

Electronic Supporting Information

CpCo(I) precatalysts for [2+2+2] cycloaddition reactions: synthesis and reactivity

Fabian Fischer,^a Tobias Pientka,^a Haijun Jiao,^a Anke Spannenberg^a and Marko Hapke^{*a,b}

^a *Leibniz-Institut für Katalyse e.V. (LIKAT Rostock), Albert-Einstein-Strasse 29a, D-18059 Rostock (Germany)*

^b *Johannes Kepler Universität Linz, Institut für Katalyse (INCA), Altenberger Strasse 69, A-4040 (Austria)*

E-mail: marko.hapke@jku.at

Marko Hapke: orcid.org/0000-0001-7454-9184, ResearcherID I-7444-2012

Table of contents

| | |
|--|-------|
| 1. General methods and materials..... | SI-3 |
| 2. Synthesis of ligands | SI-3 |
| 3. Synthesis and data of CpCo(CO)-phosphite complexes..... | SI-5 |
| 4. NMR and IR Spectra of the CpCo(CO)-phosphite complexes (2a-e and 2g) and of CpCo(CO)-phosphoramidite complex 2f | SI-9 |
| 5. SC-XRD of CpCo(CO)-phosphite complexes 2b and 2c | SI-19 |
| 6. Synthesis and analytical data of CpCo-olefin-phosphite complexes..... | SI-21 |
| 7. NMR and IR Spectra of the CpCo-olefin-phosphite complexes | SI-28 |
| 8. ³¹ P NMR shifts of phosphites, CpCo(CO)-phosphite and CpCo-olefin-phosphite complexes: Compilation of NMR shift data | SI-41 |
| 9. SC-XRD of CpCo-olefin-phosphite complexes 3e , 3h , 3j and 3k | SI-43 |
| 10. Precatalyst screening in [2+2+2] cycloaddition reactions – Reactions and products... | SI-48 |
| 11. Theoretical calculations on ligand exchange reactions..... | SI-62 |
| References..... | SI-68 |

1. General methods and materials

All experiments were carried out under inert gas atmosphere (argon) in flame dried Schlenk tubes or glass reaction vials. The anhydrous solvents (diethylether, THF, toluene, dichloromethane and *n*-hexane) were dried in a solvent purification system MD-5 from Inert (former Innovative Technology). All NMR spectra were recorded on a Bruker AV 300, AV 400 or Fourier 300 NMR spectrometer. HRMS (ESI-TOF) was performed at a Agilent 6210 Time-of-Flight LC/MS. Elemental analysis was performed at a Perkin Elmer AAS-Analyst 300 (Co), Leco Microanalyser-TruSpec CHNS (C, H), Radiometer Analytical SAS (Titrator) Titrablab 870-TIM 870 (Br) and a Perkin Elmer UV/VIS-spectrometer Lambda 2 (P).

Photochemistry was performed in a thermostated glass reaction vessel (two mercury medium pressure lamps, ca. 900 W total).¹

SC-XRD (Single Crystal X-ray Diffraction): Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods² and refined by full-matrix least-squares procedures on F^2 .³ XP (Bruker AXS) was used for graphical representations.

The phosphites P(O*i*Pr)₃ (**L^{1a}**), P[OCH₂(CF₃)₂]₃ (**L^{1b}**) and P(OCH₂*t*Bu)₃ (**L^{1e}**) as well as 2,4-bis(*tert*-butyl)phenyl]phosphite (**L^{1g}**) are commercially available and have been dried by addition of spherical molecular sieve A4. They were only distilled in vacuum, if the purity was <98%. The olefins used in this study, **L^{2a}** to **L^{2e}**, are commercially available, except compound **L^{1e}** (N,N'-diacetyl imidazole-2-one), which was synthesised according to a literature procedure and sublimed for purification.⁴

2. Synthesis of ligands

Tri-*tert*-butylphosphite (**L^{1c}**)⁵

Ligand **L^{1c}** was synthesised in accordance to a procedure reported by Bornhop et al. PCl₃ (7.54 g, 55 mmol, 0.33 equiv.) dissolved in anhydrous Et₂O (20 ml) is added slowly and dropwise at 0 °C to a mixture of *tert*-butanol (12.27 g, 165 mmol, 1.0 equiv.) and triethylamine (18.21 g, 180 mmol, 1.1 equiv.) dissolved in anhydrous Et₂O (100 ml). The reaction mixture is then stirred for further 2 h at 0 °C, resulting in the formation of a white suspension. After further addition of additional 50 ml of anhydrous Et₂O the suspension is stirred for additional 18 h. Subsequent filtration over celite and evaporation of the solvent in vacuum, followed by removal of residual solvent in high vacuum gave the product **L^{1c}** as colourless oil (7.5 g, 54%). The purity was sufficient for the ligand exchange experiments.

¹H NMR (300 MHz, CDCl₃): δ = 1.34 (s, 27H) ppm. ³¹P NMR (122 MHz, CDCl₃): δ = 140.6 ppm. The data are in accordance to the literature data.⁵

Tricyclohexylphosphite (L^{1d})⁶

A solution of PCl₃ (45 g, 450 mmol, 1.0 equiv.) in anhydrous Et₂O was added dropwise at 0 °C to a solution of cyclohexanol (20.6 g, 150 mmol, 0.33 equiv.) and N,N-dimethylaniline (55 g, 450 mmol, 1.0 equiv.) in anhydrous Et₂O. The reaction was stirred for 110 h at 25 °C and then the solid reaction products filtered off and washed with diethyl ether. The filtrate was dried with Na₂SO₄, filtered again and the solvent removed under reduced pressure. Isolation of pure product was accomplished by distillation at 160 °C in high vacuum (ca. 2.5 · 10⁻³ mbar), yielding 28.9 g (59%) Tri-*cyclo*-hexylphosphite (L^{1c}) as colourless solid.

¹H NMR (300 MHz, CDCl₃): δ = 4.07 (qt, *J* = 9.3, 4.0 Hz, 3H), 2.03-1.64 (m, 12H), 1.57-1.09 (m, 18H) ppm. ³¹P NMR (122 MHz, CDCl₃): δ = 139.6 ppm. The data are in accordance to the literature data.⁶

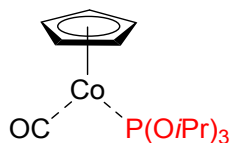
N,N-diethyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L^{1f})⁷

According to a procedure by Wills *et al.*,⁸ tris(diethylamino)phosphine (5.1 g, 20.6 mmol, 1.5 equiv.) and (*S*)-BINOL (3.93 g, 13.7 mmol, 1.0 equiv.) were dissolved in toluene (100 ml) and heated to 110 °C for 16 h. The resulting white solid was filtered off over silica gel and washed with a mixture of ethyl acetate and petrol ether (1:4, v/v). The remaining solid was dissolved in dichloromethane, separated from the silica gel by filtration and the solvent removed under reduced pressure. The remaining solid was dried thoroughly in high vacuum and 4.9 g (92%) of the phosphoramidite L^{1f} obtained as white solid.

¹H NMR (300 MHz, CDCl₃): δ = 8.04-7.86 (m, 4H), 7.57-7.21 (m, 8H), 3.16-2.76 (m, 4H), 1.06 (t, *J* = 7.1 Hz, 6H) ppm. ³¹P NMR (122 MHz, CDCl₃): δ = 150.2 ppm. The data are in accordance to the literature data.⁷

3. Synthesis and data of CpCo(CO)-phosphite complexes

General synthetic procedure as exemplified for the synthesis of compound 2a:

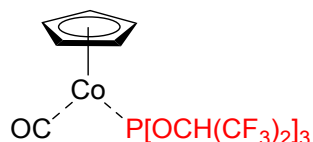


CpCo(CO)₂ (900 mg, 5.0 mmol, 1.0 equiv.) and triisopropylphosphite (**L^{1a}**) (1.04 g, 5.0 mmol, 1.0 equiv.) were stirred without solvent at room temperature for 21 h under slight under-pressure, before heated to 65 °C for 7 h. The solution was filtered over a small amount of neutral Al₂O₃ (Brockman Type I), which was afterwards washed with THF (20 ml). After removal of the solvent the deep red liquid was dried under vacuum (yield: 1.8 g, >99%).

¹H NMR (300 MHz, THF-*d*₈): δ = 4.82–4.69 (m, 8H), 1.24 (d, *J* = 6.3 Hz, 18H) ppm. ¹³C NMR (75 MHz, THF-*d*₈): δ = 82.9 (d, *J* = 1.7 Hz), 69.7 (d, *J* = 2.6 Hz), 24.5 (d, *J* = 4.1 Hz) ppm. ³¹P NMR (122 MHz, THF-*d*₈): δ = 168.9 ppm.

IR: ν_{max} = 2975, 2934, 1921, 1382, 1289, 1139, 1105, 954, 875, 800, 766, 725, 596, 557 cm⁻¹.

Synthesis of compound 2b:

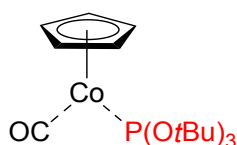


CpCo(CO)₂ (633 mg, 3.51 mmol, 1.0 equiv.) and tris-(3,3,3,6,6,6-hexafluoro-isopropyl) phosphite (**L^{1b}**) (1.867 g, 3.51 mmol, 1.0 equiv.) were stirred at room temperature without solvent for 24 h under slight under-pressure, before heated to 65 °C for 3 h. The solution was filtered over a small amount of neutral Al₂O₃ (Brockman Type I) under inert conditions, which was washed with THF (20 ml). All volatile substances were removed under high vacuum, affording a red oily product, which was crystallized from Et₂O to furnish a red crystalline product (yield: 2.16 g, 90%).

¹H NMR (400 MHz, toluene-*d*₈): δ = 5.53–5.41 (m, 3H), 4.46 (s, 5H) ppm. ¹³C NMR (100 MHz, toluene-*d*₈): δ = 120.8 (d, *J* = 284 Hz), 84.6, 72.3 (hept, *J* = 35.6 Hz) ppm. ¹⁹F NMR (282 MHz, toluene-*d*₈) δ = -73.4 ppm. ³¹P NMR (162 MHz, toluene-*d*₈): δ = 189.1 ppm.

IR: ν_{max} = 2910, 1966, 1375, 1289, 1194, 1086, 869, 820, 685, 626, 539, 451 cm⁻¹.

Synthesis of compound 2c:



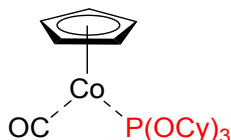
CpCo(CO)₂ (1 g, 5.56 mmol, 1.0 equiv.) and tri-*tert*-butylphosphite (**L^{1c}**) (1.32 g, 5.56 mmol, 1.0 equiv.) were stirred at room temperature for 21 h, before heated to 65 °C for 3 h. The solution was filtered over a small amount of neutral Al₂O₃ (Brockman Type I), which was

washed with THF (20 ml). All volatile substances were removed under high vacuum, affording a red solid (yield: 530 mg, 24%).

^1H NMR (300 MHz, THF- d_8): δ = 4.66 (s, 5H), 1.53 (s, 27H) ppm. ^{13}C NMR (75 MHz, THF- d_8): δ = 83.8 (d, J = 1.7 Hz), 81.1 (d, J = 9.9 Hz), 31.4 (d, J = 3.9 Hz) ppm. ^{31}P NMR (122 MHz, THF- d_8): δ = 142.6 ppm.

IR: ν_{max} = 2974, 1923, 1389, 1364, 1240, 1172, 1033, 945, 906, 800, 692, 553, 495 cm^{-1} .

Synthesis of compound 2d:

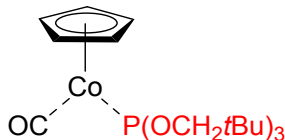


According to the general procedure, CpCo(CO) $_2$ (822 mg, 4.6 mmol, 1.0 equiv.) and tricyclohexylphosphite (**L^{1d}**) (1.51 g, 4.6 mmol, 1.0 equiv.) were stirred at room temperature for 23 h, before heated to 60 °C for 3 h. The solution was filtered over a small amount of neutral Al $_2$ O $_3$ (Brockman Type I), which was washed with THF (20 ml). A red solid was afforded and recrystallised in *n*-pentane at -78 °C (yield: 1.74 g, 79%).

^1H NMR (300 MHz, THF- d_8): δ = 4.78 (s, 5H), 4.58-4.44 (m, 3H), 1.97-1.63 (m, 12H), 1.60-1.19 (m, 18H) ppm. ^{13}C NMR (75 MHz, THF- d_8): δ = 82.9 (d, J = 1.3 Hz), 74.6 (d, J = 3.0 Hz), 34.8 (d, J = 3.5 Hz), 26.6, 24.7 ppm. ^{31}P NMR (122 MHz, THF- d_8): δ = 168.8 ppm.

IR: ν_{max} = 2929, 2854, 1915, 1447, 967, 860, 783, 640, 559 cm^{-1} .

Synthesis of compound 2e:

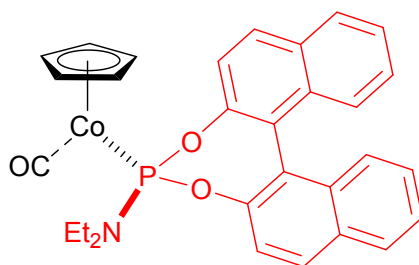


CpCo(CO) $_2$ (535 mg, 2.98 mmol, 1.0 equiv.) and tri-*neo*-pentylphosphite (**L^{1e}**) (870 mg, 2.98 mmol, 1.0 equiv.) in THF (5 ml) were stirred at room temperature for 18 h, before heated to 65 °C for 4 h. The solution was filtered over a small amount of neutral Al $_2$ O $_3$ (Brockman Type I), which was washed with THF (20 ml). After removal of the solvent the deep red liquid was dried under vacuum (yield: 1.05 g, 81%).

^1H NMR (300 MHz, THF- d_8): δ = 4.82 (s, 5H), 3.62 (d, J = 5.2 Hz, 6H), 0.96 (s, 27H) ppm. ^{13}C NMR (75 MHz, THF- d_8): δ = 82.6 (d, J = 1.7 Hz), 75.0 (d, J = 3.6 Hz), 33.0 (d, J = 7.8 Hz), 27.0 ppm. ^{31}P NMR (122 MHz, THF- d_8): δ = 170.9 ppm.

IR: ν_{max} = 2955, 2870, 1931, 1477, 1364, 1000, 816, 798, 597, 575, 525 cm^{-1} .

Synthesis of compound 2f:

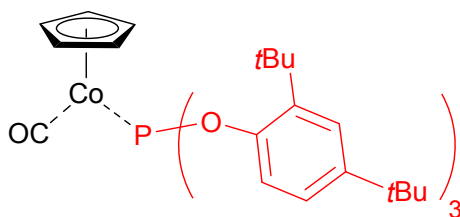


CpCo(CO)₂ (900 mg, 5.0 mmol, 1.0 equiv.) and (**L1f**) (1.04 g, 5.0 mmol, 1.0 equiv.) were stirred at room temperature for 21 h, before heated to 65 °C for 7 h. The solution was filtered over a small amount of neutral Al₂O₃ (Brockman Type I), which was washed with THF (20 ml). After removal of the solvent a deep red liquid was obtained, which was dried under high vacuum (yield: 1.8 g >99%).

¹H NMR (300 MHz, THF-*d*₈): δ = 7.98 (d, *J* = 28.6 Hz, 4H), 7.59 (dd, *J* = 8.8, 1.1 Hz, 1H), 7.43-7.17 (m, 7H), 4.55 (s, 5H), 3.58 (s, 2H), 2.89 (ddt, *J* = 14.2, 8.9, 7.0 Hz, 2H), 1.00 (t, *J* = 7.0 Hz, 6H) ppm. ³¹P NMR (122 MHz, THF-*d*₈): δ = 188.5 ppm.

IR: ν_{max} = 3051, 2967, 2929, 2861, 2019, 1926, 1230, 1204, 1166, 939, 786, 601 cm⁻¹.

Synthesis of compound 2g:

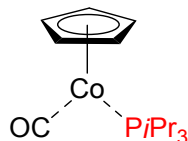


Tris[2,4-bis(*tert*-butyl)phenyl]phosphite (**L1f**) (1.87 g, 2.90 mmol, 1.0 equiv.) was added to solution of CpCo(CO)₂ (520 mg, 2.90 mmol, 1.0 equiv.) in toluene (10 ml). The solution was irradiated with light (medium pressure mercury lamp, thermostated glass reaction vessel) under reduced pressure for a total for a total of 24 h, during which the reactor was vented and partially evacuated two more times. After filtration over a small amount of neutral Al₂O₃ (Brockman Type I), which was eluted with THF (20 ml), the solvent was removed under reduced pressure and the isolated orange solid was dried in vacuum. It should be noted that the product possibly needs to be purified again with the aforementioned method to be obtained in sufficient purity for the subsequent ligand exchange step, where residues of the solid phosphite (**L1f**) can be problematic (yield: 2.15 g, 93%).

¹H NMR (300 MHz, THF-*d*₈): δ = 7.68 (dd, *J* = 8.6, 1.0 Hz, 3H), 7.35 (d, *J* = 1.8 Hz, 3H), 7.04 (dd, *J* = 8.6, 2.5 Hz, 3H), 4.60 (s, 5H), 1.50 (s, 27H), 1.22 (s, 27H) ppm. ¹³C NMR (75 MHz, THF-*d*₈): δ = 149.7 (d, *J* = 6.2 Hz), 146.6, 139.1 (d, *J* = 6.0 Hz), 125.1, 124.0, 120.9 (d, *J* = 8.1 Hz), 83.9, 36.0, 35.2, 31.9, 31.18 ppm. ³¹P NMR (122 MHz, THF-*d*₈): δ = 156.0 ppm.

IR: ν_{max} = 2955, 2867, 1955, 1488, 1360, 1186, 1081, 912, 870, 804, 774, 612, 550, 494 cm⁻¹.

Synthesis of compound **2h_{phosphine}**:⁹

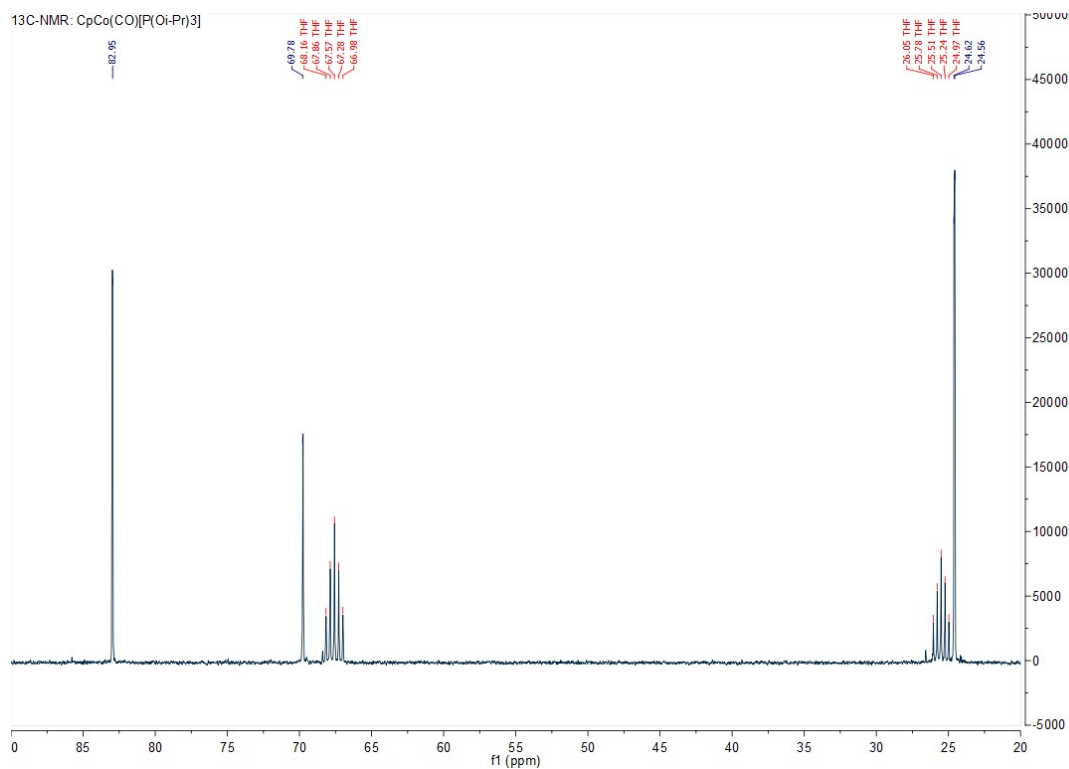
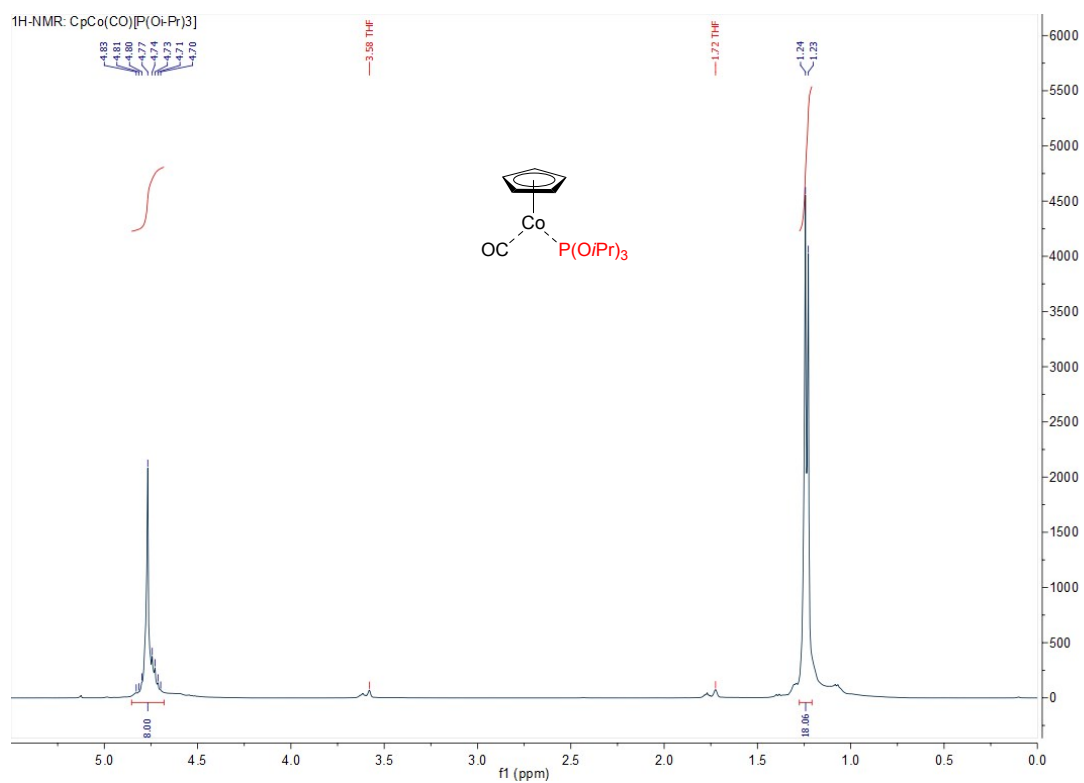


CpCo(CO)₂ (1.235 g, 6.86 mmol, 1.0 equiv.) and triisopropylphosphine (**2h_{phosphine}**) (1.10 g, 6.86 mmol, 1.0 equiv.) were stirred without solvent at room temperature for 13 h under slight reduced pressure, before heating to 70 °C for 4 h. The solution was filtered over a small amount of neutral Al₂O₃ (Brockman Type I), which was afterwards washed with THF (20 ml). After removal of the solvent the deep red liquid was dried under vacuum (yield: 2.13 g, 99%).
¹H NMR (300 MHz, THF-*d*₈): δ = 4.70 (m, 5H), 2.11-1.94 (m, 3H), 1.24-1.14 (m, 18H) ppm.
¹³C NMR (75 MHz, THF-*d*₈): δ = 82.0 (bs), 28.2 (d, *J* = 21.5 Hz), 20.2 (bs) ppm. ³¹P NMR (122 MHz, THF-*d*₈): δ = 88.0 ppm.

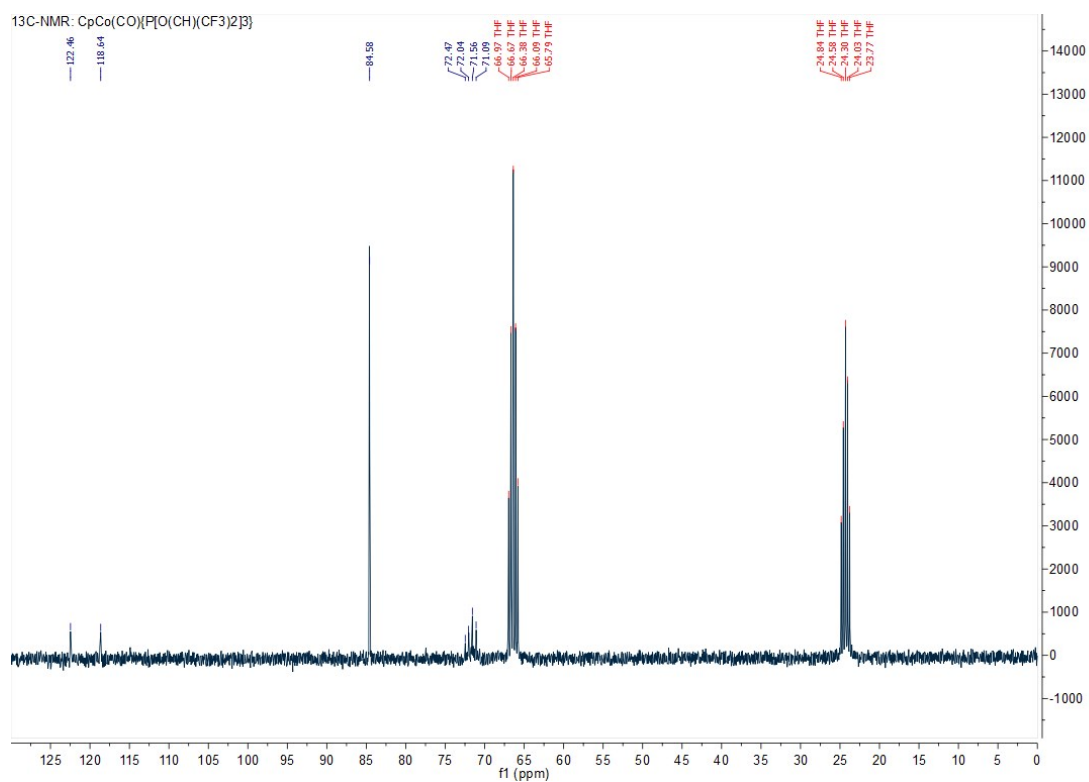
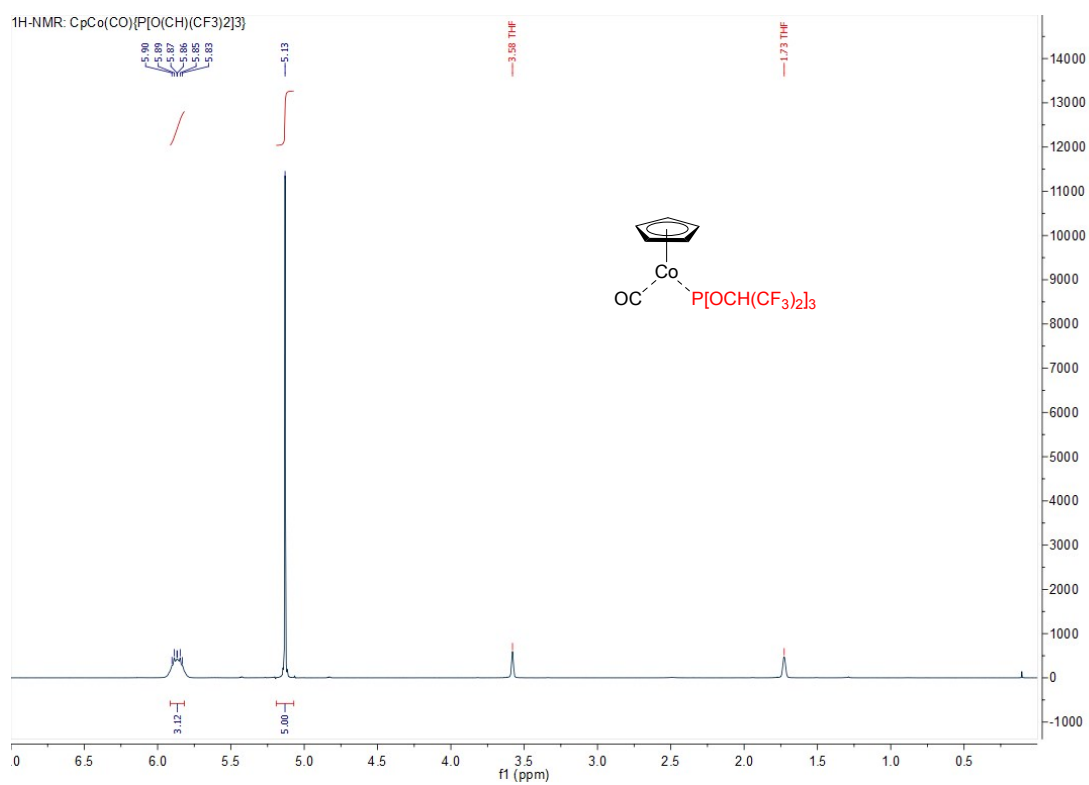
IR: ν_{max} = 2959, 2870, 2021, 1899, 1460, 1239, 1058, 1021, 883, 793, 647, 557, 491 cm⁻¹.

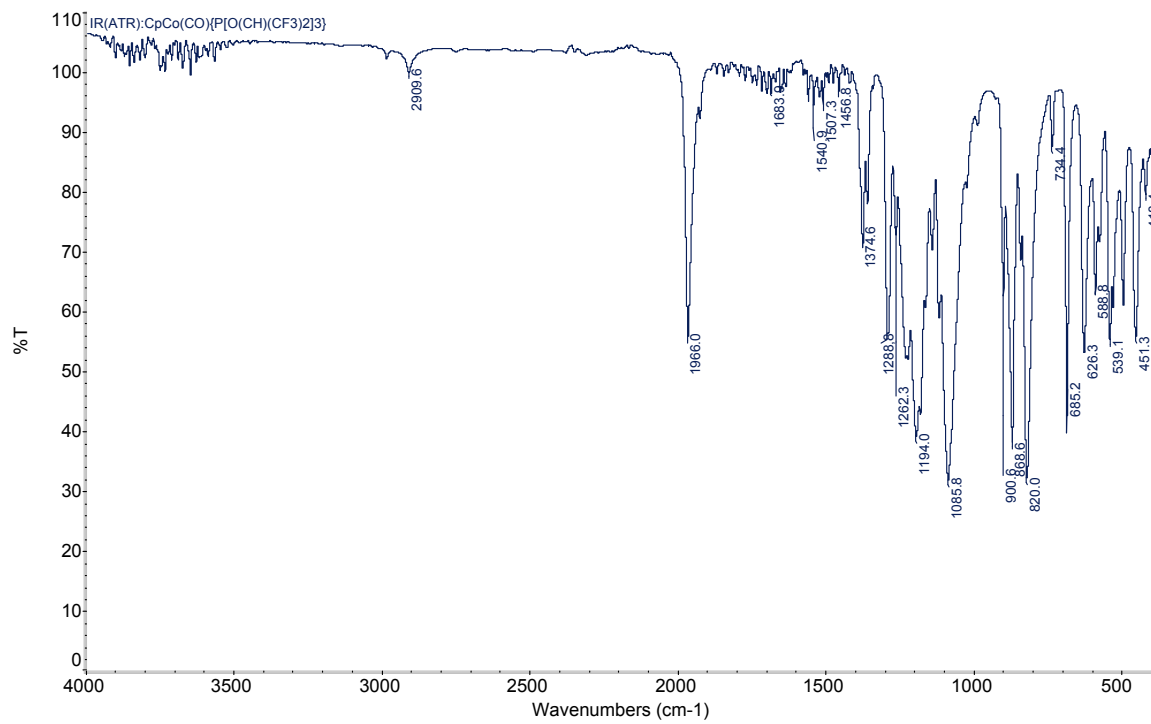
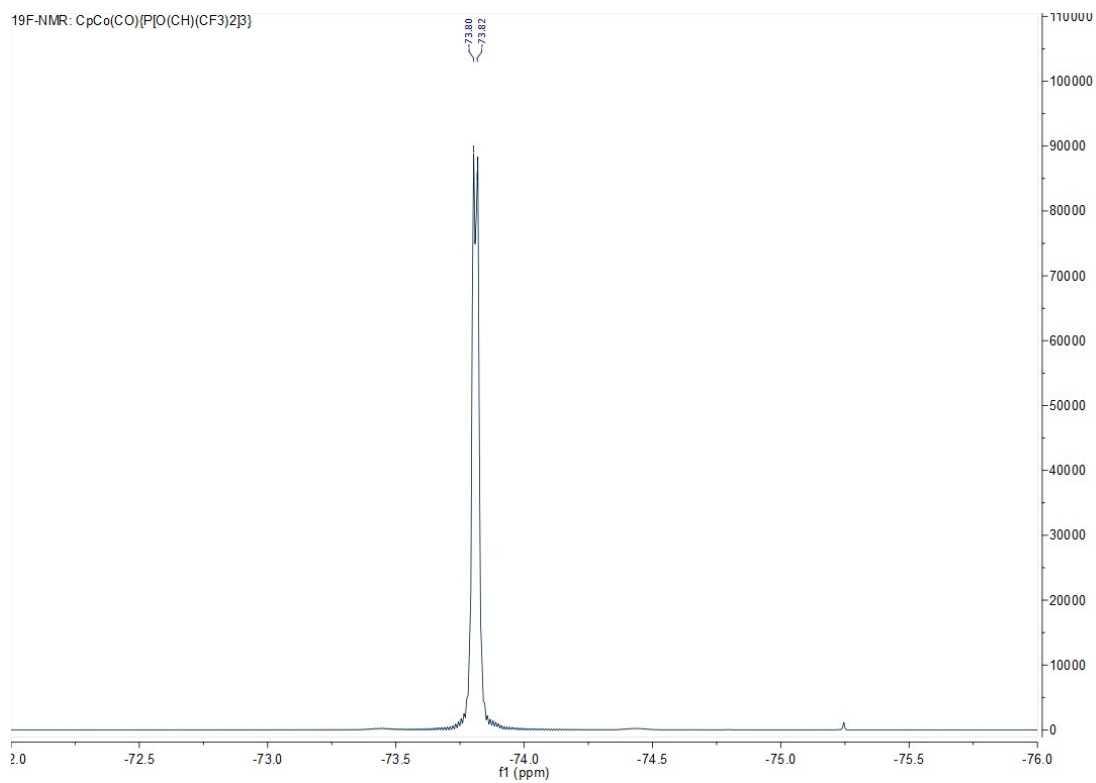
4. NMR and IR Spectra of the CpCo(CO)-phosphite complexes (2a-e and 2g) and of CpCo(CO)-phosphoramidite complex 2f

Compound 2a:

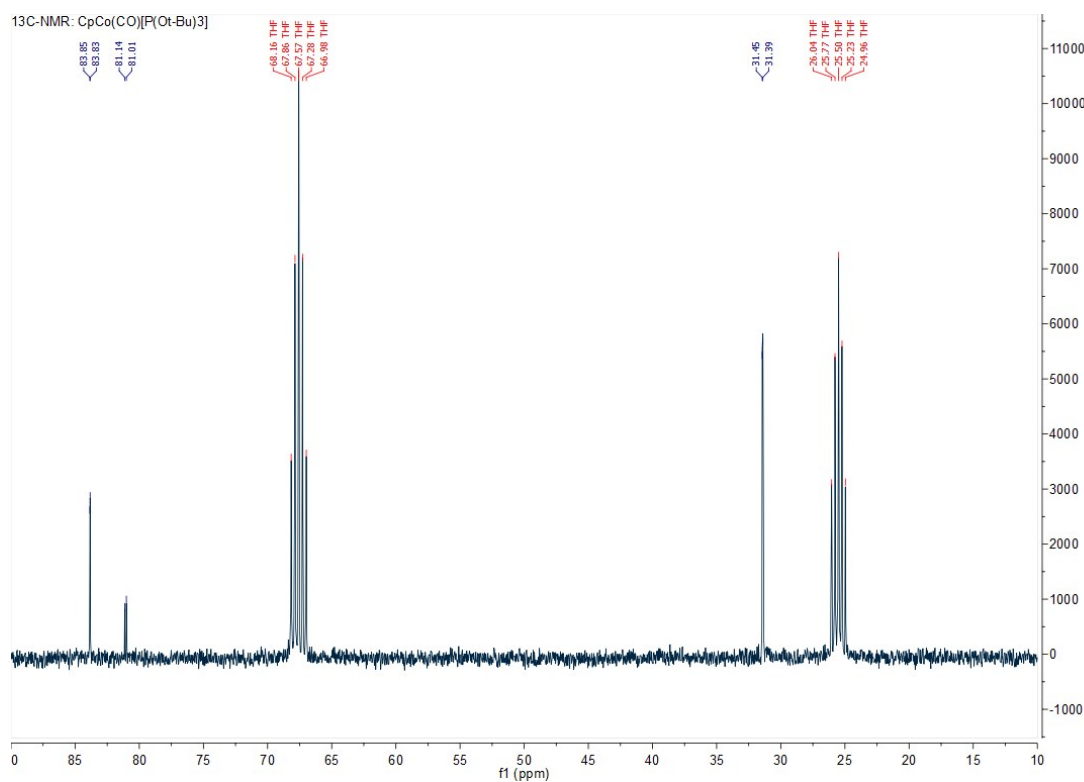
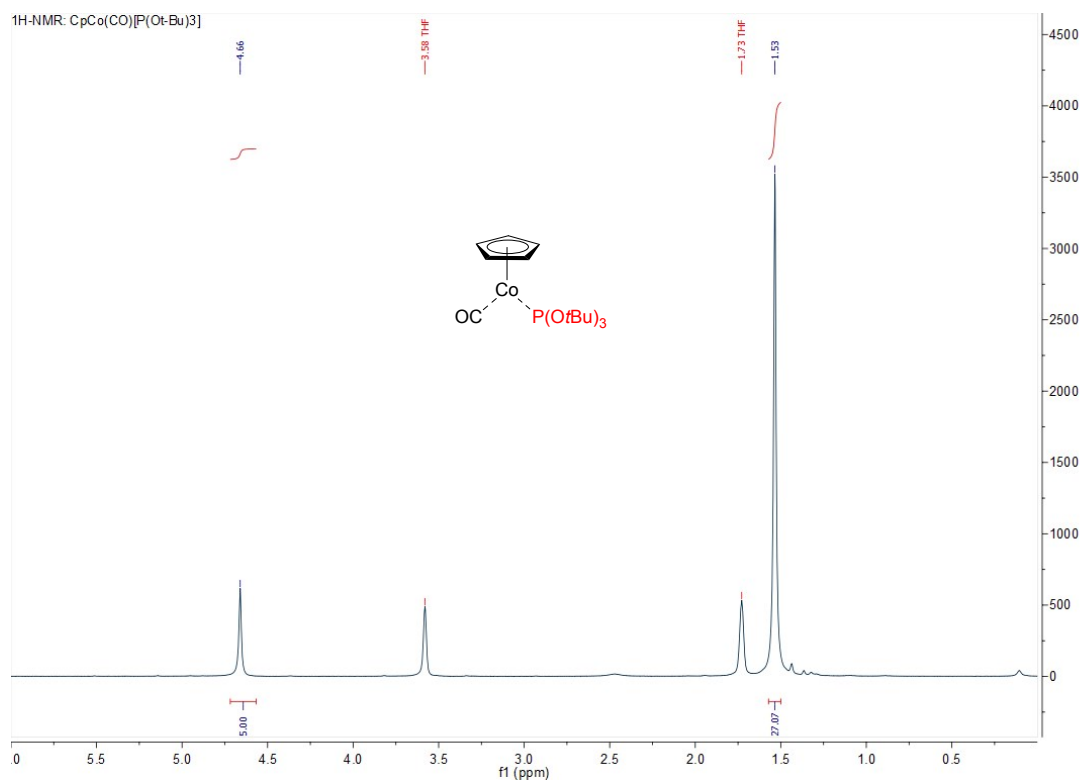


Compound 2b:

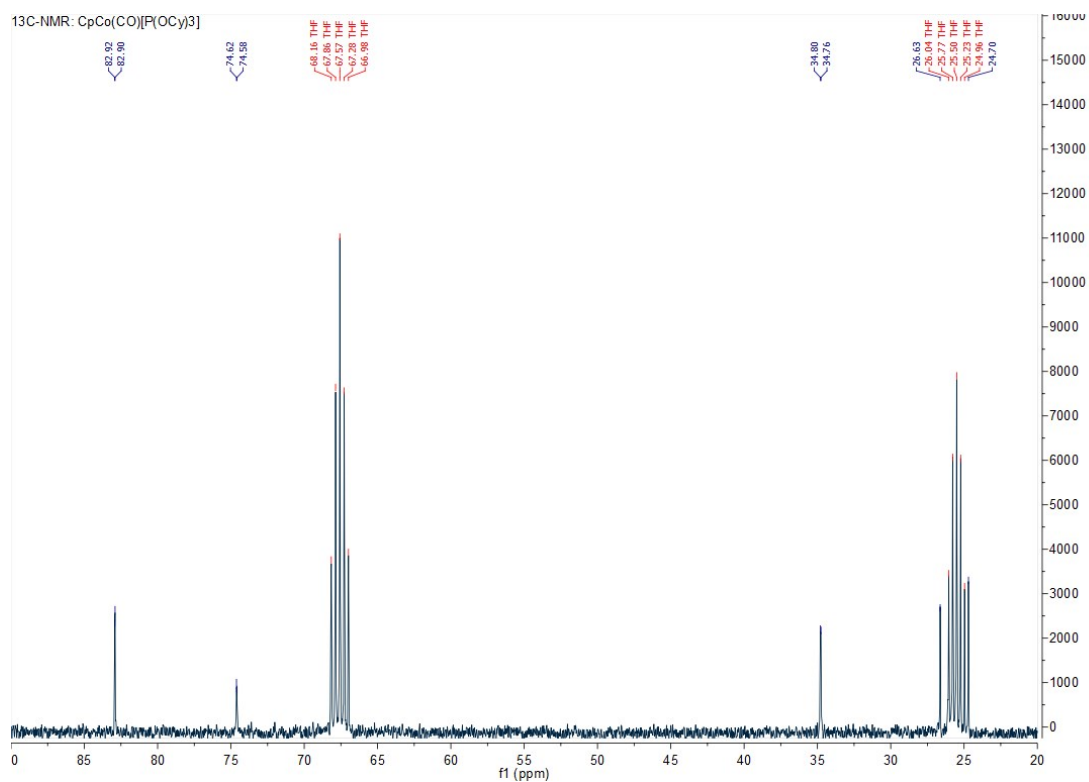
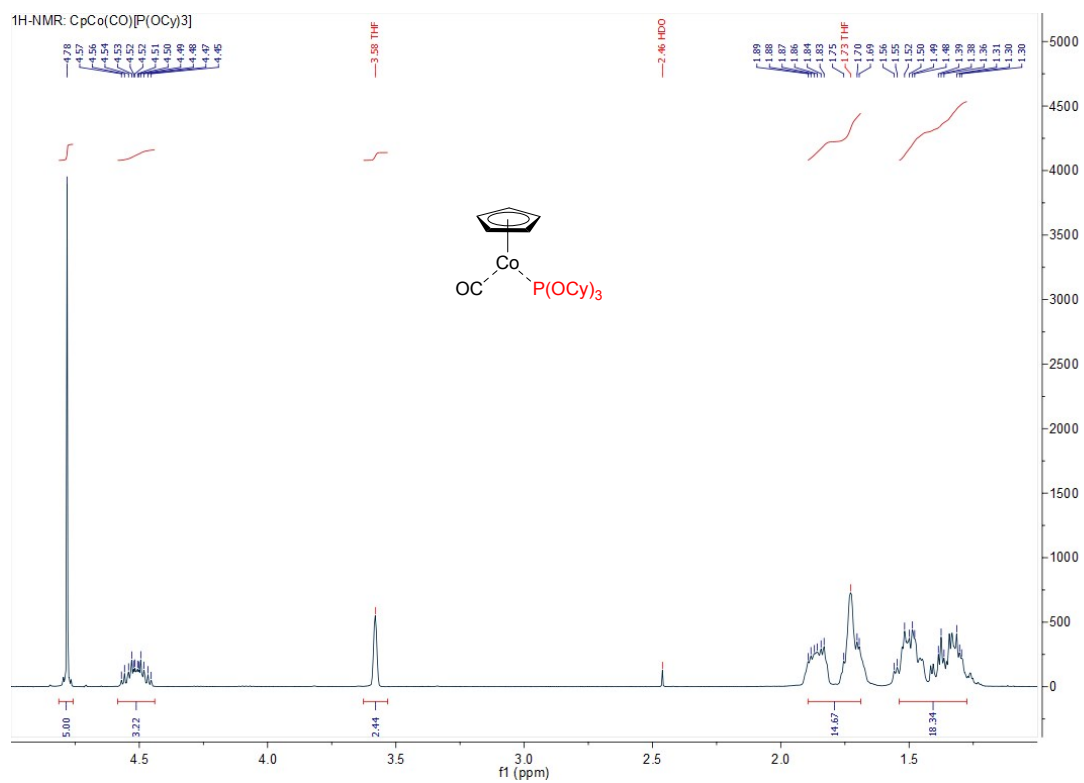


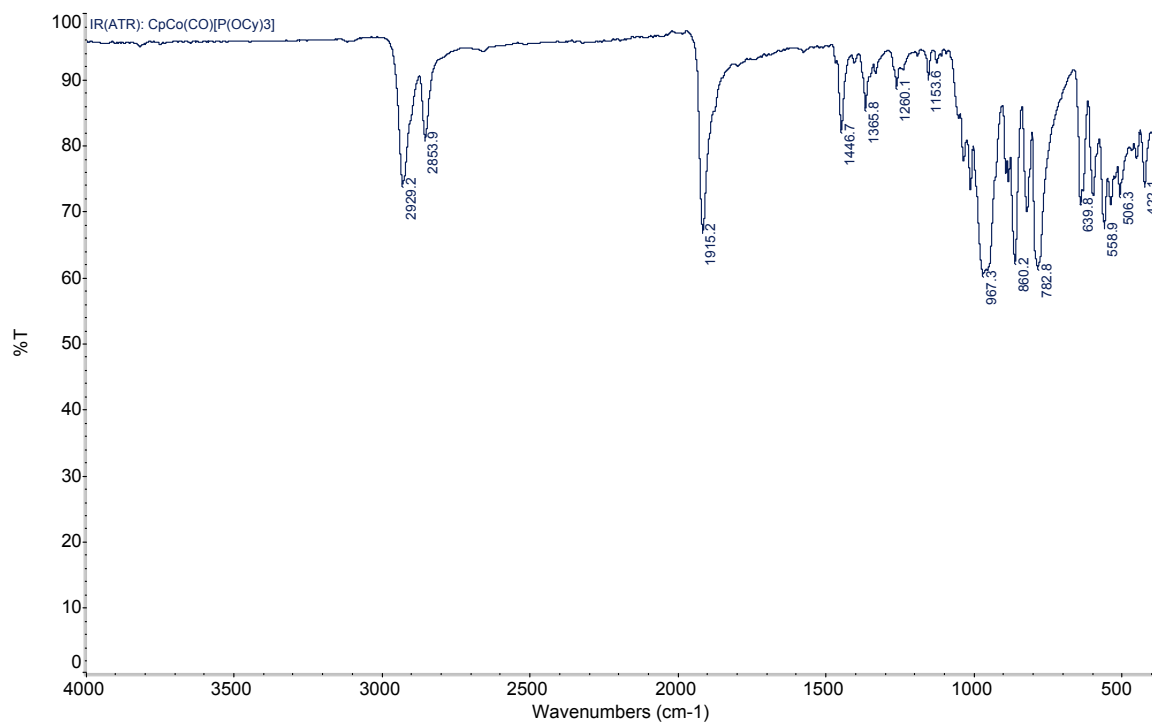


Compound 2c:

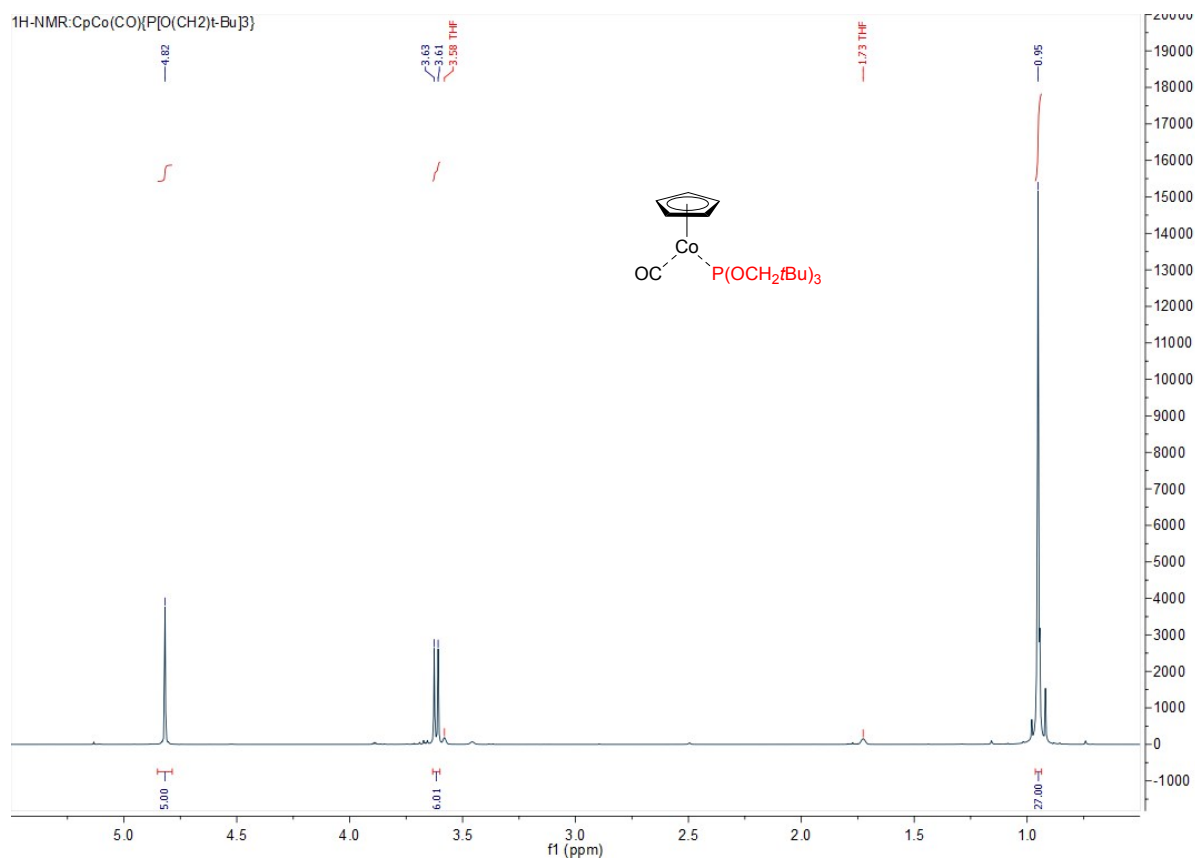


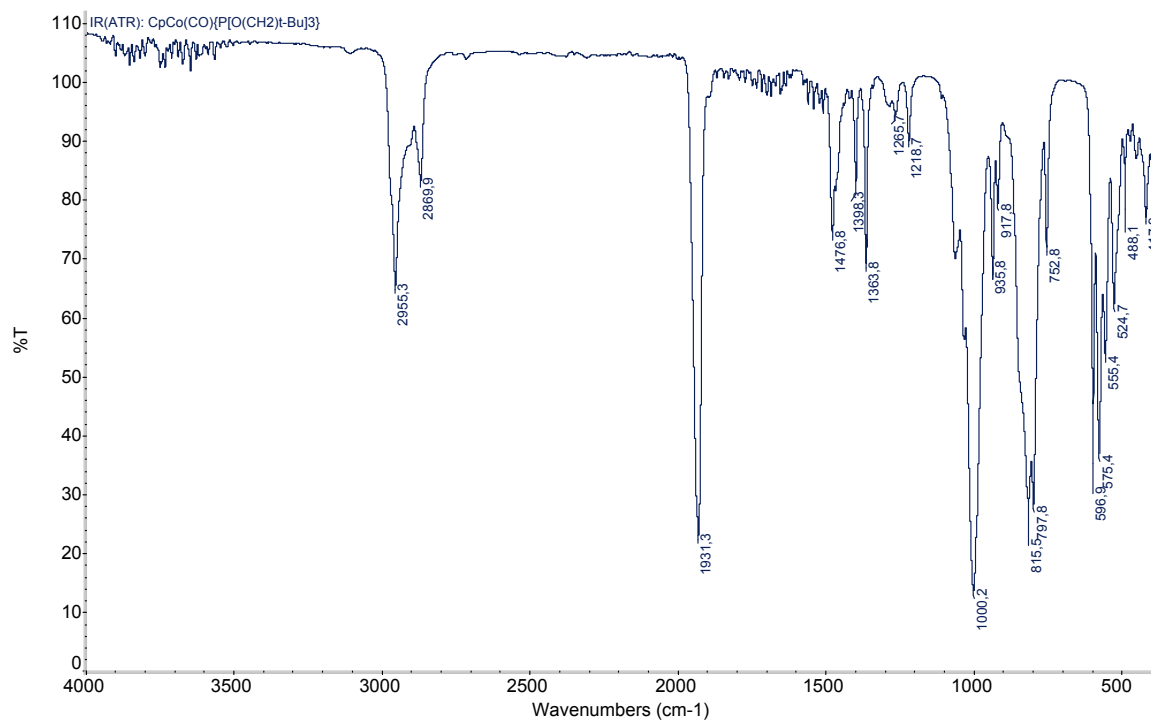
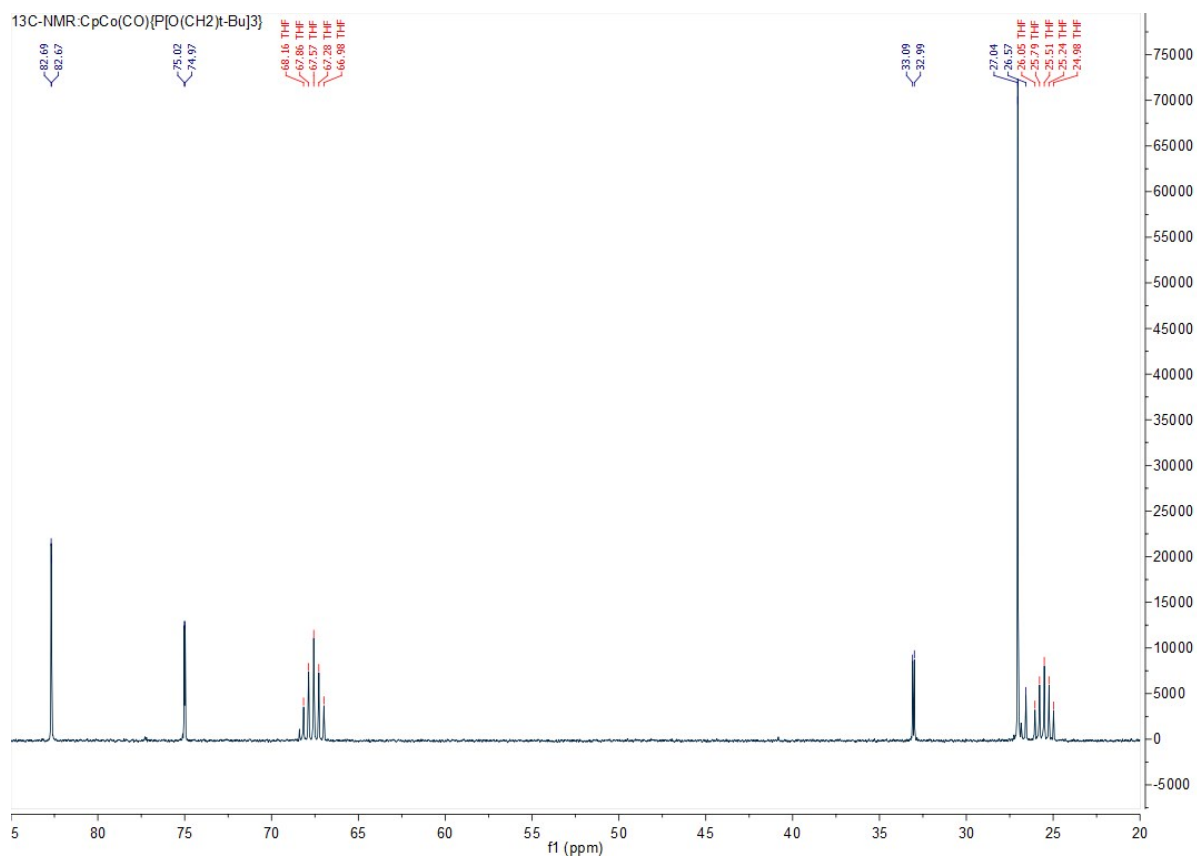
Compound 2d:





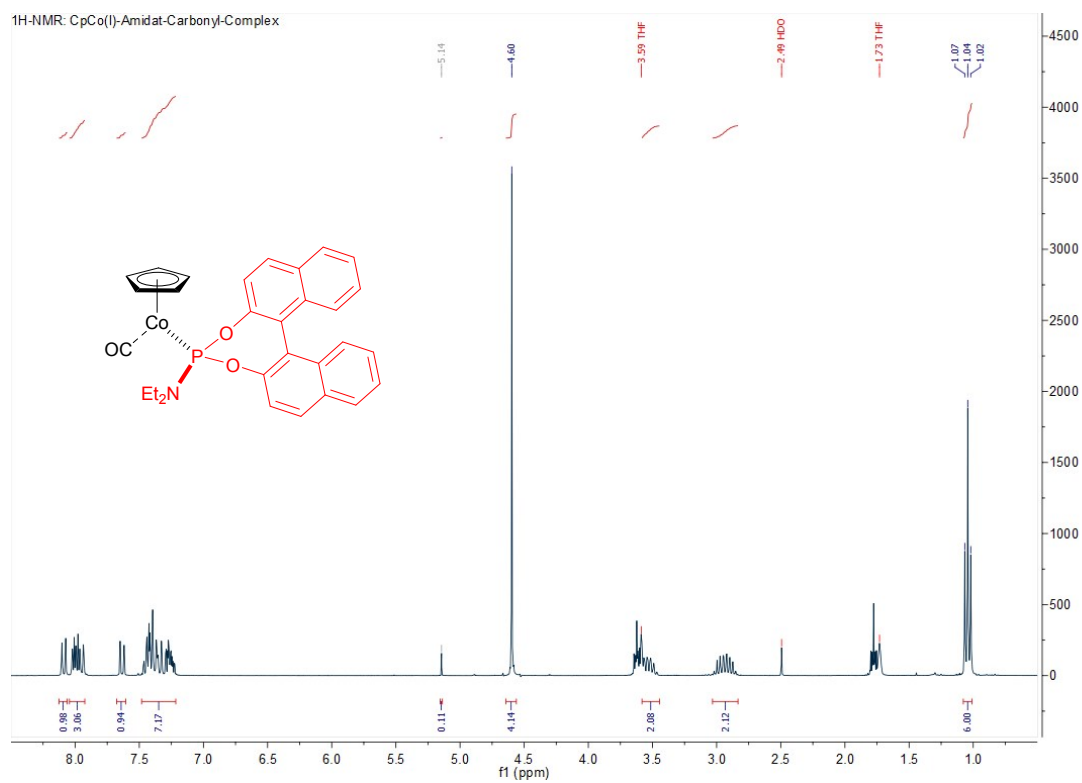
Compound 2e:



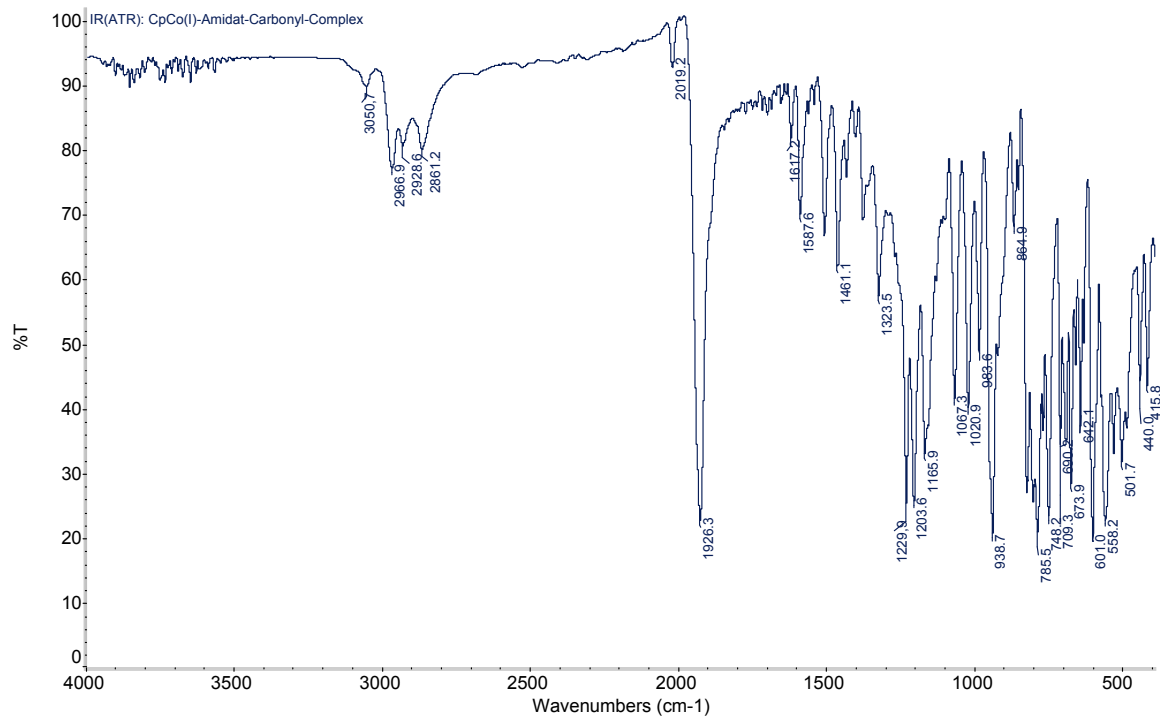


Compound 2f:

¹H-NMR: CpCo(I)-Amidat-Carbonyl-Complex

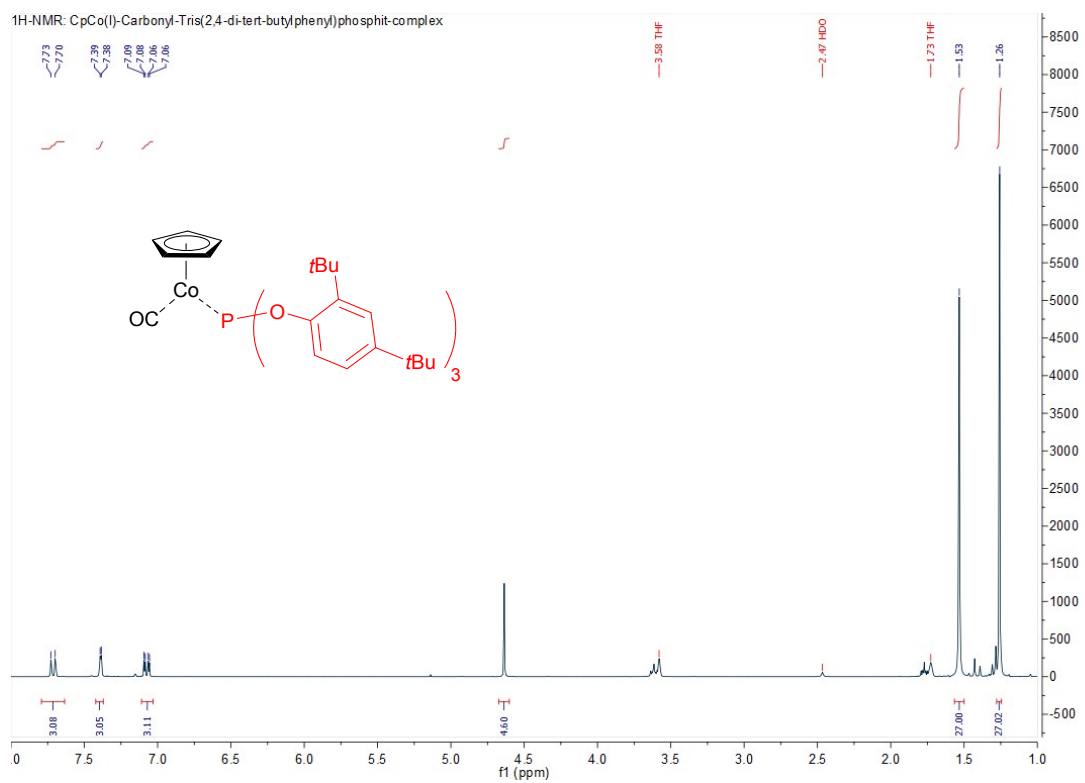


IR(ATR): CpCo(I)-Amidat-Carbonyl-Complex

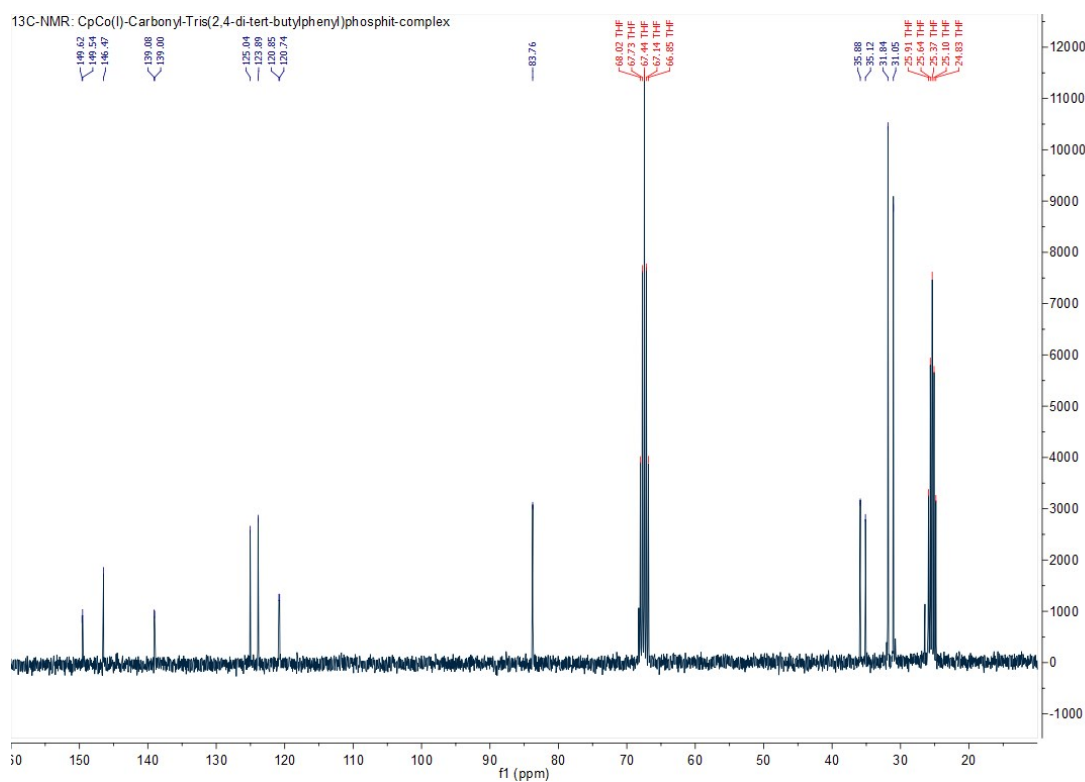


Compound 2g:

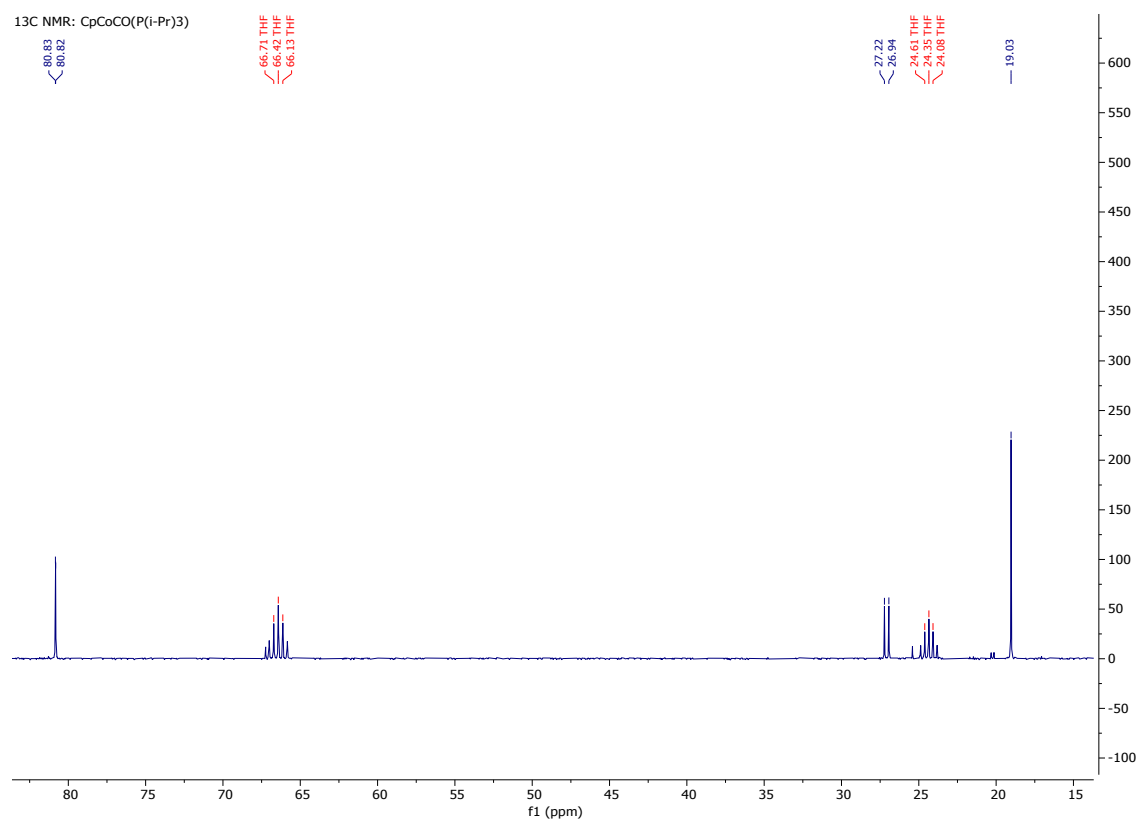
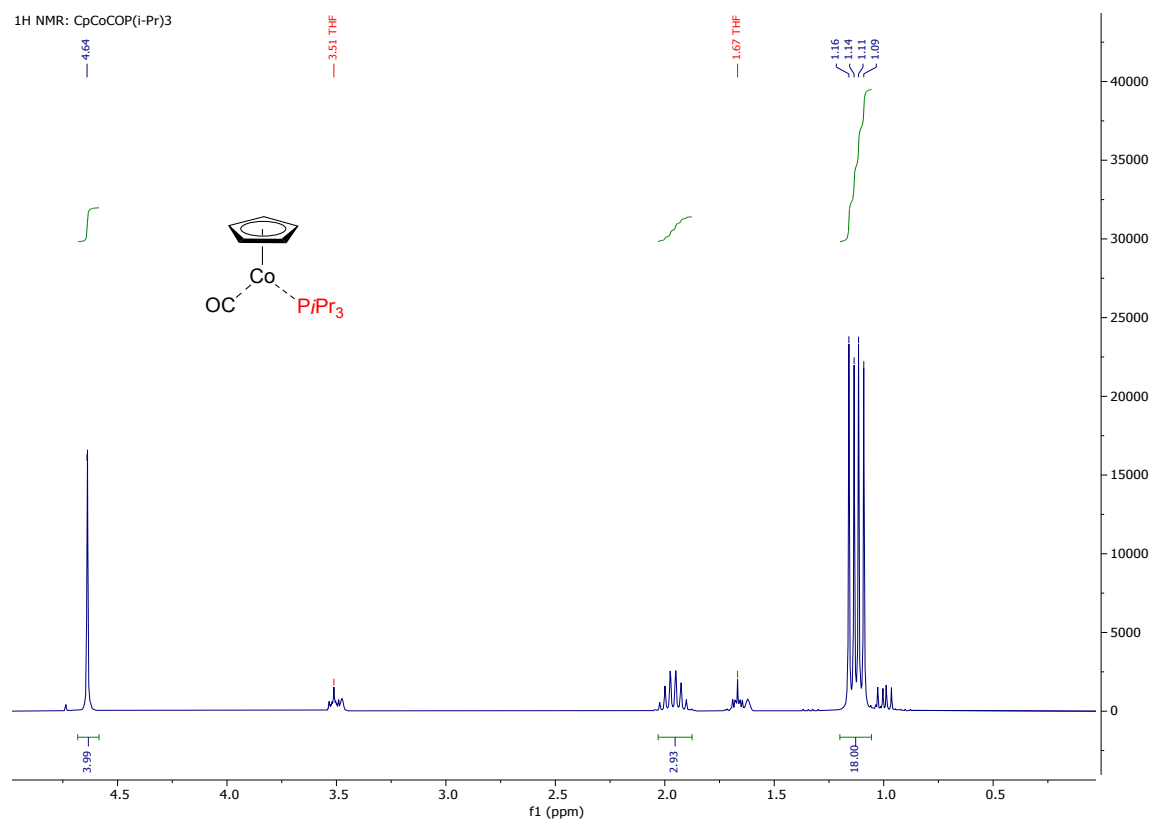
¹H-NMR: CpCo(I)-Carbonyl-Tris(2,4-di-tert-butylphenyl)phosphit-complex



¹³C-NMR: CpCo(I)-Carbonyl-Tris(2,4-di-tert-butylphenyl)phosphit-complex

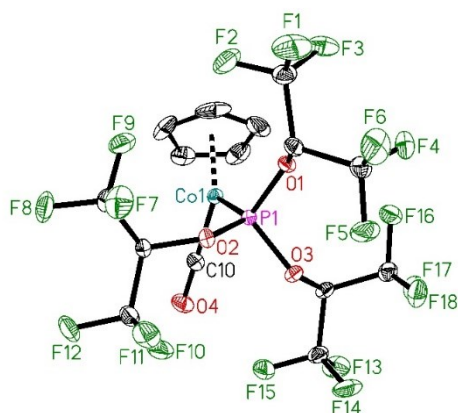


Compound 2h_{phosphine}:



5. SC-XRD of CpCo(CO)-phosphite complexes **2b** and **2c**

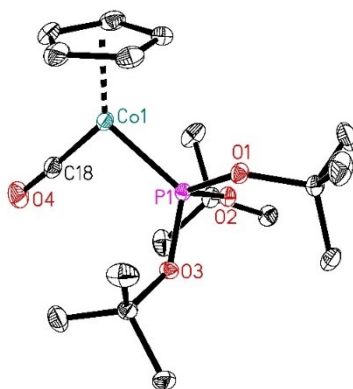
Complex **2b**:



Molecular structure of **2b** (Hydrogen atoms omitted, ellipsoids with 30% probability)

| Distance | Co1-P1 | Co1-C10 | Co1-Cp _{centroid} |
|------------|-----------|------------|----------------------------|
| Length [Å] | 2.0454(4) | 1.7281(16) | 1.7011(9) |

Complex **2c**:



Molecular structure of **2c** (Hydrogen atoms omitted, ellipsoids with 30% probability, only one of the three molecules of the asymmetric unit is depicted)

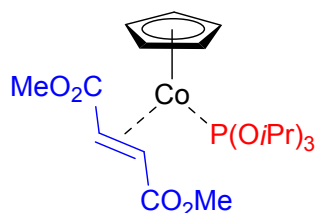
| Distance | Co1-P1 | Co1-C18 | Co1-Cp _{centroid} |
|------------|-----------|----------|----------------------------|
| Length [Å] | 2.1145(5) | 1.708(2) | 1.7057(11) |
| | 2.1065(5) | 1.707(2) | 1.7009(11) |
| | 2.1121(5) | 1.710(2) | 1.7065(11) |

| | CpCo(CO){P[O(CH)(CF₃)₂]₃} (2b) | CpCo(CO)[P(O<i>t</i>-Bu)₃] (2c) |
|---|--|---|
| Empirical formula | C ₁₅ H ₈ CoF ₁₈ O ₄ P | C ₁₈ H ₃₂ CoO ₄ P |
| Formula weight [g·mol ⁻¹] | 684.11 | 402.33 |
| Color | red | red |
| Crystal system | triclinic | triclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ |
| Unit cell dimensions: | | |
| <i>a</i> [Å] | 8.8080(9) | 9.1926(6) |
| <i>b</i> [Å] | 11.2727(11) | 18.6959(12) |
| <i>c</i> [Å] | 11.4608(11) | 18.8899(12) |
| α [°] | 87.2767(16) | 93.315(2) |
| β [°] | 86.0751(16) | 103.8784(19) |
| γ [°] | 81.5105(16) | 98.222(2) |
| Cell volume [Å ³] | 1122.03(19) | 3104.9(3) |
| <i>Z</i> | 2 | 6 |
| Calculated density [g·cm ⁻³] | 2.025 | 1.291 |
| μ (Mo K α) [mm ⁻¹] | 1.008 | 0.923 |
| Temperature [K] | 150(2) | 150(2) |
| Reflections collected | 36009 | 140910 |
| Reflections unique (<i>R</i> _{int}) | 5424 (0.0183) | 14958 (0.0326) |
| Reflections observed [<i>I</i> > 2 σ (<i>I</i>)] | 5134 | 12732 |
| Parameters | 352 | 666 |
| GOF (<i>F</i> ²) | 1.043 | 1.016 |
| <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] | 0.0273 | 0.0352 |
| <i>wR</i> ₂ (all data) | 0.0691 | 0.0936 |
| CCDC # | 1957193 | 1957192 |

6. Synthesis and analytical data of CpCo-olefin-phosphite complexes

General remark: The CpCo-olefin-phosphite complexes **3** are stable solids, which can be handled in air at least for short periods of time with the exception of precatalyst **3e**. Storage under nitrogen or argon with protection from light is recommended, as the complexes are indefinitely stable under these conditions.

General synthetic procedure as exemplified for the synthesis of compound 3a:



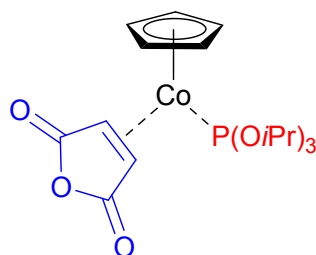
Dimethyl fumarate (**L^{2a}**) (192 mg, 1.33 mmol, 1.0 equiv.) was added to a solution of [CpCo(CO){P(O*i*Pr)₃}] (**2a**) (480 mg, 1.33 mmol, 1.0 equiv.) in toluene (10 ml). The red solution was irradiated with light in a thermostated glass reaction vessel (two mercury medium pressure lamp, ca. 900 W total) under reduced pressure for a total time of 48 h, during which the reactor was vented and partially evacuated two more times. After filtration over a small amount of neutral Al₂O₃ (Brockman Type I), using THF (20ml) as the eluent, the solvent was removed under reduced pressure and the resulting red oil was placed on a column of Al₂O₃. The first band, eluted with *n*-pentane/diethyl ether (1/1), was not collected. The second band was eluted with THF and the solvent was removed under vacuum and the product **3a** dried in high vacuum (yield: 440 mg, 70%).

¹H NMR (300 MHz, THF-*d*₈): δ = 4.68–4.47 (m, 8H), 3.56 (s, 3H), 3.47 (s, 3H), 3.35 (dd, *J* = 10.5, 3.4 Hz, 1H), 2.82–2.66 (m, 1H), 1.22 (d, *J* = 6.1 Hz, 18H) ppm. ¹³C NMR (75 MHz, THF-*d*₈): δ = 178.8(d, *J* = 42.5 Hz) 85.7, 70.3 (d, *J* = 6.0 Hz), 68.4, 51.1, 36.5 (d, *J* = 9.2 Hz), 30.2 (d, *J* = 3.0 Hz), 26.6, 25.0, 24.7 (d, *J* = 4.3 Hz) ³¹P NMR (122 MHz, THF-*d*₈): δ = 151.5 ppm.

IR: ν_{max} = 2976, 2944, 2871, 2014, 1692, 1295, 1149, 958, 876, 756, 550 cm⁻¹.

Elemental analysis for C₂₀H₃₄CoO₇P (476.39 g/mole): calc. C 50.42, H 7.19, Co 12.37, P 6.50; found C 50.61, H 7.40, Co 14.25, P 5.71.

Synthesis of compound 3b:



Maleic anhydride (**L^{2b}**) (147 mg, 1.5 mmol, 1.0 equiv.) was added to a solution of [CpCo(CO){P(O*i*Pr)₃}] (**2a**) (543 mg, 1.5 mmol, 1.0 equiv.) in toluene (10 ml). The red solution

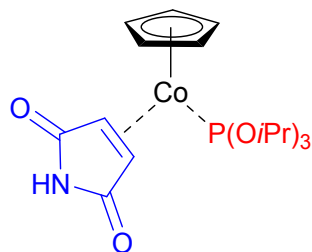
was irradiated with light under reduced pressure in a thermostated glass reactor for a total for a total of 24 h, during which the reactor was vented and partially evacuated two more times. After filtration over a small amount of neutral Al₂O₃ (Brockman Type I), which was eluted with THF (20 ml), the solvent was removed under reduced pressure and the resulting red solid was recrystallised from *n*-pentane at -78 °C and the collected fractions dried in high vacuum (yield: 300 mg, 47%).

¹H NMR (300 MHz, THF-*d*₈): δ = 4.74 (m, 3H), 4.67 (s, 5H), 2.80 (d, *J* = 8.1 Hz, 2H), 1.29 (d, *J* = 6.1 Hz, 18H) ppm. ¹³C NMR (75 MHz, THF-*d*₈): δ = 177.3 (d, *J* = 2.5 Hz), 86.3 (d, *J* = 2.7 Hz), 71.4 (d, *J* = 7.0 Hz), 33.1 (d, *J* = 9.2 Hz), 24.4 (d, *J* = 3.8 Hz) ppm. ³¹P NMR (122 MHz, THF-*d*₈): δ = 146.4 ppm.

IR: ν_{max} = 2981, 2934, 2872, 1926, 1798, 1731, 1375, 1226, 1102, 953, 566 cm⁻¹.

Elemental analysis for C₁₈H₂₈CoO₆P (M = 430.32 g/mole): calc. C 50.24, H 6.56, Co 13.70, P 7.20; found C 51.07, H 6.52, Co 13.21, P 7.03.

Synthesis of compound 3d:

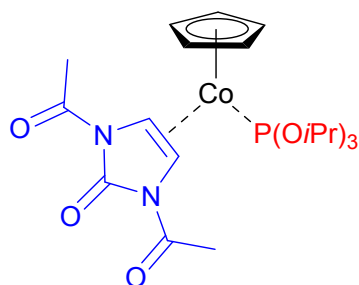


Maleimide (**L²d**) (194 mg, 2.0 mmol, 1.0 equiv.) was added to the solution of [CpCo(CO){P(O*i*Pr)₃}] (**2a**) (724 mg, 2.0 mmol, 1.0 equiv.) in toluene (10 ml). The red solution was irradiated with light under reduced pressure in a thermostated glass reactor for a total for a total of 24 h, during which the reactor was vented and partially evacuated two more times. The solvent was filtrated off the red precipitate, formed during the reaction, and the solid residue washed two more times with toluene (5 ml). The red solid, soluble in Et₂O and THF, was collected and dried under high vacuum (yield: 670 mg, 78%).

¹H NMR (300 MHz, THF-*d*₈): δ = 4.81-4.68 (m, 3H), 4.56 (s, 5H), 2.64 (d, *J* = 7.7 Hz, 2H), 1.27 (d, *J* = 6.1 Hz, 18H) ppm. ¹³C NMR (75 MHz, THF-*d*₈): δ = 183.3 (d, *J* = 2.4 Hz), 85.8 (d, *J* = 2.9 Hz), 70.8 (d, *J* = 6.4 Hz), 36.0 (d, *J* = 9.2 Hz), 24.4 (d, *J* = 3.8 Hz) ppm. ³¹P NMR (122 MHz, THF-*d*₈): δ = 150.3 ppm.

Elemental analysis for C₁₈H₂₉CoNO₅P (429.34 g/mole): calc. C 50.36, H 6.81, Co 13.73, N 3.26, P 7.21; found C 51.47, H 6.95, Co 13.13, N 3.27, P 7.04.

Synthesis of compound 3e:

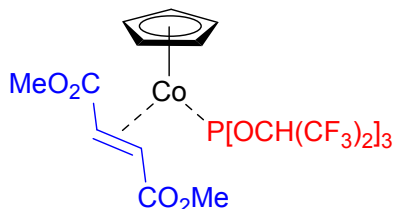


1,3-Diacetyl-1,3-dihydro-2H-imidazol-2-one (**L²d**) (292 mg, 1.5 mmol, 1.0 equiv.) was added to a solution of [CpCo(CO){P(O*i*Pr)₃}] (**2a**) (540 mg, 1.5 mmol, 1.0 equiv.) in toluene (10 ml). The red solution was irradiated with light under reduced pressure in a thermostated glass reactor for a total of 48 h, during which the reactor was vented and partially evacuated two more times. After filtration over a small amount of neutral Al₂O₃ (Brockman Type I) and elution with additional THF (20ml), the solvent was evaporated under reduced pressure and the resulting red solid was recrystallised in *n*-pentane at -78 °C (yield: 140 mg, 19%).

¹H NMR (300 MHz, THF-*d*₈): δ = 4.82 (m, 3H), 4.50 (s, 5H), 4.15 (d, *J* = 6.1 Hz, 2H), 2.44 (s, 6H), 1.26 (d, *J* = 6.1 Hz, 18H) ppm. ¹³C NMR (75 MHz, THF-*d*₈): δ = 170.1, 153.2, 84.3 (d, *J* = 2.7 Hz), 70.4 (d, *J* = 5.7 Hz), 48.2 (d, *J* = 14.0 Hz), 24.7 (d, *J* = 4.2 Hz), 24.7 ppm. ³¹P NMR (122 MHz, THF-*d*₈): δ = 155.9 ppm.

Elemental analysis for C₂₁H₃₄CoN₂O₆P (M = 500.42 g/mole): calc. C 50.40, H 6.85, Co 11.78, N 5.60; found C 49.36, H 7.23, Co 13.65, N 4.84.

Synthesis of compound 3f:

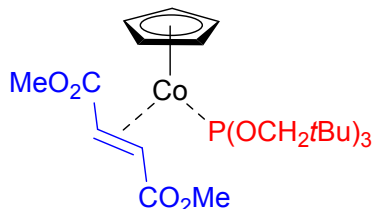


Dimethyl fumarate (**L²a**) (144 mg, 1.0 mmol, 1.0 equiv.) was added to solution of [CpCo(CO){P{OCH(CF₃)₂}₃}] (**2b**) (643 mg, 1.0 mmol, 1.0 equiv.) in toluene (10 ml). The red solution was irradiated with light under reduced pressure in a thermostated glass reactor for a total for a total of 24 h, during which the reactor was vented and partially evacuated two more times. After filtration over a small amount of neutral Al₂O₃ (Brockman Type I), followed by elution with THF (20 ml), the solvent was removed under reduced pressure, yielding a red oil. Dissolving the oil in *n*-pentane afforded the desired product by crystallisation as a deep red solid, which was dried under vacuum at 40 °C (yield: 400 mg, 50%).

¹H NMR (300 MHz, THF-*d*₈): δ = 5.81-5.63 (m, 3H), 4.97 (s, 5H), 3.70 (s, 3H), 3.63 (s, 3H), 3.44 (dd, *J* = 10.5, 3.2 Hz, 1H), 3.18 (dd, *J* = 14.1, 10.5 Hz, 1H) ppm. ¹⁹F NMR (282 MHz, THF-*d*₈): δ = -73.3 (d, *J* = 154.0 Hz) ppm. ³¹P NMR (122 MHz, THF-*d*₈): δ = 156.3 ppm.

Elemental analysis for $C_{20}H_{16}CoF_{18}O_7P$ (800.22 g/mole): calc. C 30.02, H 2.02, Co 7.36; found C 28.87, H 1.83, Co 8.70.

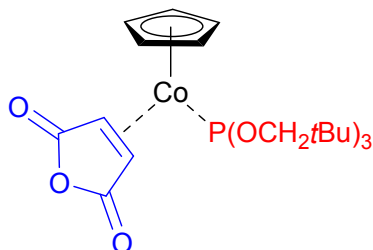
Synthesis of compound 3g:



Dimethyl fumarate (**L^{2a}**) (216 mg, 1.5 mmol, 1.0 equiv.) was added to solution of $[CpCo(CO)\{P(OCH_2tBu)_3\}]$ (**2e**) (665 mg, 1.5 mmol, 1.0 equiv.) in toluene (10 ml). The red solution was irradiated with light in a thermostated glass reactor under reduced pressure for a total of 24 h, during which the reactor was vented and partially evacuated two more times. After filtration over a small amount of neutral Al_2O_3 (Brockman Type I) and subsequent elution with THF (20 ml), the solvent was removed under reduced pressure red oil was placed on a column of Al_2O_3 . The first band, eluted with *n*-pentane/diethyl ether (1/1), was not collected. The second band was eluted with THF and the solvent was removed under vacuum and dried for the removal of residual solvent in high vacuum to give an oily substance which partially solidified (yield: 540 mg, 64%).

1H NMR (300 MHz, THF- d_8): δ = 4.69 (s, 5H), 3.72–3.65 (m, 3H), 3.61 (s, 3H), 3.56–3.50 (m, 3H), 3.49 (s, 3H), 3.44 (dd, J = 10.4, 3.4 Hz, 1H), 2.89 (dd, J = 10.7; 12.3 Hz, 1H), 0.99 (s, 27H) ppm. ^{13}C NMR (101 MHz, THF- d_8): δ = 178.7, 177.8 (d, J = 3.4 Hz), 88.3, 85.5 (d, J = 2.7 Hz), 75.2 (d, J = 5.5 Hz), 50.9 (d, J = 7.3 Hz), 36.1 (d, J = 8.2 Hz), 33.1 (d, J = 7.5 Hz), 30.7 (d, J = 4.4 Hz), 27.0 (9C, *t*-Bu), 26.6 ppm. ^{31}P NMR (122 MHz, THF- d_8): δ = 156.1 ppm. Elemental analysis for $C_{26}H_{46}CoO_7P$ (M = 560.55 g/mole): calc. C 55.71, H 8.27, Co 10.51; found C 56.32, H 8.15, Co 12.93.

Synthesis of compound 3h:



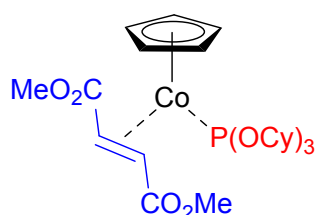
Maleic anhydride (**L^{2b}**) (110 mg, 1.12 mmol, 1.04 equiv.) was added to solution of $[CpCo(CO)\{P(OCH_2tBu)_3\}]$ (**2e**) (482 mg, 1.08 mmol, 1.00 equiv.) in toluene (10 ml). The red solution was irradiated with light in a thermostated glass reactor under reduced pressure for a total of 48 h, during which the reactor was vented and partially evacuated two more times. The reaction solution was then carefully covered with *n*-pentane and cooled to -78 °C for 24 h

afterwards. The solvent was filtered off from the crystallised product and the isolated red solid was dried in high vacuum (yield: 305 mg, 55%).

^1H NMR (300 MHz, THF- d_8): δ = 4.72 (s, 5H), 3.67 (d, J = 4.2 Hz, 6H), 2.93 (d, J = 7.9 Hz, 2H), 0.98 (s, 27H) ppm. ^{13}C NMR (75 MHz, THF- d_8): δ = 177.17 (d, J = 2.5 Hz), 86.2, 75.8 (d, J = 6.4 Hz), 33.1 (d, J = 7.3 Hz), 32.7 (d, J = 9.4 Hz), 26.7 ppm. ^{31}P NMR (122 MHz, THF- d_8) δ = 150.6 ppm.

Elemental analysis for $\text{C}_{24}\text{H}_{40}\text{CoO}_6\text{P}$ (514.48 g/mole): calc. C 56.03, H 7.84, Co 11.45; found C 56.57, H 7.95, Co 10.55.

Synthesis of compound 3i:



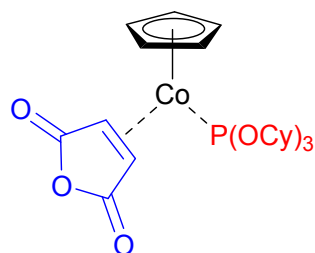
Dimethyl fumarate (**L²a**) (180 mg, 1.25 mmol, 1.0 equiv.) was added to a solution of $[\text{CpCo}(\text{CO})\{\text{P}(\text{OCy})_3\}]$ (**2d**) (600 mg, 1.25 mmol, 1.0 equiv.) in toluene (10 ml). The red solution was irradiated with light in a thermostated glass reactor under reduced pressure for 24 h totally, during which the reactor was vented and partially evacuated two more times. Afterwards, the solvent was evaporated under reduced pressure and the crude product was dissolved in a small amount of THF and subject to filtration over a small amount of neutral Al_2O_3 (Brockman Type I), followed by elution with THF (20ml). The solvent of the filtrate was removed under reduced pressure. The resulting red sticky oil was dissolved in *n*-pentane and crystallised at -78 °C. The after filtration obtained deep red solid was washed with a small amount of cold diethyl ether and dried in vacuum (yield: 180 mg, 24%).

^1H NMR (300 MHz, THF- d_8): δ = 4.62 (s, 5H), 4.37 (qt, J = 8.9, 3.6 Hz, 3H), 3.61 (s, 3H), 3.51 (s, 3H), 3.28 (m, 1H), 2.72 (dd, J = 11.7, 10.5 Hz, 1H), 1.73 (s, 12H), 1.58-1.20 (m, 18H) ppm. ^{13}C NMR (75 MHz, THF- d_8): δ = 179.2, 178.6, 85.7 (d, J = 2.9 Hz), 70.3 (d, J = 6.5 Hz), 51.0, 36.5 (d, J = 7.9 Hz), 30.2 (d, J = 4.7 Hz), 24.9, 24.6 (d, J = 5.7 Hz) ppm. ^{31}P NMR (122 MHz, THF- d_8): δ = 152.0 ppm.

IR: ν_{max} = 2927, 2855, 1926, 1688, 1432, 1297, 1151, 1032, 963, 857, 816, 581, 499 cm^{-1} .

Elemental analysis for $\text{C}_{29}\text{H}_{46}\text{CoO}_7\text{P}$ (M = 596.59 g/mole): calc. C 58.39, H 7.77, Co 9.88, P 5.19; found C 57.60, H 7.90, Co 11.00, P 5.32.

Synthesis of compound 3j:



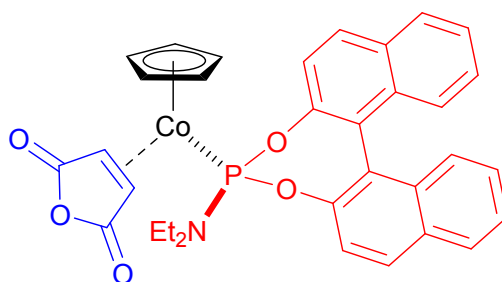
Maleic anhydride (**L^{2b}**) (98 mg, 1.02 mmol, 1.0 equiv.) was added to a solution of [CpCo(CO){P(OCy)₃}] (**2d**) (480 mg, 1.0 mmol, 1.0 equiv.) in toluene (10 ml). The red solution was irradiated for 24 h with light under reduced pressure in a thermostated glass reactor for a total of 24 h, during which the reactor was vented and partially evacuated two more times. The solvent was evaporated under reduced pressure and the crude product was dissolved in a small amount of THF and subject to filtration over a small amount of neutral Al₂O₃ (Brockman Type I), followed by elution with THF (20ml). The filtrate was evaporated under reduced pressure, furnishing a red solid as product. It was dissolved in THF (2 ml) and overlaid with *n*-pentane (35 ml). Storage for 48 h resulted in the formation of crystals. The solvent was removed by filtration and the precipitated red crystals were dried in vacuum (yield: 200 mg, 36%).

¹H NMR (300 MHz, THF-*d*₈): δ = 4.66 (s, 5H), 4.49 (s, 3H), 2.83 (d, *J* = 8.1 Hz, 2H), 1.86 (s, 12H), 1.62–1.22 (m, 18H). ¹³C NMR (101 MHz, THF-*d*₈): δ = 177.4, 86.3, 76.3, 34.7, 33.1 (d, *J* = 8.7 Hz), 26.3, 24.5 ppm. ³¹P NMR (122 MHz, THF-*d*₈): δ = 146.8 ppm.

IR: ν_{max} = 2931, 2847, 1797, 1731, 1446, 1224, 958, 865, 829, 589 cm⁻¹.

Elemental analysis for C₂₇H₄₀CoO₆P (550.52 g/mole): calc. C 58.91, H 7.32, Co 10.71, P 5.63; found C 59.71, H 7.30, Co 10.36 P: 5.57.

Synthesis of compound 3k:



Maleic anhydride (**L^{2b}**) (242 mg, 2.47 mmol, 1.0 equiv.) was added to a solution of [CpCo(CO)(**L^{1f}**)] (**2f**) (1.33 g, 2.47 mmol, 1.0 equiv.) in toluene (10 ml). The red solution was irradiated with light in a thermostated glass reactor under reduced pressure for a total of 96 h, during which the reactor was vented and partially evacuated three more times. After filtration over a small amount of neutral Al₂O₃ (Brockman Type I), elution with THF (20 ml) and evaporation of the obtained solution under reduced pressure, the resulting red solid was dissolved in a mixture of diethyl ether (5 ml) and THF (2 ml). Over this solution a layer of *n*-pentane (40 ml) was carefully introduced and the flask stored to rest for 96 h. Afterwards the

solvent was removed per syringe and the remaining deep red crystals were dried in vacuum (yield: 800 mg, 53%).

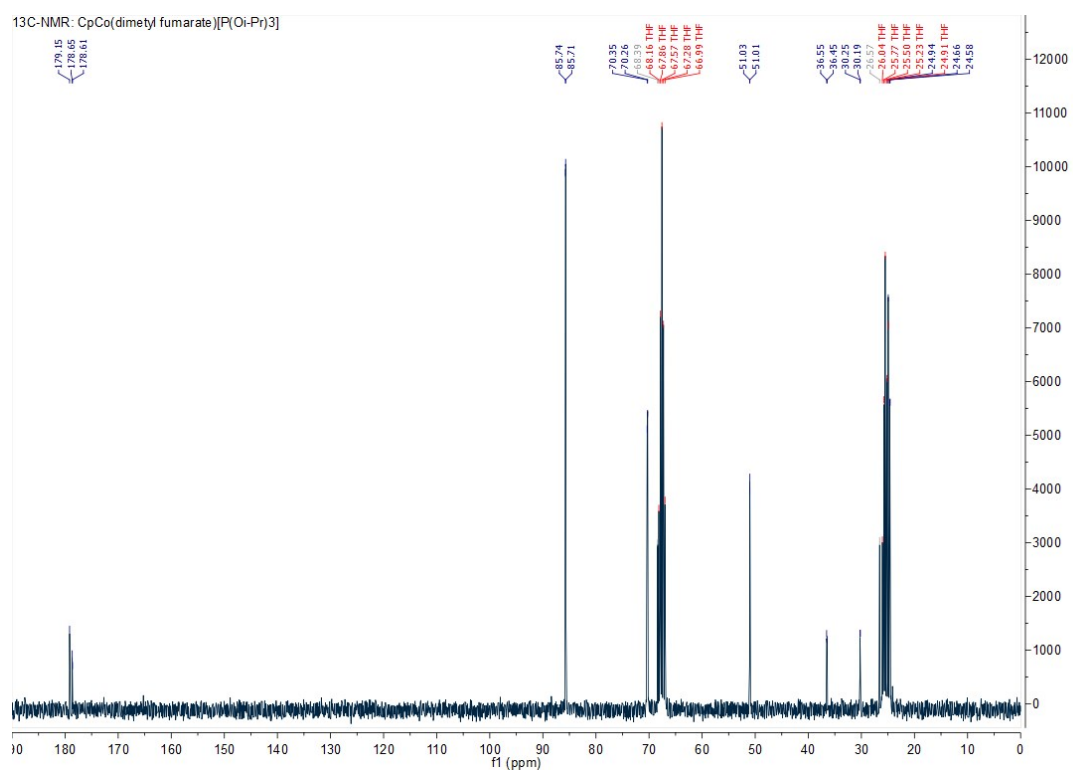
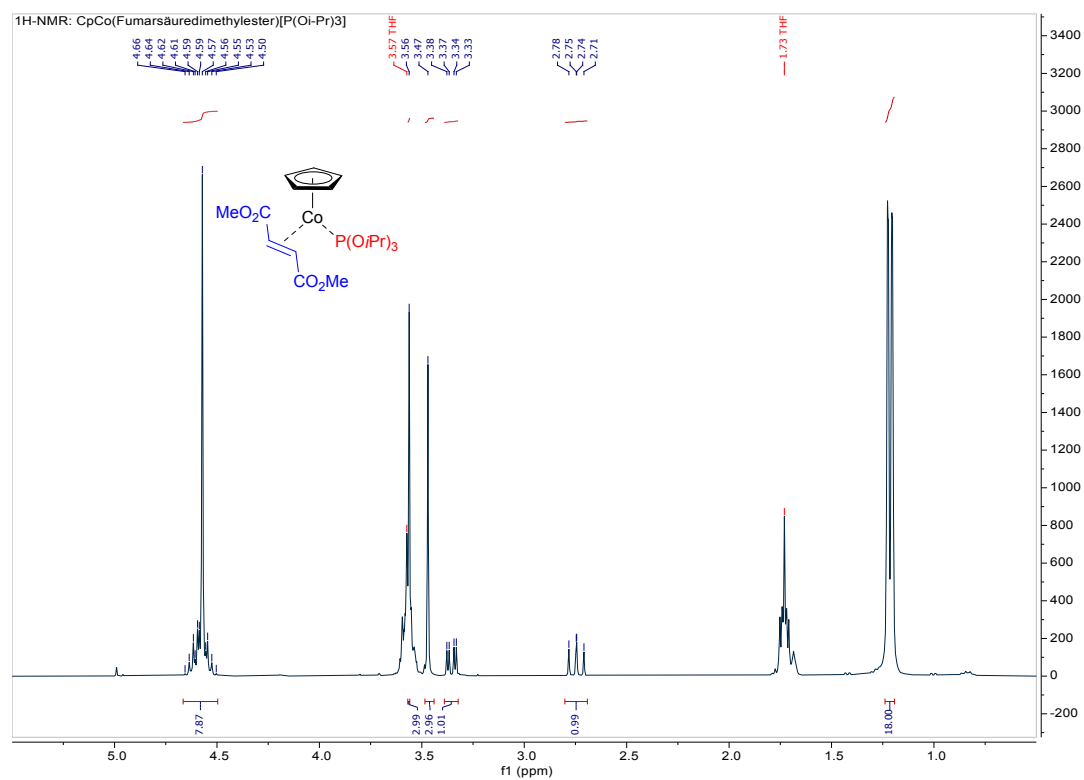
^1H NMR (300 MHz, THF- d_8): δ = 8.29 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H), 8.03-7.79 (m, 3H), 7.63-7.40 (m, 2H), 7.40-7.06 (m, 5H), 4.70 (s, 5H), 3.60-3.30 (m, 2H), 3.20 (dd, J = 9.4, 3.8 Hz, 1H), 3.03-2.77 (m, 2H), 2.31 (dd, J = 7.3, 3.8 Hz, 1H), 1.06 (t, J = 7.0 Hz, 6H) ppm. ^{13}C NMR (75 MHz, THF- d_8): δ = 177.2, 177.1, 176.8 (2x), 150.1, 149.9, 149.1 (2x), 133.6, 132.9, 132.5, 131.8, 131.5, 129.7, 129.5, 127.7, 127.6, 127.5, 126.5, 126.4, 123.8, 123.8, 123.7, 123.6, 123.1 (2x), 122.0, 87.4 (2x), 41.5, 41.4, 34.4, 34.3, 33.8, 33.7, 15.1, 15.0 ppm.

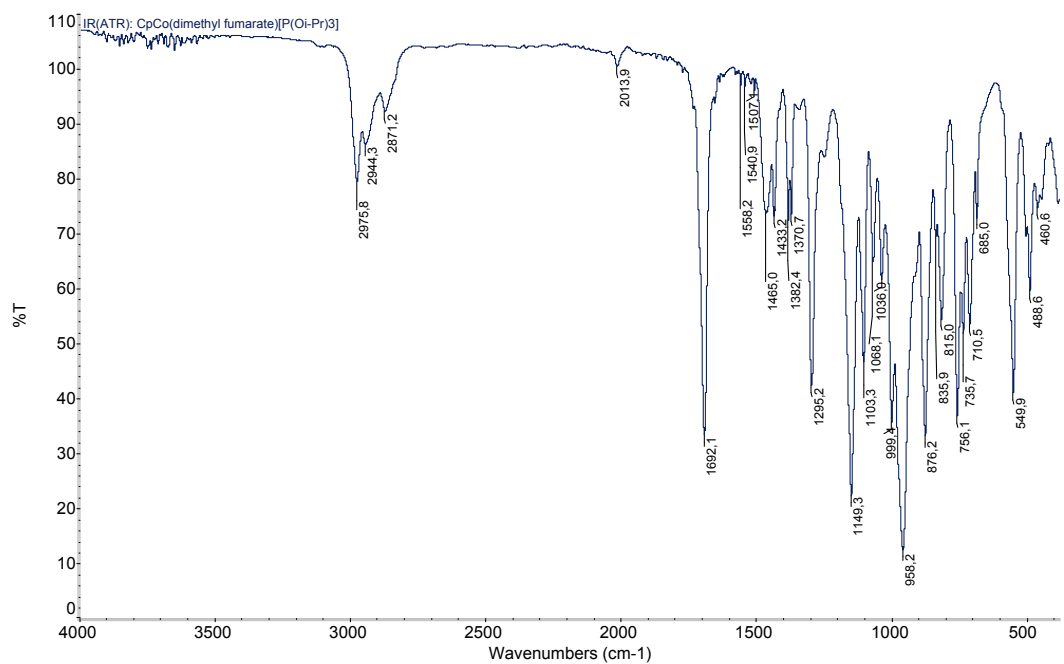
^{31}P NMR (122 MHz, THF- d_8): δ = 180.2 ppm.

Elemental analysis for $\text{C}_{33}\text{H}_{29}\text{CoNO}_5\text{P}$ (609.50 g/mole): calc. C 65.03, H 4.80, Co 9.67, N 2.30, P 5.08; found C 65.45, H 4.86, Co 9.50, N 2.10, P 5.01.

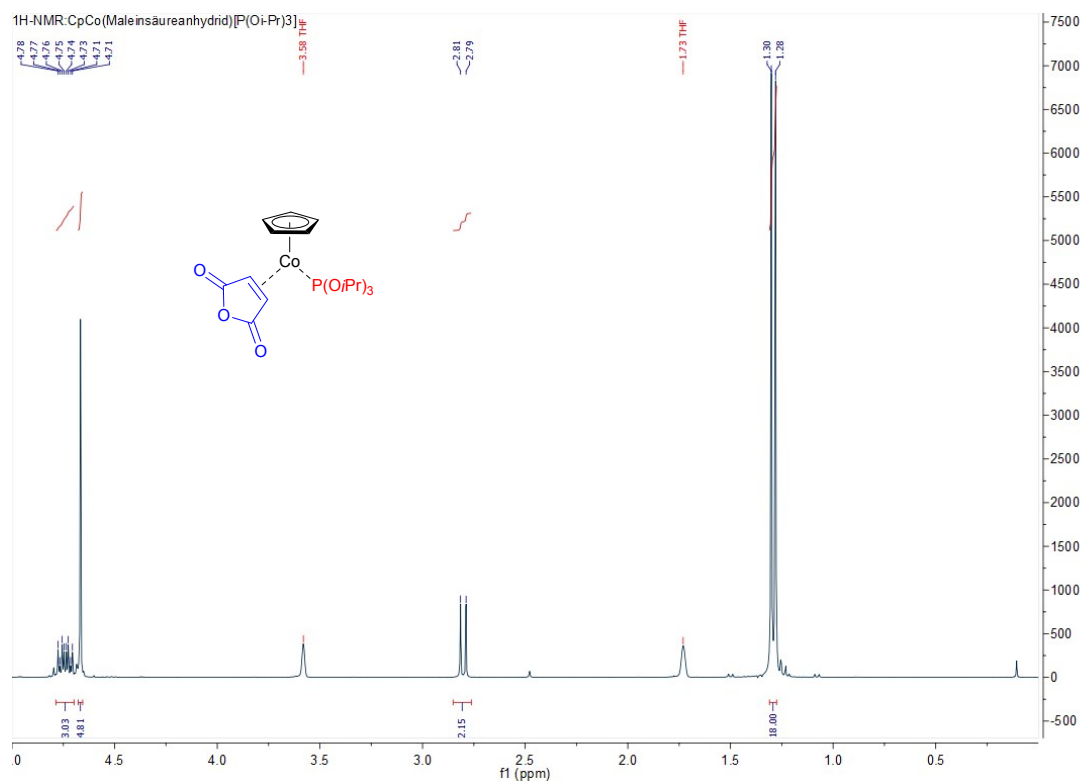
7. NMR and IR Spectra of the CpCo-olefin-phosphite complexes

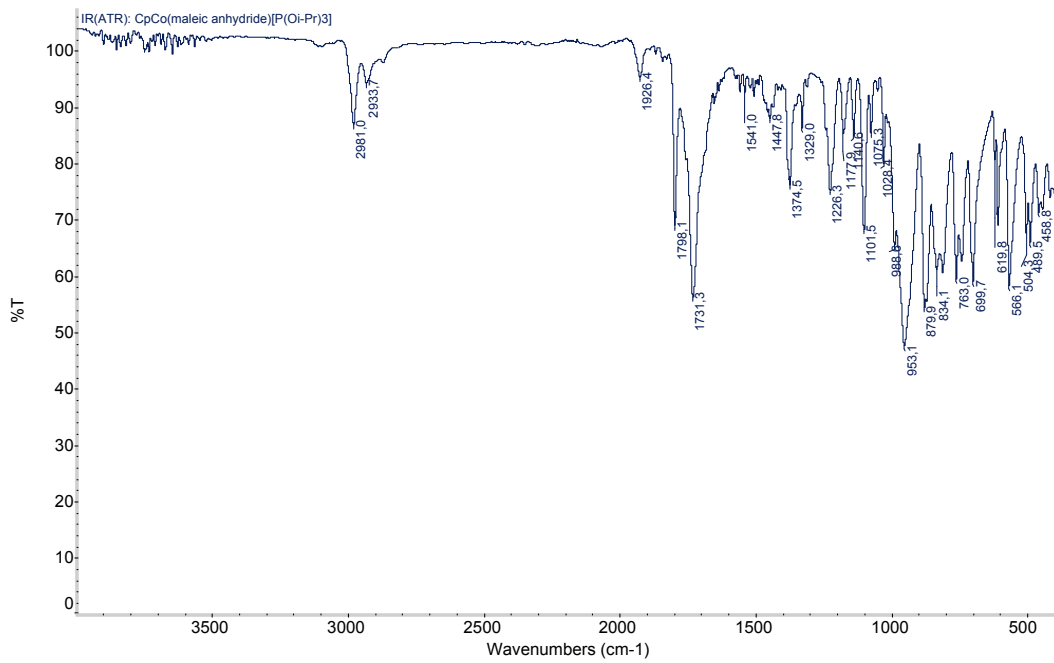
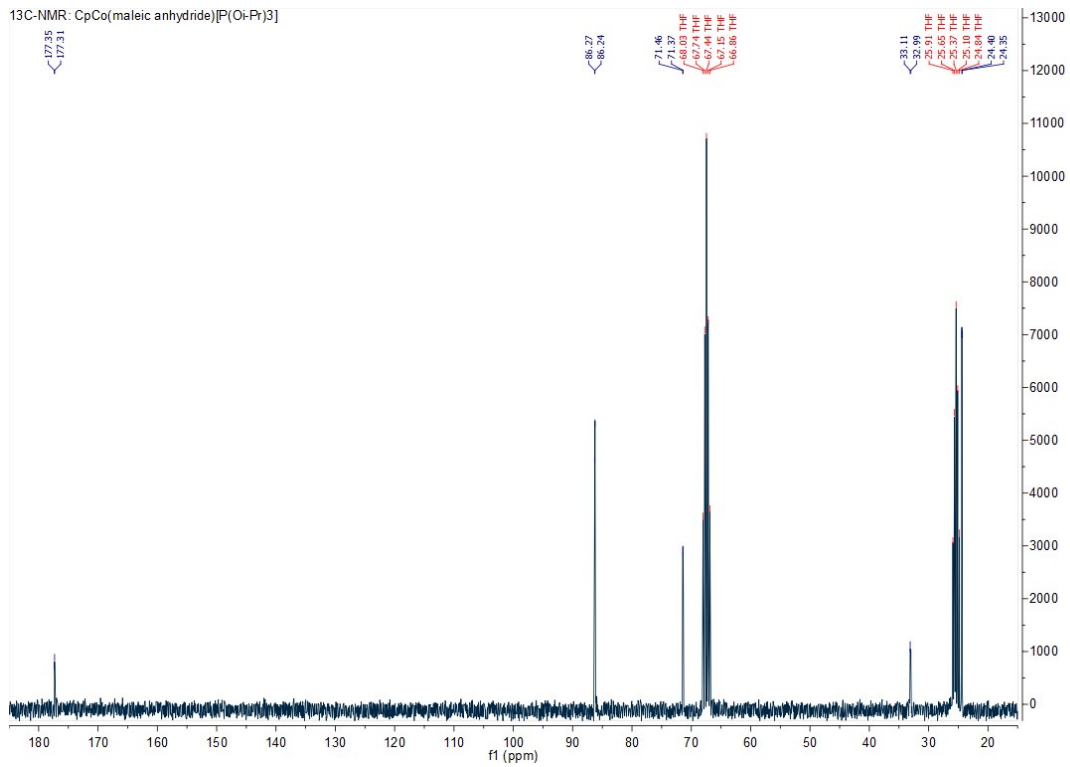
Compound 3a:



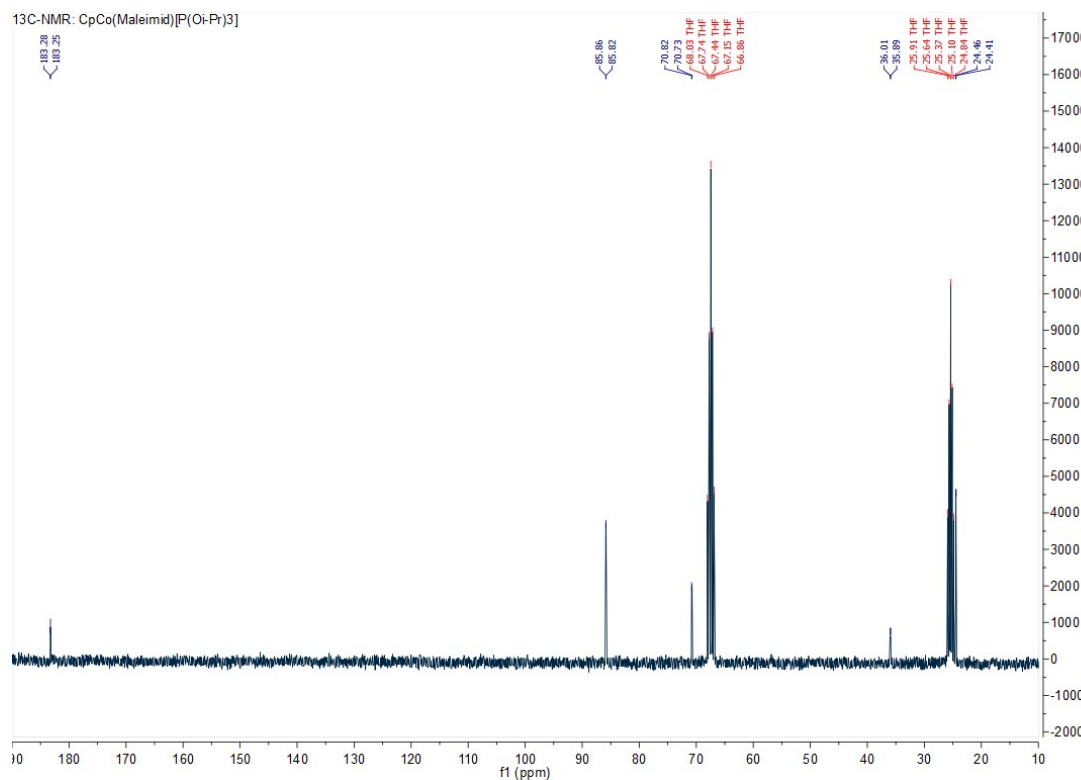
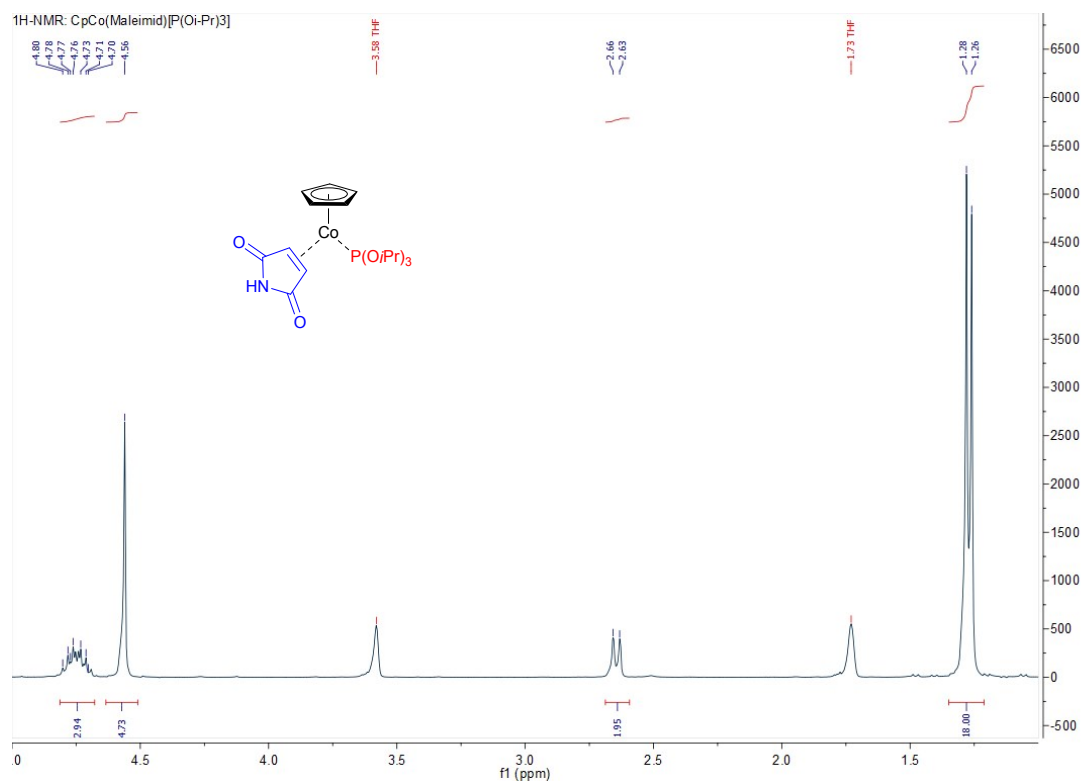


Compound 3b:

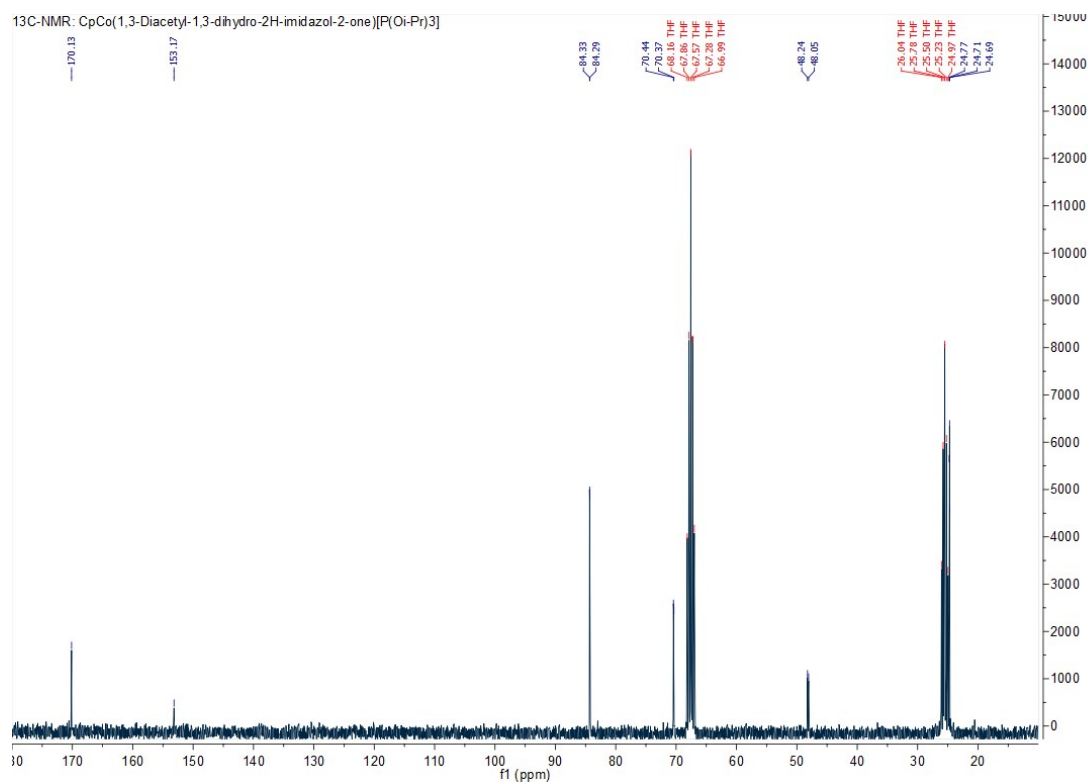
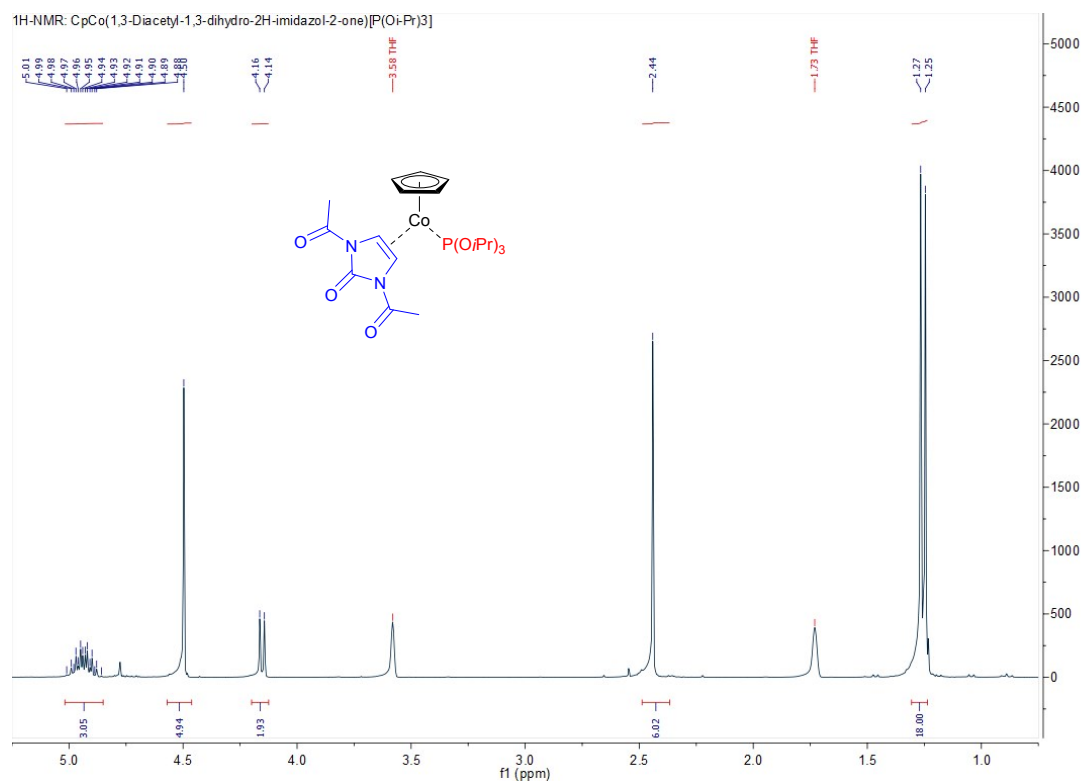




Compound 3d:

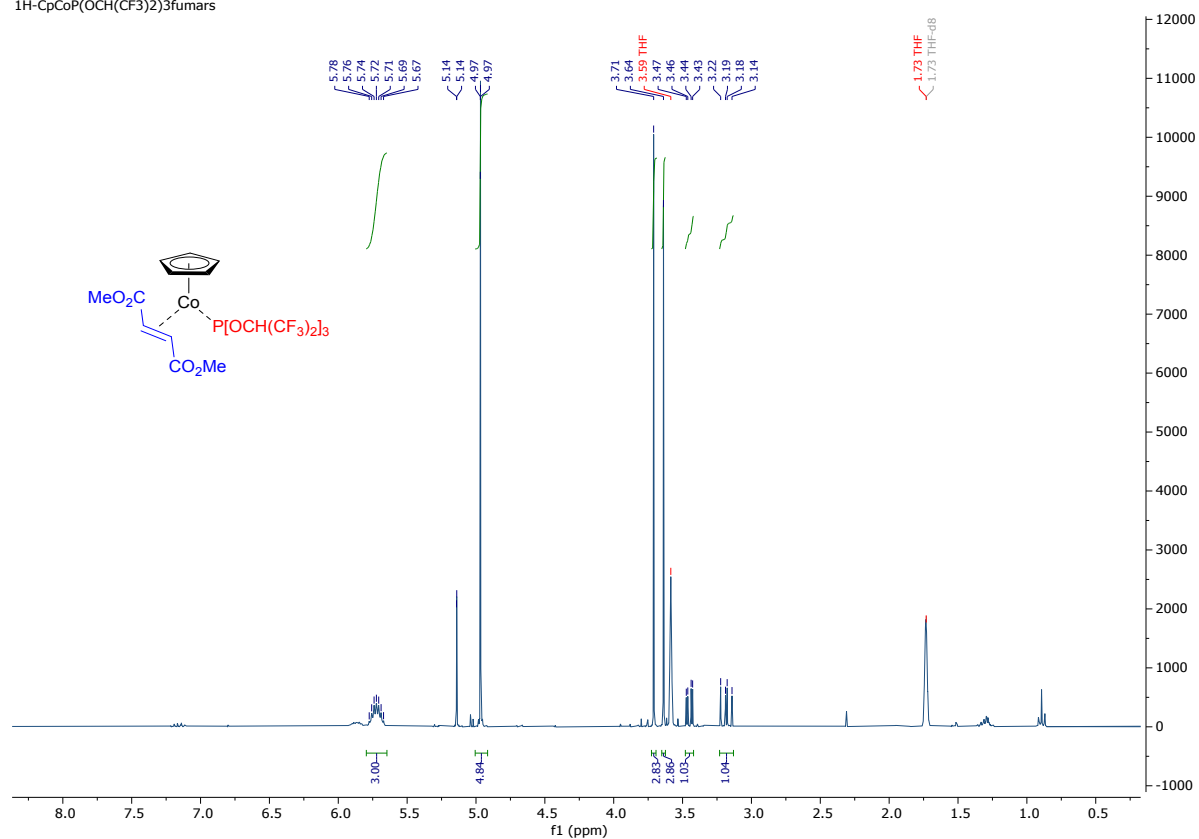


Compound 3e:

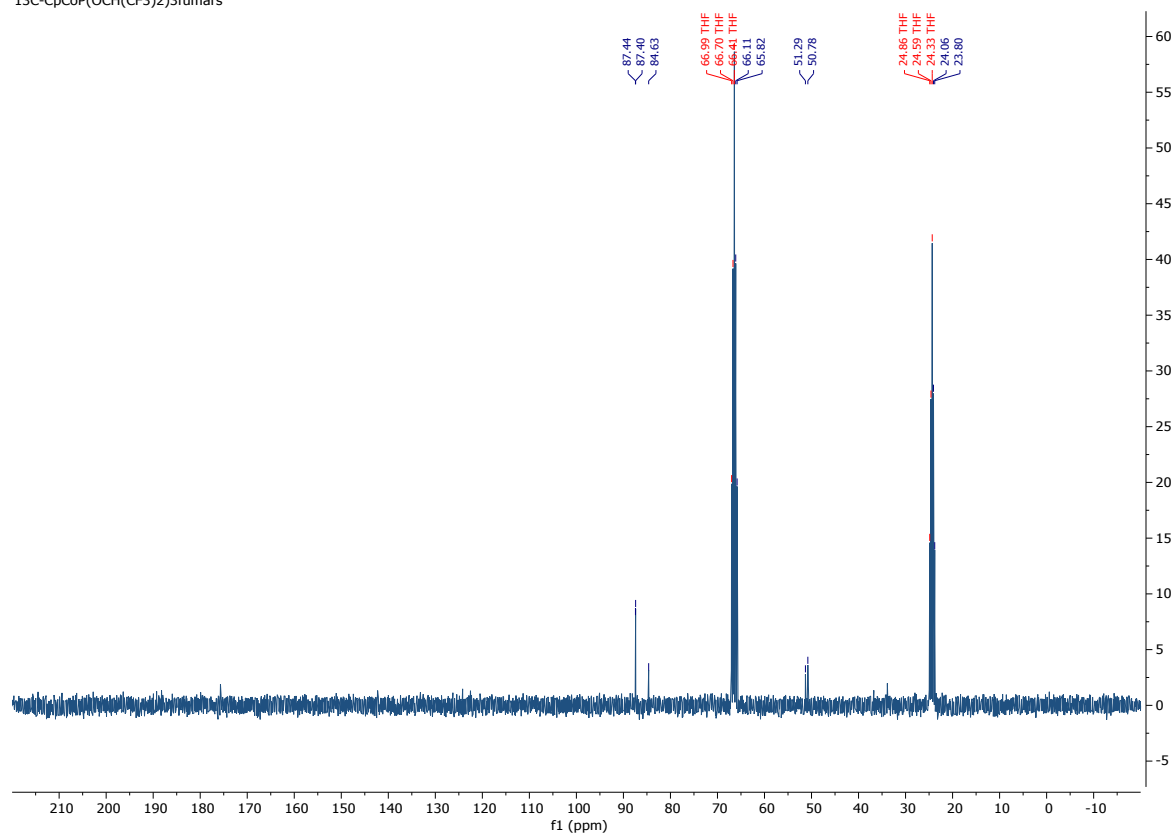


Compound 3f:

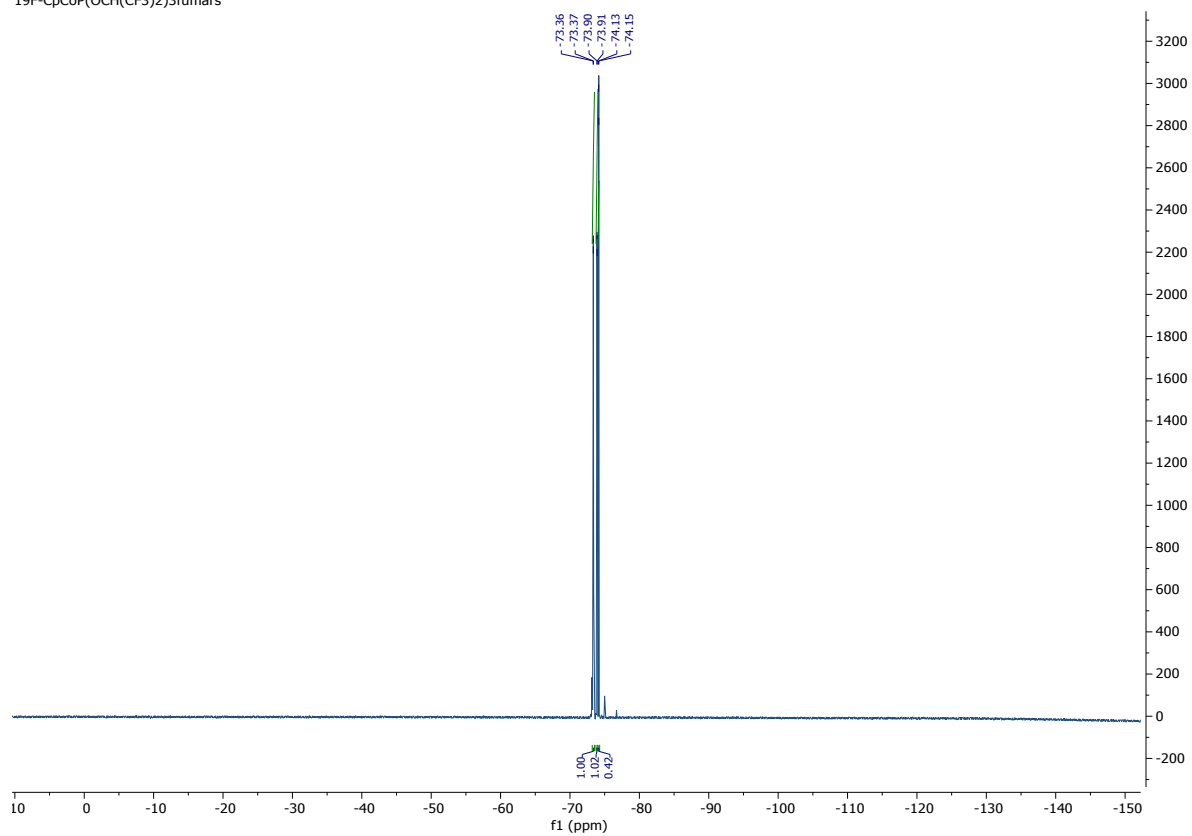
¹H-CpCoP(OCH(CF₃)₂)₃fumars



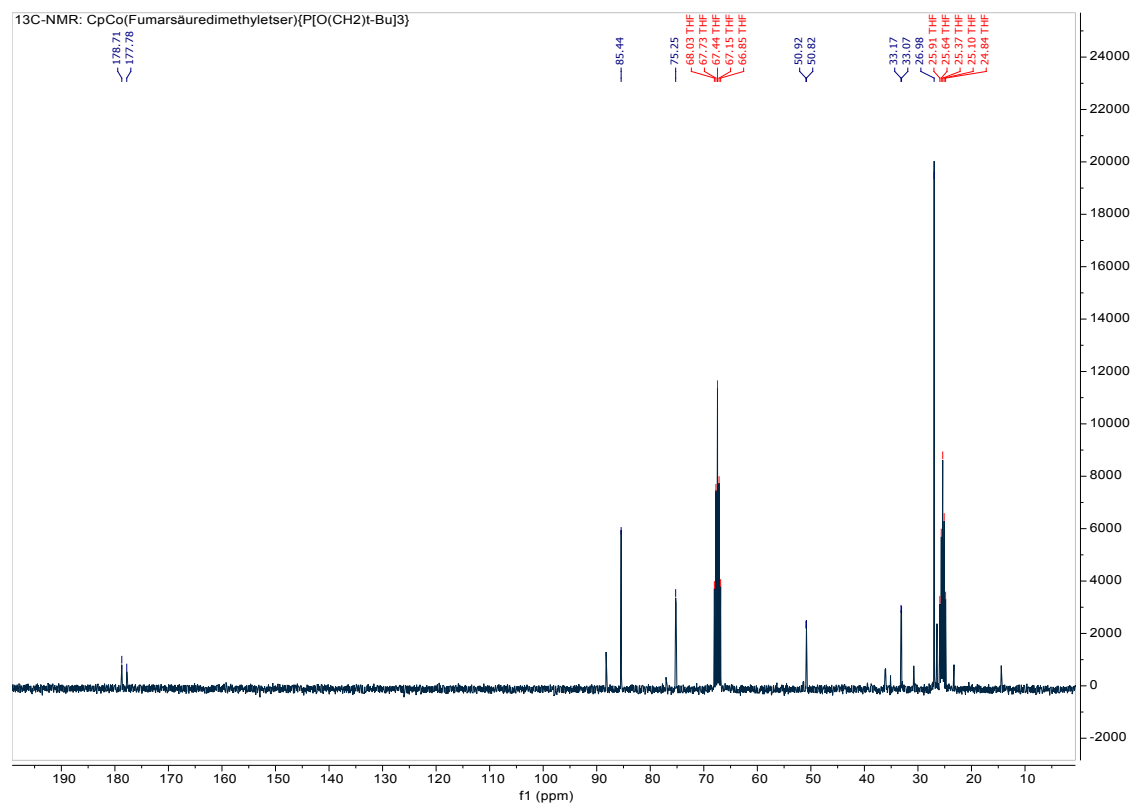
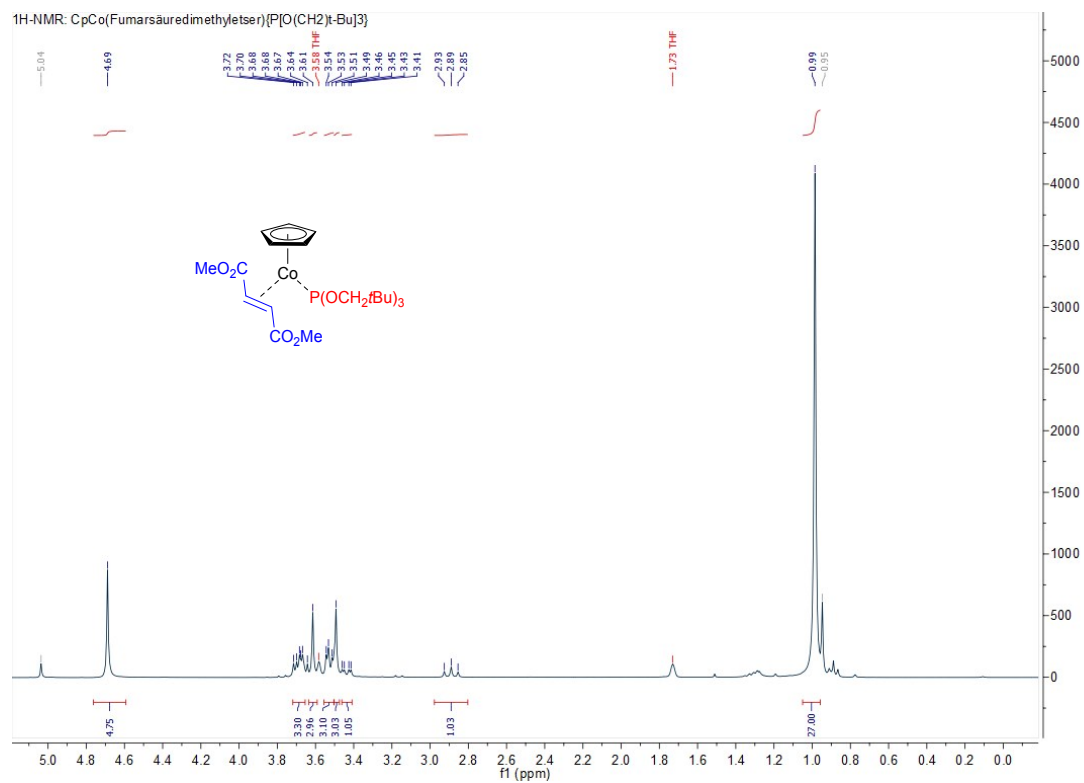
¹³C-CpCoP(OCH(CF₃)₂)₃fumars



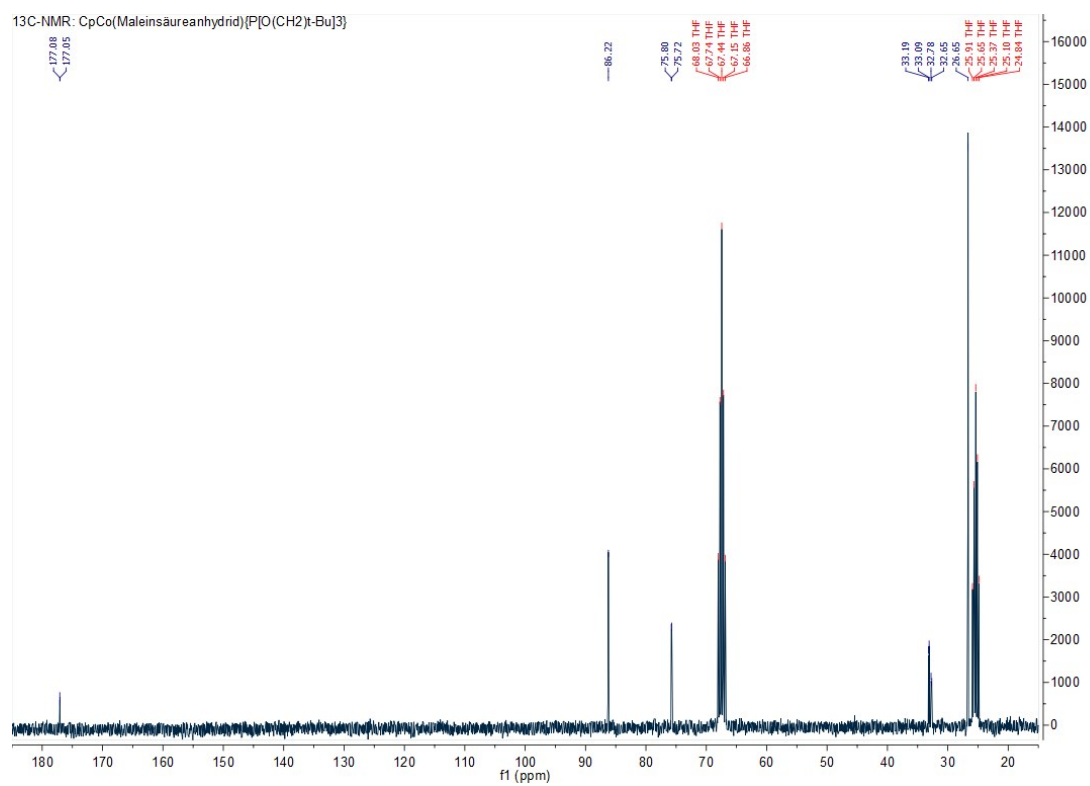
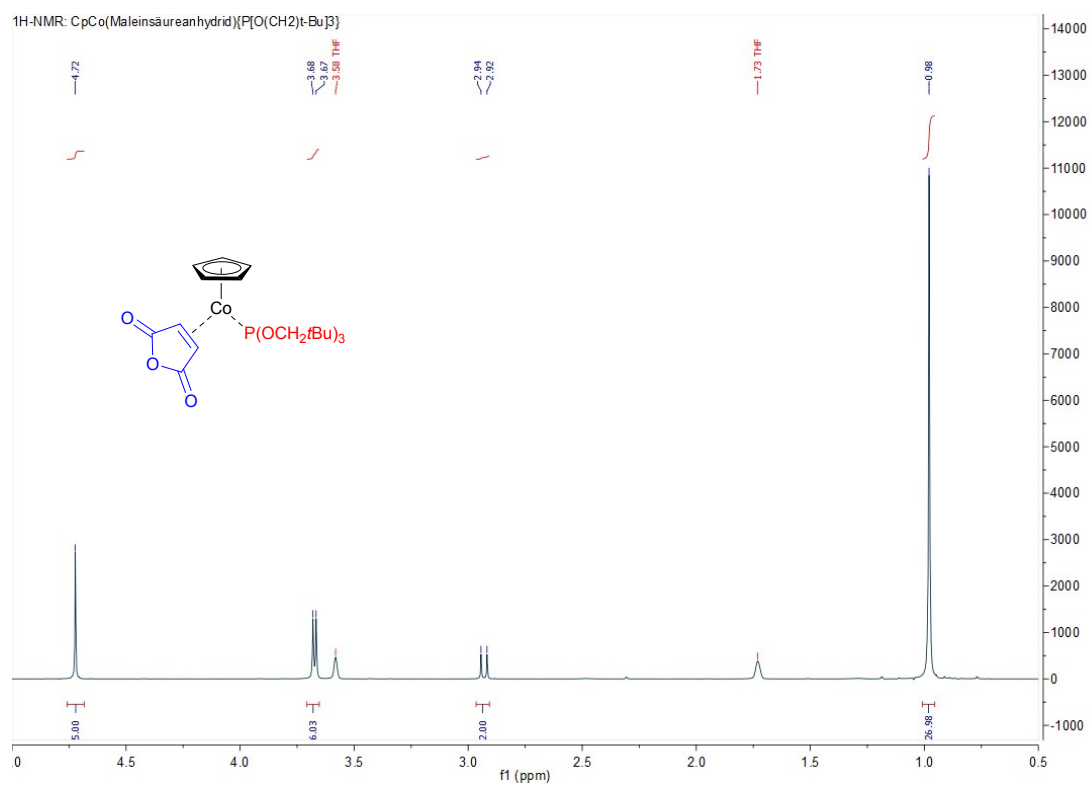
^{19}F -CpCoP(OCH(CF₃)₂)₃fumars



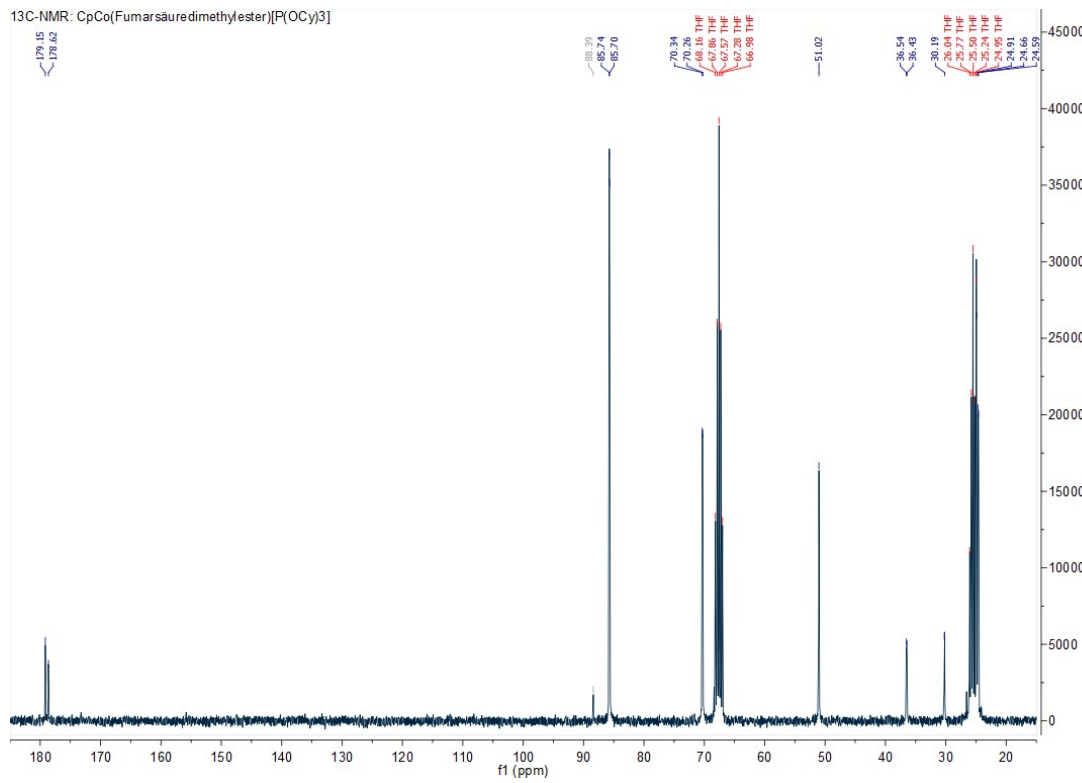
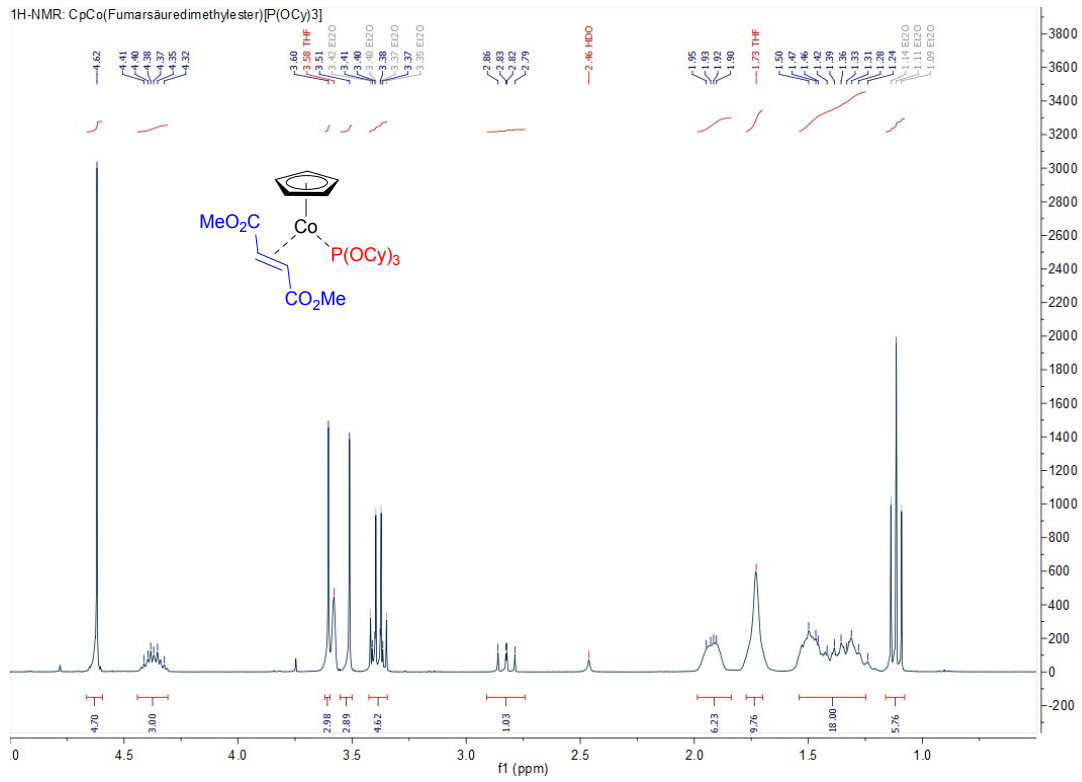
Compound 3g:

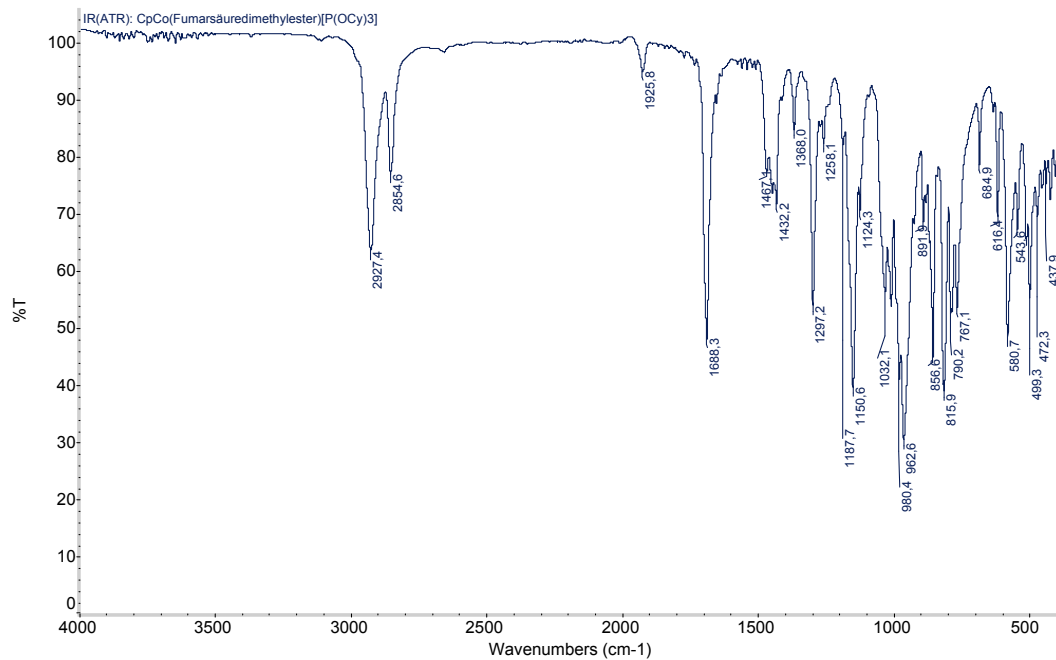


Compound 3h:

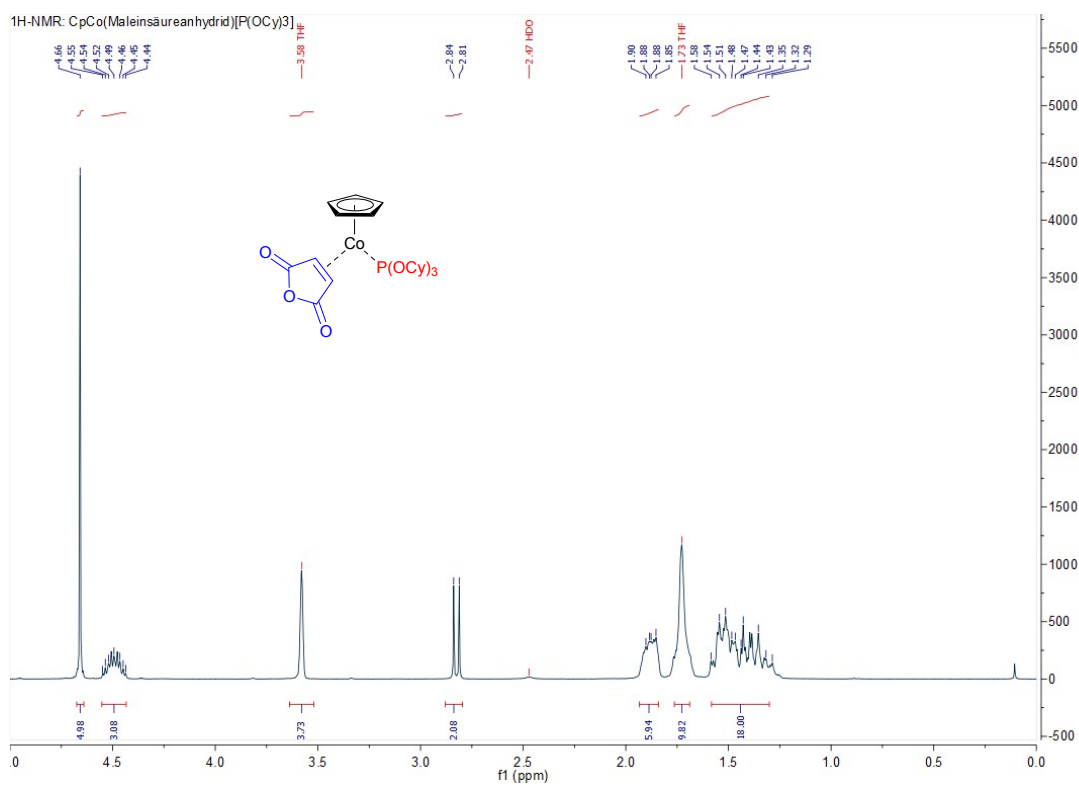


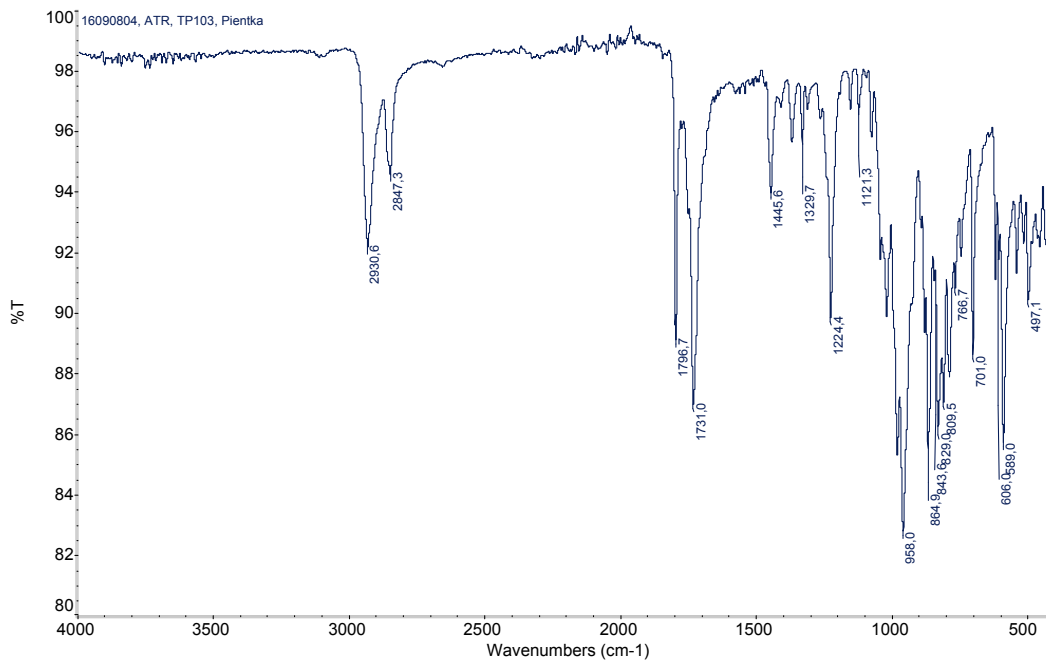
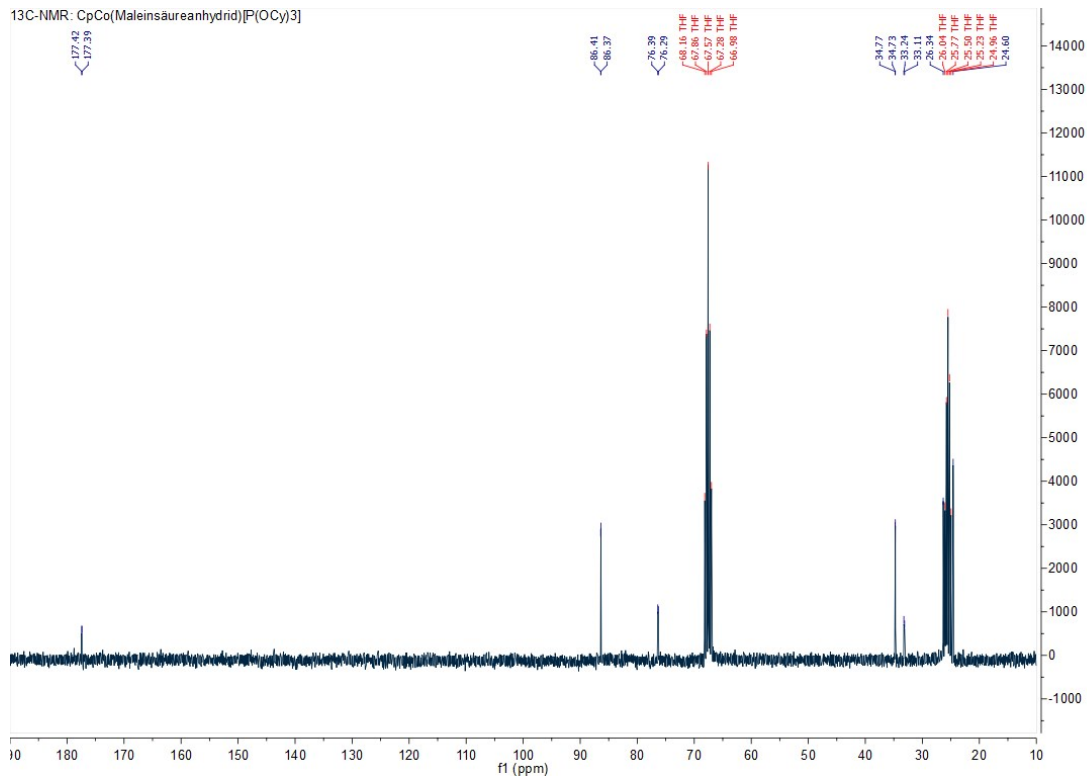
Compound 3i:



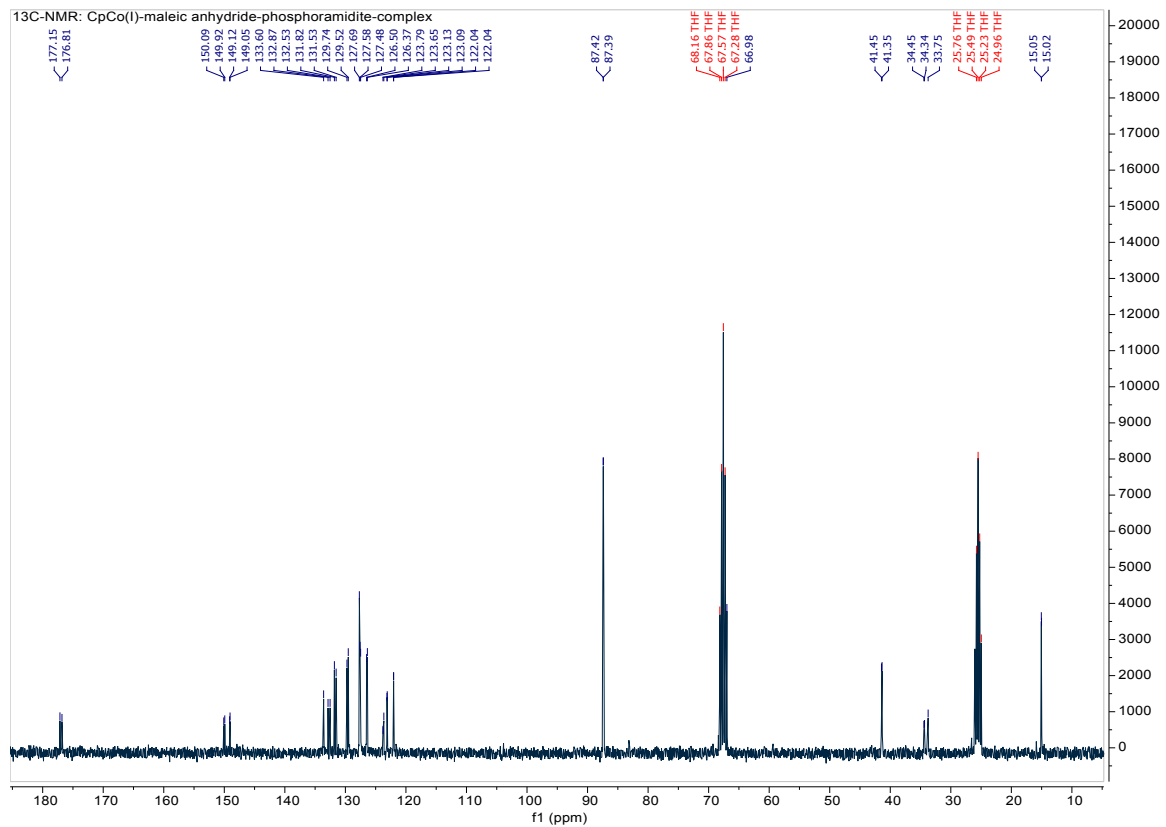
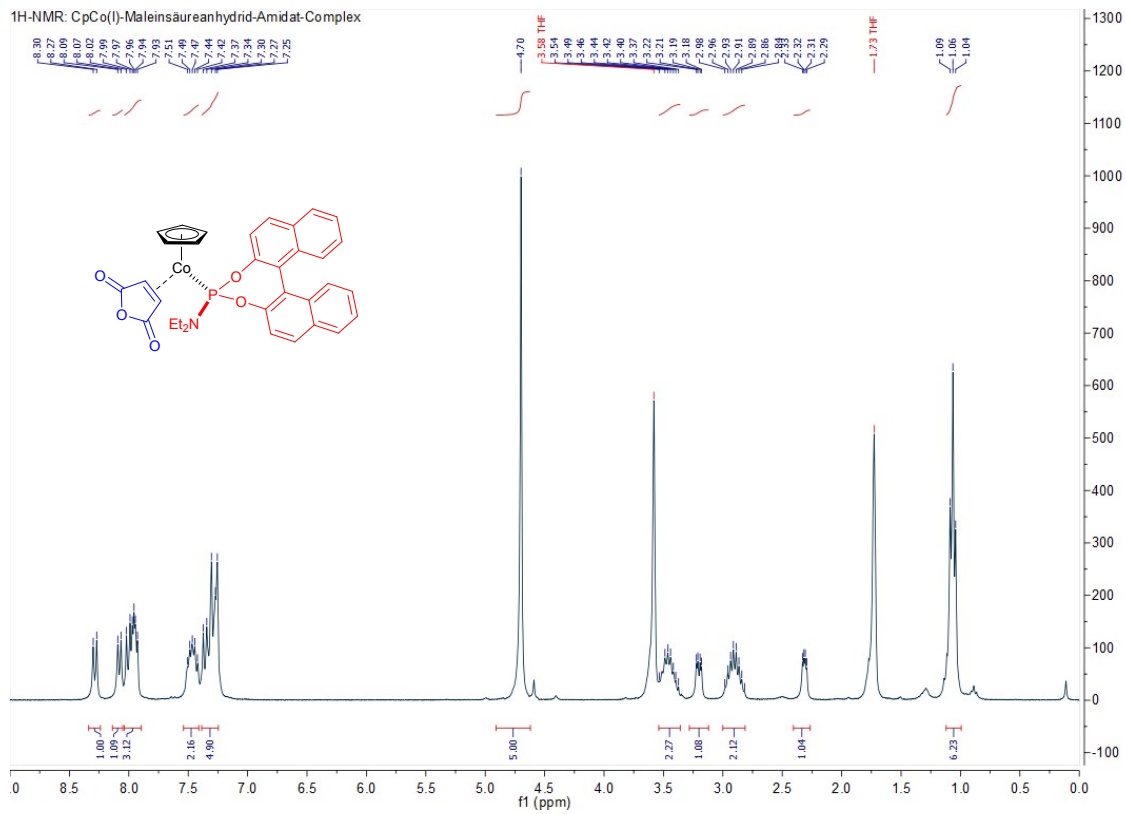


Compound 3j:



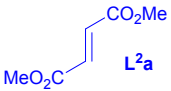
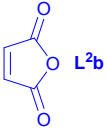


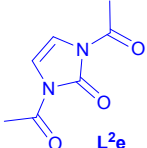
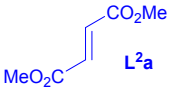
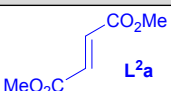
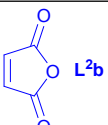


Compound 3k:

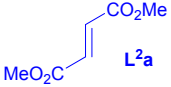
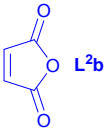
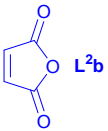


8. ³¹P NMR shifts of phosphites, CpCo(CO)-phosphite and CpCo-olefin-phosphite complexes: Compilation of NMR shift data

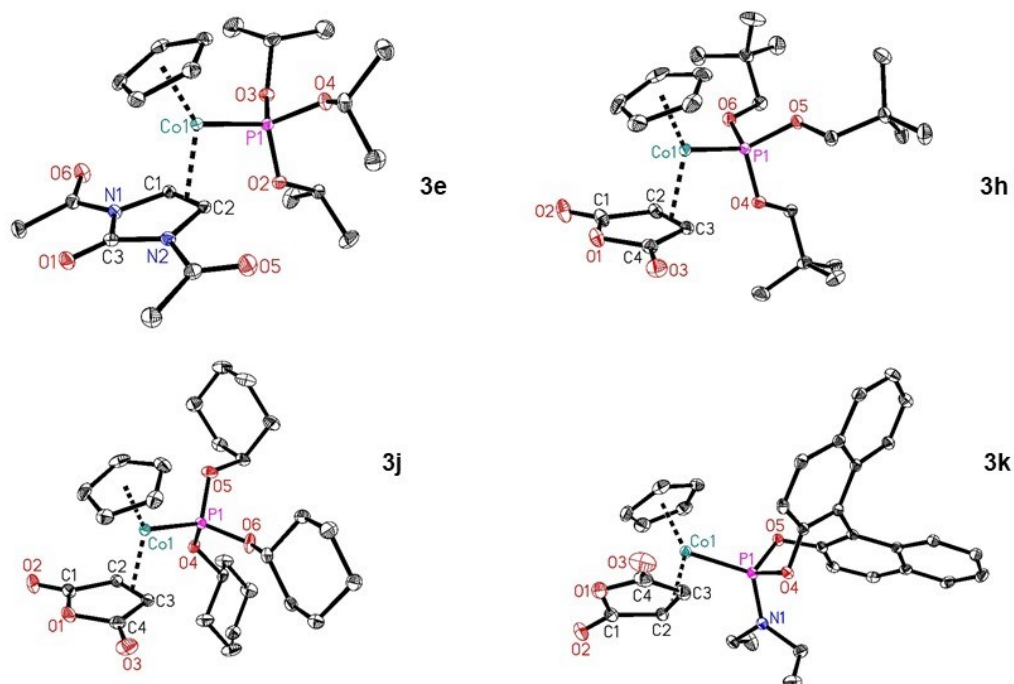
Table SI-1

| Phosphite (L ¹) | Olefin (L ²) | Phosphite δ (³¹ P) [ppm] | CpCo(CO)(L ¹) δ (³¹ P) [ppm] | CpCo(L ¹)(L ²) δ (³¹ P) [ppm] |
|--|---|--------------------------------------|--|---|
| P(O <i>i</i> Pr) ₃ (L ^{1a}) | | 139.1 (CDCl ₃) | | |
| | | | 2a : 168.9 (THF- <i>d</i> ₈) | |
| |  | | | 3a : 152.0 (THF- <i>d</i> ₈) |
| |  | | | 3b : 146.4 (THF- <i>d</i> ₈) |
| |  | | | 3c : --- |
| |  | | | 3d : 150.3 (THF- <i>d</i> ₈) |
| |  | | | 3e : 155.9 (THF- <i>d</i> ₈) |
| P[OCH(CF ₃) ₂] ₃ (L ^{1b}) | | 144.6 (CDCl ₃) | | |
| | | | 2b : 189.1 (toluene- <i>d</i> ₈) | |
| |  | | | 3f : 156.3 (THF- <i>d</i> ₈) |
| P(O <i>t</i> Bu) ₃ (L ^{1c}) | | 140.6 (CDCl ₃) | | |
| | | | 2c : 142.6 (THF- <i>d</i> ₈) | |
| P(OCH ₂ <i>t</i> Bu) ₃ (L ^{1e}) | | 138.6 (CDCl ₃) | | |
| | | | 2e : 170.9 (THF- <i>d</i> ₈) | |
| |  | | | 3g : 156.1 (THF- <i>d</i> ₈) |
| |  | | | 3h : 150.6 (THF- <i>d</i> ₈) |

Continuing **Table SI-1**

| Phosphite (L ¹) | Olefin (L ²) | Phosphite δ (³¹ P) [ppm] | CpCo(CO)(L ¹) δ (³¹ P) [ppm] | CpCo(L ¹)(L ²) δ (³¹ P) [ppm] |
|--|---|---|---|--|
| P(OCy) ₃ (L ^{1d}) | | 139.6 (CDCl ₃) | | |
| | | | 2d : 168.8 (THF- <i>d</i> ₈) | |
| |  | | | 3i : 152.0 (THF- <i>d</i> ₈) |
| |  | | | 3j : 146.8 (THF- <i>d</i> ₈) |
| L^{1f} | | 150.2 (CDCl ₃) | | |
| | | | 2f : 188.5 (THF- <i>d</i> ₈) | |
| |  | | | 3k : 180.2 (THF- <i>d</i> ₈) |
| L^{1g} | | 131.4 (CDCl ₃) | | |
| | | | 2g : 156.0 (THF- <i>d</i> ₈) | |

9. SC-XRD of CpCo-olefin-phosphite complexes **3e**, **3h**, **3j** and **3k**



Molecular structures (Hydrogen atoms omitted, ellipsoids with 30% probability)

Table SI-2

| Distance | Complexes | | | |
|--------------------------------|---------------|---------------|---------------|---------------|
| | 3e [Å] | 3h [Å] | 3j [Å] | 3k [Å] |
| Co1-P1 [Å] | 2.1118(5) | 2.1181(3) | 2.1308(5) | 2.1253(6) |
| Co1-C1 [Å] | 1.9926(14) | | | |
| Co1-C2 [Å] | | 1.9959(11) | 2.0018(18) | 2.013(2) |
| Co1-C2 [Å] | 1.9660(14) | | | |
| Co1-C3 [Å] | | 2.0036(11) | 1.9944(18) | 2.005(2) |
| C1-C2 [Å] | 1.4291(19) | | | |
| C2-C3 [Å] | | 1.4352(16) | 1.434(3) | 1.432(3) |
| Co1-Cp _{centroid} [Å] | 1.7064(8) | 1.6891(7) | 1.6924(9) | 1.6933(11) |

Complex 3e:

| | CpCo(L²e){P[Oi-Pr]₃} |
|---|---|
| Empirical Formula | C ₂₁ H ₃₄ CoN ₂ O ₆ P |
| Formula weight [g·mol ⁻¹] | 500.40 |
| Color | orange |
| Crystal system | monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> |
| Unit cell dimensions: | |
| <i>a</i> [Å] | 17.748(2) |
| <i>b</i> [Å] | 8.4442(11) |
| <i>c</i> [Å] | 16.239(2) |
| α [°] | 90 |
| β [°] | 91.117(2) |
| γ [°] | 90 |
| Cell volume [Å ³] | 2433.2(5) |
| <i>Z</i> | 4 |
| Calculated density [g·cm ⁻³] | 1.366 |
| μ (Mo K α) [mm ⁻¹] | 0.808 |
| Temperature [K] | 150(2) |
| Reflections collected | 35770 |
| Reflections unique (<i>R</i> _{int}) | 5865 (0.0321) |
| Reflections observed [<i>I</i> > 2 σ (<i>I</i>)] | 5035 |
| Parameters | 296 |
| GOF (<i>F</i> ²) | 1.028 |
| <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] | 0.0275 |
| <i>wR</i> ₂ (all data) | 0.0737 |
| CCDC # | 1957196 |

Complex 3h:

| | CpCo(L²b){P[O(CH₂t-Bu]₃} |
|---|--|
| Empirical Formula | C ₂₄ H ₄₀ CoO ₆ P |
| Formula weight [g·mol ⁻¹] | 514.46 |
| Color | red |
| Crystal system | monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> |
| Unit cell dimensions: | |
| <i>a</i> [Å] | 10.9250(2) |
| <i>b</i> [Å] | 12.6105(2) |
| <i>c</i> [Å] | 20.1341(3) |
| α [°] | 90 |
| β [°] | 104.5611(5) |
| γ [°] | 90 |
| Cell volume [Å ³] | 2684.77(8) |
| <i>Z</i> | 4 |
| Calculated density [g·cm ⁻³] | 1.273 |
| μ (Mo K α) [mm ⁻¹] | 0.732 |
| Temperature [K] | 150(2) |
| Reflections collected | 60158 |
| Reflections unique (<i>R</i> _{int}) | 7145 (0.0228) |
| Reflections observed [<i>I</i> > 2 σ (<i>I</i>)] | 6438 |
| Parameters | 306 |
| GOF (<i>F</i> ²) | 1.023 |
| <i>R</i> ₁ <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] | 0.0258 |
| <i>wR</i> ₂ (all data) | 0.0705 |
| CCDC # | 1957195 |

Complex 3j:

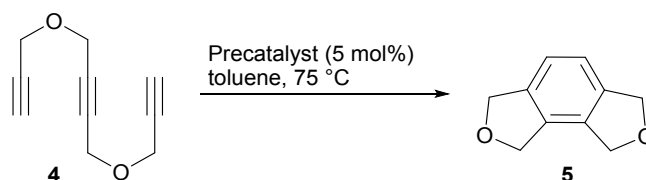
| | CpCo(L²b)[P(OCy)₃] |
|---|--|
| Empirical Formula | C ₂₇ H ₄₀ CoO ₆ P |
| Formula weight [g·mol ⁻¹] | 550.49 |
| Color | red |
| Crystal system | monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> |
| Unit cell dimensions: | |
| <i>a</i> [Å] | 9.3420(4) |
| <i>b</i> [Å] | 12.6826(6) |
| <i>c</i> [Å] | 22.4709(10) |
| α [°] | 90 |
| β [°] | 93.0410(14) |
| γ [°] | 90 |
| Cell volume [Å ³] | |
| <i>Z</i> | 4 |
| Calculated density [g·cm ⁻³] | 1.375 |
| μ (Mo K α) [mm ⁻¹] | 0.745 |
| Temperature [K] | 150(2) |
| Reflections collected | 47801 |
| Reflections unique (<i>R</i> _{int}) | 5793 (0.0248) |
| Reflections observed [<i>I</i> > 2 σ (<i>I</i>)] | 5321 |
| Parameters | 324 |
| GOF (<i>F</i> ²) | 1.092 |
| <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] | 0.0304 |
| <i>wR</i> ₂ (all data) | 0.0766 |
| CCDC # | 1957194 |

Complex 3k:

| CpCo(L²b)[phosphoramidite L¹f] | |
|--|---|
| Empirical Formula | C ₃₃ H ₂₉ CoNO ₅ P |
| Formula weight [g·mol ⁻¹] | 609.47 |
| Color | red |
| Crystal system | orthorhombic |
| Space group | <i>P</i> 2 ₁ 2 ₁ 2 ₁ |
| Unit cell dimensions: | |
| <i>a</i> [Å] | 10.7864(6) |
| <i>b</i> [Å] | 11.5313(7) |
| <i>c</i> [Å] | 22.3359(13) |
| α [°] | 90 |
| β [°] | 90 |
| γ [°] | 90 |
| Cell volume [Å ³] | 2778.2(3) |
| <i>Z</i> | 4 |
| Calculated density [g·cm ⁻³] | 1.457 |
| μ (Mo K α) [mm ⁻¹] | 0.720 |
| Temperature [K] | 150(2) |
| Reflections collected | 51424 |
| Reflections unique (<i>R</i> _{int}) | 6704 (0.0311) |
| Reflections observed [<i>I</i> > 2 σ (<i>I</i>)] | 6393 |
| Parameters | 378 |
| GOF (<i>F</i> ²) | 1.052 |
| <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] | 0.0247 |
| <i>wR</i> ₂ (all data) | 0.0612 |
| CCDC # | 1957197 |

10. Precatalyst screening in [2+2+2] cycloaddition reactions – Reactions and products

10.1 Screening of catalysts **3a**, **3b**, **3d**, **3e**, **3f** and **3k** in the cyclisation of triyne **4** (Chart 2)



General Procedure A: The CpCo(I)-precatalyst (either **3a**, **3b**, **3d**, **3e**, **3f** and **3k**, 5 mol% with regard to the triyne) was dissolved in toluene and to this solution the triyne **4** was added. It was stirred at 75 °C for 2 hours. After cooling to room temperature and evaporation of solvent, the residue was purified by column chromatography over silica gel (eluent: cyclohexane/ethyl acetate, 2:1 v/v) to give the product **5**, which was identified by NMR spectroscopy.

Precatalyst 3a: Reaction of **3a** (14.7 mg, 0.031 mmol) with triyne **4** (100 mg, 0.616 mmol) following the General Procedure A gave 48% (48 mg) isolated yield of product **5**.

Precatalyst 3b: Reaction of **3b** (13.3 mg, 0.031 mmol) with triyne **4** (100 mg, 0.616 mmol) following the General Procedure A gave 5% (5 mg) isolated yield of benzene **5** and 58% (58 mg) reisolated **4**.

Precatalyst 3d: Reaction of **3d** (13.2 mg, 0.031 mmol) with triyne **4** (100 mg, 0.616 mmol) following the General Procedure A gave 4% (4 mg) isolated yield of product **5** and 74% (74 mg) reisolated **4**.

Precatalyst 3e: Reaction of **3e** (15.4 mg, 0.031 mmol) with triyne **4** (100 mg, 0.616 mmol) following the General Procedure A gave 40% (40 mg) isolated yield of benzene **5**.

Precatalyst 3f: Reaction of **3f** (12.0 mg, 0.015 mmol) with triyne **4** (50 mg, 0.308 mmol) following the General Procedure A gave 50% (25 mg) isolated yield of product **5**.

Precatalyst 3g (5 mol%): Reaction of **3g** (17.2 mg, 0.031 mmol) with triyne **4** (100 mg, 0.616 mmol) following the General Procedure A gave 46% (46 mg) isolated yield of product **5**.

Precatalyst 3g (10 mol%): Reaction of **3g** (34.5 mg, 0.061 mmol) with triyne **4** (100 mg, 0.616 mmol) following the General Procedure A gave 43% (43 mg) isolated yield of product **5**.

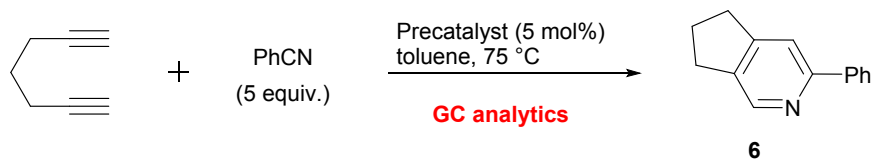
Precatalyst 3i: Reaction of **3i** (18.3 mg, 0.031 mmol) with triyne **4** (100 mg, 0.616 mmol) following the General Procedure A gave 50% (50 mg) isolated yield of benzene **5**.

Precatalyst 3i (10 mol%): Reaction of **3i** (36.7 mg, 0.061 mmol) with triyne **4** (100 mg, 0.616 mmol) following the General Procedure A gave 51% (51 mg) isolated yield of product **5**.

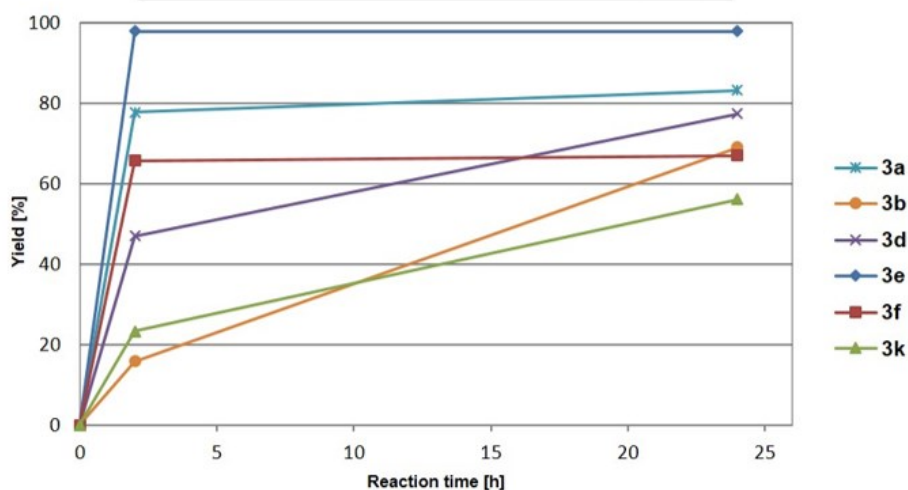
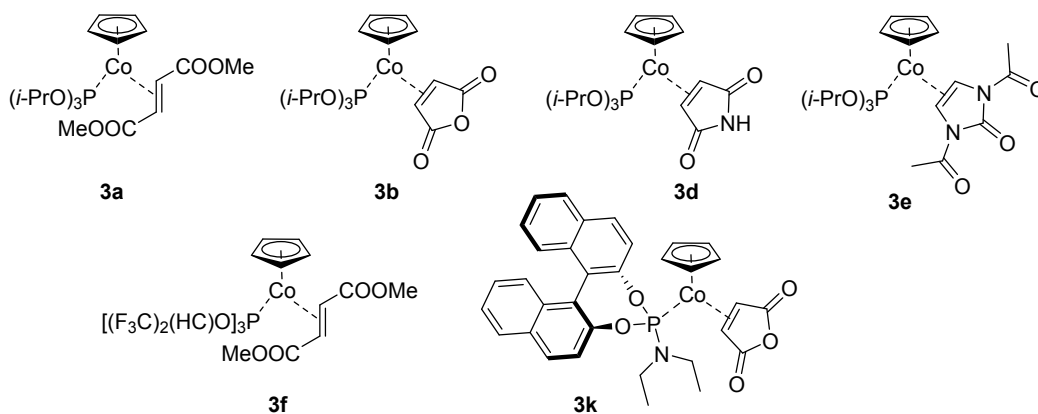
Precatalyst 3k: Reaction of **3k** (18.8 mg, 0.031 mmol) with triyne **4** (100 mg, 0.616 mmol) following the General Procedure A gave 8% (8 mg) isolated yield of product **5** and 64% (64 mg) reisolated **4**.

Precatalyst 3m: Reaction of **3l** (12.6 mg, 0.015 mmol) with triyne **4** (50 mg, 0.308 mmol) following the General Procedure A gave 50% (25 mg) isolated yield of product **5**.

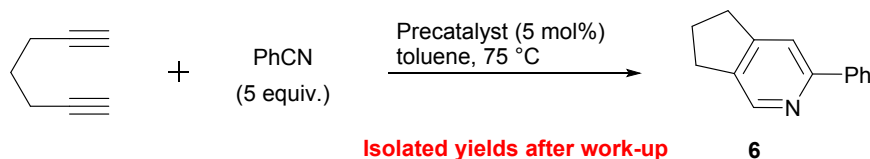
10.2 Initial screening of catalysts **3a**, **3b**, **3d-f** and **3k** in the reaction of 1,6-heptadiyne and PhCN



General methodology: The CpCo(I) precatalyst (either **3a**, **3b**, **3d-f** and **3k**, 5 mol% with regard to the diyne) was added to a solution of 1,6-heptadiyne (1.0 equiv.) and benzonitrile (5 equiv.) in toluene and was stirred at 75 °C for a specific time. After cooling to room temperature, it was filtrated over a short pad of silica and the product formation of **6** analysed GC analysis.



10.3 Screening of catalysts **3a**, **3b**, **3d-f** and **3k** in the reaction of 1,6-heptadiyne and PhCN with isolated yields (Chart 3)



General Procedure B: The CpCo(I) precatalyst (0.016 mmol of either **3a**, **3b**, **3d-f** and **3k**, 5 mol% with regard to the diyne) was added to a solution of 1,6-heptadiyne (30 mg, 0.33 mmol, 1.0 equiv.) and benzonitrile (168 mg, 1.63 mmol, 5 equiv.) in toluene and was stirred at 75 °C for 2 hours in a Schlenk flask. After cooling to room temperature the solvent was evaporated and it was purified by column chromatography over silica gel (eluent: cyclohexane:ethyl acetate, 2:1 v/v) to give the product **6**, which was identified by NMR-spectroscopy.

Precatalyst 3a: Reaction of **3a** (7.8 mg, 0.016 mmol) with 1,6-heptadiyne (30 mg, 0.33 mmol) and benzonitrile (168 mg, 1.63 mmol) following the General Procedure B gave 35% (22 mg) isolated yield of product **6**.

Precatalyst 3b: Reaction of **3b** (7.0 mg, 0.016 mmol) with 1,6-heptadiyne and benzonitrile following the General Procedure B gave 5% (3 mg) isolated yield of pyridine **6**.

Precatalyst 3d: Reaction of **3d** (7.0 mg, 0.016 mmol) with 1,6-heptadiyne and benzonitrile following the General Procedure B gave 4% (2 mg) isolated yield of product **6**.

Precatalyst 3e: Reaction of **3e** (8.2 mg, 0.016 mmol) with 1,6-heptadiyne and benzonitrile following the General Procedure B gave 70% (41 mg) isolated yield of product **6**.

Precatalyst 3f: Reaction of **3f** (13.0 mg, 0.016 mmol) with 1,6-heptadiyne and benzonitrile following the General Procedure B gave 20% (12 mg) isolated yield of pyridine **6**.

Precatalyst 3g: Reaction of **3g** (15.0 mg, 0.026 mmol) with 1,6-heptadiyne (49 mg, 0.535 mmol) and benzonitrile (275 mg, 2.675 mmol) following the General Procedure B gave 23% (23 mg) isolated yield of product **6**.

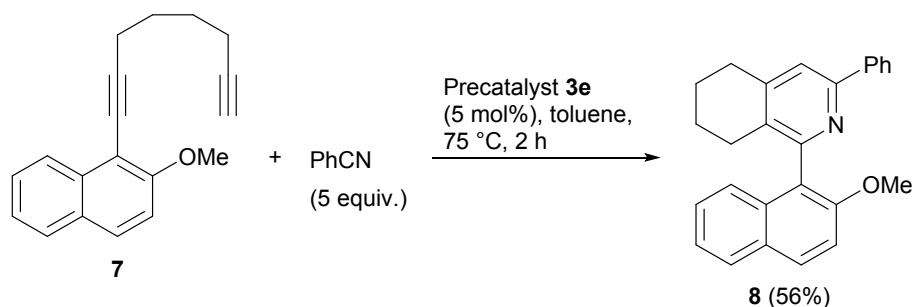
Precatalyst 3i: Reaction of **3i** (15.0 mg, 0.025 mmol) with 1,6-heptadiyne (46 mg, 0.502 mmol) and benzonitrile (258 mg, 2.51 mmol) following the General Procedure B gave 62% (61 mg) isolated yield of product **6**.

Precatalyst 3k: Reaction of **3k** (10.0 mg, 0.016 mmol) with 1,6-heptadiyne and benzonitrile following the General Procedure B gave 13% (8 mg) isolated yield of pyridine **6**.

Precatalyst 3m: Reaction of **3I** (7.6 mg, 0.009 mmol) with 1,6-heptadiyne (17 mg, 0.185 mmol) and benzonitrile (95 mg, 0.925 mmol) following the General Procedure B gave 78% (28 mg) isolated yield of product **6**.

10.4 Cyclisation reactions using precatalyst 3e

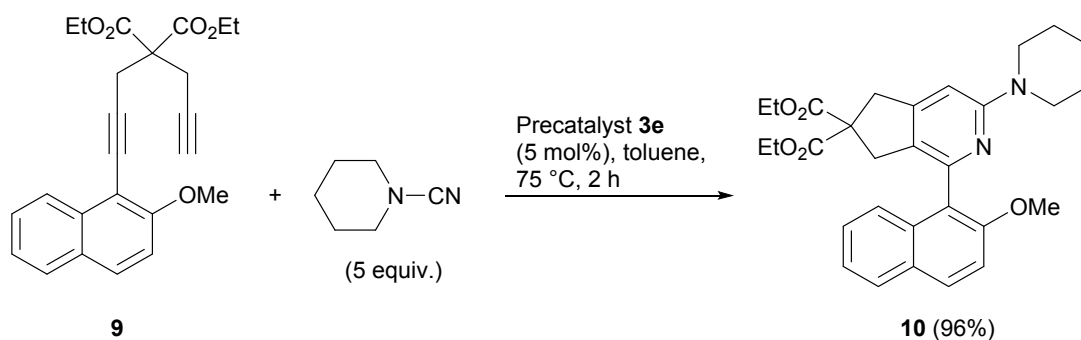
Compound 8:



Following the General Procedure B, complex **3e** (7.5 mg, 0.015 mmol), diyne **7** (78 mg, 0.30 mmol) and benzonitrile (5 equiv., 154 mg, 1.50 mmol) were dissolved in dry toluene (2 mL) and heated to 75 °C for 2 h. After that time the reaction mixture was allowed to cool, the solvent was evaporated, and the residue purified by column chromatography (eluent: cyclohexane:ethyl acetate, 6:1 v/v) to give 62 mg (56%) of **8**.

Compound **8** was identified by NMR spectra, which corresponds to the reported data.¹⁰

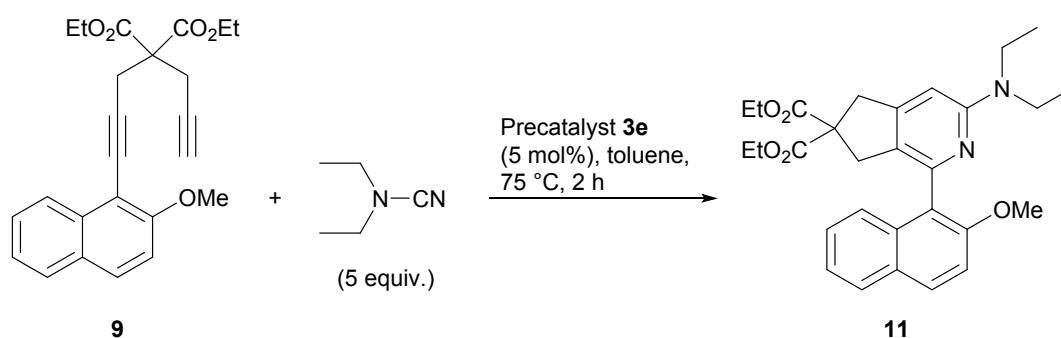
Compound 10:



Following the General Procedure B, complex **3e** (3.7 mg, 0.0075 mmol), diyne **9** (58.5 mg, 0.149 mmol) and piperidine-1-carbonitrile (5 equiv., 82.0 mg, 0.747 mmol) were dissolved in dry toluene (2 mL) and heated to 75 °C for 2 h. After that time the reaction mixture was allowed to cool, the solvent removed in vacuo and the residue purified by column chromatography (eluent: cyclohexane:ethyl acetate, 2:1 v/v) to give 72 mg (96%) of **10**.

Compound **10** was identified by NMR data, which correspond to the reported data.¹¹

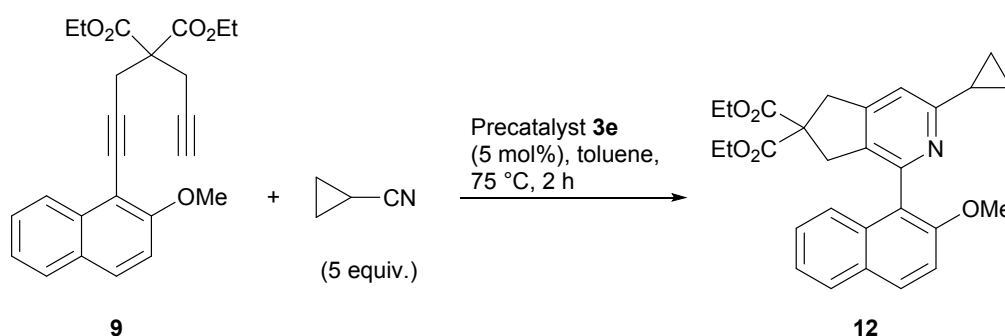
Compound 11:



In accordance to the General Procedure B, complex **3e** (3.7 mg, 0.0075 mmol), diyne **9** (58.5 mg, 0.149 mmol) and diethylcyanamide (5 equiv., 73 mg, 0.747 mmol) were dissolved in 2 mL dry toluene and heated to 75 °C for 2 h. After that time the reaction mixture was allowed to cool, the solvent evaporated and the residue purified by column chromatography (eluent: cyclohexane:ethyl acetate, 2:1 v/v) on silica gel to give 60 mg (82%) of **11**.

¹H NMR (CDCl₃, 300 MHz): δ = 1.12 (t, *J* = 7.1 Hz, 3H), 1.16 (bt, *J* = 7.0 Hz, 6H), 1.23 (t, *J* = 7.1 Hz, 3H), 2.97 (d, *J* = 16.0 Hz, 1H), 3.34 (d, *J* = 16.0 Hz, 1H), 3.47-3.38 (m, 2H), 3.62-3.51 (m, 4H), 3.89 (s, 3H), 4.15-4.03 (m, 2H), 4.19 (qd, *J* = 7.2, 0.5 Hz, 2H), 6.40 (s, 1H), 7.35-7.29 (m, 2H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.57-7.51 (m, 1H), 7.82-7.78 (m, 1H), 7.87 (d, *J* = 9.0 Hz, 1H) ppm; ¹³C NMR (CDCl₃, 75 MHz): δ = 13.2 (2C), 14.0, 14.1, 38.0, 40.9, 42.9, 56.9, 60.2, 61.7 (2C), 99.7, 114.1, 123.5, 124.1, 124.2, 125.6, 126.2, 127.8, 129.3, 129.6 (2C), 133.2, 149.2, 151.3, 154.0, 157.2, 171.7, 171.8 ppm; HRMS (ESI-TOF), C₂₉H₃₄N₂O₅ as [MH]⁺: calc.: 491.2546; found: 491.20542.

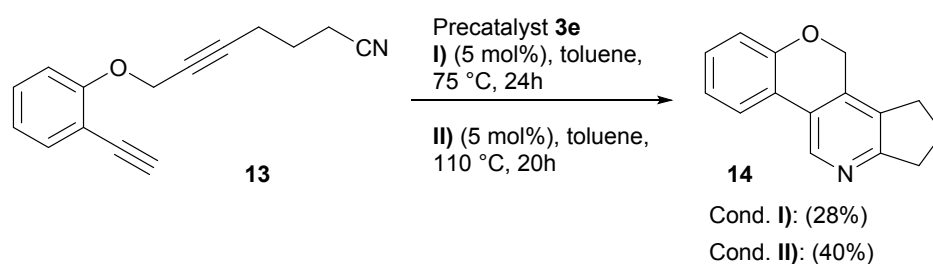
Compound 12:



Following the General Procedure B, complex **3e** (3.7 mg, 0.0075 mmol), diyne **9** (58.5 mg, 0.149 mmol) and cyclopropanecarbonitrile (5 equiv., 50 mg, 0.747 mmol) were dissolved in dry toluene (2 mL) and heated to 75 °C for 2 h. After that time the reaction mixture was allowed to cool, evaporated to dryness and the residue purified by column chromatography (eluent: cyclohexane:ethyl acetate, 2:1 v/v) on silica gel to give 57 mg (83%) of **12**.

^1H NMR (CDCl_3 , 300 MHz): δ = 1.02-0.97 (m, 4H), 1.16 (t, J = 7.1 Hz, 6H), 1.26 (t, J = 7.1 Hz, 3H), 2.24-2.11 (m, 1H), 3.09 (d, J = 16.8 Hz, 1H), 3.45 (d, J = 16.8 Hz, 1H), 3.69-3.66 (m, 2H), 3.90 (s, 3H), 4.18-4.07 (m, 2H), 4.22 (qd, J = 7.1, 0.4 Hz, 2H), 7.00 (bs, 1H), 7.38 (d, J = 9.0 Hz, 1H), 7.38-7.32 (m, 3H), 7.86-7.81 (m, 1H), 7.93 (d, J = 9.0 Hz, 1H) ppm; ^{13}C NMR (CDCl_3 , 75 MHz): δ = 10.0 (2C), 14.0, 14.1, 17.5, 38.5, 42.9, 56.8, 59.9, 61.8 (2C), 113.8, 114.9, 123.7, 124.9, 126.6, 127.9, 129.3, 130.1 (2C), 133.1, 134.0, 150.0, 151.1, 154.2, 161.7, 171.4, 171.5 ppm; HRMS (ESI-TOF), $\text{C}_{28}\text{H}_{29}\text{NO}_5$ as $[\text{MH}]^+$: calc.: 460.2124; found: 460.2119.

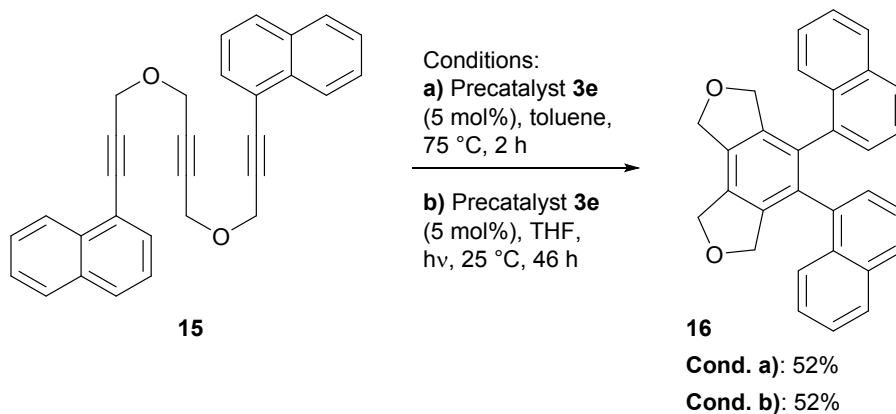
Compound 14:



Following the General Procedure B, complex **3e** (2.8 mg, 0.056 mmol) and cyanodiene **13** (25.0 mg, 0.112 mmol) were dissolved in dry toluene (2 mL) and heated to either 75 °C for 24 h or 110 °C for 20 h. After that time the reaction mixture was allowed to cool to room temperature, the solvent was evaporated and purification performed by column chromatography (eluent: cyclohexane:ethyl acetate, 2:1 v/v) on silica gel, in case of the reaction at 110 °C to give 10 mg (40%) of **14** and 4 mg (16%) reisolated substrate **13**.

^1H NMR (CDCl_3 , 300 MHz): δ = 2.15-2.25 (m, 2H), 2.88 (t, J = 7.8 Hz, 2H), 3.05 (t, J = 7.8 Hz, 2H), 5.07 (s, 2H), 6.96 (dd, J = 7.0, 1.6 Hz, 1H), 7.03-7.09 (m, 1H), 7.22-7.29 (m, 1H), 7.77 (dd, J = 7.7, 1.6 Hz, 1H), 8.71 (s, 1H) ppm; ^{13}C NMR (CDCl_3 , 75 MHz): δ = 23.2, 28.3, 34.1, 65.0, 117.7, 120.8, 122.6, 123.0, 123.3, 129.8, 131.8, 135.7, 141.6, 154.3, 165.4 ppm; HRMS (ESI-TOF), $\text{C}_{15}\text{H}_{13}\text{NO}$: calc.: 224.1075; found: 224.1080.

Compound 16:



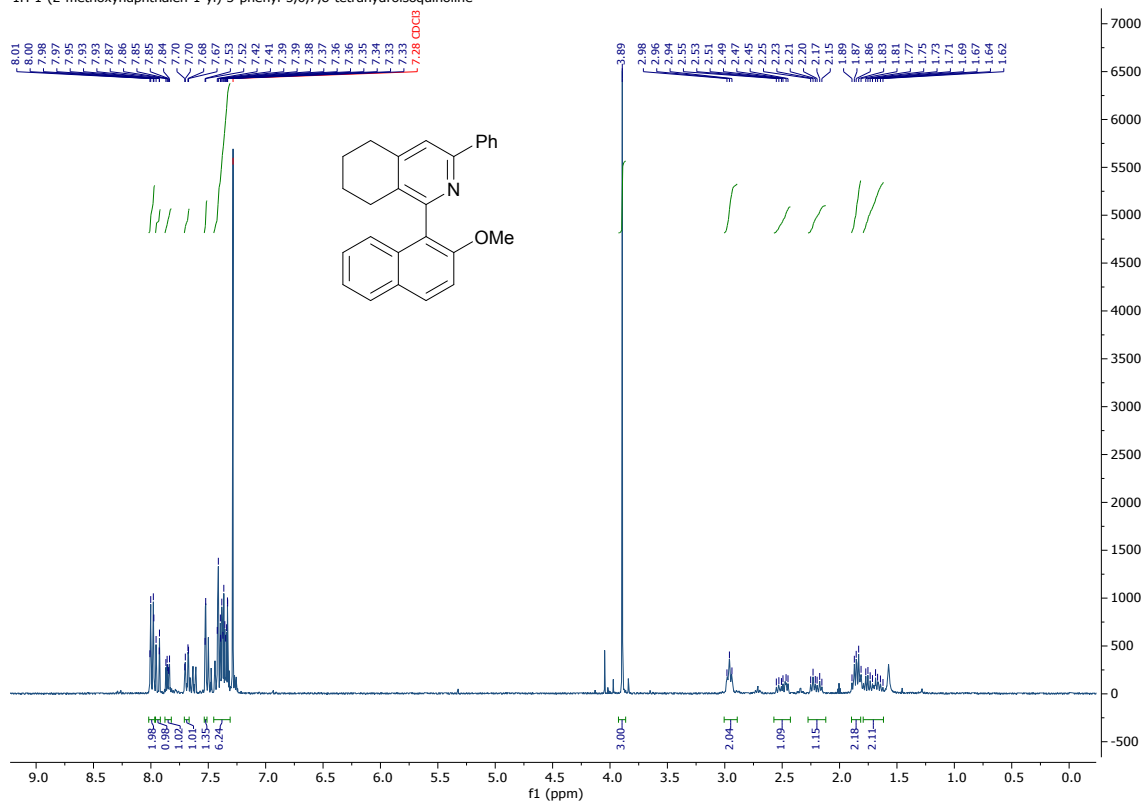
Under thermal **Cond. a)**: According to the General Procedure C, complex **3e** (3.7 mg, 0.0075 mmol) and triyne **15** (62 mg, 0.150 mmol) were dissolved in dry toluene and heated to 75 °C for 2 h. After that time the reaction mixture was allowed to cool, the solvent removed in vacuo and purified by column chromatography (eluent: cyclohexane:ethyl acetate, 2:1 v/v) to give 32 mg (52%) isolated yield of **16**, while 10 mg (16%) of starting material **15** were reisolated. Compound **16** was identified by its NMR spectra, which corresponds to the reported data.¹²

Under photochemical **Cond. b)**: A Schlenk flask was loaded with precatalyst **3e** (2.7 mg, 0.0054 mmol), triyne **15** (46 mg, 0.11 mmol) and dissolved in toluene (2 ml). The reaction mixture was irradiated for 46 h at 25 °C using LED lamps (34 W). The reaction was stopped by turning off the lamps and the reaction vessel opened to air. The reaction solution was evaporated to dryness and loaded to a small amount of silica gel, yielding a fine powder. The crude product was purified by flash chromatography, furnishing the pure product. Product **16** was isolated with 52% (24 mg) yield and 16 mg (35%) of **15** were reisolated. Identification was accomplished by NMR, as above.

10.5 NMR spectra of products from cyclisation reactions

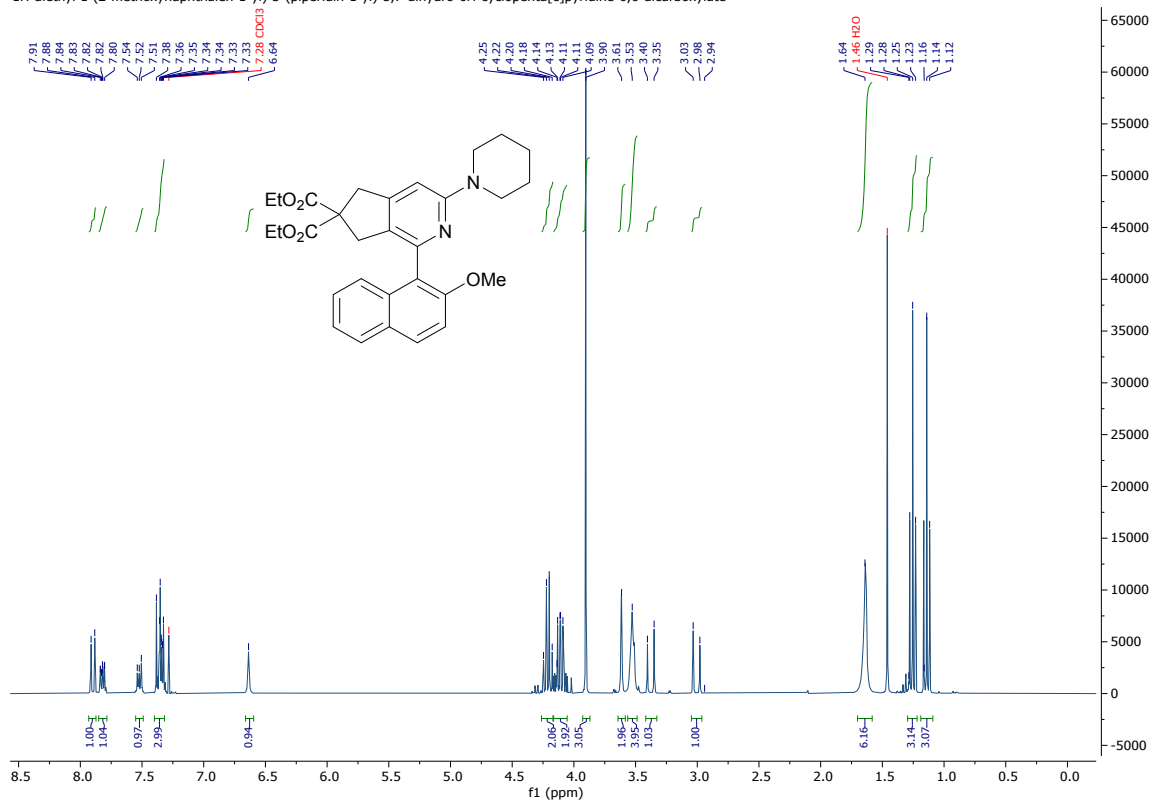
Compound 8:

1H-1-(2-methoxynaphthalen-1-yl)-3-phenyl-5,6,7,8-tetrahydroisoquinoline



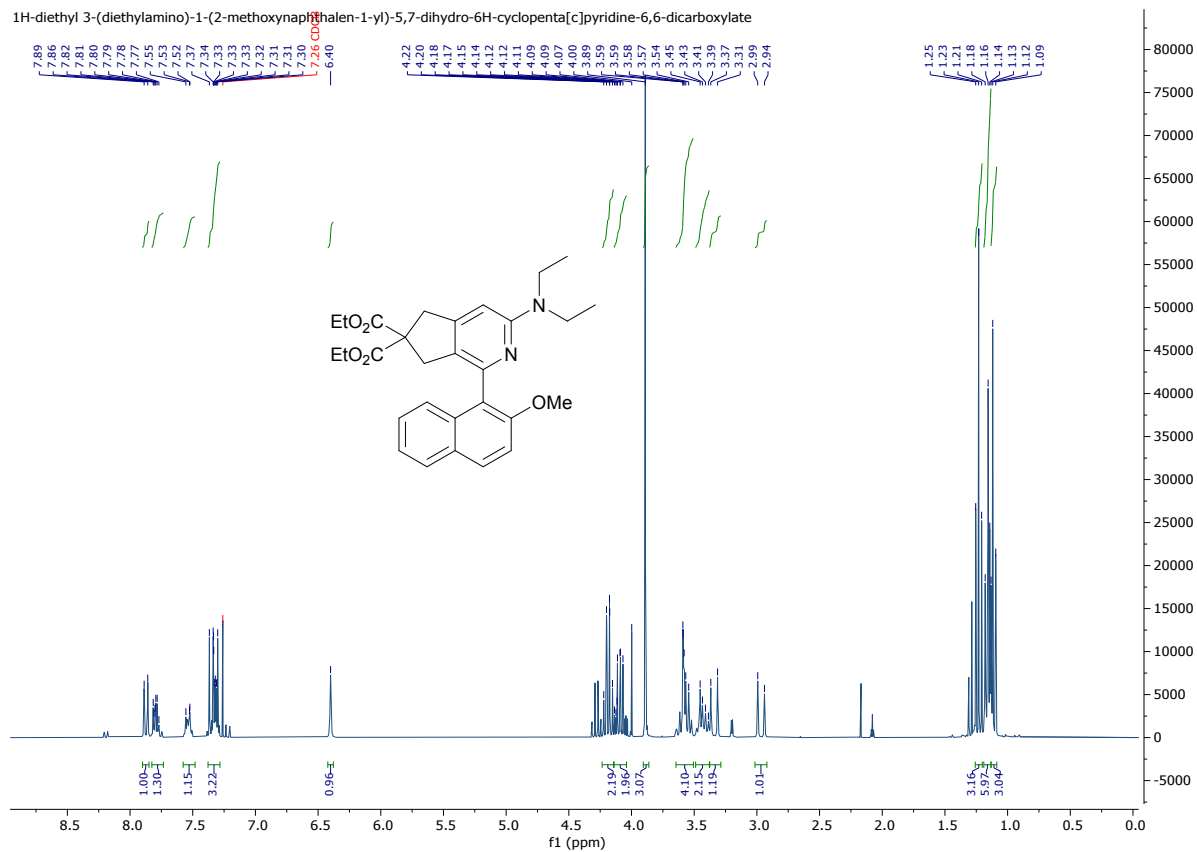
Compound 10:

1H-diethyl 1-(2-methoxynaphthalen-1-yl)-3-(piperidin-1-yl)-5,7-dihydro-6H-cyclopenta[c]pyridine-6,6-dicarboxylate

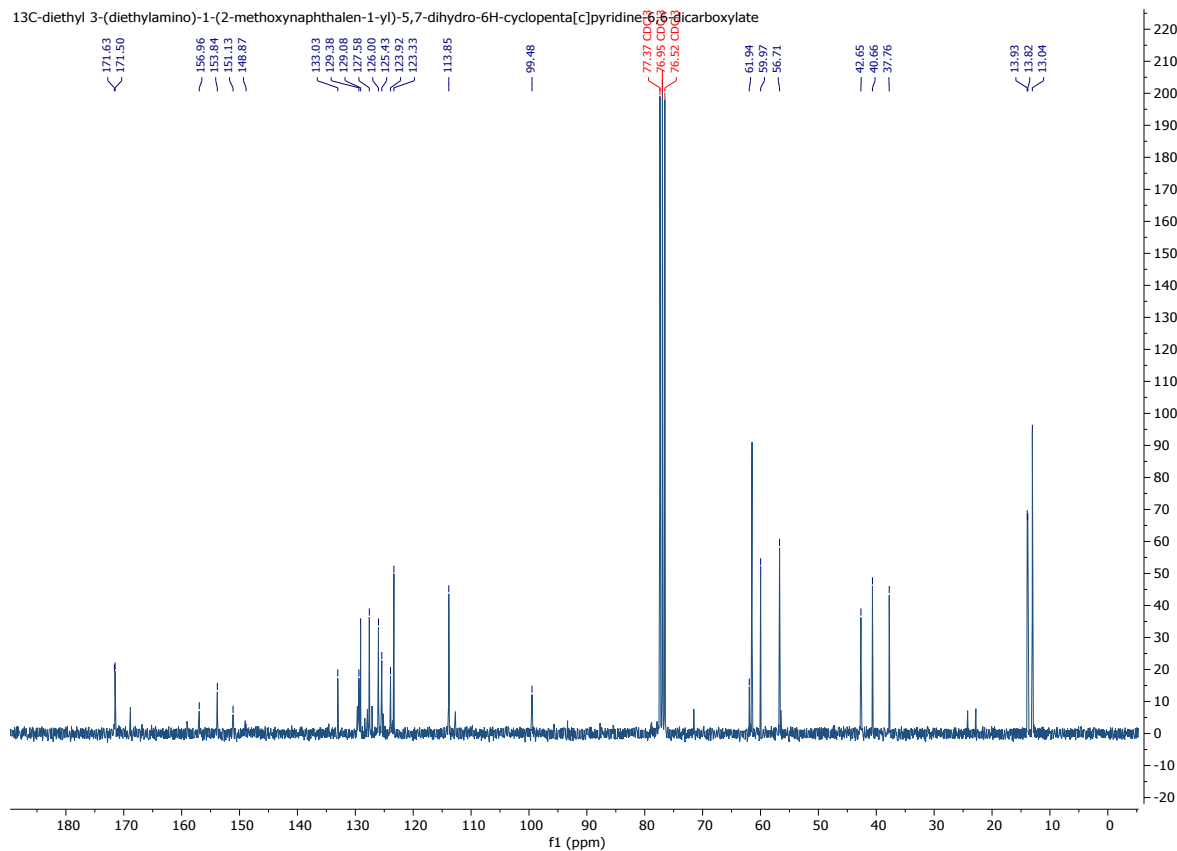


Compound 11:

¹H-diethyl 3-(diethylamino)-1-(2-methoxynaphthalen-1-yl)-5,7-dihydro-6H-cyclopenta[c]pyridine-6,6-dicarboxylate

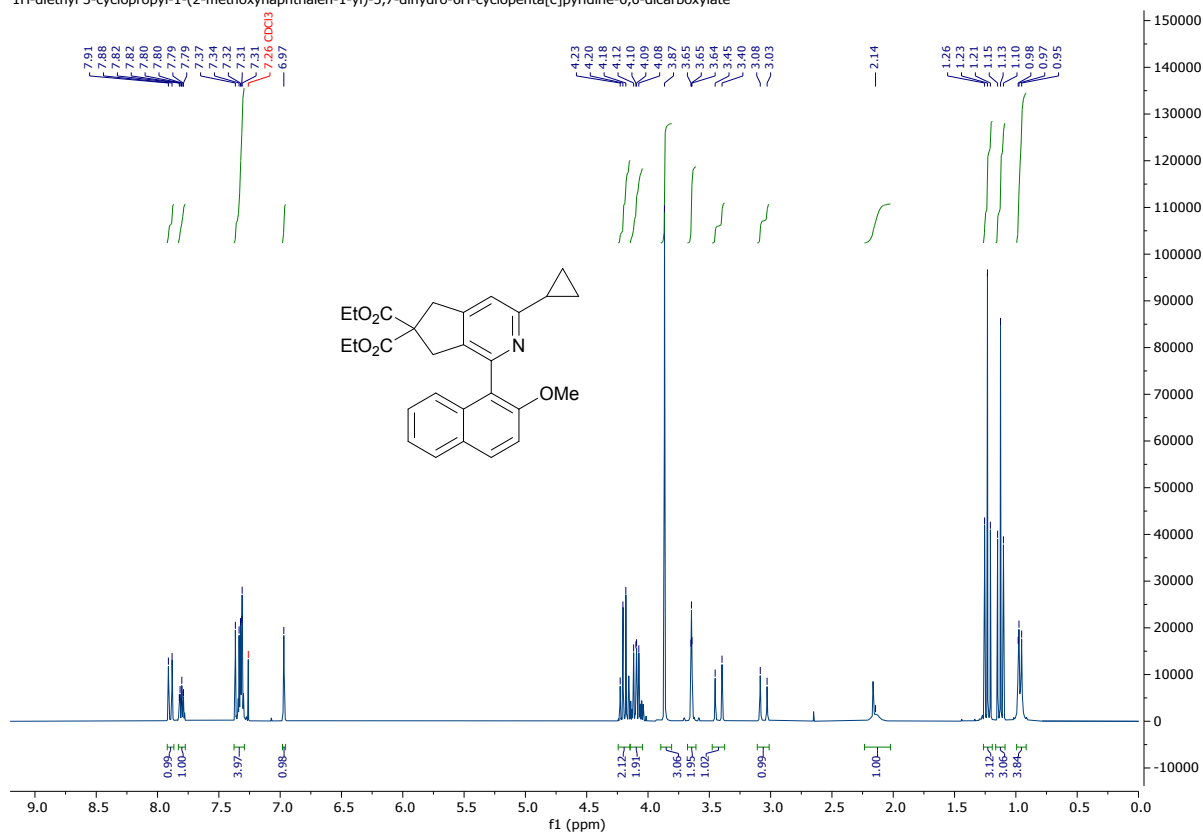


¹³C-diethyl 3-(diethylamino)-1-(2-methoxynaphthalen-1-yl)-5,7-dihydro-6H-cyclopenta[c]pyridine-6,6-dicarboxylate

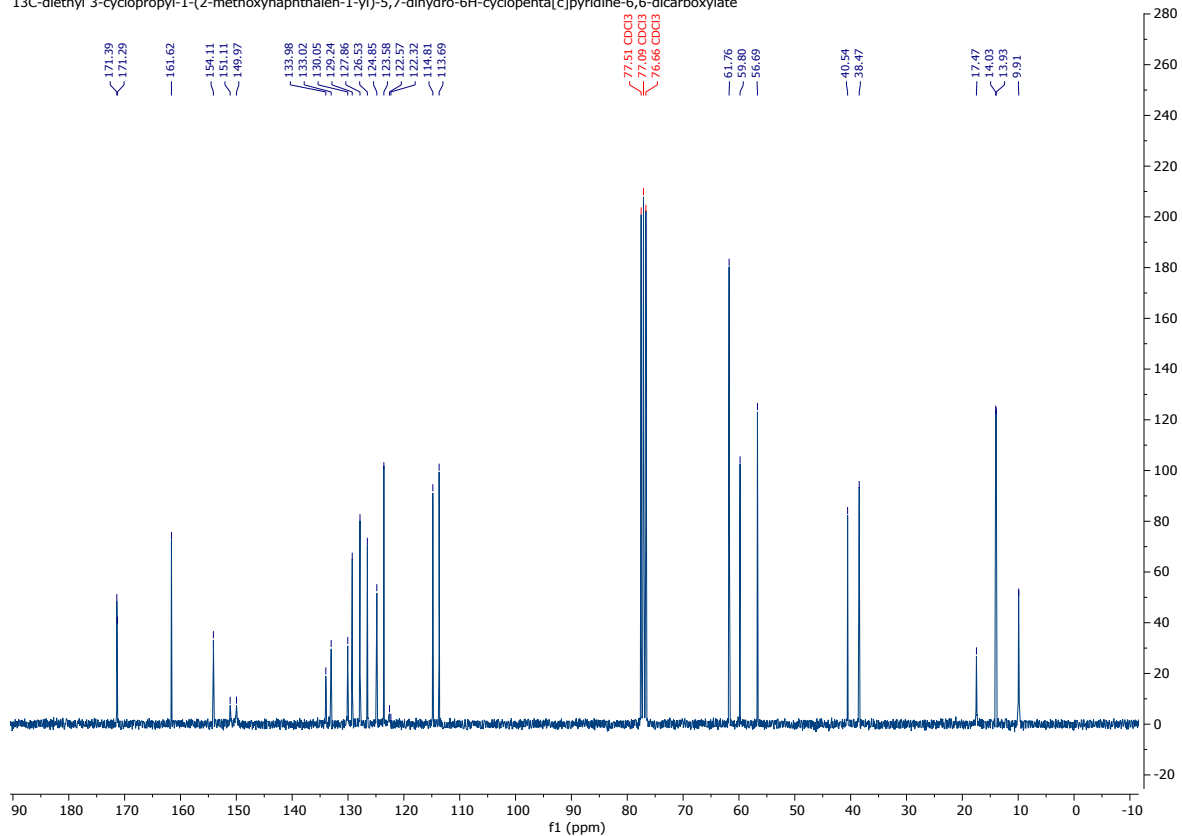


Compound 12:

1H-diethyl 3-cyclopropyl-1-(2-methoxynaphthalen-1-yl)-5,7-dihydro-6H-cyclopenta[c]pyridine-6,6-dicarboxylate

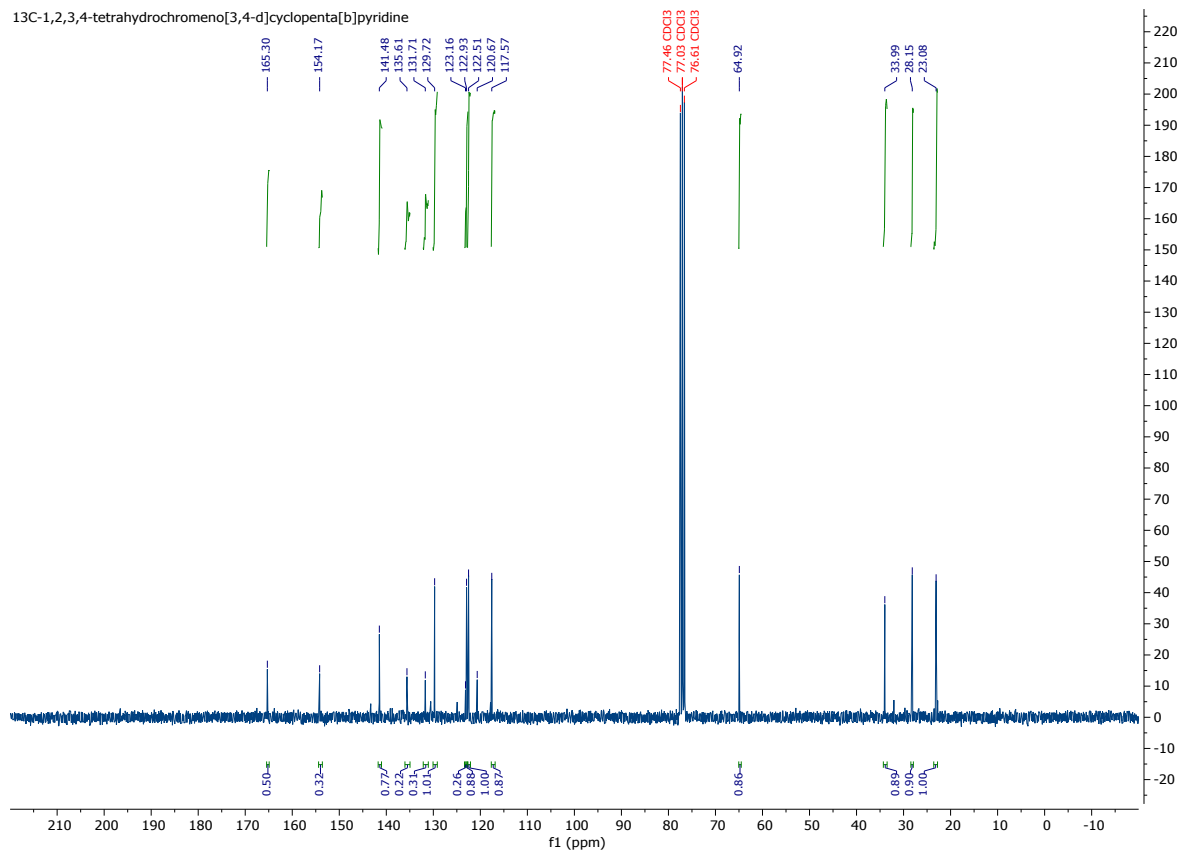
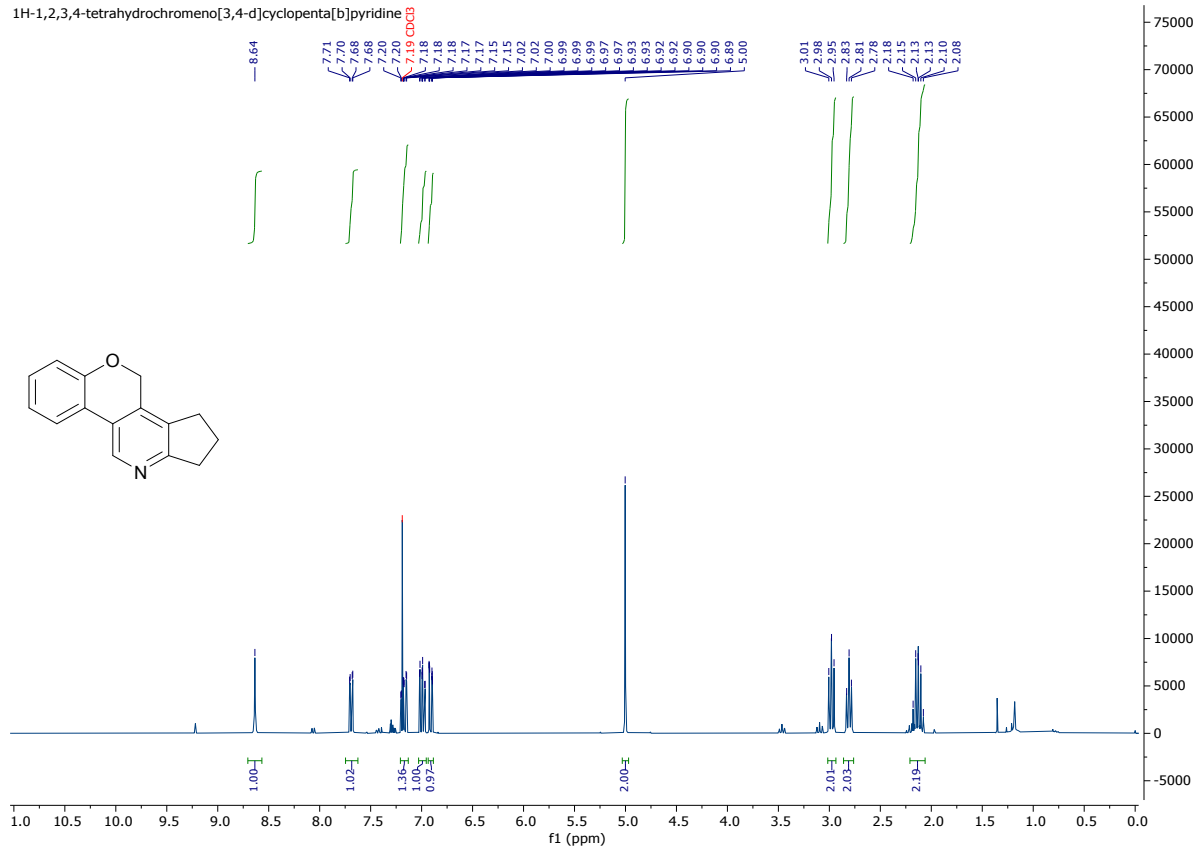


¹³C-diethyl 3-cyclopropyl-1-(2-methoxynaphthalen-1-yl)-5,7-dihydro-6H-cyclopenta[c]pyridine-6,6-dicarboxylate



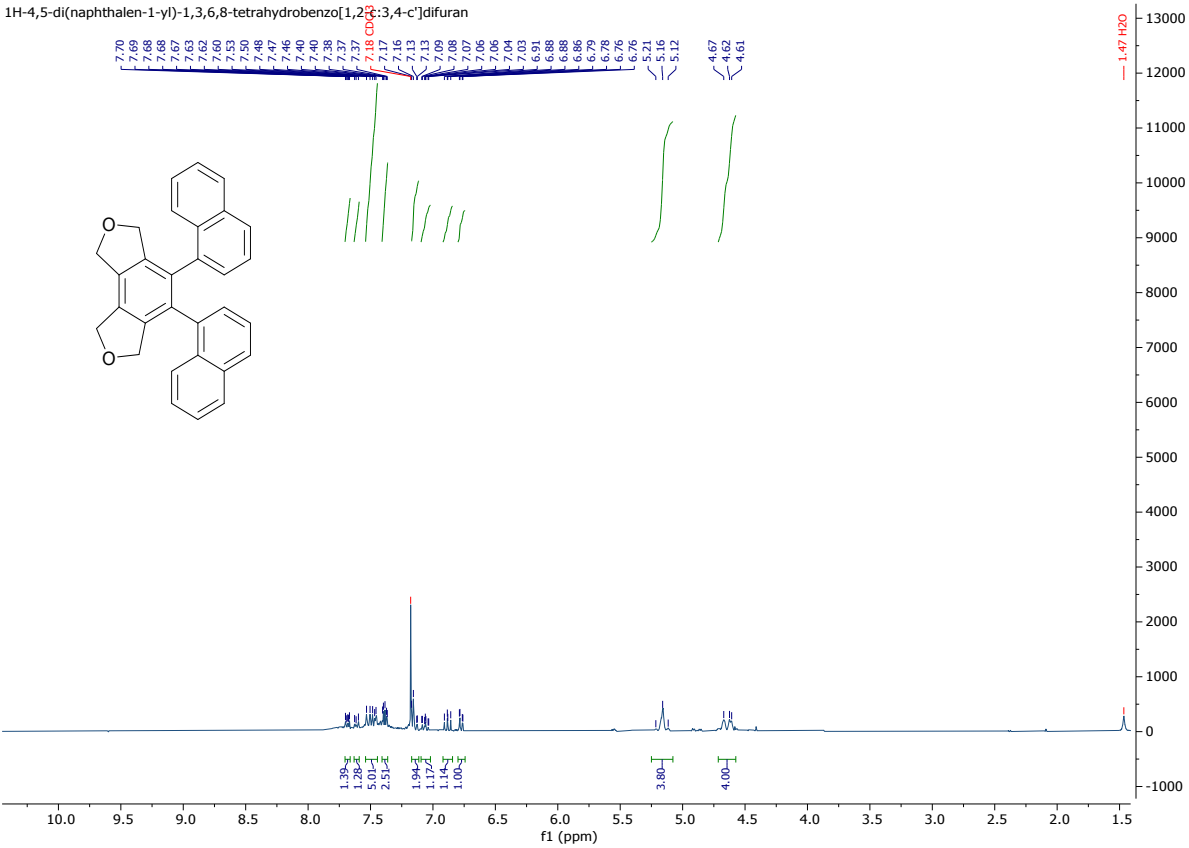
Compound 14:

¹H-1,2,3,4-tetrahydrochromeno[3,4-d]cyclopenta[b]pyridine



Compound 16:

1H-4,5-di(naphthalen-1-yl)-1,3,6,8-tetrahydrobenzo[1,2-f:3,4-c']difuran



11. Theoretical calculations on ligand exchange reactions

Ligand exchange 1:

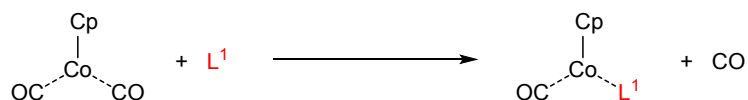
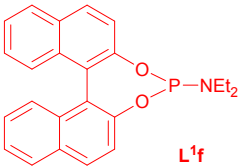
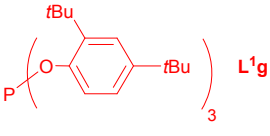
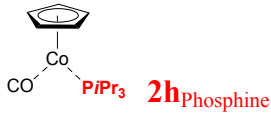
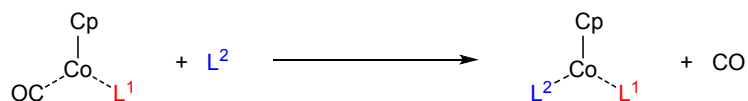


Table SI-3

| Entry | Ligand - Product | ΔG_{L^1} [kcal/mole] |
|-------|--|---------------------------------|
| 1 | $\text{P}(\text{O}i\text{Pr})_3$ (L^{1a}) - 2a | +10.37 |
| 2 | $\text{P}[\text{OCH}(\text{CF}_3)_2]_3$ (L^{1b}) - 2b | +9.64 |
| 3 | $\text{P}(\text{O}t\text{Bu})_3$ (L^{1c}) - 2c | +16.62 |
| 4 | $\text{P}(\text{OCy})_3$ (L^{1d}) - 2d | +9.12 |
| 5 | $\text{P}(\text{OCH}_2t\text{Bu})_3$ (L^{1e}) - 2e | +11.55 |
| 6 |  L^{1f} - 2f | +11.27 |
| 7 |  L^{1g} - 2g | +19.00 |
| 8 | $\text{P}i\text{Pr}_3$ -  2h_{Phosphine} | +15.77 |

Ligand exchange 2:



P ligands **L²**:

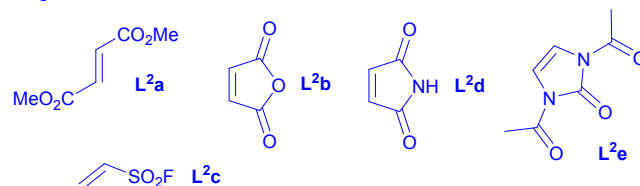
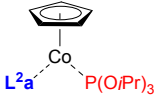
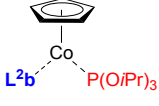
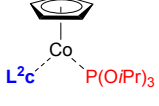
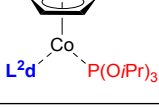
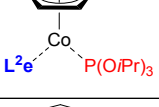
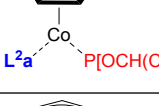
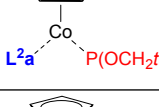
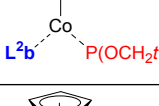
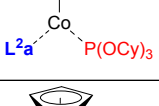
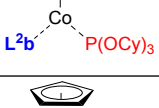
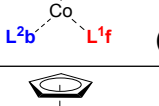
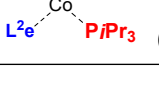
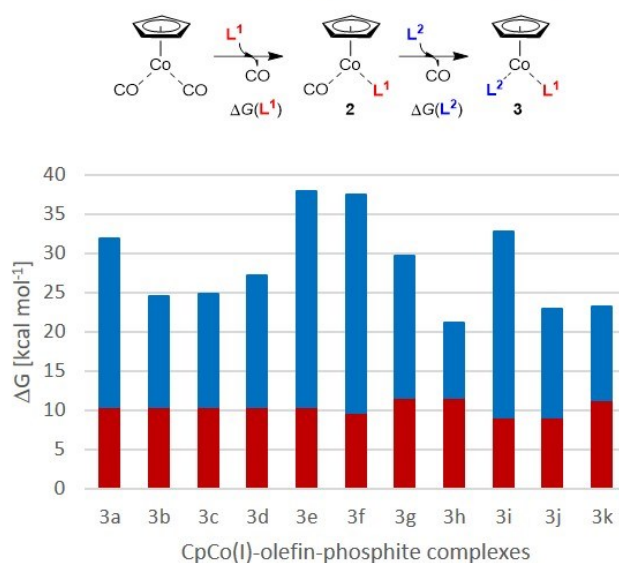


Table SI-4

| Entry | Complex 2 + Olefin L ² – | Complex 3 | ΔG_{L^2} [kcal/mole] | $\Delta G_{L^1+L^2}$ [kcal/mole] |
|-------|---|--|---------------------------------|-------------------------------------|
| 1 | 2a + L ^{2a} |  (3a) | +21.48 | 31.85 |
| 2 | 2a + L ^{2b} |  (3b) | +14.11 | 24.48 |
| 3 | 2a + L ^{2c} |  (3c) | +14.41 | 24.78 |
| 4 | 2a + L ^{2d} |  (3d) | +16.77 | 27.14 |
| 5 | 2a + L ^{2e} |  (3e) | +27.51 | 37.88 |
| 6 | 2b + L ^{2a} |  (3f) | +27.84 | 37.48 |
| 7 | 2e + L ^{2a} |  (3g) | +18.08 | 29.63 |
| 8 | 2e + L ^{2b} |  (3h) | +9.55 | 21.1 |
| 9 | 2d + L ^{2a} |  (3i) | +23.71 | 32.83 |
| 10 | 2d + L ^{2b} |  (3j) | +13.75 | 22.87 |
| 11 | 2f + L ^{2b} |  (3k) | +11.87 | 23.14 |
| 12 | 2h_{Phosphine} + L ^{2e} |  (3l _{Phosphine}) | +29.56 | 45.33 |

Energetics of ligand exchange

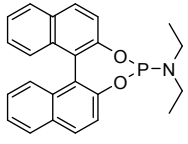
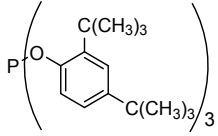
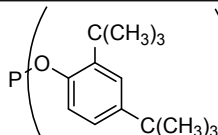
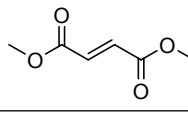
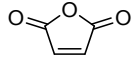




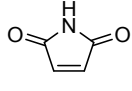
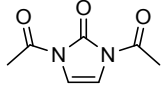
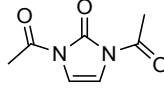
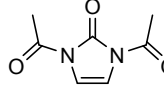
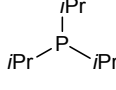
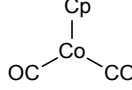
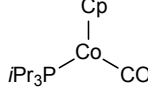
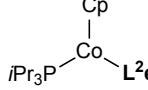
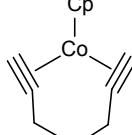
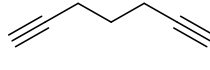
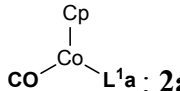
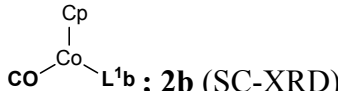
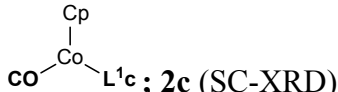
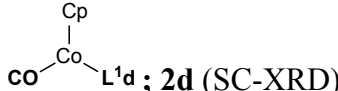
Computational details

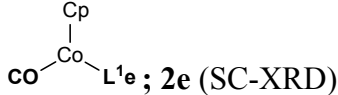
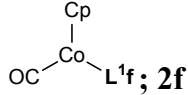
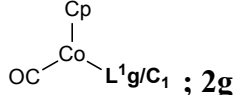
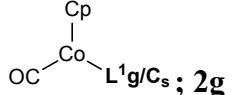
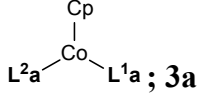
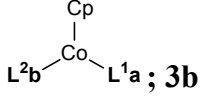
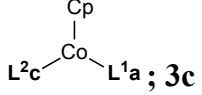
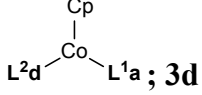
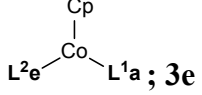
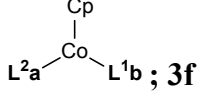
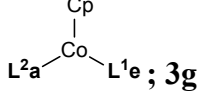
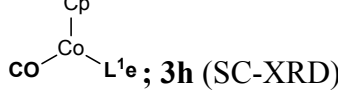
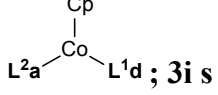
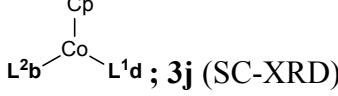
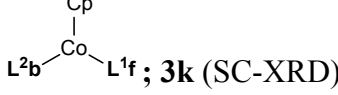
Our computations have been carried out at the BP86¹³ level of density functional theory as implemented in Gaussian 09 program,¹⁴ and all computational details are given here in the Supporting Information. For geometry optimisations we have used the SVP¹⁵ sets for all non-metal elements and the LANL2DZ¹⁶ basis set for Co (BP86/SVP). All optimised structures have been characterised either as energy minima without imaginary frequencies or transition states with only one imaginary frequency by frequency calculations at the same level. The computed Gibbs free energies (ΔG) at 298 K deduced the frequency calculations were used for discussion and comparison. In addition to the conformations of the ligands or complexes, we used either the obtained the molecular structures of SC-XRD analysis or from the more (most) conformational isomers.

Table SI-5 BP86 computed total electronic energy (HF, au), zero-point energy (ZPE, au), number of imaginary frequency (NImag), sum of electronic and thermal enthalpies (H_{tot} , au) as well as electronic and thermal free energies (G_{tot} , au)

| | BP86/SVP | BP86/SVP |
|---|---|--|
| CO | HF=-113.2238129 ZPE=3.07383 NImag=0 | Htot=-113.215609 Gtot= -113.238060 |
| P(O-CH(CH ₃) ₂) ₃ /SC-XRD (L¹a) | HF=-922.1739244 ZPE=180.24498 NImag=0 | Htot=-921.867529 Gtot= -921.934701 |
| P(O-CH(CH ₃) ₂) ₃ /anti-LP (L¹a) | HF=-922.1625169 ZPE= 180.18238 | Htot= -921.857109 Gtot= -921.921791 |

| | | |
|--|---|--|
| | NImag=0 | |
| P(O-CH(CF ₃) ₂) ₃ /C ₁ SC-XRD (L^{1b}) | HF=-2707.171452 ZPE=96.37590 NImag=0 | Htot=-2706.986467 Gtot= -2707.087009 |
| P(O-CH(CF ₃) ₂) ₃ /syn-LP (L^{1b}) | HF=-2707.1659436 ZPE=96.22161 NImag=0 | Htot=-2706.980936 Gtot= -2707.083842 |
| P(O-CH(CF ₃) ₂) ₃ (L^{1b}) | HF=-2707.1681352 ZPE=96.28292 NImag=0 | Htot=-2706.983250 Gtot= -2707.084128 |
| P(O-C(CH ₃) ₃) ₃ /C ₁ (L^{1c}) | HF=-1040.0222753 ZPE=230.14683 NImag=0 | Htot=-1039.632313 Gtot= -1039.705692 |
| P(O-C(CH ₃) ₃) ₃ /C ₃ (L^{1c}) | HF=-1040.0213029 ZPE=230.17879 NImag=0 | Htot=-1039.631277 Gtot= -1039.705669 |
| P(O-CH ₂ C(CH ₃) ₃) ₃ /SC-XRD (L^{1d}) | HF=-1157.8602857 ZPE=282.59231 NImag=0 | Htot=-1157.382618 Gtot= -1157.468075 |
| P(O-CH ₂ C(CH ₃) ₃) ₃ /C ₃ (L^{1d}) | HF=-1157.8557508 ZPE=282.14043 NImag=0 | Htot=-1157.378661 Gtot= -1157.463995 |
| P(O-Cy) ₃ /SC-XRD (L^{1e}) | HF=-1272.1293127 ZPE=301.66336 NImag=0 | Htot=-1271.624517 Gtot=-1271.703641 |
| P(O-Cy) ₃ /C ₃ (L^{1e}) | HF=-1272.1256637 ZPE= 301.45529 NImag=0 | Htot= -1271.621034 Gtot= -1271.700231 |
|  (L^{1f}) | HF=-1473.5242575 ZPE= 245.57898 NImag=0 | Htot= -1473.107496 Gtot= -1473.187449 |
|  (L^{1g})/C ₃ symm. | HF=-2204.0451427 ZPE= 582.12880 NImag=0 | Htot= -2203.062827 Gtot= -2203.206287 |
|  (L^{1g})/C _s symm. | HF=-2204.0426554 ZPE=582.24622 NImag=0 | Htot=-2203.060078 Gtot= -2203.205160 |
|  L^{2a} | HF=-533.9592511 ZPE=83.94814 NImag=0 | Htot=-533.813209 Gtot= -533.863236 |
|  L^{2b} | HF=-379.0249466 ZPE=33.85704 NImag=0 | Htot=-378.964738 Gtot=-378.999503 |
|  syn-C ₁ / L^{2c} | HF=-726.077284 ZPE=33.19433 NImag=0 | Htot=-726.017129 Gtot= -726.054732 |

| | | |
|--|--|---|
|  anti-C _s /L ^{2c} | HF=-726.0715924 ZPE=32.81196 NImag=0 | Htot=-726.012669 Gtot= -726.048860 |
|  L ^{2d} | HF=-359.1817309 ZPE= 41.62829 NImag=0 | Htot= -359.108951 Gtot= -359.144017 |
|  syn-syn/L ^{2e} | HF=-606.3262574 ZPE=90.92987 NImag=0 | Htot=-606.168565 Gtot= -606.219406 |
|  anti-syn/L ^{2e} | HF=-606.3385276 ZPE=91.17813 NImag=0 | Htot=-606.180550 Gtot= -606.231496 |
|  anti-anti/L ^{2e} | HF=-606.3491833 ZPE=91.39787 NImag= | Htot=-606.190951 Gtot= -606.240777 |
|  iPr ₃ P | HF=-696.6063847 ZPE=171.77822 NImag=0 | Htot= -696.316720 Gtot= -696.371966 |
|  Cp OC-Co-CO | HF=-565.1292958 ZPE=61.37654 NImag=0 | Htot=-565.021787 Gtot= -565.065742 |
| CO | HF=-113.2238129 ZPE=3.07383 NImag=0 | Htot=-113.215609 Gtot= -113.238060 |
|  Cp iPr ₃ P-Co-CO | HF=-1148.489748 ZPE=229.72411 NImag=0 | Htot=-1148.099272 Gtot= -1148.174523 |
|  Cp iPr ₃ P-Co-L ^{2e} | HF=-1641.5741973 ZPE=317.60347 NImag=0 | Htot=-1641.033655 Gtot= -1641.130127 |
|  Cp Co-CO-CO-CO | HF=-609.8309074 ZPE=0.202066 NImag=0 | Htot=-609.614844 Gtot=-609.667217 |
|  | HF=-271.210036 ZPE=0.118802 NImag=0 | Htot=-271.082004 Gtot=-271.123226 |
|  Cp CO-Co-L ^{1a} ; 2a | HF=-1374.0664054 ZPP=237.82768 NImag=0 | Htot=-1373.659736 Gtot= -1373.745864 |
|  Cp CO-Co-L ^{1b} ; 2b (SC-XRD) | HF=-3159.0630793 ZPE=153.62330 NImag=0 | Htot=-3158.778104 Gtot= -3158.899319 |
|  Cp CO-Co-L ^{1c} ; 2c (SC-XRD) | HF=-1491.9057005 ZPE=287.70045 NImag=0 | Htot=-1491.415564 Gtot= -1491.506894 |
|  Cp CO-Co-L ^{1d} ; 2d (SC-XRD) | HF=-1724.0205485 ZPE=359.00149 NImag=0 | Htot=-1723.415613 Gtot= -1723.516792 |

| | | |
|--|---|--|
|  2e (SC-XRD) | HF=-1609.7495887 ZPE=339.98724 NImag=0 | Htot=-1609.171756 Gtot= -1609.277356 |
|  2f | HF=-1925.4143568 ZPE=303.10992 NImag=0 | Htot=-1924.897316 Gtot= -1924.997174 |
|  2g | HF=-2655.9258474 ZPE= 640.00164 NImag=0 | Htot= -2654.842917 Gtot= -2655.003685 |
|  2g | HF=-2655.9230384 ZPE= 639.29713 NImag=2 (-34. -18 cm) | Htot= -2654.842525 Gtot= -2655.000317 |
|  3a | HF=-1794.7742204 ZPE=317.83208 NImag=0 | Htot=-1794.230382 Gtot= -1794.336804 |
|  3b | HF=-1639.8499561 ZPE=267.90579 NImag=0 | Htot=-1639.391629 Gtot=-1639.484808 |
|  3c | HF=-1986.9034184 ZPE=267.48512 NImag=0 | Htot=-1986.445101 Gtot= -1986.539577 |
|  3d | HF=-1620.0023249 ZPE=275.60608 NImag=0 | Htot=-1619.531528 Gtot= -1619.625104 |
|  3e | HF=-1867.1534778 ZPE=325.13444 NImag=0 | Htot=-1866.597424 Gtot= -1866.704735 |
|  3f | HF=-3579.7660473 ZPE=234.28022 NImag=0 | Htot=-3579.343376 Gtot= -3579.480134 |
|  3g | HF=-2030.4634059 ZPE= 420.25454 NImag=0 | Htot= -2029.747989 Gtot= -2029.873710 |
|  3h (SC-XRD) | HF=-1875.5395878 ZPE=370.22249 NImag=0 | Htot=-1874.909845 Gtot= -1875.023580 |
|  3i s | HF=-2144.7265414 ZPE= 439.58475 NImag=0 | Htot= -2143.983679 Gtot= -2144.101944 |
|  3j (SC-XRD) | HF=-1989.8073134 ZPE=389.25168 NImag=0 | Htot=-1989.150586 Gtot= -1989.256329 |
|  3k (SC-XRD) | HF=-2191.201736 ZPE= 333.34807 NImag=0 | Htot= -2190.632841 Gtot= -2190.739701 |

References

- [1] Details on the photochemical setup: F. Fischer, A. F. Siegle, M. Checinski, C. Fischer, K. Kral, R. Thede, O. Trapp and M. Hapke, *J. Org. Chem.* 2016, **81**, 3087 and Supporting Information.
- [2] SHELXS-97: G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.
- [3] SHELXL-2014: G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3.
- [4] S. Han and S. Z. Zard, *Org. Lett.*, 2014, **16**, 5386.
- [5] H. C. Manning, M. Bai, B. M. Anderson, R. Lisiak, L. E. Samuelson and D. J. Bornhop, *Tetrahedron Lett.* 2005, **46**, 4707.
- [6] I. Kownacki, B. Marciniak, H. Steinberger, M. Kubicki, M. Hoffmann, A. Ziarko, K. Szubert, M. Majchrzak and S. Rubinsztajn, *Appl. Catal., A* 2009, **362**.
- [7] X. Jia, X. Li, L. Xu, Q. Shi, X. Yao and A. S. C. Chan, *J. Org. Chem.* 2003, **68**, 4539.
- [8] R. Hodgkinson, A. Del Grosso, G. Clarkson and M. Wills, *Dalton Trans.* 2016, **45**, 3992.
- [9] L. Hofmann and H. Werner, *J. Organomet. Chem.* 1985, **289**, 141-155.
- [10] M. Hapke, K. Kral, C. Fischer, A. Spannenberg, A. Gutnov, D. Redkin and B. Heller, *J. Org. Chem.* 2010, **75**, 3993.
- [11] F. Fischer and M. Hapke, *Eur. J. Org. Chem.* 2018, 3193.
- [12] P. Jungk, F. Fischer, I. Thiel and M. Hapke, *J. Org. Chem.* 2015, **80**, 9781.
- [13] J. P. Perdew *Phys. Rev. B*, 1986, **33**, 8822.
- [14] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision C.01; Gaussian, Inc. Wallingford, CT, 2010.
- [15] A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.* 1992, **97**, 2571.
- [16] P. J. Hay and W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 299.