

## Supplementary Information for

# Fluorophosphoniums as Lewis acids in organometallic catalysis: application to the carbonylation of $\beta$ -lactones

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# 1 General information

## 1.1 Safety warning

Carbon monoxide was carefully handled under well-ventilated fumehoods equipped with carbon monoxide detectors.

## 1.2 General remarks

Unless otherwise stated, all reactions were performed in a recirculating *MBraun LabMaster DP* inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 120 °C or flame-dried before use.

Solvents and mesitylene were purified following literature techniques.

All other reagents were purchased from commercial suppliers (Sigma Aldrich, Carlo Erba, Thermo Fischer Scientific, Strem and Alfa Aesar), and used as received.

CO (4.7 grade) were purchased from Air Products.

## 1.3 General analytical information

NMR spectra were recorded on a *Bruker AVANCE Neo 400 MHz* spectrometer at 298 K. Chemical shifts ( $\delta$ ) value are internally referenced to solvent residual peaks for  $^1\text{H}$  and  $^{13}\text{C}$ , and externally referenced for  $^{31}\text{P}$  and  $^{19}\text{F}$ , and reported in parts per million (ppm) relative to tetramethylsilane ( $^1\text{H}$ ,  $^{13}\text{C}$ ), or phosphoric acid ( $^{31}\text{P}$ ). Coupling constants ( $J$ ) are given in Hz, multiplicities are named as singlet (s), doublet (d), triplet (t), quartet (q), multiplet or overlapping signals (m) and broad signal (br), solvent is given in parenthesis.

GC-MS spectra were recorded on a *Shimadzu GC-QP2010 Ultra gas* apparatus equipped with a *Supelco SLB<sup>TM</sup>-ms* fused silica capillary column (30 m x 0.25 mm x 0.25  $\mu\text{m}$ ). GC conditions for the analysis of all the samples: injector temperature: 250 °C; carrier gas: helium; pressure: 120.0 kPa; linear velocity: 52.9  $\text{cm}\cdot\text{s}^{-1}$ ; oven temperature: 40 °C to 100 °C at 25 °C $\cdot\text{min}^{-1}$ , then to 180 °C at 25 °C $\cdot\text{min}^{-1}$  then to 280 °C at 30 °C $\cdot\text{min}^{-1}$  (hold 5 min). Detector: MS (EI); ion source temperature: 200 °C; interface temperature: 250 °C; detector voltage: 1.5 kV.

Calibration curves were performed for all the reagents and products in GC-MS (See the corresponding section).

GC spectra were recorded on a *Shimadzu GC-2010 Plus* apparatus, equipped with a *Supelco* column CARBOXEN 1010 PLOT (30 m x 0.53 mm, T = 100 °C) and using argon as a gas carrier.

IR spectra were recorded on a Shimadzu MIRacle 10 (ATR). Absorption bands are given in wavenumber  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ).

Elemental analysis was performed by Mikoanalytisches Labor Pascher (Remagen, Germany).

For the XRD structures, data collections were performed at 100(2) K on a Bruker D8 Quest diffractometer using an Incoatec Microfocus Source ( $I\mu\text{S}$  3.0 Mo) and a PHOTON III area detector, and operated with APEX3.<sup>1</sup> The data were processed with SAINT,<sup>2</sup> and empirical absorption corrections were made with SADABS.<sup>3</sup> The structures were solved by intrinsic phasing with SHELXT,<sup>4</sup> and refined by full-matrix least-squares on  $F^2$  with SHELXL,<sup>5</sup> using

the ShelXle interface.<sup>6</sup> The hydrogen atoms were introduced at calculated positions and treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH<sub>3</sub>). Crystal data and structure refinement parameters are given in Table S4. Drawings were made with ORTEP-3.<sup>7</sup>

#### 1.4 Experimental setup

**Small-volume autoclaves** – Small-volume autoclaves allow to perform reaction on a scale of 1 to 4 mL. The vessels are made of stainless steel (SS316). The assembly is made of two parts: a part of connections, made of commercial components purchased from Swagelok France, and a part, which is the reactor itself, made in our laboratory (Figure S1).



Figure S1 – Small-scale autoclave, disassembled (left), and inside the heating block (right).

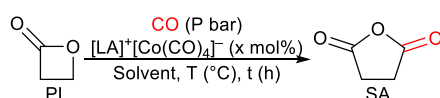
**Gas mixing and delivery system** – the gas used for the reactions was handled through a gas delivery system purchased at Parr instrument, which allows to prepare, compress, and store gas or gas mixtures.

## 2 Additional experiments

### 2.1 Catalytic experiments

Further catalytic experiments were run, and the results are reported in Table S1. The concentration of the  $\beta$ -propiolactone (PL, from 0.5 to 2 mol·L<sup>-1</sup>) did not have a significant influence on the yield (64–84 %, entries 1–3). Running the catalysis at 60 °C instead of 80 °C reduced the activity of the system: 31 % of SA were obtained instead of 91 % (Table 2, entry 5). On the other hand, increasing the temperature to 120 °C was detrimental to the selectivity (63 % after 6 h, entry 5). Finally, the application of a catalyst loading of 0.3 mol% led to only traces of product (entry 6). In ethyl acetate, the catalytic activity was maintained with good selectivity in favour of succinic anhydride (90 %, entries 7 and 8).

Table S1 – Additional catalytic experiments.<sup>a</sup>



Entry	[PL] (M)	Solvent	[LA] <sup>+</sup> [Co(CO) <sub>4</sub> ] <sup>-</sup>	x (mol%)	P (bar)	T (°C)	t (h)	Conversion PL (%)	Yield SA (%)	Selectivity SA (%)
1	0.5	Toluene	<b>IV</b>	6	15	80	18	77	68	88
2	0.5	Toluene	<b>IV</b>	6	60	80	18	75	61	81
3	1	Toluene	<b>IV</b>	3	60	80	18	84	80	95
4	2	Toluene	<b>IV</b>	3	10	60	16	20	31	>99
5	2	Toluene	<b>IV</b>	3	10	120	6	73	46	63
6	2	Toluene	<b>IV</b>	0.3	10	80	16	7	2	>99
7	0.5	EtOAc	<b>IV</b>	6	15	80	18	64	57	89
8	0.5	EtOAc	<b>IV</b>	6	60	80	18	70	76	>90

<sup>a</sup> Conditions: PL, mesitylene (internal standard, 10 mol%), and [LA]<sup>+</sup>[Co(CO)<sub>4</sub>]<sup>-</sup> (x mol%) in the solvent (1 mL), heated under CO pressure. SA yields and PL conversions measured by GC-MS analysis.

### 2.2 Mechanistic investigation of the carbonylation of $\beta$ -butyrolactone (BL)

Complex **IV** (19.6 mg, 0.05 mmol, 1 eq) and BL (4  $\mu$ L, 0.05 mmol, 1 eq) were dissolved in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL), in a Young NMR tube, under argon atmosphere. <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>19</sup>F{<sup>1</sup>H} NMR spectra of the solution were recorded (Figure S2, Figure S6, and Figure S7). The tube was set under CO atmosphere, and the mixture was analyzed by NMR (Figure S3, Figure S6, and Figure S7). The tube was then heated for 1 h at 90 °C, and the mixture was analyzed by NMR (Figure S4, Figure S6, and Figure S7). No other intermediates than complex **IV** could be identified. The shift in the NMR displacement of **IV** in the <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>19</sup>F{<sup>1</sup>H} NMR spectra suggests the formation of paramagnetic species which were not identified (Figure S5, Figure S6, and Figure S7).

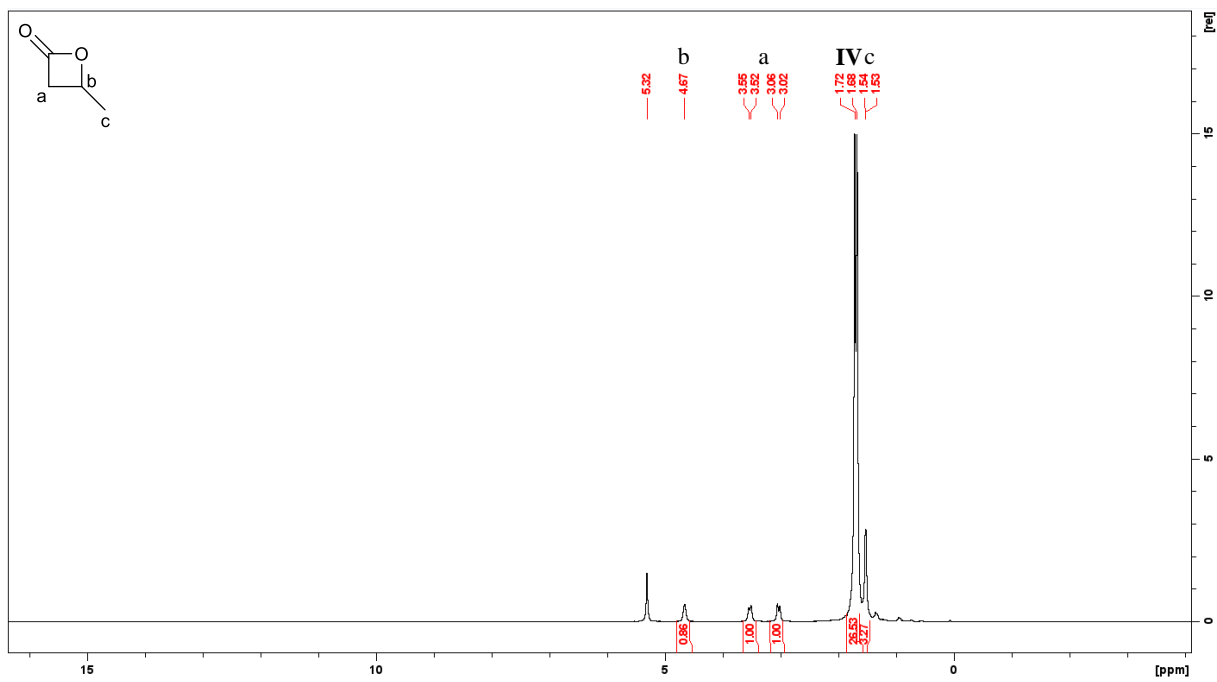


Figure S2 –  $^1\text{H}$  NMR spectrum of the stoichiometric mixture of **IV** and **BL** ( $\text{CD}_2\text{Cl}_2$ ).

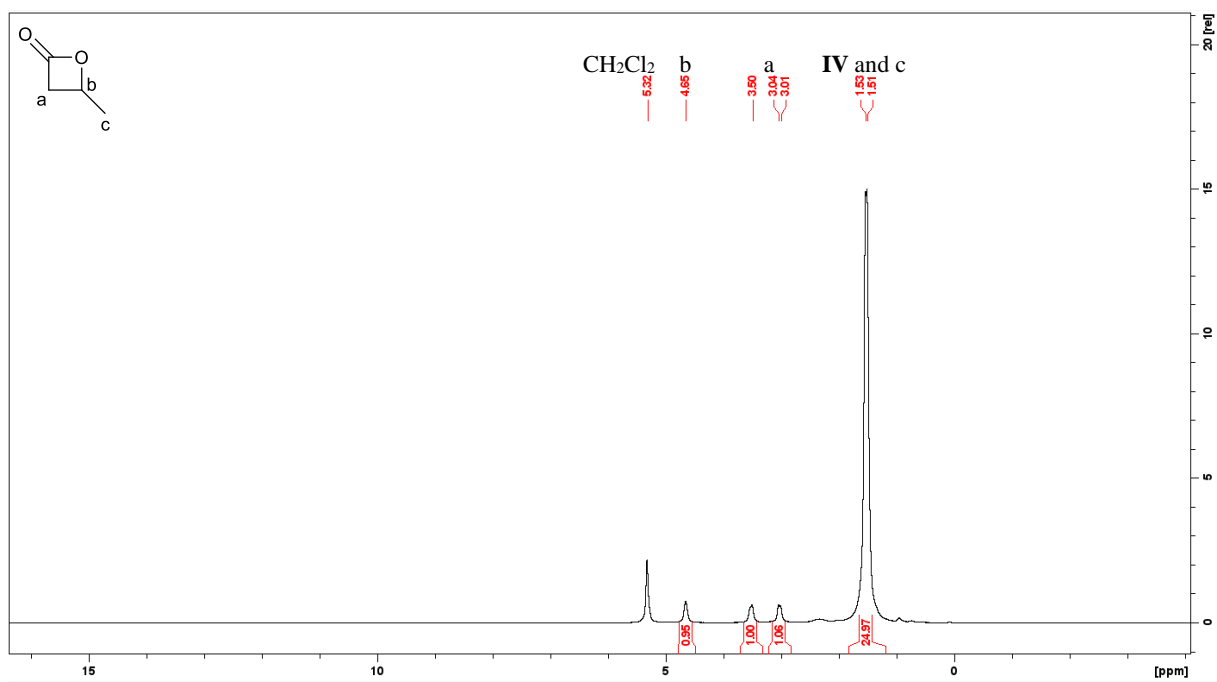


Figure S3 –  $^1\text{H}$  NMR spectrum of the stoichiometric mixture of **IV** and **BL** under  $\text{CO}$  atmosphere ( $\text{CD}_2\text{Cl}_2$ ).

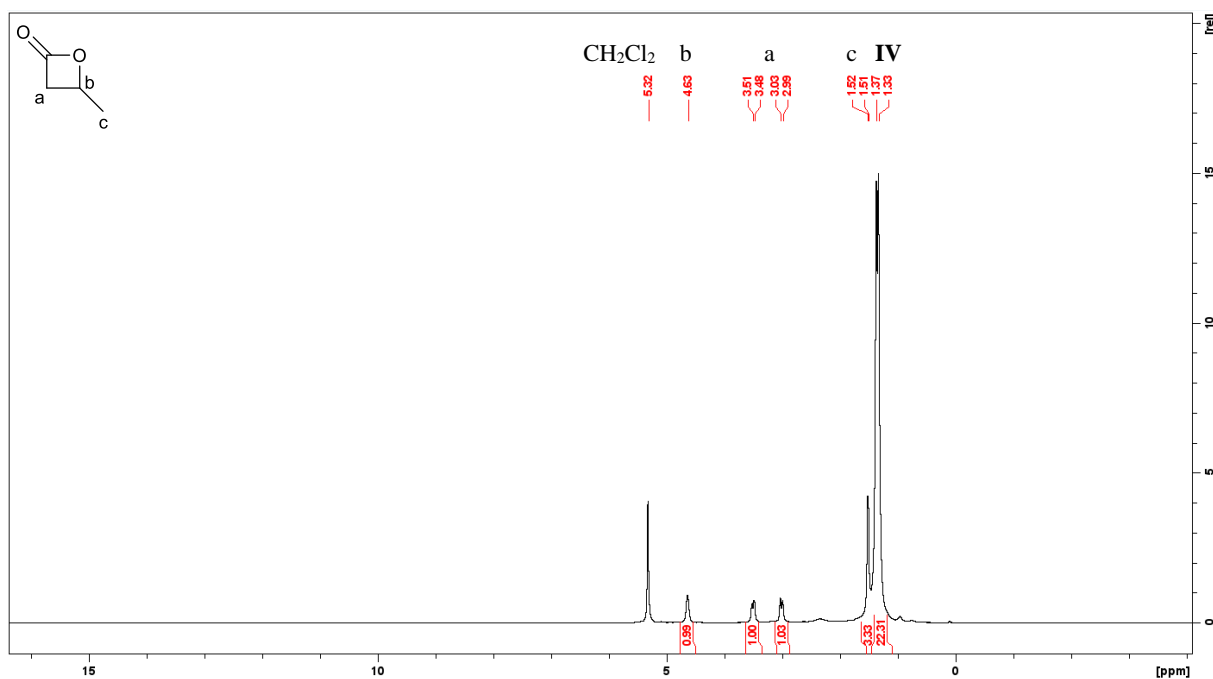


Figure S4 – <sup>1</sup>H NMR spectrum of the stoichiometric mixture of **IV** and **BL** under **CO** atmosphere, after 1 h of heating at 90 °C (CD<sub>2</sub>Cl<sub>2</sub>).

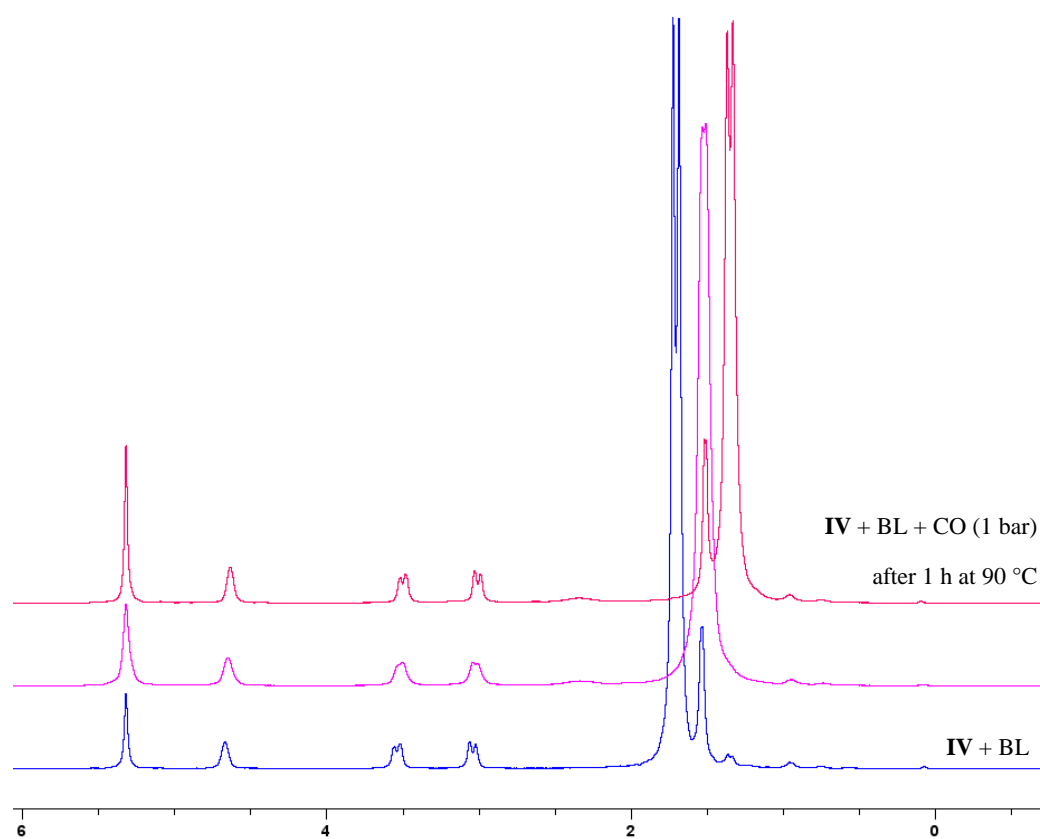


Figure S5 – Stacking of the <sup>1</sup>H NMR spectra of the stoichiometric mixture of **IV** and **BL** under argon atmosphere, under **CO** atmosphere, after 1 h of heating at 90 °C (CD<sub>2</sub>Cl<sub>2</sub>). The signal of **IV** shifts from 1.70 ppm to 1.35 ppm.

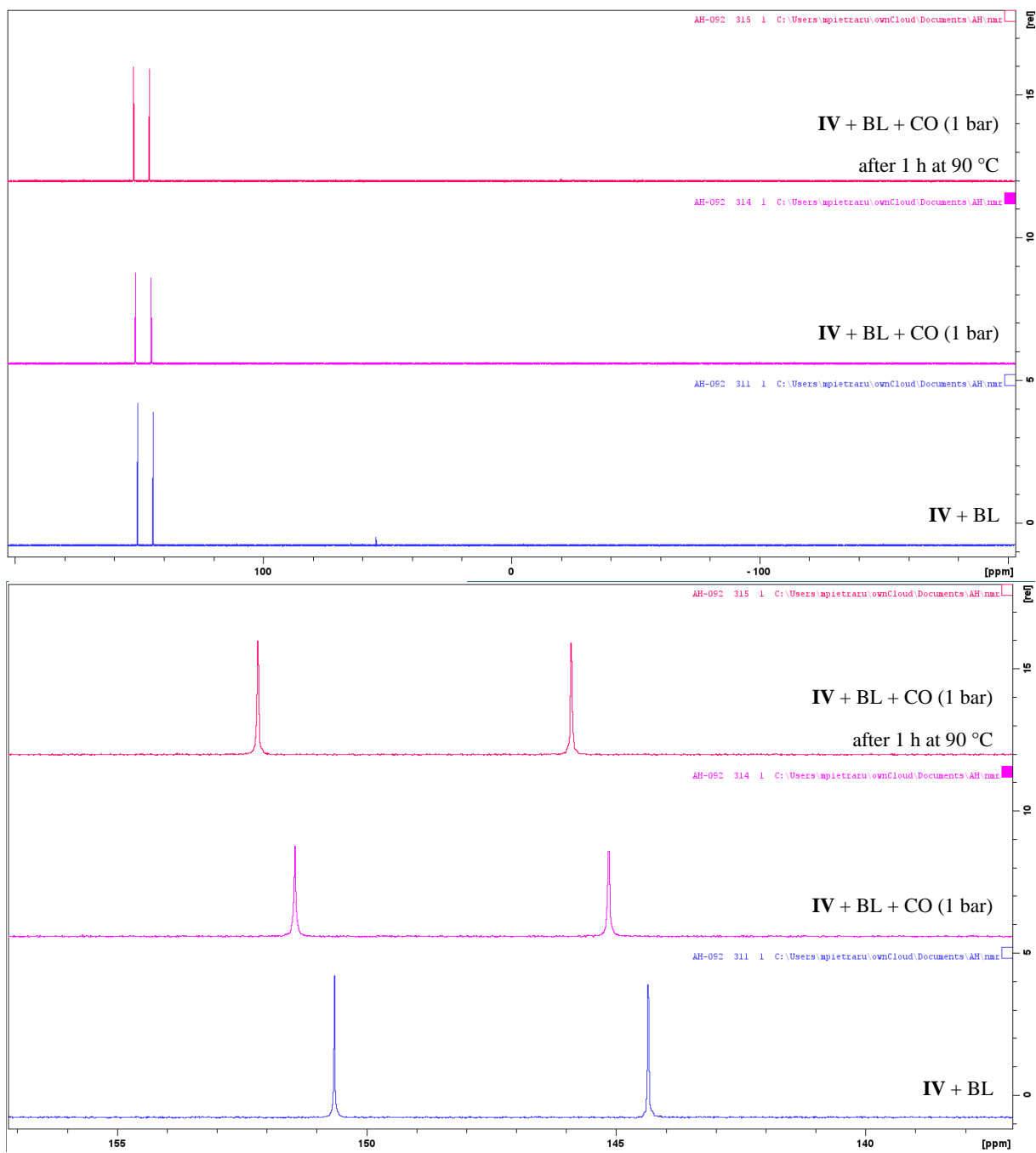


Figure S6 – Stacking of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the stoichiometric mixture of **IV** and **BL** under argon atmosphere, under CO atmosphere, after 1 h of heating at 90 °C ( $\text{CD}_2\text{Cl}_2$ ). Top: full view; bottom: focus on the 157–137 ppm area.

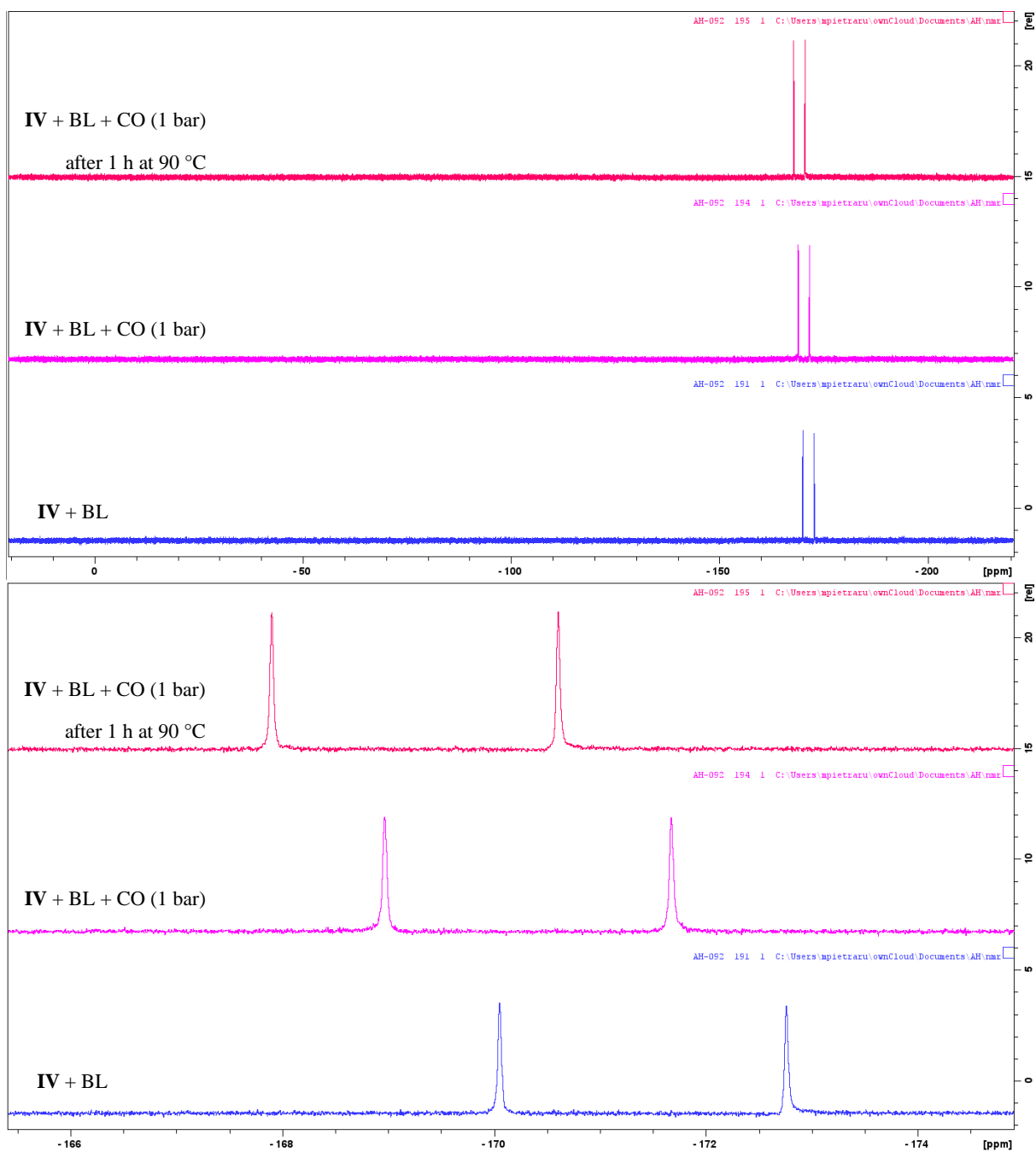
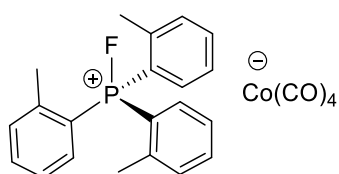


Figure S7 – Stacking of the  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra of the stoichiometric mixture of **IV** and **BL** under argon atmosphere, under **CO** atmosphere, after 1 h of heating at 90 °C ( $\text{CD}_2\text{Cl}_2$ ). Top: full view; bottom: focus on the (-164)–(-176) ppm area.



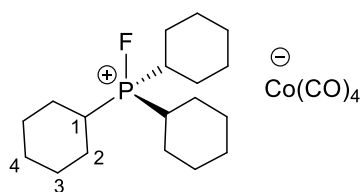
## 3 Experimental procedures

### 3.1 Syntheses of fluorophosphonium cobaltates I-IV



#### Synthesis of I

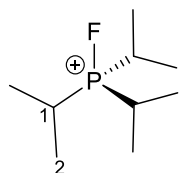
In a round-bottom flask,  $[\text{Co}_2(\text{CO})_8]$  (34.2 mg, 0.1 mmol, 0.5 eq) was dissolved in toluene (1 mL) and  $\text{Et}_3\text{SiH}$  (32  $\mu\text{L}$ , 0.2 mmol, 1.0 eq) was added. The mixture was stirred regularly for 1 h at room temperature. In a second round-bottom flask,  $\text{XeF}_2$  (33.9 mg, 0.2 mmol, 1.0 eq) was carefully added on a solution of tri(*o*-tolyl)phosphine (60.9 mg, 0.2 mmol, 1 eq) in toluene (2 mL). The mixture was stirred for 10 min at room temperature, until the evolution of xenon gas stopped. The solution containing the difluorophosphine was added to the solution containing the cobalt-silicon reagent. The mixture was stirred at room temperature overnight. When the stirring was stopped, after decantation, a colored precipitate (the product) and a red translucent supernatant were observed: the supernatant would contain some residues of starting materials, intermediates ( $[\text{Et}_3\text{SiCo}(\text{CO})_4]$ ,  $\text{F}_2\text{P}(\textit{o}\text{-Tol})_3$ ), and by-products ( $\text{Et}_3\text{SiF}$ ), and got its color from cobalt species. The supernatant was removed, and the precipitate was washed with pentane (3 x 2 mL), until the washings were clear. The powder was dried under vacuum to afford a yellow solid in 76 % yield (75.4 mg). Crystals suitable for XRD analysis were obtained by slow diffusion of pentane in a concentrated solution in DME.  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm) = 8.02 – 7.18 (m, 12 H;  $\text{C}_{\text{Ar}}\text{-H}$ ), 2.49 (quint,  $J = 20.4$  Hz, 9 H;  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm) = 145.36 (dd,  $J = 8.2, 1.4$  Hz;  $\text{C}_{\text{Ar}}$ ), 138.88 (br;  $\text{C}_{\text{Ar}}$ ), 135.80 (dd,  $J = 18.4, 2.06$  Hz;  $\text{C}_{\text{Ar}}$ ), 134.50 (d,  $J = 12.0$  Hz;  $\text{C}_{\text{Ar}}$ ), 128.44 (d,  $J = 15.7$  Hz;  $\text{C}_{\text{Ar}}$ ), 115.71 (dd,  $J = 105.3, 13.0$  Hz;  $\text{C}_{\text{Ar}}$ ), 21.76 (dd,  $J = 5.0, 2.9$  Hz;  $\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm) = 103.19 (d,  $J_{\text{PF}} = 992.8$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (375 MHz,  $\text{CD}_2\text{Cl}_2$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm) = -125.41 (d,  $J_{\text{PF}} = 993.7$  Hz). IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 1904 (m, sh;  $\text{C}\equiv\text{O}$ ), 1873 (s, sh;  $\text{C}=\text{O}$ ), 1857 (s;  $\text{C}=\text{O}$ ). **Elemental analysis** calcd (%) for  $\text{C}_{25}\text{H}_{21}\text{CoFO}_4\text{P}$ : C 60.74, H 4.28; found: C 59.79, H 4.28.



#### Synthesis of II

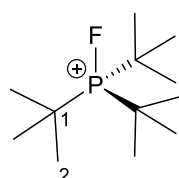
In a round-bottom flask,  $[\text{Co}_2(\text{CO})_8]$  (68.5 mg, 0.2 mmol, 0.5 eq) was dissolved in toluene (2 mL) and  $\text{Et}_3\text{SiH}$  (64  $\mu\text{L}$ , 0.4 mmol, 1.0 eq) was added. The mixture was stirred regularly for 1 h at room temperature. In a second round-bottom flask,  $\text{XeF}_2$  (67.7 mg, 0.4 mmol, 1.0 eq) was carefully added on a solution of tricyclohexylphosphine (112.2 mg, 0.4 mmol, 1 eq) in toluene (4 mL). The mixture was stirred for 10 min at room temperature, until the evolution of xenon gas stopped. The solution containing the difluorophosphine was added to the solution containing the cobalt-silicon reagent. The mixture was stirred at room temperature overnight. When the stirring was stopped, after decantation, a colored slurry (the product) and a red translucent supernatant were observed: the supernatant would contain some residues of starting materials, intermediates ( $[\text{Et}_3\text{SiCo}(\text{CO})_4]$ ,  $\text{F}_2\text{PCy}_3$ ), and by-products ( $\text{Et}_3\text{SiF}$ ), and got its color from cobalt species. The supernatant was removed. Addition of pentane allowed the precipitation of the slurry: the precipitate was washed with pentane (3 x 2 mL), until the washings were clear. The powder was dried under vacuum to afford a blue-grey solid in 89 % yield (167.6 mg). Crystals suitable for DRX analysis were obtained by slow diffusion of pentane in a concentrated solution in DME.  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm) = 2.73 – 1.39 (m, 33 H;  $\text{C}_{\text{Cy}}\text{-H}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 25  $^\circ\text{C}$ )  $\delta$  (ppm) = 33.34 (dd,  $J = 42.2, 7.4$  Hz, 3 C;  $\text{C}(1)$ ), 25.94 (d,  $J = 13.2$  Hz, 6 C;  $\text{C}(2)$ ), 25.2

(s, 9 C; C(3), C(4)).  $^{31}\text{P}\{\text{1H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  (ppm) = 133.03 (d,  $J_{\text{PF}} = 992.8$  Hz).  $^{19}\text{F}\{\text{1H}\}$  NMR (375 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  (ppm) = -171.09 (d,  $J_{\text{PF}} = 992.4$  Hz). IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 1867 (s; C $\equiv$ O). Elemental analysis calcd (%) for  $\text{C}_{22}\text{H}_{33}\text{CoFO}_4\text{P}$ : C 56.17, H 7.07; found: C 55.76, H 7.16.



### Synthesis of III

In a round-bottom flask,  $[\text{Co}_2(\text{CO})_8]$  (68.5 mg, 0.2 mmol, 0.5 eq) was dissolved in toluene (2 mL) and  $\text{Et}_3\text{SiH}$  (64  $\mu\text{L}$ , 0.4 mmol, 1.0 eq) was added. The mixture was stirred regularly for 1 h at room temperature. In a second round-bottom flask,  $\text{XeF}_2$  (67.7 mg, 0.4 mmol, 1.0 eq) was carefully added on a solution of tri(isopropyl)phosphine (64.1 mg, 0.4 mmol, 1 eq) in toluene (4 mL). The mixture was stirred for 10 min at room temperature, until the evolution of xenon gas stopped. The solution containing the difluorophosphine was added to the solution containing the cobalt-silicon reagent. The mixture was stirred at room temperature overnight. When the stirring was stopped, after decantation, a colored slurry (the product) and a red translucent supernatant were observed: the supernatant would contain some residues of starting materials, intermediates ( $[\text{Et}_3\text{SiCo}(\text{CO})_4]$ ,  $\text{F}_2\text{P}^i\text{Pr}_3$ ), and by-products ( $\text{Et}_3\text{SiF}$ ), and got its color from cobalt species. The supernatant was removed. Addition of pentane allowed the precipitation of the slurry: the precipitate was washed with pentane (3 x 2 mL), until the washings were clear. The powder was dried under vacuum to afford a green solid in 82 % yield (115.0 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  (ppm) = 3.06 (m, 3 H; H-C(1)), 1.56 (dd,  $J = 17.8, 7.0$  Hz, 18 H; H-C(2)).  $^{13}\text{C}\{\text{1H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  (ppm) = 24.25 (dd,  $J = 43.3, 7.8$  Hz, 3 C; C(1)), 15.41 (t,  $J = 2.3$  Hz, 6 C; C(2)).  $^{31}\text{P}\{\text{1H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  (ppm) = 146.43 (d,  $J_{\text{PF}} = 997.4$  Hz).  $^{19}\text{F}\{\text{1H}\}$  NMR (375 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  (ppm) = -169.43 (d,  $J_{\text{PF}} = 996.5$  Hz). IR (ATR):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ) = 1867 (s; C $\equiv$ O). Elemental analysis calcd (%) for  $\text{C}_{13}\text{H}_{21}\text{CoFO}_4\text{P}$ : C 44.59, H 6.04; found: C 43.73, H 5.82.



### Synthesis of IV

In a round-bottom flask,  $[\text{Co}_2(\text{CO})_8]$  (171.0 mg, 0.5 mmol, 0.5 eq) was dissolved in toluene (2 mL) and  $\text{Et}_3\text{SiH}$  (160  $\mu\text{L}$ , 1 mmol, 1.0 eq) was added. The mixture was stirred regularly for 1 h at room temperature. In a second round-bottom flask,  $\text{XeF}_2$  (169.3 mg, 1.0 mmol, 1.0 eq) was carefully added on a solution of tri(tert-butyl)phosphine (202.3 mg, 1.0 mmol, 1 eq) in toluene (5 mL). The mixture was stirred for 10 min at room temperature, until the evolution of xenon gas stopped. The solution containing the difluorophosphine was added to the solution containing the cobalt-silicon reagent. The mixture was stirred at room temperature overnight. When the stirring was stopped, after decantation, a colored slurry (the product) and a red translucent supernatant were observed: the supernatant would contain some residues of starting materials, intermediates ( $[\text{Et}_3\text{SiCo}(\text{CO})_4]$ ,  $\text{F}_2\text{P}^t\text{Bu}_3$ ), and by-products ( $\text{Et}_3\text{SiF}$ ), and got its color from cobalt species. The supernatant was removed. Addition of pentane allowed the precipitation of the slurry: the precipitate was washed with pentane (3 x 3 mL), until the washings were clear. The powder was dried under vacuum to afford a green solid in 95 % yield (372.7 mg). Crystals suitable for DRX analysis were obtained by slow diffusion of pentane in a concentrated solution in DME.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  (ppm) = 1.67 (d,  $J = 15.5$  Hz, 27 H; H-C(2)).  $^{13}\text{C}\{\text{1H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  (ppm) = 41.64 (dd,  $J = 26.2, 7.8$  Hz, 3 C; C(1)), 28.3 (d,  $J = 1.91$  Hz, 9 C; C(2)).  $^{31}\text{P}\{\text{1H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$  (ppm) = 150.64 (d,  $J_{\text{PF}} = 1018.4$  Hz).  $^{19}\text{F}\{\text{1H}\}$  NMR

(375 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C)  $\delta$  (ppm) = -171.38 (d,  $J_{PF}$  = 1018.6 Hz). **IR (ATR):**  $\tilde{\nu}$  (cm<sup>-1</sup>) = 1863 (s; C≡O). **Elemental analysis** calcd (%) for C<sub>16</sub>H<sub>27</sub>CoFO<sub>4</sub>P: C 48.99, H 6.94; found: C 48.19, H 6.91.

#### ***Additional comments about the synthesis of [R<sub>3</sub>PF]<sup>+</sup>[Co(CO)<sub>4</sub>]<sup>-</sup>:***

- *The difluorophosphine solution and the silyl-cobalt solution were left to react overnight for convenience, but a few hours (typically 2 h) would be enough to complete the reaction.*
- *The reaction between XeF<sub>2</sub> and a phosphine is quite exothermic: enough solvent should be used in order to absorb the heat, and good stirring should be applied immediately after addition of XeF<sub>2</sub>. It is recommended to add the crystals of XeF<sub>2</sub> one by one carefully, in order to avoid strong bubbling and overheating.*

#### ***Attempted synthesis of triarylfluorophosphonium cobaltate species***

The synthesis of [Mes<sub>3</sub>PF]<sup>+</sup>[Co(CO)<sub>4</sub>]<sup>-</sup> (Mes: mesityl) was attempted and appeared to be very slow, probably because of steric hindrance caused by the mesityl substituents: after a few days of stirring at room temperature of the difluorophosphine and the silyl-cobalt solutions, only a small amount of precipitate could be observed, while the supernatant kept a dark red ruby color.

The synthesis of [Ph<sub>3</sub>PF]<sup>+</sup>[Co(CO)<sub>4</sub>]<sup>-</sup> was unsuccessful due to the fast degradation of the product during the purification process: our observations led us to assume that [Ph<sub>3</sub>PF]<sup>+</sup>[Co(CO)<sub>4</sub>]<sup>-</sup> disproportionates to afford a mixture of products, among which F<sub>2</sub>PPh<sub>3</sub> was identified.

- During the purification process, upon addition of pentane, a brown precipitate was formed, which we thought was the product. However, contrary to **I-IV**, this precipitate was not soluble in CD<sub>2</sub>Cl<sub>2</sub>, which was unusual, and unexpected.
- Despite using the typical procedure for the purification of [Ph<sub>3</sub>PF]<sup>+</sup>[Co(CO)<sub>4</sub>]<sup>-</sup>, F<sub>2</sub>PPh<sub>3</sub> was systematically observed in <sup>19</sup>F and <sup>31</sup>P NMR spectra (see section 5.5, Figure S41 and Figure S42), which was unusual as well, since pentane was successful at washing excess of F<sub>2</sub>PR<sub>3</sub> species during the purification of **I-IV**. This suggested that F<sub>2</sub>PPh<sub>3</sub> may be continuously formed from [Ph<sub>3</sub>PF]<sup>+</sup>[Co(CO)<sub>4</sub>]<sup>-</sup>.
- When a solution of [Ph<sub>3</sub>PF]<sup>+</sup>[Co(CO)<sub>4</sub>]<sup>-</sup> in CD<sub>2</sub>Cl<sub>2</sub> is kept for a few days at room temperature, conversion of [Ph<sub>3</sub>PF]<sup>+</sup>[Co(CO)<sub>4</sub>]<sup>-</sup> into F<sub>2</sub>PPh<sub>3</sub> is observed in <sup>19</sup>F and <sup>31</sup>P NMR, among other phosphorus species (see section 5.5, Figure S43 and Figure S44).

### **3.2 Representative procedure for the carbonylation of $\beta$ -lactones**

***Preparation of the autoclave*** – Before each experiment, the autoclave was thoroughly washed with ethanol (bottom and top part), while the glass tube and the magnetic stirrer were washed with ethanol, acetone, and diluted nitric acid to eliminate any residues of metallic compounds. The bottom part of the autoclave, the glass tube, and the magnetic stirrer were dried in an oven at 120 °C for at least 30 minutes. The top part was dried as much as possible under a flow of compressed air. The bottom part of the autoclave, a glass tube, and a magnetic stirrer were cooled at room temperature, then the autoclave was locked with a 42 mm wrench. In order to remove any residual trace of washing solvents, the autoclave was put under vacuum for at least 20 minutes. Finally, the tightness of the autoclave was checked by putting it under pressure for

at least 10 minutes and checking if the pressure decreased, and the autoclave was flushed three times with 10 bar of carbon monoxide.

**Preparation of the mixture** – Inside the dry box, in a vial, **IV** (23.5 mg, 0.06 mmol, 3 mol%) was dissolved in toluene (1 mL).  $\beta$ -propiolactone (125  $\mu$ L, 2 mmol) was added in the mixture. The mixture was homogenized, then taken into a syringe. The needle of the syringe was stuck in the septum of a sealed vial to keep the mixture under inert atmosphere during the transfer outside the dry box.

**Injection in the autoclave and start of the reaction** – The mixture prepared in the dry box and collected in the syringe was injected quickly in the purged autoclave thanks to the use of a long metallic needle. The autoclave was purged one more time with 10 bar of carbon monoxide. The autoclave was then pressurized at 10 bar, and put in a heating block for 16 h at 80 °C.

**End of the reaction and analysis of the raw mixture** – The reaction was stopped by cooling the autoclave in an ice bath. After depressurization and unlocking of the autoclave, ethyl acetate, a solvent that solubilizes well succinic anhydride, was added in the glass tube (3 mL of solvent per mmol of  $\beta$ -propiolactone initially injected). According to Yang *et al.*, this volume is twice the minimal amount required to dissolve 1 mmol of SA in ethyl acetate at 288 °K.<sup>8</sup>

After addition of mesitylene (internal standard, 10 mol%, 0.2 mmol, 28  $\mu$ L) in the mixture, and homogenization, the mixture was filtered on a Celite pad, and a sample was collected for GC-MS analysis.

### 3.3 GC-MS analysis: calibration curves

Calibrations were performed in order to quantify the amount of  $\beta$ -propiolactone (PL),  $\beta$ -butyrolactone (BL), succinic anhydride (SA) and methylsuccinic anhydride (MeSA) present in the final raw mixture after carbonylation, using commercial products. Mesitylene was used as an internal standard, and introduced in the raw mixture at the end of the reaction (0.1 eq vs. initial amount of PL or BL).

We estimate that our method enables to obtain a yield with an uncertainty of 5 %.

#### **Procedure**

- SA: the calibration used herein has already been described in a previous paper of our group (see S.I. Section 3.4, Calibration n°9).<sup>9</sup> The calibration curve is reminded in Figure S8.
- PL: PL (3.06 mmol, 220.8 mg) was weighed in vial A and diluted in ethyl acetate (9 mL) (solution A, 0.33 M). 4 vials were prepared, each containing mesitylene (0.1 mmol, 14  $\mu$ L), and:
  - in vial 1, 0.75 mL of solution A and 4.25 mL of ethyl acetate;
  - in vial 2, 1.5 mL of solution A and 3.5 mL of ethyl acetate;
  - in vial 3, 2.25 mL of solution A and 2.75 mL of ethyl acetate;
  - in vial 4, 3.0 mL of solution A and 2 mL of ethyl acetate.

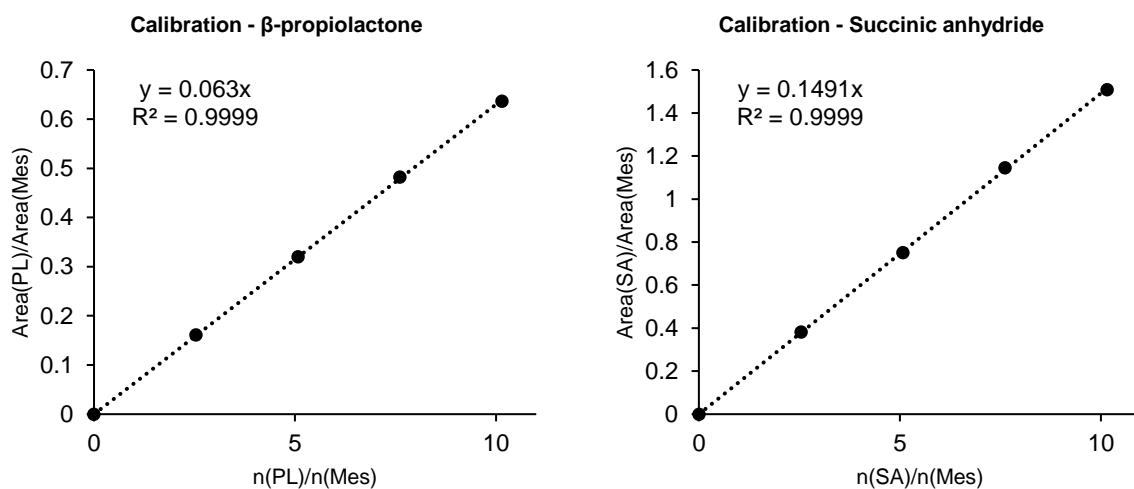
About < 0.1 mL of each vial was collected for the GC-MS analysis. The calibration curve obtained is reported in Figure S8.

- BL and MeSA: MeSA (3.02 mmol, 344.6 mg) was weighed in vial B and diluted in ethyl acetate (9 mL) (solution B, 0.33 M). BL (2.98 mmol, 256.5 mg) was weighed in

vial C and diluted in ethyl acetate (9 mL) (solution C, 0.33 M); Five vials were prepared, each containing ethyl acetate (2 mL) and mesitylene (0.1 mmol, 14  $\mu$ L), and:

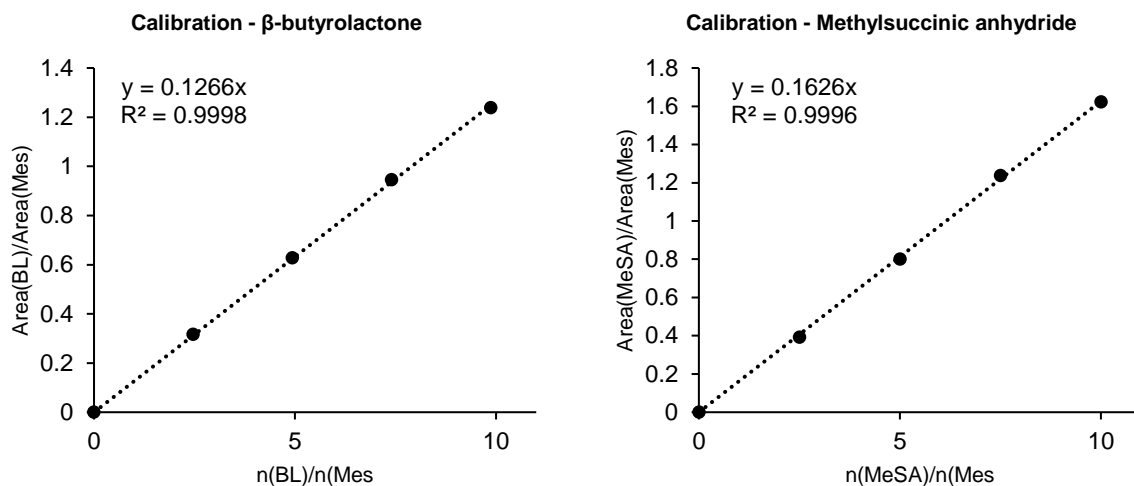
- in vial 1, 0.0 mL of solution B and 3.0 mL of solution C;
- in vial 2, 0.75 mL of solution B and 2.25 mL of solution C;
- in vial 3, 1.5 mL of solution B and 1.5 mL of solution C;
- in vial 4, 2.25 mL of solution B and 0.75 mL of solution C;
- in vial 5, 3.0 mL of solution B and 0 mL of solution C.

About < 0.1 mL of each vial was collected for the GC-MS analysis. The calibration curves obtained are reported in Figure S9.



Sample n°	Area(Mes)	Area(PL)	Area(PL)/Area(Mes)	n(PL)/n(Mes)
1	440440	71147	0.16154	2.53717
2	512917	164236	0.32020	5.07435
3	764129	368269	0.48195	7.61152
4	719693	457999	0.63638	10.14869
Sample n°	Area(Mes)	Area(SA)	Area(SA)/Area(Mes)	n(SA)/n(Mes)
1	652225	249369	0.38234	2.53779
2	628688	472506	0.75157	5.07557
3	729188	835644	1.14599	7.61336
4	717719	1082264	1.50792	10.15115

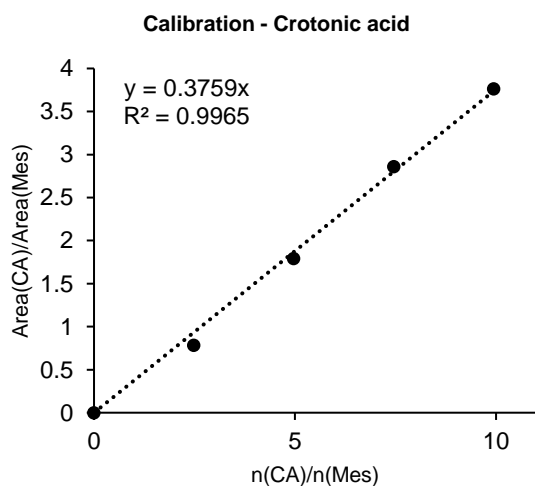
Figure S8 – Calibration curves for PL and SA.



Sample n°	Area(Mes)	Area(BL)	Area(BL) /Area(Mes)	n(BL)/n(Mes)	Area(MeSA)	Area(MeSA) /Area(Mes)	n(MeSA)/n(Mes)
1	822482	10189850	1.23891	9.86825	0	0	0
2	1141958	1080108	0.94584	7.40118	448625	0.39286	2.50078
3	1267532	796080	0.62806	4.93412	1014264	0.80019	5.00155
4	1231884	390158	0.31696	2.46706	1524594	1.23761	7.50233
5	1291581	0	0	0	2096568	1.62326	10.00311

Figure S9 – Calibration curves for BL and MeSA.

During the carbonylation of BL at 120 °C/52 h (Table S3, entry 5), and at 140 °C/16 h (Table S3, entry 6), crotonic acid (CA) was detected, and a commercial sample was used to perform a calibration (Figure S10).



Sample n°	Area(Mes)	Area(CA)	Area(CA)/Area(Mes)	n(CA)/n(Mes)
1	42257532	33164386	0.78482	2.48437
2	40093732	71946591	1.79446	4.96875
3	41645517	119210988	2.86252	7.45312
4	40981874	154278593	3.76456	9.93750

Figure S10 – Calibration curve for CA.

### 3.4 GC-MS analysis: examples of chromatograms

Commercial samples of mesitylene, PL, BL, SA, MeSA, and CA were used to establish the calibration curves reported in Section 3.3. Their mass spectra are respectively reported in Figure S11, Figure S12, Figure S13, Figure S14, Figure S15, and Figure S16.

Calibration PL - Sample 4 - Mass spectrum - Mesitylene

Peak#:2 R.Time:3.899(Scan#:661)  
 MassPeaks:228  
 RawMode:Averaged 3.897-3.903(660-662)  
 BG Mode:Calc. from Peak Group 1 - Event 1

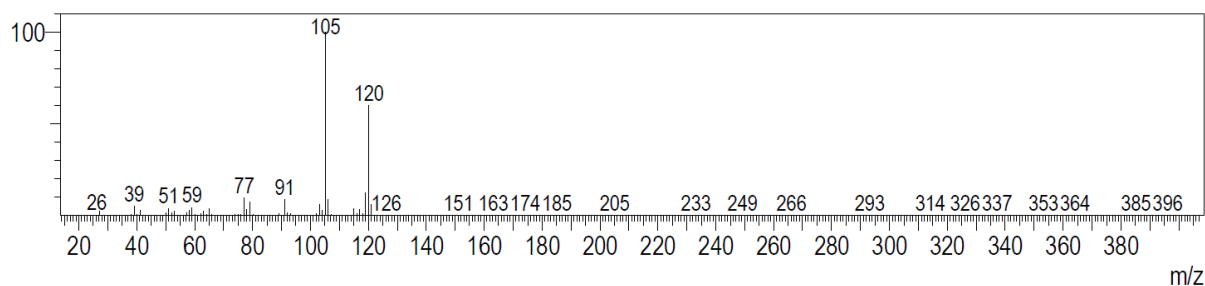


Figure S11 – Mass spectrum of a commercial sample of mesitylene, obtained during the calibration of PL.

Calibration PL - Sample 4 - Mass spectrum - PL

Peak#:1 R.Time:2.324(Scan#:188)  
 MassPeaks:175  
 RawMode:Averaged 2.320-2.327(187-189)  
 BG Mode:Calc. from Peak Group 1 - Event 1

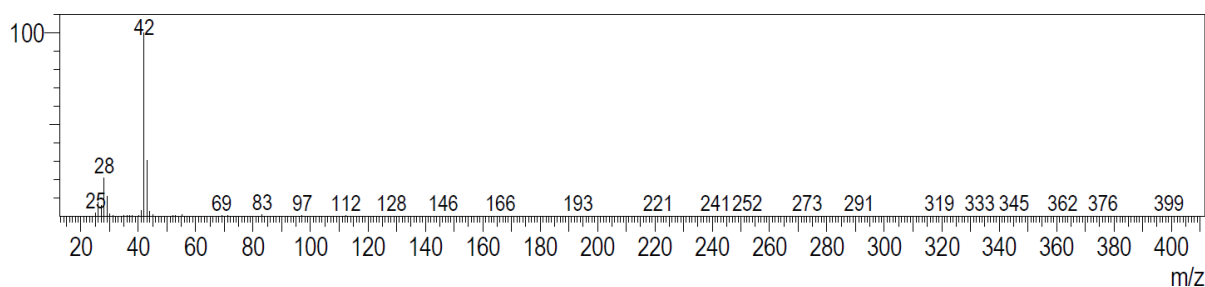


Figure S12 – Mass spectrum of a commercial sample of PL, obtained during its calibration.

Calibration BL and MeSA - Sample 3 - Mass spectrum - BL

Peak#:1 R.Time:2.626(Scan#:204)  
MassPeaks:192  
RawMode:Averaged 2.623-2.630(203-205)  
BG Mode:Calc. from Peak Group 1 - Event 1

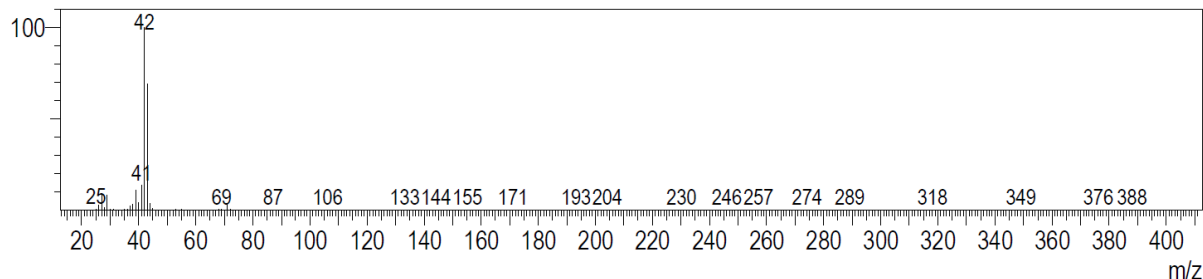


Figure S13 – Mass spectrum of a commercial sample of BL, obtained during its calibration.

Calibration - Sample 4 - Mass spectrum - Succinic anhydride

Peak#:2 R.Time:4.192(Scan#:749)  
MassPeaks:196  
RawMode:Averaged 4.190-4.197(748-750)  
BG Mode:Calc. from Peak Group 1 - Event 1

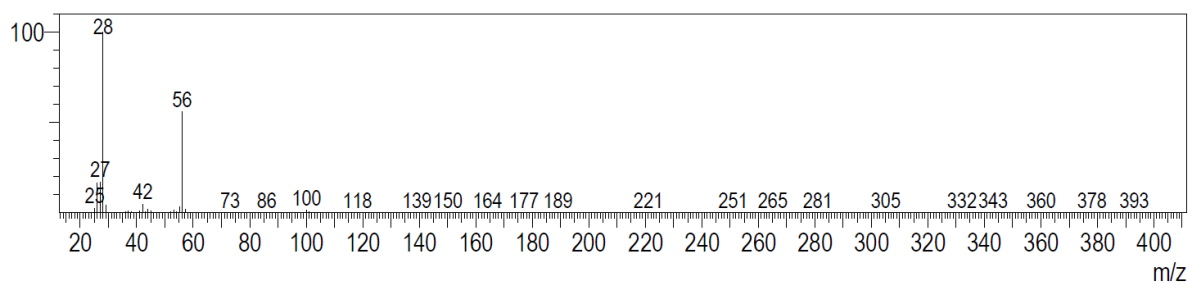


Figure S14 – Mass spectrum of a commercial sample of SA, obtained during its calibration.

Calibration BL and MeSA - Sample 3 - Mass spectrum - MeSA

Peak#:3 R.Time:4.248(Scan#:690)  
MassPeaks:243  
RawMode:Averaged 4.243-4.250(689-691)  
BG Mode:Calc. from Peak Group 1 - Event 1

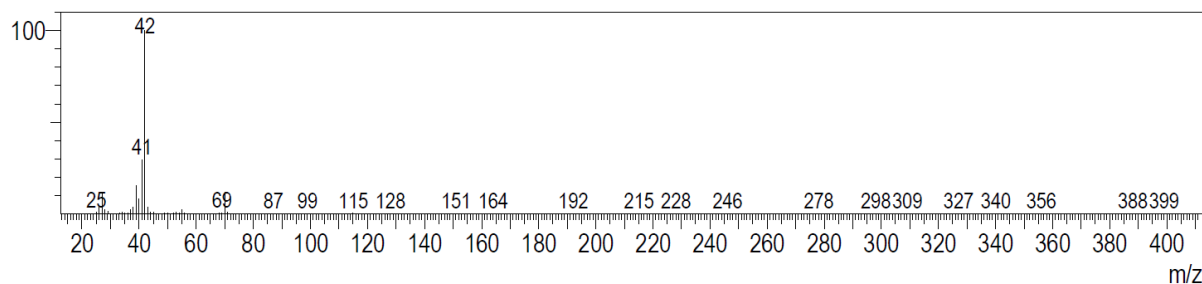


Figure S15 – Mass spectrum of a commercial sample of MeSA, obtained during its calibration.



Calibration CA - Sample 4 - Mass spectrum - Crotonic acid

Peak#:1 R.Time:2.957(Scan#:378)

MassPeaks:259

RawMode:Averaged 2.953-2.960(377-379)

BG Mode:Calc. from Peak Group 1 - Event 1

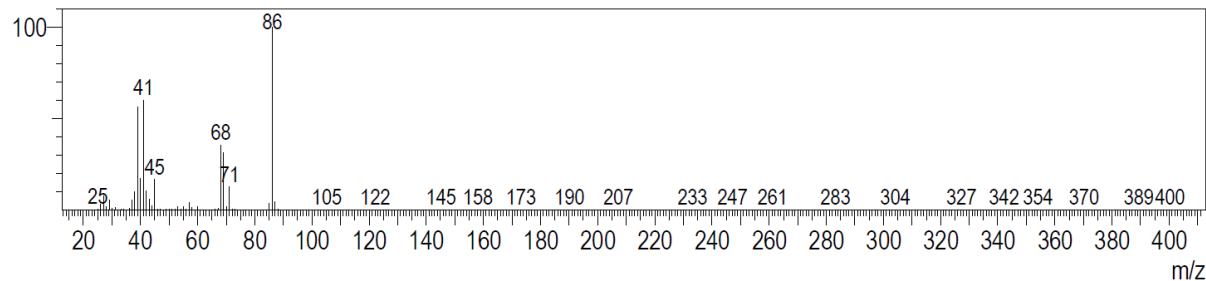
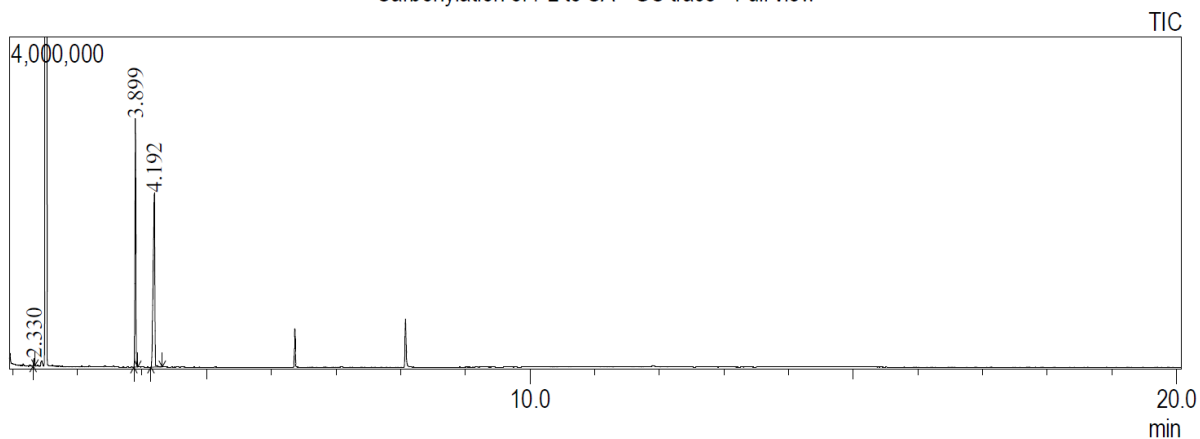


Figure S16 - Mass spectrum of a commercial sample of crotonic acid, obtained during its calibration.

GC traces and the mass spectra of the products observed are provided below to exemplify our analytical method:

- GC trace obtained after the carbonylation of PL (Figure S17; for conditions of the corresponding carbonylation see Table S2, entry 8).
- GC trace obtained after the carbonylation of BL (Figure S18; for conditions of the corresponding carbonylation see Table S3, entry 5).

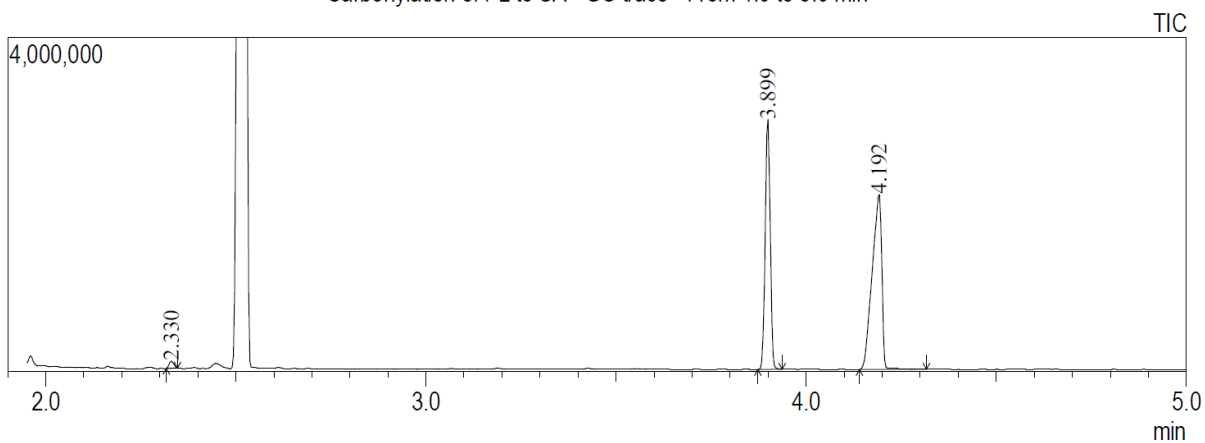
Carbonylation of PL to SA - GC trace - Full view



Peak Report TIC

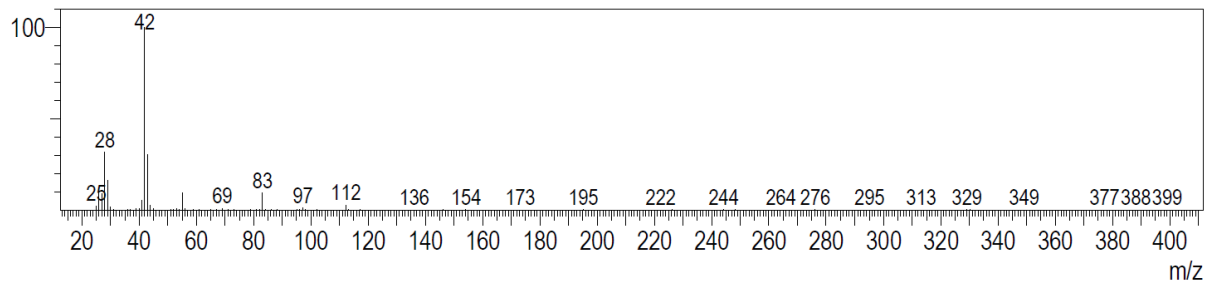
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	Name
1	2.330	2.317	2.347	74542	1.14	85006	1.64	Beta-propiolactone
2	3.899	3.873	3.937	2769293	42.31	2990991	57.85	Mesitylene
3	4.192	4.140	4.317	3702008	56.56	2094698	40.51	Succinic anhydride
				6545843	100.00	5170695	100.00	

Carbonylation of PL to SA - GC trace - From 1.9 to 5.0 min



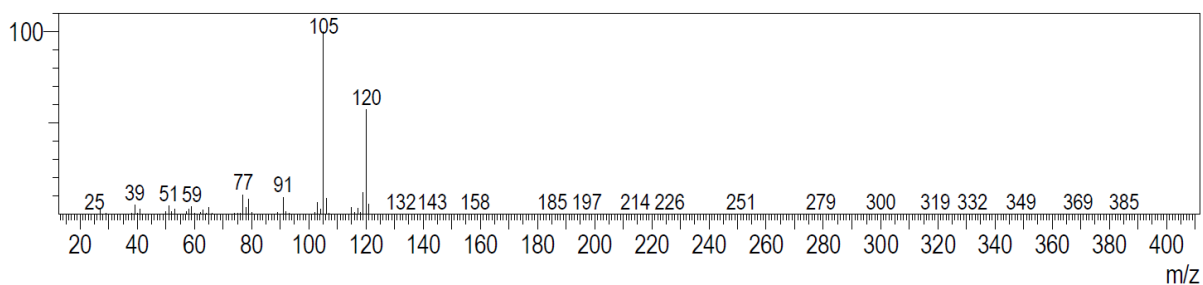
Carbonylation of PL to SA - Mass spectrum - PL

Peak#:1 R.Time:2.330(Scan#:115)  
MassPeaks:174  
RawMode:Averaged 2.327-2.333(114-116)  
BG Mode:Calc. from Peak Group 1 - Event 1



Carbonylation of PL to SA - Mass spectrum - Mesitylene

Peak#:2 R.Time:3.899(Scan#:586)  
MassPeaks:214  
RawMode:Averaged 3.897-3.903(585-587)  
BG Mode:Calc. from Peak Group 1 - Event 1



Carbonylation of PL to SA - Mass spectrum - SA

Peak#:3 R.Time:4.192(Scan#:674)  
MassPeaks:204  
RawMode:Averaged 4.190-4.197(673-675)  
BG Mode:Calc. from Peak Group 1 - Event 1

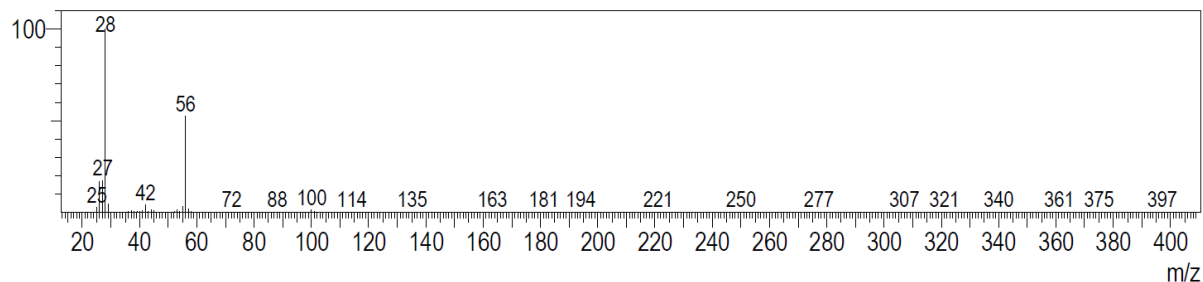
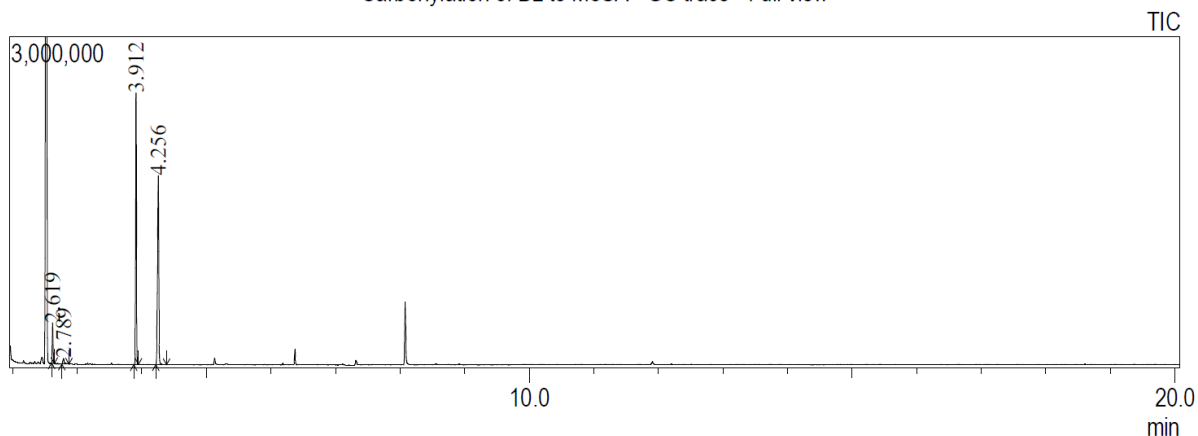


Figure S17 – GC trace and mass spectra obtained after the carbonylation of PL in presence of **IV** (3 mol%), in toluene, under CO (2 bar), 80 °C, 16 h (see Table S2, entry 8).

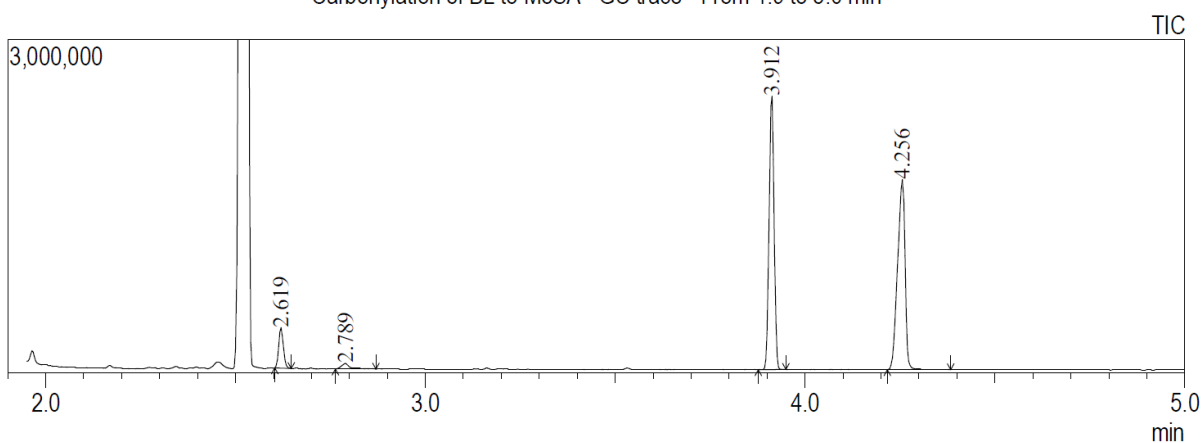
Carbonylation of BL to MeSA - GC trace - Full view



Peak Report TIC

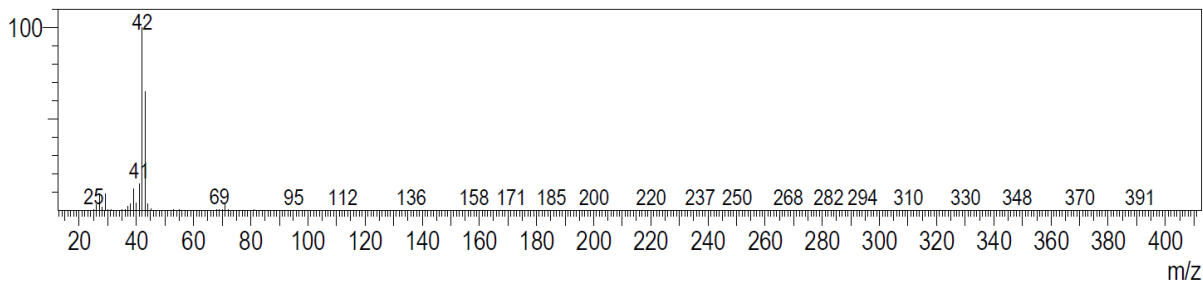
Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	Name
1	2.619	2.603	2.647	312459	6.24	364563	7.95	Beta-butyrolactone
2	2.789	2.763	2.870	78528	1.57	50691	1.11	Crotonic acid
3	3.912	3.877	3.950	2272558	45.38	2460696	53.65	Mesitylene
4	4.256	4.217	4.383	2343757	46.81	1710837	37.30	Methylsuccinic anhydrid
				5007302	100.00	4586787	100.00	

Carbonylation of BL to MeSA - GC trace - From 1.9 to 5.0 min



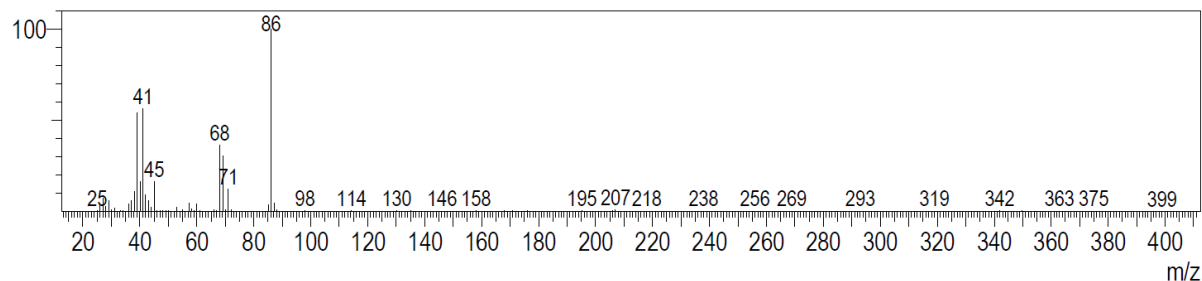
Carbonylation of BL to MeSA - Mass spectrum - BL

Peak#:1 R.Time:2.619(Scan#:202)  
 MassPeaks:190  
 RawMode:Averaged 2.617-2.623(201-203)  
 BG Mode:Calc. from Peak Group 1 - Event 1



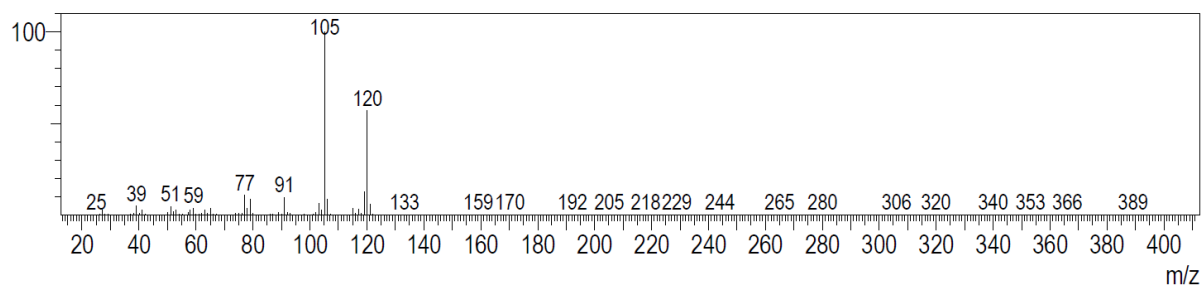
Carbonylation of BL to MeSA - Mass spectrum - CA

Peak#2 R.Time:2.789(Scan#:253)  
MassPeaks:211  
RawMode:Averaged 2.787-2.793(252-254)  
BG Mode:Calc. from Peak Group 1 - Event 1



Carbonylation of BL to MeSA - Mass spectrum - Mesitylene

Peak#3 R.Time:3.912(Scan#:590)  
MassPeaks:216  
RawMode:Averaged 3.910-3.917(589-591)  
BG Mode:Calc. from Peak Group 1 - Event 1



Carbonylation of BL to MeSA - Mass spectrum - MeSA

Peak#4 R.Time:4.256(Scan#:693)  
MassPeaks:197  
RawMode:Averaged 4.253-4.260(692-694)  
BG Mode:Calc. from Peak Group 1 - Event 1

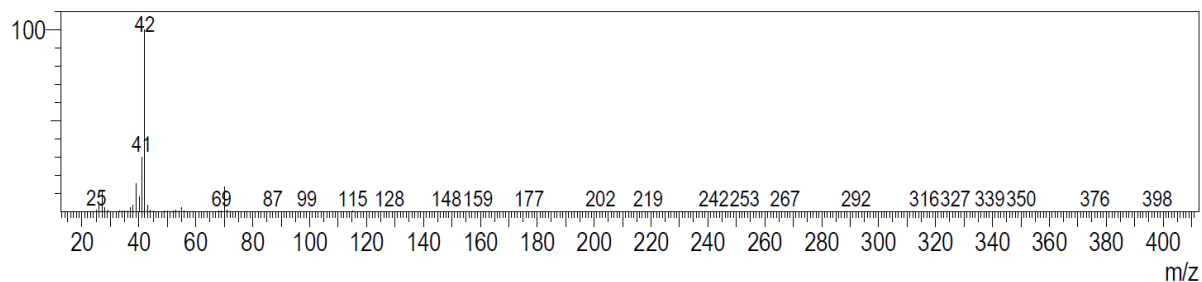


Figure S18 – GC trace and mass spectra obtained after the carbonylation of BL in presence of **IV** (3 mol%), in toluene, under CO (10 bar), 120 °C, 48 h (see Table Table S3, entry 5).

## 4 Analysis of the catalytic experiments

### 4.1 GC-MS analyses of the mixture

Table S2 – Carbonylation of  $\beta$ -propiolactone (PL) to succinic anhydride (SA).

Entry	Reaction conditions			Analysis				
	Catalyst	P <sub>CO</sub> (bar)	T (°C)	Area measured after GC-MS analysis			PL conversion (%)	SA yield (%)
				Mesitylene	PL	SA		
1	I	50	80	2635023	423820	2278844	74	58
2	II	50	80	2757524	232312	3050682	87	75
3	III	50	80	1297143	96482	1347531	88	70
4	IV	50	80	2439939	221803	2710682	85	75
5	IV	50	100	1588754	50788	1737196	95	74
6	IV	20	80	2216528	51801	2545767	96	78
7	IV	10	80	3131516	15438	4214604	99	91
8 <sup>a</sup>	IV	2	80	2769293	74542	3702008	96	90

Conditions: The catalyst (3 mol%) and PL (2 mol.L<sup>-1</sup>) were dissolved in toluene (1 mL) The mixture was injected in a previously dried and purged autoclave. The autoclave was then filled with CO, and the reaction was run at the indicated temperature for 16 h. Mesitylene (internal standard, 10 mol%) was added in the raw mixture at the end of the reaction. <sup>a</sup>The pressure was maintained constant at 2 bar over the course of the reaction, to make up for the consumption of CO (2 bar of CO in the small-volume autoclaves corresponds to about 2 mmol of CO).

Table S3 – Carbonylation of  $\beta$ -butyrolactone (BL) to methylsuccinic anhydride (MeSA).

Entry	Reaction conditions		Analysis				
	T (°C)	Duration (h)	Area measured after GC-MS analysis			BL conversion (%)	MeSA yield (%)
			Mesitylene	BL	MeSA		
1	80	16	3050617	3706732	209740	3	4
2	100	16	2733870	2295413	1445567	33	33
3	100	48	1519419	152868	1757921	92	72
4	120	16	2727030	896319	2745100	74	62
5 <sup>a</sup>	120	52	2272558	312459	2343757	89	64
6 <sup>b</sup>	140	16	3208150	547183	1474269	86	28

Conditions: The catalyst IV (3 mol%) and BL (2 mol.L<sup>-1</sup>) were dissolved in toluene (1 mL) The mixture was injected in a previously dried and purged autoclave. The autoclave was then filled with CO (10 bar), and the reaction was run at the indicated temperature for 16 h or 48 h. Mesitylene (internal standard, 10 mol%) was added in the raw mixture at the end of the reaction. <sup>a</sup>9 % of crotonic acid was also obtained (area: 78528). <sup>b</sup>49 % of crotonic acid was also obtained (area: 596170).

In some experiments, H<sub>2</sub> and CO<sub>2</sub> were also observed in the gas phase as side-products of the carbonylation of BL to MeSA (see Section 4.2).

### 4.2 GC analyses of the gas phase

At the end of each carbonylation, and after cooling and depressurization of the reactor, GC analysis of the gas phase was systematically performed. While only CO (t<sub>R</sub> ≈ 2.6 min) could be

detected after carbonylation of PL, small amounts of H<sub>2</sub> (t<sub>R</sub> ≈ 2.0 min) and CO<sub>2</sub> (t<sub>R</sub> ≈ 6.5 min) were detected after carbonylation of BL. N<sub>2</sub> (t<sub>R</sub> ≈ 2.5 min) may also be detected due to a slight leakage of the gas microsyringe.

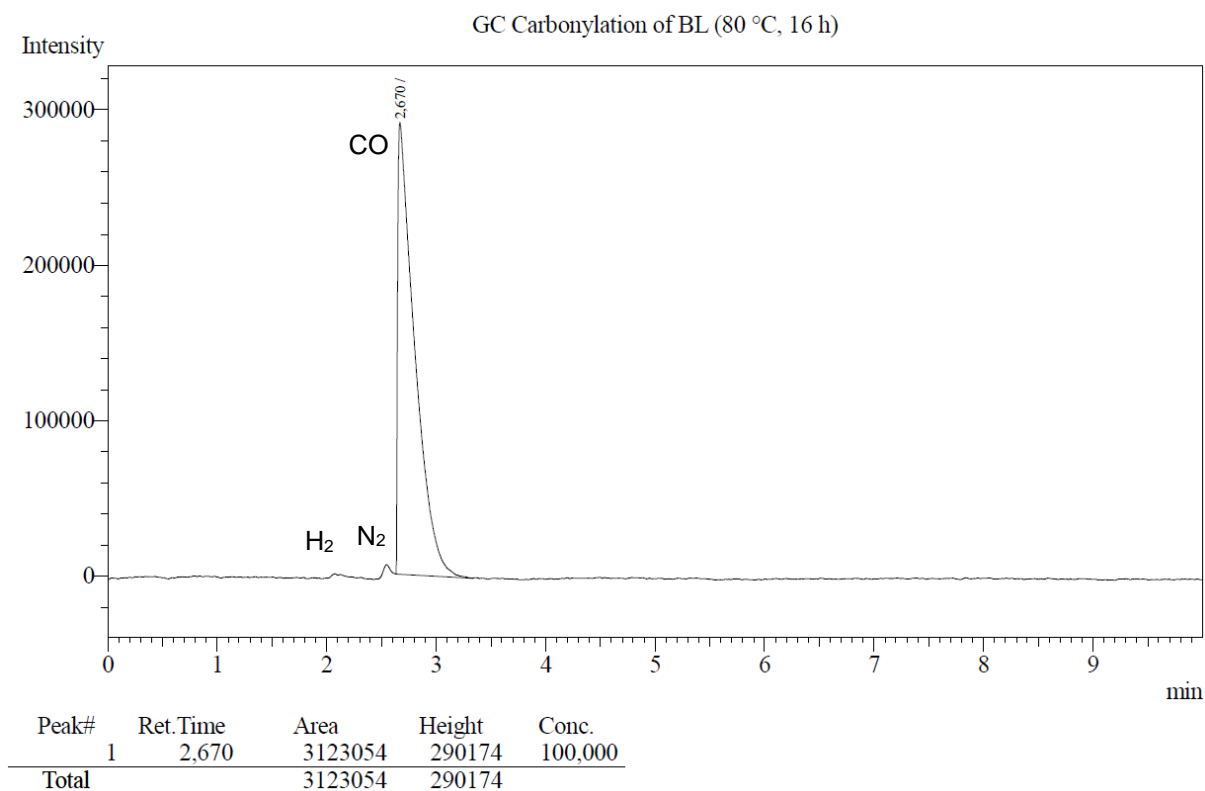


Figure S19 – GC of the gas phase after the carbonylation of BL at 80 °C, 16 h (Table S3, entry 1).

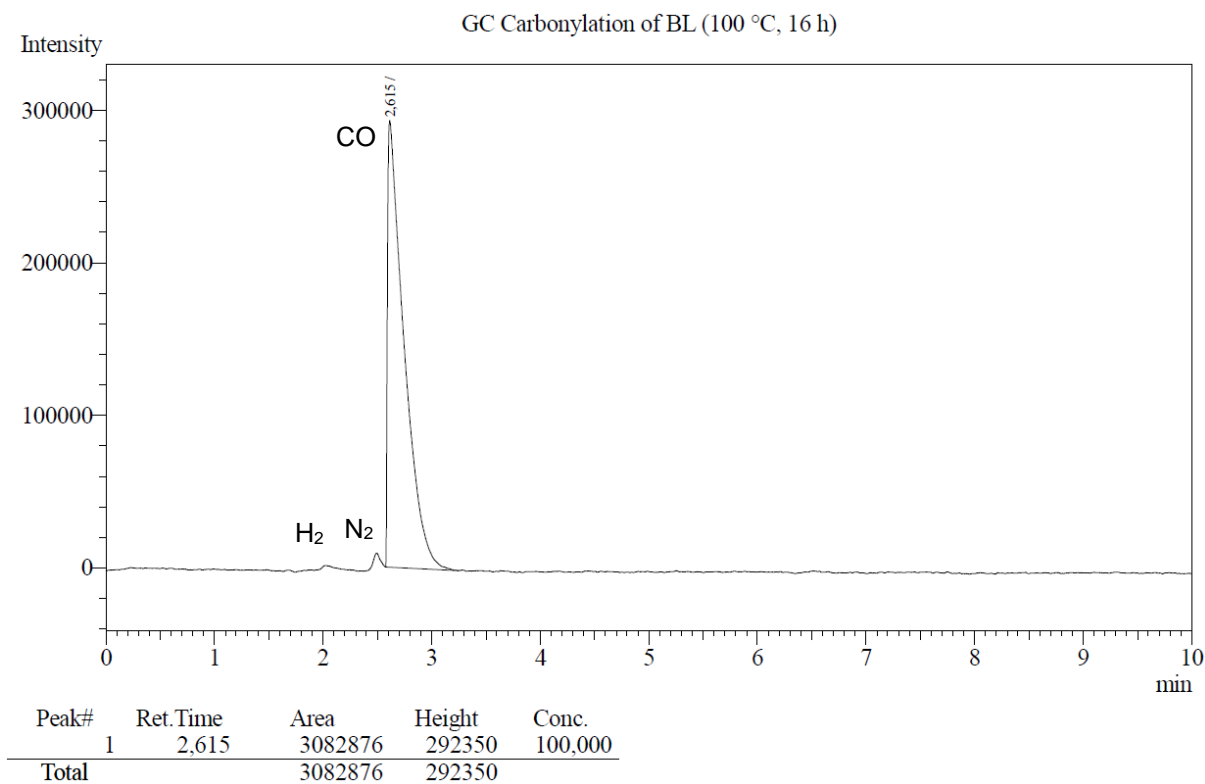
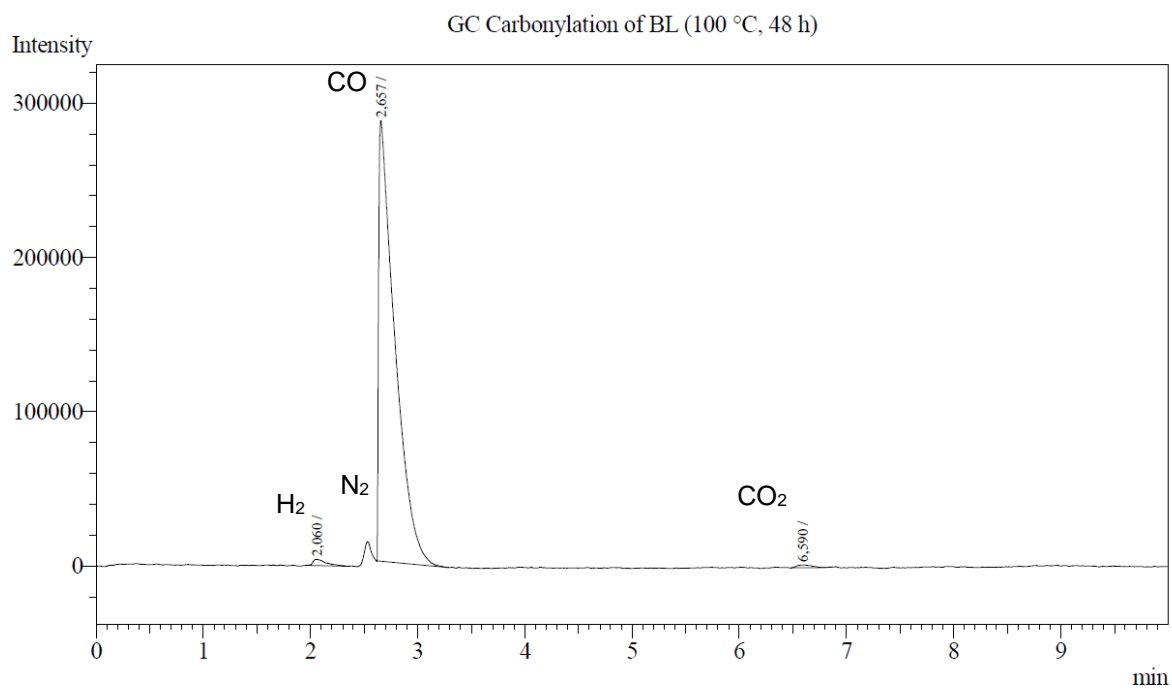
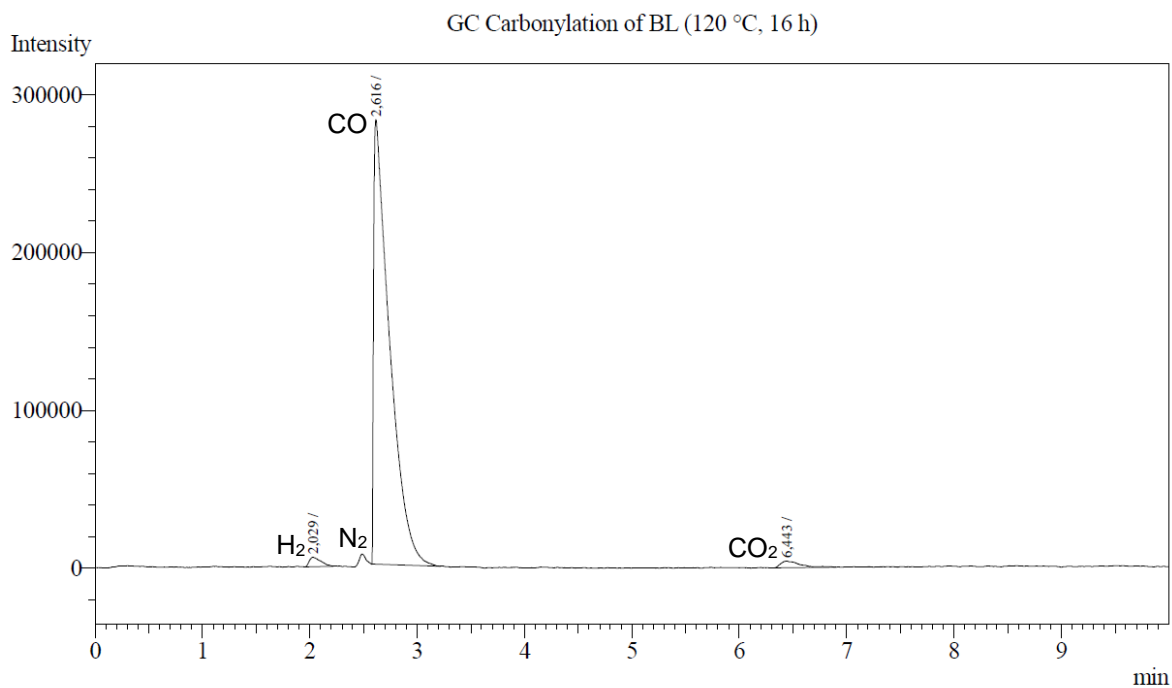


Figure S20 – GC of the gas phase after the carbonylation of BL at 100 °C, 16 h (Table S3, entry 2).



Peak#	Ret. Time	Area	Height	Conc.
1	2,060	34405	4015	1,130
2	2,657	2992480	284054	98,284
3	6,590	17849	1852	0,586
Total		3044734	289921	

Figure S21– GC of the gas phase after the carbonylation of BL at 100 °C, 48 h (Table S3, entry 3).



Peak#	Ret. Time	Area	Height	Conc.
1	2,029	43834	5925	1,463
2	2,616	2898004	280695	96,719
3	6,443	54475	4284	1,818
Total		2996313	290904	

Figure S22 – GC of the gas phase after the carbonylation of BL at 120 °C, 16 h (Table S3, entry 4).



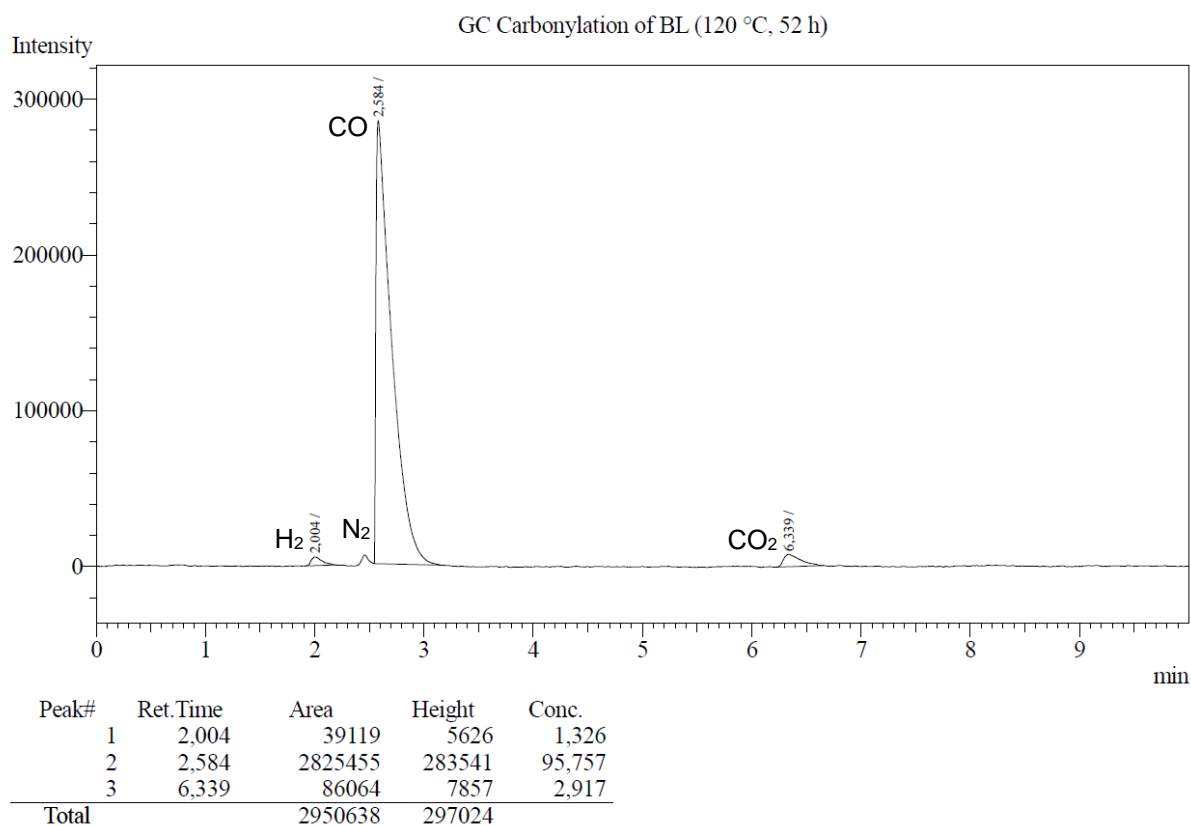


Figure S23– GC of the gas phase after the carbonylation of BL at 120 °C, 52 h (Table S3, entry 5).

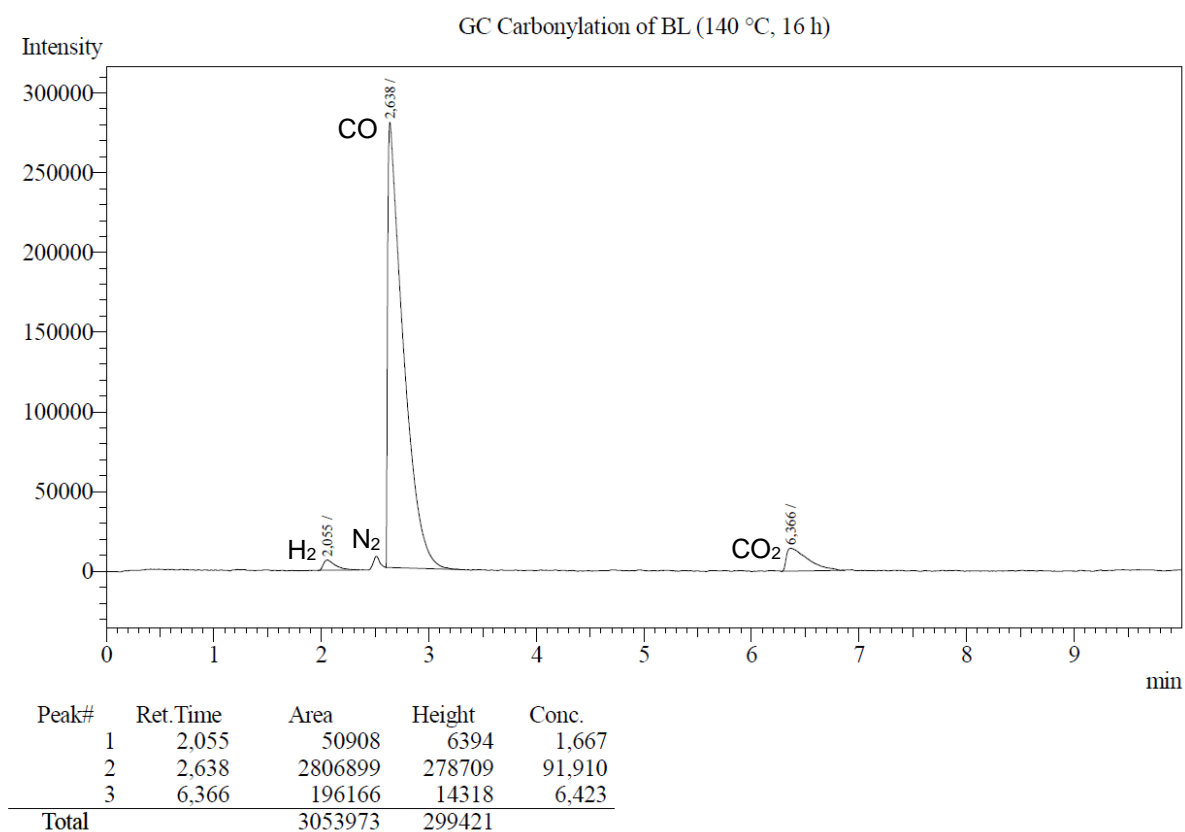


Figure S24 – GC of the gas phase after the carbonylation of BL at 140 °C, 16 h (Table S3, entry 6).

## 5 NMR spectra

### 5.1 Compound I: $[(o\text{-Tol})_3\text{PF}]^+[\text{Co}(\text{CO})_4]^-$

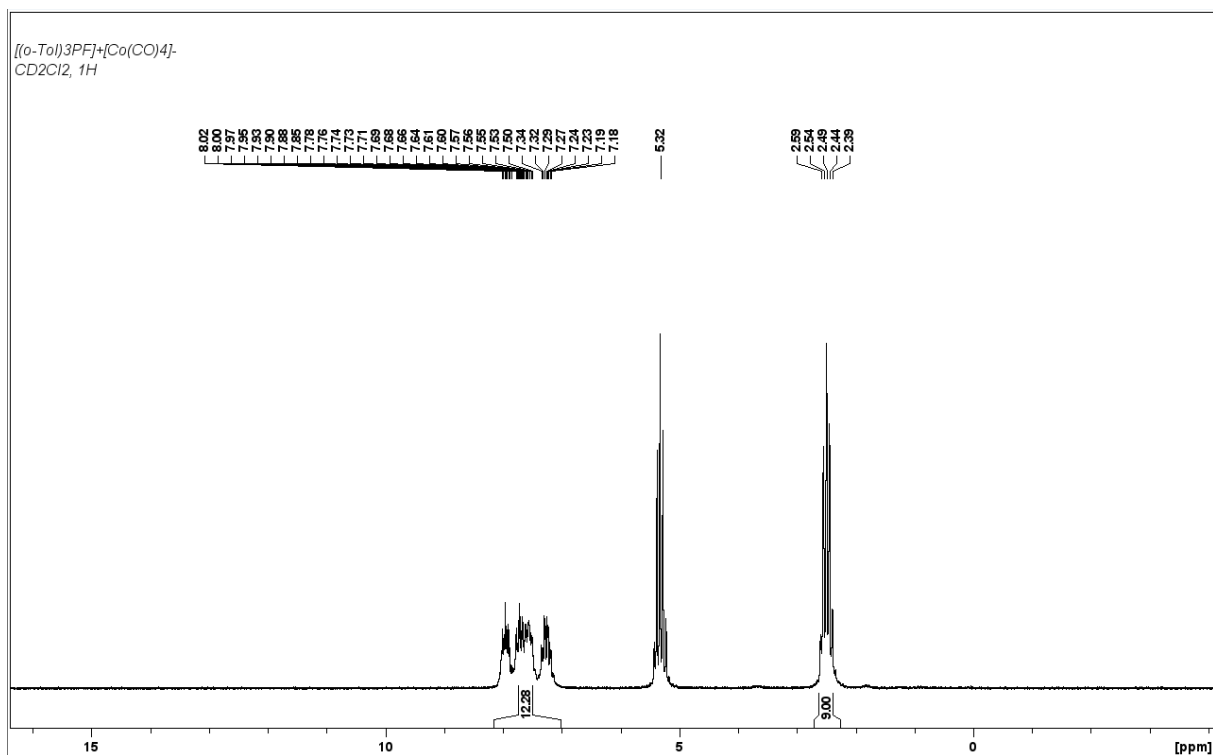


Figure S25 – <sup>1</sup>H NMR spectrum of compound I (CD<sub>2</sub>Cl<sub>2</sub>).

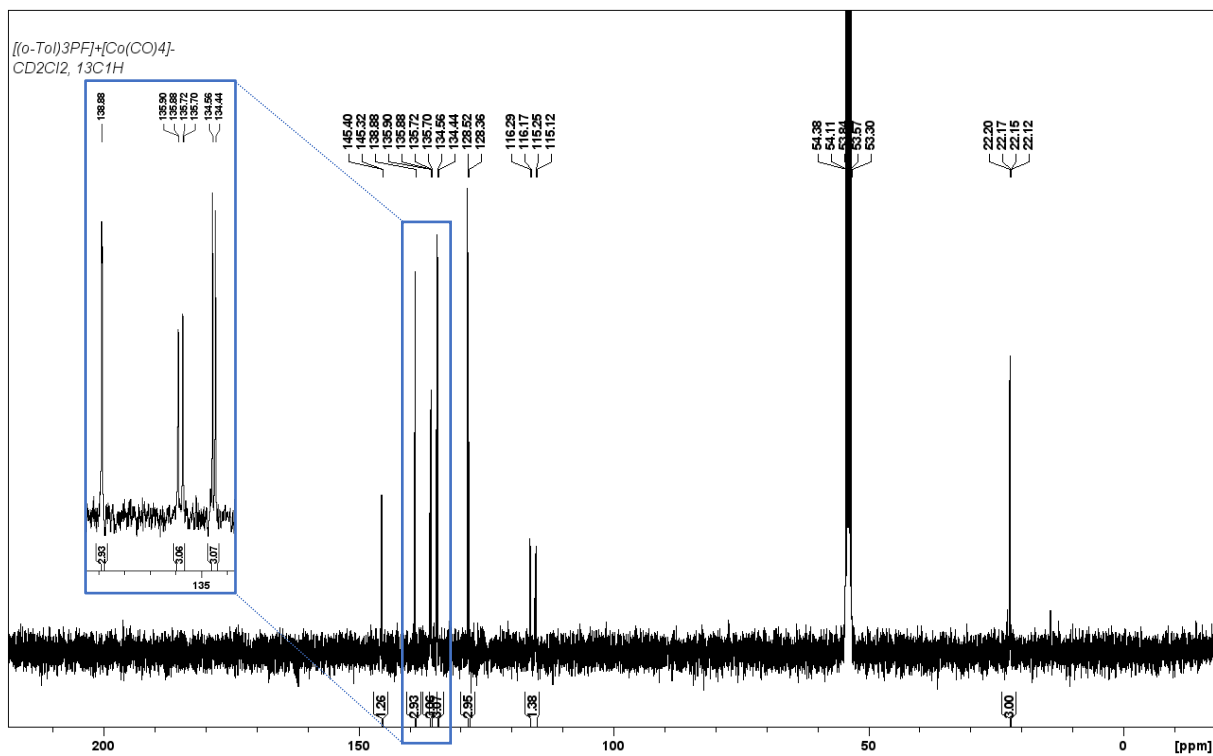


Figure S26 – <sup>13</sup>C NMR spectrum of compound I (CD<sub>2</sub>Cl<sub>2</sub>).

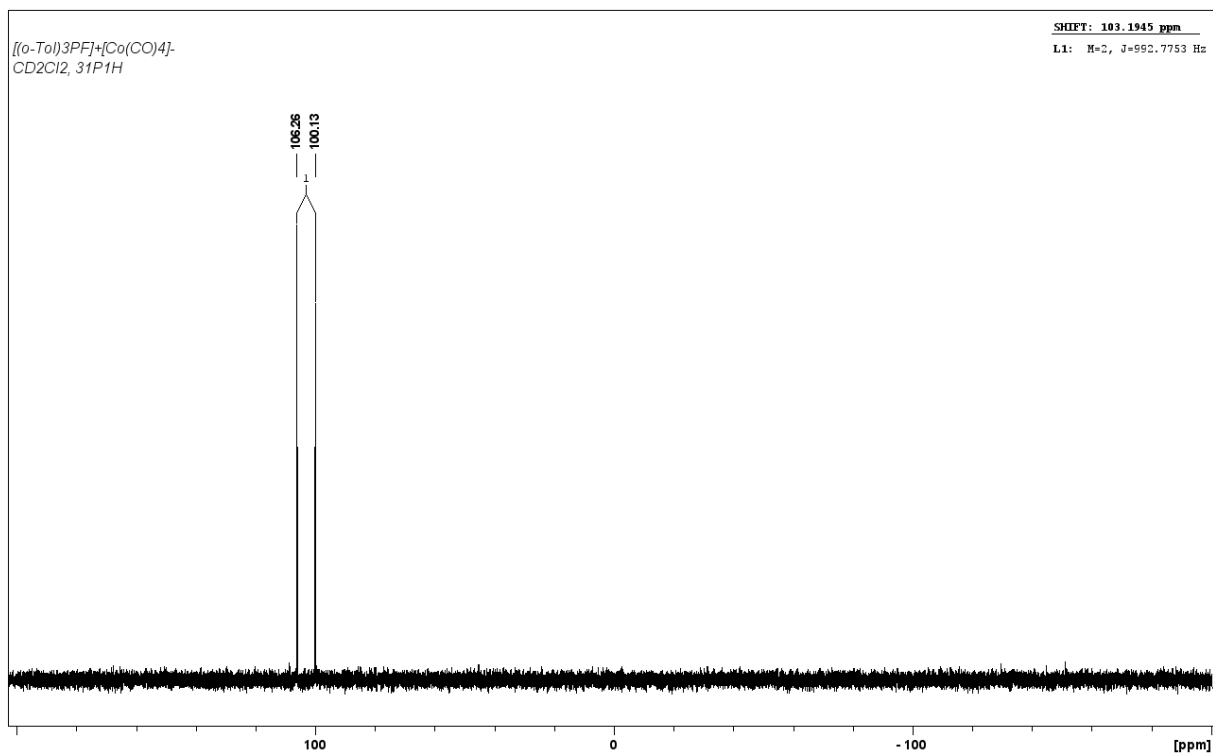


Figure S27 –  $^{31}\text{P}$  NMR spectrum of compound **I** ( $\text{CD}_2\text{Cl}_2$ ).

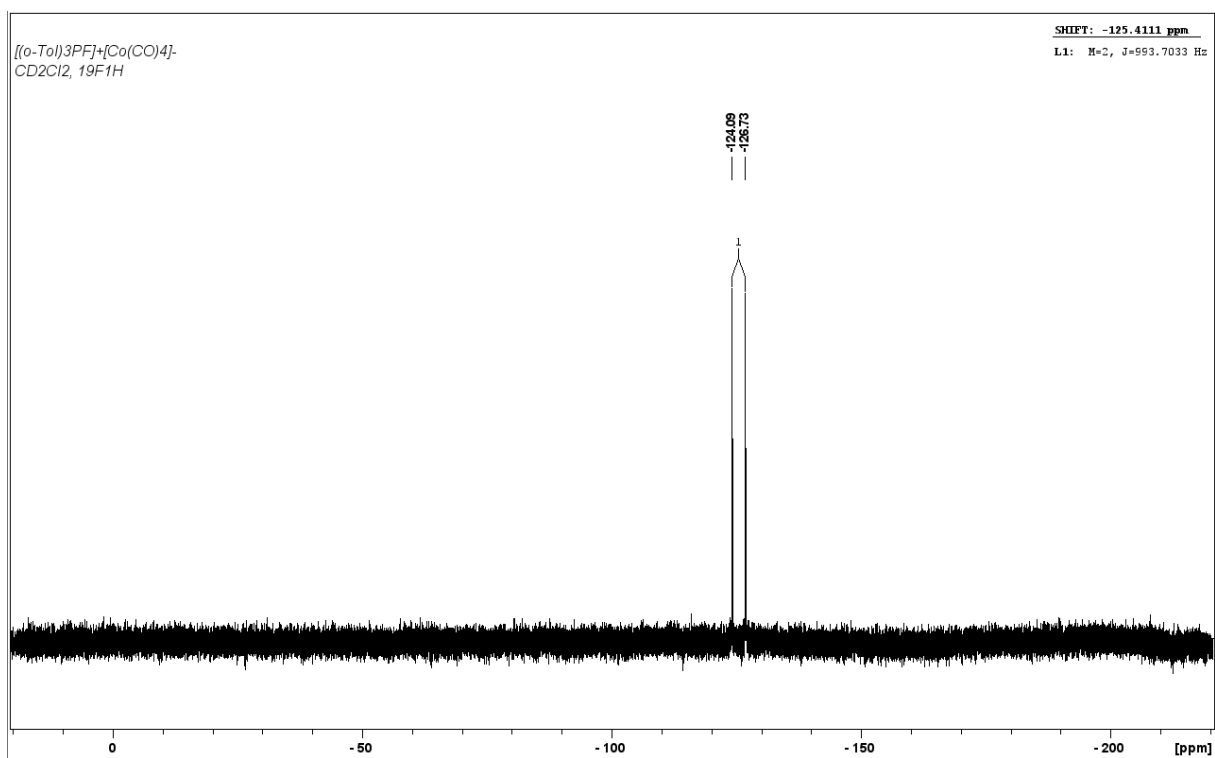


Figure S28 –  $^{19}\text{F}$  NMR spectrum of compound **I** ( $\text{CD}_2\text{Cl}_2$ ).

## 5.2 Compound II: $[\text{Cy}_3\text{PF}]^+[\text{Co}(\text{CO})_4]^-$

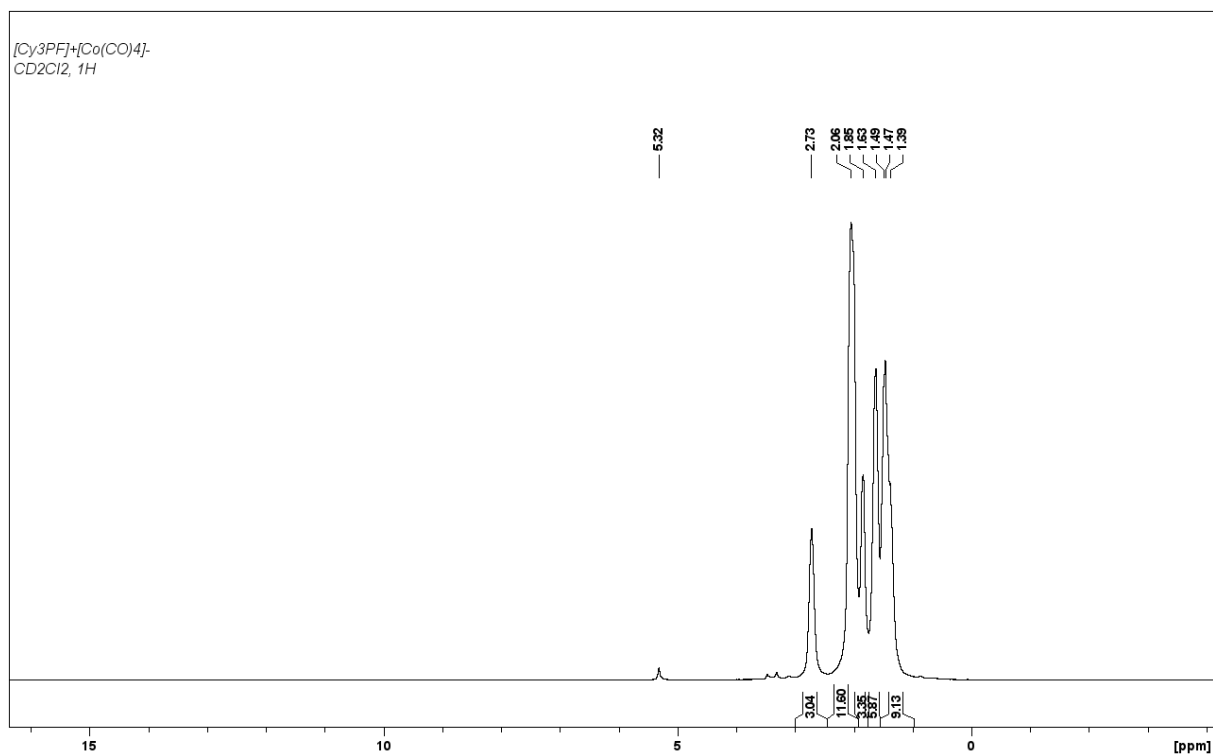


Figure S29 –  $^1\text{H}$  NMR spectrum of compound **II** ( $\text{CD}_2\text{Cl}_2$ ).

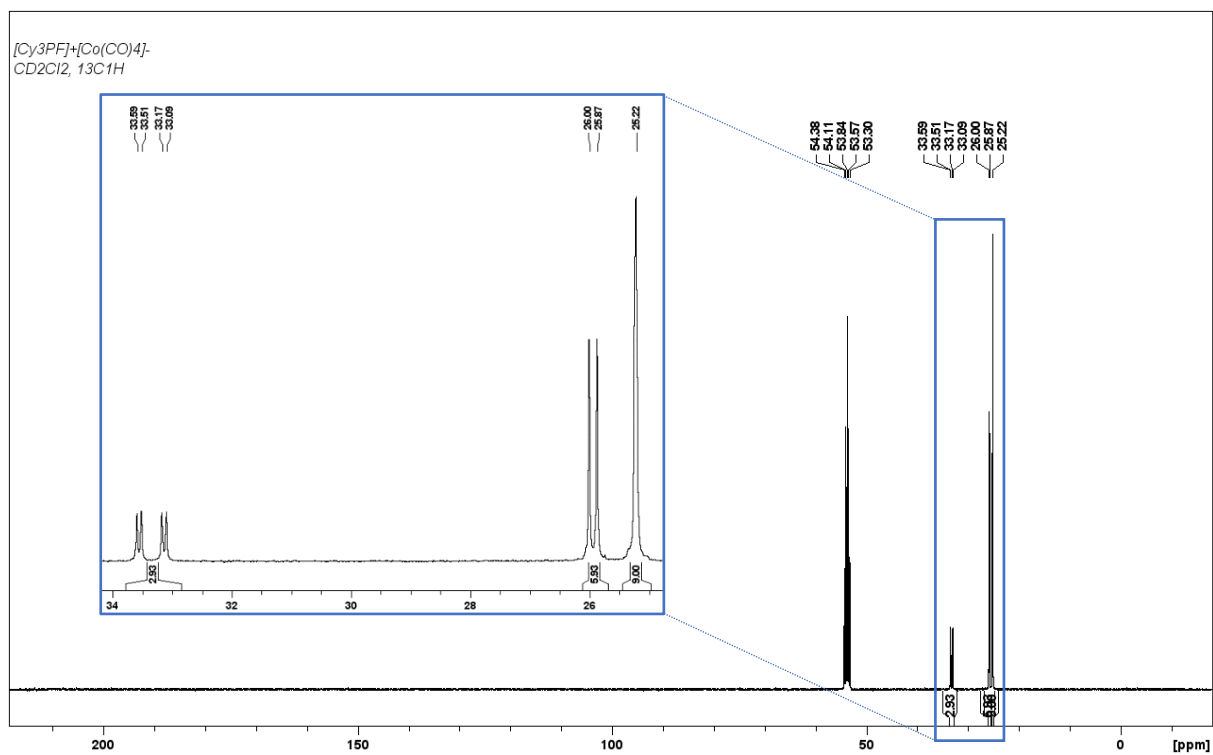


Figure S30 –  $^{13}\text{C}$  NMR spectrum of compound **II** ( $\text{CD}_2\text{Cl}_2$ ).

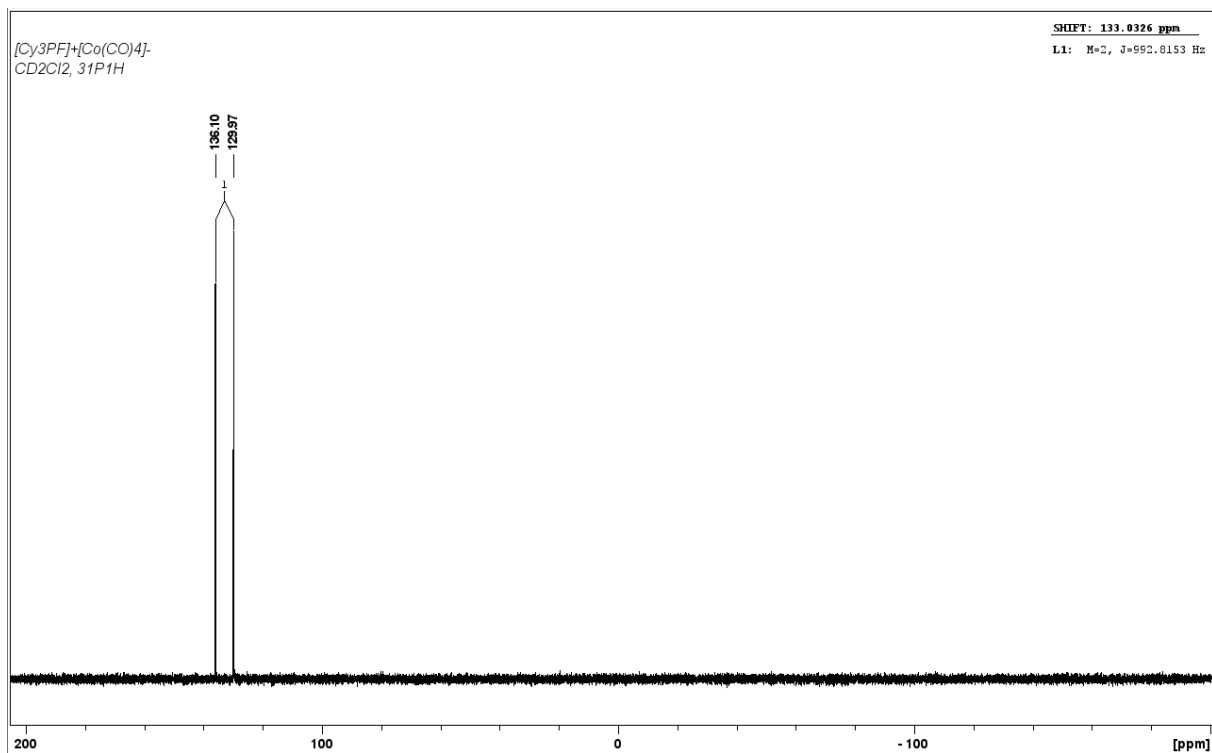


Figure S31 – <sup>31</sup>P NMR spectrum of compound **II** (CD<sub>2</sub>Cl<sub>2</sub>).

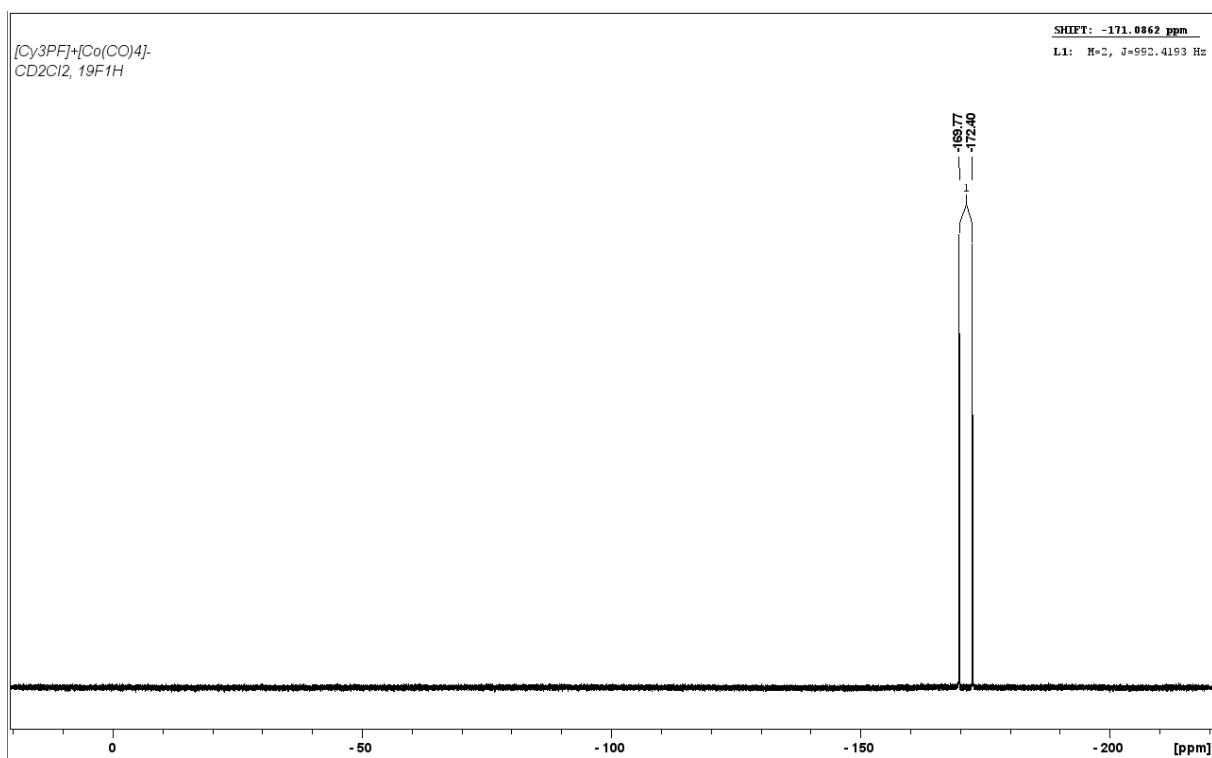


Figure S32 – <sup>19</sup>F NMR spectrum of compound **II** (CD<sub>2</sub>Cl<sub>2</sub>).

### 5.3 Compound III: $[(iPr)_3PF]^+[Co(CO)_4]^-$

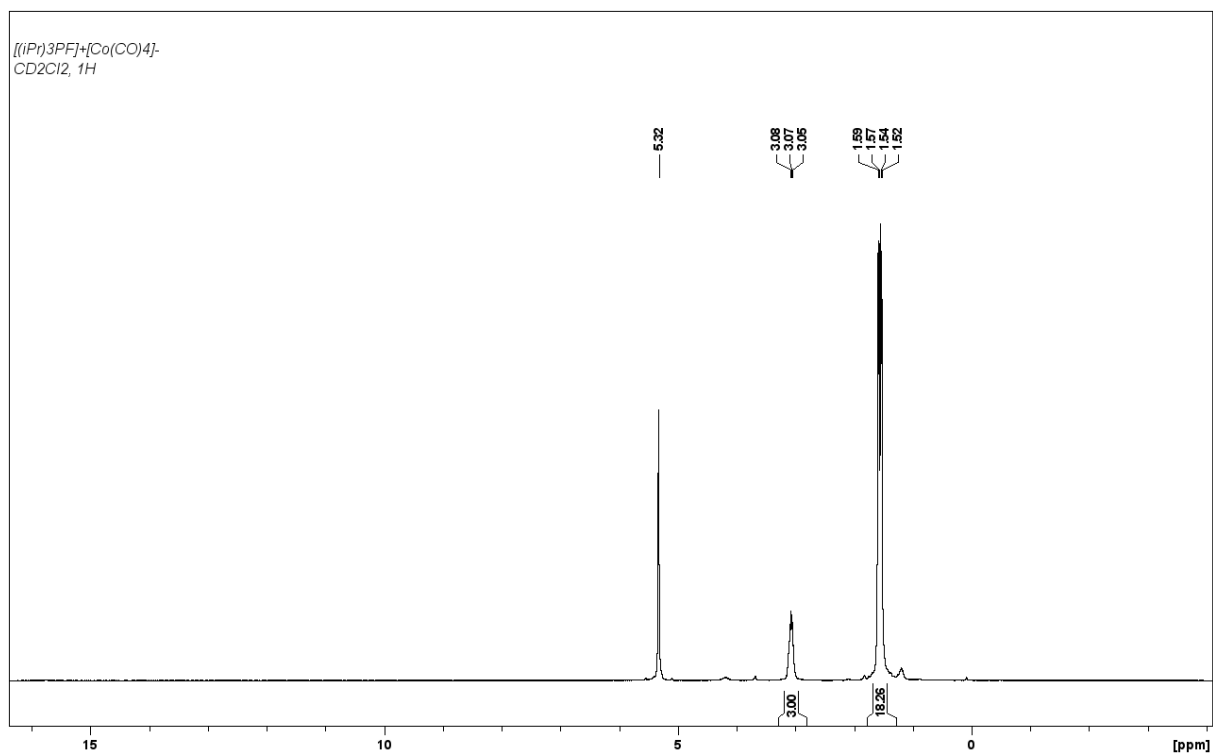


Figure S33 – <sup>1</sup>H NMR spectrum of compound III (CD<sub>2</sub>Cl<sub>2</sub>).

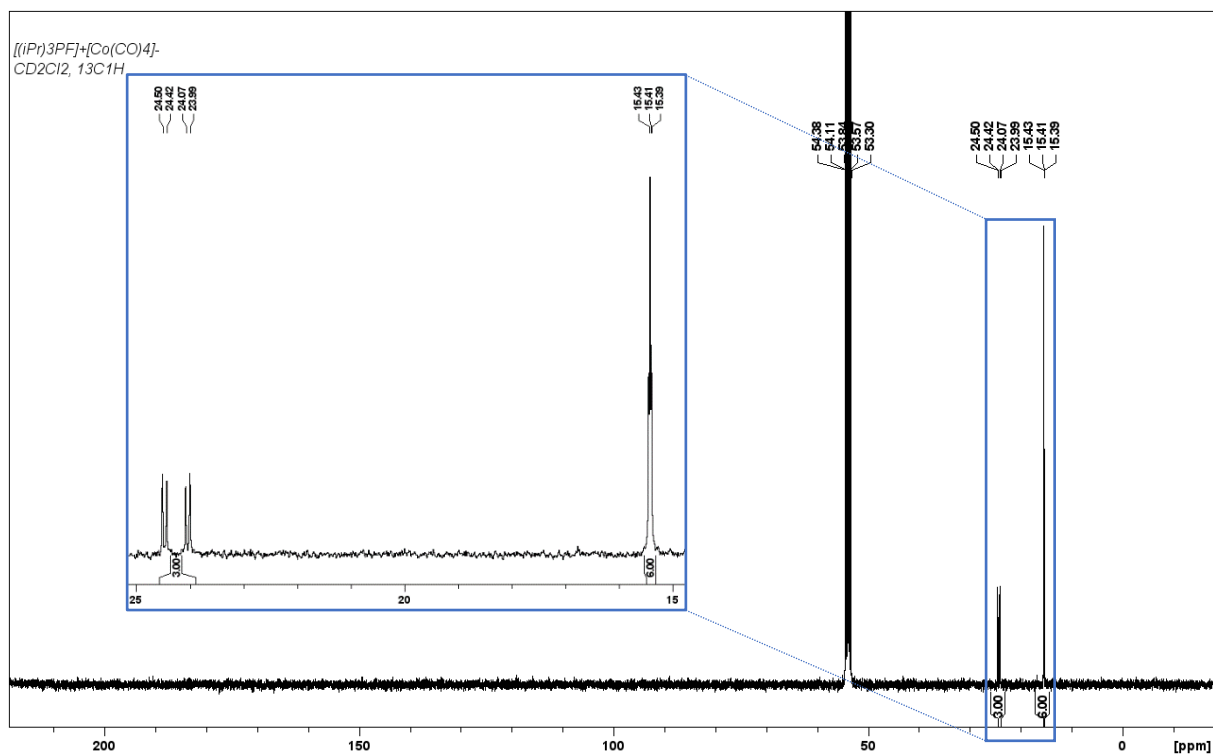


Figure S34 – <sup>13</sup>C NMR spectrum of compound III (CD<sub>2</sub>Cl<sub>2</sub>).

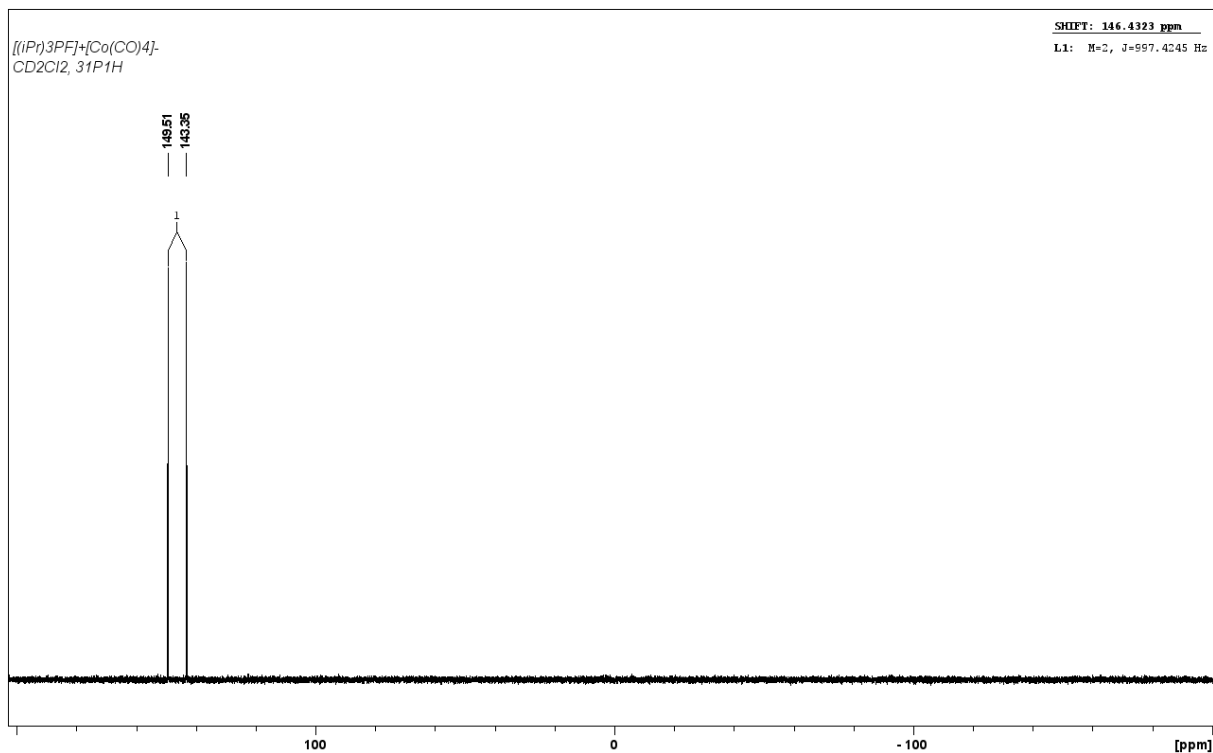


Figure S35 – <sup>31</sup>P NMR spectrum of compound **III** (CD<sub>2</sub>Cl<sub>2</sub>).

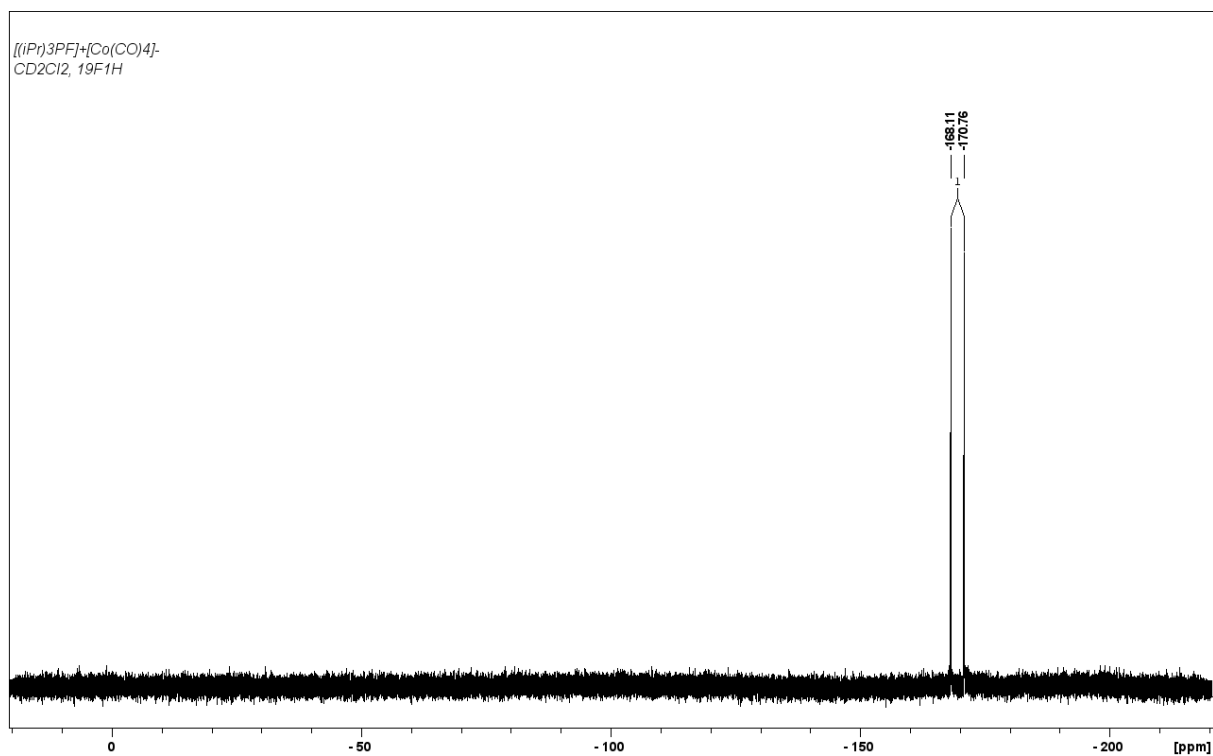


Figure S36 – <sup>19</sup>F NMR spectrum of compound **III** (CD<sub>2</sub>Cl<sub>2</sub>).

## 5.4 Compound IV: $[\text{tBu}_3\text{PF}]^+[\text{Co}(\text{CO})_4]^-$

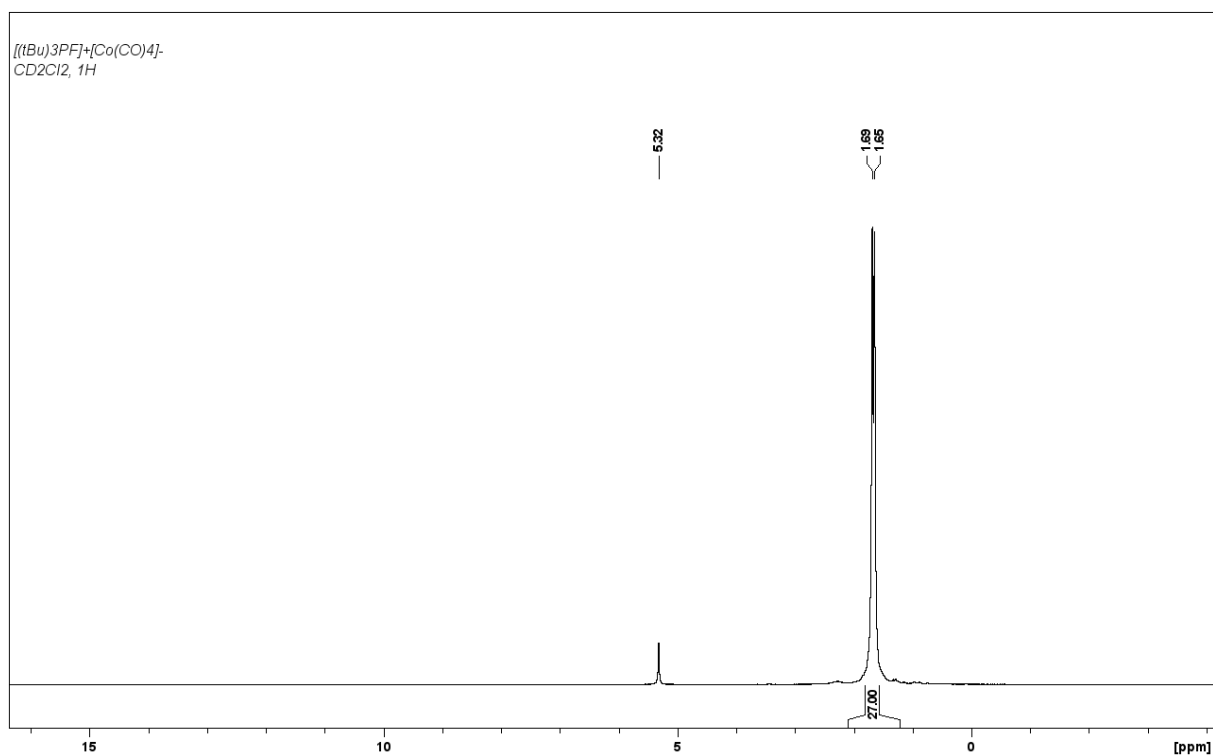


Figure S37 –  $^1\text{H}$  NMR spectrum of compound IV ( $\text{CD}_2\text{Cl}_2$ ).

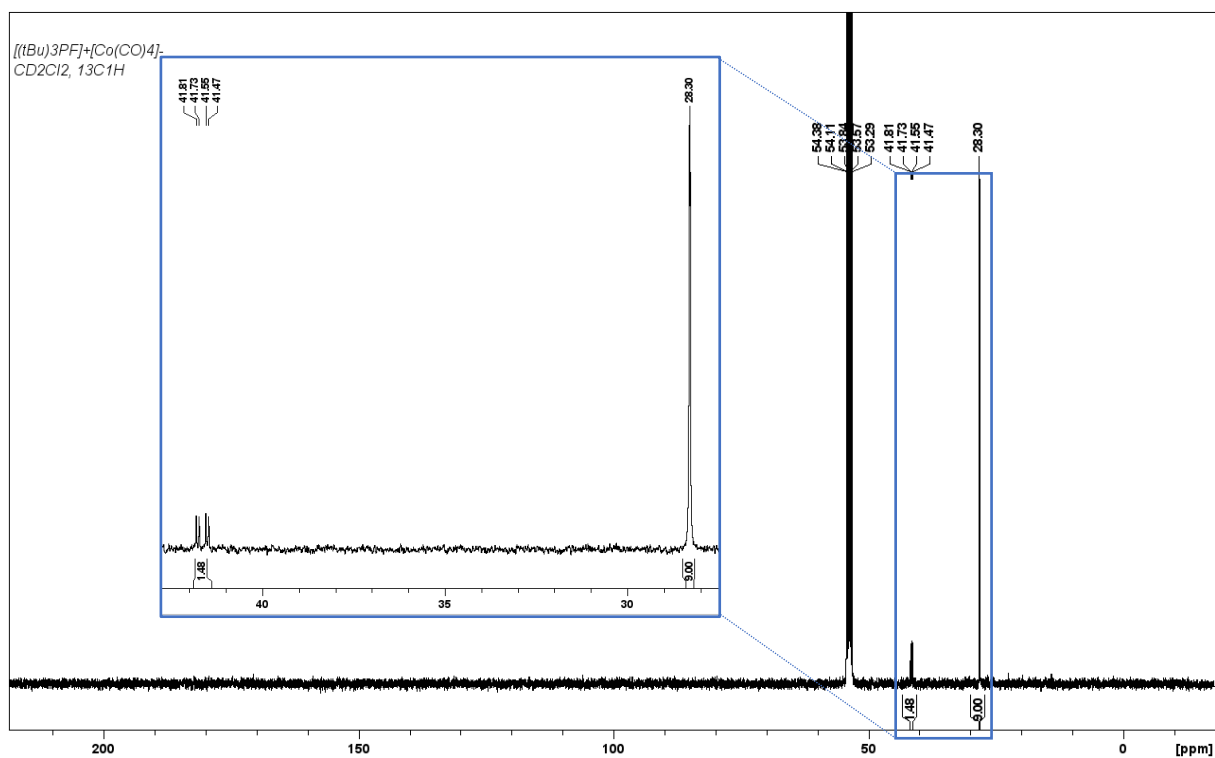


Figure S38 –  $^{13}\text{C}$  NMR spectrum of compound IV ( $\text{CD}_2\text{Cl}_2$ ).



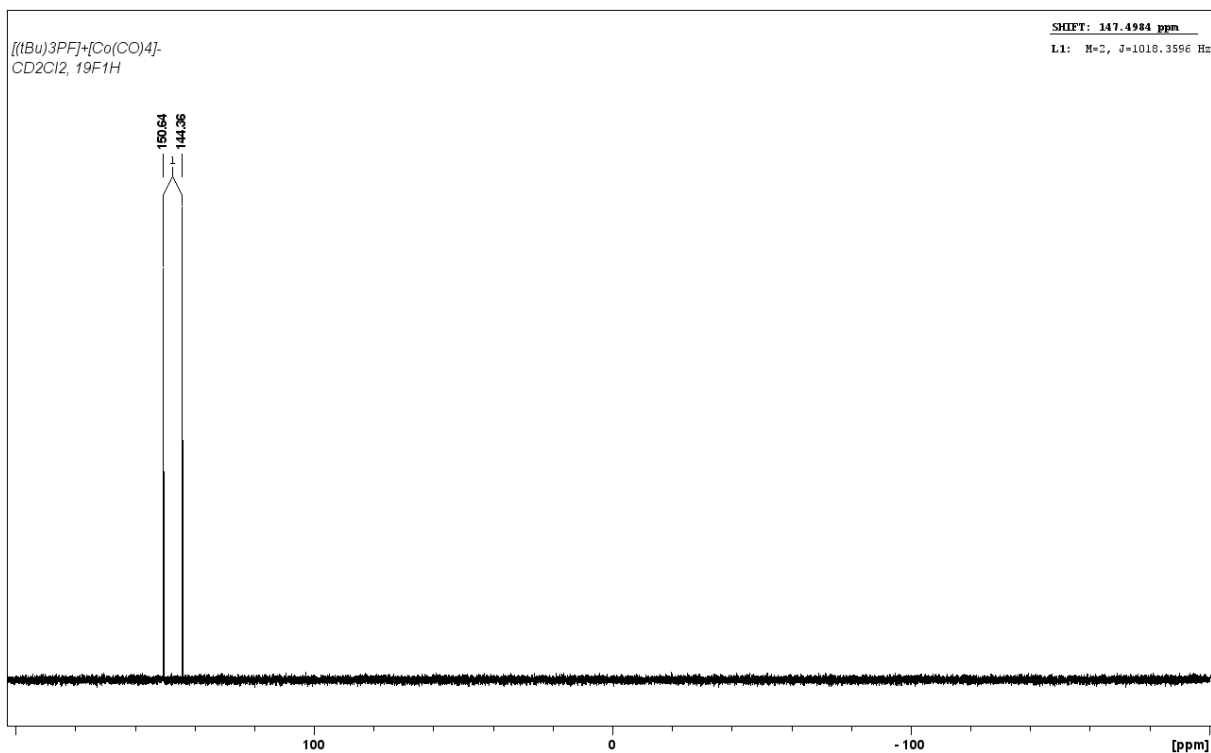


Figure S39 – <sup>31</sup>P NMR spectrum of compound IV (CD<sub>2</sub>Cl<sub>2</sub>).

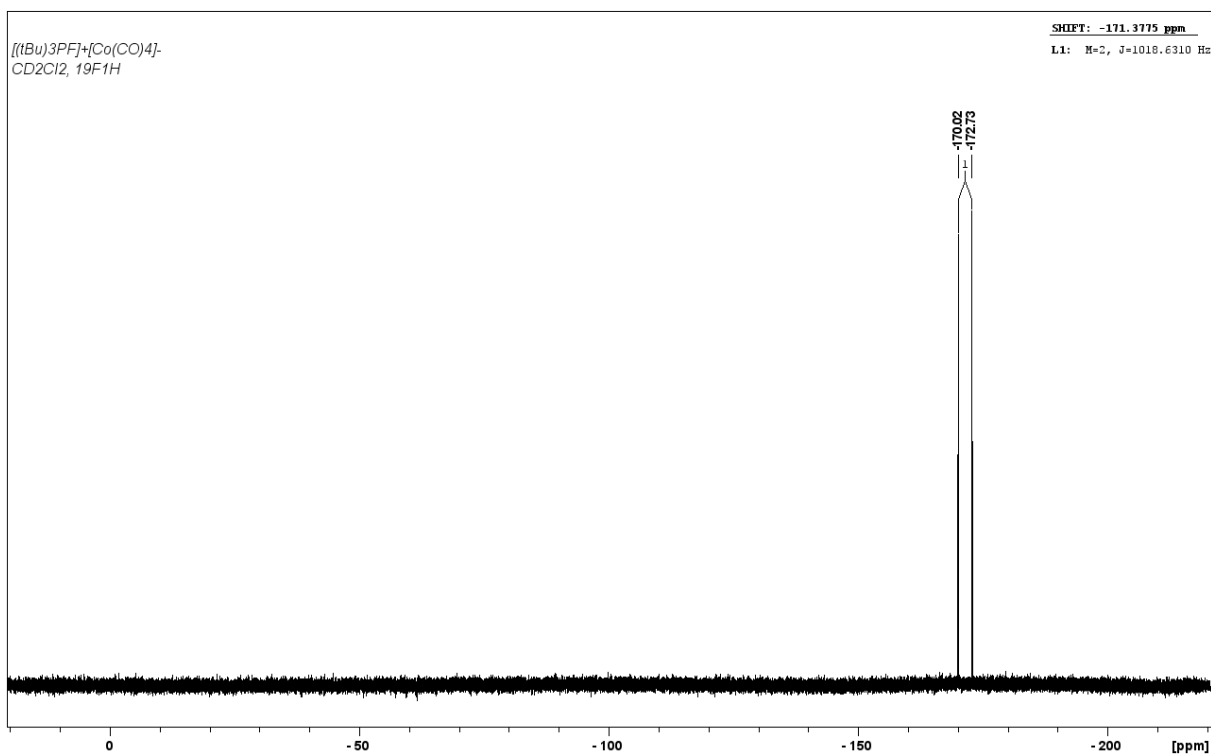


Figure S40 – <sup>19</sup>F NMR spectrum of compound IV (CD<sub>2</sub>Cl<sub>2</sub>).

## 5.5 Attempted synthesis of $[\text{Ph}_3\text{PF}]^+[\text{Co}(\text{CO})_4]^-$

As described in section 3.1, the synthesis of  $[\text{Ph}_3\text{PF}]^+[\text{Co}(\text{CO})_4]^-$  was attempted. Below are displayed the  $^{31}\text{P}$  and  $^{19}\text{F}$  NMR spectra of the best quality material obtained after several attempts of purification (Figure S41 and Figure S42), and the spectra of the same NMR tube after a few days at room temperature (Figure S43 and Figure S44).  $[\text{Ph}_3\text{PF}]^+[\text{Co}(\text{CO})_4]^-$  peak in  $^{31}\text{P}$  NMR was at 95 ppm (d,  $J_{\text{P-F}} \approx 997$  Hz), and at  $-128$  ppm (d,  $J_{\text{P-F}} \approx 996$  Hz) in  $^{19}\text{F}$  NMR. In accordance with the literature,<sup>10</sup>  $\text{F}_2\text{PPh}_3$  was observed at  $-55$  ppm (t,  $J_{\text{P-F}} \approx 660$  Hz) in  $^{31}\text{P}$  NMR, and at  $-40$  ppm (d,  $J_{\text{P-F}} \approx 650$  Hz) in  $^{19}\text{F}$  NMR. The peaks at  $65$ – $55$  ppm in  $^{31}\text{P}$  NMR could be attributed to a phosphine-ligated cobalt carbonyl complex (such as  $[\text{Co}(\text{CO})_3(\text{PPh}_3)_2][\text{Co}(\text{CO})_4]$  and/or  $[\text{Co}_2(\text{CO})_6(\text{PPh}_3)_2]$ ).<sup>11</sup>

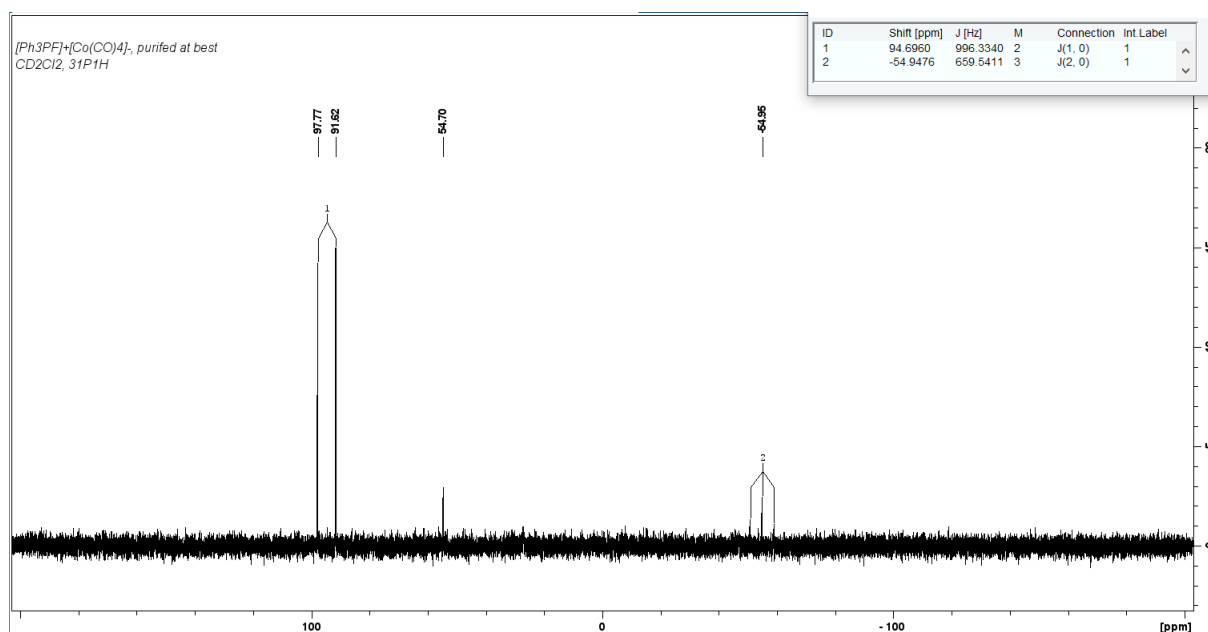


Figure S41 –  $^{31}\text{P}$  NMR spectrum of  $[\text{Ph}_3\text{PF}]^+[\text{Co}(\text{CO})_4]^-$ , purified at best ( $\text{CD}_2\text{Cl}_2$ ).

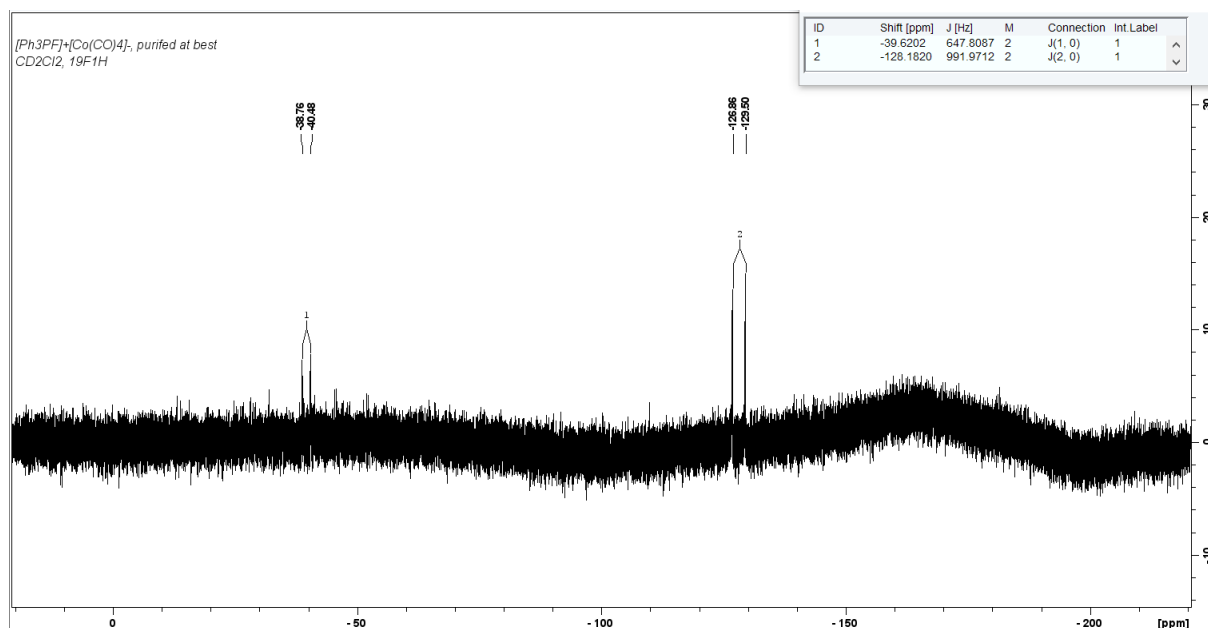


Figure S42 –  $^{19}\text{F}$  NMR spectrum of  $[\text{Ph}_3\text{PF}]^+[\text{Co}(\text{CO})_4]^-$ , purified at best ( $\text{CD}_2\text{Cl}_2$ ).

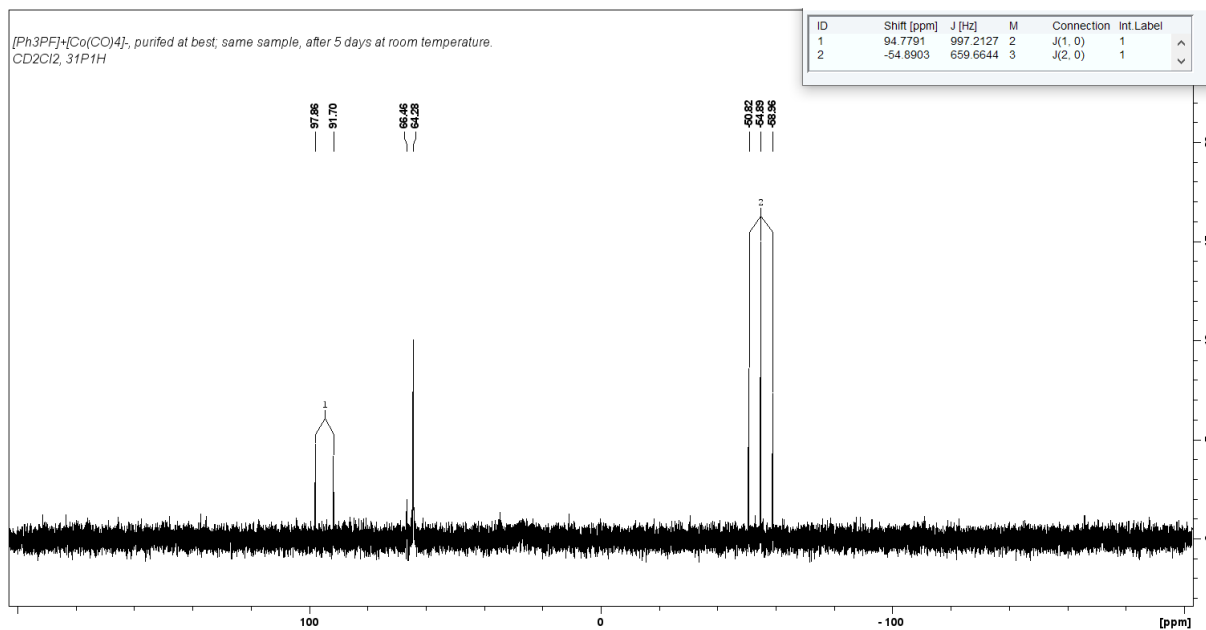


Figure S43 – <sup>31</sup>P NMR spectrum of the same sample as in Figure S41 and Figure S42, after 5 days at room temperature (CD<sub>2</sub>Cl<sub>2</sub>).

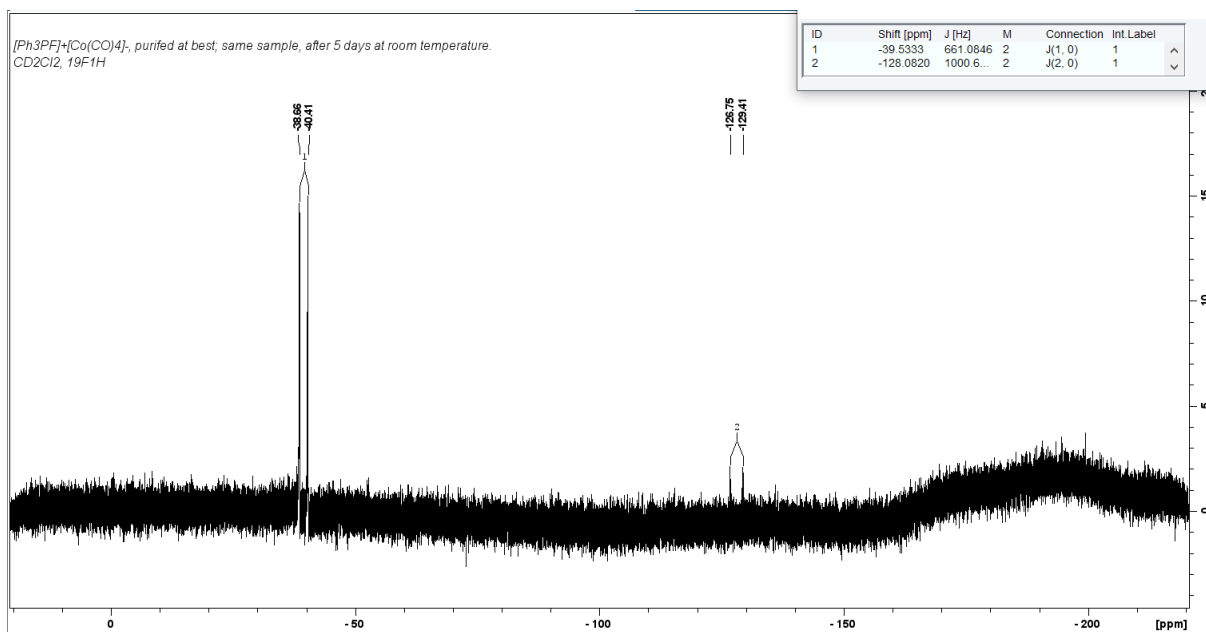


Figure S44 – <sup>19</sup>F NMR spectrum of the same sample as in Figure S41 and Figure S42, after 5 days at room temperature (CD<sub>2</sub>Cl<sub>2</sub>).

## 6 Infrared spectra

Solid samples of complexes **I-IV** stored under argon atmosphere were used to perform the infrared spectra below. The samples were analyzed under air; overall they were exposed to air for less than one minute prior to analysis. No visible degradation (change of color) was observed then.

After being exposed overnight to air, **I** kept its original yellow color, while **II** and **IV** turned light pink, and **III** turned emerald green.

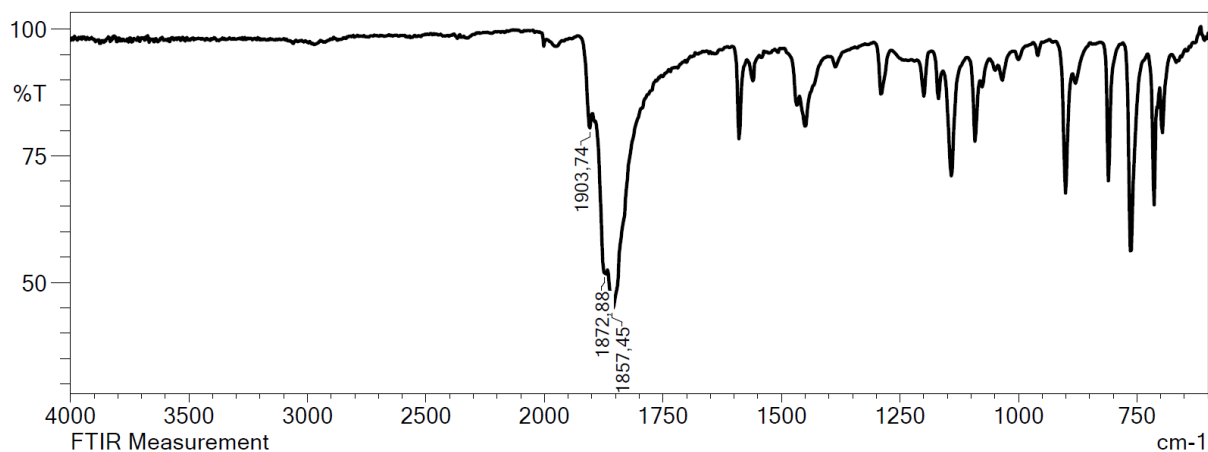


Figure S45 – Infrared spectrum of **I**.

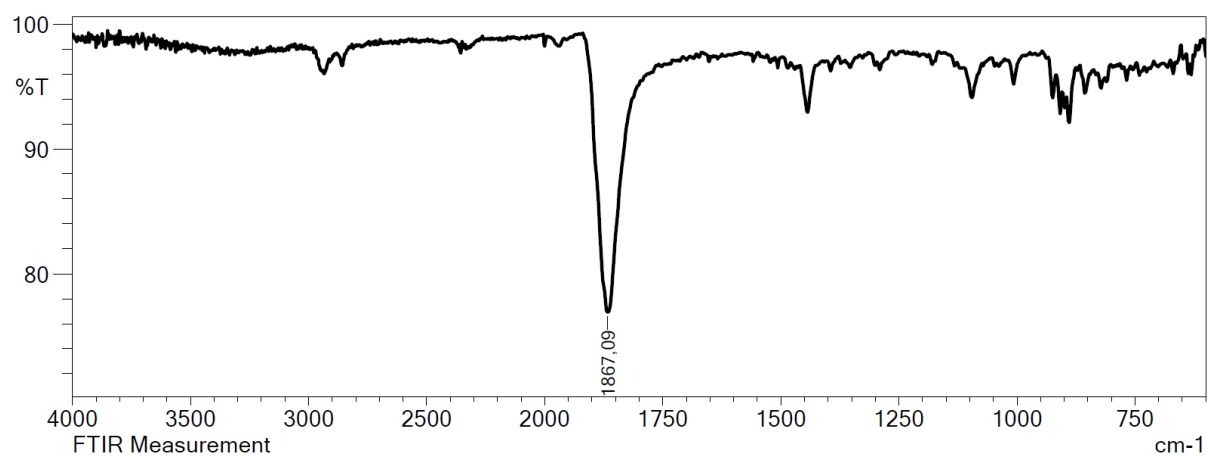


Figure S46 – Infrared spectrum of **II**.

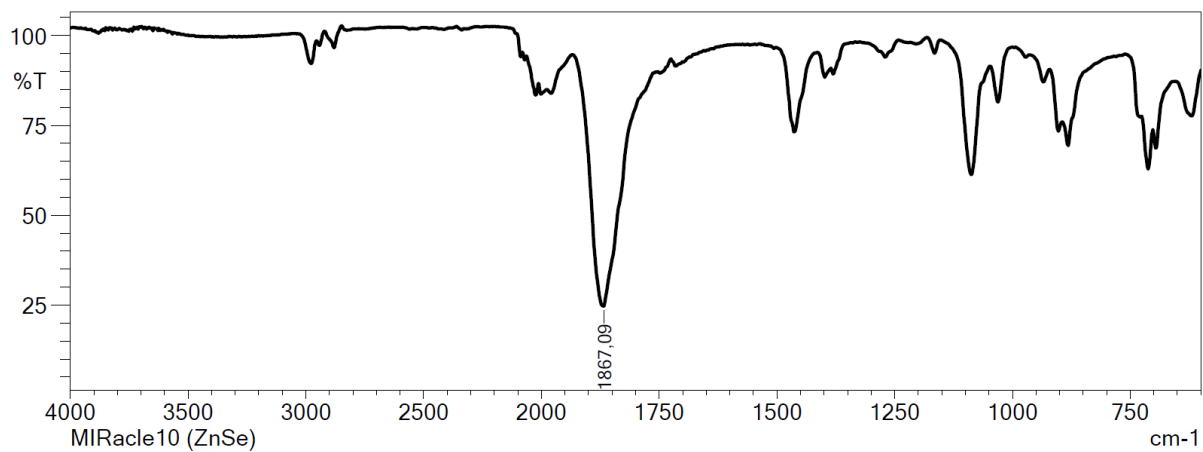


Figure S47 – Infrared spectrum of **III**.

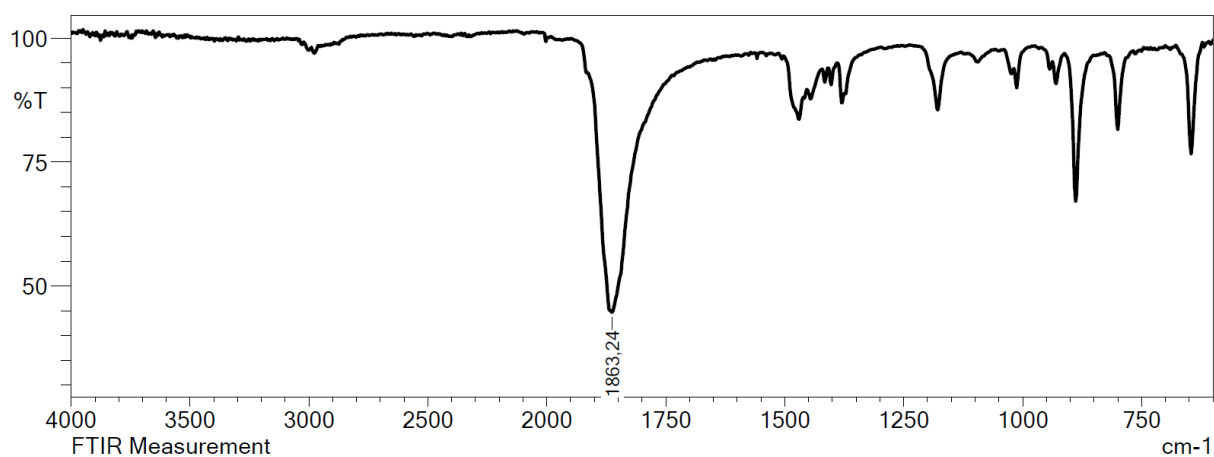


Figure S48 – Infrared spectrum of **IV**.

## 7 Crystallography

Table S4 – Crystal data and structure refinement details.

	I	II	IV
Chemical formula	C <sub>25</sub> H <sub>21</sub> CoFO <sub>4</sub> P	C <sub>22</sub> H <sub>33</sub> CoFO <sub>4</sub> P	C <sub>16</sub> H <sub>27</sub> CoFO <sub>4</sub> P
<i>M</i> /g mol <sup>-1</sup>	494.32	470.38	392.27
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	<i>C2/c</i>	<i>Pnma</i>	<i>Pbca</i>
<i>a</i> /Å	20.3694(10)	16.5748(4)	14.9882(5)
<i>b</i> /Å	11.8516(6)	13.6875(3)	15.8456(5)
<i>c</i> /Å	19.7496(10)	10.2341(3)	16.4634(5)
$\alpha$ /°	90	90	90
$\beta$ /°	106.8546(18)	90	90
$\gamma$ /°	90	90	90
<i>V</i> /Å <sup>3</sup>	4562.9(4)	2321.79(10)	3910.0(2)
<i>Z</i>	8	4	8
Reflections collected	134848	72276	145437
Independent reflections	6955	3679	5975
Observed reflections [ <i>I</i> > 2σ( <i>I</i> )]	5730	3234	4607
<i>R</i> <sub>int</sub>	0.079	0.043	0.100
Parameters refined	292	148	217
<i>R</i> <sub>1</sub>	0.031	0.026	0.035
w <i>R</i> <sub>2</sub>	0.082	0.071	0.080
<i>S</i>	1.046	1.076	1.087
$\Delta\rho_{\text{min}}$ /e Å <sup>-3</sup>	-0.53	-0.41	-0.43
$\Delta\rho_{\text{max}}$ /e Å <sup>-3</sup>	0.68	0.38	0.42

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