Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

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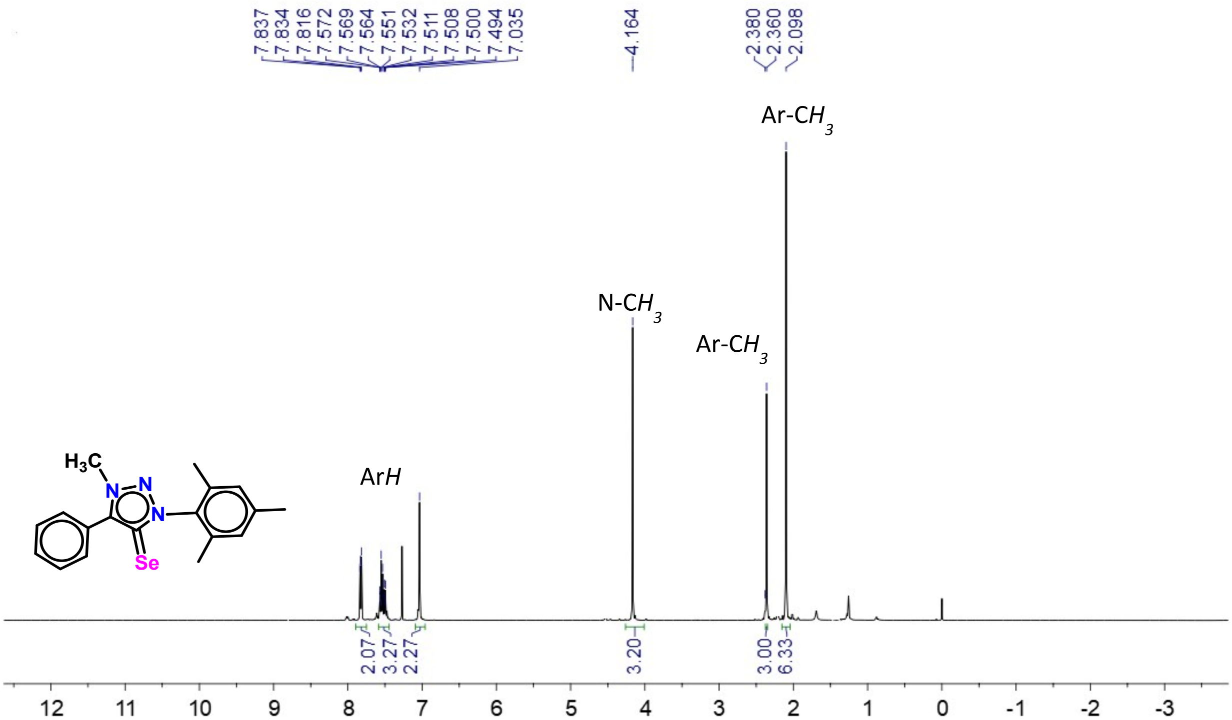


Fig. S1 ^{1}H NMR spectrum of **L^{1}** in $CDCl_3$

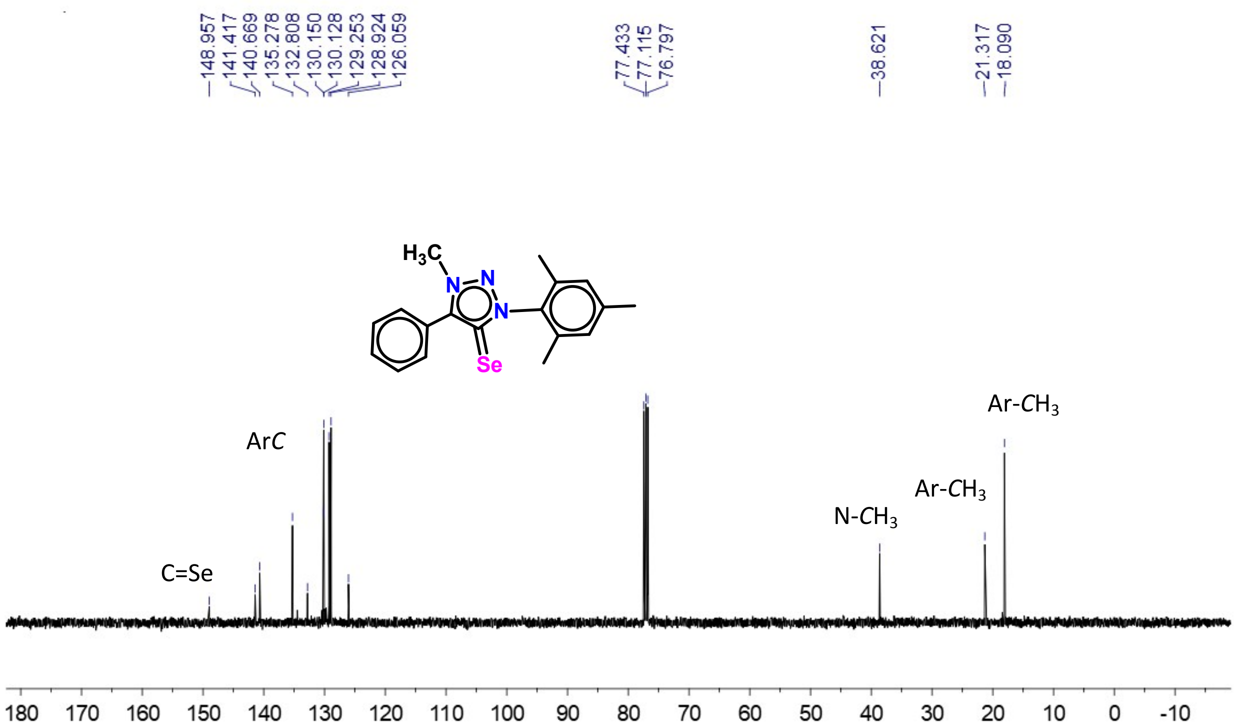


Fig. S2 ^{13}C NMR spectrum of **L^{1}** in $CDCl_3$

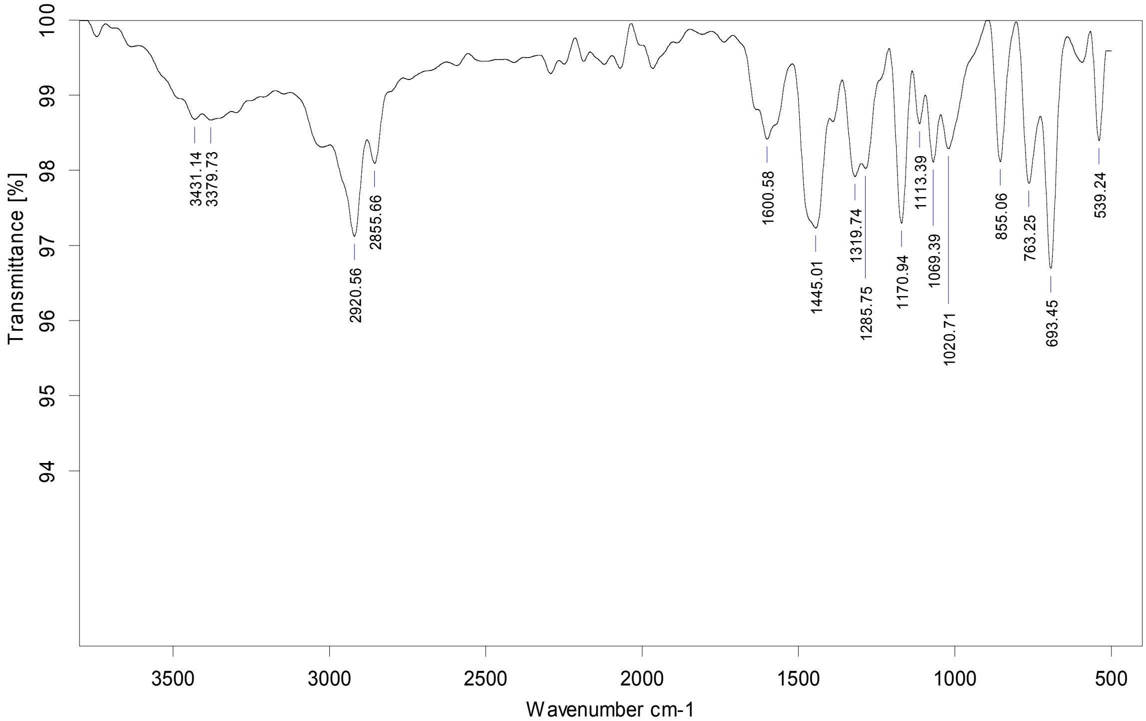


Fig. S3. Neat FT-IR spectrum of **L¹**

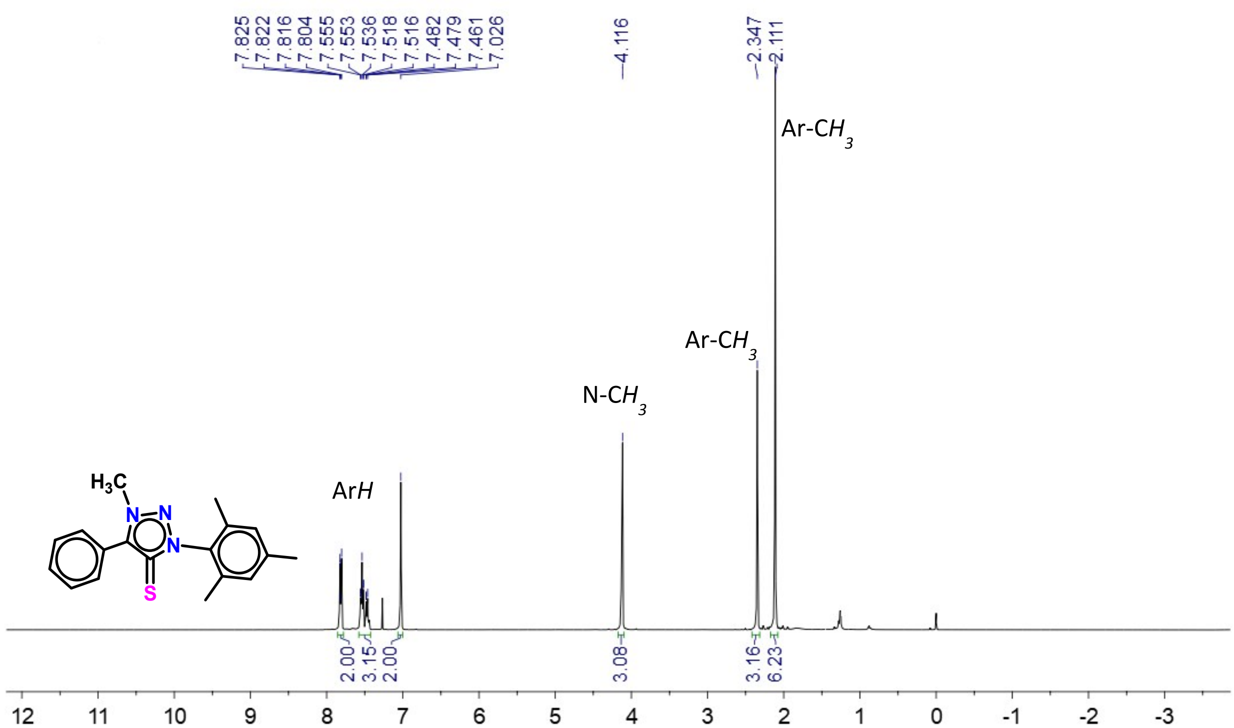


Fig. S4 ^{1}H NMR spectrum of **L²** in $CDCl_3$

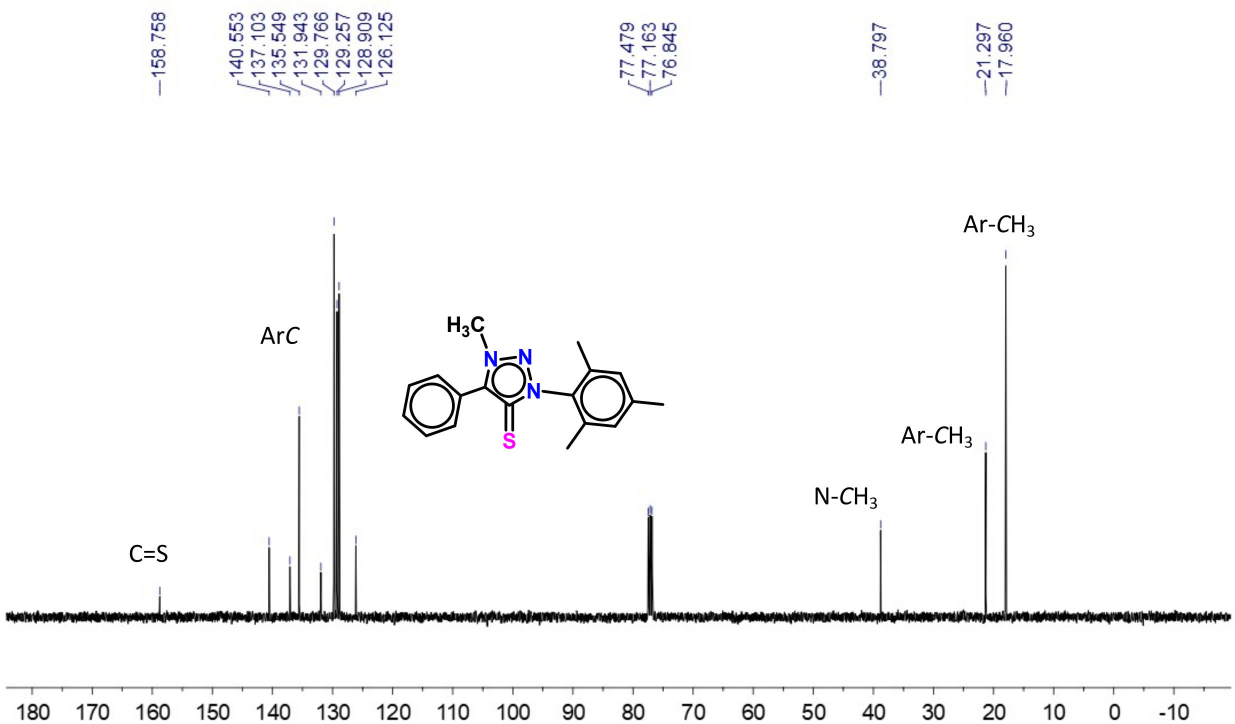


Fig. S5 ^{13}C NMR spectrum of **L^2** in $CDCl_3$

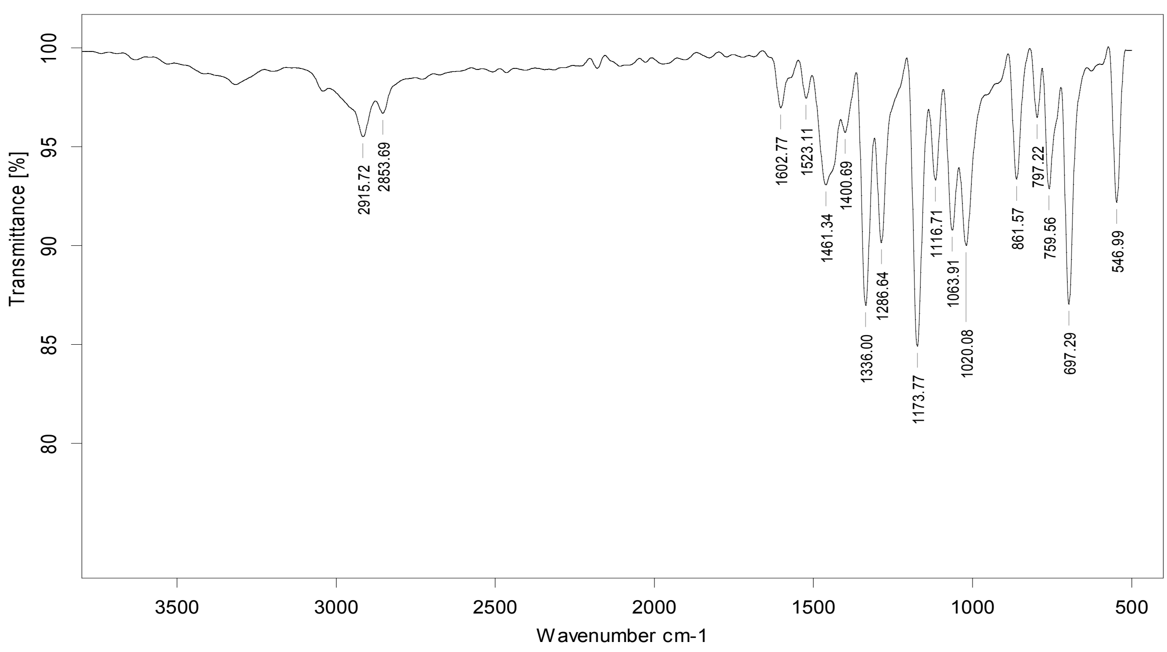


Fig. S6. Neat FT-IR spectrum of **L^2**

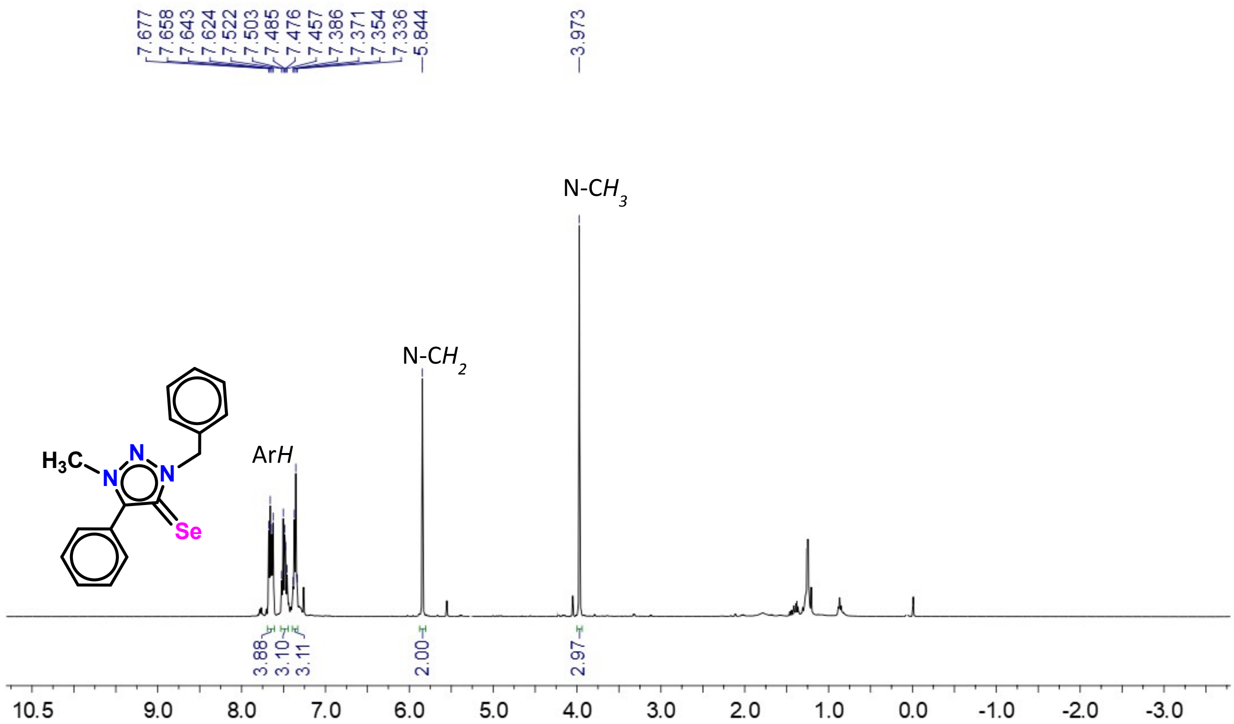


Fig. S7 ^{1}H NMR spectrum of **L³** in $CDCl_3$

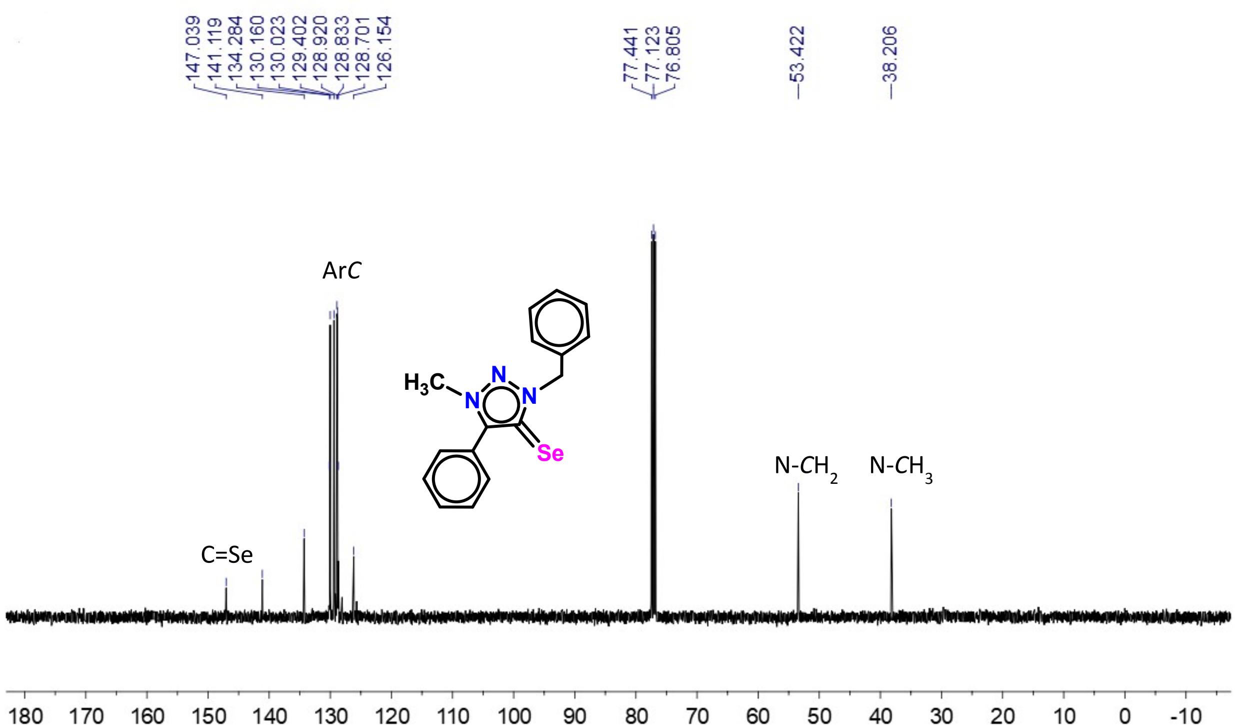


Fig. S8 ^{13}C NMR spectrum of **L³** in $CDCl_3$

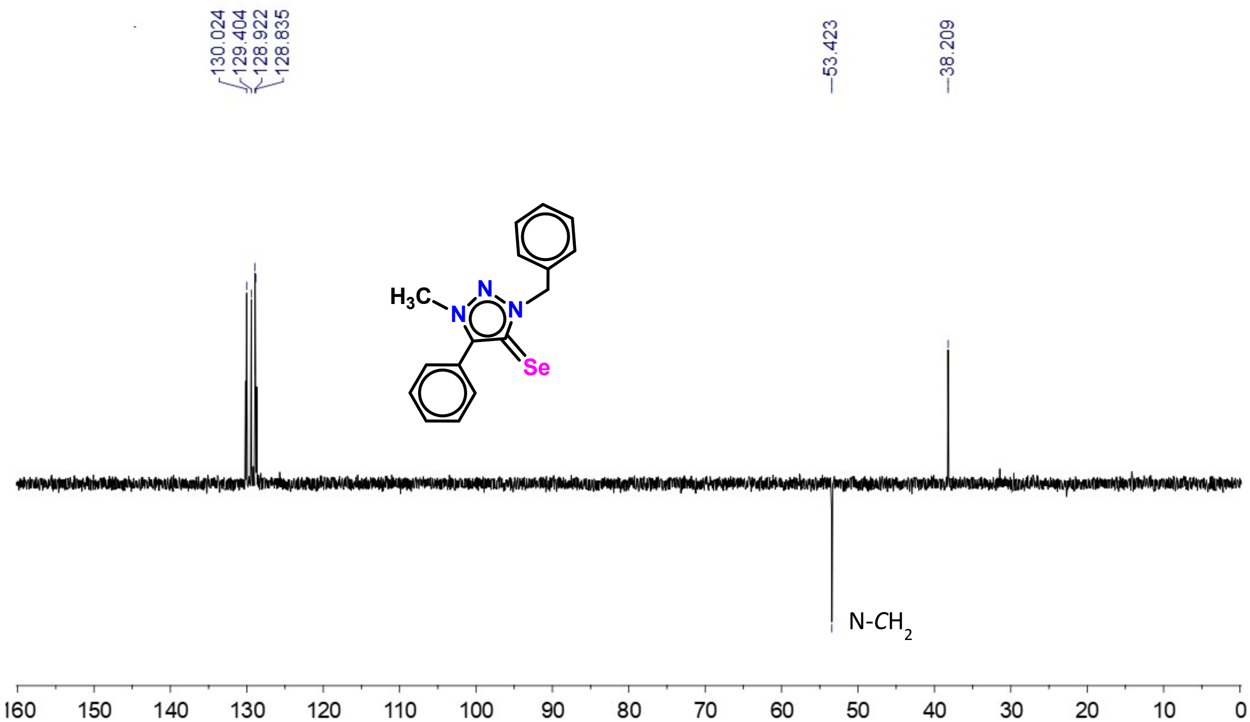


Fig. S9 DEPT NMR spectrum of **L³** in $CDCl_3$

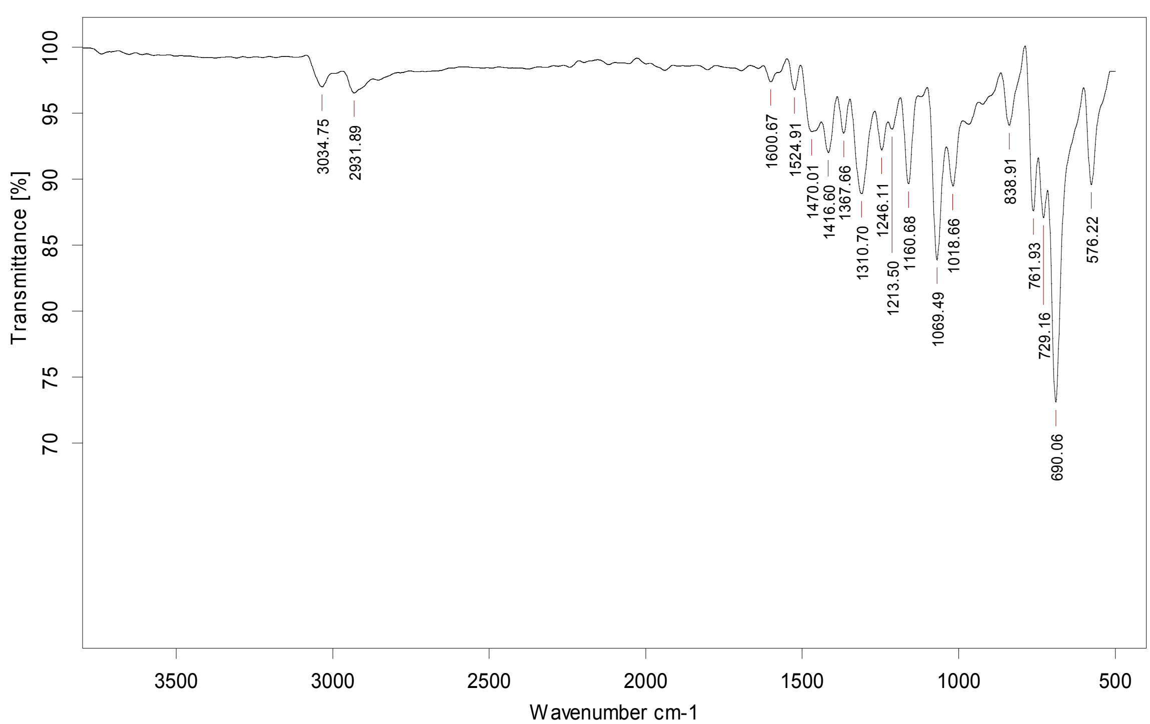


Fig. S10 Neat FT-IR spectrum of **L³**

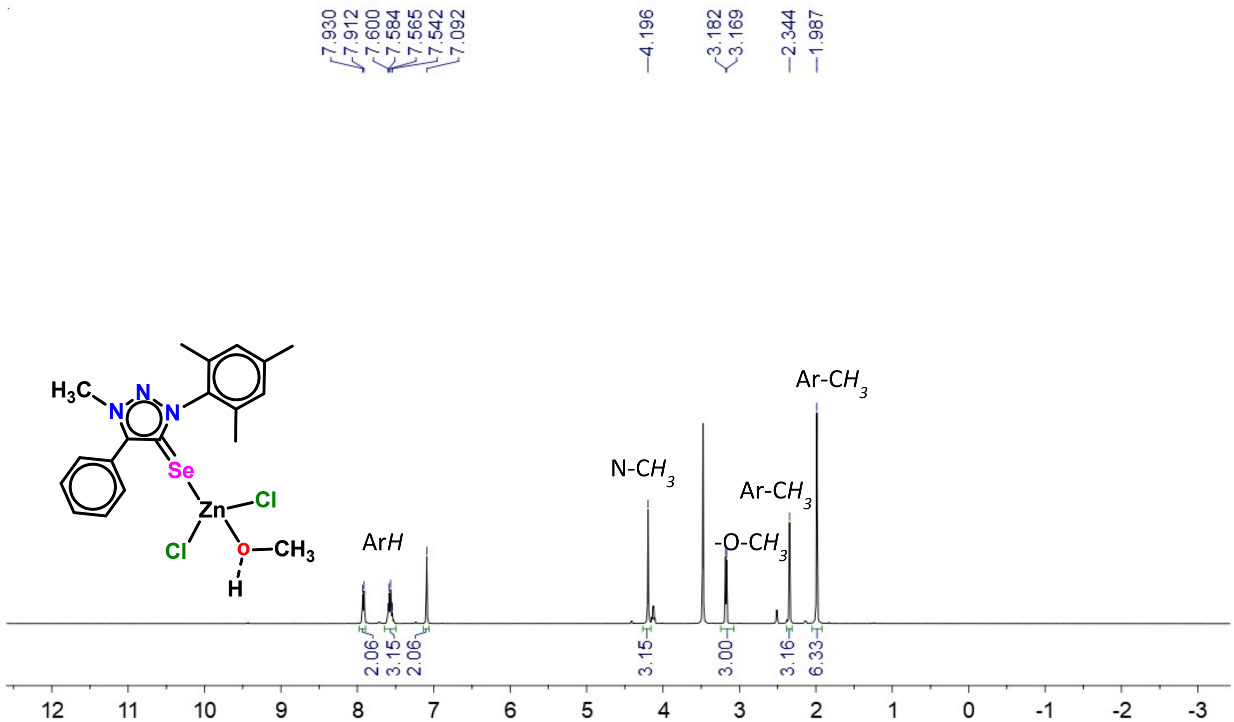


Fig. S11 [1]H NMR spectrum of complex **1** in DMSO-d_6

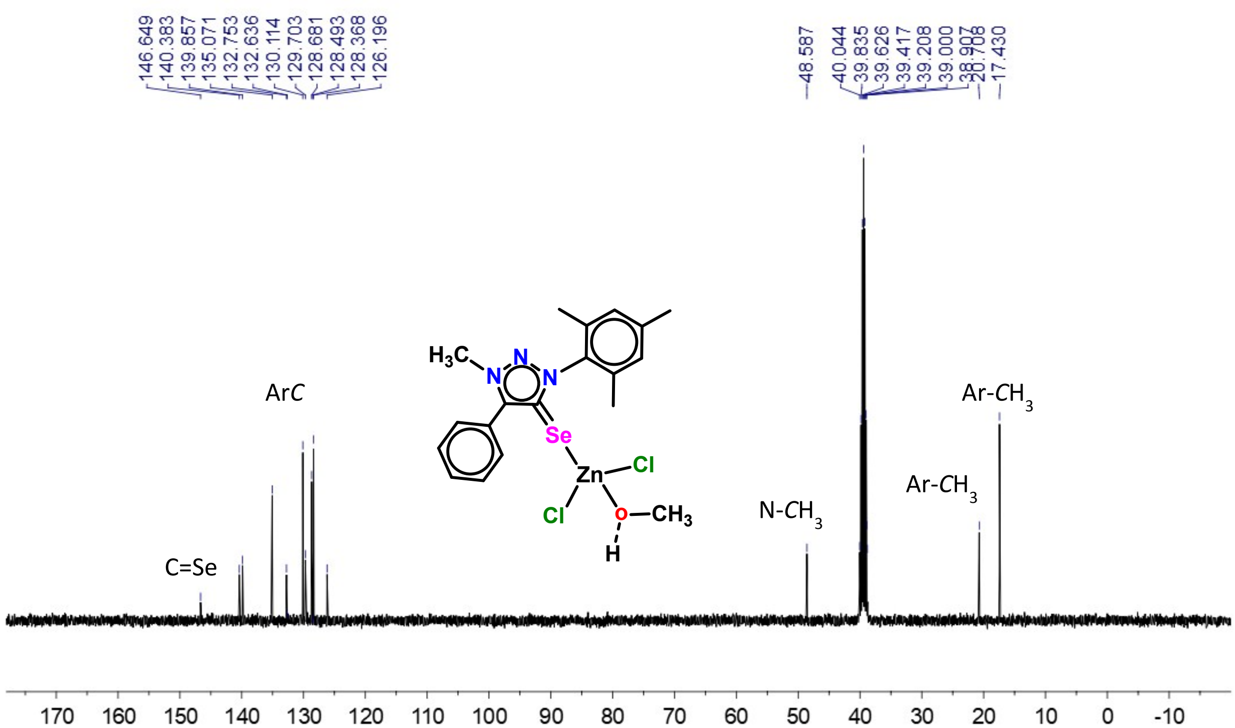


Fig. S12 [13] C NMR spectrum of complex **1** in DMSO-d_6

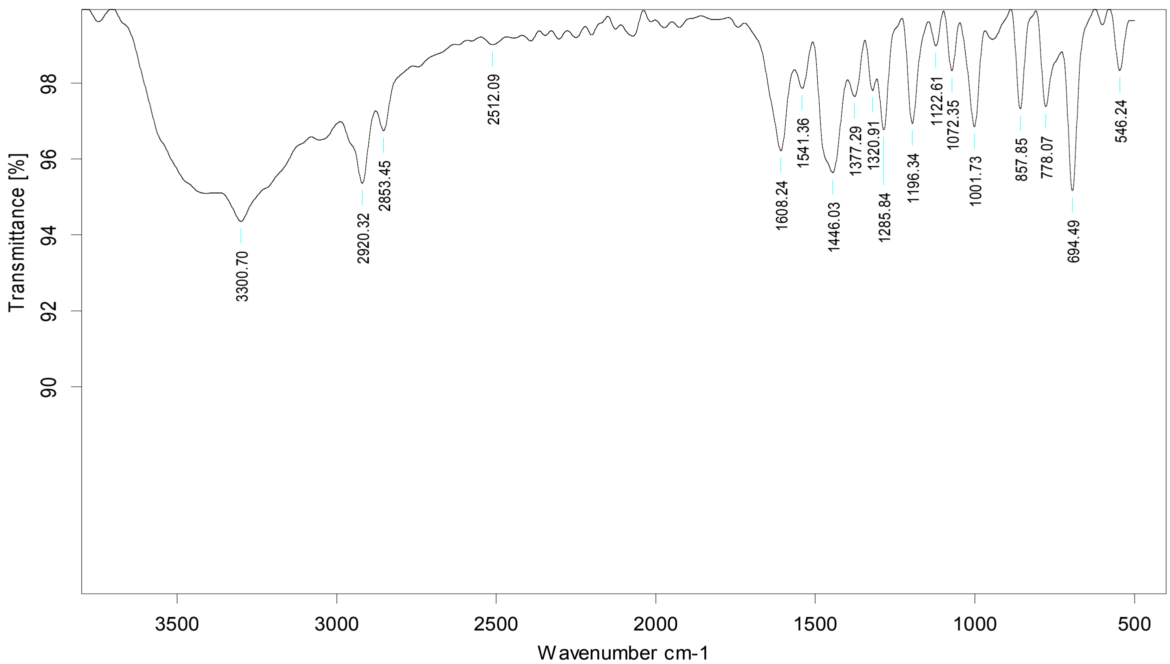


Fig. S13. Neat FT-IR spectrum of complex **1**

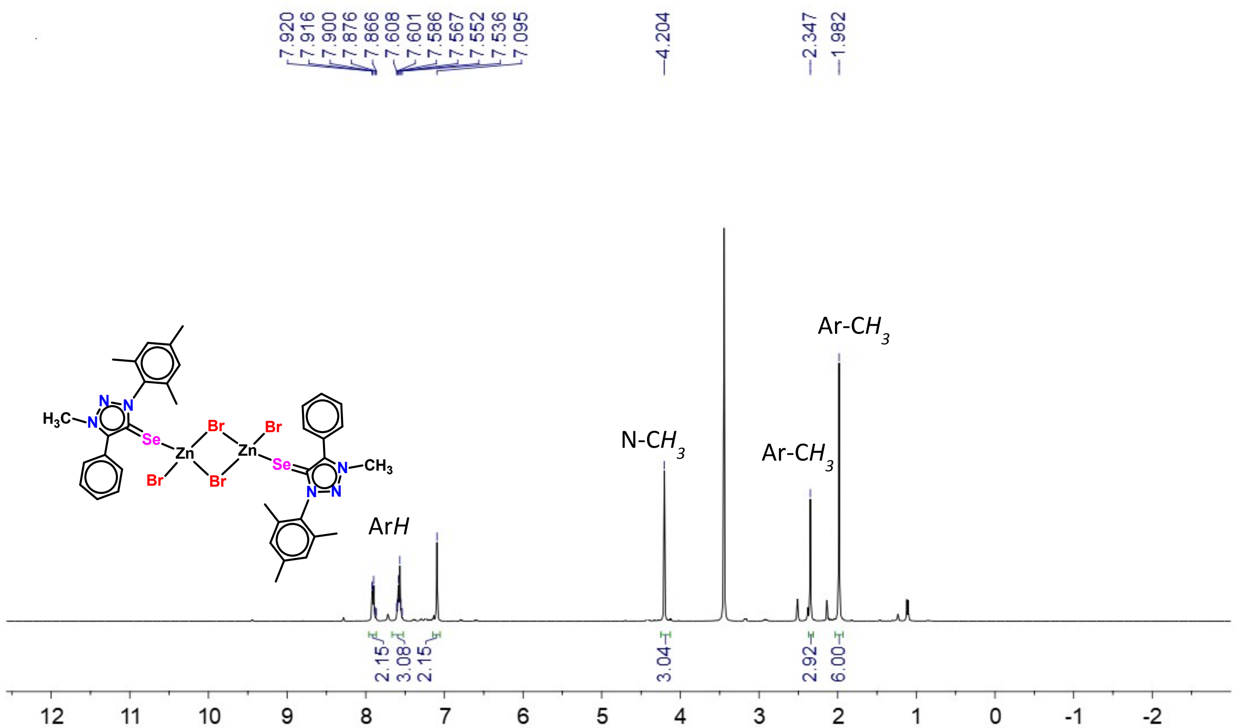


Fig. S14 ^{1}H NMR spectrum of complex **2** in DMSO-d_6

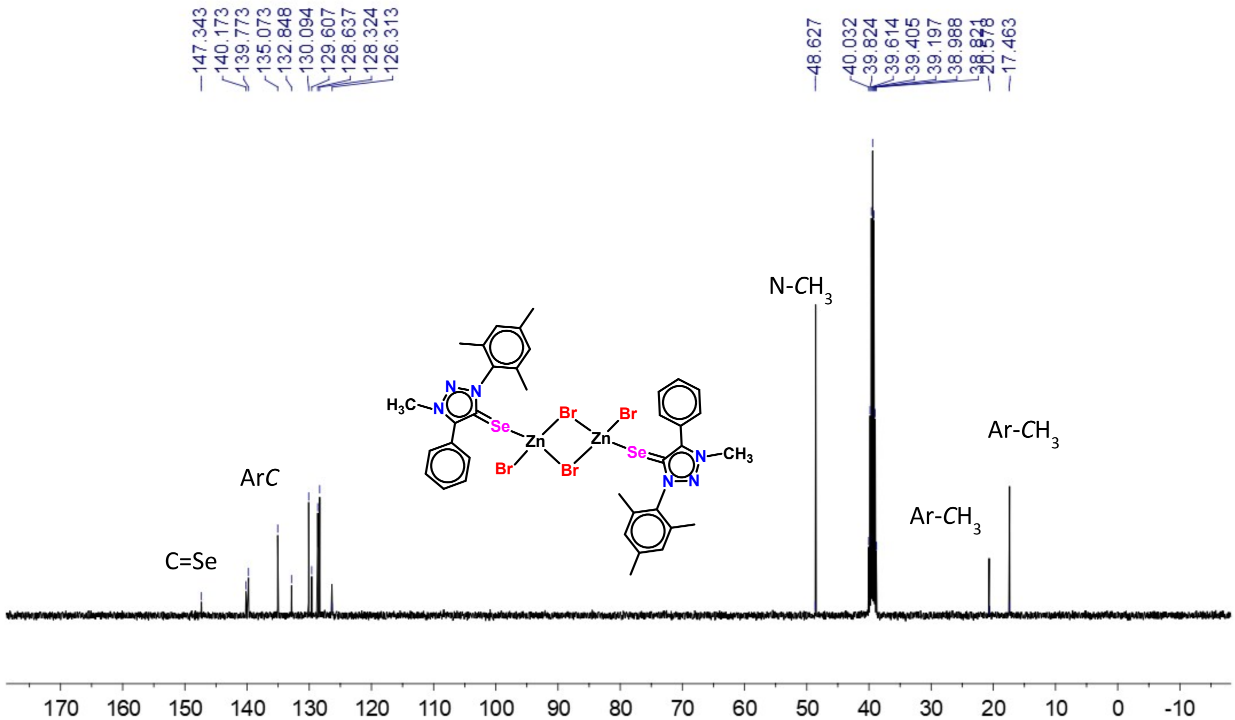


Fig. S15 ^{13}C NMR spectrum of complex **2** in DMSO-d_6

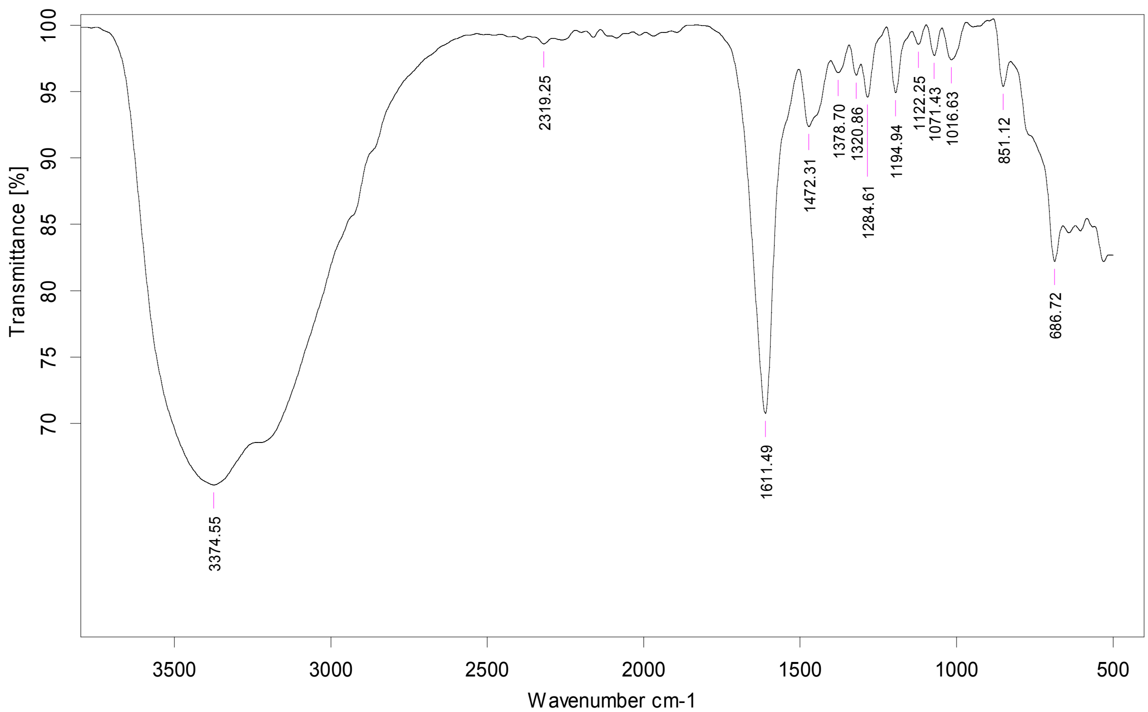


Fig. S16. Neat FT-IR spectrum of complex **2**

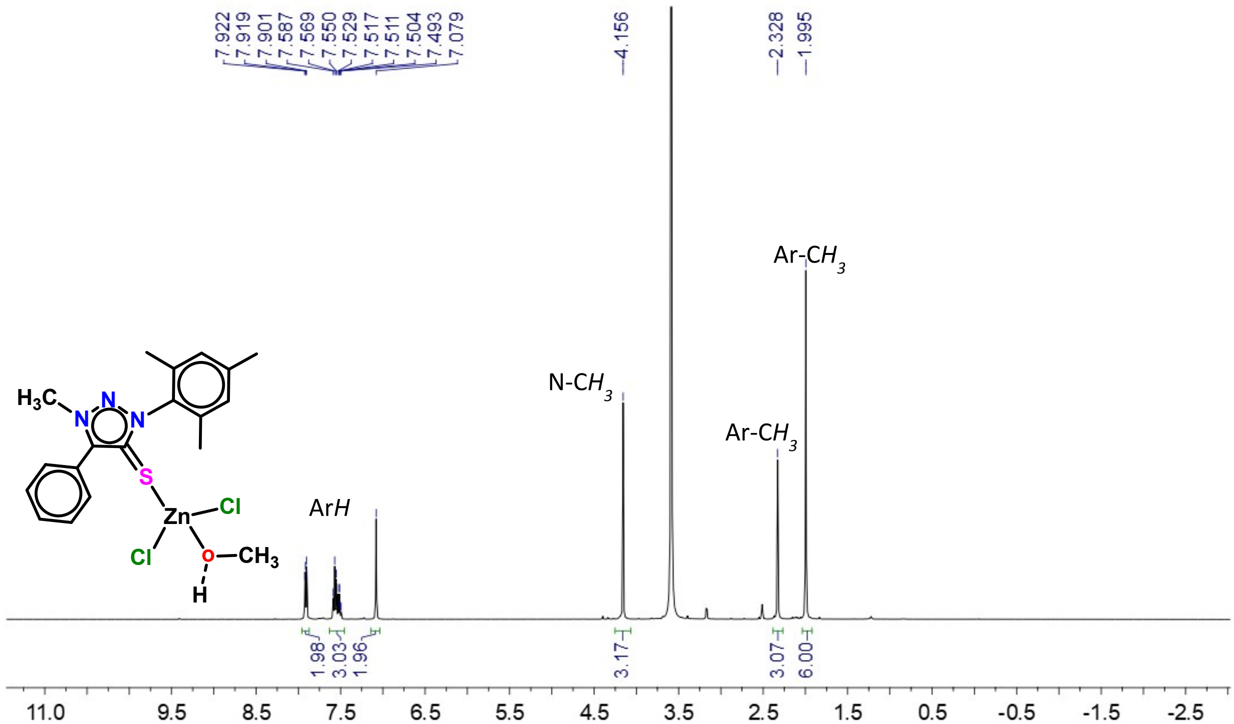


Fig. S17 ^{1}H NMR spectrum of complex **3** in DMSO-d_6

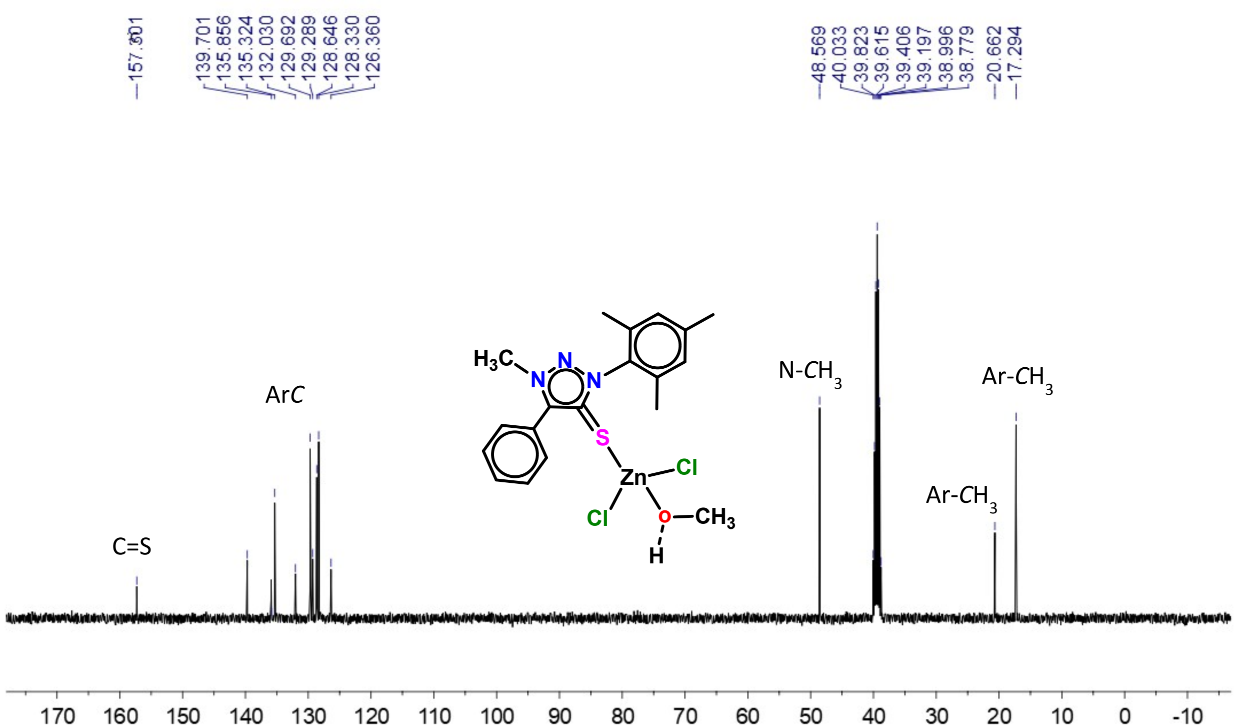


Fig. S18 ^{13}C NMR spectrum of complex **3** in DMSO-d_6

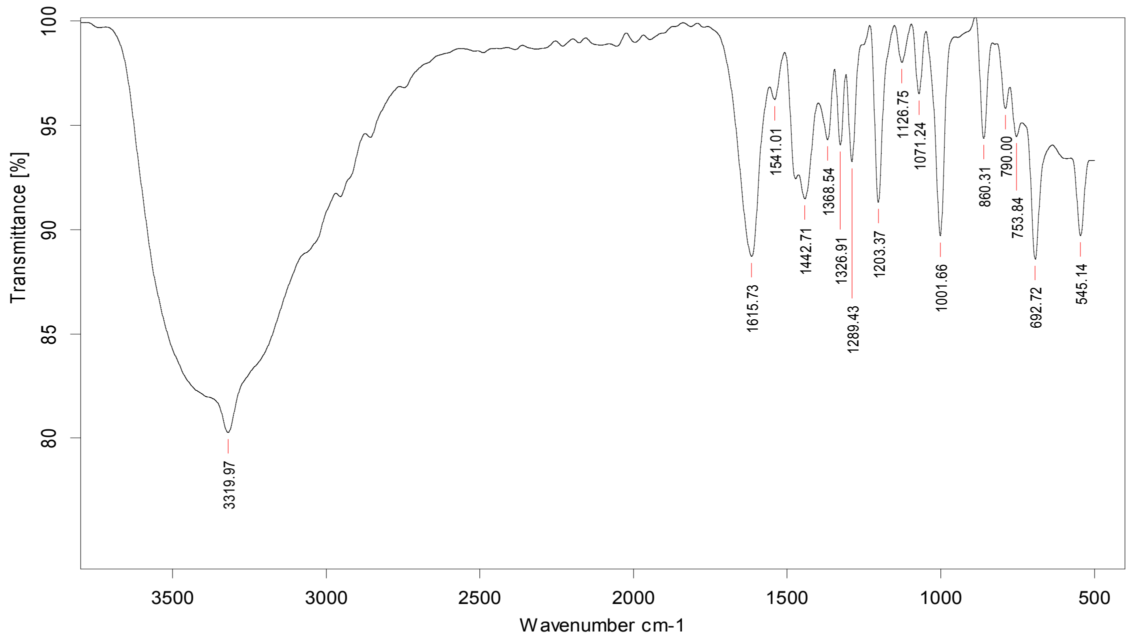


Fig.S19. Neat FT-IR spectrum of complex **3**

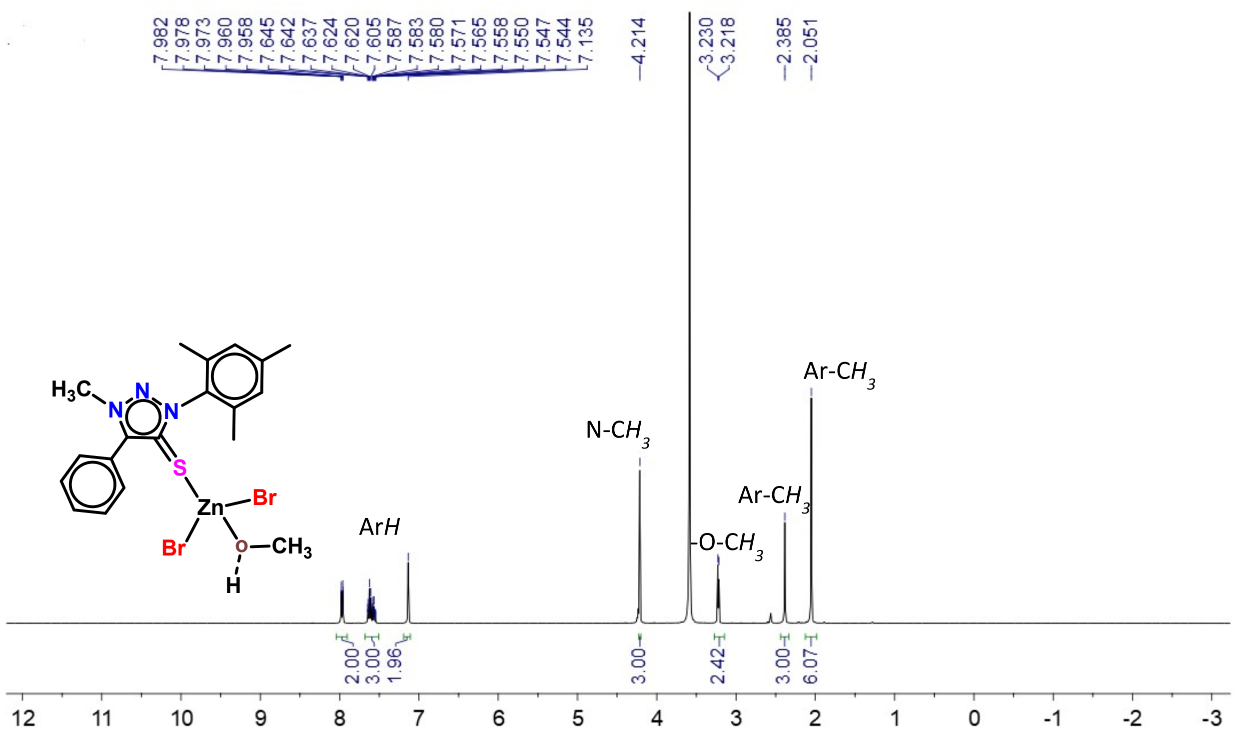


Fig. S20 [1]H NMR spectrum of complex **4** in DMSO-d_6

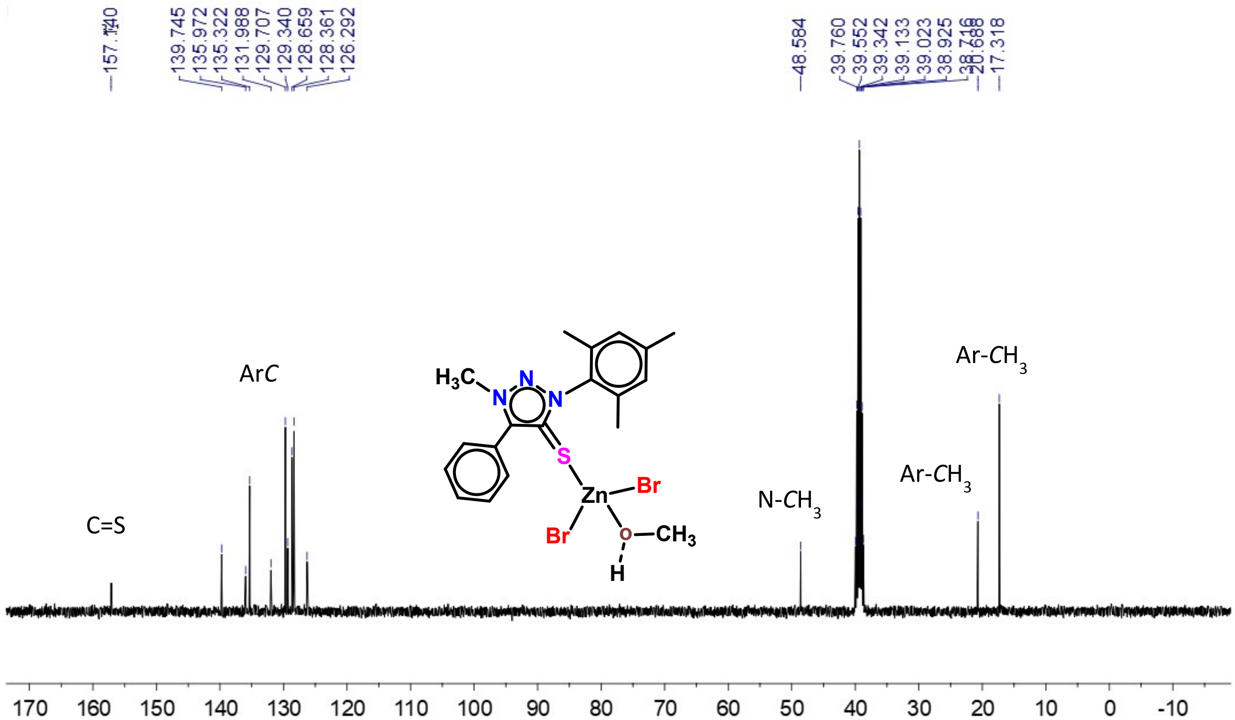


Fig. S21 ^{13}C NMR spectrum of complex **4** in DMSO-d_6

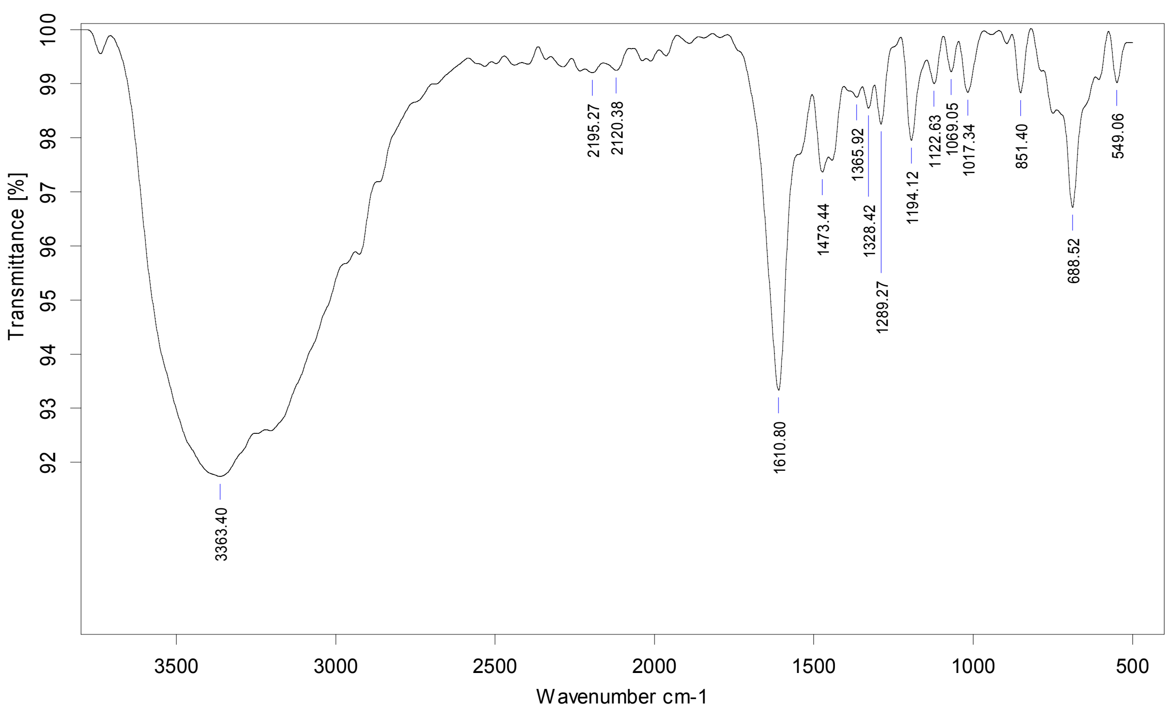


Fig. S22. Neat FT-IR spectrum of complex **4**

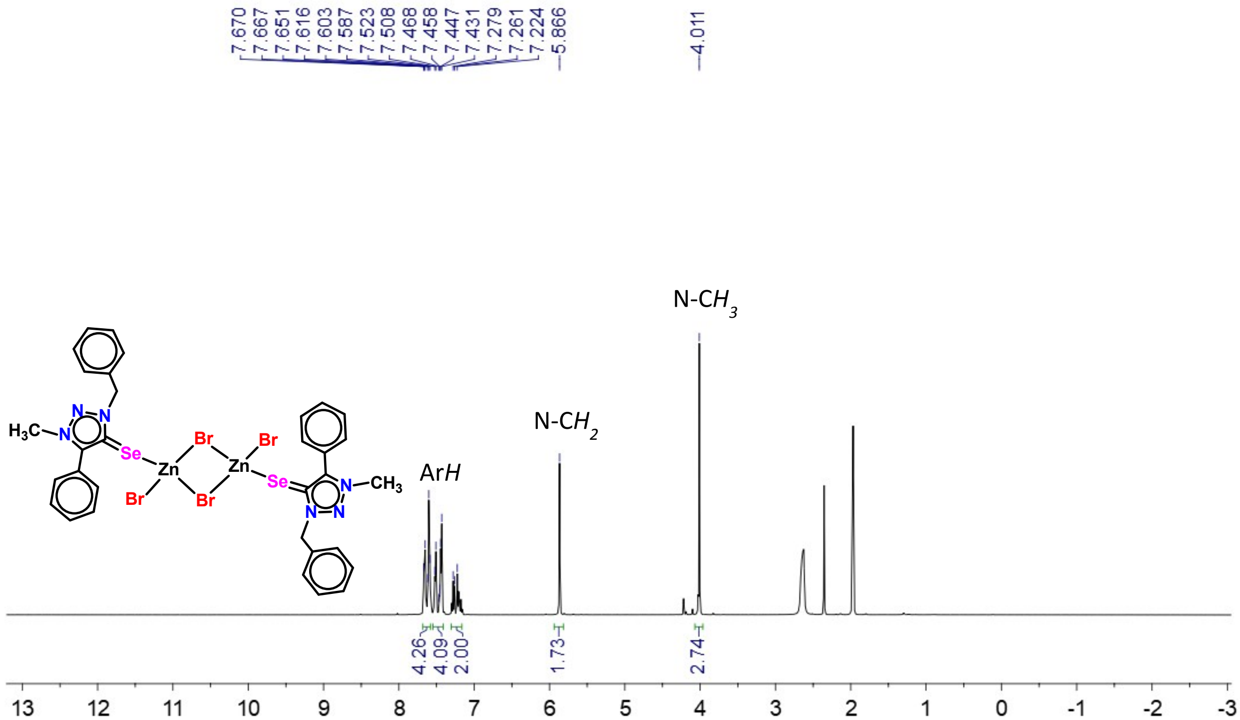


Fig. S23 ^{1}H NMR spectrum of complex **5** in CD_3CN

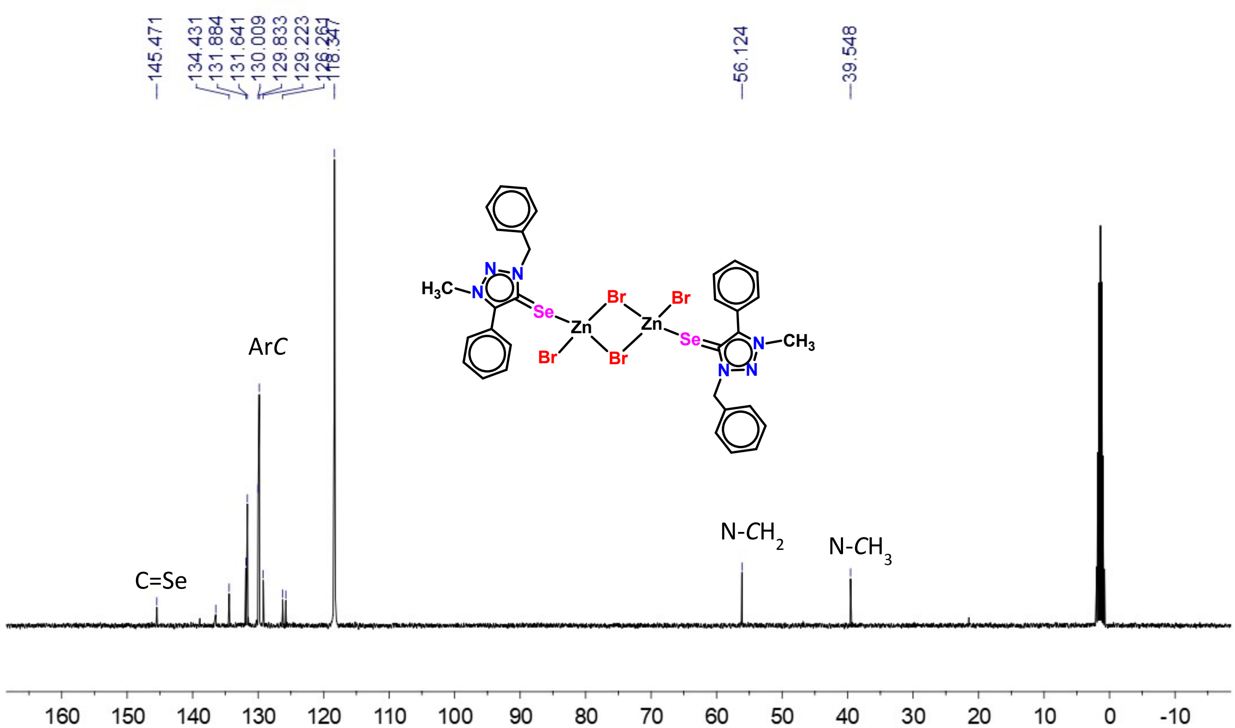


Fig. S24 ^{13}C NMR spectrum of complex **5** in CD_3CN

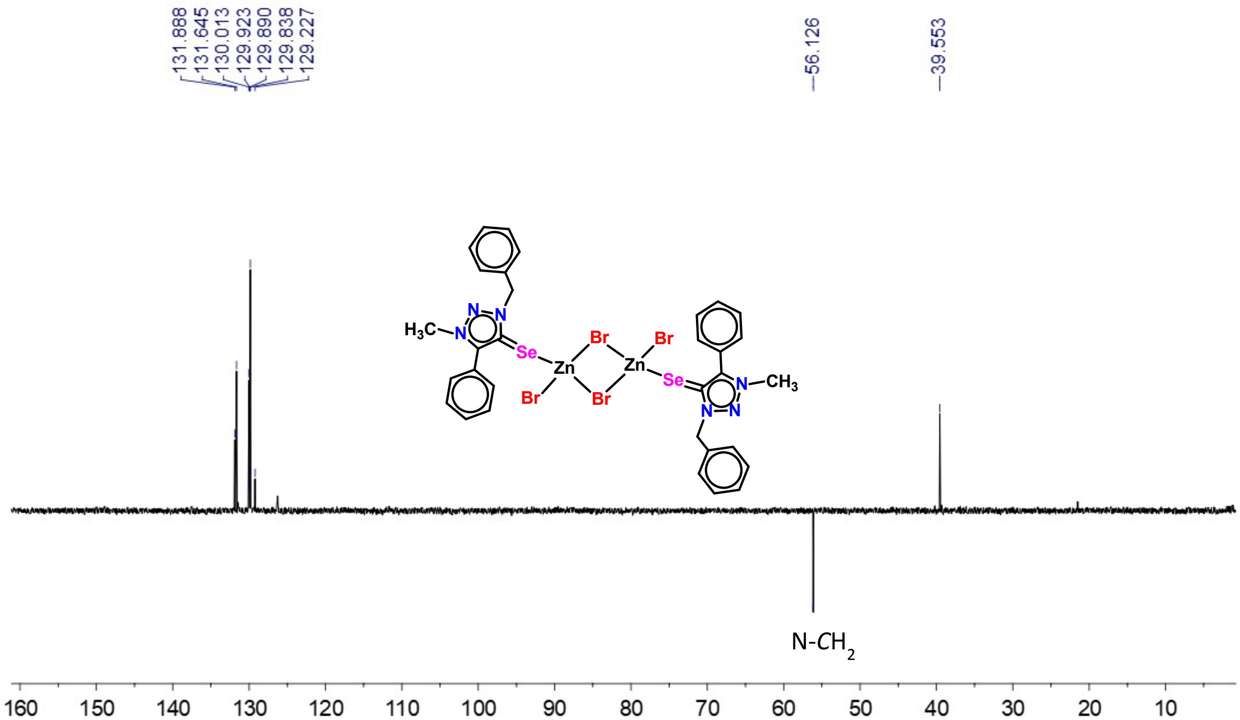


Fig. S25 DEPT NMR spectrum of complex **5** in CD_3CN

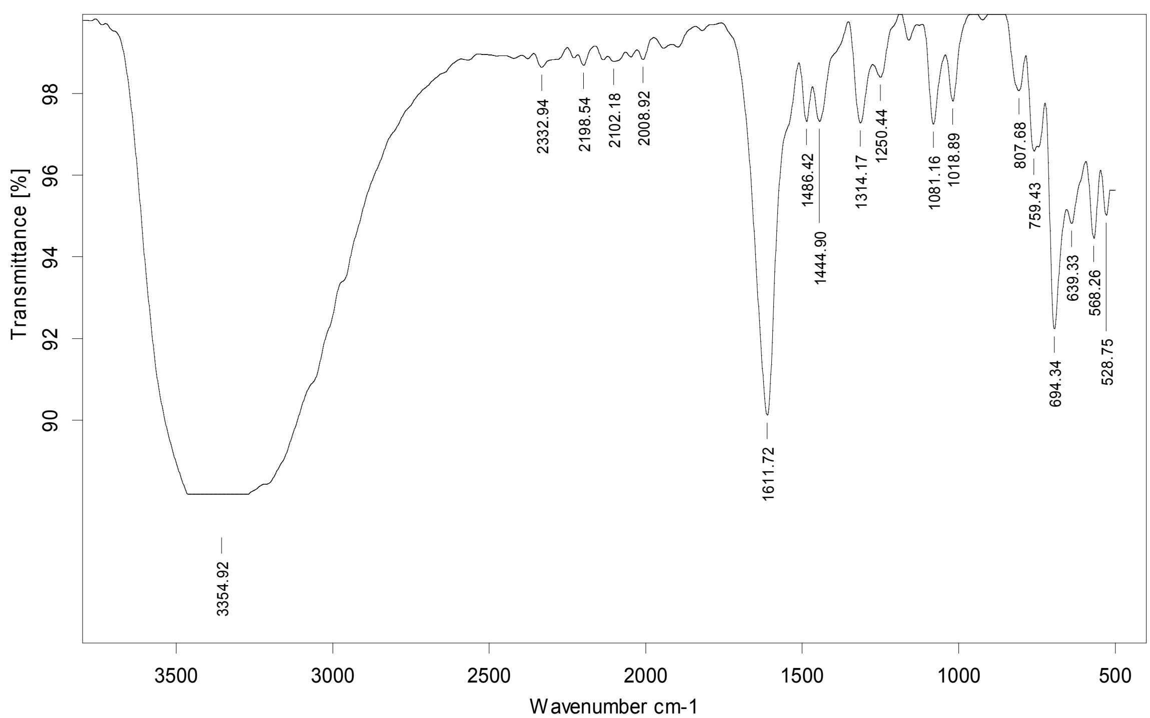
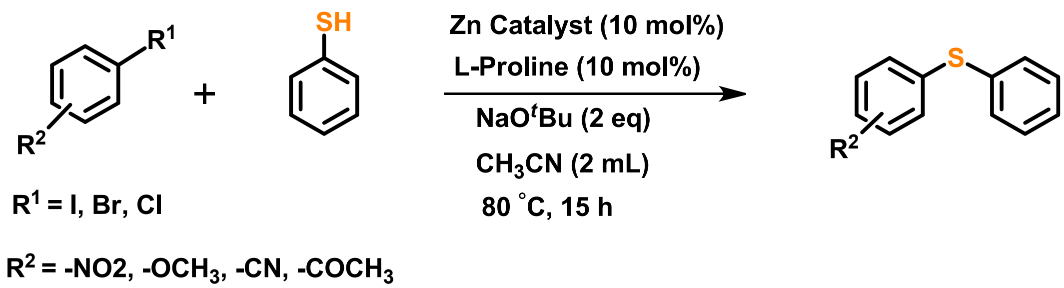
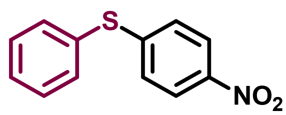


Fig. S26 Neat FT-IR spectrum of complex **5**

Zn Catalysed C-S cross coupling reactions

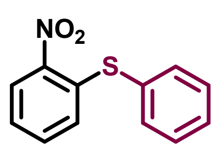


1. Compound characterisation data (1a):



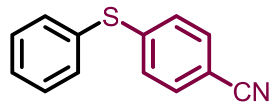
(4-nitrophenyl) (phenyl) sulfane : Chemical Formula: C12H9NO$_2$S; yellow Colour solid; Yield: 110 mg (95 %); **M. P**: 86-90 ° C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.06 (d, *J*=9.0 Hz, 2H, ArC*H*), 7.49 (m, 5H, ArC*H*) 7.17 (d, *J*=9.1 Hz, 2H, ArC*H*). **^{13}C NMR (CDCl$_3$, 100 MHz):** 148.72 (Ar*C*), 144.86 (Ar*C*), 135.06 (Ar*C*), 130.63 (Ar*C*), 129.98 (Ar*C*), 127.13 (Ar*C*), 126.48 (Ar*C*), 124.26 (Ar*C*). **FT-IR (neat, $\bar{\upsilon}$):** 1577(s), 1507(s), 1327(s), 1177(m), 1076(s), 1012(m), 840(s), 739(s), 685(s), 507(s).

2. Compound characterisation data (2a):



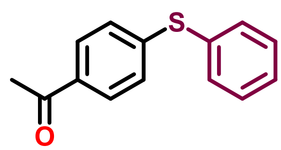
(3-nitrophenyl) (phenyl)sulfane: Chemical Formula: C12H9O$_2$NS; yellow Colour solid; Yield: 103 mg (83 %); **M. P**: 82-85 ° C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.20 (d, *J*= 8.2 Hz, 1H, ArC*H*), 7.44-7.58 (m, 5H, ArC*H*), 7.33 (t, *J*= 7.7 Hz, 1H, ArC*H*), 7.20 (t, *J*= 7.7 Hz, 1H, ArC*H*), 6.86 (d, *J*= 8.2 Hz, 1H, ArC*H*). **^{13}C NMR (CDCl$_3$, 100 MHz):** 145.00 (Ar*C*), 139.48 (Ar*C*), 135.91 (Ar*C*), 133.61 (Ar*C*), 131.17 (Ar*C*), 130.79 (Ar*C*), 130.16 (Ar*C*), 128.48 (Ar*C*), 125.84 (Ar*C*), 124.82(Ar*C*). **FT-IR (neat, $\bar{\upsilon}$):** 1583(s), 1510(s), 1447(m), 1333(s), 1299(m), 1165(w), 1104(s), 1043(s), 906(s), 851(m), 724(s), 485(s).

3. Compound characterisation data (3a):



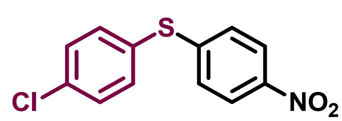
4-(phenylthio)benzonitrile : Chemical Formula: C13H9NS; Colourless solid; Yield: 135 mg (82 %); **M. P**: 80-83 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.60 (d, *J*=8.7 Hz, 1H, ArC*H*), 7.48-7.50 (m, 3H, ArC*H*), 7.38-7.44(m, 3H, ArC*H*), 7.15-7.20(m,2H, ArC*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** 144.96 (Ar*C*), 135.79 (Ar*C*), 135.56 (Ar*C*), 132.65 (Ar*C*), 130.06 (Ar*C*), 129.62 (Ar*C*), 127.57 (Ar*C*), 118.66 (Ar*C*), 109.05 (Ar*C*). **FT-IR (neat, $\bar{\upsilon}$):** 2217, 1581(s), 1470(s), 1389(m), 1180(m), 1078(s), 1006(m), 814(s), 740(m), 583(m), 537(m), 496(s).

4. Compound characterisation data(4a):



1-(4-Phenylsulfanylphenyl) ethanone: Chemical Formula: C14H12OS; Colourless solid; Yield: 95 mg (79 %); **M. P**: 69-72 ° C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.82 (d, *J*= 8.4 Hz, 2H, ArC*H*), 7.50 (m, 2H, ArC*H*), 7.40 (m, 3H, ArC*H*), 7.21 (d, *J*= 8.8 Hz, 2H, ArC*H*), 2.55 (s, 3H, Ar-CO-C*H₃*). **^{13}C NMR** (100MHz, CDCl3): δ 197.17 (Ar-*CO*), 144.89 (Ar*C*), 134.30 (Ar*C*), 133.91 (Ar*C*), 132.06 (Ar*C*), 129.70 (Ar*C*), 128.87 (Ar*C*), 127.45 (Ar*C*), 26.15 (Ar-CO-*C*H_3). **FT-IR (neat, $\bar{\upsilon}$):** 3337(w), 1678(s), 1585(s), 1474(w), 1398(w), 1358(m), 1264(s), 1090(m), 1016(s), 957(m), 821(m), 748(m), 692(m), 587(w).

5. Compound characterisation data (5a):



(4-chlorophenyl) (4-nitrophenyl) sulfane: Chemical Formula: C12H8NO_2SCl; Colourless solid; Yield: 120 mg (90 %); **M. P**: 90-93 ° C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.08 (d, *J*= 6.8 Hz, 2H, ArC*H*), 7.41-7.48 (m, 4H, ArC*H*), 7.18 (d, *J*=8.8 Hz, 2H, ArC*H*). **^{13}C NMR ($CDCl_3$, 100 MHz):** 147.65 (Ar*C*), 144.94 (Ar*C*), 136.08 (Ar*C*), 135.81 (Ar*C*), 130.49 (Ar*C*), 128.85 (Ar*C*), 126.61 (Ar*C*), 123.29 (Ar*C*). **FT-IR (neat, $\bar{\upsilon}$):** 1576(s), 1501(s), 1388(m), 1327(s), 1079(s), 1007(m), 834(m), 812(m), 737(s), 677(w), 533(w).

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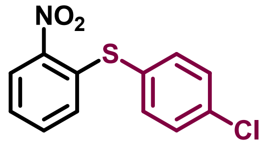
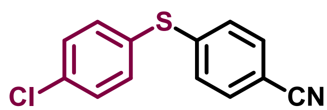


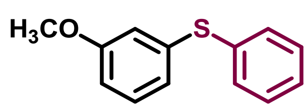
(4-chlorophenyl) (3-nitrophenyl) sulfane: Chemical Formula: $C_{12}H_8NO_2SCl$; yellow colour solid; Yield: 139 mg (80 %); **M. P**: 93-95 ^oC. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.23 (d, *J*= 8.2 Hz, & 1.5 Hz, 1H, ArC*H*), 7.45-7.53 (m, 2H, ArC*H*), 7.46(m, 2H, ArC*H*), 7.36 (dd, *J*= 8.3 Hz & 1.4Hz, 1H, ArC*H*), 7.25 (dd, *J*= 8.3 Hz & 1.2 Hz, 1H, ArC*H*), 6.86 (dd, *J*= 8.2 Hz & 1.2 Hz, 1H, ArC*H*). **^{13}C NMR (CDCl$_3$, 100 MHz):** 144.86 (Ar*C*), 138.56 (Ar*C*), 137.27 (Ar*C*), 136.36(Ar*C*), 133.76 (Ar*C*), 130.27 (Ar*C*), 129.79 (Ar*C*), 127.78 (Ar*C*), 125.85 (Ar*C*), 125.54 (Ar*C*). **FT-IR (neat, $\bar{\upsilon}$):** 1570(s), 1499(s), 1330(m), 1295(s), 1085(s), 815(m), 727(s), 490(m).

7. Compound characterisation data (7a):



4-((4-chlorophenyl) thio)benzonitrile: Chemical Formula: C13H8NSCl; Colourless solid; Yield: 158 mg (80 %); **M. P**: 88-92 ^{o} C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.42-7.50 (m, 6H, ArC*H*), 7.15 (d, *J*=8.7 Hz, 2H, ArC*H*). **^{13}C NMR (CDCl$_3$, 100 MHz):** 145.66 (Ar*C*), 134.13 (Ar*C*), 132.19 (Ar*C*), 129.96 (Ar*C*), 129.34 (Ar*C*), 118.59 (Ar*C*), 108.57 (Ar*C*). **FT-IR (neat, $\bar{\upsilon}$):** 2217, 1582(s), 1471(s), 1389(m), 1327(s), 1079(s), 1008(m), 815(s), 737(s), 539(m), 485(s).

8. Compound characterisation data (8a):



(3-methoxyphenyl) (phenyl)sulfane: Chemical Formula: $C_{13}H_{12}OS$; Colourless liquid; Yield: 80 mg (65%). **M. P**: 95-100 ^oC.**^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.18-7.36 (m, 6H, ArC*H*), 6.76-6.91 (m, 3H, ArC*H*), 3.71 (s, 3H, Ar-OC*H$_3$*). **^{13}C NMR (CDCl$_3$, 100 MHz):** 160.02 (Ar*C*), 137.25 (Ar*C*), 135.26 (Ar*C*), 131.44 (Ar*C*), 129.97 (Ar*C*), 129.25 (Ar*C*), 127.28 (Ar*C*), 122.96 (Ar*C*), 115.90 (Ar*C*), 112.80 (Ar*C*), 55.29 (Ar-O*C*H$_3$). **FT-IR (neat, $\bar{\upsilon}$):** 2922(m), 1580(s), 1470(s), 1283(m), 1236(s), 1179(m), 1035(s), 966(m), 852(s), 740(s), 685(s), 560(m), 502(s).

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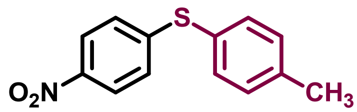

(4-nitrophenyl) (p-tolyl) sulfane: Chemical Formula: $C_{13}H_{11}NO_2S$; yellow colour liquid; Yield: 100 mg (81 %). **M. P**: 85-90 ° C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.96 (d, *J*= 9.1 Hz, 2H, ArC*H*), 7.49-7.29 (m, 2H, ArC*H*), 7.27-7.11 (m, 2H, ArC*H*), 7.09-6.97 (m, 2H, ArC*H*), 2.34 (s, 3H, Ar-C*H₃*). **^{13}C NMR ($CDCl_3$, 100 MHz):** 148.60 (Ar*C*), 143.81 (Ar*C*), 138.45 (Ar*C*), 134.05 (Ar*C*), 131.59 (Ar*C*), 129.59 (Ar*C*), 128.85 (Ar*C*), 125.46 (Ar*C*), 123.87 (Ar*C*), 122.85 (Ar*C*), 20.31(Ar*C*H_3). **FT-IR (neat, $\bar{\upsilon}$):** 2894(m), 2818(m), 2231(w), 1563(s), 1495(s), 1456(w), 1321(s), 1263(m), 1072(m), 1009(m), 895(s), 836(m).

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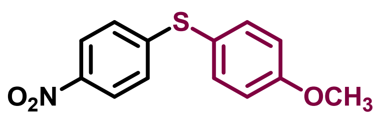
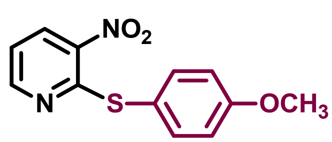


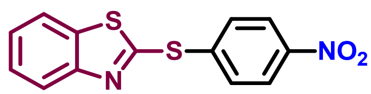
(4-methoxyphenyl) (4-nitrophenyl) sulfane: Chemical Formula: $C_{13}H_{11}NO_3S$; yellow colour solid; Yield: 92 mg (70 %); **M. P**: 82-85 ° C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.04 (d, *J*= 9.1 Hz 2H), 7.57-7.44 (m, 2H), 6.98-7.17 (m, 4H, ArC*H*), 3.82 (s, 3H, Ar-O-CH_3).**^{13}C NMR ($CDCl_3$, 100 MHz):** 159.73 (Ar*C*), 147.98 (Ar*C*), 145.17 (Ar*C*), 136.87 (Ar*C*), 132.01 (Ar*C*), 126.15 (Ar*C*), 123.86 (Ar*C*), 121.68 (Ar*C*), 117.64 (Ar*C*), 111.80 (Ar*C*), 55.98 (Ar-O-*C*H_3). **FT-IR (neat, $\bar{\upsilon}$):** 2892(s), 2822(m), 1561(s), 1493(s), 1452(s), 1317(s), 1259(s), 1230(m), 1061(s), 1005(s), 833(s).

11. Compound characterisation data (11a):



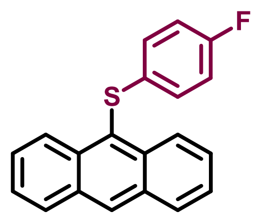
2-((4-methoxyphenyl) thio)-3-nitropyridine: Chemical Formula: C12H10N_2O_3S; yellow Colour solid; Yield: 96 mg (62 %); **M. P**: 138-140 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.84(dd, *J*= 6.8 Hz &1.3 Hz, 2H, ArC*H*), 7.51-7.57 (m, 3H, ArC*H*), 7.05 (m, 2H, ArC*H*), 4.18 (s, 3H, Ar-OCH_3). **^{13}C NMR ($CDCl_3$, 100 MHz):** 158.88 (Ar*C*), 140.57 (Ar*C*), 137.25 (Ar*C*), 135.54 (Ar*C*), 131.87 (Ar*C*), 129.88 (Ar*C*), 129.79 (Ar*C*), 128.93 (Ar*C*), 126.07, 60.41 (Ar O*C*H_3). **FT-IR (neat, $\bar{\upsilon}$):** 2920(s), 2854(m), 1706(s), 1580(m), 1458(s), 1338(s), 1286(s), 1175(s), 1120(m), 1071(m), 1025(m), 966(m), 852(s), 740(m), 696(s), 614(m), 547(m), 511(m).

12. Compound characterisation data (12a):



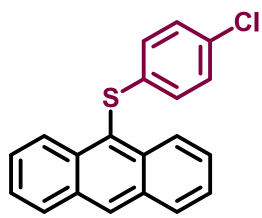
2-((4-nitrophenyl)thio)-1,3-benzothiazole: Chemical Formula: $C_{13}H_8N_2O_2S_2$; Colourless solid; Yield: 145 mg (86 %); **M. P**: 85-90 ^{o} C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.09 (d, *J*=9.6 Hz, 2H, ArC*H*), 7.41-7.49 (m, 4H, ArC*H*), 7.17-7.20 (m, 2H, ArC*H*). **^{13}C NMR (CDCl$_3$, 100 MHz):** 162.78 (Ar*C*), 153.41 (Ar*C*), 140.09 (Ar*C*), 136.22 (Ar*C*), 132.68 (Ar*C*), 131.14 (Ar*C*), 126.69 (Ar*C*), 125.57 (Ar*C*), 124.65 (Ar*C*), 122.84 (Ar*C*), 121.20 (Ar*C*). **FT-IR (neat, $\bar{\upsilon}$):** 1570(s), 1502(s), 1388(m), 1329(s), 1080(s), 1009(m), 844(m), 814(m), 738(s), 504(w).

13. Compound characterisation data (13a):



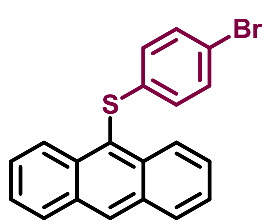
anthracen-9-yl(4-fluorophenyl) sulfane: Chemical Formula: $C_{20}H_{13}FS$; light yellow solid; Yield: 80 mg (72 %); **M. P**: 152-155 ^{o} C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.61- 8.77 (m, 3H, ArC*H*), 8.06 (d, *J*= 9.7 Hz, 2H, ArC*H*), 7.50-7.57 (m, 4H, ArC*H*), 7.04 (d, *J*= 8.7 Hz, 2H, ArC*H*), 6.83 (m, 2H, ArC*H*). **^{13}C NMR (CDCl$_3$, 100 MHz):** 139.49 (Ar*C*), 137.30 (Ar*C*), 134.90 (Ar*C*), 132.00 (Ar*C*), 130.73 (Ar*C*), 129.03 (Ar*C*), 128.99 (Ar*C*), 127.49 (Ar*C*), 126.58 (Ar*C*), 125.67 (Ar*C*), 124.70 (Ar*C*). **FT-IR (neat, $\bar{\upsilon}$):** 3019(m), 2893(s), 2838(m), 1706(s), 1655(m), 1542(w), 1453(s), 1371(s), 1292(s), 1204(s), 1157(s), 1071(s), 996(s), 939(s), 884(s), 8338(m).

14. Compound characterisation data (14a):



anthracen-9-yl(4-chlorophenyl) sulfane: Chemical Formula: $C_{20}H_{13}ClS$; light yellow solid; Yield: 92 mg (74 %); **M. P**: 158-162 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.61- 8.78 (m, 3H, ArC*H*), 8.07 (d, *J*= 8.0 Hz, 2H, ArC*H*), 7.50-7.58 (m, 4H, ArC*H*), 7.05 (d, *J*= 8.7 Hz, 2H, ArC*H*), 6.85 (d, *J*= 8.7 Hz, 2H, ArC*H*). **^{13}C NMR (CDCl$_3$, 100 MHz):** 137.35 (Ar*C*), 137.30 (Ar*C*), 137.17 (Ar*C*), 134.90 (Ar*C*), 132.00 (Ar*C*), 130.73 (Ar*C*), 130.53 (Ar*C*), 129.03 (Ar*C*), 127.66(Ar*C*), 127.49 (Ar*C*), 126.58(Ar*C*), 125.67 (Ar*C*), 124.59 (Ar*C*). **FT-IR (neat, $\bar{\upsilon}$):** 3018(w), 2925(s), 2835(m), 1707(s), 1501(m), 1452(w), 1369(s), 1263(s), 1165(s), 1070(s), 1003(m), 939(s), 895(s).

15. Compound characterisation data (15a):



anthracen-9-yl(4-bromophenyl) sulfane: Chemical Formula: $C_{20}H_{13}BrS$; light yellow solid; Yield: 100 mg (70 %); **M. P**: 160-163 ^{o}C. **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 8.60- 8.76 (m, 3H, ArC*H*), 8.07 (d, *J*= 9.7 Hz, 2H, ArC*H*), 7.50-7.58 (m, 4H, ArC*H*), 7.06 (d, *J*= 8.7 Hz, 2H, ArC*H*), 6.84 (m, 2H, ArC*H*).**^{13}C NMR (CDCl$_3$, 100 MHz):** 134.89, 131.99, 130.89, 130.53, 129.02, 128.98, 128.81, 127.48, 126.57, 125.67. **FT-IR (neat, $\bar{\upsilon}$):** 3019(m), 2893(s), 2333(m), 1655(m), 1606(w), 15401(w), 1453(s), 1371(s), 1292(s), 1204(s), 1157(s), 1071(s), 996(s), 939(s), 884(s), 838(m).

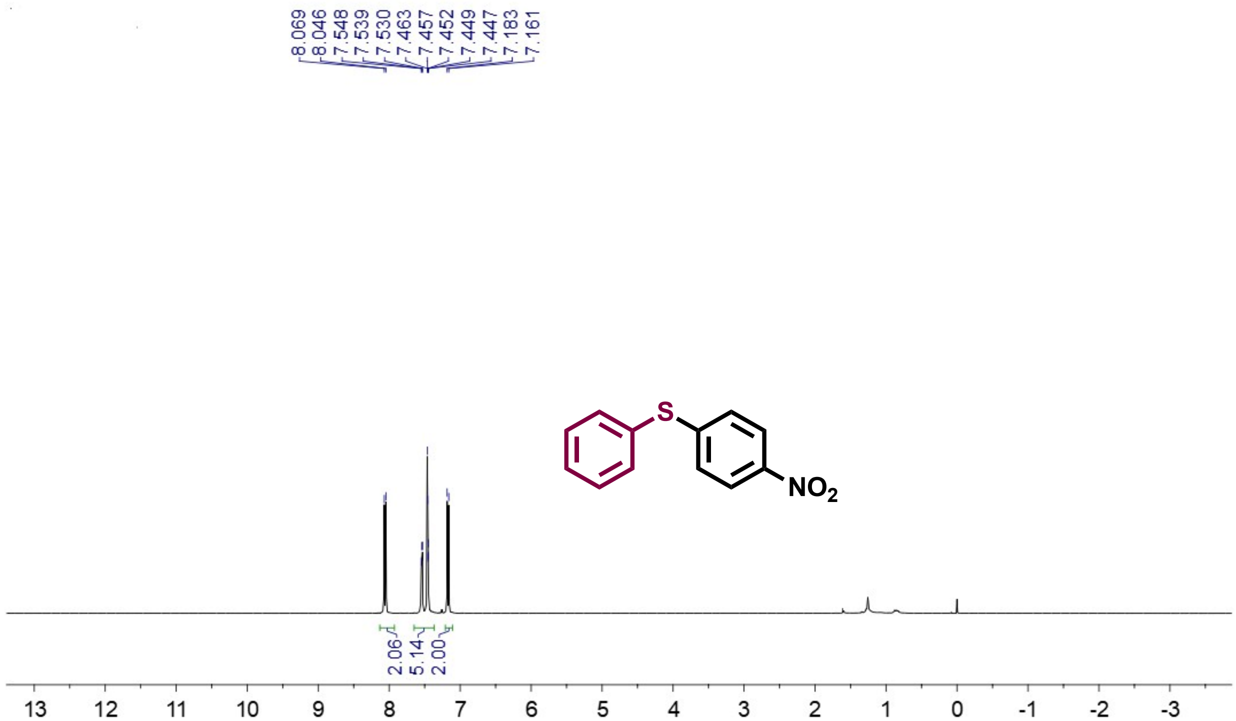


Fig. S27 ^{1}H NMR spectrum of compound **1a** in $CDCl_3$

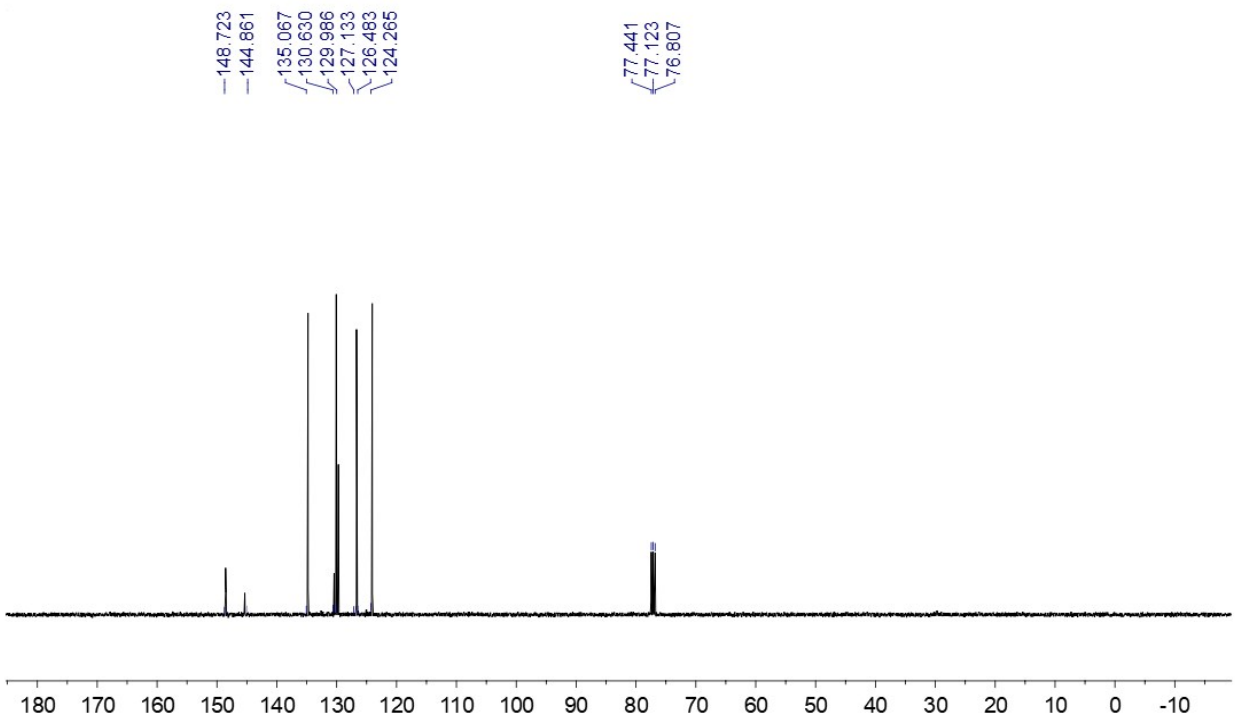


Fig. S28 ^{13}C NMR spectrum of compound **1a** in $CDCl_3$

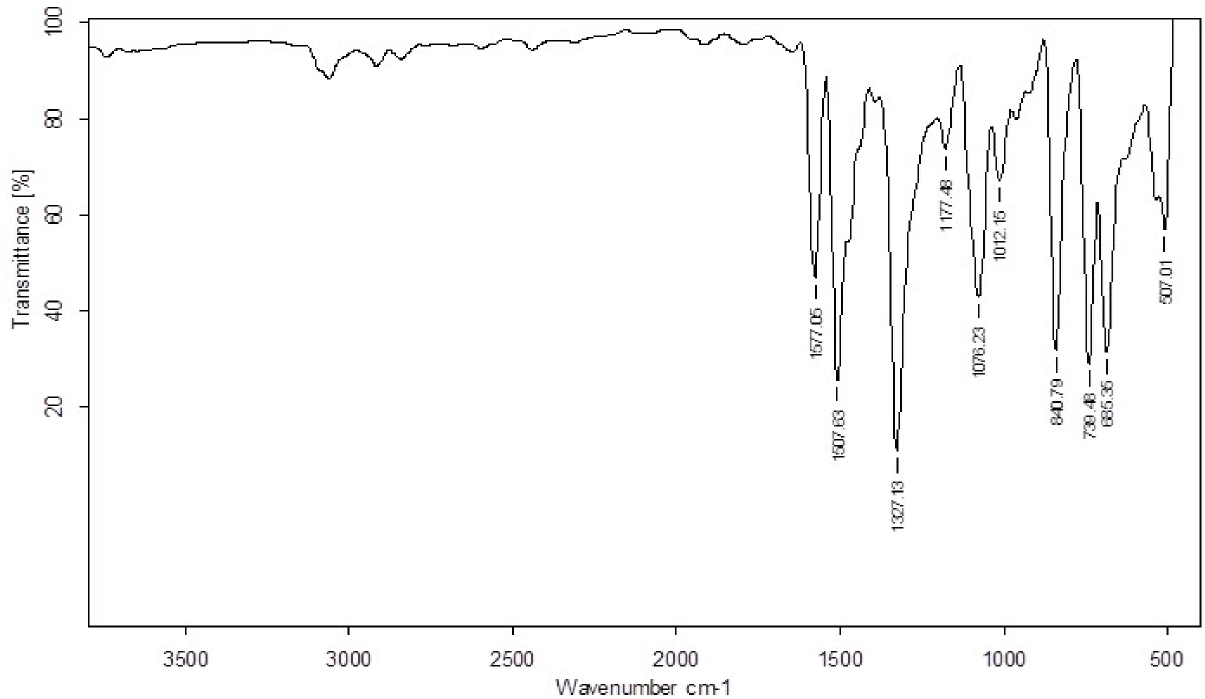


Fig. S29. Neat FT-IR spectrum of complex **1a**

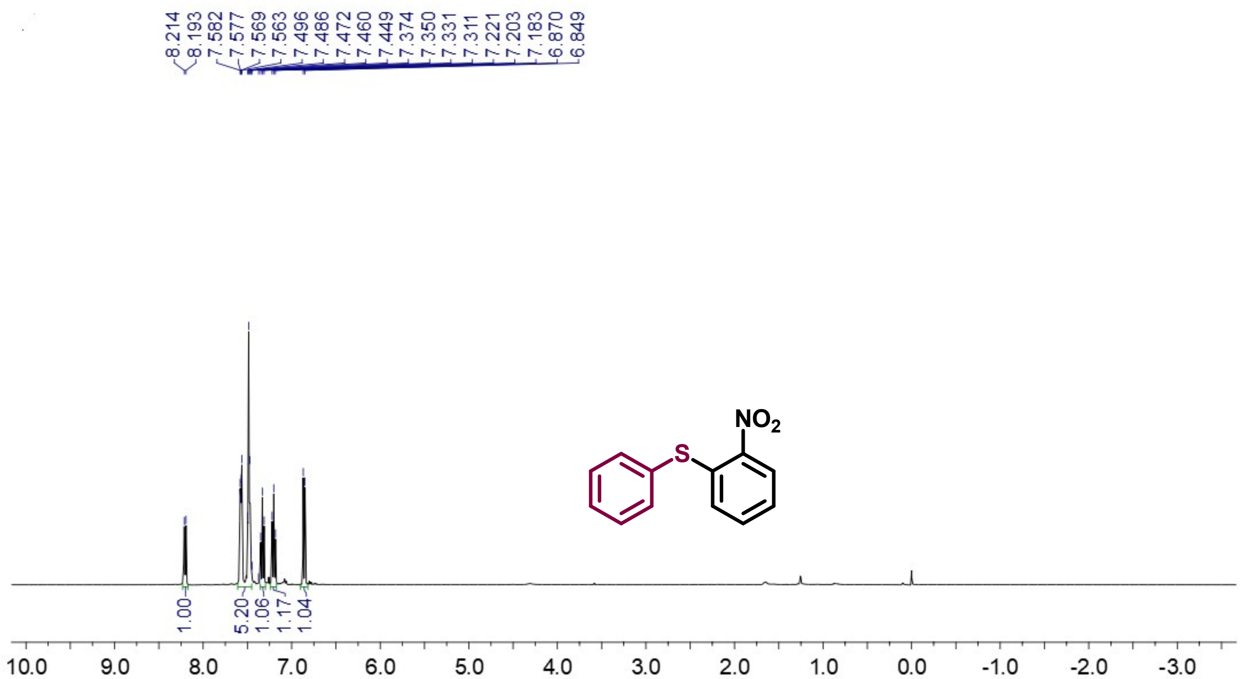


Fig. S30 ^{1}H NMR spectrum of compound **2a** in $CDCl_3$

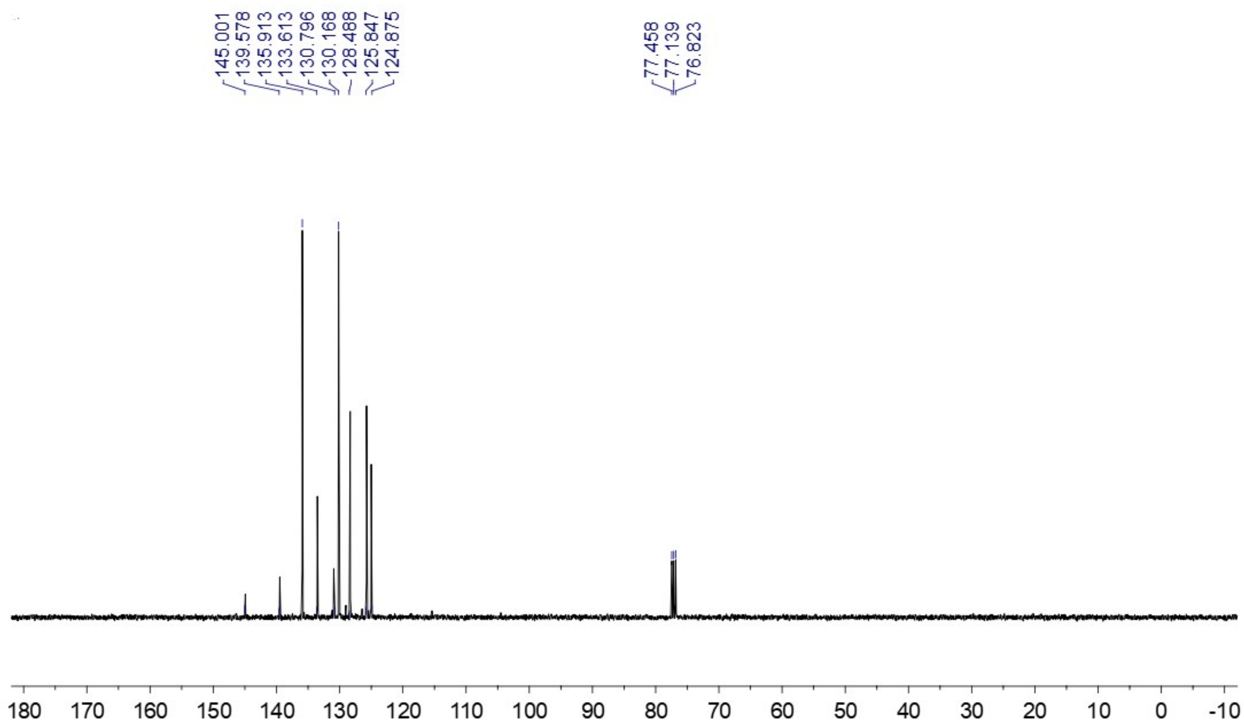


Fig. S31 ^{13}C NMR spectrum of compound **2a** in $CDCl_3$

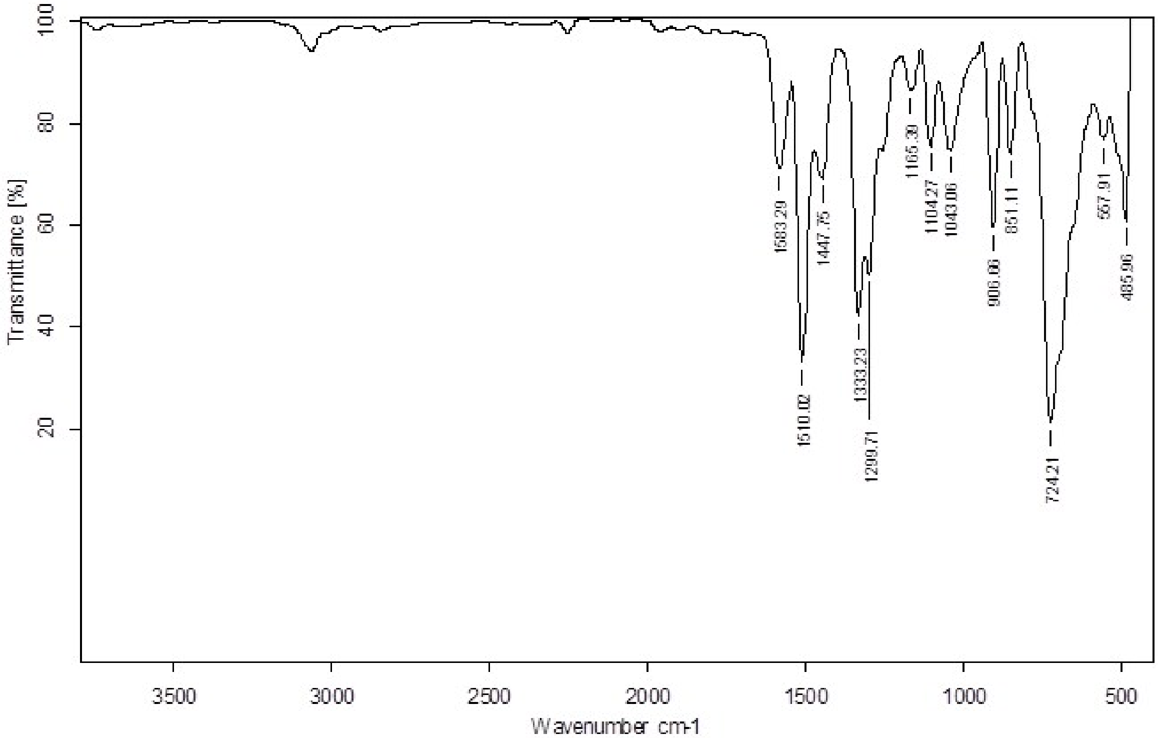


Fig. S32. Neat FT-IR spectrum of compound **2a**

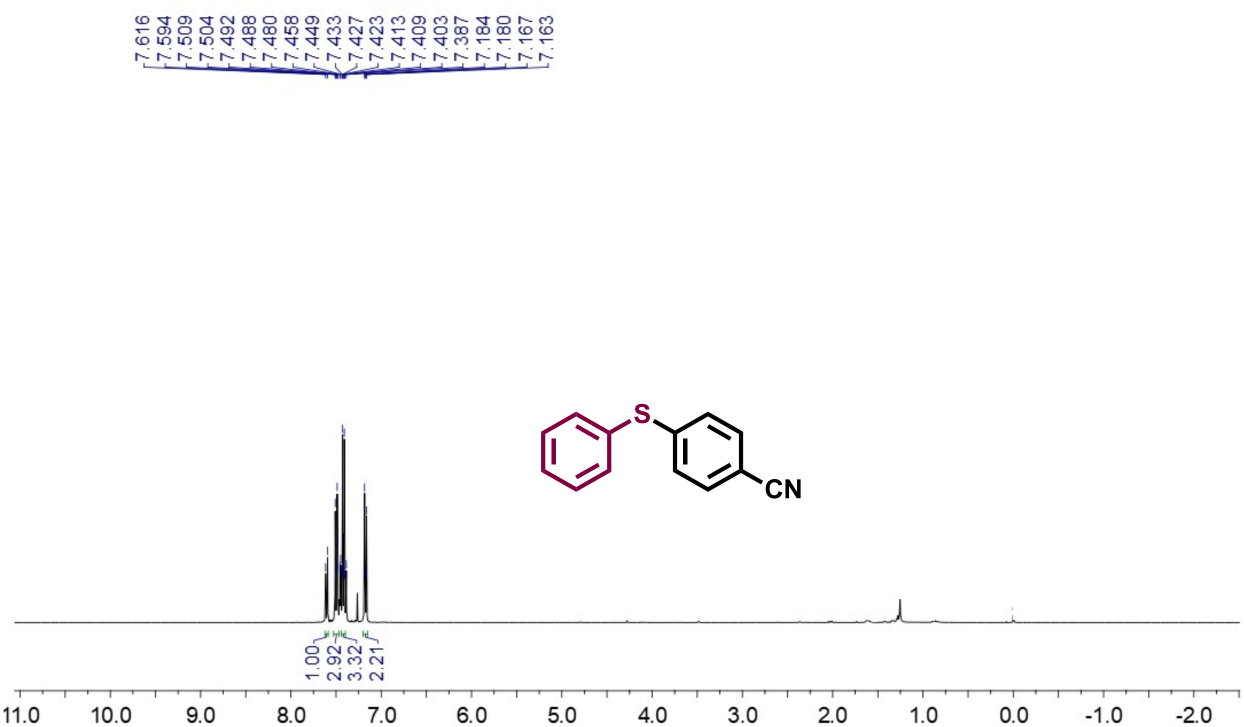


Fig. S33 ^{1}H NMR spectrum of compound **3a** in $CDCl_3$

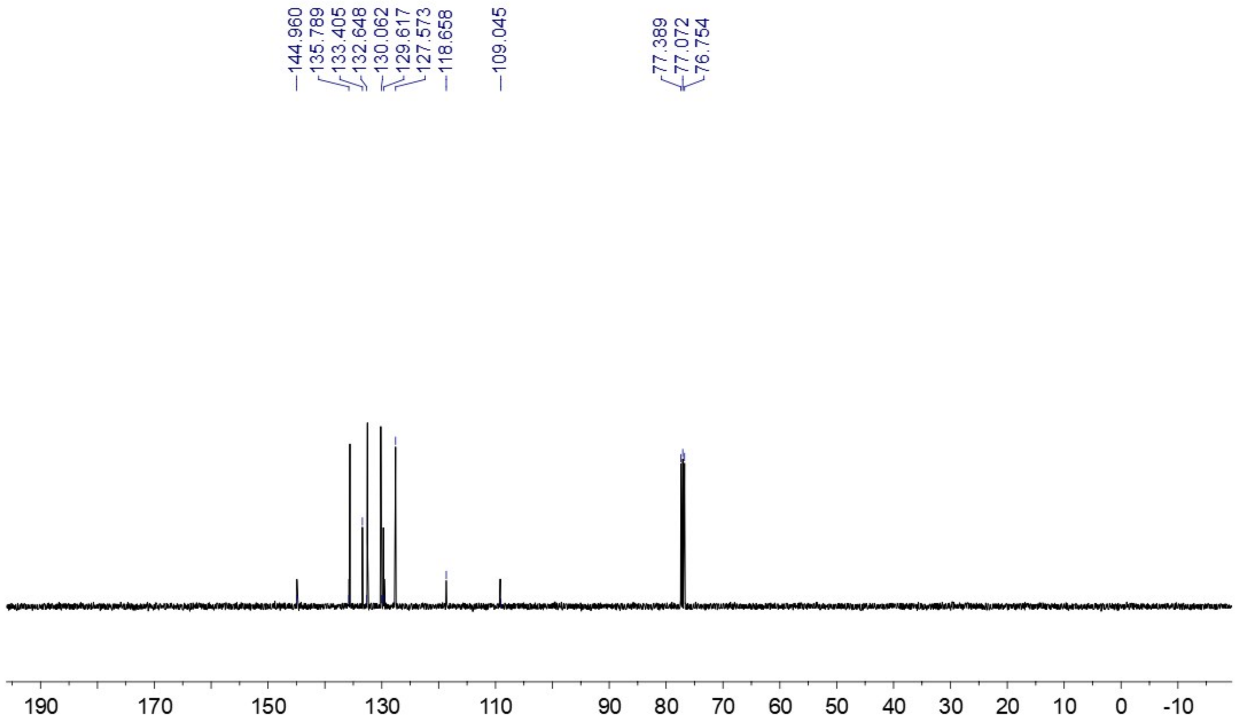


Fig. S34 ^{13}C NMR spectrum of compound **3a** in $CDCl_3$

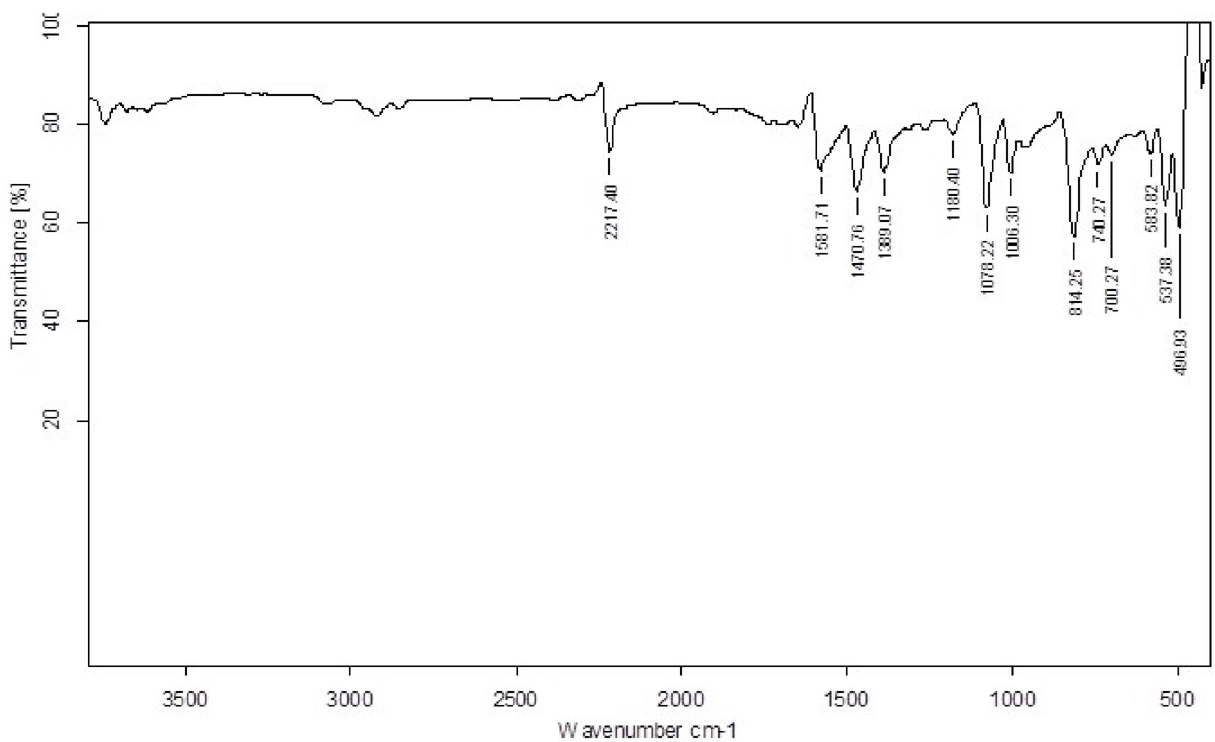


Fig. S35. Neat FT-IR spectrum of compound **3a**

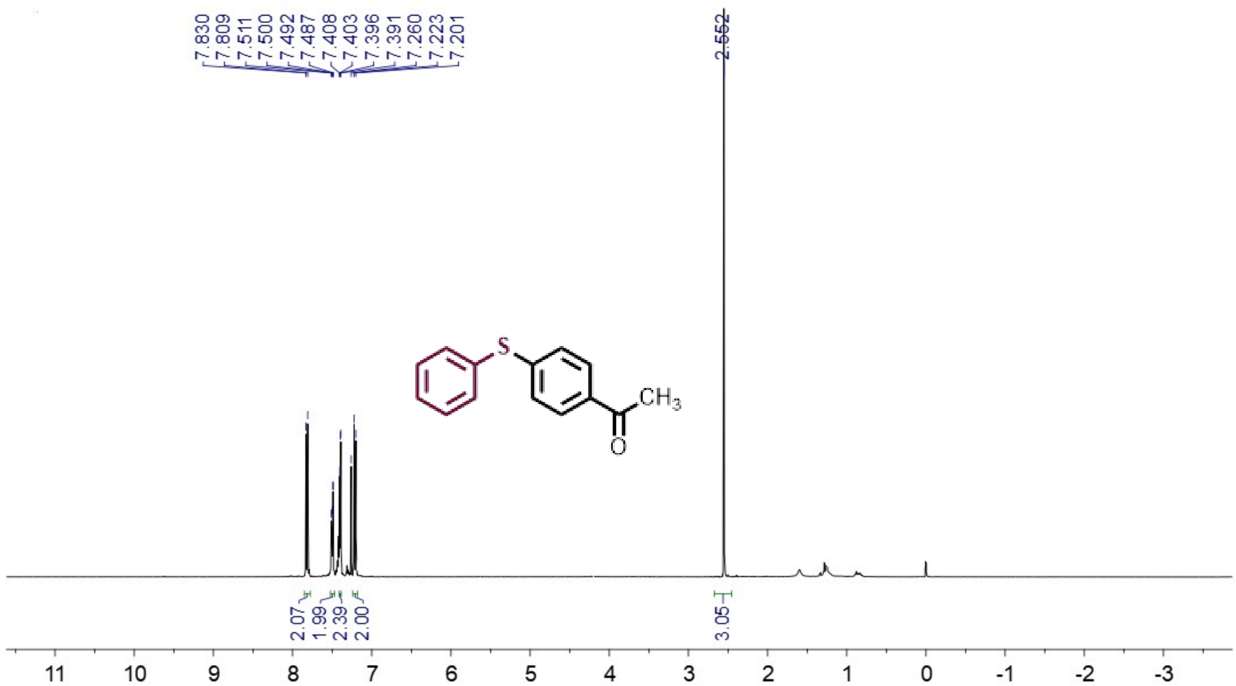


Fig. S36 ^{1}H NMR spectrum of compound **4a** in $CDCl_3$

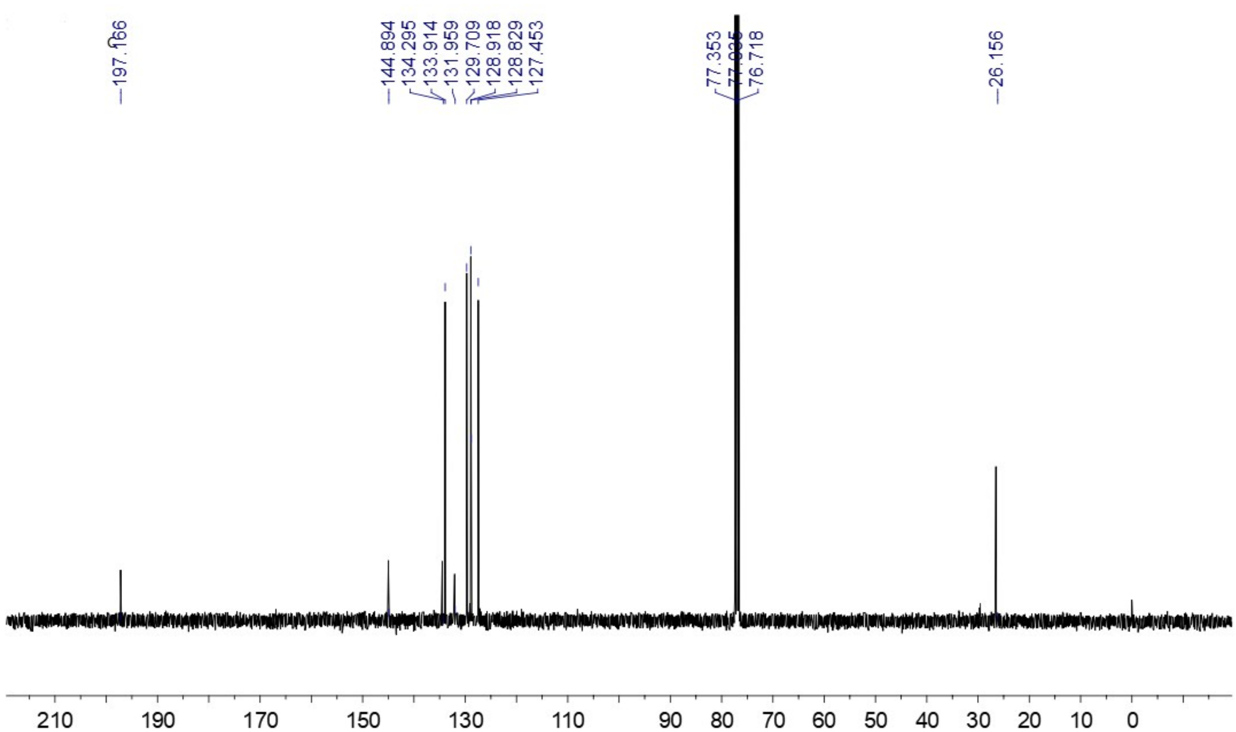


Fig. S37 ^{13}C NMR spectrum of compound **4a** in $CDCl_3$

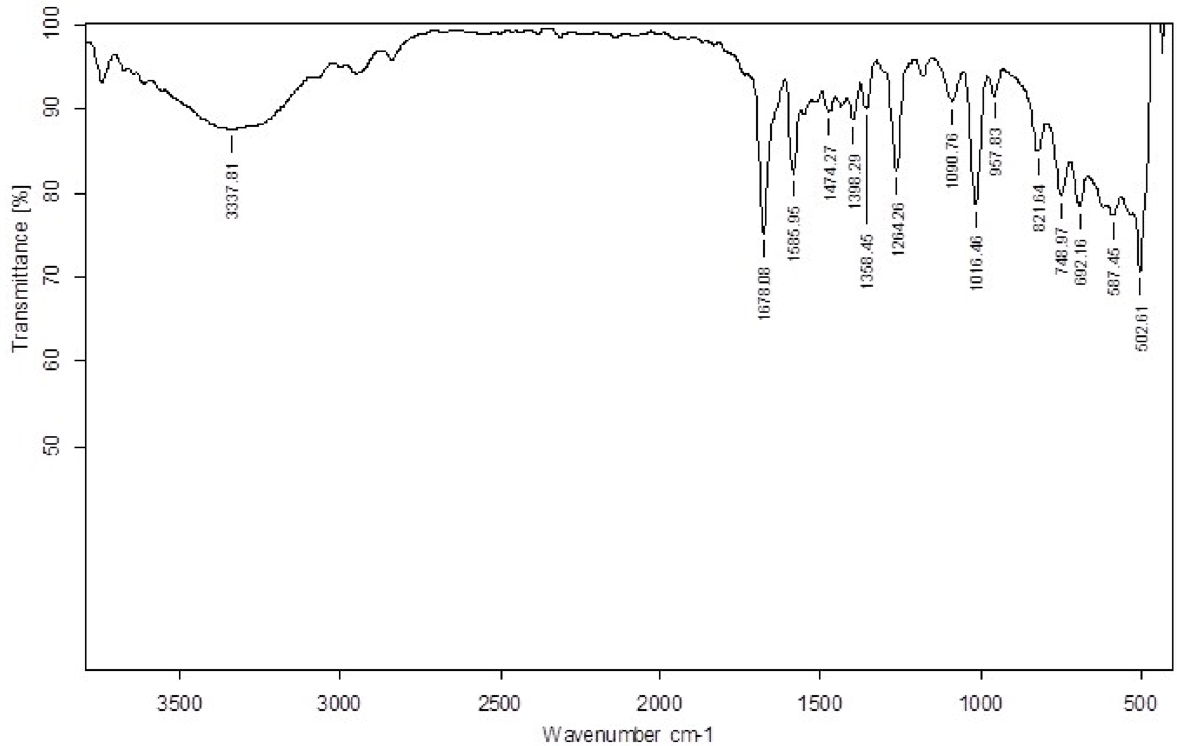


Fig. S38. Neat FT-IR spectrum of complex **4a**

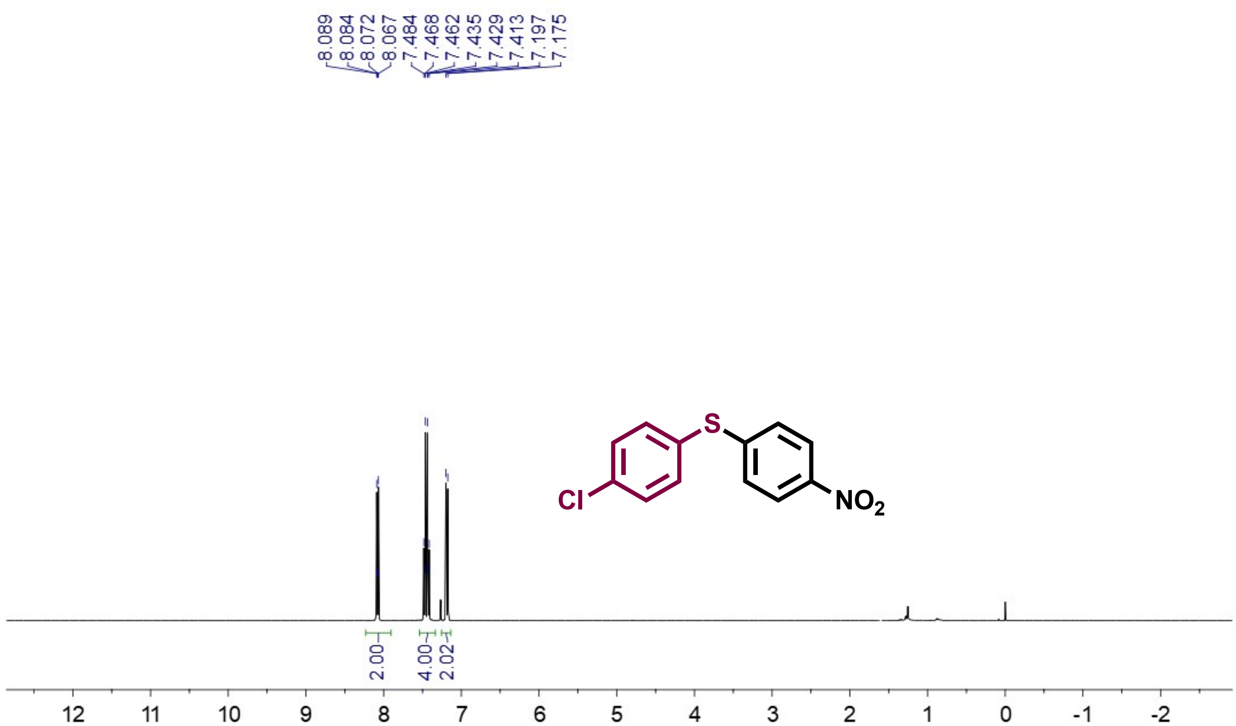


Fig. S39 ^{1}H NMR spectrum of compound **5a** in $CDCl_3$

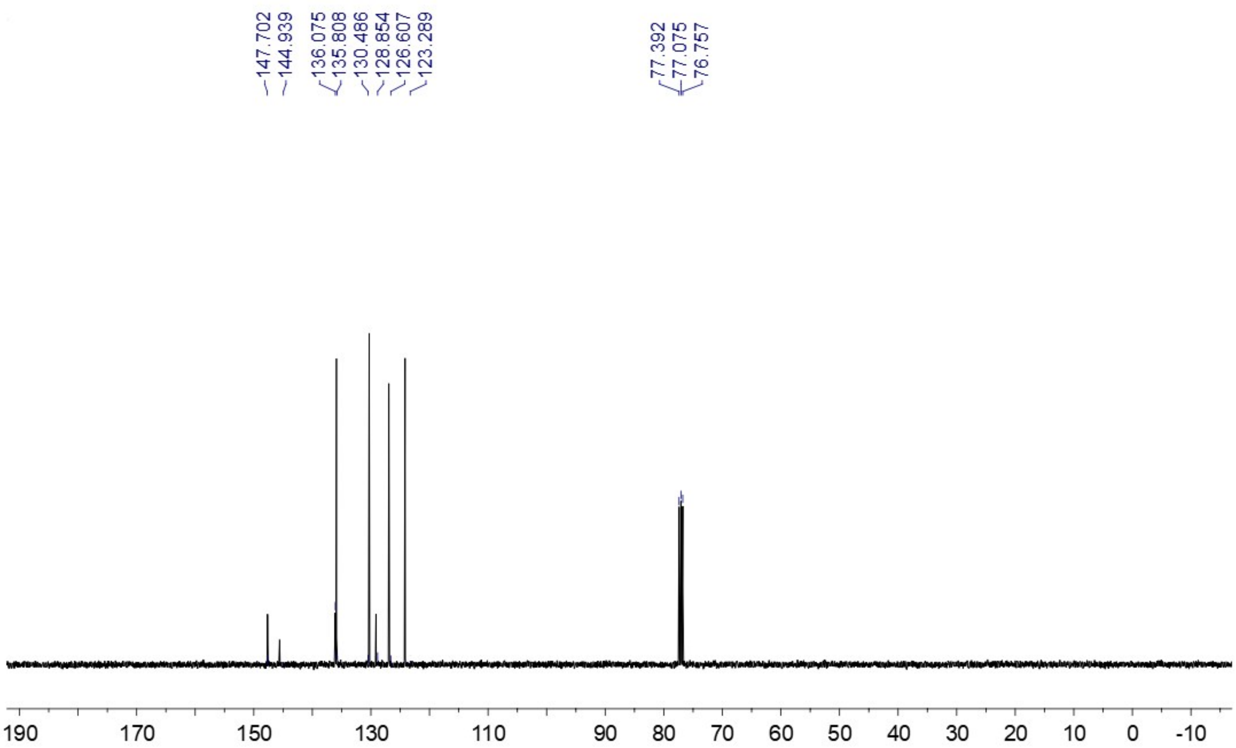


Fig. S40 ^{13}C NMR spectrum of compound **5a** in $CDCl_3$

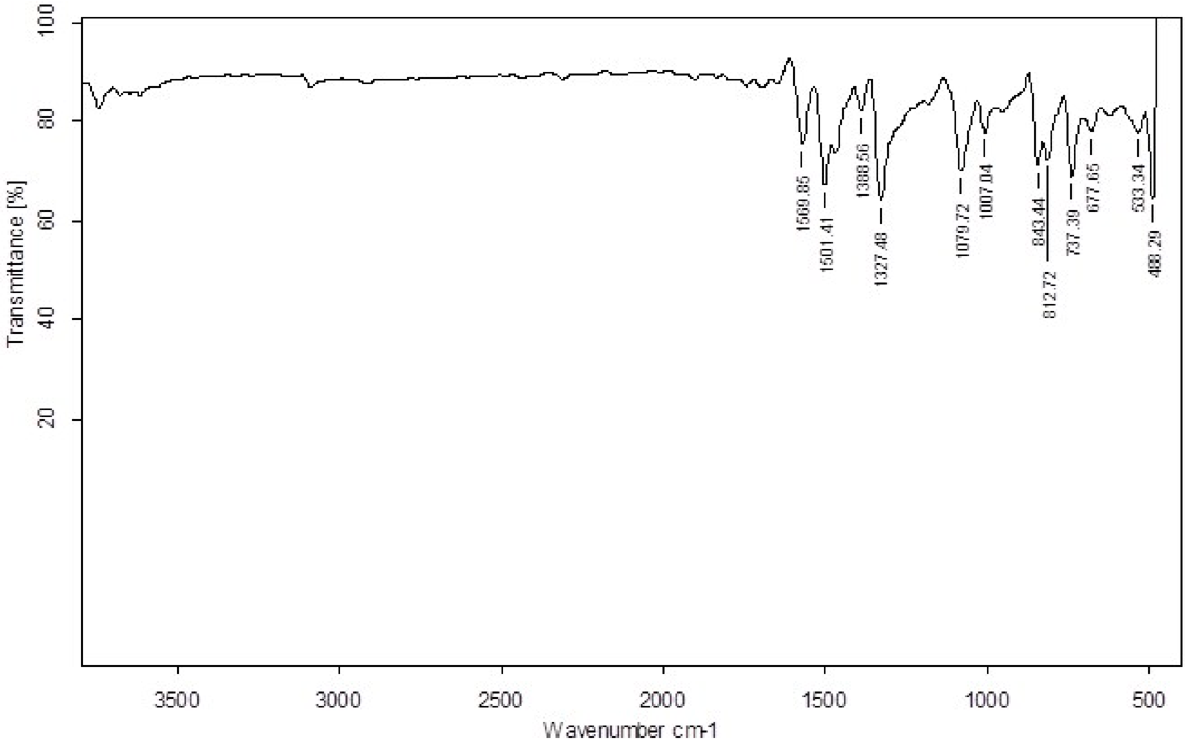


Fig. S41. Neat FT-IR spectrum of compound **5a**

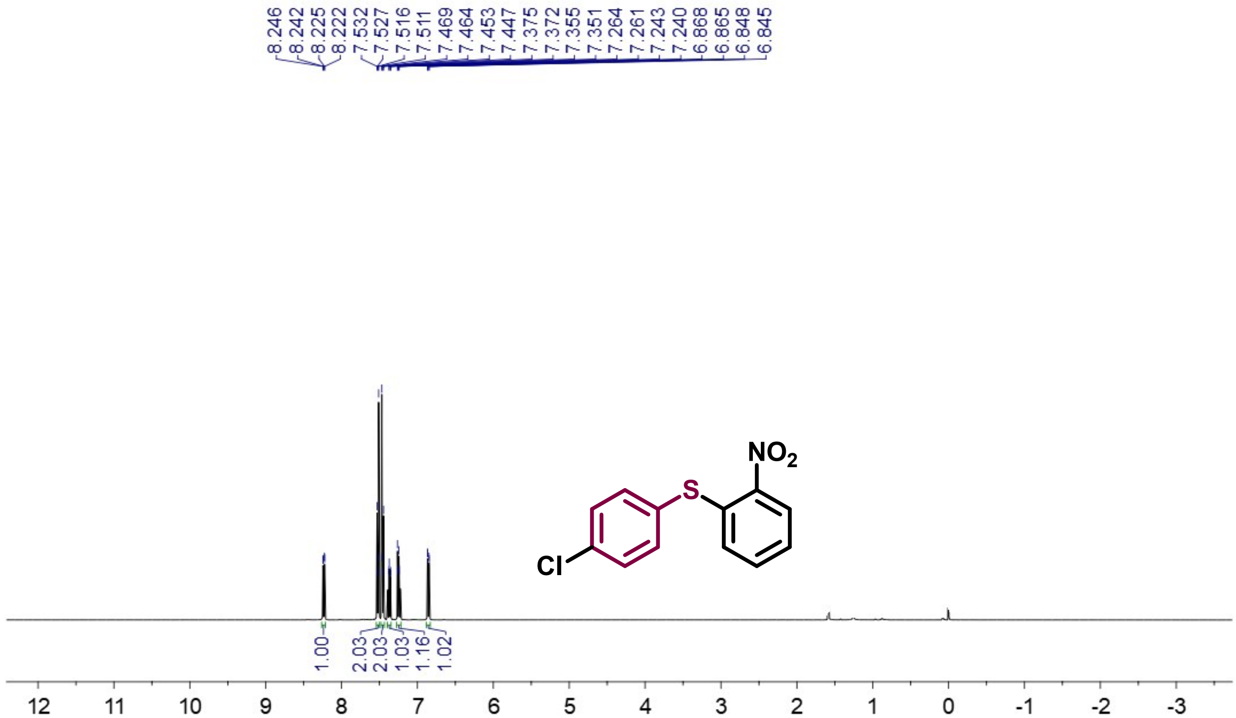


Fig. S42 ^{1}H NMR spectrum of compound **6a** in $CDCl_3$

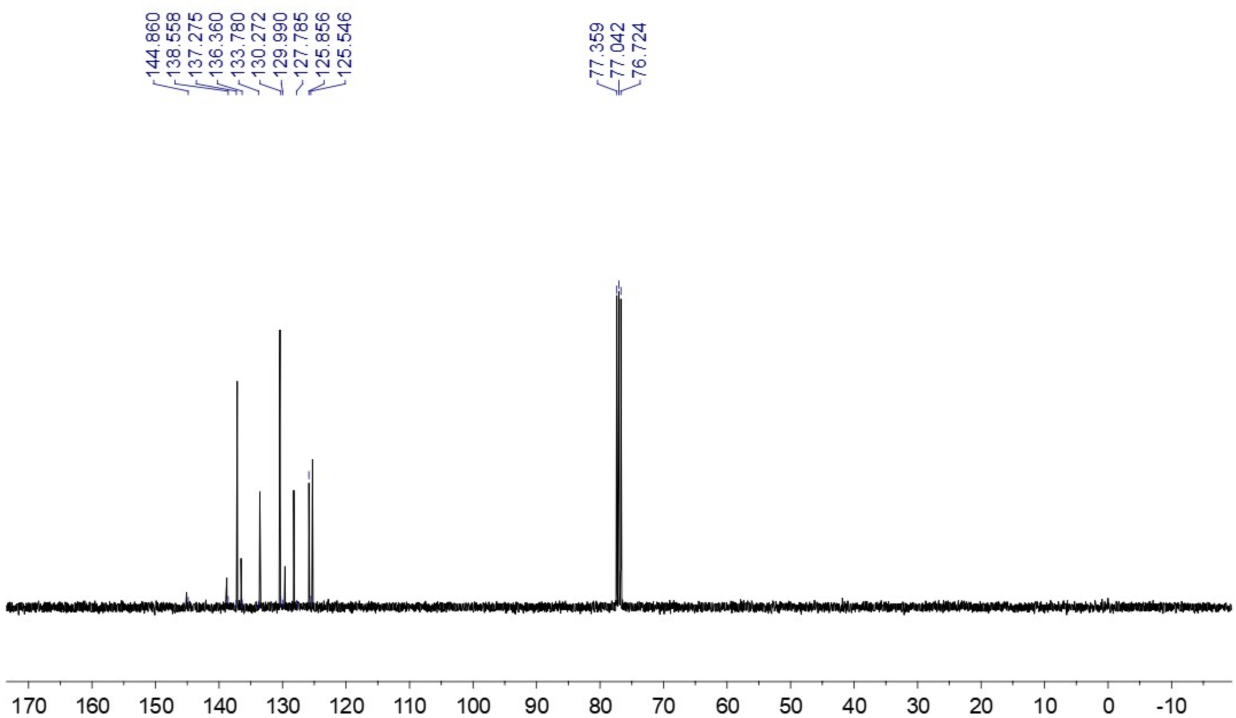


Fig. S43 ^{13}C NMR spectrum of compound **6a** in $CDCl_3$

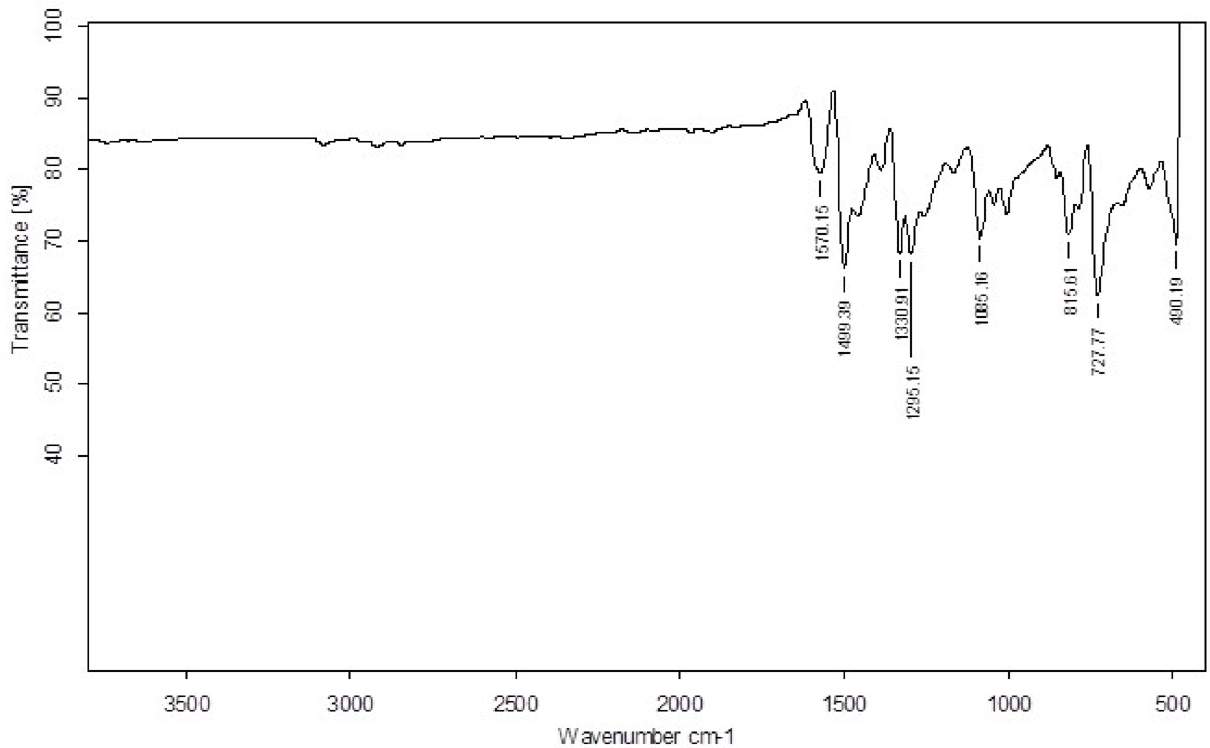


Fig. S44. Neat FT-IR spectrum of compound **6a**

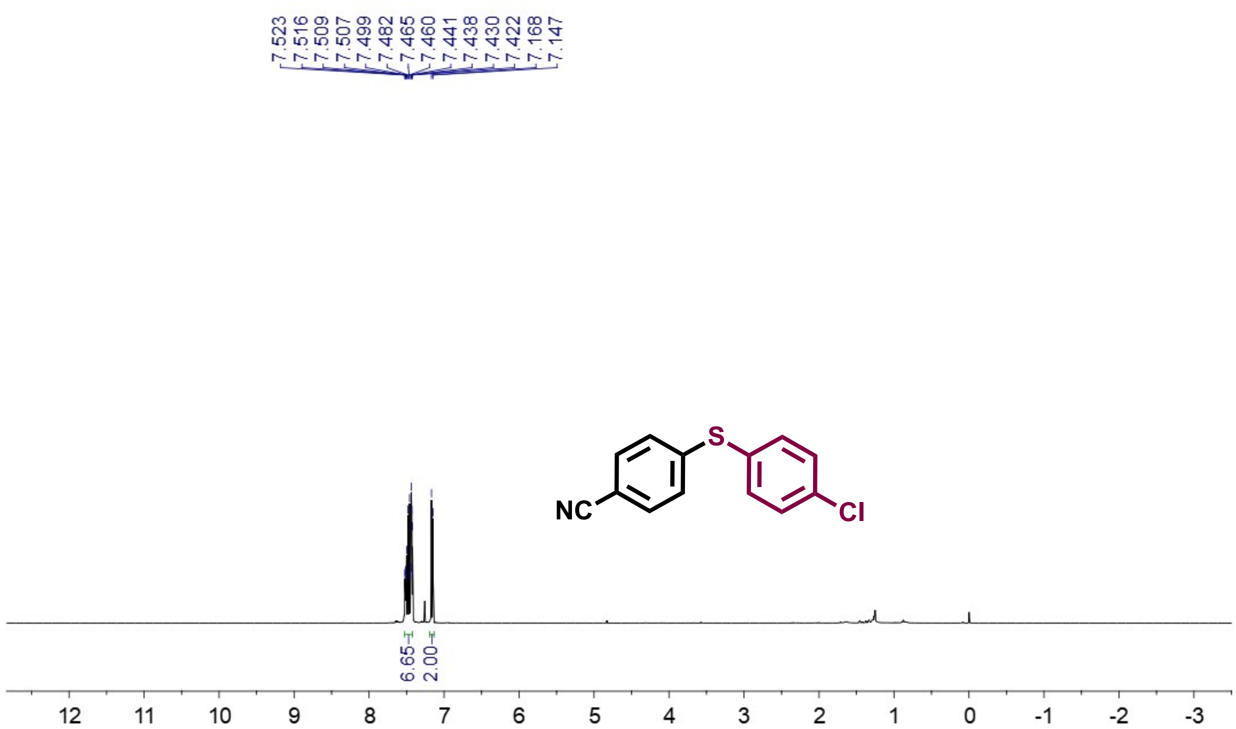


Fig. S45 ^{1}H NMR spectrum of compound **7a** in $CDCl_3$

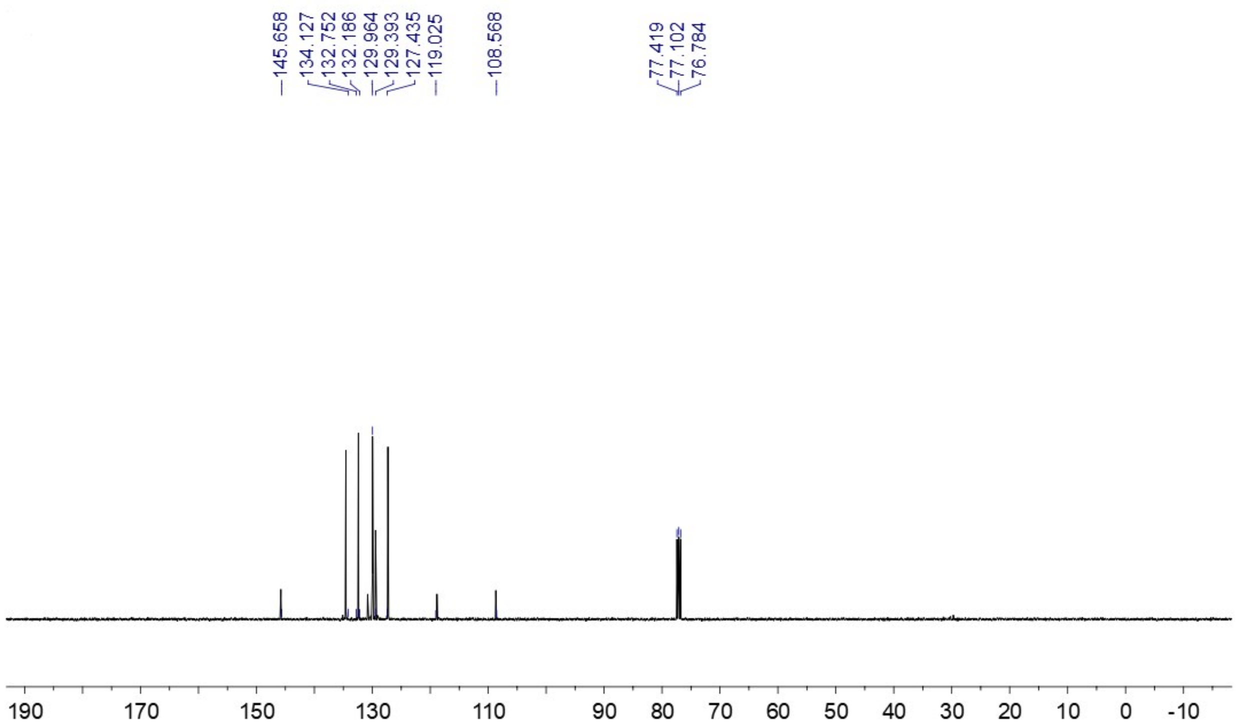


Fig. S46 ^{13}C NMR spectrum of compound **7a** in $CDCl_3$

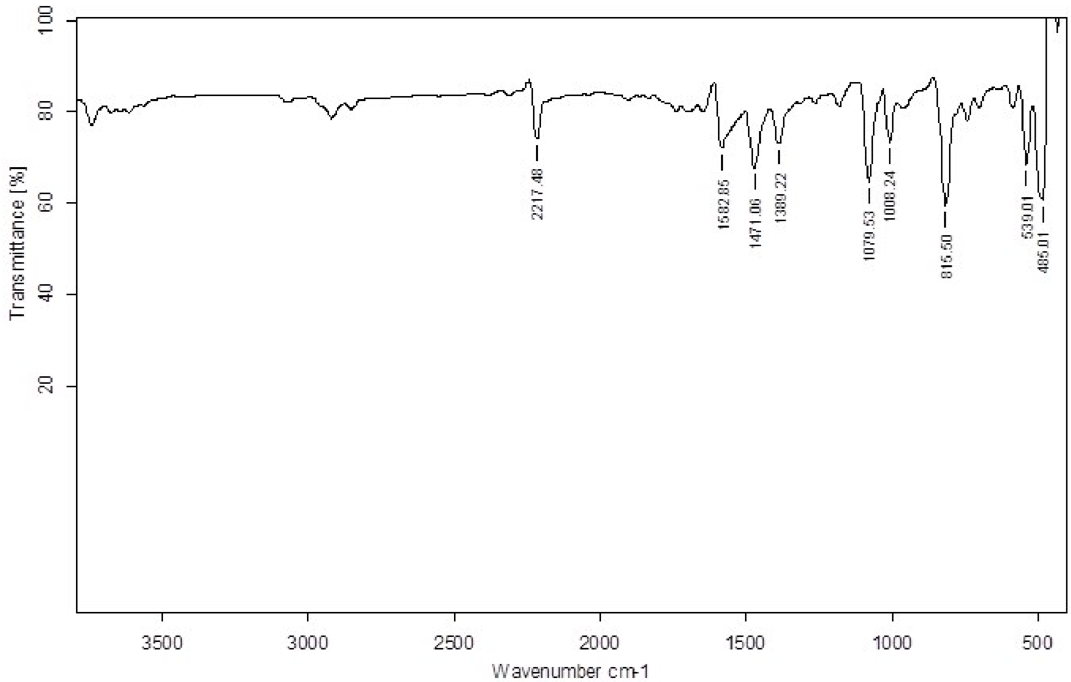


Fig. S47. Neat FT-IR spectrum of compound **7a**

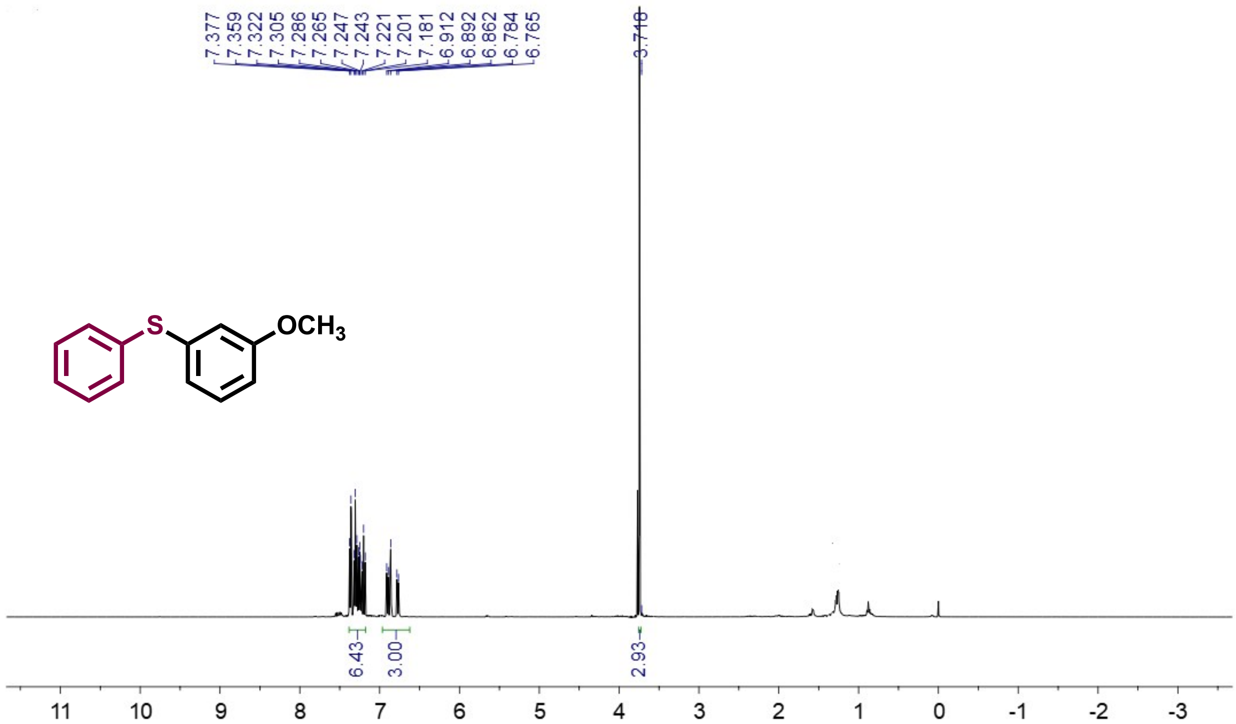


Fig. S48 ^{1}H NMR spectrum of compound **8a** in $CDCl_3$

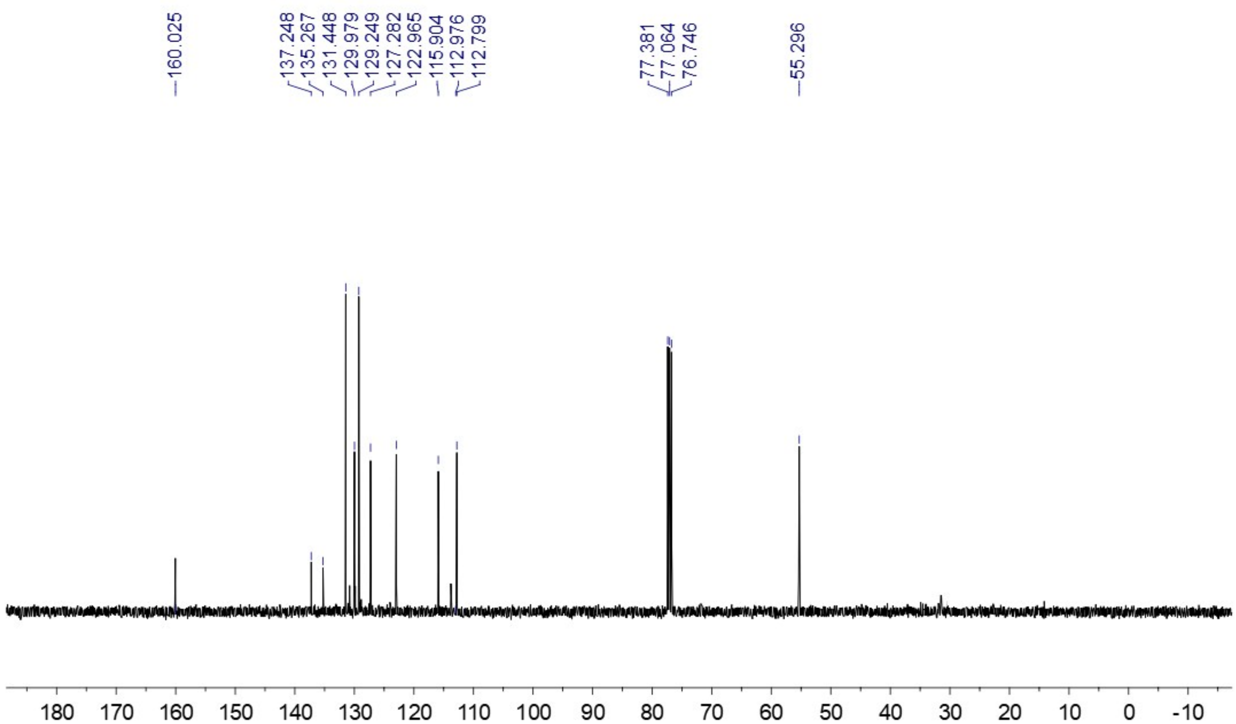


Fig. S49 ^{13}C NMR spectrum of compound **8a** in $CDCl_3$

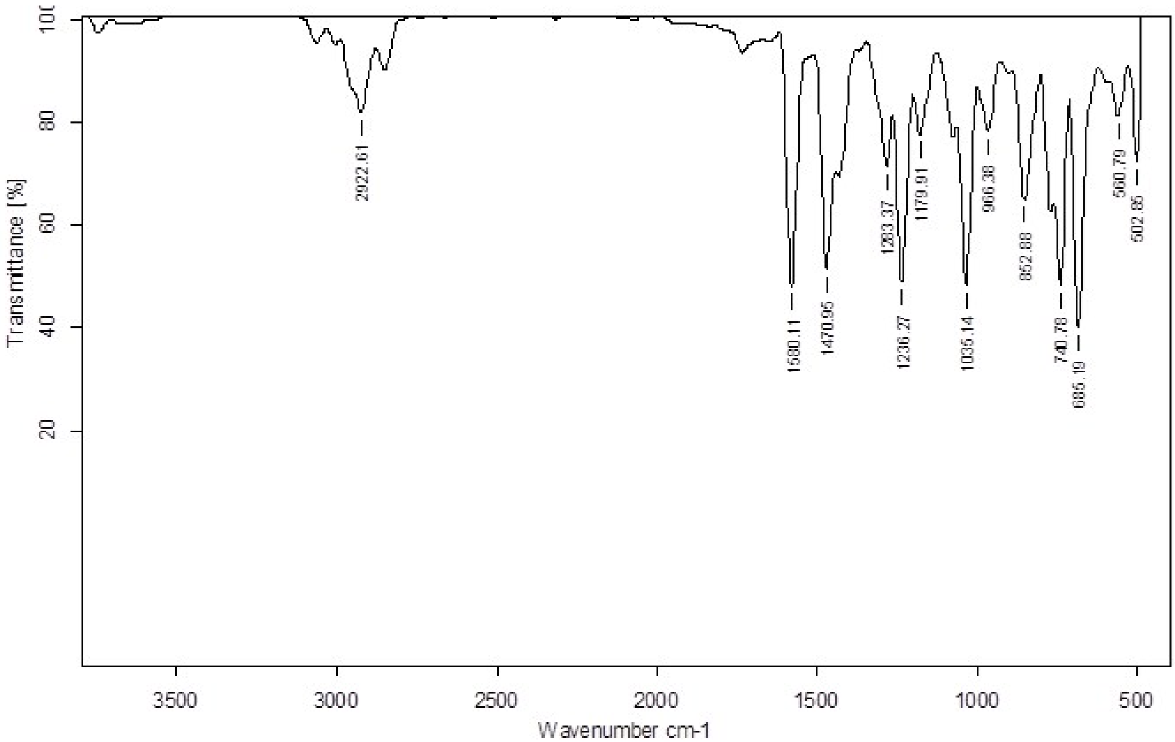


Fig. S50. Neat FT-IR spectrum of compound **8a**

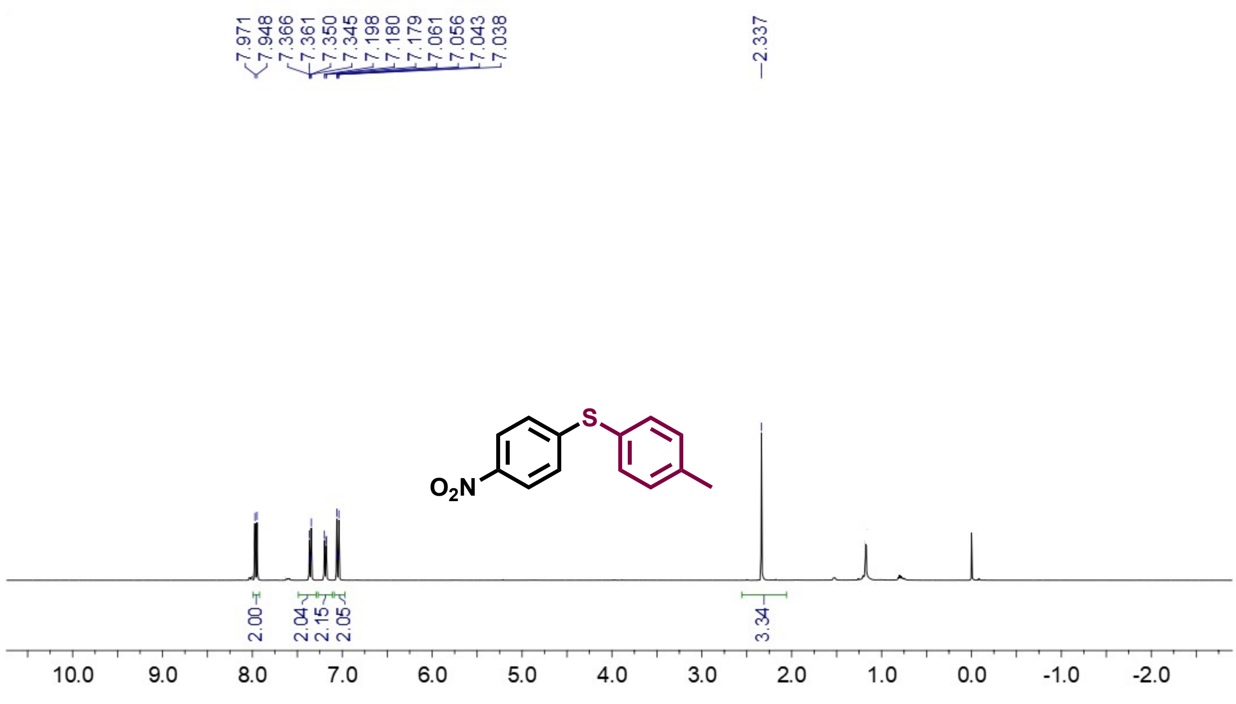


Fig. S51 ^{1}H NMR spectrum of compound **9a** in $CDCl_3$

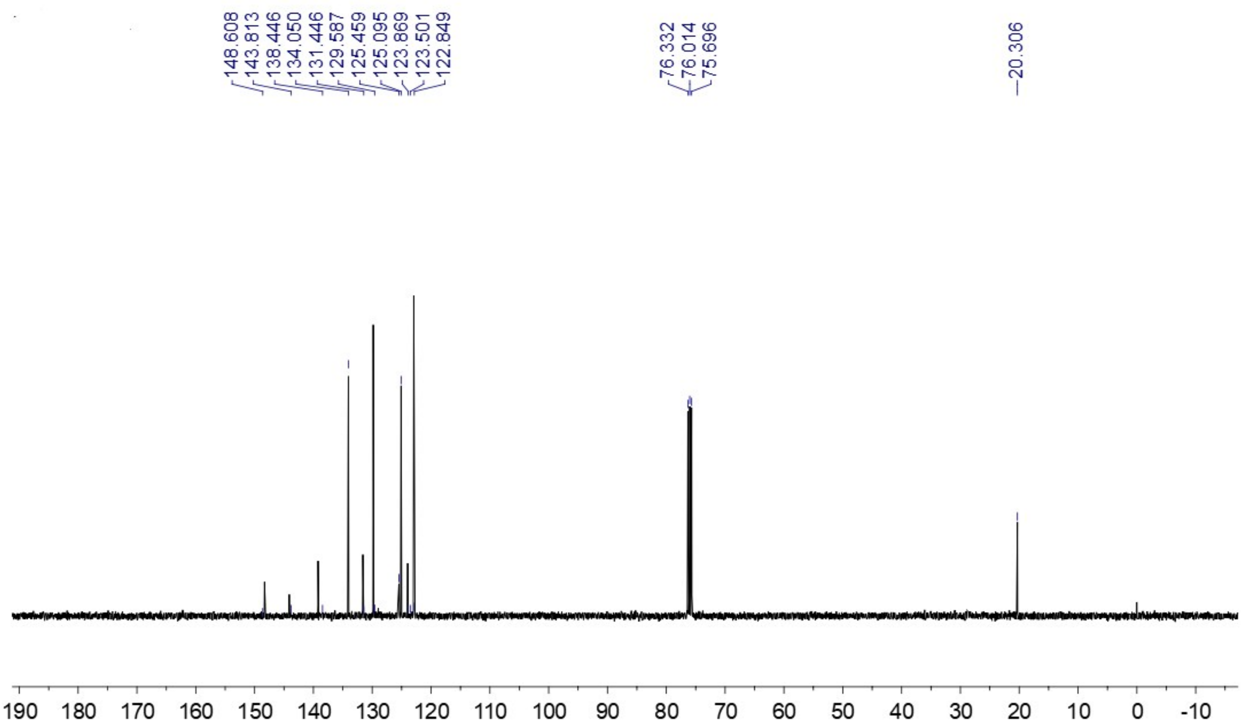


Fig. S52 ^{13}C NMR spectrum of compound **9a** in $CDCl_3$

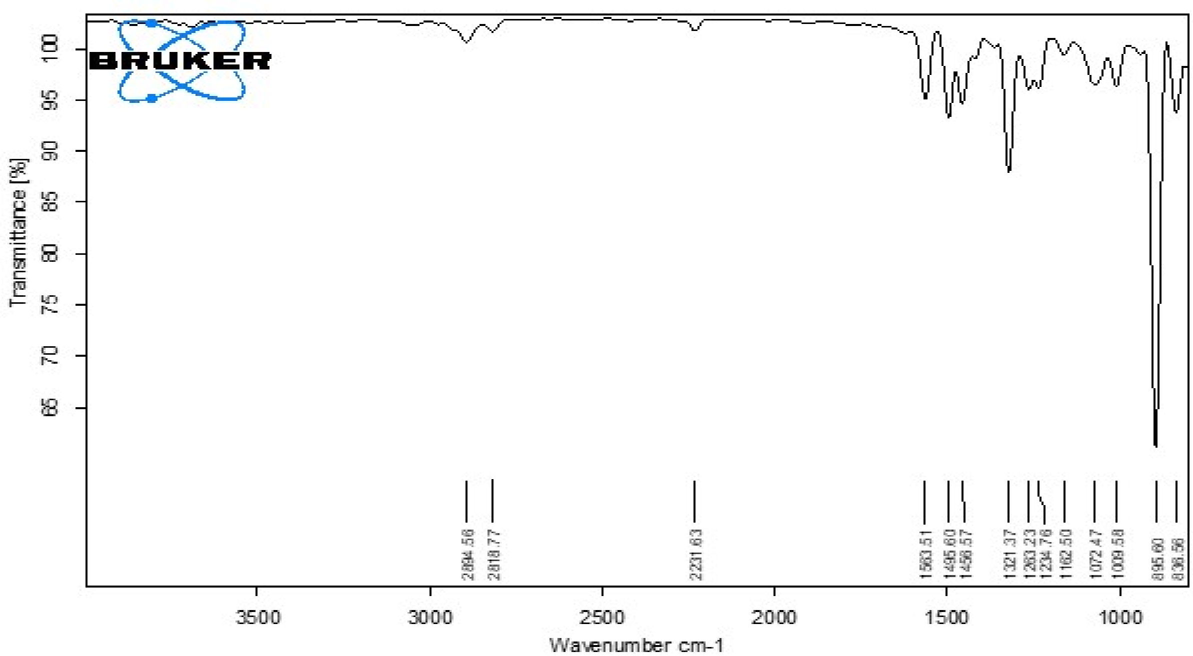


Fig. S53. Neat FT-IR spectrum of compound **9a**

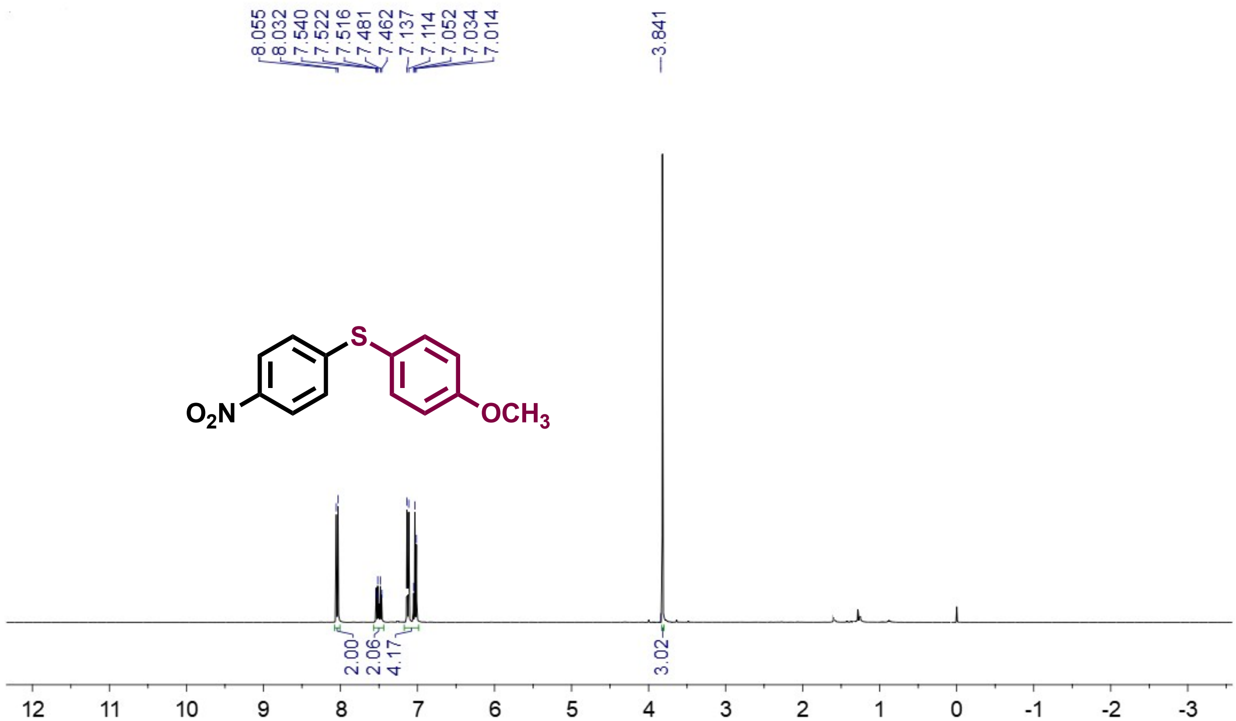


Fig. S54 ^{1}H NMR spectrum of compound **10a** in $CDCl_3$

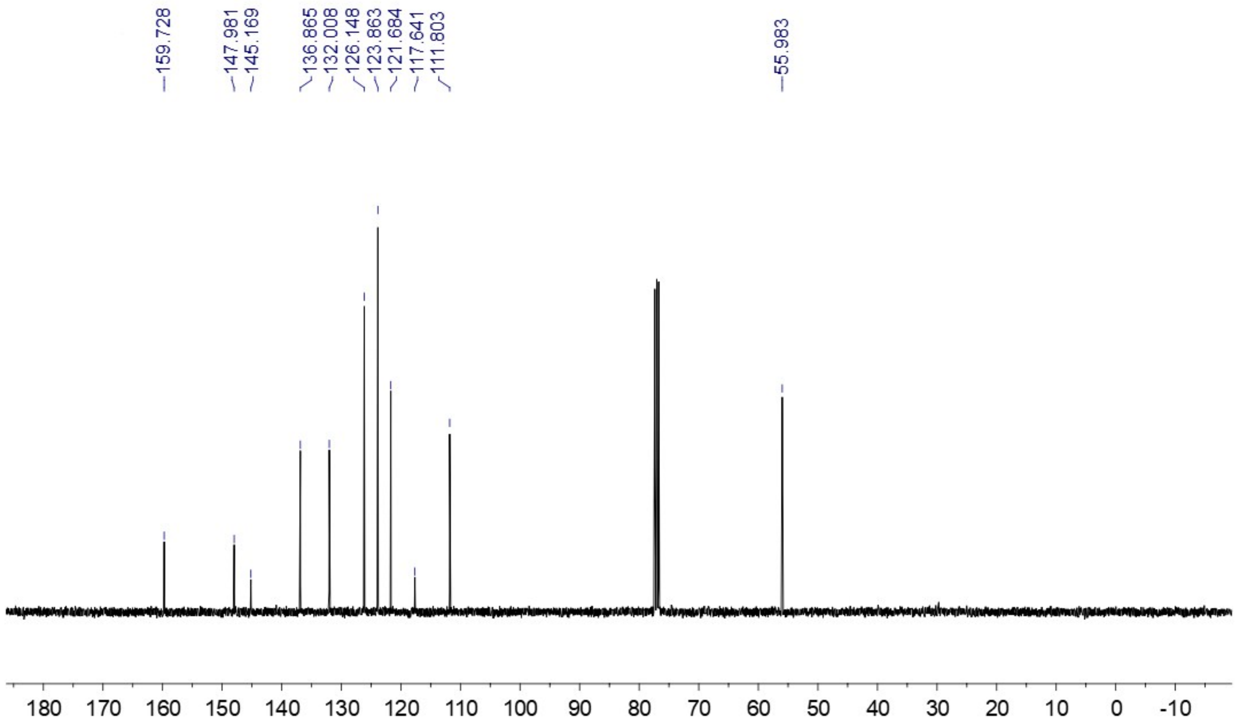


Fig. S55 ^{13}C NMR spectrum of compound **10a** in $CDCl_3$

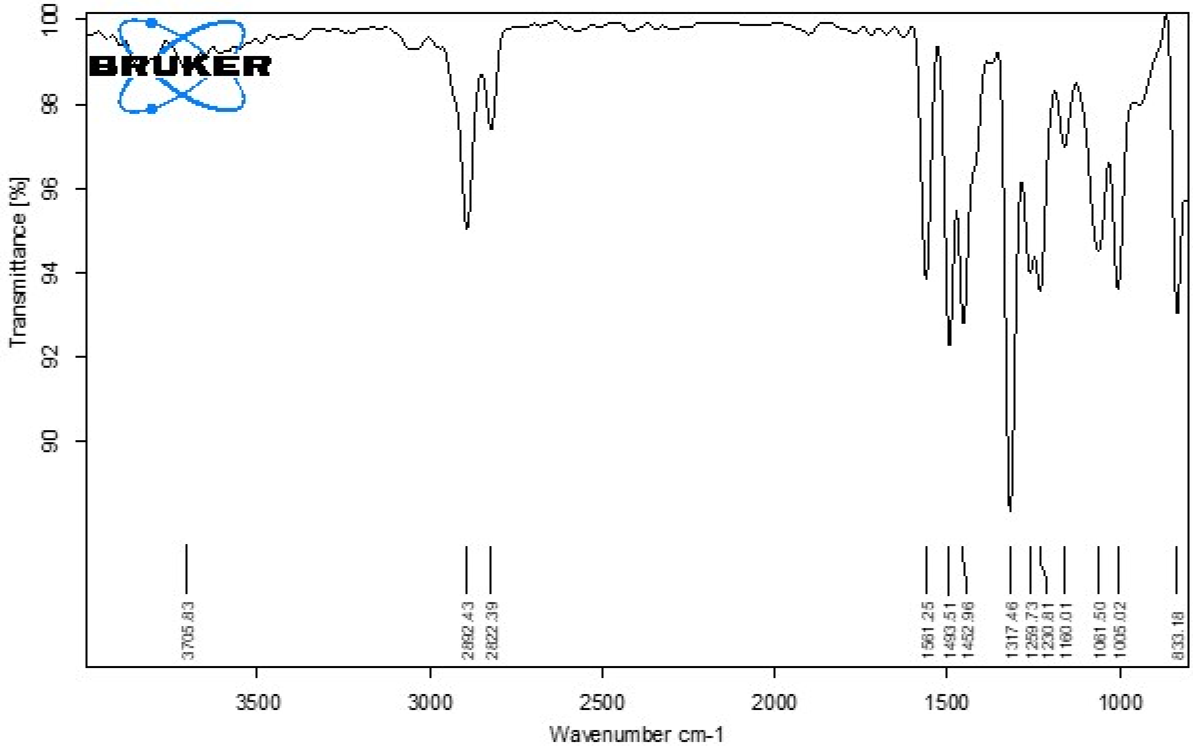


Fig. S56. Neat FT-IR spectrum of compound **10a**

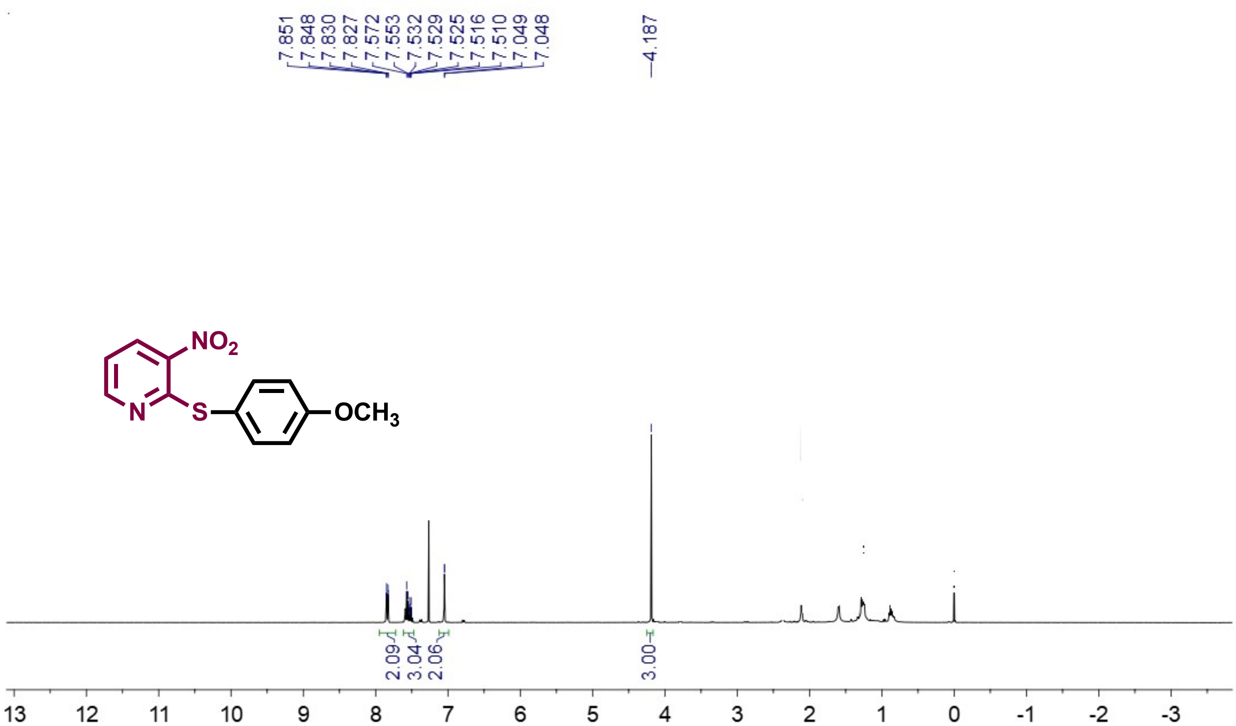


Fig. S57 ^{1}H NMR spectrum of compound **11a** in $CDCl_3$

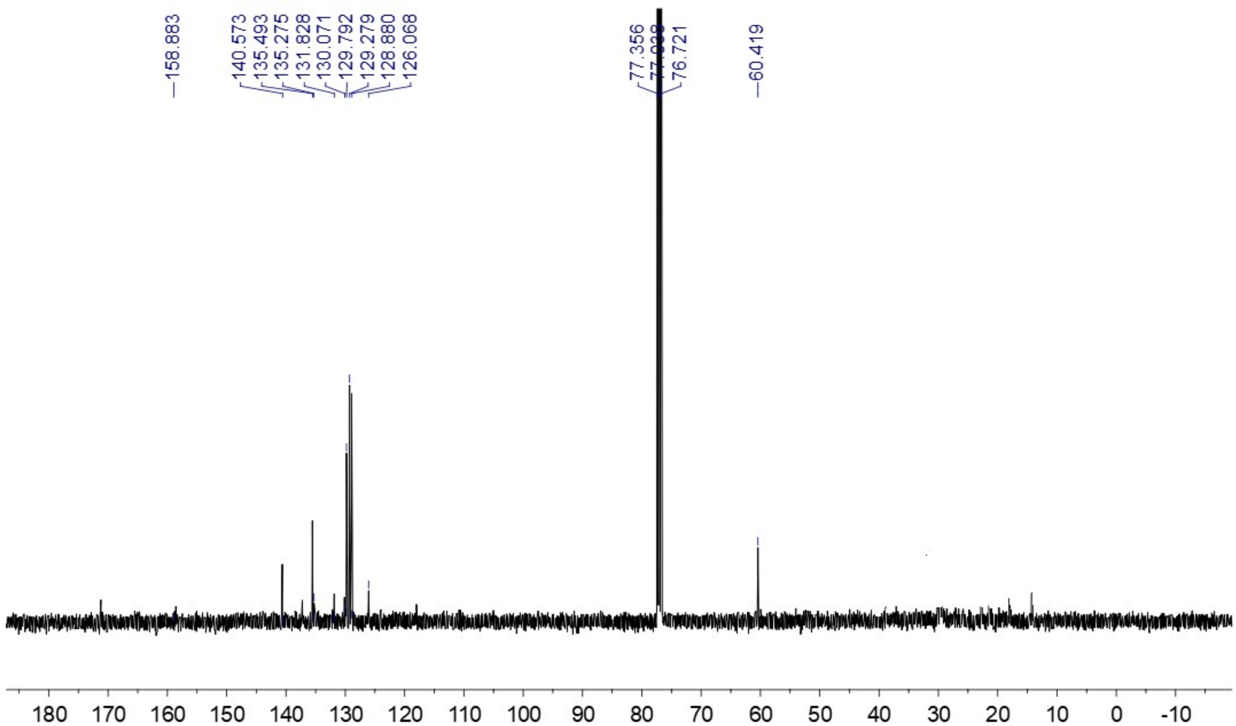


Fig. S58 ^{13}C NMR spectrum of compound **11a** in $CDCl_3$

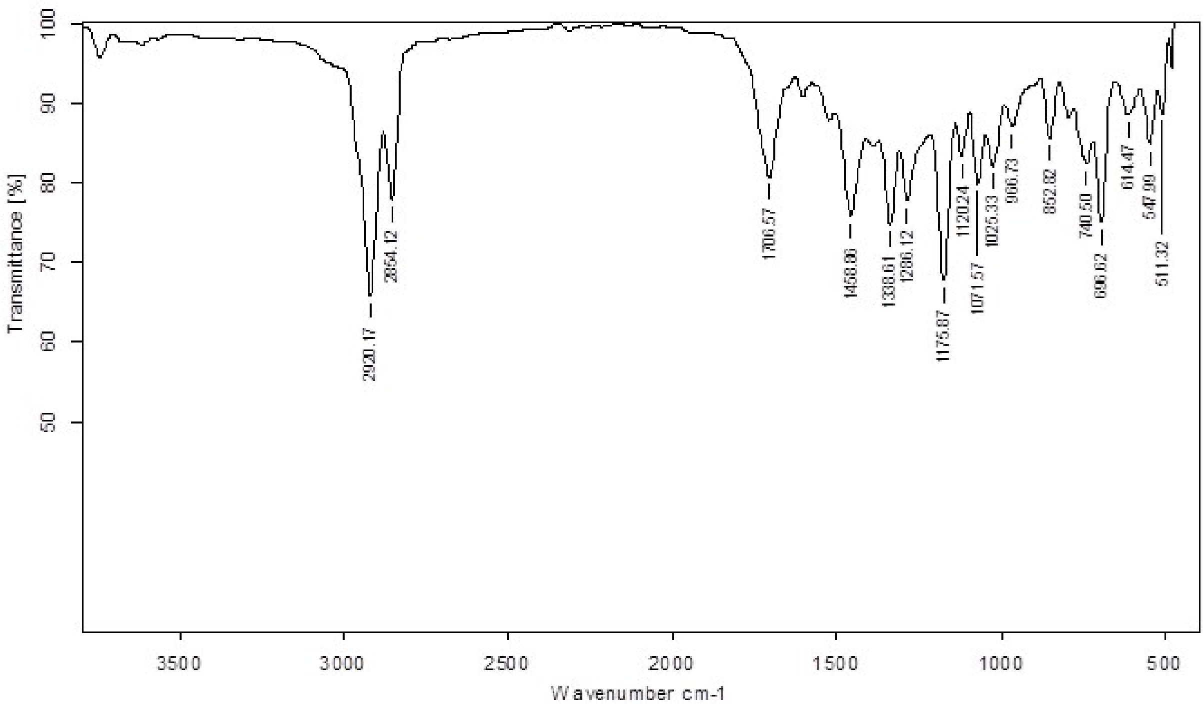


Fig. S59. Neat FT-IR spectrum of complex **11a**

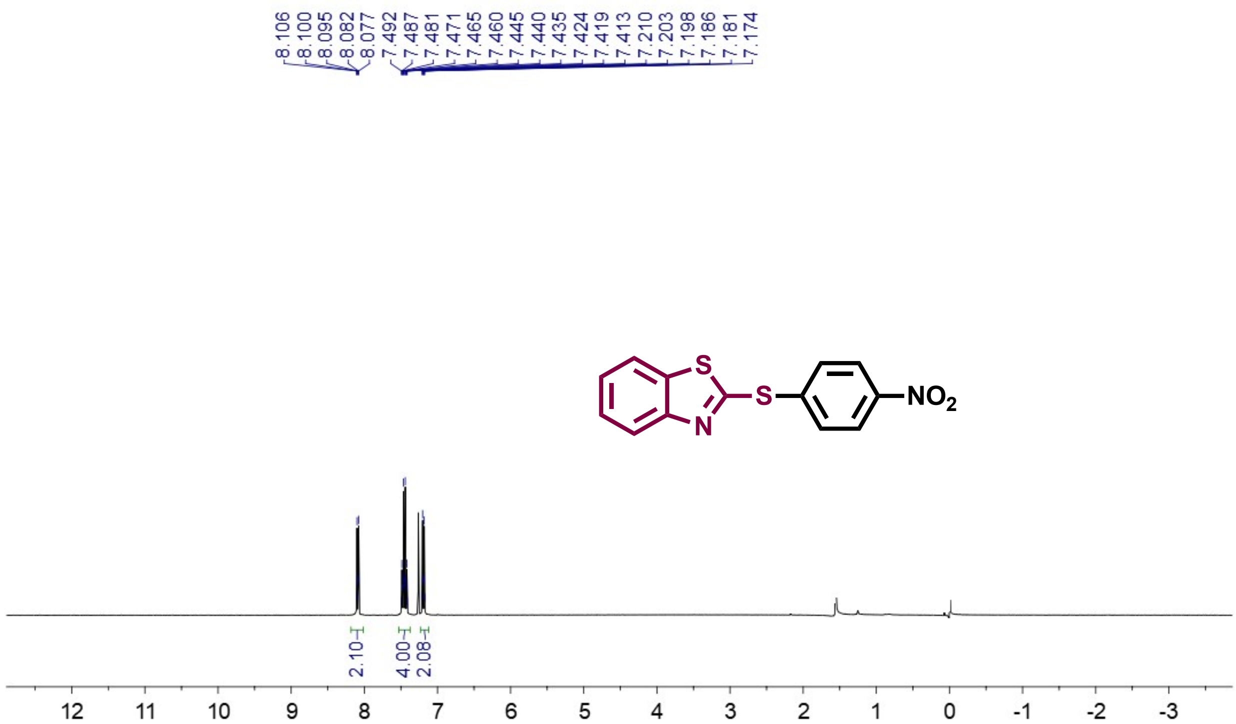


Fig. S60 ^{1}H NMR spectrum of compound **12a** in $CDCl_3$

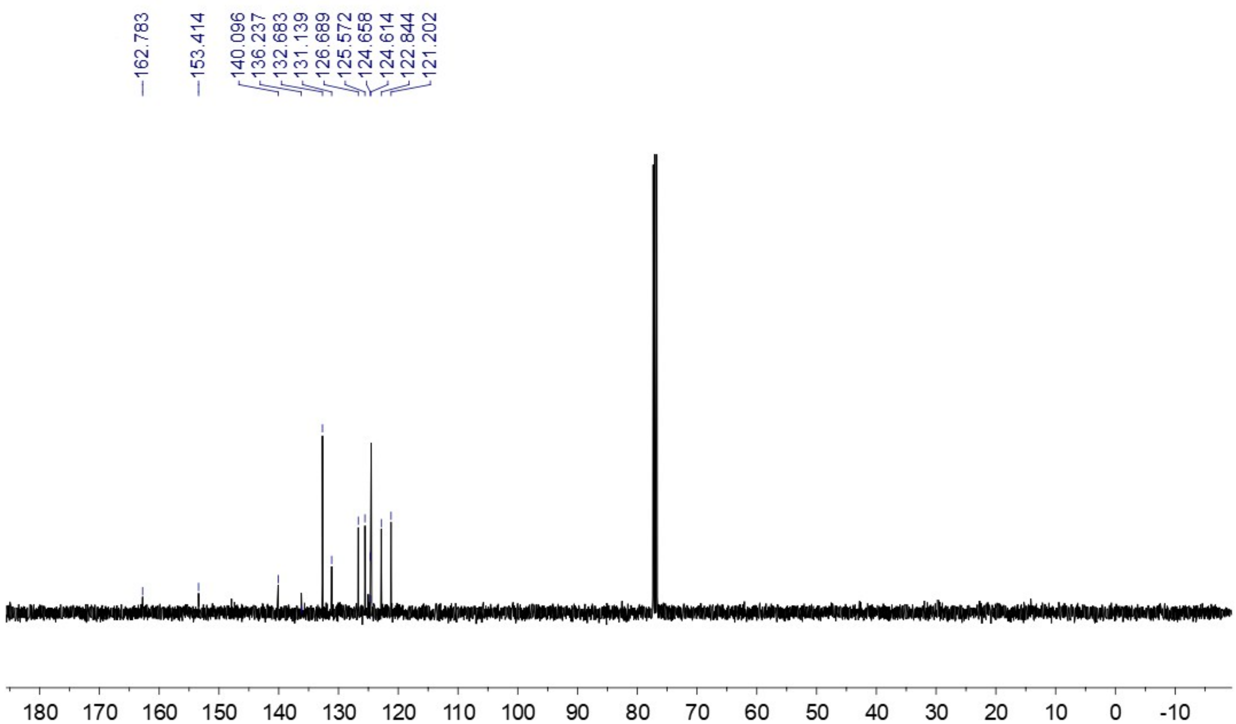


Fig. S61 ^{13}C NMR spectrum of compound **12a** in $CDCl_3$

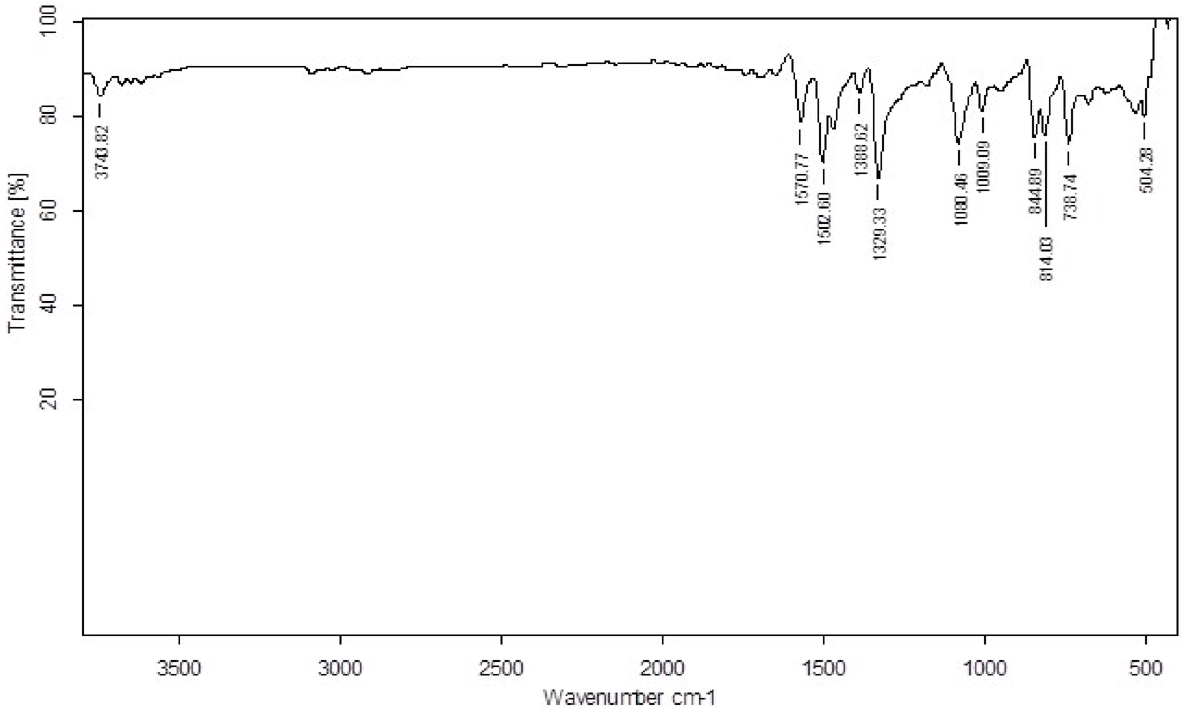


Fig. S62. Neat FT-IR spectrum of compound **12a**

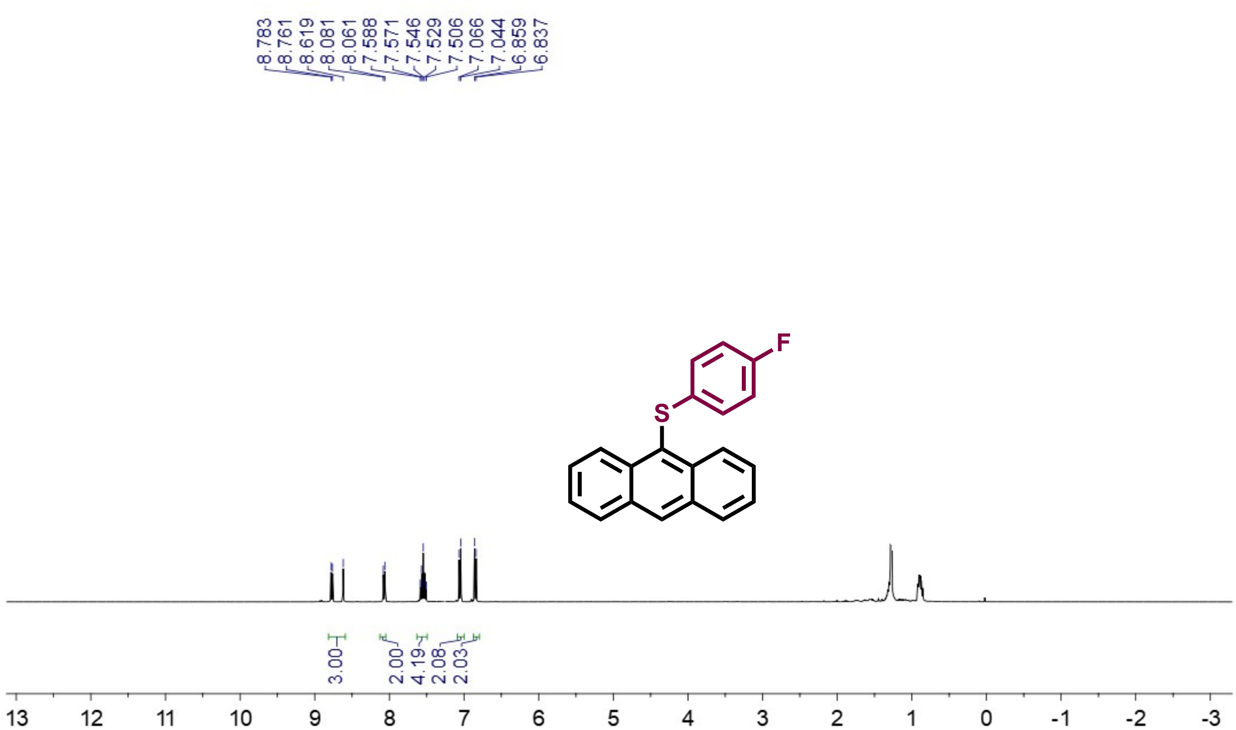


Fig. S63 ^{1}H NMR spectrum of compound **13a** in $CDCl_3$

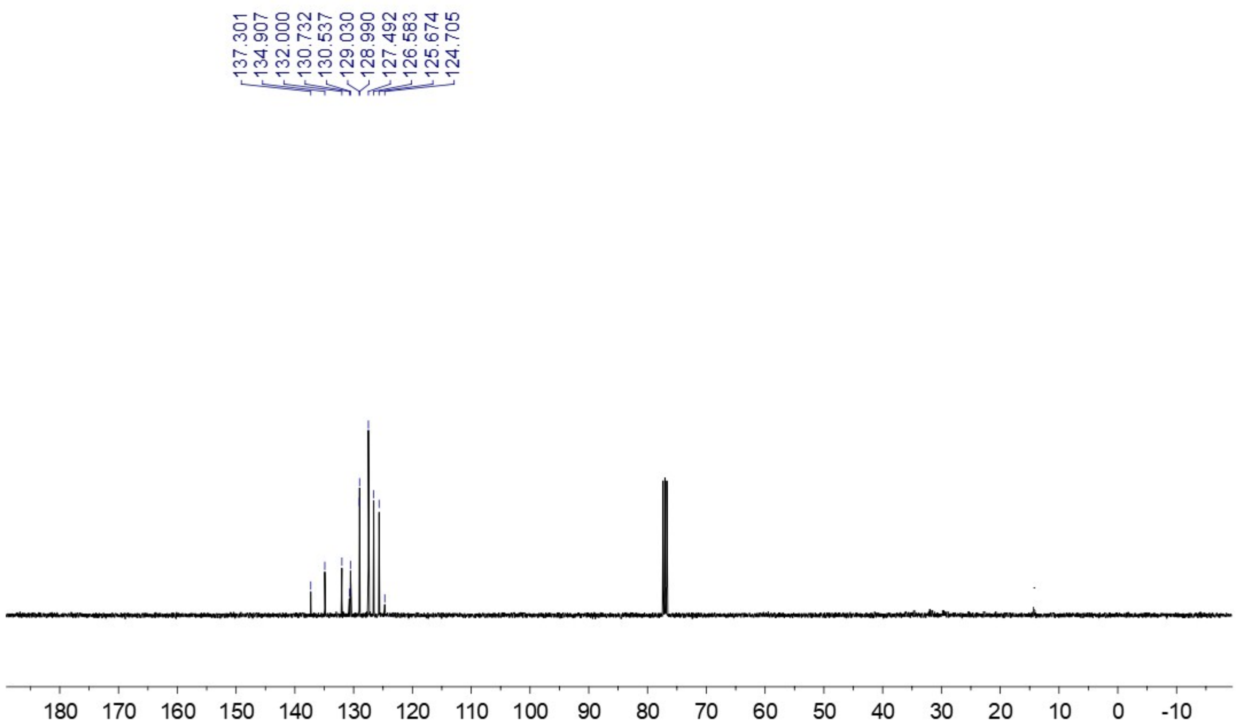


Fig. S64 ^{13}C NMR spectrum of compound 1**3a** in $CDCl_3$

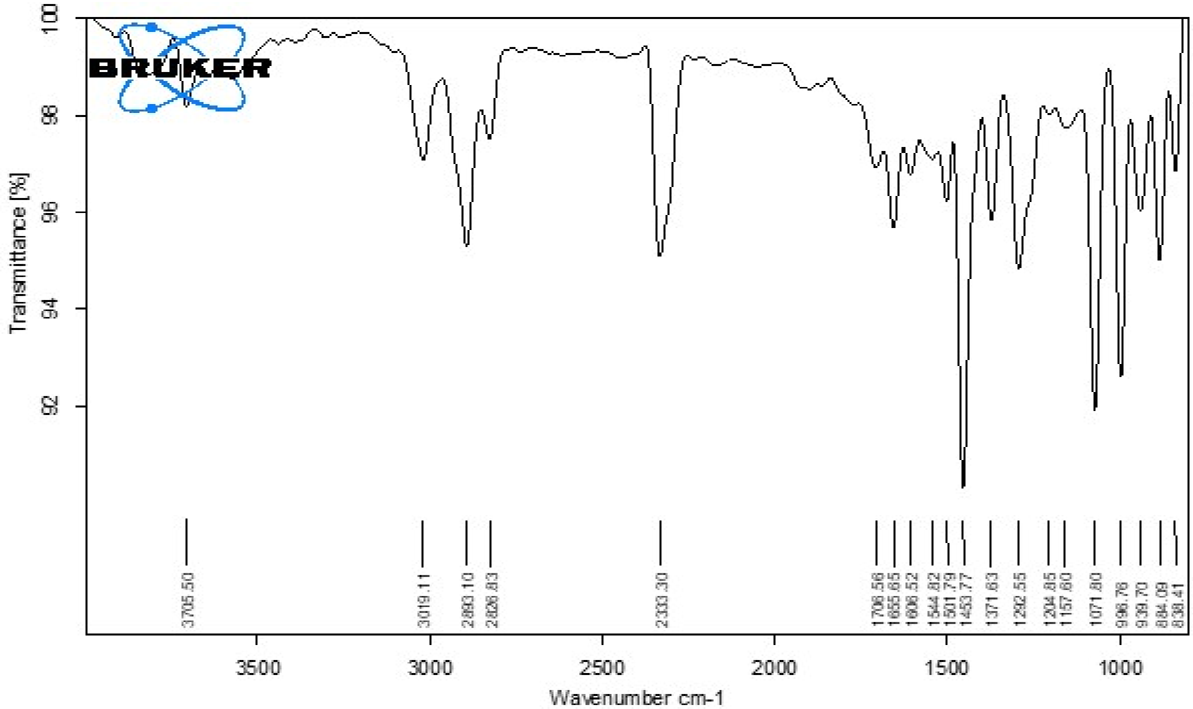


Fig. S65. Neat FT-IR spectrum of compound **13a**

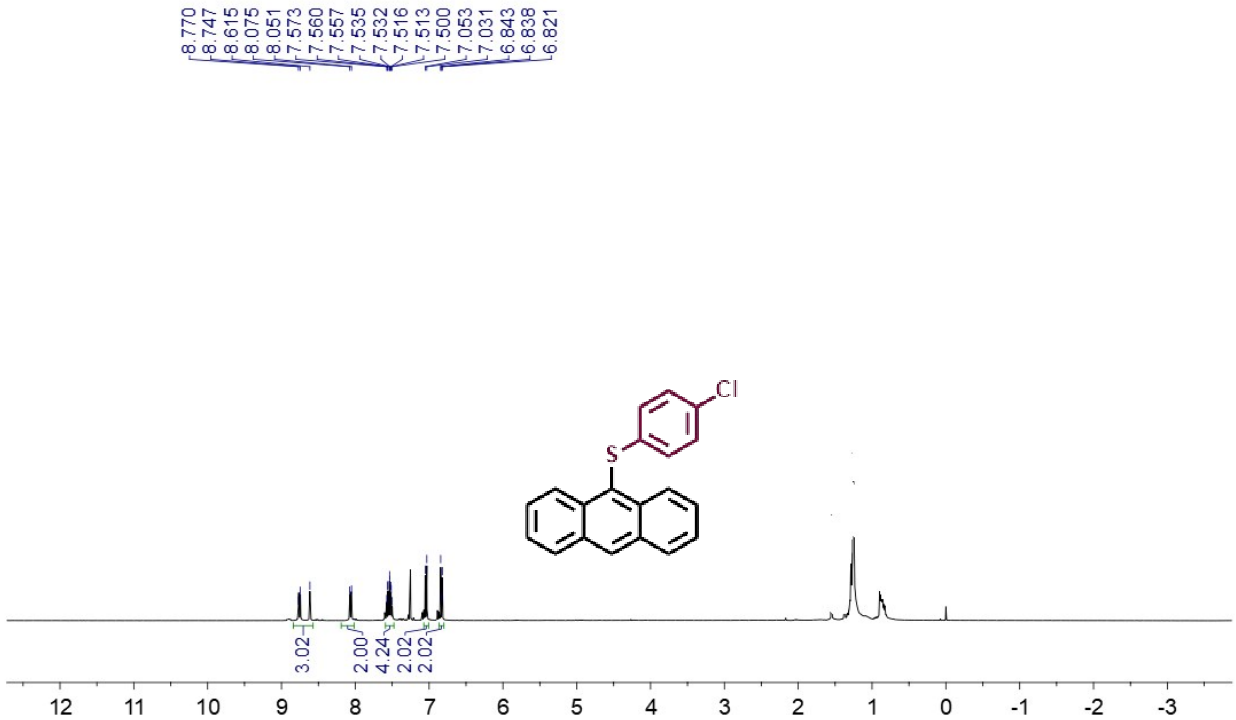


Fig. S66 ^{1}H NMR spectrum of compound **14a** in $CDCl_3$

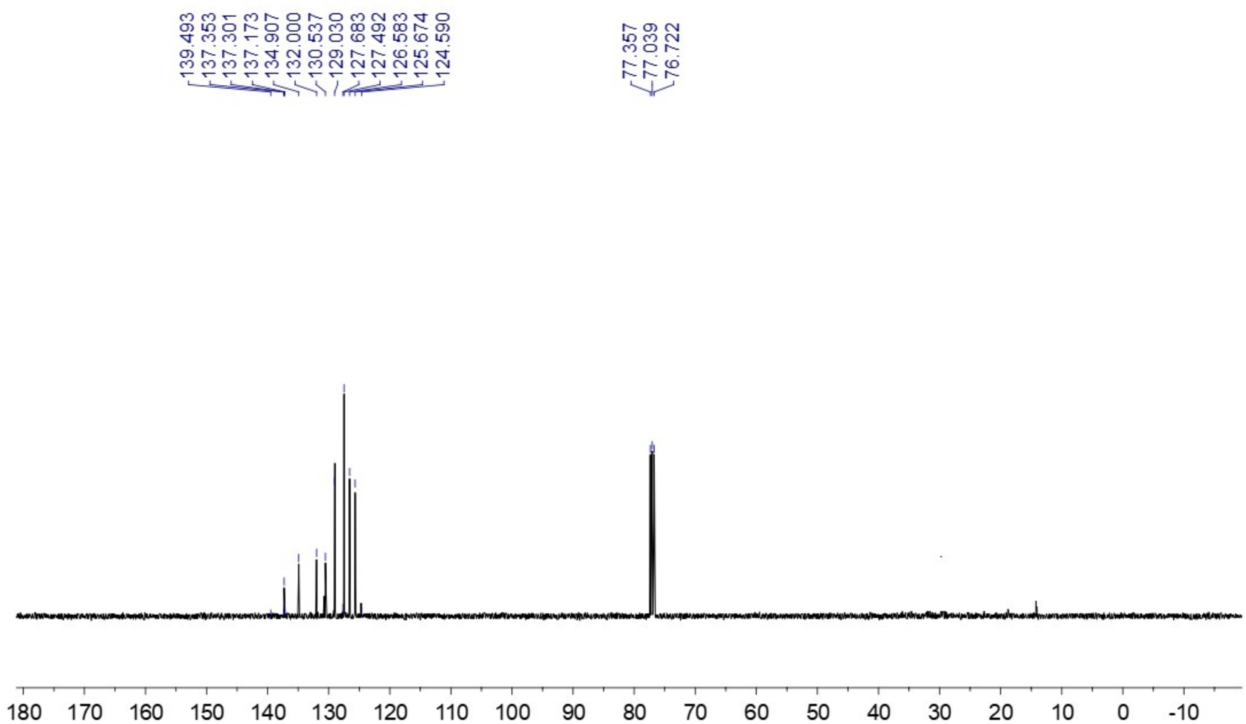


Fig. S67 ^{13}C NMR spectrum of compound **14a** in $CDCl_3$

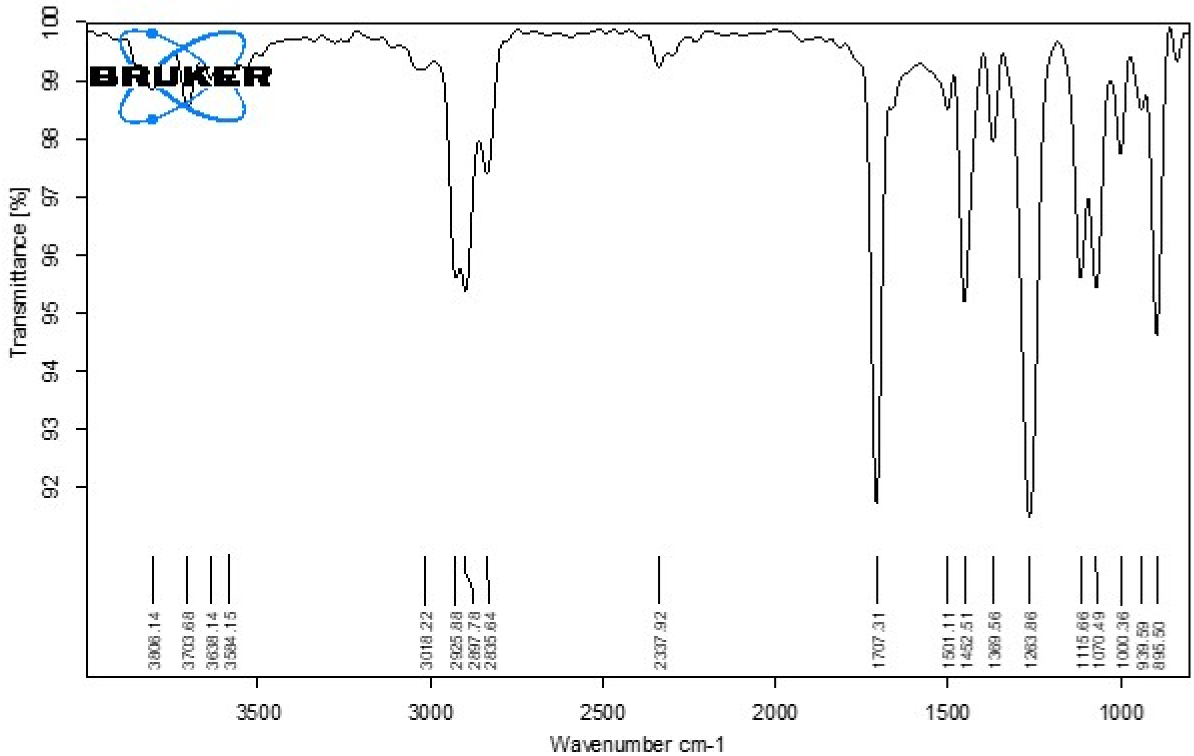


Fig. S68. Neat FT-IR spectrum of compound **14a**

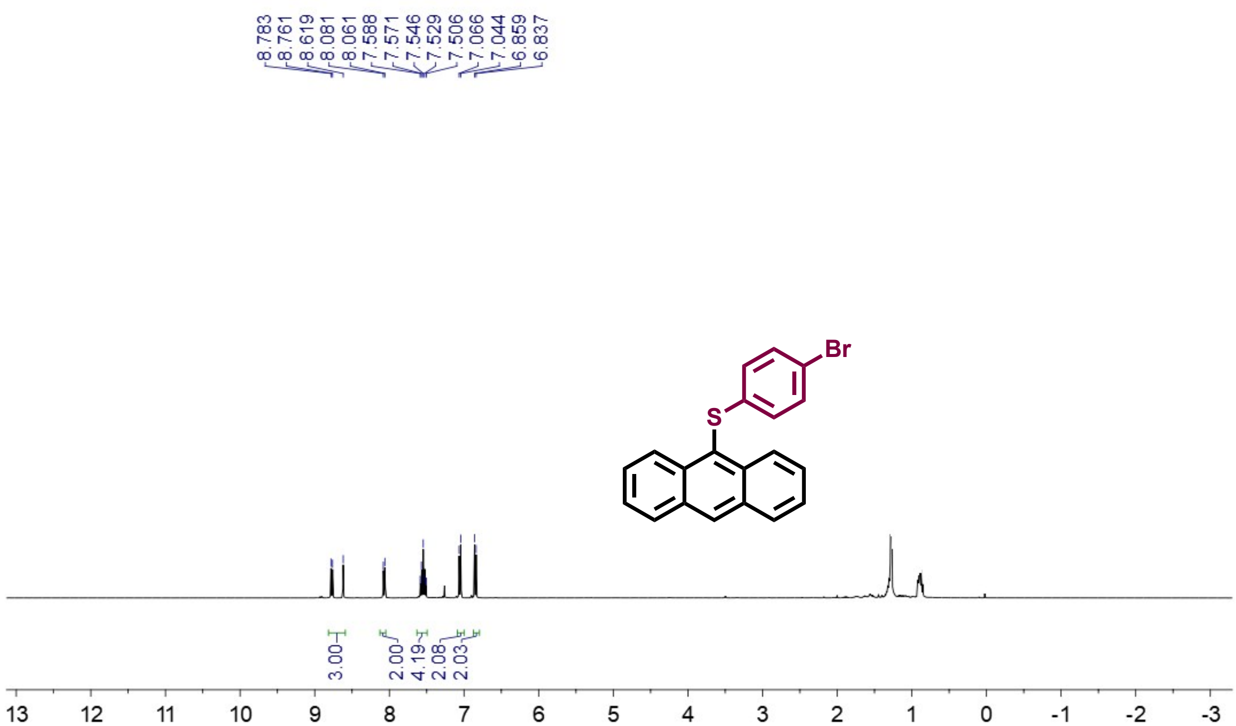


Fig. S69 ^{1}H NMR spectrum of compound **15a** in $CDCl_3$

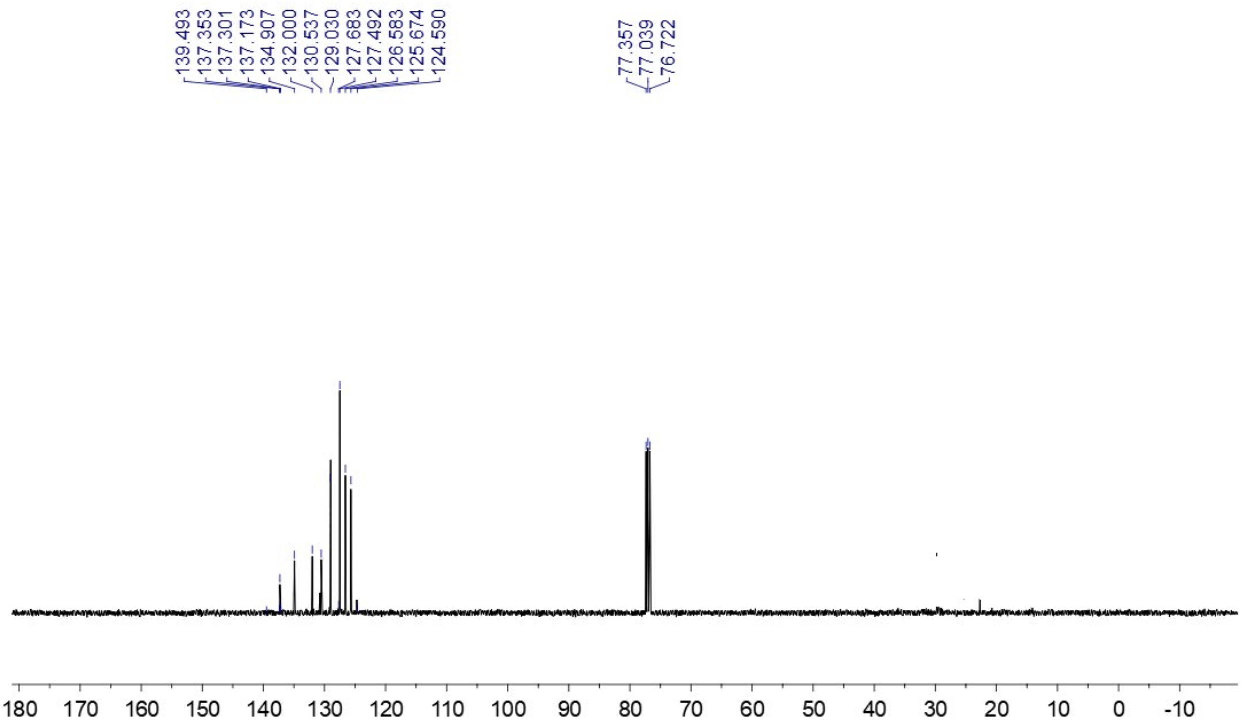


Fig. S70 ^{13}C NMR spectrum of compound **15a** in $CDCl_3$

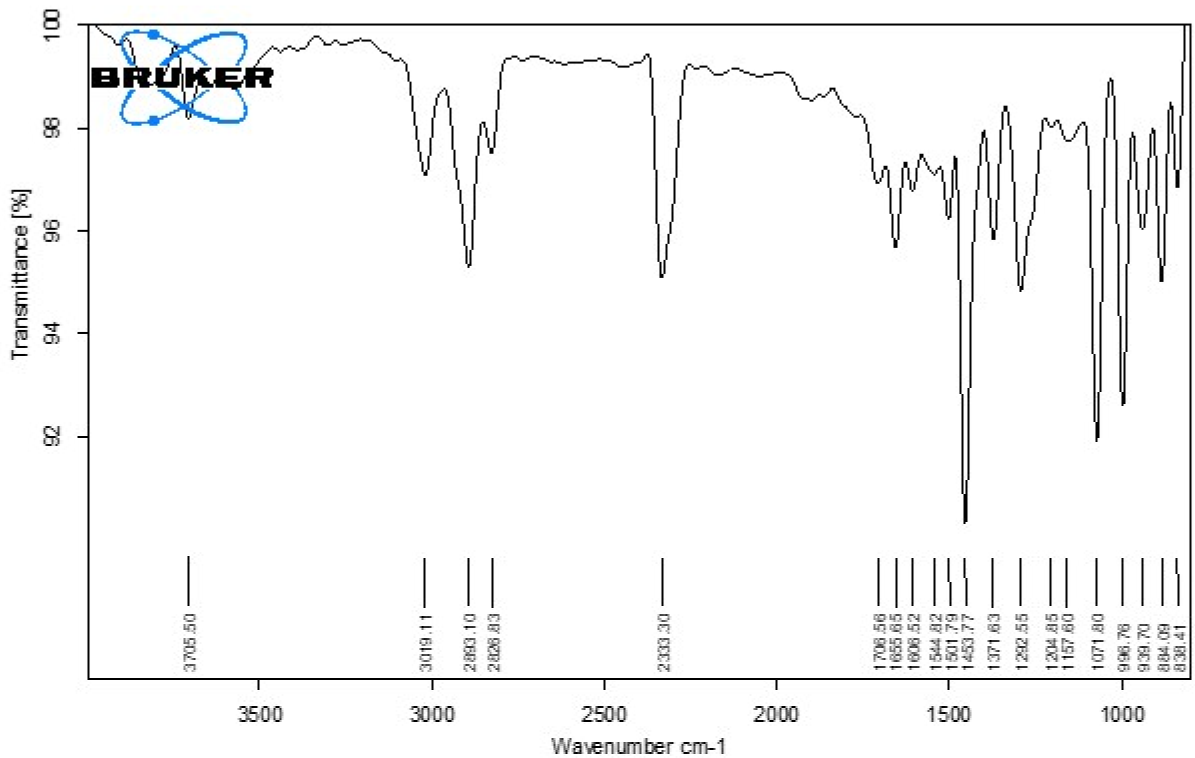


Fig. S71. Neat FT-IR spectrum of compound **15a**

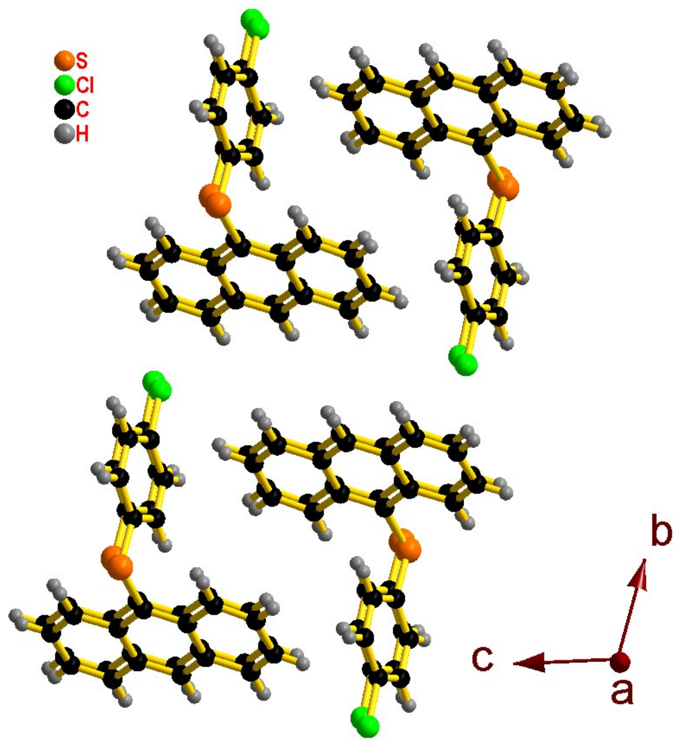


Fig. S72. Molecular packing of **E14.**

Table S1. Structural parameters of compounds **L**[1], **L**[2], **L**[3] and **1**.

	L[1]	**L**[2]	**L**[3]	**1**
Empirical formula	$C_{18}H_{19}N_3Se$	$C_{18}H_{19}N_3S$	$C_{16}H_{15}N_3Se$	$C_{19}H_{23}N_3SeCl_2OZn$
Formula weight	356.33	309.44	328.28	524.67
Temperature (K)	293	293	293	293
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	Pna21	Pbca	$P2_1/c$	$P2_1/n$
a/Å	14.5860(4)	15.9130(6)	11.1018(3)	11.2044(3)
b/Å	14.6224(4)	7.5636(2)	7.9784(2)	13.7372(3)
c/Å	7.9425(3)	27.8228(9)	16.7114(5)	15..1908(4)
α/°	90	90	90	90
β/°	90	90	92.665(3)	104.509(3)
γ/°	90	90	90	90
Volume (Å^3)	1694.00(9)	3348.75(19)	1478.61(7)	2263.58(10)
Z	4	8	4	4
ρ_{calc}/mg mm^{-3}	1.3971	1.2274	1.4746	1.5395
Absorption coefficient (μ/mm^{-1})	2.217	0.193	3.373	2.943
F(000)	727.9	1313.4	662.3	1058.4
Reflections collected	5934	12082	4733	11099
R_{int}	0.0386	0.0443	0.0195	0.0451
GOF on F^2	1.028	1.053	1.260	1.038
R_1 (I>2σ(I))	0.0490	0.0567	0.0617	0.0454
wR_2 (I>2σ(I))	0.0706	0.1242	0.2073	0.0740
R_1 values (all data)	0.0830	0.1003	0.0763	0.0839
R_2 values (all data)	0.0866	0.1514	0.2787	0.0932
2Θ range for data collection/°	5.84 to 58.18	5.86 to 57.9	7.98 to 141.6	5.94 to 57.96
Largest diff. peak/hole / e Å^{-3}	0.45/-0.35	0.34/-0.41	0.54/-1.47	0.74/-0.69
Independent reflections	3271 [R_{int} = 0.0386, R_{sigma} = 0.0698]	3933 [R_{int} = 0.0443, R_{sigma} = 0.0504]	2633 [R_{int} = 0.0195, R_{sigma} = 0.0260]	5224 [R_{int} = 0.0451, R_{sigma} = 0.0727]
Flack parameter	0.32 (19)	-	-	-

Table S2. Structural parameters of compounds **2-5**.

	2	**3**	**4**	**5**
Empirical formula	$C_{36}H_{38}N_6Se_2Br_4Zn_2$	$C_{19}H_{23}N_3SCl_2OZn$	$C_{19}H_{23}N_3SBr_2OZn$	$C_{38}H_{35}N_6Se_2Br4 Zn_2$
Formula weight	1163.07	477.78	566.68	1185.07
Temperature (K)	293	293	293	293
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	10.0434(3)	11.1565(4)	11.3268(7)	7.5364(5)
b/Å	13.9747(4)	13.8114(5)	14.1364(8)	12.0785(11)
c/Å	15.7202(5)	15.0162(5)	15.1166(8)	13.2048(12)
α/°	90	90	90	70.474(8)
β/°	102.367(3)	104.487(3)	105.480(6)	77.488(7)
γ/°	90	90	90	76.996(7)
Volume (Å^3)	2155.19(11)	2240.23(13)	2332.7(2)	1090.67(17)
Z	2	4	4	1
ρ_{calc}/mg mm^{-3}	1.7921	1.4165	1.6135	1.685
Absorption coefficient (μ/mm^{-1})	6.542	1.442	4.581	6.459
F(000)	1127.3	987.2	1127.9	531.6
Reflections collected	10913	10646	10469	8943
R_{int}	0.0409	0.0395	0.0746	0.0368
GOF on F^2	1.040	1.045	0.904	1.015
R_1 (I>2σ(I))	0.0539	0.0468	0.0586	0.0467
wR_2 (I>2σ(I))	0.1069	0.0846	0.0912	0.0850
R_1 values (all data)	0.1067	0.0833	0.1345	0.0836
R_2 values (all data)	0.1316	0.1062	0.1278	0.1039
2Θ range for data collection/°	6 to 58.1	5.9 to 57.88	5.96 to 58.08	6 to 58.14
Largest diff. peak/hole / e Å^{-3}	1.23/-1.55	0.53/-0.55	1.41/-1.24	0.94/-0.98
Independent reflections	4978 [R_{int} = 0.0409, R_{sigma} = 0.0668]	5218 [R_{int} = 0.0395, R_{sigma} = 0.0678]	5350 [R_{int} = 0.0746, R_{sigma} = 0.1468]	4952 [R_{int} = 0.0368, R_{sigma} = 0.0711]
Flack parameter	0.32 (19)	-	-	-

Table S3. Structural parameters of **E14**

Empirical formula	$C_{20}H_{13}S_1Cl_1$
Formula weight	320.84
Temperature/K	293
Crystal system	triclinic
Space group	P-1
a/Å	5.5355(3)
b/Å	11.3824(10)
c/Å	13.4351(10)
α/°	107.316(7)
β/°	94.243(6)
γ/°	99.600(6)
Volume/Å^3	789.92(11)
Z	2
ρ_{calc}g/cm^3	1.3488
μ/mm^{-1}	3.296
F(000)	334.2
Crystal size/mm^3	0.07 × 0.07 × 0.06
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.96 to 139.94
Index ranges	$-6 \le h \le 6$, $-13 \le k \le 13$, $-16 \le l \le 15$
Reflections collected	6327
Independent reflections	2976 [R_{int} = 0.0142, R_{sigma} = 0.0175]
Data/restraints/parameters	2976/0/199

Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	$R_1 = 0.0370$, $wR_2 = 0.1055$
Final R indexes [all data]	$R_1 = 0.0445$, $wR_2 = 0.1133$
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.26

Table S4: The absorption wavelength and the molar extinction coefficient of **L^1-L^3** and **1-5**.

Compound	**$\lambda_{(abs)\ max}$(nm)**	**ϵ ($L.mol^{-1}.cm^{-1}$)**
L^1	310, 380	800, 500
L^2	300, 370	1600, 1300
L^3	310, 370	1040, 600
1	310, 380	1400, 840
2	310, 380	500, 320
3	300, 370	1400, 1160
4	300, 370	720, 560
5	310, 370	1600, 900

Table S5. Screening effect of zinc sources on C-S cross coupling reactions[a]

Entry	Catalyst	Solvent	Time (h)	Yield (%)[b]
1	$ZnCl_2$	CH_3CN	24	nd[c]
2	$ZnBr_2$	CH_3CN	24	nd[c]
3	$ZnX_2.6H_2O$	CH_3CN	24	nd[c]
4	$ZnBr_2$/NaO^{t}Bu(2 eq)	CH_3CN	24	25
5	$ZnX_2.6H_2O$/NaO^{t}Bu(2eq)	CH_3CN	24	trace

[a]Reaction condition: 1-bromo-4-nitro benzene (1 mmol), thiophenol (1 mmol), L-proline 80 ^oC. b Isolated yield, c Not detected.

Table S6. Effect of the amount of catalyst **1** on C-S cross coupling reactions[a]

Entry	Zn catalyst 1 (mol %)	L- proline (mol%)	Solvent	Yield (%)[b]
1	10	10	CH_3CN	90
2	5	5	CH_3CN	65
3	2.5	2.5	CH_3CN	36

[a]Reaction condition: 1-bromo-4-nitro benzene (1 mmol), thiophenol (1 mmol), NaO^{t}Bu (2 equiv.), 80 ^oC, 15 h. b Isolated yield.

DFT (B3LYP) Calculation

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1,3,4-methyl-1,2,3-triazolin-5-ylidene (I)

Sl. No	Occupancy	Bond orbital	Coefficients	Hybrids
1	0.99323	BD(1)N1-N2	(54.86%) 0.7407* N1	s(28.40%)p 2.52(71.52%)d 0.00(0.08%)
			(45.14%) 0.6719* N2	s(25.05%)p 2.99(74.78%)d 0.01(0.16%)
2	0.99210	BD(1)N1-C5	(64.59%) 0.8037* N1	s(38.01%)p 1.63(61.96%)d 0.00(0.02%)
			(35.41%) 0.5951* C5	s(24.95%)p 3.00(74.91%)d 0.01(0.14%)
3	0.99487	BD(1)N1-C7	(64.21%) 0.8013* N1	s(33.55%)p 1.98(66.43%)d 0.00(0.02%)
			(35.79%) 0.5983* C7	s(21.63%)p 3.62(78.21%)d 0.01(0.16%)
4	0.99350	BD (1)N2-N3	(46.62%) 0.6828* N2	s(25.49%)p 2.92(74.34%)d 0.01(0.17%)
			(53.38%) 0.7306* N3	s(27.21%)p 2.67(72.70%)d 0.00(0.09%)
5	0.80330	BD*(1)N2-C5	(62.25%) 0.7890* N2	s(0.00%)p 1.00(99.86%)d 0.00(0.14%)
			(37.75%) -0.6144* C5	s(0.00%)p 1.00(99.98%)d 0.00(0.02%)
6	0.99052	BD(1)N3-C4	(68.17%) 0.8257* N3	s(39.60%)p 1.52(60.38%)d 0.00(0.02%)
			(31.83%) 0.5641* C4	s(22.50%)p 3.43(77.26%)d 0.01(0.24%)
7	0.99473	BD(1)N3-C6	(64.11%) 0.8007* N3	s(33.17%)p 2.01(66.81%)d 0.00(0.02%)
			(35.89%) 0.5991* C6	s(22.07%)p 3.52(77.77%)d 0.01(0.16%)
8	0.98192	BD(1)C4-C5	(44.25%) 0.6652* C4	s(32.21%)p 2.10(67.66%)d 0.00(0.13%)
			(55.75%) 0.7467* C5	s(38.14%)p 1.62(61.82%)d 0.00(0.04%)
9	0.99305	BD(1)C5-C8	(51.00%) 0.7142* C5	s(36.87%)p 1.71(63.10%)d 0.00(0.03%)
			(49.00%) 0.7000* C8	s(27.52%)p 2.63(72.43%)d 0.00(0.05%)
30	0.95224	LP(1)C4		s(46.17%)p 1.16(53.77%)d 0.00(0.06%)
31	0.36069	LP*(2)C4		s(0.00%)p 1.00(99.75%)d 0.00(0.25%)

193	0.36330	BD(1)N2-C5	(37.75%) 0.6144* N2	s(0.00%)p 1.00(99.86%)d 0.00(0.14%)
			(62.25%) 0.7890* C5	s(0.00%)p 1.00(99.98%)d 0.00(0.02%)
194	0.01201	BD*(1)N3 -C4	(31.83%) 0.5641* N3	s(39.60%)p 1.52(60.38%)d 0.00(0.02%)
			(68.17%) -0.8257* C4	s(22.50%)p 3.43(77.26%)d 0.01(0.24%)

1,3,4-methyl-1,2,3-triazolin-5-thione (II)

Sl No	Occupancy	Bond orbital	Coefficients	Hybrids
1	0.99259	BD(1)N1-N2	(55.04%) 0.7419* N1	s(28.40%)p 2.52(71.52%)d 0.00(0.08%)
			(44.96%) 0.6705* N2	s(24.91%)p 3.01(74.93%)d 0.01(0.17%)
2	0.99180	BD(1)N1-C5	(63.76%) 0.7985* N1	s(37.94%)p 1.63(62.03%)d 0.00(0.03%)
			(36.24%) 0.6020* C5	s(25.99%)p 2.84(73.88%)d 0.00(0.13%)
3	0.99456	BD(1)N1-C7	(64.65%) 0.8041* N 1	s(33.60%)p 1.98(66.37%)d 0.00(0.02%)
			(35.35%) 0.5945* C7	s(21.30%)p 3.69(78.54%)d 0.01(0.16%)
4	0.99242	BD(1)N2-N3	(45.86%) 0.6772* N2	s(24.98%)p 3.00(74.85%)d 0.01(0.17%)
			(54.14%) 0.7358* N3	s(28.18%)p 2.55(71.73%)d 0.00(0.09%)
5	0.81054	BD*(1)N2-C5	(63.43%) 0.7964* N2	s(0.00%)p 1.00(99.86%)d 0.00(0.14%)
			(36.57%) -0.6047* C5	s(0.00%)p 1.00(99.97%)d 0.00(0.03%)
6	0.99217	BD(1)N3-C4	(63.85%) 0.7991* N3	s(36.95%)p 1.71(63.02%)d 0.00(0.03%)
			(36.15%) 0.6013* C4	s(25.51%)p 2.91(74.35%)d 0.01(0.14%)
7	0.99466	BD(1)N3-C6	(64.96%) 0.8060* N3	s(34.81%)p 1.87(65.17%)d 0.00(0.02%)
			(35.04%) 0.5920* C6	s(21.07%)p 3.74(78.77%)d 0.01(0.16%)
8	0.98462	BD(1)C4-C5	(49.16%) 0.7012* C4	s(34.84%)p 1.87(65.10%)d 0.00(0.06%)
			(50.84%) 0.7130* C5	s(35.54%)p 1.81(64.41%)d 0.00(0.05%)

9	0.99111	BD(1)C4-S18	(60.81%) 0.7798* C4	s(39.62%)p 1.52(60.32%)d 0.00(0.06%)
			(39.19%) 0.6260* S18	s(17.63%)p 4.63(81.65%)d 0.04(0.72%)
10	0.99183	BD(1)C5-C8	(52.04%) 0.7214* C5	s(38.43%)p 1.60(61.54%)d 0.00(0.02%)
			(47.96%) 0.6926* C8	s(26.47%)p 2.78(73.48%)d 0.00(0.05%)
11	0.51219	LP*(1) C4		s(0.00%)p 1.00(99.99%)d 0.00(0.01%)
12	0.99397	LP (1)S18		s(83.06%)p 0.20(16.92%)d 0.00(0.02%)
13	0.93645	LP(2)S18		s(0.04%)p99.99(99.91%)d 1.08(0.05%)
14	0.83280	LP(3)S18		s(0.00%)p 1.00(99.90%)d 0.00(0.10%)
215	0.36110	BD(1)N2-C5	(36.57%) 0.6047* N2	s(0.00%)p 1.00(99.86%)d 0.00(0.14%)
			(63.43%) 0.7964* C5	s(0.00%)p 1.00(99.97%)d 0.00(0.03%)
216	0.04394	BD*(1)N3-C4	(36.15%) 0.6013* N3	s(36.95%)p 1.71(63.02%)d 0.00(0.03%)
			(63.85%) -0.7991* C4	s(25.51%)p 2.91(74.35%)d 0.01(0.14%)

1,3,4-methyl-1,2,3-triazolin-5-selone (III)

Sl. No	Occupancy	Bond orbital	Coefficients	Hybrids
1	0.99271	BD(1)N1-N2	(55.01%) 0.7417* N1	s(28.36%)p 2.52(71.56%)d 0.00(0.08%)
			(44.99%) 0.6707* N2	s(24.90%)p 3.01(74.94%)d 0.01(0.17%)
2	0.99154	BD(1)N1-C5	(63.75%) 0.7984* N1	s(37.92%)p 1.64(62.05%)d 0.00(0.03%)
			(36.25%) 0.6021* C5	s(25.75%)p 2.88(74.12%)d 0.00(0.13%)
3	0.99458	BD(1)N1-C7	(64.70%) 0.8044* N1	s(33.67%)p 1.97(66.31%)d 0.00(0.02%)
			(35.30%) 0.5941* C7	s(21.28%)p 3.69(78.56%)d 0.01(0.16%)
4	0.99238	BD(1)N2-N3	(45.84%) 0.6770* N2	s(25.01%)p 2.99(74.82%)d 0.01(0.17%)
			(54.16%) 0.7359* N3	s(28.03%)p 2.56(71.88%)d 0.00(0.09%)
5	0.80270	BD*(1)N2-C5	(64.01%) 0.8001* N2	s(0.00%)p 1.00(99.86%)d

				0.00(0.14%)
			(35.99%) -0.5999* C5	s(0.00%)p 1.00(99.97%)d 0.00(0.03%)
6	0.99212	BD(1)N3-C4	(64.10%) 0.8006* N3	s(37.24%)p 1.68(62.74%)d 0.00(0.03%)
			(35.90% 0.5991* C4	s(25.65%)p 2.89(74.20%)d 0.01(0.15%)
7	0.99457	BD(1)N3-C6	(65.10%) 0.8069* N3	s(34.67%)p 1.88(65.31%)d 0.00(0.02%)
			(34.90%) 0.5907* C6	s(21.00%)p 3.75(78.84%)d 0.01(0.16%)
8	0.98486	BD(1)C4-C5	(48.80%) 0.6986* C4	s(35.17%)p 1.84(64.76%)d 0.00(0.06%)
			(51.20%) 0.7155* C5	s(35.96%)p 1.78(64.00%)d 0.00(0.05%)
9	0.98930	BD(1)C4-Se18	(64.06%) 0.8003* C4	s(39.19%)p 1.55(60.79%)d 0.00(0.03%)
			(35.94%) 0.5995*Se18	s(13.70%)p 6.28(85.96%)d 0.03(0.34%)
10	0.99179	BD(1)C5-C8	(52.16%) 0.7223* C5	s(38.27%)p 1.61(61.71%)d 0.00(0.02%)
			(47.84%) 0.6916* C8	s(26.40%)p 2.79(73.55%)d 0.00(0.06%)
45	0.51192	LP*(1)C4		s(0.00%)p 1.00(99.98%)d 0.00(0.02%)
46	0.99467	LP(1)Se18		s(87.12%)p 0.15(12.88%)d 0.00(0.00%)
47	0.94362	LP(2)Se18		s(0.05%)p99.99(99.92%)d 0.59(0.03%)
48	0.84684	LP(3)Se18		s(0.00%)p 1.00(99.90%)d 0.00(0.10%)
226	0.36069	BD(1)N2-C5	(35.99%) 0.5999* N2	s(0.00%)p 1.00(99.86%)d 0.00(0.14%)
			(64.01%) 0.8001* C5	s(0.00%)p 1.00(99.97%)d 0.00(0.03%)
227	0.03953	BD*(1)N3-C4	(35.90%) 0.5991* N3	s(37.24%)p 1.68(62.74%)d 0.00(0.03%)
			(64.10%) -0.8006* C4	s(25.65%)p 2.89(74.20%)d 0.01(0.15%)