

Supporting Information

Synthesis of 4-Hydroxy-5-phenylaminoimidazoles Through a Three-component Reaction of Sulfur ylides, Nitrosobenzenes and Amidines

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1. General Information

All reagents and solvents were purchased from commercial source and used directly without further purification. Melting points were recorded on a BüCHI B-540 melting point apparatus. NMR spectra were recorded for ^1H NMR at 400 MHz and for $^{13}\text{C}\{^1\text{H}\}$ NMR at 100 MHz. For ^1H NMR, CDCl_3 , DMSO-D_6 or CD_3OD was served as internal standard ($\delta = 7.26, 2.50$ or 3.31) and data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hz and integration. For $^{13}\text{C}\{^1\text{H}\}$ NMR, CDCl_3 ($\delta = 77.26$) or DMSO-D_6 ($\delta = 33.95$) was served as internal standard and spectra were obtained with complete proton decoupling. HRMS data were obtained on an Agilent 1290 HPLC-6224 Time of Flight Mass Spectrometer. The substrates **1** and **2** were prepared according to the known literature procedures.^{1,2} The reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. Column chromatography was performed on silica gel (200-300 mesh) using a mixture of petroleum ether/ethyl acetate.

2. General procedure for the synthesis of target compound **4**

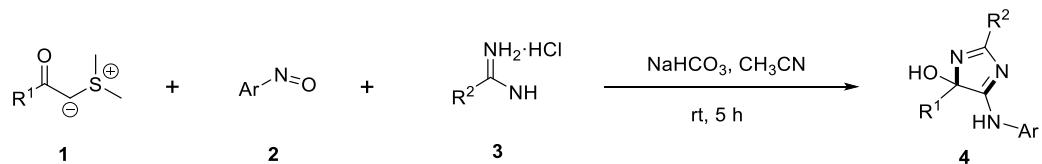


Fig S1. General procedure for the synthesis of target compound **4**

In a 25 mL sealed tube, sulfur ylide (1.0 mmol, 1.0 equiv) and nitrosobenzene (1.0 mmol, 1.0 equiv) were mixed with 5 mL acetonitrile (CH_3CN), the resulting mixture was stirred at r.t. for 10 minutes. Subsequently, amidine hydrochloride (1.5 mmol, 1.5 equiv) and NaHCO_3 (1.5 mmol, 1.5 equiv) were then added to the aforementioned reaction mixture, and the stirring was continued for an additional 5h. Upon completion of the reaction, the mixture was filtrated to afford the crude product as white solid. The crude product was then washed with petroleum ether (10 mL*3) and water (10 mL*3) respectively to afford the desired product **4**.

3. General procedure for the scale-up synthesis of **4a**, further transformations and the synthesis of nitrone intermediate **I**

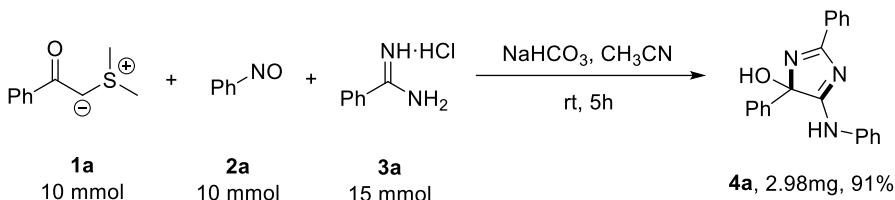


Fig S2. Scale-up synthesis of **4a**

In a 100 mL three-neck flask, sulfur ylide **1a** (10.0 mmol, 1.0 equiv) and nitrosobenzene **2a** (10.0 mmol, 1.0 equiv) were mixed with 50 mL acetonitrile (CH_3CN), the resulting mixture was stirred at r.t. for 10 minutes. Subsequently, amidine hydrochloride **3a** (15.0 mmol, 1.5 equiv) and NaHCO_3 (15.0 mmol, 1.5 equiv) were then added to the aforementioned reaction mixture, and the stirring was continued for an additional 5 hours. Upon completion of the reaction, the mixture was filtrated to afford the crude product as white solid. The crude product was then washed with petroleum ether (30 mL*3) and water (30 mL*3) respectively to afford the desired product **4a**.

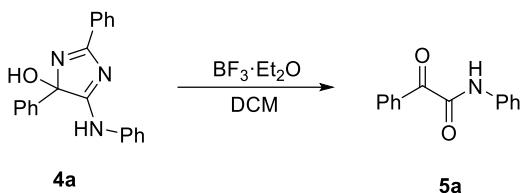


Fig S3. Procedure for the synthesis of **5a**

In a 25 mL sealed tube, 4-hydroxy-5-phenylaminoimidazole **4a** (1.0 mmol, 1.0 equiv) was dissolved in 15 mL dichloromethane (DCM), the resulting solution was cooled to 0 °C. Subsequently, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (15.0 mmol, 15.0 equiv) was then added to the aforementioned reaction mixture dropwise, and the stirring was continued for an additional 0.5 hour at 0 °C, and then 2 hours under room temperature. Upon the completion of the reaction, the reaction was quenched with water and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4 and were concentrated under reduced pressure. The crude product was then purified via column chromatography (silica gel, 200-300 mesh;

petroleum ether/ethyl acetate = 10:1) to afford the desired product **5b-5g**.

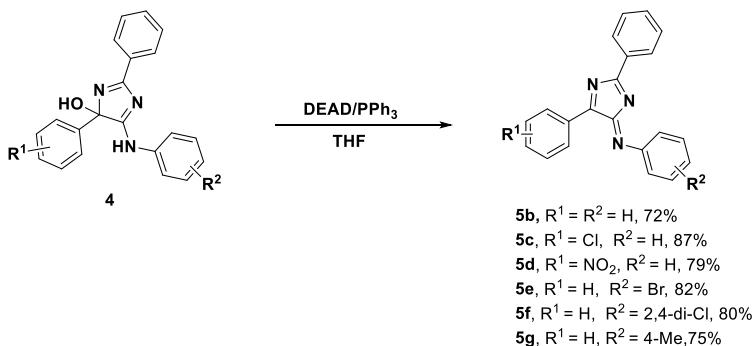


Fig S4. Procedure for the synthesis of **5b-5g**

In a 25 mL sealed tube, 4-hydroxy-5-phenylaminoimidazole **4** (1.0 mmol, 1.0 equiv) was dissolved in 5 mL tetrahydrofuran (THF), PPh_3 (1.2 mmol, 1.2 equiv) was added to the solution. The reaction mixture was stirred at 0 °C. Then, DEAD (1.2 mmol, 1.2 equiv) was added and warmed slowly to room temperature and stirred overnight. The crude mixture was extracted with ethyl acetate (10 mL), washed with saturated brine (5 mL). The organic layer was dried over Na_2SO_4 , filtered and concentrated, the crude product was then purified via column chromatography (silica gel, 200-300 mesh; petroleum ether/ethyl acetate = 10:1) to afford the desired product **5b**.

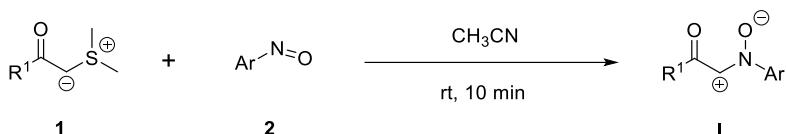


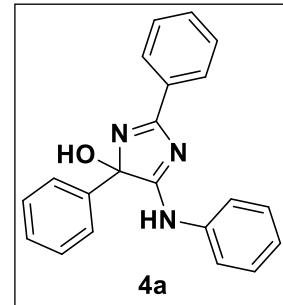
Fig S5. General procedure for the synthesis of nitrone intermediate **I**

In a 25 mL sealed tube, sulfur ylide (1.0 mmol, 1.0 equiv) and nitrosobenzene (1.0 mmol, 1.0 equiv) were mixed with 5 mL acetonitrile (CH_3CN), the resulting mixture was stirred at r.t. for 10 minutes. Upon completion of the reaction, the mixture was concentrated under reduced pressure. The crude product was then purified via column chromatography (silica gel, 200-300 mesh; petroleum ether/ethyl acetate = 4:1) to afford the desired nitrone intermediate **I**.

4. Characterization of compounds 4, 5 and intermediate I

2,4-diphenyl-5-(phenylamino)-4*H*-imidazol-4-ol, (4a)

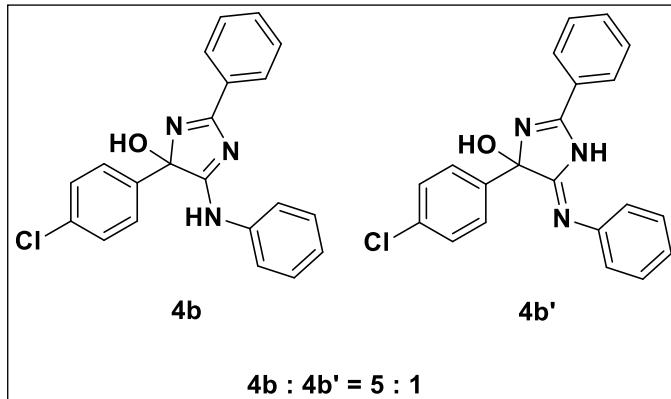
White solid (301 mg, 92%); mp 155.3–155.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.29 (d, *J* = 6.8 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.35 (m, 2H), 7.30 (m, 2H), 7.19 – 7.14 (m, 2H), 7.10 (m, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 181.7, 176.0, 138.5, 138.4, 132.0, 131.4, 129.6, 128.9, 128.6, 128.4, 128.4, 124.8, 124.2, 119.7, 102.4; HRMS calcd for C₂₁H₁₇N₃O+H⁺: 328.1444, found: 328.1442.



4-(4-chlorophenyl)-2-phenyl-5-(phenylamino)-4*H*-imidazol-4-ol, (4b) and (Z)-4-(4-chlorophenyl)-2-phenyl-5-(phenylimino)-4,5-dihydro-1*H*-imidazol-4-ol. (4b')

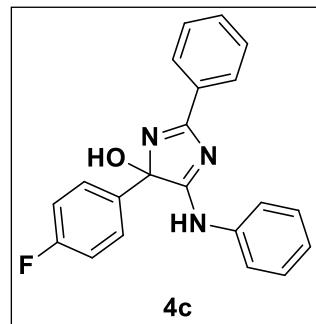
(5:1 ratio)

White solid (332 mg, 92%); mp 151.9–152.3 °C; ¹H NMR (400 MHz, DMSO-D₆): δ 10.21 (s, 1H), 8.26 (d, *J* = 6.7 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.50 (m, 4H), 7.42 (m, 4H), 7.36 (m, 2H), 7.09 (t, *J* = 7.3 Hz, 1H). ¹³C{¹H} NMR (100 MHz, DMSO-D₆): δ 182.8, 173.0, 140.1, 139.2, 133.0, 132.9, 131.9, 129.2, 129.2, 129.0, 128.6, 127.7, 123.9, 120.2, 103.2; HRMS calcd for C₂₁H₁₆ClN₃O+H⁺: 362.1055 and 364.1026, found: 362.1053 and 364.1026.



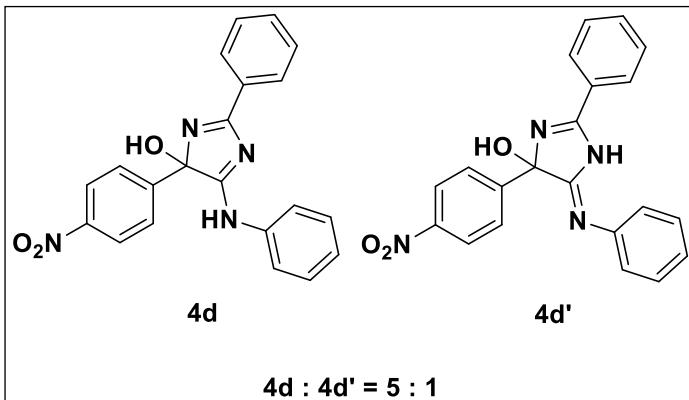
4-(4-fluorophenyl)-2-phenyl-5-(phenylamino)-4*H*-imidazol-4-ol, 4c

White solid (304 mg, 88%); mp 162.4–162.8 °C; ^1H NMR (400 MHz, CD₃OD): δ 8.30 – 8.24 (m, 2H), 7.83 (d, J = 7.9 Hz, 2H), 7.60 – 7.54 (m, 3H), 7.51 (t, J = 7.3 Hz, 2H), 7.37 (t, J = 7.9 Hz, 2H), 7.15 – 7.07 (m, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO-D₆): δ 182.9, 172.8, 162.3 (d, J = 242.3 Hz), 140.2, 136.5, 132.9, 131.9, 129.2, 129.1, 129.0, 127.9 (d, J = 8.3 Hz), 123.9, 120.2, 115.4 (d, J = 21.4 Hz), 103.2; HRMS calcd for C₂₁H₁₆FN₃O+H⁺: 346.1351, found: 346.1363.



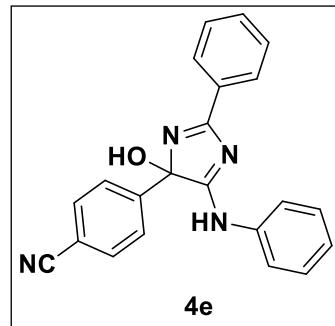
4-(4-nitrophenyl)-2-phenyl-5-(phenylamino)-4*H*-imidazol-4-ol, (4d) and (*Z*)-4-(4-nitrophenyl)-2-phenyl-5-(phenylimino)-4,5-dihydro-1*H*-imidazol-4-ol (4d') (5:1 ratio).

White solid (320 mg, 86%); mp 173.1–173.6 °C; ^1H NMR (400 MHz, DMSO-D₆): δ 10.35 (s, 1H), 8.28 (d, J = 6.8 Hz, 2H), 8.23 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.61 – 7.54 (m, 4H), 7.39 (t, J = 7.9 Hz, 2H), 7.10 (t, J = 7.3 Hz, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO-D₆): δ 182.4, 173.8, 147.6, 147.2, 140.0, 132.6, 132.1, 129.2, 129.0, 127.1, 124.1, 124.0, 120.2, 103.1; HRMS calcd for C₂₁H₁₆N₄O₃+H⁺: 373.1296, found: 373.1291.



4-(4-hydroxy-2-phenyl-5-(phenylamino)-4*H*-imidazol-4-yl)benzonitrile, 4e

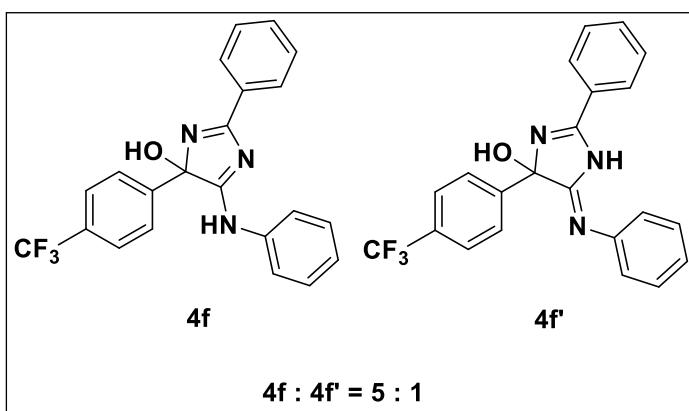
White solid (299 mg, 85%); mp 178.2–179.1 °C; ^1H NMR (400 MHz, CD₃OD): δ 8.27 (d, J = 7.4 Hz, 2H), 7.82 (d, J = 5.0 Hz, 2H), 7.73 (q, J = 8.4 Hz, 4H), 7.59 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.37 (t, J = 7.9 Hz, 2H), 7.13 (t, J = 7.4 Hz, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO-D₆): δ 182.5, 173.7, 145.4, 140.0, 132.8, 132.7, 132.1, 129.3, 129.3, 129.0, 126.7, 124.1, 120.2, 119.2, 111.2, 103.2; HRMS calcd for C₂₂H₁₆N₄O+H⁺: 353.1397, found: 353.1391.



2-phenyl-5-(phenylamino)-4-(4-(trifluoromethyl)phenyl)-4*H*-imidazol-4-ol, (4f)

and (*Z*)-2-phenyl-5-(phenylimino)-4-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-4-ol (4f') (5:1 ratio).

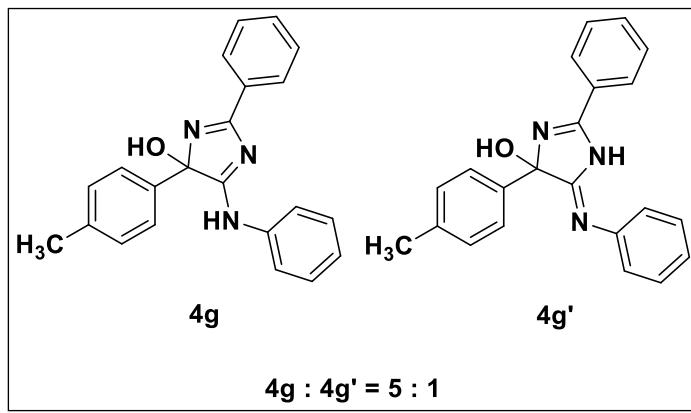
White solid (269 mg, 68%); mp 173.9–174.7 °C; ^1H NMR (400 MHz, DMSO-D₆): δ 10.37 (s, 1H), 9.45 (s, 1H), 8.26 (d, J = 6.8 Hz, 2H), 8.06 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.3



Hz, 2H), 7.58 – 7.52 (m, 3H), 7.39 (t, J = 7.8 Hz, 2H), 7.09 (t, J = 7.3 Hz, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO-D₆): δ 182.7, 173.4, 144.7, 140.1, 132.8, 132.0, 129.2, 129.0, 128.7 (d, J = 22.8 Hz), 127.1, 126.6, 125.7 (d, J = 3.3 Hz), 124.4 (d, J = 210.1 Hz), 124.0, 120.2, 103.2; HRMS calcd for C₂₂H₁₆F₃N₃O+H⁺: 396.1319, found: 396.1314.

2-phenyl-5-(phenylamino)-4-(p-tolyl)-4*H*-imidazol-4-ol, (4g) and (*Z*)-2-phenyl-5-(phenylimino)-4-(p-tolyl)-4,5-dihydro-1*H*-imidazol-4-ol (4g') (5:1 ratio)

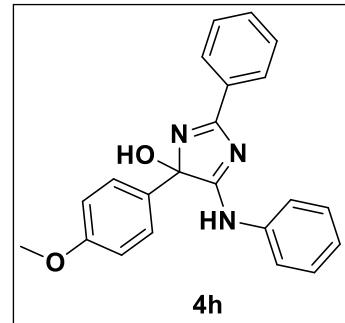
White solid (310 mg, 91%);
mp 167.7-167.9 °C; ^1H NMR
(400 MHz, DMSO- D_6): δ
10.09 (s, 1H), 8.26 (d, $J = 6.3$
Hz, 2H), 8.08 (d, $J = 8.0$ Hz,
2H), 7.55 (t, $J = 7.0$ Hz, 3H),
7.38 (t, $J = 7.8$ Hz, 2H), 7.32



(d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 3H), 7.08 (t, $J = 7.3$ Hz, 1H), 2.27 (s, 3H);
 $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ 183.2, 172.4, 140.3, 137.5, 137.3, 133.1,
131.7, 129.2, 129.1, 129.1, 128.9, 125.6, 123.8, 120.1, 103.6, 21.2.; HRMS calcd for
 $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}+\text{H}^+$: 342.1601, found: 342.1601.

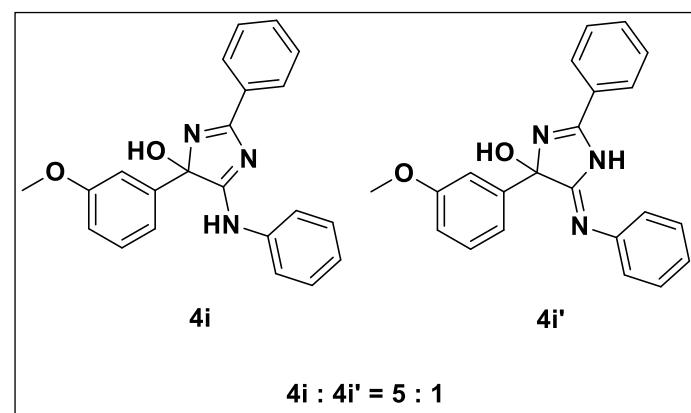
4-(4-methoxyphenyl)-2-phenyl-5-(phenylamino)-4*H*-imidazol-4-ol, **4h**

White solid (275mg, 77%); mp 168.4-169.3 °C; ^1H
NMR (400 MHz, CD₃OD): δ 8.27 (d, $J = 7.2$ Hz, 2H),
7.86 (d, $J = 1.4$ Hz, 2H), 7.57 (t, $J = 7.3$ Hz, 1H), 7.50
(m, 2H), 7.46 (d, $J = 8.7$ Hz, 2H), 7.37 (t, $J = 7.9$ Hz,
2H), 7.12 (t, $J = 7.4$ Hz, 1H), 6.92 (d, $J = 8.8$ Hz, 2H),
4.89 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ
183.2, 172.2, 159.4, 140.3, 133.1, 132.3, 131.7, 129.2, 129.1, 128.9, 127.0, 123.7,
120.1, 113.9, 103.5, 55.5; HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_2+\text{H}^+$: 358.1551, found:
358.1550.



4-(3-methoxyphenyl)-2-phenyl-5-(phenylamino)-4*H*-imidazol-4-ol, (**4i**) and (*Z*)-4-

(3-methoxyphenyl)-2-phenyl-
5-(phenylimino)-4,5-dihydro-
1*H*-imidazol-4-ol (**4i'**) (5:1



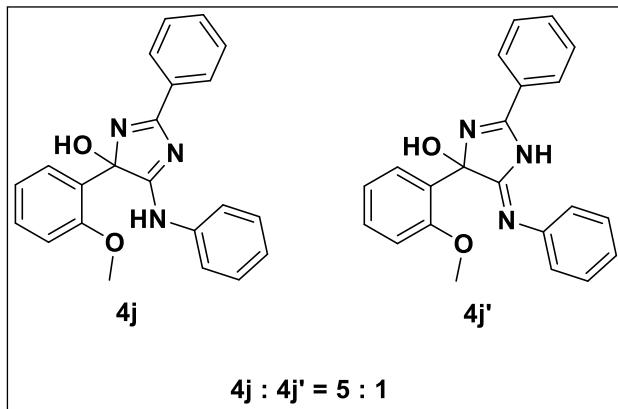
ratio)

White solid (218 mg, 61%); mp 179.9–180.5 °C; ^1H NMR (400 MHz, DMSO- D_6): δ 10.14 (s, 1H), 8.26 (d, J = 6.7 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H), 7.55 – 7.52 (m, 3H), 7.37 (t, J = 7.7 Hz, 2H), 7.23 (d, J = 6.2 Hz, 2H), 7.16 (s, 1H), 7.09 (t, J = 7.3 Hz, 1H), 6.85 (t, J = 9.6 Hz, 2H), 3.75 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ 183.1, 172.8, 159.6, 141.8, 140.2, 133.0, 131.8, 129.7, 129.2, 129.1, 129.0, 123.8, 120.2, 117.7, 113.5, 111.9, 103.5, 55.5; HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_2+\text{H}^+$: 358.1551, found: 358.1548.

4-(2-methoxyphenyl)-2-phenyl-5-(phenylamino)-4*H*-imidazol-4-ol, (4j) and (*Z*)-4-(2-methoxyphenyl)-2-phenyl-5-(phenylimino)-4,5-dihydro-1*H*-imidazol-4-ol (4j')

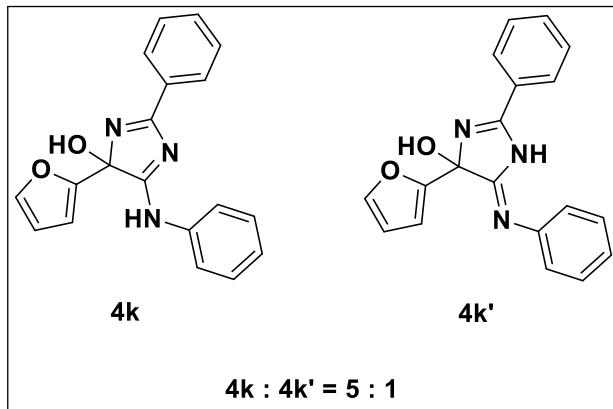
(5:1 ratio)

White solid (254 mg, 71%); mp 163.7–164.7 °C; ^1H NMR (400 MHz, DMSO- D_6): δ 10.13 (s, 1H), 8.28 – 8.24 (m, 2H), 8.07 (d, J = 7.9 Hz, 2H), 7.59 – 7.55 (m, 2H), 7.54 (s, 1H), 7.38 (t, J = 7.9 Hz, 2H), 7.23 (d, J = 5.4 Hz, 2H), 7.15 (d, J = 1.7 Hz, 1H), 7.08 (t, J = 7.3 Hz, 1H), 6.87 (m, 1H), 6.83 (d, J = 7.9 Hz, 1H), 3.75 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ 183.0, 172.8, 159.6, 141.8, 140.2, 133.0, 131.8, 129.7, 129.2, 129.1, 129.0, 123.8, 120.1, 117.6, 113.5, 111.9, 103.5, 55.5; HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_2+\text{H}^+$: 358.1551, found: 358.1556.



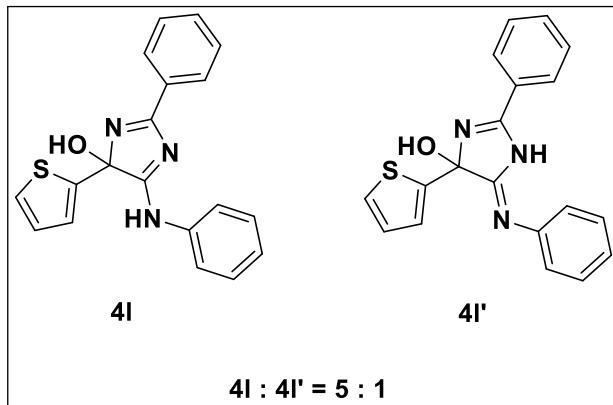
4-(furan-2-yl)-2-phenyl-5-(phenylamino)-4*H*-imidazol-4-ol, (4k) and (*Z*)-4-(furan-2-yl)-2-phenyl-5-(phenylimino)-4,5-dihydro-1*H*-imidazol-4-ol (4k') (5:1 ratio)

White solid (260 mg, 82%); mp 188.1–188.6 °C; ^1H NMR (400 MHz, DMSO- D_6): δ 10.42 (s, 1H), 8.24 (d, J = 7.2 Hz, 2H), 8.11 (d, J = 8.2 Hz, 2H), 7.61 (s, 1H), 7.55 (m, 3H), 7.40 (t, J = 7.9 Hz, 2H), 7.36 (s, 1H), 7.11 (t, J = 7.4 Hz, 1H), 6.46 (m, 2H).; $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ 180.8, 173.5, 152.8, 143.3, 140.1, 132.9, 131.9, 129.2, 129.2, 129.0, 124.0, 120.2, 110.9, 108.0, 100.1; HRMS calcd for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_2+\text{H}^+$: 318.1238, found: 318.1237.



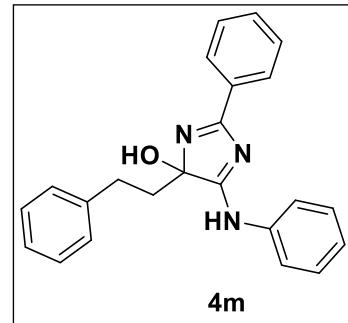
2-phenyl-5-(phenylamino)-4-(thiophen-2-yl)-4H-imidazol-4-ol, (4l) and (*Z*)-2-phenyl-5-(phenylimino)-4-(thiophen-2-yl)-4,5-dihydro-1*H*-imidazol-4-ol (4l') (5:1 ratio)

White solid (270 mg, 81%); mp 166.6–167.1 °C; ^1H NMR (400 MHz, DMSO- D_6): δ 10.45 (s, 1H), 8.29 – 8.21 (m, 2H), 8.12 (d, J = 8.0 Hz, 2H), 7.58 – 7.52 (m, 3H), 7.48 – 7.43 (m, 2H), 7.41 (t, J = 7.9 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.11 (t, J = 7.4 Hz, 1H), 6.99 (m, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ 181.8, 172.8, 144.9, 140.2, 132.9, 131.9, 129.2, 129.1, 129.0, 127.2, 126.3, 125.0, 124.0, 120.3, 101.6; HRMS calcd for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{OS}+\text{H}^+$: 334.1009, found: 334.1009.



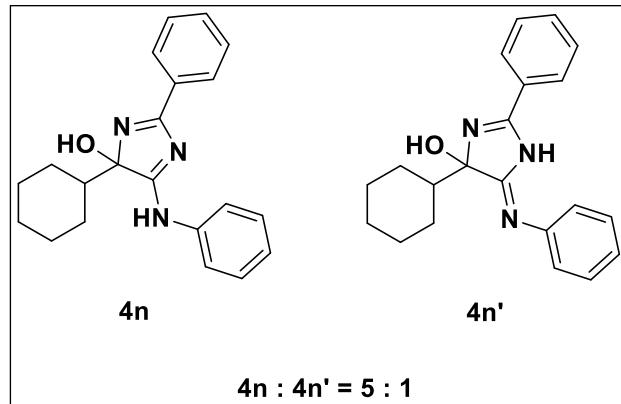
4-phenethyl-2-phenyl-5-(phenylamino)-4H-imidazol-4-ol, 4m

White solid (330 mg, 93%); mp 172.2–173.2 °C; ^1H NMR (400 MHz, DMSO- D_6): δ 10.32 (s, 1H), 8.31 – 8.23 (m, 2H), 8.09 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 6.5 Hz, 3H), 7.40 (t, J = 7.8 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.13 (d, J = 7.1 Hz, 3H), 7.09 (d, J = 7.3 Hz, 1H), 6.57 (s, 1H), 2.58 (dd, J = 18.8, 6.5 Hz, 1H), 2.45 – 2.31 (m, 2H), 2.06 (dd, J = 18.3, 6.3 Hz, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ 182.5, 171.9, 142.0, 140.4, 133.3, 131.5, 129.2, 129.0, 128.8, 128.7, 128.5, 126.1, 123.7, 120.0, 103.0, 39.6, 29.6.; HRMS calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}+\text{H}^+$: 356.1758, found: 356.1753.



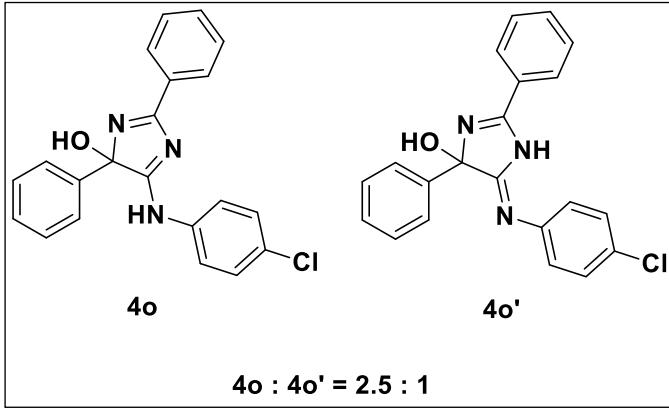
4-cyclohexyl-2-phenyl-5-(phenylamino)-4*H*-imidazol-4-ol, (4n) and (Z)-4-cyclohexyl-2-phenyl-5-(phenylimino)-4,5-dihydro-1*H*-imidazol-4-ol (4n') (5:1 ratio)

White solid (317 mg, 95%); mp 160.2–160.9 °C; ^1H NMR (400 MHz, DMSO- D_6): δ 10.14 (s, 1H), 8.25 – 8.18 (m, 2H), 8.08 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 6.6 Hz, 3H), 7.38 (t, J = 7.8 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 6.31 (s, 1H), 2.30 (d, J = 12.6 Hz, 1H), 1.93 (t, J = 11.6 Hz, 1H), 1.80 (d, J = 12.2 Hz, 1H), 1.61 – 1.52 (m, 2H), 1.41 (td, J = 13.0, 2.6 Hz, 1H), 1.20 (d, J = 12.6 Hz, 1H), 1.08 (t, J = 13.2 Hz, 3H), 0.72 – 0.56 (m, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ 183.3, 172.0, 140.4, 133.4, 131.4, 129.2, 129.0, 128.8, 123.5, 119.9, 105.2, 44.8, 27.2, 26.5, 26.5, 25.9, 25.7; HRMS calcd for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}+\text{H}^+$: 334.1914, found: 334.1910.



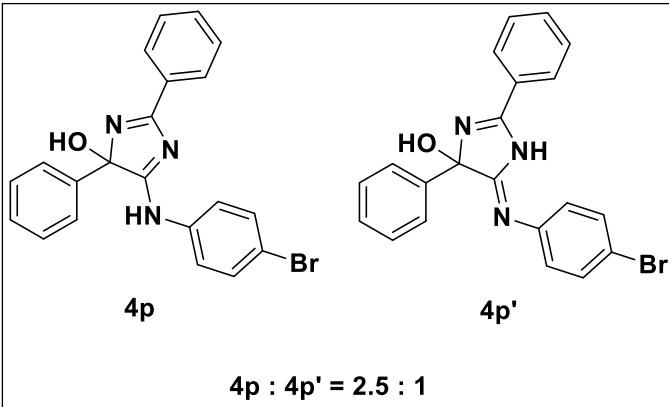
5-((4-chlorophenyl)amino)-2,4-diphenyl-4*H*-imidazol-4-ol, (4o) and (Z)-5-((4-chlorophenyl)imino)-2,4-diphenyl-4,5-dihydro-1*H*-imidazol-4-ol (4o') (2.5:1 ratio)

White solid (271 mg, 75%); mp 167.5–168.1 °C; ^1H NMR (400 MHz, CD₃OD): δ 8.26 (d, $J = 7.4$ Hz, 2H), 7.82 (s, 1H), 7.80 (d, $J = 1.3$ Hz, 2H), 7.75 (t, $J = 7.5$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 2H), 7.55 – 7.53 (m, 2H), 7.52 (s, 1H), 7.38 (s, 1H), 7.36 (s, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO-D₆): δ 183.1, 172.3, 140.0, 139.2, 132.9, 131.9, 129.1, 129.0, 128.7, 128.5, 126.1, 125.9, 125.7, 121.8, 103.8; HRMS calcd for C₂₁H₁₆ClN₃O+H⁺: 362.1055 and 354.1026, found: 362.1055 and 354.1025.



5-((4-bromophenyl)amino)-2,4-diphenyl-4H-imidazol-4-ol, (4p) and (Z)-5-((4-bromophenyl)imino)-2,4-diphenyl-4,5-dihydro-1H-imidazol-4-ol (4p') (2.5:1 ratio)

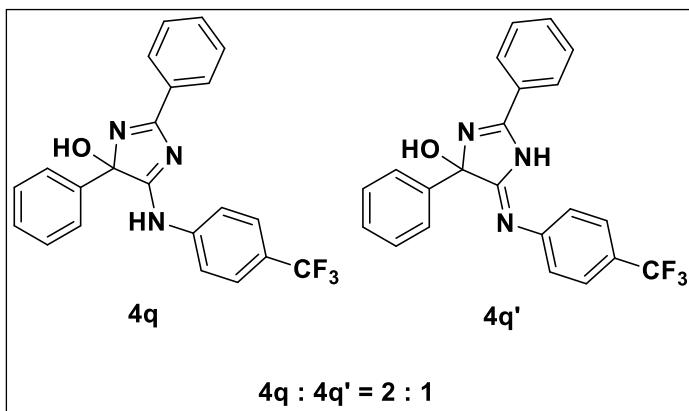
White solid (300 mg, 74%); mp 182.6–183.1 °C; ^1H NMR (400 MHz, CD₃OD): δ 8.28 – 8.23 (m, 2H), 7.76 (m, 2H), 7.59 (t, $J = 6.7$ Hz, 1H), 7.55 (s, 1H), 7.54 – 7.52 (m, 2H), 7.51 (d, $J = 4.2$ Hz, 2H), 7.48 (s, 1H), 7.39 (d, $J = 7.0$ Hz, 1H), 7.36 (s, 1H), 7.33 (d, $J = 2.6$ Hz, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO-D₆): δ 183.2, 172.3, 139.9, 139.6, 132.0, 131.4, 129.1, 129.0, 128.7, 128.5, 126.3, 125.7, 122.2, 115.7, 103.8; HRMS calcd for C₂₁H₁₆BrN₃O+H⁺: 406.0550 and 408.0530, found: 406.0445 and 408.0429.



2,4-diphenyl-5-((4-(trifluoromethyl)phenyl)amino)-4H-imidazol-4-ol, (4q) and (Z)-2,4-diphenyl-5-((4-(trifluoromethyl)phenyl)imino)-4,5-dihydro-1H-imidazol-

4-ol (4q') (2:1 ratio)

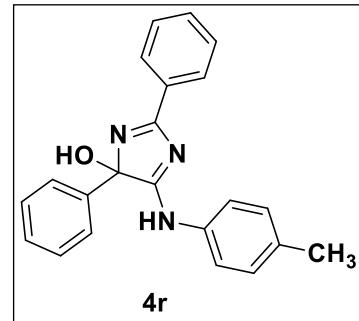
White solid (300 mg, 76%);
mp 166.7–167.7 °C; ^1H NMR (400 MHz, DMSO- D_6): δ 10.52 (s, 1H), 8.28 (s, 2H), 7.76 (d, J = 8.7 Hz, 2H), 7.59 (s, 1H), 7.57 (d, J = 3.0 Hz, 2H), 7.52 (s, 1H), 7.43 (d, J =



6.9 Hz, 2H), 7.35 (s, 2H), 7.32 (s, 2H), 7.31 (s, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ 183.5, 172.2, 143.6, 139.7, 132.7, 132.0, 129.3, 129.2, 129.1, 129.0, 128.7 (d, J = 18.4 Hz), 126.6 (d, J = 3.5 Hz), 125.7, 125.0 (d, J = 207.7 Hz), 120.3, 104.0; HRMS calcd for C₂₂H₁₆F₃N₃O+H⁺: 396.1319, found: 396.1318.

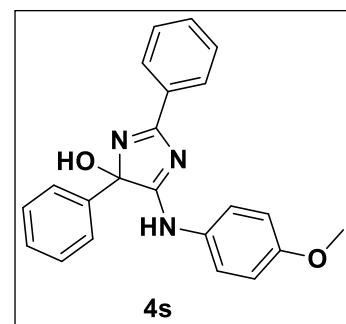
2,4-diphenyl-5-(*p*-tolylamino)-4*H*-imidazol-4-ol, 4r

White solid (229 mg, 67%); mp 154.7–155.4 °C; ^1H NMR (400 MHz, DMSO- D_6): δ 10.03 (s, 1H), 8.25 (d, J = 6.4 Hz, 2H), 7.95 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 7.0 Hz, 4H), 7.43 (d, J = 7.0 Hz, 2H), 7.38 – 7.26 (m, 4H), 7.22 – 7.11 (m, 4H), 2.28 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ 182.9, 172.7, 140.4, 137.8, 133.2, 132.8, 131.7, 129.6, 129.1, 128.9, 128.6, 128.3, 125.7, 120.2, 103.5, 20.9; HRMS calcd for C₂₂H₁₉N₃O+H⁺: 342.1601, found: 342.1578.



5-((4-methoxyphenyl)amino)-2,4-diphenyl-4*H*-imidazol-4-ol, 4s

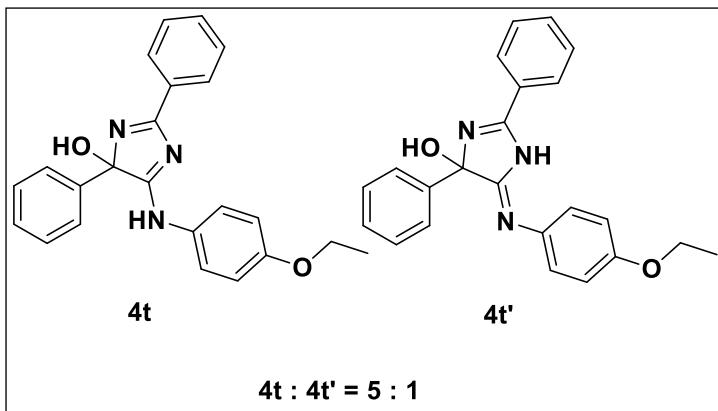
White solid (232 mg, 65%); mp 170.7–171.3 °C; ^1H NMR (400 MHz, DMSO- D_6): δ 10.06 (s, 1H), 8.24 (d, J = 6.5 Hz, 2H), 8.00 (d, J = 0.6 Hz, 2H), 7.54 (d, J = 6.6 Hz, 3H), 7.44 (d, J = 5.6 Hz, 2H), 7.35 (t, J = 7.3 Hz, 2H), 7.30 (d, J = 7.0 Hz, 1H), 7.17 (s, 1H), 6.95 (d, J = 5.7 Hz,



2H), 3.74 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ 182.7, 172.8, 155.8, 140.6, 133.7, 133.3, 131.7, 129.1, 128.9, 128.6, 128.3, 125.7, 121.6, 114.4, 103.4, 55.7; HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_2+\text{H}^+$: 358.1551, found: 358.1559.

5-((4-ethoxyphenyl)amino)-2,4-diphenyl-4*H*-imidazol-4-ol, (4t**) and (*Z*)-5-((4-ethoxyphenyl)imino)-2,4-diphenyl-4,5-dihydro-1*H*-imidazol-4-ol (**4t'**) (5:1 ratio)**

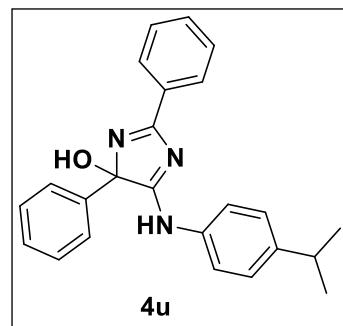
White solid (219 mg, 59%); mp 162.3–163.1 °C; ^1H NMR (400 MHz, DMSO- D_6): δ 8.26 (d, $J = 7.4$ Hz, 2H), 7.75 (d, $J = 7.9$ Hz, 2H), 7.60 – 7.54 (m, 2H), 7.53 (d, $J = 3.9$ Hz, 2H),



7.49 (d, $J = 7.0$ Hz, 1H), 7.38 (t, $J = 7.3$ Hz, 2H), 7.34 – 7.30 (m, 1H), 6.92 (d, $J = 9.0$ Hz, 2H), 4.03 (q, $J = 7.0$ Hz, 2H), 1.38 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO): δ 182.6, 172.8, 155.0, 140.6, 133.5, 133.3, 131.6, 129.1, 128.9, 128.6, 128.3, 125.7, 121.5, 114.8, 103.4, 63.6, 15.1; HRMS calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_2+\text{H}^+$: 372.1707, found: 372.1704.

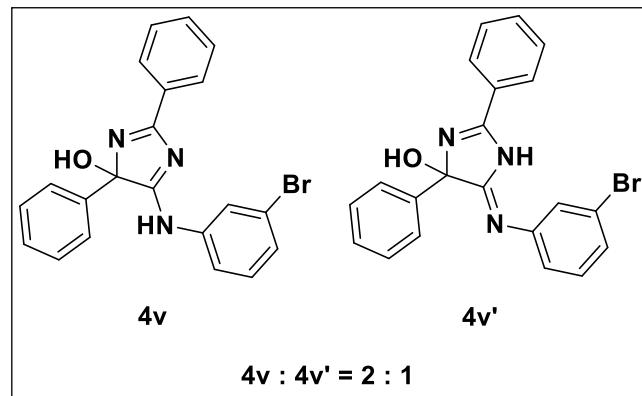
5-((4-isopropylphenyl)amino)-2,4-diphenyl-4*H*-imidazol-4-ol, **4u**

White solid (288 mg, 78%); mp 174.4–174.7 °C; ^1H NMR (400 MHz, DMSO- D_6): δ 10.06 (s, 1H), 8.25 (d, $J = 6.4$ Hz, 2H), 7.97 (d, $J = 7.8$ Hz, 2H), 7.54 (d, $J = 7.1$ Hz, 3H), 7.43 (d, $J = 7.0$ Hz, 2H), 7.36 – 7.29 (m, 3H), 7.28 – 7.22 (m, 2H), 7.16 (s, 1H), 2.86 (dt, $J = 13.7, 6.9$ Hz, 1H), 1.20 (s, 3H), 1.19 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO- D_6): δ 182.9, 172.7, 143.9, 140.5, 138.1, 133.2, 131.7, 129.1, 128.9, 128.5, 128.3, 126.9, 125.7, 120.3, 103.5, 33.3, 24.4; HRMS calcd for $\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}+\text{H}^+$: 370.1914, found: 370.1907.



5-((3-bromophenyl)amino)-2,4-diphenyl-4*H*-imidazol-4-ol, (4v**) and (*Z*)-5-((3-bromophenyl)imino)-2,4-diphenyl-4,5-dihydro-1*H*-imidazol-4-ol (**4v'**) (2:1 ratio)**

White solid (219 mg, 54%); mp 164.9–165.9 °C; ¹H NMR (400 MHz, DMSO-_D6): δ 10.28 (s, 1H), 8.40 (s, 1H), 8.24 (d, *J* = 6.6 Hz, 2H), 8.15 (d, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 3H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 3H), 7.25 (d, *J* = 3.3 Hz, 2H); ¹³C{¹H} NMR (100 MHz, DMSO-_D6): δ 183.3, 172.2, 141.7, 139.8, 131.9, 131.2, 129.3, 129.0, 128.7, 128.5, 126.4, 126.1, 125.7, 122.6, 122.0, 119.0, 103.9; HRMS calcd for C₂₁H₁₆BrN₃O+H⁺: 406.0550 and 408.0530, found: 406.0557 and 408.0537.

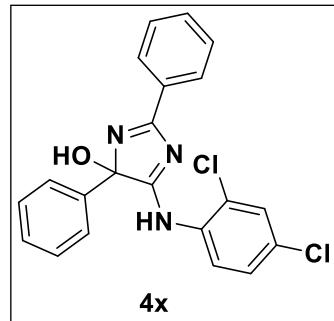


N-(2-chlorophenyl)-2-(4-chlorophenyl)-2-oxoethanethioamide, (4w**) and (*Z*)-2,4-diphenyl-5-(*m*-tolylimino)-4,5-dihydro-1*H*-imidazol-4-ol (**4w'**) (5:1 ratio)**

White solid (205 mg, 60%); mp 165.3–166.1 °C; ¹H NMR (400 MHz, DMSO-_D6): δ 10.02 (s, 1H), 8.27 – 8.22 (m, 2H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.85 (s, 1H), 7.56 (d, *J* = 6.8 Hz, 2H), 7.53 (s, 1H), 7.44 – 7.40 (m, 2H), 7.33 (m, 3H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.17 (s, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 2.32 (s, 3H); ¹³C{¹H} NMR (100 MHz, DMSO-_D6): δ 183.1, 172.6, 140.3, 140.2, 138.3, 133.1, 131.8, 129.1, 129.0, 128.9, 128.6, 128.3, 125.7, 124.5, 120.7, 117.4, 103.6, 21.8; HRMS calcd for C₂₂H₁₉N₃O+H⁺: 342.1601, found: 342.1605.

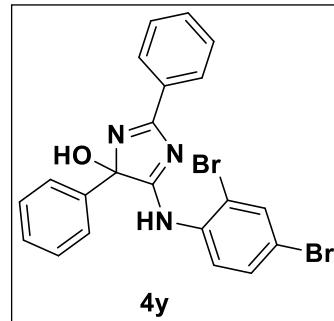
5-((2,4-dichlorophenyl)amino)-2,4-diphenyl-4*H*-imidazol-4-ol, 4x

White solid (198mg, 50%); mp 169.9-170.3 °C; ¹H NMR (400 MHz, DMSO-D₆): δ 10.53 (s, 1H), 8.11 (d, *J* = 7.4 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 (m, 4H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.25 (d, *J* = 8.6 Hz, 1H); ¹³C{¹H} NMR (100 MHz, DMSO-D₆): δ 175.4, 172.2, 147.2, 141.4, 133.7, 129.3, 129.1, 128.8, 128.6, 128.4, 128.3, 127.5, 127.4, 127.1, 126.3, 125.3, 90.1; HRMS calcd for C₂₁H₁₅Cl₂N₃O+H⁺: 396.0665 and 398.0636, found: 396.0673 and 398.0635.



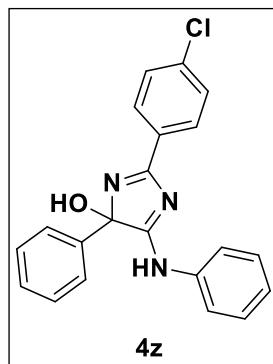
5-((2,4-dibromophenyl)amino)-2,4-diphenyl-4*H*-imidazol-4-ol, 4y

White solid (367 mg, 76%); mp 133.5-134.3 °C; ¹H NMR (400 MHz, DMSO-D₆): δ 10.53 (s, 1H), 8.11 (d, *J* = 7.4 Hz, 2H), 7.72 (d, *J* = 2.1 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.61 – 7.53 (m, 4H), 7.47 (m, 1H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.34 (d, *J* = 7.1 Hz, 1H), 7.30 (s, 1H), 7.18 (d, *J* = 8.5 Hz, 1H); ¹³C{¹H} NMR (100 MHz, DMSO-D₆): δ 175.1, 172.3, 148.9, 141.2, 134.2, 133.8, 130.9, 129.3, 129.1, 128.6, 128.4, 128.3, 126.4, 125.7, 118.3, 115.0, 90.1; HRMS calcd for C₂₁H₁₅Br₂N₃O+H⁺: 483.9655 and 485.9635, found: 483.9652 and 485.9637.



2-(4-chlorophenyl)-4-phenyl-5-(phenylamino)-4*H*-imidazol-4-ol, 4z

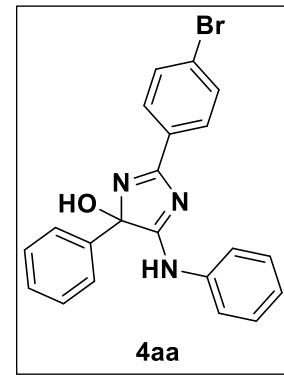
White solid (354 mg, 98%); mp 166.8-167.1 °C; ¹H NMR (400 MHz, DMSO-D₆): δ 10.18 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 2H), 8.06 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 6.7 Hz, 2H), 7.37 (d, *J* = 10.6 Hz, 3H), 7.33 (d, *J* = 5.0 Hz, 1H), 7.30 (s, 1H), 7.22 (s, 1H), 7.09 (t, *J* = 6.6 Hz, 1H); ¹³C{¹H} NMR (100 MHz, DMSO-D₆): δ 183.3, 171.7, 140.1, 140.1, 136.5, 131.9, 130.8, 129.2, 129.1, 128.6, 128.4, 125.7, 124.0, 103.8; HRMS calcd for



$C_{21}H_{16}ClN_3O + H^+$: 362.1055 and 364.1026, found: 362.1049 and 364.1025.

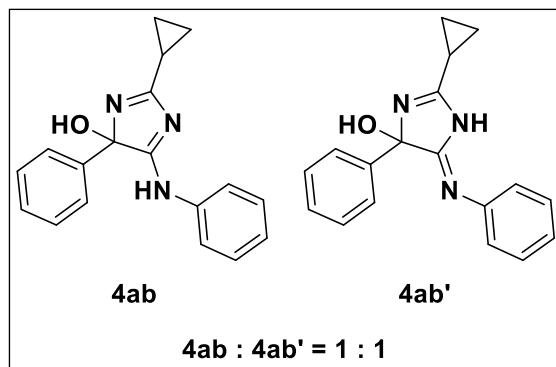
2-(4-bromophenyl)-4-phenyl-5-(phenylamino)-4*H*-imidazol-4-ol, 74aa

White solid (389mg, 96%); mp 175.7–176.3 °C; 1H NMR (400 MHz, DMSO- D_6): δ 10.18 (s, 1H), 8.18 (d, J = 8.0 Hz, 2H), 8.06 (d, J = 7.8 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 7.2 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.32 (d, J = 5.1 Hz, 1H), 7.28 (d, J = 14.9 Hz, 1H), 7.22 (s, 1H), 7.09 (t, J = 7.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO- D_6): δ 183.3, 171.8, 140.1, 140.0, 132.3, 132.1, 131.0, 129.2, 128.6, 128.4, 125.7, 125.5, 124.0, 120.3, 103.8; HRMS calcd for $C_{21}H_{16}BrN_3O + H^+$: 406.0550 and 408.0530, found: 406.0542 and 408.0534.



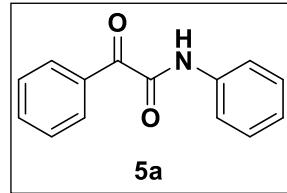
2-cyclopropyl-4-phenyl-5-(phenylamino)-4*H*-imidazol-4-ol, (4ab) and (Z)-2-cyclopropyl-4-phenyl-5-(phenylimino)-4,5-dihydro-1*H*-imidazol-4-ol (4ab') (1:1 ratio)

White solid (224 mg, 77%); mp 169.6–170.4 °C; 1H NMR (400 MHz, DMSO- D_6): δ 9.79 (d, J = 12.0 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.36 (d, J = 7.6 Hz, 2H), 7.33 – 7.25 (m, 3H), 7.19 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.95 – 6.90 (m, 1H), 1.85 – 1.74 (m, 1H), 1.08 (d, J = 9.8 Hz, 3H), 0.95 (d, J = 7.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO- D_6): δ 181.0, 173.4, 150.2, 142.2, 128.4, 128.4, 128.3, 126.0, 123.9, 123.0, 89.5, 11.0, 9.9, 7.6; HRMS calcd for $C_{18}H_{17}N_3O + H^+$: 292.1445, found: 292.1447.



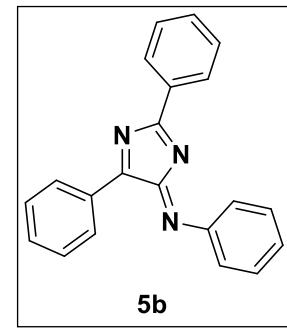
2-oxo-*N*,2-diphenylacetamide, 5a

Yellow solid (224 mg, 77%); mp 60.3-60.9 °C; Purified by column chromatography (silica gel 200-300 mesh, petroleum ether/ethyl acetate, v/v = 10/1); ^1H NMR (400 MHz, CDCl_3): δ 9.02 (s, 1H), 8.40 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.65 (m, 1H), 7.50 (m, 2H), 7.40 (m, 2H), 7.19 (m, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 187.4, 158.9, 136.6, 134.6, 133.1, 131.5, 129.2, 128.6, 125.3, 119.9; HRMS calcd for $\text{C}_{14}\text{H}_{11}\text{NO}_2+\text{H}^+$: 225.0790, found: 225.0795.



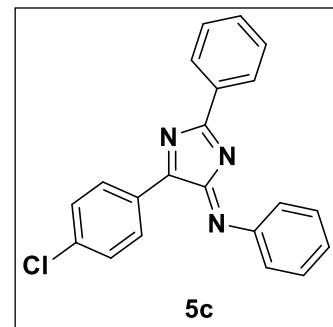
(Z)-N,2,5-triphenyl-4H-imidazol-4-imine, 5b

Red solid (223 mg, 72%); mp 124.1-124.7 °C; Purified by column chromatography (silica gel 200-300 mesh, petroleum ether/ethyl acetate, v/v = 10/1); ^1H NMR (400 MHz, CDCl_3): δ 8.74 (d, J = 7.4 Hz, 2H), 8.61 (d, J = 7.5 Hz, 2H), 7.93 (d, J = 7.8 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.62 – 7.56 (m, 3H), 7.56 – 7.47 (m, 4H), 7.38 (t, J = 7.2 Hz, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 182.5, 176.2, 166.7, 147.7, 134.0, 132.8, 131.3, 131.2, 131.0, 130.9, 129.2, 129.0, 128.9, 128.8, 127.5. HRMS calcd for $\text{C}_{21}\text{H}_{15}\text{N}_3+\text{H}^+$: 310.1339, found: 310.1348.



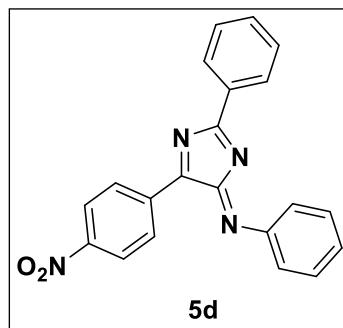
(Z)-5-(4-chlorophenyl)-N,2-diphenyl-4H-imidazol-4-imine, 5c

Red solid (298 mg, 87%); mp 164.2-164.9 °C; Purified by column chromatography (silica gel 200-300 mesh, petroleum ether/ethyl acetate, v/v = 10/1); ^1H NMR (400 MHz, CDCl_3): δ 8.71 (d, J = 8.6 Hz, 2H), 8.61 – 8.54 (m, 2H), 7.93 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 7.50 (t, J = 8.6 Hz, 4H), 7.38 (t, J = 7.4 Hz, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 182.3, 174.9, 166.3, 147.3, 139.3, 134.0, 132.3, 130.8, 129.6, 129.4, 129.0, 129.0, 128.8, 127.6. HRMS calcd for $\text{C}_{21}\text{H}_{14}\text{ClN}_3+\text{H}^+$: 344.0950 and 346.0920, found: 344.0949 and 346.0917.



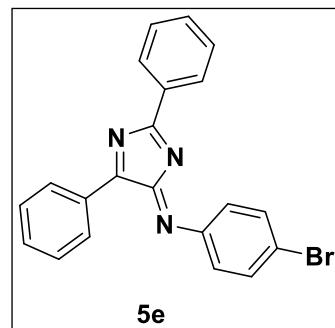
(Z)-5-(4-nitrophenyl)-N,2-diphenyl-4H-imidazol-4-imine, 5d

Red solid (280 mg, 79%); mp 187.3-188.0 °C; Purified by column chromatography (silica gel 200-300 mesh, petroleum ether/ethyl acetate, v/v = 10/1); ^1H NMR (400 MHz, CDCl_3): δ 8.90 (d, J = 8.7 Hz, 2H), 8.59 (d, J = 7.6 Hz, 2H), 8.37 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 7.9 Hz, 2H), 7.68 (t, J = 7.2 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.52 (t, J = 7.7 Hz, 2H), 7.42 (t, J = 7.3 Hz, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 181.7, 173.9, 165.6, 149.9, 147.1, 136.5, 134.4, 131.8, 130.8, 130.4, 130.1, 129.1, 129.0, 128.1, 123.6. HRMS calcd for $\text{C}_{21}\text{H}_{14}\text{N}_4\text{O}_2+\text{H}^+$: 355.1190, found: 355.1182.



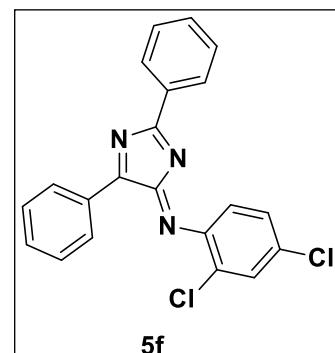
(Z)-N-(4-bromophenyl)-2,5-diphenyl-4H-imidazol-4-imine, 5e

Red solid (317 mg, 82%); mp 119.4-120.0 °C; Purified by column chromatography (silica gel 200-300 mesh, petroleum ether/ethyl acetate, v/v = 10/1); ^1H NMR (400 MHz, CDCl_3): δ 8.74 – 8.67 (m, 2H), 8.64 – 8.57 (m, 2H), 7.86 – 7.78 (m, 2H), 7.67 (m, 1H), 7.65 – 7.62 (m, 2H), 7.61 (d, J = 2.2 Hz, 1H), 7.59 – 7.52 (m, 4H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 182.6, 176.1, 166.9, 146.4, 134.2, 132.9, 132.1, 131.1, 131.0, 130.9, 130.7, 129.0, 128.9, 128.7, 123.4. HRMS calcd for $\text{C}_{21}\text{H}_{14}\text{BrN}_3+\text{H}^+$: 388.0444 and 390.0424, found: 388.0451 and 390.0425.



(Z)-N-(2,4-dichlorophenyl)-2,5-diphenyl-4H-imidazol-4-imine, 5f

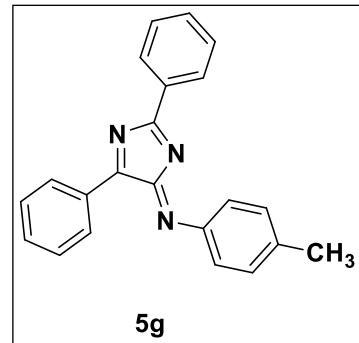
Red solid (302 mg, 80%); mp 178.5-178.9 °C; Purified by column chromatography (silica gel 200-300 mesh, petroleum ether/ethyl acetate, v/v = 10/1); ^1H NMR (400 MHz, CDCl_3): δ 8.82 (d, J = 7.9 Hz, 2H), 8.59 (d, J = 7.8 Hz, 2H), 8.06 (d, J = 8.7 Hz, 1H), 7.67 (t, J = 6.9 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.59 – 7.52 (m, 5H), 7.36 (d, J = 8.7 Hz, 1H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 183.6, 176.0, 167.5, 143.1, 134.5, 134.5, 134.1, 133.2, 131.4, 131.1, 130.7, 130.5, 129.9, 128.9, 128.8, 127.5, 126.9. HRMS



calcd for C₂₁H₁₃Cl₂N₃+H⁺: 378.0560, found: 378.0571.

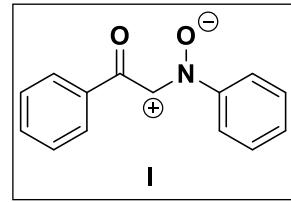
(Z)-2,5-diphenyl-N-(*p*-tolyl)-4*H*-imidazol-4-imine, 5g

Red solid (242 mg, 75%); mp 114.8–115.3 °C; Purified by column chromatography (silica gel 200–300 mesh, petroleum ether/ethyl acetate, v/v = 10/1); ¹H NMR (400 MHz, CDCl₃): δ 8.77–8.70 (m, 2H), 8.65–8.59 (m, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.61–7.52 (m, 5H), 7.31 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 181.7, 176.1, 165.7, 145.2, 140.3, 133.7, 132.5, 131.3, 131.1, 130.6, 129.7, 128.8, 128.6, 128.3, 21.6. HRMS calcd for C₂₂H₁₇N₃+H⁺: 324.1496, found: 324.1487.



(Z)-2-oxo-*N*,2-diphenylethan-1-imine oxide, I

Yellow solid (201 mg, 89%); mp 104.1–104.4 °C; Purified by column chromatography (silica gel 200–300 mesh, petroleum ether/ethyl acetate, v/v = 4/1); ¹H NMR (400 MHz, CDCl₃): δ 8.34 (s, 1H), 7.94 (d, *J* = 7.4 Hz, 2H), 7.79 (d, *J* = 7.3 Hz, 2H), 7.62–7.52 (m, 3H), 7.51 (s, 1H), 7.49 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 184.1, 148.9, 137.1, 133.5, 131.6, 129.5, 129.1, 128.9, 128.3, 121.9. HRMS calcd for C₁₄H₁₁ON₂+H⁺: 226.0863, found: 226.0862.



5. ^1H and ^{13}C NMR Spectra of target compounds 4, 5 and intermediate I

4a

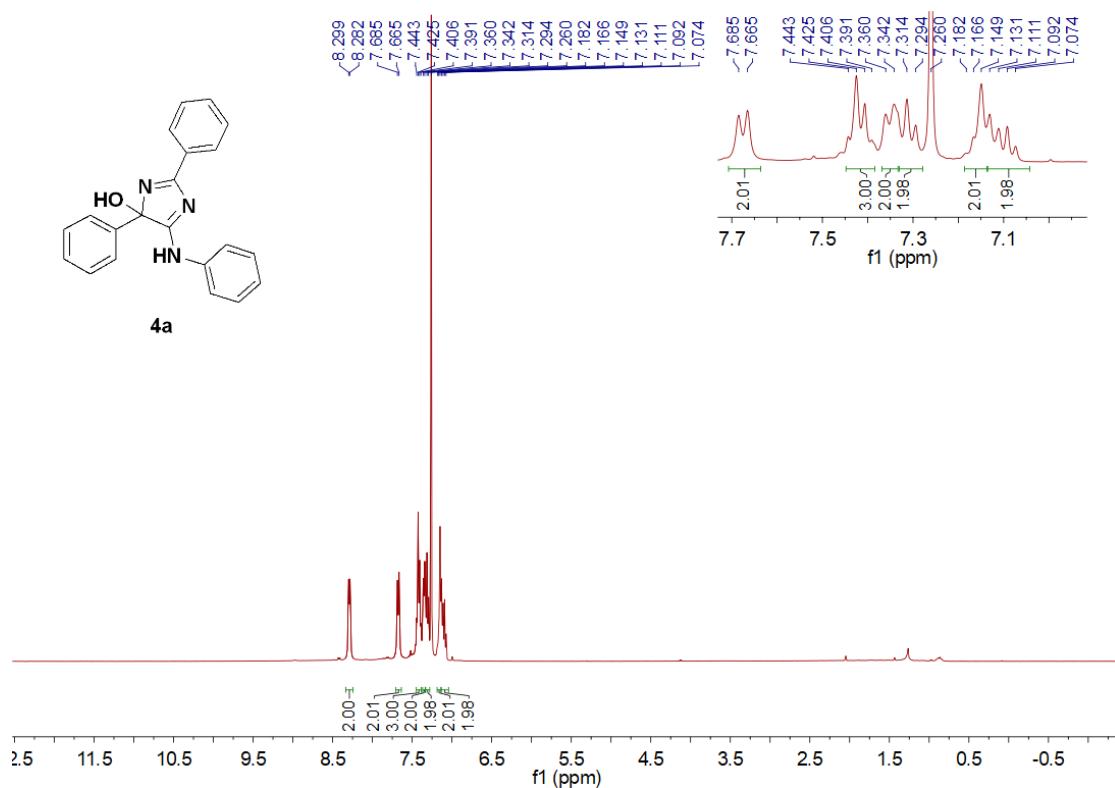


Fig S6. ^1H NMR (400 MHz) spectrum of **4a** (CDCl_3 , rt)

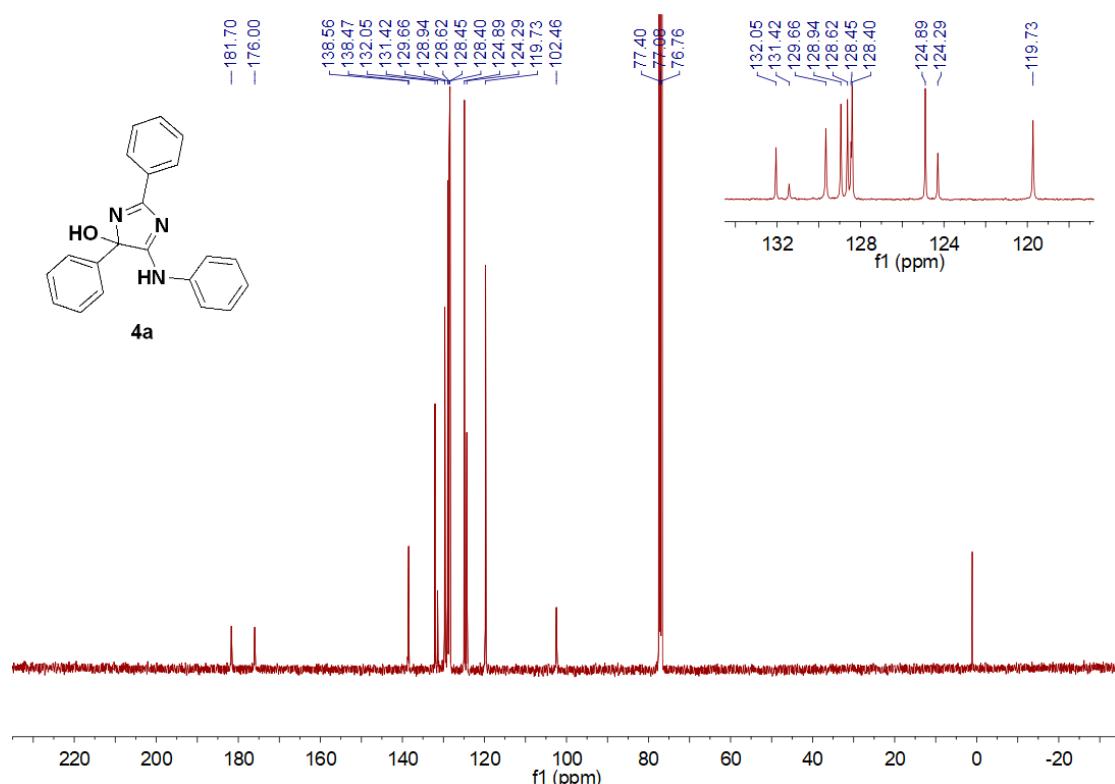


Fig S7. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4a** (CDCl_3 , rt)

Mixture of **4b and **4b'** (5:1 ratio)**

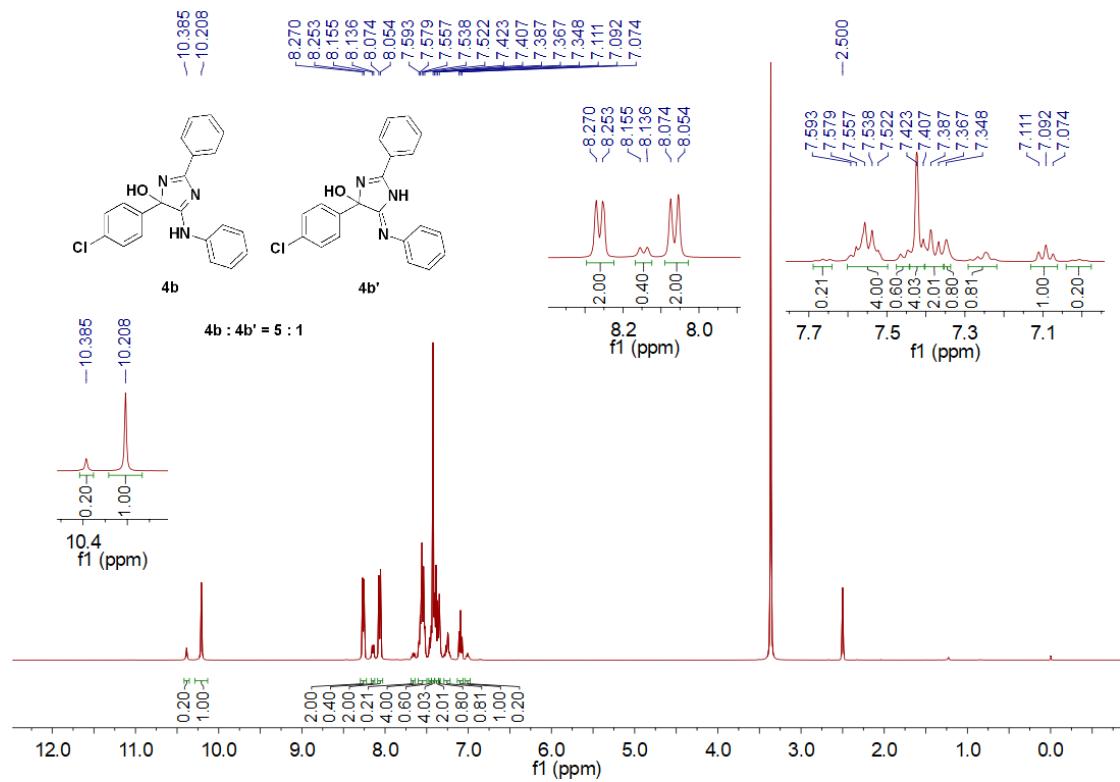


Fig S8. ^1H NMR (400 MHz) spectrum of **4b** and **4b'** (5:1 ratio) (DMSO- D_6 , rt)

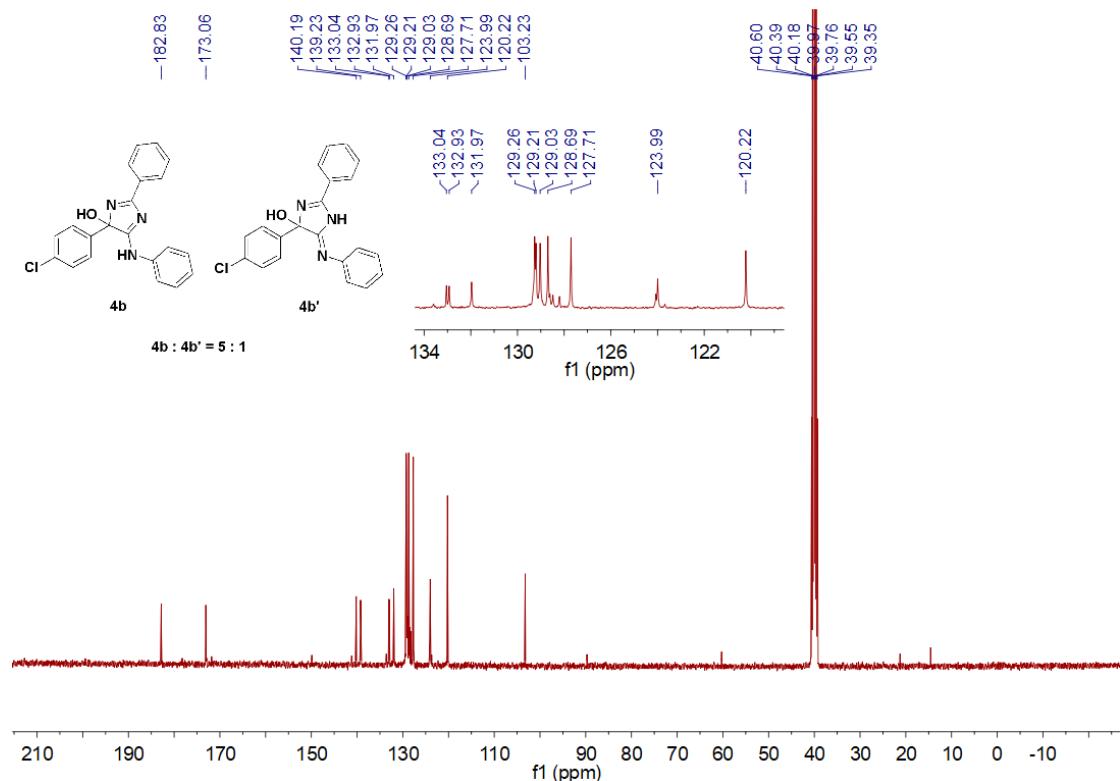


Fig S9. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4b** and **4b'** (5:1 ratio) (DMSO- D_6 , rt)

4c

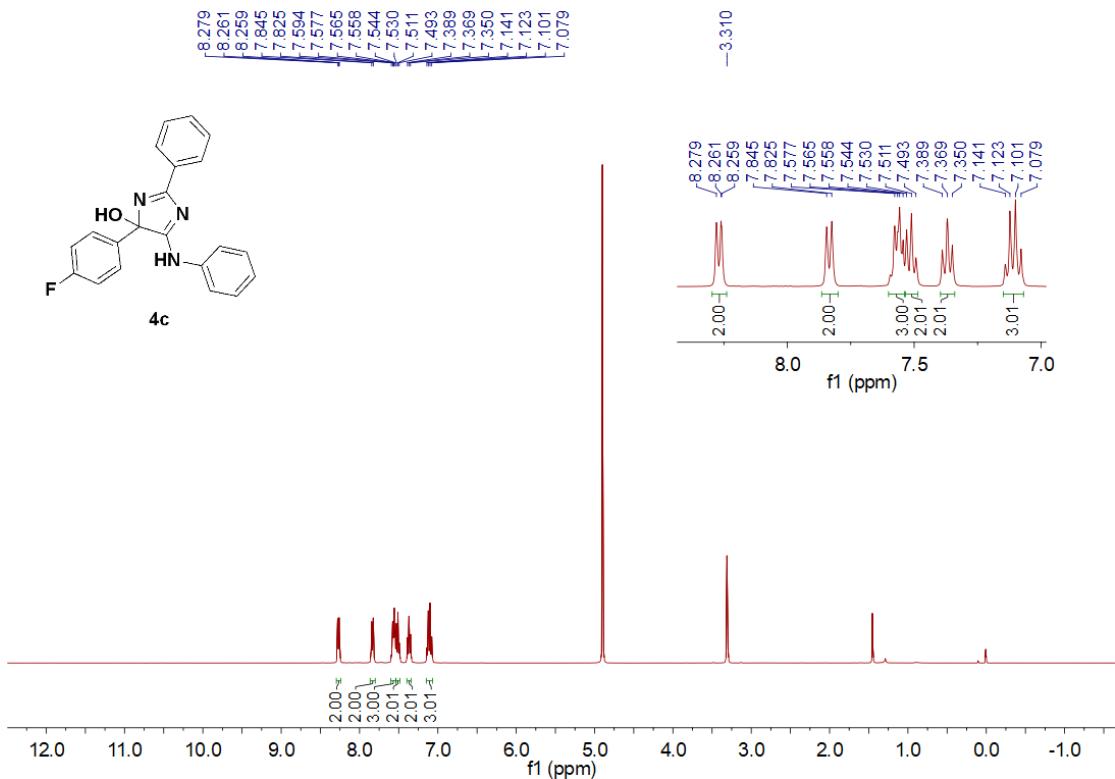


Fig S10. ¹H NMR (400 MHz) spectrum of **4c** (CD₃OD, rt)

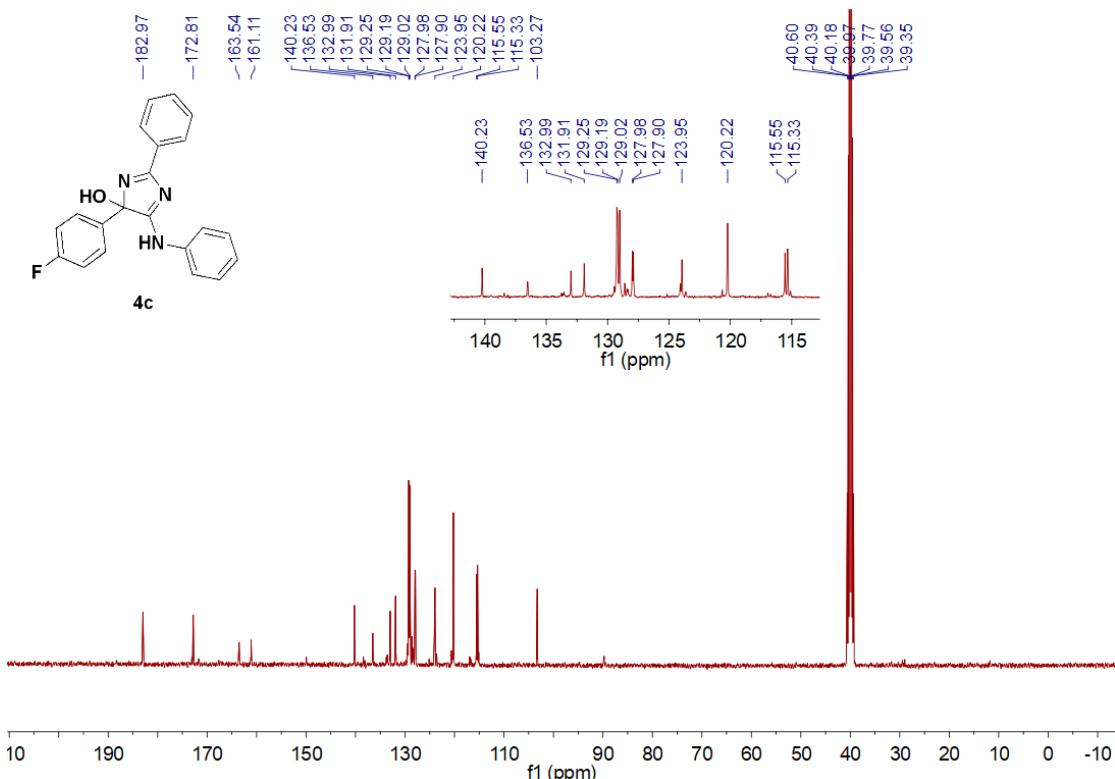


Fig S11. ¹³C{¹H} NMR (100 MHz) spectrum of **4c** (DMSO-D₆, rt)

Mixture of 4d and 4d' (5:1 ratio)

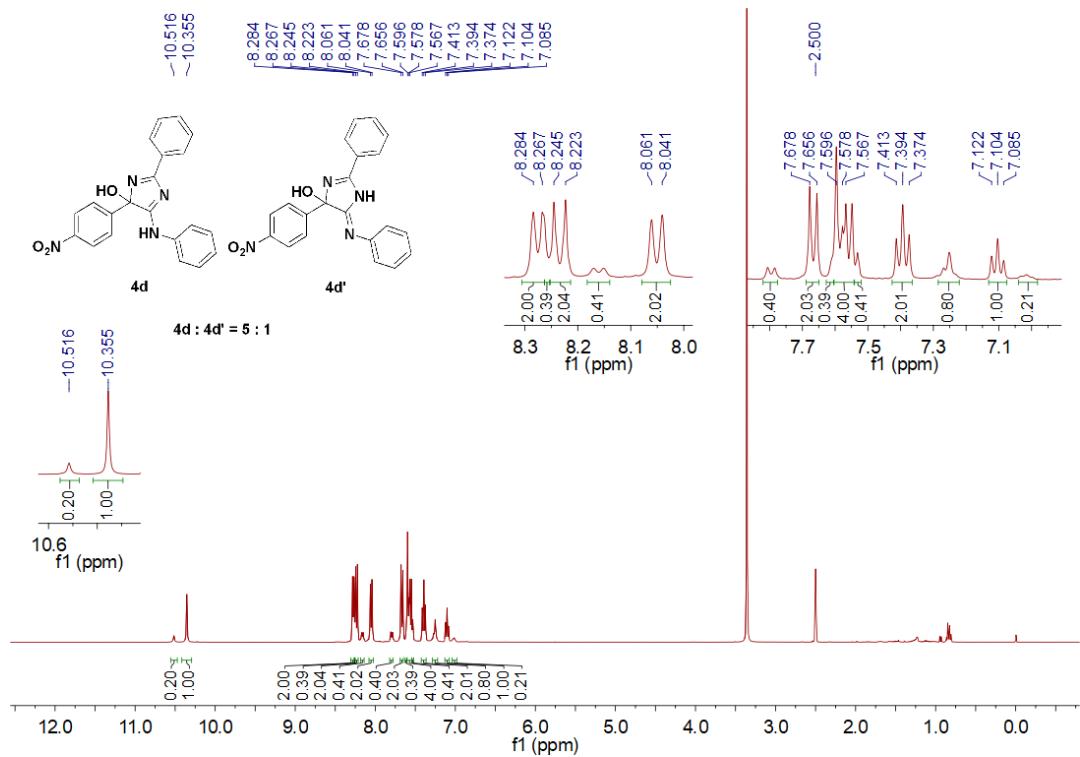


Fig S12. ^1H NMR (400 MHz) spectrum of **4d and 4d'** (**5:1 ratio**) (DMSO- D_6 , rt)

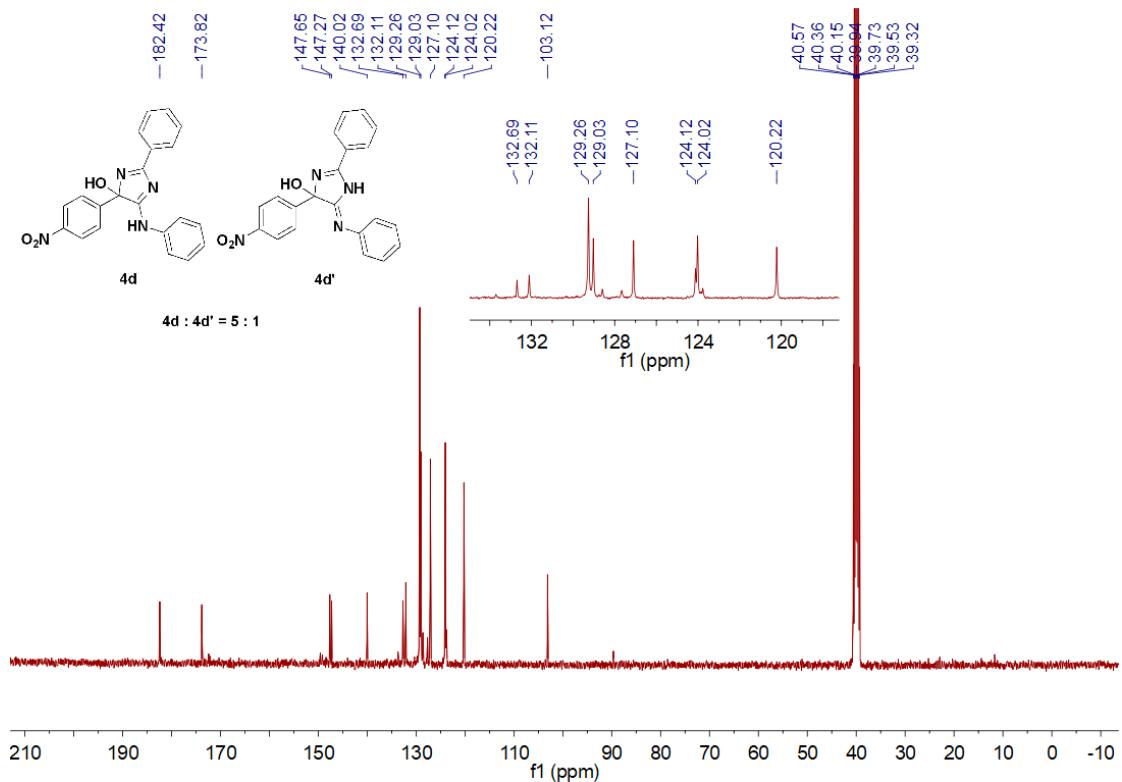


Fig S13. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4d and 4d'** (**5:1 ratio**) (DMSO- D_6 , rt)

4e

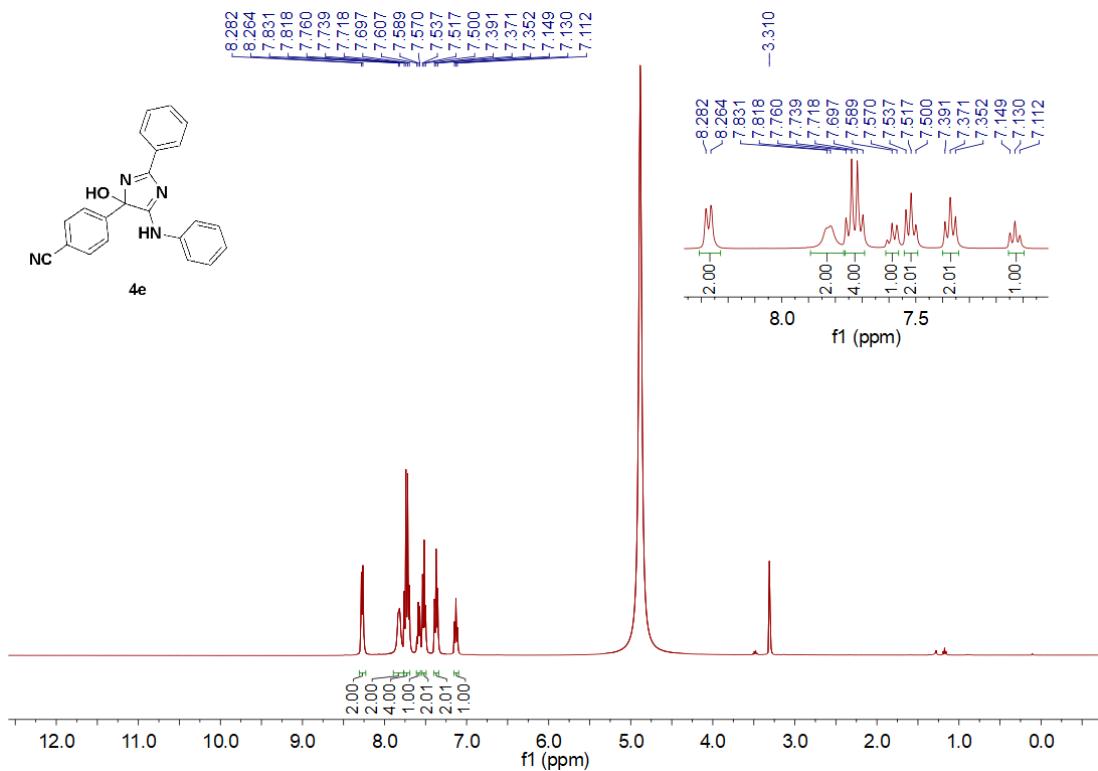


Fig S14. ^1H NMR (400 MHz) spectrum of **4e** (CD_3OD , rt)

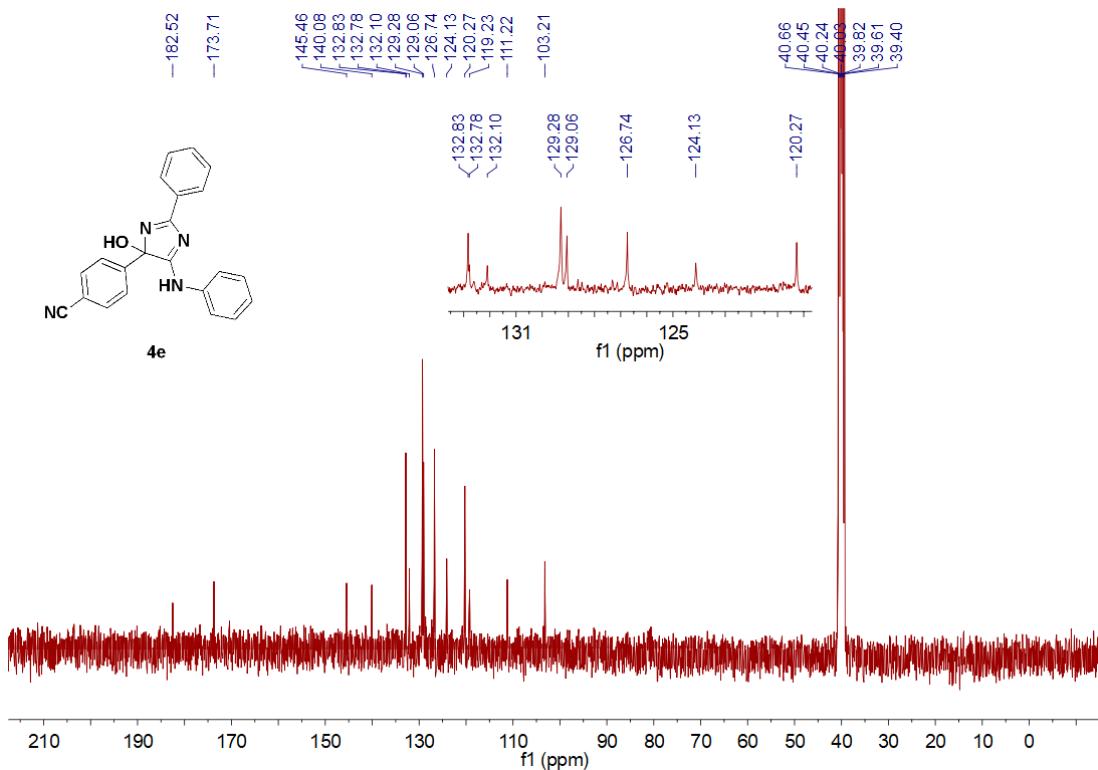


Fig S15. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4e** (DMSO-D_6 , rt)

Mixture of **4f and **4f'** (5:1 ratio)**

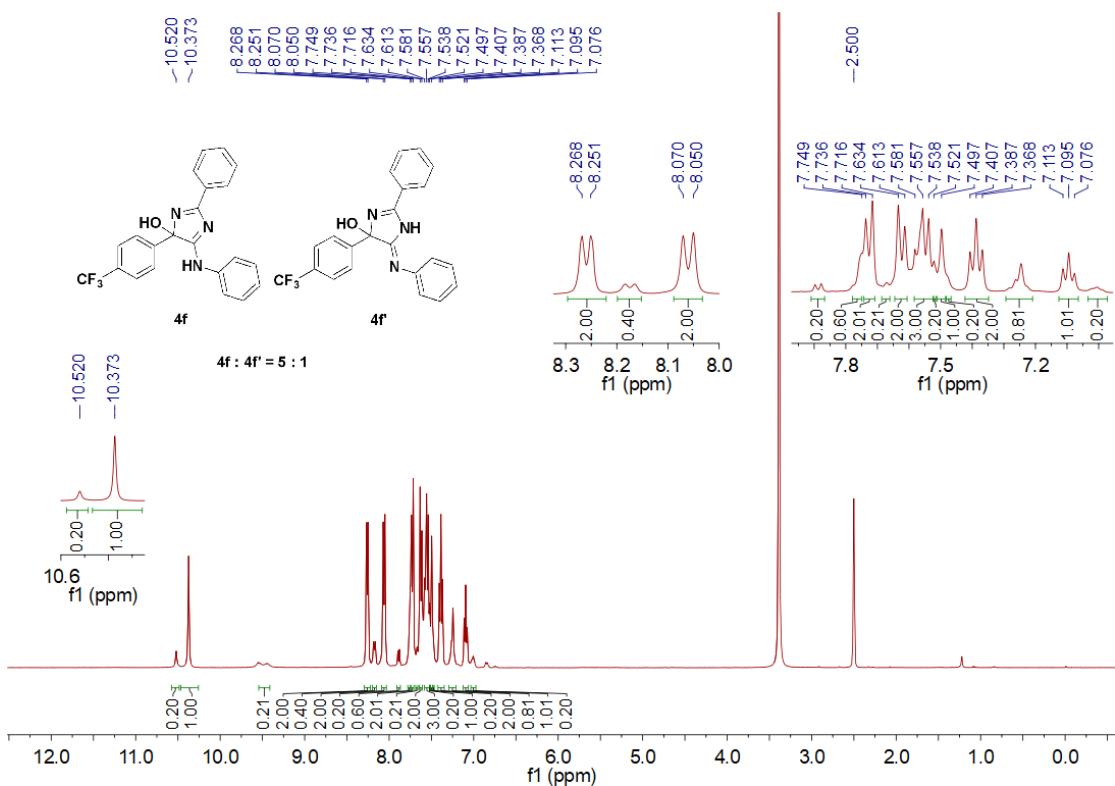


Fig S16. ^1H NMR (400 MHz) spectrum of **4f** and **4f'** (5:1 ratio) (DMSO- D_6 , rt)

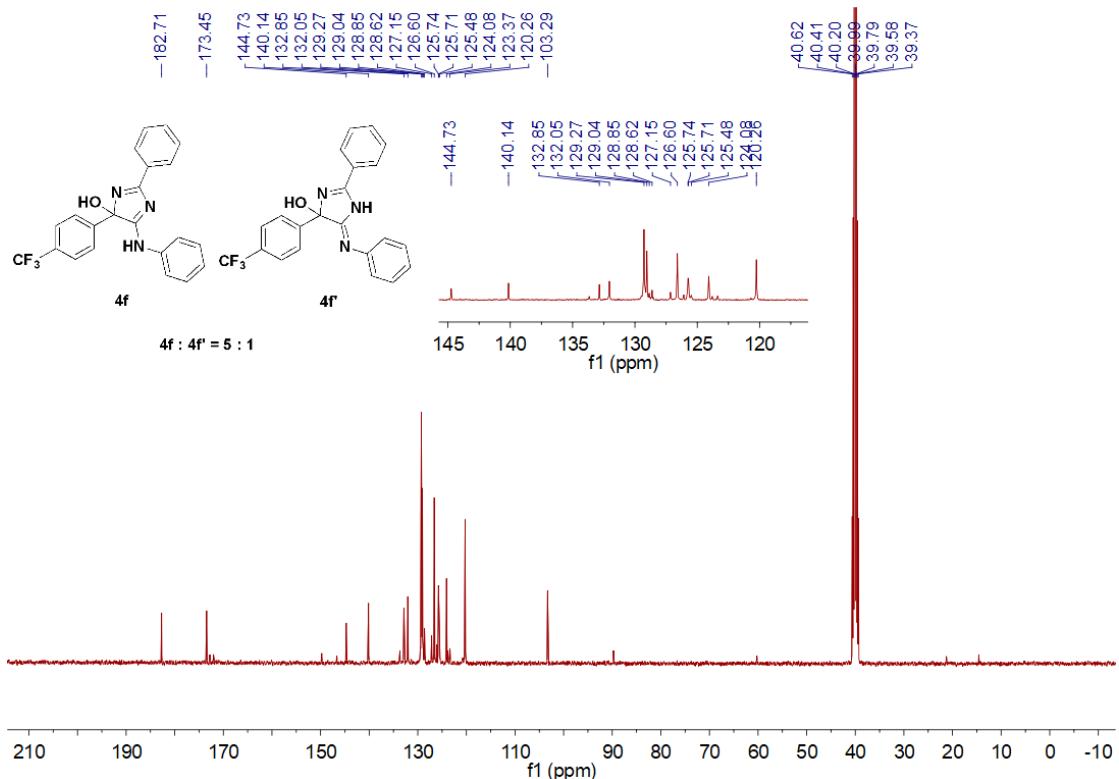


Fig S17. $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz) spectrum of **4f** and **4f'** (5:1 ratio) (DMSO- D_6 , rt)

Mixture of **4g and **4g'** (5:1 ratio)**

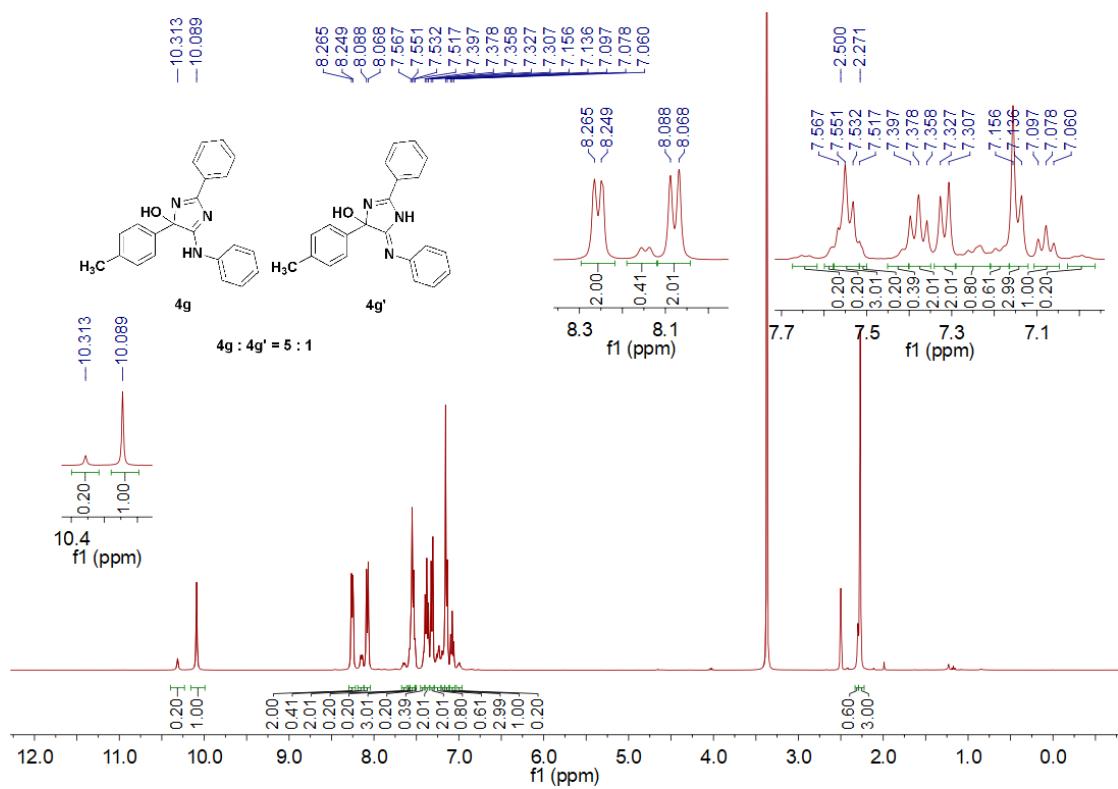


Fig S18. ^1H NMR (400 MHz) spectrum of **4g** and **4g'** (5:1 ratio) (DMSO- D_6 , rt)

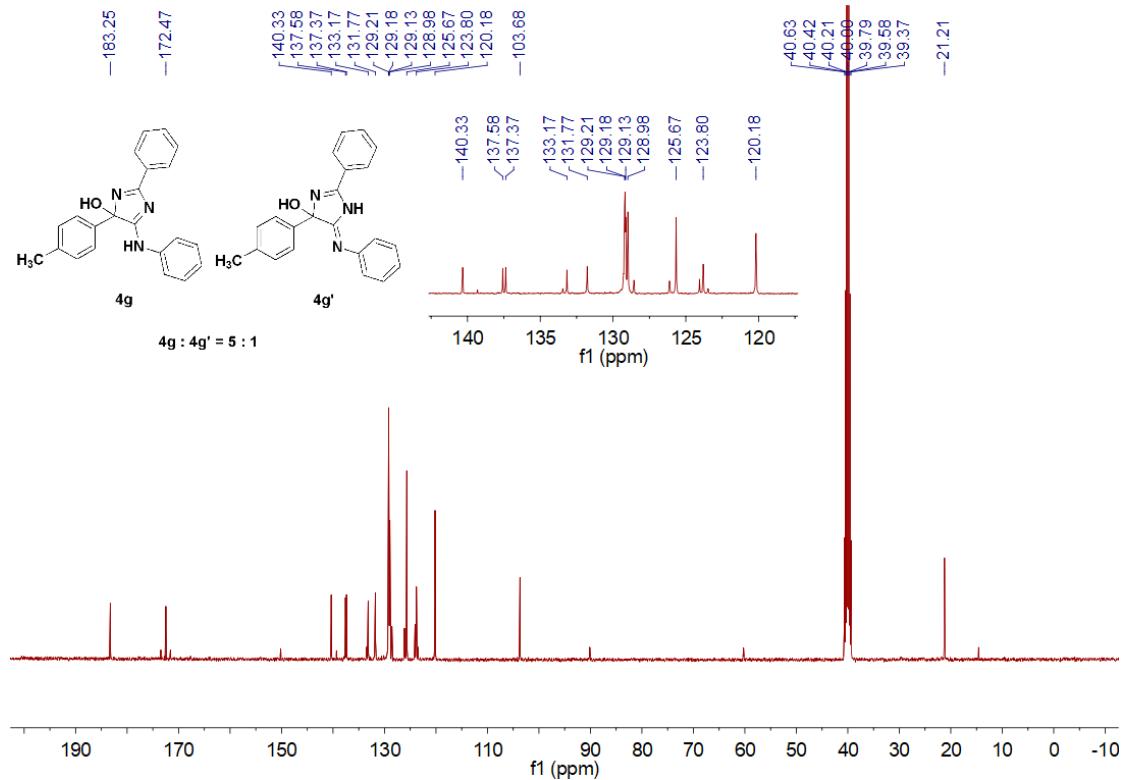


Fig S19. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4g** and **4g'** (5:1 ratio) (DMSO- D_6 , rt)

4h

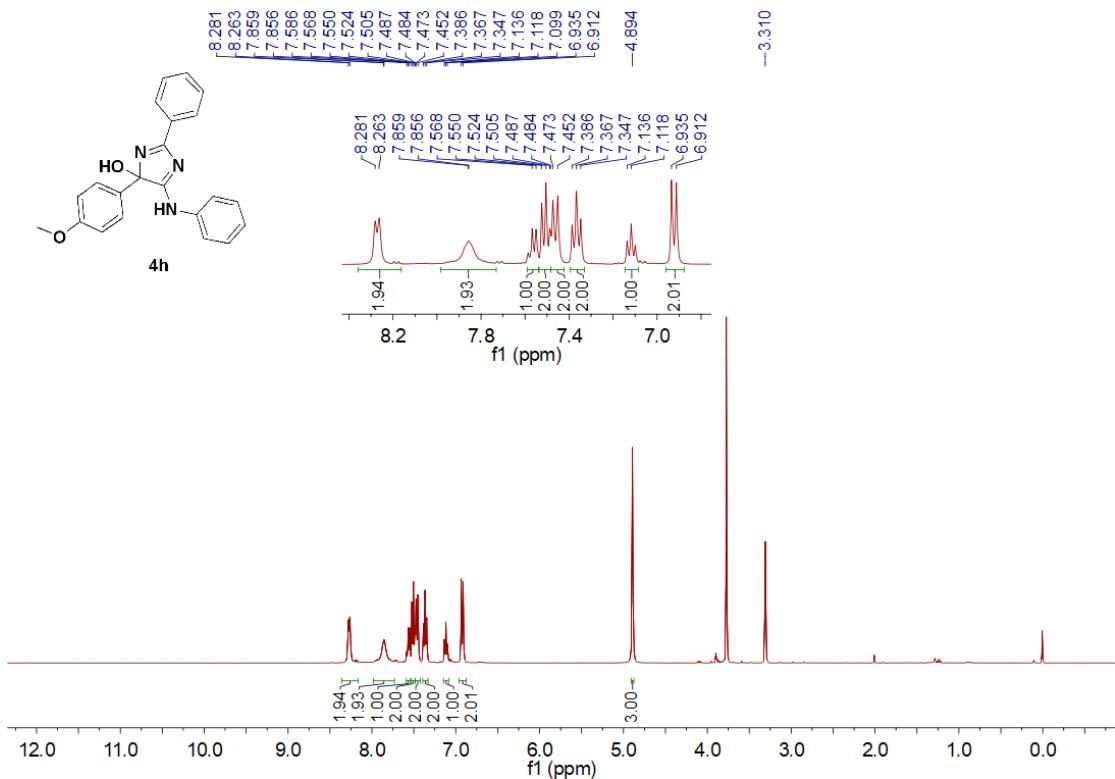


Fig S20. ¹H NMR (400 MHz) spectrum of **4h** (CD₃OD, rt)

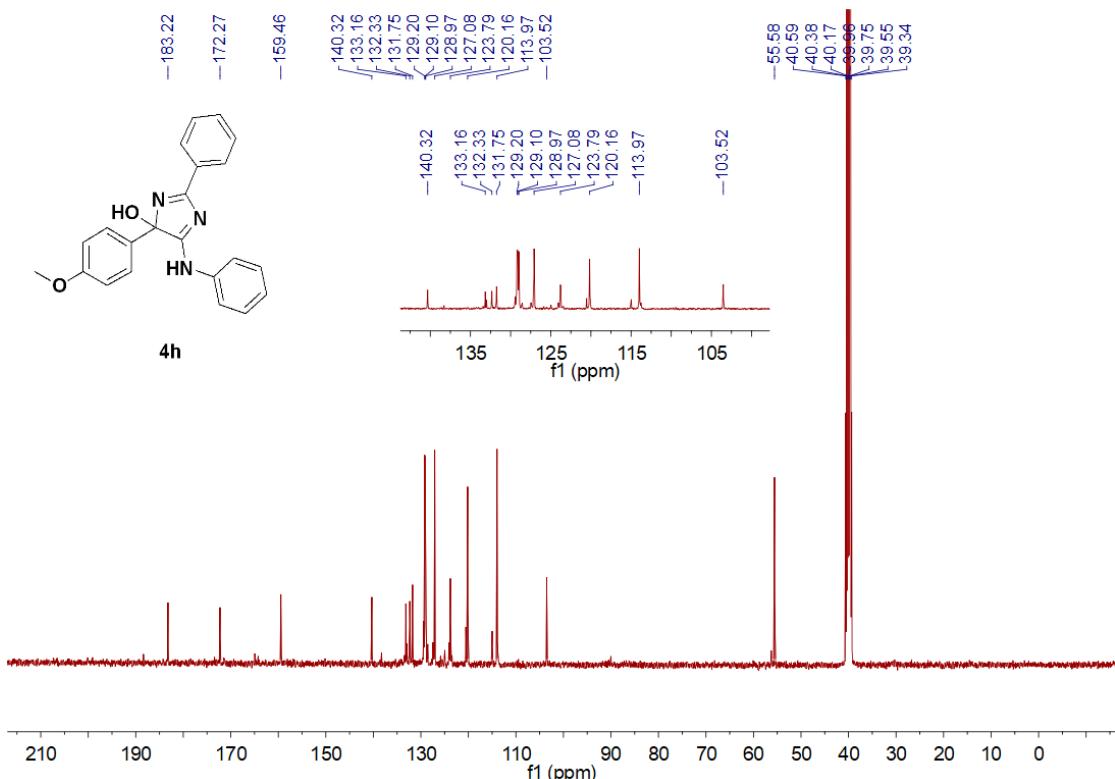


Fig S21. ¹³C{¹H} NMR (100 MHz) spectrum of **4h** (DMSO-D₆, rt)

Mixture of **4i and **4i'** (5:1 ratio)**

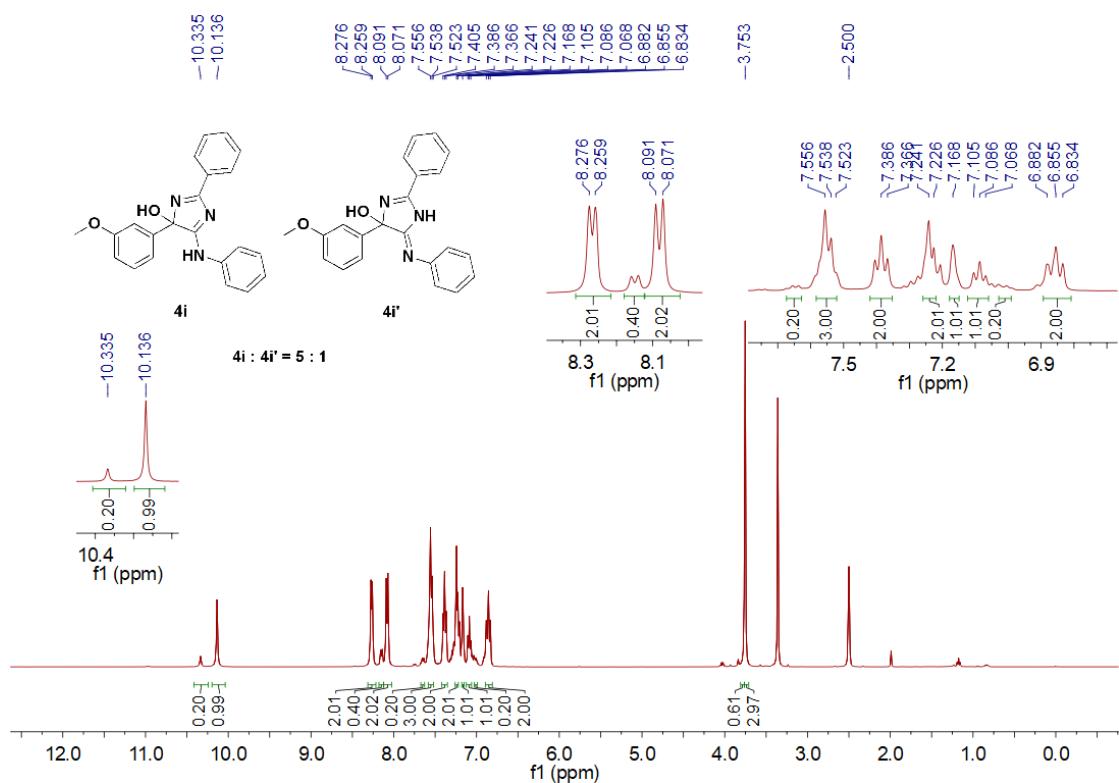


Fig S22. ^1H NMR (400 MHz) spectrum of **4i** and **4i'** (5:1 ratio) (DMSO- D_6 , rt)

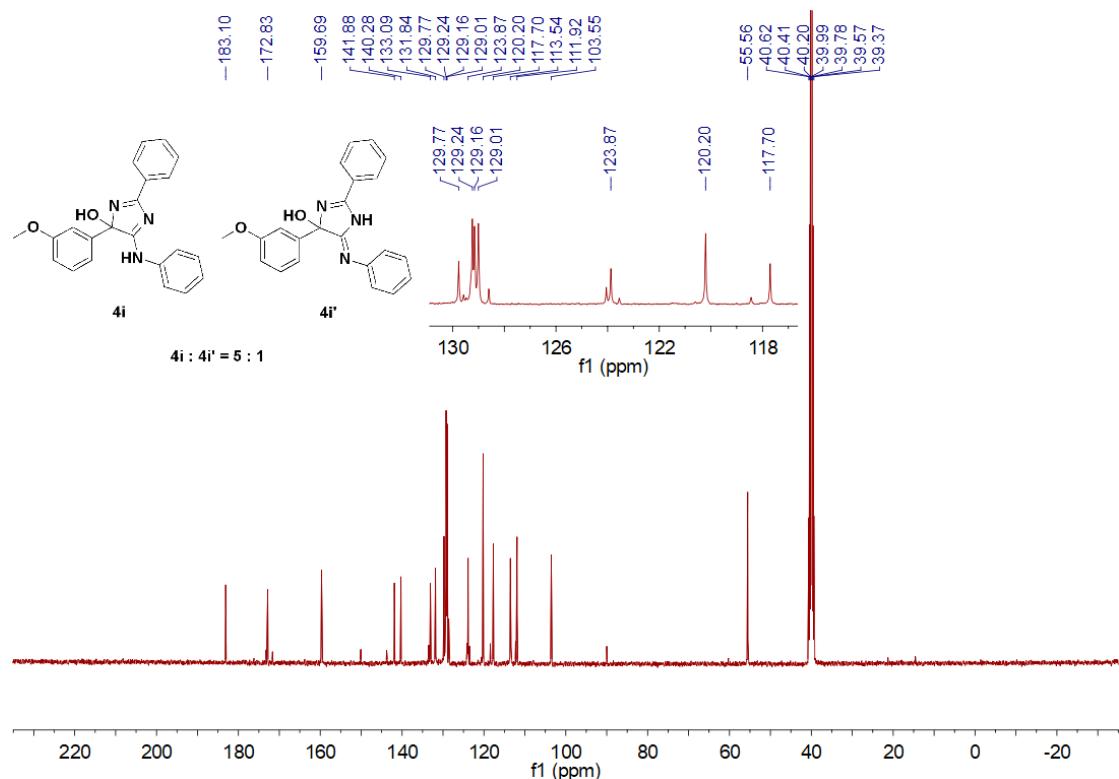


Fig S23. $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz) spectrum of **4i** and **4i'** (5:1 ratio) (DMSO- D_6 , rt)

Mixture of **4j and **4j'** (5:1 ratio)**

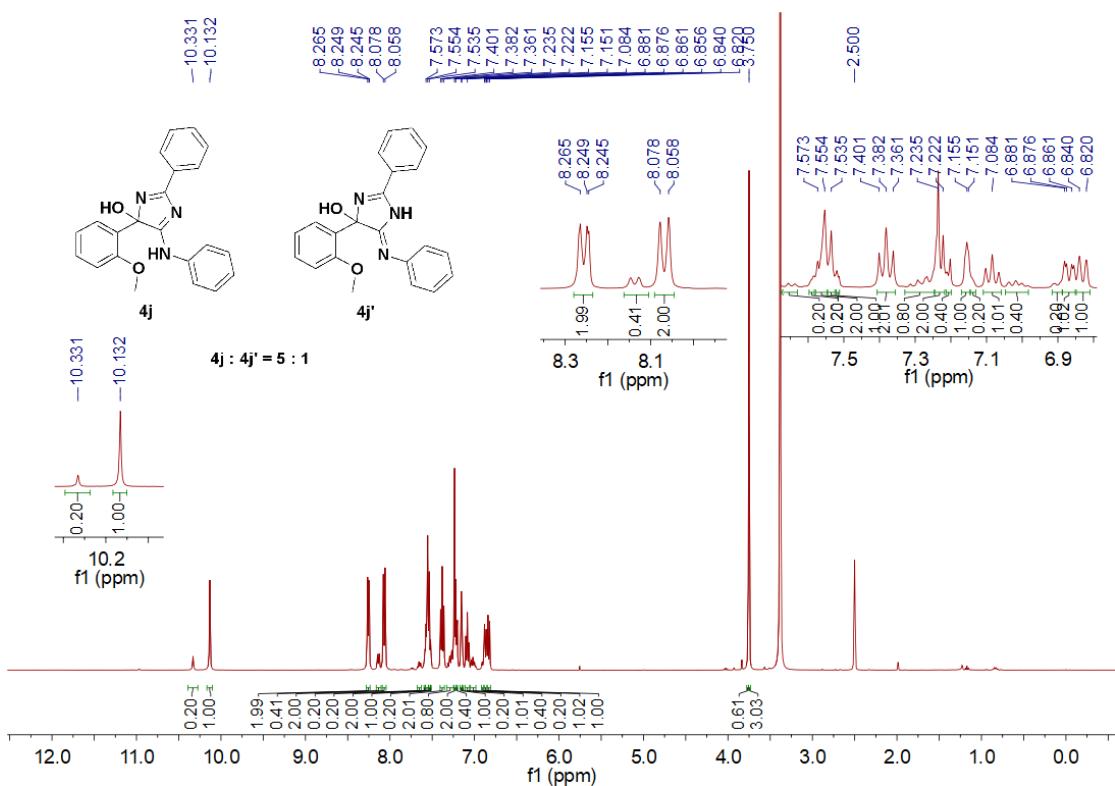


Fig S24. ^1H NMR (400 MHz) spectrum of **4j** and **4j'** (5:1 ratio) (DMSO- D_6 , rt)

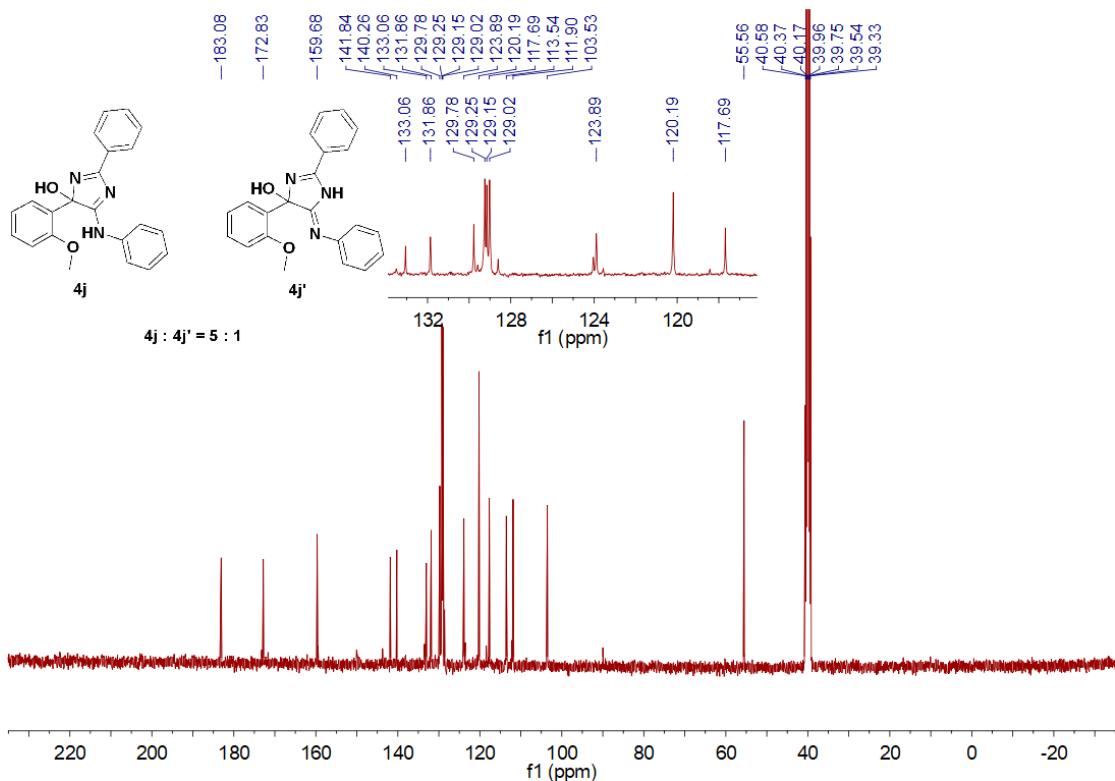


Fig S25. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4j** and **4j'** (5:1 ratio) (DMSO- D_6 , rt)

Mixture of **4k and **4k'** (5:1 ratio)**

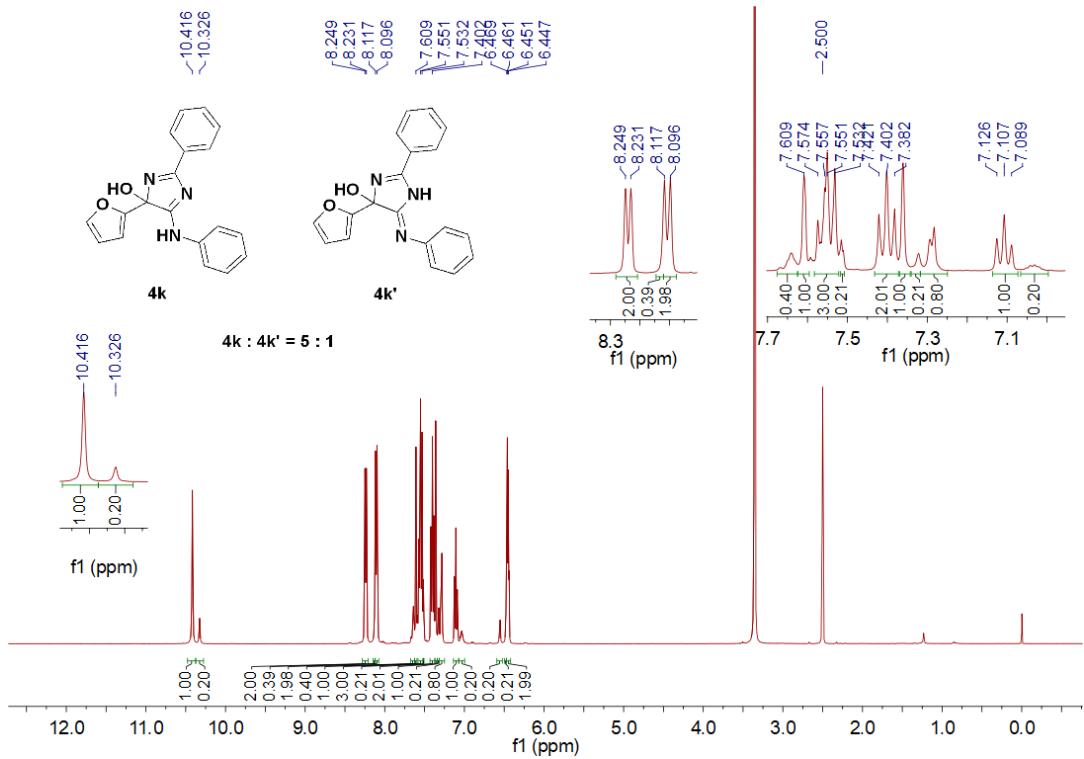


Fig S26. ¹H NMR (400 MHz) spectrum of **4k** and **4k'** (5:1 ratio) (DMSO-D₆, rt)

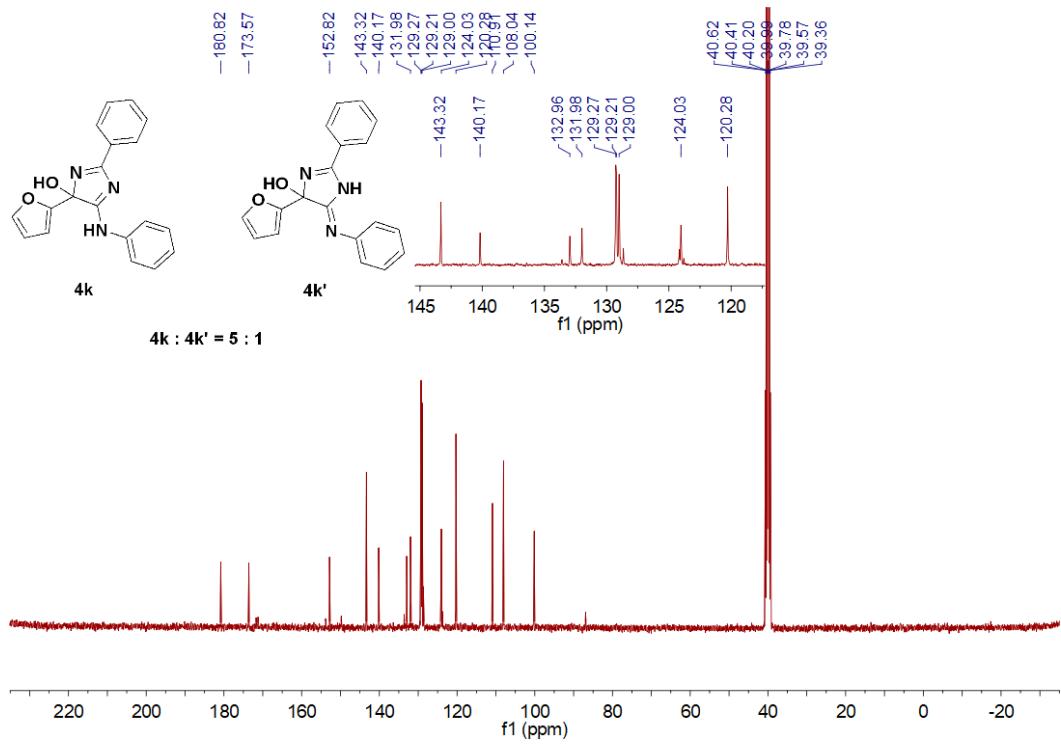


Fig S27. ¹³C{¹H} NMR (100 MHz) spectrum of **4k** and **4k'** (5:1 ratio) (DMSO-D₆, rt)

Mixture of **4l and **4l'** (5:1 ratio)**

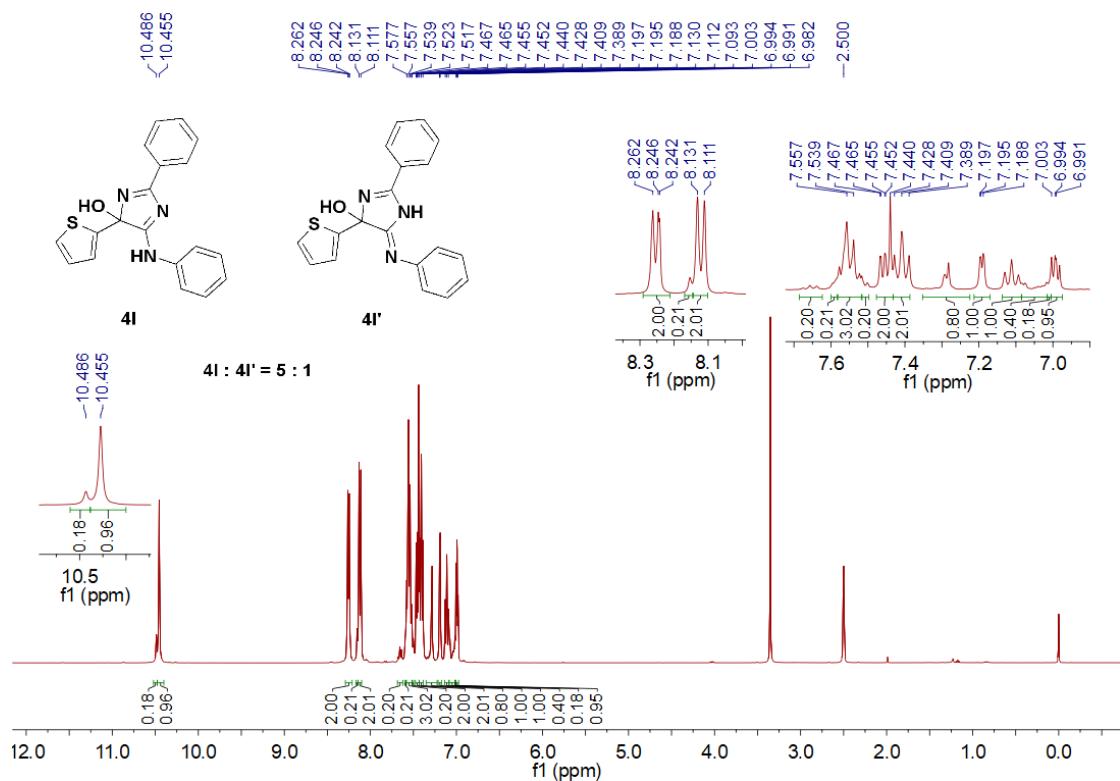


Fig S28. ^1H NMR (400 MHz) spectrum of **4l** and **4l'** (5:1 ratio) (DMSO- D_6 , rt)

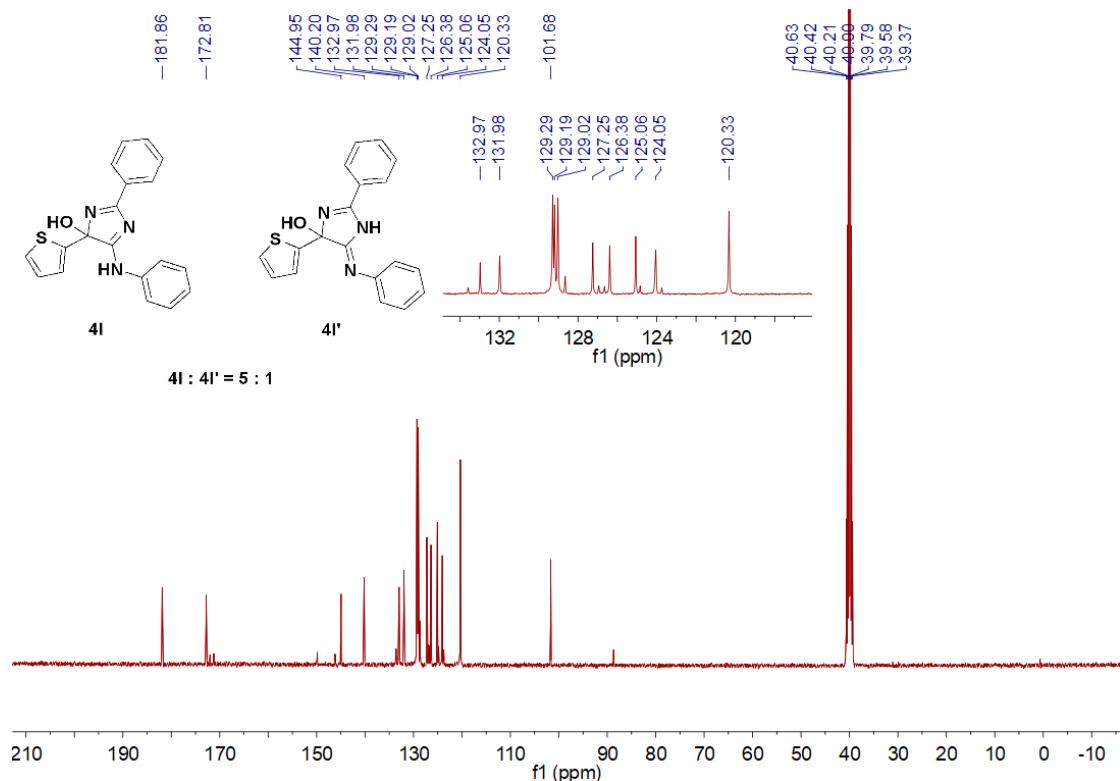


Fig S29. $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz) spectrum of **4l** and **4l'** (5:1 ratio) (DMSO- D_6 , rt)

4m

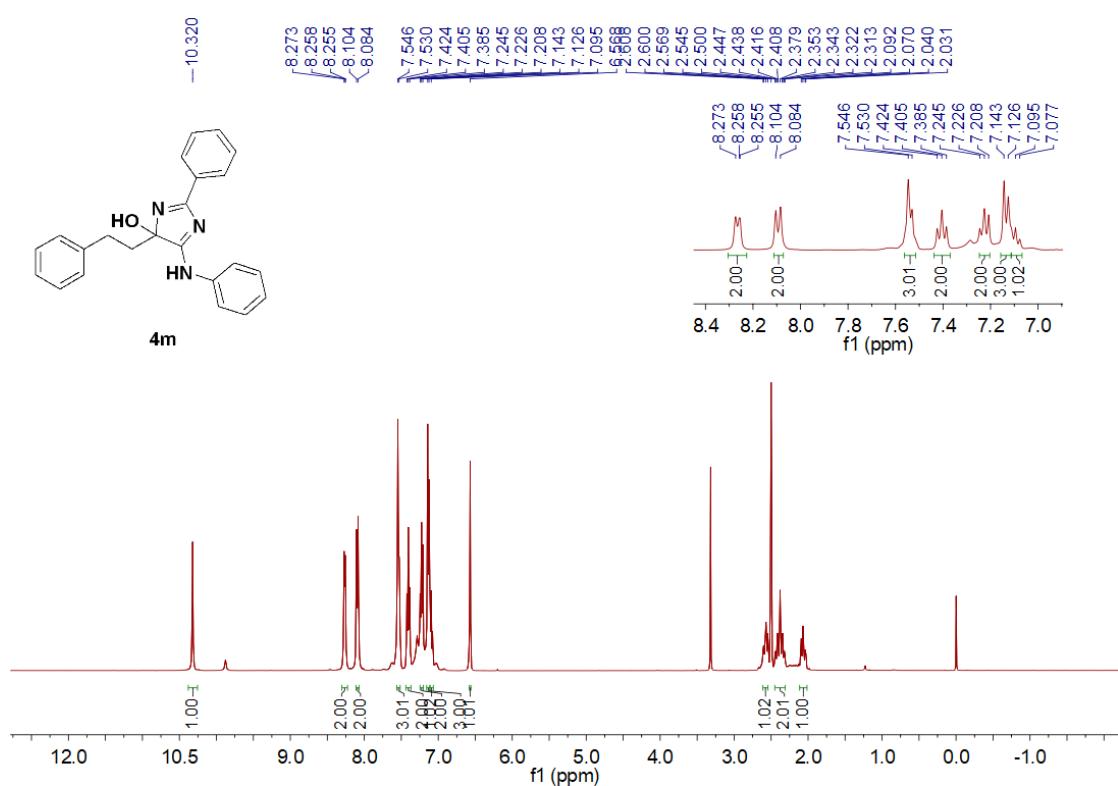


Fig S30. ¹H NMR (400 MHz) spectrum of **4m** (DMSO-D₆, rt)

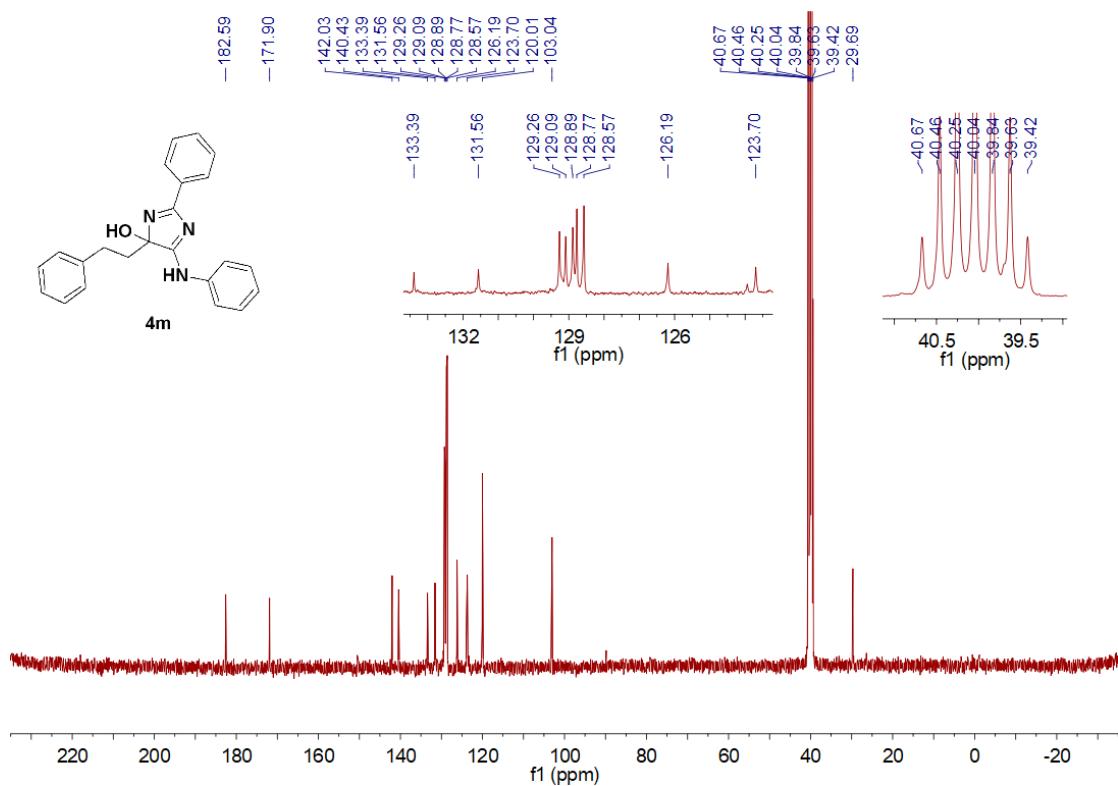


Fig S31. ¹³C{¹H} NMR (100 MHz) spectrum of **4m** (DMSO-D₆, rt)

Mixture of 4n and 4n' (5:1 ratio)

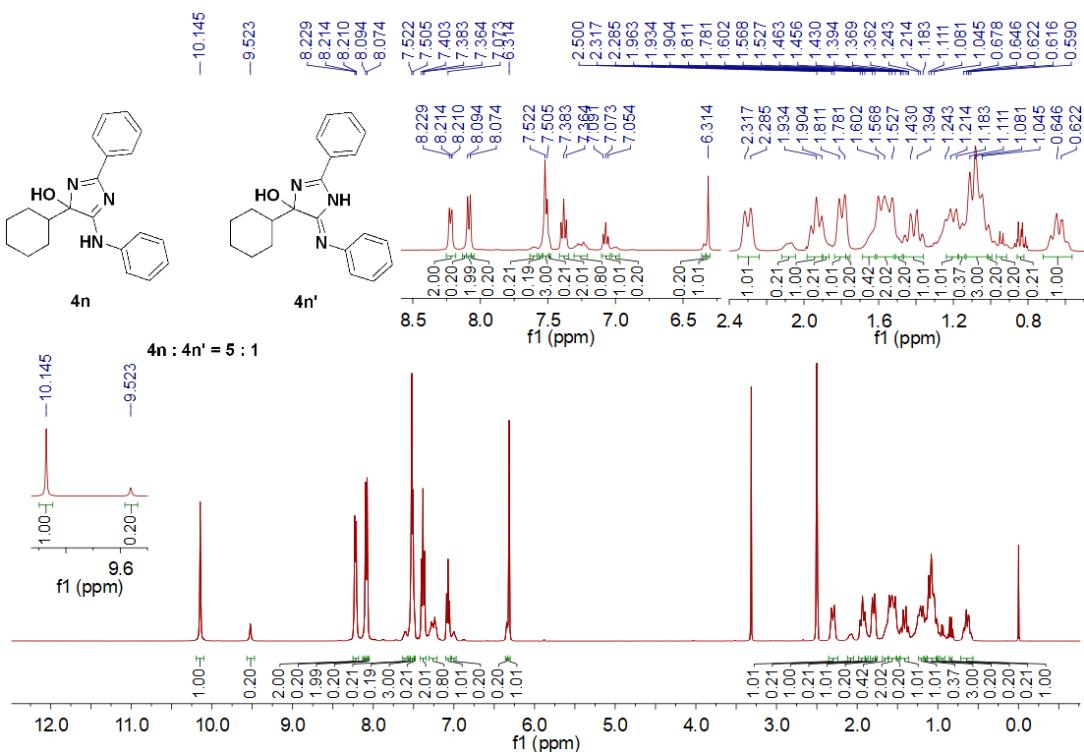


Fig S32. ^1H NMR (400 MHz) spectrum of **4n and 4n'** (**5:1 ratio**) (DMSO- D_6 , rt)

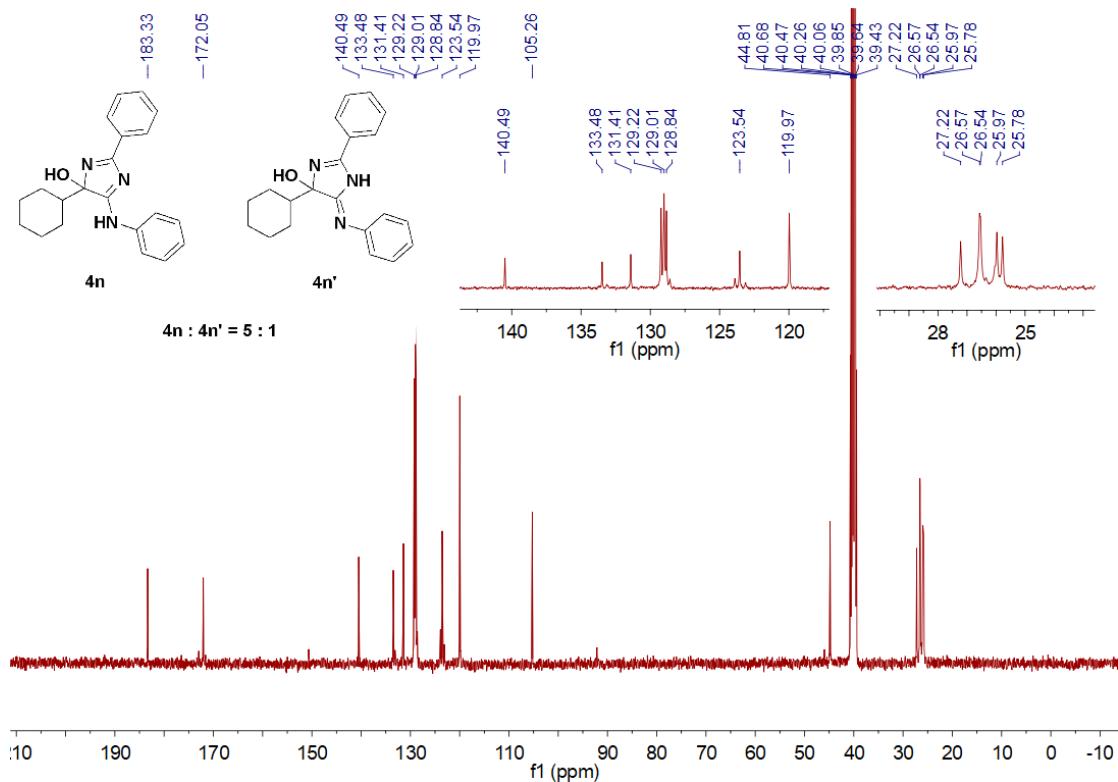


Fig S33. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4k and 4k'** (**5:1 ratio**) (DMSO- D_6 , rt)

Mixture of **4o and **4o'** (2.5:1 ratio)**

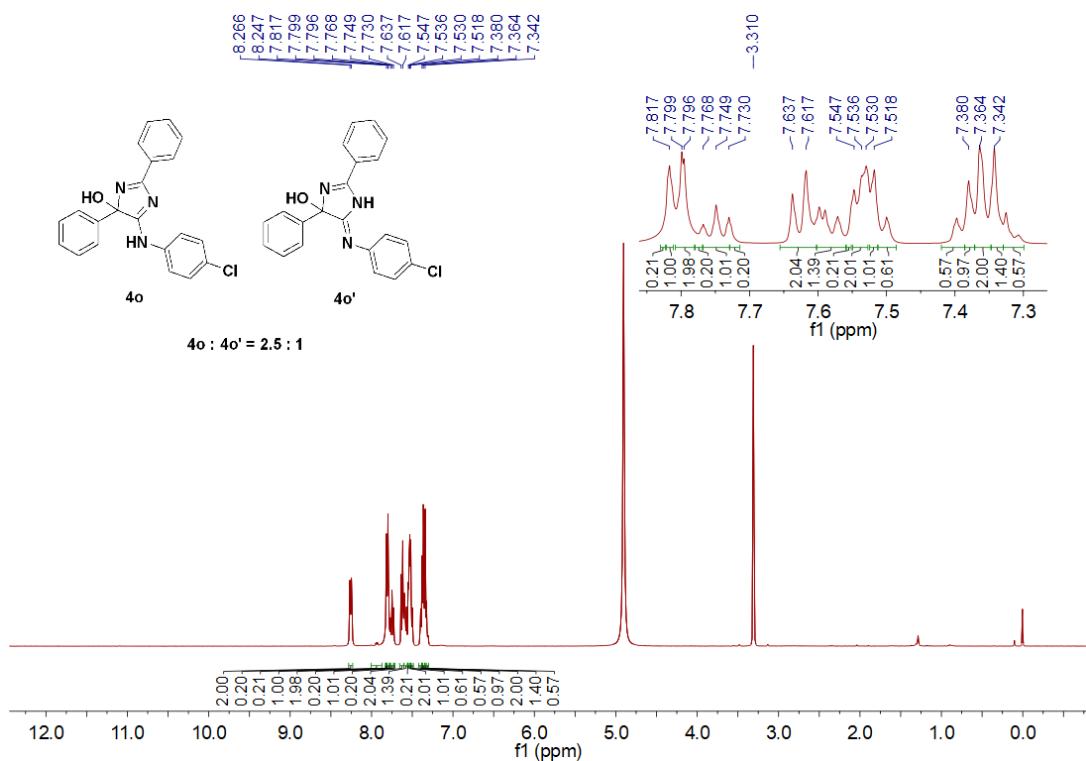


Fig S34. ^1H NMR (400 MHz) spectrum of **4o** and **4o'** (2.5:1 ratio) (CD_3OD , rt)

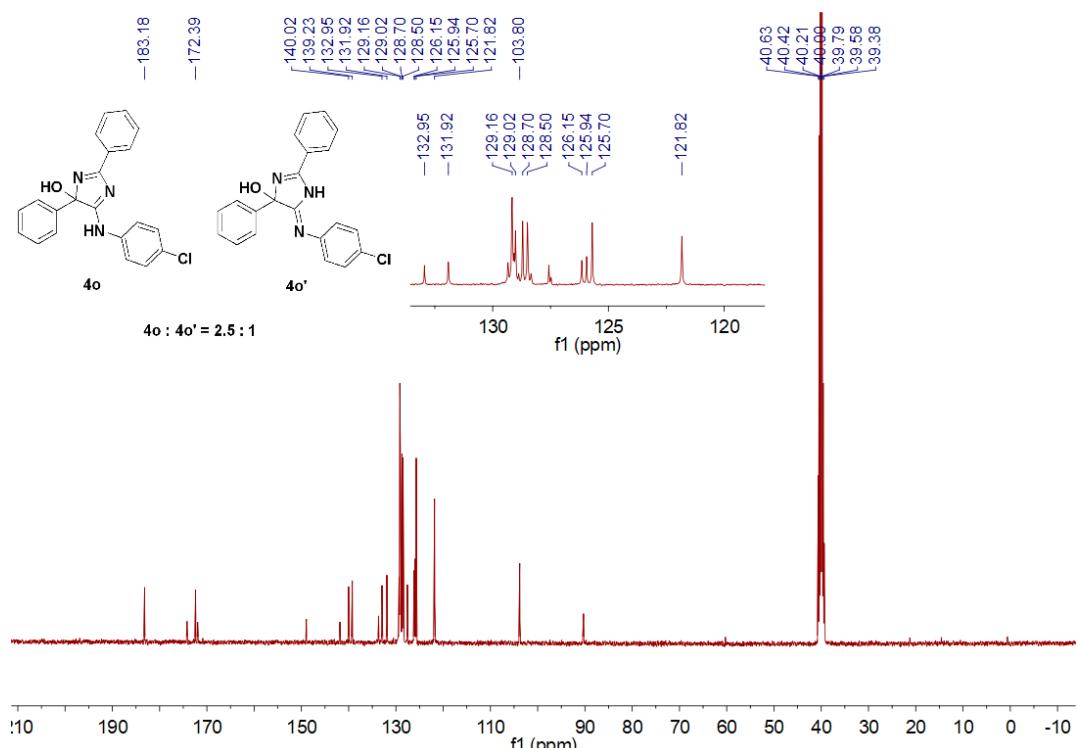


Fig S35. $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz) spectrum of **4o** and **4o'** (2.5:1 ratio) (DMSO-D_6 , rt)

Mixture of 4p and 4p' (2.5:1 ratio)

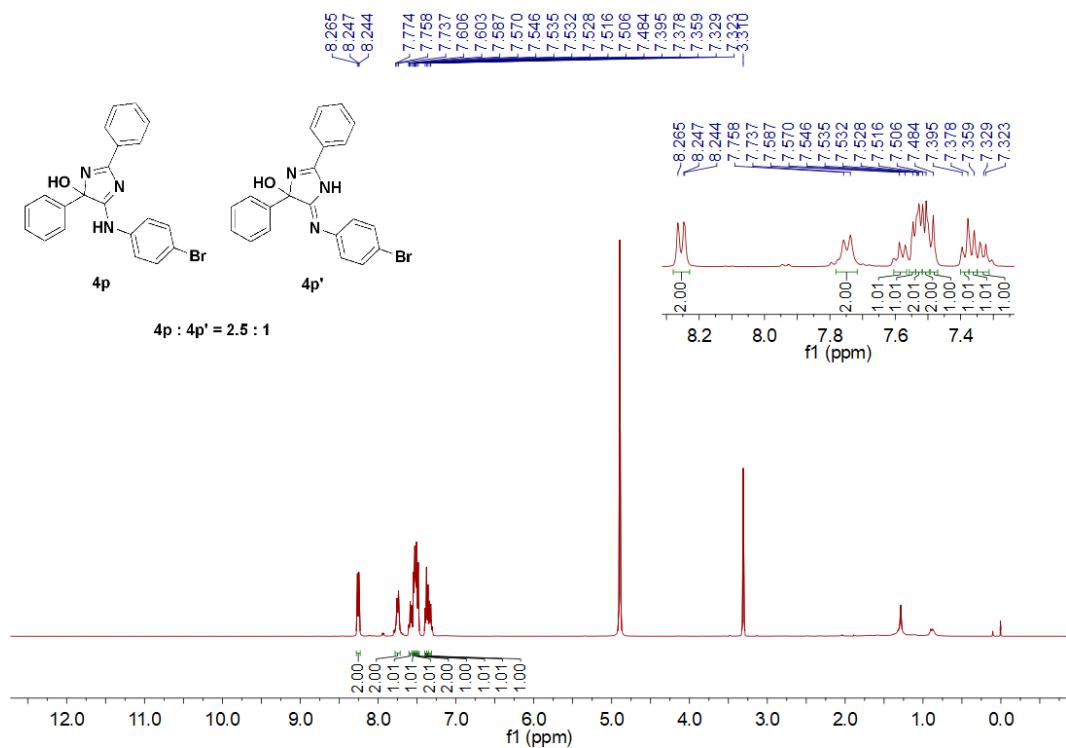


Fig S36. ¹H NMR (400 MHz) spectrum of **4p and 4p'** (2.5:1 ratio) (CD₃OD, rt)

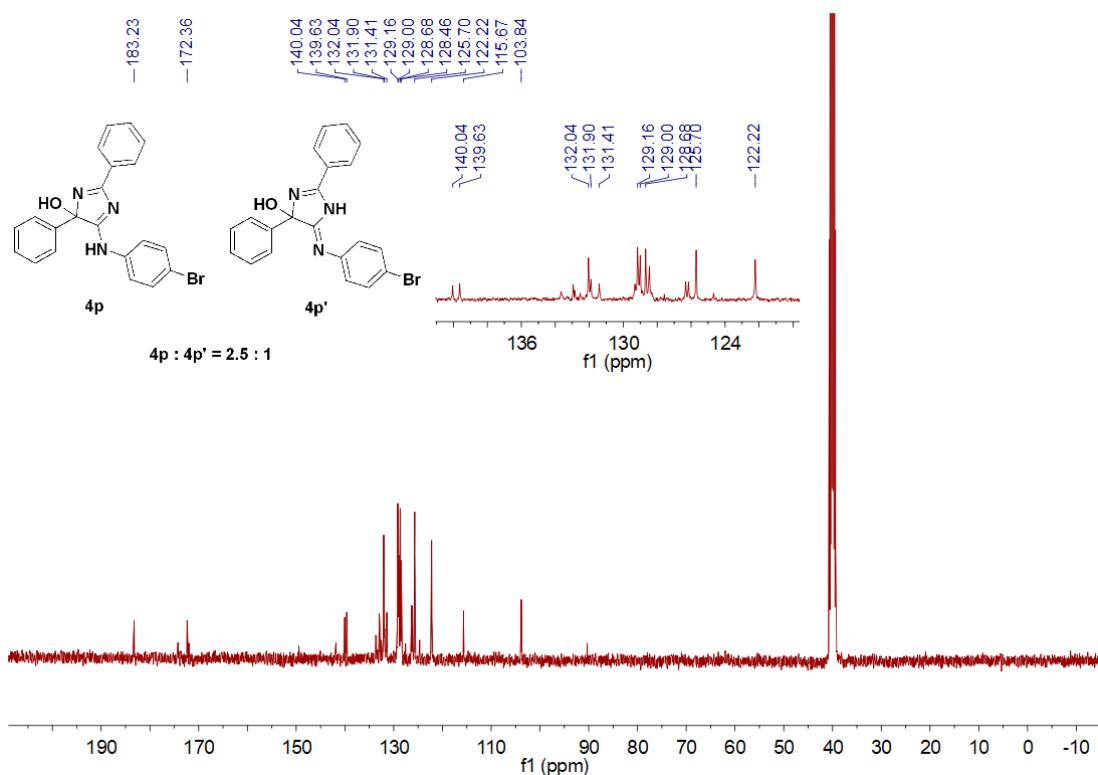


Fig S37. ¹³C{¹H} NMR (100 MHz) spectrum of **4p and 4p'** (2.5:1 ratio) (DMSO-D₆, rt)

Mixture of **4q** and **4q'** (2:1 ratio)

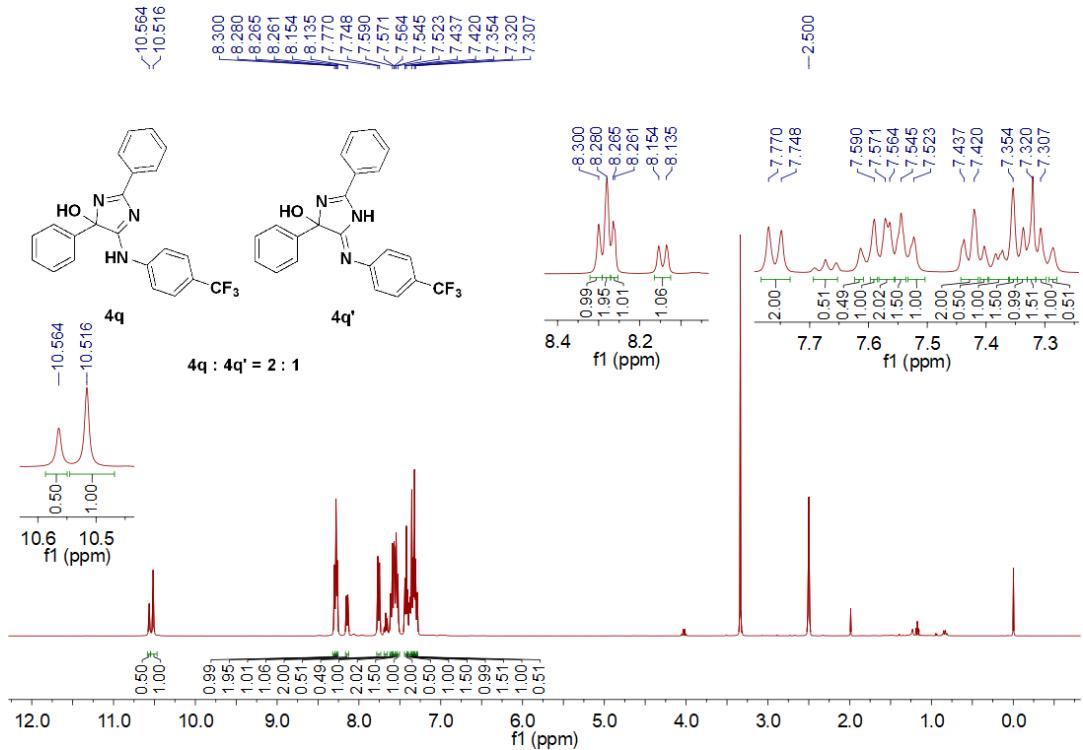


Fig S38. ^1H NMR (400 MHz) spectrum of **4q** and **4q'** (2:1 ratio) (DMSO- D_6 , rt)

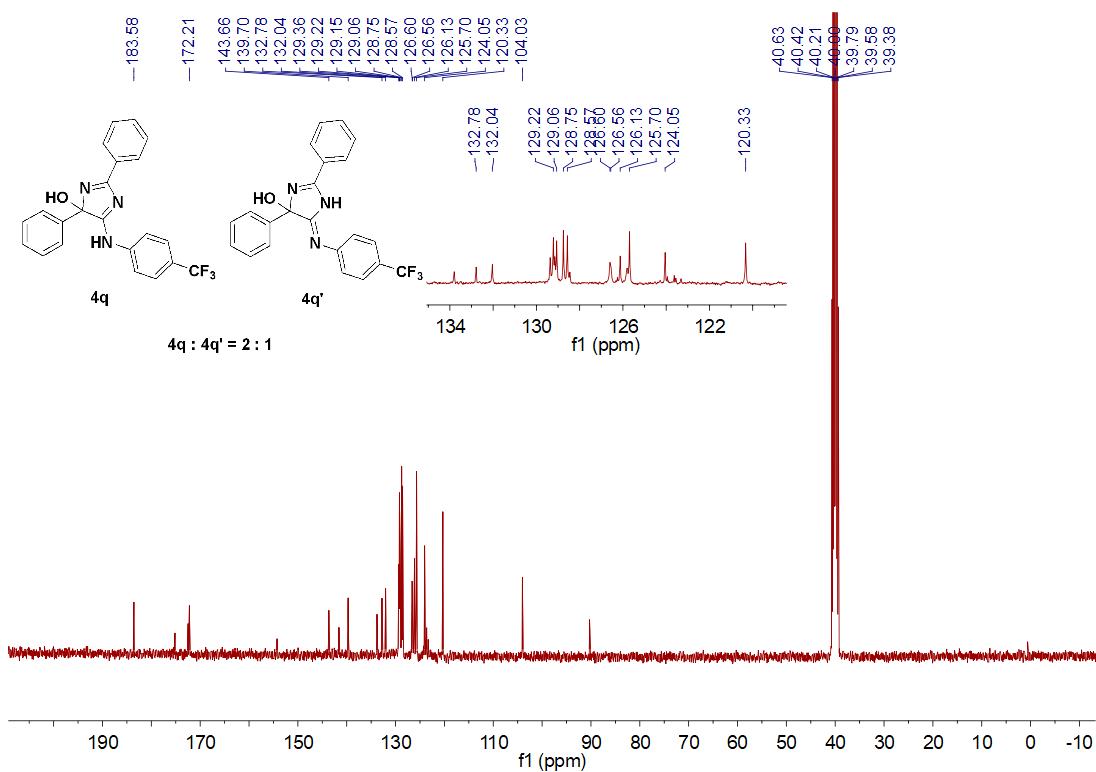


Fig S39. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4q** and **4q'** (2:1 ratio) (DMSO- D_6 , rt)

4r

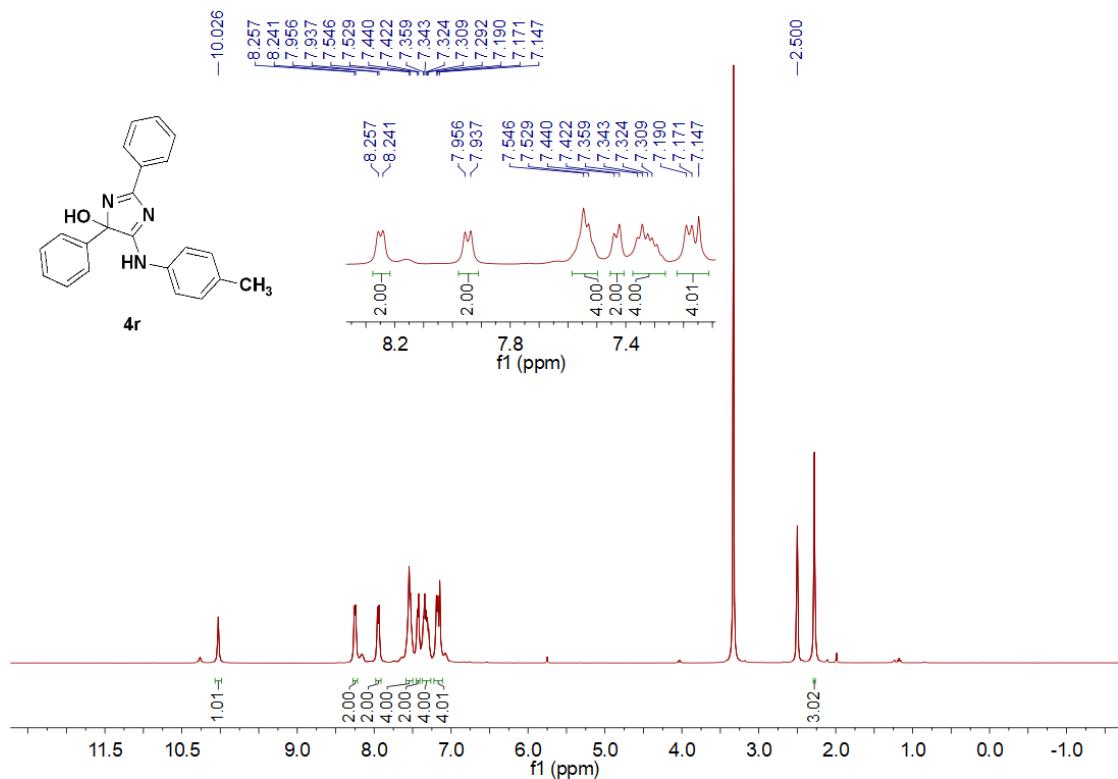


Fig S40. ^1H NMR (400 MHz) spectrum of **4r** (DMSO- D_6 , rt)

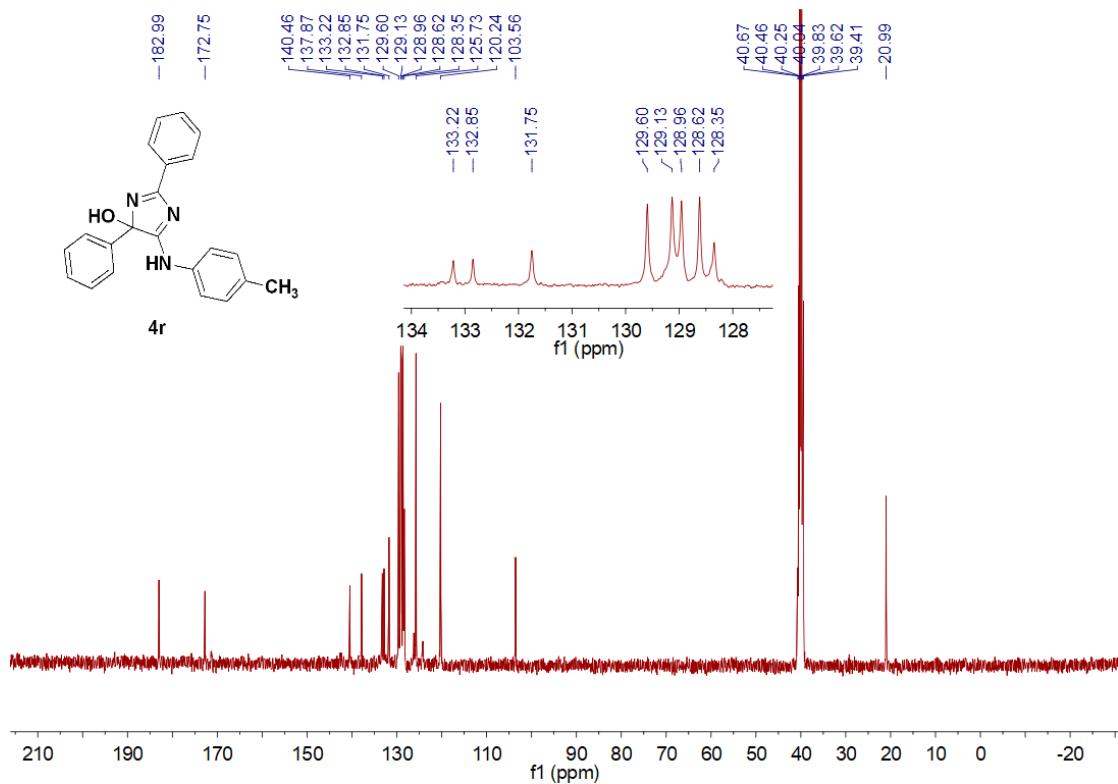


Fig S41. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4r** (DMSO- D_6 , rt)

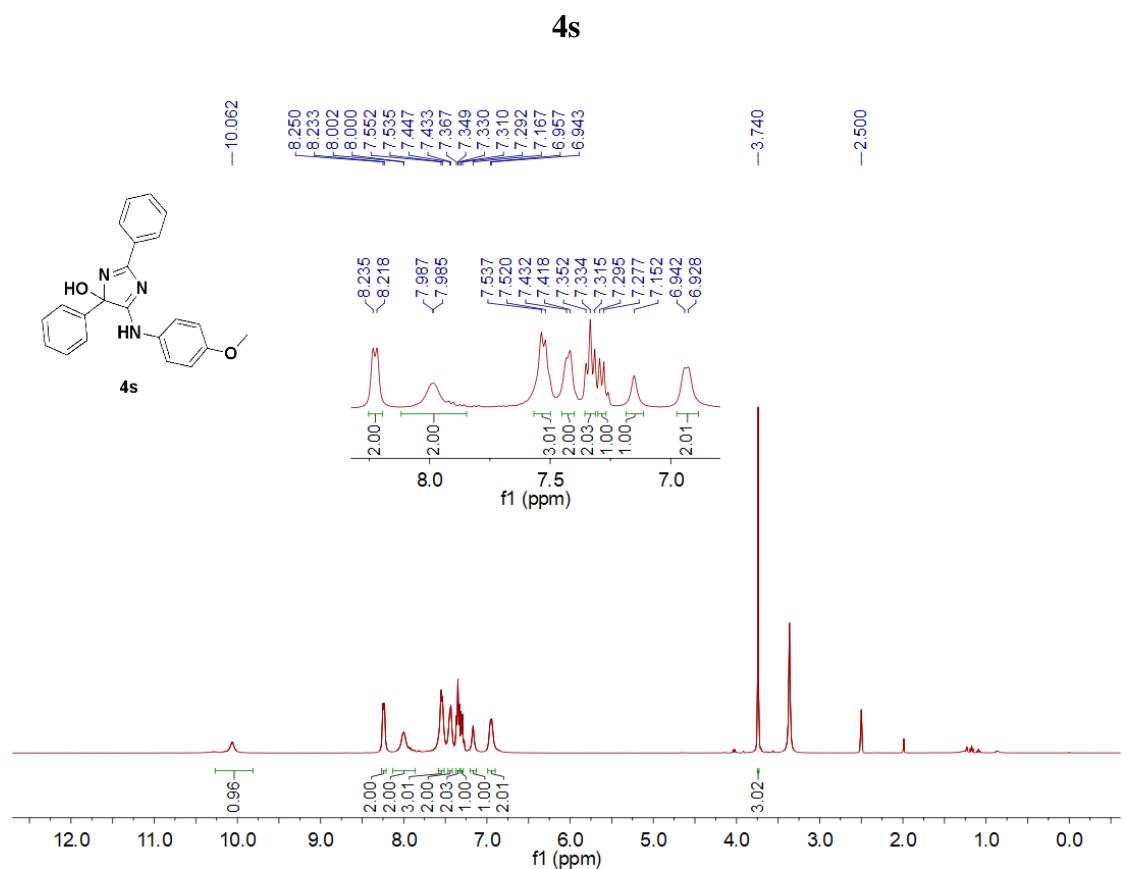


Fig S42. ^1H NMR (400 MHz) spectrum of **4s** (DMSO- D_6 , rt)

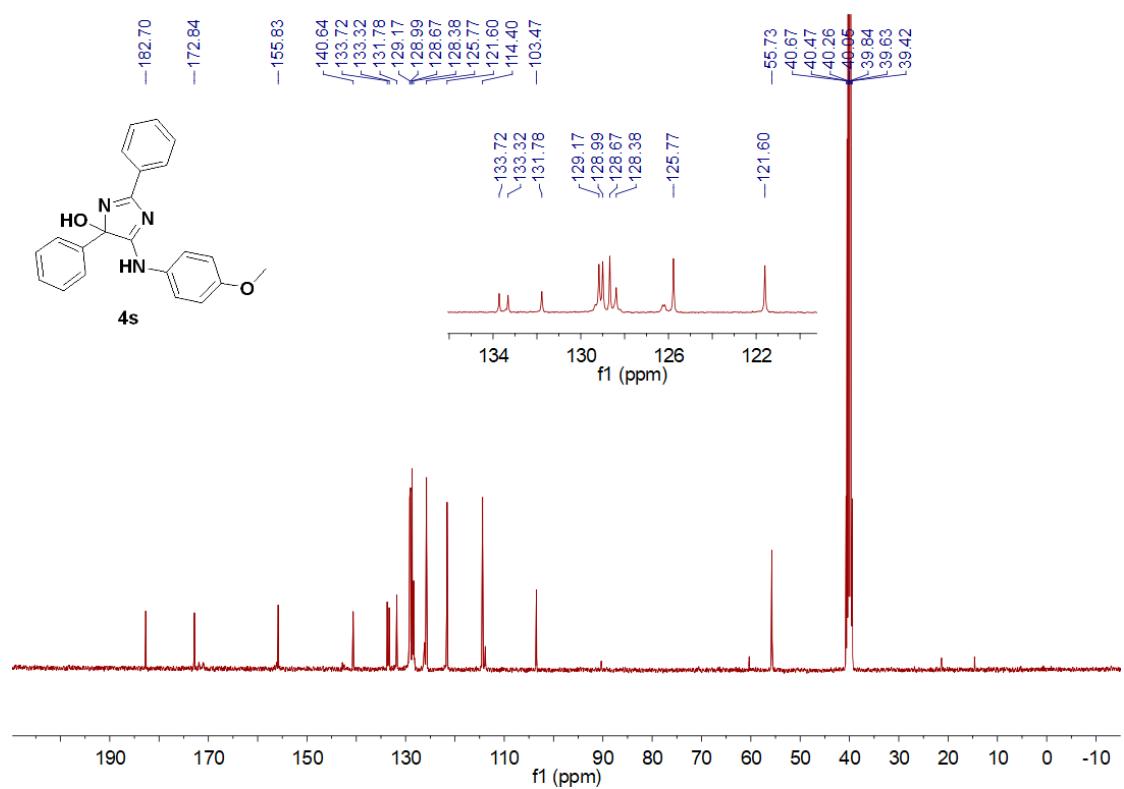


Fig S43. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4s** (DMSO- D_6 , rt)

Mixture of **4t and **4t'** (5:1 ratio)**

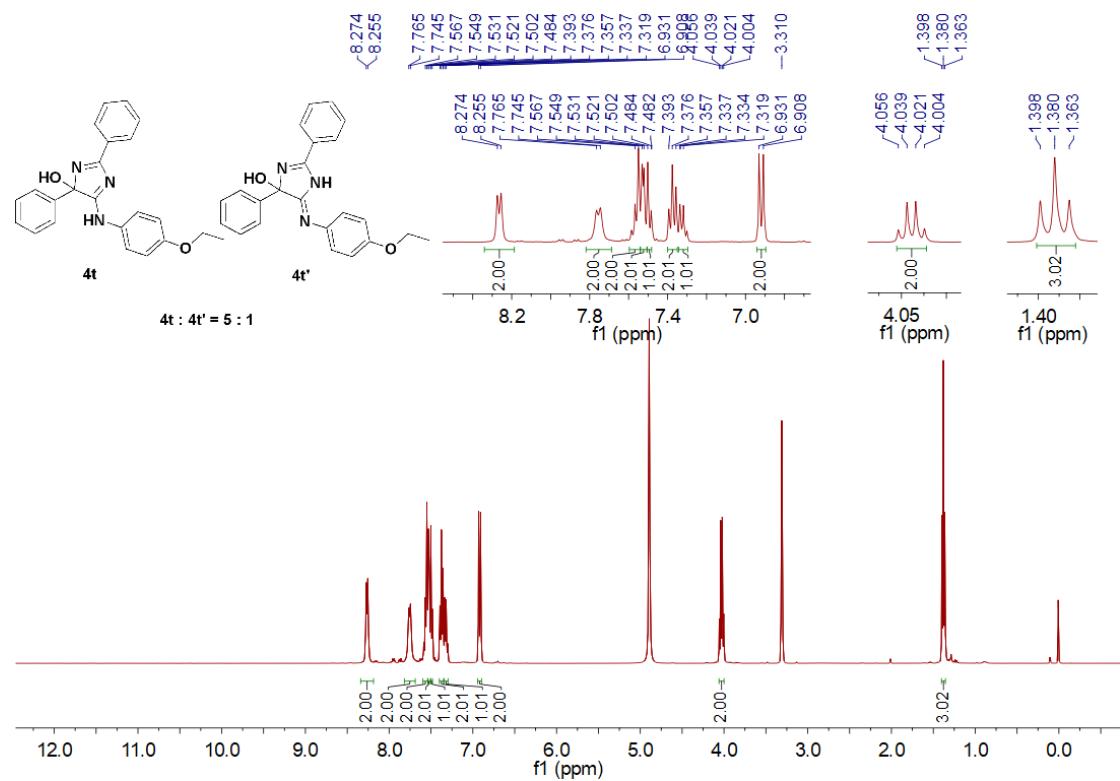


Fig S44. ¹H NMR (400 MHz) spectrum of **4t** and **4t'** (5:1 ratio) (CD₃OD, rt)

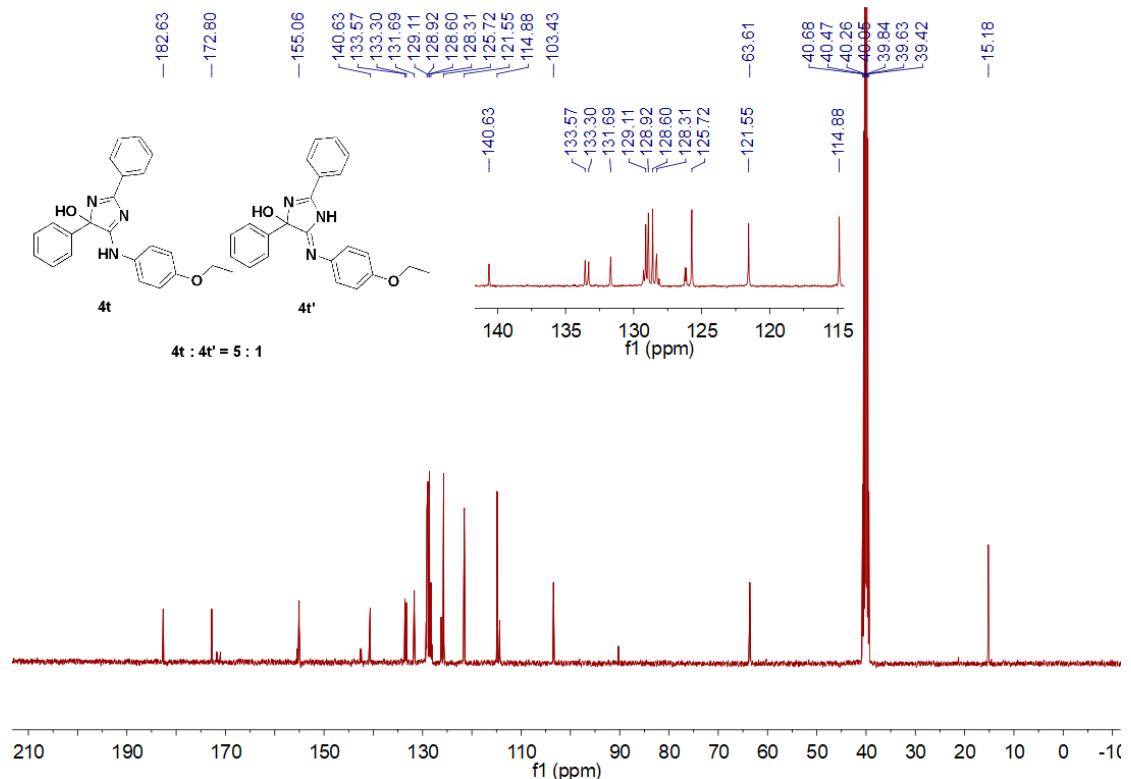


Fig S45. ¹³C{¹H} NMR (100 MHz) spectrum of **4t** and **4t'** (5:1 ratio) (DMSO-CD₃, rt)

4u

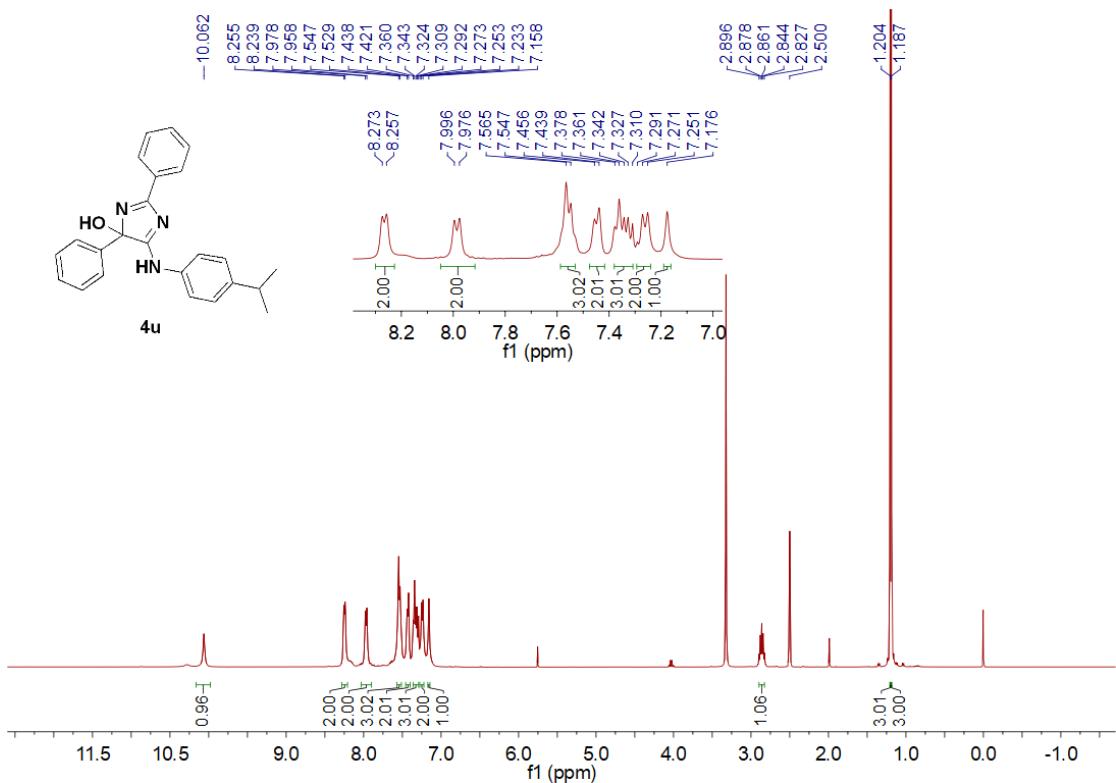


Fig S46. ¹H NMR (400 MHz) spectrum of **4u** (DMSO-D₆, rt)

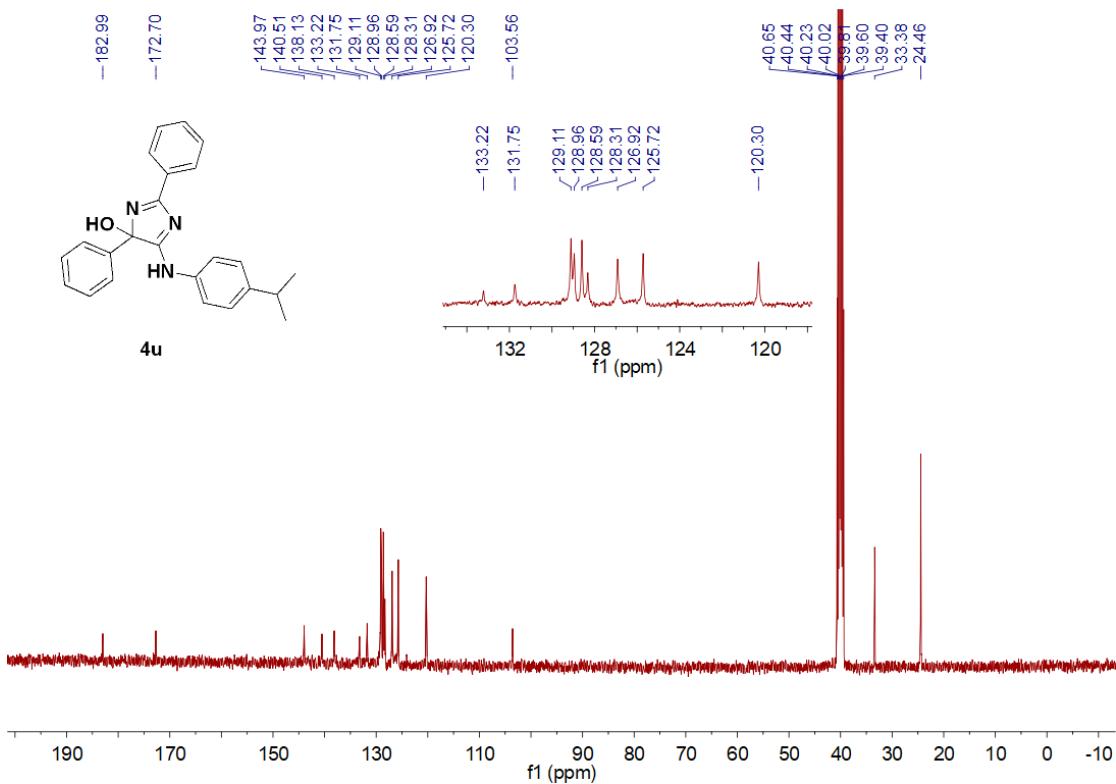


Fig S47. ¹³C{¹H} NMR (100 MHz) spectrum of **4u** (DMSO-D₆, rt)

Mixture of **4v and **4v'** (2:1 ratio)**

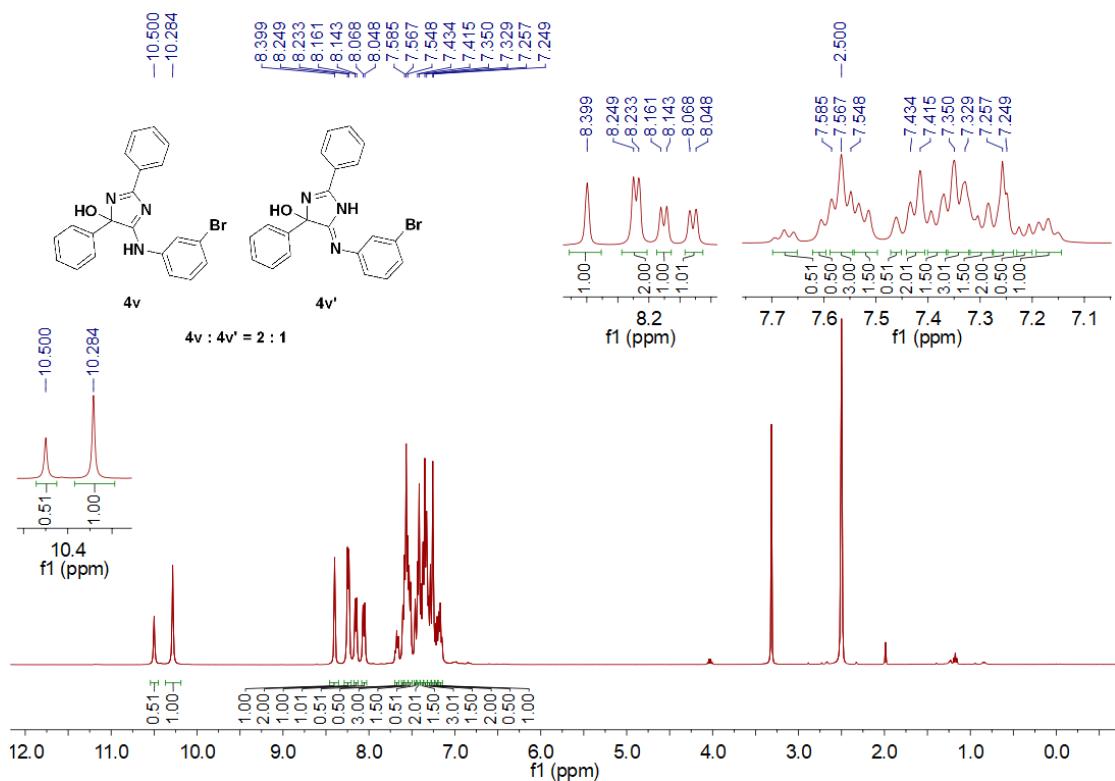


Fig S48. ^1H NMR (400 MHz) spectrum of **4v** and **4v'** (2:1 ratio) (DMSO- D_6 , rt)

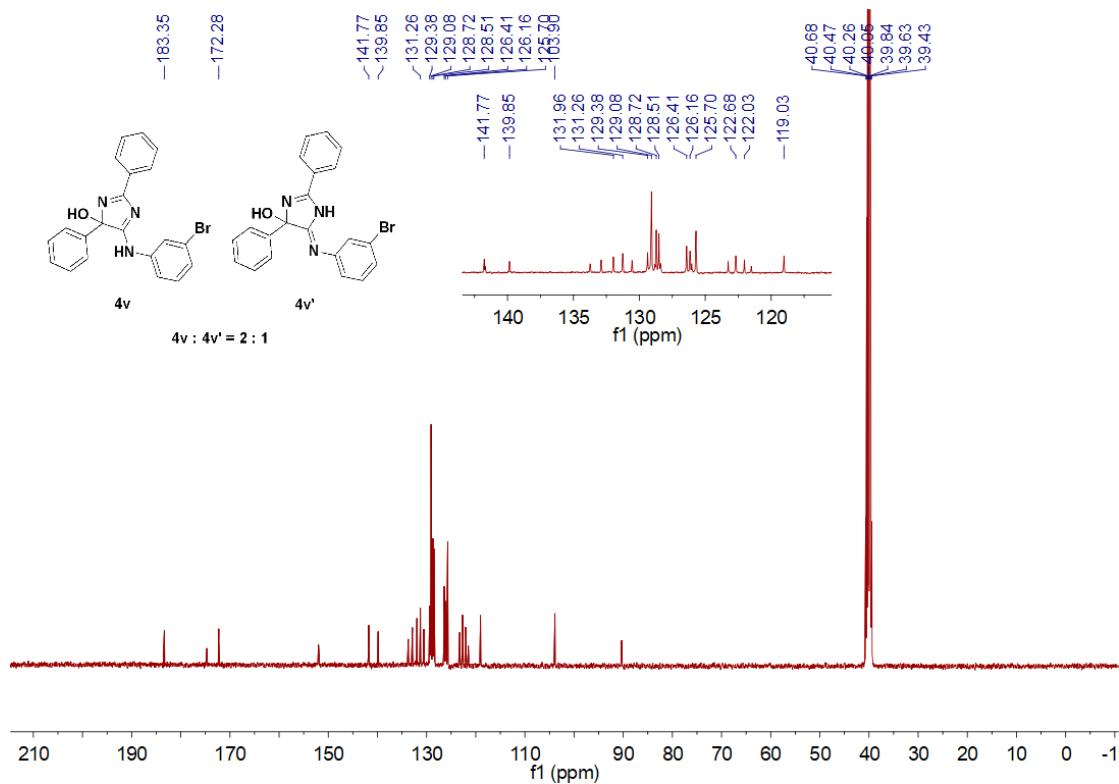


Fig S49. $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz) spectrum of **4v** and **4v'** (2:1 ratio) (DMSO- D_6 , rt)

Mixture of **4w** and **4w'** (5:1 ratio)

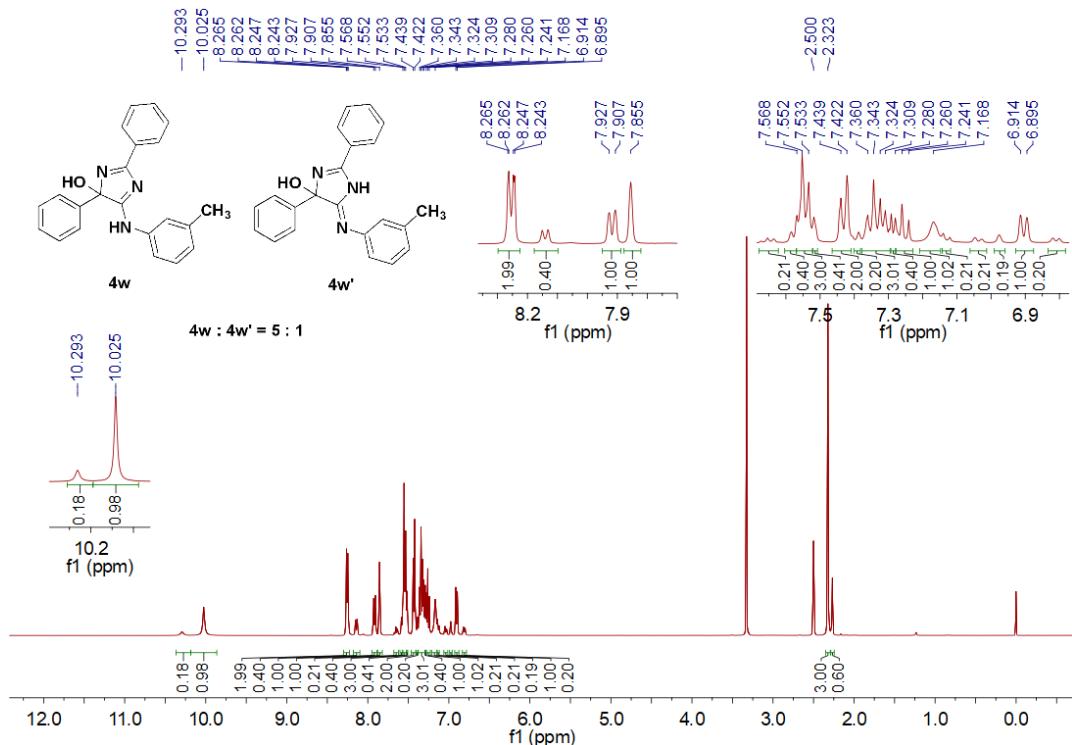


Fig S50. ^1H NMR (400 MHz) spectrum of **4w** and **4w'** (5:1 ratio) (DMSO- D_6 , rt)

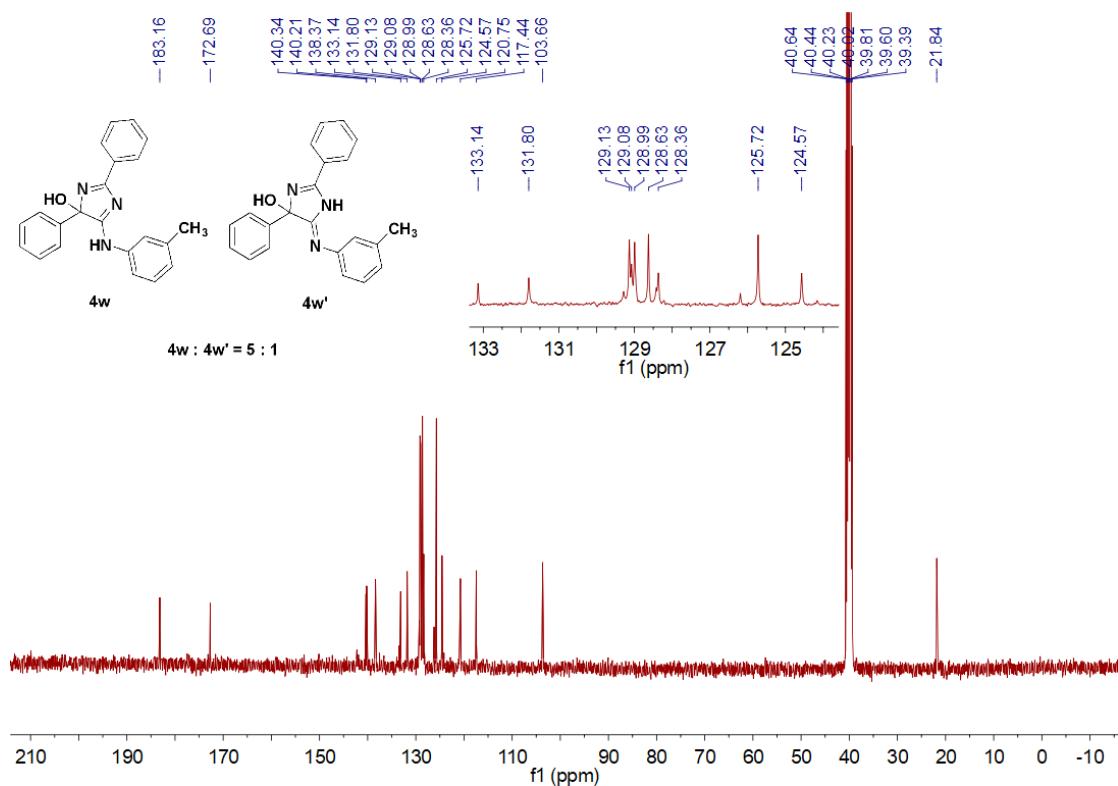


Fig S51. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4w** and **4w'** (5:1 ratio) (DMSO- D_6 , rt)

4x

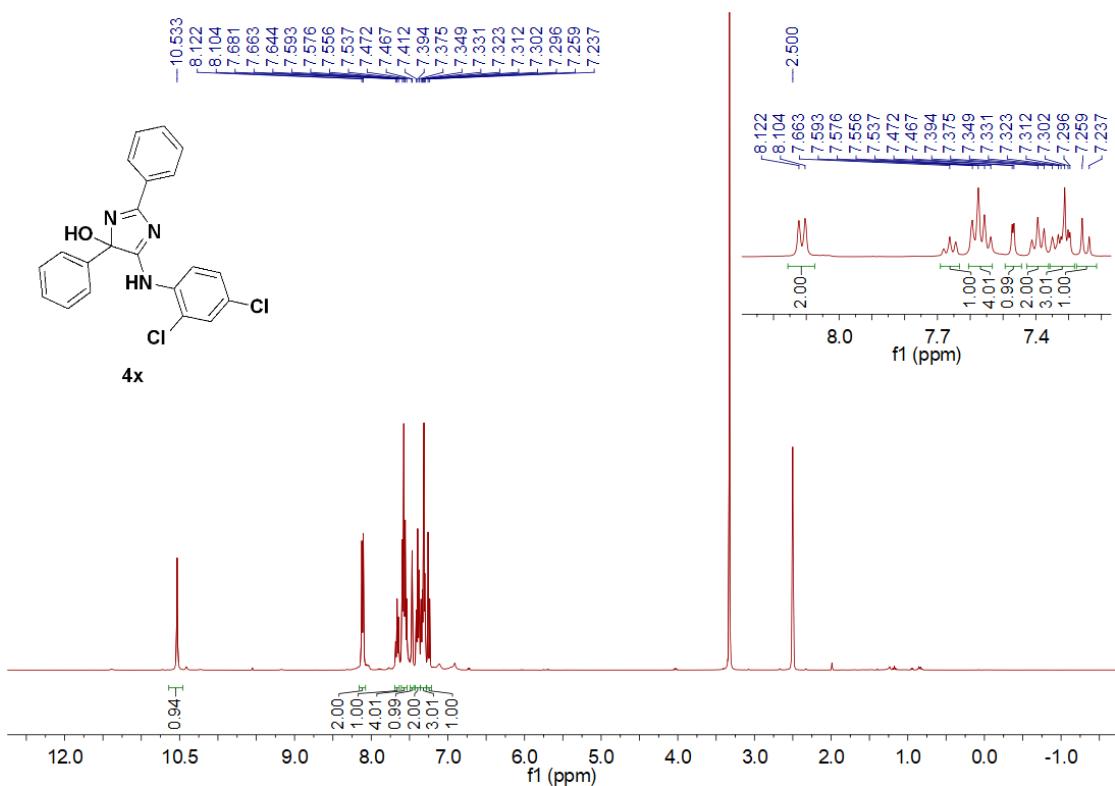


Fig S52. ^1H NMR (400 MHz) spectrum of **4x** (DMSO- D_6 , rt)

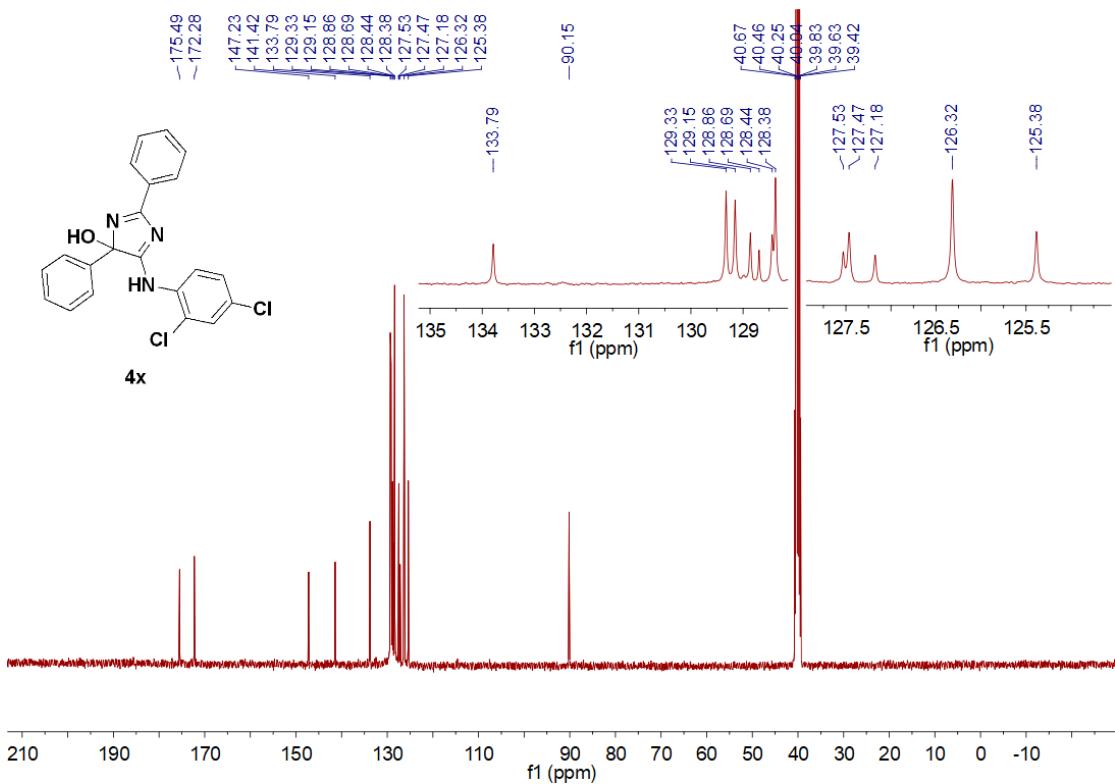


Fig S53. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **4x** (DMSO- D_6 , rt)

4y

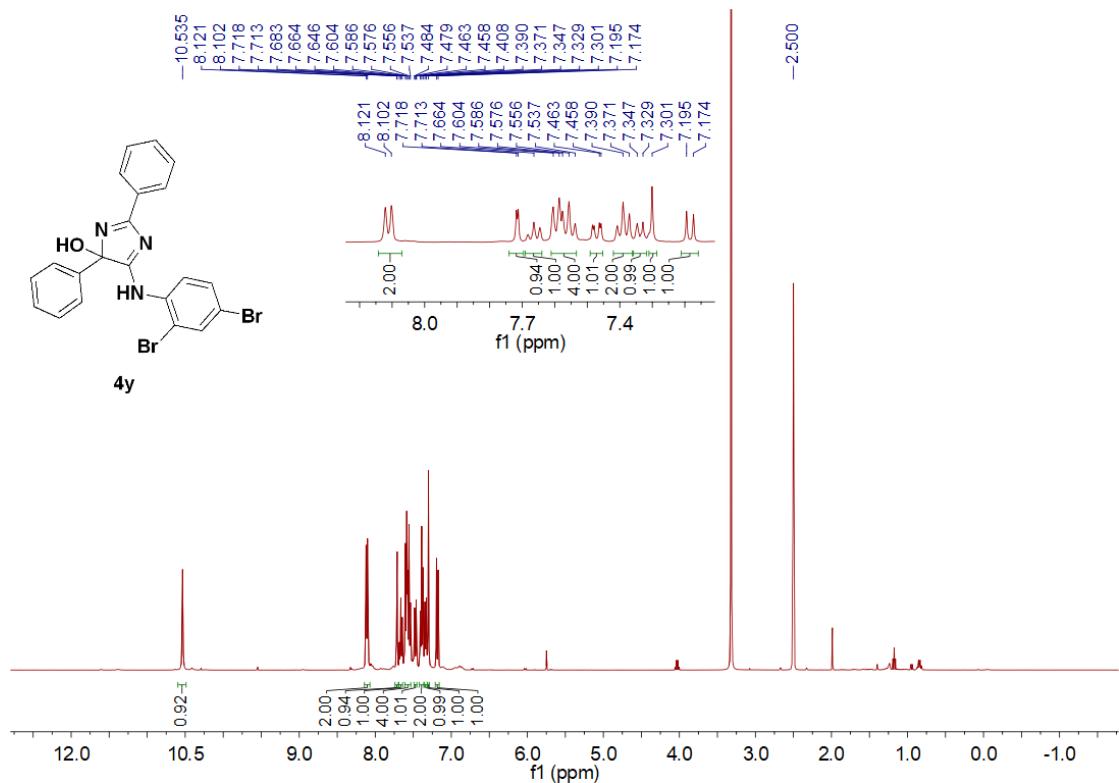


Fig S54. ¹H NMR (400 MHz) spectrum of **4y** (DMSO-D₆, rt)

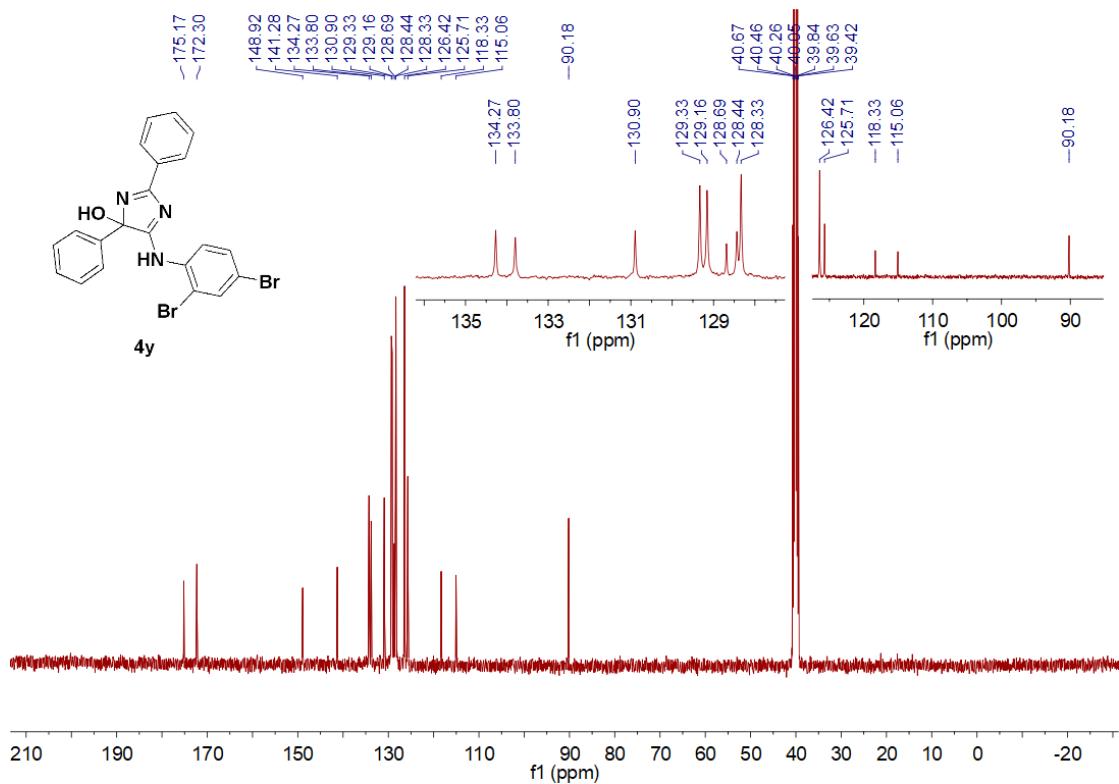


Fig S55. ¹³C{¹H} NMR (100 MHz) spectrum of **4y** (DMSO-D₆, rt)

4z

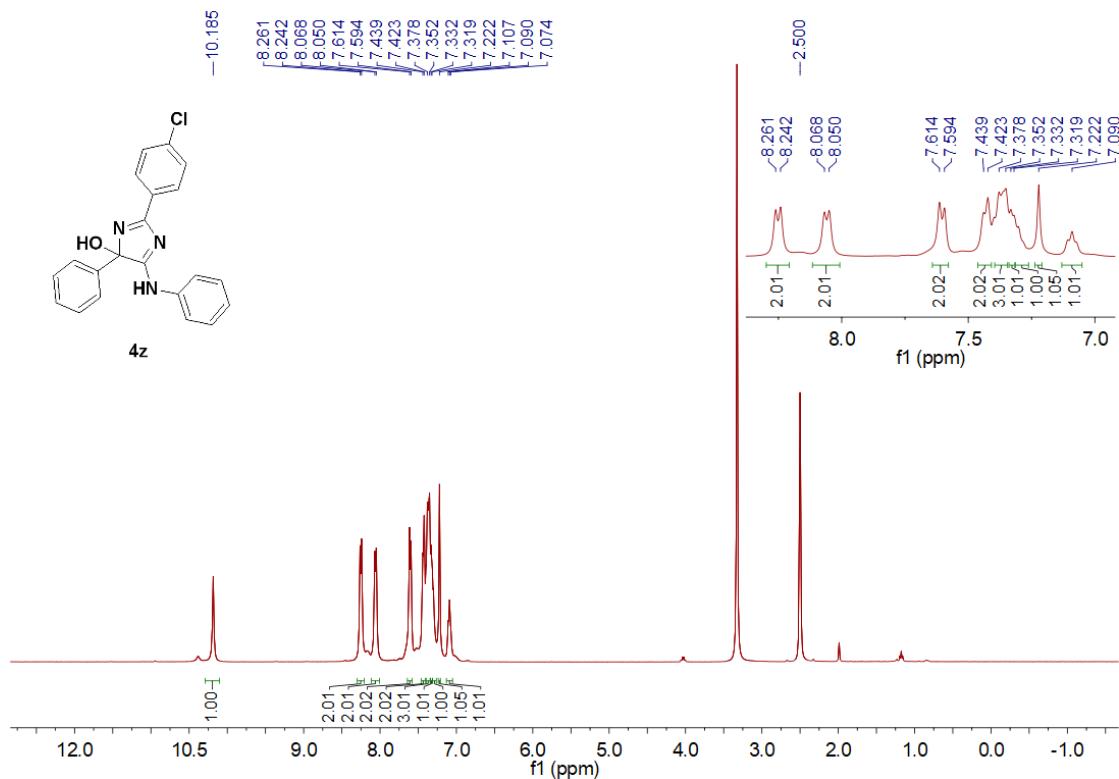


Fig S56. ¹H NMR (400 MHz) spectrum of **4z** (DMSO-D₆, rt)

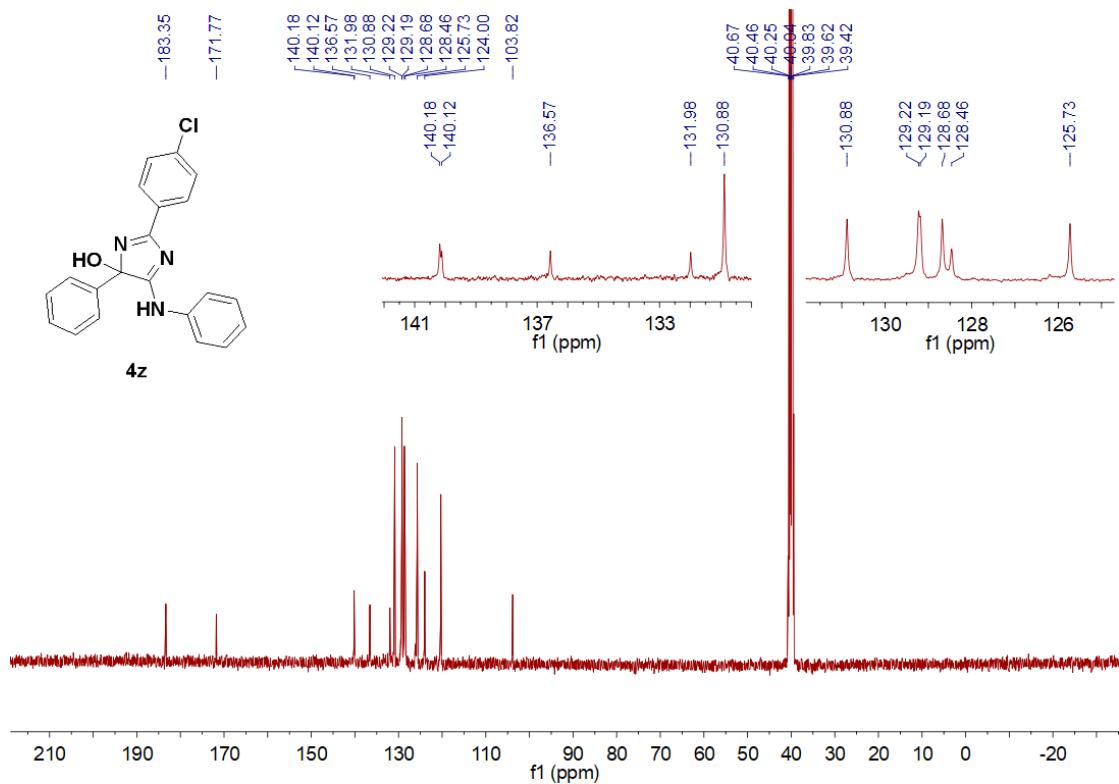


Fig S57. ¹³C{¹H} NMR (100 MHz) spectrum of **4z** (DMSO-D₆, rt)

4aa

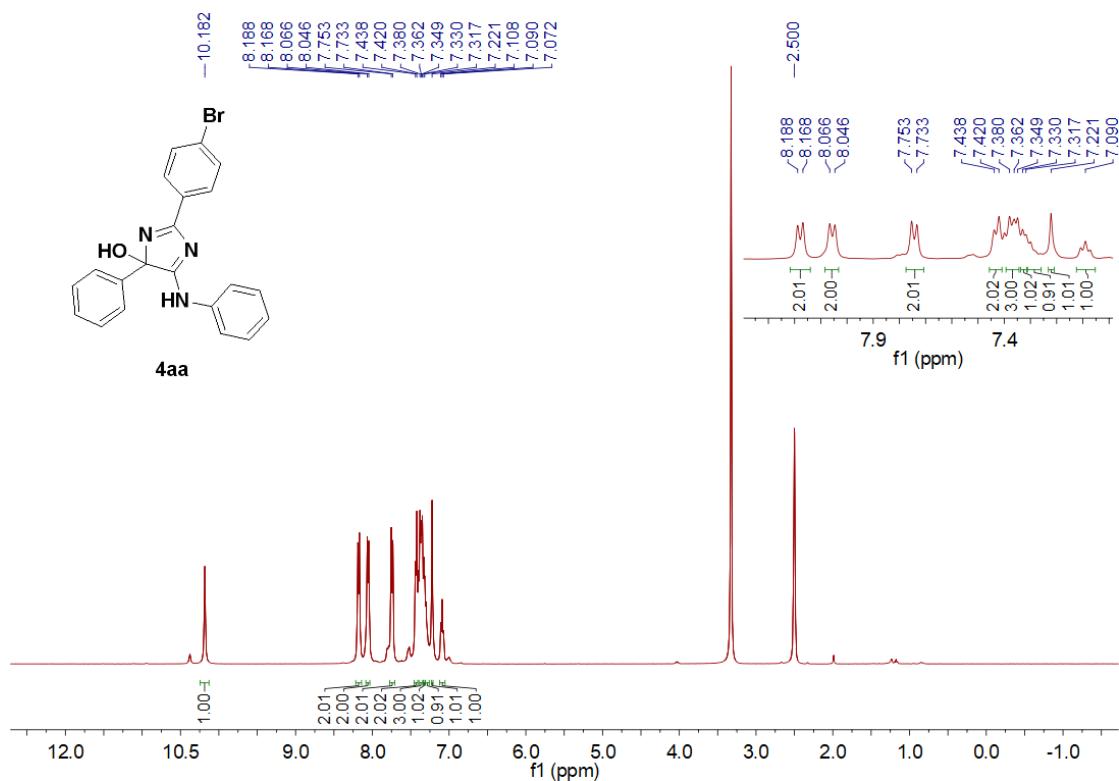


Fig S58. ¹H NMR (400 MHz) spectrum of **4aa** (DMSO-D₆, rt)

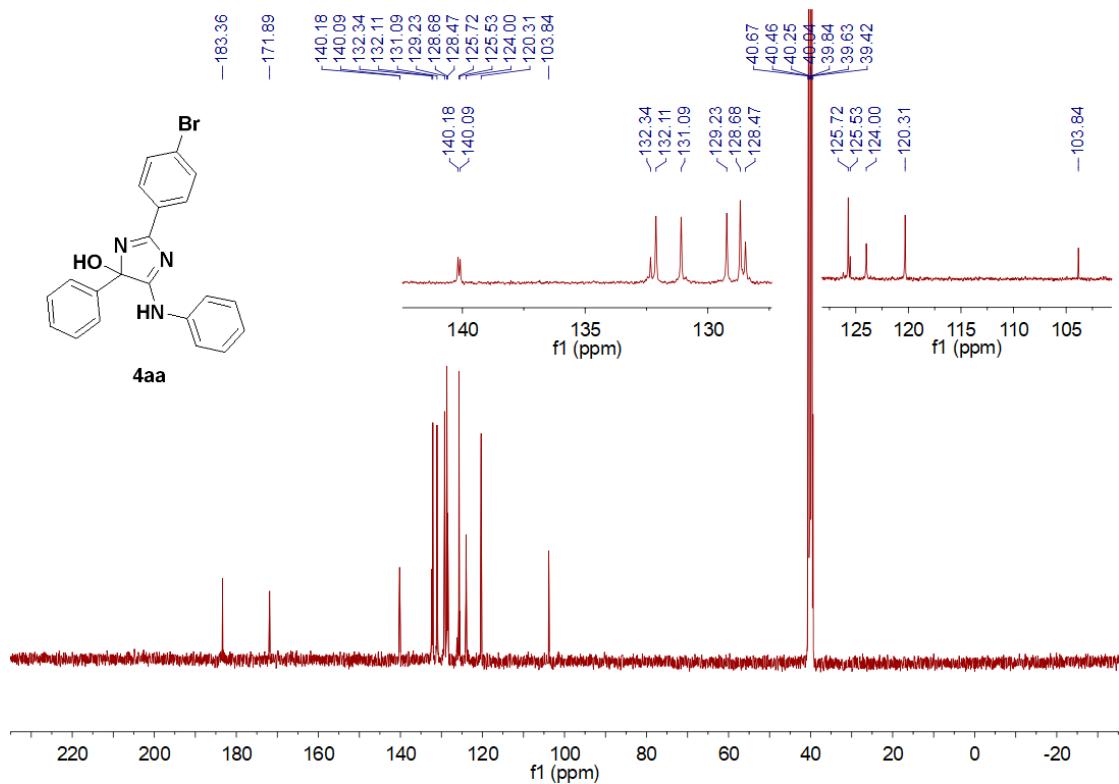


Fig S59. ¹³C{¹H} NMR (100 MHz) spectrum of **4aa** (DMSO-D₆, rt)

Mixture of 4ab and 4ab' (1:1 ratio)

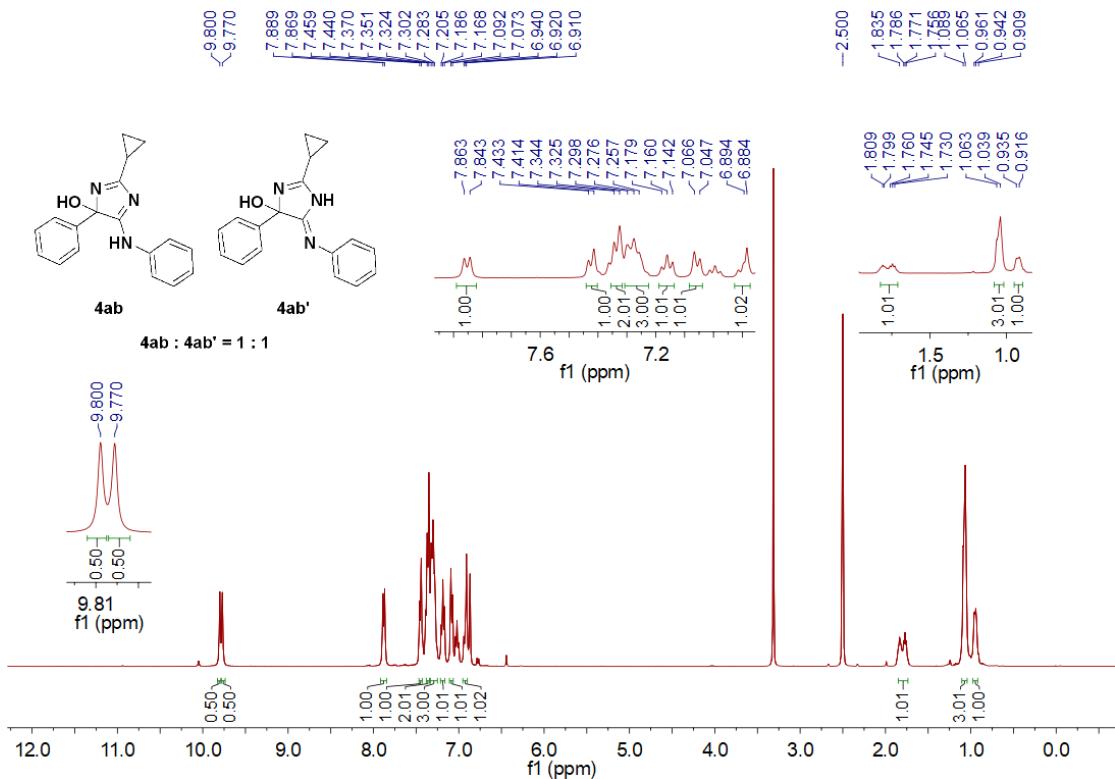


Fig S60. ^1H NMR (400 MHz) spectrum of **4ab and 4ab' (1:1 ratio)** (DMSO- D_6 , rt)

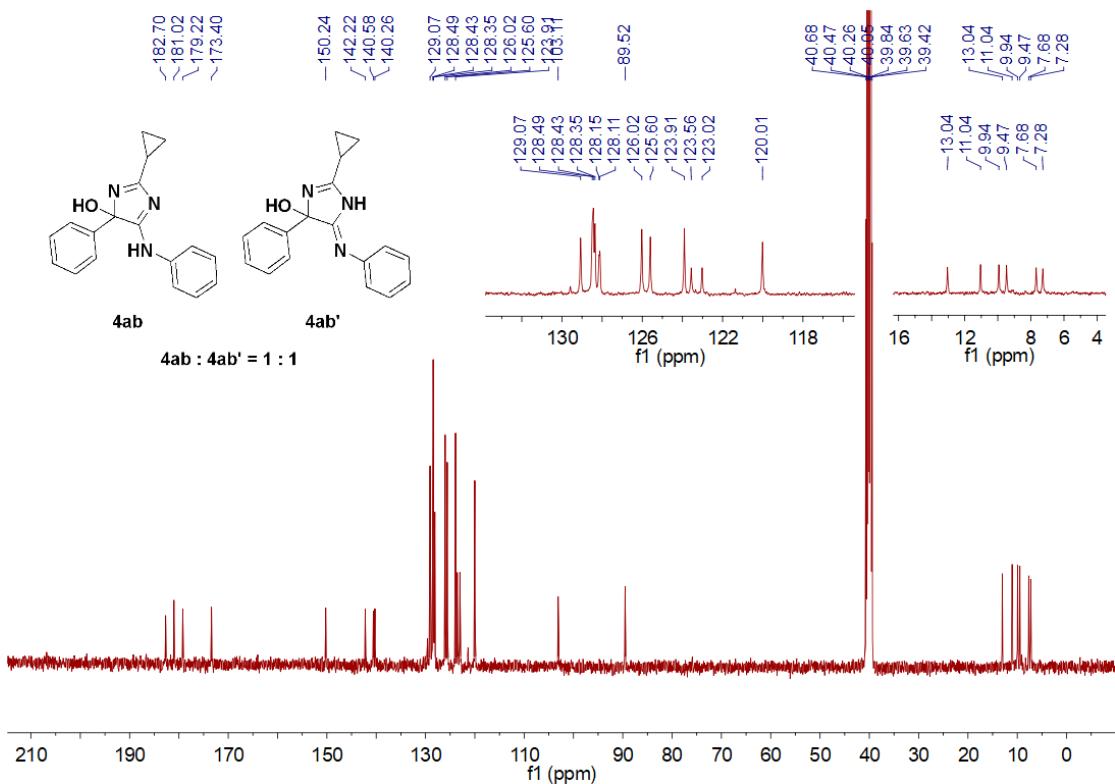


Fig S61. $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz) spectrum of **4ab and 4ab' (1:1 ratio)** (DMSO- D_6 , rt)

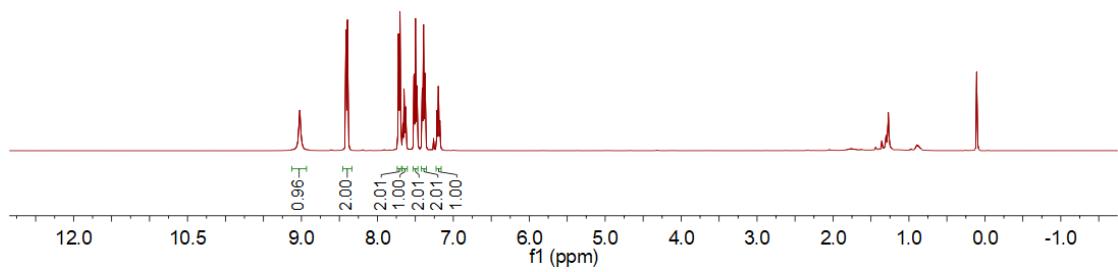
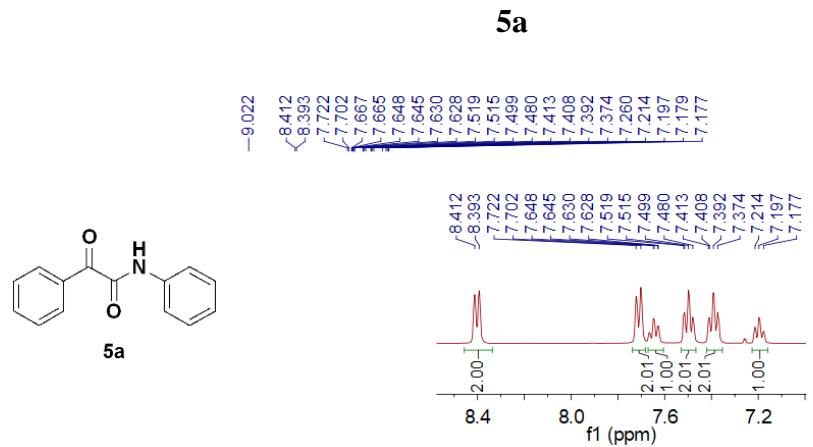


Fig S62. ^1H NMR (400 MHz) spectrum of **5a** (CDCl_3 , rt)

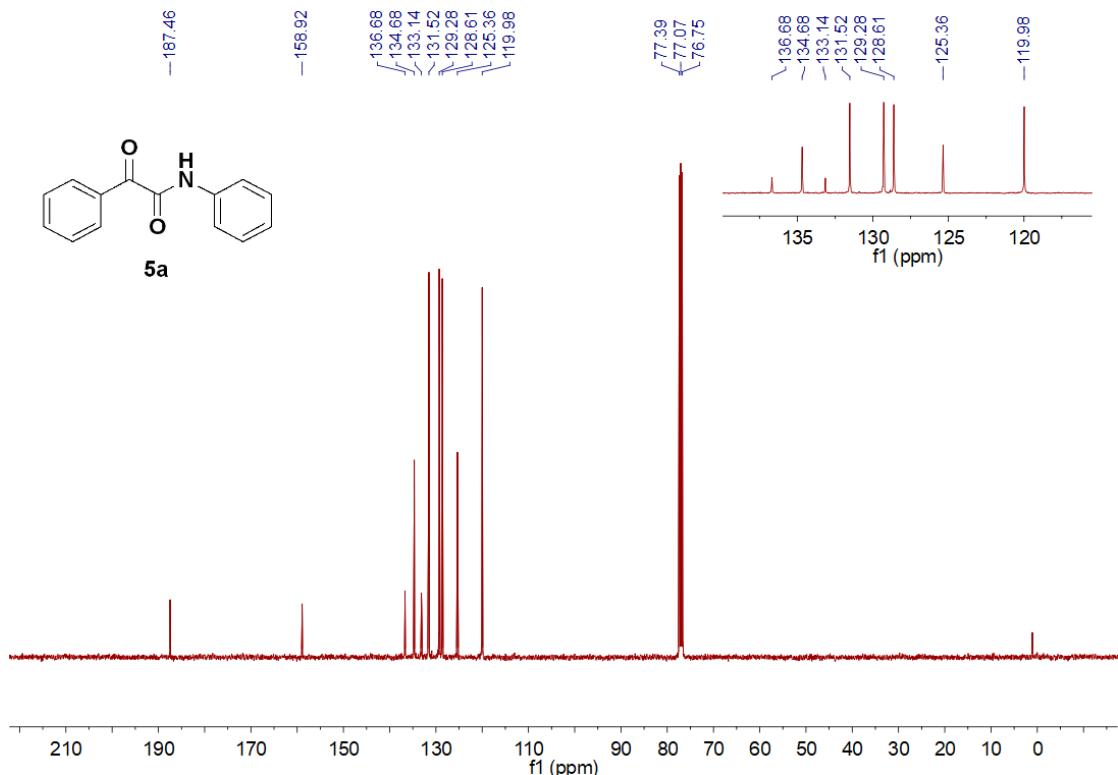


Fig S63. $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz) spectrum of **5a** (CDCl_3 , rt)

5b

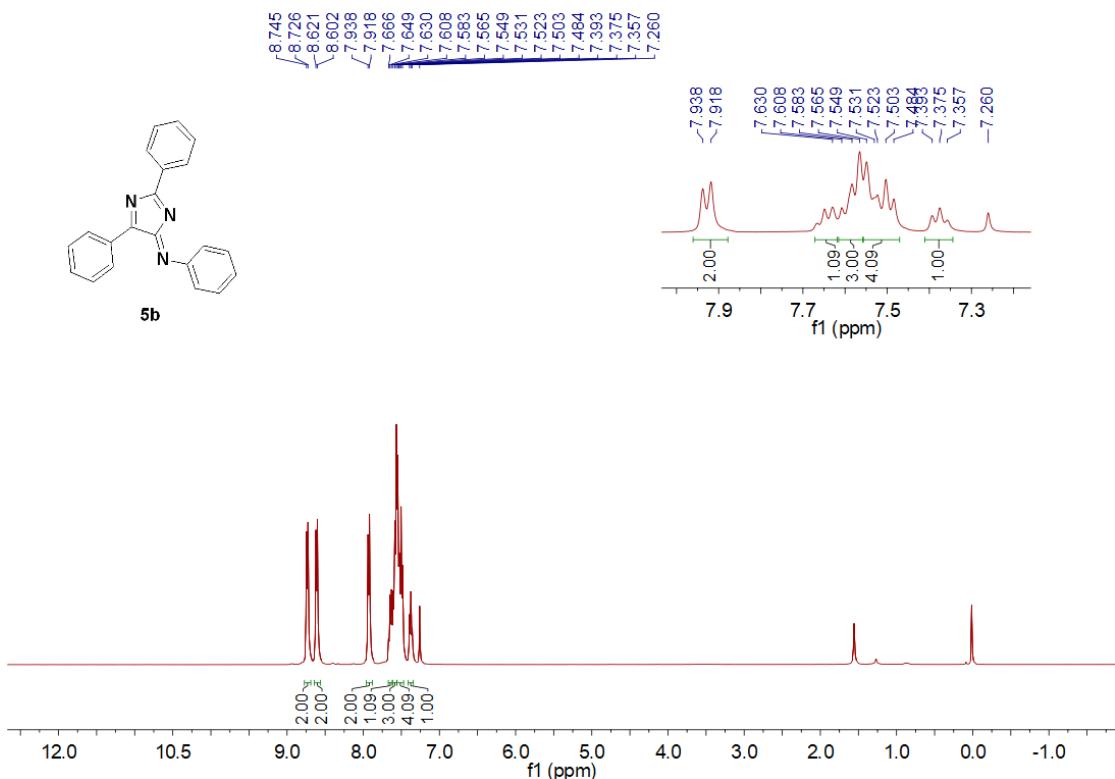


Fig S64. ¹H NMR (400 MHz) spectrum of **5b** (CDCl₃, rt)

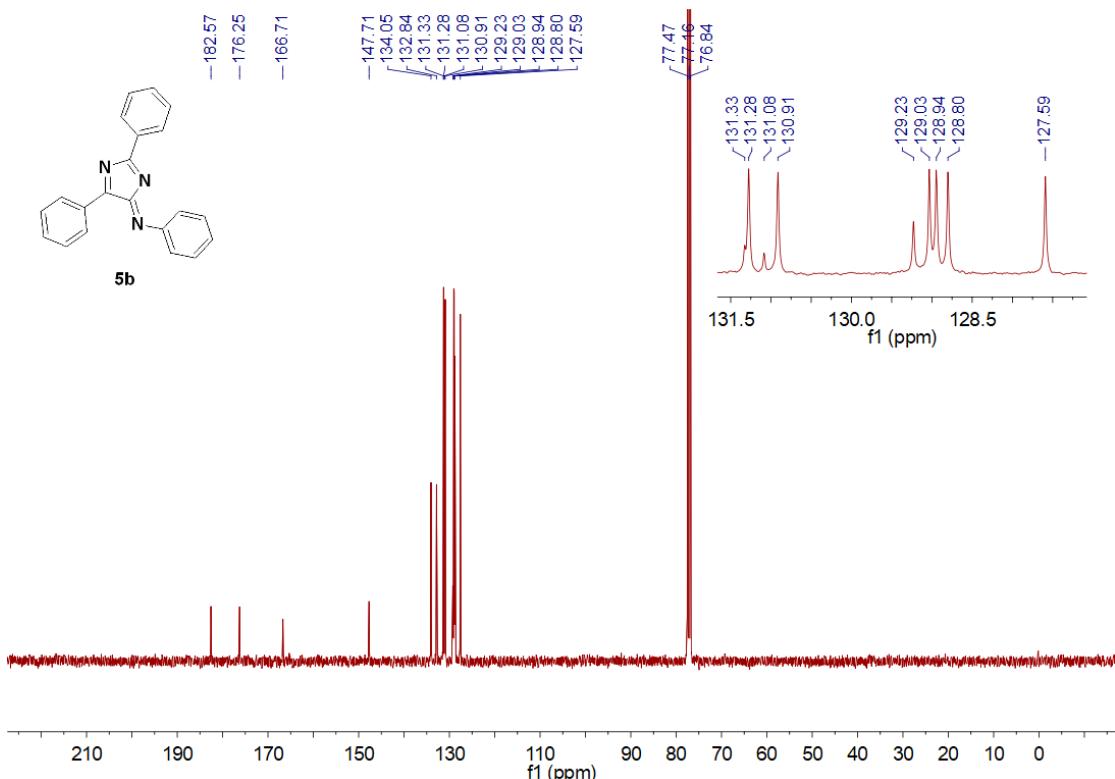


Fig S65. ¹³C{¹H} NMR (100 MHz) spectrum of **5b** (CDCl₃, rt)

5c

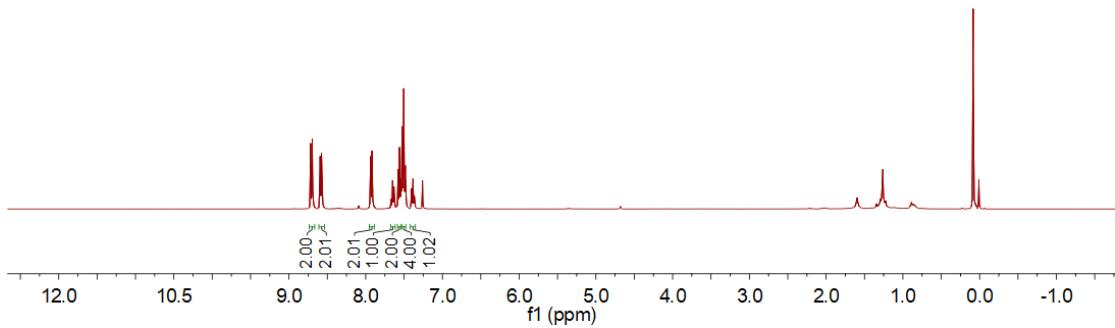
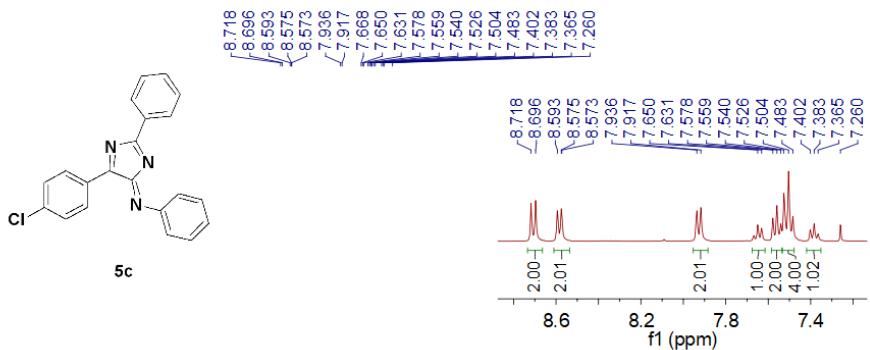


Fig S66. ^1H NMR (400 MHz) spectrum of **5c** (CDCl_3 , rt)

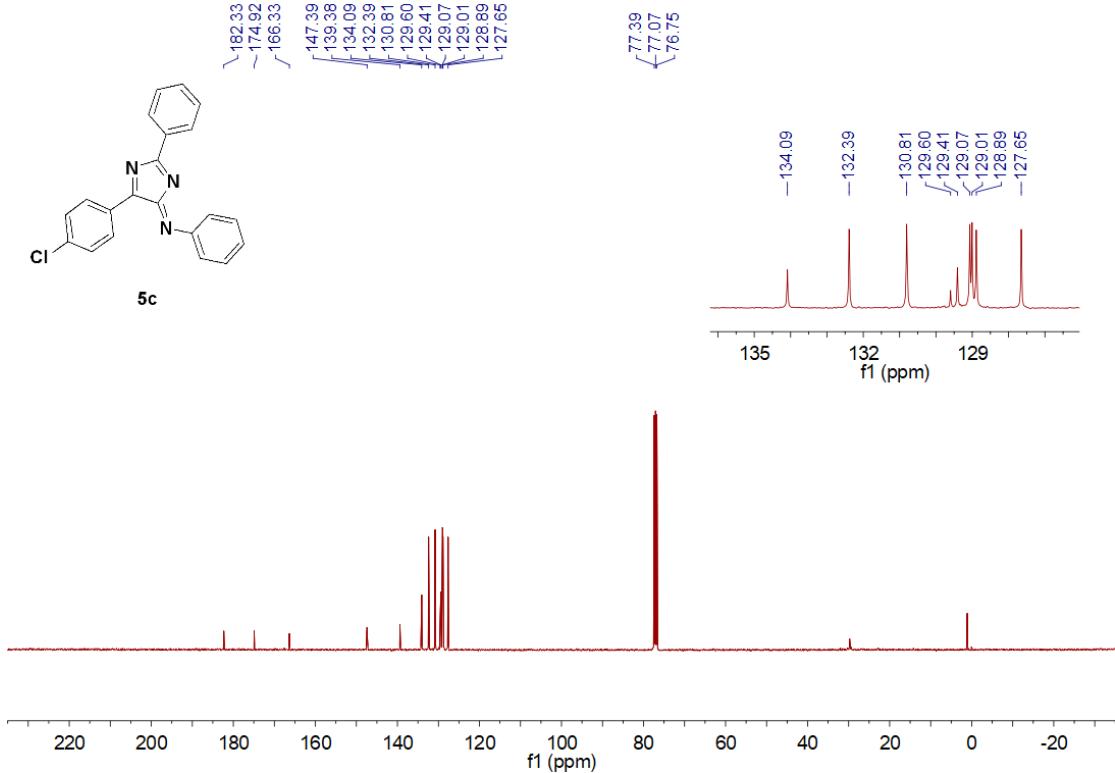


Fig S67. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **5c** (CDCl_3 , rt)

5d

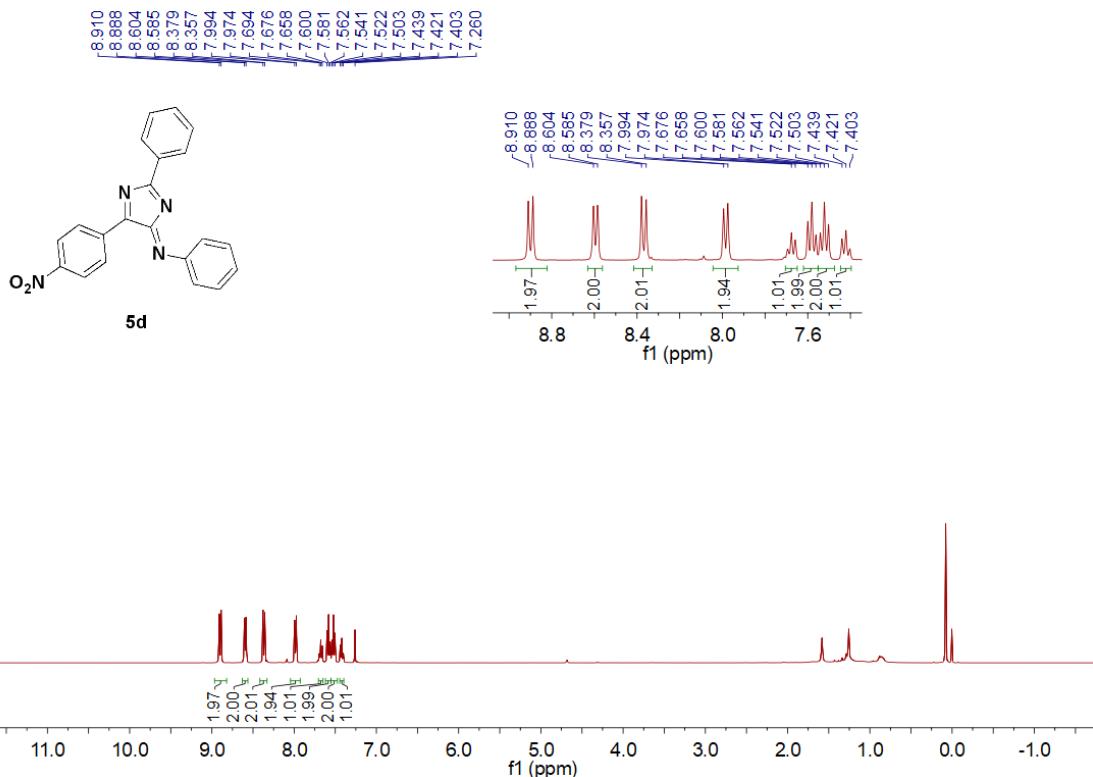


Fig S68. ¹H NMR (400 MHz) spectrum of **5d** (CDCl₃, rt)

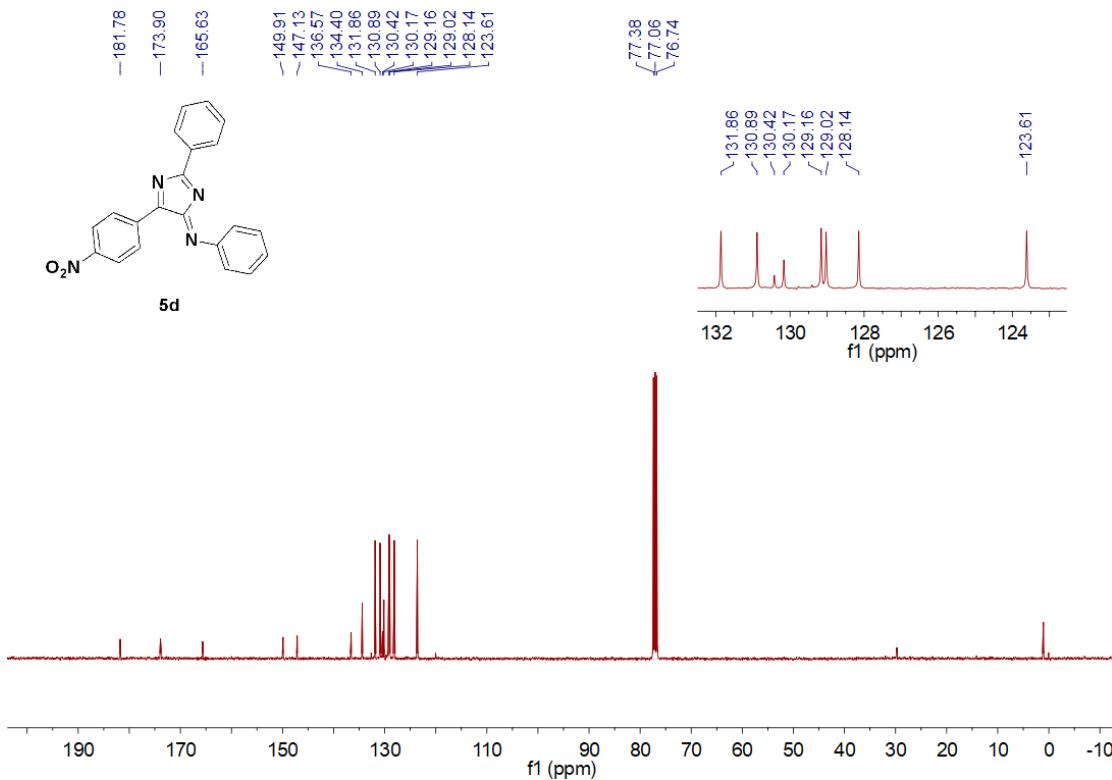


Fig S69. ¹³C{¹H} NMR (100 MHz) spectrum of **5d** (CDCl₃, rt)

5e

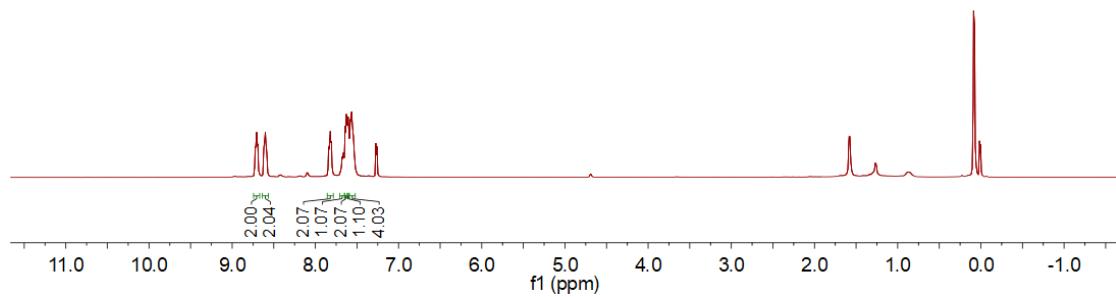
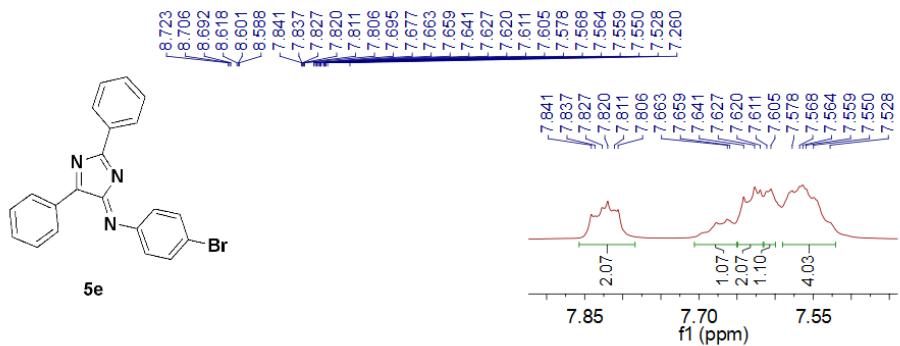


Fig S70. ¹H NMR (400 MHz) spectrum of **5e** (CDCl₃, rt)

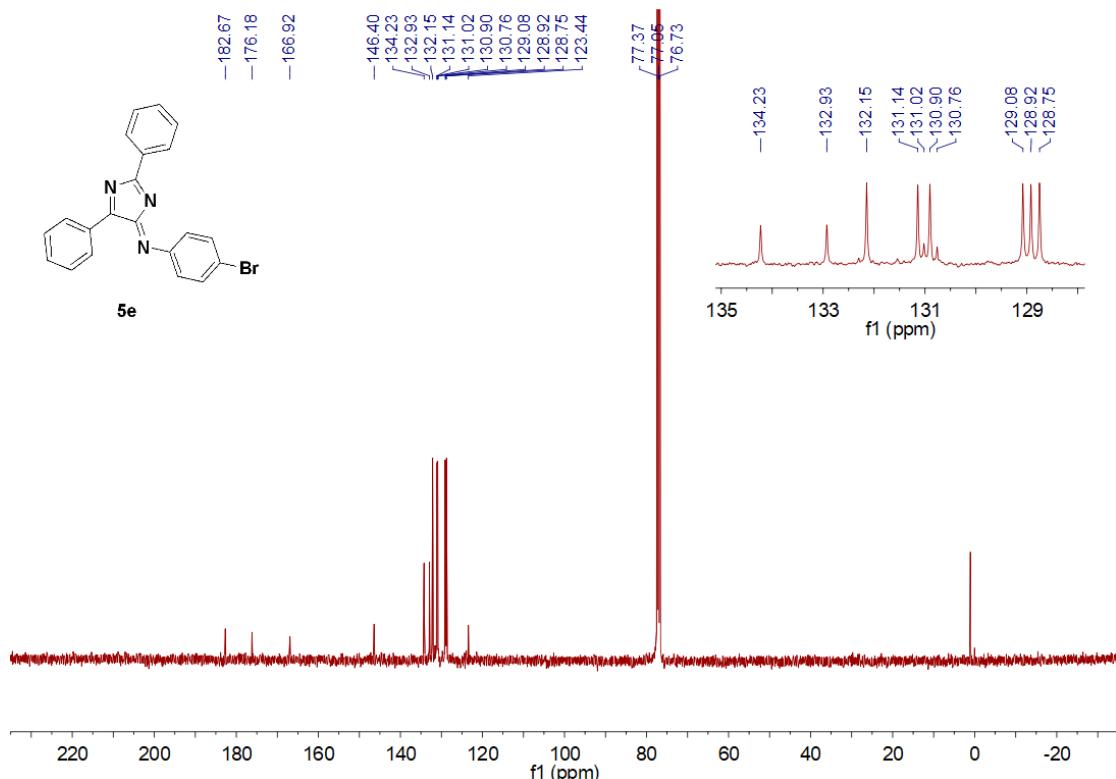


Fig S71. ¹³C{¹H} NMR (100 MHz) spectrum of **5e** (CDCl₃, rt)

5f

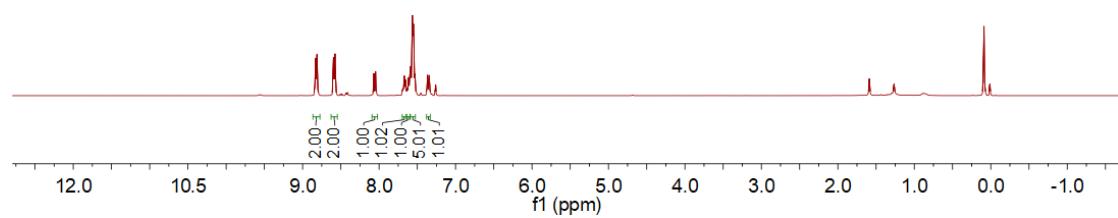
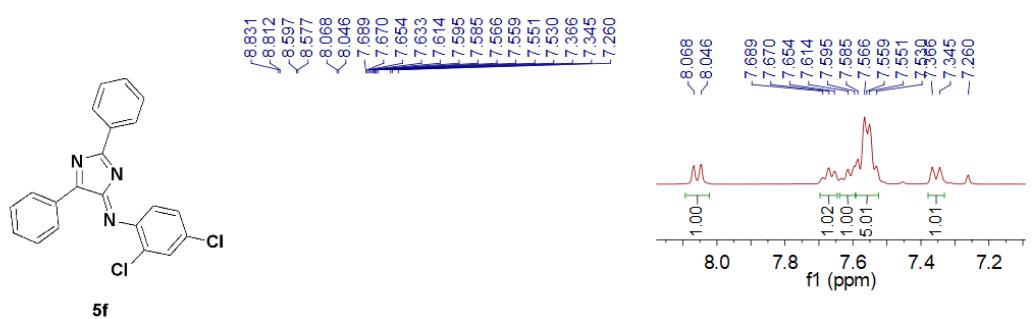


Fig S72. ¹H NMR (400 MHz) spectrum of **5f** (CDCl₃, rt)

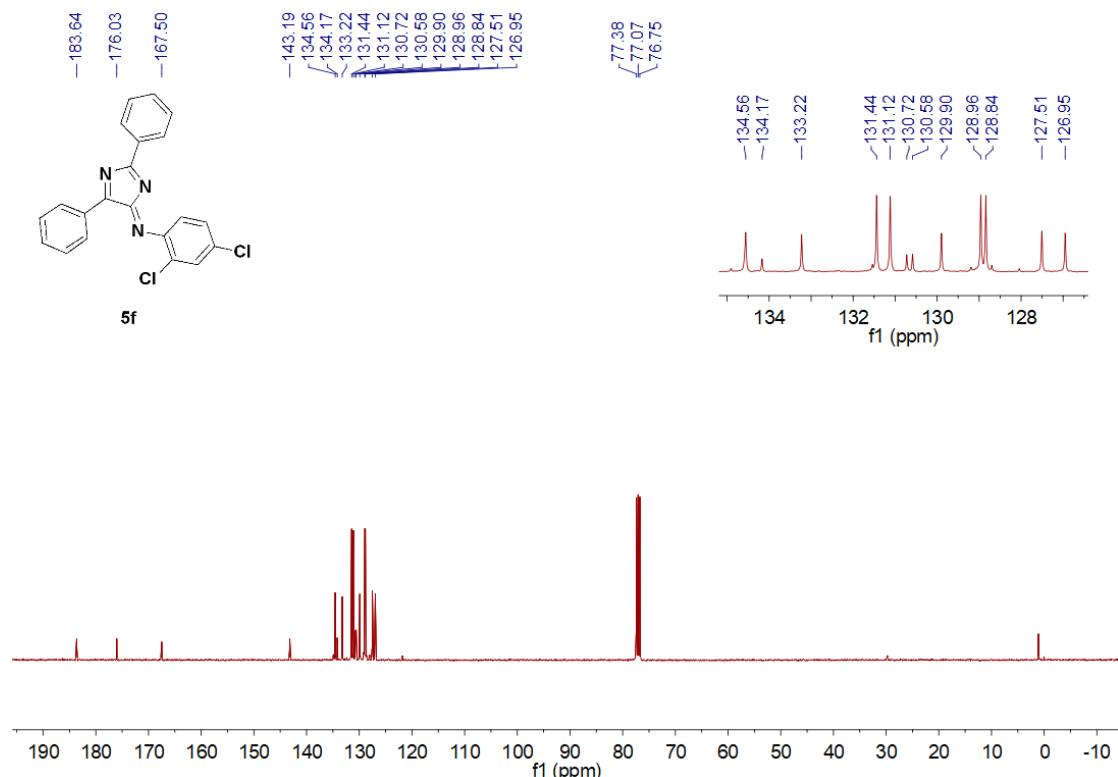
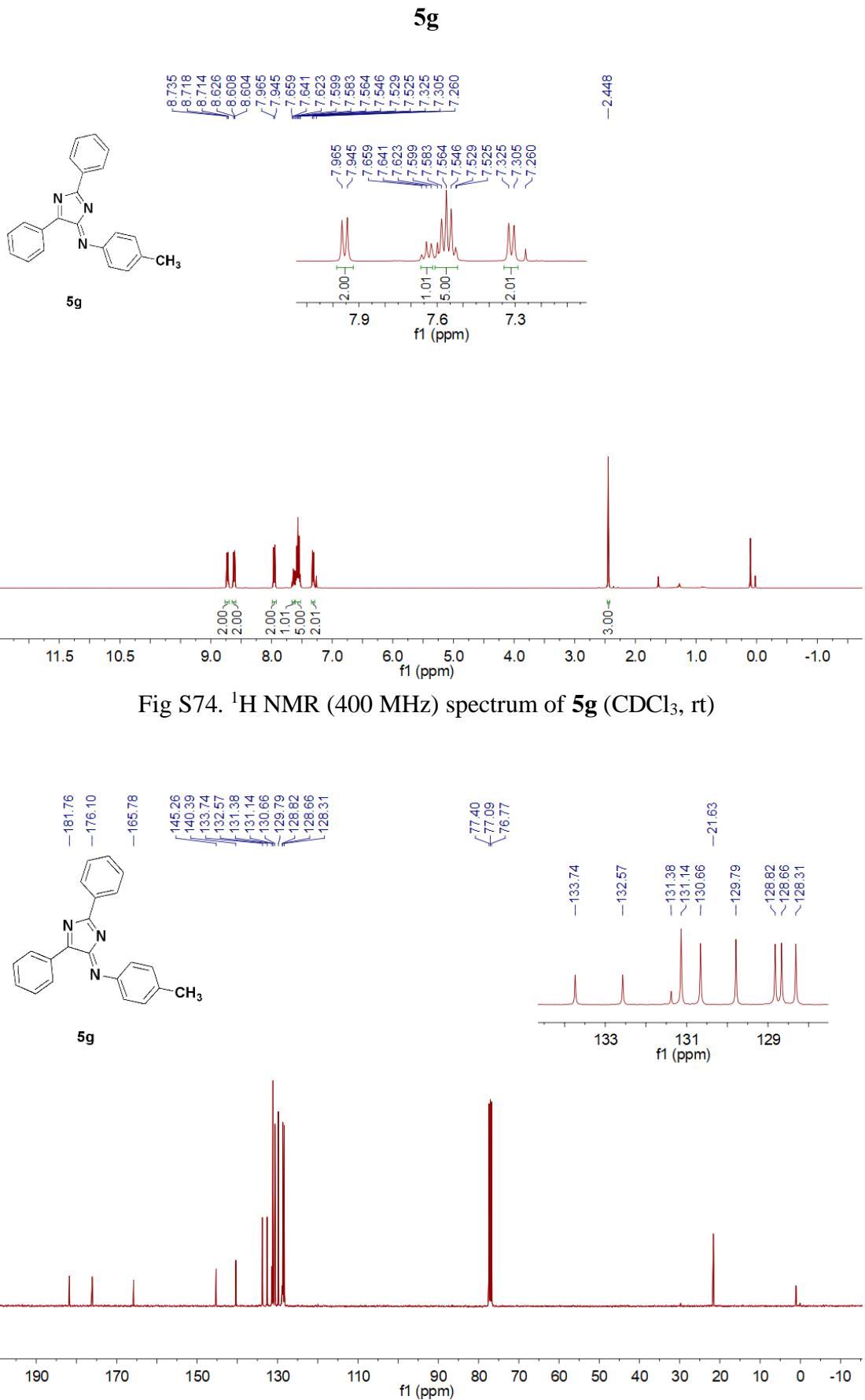


Fig S73. ¹³C{¹H} NMR (100 MHz) spectrum of **5f** (CDCl₃, rt)



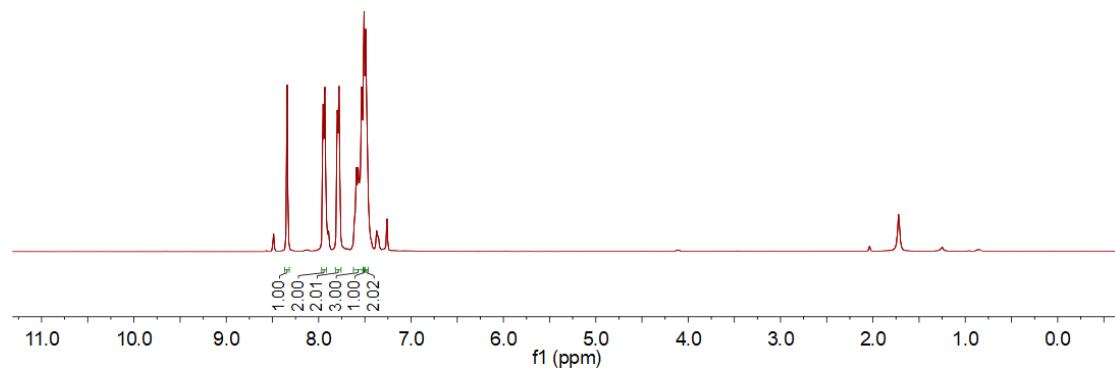
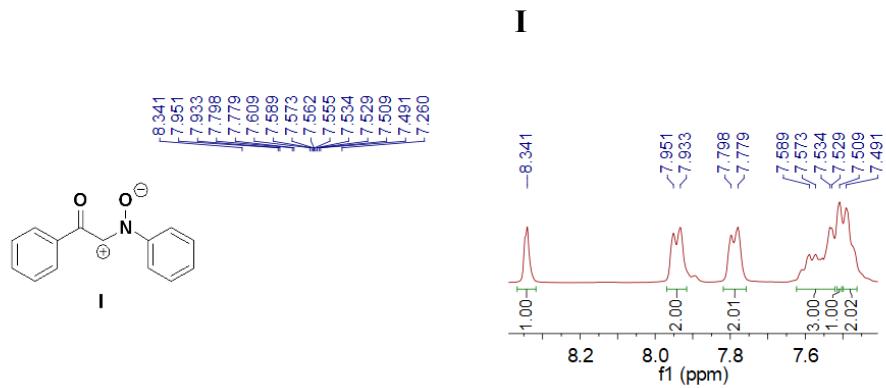


Fig S76. ^1H NMR (400 MHz) spectrum of **I** (CDCl_3 , rt)

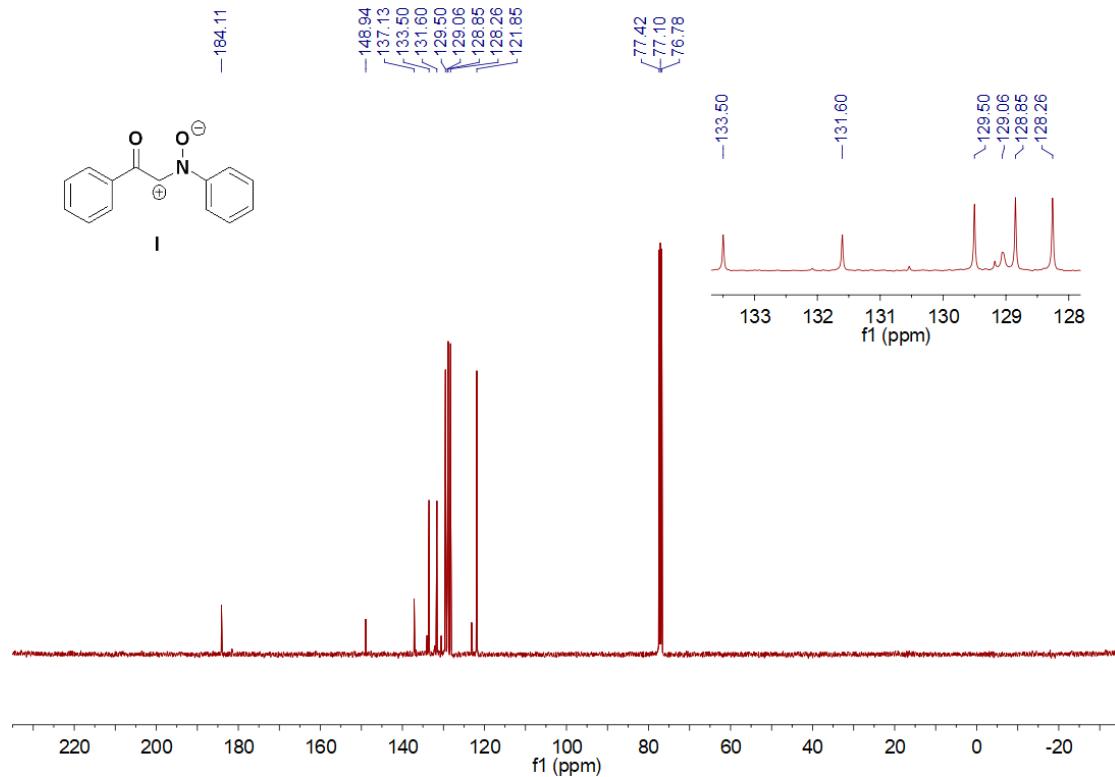


Fig S77. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz) spectrum of **I** (CDCl_3 , rt)

5. X-ray Crystallography Data of **4c**

Single crystals of compound **4c** was measured on a Rigaku PAXIS-PAPID single-crystal diffractometer. The recrystallization solvent of **4c** was methanol.

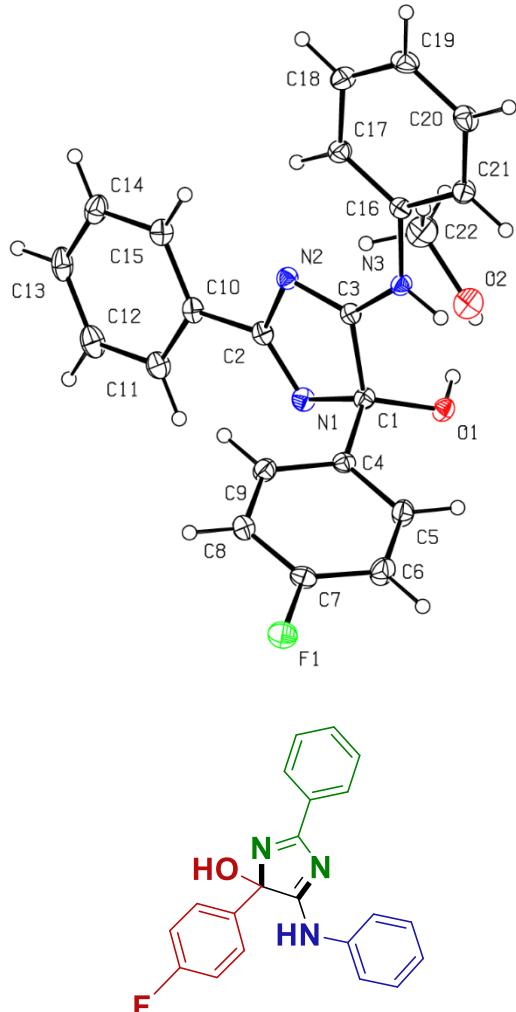


Figure S1 X-ray crystallography of **4c** (the ellipsoid contour probability level is 50%)
Table S1 X-ray crystallography data of **4c**

Formula moiety	C ₂₂ H ₂₀ FN ₃ O ₂
Formula sum	C ₂₂ H ₂₀ FN ₃ O ₂
Formula weight	377.41
Temperature	170K
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a=8.7169(2) b=22.5676(7)

	c=10.2298(3)
	alpha=90
	beta=111.7690(10)
	gamma=90
Volume	1868.89(9)
Z	4
Calculated density	1.341 g/cm ³
Absorption coefficient	0.094
F(000)	792.0
Crystal size	0.45 × 0.29 × 0.23 mm
Theta range for data collection	4.652 to 55.004
Reflections collected	21398
Independent reflections	4290 [R _{int} = 0.0381, R _{sigma} = 0.0276]
Data / restraints / parameters	4290/0/256
Goodness-of-fit on F ²	1.064
Final R indexes [I>=2σ (I)]	R ₁ = 0.0427, wR ₂ = 0.0944
Final R indexes [all data]	R ₁ = 0.0545, wR ₂ = 0.1020
Largest diff. peak/hole / e Å ⁻³	0.28/-0.22

6. References

- (1) Qiu, F.K.; Wang, Z.; Zhao, D.; Zeng, L.H.; Zhang, C.; Zhu, H.J.; Zhang, J.K.; Shao J.A. *J. Org. Chem.* **2023**, *88*, 10810-10817.
- (2) Zhao, Y.R., Li, L.; Xuan, J. *Synlett.*, **2023**, *34*, 2022-2028.