Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Additive-Free Cobalt-Catalysed Hydrogenation of Carbonates to Methanol and Alcohols

Francesco Ferretti,[a,b] Florian Korbinian Scharnagl,[a] Anna Dall'Anese,[a,c] Ralf Jackstell[a], Sarim Dastgir,[d] and Matthias Beller[a]*

[a] *Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany*

[b] *Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133 Milano, Italy*

[c] *Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via Licio Giorgieri 1, 34127 Trieste, Italy*

[d] *Qatar Environment and Energy Research Institute (QEERI), Hamad bin Khalifa University (HBKU), Qatar Foundation, Doha, Qatar*

General

All chemicals were purchased from commercial sources and were used as received without additional purification, if not stated otherwise. Molecular hydrogen was purchased by Linde. All experiments were carried out under argon atmosphere by using standard Schlenk-techniques, unless stated otherwise. Solvents were dried and distilled or directly used from a solvent purification system (MBraun). THF was stored over molecular sieves 3 Å. Diethyl carbonate was distilled prior to use. The ligands **L2** – **L6**,[37] **L7** – **L9**,[40] **L11**,[40] **L15**,[41] **L16**,[42] **L17**,[43] **L19**,[44] and **L20**[45] have been synthesised according to literature-reported procedures. All other ligands have been purchased from commercial sources.

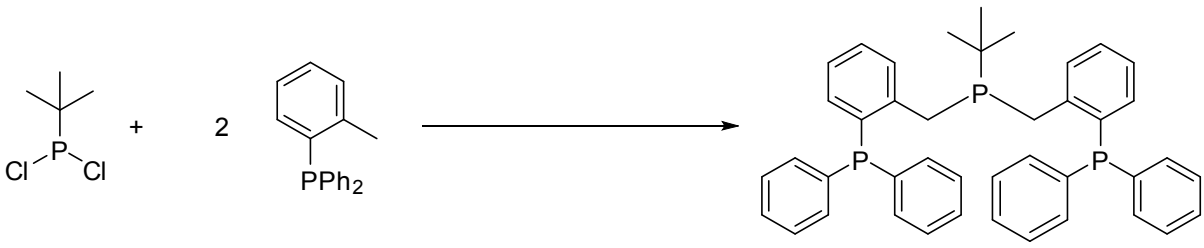
Catalytic experiments were conducted in 4 mL screw cap vials, closed with a polytetrafluoroethylene (PTFE)/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere by a needle, inside a 300 mL Parr autoclave and stirred with a magnetic stirring bar. GC measurements were carried out on a 7890A GC-System with HP-5 column (polydimethylsiloxane with 5% phenyl groups, length 30 m, i.d. 0.32 mm, film 0.25 µm) and with a FID coupled with a 7693 autosampler from Agilent Technologies. Argon was used as carrier gas. GC-analyses for methanol quantification were performed on an Agilent HP-6890 chromatograph with a FID detector and an Agilent HP Ultra 1 column (19091A-105, 50 m, 0.20mm i.d., 0.33 mm film thickness, 100% dimethylpolysiloxane) using argon as carrier gas.

Catalytic Experiments

In a typical catalytic experiment, $Co(BF_4)_2{\cdot}_6H_2O$ (6.81 mg, 2.0 mmol) and ligand (2.4 mmol) were fast weighed in the air and transferred into a 4 mL glass vial. If used, solid substrates were also weighed in the air and added into the vial. The vial was subsequently set under argon. 2.0 mL solvent were added and the mixture stirred for 5-10 min. Then, liquid substrates were added and the vials were placed in a metal plate inside a 300 mL autoclave. After closing, the reactor was pressurised with hydrogen (about 20 bar), which was released again. This procedure was carried out three times, after which 50 bar H_2 were introduced. The autoclave was then heated inside an aluminium block to 120 °C for 18 h. Afterwards the reaction was quenched with an ice-bath and the reactor vented. Hexadecane (30 µL) was added to the reaction as internal standard for GC, along with 2 mL THF. After proper mixing, GC was measured of the sample.

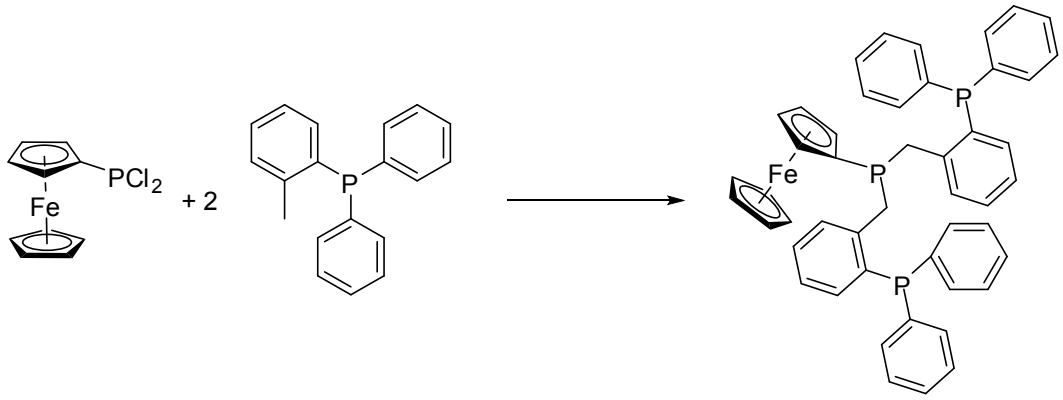
Ligand Synthesis

L10



1.73 g (6.26 mmol) diphenyl(*o*-tolyl)phosphine are dissolved in 20 mL Et_2O inside a 100 mL three-necked round bottom flask equipped with a magnetic stirring bar under argon. At room-temperature, 0.7 g (1 mL) TMEDA is added while stirring. In a 50 mL Schlenk-flask, 4 mL (6.2 mmol) of a 1.6 M *n*-BuLi solution in hexane are dried under vacuum and 5 mL Et_2O are added to the oily residue. This ethereal solution is added to the phosphine-solution *via* syringe at room-temperature under argon and while stirring, which leads to a change of colour to orange. The stirring is stopped and orange crystals are obtained within two hours. The liquid is filtered off and 20 mL Et_2O is added to the crystals. To this suspension, a solution of 0.5 g (3.13 mmol) *tert*-butyldichlorophosphine in 10 mL Et_2O is added while stirring. The orange crystals dissolve and lithium chloride precipitates. The exothermic reaction is cooled with a water-bath. After one hour the crystals are dissolved completely. Afterwards, the reaction mixture is washed three times with distilled water and the organic fraction is dried under vacuum. 30 mL methanol is added and the mixture shortly heated to 70 °C while stirring. After cooling down to room-temperature, the mixture is filtrated under argon and the solid dried under vacuum. The product is obtained as white solid (1.6 g, 80%).

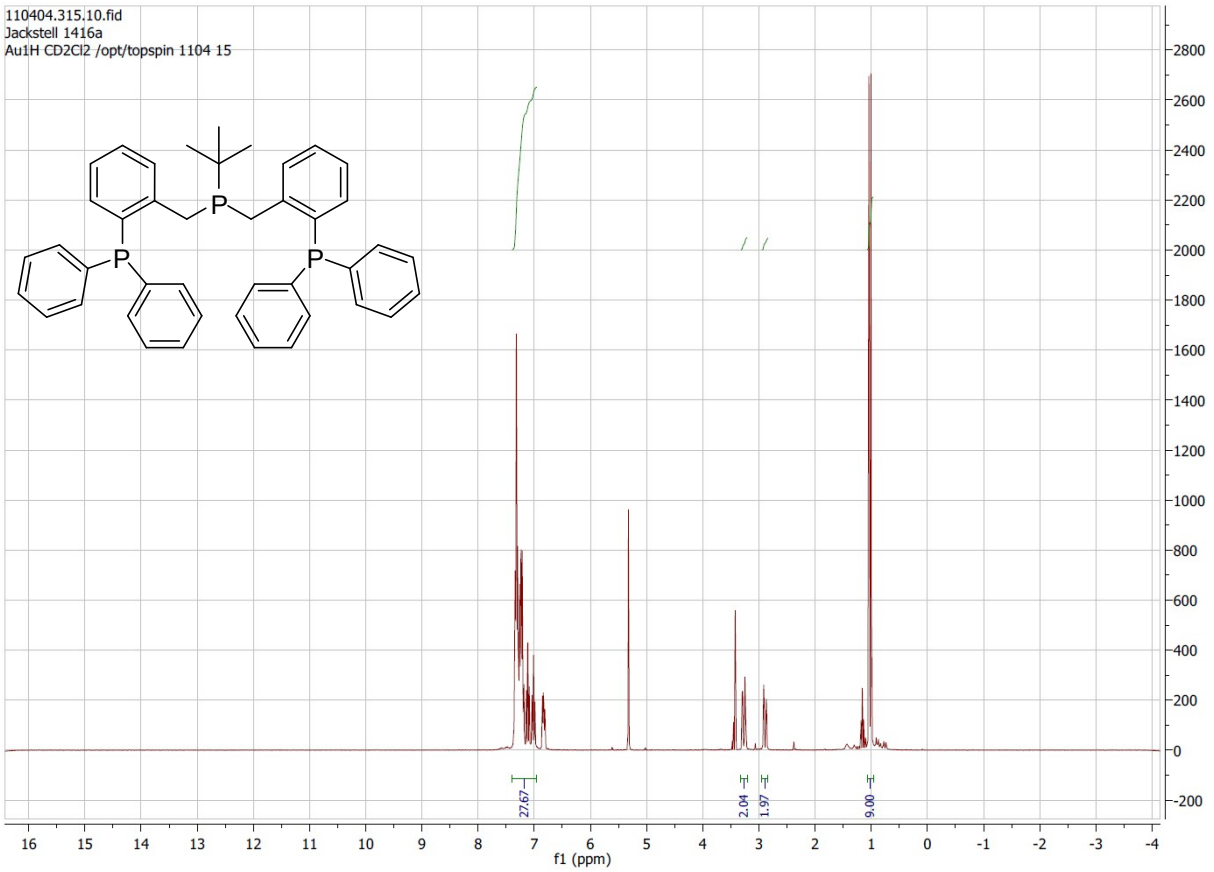
L13



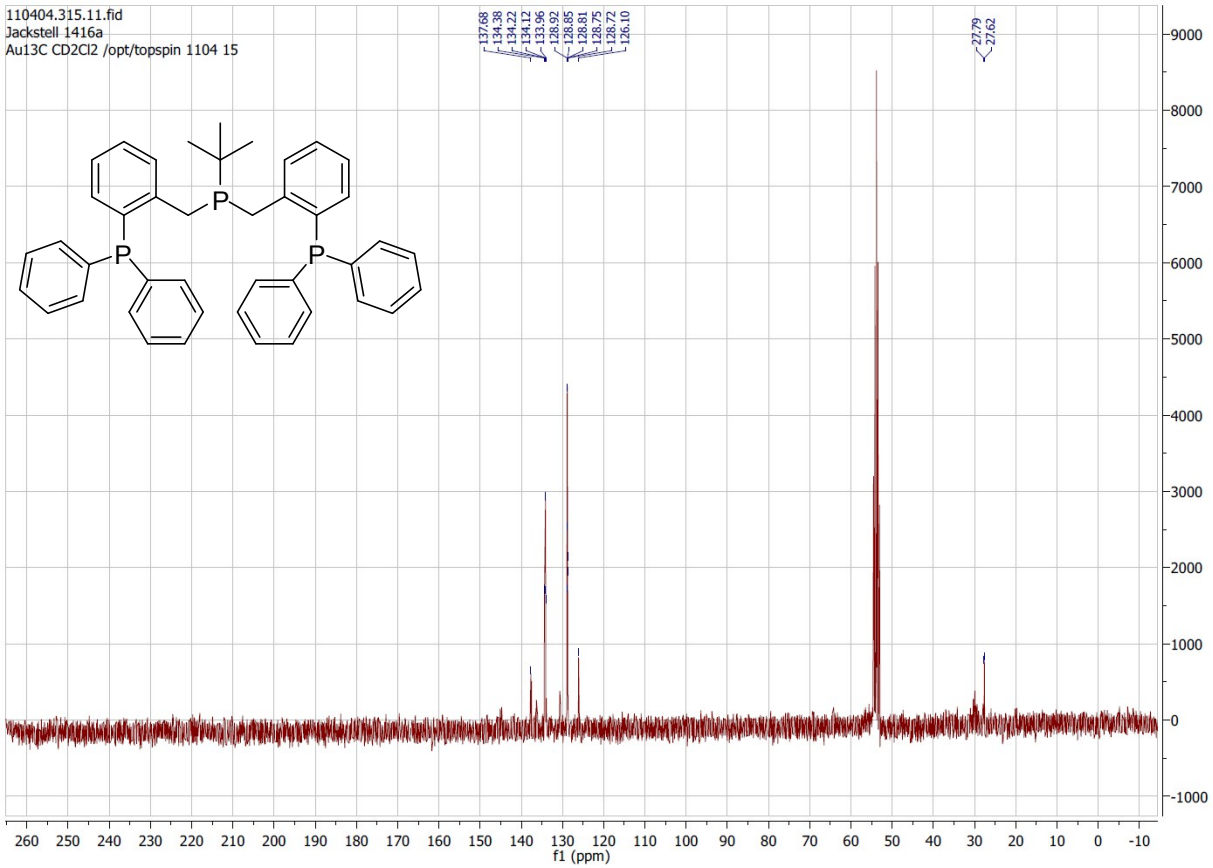
2.0 g (6.57 mmol) diphenyl(*o*-tolyl)phosphine are dissolved in 20 mL Et_2O inside a 50 mL Schlenk-flask equipped with a magnetic stirring bar under argon. At room-temperature, 0.8 g (1.3 mL) TMEDA is added while stirring. In a 50 mL Schlenk-flask, 5 mL (7.8 mmol) of a 1.6 M *n*-BuLi solution in hexane are dried under vacuum and 10 mL Et_2O is added to the oily residue. This ethereal solution is added to the phosphine-solution *via* syringe at room-temperature under argon and while stirring. The stirring is stopped and orange crystals are obtained within two hours. The liquid is decanted off and 20 mL Et_2O is added to the crystals. To this suspension, a solution of 0.9 g (3.14 mmol) *P*,*P*-Dichloroferrocenylphosphine in 10 mL heptane is added and stirred for 1 h. Additional 3 mL THF are added to complete the reaction. After an additional hour, the reaction solution is dried under vacuum. 20 mL toluene is added and the mixture is washed three times with distilled water and dried over Na_2SO_4. After filtration, the solution is evaporated to dryness, dissolved in ether and filtered over silica 60 G. After evaporation under argon, the product is obtained as an orange solid (1.6 g, 60%).

NMR spectra

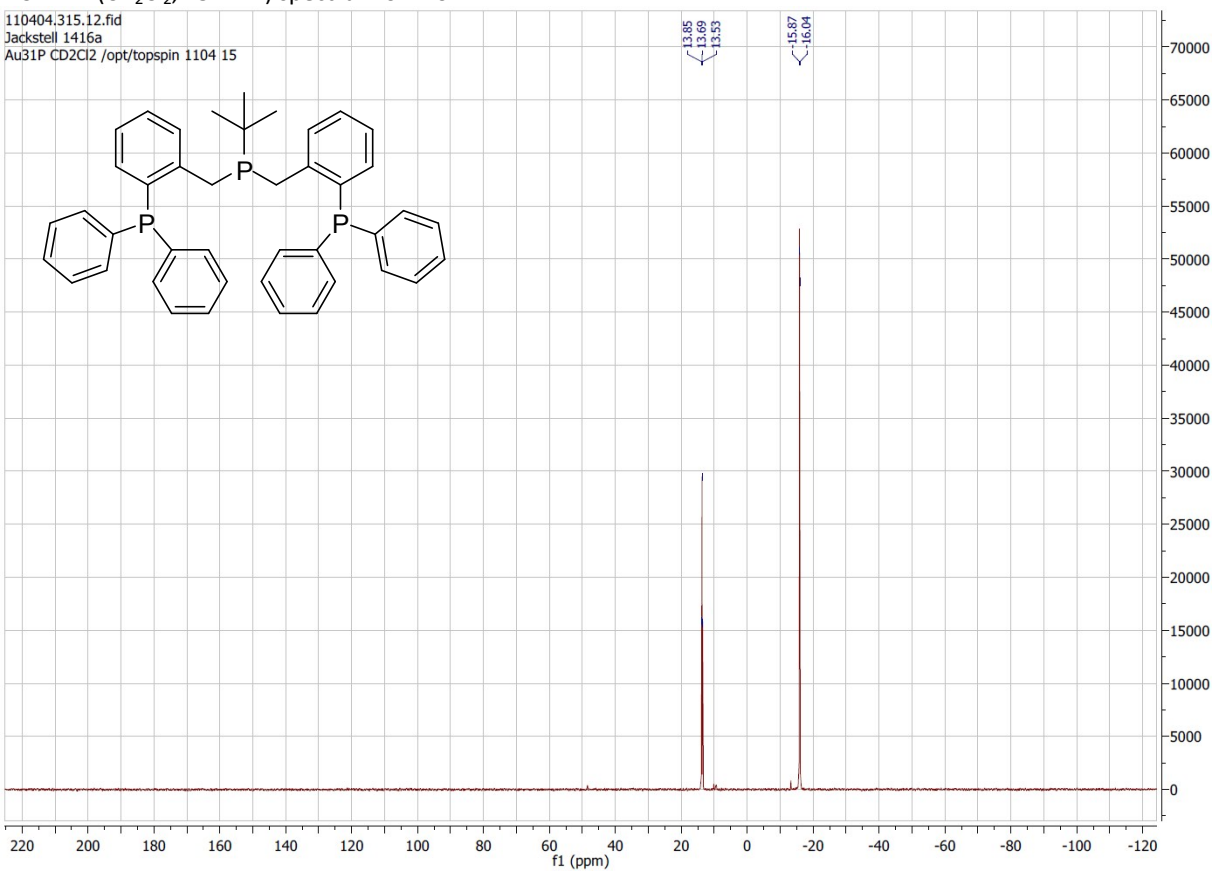
L10



^{1}H NMR (CD_2Cl_2, 300 MHz) spectrum of **L10**.

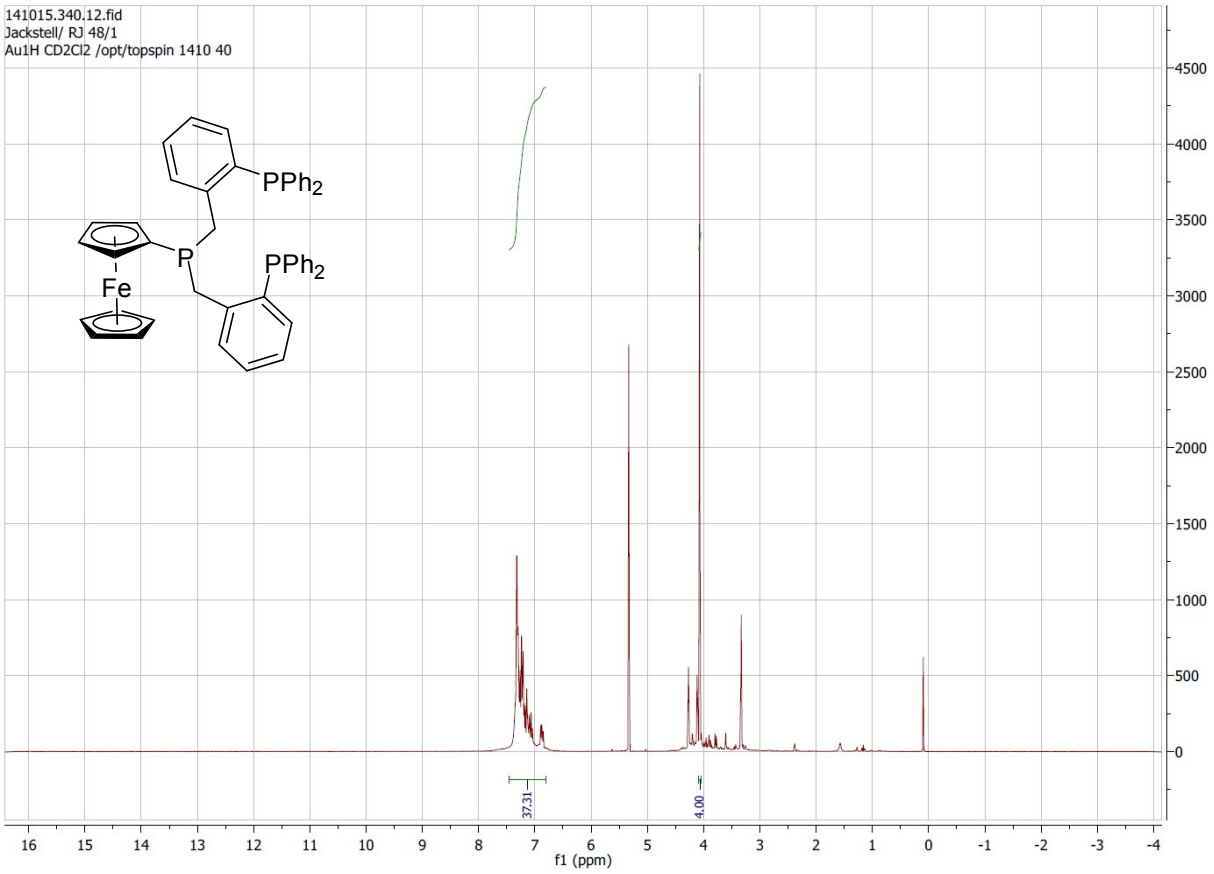


^{13}C NMR (CD_2Cl_2, 75 MHz) spectrum of **L10**.

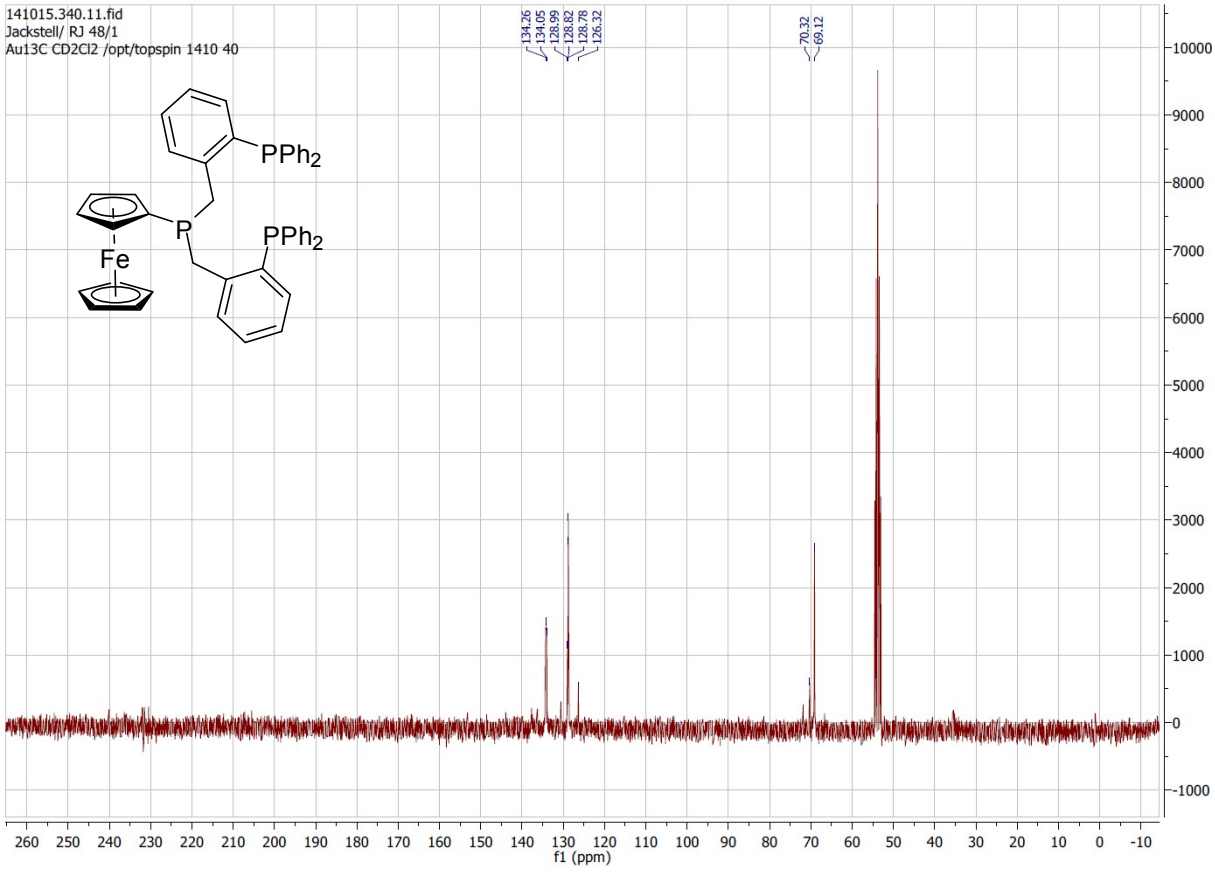


^{31}P NMR (CD_2Cl_2, 121 MHz) spectrum of **L10**.

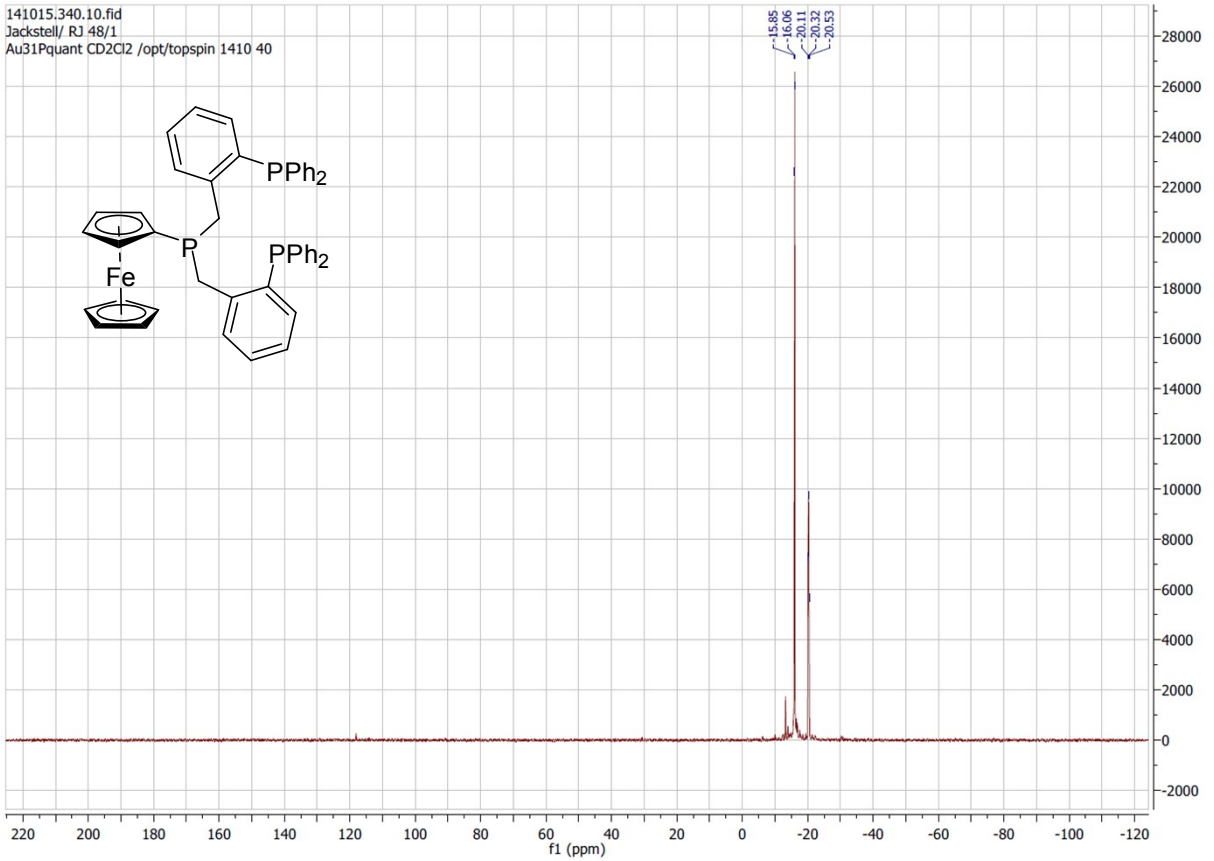
L13



^{1}H NMR (CD_2Cl_2, 300 MHz) spectrum of **L13**.



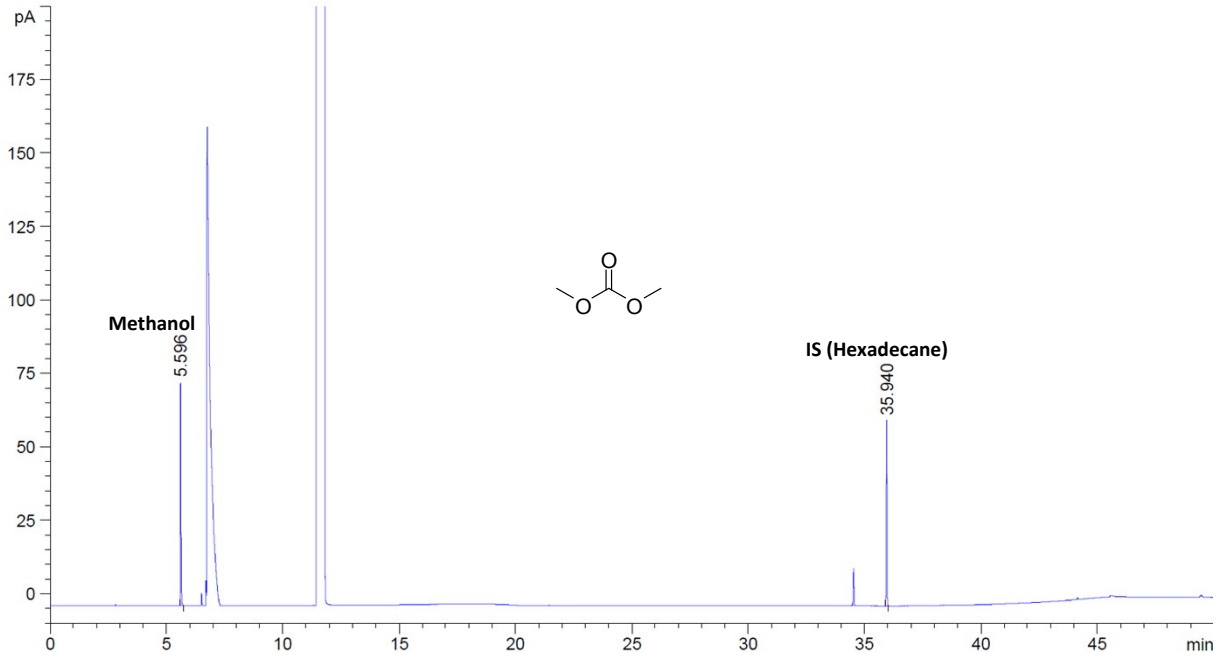
^{13}C NMR (CD_2Cl_2, 75 MHz) spectrum of **L13**.



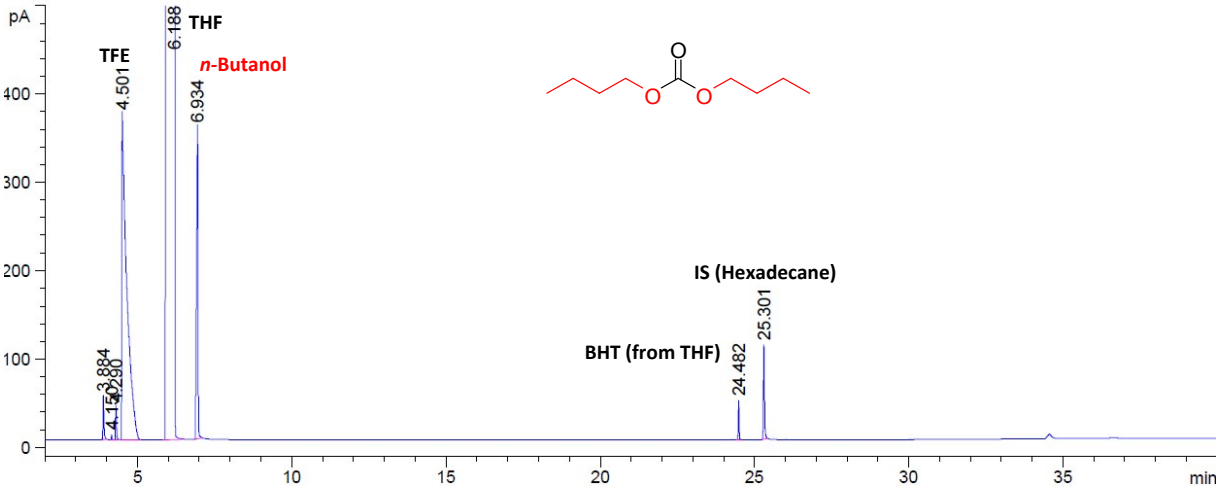
^{31}P NMR (CD_2Cl_2, 121 MHz) spectrum of **L13**.

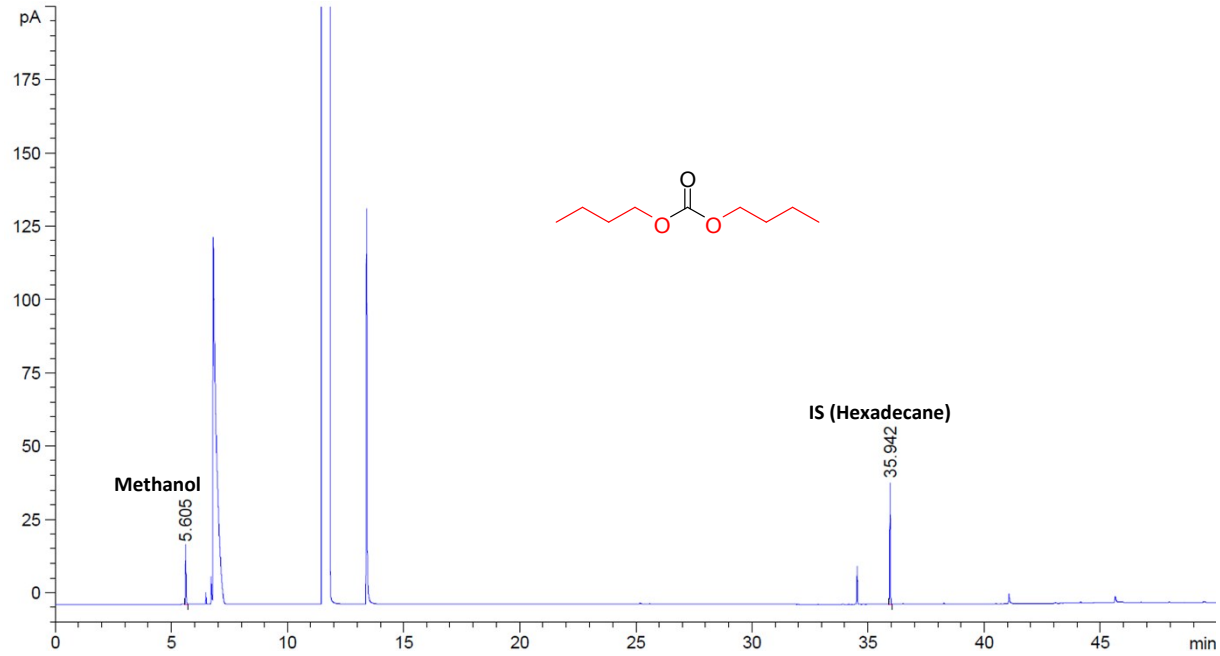
GC Chromatograms

Dimethyl carbonate (**1**)

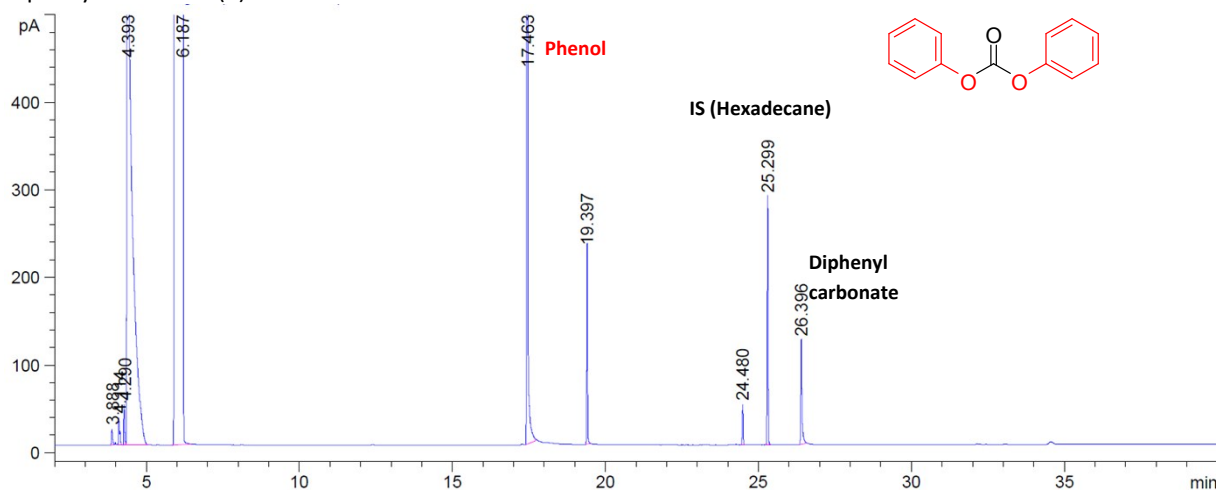


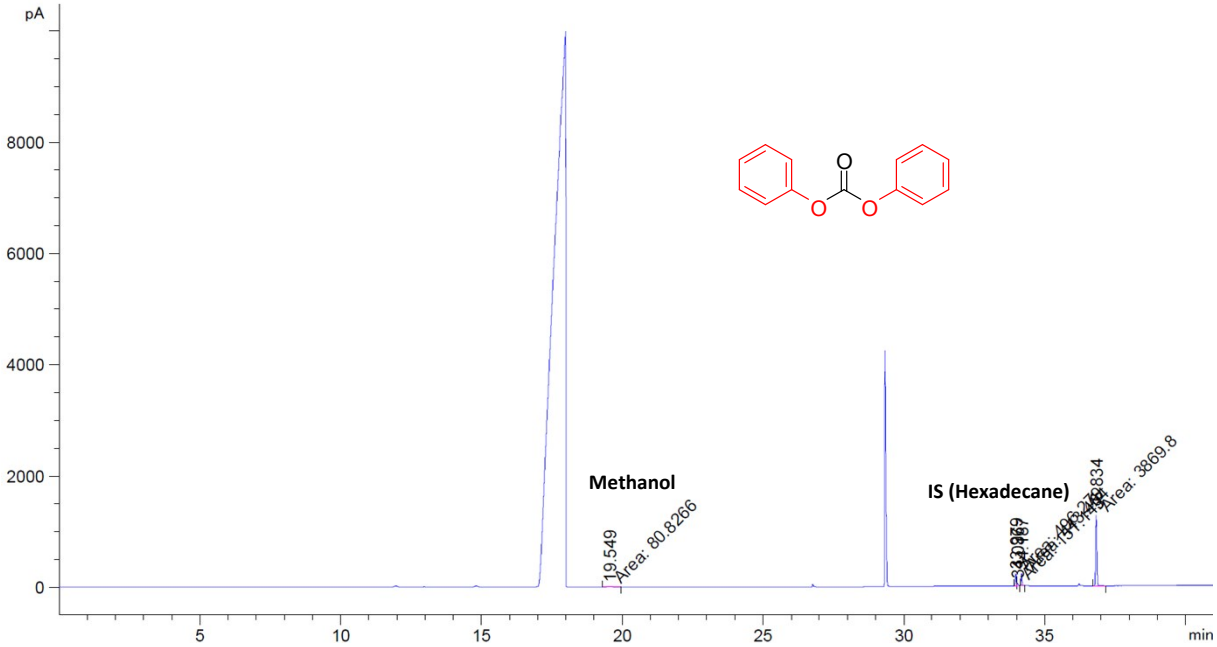
Dibutyl carbonate (**2**)



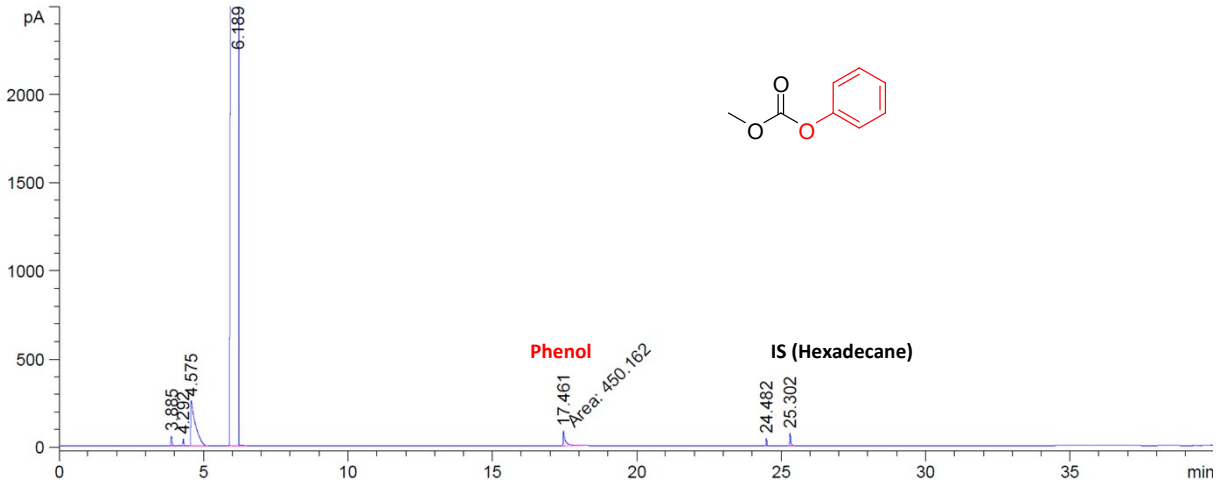


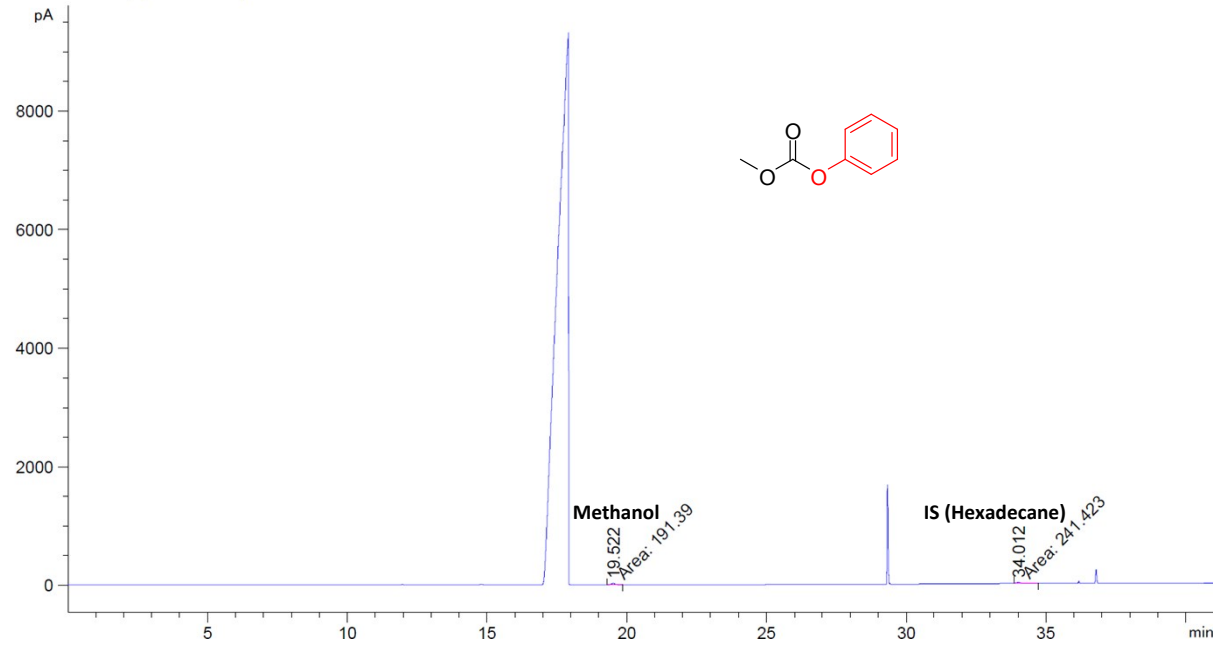
Diphenyl carbonate (**3**)



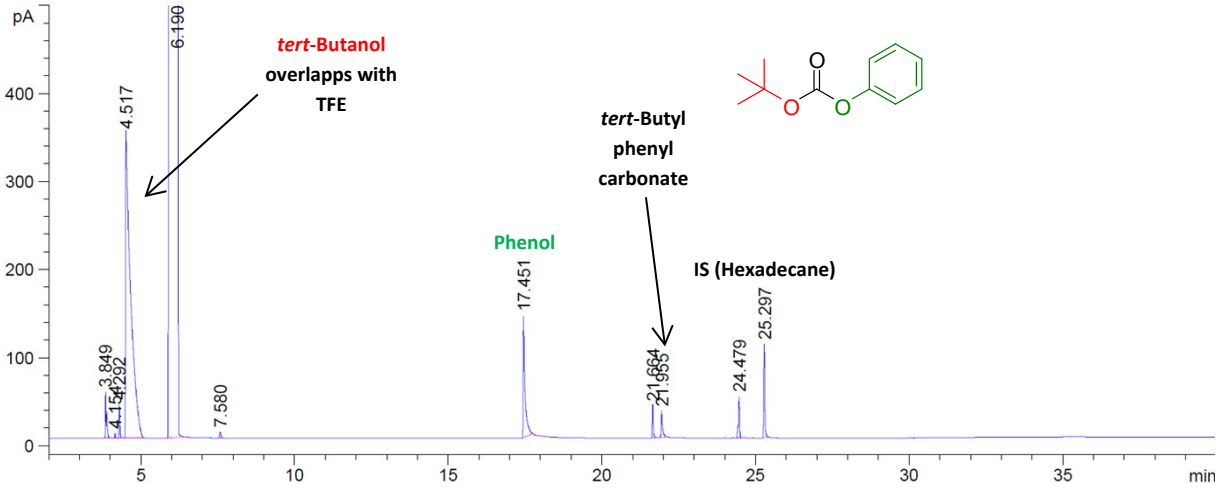


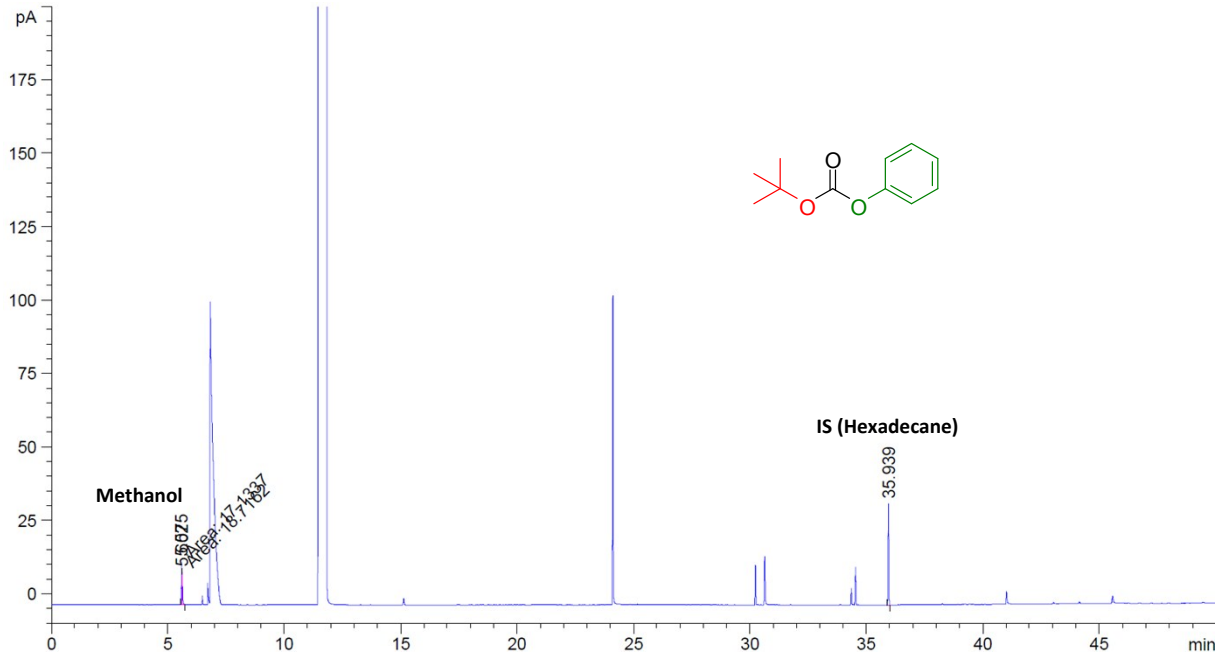
Methyl phenyl carbonate (**4**)



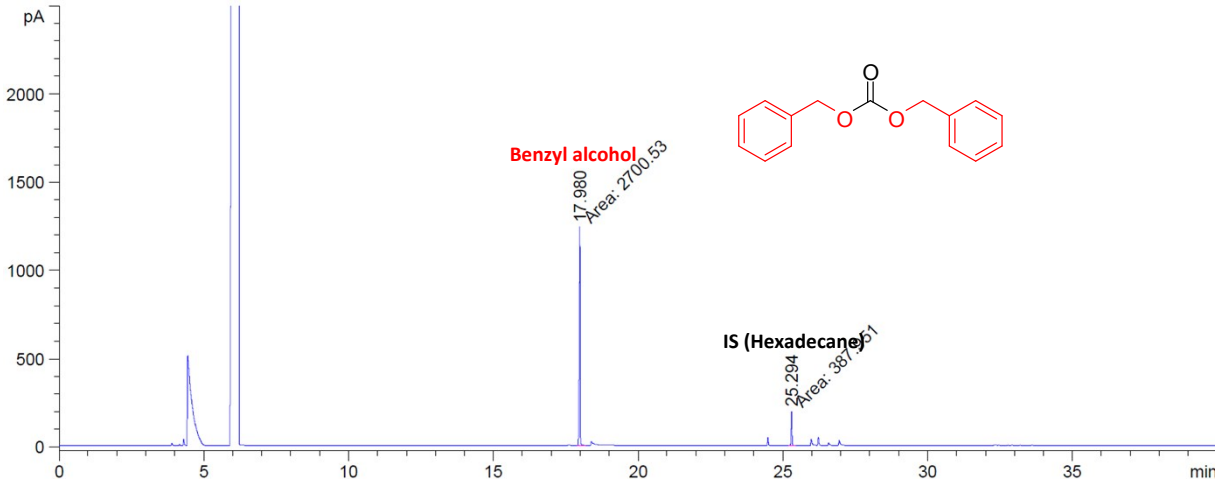


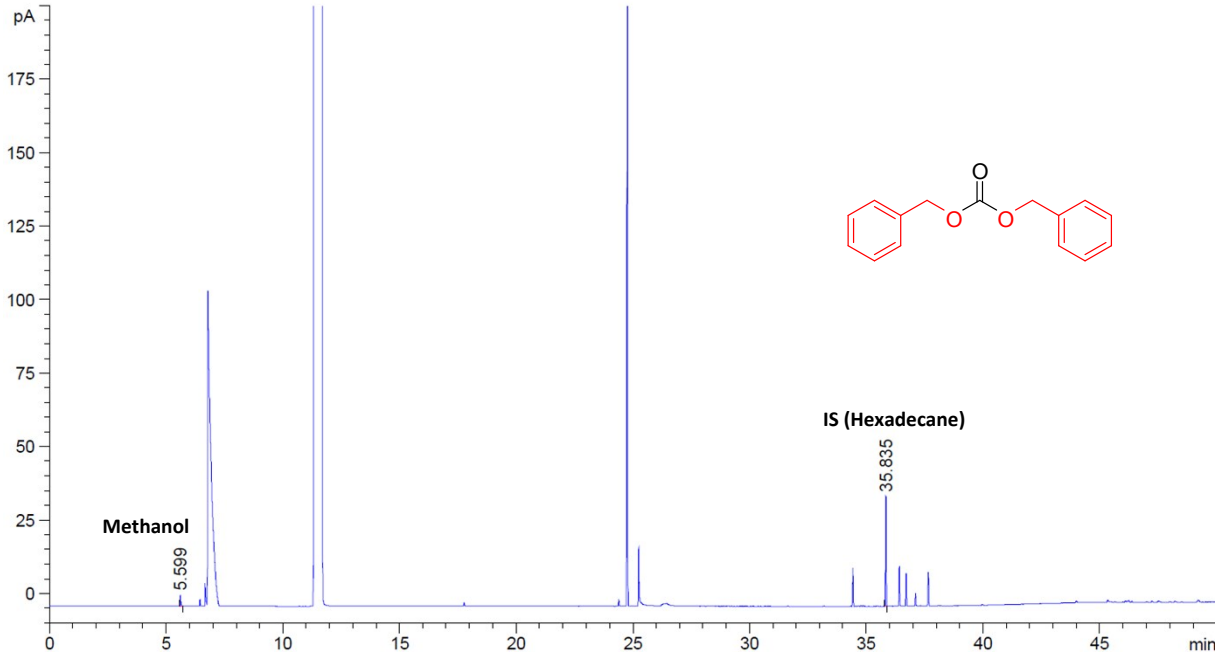
tert-Butyl phenyl carbonate (**5**)



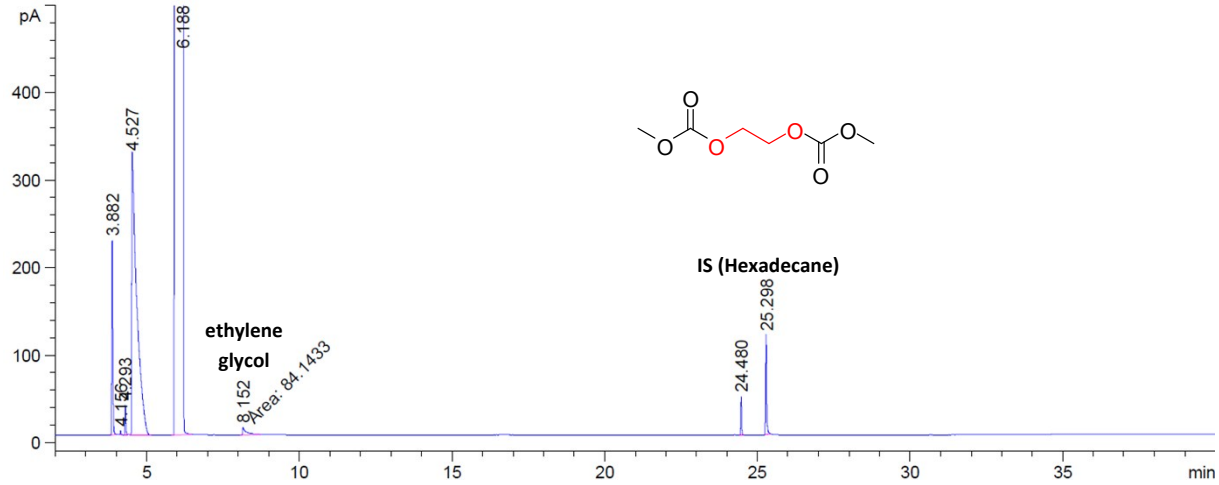


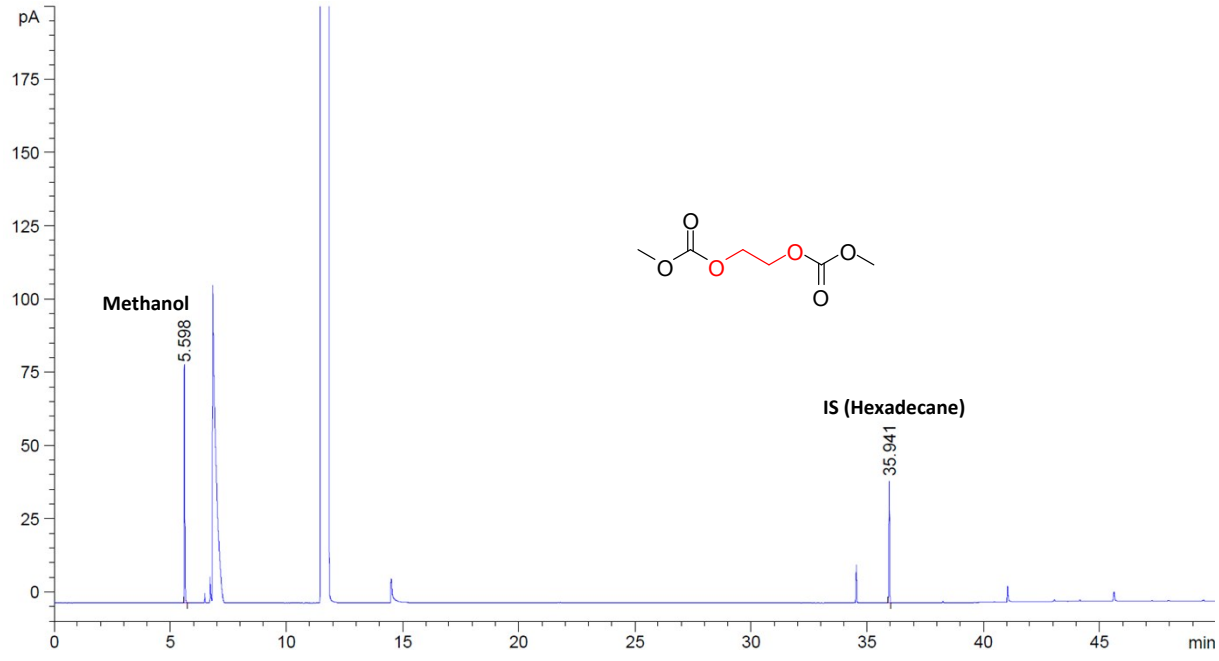
Dibenzyl carbonate (**6**)



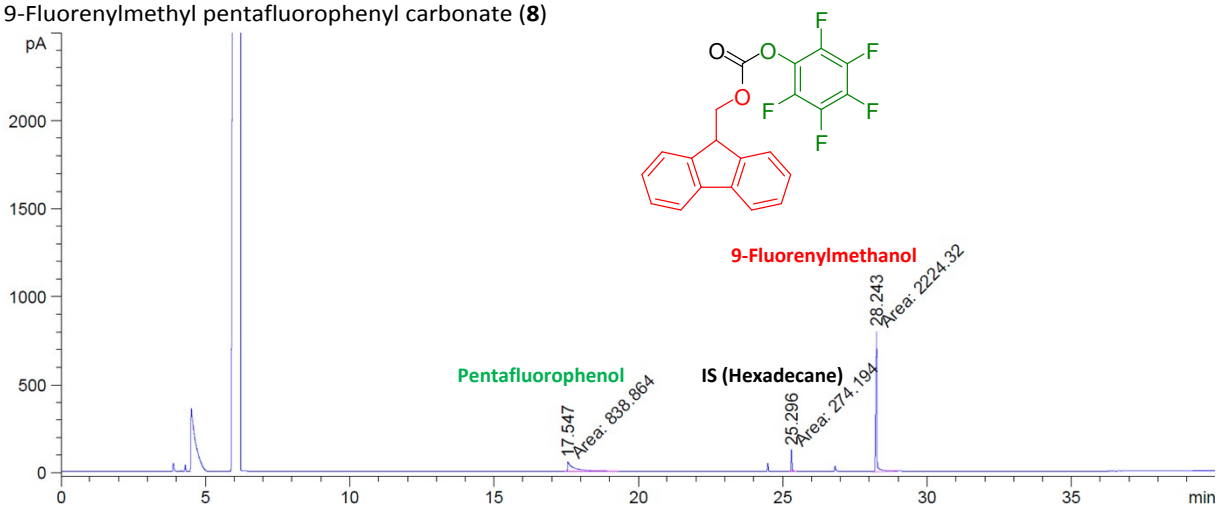


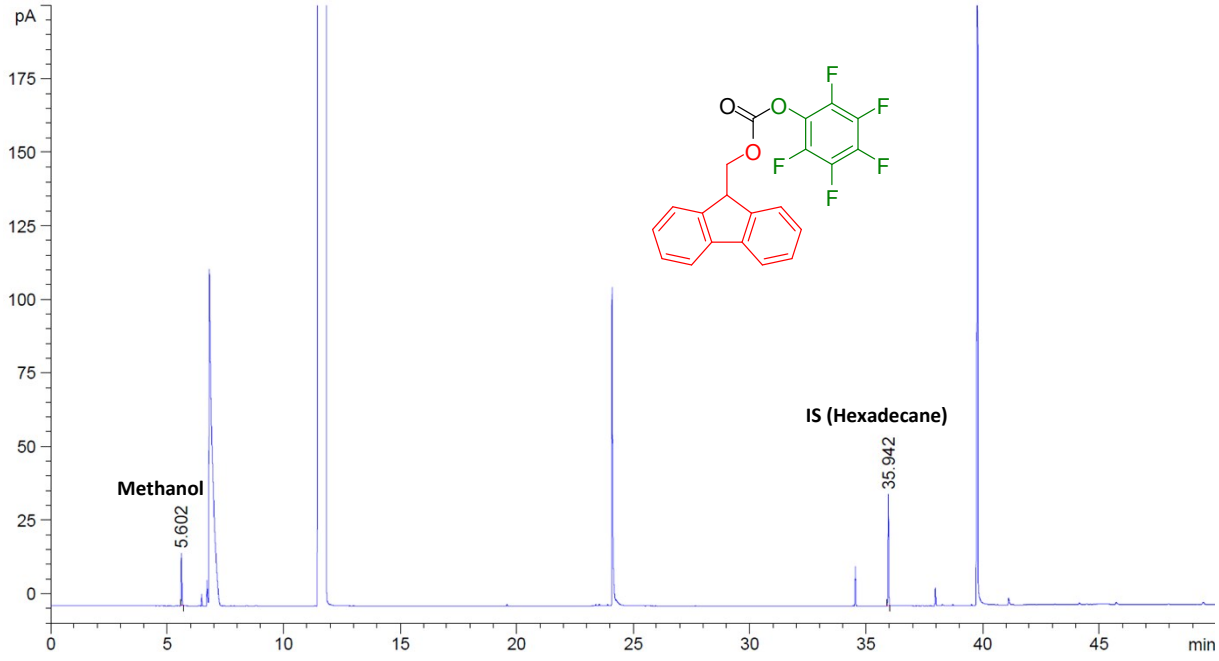
Dimethyl-2,5-dioxahexanedioate (**7**)



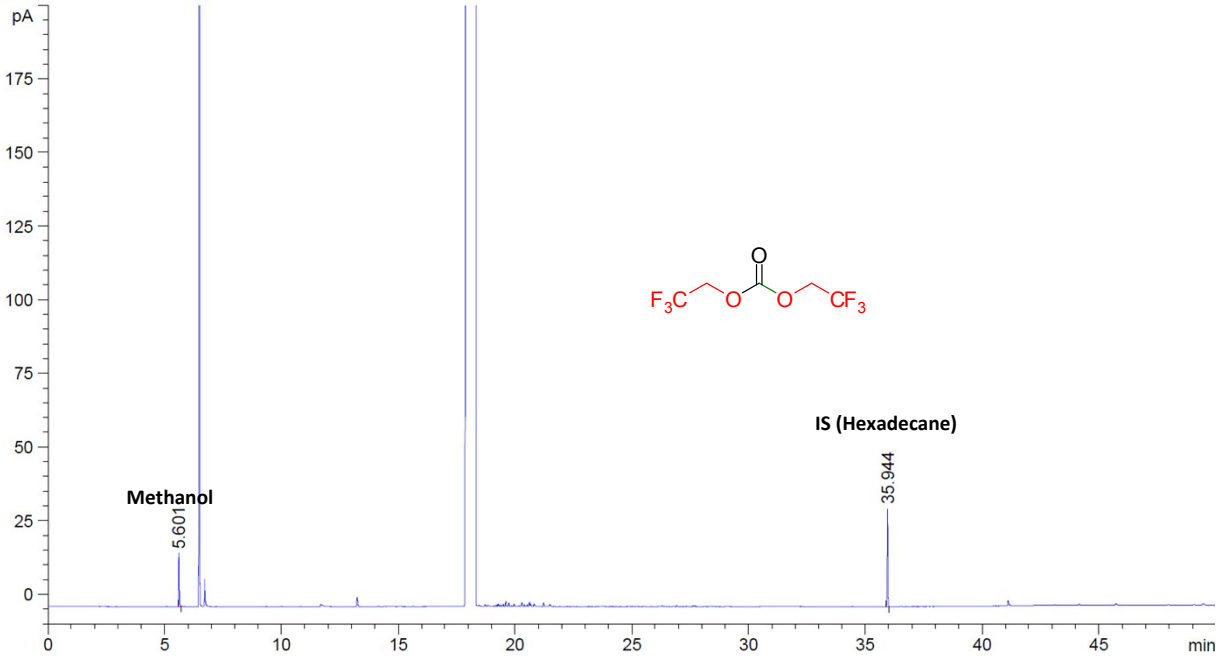


9-Fluorenylmethyl pentafluorophenyl carbonate (**8**)

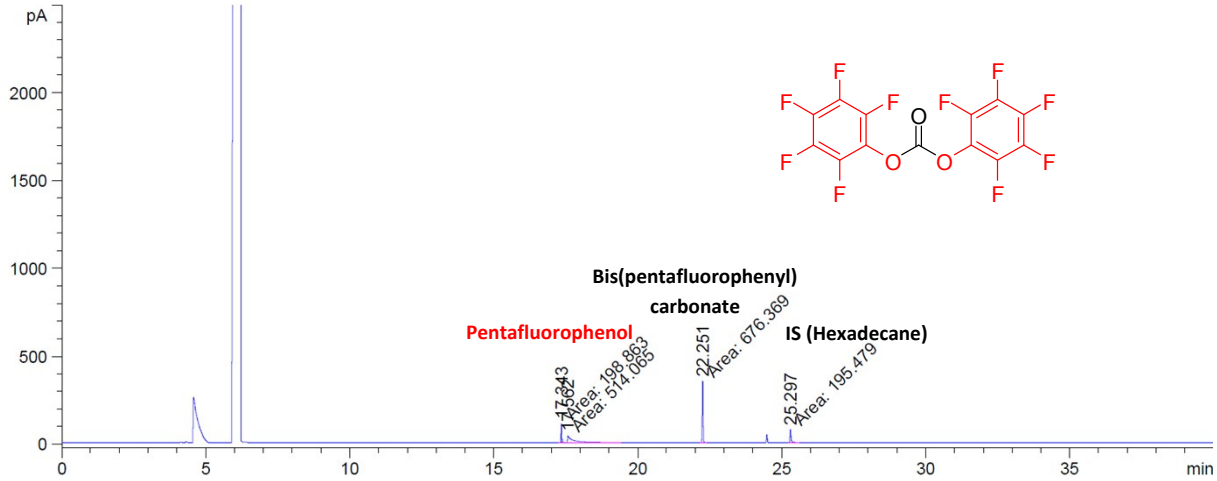


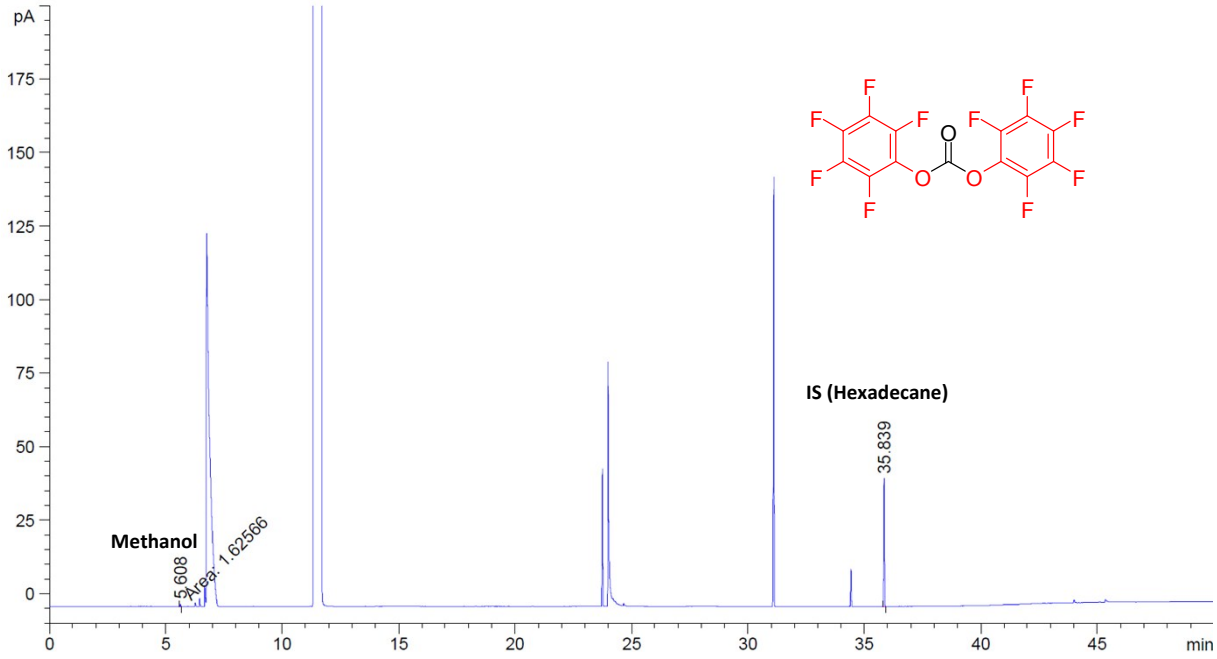


Bis(2,2,2-trifluoroethyl) carbonate (**9**)

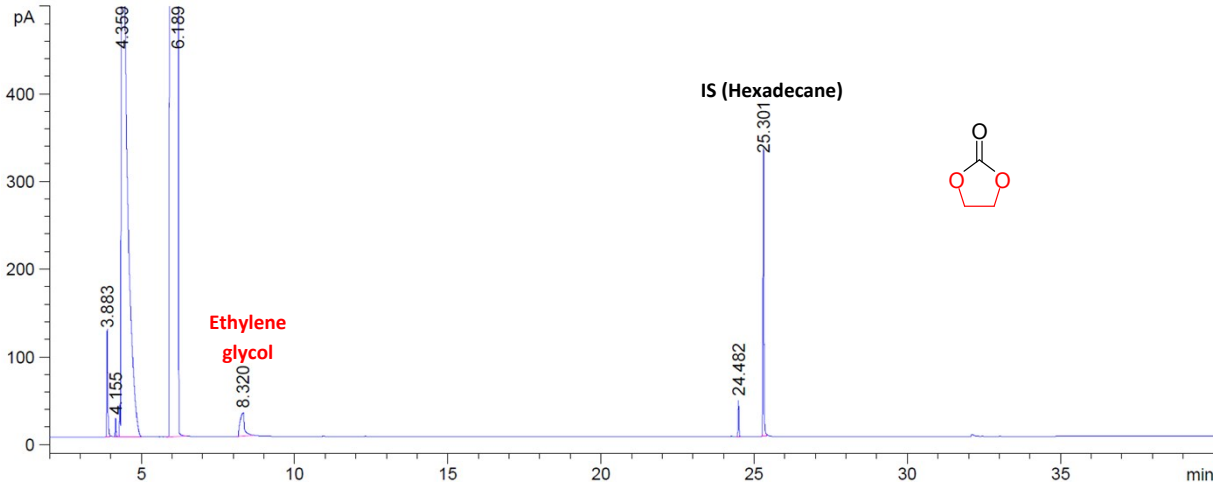


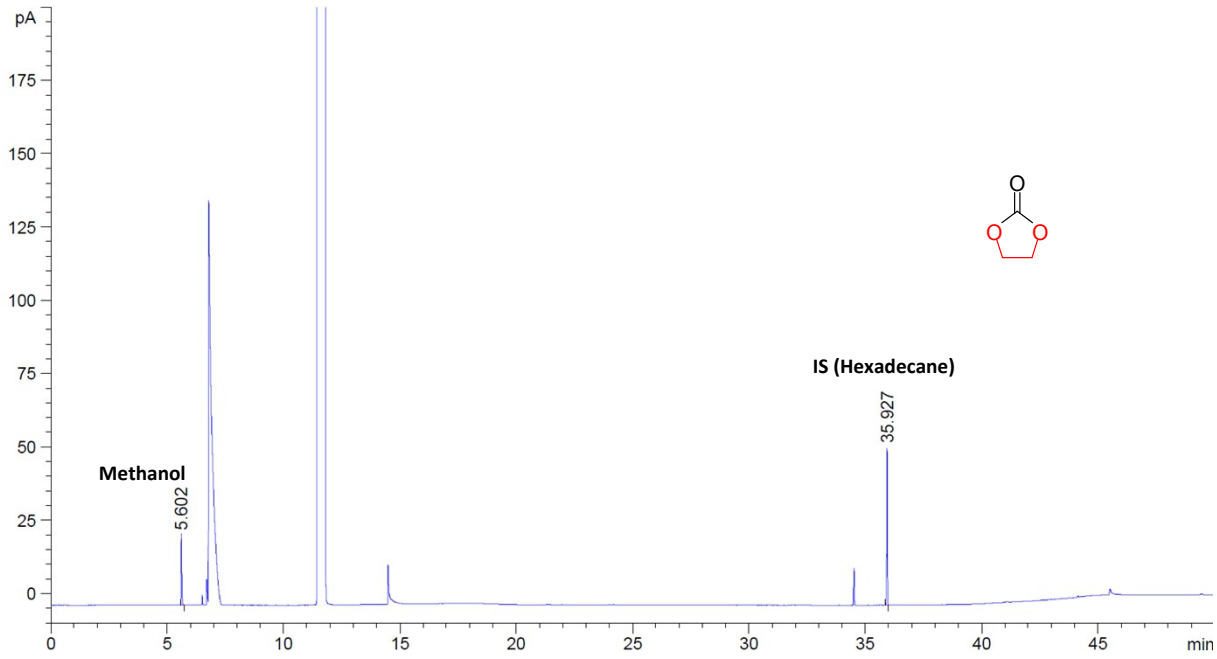
Bis(pentafluorophenyl) carbonate (**10**)



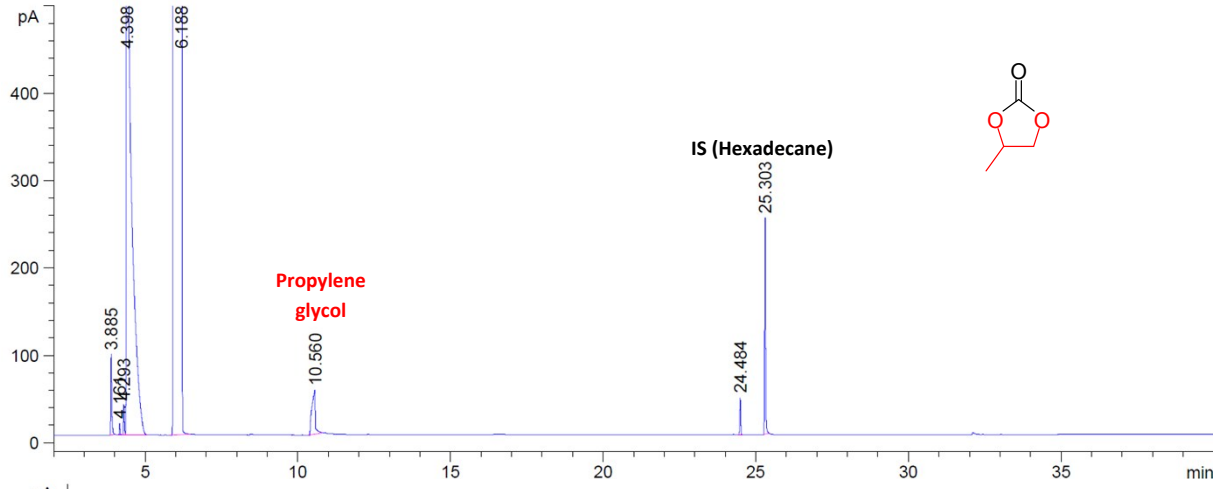


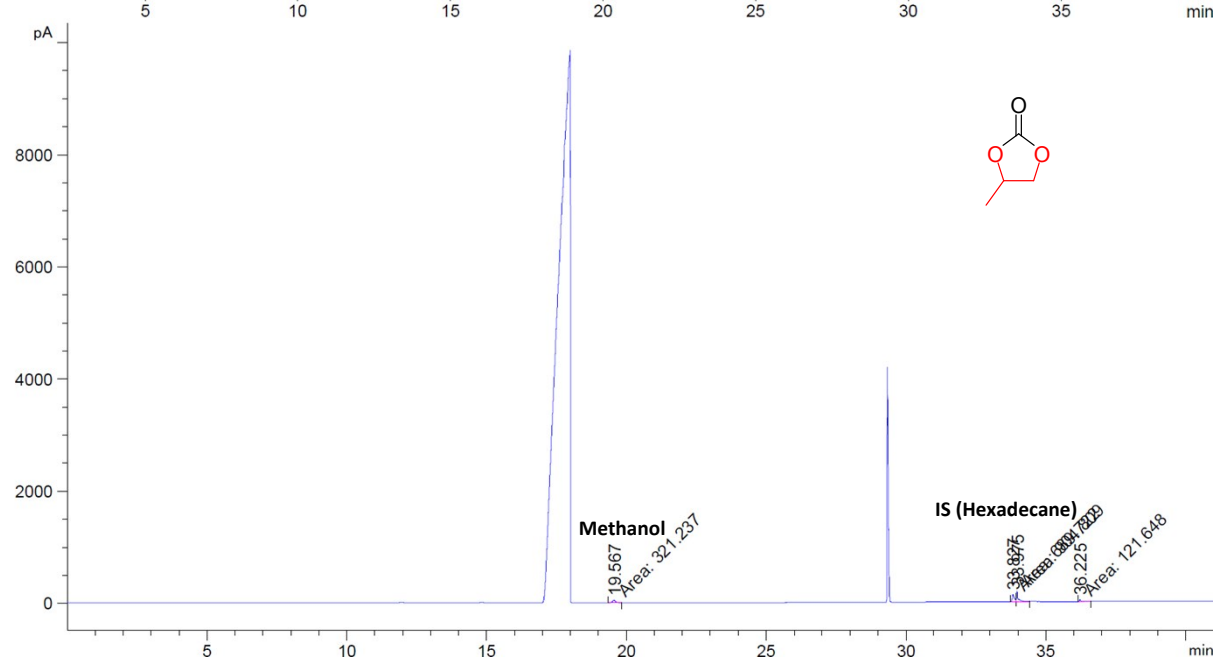
Ethylene carbonate (**11**)



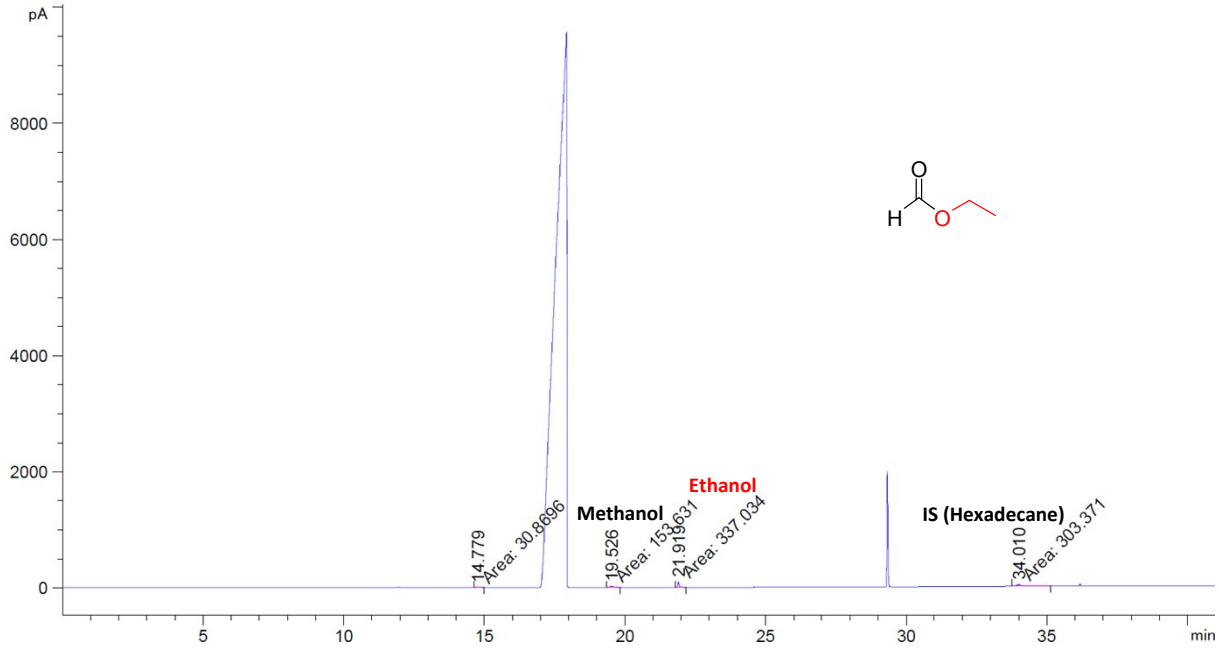


Propylene carbonate (**12**)





Ethylformate



para-Formaldehyde