Supporting Information

Synthesis of 2*H*-imidazoles *via* Copper-Catalyzed Homo/Cross-Coupling of Oxime Acetates

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Contents:

General information

All reactions were carried out under air atmosphere using standard Schlenk technique in the parallel synthesizer. All reagent/reactant were commercially available unless other noted, DCE (99.5%, Extra Dry, with molecular sieves) and the related dry solvents screened were purchased from Energy Chemical (Note: the solvents used above could be altered to normal solvent with the additive of 4A Ms.). Column chromatography was performed using Silica Gel 60 (particle sizeand 37-54 μm). The pure products were obtained by column chromatography using ethyl acetate/petroleum ether as the eluent and characterized by NMR spectroscopy using $CDCl_3$ as the deuterium reagent. GC analysis was performed on GC 7820A (Shimadzu). GC-MS results were recorded on GC-MS QP2030 (Shimadzu). The ^1H NMR and ^{13}C NMR data were acquired on a Brucker ADVANCE III spectrometer (400 MHz for ^1H NMR spectroscopy and 100 MHz for ^{13}C NMR spectroscopy). HRMS analysis was conducted at the College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, 325000, China.

Typical procedure for preparation of oxime acetates

General Procedure for oximes：To a solution of aromatic ketones (2 mmol) in the mixture of C_2H_5OH/H_2O (v/v = 1:1) was added hydroxylamine hydrochloride (2.2 mmol), NaOAc (3 mmol) in one portion, and the reaction mixture was stirred at 100 ^oC for 6-8 h. Upon completion of the reaction as indicated by TLC, the reaction mixture was diluted with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was removed and concentrated under reduced pressure to give oximes.

General Procedure for oxime acetates: The mixture of ketoximes (2.0 mmol), anhydride (4.0 mmol, 2.0 equiv) was stirred in CH_2Cl_2 (10 mL) at room temperature for 24 h. Upon completion of the reaction as indicated by TLC, the reaction mixture was diluted with EtOAc (25 mL), washed with H_2O (20 mL) and aq. $NaHCO_3$ (10 mL). Neutralization with $NaHCO_3$ and dried over anhydrous Na_2SO_4 and evaporated in vacuo. The crude residue was purified by column chromatography using silica gel with hexane as the eluent to give oxime acetates.

Typical procedure for the synthesis of 2*H*-imidazoles

Process a: the synthesis of 2-methyl-2,4-diphenyl-2*H*-imidazole

An oven-dried Schlenk tube containing a stir bar was charged with **1a** 1-phenylethan-1-one O-acetyl oxime (0.3 mmol, 53.1 mg) and CuCl (0.03 mmol, 2.97 mg), for which then were dissolved in 2 mL anhydrous DCE. The mixture was stirred at 120 ^oC for 4 h under air. After reaction, the mixture was diluted with 3-5 mL EA, then the volatiles was removed and the residues were passed through a short silica chromatography column (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product **3a**.

Process b**:** the synthesis of 2,2,4-triphenyl-2*H*-imidazole

An oven-dried Schlenk tube containing a stir bar was charged with **1a** 1-phenylethan-1-one O-acetyl oxime (0.15 mmol, 26.5 mg), **4a** diphenylmethanone O-acetyl oxime (0.15 mmol, 35.8 mg) and CuCl (0.03 mmol, 2.97 mg), for which then were dissolved in 2 mL anhydrous DCE. The mixture was stirred at 120 ^oC for 8 h under air. After reaction, the mixture was diluted with 3-5 mL EA, then the volatiles was removed and the residues were passed through a short silica

chromatography column (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product **4aa**.

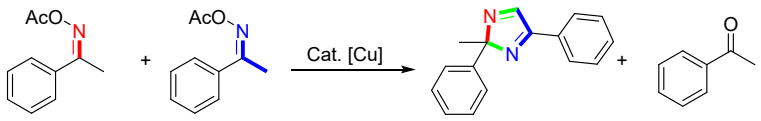
Typical procedure for the scale-up synthesis of 2*H*-imidazoles

An oven-dried 100 mL Schlenk tube containing a stir bar was charged with **1a** 1-phenylethan-1-one O-acetyl oxime (6 mmol, 1062 mg) and CuCl (0.6 mmol, 59.4 mg), for which then were dissolved in 20 mL anhydrous DCE. The mixture was stirred at 120 °C for 12 h under air. After reaction, the volatiles was removed and the residues were passed through a short silica chromatography column (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product **3a**, 582.7mg, 83% yield.

Typical procedure for the scale-up synthesis of 5aa

To a solution of 2,2,4-triphenyl-2*H*-imidazole **4aa** (1.0 mmol), dry CH_3CN (2 mL) and m-CPBA (344 mg, 2.0 equiv) were added to a 10 mL screw-capped tube at 80 °C. Upon completion of the reaction as indicated by TLC, the solvent was removed and concentrated under reduced pressure to give crude raffinate. The crude raffinate was purified by column chromatography using silica gel with eluent (petroleum ether: EtOAc = 5 : 1) to afford **5aa** (188 mg, 60% yield).

Condition screening

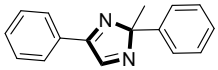


1a **1a** **3a** **4a**

Entry	Acids/ 2 eq.	Yield **3a**/%	Yield **4a**/%
1	CF_3COOH	trace	95
2	CH_3COOH	trace	94
3	PTSA	trace	98
4	Citric acid	trace	98
5	H_3PO_4	trace	87
6	NH_4Cl	6	93

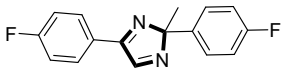
[a] Reaction conditions: **1a** 0.15 mmol, **2a** 0.15 mmol, cat. 0.03 mmol, additives 0.3 mmol, solvent 2.0 mL, under air, 4 h. GC yield using tridecane as the internal standard based on 0.15 mmol of **1a**.

Characterization and analytical data of products



3a[1]

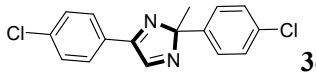
Yield 93%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.07 (d, *J* = 6.8 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.53-7.51 (m, 3H), 7.38-7.27 (m, 3H), 1.87 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.7, 154.3, 140.0, 131.4, 131.0, 129.0, 128.3, 128.3, 127.6, 126.9, 109.1, 27.0.



3b

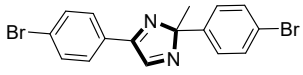
Yield 87%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.06 (t, *J* = 6.4 Hz, 2H), 7.68 (t, *J* = 6.4 Hz,

2H), 7.19 (t, J = 8.0 Hz, 2H), 7.02 (t, J = 8.0 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 166.0 (d, $J_{F\text{-}C}$ = 251.3 Hz), 163.4 (d, $J_{F\text{-}C}$ = 244.8 Hz), 162.6, 154.1, 135.9 (d, $J_{F\text{-}C}$ = 3.2 Hz), 130.5 (d, $J_{F\text{-}C}$ = 8.8 Hz), 128.7 (d, $J_{F\text{-}C}$ = 8.0 Hz), 127.2 (d, $J_{F\text{-}C}$ = 3.3 Hz), 116.4 (d, $J_{F\text{-}C}$ = 142.0 Hz), 116.2 (d, $J_{F\text{-}C}$ = 98.8 Hz), 108.7, 27.2;^{19}F NMR(377 MHz, $CDCl_3$), δ -107.4, -114.6. HRMS (ESI): calcd for $C_{16}H_{12}F_2N_2$: [M+H$^+$] 271.1041, found 271.1047.



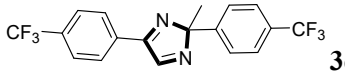
3c

Yield 84%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.97 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 1.79 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 162.8, 154.1, 138.4, 137.7, 133.5, 129.5,129.3, 129.2, 128.3, 128.3, 108.7, 27.0. HRMS (ESI): calcd for $C_{16}H_{12}Cl_2N_2$: [M+H$^+$] 303.0450, found 303.0456.



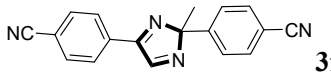
3d

Yield 82%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 1.79 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.0, 154.1, 138.9, 132.3, 131.4, 129.7, 129.7, 128.7, 126.2, 121.8, 108.9, 27.0. HRMS (ESI): calcd for $C_{16}H_{12}Br_2N_2$: [M+H$^+$] 390.9440, found 390.9444.



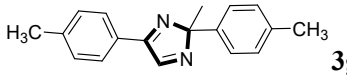
3e

Yield 62%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.19 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 1.85 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.0, 154.2, 143.7, 134.0, 133.4 (d, $J_{F\text{-}C}$ = 32.6 Hz), 130.2 (d, $J_{F\text{-}C}$ = 32.2 Hz) , 128.7, 127.5, 126.1 (q, $J_{F\text{-}C}$ = 3.7 Hz), 125.4 (d, $J_{F\text{-}C}$ = 36.8 Hz), 125.3 (q, $J_{F\text{-}C}$ = 3.7 Hz), 122.7 (d, $J_{F\text{-}C}$ = 37.4 Hz), 109.2, 27.2;^{19}F NMR(377 MHz, $CDCl_3$), δ -62.6, -63.0. HRMS (ESI): calcd for $C_{18}H_{12}F_6N_2$: [M+H$^+$] 371.0977, found 371.0982.



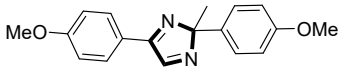
3f

Yield 76%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.17 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 7.6 Hz, 2H), 1.81 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 162.8, 154.1, 144.7, 134.5, 132.8, 132.1, 128.9, 127.9, 118.5, 117.9, 115.1, 111.7, 109.2, 27.1. HRMS (ESI): calcd for $C_{18}H_{12}N_4$: [M+H$^+$] 285.1135, found 285.1141.



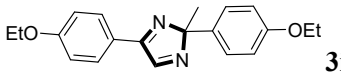
3g[1]

Yield 91%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H), 2.33 (s, 3H), 1.84 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.6, 154.3, 141.9, 137.4, 137.3, 129.8, 129.0, 128.4, 128.3, 126.8, 1008.9, 27.0, 21.6, 21.1.



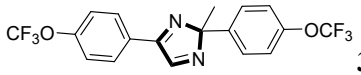
3h

Yield 67%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H), 3.77 (s, 3H), 1.81 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 162.9, 162.0, 158.9, 154.1, 132.4, 129.9, 127.9, 123.7, 114.3, 113.5, 108.4, 55.3, 55.1,26.9. HRMS (ESI): calcd for $C_{18}H_{18}N_2O_2$: [M+H$^+$] 295.1441, found 295.1447.



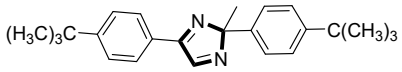
3i

Yield 72%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.10-4.05 (dd, J_1 = 6.8 Hz, J_2 = 14 Hz, 2H), 4.02-3.97 (dd, J_1 = 6.8 Hz, J_2 = 14 Hz, 2H),1.81 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 162.9, 161.4, 158.2, 154.1, 132.2, 129.9, 127.9, 123.5, 114.8, 114.1, 108.4, 63.5, 63.3, 26.9, 14.7, 14.6. HRMS (ESI): calcd for $C_{20}H_{22}N_2O_2$: [M+H$^+$] 323.1754, found 323.1757.



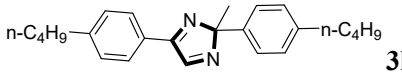
3j

Yield 73%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.1 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.04 Hz, 2H), 1.82 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 162.7, 154.1, 151.5, 148.7, 138.7, 130.1, 129.4, 128.5, 121.7 (d, $J_{F\text{-}C}$ = 265 Hz), 121.6 (d, $J_{F\text{-}C}$ = 247 Hz), 119.1, 119.1, 108.9, 27.2. ^{19}F NMR(377 MHz, $CDCl_3$), δ -57.7, -57.9. HRMS (ESI): calcd for $C_{18}H_{12}F_6N_2O_2$: [M+H$^+$] 403.0876, found 403.0881.



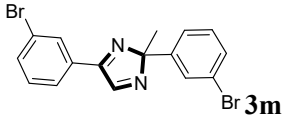
3k[2]

Yield 60%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0, 2H), 1.86 (s, 3H), 1.38 (s, 9H), 1.32 (s, 9H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.5, 154.9, 154.3, 150.4, 137.1, 128.3, 128.1, 126.5, 125.9, 125.2, 108.8, 34.9, 34.4, 31.3, 31.1, 26.8.



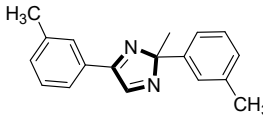
3l

Yield 53%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.6, 2H), 2.69 (t, *J* = 7.6, 2H), 2.59 (t, *J* = 7.6, 2H), 1.84 (s, 3H), 1.68-1.54 (m, 4H), 1.42-1.30 (m, 4H), 0.97-0.90 (m, 6H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.5, 154.3, 146.8, 142.3, 137.3, 129.1, 128.5, 128.3, 128.3, 126.7, 108.9, 35.5, 35.2, 33.5, 33.3, 26.9, 22.3, 22.2, 13.88, 13.87. HRMS (ESI): calcd for $C_{24}H_{30}N_2$: [M+H$^+$] 347.2482, found 347.2488.



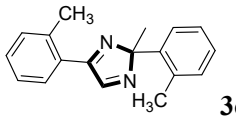
3m

Yield 62%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.22 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.86 (s, 1H), 7.67 (t, *J* = 7.2 Hz, 2H), 7.42-7.36 (m, 2H), 7.23 (t, *J* = 8.0 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 162.7, 154.2, 141.9, 134.5, 132.7, 131.2, 130.8, 130.5, 130.1, 129.9, 126.8, 125.7, 123.3, 122.3, 108.7, 27.1. HRMS (ESI): calcd for $C_{16}H_{12}Br_2N_2$: [M+H$^+$] 390.9440, found 390.9445.



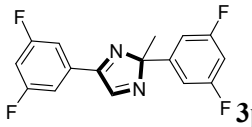
3n

Yield 80%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.95 (s, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 6.8 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 2.48 (s, 3H), 2.40 (s, 3H), 1.89 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.9, 154.4, 139.9, 138.9, 137.9, 132.2, 130.9, 128.8, 128.8, 128.4, 128.2, 127.5, 125.4, 124.0, 123.9, 26.9, 21.4, 21.3. HRMS (ESI): calcd for $C_{18}H_{18}N_2$: [M+H$^+$] 263.1543, found 263.1547.



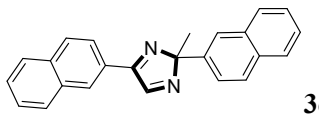
3o

Yield 94%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.36-7.27 (m, 3H), 7.22-7.16 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 2.88 (s, 3H), 2.61 (s, 3H), 1.83 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.9, 155.6, 138.9, 138.6, 137.1, 132.3, 131.7, 130.7, 130.4, 129.6, 128.4, 127.8, 126.1, 125.8, 110.3, 25.5, 22.2, 21.7. HRMS (ESI): calcd for $C_{18}H_{18}N_2$: [M+H$^+$] 263.1543, found 263.1547



3p

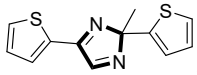
Yield 65%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.59 (d, *J* = 5.6 Hz, 2H), 7.27 (d, *J* = 6.0 Hz, 2H), 7.03 (t, *J* = 8.8 Hz, 1H), 6.77 (t, *J* = 8.8 Hz, 1H), 1.80 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 164.6 (d, $J_{F\text{-}C}$ = 12.3 Hz), 164.0 (d, $J_{F\text{-}C}$ = 185.0 Hz), 163.9 (d, $J_{F\text{-}C}$ = 184.7 Hz), 162.4 (t, $J_{F\text{-}C}$ = 3.3 Hz), 161.2 (d, $J_{F\text{-}C}$ = 12.6 Hz), 154.1, 143.0 (t, $J_{F\text{-}C}$ = 9.3 Hz), 133.6 (t, $J_{F\text{-}C}$ = 9.3 Hz), 111.5 (d, $J_{F\text{-}C}$ = 26.5 Hz), 111.4 (d, $J_{F\text{-}C}$ = 11.3 Hz), 110.5 (d, $J_{F\text{-}C}$ = 26.4 Hz), 110.4 (d, $J_{F\text{-}C}$ = 11.9 Hz), 108.7, 107.1 (t, $J_{F\text{-}C}$ = 25.1 Hz), 103.2 (t, $J_{F\text{-}C}$ = 25.1 Hz), 27.1; ^{19}F NMR(470 MHz, $CDCl_3$), δ -107.6, -109.3. HRMS (ESI): calcd for $C_{16}H_{10}F_4N_2$: [M+H$^+$] 307.0853, found 307.0859.



3q

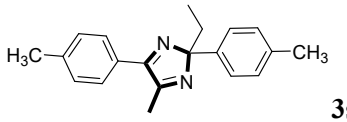
Yield 60%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 9.58 (d, *J* = 8.8 Hz, 1H), 8.99 (d, *J* = 8.0 Hz, 1H), 8.56 (s, 1H), 8.03-7.89 (m, 5H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.70-7.53 (m, 5H), 7.44 (t, *J* = 7.6 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.4, 155.99, 137.0, 134.63, 133.99, 131.69, 131.59, 131.3, 129.0, 128.8, 128.7, 128.3, 127.8, 127.6, 126.6, 125.9, 125.8, 125.7, 125.4, 125.2, 124.9,

110.7, 26.5. HRMS (ESI): calcd for $C_{24}H_{18}N_2$: [M+H$^+$] 335.1543, found 335.1547



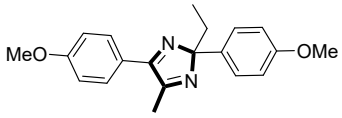
3r

Yield 35%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.22-7.17 (m, 3H), 6.98 (t, *J* = 4.0 Hz, 1H), 1.91 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 158.6, 154.4, 141.0, 134.6, 131.0, 130.6, 128.0, 126.7, 125.0, 124.8, 106.9, 27.1. HRMS (ESI): calcd for $C_{12}H_{10}N_2S_2$: [M+H$^+$] 247.0358, found 247.0362.



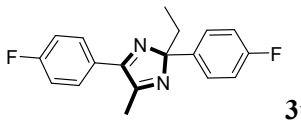
3s

Yield 87%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 2.51 (s, 3H), 2.41 (s, 3H), 2.32 (s, 3H), 2.24-2.20 (m, 2H), 0.75 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 165.6, 163.9, 140.7, 137.6, 137.0, 129.4, 129.3, 128.8, 128.4, 127.5, 106.9, 33.9, 21.4, 21.0, 17.5, 8.5. HRMS (ESI): calcd for $C_{20}H_{22}N_2$: [M+H$^+$] 291.1856, found 291.1860



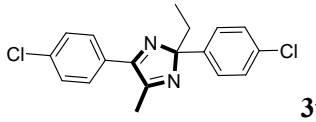
3t

Yield 62%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.78 (s, 3H), 2.52 (s, 3H), 2.23-2.15 (m, 2H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 164.9, 163.7, 161.3, 158.7, 132.8, 130.0, 128.6, 124.7, 114.0, 113.4, 106.0, 55.3, 55.1, 33.9, 17.7, 8.5. HRMS (ESI): calcd for $C_{20}H_{22}N_2O_2$: [M+H$^+$] 323.1754, found 323.1758.



3u

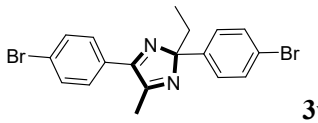
Yield 85%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.83 (t, *J* = 7.2 Hz, 2H),7.71 (d, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 8.4 Hz, 2H), 2.52 (s, 3H), 2.20-2.13 (m, 2H), 0.74 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 165.4 (d, $J_{F\text{-}C}$ = 211.3 Hz), 164.7 (d, $J_{F\text{-}C}$ = 104.1 Hz), 162.9, 160.8, 136.1, 130.5 (d, $J_{F\text{-}C}$ = 8.6 Hz), 129.3 (d, $J_{F\text{-}C}$ = 7.9 Hz), 128.3 (d, $J_{F\text{-}C}$ = 3.3 Hz), 115.9 (d, $J_{F\text{-}C}$ = 21.7 Hz), 114.9 (d, $J_{F\text{-}C}$ = 21.1 Hz), 106.4, 34.1, 17.5, 8.5; ^{19}F NMR(377 MHz, $CDCl_3$), δ -109.3, -115.1; HRMS (ESI): calcd for $C_{18}H_{16}F_2N_2$: [M+H$^+$] 299.1354, found 299.1357.



3v

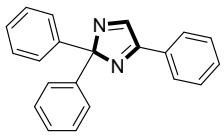
Yield 83%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H),7.59 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.11-2.06 (m, 2H), 0.65 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 164.8, 163.7, 138.6, 136.8, 133.3, 130.5, 129.7, 129.0, 129.0,

128.2, 106.6, 34.1, 17.5, 8.5. HRMS (ESI): calcd for $C_{18}H_{16}Cl_2N_2$: [M+H$^+$] 331.0763, found 331.0769.



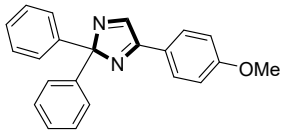
3w

Yield 80%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.63-7.59 (m, 4H), 7.46 (d, *J* = 8.4 Hz, 2H), 2.51 (s, 3H), 2.17-2.14 (m, 2H), 0.74 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 164.9, 163.6, 139.1, 131.9, 131.1, 130.9, 129.9, 129.4, 125.2, 121.5, 106.6, 34.0, 17.4, 8.5. HRMS (ESI): calcd for $C_{18}H_{16}Br_2N_2$: [M+H$^+$] 418.9752, found 417.9758.



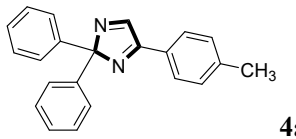
4aa[1]

Yield 77%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.06 (d, *J* = 4.8 Hz, 2H), 7.69 (d, *J* = 6.4 Hz, 4H), 7.45 (s, 3H), 7.28-7.21 (m, 6H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 164.3, 163.3, 155.1, 148.7, 140.9, 133.6, 131.6, 131.5, 131.0, 129.6, 129.1, 128.6, 128.4, 127.8, 126.5, 112.7.



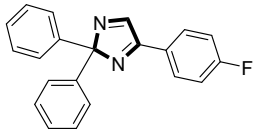
4ab

Yield 60%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 4H), 7.30-7.20 (m, 6H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.5, 162.2, 155.0, 141.0, 130.2, 128.2, 127.6, 127.6, 123.6, 114.4, 112.3, 55.3. HRMS (ESI): calcd for $C_{22}H_{18}N_2O$: [M+H$^+$] 327.1491, found 327.1495.



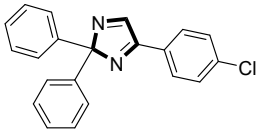
4ac[3]

Yield 72%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 4H), 7.30-7.26 (m, 6H), 7.23 (t, *J* = 7.2 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 164.2, 155.2, 142.1, 141.0, 129.8, 128.6, 128.3, 127.8, 127.7, 112.6, 21.7.



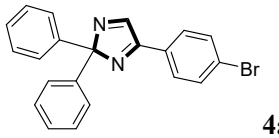
4ad[3]

Yield 73%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.98-7.95 (m, 2H), 7.58 (d, *J* = 7.2 Hz, 4H), 7.20-7.10 (m, 6H), 7.2307 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 166.1 (t, J_{F-C} = 251.3 Hz), 163.1, 154.7, 140.8, 130.8, 130.7, 128.4, 127.8, 127.7, 116.3 (d, J_{F-C} = 27.5 Hz), 112.8.



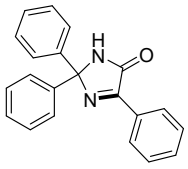
4ae[3]

Yield 71%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 4H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 4H), 7.10 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.1, 154.5, 140.6, 137.7, 129.7, 129.3, 128.3, 127.7, 127.6, 112.7.



4af[3]

Yield 70%**.** ^{1}H NMR(400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 4H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 4H), 7.21 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR(100 MHz, $CDCl_3$), δ 163.2, 154.4, 140.5, 132.2, 129.9, 129.7, 128.3, 127.8, 127.6, 112.8.



5aa[3]

Yield 60%, ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 9.83 (s, 1H), 8.54 (d, *J* = 7.0 Hz, 2H), 7.56-7.53 (m, 1H), 7.50-7.49 (m, 6H), 7.36-7.31 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 160.9, 141.3, 131.9, 130.3, 128.8, 128.6, 128.6, 128.3, 126.8, 87.5.

Reference

1. Z. Zhu, X. Tang, J. Li, X. Li, W. Wu, G. Deng and H. Jiang, *Org. Lett*., 2017, **19**, 1370-1373;
2. F. Geng, S. Wu, X. Gan, W. Hou, J. Dong and Y. Zhou, *Org. Biomol. Chem*., 2022, **20**, 5416-5422;
3. Z. Zhu, H. Lin, B. Liang, J. Huang, W. Liang, L. Chen, Y. Huang, X. Chen and Y. Li, *Chem. Commu*n., 2020, **56**, 5621-5624

Copies of ^{1}H NMR and ^{13}C NMR spectroscopies

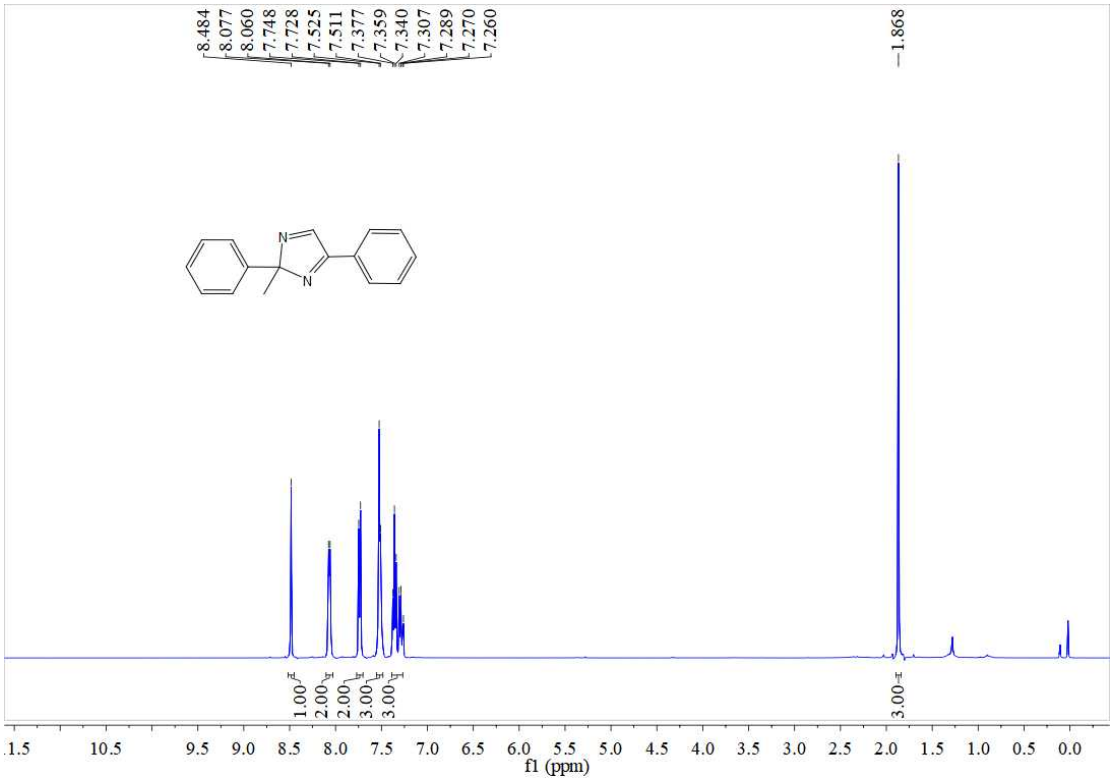


Figure S1 ^{1}H NMR of **3a**

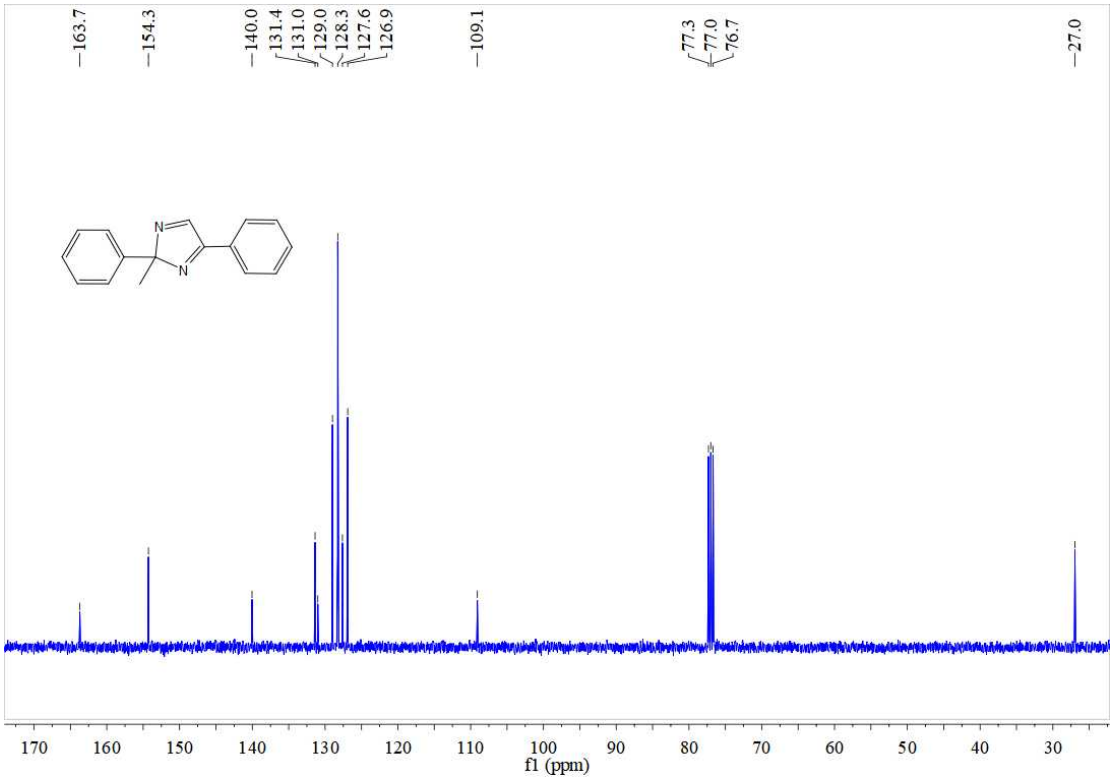


Figure S2 ^{13}C NMR of **3a**

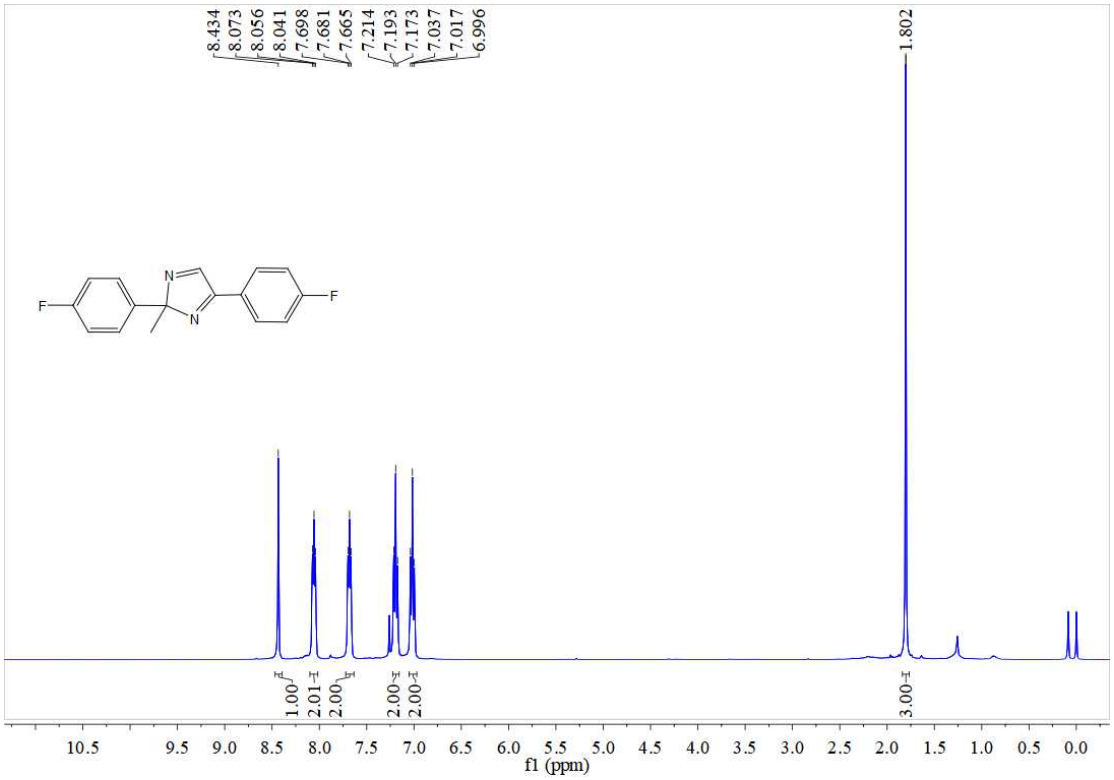


Figure S3 ^{1}H NMR of **3b**

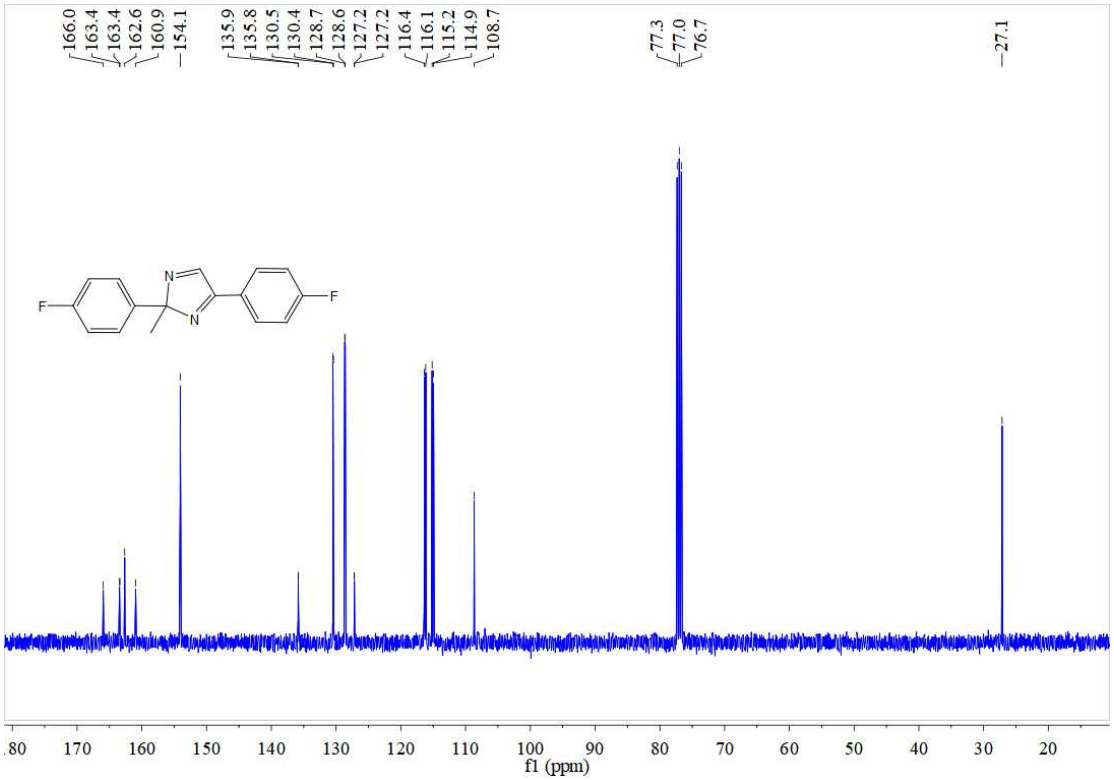


Figure S4 ^{13}C NMR of **3b**

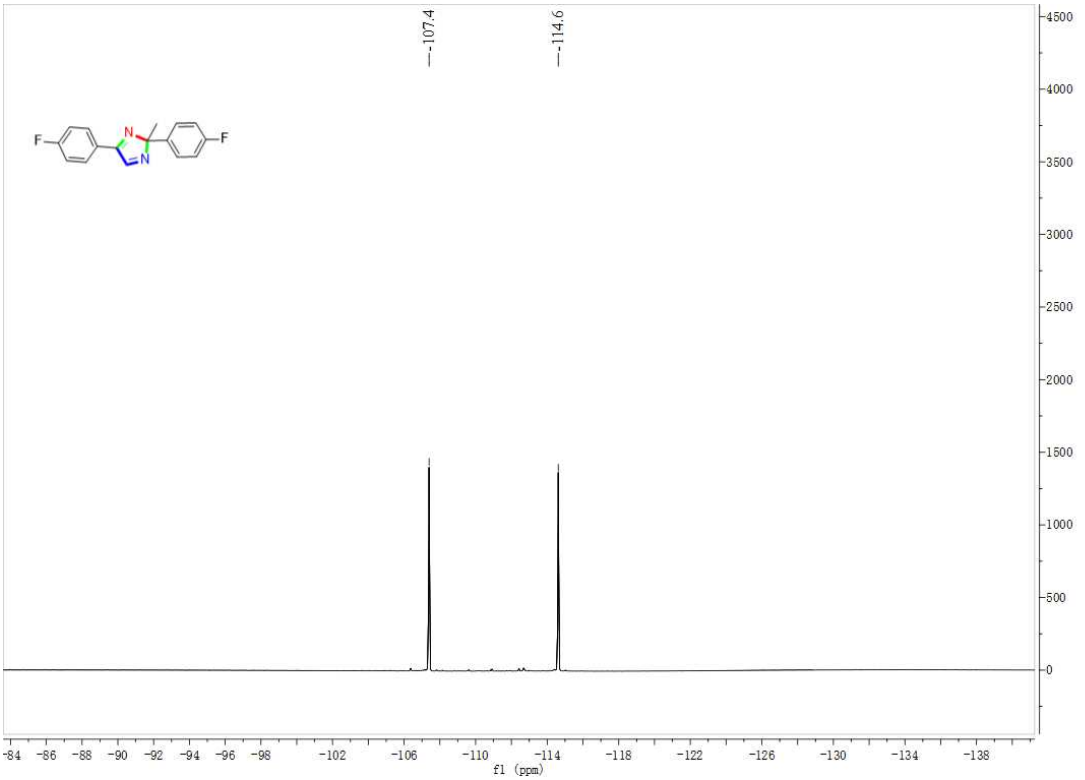


Figure S5 ^{19}F NMR of **3b**

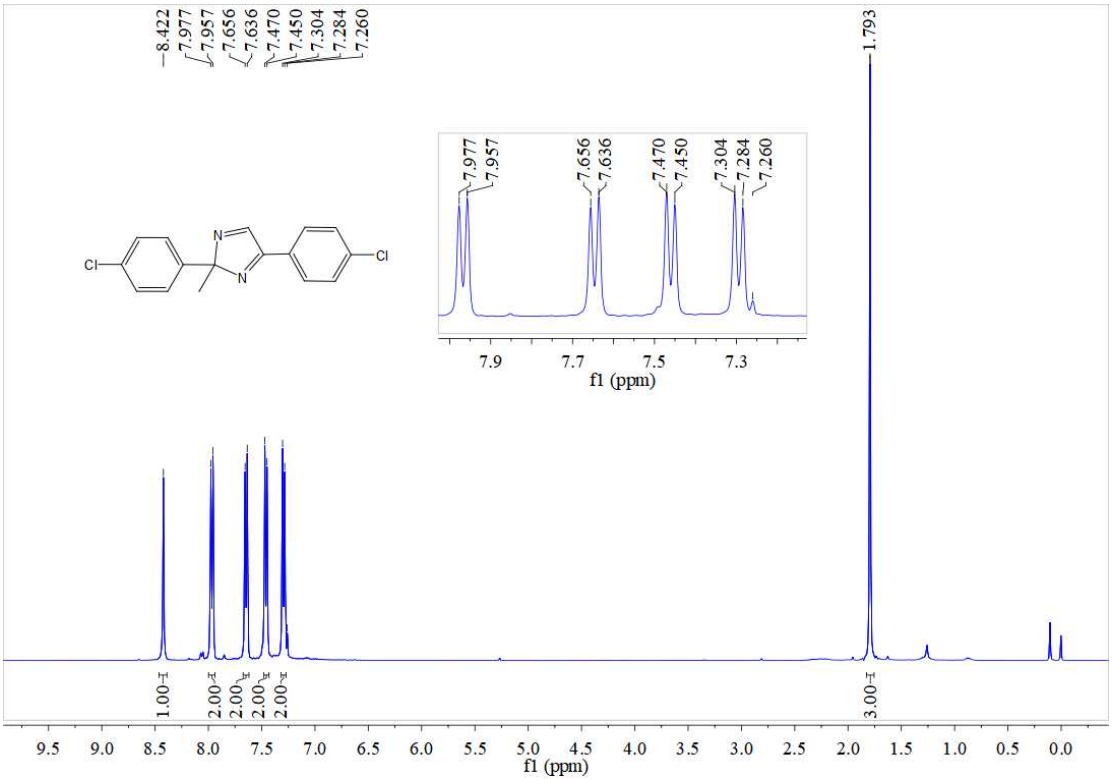


Figure S6 ^{1}H NMR of **3c**

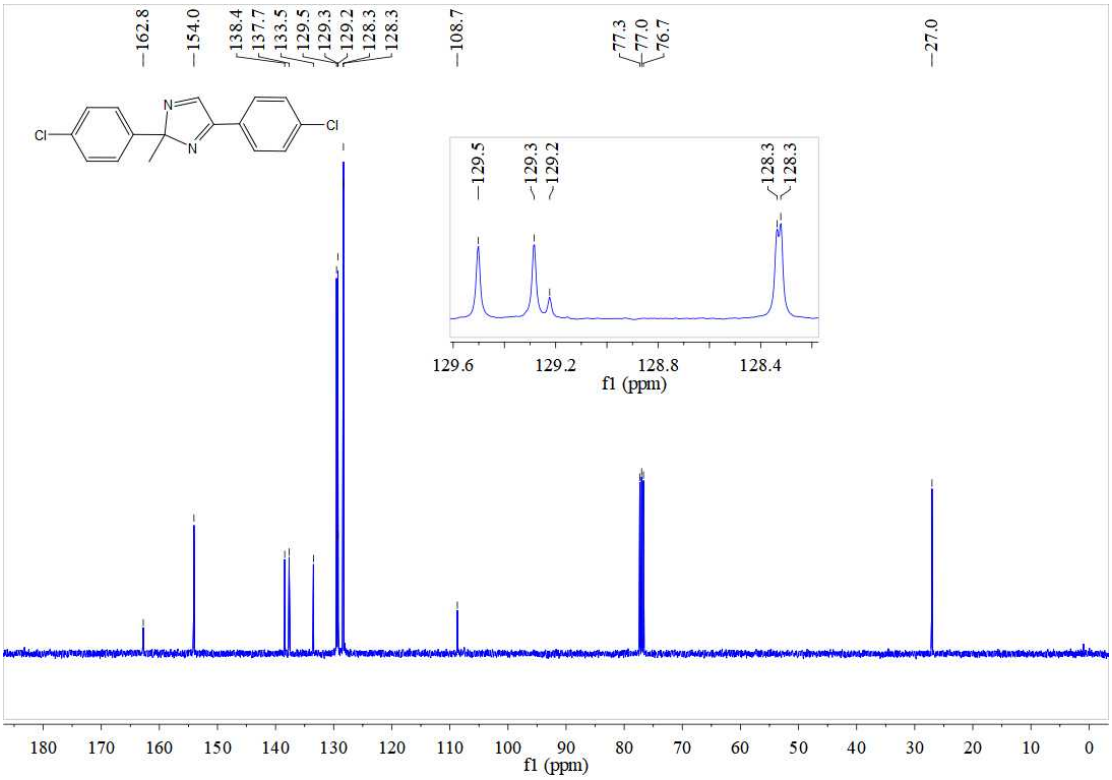


Figure S7 ^{13}C NMR of **3c**

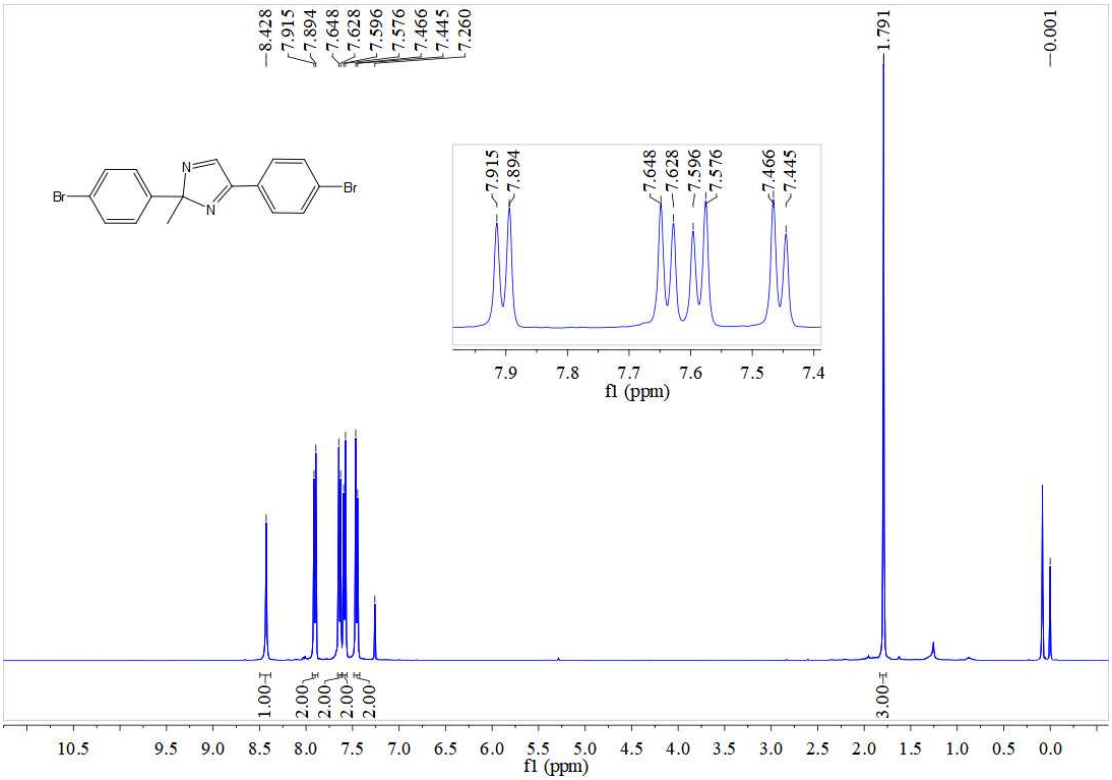


Figure S8 ^{1}H NMR of **3d**

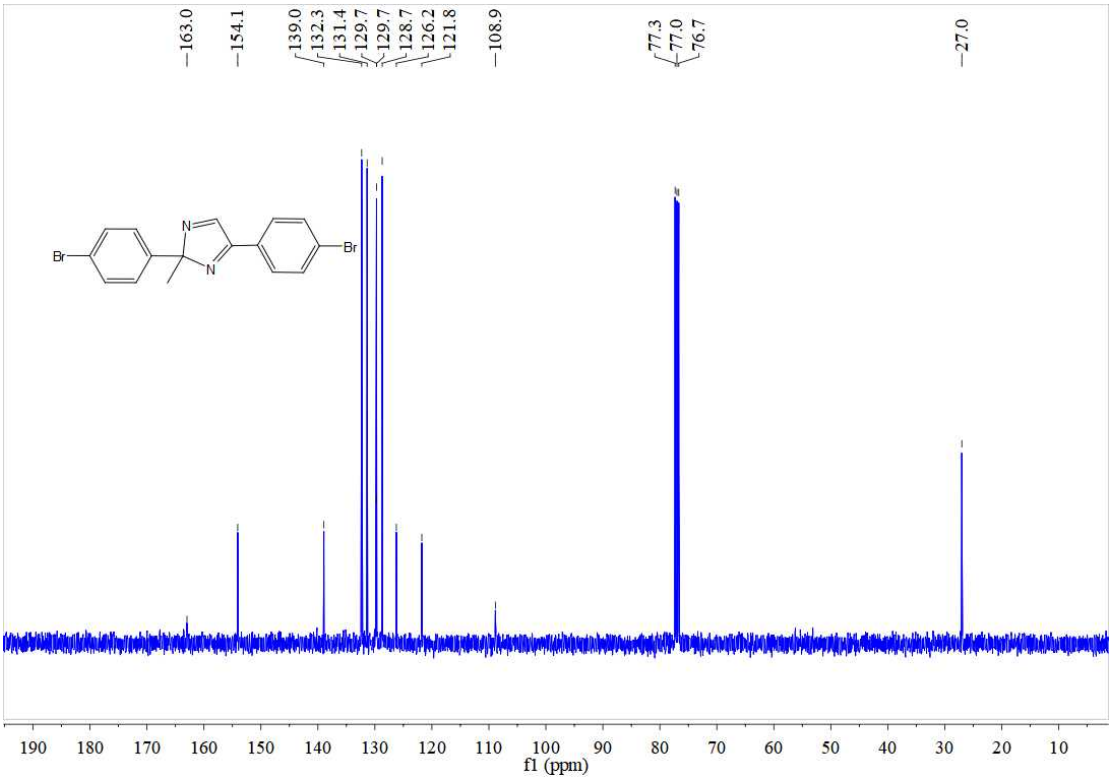


Figure S9 ^{13}C NMR of **3d**

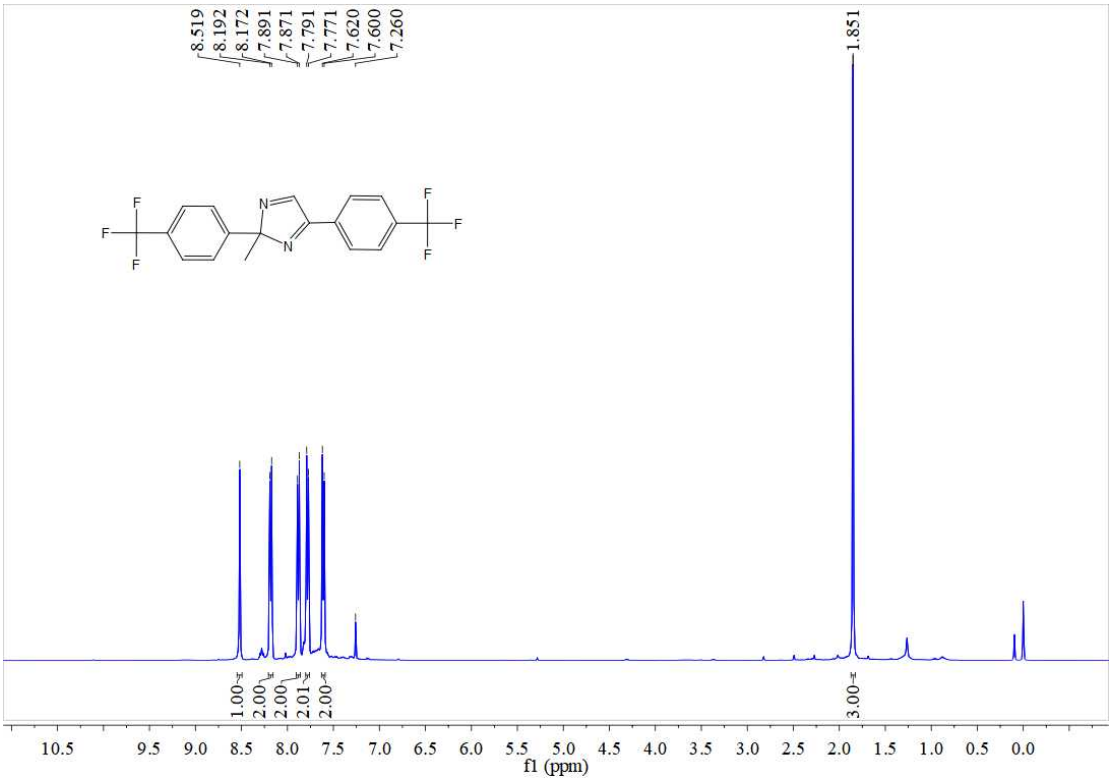


Figure S10 ^{1}H NMR of **3e**

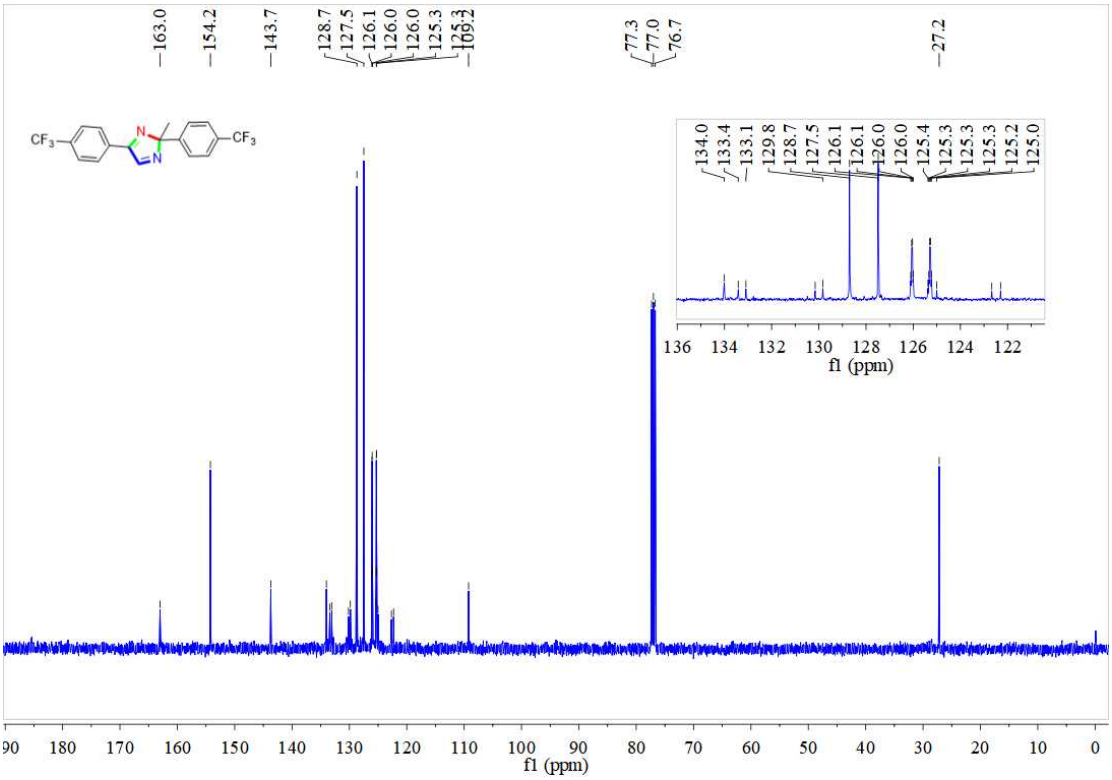


Figure S12 ^{13}C NMR of **3e**

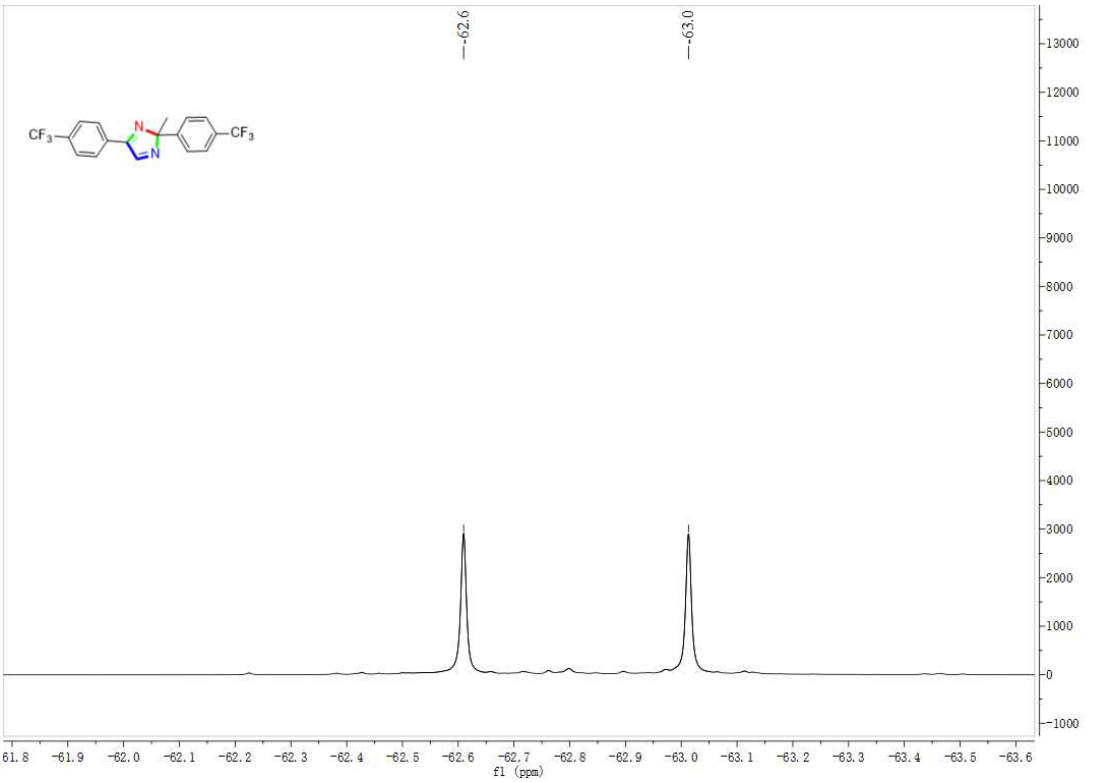


Figure S13 ^{19}F NMR of **3e**

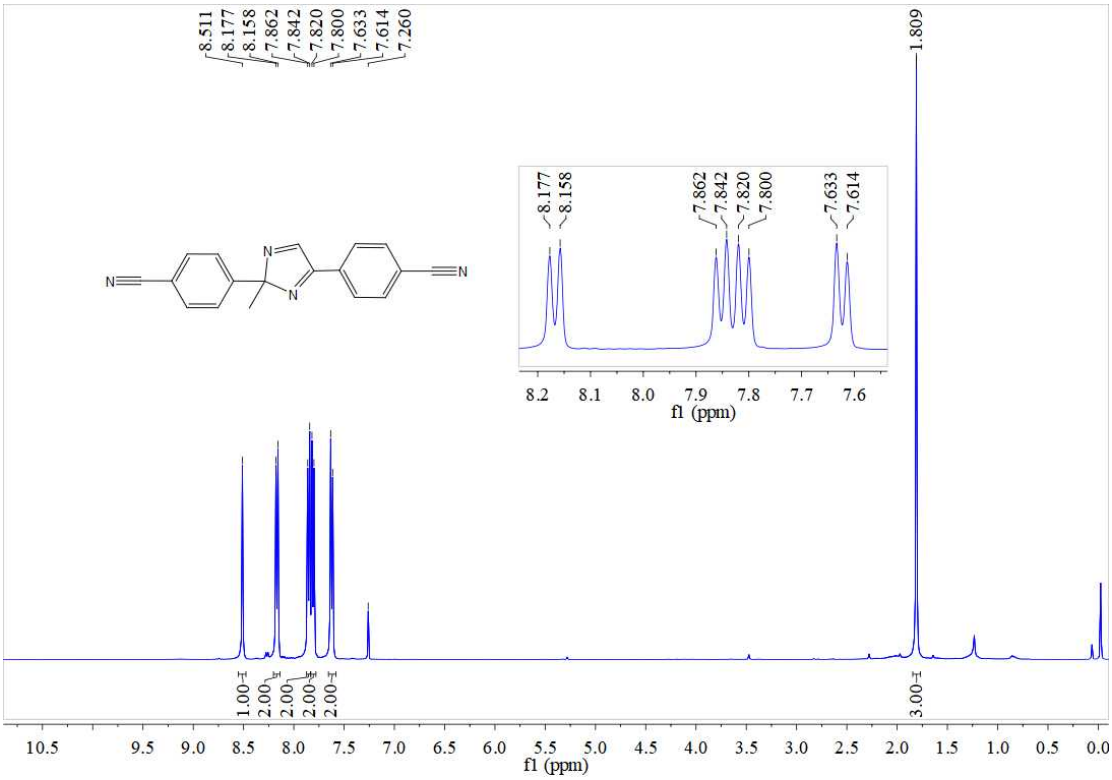


Figure S14 ^{1}H NMR of **3f**

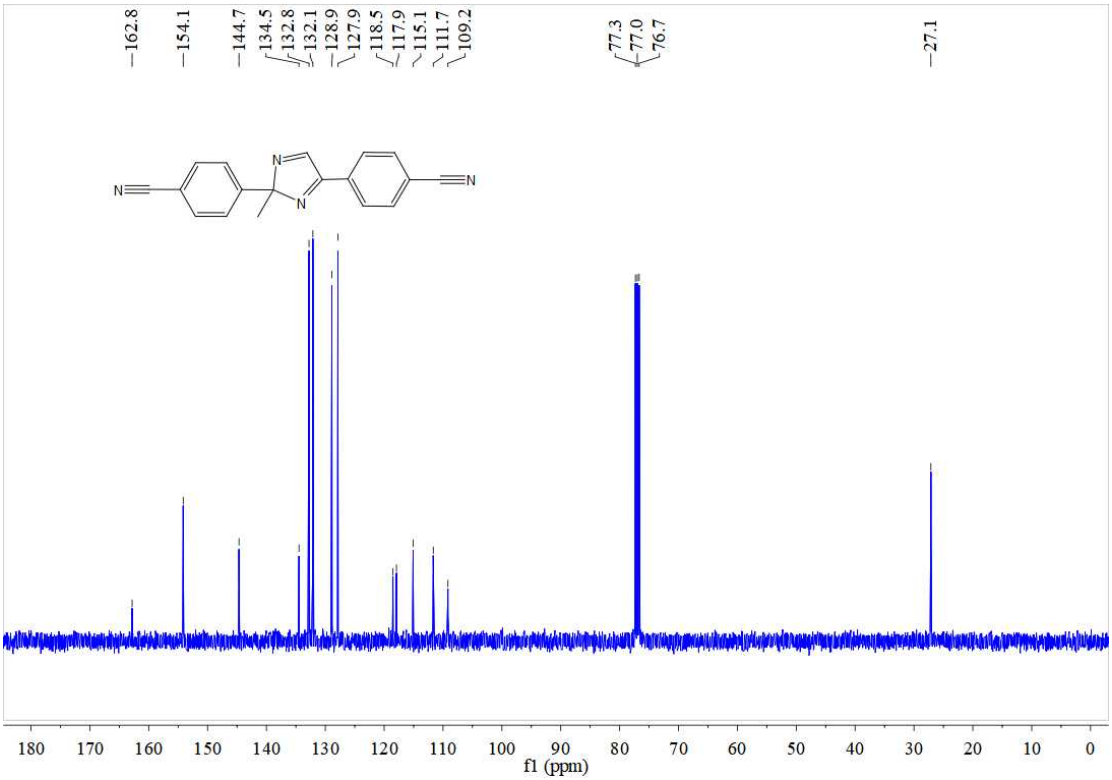


Figure S15 ^{13}C NMR of **3f**

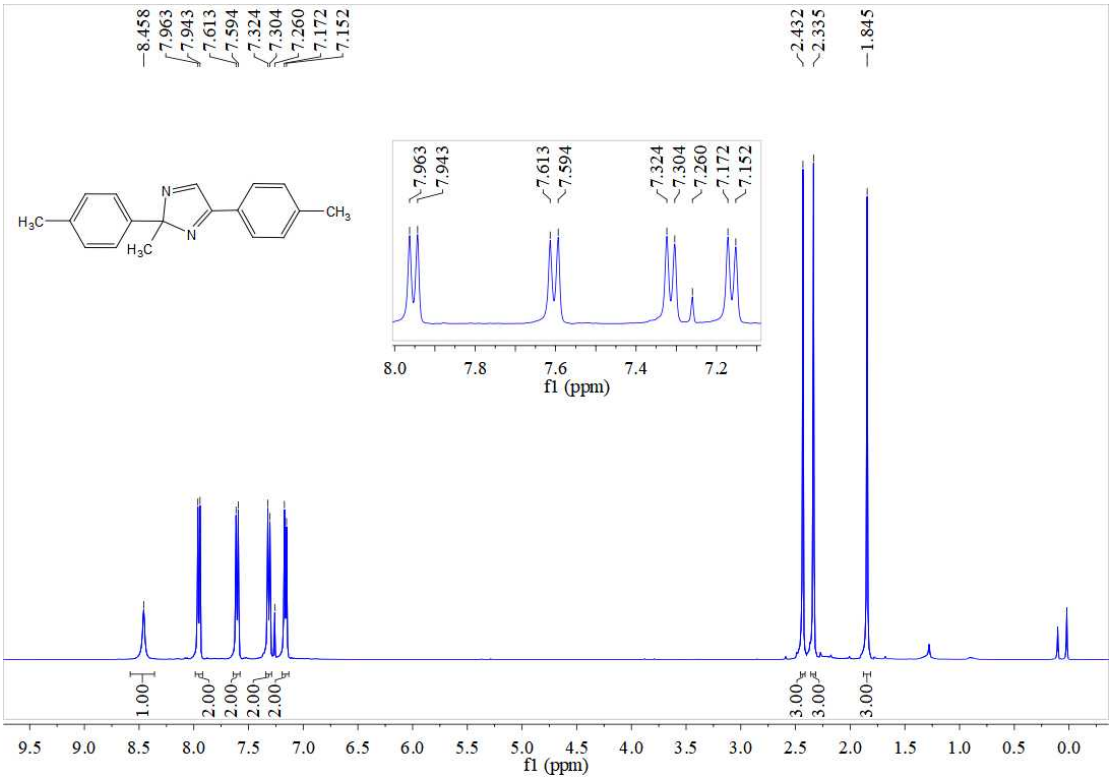


Figure S16 ^{1}H NMR of **3g**

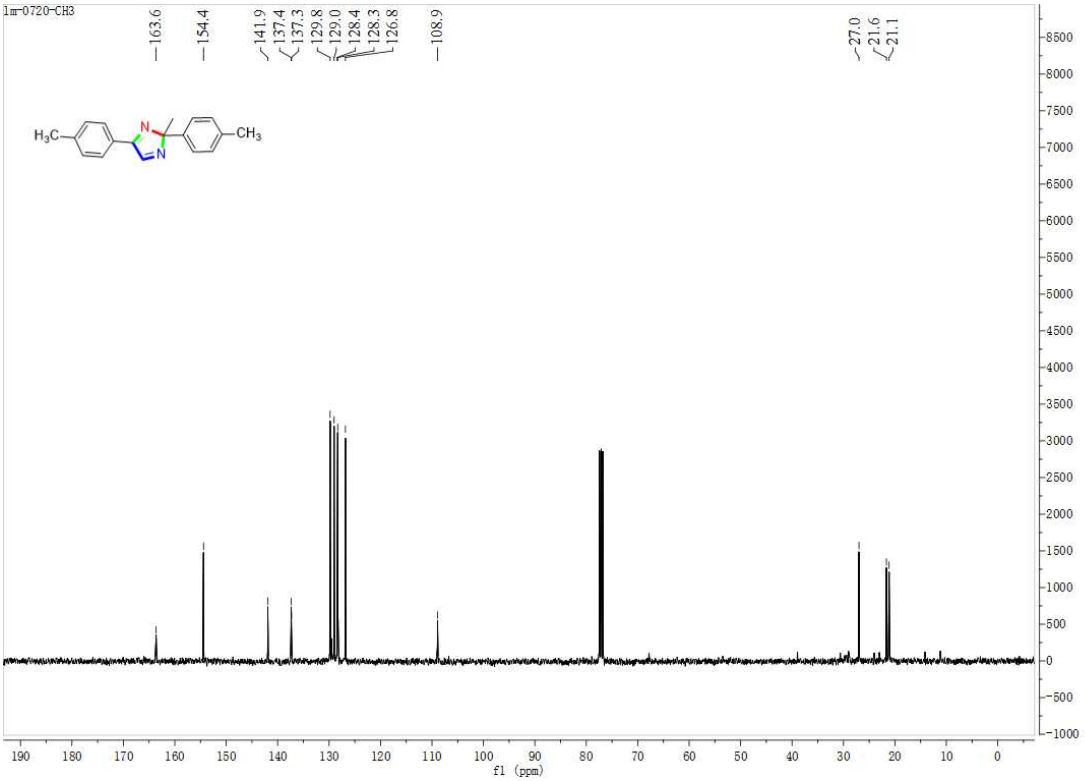


Figure S17 ^{13}C NMR of **3g**

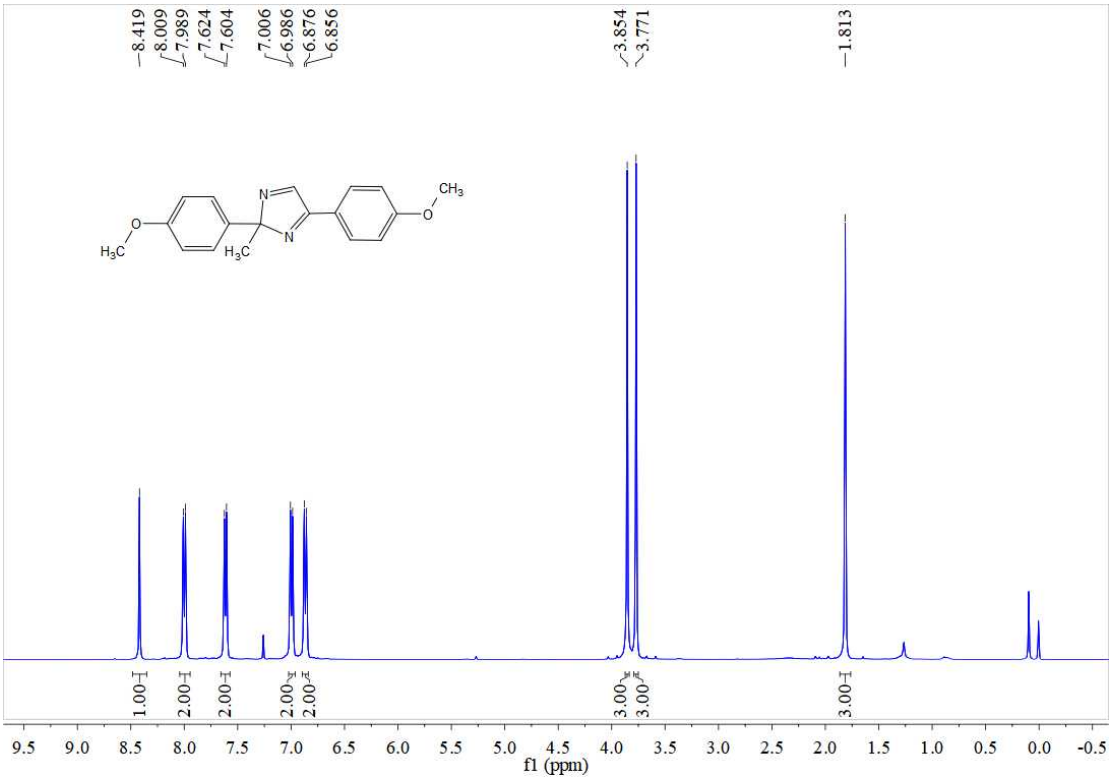


Figure S18 ^{1}H NMR of **3h**

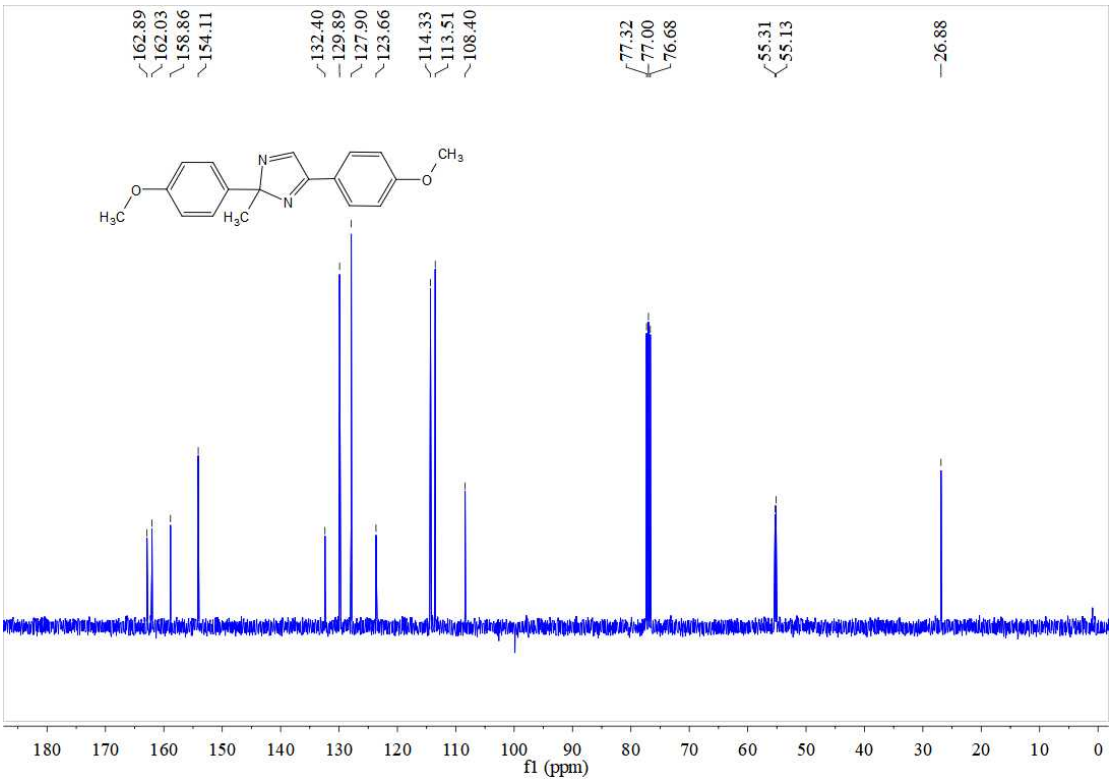


Figure S19 ^{13}C NMR of **3h**

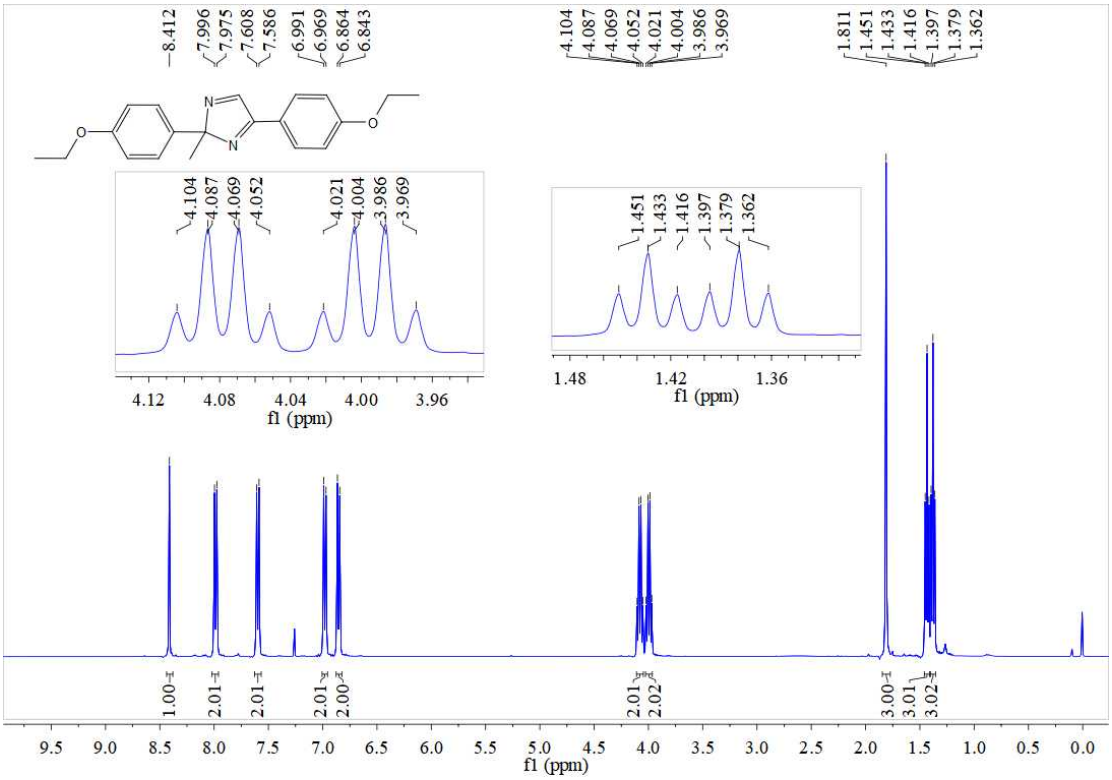


Figure S20 ^{1}H NMR of **3i**

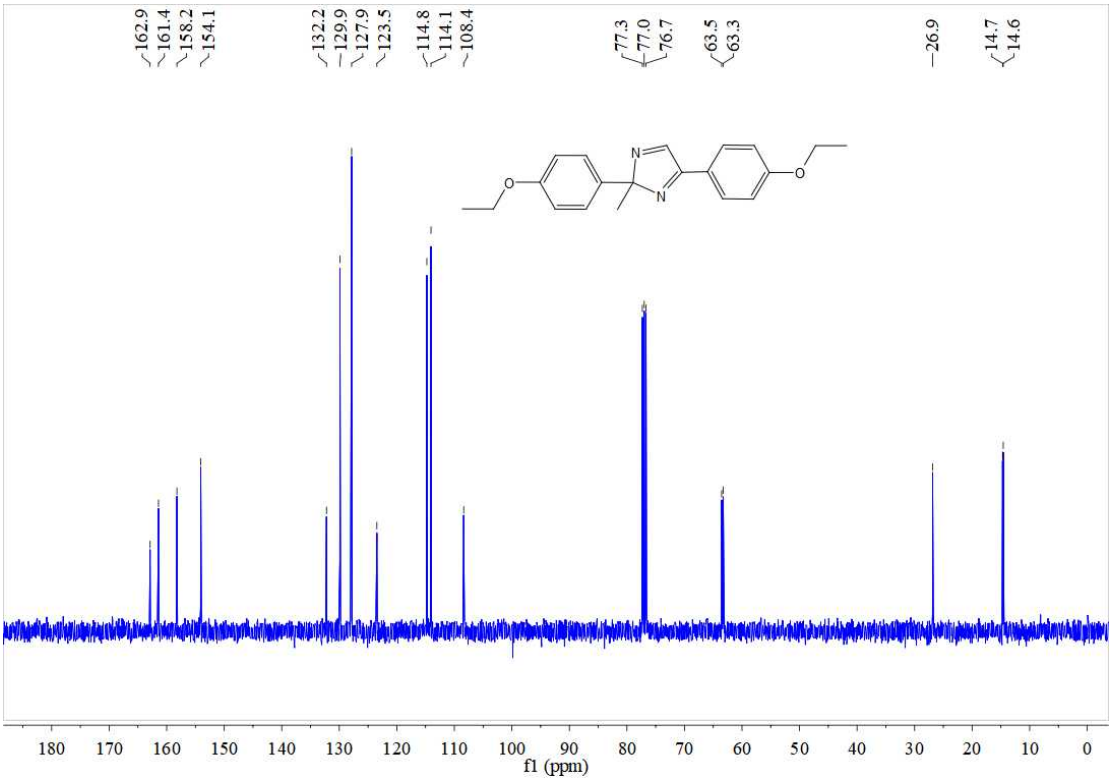


Figure S21 ^{13}C NMR of **3i**

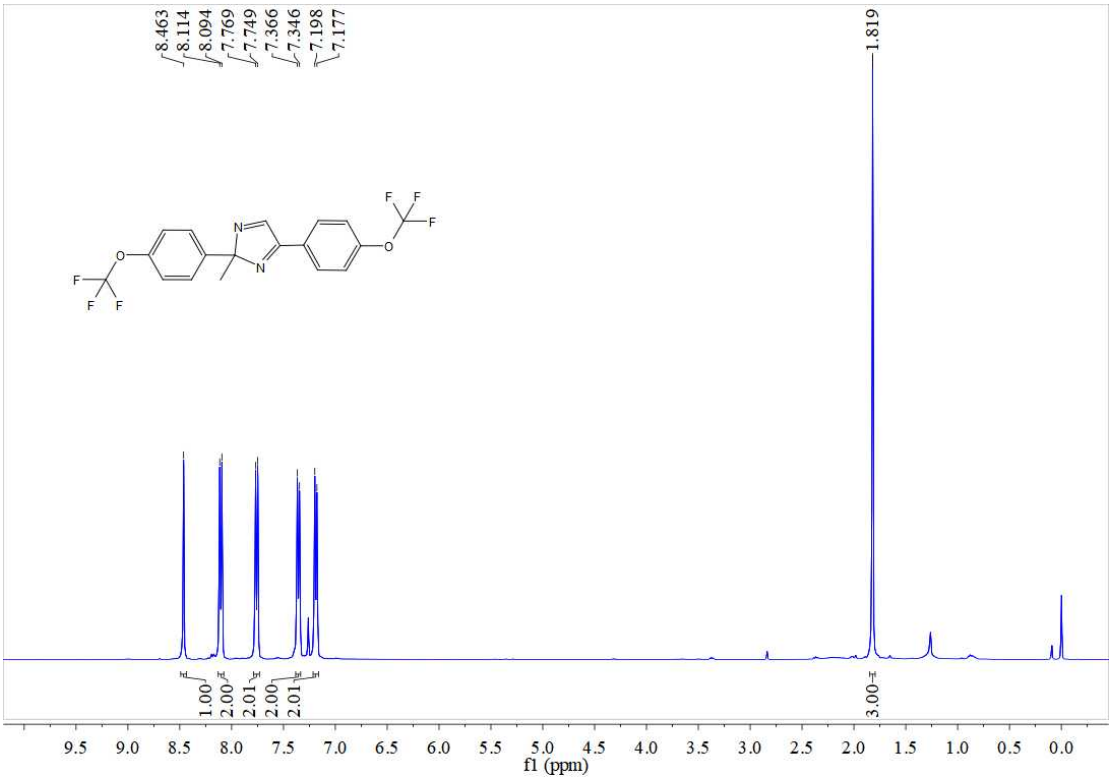


Figure S22 ^{1}H NMR of **3j**

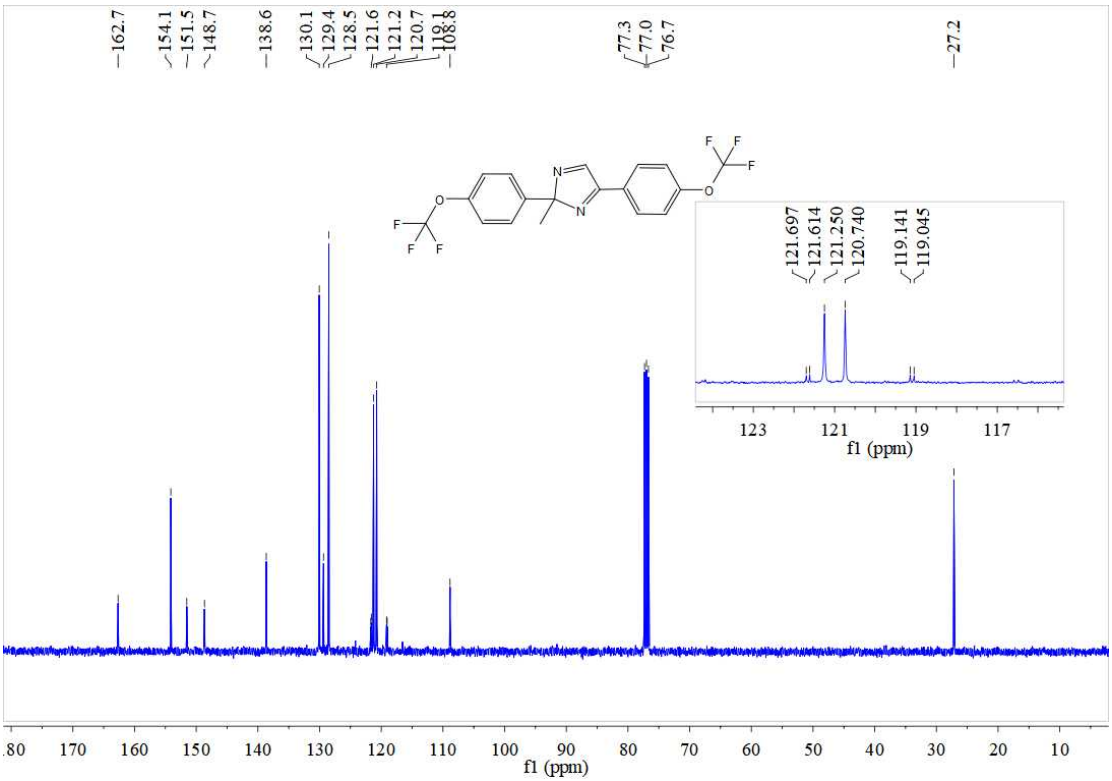


Figure S23 ^{13}C NMR of **3j**

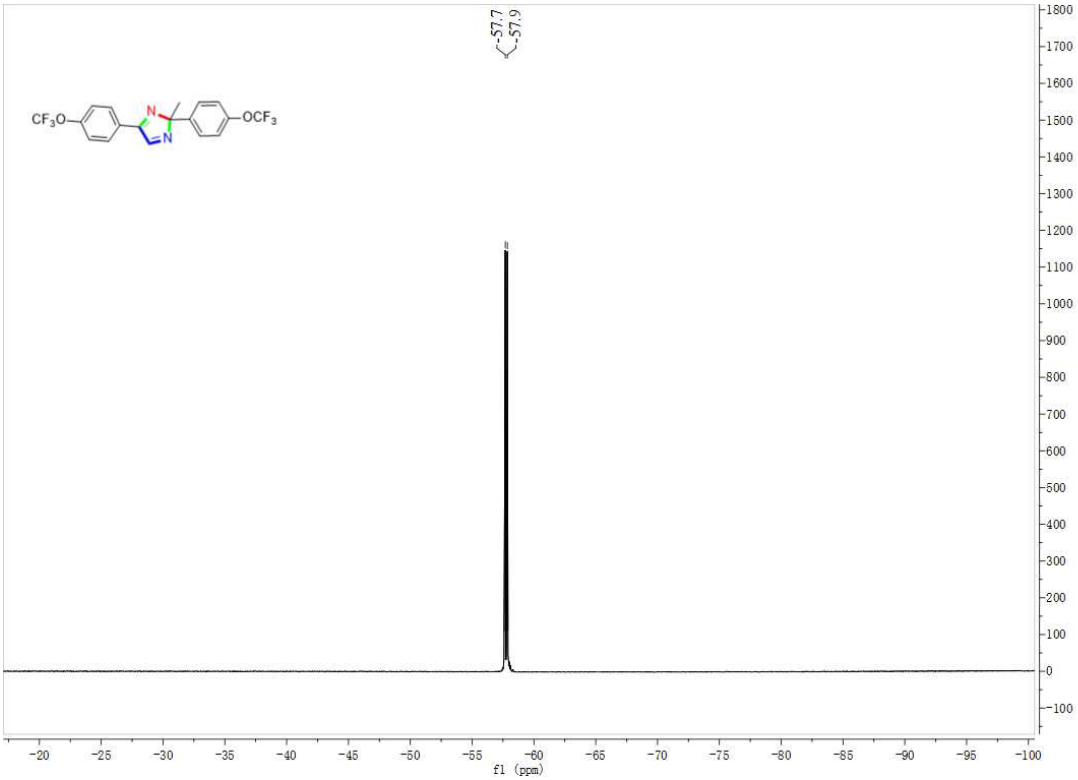


Figure S24 ^{19}F NMR of **3j**

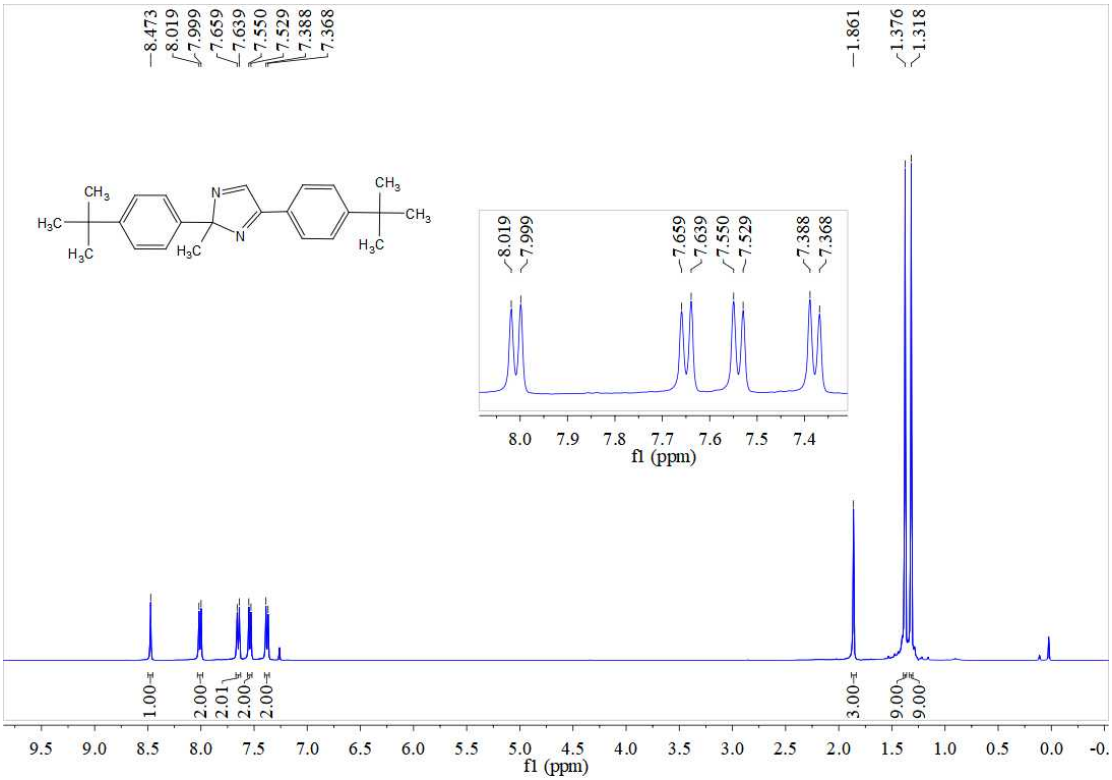


Figure S25 ^{1}H NMR of **3k**

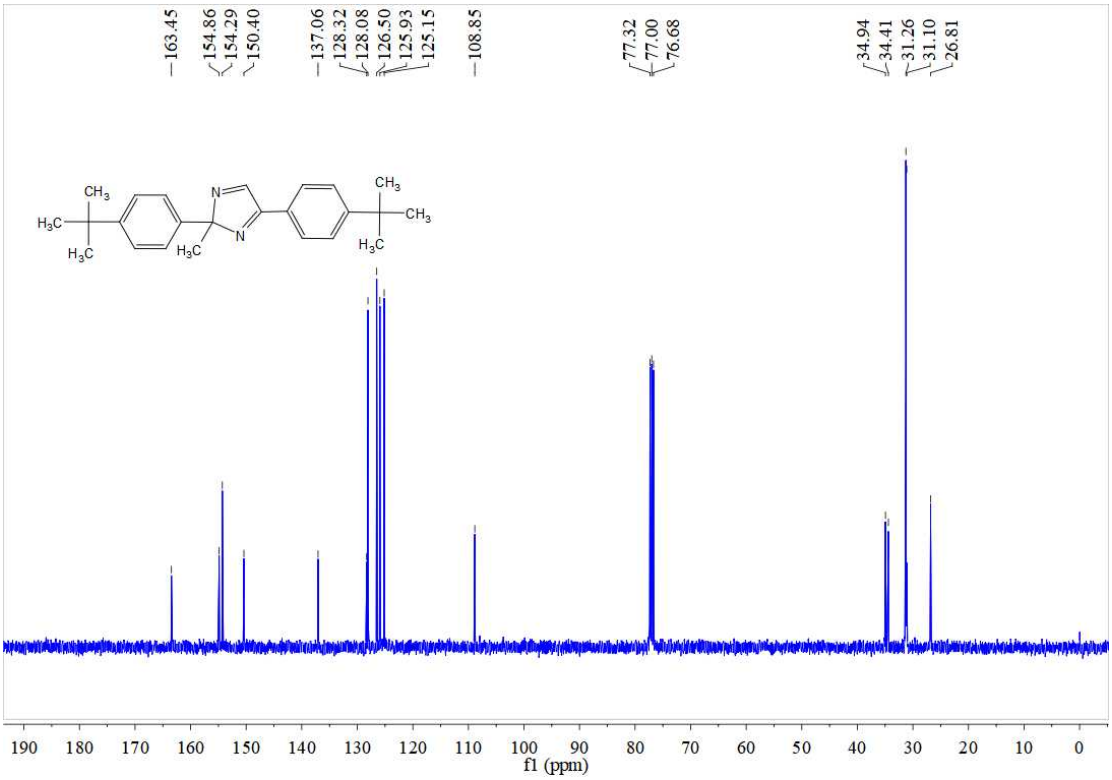


Figure S26 ^{13}C NMR of **3k**

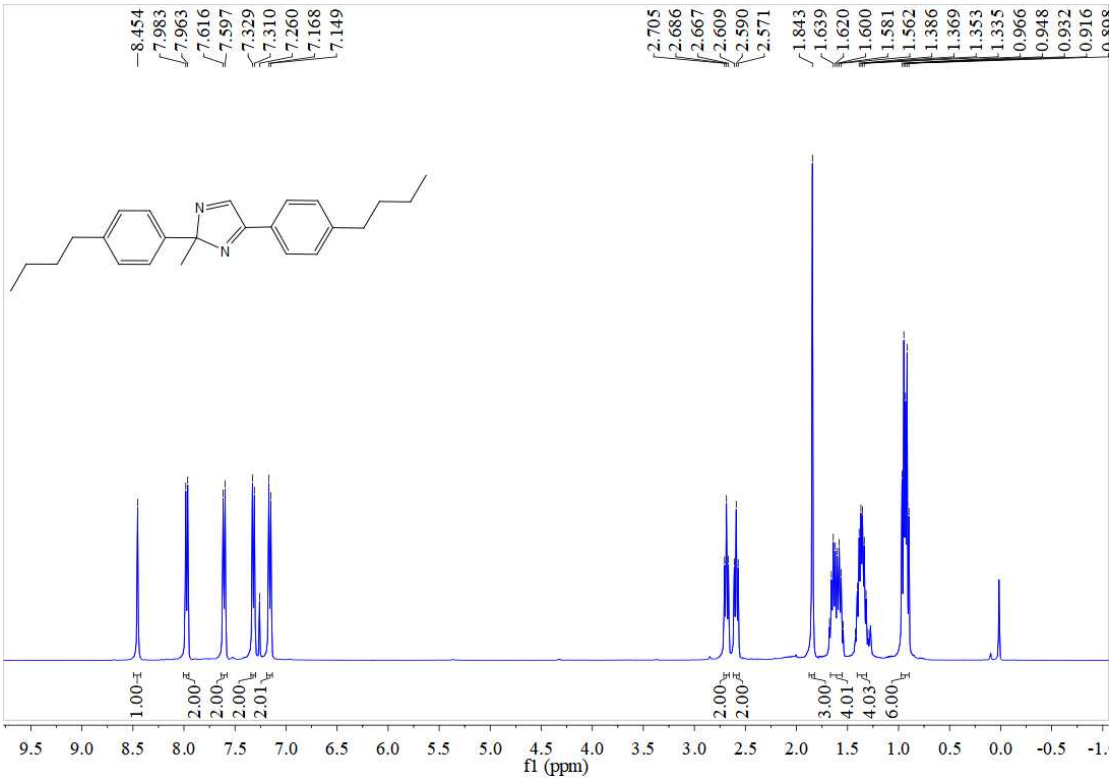


Figure S27 ^{1}H NMR of **3l**

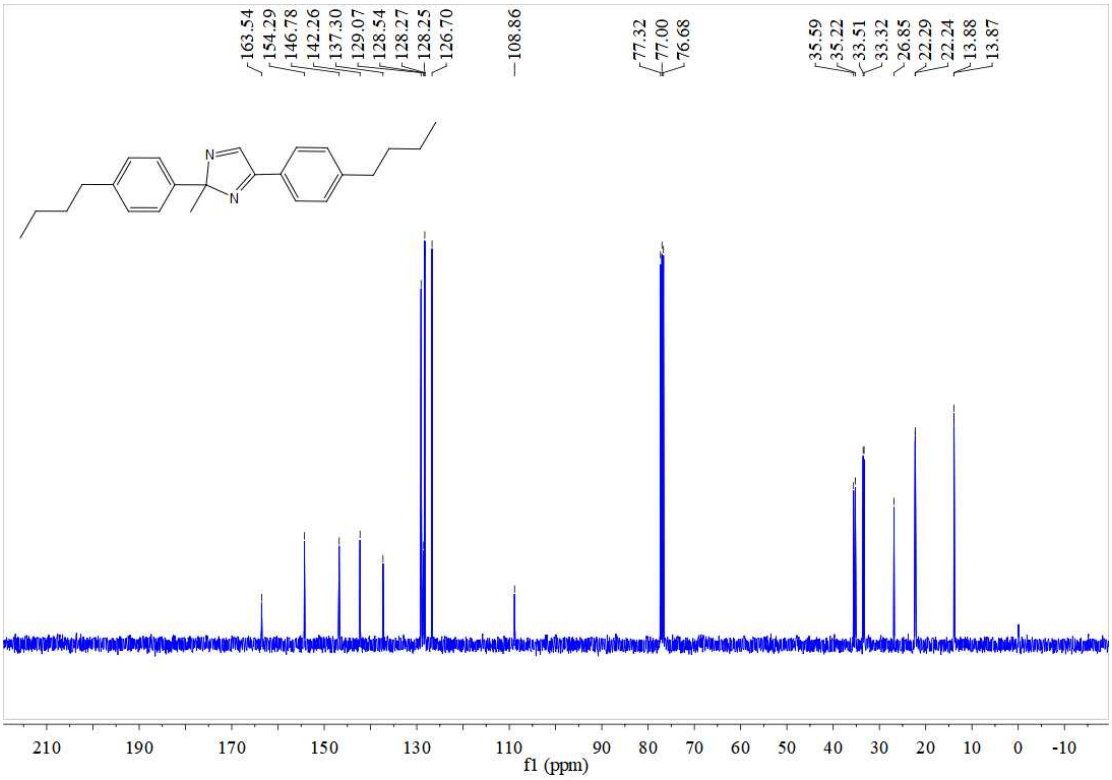


Figure S28 ^{13}C NMR of **3l**

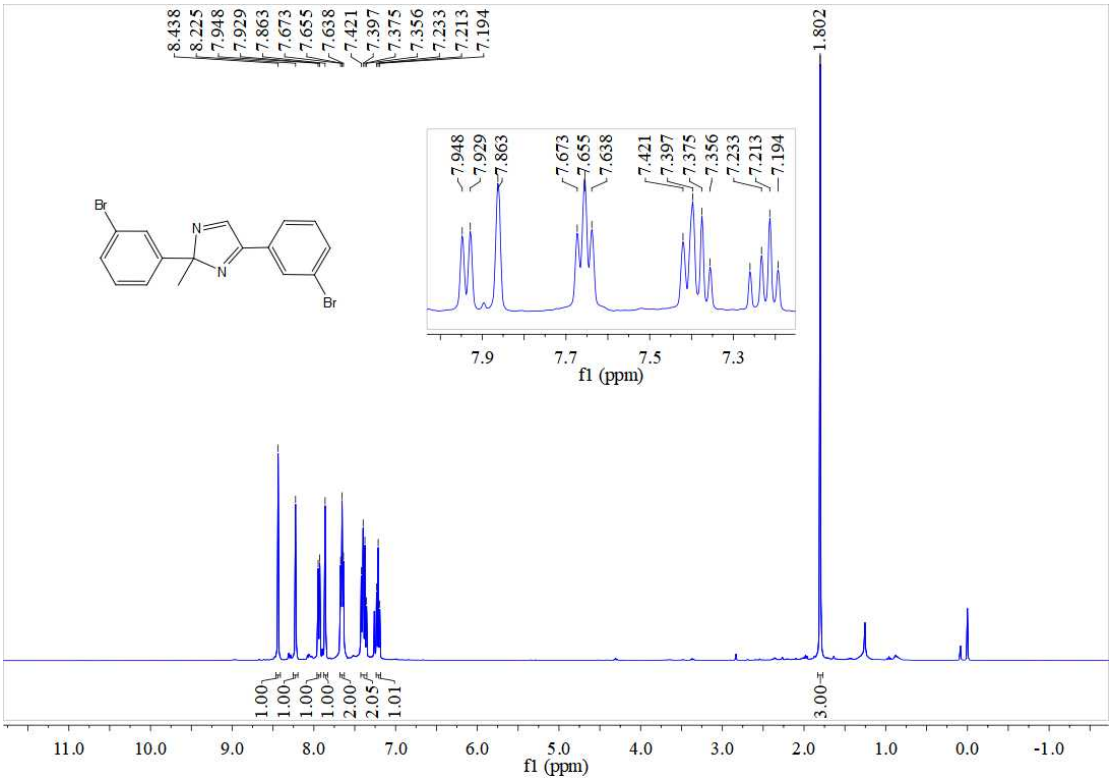


Figure S29 ^{1}H NMR of **3m**

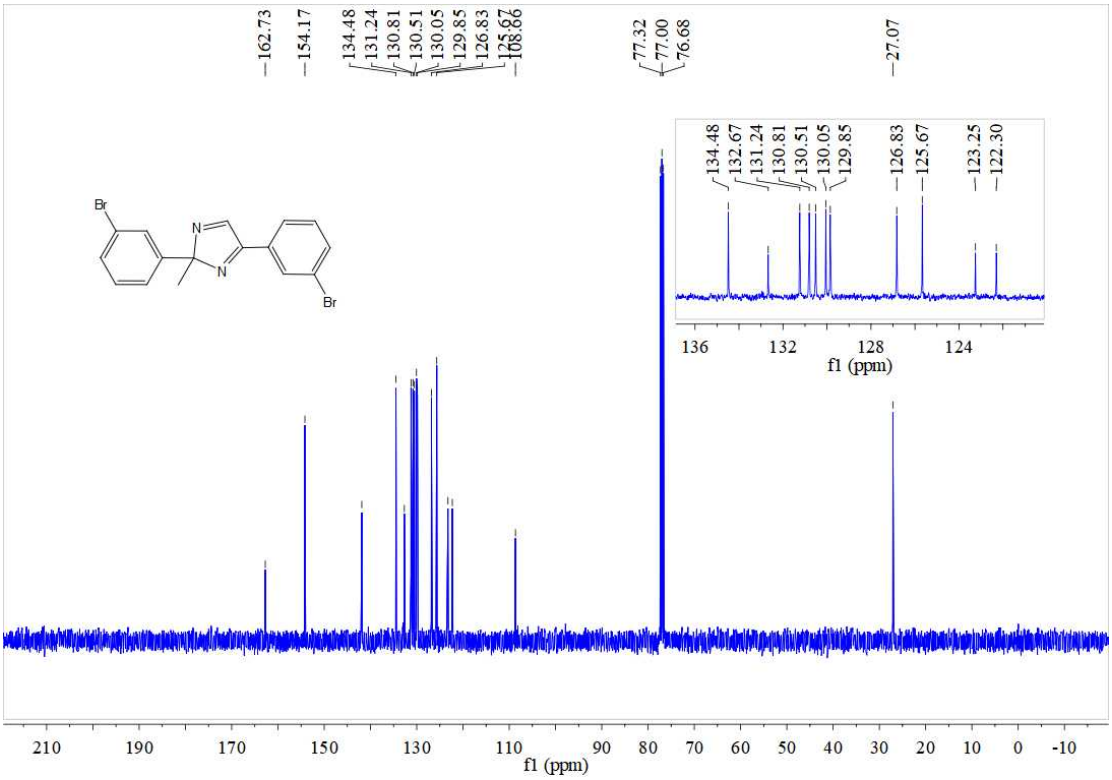


Figure S30 ^{13}C NMR of **3m**

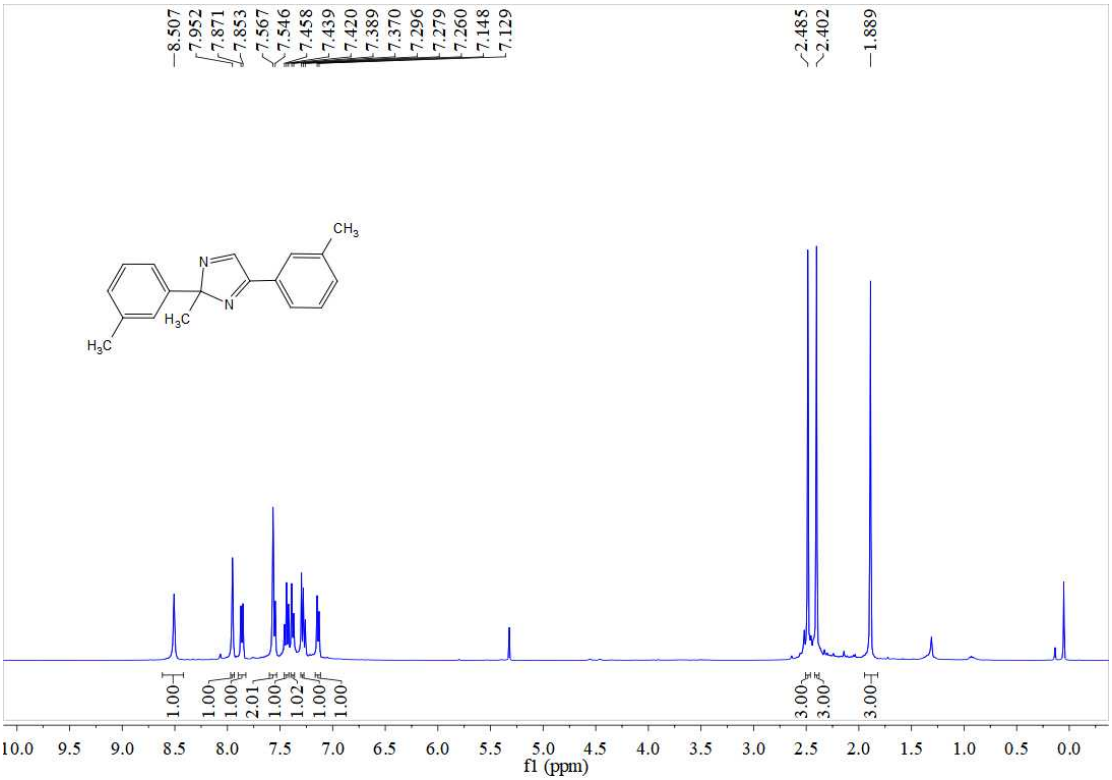


Figure S31 ^{1}H NMR of **3n**

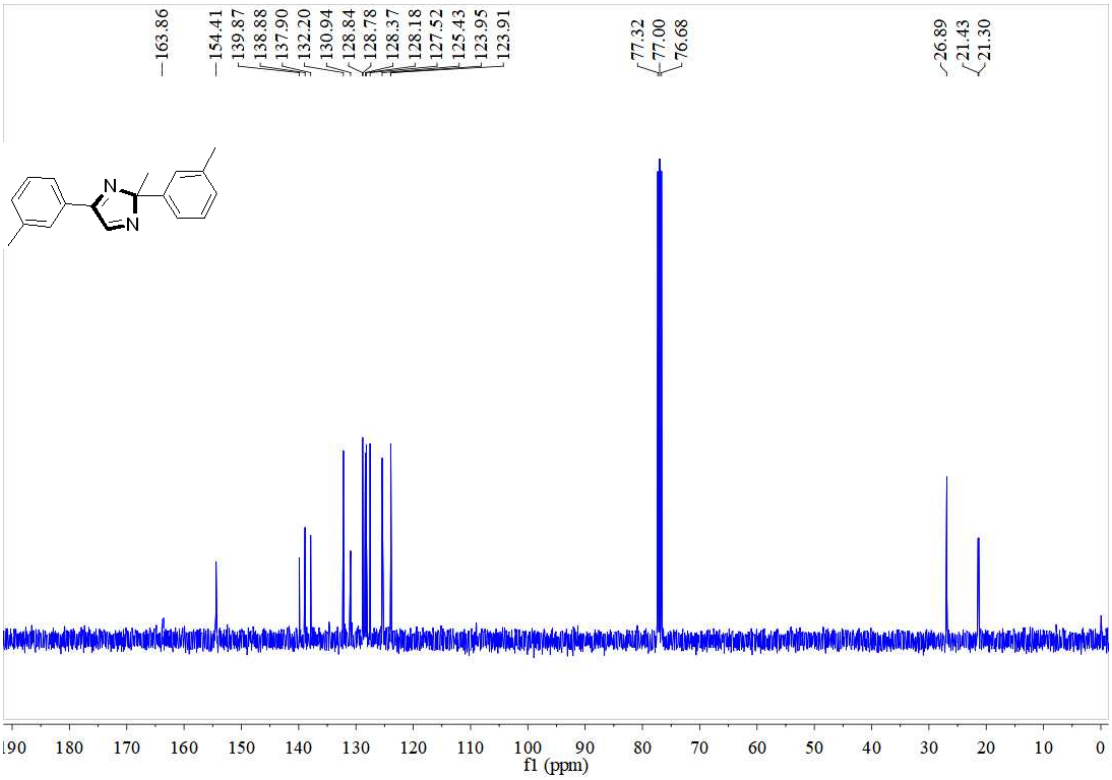


Figure S32 ^{13}C NMR of **3n**

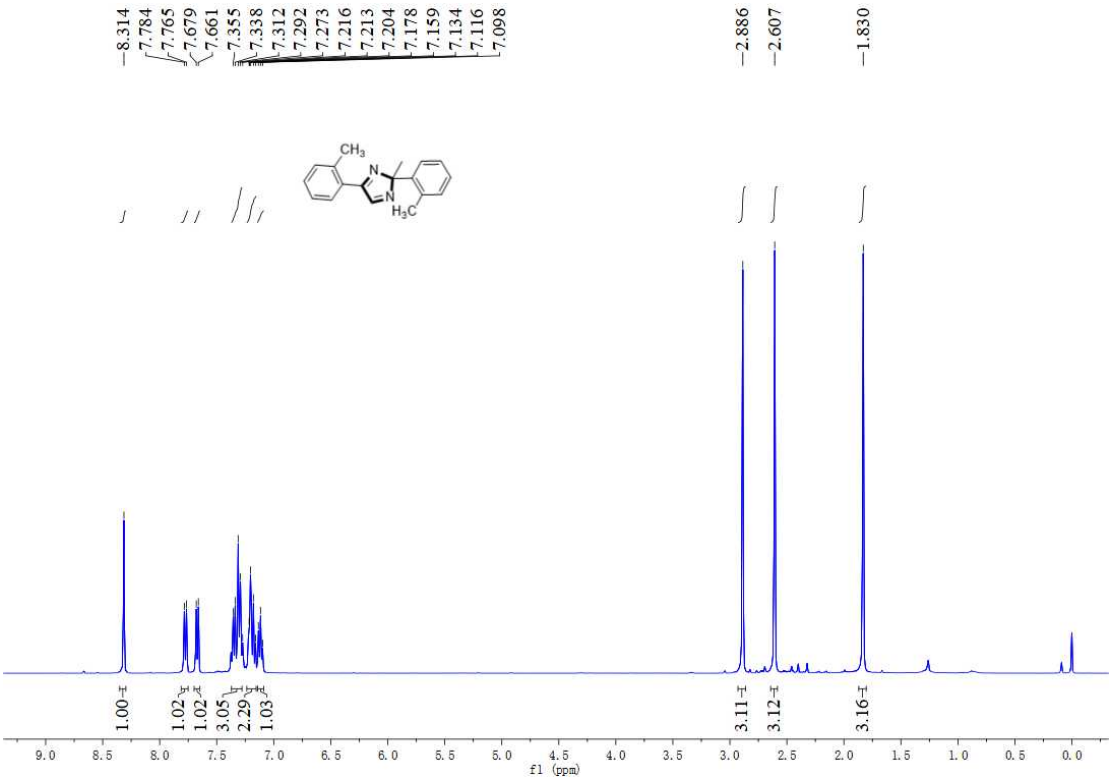


Figure S33 ^{1}H NMR of **3o**

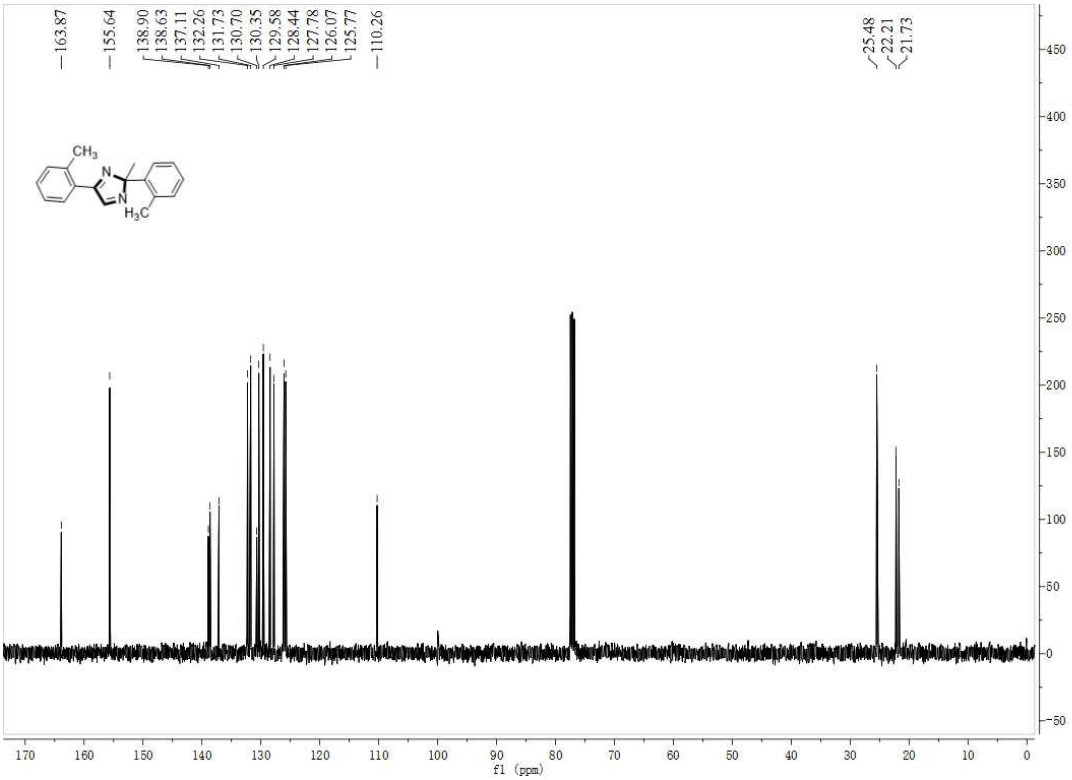


Figure S34 ^{13}C NMR of **3o**

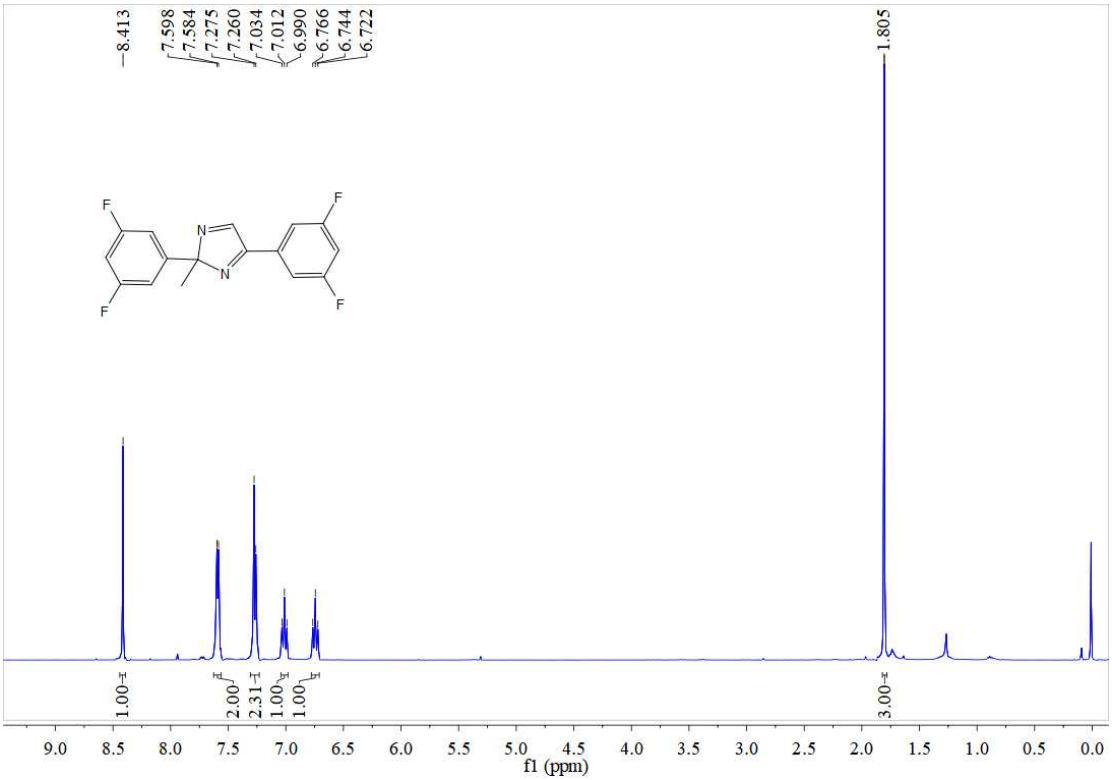


Figure S35 ^{1}H NMR of **3p**

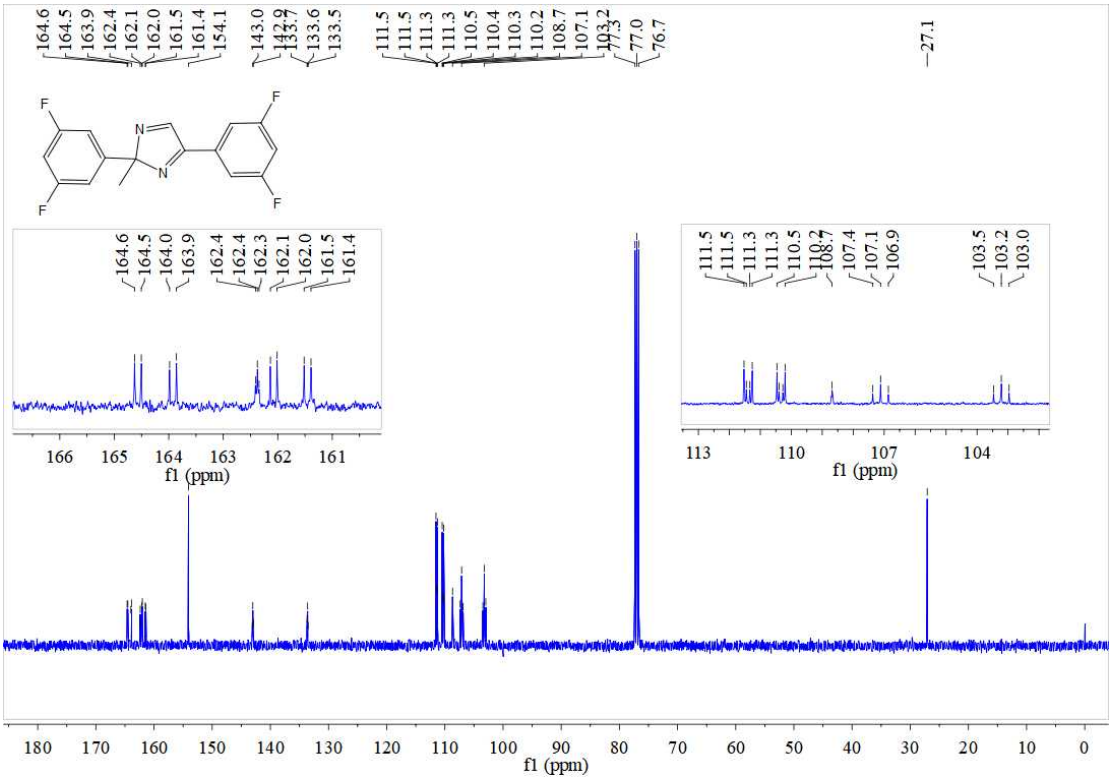


Figure S36 ^{13}C NMR of **3p**

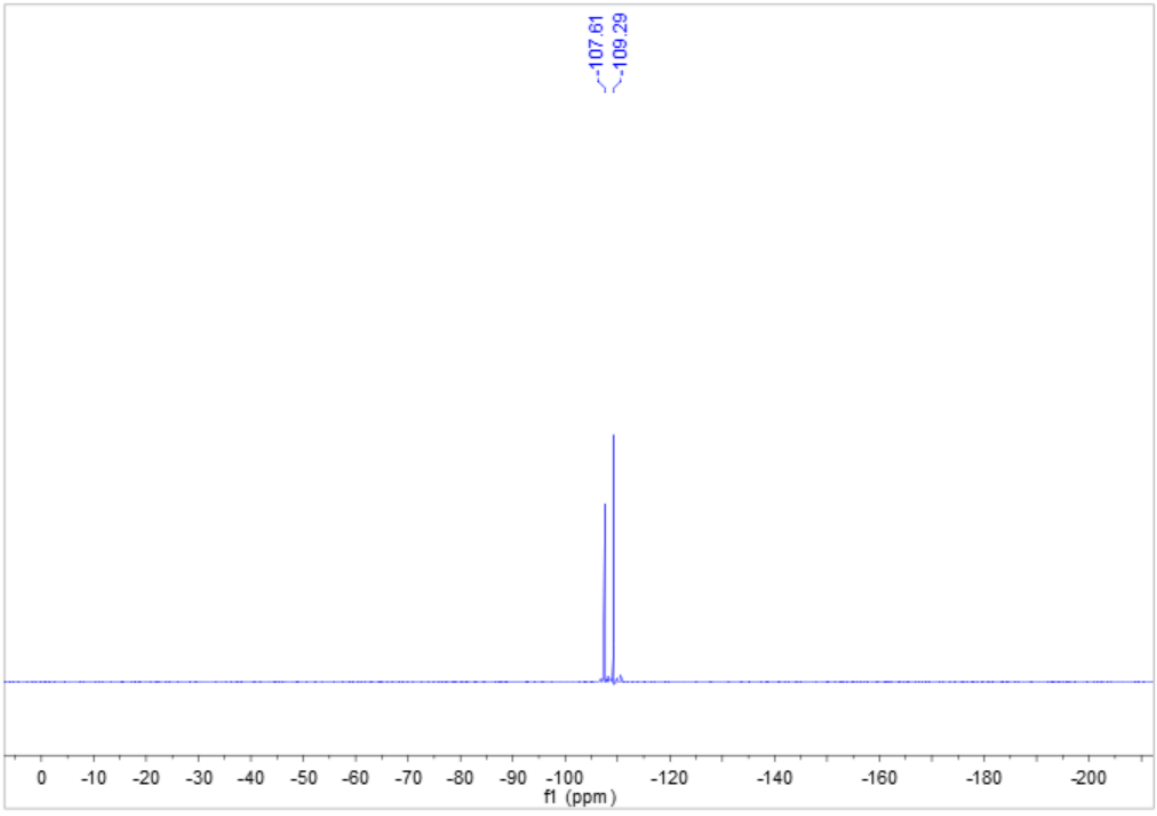


Figure S37 ^{19}F NMR of **3p**

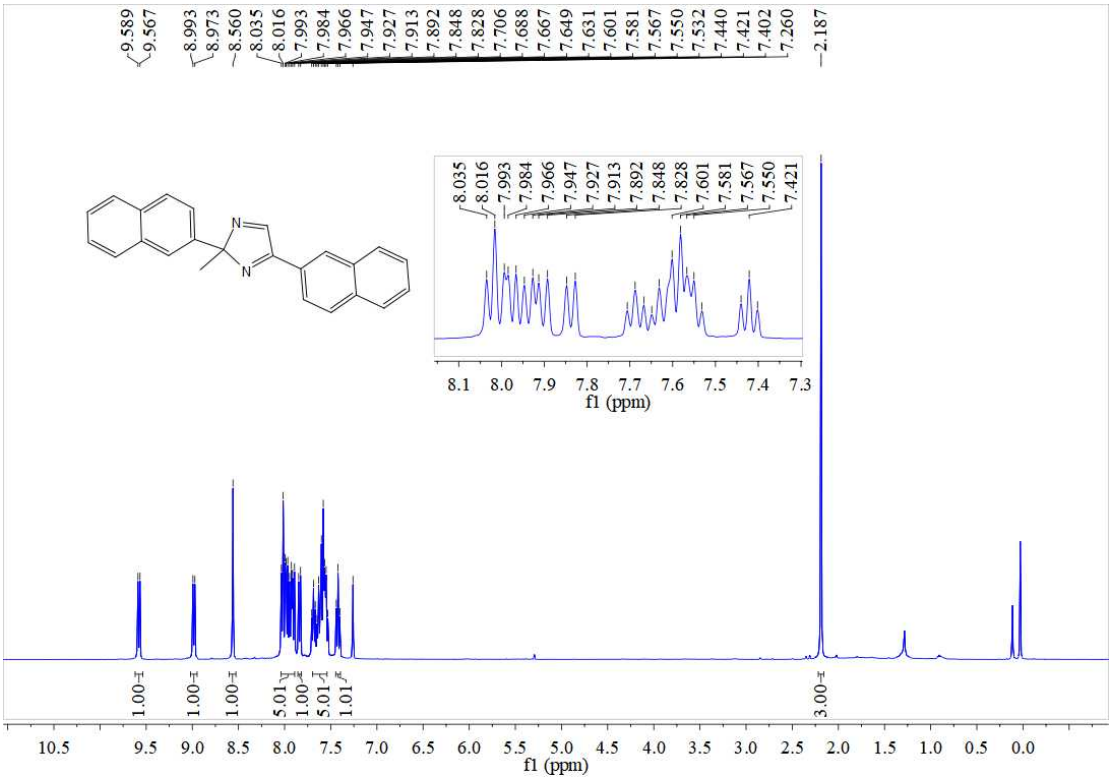


Figure S38 ^{1}H NMR of **3q**

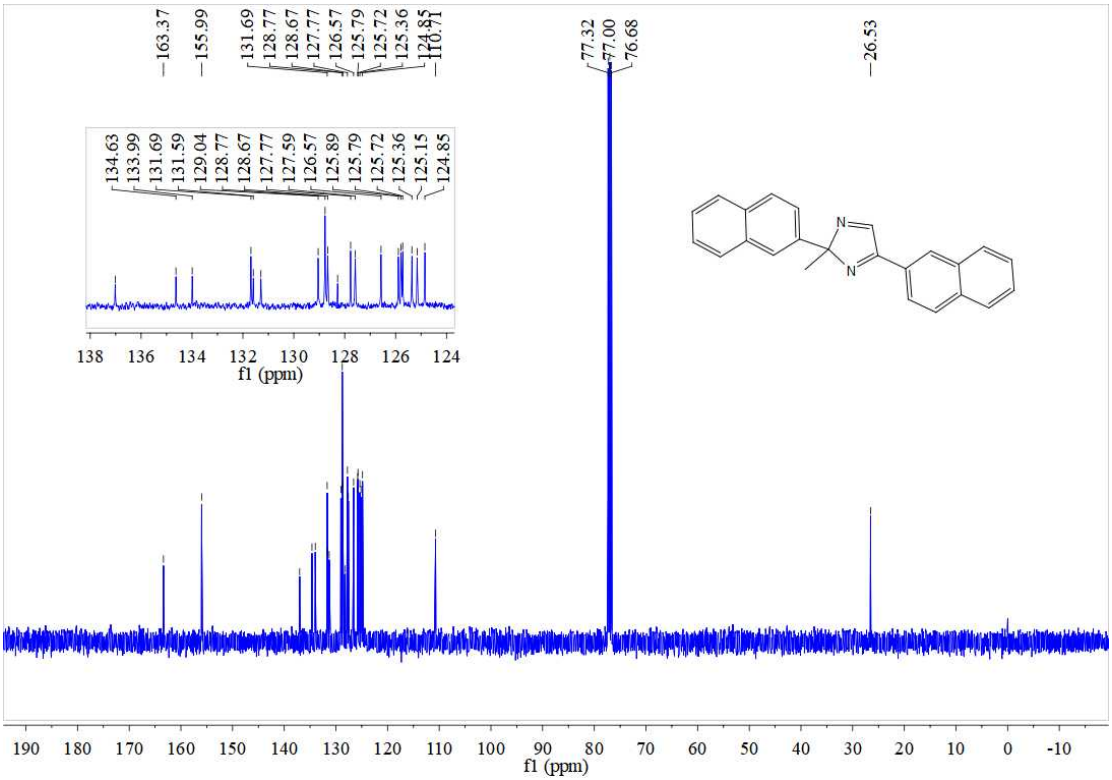


Figure S39 ^{13}C NMR of **3q**

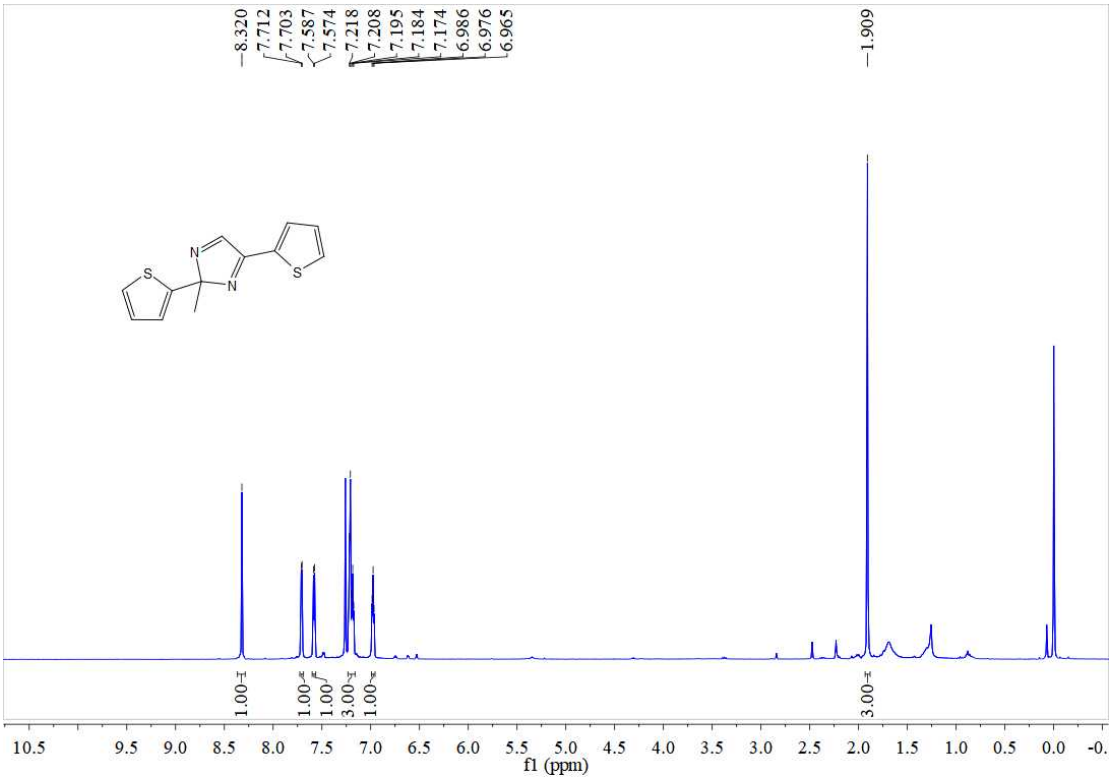


Figure S40 ^{1}H NMR of **3r**

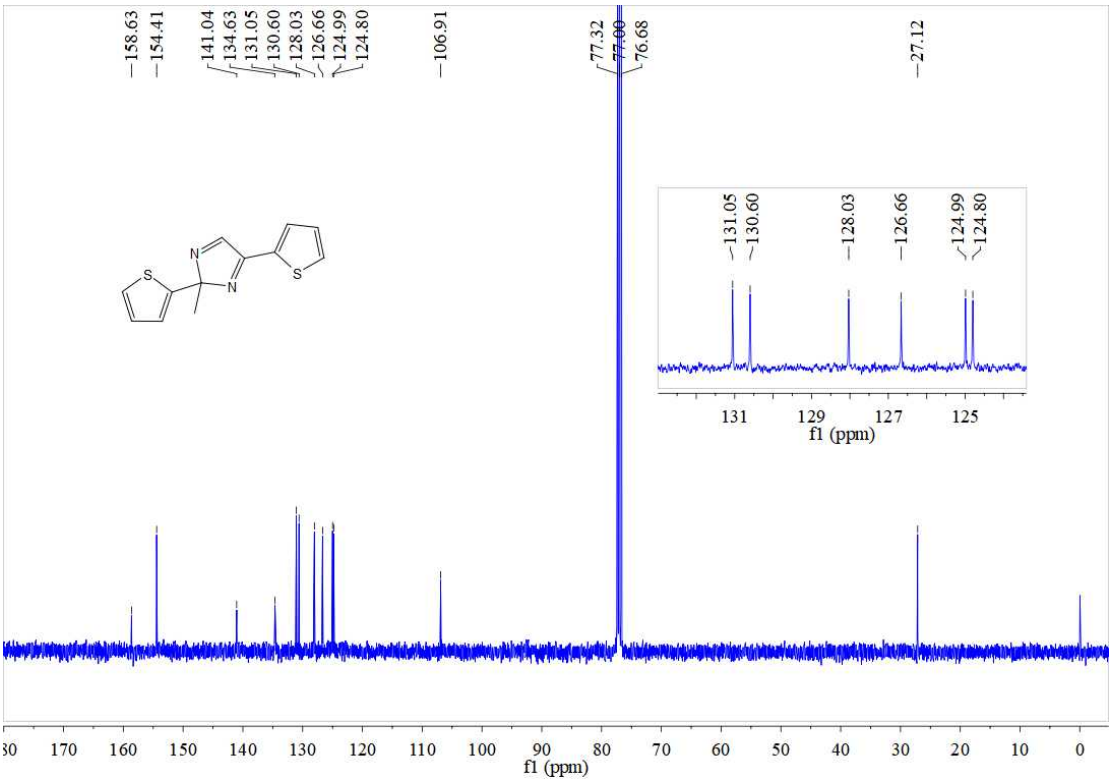


Figure S41 ^{13}C NMR of **3r**

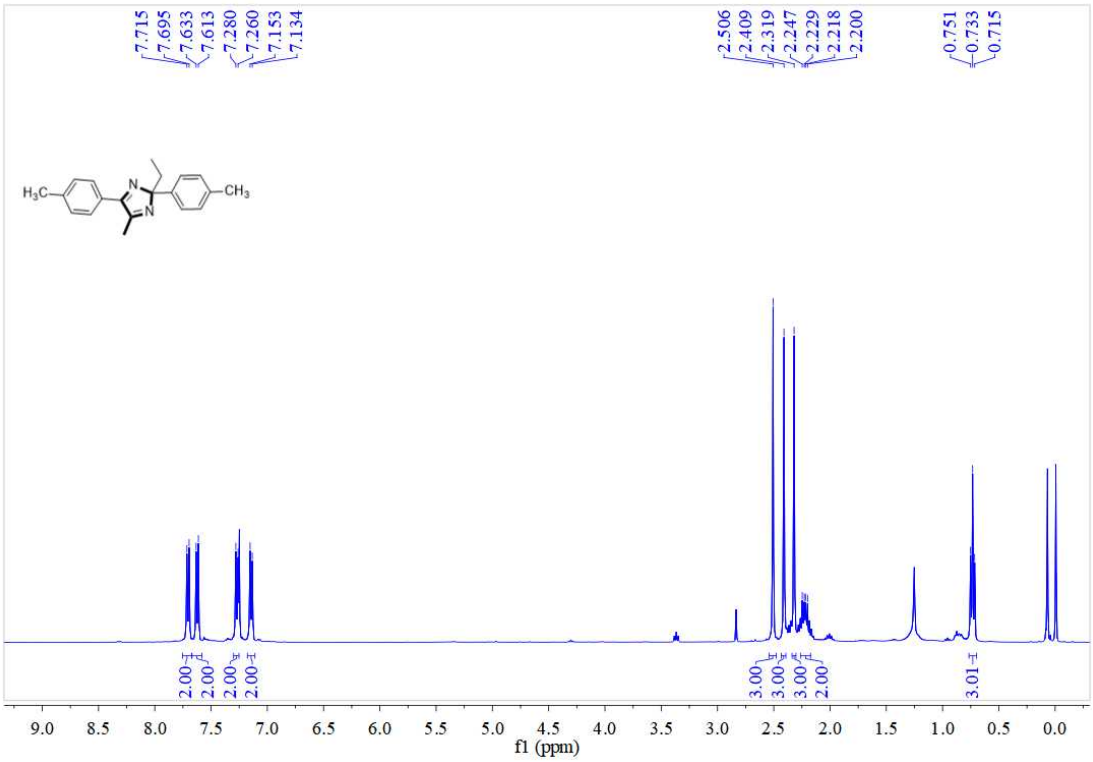


Figure S42 ^{1}H NMR of **3s**

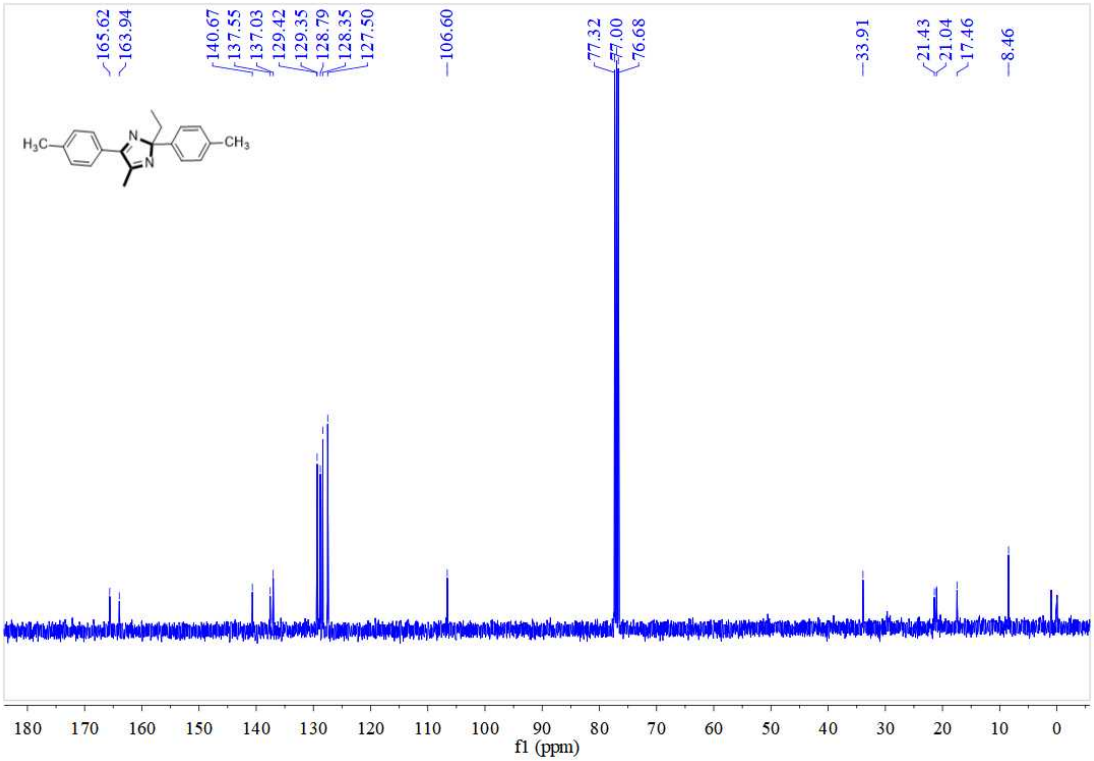


Figure S43 ^{13}C NMR of **3s**

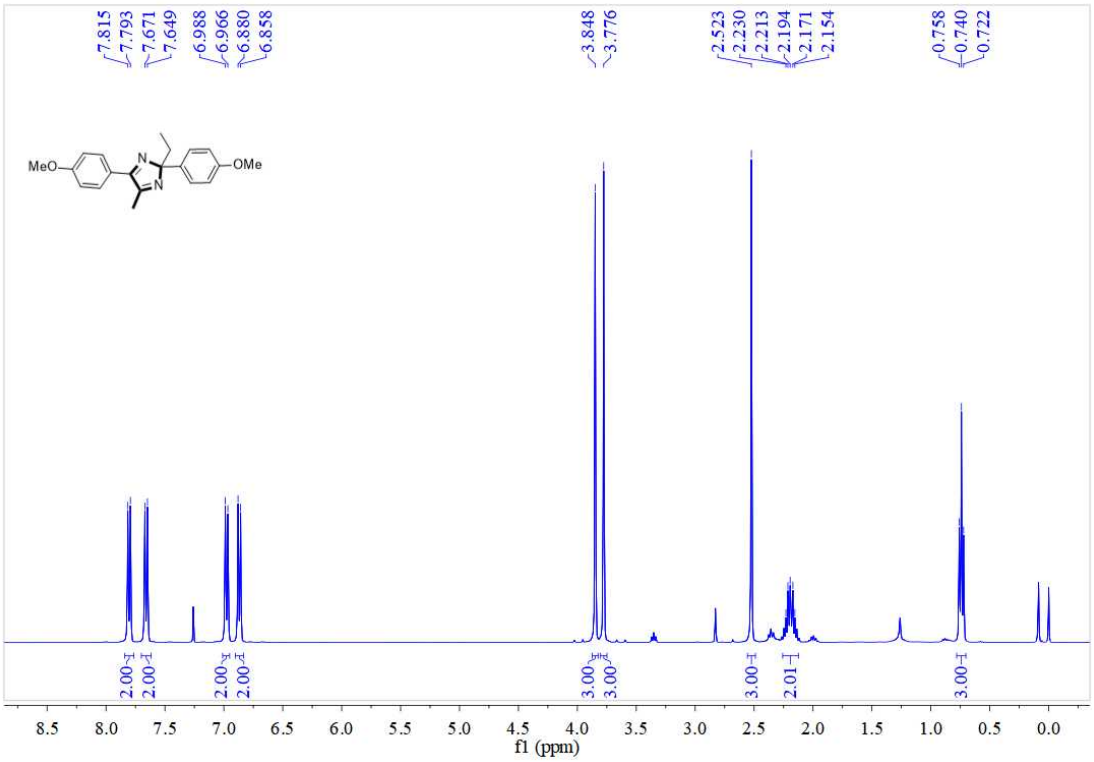


Figure S44 ^{1}H NMR of **3t**

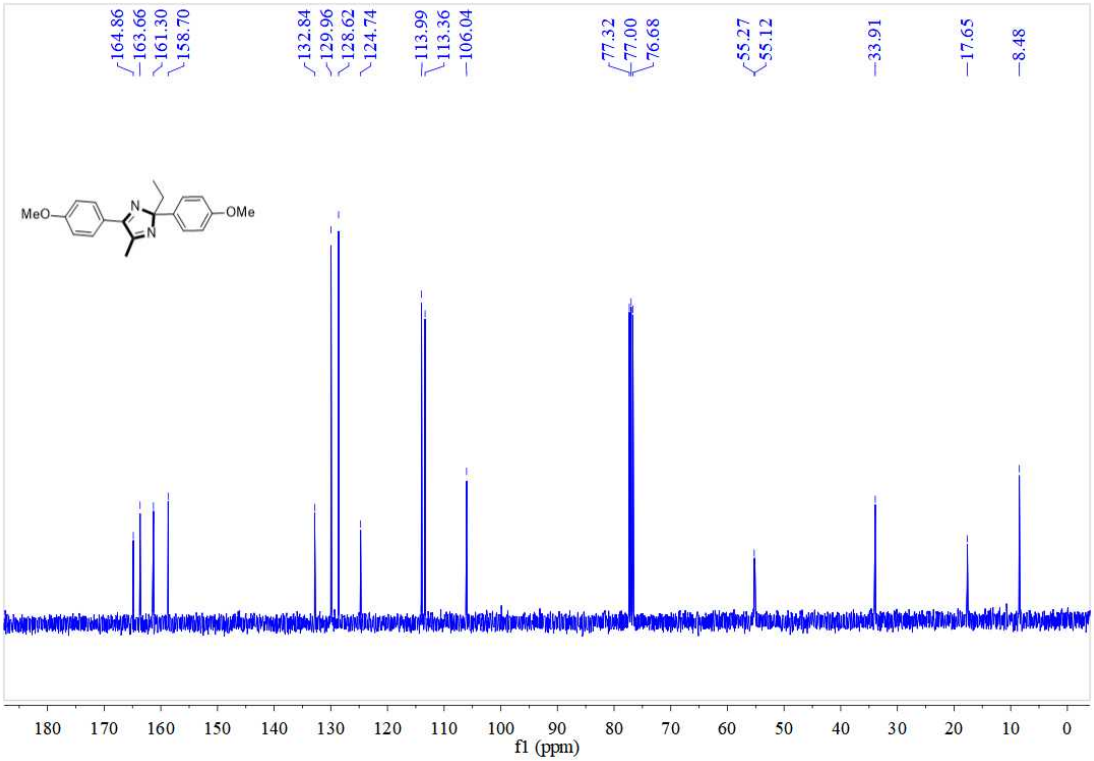


Figure S45 ^{13}C NMR of **3t**

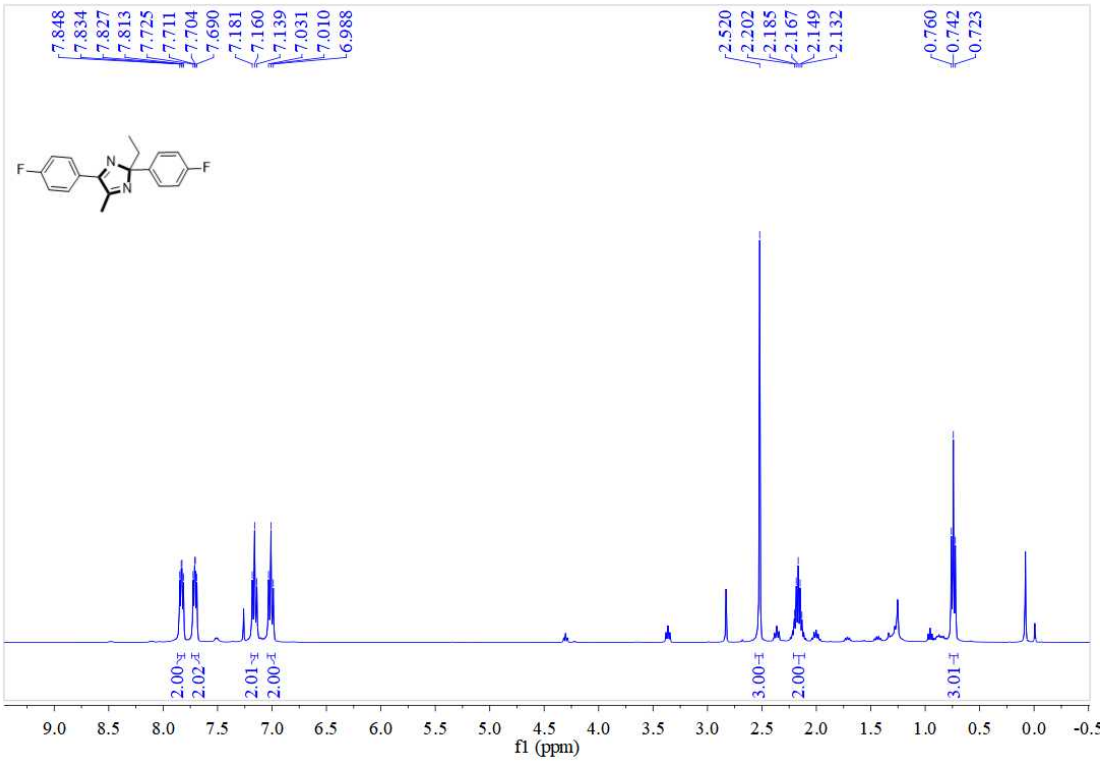


Figure S46 ^{1}H NMR of **3u**

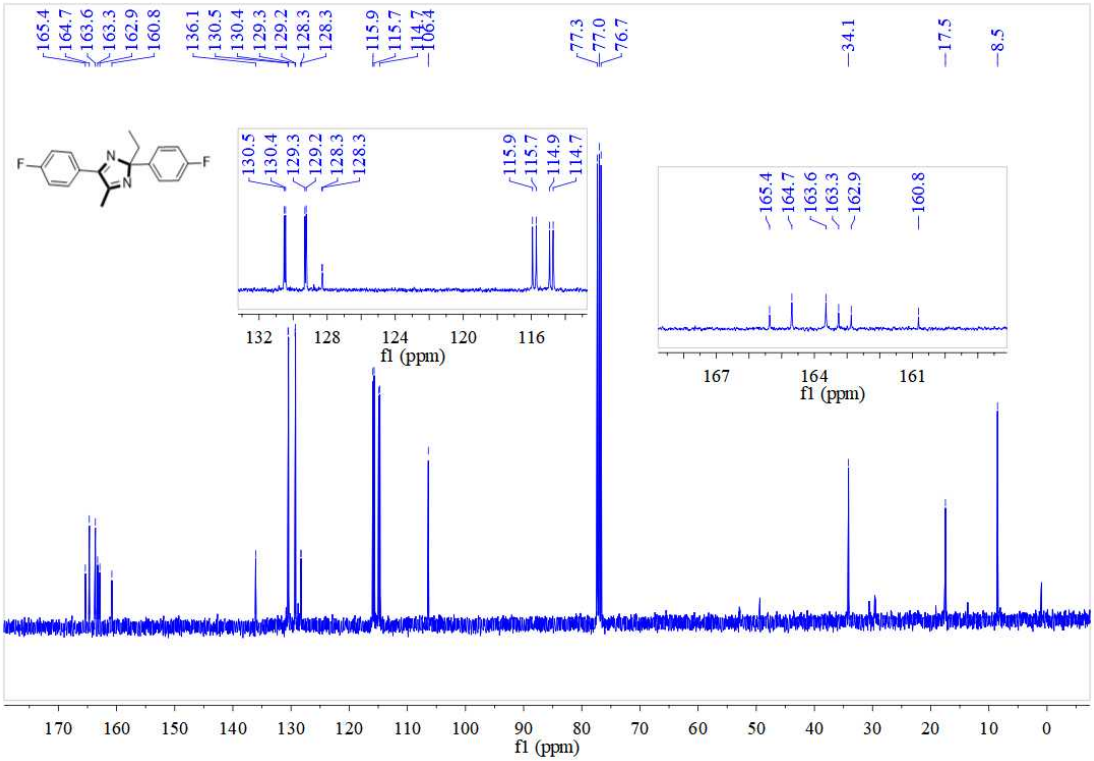


Figure S47 ^{13}C NMR of **3u**

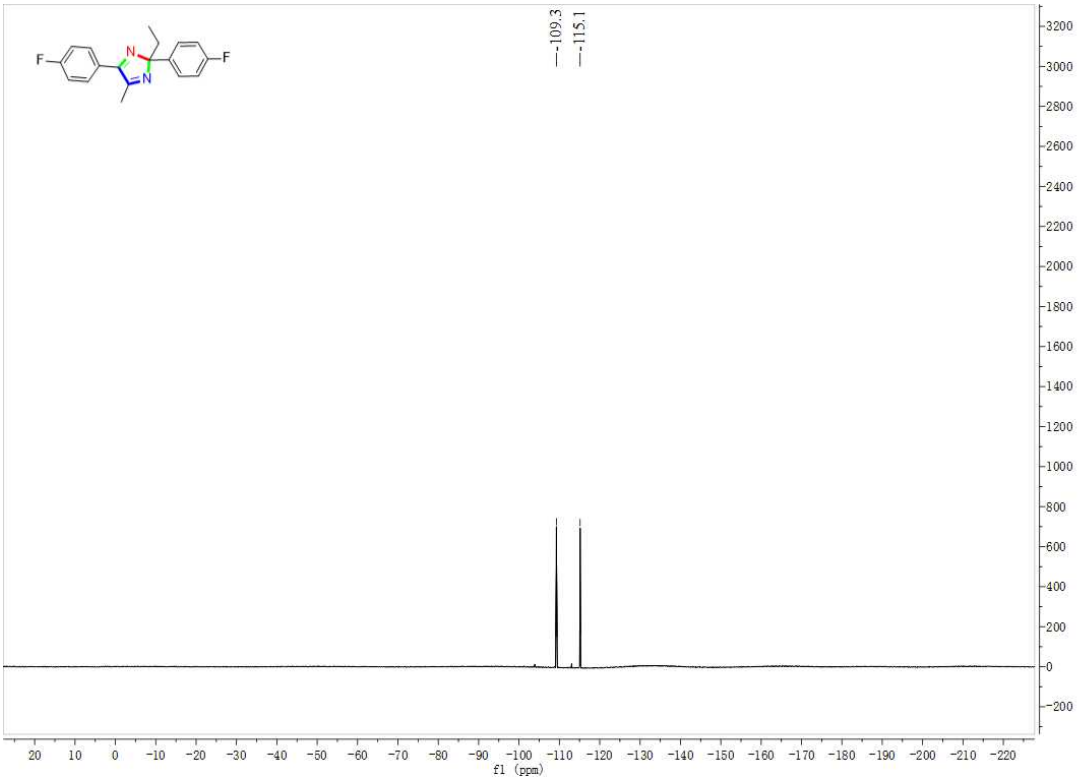


Figure S48 ^{19}F NMR of **3u**

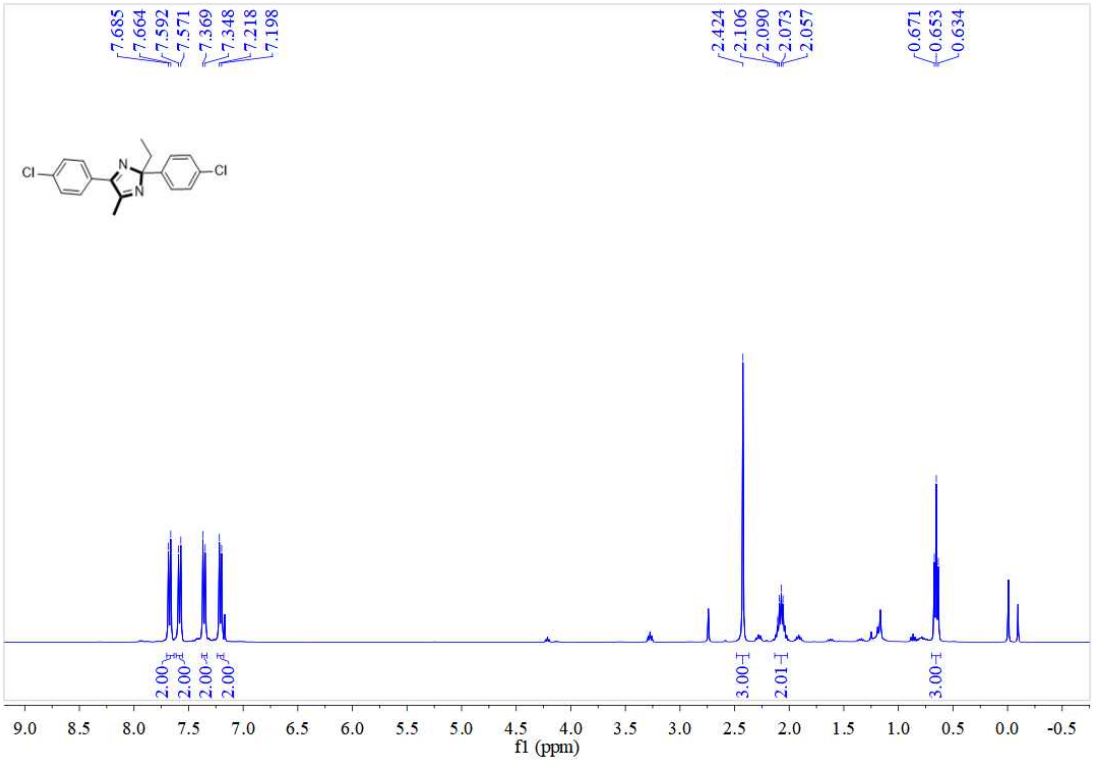


Figure S49 ^{1}H NMR of **3v**

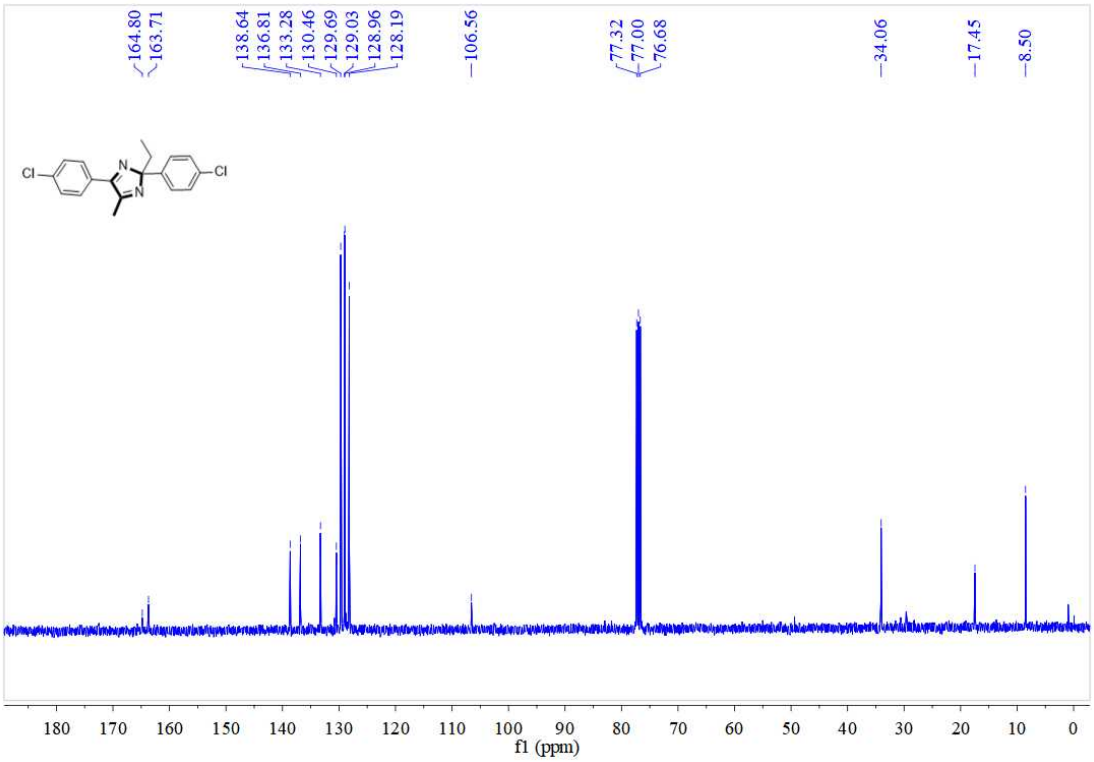


Figure S50 ^{13}C NMR of **3v**

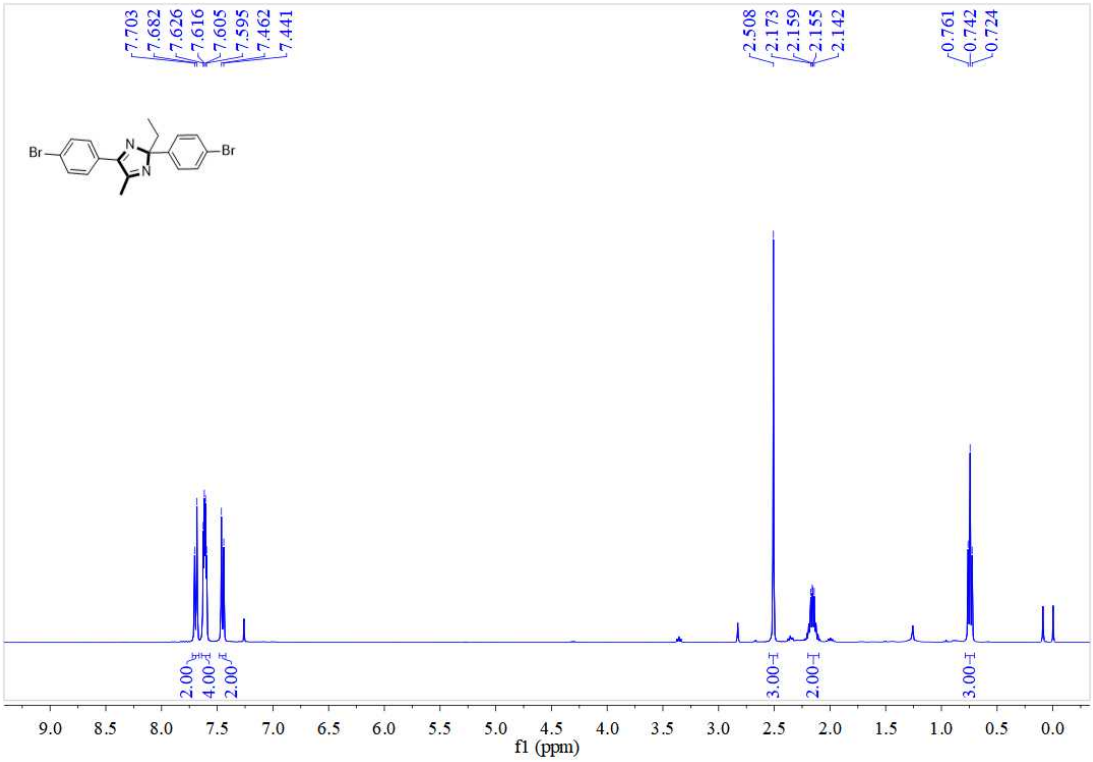


Figure S51 ^{1}H NMR of **3w**

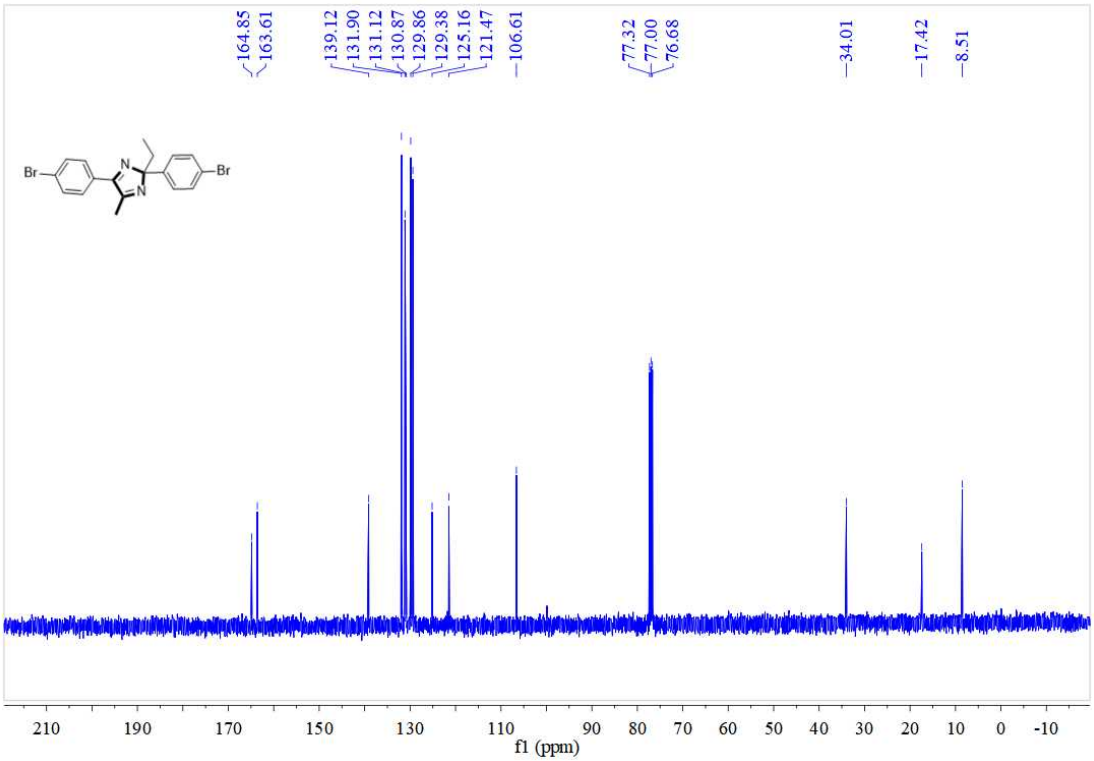


Figure S52 ^{13}C NMR of **3w**

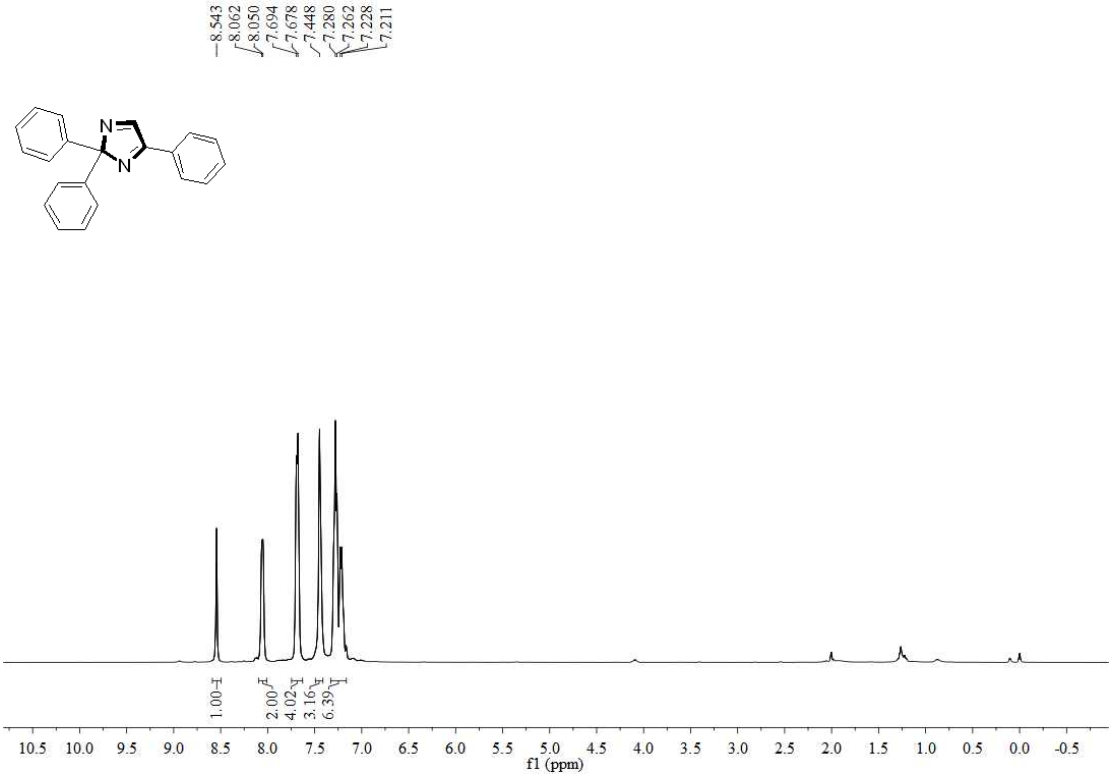


Figure S53 ^{1}H NMR of **4aa**

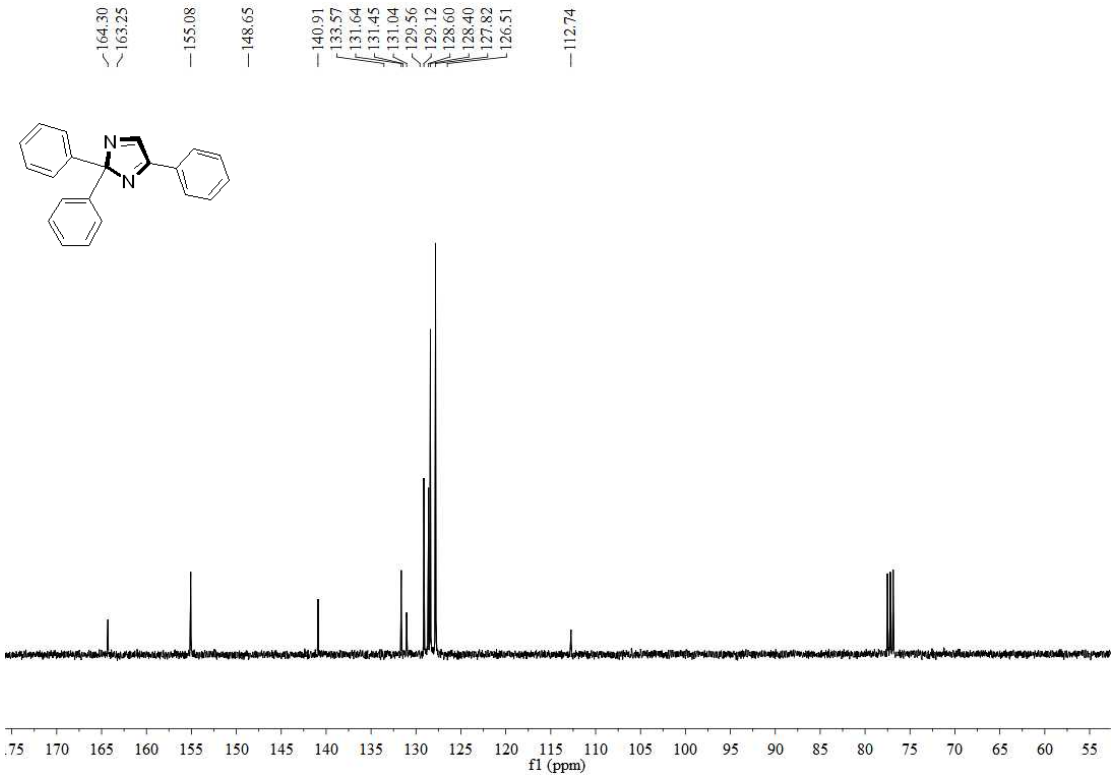


Figure S54 ^{13}C NMR of **4aa**

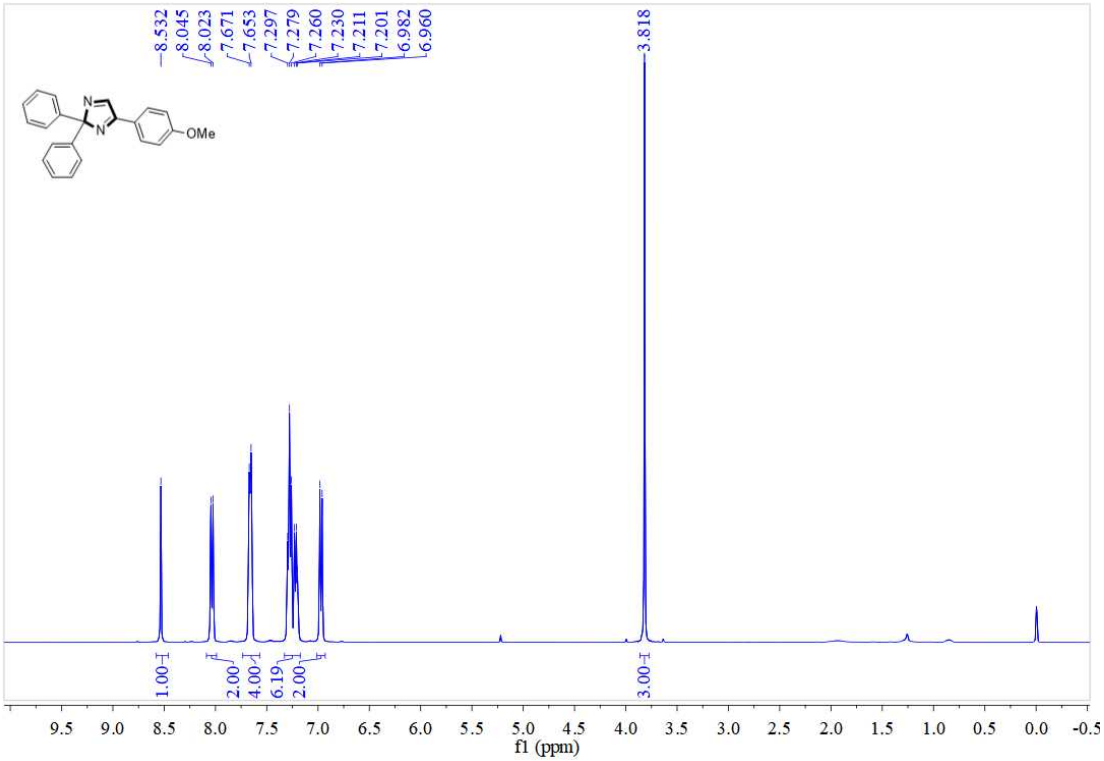


Figure S55 ^{1}H NMR of **4ab**

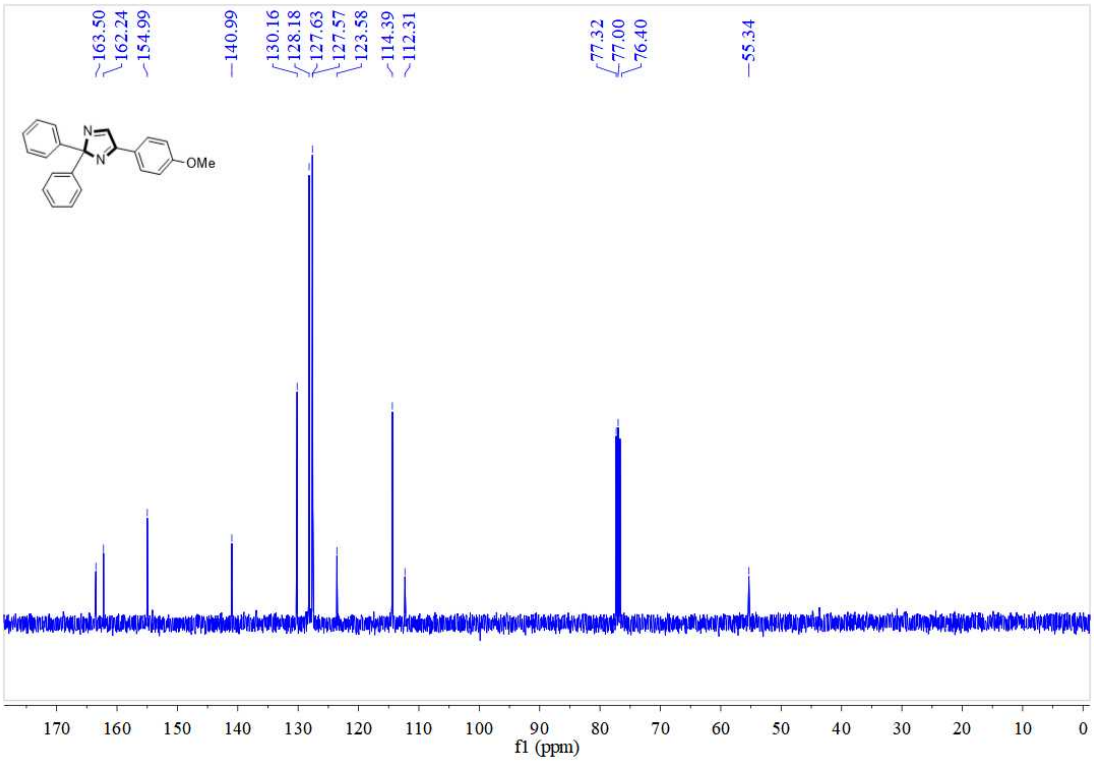


Figure S56 ^{13}C NMR of **4ab**

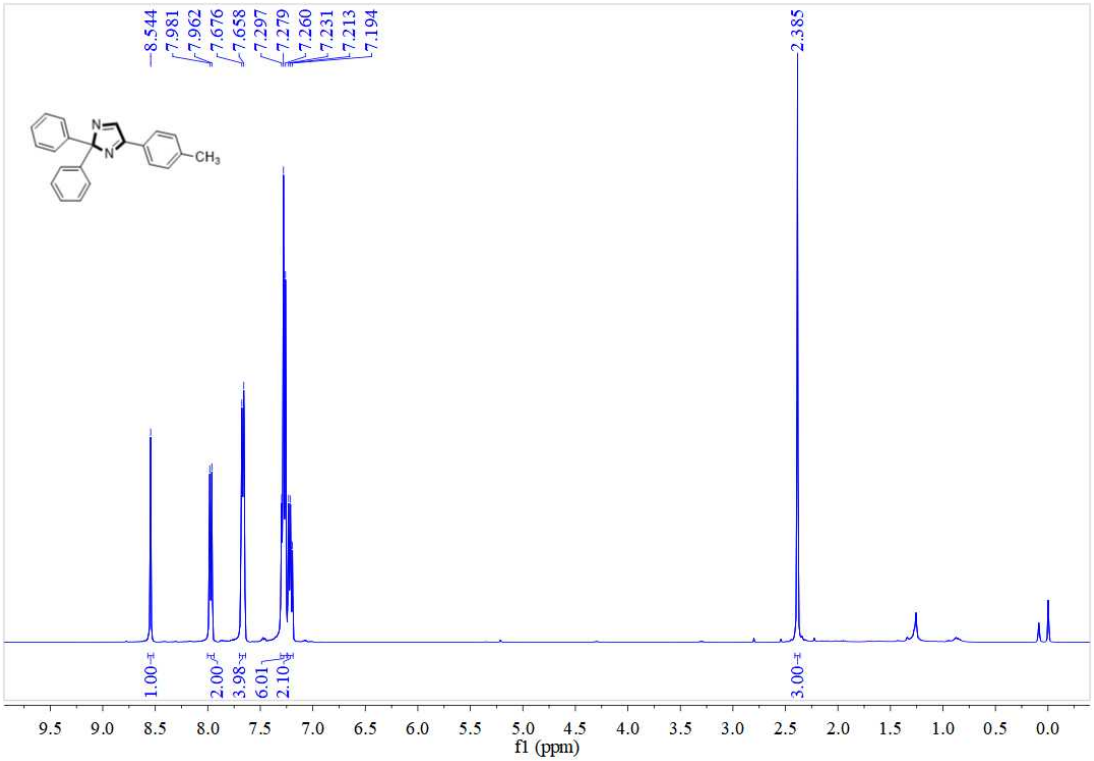


Figure S57 ^{1}H NMR of **4ac**

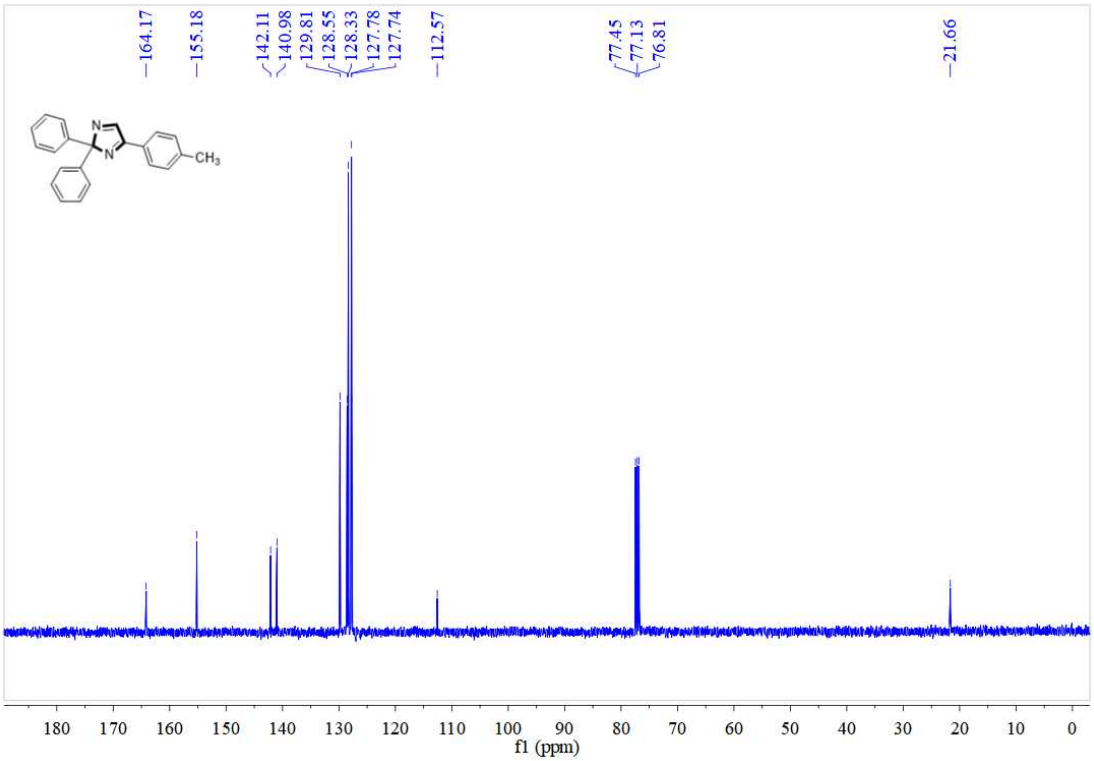


Figure S58 ^{13}C NMR of **4ac**

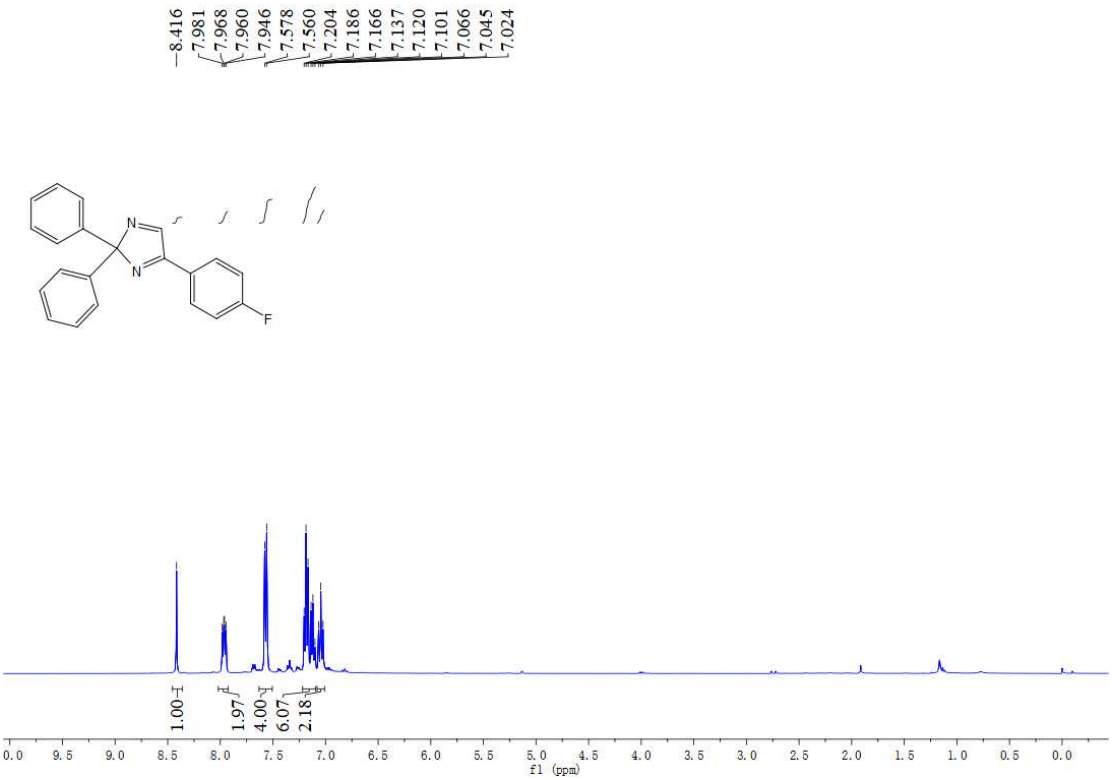


Figure S59 ^{1}H NMR of **4ad**

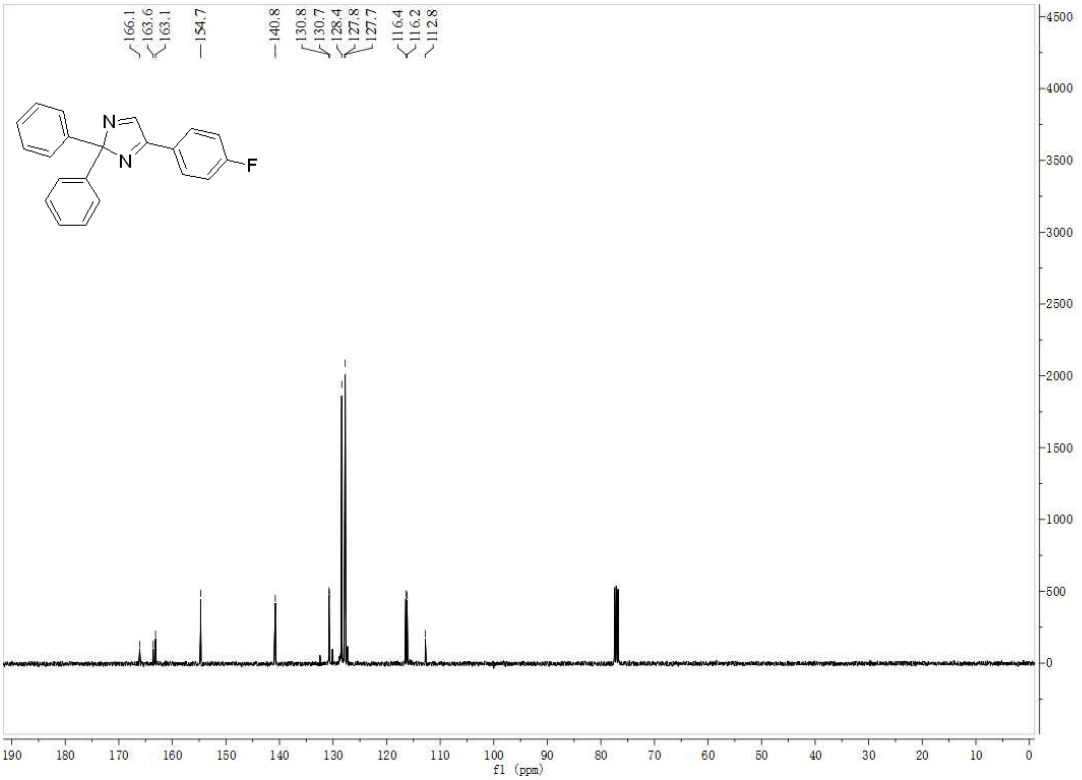


Figure S60 ^{13}C NMR of **4ad**

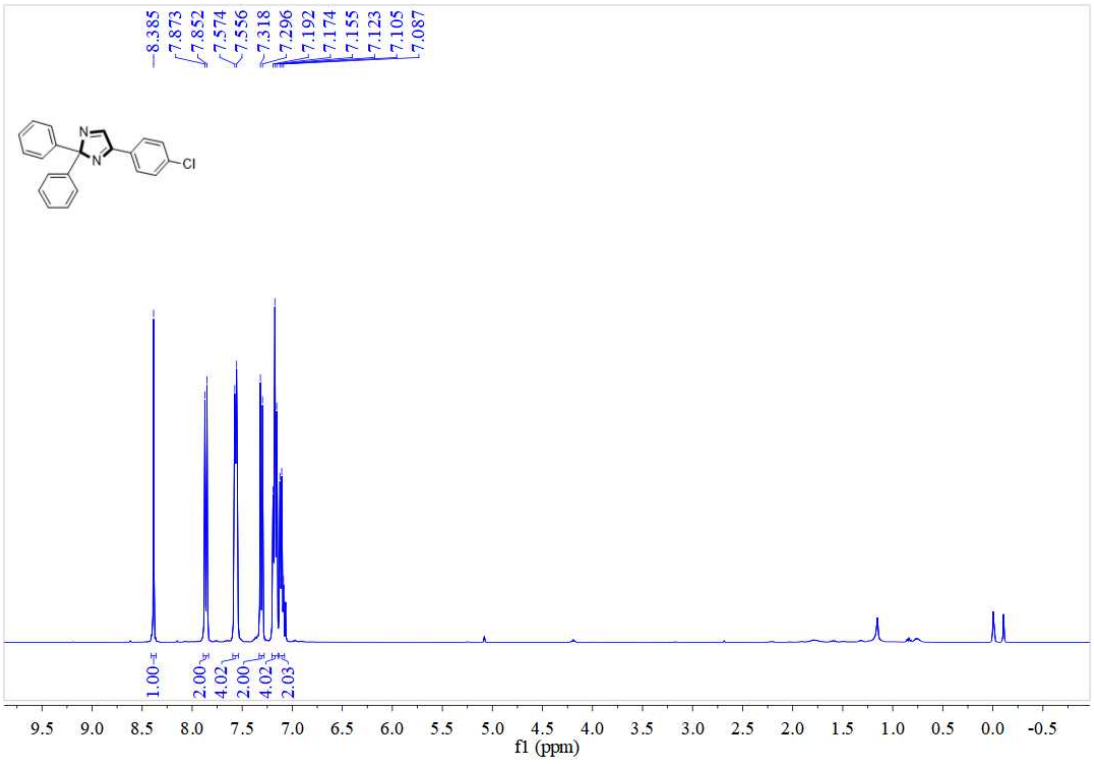


Figure S61 ^{1}H NMR of **4ae**

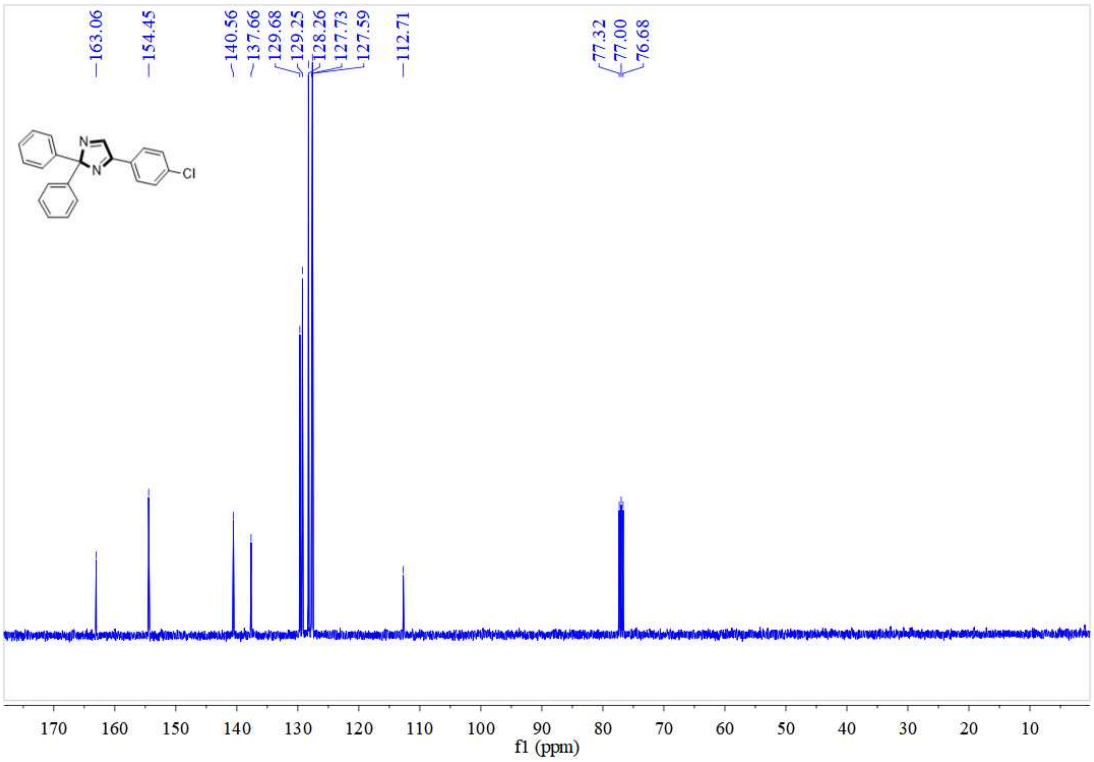


Figure S62 ^{13}C NMR of **4ae**

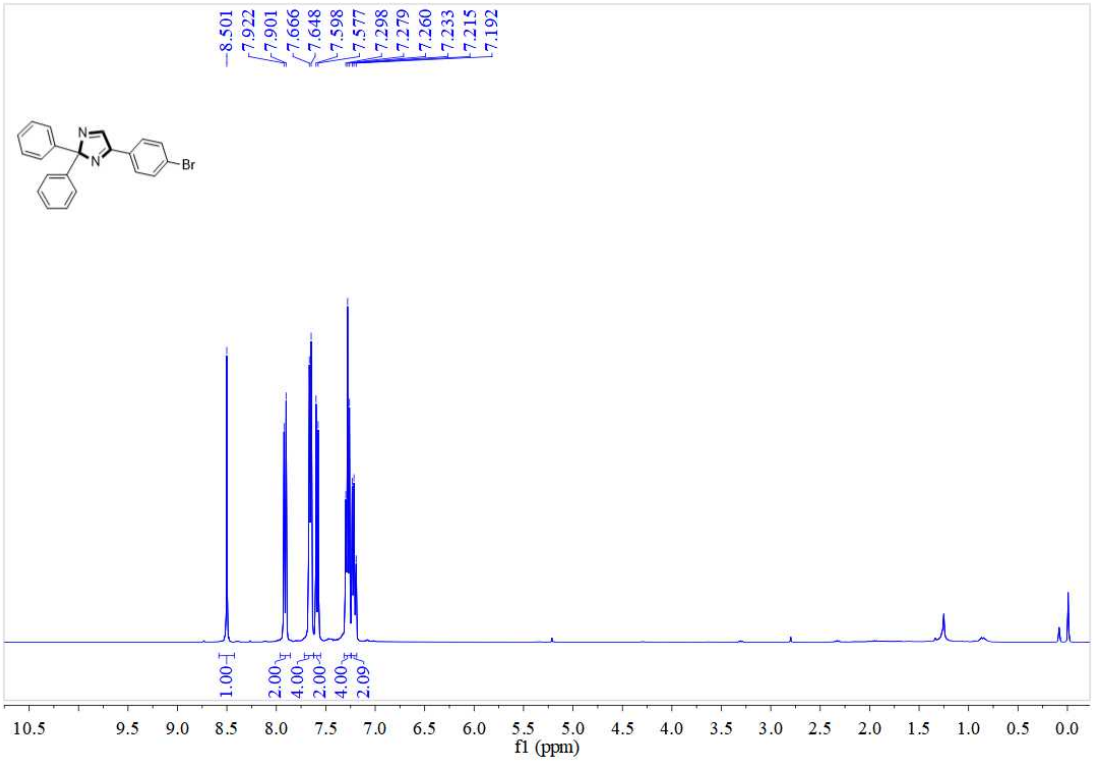


Figure S63 ^{1}H NMR of **4ae**

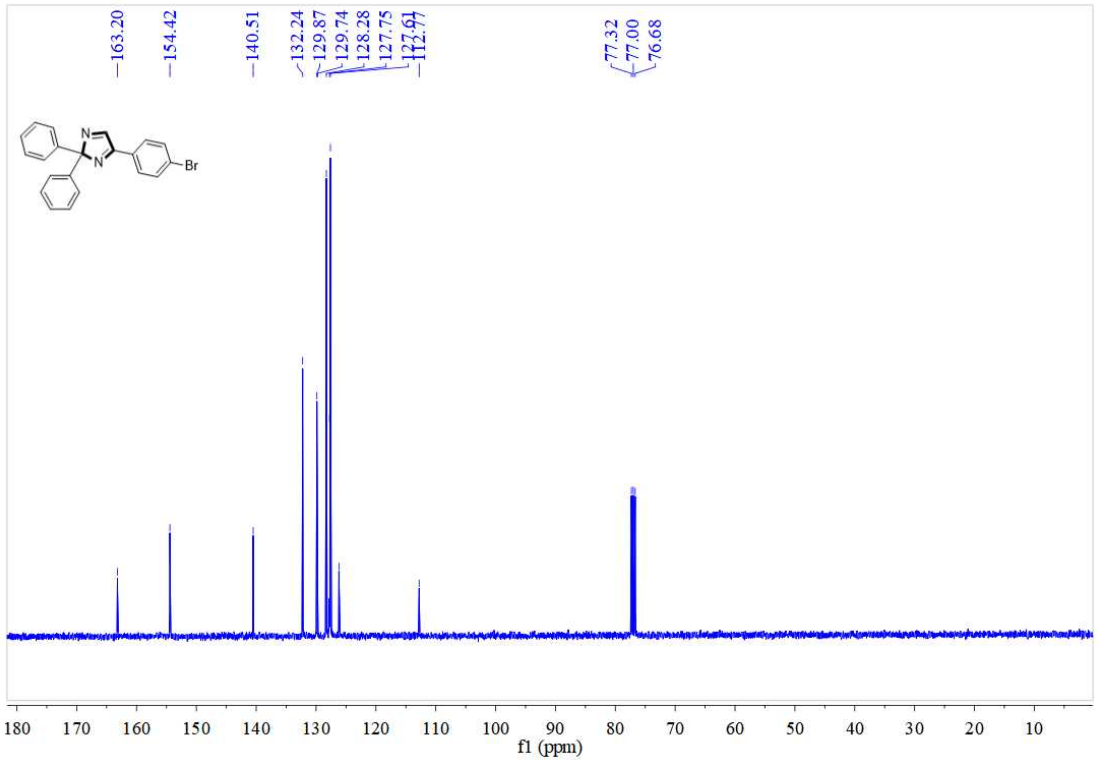


Figure S64 ^{13}C NMR of **4ae**

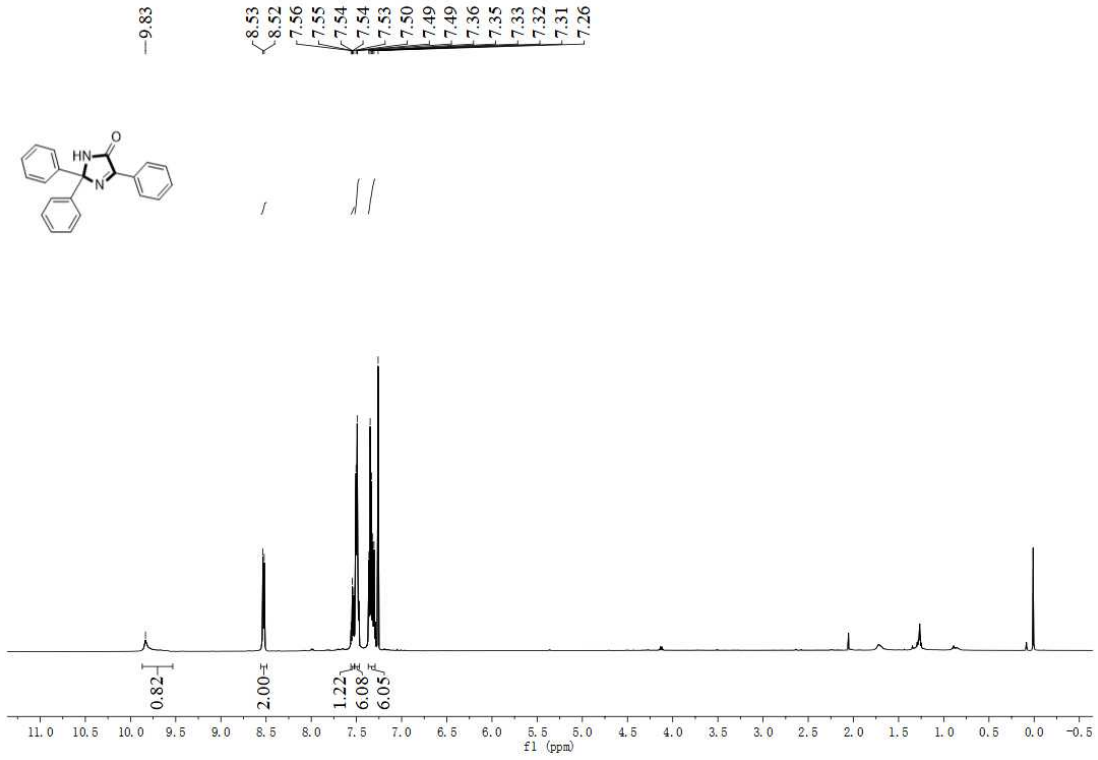


Figure S65 ^{1}H NMR of **5aa**

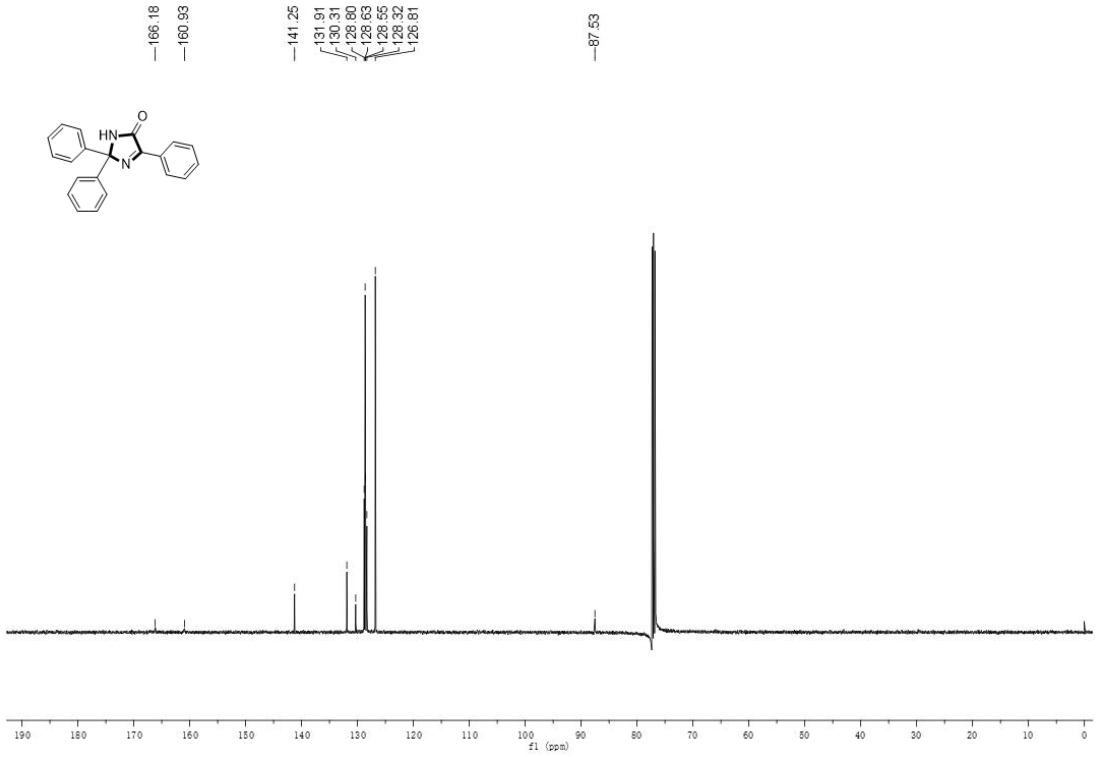


Figure S66 ^{13}C NMR of **5aa**