Electronic Supplementary Material (ESI) for RSC Advances.

Role of C, S, Se and P Donor Ligands in Copper(I) Mediated C–N and C–Si Bond Formation Reactions

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Supporting Information: Part 1

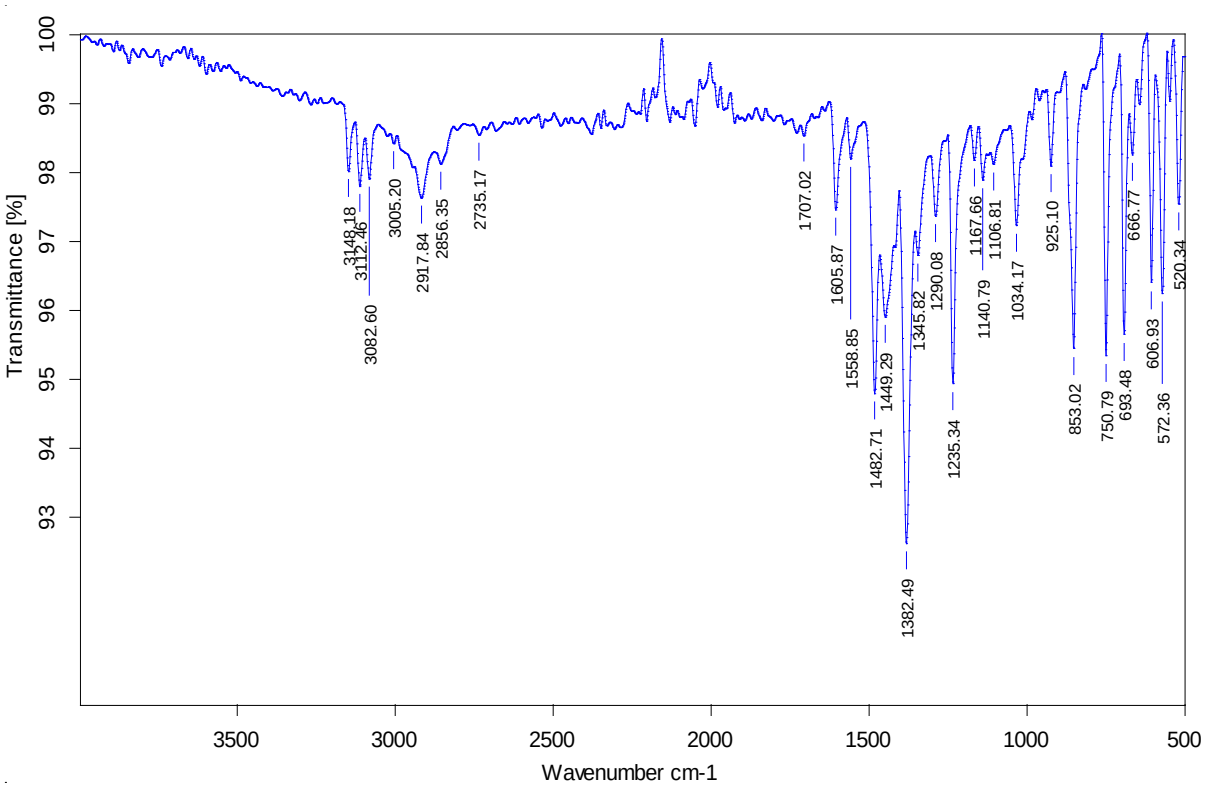


Fig. S1. Neat FT-IR spectrum of **[(IMes=S)Cu]Cl** (**1**) at room temperature.

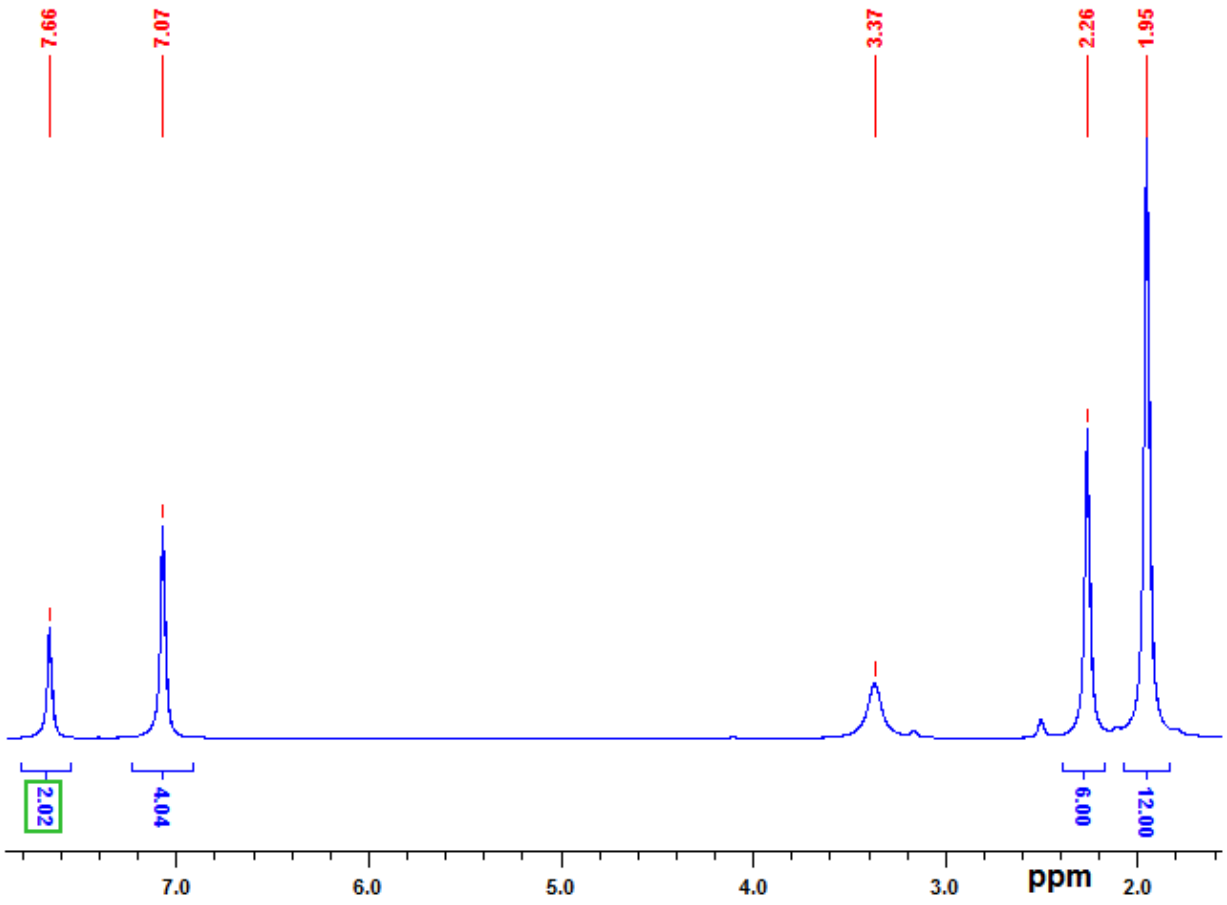


Fig. S2. ^{1}H NMR spectrum of **[(IMes=S)Cu]Cl** (**1**) in DMSO-d_6 at room temperature.

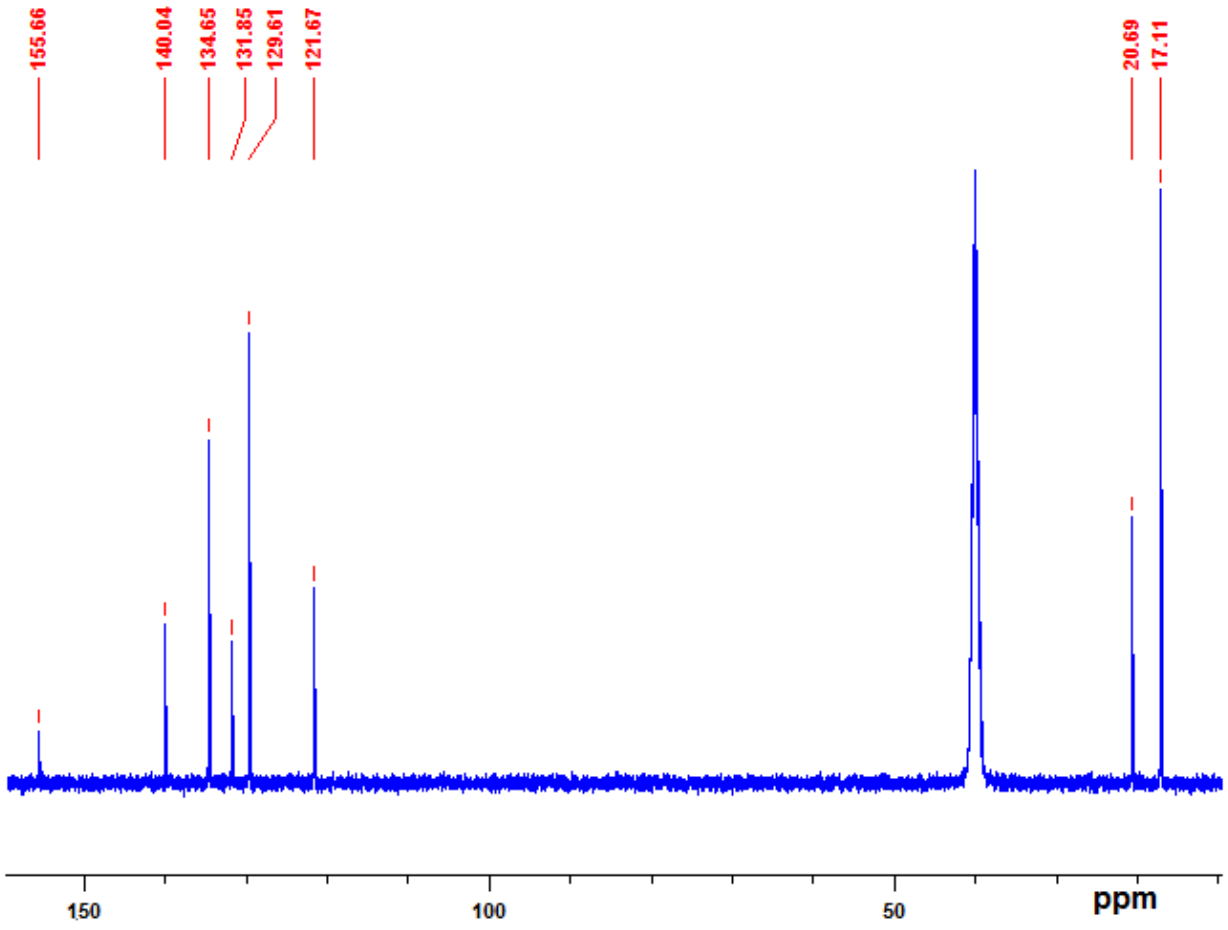


Fig. S3. ^{13}C NMR spectrum of **[(IMes=S)Cu]Cl** (**1**) in DMSO-d_6 at room temperature.

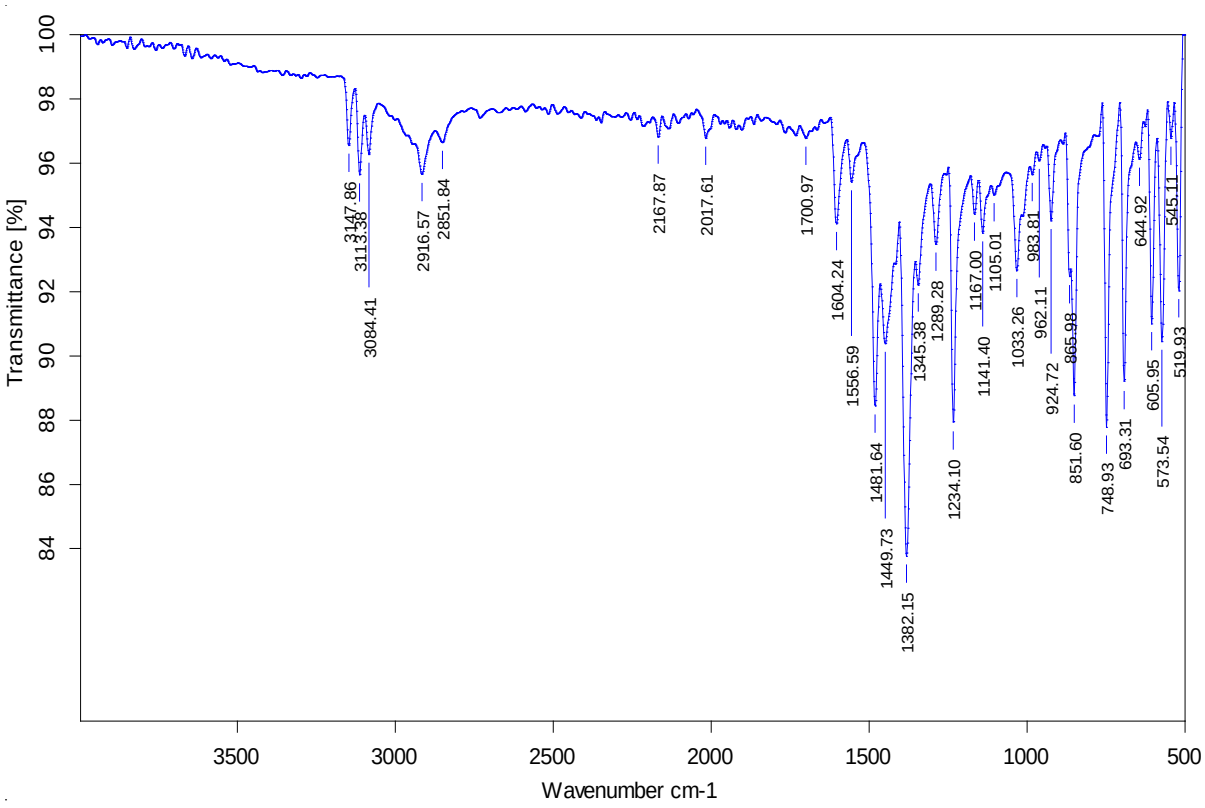


Fig. S4. Neat FT-IR spectrum of **[(IMes=S)Cu]Br** (**2**) at room temperature.

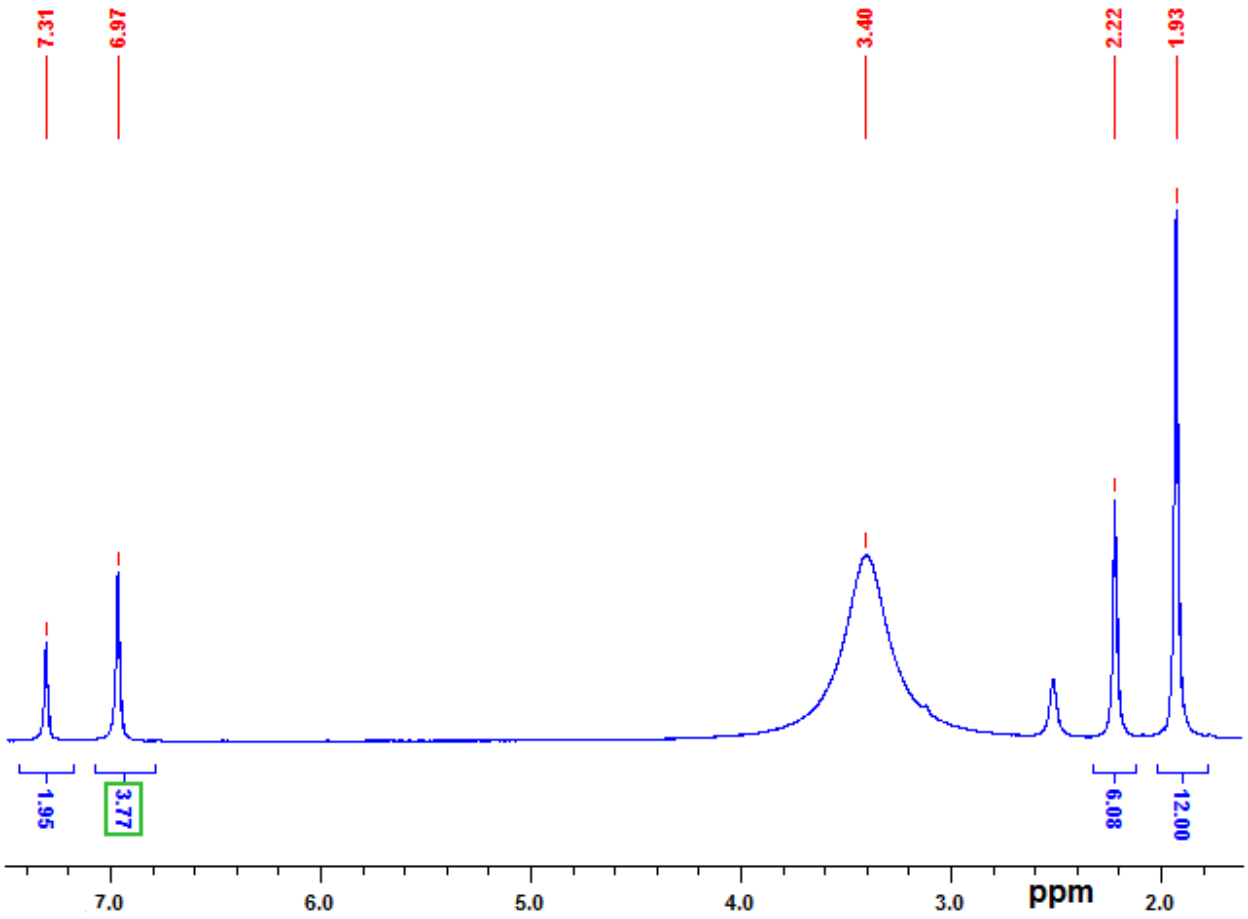


Fig. S5. ^{1}H NMR spectrum of **[(IMes=S)Cu]Br** (**2**) in DMSO-d_6 at room temperature.

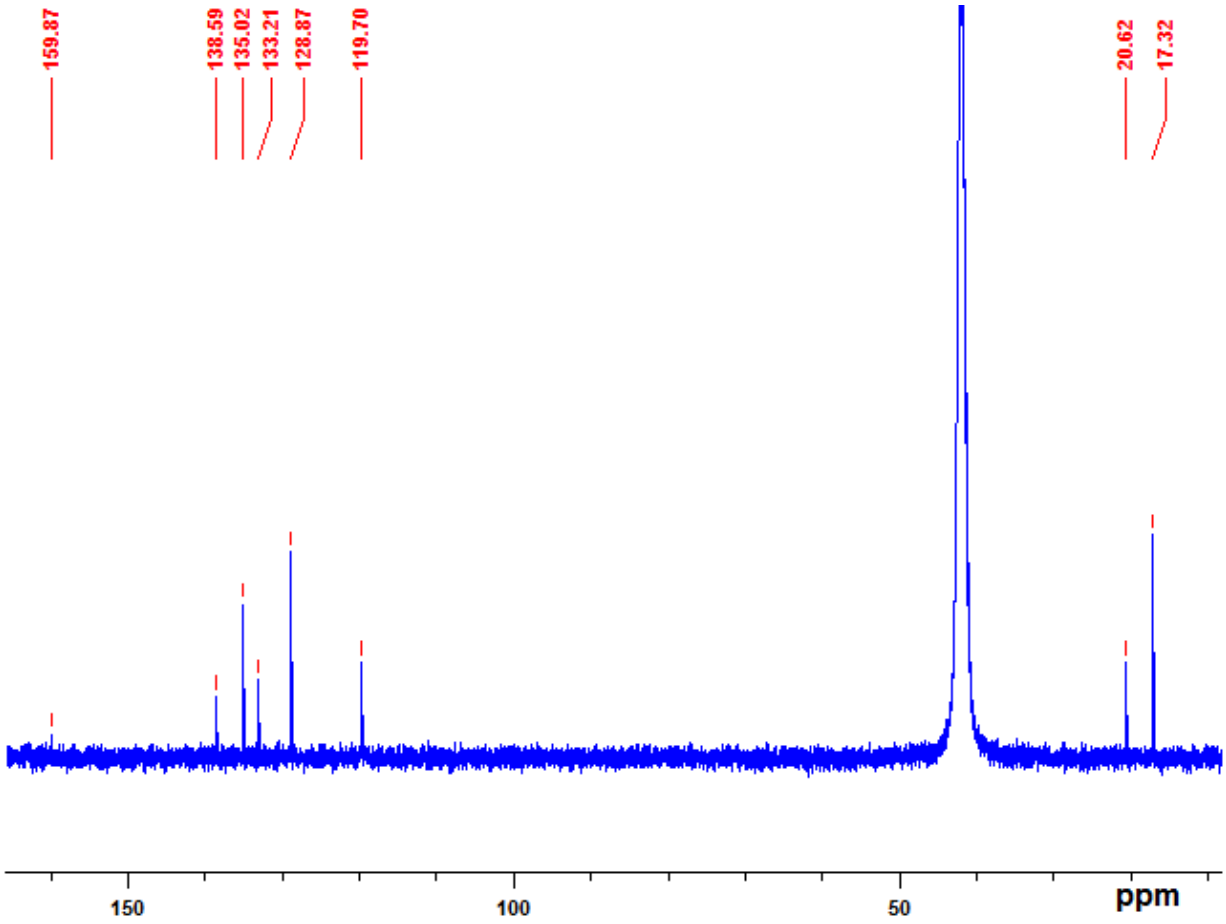


Fig. S6. ^{13}C NMR spectrum of **[(IMes=S)Cu]Br** (**2**) in DMSO-d_6 at room temperature.

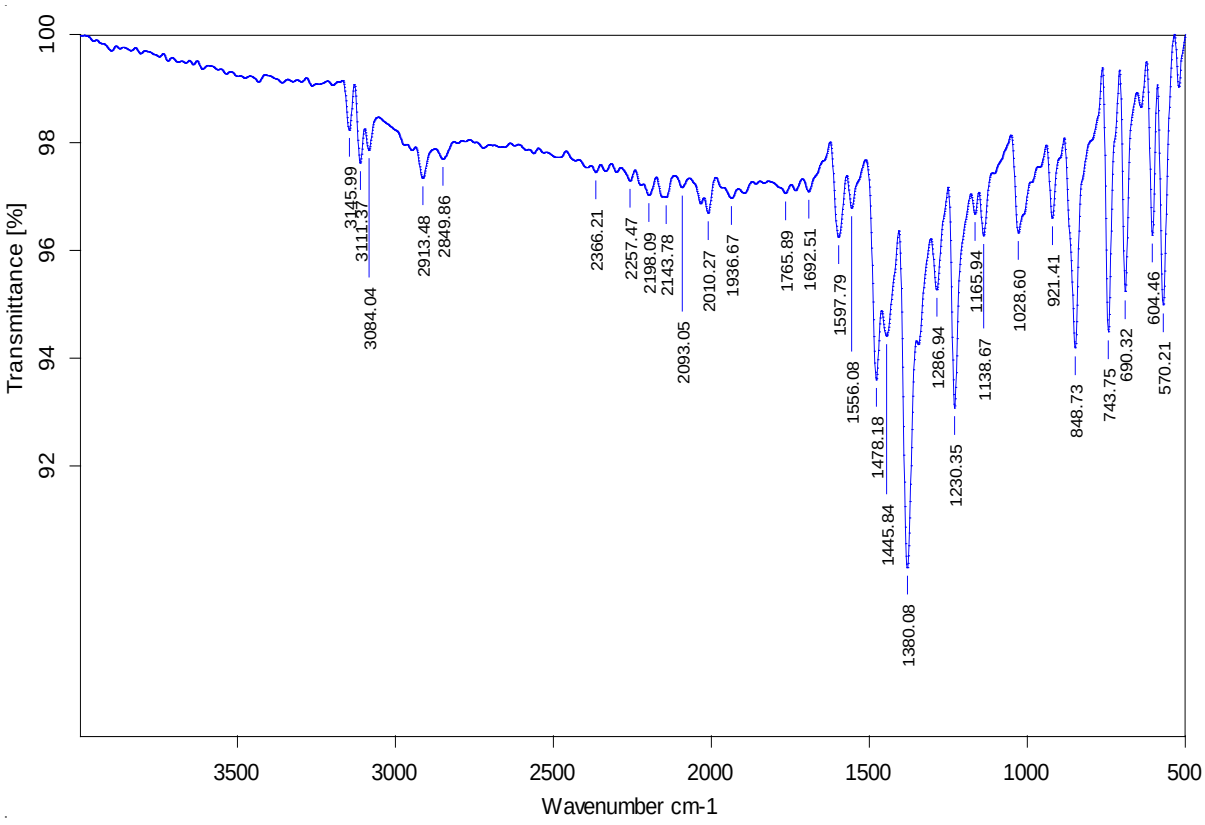


Fig. S7. Neat FT-IR spectrum of **[(IMes=S)Cu]I** (**3**) at room temperature.

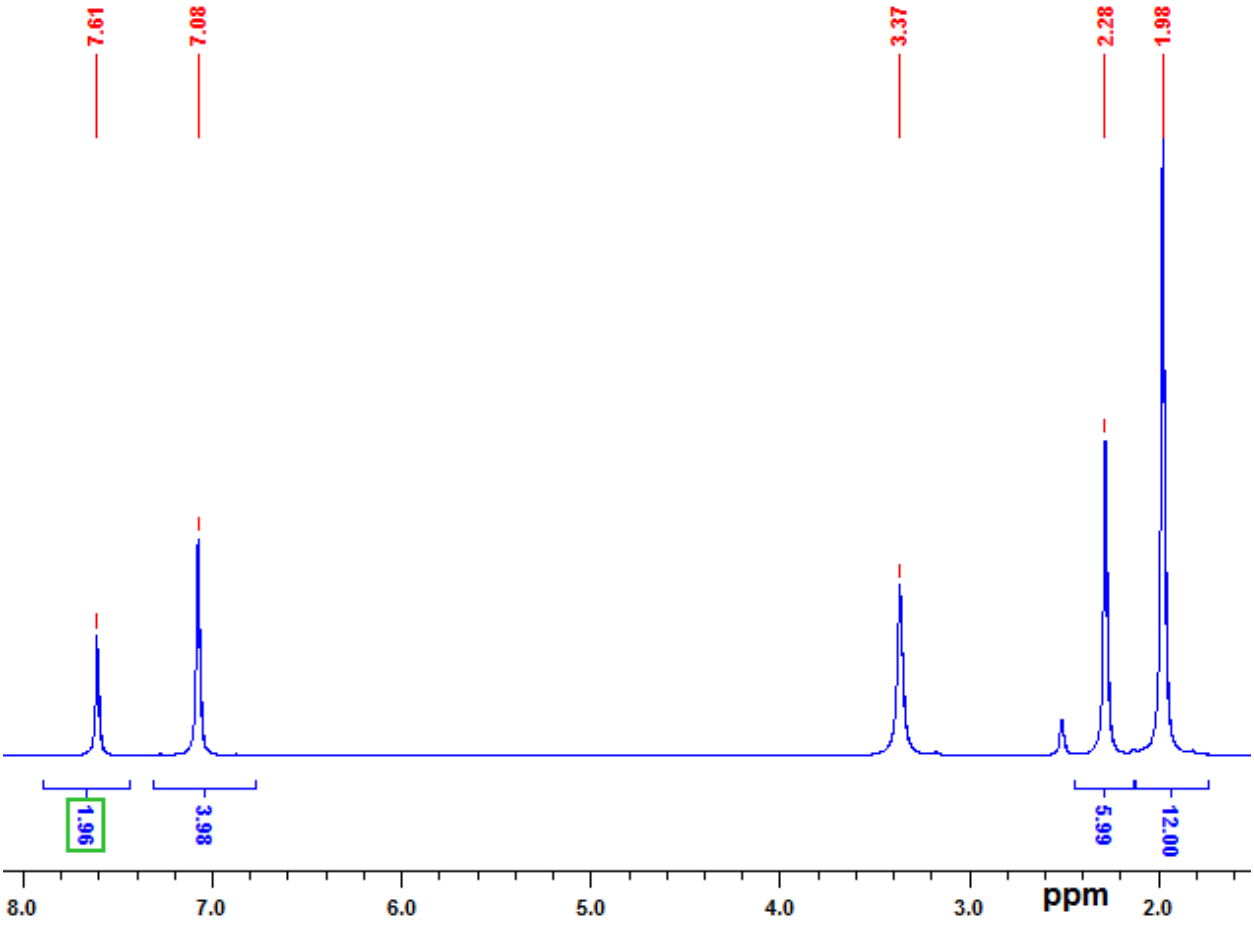


Fig. S8. ^{1}H NMR spectrum of **[(IMes=S)Cu]I** (**3**) in DMSO-d_6 at room temperature.

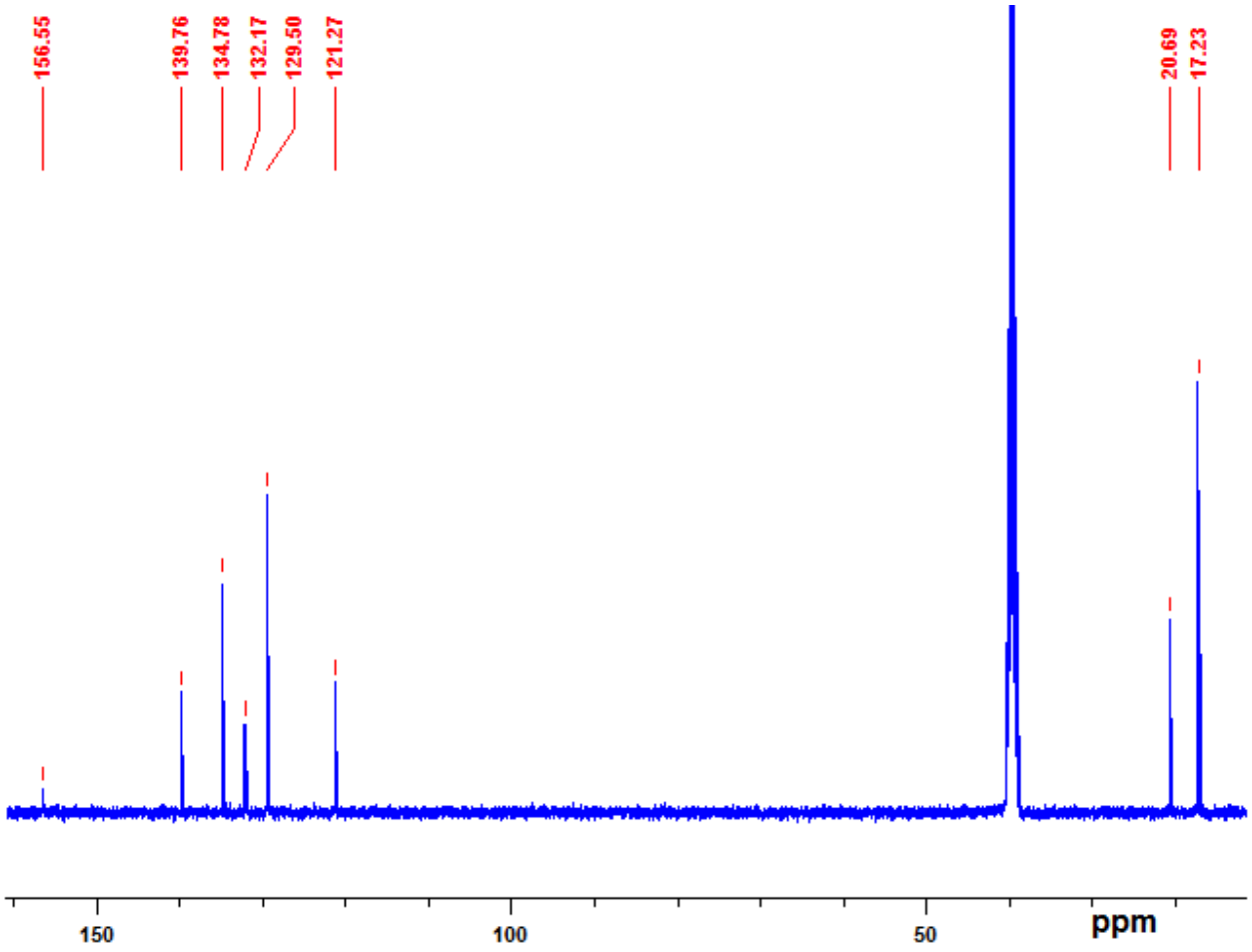


Fig. S9. ^{13}C NMR spectrum of **[(IMes=S)Cu]I** (**3**) in DMSO-d_6 at room temperature.

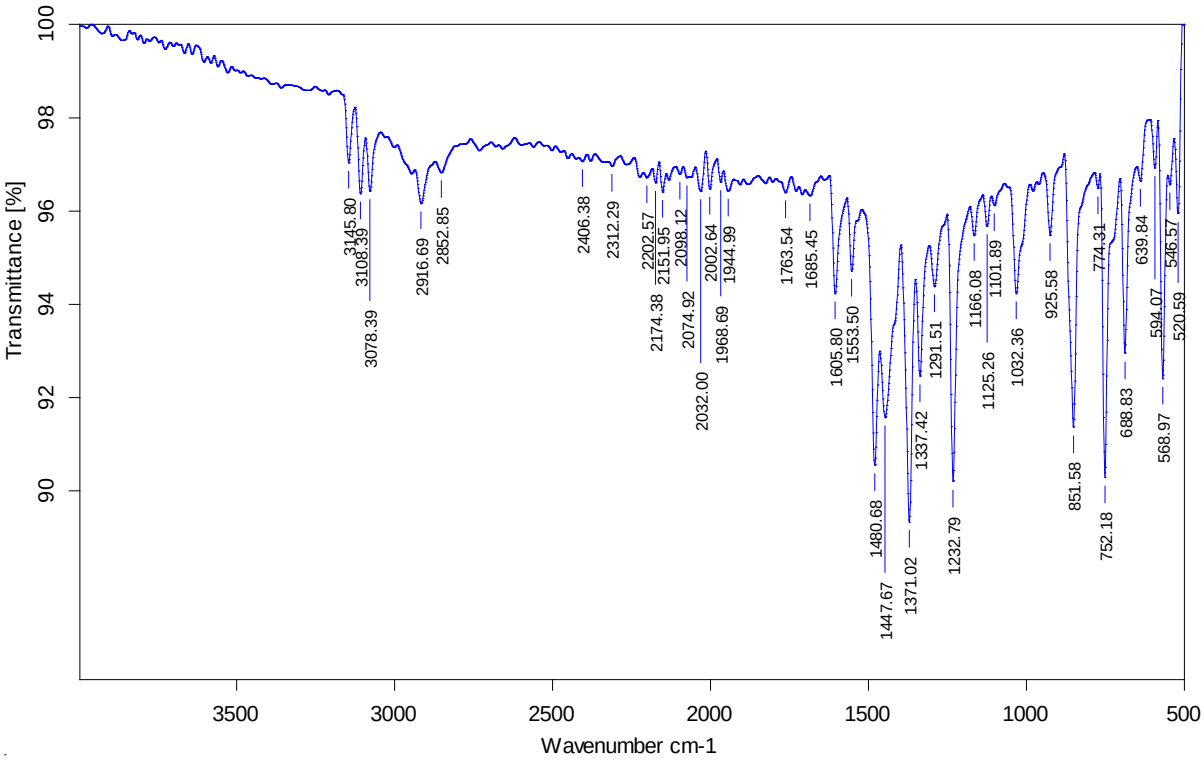


Fig. S10. Neat FT-IR spectrum of **[(IMes=Se)Cu]Br** (**4**) at room temperature.

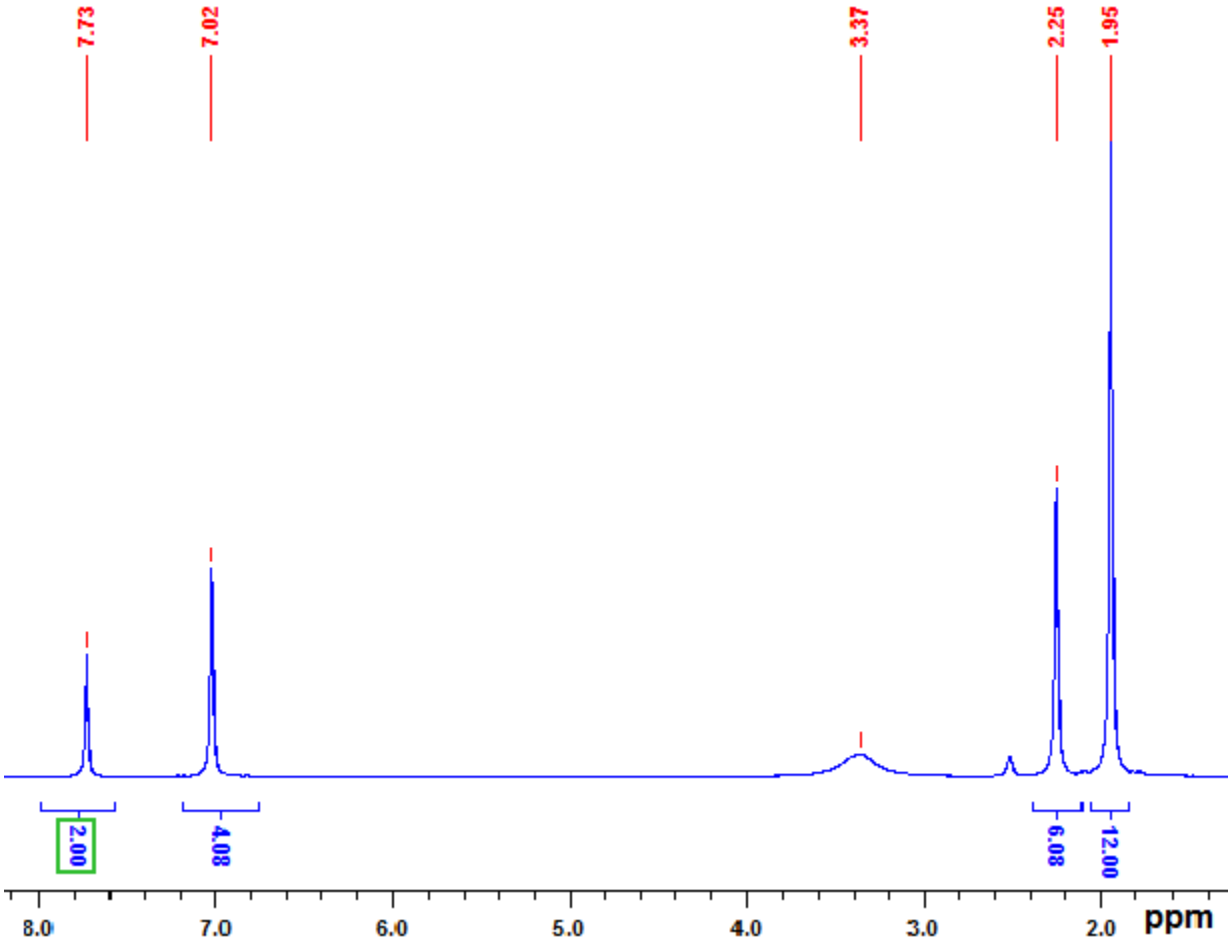


Fig. S11. ^{1}H NMR spectrum of **[(IMes=Se)Cu]Br** (**4**) in DMSO-d_6 at room temperature.

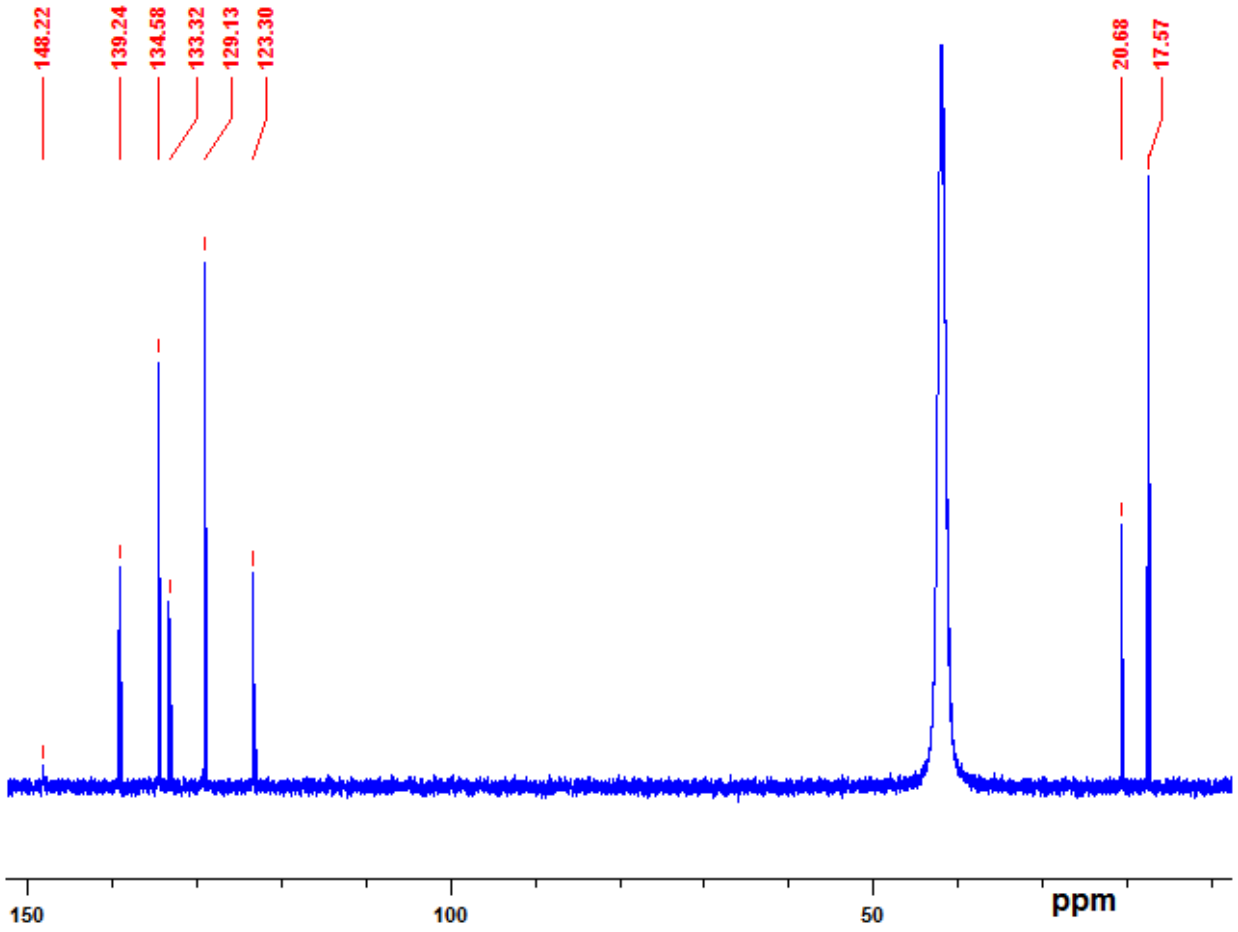


Fig. S12. ^{13}C NMR spectrum of **[(IMes=Se)Cu]Br** (**4**) in DMSO-d_6 at room temperature.

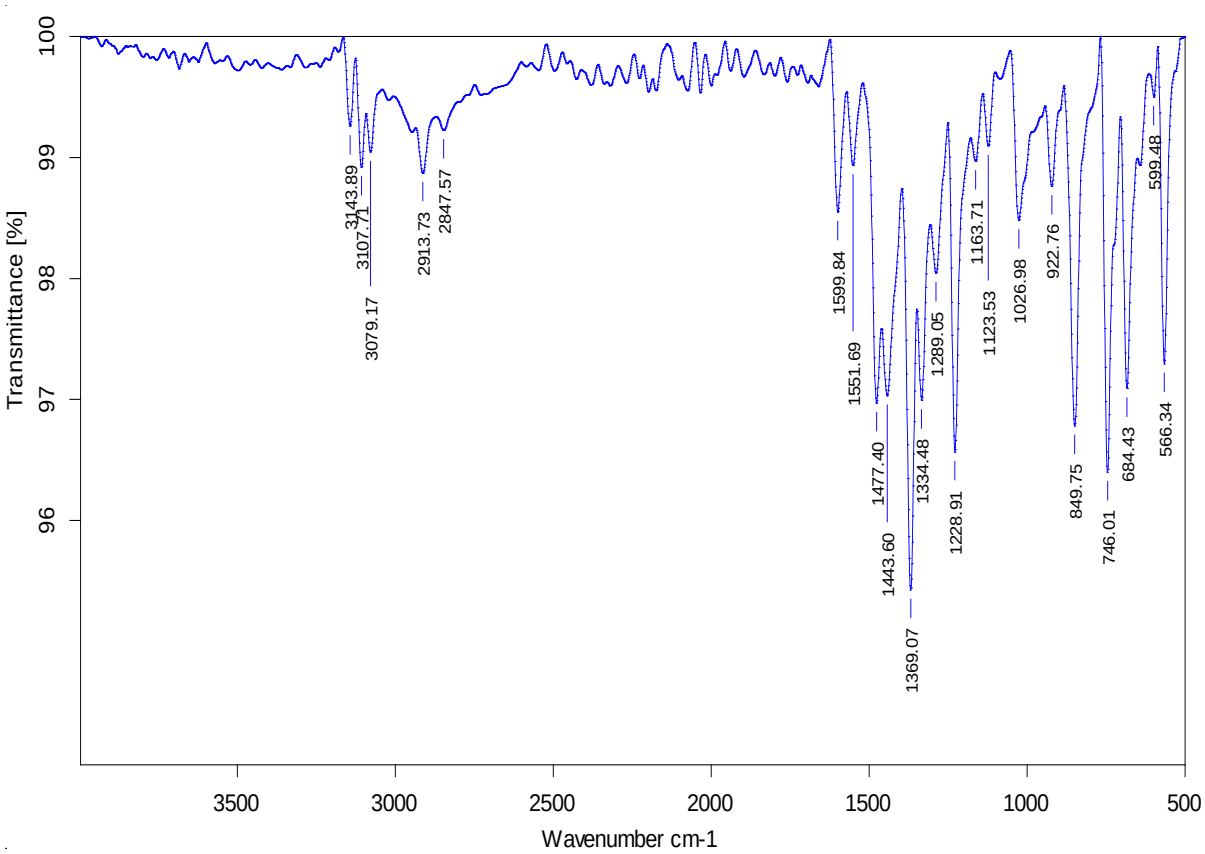


Fig. S13. Neat FT-IR spectrum of **[(IMes=Se)Cu]I** (**5**) at room temperature.

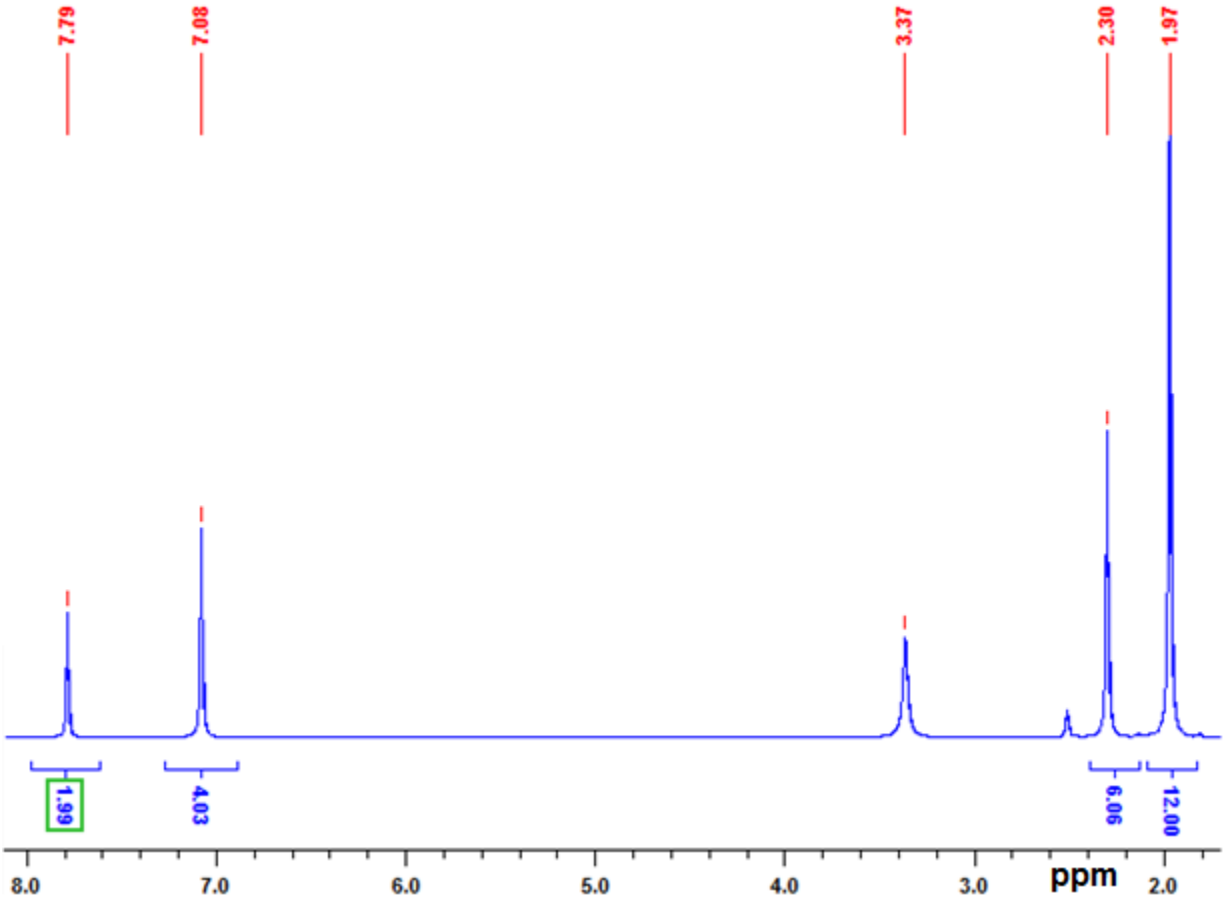


Fig. S14. ^{1}H NMR spectrum of **[(IMes=Se)Cu]I** (**5**) in DMSO-d_6 at room temperature.

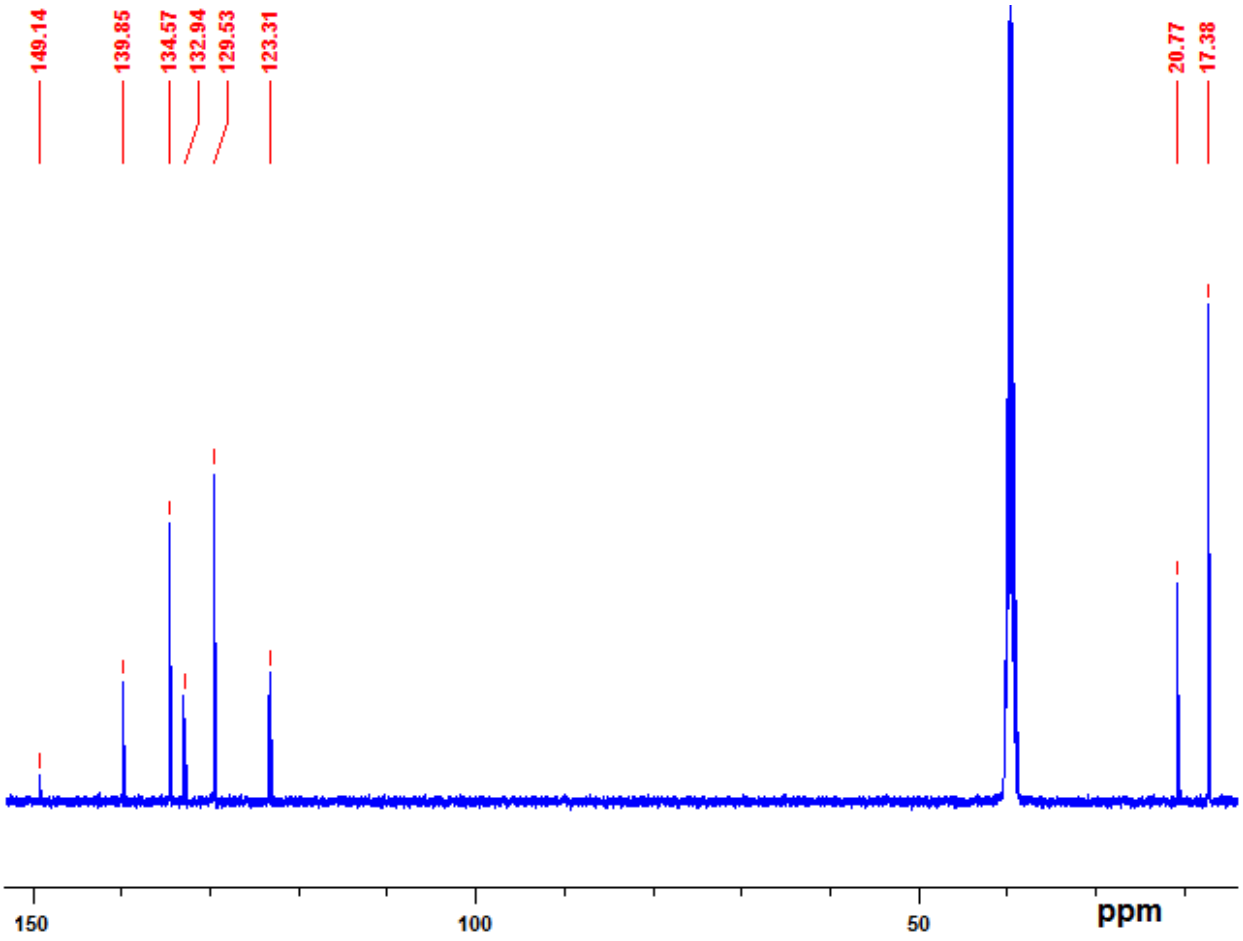


Fig. S15. ^{13}C NMR spectrum of **[(IMes=Se)Cu]I** (**5**) in DMSO-d_6 at room temperature.

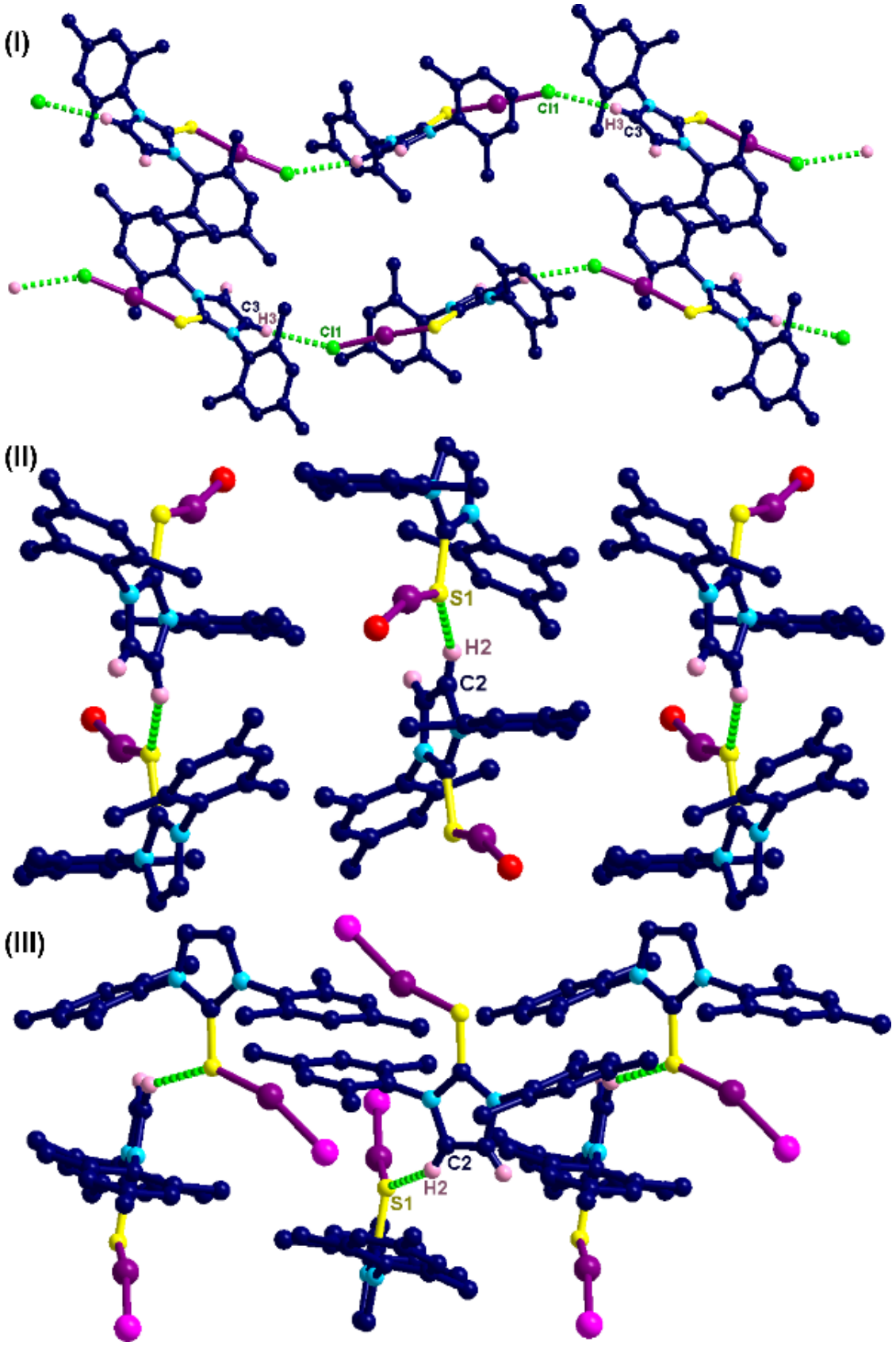

(I)
Cl1
H3
C3
C3
H3
Cl1
(II)
S1
H2
C2
(III)
C2
H2
S1

Fig. 16. (I) Molecular packing arrangement of **1** with extended C–H···Cl hydrogen bonding interactions. Non-interacting hydrogen atoms have been omitted for the clarity. D···A distances [Å]: H(3)···Cl(1), 2.8116(2); C–D···A angles [°]: C(3)–H(3)···Cl(1), 164.549(3). (II) Molecular packing arrangement of **2** with extended C–H···S hydrogen bonding interactions. Non-interacting hydrogen atoms have been omitted for the clarity. D···A distances [Å]: H(2)···S(1), 3.1008(1); C–D···A angles [°]: C(2)–H(2)···S(1), 134.838(1); C(1)–S(1)···H(2), 106.654(1). (III) Molecular packing arrangement of **3** with extended C–H···S hydrogen bonding interactions. Non-interacting hydrogen atoms have been omitted for the clarity. D···A distances [Å]: H(2)···S(1), 3.0441(3); C–D···A angles [°]: C(2)–H(2)···S(1), 136.506(7); C(1)–S(1)···H(2), 106.816(4).

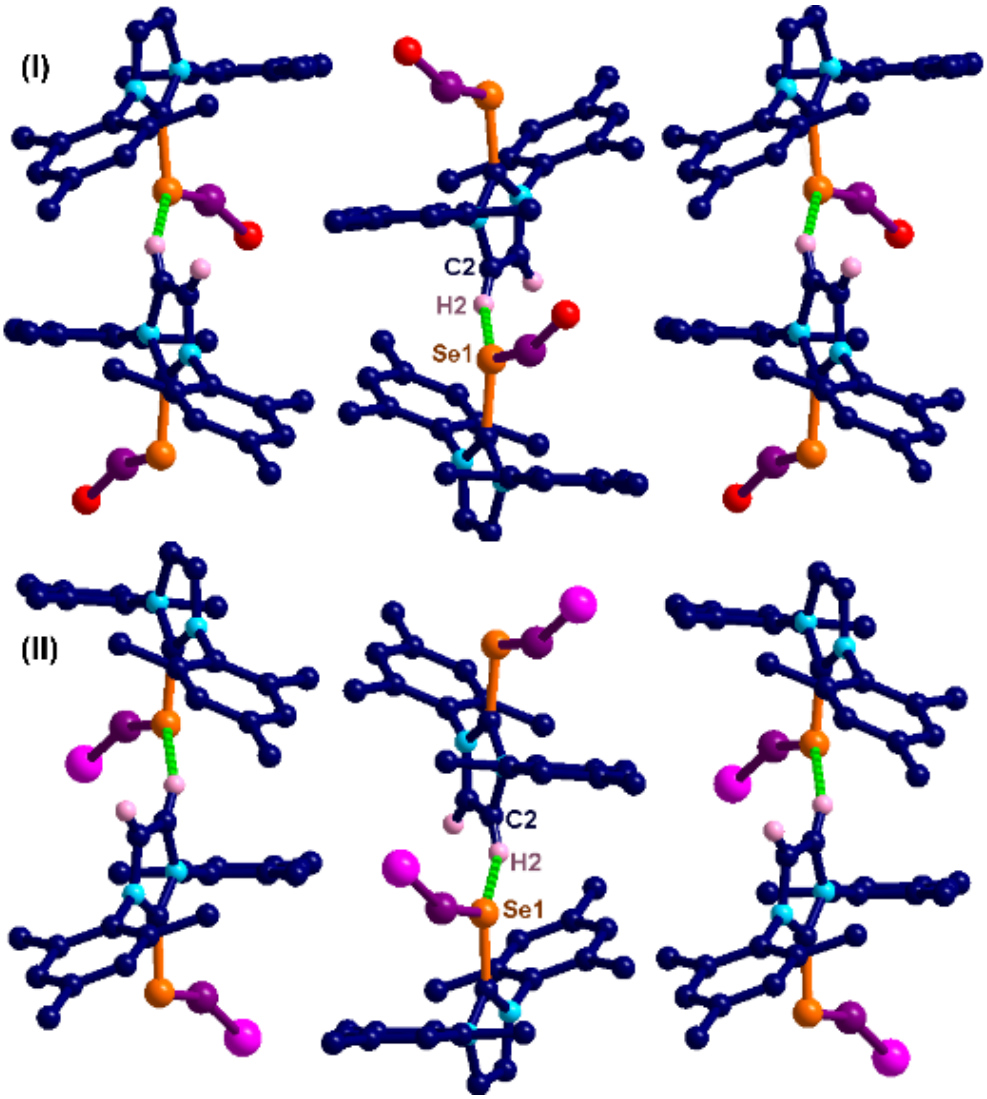


Fig. 17. (I) Molecular packing arrangement of **4** with extended C–H···Se hydrogen bonding interactions. Non-interacting hydrogen atoms have been omitted for the clarity. D···A distances [Å]: H(2)···Se(1), 3.1576(1); C–D···A angles [°]: C(2)–H(2)···Se(1), 132.740(3); C(1)–Se(1)···H(2), 105.844(2). (II) Molecular packing arrangement of **3** with extended C–H···Se hydrogen bonding interactions. Non-interacting hydrogen atoms have been omitted for the clarity. D···A distances [Å]: H(2)···Se(1), 3.1241(1); C–D···A angles [°]: C(2)–H(2)···Se(1), 132.134(3); C(1)–Se(1)···H(2), 104.541(1).

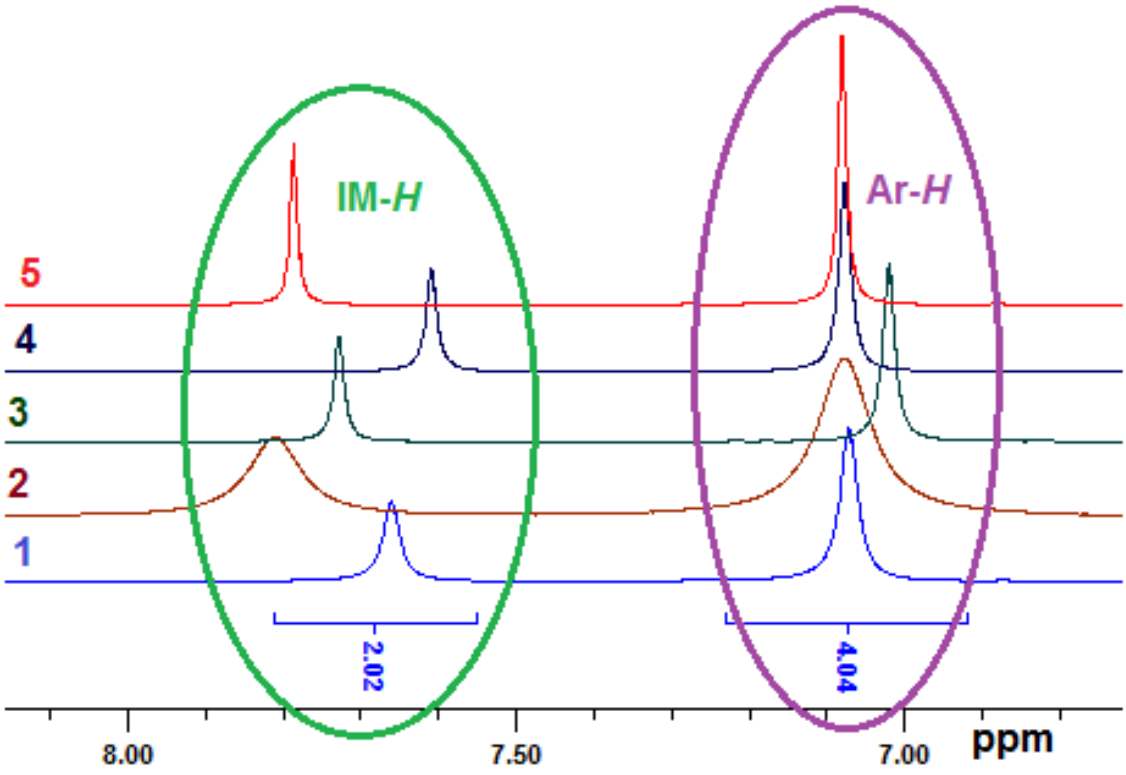


Fig. 18. Section of ^{1}H NMR spectra (400 MHz, DMSO-d_6) displays the aryl region among **1-5**.

Synthesis of [(IMes)CuCl] (6)

6 was synthesized as reported earlier and the spectral data matching with the reports.[ref] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (s, 2H, Im*H*), 6.99 (s, 4H, CH_{meta}), 2.34 (s, 6H, CH_{3para}), 2.10 (s, 12H, CH_{3ortho}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.66 (*C*–Cu), 139.50, 135.08, 134.57, 129.49, 122.30 (Ar*C*), 21.12 (*p*-CH_3), 17.77 (*o*-CH_3) ppm. FT-IR (neat): $\bar{\upsilon}$ = 3096(m), 2913(w), 1690(s), 1562(w), 1481(s), 1402(w), 1242(s), 1170(m), 1043(w), 928(w), 859(s), 736(s), 567(m) cm^{-1}.

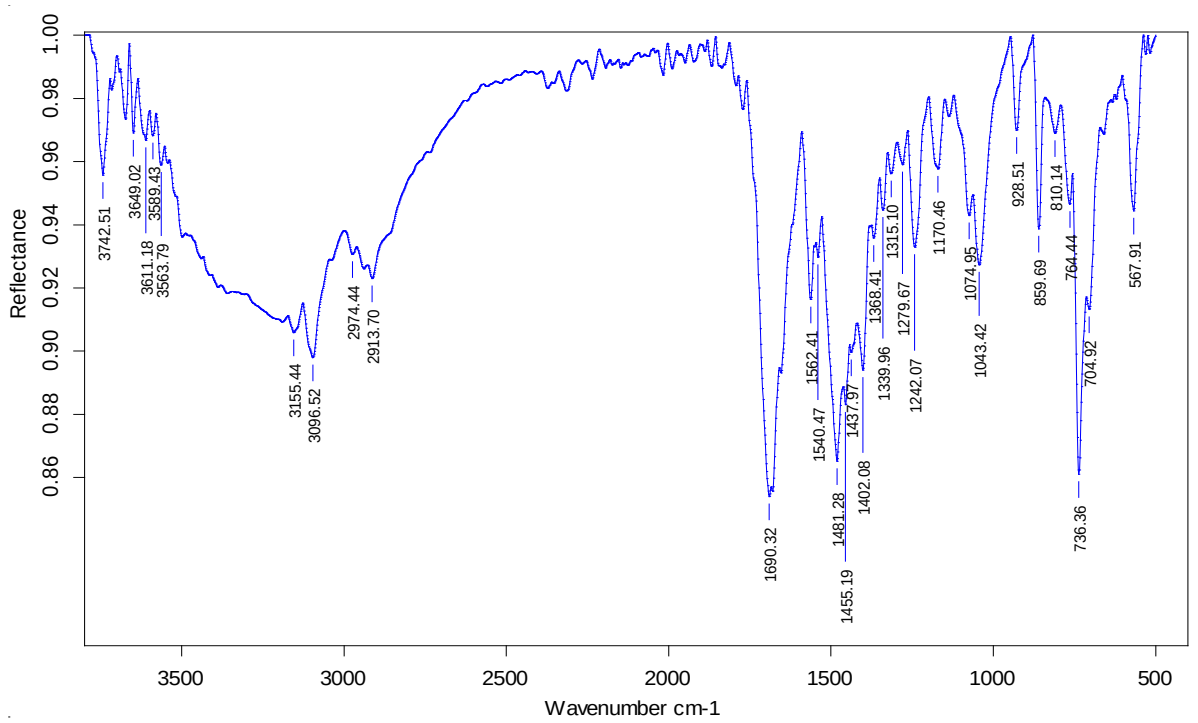


Fig. S19. Neat FT-IR spectrum of **[(IMes)CuCl]** (**6**) at room temperature.

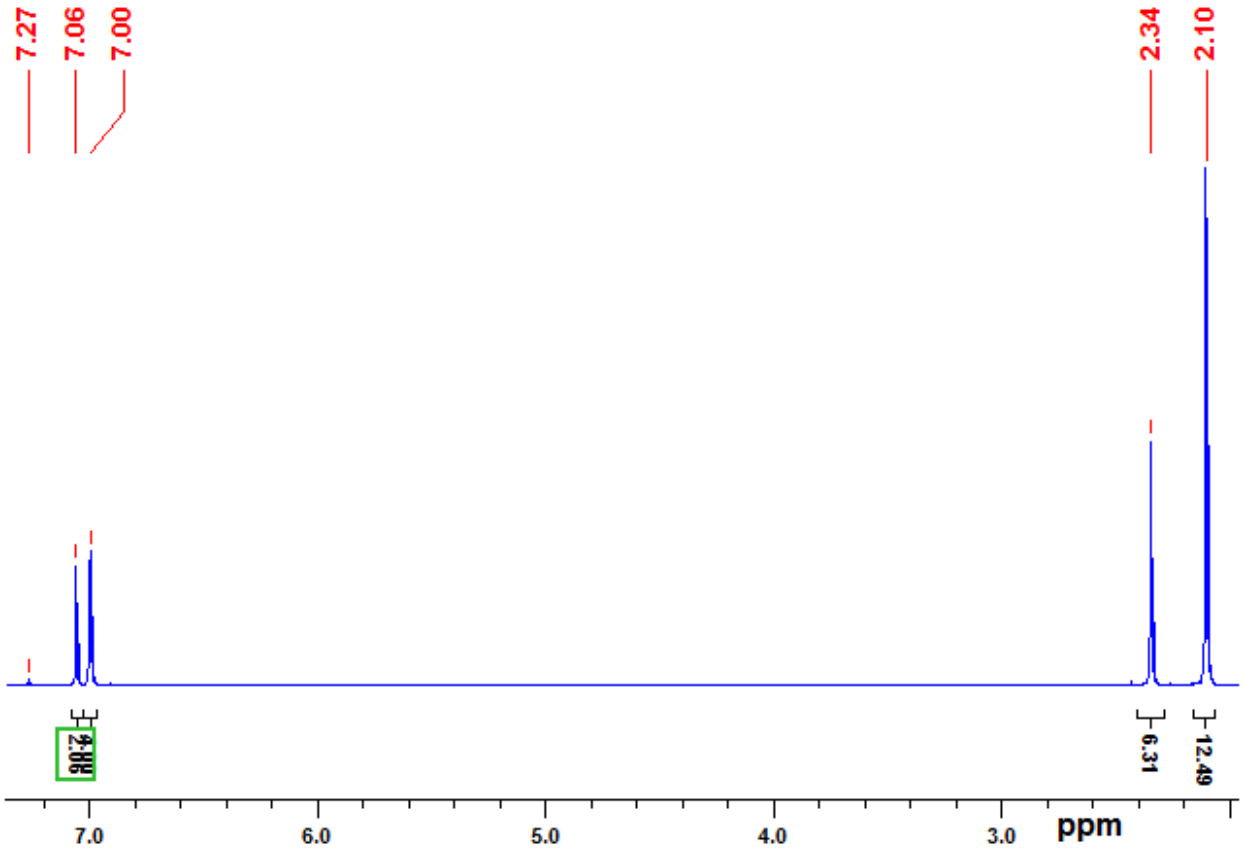


Fig. S20. ^{1}H NMR spectrum of **[(IMes)CuCl]** (**6**) in CDC_3 at room temperature.

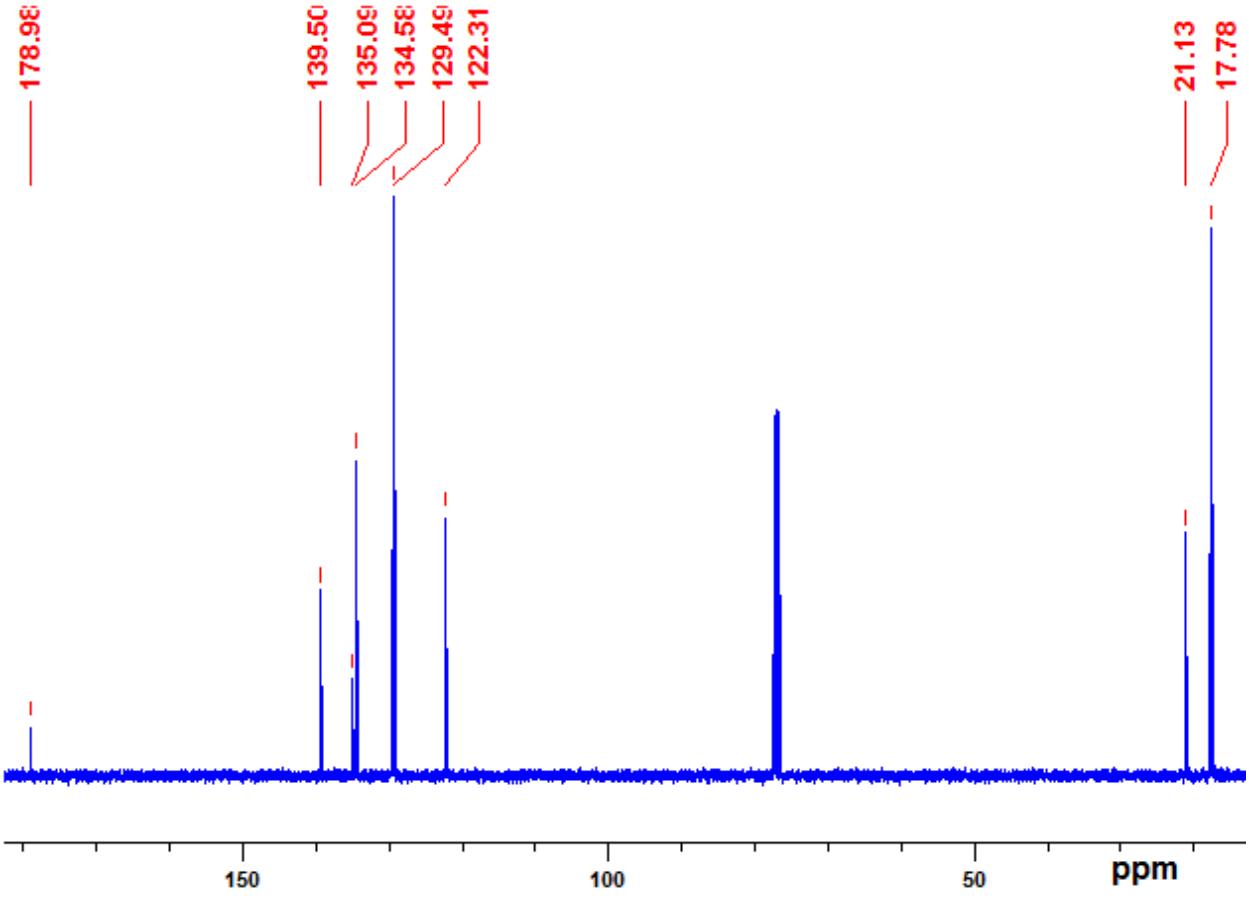


Fig. S21. ^{13}C NMR spectrum of **[(IMes)CuCl]** (**6**) in $CDCl_3$ at room temperature.

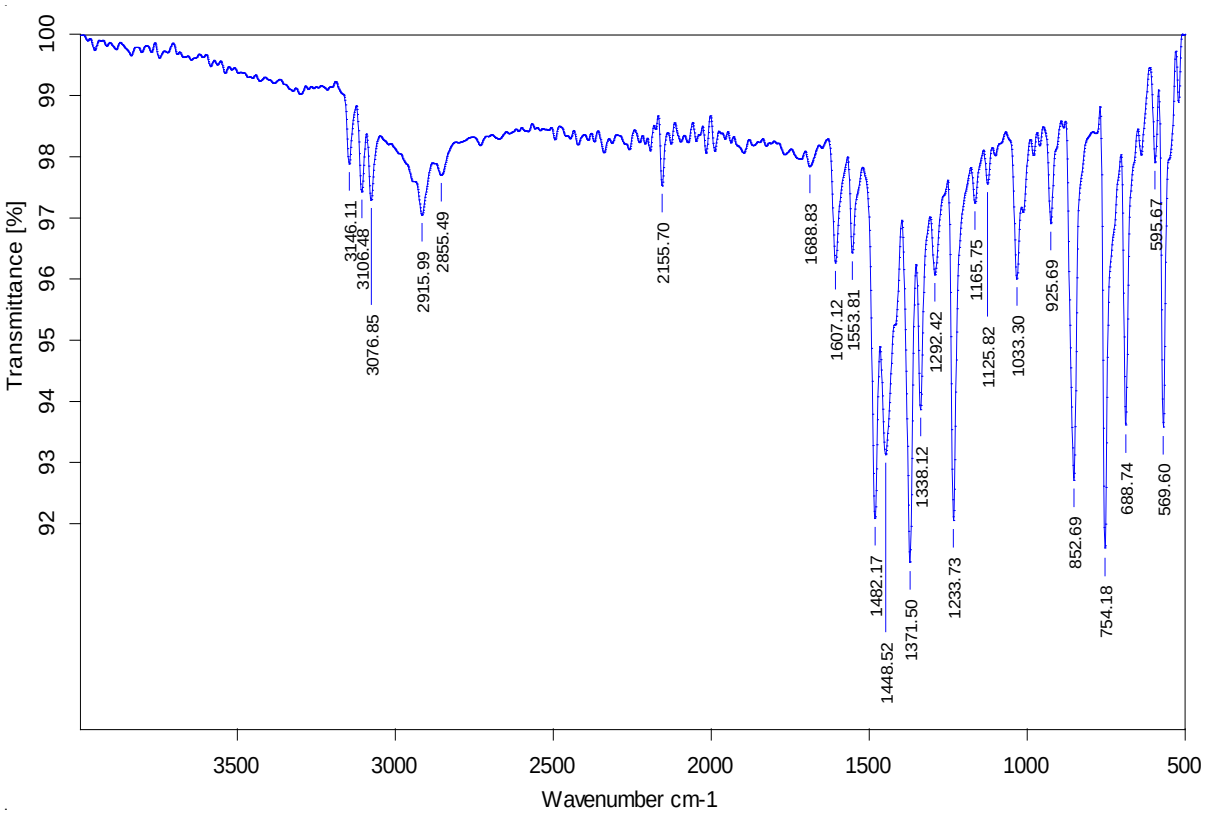


Fig. S22. Neat FT-IR spectrum of **[(IMes=Se)$_2$Cu][CuCl$_2$]** (**7**) at room temperature.

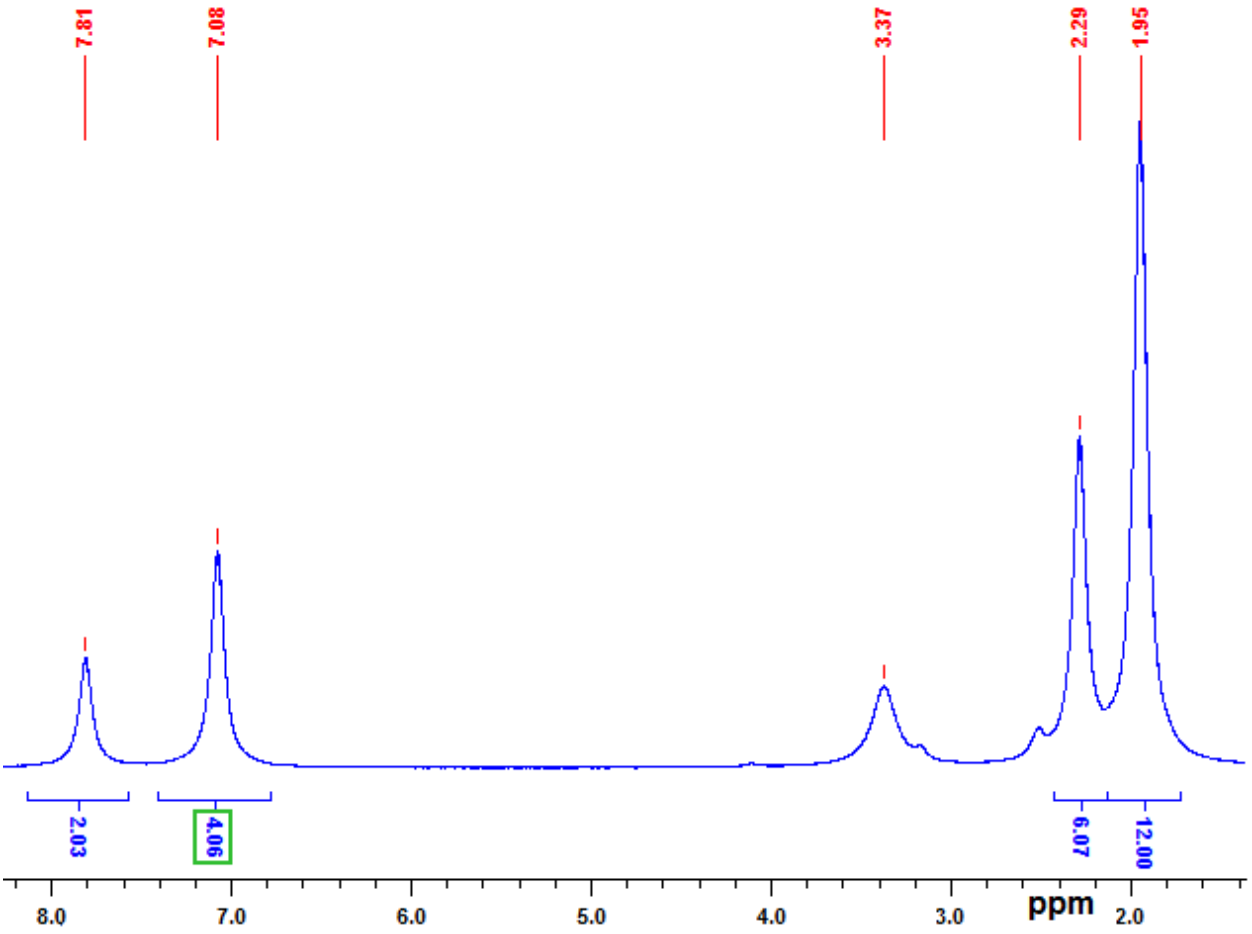


Fig. S23. ^{1}H NMR spectrum of **[(IMes=Se)$_2$Cu][CuCl$_2$]** (**7**) in DMSO-d_6 at room temperature.

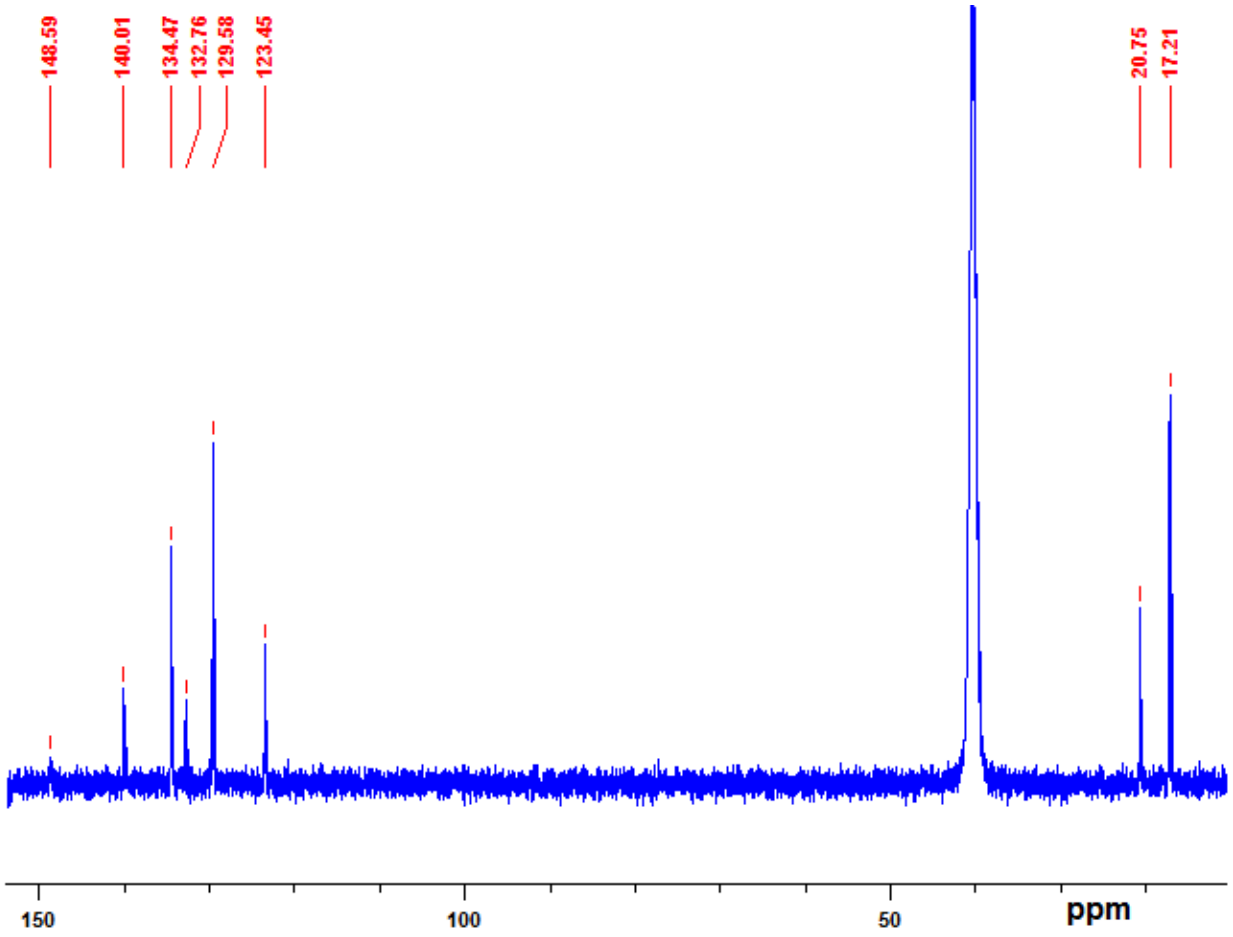


Fig. S24. ^{13}C NMR spectrum of **[(IMes=Se)$_2$Cu][CuCl$_2$]** (**7**) in DMSO-d_6 at room temperature.

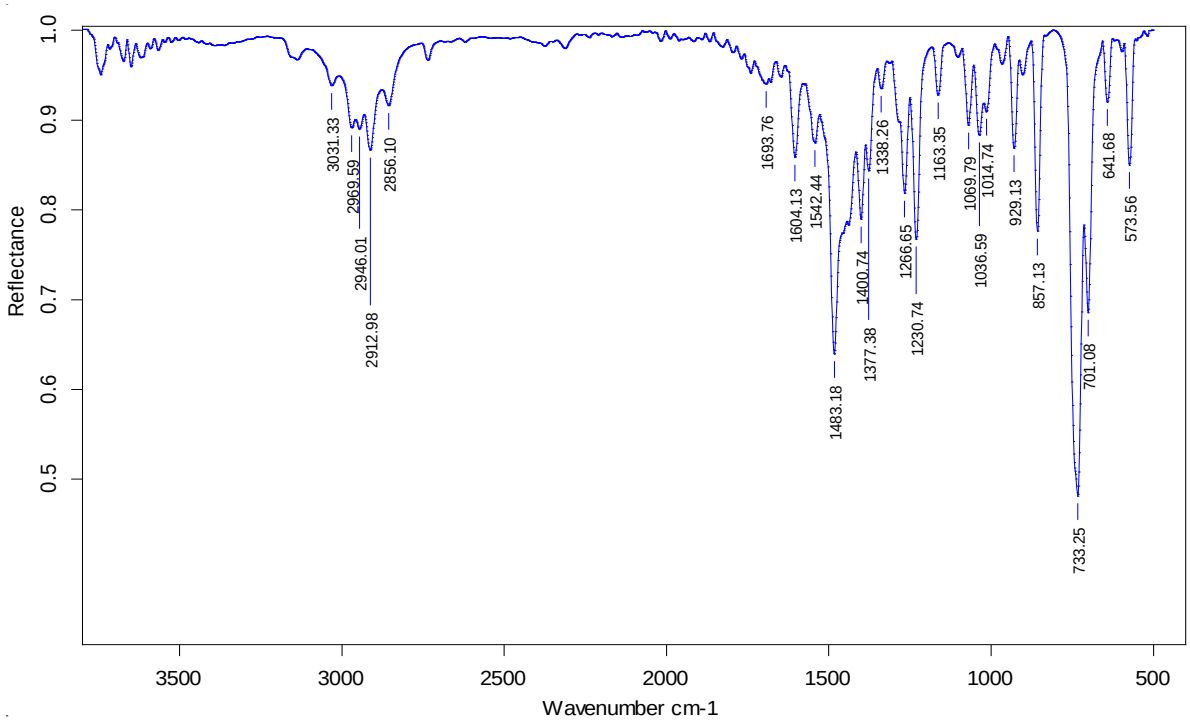


Fig. S25. Neat FT-IR spectrum of **[(IMes)$_2$Cu][Cl]** (**8**) at room temperature.

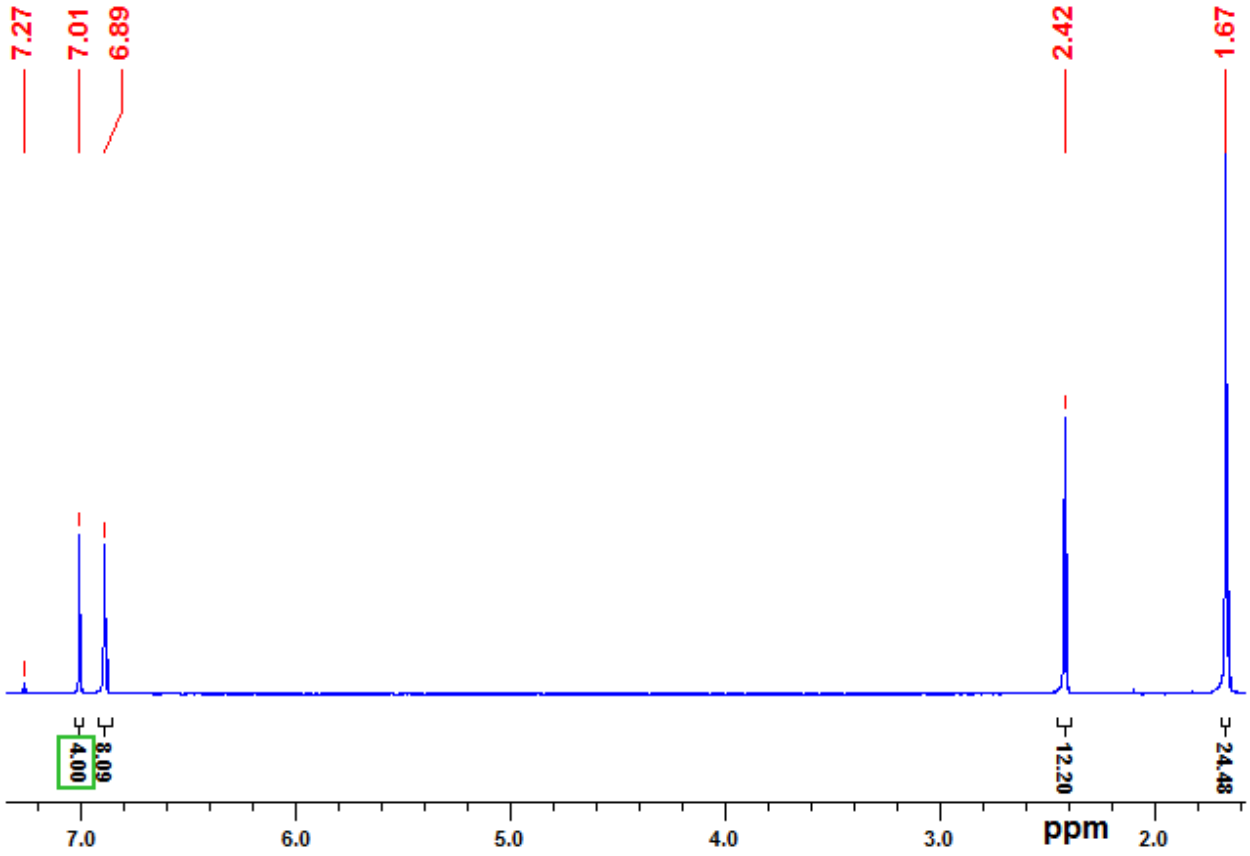


Fig. S26. ^{1}H NMR spectrum of **[(IMes)$_2$Cu][Cl]** (**8**) in CDC_3 at room temperature.

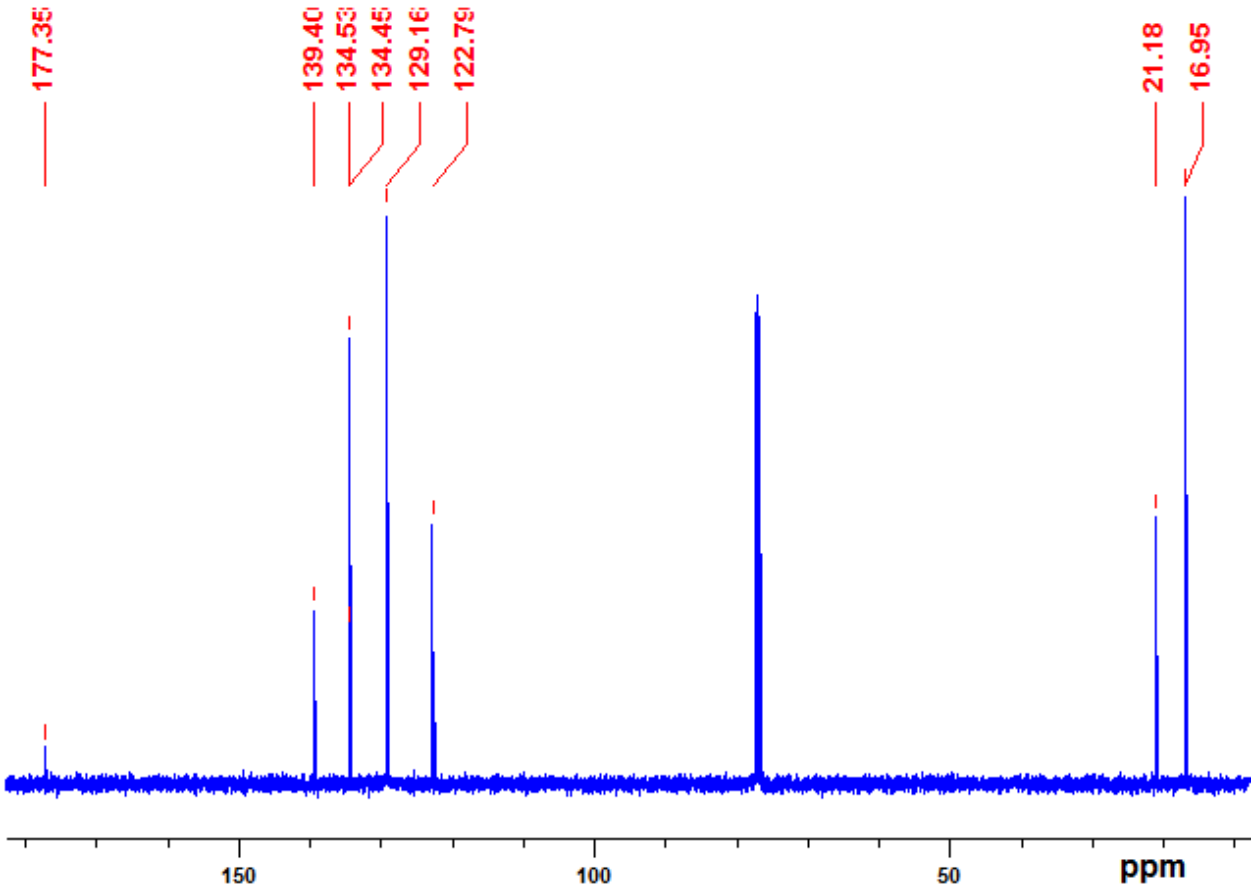


Fig. S27. ^{13}C NMR spectrum of **[(IMes)$_2$Cu][Cl]** (**8**) in $CDCl_3$ at room temperature.

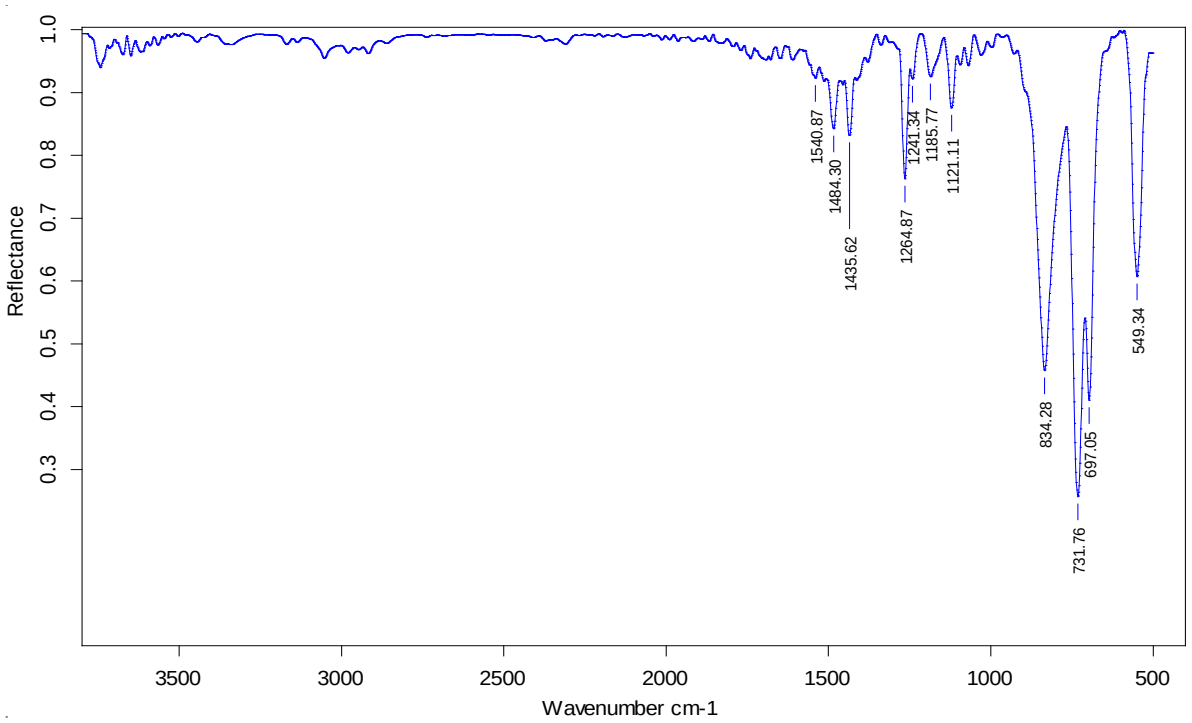


Fig. S28. Neat FT-IR spectrum of **[(IMes=Se)$_2$Cu][PF$_6$]** (**9**) at room temperature.

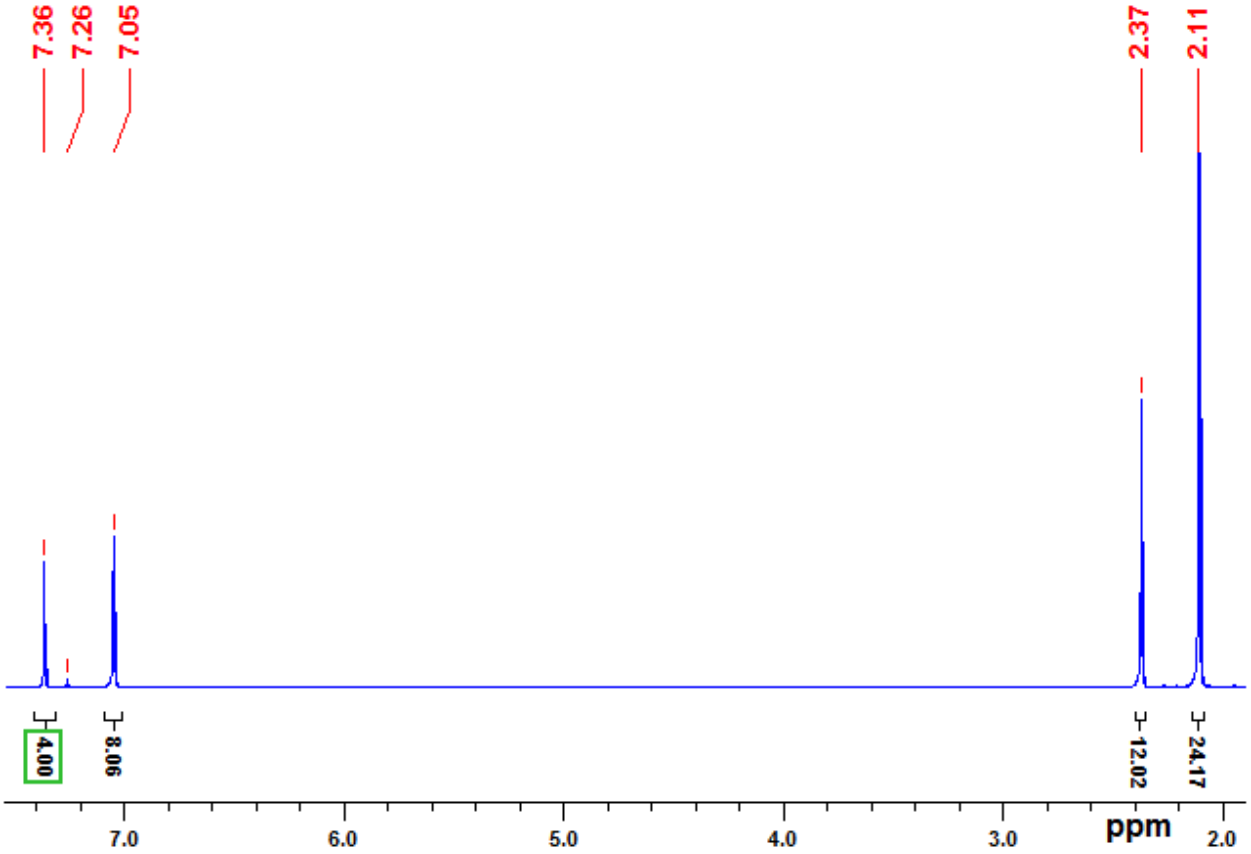


Fig. S29. ^{1}H NMR spectrum of **[(IMes=Se)$_2$Cu][PF$_6$]** (**9**) in CDC_3 at room temperature.

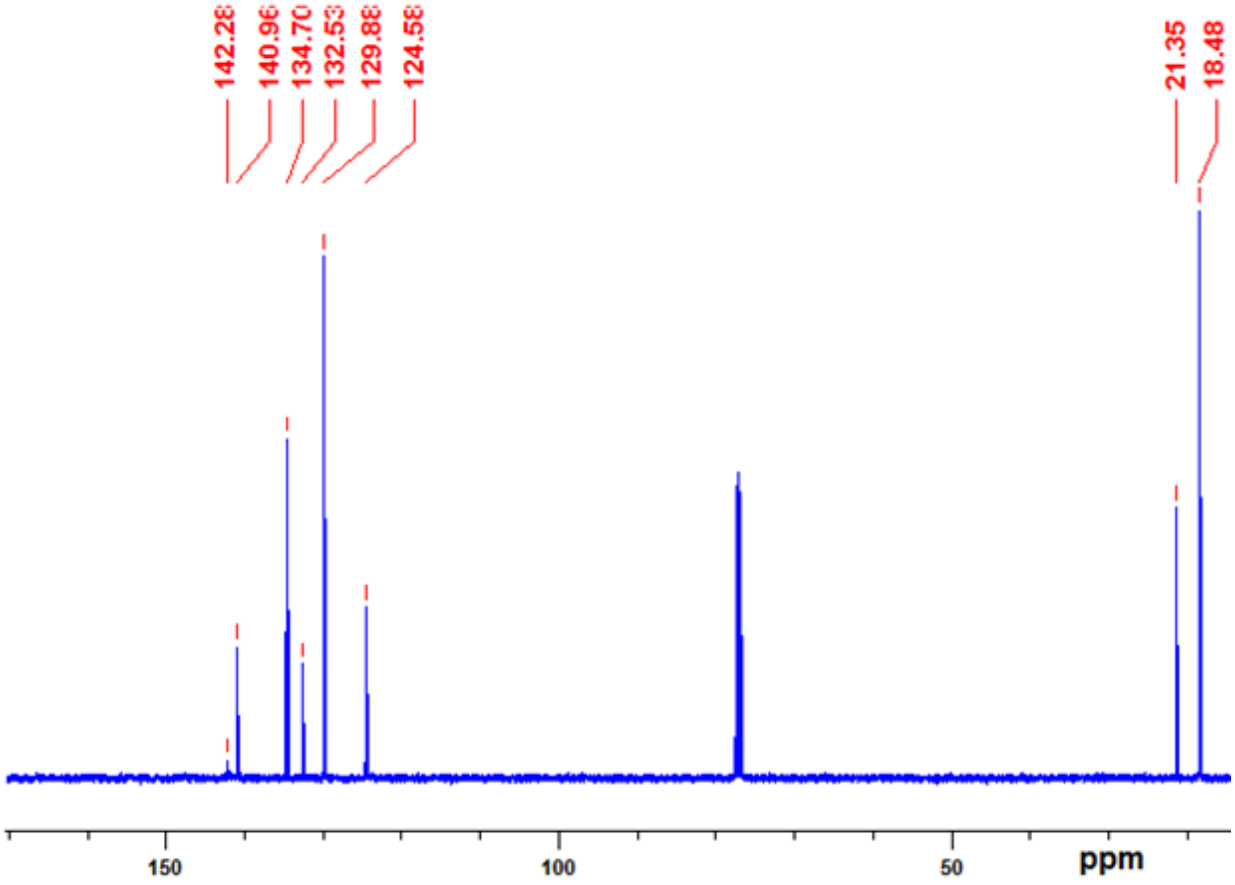


Fig. S30. ^{13}C NMR spectrum of **[(IMes=Se)$_2$Cu][PF$_6$]** (**9**) in $CDCl_3$ at room temperature.

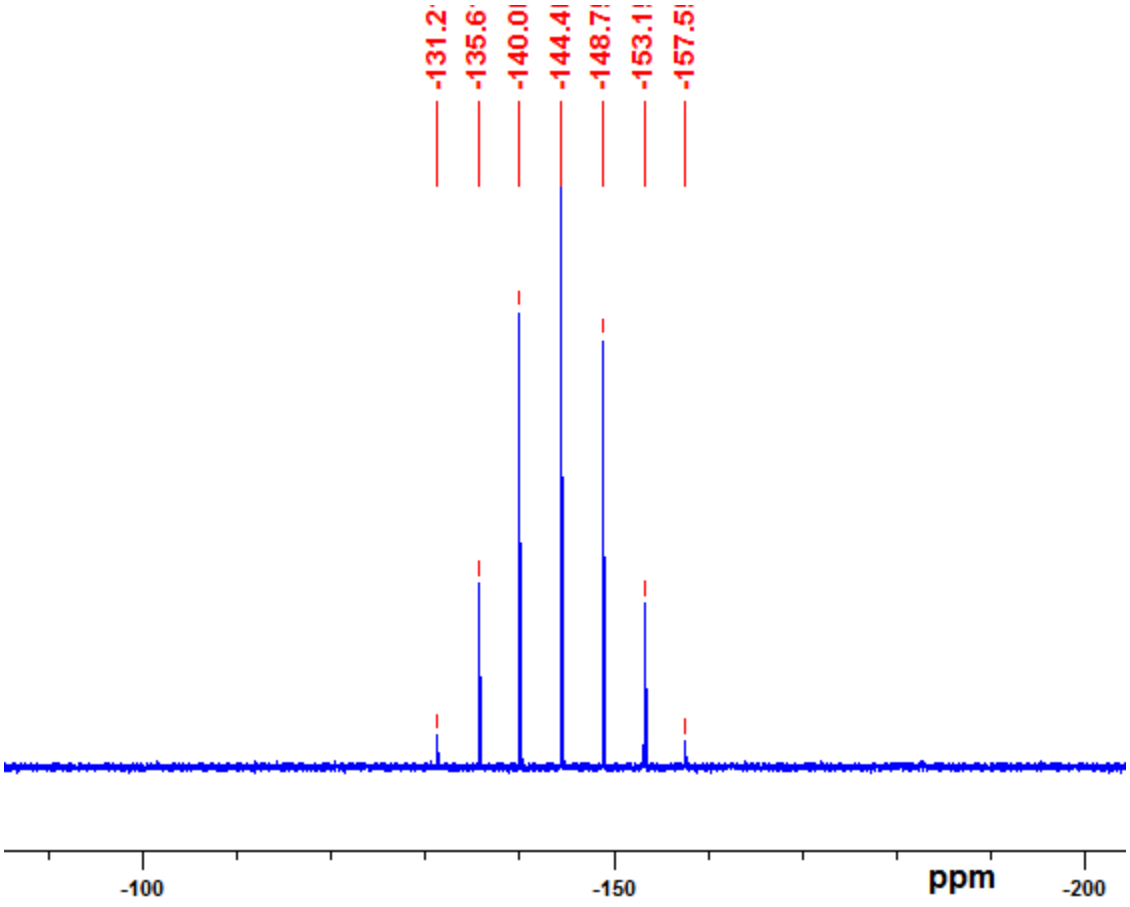


Fig. S31. ^{31}P NMR spectrum of **[(IMes=Se)$_2$Cu][PF$_6$]** (**9**) in $CDCl_3$ at room temperature.

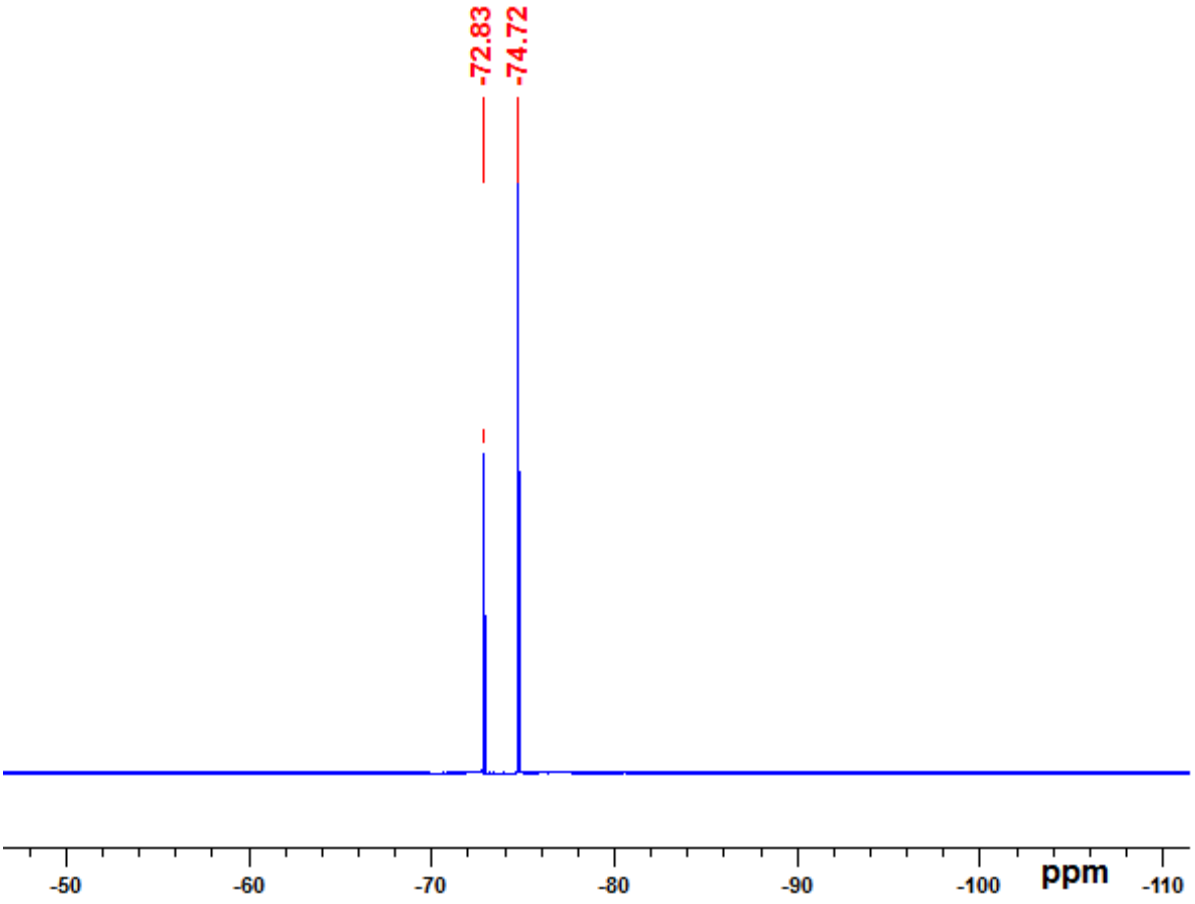


Fig. S32. ^{19}F NMR spectrum of **[(IMes=Se)$_2$Cu][PF$_6$]** (**9**) in $CDCl_3$ at room temperature.

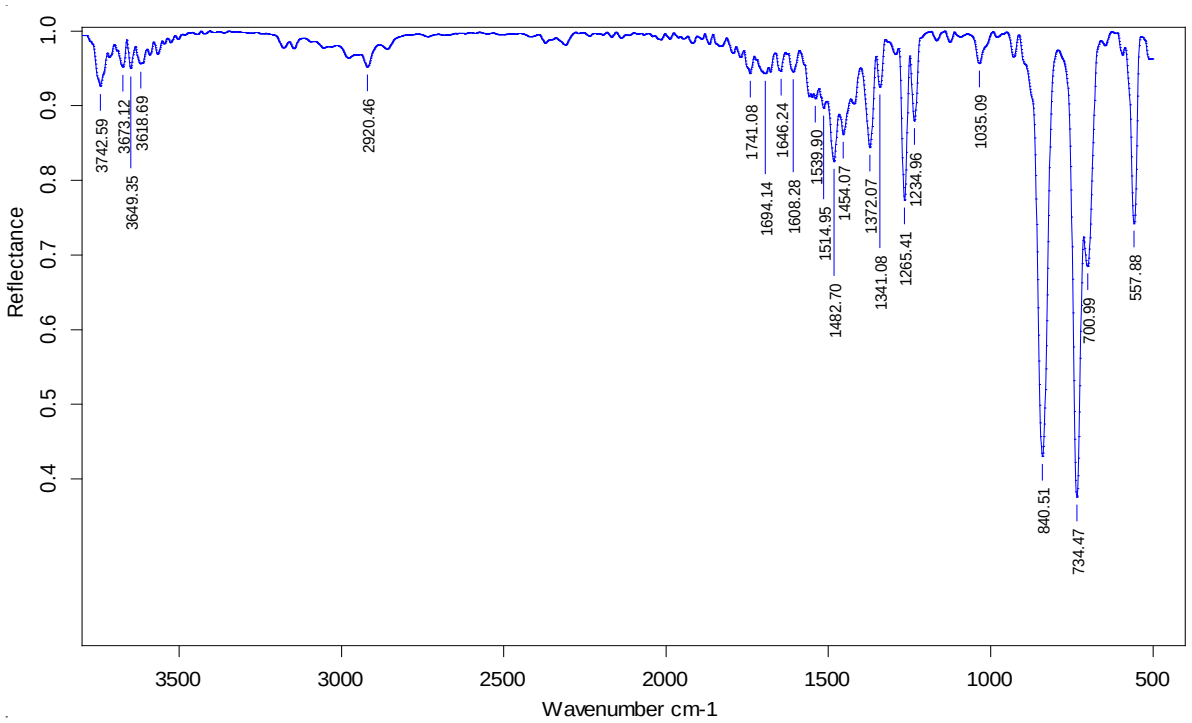


Fig. S33. Neat FT-IR spectrum of **[(IMes)$_2$Cu][PF$_6$]** (**10**) at room temperature.

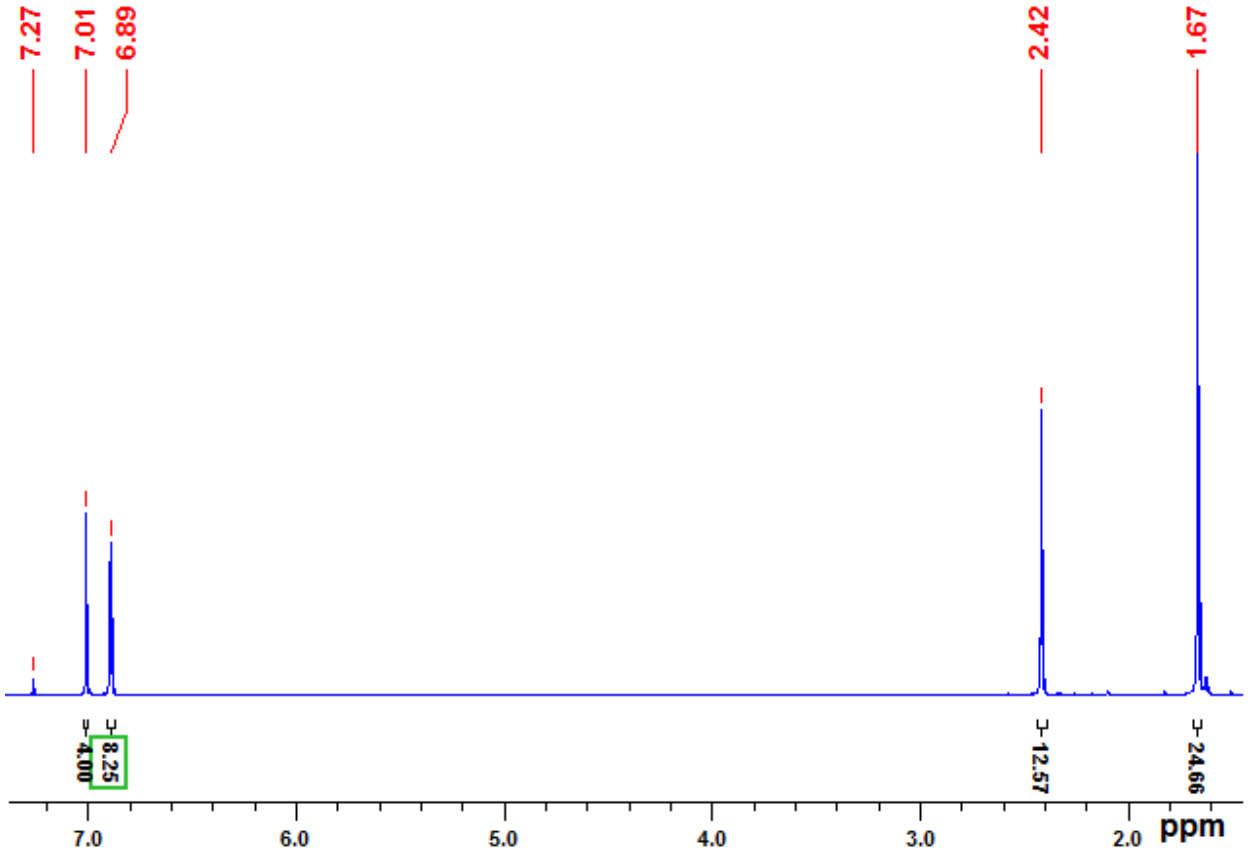


Fig. S34. ^{1}H NMR spectrum of **[(IMes)$_2$Cu][PF$_6$]** (**10**) in CDC_3 at room temperature.

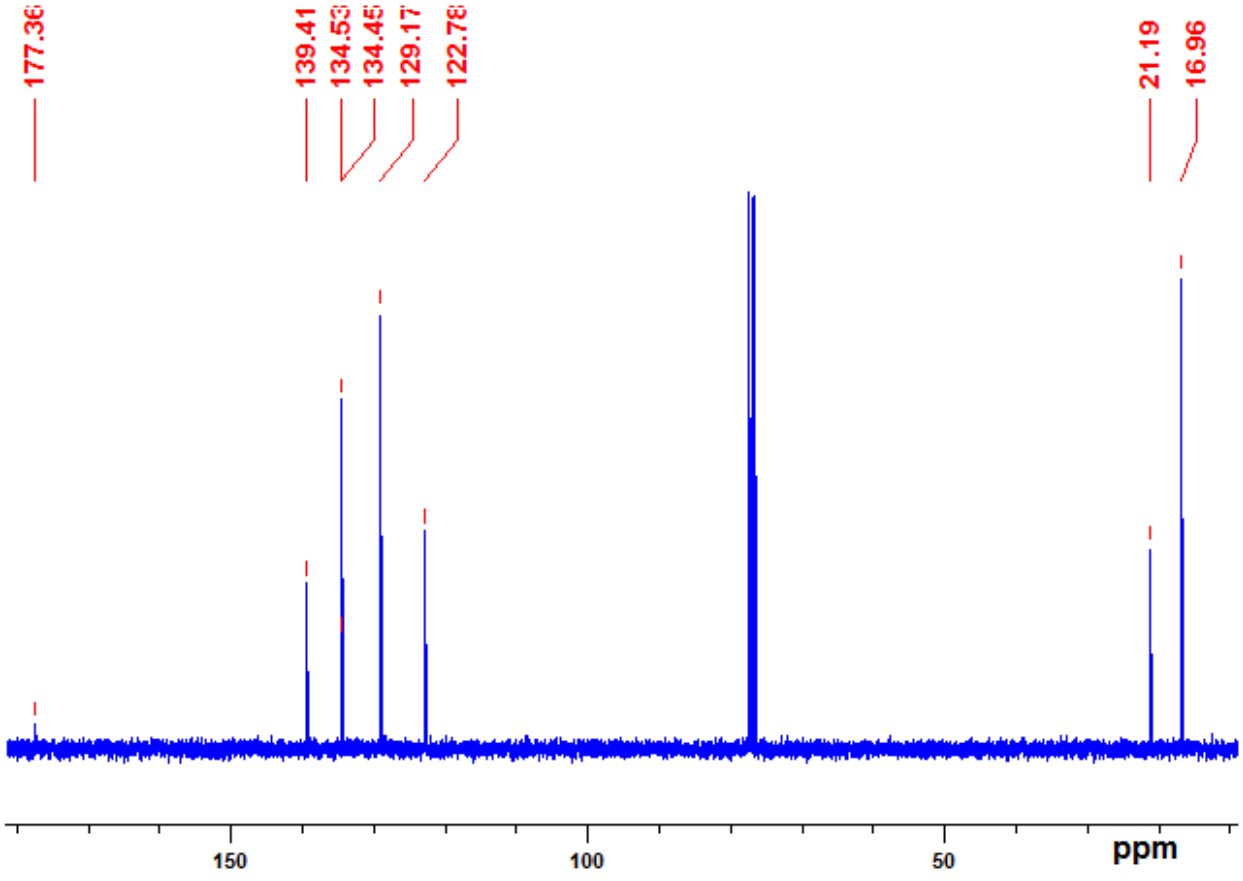


Fig. S35. ^{13}C NMR spectrum of **[(IMes)$_2$Cu][PF$_6$]** (**10**) in $CDCl_3$ at room temperature.

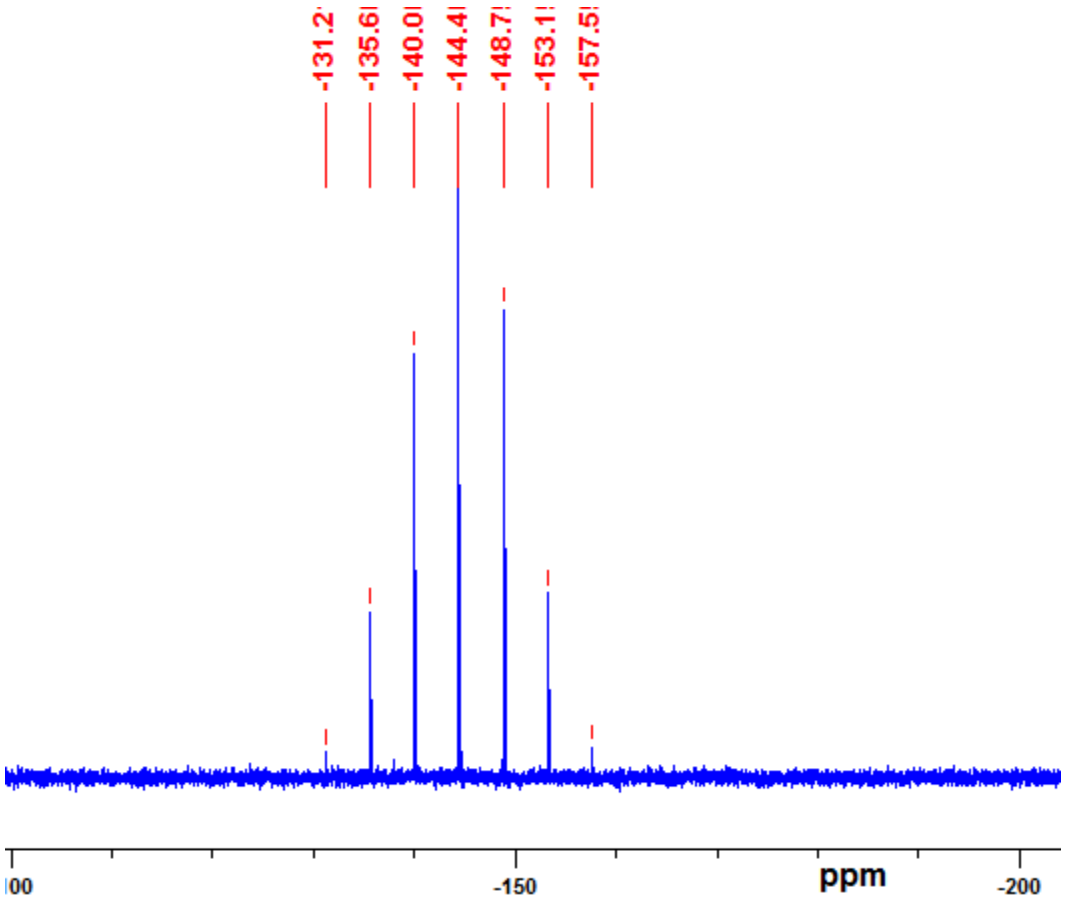


Fig. S36. ^{31}P NMR spectrum of **[(IMes)$_2$Cu][PF$_6$]** (**10**) in $CDCl_3$ at room temperature.

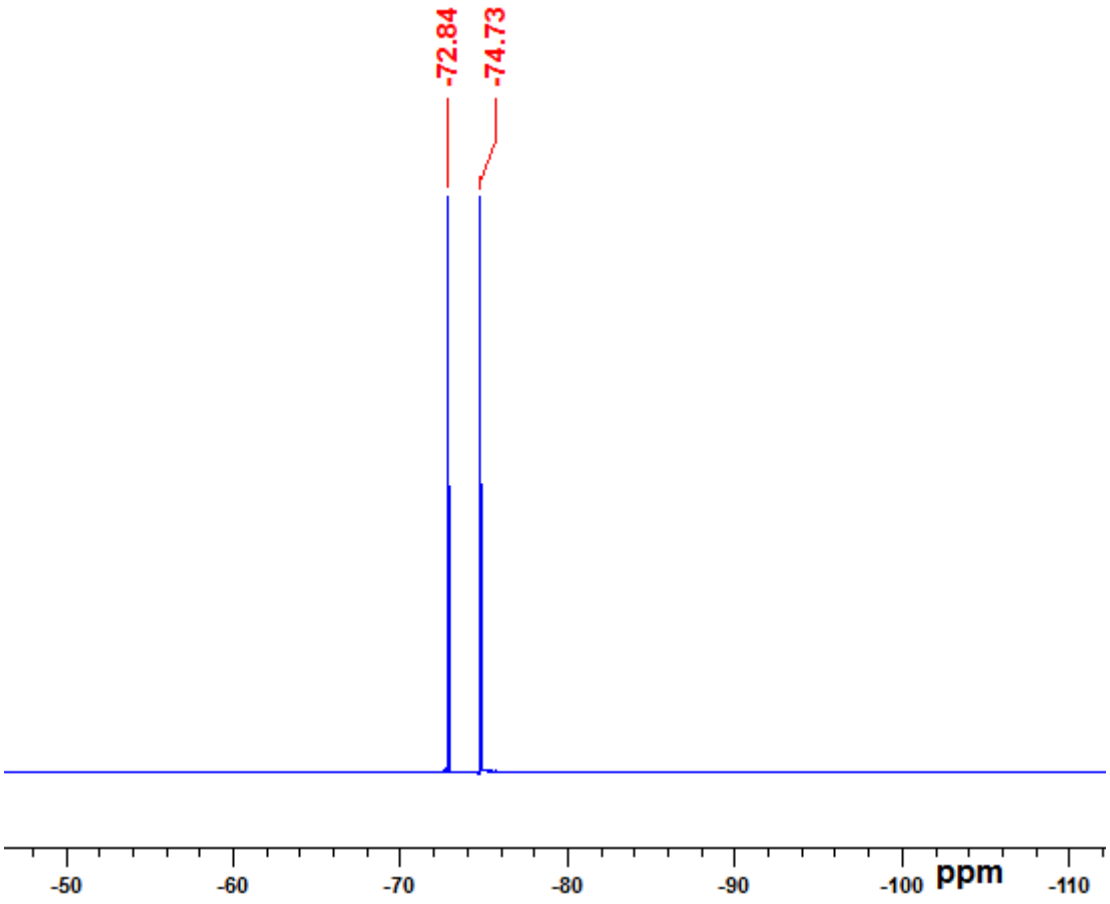


Fig. S37. ^{19}F NMR spectrum of **[(IMes)$_2$Cu][PF$_6$]** (**10**) in $CDCl_3$ at room temperature.

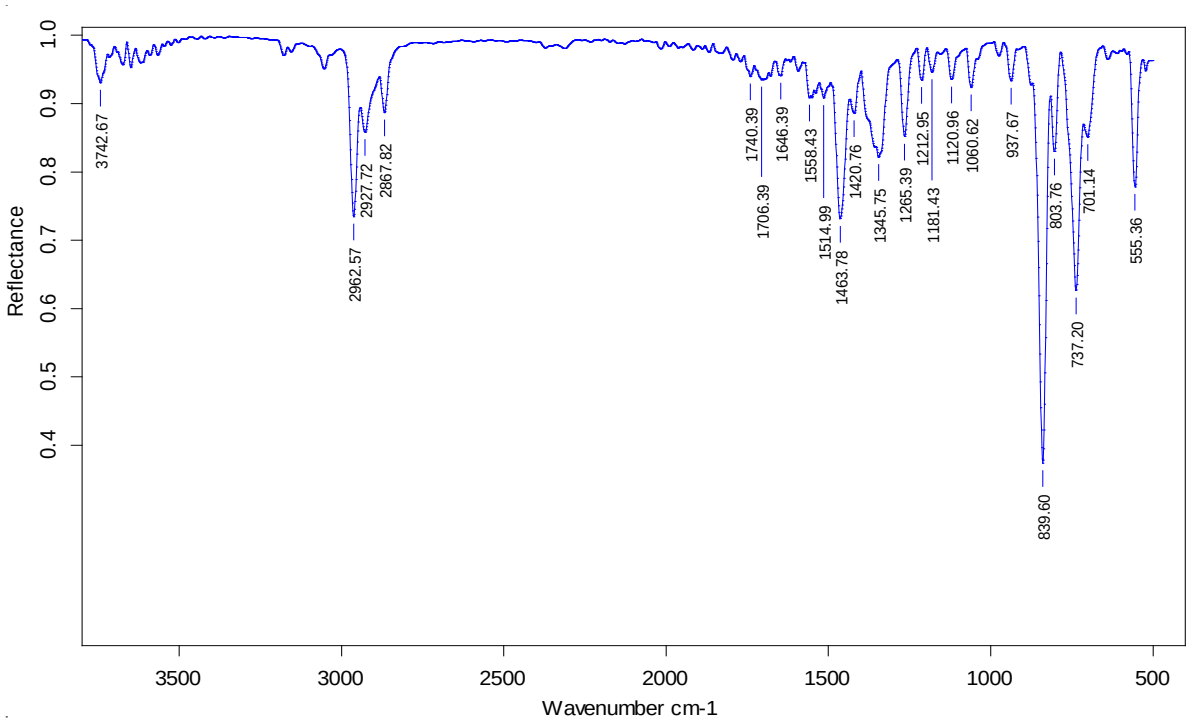


Fig. S38. Neat FT-IR spectrum of **[(IPr=Se)$_2$Cu][PF$_6$]** (**11**) at room temperature.

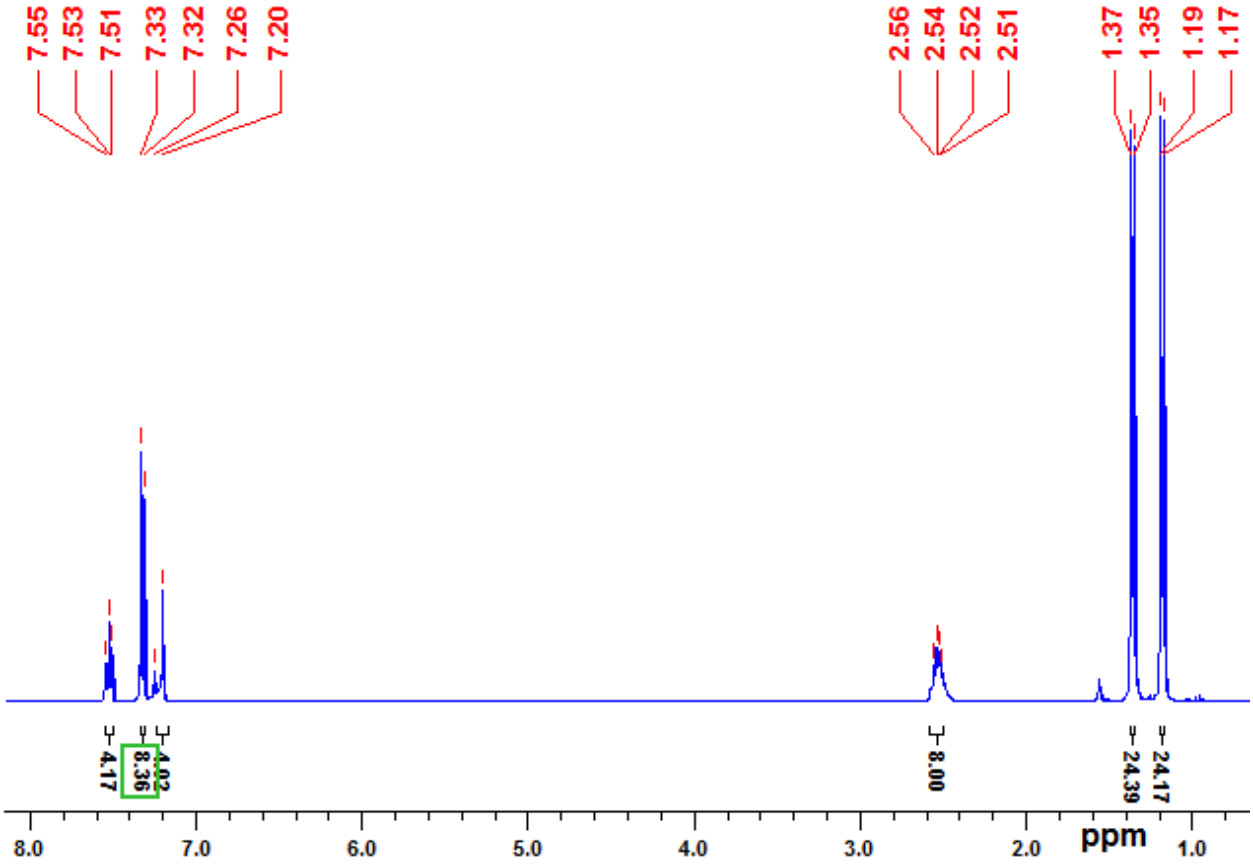


Fig. S39. ^{1}H NMR spectrum of **[(IPr=Se)$_2$Cu][PF$_6$]** (**11**) in CDC_3 at room temperature.

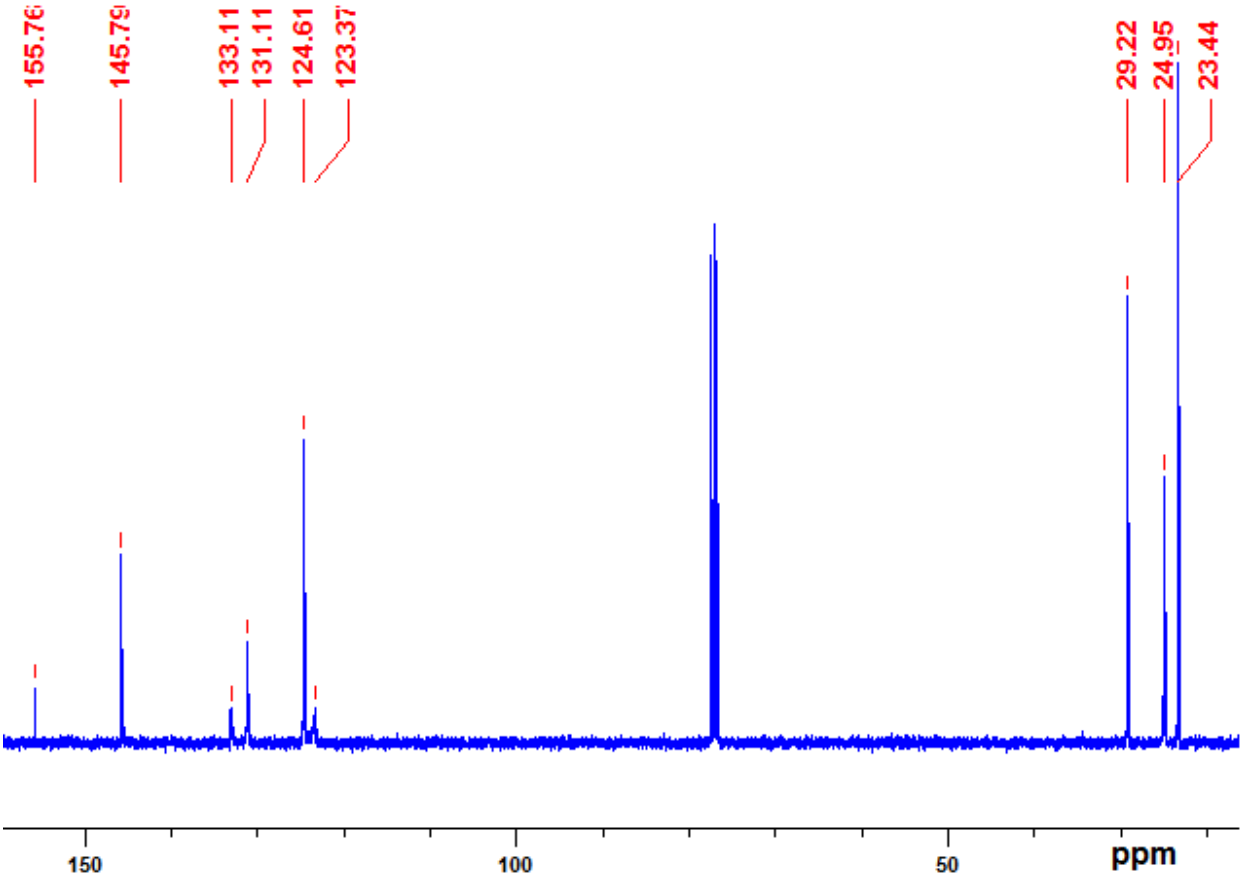


Fig. S40. ^{13}C NMR spectrum of **[(IPr=Se)$_2$Cu][PF$_6$]** (**11**) in $CDCl_3$ at room temperature.

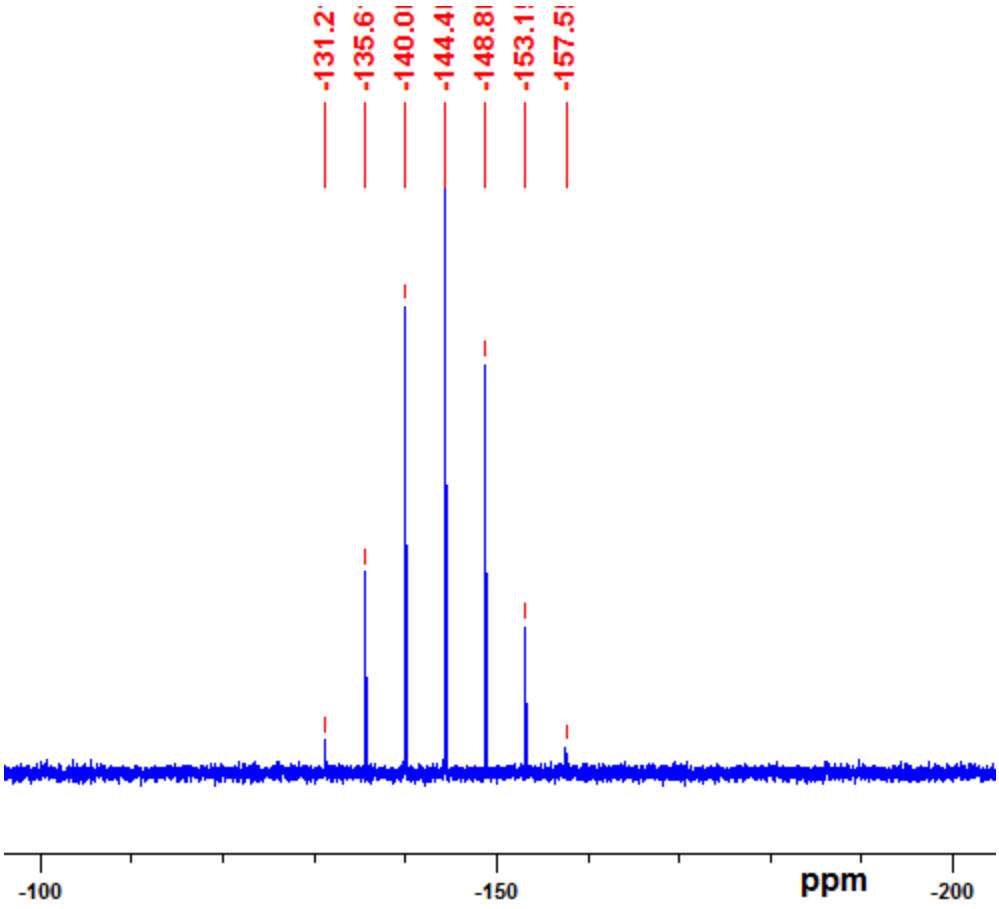


Fig. S41. ^{31}P NMR spectrum of **[(IPr=Se)$_2$Cu][PF$_6$]** (**11**) in $CDCl_3$ at room temperature.

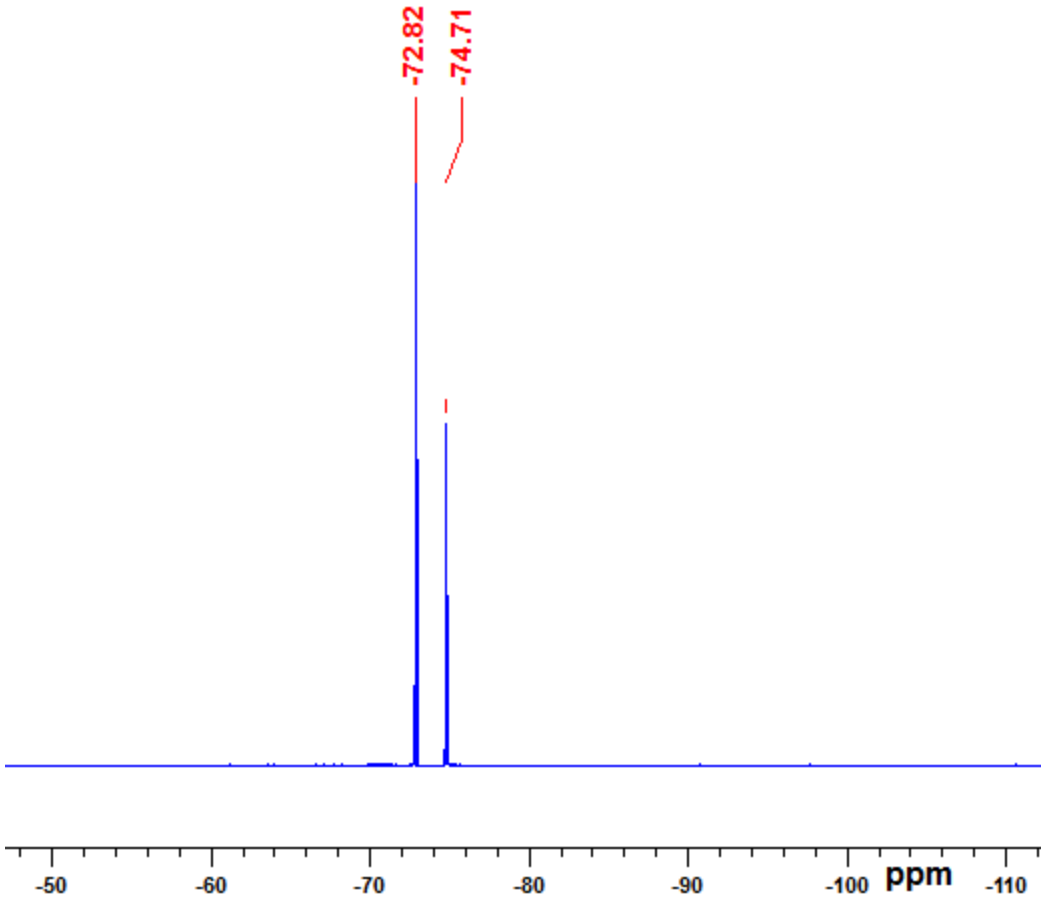


Fig. S42. ^{19}F NMR spectrum of **[(IPr=Se)$_2$Cu][PF$_6$]** (**11**) in $CDCl_3$ at room temperature.

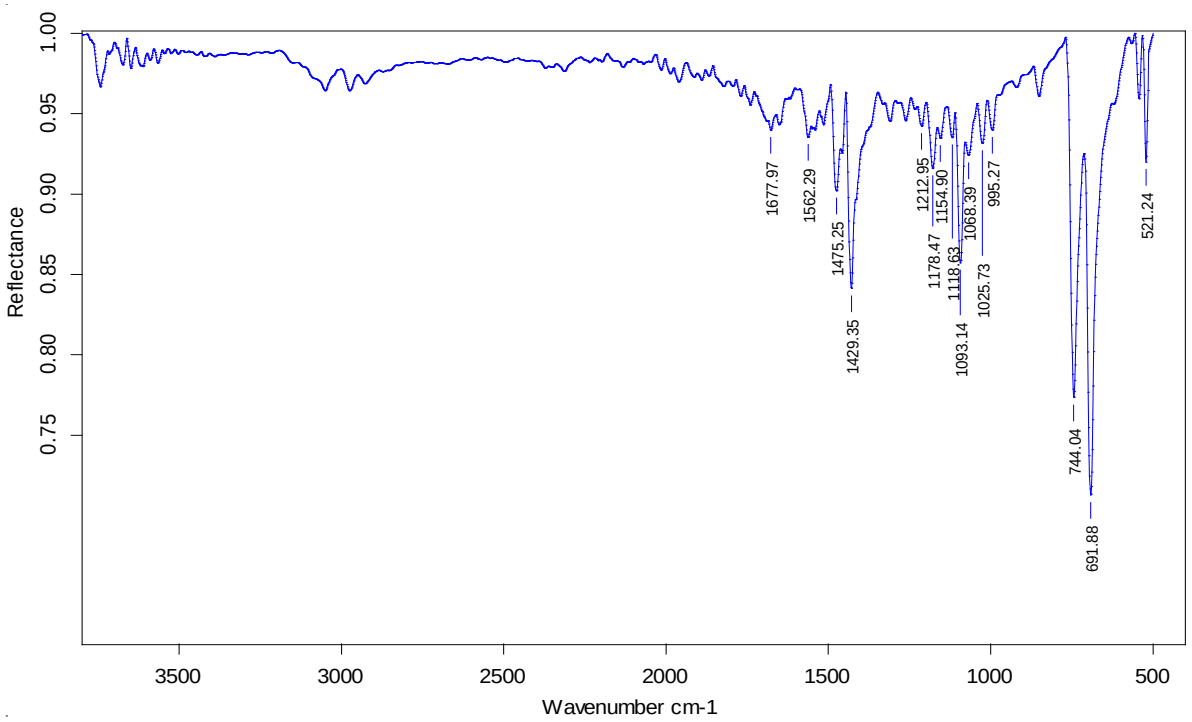


Fig. S43. Neat FT-IR spectrum of **[(PPh$_3$)$_4$Cu$_4$I$_4$]** (**12**) at room temperature.

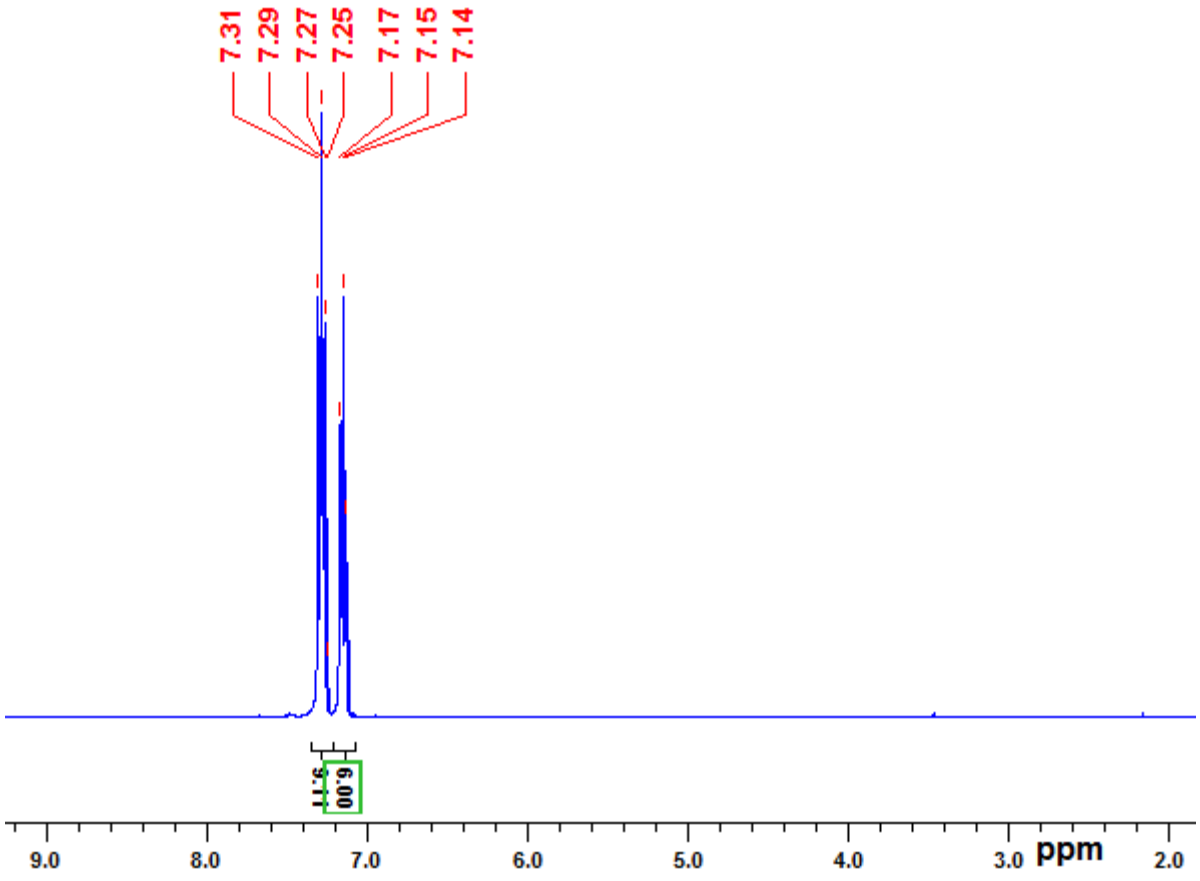


Fig. S44. ^{1}H NMR spectrum of **[(PPh$_3$)$_4$Cu$_4$I$_4$]** (**12**) in CDC_3 at room temperature.

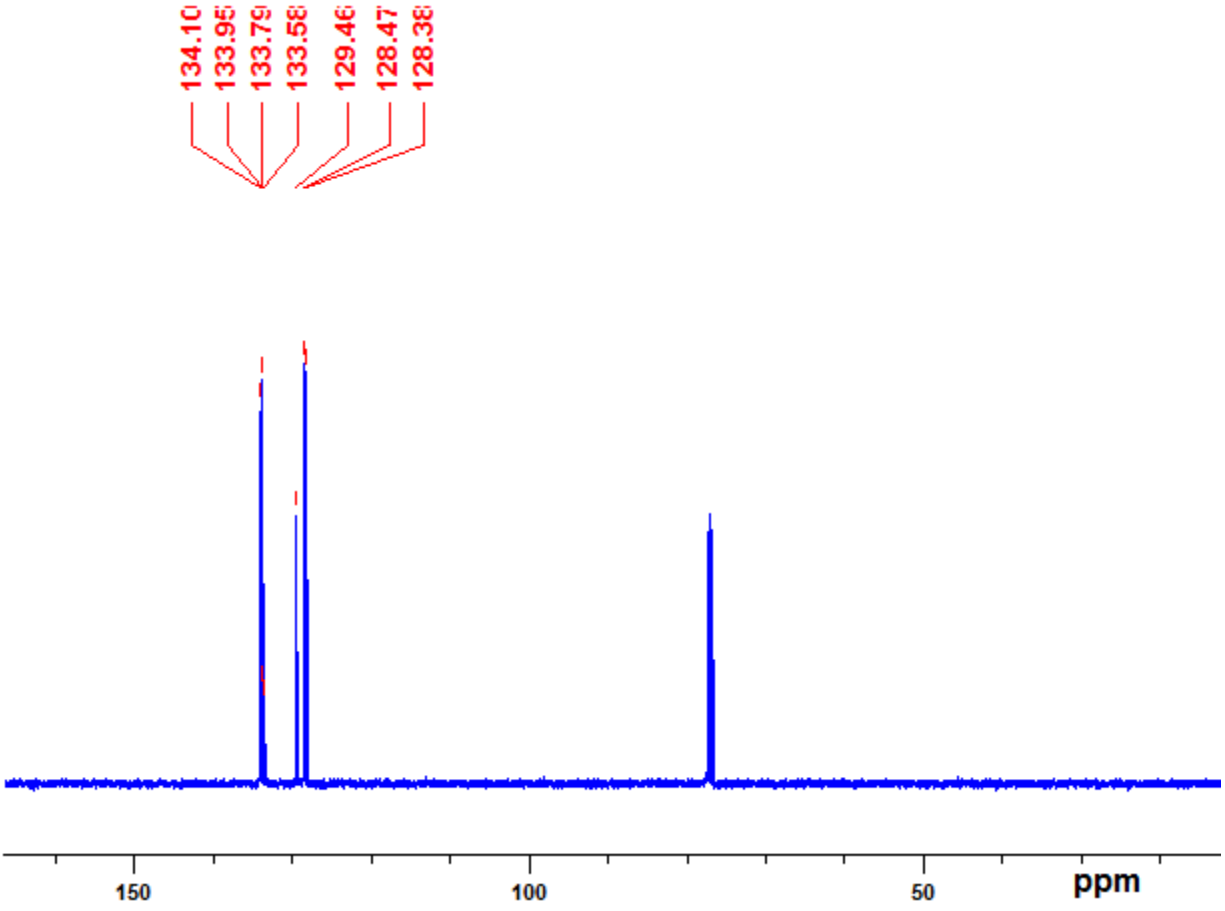


Fig. S45. ^{13}C NMR spectrum of **[(PPh$_3$)$_4$Cu$_4$I$_4$]** (**12**) in $CDCl_3$ at room temperature.

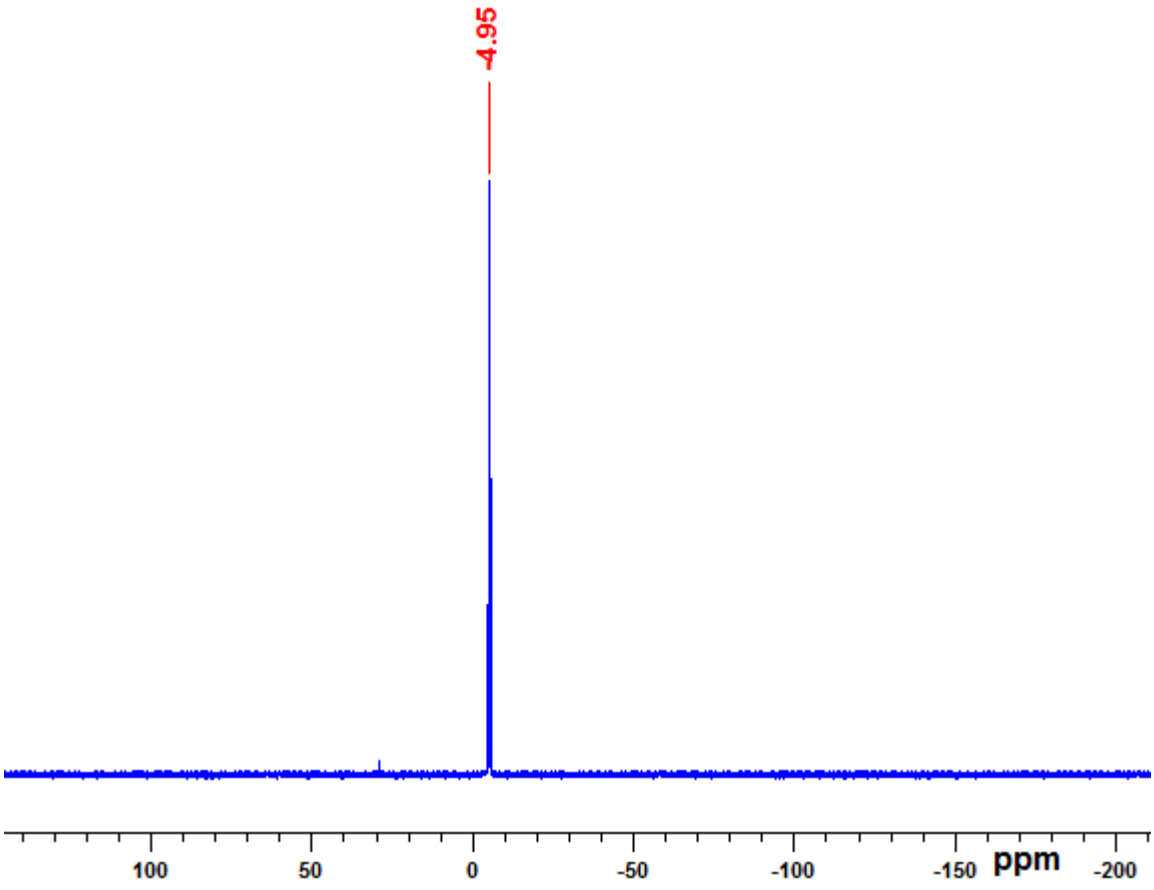


Fig. 46. ^{31}P NMR spectrum of **[(PPh$_3$)$_4$Cu$_4$I$_4$]** (**12**) in $CDCl_3$ at room temperature.

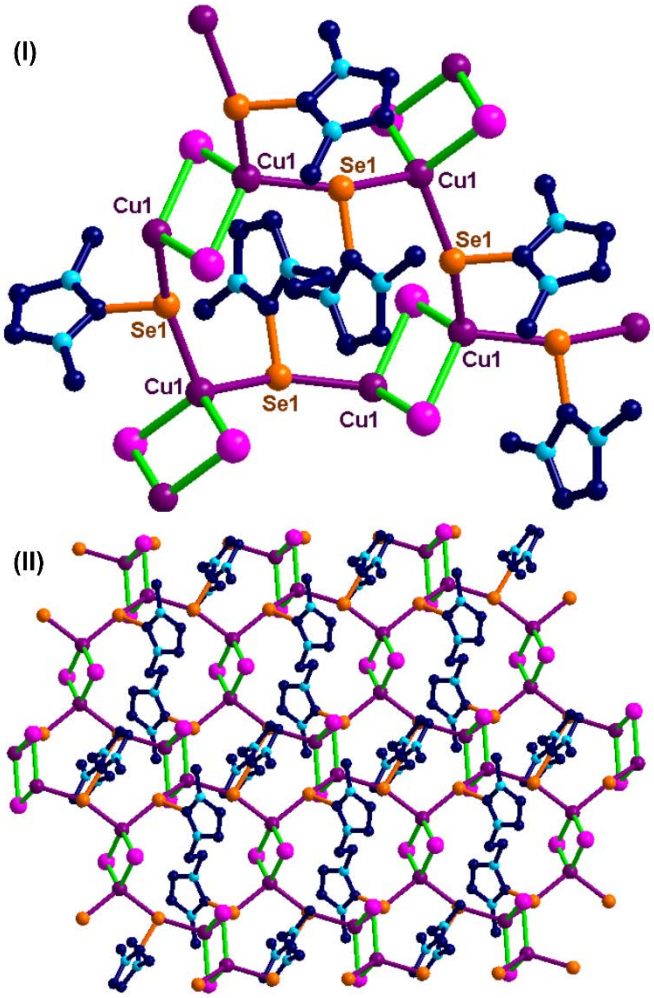


Fig. 47. Packing arrangement of molecule **13**.

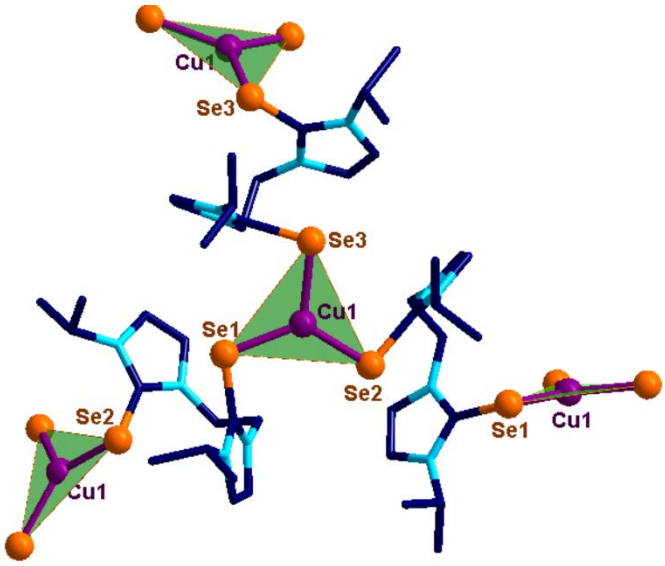


Fig. 48. Polyhedron view of molecule **14**.

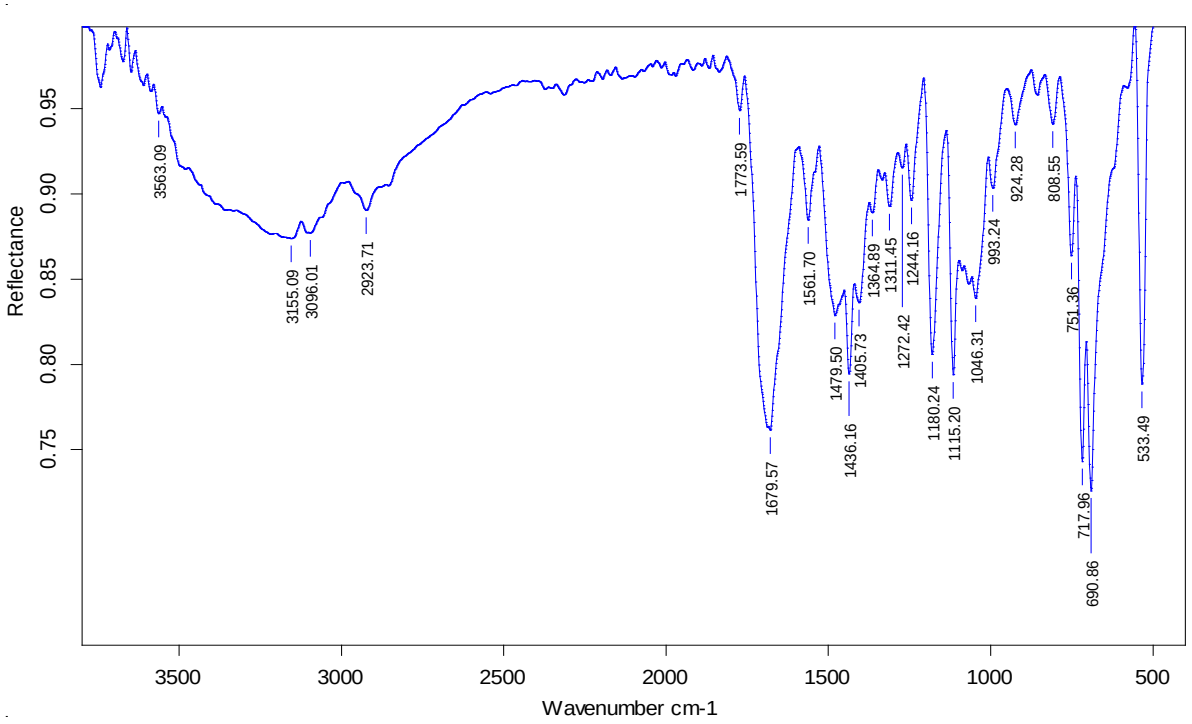


Fig. S49. Neat FT-IR spectrum of **[(Ebis)CuI]$_n$** (**13**) at room temperature.

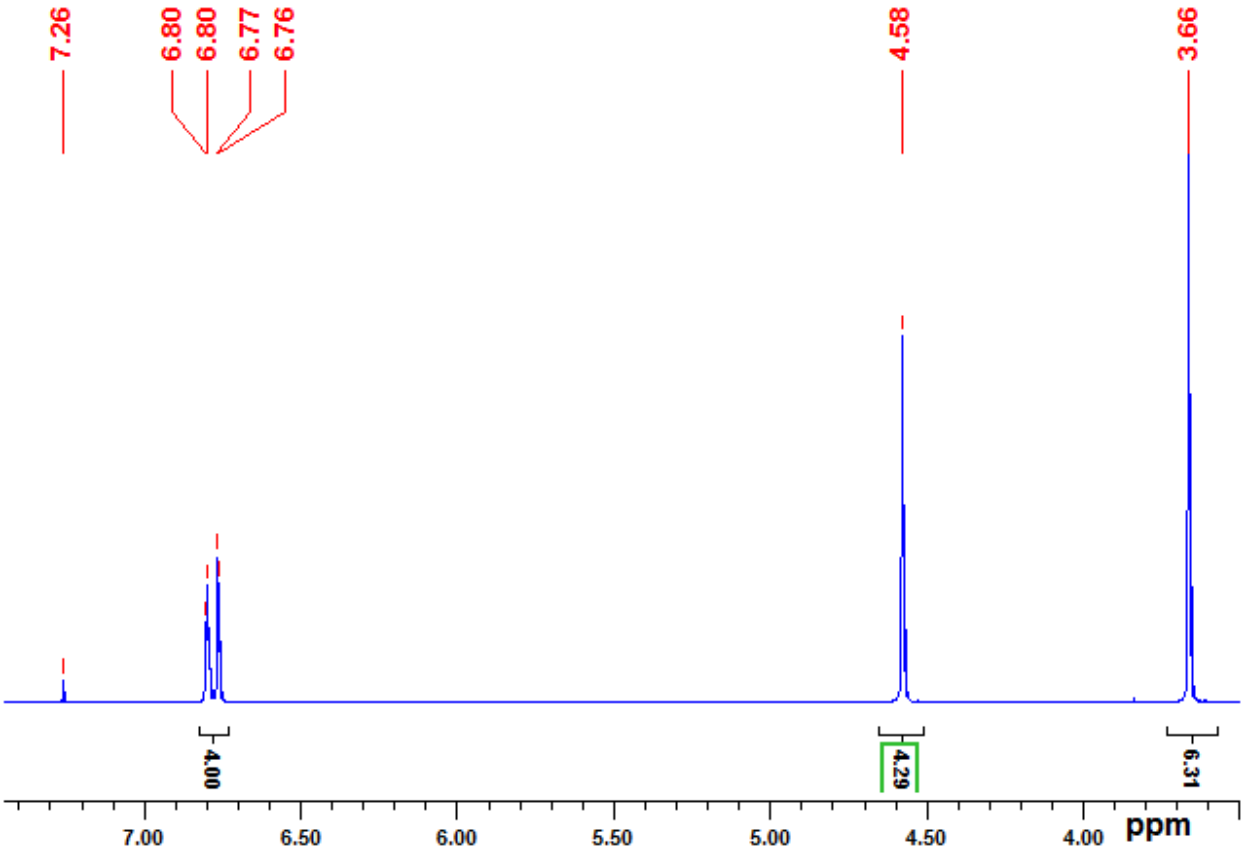


Fig. S50. ^{1}H NMR spectrum of **[(Ebis)CuI]$_n$** (**13**) in CDC_3 at room temperature.

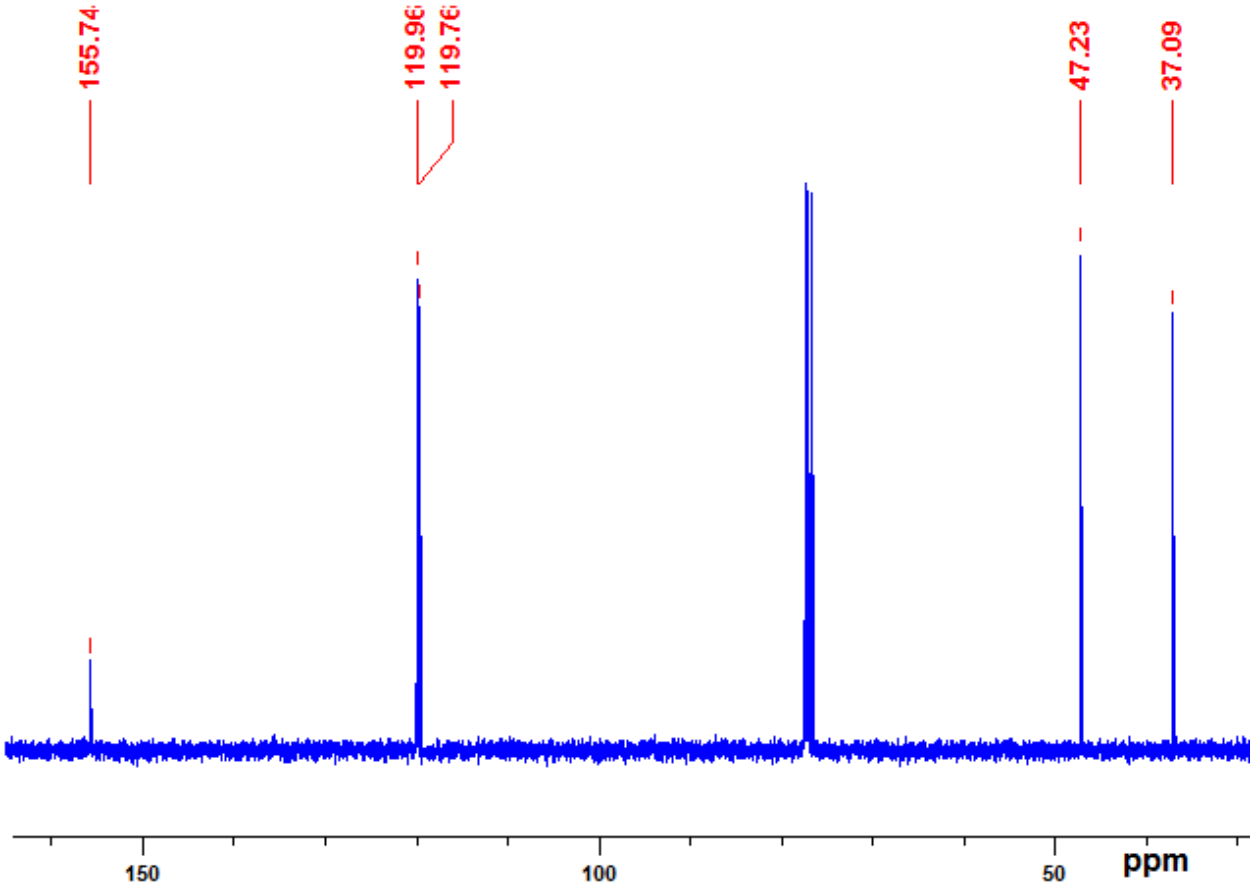


Fig. S51. ^{13}C NMR spectrum of **[(Ebis)CuI]$_n$** (**13**) in $CDCl_3$ at room temperature.

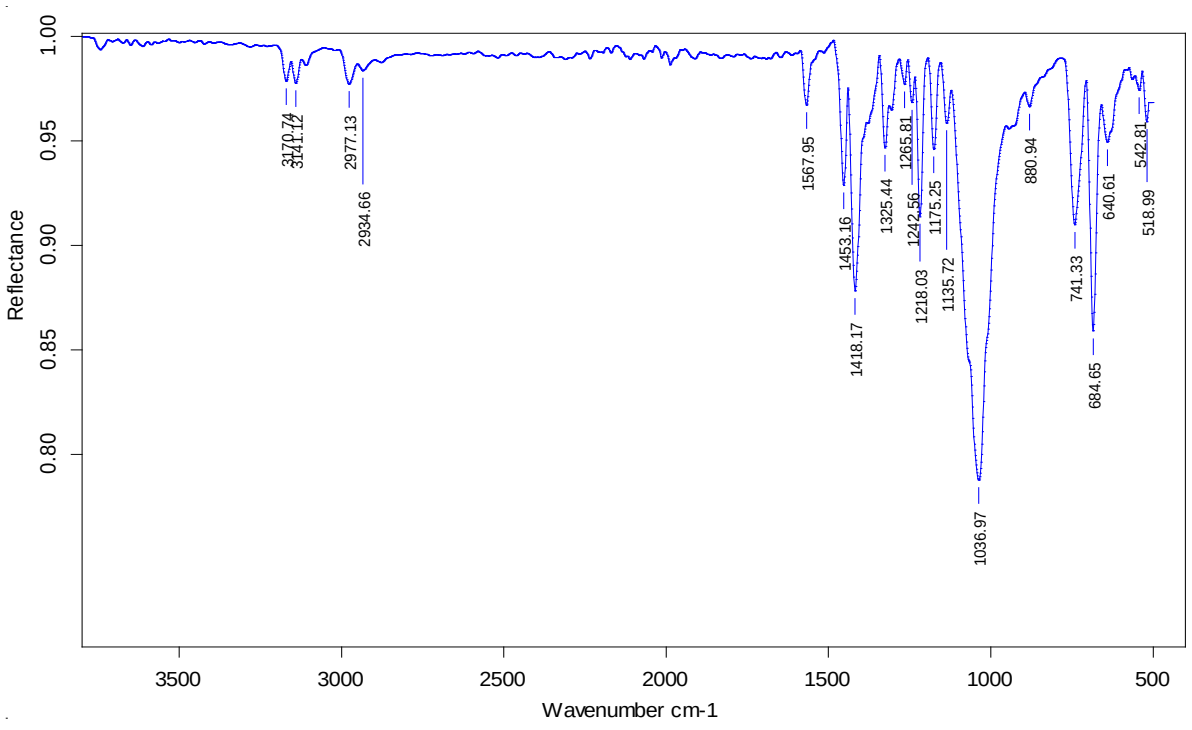


Fig. S52. Neat FT-IR spectrum of **{[(Ebpis)$_{1.5}$Cu][BF$_4$]}$_n$** (**14**) at room temperature.

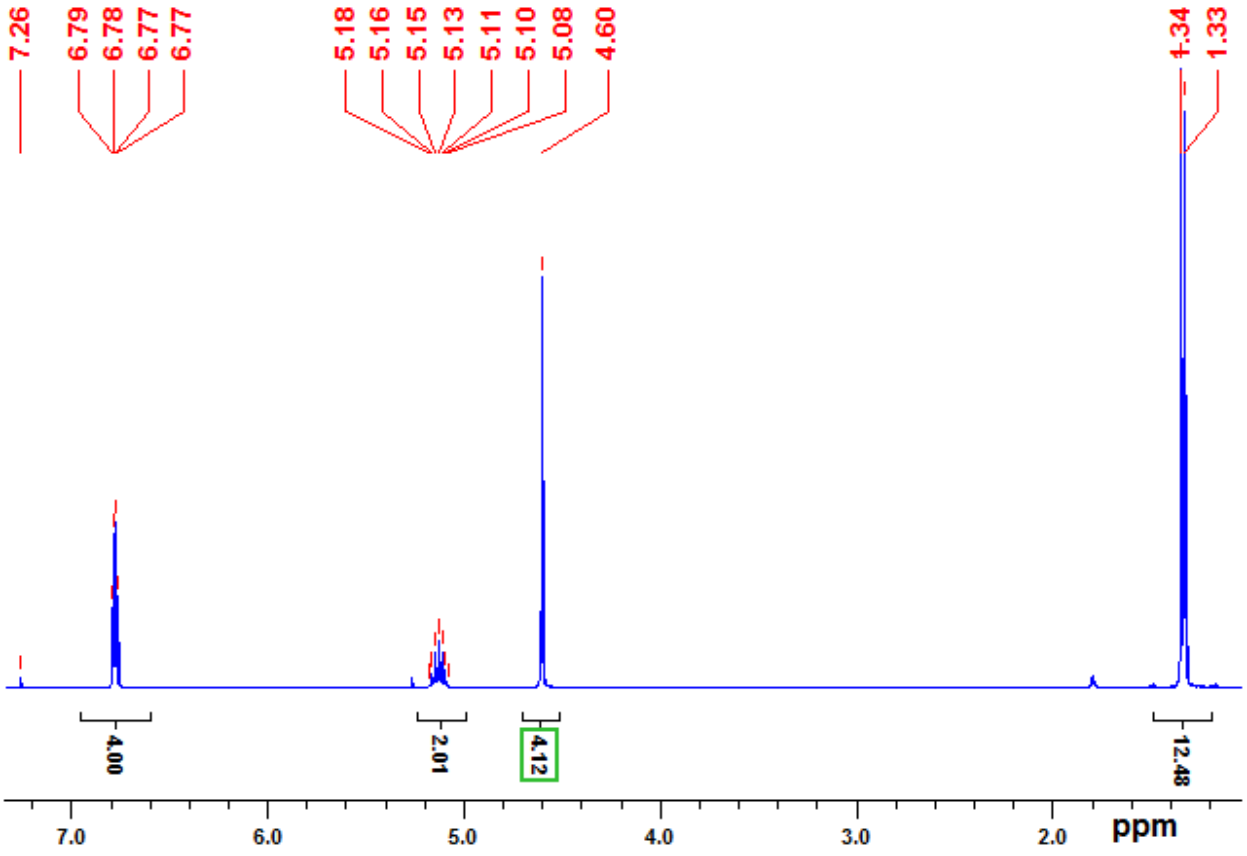


Fig. S53. ^{1}H NMR spectrum of **{[(Ebpis)$_{1.5}$Cu][BF$_4$]}$_n$** (**14**) in CDC_3 at room temperature.

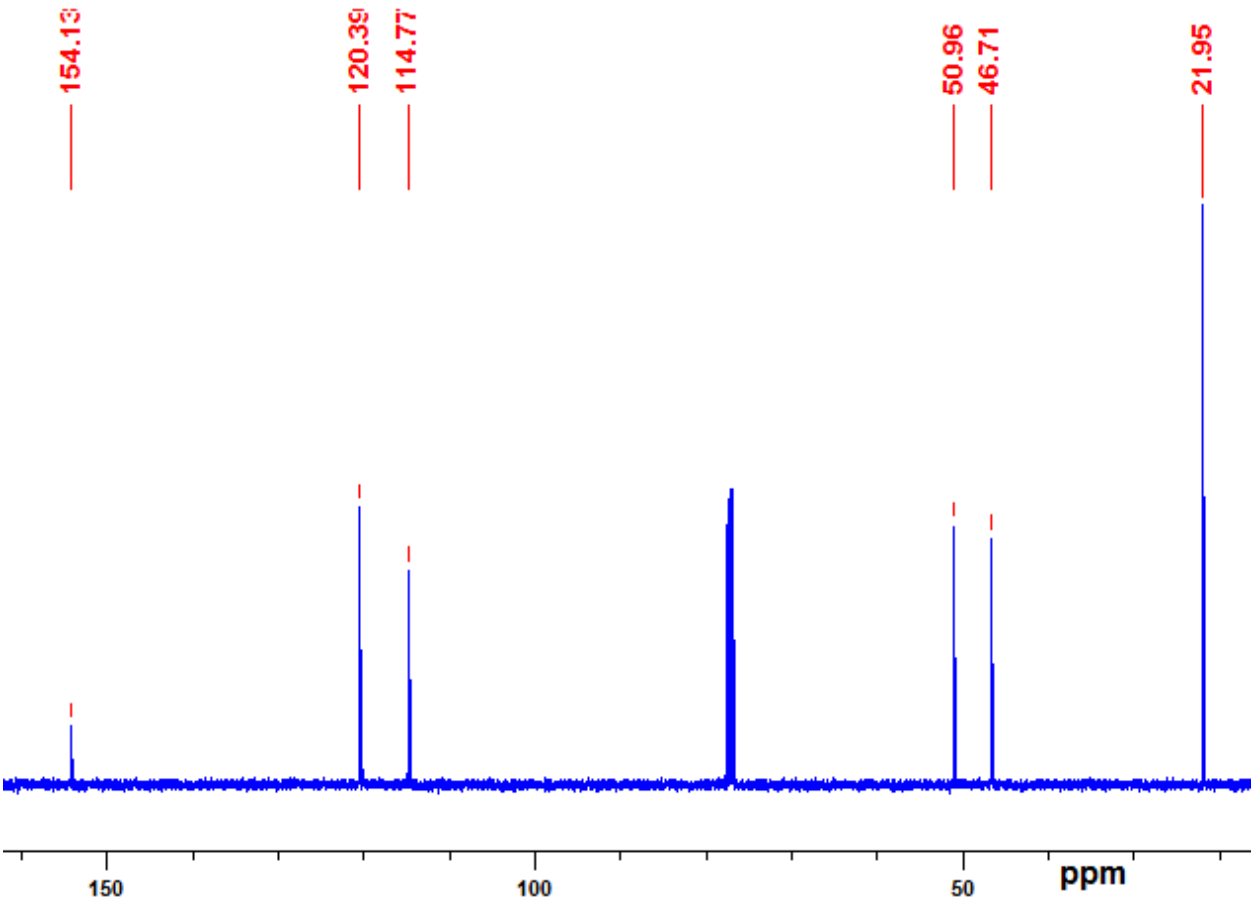


Fig. S54. ^{13}C NMR spectrum of **{[(Ebpis)$_{1.5}$Cu][BF$_4$]}$_n$** (**14**) in $CDCl_3$ at room temperature.

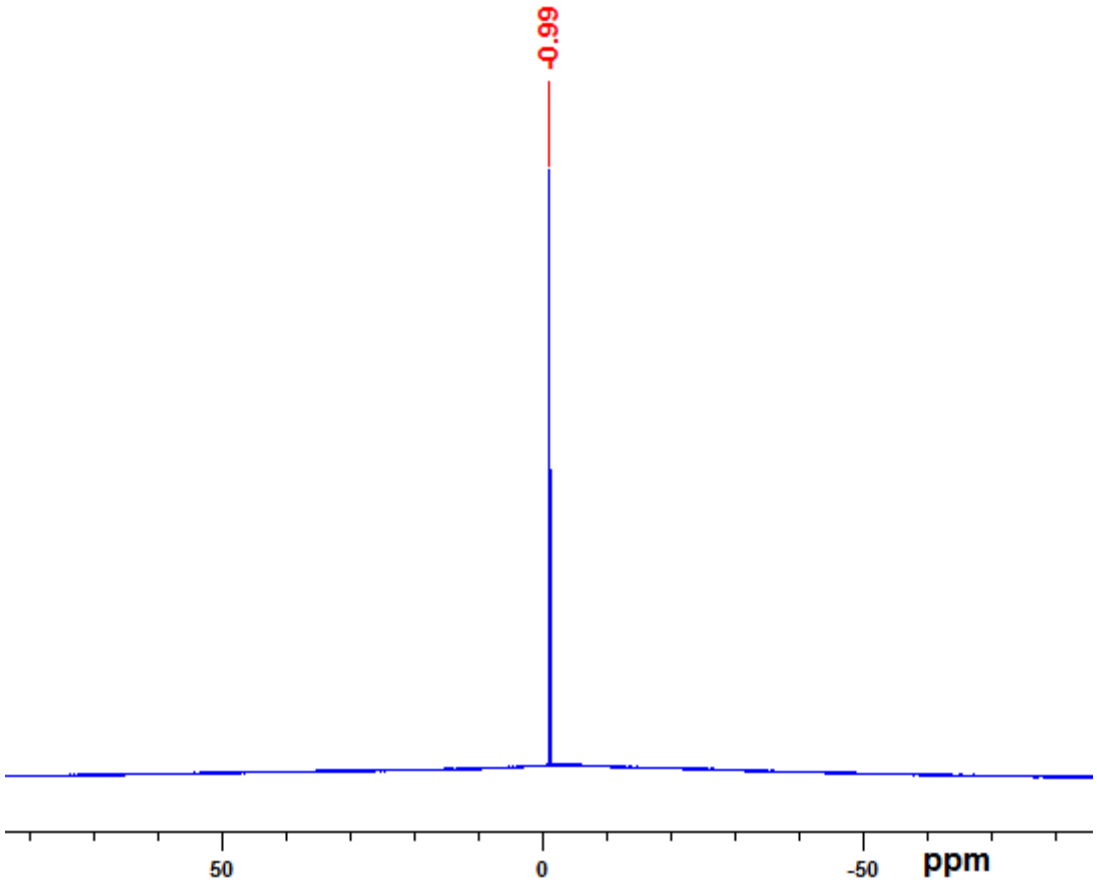


Fig. S55. ^{11}B NMR spectrum of **{[(Ebpis)$_{1.5}$Cu][BF$_4$]}$_n$** (**14**) in $CDCl_3$ at room temperature.

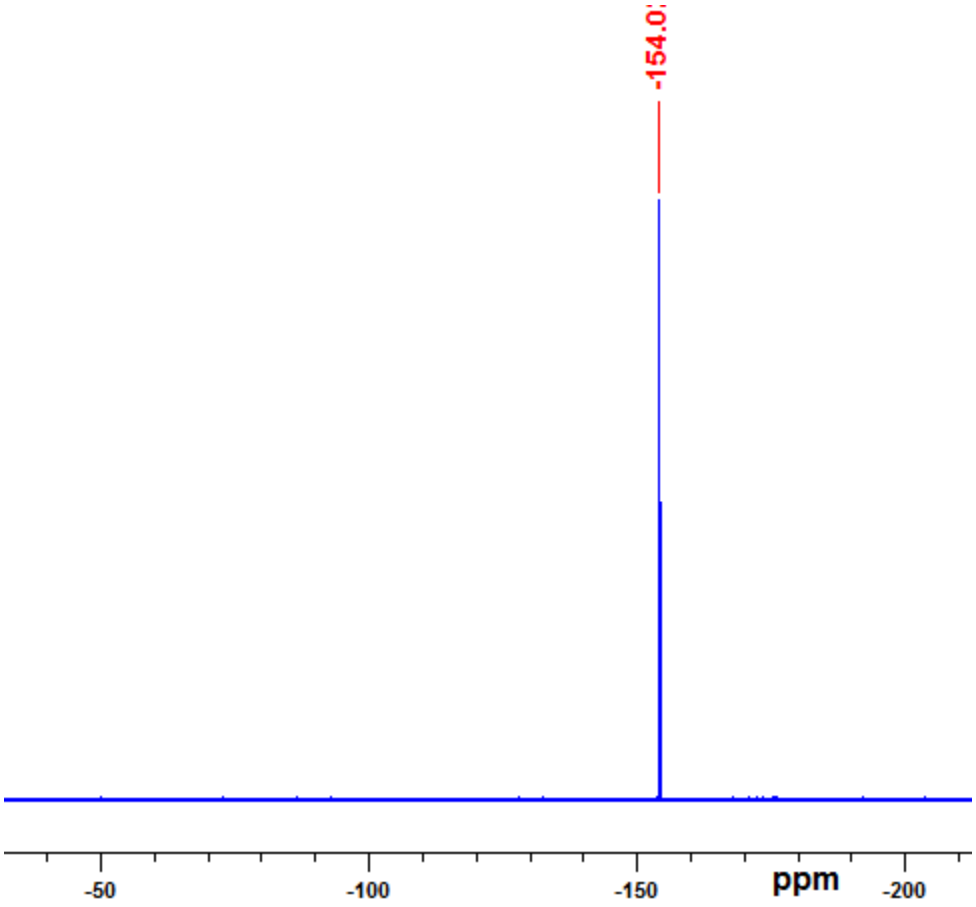


Fig. S56. ^{19}F NMR spectrum of **{[(Ebpis)$_{1.5}$Cu][BF$_4$]}$_n$** (**14**) in $CDCl_3$ at room temperature.

Table S1. Structural parameters of compounds **1-5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{21}H_{31}N_2SCuCl$	$C_{21}H_{24}N_2SCuBr$	$C_{21}H_{24}N_2SeCuBr$	$C_{21}H_{24}N_2SCuI$	$C_{21}H_{24}N_2SeCuI$
Formula weight	435.50	479.93	526.85	526.95	573.85
Temperature (K)	298	298	298	298	298
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	11.0627(5)	11.2039(4)	11.204(2)	11.5024(12)	11.5428(5)
b/Å	15.3677(6)	15.3755(6)	15.341(2)	15.4127(14)	15.3915(8)
c/Å	13.7074(6)	13.6204(6)	13.7742(11)	13.6155(16)	13.7448(7)
α/°	90	90	90	90	90
β/°	113.378(5)	112.795(5)	112.615(15)	112.632(13)	112.364(5)
γ/°	90	90	90	90	90
Volume ($Å^3$)	2139.06(18)	2163.07(14)	2185.3(6)	2227.9(5)	2258.3(2)
Z	4	4	4	4	4
ρ_{calc}/mg mm^{-3}	1.3522	1.474	1.6012	1.5709	1.6877
Absorption coefficient (μ/mm^{-1})	3.540	4.529	5.495	13.179	13.981
F(000)	900.7	976.0	1036.0	1042.9	1110.4
Reflections collected	5620	8986	5465	8950	9201
R_{int}	0.0214	0.0242	0.0206	0.0442	0.0314
GOF on F^2	1.062	1.054	1.017	1.063	1.021
R_1 ($I>2\sigma(I)$)	0.0506	0.0458	0.0556	0.0850	0.0490
wR_2 ($I>2\sigma(I)$)	0.1450	0.1207	0.2110	0.3193	0.1503
R_1 values (all data)	0.0656	0.0546	0.0674	0.1158	0.0623
R_2 values (all data)	0.1700	0.1309	0.2111	0.3194	0.1504

Table S2. Structural parameters of compounds **7**, **9** and **10**.

	7	**9**	**11**
Empirical formula	$C_{42}H_{48}N_4Cl_2Cu_2Se_2$	$C_{42}H_{48}N_4F_6PCuSe_2$	$C_{54}H_{72}N_4PCuSe_2F_6$
Formula weight	964.79	975.30	1143.63
Temperature (K)	298	298	298
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	C2/c
a/Å	8.3465(2)	8.4401(2)	19.5751(8)
b/Å	19.3330(5)	18.3180(4)	16.3426(4)
c/Å	13.4761(3)	14.4474(3)	20.4314(10)
α/°	90	90	90
β/°	96.742(2)	98.023(2)	113.637(5)
γ/°	90	90	90
Volume (Å^3)	2159.51(10)	2211.79(9)	5987.8(5)
Z	2	2	4
ρ_{calc}/mg mm^{-3}	1.4836	1.4644	1.2685
Absorption coefficient (μ/mm^{-1})	4.531	3.421	2.601
F(000)	968.2	984.1	2353.1
Reflections collected	8771	7598	10607
R_{int}	0.0497	0.0193	0.0223
GOF on F^2	1.046	1.040	1.045
R_1 ($I>2\sigma(I)$)	0.0463	0.0472	0.0542
wR_2 ($I>2\sigma(I)$)	0.1347	0.1319	0.1516
R_1 values (all data)	0.0545	0.0588	0.0665
R_2 values (all data)	0.1525	0.1522	0.1697

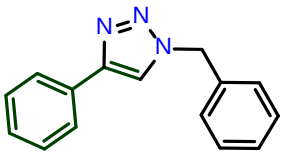
Table S3. Structural parameters of compounds **12-14**.

	12	**13**	**14**
Empirical formula	$C_{74}H_{63}NP_4Cu_4I_4$	$C_5H_7CuIN_2Se$	$C_{21}H_{33}N_6BF_4CuSe_3$
Formula weight	1887.03	364.53	756.78
Temperature (K)	298	298	298
Crystal system	Monoclinic	Monoclinic	Tetragonal
Space group	C2/c	$P2_1/c$	$P4_12_12$
a/Å	26.6333(12)	9.8486(4)	16.4174(2)
b/Å	16.1396(6)	10.7720(3)	16.4174(2)
c/Å	18.2784(8)	8.0970(3)	22.1831(4)
α/°	90	90	90
β/°	110.048(5)	103.735(4)	90
γ/°	90	90	90
Volume (Å^3)	7380.9(6)	834.44(5)	5979.02(16)
Z	4	4	8
ρ_{calc}/mg mm^{-3}	1.6980	2.9015	1.6813
Absorption coefficient (μ/mm^{-1})	15.579	10.604	5.613
F(000)	3650.2	667.7	2955.9
Reflections collected	13446	3108	12308
R_{int}	0.0691	0.0326	0.0230
GOF on F^2	1.027	1.007	1.047
R_1 ($I>2\sigma(I)$)	0.0790	0.0443	0.0395
wR_2 ($I>2\sigma(I)$)	0.2104	0.1237	0.1025
R_1 values (all data)	0.0917	0.0572	0.0478
R_2 values (all data)	0.2419	0.1395	0.1121

Supporting Information: Part 2

Cu(I)–catalyzed azide–alkyne cycloaddition reactions (CuAAC).

1. 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (Ia)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.79 (d, 2H), 7.66 (s, 1H), 7.27-7.39 (m, 8H), 5.53 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.74, 130.58, 129.16, 128.83, 128.78, 128.18, 128.07, 125.71, 119.62, 54.21 ppm.

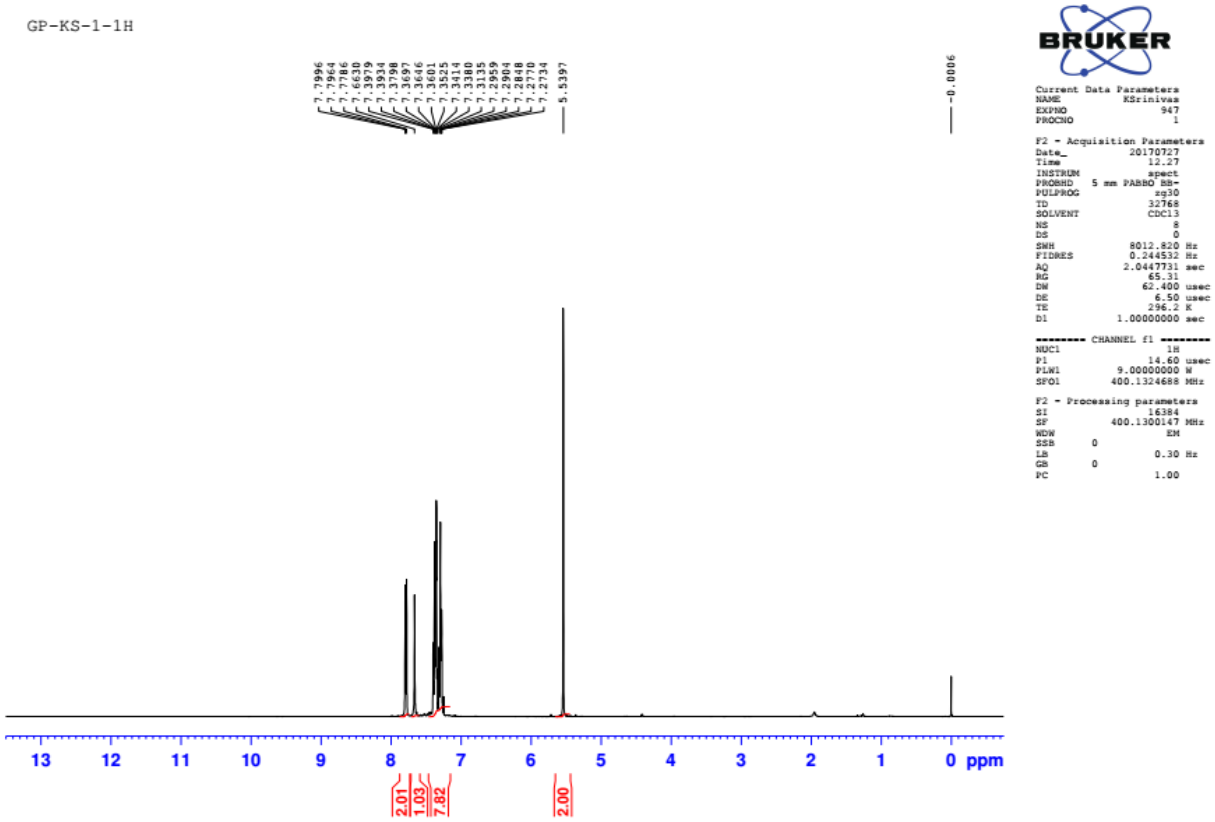


Fig. S57. ^{1}H NMR spectrum of **Ia** in $CDCl_3$ at room temperature.

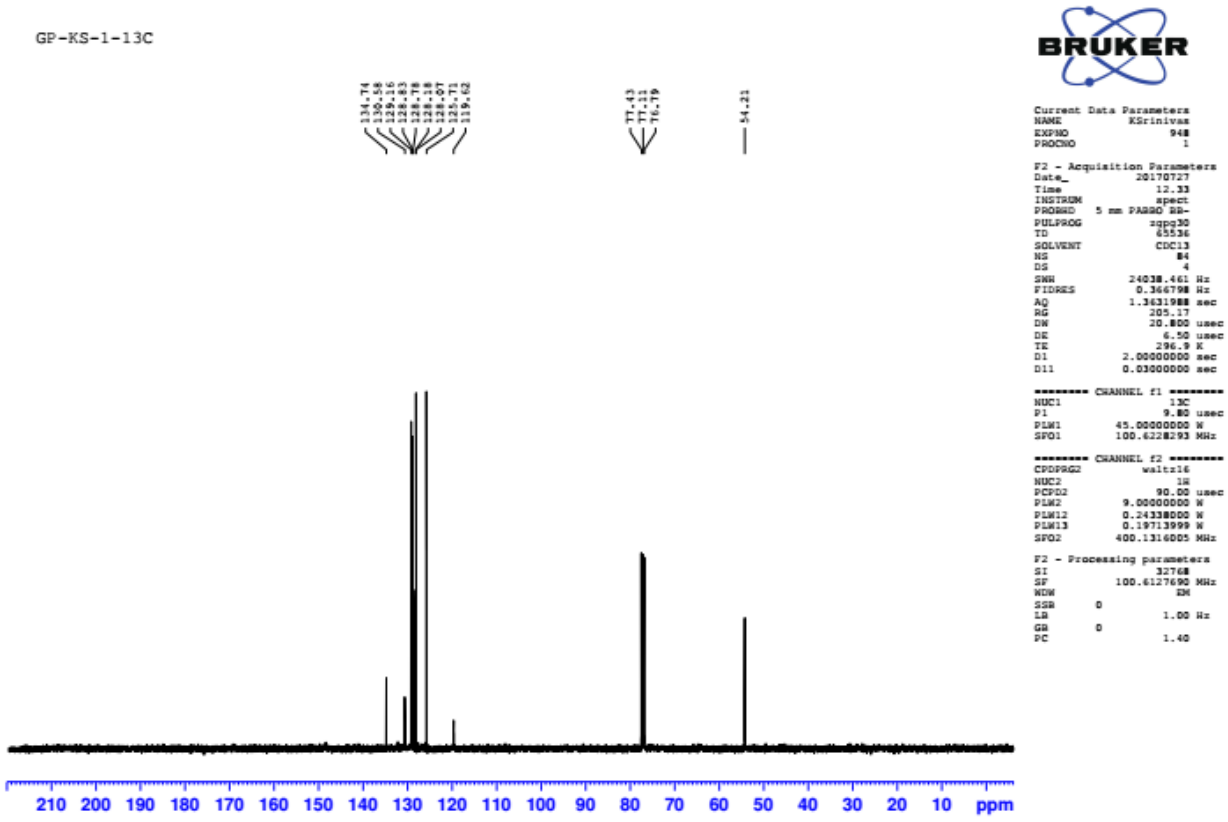
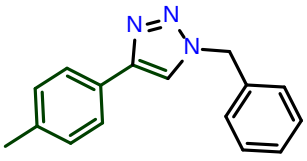


Fig. S58. ^{13}C NMR spectrum of **Ia** in $CDCl_3$ at room temperature.

2. 1-benzyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (Ib)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.68 (m, 3H), 7.17-7.36 (m, 7H), 5.52 (s, 2H), 2.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.01, 134.79, 129.50, 129.14, 128.74, 128.06, 127.76, 125.62, 119.28, 54.18, 21.29 ppm.

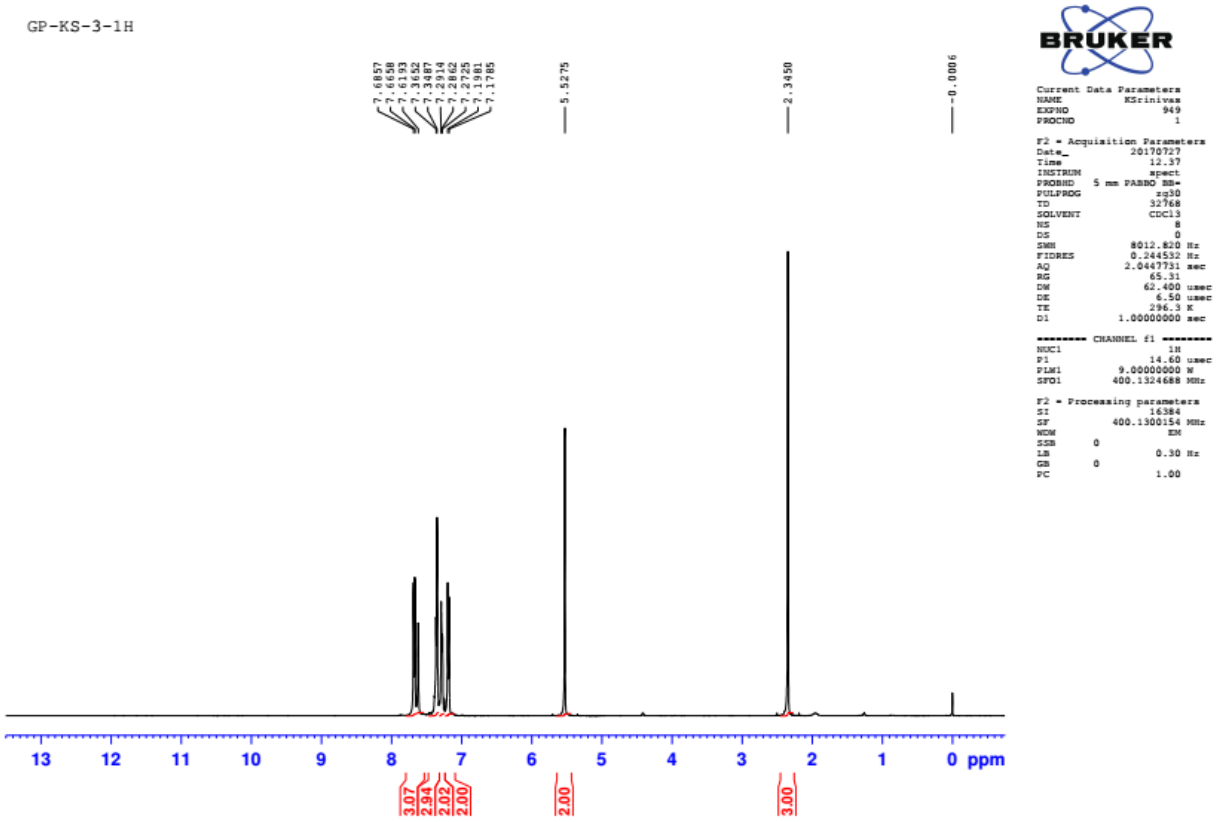


Fig. S59. ^{1}H NMR spectrum of **Ib** in $CDCl_3$ at room temperature.

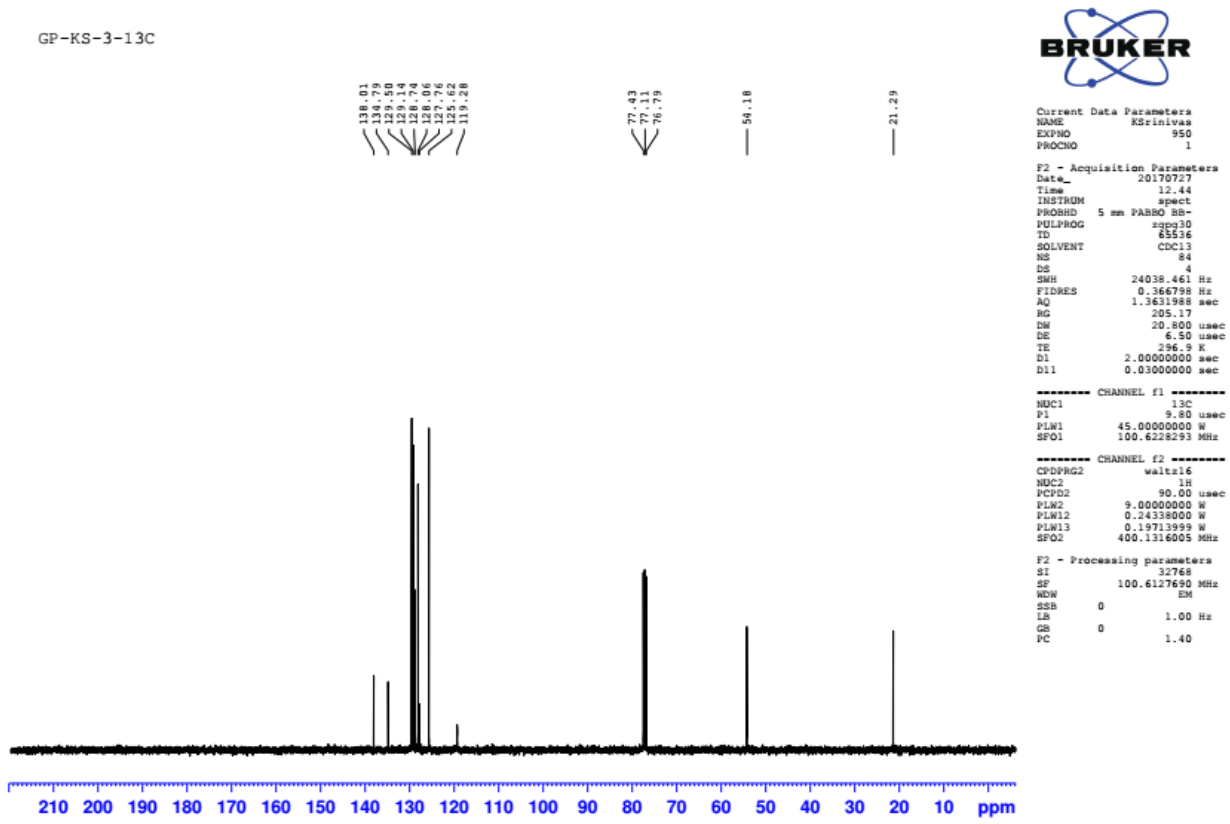
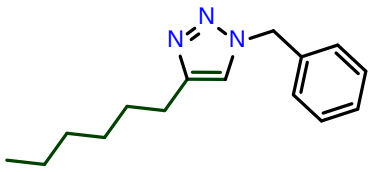


Fig. S60. ^{13}C NMR spectrum of **Ib** in $CDCl_3$ at room temperature.

3. 1–benzyl–4–hexyl–1H–1,2,3–triazole (Ic)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.36 (m, 3H), 7.23-7.25 (m, 2H), 7.19 (s, 1H), 5.48 (s, 2H), 2.65-2.69 (t, 2H), 1.59-1.66 (m, 2H), 1.27-1.34 (m, 6H), 0.84-0.87 (t, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.03, 129.03, 128.58, 127.94, 120.59, 53.97, 31.54, 29.36, 28.91, 25.75, 22.53, 14.04 ppm.

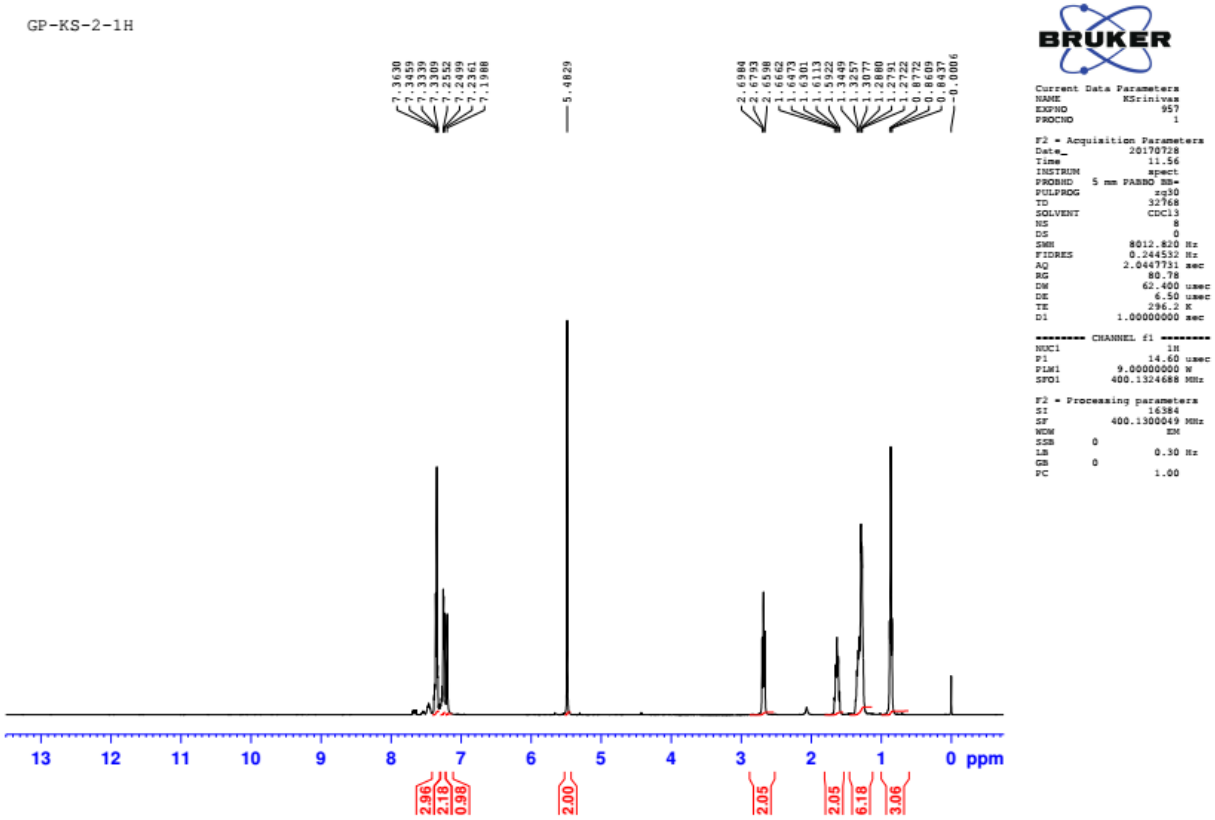


Fig. S61. ^{1}H NMR spectrum of **Ic** in $CDCl_3$ at room temperature.

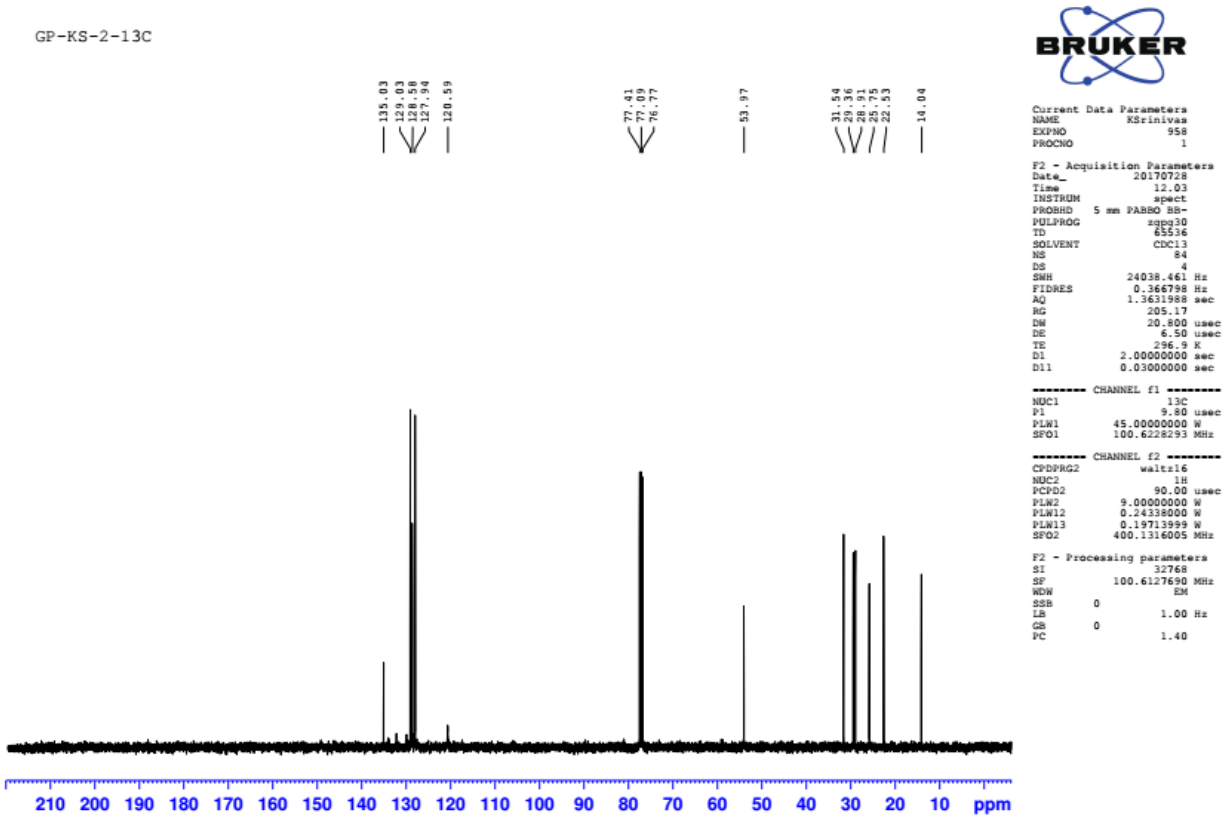
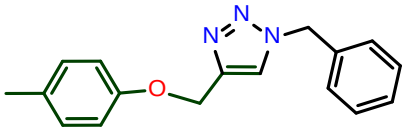


Fig. S62. ^{13}C NMR spectrum of **Ic** in $CDCl_3$ at room temperature.

4. 1-benzyl-4-((*p*-tolyloxy)methyl)-1*H*-1,2,3-triazole (Id)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.34-7.37 (m, 3H), 7.24-7.27 (t, 2H), 7.05-7.07 (d, 2H), 6.84-6.86 (d, 2H), 5.50 (s, 2H), 5.14 (s, 2H), 2.27 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.12, 134.52, 130.53, 129.97, 129.15, 128.80, 128.13, 122.58, 114.66, 62.26, 54.24, 20.48 ppm..

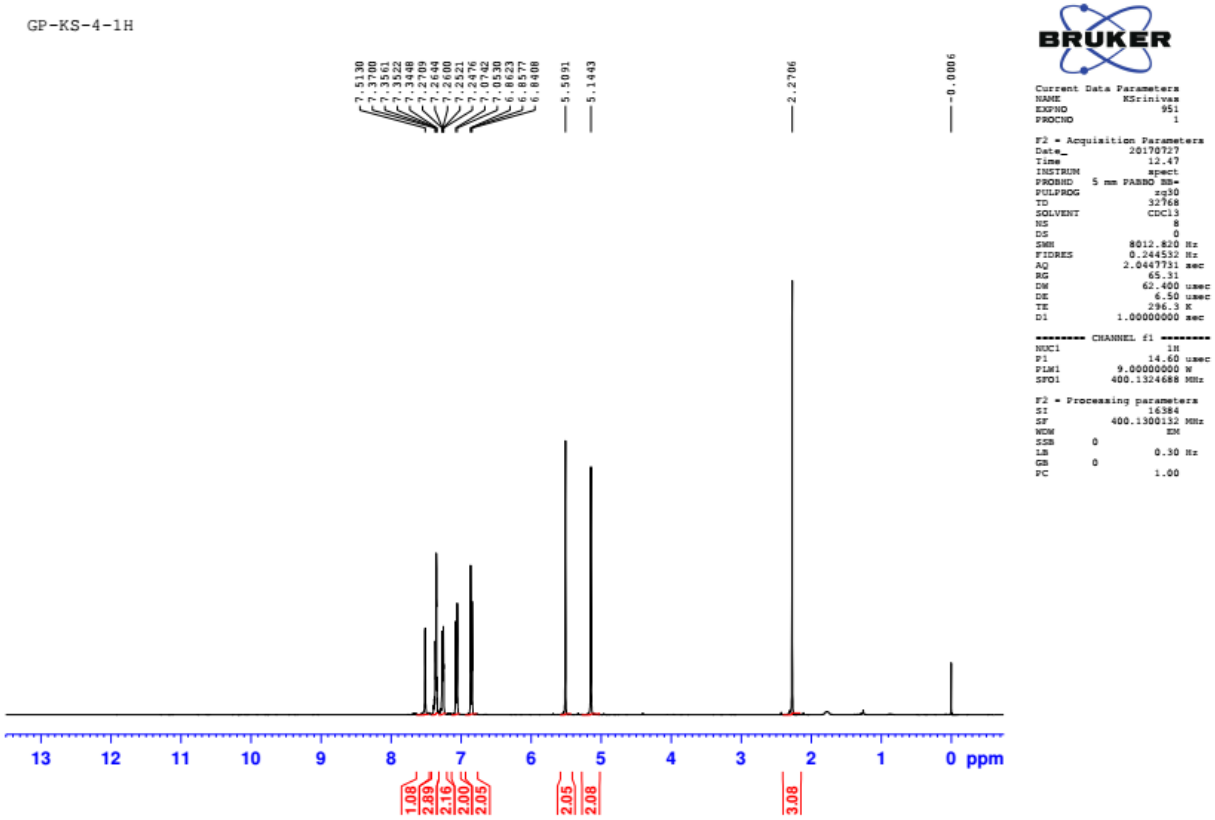


Fig. S63. ^{1}H NMR spectrum of **Id** in $CDCl_3$ at room temperature.

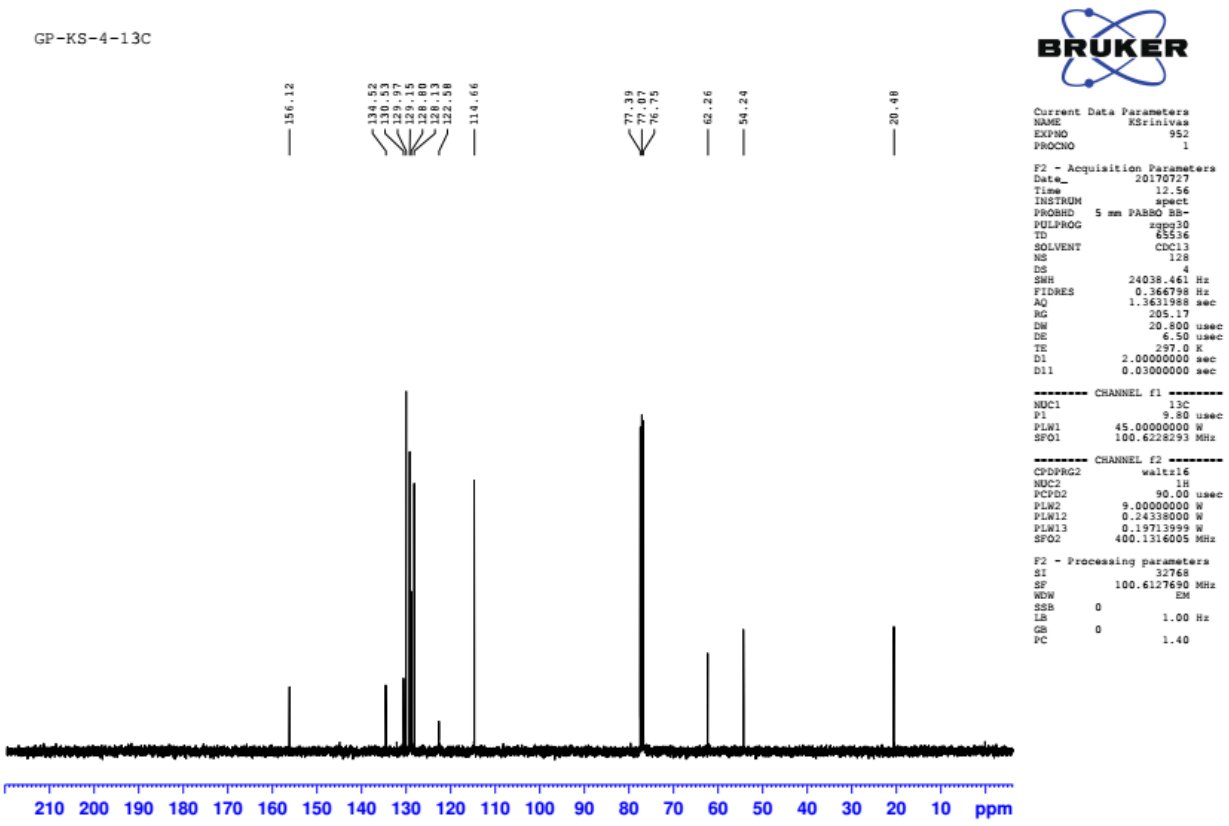
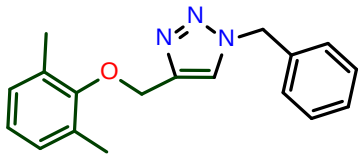


Fig. S64. ^{13}C NMR spectrum of **Id** in $CDCl_3$ at room temperature.

5. 1-benzyl-4-((2,6-dimethylphenoxy)methyl)-1*H*-1,2,3-triazole (Ie)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.68 (m, 6H), 6.91-7.00 (m, 3H), 5.54 (s, 2H), 4.94 (s, 2H), 2.25 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.30, 145.11, 134.59, 132.15, 132.05, 131.98, 131.05, 129.15, 128.89, 128.80, 128.59, 128.47, 128.11, 124.24, 122.54, 65.63, 54.23, 16.36 ppm.

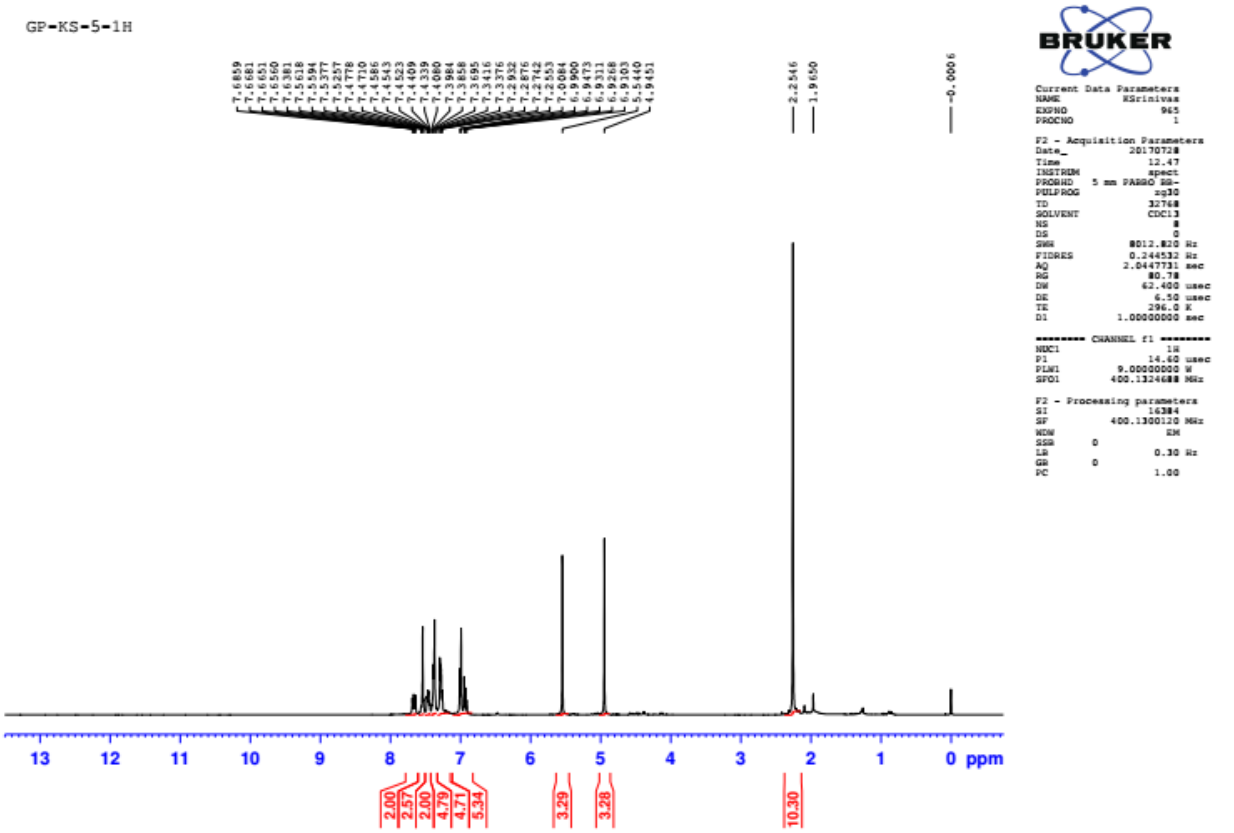


Fig. S65. ^{1}H NMR spectrum of **Ie** in $CDCl_3$ at room temperature.

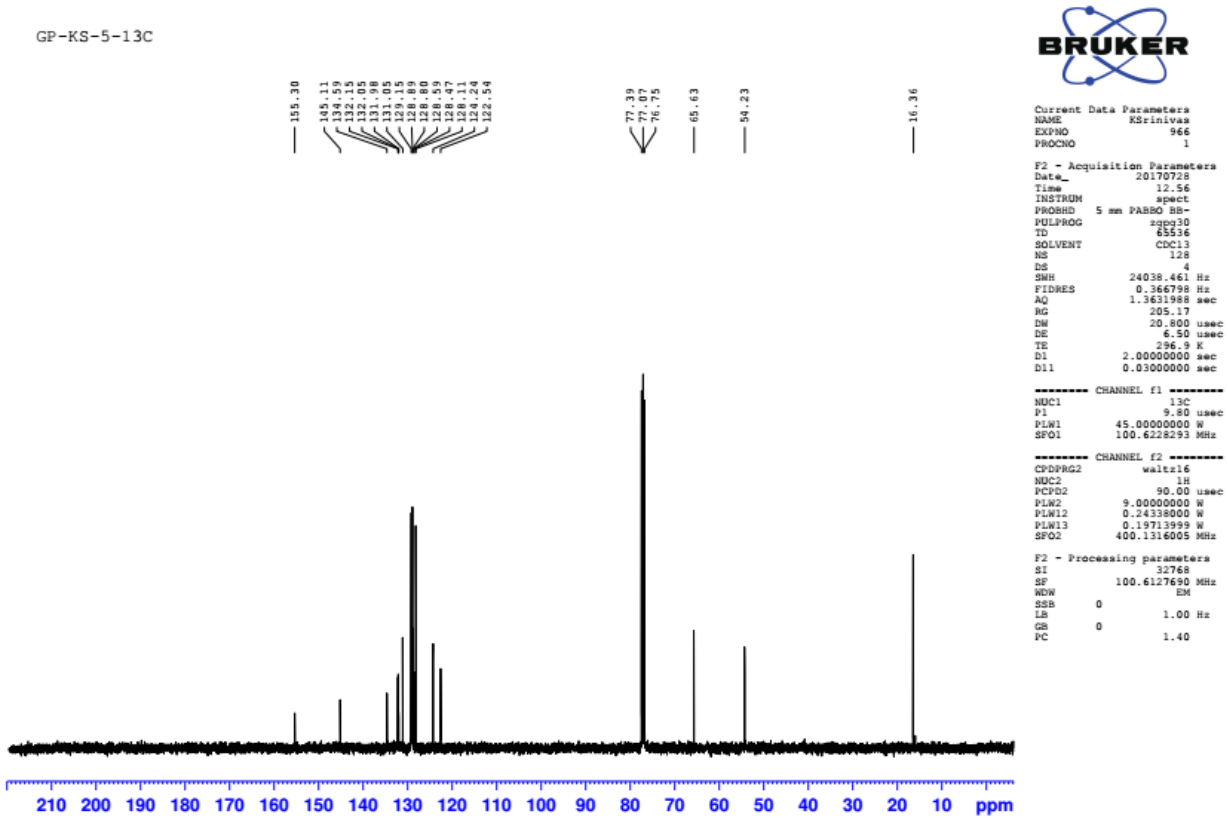
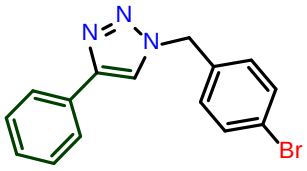


Fig. S66. ^{13}C NMR spectrum of **Ie** in $CDCl_3$ at room temperature.

6. 1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (IIa)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.79 (m, 10H), 5.49 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.38, 133.75, 132.32, 130.38, 129.66, 128.86, 128.30, 125.72, 122.93, 119.54, 53.50 ppm.

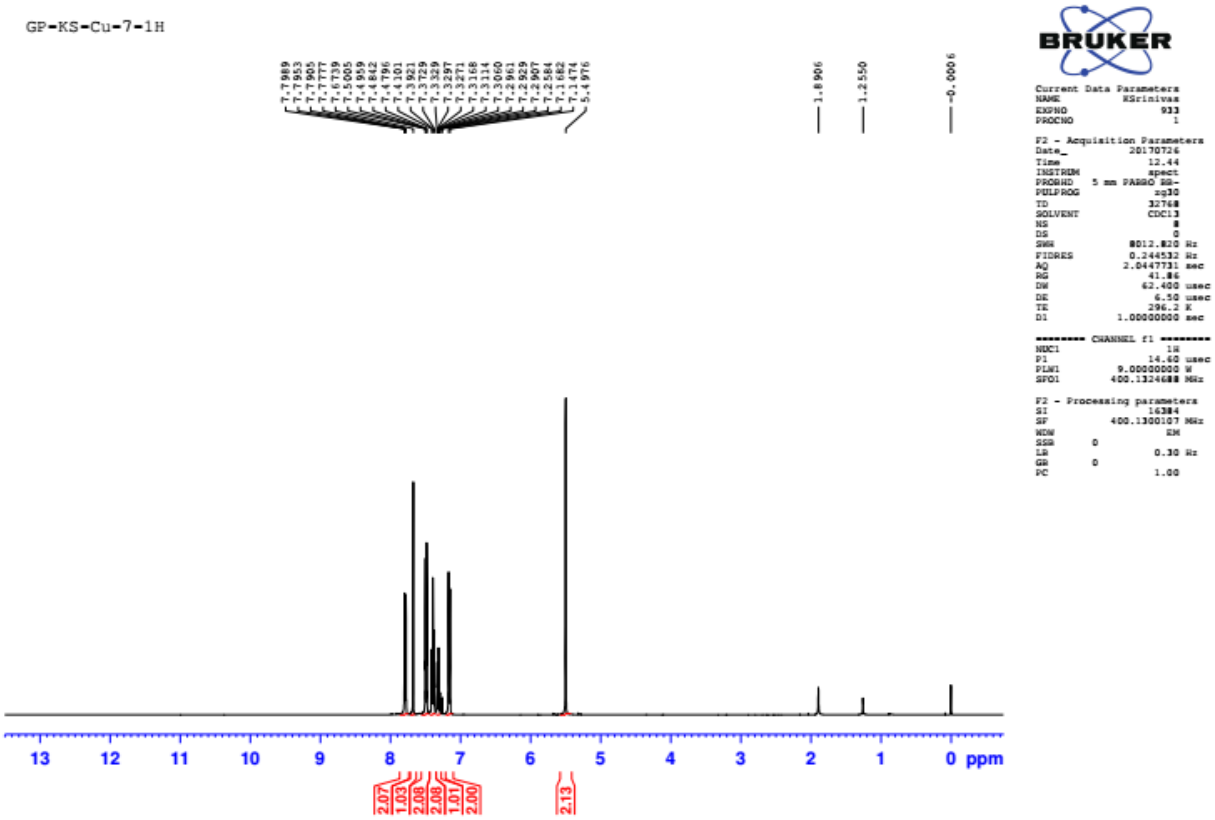


Fig. S67. ^{1}H NMR spectrum of **IIa** in $CDCl_3$ at room temperature.

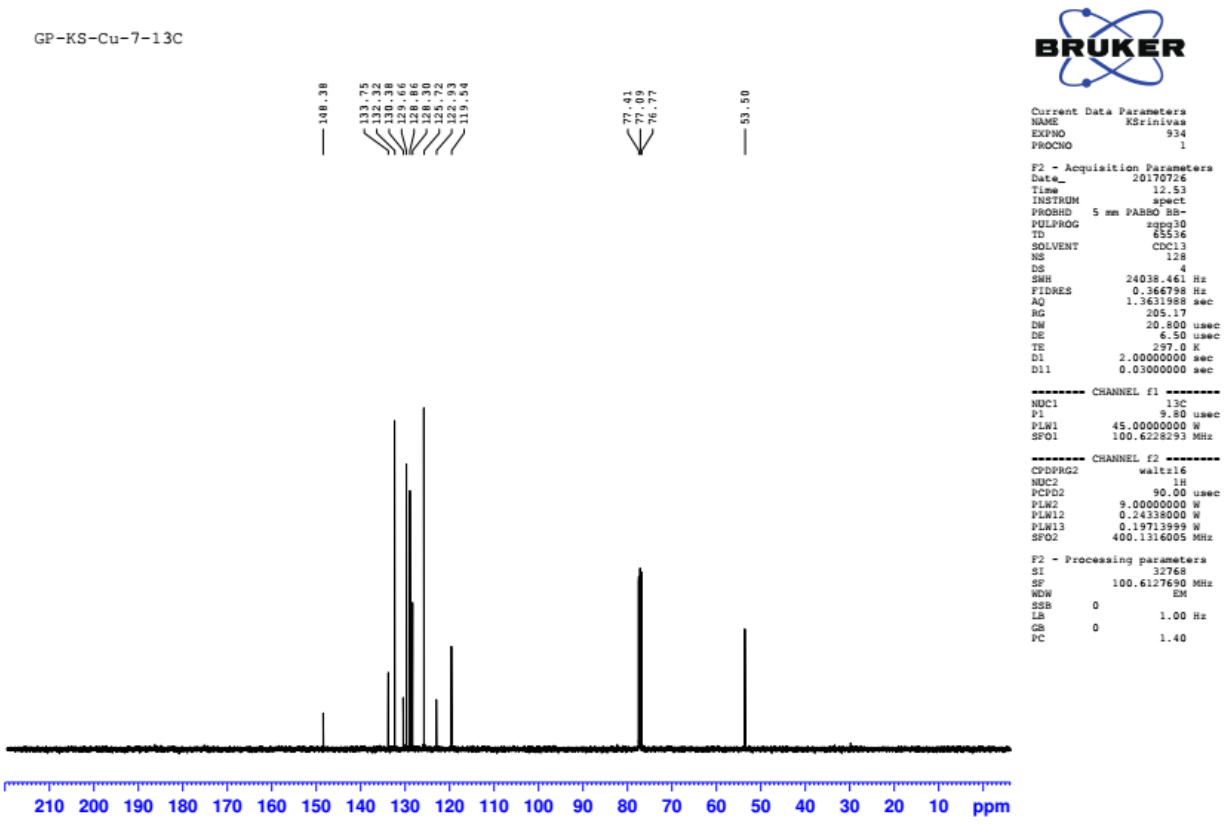
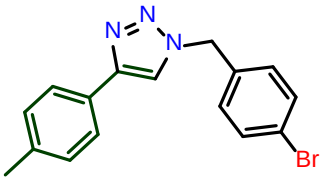


Fig. S68. ^{13}C NMR spectrum of **IIa** in $CDCl_3$ at room temperature.

7. 1-(4-nitrobenzyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (IIb)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.68 (m, 3H), 7.47-7.51 (m, 2H), 7.15-7.21 (m, 4H), 5.49 (s, 2H), 2.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.48, 138.16, 133.80, 132.30, 129.65, 128.53, 127.55, 125.62, 122.90, 119.14, 53.48, 21.30 ppm.

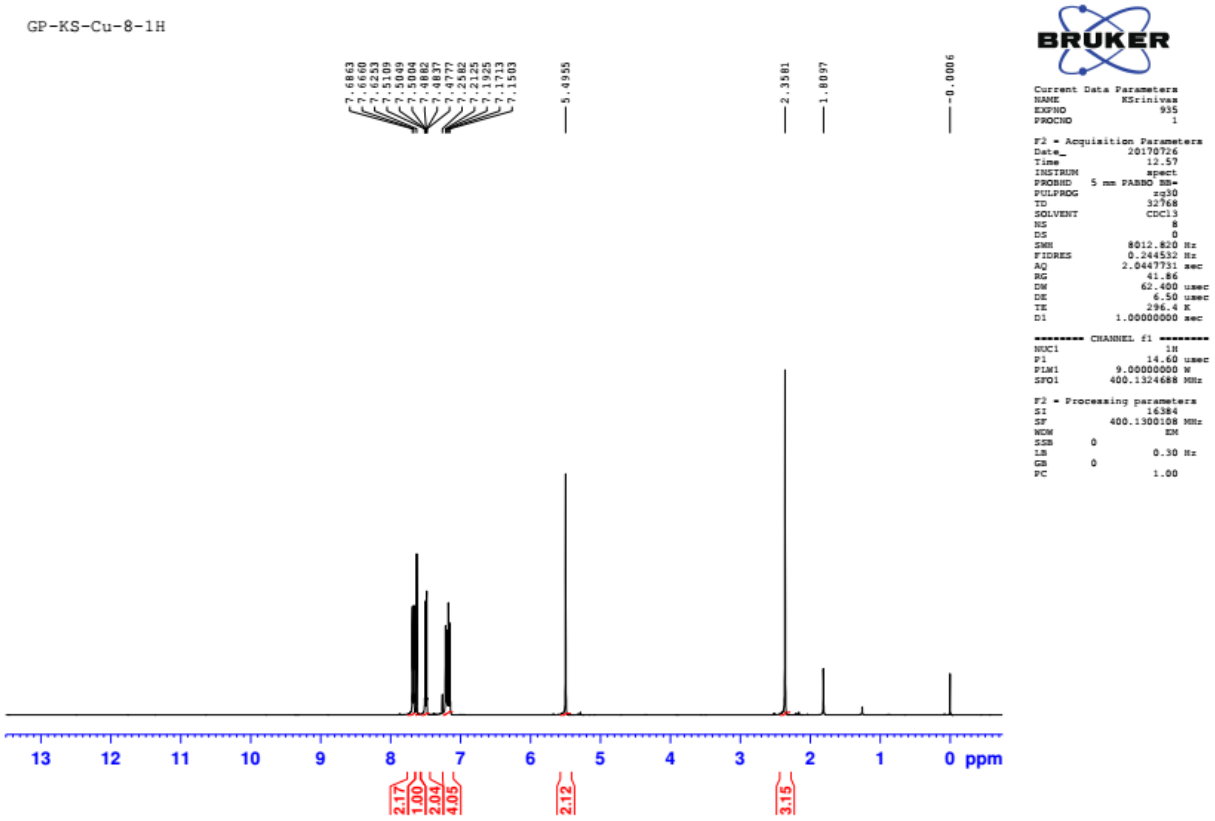


Fig. S69. ^{1}H NMR spectrum of **IIb** in $CDCl_3$ at room temperature.

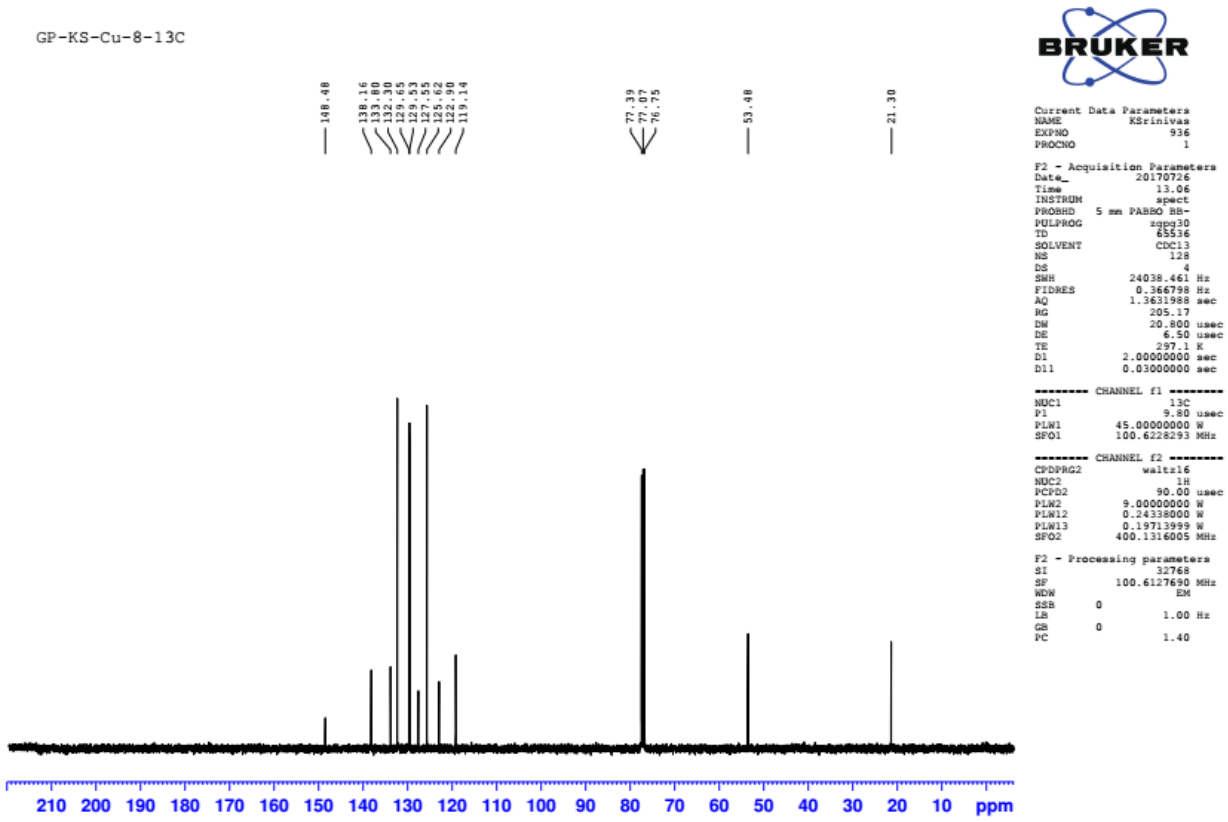
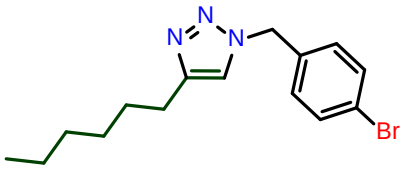


Fig. S70. ^{13}C NMR spectrum of **IIb** in $CDCl_3$ at room temperature.

8. 4-hexyl-1-(4-nitrobenzyl)-1H-1,2,3-triazole (IIc)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.49 (m, 2H), 7.11-7.19 (m, 3H), 5.44 (s, 2H), 2.66-2.70 (t, 2H), 1.59-1.64 (m, 2H), 1.25-1.34 (m, 6H), 0.84-0.88 (t, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.25, 134.04, 132.21, 129.55, 128.57, 128.45, 122.74, 120.49, 53.28, 31.52, 29.34, 28.90, 25.71, 22.53, 14.04 ppm.

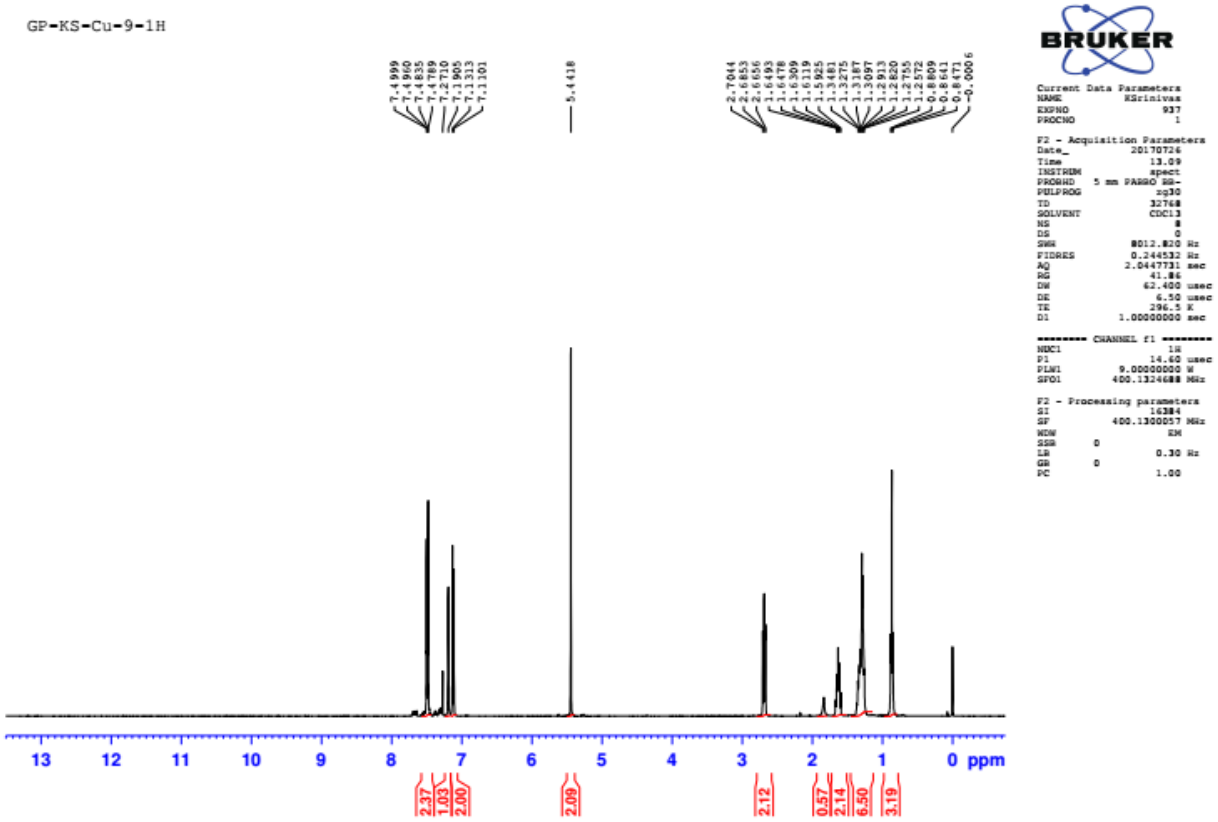


Fig. S71. ^{1}H NMR spectrum of **IIc** in $CDCl_3$ at room temperature.

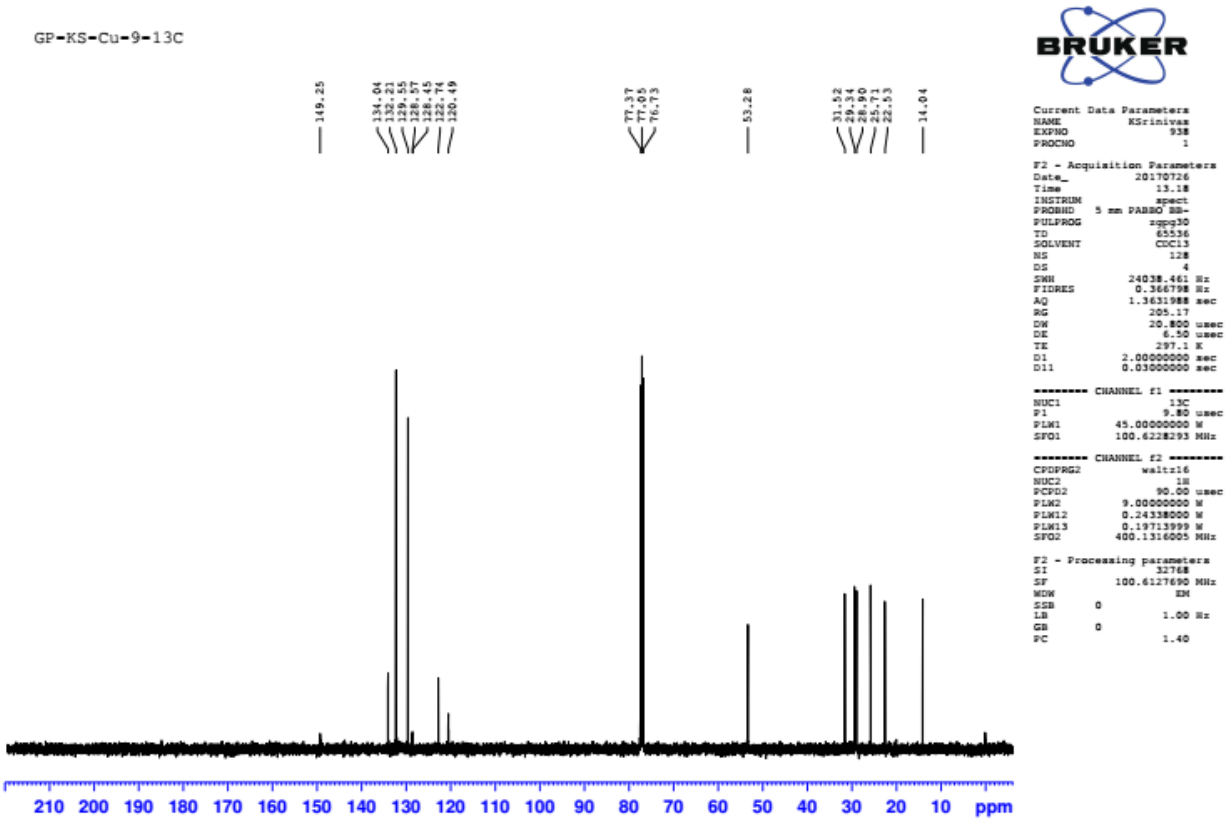
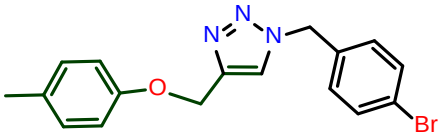


Fig. S72. ^{13}C NMR spectrum of **IIc** in $CDCl_3$ at room temperature.

9. 1-(4-nitrobenzyl)-4-((*p*-tolyloxy)methyl)-1*H*-1,2,3-triazole (IId)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.51 (m, 3H), 7.05-7.14 (m, 4H), 6.83-6.86 (m, 2H), 5.46 (s, 2H), 5.15 (s, 2H), 2.27 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.06, 145.13, 133.54, 132.32, 130.60, 129.98, 129.70, 122.98, 122.53, 114.66, 62.20, 53.52, 20.48 ppm.

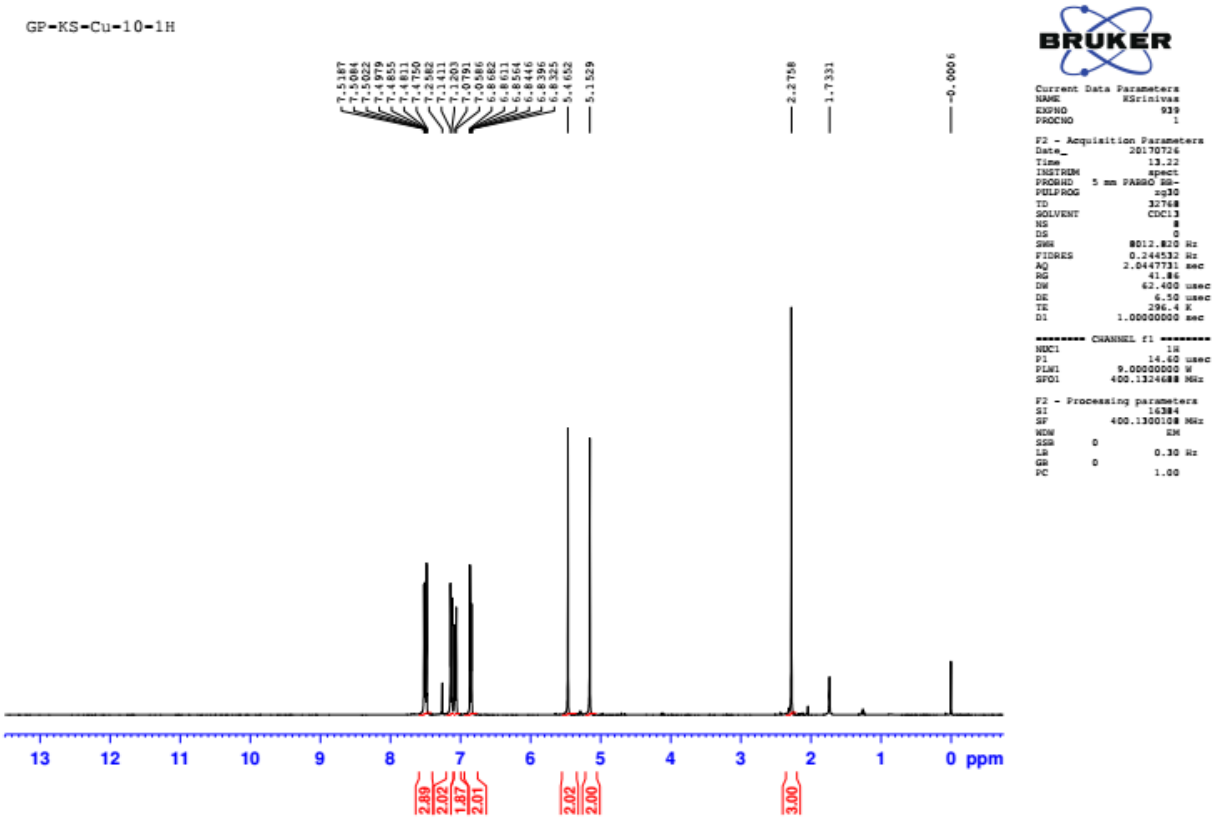


Fig. S73. ^{1}H NMR spectrum of **IId** in $CDCl_3$ at room temperature.

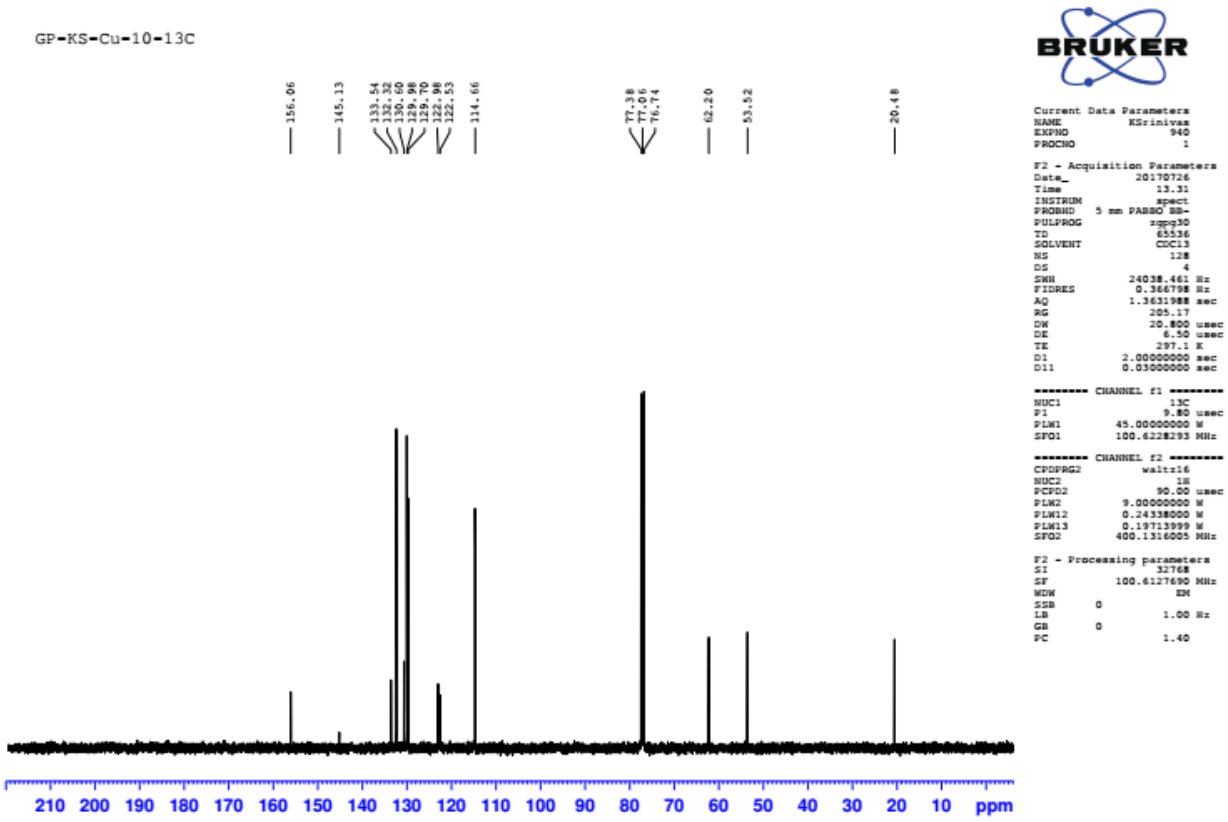
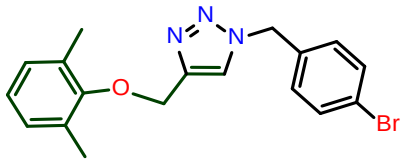


Fig. S74. ^{13}C NMR spectrum of **IId** in $CDCl_3$ at room temperature.

10. 4-((2,6-dimethylphenoxy)methyl)-1-(4-nitrobenzyl)-1*H*-1,2,3-triazole (IIe)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.54 (m, 3H), 7.14-7.16 (m, 2H), 6.91-7.01 (m, 3H), 5.50 (s, 2H), 4.95 (s, 2H), 2.25 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.24, 145.35, 133.61, 132.33, 131.02, 129.69, 128.91, 124.29, 122.98, 122.47, 65.56, 53.52, 16.36 ppm.

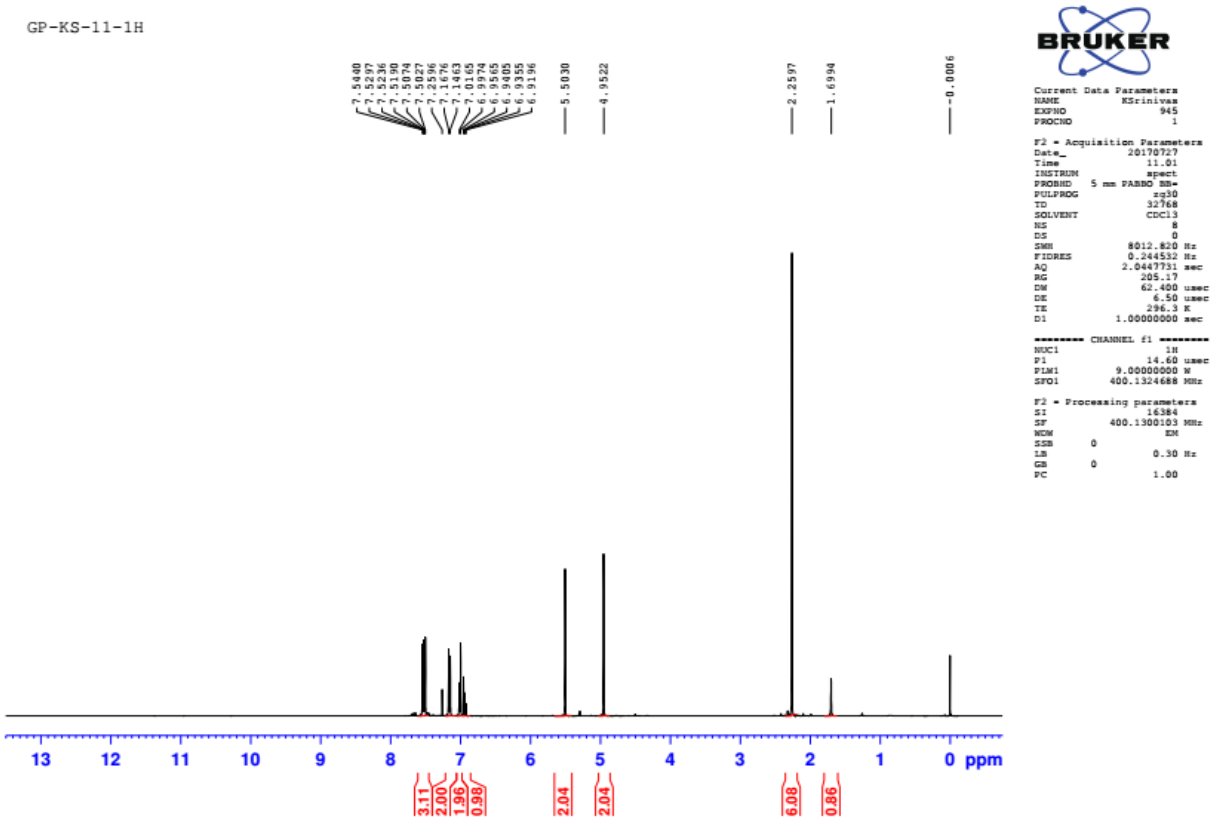


Fig. S75. ^{1}H NMR spectrum of **IIe** in $CDCl_3$ at room temperature.

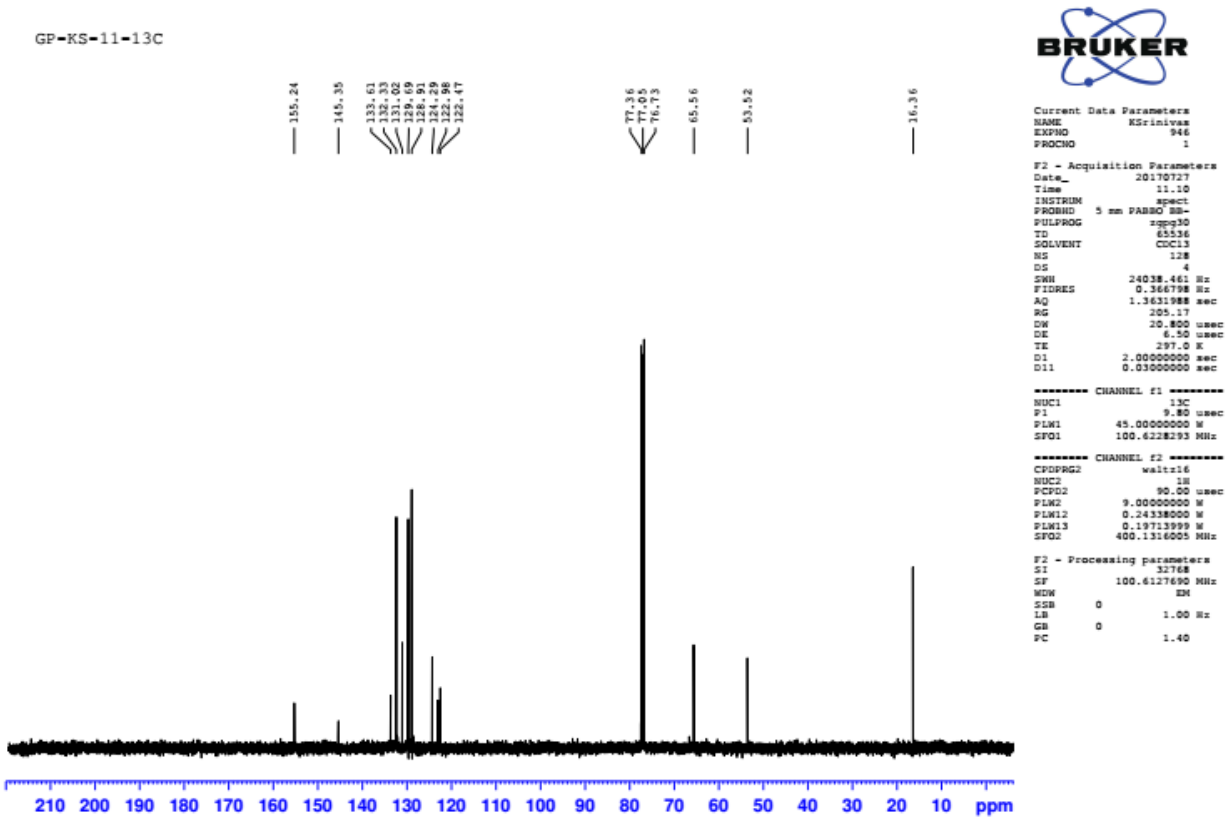
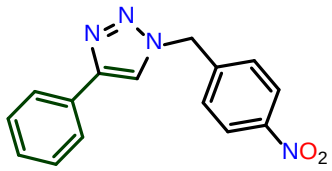


Fig. S76. ^{13}C NMR spectrum of **IIe** in $CDCl_3$ at room temperature.

11. 1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (IIIa)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21-8.23 (d, 2H), 7.76-7.81 (m, 3H), 7.33-7.44 (m, 5H), 5.69 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.71, 148.09, 141.78, 132.13, 132.03, 130.11, 128.93, 128.77, 128.57, 125.50, 125.75, 124.33, 119.76, 53.18 ppm.

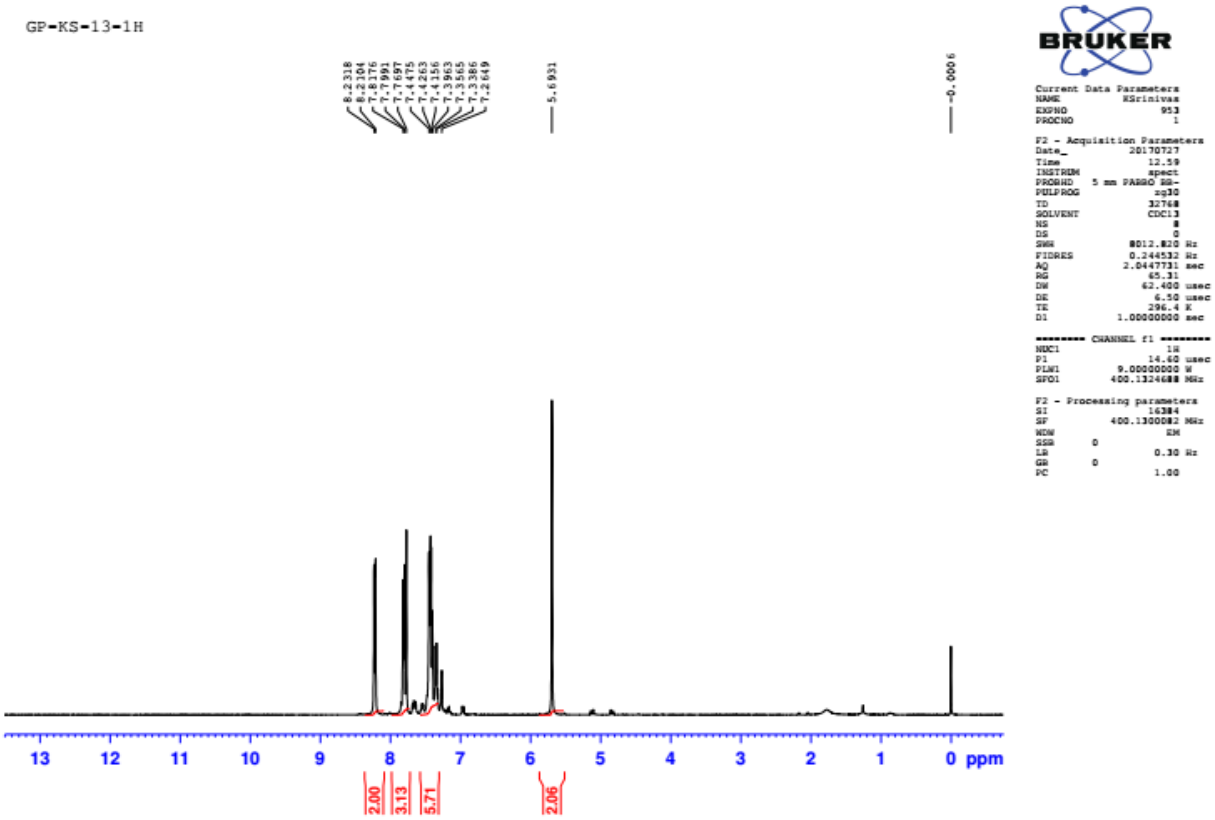


Fig. S77. ^{1}H NMR spectrum of **IIIa** in $CDCl_3$ at room temperature.

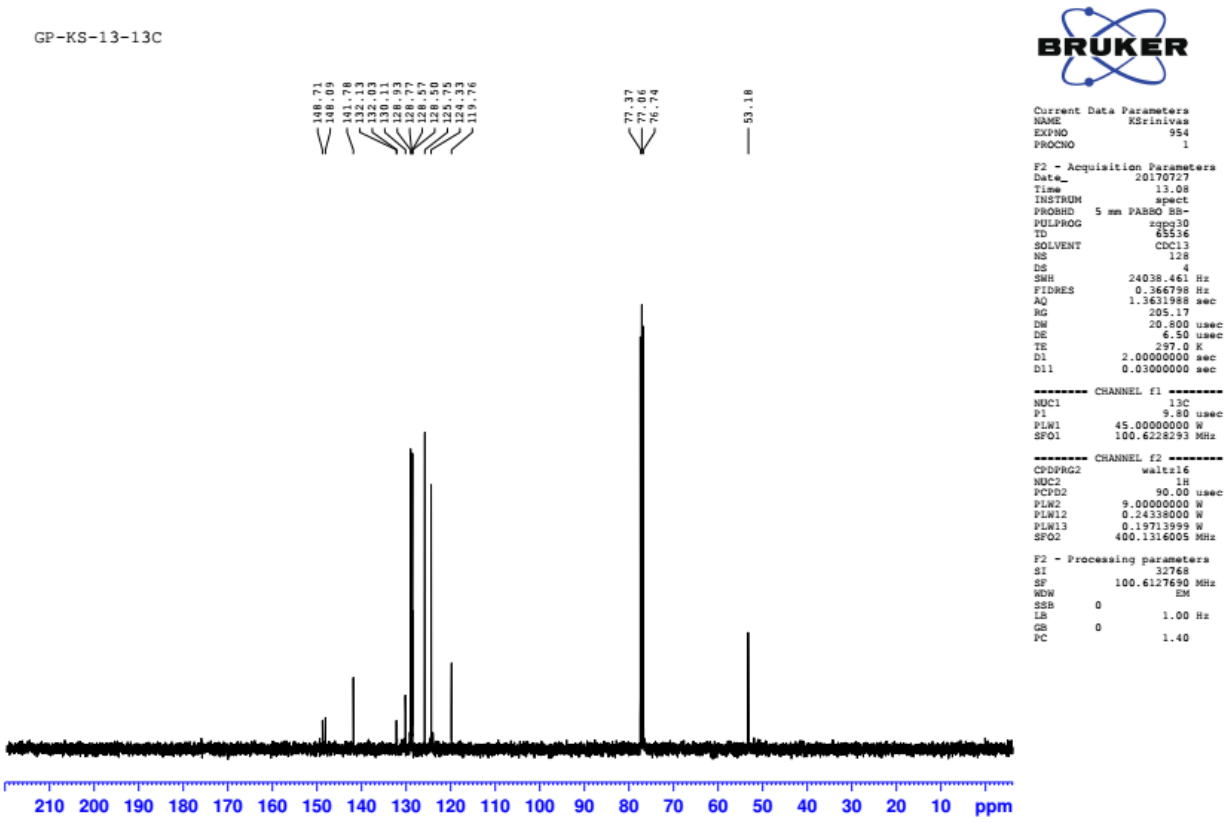
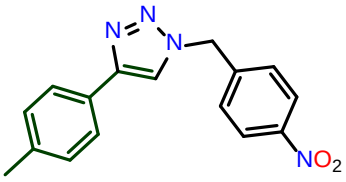


Fig. S78. ^{13}C NMR spectrum of **IIIa** in $CDCl_3$ at room temperature.

12. 1-(4-nitrobenzyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (IIIb)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.22 (d, 2H), 7.69-7.75 (m, 3H), 7.41-7.43 (d, 2H), 7.21-7.22 (d, 2H), 5.68 (s, 2H), 2.36 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.06, 141.84, 138.42, 132.13, 129.60, 128.57, 127.33, 125.64, 124.31, 53.19, 21.30 ppm.

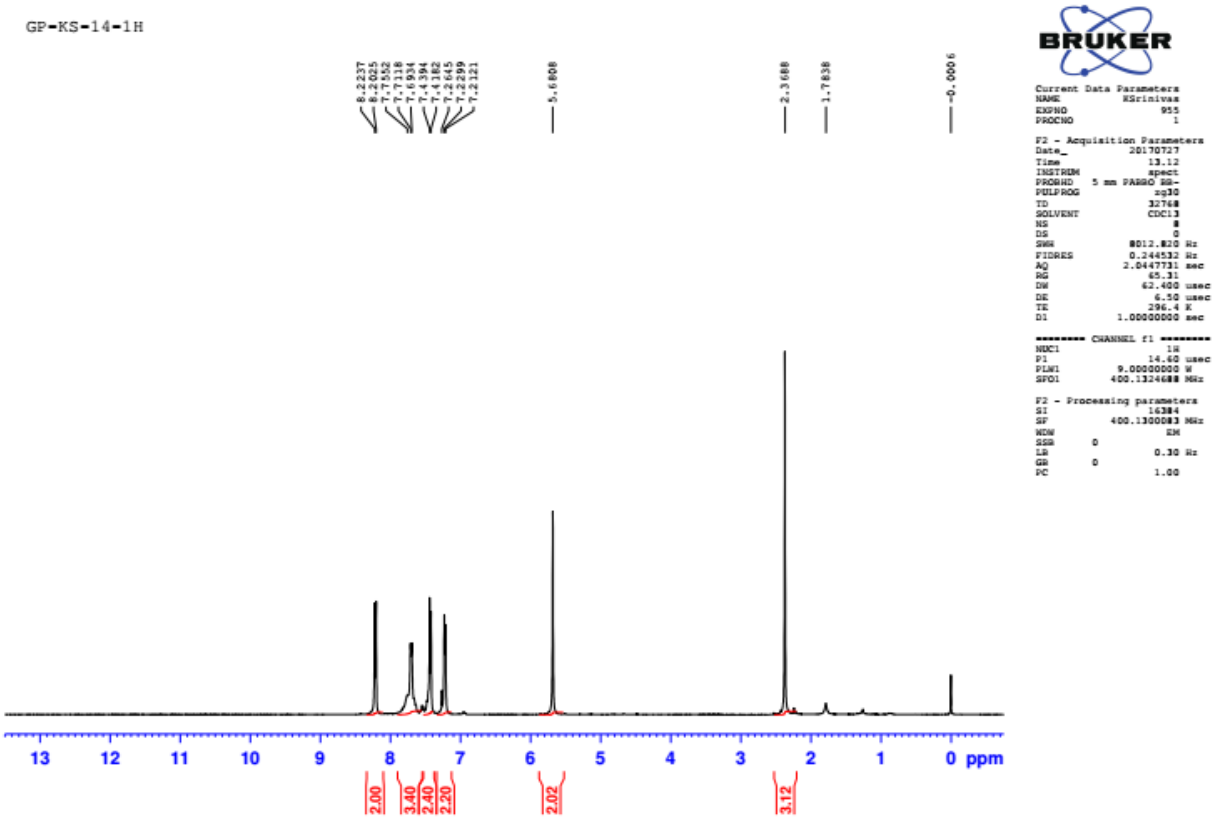


Fig. S79. ^{1}H NMR spectrum of **IIIb** in $CDCl_3$ at room temperature.

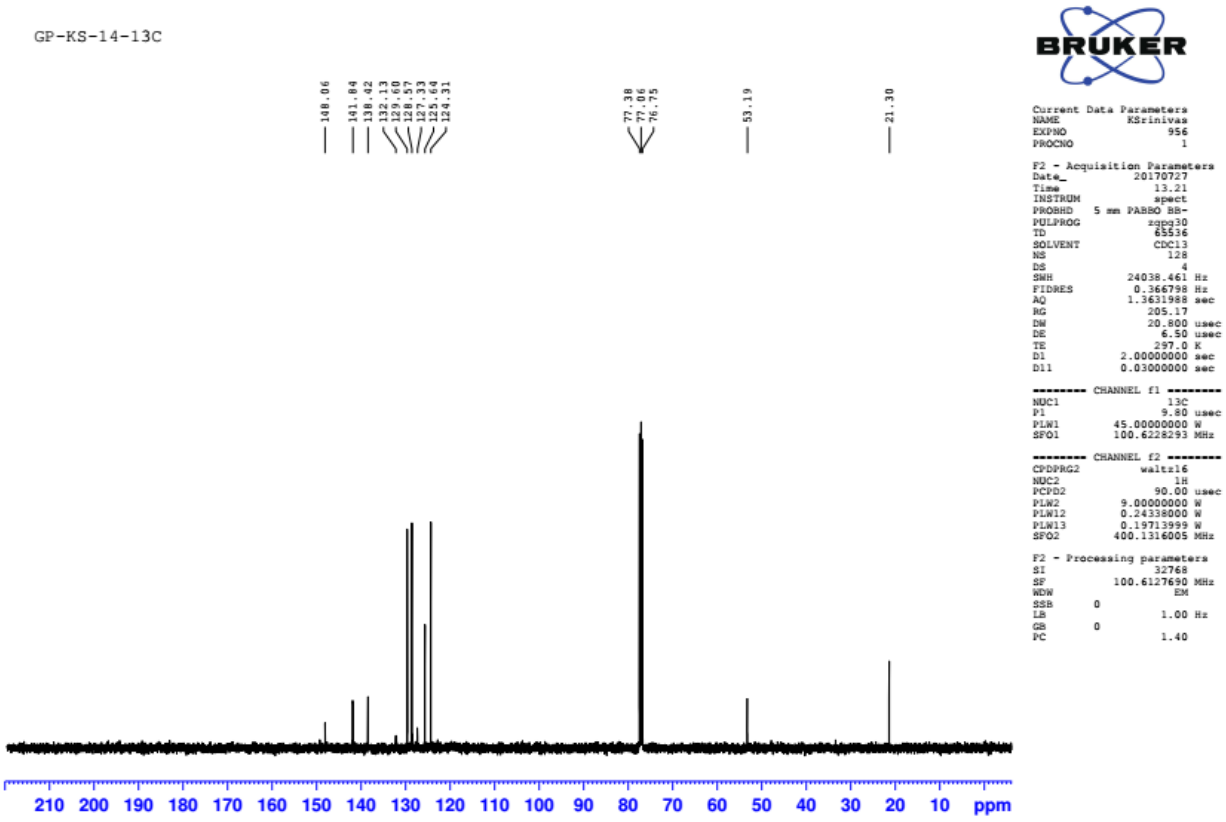
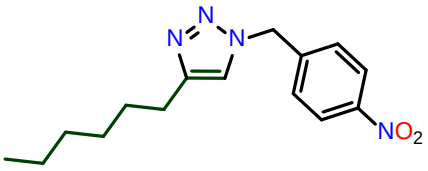


Fig. S80. ^{13}C NMR spectrum of **IIIb** in $CDCl_3$ at room temperature.

13. 4-hexyl-1-(4-nitrobenzyl)-1H-1,2,3-triazole (IIIc)



^1H NMR (400 MHz, $CDCl_3$): δ 8.19-8.21 (d, 1H), 7.28-7.64 (m, 4H), 5.62 (s, 2H), 2.71 (t, 2H), 1.65 (m, 2H), 1.29 (m, 6H), 0.86 (t, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.96, 142.15, 132.08, 131.97, 128.64, 128.46, 124.23, 52.96, 31.51, 29.28, 28.88, 25.70, 22.52, 14.03 ppm.

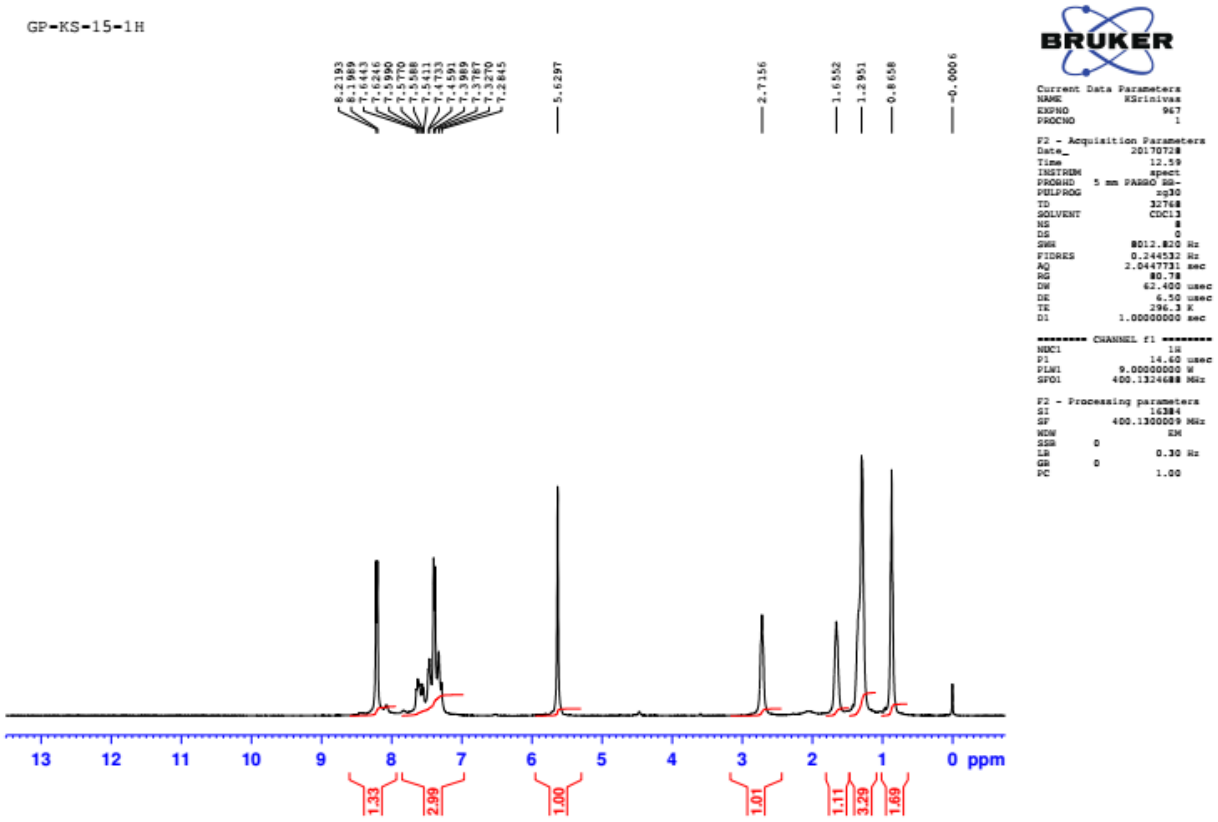


Fig. S81. ^{1}H NMR spectrum of **IIIc** in $CDCl_3$ at room temperature.

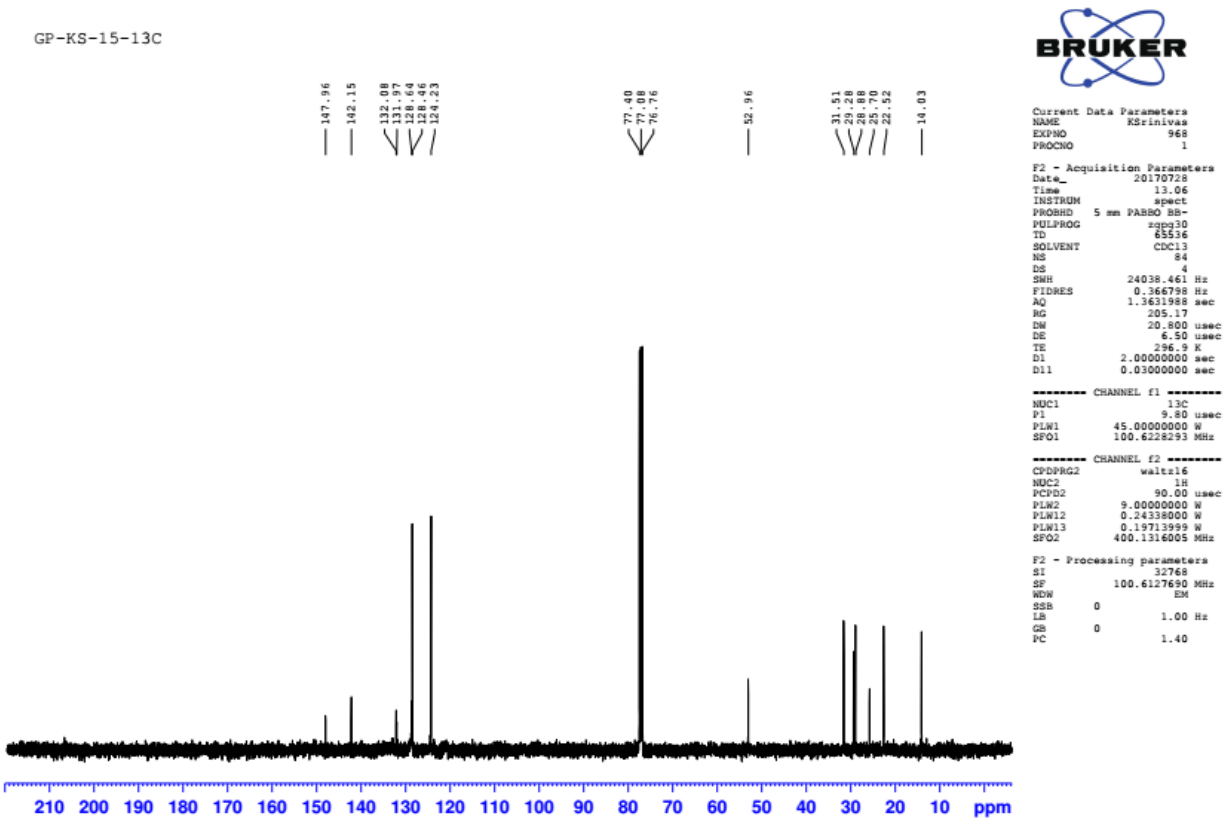
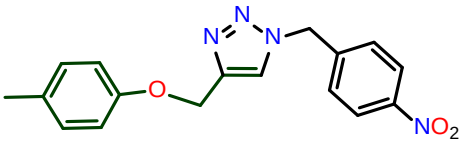


Fig. S82. ^{13}C NMR spectrum of **IIIc** in $CDCl_3$ at room temperature.

14. 1-(4-nitrobenzyl)-4-((*p*-tolyloxy)methyl)-1*H*-1,2,3-triazole (IIId)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-8.99 (d, 2H), 7.62 (s, 1H), 7.40-7.38 (d, 2H), 7.08-7.06 (d, 2H), 6.86-6.83 (d, 2H), 5.64 (s, 2H), 5.18 (s, 2H), 2.27 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.94, 148.06, 141.58, 132.08, 131.98, 130.72, 130.02, 128.70, 128.62, 124.32, 122.95, 114.61, 62.08, 53.17, 20.49 ppm.

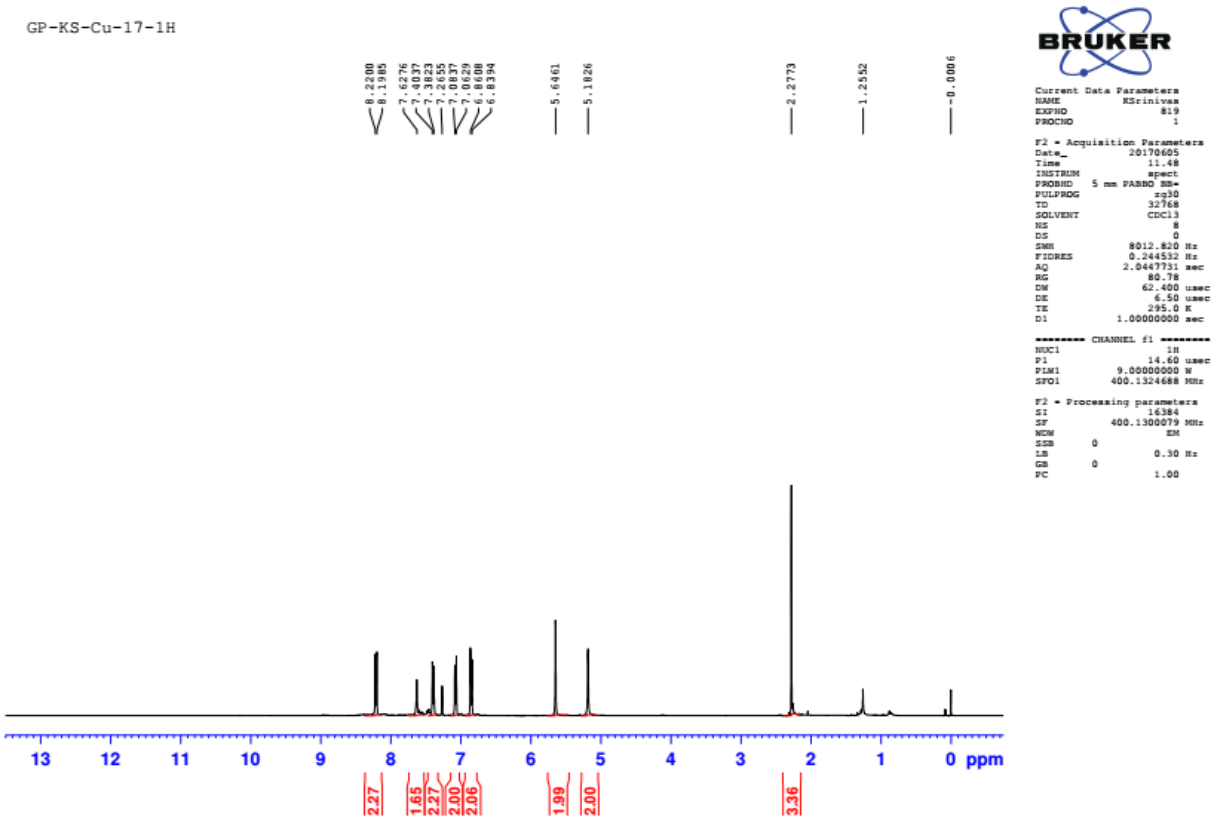


Fig. S83. ^{1}H NMR spectrum of **IIId** in $CDCl_3$ at room temperature.

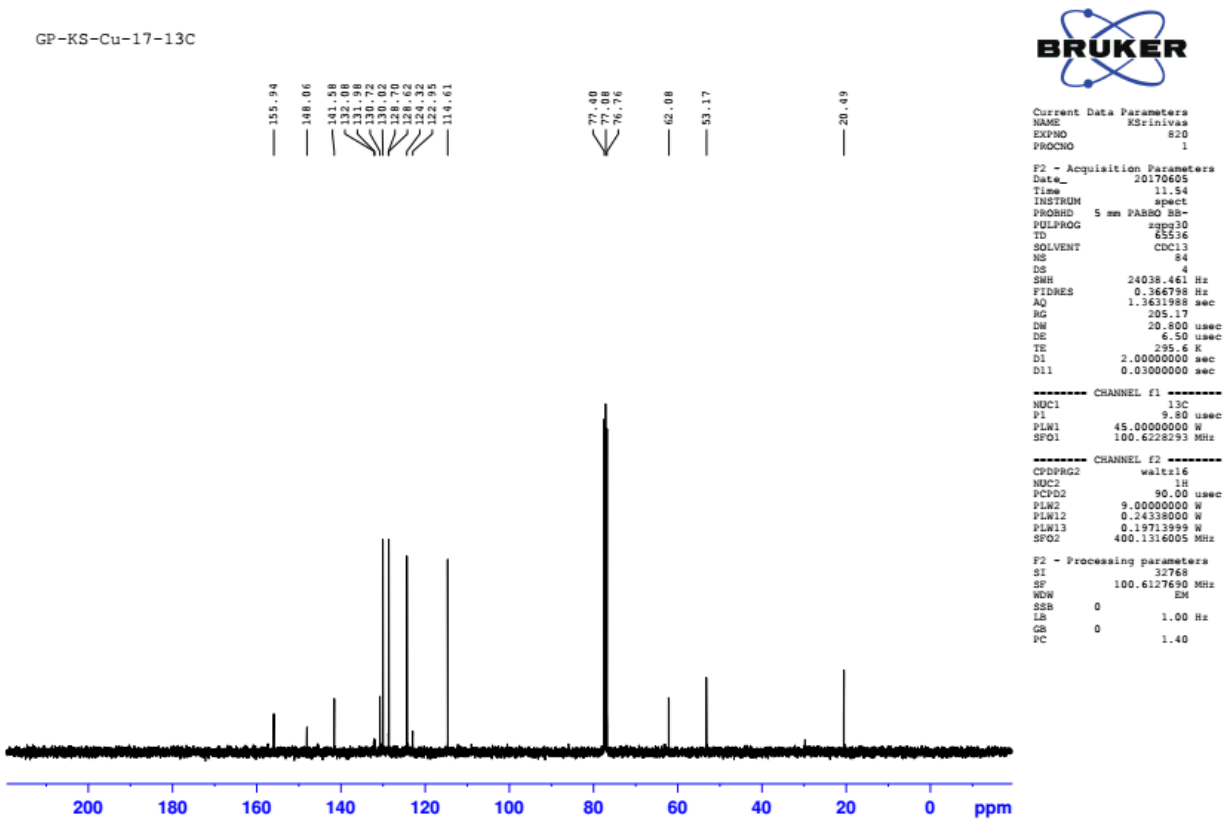
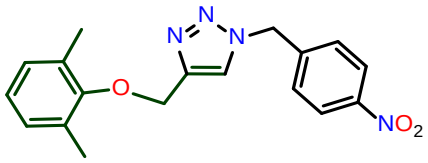


Fig. S84. ^{13}C NMR spectrum of **IIId** in $CDCl_3$ at room temperature.

15. 4-((2,6-dimethylphenoxy)methyl)-1-(4-nitrobenzyl)-1*H*-1,2,3-triazole (IIIe)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17-8.15 (d, 2H), 7.73 (s, 1H), 7.40-7.38 (m, 2H), 7.00-6.92 (m, 3H), 5.67 (s, 2H), 4.96 (s, 2H), 2.26 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.18, 147.93, 141.90, 132.17, 132.05, 131.95, 130.95, 128.95, 128.64, 128.57, 124.36, 124.21, 123.26, 65.39, 53.06, 16.36 ppm.

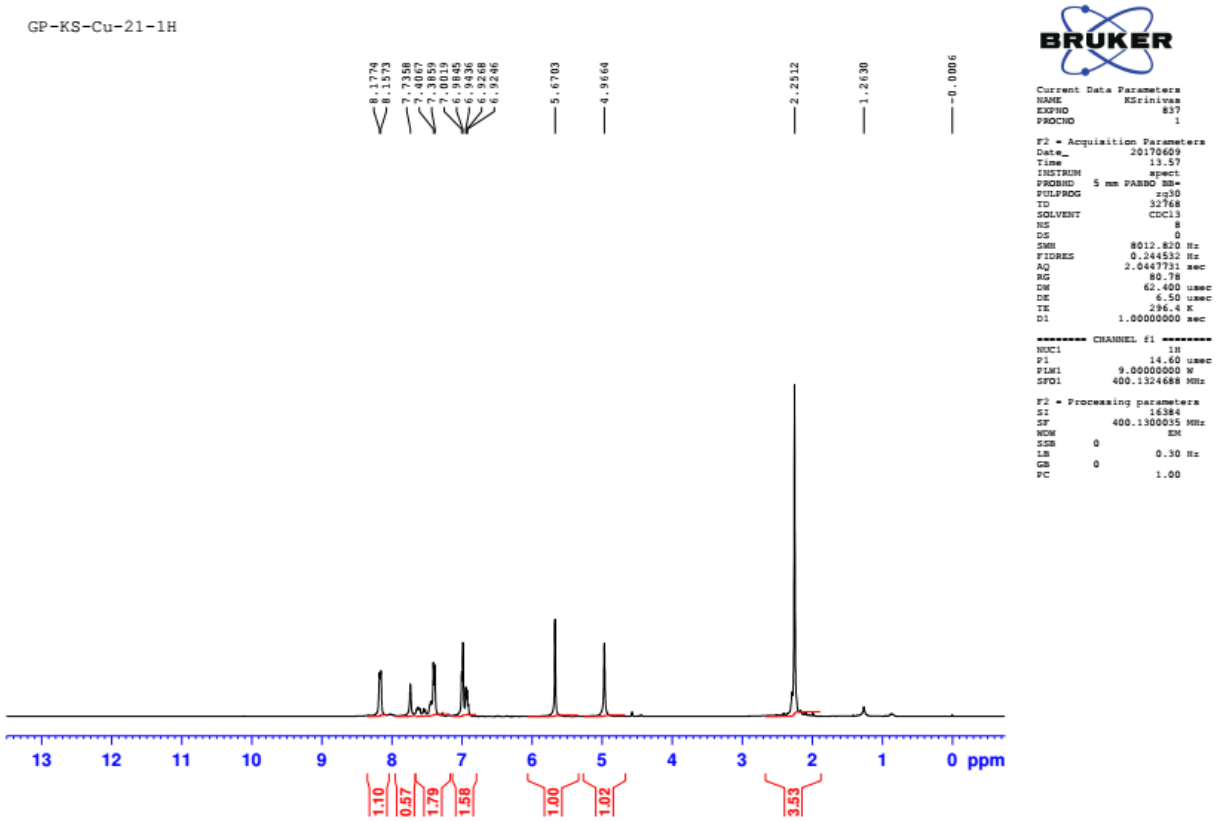


Fig. S85. ^{1}H NMR spectrum of **IIIe** in $CDCl_3$ at room temperature.

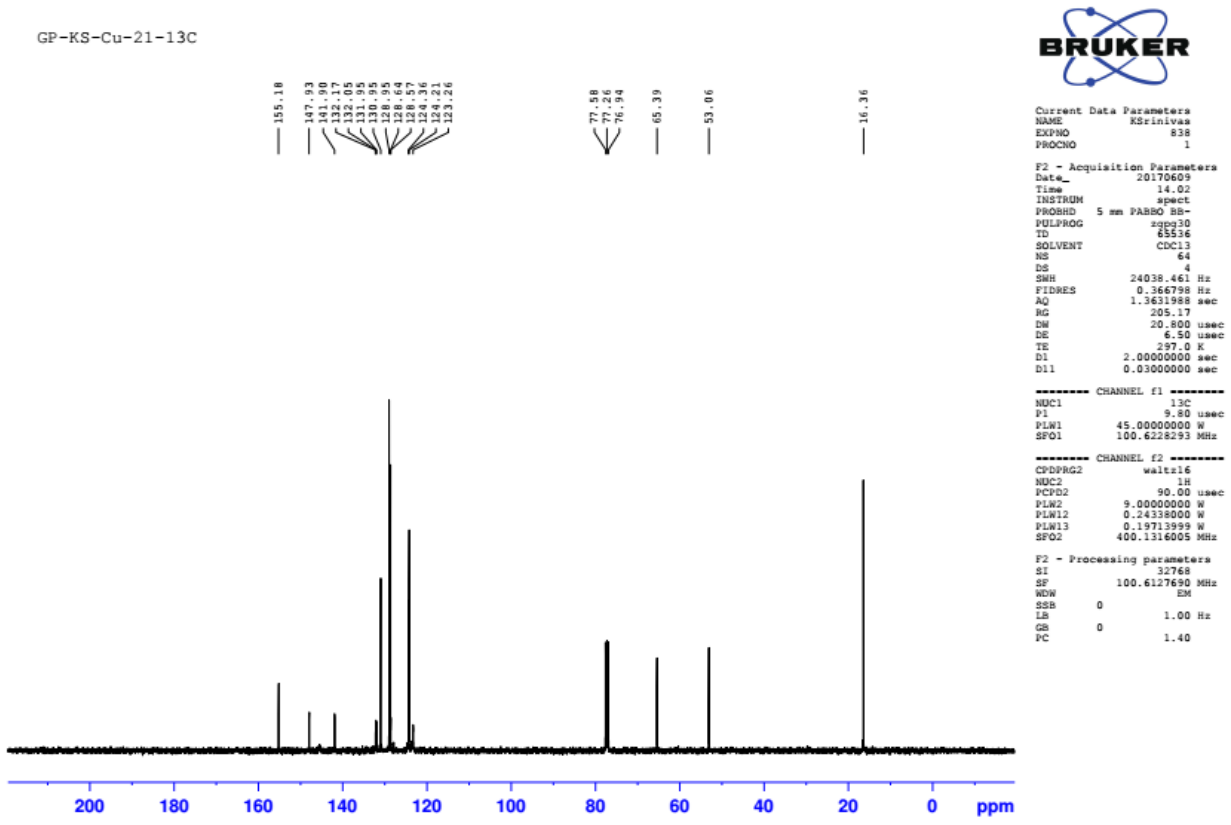
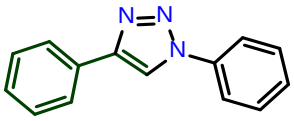


Fig. S86. ^{13}C NMR spectrum of **IIIe** in $CDCl_3$ at room temperature.

16. 1,4-diphenyl-1*H*-1,2,3-triazole (IVa)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.90-7.92 (d, 2H), 7.78-7.80 (d, 2H), 7.52-7.56 (t, 2H), 7.43-7.47 (m, 3H), 7.34-7.38 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.09, 130.27, 129.80, 128.94, 128.79, 128.44, 125.87, 120.55, 117.62 ppm.

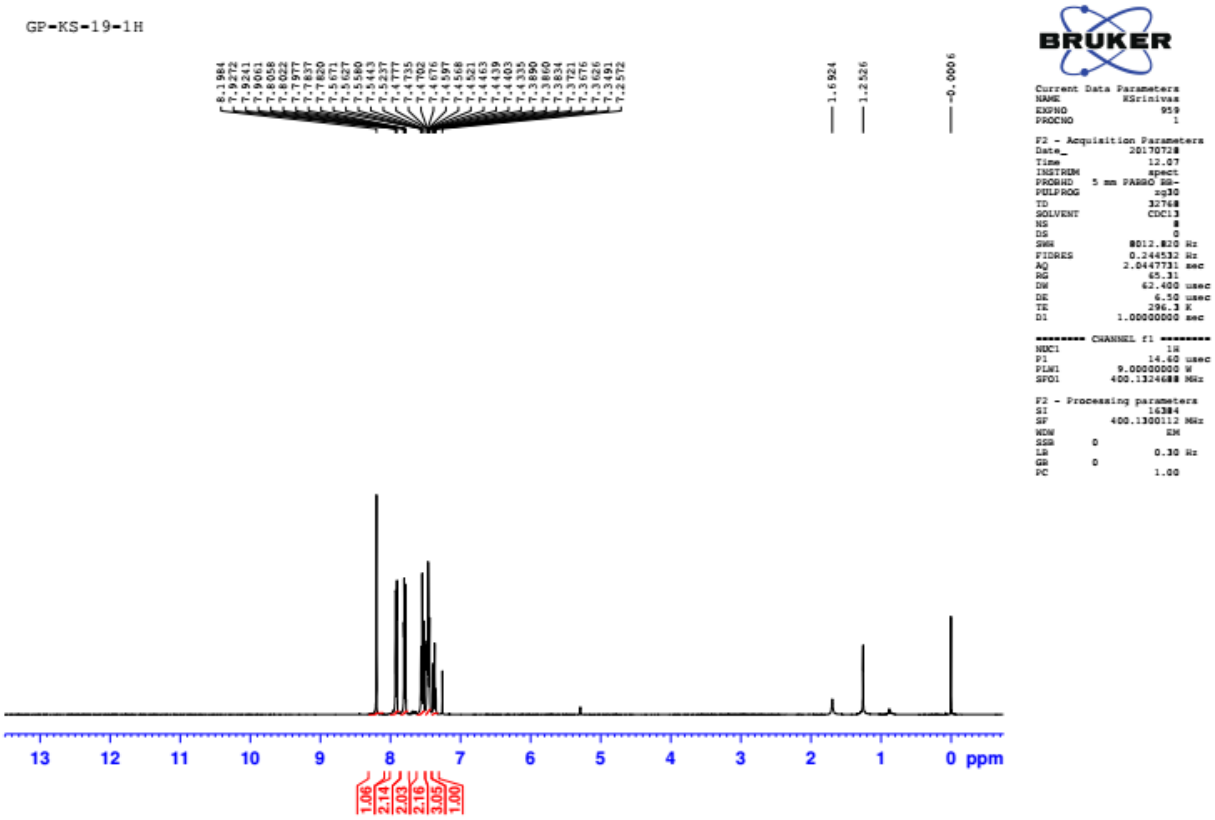


Fig. S87. ^{1}H NMR spectrum of **IVa** in $CDCl_3$ at room temperature.

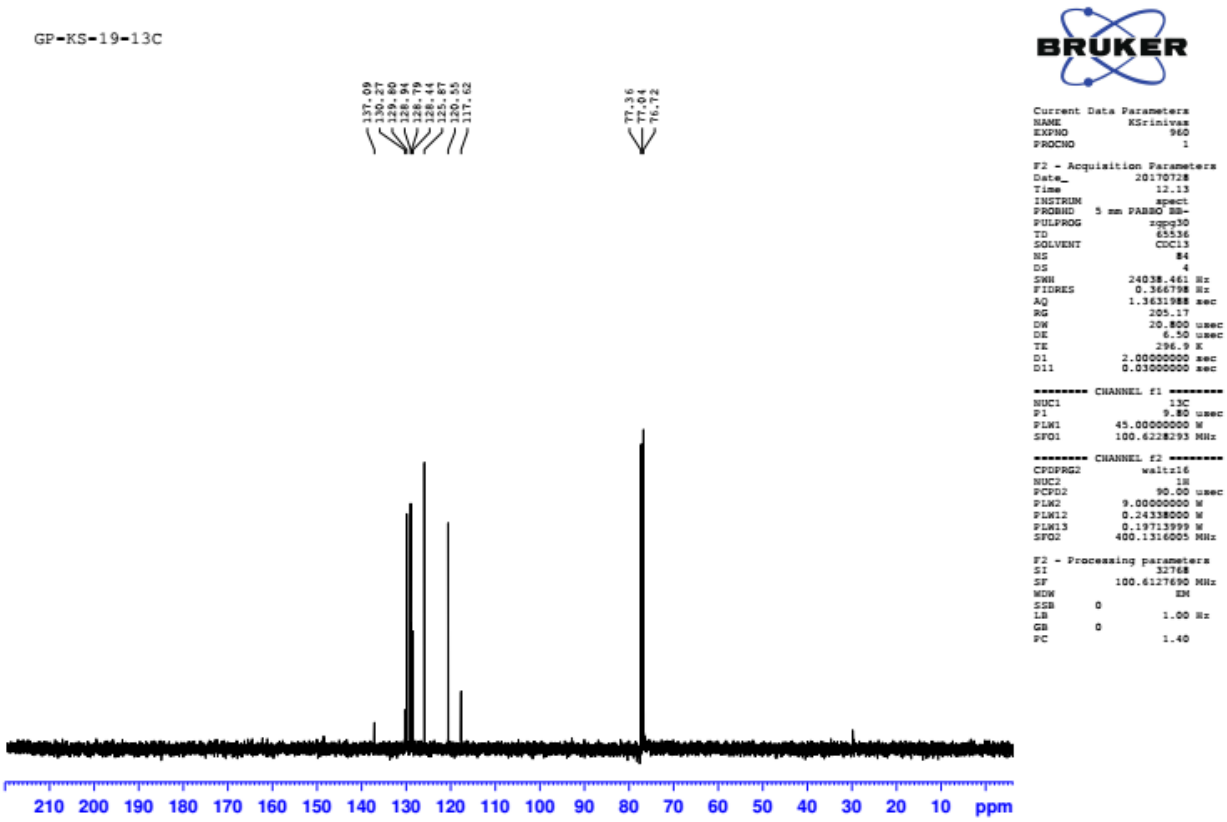
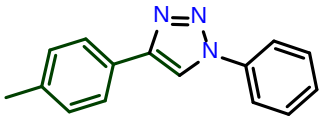


Fig. S88. ^{13}C NMR spectrum of **IVa** in $CDCl_3$ at room temperature.

17. 1-phenyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (IVb)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.76-7.80 (t, 4H), 7.50-7.54 (t, 2H), 7.41-7.45 (t, 1H), 7.24-7.25 (m, 2H), 2.38 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.50, 138.33, 137.12, 129.77, 129.61, 128.70, 127.43, 125.78, 120.50, 117.28, 21.34 ppm.

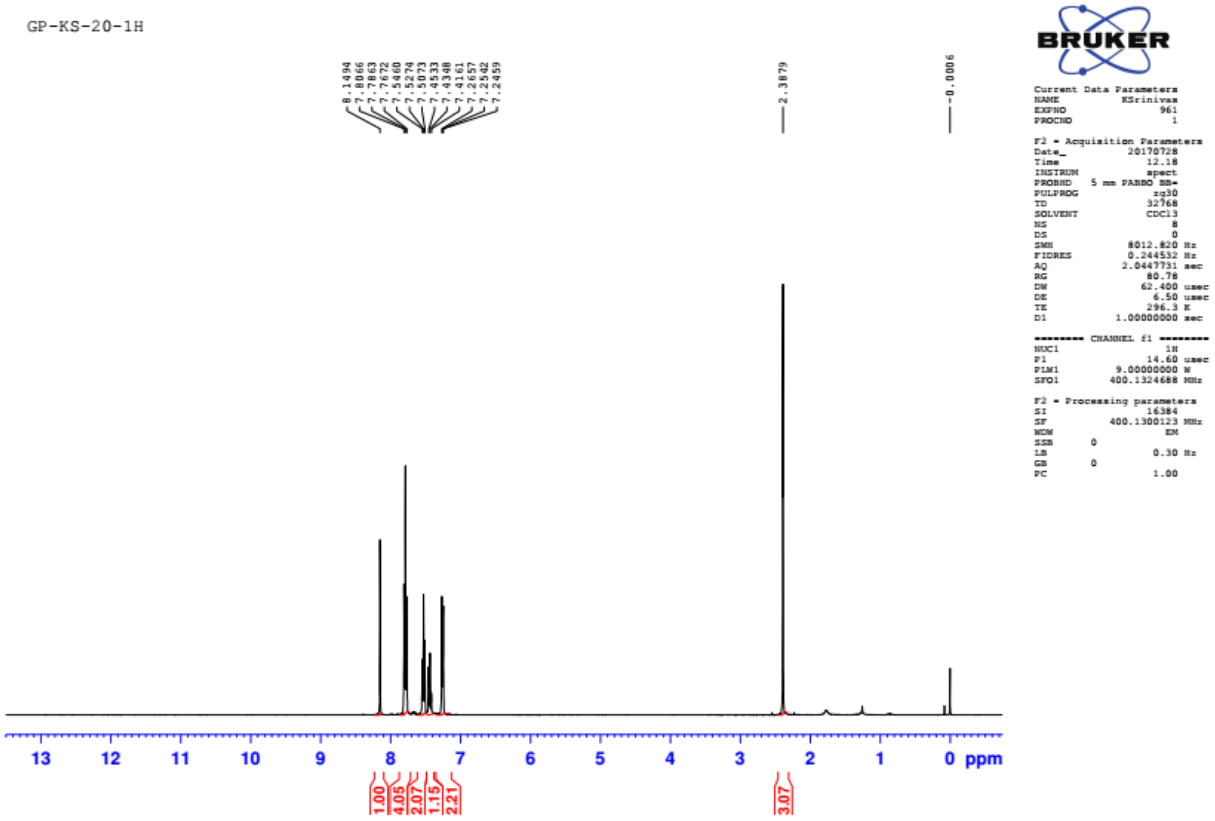


Fig. S89. ^{1}H NMR spectrum of **IVb** in $CDCl_3$ at room temperature.

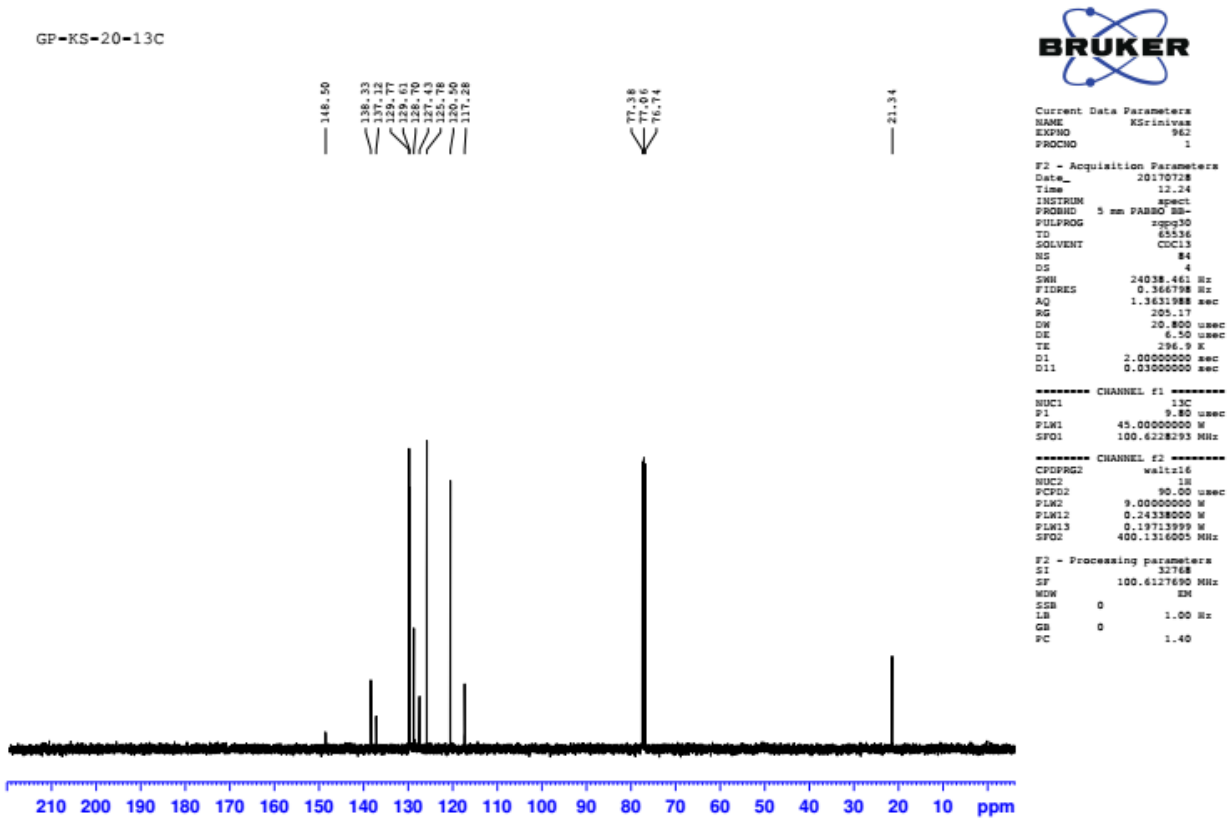
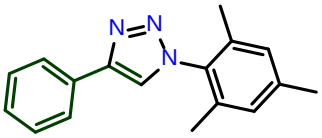


Fig. S90. ^{13}C NMR spectrum of **IVb** in $CDCl_3$ at room temperature.

18. 1-mesityl-4-phenyl-1*H*-1,2,3-triazole (Va)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.93 (d, 2H), 7.83 (s, 1H), 7.42-7.46 (m, 2H), 7.32-7.36 (m, 1H), 6.99 (s, 2H), 2.35 (s, 3H), 2.00 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.57, 140.08, 135.11, 133.53, 130.55, 129.13, 128.93, 128.27, 125.76, 121.55, 21.17, 17.35 ppm.

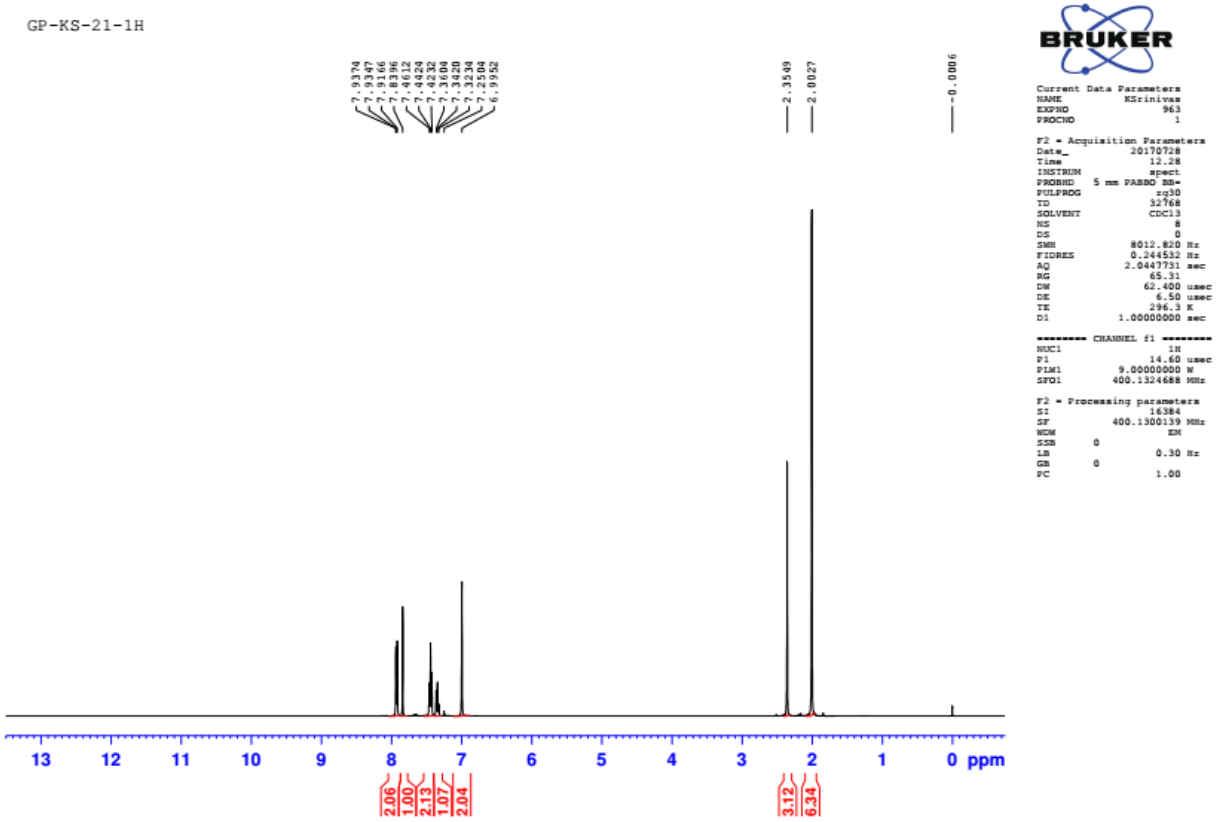


Fig. S91. ^{1}H NMR spectrum of **Va** in $CDCl_3$ at room temperature.

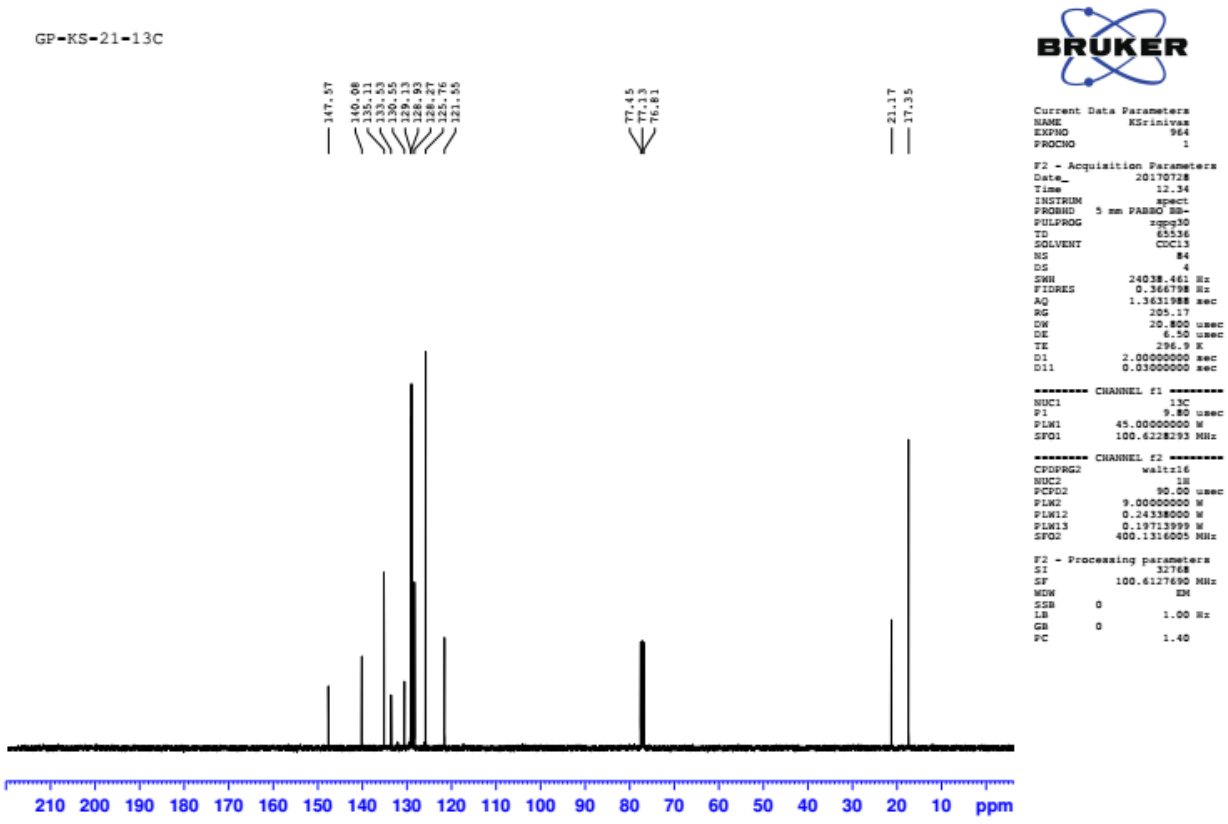
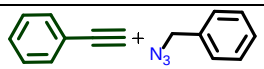
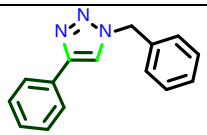
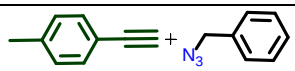
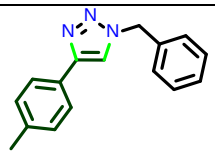
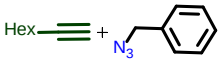
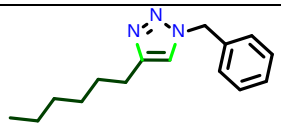
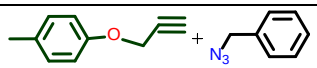
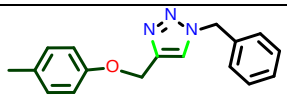
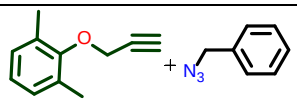
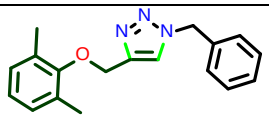
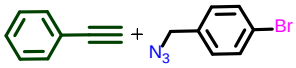
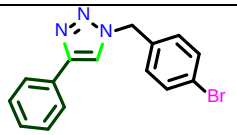
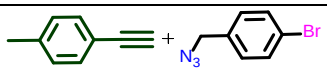
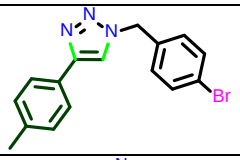
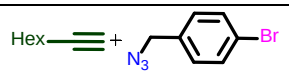
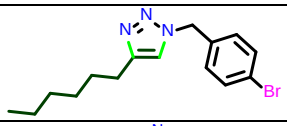
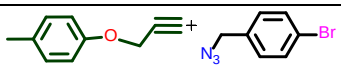
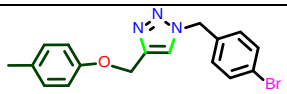
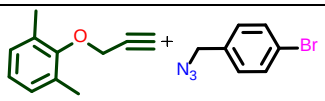
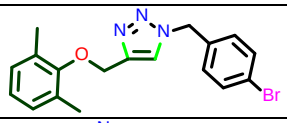
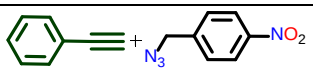
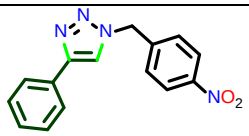
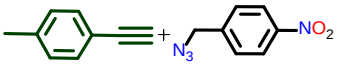
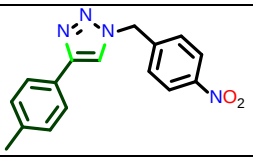


Fig. S92. ^{13}C NMR spectrum of **Va** in $CDCl_3$ at room temperature.

Table S4: 1,2,3-triazoles isolated by click catalysis by **3**, **6** and **12** in water**.**

Entry	Starting Materials	Product	Isolated Yields (%) **3** **6** **12**
1			90 92 95
2			89 85 98
3			85 88 92
4			79 82 85
5			80 83 86
6			86 82 86
7			82 84 88
8			75 78 83
9			84 89 85
10			80 83 86
11			79 80 84
12			82 80 85

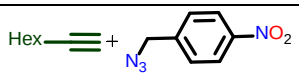
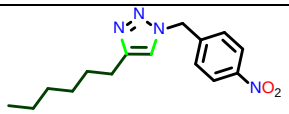
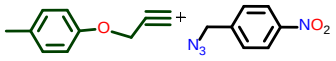
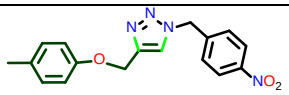
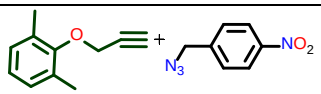
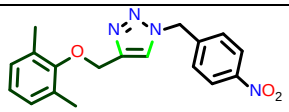
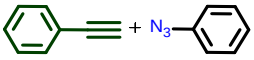
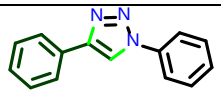
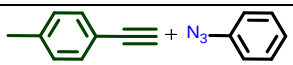
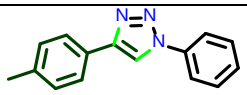
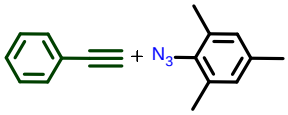
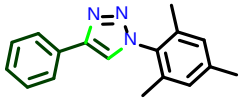
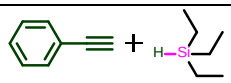
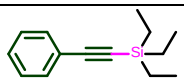
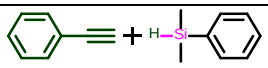
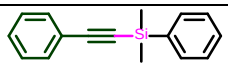
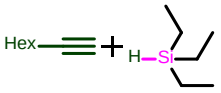
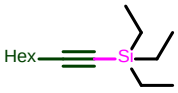
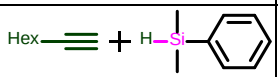
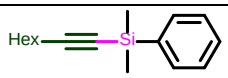
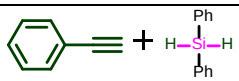
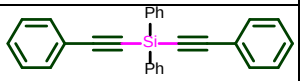
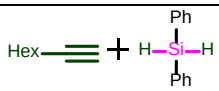
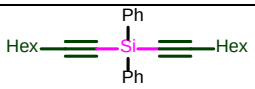
13			85 88 90
14			75 80 82
15			88 84 86
16			76 79 78
17			79 80 85
18			85 82 89

Table S5: Alkynylsilanes isolated by **3, 6** and **12**. Reaction conditions for X and XI: Phenylacetylene (0.80 mmol), diphenylsilane (0.40 mmol), Catalyst (1 mol%), base (20 mol%), solvent (1.0 mL).

Entry	Starting Materials	Product	Isolated Yields (%) **3** **6** **12**
1			98 95 92
2			92 99 95
3			90 96 94
4			94 96 93
5			90 98 94
6			93 95 96