Electronic supplementary information for

A highly active diradical cobalt(III) catalyst for the cycloisomerization of alkynoic acids

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Table of contents:

1. General

1.1 Materials and methods

All reagents were purchased from Acros, Alfa-Aesar, Sigma-Aldrich or TCI and were used as received unless otherwise noted. HMPA was distilled from CaH_2 under reduced pressure prior to use. Deuterated solvents were purchased from Euriso-Top. Anhydrous solvents were distilled over the suitable drying agent under an argon atmosphere prior to use: CH_2Cl_2 and $CHCl_3$ over CaH_2; THF over sodium in the presence of benzophenone as an indicator of dryness.

NMR spectra were recorded on Brüker Avance 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) or 500 (^{1}H at 500 MHz, ^{13}C at 125 MHz) spectrometers. Chemical shifts are given relative to solvent residual peaks. Mass spectra were recorded on a Brüker Esquire 3000 (ESI/Ion Trap) equipment. Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer equipped with an ATR sampling accessory. Microanalyses were performed by the Service Central d'Analyze du CNRS (Lyon, France).

1.2 Crystal structure analysis

Single crystals were coated with a parafin mixture, picked up with nylon loops and mounted in the nitrogen cold stream of a Nonius 4 circles diffractometer at 200 K. Mo-Kα radiation (λ = 0.71073Å) from an Incoatec micro Mo-target X-ray source equipped with Montel optics was used. The data were collected with a Bruker APEXII detector. Final cell parameters were obtained from refinements using the whole data. Intensities were corrected for Lorentz and polarisation effects using EVAL, then for absorption using a multiscans method implemented with the program SADABS. The resulting data was merged with XPREP. The structures were solved by charge flipping methods. The SHELX2013 software implemented in OLEX was used for the refinement.[1] All non-hydrogen atoms were anisotropically refined and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. CCDC-1546379, CCDC-1546380 and CCDC-1546381 contain the crystallographic data for **1**•H_2O, **2**•CH_3CN and **7m**, respectively; these data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html

1.3 Computational details

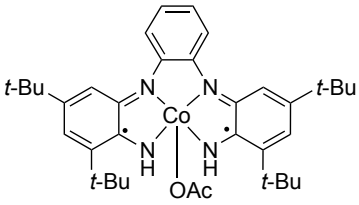
Full geometric optimizations were performed with the Gaussian 9.0 program,[2] by using the B3LYP functional[3,4] in combination with the 6-31g* basis set[5] for all atoms. Frequency calculations were performed in order to ensure that the optimized structures correspond to a real energy minimum

and not a saddle point. Thermochemistry has been computed at 298 K. The relative energies are given in the gas phase at the B3LYP/6-31g* level of theory.

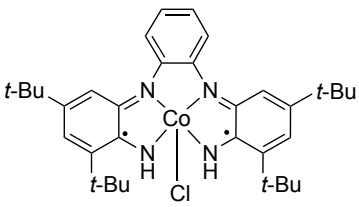
2. Synthesis of catalysts and substrates

Synthetic procedures for the preparation of $^{H}LH_4$,[6] [Co^{III}-salen(OAc)] **4**[7] and [Co^{III}-salophen(OAc)] **5**[8] were reported elsewhere. 2-Isopropyl-4-pentynoic acid **6b**,[9] 2-phenyl-4-pentynoic acid **6c**,[10] 2-methoxycarbonyl-4-pentynoic acid **6d**,[11] *N*-Boc DL-propargylglycine **6e**,[12] 3-phenyl-4-pentynoic acid **6g**,[13] 2-phenyl-4-hexynoic acid **6l**,[10] ethyl 3,3-dimethyl-4-pentynoate **6h**,[14] 4-hexynoic acid **6i**,[15] 5-phenyl-4-pentynoic acid **6k**,[16] 2-phenethynylbenzoic acid **6n**,[17] 2,2-dimethyl-5-[4-methyl-1-(trimethylsilyl)pent-1-yn-3-yl]-1,3-dioxane-4,6-dione **9**,[18] were prepared according to reported procedures.

2.1 Synthesis of catalysts 1 and 2

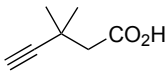


1. Under air atmosphere, Et_3N (325 µL, 2.33 mmol, 4.0 equiv.) and the ligand $^{H}LH_4$ (300 mg, 0.58 mmol, 1.0 equiv.) were successively added to a vigorously stirred suspension of $Co(OAc)_2.4H_2O$ (145 mg, 0.58 mmol, 1.0 equiv.) in CH_3CN (100 mL). Upon addition of the ligand, an immediate color change from pink to dark purple was noticed. The resulting mixture was stirred at rt for 2h and cooled to 5°C with an ice bath. The dark precipitate that formed was filtrated through a frit, rinsed with cold CH_3CN and dried under vacuum. Suitable crystals for X-Ray analysis were obtained by vapour diffusion of CH_3CN into a benzene solution. Yield: 77%, ^{1}H NMR (500 MHz, $CDCl_3$): ð (ppm)= 12.87 (s, 2H), 8.21 (br s, 2H), 7.56 (s, 2H), 7.48 (br s, 2H), 7.09 (s, 2H), 1.71 (s, 3H), 1.61 (s, 18H), 1.29 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): ð (ppm)= 179.6, 171.0, 155.1, 153.8, 145.9, 140.4, 128.4, 124.3, 121.8, 116.0, 37.2, 36.0, 30.5, 28.7, 25.7. MS (ESI): m/z= 569 $[M - OAc]^+$. IR: n (cm^{-1})= 3266, 2951, 2904, 2869, 1572, 1384, 1360, 1331, 1248, 1198, 1145, 1104. Anal. Calcd for $C_{36}H_{49}CoN_4O_2$: C, 68.77; H, 7.86; N, 8.91. Found: C, 69.14; H, 7.98; N, 9.18.



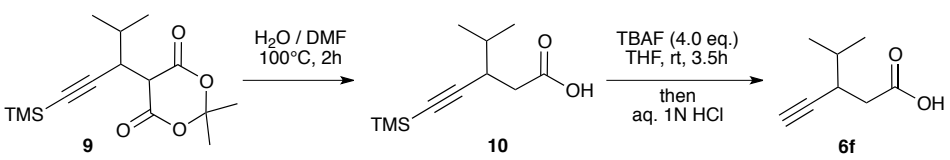
2•CH_3CN. Under air atmosphere, ligand $^{H}LH_4$ (97 mg, 188 µmol, 1.0 equiv.) was added to a vigorously stirred solution of $CoCl_2.6H_2O$ (45 mg, 189 µmol, 1.0 equiv.) and Et_3N (105 µL, 753 µmol, 4.0 equiv.) in CH_3CN (30 mL). The mixture was stirred at rt for 1h and tetramethylammonium chloride (62 mg, 566 µmol, 3.0 equiv.) was added. After 2 additional hours at rt, the mixture was cooled to 5°C with an ice bath. The black precipitate that formed was filtrated through a frit, rinsed with cold CH_3CN and dried under vacuum. Suitable crystals for X-Ray analysis were obtained by vapour diffusion of CH_3CN into a benzene solution. Yield: 46%. ^{1}H NMR (500 MHz, $CDCl_3$): ð (ppm)= 11.83 (br s, 2H), 8.25-8.21 (m, 2H), 7.68 (s, 2H), 7.59-7.56 (m, 2H), 7.20 (s, 2H), 2.00 (s, 3H), 1.64 (s, 18H), 1.31 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): ð (ppm)= 171.0, 155.4, 154.2, 146.3, 140.7, 129.2, 124.7, 121.4, 116.5, 115.4, 36.8, 35.9, 31.0, 29.0, 2.1. MS (ESI): m/z= 569 $[M - Cl]^+$, 639 $[M + {}^{35}Cl]^-$, 641 $[M + {}^{37}Cl]^-$. IR: n (cm^{-1})= 3297, 2952, 2905, 2867, 1587, 1461, 1359, 1321, 1239, 1195, 1144, 1100. Anal. Calcd for $C_{34}H_{46}CoN_4Cl$, CH_3CN C, 66.91; H, 7.64; N, 10.84. Found: C, 66.99; H, 7.87; N, 10.54.

2.2 Preparation of alkynoic acids



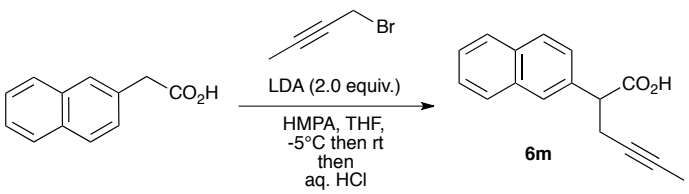
3,3-Dimethyl-4-pentynoic acid (6h).[19] 2N aq. KOH (3.25 mL, 6.5 mmol, 1.6 eq.) was added dropwise to a solution of ethyl 3,3-dimethyl-4-pentynoate (626 mg, 4.06 mmol) in MeOH (8 mL) at rt. The mixture was stirred at rt for 24 hours (TLC monitoring, eluent: Pentane/Et_2O, 8:2, v:v). The volatiles were removed under reduced pressure and the remaining aqueous phase was diluted with H_2O and washed with Et_2O (2x25mL). The aqueous phase was acidified to pH= 1 with aq. 37% HCl and extracted with CH_2Cl_2 (3x 25 mL). The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to afford the desired compound as a light yellow oil. Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 2.54 (s, 2H), 2.20 (s, 1H), 1.41(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): ð (ppm)= 176.6, 89.9, 68.7, 46.8, 29.6, 29.2. MS (ESI): m/z= 125.0 $[M - H]^-$. IR: n (cm^{-1})= 3297, 2971, 2936, 1705, 1245. HRMS (ESI) calcd for $[M – H]^-$ ($C_7H_9O_2$): 125.0603, found: 125.0604.

3-*Iso*-propyl-4-pentynoic acid (6f).



3-Isopropyl-5-trimethylsilyl-4-pentynoic acid (10). A solution of 2,2-dimethyl-5-[4-methyl-1-(trimethylsilyl)pent-1-yn-3-yl]-1,3-dioxane-4,6-dione **9**[18] (1.275g, 4.3 mmol) in DMF/H_2O (37.4 ml; 10:1) was stirred at 100°C for 2h. After cooling to rt the reaction mixture was treated with H_2O/sat. aq. NH_4Cl soln. (1:1) and extracted three times with Et_2O. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. If the remaining residue contained traces of DMF, it was dissolved in EtOAc (50 mL), washed with H_2O (3x 15 mL) and brine (3x 15 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The remaining yellow oil was used in the next step without any further purification. Yield: 91%. ^{1}H NMR (300 MHz, $CDCl_3$): ∂ (ppm)= 2.85-2.78 (m, 1H), 2.59-2.45 (m, 2H), 1.84-1.68 (m, 1H), 1.00 (d, *J*= 6.6 Hz, 3H), 0.96 (d, *J*= 6.6 Hz, 3H), 0.14 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): ∂ (ppm)= 178.2, 106.6, 87.5, 38.0, 35.8, 31.1, 21.1, 18.0, 0.3. HRMS (ESI) calcd for $[M - H]^-$ ($C_{11}H_{19}O_2Si$): 211.1154, found: 211.1024. IR: n (cm^{-1})= 3003, 2965, 2933, 2173, 1708, 1249.

3-Isopropyl-4-pentynoic acid (6f). A 1M solution of TBAF in THF (13.4 mL, 13.4 mmol, 4.0 eq.) was added dropwise to a stirred solution of 3-isopropyl-5-trimethylsilyl-4-pentynoic acid **10** (710 mg, 3.34 mmol) in THF (13 mL) at rt for 3.5h. After cooling to 5°C the mixture was hydrolyzed with 1N HCl (25 mL) and extracted with Et_2O (3x 15 mL). The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. If impurities were still present, the oily residue was dissolved in MeOH (7 mL) and 2N aq. KOH (3.4 mL, 6.8 mmol, 2.0 equiv.) was added dropwise. The mixture was stirred at rt during 30 min and the volatiles were removed under reduced pressure. The aqueous phase was diluted with water (30 mL), washed with Et_2O (3x 25 mL), acidified with conc. HCl to pH= 1 and extracted with CH_2Cl_2 (3x 25 mL) to give a yellow oil. Yield: 99%. ^{1}H NMR (300 MHz, $CDCl_3$): ∂ (ppm)= 2.84-2.78 (m, 1H), 2.60-2.49 (m, 2H), 2.10 (d, *J*= 2.4 Hz, 1.84-1.73 (m, 1H), 1.03 (d, *J*= 6.8 Hz, 3H), 0.98 (d, *J*= 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): ∂ (ppm)= 177.6, 84.0, 71.1, 37.8, 34.7, 31.1, 21.0, 18.0. HRMS (ESI) calcd for $[M - H]^-$ ($C_8H_{11}O_2$): 139.0759, found: 139.0761. IR: n (cm^{-1})= 3303, 2962, 2933, 1705, 1271.



2-Naphthyl-4-hexynoic acid (6m). Under argon, at rt, in a flame-dried three-necked round bottom flask equipped with a stirring bar and a thermometer, a 2.0 M solution of LDA in THF (11 mL, 20 mmol, 2.0 equiv.) was diluted in THF (20 mL). The resulting brown solution was cooled to -12°C with an ice+salt bath and a solution of 2-naphthylacetic acid (1.86 g, 10 mmol, 1.0 equiv.) in THF (15 mL)

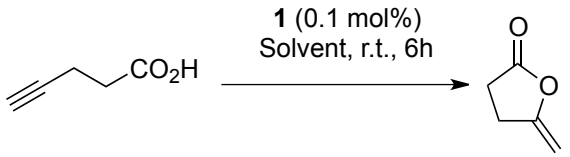
was added dropwise, while the temperature was kept below 0°C. After stirring at -5°C for 1h, freshly distilled HMPA (2 mL, 11,5 mmol, 1.15 eq.) and a solution of 1-bromo-2-butyne (880 µL, 10 mmol, 1.0 equiv.) in THF (5 mL) were successively added to the solution, taking care of keeping the temperature below 0°C. The resulting yellow mixture was allowed to warm to 20°C. After stirring for additional 4h, the reaction mixture was quenched with cold 6N HCl and extracted with Et_2O. The combined organic phase was successively washed with 1N HCl, H_2O and brine, then dried over Na_2SO_4, filtrated through cotton and concentrated under reduced pressure. The remaining crude material was dissolved in a minimum of CH_2Cl_2 and pentane was added until the precipitation of the desired compound that was recovered by filtration (m= 1.75 g). White fluffy solid, yield= 74%. ^{1}H NMR (300 MHz, $CDCl_3$): ð (ppm)= 7.83-7.78 (m, 4H, H_{Ar}), 7.51-7.43 (m, 3H, H_{Ar}), 3.95 (dd, ^3J= 7.2, 6.6 Hz, 1H, H_2), 3.03-2.93 (m, 1H, H_{3a}), 2.74-2.63 (m, 1H, H_{3b}), 1.71 (dd, ^5J= 2.4, 2.7 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): ð (ppm)= 178.6 (C_1), 134.8 (C_{Ar}), 133.5 (C_{Ar}), 133.0 (C_{Ar}), 128.6 (C_{Ar}), 128.1 (C_{Ar}), 127.8 (C_{Ar}), 127.1 (C_{Ar}), 126.4 (C_{Ar}), 126.3 (C_{Ar}), 125.8 (C_{Ar}), 77.9 (C_4), 75.9 (C_5), 51.5 (C_2), 23.2 (C_3), 3.6 (CH$_3$). MS (ESI): m/z= 239 [M + H]$^+$, 261 [M + Na]$^+$. IR: n (cm^{-1})= 3054, 2951, 2913 (br), 1693, 1431, 1416, 1233. Anal. Calcd for $C_{16}H_{14}O_2$, 0.125 CH_2Cl_2: C, 77.81; H, 5.77. Found: C, 77.55; H, 5.91.

3. Catalytic experiments and products characterization

3.1 General procedure for the cyclisation of alkynoic acids.

Under argon, at rt, in a flame-dried round bottom flask, catalyst **1** (x mol%) was added in one portion to a vigorously stirred solution of the alkynoic acid (1 mmol) in freshly distilled CH_2Cl_2 (10 mL). Reaction completion was monitored by TLC (Eluent: Pentane / Et_2O; 7:3, v:v). After full conversion of the starting material, the volatiles were removed under reduced pressure. Purification of the crude by flash chromatography on silica gel (Eluent: Pentane / Et_2O; 9:1, v:v) afforded the desired γ-vinyllactone.

Table S1. Solvents screening[a]



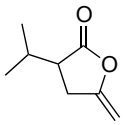
6a **7a**

Entry	Solvent	Conversion (%)[b]
1	$CDCl_3$	65
2[c]	$CDCl_3$	31
3	CD_2Cl_2	70
4	THF-d_8	0
5	DMSO-d_6	0
6	DMF-d_7	0
7	Benzene-d_6	16
8	Acetone-d_6	0
9	MeOD	0
10	CD_3CN	< 1

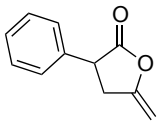
[a] Conditions: 4-pentynoic acid (0.2 mmol), [CoL(OAc)] (0.2 µmol), solvent (2 mL), 25°C, argon. [b] Mean of 2 runs. Determined by ^{1}H NMR (Internal standard: PhTMS, 5 mM). [c] Run performed at 50°C.

The influence of the solvent on the 5-exo-dig cyclization of 4-pentynoic acid was evaluated in the presence of 0.1 mol% of catalyst **1**. In each case, the reaction mixture was analyzed after 6h stirring under argon.

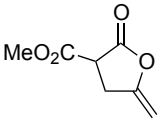
3.2 Products characterization.



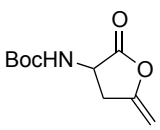
3-*iso*-Propyl-5-methylenedihydrofuran-2-one (7b).[20] The reaction went to completion within 30min using 0.5 mol% of catalyst. Pale yellow oil, yield= 96%. ^{1}H NMR (300 MHz, $CDCl_3$): ð (ppm)= 4.71-4.69 (m, 1H, H_{5a}), 4.30-4.28 (m, 1H, H_{5b}), 2.94-2.78 (m, 1H, H_{3a}), 2.75-2.61 (m, 2H, H_2 & H_{3b}), 2.27-2.12 (m, 1H, CH_{iPr}), 1.02 (d, ^{3}J= 6.8 Hz, 3H, CH_3), 0.95 (d, ^{3}J= 6.8 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): ð (ppm)= 176.5 (C_1), 154.9 (C_4), 88.4 (C_5), 46.1 (C_2), 29.1 (CH$_{iPr}$), 27.9 (C_3), 20.2 (CH$_3$), 18.3 (CH$_3$).



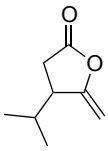
3-Phenyl-5-methylenedihydrofuran-2-one (7c).[20] The reaction went to completion within 2.5h using 0.5 mol% of catalyst. Colorless oil, yield= 84%. ^{1}H NMR (300 MHz, $CDCl_3$): ð (ppm)= 7.41-7.27 (m, 5H, H_{Ar}), 4.84 (dd, ^{2}J= 2.7 Hz, ^{3}J= 1.8 Hz, 1H, H_{5a}), 4.42 (dd, ^{2}J= 2.7 Hz, ^{3}J= 1.8 Hz, 1H, H_{5b}), 3.99 (dd, ^{3}J= 10.2, 7.8 Hz, 1H, H_2), 3.35 (ddt, ^{2}J= 16.3 Hz, ^{3}J= 10.2 Hz, ^{4}J= 1.8 Hz, 1H, H_{3a}), 3.02 (ddt, ^{2}J= 16.3 Hz, ^{3}J= 7.8 Hz, ^{4}J= 1.8 Hz, 1H, H_{3b}). ^{13}C NMR (75 MHz, $CDCl_3$): ð (ppm)= 175.0 (C_1), 154.2 (C_4), 136.8 (C_{qAr}), 129.2 (C_{Ar}), 128.1 (C_{Ar}), 127.7 (C_{Ar}), 89.3 (C_5), 46.2 (C_2), 34.6 (C_3).



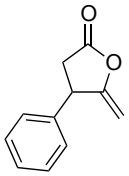
3-(Methoxycarbonyl)-5-methylenedihydrofuran-2-one (7d).[11] $CHCl_3$ was used as solvent instead of CH_2Cl_2. The reaction went to completion within 1.5h using 0.5 mol% of catalyst. Colorless oil, yield= 87%. ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 4.82 (ddd, ^{2}J= 2.6 Hz, ^{4}J= 2.2 Hz, ^{4}J= 1.6 Hz, 1H), 4.41 (ddd, ^{2}J= 2.6 Hz, ^{4}J= 2.0 Hz, ^{4}J= 1.8 Hz, 1H), 3.83 (s, 3H), 3.76 (dd, ^{2}J= 10.4 Hz, ^{3}J= 7.6 Hz, 1H), 3.31 (dddd, ^{2}J= 16.6 Hz, ^{4}J= 7.6 Hz, ^{4}J= 2.2 Hz, ^{4}J= 1.8 Hz, 1H), 3.09 (dddd, ^{2}J= 16.6 Hz, ^{4}J= 10.4 Hz, ^{4}J= 2.0 Hz, ^{4}J= 1.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): ð (ppm)= 169.6, 167.4, 153.2, 90.0, 53.5, 46.4, 29.5.



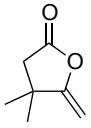
***N*-(*tert*-Butoxycarbonyl)-3-amino-5-methylenedihydrofuran-2-one (7e).**[11, 21] $CHCl_3$ was used as solvent instead of CH_2Cl_2. The reaction went to completion within 1.5h using 0.5 mol% of catalyst. White solid, yield= 99%. ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 5.14 (br s, 1H), 4.81-4.79 (m, 1H), 4.45 (br s, 1H), 4.40-4.39 (m, 1H), 3.30-3.24 (m, 1H), 2.90-2.84 (m, 1H), 1.45 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): ð (ppm)= 173.2, 155.3, 152.4, 90.5, 81.1, 50.6, 33.5, 28.4.



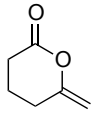
4-Isopropyl-5-methylenedihydrofuran-2-one (7f). The reaction went to completion within 4h using 0.5 mol% of catalyst. Colorless oil, yield= 93%. ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 4.81-4.80 (m, 1H, H_{6a}), 4.29 (dd, ^2J= 2.4 Hz, ^3J= 1.2 Hz, 1H, H_{6b}), 3.02-2.97 (m, 1H, H_4), 2.69 (dd, ^2J= 18.4 Hz, ^3J= 10.0 Hz, 1H, H_{3a}), 2.42 (dd, ^2J= 18.4 Hz, ^3J= 4.8 Hz, 1H, H_{3b}), 1.97-1.86 (m, 1H, CH_{iPr}), 0.95 (d, ^3J= 6.8 Hz, CH_3), 0.92 (d, ^3J= 6.8 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): ð (ppm)= 174.6 (C_2), 159.0 (C_5), 89.4 (C_6), 43.9 (C_3), 31.4 (C_4), 30.8 (CH$_{iPr}$), 19.6 (CH$_3$), 17.5 (CH$_3$). HRMS (ESI) calcd for $[M + H]^+$ ($C_8H_{13}O_2$): 141.0916, found: 141.0920. IR: n (cm^{-1})= 2962, 2933, 2873, 1796, 1660, 1131, 970.



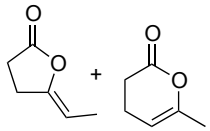
4-Phenyl-5-methylenedihydrofuran-2-one (7g). The reaction went to completion within 1h using 1 mol% of catalyst. Colorless oil, yield= 93%. ^{1}H NMR (500 MHz, $CDCl_3$): ð (ppm)= 7.39-7.35 (m, 2H, H_{Ar}), 7.33-7.29 (m, 1H, H_{Ar}), 7.28-7.26 (m, 2H, H_{Ar}), 4.88 (dd, ^2J= 2.7 Hz, ^4J= 2.5 Hz, 1H, H_{6a}), 4.27 (dddd, ^3J= 10.2 Hz, ^3J= 7.5 Hz, ^4J= 2.5 Hz, ^4J= 2.0 Hz, 1H, H_4), 4.17 (dd, ^2J= 2.7 Hz, ^4J= 2.0 Hz, 1H, H_{6b}), 3.11 (dd, ^2J= 18.2 Hz, ^3J= 10.2 Hz, 1H, H_{3a}), 2.77 (dd, ^2J= 18.2 Hz, ^3J= 7.5 Hz, 1H, H_{3b}). ^{13}C NMR (125 MHz, $CDCl_3$): ð (ppm)= 173.3, 159.9, 140.0, 129.3, 127.9, 127.5, 90.7, 44.3, 37.4. MS (EI): m/z= 174 $[M]^{+\bullet}$. IR: n(cm^{-1})= 3063, 3031, 1796, 1666, 1122, 973, 833. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.83; H, 5.80. Found: C, 75.79; H, 5.94.



4,4-Dimethyl-5-methylenedihydrofuran-2-one (7h).[19] The reaction went to completion within 4h using 5 mol% of catalyst. Pale yellow oil, yield= 71%. ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 4.67 (d, J= 3.2 Hz, 1H), 4.29 (d, J= 3.2 Hz, 1H), 2.49 (s, 2H), 1.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): ð (ppm)= 173.2, 166.0, 86.4, 43.2, 39.2, 28.1. MS (EI): m/z= 126.1 $[M]^{+\bullet}$. IR: n (cm^{-1})= 2968, 2930, 1780, 1667, 1255, 1230, 1198, 1097, 976, 840.



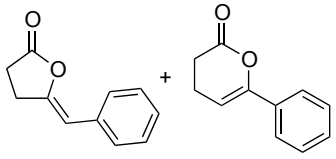
6-Methylenetetrahydropyran-2-one (7i).[11] The reaction went to completion within 8h using 5 mol% of catalyst. Colorless oil, yield= 92%. ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 4.64 (ddd, *J*= 2.4 Hz, *J*= 1.6 Hz, *J*= 0.8 Hz, 1H), 4.29 (dt, *J*= 2.4 Hz, *J*= 1.2 Hz, 1H), 2.63 (t, *J*= 6.6 Hz, 2H), 2.48 (ddd, *J*= 6.6 Hz, *J*= 1.2 Hz, *J*= 0.8 Hz, 2H), 1.91-1.84 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): ð (ppm)= 168.2, 155.4, 93.9, 30.4, 26.9, 18.7.



(*Z*)-5-Ethylidenedihydrofuran-2-one (7j) and 6-methyl-3,4-dihydropyran-2-one (8j).[22] The reaction went to completion within 6h using 1 mol% of catalyst. Colorless oil, yield= 90%. The (*Z*)-5-*exo-dig* and 6-*endo-dig* isomers were obtained in a 80:20 ratio.

(*Z*)-5-*exo-dig* cycloadduct: ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 4.61 (tq, ^{3}J= 6.8 Hz, ^{4}J= 2.0 Hz, ^{4}J= 1.6 Hz), 2.83-2.77 (m, 2H), 2.65-2.61 (m, 2H), 1.67 (dt, ^{3}J= 6.8 Hz, ^{5}J= 1.6 Hz, ^{5}J= 2.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): ð (ppm)= 175.3, 148.4, 99.4, 28.2, 25.1, 10.5.

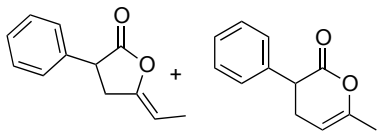
6-*endo-dig* cycloadduct: ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 5.00 (m, 1H), 2.61-2.55 (m, 2H), 2.31-2.26 (m, 2H), 1.89-1.88 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): ð (ppm)= 169.3, 150.2, 99.9, 28.5, 18.9, 18.8.



5-Benzylidenedihydrofuran-2-one (7k) and 6-phenyl-3,4-dihydropyran-2-one (8k).[19,23] The reaction went to completion within 8h using 2 mol% of catalyst. Colorless oil, yield: 97%. The (*Z*)-5-*exo-dig* and 6-*endo-dig* isomers were obtained in a 60:40 ratio.

(*Z*)-5-*exo-dig* cycloadduct: ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 7.57-7.54 (m, 2H), 7.35-7.31 (m, 2H), 7.23-7.19 (m, 1H), 5.54 (t, *J*= 1.6 Hz, 1H), 3.03-2.98 (m, 2H), 2.70-2.66 (m, 2H).

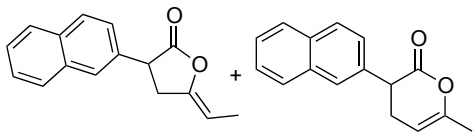
6-*endo-dig* cycloadduct: ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 7.63-7.59 (m, 2H), 7.40-7.34 (m, 3H), 5.83 (t, *J*= 4.8 Hz, 1H), 2.71-2.68 (m, 2H), 2.54-2.49 (m, 2H).



(*Z*)-3-Phenyl-5-ethylidenedihydrofuran-2-one (7l) and 3-phenyl-6-methyl-3,4-dihydropyran-2-one (8l).[10,24] The reaction went to completion within 8h using 0.5 mol% of catalyst. Pale yellow oil, yield= 82%. The (*Z*)-5-*exo-dig* and 6-*endo-dig* isomers were obtained in a 85:15 ratio.

(*Z*)-5-*exo-dig* cycloadduct: ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 7.39-7.26 (m, 5H), 4.76-4.70 (m, 1H), 3.98-3.93 (m, 1H), 3.30-3.23 (m, 1H), 3.00-2.92 (m, 1H), 1.75-1.73 (m, 1H).

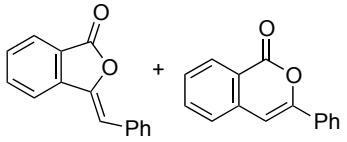
6-*endo-dig* cycloadduct: ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 7.39-7.25 (m, 5H), 5.12-5.09 (m, 1H), 3.81-3.76 (m, 1H), 2.65-2.53 (m, 2H), 1.94 (br s, 3H).



(*Z*)-3-(2-Naphthyl)-5-ethylidenedihydrofuran-2-one (7m) and 3-(2-naphthyl)-6-methyl-3,4-dihydropyran-2-one (8m). The reaction went to completion within 5h using 1 mol% of catalyst. White solid, yield: 95%. The (*Z*)-5-*exo-dig* and 6-*endo-dig* isomers were obtained in an 84:16 ratio.

(*Z*)-5-*exo-dig* cycloadduct: Suitable crystals for X-ray diffraction were successfully obtained from an EtOH / H_2O mixture. ^{1}H NMR (300 MHz, $CDCl_3$): ð (ppm)= 7.87-7.74 (m, 4H, H_{Ar}), 7.53-7.45 (m, 2H, H_{Ar}), 7.38 (dd, *J*= 8.4, 1.8 Hz, 1H, H_{Ar}), 4.76 (ddq, ^{3}J= 6.9 Hz, ^{4}J= 2.1, 1.5 Hz, 1H, H_5), 4.12 (dd, *3J*= 10.2, 8.4 Hz, 1H, H_2), 3.38-3.27 (m, 1H, H_{3a}), 3.10-3.00 (m, 1H, H_{3b}), 1.77 (ddd, ^{3}J= 6.9 Hz, ^{5}J= 2.1, 1.5 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): ð (ppm)= 175.2 (C_1), 146.8 (C_4), 134.2 ($C_{q\,Ar}$), 133.5 ($C_{q\,Ar}$), 132.9 ($C_{q\,Ar}$), 129.1 (C_{Ar}), 128.0 (C_{Ar}), 127.8 (C_{Ar}), 126.8 (C_{Ar}), 126.6 (C_{Ar}), 126.4 (C_{Ar}), 125.3 (C_{Ar}), 99.9 (C_5), 46.3 (C_2), 34.5 (C_3), 10.6 (CH_3). MS (ESI): m/z= 261 $[M + Na]^+$. IR: n (cm^{-1})= 2920, 1780, 1708, 1226, 1198, 1119, 1071, 986, 967, 815. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.93. Found: C, 80.29; H, 6.09.

6-*endo-dig* cycloadduct: ^{1}H NMR (400 MHz, $CDCl_3$): ð (ppm)= 7.87-7.79 (m, 3H, H_{Ar}), 7.70 (br s, 1H, H_{Ar}), 7.50-7.45 (m, 2H, H_{Ar}), 7.38 (dd, *J*= 8.4, 1.6 Hz, 1H, H_{Ar}), 5.15-5.13 (m, 1H, H_4), 3.96 (dd, *J*= 10.8, 7.2 Hz, 1H, H_2), 2.78-2.68 (m, 1H, H_{3a}), 2.66-2.58 (m, 1H, H_{3b}), 1.96 (m, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): ð (ppm)= 170.0 (C_1), 150.3 (C_5), 134.9 (C_{Ar}), 133.5(C_{Ar}), 132.9 (C_{Ar}), 128.7 (C_{Ar}), 128.0 (C_{Ar}), 127.8 (C_{Ar}), 127.1 (C_{Ar}), 126.4 (C_{Ar}), 126.24 (C_{Ar}), 126.17 (C_{Ar}), 100.1 (C_4), 45.4 (C_2), 27.4 (C_3), 18.8(CH_3). MS (ESI): m/z= 261 $[M + Na]^+$, 277 $[M + K]^+$. IR: n (cm^{-1})= 3052, 2944, 2919, 1762, 1697, 1180, 1116, 1063, 983, 814. Anal. Calcd for $C_{16}H_{14}O_2$, 0.9 H_2O C, 75.51; H, 6.26. Found: C, 75.67; H, 5.89.



(*Z*)-5-Benzylidenebenzofuran-2-one (7n) and 3-phenyl-isochromen-1-one (8n).[25] The reaction went to completion within 4h using 5 mol% of catalyst. White solid, yield: 74%. The (*Z*)-5-*exo-dig* and 6-*endo-dig* isomers were obtained in a 40:60 ratio.

(*Z*)-5-*exo-dig* cycloadduct: ^{1}H NMR (400 MHz, $CDCl_3$): ∂ (ppm)= 7.95 (ddd, *J*= 7.8 Hz, *J*= 1.2 Hz, *J*= 0.8 Hz, 1H), 7.89-7.85 (m, 2H), 7.80-7.74 (m, 2H), 7.55 (td, *J*= 7.8 Hz, *J*= 1.2 Hz, 1H), 7.44-7.42 (m, 2H), 7.35-7.30 (m, 1H), 6.44 (s, 1H).

6-*endo-dig* cycloadduct: ^{1}H NMR (400 MHz, $CDCl_3$): ∂ (ppm)= 8.32 (d, *J*= 8.4 Hz, 1H), 7.91-7.88 (m, 2H), 7.73-7.71 (m, 1H), 7.53-7.40 (m, 5H), 6.96 (s, 1H).

4. X-Ray data

Figure S1. X-Ray structure of **2•CH_3CN**. The solvent molecule and H atoms were omitted for clarity, except the anilido ones. Right: Atoms numbering in **2**. Selected bond lengths (Å): Co-N1 1.8441(15), Co-N2 1.8592(14), Co-N3 1.8431(14), Co-N4 1.8609(15), Co-Cl1 2.3064(7), N1-C1 1.334(2), N2-C2 1.346(2), N3-C8 1.343(2), N4-C7 1.331(2), N2-C13 1.407(2), N3-C14 1.409(2).

Table S2. Crystallographic data and structure refinement for **1** and **2**.

	1 • H_2O, 0.125 C_6H_6	**2**, CH_3CN
Empirical formula	$C_{36.75}H_{51.75}CoN_4O_3$	$C_{36}H_{49}ClCoN_5$
Formula weight	656.50	646.18
Temperature/K	200	200
Crystal system	triclinic	monoclinic
Space group	P-1	P21/n
a/Å	10.455(2)	14.519(3)
b/Å	14.036(3)	16.983(3)
c/Å	14.199(3)	14.819(3)
α/°	107.28(3)	90
β/°	110.92(3)	108.83(3)
γ/°	97.29(3)	90
Volume/$Å^3$	1794.2(8)	3458.5(13)
Z	2	4
$\rho_{calc}g/cm^3$	1.215	1.241
μ/mm^{-1}	0.517	0.605
F(000)	702.0	1376.0
Crystal size/mm^3	0.44 × 0.34 × 0.1	0.5 × 0.5 × 0.3
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.634 to 49.994	5.342 to 55.994
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16	-17 ≤ h ≤ 19, -22 ≤ k ≤ 20, -19 ≤ l ≤ 19
Reflections collected	21656	38863
Independent reflections	6175 [Rint = 0.0657, Rsigma = 0.0588]	8257 [Rint = 0.0394, Rsigma = 0.0307]
Data/restraints/parameters	6175/11/444	8257/0/401
Goodness-of-fit on F^2	1.082	1.142
Final R indexes [I>=2σ (I)]	R1 = 0.0733, wR2 = 0.1851	R1 = 0.0350, wR2 = 0.0770
Final R indexes [all data]	R1 = 0.0975, wR2 = 0.2089	R1 = 0.0555, wR2 = 0.0918
Largest diff. peak/hole / e $Å^{-3}$	0.85/-0.80	0.41/-0.32

Table S3. Crystallographic data and structure refinement for **7m**.

	7m
Empirical formula	$C_{16}H_{14}O_2$
Formula weight	238.27
Temperature/K	200
Crystal system	orthorhombic
Space group	Pna21
a/Å	17.365(4)
b/Å	12.283(3)
c/Å	5.6968(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1215.1(4)
Z	4
ρ_{calc}g/cm^3	1.303
μ/mm^{-1}	0.085
F(000)	504.0
Crystal size/mm^3	0.38 × 0.22 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.692 to 49.986
Index ranges	-19 ≤ h ≤ 20, -14 ≤ k ≤ 14, -6 ≤ l ≤ 6
Reflections collected	14944
Independent reflections	2120 [Rint = 0.1311, Rsigma = 0.0593]
Data/restraints/parameters	2120/1/164
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R1 = 0.0441, wR2 = 0.1017
Final R indexes [all data]	R1 = 0.0579, wR2 = 0.1141
Largest diff. peak/hole / e Å^{-3}	0.20/-0.21
	-0.2(10)

5. Computational details

- XYZ Coordinates for the singlet **1**:

Co	0.000711743	-0.286609277	0.457654181
N	-1.430967249	-1.321857251	-0.087260799
H	-1.406894976	-2.333516090	-0.123731166
N	-1.241874226	1.079286104	0.368788917
C	-6.035017282	1.897067099	-0.998860158
N	1.432009199	-1.322643079	-0.086823170
H	1.407487126	-2.334286043	-0.123534841
C	-6.498174378	1.599265194	-2.445981072
H	-7.381494505	2.200747106	-2.693231204
H	-6.764590780	0.546328942	-2.584136023
H	-5.708752520	1.841873912	-3.166347416
C	-1.402647271	3.459231148	1.185929078
H	-2.482142929	3.448655011	1.262205216
C	3.281925018	-3.378842244	-1.815311331
H	3.611474384	-2.930898995	-2.759720209
H	2.207531158	-3.198041429	-1.728418310
H	3.430412155	-4.463104202	-1.884105961
C	4.929907329	-0.392826264	-0.726758275
H	5.906022390	-0.788938189	-0.973557019
N	1.244279866	1.078557956	0.369932998
C	4.807823491	1.033872113	-0.662745291
C	-0.693233309	4.595610185	1.599066223
H	-1.240559221	5.469593509	1.940419946
C	3.896900421	-1.281867855	-0.518965186
C	-4.928056267	-0.390160269	-0.728790316
H	-5.904383528	-0.785804931	-0.975522912
C	-7.181953406	1.562324918	-0.013998855
H	-7.479873847	0.510263925	-0.070417087
H	-8.066366813	2.169728323	-0.241990110
H	-6.883581577	1.770334969	1.019751018
C	-0.711954012	2.333472168	0.738446213
C	-4.804861157	1.036489952	-0.666270141
C	7.184772333	1.556765382	-0.007886858
H	7.481773593	0.504503831	-0.065353919
H	6.885684527	1.763753063	1.025857194
H	8.069929763	2.163654956	-0.234357787
C	-3.895777507	-1.279758026	-0.519588028
C	3.594107316	1.580590000	-0.304270039
H	3.458926341	2.651069007	-0.272662811
C	-3.282402336	-3.379181447	-1.812909396
H	-2.207882003	-3.198924096	-1.726512214
H	-3.611833166	-2.932539973	-2.757973395
H	-3.431588516	-4.463458221	-1.879930223
C	6.503106310	1.597318880	-2.440412011
H	5.714499385	1.841448983	-3.161160420
H	6.768782393	0.544335002	-2.579613145
H	7.387126538	2.198373217	-2.686194205

C	3.709824092	-3.505499231	0.698824067
H	3.882434302	-4.585105487	0.613493177
H	2.665274241	-3.365102157	0.988053830
H	4.330366439	-3.130705211	1.520940082
C	0.696489866	4.595219123	1.599726108
H	1.243988289	5.468891290	1.941597894
C	-2.608455951	-0.702942124	-0.204213205
C	-3.590958182	1.582610928	-0.307389010
H	-3.454948516	2.653017967	-0.276628994
C	6.038989287	1.893769267	-0.993323906
C	2.609886317	-0.704425937	-0.203238989
C	0.714788815	2.333063114	0.739137319
C	-2.491033107	0.738138232	-0.013143175
C	4.102533408	-2.806816455	-0.629937889
C	1.405667285	3.458441086	1.187271072
H	2.485075100	3.447302434	1.264637844
C	-3.710131544	-3.501669046	0.701490062
H	-4.330663308	-3.125344116	1.522938255
H	-2.665475328	-3.361543440	0.990576947
H	-3.883350308	-4.581300174	0.617782158
C	5.746565410	3.402173140	-0.886587267
H	5.441943468	3.687317125	0.126932159
H	4.960541399	3.715385216	-1.583003048
H	6.650072590	3.971660466	-1.131237022
C	-5.741332376	3.405340266	-0.893741214
H	-6.644116700	3.975335073	-1.139871078
H	-4.954436282	3.716977510	-1.589880236
H	-5.437309463	3.691479104	0.119678197
C	-4.102458265	-2.804716150	-0.628333953
C	5.578072199	-3.170029431	-0.899147289
H	5.936555388	-2.766654018	-1.852867041
H	5.676810323	-4.259917072	-0.946856852
H	6.239433691	-2.813338035	-0.101666062
C	2.493360428	0.736690932	-0.011400065
C	-5.578286515	-3.167272417	-0.896831080
H	-5.936520463	-2.765138455	-1.851167323
H	-6.239323622	-2.808782348	-0.099886968
H	-5.677852273	-4.257160058	-0.942803883
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O	-0.002261174	-3.076639172	1.670396142
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C	-0.026675825	-2.472328278	4.003418509
H	-0.987106073	-2.159443234	4.428215546
H	0.755711150	-1.909692210	4.521793134
H	0.109269810	-3.543221102	4.165934134

- XYZ Coordinates for the triplet **1**:

Co	0.001205995	-0.273488327	0.449714935
N	-1.420855731	-1.292157707	-0.172480562
H	-1.395385900	-2.304869609	-0.158501286
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N	1.424042436	-1.293921984	-0.163232660
H	1.398211707	-2.306572501	-0.145922743
C	-6.580075670	1.619585601	-2.364903180
H	-7.472619885	2.218650760	-2.583383003
H	-6.842515305	0.566773705	-2.511533433
H	-5.809086643	1.877477487	-3.099819781
C	-1.408565060	3.488448082	1.151285431
H	-2.487583400	3.479435664	1.231611363
C	3.294944896	-3.347270471	-1.839306344
H	3.642195240	-2.894711208	-2.775198643
H	2.220634645	-3.160448148	-1.767548322
H	3.438827660	-4.431816068	-1.913453073
C	4.953945734	-0.379398391	-0.701789576
H	5.928733619	-0.786699770	-0.935383760
N	1.256113857	1.116543357	0.351668445
C	4.844677512	1.039090329	-0.633378599
C	-0.700611627	4.617720269	1.538098654
H	-1.241178358	5.497522955	1.875176624
C	3.902411802	-1.262086681	-0.517341671
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H	-8.100487104	2.146908612	-0.116531710
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H	6.887007999	1.739220935	1.110044003
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C	-3.292507505	-3.342045904	-1.851797573
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H	5.813021605	1.869335037	-3.101608400
H	6.846441801	0.560598207	-2.508958457
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H	3.861888996	-4.572820638	0.593890864
H	2.629000199	-3.364529587	0.946371596

H	4.280680400	-3.119955504	1.517653362
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H	1.244963034	5.497737271	1.871898371
C	-2.616390434	-0.673833671	-0.241630270
C	-3.617480545	1.593338409	-0.297562717
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C	-3.676708709	-3.496332823	0.667565566
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H	5.032583061	3.730712306	-1.520752224
H	6.711991620	3.972928904	-1.025921224
C	-5.798547020	3.407192386	-0.803333398
H	-6.710483465	3.975013862	-1.018840833
H	-5.030630397	3.734933023	-1.513216211
H	-5.472269029	3.679798575	0.206979743
C	-4.095995423	-2.786702957	-0.647097520
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H	5.668117529	-4.250204553	-0.938582107
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H	0.039135303	-3.790324123	4.029756719

- XYZ Coordinates for the quintet **1**:

Co	0.000599000	-0.305349000	0.373482000
N	-1.472602000	-1.352094000	-0.136398000
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N	1.473638000	-1.352912000	-0.135282000
H	1.455252000	-2.364343000	-0.126622000
C	-6.552639000	1.653446000	-2.384949000
H	-7.431857000	2.268432000	-2.612593000
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H	-5.770581000	1.895379000	-3.113557000
C	-1.403167000	3.469148000	1.161936000
H	-2.482084000	3.462137000	1.241906000
C	3.354216000	-3.361367000	-1.841132000
H	3.692647000	-2.905699000	-2.778792000
H	2.278031000	-3.187848000	-1.765086000
H	3.511114000	-4.444082000	-1.914798000
C	4.975757000	-0.369378000	-0.708951000
H	5.955779000	-0.760513000	-0.947773000
N	1.275031000	1.078894000	0.423465000
C	4.843664000	1.047475000	-0.634353000
C	-0.696475000	4.612213000	1.536118000
H	-1.242429000	5.495329000	1.855348000
C	3.938856000	-1.268104000	-0.520870000
C	-4.974210000	-0.367327000	-0.710650000
H	-5.954396000	-0.758126000	-0.949364000
C	-7.202801000	1.593123000	0.055760000
H	-7.513549000	0.545396000	-0.011177000
H	-8.083121000	2.213855000	-0.151160000
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C	-4.841405000	1.049516000	-0.636914000
C	7.205063000	1.589370000	0.059540000
H	7.515245000	0.541512000	-0.007944000
H	6.889498000	1.779036000	1.091674000
H	8.085808000	2.209746000	-0.146645000
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C	3.613148000	1.580954000	-0.282155000
H	3.473626000	2.649486000	-0.231445000
C	-3.354122000	-3.361202000	-1.840241000
H	-2.277853000	-3.188139000	-1.764410000
H	-3.692390000	-2.906254000	-2.778309000
H	-3.511545000	-4.443909000	-1.912874000
C	6.555854000	1.651636000	-2.381380000
H	5.774176000	1.894392000	-3.110121000
H	6.836323000	0.603529000	-2.528380000
H	7.435441000	2.266356000	-2.608318000
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H	3.945466000	-4.581308000	0.585510000
H	2.708181000	-3.382390000	0.958115000

H	4.363966000	-3.128358000	1.508963000
C	0.699265000	4.611803000	1.536808000
H	1.245424000	5.494596000	1.856577000
C	-2.647650000	-0.703910000	-0.222919000
C	-3.610759000	1.582594000	-0.284542000
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C	0.720779000	2.311774000	0.762829000
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H	-4.363628000	-3.124603000	1.509646000
H	-2.707862000	-3.380054000	0.959024000
H	-3.945804000	-4.578595000	0.587593000
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H	6.657464000	4.011866000	-1.042956000
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H	-6.653476000	4.014602000	-1.048152000
H	-4.972553000	3.743739000	-1.522730000
H	-5.434530000	3.701749000	0.192335000
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H	5.745512000	-4.229434000	-0.954076000
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C	2.523228000	0.731625000	-0.007172000
C	-5.637898000	-3.138713000	-0.897472000
H	-6.003594000	-2.725702000	-1.844356000
H	-6.287968000	-2.783359000	-0.090111000
H	-5.745770000	-4.227334000	-0.952182000
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O	-0.002781000	-3.129174000	1.603281000
C	-0.003951000	-2.249616000	2.486013000
C	-0.020133000	-2.642193000	3.961404000
H	-0.950481000	-2.295766000	4.425446000
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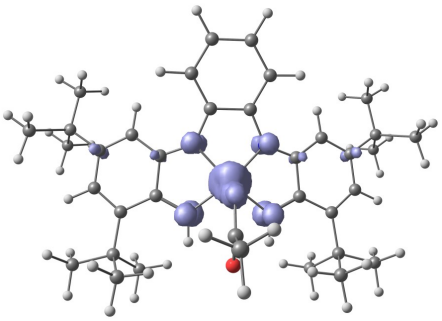


Fig. S2 Spin density plot for the quintet **1**

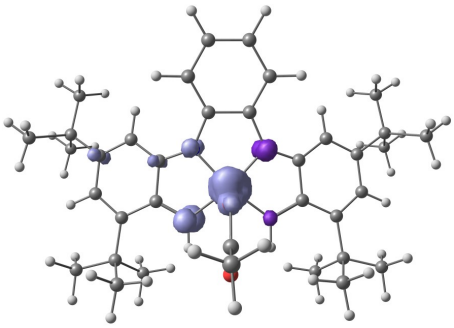


Fig. S3 Spin density plot for the "BS(3,1)" triplet **1**

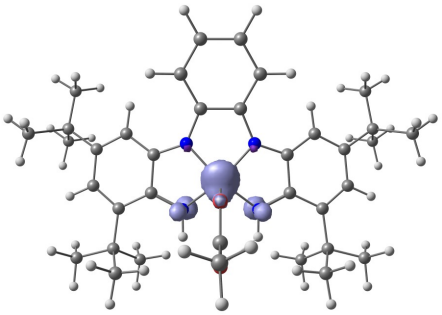


Fig. S4 Spin density plot for the triplet **1**

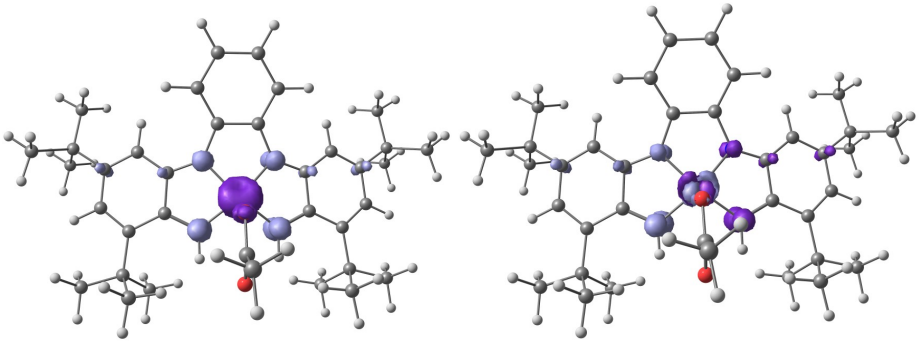


Fig. S5 Spin density plot for the two open-shell singlets $\mathbf{1}_A$ (left) and $\mathbf{1}_B$ (right), showing the diradical character of the ligand.

Table S4. Structural parameters for the optimized **1** and the X-Ray crystal structure

Configuration	Co-O1	Co-N1	Co-N2	C1-N1	C2-N2
Quintet	2.020	1.878	1.882	1.345	1.365
Triplet	1.981	1.857	1.876	1.348	1.366
Singlet	1.898	1.849	1.849	1.335	1.350
X-Ray crystal structure	1.978	1.863	1.839	1.325	1.353

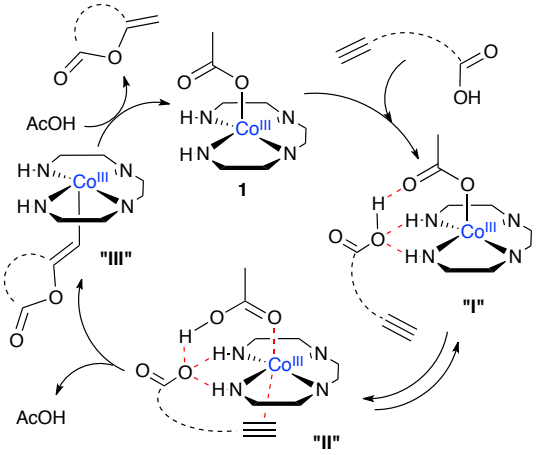
Table S5. Energetic analysis for **1** [a]

Configuration	$<S^2>$ [b]	Electronic	Electronic+ZPE	Electronic +Thermal Free Energies
Quintet	6.0329	-3153.54155	-3152.75312	-3152.83216
« BS(3,1) » triplet	2.6568	-3153.55196	-	-
Triplet	2.2897	-3153.55403	-3152.76489	-3152.84454
Closed-shell singlet	0	-3153.55573	-3152.76483	-3152.84119
Open-shell singlet $\mathbf{1_A}$	1.2216	-3153.56053	-	-
Open-shell singlet $\mathbf{1_B}$	0.8523	-3153.56045	-	-

[a] The energies are given in Ha [b] The deviations from the theoretical $<S^2>$ values (6 for the quintet, 2 for the triplet) are consistent with a multiconfigurational character of **1**.

6. Speculative mechanism

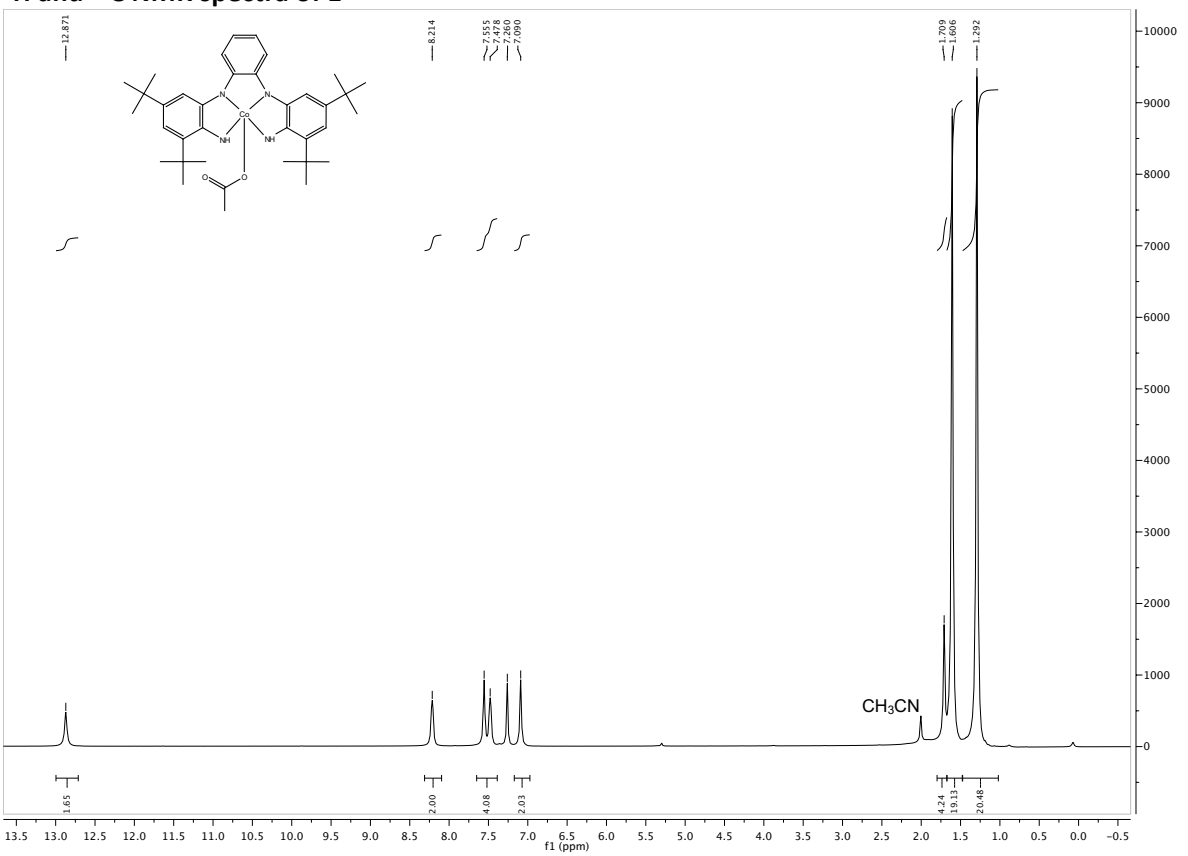
A possible mechanism is speculated in scheme S1. The N-H groups would favour both the binding and positioning of the substrate by acting as donors in a H-bond network that involves the carbonyl moiety (intermediate **"I"**). This would not only favour the approach of the alkynoic acid, but also the proton transfer to the acetate. This hypothesis is fully consistent with the fact that **2** is a poor catalyst. The acetylenic bond would then be activated by the Lewis acidity of the metal center (intermediate **"II"**). Cyclization and concomitant carboxylic proton migration from the substrate to the acetate would lead to the cyclized organometallic intermediate **"III"**. A final protonation step would release the product and regenerate the catalyst. In such a scheme, **1** would act as a bifunctional catalyst, the acetate moiety being a proton relay.

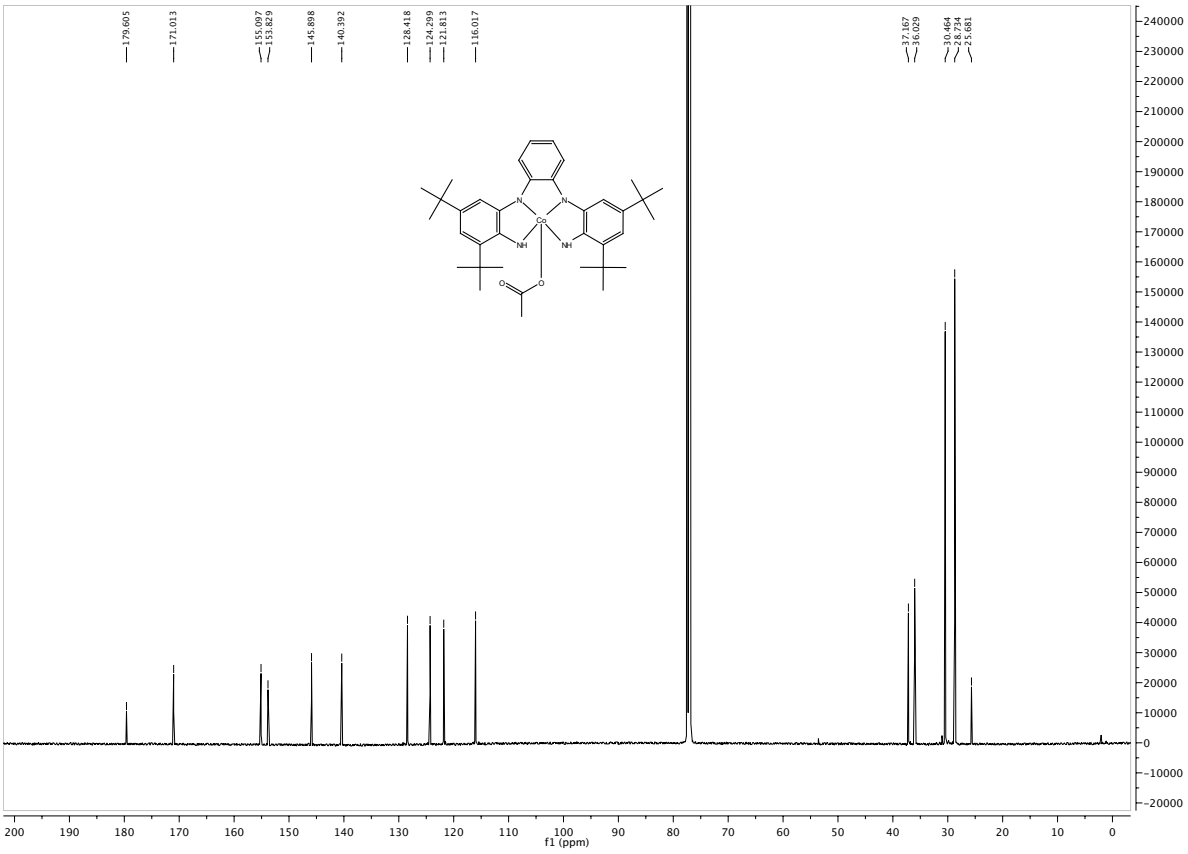


Scheme S1. Speculative reaction mechanism

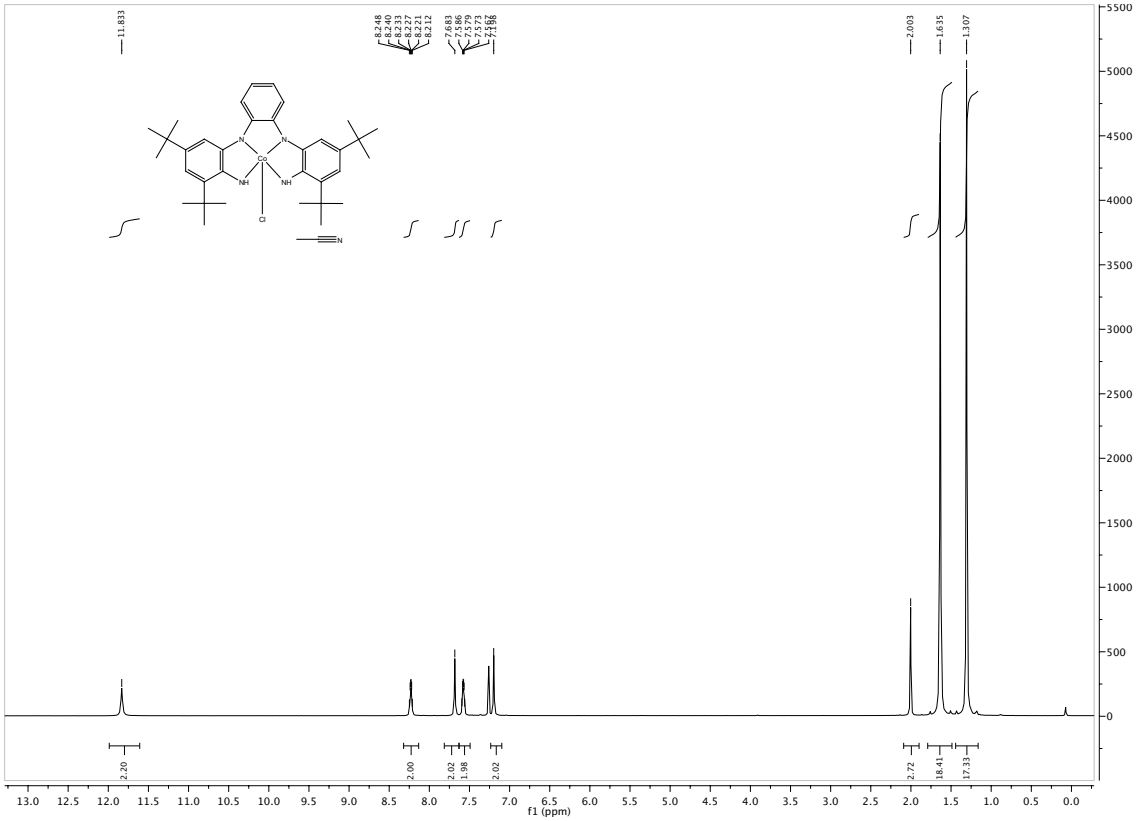
7. NMR Spectra

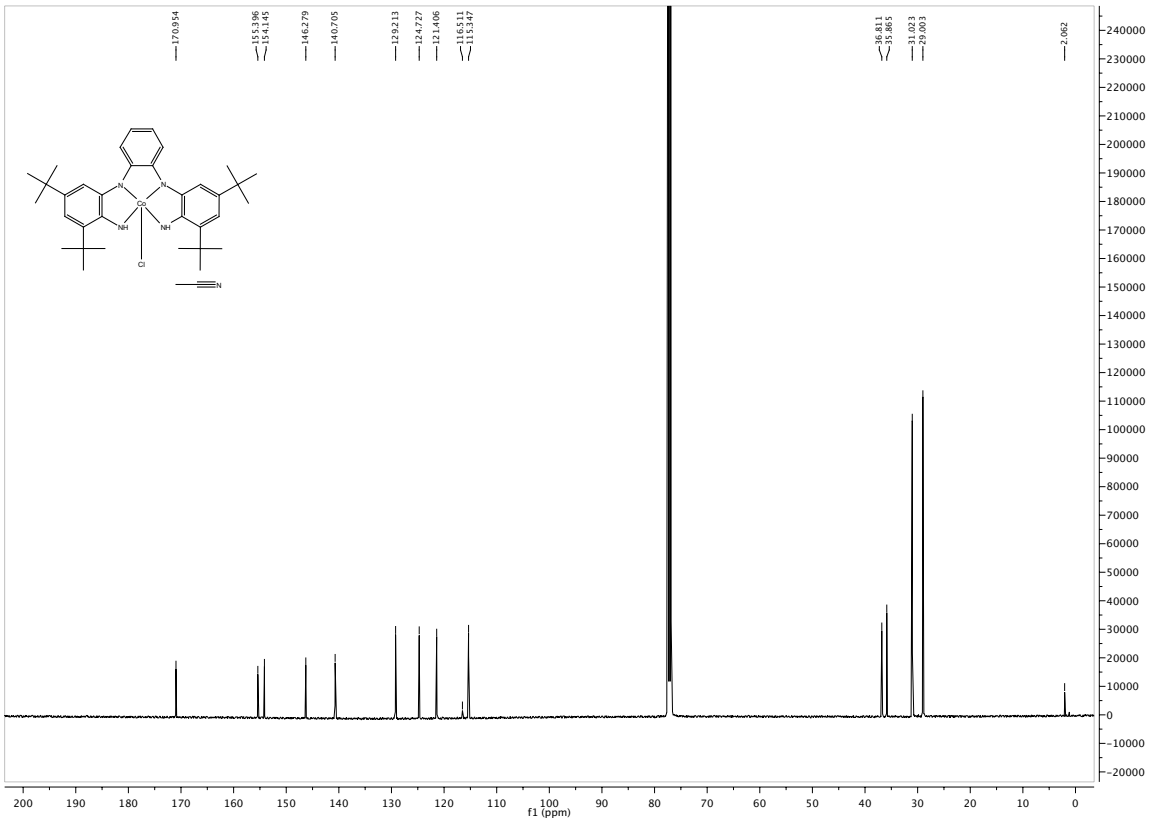
^{1}H and ^{13}C NMR spectra of 1



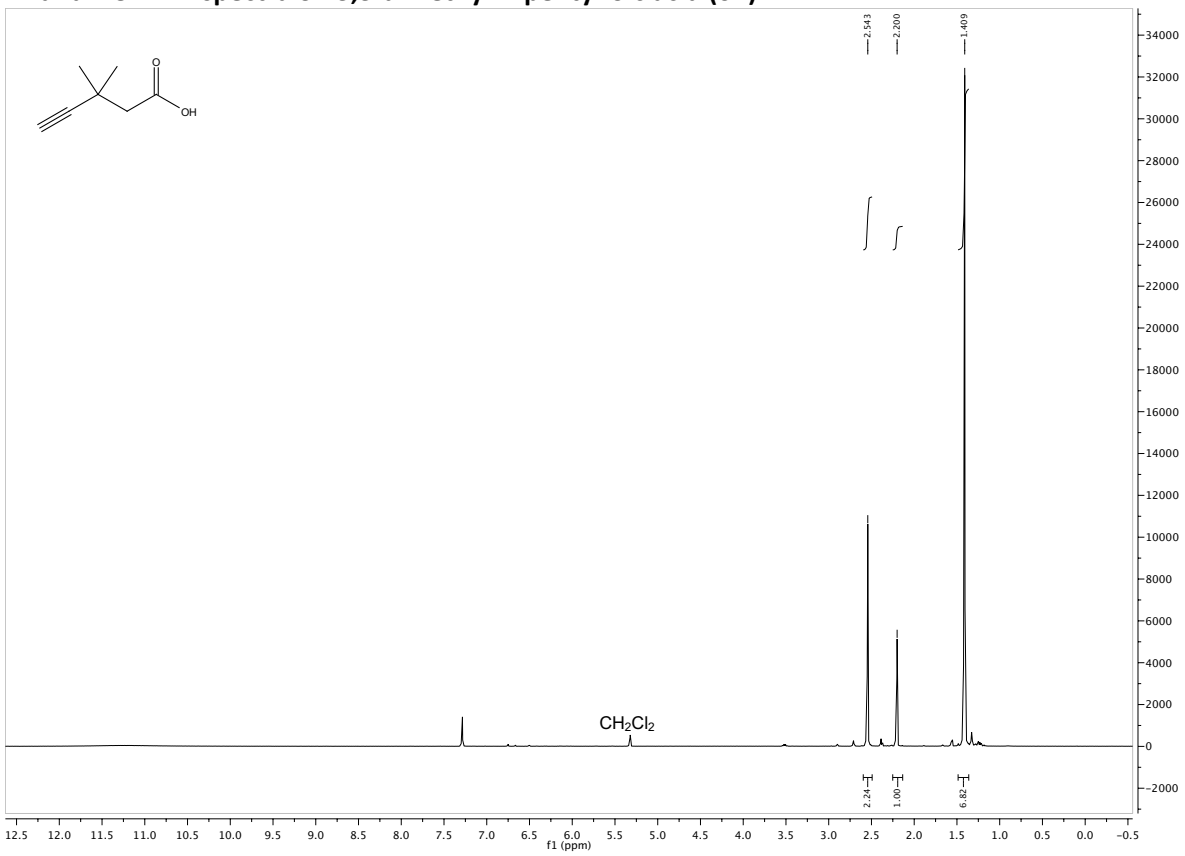


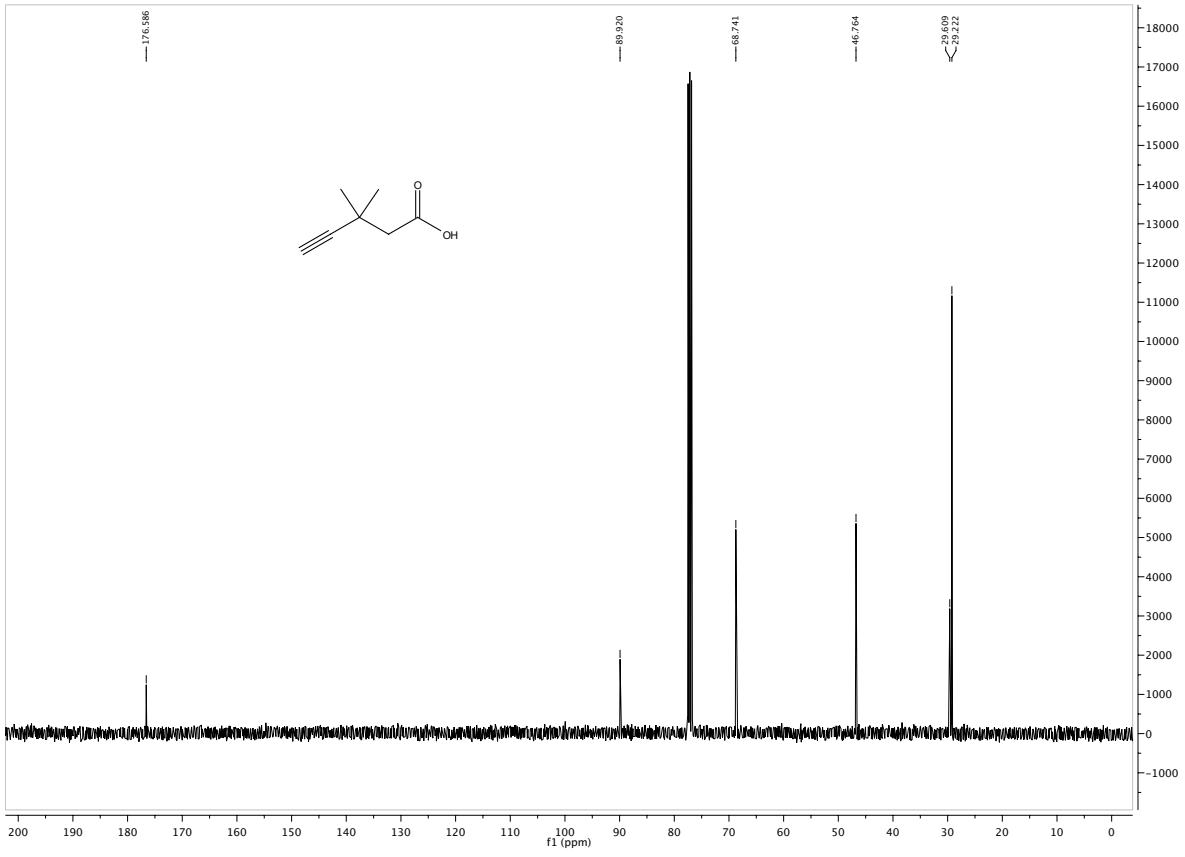
^{1}H and ^{13}C NMR spectra of 2



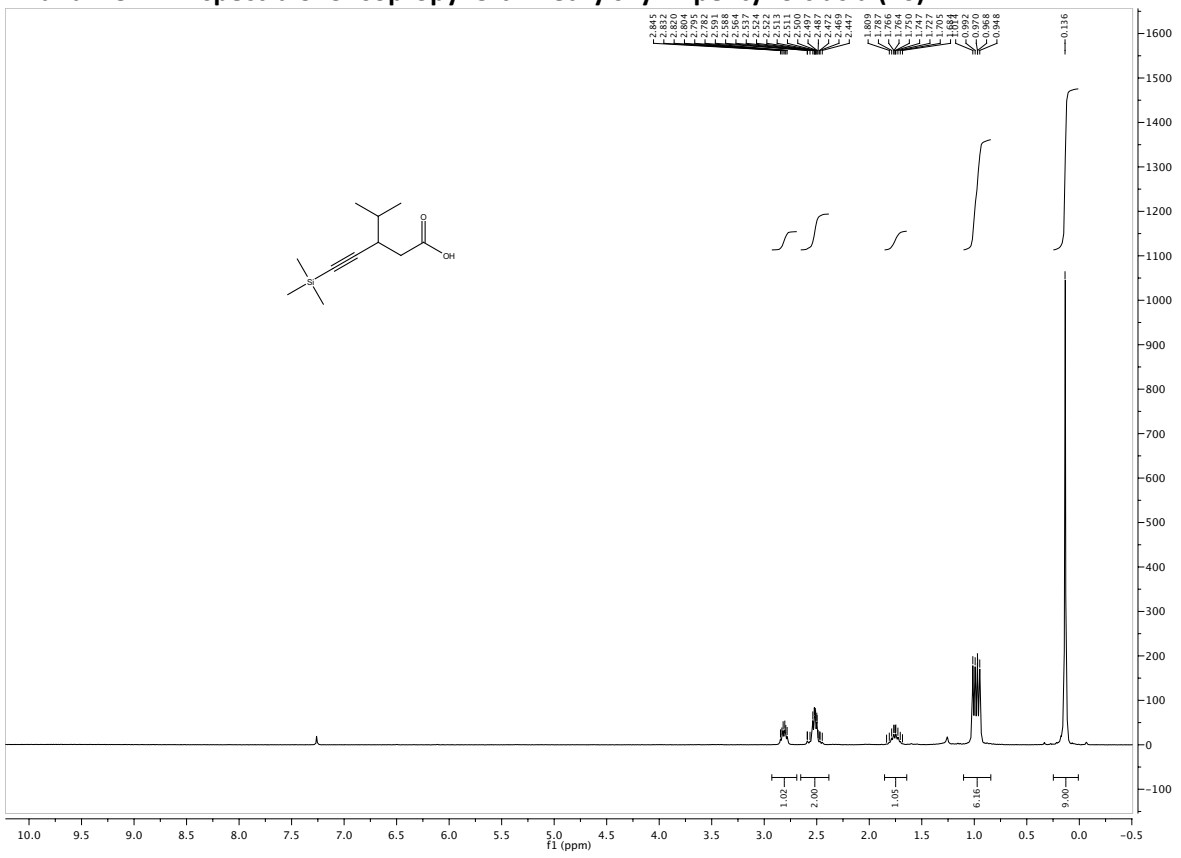


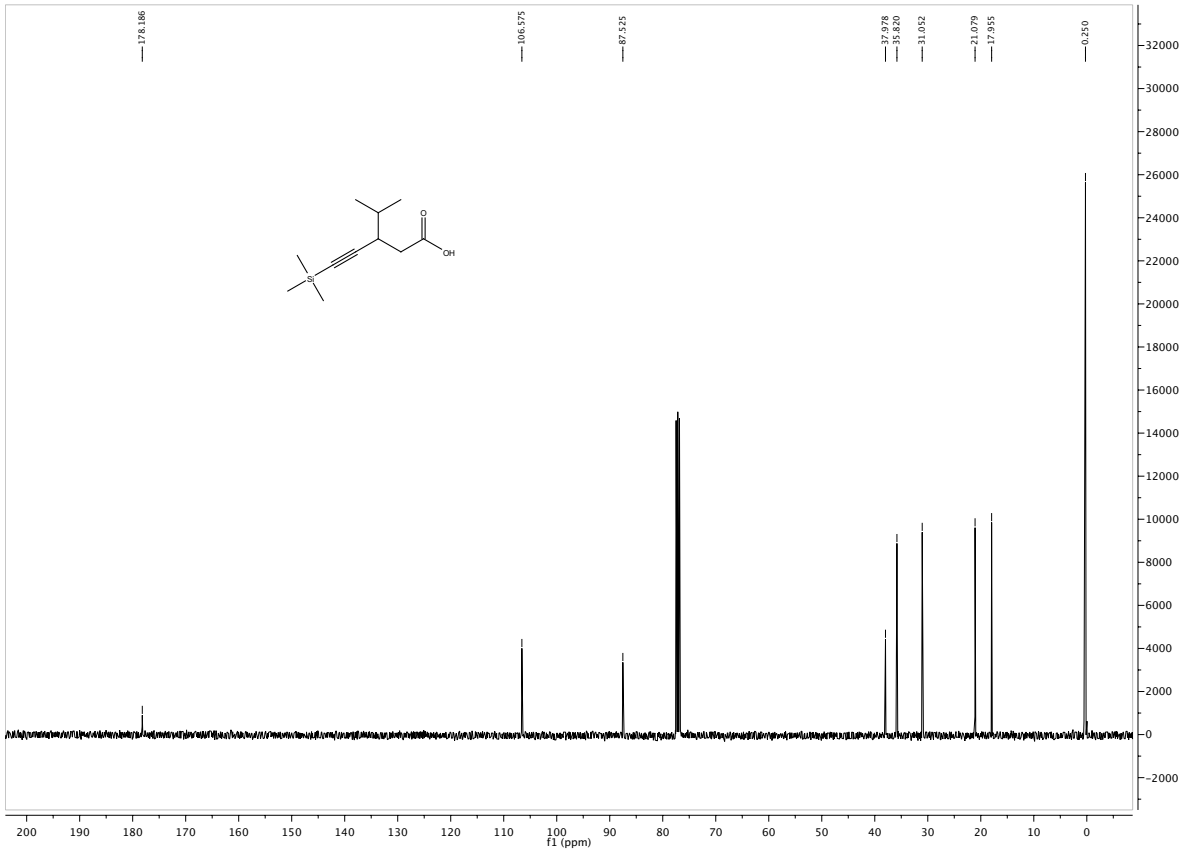
^{1}H and ^{13}C NMR spectra of 3,3-dimethyl-4-pentynoic acid (6h)



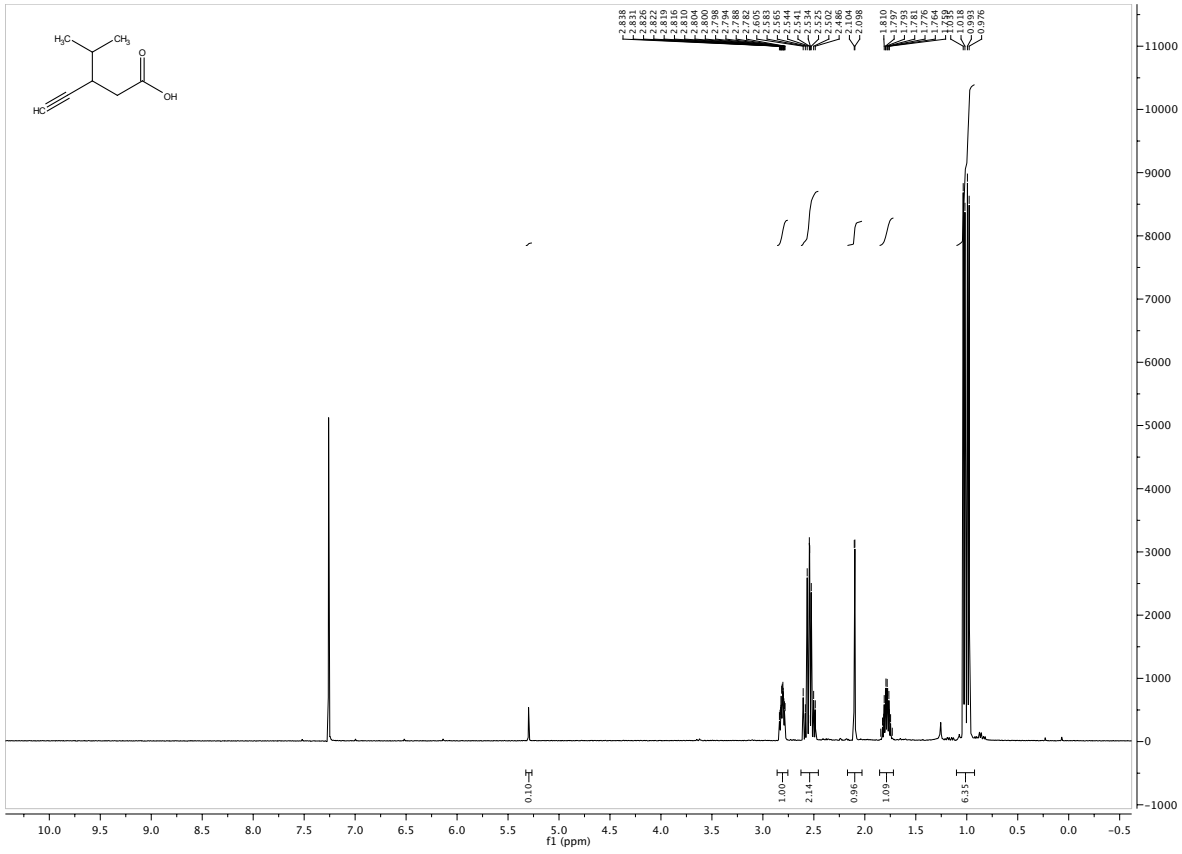


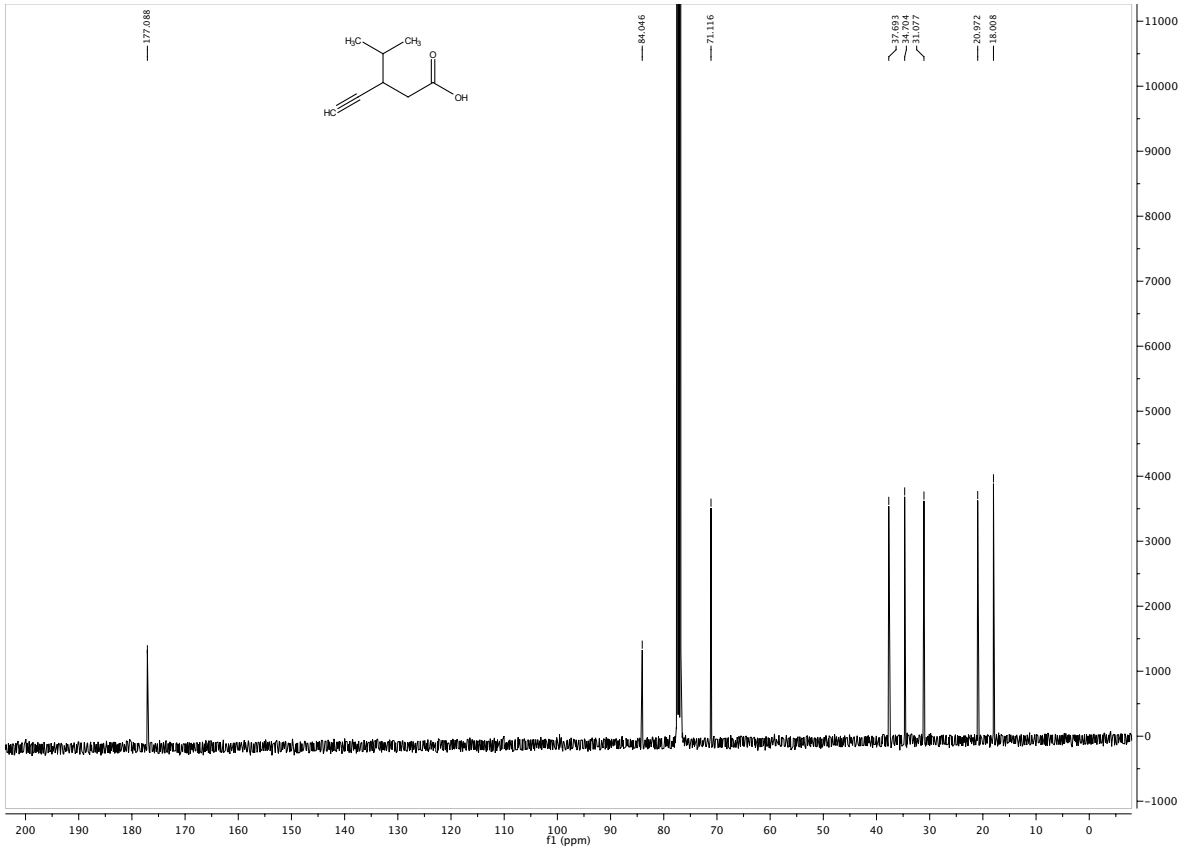
^{1}H and ^{13}C NMR spectra of 3-isopropyl-5-trimethylsilyl-4-pentynoic acid (10)



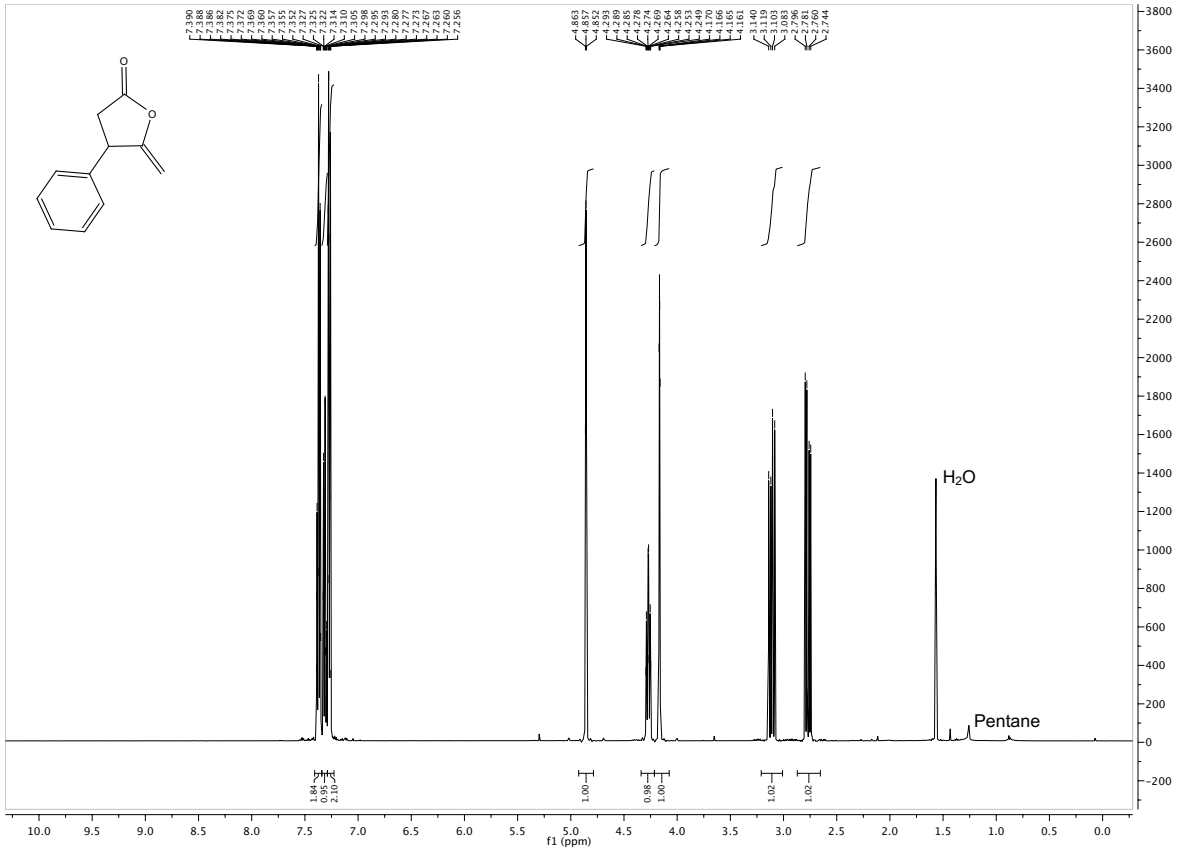


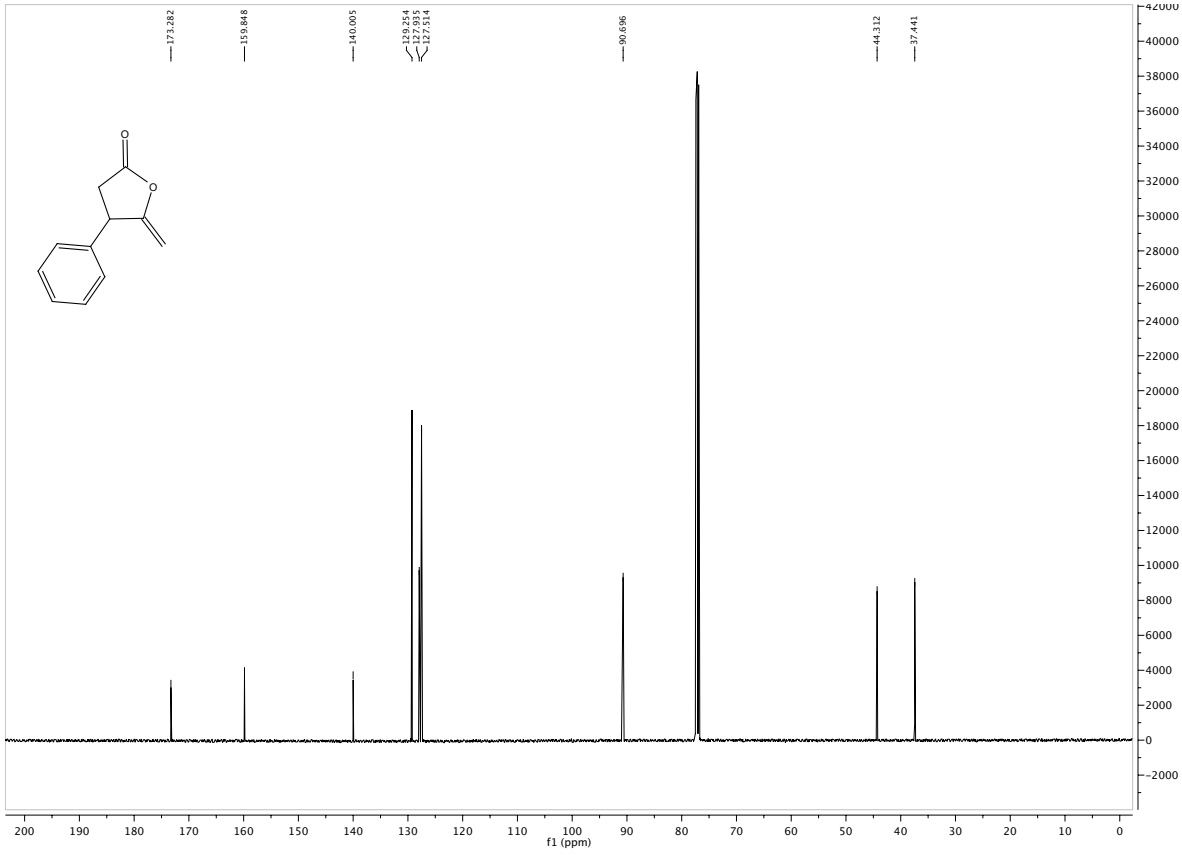
^{1}H and ^{13}C NMR spectra of 3-isopropyl-4-pentynoic acid (6f)



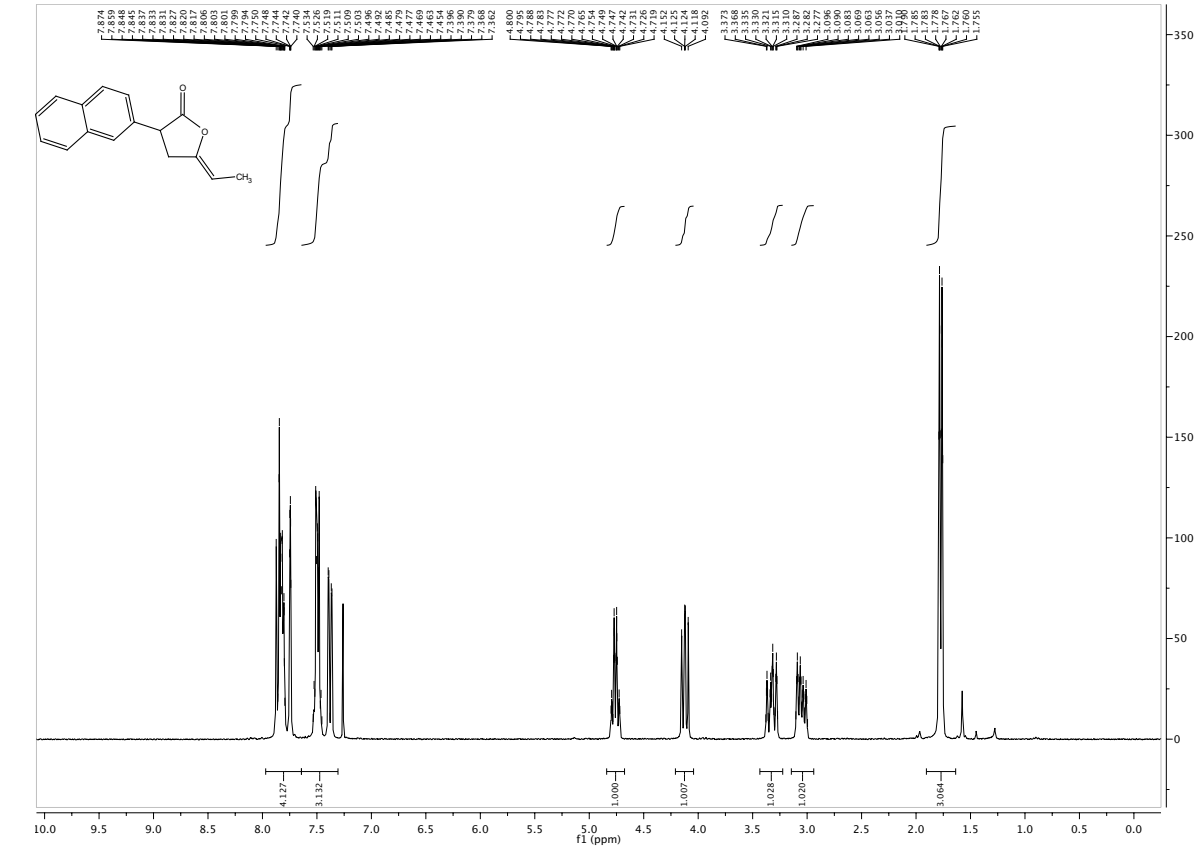


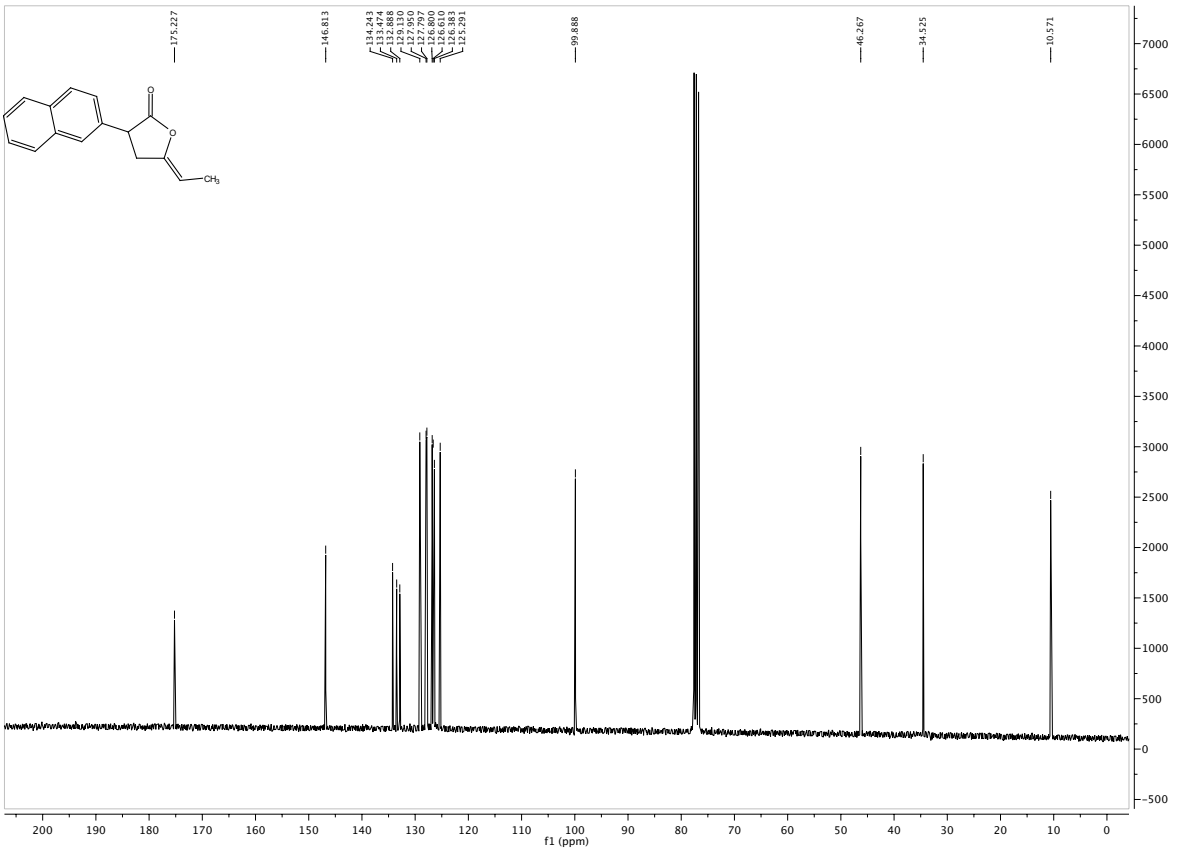
^{1}H and ^{13}C NMR spectra of 4-phenyl-5-methylenedihydrofuran-2-one (7g)



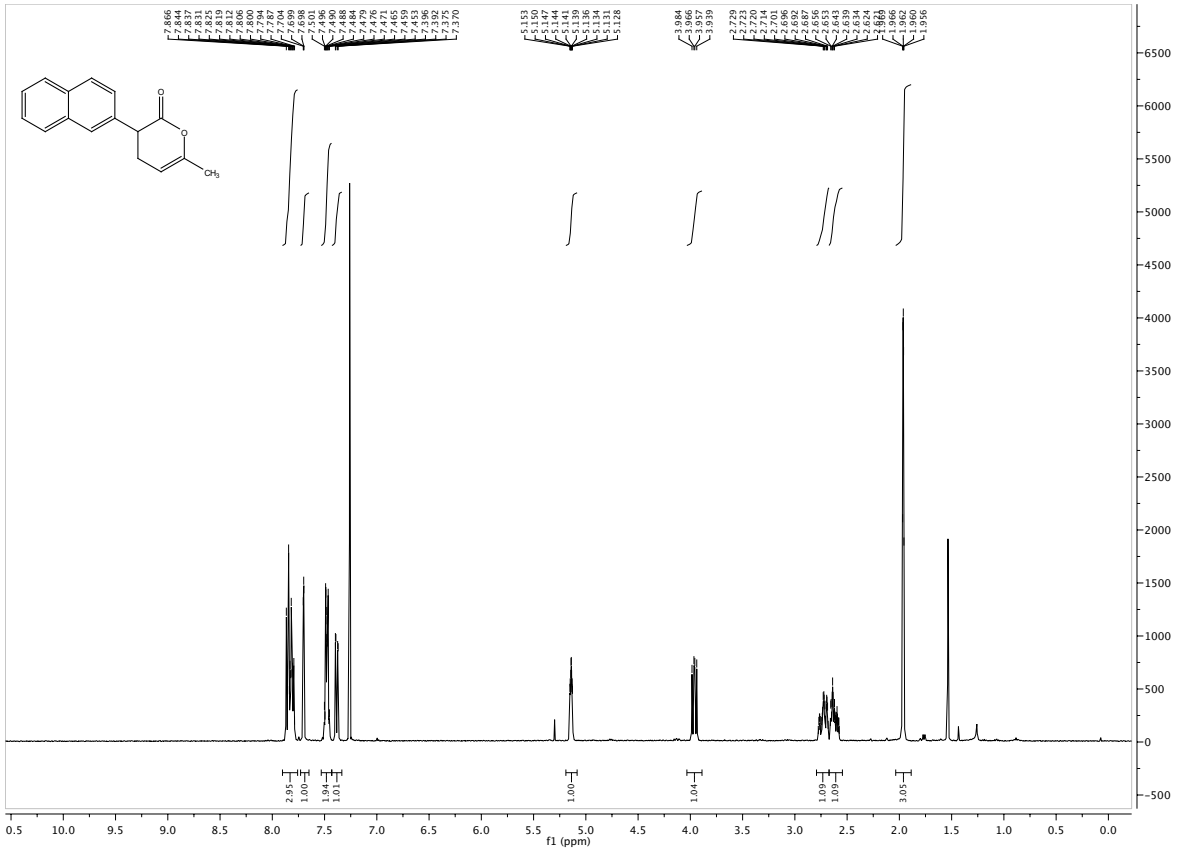


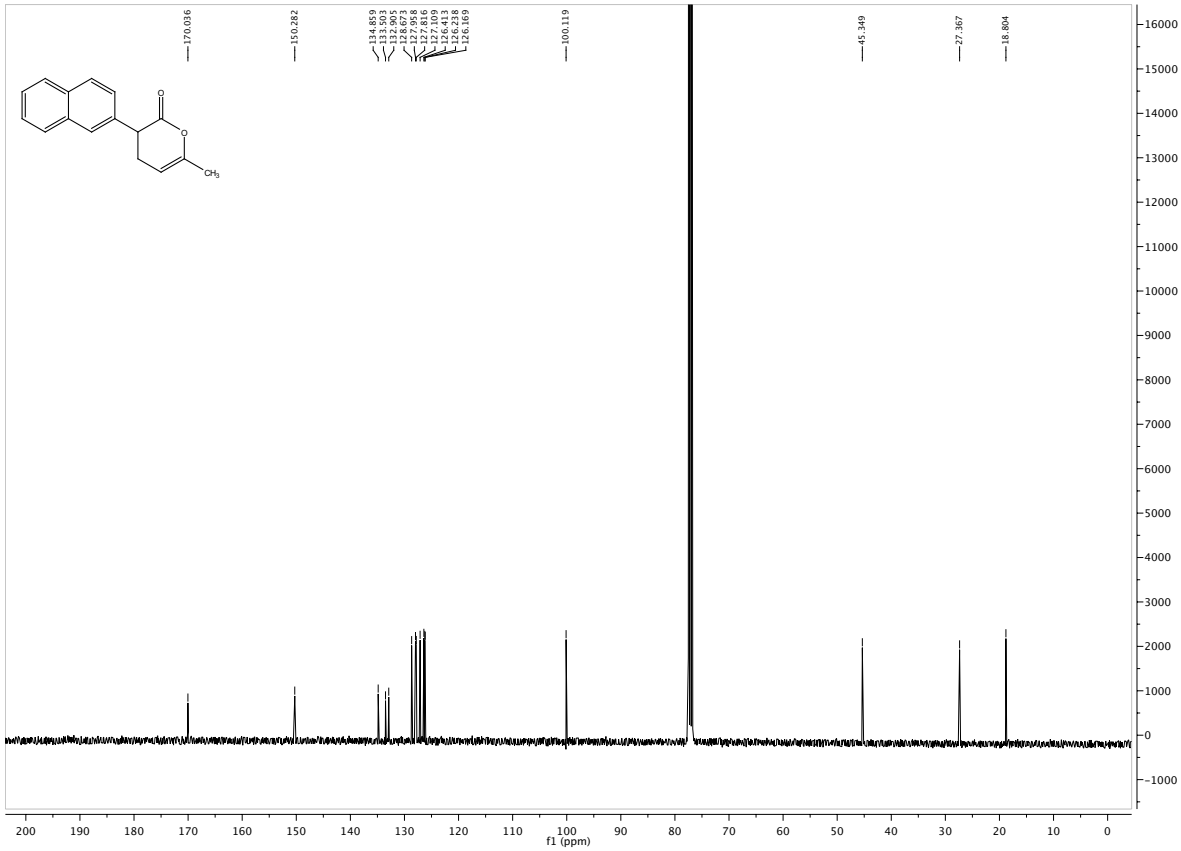
^{1}H and ^{13}C NMR spectra of 3-(2-naphthyl)-5-ethylidenedihydrofuran-2-one (7m)





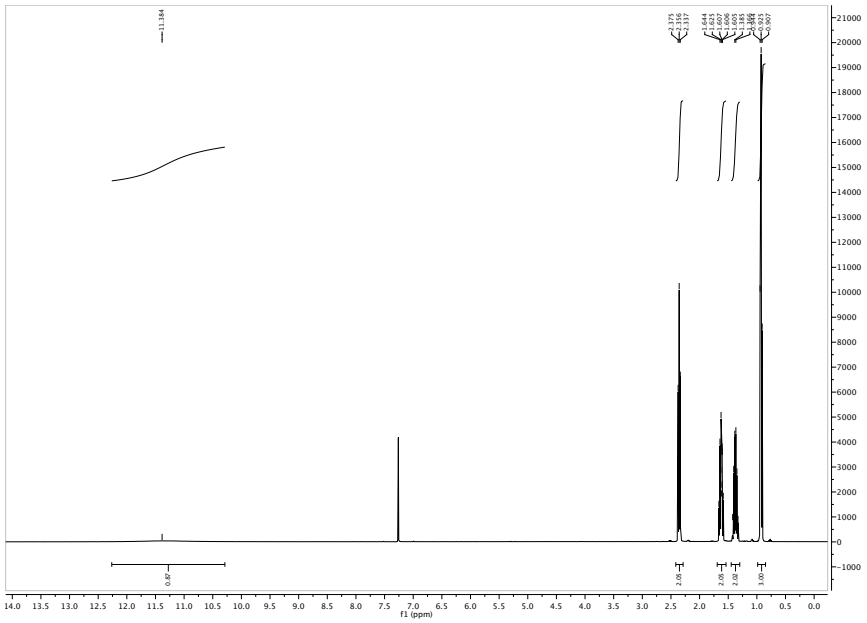
^{1}H and ^{13}C NMR spectra of 3-(2-naphthyl)-6-methyl-3,4-dihydropyran-2-one (8m)



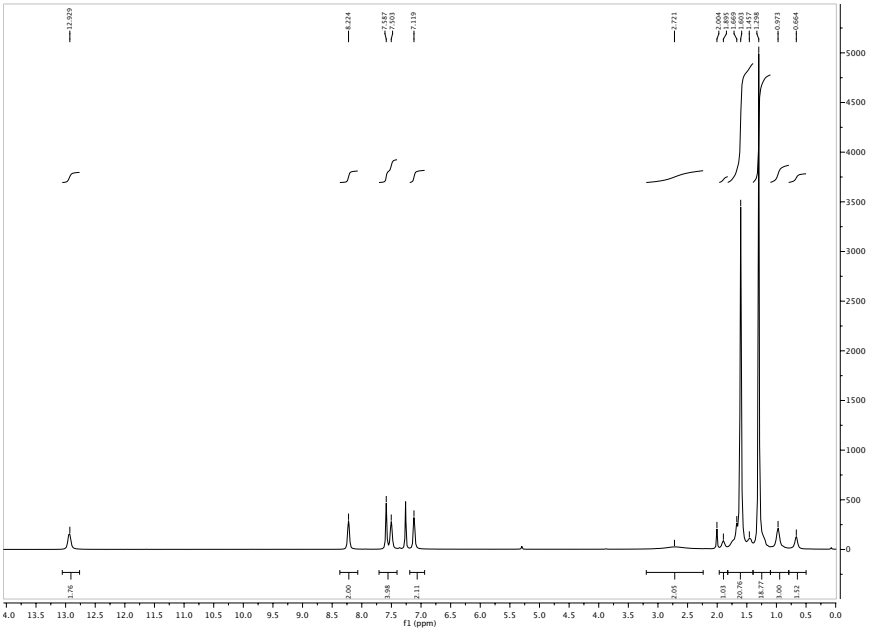


8. Reaction of complexes 1 and 2 with valeric acid

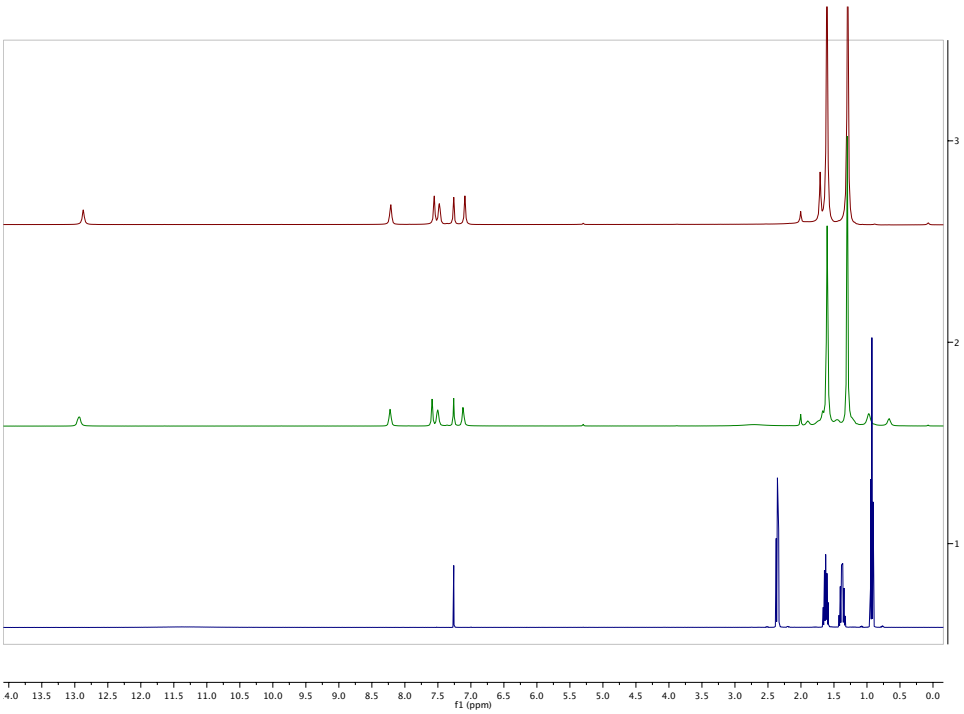
Complexes **1** and **2** were mixed with an equimolar amount of valeric acid, an unreactive analog of 4-pentynoic acid.



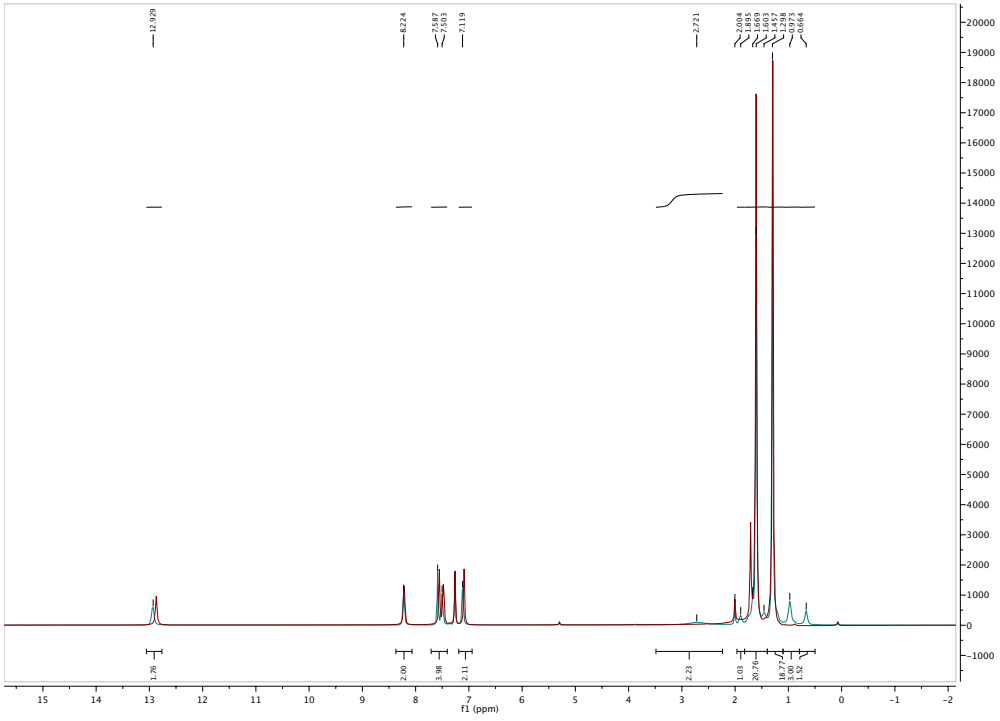
^{1}H NMR spectrum of valeric acid.



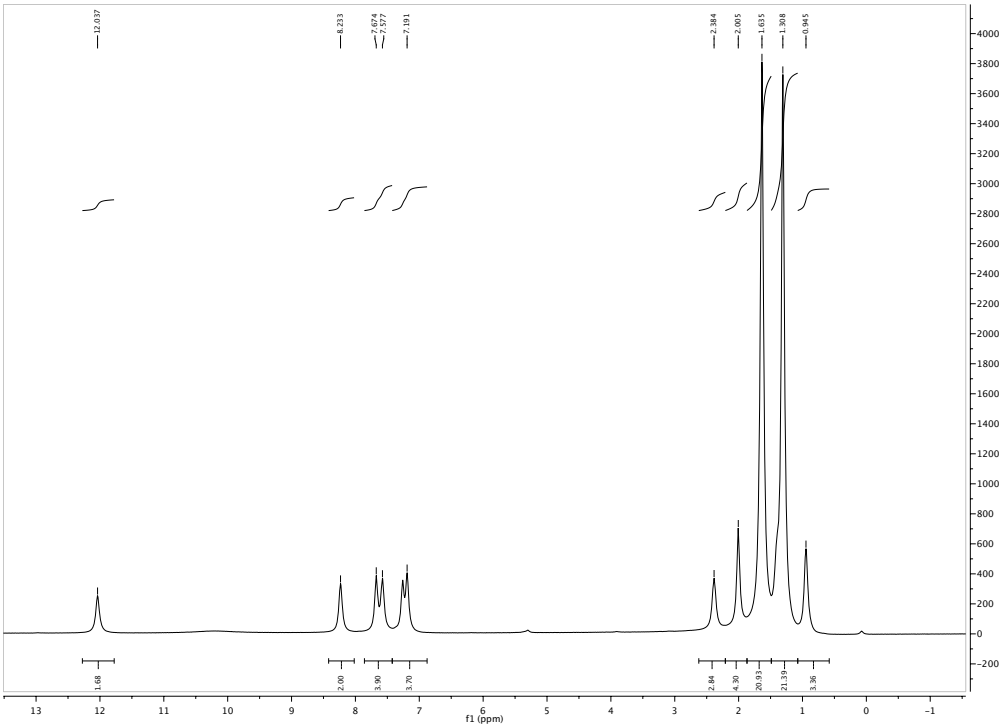
^{1}H NMR spectrum of **1** + 1.0 equivalent of valeric acid



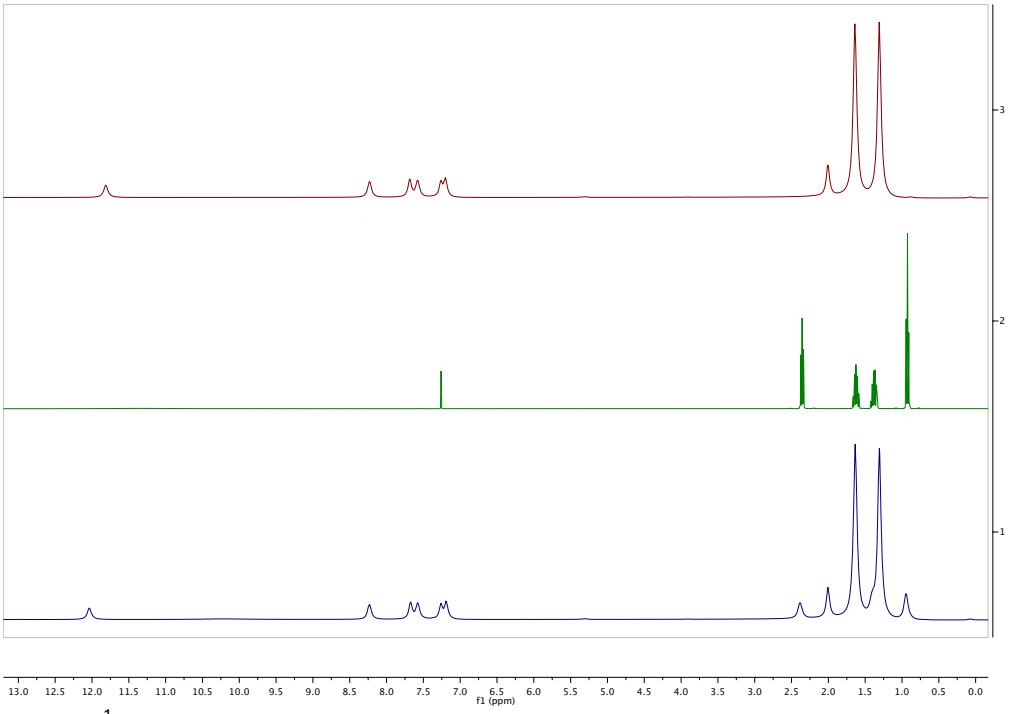
Stacked ^{1}H NMR spectra of **1** (red), **1**+valeric acid (green), valeric acid (blue).



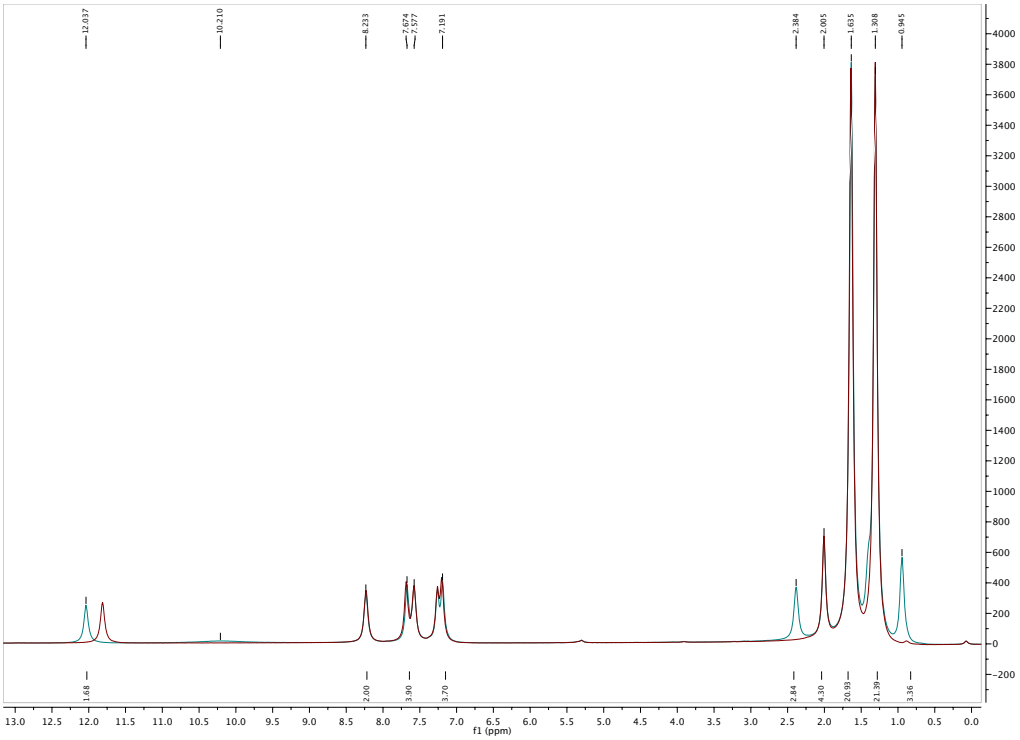
Superimposed ^{1}H NMR spectra of **1** (red) and **1** + 1.0 equivalent of valeric acid (blue)



^{1}H NMR spectrum of **2** + 1.0 equivalent of valeric acid



Stacked ^{1}H NMR spectra of **2** (red), valeric acid (green), **2**+ 1equiv. valeric acid (blue)



Superimposed ^{1}H NMR spectra of **2** (red) and **2** + 1.0 equivalent of valeric acid

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