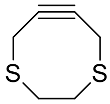
Electronic Supplementary Material (ESI) for RSC Advances.

## Supporting Information

Solvents and chemicals used were purchased from commercial suppliers. Solvents were dried under standard conditions. All materials were used without further purification. Thin-layer chromatography (TLC) was carried out on silica gel plates (Silica gel 60, F254, Merck) with detection by UV. Purification was performed with preparative chromatography using normal-phase silica gel (Silica gel 60, 230-400 mesh, Merck). $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM 400 or Bruker DRX 250, respectively. Chemical shifts are reported as δ values (ppm). The signal abbreviations include: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, H-Ar = aromatic proton. The signals of $^{13}$C NMR spectra were allocated through DEPT-technology (DEPT = Distortionless Enhancement by Polarisation Transfer). The signal abbreviations include: C-Ar = aromatic carbon, + = primary or tertiary carbon, − = secondary carbon, $C_{quart}$ = quaternary carbon. MS (EI) (electron impact mass spectrometry), FAB (fast atom bombardment mass spectrometry) and HRMS (high resolution mass spectrometry) were carried out on a Finnigan MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (m/z), the intensities as a percentage value relative to the intensity of the base signal (100%). The abbreviation $[M]^+$ refers to the molecular ion. Descriptions without nominated temperature were done at room temperature (r.t.), and the following abbreviations were used: calcd. (theoretical value), found (measured value). Intensity is given in mass percent. IR (infrared spectroscopy) was carried out on a FT-IR Bruker Alpha-T. IR spectra of solids were recorded with a Diamond ATR technique, and as thin films on KBr for oils. The deposit of the absorption band was given in wavenumbers ν in cm$^{-1}$. The forms and intensities of the bands were characterized as follows: s = strong 10–40% transmission, m = medium 40–70% transmission, w = weak 70–90% transmission, vw = very weak 90–100% transmission, br = broad.

### *4,7-Dithiacyclooctyne (4)*

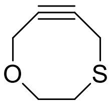


In 100 mL of dry dichloromethane 0.500 g 2-butyne-1,4-diol-dicobalthexacarbonyl complex (1.34 mmol, 1.00 equiv.) were dissolved under argon atmosphere and 0.13 mL ethane dithiol (0.146 g, 1.55 mmol, 1.16 equiv.) were added. Few drops of $HBF_4$-etherate were added and the mixture was stirred for 48 h. Then one spatula tip of sodium bicarbonate and sodium sulfate were added and the mixture was filtered. The solvent of the filtrate was removed and the crude intermediate was purified by flash-column chromatography (20 x 2 cm, silica gel, pentane/dichloromethane 9:1) and the colored fraction was collected. Of the intermediate 0.403 g (0.940 mmol) were obtained which were used directly without further characterization. The red/brown oil was dissolved in 20 mL of methanol and cooled to 0 °C. Then a solution of 1.89 g ferric nitrate nonahydrate (4.69 mmol, 5.00 equiv.) in 5 mL methanol was added and the mixture was stirred for

3 h. The solution was diluted with 50 mL diethyl ether and washed with 2 x 30 mL water. The organic phase was dried over sodium sulfate and the crude product was purified by flash column chromatography (20 x 1, silica gel, pentane/dichloromethane 5:1) to obtain 0.050 g of a colorless oil (26% yield over two steps).

*R*$_f$ = 0.33 (pentane/DCM). – $^1$H NMR: (400 MHz, $CDCl_3$): δ(ppm) = 3.34 (s, 4 H, CCC*H*$_2$); 3.14 (s, 4 H, S(C*H*$_2$)$_2$S). – $^{13}$C NMR (100 MHz, $CDCl_3$), δ (ppm) = 90.9 (C$_{quart}$, *C*-alkyne); 35.0 (–, S(*C*H$_2$)$_2$S); 20.8 (–, CC*C*H$_2$). – IR (ATR Platinum Diamond) ν (cm$^{-1}$) = 2946 (w), 2920 (w), 2221 (w), 1668 (s), 1499 (w), 1399 (m). – MS (70 eV, EI), *m/z* (%): 144 [M$^+$] (100), 116 (15), 111 (14). – HRMS ($C_6H_8S_2$): calcd. 144.0069; found 144.0067.

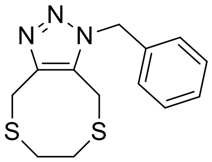
***4-Thia-7-oxa-cyclooctyne (5)***



In 100 mL of dry dichloromethane 0.500 g 2-butyne-1,4-diol-dicobalthexacarbonyl complex (1.34 mmol, 1.00 equiv.) were dissolved under argon atmosphere and 0.098 mL mercaptoethanol (0.081 g, 1.40 mmol, 1.04 equiv.) were added. Few drops of $HBF_4$-etherate were added and the mixture was stirred for 48 h. Then one spatula tip of sodium bicarbonate and sodium sulfate were added and the mixture was filtered. The solvent of the filtrate was removed and the crude intermediate was purified by flash-column chromatography (20 x 2 cm, silica gel, pentane/dichloromethane 9:1to 3:1) and the colored fraction was collected (R$_f$ = 0.28 (pentane/DCM 3:1)). The intermediate (0.385 g, 0.930 mmol) was obtained which was used directly without further characterization. The red/brown oil was dissolved in 20 mL of methanol and cooled to 0 °C. Then a solution of 1.89 g ferric nitrate nonahydrate (4.69 mmol, 5.00 equiv.) in 5 mL methanol was added and the mixture was stirred for 3 h. The solution was diluted with 50 mL diethyl ether and washed with 2 x 30 mL water. The organic phase was dried over sodium sulfate and the crude product was purified by flash column chromatography (20 x 1, silica gel, pentane/DCM 1:1) to obtain 0.023 g of a colorless oil (13% yield over two steps), 80% purity (see NMR spectra). The compound is sensitive and decomposes at room temperature within few days.

*R*$_f$ = 0.24 (pentane/DCM 1:1). – $^1$H NMR: (400 MHz, $CDCl_3$): δ (ppm) = 4.18 (t, $^5J$ = 2.5 Hz, 2 H, CCC*H*$_2$O); 4.07 (t, $^3J$ = 4.6 Hz, 2 H, OC*H*$_2$CH$_2$); 3.37 (t, $^5J$ = 2.5 Hz, 2 H, CCC*H*$_2$S); 2.98 (t, $^3J$ = 4.6 Hz, 2 H, SC*H*$_2$CH$_2$). – $^{13}$C NMR (100 MHz, $CDCl_3$), δ (ppm) = 97.1 (C$_{quart}$, C-alkyne); 95.9 (C$_{quart}$, C-alkyne); 74.1 (–, O*C*H$_2$CH$_2$); 60.2 (–, CC*C*H$_2$O); 34.1 (–, S*C*H$_2$CH$_2$); 20.9 (–, CC*C*H$_2$S). – IR (Film KBr) ν (cm$^{-1}$) = 2916 (s), 2852 (s), 2207 (w), 1636 (w), 1449 (m). – MS (70 eV, EI), *m/z* (%): 128 [M$^+$] (97), 98 (37), 97 (43), 52 (100). – HRMS (128.0298): calcd. 128.0298; found 128.0296.

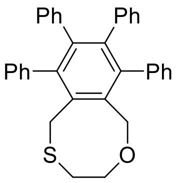
### ***1-Benzyl-4,6,7,9-tetrahydro-1H-[1,4]dithiocino[6,7-d][1,2,3]triazole (6)***



In 5 mL of dichloromethane 0.034 g 4,7-dithiacyclooctyne (0.236 mmol, 1,00 equiv.) were dissolved with 0.063 g benzyl azide (0.473 mmol, 2.00 equiv.) and stirred for 12 h. The solvent was removed and the crude product was purified by flash- column chromatography (20 x 1, silica gel, cyclohexane/ethyl acetate 3:1) to obtain 0.032 g of a white solid (49%).

R$_f$ = 0.26 (CH/EE 3:1). – mp 108 °C – $^1$H NMR: (400 MHz, CDCl$_3$): δ (ppm) = 7.38 – 7.27 (m, 3 H, H-Ar); 1.20 – 7.21 (m, 2 H, H-Ar); 5.51 (s, 2 H, CH$_2$Ph); 4.08 (s, 2 H, SCH$_2$); 3.86 (s, 2 H, SCH$_2$); 2.88 – 2.83 (m, 2 H, SCH$_2$CH$_2$S); 2.75 – 2.70 (m, 2 H, SCH$_2$CH$_2$S). – $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) = 143.9 (C$_{quart.}$, C-Ar); 134.5 (C$_{quart.}$, C-Ar (triazole)); 130.6 (C$_{quart.}$, C-Ar (triazole)); 129.0 (+, C-Ar,); 128.5 (+, C-Ar); 127.1 (+, C-Ar); 52.0 (–, CH$_2$-Ph); 33.7 (–, CH$_2$); 33.2 (–, CH$_2$); 27.2 (–, CH$_2$); 23.0 (–, CH$_2$). – IR (ATR Platinum Diamond): 2968 (vw), 2929 (vw), 1573 (vw), 1497 (vw), 1477 (vw), 1455 (vw), 1425 (vw), 1345 (vw), 1312 (vw), 1272 (vw), 1231(vw), 1210(vw), 1184 (vw), 1125 (vw), 1077 (vw), 1056 (vw), 1030 (vw). – MS (70 eV, EI), *m/z* (%): 278 [(M+H)$^+$] (100), 250 [(M-N$_2$+H)$^+$]. – HRMS (C$_{13}$H$_{16}$N$_3$S$_2$): calcd. 278.0786, found 278.0784.

### ***7,8,9,10-Tetraphenyl-1,3,4,6-tetrahydrobenzo[f][1,4]oxathiocine (7)***

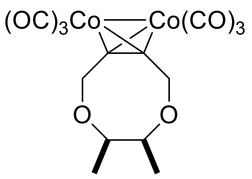


In 100 mL of dry dichloromethane 0.500 g 2-butyne-1,4-diol-dicobalthexacarbonyl complex (1.34 mmol, 1.00 equiv.) were dissolved under argon atmosphere and 0.098 mL mercaptoethanol (0.081 g, 1.40 mmol, 1.04equiv.) were added. Few drops of HBF$_4$-etherate were added and the mixture was stirred for 48 h. Then one spatula tip of sodium bicarbonate and sodium sulfate were added and the mixture was filtered. The solvent of the filtrate was removed and the crude intermediate was purified by flash- column chromatography (20 x 2 cm, silica gel, pentane/dichloromethane 9:1 to 3:1) and the colored fraction was collected ($R_f$ = 0.28 (pentane/DCM 3:1)). Of the intermediate 0.385 g (0.930 mmol) were obtained which were used directly without further characterization. The red/brown oil was dissolved in 20 mL of methanol and cooled to 0 °C. Then a solution of 1.89 g ferric nitrate nonahydrate (4.69 mmol, 5.00 equiv.) in methanol was added and the mixture was stirred for 3 h. The solution was diluted with 50 mL diethyl ether and washed with 2 x 30 mL water. The organic phase was dried over sodium sulfate and to the solution was added 1.03 g tetracyclone (2.68 mmol, 2.00 equiv.). The solution was stirred for 24 h, the solvent was removed and the crude product was purified by flash column chromatography (20 x 2, silica gel, cyclohexane/ethyl acetate 100:1-30:1) to obtain 0.060 g of a white solid (9.3% over 3 steps).

$R_f$ = 0.15 (CH/EE 100:1). – mp = 216°C. – $^1$H NMR: (400 MHz, CDCl$_3$): δ (ppm) = 7.24 – 7.15 (m, 6 H, H-Ar); 7.15 – 7.06 (m, 4 H, H-Ar); 6.87 – 6.72 (m, 10 H, H-Ar); 4.63 (s, 2 H, Ar-CH$_2$-O); 4.11 – 3.99 (m, 4 H, CH$_2$); 2.83 – 2.75 (m, 2 H, CH$_2$). – $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) = 141.8 (C$_{quart}$, *C*-Ar); 141.6 (C$_{quart}$, *C*-Ar); 140.3 (C$_{quart}$, *C*-Ar); 140.2 (C$_{quart}$, *C*-Ar); 140.2 (C$_{quart}$, *C*-Ar); 140.0 (C$_{quart}$, *C*-Ar); 139.6 (C$_{quart}$, *C*-Ar); 139.6 (C$_{quart}$, *C*-Ar); 135.0 (C$_{quart}$, *C*-Ar); 134.4 (C$_{quart}$, *C*-Ar); 131.0

(+, *C*-Ar); 130.9 (+, *C*-Ar); 130.6 (+, *C*-Ar); 130.2 (+, *C*-Ar); 127.4 (+, *C*-Ar); 127.2 (+, *C*-Ar); 126.4 (+, *C*-Ar); 126.4 (+, *C*-Ar); 126.3 (+, *C*-Ar); 125.2 (+, *C*-Ar); 73.1 (–, *C*H$_2$-O); 69.5 (–, *C*H$_2$-O); 31.6 (–, *C*H$_2$-S); 30.4 (–, *C*H$_2$-S). – IR (ATR Platinum Diamond): 3055 (vw), 2906 (vw), 2835 (vw), 1599 (vw), 1576 (vw), 1494 (vw), 1440 (vw), 1409 (vw), 1363 (vw), 1233 (vw), 1180 (vw), 1108 (w), 1094 (w), 1041 (w), 1025 (w). ). – MS (70 eV, EI), *m/z* (%): 484 [M$^+$] (8); 400 (20); 166 (100). HRMS ($C_{34}H_{28}OS$): calcd 484.1861, found 484.1864.

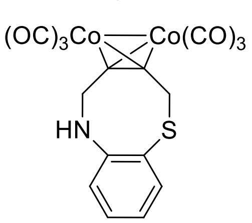
### ***meso-5,6-Dimethyl-4,7-dioxocyclooctyne-dicobalthexacarbonyl-complex (8)***



In 100 mL of dry dichloromethane 0.500 g 2-butyne-1,4-diol-dicobalthexacarbonyl complex (1.34 mmol, 1.00 equiv.) were dissolved under argon atmosphere and 0.126 g meso-2,3-butanediol (1.40 mmol, 1.04equiv.) were added. Few drops of HBF$_4$-etherate were added and the mixture was stirred for 24 h. Then one spatula tip of sodium bicarbonate and sodium sulfate were added and the mixture was filtered. The solvent of the filtrate was removed and the crude product was purified by flash column chromatography (20 x 2 cm, silica gel, dichloromethane) to obtain 0.175 g of a red/brown oil (30% yield).

$R_f$ = 0.61 (DCM). – $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) = 199.3 (C$_{quart}$, *C*O); 96.0 (C$_{quart}$, *C*-complexed alkyne); 77.3 (+, *C*HO); 71.1 (–, *C*H$_2$); 15.6 (+, *C*H$_3$). – IR (ATR Platinum Diamond): ν = 2984 (w), 2845 (w), 2090 (m), 2032 (m), 2003 (s), 1586 (w), 1442 (m), 1388 (w), 1343 (w), 1247 (m), 1171 (w), 1114 (m), 1086 (s), 1047 (s), 1011 (m). – MS (70 eV, EI), *m/z* (%): 426 [M$^+$] (9), 398 [(M-CO)$^+$] (28), 370 [(M-2CO)$^+$] (39), 342 [(M-3CO)$^+$] (100), 314 [(M-4CO)$^+$] (63), 286 [(M-5CO)$^+$] (12), 258 [(M-6CO)$^+$] (21). – HRMS ($C_{14}H_{12}Co_2O_8$): calcd. 425.9196; found 425.9198.

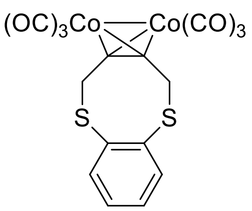
### ***3,4-Didehydro-5,6-dihydro-2H-1,6-benzothiazocin-dicobalthexacarbonyl-complex (9)***



In 300 mL of dry dichloromethane 0.475 g 2-butyne-1,4-diol-dicobalthexacarbonyl complex (1.27 mmol, 1.00 equiv.) were dissolved under argon atmosphere and the solution was cooled to – 78 °C. Afterwards 0,5 mL HBF$_4$-etherate were added and the mixture was stirred for 30 min. Then 0.159 g 2-aminothiophenol (1.27 mmol, 1.00 equiv.) were added, the solution was warmed to r. t. and stirred for 12 h. Then one spatula tip of sodium bicarbonate and sodium sulfate were added and the mixture was filtered. The solvent of the filtrate was removed and the crude product was purified by flash column chromatography (20 x 2, silica gel, cyclohexane/DCM 4:1 to 1:1) to obtain 0.182 g of a red/brown oil (31%).

$R_f$ = 0.48 (CH/DCM 1:1). – $^1$H NMR: (500 MHz, $CDCl_3$): δ(ppm) = 7.69 (bs, 1 H, *H*-Ar); 7.36 (bs, 1 H, *H*-Ar); 7.28 (1 H, *H*-Ar); 7.06 (bs, 1 H, *H*-Ar); 5.09 (bs, 1 H, N*H*); 4.71 (bs, 2 H, C$H_2$); 4.19 (bs, 2 H, C$H_2$). – $^{13}$C NMR (125 MHz, $CDCl_3$), δ (ppm) = 199.0 ($C_{quart}$, 6 C, *C*O); 152.9 ($C_{quart}$, N-*C*-Ar); 136.6 (+, *C*-Ar); 131.3 (+, *C*-Ar); 129.2 ($C_{quart}$, S-*C*-Ar); 124.5 (+, *C*-Ar); 124.4 (+, *C*-Ar); 97.0 ($C_{quart}$, *C*-complexed alkyne); 94.2 ($C_{quart}$, *C*-complexed alkyne); 59.5 (–, N-$CH_2$); 44.6 (–, S-$CH_2$). – IR (ATR Platinum Diamond): 3287 (w), 2924 (w), 2089 (s), 2039 (s), 1984 (vs), 1594 (m), 1479 (m), 1453 (m), 1422 (m), 1400 (m), 1316 (m), 1286 (m), 1224 (m), 1205 (m), 1186 (m), 1224 (m). – MS (70 eV, EI), *m/z* (%): 461 [$M^+$] (2), 433 [$(M\text{-}CO)^+$] (10), 405 [$(M\text{-}2\ CO)^+$] (54), 377 [$(M\text{-}3\ CO)^+$] (21), 349 [$(M\text{-}4\ CO)^+$] (25), 321 [$(M\text{-}5\ CO)^+$] (44), 293 [$(M\text{-}6\ CO)^+$] (100). HRMS ($C_{16}H_9NSCo_2$): calcd 460.8814, found 460.8810.

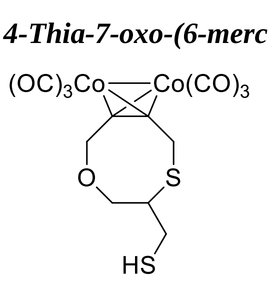
### *3,4-Didehydro-2,5-dihydro-1,6-benzodithiocin-dicobalthexacarbonyl-complex (10)*



In 100 mL of dry dichloromethane 0.500 g 2-butyne-1,4-diol-dicobalthexacarbonyl complex (1.34 mmol, 1.00 equiv.) were dissolved under argon atmosphere and 0.200 g 1,2-benzenedithiol (1.41 mmol, 1.05equiv.) were added and the solution was cooled to – 78 °C. Few drops of $HBF_4$-etherate were added and the mixture was stirred for 2 h. Then one spatula tip of sodium bicarbonate and sodium sulfate were added and the mixture was filtered. The solvent of the filtrate was removed and the crude product was purified by flash column chromatography (20 x 2 cm, silica gel, cyclohexane/ethyl acetate 10:1) to obtain 0.326 g of a red/brown solid (51%).

$R_f$ = 0.68 (CH/EE 50:1). – $^1$H NMR: (400 MHz, $CDCl_3$): δ(ppm) = 7.95 (bs, 2 H, H-Ar); 7.45 (bs, 2 H, H-Ar); 4.32 (bs, 4 H, $CH_2$). – $^{13}$C NMR (100 MHz, $CDCl_3$), δ (ppm) = 199.2 ($C_{quart}$, 6 C, CO); 142.8 ($C_{quart}$, 2 C, C-Ar); 138.4 (+, 2 C, C-Ar); 130.5 (+, 2 C, C-Ar); 96.6 ($C_{quart}$, 2 C, C-Alkin); 46.1 (–, 2 C, $CH_2$). – MS (70 eV, EI), *m/z* (%):422 [$(M\text{-}2\ CO)^+$] (47), 394 [$(M\text{-}3\ CO)^+$] (9), 366 [$(M\text{-}4\ CO)^+$] (19), 338 [$(M\text{-}5\ CO)^+$] (32), 310 [$(M\text{-}6\ CO)^+$] (96) 258 (100). HRMS ($C_{16}H_9NSCo_2$): calcd. 477.8421, found 477.8421.

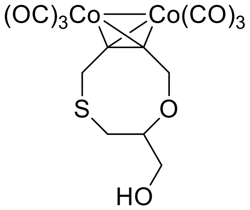
### *4-Thia-7-oxo-(6-mercaptomethyl)cyclooctyne-dicobalthexacarbonyl-complex (11)*



In 100 mL of dry dichloromethane 0.500 g 2-butyne-1,4-diol-dicobalthexacarbonyl complex (1.34 mmol, 1.00 equiv.) were dissolved under argon atmosphere and 0.174 g 2,3-dimercapto propanol (1.40 mmol, 1.05 equiv.) were added. Few drops of $HBF_4$-etherate were added and the mixture was stirred for 48 h. Then one spatula tip of sodium bicarbonate and sodium sulfate were added and the mixture was filtered. The solvent of the filtrate was removed and the crude product was purified by flash column chromatography (20 x 2 cm, silica gel, pentane/dichloromethane 2:1 to 0:1) to obtain 0.195 g of a brown oil (32%)

*R*$_f$ = 0.15 (pentane/DCM 2:1). –$^1$H NMR: (400 MHz, $CDCl_3$): δ(ppm) = 4.01 (bs, 4 H); 3.76 (bs, 1 H); 3.62 (bs, 1 H); 3.28 (bs, 1 H); 3.05 (bs, 1 H); 2.71 (bs, 1 H); 2.28 (bs, 1 H). – $^{13}$C NMR (100 MHz, $CDCl_3$), δ (ppm) = 199.2 ($C_{quart}$, 6 C, *C*O); 97.3 ($C_{quart}$, *C*-complexed alkyne); 96.9 ($C_{quart}$, *C*-complexed alkyne); 65.0 (–, *C*H$_2$-O); 54.1 (–, *C*H$_2$-O); 38.7 (–, *C*H$_2$-S); 37.6 (+, *C*H-S); 36.5 (–, *C*H$_2$-S). ). – IR (ATR Platinum Diamond): 3461 (vw), 2927 (w), 2889 (w), 2042 (s), 1994 (vs), 1615 (m), 1404 (m), 1380 (m), 1343 (m), 1307 (w), 1278 (m), 1226 (m), 1176 (w), 1140 (w), 1062 (m), 1049 (m). – MS (70 eV, EI), *m/z* (%): 460 [M$^+$] (<1), 432 [(M-CO)$^+$] (<1), 404 [(M-2 CO)$^+$] (71), 376 [(M-3 CO)$^+$] (40), 348 [(M-4 CO)$^+$] (19), 320 [(M-5 CO)$^+$] (17), 292 [(M-6 CO)$^+$] (100). – HRMS ($C_{13}H_{10}S_2Co_2O_7$): calcd. 459.8532, found 459.8535.

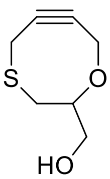
***4-Thia-7-oxo-(6-hydroxymethyl)cyclooctyne-dicobalthexacarbonyl-complex (13)***



In 200 mL of dry dichloromethane 1.00 g 2-butyne-1,4-diol-dicobalthexacarbonyl complex (2.68 mmol, 1.00 equiv.) were dissolved under argon atmosphere and 0.302 g 1-thio glycerol (2.80 mmol, 1.05 equiv.) were added. Few drops of $HBF_4$-etherate were added and the mixture was stirred for 24 h. Then one spatula tip of sodium bicarbonate and sodium sulfate were added and the mixture was filtered. The solvent of the filtrate was removed and the crude product was purified by flash- column chromatography (20 x 2 cm, silica gel, cyclohexane/ethyl acetate 5:1) to obtain 0.453 g of a red/brown oil (38%)

*R*$_f$ = 0.21 (cyclohexane/ethyl acetate 5:1). – $^1$H NMR: (400 MHz, $CDCl_3$): δ(ppm) = 5.75 – 4.21 (bs, 1 H); 4.26 – 2.95 (bs, 4 H); 2.69 (bs, 2 H); 2.19 – 0.88 (bs, 3 H). – $^{13}$C NMR (100 MHz, $CDCl_3$), δ (ppm) = 199.3 ($C_{quart}$, 6 C, *C*O); 97.8 ($C_{quart}$, *C*-complexed alkyne); 94.8 ($C_{quart,}$ *C*-complexed alkyne); 83.6 (+, *C*H-O); 73.4 (–, *C*H$_2$-O); 65.2 (–, *C*H$_2$-O); 39.3 (–, *C*H$_2$-S); 36.7 (–, *C*H$_2$-S). – IR (ATR Platinum Diamond): 3380 (w), 2916 (w), 2088 (m), 2042 (m); 1987 (s), 1597 (m), 1435 (m), 1401 (m), 1337 (m), 1268 (w), 1249 (w), 1223 (m), 1156 (w), 1096 (m), 1035 (m). ). – MS (70 eV, EI), *m/z* (%): 444 [M$^+$] (<1), 388 [(M-2 CO)$^+$] (67), 360 [(M-3 CO)$^+$] (68), 332 [(M-4 CO)$^+$] (19), 304 [(M-5 CO)$^+$] (10), 276 [(M-6 CO)$^+$] (100). – HRMS ($C_{11}H_{10}O_6SCo_2$): calcd 387.8857, found 387.8856.

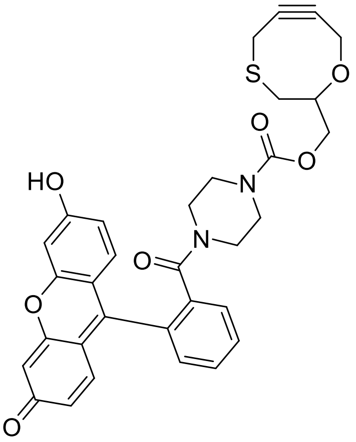
***4-Thia-7-oxo-(6-hydroxymethyl)cyclooctyne (14)***



In 175 ml methanol 3.80 g of the complex **13** (8.56 mmol, 1.00 equiv.) were dissolved and 17.2 g ferric nitrate nonahydrate (42.8 mmol, 5.00 equiv.) dissolved in 10 mL of methanol was added. The solution was stirred for 3 h and was then diluted with diethyl ether, washed with 2 x 100 mL of water. The organic phase was dried over sodium sulfate. The solvent was removed and the crude product was purified by flash- column chromatography (20 x 2, silica gel, cyclohexane/ethyl acetate 5:1) to obtain 0.525 g of a colorless oil (39%).

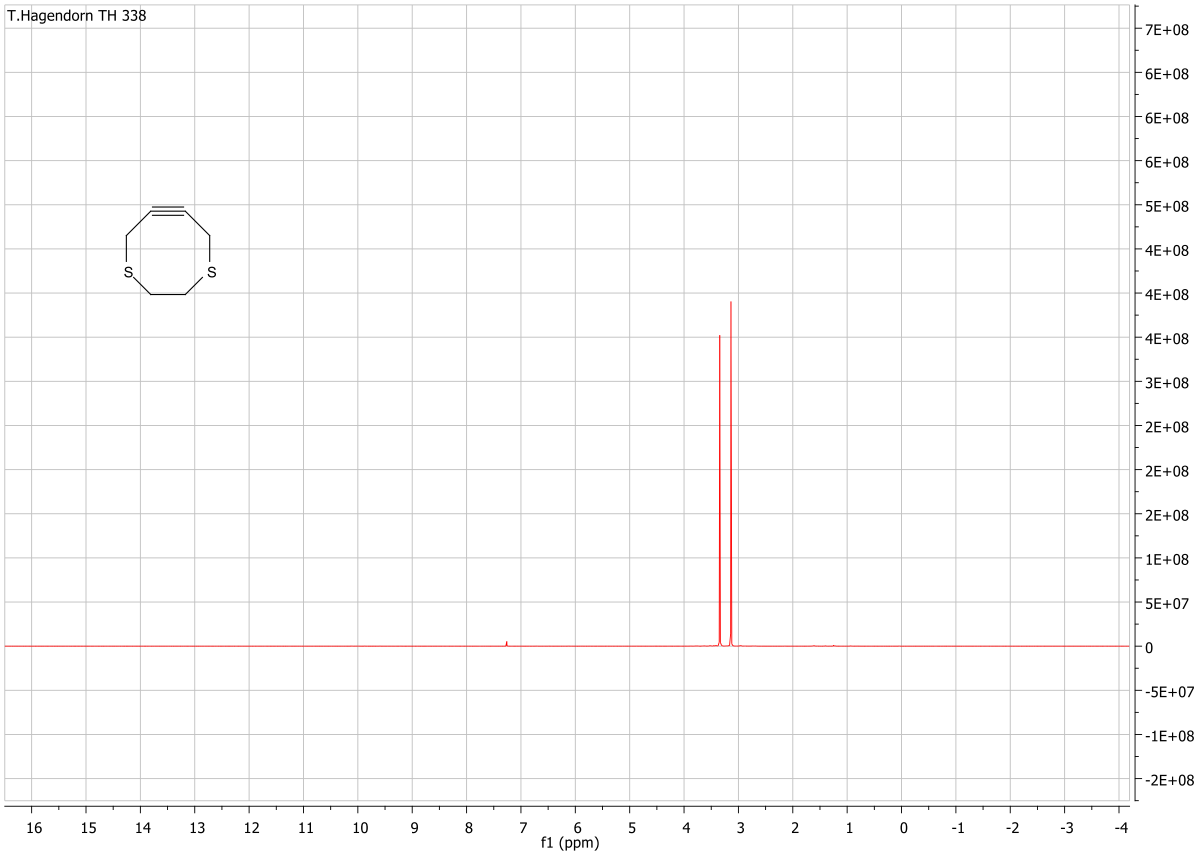
$R_f$ = 0.10 (CH/EE 5:1). –$^1$H NMR: (400 MHz, MeOD): δ(ppm) = 4.32 – 4.28 (m, 2 H, *C*H$_2$-O); 3.95 – 3.87 (m, 1 H, CH-O); 3.70 – 3.62 (m, 1 H, CH$_2$-O); 3.50 – 3.36 (m, 2 H, CH$_2$-O, CH$_2$-S); 3.24 – 3.14 (m, 1 H, CH$_2$-S); 2.96 – 2.88 (m, 1 H, CH$_2$-S); 2.65 – 2.56 (m, 1 H, CH$_2$-S). – $^{13}$C NMR (100 MHz, MeOD), δ (ppm) = 98.2 ($C_{quart}$, *C*-alkyne); 96.8 ($C_{quart}$, *C*-alkyne); 87.4 (+, *C*H-O); 65.7 (–, *C*H$_2$-O); 61.0 (–, *C*H$_2$-O); 36.1 (–, *C*H$_2$-S); 21.3 (–, *C*H$_2$-S-C-alkyne). – IR (ATR Platinum Diamond): 3357 (w), 2915 (w), 1635 (vw), 1408 (vw), 1344 (vw), 1225 (vw), 1174 (vw), 1041 (w), 2862 (w). – MS (70 eV, EI), *m/z* (%): 158 [M$^+$] (100). – HRMS ($C_7H_{10}O_2S$): calcd. 158.0396, found 158.0397.

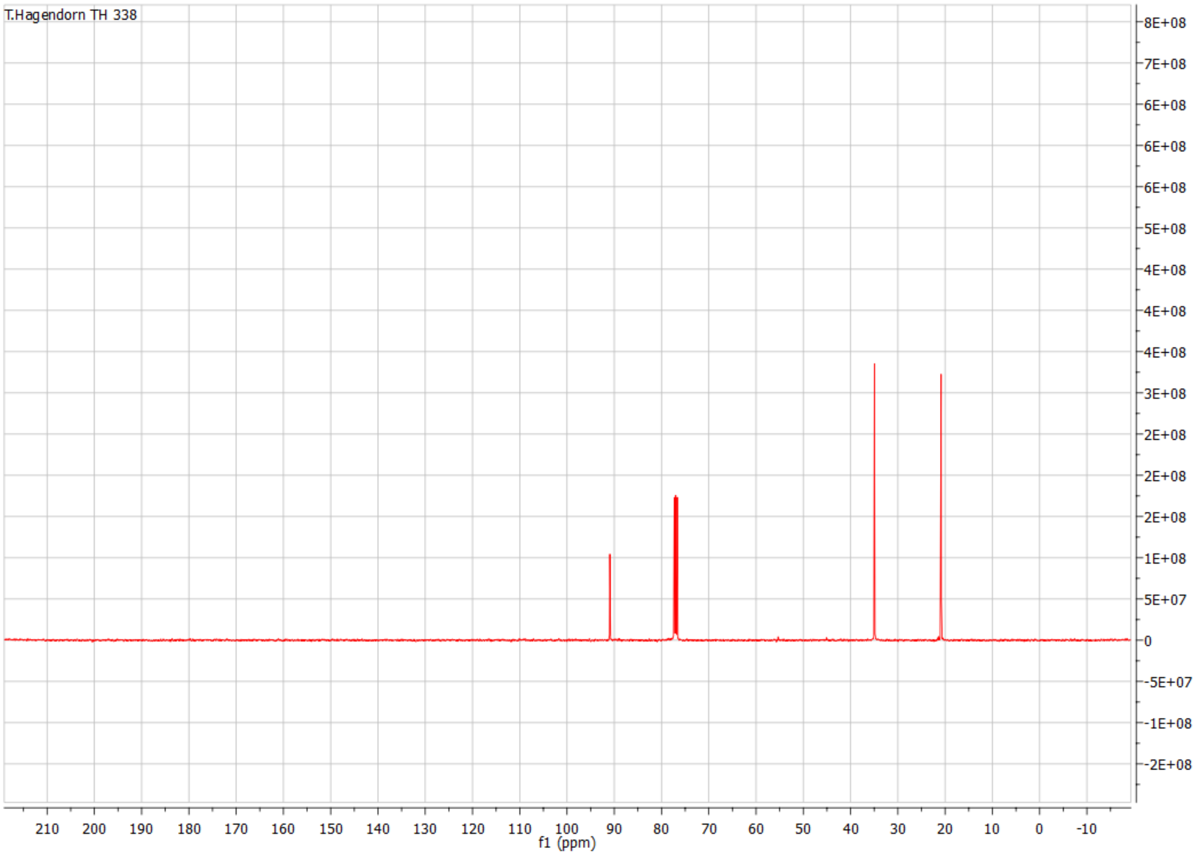
### *4-(2-(6-Hydroxy-3-oxo-3H-xanthen-9-yl)benzoyl)piperazin-1-carboxylic acid-(4-thia-7-oxo-(6-hydroxymethyl)cyclooctynyl-ester (15)*

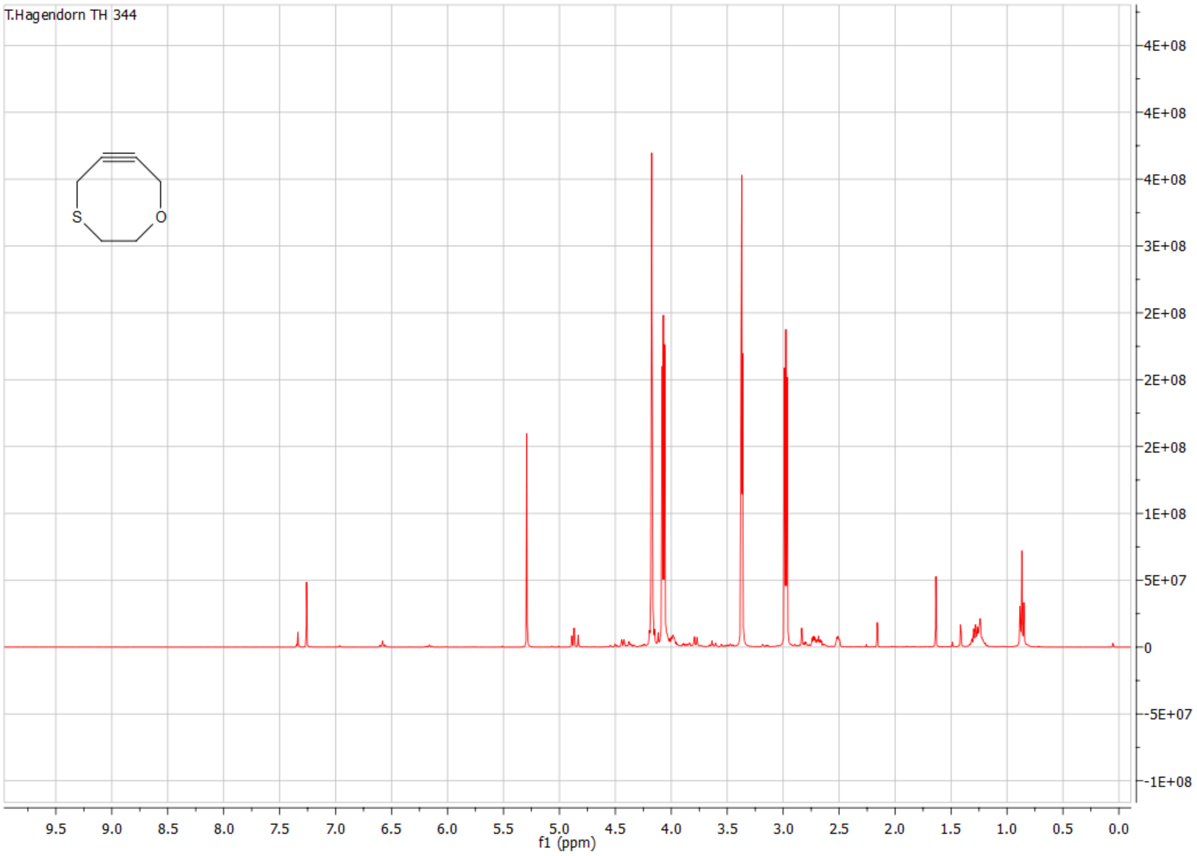


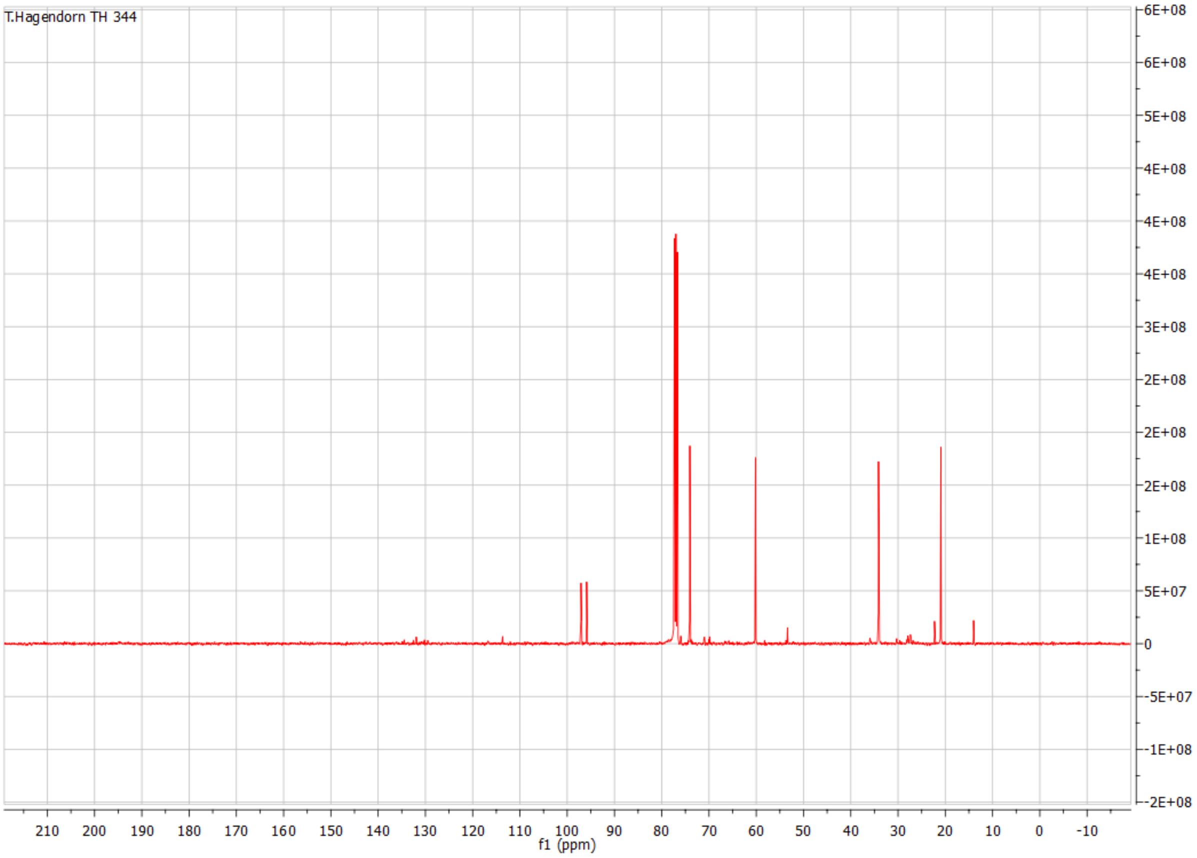
In 2 mL of dry DMF 0.094 g alcohol **14** (0.595 mmol, 1.00 equiv.) was dissolved and 0.117 g carbonyldiimidazole (0.722 mmol, 1.21 equiv.) were added. The mixture was stirred for 2 h then 0.288 g fluorescein-piperazine amide (0.722 mmol, 1.21 equiv.) were added and the solution was stirred for further 12 h. The solvent was removed and the crude product was purified by flash- column chromatography (20 x 1, silica gel, dichloromethane/methanol 20:1-10:1) to obtain 0.065 g of an orange solid (20%). (Despite extended drying under high vacuum before and after the chromatography traces of DMF remained in the product).

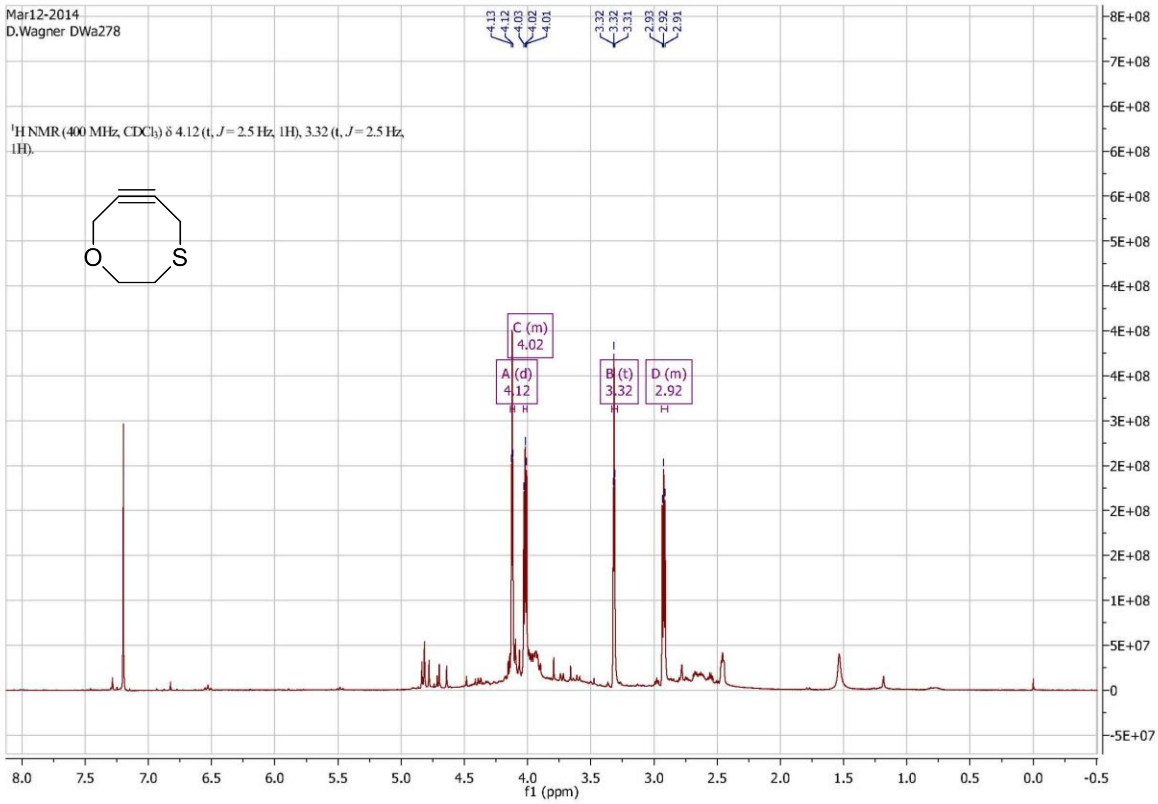
$R_f$ = 0.63 (DCM/MeOH 10:1). – mp = 220°C (decomposition) – $^1$H NMR: (400 MHz, CDCl$_3$): δ(ppm) = 7.64 – 7.52 (m, 2 H, *H*-Ar), 7.52 – 7.39 (m, 1 H, *H*-Ar), 7.39 – 7.28 (m, 1 H, *H*-Ar), 6.98 (d, $^3J$ = 9.5 Hz, 2 H, H-Ar), 6.73 – 6.65 (m, 4 H, *H*-Ar), 6.31 (bs, 1 H, OH), 4.19 – 4.10 (m, 2 H), 4.10 – 4.00 (m, 2 H), 3.93 – 3.84 (m, 1 H, OC*H*), 3.56 (dt, $^3J$ = 15.4, 3.0 Hz, 1 H, OCH$_2$), 3.46 – 3.14 (m, 8 H, CH$_2$-piperazin), 3.09 (d, $^3J$ = 15.5 Hz, 1 H, C*H*$_2$), 2.95 (d, $^3J$ = 16.3 Hz, 1 H, C*H*$_2$), 2.54 (dd, $^3J$ = 16.3, 3.4 Hz, 1 H, CH$_2$). – $^{13}$C NMR (100 MHz, CDCl$_3$), δ (ppm) = 175.3 ($C_{quart}$, CO); 167.9 ($C_{quart}$, CO); 157.4 ($C_{quart}$, C-Ar); 154.5 ($C_{quart}$, C-Ar); 151.2 ($C_{quart}$, C-Ar); 135.1 ($C_{quart}$, C-Ar); 131.6 ($C_{quart}$, C-Ar); 130.7 (+, C-Ar); 130.6 (+, C-Ar); 129.9 (+, C-Ar); 129.6 (+, C-Ar); 127.4 (+, C-Ar); 122.0 (+, C-Ar); 115.1 ($C_{quart}$, C-Ar); 103.9 (+, C-Ar); 96.9 ($C_{quart}$, C-alkyne); 95.5 ($C_{quart}$, C-alkyne); 82.3 (+, CH-O); 67.2 (–, CH$_2$-O); 60.2 (–, CH$_2$-O); 47.2 (–, CH$_2$-piperazine); 43.6 (–, CH$_2$-piperazine); 43.3 (–, CH$_2$-piperazine); 41.6 (–, CH$_2$-piperazine); 35.5 (–, CH$_2$-S); 21.0 (–, CH$_2$-S). – IR (ATR Platinum Diamond): 2919 (w), 2851 (w), 1695 (w), 1633 (w), 1588 (w), 1455 (w), 1418 (w), 1378 (w), 1308 (w), 1240 (w), 1202 (m), 1104 (w), 1003 (w). – MS (FAB): 585 [(M+H)$^+$]. – HRMS ($C_{32}H_{29}O_7N_2S$): calcd. 585.1690, found 585.1692.

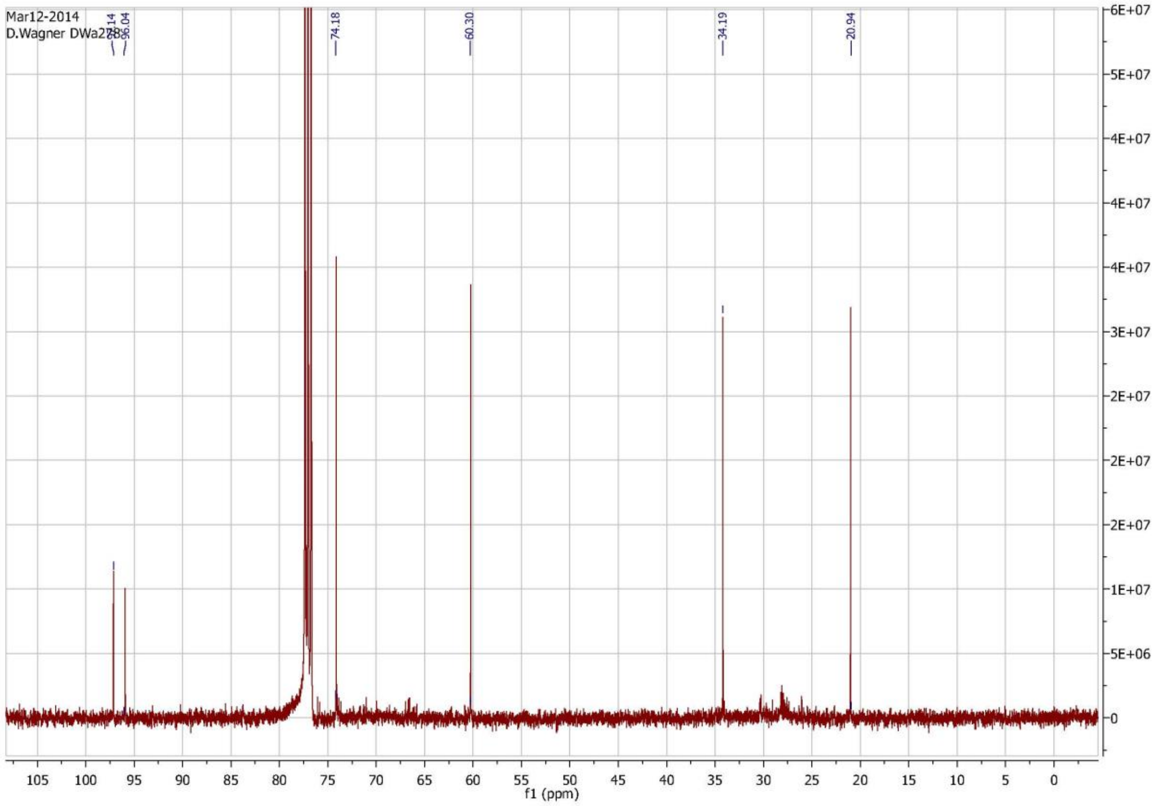

T.Hagendorn TH 338
S
S
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
-1E+08
-2E+08
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

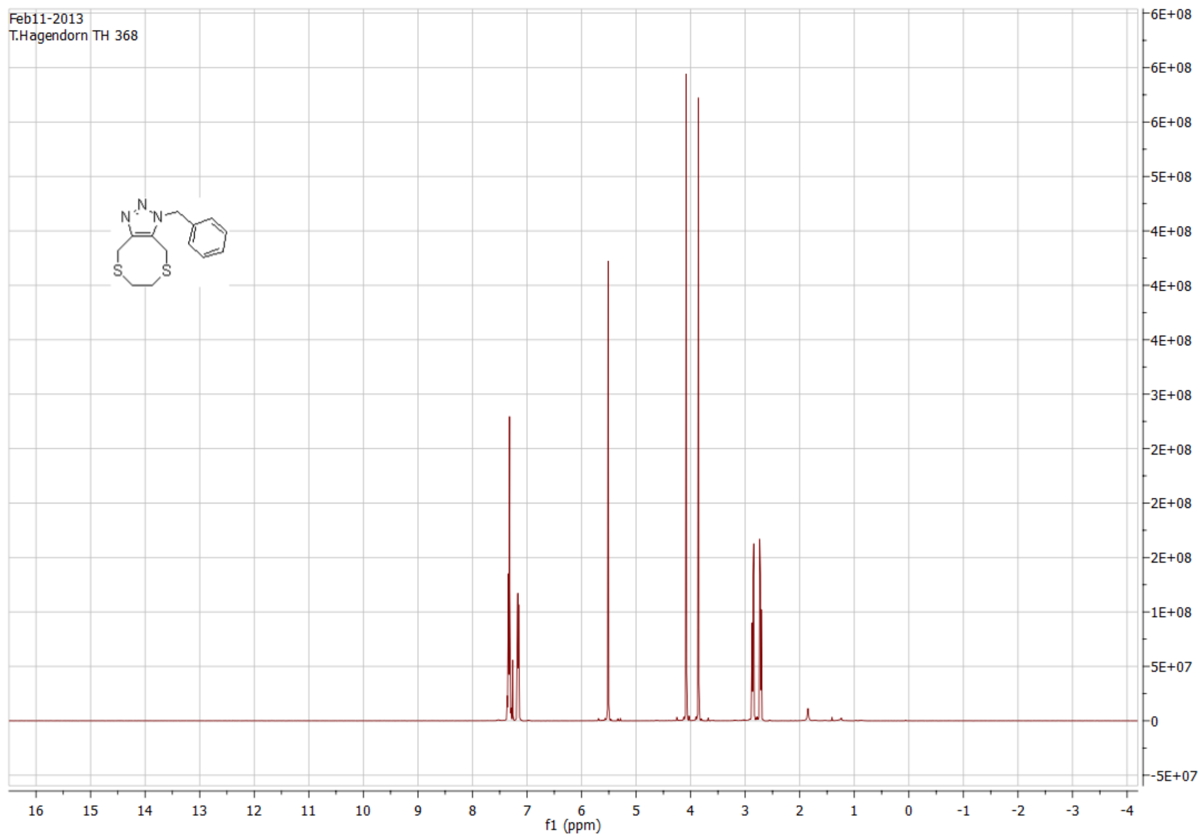

T.Hagendorn TH 338
8E+08
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
-1E+08
-2E+08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

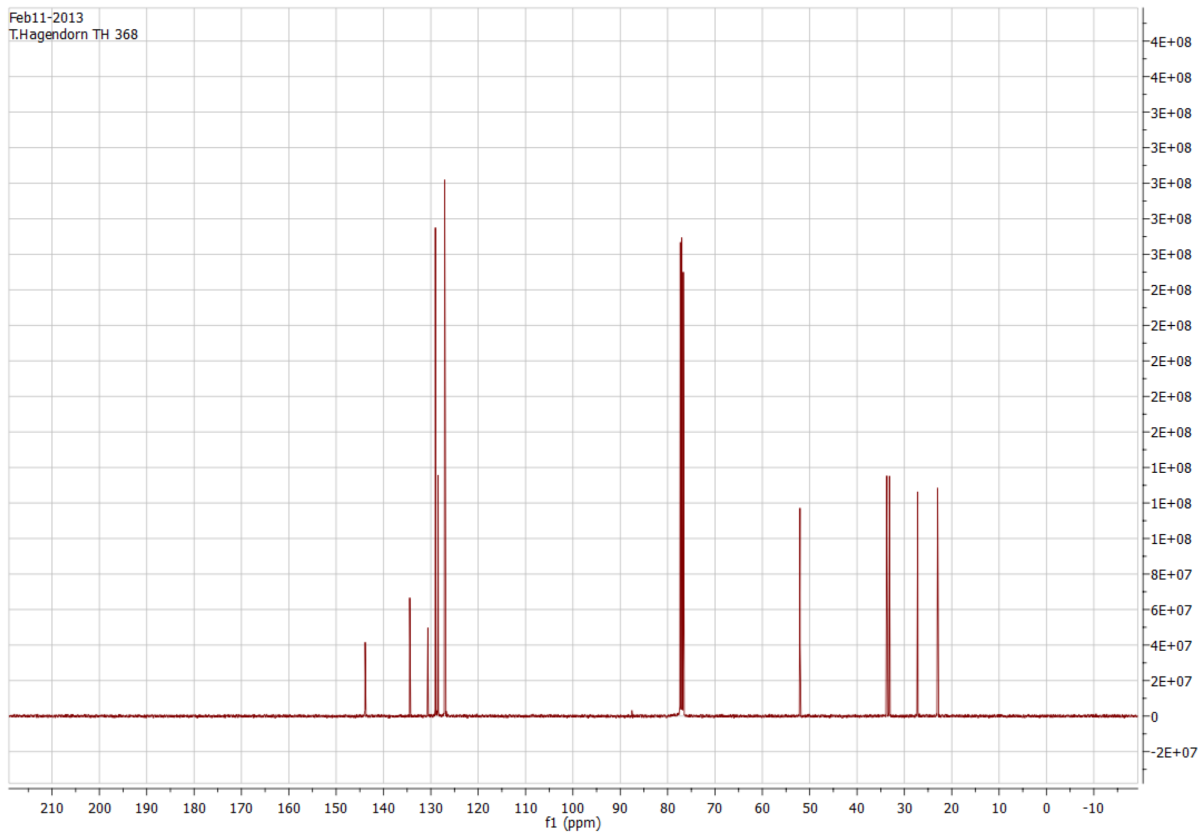

T.Hagendorn TH 344
S
O
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
-1E+08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


T.Hagendorn TH 344
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
-1E+08
-2E+08
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


$^1$H NMR (400 MHz, $CDCl_3$) δ 4.12 (t, $J$ = 2.5 Hz, 1H), 3.32 (t, $J$ = 2.5 Hz, 1H).




Feb11-2013
T.Hagendorn TH 368
N
N
N
S
S
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


Feb11-2013
T.Hagendorn TH 368
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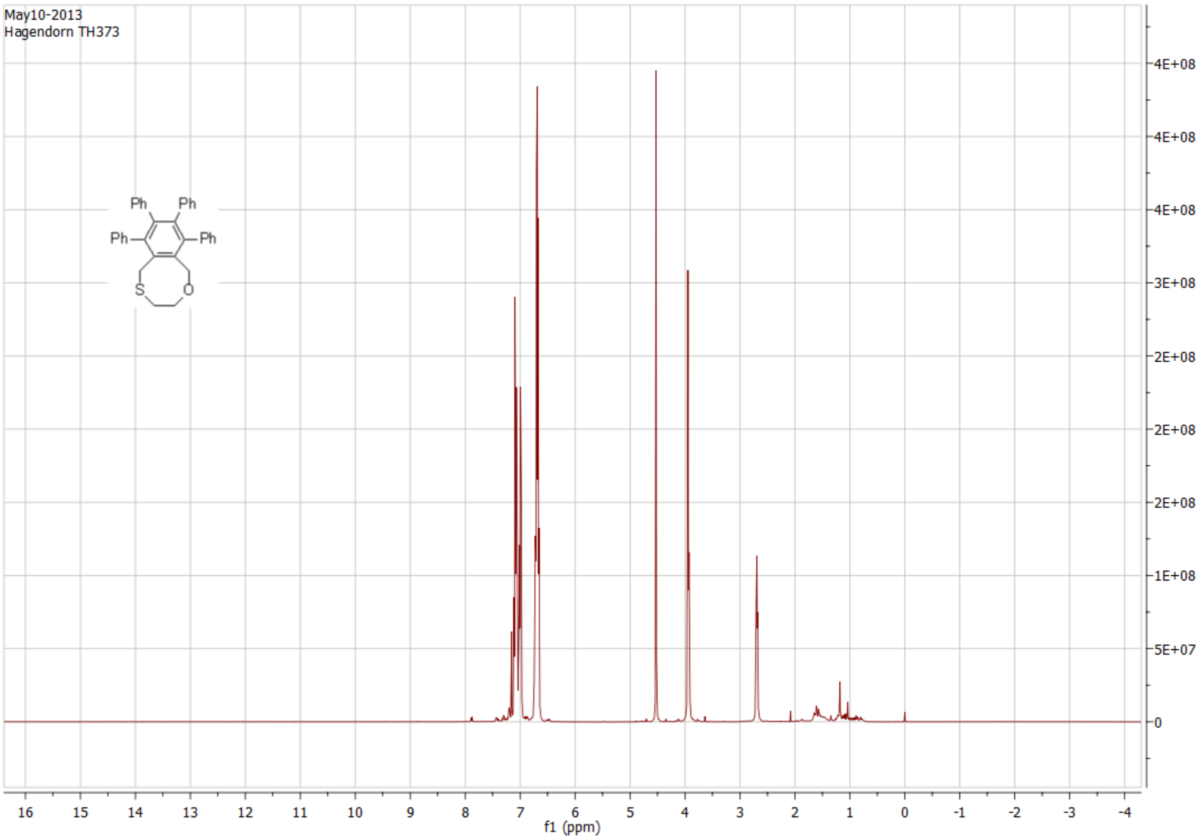
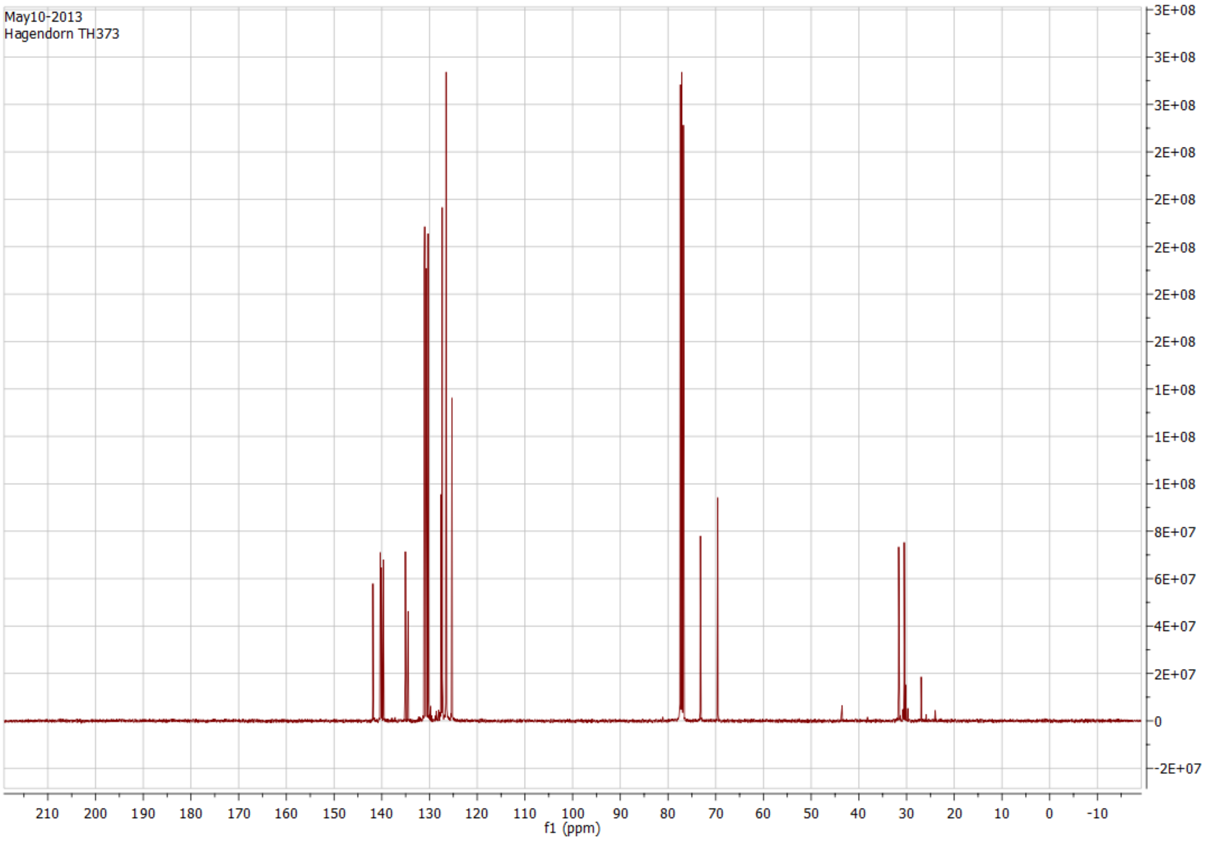
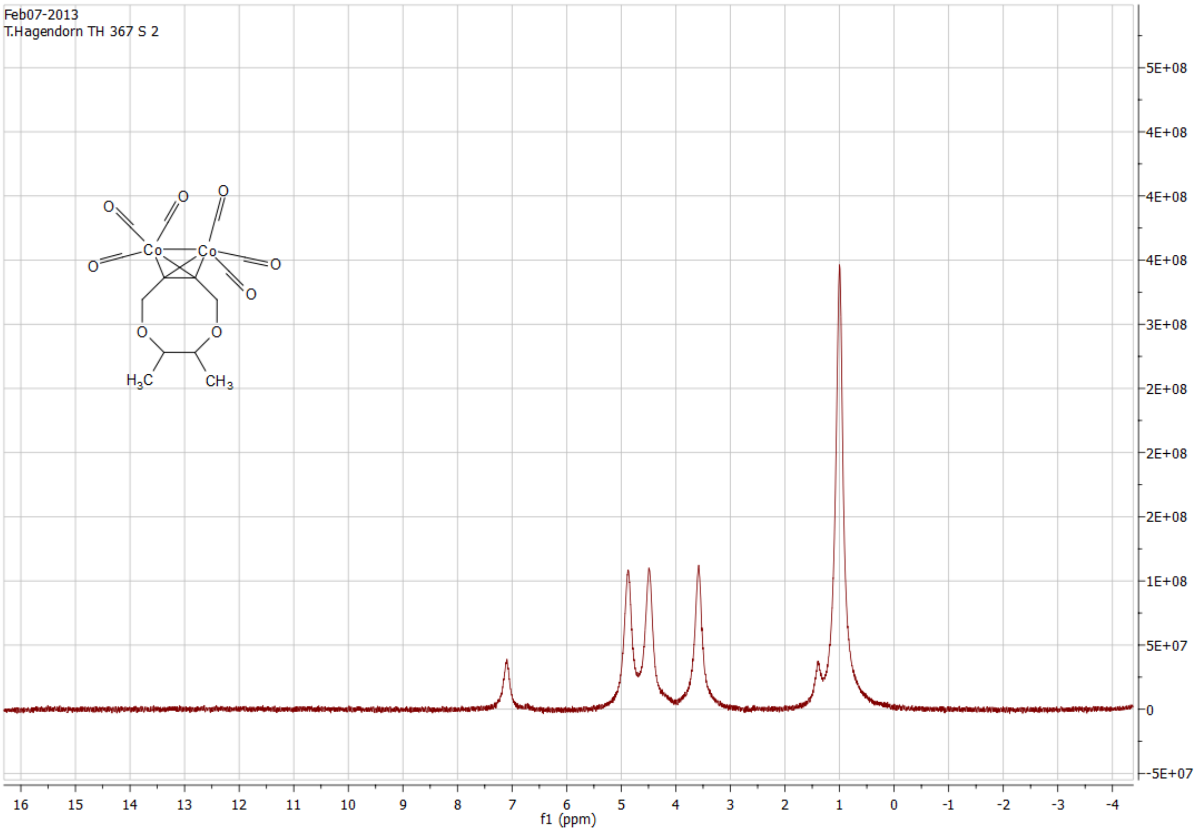
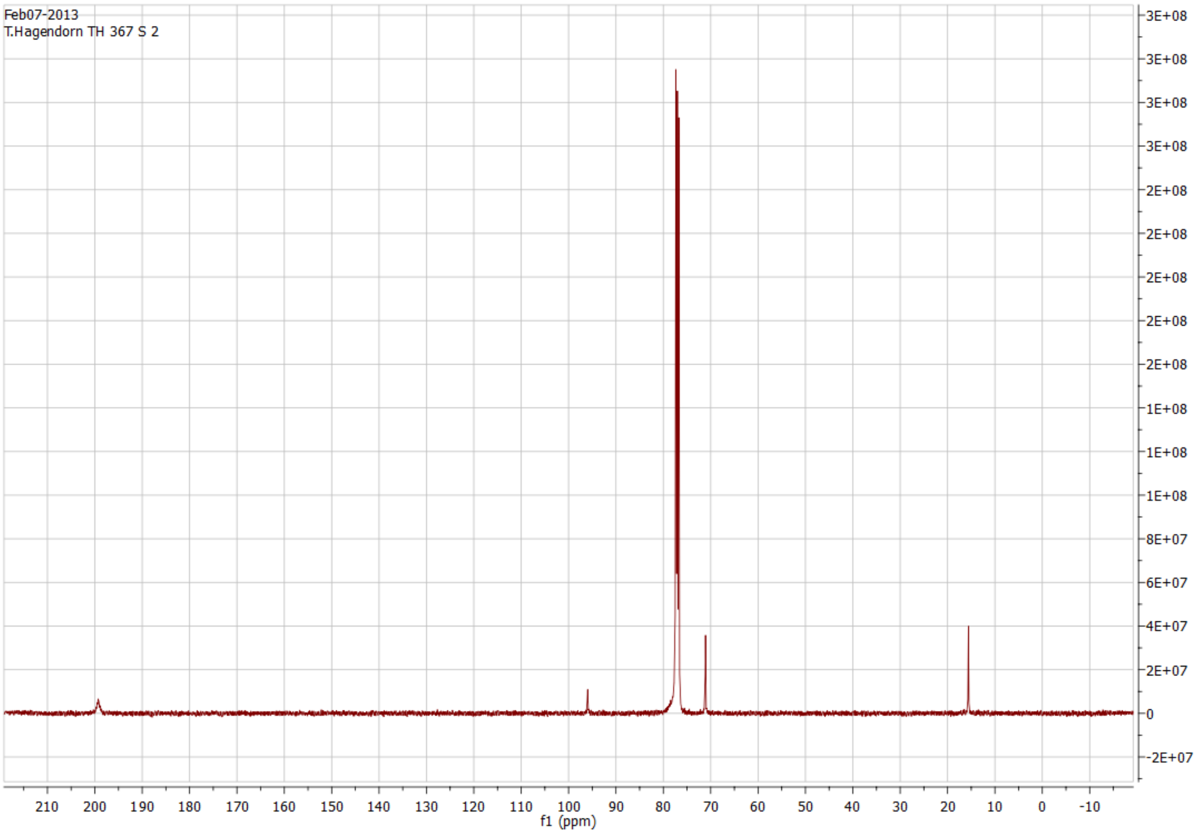
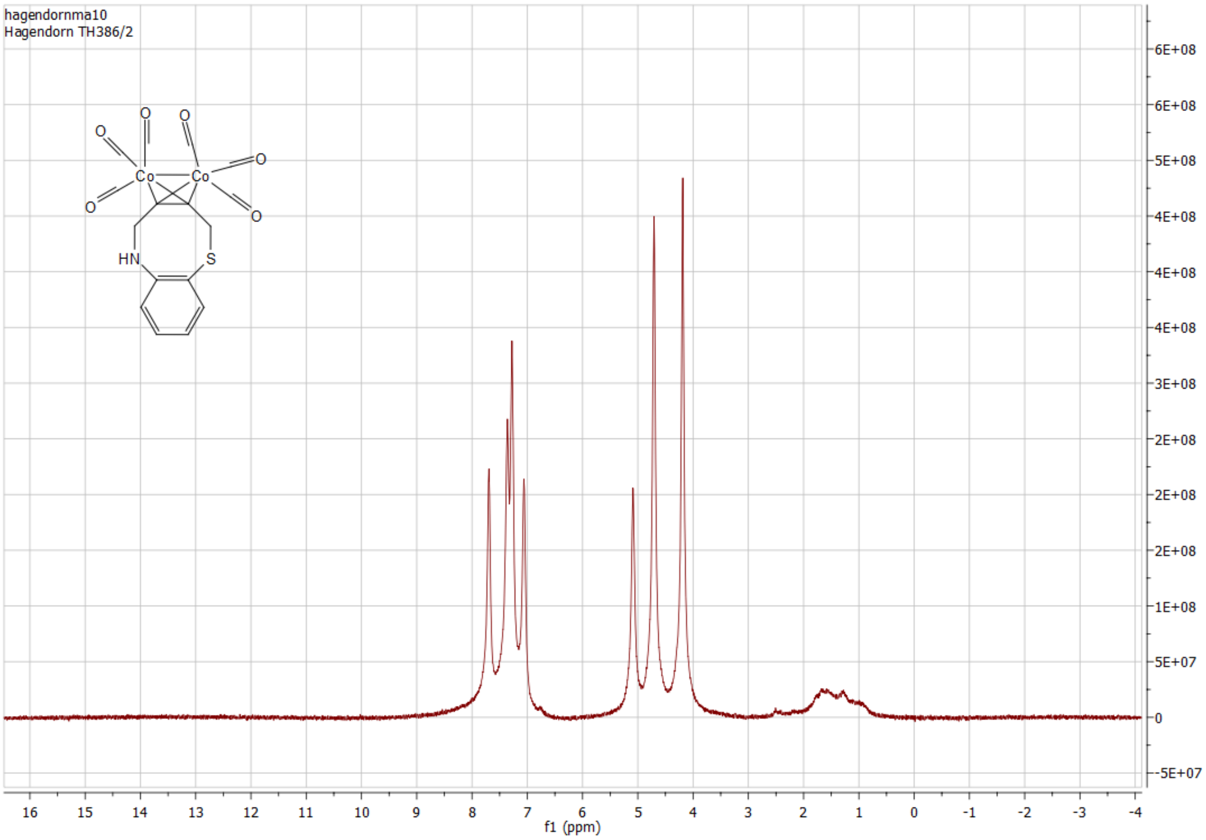
4E+08
3E+08
3E+08
3E+08
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

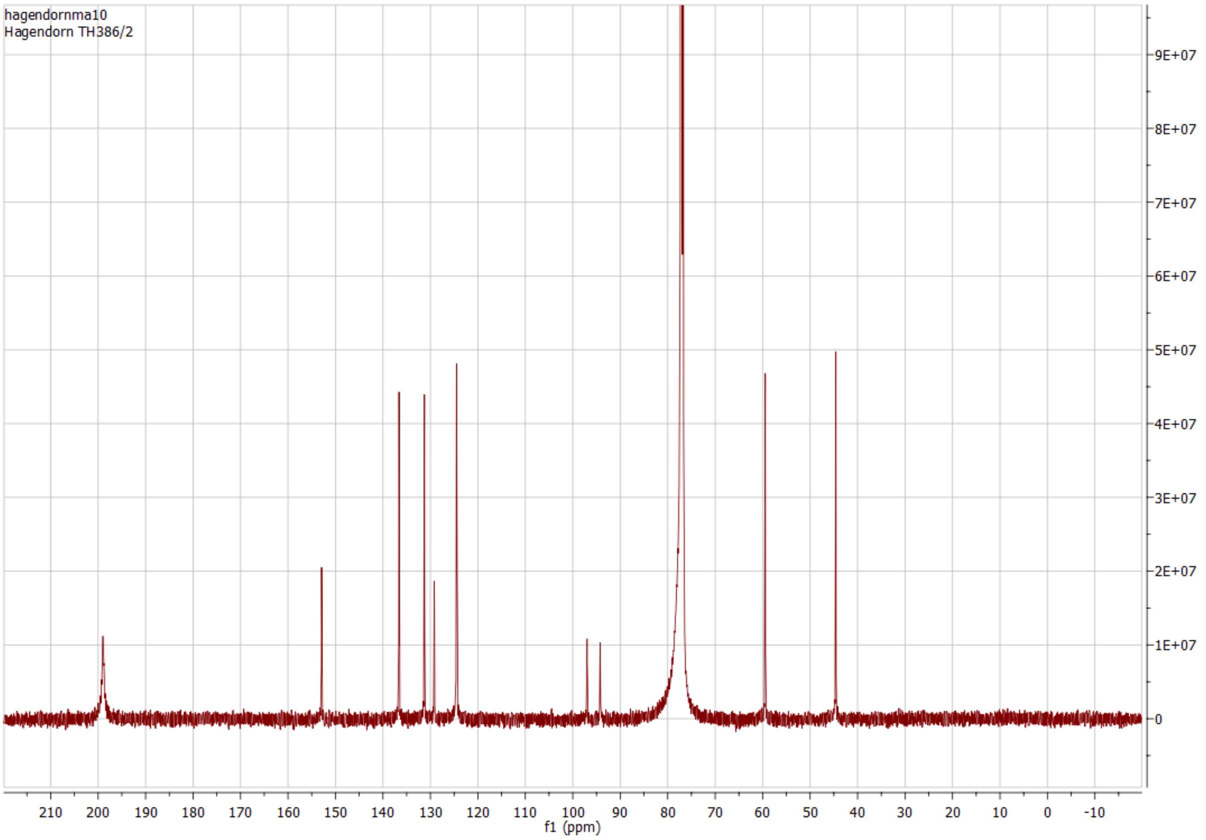

May10-2013
Hagendorn TH373
Ph
Ph
Ph
Ph
S
O
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

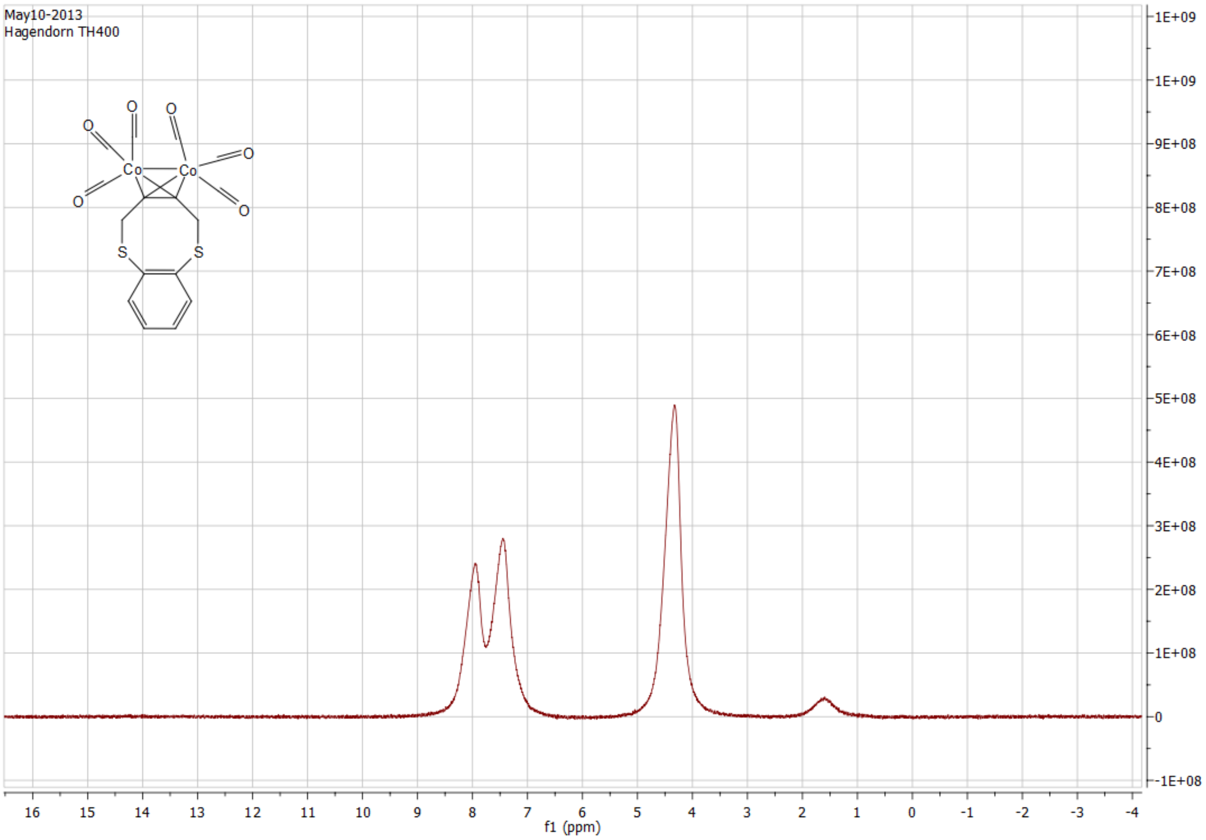

May10-2013
Hagendorn TH373
3E+08
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

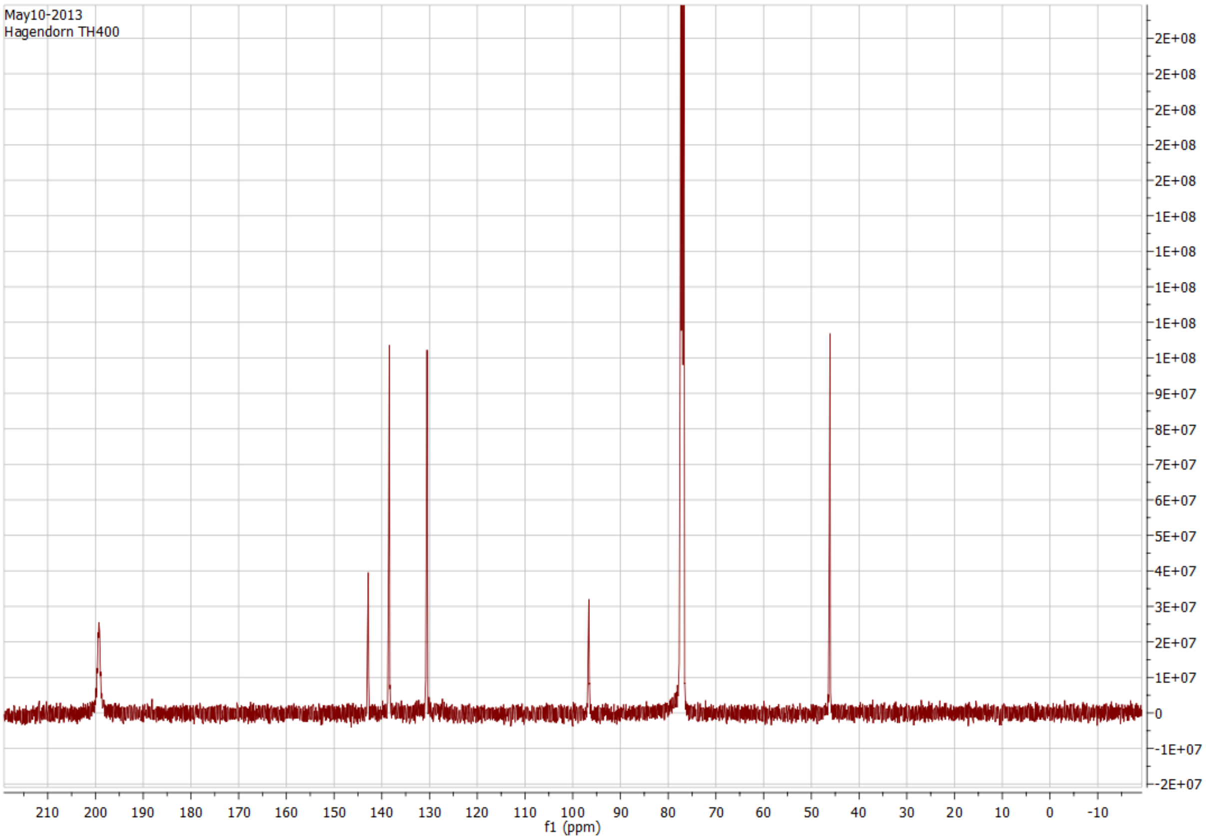

Feb07-2013
T.Hagendorn TH 367 S 2
O
O
O
Co
Co
O
O
O
O
O
H3C
CH3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


Feb07-2013
T.Hagendorn TH 367 S 2
3E+08
3E+08
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


hagendornma10
Hagendorn TH386/2
O
O
O
O
O
O
Co
Co
HN
S
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


hagendornma10
Hagendorn TH386/2
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


May10-2013
Hagendorn TH400
O
O
O
O
O
O
Co
Co
S
S
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


May10-2013
Hagendorn TH400
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
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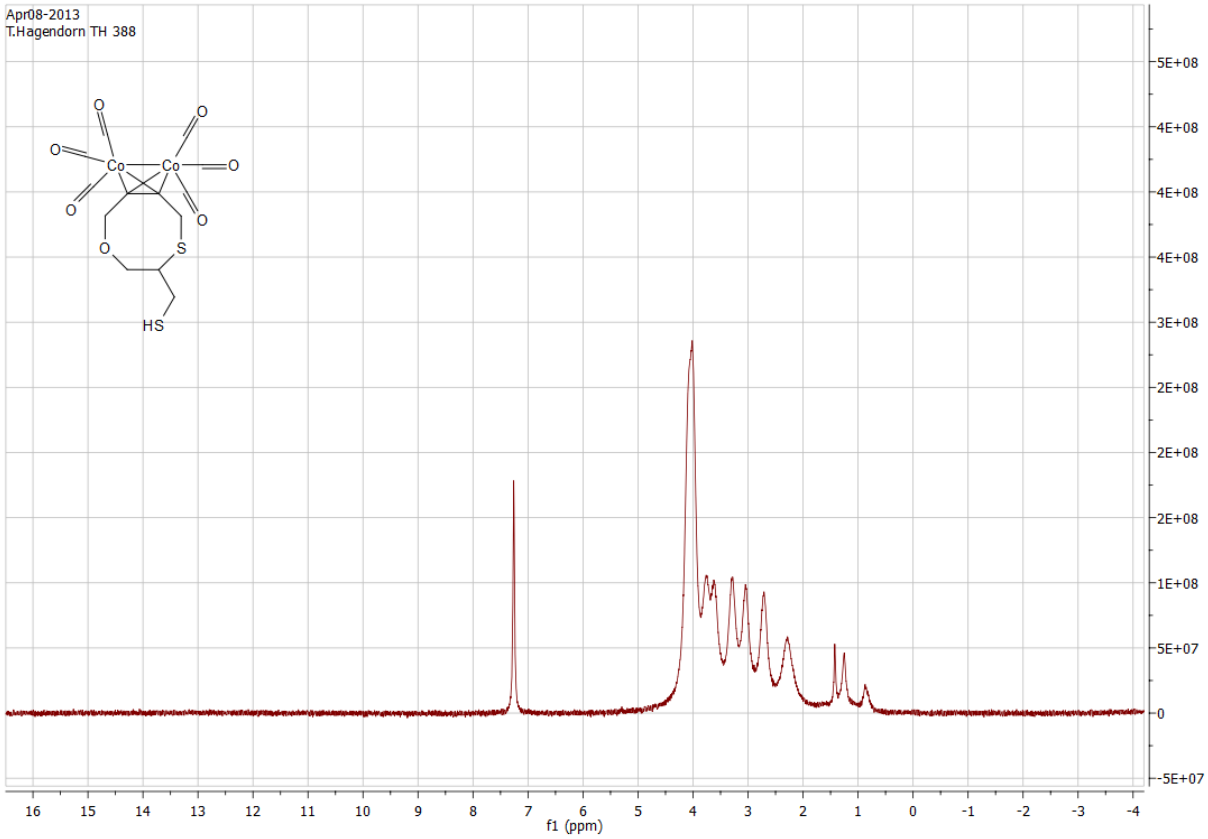
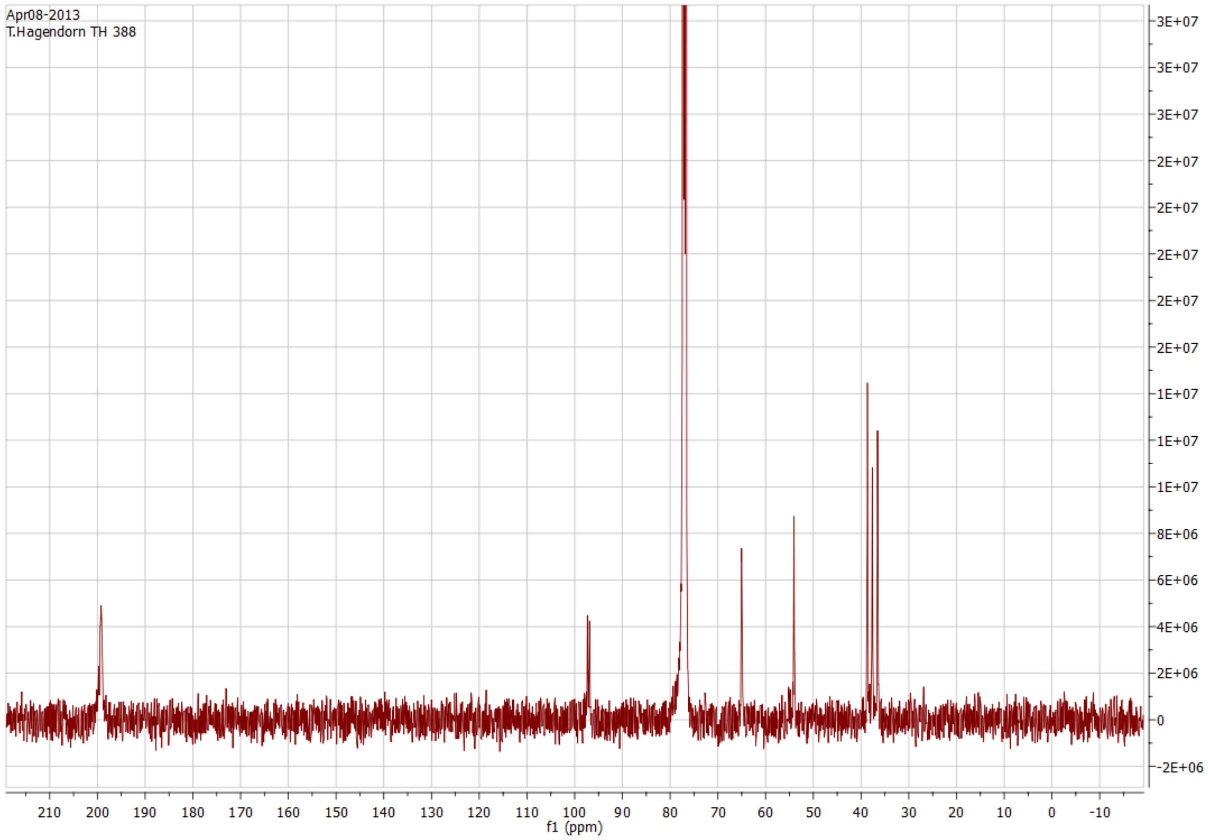
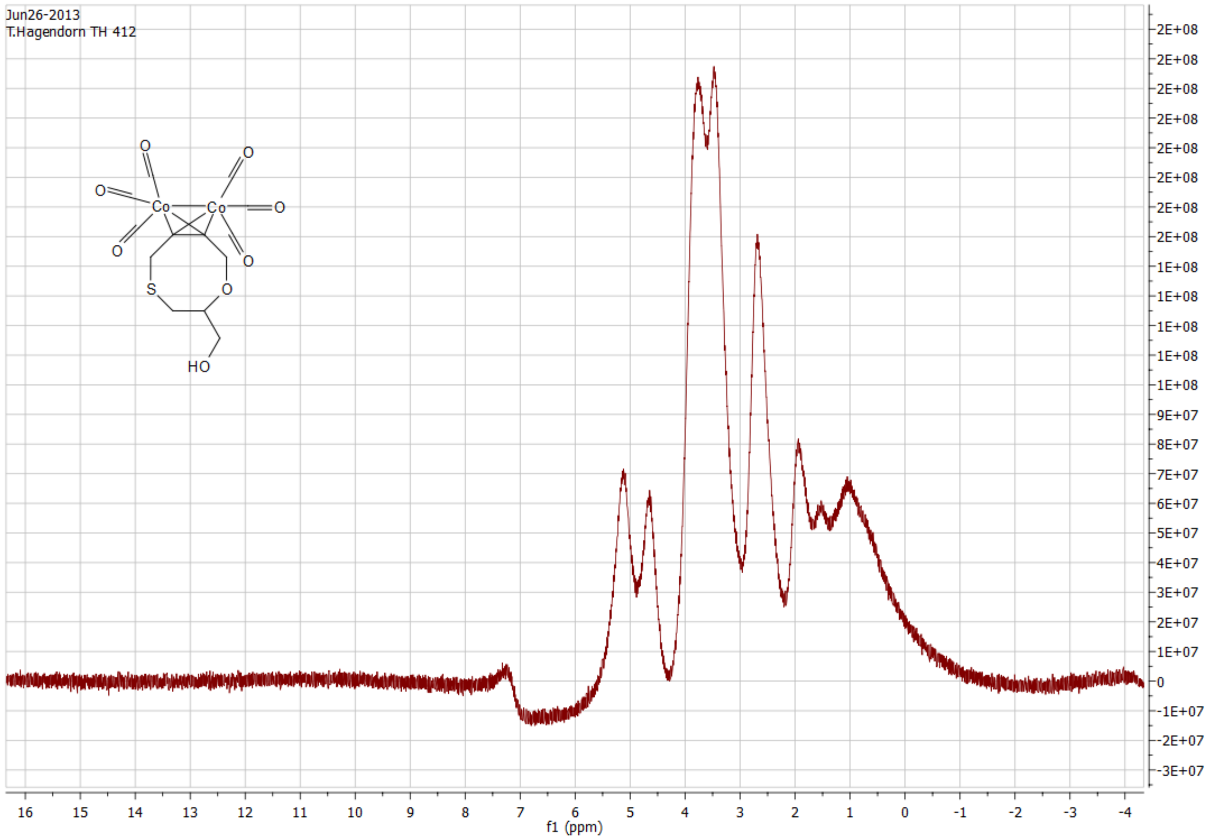
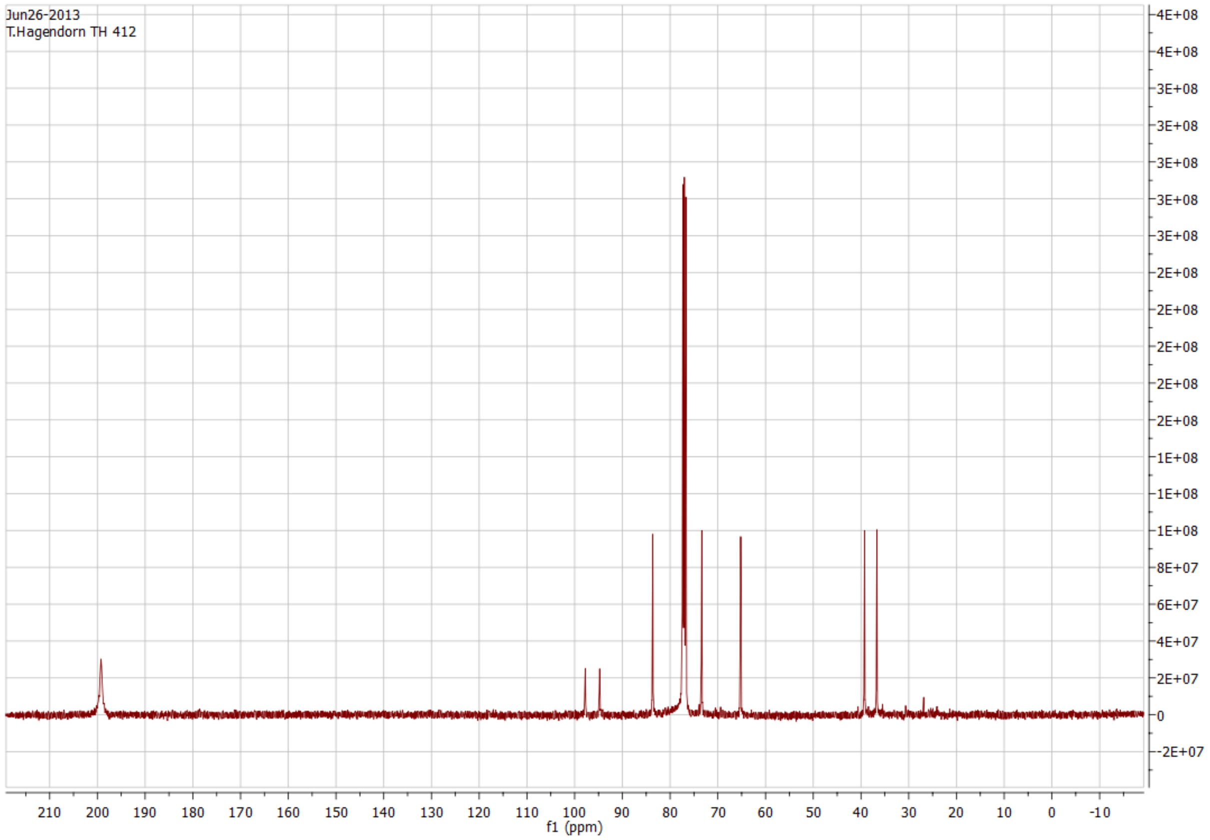
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
-2E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Apr08-2013
T.Hagendorn TH 388
O
O
O
O
Co
Co
O
O
O
S
HS
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


Apr08-2013
T.Hagendorn TH 388
3E+07
3E+07
3E+07
2E+07
2E+07
2E+07
2E+07
2E+07
1E+07
1E+07
1E+07
8E+06
6E+06
4E+06
2E+06
0
-2E+06
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Jun26-2013
T.Hagendorn TH 412
O
O
O
O
O
O
Co
Co
S
O
HO
2E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
-2E+07
-3E+07
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


Jun26-2013
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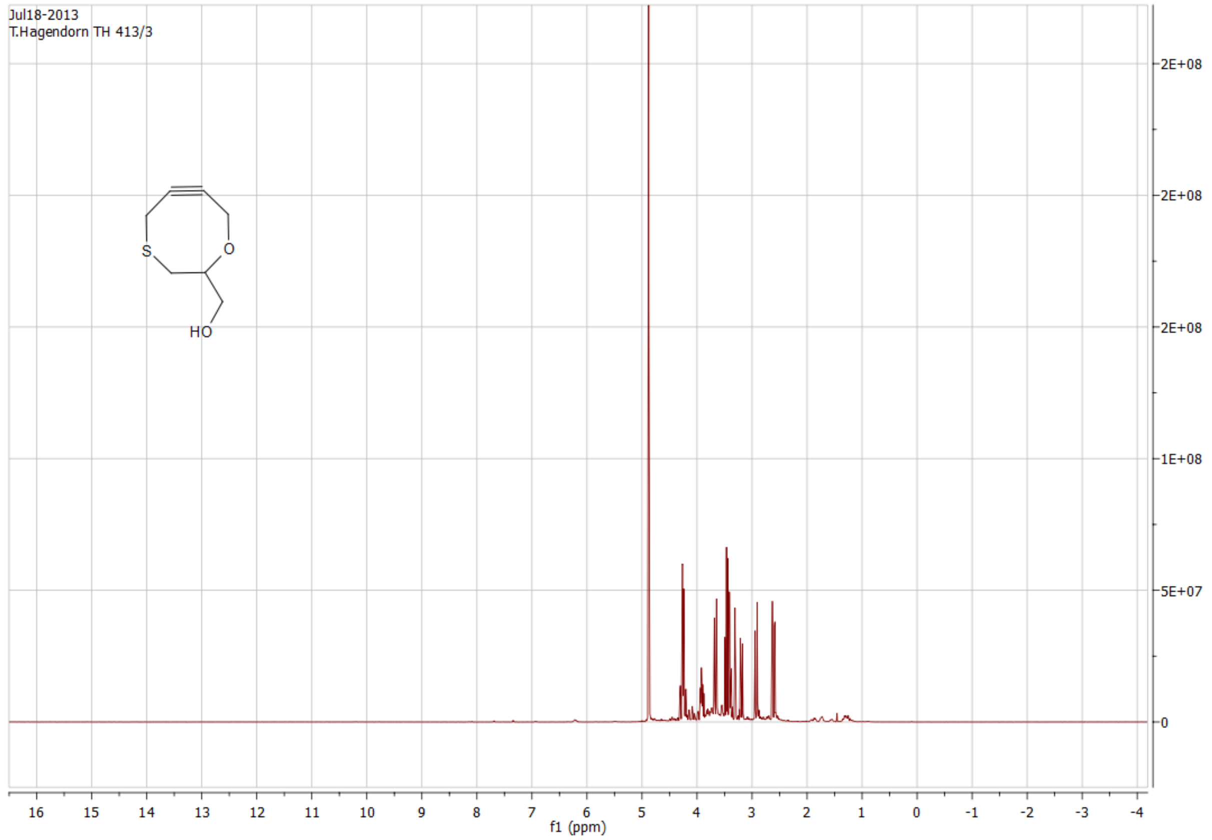
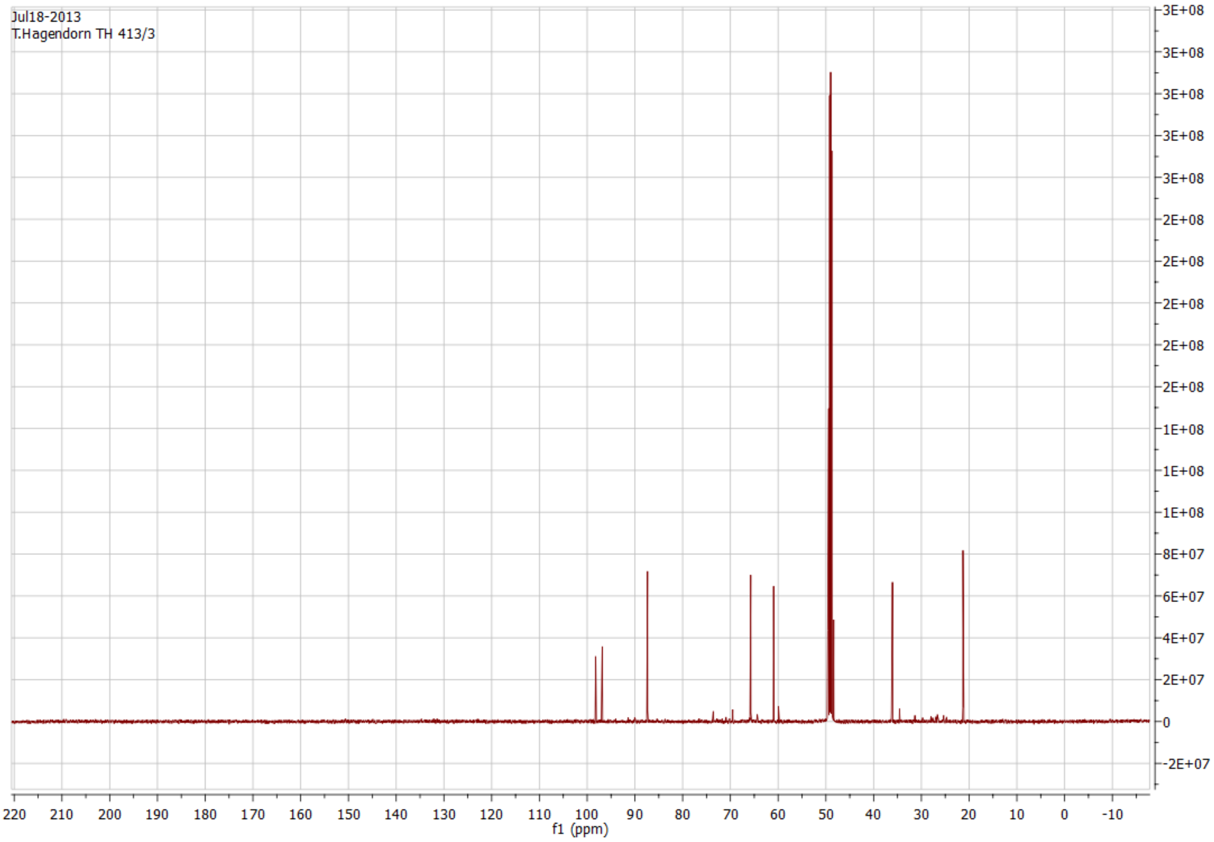
4E+08
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Jul18-2013
T.Hagendorn TH 413/3
S
O
HO
2E+08
2E+08
2E+08
1E+08
5E+07
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


Jul18-2013
T.Hagendorn TH 413/3
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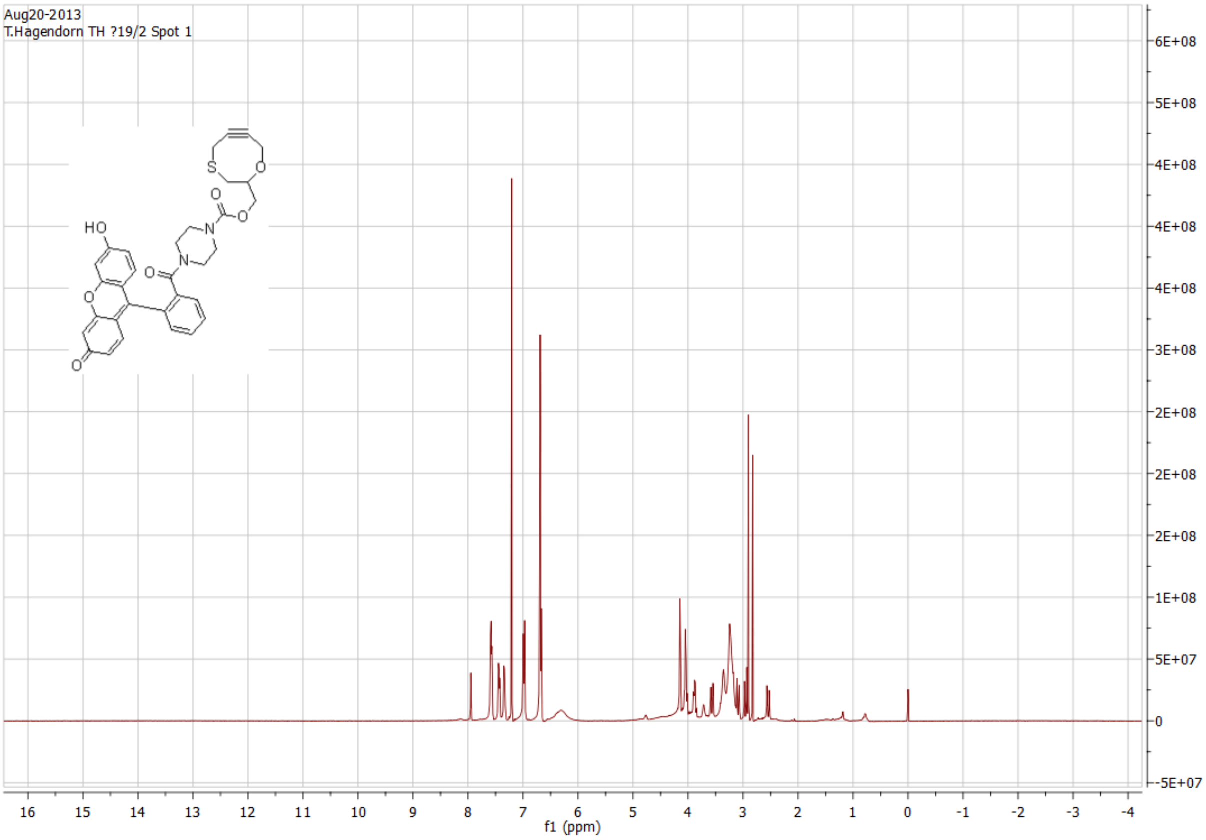
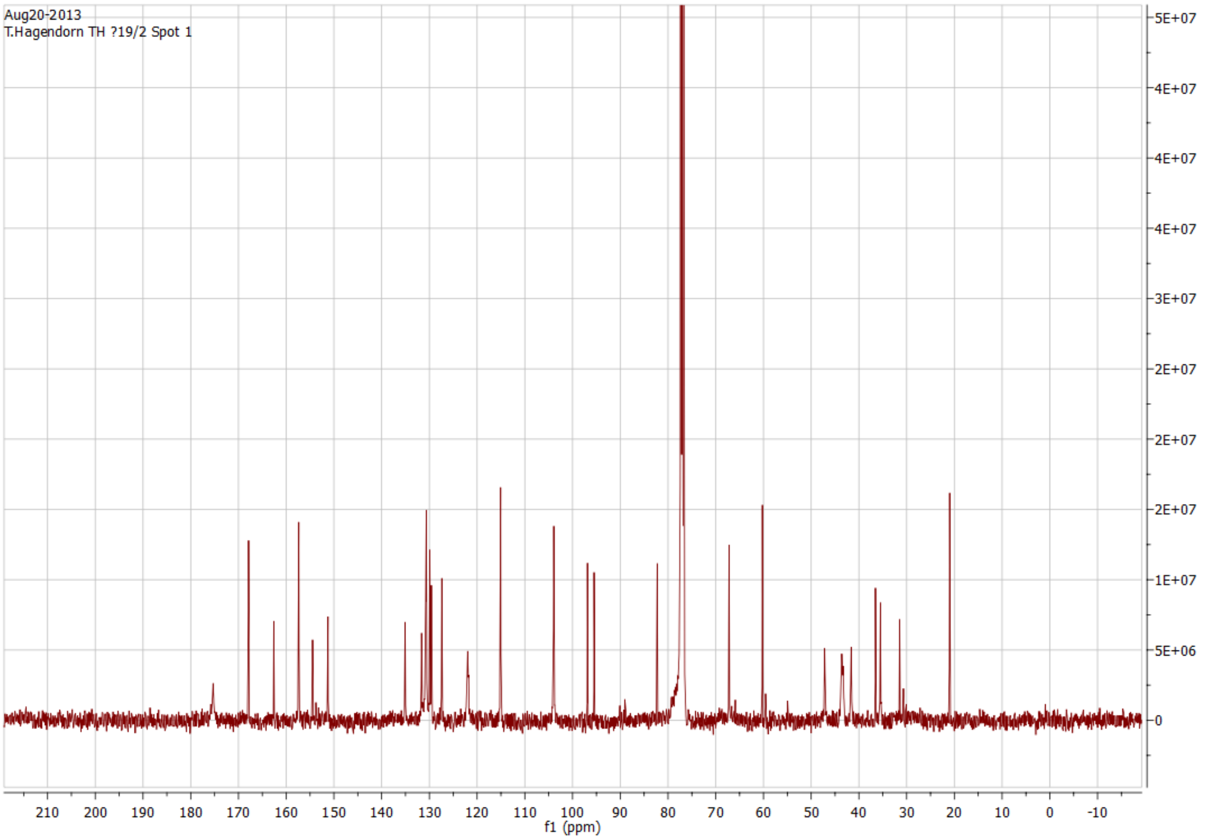
3E+08
3E+08
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Aug20-2013
T.Hagendorn TH ?19/2 Spot 1
HO
O
O
O
N
N
O
O
S
O
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


Aug20-2013
T.Hagendorn TH ?19/2 Spot 1
5E+07
4E+07
4E+07
4E+07
3E+07
2E+07
2E+07
2E+07
1E+07
5E+06
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)