

Electronic Supporting Information

Improved synthetic routes to *N*-heterocyclic carbene-metal-diketonate complexes of gold and copper

Ishfaq Ibni Hashim, Nikolaos V. Tzouras, Xinyuan Ma, Laurens Bourda, Kristof Van Hecke, Steven P. Nolan, Catherine S. J. Cazin

Contents

1. Procedures for one-pot, gram scale and mechanochemical reactions	S2
2. NMR spectra of the reported complexes	S3
3. References	S14

1. Procedures for one-pot, gram scale and mechanochemical reactions

One-pot reactions:

Reaction 1 (Scheme 2). A 4 mL screw cap vial was charged under air with [IPr•HCl] (100 mg, 0.235 mmol), CuCl (23.3 mg, 0.235 mmol, 1 equiv.), K₂CO₃ (97.4 mg, 0.705 mmol, 3 equiv.), and the solids were suspended in acetone (0.5 mL). The reaction mixture was stirred at 60 °C for 20 hours. Then, the reaction was cooled to room temperature and DBMH (58.0 mg, 0.259 mmol, 1.1 equiv.), K₂CO₃ (65.0 mg, 0.471 mmol, 2 equiv.) and 0.5 mL of acetone were added. The reaction mixture was stirred at room temperature for 2h. After this time the solvent was removed under vacuum and the residue was taken up in THF (3 mL) and filtered through celite which was washed using THF (2 mL). The filtrate was concentrated to dryness, and the resulting solid was recrystallized from DCM/pentane yielding orange precipitate which was washed with pentane and dried under vacuum, affording the desired complex as bright orange solid in 80% yield (127 mg).

Reaction 2 (Scheme 2). A 4 mL screw cap vial was charged under air with [IPr•HCl] (100 mg, 0.235 mmol), CuCl (23.3 mg, 0.235 mmol, 1 equiv.), DBMH (58.0 mg, 0.259 mmol, 1.1 equiv.), K₂CO₃ (162.6 mg, 1.18 mmol, 5 equiv.), and the solids were suspended in acetone (1.0 mL). The reaction mixture was stirred at 60 °C for 20 hours. Then, the reaction was cooled to room temperature. After that the solvent was removed under vacuum and the residue was taken up in THF (3 mL) and filtered through celite which was washed using THF (2 mL). The filtrate was concentrated to dryness, and the resulting solid was recrystallized from DCM/pentane yielding orange precipitate which was washed with pentane and dried under vacuum, affording the desired complex as bright orange solid in 78% yield (125 mg).

Gram-scale reaction (Scheme 2)

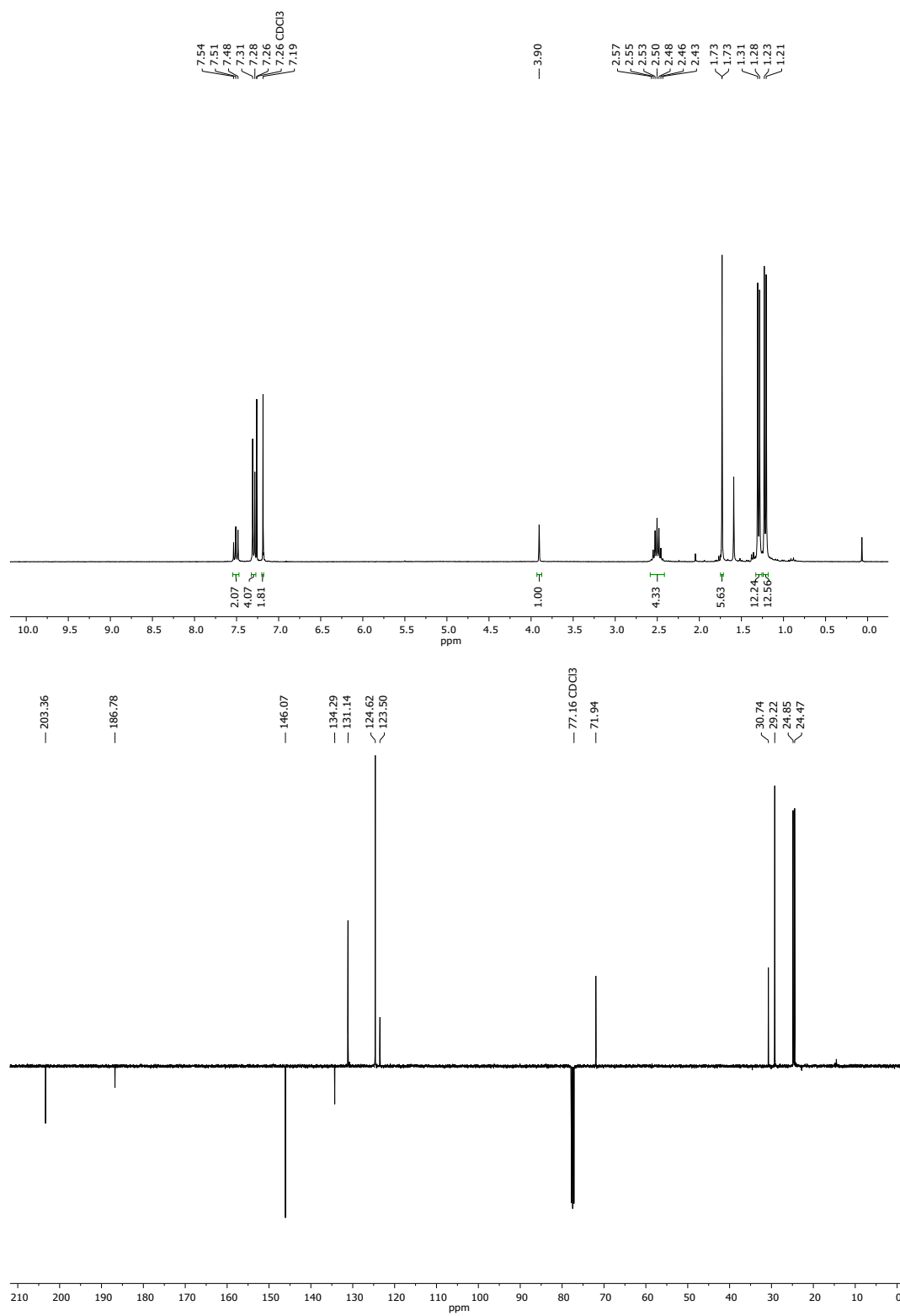
A 40 mL scintillation vial equipped with a septum cap and a stirring bar under air was charged with [Cu(Cl)(IPr)] (1.00 g, 2.05 mmol, 1 equiv.), DBMH (0.506 g, 2.26 mmol, 1.1 equiv.), and K₂CO₃ (0.850 g, 6.15 mmol, 3 equiv.) and solids suspended in acetone (10 mL). Full conversion had been achieved in one hour, as judged by NMR analysis of an aliquot. After concentrating the reaction mixture to dryness, purification of the product was carried out by filtration through a pad of Celite (3 cm) with THF (40 mL). Evaporation of the solvent to minimum and addition of pentane (30 mL) resulted in orange precipitate. The solid was additionally recrystallized from DCM/pentane, washed with pentane (3 x 20 mL) and dried under high vacuum to afford the pure product as bright orange solid in 96 % yield (1.33 g).

Mortar and pestle reaction (mechanochemical reaction)

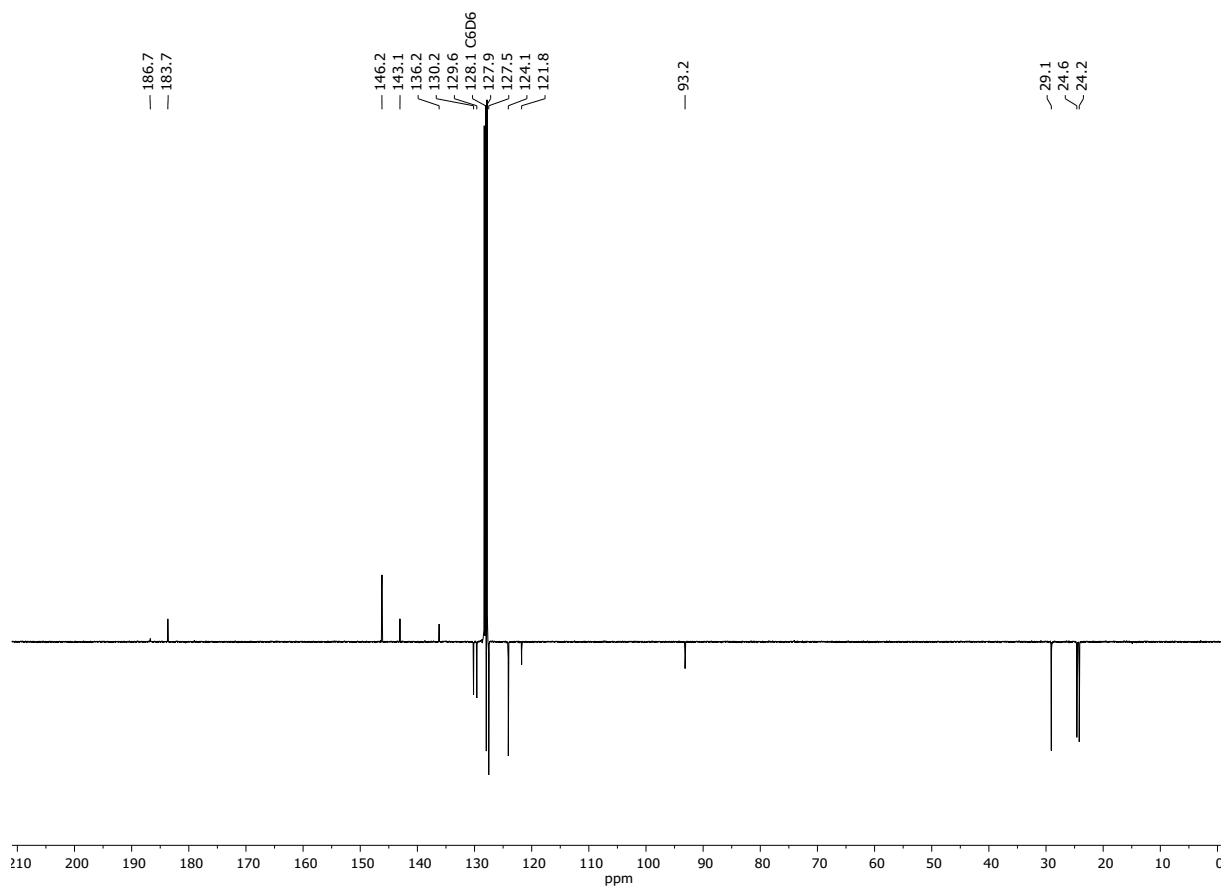
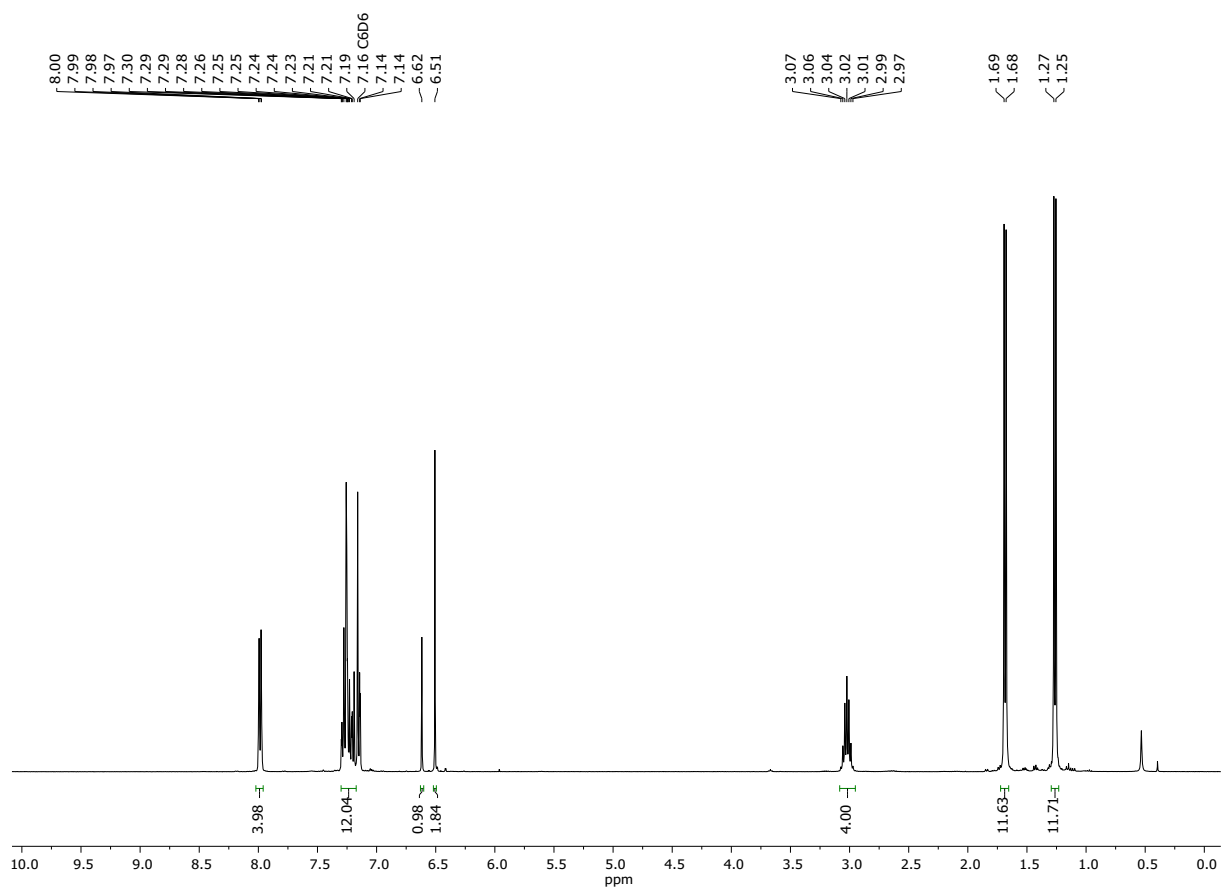
In air, [Cu(Cl)(IPr)] (50 mg, 0.103 mmol), DBMH (25.3 mg, 0.113 mmol, 1.1 equiv.) and K₂CO₃ (42.5 mg, 0.308 mmol, 3 equiv.) were added to a mortar. The solids displaying a white color were then ground using a pestle for 15 min yielding an orange powder. The crude product was suspended in DCM (5 mL) and filtered through celite. After concentrating to a minimum volume (ca. 1 mL), 8 mL of pentane were added resulting in the precipitation of an orange microcrystalline solid. The precipitate was collected by filtration on a medium porosity frit, washed with pentane (3 x 2 mL) and dried under vacuum to produce a bright orange solid in 95% yield (66 mg).

2. NMR spectra of the reported complexes

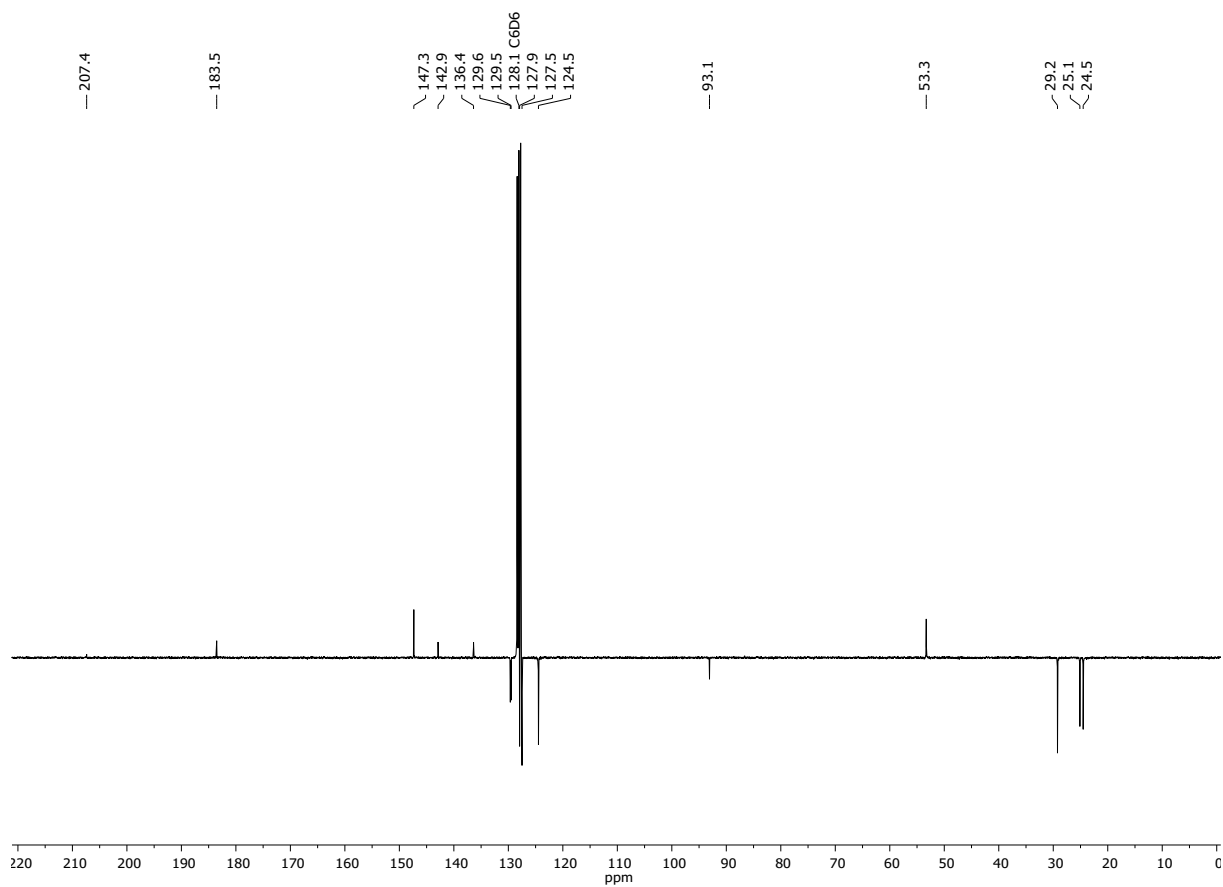
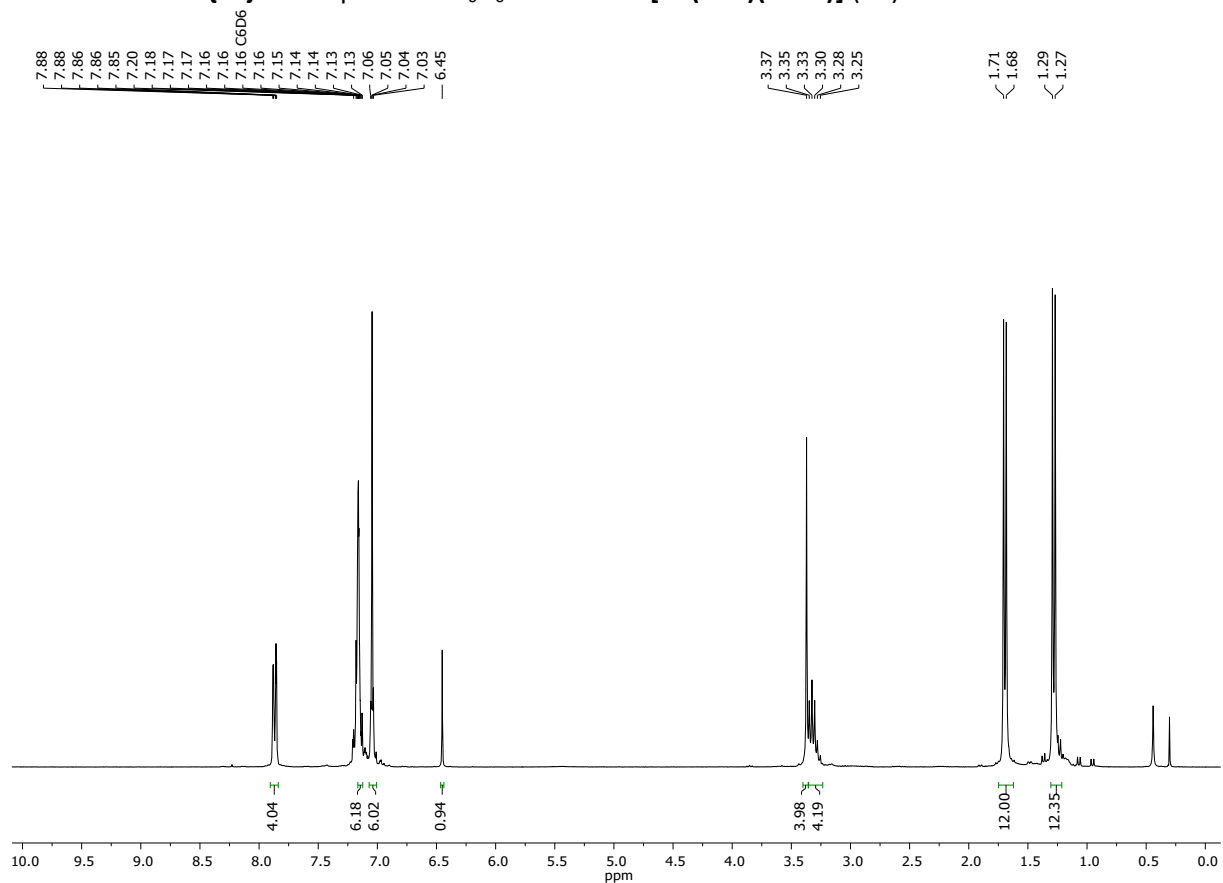
^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra in CDCl_3 at 298K for $[\text{Au}(\text{acac})(\text{IPr})]$ (**1**)¹



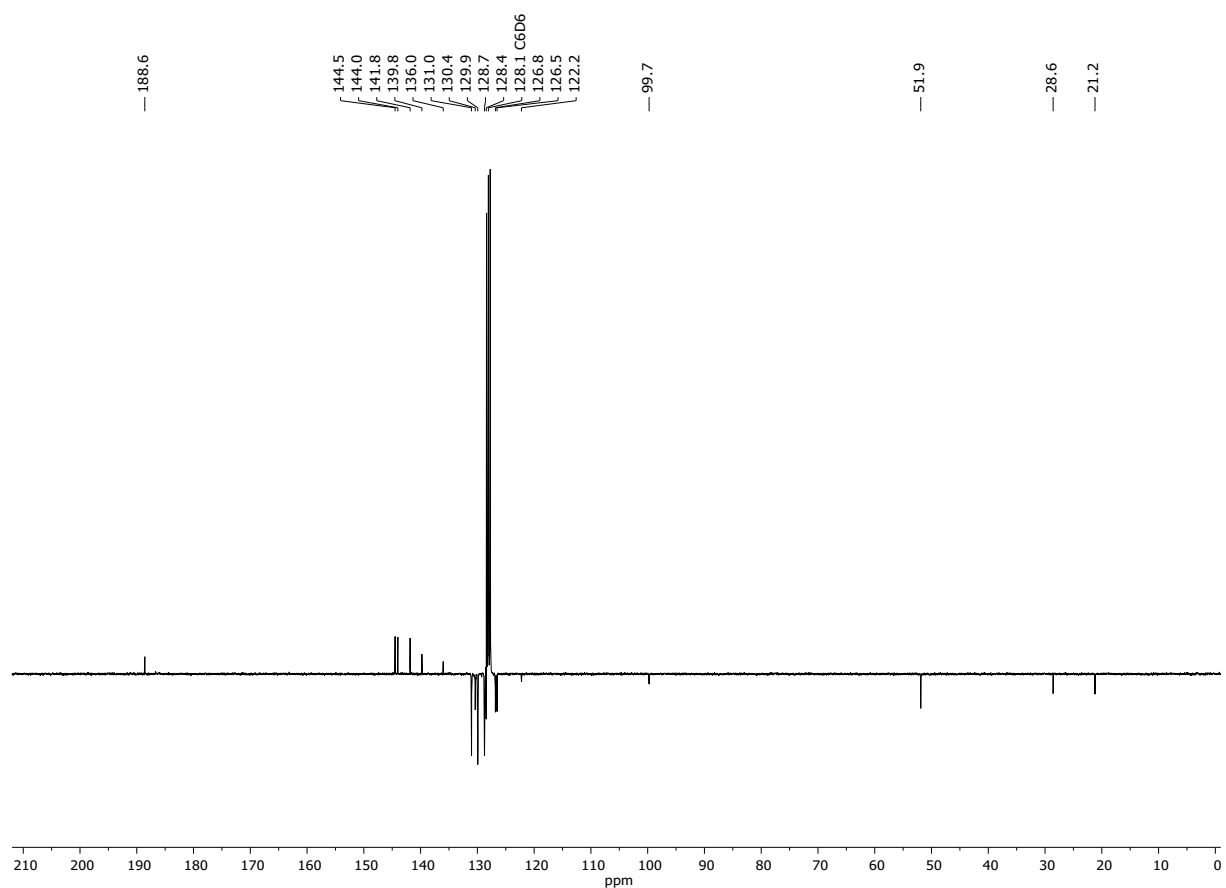
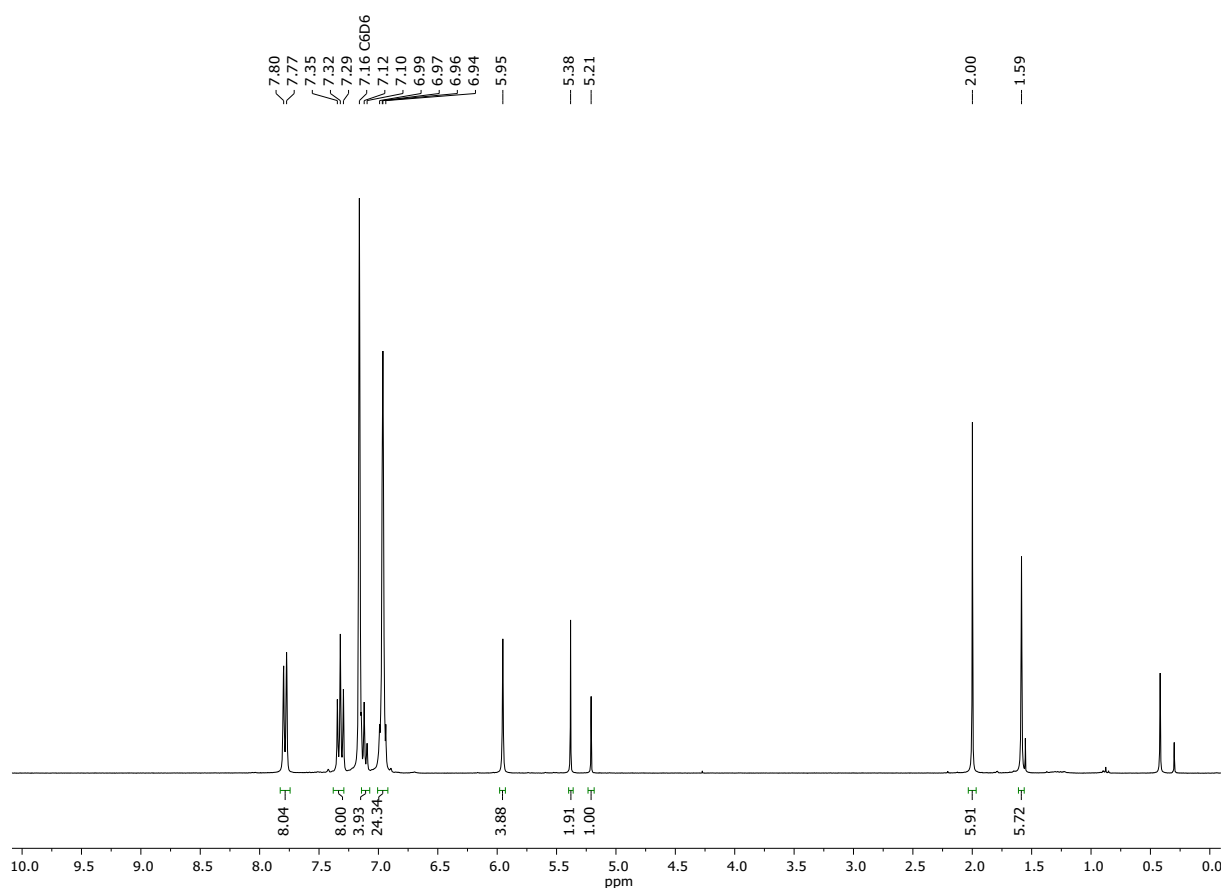
^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra in C_6D_6 at 298K for $[\text{Cu}(\text{DBM})(\text{IPr})] (\mathbf{2a})^2$



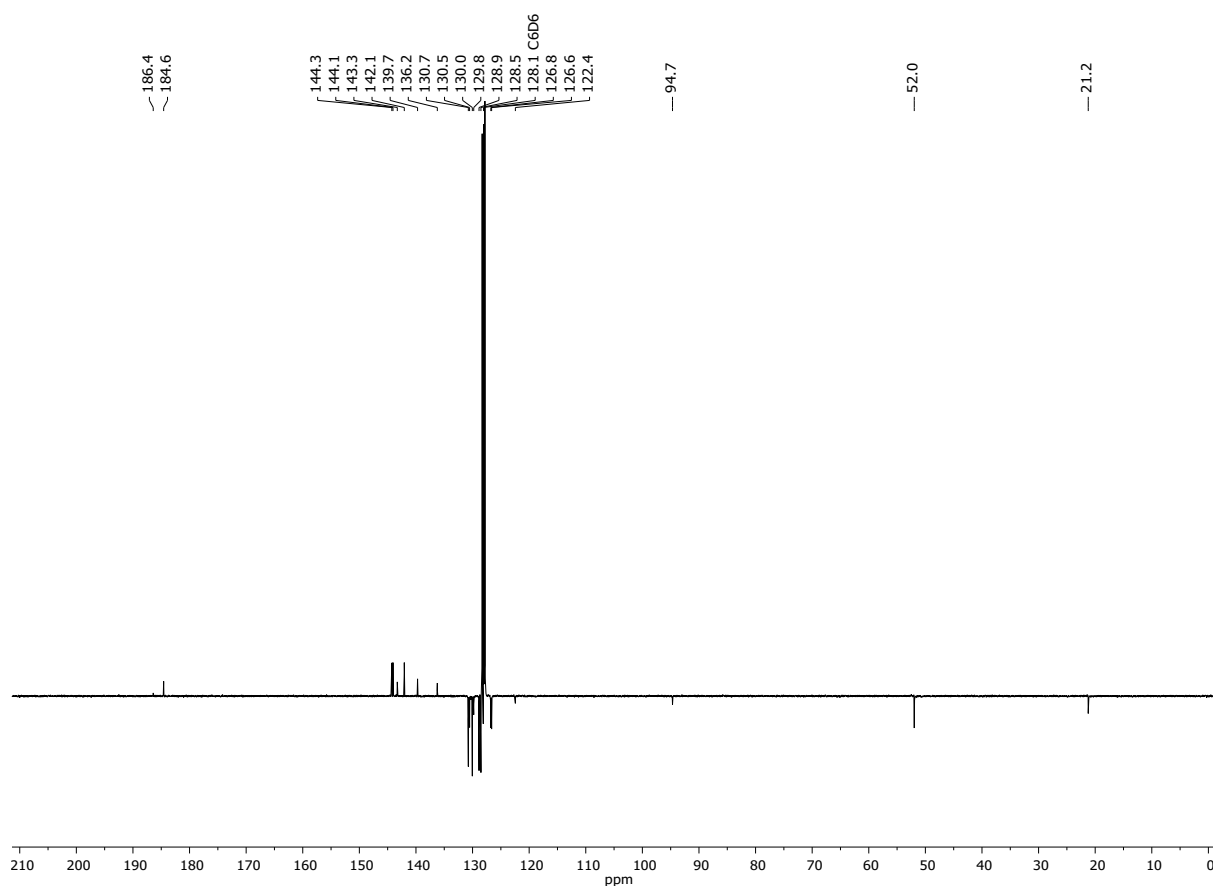
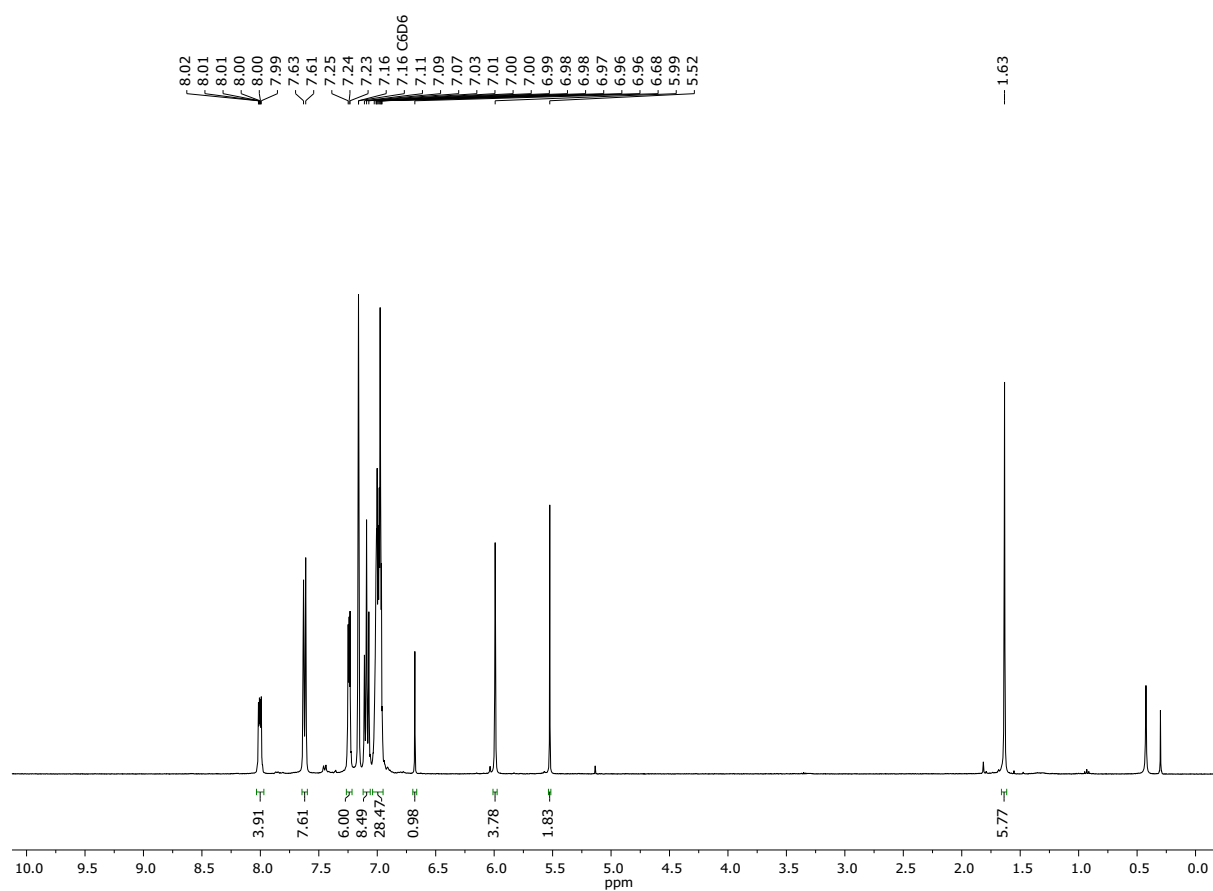
^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra in C_6D_6 at 298K for $[\text{Cu}(\text{SIPr})(\text{DBM})]$ (**2b**)



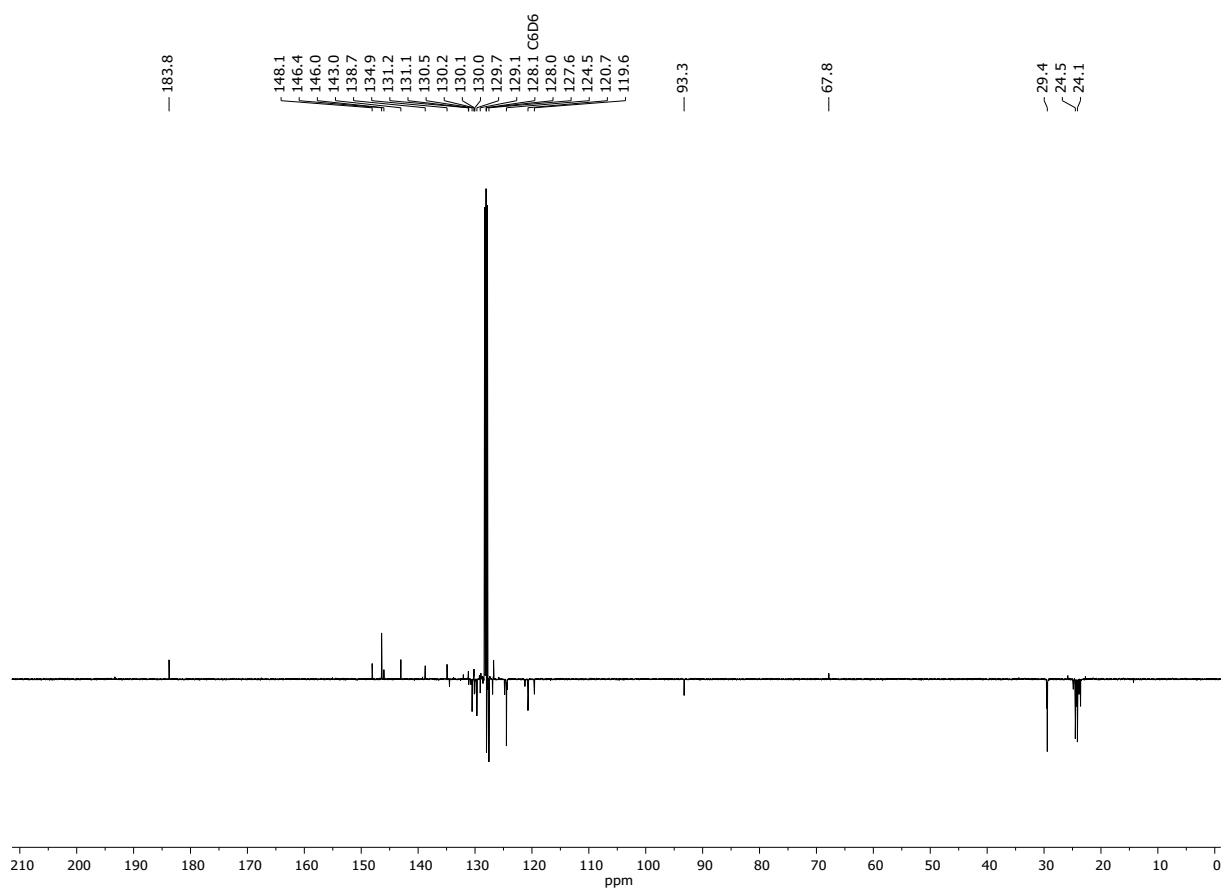
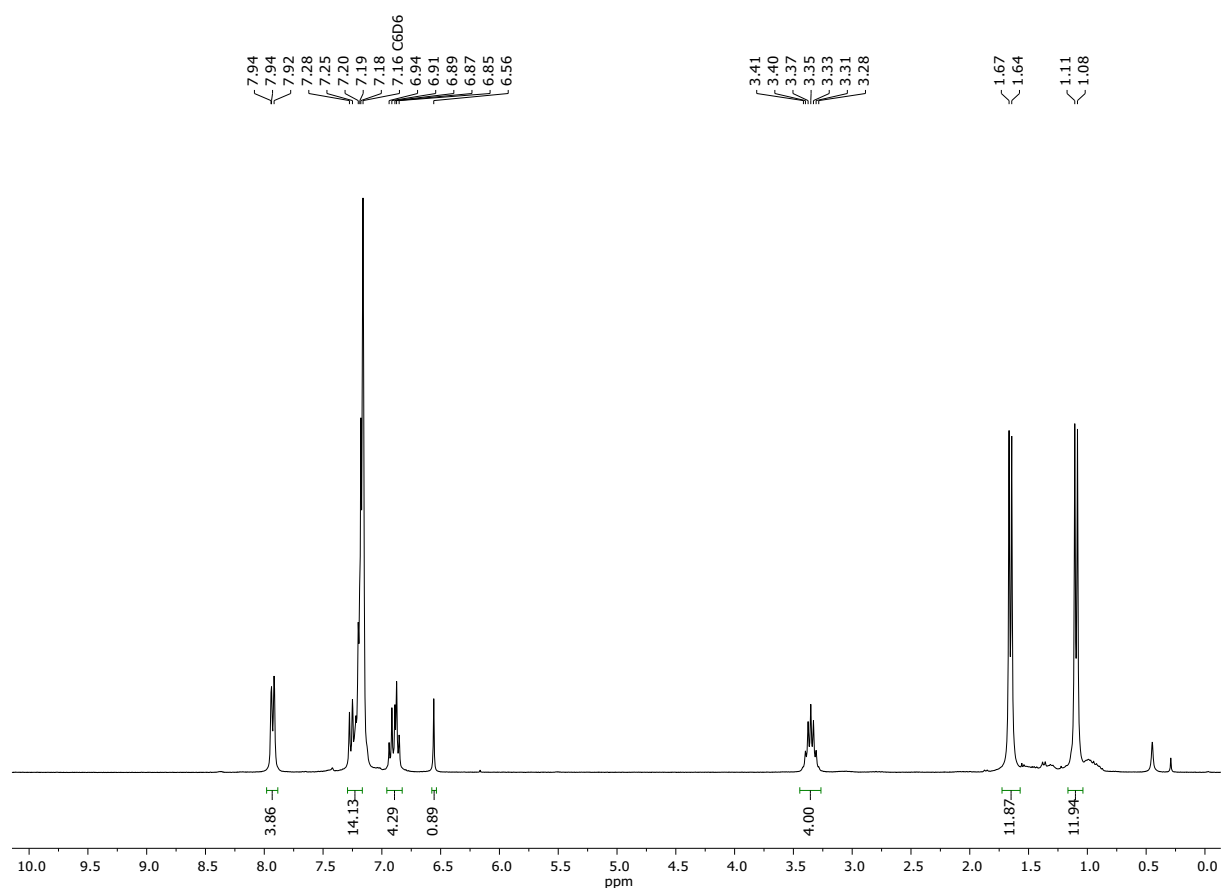
^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra in C_6D_6 at 298K for $[\text{Cu}(\text{acac})(\text{IPr}^*)]$ (**2c**)



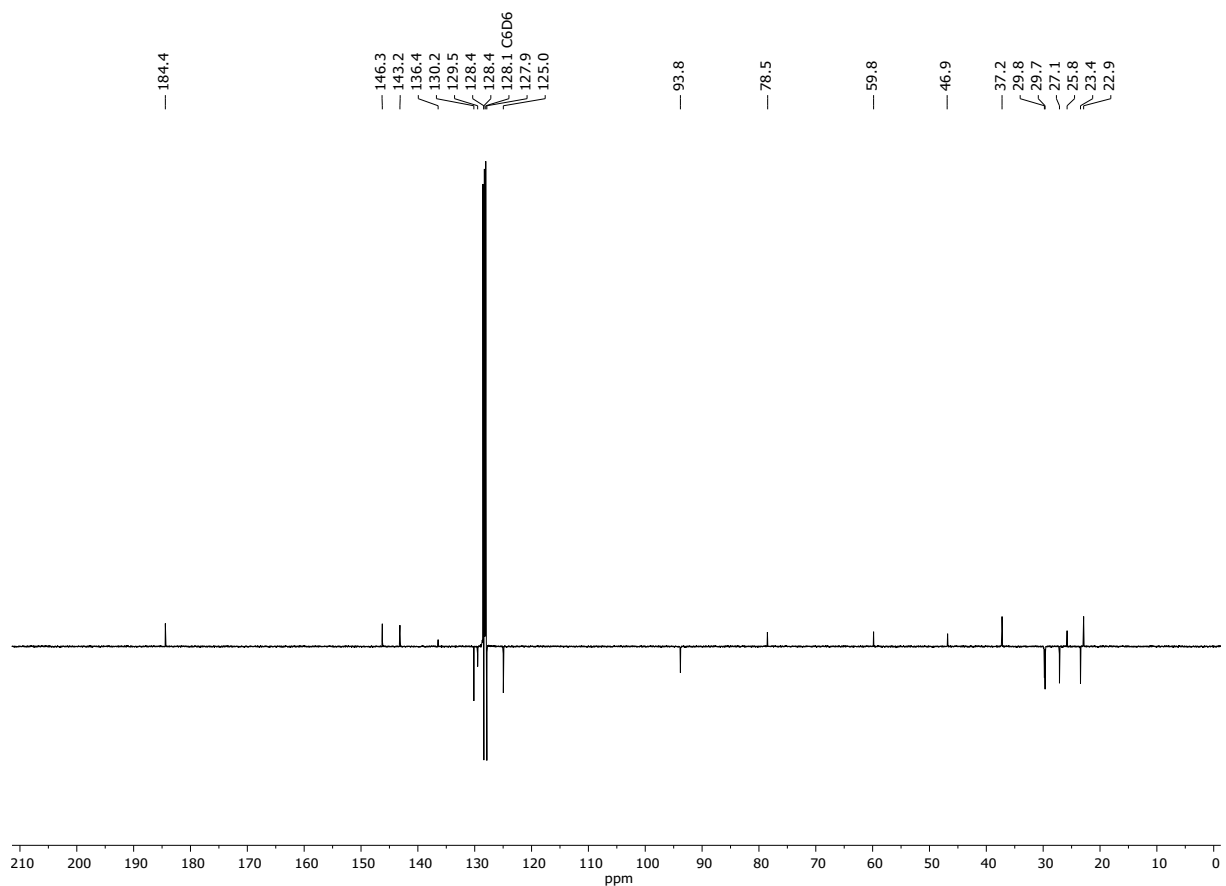
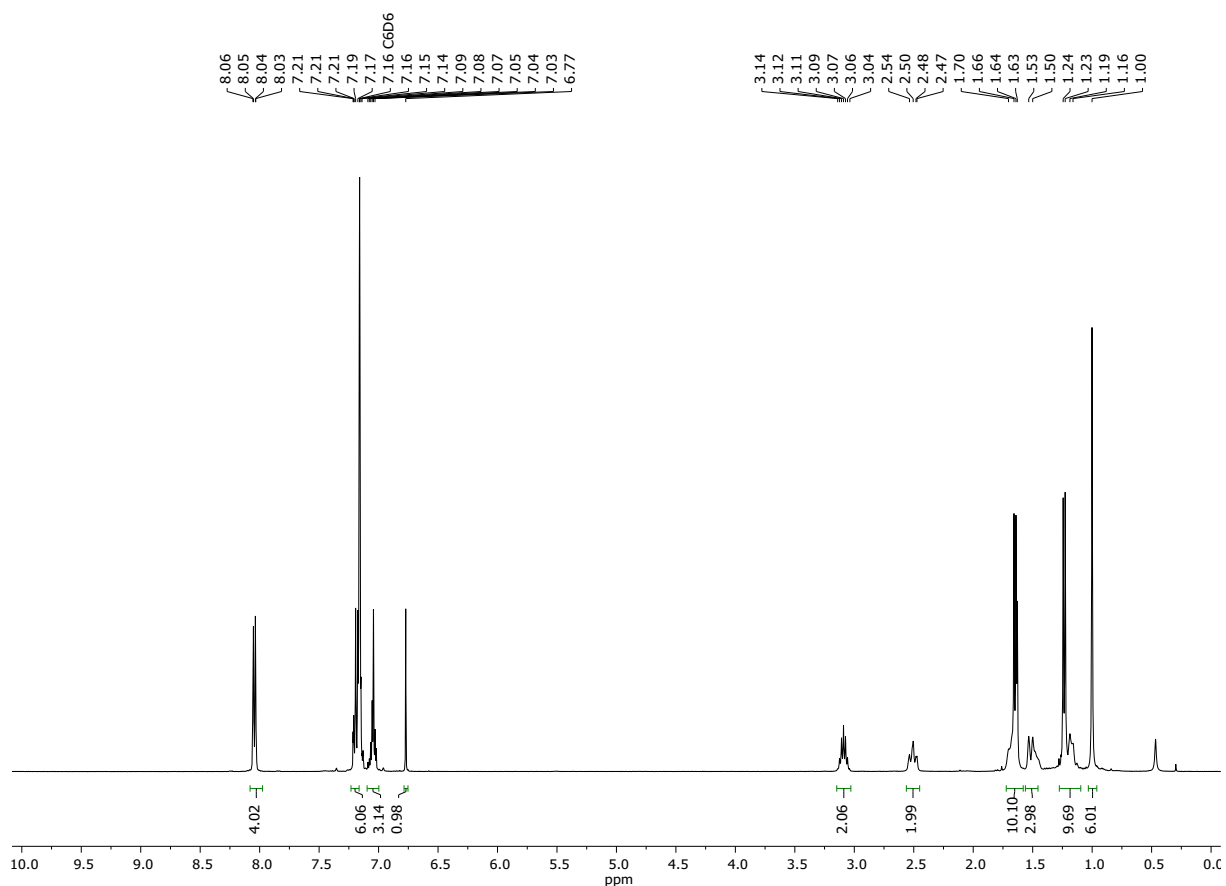
^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra in C_6D_6 at 298K for $[\text{Cu}(\text{DBM})(\text{IPr}^*)]$ (2d)



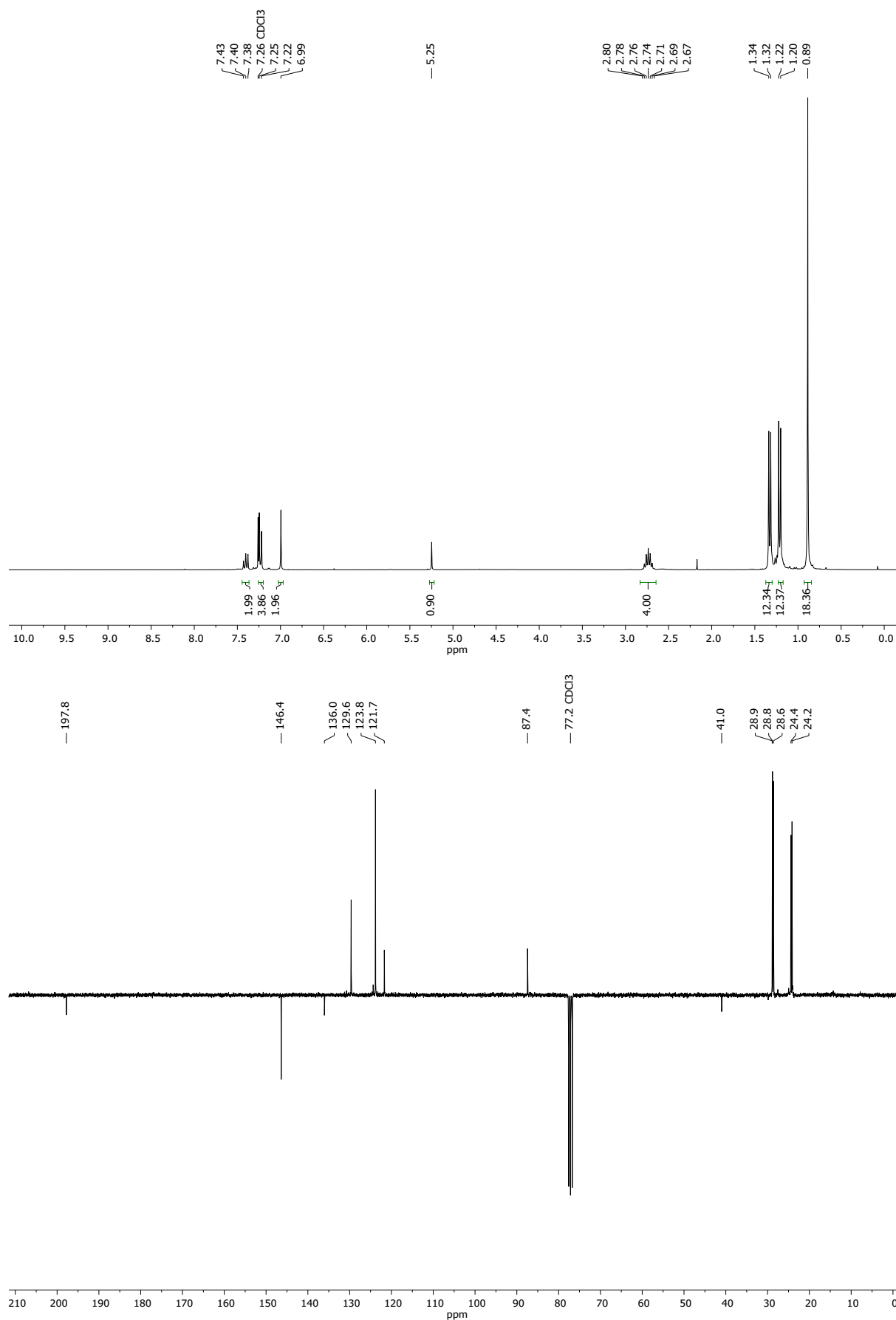
^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra in C_6D_6 at 298K for $[\text{Cu}(\text{DBM})(\text{BIAN-IPr})]$ (**2e**)



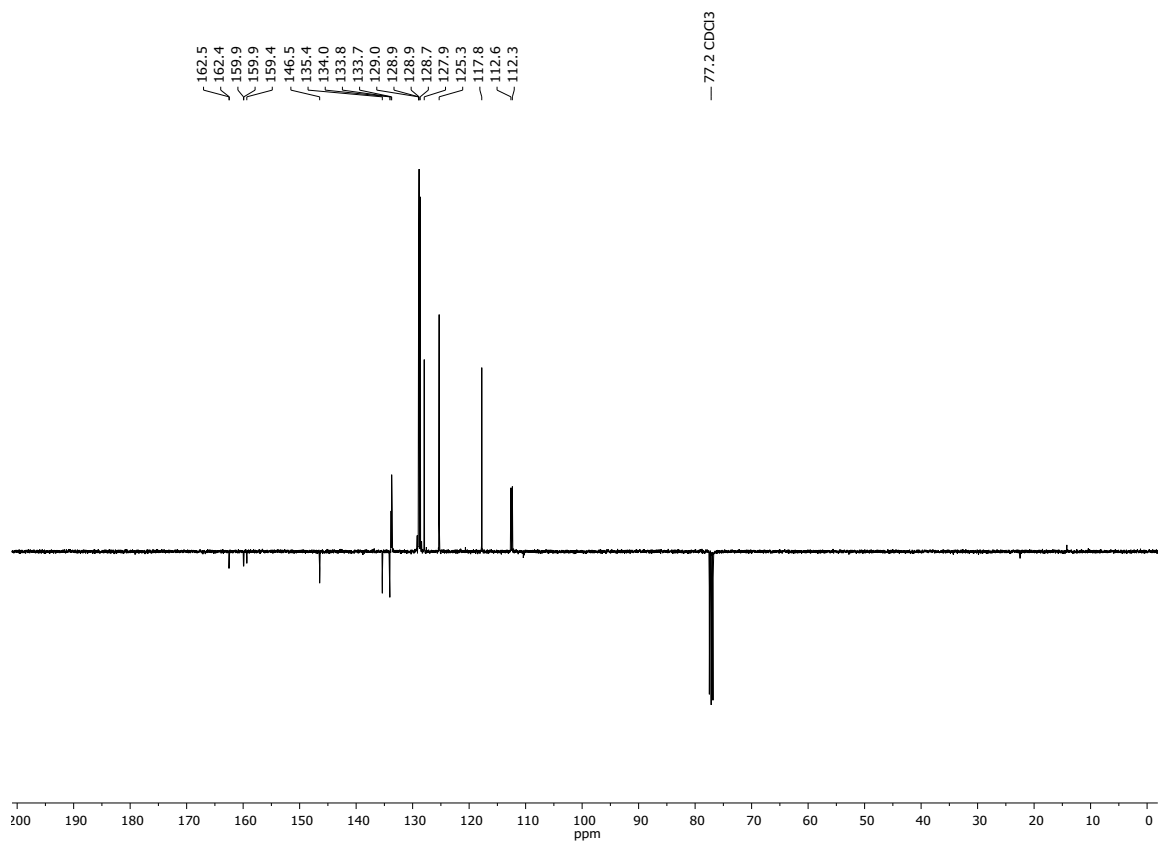
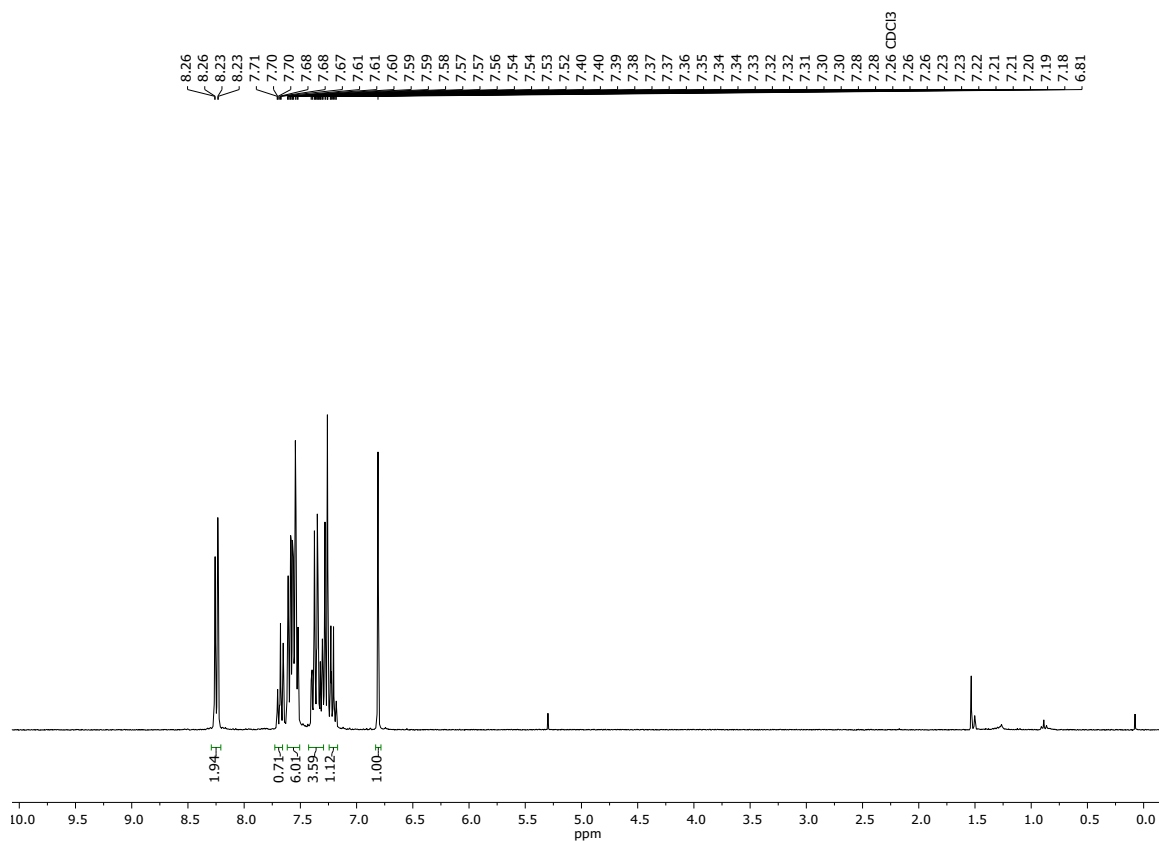
^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra in C_6D_6 at 298K for $[\text{Cu}(\text{DBM})(\text{CAAC}^{\text{Cy}})]$ (2f)



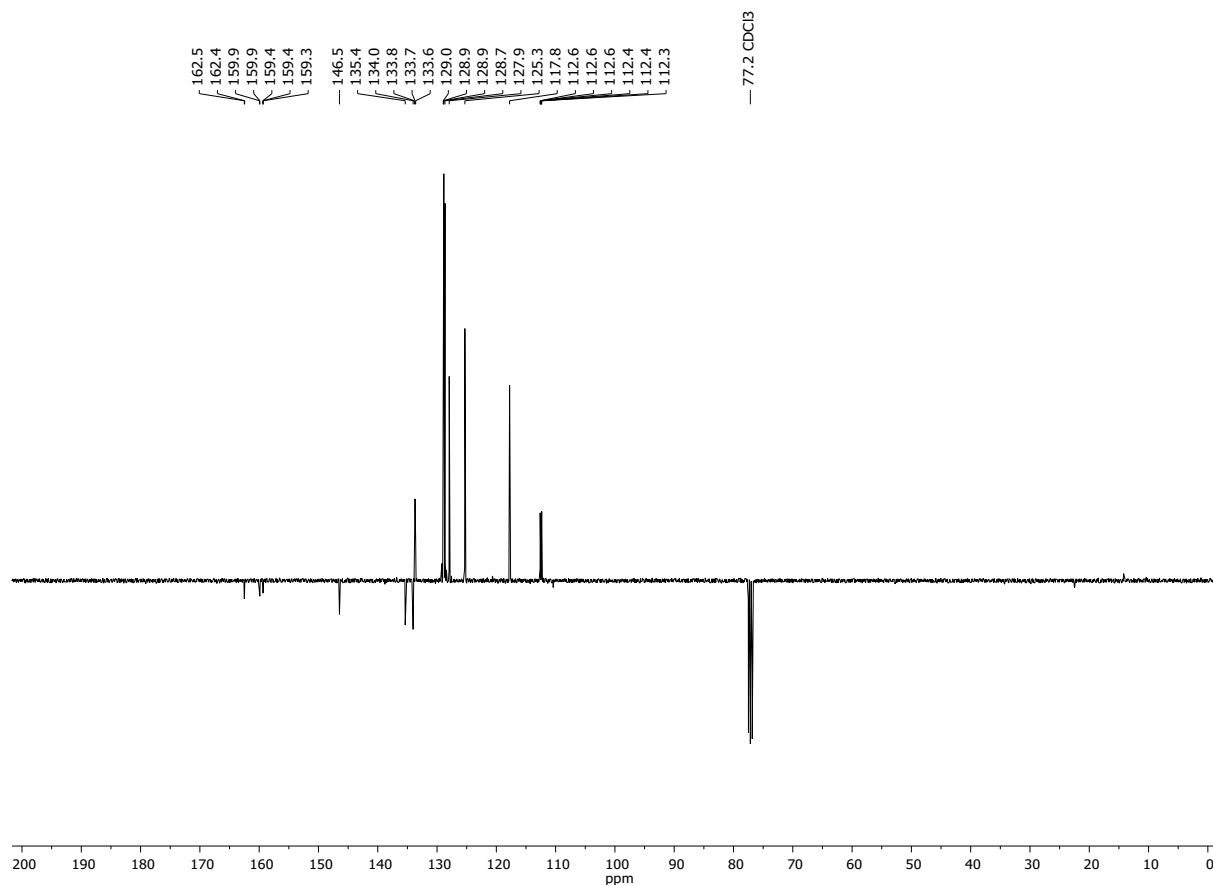
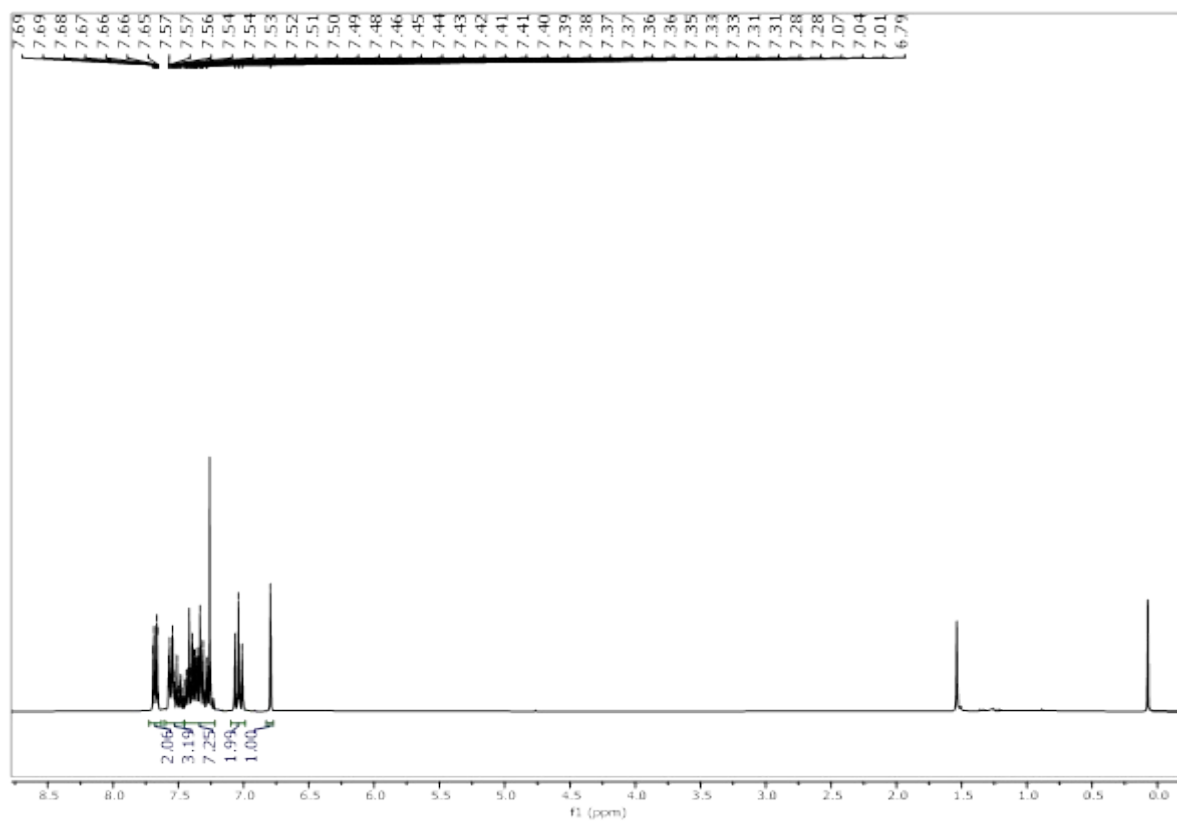
^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra in CDCl_3 at 298K for $[\text{Cu}(\text{DPM})(\text{IPr})]$ (2g)

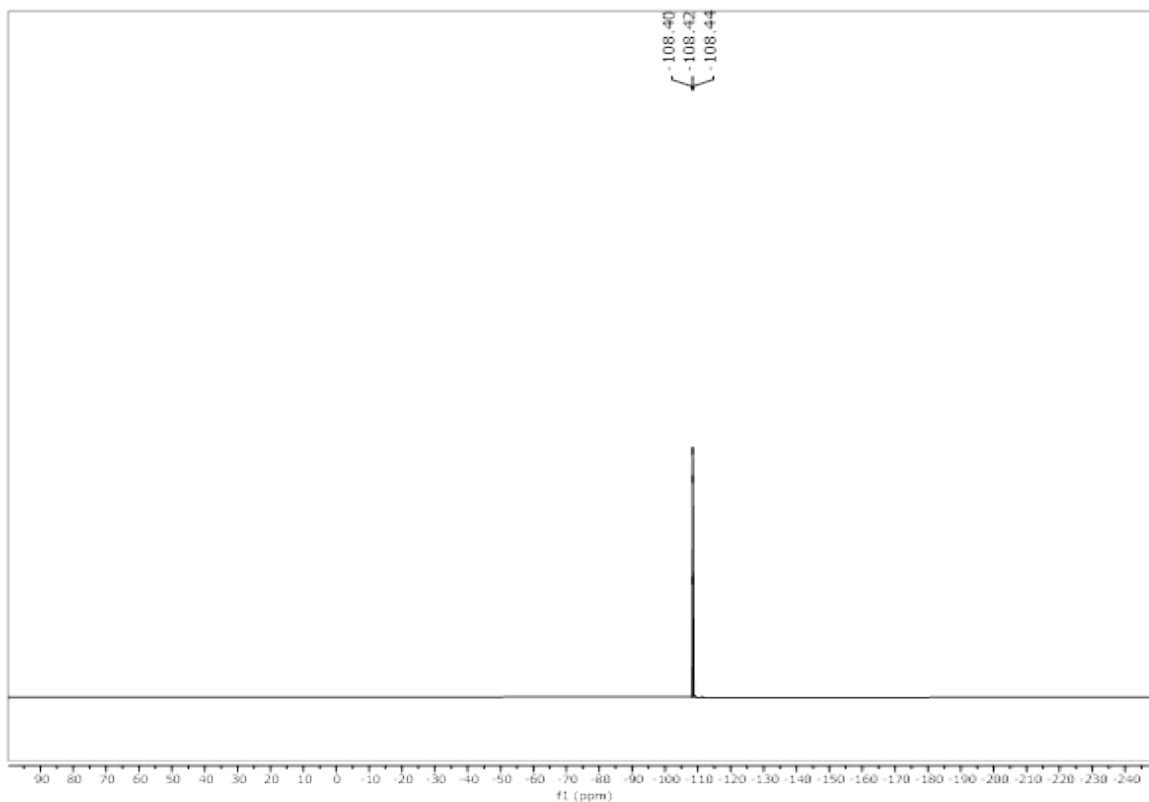


^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra in CDCl_3 at 298K for (Z)-1,2-diphenylvinyl benzoate (3a)³

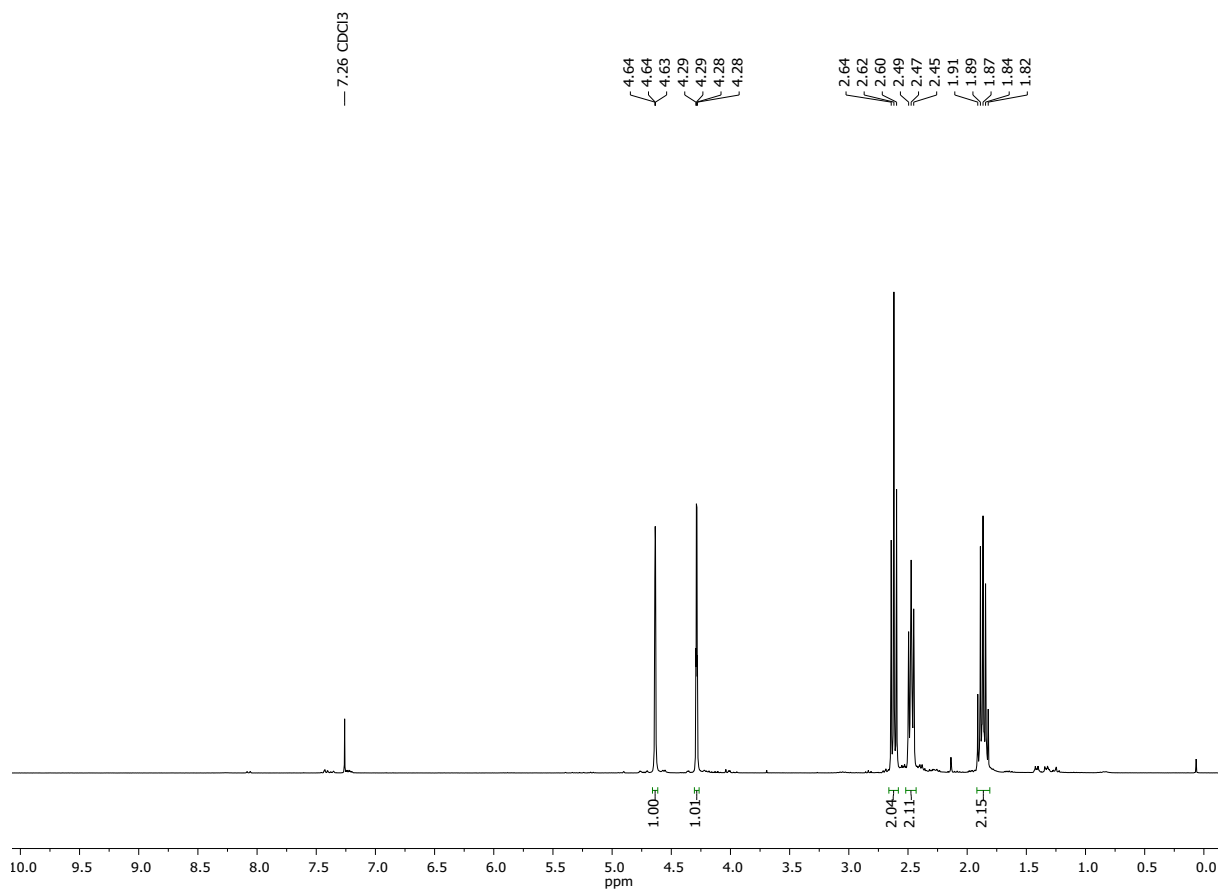


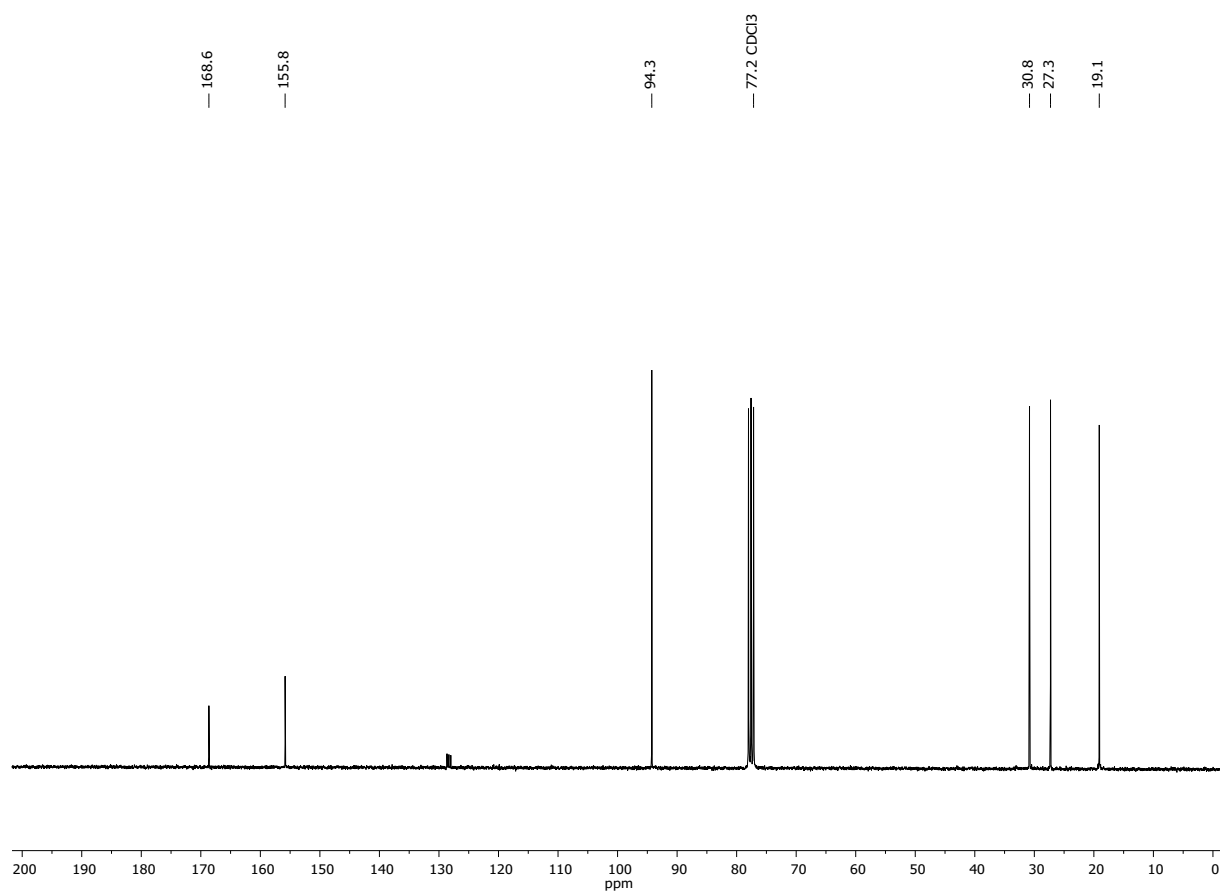
^1H NMR, ^{13}C $\{^1\text{H}\}$ and ^{19}F NMR spectra in CDCl_3 at 298K for **1,2-diphenylvinyl 2,6-difluorobenzoate (3b)**





^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra in CDCl_3 at 298K for 6-methylenetetrahydro-2H-pyran-2-one (4a)⁴





3. References

- 1 D. Gasperini, A. Collado, A. Gómez-Suárez, D. B. Cordes, A. M. Z. Slawin and S. P. Nolan, *Chem. - A Eur. J.*, 2015, **21**, 5403–5412.
- 2 A. Welle, S. Díez-González, B. Tinant, S. P. Nolan and O. Riant, *Org. Lett.*, 2006, **8**, 6059–6062.
- 3 S. Dupuy, D. Gasperini and S. P. Nolan, *ACS Catal.*, 2015, **5**, 6918–6921.
- 4 D. Gasperini, L. Maggi, S. Dupuy, R. M. P. Veenboer, D. B. Cordes, A. M. Z. Slawin and S. P. Nolan, *Adv. Synth. Catal.*, 2016, **358**, 3857–3862.