

# Catalytic Hydrogenations with Cationic Heteroleptic Copper(I)/N-Heterocyclic Carbene Complexes

Niklas O. Thiel, [Johannes Teichert](#)

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A new heteroleptic cationic copper(I) complex bearing two N-heterocyclic carbene (NHC) ligands has been prepared. In situ, a Cu–O-bond can be generated which enables the complex to catalytically activate H<sub>2</sub>. The resulting complex shows activity in catalytic chemo- and stereoselective alkyne semihydrogenations as well as conjugate reductions of enones.

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# Catalytic Hydrogenations with Cationic Heteroleptic Copper(I)/N-Heterocyclic Carbene Complexes

Niklas O. Thiel<sup>a,1</sup>, Johannes F. Teichert<sup>\*a</sup>

<sup>a</sup> Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 115, 10623 Berlin, Germany.

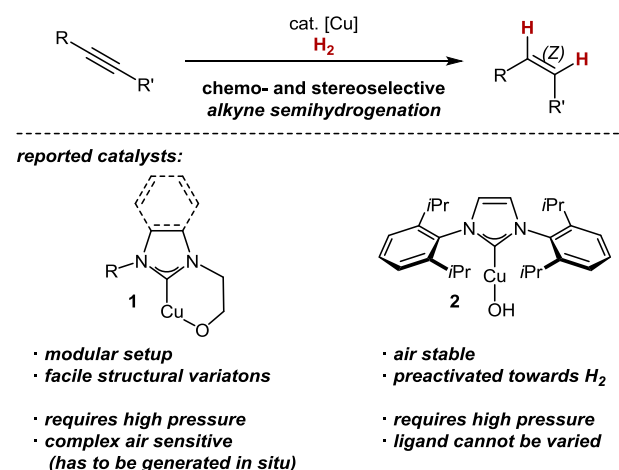
[johannes.teichert@chem.tu-berlin.de](mailto:johannes.teichert@chem.tu-berlin.de)

## Abstract

A new heteroleptic cationic copper(I) complex bearing two N-heterocyclic carbene (NHC) ligands has been prepared. In situ, a Cu–O-bond can be generated which enables the complex to catalytically activate H<sub>2</sub>. The resulting complex shows activity in catalytic chemo- and stereoselective alkyne semihydrogenations as well as conjugate reductions of enones.

Well-defined copper(I) complexes bearing N-heterocyclic carbene (NHC) ligands have emerged as powerful catalysts for a variety of transformations.<sup>2</sup> While the vast majority of the complexes reported bear one NHC ligand (leading to NHCCuX complexes, where X is an additional anionic ligand), also the corresponding cationic complexes of the general formula (NHC)<sub>2</sub>Cu<sup>+</sup> have been investigated as catalysts, albeit to a much lesser extent.<sup>3,4</sup> Our group and others have identified copper(I)/NHC complexes bearing a Cu–O-bond as useful catalysts for the activation of H<sub>2</sub> and subsequent hydrogenations or other reductive transformations.<sup>5–7</sup> For catalytic chemo- and stereoselective alkyne semihydrogenations, two general types of complexes have been disclosed: i) Copper(I) complexes such as **1** based on bidentate (“tethered”) NHC ligands bearing additional heteroatom tethers<sup>6a,6e,8</sup> that were generated in situ from the corresponding imidazol(in)ium salts and a suitable copper(I) precursor (Scheme 1, bottom left). ii) The simple and preactivated copper(I) hydroxide complex [IPrCuOH]<sup>9</sup> (**2**, Scheme 1, bottom right).<sup>6b,6d</sup> Both catalysts lead to a variety of Z-alkenes from internal alkynes in a highly stereoselective manner and are characterized by their negligible tendency for an overreduction to the corresponding alkanes. For a systematic optimization, however, both catalysts pose particular challenges: Complexes of the type **1** with a tethered ligand have so far not been isolated due to their tendency to oxidize to the corresponding (inactive) copper(II) counterparts.<sup>6a</sup> In addition, this catalyst requires high H<sub>2</sub> pressure (generally 50–100 bar), which impedes the practicability of the overall catalytic hydrogenation. However, this catalyst type is modular and can easily be varied both structurally as well as electronically through a variety of substituents.<sup>6c</sup> While

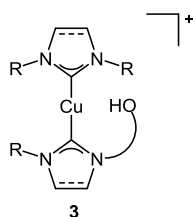
the second type of catalyst (**2**) is air-stable and can therefore be operated without special precautions, it shares the limitation of being active only at elevated H<sub>2</sub> pressure.<sup>6b,6d</sup> In addition, with the exception of one closely related complex,<sup>10</sup> copper(I) hydroxide/NHC complexes based on other NHC ligands are highly unstable, which hampers their use and systematic optimization.



**Scheme 1.** Reported copper(I)/NHC catalysts for alkyne semihydrogenations.

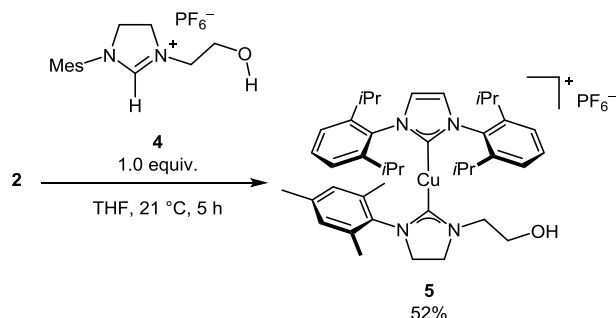
We therefore decided to investigate cationic copper(I)/NHC complexes **3** (Figure 1), with the aim to take advantage of a possible air-stability while maintaining viable pathways for derivatizations. Such a setup, with two different NHC ligands coordinated to one copper(I) atom (heteroleptic complex), could serve as ideal platform for rapid and systematic optimization of

catalysts for a catalytic transformation of choice. At the same time, at least one of the NHC moieties would have to be bidentate, with an additional alkoxide moiety available for the generation of a Cu–O-bond required for H<sub>2</sub> activation.

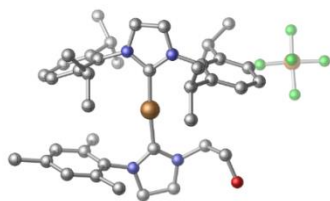


**Figure 1.** Envisaged heteroleptic cationic copper(I)/(NHC)<sub>2</sub> complexes.

We decided to take advantage of the high basicity<sup>9a</sup> of the [IPrCuOH] complex for the preparation of the envisaged cationic copper(I) complexes, and therefore anticipated that **2** could itself deprotonate an imidazolium salt such as **4**<sup>11</sup> to generate the desired complex **5** (Scheme 2). Indeed, when [IPrCuOH] (**2**) and imidazolium salt **4** were reacted in THF at room temperature, we were able to isolate the new heteroleptic cationic copper(I) complex **5** in 52% yield. We did not detect any copper(I) alkoxide complex which could form through direct deprotonation of the alcohol moiety of ligand precursor **4**.<sup>12</sup> Heteroleptic cationic copper(I) complex **5** was susceptible to X-ray crystal structure analysis (Figure 2).<sup>13</sup> The C–Cu–C angle was found to be 175° and no interaction between the copper and the oxygen atom was found.

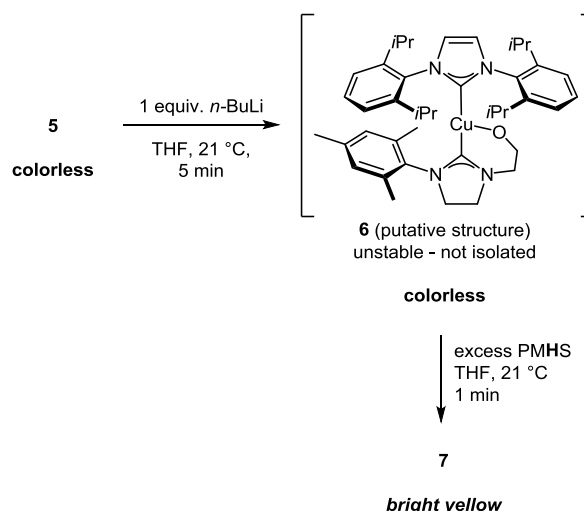


**Scheme 2.** Synthesis of cationic heteroleptic copper(I)/NHC complex **5**.



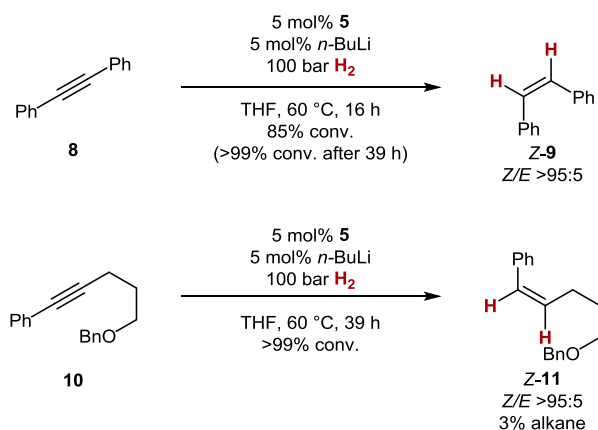
**Figure 2.** X-ray crystal structure of complex **5**. (Hydrogen atoms omitted for clarity)

For catalytic activity with H<sub>2</sub>, the formation of a Cu–O-bond emanating from complex **5** was necessary. We therefore decided to deprotonate **5** with *n*-butyllithium as in our earlier protocol.<sup>6a,6e</sup> While full conversion of **5** was detected after 5 minutes, the new complex **6** turned out to be too reactive to be isolated (Scheme 3). When polymethylhydrosiloxane (PMHS) was added to the reaction mixture at room temperature, a fast appearance of a yellow color, indicative for a copper(I) hydride complex **7**, could be observed.<sup>14,15</sup> Copper(I) hydrides are known to be formed from complexes bearing a Cu–O-bond in the presence of hydrosilanes.<sup>16</sup> We therefore reasoned that the unknown intermediate **6** does indeed possess a Cu–O-bond in a possible T-shape coordination.<sup>17</sup>



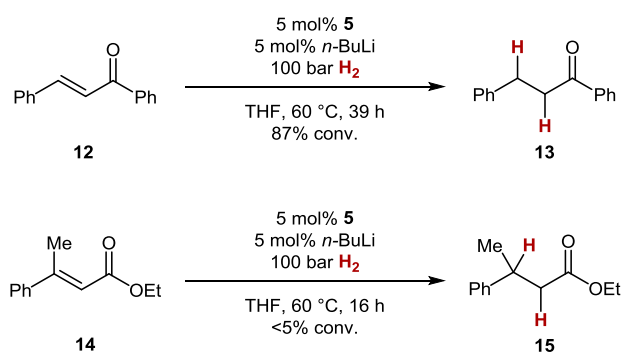
**Scheme 3.** Attempted isolation of copper(I)/alkoxide complex **6** and evidence for copper(I) hydride formation. (PMHS = polymethylhydrosiloxane)

To assess the catalytic activity of the new cationic complex **5**, we decided to activate it in situ to generate the putative active complex **6** and then directly carry out an alkyne semihydrogenation with tolane (**8**) and pentynol-derivative **10** as representative internal alkynes. With 100 bar H<sub>2</sub> pressure at 60 °C, we found that tolane (**8**) showed 85% conversion to *Z*-stilbene (**9**) with excellent stereoselectivity (*E/Z* >95:5, Scheme 4), and no overreduction to the corresponding alkane (not shown) detected. Full conversion of **8** was reached after 39 h reaction time. Under these conditions, alkyne **10** was also fully converted with similar stereoselectivity, albeit in this case with 3% alkane detected in the reaction mixture. Cationic complex **5** therefore shows the known characteristics of a copper(I)/NHC complex in catalytic alkyne semihydrogenations (high chemo- and stereoselectivity), while being slightly less active than the parent complexes **1** and **2**, both of which gave full conversion at 40 °C and 80–100 bar H<sub>2</sub>.<sup>6a,b,d,e</sup>



**Scheme 4.** Alkyne semihydrogenations catalyzed by cationic copper(I) complex **5**.

One of the hallmark reactions of the so-called “copper hydride catalysis” is the conjugate reduction of  $\alpha,\beta$ -unsaturated carbonyl or carboxyl derivatives.<sup>15</sup> We therefore decided to test the new cationic complex for these transformations as well. Chalcone (**12**) and cinnamic ester **14** were chosen as model substrates. Under similar reaction conditions as before (100 bar  $H_2$ , 60 °C, THF), chalcone (**12**) could be reduced to ketone **13** with 87% conversion, while no 1,2-reduction of the ketone was observed. The less reactive and sterically more demanding enoate **14** showed negligible conversion, displaying that the activity of the cationic complex **5** is limited at present in comparison to related neutral copper(I)/NHC complexes.<sup>6f</sup> Nevertheless, the observed reactivity of the new catalyst with enone **12** gives an important indication that copper(I) hydride complexes are indeed present after  $H_2$  activation.



**Scheme 5.** Catalytic conjugate reductions with cationic complex **5**.

In summary, we have demonstrated that cationic, heteroleptic copper(I) complexes bearing two NHC ligands can be employed as catalysts for  $H_2$  activation and alkyne semihydrogenations as well as conjugate reductions. The new complex presented herein serves as an ideal platform for further systematic development of well-defined copper(I)/NHC catalyst, as it offers several advantages: The catalyst precursor is air-stable and does not require special handling, and additionally bears a

multitude of sites for systematic variation of electronic and steric parameters of the resulting catalysts. This variation could stem from different NHC backbones, N-substituents and/or the alkoxide tether.

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## References and Notes

- (1) Present address: Stratingh Institute for Chemistry, Rijksuniversiteit Groningen, the Netherlands.
- (2) For reviews, see: (a) Egbert, J. D.; Cazin, C. S. J.; Nolan, S. P., *Catal. Sci. Technol.* **2013**, *3*, 912–926. (b) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B., *Chem. Rev.* **2009**, *109*, 3561–3598.
- (3) For a review, see: Lazreg, F.; Nagra, F.; Cazin, C. S. J., *Coord. Chem. Rev.* **2015**, *293–294*, 48–79.
- (4) For selected examples, see: (a) Grandbois, A.; Mayer, M.-E.; Bédard, M.; Collins, S. K.; Michel, T., *Chem. Eur. J.* **2009**, *15*, 9655–9659. (b) Díez-González, S.; Stevens, E. D.; Scott, N. M.; Petersen, J. L.; Nolan, S. P., *Chem. Eur. J.* **2008**, *14*, 158–168. (c) Díaz Velázquez, H.; Ruiz García, Y.; Vandichel, M.; Madder, A.; Verpoort, F., *Org. Biomol. Chem.* **2014**, *12*, 9350–9356.
- (5) For the formulation of the mechanistic hypothesis of  $H_2$ -activation along Cu–O-bonds, see: (a) Halpern, J., *J. Phys. Chem.* **1959**, *63*, 398–403. (b) Chalk, A. J.; Halpern, J., *J. Am. Chem. Soc.* **1959**, *81*, 5852–5854. (c) Goeden, G. V.; Caulton, K. G., *J. Am. Chem. Soc.* **1981**, *103*, 7354–7355.
- (6) For catalytic hydrogenations with copper(I)/NHC complexes, see: (a) Pape, F.; Thiel, N. O.; Teichert, J. F., *Chem. Eur. J.* **2015**, *21*, 15934–15938. (b) Thiel, N. O.; Teichert, J. F., *Org. Biomol. Chem.* **2016**, *14*, 10660–10666. (c) Wakamatsu, T.; Nagao, K.; Ohmiya, H.; Sawamura, M., *Organometallics* **2016**, *35*, 1354–1357. (d) Thiel, N. O.; Kemper, S.; Teichert, J. F., *Tetrahedron* **2017**, *73*, 5023–5028. (e) Pape, F.; Teichert, J. F., *Synthesis* **2017**, *49*, 2470–2482. (f) Zimmermann, B. M.; Teichert, J. F., *ChemRxiv* **2018**, DOI: 10.26434/chemrxiv.7461569. For a related copper(I)-catalyzed alkyne semihydrogenation employing phosphine ligands, see: (g) Semba, K.; Kameyama, R.; Nakao, Y., *Synlett* **2015**, *26*, 318–322.
- (7) For related reductive transformations with copper(I)/NHC complexes, see: (a) Nguyen, T. N. T.; Thiel, N. O.; Pape, F.; Teichert, J. F., *Org. Lett.* **2016**, *18*, 2455–2458. (b) Korytiakova, E.; Thiel, N. O.; Pape, F.; Teichert, J. F., *Chem. Commun.* **2017**, *53*, 732–735. (c) Nguyen, T. N. T.; Thiel, N. O.; Teichert, J. F., *Chem. Commun.* **2017**, *53*, 11686–11689. (d) Das, M.; Kaicharla, T.; Teichert, J. F., *Org. Lett.* **2018**, *20*, 4926–4929. (e) Pape, F.; Brechmann, L. T.; Teichert, J. F., *Chem. Eur. J.* **2018**, DOI: 10.1002/chem.201805530.
- (8) For reviews on “tethered” NHC ligands, see: (a) Pape, F.; Teichert, J. F., *Eur. J. Org. Chem.* **2017**, 4206–4229. (b) Hameury, S.; Frémont, P. de; Braunstein, P., *Chem. Soc. Rev.* **2017**, *46*, 632–733. (c) Liddle, S. T.; Edworthy, I. S.; Arnold, P. L., *Chem. Soc. Rev.* **2007**, *36*, 1732.

- (9) (a) Fortman, G. C.; Slawin, A. M. Z.; Nolan, S. P., *Organometallics* **2010**, *29*, 3966–3972. For a review on transition metal hydroxides, see: (b) Nelson, D. J.; Nolan, S. P., *Coord. Chem. Rev.* **2017**, *353*, 278–294.
- (10) Santoro, O.; Lazreg, F.; Minenkov, Y.; Cavallo, L.; Cazin, C. S. J., *Dalton Trans.* **2015**, *44*, 18138–18144.
- (11) Clavier, H.; Coutable, L.; Toupet, L.; Guillemin, J.-C.; Mauduit, M., *J. Organomet. Chem.* **2005**, *690*, 5237–5254.
- (12) For an investigation of the deprotonation behavior of “tethered” NHC precursors, see: Arnold, P. L.; Casely, I. J.; Turner, Z. R.; Carmichael, C. D., *Chem. Eur. J.* **2008**, *14*, 10415–10422.
- (13) CCDC 1890624.
- (14) Mankad, N. P.; Laitar, D. S.; Sadighi, J. P., *Organometallics* **2004**, *23*, 3369–3371.
- (15) For reviews on copper(I) hydride chemistry, see: (a) Jordan, A. J.; Lalic, G.; Sadighi, J. P., *Chem. Rev.* **2016**, *116*, 8318–8372. (b) Deutsch, C.; Krause, N., *Chem. Rev.* **2008**, *108*, 2916–2927. (c) Rendler, S.; Oestreich, M., *Angew. Chem. Int. Ed.* **2007**, *46*, 498–504.
- (16) (a) Rendler, S.; Plefka, O.; Karatas, B.; Auer, G.; Fröhlich, R.; Mück-Lichtenfeld, C.; Grimme, S.; Oestreich, M., *Chem. Eur. J.* **2008**, *14*, 11512–11528. (b) Gathy, T.; Peeters, D.; Leyssens, T., *J. Organomet. Chem.* **2009**, *694*, 3943–3950. (c) Vergote, T.; Nahra, F.; Merschaert, A.; Riant, O.; Peeters, D.; Leyssens, T., *Organometallics* **2014**, *33*, 1953–1963.
- (17) For a related T-shaped copper(I) complex, see: Lake, B. R. M.; Willans, C. E., *Chem. Eur. J.* **2013**, *19*, 16780–16790. A trigonal planar coordination of the ligands in **6** would also be viable. However, the steric demand of the two bulky NHC ligands makes such coordination mode unlikely.

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**Supporting Information for**  
**Catalytic Hydrogenations with Cationic Heteroleptic Copper(I)/N-Heterocyclic Carbene**  
**Complexes**

Niklas O. Thiel, Johannes F. Teichert

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# 1 General Information

All reactions were carried out in flame dried glassware under a nitrogen atmosphere using standard Schlenk techniques. Glassware and stir bars contaminated with transition metals were treated with *aqua regia* (conc. HCl/conc. HNO<sub>3</sub> 3:1) prior to cleaning. For cleaning, glassware and stir bars were kept in a *iso*-PrOH/KOH bath overnight, rinsed with H<sub>2</sub>O, kept in a citric acid/H<sub>2</sub>O bath overnight and finally rinsed with deionized H<sub>2</sub>O and dried at 120 °C. Solutions and reagents were added with nitrogen-flushed disposable syringes/needles. Solvents were added using glass syringes and stainless steel needles (stored at 120 °C). Analytical thin layer chromatography (TLC) was performed on silica gel 60 G/UV<sub>254</sub> aluminium sheets (*Macherey-Nagel*). Flash column chromatography was performed on silica gel Davisil LC60A (40-63 µm, pore size 60 Å, *Grace*) using the indicated solvents. NMR spectra were recorded on AV400, AV500 or AV700 instruments (*Bruker*) at the Institut für Chemie of *Technische Universität Berlin*. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard according to the standard literature.<sup>[1,2]</sup> Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m<sub>c</sub> = centrosymmetric multiplet), coupling constants (Hz), integration and – if possible – atom assignment. The assignment refers to the atom number shown in the corresponding molecule figure and was achieved by analysis of DEPT (DEPT 135) and 2D-NMR spectra (COSY, HMQC, HSQC, HMBC, NOESY). If a distinct assignment was not possible, atoms were marked with “\*” and are interchangeable. Infrared (IR) spectra were recorded on a Cary 630 FT-IR spectrometer equipped with an ATR unit (*Agilent Technologies*). Mass spectra (HRMS) were obtained from the Analytical Facility at the Institut für Chemie at *Technische Universität Berlin* (ESI/APCI: LTQ Orbitrap XL, *Thermo Scientific*; EI: GC-system 5975C, HP-5MS, *Agilent Technologies*). Analytical gas chromatography (GC) of reaction mixtures and pure substances was performed using a gas chromatograph 430-GC (*Varian Inc.*). The instrument was equipped with a FactorFour VF-WAXms capillary column (*Varian Inc.*, length: 30 m, inner diameter: 0.25 mm, film thickness of the stationary phase: 0.25 µm). The following temperature program was used for the analysis: carrier gas N<sub>2</sub>; injection temperature 270 °C; detector temperature 270 °C; flow rate 4.0 mL/min; temperature program: 40 °C start temperature, 20 °C/min heating rate to 250 °C for 10 min, then 20 °C/min heating rate to final temperature 260 °C for 5 min. The data was recorded with the program Galaxie 1.9.302.952 (*Varian Inc.*).

## 1.1 Solvents

THF was dried over sodium/benzophenone and distilled under N<sub>2</sub> atmosphere prior to use. CH<sub>2</sub>Cl<sub>2</sub> was dried over CaH<sub>2</sub> and distilled under N<sub>2</sub> atmosphere prior to use. Solvents (technical grade) for extraction/chromatography (*n*-pentane, cyclohexane, CH<sub>2</sub>Cl<sub>2</sub>, *tert*-butyl methyl ether, MeOH) were distilled under reduced pressure prior to use. Liquid substrates for hydrogenation reactions were degassed prior to use.

## 1.2 Reactions under H<sub>2</sub> pressure

All reactions under H<sub>2</sub> pressure were carried out in glass vials (50 x 14 mm, *Schütt*), equipped with a magnetic stir bar and a rubber septum in autoclaves BR-100 or Br-300 (including the appropriate heating blocks, *Berghof*). The autoclave was purged with N<sub>2</sub> (3 x 10 bar) before the vials were placed in the autoclave and the septum was pierced under a

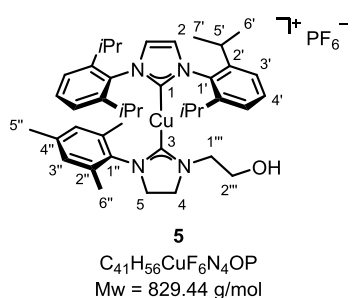
counter flow of N<sub>2</sub>. The autoclave was purged with N<sub>2</sub> (1 x 1 bar, 3 x 10 bar) and H<sub>2</sub> (3 x 10 bar) H<sub>2</sub> pressure was applied (pressure is given as initial pressure before heating). The heating block was pre-heated before the autoclave was placed inside. After the respective reaction time the autoclave was allowed to cool to rt and H<sub>2</sub> was released. The autoclave was purged with N<sub>2</sub> (3 x 10 bar) before the vials were taken out.

### 1.3 Chemicals

All reagents were purchased from established commercial suppliers (*Sigma-Aldrich*, *Alfa Aesar*, *TCI*, *Acros*, *Strem*, *Merck*, *ABCR*, *Fluka*, *Fisher Scientific*) and used without further purification. H<sub>2</sub> (99.999%) was purchased from *Air Liquide*. Tolane (**8**, *ABCR*) and chalcone (**12**, *Sigma Aldrich*) were purchased from commercial suppliers and used without further purification. Synthesis of alkyne **10**: (5-(benzyloxy)pent-1-yn-1-yl)benzene (**10**) was prepared according to a literature procedure.<sup>[3]</sup> Synthesis of **4** (Ligand precursor): 1-(2-Hydroxyethyl)-3-mesityl-4,5-dihydro-1*H*-imidazol-3-iumhexafluorophosphate (**4**) was prepared according to a literature procedure.<sup>[3]</sup> Synthesis of [IPrCuOH] (**2**): The copper(I) hydroxide/NHC complex **2** was prepared according to a literature procedure.<sup>[4]</sup>

## 2 Synthesis of compound 5

### (1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene)(1-(2-hydroxy-ethyl)-3-mesitylimidazolidine-2-ylidene)copper(I)hexafluorophosphate (**5**)



To a solution of 1-(2-Hydroxyethyl)-3-mesityl-4,5-dihydro-1*H*-imidazol-3-iumhexafluorophosphate (**4**, 0.38 g, 1.0 mmol, 1.0 equiv) in THF (10 mL) was added a solution of [IPrCuOH] (**2**, 0.47 g, 1.0 mmol, 1.0 equiv) in THF (5 mL) at 21 °C. The resulting mixture was stirred for 5 h. In the following, all volatiles were removed under reduced pressure. The crude product was purified via flash column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 20:1, 14.5 x 4 cm) and gave the title compound (**5**, 0.43 g,

0.52 mmol, 52%) as white solid. Single crystals for X-ray crystal structure analysis were obtained by crystallization through slow diffusion of *n*-pentane into a saturated solution of **5** in CH<sub>2</sub>Cl<sub>2</sub>.

$R_f = 0.42$  (SiO<sub>2</sub>, MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 20:1).

**<sup>1</sup>H NMR** (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 1.09 (d,  $^3J_{6',5'} = 6.9$  Hz, 12H, H-6')\*, 1.19 (d,  $^3J_{7',5'} = 6.9$  Hz, 12H, H-7')\*, 1.57 (br s, 1H, OH), 1.83 (s, 6H, H-6''), 2.31 (s, 3H, H-5''), 2.41 (sept,  $^3J_{5',6'/7'} = 6.9$  Hz, 4H, H-5'), 2.85 (m<sub>c</sub>, 2H, H-1'''), 3.35 (m<sub>c</sub>, 2H, H-2'''), 3.55–3.60 (m, 2H, H-5), 3.69–3.73 (m, 2H, H-4), 6.64 (s, 2H, H-2), 7.20 (s, 2H, H-3''), 7.27 (d,  $^3J_{3',4'} = 7.8$  Hz, 4H, H-3'), 7.55 (t,  $^3J_{4',3'} = 7.8$  Hz, 2H, H-4') ppm.

**<sup>13</sup>C NMR** (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 17.8 (C-6''), 21.3 (C-5''), 24.0 (C-7'')\*, 24.9 (C-6'')\*, 29.1 (C-5'), 49.5 (C-4), 51.7 (C-5), 52.2 (C-1'''), 60.5 (C-2'''), 124.3 (C-3''), 124.5 (C-3'), 130.1 (C-2), 131.1 (C-4'), 134.4 (C-1'), 135.4 (C-2''), 138.3 (C-4''), 146.0 (C-2'), 179.6 (C-1), 200.0 (C-3) ppm. The signal for C-1'' was not detected.

**<sup>31</sup>P-NMR** (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = −144.5 (sept,  $^1J_{P,F} = 711$  Hz) ppm.

**<sup>19</sup>F-NMR** (471 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = −73.6 (d,  $^1J_{F,P} = 711$  Hz) ppm.

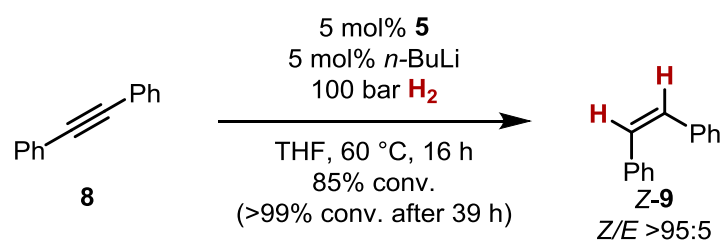
**HRMS** (ESI) calculated for C<sub>41</sub>H<sub>56</sub>CuN<sub>4</sub>O<sup>+</sup> [(M-PF<sub>6</sub>)<sup>+</sup>]: 683.3750, found 683.3731.

**IR** (ATR):  $\nu$  = 2958 (w), 1648 (m), 1458 (m), 1327 (w), 1270 (w), 1059 (w), 836 (s), 759 (s) cm<sup>−1</sup>.

### 3 General procedure for catalytic hydrogenation with complex 5

Also compare the general information on hydrogenation reactions (section 1.2). In a 10 mL glass vial equipped with a rubber septum which was flushed with N<sub>2</sub>, complex **5** (5 mol%, 18 μmol, 14.9 mg) was dissolved in 1 mL THF at 21 °C. Then, a solution of *n*-BuLi (c = 1.81 mol/L,<sup>[5]</sup> 18 μmol, 0.01 mL) in hexanes was added and the mixture was stirred for 30 minutes at 21 °C. Afterwards, the appropriate substrate (0.36 mmol) was added as a solution in 1 mL THF. The reaction vessel was placed in the autoclave, and just before the above mentioned protocol of flushing with N<sub>2</sub> and H<sub>2</sub>, the septum was pierced with a needle. The autoclave was then pressurized with 100 bar H<sub>2</sub> and the reaction was allowed to stir at 100 bar H<sub>2</sub> (750 rpm stirring speed) and 60 °C for the given amount of time (16 or 39 h). After this time, the reaction was allowed to cool to 21 °C, and was removed from the autoclave. The reaction mixture was filtered in a pipette through a pad of silica (2 cm) and washed with *tert*-butyl methyl ether (5 mL). All volatiles were removed under reduced pressure and the crude mixture was analyzed by GC chromatography.

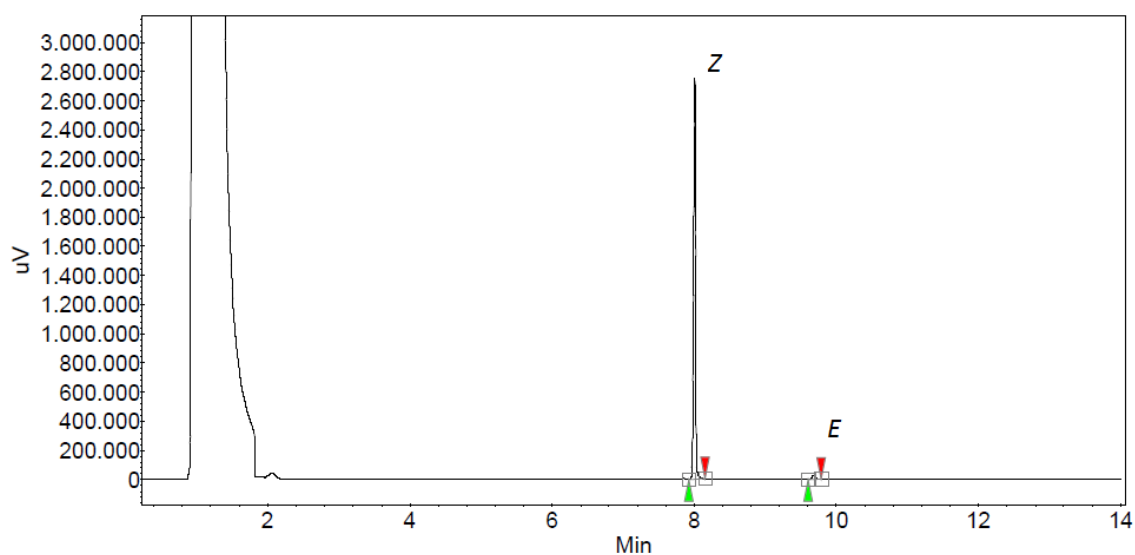
## 4 Analytical data for catalytic reactions



### GC

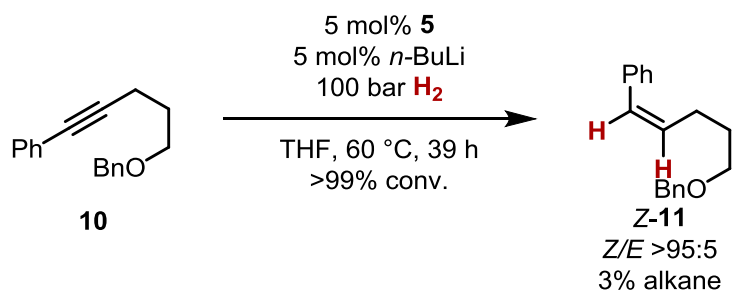
System : GC\_2  
 Method : GC2\_40\_20\_250\_10  
 User : User1

Acquired : 21.11.2016 09:33:05  
 Processed : 21.11.2016 09:49:06  
 Printed : 21.09.2018 09:27:48



#### Peak results :

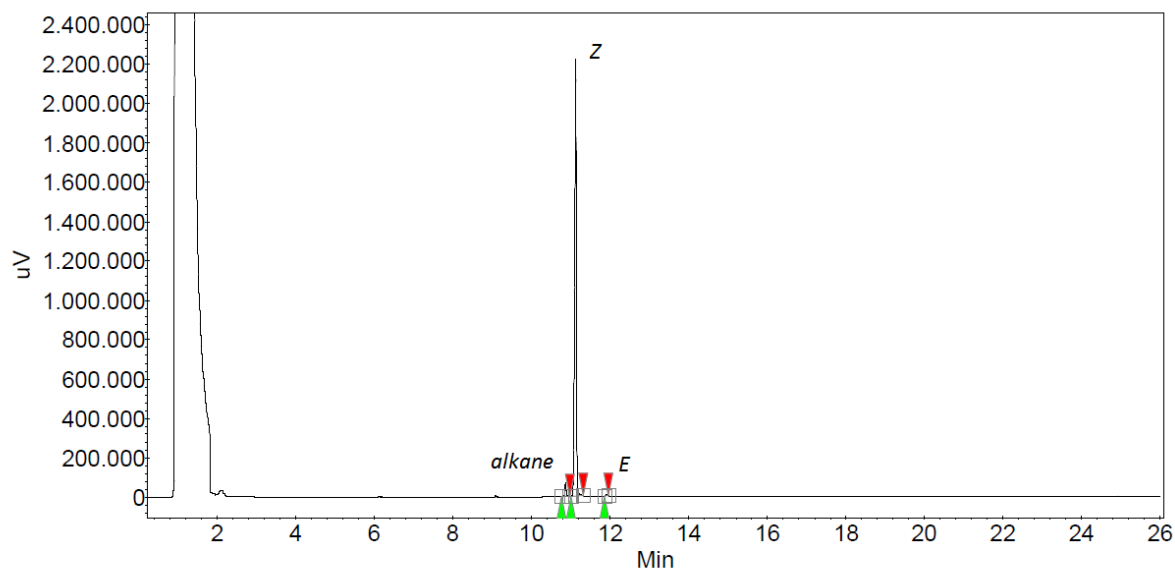
Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	8.01	98.36	2750496.6	86973.1	98.355
2	UNKNOWN	9.67	1.64	25589.9	1454.5	1.645
Total			100.00	2776086.4	88427.7	100.000



## GC

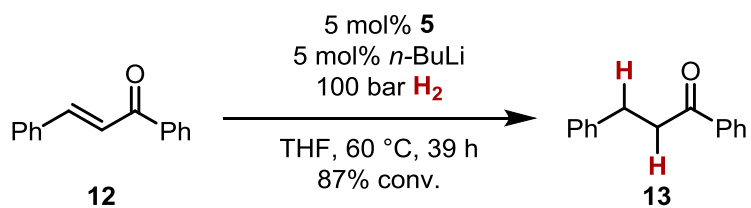
System : GC\_2  
 Method : GC2\_40\_20\_250\_10  
 User : User1

Acquired : 21.11.2016 09:54:13  
 Processed : 21.11.2016 13:32:19  
 Printed : 21.09.2018 09:28:11



### Peak results :

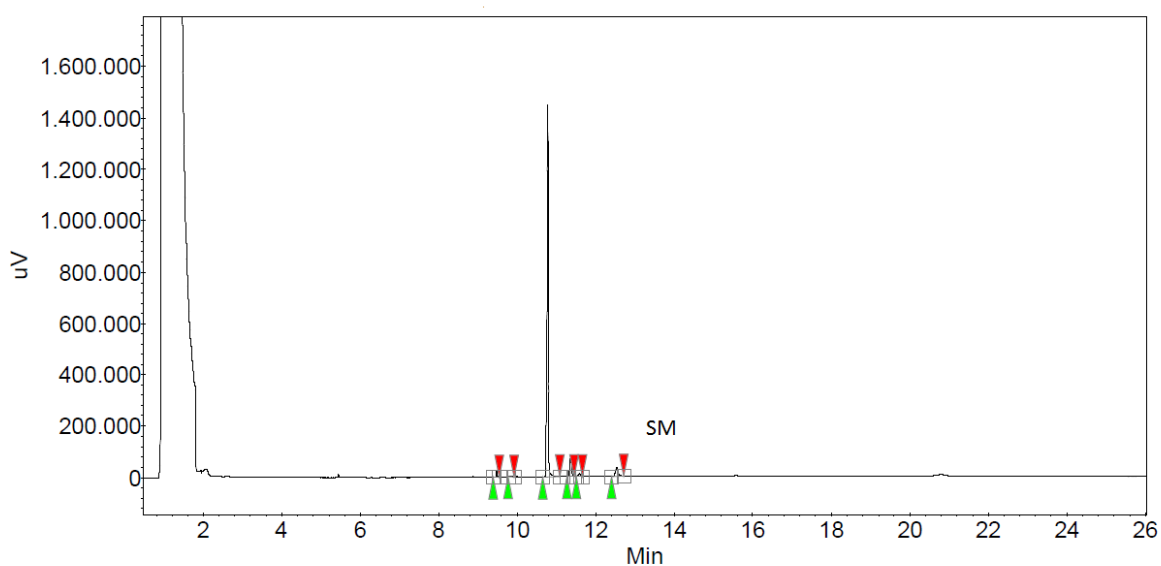
Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	10.87	2.74	68438.1	3136.7	2.741
2	UNKNOWN	11.13	97.01	2220592.8	111013.2	97.006
3	UNKNOWN	11.90	0.25	5473.8	290.1	0.254
Total			100.00	2294504.7	114440.0	100.000



## GC

System : GC\_2  
 Method : GC2\_40\_20\_250\_10  
 User : User1

Acquired : 21.11.2016 08:59:52  
 Processed : 21.11.2016 09:48:40  
 Printed : 21.09.2018 09:28:35

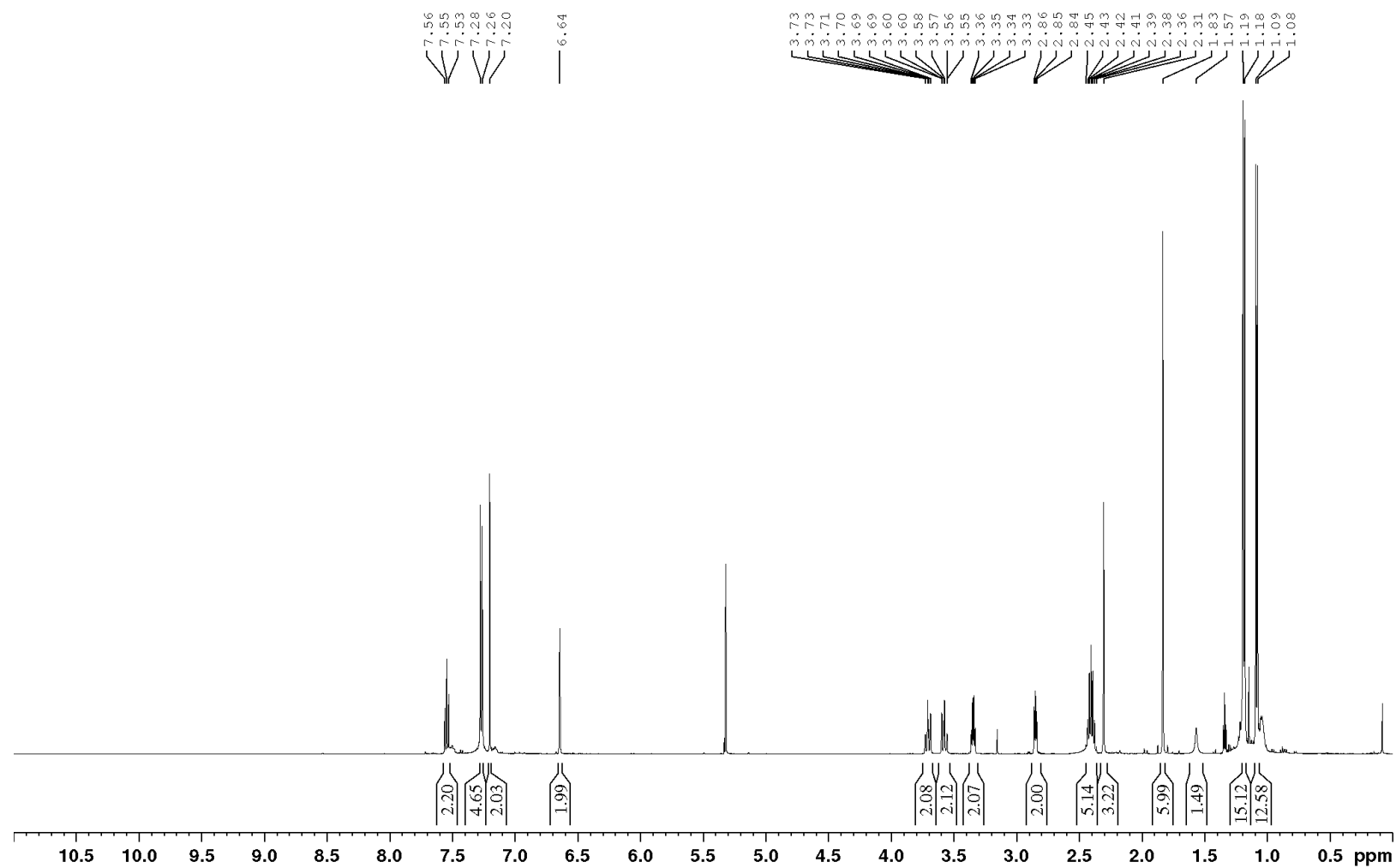


### Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
4	UNKNOWN	9.48	1.05	21161.6	662.4	1.051
5	UNKNOWN	9.86	0.39	4202.5	243.2	0.386
1	UNKNOWN	10.78	87.17	1448740.1	54954.0	87.175
2	UNKNOWN	11.36	5.75	71224.3	3623.6	5.748
6	UNKNOWN	11.58	1.01	12624.0	637.0	1.011
3	UNKNOWN	12.53	4.63	35363.6	2918.5	4.630
Total			100.00	1593316.2	63038.7	100.000

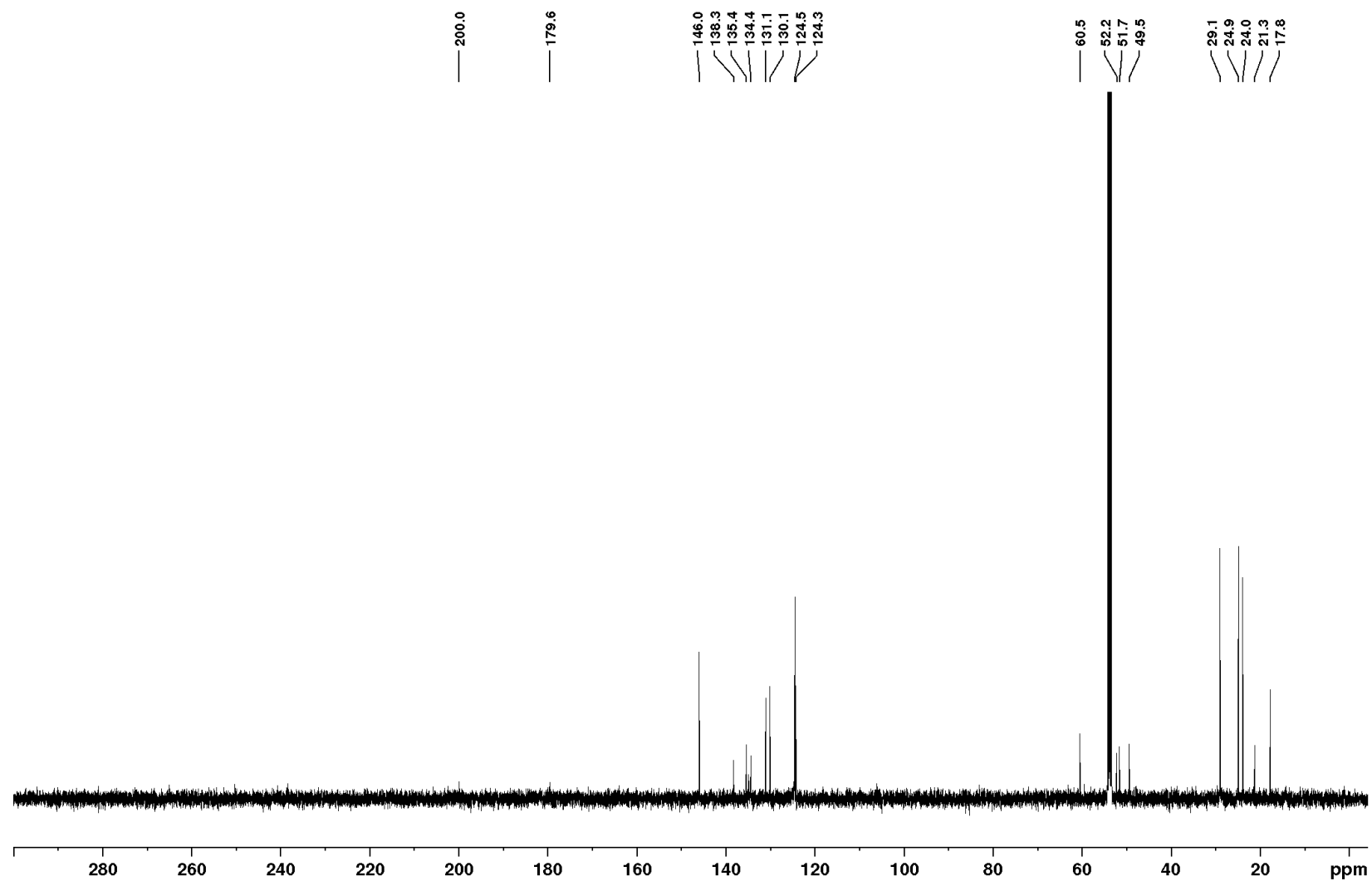
## 5 Spectra of complex 5

$^1\text{H}$  NMR

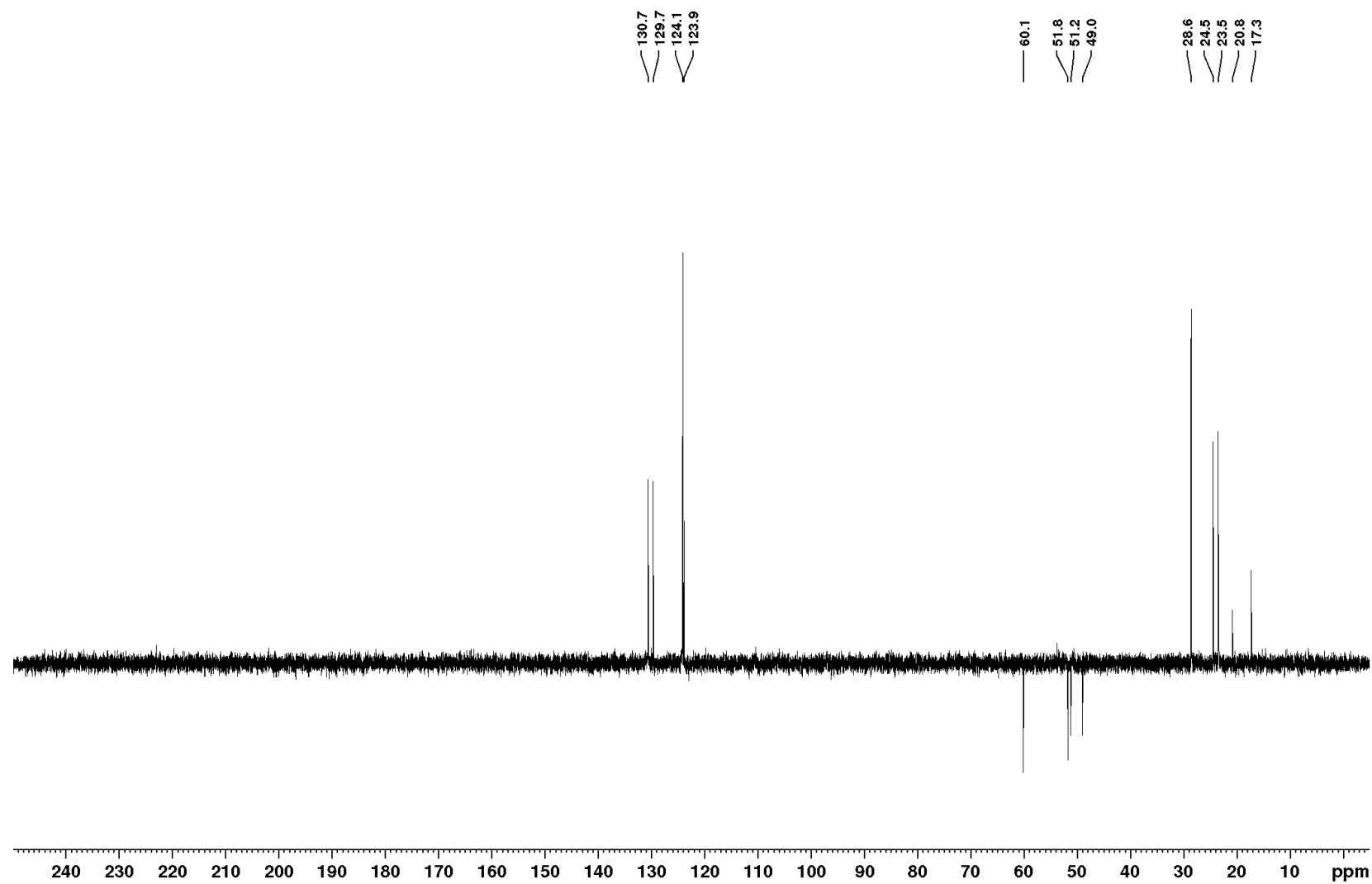




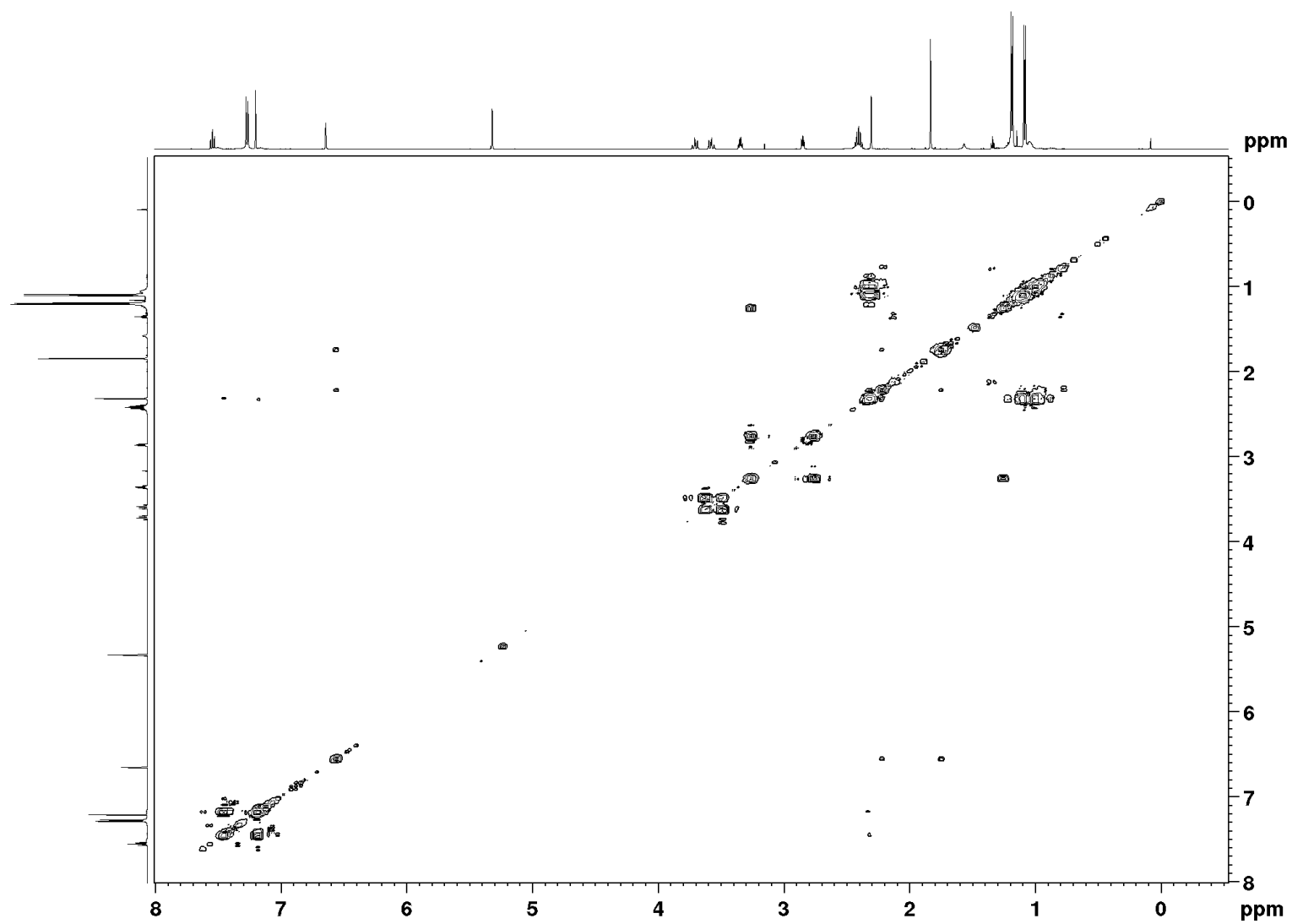
<sup>13</sup>C NMR



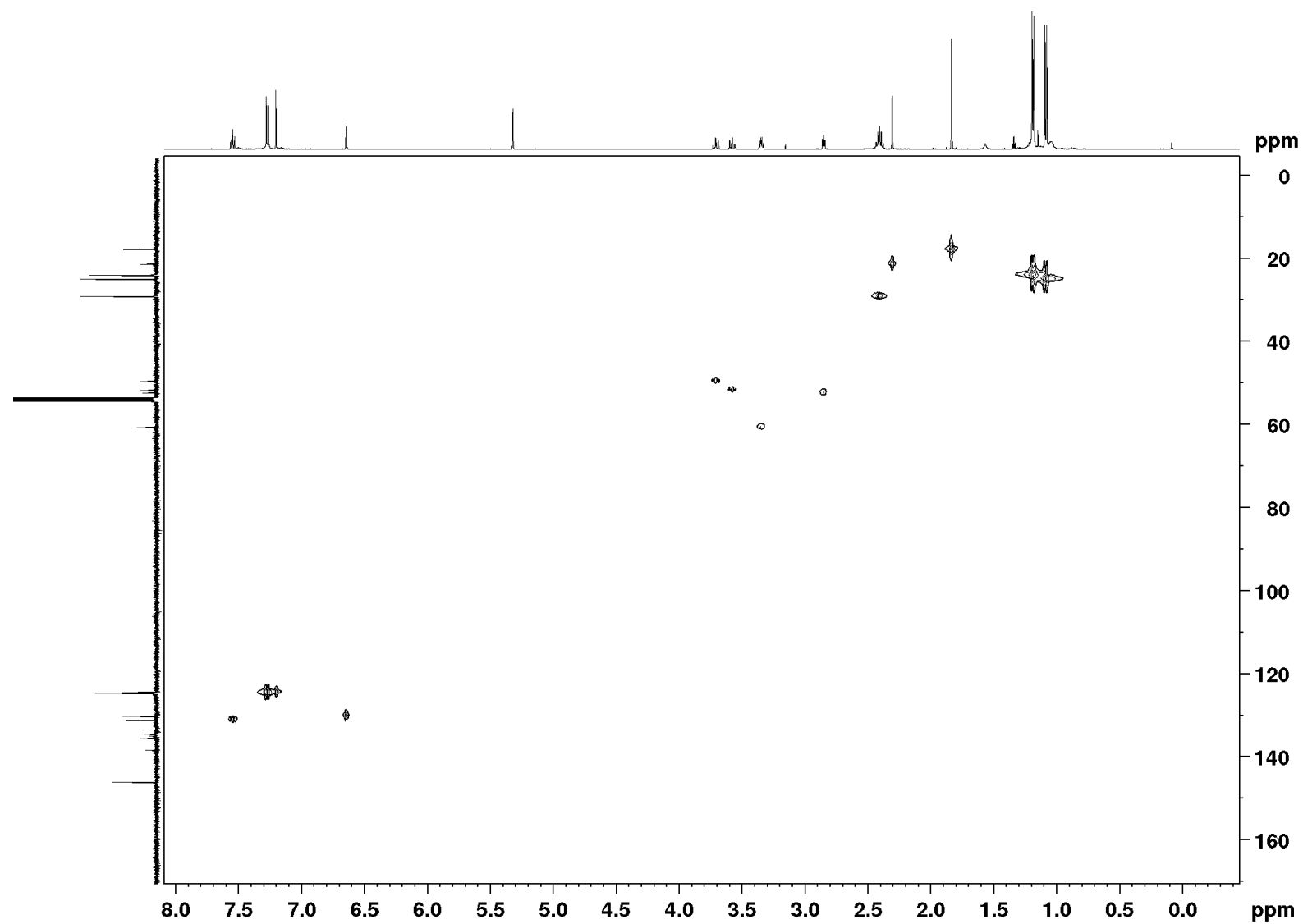
<sup>13</sup>C-DEPT-NMR



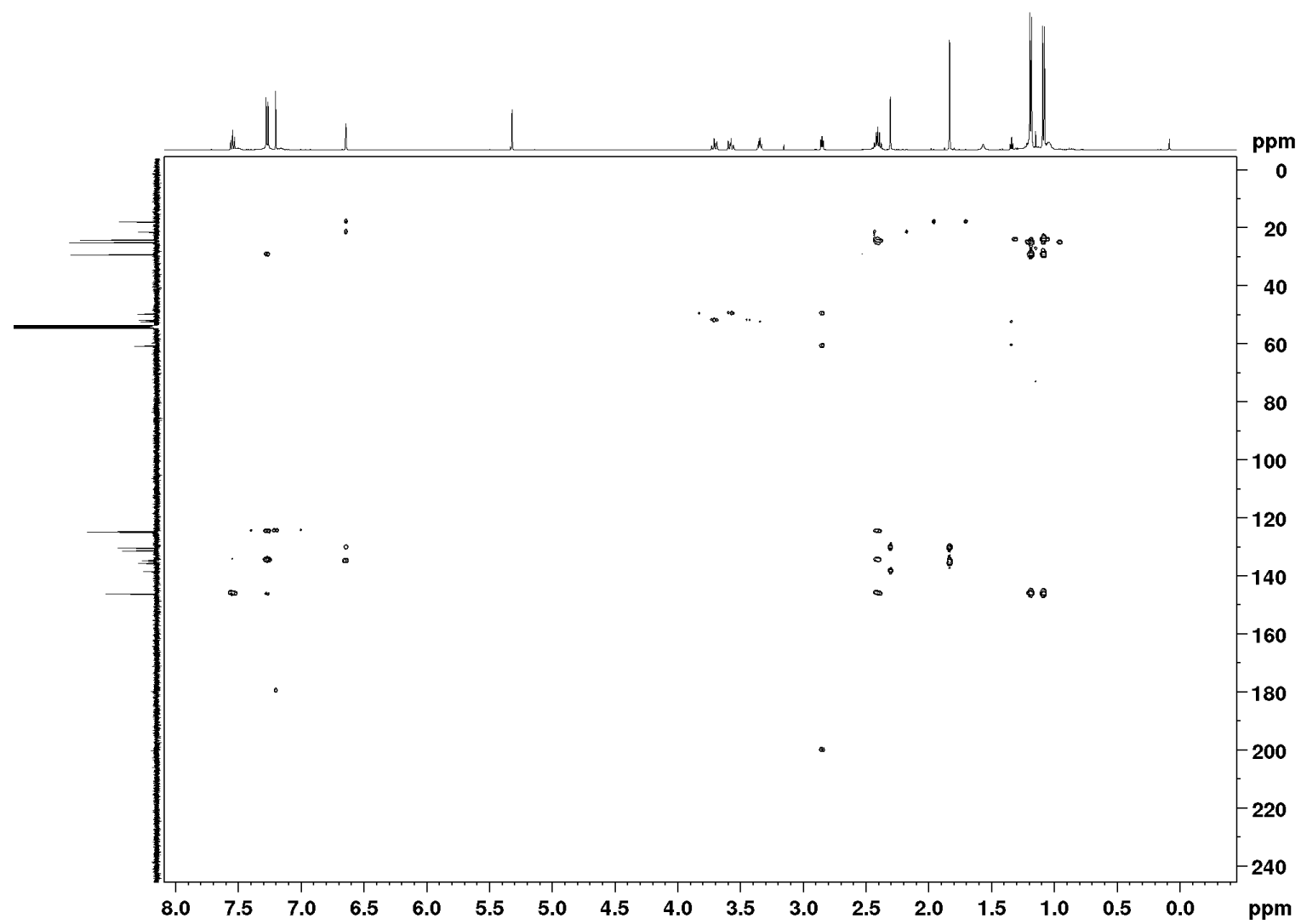
$^1\text{H}, ^1\text{H}$ -COSY-NMR



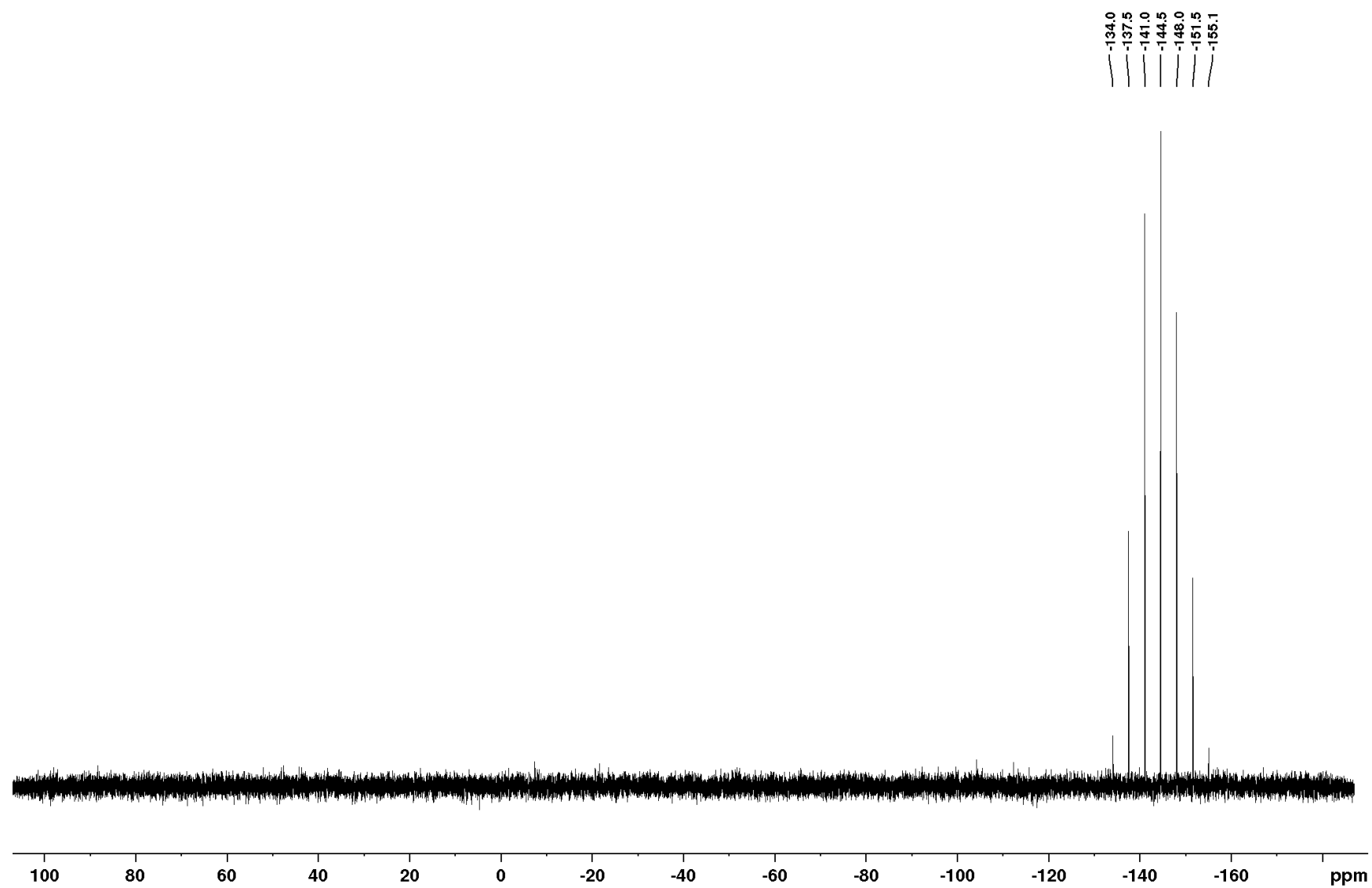
$^1\text{H}, ^{13}\text{C}$ -HSQC-NMR



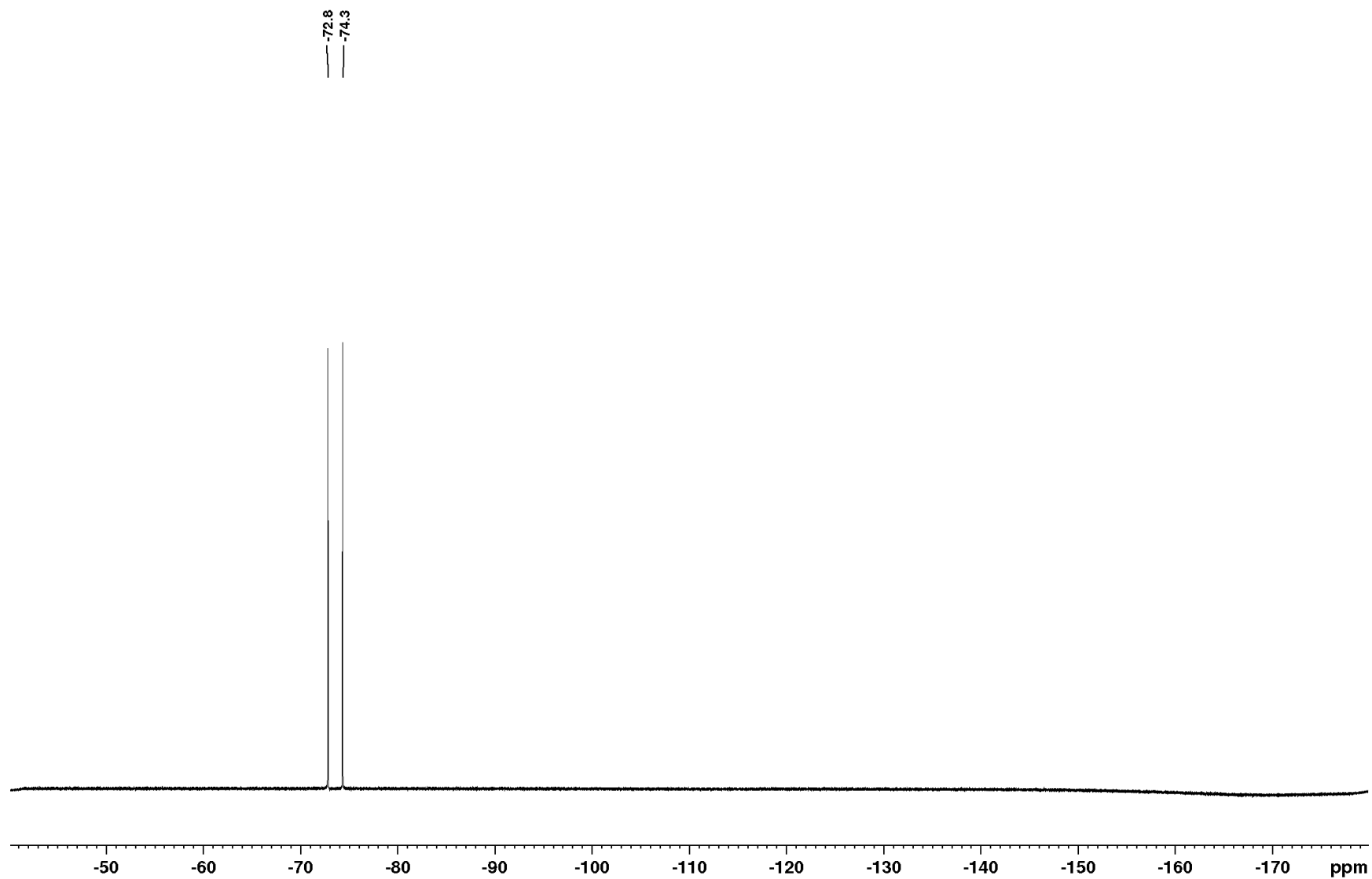
$^1\text{H}, ^{13}\text{C}$ -HMBC-NMR



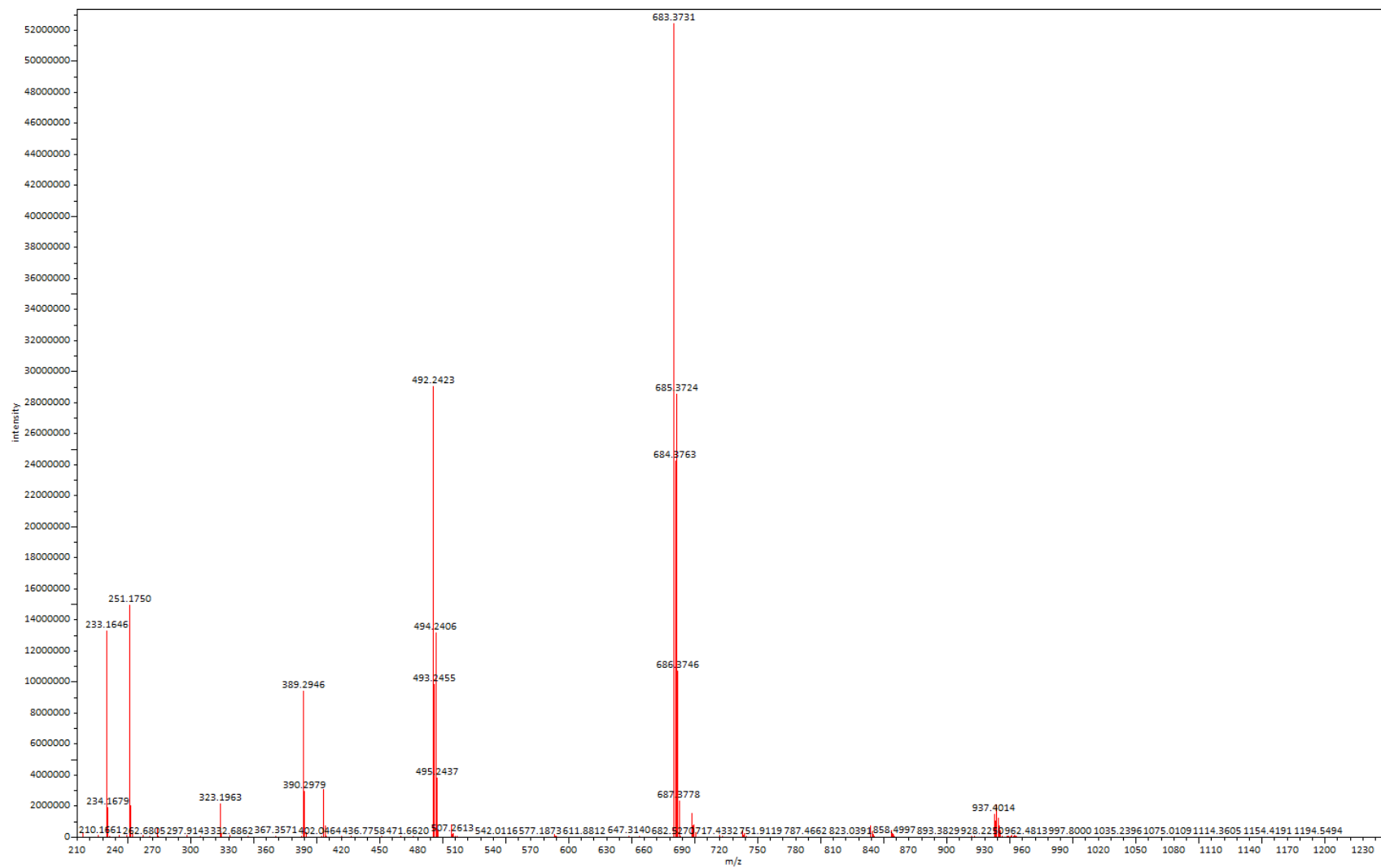
<sup>19</sup>F NMR



$^{31}\text{P}$  NMR

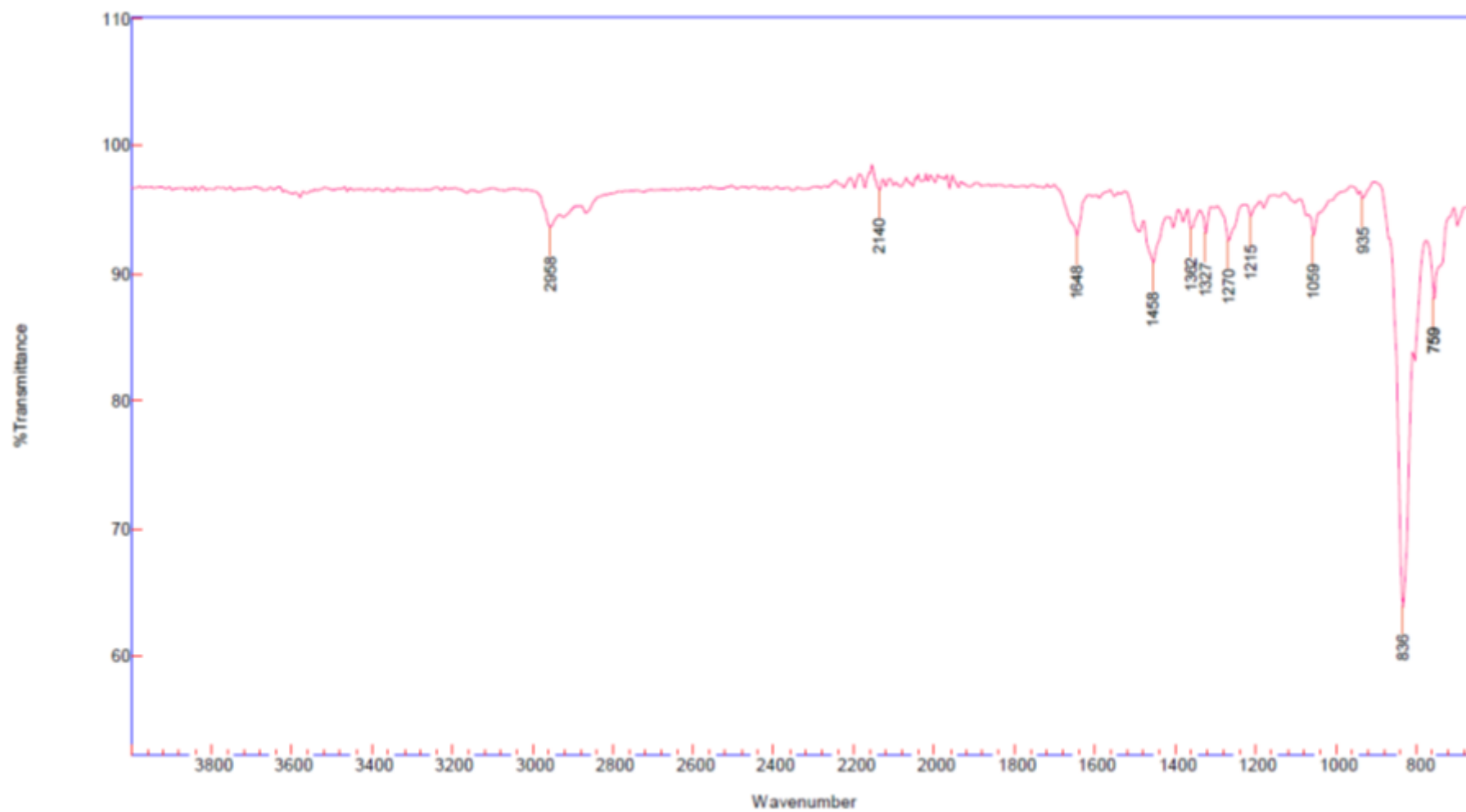


## HRMS

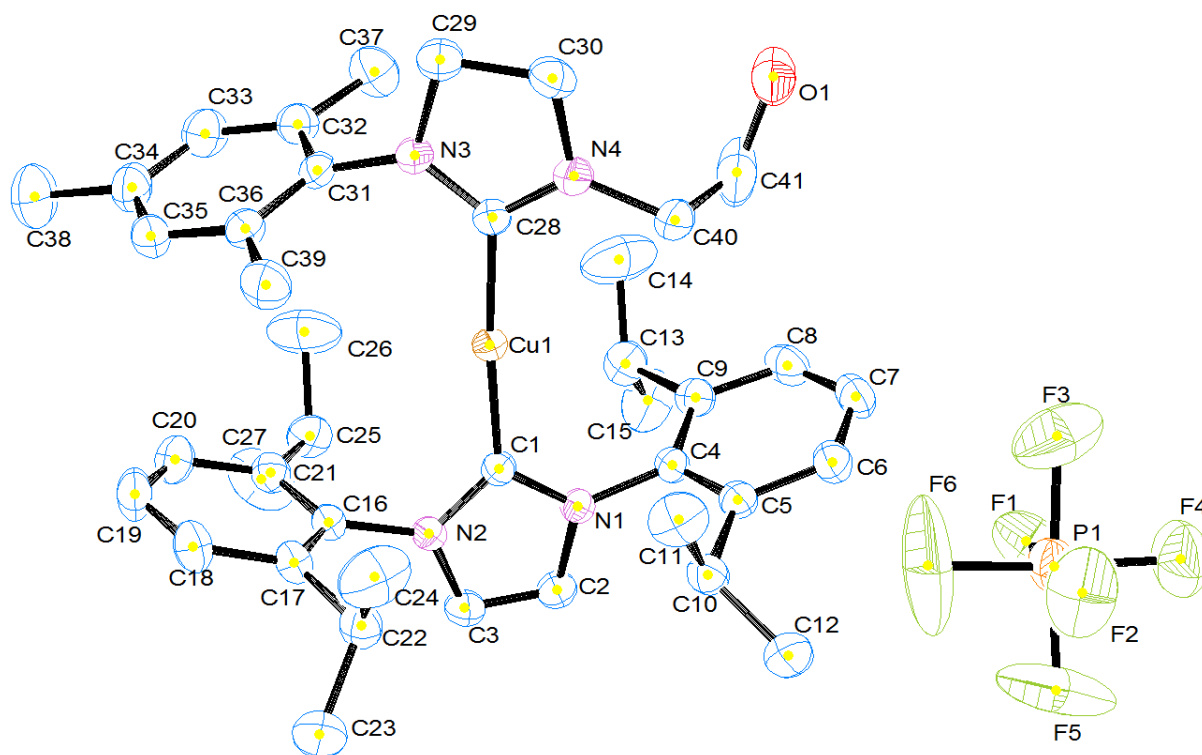




IR



## 6 X-Ray data for complex 5



X-Ray crystal structure of **5**. Hydrogen atoms have been omitted for clarity.

Table 1. Crystal data und structure refinement for cu-2045.

Identification code	cu-2045	
Empirical formula	C <sub>41</sub> H <sub>56</sub> Cu F <sub>6</sub> N <sub>4</sub> O P	
Formula weight	829.41	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 10.7213(4)$ Å	$\alpha = 72.433(3)^\circ$ .
	$b = 12.3889(3)$ Å	$\beta = 74.558(3)^\circ$ .
	$c = 17.3965(5)$ Å	$\gamma = 82.459(2)^\circ$ .
Volume	$2120.17(11)$ Å <sup>3</sup>	
Z	2	
Density (calculated)	1.299 Mg/m <sup>3</sup>	
Absorption coefficient	1.609 mm <sup>-1</sup>	
F(000)	872	

Crystal size	0.37 x 0.17 x 0.12 mm <sup>3</sup>
Theta range for data collection	2.74 to 67.49°.
Index ranges	-12<=h<=12, -10<=k<=14, -20<=l<=20
Reflections collected	14129
Independent reflections	7630 [R(int) = 0.0173]
Completeness to theta = 67.49°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. und min. transmission	0.8328 und 0.5874
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	7630 / 0 / 496
Goodness-of-fit on F <sup>2</sup>	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.1153
R indices (all data)	R1 = 0.0466, wR2 = 0.1185
Largest diff. peak und hole	1.017 und -0.610 e.Å <sup>-3</sup>

Table 2. Atomic coordinates ( x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for cu-2045. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

	x	y	z	U(eq)
Cu(1)	6295(1)	2663(1)	2863(1)	27(1)
O(1)	4537(2)	6213(2)	3987(1)	62(1)
N(1)	9057(2)	2352(1)	2792(1)	26(1)
N(2)	8471(2)	1086(1)	2379(1)	26(1)
N(3)	3605(2)	3329(1)	2830(1)	28(1)
N(4)	4225(2)	3930(2)	3702(1)	38(1)
C(1)	7997(2)	1982(2)	2684(1)	24(1)
C(2)	10159(2)	1709(2)	2548(1)	34(1)
C(3)	9793(2)	907(2)	2292(1)	35(1)
C(4)	9033(2)	3264(2)	3153(1)	27(1)
C(5)	8973(2)	2978(2)	4004(1)	30(1)
C(6)	9013(2)	3859(2)	4339(2)	36(1)
C(7)	9135(2)	4962(2)	3835(2)	41(1)
C(8)	9173(2)	5222(2)	3002(2)	40(1)
C(9)	9108(2)	4378(2)	2638(1)	34(1)
C(10)	8810(2)	1762(2)	4553(1)	35(1)
C(11)	7378(3)	1575(2)	4957(2)	51(1)
C(12)	9609(3)	1438(2)	5204(2)	53(1)

C(13)	9140(2)	4666(2)	1720(2)	42(1)
C(14)	8099(4)	5569(4)	1476(2)	90(1)
C(15)	10473(3)	5012(3)	1190(2)	68(1)
C(16)	7676(2)	434(2)	2155(1)	28(1)
C(17)	7109(2)	-516(2)	2753(1)	32(1)
C(18)	6313(2)	-1100(2)	2520(2)	41(1)
C(19)	6109(3)	-757(2)	1730(2)	46(1)
C(20)	6708(3)	173(2)	1146(2)	44(1)
C(21)	7509(2)	795(2)	1343(1)	34(1)
C(22)	7365(2)	-929(2)	3616(1)	36(1)
C(23)	8020(3)	-2114(2)	3755(2)	55(1)
C(24)	6134(3)	-890(3)	4289(2)	70(1)
C(25)	8157(2)	1818(2)	703(1)	40(1)
C(26)	7163(3)	2743(3)	439(2)	75(1)
C(27)	9063(4)	1501(3)	-44(2)	78(1)
C(28)	4611(2)	3374(2)	3125(1)	28(1)
C(29)	2411(2)	3913(2)	3207(2)	38(1)
C(30)	2834(2)	4262(2)	3859(1)	37(1)
C(31)	3641(2)	2854(2)	2166(1)	28(1)
C(32)	3769(2)	3579(2)	1365(1)	35(1)
C(33)	3707(3)	3118(2)	740(2)	44(1)
C(34)	3553(2)	1971(2)	894(2)	45(1)
C(35)	3465(2)	1271(2)	1690(2)	39(1)
C(36)	3501(2)	1697(2)	2341(1)	32(1)
C(37)	4024(3)	4810(2)	1173(2)	48(1)
C(38)	3511(4)	1493(3)	199(2)	71(1)
C(39)	3378(3)	914(2)	3201(2)	45(1)
C(40)	5083(3)	4211(3)	4129(2)	59(1)
C(41)	5508(3)	5410(3)	3779(2)	69(1)
P(1)	7626(1)	2363(1)	7629(1)	46(1)
F(1)	8412(2)	3073(1)	6738(1)	62(1)
F(2)	6826(2)	1662(2)	8504(1)	81(1)
F(3)	6411(2)	3274(2)	7532(1)	92(1)
F(4)	8090(2)	3134(2)	8058(1)	76(1)
F(5)	8821(3)	1529(2)	7732(2)	129(1)
F(6)	7090(4)	1657(3)	7189(2)	147(2)

Table 3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for cu-2045.

---

Cu(1)-C(1)	1.8955(19)
Cu(1)-C(28)	1.905(2)
O(1)-C(41)	1.396(4)
N(1)-C(1)	1.357(2)
N(1)-C(2)	1.378(3)
N(1)-C(4)	1.443(2)
N(2)-C(1)	1.354(2)
N(2)-C(3)	1.380(3)
N(2)-C(16)	1.442(2)
N(3)-C(28)	1.327(3)
N(3)-C(31)	1.434(3)
N(3)-C(29)	1.479(3)
N(4)-C(28)	1.332(3)
N(4)-C(40)	1.458(3)
N(4)-C(30)	1.469(3)
C(2)-C(3)	1.342(3)
C(4)-C(9)	1.400(3)
C(4)-C(5)	1.400(3)
C(5)-C(6)	1.393(3)
C(5)-C(10)	1.524(3)
C(6)-C(7)	1.384(3)
C(7)-C(8)	1.378(4)
C(8)-C(9)	1.394(3)
C(9)-C(13)	1.520(3)
C(10)-C(11)	1.525(3)
C(10)-C(12)	1.527(3)
C(13)-C(15)	1.515(4)
C(13)-C(14)	1.522(4)
C(16)-C(17)	1.396(3)
C(16)-C(21)	1.400(3)
C(17)-C(18)	1.392(3)
C(17)-C(22)	1.520(3)
C(18)-C(19)	1.379(4)
C(19)-C(20)	1.383(4)
C(20)-C(21)	1.392(3)
C(21)-C(25)	1.515(3)
C(22)-C(24)	1.519(4)

C(22)-C(23)	1.520(3)
C(25)-C(26)	1.511(4)
C(25)-C(27)	1.524(4)
C(29)-C(30)	1.517(3)
C(31)-C(36)	1.393(3)
C(31)-C(32)	1.394(3)
C(32)-C(33)	1.392(3)
C(32)-C(37)	1.504(3)
C(33)-C(34)	1.388(4)
C(34)-C(35)	1.382(4)
C(34)-C(38)	1.511(3)
C(35)-C(36)	1.396(3)
C(36)-C(39)	1.500(3)
C(40)-C(41)	1.506(5)
P(1)-F(5)	1.551(2)
P(1)-F(6)	1.566(2)
P(1)-F(4)	1.5721(18)
P(1)-F(2)	1.5838(18)
P(1)-F(1)	1.6007(17)
P(1)-F(3)	1.617(2)
C(1)-Cu(1)-C(28)	174.96(8)
C(1)-N(1)-C(2)	111.19(17)
C(1)-N(1)-C(4)	124.68(16)
C(2)-N(1)-C(4)	124.07(16)
C(1)-N(2)-C(3)	111.66(16)
C(1)-N(2)-C(16)	123.17(16)
C(3)-N(2)-C(16)	125.15(16)
C(28)-N(3)-C(31)	125.47(17)
C(28)-N(3)-C(29)	113.16(17)
C(31)-N(3)-C(29)	121.19(16)
C(28)-N(4)-C(40)	124.25(19)
C(28)-N(4)-C(30)	113.21(18)
C(40)-N(4)-C(30)	122.53(18)
N(2)-C(1)-N(1)	103.81(16)
N(2)-C(1)-Cu(1)	129.85(14)
N(1)-C(1)-Cu(1)	126.23(14)
C(3)-C(2)-N(1)	107.07(18)
C(2)-C(3)-N(2)	106.27(18)

C(9)-C(4)-C(5)	123.35(19)
C(9)-C(4)-N(1)	118.88(18)
C(5)-C(4)-N(1)	117.74(17)
C(6)-C(5)-C(4)	117.29(19)
C(6)-C(5)-C(10)	121.1(2)
C(4)-C(5)-C(10)	121.56(18)
C(7)-C(6)-C(5)	120.4(2)
C(8)-C(7)-C(6)	121.1(2)
C(7)-C(8)-C(9)	121.0(2)
C(8)-C(9)-C(4)	116.9(2)
C(8)-C(9)-C(13)	120.9(2)
C(4)-C(9)-C(13)	122.21(19)
C(5)-C(10)-C(11)	109.82(18)
C(5)-C(10)-C(12)	113.0(2)
C(11)-C(10)-C(12)	111.1(2)
C(15)-C(13)-C(9)	110.9(2)
C(15)-C(13)-C(14)	111.1(3)
C(9)-C(13)-C(14)	112.3(2)
C(17)-C(16)-C(21)	123.33(19)
C(17)-C(16)-N(2)	118.80(18)
C(21)-C(16)-N(2)	117.86(18)
C(18)-C(17)-C(16)	117.0(2)
C(18)-C(17)-C(22)	120.6(2)
C(16)-C(17)-C(22)	122.35(19)
C(19)-C(18)-C(17)	121.2(2)
C(18)-C(19)-C(20)	120.4(2)
C(19)-C(20)-C(21)	121.1(2)
C(20)-C(21)-C(16)	116.9(2)
C(20)-C(21)-C(25)	121.0(2)
C(16)-C(21)-C(25)	122.1(2)
C(24)-C(22)-C(23)	111.3(2)
C(24)-C(22)-C(17)	111.8(2)
C(23)-C(22)-C(17)	110.3(2)
C(26)-C(25)-C(21)	111.0(2)
C(26)-C(25)-C(27)	111.2(3)
C(21)-C(25)-C(27)	111.7(2)
N(3)-C(28)-N(4)	108.42(18)
N(3)-C(28)-Cu(1)	127.06(15)

N(4)-C(28)-Cu(1)	124.30(15)
N(3)-C(29)-C(30)	102.23(17)
N(4)-C(30)-C(29)	102.65(16)
C(36)-C(31)-C(32)	121.76(19)
C(36)-C(31)-N(3)	119.56(18)
C(32)-C(31)-N(3)	118.64(18)
C(33)-C(32)-C(31)	117.8(2)
C(33)-C(32)-C(37)	120.9(2)
C(31)-C(32)-C(37)	121.2(2)
C(34)-C(33)-C(32)	121.9(2)
C(35)-C(34)-C(33)	118.8(2)
C(35)-C(34)-C(38)	120.6(3)
C(33)-C(34)-C(38)	120.6(3)
C(34)-C(35)-C(36)	121.4(2)
C(31)-C(36)-C(35)	118.3(2)
C(31)-C(36)-C(39)	121.8(2)
C(35)-C(36)-C(39)	119.9(2)
N(4)-C(40)-C(41)	114.1(2)
O(1)-C(41)-C(40)	113.3(2)
F(5)-P(1)-F(6)	93.2(2)
F(5)-P(1)-F(4)	90.61(16)
F(6)-P(1)-F(4)	176.19(18)
F(5)-P(1)-F(2)	90.05(14)
F(6)-P(1)-F(2)	90.22(12)
F(4)-P(1)-F(2)	90.25(11)
F(5)-P(1)-F(1)	90.69(12)
F(6)-P(1)-F(1)	89.05(12)
F(4)-P(1)-F(1)	90.43(11)
F(2)-P(1)-F(1)	178.98(12)
F(5)-P(1)-F(3)	177.43(17)
F(6)-P(1)-F(3)	89.32(19)
F(4)-P(1)-F(3)	86.89(13)
F(2)-P(1)-F(3)	90.58(12)
F(1)-P(1)-F(3)	88.70(10)

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for cu-2045. The anisotropic



displacement factor exponent takes the form:  $-2 \pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
Cu(1)	23(1)	26(1)	35(1)	-12(1)	-10(1)	2(1)
O(1)	83(2)	55(1)	65(1)	-27(1)	-38(1)	1(1)
N(1)	23(1)	25(1)	31(1)	-9(1)	-7(1)	-2(1)
N(2)	26(1)	23(1)	31(1)	-9(1)	-8(1)	0(1)
N(3)	23(1)	31(1)	33(1)	-13(1)	-7(1)	1(1)
N(4)	39(1)	43(1)	41(1)	-23(1)	-20(1)	13(1)
C(1)	26(1)	21(1)	26(1)	-4(1)	-8(1)	-4(1)
C(2)	21(1)	39(1)	46(1)	-17(1)	-9(1)	1(1)
C(3)	26(1)	36(1)	44(1)	-17(1)	-8(1)	5(1)
C(4)	20(1)	26(1)	38(1)	-12(1)	-7(1)	-3(1)
C(5)	23(1)	30(1)	37(1)	-12(1)	-7(1)	-1(1)
C(6)	33(1)	39(1)	42(1)	-19(1)	-9(1)	0(1)
C(7)	37(1)	34(1)	59(2)	-24(1)	-9(1)	-3(1)
C(8)	38(1)	26(1)	56(1)	-10(1)	-10(1)	-5(1)
C(9)	27(1)	29(1)	44(1)	-8(1)	-8(1)	-6(1)
C(10)	42(1)	30(1)	34(1)	-9(1)	-12(1)	1(1)
C(11)	51(2)	45(1)	46(1)	6(1)	-8(1)	-13(1)
C(12)	67(2)	49(1)	50(2)	-17(1)	-30(1)	14(1)
C(13)	46(1)	35(1)	42(1)	-2(1)	-12(1)	-11(1)
C(14)	79(2)	118(3)	52(2)	-4(2)	-24(2)	32(2)
C(15)	58(2)	97(2)	47(2)	-20(2)	-1(1)	-22(2)
C(16)	29(1)	25(1)	33(1)	-12(1)	-9(1)	0(1)
C(17)	37(1)	27(1)	35(1)	-12(1)	-8(1)	-4(1)
C(18)	47(1)	34(1)	46(1)	-14(1)	-10(1)	-12(1)
C(19)	50(1)	46(1)	54(2)	-25(1)	-18(1)	-10(1)
C(20)	53(1)	49(1)	39(1)	-19(1)	-20(1)	-1(1)
C(21)	37(1)	34(1)	32(1)	-12(1)	-9(1)	0(1)
C(22)	44(1)	30(1)	35(1)	-5(1)	-11(1)	-7(1)
C(23)	66(2)	39(1)	62(2)	-8(1)	-29(1)	3(1)
C(24)	62(2)	104(3)	37(1)	-18(2)	-9(1)	11(2)
C(25)	45(1)	39(1)	33(1)	-5(1)	-10(1)	-3(1)
C(26)	58(2)	50(2)	86(2)	16(2)	-8(2)	5(1)
C(27)	87(2)	68(2)	55(2)	-15(2)	19(2)	-6(2)
C(28)	30(1)	27(1)	29(1)	-8(1)	-10(1)	2(1)

C(29)	26(1)	47(1)	45(1)	-21(1)	-5(1)	4(1)
C(30)	36(1)	36(1)	36(1)	-14(1)	-5(1)	6(1)
C(31)	22(1)	33(1)	32(1)	-12(1)	-8(1)	0(1)
C(32)	34(1)	36(1)	35(1)	-10(1)	-9(1)	1(1)
C(33)	51(1)	51(1)	33(1)	-13(1)	-14(1)	1(1)
C(34)	43(1)	56(2)	46(1)	-28(1)	-15(1)	0(1)
C(35)	35(1)	37(1)	52(1)	-21(1)	-13(1)	-1(1)
C(36)	25(1)	33(1)	40(1)	-12(1)	-9(1)	-1(1)
C(37)	62(2)	37(1)	40(1)	-5(1)	-9(1)	-6(1)
C(38)	87(2)	84(2)	62(2)	-45(2)	-27(2)	-1(2)
C(39)	55(2)	33(1)	46(1)	-5(1)	-15(1)	-4(1)
C(40)	61(2)	71(2)	73(2)	-51(2)	-47(2)	34(1)
C(41)	48(2)	109(3)	76(2)	-64(2)	-10(1)	-14(2)
P(1)	56(1)	32(1)	50(1)	-10(1)	-12(1)	-12(1)
F(1)	67(1)	43(1)	60(1)	-7(1)	2(1)	-7(1)
F(2)	102(2)	79(1)	55(1)	1(1)	-11(1)	-46(1)
F(3)	57(1)	133(2)	69(1)	-10(1)	-16(1)	16(1)
F(4)	93(1)	63(1)	83(1)	-27(1)	-27(1)	-23(1)
F(5)	129(2)	74(2)	121(2)	7(1)	5(2)	60(2)
F(6)	252(4)	139(2)	75(2)	-42(2)	-4(2)	-137(3)

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## 7 Literature

- [1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, 29, 2176.
- [2] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, 62, 7512.
- [3] F. Pape, N. O. Thiel, J. F. Teichert, *Chem. Eur. J.* **2015**, 21, 15934.
- [4] G. C. Fortman, A. M. Z. Slawin, S. P. Nolan, *Organometallics* **2010**, 29, 3966.
- [5] Concentration of *n*-BuLi solution was determined by titration with *suffert's reagent* (Suffert, J., *J. Org. Chem.*, **1989**, 54, 509)

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