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Supplementary Information

Incorporating Cobalt Carbonyl moieties onto Ethynylthiophene-based Dithienylcyclopentene Switches Part 1: Photochemistry

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S1. Experimental Section

Photocyclization/cycloreversion: Solutions of the compounds were made-up in THF at a concentration of 1.4×10^{-5} mol/L, and purged with nitrogen. Cyclization experiments were performed by irradiating the solution with monochromatic light at $\lambda = 313$ nm and recording the UV/vis absorption spectra at specific time intervals. Irradiation was carried out until the photostationary state (PSS) of the compounds was achieved, or until no more changes were endured in the UV-vis spectra. Following this, cyclo-reversion was induced by irradiation of the same solution with broadband visible light ($\lambda > 550$ nm) and the absorption spectra were recorded over time, until no further changes were observed in the spectra.

^1H NMR Studies: Solutions of these switches, in deuterated acetone, were irradiated with monochromatic light at 313 nm, under air, in a sealed NMR tube. The changes in the ^1H NMR spectra were observed over recorded irradiation time intervals. The integration of the signals associated with the open isomers, closed isomers and by-product (in the case of **1Ho**) was used to calculate the % conversion from the open to the closed isomers and by-product. Reference to the residual solvent signal confirms that the mass balance was maintained.

Fatigue Resistance: Solutions of these switches in THF, at a concentration of 1.4×10^{-5} mol/L, were purged with nitrogen and placed in a sealed 1 cm quartz cell. Cyclisation to the closed isomer was induced by irradiation with a monochromatic light source at a wavelength of 313 nm, and cycloreversion back to the open isomer was carried out using broadband filtered light > 550 nm. This process counted as one cycle, and the fatigue resistance properties were measured over five consecutive cycles, by UV-vis spectrophotometry.

Thermal Stability: The switches were irradiated with monochromatic light at $\lambda = 313$ nm, in a solution of toluene, until the PSS of the closed isomer was reached, as monitored in the UV-vis absorption spectra. The stability of the switches, at room temperature, was measured by storing the solutions of the closed-switches under air in sealed glass vials, in the dark. After 10 weeks, the absorption spectra of these compounds were recorded and compared to the spectra measured initially. The stability of these switches was also measured at elevated temperatures (60°C, 80°C and 100°C) by placing non-degassed solutions of the closed isomers, in toluene, on a temperature

controlled heating mantel and measuring their absorption spectra at specific time intervals (minutes).

Steady-state Photolysis: Solutions of the cobalt carbonyl complexes were made-up in spectroscopic-grade THF, and purged with nitrogen for 20 minutes. The solutions were placed in a liquid IR cell, and irradiated with monochromatic light at two different wavelengths, 313 nm and 365 nm. The changes observed in the carbonyl stretches in the IR spectrum were recorded. These experiments were repeated in the presence of a large excess of triphenylphosphine (PPh₃), which was used as a trapping ligand.

Synthesis: All reactions were performed under nitrogen, which was supplied by Air Products Ltd. 1,2-Bis(5'-chloro-2'-methylthien-3'-yl)cyclopentene, 1,2-Bis(5'-chloro-2'-methylthien-3'-yl)perfluorocyclopentene, 1,2-Bis(5'-iodo-2'-methylthien-3'-yl)cyclopentene and 1,2-Bis(5'-iodo-2'-methylthien-3'-yl)perfluorocyclopentene were synthesized according to previous literature procedures.^{1,2,3} All other reagents and solvents were purchased from Sigma Aldrich and used without further purification. n-Butyllithium, tert-butyllithium, DMF and triethylamine were of anhydrous grade, and the rest of the solvents were analytical grade. Dry THF and diethyl ether were distilled from sodium/benzophenone. Octaperfluoro-cyclopentene was sourced from Rijksuniversiteit Groningen, Holland. Column chromatography was performed using neutral silica gel. All glassware used for synthesis was dried in an oven at ~150°C overnight. ¹H NMR spectra were recorded on a Bruker model AC 400 MHz spectrometer. ¹³C and ³¹P NMR spectra were recorded on a Bruker Avance III 600 ultrashield spectrometer (at 150 MHz and 242.9 MHz, respectively). ¹⁹F NMR spectra were recorded on a Bruker model AC 400 MHz spectrometer (at 376.5 MHz). All NMR spectra were obtained in the designated deuterated solvent and each spectrum was calibrated according to the deuterated solvent peak. The splitting patterns are designated as follows: s (singlet); d (doublet); dd (doublet of doublets); t (triplet); quintet; m (multiplet) and br (broad). In the case of the ¹³C NMR data, a quaternary carbon is denoted by "Cq". Infra-red spectroscopy was carried out on a Perkin Elmer "Spectrum GX" FT-IR spectrometer. For the IR data, "sh" denotes a shoulder band. Elemental analysis was carried out at Rijksuniversiteit Groningen, The Netherlands.

S2. Synthetic Procedures

1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)-cyclopentene (1Ho). Anhydrous DMF (60 mL), anhydrous triethylamine (7 mL) and distilled, dry THF (7 mL) were added to an oven-dried round-bottomed flask. 1,2-Bis(5'-iodo-2'-methylthien-3'-yl)-cyclopentene (0.300 g, 0.586 mmol) was added to the flask, and after the solution was purged with nitrogen for 20 minutes, CuI (0.09 g, 0.473 mmol), tetra-butylammonium iodide (TBAI) (1.704 g, 4.613 mmol) and $[(\text{CH}_3)_3\text{C}_6\text{H}_2]_3\text{P}$ (0.18 g, 0.463 mmol), were also added to the reaction flask. The mixture was then freeze-evacuated three times, followed by the addition of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (0.035 g, 0.051 mmol) under nitrogen, and was left to stir for 5 minutes at room temperature. Subsequently, the flask was cooled to -20°C and 3-ethynylthiophene (0.127 ml, 1.29 mmol) was added. The solution was then allowed to warm up to room temperature and left to stir for 24 hours, under nitrogen. The reaction mixture was quenched with water, and the solvent was removed by vacuum distillation. The crude product was extracted three times with brine/dichloromethane, the organic extracts were combined, dried over MgSO_4 and filtered. The crude product was purified by column chromatography, using silica gel, and eluted with 100% hexane followed by a 9:1 mixture of hexane: CH_2Cl_2 respectively. The pure product was found to be the 4th band on the column, and a purple solid was obtained (0.2721 g, 98%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): δ = 1.89 (s, 6H, CH_3), 2.01 (quintet, $J=7.5$ Hz, 2H, CH_2), 2.77 (t, $J=7.5$ Hz, 4H, CH_2), 7.13 (s, 2H, thienyl-H4), 7.24 (dd, $J=4.9$ Hz, 1.2 Hz, 2H, ethynylthiophene-H4), 7.65 (dd, $J=4.9$ Hz, 3 Hz, 2H, ethynyl-thiophene-H5), 7.90 (dd, $J=3$ Hz, 1.2 Hz, 2H, ethynylthiophene-H2) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ = 14.52 (s, 2C, CH_3), 23.02 (s, 1C, CH_2), 38.71 (s, 2C, CH_2), 82.54 (s, 2C, Cq), 87.78 (s, 2C, Cq), 119.18 (s, 2C, Cq), 122.26 (s, 2C, Cq), 125.50 (s, 2C, CH), 128.63 (s, 2C, CH), 129.85 (s, 2C, CH), 133.05 (s, 2C, CH), 134.63 (s, 2C, Cq), 135.87 (s, 2C, Cq), 137.16 (s, 2C, Cq) ppm. Anal. calc. for $\text{C}_{27}\text{H}_{20}\text{S}_4$ (%): C 68.60, H 4.26; found: C 67.59, H 4.36 (see footnote at end of this section).

1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)-perfluorocyclopentene (1Fo). 1,2-Bis(5'-iodo-2'-methylthien-3'-yl)perfluorocyclopentene (0.300 g, 0.484 mmol), CuI (0.075 g,

0.394 mmol), TBAI (1.42 g, 3.84 mmol) and $[(\text{CH}_3)_3\text{C}_6\text{H}_2]_3\text{P}$ (0.15 g, 0.386 mmol), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (0.044 g, 0.043 mmol), and 3-ethynylthiophene (0.104 mL, 1.06 mmol) were all dissolved in DMF (50 mL), THF (6 mL) and triethylamine (6 mL). The reaction was carried out using the same synthetic method as described for **1Ho**. Purification of the crude product was carried out on a silica gel column, using 100% hexane as the eluent, followed by a 9:1 mixture of hexane: CH_2Cl_2 . The 4th band on the column was collected, and the pure product was obtained as a blue solid (0.1583 g, 56%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$): δ = 1.97 (s, 6H, CH_3), 7.28 (dd, $J=5$ Hz, 1.2 Hz, 2H, ethynylthiophene-H4), 7.39 (s, 2H, thienyl-H4), 7.67 (dd, $J=5$ Hz, 3 Hz, 2H, ethynylthiophene-H5), 7.97 (dd, $J=3$ Hz, 1.2 Hz, 2H, ethynylthiophene-H2) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ = 14.66 (s, 2C, CH_3), 81.11 (s, 2C, Cq), 89.33 (s, 2C, Cq), 121.60 (s, 2C, Cq), 121.95 (s, 2C, Cq), 124.93 (s, 2C, Cq), 125.80 (s, 2C, CH), 129.40 (s, 2C, CH), 129.75 (s, 2C, CH), 131.39 (s, 2C, CH), 143.25 (s, 2C, Cq) ppm (C-F resonances not located). ^{19}F NMR (376.5 MHz, CDCl_3) δ = -110.24 (t, $J=5.2$ Hz, 4F), -131.81 (quintet, $J=5.2$ Hz, 2F). Anal. calc. for $\text{C}_{27}\text{H}_{14}\text{F}_6\text{S}_4$ (%): C 55.85, H 2.43; found: C 55.51, H 2.25.

1,2-Bis(5'-(4''-bromophenyl)-2'-methylthien-3'-yl)-cyclopentene. An oven-dried flask was charged with a solution of 1,2-Bis(5'-chloro-2'-methylthien-3'-yl)cyclopentene (0.754 g, 2.29 mmol), in distilled, dry THF (80 mL), under an atmosphere of nitrogen. *n*-Butyllithium (3.6 mL of 1.6 M solution in hexane, 5.73 mmol) was added to the reaction flask, and after 1 hour of stirring, $\text{B}(\text{O}i\text{Bu})_3$ (1.85 mL, 6.87 mmol) was added and the mixture was allowed to stir for a further 1 hour, in order to produce a boronic ester intermediate. In a separate 500 mL round-bottomed flask, a solution of 1,4-dibromobenzene (2.59 g, 9.16 mmol), dissolved in THF (200 mL), was purged with nitrogen. $\text{Pd}(\text{PPh}_3)_4$ (0.281 g, 0.252 mmol), 2M Na_2CO_3 (15 mL) and ethylene glycol (15 drops) were added to the flask, and purging was continued for 10 minutes. Then, the boronic ester intermediate was added dropwise, via a syringe, and the reaction was refluxed overnight, under an inert atmosphere. The mixture was extracted with water and diethyl ether, the organic layers were dried over MgSO_4 , filtered and the solvent was removed. The crude product was purified on silica gel, and eluted with hexane, yielding a pale pink/purple solid (0.58 g, 44%). ^1H NMR (400 MHz, CDCl_3): δ = 1.99 (s, 6H, CH_3), 2.08 (quintet, $J=7.5$ Hz,

2H, CH₂), 2.83 (t, J=7.5 Hz, 4H, CH₂), 7.00 (s, 2H, thienyl-H4), 7.34 (d, J=8.5 Hz, 4H, phenyl-H2,6), 7.44 (d, J=8.5 Hz, 4H, phenyl-H3,5) ppm. ¹³C NMR (150 MHz, CDCl₃) δ = 14.60 (s, 2C, CH₃), 23.17 (s, 1C, CH₂), 38.57 (s, 2C, CH₂), 120.84 (s, 2C, Cq), 124.55 (s, 2C, CH), 126.91 (s, 4C, CH), 132.00 (s, 4C, CH), 133.57 (s, 2C, Cq), 134.86 (s, 2C, Cq), 135.17 (s, 2C, Cq), 136.95 (s, 2C, Cq), 138.55 (s, 2C, Cq) ppm.

1,2-Bis(5'-(4''-iodophenyl)-2'-methylthien-3'-yl)-cyclopentene. Distilled, dry THF (20 mL) was placed in a 50 mL oven-dried round-bottomed flask, and 1,2-bis(5'-(4''-bromophenyl)-2'-methylthien-3'-yl)-cyclopentene (0.4 g, 0.701 mmol) was added, under an atmosphere of nitrogen. The reaction flask was submerged in a bath of liquid nitrogen and acetone, and cooled to -78°C. tert-Butyllithium (1.03 mL of 1.7 M in hexane, 1.75 mmol) was added dropwise, via a syringe, and the solution was allowed to stir for 1 hour, under an inert atmosphere. In a separate 25 mL oven-dried flask, iodine (0.89 g, 3.51 mmol) was added to distilled, dry THF (10 mL), under N₂. The iodine solution was added dropwise, via a syringe, into the reaction flask, and the mixture was stirred for a further 1 hour at -78°C. Then the flask was allowed to warm-up to room temperature, and it was left stirring overnight under inert conditions. Water (20 mL) was added to the flask to quench the reaction, and it was extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed with a 50% aqueous solution of sodium thiosulphate pentahydrate, in order to remove the excess iodine, washed with water, dried over MgSO₄ and filtered. The solvent was removed under reduced pressure, and the crude product was recrystallised in 4:1 methanol:CH₂Cl₂ and vacuum filtered, yielding a light purple-brown pure product (0.3921 g, 84%). ¹H NMR (400 MHz, CDCl₃) δ=1.98 (s, 6H, CH₃), 2.08 (quintet, J=7.5 Hz, 2H, CH₂), 2.83 (t, J=7.5 Hz, 4H, CH₂), 7.01 (s, 2H, thienyl-H4), 7.22 (d, J=8.5 Hz, 4H, phenyl-H2,6), 7.64 (d, J=8.5 Hz, 4H, phenyl-H3,5).

Synthesis of 1,2-Bis(5'-(4''-phenyl-3''-ethynylthiophene)-2'-methylthien-3'-yl)cyclopentene (2Ho). The same procedure described for **1Ho** was followed, starting from 1,2-Bis(5'-(4''-iodophenyl)-2'-methylthien-3'-yl)-cyclopentene (0.392 g, 0.59 mmol), CuI (0.09 g, 0.473 mmol), TBAI (1.704 g, 4.61 mmol), [(CH₃)₃C₆H₂]₃P (0.18 g, 0.463 mmol), Pd₂(dba)₃.CHCl₃

(0.053 g, 0.051 mmol and 3-ethynylthiophene (0.145 mL, 1.475 mmol). Anhydrous DMF (60 mL), anhydrous triethylamine (7 mL) and distilled dry THF (7 mL) were used as the solvent mixture. The resulting crude product was purified by column chromatography, using silica gel and 100% hexane, followed by 8:2 hexane:CH₂Cl₂, yielding a purple solid (0.191 g, 52%). ¹H NMR (400 MHz, (CD₃)₂SO): δ = 1.91 (s, 6H, CH₃), 2.05 (quintet, J=7.5 Hz, 2H, CH₂), 2.85 (t, J=7.5 Hz, 4H, CH₂), 7.27 (dd, J=5 Hz, 1.2 Hz, 2H, ethynylthiophene-H4), 7.41 (s, 2H, thienyl-H4), 7.51 (d, J=8.4 Hz, 4H, phenyl-H2,6), 7.60 (d, J=8.4 Hz, 4H, phenyl-H3,5), 7.66 (dd, J=5 Hz, 3 Hz, 2H, ethynylthiophene-H5), 7.90 (dd, J=3 Hz, 1.2 Hz, 2H, ethynylthiophene-H2) ppm. ¹³C NMR (150 MHz, CDCl₃) δ = 14.67 (s, 2C, CH₃), 23.16 (s, 1C, CH₂), 38.64 (s, 2C, CH₂), 85.38 (s, 2C, Cq), 89.03 (s, 2C, Cq), 121.66 (s, 2C, Cq), 122.46 (s, 2C, Cq), 124.64 (s, 2C, CH), 125.15 (s, 4C, CH), 125.52 (s, 2C, CH), 128.70 (s, 2C, CH), 130.00 (s, 2C, CH), 132.07 (s, 4C, CH), 134.33 (s, 2C, Cq), 134.82 (s, 2C, Cq), 135.42 (s, 2C, Cq), 137.01 (s, 2C, Cq), 139.13 (s, 2C, Cq) ppm. Anal. calc. for C₃₉H₂₈S₄ (%): C 74.96, H 4.52; found: C 74.73, H 4.61.

Synthesis of 1-(3-thienylethynyl)-4-bromobenzene. 1-Iodo-4-bromobenzene (0.200 g, 0.707 mmol), CuI (0.113 g, 0.593 mmol), TBAI (2.13 g, 5.766 mmol), [(CH₃)₃C₆H₂]₃P (0.225 g, 0.579 mmol), Pd₂(dba)₃.CHCl₃ (0.066 g, 0.064 mmol) and 3-ethynylthiophene (0.077 mL, 0.778 mmol) were all dissolved in anhydrous DMF (75 mL), anhydrous triethylamine (9 mL) and dry THF (9 mL), and the reaction was carried out under the same conditions as described for **1Ho**. Purification of the crude product was carried out on a silica gel column, using 100% hexane as the eluent, followed by a 8:2 mixture of hexane:CH₂Cl₂. A white solid was obtained (0.113 g, 61%). ¹H NMR (400 MHz, (CD₃)₂CO) δ = 7.24 (dd, J=5 Hz, 1.2 Hz, 1H, ethynylthiophene-H4), 7.47 (d, J=8.6 Hz, 2H, phenyl-H2,6), 7.57 (dd, J=5 Hz, 3 Hz, 1H, ethynylthiophene-H5), 7.60 (d, J=8.6 Hz, 2H, phenyl-H3,5), 7.77 (dd, J=3 Hz, 1.2 Hz, 1H, ethynylthiophene-H2) ppm. ¹³C NMR (150 MHz, CDCl₃) δ = 85.75 (s, 1C, Cq), 87.90 (s, 1C, Cq), 121.79, (s, 1C, Cq), 122.10 (s, 1C, Cq), 122.34 (s, 1C, Cq), 125.67 (s, 1C, CH), 129.01 (s, 1C, CH), 129.97 (s, 1C, CH), 131.73 (s, 2C, CH), 133.06 (s, 2C, CH). Anal. calc. for C₁₂H₇SBr (%): C 54.77, H 2.68; found: C 54.81, H 2.69.

Synthesis of 1,2-Bis(5'-(4''-phenyl-3'''-ethynylthiophene)-2'-methylthien-3'-yl)perfluorocyclopentene (2Fo). Using the Suzuki reaction conditions, as described already for 1,2-bis(5'-(4''-bromophenyl)-2'-methylthien-3'-yl)-cyclopentene, the following reagents were reacted together in flask 1: 1,2-Bis(5'-chloro-2'-methylthien-3'-yl)perfluorocyclopentene (0.1208 g, 0.276 mmol), t-Butyllithium (0.41 mL of 1.7M solution in hexane, 0.69 mmol), B(OBu)₃ 0.223 mL, 0.828 mmol) in distilled, dry diethyl ether (20 mL), to form the boronic ester intermediate. In a separate flask, 1-(3-thienylethynyl)-4-bromobenzene (0.16 g, 0.608 mmol), Pd(PPh₃)₄ (0.0339 g, 0.03 mmol), 2M Na₂CO₃ (4 mL) and ethylene glycol (4 drops) and distilled, dry diethyl ether (40 mL) were added together, followed by the addition of the boronic ester intermediate from flask 1, using the same procedure as described for 1,2-Bis(5'-(4''-bromophenyl)-2'-methylthien-3'-yl)-cyclopentene. The crude product was purified on a silica gel column, using 100% hexane, followed by a solvent mixture of 9:1 hexane:CH₂Cl₂. The 2nd blue band was collected from the column, and the pure product was obtained as a blue solid (0.07 g, 35%). ¹H NMR (400 MHz, (CD₃)₂SO): δ = 2.00 (s, 6H, CH₃), 7.29 (dd, J=5 Hz, 1.0 Hz, 2H, ethynylthiophene-H4), 7.57 (d, J=8.4 Hz, 4H, phenyl-H2,6), 7.62 (s, 2H, thienyl-H4), 7.67 (dd, J=5 Hz, 2.8 Hz, 2H, ethynylthiophene-H5), 7.70 (d, J=8.4 Hz, 4H, phenyl-H3,5), 7.93 (dd, J=2.8 Hz, 1.0 Hz, 2H, ethynylthiophene-H2) ppm. ¹³C NMR (150 MHz, CDCl₃) δ = 14.21 (s, 2C, CH₃), 85.97 (s, 2C, Cq), 88.71 (s, 2C, Cq), 122.28 (s, 2C, Cq), 122.82 (s, 2C, CH), 122.96 (s, 2C, Cq), 125.50 (s, 4C, CH), 125.62 (s, 2C, CH), 126.16 (s, 2C, Cq), 128.96 (s, 2C, CH), 129.98 (s, 2C, CH), 132.25 (s, 4C, CH), 133.06 (s, 2C, Cq), 141.73 (s, 2C, Cq), 141.99 (s, 2C, Cq) ppm (C-F resonances not located). ¹⁹F NMR (376.5 MHz, CDCl₃) δ = -110.01 (t, J=5.0 Hz, 4F), -131.83 (quintet, J=5.0 Hz, 2F). Anal. calc. for C₃₉H₂₂F₆S₄ (%): C 63.92, H 3.03; found: C 60.22, H 2.97(see footnote at end of this section).

Synthesis of 1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)-cyclopentene [Co₂(CO)₆]₂ (3Ho). A 100 ml oven-dried round-bottomed flask was filled with a solution of 1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)-cyclopentene (**1Ho**) (0.08 g, 0.169 mmol), dissolved in hexane (20 mL) and dry THF (15 mL), and the solution was purged with nitrogen for 20 minutes. Co₂(CO)₈ (0.127 g, 0.372 mmol) was weighed out under nitrogen, and

added to the flask. The reaction mixture was allowed to stir overnight at room temperature, under an inert atmosphere. The solvent was removed under reduced pressure, and the crude product was purified on silica gel, and eluted with 100% hexane, followed by 9:1 hexane:diethyl ether. A pure brown/black product was obtained (0.1432 g, 81%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 2.03 (s, 6H, CH_3), 2.07 (quintet, $J=7.5$ Hz, 2H, CH_2), 2.84 (t, $J=7.5$ Hz, 4H, CH_2), 7.25 (s, 2H, thienyl-H4), 7.36 (dd, $J=5$ Hz, 1.2 Hz, 2H, ethynylthiophene-H4), 7.62 (dd, $J=5$ Hz, 3 Hz, 2H, ethynylthiophene-H5), 7.82 (dd, $J=3$ Hz, 1.2 Hz, 2H, ethynylthiophene-H2) ppm. Anal. calc. for $\text{C}_{39}\text{H}_{20}\text{Co}_4\text{O}_{12}\text{S}_4$ (%): C 44.88, H 1.93; found: C 43.85, H 2.08 (see footnote at end of this section). IR (THF, cm^{-1}) ν_{CO} = 2089, 2055, 2025.

Synthesis of 1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)-perfluorocyclopentene $[\text{Co}_2(\text{CO})_6]_2$ (3Fo). 1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)perfluorocyclopentene (**1Fo**) (0.16 g, 0.276 mmol) and $\text{Co}_2(\text{CO})_8$ (0.207 g, 0.606 mmol) were reacted together in hexane (30 mL) and THF (20 mL), under the same conditions as described for **3Ho**. Purification of the crude product was achieved by column chromatography on silica gel, using 100% hexane as the eluent, yielding a dark brown/black solid (0.1564 g, 49%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ = 2.08 (s, 6H, CH_3), 7.36 (dd, $J=5.1$ Hz, 1.4 Hz, 2H, ethynylthiophene-H4), 7.51 (s, 2H, thienyl-H4), 7.65 (dd, $J=5.1$ Hz, 2.9 Hz, 2H, ethynylthiophene-H5), 7.84 (dd, $J=2.9$ Hz, 1.4 Hz, 2H, ethynylthiophene-H2) ppm. ^{19}F NMR (376.5 MHz, CDCl_3) δ = -110.06 (t, $J=5.0$ Hz, 4F), -131.79 (quintet, $J=5.0$ Hz, 2F). Anal. calc. for $\text{C}_{39}\text{H}_{14}\text{Co}_4\text{F}_6\text{O}_{12}\text{S}_4$ (%): C 40.68, H 1.23; found: C 39.76, H 1.33 (see footnote at end of this section). IR (THF, cm^{-1}) ν_{CO} = 2092, 2058, 2029.

Synthesis of the closed isomer of 1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)-perfluorocyclopentene $[\text{Co}_2(\text{CO})_6]_2$ (3Fc). 1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)perfluorocyclopentene (**1Fo**) (0.01 g, 0.017 mmol) was irradiated with UV light at 313 nm in deuterated acetone, and was monitored in the ^1H NMR until the open isomer converted to the closed isomer (**1Fc**). The solvent was removed, and the closed isomer **1Fc** was dissolved in a degassed solution of hexane (12 mL) and THF (3 mL) in the dark. $\text{Co}_2(\text{CO})_8$ (0.15 g, 0.043 mmol) was added to the reaction flask, and the mixture was stirred overnight, under an inert

atmosphere, in the dark. The crude product was purified on a silica gel column (covered with tin-foil), and eluted with 100% hexane, followed by 9:1 hexane:CH₂Cl₂. A dark blue product was obtained (0.009 g, 45%). ¹H NMR (400 MHz, (CD₃)₂CO): δ = 2.30 (s, 6H, CH₃), 6.67 (s, 2H, thienyl-H4), 7.36 (dd, J=5 Hz, 1.4 Hz, 2H, ethynylthiophene-H4), 7.65 (dd, J=5 Hz, 2.9 Hz, 2H, ethynylthiophene-H5), 7.87 (dd, J=2.9 Hz, 1.4 Hz, 2H, ethynylthiophene-H2) ppm. IR (THF, cm⁻¹) ν_{CO} = 2094, 2063, 2035.

* It should be noted that the amount of **3Fc**, prepared was only sufficient for characterization by ¹H NMR and IR spectroscopy. In the following sections, a logic is provided to confirm that the complex **3Fc**, bears ligands in the closed form, and the ¹H NMR spectrum obtained for this compound is provided.

Synthesis of 1,2-Bis(5'-(4''-phenyl-3''')-ethynylthiophene)-2'-methylthien-3'-yl)cyclopentene [Co₂(CO)₆]₂ (4Ho). Using the same procedure as described for **3Ho**, 1,2-Bis(5'-(4''-phenyl-3''')-ethynylthiophene)-2'-methylthien-3'-yl)-cyclopentene (**2Ho**) (0.100 g, 0.16 mmol) and Co₂(CO)₈ (0.121 g, 0.352 mmol) were reacted together. The crude product was purified on silica gel, with 100% hexane, followed by 9:1 hexane:diethyl ether, yielding a black solid as the pure product (0.174 g, 91%). ¹H NMR (400 MHz, (CD₃)₂CO): δ = 2.05 (s, 6H, CH₃), 2.09 (quintet, J=7.4 Hz, 2H, CH₂), 2.90 (t, J=7.4 Hz, 4H, CH₂), 7.35 (m, 4H, thienyl-H4 & ethynylthiophene-H4), 7.63-7.69 (m, 10H, ethynylthiophene-H5 & phenyl-H2,3,5,6), 7.80 (dd, 2H, J=3 Hz, 1.2 Hz, ethynylthiophene-H2) ppm. Anal. calc. for C₅₁H₂₈ Co₄O₁₂ S₄ (%): C 51.23, H 2.36; found: C 51.89, H 3.15 (see footnote at end of this section). IR (THF, cm⁻¹) ν_{CO} = 2089, 2054, 2025.

Synthesis of the closed isomer of 1,2-Bis(5'-(4''-phenyl-3''')-ethynyl-thiophene)-2'-methylthien-3'-yl)cyclopentene [Co₂(CO)₆]₂ (4Hc_s). The open isomer of 1,2-Bis(5'-(4''-

phenyl-3'''-ethynylthiophene)-2'-methylthien-3'-yl)-cyclopentene (**2Ho**) (0.01 g, 0.016 mmol) was converted to the closed isomer **4Hc** following irradiation with UV light ($\lambda=313$ nm) in deuterated acetone, whilst monitoring in the ^1H NMR. **4Hc** was reacted with $\text{Co}_2(\text{CO})_8$ (0.014 g, 0.04 mmol), in a solvent mixture of hexane (12 mL) and THF (3 mL), following the same reaction procedure as described for **3Fc**. Purification of the crude product was carried out on a silica gel column, and eluted with 100% hexane, followed by 9:1 hexane: CH_2Cl_2 , yielding a dark purple product (0.015 g, 78%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 2.09$ (s, 6H, CH_3), 2.12 (quintet, $J=7.4$ Hz, 2H, CH_2), 2.92 (t, $J=7.4$ Hz, 4H, CH_2), 6.82 (s, 2H, thienyl-H4), 7.35 (dd, $J=5$ Hz, 1.2 Hz, 2H, ethynylthiophene-H4), 7.65-7.72 (m, 10H, ethynylthiophene-H5 & phenyl-H2,3,5,6), 7.82 (dd, $J=3$ Hz, 1.2 Hz, 2H, ethynylthiophene-H2) ppm. IR (THF, cm^{-1}) $\nu_{\text{CO}} = 2089, 2055, 2026$.

* It should be noted that the amount of **4Hc**, prepared was only sufficient for characterization by ^1H NMR and IR spectroscopy. In the following sections, a logic is provided to confirm that the complex **4Hc**, bears ligands in the closed form, and the ^1H NMR spectrum obtained for this compound is provided.

Synthesis of 1,2-Bis(5'-(4''-phenyl-3'''-ethynylthiophene)-2'-methylthien-3'-yl)-perfluorocyclopentene [$\text{Co}_2(\text{CO})_6$]₂ (4Fo). 1,2-Bis(5'-(4''-phenyl-3'''-ethynylthiophene)-2'-methylthien-3'-yl)perfluoro-cyclopentene (**2Fo**) (0.06 g, 0.082 mmol) and $\text{Co}_2(\text{CO})_8$ (0.062 g, 0.180 mmol) were reacted together using the same method as described for **3Ho**. Column chromatography was used to purify the crude product, using silica gel and a solvent mixture of 9:1 hexane: CH_2Cl_2 , yielding a dark brown/black solid (0.0137 g, 13%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 2.04$ (s, 6H, CH_3), 7.35 (dd, $J=5$ Hz, 1.3 Hz, 2H, ethynylthiophene-H4), 7.61 (s, 2H, thienyl-H4), 7.65 (dd, $J=5$ Hz, 3 Hz, 2H, ethynylthiophene-H5), 7.73-7.78 (m, 8H, phenyl-H2,3,5,6), 7.82 (dd, $J=3$ Hz, 1.3 Hz, 2H, ethynylthiophene-H2) ppm. ^{19}F NMR (376.5 MHz, CDCl_3) $\delta = -110.04$ (t, $J=5.0$ Hz, 4F), -131.81 (quintet, $J=5.0$ Hz, 2F). IR (THF, cm^{-1}) $\nu_{\text{CO}} = 2090, 2055, 2026$.

* Synthesis of the free ligand compound **2Fo** proved to be difficult, therefore, due to a low amount of **2Fo** available for further reactions, only a small amount of **4Fo** was synthesised. Hence, the amount of **4Fo**

prepared was only sufficient for characterization by ^1H and ^{19}F NMR and IR spectroscopy. The ^1H NMR spectrum obtained for this compound is shown at the end of this section.

Synthesis of 1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)-cyclopentene [Co₂(CO)₄dppm]₂ (5Ho). Bis(diphenylphosphino)methane {dppm} (0.101 g, 0.263 mmol) was added to heptane (65 mL) in an oven-dried round-bottomed flask and the solution was purged with nitrogen for 20 minutes. The reaction mixture was heated and, once the solution began to reflux, 1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)-cyclopentene [Co₂(CO)₆]₂ (**3Ho**) (0.1247 g, 0.119 mmol) was added to the flask. The solution was left to reflux for 40 minutes under an inert atmosphere. Once the flask had cooled, the solvent was removed under vacuum, and the product was purified by column chromatography. It was passed through a silica gel column, with a mobile phase consisting of 7:3 hexane:CH₂Cl₂, and the pure product was obtained as a pink/brown solid (0.0662 g, 33%). ^1H NMR (600 MHz, (CD₃)₂CO): δ = 1.84 (s, 6H, CH₃), 2.03 (quintet, J=7.5 Hz, 2H, CH₂), 2.67 (t, J=7.5 Hz, 4H, CH₂), 3.64 (t, J=10.6 Hz, 4H, dppm-CH₂), 6.82 (s, 2H, thienyl-H4), 7.15-7.44 (m, 46H, ethynylthiophene-H2,4,5 & phenyl-dppm) ppm. ^{13}C NMR (150 MHz, CDCl₃) δ = 14.38 (s, 2C, CH₃), 22.82 (s, 1C, CH₂), 34.36 (t, 2C, CH₂), 38.94 (s, 2C, CH₂), 83.19 (s, 2C, Cq), 88.12 (s, 2C, Cq), 121.24 (s, 2C, CH), 125.43 (s, 2C, CH), 127.80 (s, 2C, CH), 128.26 (m, 8C, CH), 128.36 (m, 8C, CH), 129.27 (s, 2C, CH), 129.51 (s, 4C, CH), 129.66 (s, 4C, CH), 131.50 (m, 8C, CH), 131.97 (m, 8C, CH), 134.38 (s, 2C, Cq), 134.44 (s, 2C, Cq), 136.19 (s, 2C, Cq), 136.44 (br, 4C, Cq), 136.97 (br, 4C, Cq), 142.17 (s, 2C, Cq), 143.16 (s, 2C, Cq), 204.43 (br, 4C, CO), 207.51 (br, 4C, CO) ppm. ^{31}P NMR (242.9 MHz, CDCl₃): δ = 37.37 (s, 4P) ppm. Anal. calc. for C₈₅H₆₄Co₄O₈P₄S₄ (%): C 60.04, H 3.79; found: C 56.03, H 3.94 (see footnote at end of this section). IR (THF, cm⁻¹) ν_{CO} = 2022, 1998, 1971, 1952 (sh).

Synthesis of 1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)-perfluorocyclopentene [Co₂(CO)₄dppm]₂ (5Fo). Using the same procedure as described for **5H**, 1,2-Bis(5'-(3''-ethynylthiophene)-2'-methylthien-3'-yl)perfluorocyclopentene [Co₂(CO)₆]₂ (**3Fo**) (0.1138 g, 0.099 mmol) and bis(diphenylphosphino)methane (0.0835 g, 0.217 mmol) were reacted together, and the crude product was purified on a silica gel column, with a solvent mixture of 7:3

hexane:CH₂Cl₂. A pink/brown solid was obtained (0.0734 g, 41%). ¹H NMR (400 MHz, (CD₃)₂CO): δ = 1.87 (s, 6H, CH₃), 3.58-3.75 (m, 4H, dppm-CH₂), 7.04 (s, 2H, thienyl-H4), 7.13-7.50 (m, 46H, ethynylthiophene-H2,4,5 & phenyl-dppm) ppm. ¹³C NMR (150 MHz, CDCl₃) δ = 14.28 (s, 2C, CH₃), 34.29 (t, 2C, CH₂), 81.82 (s, 2C, Cq), 88.78 (s, 2C, Cq), 121.54 (s, 2C, CH), 124.89 (s, 2C, Cq), 125.62 (s, 2C, CH), 128.33 (m, 8C, CH), 128.43 (m, 8C, CH), 128.84 (s, 2C, CH), 129.06 (s, 2C, CH), 129.65 (s, 4C, CH), 129.77 (s, 4C, CH), 131.30 (m, 8C, CH), 131.96 (m, 8C, CH), 136.04 (br, 4C, Cq), 136.77 (br, 4C, Cq), 141.10 (s, 2C, Cq), 142.80 (s, 2C, Cq), 145.35 (s, 2C, Cq), 203.46 (br, 4C, CO), 204.81 (br, 4C, CO) ppm. ¹⁹F NMR (376.5 MHz, CDCl₃) δ = -110.07 (t, J=5.3 Hz, 4F), -131.69 (quintet, J=5.3 Hz, 2F). ³¹P NMR (242.9 MHz, CDCl₃): δ = 36.90 (s, 4P) ppm. Anal. calc. for C₈₅H₅₈ Co₄F₆O₈P₄S₄ (%): C 56.46, H 3.23; found: C 56.98, H 3.49. IR (THF, cm⁻¹) ν_{CO} = 2025, 2000, 1974, 1954 (sh).

Synthesis of 1,2-Bis(5'-(4''-phenyl-3'''-ethynylthiophene)-2'-methylthien-3'-yl)-cyclopentene [Co₂(CO)₄dppm]₂ (6Ho). 1,2-Bis(5'-(4''-phenyl-3'''-ethynylthiophene)-2'-methylthien-3'-yl)-cyclopentene [Co₂(CO)₆]₂ (**4Ho**) (0.113 g, 0.094 mmol) and bis(diphenylphosphino)methane (0.08 g, 0.208 mmol) were added to a reaction flask and refluxed in heptane (65 mL) under the same reaction conditions as described for **5Ho**. The crude product was purified by passing it through a silica gel column, using a solvent mixture of 7:3 hexane:CH₂Cl₂ as the eluent, yielding a pink-brown solid (0.096 g, 55%). ¹H NMR (400 MHz, (CD₃)₂CO): δ = 2.03 (s, 6H, CH₃), 2.09 (quintet, J=7.5 Hz, 2H, CH₂), 2.89 (t, J=7.5 Hz, 4H, CH₂), 3.58 (t, J=10.4 Hz, 4H, dppm-CH₂), 7.02 (s, 2H, thienyl-H4), 7.13-7.49 (m, 54H, phenyl-H2,3,5,6 & ethynylthiophene-H2,4,5 & phenyl-dppm) ppm. ¹³C NMR (150 MHz, CDCl₃) δ = 14.72 (s, 2C, CH₃), 23.11 (s, 1C, CH₂), 34.34 (t, 2C, CH₂), 38.78 (s, 2C, CH₂), 87.58 (s, 2C, Cq), 94.06 (s, 2C, Cq), 121.11 (s, 2C, CH), 123.63 (s, 2C, CH), 125.41 (s, 4H, CH), 125.60 (s, 2C, CH), 128.25 (m, 8C, CH), 128.39 (m, 8C, CH), 129.30 (s, 2C, CH), 129.52 (s, 4C, CH), 129.65 (s, 4C, CH), 129.73 (s, 4C, CH), 131.40 (m, 8C, CH), 131.91 (m, 8C, CH), 132.27 (s, 2C, Cq), 134.28 (s, 2C, Cq), 134.69 (s, 2C, Cq), 136.03 (br, 4C, Cq), 136.92 (s, 2C, Cq), 137.10 (br, 4C, Cq), 140.11 (s, 2C, Cq), 142.03 (s, 2C, Cq), 143.28 (s, 2C, Cq), 204.25 (br, 4C, CO), 205.11 (br, 4C, CO) ppm. ³¹P NMR (242.9 MHz, CDCl₃): δ = 36.92 (s, 4P) ppm. Anal. calc. for C₉₇H₇₂

Co₄O₈P₄S₄ (%): C 62.89, H 3.92; found: C 62.15, H 4.08 (see footnote at end of this section). IR (THF, cm⁻¹) ν_{CO} = 2021, 1996, 1970, 1949 (sh).

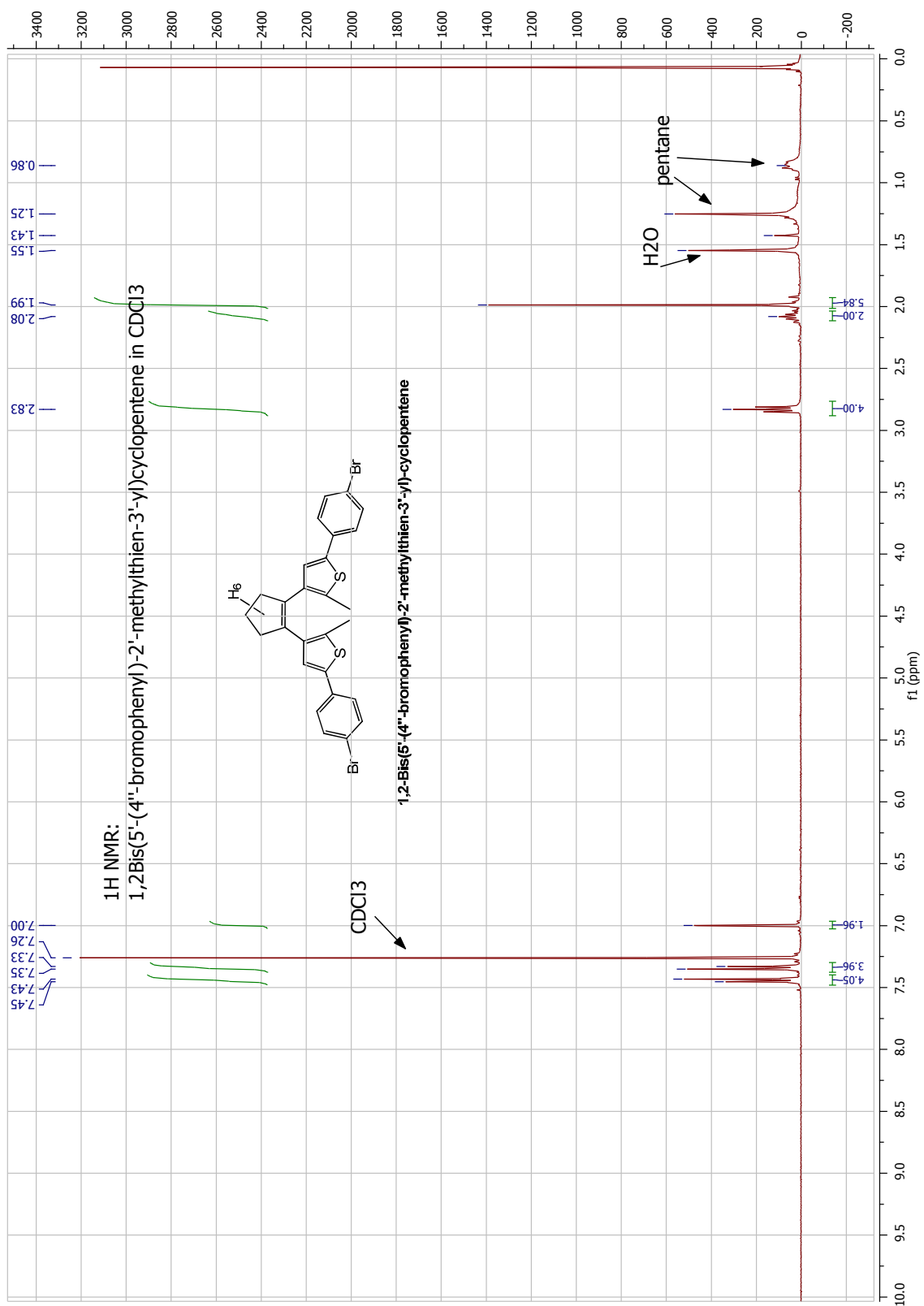
*NOTE: Although the elemental analysis results for **1Ho**, **2Fo**, **3Ho**, **3Fo**, **4Ho**, **5Ho**, **6Ho** are outside the range viewed as establishing analytical purity, they are provided to illustrate the best values obtained to date. We have therefore included the ¹H NMR spectra of these compounds to demonstrate composition.

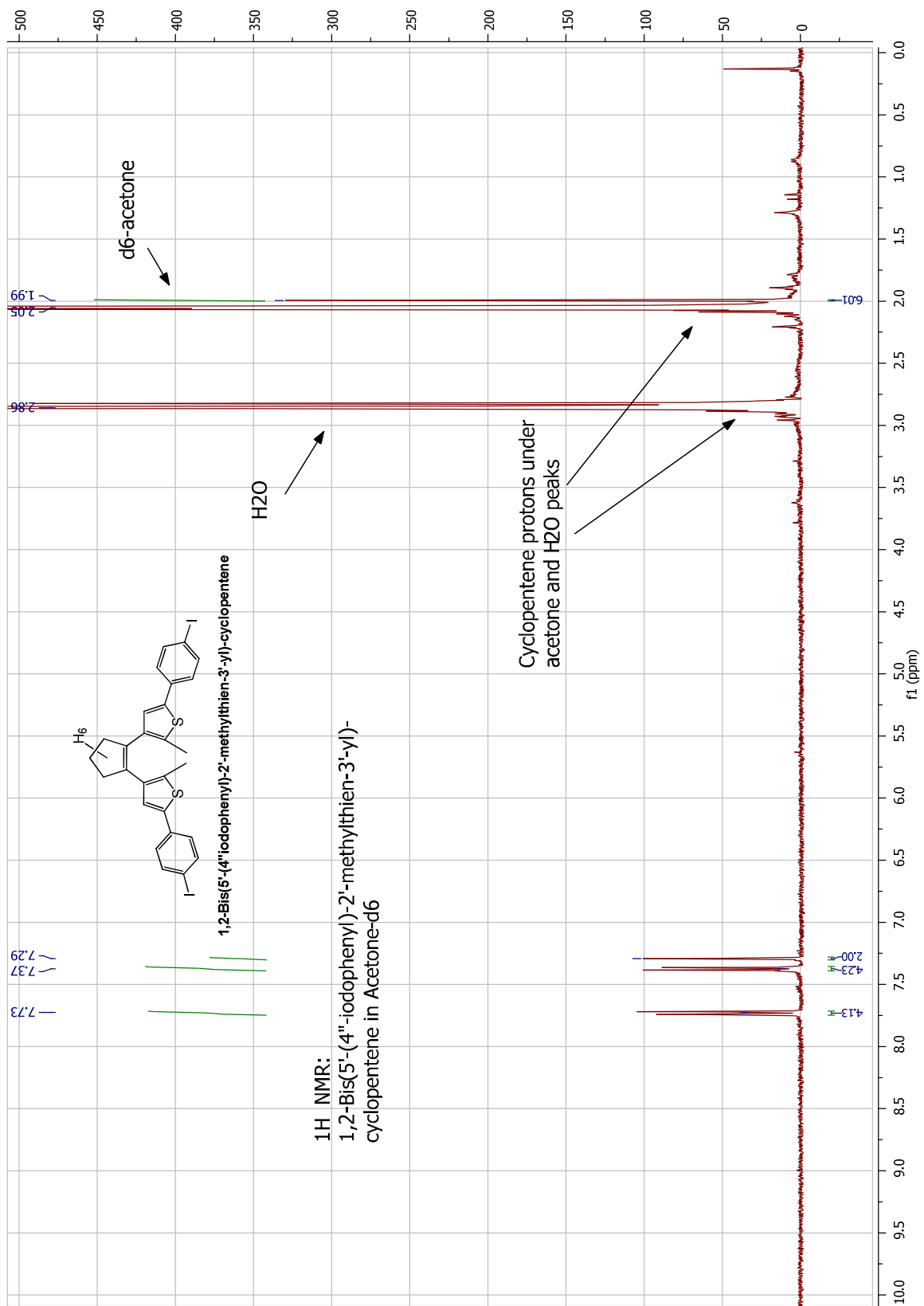
S3. Characterization of 3Fc_s and 4Hc_s

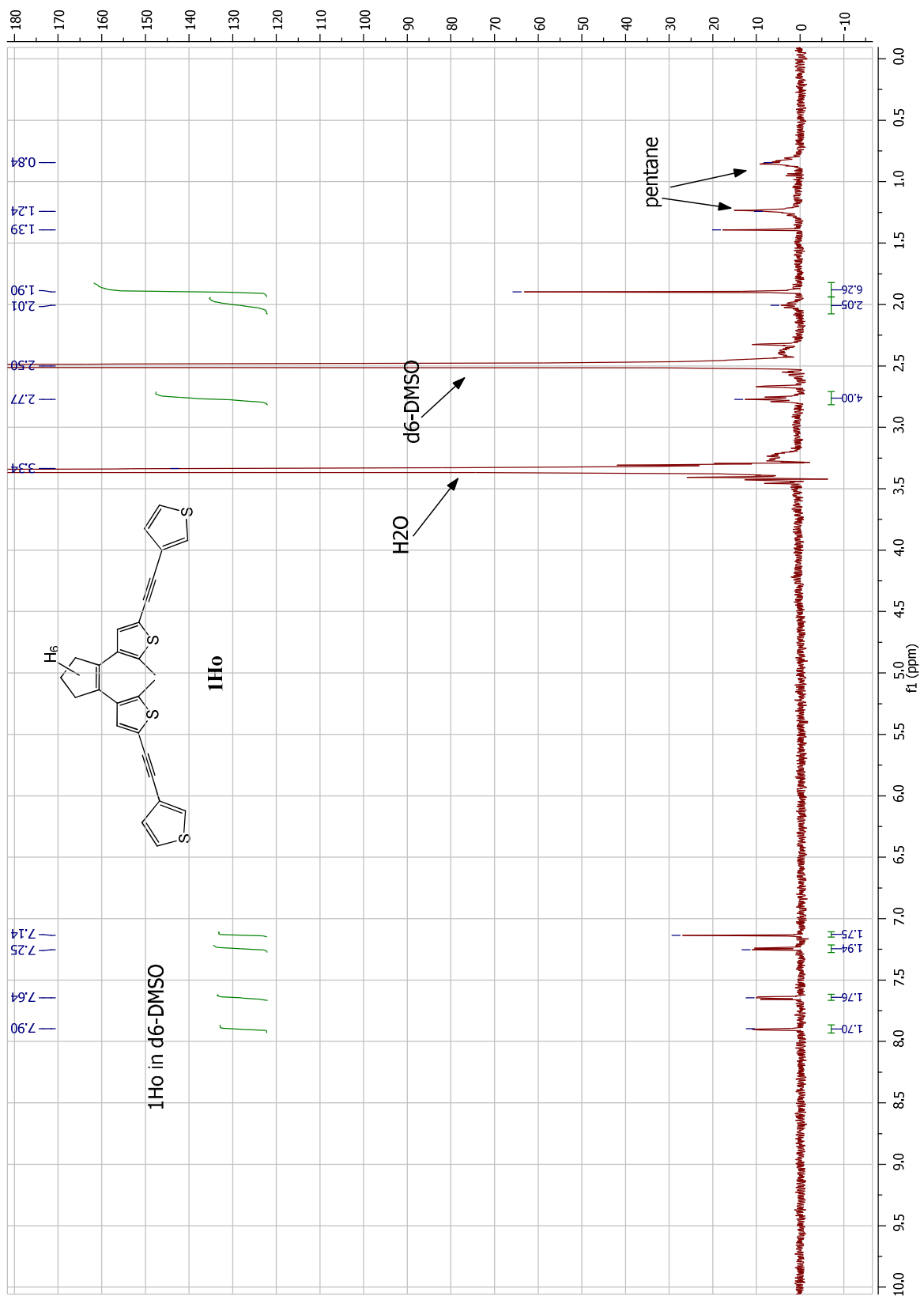
The following spectroscopic techniques were used to verify that the Co₂(CO)₆ complexes of the closed switches, **3Fc_s** and **4Hc_s**, were synthesized:

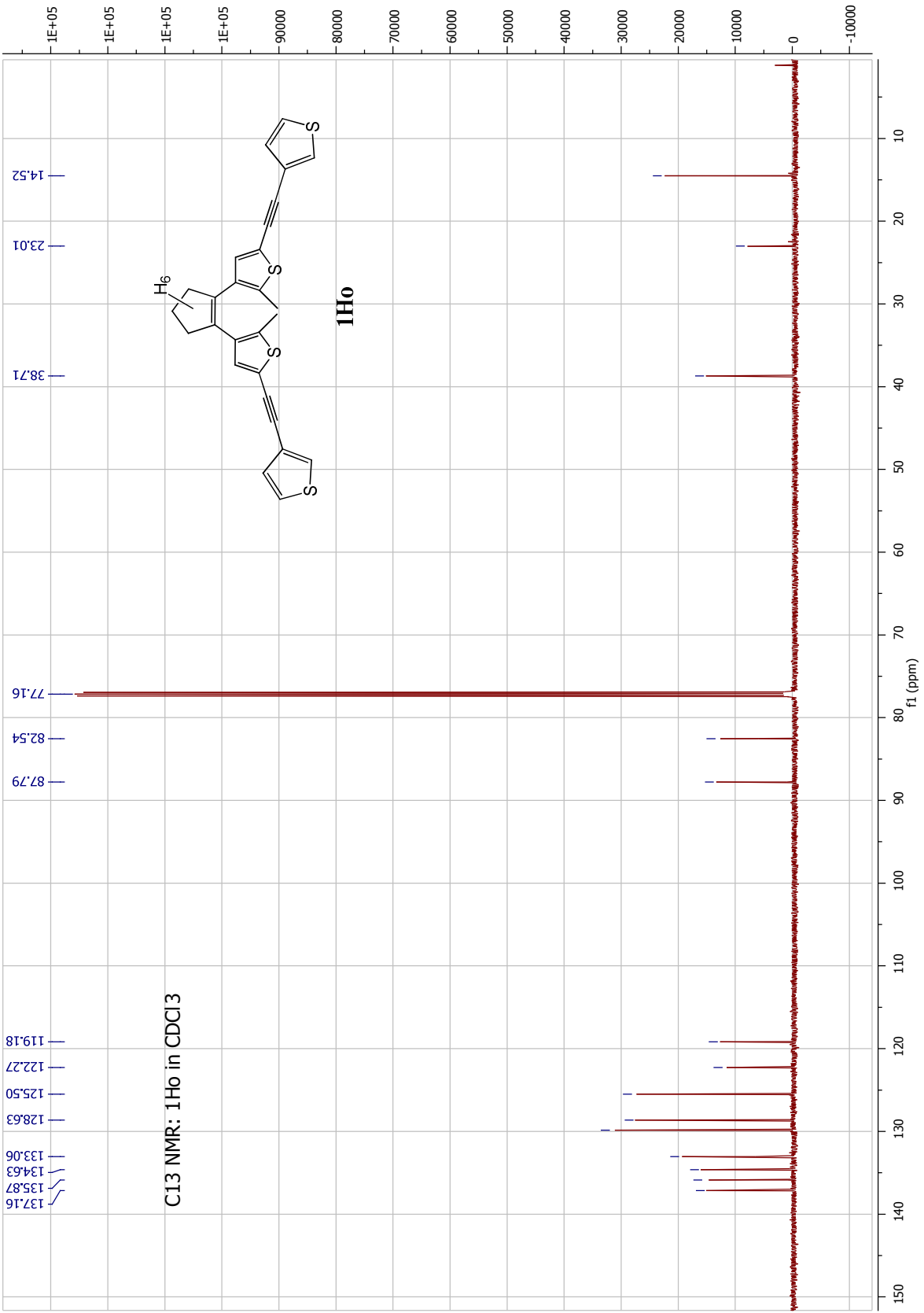
¹ H NMR (ppm)			
3Fo	3Fc_s	4Ho	4Hc_s
2.08, 7.36, 7.51 , 7.65, 7.84	2.30, 6.67 , 7.36, 7.65, 7.87	2.05, 2.09, 2.90, 7.35 , 7.63-7.69, 7.80	2.09, 2.12, 2.92, 6.82 , 7.35, 7.65- 7.72, 7.82
From comparison of the open and closed Co ₂ (CO) ₆ switches, the ¹ H NMR (in acetone-d ⁶) spectroscopic data show that the peak associated with the thienyl-H4 proton is shifted upfield i.e. 7.51 (3Fo) to 6.67 ppm (3Fc_s); and 7.35 (4Ho) to 6.82 ppm (4Hc_s). This corresponds to the expected changes in the ¹ H NMR spectra following ring-closing and hence gives strong evidence of the successful synthesis of 3Fc_s and 4Hc_s .			
IR Spectra (cm ⁻¹)			
3Fo	3Fc_s	4Ho	4Hc_s
2092, 2058, 2029	2094, 2063, 2035	2089, 2054, 2025	2089, 2055, 2026
The IR spectra (in THF) of 3Fc_s and 4Hc_s show three bands in the carbonyl region of the IR, thus indicating that the Co ₂ (CO) ₆ moieties are attached to the closed ring isomers. Furthermore, the carbonyl IR bands for 3Fc_s are shifted to higher wavenumbers in comparison to 3Fo which confirms that 3Fc_s is in fact the closed-ring isomer as the extended conjugation of the system in the closed form reduces electron-density from the system, hence shifting the carbonyl bands to higher energy. This effect is not seen in the case of the closed-ring isomer 4Hc_s , as the IR bands are similar to the values recorded for its related open-ring form 4Ho , due to the presence of the phenyl-rings in 4Hc_s , which act as spacer groups between the cobalt carbonyl moieties and the switching unit. Hence, the influence of the conjugated closed switch on the Co ₂ (CO) ₆ units is reduced, in comparison to 3Fc_s .			

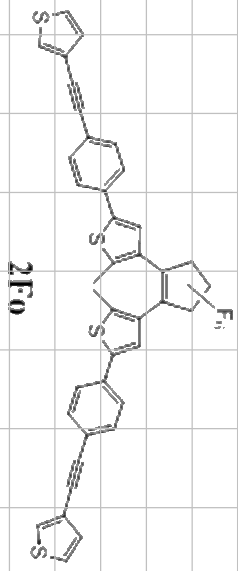
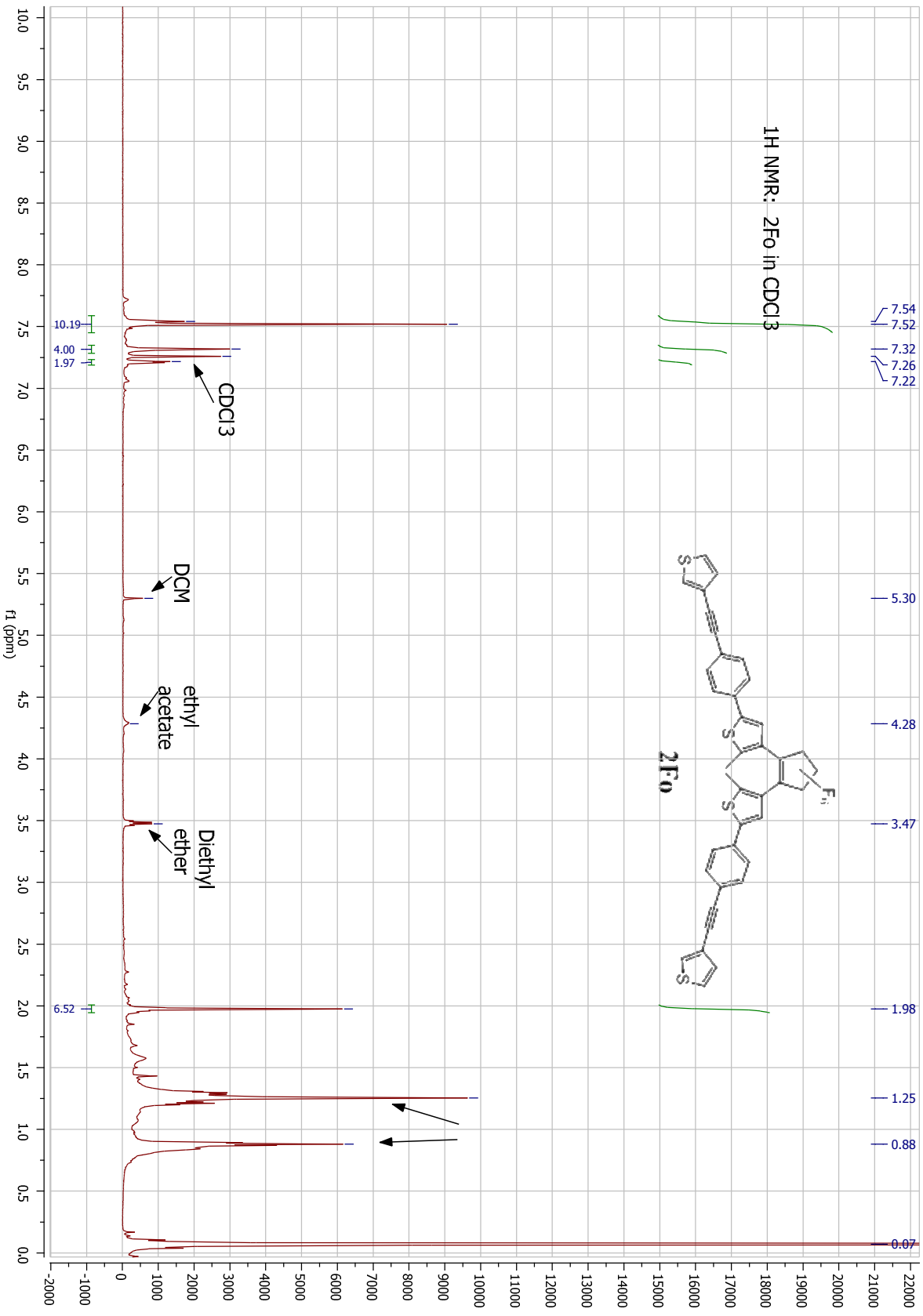
S4. NMR Spectra

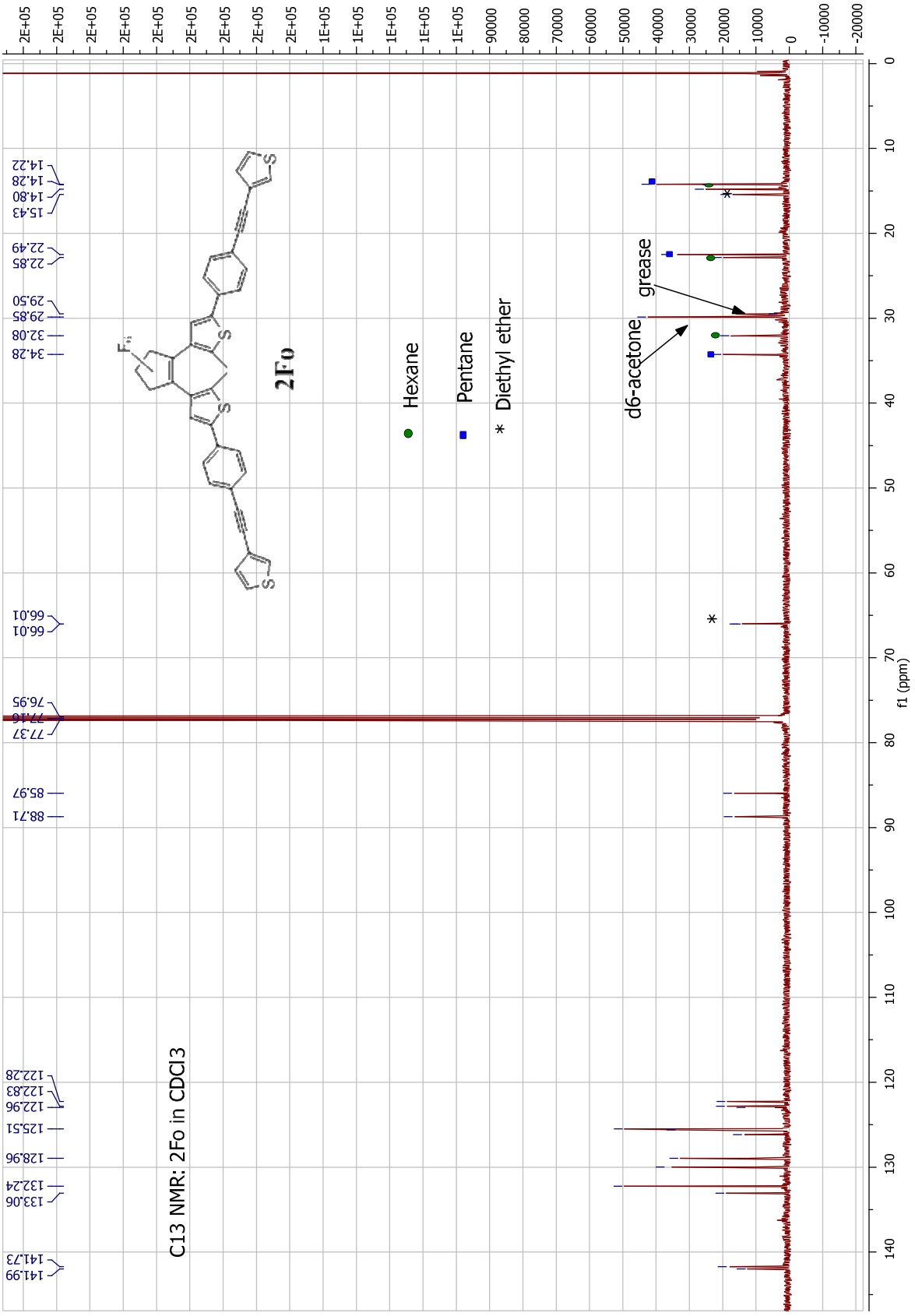


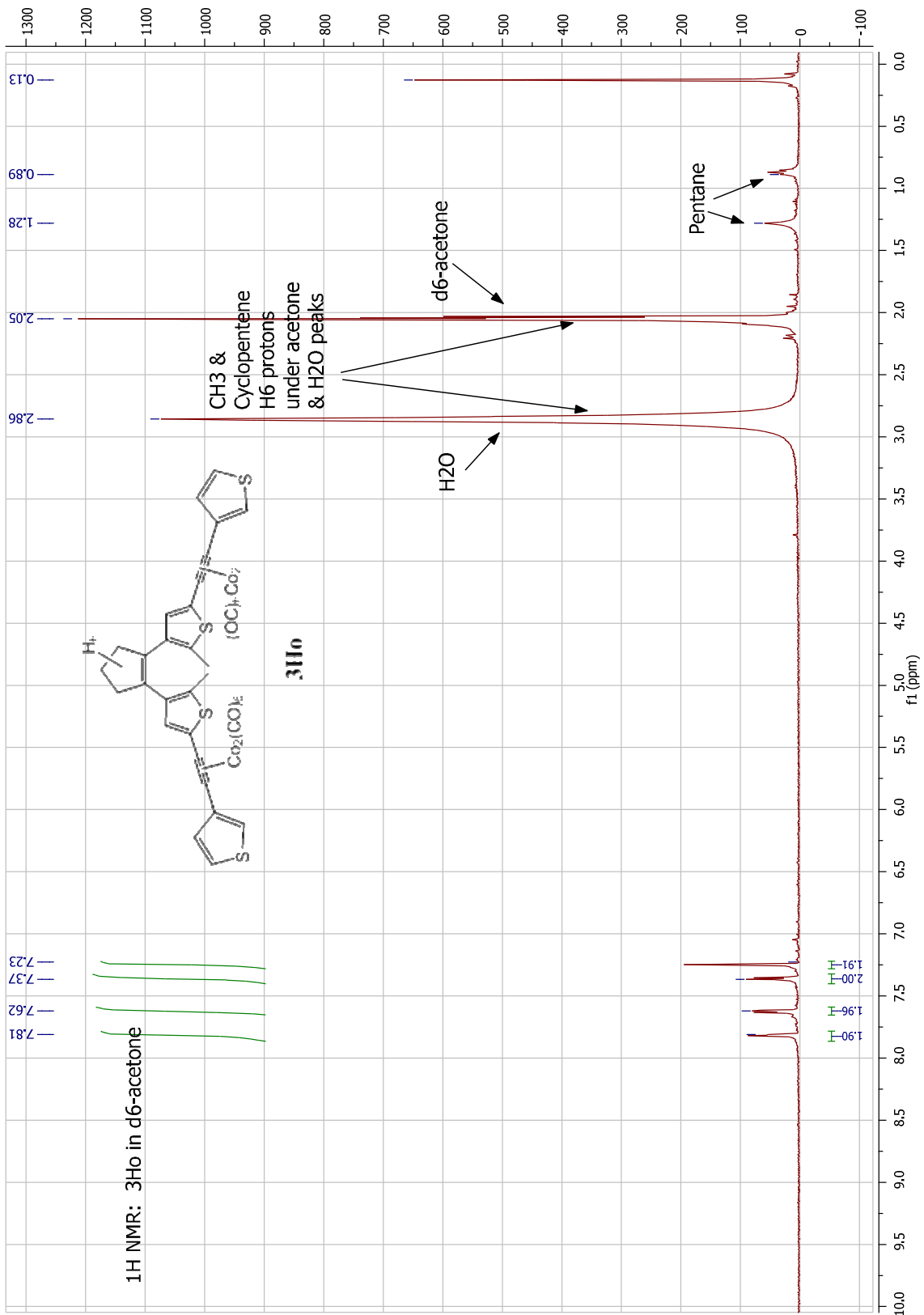


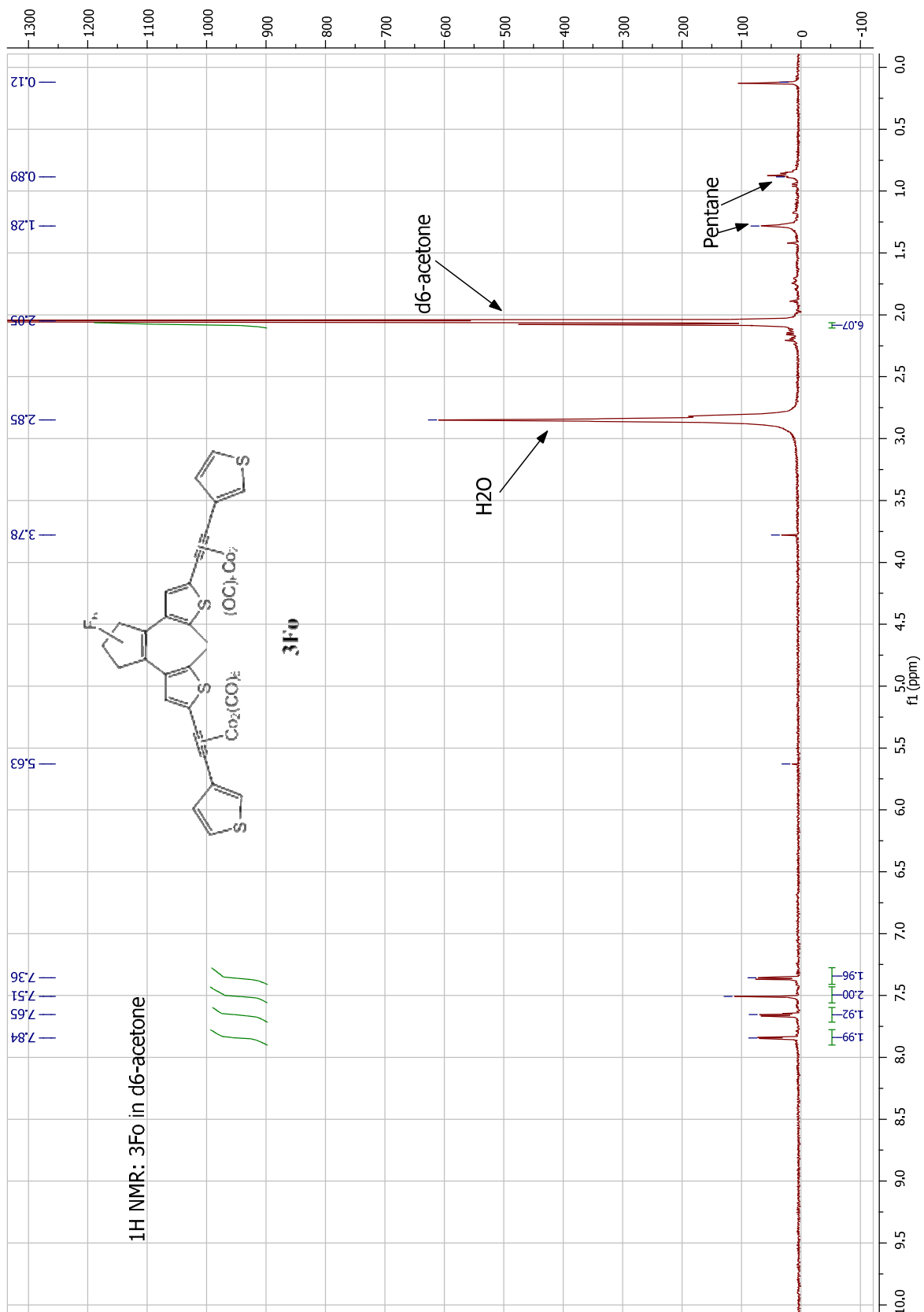


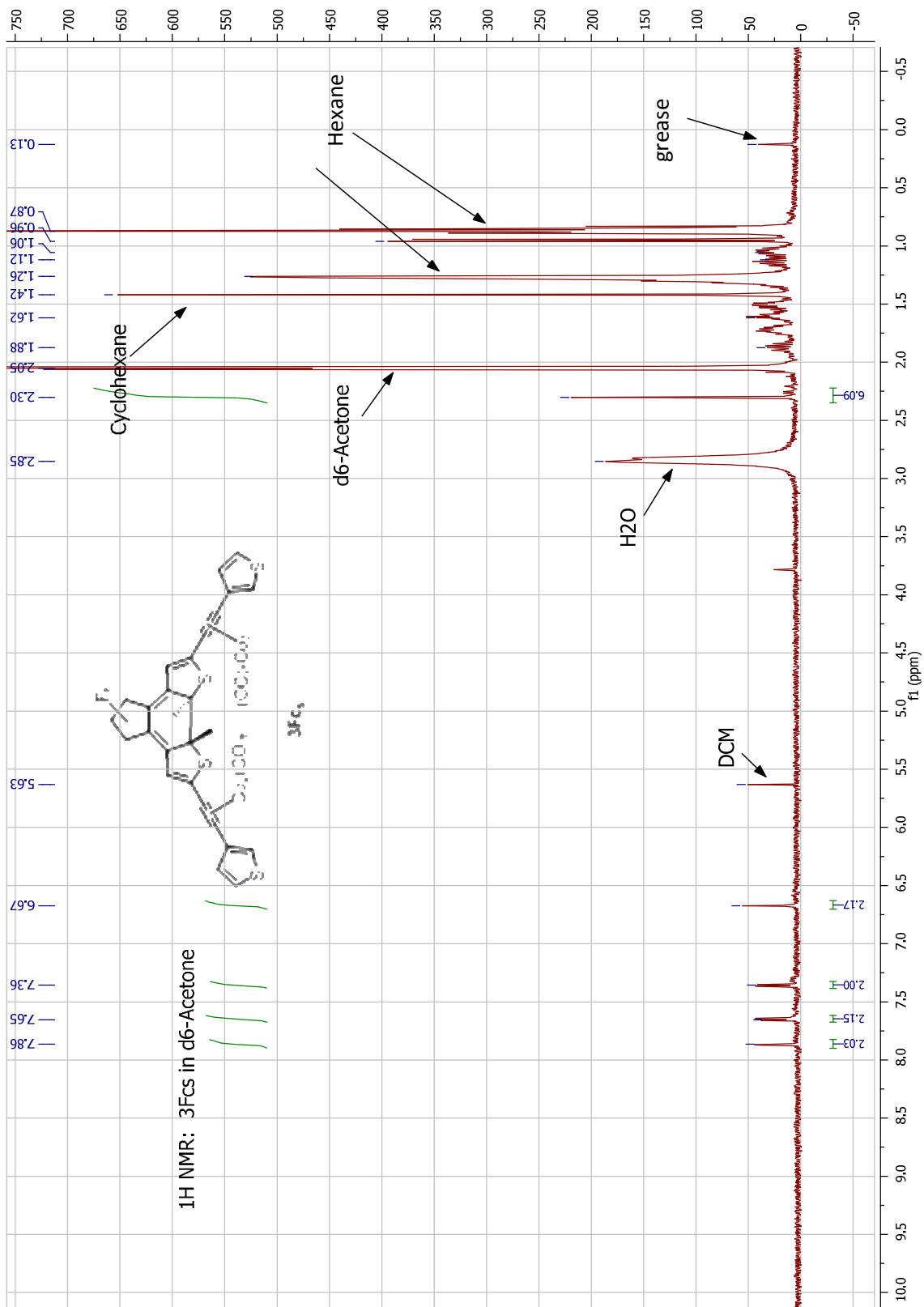


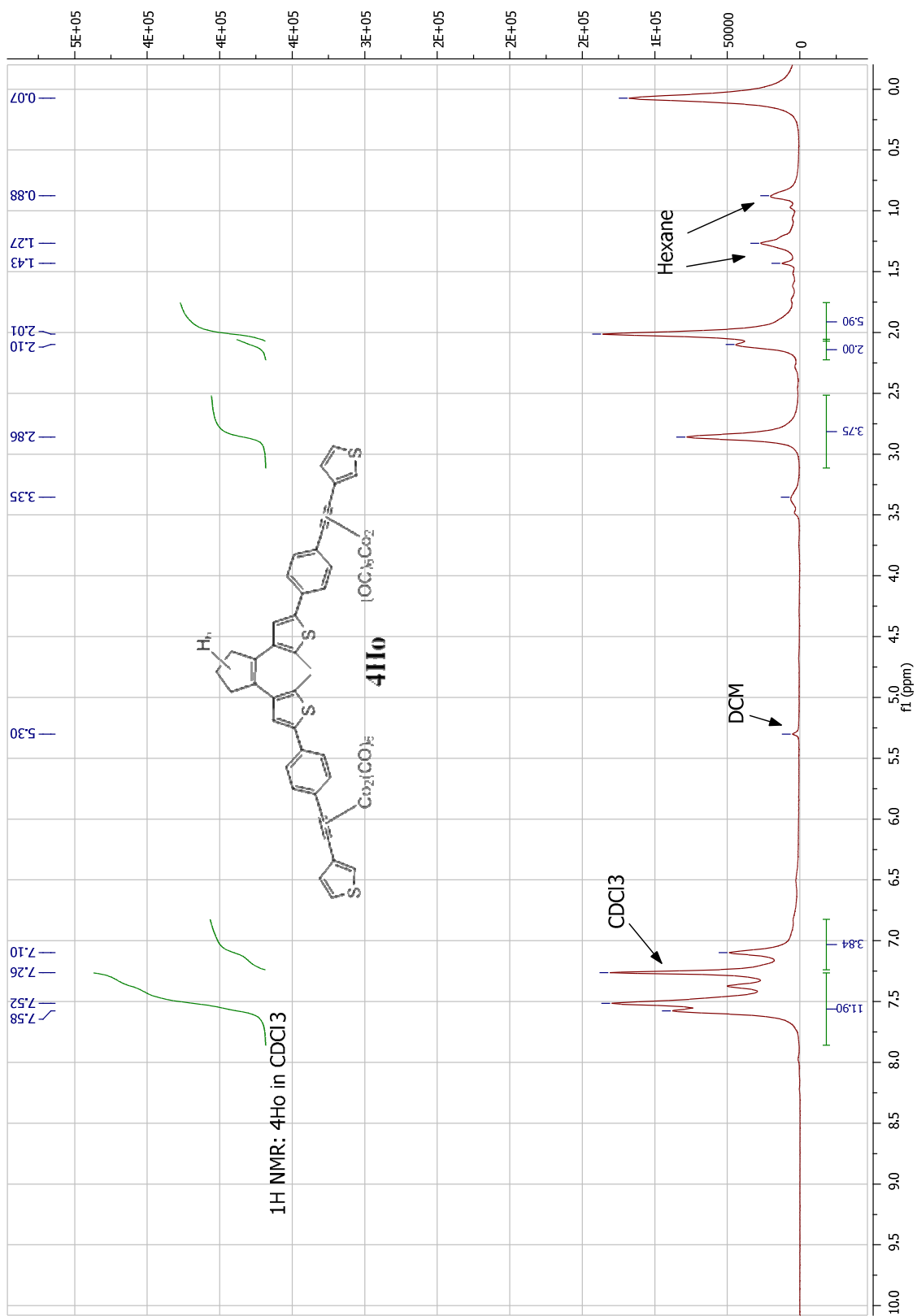


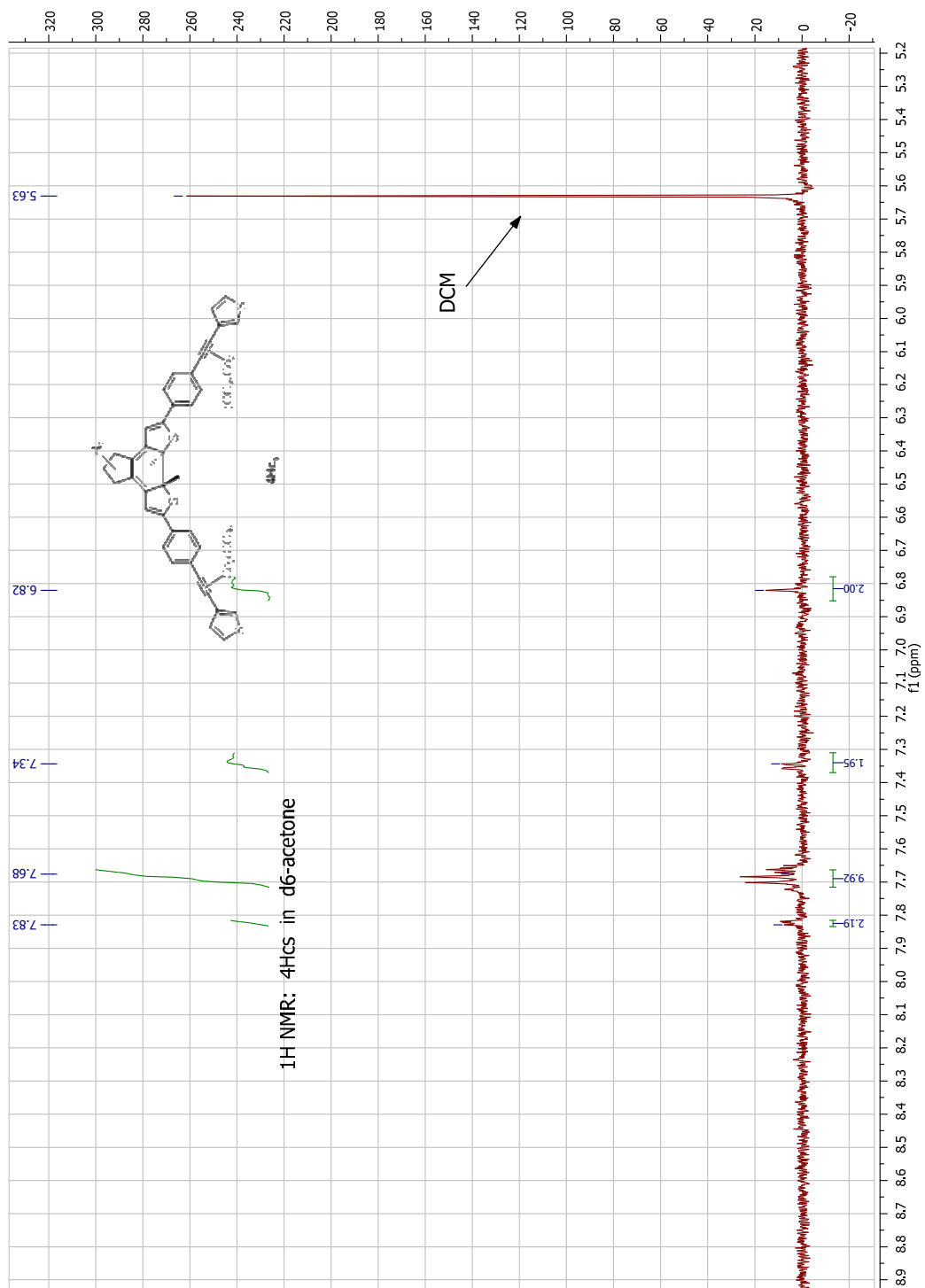




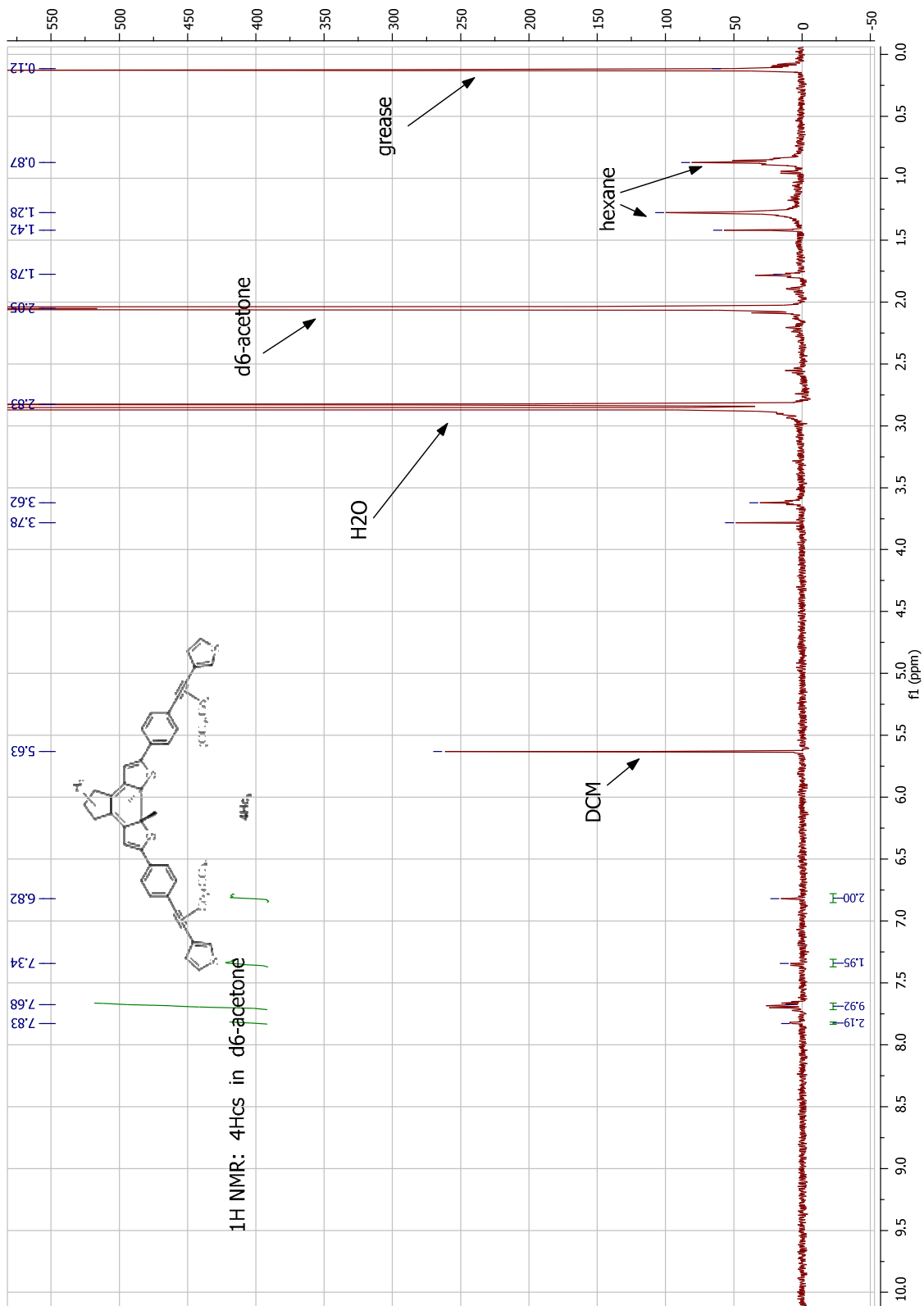


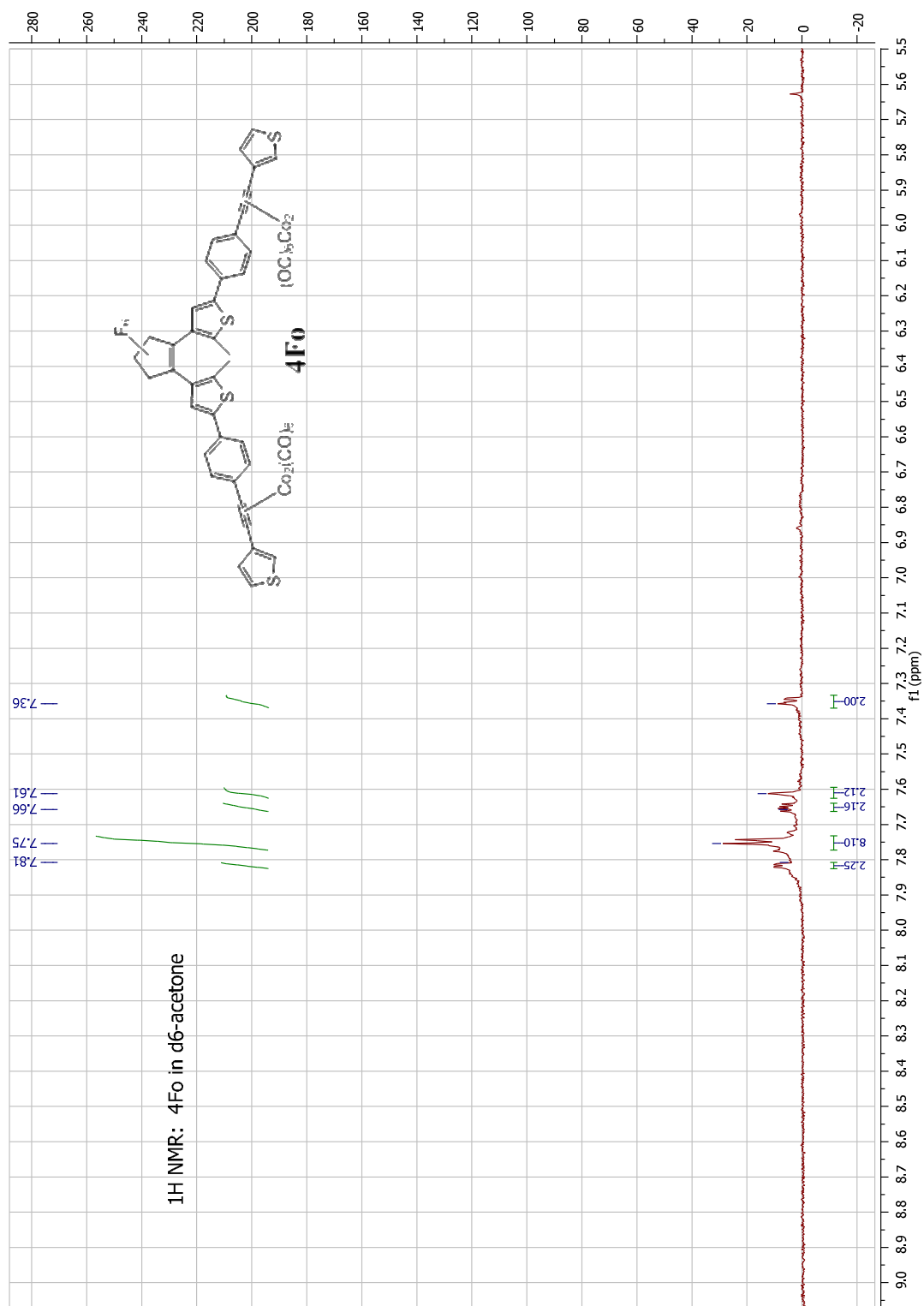




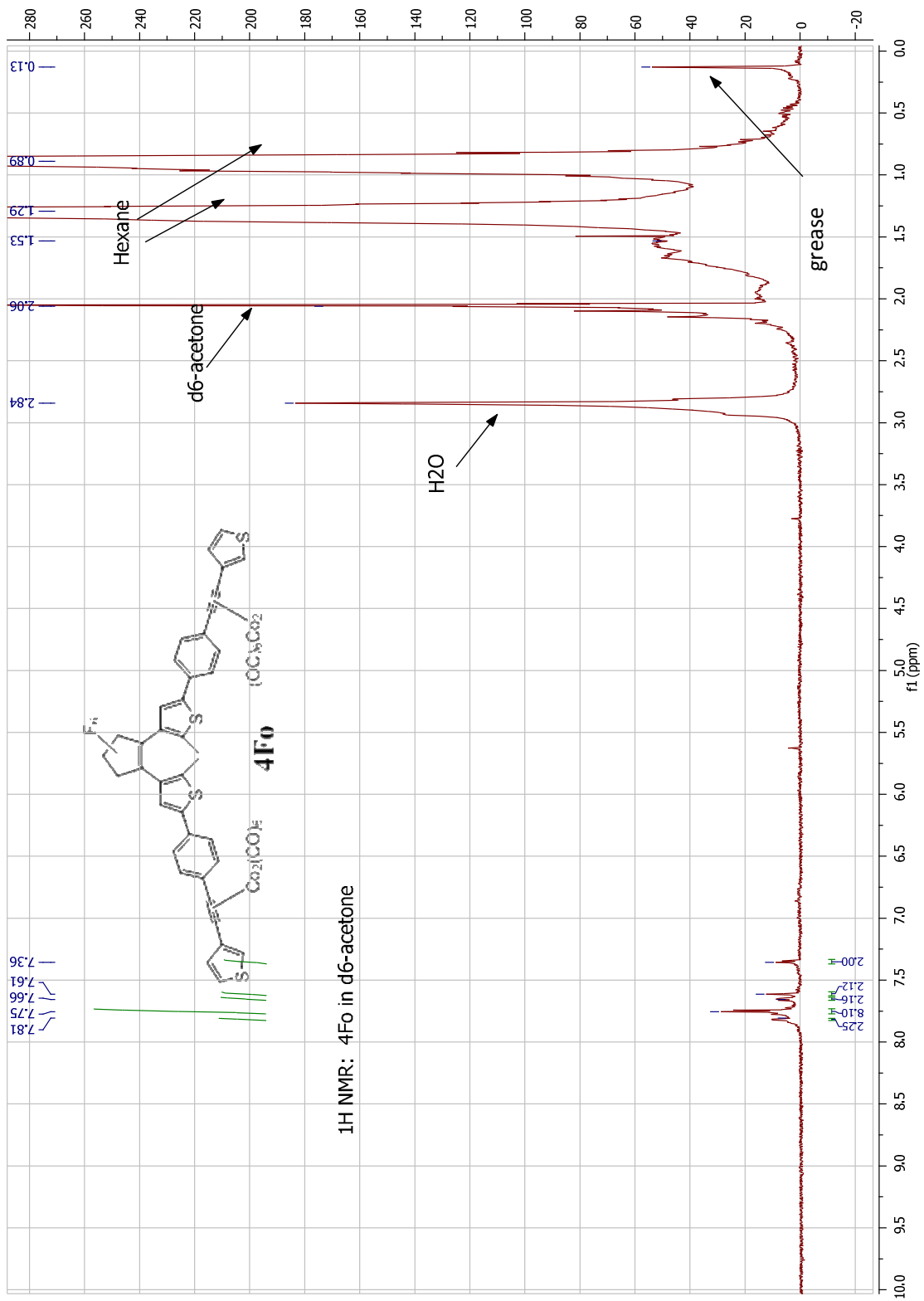


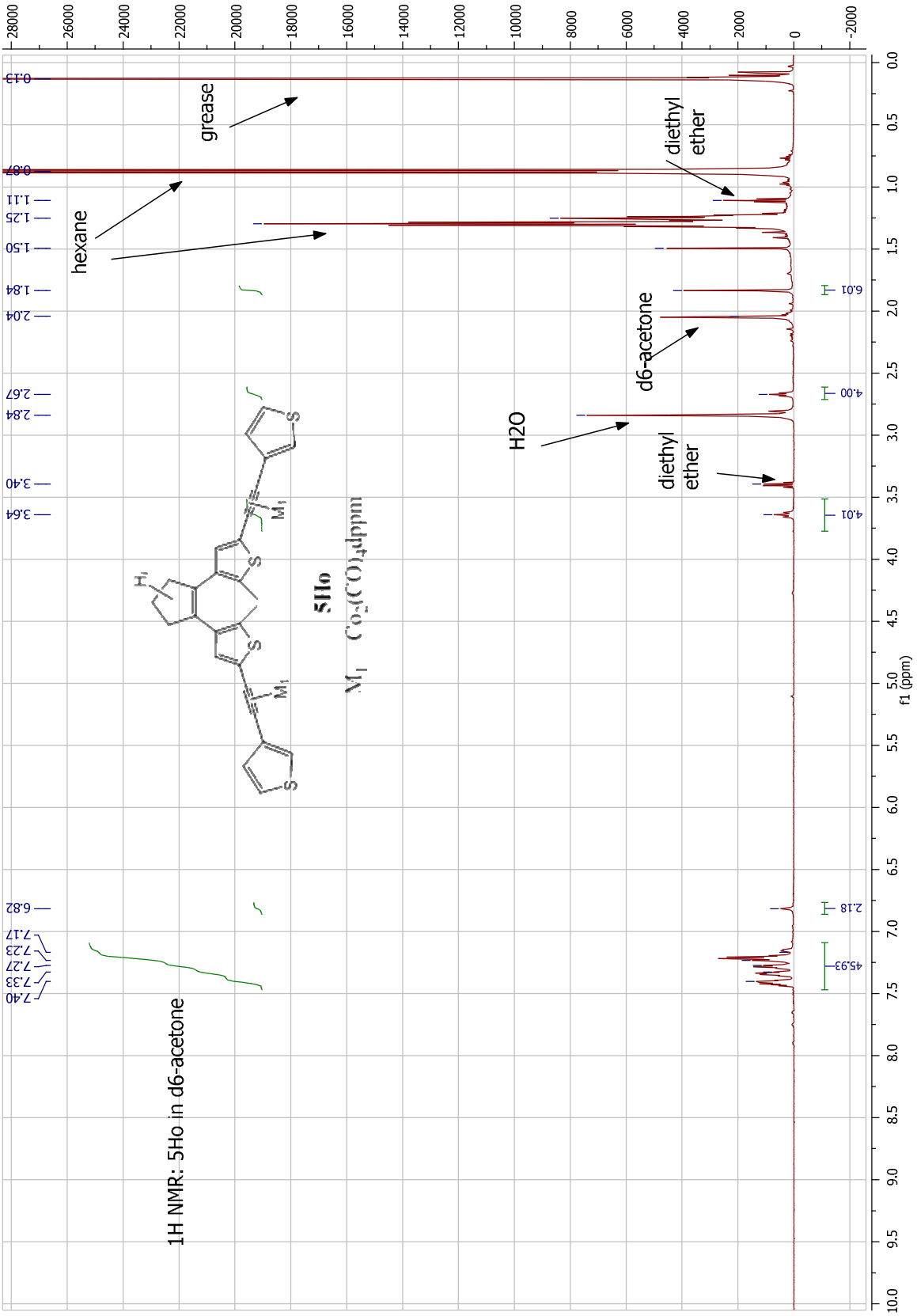
Due to the intensity of residual solvent from purification, only the aromatic region is shown here.

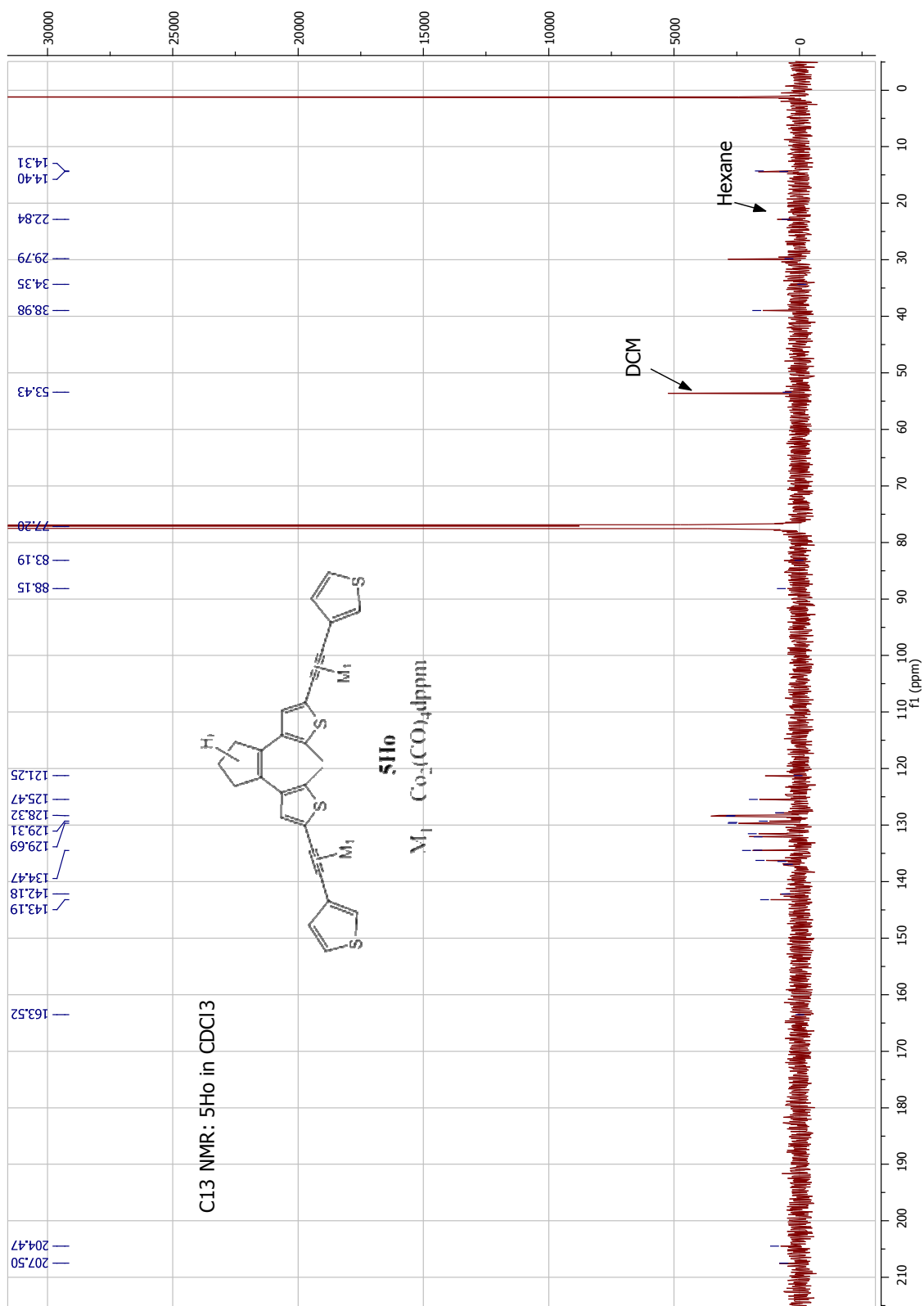


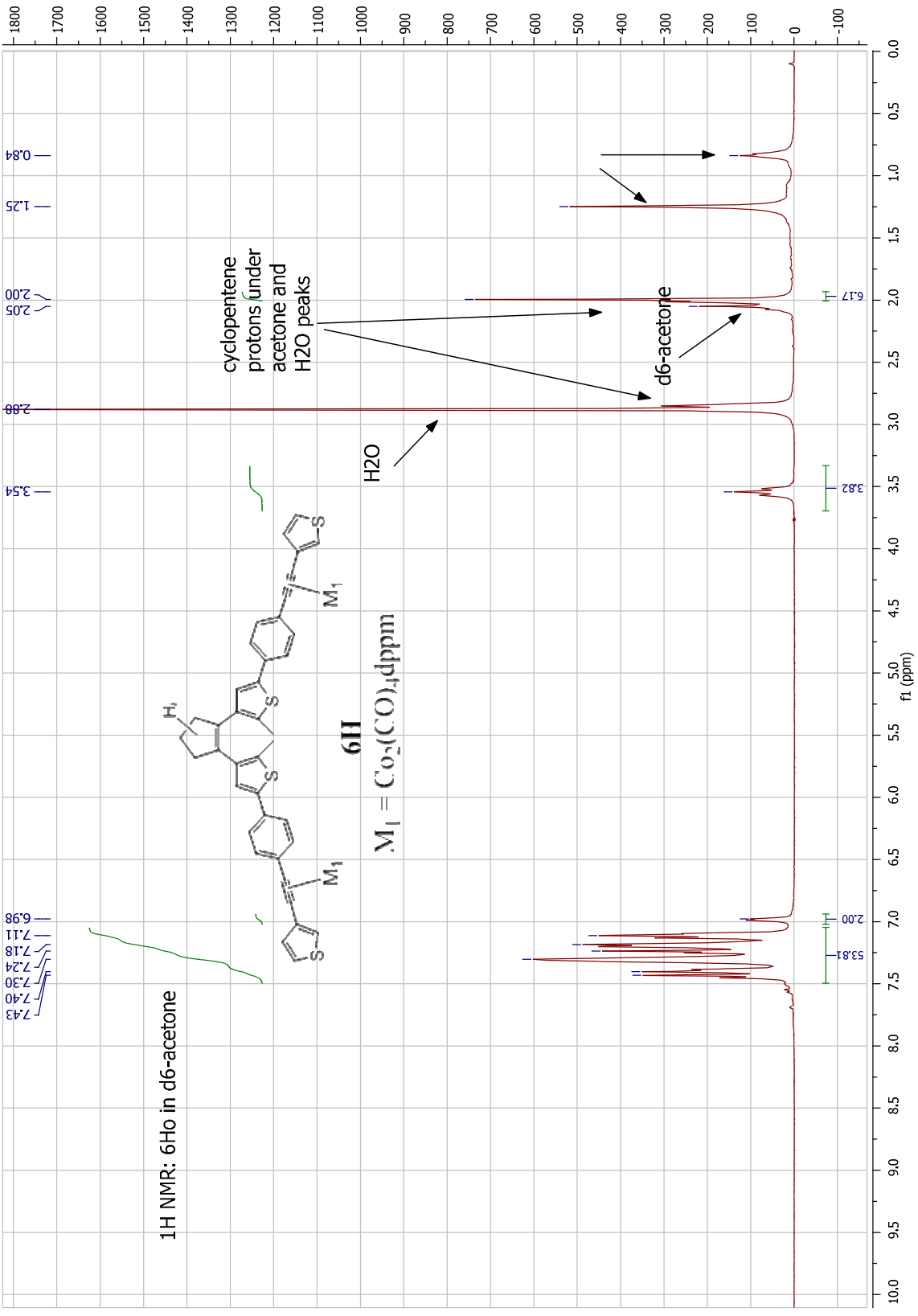


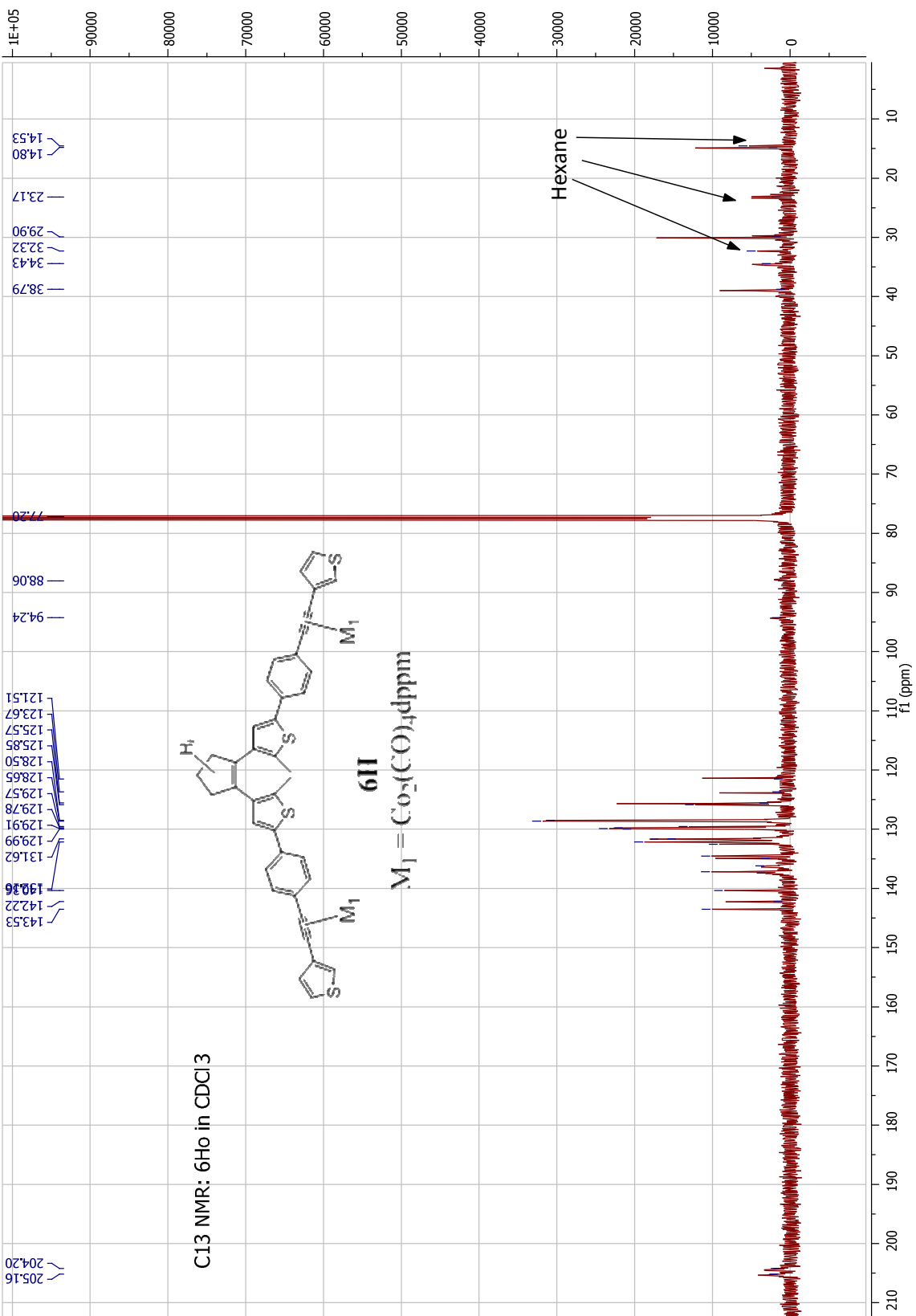
Due to the intensity of residual solvent from purification, only the aromatic region is shown here.











S5. UV-vis Absorption Spectra

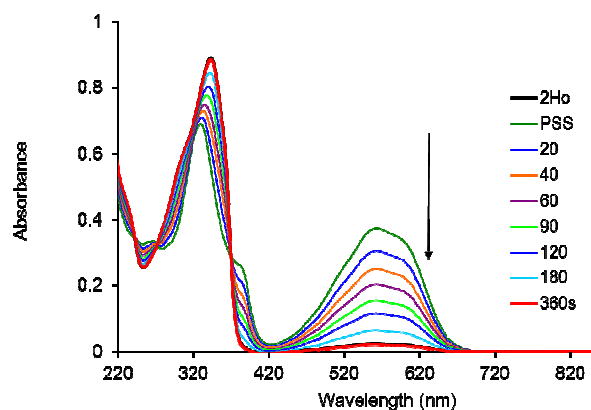


Figure S1: Absorption spectra of the cycloreversion process of **2Hc**, from the closed to the open isomer, in THF ($C=1.4 \times 10^{-5}$ mol/L), following irradiation with broadband light $\lambda > 550$ nm for 360 seconds (red line). The open isomer (**2Ho**) recorded at the start of the experiment (before any irradiation takes place) is denoted by the black line.

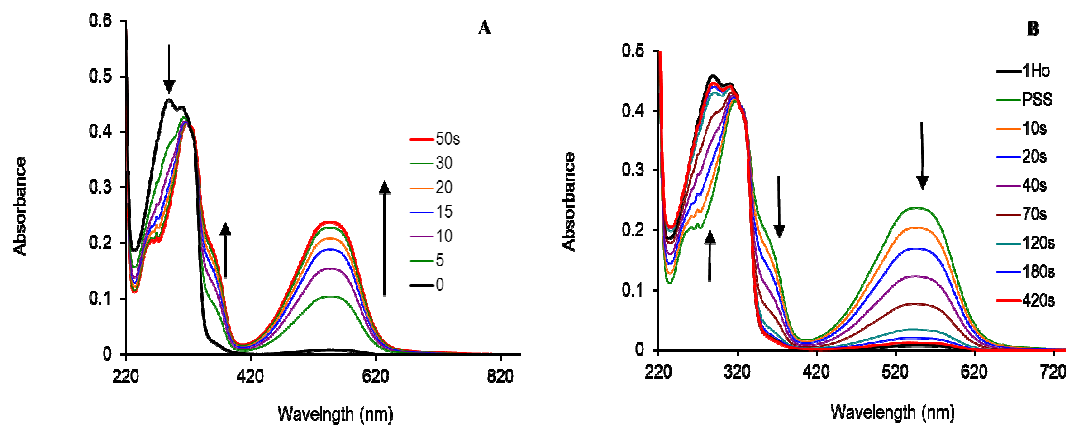


Figure S2: Absorption spectra of **1H** following cyclisation ($\lambda_{irr} = 313$ nm) to the closed isomer (A) and cycloreversion ($\lambda_{irr} > 550$ nm) back to the open isomer (B), in THF ($C=1.4 \times 10^{-5}$ mol/L). In graph B, the open isomer (**1Ho**) recorded at the start of the experiment (before any irradiation takes place) is denoted by the black line.

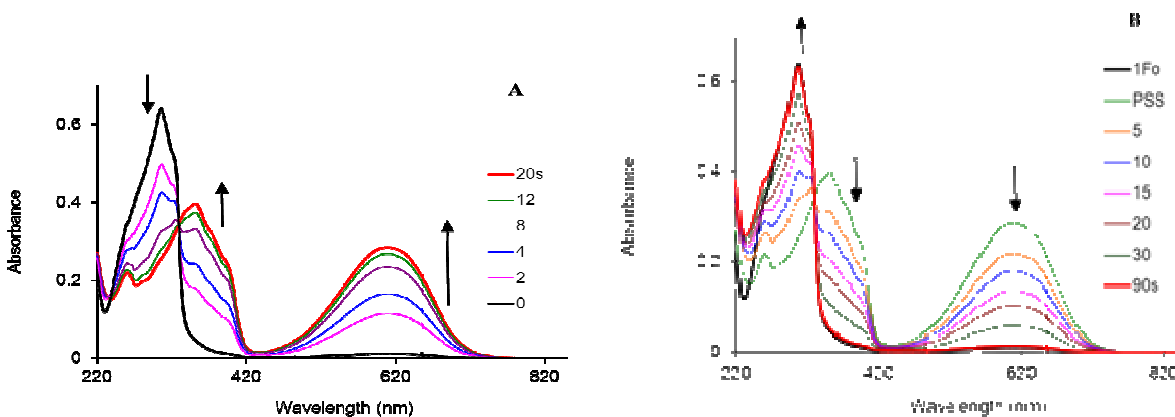


Figure S3: Absorption spectra of **1F** following cyclisation ($\lambda_{\text{irr}} = 313 \text{ nm}$) to the closed isomer (A) and cycloreversion ($\lambda_{\text{irr}} > 550 \text{ nm}$) back to the open isomer (B), in THF ($C=1.4 \times 10^{-5} \text{ mol/L}$). In graph B, the open isomer (**1Fo**) recorded at the start of the experiment (before any irradiation takes place) is denoted by the black line.

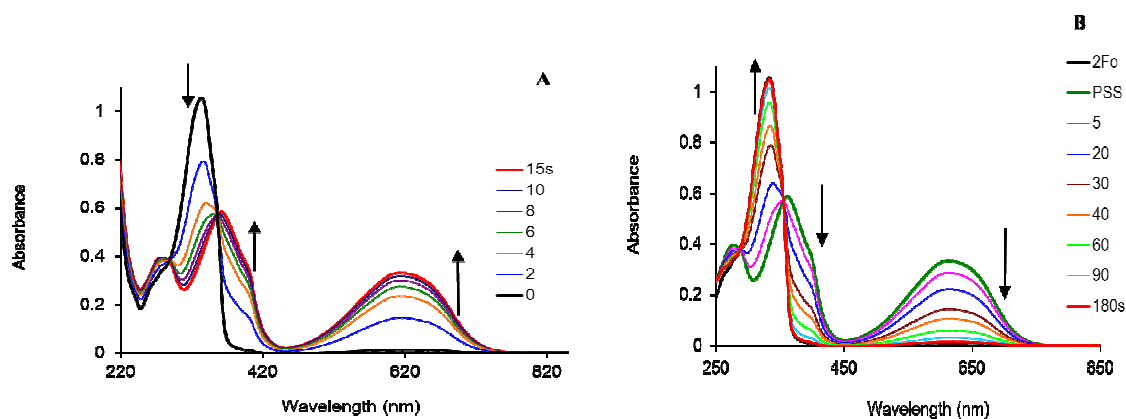


Figure S4: Absorption spectra of **2F** following cyclisation ($\lambda_{\text{irr}} = 313 \text{ nm}$) to the closed isomer (A) and cycloreversion ($\lambda_{\text{irr}} > 550 \text{ nm}$) back to the open isomer (B), in THF ($C=1.4 \times 10^{-5} \text{ mol/L}$). In graph B, the open isomer (**2Fo**) recorded at the start of the experiment (before any irradiation takes place) is denoted by the black line.

S6. ¹H NMR Spectroscopy

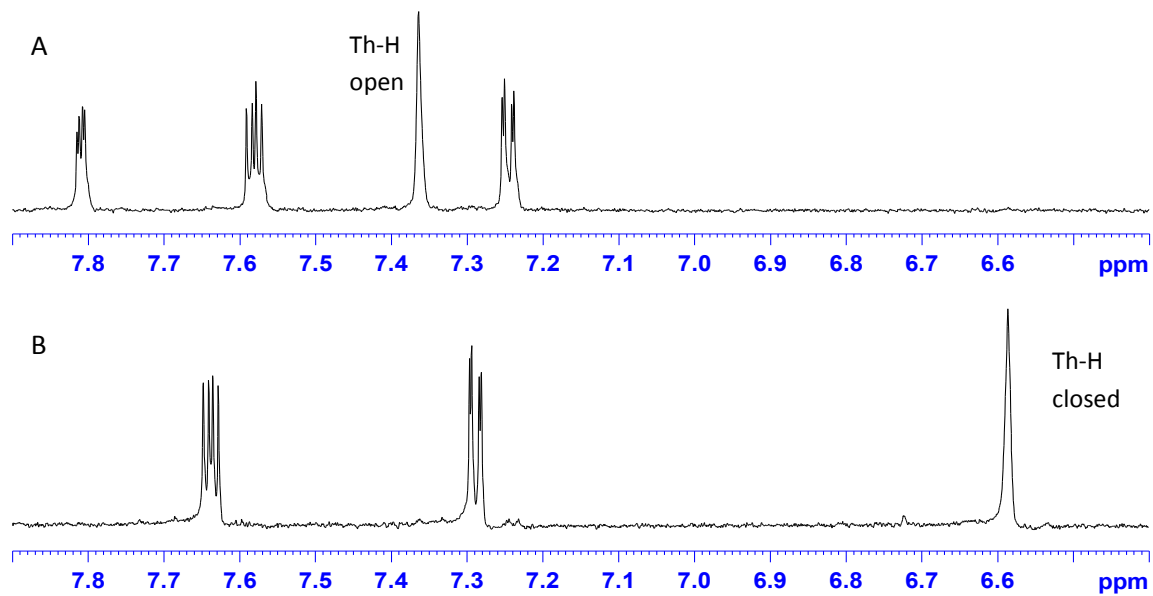


Figure S6(a): ¹H NMR spectral changes of **1F**, in deuterated acetone, upon irradiation at $\lambda = 313$ nm. A: open isomer **1Fo** before irradiation. B: closed isomer **1Fc** after 100 minutes of irradiation.

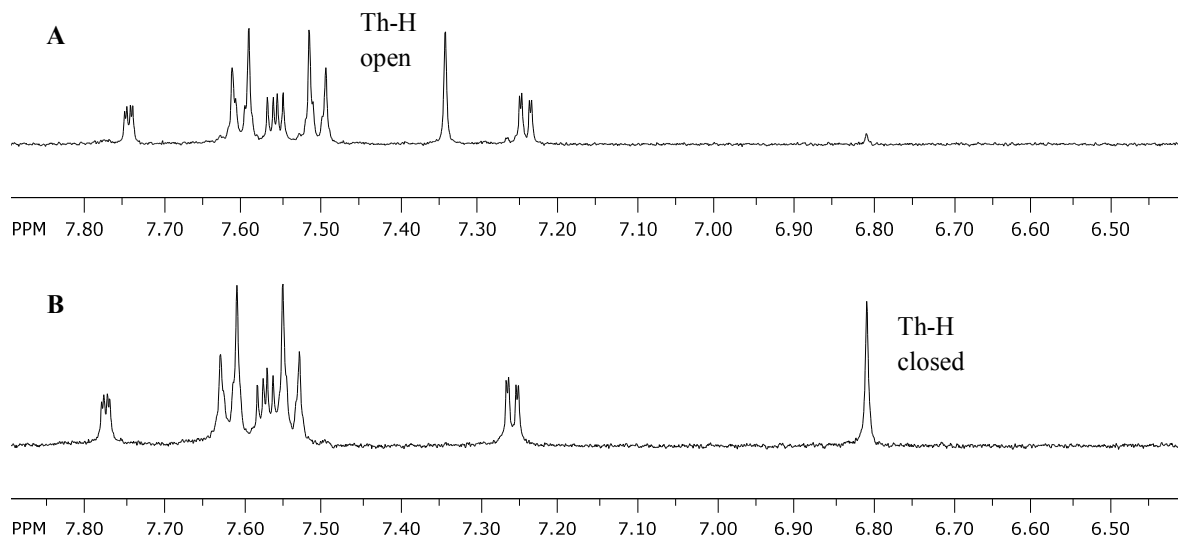


Figure S6(b): ^1H NMR spectral changes of **2Ho**, in deuterated acetone, upon irradiation at $\lambda = 313$ nm. A: open isomer **2Ho** before irradiation. B: closed isomer **2Hc** after 100 minutes of irradiation.

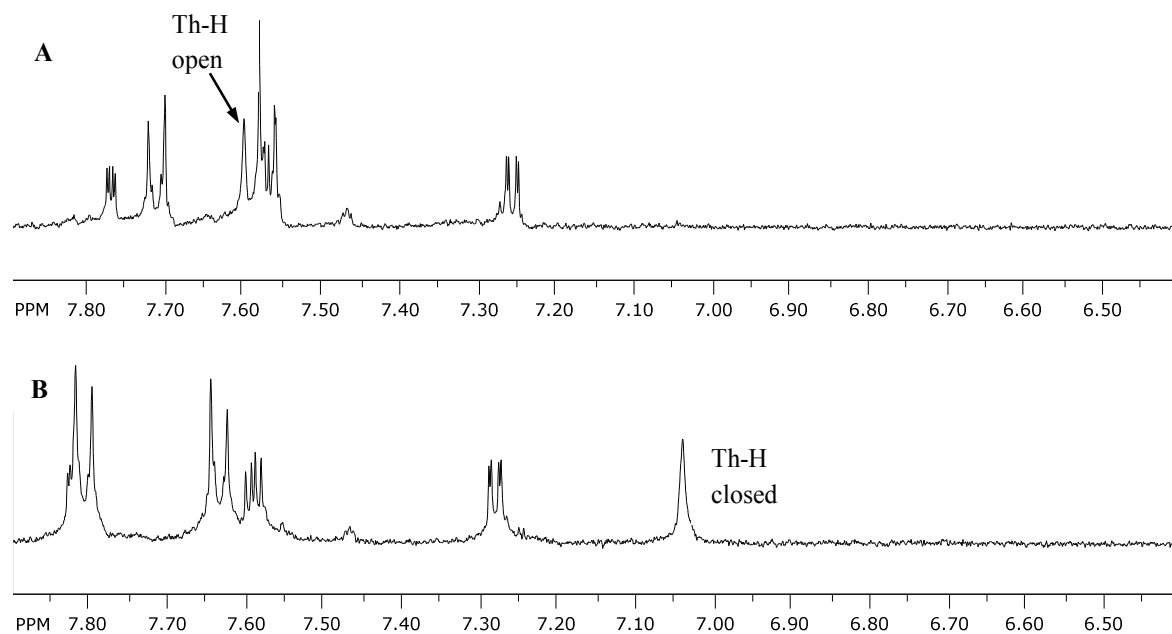


Figure S6(c): ^1H NMR spectral changes of **2Fo**, in deuterated acetone, upon irradiation at $\lambda = 313$ nm. A: open isomer **2Fo** before irradiation. B: closed isomer **2Fc** after 100 minutes of irradiation.

Table S1: ^1H NMR spectroscopic data (in ppm) for the thiophene-hydrogen at the 4-position for compounds **1H/F** and **2H/F**, before and after irradiation ($\lambda_{\text{irr}} = 313$ nm), in deuterated acetone.

Compound	Irradiation Time	δ Th-H open	δ Th-H closed	% [a]	δ Th-H by-product	% [b]
1F	100 min	7.36	6.59	> 95	-	-
2H	100 min	7.34	6.81	> 95	-	-
2F	100 min	7.60	7.04	> 95	-	-
1H	30 min	7.06	6.34	70	-	-
	60 min	7.06	6.34	85	6.53	4
	125 min	7.06	6.34	85	6.53	11
	220 min	7.06	6.34	78	6.53	18

[a] % conversion from the open isomer to the closed isomer

[b] % conversion to the by-product, in the case of **1H**.

(-) indicates absence of the photostable by-product.

S7. Thermal Stability

The absorption bands in the visible region, indicative of the closed isomer, decreased over time and the decay curves of the closed-isomers were plotted $\{\ln([c]/[c]_0) \text{ vs. time}\}$. The thermal stability of these compounds was found to increase in the order of: **2Hc** > **1Fc** > **1Hc** > **2Fc**. Noticeably, the absorption bands in the UV region (representing the open isomer) did not recover completely, indicating that thermal cycloreversion also involves some thermal degradation. Furthermore, the thermal stability plot obtained for **2H** was not linear indicating that this switch may undergo oxidative opening, catalytically. (It should be noted however, that the closed isomers were stable at room temperature, in solution, over a ten week period).

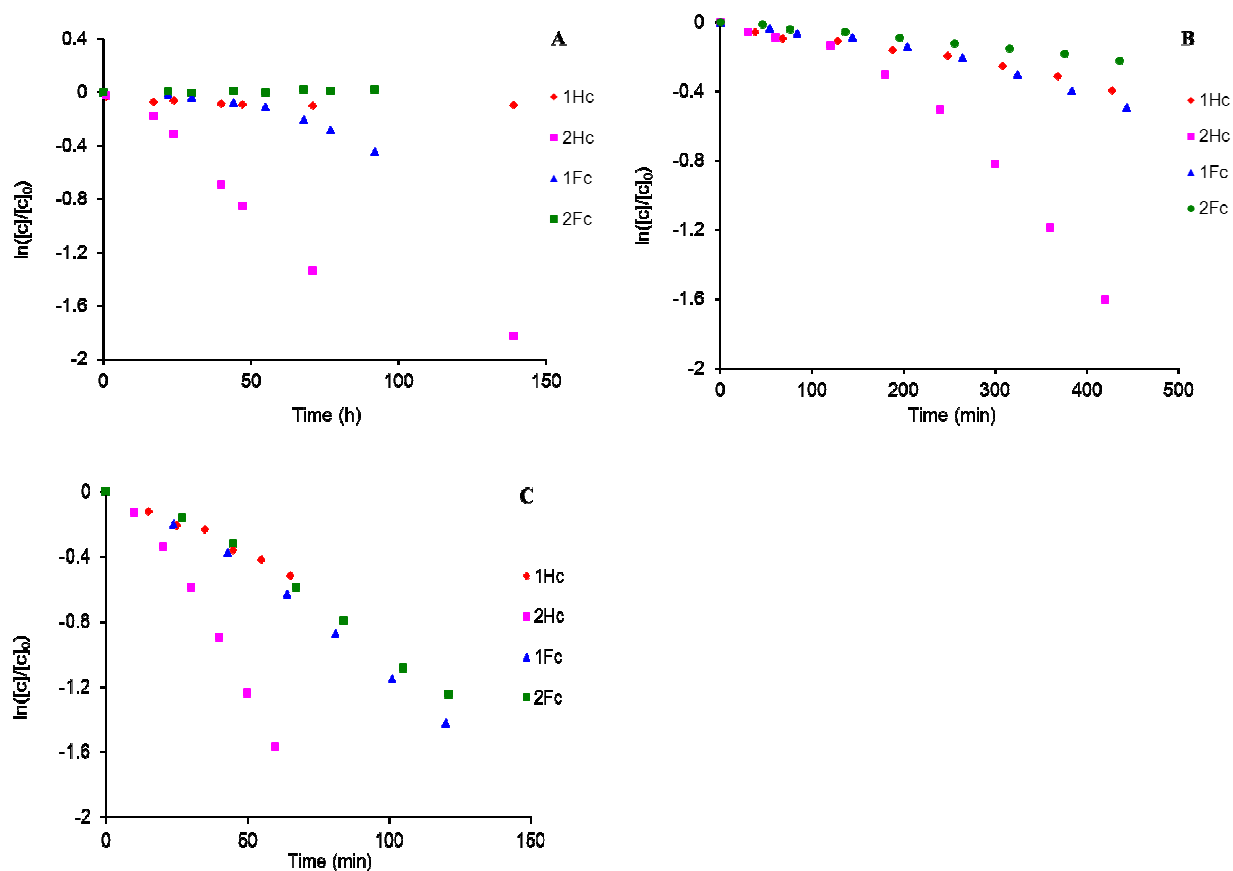


Figure S7: Thermal Stability of compounds **1Hc/Fc** and **2Hc/Fc**, in Toluene ($C=1.4 \times 10^{-5}$ mol/L), at 60°C for 140 hours (A), 80 °C for 7 hours (B), and at 100°C for 120 minutes (C).

S8. Co₂(CO)₆ Complexes: UV-vis Absorption Spectra

Table S2: UV-vis absorption data for the Co₂(CO)₆ complexes {**3Ho**, **3Fo**, **4Ho**, **4Fo**} and

Co ₂ (CO) ₆ Complexes λ_{abs} [nm] ($\epsilon \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)		Co ₂ (CO) ₄ dppm Complexes λ_{abs} [nm] ($\epsilon \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	
3Ho	259 (50.8), 327 (27.4), 462 (3.6), 569 (2.1)	5Ho	260 (46.8), 348 (23.3), 474 (2.5), 555 (2.2)
3Fo	275 (37.3), 326 (23.2), 452 (2.0), 555 (1.0)	5Fo	272(54.4), 340 (32.1), 474 (3.2), 555 (2.4)
4Ho	274 (51.2), 341 (53.0), 455 (4.7), 558 (2.4)	6Ho	279 (51.2), 351 (53.2), 474 (4.2), 555 (3.3)
4Fo	274, 328, 450, 559		

Co₂(CO)₄dppm complexes {**5Ho**, **5Fo**, **6Ho**, **6Fo**}, in THF.

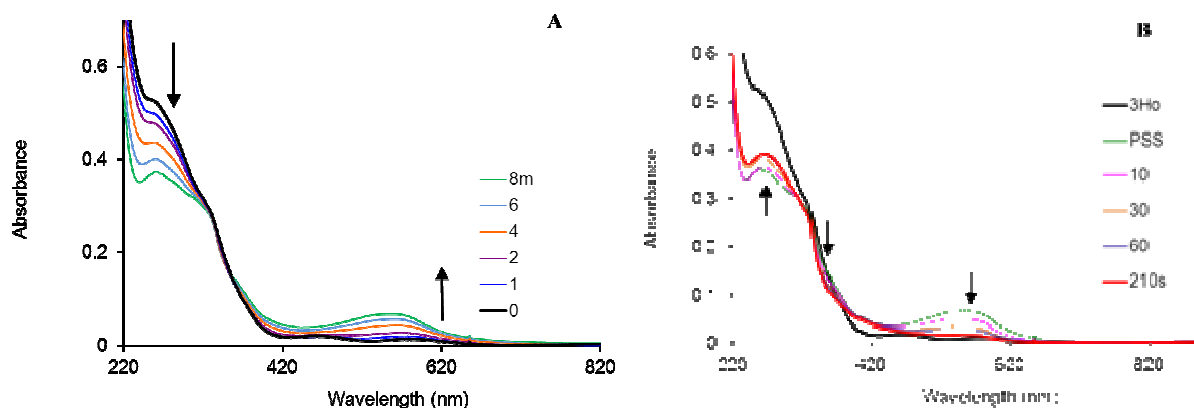


Figure S8: UV-vis absorption spectrum of **3H**, in THF ($c = 1.4 \times 10^{-5} \text{ mol/L}$), following irradiation at $\lambda = 313 \text{ nm}$ for 8 minutes (A), and subsequent cycloreversion at $\lambda_{\text{irr}} > 550 \text{ nm}$ (B).

In graph B, the open isomer (**3Ho**) recorded at the start of the experiment (before any irradiation takes place) is denoted by the black line.

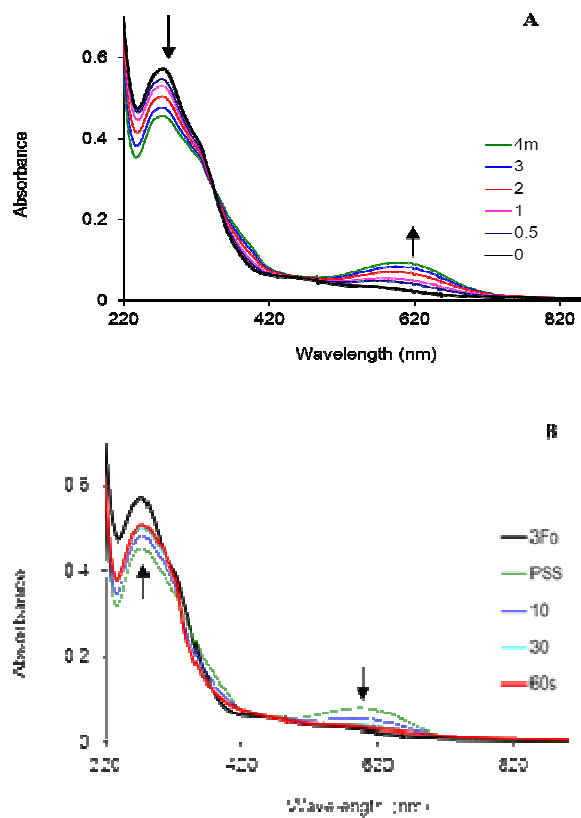


Figure S9: UV-vis absorption spectrum of **3F**, in THF ($c = 1.4 \times 10^{-5}$ mol/L), following irradiation at $\lambda = 313$ nm for 8 minutes (A), and subsequent cycloreversion at $\lambda_{\text{irr}} > 550$ nm (B). In graph B, the open isomer (**3Fo**) recorded at the start of the experiment (before any irradiation takes place) is denoted by the black line.

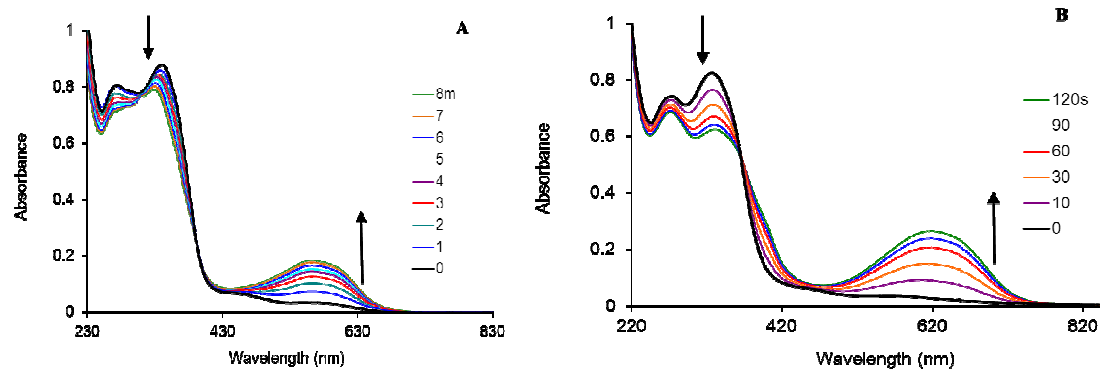


Figure S10: UV-vis absorption spectrum of **4Ho** (A) and **4Fo** (B), in THF ($c = 1.4 \times 10^{-5}$ mol/L), following irradiation to the PSS, at $\lambda = 313$ nm, for 8 minutes and 120 seconds, respectively.

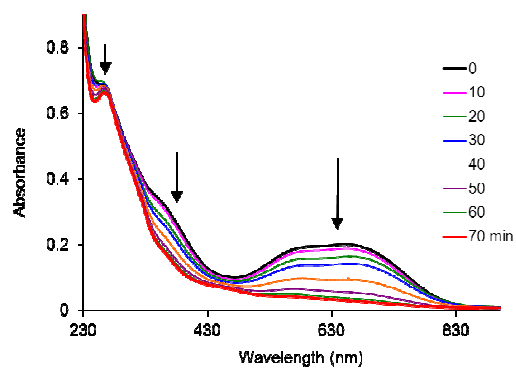


Figure S11: UV-vis absorption spectrum of the closed isomer **3Fc_s**, in THF, following irradiation at $\lambda > 650$ nm, for 70 minutes.

S9. Co₂(CO)₄dppm Complexes: UV-vis Absorption Spectra

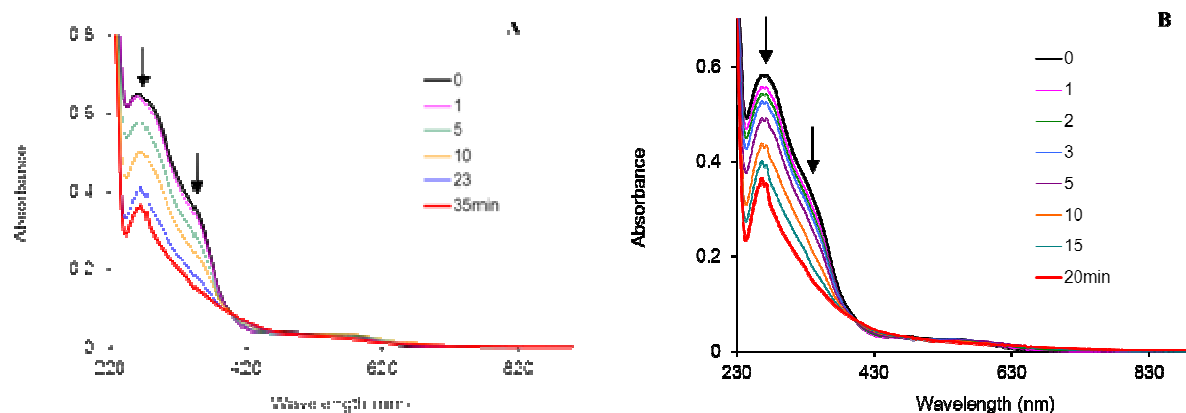


Figure S12: UV-vis absorption spectrum of **5Ho** (A) and **5Fo** (B), in THF ($c = 1.4 \times 10^{-5}$ mol/L), following irradiation to the PSS, at $\lambda = 313$ nm, for 35 and 20 minutes, respectively.

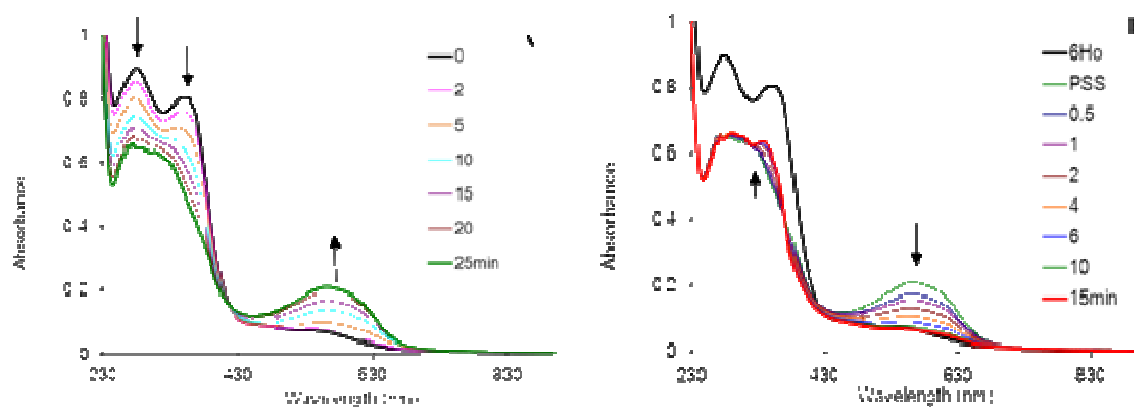


Figure S13: UV-vis absorption spectrum of **6H**, in THF ($c = 1.4 \times 10^{-5}$ mol/L). A: Cyclisation process at $\lambda_{\text{irr}} = 313$ nm for 25 minutes. B: Cycloreversion process at $\lambda_{\text{irr}} > 550$ nm for 15 minutes. In graph B, the open isomer (**6Ho**) recorded at the start of the experiment (before any irradiation takes place) is denoted by the black line.

S10. IR Absorption Spectra

Table S3: Changes observed in the carbonyl FT-IR absorptions upon irradiation at $\lambda = 313$ or 365 nm, for the $\text{Co}_2(\text{CO})_6$ complexes **3Ho** and **4Ho**, and their corresponding $\text{Co}_2(\text{CO})_4\text{dppm}$ complexes **5Ho** and **6Ho**, in THF and in the presence of PPh_3 .

	IR bands $\nu_{(\text{CO})} \text{ cm}^{-1}$	λ_{irr} (nm)	Photoproducts $\nu_{(\text{CO})} \text{ cm}^{-1}$
3Ho	2089 ^a , 2054 ^a , 2025 ^a ,	365	2061 ^b , 2010 ^b , 1995 ^b , 1960 ^c
		313	2061 ^b , 2010 ^b , 1995 ^b , 1973 ^c , 1960 ^c , 1918 ^d , 1885 ^d
4Ho	2089 ^a , 2053 ^a , 2025 ^a	365	2060 ^b , 2010 ^b , 1995 ^b , 1962 ^c
		313	2060 ^b , 2010 ^b , 1997 ^b , 1962 ^c , 1927 ^d , 1885 ^d , 1842 ^d
4Hc_s	2089 ^a , 2055 ^a , 2026 ^a	> 650	2011 ^b , 1996 ^b , 1964 ^c
5Ho	2021 ^a , 1997 ^a , 1969 ^a	365	1989 ^e , 1951 ^e , 1915 ^e
		313	1989 ^e , 1951 ^e , 1915 ^e
6Ho	2020 ^a , 1996 ^a , 1969 ^a	365	1987 ^e , 1950 ^e , 1914 ^e
		313	1987 ^e , 1950 ^e , 1914 ^e

a = parent bands

b = (Switch)[$\text{Co}_2(\text{CO})_5\text{PPh}_3$]₂

c = (Switch)[$\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2$]₂

d = (Switch)[$\text{Co}_2(\text{CO})_3(\text{PPh}_3)_3$]₂ or (Switch)[$\text{Co}_2(\text{CO})_2(\text{PPh}_3)_4$]₂

e = (Switch)[$\text{Co}_2(\text{CO})_3(\text{dppm})\text{PPh}_3$]₂

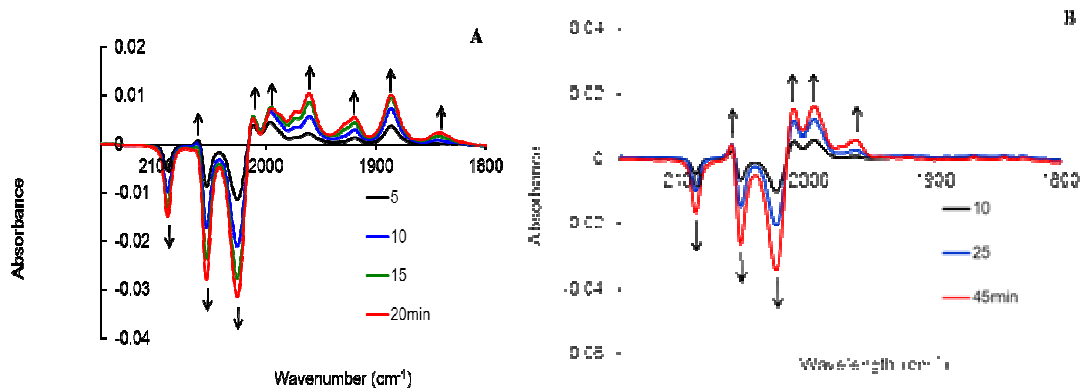


Figure S14: The IR difference spectra of the $\text{Co}_2(\text{CO})_6$ complex **3Ho** in THF (in the presence of PPh_3); (A) following irradiation at $\lambda = 313$ nm for 20 minutes, and (B) at $\lambda = 365$ nm for 45 minutes. Negative bands indicate bleaching of the parent bands and the positive bands indicate formation of the photoproducts, following CO loss.

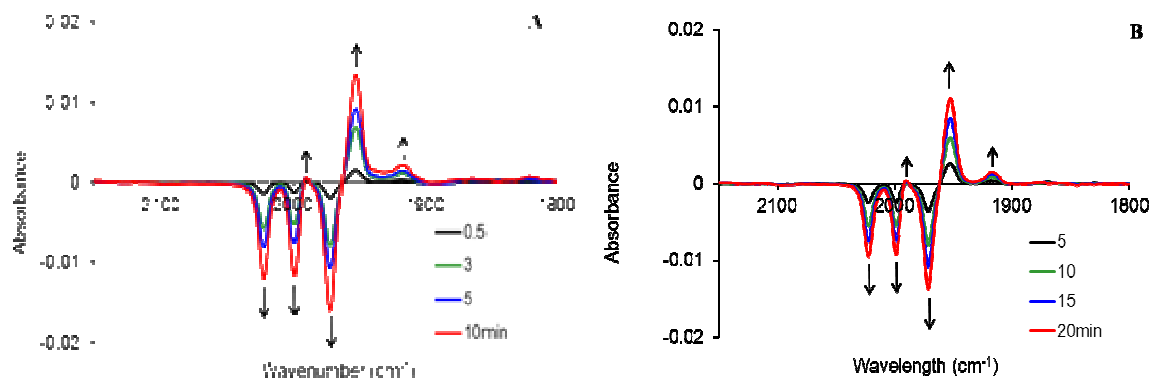


Figure S15: The IR difference spectra of the $\text{Co}_2(\text{CO})_4\text{dppm}$ complex **5Ho** in THF (in the presence of PPh_3); (A) following irradiation at $\lambda = 313$ nm for 10 minutes, and (B) at $\lambda = 365$ nm for 20 minutes. Negative bands indicate bleaching of the parent bands and the positive bands indicate formation of the photoproducts, following CO loss.

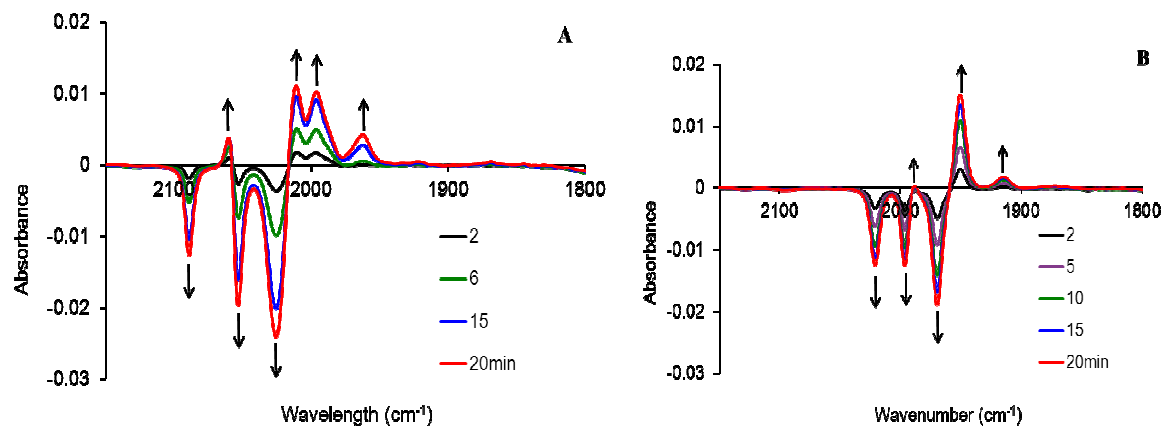


Figure S16: The IR difference spectra of the Co₂(CO)₆ complex **4Ho** (Graph A), and the Co₂(CO)₄dppm complex **6Ho** (Graph B), in THF, following irradiation at 365 nm for 20 minutes, in the presence of PPh₃. Negative bands indicate bleaching of the parent bands and the positive bands indicate formation of the photoproducts, following CO loss.