Supporting Information

Contents

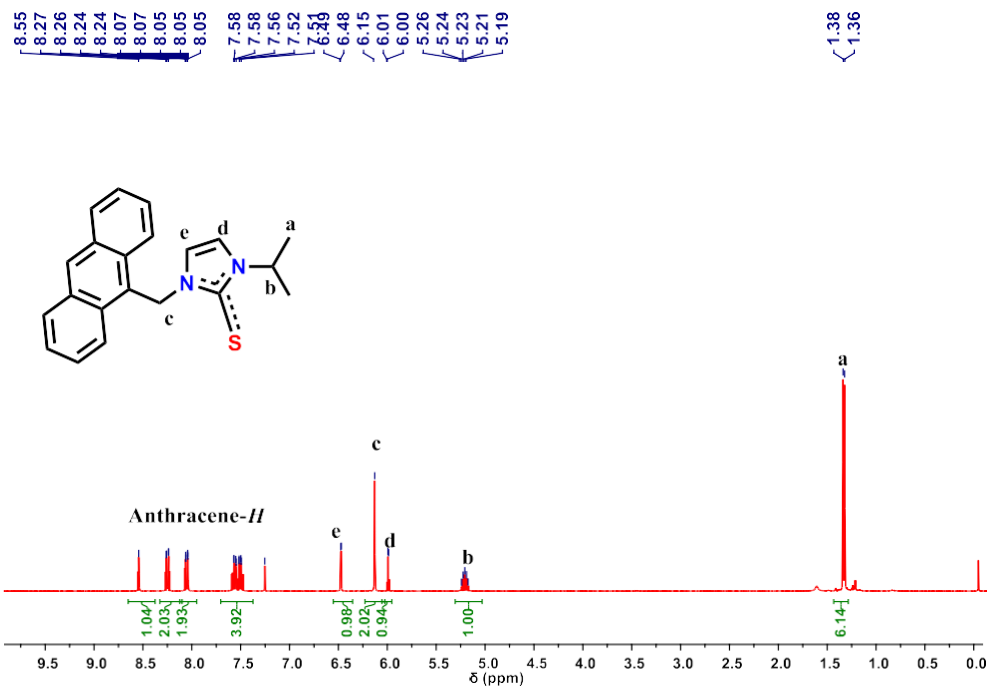


Fig. S1. ^{1}H NMR of **L^{1}** in $CDCl_3$ at 25 °C

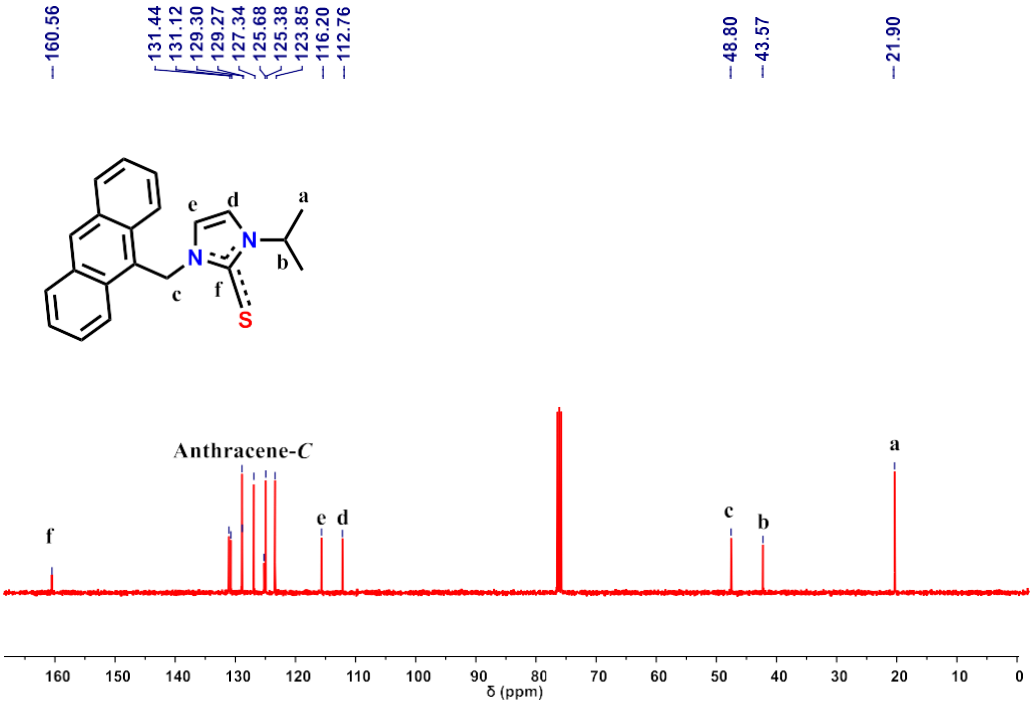


Fig. S2. ^{13}C NMR of **L^{1}** in $CDCl_3$ at 25 °C

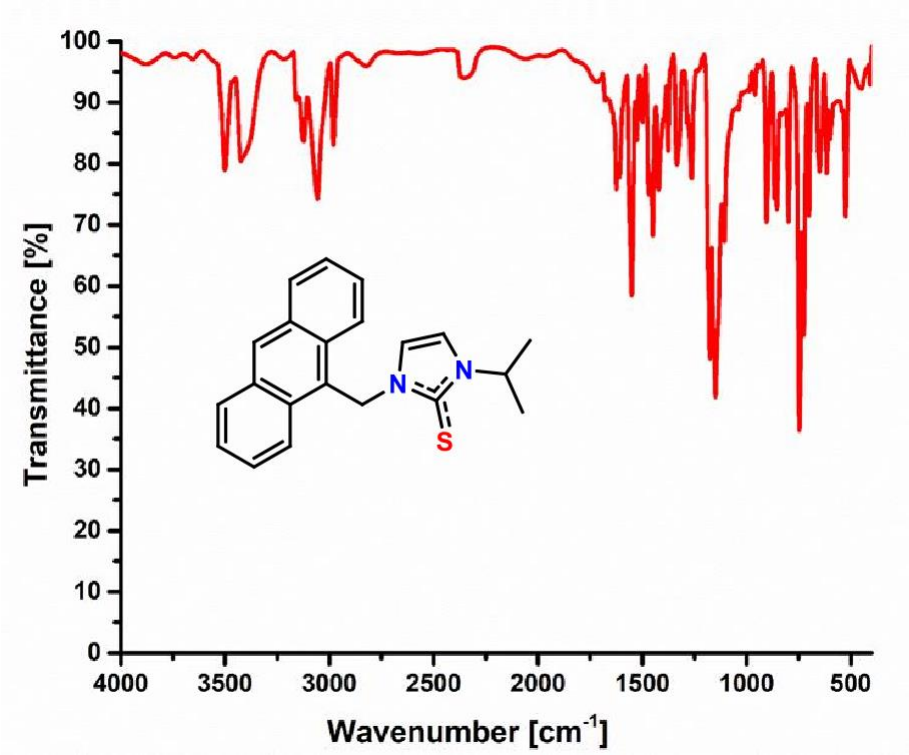


Fig. S3. FT-IR spectrum of **L¹** (KBr method) at 25 °C

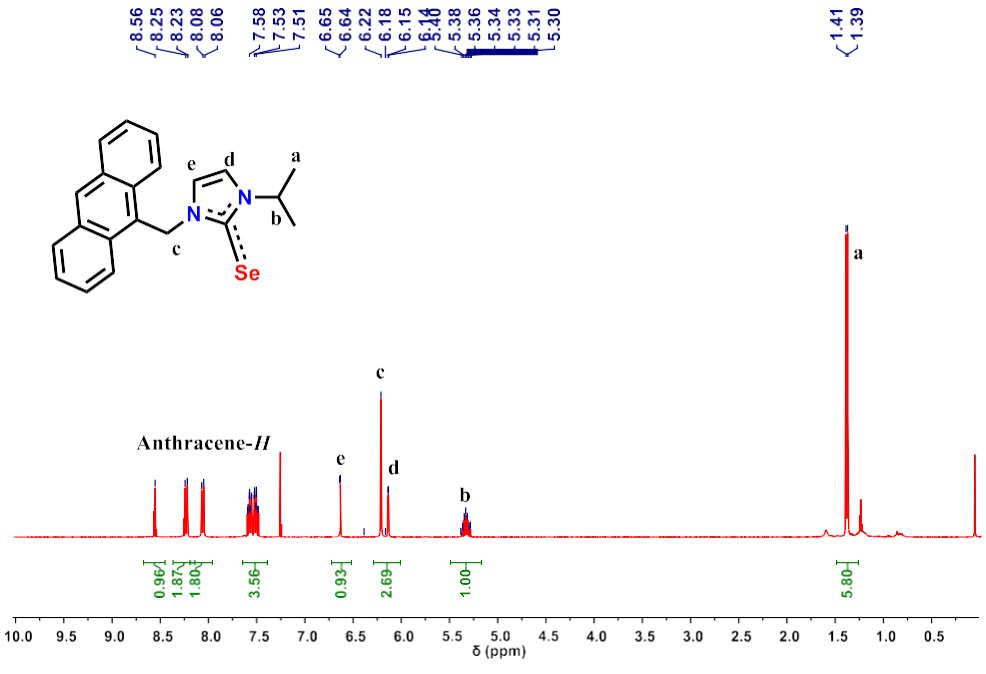


Fig. S4. ^{1}H NMR of **L²** in $CDCl_3$ at 25 °C

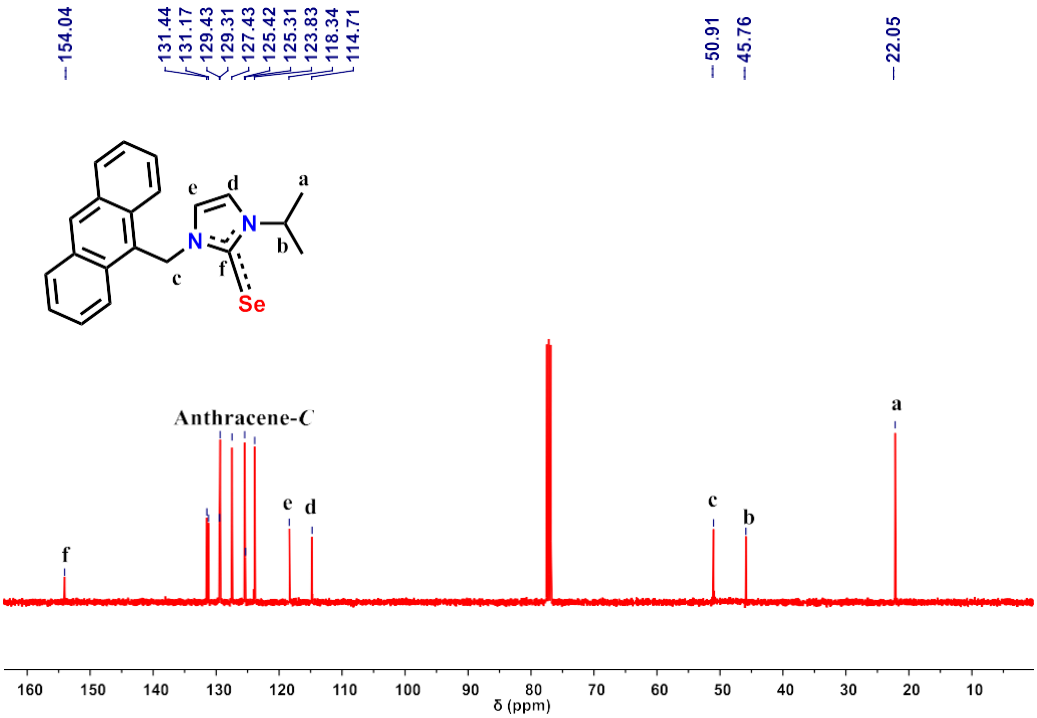


Fig. S5. ^{13}C NMR of **L²** in $CDCl_3$ at 25 °C

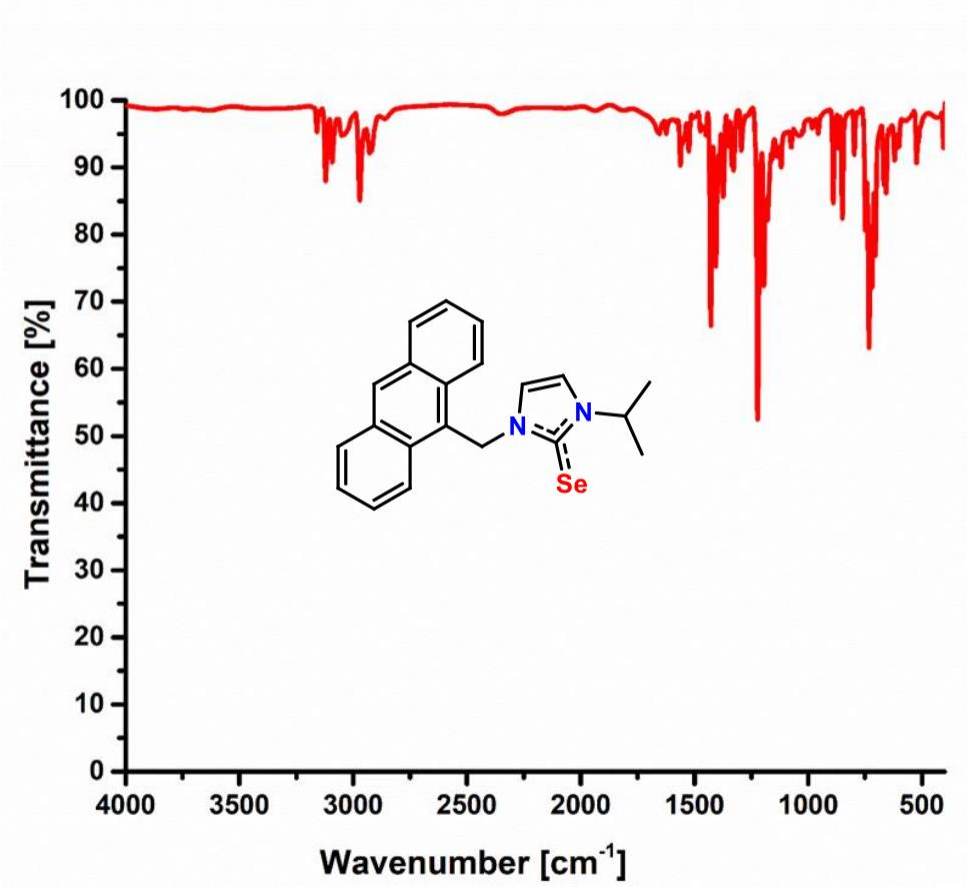


Fig. S6. FT-IR of **L²** (KBr method) at 25 °C

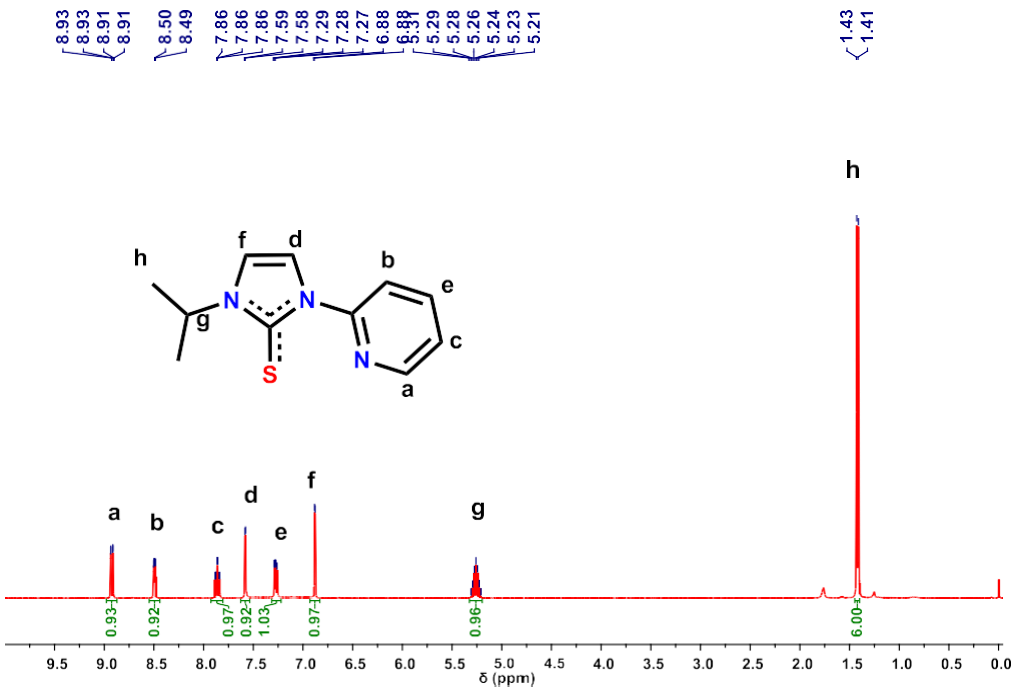


Fig. S7. ^{1}H NMR of **L^{3}** in $CDCl_3$ at 25 °C

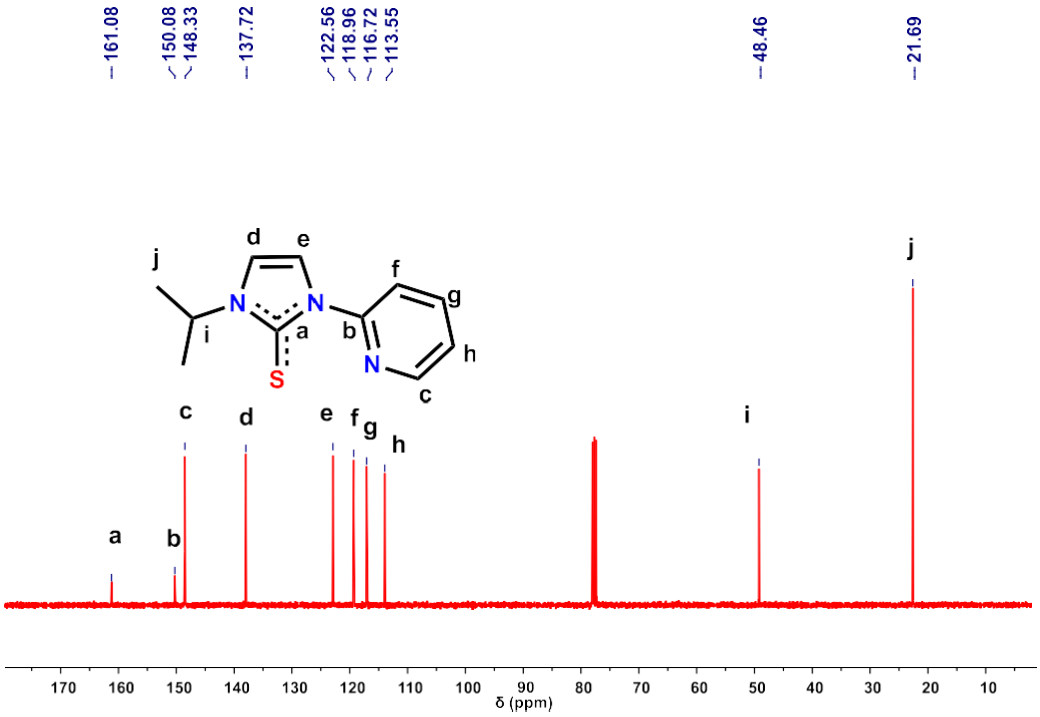


Fig. S8. ^{13}C NMR of **L^{3}** in $CDCl_3$ at 25 °C

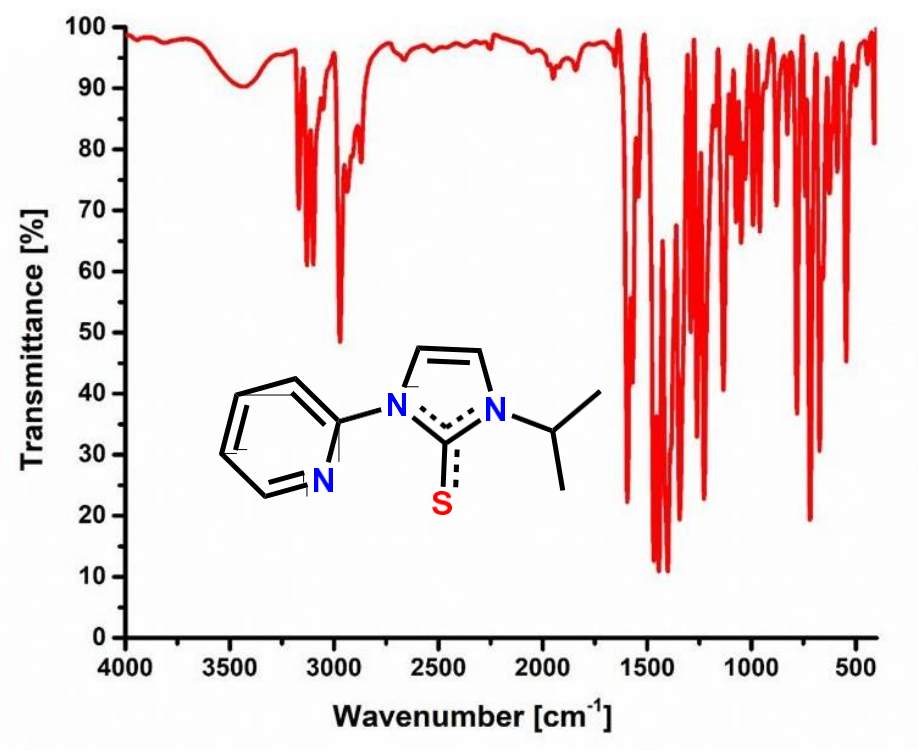


Fig. S9. FT-IR spectrum of **L³** (KBr method) at 25 °C

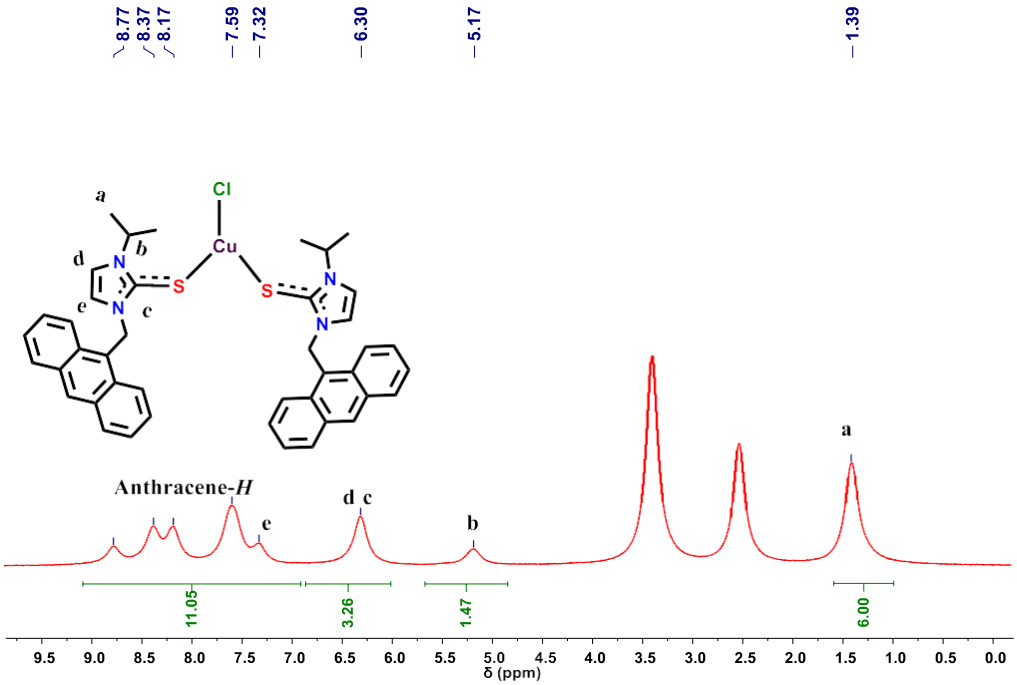


Fig. S10. ^{1}H NMR of **1** in DMSO-d_6 at 25 °C

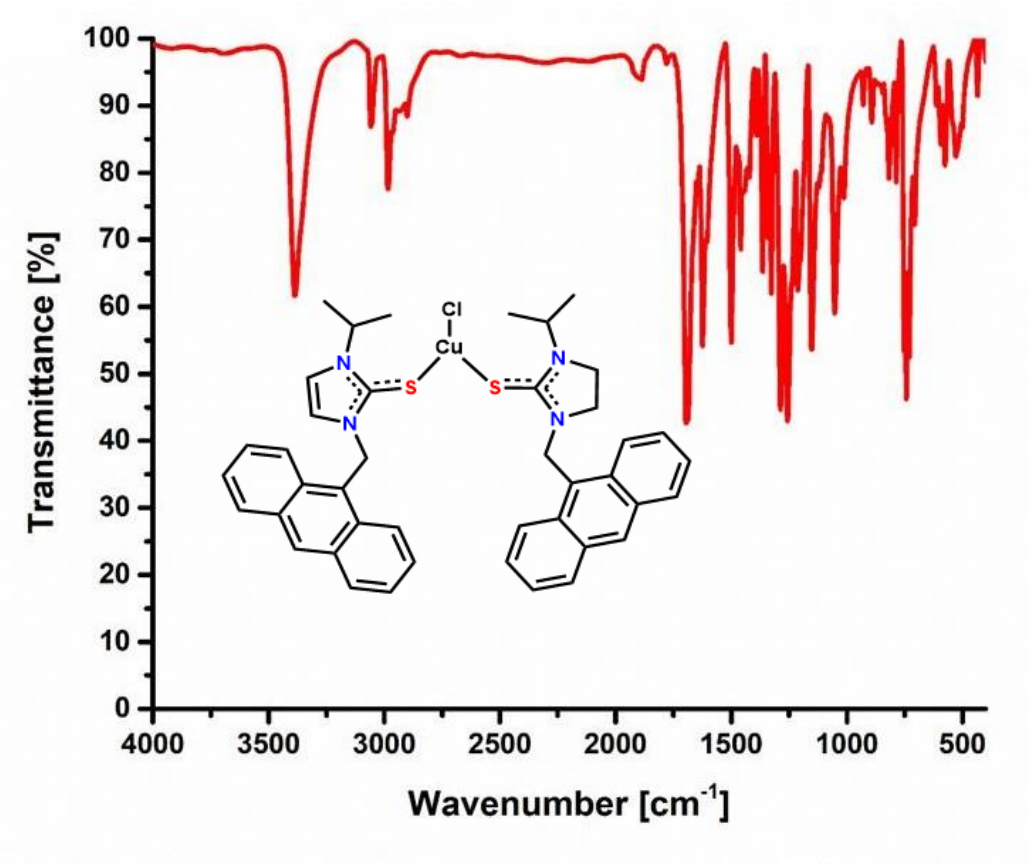


Fig. S11. FT-IR spectrum of **1** (KBr method) at 25 °C

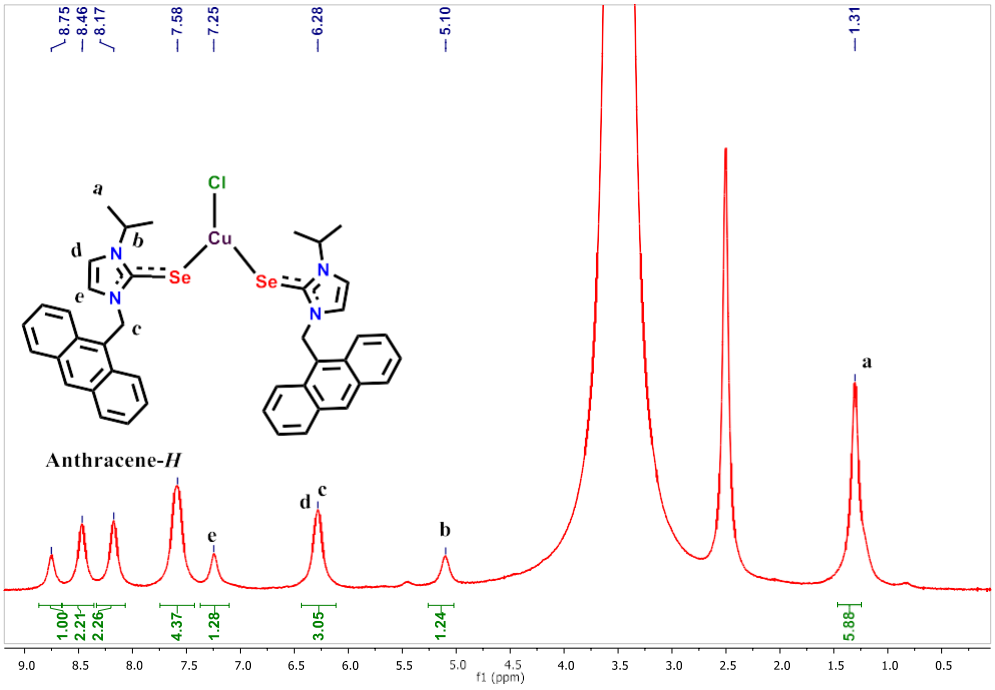


Fig S12. ^{1}H NMR of **2** in DMSO-d_6 at 25 °C

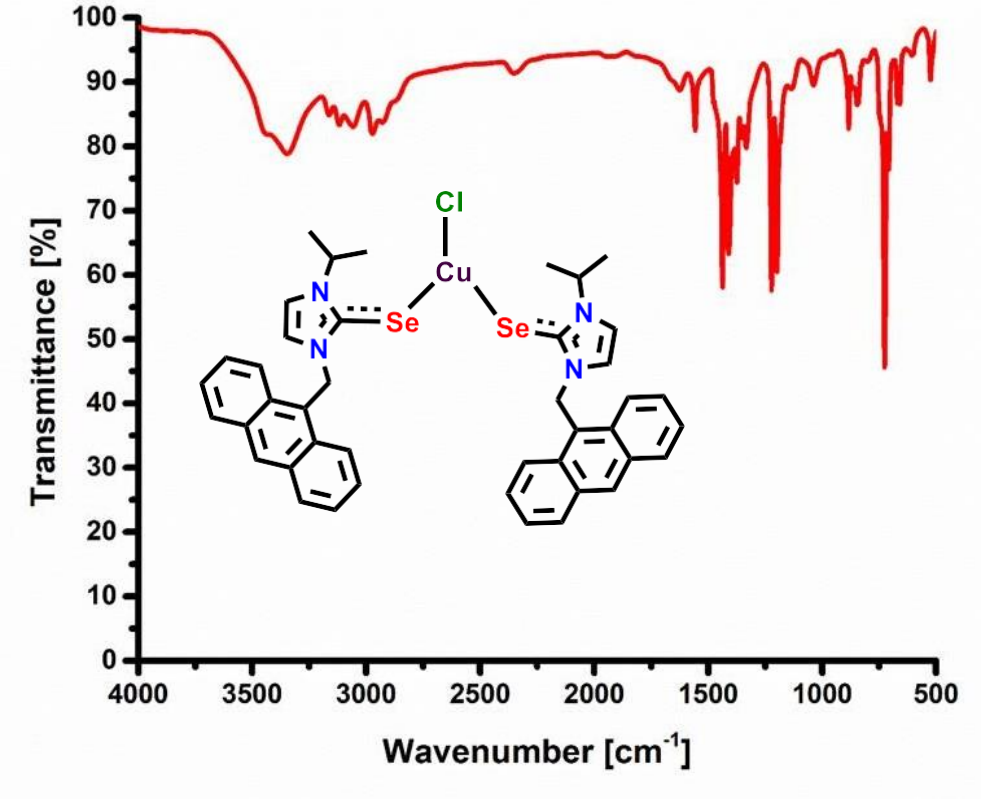


Fig. S13. FT-IR spectrum of **2** (KBr method) at 25 °C

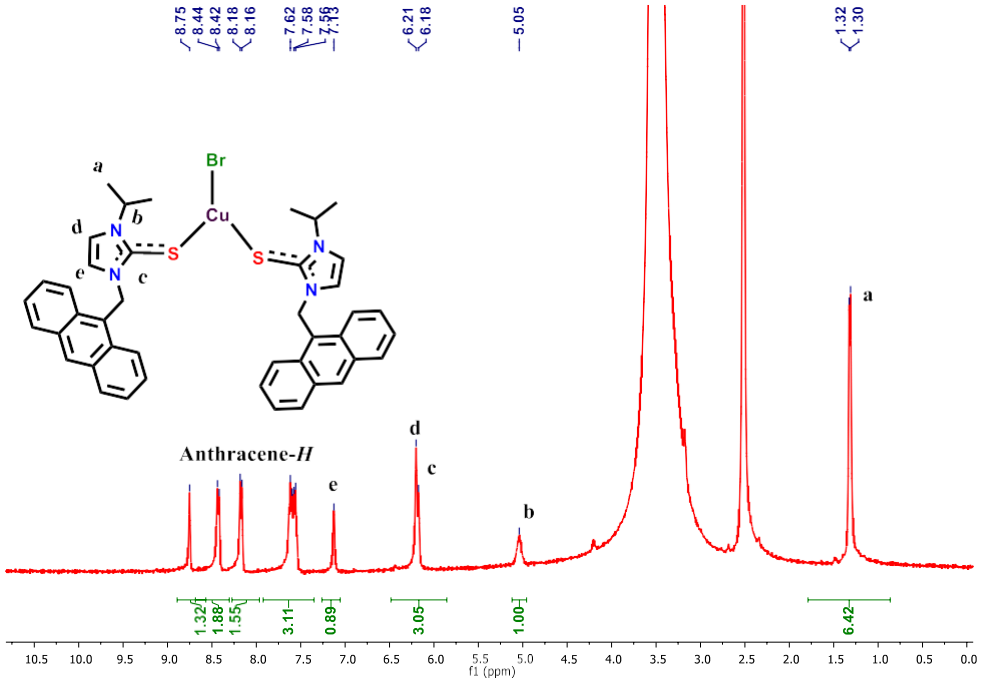


Fig. S14. ^{1}H NMR of **3** in DMSO-d_6 at 25 °C

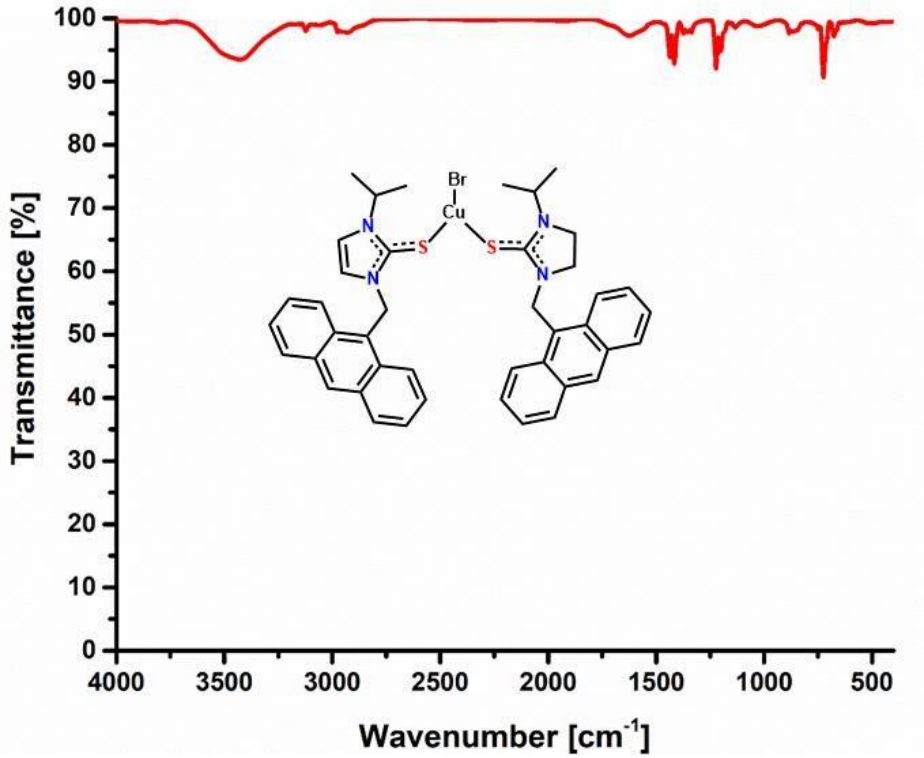


Fig. S15. FT-IR spectrum of **3** (KBr method) at 25 °C

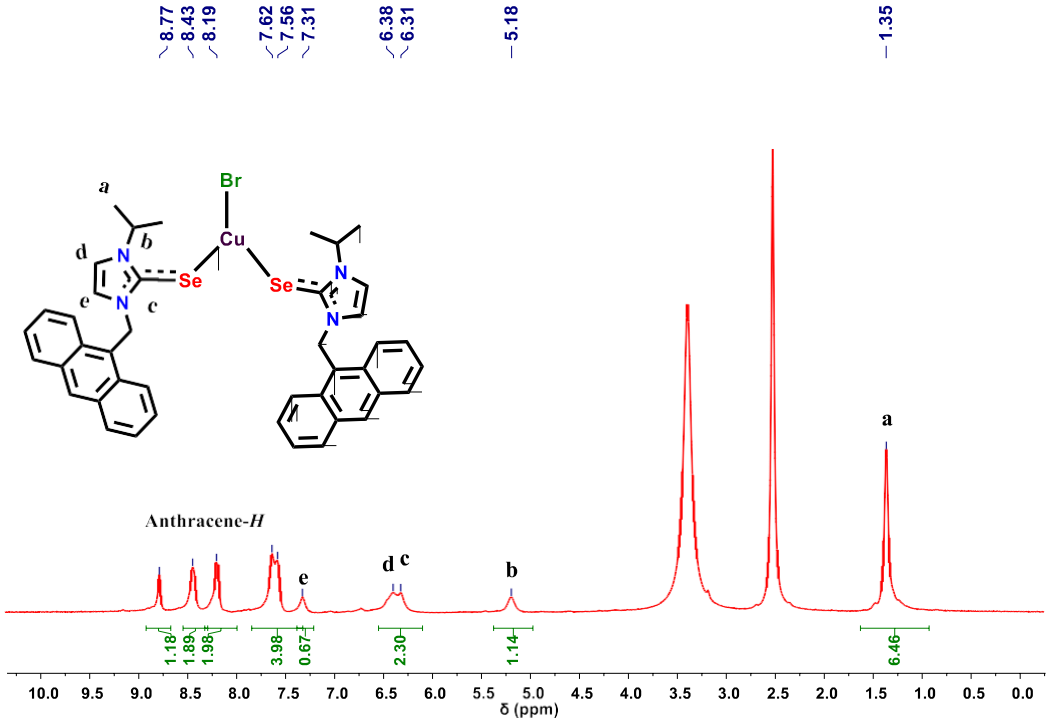


Fig. S16. ^{1}H NMR of **4** in DMSO-d_6 at 25 °C

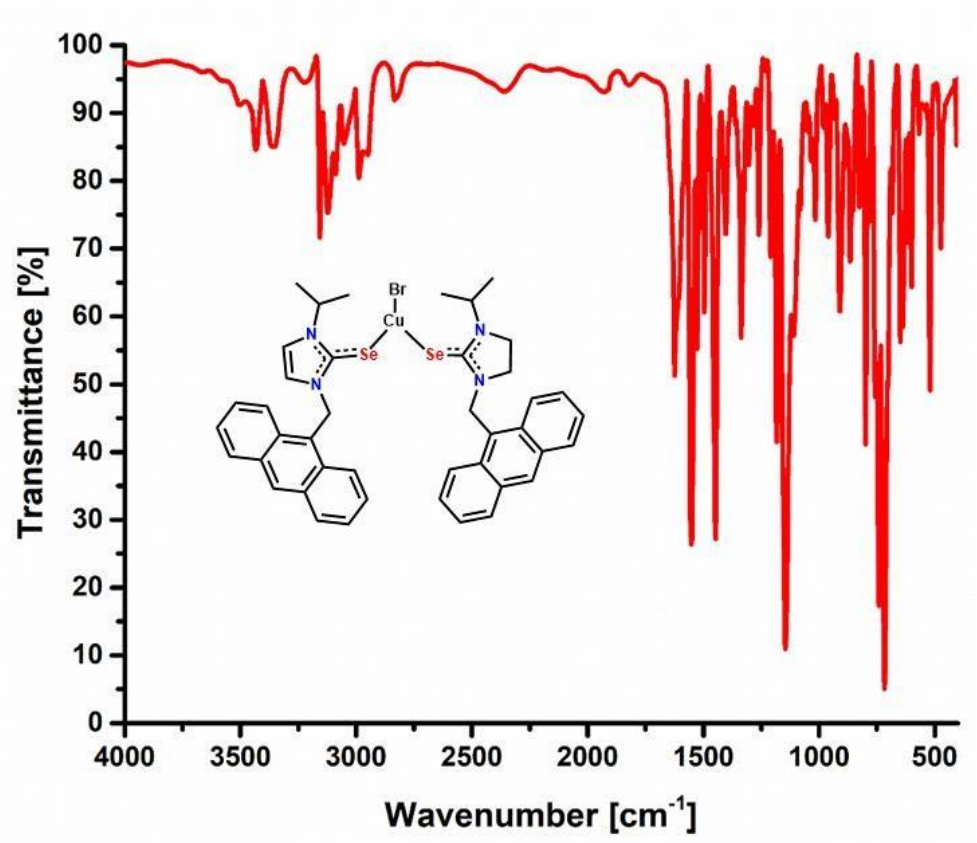


Fig. S17. FT-IR spectrum of **4** (KBr method) at 25 °C

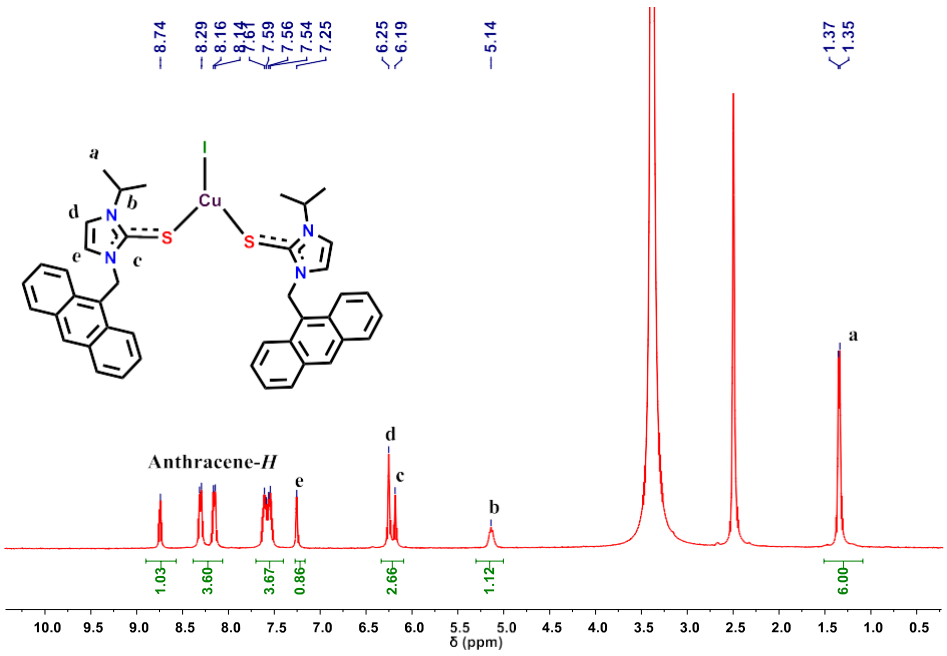


Fig. S18. ^{1}H NMR of **5** in DMSO-d_6 at 25 °C

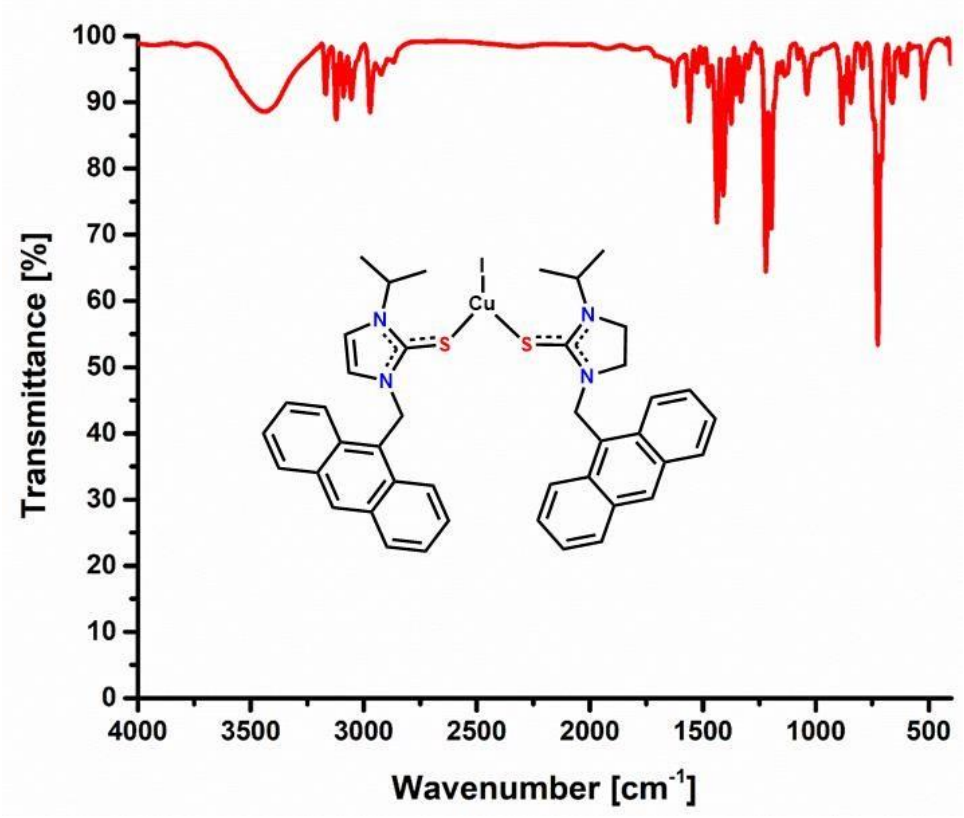


Fig. S19. FT-IR spectrum of **5** (KBr method) at 25 °C

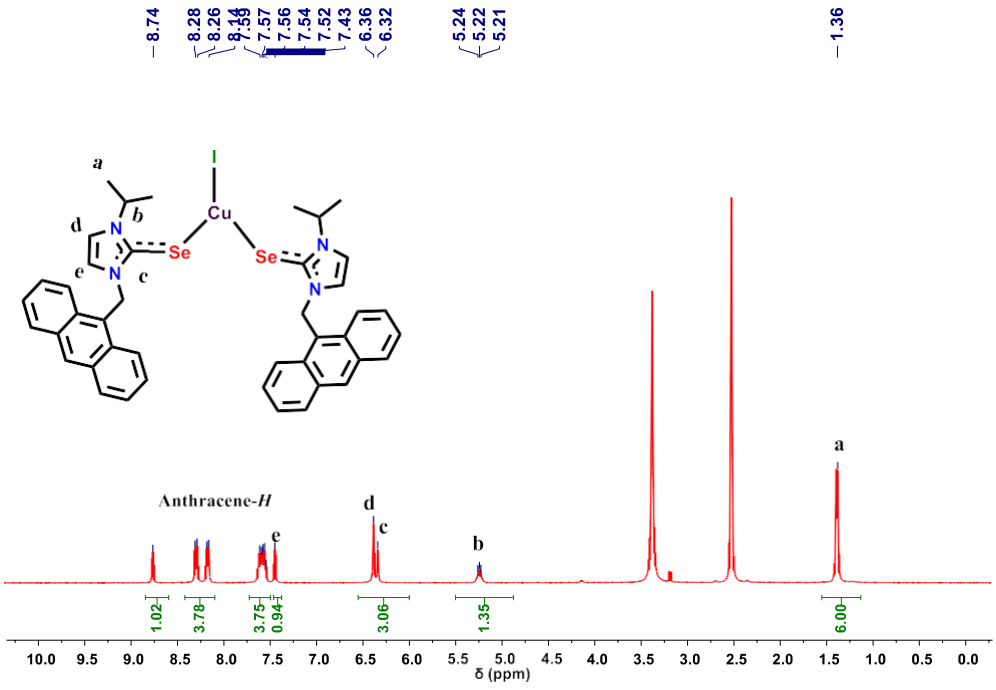


Fig S20. ^{1}H NMR of **6** in DMSO-d_6 at 25 °C

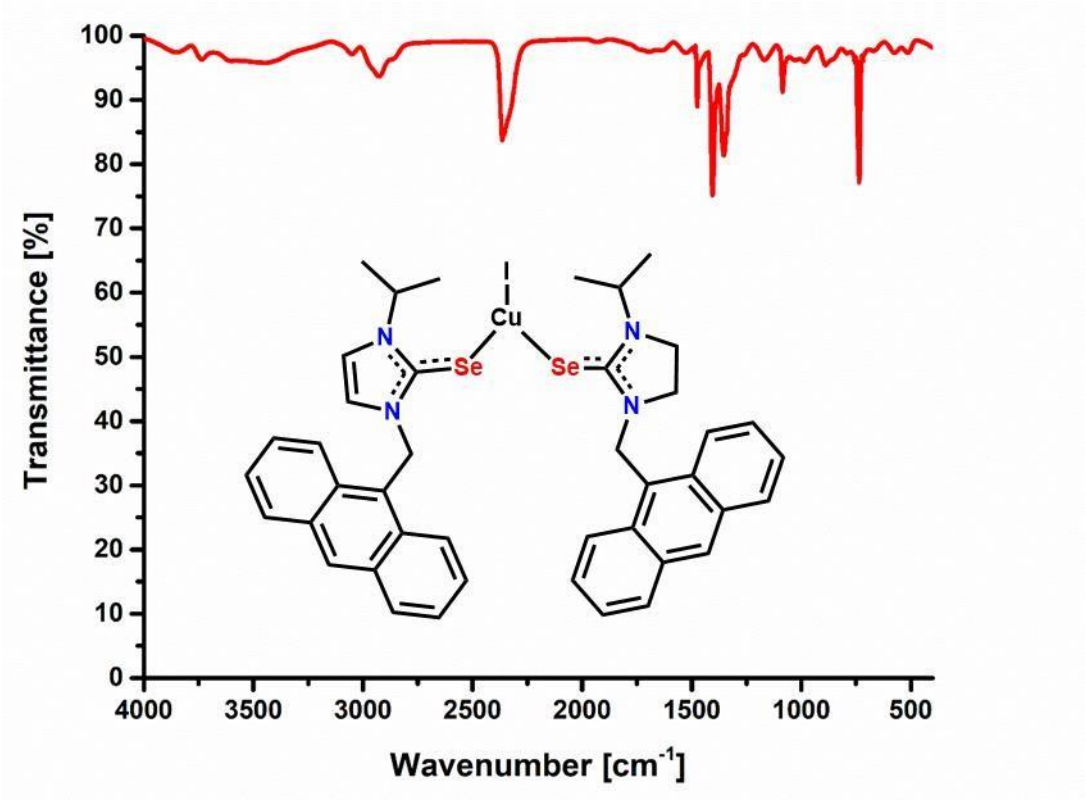


Fig. S21. FT-IR spectrum of **6** (KBr method) at 25 °C

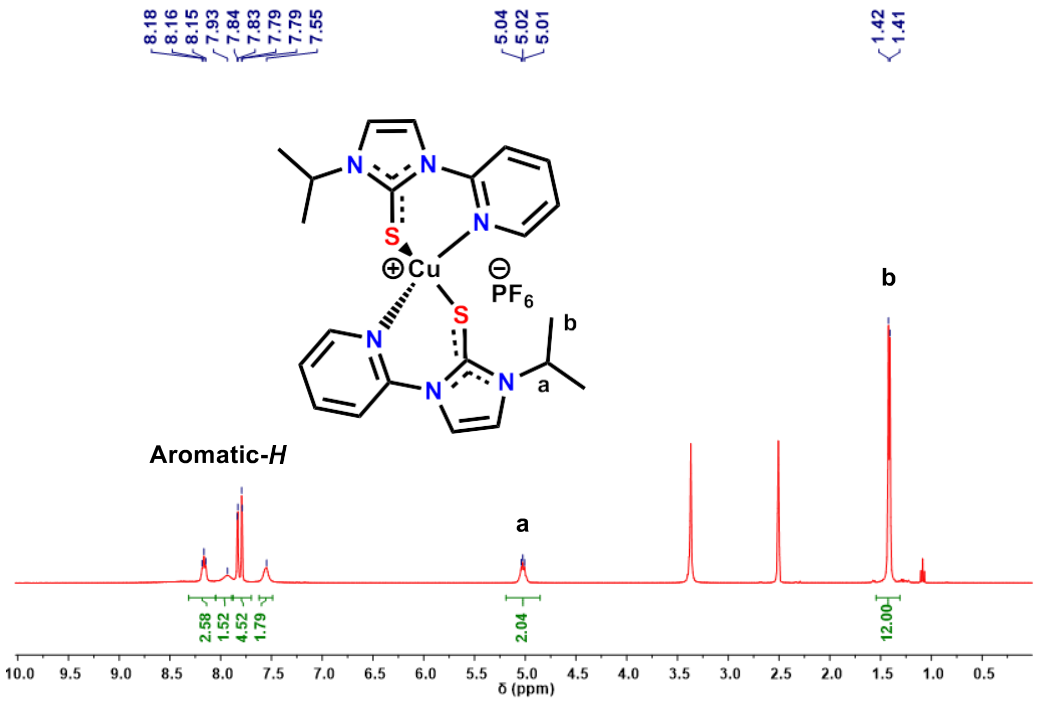


Fig. S22. ^{1}H NMR of **7** in DMSO-d_6 at 25 °C

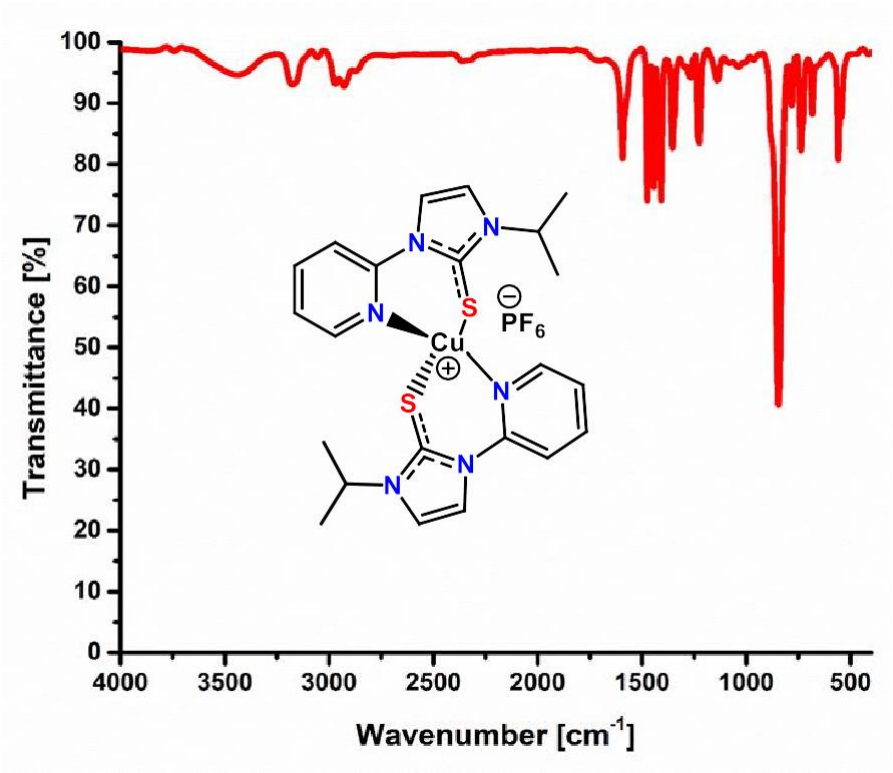


Fig. S23. FT-IR spectrum of **7** (KBr method) at 25 °C

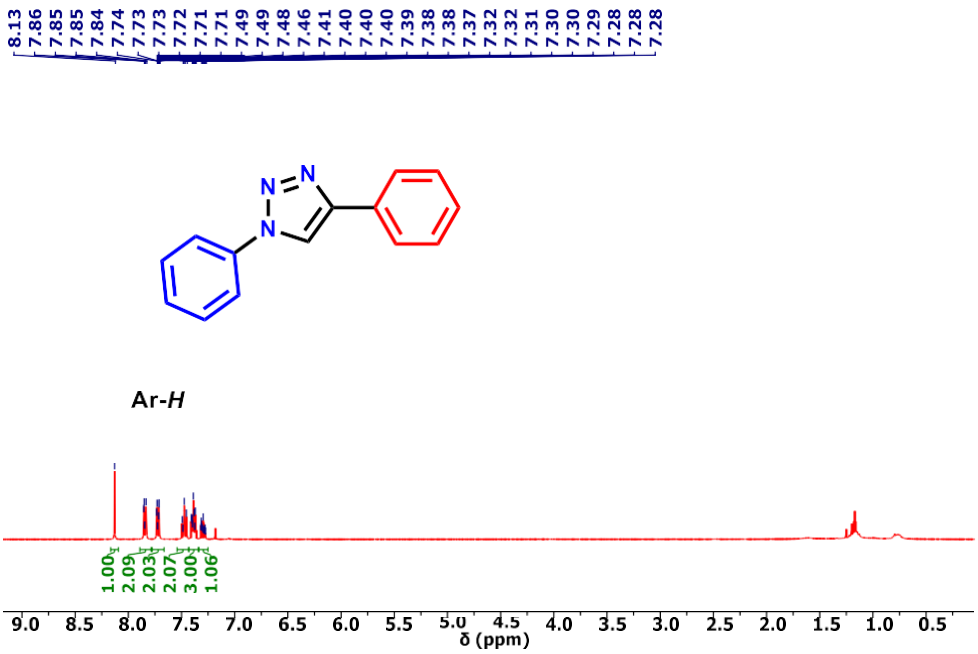


Fig. S24. ^{1}H NMR of **1a** in $CDCl_3$ at 25 °C

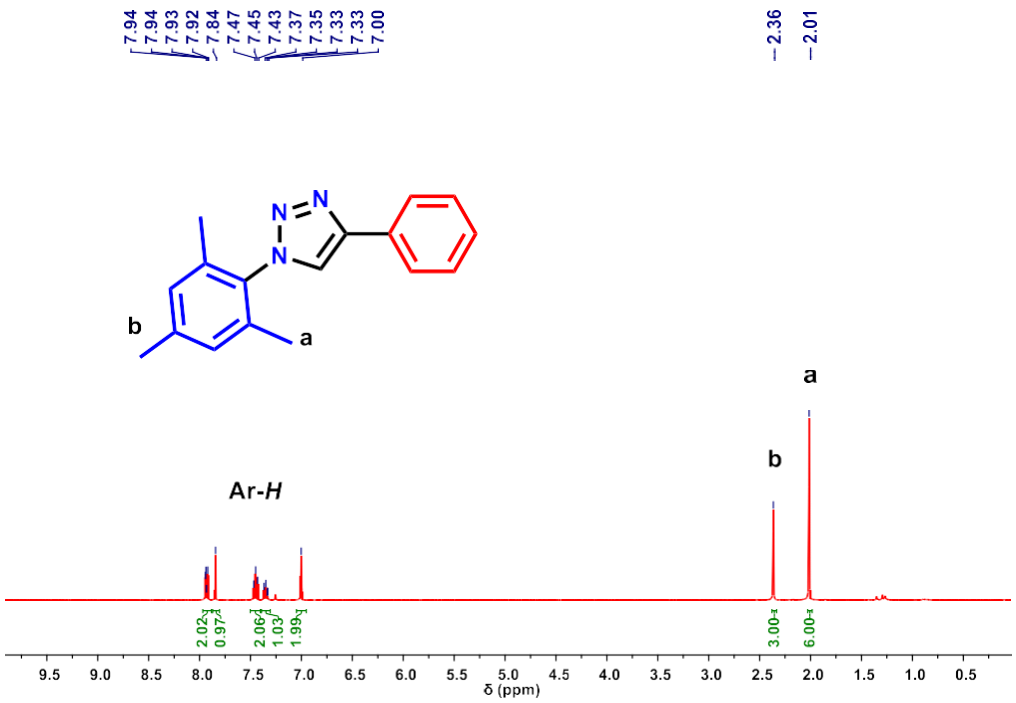


Fig. S25. ^{1}H NMR of **1b** in $CDCl_3$ at 25 °C.

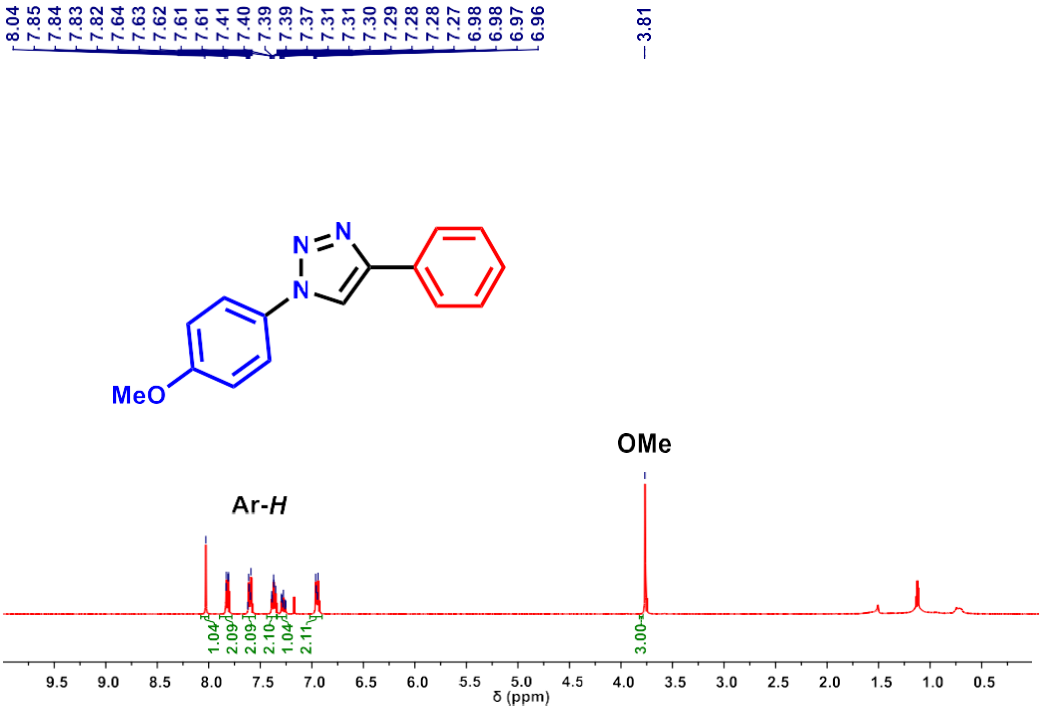


Fig. S26. ^{1}H NMR of **1c** in $CDCl_3$ at 25 °C.

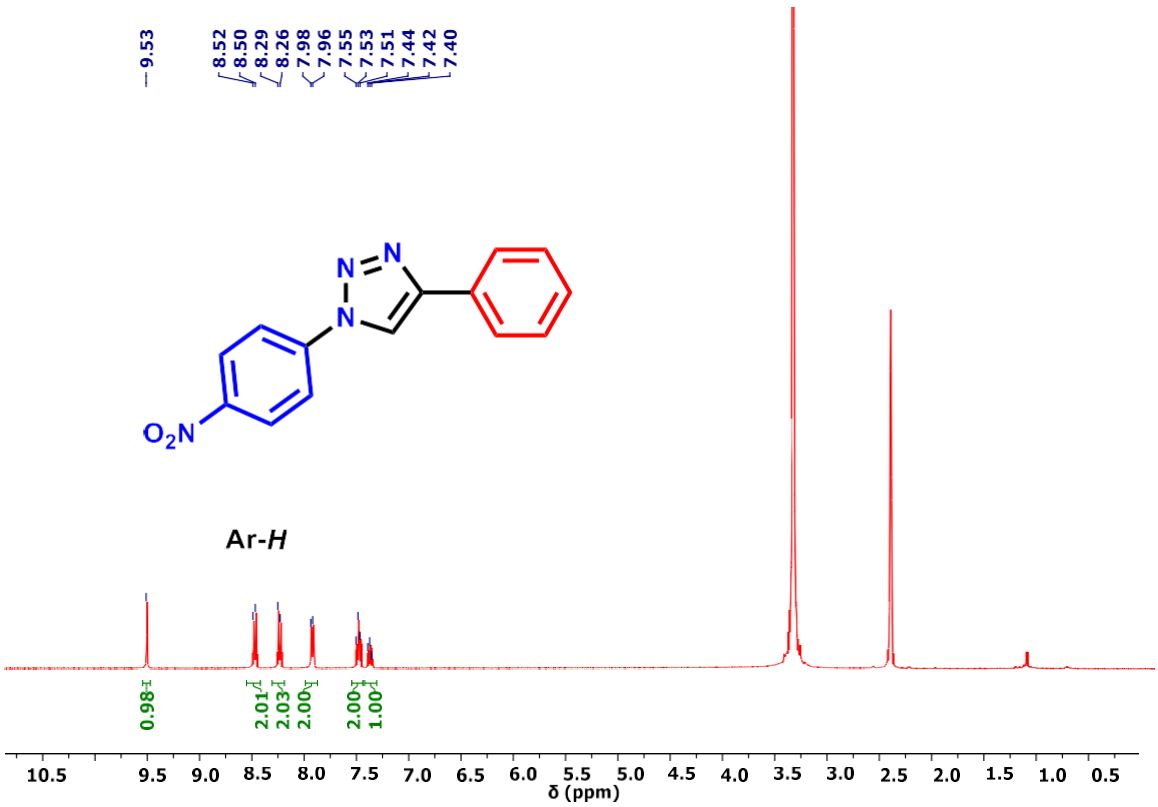


Fig. S27. ^{1}H NMR of **1d** in DMSO-d_6 at 25 °C

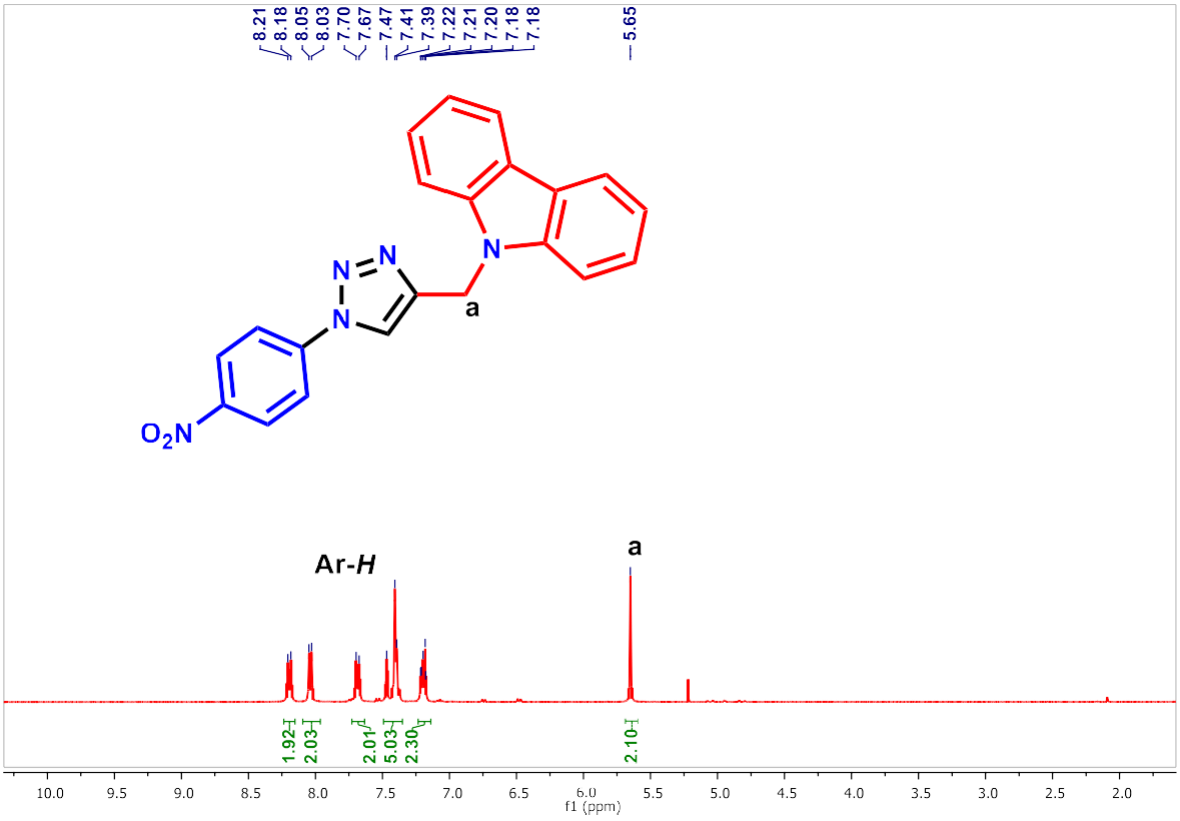


Fig. S28. ^{1}H NMR of **1e** in $CDCl_3$ at 25 °C.

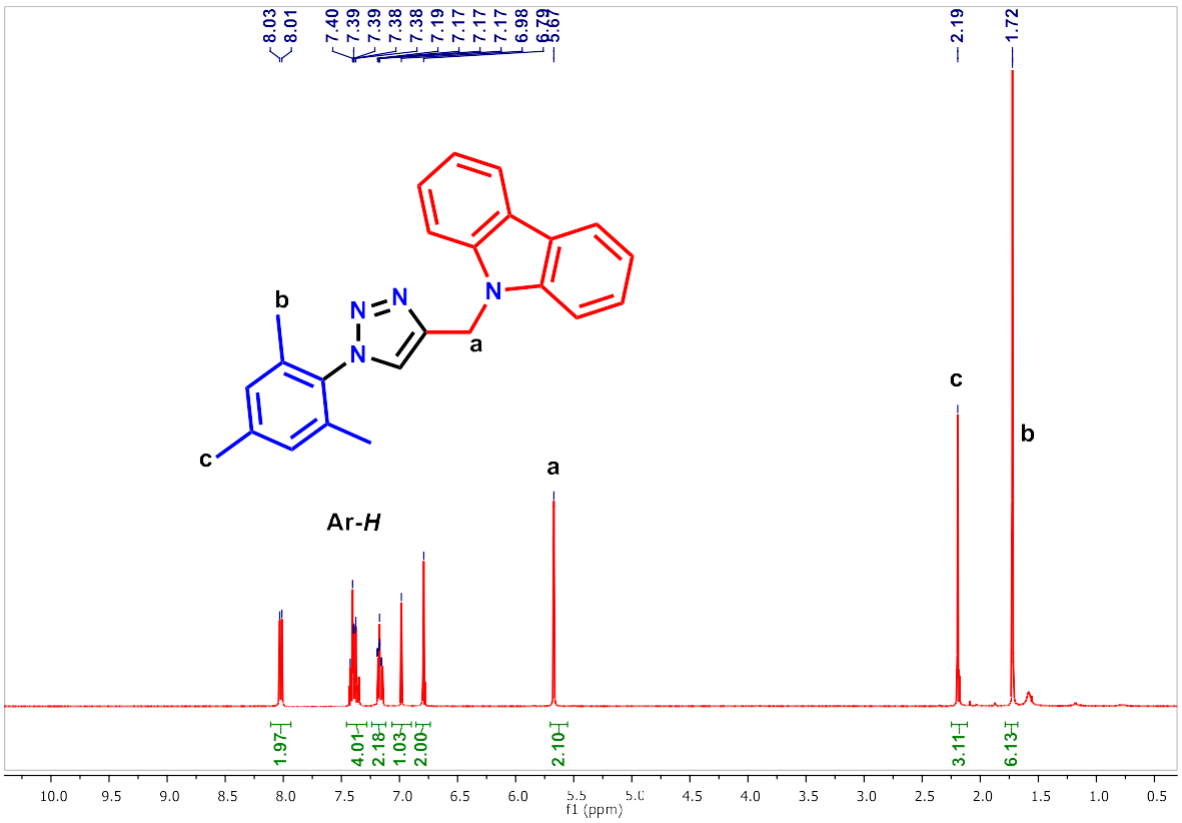


Fig. S29. ^{1}H NMR of **1f** in $CDCl_3$ at 25 °C.

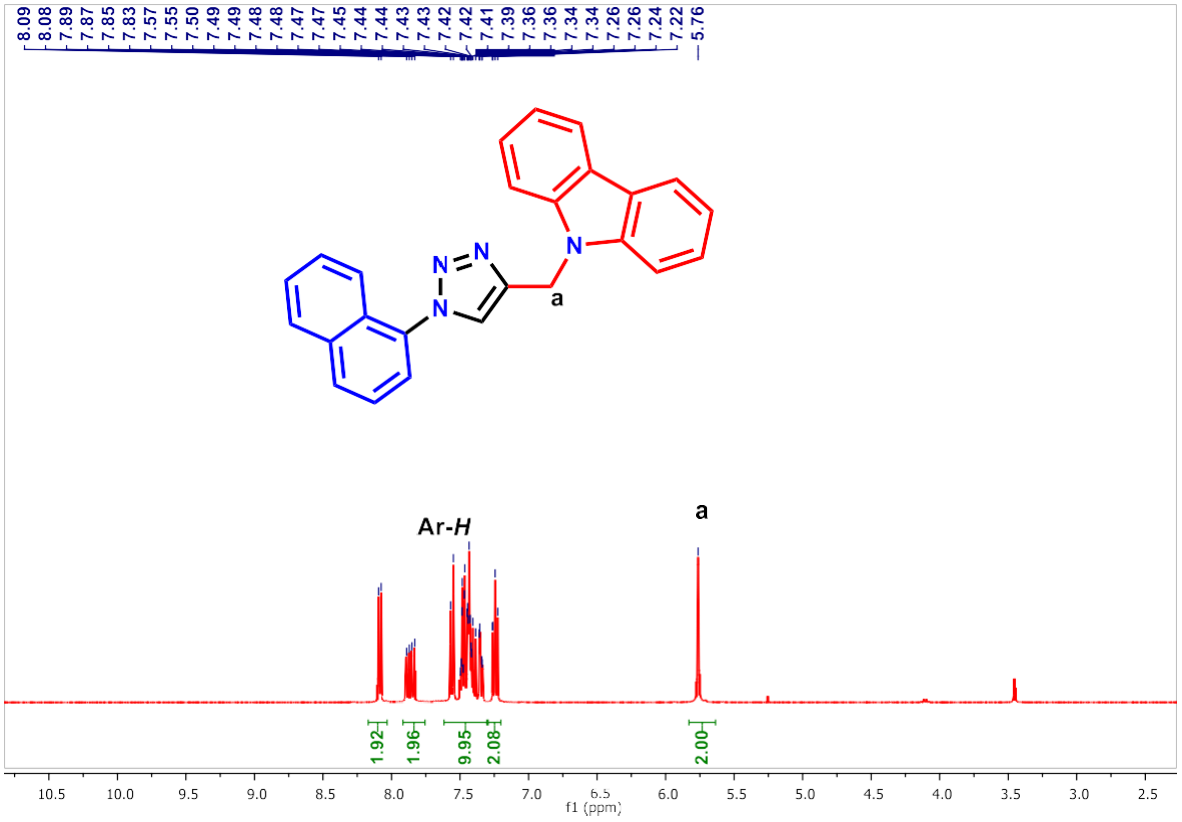


Fig. S30. ^{1}H NMR of **1g** in $CDCl_3$ at 25 °C.

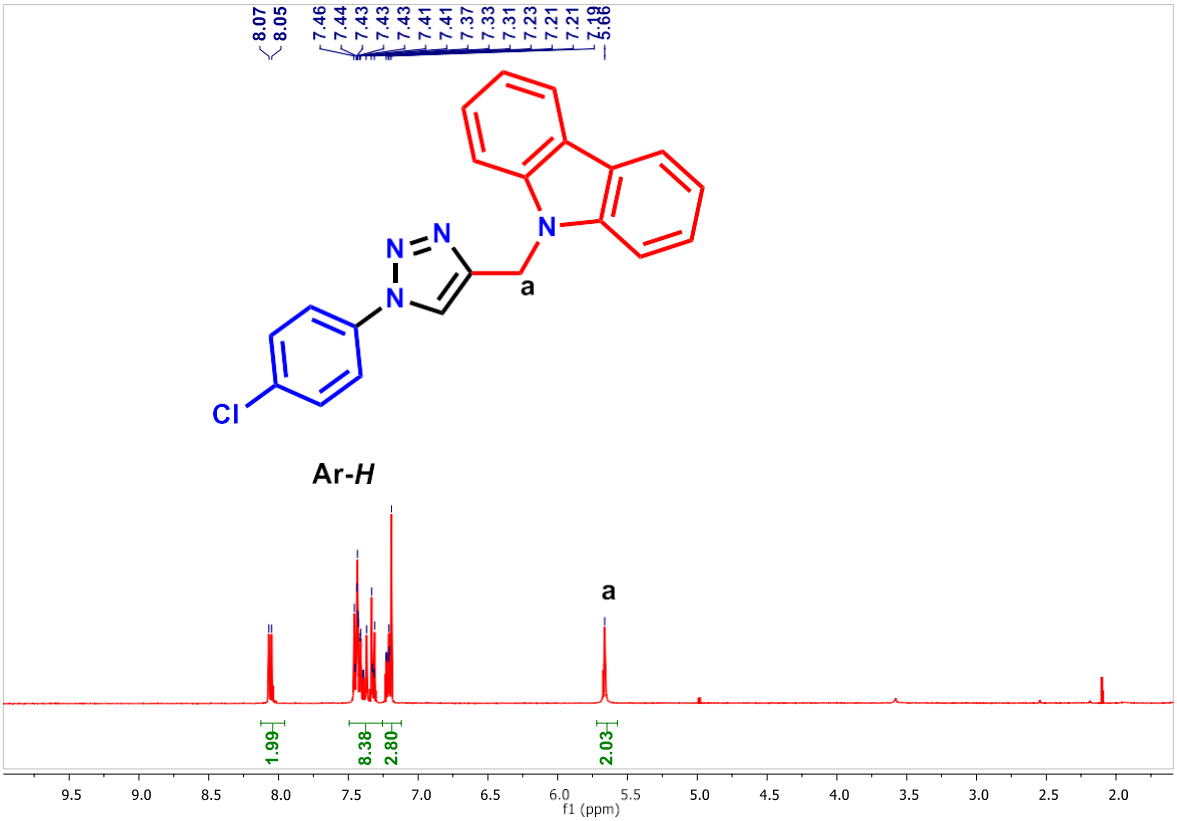


Fig. S31. ^{1}H NMR of **1h** in $CDCl_3$ at 25 °C

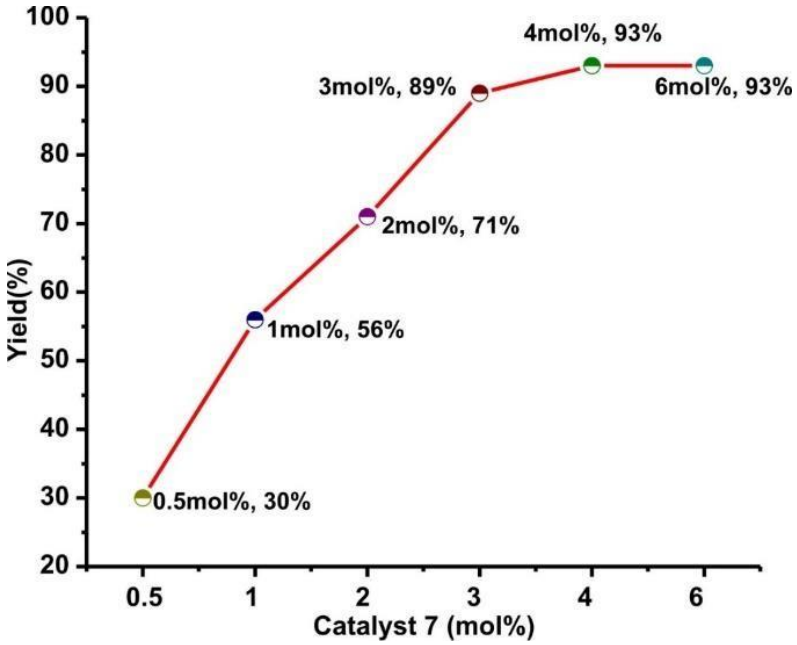


Fig. S32. Effect of catalyst **7** loading on [3+2] cycloaddition reaction between mesityl azide and phenylacetylene at ambient temperature, 2 h in DCM and MeOH mixture.

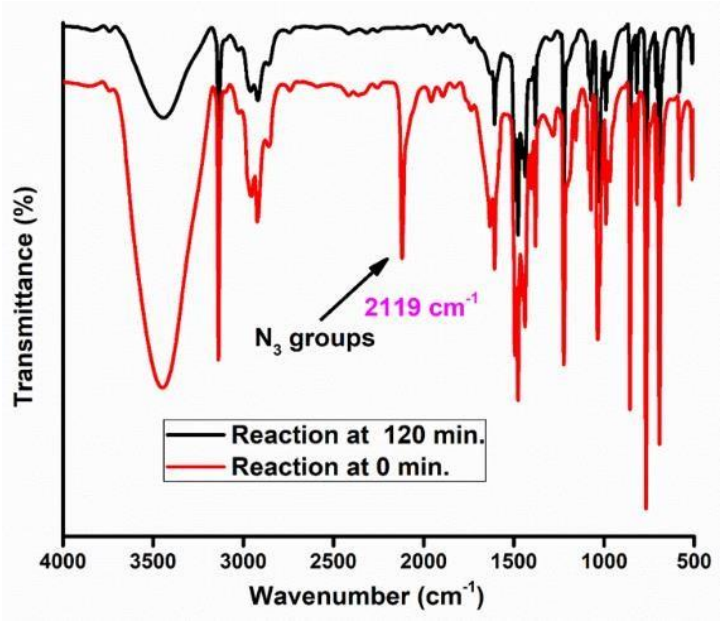
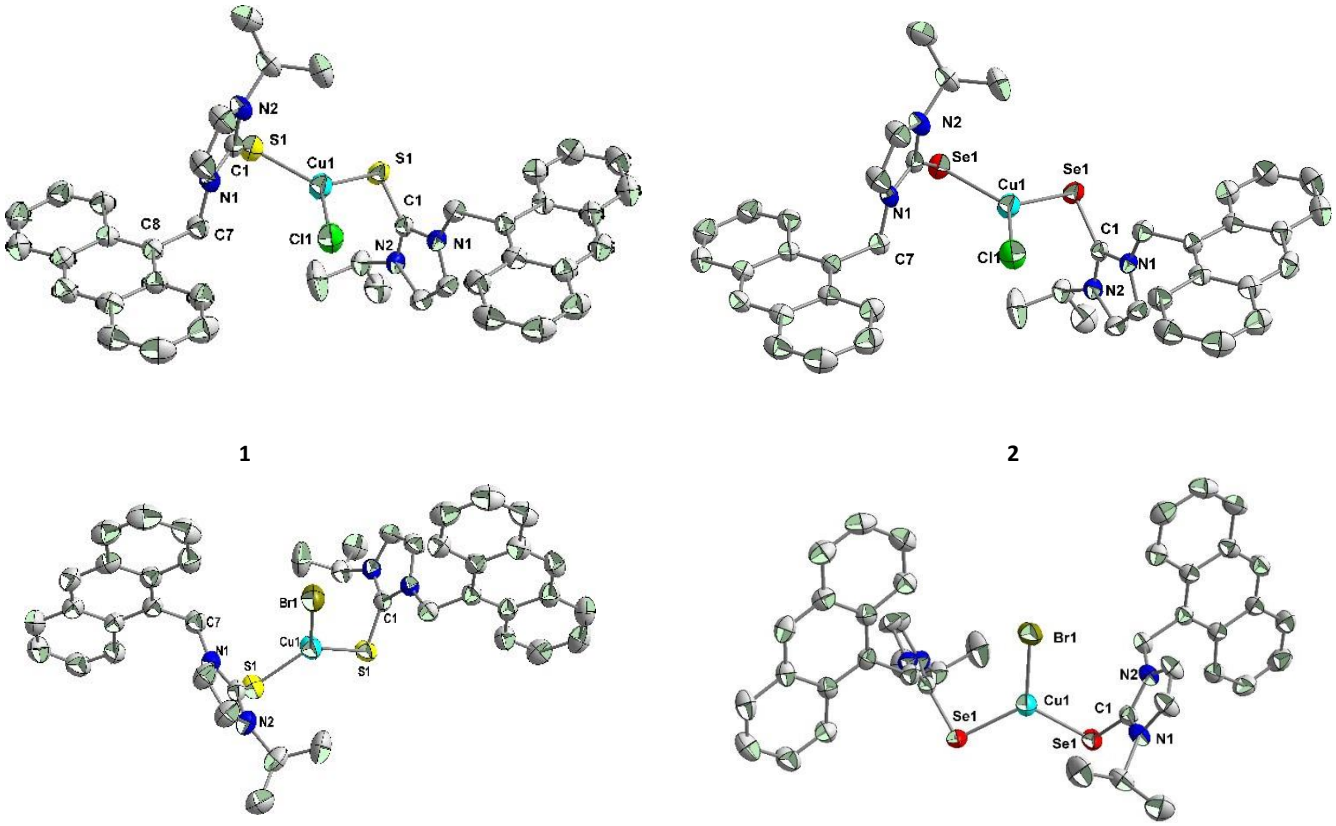


Fig. S33. FT-IR spectra of a mixture of phenylacetylene and mesityl azide in 0 min. and 120 min



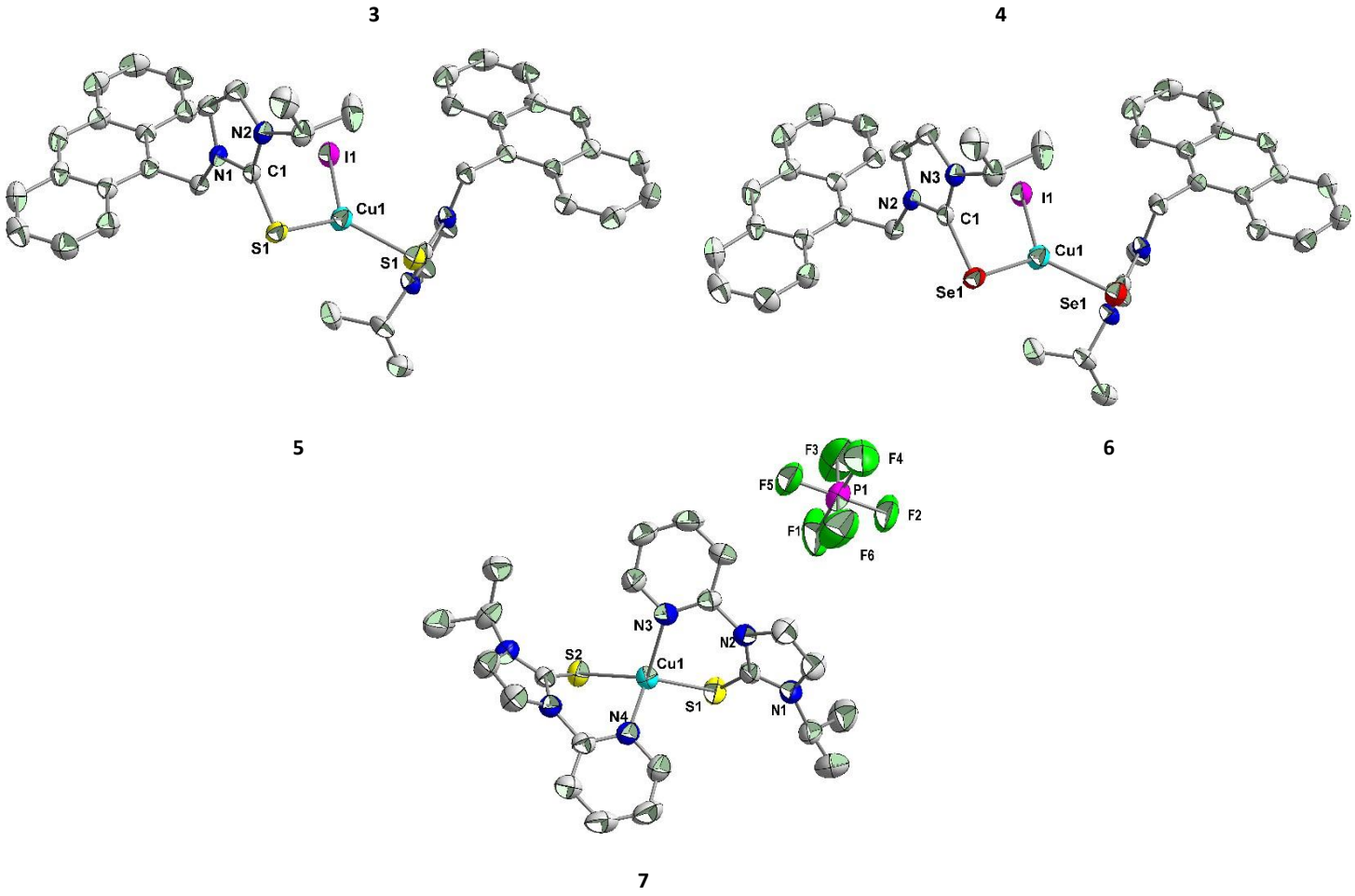


Fig. 34. The tthermal ellipsoidal structures of **1**-**7**. The hydrogen atoms have been omitted for clarity.

Table S1. The structural parameters of **1**-**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{42}H_{40}N_4S_2ClCu$	$C_{42}H_{40}N_4S_2ClCu$	$C_{42}H_{40}N_4S_2BrCu$	$C_{42}H_{40}N_4Se_2BrCu$
Formula weight	763.89	857.69	812.35	902.15
Temperature/K	273.15	299	273.15	273.15
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	C2/c	C2/c	C2/c
a/ Å	28.019(3)	28.106(7)	28.070(16)	28.090(19)
b/ Å	10.1880(9)	10.306(3)	10.219(5)	10.332(6)
c/ Å	14.114(12)	14.197(3)	14.185(8)	14.202(9)
α/	90	90	90	90
β/°	115.370(3)	116.160(10)	114.84(3)	115.758(4)
γ/°	90	90	90	90
Volume/$Å^3$	3640.4(6)	3691.6(16)	3693(3)	3712.5(4)
Z	4	4	4	4
$\rho_{calc}g/cm^3$	1.394	1.543	1.461	1.614
μ/mm^{-1}	0.825	2.672	1.825	3.662
F(000)	1592.0	1736.0	1672.0	1808.0
Crystal size/mm^3	0.117× 0.065 × 0.035	0.28 × 0.25 × 0.17	0.28 × 0.17 × 0.17	0.28 × 0.17 × 0.17
Radiation	MoKα (λ=0.71073)	MoKα (λ=0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.31 to 54.208	4.268 to 54.44	4.294 to 54.536	4.258 to 54.244
Index ranges	-35 ≤ h ≤ 35, -13 ≤ k ≤ 13, -16 ≤ l ≤ 18	-35 ≤ h ≤ 36, -13 ≤ k ≤ 12, -18 ≤ l ≤ 16	-35 ≤ h ≤ 36, -10 ≤ k ≤ 13, -18 ≤ l ≤ 18	-36 ≤ h ≤ 36, -12 ≤ k ≤ 13, -18 ≤ l ≤ 18
Reflections collected	29121	22075	31839	36317
Independent reflections	4013 [R_{int} = 0.0945, R_{sigma} = 0.0580]	4099 [R_{int} = 0.0559, R_{sigma} = 0.0429]	4106 [R_{int} = 0.0922, R_{sigma} = 0.0540]	4114 [R_{int} = 0.1008, R_{sigma} = 0.0532]
Data/restraints/parameters	4013/0/229	4099/0/229	4106/0/229	4114/0/229
Goodness-of-fit on F^2	1.017	1.034	1.014	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0406, wR_2 = 0.0838	R_1 = 0.0332, wR_2 = 0.0693	R_1 = 0.0460, wR_2 = 0.1111	R_1 = 0.0342, wR_2 = 0.0767
Final R indexes [all data]	R_1 = 0.0961, wR_2 = 0.1041	R_1 = 0.0585, wR_2 = 0.0776	R_1 = 0.0983, wR_2 = 0.1365	R_1 = 0.0663, wR_2 = 0.0899
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.31	0.32/-0.35	0.38/-0.57	0.39/-0.52

Table S2. The structural parameters of **5**-**7**.

	5	**6**	**7**
Empirical formula	$C_{42}H_{40}N_4S_2ICu$	$C_{42}H_{40}N_4Se_2ICu$	$C_{22}H_{26}CuF_6N_6PS_2$
Formula weight	855.34	949.14	647.12
Temperature/K	273.15	273.15	273.15
Crystal system	monoclinic	monoclinic	triclinic
Space group	C2/c	C2/c	P-1
a/Å	28.154(6)	28.1758(15)	11.7935(7)
b/Å	10.252(2)	10.3689(4)	12.0809(7)
c/Å	14.169(3)	14.2314(6)	12.2924(7)
α/°	90	90	102.000(2)
β/°	114.508(12)	115.236(3)	110.065(2)
γ/°	90	90	111.341(2)
Volume/$Å^3$	3721.0(14)	3760.9(3)	1417.11(15)
Z	4	4	2
$\rho_{calc}g/cm^3$	1.527	1.676	1.517
μ/mm^{-1}	1.565	3.373	1.037
F(000)	1736.0	1880.0	660.0
Crystal size/mm^3	0.28 × 0.17 × 0.17	0.28 × 0.17 × 0.17	0.08 × 0.07 × 0.06
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.28 to 54.668	4.24 to 54.222	3.814 to 54.206
Index ranges	-36 ≤ h ≤ 36, -13 ≤ k ≤ 13, -17 ≤ l ≤ 18	-36 ≤ h ≤ 36, -13 ≤ k ≤ 13, -18 ≤ l ≤ 18	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -14 ≤ l ≤ 15
Reflections collected	35507	42344	33022
Independent reflections	4179 [R_{int} = 0.0665, R_{sigma} = 0.0380]	4162 [R_{int} = 0.0476, R_{sigma} = 0.0228]	6254 [R_{int} = 0.0605, R_{sigma} = 0.0438]
Data/restraints/parameters	4179/0/229	4162/0/229	6254/0/347
Goodness-of-fit on F^2	1.038	1.026	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0273, wR_2 = 0.0709	R_1 = 0.0241, wR_2 = 0.0518	R_1 = 0.0497, wR_2 = 0.1230
Final R indexes [all data]	R_1 = 0.0303, wR_2 = 0.0729	R_1 = 0.0339, wR_2 = 0.0551	R_1 = 0.0830, wR_2 = 0.1421
Largest diff. peak/hole / e $Å^{-3}$	0.51/-0.73	0.47/-0.59	0.58/-0.51

Table 3. Selected bond lengths of **1**-**6.**

	1	**2**	**3**	**4**	**5**	**6**
			Bond Lengths [Å]			
C1-E1	1.708(2)	1.867(2)	1.719(3)	1.865(3)	1.7174(18)	1.867(2)
Cu1-E1	2.2603(7)	2.3742(4)	2.2583(14)	2.3661(4)	2.2544(6)	2.3654(3)
Cu1-X1	2.2555(11)	2.2426(12)	2.4036(14)	2.3883(7)	2.5793(7)	2.5641(5)

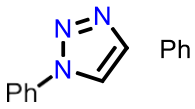
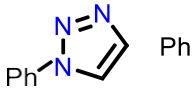
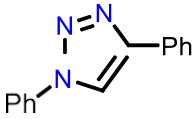
Table 4. Selected bond angles of **1-6.**

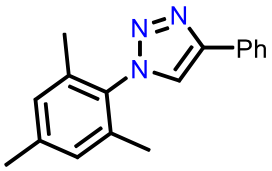
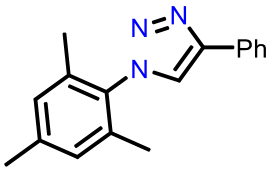
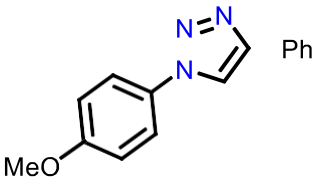
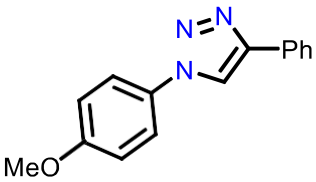
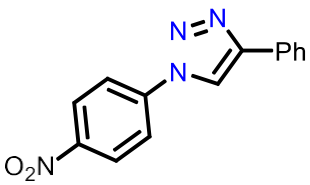
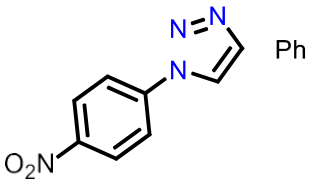
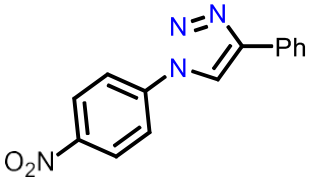
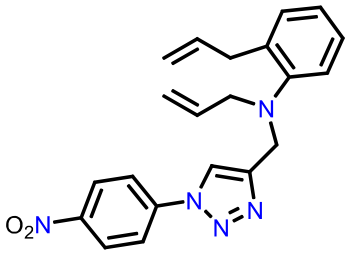
	1	**2**	**3**	**4**	**5**	**6**
			Bond angles [°]			
N1-C1-E1	127.0(2)	126.44(18)	126.7(3)	127.1(2)	126.79(14)	126.67(16)
C1-E1-Cu1	96.75(9)	93.43(7)	97.41(12)	93.85(8)	97.97(6)	94.34(6)
E1-Cu1-X1	120.76(2)	122.35(12)	118.59(3)	120.060(14)	116.610(16)	118.100(10)
E1-Cu1-E1’	118.48(4)	115.29(2)	122.83(6)	119.88(3)	126.78(3)	123.80(2)

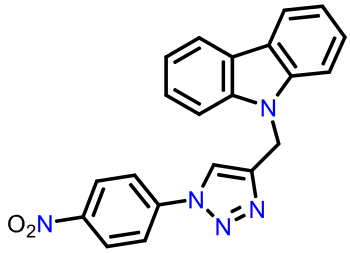
Table 5. Selected bond lengths (Å) and bond angles (°) of **7.**

Bond length (Å)		*Bond angle (°)*	
Cu1-S1	2.2476(10)	S1-Cu1-S2	128.82(4)
Cu1-S2	2.2721(9)	N3-Cu1-S1	95.92(8)
Cu1-N3	1.711(3)	N3-Cu1-S2	112.17(8)
Cu1-N4	2.124(3)	N3-Cu1-N4	116.25(11)
S1-C1	1.693(3)		

Table S6. Comparison of catalytic efficiency of **7** with known Cu(I) catalysts for the formation of triazole product.

Catalyst	**Solvent**	**T/°C**	**t/h**	**Cu/mmol**	**Trizole product**	**Yield/%**	**ESI Ref.**
CuI-USY	$PhCH_3$	25 °C	15 h	10		59	[1]
[Cu(Bn2-imy)(IPr)]PF_6	H_2O	60 °C	16 h	1		71	[2]
$MeCN)_4CuBF_4$	DCM	rt	24 h	5		46	[3]
Cat.**7**	DCM:MeOH	25 °C	2 h	4		86	**This work**

[Cu(Bn2-imy)(IPr)]PF_6	H2O	60 °C	16 h	1		71	[2]
Cat.**7**	DCM:MeOH	25 °C	2 h	4		93	**This work**
[Cu]	H_2O	60 °C	16 h	1		83	[1]
Cat.**7**	DCM:MeOH	25 °C	2 h	4		91	**This work**
CuI	[bmim][BF4]/ H_2O	25 °C	12 h	15		68	[4]
[Cu]	H_2O	60 °C	16 h	1		trace	[1]
Cat.**7**	DCM:MeOH	25 °C	2 h	4		82	**This work**
$CuSO_4 \cdot 5H_2O$ (20 mol%) sodium ascorbate (20 mol%)	Add *t*-butanol: water (1:1, v/v, 4 mL)	25 °C	8-10 h	20		87	

Cat.**7**	DCM:MeOH	25 °C	2 h	4		84	**This work**

References

1 S. Chassaing, M. Kumarraja, A. Sani Souna Sido, P. Pale and J. Sommer, *Org. Lett.*, 2007, **9**, 883–886.

2 S. Guo, M. H. Lim and H. V. Huynh, *Organometallics*, 2013, **32**, 7225–7233.

3 K. Sugiyama, Y. Sakata, T. Niwa, S. Yoshida and T. Hosoya, *Chem. Commun.*, 2022, **58**, 6235–6238.

4 Y.-B. Zhao, Z.-Y. Yan and Y.-M. Liang, *Tetrahedron Letters*, 2006, **47**, 1545–1549.