Supplementary Material (ESI) for Chemical Science

Supplementary Information for

High-Contrast Cu(I)-Selective Fluorescent Probes Based on Synergistic Electronic and Conformational Switching

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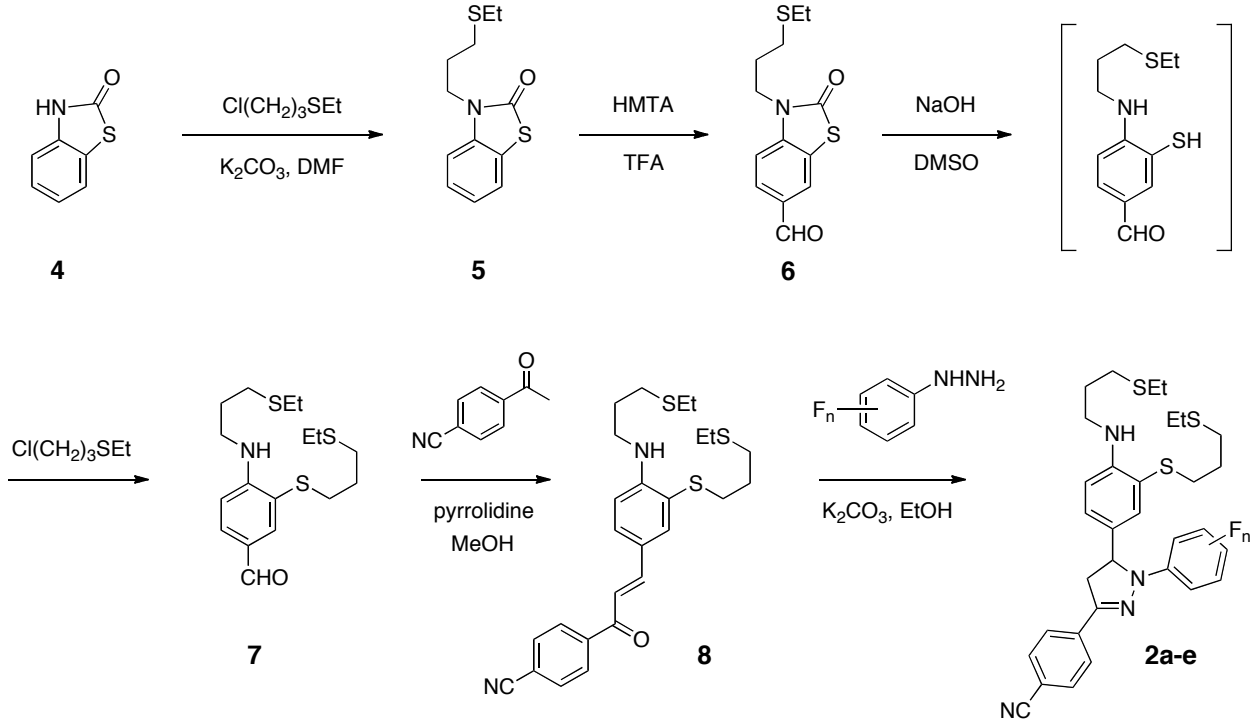
1. Synthesis

Materials and Reagents. Benzothiazol-2(3H)-one, 1-bromo-3-chloropropane, ethanethiol, hexamethylenetetramine, trifluoroacetic acid, and 4-acetylbenzonitrile were purchased from Sigma-Aldrich; 3-fluorophenylhydrazine hydrochloride**,** 2,5-difluorophenylhydrazine, and 2,3,5,6-tetra-fluorophenylhydrazine, and pentafluorophenylhydrazine were purchased from Oakwood Products (West Columbia, SC); 2,3,5-trifluorophenylhydrazine[1], 4-cinnamoylbenzonitrile[2] and 1-chloro-3-(ethylthio)propane[3] were synthesized as described in the literature. NMR: δ in ppm vs $SiMe_4$ (0 ppm, ^1H, 400 MHz), $CDCl_3$ (77.0 ppm, ^{13}C, 100 MHz), and $CFCl_3$ (0 ppm, ^{19}F, 376 MHz). MS: selected peaks; m/z. Melting points are uncorrected. Flash chromatography: Merck silica gel (70-230 mesh). TLC: 0.25 mm, Merck silica gel 60 F_{254}, visualizing at 254 nm or with 2% $KMnO_4$ solution.



Scheme S1: Reaction sequence and intermediates for the synthesis of pyrazoline derivatives **2a-e**.

3-(3-(Ethylthio)propyl)-2(3*H*)-benzothiazolone (5). A solution of benzothiazol-2(3H)-one (1.0 g, 6.61 mmol), 1-chloro-3-(ethylthio)-propane[3] (1.09 g, 7.93 mmol), and anhydrous K_2CO_3 (2.74 g) in anhydrous dimethylformamide (6 mL) was stirred at 80°C for 8 hours. After cooling to room temperature the reaction mixture was diluted with water (50 mL) and extracted with *tert*-butylmethyl ether. The combined organic layers were dried with anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified on silica gel (10:1 hexanes/EtOAc) to afford 1.30 g (5.13 mmol, 77% yield) of benzothiazolone **5** as colorless oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.26 (t, J = 7.3 Hz, 3H), 2.03 (p, J = 7.3 Hz, 2H), 2.56 (q, J = 7.3 Hz, 2H), 2.61 (t, J = 7.3 Hz, 2H), 4.07 (t, J = 7.3 Hz, 2H), 7.14 (d, J = 8.0 Hz, 1H), 7.16 (td, J = 7.6, 1.1 Hz, 1H), 7.33 (td, J = 7.8, 1.3 Hz, 1H), 7.43 (ddd, J = 7.8, 1.3, 0.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ14.7, 26.0, 27.3, 28.7, 41.7, 110.5, 122.6, 122.7, 123.0, 126.3, 137.0, 169.9. IR (NaCl) 2926, 2868, 1683, 1590, 1472, 1324, 1233, 745 cm^{-1}. EI-MS *m/z* 253 (100, $[M]^+$), 192 (78), 164 (44), 151 (42), 136 (46), 109 (45). EI-HRMS *m/z* calcd for $[M]^+$ $C_{12}H_{15}NOS_2$ 253.0595, found 253.0602.

3-(3-(Ethylthio)propyl)-2(3*H*)-benzothiazolone-6-carboxaldehyde (6). A solution of benzothiazolone **5** (208 mg, 0.82 mmol) and hexamethylenetetramine (233 mg, 1.66 mmol) in TFA (3 mL) was stirred in a sealed tube at 80°C for 45 hours. The reaction mixture was concentrated under reduced pressure and diluted with ice-cold water (20 mL). After stirring for 30 minutes, the solution was neutralized with Na_2CO_3 and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried ($MgSO_4$), concentrated under reduced pressure, and the residue was purified on silica gel, affording 200 mg (0.71 mmol, 87% yield) of aldehyde **6** as yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27 (t, *J* = 7.4 Hz, 3H), 2.05 (p, *J* = 6.9 Hz, 2H), 2.57 (q, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 7.0 Hz, 2H), 4.13 (t, *J* = 7.3 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.99 (d, *J* = 1.6 Hz, 1H), 9.95 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ14.7, 26.1, 27.2, 28.6, 42.1, 110.6, 123.7, 124.0, 129.1, 131.9, 141.8, 169.9, 190.2. IR (NaCl) 2962, 2927, 1683, 1593, 1489, 1385, 1328, 1234, 1199, 817, 741, 699 cm^{-1}. EI-MS *m/z* 281 (97, $[M]^+$), 221 (100), 192 (58), 180 (51), 164 (52), 109 (44). EI-HRMS *m/z* calcd for $[M]^+$ $C_{13}H_{15}NO_2S_2$ 281.0544, found 281.0561.

4-(3-(Ethylthio)propylamino)-3-(3-(ethylthio)propylthio)benzaldehyde (7). To a solution of **6** (175 mg, 0.62 mmol) in DMSO (2 mL) was added 20% aq. NaOH (0.5 mL) and the resulting mixture was stirred at 80 °C under nitrogen atmosphere until completion of hydrolysis (75 min). Then a solution of 1-chloro-3-(ethylthio)propane[3] (172 mg, 1.24 mmol) in DMSO (0.5 mL) was added and the reaction mixture was stirred for an additional 80 min. After cooling to room temperature, the reaction mixture was diluted with water and extracted with dichloromethane. The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel, gradient 9/1 –> 7/3 hexane/EtOAc) to afford 54 mg of **7** as a colorless oil (0.15 mmol, 24%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.23 (t, *J* = 7.4 Hz, 3H), 1.27 (t, *J* = 7.4 Hz, 3H), 1.82 (p, *J* = 7.1 Hz, 2H), 1.98 (p, *J* = 6.9 Hz, 2H), 2.49 (q, *J* = 7.4 Hz, 2H), 2.57 (q, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 7.0 Hz, 2H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 3.40 (q, *J* = 6.8 Hz, 2H), 5.89 (t, *J* = 5.6 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 1H), 7.71 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 9.69 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.68, 14.71, 25.8, 26.1, 28.5, 28.9, 29.0, 30.2, 33.7, 42.1, 109.0, 117.4, 126.0, 132.8, 138.3, 153.4, 189.0. IR (NaCl) 3352, 2962, 2925, 1674, 1589, 1525, 1418, 1337, 1254, 1190, 814 cm^{-1}. EI-MS *m/z* 357 (64, $[M]^+$), 103 (100); EI-HRMS *m/z* calcd for $[M]^+$ $C_{17}H_{27}NOS_3$ 357.1255, found 357.1259.

(*E*)-4-(3-(4-(3-(Ethylthio)propylamino)-3-(3-(ethylthio)propylthio)phenyl)acryloyl)-benzonitrile (8). Aldehyde **7** (108 mg, 0.3 mmol) was dissolved in dichloromethane (1 mL) and a solution of 4-acetylbenzonitrile (50 mg, 0.34 mmol) and pyrrolidine (150 µL, 1.8 mmol) in methanol (14 mL) was added. After stirring at room temperature for 6 hours, the reaction mixture was concentrated to half of its volume. The mixture was diluted with water (20 mL) and extracted with EtOAc (3 x 15 mL). The combined fractions were dried (Na_2SO_4) and concentrated under reduced pressure. The resulting residue was purified on silica gel (gradient CH_2Cl_2/EtOAc 1500:1 -> 100:1) to give 64 mg (43% yield) of chalcone **8** as orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.24 (t, *J* = 7.4 Hz, 3H), 1.28 (t, *J* = 7.4 Hz, 3H), 1.84 (p, *J* = 7.1 Hz, 2H), 1.98 (p, *J* = 6.9 Hz, 2H), 2.50 (q, *J* = 7.4 Hz, 2H), 2.58 (q, *J* = 7.4 Hz, 2H), 2.64 (t, *J* = 7.0 Hz, 2H), 2.66 (t, *J* = 7.0 Hz, 2H), 2.83 (t, *J* = 7.2 Hz, 2H), 3.39 (q, *J* = 6.8 Hz, 2H), 5.69 (t, *J* = 5.7 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 7.26 (d, *J* = 15.6 Hz, 1H), 7.51 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.74 (d, *J* = 15.6 Hz, 1H), 7.74 (d, *J* = 2.1 Hz, 1H), 7.79 (d, *J* = 8.6 Hz, 2H), 8.07 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ14.67, 14.71, 25.8, 26.0, 28.6, 28.9, 29.0, 30.2, 33.7, 42.1, 109.7, 115.3, 116.2, 117.7, 118.2, 122.8,

128.6, 131.9, 132.3, 137.2, 142.2, 146.7, 151.3, 188.8. IR (NaCl) 3359, 2924, 2229, 1655, 1573, 1519, 1410, 1330, 1212, 1175, 1034, 1015, 811 cm^{-1}. EI-MS *m/z* 484 (88, $[M]^+$), 103 (100); EI-HRMS *m/z* calcd for $[M]^+$ $C_{26}H_{32}N_2OS_3$ 484.1677, found 484.1690.

Synthesis of racemic 1,3,5-triarylpyrazolines 2a-e from chalcone 8 and polyfluorophenylhydrazines (General method). A mixture of the chalcone **8** (60 μmol), anhydrous K_2CO_3 (77 μmol), and the corresponding fluoro-substituted phenylhydrazine hydrochloride salt (1.3 molar equiv) in ethanol (750 μl) was stirred at 90°C for 3 hours. The reaction mixture was diluted with ice-cold water (10 mL) and the product extracted with EtOAc (3 x 5 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by flash chromatography and analytical purity was verified by reversed-phase HPLC (Varian ProStar system with UV detector, acetonitrile-water, gradient 20% –> 2% water).

(±)-4-(5-(4-(3-(Ethylthio)propylamino)-3-(3-(ethylthio)propylthio)phenyl)-1-(3-fluorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl)benzonitrile (2a). Synthesized from chalcone **8** and 3-fluorophenyl hydrazine. Yield 66%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, *J* = 7.4 Hz, 3H), 1.26 (t, *J* = 7.4 Hz, 3H), 1.68 (p, *J* = 7.1 Hz, 2H), 1.92 (p, *J* = 6.9 Hz, 2H), 2.45 (q, *J* = 7.4 Hz, 2H), 2.52 (q, 6.9 Hz, 2H), 2.55 (q, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 7.0 Hz, 2H), 2.73 (t, *J* = 7.1 Hz, 2H), 3.12 (dd, *J* = 17.2, 6.7, 1H), 3.26 (t, *J* = 6.6 Hz, 2H), 3.78 (dd, *J* = 17.2, 12.4 Hz, 1H), 5.11 (br s, 1H), 5.23 (dd, *J* = 12.4, 6.7 Hz, 1H), 6.50 (tdd, *J* = 8.4, 2.4, 0.8 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 1H), 6.77 (ddd, *J* = 8.3, 2.1, 0.8 Hz, 1H), 6.88 (dt, *J* = 11.7, 2.3 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.10 (td, *J* = 8.3, 6.6 Hz, 1H), 7.25 (d, *J* = 2.2 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.78 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ14.70, 14.74, 25.8, 26.0, 28.8, 28.9, 29.1, 30.0, 33.2, 42.5, 43.0, 64.1, 101.1 (d, J_{CF} = 26.8 Hz), 106.3 (d, J_{CF} = 21.8 Hz), 109.2 (d, J_{CF} = 2.3 Hz), 110.6, 111.3, 117.6, 118.9, 125.9, 127.5, 129.0, 130.0 (d, J_{CF} = 9.9 Hz), 132.3, 133.4, 136.8, 145.2, 145.4 (d, J_{CF} = 11.1 Hz), 148.6, 163.5 (d, J_{CF} = 243.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –112.7 (ddd, *J* = 12.1, 8.4, 6.5 Hz, 1F). IR (NaCl) 2918, 2849, 2224, 1605, 1575, 1516, 1490, 1324, 1272, 1185, 1125, 839 cm^{-1}. EI-MS *m/z* 592 (100, $[M]^+$), 103 (62); EI-HRMS *m/z* calcd for $[M]^+$ $C_{32}H_{37}FN_4S_3$ 592.2164, found 592.2153.

(±)-4-(5-(4-(3-(Ethylthio)propylamino)-3-(3-(ethylthio)propylthio)phenyl)-1-(2,5-difluorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl)benzonitrile (2b). Synthesized from chalcone **8** and 2,5-difluorophenyl hydrazine. Yield 73%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (t, *J* = 7.8 Hz, 3H), 1.24 (t, *J* = 7.5 Hz, 3H), 1.58 (p, *J* = 7.1 Hz, 2H), 1.88 (p, *J* = 6.9 Hz, 2H), 2.46 (q, *J* = 7.4 Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.53 (q, *J* = 7.4 Hz, 2H), 2.59 (t, *J* = 7.0 Hz, 2H), 2.65 (t, *J* = 7.0 Hz, 2H), 3.20 (br t, *J* = 7.1 Hz, 2H), 3.26 (dd, *J* = 17.1, 4.1 Hz, 1H), 3.73 (dd, *J* = 17.1, 3.8 Hz, 1H), 5.04 (br s, 1H), 5.61 (dt, *J* = 11.9, 3.8 Hz, 1H), 6.44-6.50 (m, 2H), 6.82 (ddd, *J* = 12.0, 6.8, 5.0 Hz, 1H), 6.96 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.13 (d, *J* = 2.1 Hz, 1H), 7.33 (ddd, *J* = 10.0, 6.6, 3.1 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ14.68, 14.74, 25.8, 26.0, 28.6, 28.8, 29.1, 30.1, 33.2, 42.3, 42.4, 65.8 (d, J_{CF} = 8.1 Hz), 106.6 (dd, J_{CF} = 28.5, 3.8 Hz), 107.7 (dd, J_{CF} = 24.4, 7.6 Hz), 110.0, 111.7, 116.6 (dd, J_{CF} = 23.2, 10.1 Hz), 116.9, 118.8, 126.2, 127.9, 128.9, 132.3, 133.4 (t, J_{CF} = 10.9 Hz), 133.8, 136.6, 146.9, 147.0 (dd, J_{CF} = 240.0, 2.2 Hz), 148.6, 159.0 (dd, J_{CF} = 240.4, 1.5 Hz). IR (NaCl) 2925, 2855, 2225, 1604, 1504, 1446, 1324, 1252, 1176, 1107, 1011, 835 cm^{-1}. EI-MS *m/z* 610 (100, $[M]^+$), 103 (75); EI-HRMS *m/z* calcd for $[M]^+$ $C_{32}H_{36}F_2N_4S_3$ 610.2070, found 610.2071.

(±)-4-(5-(4-(3-(Ethylthio)propylamino)-3-(3-(ethylthio)propylthio)phenyl)-1-(2,3,5-trifluorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl)benzonitrile (2c). Synthesized from chalcone **8** and 2,3,5-trifluorophenyl hydrazine[1]. Yield 83%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (t, *J* = 7.4 Hz, 3H), 1.24 (t, *J* = 7.4 Hz, 3H), 1.61 (p, *J* = 7.1 Hz, 2H), 1.89 (p, *J* = 7.0 Hz, 2H), 2.45 (q, *J* = 7.0 Hz, 2H), 2.50-2.56 (m, 4H), 2.60 (t, *J* = 7.0 Hz, 2H), 2.68 (ddd, *J* = 7.9, 6.8, 1.3 Hz, 2H), 3.22 (br dd, *J* = 11.5, 6.6 Hz, 2H), 3.28 (dd, *J* = 17.2, 4.0 Hz, 1H), 3.75 (dd, *J* = 17.1, 11.9 Hz, 1H), 5.08 (br m, 1H), 5.61 (dt, *J* = 11.9, 3.8 Hz, 1H), 6.46 (d, *J* = 8.5 Hz, 1H), 6.38 (dddd, *J* = 10.4, 8.0, 5.8, 3.1 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.09-7.16 (m, 2H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –115.7 (dddd, *J* = 11.3, 10.8, 9.1, 2.9 Hz, 1F), –134.9 (dd, *J* = 20.2, 10.0 Hz, 1F), –156.0 (m, 1F). IR (NaCl) 2924, 2853, 2226, 1635, 1603, 1507, 1458, 1245, 1144, 1110, 840 cm^{-1}. EI-MS *m/z* 628 (100, $[M]^+$), 103 (42); EI-HRMS *m/z* calcd for $[M]^+$ $C_{32}H_{35}F_3N_4S_3$ 628.1976, found 628.1990.

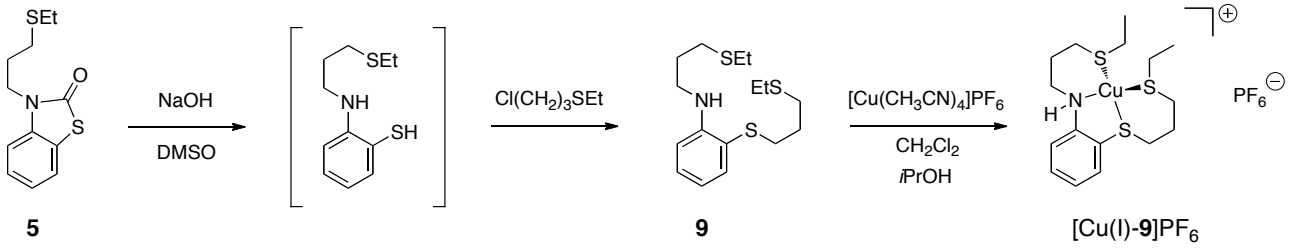
(±)-4-(5-(4-(3-(Ethylthio)propylamino)-3-(3-(ethylthio)propylthio)phenyl)-1-(2,3,5,6-tetrafluorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl)benzonitrile (2d). Synthesized from chalcone **8** and 2,3,5,6-tetrafluorophenyl hydrazine. Yield 79%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (t, *J* = 7.4 Hz, 3H), 1.25 (t, *J* = 7.4, 3H), 1.62-1.70 (m, 2H), 1.89 (p, *J* = 6.9 Hz, 2H), 2.47 (q, *J* = 7.4 Hz, 2H), 2.54 (q, *J* = 7.4 Hz, 2H), 2.56 (t, *J* = 7.0 Hz, 2H), 2.61 (t, *J* = 7.0 Hz, 2H), 2.72 (t, *J* = 7.0 Hz, 2H), 3.23 (t, *J* = 6.8 Hz, 2H), 3.29 (dd, *J* = 17.1, 7.4 Hz, 1H), 3.71 (dd, *J* = 17.1, 12.0 Hz, 1H), 5.11 (br s, 1H), 5.46 (dd, *J* = 12.0, 7.4 Hz, 1H), 6.49 (d, *J* = 8.5 Hz, 1H), 6.71 (tt, *J* = 9.8, 7.1 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –140.3 (dt, *J* = 21.0, 9.5 Hz, 2F), –148.9 (dt, *J* = 20.6, 8.5, 2F). IR (NaCl) 2926, 2869, 2226, 1641, 1602, 1580, 1412, 1324, 1262, 1170, 1151, 1104, 934, 839, 710 cm^{-1}. EI-MS *m/z* 646 (100, $[M]^+$), 103 (72); EI-HRMS *m/z* calcd for $[M]^+$ $C_{32}H_{34}F_4N_4S_3$ 646.1882, found 646.1879.

(±)-4-(5-(4-(3-(Ethylthio)propylamino)-3-(3-(ethylthio)propylthio)phenyl)-1-(2,3,4,5,6-pentafluorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl)benzonitrile (2e). Synthesized from chalcone **8** and pentafluorophenyl hydrazine. Yield 65%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (t, *J* = 7.4 Hz, 3H), 1.26 (t, *J* = 7.4 Hz, 3H), 1.66-1.73 (m, 2H), 1.91 (p, *J* = 6.9 Hz, 2H), 2.48 (q, *J* = 7.4 Hz, 2H), 2.55 (q, *J* = 7.4 Hz, 2H), 2.57 (t, *J* = 7.1 Hz, 2H), 2.62 (t, *J* = 7.0 Hz, 2H), 2.72 (t, *J* = 7.1 Hz, 2H), 3.22-3.27 (m, 2H), 3.29 (dd, *J* = 17.1, 8.3 Hz, 1H), 3.70 (dd, *J* = 17.1, 11.8 Hz, 1H), 5.13 (br s, 1H), 5.32 (dd, *J* = 11.8, 8.3 Hz, 1H), 6.50 (d, *J* = 8.5 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –148.1 (dd, *J* = 21.8, 5.0 Hz, 2F), –160.5 (t, *J* = 21.8 Hz, 1F), –163.4 (td, *J* = 21.8 , 5.0 Hz, 2F). IR (NaCl) 2927, 2869, 2226, 1603, 1581, 1519, 1516, 1505, 1412, 1320, 1101, 1060, 981, 839 cm^{-1}. EI-MS *m/z* 664 (100, $[M]^+$), 103 (75); EI-HRMS *m/z* calcd for $[M]^+$ $C_{32}H_{33}F_5N_4S_3$ 664.1788, found 664.1790.

(±)-4-(5-Phenyl-1-(2,5-difluorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]benzonitrile (3b). Synthesized according to reference 2.

(±)-4-(5-Phenyl-1-(2,3,5-trifluorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl)benzonitrile (3c). Synthesized from 4-cinnamoylbenzonitrile[2] and 2,3,5-trifluorophenylhydrazine[1] following the procedure as described above for **2a-e**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.28 (dd, *J* = 17.2, 3.9 Hz, 1H), 3.82 (dd, *J* = 16.9, 12.0 Hz, 1H), 5.76 (dt, *J* = 11.8, 3.5 Hz, 1H), 6.35-6.42 (m, 1H), 7.13-7.19 (m, 4H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –115.6 -

–115.7 (m, 1F), –134.8 (dd, *J* = 19.6, 10.0 Hz, 1F), –156.8 - –156.9 (m, 1F). IR (NaCl) 3080, 2226, 1629, 1581, 1508, 1457, 1224, 1144, 1109, 994, 840, 804, 763, 702 cm^{-1}. EI-MS *m/z* 377 (100, $[M]^+$), 300 (32), 231 (28), 145 (27); EI-HRMS *m/z* calcd for $[M]^+$ $C_{22}H_{14}F_3N_3$ 377.1140, found 377.1134.

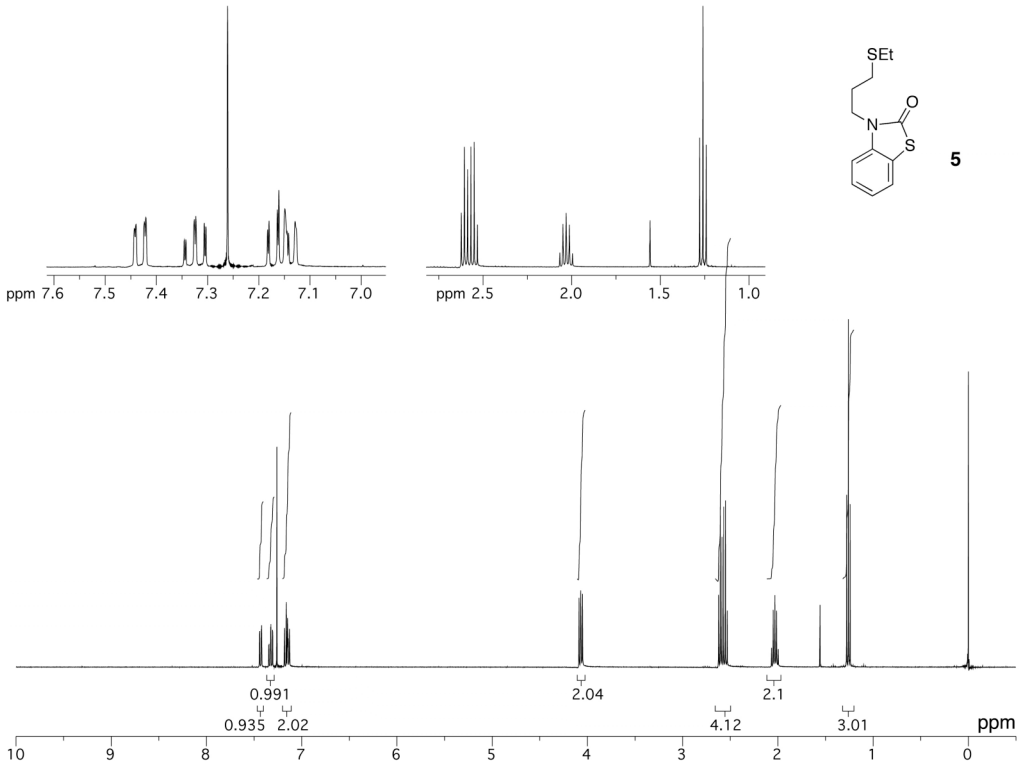


Scheme S2: Reaction sequence and intermediates for the synthesis of complex [Cu(I)-**9**]PF_6.

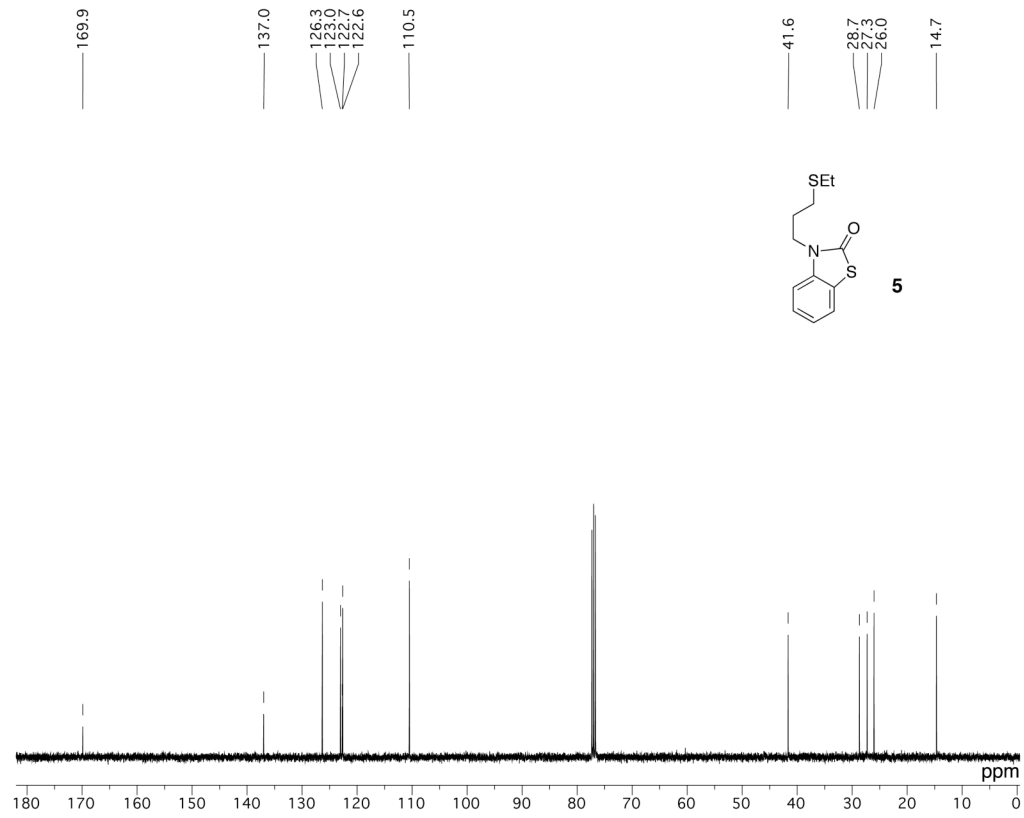
N-(3-(Ethylthio)propyl)-2-((3-ethylthio)propy)thio)aniline (9). A mixture of **5** (1.15 g, 4.54 mmol), NaOH (760 mg) in 30 mL DMSO-H_2O (2:1) was heated under an argon atmosphere for 4 hours at 90°C. A solution of 1-chloro-3-(ethylthio)-propane[3] in DMSO (2 mL) was added, and the mixture was stirred at 90°C for an additional 2.5 hours. After cooling to room temperature, the reaction mixture was diluted with ice cold $NaHPO_4$ (0.1 M, 50 mL), and extracted with *tert*-butylmethyl ether (3 x 50 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated under reduced pressure. The residual oil was purified on silica (hexanes-*tert*-butylmethyl ether 40:1) to give 1.08 g (72% yield) of ligand **9** as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.23 (t, *J* = 7.4 Hz, 3H), 1.27 (t, *J* = 7.4 Hz, 3H), 1.81 (p, *J* = 7.2 Hz, 2H), 1.95 (p, *J* = 7.0 Hz, 2H), 2.50 (q, *J* = 7.4 Hz, 2H), 2.56 (q, *J* = 7.4 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.1 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 3.29 (q, *J* = 6.7 Hz, 2H), 5.11 (t, *J* = 5.7 Hz, 1H), 6.59-6.63 (m, 2H), 7.20 (td, *J* = 7.8, 1.6 Hz, 1H), 7.38 (ddd, *J* = 7.3, 1.5, 0.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ14.72, 14.75, 25.8, 26.0, 28.9, 29.1, 29.2, 30.2, 33.5, 42.5, 110.0, 116.6, 117.0, 130.1, 136.2, 149.0. IR (NaCl) cm^{-1} 3369, 2924, 1589, 1501, 1450, 1373, 1320, 1260, 1037, 747. EI-MS *m/z* 329 (59, $[M]^+$), 136 (24), 103 (100), 75 (30). EI-HRMS *m/z* calcd for $[M]^+$ $C_{12}H_{27}NS_3$ 329.1306, found 329.1267.

Copper(I) N-(3-(ethylthio)propyl)-2-((3-ethylthio)propy)thio)aniline hexafluorophosphate ([Cu(I)-9]PF_6). To a solution of ligand **9** (200 mg, 0.607 mmol) in dichloromethane (5 mL) was added $[Cu(I)(CH_3CN)_4]PF_6$ (226 mg, 0.607 mmol). The mixture was stirred at room temperature for 15 min, filtered, and diluted with 10 mL isopropanol. Upon concentration of the clear solution under reduced pressure, the copper complex started to crystallize. The product was filtered off, washed with isopropanol and hexane, and dried in vacuo to give 272 mg (0.50 mmol, 83% yield) of ([Cu-**9**]PF_6) as colorless needles. A sample was recrystallized from methanol to afford colorless needles suitable for x-ray diffraction structural analysis. ^{1}H NMR (CD_3OD, 400 MHz) δ 1.23 (t, *J* = 7.4 Hz, 3H), 1.43 (t, *J* = 7.4 Hz, 3H), 1.82-1.87 (m, 2H), 2.05-2.09 (m, 2H), 2.55 (q, *J* = 7.4 Hz, 2H), 2.86-2.89 (m, 2H), 2.92 (q, *J* = 7.4 Hz, 2H), 2.98-3.00 (m, 4H), 3.42-3.45 (m, 2H), 7.34-7.45 (m, 3H), 7.72 (dt, *J* = 7.6, 1.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.2, 13.7, 21.7, 25.3, 28.8, 29.5, 31.2, 33.3, 37.2, 58.2, 125.8, 127.6, 128.1, 130.2, 130.6, 148.8. IR (KBr) cm^{-1}. 3304, 2928, 2858, 1589, 1502, 1452, 1416, 1265, 1178, 1091, 979, 908, 840, 767, 739, 558. MALDI-MS (MC); isotopic envelope for [Cu-**9**]$^+$ *m/z* 392 (100), 393 (25), 394 (63), 395 (14); calcd 392 (100), 393 (21), 394 (60), 395 (12).

^{1}H-NMR ($CDCl_3$, 400 MHz)



^{13}C-NMR ($CDCl_3$, 100 MHz)



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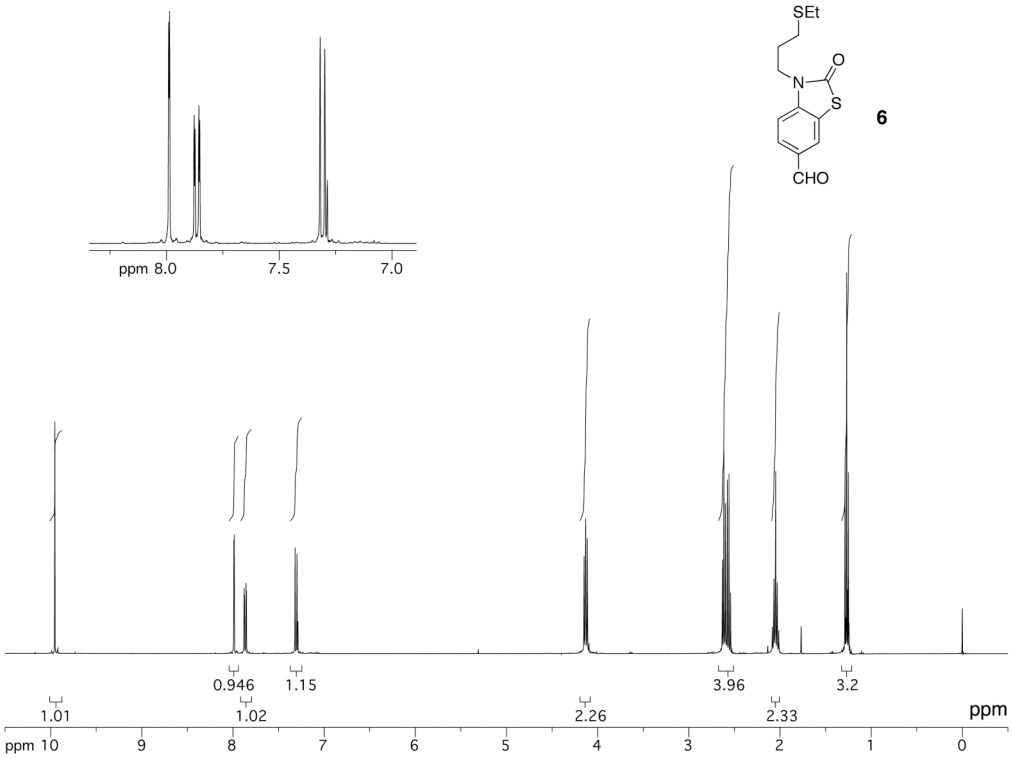

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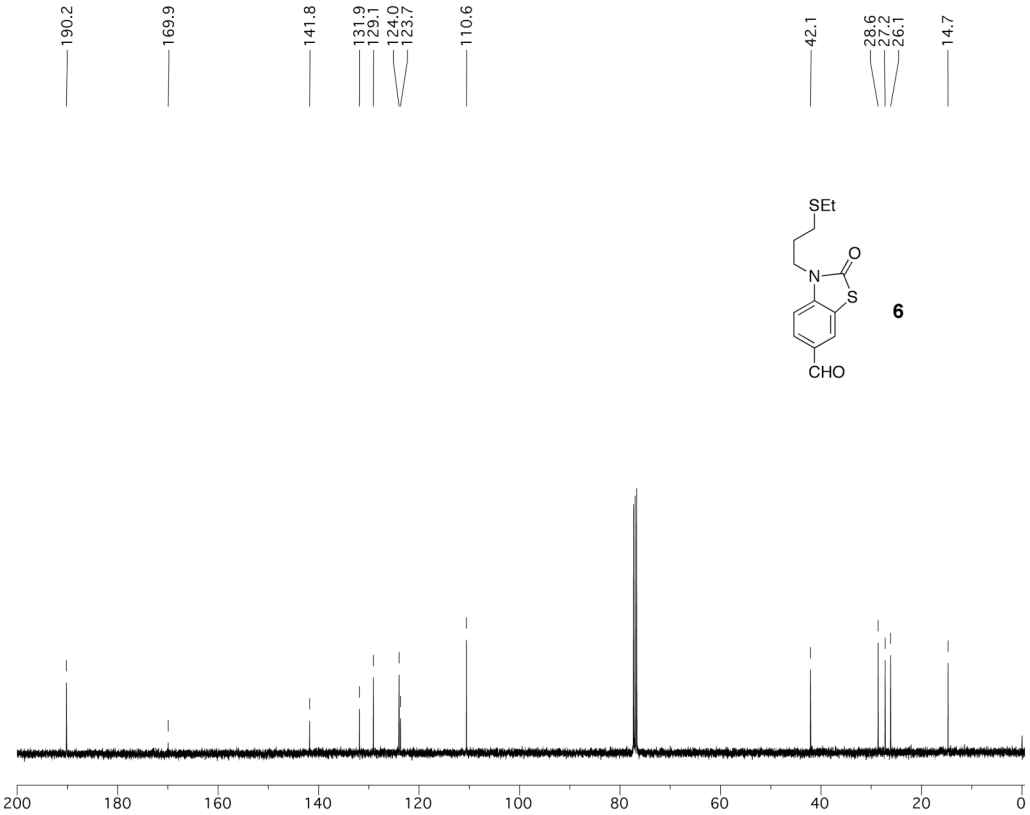

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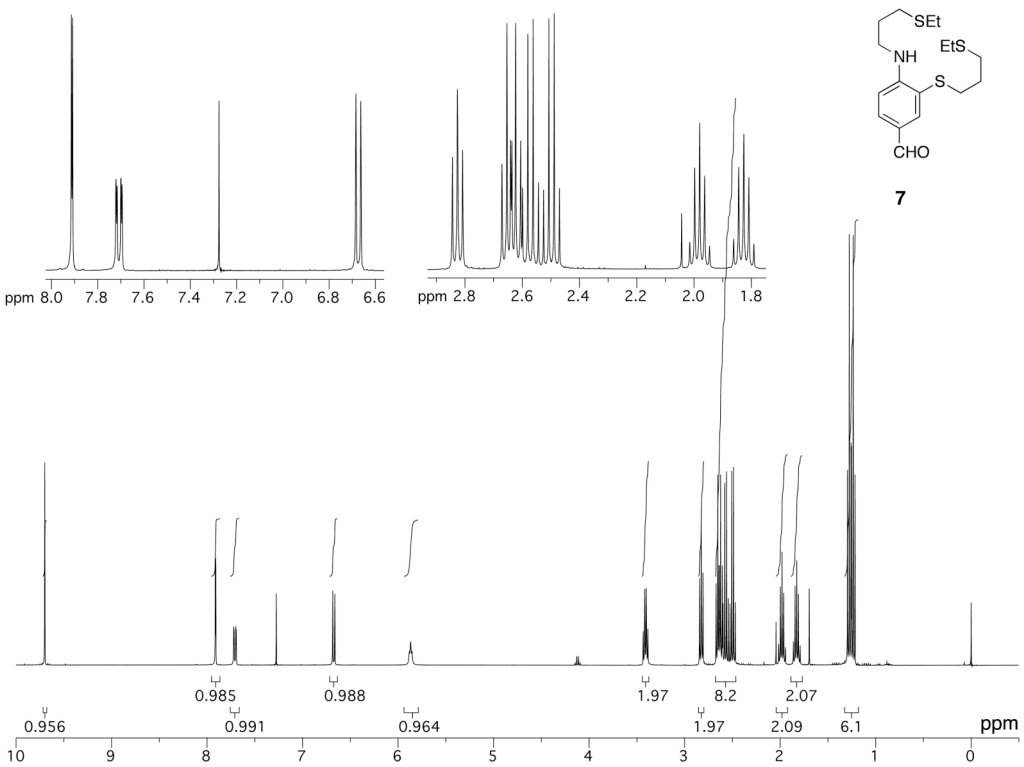
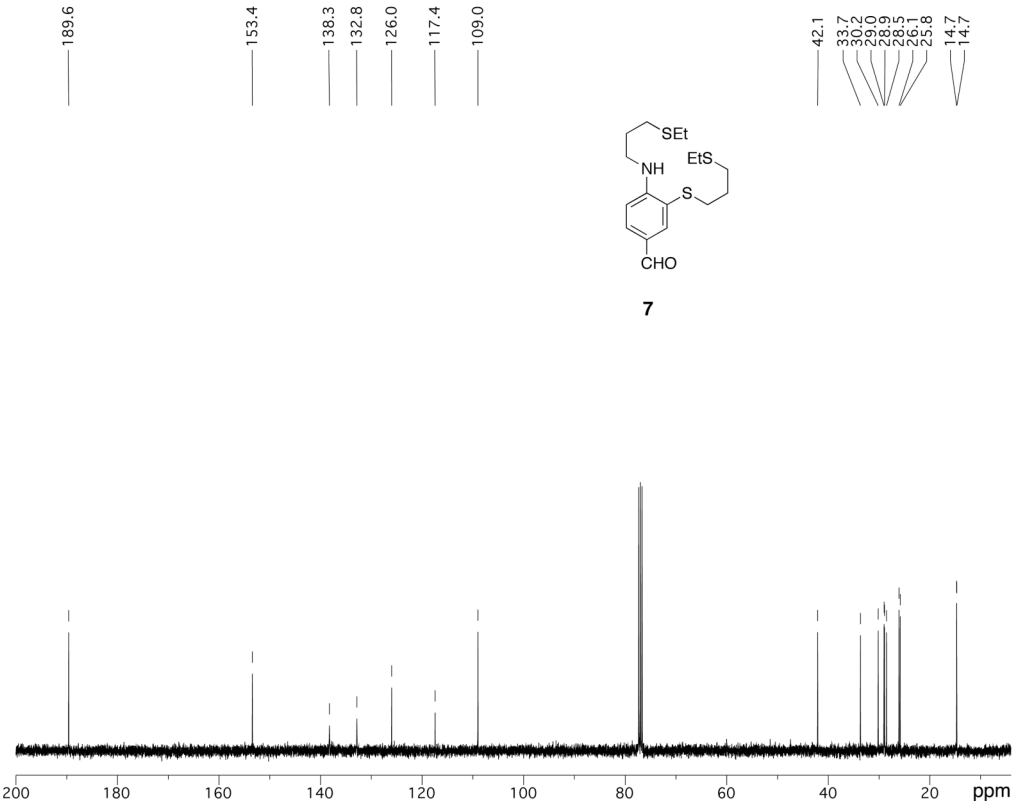


^{13}C-NMR ($CDCl_3$, 100 MHz)



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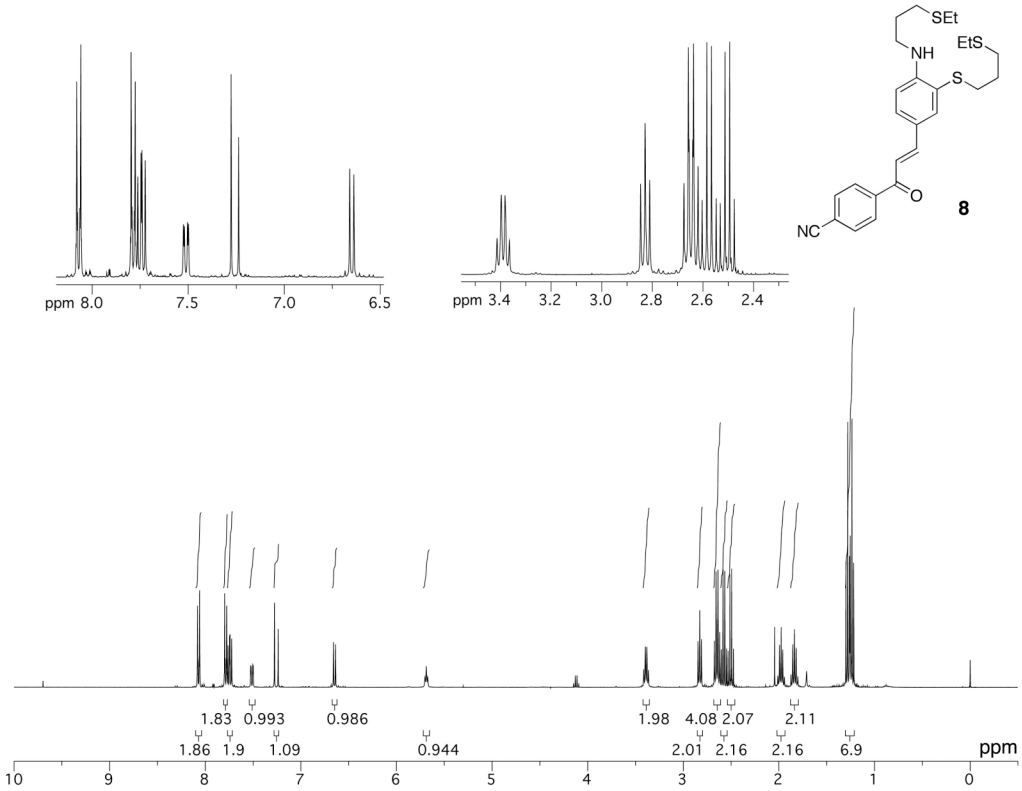

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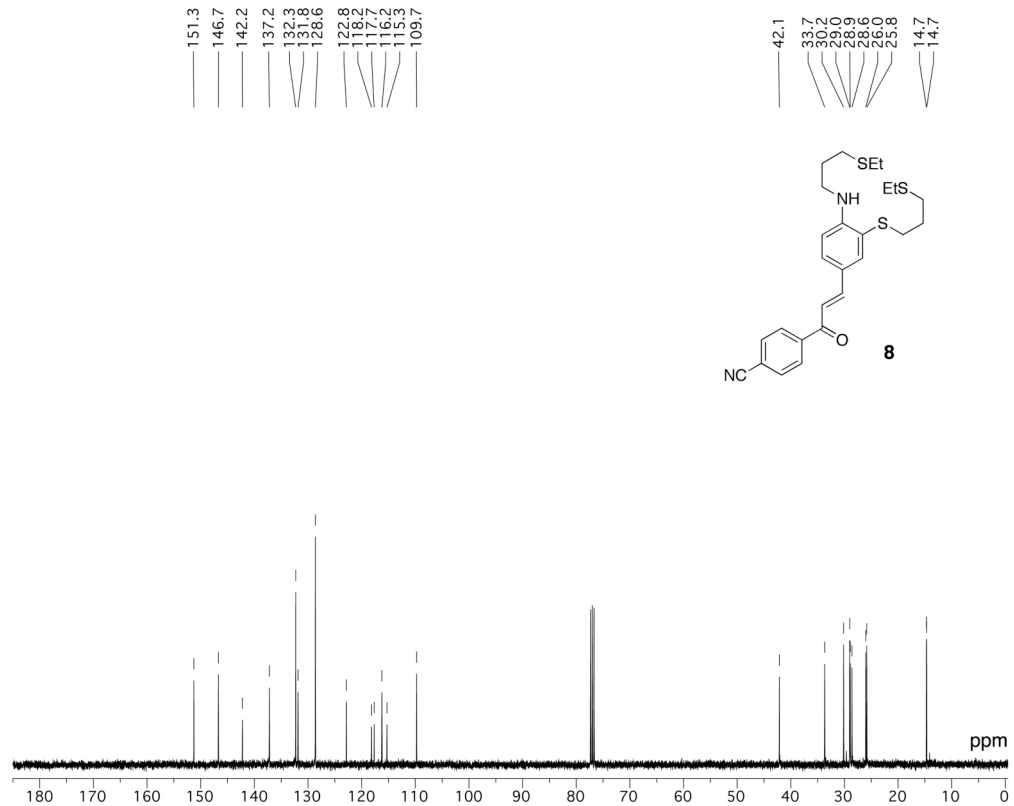

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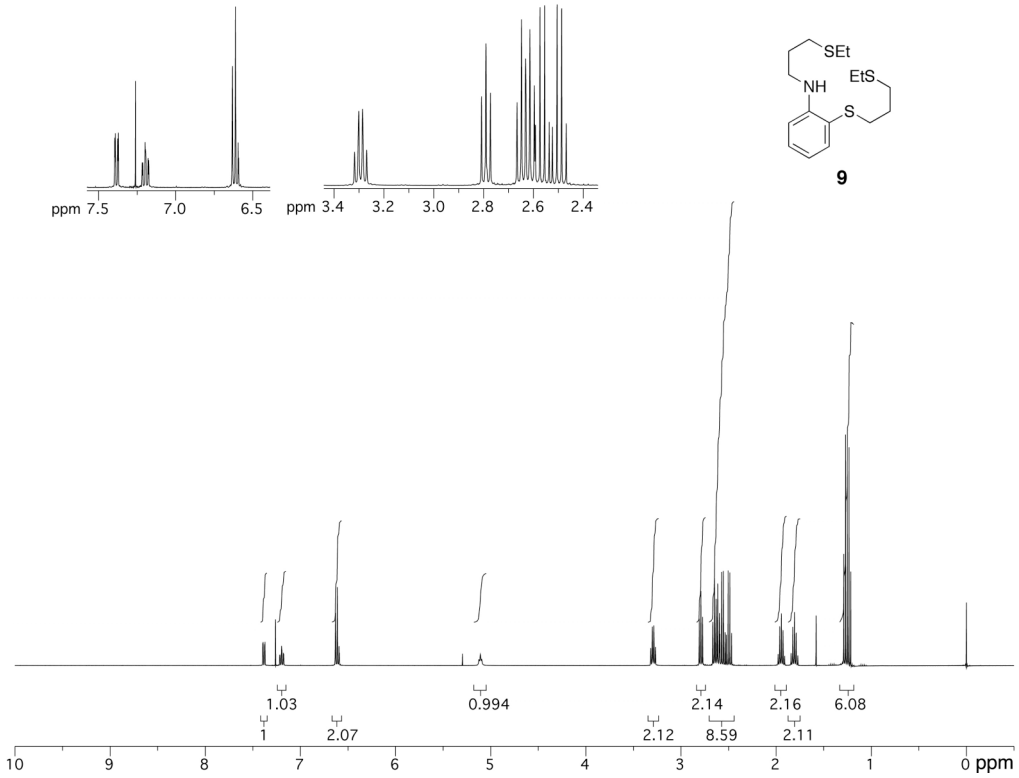

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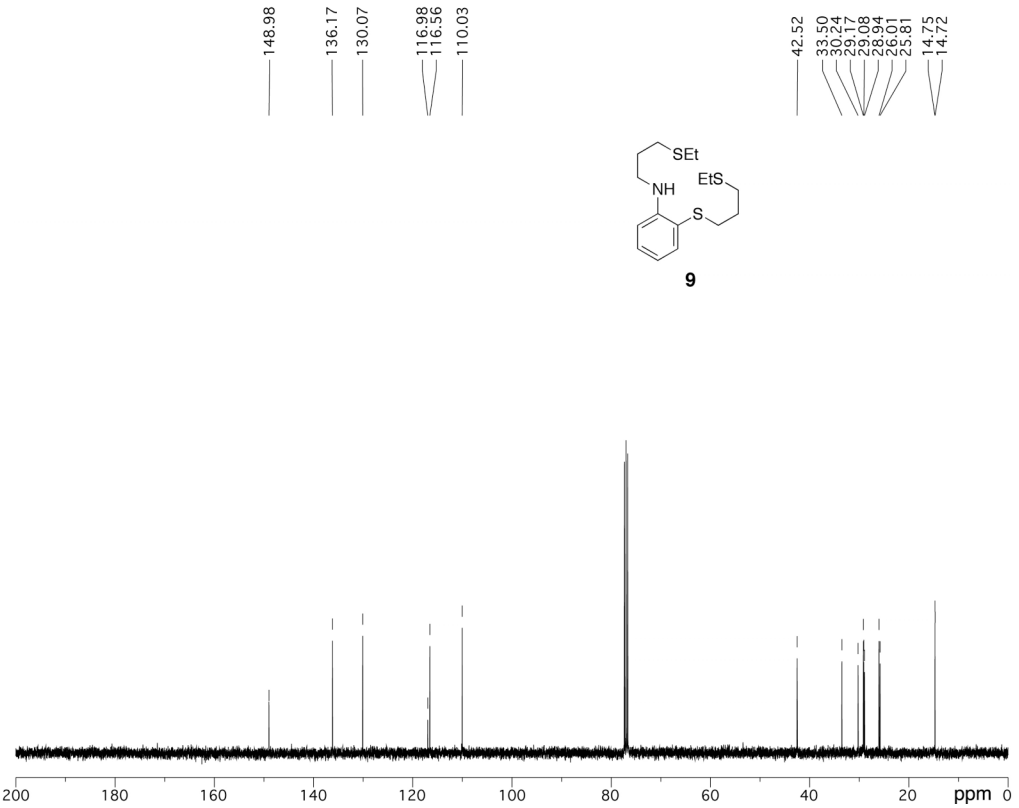
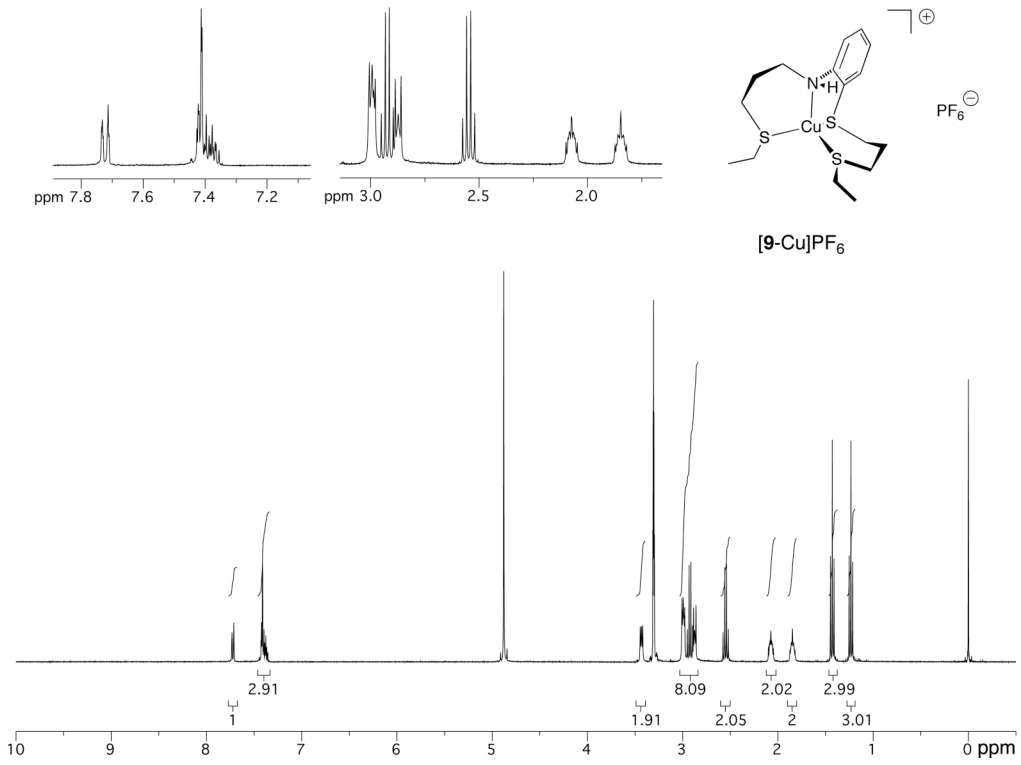


^{1}H-NMR (CD_3OD, 400 MHz)



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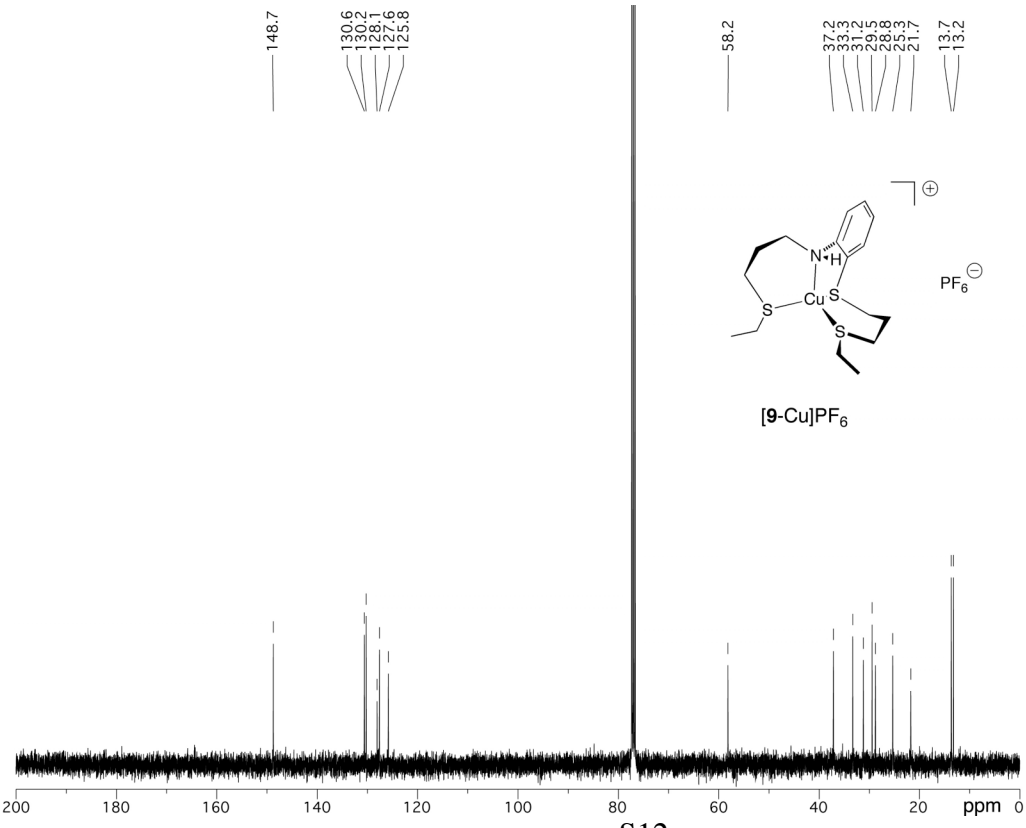

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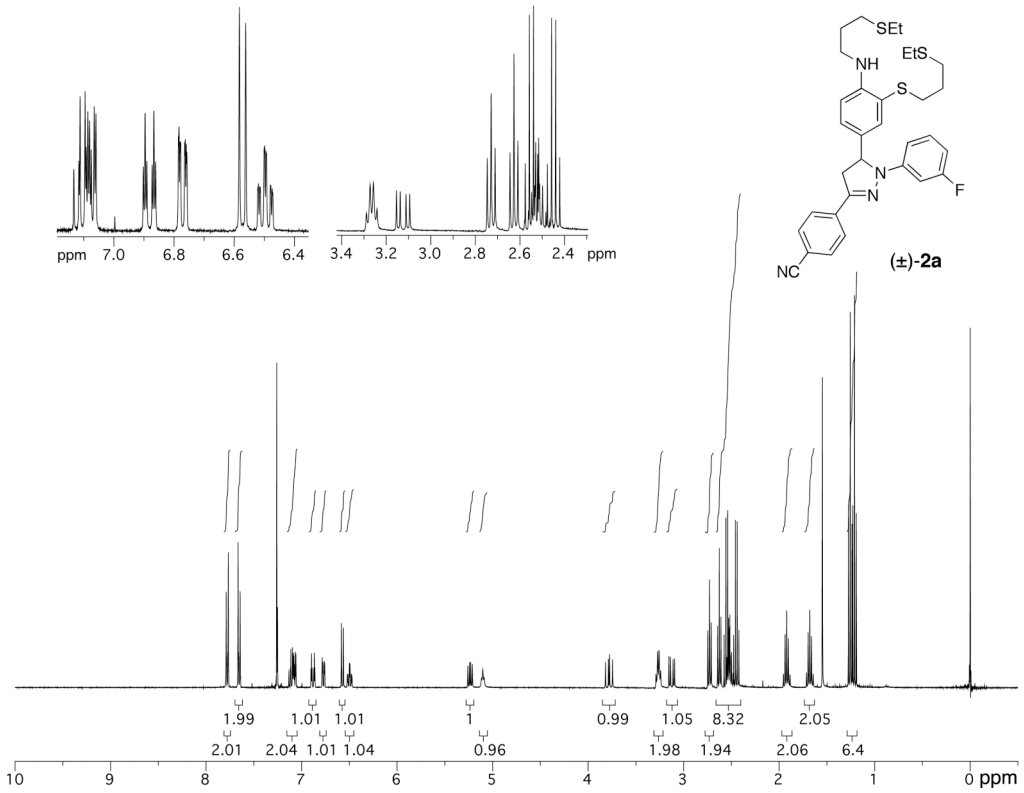
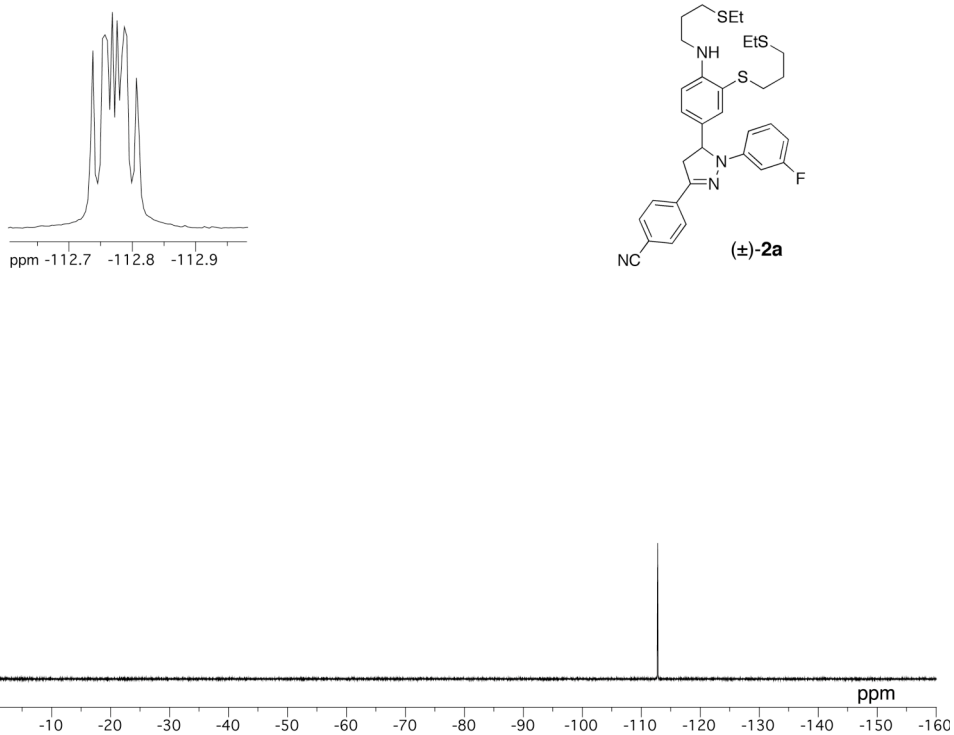


^{19}F-NMR ($CDCl_3$, 376 MHz)



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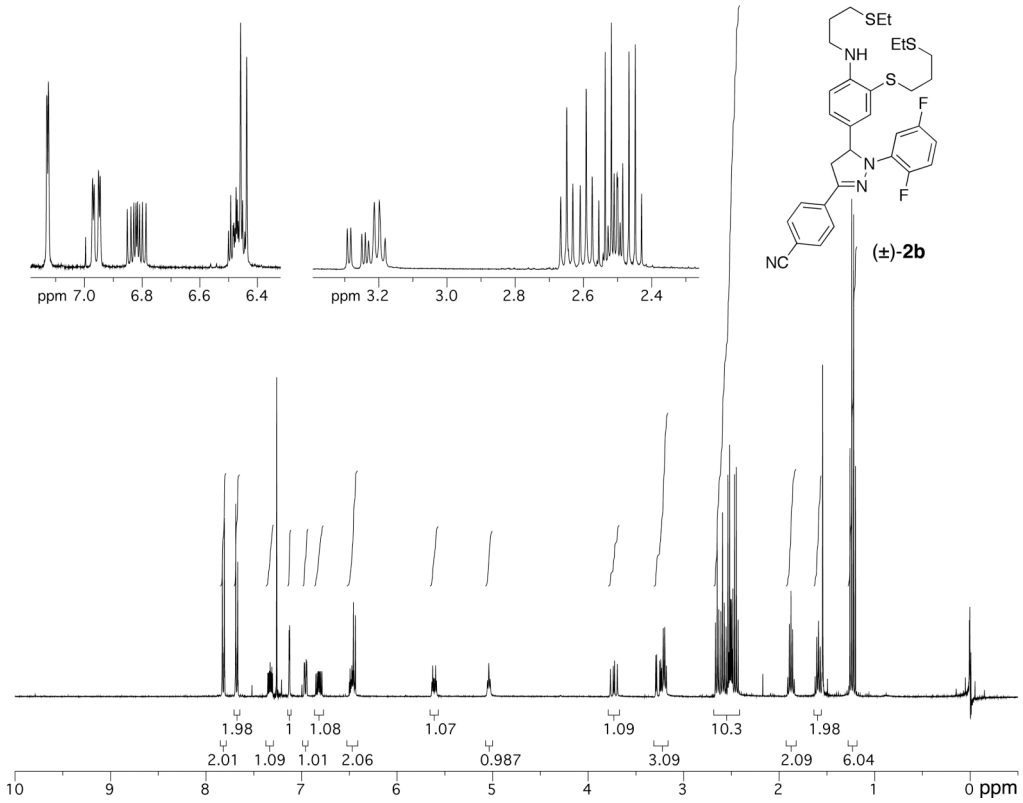
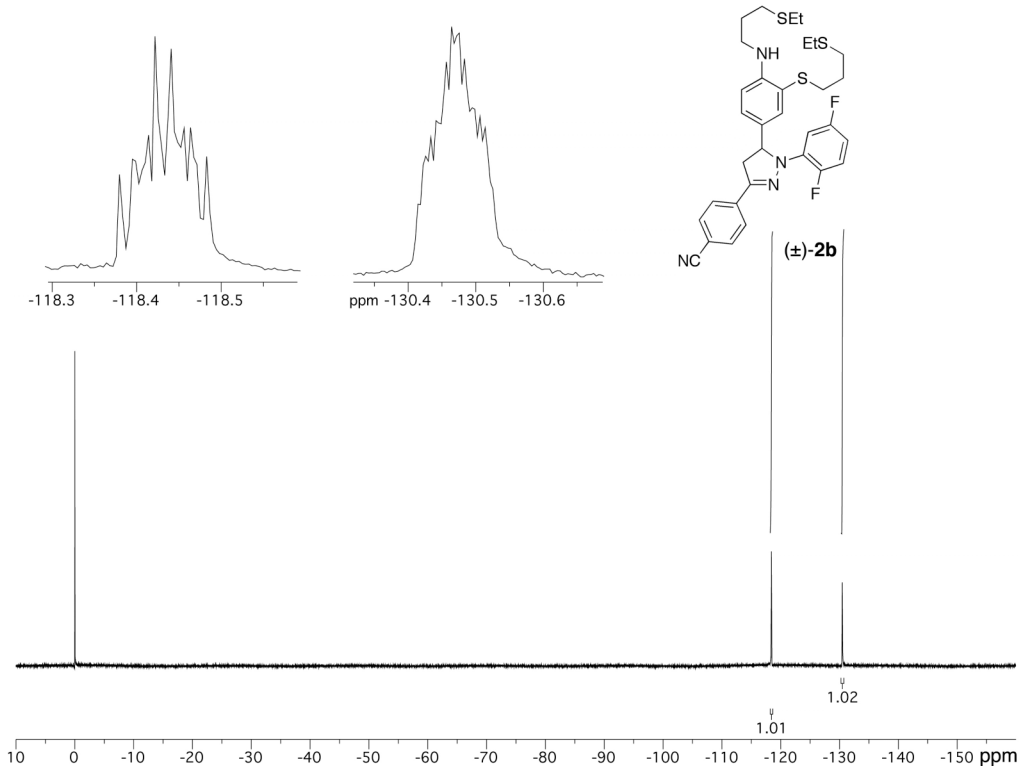


^{19}F-NMR ($CDCl_3$, 376 MHz)



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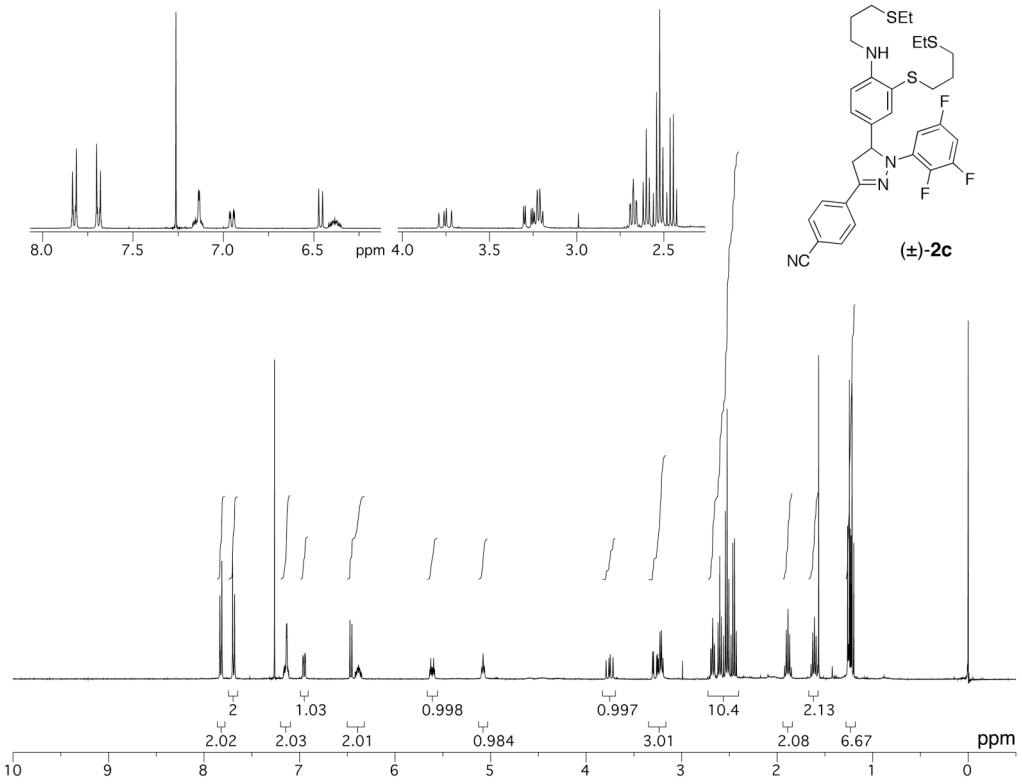

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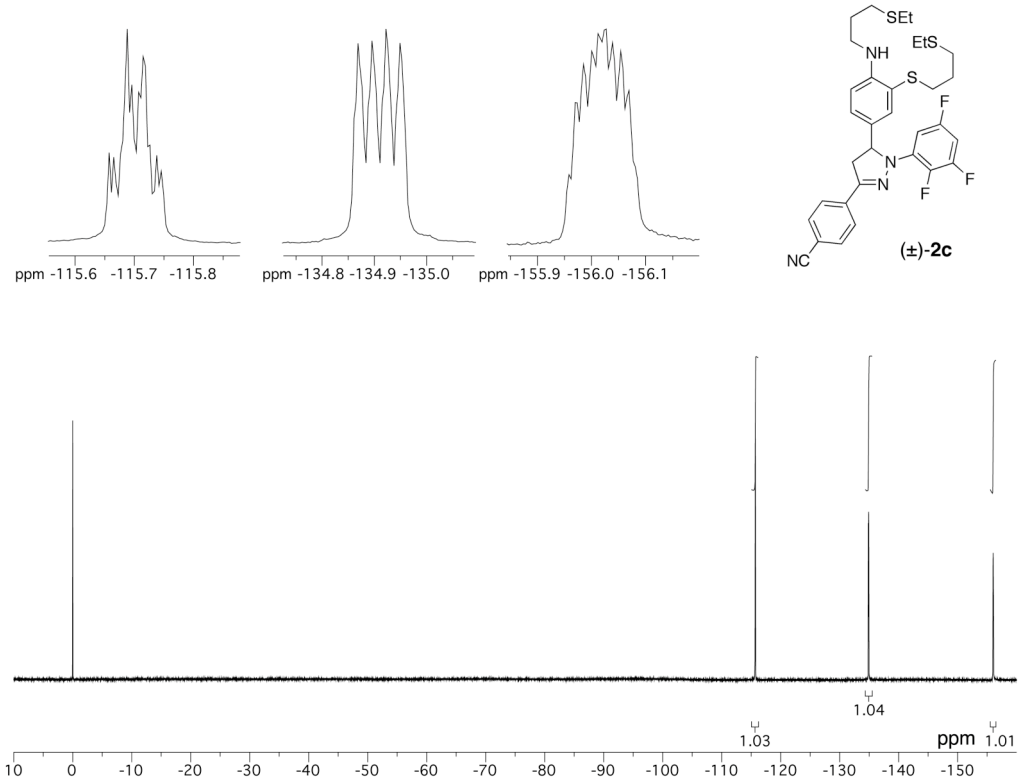

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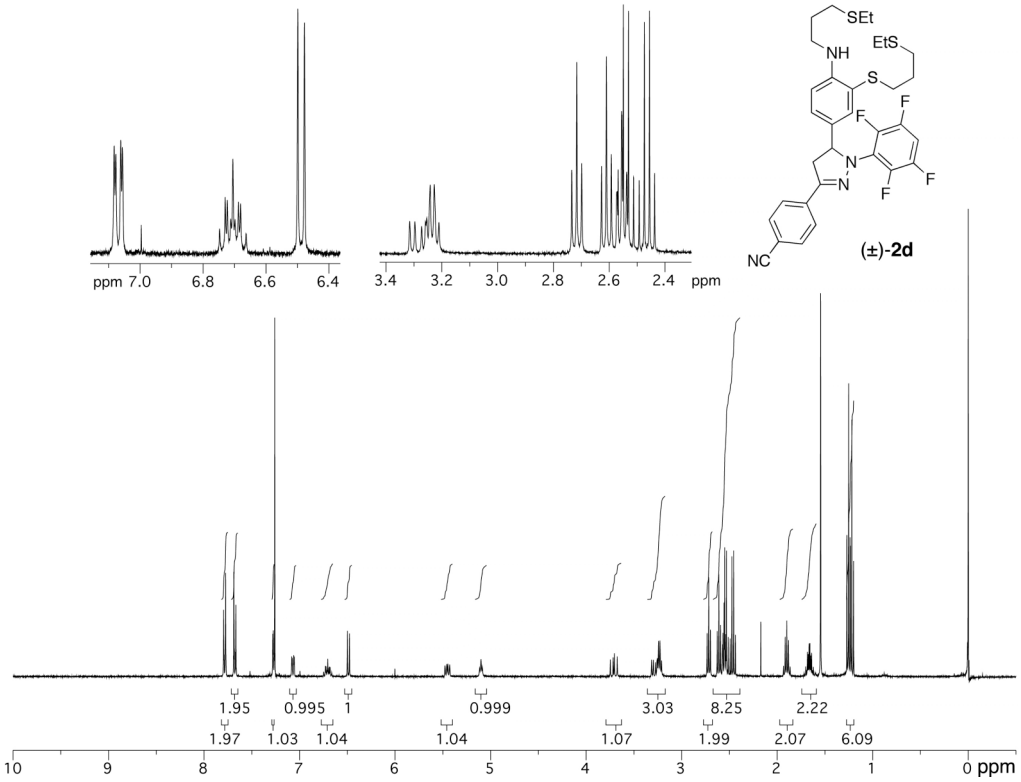

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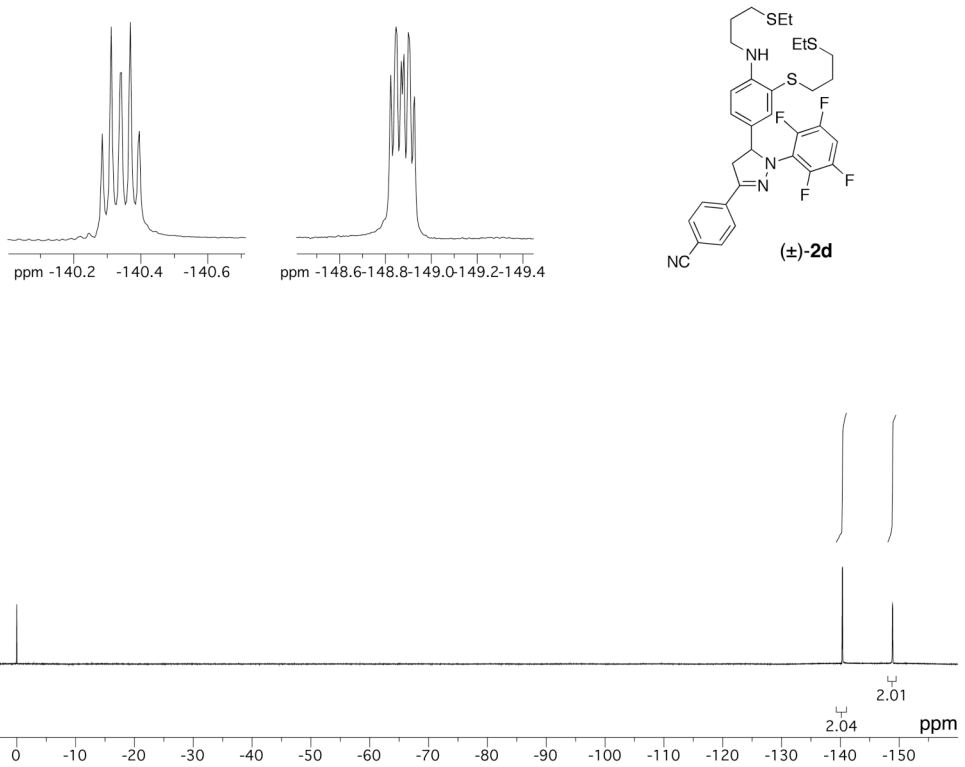

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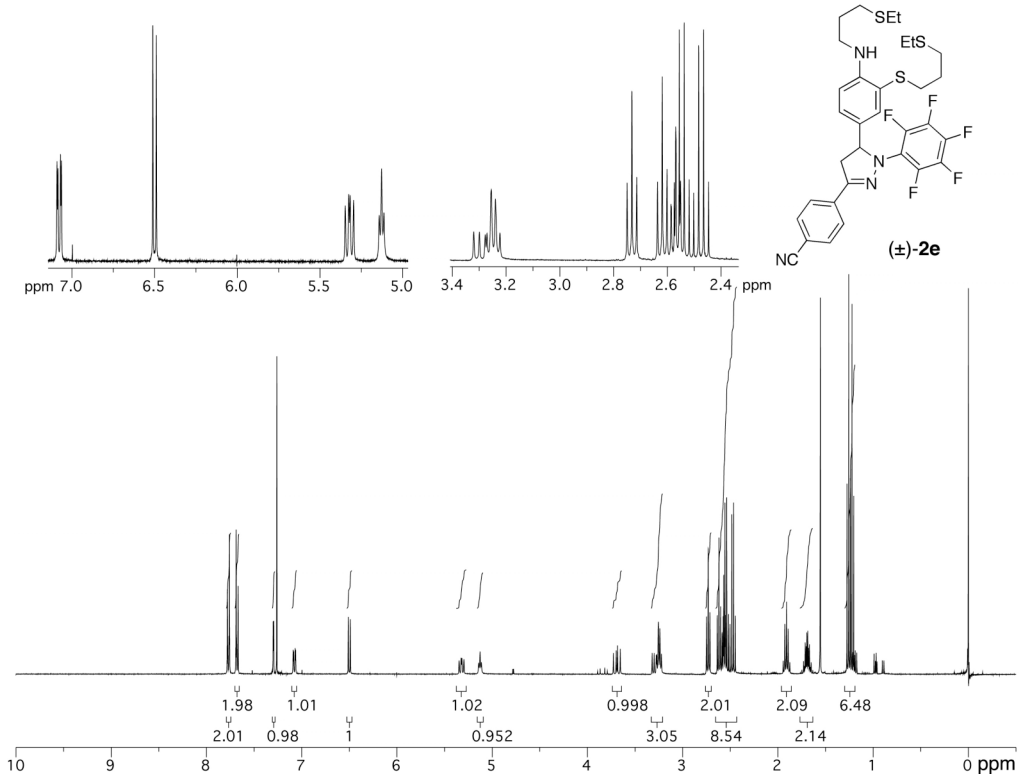
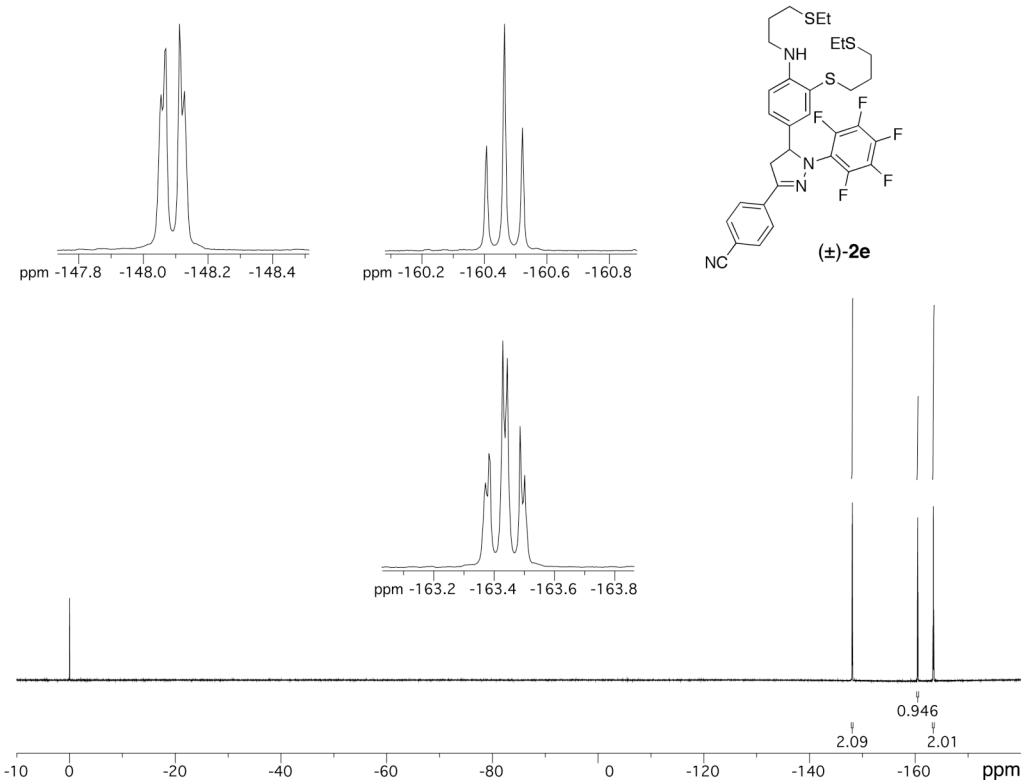


^{19}F-NMR ($CDCl_3$, 376 MHz)



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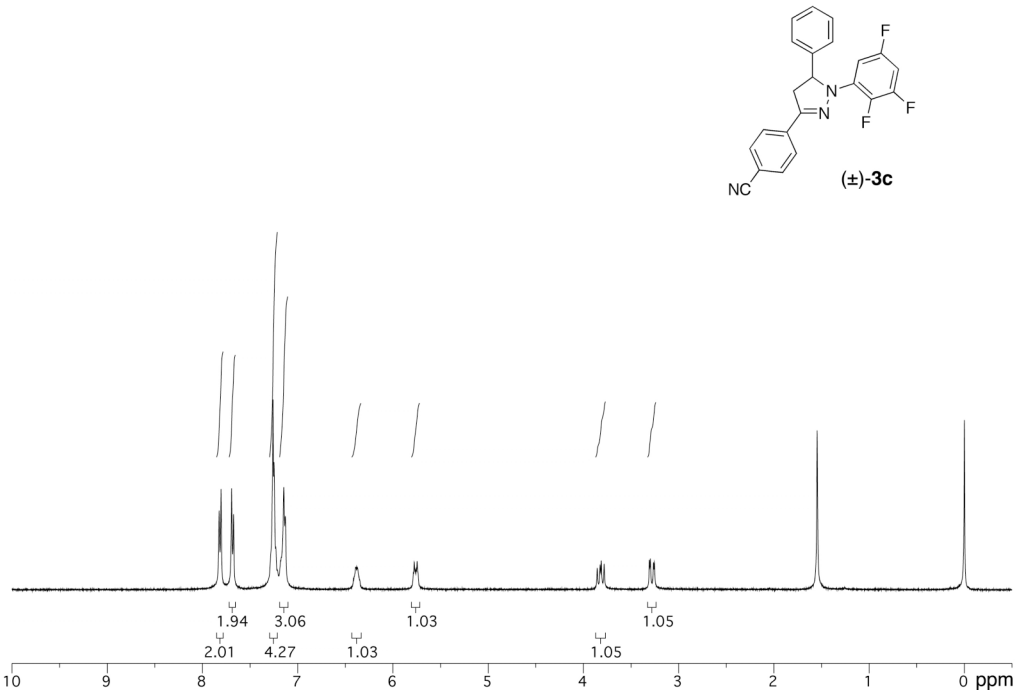

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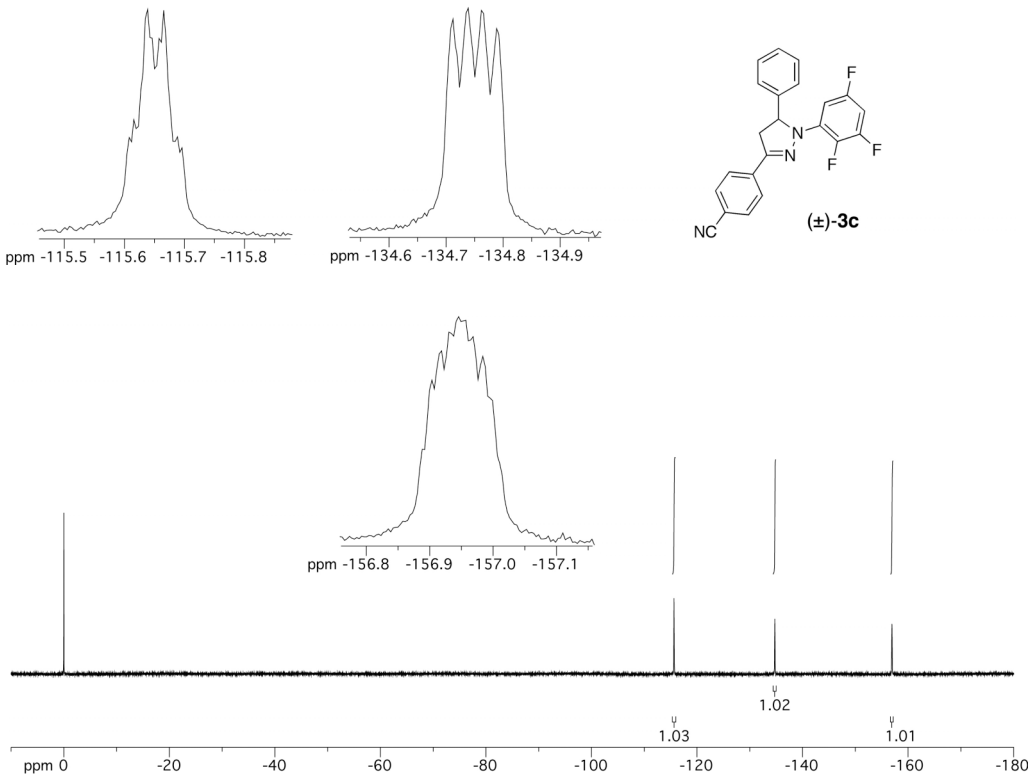

2. 2D [^{1}H,^{15}N]-HSQC NMR Spectra (DMSO-d_6)

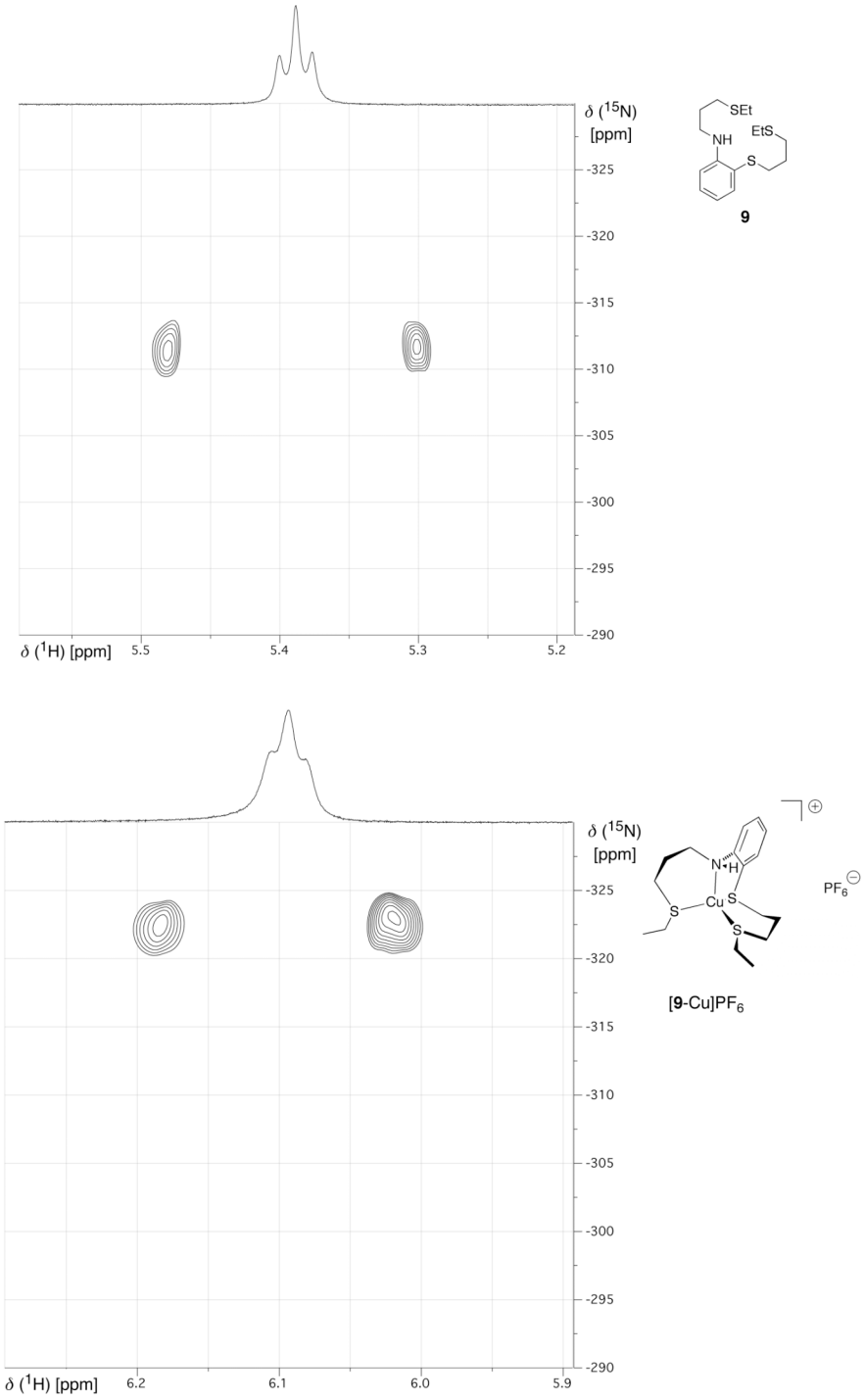

Figure S1: 2D [^{1}H,^{15}N] HSQC NMR spectra of ligand **9** (top) and [Cu(I)-**9**]PF_6 (bottom) in DMSO-d_6. The ^{15}N chemical shift was referenced relative to $CH_3{}^{15}NO_2$.

3. Electrochemistry

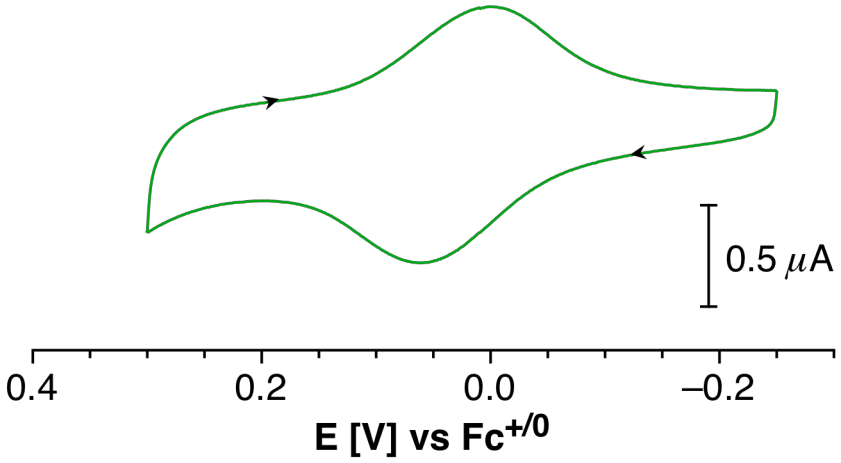

Figure S2: Cyclic voltammogram of **2c** in the presence of 1 molar equiv of $[Cu(I)(CH_3CN)_4]PF_6$ in methanol (0.1 M Bu_4NPF_6, glassy carbon working electrode, Pt counter electrode, aqueous Ag/AgCl/3M KCl reference electrode, scan rate 50 mV/s, sweep direction indicated by black arrows). The voltammogram was referenced against $Fc^{+/0}$ (ferrocene) measured under the same conditions.

4. Time-resolved Fluorescence Emission Decay Data

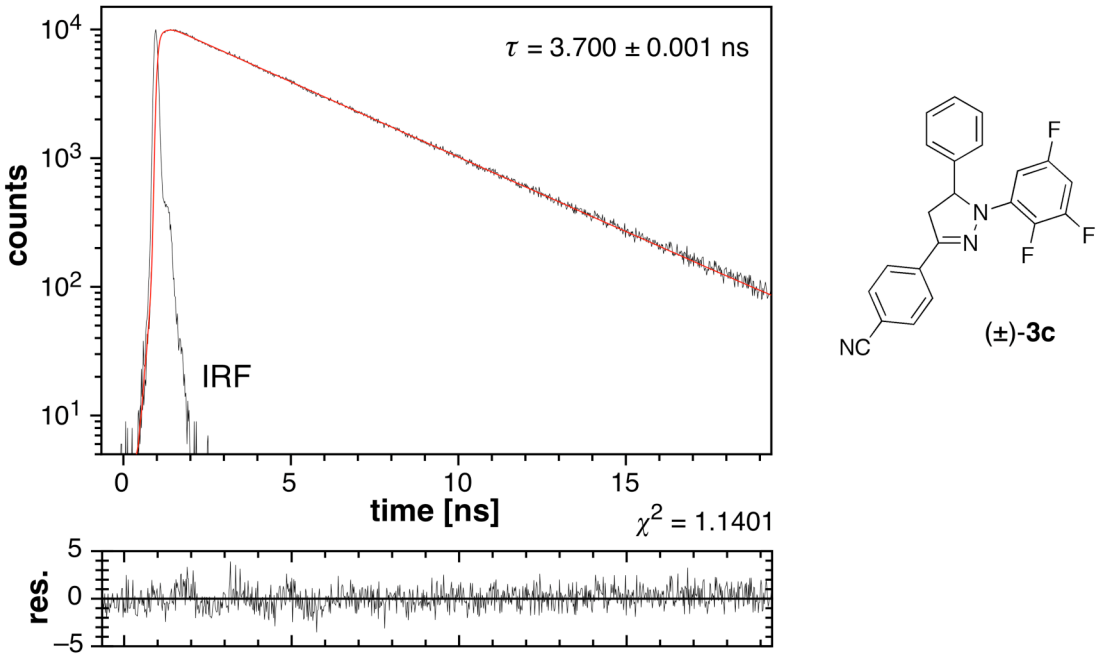

Figure S3: Fluorescence decay profile for pyrazoline derivative (±)-**3c** in methanol at 298 K (excitation at 372 nm, fluorescence emission acquired at 460 nm; IRF = instrument response function; curve fit for a monoexponential decay shown in red).

5. Photophysical Model Approximations

a) Photoinduced electron transfer driving force

The free energy change ΔG_{et} of the PET process was estimated based on the Rehm-Weller formalism (S1)[4] using the experimental ground state donor and acceptor potentials, $E(D^+/D)$ and $E(A/A^-)$, respectively, and the excited state energy ΔE_{00},

$$\Delta G_{et} = E(D^+/D) - E(A/A^-) - \Delta E_{00} + w_p \qquad \text{(S1)}$$

The term w_p corresponds to the Coulombic stabilization energy of the radical ion pair intermediate formed in the course of the PET reaction. According to earlier studies, the ion pair stabilization energy of structurally closely related derivatives was estimated to be $w_p = -0.045$ eV.[2]
Because the acceptor potential of the pyrazoline derivatives **2a-e** reside outside the accessible potential window of methanol, we utilized acetonitrile as a substitute. To estimate the solvation energy difference ΔG_{solv} for this change, we utilized the Born equation (S2) for a spherical charge,

$$\Delta G_{solv} = -\frac{e^2}{2}\left(\frac{1}{r_D} + \frac{1}{r_A}\right)\left(\frac{1}{\varepsilon_{MeCN}} - \frac{1}{\varepsilon_{MeOH}}\right) \qquad \text{(S2)}$$

where r_D and r_A are the ionic radii of the donor and acceptor portion of the radical ion pair and ε_{MeCN} and ε_{MeOH} are the vacuum permittivities of the two solvents.[5] With an average D-A distance of 8.6 Å and permittivities of 35.94 and 32.66 for acetonitrile and methanol, respectively, we obtained $\Delta G_{solv} = 0.0094$ eV. The experimental donor and acceptor potential as well as the PET driving force $-\Delta G_{et}$ estimated according to equations S1 and S2 are compiled in Table S1.

Table S1: Donor and Acceptor Reduction Potentials and Electron Transfer Parameters of Pyrazoline Derivatives **2a-2e**.

	$E_{1/2}(D^+/D)$ [a] (V)	$E_{1/2}(A/A^-)$ [a] (V)	ΔE_{00} [b] (eV)	$-\Delta G_{et}$ [c] (eV)
2a	0.513	–2.205	2.86	0.18
2b	0.510	–2.181	2.93	0.27
2c	0.538	–2.148	3.01	0.36
2d	0.521	–2.211	3.16	0.46
2e	0.535	–2.180	3.23	0.55

[a] Half-wave potential in acetonitrile/0.1 M Bu_4NPF_6 vs $Fc^{+/0}$ at 298K. [b] Zero-zero transition energy in methanol; estimated based on $\Delta E_{00} = (E_{abs}(max)+E_{em}(max))/2$. [c] PET driving force calculated on the basis of the Rehm-Weller equation (S1) with $w_p = -0.045$ eV. To account for the solvation energy difference between acetonitrile and methanol, a correction of $\Delta G_{solv} = 0.0094$ eV was applied (according to equation S2).

b) Relationship between the fluorescence enhancement factor f_e, the electron transfer driving force $-\Delta G_{et}$, and the difference in donor potential $\Delta E(D^+/D)$ between metal-bound and free probe:

The fluorescence enhancement factor upon binding of the metal ion can be expressed as a function of the two electron transfer rate constants for the free (k_{et}) and bound form (k_{et}')

$$f_e = \frac{\Phi'_f}{\Phi_f} = \frac{k_0 + k_{et}}{k_0 + k'_{et}} \tag{S3}$$

where Φ'_f and Φ_f refer to the quantum yield of the bound and free probe, respectively, and k_0 is the excited state deactivation rate constant (= the inverse of the fluorescence lifetime τ_f). According to semi-classical Marcus theory, the rate constant for the electron transfer reaction of the free probe can be approximated by

$$k_{et} = \left(\frac{4\pi^3}{h^2 \lambda k_B T}\right)^{1/2} H_{DA}^2 \exp\left[-\frac{\left(\Delta G_{et} + \lambda\right)^2}{4\lambda k_B T}\right]. \tag{S4}$$

where k_{et} refers to the rate constant of the electron transfer reaction at temperature T with driving force $-\Delta G_{et}$, reorganization energy λ, and electronic coupling H_{DA}.[6,7] Assuming that the change in the ET rate upon binding of the analyte is predominantly caused by an increase in the donor potential $\Delta E(D^+/D)$, thus neglecting differences in the reorganization energy λ and electronic coupling H_{DA}, k_{et}' can be approximated as

$$k'_{et} = \left(\frac{4\pi^3}{h^2 \lambda k_B T}\right)^{1/2} H_{DA}^2 \exp\left[-\frac{\left(\Delta G_{et} + \Delta E(D^+/D) + \lambda\right)^2}{4\lambda k_B T}\right]. \tag{S5}$$

Combining equations S3-S5 and solving for $\Delta E(D^+/D)$ yields equation (S6) which was used for the contour plot shown in Figure 6A in main text:

$$\Delta E(D^+/D) = \left(-4\lambda k_B T \ln\left[\frac{(1-f_e)}{f_e}\frac{k_0}{H_{DA}^2}\left(\frac{h^2 \lambda k_B T}{4\pi^3}\right)^{1/2} + \frac{1}{f_e}\exp\left[-\frac{\left(\Delta G_{et} + \lambda\right)^2}{4\lambda k_B T}\right]\right]\right)^{1/2} - \lambda - \Delta G_{et}. \tag{S6}$$

c) Fluorescence enhancement factor f_e as a function of the electron transfer driving force $-\Delta G_{et}$ at a fixed donor potential $\Delta E(D^+/D)$:

Based on equations S3-5, the fluorescence enhancement factor can be expressed as a function of the electron transfer driving force and difference in donor potential:

$$f_e = f(\Delta G_{et}, \Delta E(\mathrm{D}^+/\mathrm{D})) = \frac{k_0 + \left(\frac{4\pi^3}{h^2 \lambda k_B T}\right)^{1/2} H_{DA}^2 \exp\left[-\frac{\left(\Delta G_{et} + \lambda\right)^2}{4\lambda k_B T}\right]}{k_0 + \left(\frac{4\pi^3}{h^2 \lambda k_B T}\right)^{1/2} H_{DA}^2 \exp\left[-\frac{\left(\Delta G_{et} + \Delta E(\mathrm{D}^+/\mathrm{D}) + \lambda\right)^2}{4\lambda k_B T}\right]} \qquad \text{(S7)}$$

The plot in Figure 6B (solid trace) was obtained using equation (S7) by inserting the following values: $\Delta E(\mathrm{D}^+/\mathrm{D}) = 0.46$ V, $k_0 = 1/\tau_f = 2.8 \times 10^8$ s^{-1}, $\lambda = 0.54$ eV, $H_{AD} = 18$ cm^{-1}, and T = 298 K.

d) Fluorescence quantum yield recovery upon metal-binding as a function of electron transfer driving force $-\Delta G_{et}$ at a fixed donor potential $\Delta E(D^+/D)$:

The fluorescence quantum yield Φ_f' of the metal-bound fluorophore can be expressed as a function of the excited state deactivation rate k_0, the quantum yield Φ_f^0 of the unquenched fluorophore, and the electron transfer rate k_{et}':

$$\Phi_f' = \frac{\Phi_f^0 k_0}{k_0 + k_{et}'} \qquad \text{(S8)}$$

Substituting k_{et}' with the expression in equation (S5) yields

$$\Phi_f' = \frac{\Phi_f^0 k_0}{k_0 + \left(\frac{4\pi^3}{h^2 \lambda k_B T}\right)^{1/2} H_{DA}^2 \exp\left[-\frac{\left(\Delta G_{et} + \Delta E(\mathrm{D}^+/\mathrm{D}) + \lambda\right)^2}{4\lambda k_B T}\right]} \qquad \text{(S9)}$$

The plot in Figure 6B (dotted trace) was obtained using equation (S9) by inserting the following values: $\Phi_f^0 = 0.64$, $\Delta E(\mathrm{D}^+/\mathrm{D}) = 0.46$ V, $k_0 = 1/\tau_f = 2.8 \times 10^8$ s^{-1}, $\lambda = 0.54$ eV, $H_{AD} = 18$ cm^{-1}, and T = 298 K.

6. Dynamic ^{1}H NMR Study of the Complexation Equilibrium of Cu(I) with Ligand 9

In the presence of 0.5 molar equiv Cu(I) ions, the protons of ligand **9** encounter two distinct chemical environments A and B corresponding to the uncomplexed and Cu(I)-bound form, respectively. The two-site exchange equilibrium can be described by

$$\mathrm{A} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} \mathrm{B} \tag{S10}$$

where k_a and k_b refer to the pseudo first order rate constant of the forward and reverse exchange process, respectively. At equilibrium, the forward and reverse rates are identical, therefore we can write:

$$k_a[\mathrm{A}] = k_b[\mathrm{B}] \quad \text{or} \quad k_a[\mathrm{A}] - k_b[\mathrm{B}] = 0 \tag{S11}$$

To extract chemically meaningful rate constants from the observed ^{1}H NMR exchange rates, we may considered two main exchange pathways corresponding to an associative (equation S12) and dissociative (equation S13) mechanism, respectively:

$$\mathrm{Cu(I)L} + \mathrm{L^*} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cu(I)L^*} + \mathrm{L} \tag{S12}$$

$$\mathrm{Cu(I)} + \mathrm{L} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Cu(I)L} \tag{S13}$$

The observed exchange rate constants k_a and k_b are related to the microscopic rate constants according to equations S14 – S16:[8,9]

$$k_a = k_1[\mathrm{Cu(I)L}] + k_2[\mathrm{Cu(I)}] = [\mathrm{Cu(I)L}]\left(k_1 + \frac{k_{-2}}{[\mathrm{L}]}\right) \tag{S14}$$

$$k_b = k_1[\mathrm{L}] + k_{-2} \tag{S15}$$

$$k_a + k_b = k_1[\mathrm{L}]_{\mathrm{total}} + k_{-2}\left(\frac{[\mathrm{L}]_{\mathrm{total}}}{[\mathrm{L}]}\right) \tag{S16}$$

If complex formation is quantitative ($K > 10^4$ M^{-1}) and the ratio of complexed and free ligand is unity, we obtain:

$$k_a + k_b = k_1[\mathrm{L}]_{\mathrm{total}} + 2k_{-2} \tag{S17}$$

Hence, the bimolecular exchange rate constant k_1 corresponds to the slope of a linear regression analysis of the observed exchange rate constants ($k_a + k_b$) vs $[L]_{total}$. Because at millimolar ligand concentration $k_1[L]_{total} >> 2k_{-2}$, equation S17 can be reduced to

$$k_a + k_b = k_1[L]_{total} \quad . \tag{S18}$$

Table S2: Exchange rate constants (k_a+k_b) obtained from full line shape analysis of ^{1}H NMR spectra of solutions with varying concentrations of ligand **9** and equal ligand to Cu(I) ratio ([L] = [Cu(I)L]).

Concentration $[L]_{total}$ [mM]	$k_a + k_b$ [s^{-1}]
3.6	9,400
7.2	19,000
10.8	24,800
15.0	32,200

7. Crystallographic Structural Determination of Complex [Cu(I)-9]PF_6

Table S3: Crystal data and structure refinement

Empirical formula	$C_{16}H_{27}CuF_6NPS_3$	
Formula weight	538.08	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.503(3) Å	α = 90°
	b = 13.996(3) Å	β = 109.377(3)°
	c = 10.645(2) Å	γ = 90°
Volume	2178.9(8) $Å^3$	
Z	4	
Density (calculated)	1.640 Mg/m^3	
Absorption coefficient	1.416 mm^{-1}	
F(000)	1104	
Crystal size	0.54 x 0.07 x 0.06 mm^3	
Theta range for data collection	1.39 to 27.48°	
Index ranges	-20<=h<=20, -18<=k<=18, -13<=l<=13	
Reflections collected	34458	
Independent reflections	4987 [R(int) = 0.1632]	
Completeness to theta = 27.48°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9173 and 0.5129	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4987 / 0 / 238	
Goodness-of-fit on F^2	1.803	
Final R indices [I>2sigma(I)]	R1 = 0.0795, wR2 = 0.2037	
R indices (all data)	R1 = 0.1615, wR2 = 0.2765	
Extinction coefficient	0.0031(14)	
Largest diff. peak and hole	1.330 and -1.123 $e.Å^{-3}$	

Table S4: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom Label	x	y	z	U(eq)
C(1)	486(6)	3342(6)	8845(9)	37(2)
C(2)	684(6)	4205(6)	8329(9)	39(2)
C(3)	115(7)	4493(7)	7065(10)	45(2)
C(4)	-613(7)	3942(8)	6316(11)	55(3)
C(5)	-800(7)	3093(8)	6864(11)	53(3)
C(6)	-273(6)	2818(6)	8101(9)	42(2)
C(7)	1387(6)	1730(6)	10267(9)	38(2)
C(8)	1915(6)	1462(6)	9348(9)	37(2)
C(9)	2906(6)	1739(5)	9816(9)	35(2)
C(10)	4296(6)	3008(6)	9716(9)	39(2)
C(11)	4773(7)	2346(7)	9041(11)	51(2)
C(12)	1166(7)	5517(6)	9875(10)	43(2)
C(13)	1959(6)	6128(5)	10714(10)	39(2)
C(14)	2501(7)	5732(6)	12066(10)	46(2)
C(15)	4199(6)	5275(7)	11834(9)	43(2)
C(16)	4770(8)	5828(8)	13024(11)	59(3)
Cu(1)	2467(1)	3872(1)	10327(1)	37(1)
F(1)	3274(13)	5275(12)	8335(18)	95(2)
F(2)	2661(13)	6797(12)	6045(17)	95(2)
F(3)	4018(12)	6286(12)	7482(17)	95(2)
F(4)	1906(11)	5900(12)	6958(16)	95(2)
F(5)	2987(11)	5241(11)	6167(15)	95(2)
F(6)	2985(11)	6827(11)	8229(16)	95(2)
F(4B)	3552(17)	6957(18)	7580(20)	95(2)
F(3B)	2222(16)	5224(18)	6660(20)	95(2)
F(2B)	2630(19)	6477(19)	5690(30)	95(2)
F(1B)	3273(19)	5614(19)	8640(30)	95(2)
F(5B)	2163(17)	6463(18)	7550(20)	95(2)
F(6B)	3966(17)	5851(18)	7040(30)	95(2)
N(1)	1449(5)	4776(5)	9095(8)	39(2)
P(1)	2989(2)	6024(2)	7161(2)	39(1)
S(1)	1201(2)	2998(2)	10470(2)	37(1)
S(2)	3059(2)	2907(1)	9134(2)	35(1)
S(3)	3229(2)	4713(1)	12127(2)	38(1)

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