Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Expedient Synthesis of a Symmetric Cycloheptyne-$Co_2(CO)_6$ Complex for Orthogonal Huisgen Cycloadditions.

Supplementary Information

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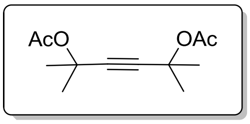
General methods

All commercial materials were used without further purification, unless indicated. ^1H NMR and ^{13}C NMR spectra were recorded on a BRUKER AVANCE I 300 Mhz (^1H: 300MHz, ^{13}C: 75.3MHz), spectrometer. The chemical shifts for the NMR spectra are reported in ppm relative to the solvent residual peak. Coupling constants J are reported in hertz (Hz). The following abbreviations are used for the multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublet; td, triplet of doublet. Yields refer to isolated material determined to be pure by NMR spectroscopy and thin-layer chromatography (TLC), unless specified in the text. Analytical TLCs were performed on Fluka Silica Gel 60 F254. Melting points were determined using a Stuart Scientific apparatus (SMP3). High resolution mass spectra were performed by the CESAMO (Talence, France) and were recorded on Qq-TOF tandem mass spectrometer (API Q-STAR Pulsari, Applied Biosystems). IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer.

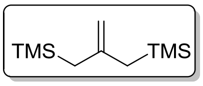
Procedures

2,5-Dimethylhex-3-yne-2,5-diyl diacetate (5)



The product was prepared by using the modified procedure reported by Nevado *et al.*[1]
To a solution of diol **4** (5 mmol, 710 mg, 1 equiv.) in dry dichloromethane under nitrogen (C = 0.1 M), were added Et_3N (50 mmol, 6.9 mL, 10 equiv.), DMAP (5 mmol, 610mg, 1 equiv.) and then Ac_2O (25 mmol, 2.5 mL, 5 equiv.) at room temperature. The solution was stirred for 16 h at this temperature. After evaporation of volatiles under vacuum, the crude solution was directly poured into a silica column chromatography (petroleum ether/Et_2O 7:3) to afford the compound **5** as a colorless liquid (m = 848 mg, yield = 75%). Analytical data was conformed to the literature.[2] **^1H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 2.00 (s, 6H), 1.62 (s, 12H).

(2-Methylenepropane-1,3-diyl)bis(trimethylsilane) (2c)



The product was prepared by using the modified procedure reported by Yus *et al.*[3]
A solution of 3-chloro-2-chloromethylprop-1-ene (8 mmol, 1 mL, 1 equiv.) and TMS-Cl (16 mmol, 2 mL, 2 equiv.) in THF (5 mL) was added under nitrogen to a suspension of freshly cut lithium pieces (56 mmol, 400 mg, 7 equiv.) and naphthalene (0.8 mmol, 100 mg, 0.1 equiv.) in THF (10 mL) at -78 °C. The mixture was allowed to reach room temperature, while continuing the stirring for 24 h until a reddish solution appeared. Then, the mixture was quenched with water (10 mL), extracted with Et_2O (3 x 20 mL), and the organic phase was dried over anhydrous sodium sulfate. The crude bis-trimethylsilyl derivative **2c** was obtained and used without any further purification (m = 1.1 g, crude yield = 68%). Analytical data was conformed to the literature.[3]
^1H NMR (300 MHz, $CDCl_3$): δ [ppm] = 4.39 (s, 2H), 1.49 (s, 4H), 0.05 (s, 18H).

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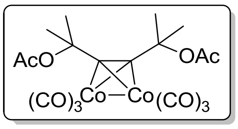
[1] X. Huang, T. De Haro and C. Nevado, *Chem. Eur. J.*, 2009*,* **15***,* 5904.

[2] D. R. Paulson, L. S. Gilliam, V. O. Terry, S. M. Farr, E. J. Parker, F. Y. N. Tang, R. Ullman and G. Ribar, *J. Org. Chem.,* 1978*,* **43***,* 1783.

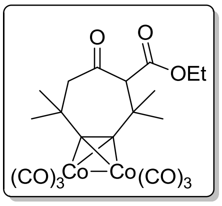
[3] E. Lorenzo, F. Alonso and M. Yus, *Tetrahedron*, 2000*,* **56***,* 1745.

Complex 1



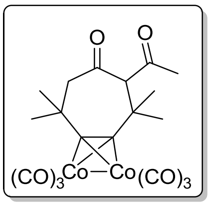
To a solution of **5** (1.2 mmol, 270 mg, 1 equiv.) in dry dichloromethane (C = 0.1 M) under nitrogen was added Co_2CO_8 (1.2 mmol, 450 mg, 1 equiv.) at room temperature. The solution was stirred for 4 h at this temperature, and then the solvent was removed under vacuum. The complex was then purified by flash chromatography on silica gel (petroleum ether/Et_2O, 8:2) to give **1** as a red solid (m= 660 mg, yield = 99%). **Mp**(°C): 86-88. **R*f***: 0.62 (8:2 cyclohexane/Et_2O).^{1}**H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 2.01 (s, 6H), 1.93 (m, 12H).^{13}**C NMR** (75 MHz, $CDCl_3$): δ [ppm] = 170.0, 83.6, 28.9, 22.3. **HRMS:** Not detected after several trials (ESI, EI, FD). **FT-IR (ν/cm^{-1}, KBr):** 2992, 2094, 2053, 2025, 1740, 1453, 1368, 1228, 1135, 1018, 937.

Complex 3a



To a solution of **1** (1.2 mmol, 660 mg, 1 equiv.) in dry dichloromethane (C = 0.1 M) under nitrogen was added the bis-silylenol ether **2a**[4] (1.2 mmol, 328 mg, 1 equiv.). The solution was cooled down to -40 °C and $BF_3 \cdot OEt_2$ (2.4 mmol, 0.72 mL, 2 equiv., C = 46.5%) was added. The solution was stirred for 1 h at -40 °C, and the solvent was removed under vacuum. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/Et_2O, 9:1) to give **3a** as a red solid (m= 190mg, yield = 30%). **R*f***: 0.46 (9:1 petroleum ether/Et_2O).^{1}**H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 4.25 – 4.10 (m, 2H), 3.71 (s, 1H), 2.87 (d, *J* = 10.9 Hz, 1H), 2.63 (d, *J* = 10.9 Hz, 1H), 2.17 (s, 3H), 1.45 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H), 1.28 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).^{13}**C NMR** (75 MHz, $CDCl_3$): δ [ppm] = 203.9, 167.2, 77.6, 77.2, 76.7, 67.4, 61.1, 59.4, 40.0, 37.8, 33.1, 31.8, 30.7, 27.5, 14.2. **HRMS (ESI)** $C_{20}H_{20}Co_2O_9$ calculated for [M+Na]: 544.9663 found 544.9678. **FT-IR (ν/cm^{-1}, KBr):** 2968, 2933, 2091, 2049, 2023, 1751, 1706, 1463, 1323, 1164, 1119.

Complex 3b



To a solution of **1** (1.2 mmol, 660 mg, 1 equiv.) in dry dichloromethane (C = 0.1 M) under nitrogen, was added the bis-silylenol ether[4] **2b** (1.2 mmol, 293 mg, 1 equiv.). The solution was cooled down to -40 °C and $BF_3 \cdot OEt_2$ (2.4 mmol, 0.72 mL, 2 equiv., C = 46.5%). The solution was stirred for 1 h at -40 °C, and the solvent was removed under vacuum. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/Et_2O, 9:1) to give to give **3b** as a red solid (m= 176 mg, yield = 30%). **R*f***: 0.35 (9:1 petroleum ether /Et_2O).^{1}**H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 3.89 (s, 1H), 2.92 (d, *J* = 10.7 Hz, 1H), 2.66 (d, *J* = 10.7 Hz, 1H), 2.13 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.28 (s, 3H).^{13}**C NMR** (75 MHz, $CDCl_3$): δ [ppm] = 205.3, 201.0, 74.4, 59.8, 40.6, 38.1, 33.2,

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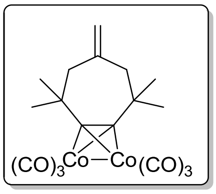
[4] Prepared following this procedure : G. A. Molander and K. O. Cameron, *J. Am. Chem. Soc.*, 1993, **115**, 830.

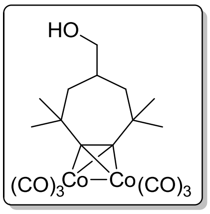
32.3, 31.8, 30.6, 27.4 . **HRMS (ESI)** $C_{19}H_{18}Co_2O_8$ calculated for [M+Na]: 514.9557 found 514.9563. **FT-IR (ν/cm^{-1}, KBr):** 2986, 2970, 2936, 2090, 2041, 2016, 1731, 1693, 1575, 1453, 1360, 1317, 1158, 1126, 1069, 995.

Complex 3c



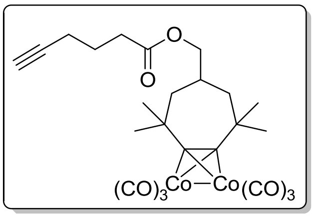
To a solution of **1** (1.2 mmol, 660 mg, 1 equiv.) in dry dichloromethane (C = 0.1 M) under nitrogen was added the bis-allylsilane **2c** (1.2 mmol, 240 mg, 1 equiv.). The solution was cooled down to -40 °C and $BF_3 \cdot OEt_2$ (2.4 mmol, 0.72 mL, 2 equiv., C= 46.5%). The solution was stirred for 1 h at -40 °C, and the solvent was removed under vacuum. The crude mixture was purified by flash chromatography on silica gel (petroleum ether pure) to give **3c** as a red pasty solid (m= 245 mg, yield = 45%). **R*f***: 0.71 (petroleum ether pure).**^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 4.96 (s, 2H), 2.28 (s, 4H), 1.27 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ [ppm] = 143.9, 118.8, 52.6, 37.9, 32.1. **HRMS:** Not detected after several trials (ESI, EI, FD). **FT-IR (ν/cm^{-1}, KBr):** 2960, 2087, 2045, 2020, 1862, 1453, 1379, 1247, 836.

Complex 6



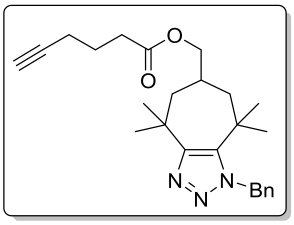
To a solution of **3c** (0.5 mmol, 227 mg, 1 equiv.) in dry THF (C = 0.1 M) under nitrogen was added $BH_3 \cdot THF$ (0.75 mmol, 0.75 mL, 1.5 equiv., C = 1 M in THF) at 0 °C. The solution was stirred at r.t. until full conversion of the starting material (16 h, TLC monitoring), then $NaBO_3 \cdot 4H_2O$ (2.5 mmol, 382 mg, 5 equiv.) in a water suspension (2 mL) was added to the mixture at r.t. The solution was vigorously stirred for 4 h at r.t. (biphasic mixture). Then, the mixture was quenched with water (10 mL), extracted with EtOAc (3 x 10 mL), and the combined organic phases were dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/Et_2O, 8:2) to give **6** as a red pasty solid (m = 142 mg, yield = 60%). **R*f***: 0.25 (7:3 cyclohexane/AcOEt).**^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 3.45 (t, *J* = 6.1 Hz, 2H), 2.13-1.96 (m, 1H), 1.79 (d, *J* = 13.5 Hz, 2H), 1.34 (d, *J* = 13.3 Hz, 2H), 1.29 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ [ppm] = 69.1, 46.9, 37.9, 35.6, 33.8, 31.9. **HRMS:** Not detected after several trials (ESI, EI, FD). **FT-IR (ν/cm^{-1}, KBr):** 3371, 2994, 2929, 2086, 2043, 2019, 1591, 1469, 1379, 1362, 1248, 858, 837

Complex 7



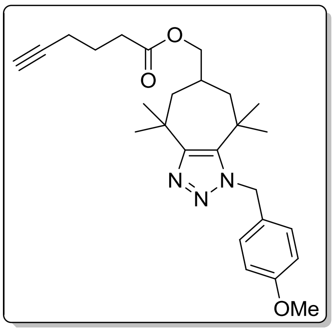
To a solution of **6** (0.3 mmol, 141 mg, 1 equiv.) in dry dichloromethane (C = 0.1 M) under nitrogen, was added 5-hexynoic acyl chloride (0.45 mmol, 59 mg, 1.5 equiv.) and Et_3N (0.3 mmol, 41μL, 1 equiv.) at room temperature. The solution was stirred at r.t. until full conversion of the starting material (1 h, TLC monitoring). After evaporation of volatiles under vacuum, the residue was directly purified by silica column chromatography (petroleum ether/Et_2O 8:2) to afford compound **7** as a red pasty solid (m = 86 mg, yield = 51%). **R*f***: 0.44 (8:2 petroleum ether/Et_2O).**^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 3.94 (d, *J* = 6.4 Hz, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 2.30 (td, *J* = 6.9, 2.6 Hz, 2H), 2.00 (t, *J* = 2.6 Hz, 1H), 1.94 – 1.83 (m, 2H), 1.74 (d, *J* = 13.0 Hz, 2H), 1.47 – 1.39 (m, 2H), 1.32 (s, 12H).**^{13}C NMR** (75 MHz, $CDCl_3$): δ [ppm] = 173.0, 109.9, 70.1, 69.2, 46.8, 37.7, 33.6, 32.9, 32.2, 31.7, 23.6, 17.9. **HRMS:** Not detected after several trials (ESI, EI, FD). **FT-IR (ν/cm^{-1}, KBr):** 3313, 2966, 2937, 2086, 2044, 2019, 1737, 1591, 1469, 1451, 1381, 1363, 1157, 858.

Click-product 8a



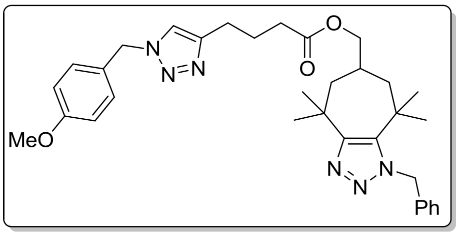
To a solution of complex **7** (0.107 mmol, 60 mg, 1 equiv.) and BnN_3 (0.22 mmol, 30 mg, 2 equiv.) in CH_3CN (C = 0.05 M) under nitrogen was added TMANO (0.55 mmol, 41 mg, 5 equiv.) at 0°C. The solution was stirred at r.t. for 16 h, the mixture becoming black. Then, the mixture was quenched with water (10 mL), extracted with EtOAc (3 x 10 mL), and the combined organic phases were dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude was purified by flash chromatography on silica gel (petroleum ether/Et_2O, 8:2) to give **8a** as a colorless oil (m = 18 mg, yield = 41%). **R*f***: 0.33 (9:1 cyclohexane/AcOEt).**^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] =7.35-7.28 (m, 3H), 7.03-6.98 (m, 2H), 5.72 (s, 2H), 3.98-3.87 (m, 2H), 2.48 (t, *J* = 7.4 Hz, 1H), 2.27 (td, *J* = 6.9, 2.7 Hz, 2H), 2.23-2.16 (m, 1H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.91-1.79 (m, 2H), 1.74-1.63 (m, 2H), 1.61(s, 3H), 1.58-1.45 (m, 2H), 1.34 (s, 3H), 1.28 (s, 3H), 1.03 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ [ppm] = 173.2, 150.9, 138.3, 136.9, 128.9, 127.9, 126.5, 83.3, 69.9, 69.4, 54.5, 49.4, 45.9, 35.0, 33.8, 33.0, 31.9, 31.6, 31.2, 31.1, 27.7, 23.8, 18.0. **HRMS (ESI)** $C_{25}H_{33}N_3O_2$ calculated for [M+Na]: 430.2464 found 430.2470.

Click-product 8b



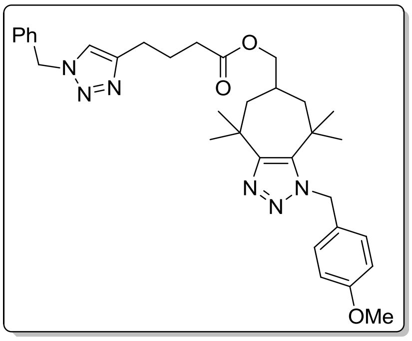
To a solution of complex **7** (0.107 mmol, 60 mg, 1 equiv.) and *p*$MeOC_6H_4CH_2N_3$ (0.22 mmol, 36 mg, 2 equiv.) in CH_3CN (C = 0.05 M) under nitrogen was added TMANO (0.55 mmol, 41 mg, 5 equiv.) at 0°C. The solution was stirred at r.t. for 16 h, the mixture becoming black. Then, the mixture was quenched with water (10 mL), extracted with EtOAc (3 x 10 mL), and the combined organic phases were dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude was purified by flash chromatography on silica gel (petroleum ether/Et_2O, 8:2) to give **8b** as a colorless oil (m= 21 mg, yield = 45%). **R*f***: 0.29 (8:2 petroleum ether/AcOEt).**^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 6.96 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.74-5.58 (m, 2H), 3.92 (dd, *J* = 6.7, 3.6 Hz, 2H), 3.79 (s, 3H), 2.48 (t, *J* = 7.4 Hz, 2H), 2.27 (td, *J* = 6.9, 2.7 Hz, 2H), 2.24-2.17 (m, 1H), 1.97 (t, *J* = 2.7 Hz, 1H), 1.88-1.81 (m, 2H), 1.73-1.61 (m, 2H), 1.60 (s, 3H), 1.54-1.45 (m, 2H), 1.36 (s, 3H), 1.27 (s, 3H), 1.02 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ [ppm] =173.2, 159.3, 150.9, 138.2, 128.8, 127.9, 114.3, 83.3, 69.9, 69.4, 55.4, 54.1, 49.4, 45.9, 34.9, 33.8, 33.0, 31.9, 31.6, 31.2, 27.7, 23.8, 18.0, 1.2. **HRMS (ESI)** $C_{26}H_{35}N_3O_3$ calculated for [M+Na]: 460.2570 found 460.2574.

Click-product 9a



To a solution of **8a** (0.022 mmol, 9 mg, 1 equiv.) and *p*$MeOC_6H_4CH_2N_3$ (0.026 mmol, 4.3 mg, 1.2 equiv.) in *t*BuOH/H_2O (3:1, C = 0.05 M) under nitrogen was added $CuSO_4$ (2.6 µmol, 0.4 mg, 0.1 equiv.) and sodium ascorbate (0.026 mmol, 5.2 mg, 1 equiv.). The solution was stirred at r.t. for 16 h. Then, the mixture was quenched with water (10 mL), extracted with EtOAc (3 x 10 mL), and the combined organic phases were dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude was purified by flash chromatography on silica gel (dichloromethane/MeOH, 95:5) to give **9a** as a colorless oil (m = 8 mg, yield = 64%). **R*f***: 0.59 (95:5 dichloromethane/MeOH).**^{1}H NMR** (300 MHz, $CDCl_3$): δ [ppm] = 7.36-7.28 (m, 3H), 7.23-7.13 (m, 3H), 7.03-6.96 (m, 2H), 6.91-6.85 (m, 2H), 5.71 (s, 2H), 5.41 (s, 2H), 3.92-3.87 (m, 2H), 3.80 (s, 3H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.38 (t, *J* = 7.5 Hz, 2H), 2.26-2.16 (m, 1H), 2.04-1.91 (m, 2H), 1.67 (d, *J* = 13.6 Hz, 2H), 1.60 (s, 3H), 1.56-1.45 (m, 2H), 1.32 (s, 3H), 1.26 (s, 3H), 1.01 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ [ppm] =173.4, 160.0, 150.9, 147.6, 138.4, 136.9, 129.7, 128.9, 127.9, 126.9, 126.5, 120.6, 114.6, 69.8, 55.5, 54.5, 53.8, 49.3, 45.9, 34.9, 33.8, 33.7, 31.9, 31.6, 31.2, 31.1, 27.7, 25.2, 24.8. **HRMS (ESI)** $C_{33}H_{42}N_6O_3Na$ calculated for [M+Na]: 593.3210 found 593.3201.

Click-product 9b



Via sequence B

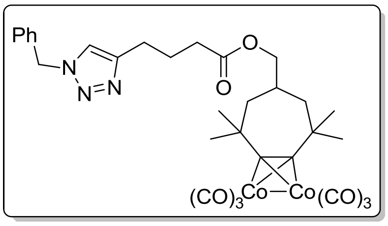
To a solution of **8b** (0.085 mmol, 37 mg, 1 equiv.) and BnN_3 (0.11 mmol, 15 mg, 1.3 equiv.) in *t*BuOH/H_2O (3:1, C = 0.05 M) under nitrogen was added $CuSO_4$ (0.01 mmol, 1.5 mg, 0.1 equiv.) and sodium ascorbate (0.085 mmol, 17 mg, 1 equiv.). The solution was stirred at r.t. for 16 h. Then, the mixture was quenched with water (10 mL), extracted with EtOAc (3 x 10 mL), and the combined organic phases were dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude was purified by flash chromatography on silica gel (dichloromethane/MeOH, 95:5) to give **9b** as a colorless oil (m = 20 mg, yield = 41%).

Via sequence C

To a solution of complex **10** (0.028 mmol, 20 mg, 1 equiv.) and *p*MeOC$_6$H$_4$CH$_2$N$_3$ (0.56 mmol, 10 mg, 2 equiv.) in CH$_3$CN (C = 0.05 M) under nitrogen was added TMANO (0.28 mmol, 21 mg, 10 equiv.) at 0°C. The solution was stirred at r.t. for 16 h, the mixture becoming black. Then, the mixture was quenched with water (10 mL), extracted with EtOAc (3 x 10 mL), and the combined organic phases were dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude was purified by flash chromatography on silica gel (dichloromethane/MeOH, 95:5) to give **9b** as a colorless oil (m = 10 mg, yield = 63%)

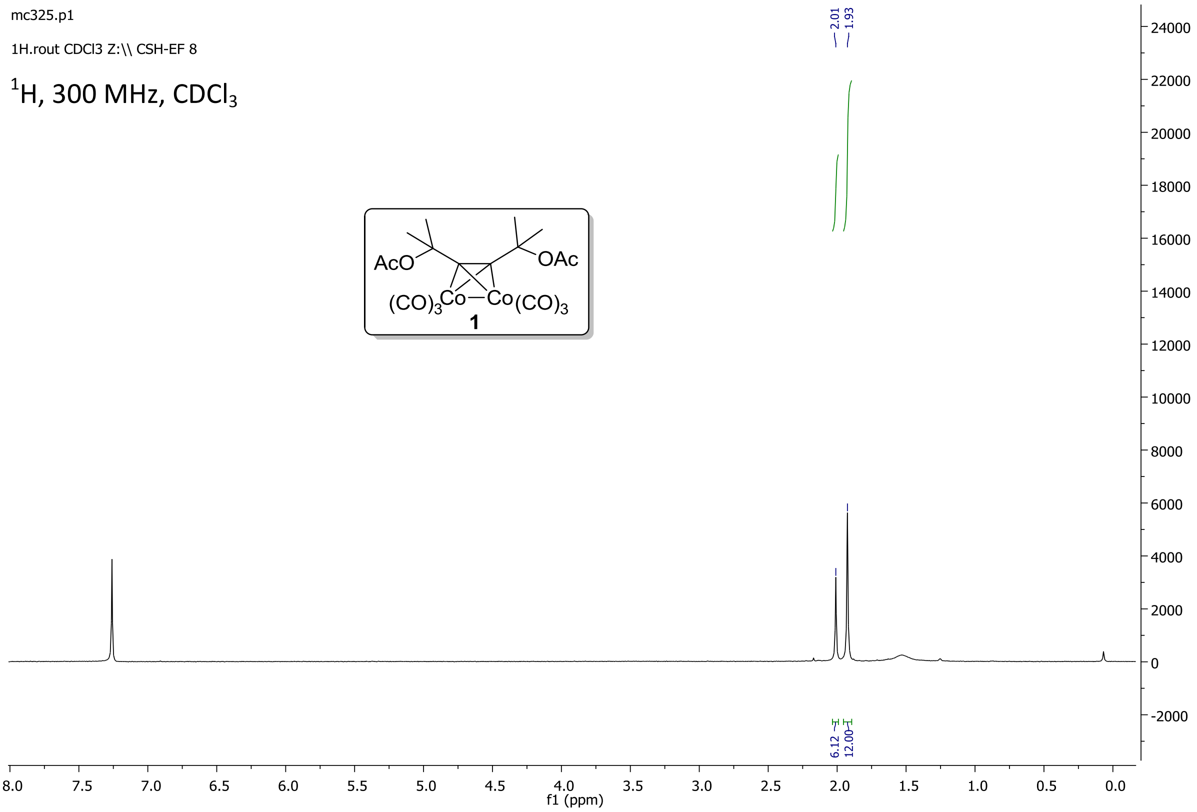
R*f*: 0.61 (95:5 dichloromethane /MeOH).^{1}**H NMR** (300 MHz, CDCl$_3$): δ [ppm] = 7.39-7.33 (m, 3H), 7.25-7.21 (m, 2H), 7.21 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.73-5.56 (m, 2H), 5.49 (s, 2H), 3.96-3.85 (m, 2H), 3.78 (s, 3H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.25-2.15 (m, 1H), 2.02-1.94 (m, 2H), 1.67 (d, *J* = 13.5 Hz, 2H), 1.59 (s, 3H), 1.49 (d, *J* = 13.6 Hz, 2H), 1.35 (s, 3H), 1.25 (s, 3H), 1.00 (s, 3H).^{13}**C NMR** (75 MHz, CDCl$_3$): δ [ppm] = 173.3, 159.2, 150.6, 143.4, 141.4, 138.1, 134.8, 129.1, 128.7, 128.0, 127.7, 120.7, 114.2, 69.7, 55.3, 54.1, 53.9, 49.2, 45.7, 34.9, 33.7, 33.6, 31.8, 31.5, 31.1, 31.0, 27.6, 25.1, 24.7. **HRMS (ESI)** C$_{33}$H$_{42}$N$_6$O$_3$ calculated for [M+Na]: 593.3210 found 593.3214.

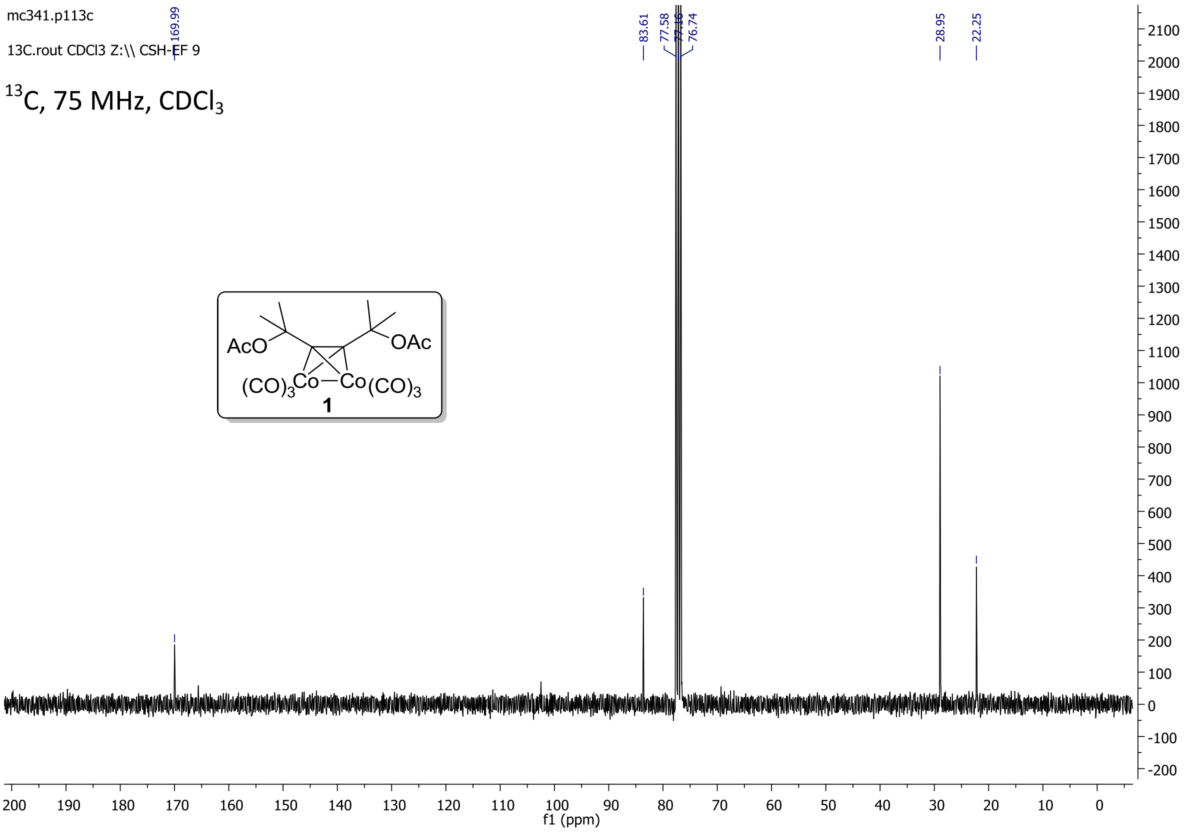
Complex 10

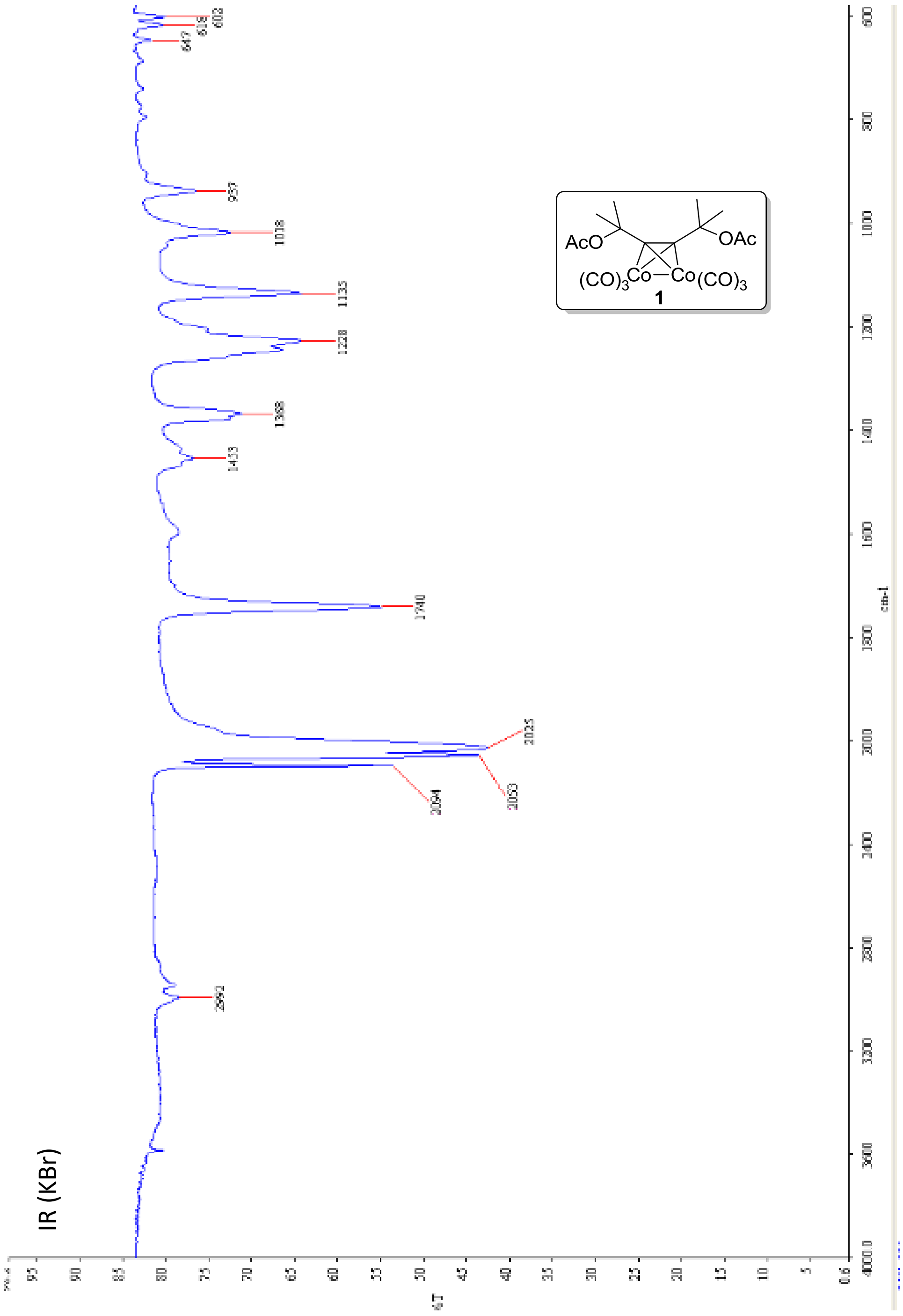


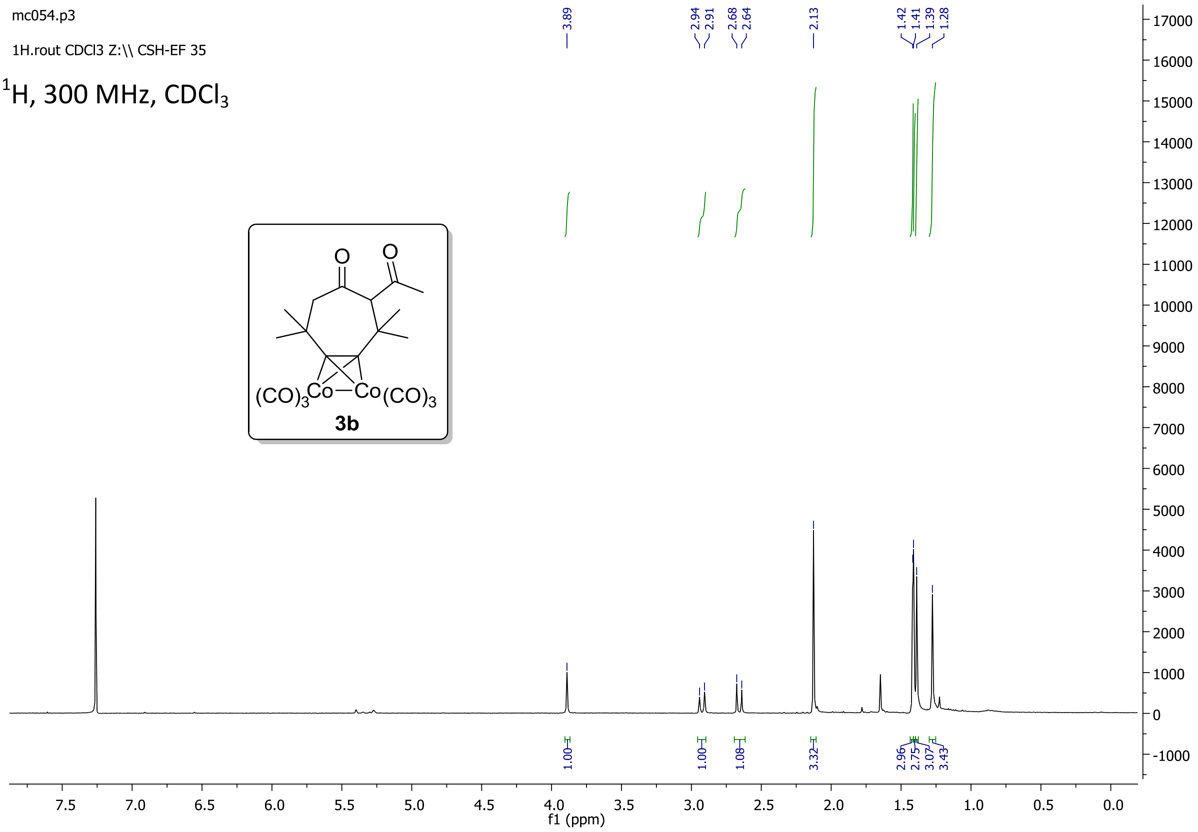
To a solution of complex **7** (0.089 mmol, 50 mg, 1 equiv.) and BnN$_3$ (0.11 mmol, 15 mg, 1.3 equiv.) in *t*BuOH/H$_2$O (3:1, C = 0.05 M) under nitrogen was added the CuSO$_4$ (0.009 mmol, 1.5 mg, 0.1 equiv.) and sodium ascorbate (0.089 mmol, 17 mg, 1 equiv.). The solution was stirred at r.t. for 16 h. Then, the mixture was quenched with water (10 mL), extracted with EtOAc (3 x 10 mL), and the combined organic phases were dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude was purified by flash chromatography on silica gel (petroleum ether/Et$_2$O, 8:2) to give **10** as a red pasty solid (m= 32 mg, yield = 54%). **R*f***: 0.5 (6:4 petroleum ether/AcOEt).^{1}**H NMR** (300 MHz, CDCl$_3$): δ [ppm] = 7.42-7.34 (m, 3H), 7.31-7.23 (m, 2H), 7.21 (s, 1H), 5.49 (s, 2H), 3.88 (d, *J* = 6.4 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.39 (t, *J* = 7.4 Hz, 2H), 2.25-2.11 (m, 1H), 2.07-1.92 (m, 2H), 1.70 (d, *J* = 13.7 Hz, 2H), 1.39 (d, *J* = 13.6 Hz, 2H), 1.27 (s, 12H). ^{13}**C NMR** (75 MHz, CDCl$_3$): δ [ppm] = 173.4, 147.8, 134.9, 129.2, 128.8, 128.2, 120.8, 110.0, 70.2, 54.2, 46.9, 37.8, 33.7, 33.6, 32.3, 31.9, 25.2, 24.7. **HRMS (ESI)** C$_{31}$H$_{33}$Co$_2$N$_3$O$_8$ calculated for [M+]: 693.0932 found 693.0935. **FT-IR (ν/cm^{-1}, KBr):** 2965, 2935, 2086, 2043, 2018, 1734, 1591, 1455, 1380, 1362, 1176, 1050, 858.

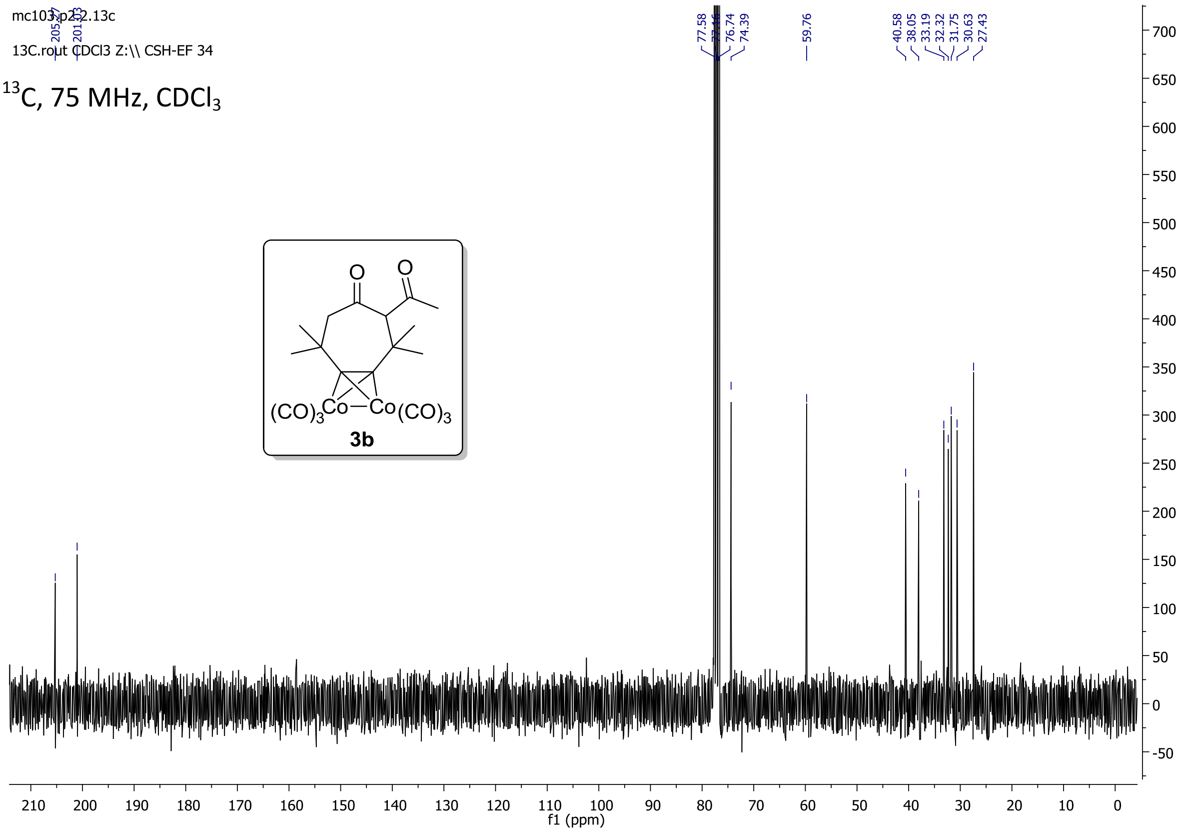
^{1}H, ^{13}C NMR and IR spectra

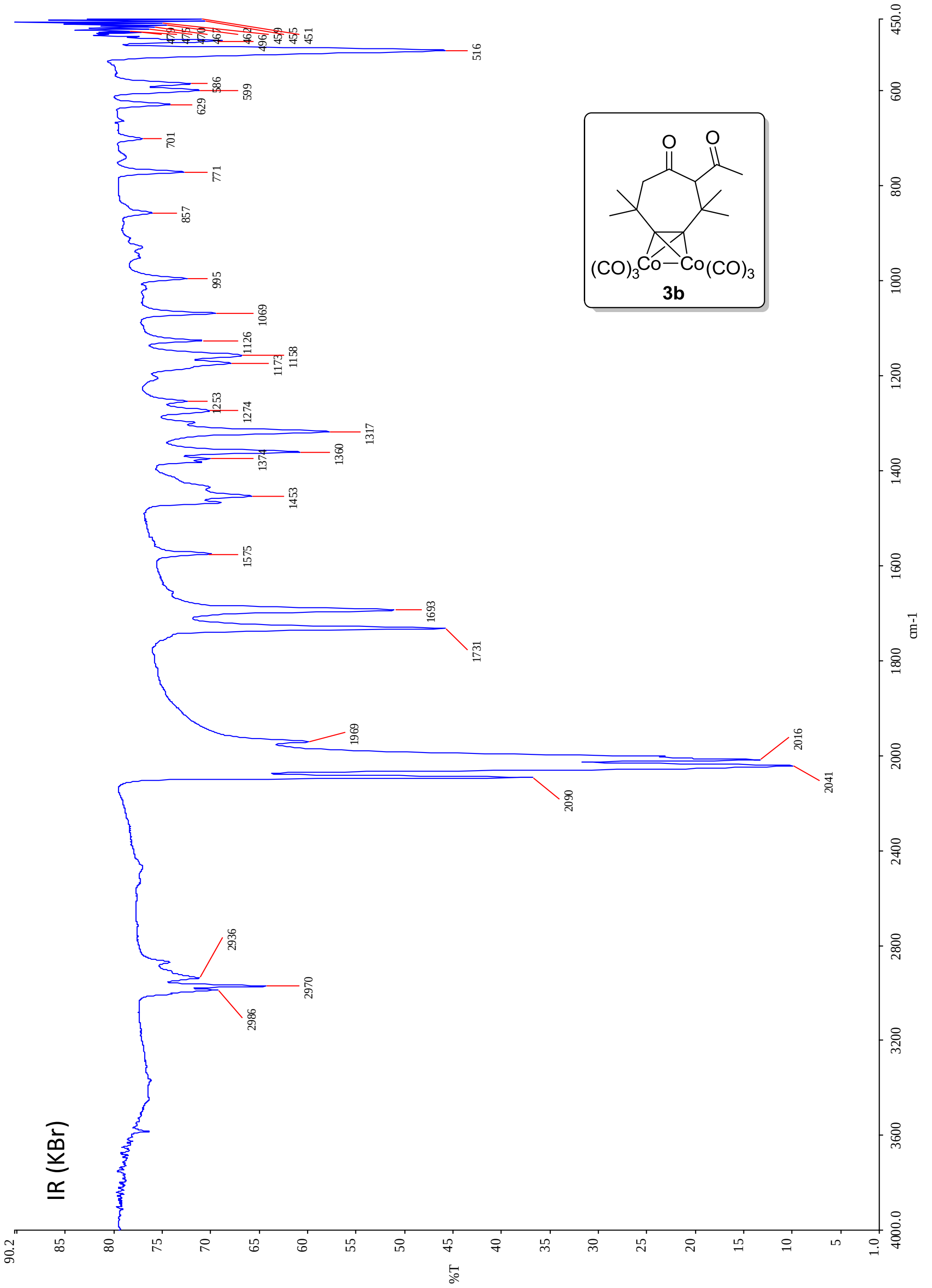


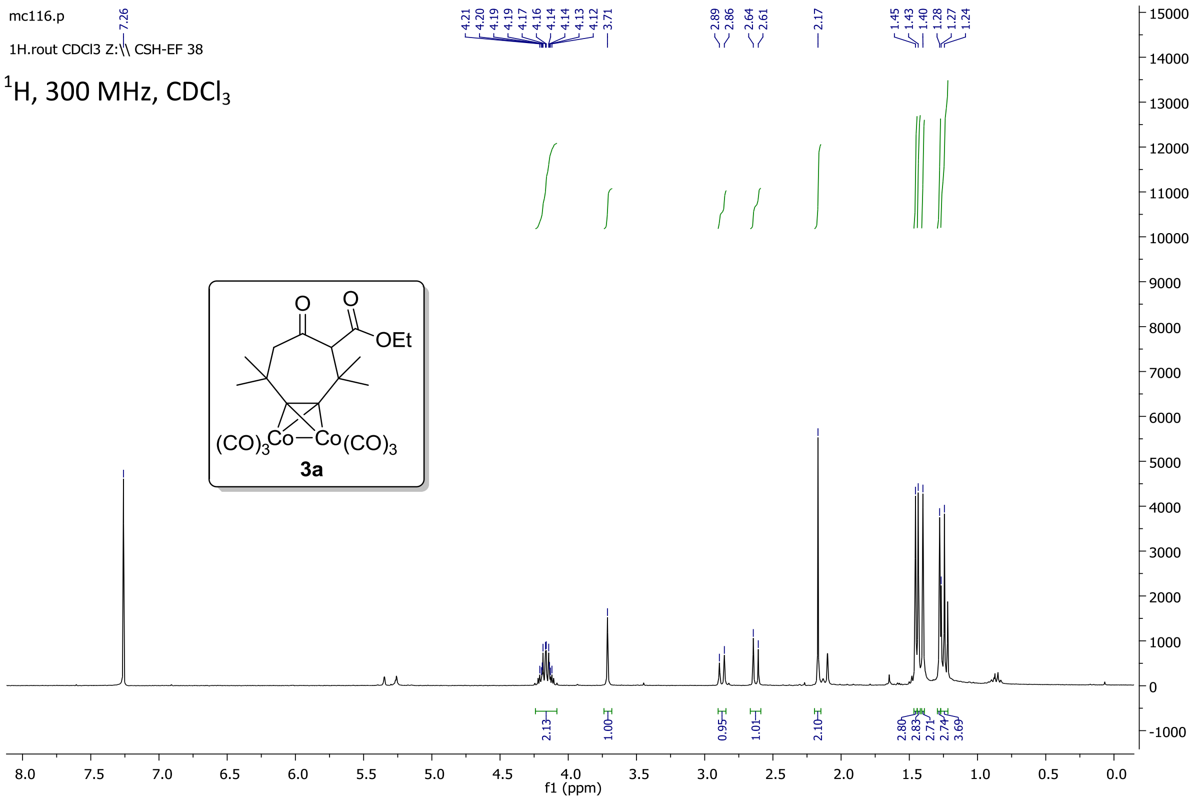


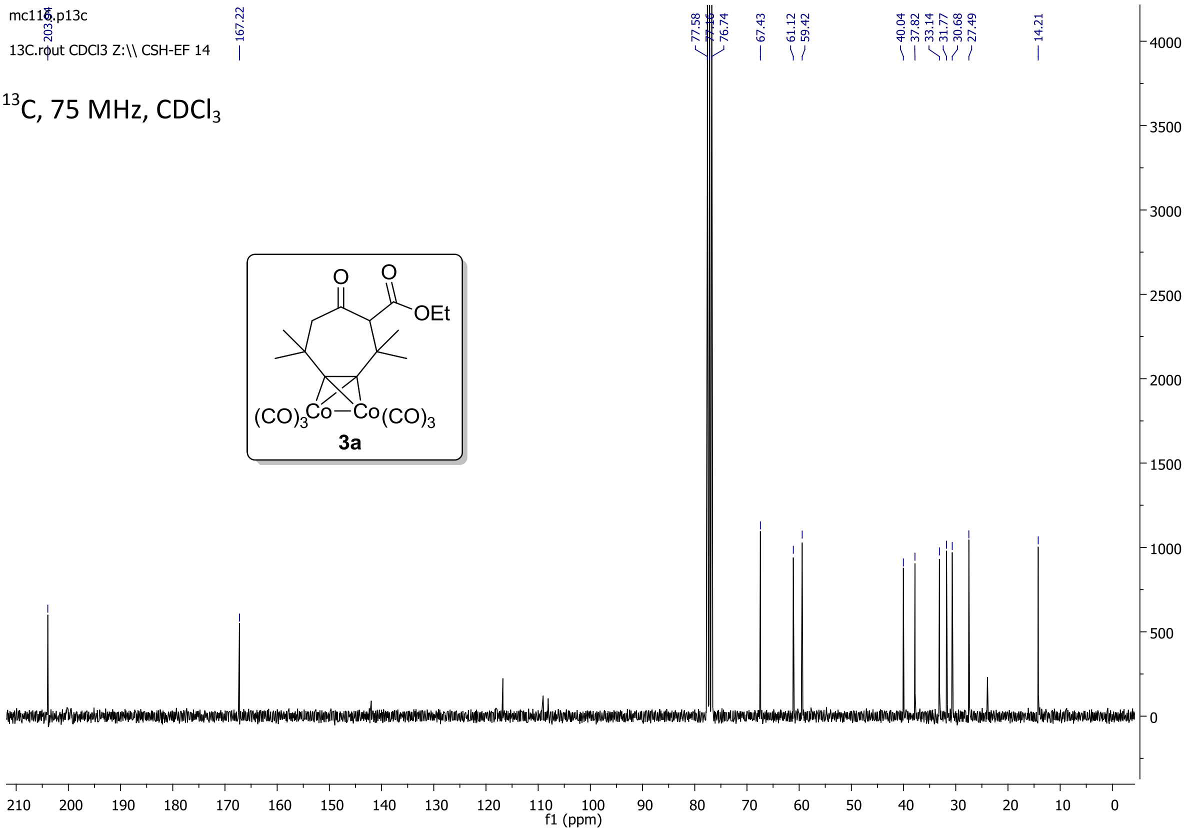

IR (KBr)
%T
cm-1
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
0.6
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
2962
2094
2053
2025
1740
1453
1368
1228
1135
1018
957
647
618
602
AcO
OAc
(CO)3Co
Co(CO)3
1

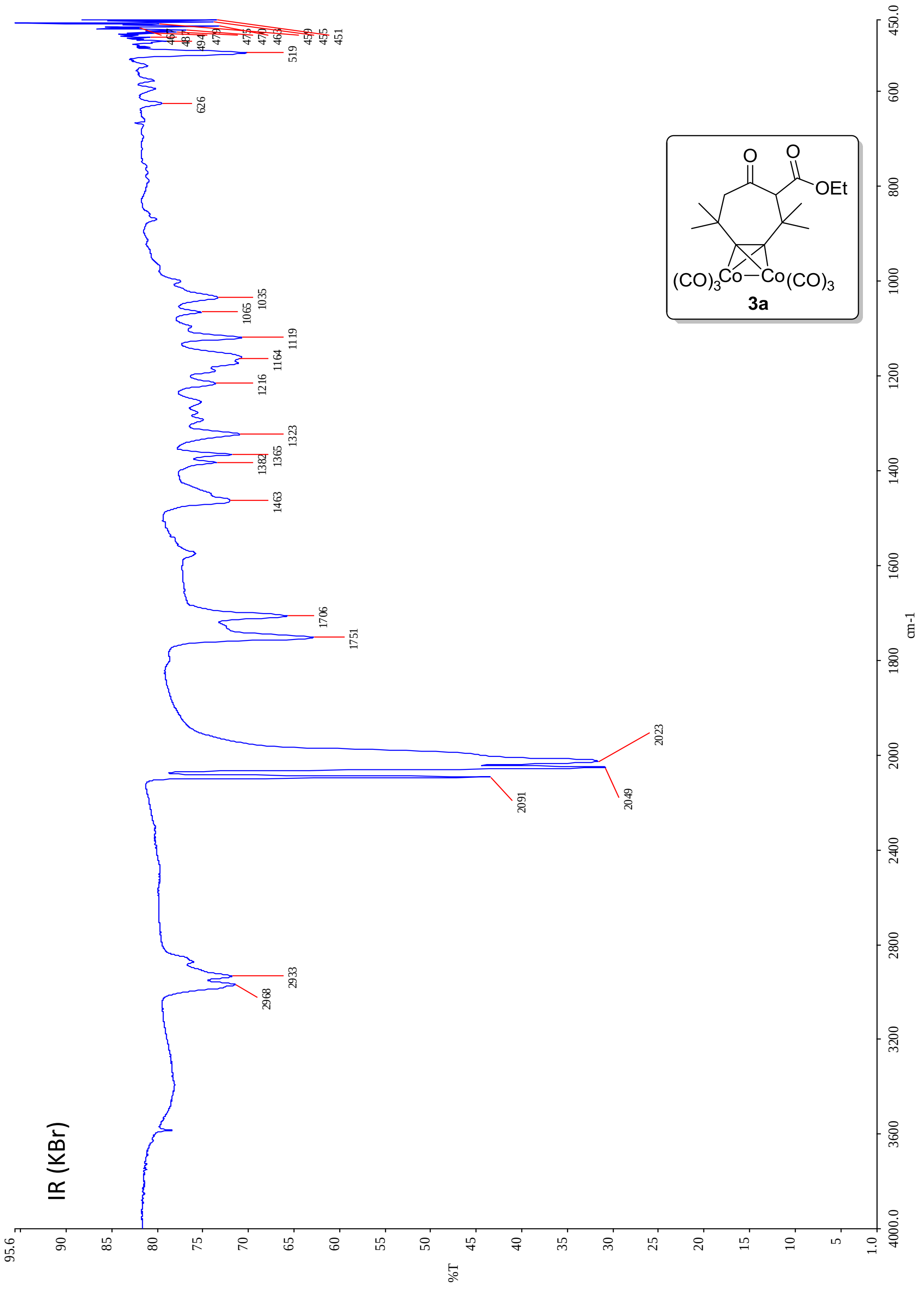

mc054.p3
1H.rout CDCl3 Z:\\ CSH-EF 35
^{1}H, 300 MHz, CDCl$_3$
3.89
2.94
2.91
2.68
2.64
2.13
1.42
1.41
1.39
1.28
O
O
(CO)$_3$Co
Co(CO)$_3$
3b
1.00
1.00
1.08
3.32
2.96
2.75
3.07
3.43
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

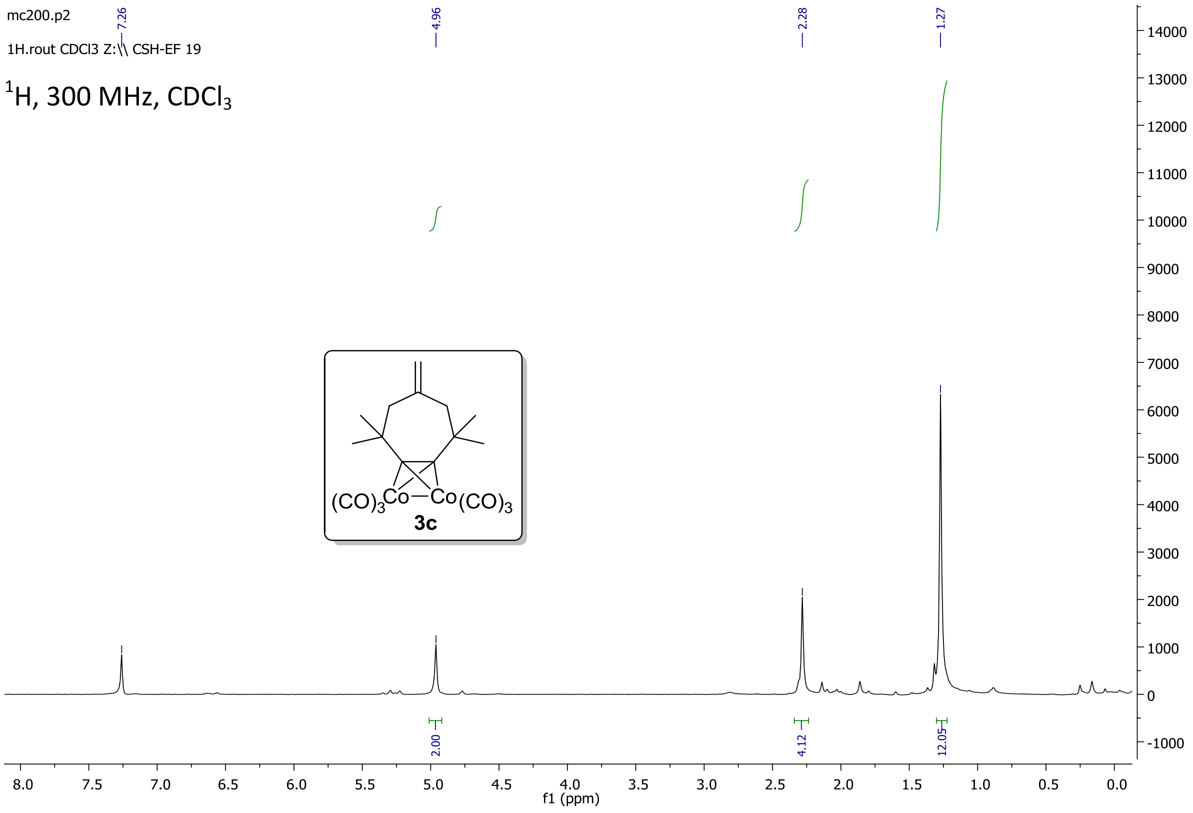

mc103.p2.2.13c
13C.rout CDCl3 Z:\\ CSH-EF 34
^{13}C, 75 MHz, CDCl$_3$
205.27
201.03
77.58
77.16
76.74
74.39
59.76
40.58
38.05
33.19
32.32
31.75
30.63
27.43
O
O
(CO)$_3$Co
Co(CO)$_3$
3b
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

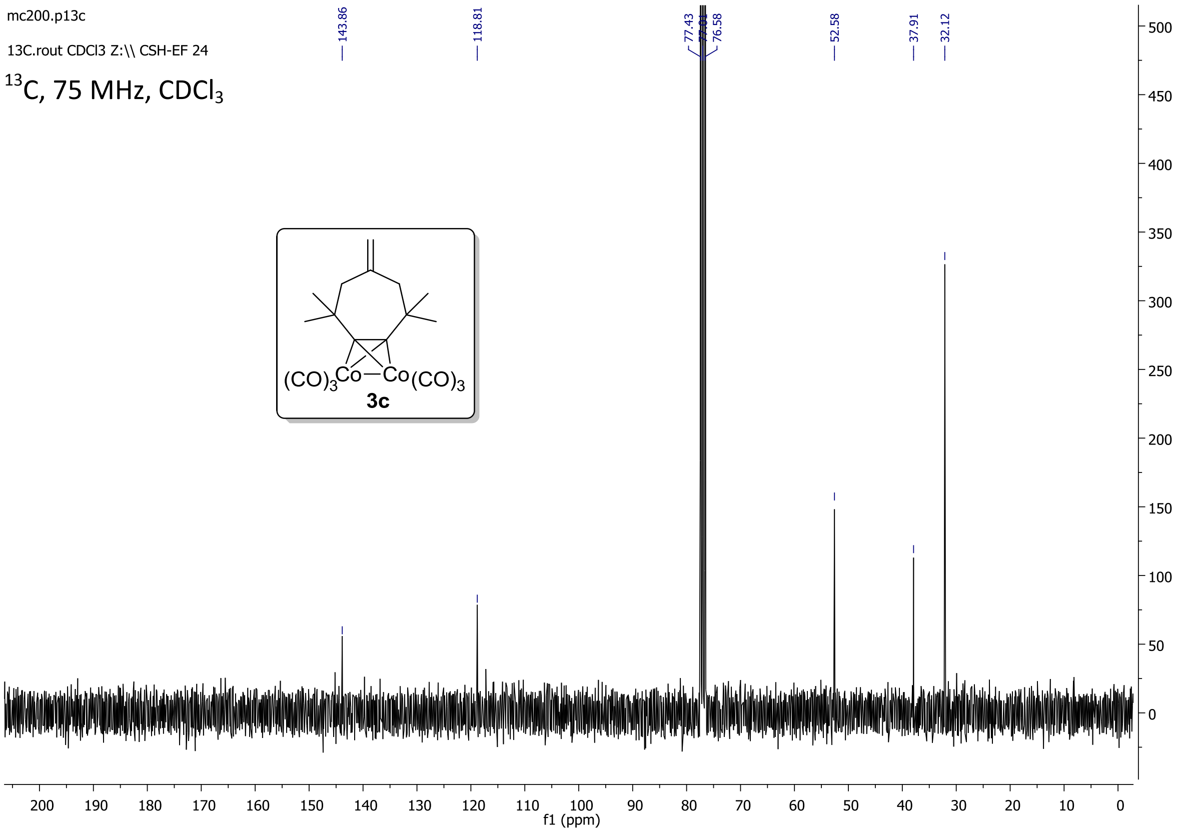

IR (KBr)
%T
cm-1
90.2
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1.0
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
2986
2970
2936
2090
2041
2016
1969
1731
1693
1575
1453
1374
1360
1317
1274
1253
1173
1158
1126
1069
995
857
771
701
629
599
586
516
496
479
475
470
467
462
459
455
451
O
O
$(CO)_3$Co—Co$(CO)_3$
3b

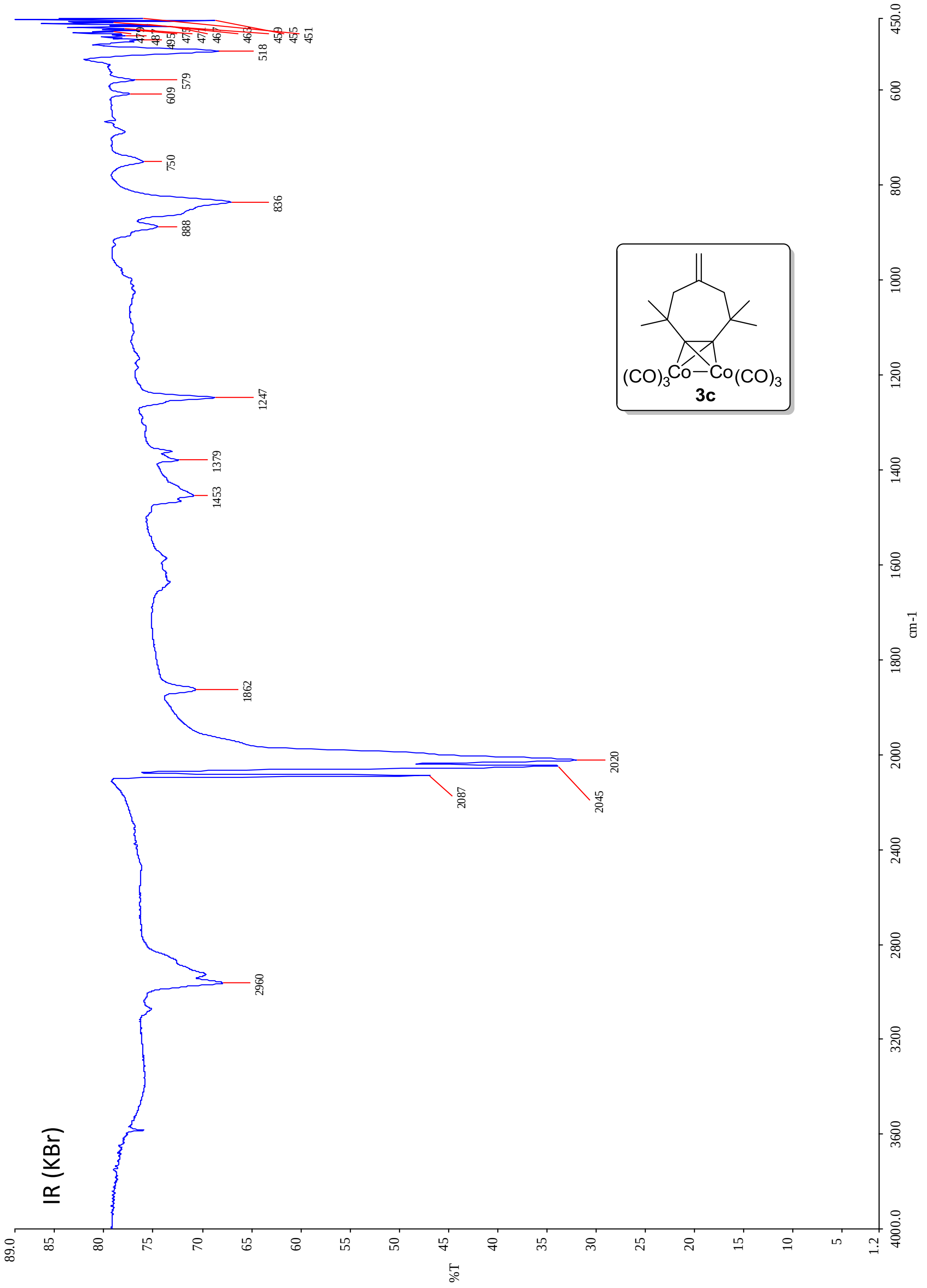

mc116.p
1H.rout CDCl3 Z:\\ CSH-EF 38
^{1}H, 300 MHz, CDCl$_3$
7.26
4.21
4.20
4.19
4.19
4.17
4.16
4.14
4.14
4.13
4.12
3.71
2.89
2.86
2.64
2.61
2.17
1.45
1.43
1.40
1.28
1.27
1.24
O
O
OEt
(CO)$_3$Co
Co(CO)$_3$
3a
2.13
1.00
0.95
1.01
2.10
2.80
2.83
2.71
2.74
3.69
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

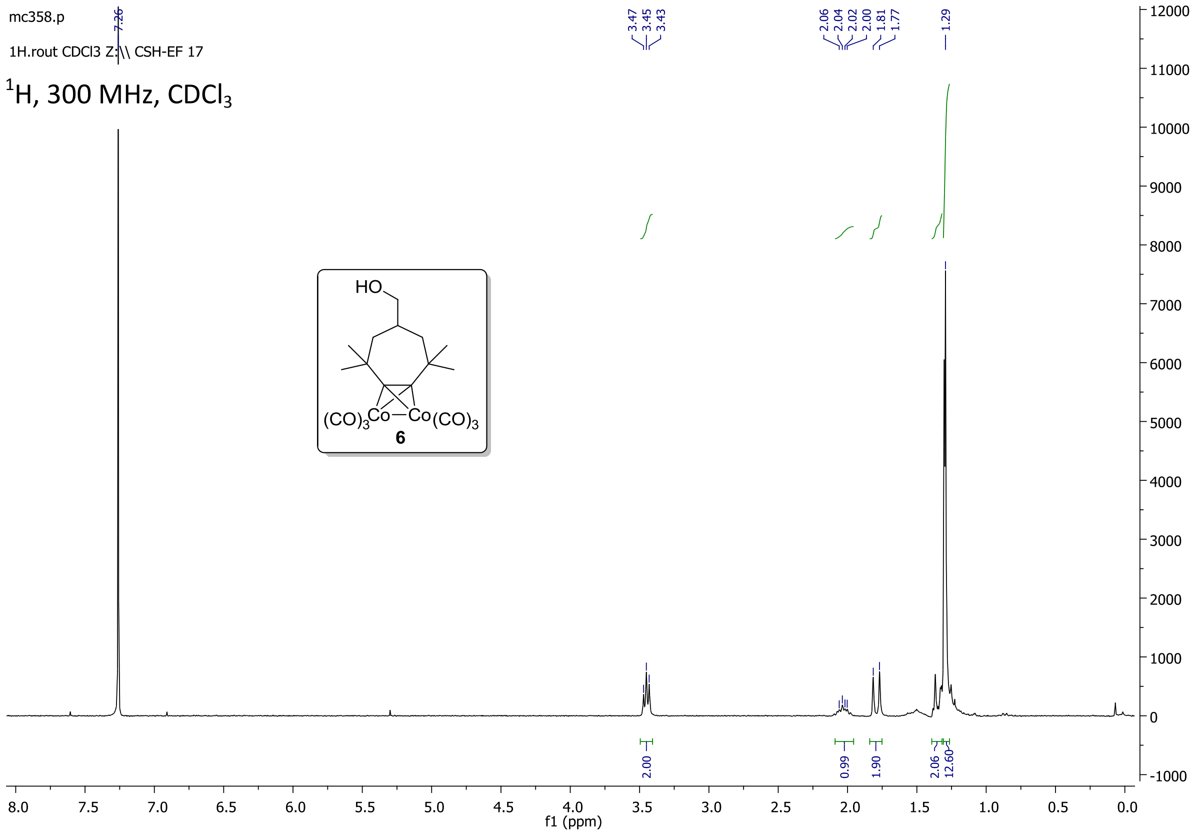

mc116.p13c
13C.rout CDCl3 Z:\\ CSH-EF 14
^{13}C, 75 MHz, CDCl$_3$
203.94
167.22
77.58
77.16
76.74
67.43
61.12
59.42
40.04
37.82
33.14
31.77
30.68
27.49
14.21
O
O
OEt
(CO)$_3$Co
Co(CO)$_3$
3a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0

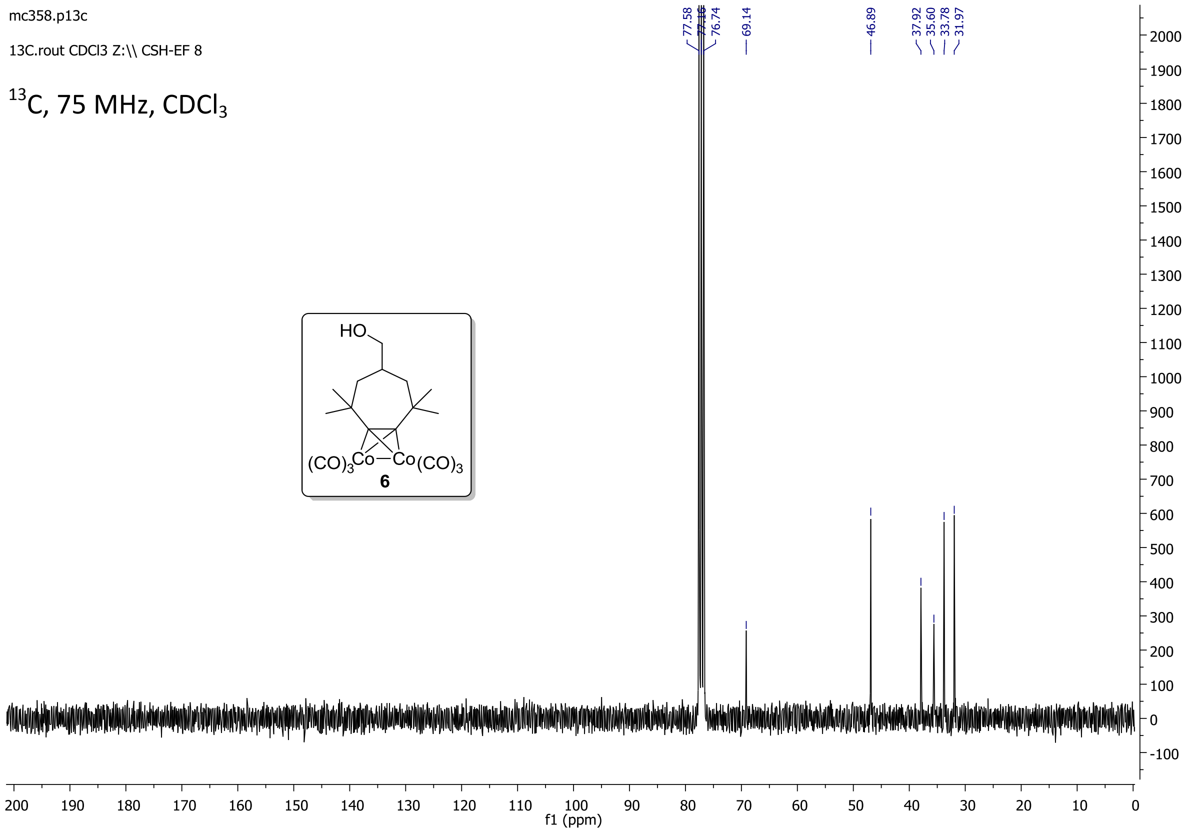

IR (KBr)
%T
cm-1
95.6
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1.0
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
2968
2933
2091
2049
2023
1751
1706
1463
1382
1365
1323
1216
1164
1119
1065
1035
626
519
487
481
494
479
475
470
463
459
455
451
O
O
OEt
(CO)3Co
Co(CO)3
3a

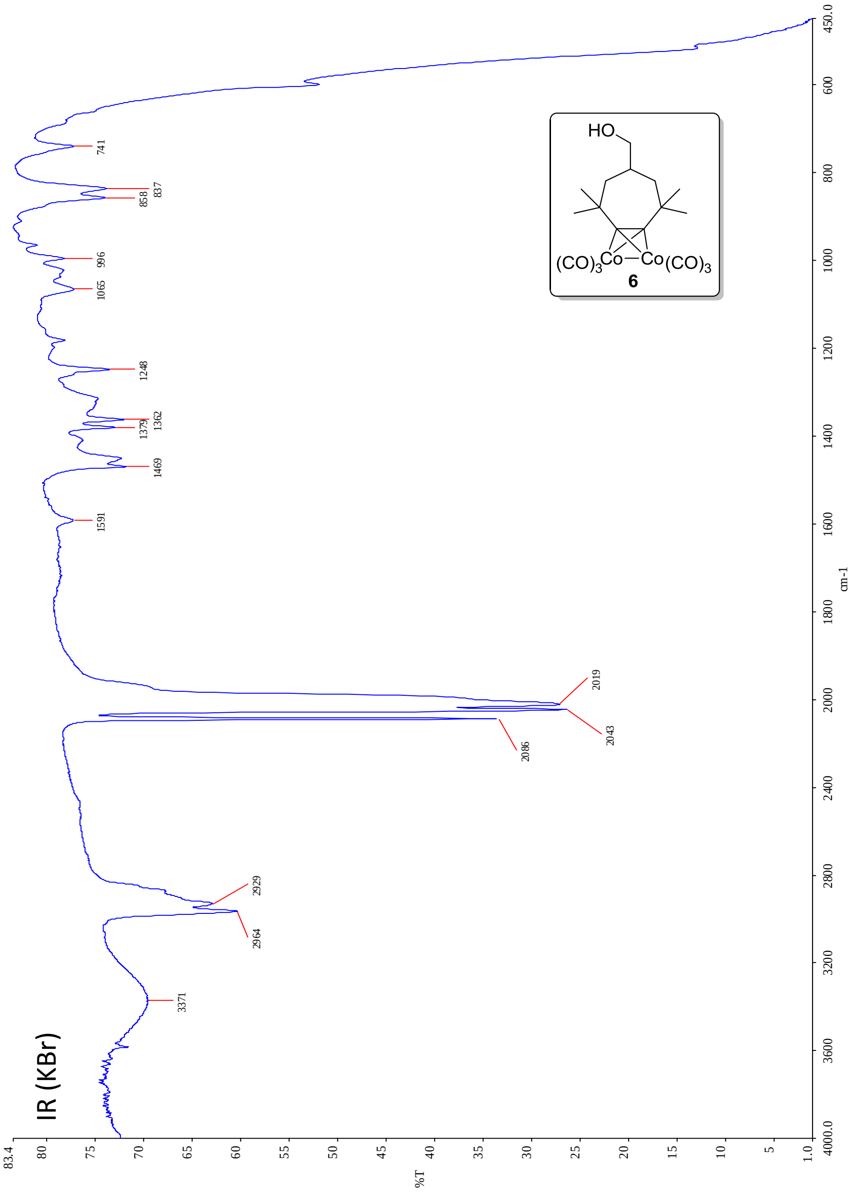

mc200.p2
1H.rout CDCl3 Z:\\ CSH-EF 19
^{1}H, 300 MHz, CDCl$_3$
7.26
4.96
2.28
1.27
(CO)$_3$Co—Co(CO)$_3$
3c
2.00
4.12
12.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

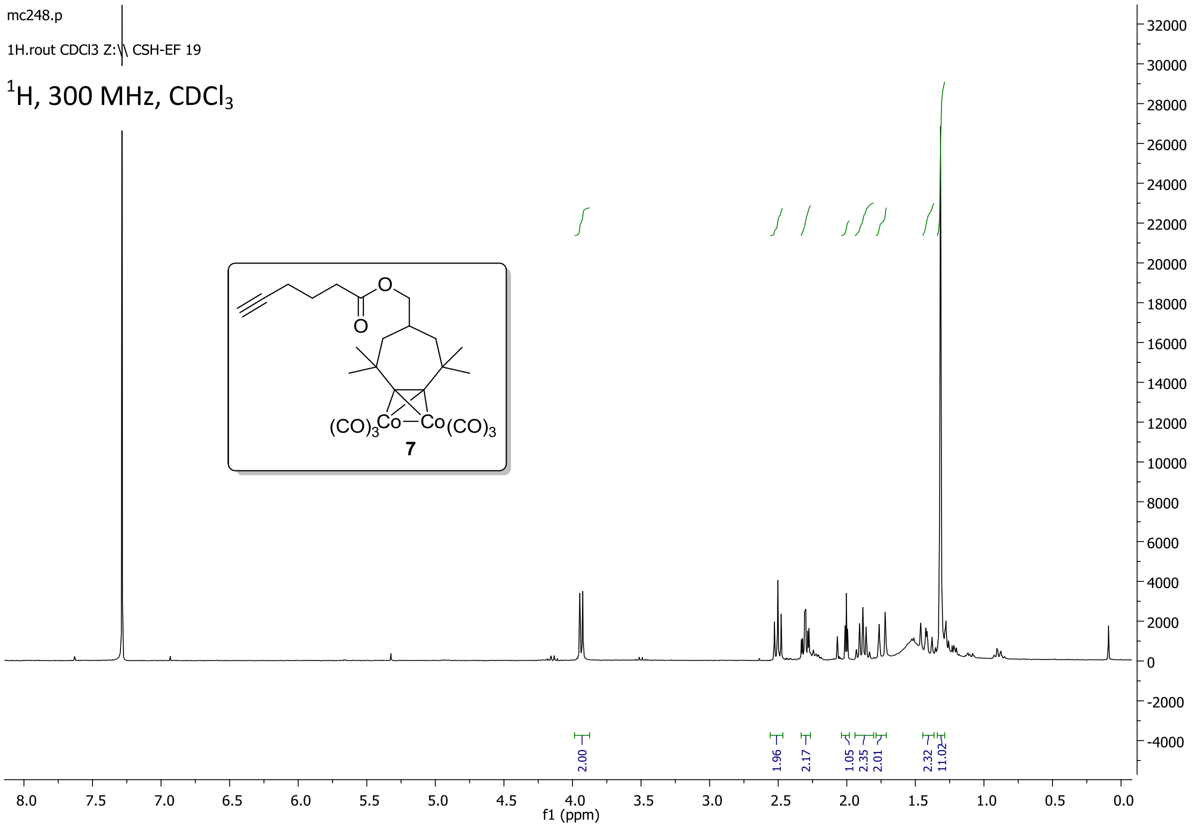

mc200.p13c
13C.rout CDCl3 Z:\\ CSH-EF 24
^{13}C, 75 MHz, CDCl$_3$
143.86
118.81
77.43
77.01
76.58
52.58
37.91
32.12
(CO)$_3$Co—Co(CO)$_3$
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0

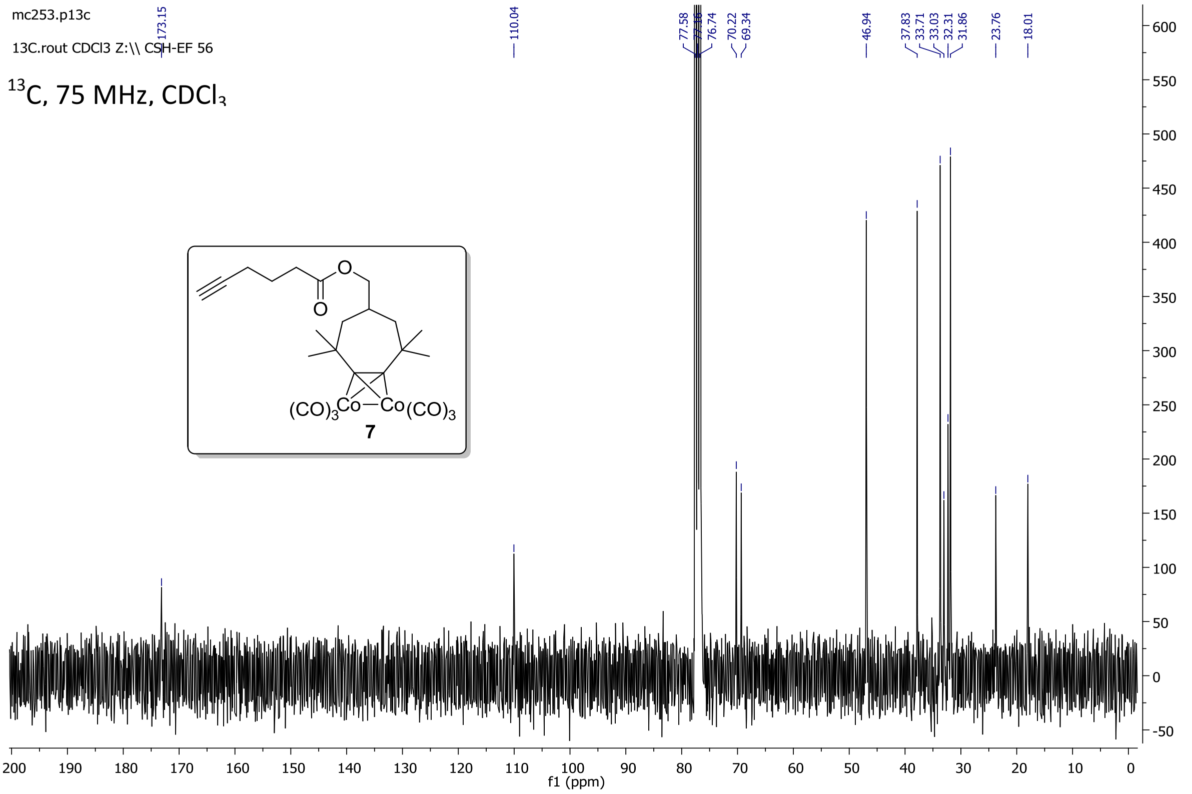

IR (KBr)
%T
cm-1
89.0
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1.2
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
2960
2087
2045
2020
1862
1453
1379
1247
888
836
750
609
579
518
479
487
495
475
471
467
463
459
455
451
(CO)3Co
Co(CO)3
3c

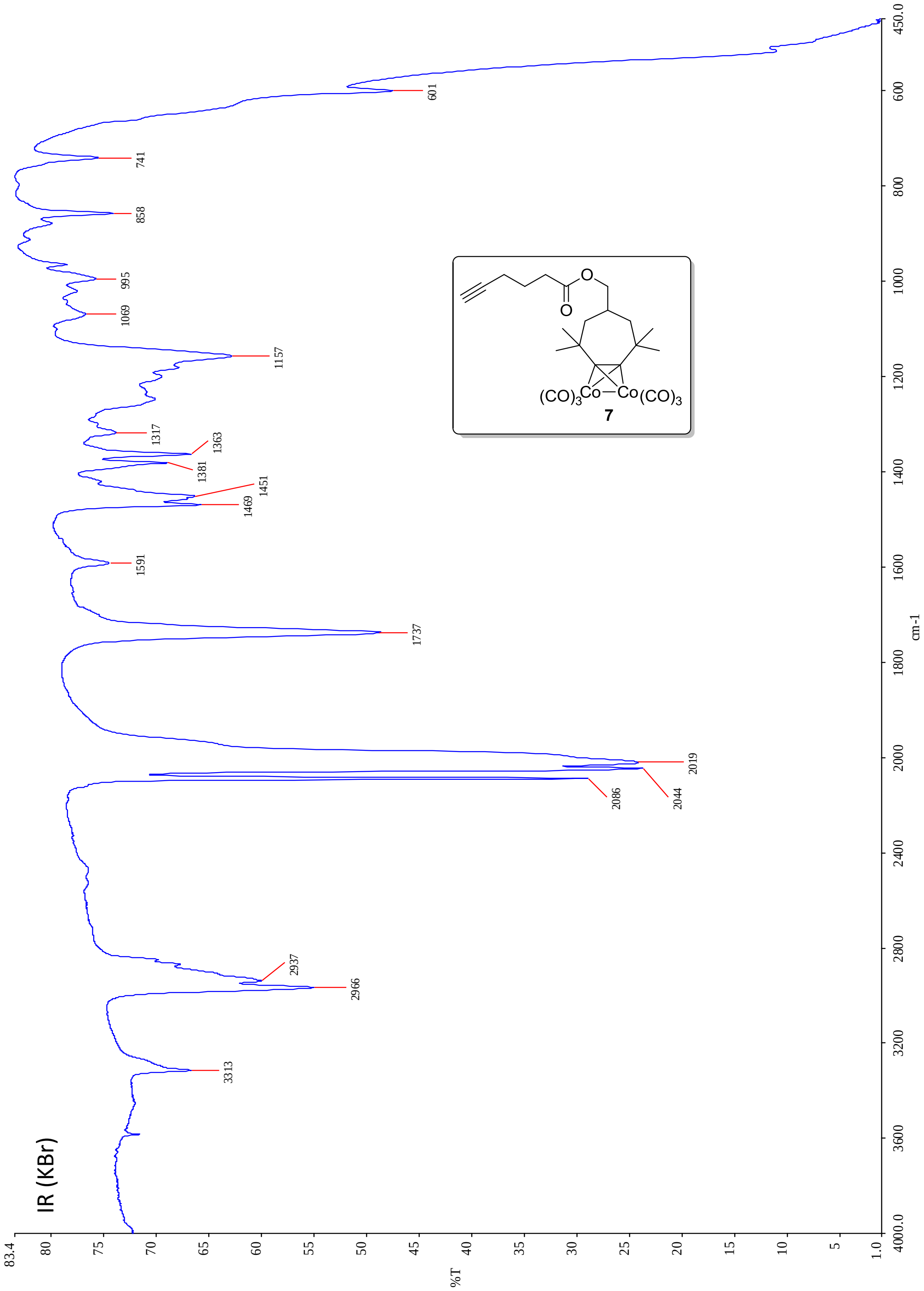

mc358.p
1H.rout CDCl3 Z:\\ CSH-EF 17
^{1}H, 300 MHz, CDCl$_3$
7.26
3.47
3.45
3.43
2.06
2.04
2.02
2.00
1.81
1.77
1.29
HO
(CO)$_3$Co—Co(CO)$_3$
6
2.00
0.99
1.90
2.06
12.60
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000

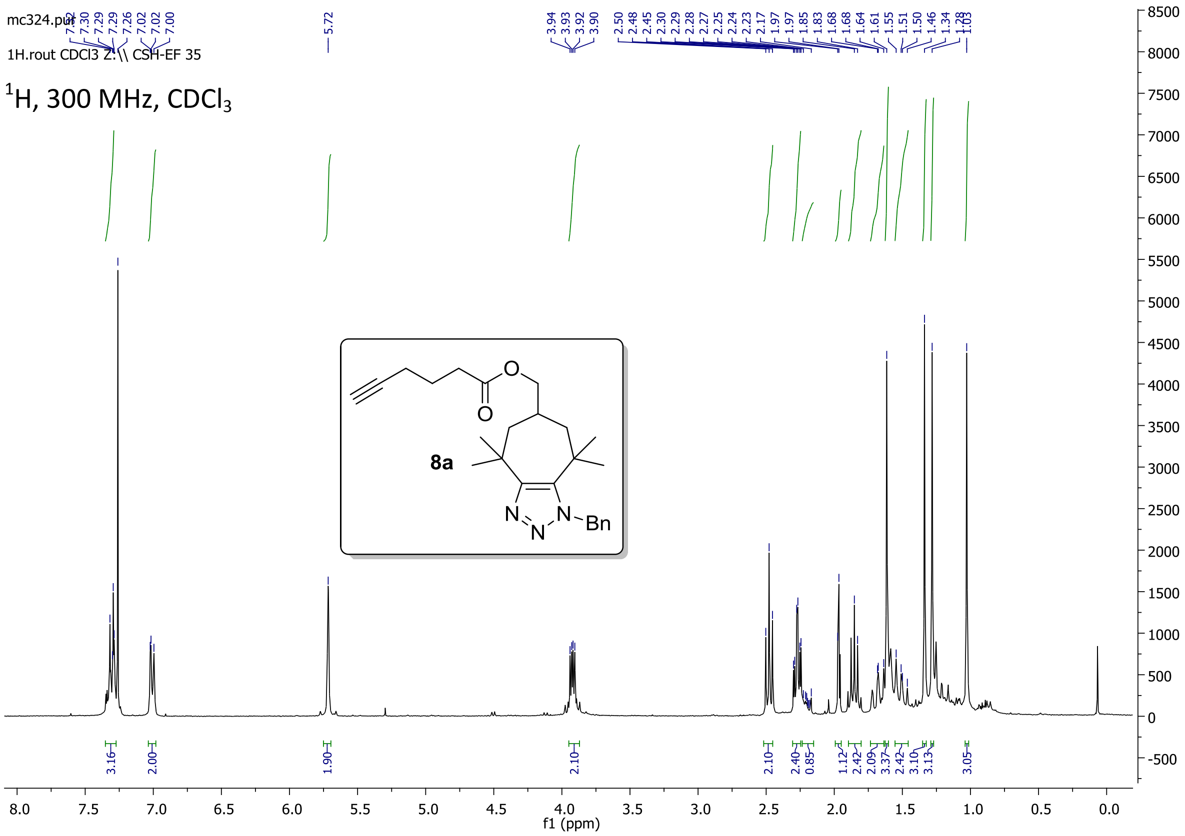

mc358.p13c
13C.rout CDCl3 Z:\\ CSH-EF 8
^{13}C, 75 MHz, CDCl$_3$
77.58
77.16
76.74
69.14
46.89
37.92
35.60
33.78
31.97
HO
(CO)$_3$Co—Co(CO)$_3$
6
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

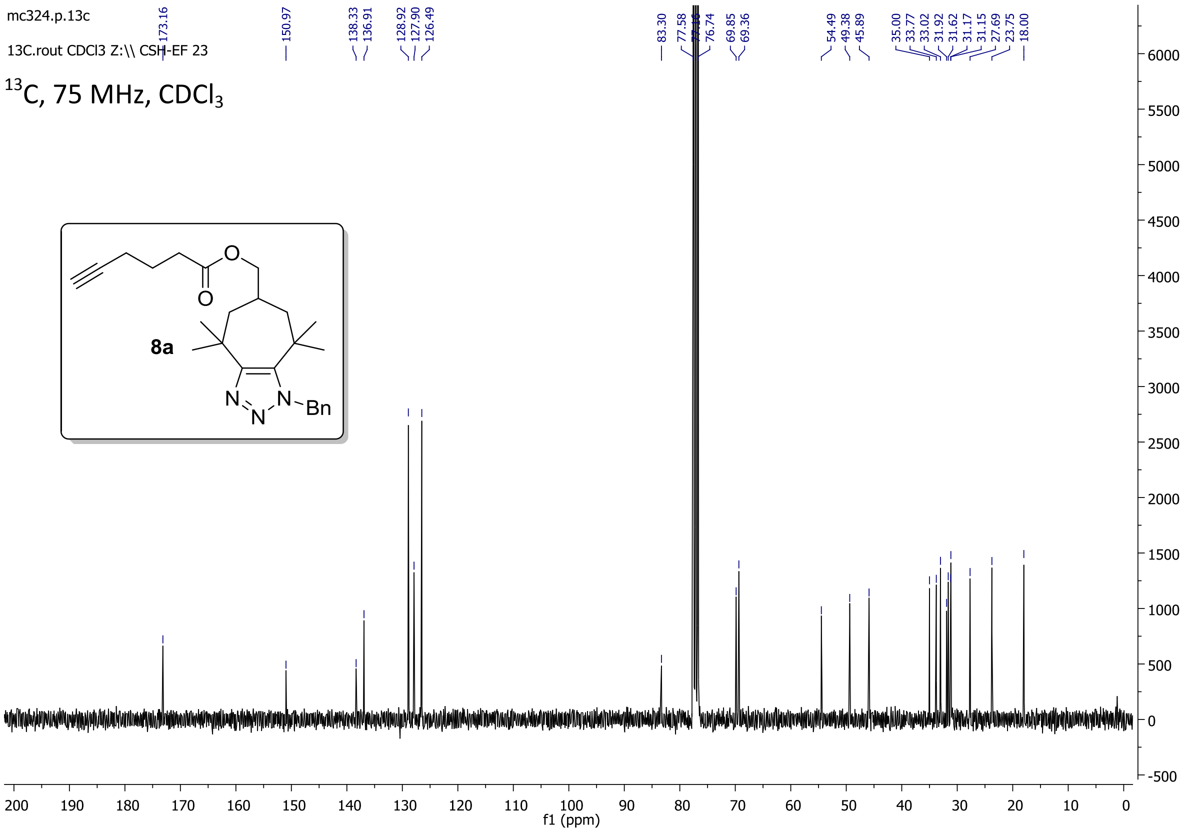

IR (KBr)
%T
cm-1
83.4
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1.0
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
3371
2964
2929
2086
2043
2019
1591
1469
1379
1362
1248
1065
996
858
837
741
HO
(CO)3Co
Co(CO)3
6

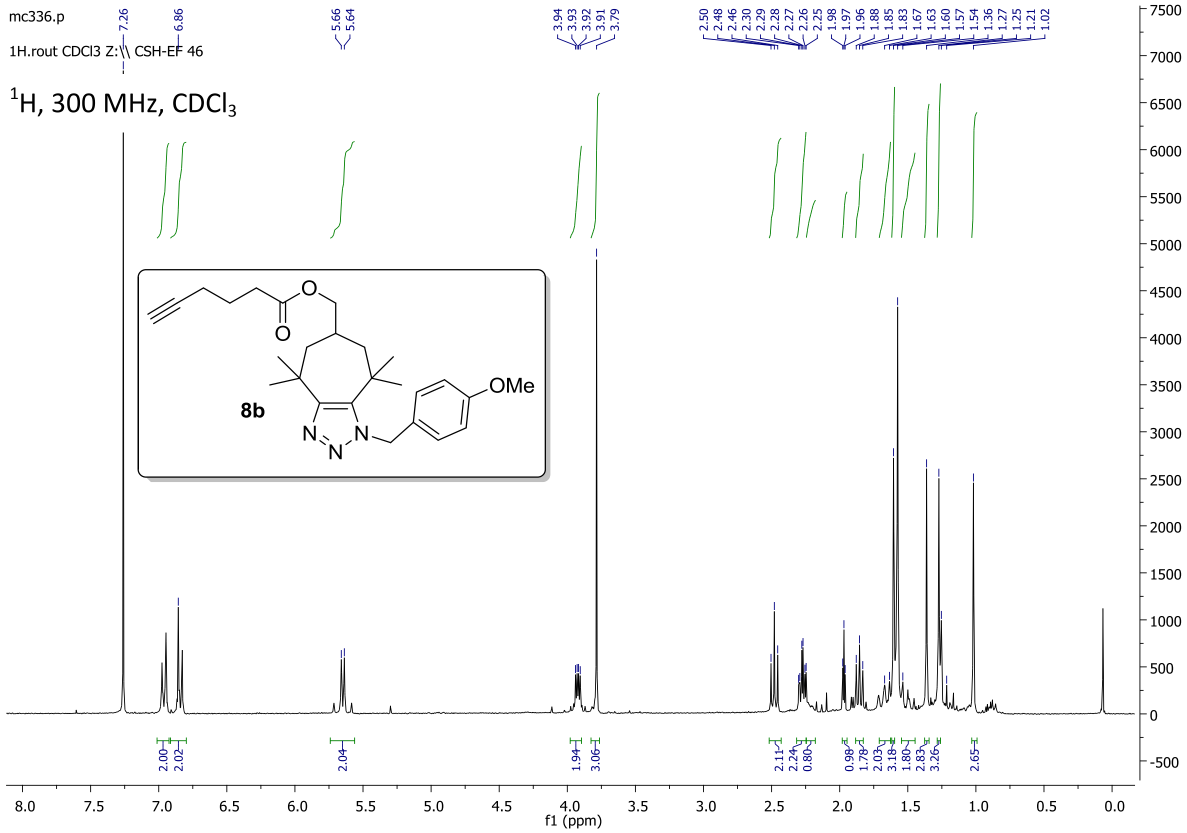

mc248.p
1H.rout CDCl3 Z:\\ CSH-EF 19
^{1}H, 300 MHz, CDCl$_3$
(CO)$_3$Co
Co(CO)$_3$
O
O
7
2.00
1.96
2.17
1.05
2.35
2.01
2.32
11.02
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000

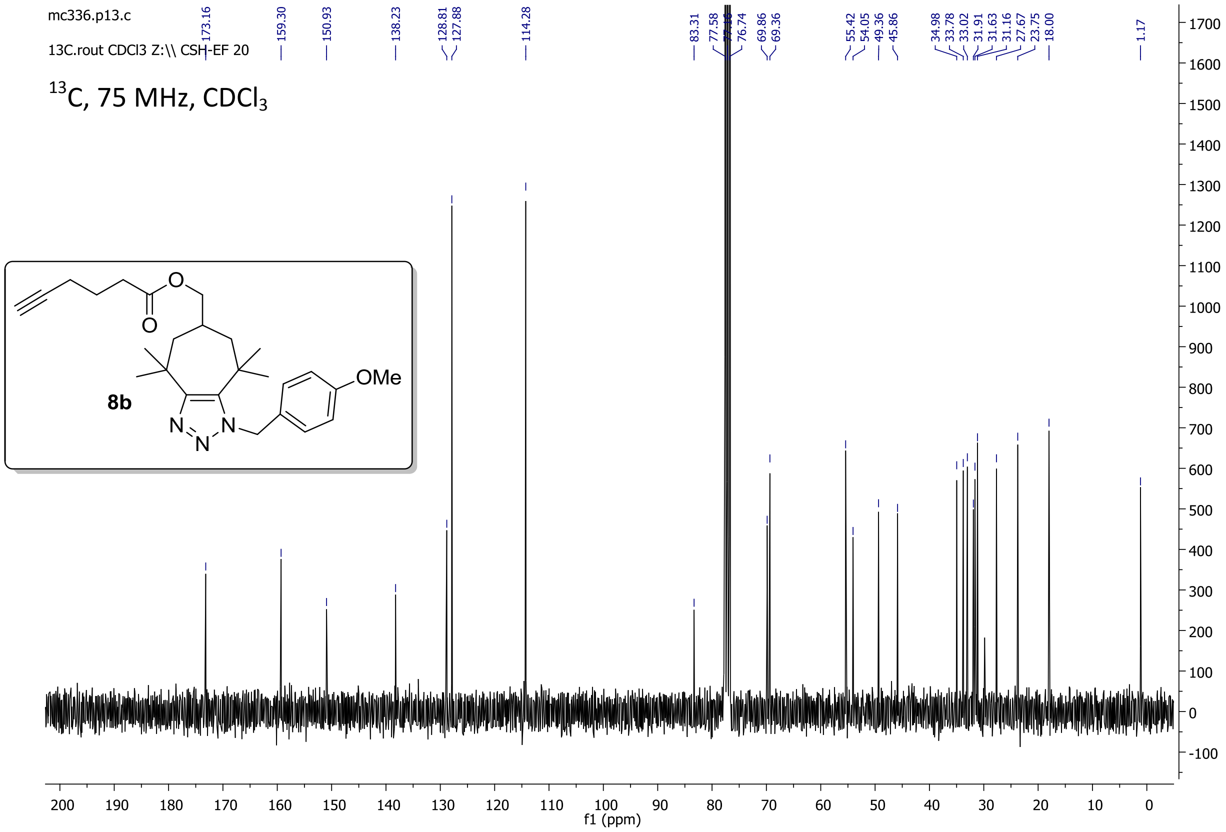

mc253.p13c
13C.rout CDCl3 Z:\\ CSH-EF 56
^{13}C, 75 MHz, CDCl$_3$
173.15
110.04
77.58
77.16
76.74
70.22
69.34
46.94
37.83
33.71
33.03
32.31
31.86
23.76
18.01
(CO)$_3$Co
Co(CO)$_3$
O
O
7
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

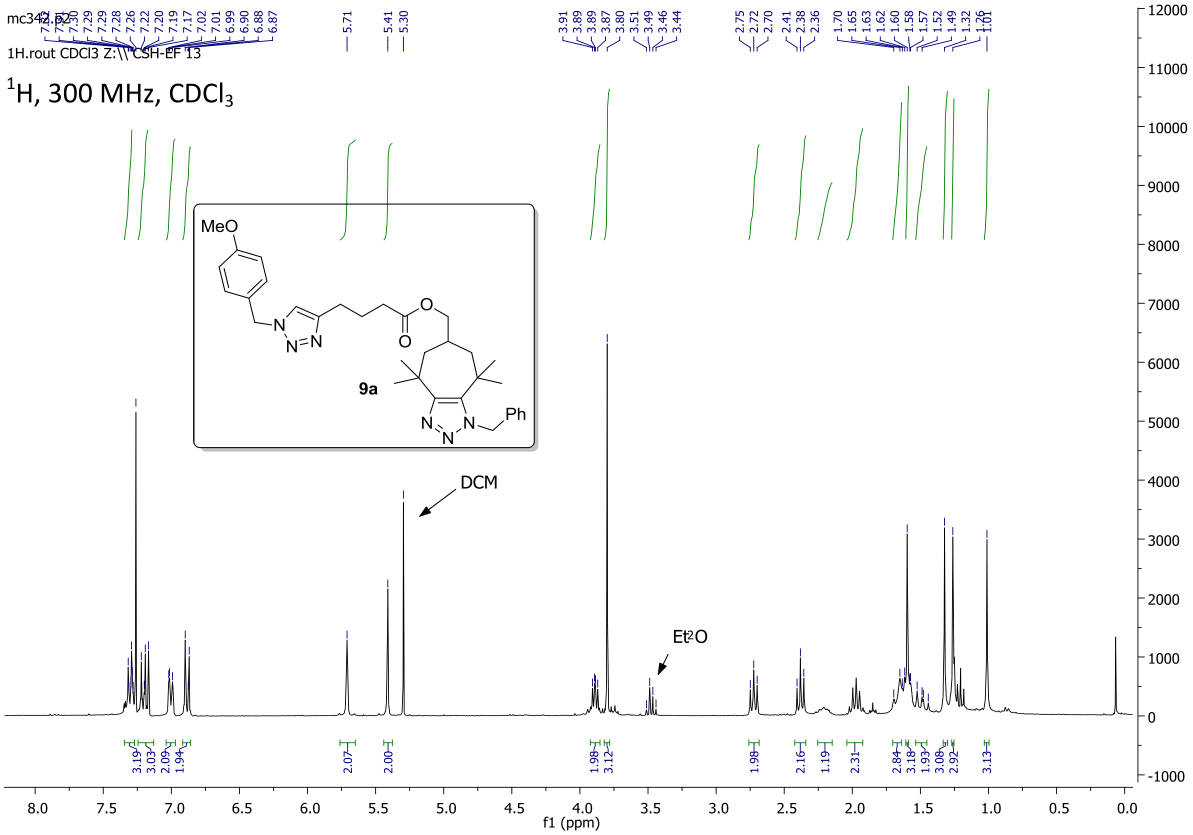

IR (KBr)
%T
cm-1
83.4
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1.0
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
3313
2966
2937
2086
2044
2019
1737
1591
1469
1451
1381
1363
1317
1157
1069
995
858
741
601
O
O
(CO)3Co
Co(CO)3
7

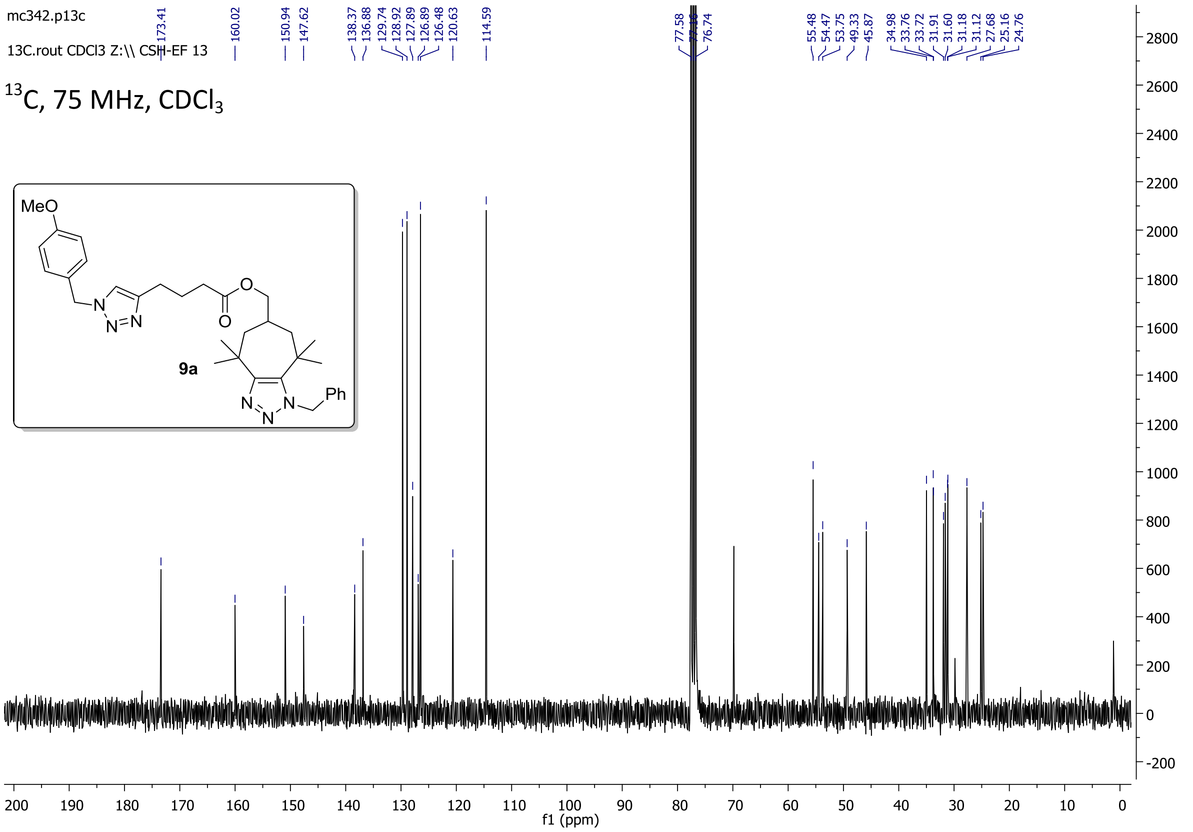

mc324.pur
1H.rout CDCl3 Z:\\ CSH-EF 35
^{1}H, 300 MHz, CDCl$_3$
7.32 7.30 7.29 7.29 7.26 7.02 7.02 7.00 5.72 3.94 3.93 3.92 3.90 2.50 2.48 2.45 2.30 2.29 2.28 2.27 2.25 2.24 2.23 2.17 1.97 1.97 1.85 1.83 1.68 1.68 1.64 1.61 1.55 1.51 1.50 1.46 1.34 1.28 1.03
3.16 2.00 1.90 2.10 2.10 2.40 0.85 1.12 2.42 2.09 3.37 2.42 3.10 3.13 3.05
8a
O
O
N
N
N
Bn
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)
8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

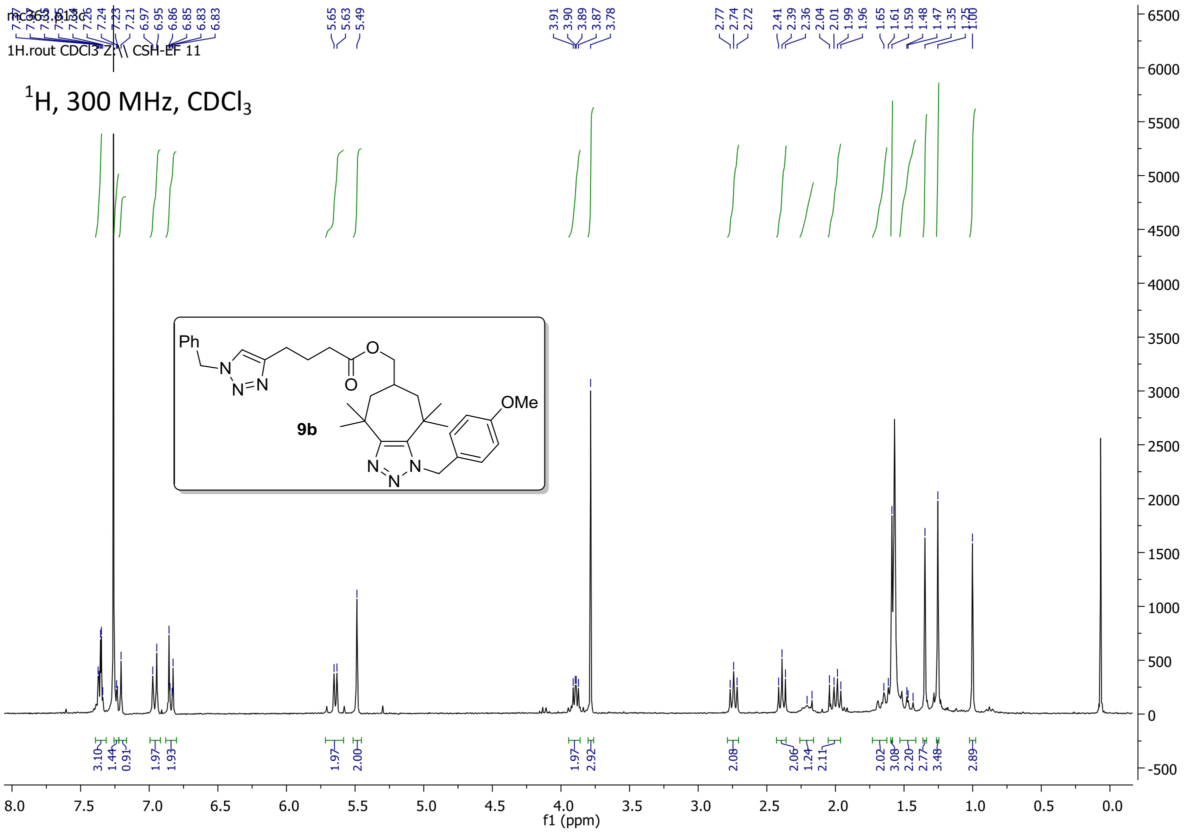

mc324.p.13c
13C.rout CDCl3 Z:\\ CSH-EF 23
^{13}C, 75 MHz, CDCl$_3$
173.16 150.97 138.33 136.91 128.92 127.90 126.49 83.30 77.58 77.16 76.74 69.85 69.36 54.49 49.38 45.89 35.00 33.77 33.02 31.92 31.62 31.17 31.15 27.69 23.75 18.00
8a
O
O
N
N
N
Bn
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

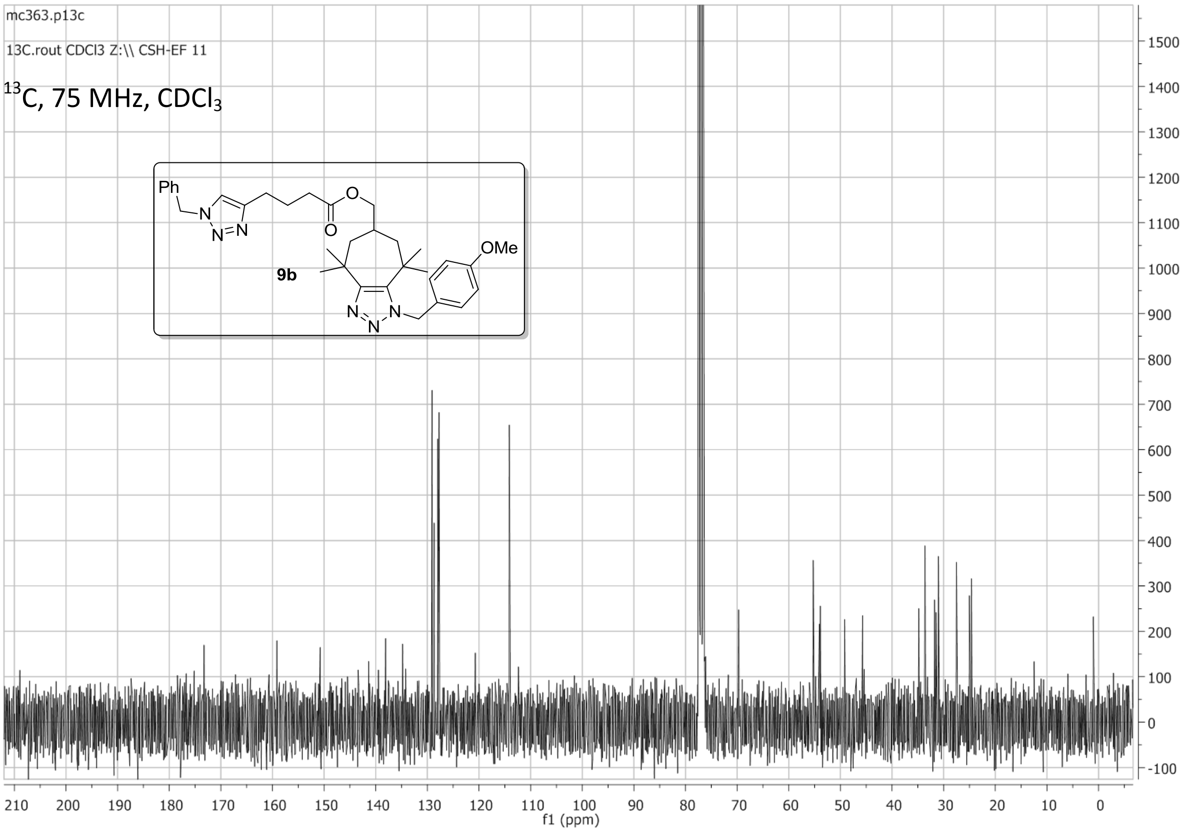

mc336.p
1H.rout CDCl3 Z:\\ CSH-EF 46
^{1}H, 300 MHz, CDCl$_3$
7.26
6.86
5.66
5.64
3.94
3.93
3.92
3.91
3.79
2.50
2.48
2.46
2.30
2.29
2.28
2.27
2.26
2.25
1.98
1.97
1.96
1.88
1.85
1.83
1.67
1.63
1.60
1.57
1.54
1.36
1.27
1.25
1.21
1.02
OMe
O
O
N
N
N
8b
2.00
2.02
2.04
1.94
3.06
2.11
2.24
0.80
0.98
1.78
2.03
3.18
1.80
2.83
3.26
2.65
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)
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

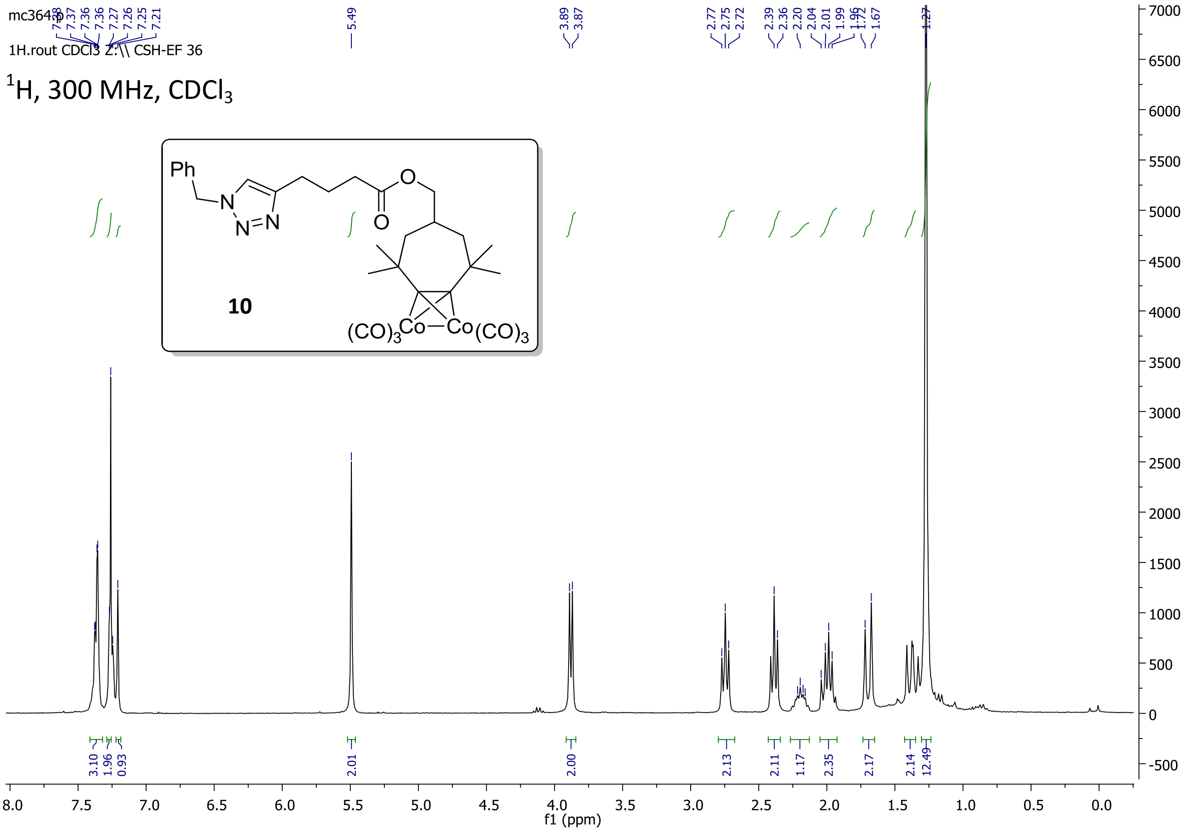

mc336.p13.c
13C.rout CDCl3 Z:\\ CSH-EF 20
^{13}C, 75 MHz, CDCl$_3$
173.16
159.30
150.93
138.23
128.81
127.88
114.28
83.31
77.58
77.16
76.74
69.86
69.36
55.42
54.05
49.36
45.86
34.98
33.78
33.02
31.91
31.63
31.16
27.67
23.75
18.00
1.17
OMe
O
O
N
N
N
8b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

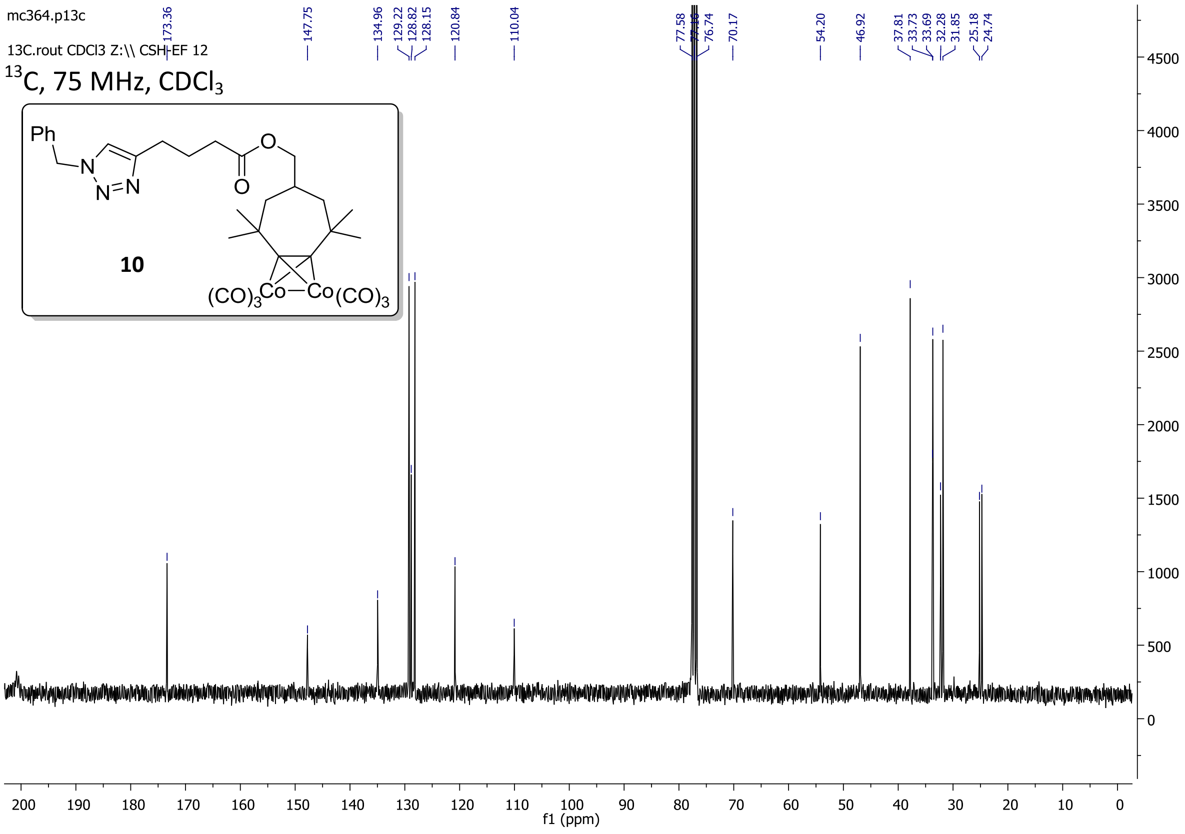

mc342.p2
1H.rout CDCl3 Z:\\ CSH-EF 13
^{1}H, 300 MHz, CDCl$_3$
7.32 7.31 7.30 7.29 7.29 7.28 7.26 7.22 7.20 7.19 7.17 7.02 7.01 6.99 6.90 6.88 6.87
5.71 5.41 5.30
3.91 3.89 3.89 3.87 3.80 3.51 3.49 3.46 3.44
2.75 2.72 2.70 2.41 2.38 2.36 1.70 1.65 1.63 1.62 1.60 1.58 1.57 1.52 1.49 1.32 1.26 1.01
MeO
N
N=N
O
O
9a
N
N
N
Ph
DCM
Et2O
3.19 3.03 2.09 1.94 2.07 2.00 1.98 3.12 1.98 2.16 1.19 2.31 2.84 3.18 1.93 3.08 2.92 3.13
12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
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)

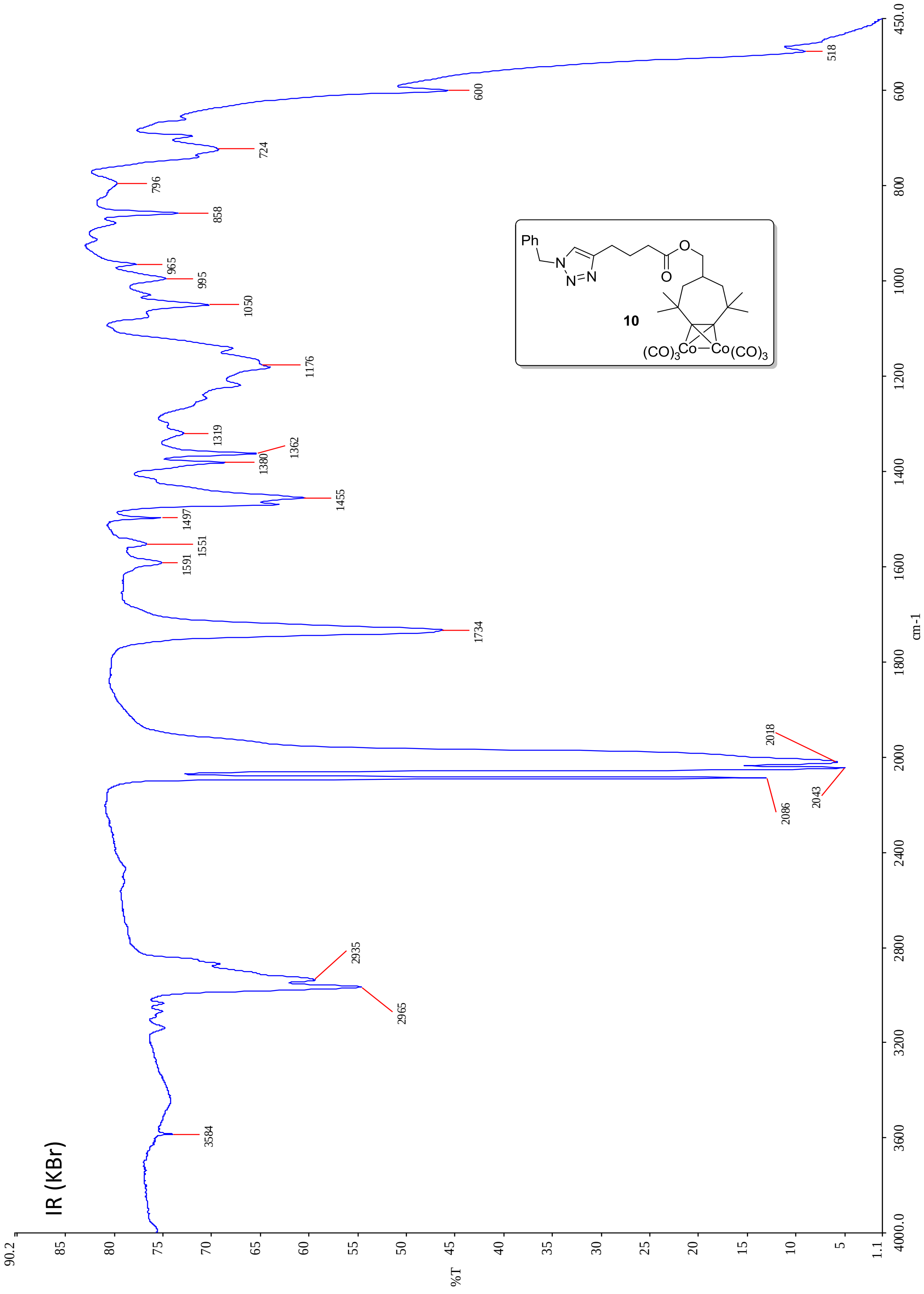

mc342.p13c
13C.rout CDCl3 Z:\\ CSH-EF 13
^{13}C, 75 MHz, CDCl$_3$
173.41 160.02 150.94 147.62 138.37 136.88 129.74 128.92 127.89 126.89 126.48 120.63 114.59
77.58 77.16 76.74
55.48 54.47 53.75 49.33 45.87 34.98 33.76 33.72 31.91 31.60 31.18 31.12 27.68 25.16 24.76
MeO
N
N=N
O
O
9a
N
N
N
Ph
2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


mc363.p13c
1H.rout CDCl3 Z:\\ CSH-EF 11
^{1}H, 300 MHz, CDCl$_3$
7.24
7.21
6.97
6.95
6.86
6.85
6.83
6.83
5.65
5.63
5.49
3.91
3.90
3.89
3.87
3.78
2.77
2.74
2.72
2.41
2.39
2.36
2.04
2.01
1.99
1.96
1.65
1.61
1.59
1.48
1.47
1.35
1.25
1.00
Ph
N
N=N
O
O
OMe
9b
N
N
N
3.10
1.44
0.91
1.97
1.93
1.97
2.00
1.97
2.92
2.08
2.06
1.24
2.11
2.02
3.08
2.20
2.77
3.48
2.89
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)
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


mc363.p13c
13C.rout CDCl3 Z:\\ CSH-EF 11
^{13}C, 75 MHz, CDCl$_3$
Ph
N
N=N
O
O
OMe
9b
N
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


mc364.p
1H.rout CDCl3 Z:\\ CSH-EF 36
^{1}H, 300 MHz, CDCl$_3$
7.38
7.37
7.36
7.36
7.27
7.26
7.25
7.21
5.49
3.89
3.87
2.77
2.75
2.72
2.39
2.36
2.20
2.04
2.01
1.99
1.96
1.72
1.67
1.27
Ph
N
N=N
O
O
10
(CO)$_3$Co—Co(CO)$_3$
3.10
1.96
0.93
2.01
2.00
2.13
2.11
1.17
2.35
2.17
2.14
12.49
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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)


mc364.p13c
13C.rout CDCl3 Z:\\ CSH-EF 12
^{13}C, 75 MHz, CDCl$_3$
173.36
147.75
134.96
129.22
128.82
128.15
120.84
110.04
77.58
77.16
76.74
70.17
54.20
46.92
37.81
33.73
33.69
32.28
31.85
25.18
24.74
Ph
N
N=N
O
O
10
(CO)$_3$Co—Co(CO)$_3$
4500
4000
3500
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


IR (KBr)
%T
90.2
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
1.1
cm-1
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
450.0
3584
2965
2935
2086
2043
2018
1734
1591
1551
1497
1455
1380
1362
1319
1176
1050
995
965
858
796
724
600
518
Ph
N
N
N
O
O
(CO)3Co
Co(CO)3
10