Supporting Information

for

Highly efficient catalytic hydrodehalogenation of polychlorinated biphenyls (PCBs)

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1. General Information

All manipulations were performed under inert atmosphere using standard Schlenk and glovebox techniques. The palladium complexes $[Pd(\mu\text{-}Cl)Cl(IPr)]_2$ **1**,[1] $[Pd(\mu\text{-}Cl)Cl(SIPr)]_2$ **2**,[2] $[Pd(\mu\text{-}Cl)Cl(IMes)]_2$ **3**,[3] $[Pd(\mu\text{-}Cl)Cl(SIMes)]_2$ **4**,[3] $[Pd(\eta^3\text{-}cinnamyl)Cl(IPr)]$ **5**,[4] $[Pd(\eta^3\text{-}allyl)Cl(IPr)]$ **6**[5] were prepared according to the literature. Chlorinated biphenyl substrates were synthesised as described below (section 4.), by modification of published procedures.[6] All other chemicals were purchased and used as received. NMR spectra were recorded on a Bruker Avance 300 spectrometer at 298 K. GC analyses were performed on an Agilent 7890A apparatus equipped with a flame ionization detector and a (5%-Phenyl)-methylpolysiloxane column (30 m, 320 μm, film: 0.25 μm). HRMS analyses were recorded on a Micromass GCT operating in EI^+ mode.

2. Optimisation studies (Table 1 and Table 2)

In a glovebox, a 5 mL screwcap-vial fitted with a septum equipped with a magnetic stirring bar was charged with the required amount of base, substrate, and catalyst (stock solution) and solvent. The reaction mixture was stirred at the indicated temperature for 24h (unless otherwise indicated) and analysed by GC.

3. Hydrodehalogenation of the PCBs

3.1. General Procedure

A Schlenk flask equipped with a magnetic stirring bar was charged with the chlorinated biphenyl and sodium hydroxide. The flask was evacuated and purged with nitrogen three times, ^{i}PrOH was added, followed by $[Pd(\mu\text{-}Cl)Cl(IPr)]_2$ **1** (stock solution in ^{i}PrOH). The reaction mixture was stirred at 80°C for 24h. The solvent was removed *in vacuo* and the crude product was purified by flash column chromatography (SiO_2, hexanes).

3.2. Hydrodehalogenation of 4-chlorobiphenyl (Table 3, entry 1)

Following the procedure described above (3.1.):

4-chlorobiphenyl (100 mg, 0.530 mmol), NaOH (23 mg, 0.583 mmol), ^{i}PrOH (2.65 mL).

$[Pd(\mu\text{-}Cl)Cl(IPr)]_2$ **1** (0.04 mol% Pd, 0.106 μmol; 120 μL of a solution of $[Pd(\mu\text{-}Cl)Cl(IPr)]_2$ **1** (10 mg, 8.84 μmol) in ^{i}PrOH (10 mL)).

Biphenyl was obtained as a colourless solid (75 mg, 92%).

3.3. Hydrodehalogenation of 2,3',4'-trichlorobiphenyl (Table 3, entry 2)

Following the procedure described above (3.1.):

2,3',4'-trichlorobiphenyl (100 mg, 0.388 mmol), NaOH (51 mg, 1.28 mmol), ^{i}PrOH (1.94 mL).

[Pd(μ-Cl)Cl(IPr)]$_2$ **1** (0.04 mol% Pd, 0.078 μmol; 88 μL of a solution of [Pd(μ-Cl)Cl(IPr)]$_2$ **1** (10 mg, 8.84 μmol) in ^{i}PrOH (10 mL)).

Biphenyl was obtained as a colourless solid (54 mg, 91%).

3.4. Hydrodehalogenation of 3,3',4,4'-tetrachlorobiphenyl (Table 3, entry 3)

Following the procedure described above (3.1.):

3,3',4,4'-tetrachlorobiphenyl (100 mg, 0.342 mmol), NaOH (60 mg, 1.51 mmol), ^{i}PrOH (2.71 mL).

Pd(μ-Cl)Cl(IPr)]$_2$ **1** (0.04 mol% Pd, 0.068 μmol; 78 μL of a solution of [Pd(μ-Cl)Cl(IPr)]$_2$ **1** (10 mg, 8.84 μmol) in ^{i}PrOH (10 mL)).

Biphenyl was obtained as a colourless solid (50 mg, 95%).

3.5. Hydrodehalogenation of decachlorobiphenyl (Table 3, entry 4)

Following the procedure described above (3.1.):

Decachlorobiphenyl (100 mg, 0.201 mmol), NaOH (88 mg, 2.21 mmol), ^{i}PrOH (2 mL).

[Pd(μ-Cl)Cl(IPr)]$_2$ **1** (1 mol% Pd, 1 μmol; 1.13 mL of a solution of [Pd(μ-Cl)Cl(IPr)]$_2$ **1** (10 mg, 8.84 μmol) in ^{i}PrOH (10 mL).

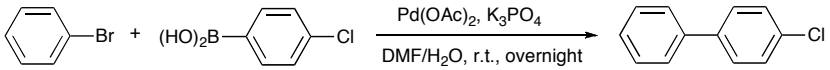
Biphenyl was obtained of biphenyl as a colourless solid (26 mg, 84%).

4. Synthesis of the PCB substrates

4.1. General Procedure[6]

A Schlenk flask equipped with a magnetic stirring bar was charged with $Pd(OAc)_2$, the chloroarylboronic acid and K_3PO_4. The flask was evacuated and purged with nitrogen three times, the aryl bromide and a mixture of DMF/H_2O were added. The reaction mixture was stirred at room temperature. The aqueous phase was extracted with EtOAc/Hexane (1/4, 3 x 65 mL), the combined organic extracts were washed with H_2O (3 x 200 mL), dried over Na_2SO_4 and the solvents were removed *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, hexanes).

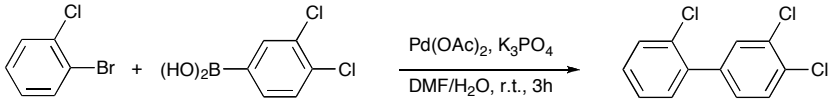
4.2. Synthesis of 4-chlorobiphenyl[7]



Following the procedure described above (4.1.):

Bromobenzene (335 μL, 3.18 mmol), 4-chlorophenylboronic acid (548 mg, 3.50 mmol) K_3PO_4 (1.35 g, 6.37 mmol), $Pd(OAc)_2$ (10.7 mg, 0.048 mmol), DMF/H_2O (1/1, 16mL), r.t., overnight. Product obtained as a colourless solid (528 mg, 88%). HRMS (EI^+): *m/z* calcd for $C_{12}H_9Cl$ ($[M]^+$): 188.0393, found 188.0388. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ (ppm) 127.0 (CH), 127.6 (CH), 128.4 (CH), 128.9 (CH), 133.3 (C-Cl), 139.60 (C), 140.0 (C).

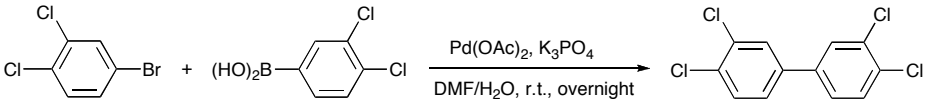
4.3. Synthesis of 2,3',4'-trichlorobiphenyl[8]



Following the procedure described above (4.1.):

1-Bromo-2-chlorobenzene (305 μL, 2.61 mmol), 3,4-dichlorophenylboronic acid (498 mg, 2.61 mmol), K_3PO_4 (1.11 g, 5.22 mmol), 1.5 mol% $Pd(OAc)_2$ (8.8 mg, 0.039 mmol), DMF/H_2O (1/1, 13 mL), r.t., 3h. Product obtained as a colourless solid (655 mg, 97%). HRMS (EI^+): *m/z* calcd for $C_{12}H_7{}^{35}Cl_3$ ($[M^+]$, 100%): 255.9613, found 255.9615; calcd for $C_{12}H_7{}^{35}Cl_2{}^{37}Cl$ ($[M^+]$, 79%): 257.9584, found 257.9577. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ(ppm) 127.0 (CH), 128.9 (CH), 129.3 (CH), 130.0 (CH), 130.1 (CH), 131.0 (CH), 131.3 (CH), 131.9 (C-Cl), 132.2 (C-Cl), 132.3 (C-Cl), 138.1 (C), 139.2 (C).

4.4. Synthesis of 3,3',4,4'-tetrachlorobiphenyl[9]

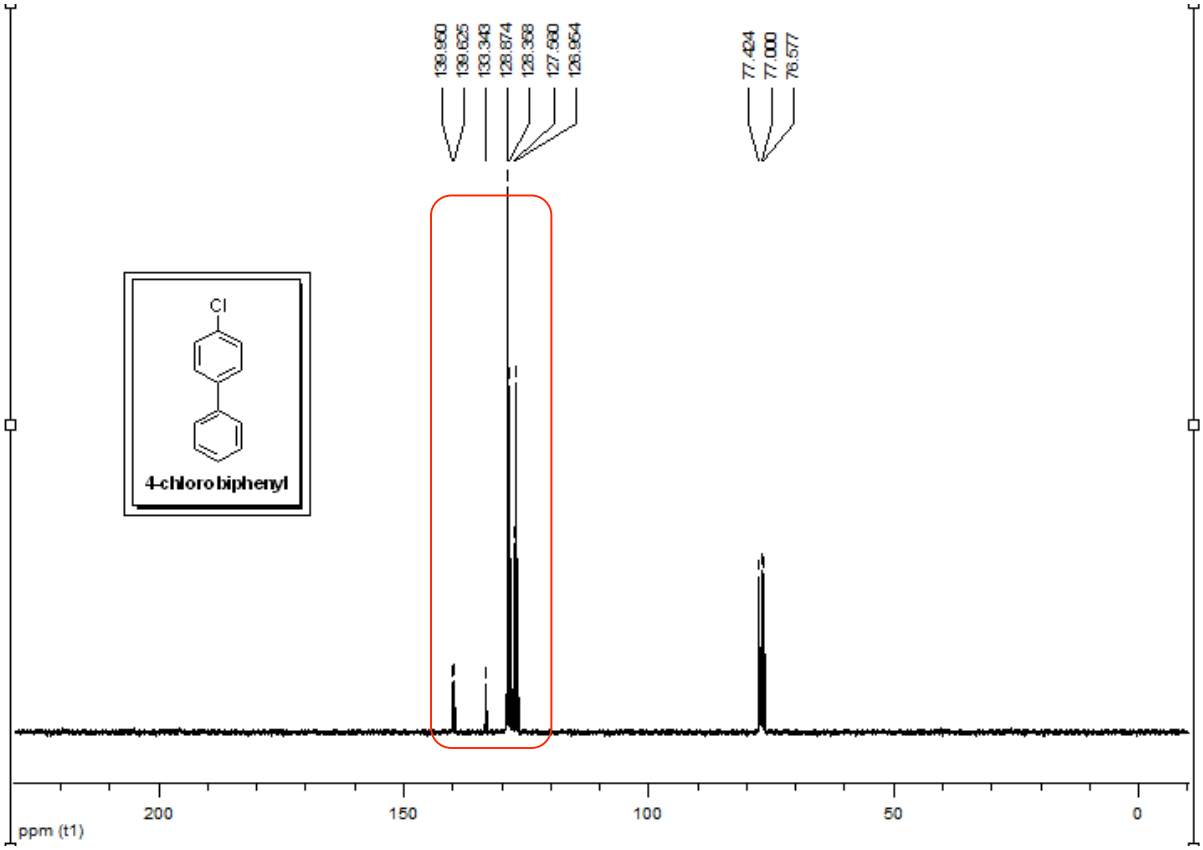


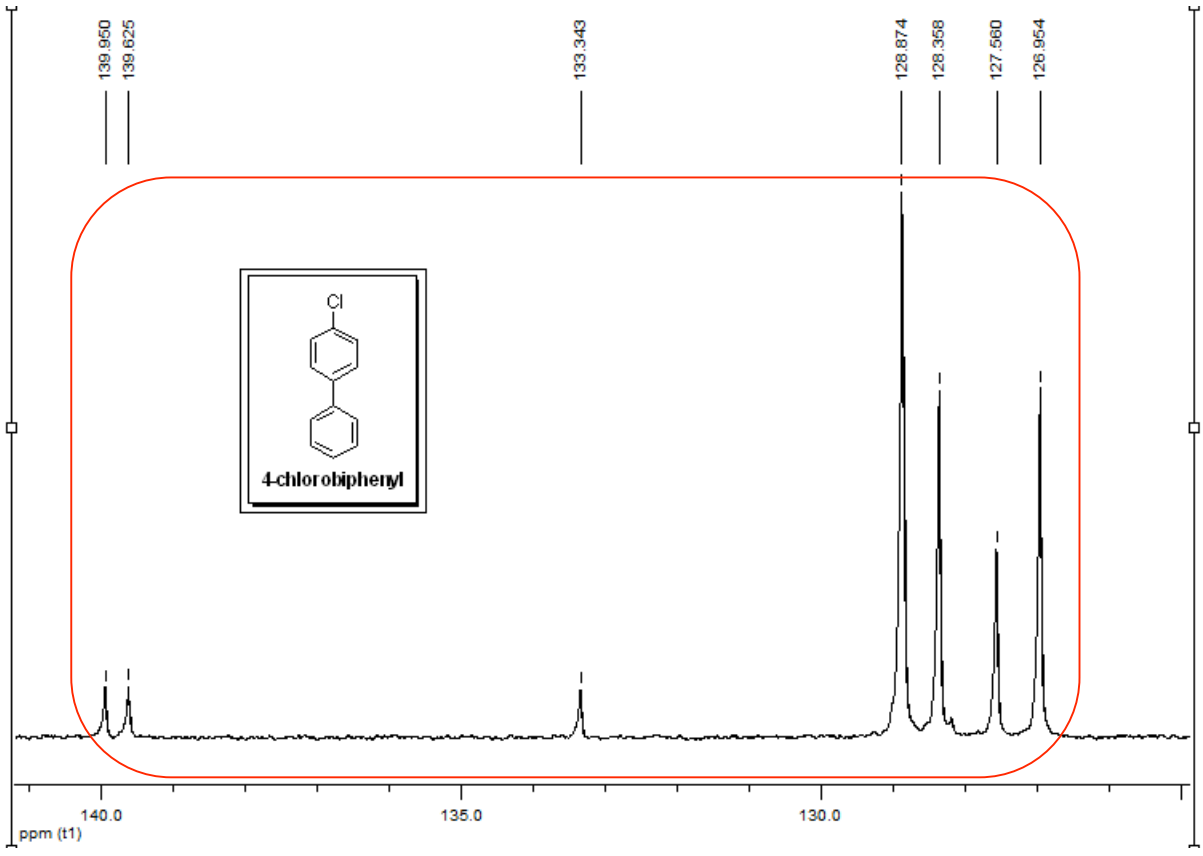
Following the procedure described above (4.1.):

4-Bromo-1,2-dichlorobenzene (284 μL, 2.21 mmol), 3,4-dichlorophenylboronic acid (465 mg, 2.43 mmol), K_3PO_4 (940 mg, 4.43 mmol), 1.5 mol% $Pd(OAc)_2$ (7.5 mg, 0.033 mmol) DMF/H_2O (1/1, 11 mL), r.t. overnight. Product obtained as a colourless solid (660 mg, 97%). HRMS (EI^+): *m/z* calcd for $C_{12}H_6{}^{35}Cl_4$ ($[M^+]$, 52.5%): 289.9224, found: 289.9225; calcd for $C_{12}H_6{}^{35}Cl_3{}^{37}Cl$ ($[M^+]$, 100%): 291.9194, found: 291.9202. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ(ppm) 126.1 (CH), 128.8 (CH), 130.9 (CH), 132.4 (C-Cl), 133.2 (C-Cl), 138.7 (C).

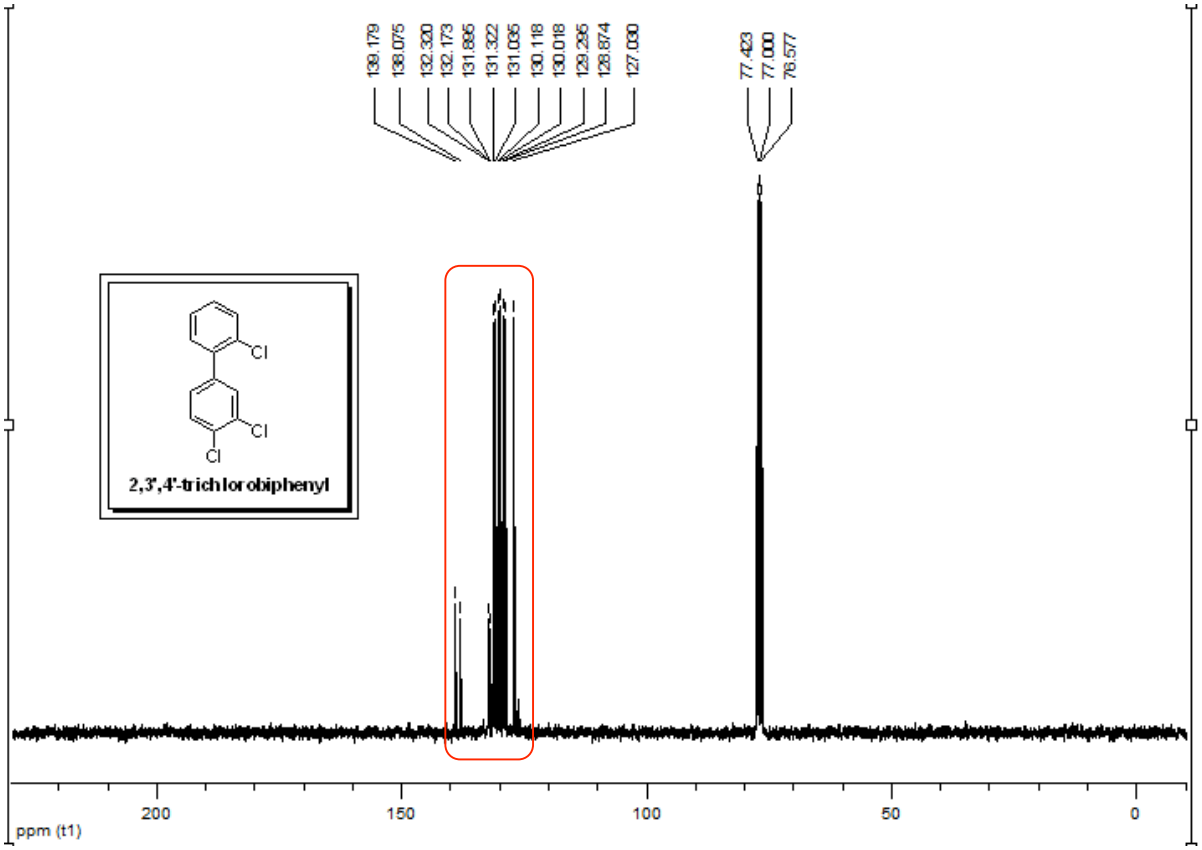
5. $^{13}C\{^{1}H\}$ NMR spectra

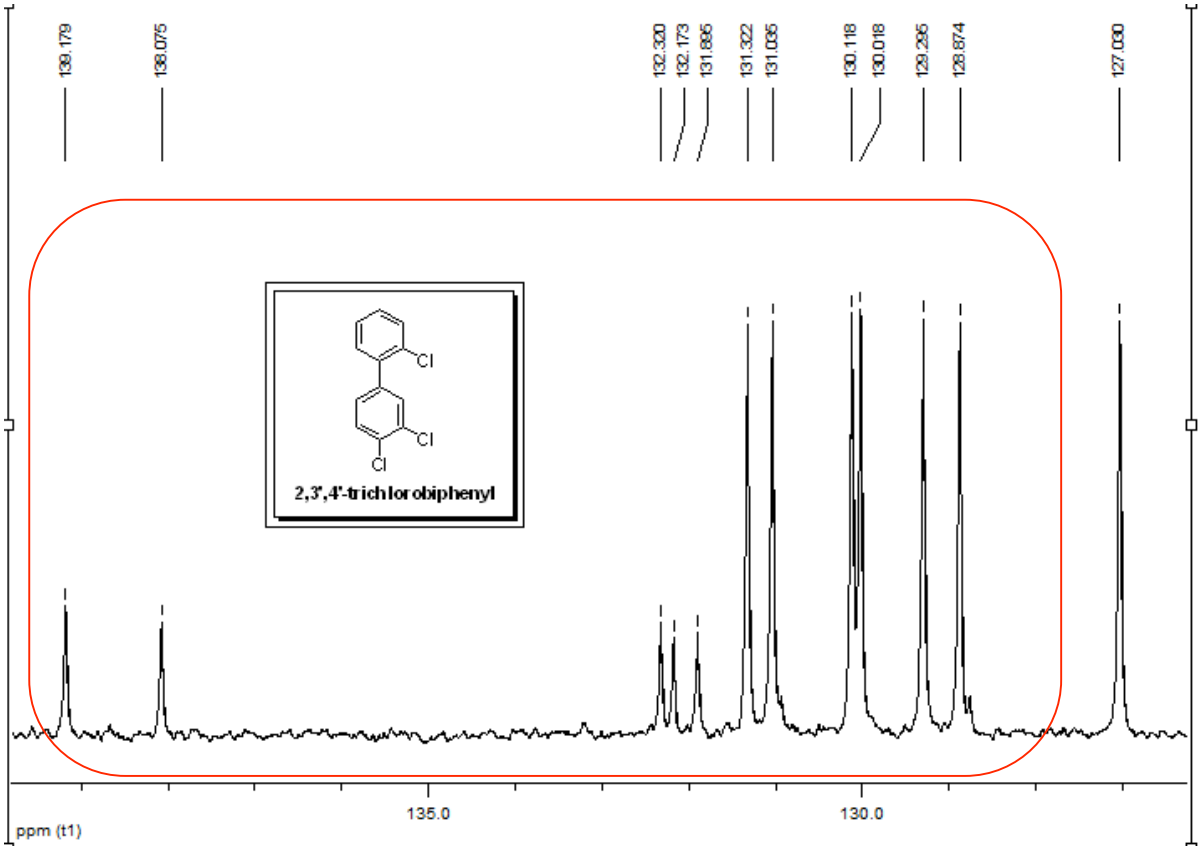
5.1. 4-chlorobiphenyl



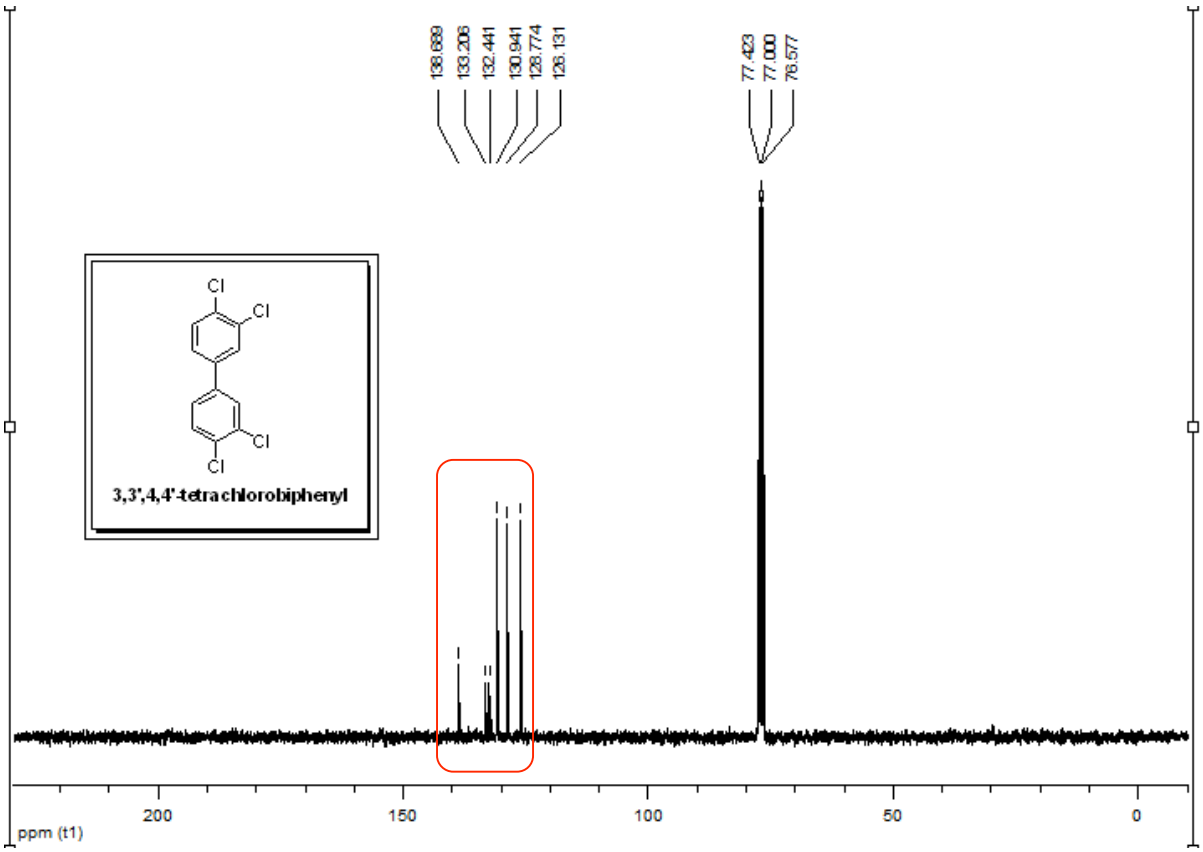


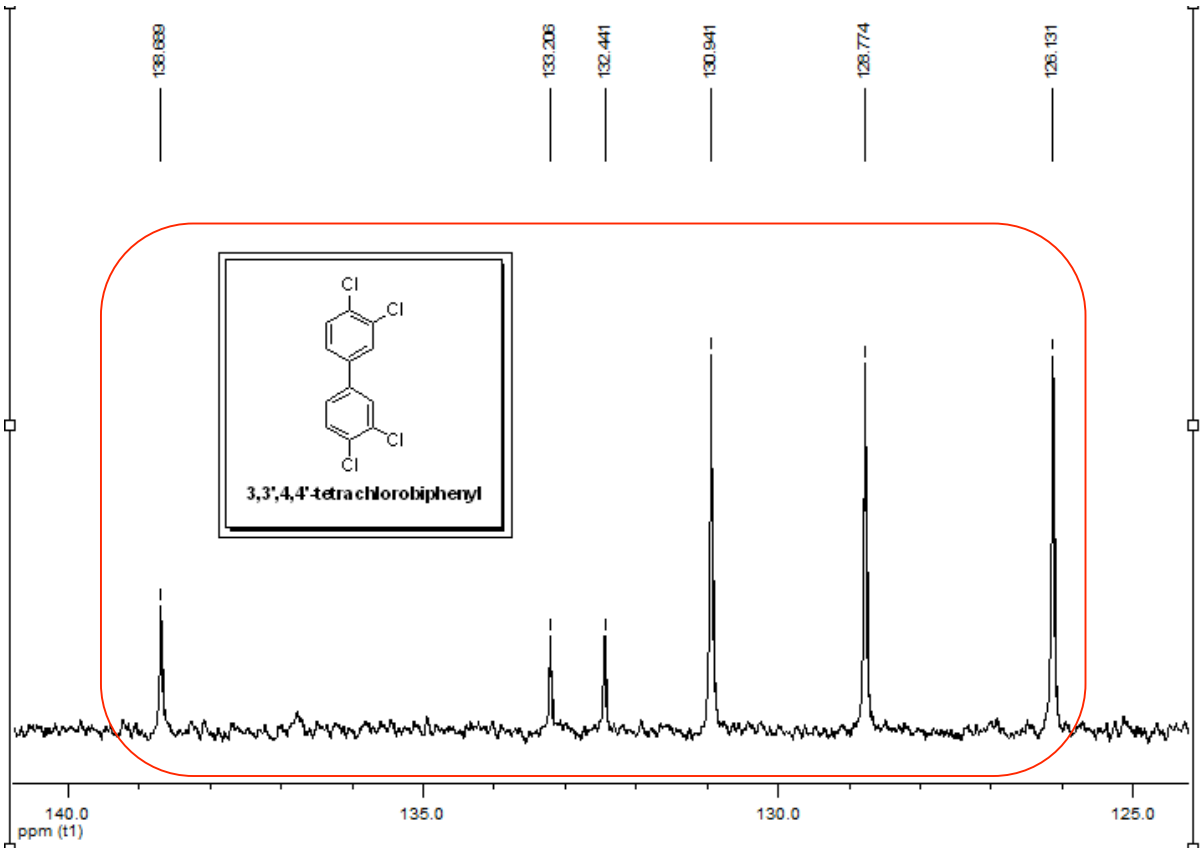
5.2. 2,3',4'-trichlorobiphenyl





5.3. 3,3',4,4'-tetrachlorobiphenyl





References

1 M. S. Viciu, R. M. Kissling, E. D. Stevens and S. P. Nolan, *Org. Lett.,* 2002*,* **4***,* 2229.

2 Y. Iwai, K. M. Gligorich and M. S. Sigman, *Angew. Chem. Int. Ed.,* 2008, **47**, 3219.

3 D. R. Jensen and M. S. Sigman, *Org. Lett.*, 2003, **5**, 63.

4 N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott and S. P. Nolan, *J. Am. Chem. Soc.,* 2006*,* **128***,* 4101.

5 M. S. Viciu, O. Navarro, R. F. Germaneau, R. A. Kelly, W. Sommer, N. Marion, E. D. Stevens; L. Cavallo and S. P. Nolan, *Organometallics,* 2004*,* **23***,* 1629.

6 J. M. A. Miguez, L. A. Adrio, A. Sousa-Pedrares, J. M. Vila and K. K. Hii, *J. Org. Chem.,* 2007, **72**, 7771.

7 S.-N. Chen, W.-Y. Wu, F.-Y. Tsai, *Tetrahedron*, 2008, **64**, 8164.

8 M. Yanagisawa, K. Hayamizu, O. Yamamoto, *Magn. Reson. Chem.,* 1986, **24**, 1013.

9 N. S. Shaikh, S. Parkin, G. Luthe, H.-J. Lehmler, *Chemosphere,* 2008, **70**, 1694.