Supplementary Information

Sulfonyl functionalized benzo[*d*]imidazo[5,1-*b*]thiazole based carbenes as building blocks for two-coordinate Cu(I) complexes exhibiting fast and efficient thermally activated delayed fluorescence

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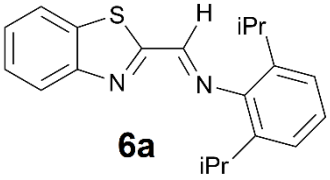
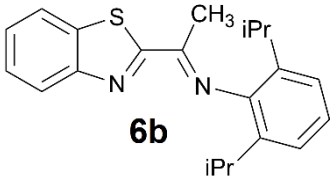
Synthesis



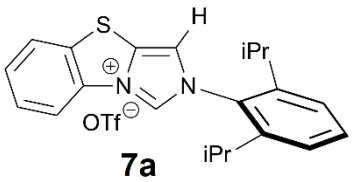
6a

*Compound **6a***, *N*-(benzo[*d*]thiazol-2-ylmethylene)-2,6-diisopropylaniline. **5a** (10.25 g, 62.81 mmol, 1.0 equiv.) and 2,6-diisopropylaniline (21.28 ml, 112.83 mmol, 1.8 equiv.) were dissolved in EtOH (190 ml) and the resulting mixture was refluxed for 24h. Then solvent was evaporated under reduced pressure and the crude product was purified by recrystallization from EtOH (45 ml) to afford product as yellow solid (9.10 g, 46%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 8.51 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.59 - 7.48 (m, 2H), 7.23 – 7.14 (m, 3H), 3.01 (hept, J = 6.8 Hz, 2H), 1.21 (d, J = 6.8 Hz, 12H). ^{13}C NMR δC ($CDCl_3$, 125.77 MHz): 167.28, 156.74, 154.02, 147.40, 137.40, 135.67, 127.14, 126.81, 125.41, 124.50, 123.38, 122.29, 28.29, 23.57.



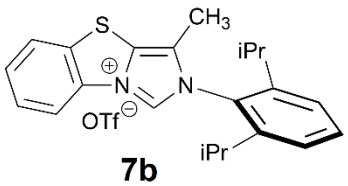
6b

*Compound **6b***, *N*-(1-(benzo[*d*]thiazol-2-yl)ethylidene)-2,6-diisopropylaniline. **5b** (22.48 g, 126.85 mmol, 1.0 equiv.) and 2,6-diisopropylaniline (31.10 ml, 164.93 mmol, 1.3 equiv.) were dissolved in MeOH (45 ml), acetic acid (15 ml) was added and the resulting mixture was refluxed for 72h. A precipitation of product was observed during reaction. After cooling to 0° C the reaction mixture was filtered to afford crude product as solid. The crude product was recrystallized with MeOH (280 ml) to afford product as yellow solid (30.71 g, 72%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 8.13 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.53 (t, J = 7.3 Hz, 1H), 7,47 (t, J = 7.2 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.16 – 7.11 (m, 1H), 2.76 (hept, J = 6.8 Hz, 2H), 2.32 (s, 3H), 1.18 (d, J = 6.9 Hz, 12H). ^{13}C NMR δC ($CDCl_3$, 125.77 MHz): 170.42, 162.63, 154.11, 145.14, 136.85, 135.92, 126.65, 126.42, 124.53, 124.36, 123.24, 122.13, 28.67, 23.22, 22.90, 17.78.



7a

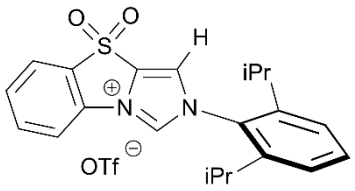
*Compound **7a***, 2-(2,6-diisopropylphenyl)-2*H*-benzo[*d*]imidazo[5,1-*b*]thiazol-9-ium triflate. To a suspension of AgOTf (2.97 g, 11.58 mmol, 1.5 equiv.) in dry DCM (37.5 ml) chloromethyl pivalate (1.69 ml, 11.75 mmol, 1.5 equiv.) was added and the resulting suspension was stirred for 45 min in the dark. The supernatant was transferred to a pressure flask containing **6a** (2.50 g, 7.75 mmol, 1 equiv.), the flask was sealed and the resulting mixture was stirred in the dark at 40° C for 2 h. The solution was cooled to room temperature, quenched with MeOH (40 ml) and the solvent was evaporated in reduced pressure. The resulting oil was dissolved in DCM (10 ml) and hexane (40 ml) was added. DCM was selectively evaporated under reduced pressure to precipitate crude product, which was collected by filtration. The crude product was purified by chromatography on silica gel (DCM-acetone, 10:1) to afford the imidazolium triflate as pale solid (2.15 g, 57%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 10.46 (s, 1H), 8.77 – 8.72 (m, 1H), 7.83 – 7.78 (m, 1H), 7.66 – 7.61 (m, 2H), 7.58 (t, J = 7.9 Hz, 1H), 7.53 (s, 1H), 7.34 (d, J = 7.9 Hz, 2H), 2.31 (hept, J = 6.8 Hz, 2H), 1.22 (d, J = 6.8 Hz, 6H), 1.16 (d, J = 6.8 Hz, 6H). ^{13}C NMR δC ($CDCl_3$, 125.77 MHz): 145.41, 132.81, 132.35, 132.08, 130.84, 130.20, 129.90, 129.76, 128.30, 124.79, 124.16, 120.70 (q, J = 320.4 Hz), 118.05, 115.49, 28.90, 24.56, 24.14. ^{19}F NMR δF ($CDCl_3$, 471 MHz): -78,55.



7b

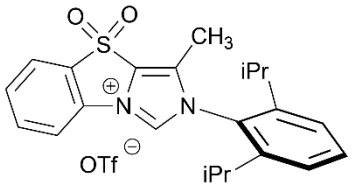
*Compound **7b***, 2-(2,6-diisopropylphenyl)-3-methyl-2*H*-benzo[*d*]imidazo[5,1-*b*]thiazol-9-ium. To a suspension of AgOTf (0.76 g, 2.97 mmol, 2 equiv.) in dry DCM (10 ml) chloromethyl pivalate (0.43 ml, 2.98 mmol, 2 equiv.) was added and the resulting suspension was stirred for 45 min in the dark. The supernatant was transferred to a pressure flask containing **6b** (0.50 g, 1.48 mmol, 1 equiv.), the flask was sealed and the resulting mixture was stirred in the dark at 40° C for 2 h. The solution was cooled to room temperature,

quenched with MeOH (10 ml) and the solvent was evaporated in reduced pressure. The resulting oil was dissolved in DCM (10 ml) and hexane (40 ml) was added. DCM was selectively evaporated under reduced pressure to precipitate crude product, which was collected by filtration. The crude product was purified by chromatography on silica gel (DCM-acetone, 10:1) to afford the imidazolium triflate as light brownish solid (0.30 g, 41%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 10.53 (s, 1H), 8.80 (d, J= 7.0 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.72 – 7.58 (m, 3H), 7.39 (d, J = 7.8 Hz, 2H), 2.23 - 2.16 (m, 5H), 1.23 (d, J = 6.5 Hz, 6H), 1.19 (d, J = 6.6 Hz, 6H). ^{13}C NMR δC ($CDCl_3$, 125.77 MHz): 145.70, 132.64, 131.30, 130.55, 129.89, 129.55, 128.59, 128.41, 125.17, 124.52, 122.35, 120.70 (q, J = 320.2 Hz), 118.39, 28.96, 24.92, 23.51, 9.66. ^{19}F NMR δF ($CDCl_3$, 471 MHz): -78.50.



9a

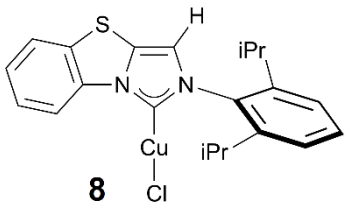
Compound ***9a***, 2-(2,6-diisopropylphenyl)-2*H*-benzo[*d*]imidazo [5,1-*b*]thiazol-9-ium 4,4-dioxide triflate. Triflate salt **7a** (4.68 g, 9.66 mmol, 1 equiv.) was dissolved in 180 ml MeOH-water solution (1:1) and oxone (14.70 g, 96.58 mmol, 10 equiv.) was added. The mixture was stirred for 5 h in 70° C, adding additional oxone (5.88 g, 37.64 mmol, 4 equiv.) every 1 h. Reaction mixture was cooled to room temperature and solvent was evaporated in reduced pressure. The resulting mixture was washed with DCM and filtrated. DCM was dried over Na_2SO_4 and evaporated in reduced pressure to afford crude product as oil. The resulting crude product was purified by chromatography on silica gel (DCM-acetone, 6:1) to afford product as white solid (2.18 g, 44%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 10.73 (s, 1H), 8.74 (d, J = 8.2 Hz, 1H), 8.01 – 7.93 (m, 2H), 7.86 (s, 1H), 7.80 (t, J = 7.7 Hz, 1H), 7.63 (t, J = 7.9 Hz, 1H), 7.38 (d, J = 7.9 Hz, 2H), 2.40 (hept, J = 6.7 Hz, 2H), 1.27 (d, J = 6.7 Hz, 6H), 1.18 (d, J = 6.7 Hz, 6H). ^{13}C NMR δC ($CDCl_3$, 125.77 MHz): 145.15, 137.11, 134.93, 133.19, 132.32, 130.48, 129.63, 129.08, 125.27, 123.48, 122.40, 120.44 (q, J = 319.9 Hz), 119.39, 29.15, 24.55, 23.95. ^{19}F NMR δF ($CDCl_3$, 471 MHz): -78.67.



9b

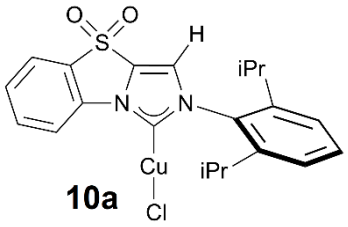
Compound ***9b***, 2-(2,6-diisopropylphenyl)-3-methyl-2*H*-benzo[*d*]imidazo[5,1-*b*]thiazol-9-ium 4,4-dioxide triflate. Triflate salt **7b** (4.40 g, 8.82 mmol, 1 equiv.) was dissolved in 150 ml MeOH-water solution (1:1) and oxone (13.43 g, 88.23 mmol, 10 equiv.) was added. The mixture was stirred for 5 h in 70° C, adding additional oxone (5.37 g, 35.28 mmol, 4 equiv.) every 1 h. Reaction mixture was cooled to room temperature and solvent was evaporated in reduced pressure. The resulting mixture was washed with DCM and filtrated. DCM was dried over Na_2SO_4 and evaporated in reduced pressure to afford crude product as oil. The resulting crude product was purified by chromatography on silica gel (DCM-acetone, 6:1) to afford product as light brown solid (1.92 g, 41%).^{1}H NMR δH ($CDCl_3$, 500 MHz): 10.73 (s, 1H), 8.74 (d, J = 8.2 Hz, 1H), 8.01 – 7.93 (m, 2H), 7.80 (t, J = 7.7 Hz, 1H), 7.67 (t, J = 7.9 Hz, 1H), 7.43 (d, J = 7.9 Hz, 2H), 2.33 (s, 3H), 2.28 (hept, J = 6.8 Hz, 2H), 1.27 (d, J = 6.8 Hz, 6H), 1.23 (d, J = 6.8 Hz, 6H). ^{13}C NMR δC ($CDCl_3$, 125.77 MHz): 145.77, 137.12, 134.57, 133.51, 132.99, 132.60, 132.18, 129.27, 127.39, 127.02, 125.75, 123.34, 119.50, 29.39, 24.72, 23.56, 9.37. ^{19}F NMR δF ($CDCl_3$, 471 MHz): -78.60.

General method (A) for synthesis of complexes ***8, 10a and 10b****.* To a mixture of imidazolium triflate (**7a**, **9a** or **9b**), CuCl (3 equiv.) and K_2CO_3 (3 equiv.) acetone was added and the resulting mixture was refluxed for 20 minutes. Reaction mixture was cooled to room temperature and evaporated under reduced pressure. DCM was added and the resulting mixture was filtered through a short pad of silica gel. Hexane was added to the filtrate and the residual DCM was selectively evaporated under reduced pressure to precipitate the product. The mixture was filtered and washed with hexane to afford product.



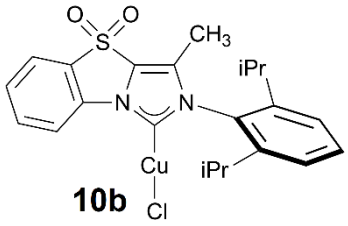
8

*Compound **8**. General Method (A):* A solution of imidazolium triflate **7a** (0.300 g, 0.62 mmol), CuCl (0.183 g, 1.85 mmol) and K_2CO_3 (0.256 g, 1.85 mmol) in acetone (15 ml). White solid (0.163 g, 61%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 8.78 (d, J = 7.9 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.30 (d, J = 7.8 Hz, 2H), 7.02 (s, 1H), 2.43 (hept, J =6.8 Hz, 2H), 1.28 (d, J = 6.8 Hz, 6H), 1.15 (d, J = 6.8 Hz, 6H). ^{13}C NMR δC ($CDCl_3$, 125.77 MHz): 168.75, 145.73, 135.44, 133.46, 131.90, 130.91, 130.18, 127.88, 127.11, 124.40, 124.03, 116.27, 113.39, 28.48, 24.93, 24.41.



10a

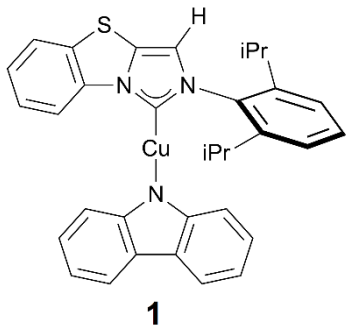
*Compound **10a**. General Method (A):* A solution of imidazolium triflate **9a** (1.30 g, 2.52 mmol), CuCl (0.75 g, 7.57 mmol) and K_2CO_3 (1.04 g, 7.52 mmol) in acetone (60 ml). White solid (0.90 g, 77%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 8.76 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.87 (t, J = 7.9 Hz, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.47 (s, 1H), 7.34 (d, J = 7.9 Hz, 2H), 2.47 (hept, J = 6.8 Hz, 2H), 1.30 (d, J = 6.8 Hz, 6H), 1.18 (d, J = 6.8 Hz, 6H). ^{13}C NMR δC ($CDCl_3$, 125.77 MHz): 145.47, 135.92, 133.89, 133.00, 132.92, 131.84, 130.05, 124.94, 123.37, 121.57, 116.44, 28.81, 24.86, 24.30.



10b

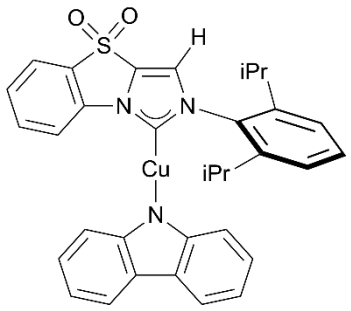
*Compound **10b**. General Method (A):* A solution of imidazolium triflate **9b** (2.00 g, 3.77 mmol), CuCl (1.11 g, 11.21 mmol) and K_2CO_3 (1.56 g, 11.21 mmol) in acetone (60 ml). Greenish solid (1.52 g, 84%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 8.68, (d, J = 8.2 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.83 (t, J = 7.9 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.57 (t, J = 7.8 Hz, 1H), 7.36 (d, J = 7.8 Hz, 2H), 2.37 (hept, J = 6.8 Hz, 2H), 2.19 (s, 3H), 1.29 (d, J = 6.8 Hz, 6H), 1.20 (d, J = 6.8 Hz, 6H). ^{13}C NMR δC ($CDCl_3$, 125.77 MHz): 172.44, 145.77, 135.71, 133.20, 132.99, 132.19, 131.93, 131.26, 129.70, 126.39, 125.17, 123.22, 116.01, 28.80, 25.58, 23.45, 9.84.

*General Method (B) for synthesis of complexes **1, 3** and **4**.* The synthesis and purification of complexes **1**, **3** and **4** was carried out using dry, deoxygenated solvents and Schlenk technique. Carbazole (3-cyanocarbazole) and KOtBu were dissolved in THF and stirred for 30 minutes under argon atmosphere. Then Cu(I) complex (**8** or **10b**) was added to the solution of carbazole amide. The resulting mixture was stirred for 2 hours at room temperature under argon atmosphere and then filtered through a syringe filter into hexane to precipitate the product. The resulting mixture was filtered to afford product as solid.



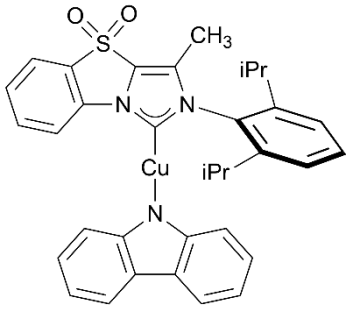
1

*Compound **1**. General Method (B):* A solution of carbazole (0.042 g, 0.25 mmol) and KOtBu (0.028 g, 0.25 mmol) in THF (10 ml) and **8** (0.100 g, 0.23 mmol). Off-white solid (0.067 g, 52%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 8.91 (d, J = 7.8 Hz, 1H), 8.05 (d, J = 7.6 Hz, 2H), 7.76 (d, J = 7.9 Hz, 1H), 7.65 – 7.51 (m, 3H), 7.40 (d, J = 7.8 Hz, 2H), 7.21 – 7.12 (m, 3H), 7.08 (d, J = 8.0 Hz, 2H), 6.99 (t, J = 7.3 Hz, 2H), 2.60 (hept, J = 6.8 Hz, 2H), 1.30 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.8 Hz, 6H). ^{13}C NMR δC ($CDCl_3$, 75.47 MHz): 150.20, 146.13, 135.82, 133.72, 132.08, 131.02, 130.29, 127.90, 127.23, 125.93, 124.56, 124.23, 123.61, 119.76, 116.22, 115.55, 114.42, 113.53, 28.70, 24.91, 24.51. Elemental analysis calculated for $C_{33}H_{30}CuN_3S$: C, 70.25; H, 5.36; Cu, 11.26; N, 7.45; S, 5.68. Found: C, 70.05; H, 5.77; N, 7.29.



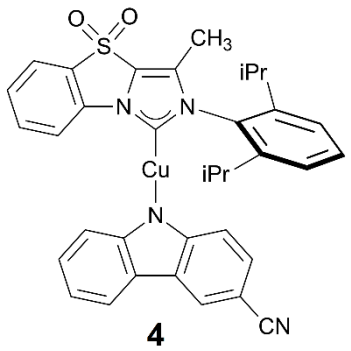
2

*Compound **2**.* A mixture of **10a** (0.180 g, 0.39 mmol, 1 equiv.), carbazole (0.097 g, 0.58 mmol, 1.5 equiv.), K_2CO_3 (0.213 g, 1.54 mmol, 4 equiv.) in absolute ethanol (20 ml) was stirred at r.t. for 24h. Then the solvent was removed under reduced pressure and dry THF was added to dissolve the product. The resulting mixture was filtered and hexane (200 ml) was added to the filtrate to precipitate the product. The mixture was filtered and washed with hexane to afford crude product. The crude product (0.13 g) was purified by crystallization from chlorobenzene (3 ml) to afford product as light-yellow solid (0.027 g, 12%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 8.84 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 7.6 Hz, 2H), 7.97 (d, J = 7.8 Hz, 1H), 7.89 (t, J = 7.8 Hz, 1H), 7.68 (t, J = 7.8 Hz, 2H), 7.59 (s, 1H), 7.44 (d, J = 7.9 Hz, 2H), 7.18 (t, J = 7.4 Hz, 2H), 7.04 – 6.94 (m, 4H), 2.63 (hept, J = 6.8 Hz, 2H), 1.32 (d, J = 6.8 Hz, 6H), 1.25 (d, J = 6.8 Hz, 6H). ^{13}C NMR δC ($CDCl_3$, 75.47 MHz): 174.70, 149.90, 145.88, 135.94, 134.26, 133.19, 133.10, 131.93, 130.24, 130.05, 125.09, 124.54, 123.82, 123.59, 121.70, 119.91, 116.30, 115.94, 114.07, 29.01, 24.82, 24.35. Elemental analysis calculated for $C_{33}H_{30}CuN_3O_2S$: C, 66.48; H, 5.07; Cu, 10.66; N, 7.05; O, 5.37; S, 5.38. Found: C, 66.13; H, 5.38; N, 7.46.



3

*Compound **3**. General Method (B):* A solution of carbazole (0.115 g, 0.69 mmol) and KOtBu (0.070 g, 0.62 mmol) in THF (40 ml) and **10b** (0.300 g, 0.62 mmol). Light yellow solid (0.34 g, 90%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 8.80 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 7.6 Hz, 2H), 7.96 (d, J = 7.8 Hz, 1H), 7.86 (t, J = 7.8 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.47 (d, J = 7.9 Hz, 2H), 7.18 (t, J = 7.5 Hz, 2H), 7.00 (t, J = 7.3 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 2.54 (hept, J = 6.8 Hz, 2H), 2.31 (s, 3H), 1.32 (d, J = 6.8 Hz, 6H), 1.27 (d, J = 6.9 Hz, 6H). ^{13}C NMR δC ($CDCl_3$, 125.77 MHz): 173.53, 149.92, 146.12, 135.74, 133.37, 133.19, 132.35, 131.98, 131.61, 129.70, 126.52, 125.34, 124.54, 123.77, 123.42, 119.88, 115.92, 115.88, 114.11, 28.97, 25.53, 23.54, 9.90. Elemental analysis calculated for $C_{34}H_{32}CuN_3O_2S$: C, 66.92; H, 5.29; Cu, 10.41; N, 6.89; O, 5.24; S, 5.25. Found: C, 67.06; H, 5.35; N, 6.91.



4

*Compound **4**. General Method (B):* A solution of 3-cyanocarbazole (0.088 g, 0.46 mmol) and KOtBu (0.047 g, 0.42 mmol) in THF (30 ml) and **10b** (0.200 g, 0.42 mmol). Off-white solid (0.19 g, 71%). ^{1}H NMR δH ($CDCl_3$, 500 MHz): 8.70 (d, J = 8.2 Hz, 1H), 8.31 (s, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.91 (t, J = 7.8 Hz, 1H), 7.75 - 7.66 (m, 2H), 7.48 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.4 Hz, 1H), 7.29-7.26 (m, 1H), 7.10 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 8.1 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H), 2.51 (hept, J = 6.7 Hz, 2H), 2.31 (s, 3H), 1.29 – 1.25 (m, 12H). ^{13}C NMR δC ($CDCl_3$, 125.77 MHz): 172.96, 151.92, 150.47, 146.27, 135.70, 133.51, 133.10, 133.52, 132.12, 131.64, 129.92, 127.00, 126.73, 125.47, 125.32, 125.09, 124.62, 123.93, 123.67, 122.39, 120.28, 117.80, 115.56, 114.62, 114.39, 97.49, 29.00, 25.52, 23.54, 9.91. Elemental analysis calculated for $C_{35}H_{31}CuN_4O_2S$: C, 66.17; H, 4.92; Cu, 10.00; N, 8.82; O, 5.04; S, 5.05. Found: C, 65.84; H, 5.16; N, 8.61.

Thermal Analysis

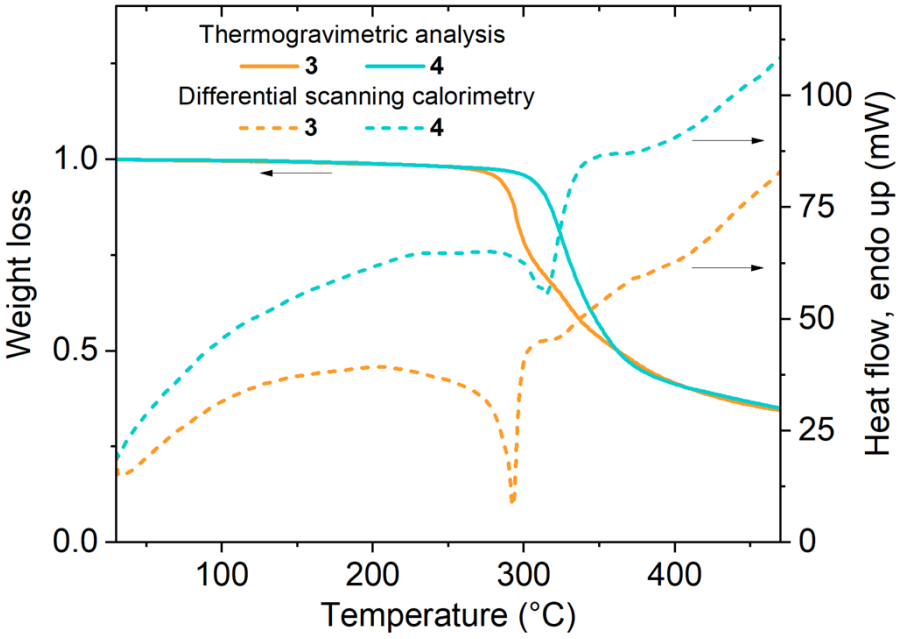


Figure S1. Thermogravimetric analysis (solid line) and differential scanning calorimetry (dashed line) of complexes **3** and **4**.

X-Ray Crystallographic Data

Table S1. Crystallographic data and structure refinement for compounds **10a** and **10b**.

	Compound **10a**	Compound **10b**
Empirical formula	$C_{21}H_{22}ClCuN_2O_2S$	$C_{22}H_{24}ClCuN_2O_2S \cdot ¼(C_6H_6)$
Formula weight	465.49	507.50
Temperature/K	140.0(3)	150.0(1)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	*Pnma*
a/Å	14.8826(3)	9.1386(3)
b/Å	14.9987(3)	37.6851(13)
c/Å	9.7655(2)	15.4208(5)
α/°	90	90
β/°	106.406(2)	90
γ/°	90	90
Volume/Å^3	2091.10(8)	5310.8(3)
Z	4	8
ρ_{calc}mg/mm^3	1.4785	1.269
μ/mm^{-1}	3.737	3.009
F(000)	960	2096
Crystal size/mm^3	0.21 × 0.18 × 0.02	0.21 × 0.16 × 0.02
Radiation	Cu Kα (λ = 1.54184 Å)	CuKα (λ = 1.54184 Å)
2Θ max. for data collection	160	170
Index ranges	$-18 \le h \le 19$, $-19 \le k \le 19$, $-10 \le l \le 12$	$-10 \le h \le 11$, $0 \le k \le 47$, $0 \le l \le 19$
Reflections collected	26094	5770
Independent reflections	4532 [R_{int} = 0.0300, R_{sigma} = 0.0209]	5583 [R_{int} = 0.0816, R_{sigma} = 0.1484]
Data/restraints/parameters	4532/0/257	5583/0/279
Goodness-of-fit on F^2	1.024	1.042
Final *R* indexes [$I > 2\sigma(I)$]	R_1 = 0.0305, wR_2 = 0.0836	R_1 = 0.1093, wR_2 = 0.2658
Final *R* indexes [all data]	R_1 = 0.0319, wR_2 = 0.0846	R_1 = 0.1333, wR_2 = 0.2787
Largest diff. peak/hole / e Å^{-3}	0.49/-0.45	1.64/-0.60
CCDC deposition number	CCDC 2304552	CCDC 2304553

Table S2. Crystallographic data and structure refinement for compounds **3** and **4**.

	Compound **3**	Compound **4**
Empirical formula	$C_{34}H_{32}CuN_3O_2S$	$C_{35}H_{31}CuN_4O_2S$
Formula weight	610.26	635.27
Temperature/K	140.0(1)	150.0(4)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	10.3882(1)	10.2939(3)
b/Å	23.1584(3)	22.4671(5)
c/Å	12.3933(1)	13.2769(4)
α/°	90	90
β/°	93.805(1)	91.856(2)
γ/°	90	90
Volume/Å^3	2974.93(5)	3068.99(15)
Z	4	4
ρ_{calc}mg/mm^3	1.3624	1.3748
μ/mm^{-1}	1.969	0.818
F(000)	1272	1320
Crystal size/mm^3	0.18 × 0.16 × 0.03	0.21 × 0.09 × 0.08
Radiation	Cu Kα (λ = 1.54184 Å)	Mo Kα (λ = 0.71073 Å)
2Θ max. for data collection	160	65.0
Index ranges	$-13 \le h \le 13$, $-29 \le k \le 29$, $-15 \le l \le 15$	$-14 \le h \le 13$, $-30 \le k \le 33$, $-17 \le l \le 18$
Reflections collected	40445	30895
Independent reflections	6494 [R_{int} = 0.0340, R_{sigma} = 0.0247]	9874 [R_{int} = 0.0426, R_{sigma} = 0.0551]
Data/restraints/parameters	6494/0/379	9874/0/393
Goodness-of-fit on F^2	1.030	1.005
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0464, wR_2 = 0.1294	R_1 = 0.0481, wR_2 = 0.1173
Final R indexes [all data]	R_1 = 0.0492, wR_2 = 0.1319	R_1 = 0.0791, wR_2 = 0.1311
Largest diff. peak/hole / e Å^{-3}	0.98/-0.46	0.74/-0.68
CCDC deposition number	CCDC 2304555	CCDC 2304554

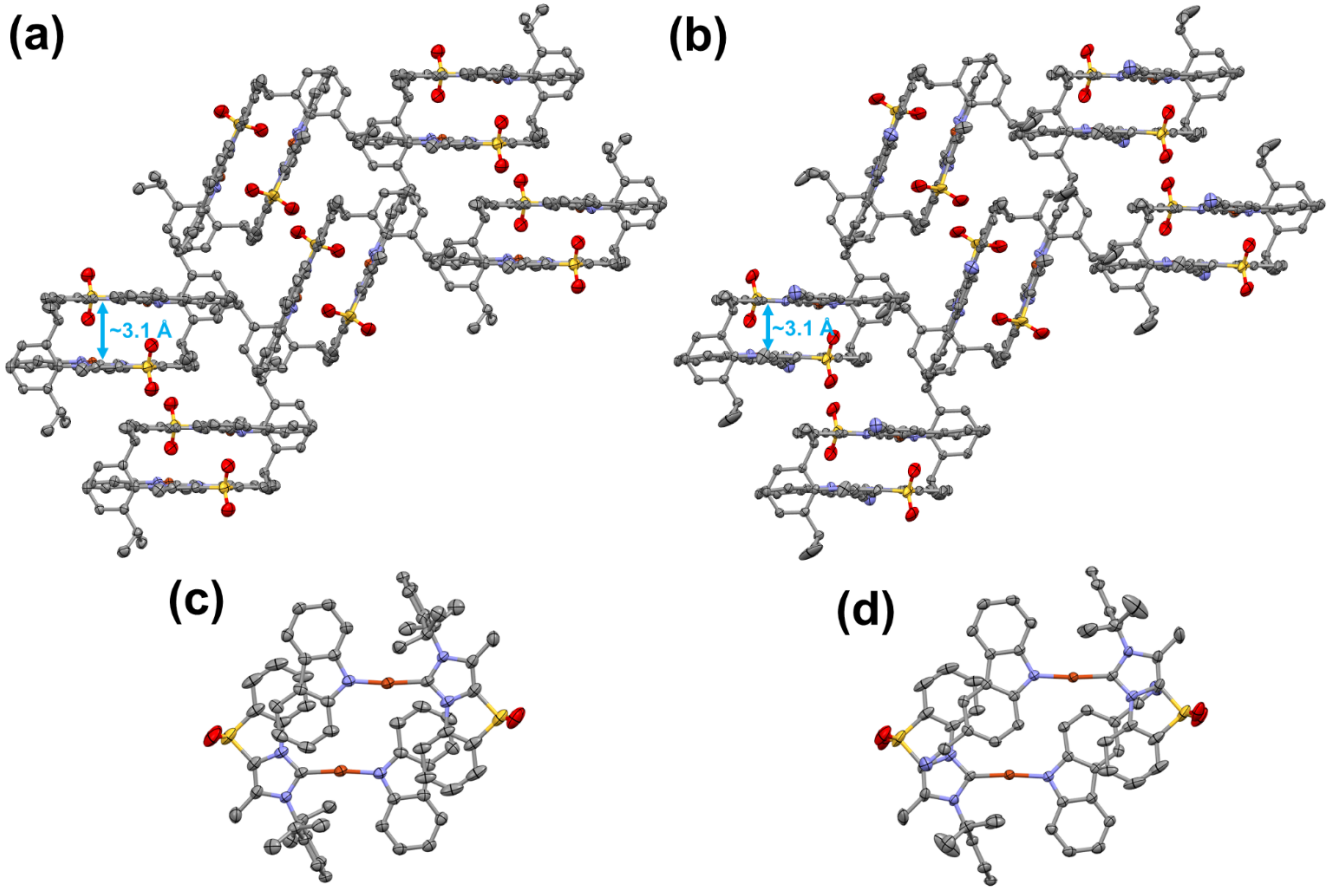


Figure S2. Molecular packing pattern of complex molecules **3** (a) and **4** (b) in crystal structure (side view). The approximate distance between two molecular planes is shown. Packing of individual molecular pairs (top view) of complexes **3** (c) and **4** (d). Ellipsoids are shown at 50% probability level; hydrogen atoms are removed for clarity.

Cyclic Voltammetry

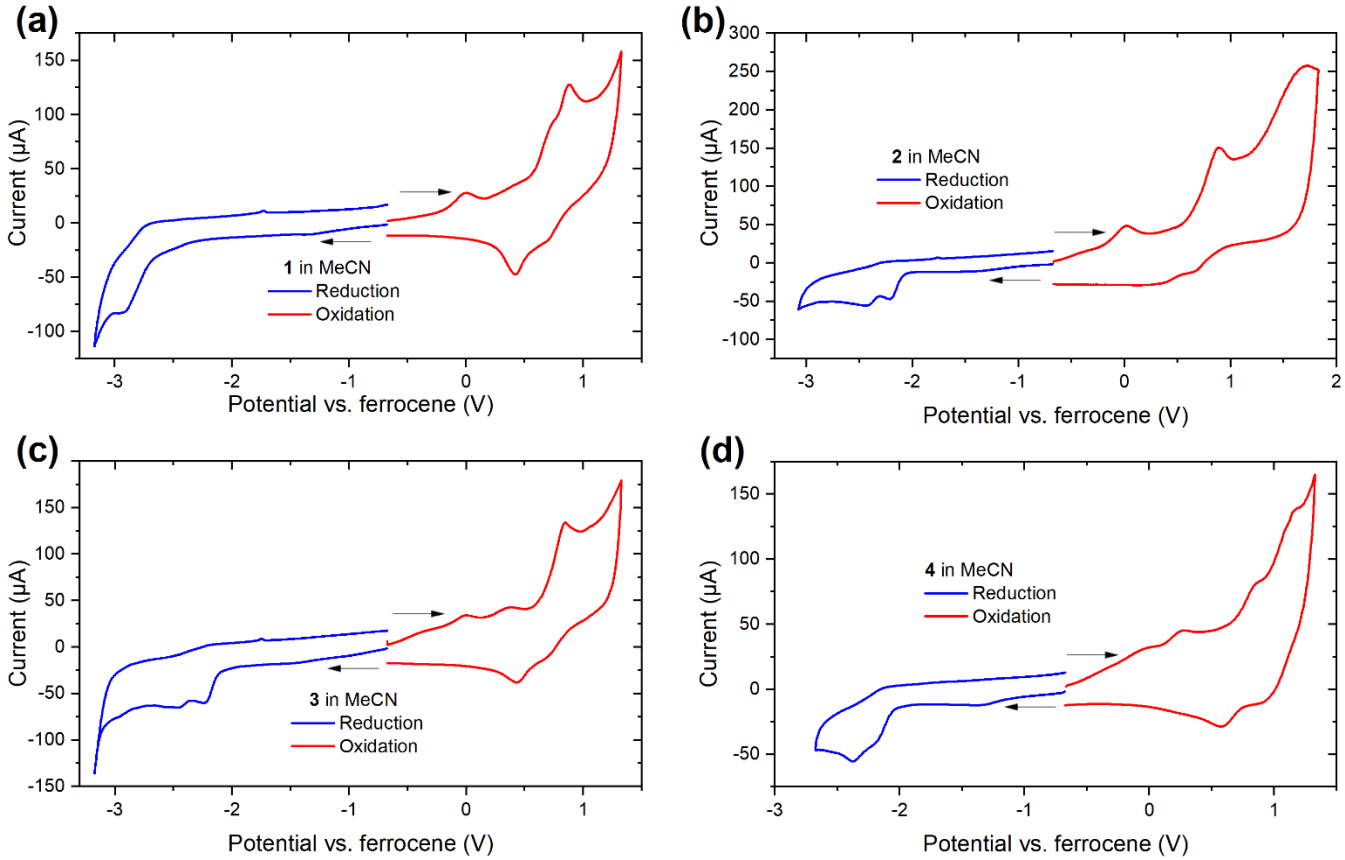


Figure S3. Cyclic voltammograms of complexes **1**−**4**. Measured in CH_3CN; supporting electrolyte – TBAF (0.1 M); scan rate of 50 mV/s; glassy carbon disk-working electrode; Pt wire-counter electrode; Ag/Ag+ (0.1M)-reference electrode. The potentials were calibrated against Fc/Fc^+ redox couple.

Photophysical Properties

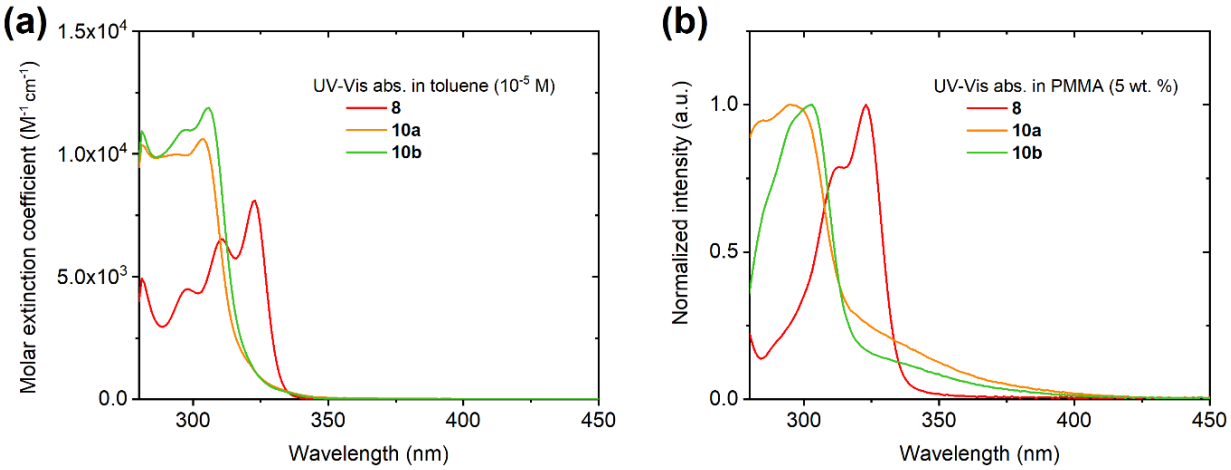


Figure S4. UV-Vis absorption spectra of compounds **8**, **10a** and **10b** in toluene (a) and PMMA films (b).

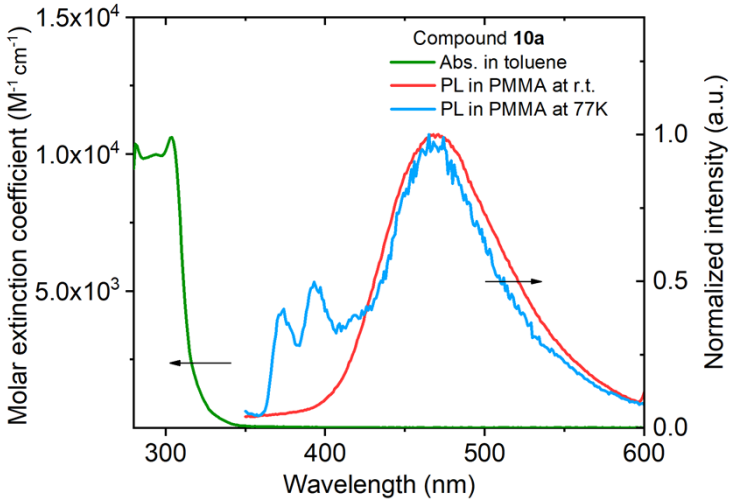


Figure S5. UV-Vis absorption spectra of **10a** in toluene (10^{-5} M) and photoluminescence of **10a** in PMMA (a 5-weight percent doping concentration) films at r.t. and 77K.

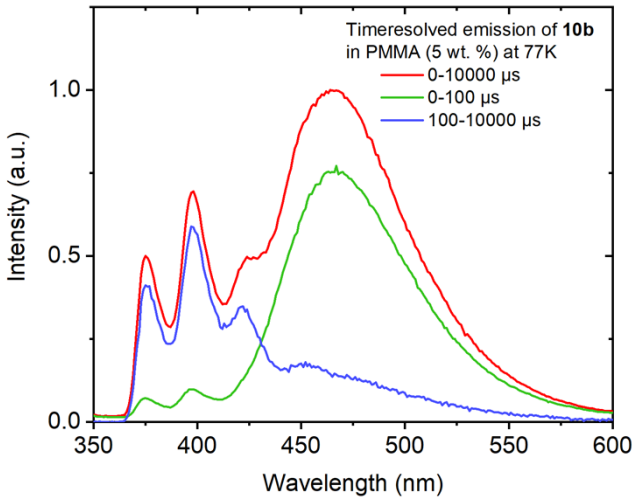


Figure S6. Time-resolved photoluminescence spectra of **10b** in PMMA (a 5-weight percent doping concentration) films at 77K.

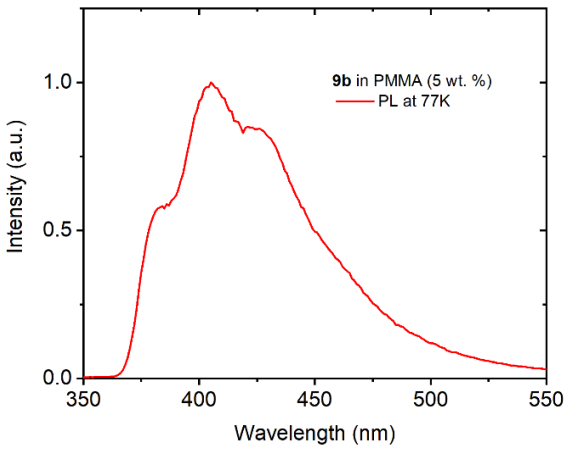


Figure S7. Photoluminescence spectra of **9b** in PMMA (a 5-weight percent doping concentration) films at 77K.

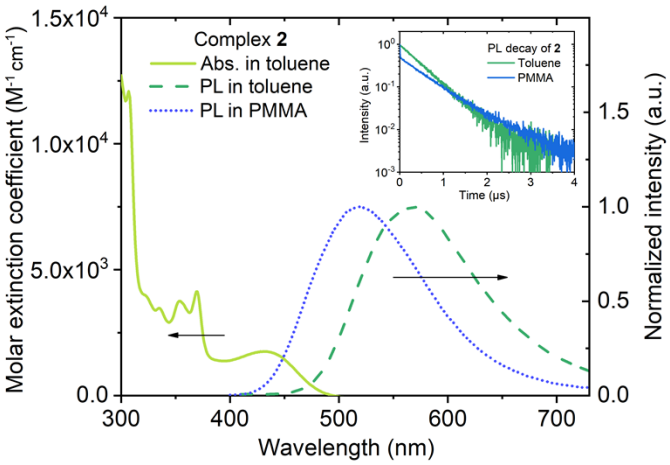


Figure S8. Photophysical properties of complex **2**. UV-Vis absorption spectra in toluene (10^{-5} M), photoluminescence in toluene (10^{-4} M) and PMMA films (a 5-weight percent doping concentration). Inset– photoluminescence decay in toluene and PMMA films.

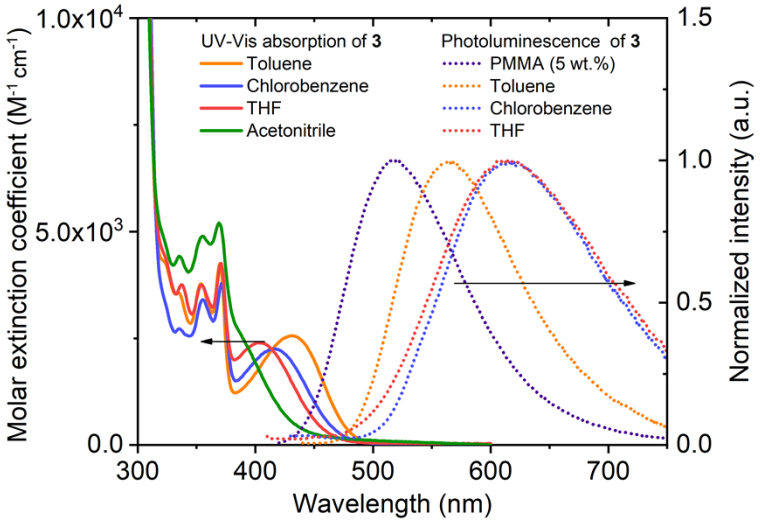


Figure S9. Solvatochromism of complex **3**. Solvatochromic response for UV-Vis absorption in solutions, $c = 10^{-5}$ M, (solid line) and photoluminescence in solutions, $c = 10^{-4}$ M, and PMMA films, a 5-weight percent doping concentration (dotted line).

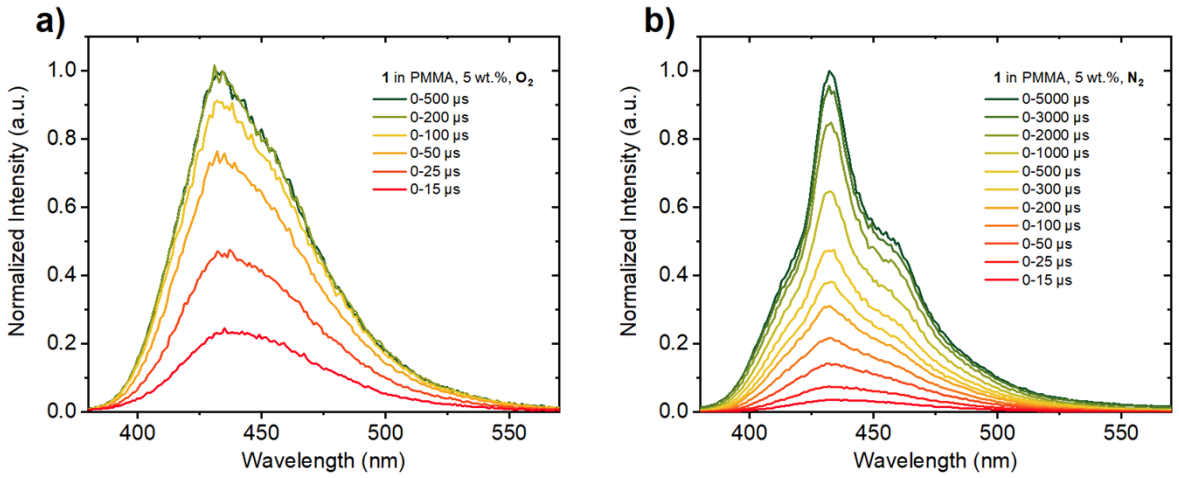


Figure S10. Time-resolved photoluminescence spectra of **1** in PMMA (a 5-weight percent doping concentration) films at ambient air (a) and N_2 (b) atmosphere.

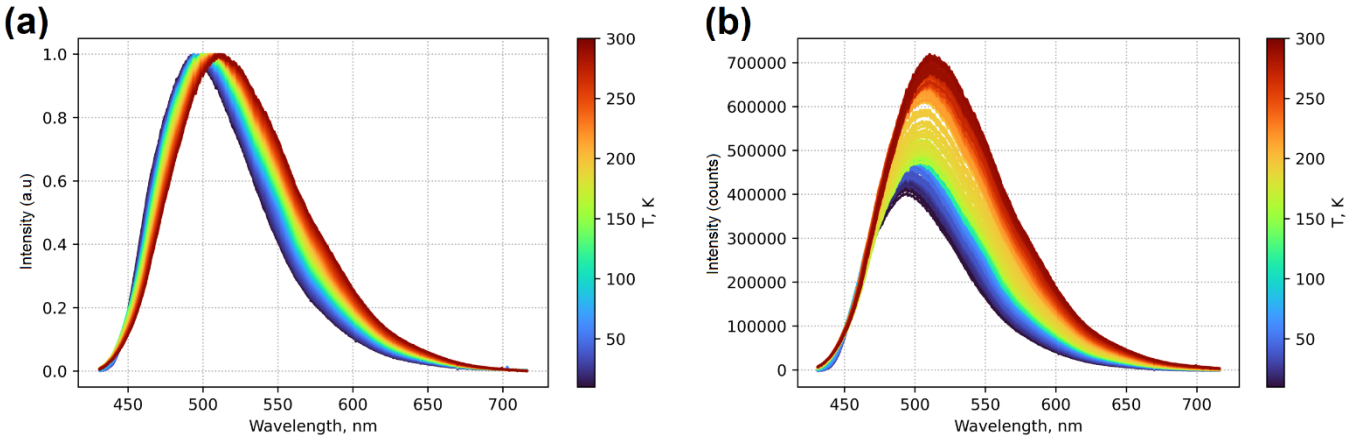


Figure S11. PL of complex **3** (PMMA, a 5-weight percent doping concentration) at 10-300 K temperature range. (a) Normalized PL spectra; (b) PL spectra with absolute intensity values.

Theoretical Calculations

Table S3. DFT calculated properties of compounds **8**, **10b**, **1**, **3** and **4**. PBE0, LACVP** theory level, PCM solvation in benzene.

Compound	E_{HOMO}, eV	E_{LUMO}, eV	S_1, eV	$f_{S0\rightarrow S1}$	^{3}CT, eV	^{3}LE, eV	ΔE_{ST}, eV
8	-6.10	-1.10	4.19 (MLCT)	0.026	3.97 (MLCT)	3.46	0.22
10b	-6.49	-1.98	3.85 (MLCT)	0.014	3.66 (MLCT)	3.56	0.19
1	-4.36	-1.33	2.95 (LLCT)	0.092	2.85 (LLCT)	3.15 (Cbz)	0.10
3	-4.57	-2.08	2.44 (LLCT)	0.072	2.36 (LLCT)	3.17 (Cbz)	0.08
4	-5.3	-1.98	2.76 (LLCT)	0.074	2.69 (LLCT)	3.16 (Cbz)	0.07

Table S4. Comparison of DFT calculated and experimental parameters between selected CMA emitters with different carbene ligands.

Compound	S_{HL}[a,b]	$f_{S0\rightarrow S1}$[a]	$k_{r(TADF)}$,[c] $\times 10^5$ s^{-1}
3	0.118	0.072	13.0
CAAC	0.302	0.110	3.0
PZI	0.258	0.124	21.5
TZL	0.278	0.120	3.6
MAC	0.298	0.117	6.4
PAC	0.211	0.083	7.9

[a] DFT calculated values.
[b] HOMO-LUMO overlap integral.
[c] Experimental values.

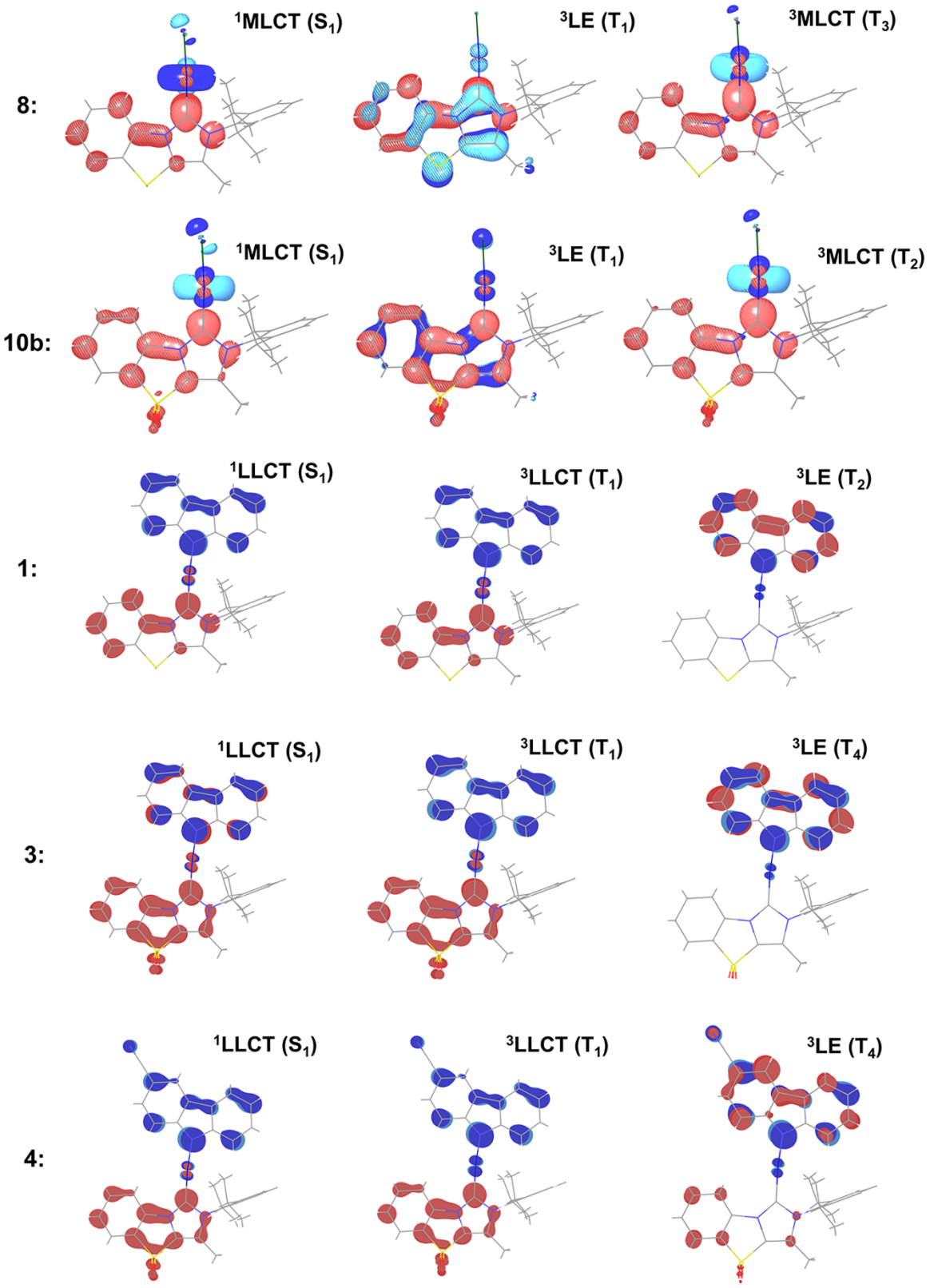


Figure S12. Natural transition orbitals for selected excitations for compounds **8**, **10b**, **1**, **3** and **4**. The blue regions represent hole, while the red are assigned to electron.

NMR spectra

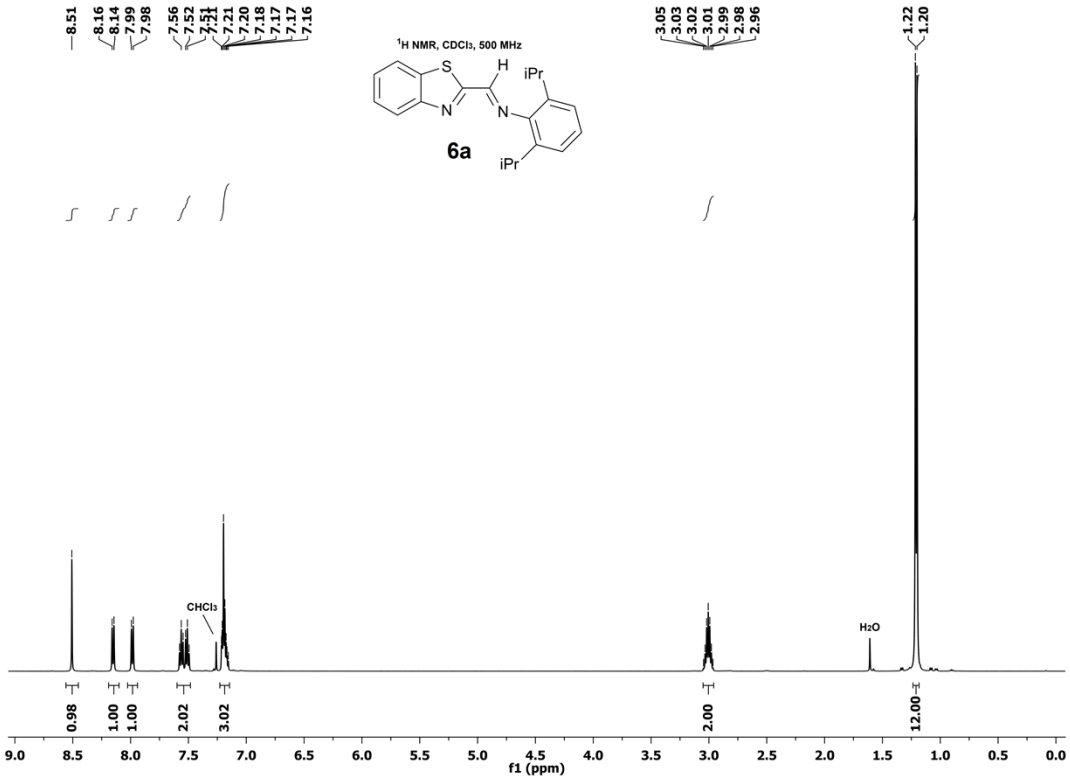


Figure S13. ^{1}H NMR spectrum of **6a** ($CDCl_3$, 500 MHz).

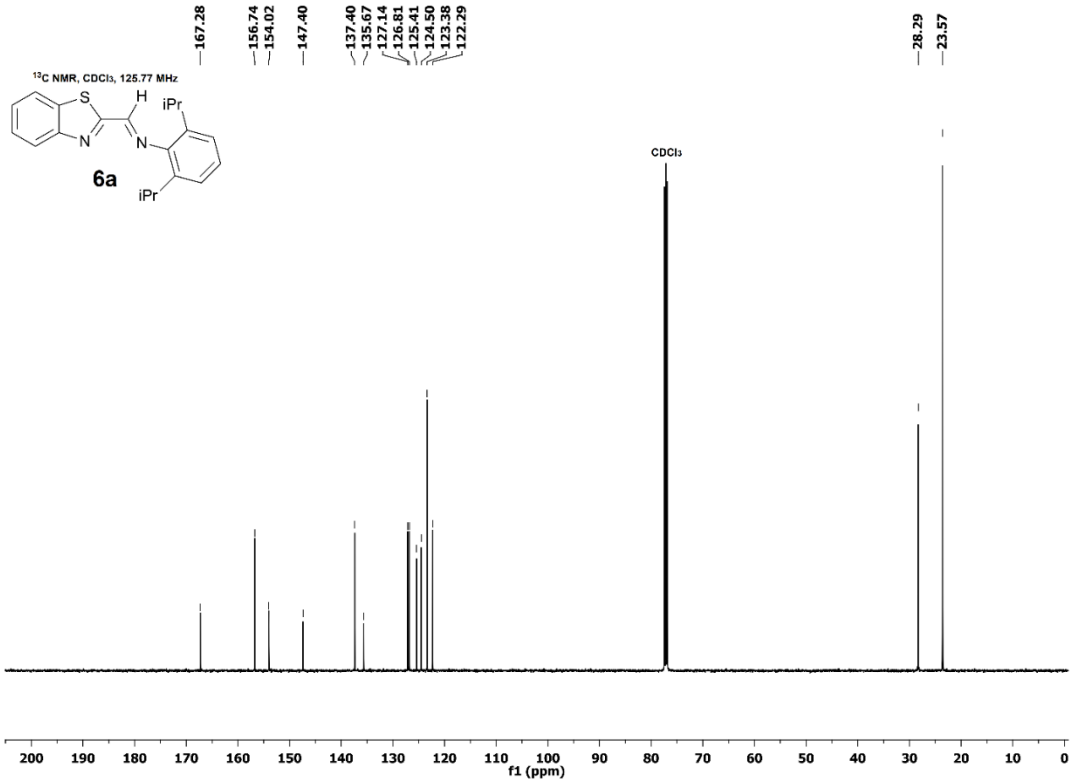


Figure S14. ^{13}C NMR spectrum of **6a** ($CDCl_3$, 125.77 MHz).

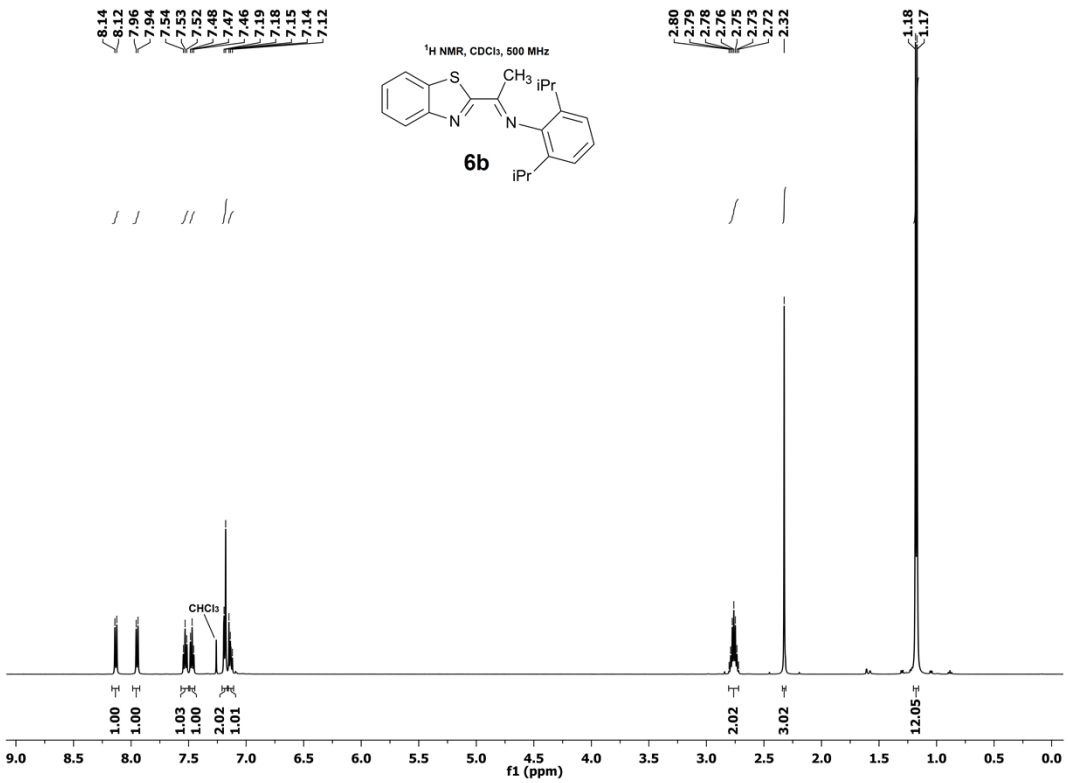


Figure S15. ^{1}H NMR spectrum of **6b** ($CDCl_3$, 500 MHz).

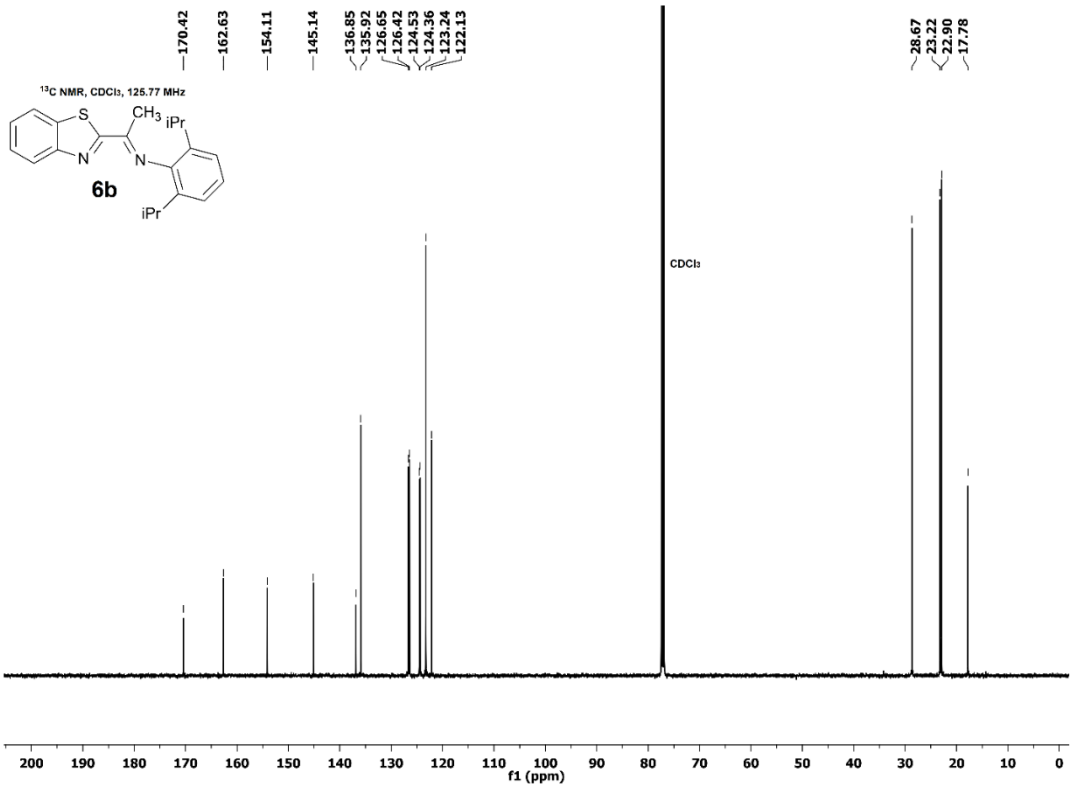


Figure S16. ^{13}C NMR spectrum of **6b** ($CDCl_3$, 125.77 MHz).

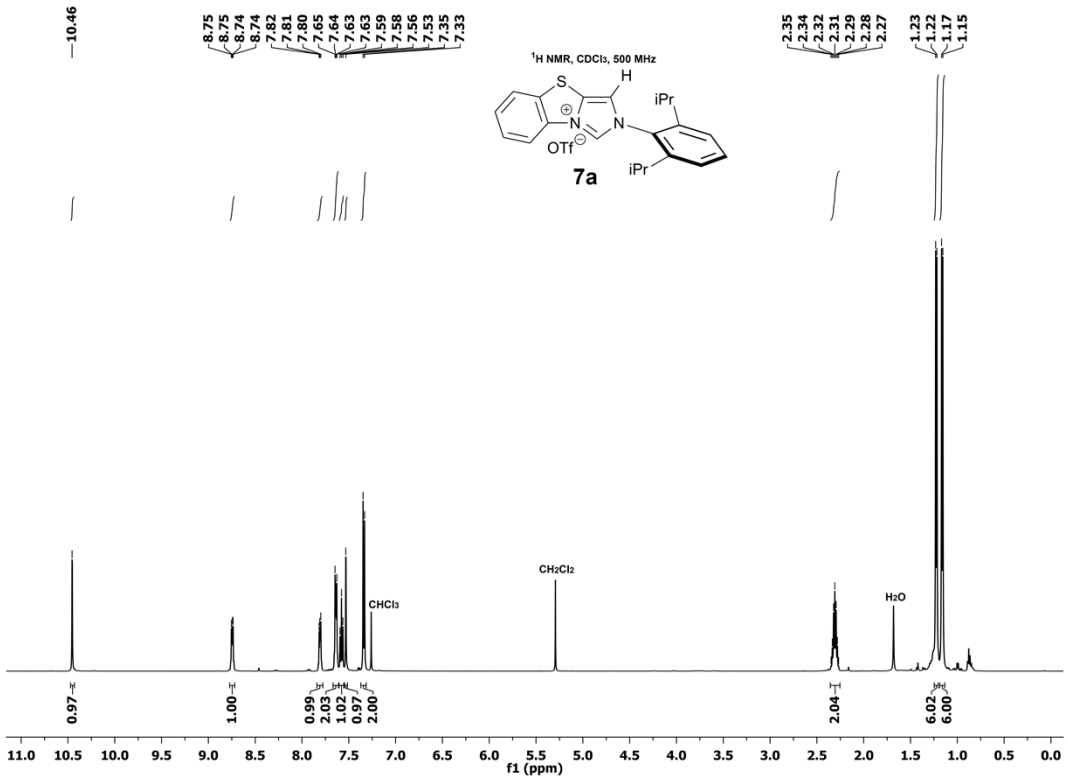


Figure S17. ^{1}H NMR spectrum of **7a** ($CDCl_3$, 500 MHz).

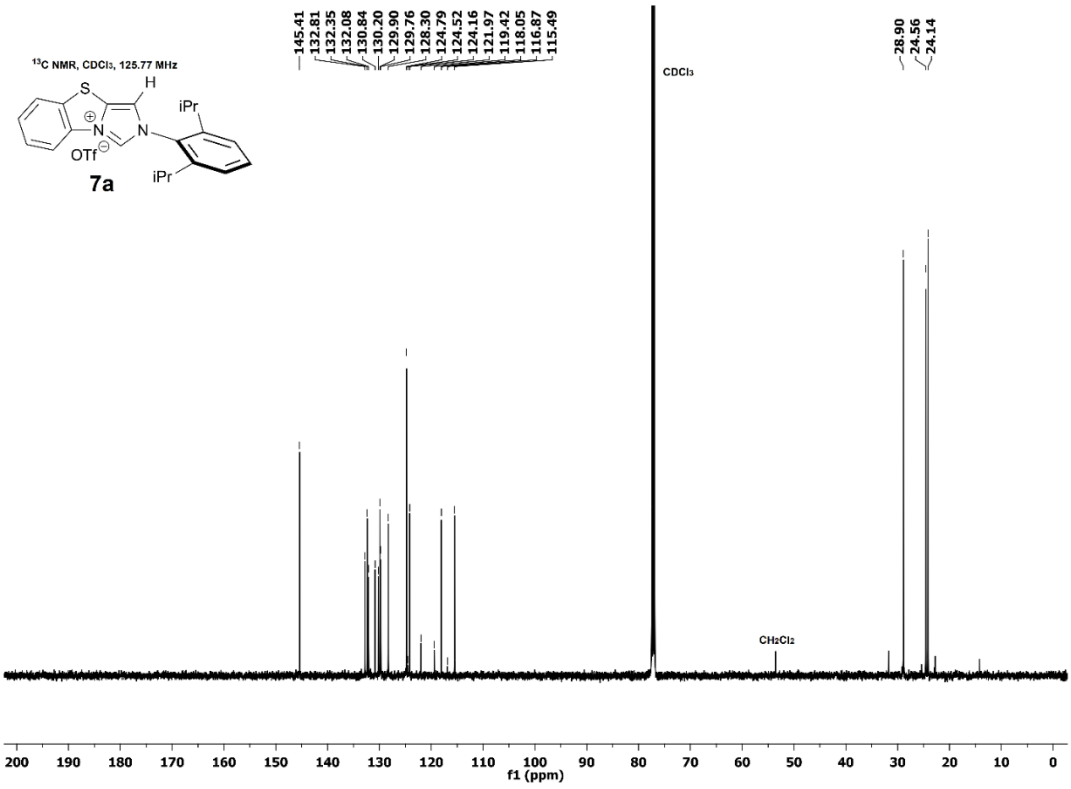


Figure S18. ^{13}C NMR spectrum of **7a** ($CDCl_3$, 125.77 MHz).

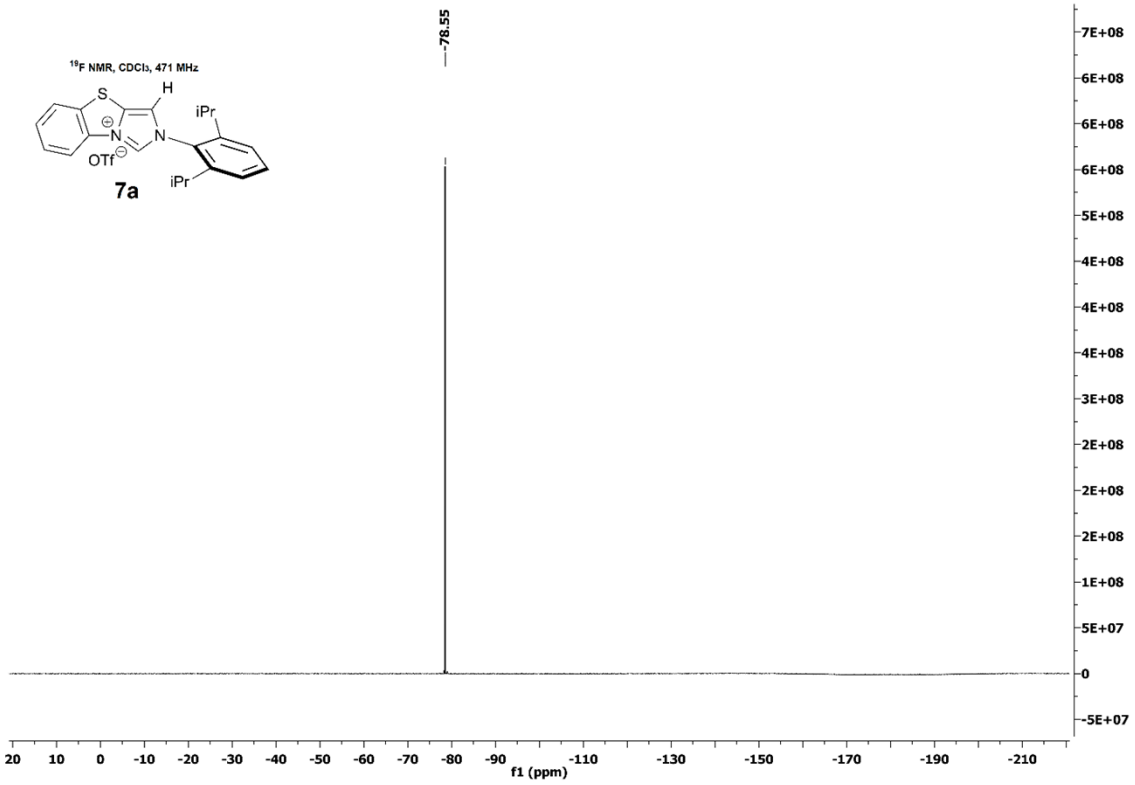


Figure S19. ^{19}F NMR spectrum of **7a** ($CDCl_3$, 471 MHz).

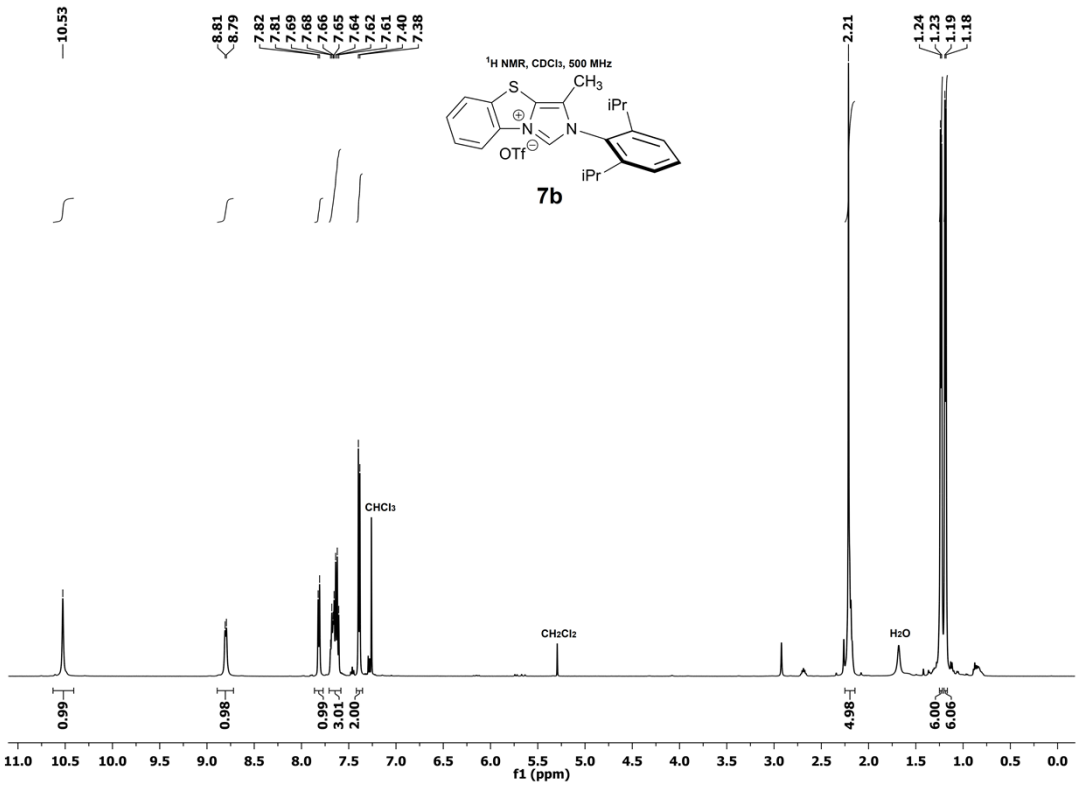


Figure S20. ^{1}H NMR spectrum of **7b** ($CDCl_3$, 500 MHz).

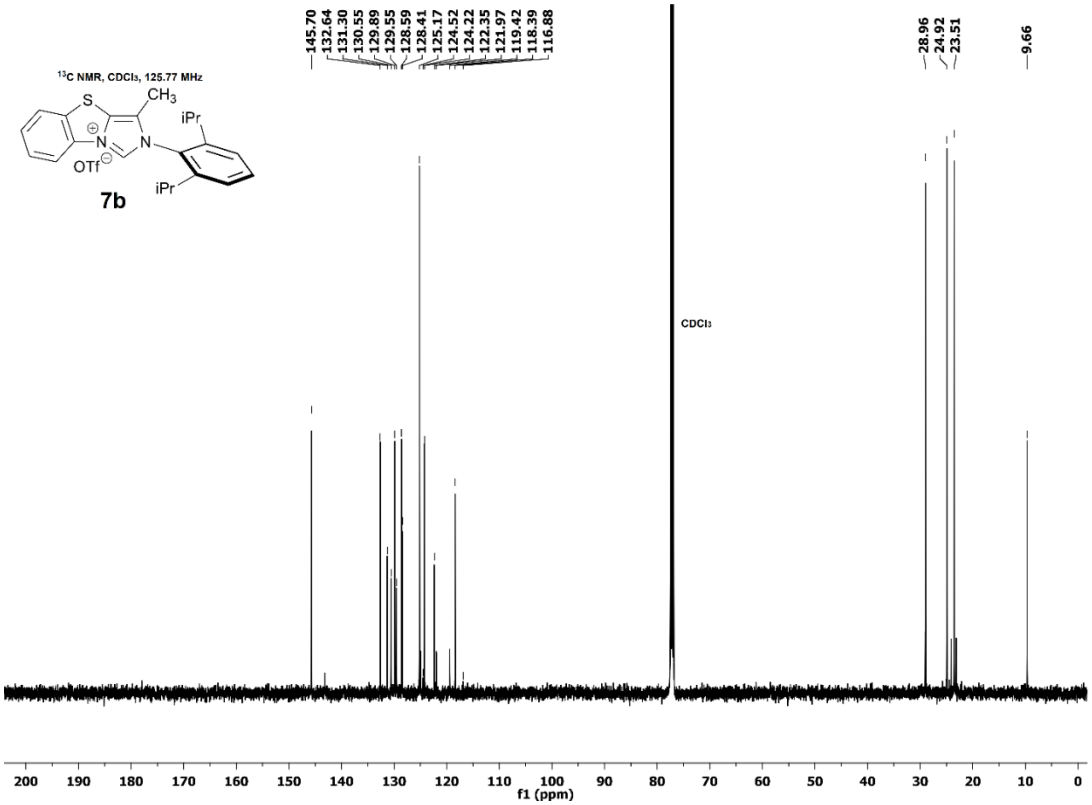


Figure S21. ^{13}C NMR spectrum of **7b** ($CDCl_3$, 125.77 MHz).

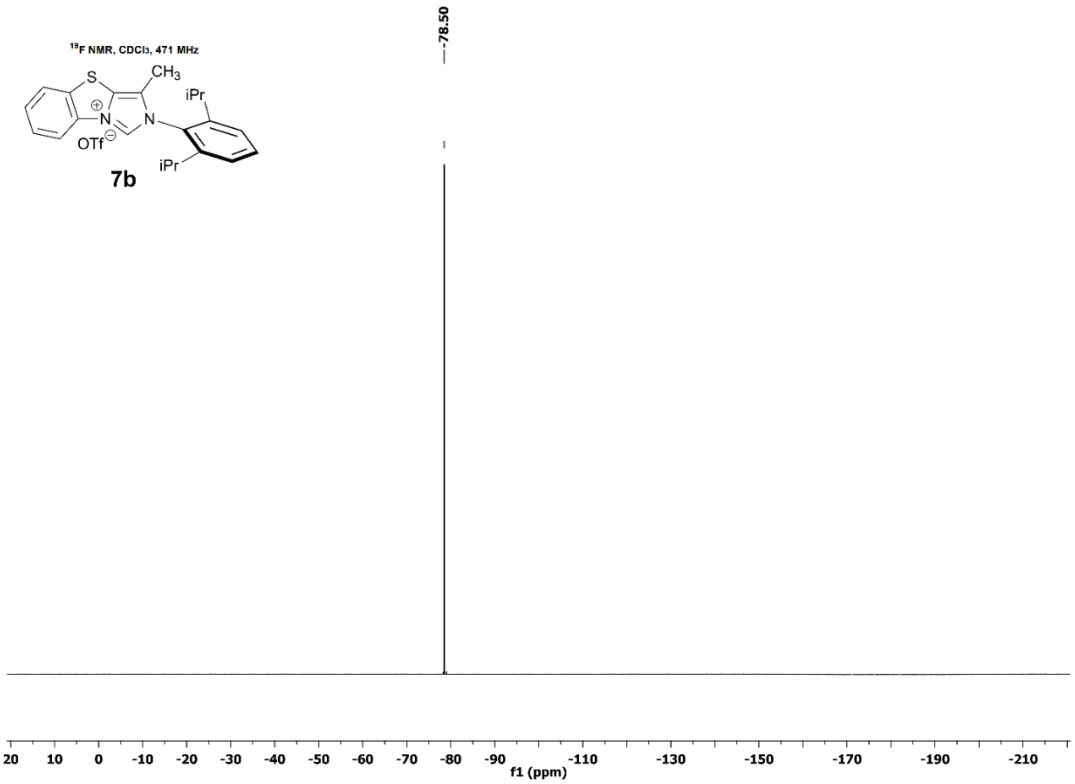


Figure S22. ^{19}F NMR spectrum of **7b** ($CDCl_3$, 471 MHz).

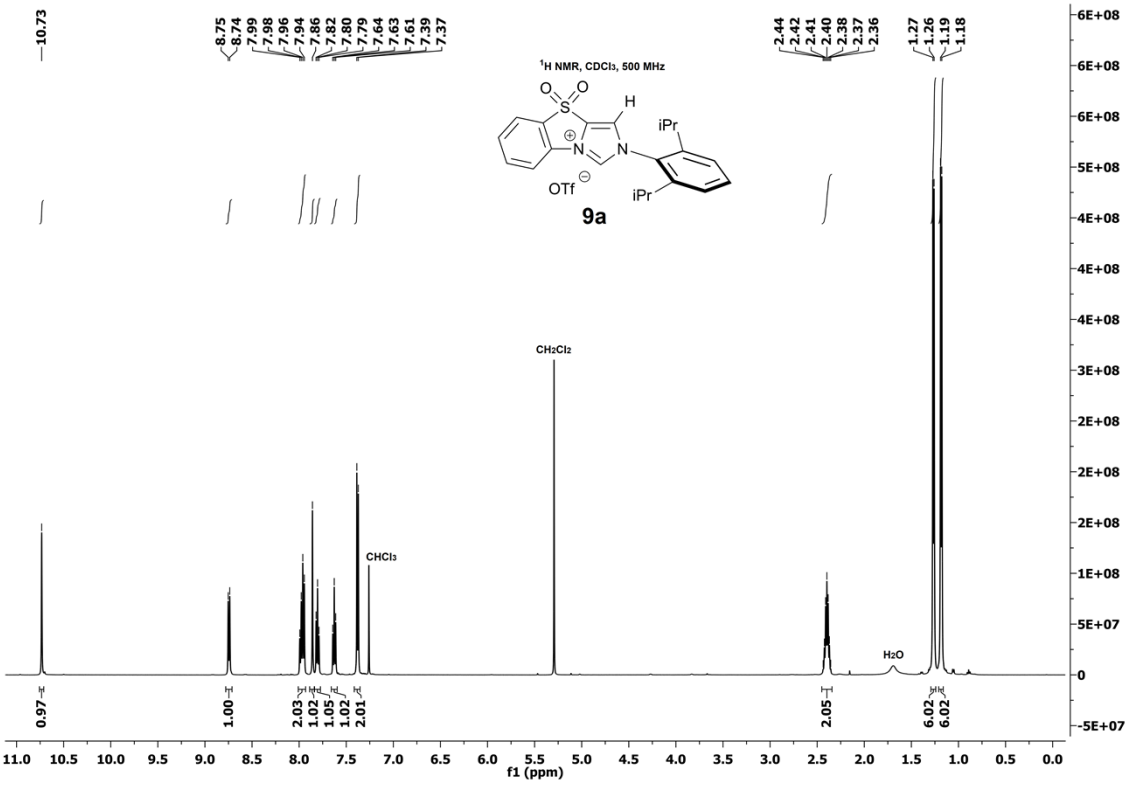


Figure S23. ^{1}H NMR spectrum of **9a** ($CDCl_3$, 500 MHz).

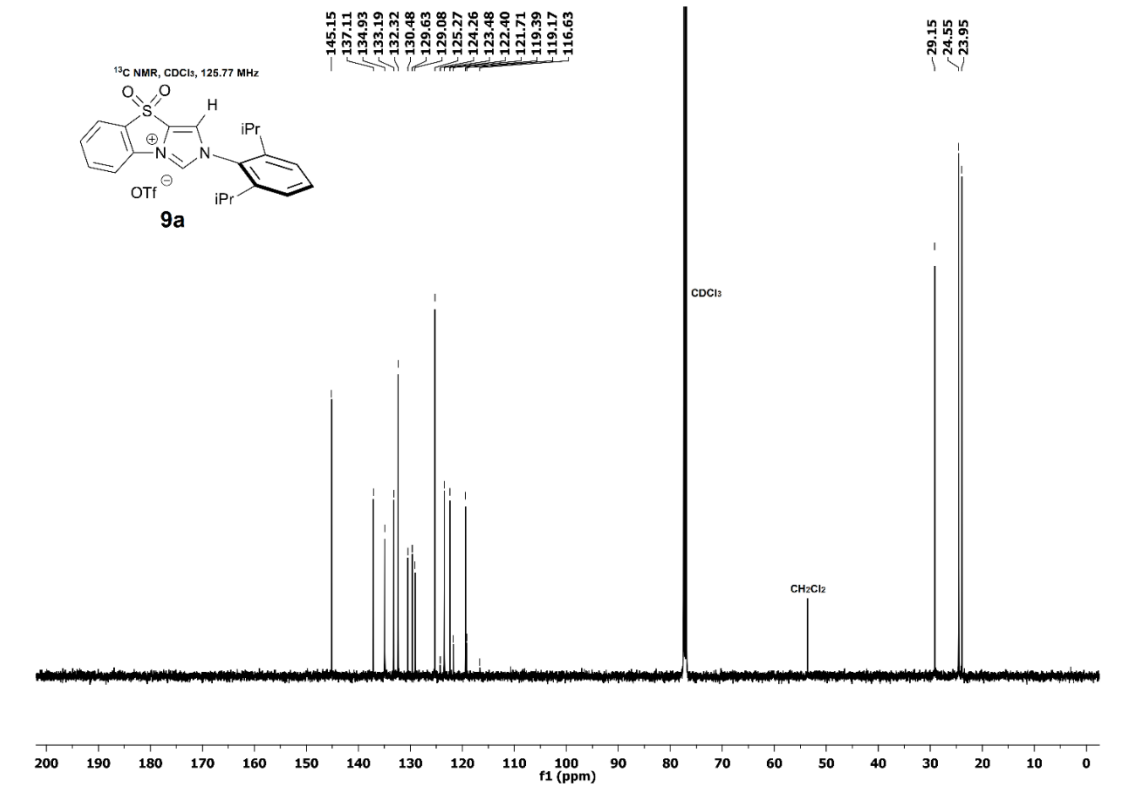


Figure S24. ^{13}C NMR spectrum of **9a** ($CDCl_3$, 125.77 MHz).

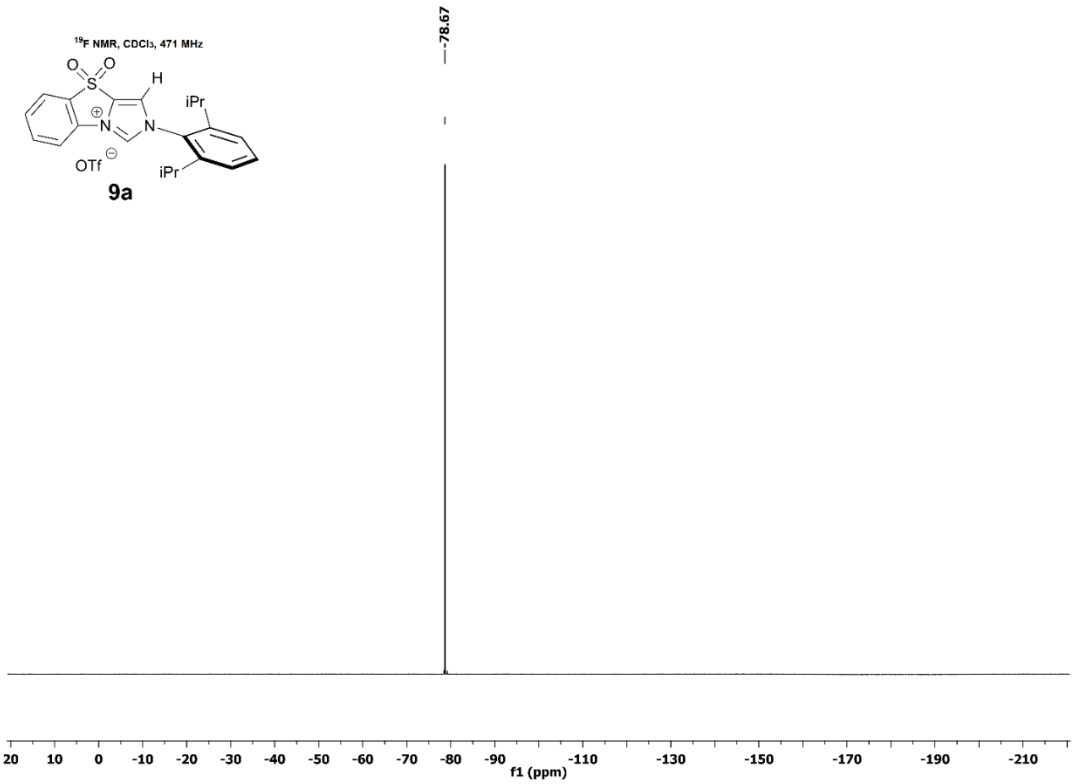


Figure S25. ^{19}F NMR spectrum of **9a** ($CDCl_3$, 471 MHz).

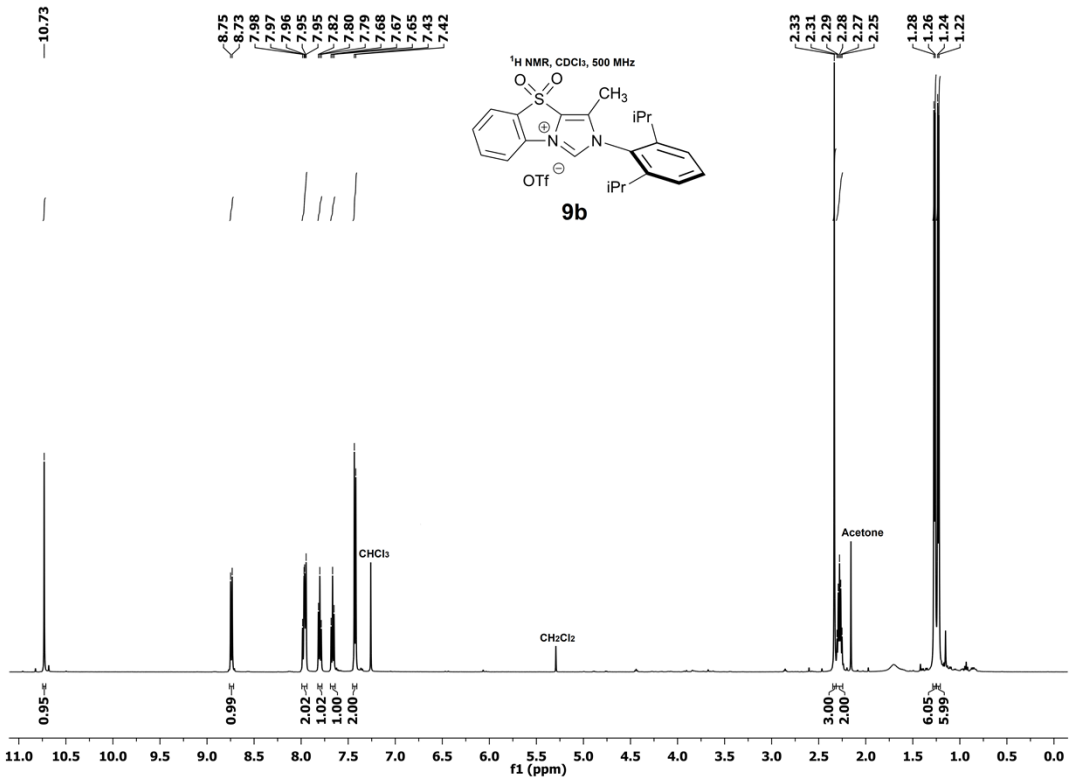


Figure S26. ^{1}H NMR spectrum of **9b** ($CDCl_3$, 500 MHz).

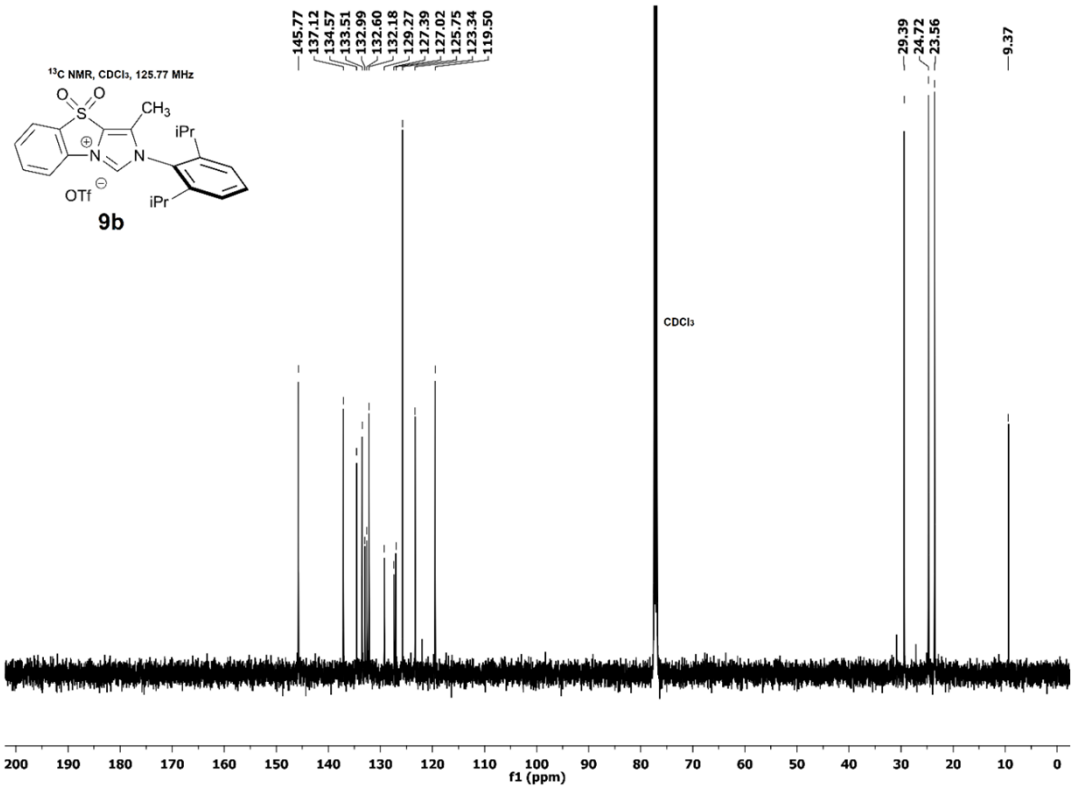


Figure S27. ^{13}C NMR spectrum of **9b** ($CDCl_3$, 125.77 MHz).

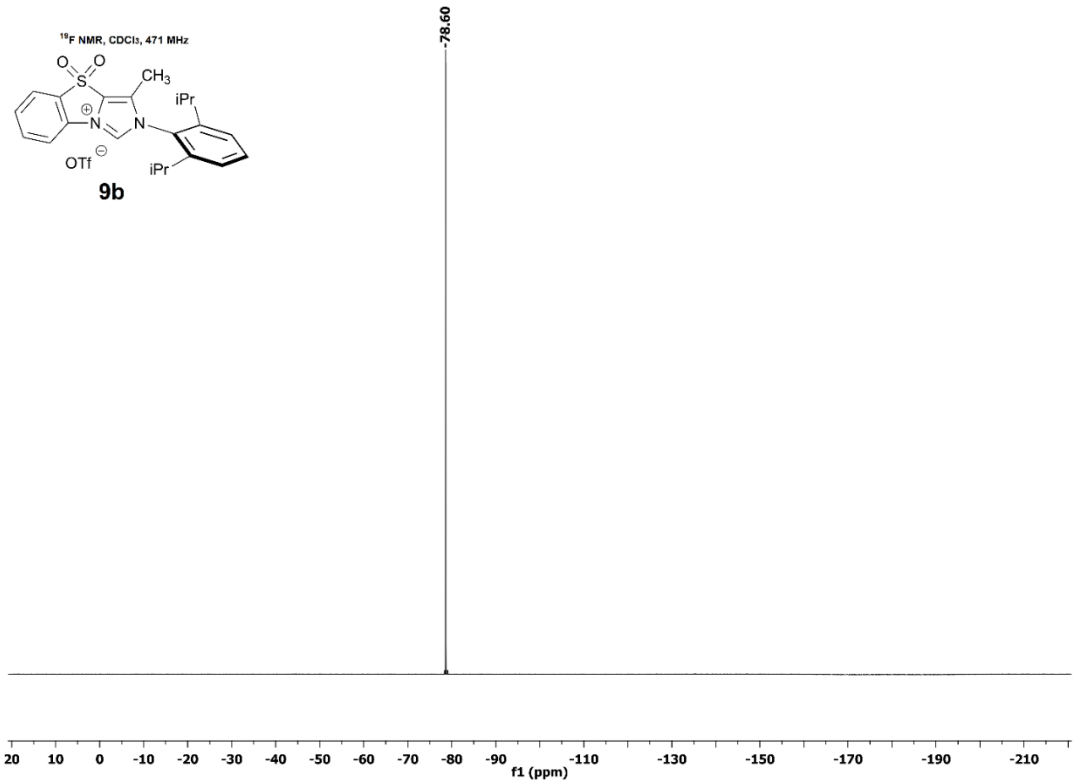


Figure S28. ^{19}F NMR spectrum of **9b** ($CDCl_3$, 471 MHz).

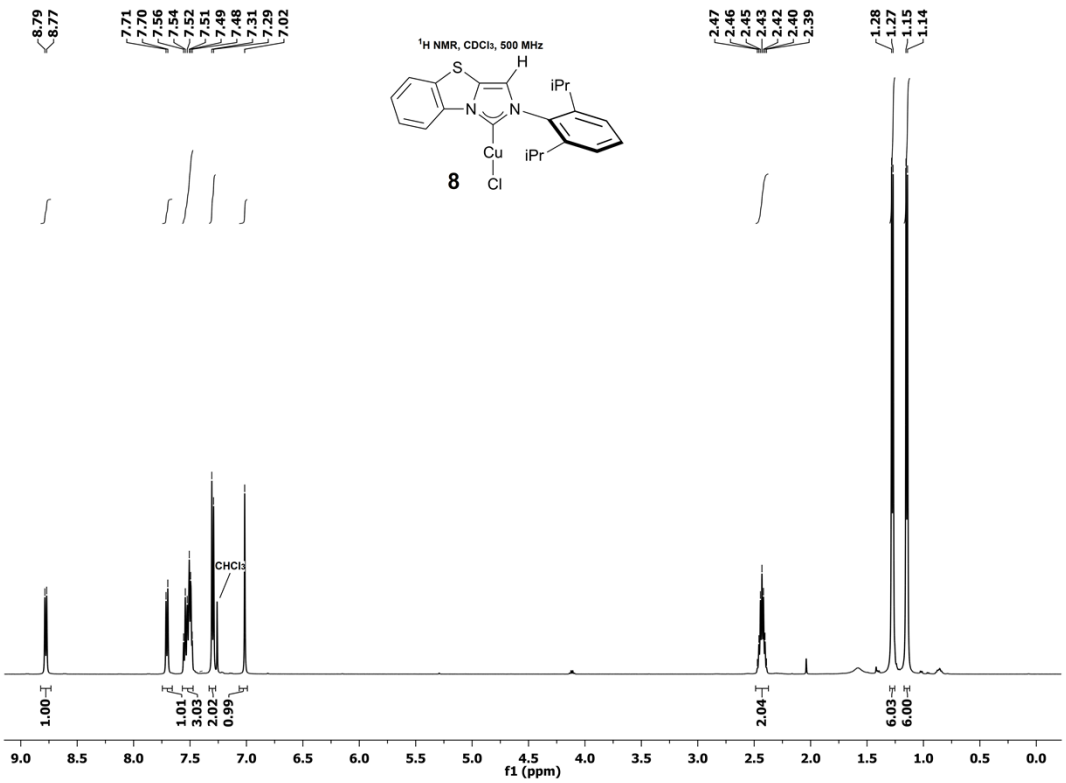


Figure S29. ^{1}H NMR spectrum of **8** ($CDCl_3$, 500 MHz).

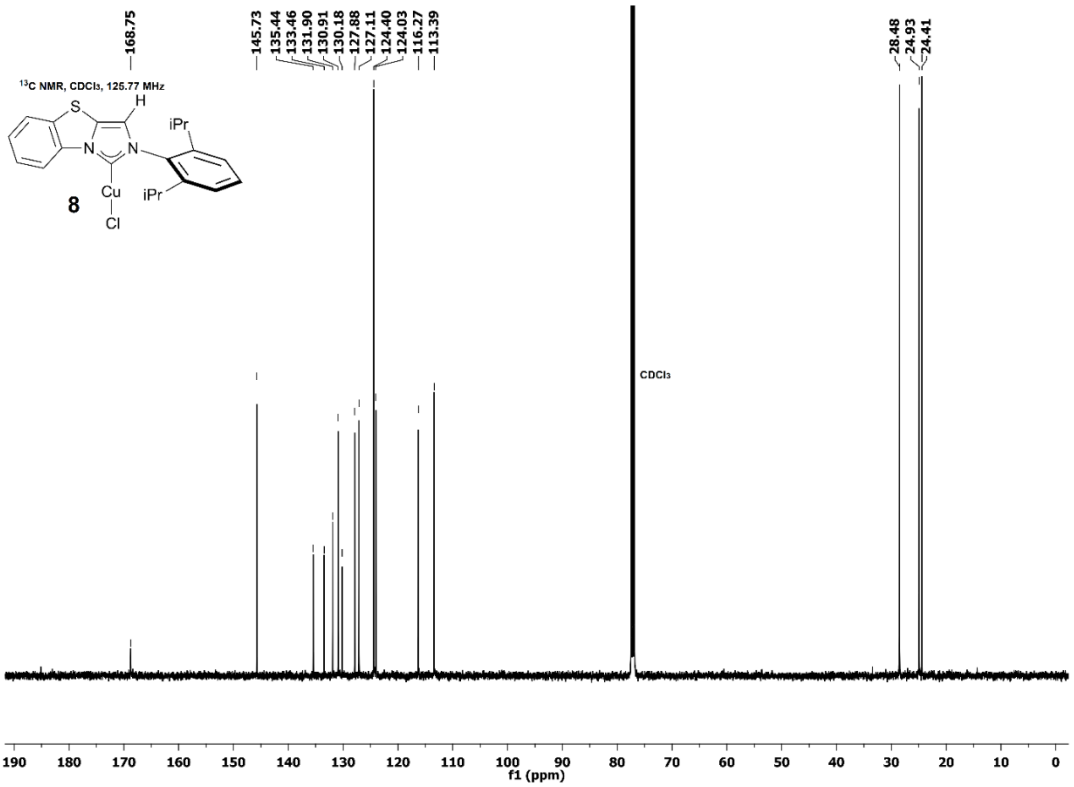


Figure S30. ^{13}C NMR spectrum of **8** ($CDCl_3$, 125.77 MHz).

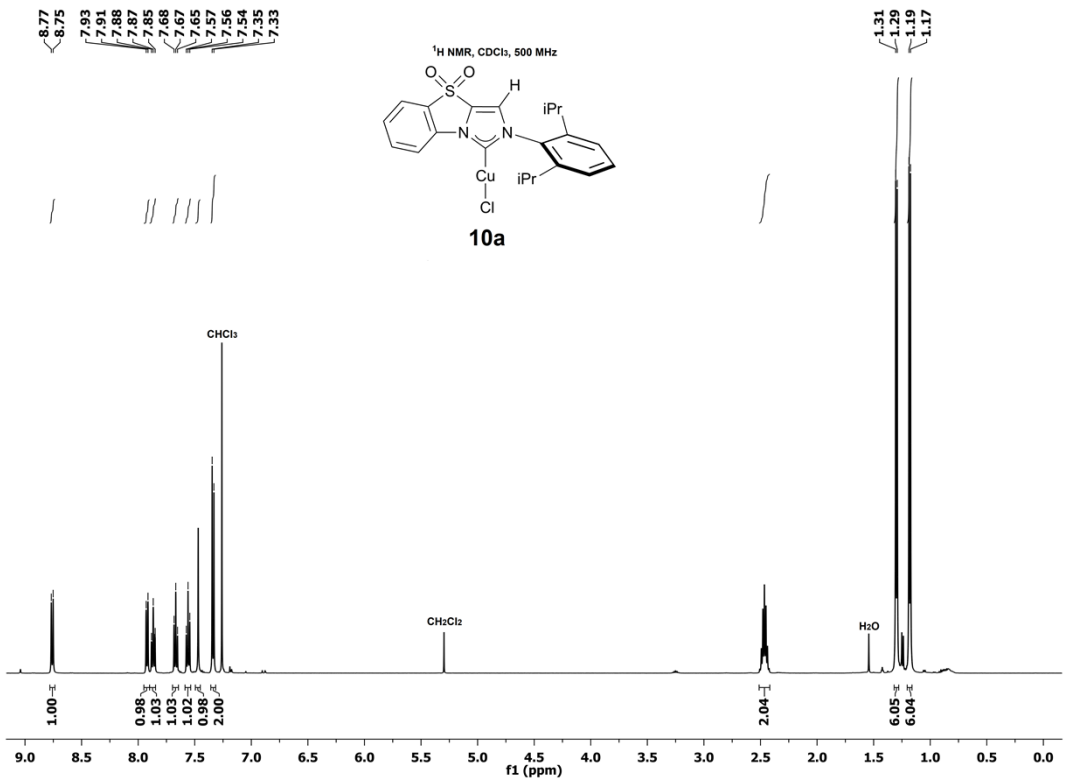


Figure S31. ^{1}H NMR spectrum of **10a** ($CDCl_3$, 500 MHz).

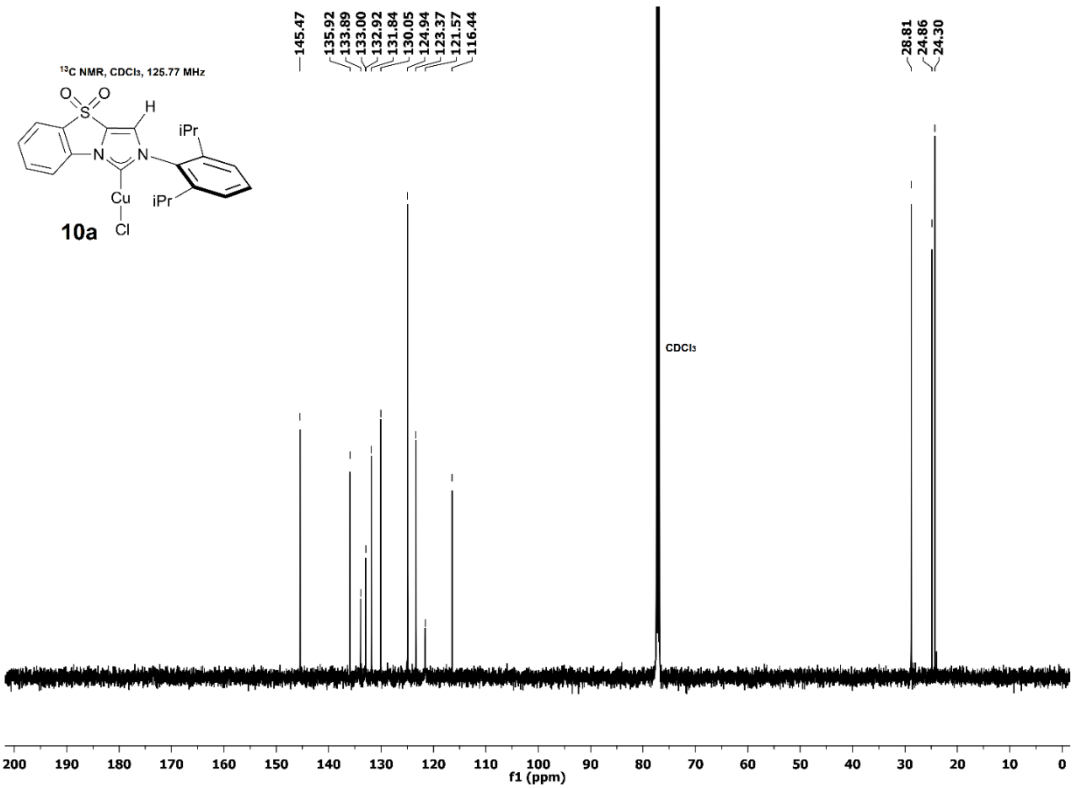


Figure S32. ^{13}C NMR spectrum of **10a** ($CDCl_3$, 125.77 MHz).

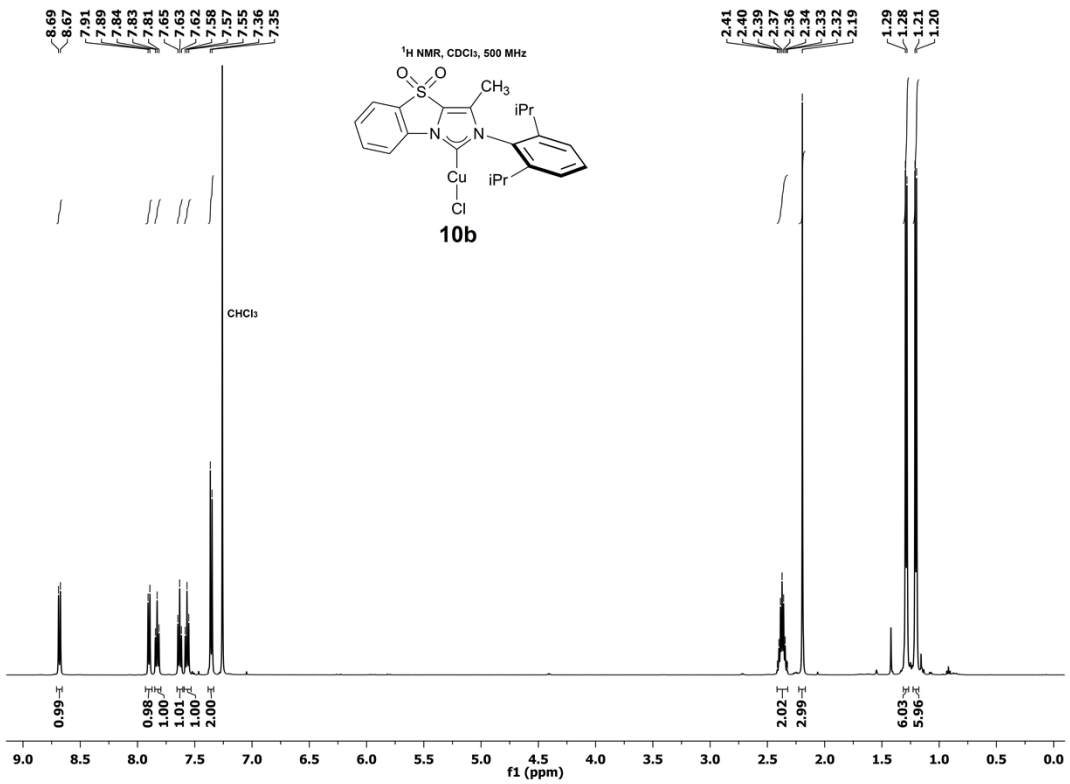


Figure S33. ^{1}H NMR spectrum of **10b** ($CDCl_3$, 500 MHz).

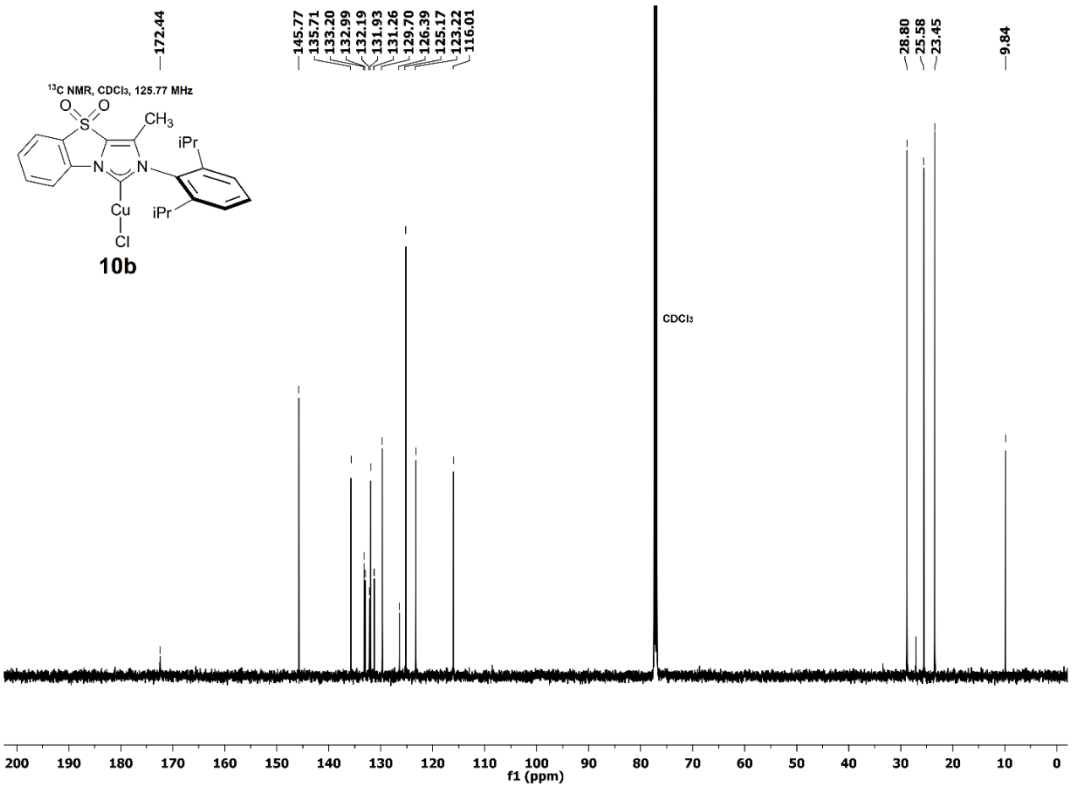


Figure S34. ^{13}C NMR spectrum of **10b** ($CDCl_3$, 125.77 MHz).

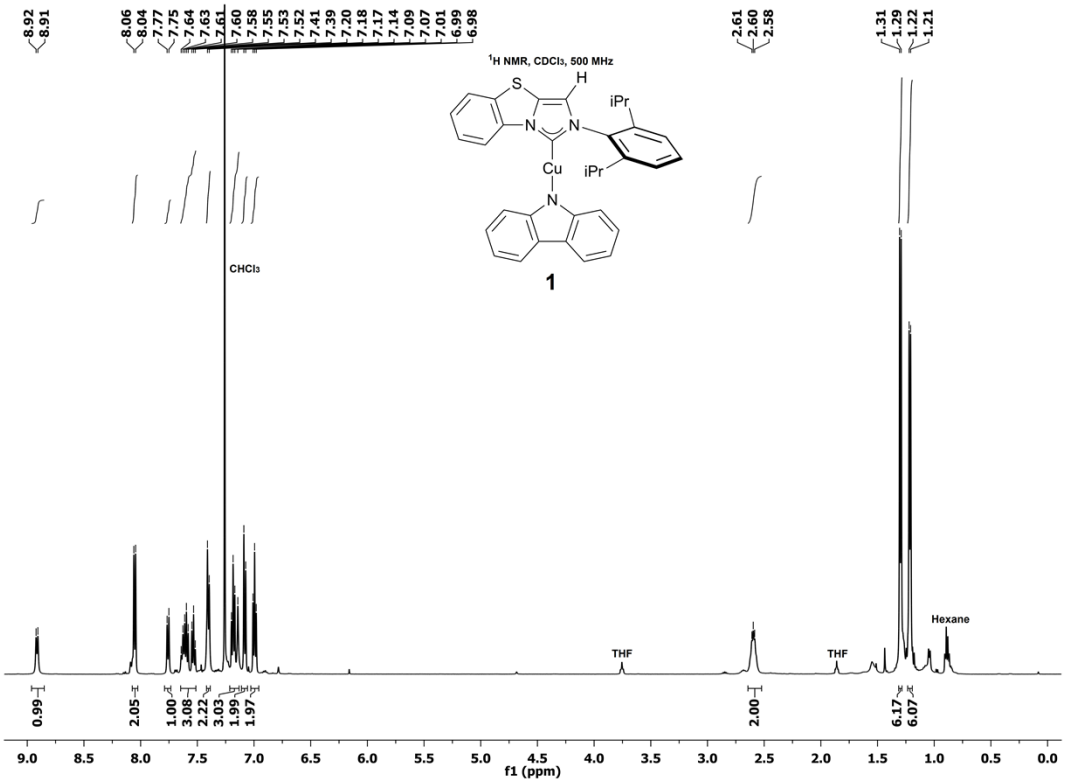


Figure S35. ^{1}H NMR spectrum of **1** ($CDCl_3$, 500 MHz).

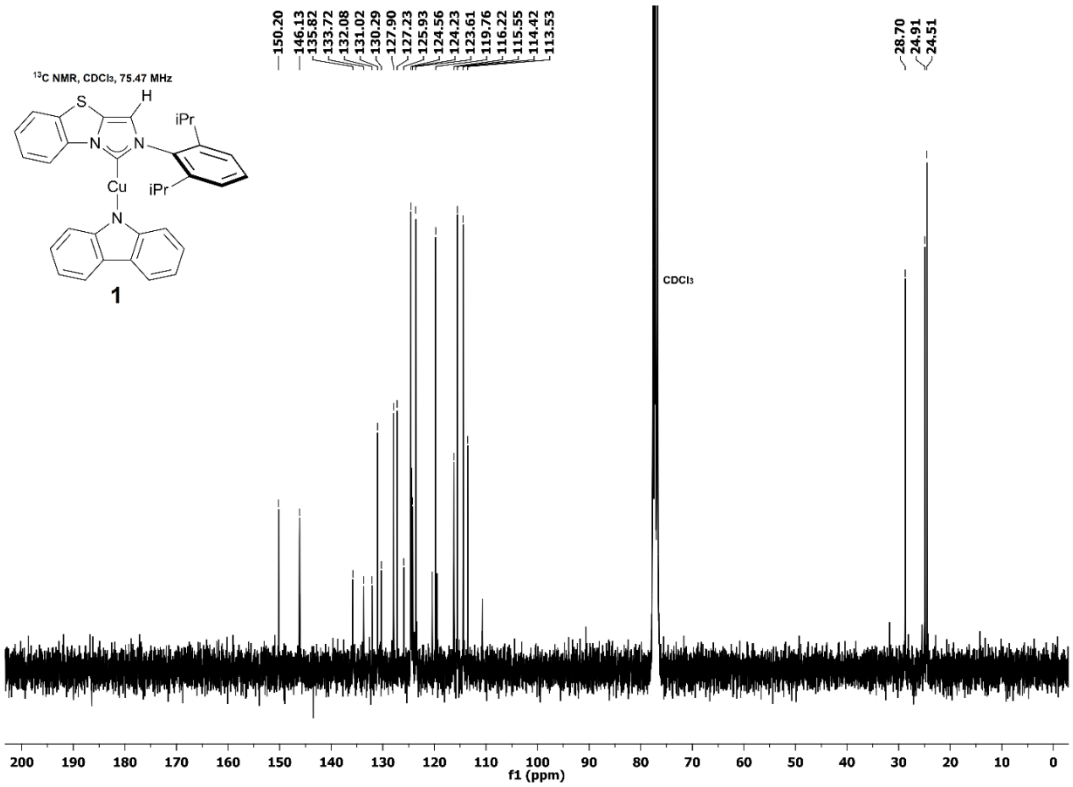


Figure S36. ^{13}C NMR spectrum of **1** ($CDCl_3$, 75.47 MHz).

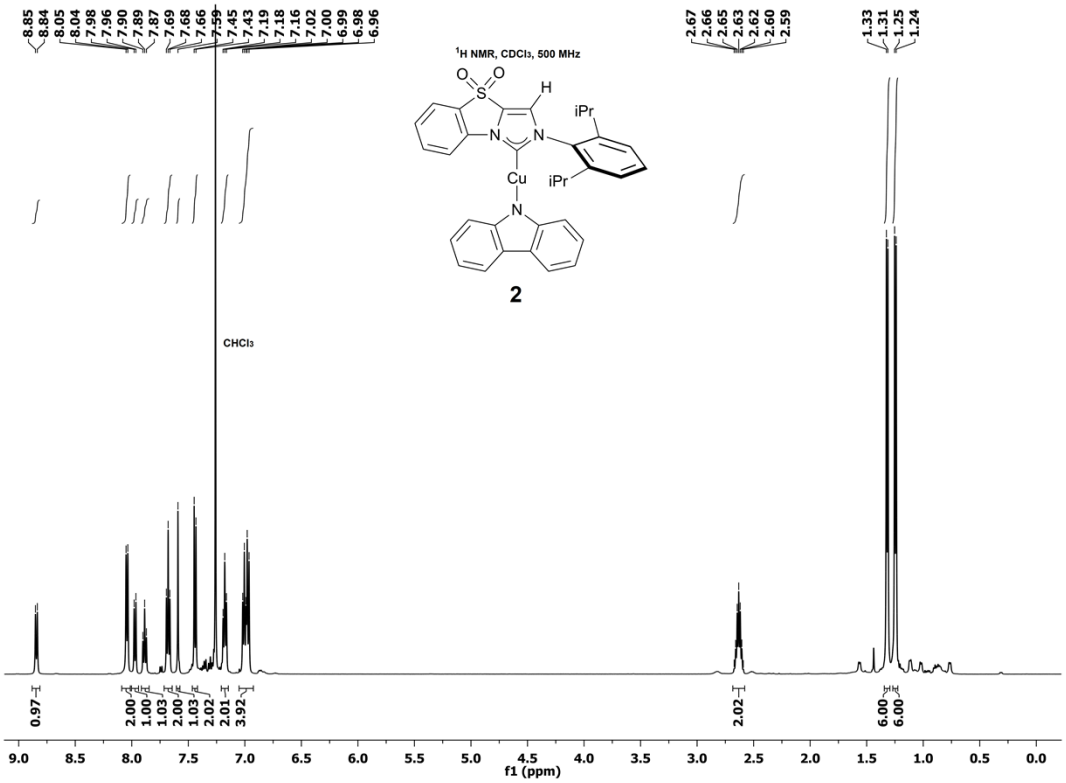


Figure S37. ^{1}H NMR spectrum of **2** ($CDCl_3$, 500 MHz).

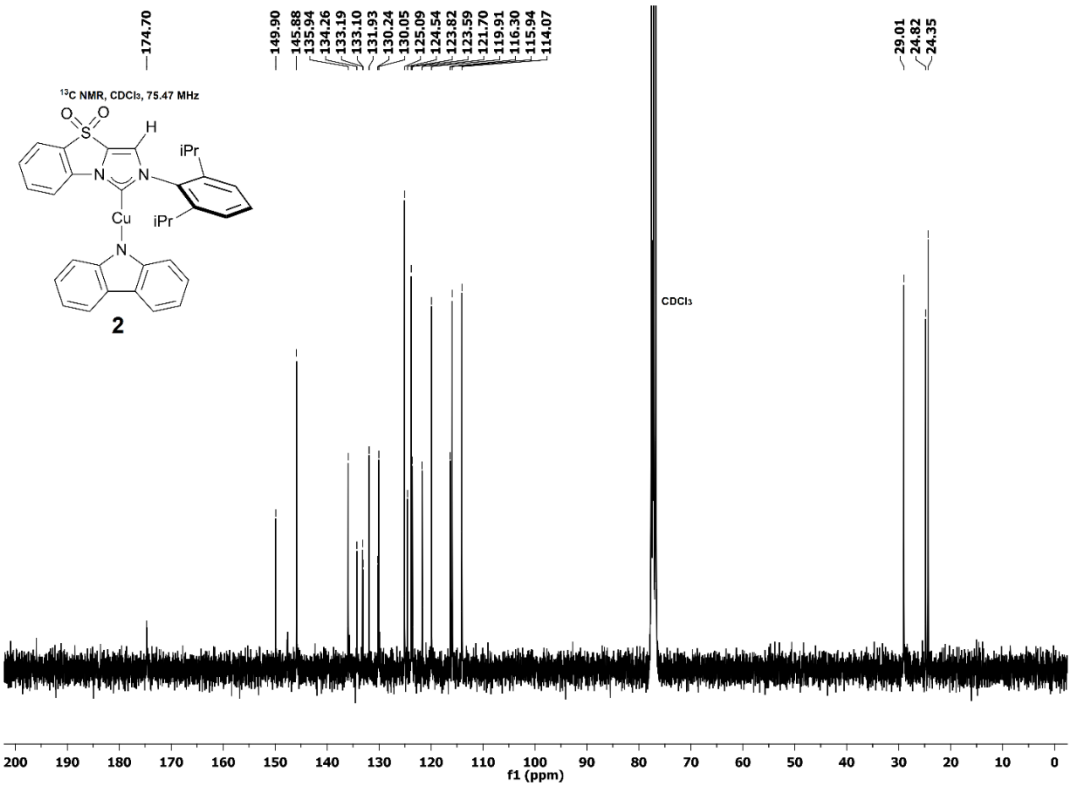


Figure S38. ^{13}C NMR spectrum of **2** ($CDCl_3$, 75.47 MHz).

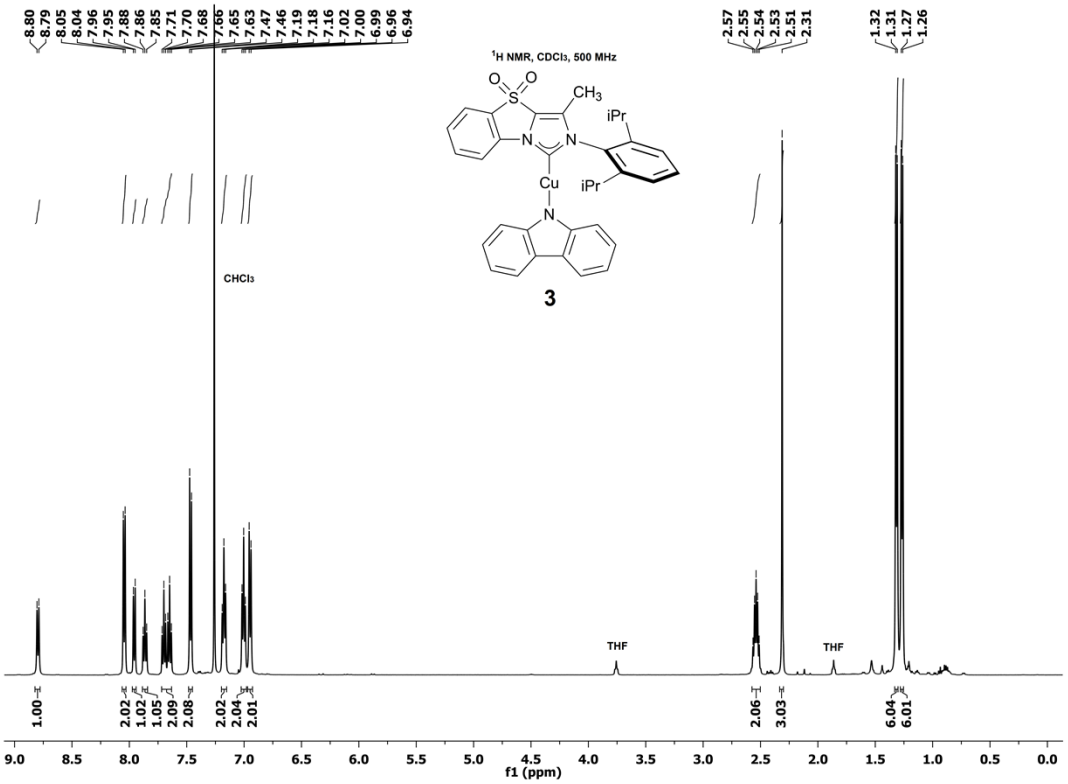


Figure S39. ^{1}H NMR spectrum of **3** ($CDCl_3$, 500 MHz).

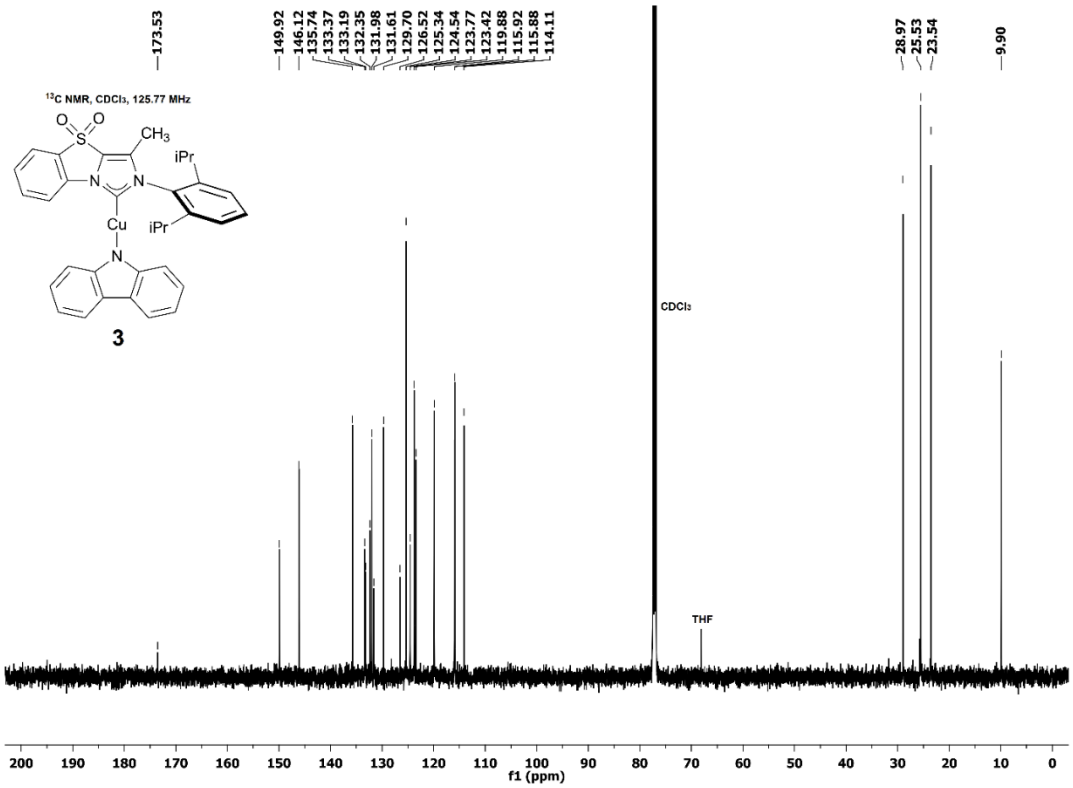


Figure S40. ^{13}C NMR spectrum of **3** ($CDCl_3$, 125.77 MHz).

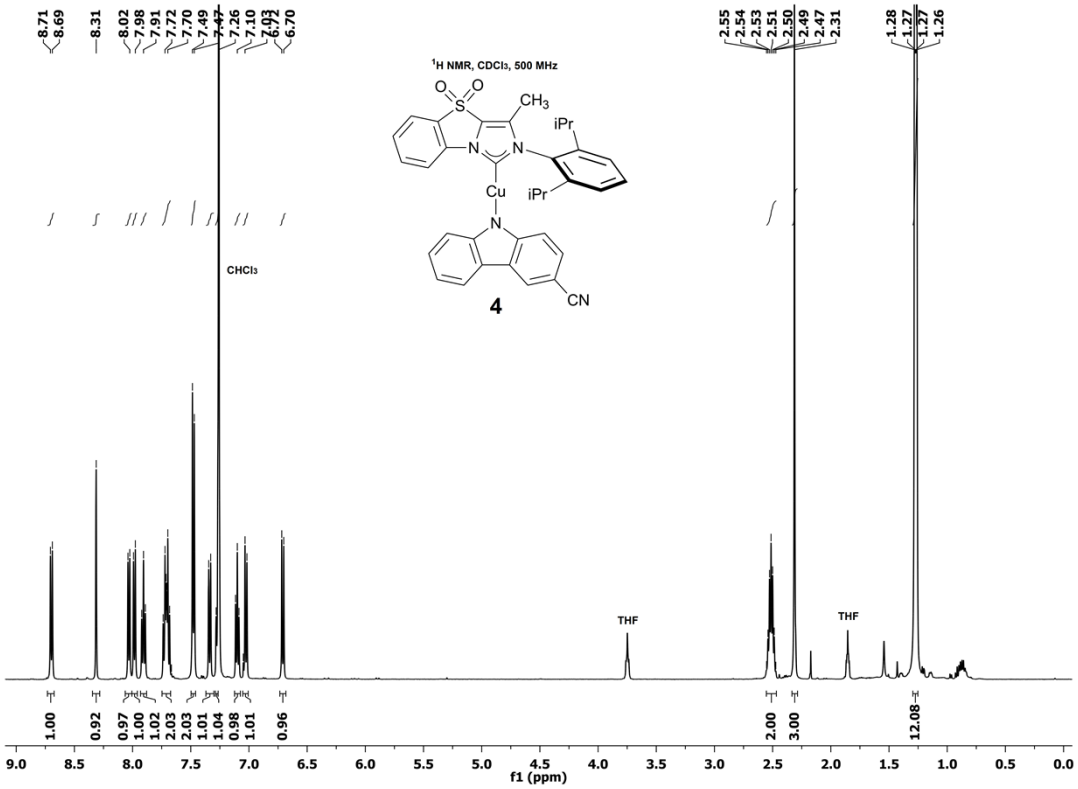


Figure S41. ^{1}H NMR spectrum of **4** ($CDCl_3$, 500 MHz).

Figure S42. ^{13}C NMR spectrum of **4** ($CDCl_3$, 125.77 MHz).