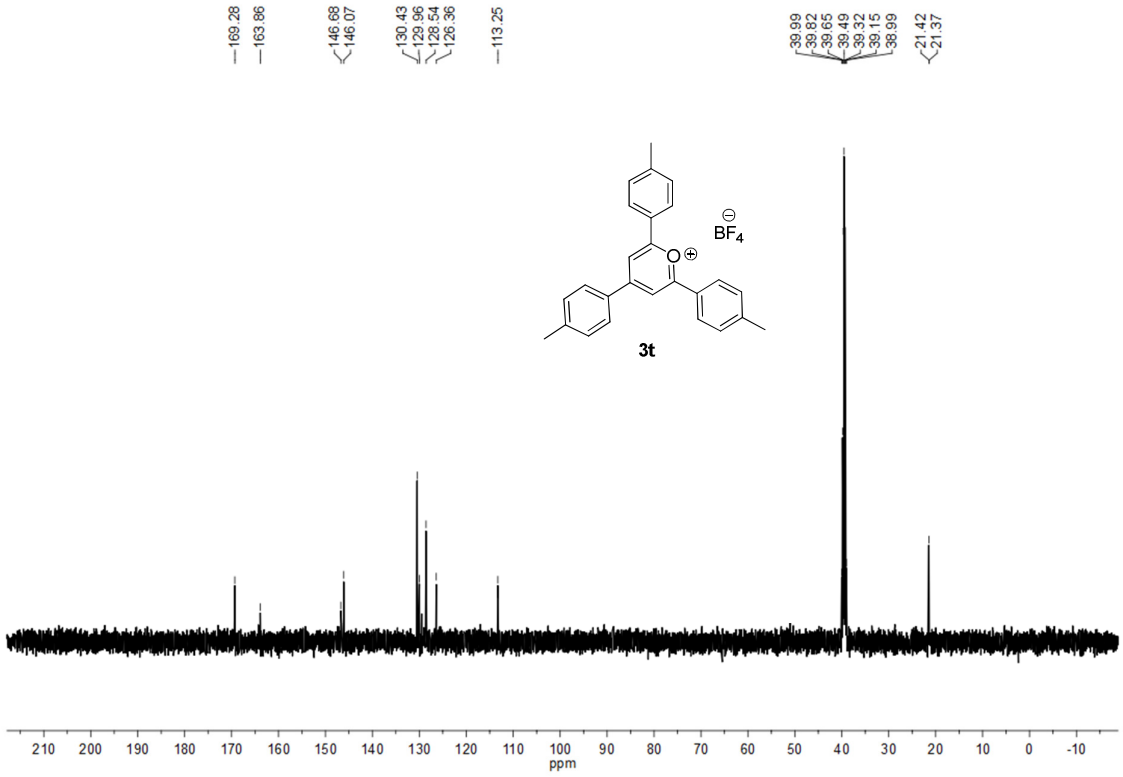

Fig S38. ^{13}C NMR of 3t

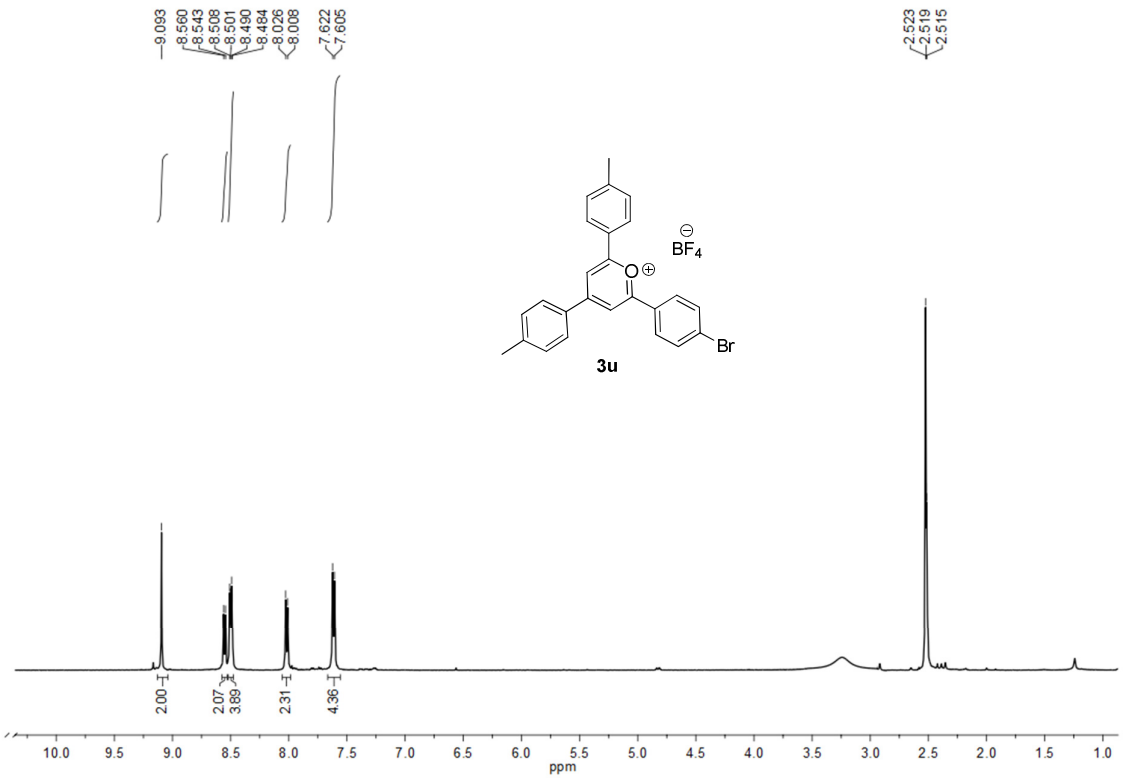

Fig S39. ^{1}H NMR of 3u

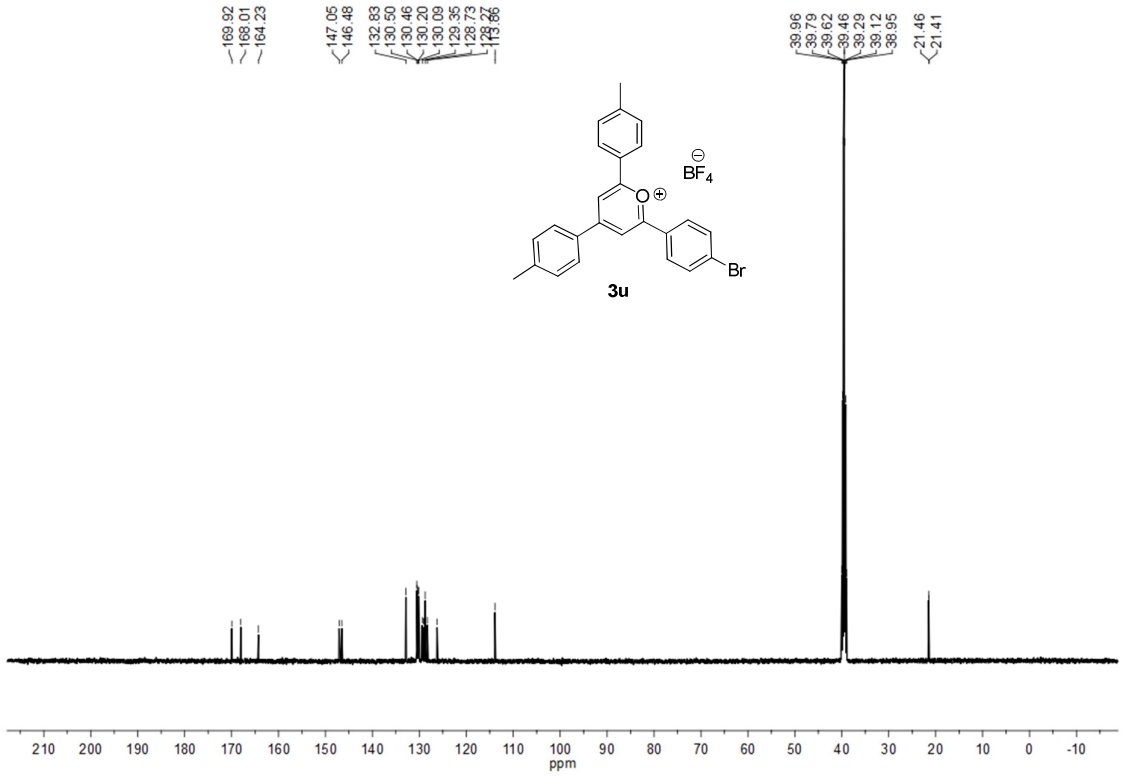

Fig S40. ^{13}C NMR of 3u

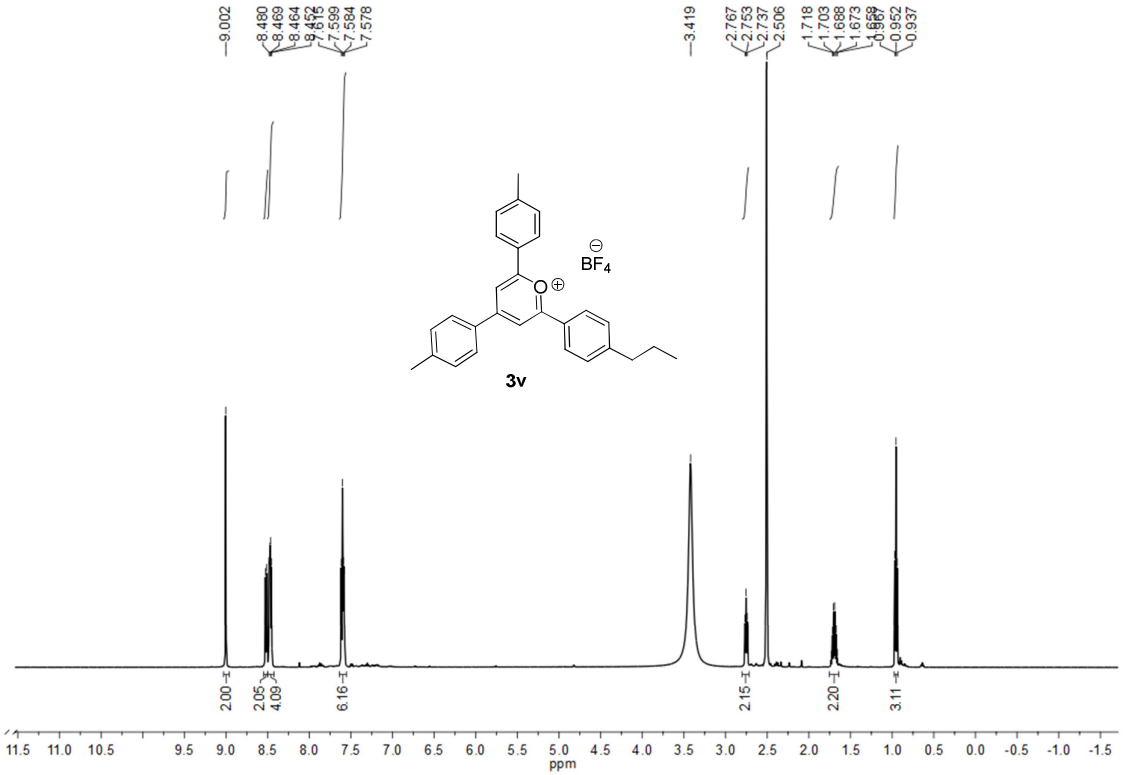

Fig S41. ^{1}H NMR of 3v

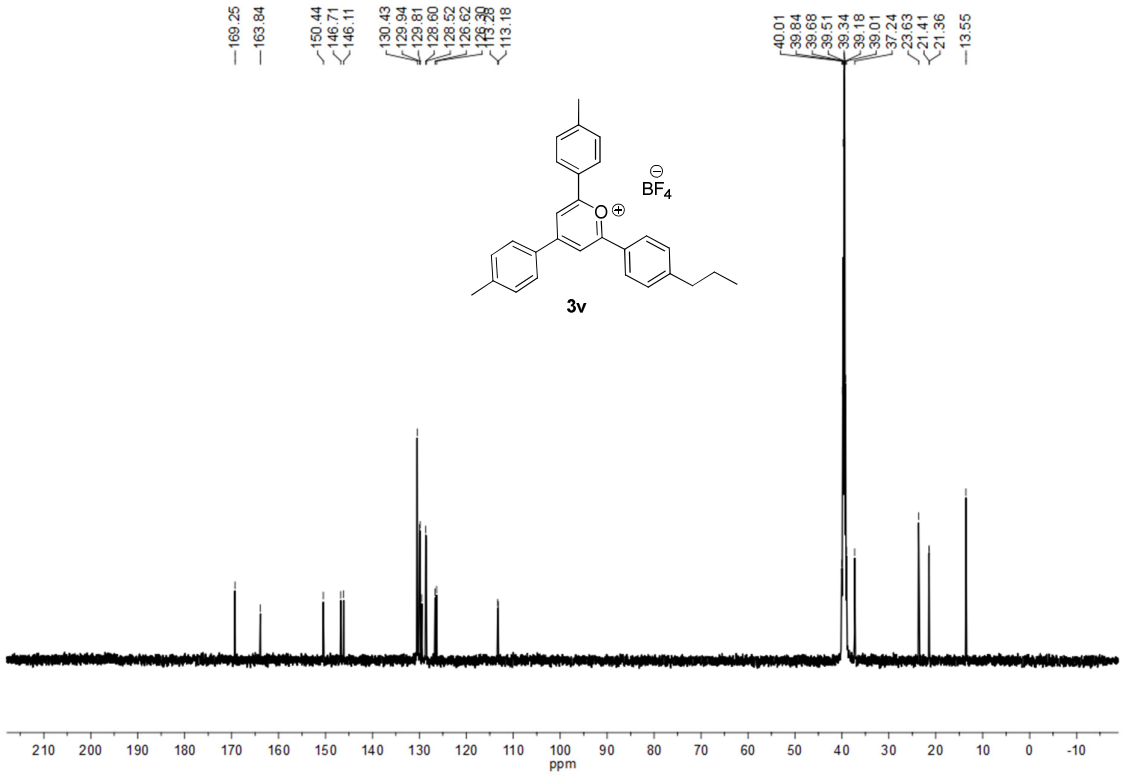

Fig S42. ^{13}C NMR of 3v

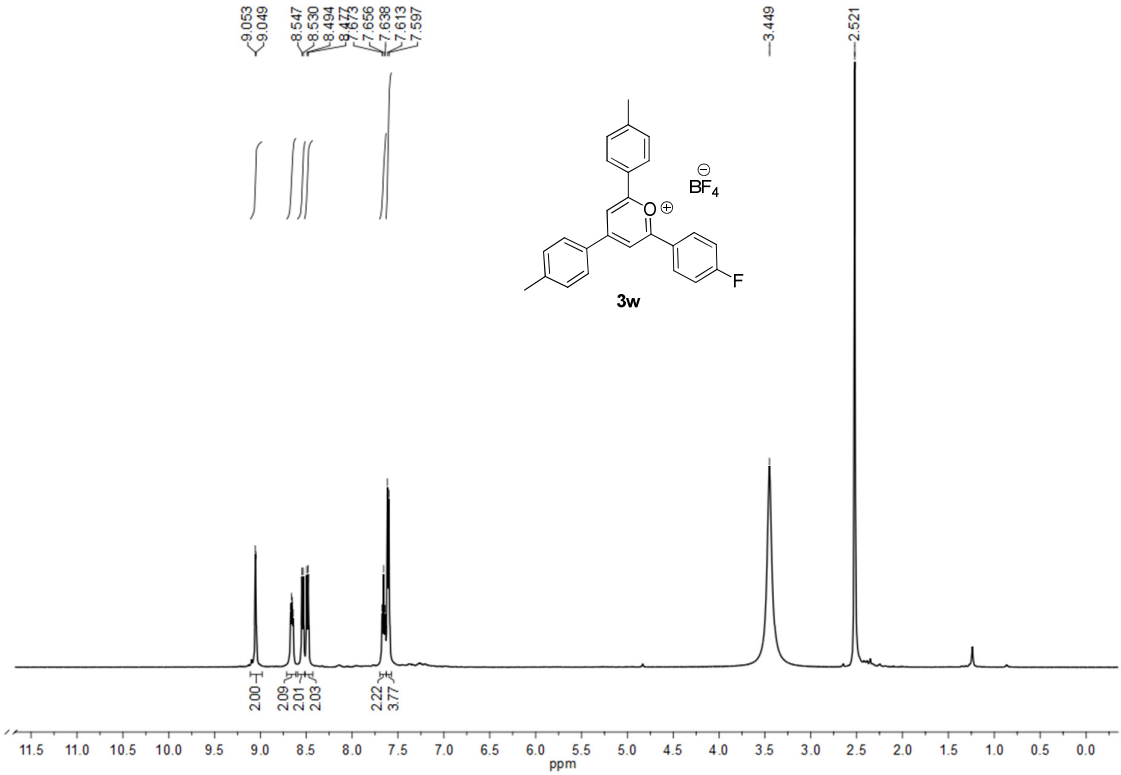

Fig S43. ^{1}H NMR of 3w

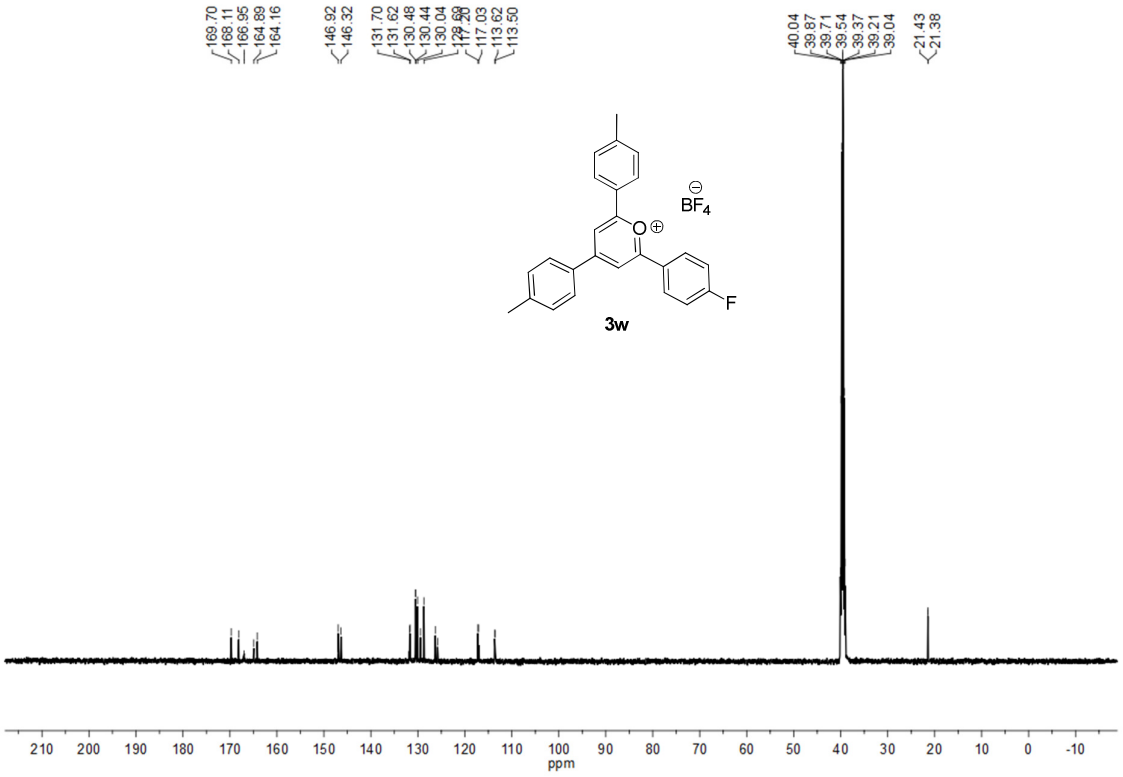

Fig S44. ^{13}C NMR of 3w

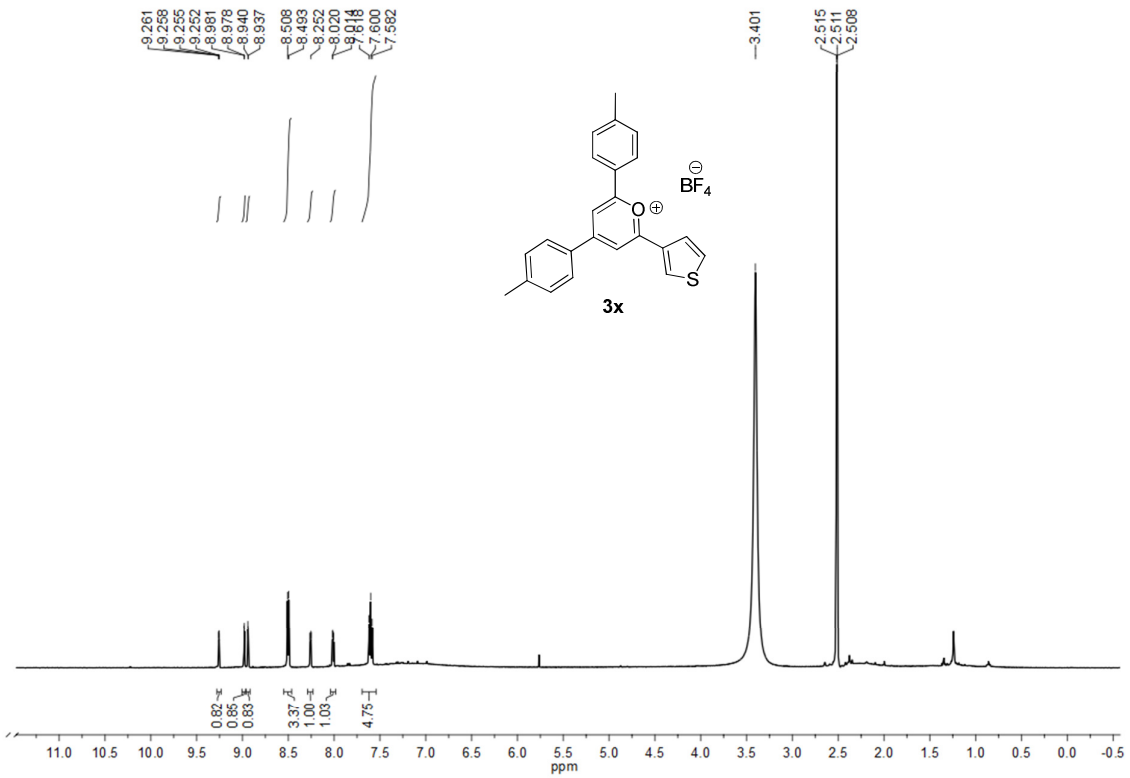

Fig S45. ^{1}H NMR of 3x

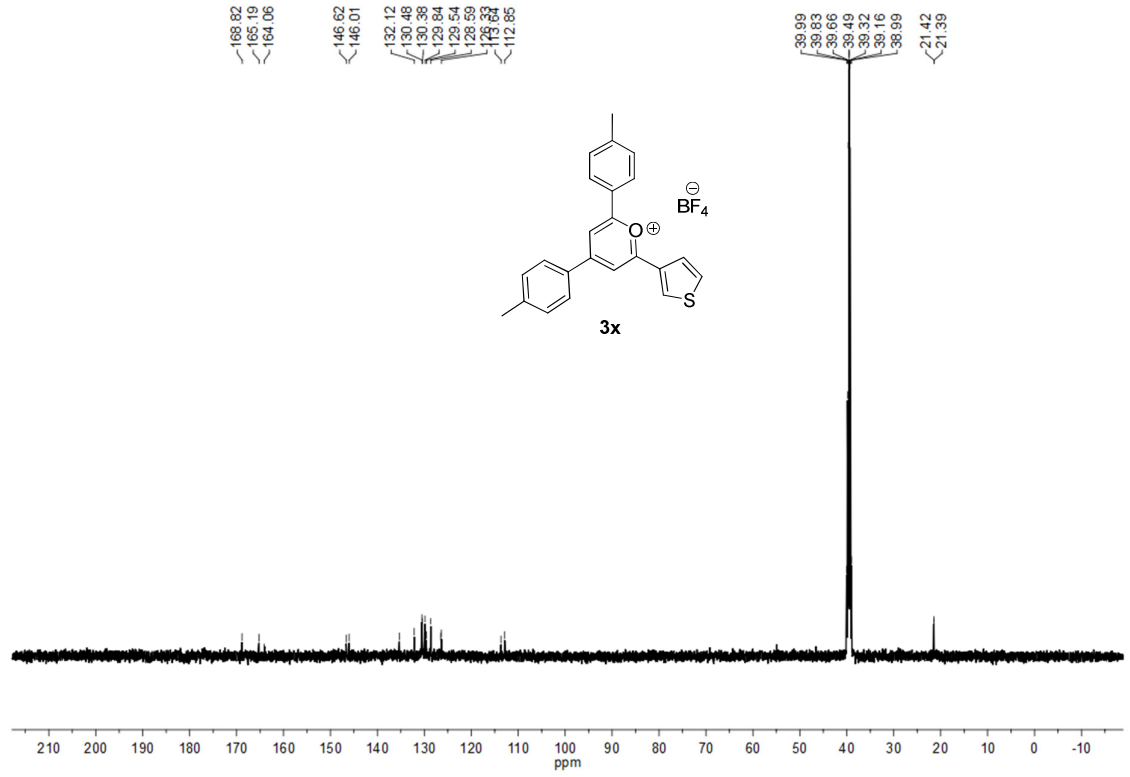

Fig S46. ^{13}C NMR of 3x

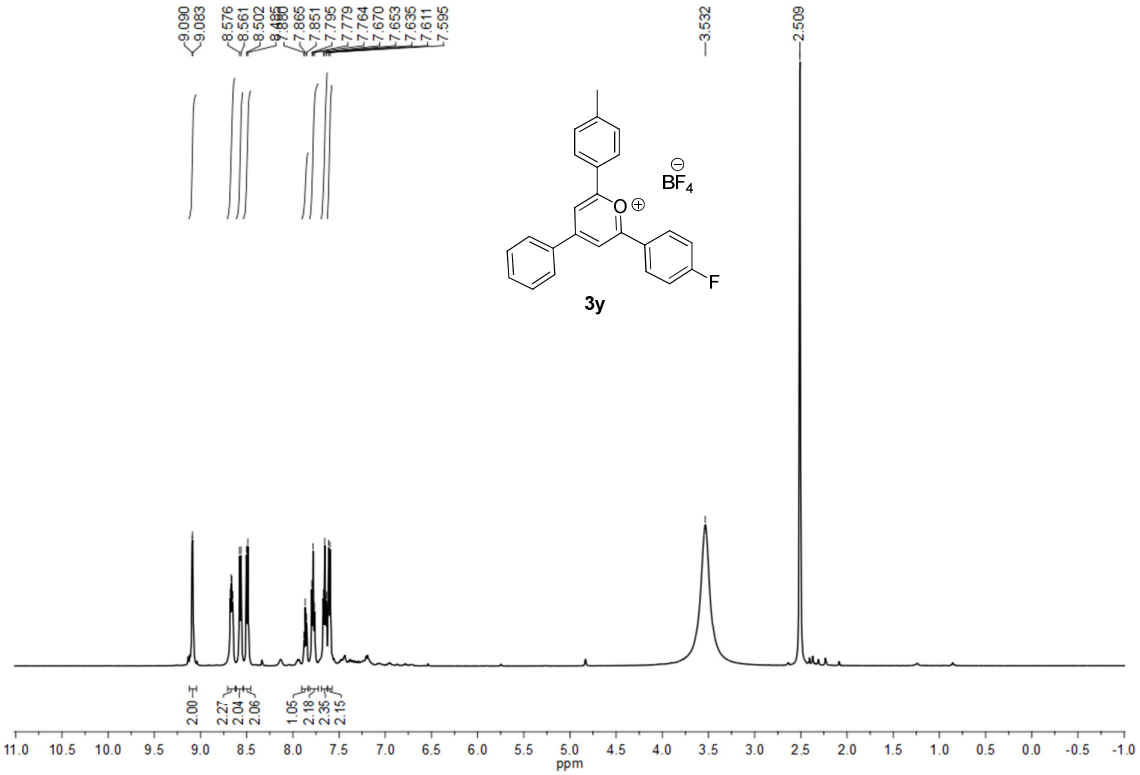

Fig S47. ^{1}H NMR of 3y

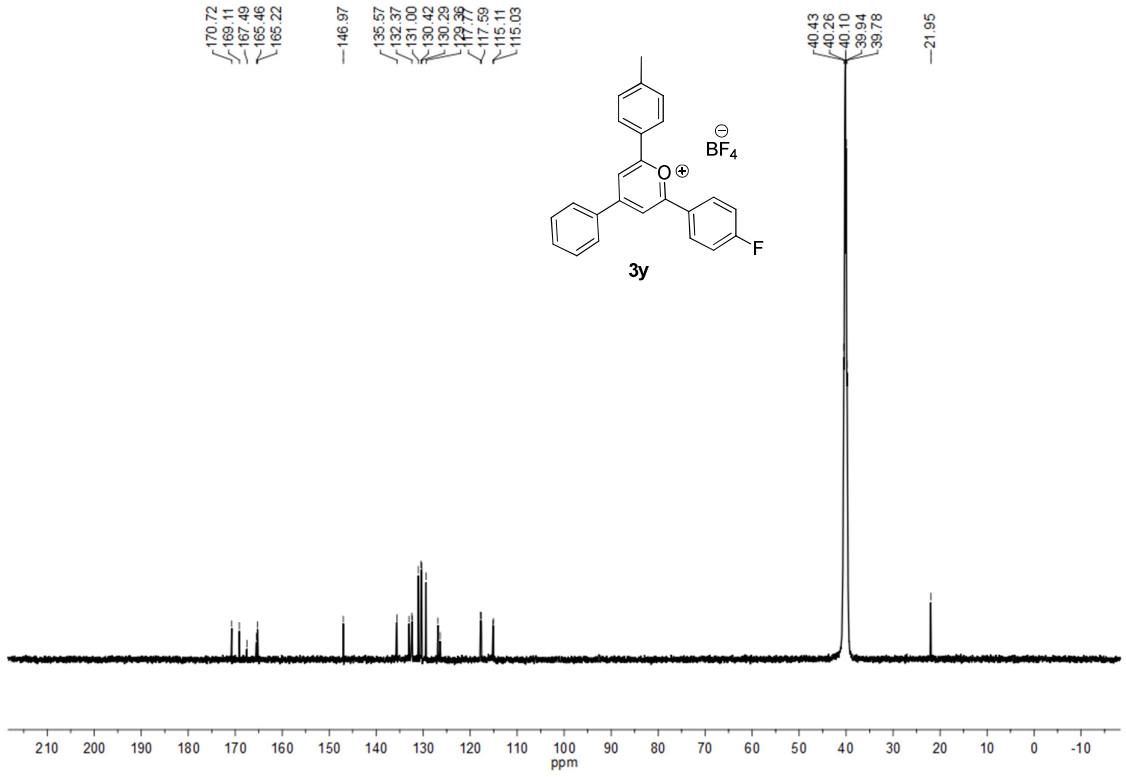

Fig S48. ^{13}C NMR of 3y

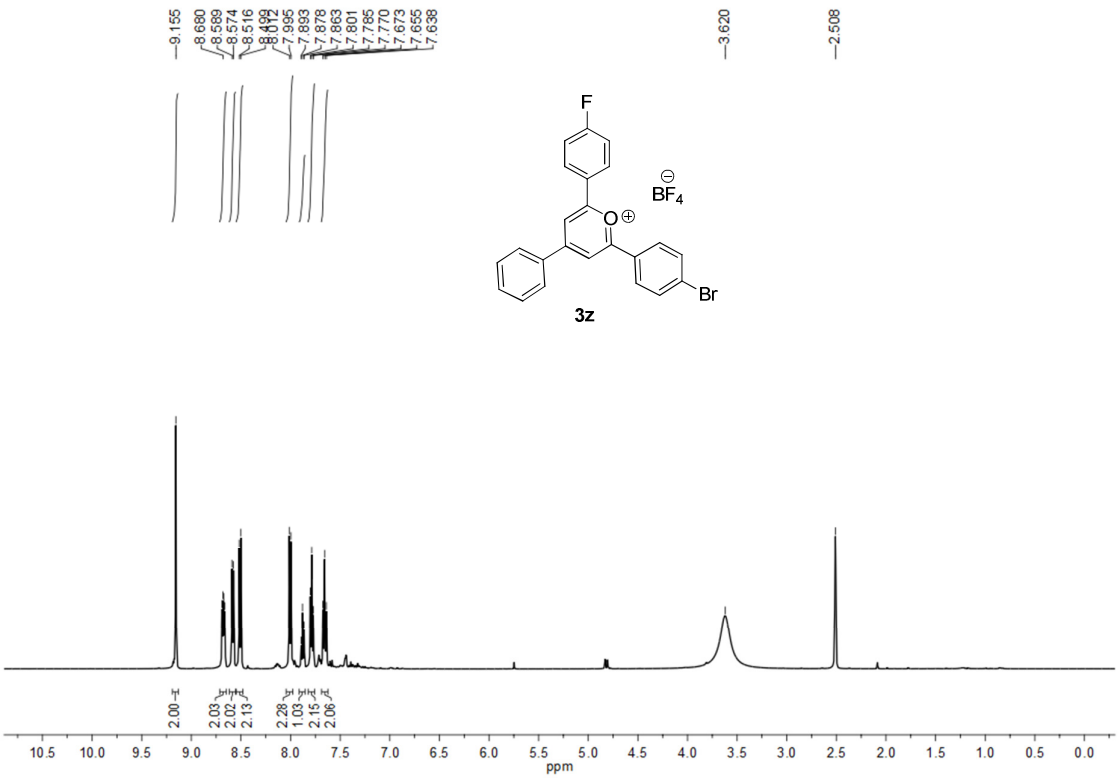

Fig S49. ^{1}H NMR of 3z

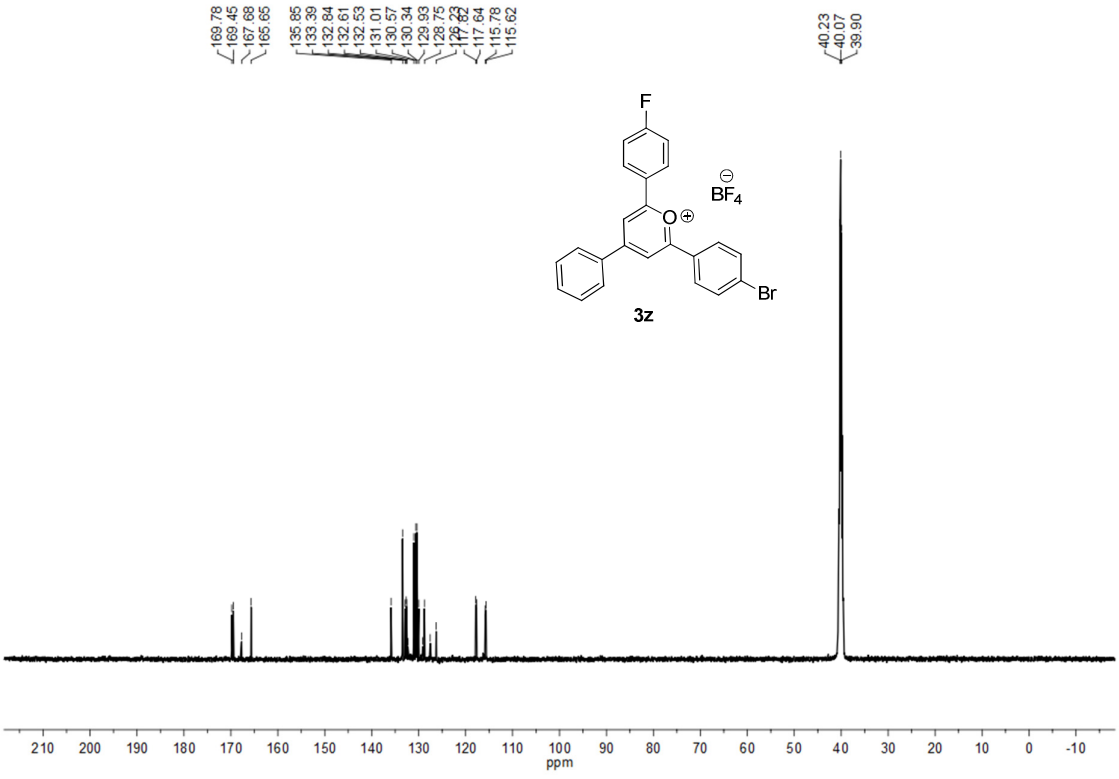

Fig S50. ^{13}C NMR of 3z

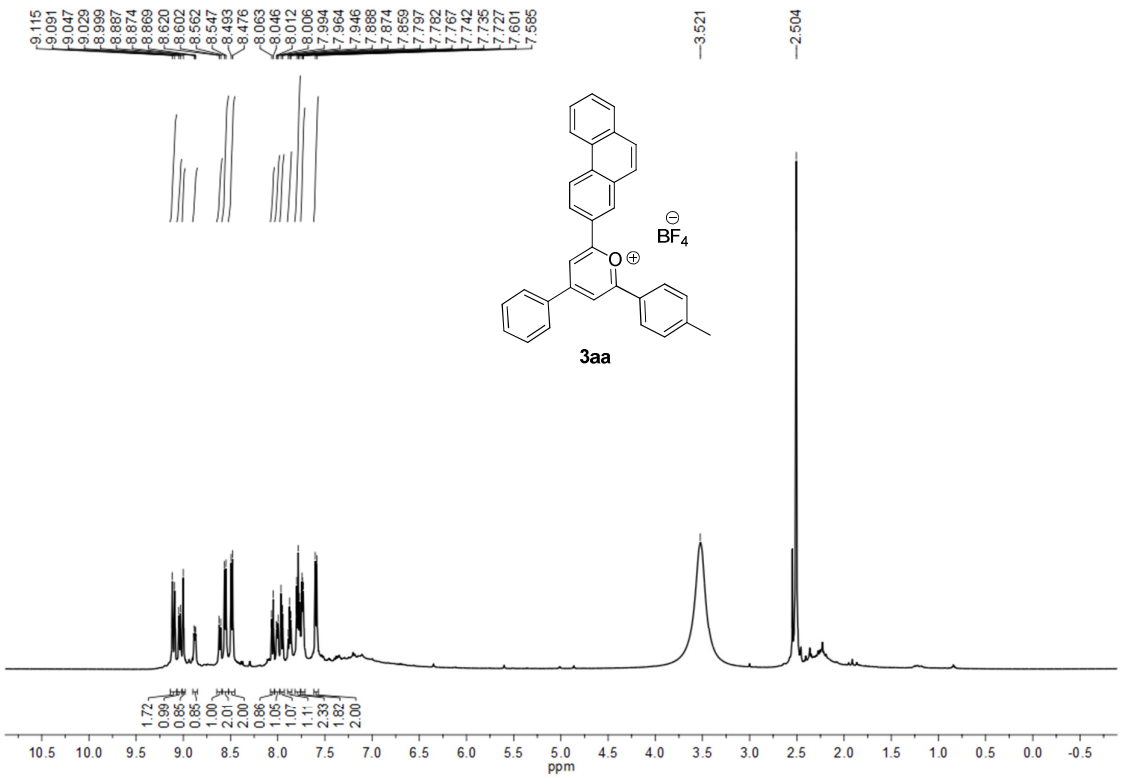

Fig S51. ^{1}H NMR of 3aa

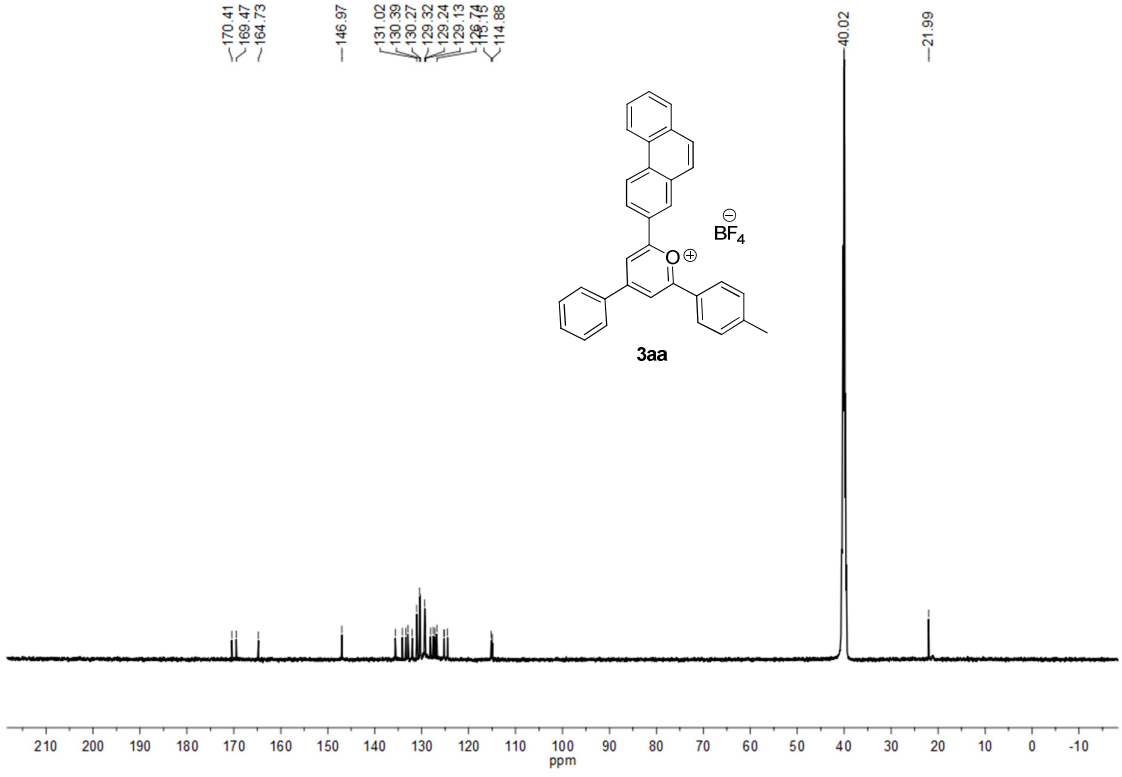

Fig S52. ^{13}C NMR of 3aa

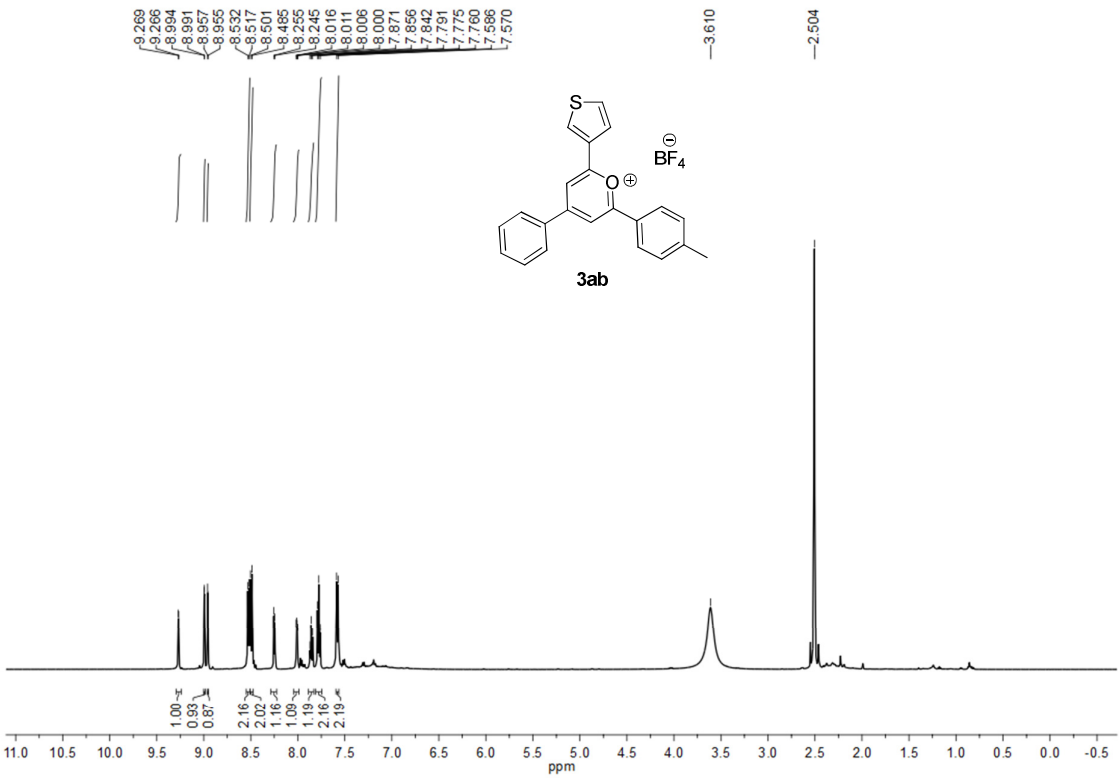

Fig S53. ^{1}H NMR of 3ab

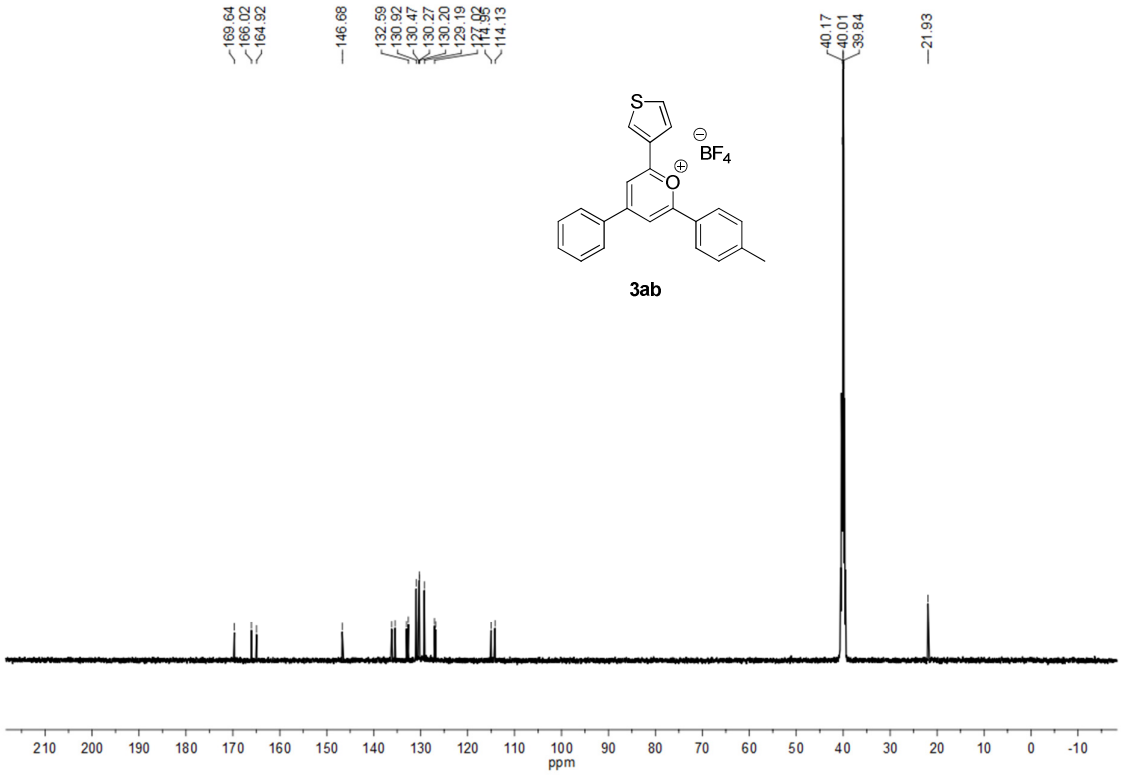

Fig S54. ^{13}C NMR of 3ab

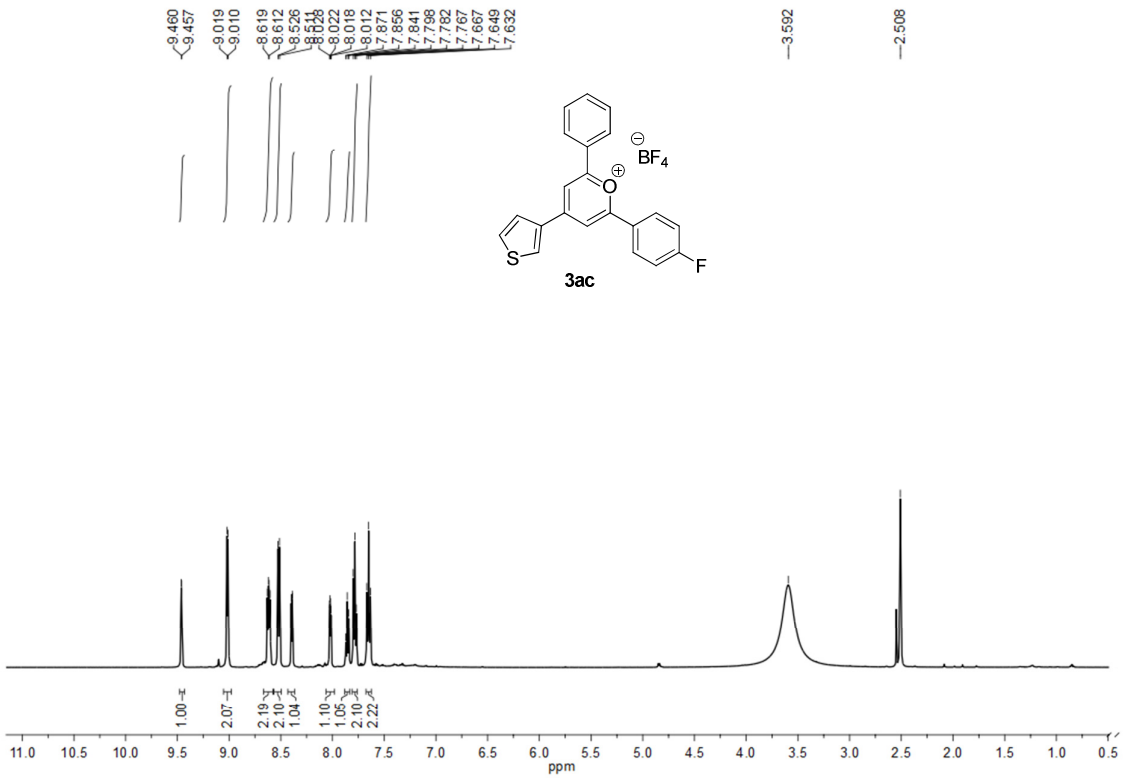

Fig S55. ^{1}H NMR of 3ac

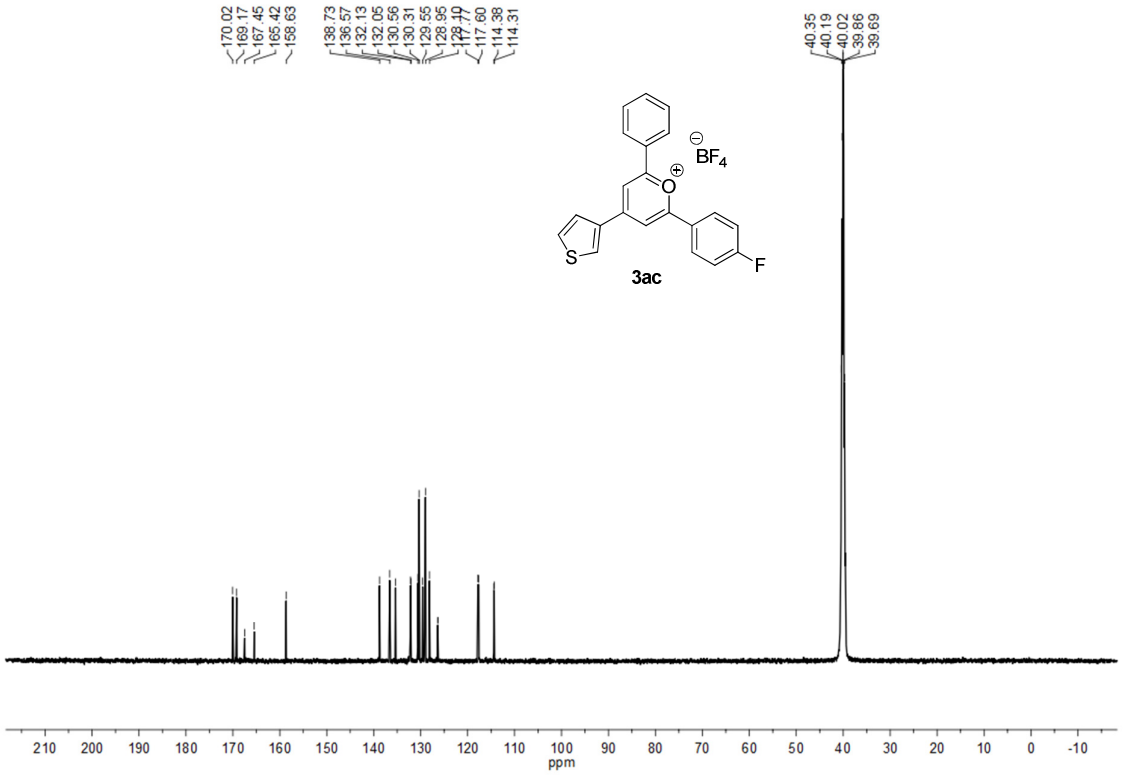

Fig S56. ^{13}C NMR of 3ac

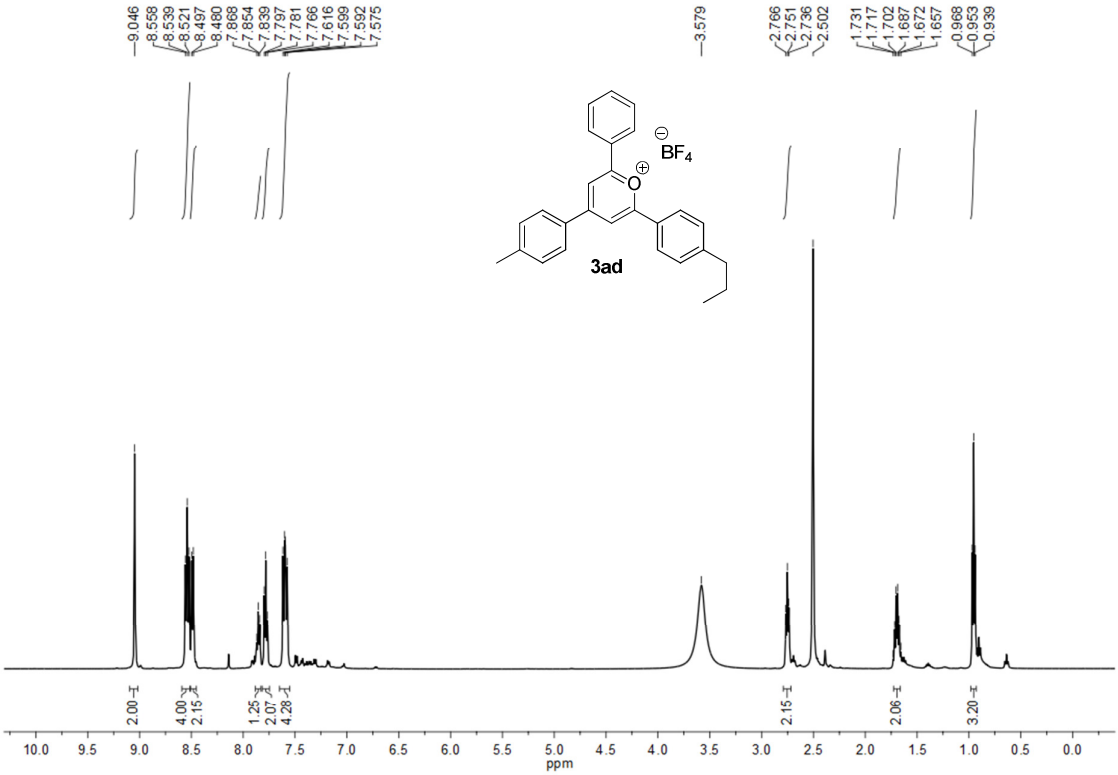

Fig S57. ^{1}H NMR of 3ad

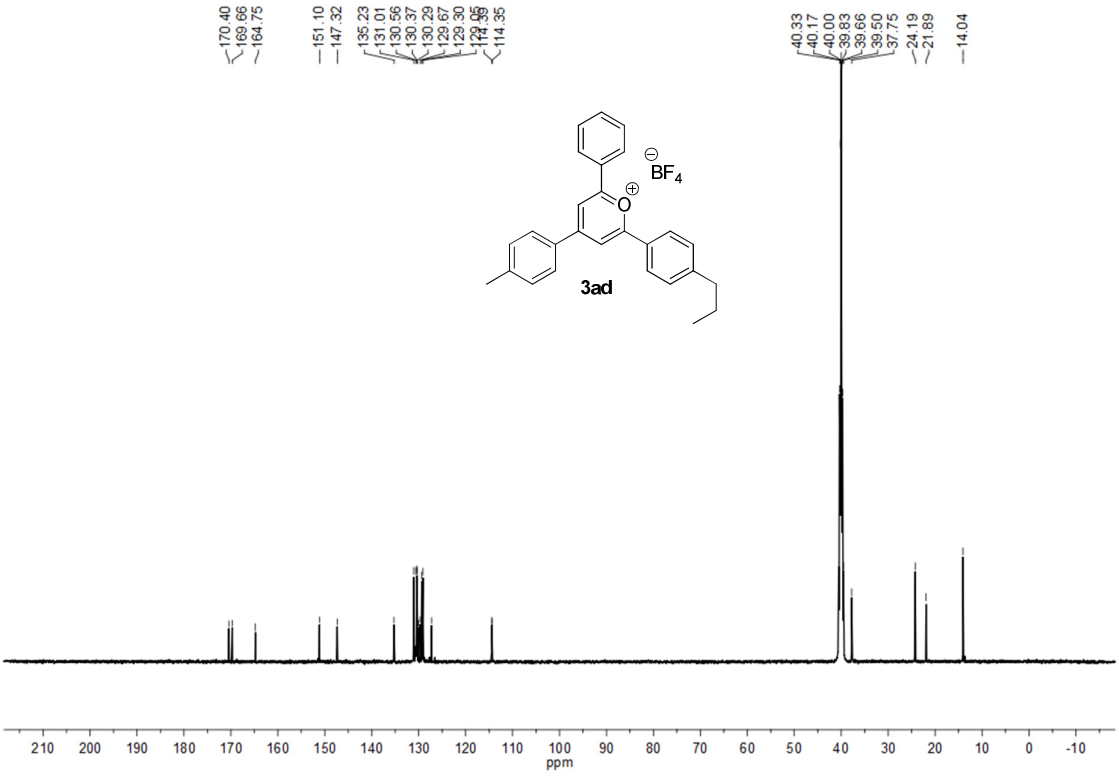

Fig S58. ^{13}C NMR of 3ad

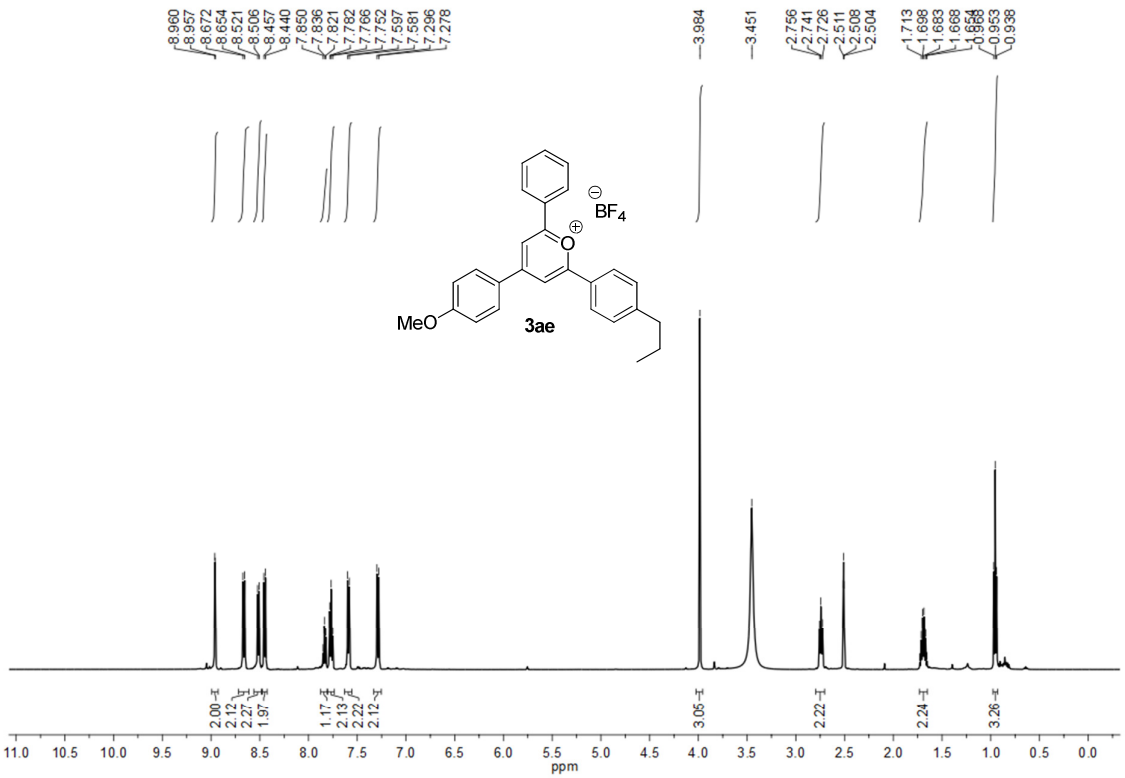

Fig S59. ^{1}H NMR of 3ae

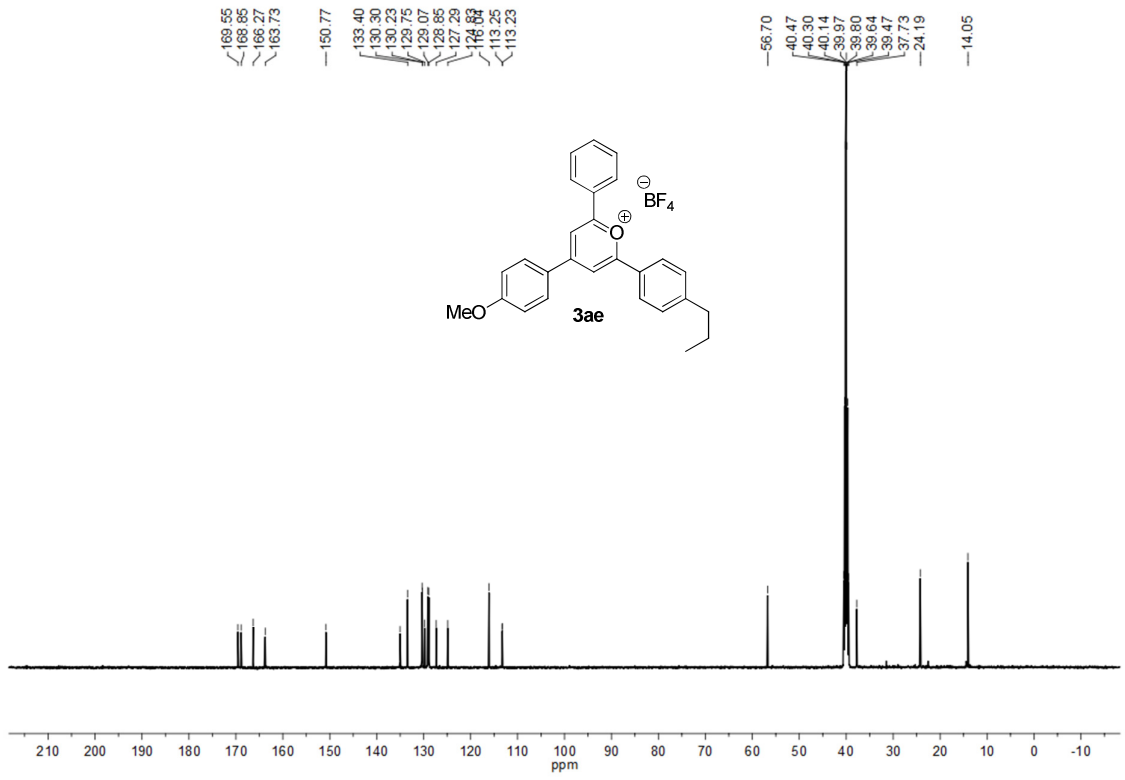

Fig S60. ^{13}C NMR of 3ae

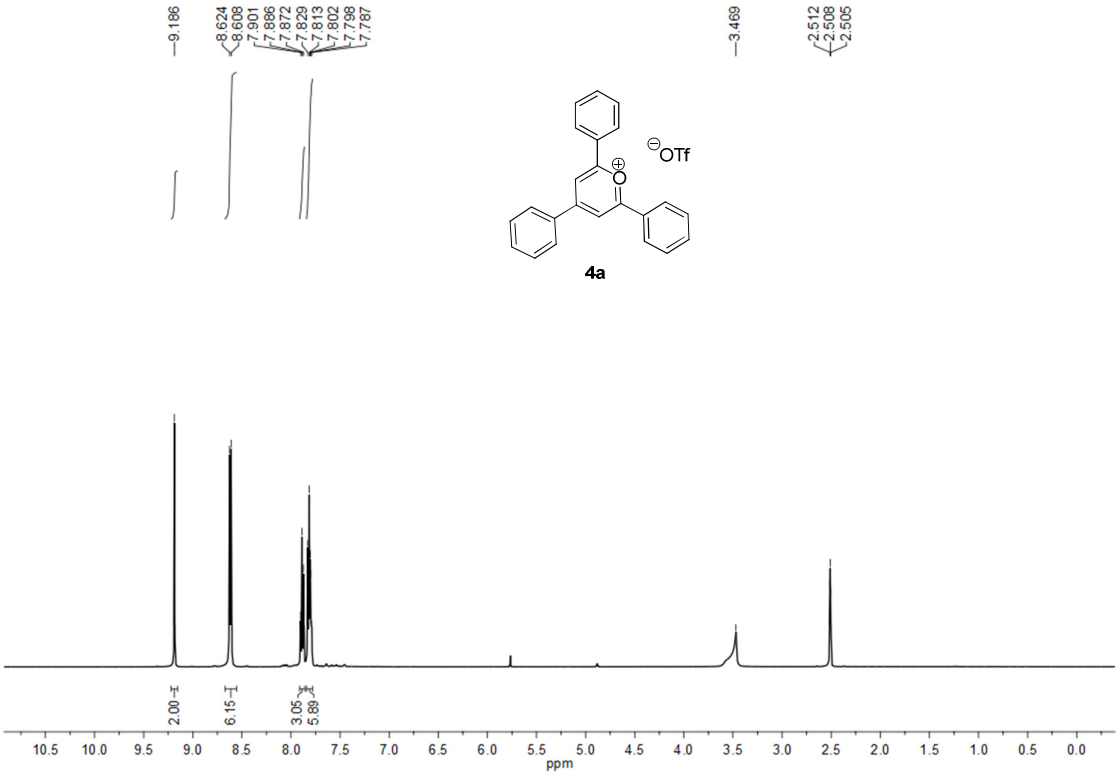

Fig S61. ^{1}H NMR of 4a

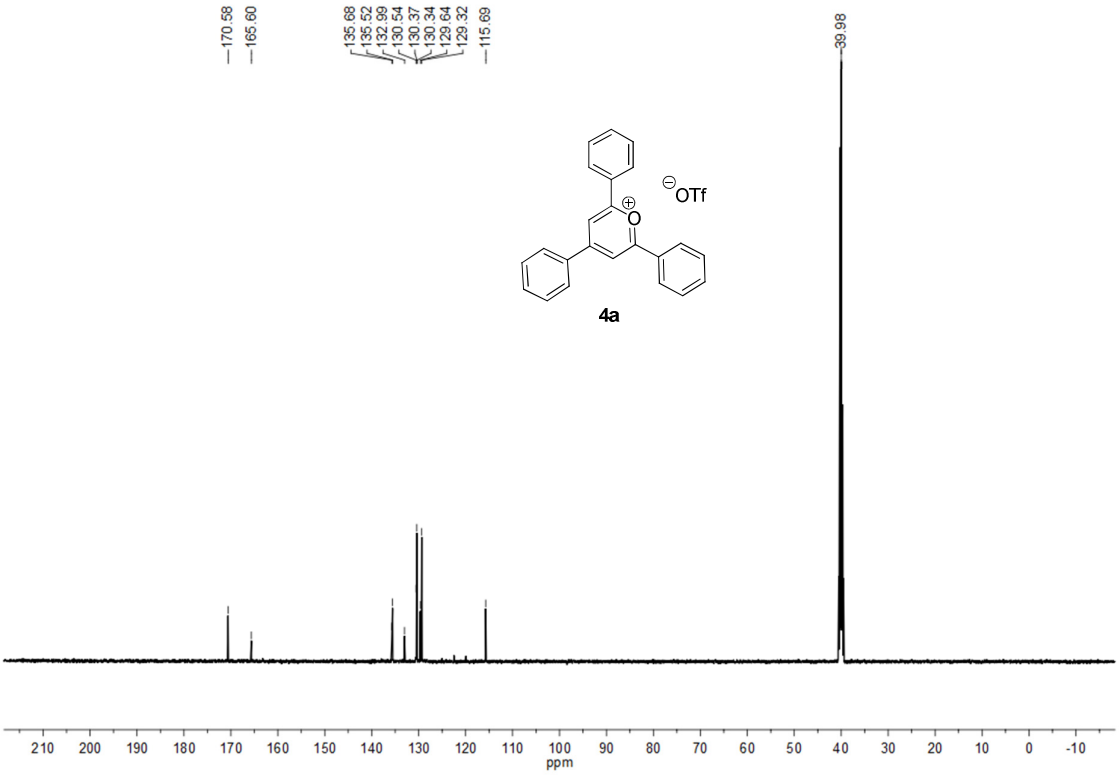

Fig S62. ^{13}C NMR of 4a

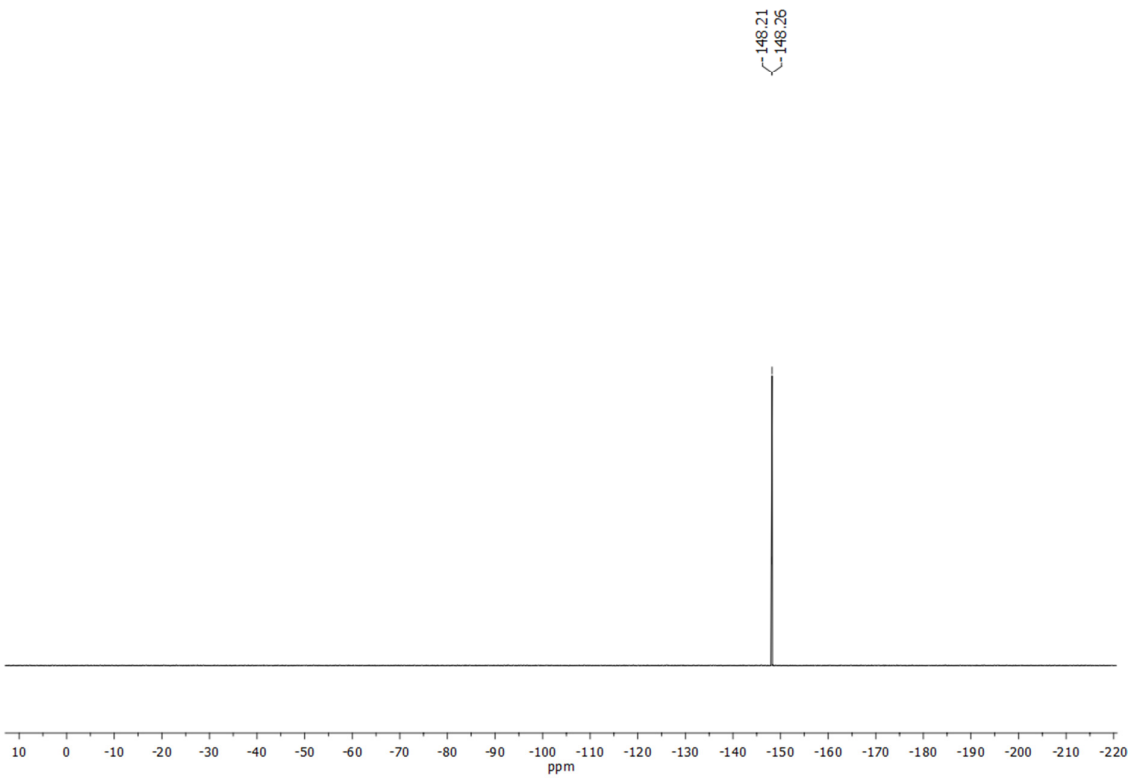

Fig S63. ^{19}F NMR of 3b

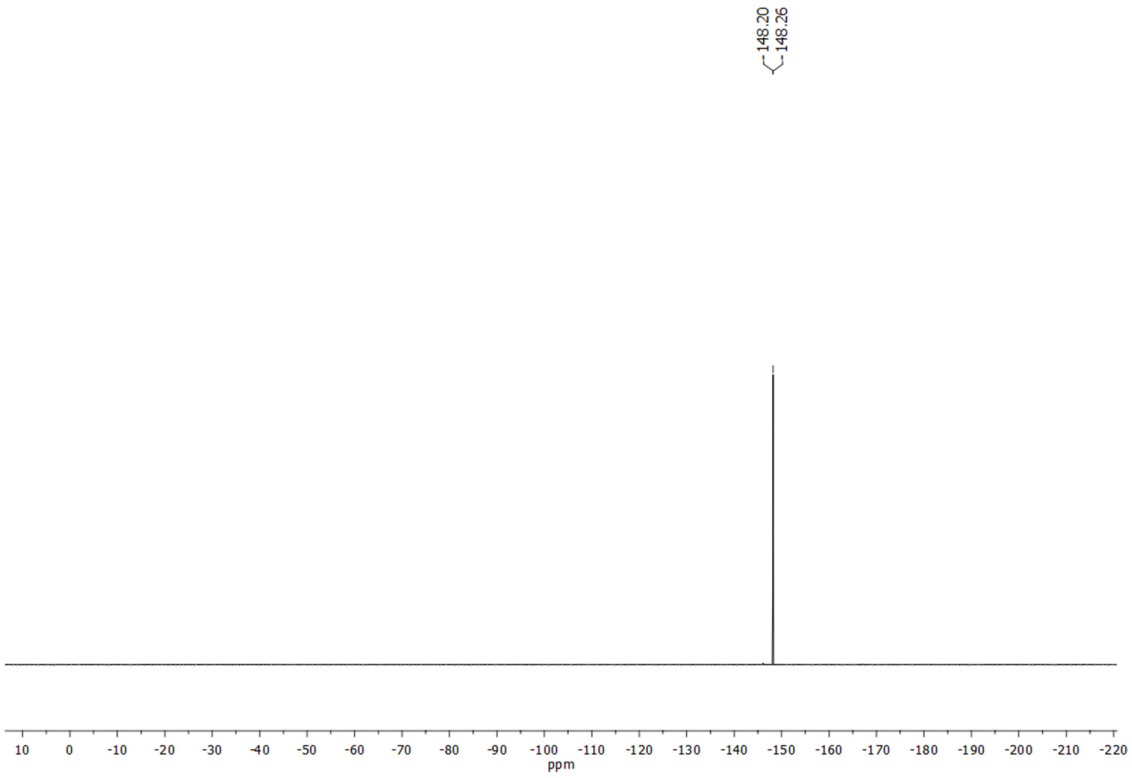

Fig S64. ^{19}F NMR of 3c

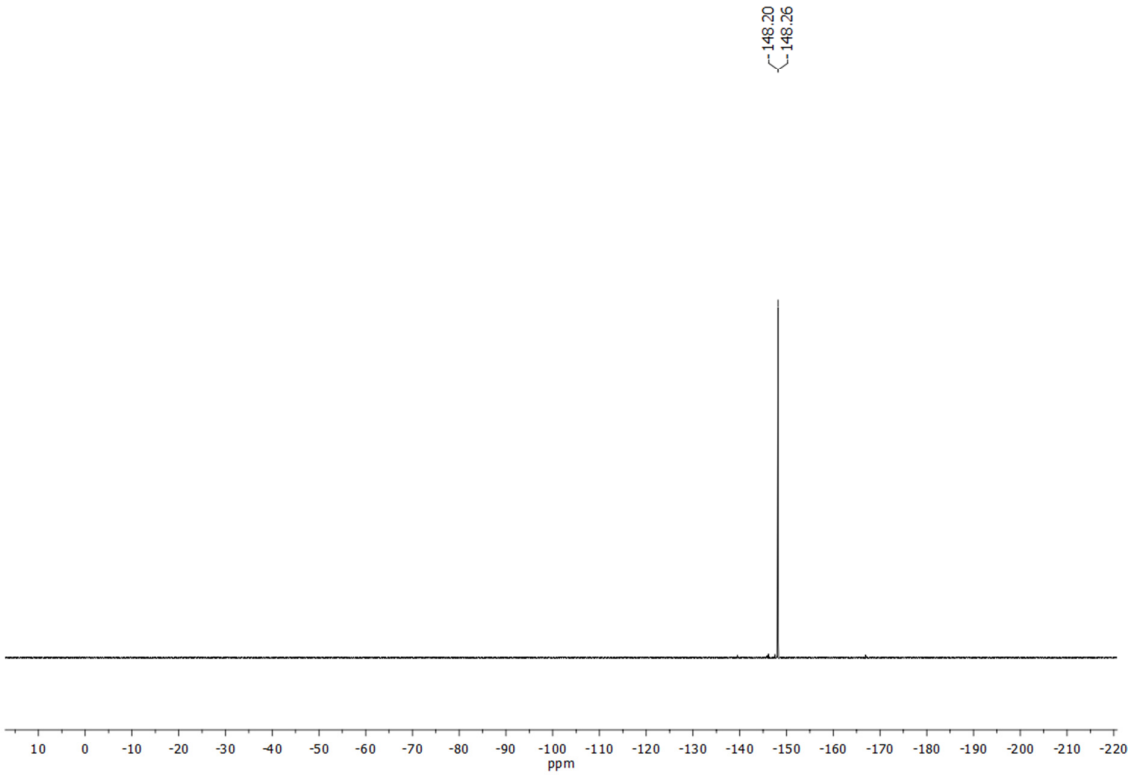

Fig S65. ^{19}F NMR of 3d

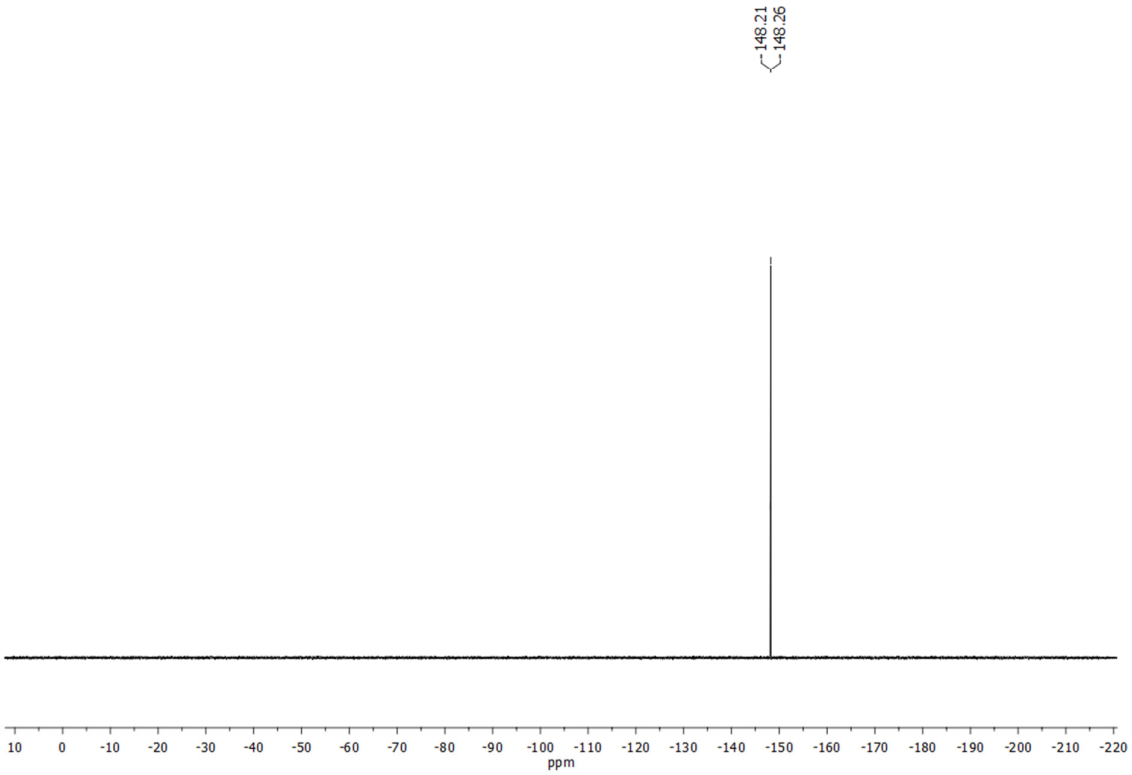

Fig S66. ^{19}F NMR of 3e

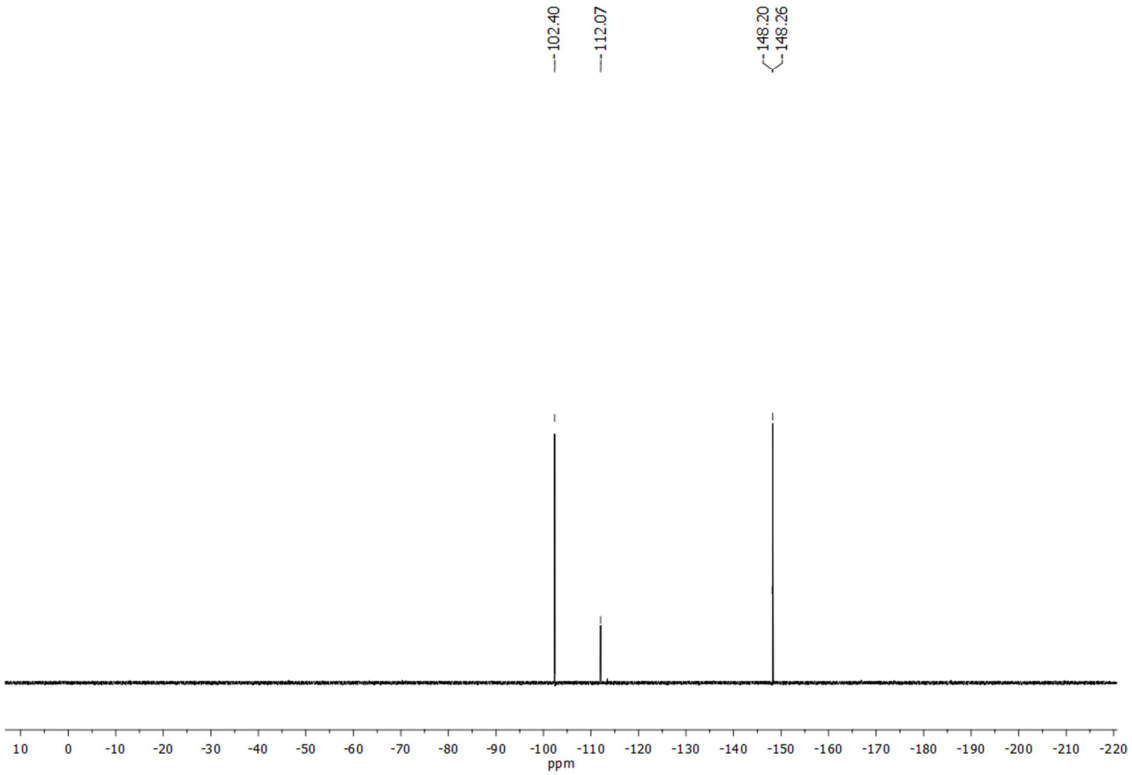

Fig S67. ^{19}F NMR of 3g

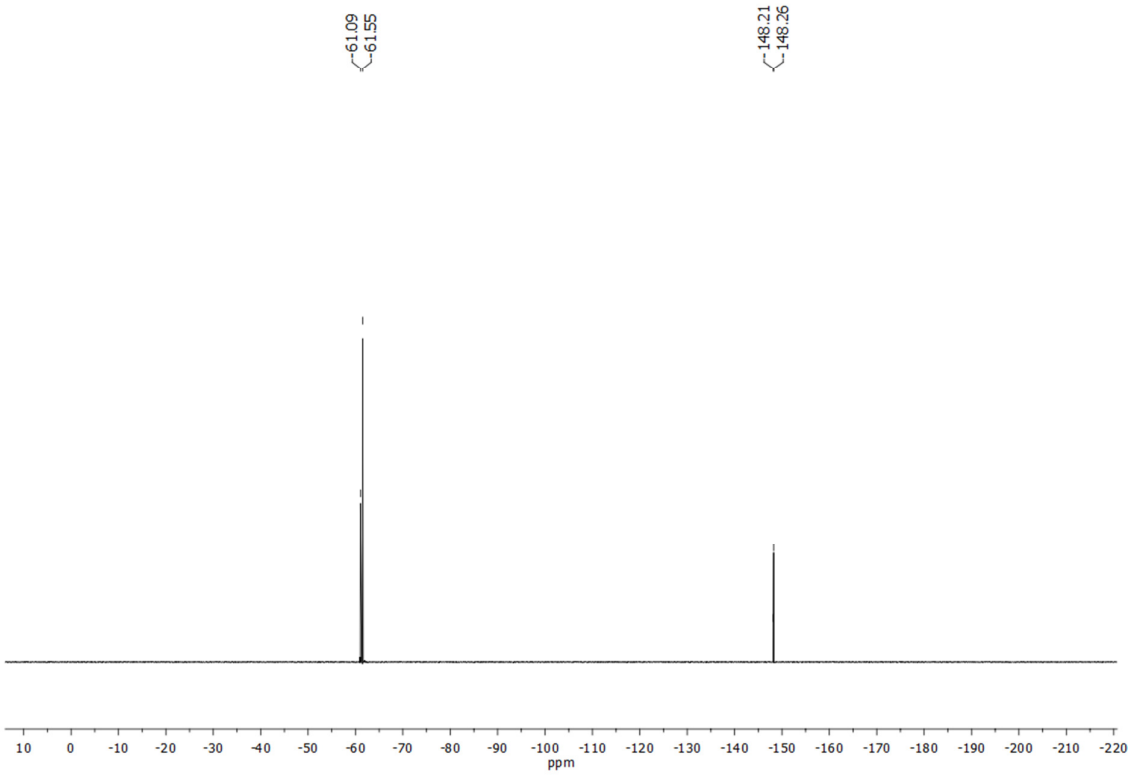

Fig S68. ^{19}F NMR of 3h

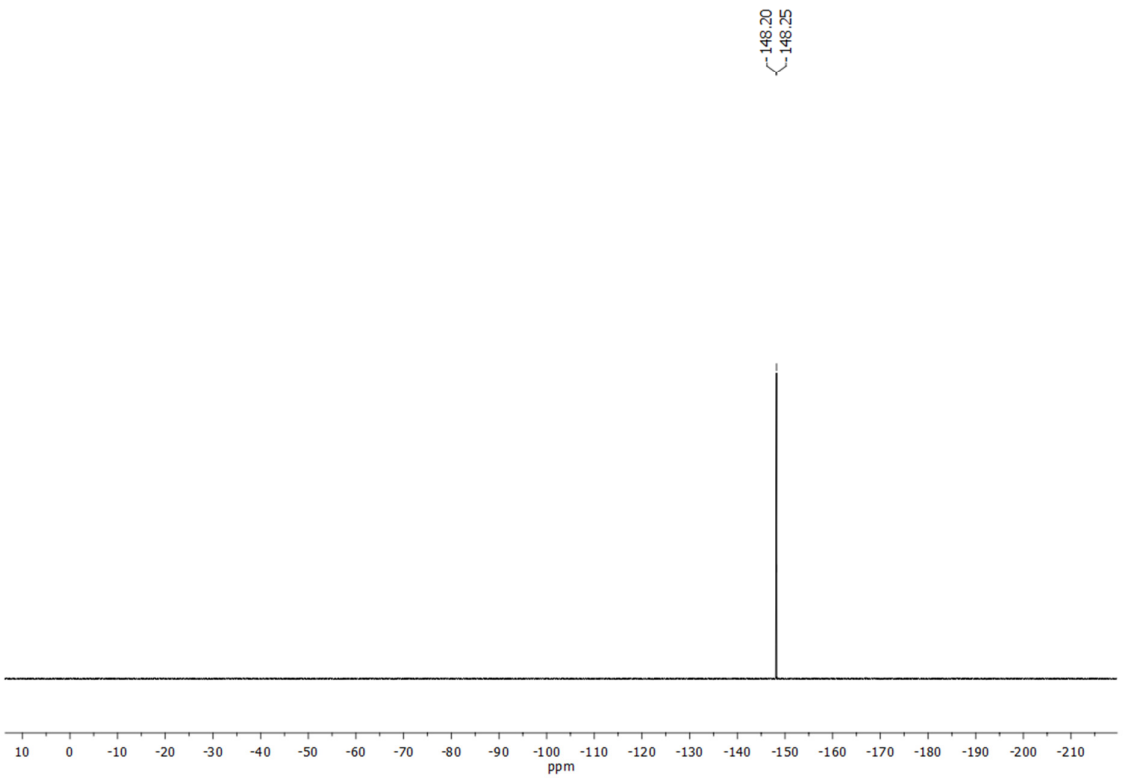

Fig S69. ^{19}F NMR of 3i

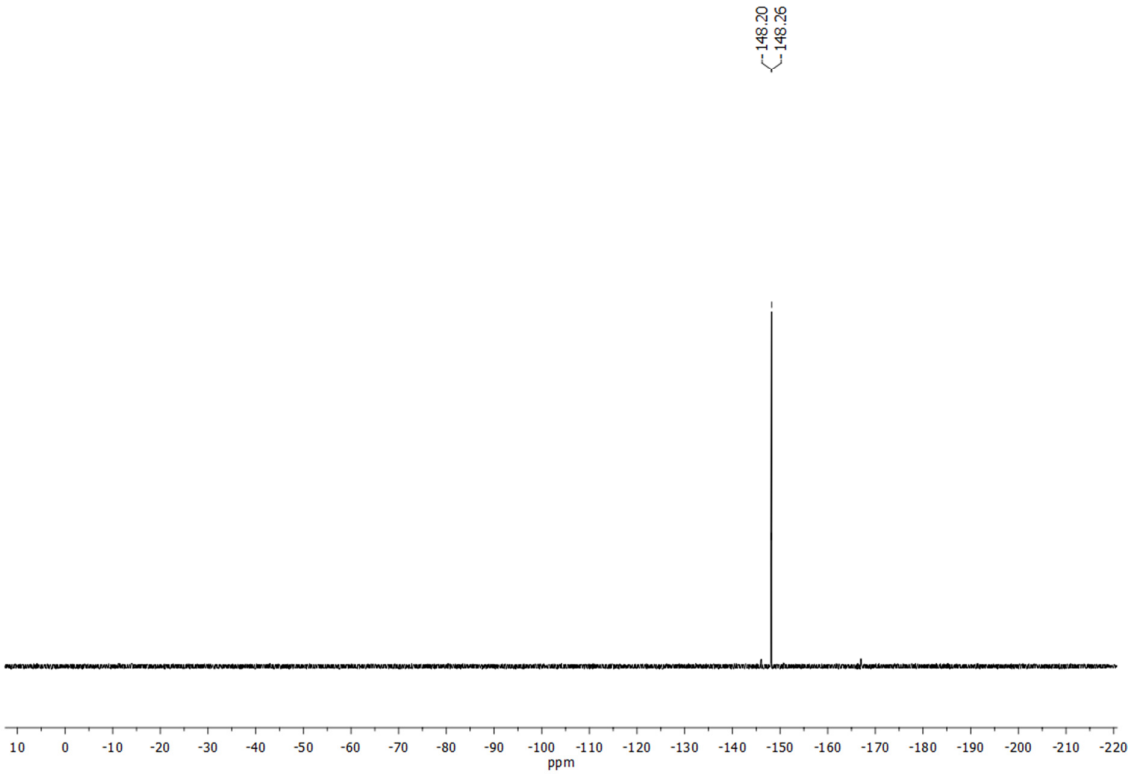

Fig S70. ^{19}F NMR of 3j

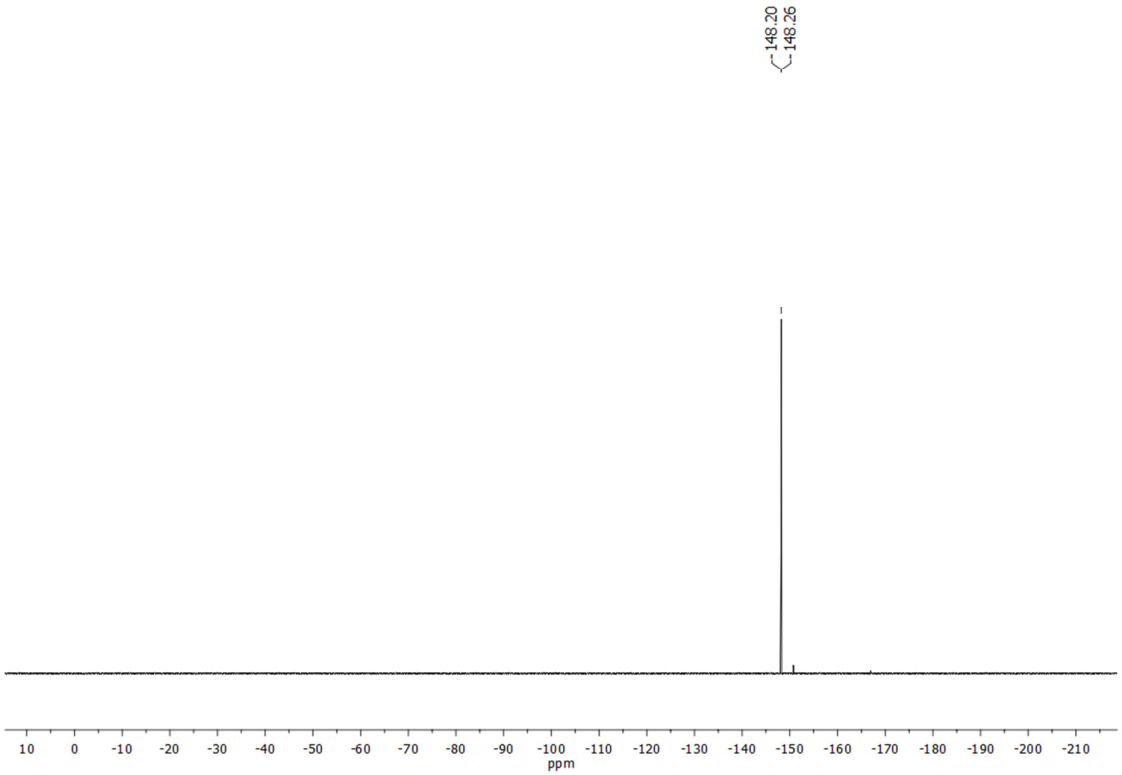

Fig S71. ^{19}F NMR of 3m

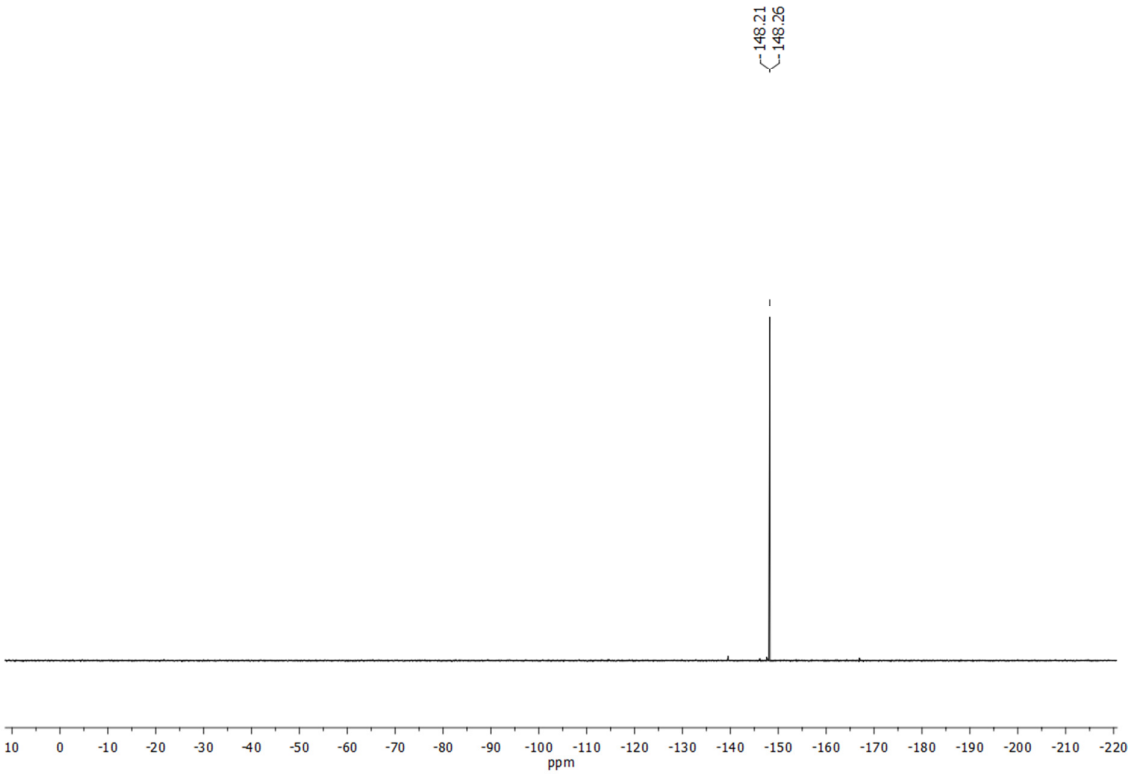

Fig S72. ^{19}F NMR of 3v

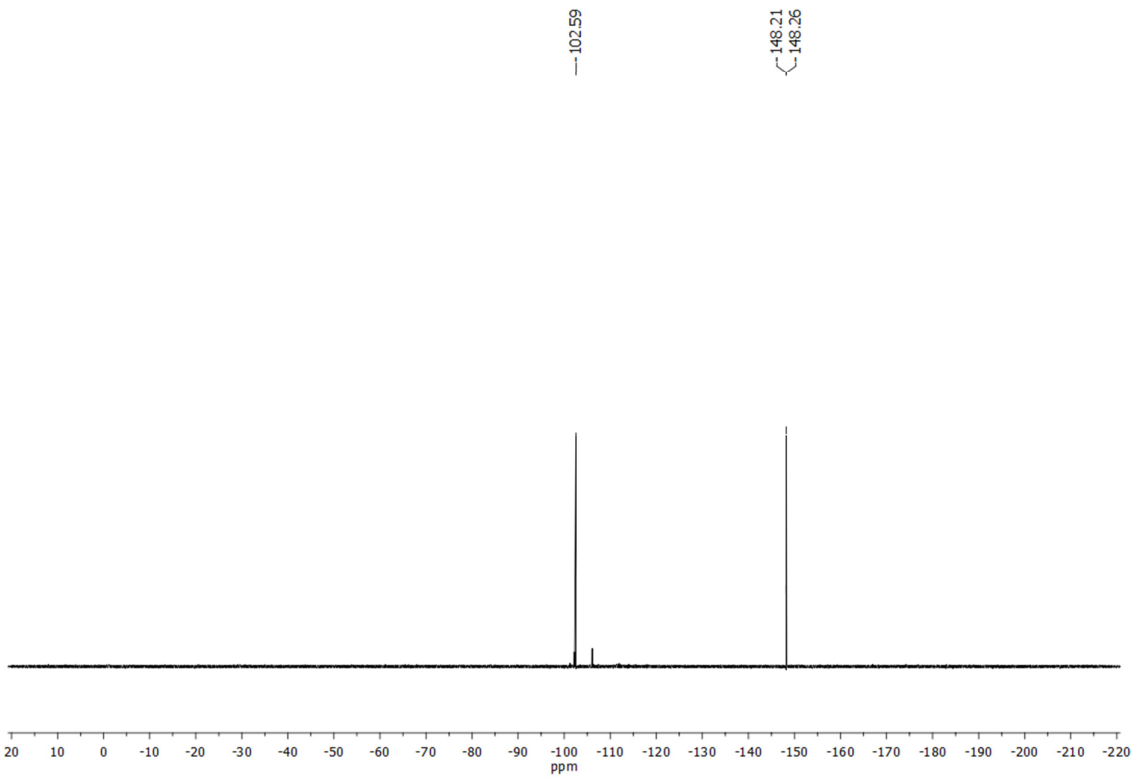

Fig S73. ^{19}F NMR of 3y

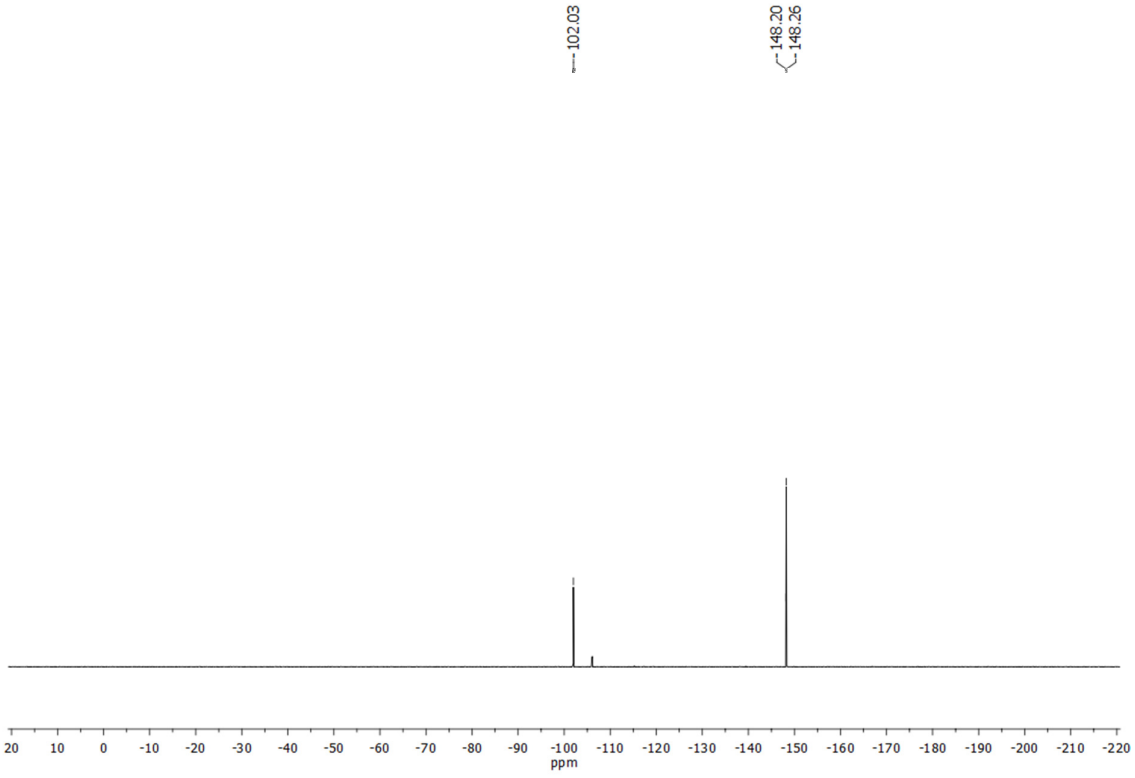

Fig S74. ^{19}F NMR of 3z

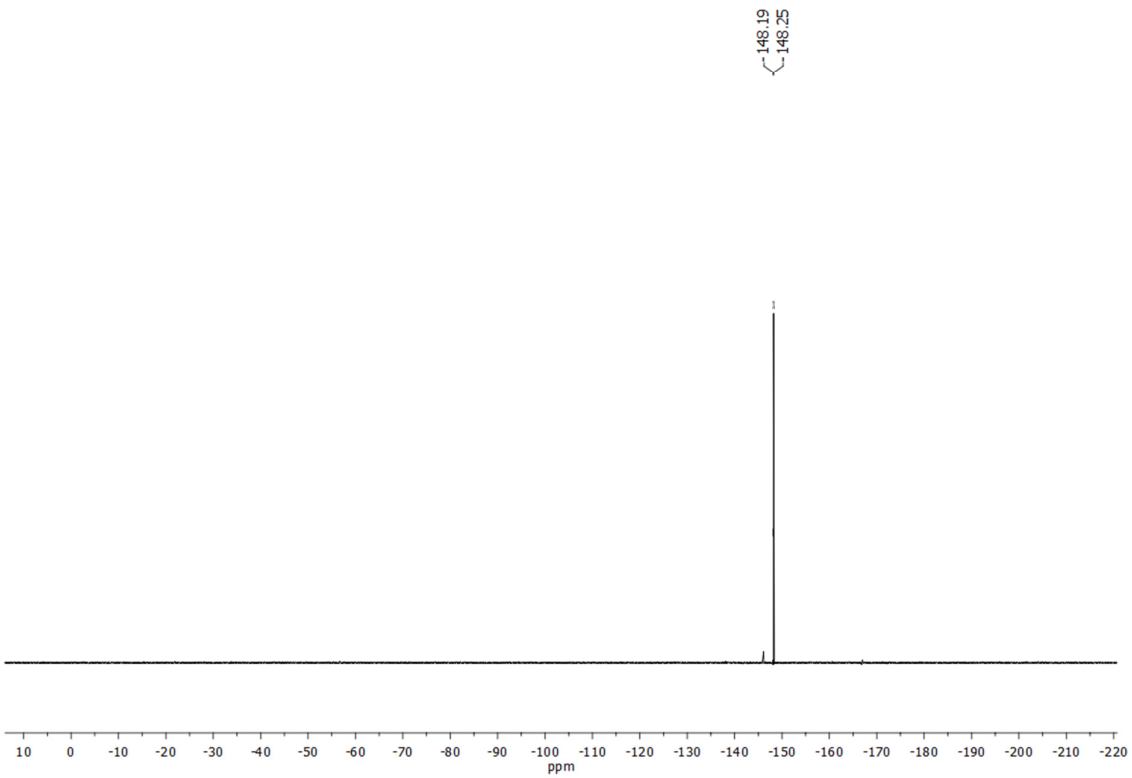

Fig S75. ^{19}F NMR of 3ab

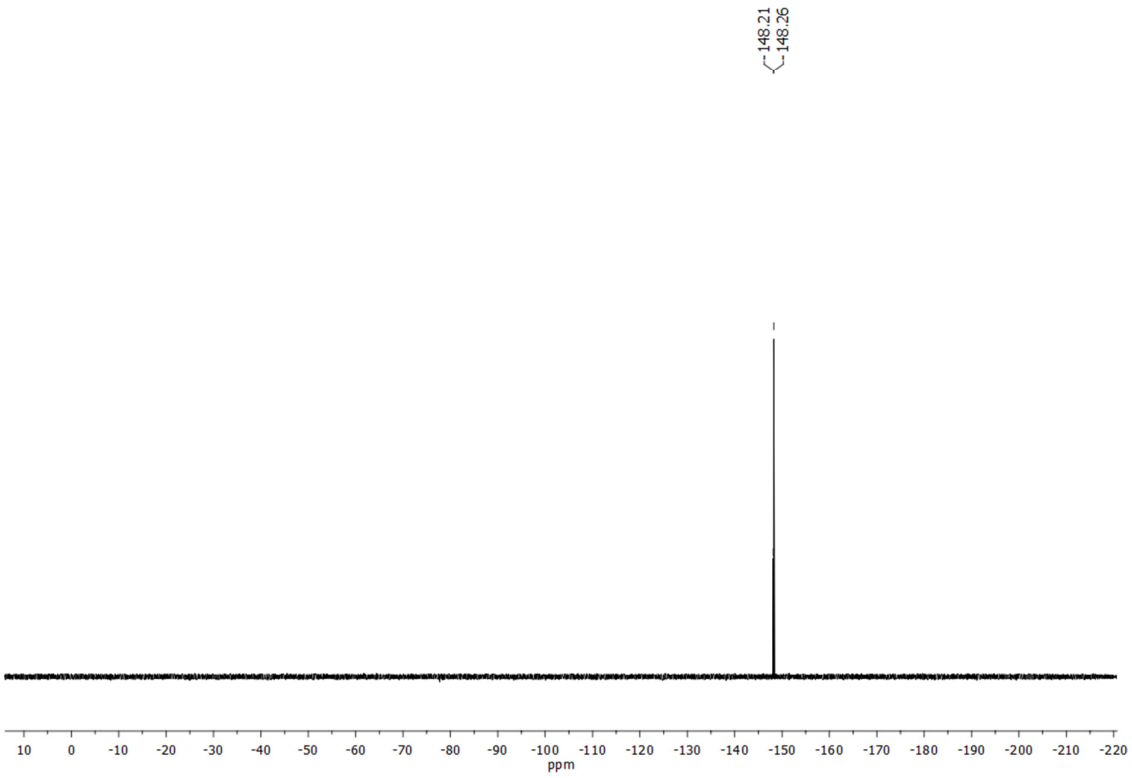

Fig S76. ^{19}F NMR of 3ad

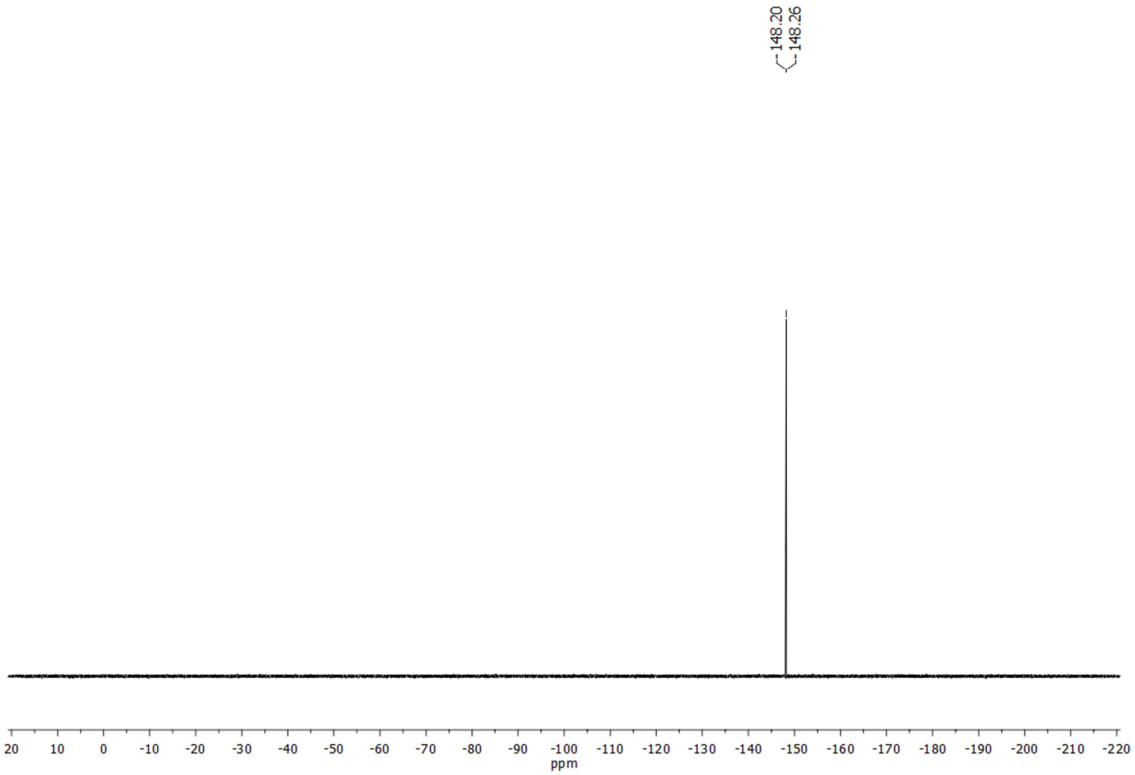

Fig S77. ^{19}F NMR of 3ae

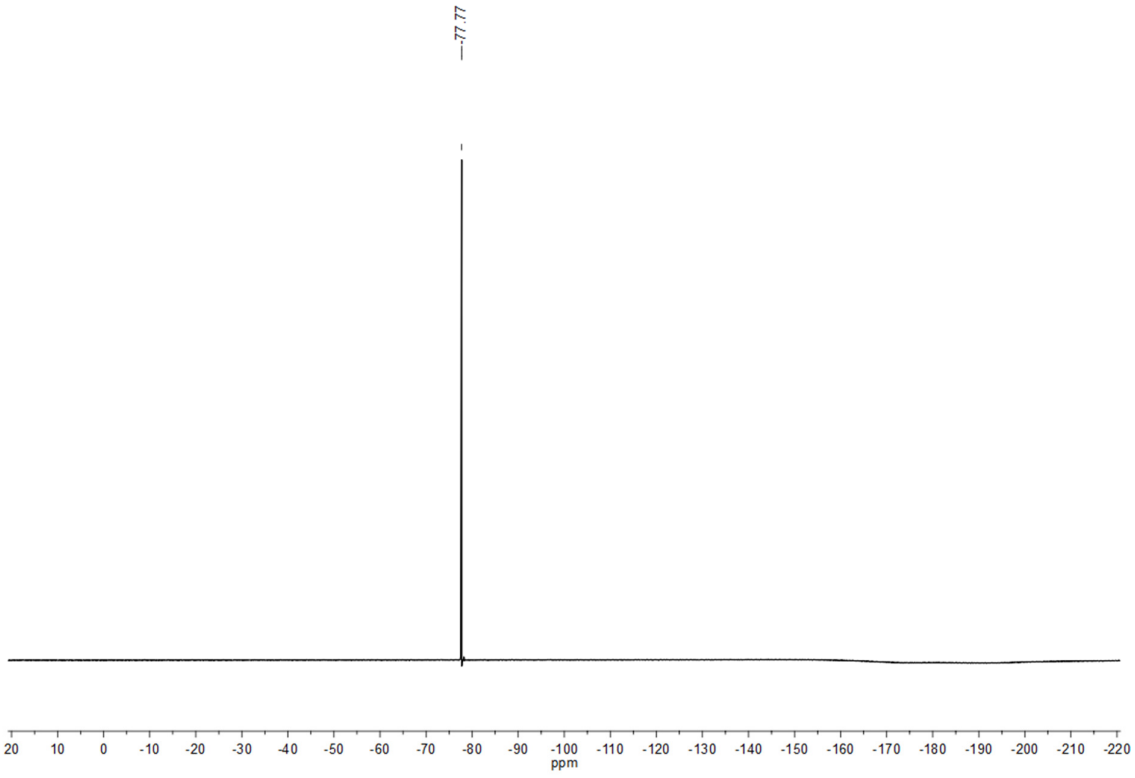

Fig S78. ^{19}F NMR of 4a

ORTEP drawing of compound 3f

CCDC 1574744

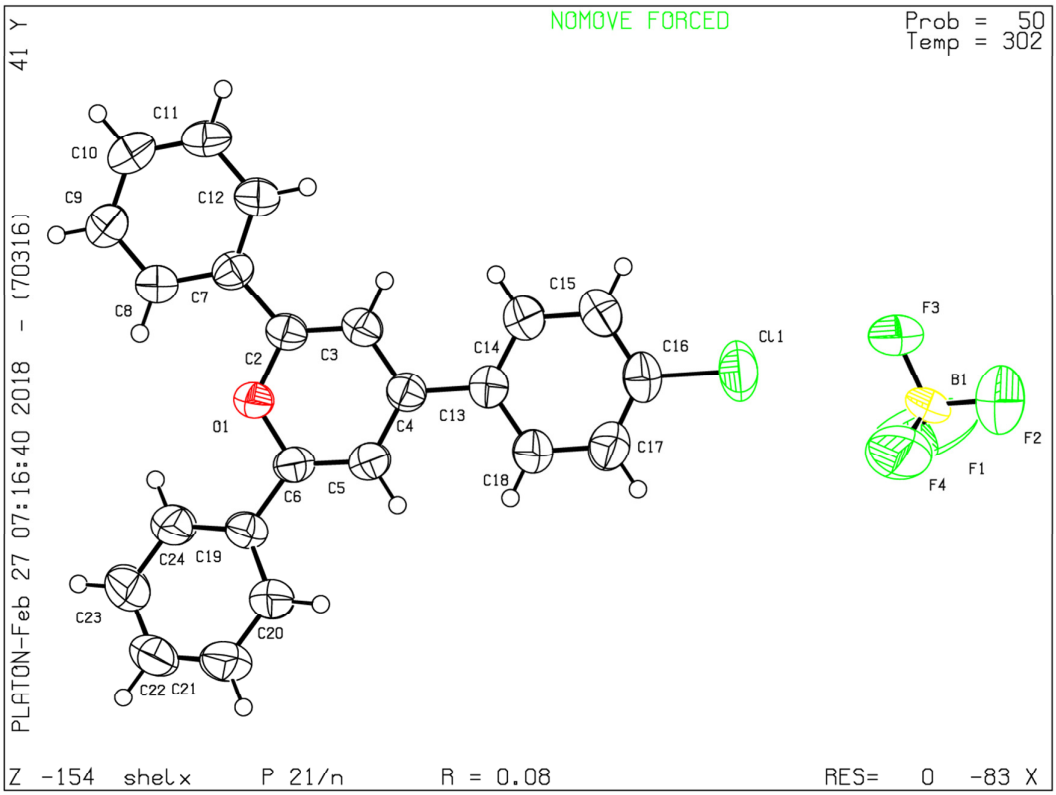

Fig S64. ORTEP drawing of compound 3f

Density Functional Theory (DFT) Calculations

Gaussian 09 suite of programs[1] have been used for all the calculations at the DFT level by the application of Minnesota functional[2] M06-2X in conjunction with valence triple-zeta polarized basis set 6-311++G(d,p).[3] M06-2X is hybrid meta exchange-correlation functional recommended for thermochemistry, thermochemical kinetics, and noncovalent interactions.[4,5] The geometries of all structures were optimized at this level under standard conditions (298.15 K, 1.0 atm). Vibrational analysis was done for all the structures. All the transition state geometries were confirmed with one imaginary frequency along the bond breaking/forming reaction coordinate while all the stationary points showed zero imaginary frequency. For the transition states, simulation of the structure along the forward and reverse directions were performed

to verify their connectivity to the proper reactants and intermediate products. Further, the solvation model SMD[6], an integral equation formalism variant of the polarizable continuum model (IEFPCM)[7] is used along with the DFT method to do single point calculations on optimized geometries to obtain more accurate energies. The SMD model simulate the effect of the solvent cyclohexane. The energetics reported in the paper is at M06-2X/6-311+G(d,p)/SMD//M06-2X/6-311+G(d,p) level.

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(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision **D.01**, Gaussian, Inc., Wallingford CT, 2009.

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(7) Scalmani, G.; Frisch, M. J. *J. Chem. Phys*. **132**, 114110 (2010).

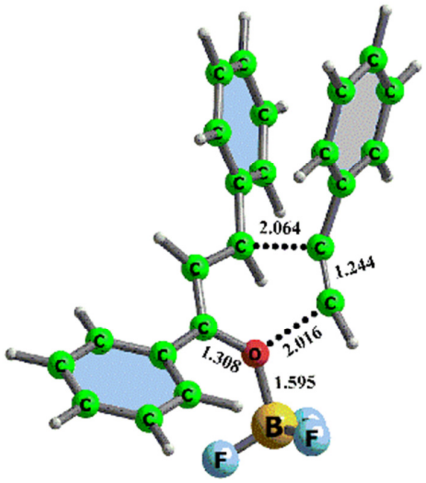


Fig S65. Optimized geometry of **ts1′** at M06-2X/6-311++G(d,p) level of DFT. All bond lengths in Å.

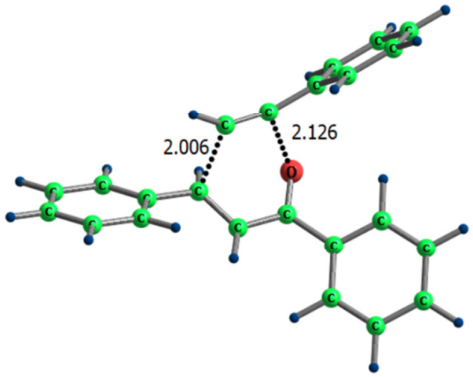


Fig S66. Optimized geometry of transition state for normal [4 + 2] cycloaddition to yield 2,4,6-triaryl-*4H*-pyran, at M06-2X/6-311++G(d,p) level of DFT. All bond lengths in Å.

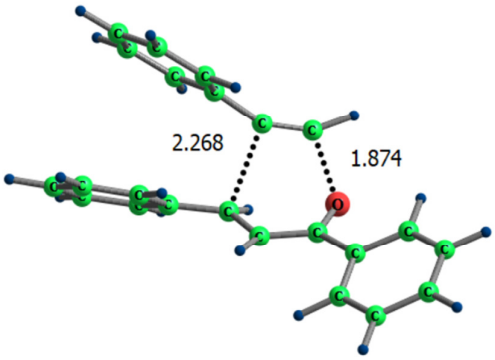
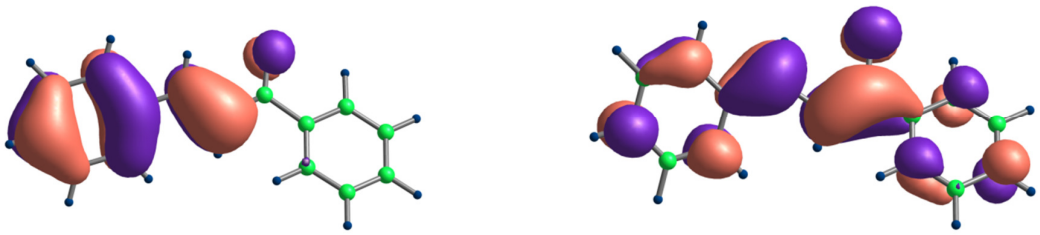


Fig S67. Optimized geometry of transition state for normal [4 + 2] cycloaddition to yield 2,4,5-triaryl-*4H*-pyran, at M06-2X/6-311++G(d,p) level of DFT. All bond lengths in Å.



HOMO -7.95 eV
HOMO-LUMO Gap = 6.39 eV

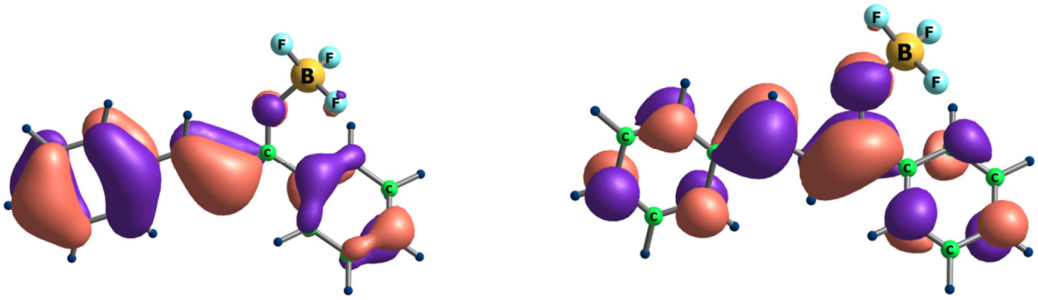
LUMO -1.56 eV

Fig S68. HOMO and LUMO of *(E)*-chalcone.

HOMO -8.00 eV
HOMO-LUMO Gap = 7.67 eV

LUMO -0.33 eV

Fig S69. HOMO and LUMO of aryl acetylene.

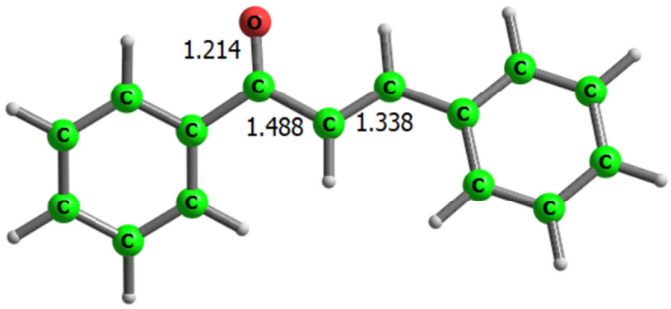


HOMO -8.57 eV
HOMO-LUMO Gap = 5.90 eV

LUMO -2.67 eV

Fig S70. HOMO and LUMO of BF_3 coordinated *(E)*-chalcone.

Cartesian coordinates of optimized geometries (in Å) of molecules at M06-2X/6-311++G(d,p) level

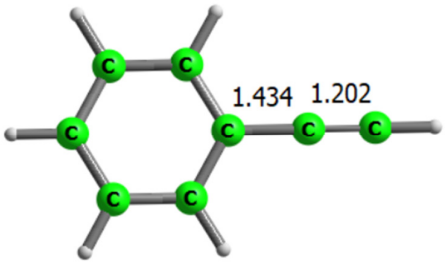


(E)-chalcone

E at M06-2X/6-311++G(d,p) level = -653.9217373 a.u.
E at M06-2X/6-311++G(d,p)/SMD//M06-2X/6-311++G(d,p) level = -653.9398306 a.u.
Number of imaginary frequency = 0

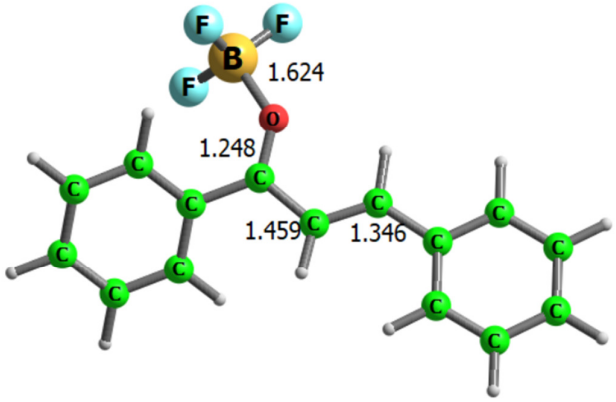
C	-2.483036000	0.229212000	-0.008790000
C	-2.571492000	-1.111196000	-0.388114000
C	-3.645341000	0.922819000	0.337413000
C	-3.806823000	-1.750124000	-0.418377000
C	-4.874739000	0.280591000	0.322791000
C	-4.956853000	-1.057915000	-0.055775000
H	-1.685944000	-1.657443000	-0.689233000
H	-3.559093000	1.966628000	0.614219000
H	-3.870687000	-2.786958000	-0.725826000
H	-5.771211000	0.820893000	0.602489000
H	-5.917678000	-1.558883000	-0.071681000
C	-1.184785000	0.981878000	0.012616000
O	-1.183947000	2.195224000	-0.009968000
C	0.082027000	0.204367000	0.081514000
H	0.026482000	-0.860378000	0.268267000
C	1.254267000	0.833041000	-0.064912000
H	1.212364000	1.903745000	-0.253422000
C	2.592928000	0.238201000	-0.006544000
C	3.696376000	1.043776000	-0.307357000
C	2.817273000	-1.100787000	0.340611000
C	4.987174000	0.529450000	-0.274145000
C	4.104229000	-1.614621000	0.376006000
C	5.194100000	-0.801975000	0.066605000
H	3.533562000	2.083092000	-0.571575000
H	1.981629000	-1.742518000	0.593244000
H	5.829328000	1.167982000	-0.512214000
H	4.262434000	-2.651266000	0.648564000

H	6.198564000	-1.206993000	0.095661000



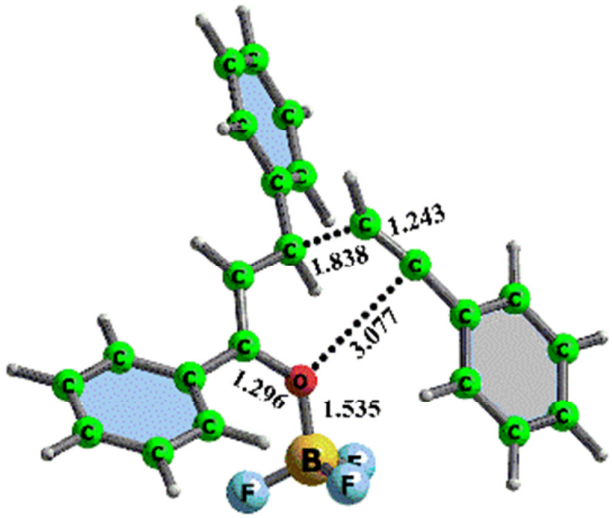
Aryl acetylene
E at M06-2X/6-311++G(d,p) level = -308.337582 a.u.
E at M06-2X/6-311++G(d,p)/SMD//M06-2X/6-311++G(d,p) level = -308.3462251 a.u.
Number of imaginary frequency = 0

C	0.585846000	-0.000013000	0.000011000
C	-0.118810000	1.208787000	0.000007000
C	-0.118831000	-1.208800000	0.000007000
C	-1.507241000	1.204874000	-0.000007000
C	-1.507259000	-1.204862000	-0.000007000
C	-2.204174000	0.000013000	-0.000018000
H	0.431825000	2.141439000	0.000019000
H	0.431793000	-2.141460000	0.000019000
H	-2.046385000	2.144591000	-0.000010000
H	-2.046420000	-2.144569000	-0.000010000
H	-3.287586000	0.000021000	-0.000031000
C	2.020217000	-0.000026000	0.000055000
C	3.222118000	0.000044000	0.000003000
H	4.285583000	-0.000119000	-0.000298000



BF_3 coordinated *(E)*-chalcone
E at M06-2X/6-311++G(d,p) level = -978.5086129 a.u.
E at M06-2X/6-311++G(d,p)/SMD//M06-2X/6-311++G(d,p) level = -978.5304913 a.u.
Number of imaginary frequency =0

C	-1.814321000	0.906102000	-0.052804000
C	-1.677537000	2.103630000	0.659592000
C	-3.008846000	0.624154000	-0.724250000
C	-2.732785000	3.001734000	0.715263000
C	-4.047603000	1.542180000	-0.689999000
C	-3.914227000	2.724272000	0.032800000
H	-0.763621000	2.313248000	1.202818000
H	-3.114117000	-0.302920000	-1.273088000
H	-2.635725000	3.915097000	1.288829000
H	-4.968056000	1.328648000	-1.218723000
H	-4.734707000	3.431372000	0.067355000
C	-0.688815000	-0.042807000	-0.114553000
O	-0.837476000	-1.279151000	-0.199932000
C	0.673326000	0.480001000	-0.123183000
H	0.796431000	1.550618000	-0.211218000
C	1.719372000	-0.363456000	-0.038679000
H	1.489721000	-1.422343000	0.056895000
C	3.134533000	-0.011733000	-0.051435000
C	4.072381000	-1.031179000	0.153752000
C	3.592581000	1.297186000	-0.261712000
C	5.433049000	-0.753081000	0.159328000
C	4.949682000	1.573440000	-0.258590000
C	5.872958000	0.549528000	-0.046187000
H	3.723770000	-2.045914000	0.311839000
H	2.886509000	2.099972000	-0.436876000
H	6.147461000	-1.550738000	0.321316000
H	5.294260000	2.586861000	-0.424464000
H	6.933640000	0.770425000	-0.044843000
B	-2.089635000	-2.261044000	0.125591000
F	-2.719648000	-2.441944000	-1.080306000
F	-2.850207000	-1.602064000	1.055410000
F	-1.462375000	-3.371073000	0.599963000



ts1

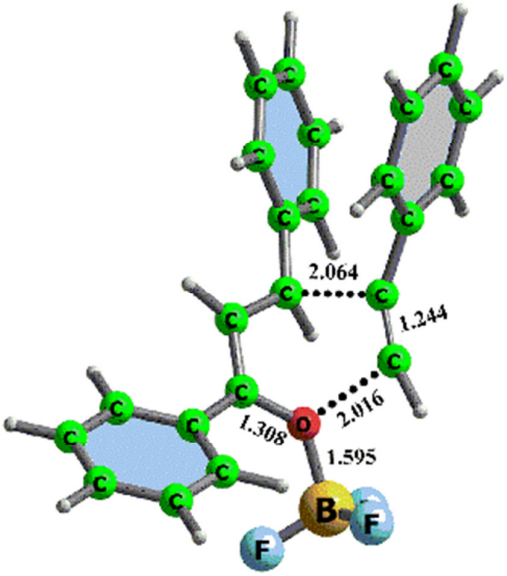
E at M06-2X/6-311++G(d,p) level = -1286.825638 a.u.

E at M06-2X/6-311++G(d,p)/SMD//M06-2X/6-311++G(d,p) level = -1286.855453 a.u.

Number of imaginary frequency = 1

C	2.633387000	1.188232000	-0.134367000
C	2.980131000	2.495080000	0.220751000
C	3.608846000	0.333266000	-0.653875000
C	4.282542000	2.944514000	0.050590000
C	4.906594000	0.791591000	-0.834544000
C	5.246592000	2.094727000	-0.483816000
H	2.235626000	3.146507000	0.663411000
H	3.348916000	-0.686829000	-0.907022000
H	4.548102000	3.952883000	0.344491000
H	5.657695000	0.125014000	-1.240658000
H	6.263539000	2.444798000	-0.616759000
C	1.233230000	0.727042000	0.002609000
O	0.943351000	-0.515556000	0.232267000
C	0.177716000	1.601648000	-0.199208000
H	0.366669000	2.593923000	-0.582580000
C	-1.157012000	1.132052000	0.006101000
H	-1.215904000	0.312174000	0.715184000
C	-2.285410000	2.099221000	0.135589000
C	-3.313820000	1.827315000	1.038587000
C	-2.342095000	3.268421000	-0.627671000
C	-4.370782000	2.717500000	1.193275000
C	-3.399720000	4.154655000	-0.478056000
C	-4.415916000	3.882032000	0.435199000
H	-3.275876000	0.918157000	1.629383000
H	-1.556758000	3.487497000	-1.343795000
H	-5.157616000	2.501357000	1.905861000
H	-3.432919000	5.059949000	-1.072254000
H	-5.239653000	4.575738000	0.552844000

C	-1.706455000	-2.288714000	-0.908535000
C	-0.526080000	-3.053047000	-0.842851000
C	-2.941448000	-2.846387000	-0.510415000
C	-0.583887000	-4.355291000	-0.379190000
C	-2.981727000	-4.147908000	-0.051424000
C	-1.803700000	-4.897980000	0.015032000
H	0.419410000	-2.604456000	-1.115680000
H	-3.839083000	-2.242740000	-0.569361000
H	0.329837000	-4.929260000	-0.294774000
H	-3.921601000	-4.584305000	0.262493000
H	-1.840971000	-5.913981000	0.390730000
C	-1.658235000	-0.962446000	-1.348556000
C	-1.602994000	0.262259000	-1.550912000
H	-1.715471000	0.991888000	-2.329516000
B	1.735145000	-1.581567000	1.002890000
F	2.669611000	-0.967054000	1.804520000
F	0.773925000	-2.270676000	1.721323000
F	2.325907000	-2.420352000	0.048551000



ts1′

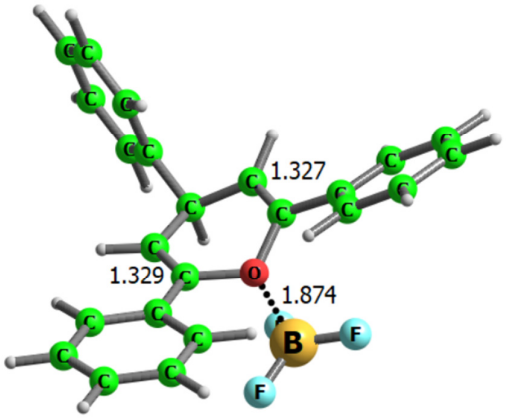
E at M06-2X/6-311++G(d,p) level = -1286.813646 a.u.

E at M06-2X/6-311++G(d,p)/SMD//M06-2X/6-311++G(d,p) level = -1286.83867 a.u.

Number of imaginary frequency = 1

C	2.844820000	1.005067000	0.084092000
C	3.081384000	2.238569000	0.697254000
C	3.712704000	0.548461000	-0.910222000
C	4.169435000	3.010808000	0.314667000
C	4.793447000	1.330173000	-1.295843000
C	5.024438000	2.559734000	-0.686827000

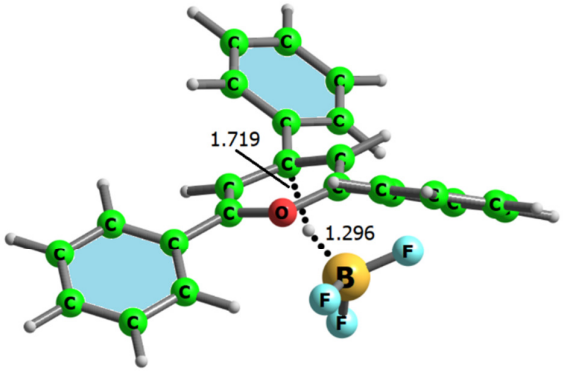
H	2.430350000	2.576458000	1.495637000
H	3.544228000	-0.414735000	-1.375310000
H	4.356389000	3.958880000	0.804254000
H	5.462540000	0.972805000	-2.069045000
H	5.874918000	3.161447000	-0.984543000
C	1.659202000	0.218215000	0.471745000
O	1.620677000	-1.081944000	0.336514000
C	0.450179000	0.788710000	0.814165000
H	0.308260000	1.858882000	0.754567000
C	-0.629549000	-0.093497000	1.047269000
H	-0.361535000	-1.044397000	1.495429000
C	-1.982535000	0.382133000	1.372815000
C	-2.790133000	-0.397909000	2.204797000
C	-2.507675000	1.553736000	0.817084000
C	-4.093495000	-0.009980000	2.489913000
C	-3.815379000	1.930535000	1.084522000
C	-4.609840000	1.150125000	1.922478000
H	-2.389628000	-1.314399000	2.625738000
H	-1.902483000	2.149602000	0.143216000
H	-4.707919000	-0.617111000	3.143682000
H	-4.220725000	2.828322000	0.633791000
H	-5.631407000	1.446406000	2.129256000
C	0.222854000	-1.652049000	-0.999209000
C	-0.832148000	-1.030051000	-0.781362000
B	2.756579000	-2.196049000	0.451369000
F	2.118694000	-3.208337000	1.114901000
F	3.051738000	-2.542796000	-0.859766000
F	3.79929000	-1.631905000	1.123406000
C	-2.118306000	-0.659518000	-1.350267000
C	-2.169125000	0.384709000	-2.277903000
C	-3.301592000	-1.270362000	-0.928312000
C	-3.394884000	0.816785000	-2.770354000
C	-4.522282000	-0.828268000	-1.420475000
C	-4.573643000	0.218595000	-2.337090000
H	-1.246404000	0.854434000	-2.598826000
H	-3.258957000	-2.078729000	-0.208539000
H	-3.427369000	1.624670000	-3.491717000
H	-5.436981000	-1.301521000	-1.083960000
H	-5.528615000	0.561967000	-2.716133000
H	0.952179000	-2.308175000	-1.430948000



4H-pyran…BF_3 adduct
E at M06-2X/6-311++G(d,p) level = -1286.898702 a.u.
E at M06-2X/6-311++G(d,p)/SMD//M06-2X/6-311++G(d,p) level = -1286.922381 a.u.
Number of imaginary frequency = 0

C	1.012039000	2.322987000	-0.308718000
C	0.449409000	3.574404000	-0.584820000
C	2.384740000	2.146000000	-0.498196000
C	1.239266000	4.616712000	-1.044931000
C	3.173007000	3.193302000	-0.961462000
C	2.605727000	4.430290000	-1.238922000
H	-0.610166000	3.742587000	-0.438952000
H	2.842798000	1.195155000	-0.261431000
H	0.786779000	5.578942000	-1.252358000
H	4.236791000	3.039797000	-1.097209000
H	3.221550000	5.246138000	-1.597619000
C	0.164783000	1.207985000	0.153109000
O	0.897388000	0.021742000	0.392120000
C	-1.150413000	1.179359000	0.339496000
H	-1.739460000	2.068490000	0.160031000
C	-1.877808000	-0.089007000	0.724945000
H	-1.938056000	-0.145791000	1.819129000
C	-3.286506000	-0.097320000	0.161982000
C	-4.394981000	-0.116330000	1.003977000
C	-3.484122000	-0.077515000	-1.220118000
C	-5.683954000	-0.116339000	0.476028000
C	-4.768657000	-0.077819000	-1.749374000
C	-5.872943000	-0.097198000	-0.900602000
H	-4.249562000	-0.131829000	2.079081000
H	-2.621627000	-0.062676000	-1.880032000
H	-6.538617000	-0.131957000	1.141989000
H	-4.909956000	-0.063289000	-2.823674000
H	-6.875084000	-0.097790000	-1.312356000
C	1.155792000	-2.222074000	-0.441390000
C	2.271943000	-1.867865000	-1.201777000
C	0.898977000	-3.570010000	-0.184117000
C	3.106972000	-2.851765000	-1.714628000

C	1.734846000	-4.551025000	-0.701236000
C	2.839581000	-4.194911000	-1.468608000
H	2.475613000	-0.822076000	-1.396861000
H	0.059928000	-3.844657000	0.444369000
H	3.968847000	-2.569477000	-2.307224000
H	1.532890000	-5.594354000	-0.490703000
H	3.495223000	-4.960961000	-1.864841000
C	0.240925000	-1.186221000	0.062205000
C	-1.073858000	-1.264045000	0.221146000
H	-1.588239000	-2.172114000	-0.067297000
B	1.540929000	-0.059935000	2.150007000
F	2.063284000	1.167831000	2.261370000
F	0.381699000	-0.287014000	2.796611000
F	2.383686000	-1.091703000	2.021466000

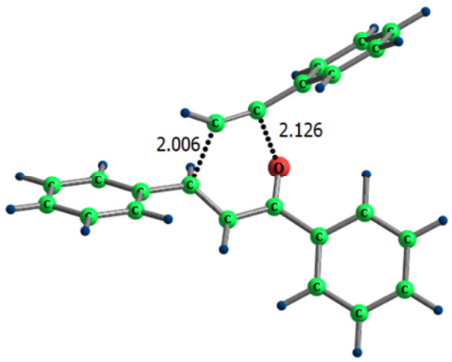


ts2

E at M06-2X/6-311++G(d,p) level = -1286.845452 a.u.
E at M06-2X/6-311++G(d,p)/SMD//M06-2X/6-311++G(d,p) level = -1286.87429 a.u.
Number of imaginary frequency = 1

C	2.051412000	2.160900000	-0.137335000
C	1.891662000	3.484217000	-0.554975000
C	3.259661000	1.752369000	0.433231000
C	2.930069000	4.391727000	-0.398457000
C	4.292737000	2.666478000	0.591123000
C	4.130777000	3.984726000	0.176153000
H	0.965530000	3.796812000	-1.023114000
H	3.370231000	0.729449000	0.771081000
H	2.805363000	5.414941000	-0.730978000
H	5.223430000	2.350571000	1.046191000
H	4.939359000	4.695096000	0.299744000
C	0.950659000	1.196391000	-0.272217000
O	1.381606000	-0.065881000	-0.437245000
C	-0.372321000	1.487785000	-0.216492000
H	-0.681034000	2.504138000	-0.016249000
C	-1.338599000	0.437122000	-0.259049000
H	-1.629614000	0.285548000	1.428581000
C	-2.773423000	0.725784000	-0.529935000
C	-3.761340000	-0.141760000	-0.055953000

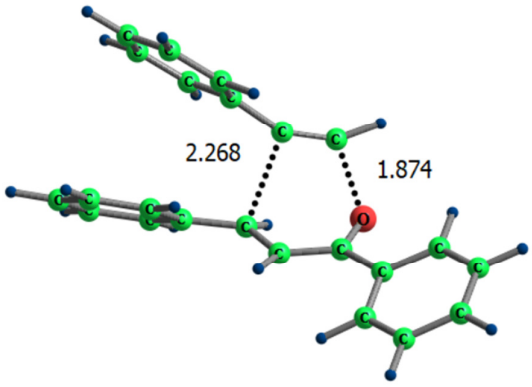
C	-3.132917000	1.826511000	-1.305345000
C	-5.093338000	0.094601000	-0.358216000
C	-4.471498000	2.057799000	-1.609881000
C	-5.451115000	1.194300000	-1.137116000
H	-3.474063000	-0.970886000	0.583687000
H	-2.368352000	2.489489000	-1.694093000
H	-5.857211000	-0.571284000	0.024370000
H	-4.744729000	2.912024000	-2.217435000
H	-6.493306000	1.377572000	-1.369623000
C	1.144380000	-2.391544000	-0.691831000
C	2.369000000	-2.533260000	-1.349550000
C	0.519522000	-3.500572000	-0.115649000
C	2.948910000	-3.789076000	-1.458701000
C	1.111473000	-4.752560000	-0.224333000
C	2.319069000	-4.898808000	-0.899964000
H	2.852136000	-1.663478000	-1.778599000
H	-0.391294000	-3.361521000	0.456971000
H	3.892400000	-3.904209000	-1.978171000
H	0.637283000	-5.611687000	0.233974000
H	2.777362000	-5.877224000	-0.982251000
C	0.506517000	-1.078182000	-0.565733000
C	-0.831180000	-0.856397000	-0.574236000
H	-1.504588000	-1.684967000	-0.735193000
B	-1.105244000	-0.511892000	2.305754000
F	0.278239000	-0.372474000	2.143947000
F	-1.543862000	-0.149256000	3.553992000
F	-1.517290000	-1.804402000	1.939513000



Transition state for normal [4 + 2] cycloaddition to yield 2,4,6-triaryl-*4H*-pyran
E at M06-2X/6-311++G(d,p) level = -962.2209272 a.u.
E at M06-2X/6-311++G(d,p)/SMD//M06-2X/6-311++G(d,p) level = -962.2440938 a.u.
Number of imaginary frequency = 1

C	1.227713000	2.025729000	0.364291000
C	0.847597000	3.360054000	0.215827000
C	2.559832000	1.662189000	0.158380000
C	1.787394000	4.319733000	-0.142603000
C	3.495257000	2.620647000	-0.210352000

C	3.111428000	3.950736000	-0.361397000
H	-0.179501000	3.653326000	0.403525000
H	2.842221000	0.622973000	0.289554000
H	1.488343000	5.356105000	-0.246187000
H	4.526254000	2.331771000	-0.377728000
H	3.843046000	4.698812000	-0.643359000
C	0.247865000	0.967256000	0.749904000
O	0.672260000	-0.105227000	1.248143000
C	-1.115915000	1.060477000	0.406311000
H	-1.481273000	1.860628000	-0.224232000
C	-1.887275000	-0.080383000	0.647559000
H	-1.653987000	-0.619142000	1.561034000
C	-3.304068000	-0.154461000	0.211751000
C	-4.250990000	-0.769747000	1.031928000
C	-3.711372000	0.362573000	-1.021269000
C	-5.584654000	-0.841370000	0.643632000
C	-5.041722000	0.286910000	-1.412692000
C	-5.983163000	-0.311607000	-0.578674000
H	-3.938801000	-1.185789000	1.983895000
H	-2.976174000	0.811837000	-1.680720000
H	-6.311123000	-1.312909000	1.294704000
H	-5.345466000	0.690115000	-2.371511000
H	-7.020793000	-0.370451000	-0.884722000
C	1.607109000	-2.115876000	-0.162463000
C	2.278201000	-2.136040000	-1.390232000
C	2.274160000	-2.522816000	0.999522000
C	3.597925000	-2.567458000	-1.453583000
C	3.589300000	-2.954821000	0.925701000
C	4.255025000	-2.979007000	-0.299055000
H	1.759672000	-1.808530000	-2.283106000
H	1.755677000	-2.469209000	1.948126000
H	4.112701000	-2.579823000	-2.406845000
H	4.102298000	-3.267267000	1.827409000
H	5.284071000	-3.314126000	-0.350492000
C	0.240625000	-1.676637000	-0.117851000
C	-0.971343000	-1.553656000	-0.359004000
H	-1.798814000	-1.971055000	-0.898265000

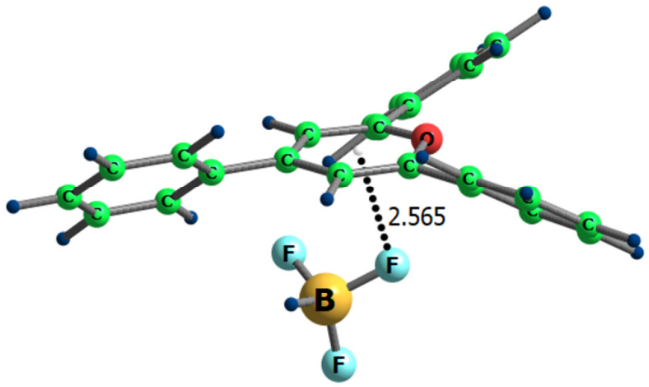


Transition state for normal [4 + 2] cycloaddition to yield 2,4,5-triaryl-*4H*-pyran

E at M06-2X/6-311++G(d,p) level = -962.2213871 a.u.
E at M06-2X/6-311++G(d,p)/SMD//M06-2X/6-311++G(d,p) level = -962.243348 a.u.
Number of imaginary frequency = 1

C	-3.436514000	0.249298000	-0.134511000
C	-3.846150000	1.218934000	0.784598000
C	-4.298050000	-0.806105000	-0.441199000
C	-5.088223000	1.123623000	1.399137000
C	-5.535881000	-0.905344000	0.180955000
C	-5.933853000	0.058004000	1.103662000
H	-3.202379000	2.063449000	1.002637000
H	-3.982162000	-1.539791000	-1.172700000
H	-5.400108000	1.884456000	2.104789000
H	-6.194345000	-1.732428000	-0.056990000
H	-6.902079000	-0.016190000	1.584389000
C	-2.112185000	0.326681000	-0.803891000
O	-1.916504000	-0.359202000	-1.860434000
C	-1.020390000	0.994085000	-0.229162000
H	-1.074417000	1.395952000	0.774405000
C	0.185010000	0.914236000	-0.911934000
H	0.121086000	0.817092000	-1.990030000
C	1.465269000	1.399116000	-0.387523000
C	2.436137000	1.869970000	-1.276610000
C	1.775140000	1.327661000	0.975371000
C	3.680906000	2.280801000	-0.816148000
C	3.024729000	1.718381000	1.433977000
C	3.979713000	2.198205000	0.539947000
H	2.207628000	1.909249000	-2.336731000
H	1.046762000	0.922809000	1.668917000
H	4.421113000	2.651716000	-1.515142000
H	3.261869000	1.635765000	2.487967000
H	4.956245000	2.499691000	0.900166000
C	-0.624258000	-1.689250000	-1.592527000

C	0.414375000	-1.339899000	-1.005882000
C	1.631433000	-1.595964000	-0.285571000
C	1.560329000	-2.002770000	1.053947000
C	2.888354000	-1.369300000	-0.860988000
C	2.720964000	-2.175328000	1.797336000
C	4.042698000	-1.537553000	-0.109241000
C	3.965682000	-1.936762000	1.222795000
H	0.587445000	-2.172128000	1.500804000
H	2.948636000	-1.046439000	-1.893417000
H	2.651297000	-2.492877000	2.831299000
H	5.007983000	-1.348106000	-0.564087000
H	4.869415000	-2.062964000	1.806694000
H	-1.243368000	-2.419959000	-2.068718000



Pyrrilium cation...HBF_3^- ion-pair complex

E at M06-2X/6-311++G(d,p) level = -1286.85883654 a.u.
E at M06-2X/6-311++G(d,p)/SMD//M06-2X/6-311++G(d,p) level = -1286.89226906 a.u.
Number of imaginary frequency = 0

C	-1.784765000	-2.348015000	-0.189529000
C	-1.590860000	-3.663512000	-0.617253000
C	-2.923355000	-2.004873000	0.545242000
C	-2.539102000	-4.631561000	-0.318609000
C	-3.862809000	-2.981151000	0.845519000
C	-3.673869000	-4.290667000	0.412636000
H	-0.714146000	-3.921090000	-1.200537000
H	-3.036873000	-0.989371000	0.905430000
H	-2.395980000	-5.649892000	-0.658163000
H	-4.737501000	-2.722579000	1.429256000
H	-4.410059000	-5.049340000	0.649840000
C	-0.780812000	-1.319284000	-0.465757000
O	-1.302251000	-0.107138000	-0.654864000
C	0.575733000	-1.500181000	-0.491088000
H	0.982142000	-2.477639000	-0.272408000

C	1.415852000	-0.388093000	-0.658428000
H	1.580883000	-0.234168000	2.187131000
C	2.878152000	-0.530751000	-0.631040000
C	3.644945000	0.414805000	0.058934000
C	3.499608000	-1.610599000	-1.264870000
C	5.025685000	0.274433000	0.102181000
C	4.882017000	-1.731706000	-1.233021000
C	5.644587000	-0.789630000	-0.547909000
H	3.144147000	1.206013000	0.608766000
H	2.902940000	-2.336098000	-1.807353000
H	5.618740000	0.991261000	0.656655000
H	5.364180000	-2.558648000	-1.739849000
H	6.722933000	-0.890483000	-0.514296000
C	-1.294192000	2.233027000	-0.809323000
C	-2.546559000	2.282674000	-1.428588000
C	-0.749618000	3.372409000	-0.210046000
C	-3.238205000	3.483696000	-1.477977000
C	-1.457491000	4.566153000	-0.255980000
C	-2.692336000	4.625191000	-0.894857000
H	-2.963377000	1.388237000	-1.876244000
H	0.179015000	3.290836000	0.344756000
H	-4.202889000	3.531158000	-1.967982000
H	-1.051392000	5.447235000	0.225111000
H	-3.238595000	5.560404000	-0.928629000
C	-0.543223000	0.981595000	-0.748975000
C	0.824697000	0.867610000	-0.800863000
H	1.422487000	1.759397000	-0.913282000
B	0.805769000	0.690374000	2.375906000
F	-0.478325000	0.370123000	1.801388000
F	0.639427000	1.006741000	3.716603000
F	1.276458000	1.866534000	1.671874000
X	0.031666000	-0.244248500	-0.636662500