Supporting Information

Pd-catalysed Hydrodehalogenation of Aryl Chlorides: A Mild Method for Deuteration and Detoxification

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1. General Methods

1.1. Analytical Methods

NMR spectroscopy. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance III 400 spectrometer at 25 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the *δ*-scale. All spin-spin coupling constants (*J*) are printed in Hertz (*Hz*). To display multiplicities and signal forms correctly, the following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, br = broad signal. Deuterated solvents ethanol-d_6, CD_2Cl_2 and $CDCl_3$ were used as received from Sigma Aldrich and Acros Organics.

GC analyses were performed on an Agilent 8890 GC system with MSD 5977B using a DB-5 capillary column ((5%-phenyl)-methylpolysiloxane, 30 m DB-5, 0.25 µm film thickness, 0.25 mm ID, start at 50 °C, heating rate 20 °C/min until 250 °C, 5 min at 250 °C). Yields were determined by GC-FID using *n*-tetradecane or *n*-hexadecane as internal standard. Response factors were measured with authentic samples for evaluation of the GC spectrum.

Column chromatography was performed *via* filtration over silica with hexane or pentane, or on a Reveleris X2 (BÜCHI) Flash Chromatography-System using Reveleris packed columns and a gradient of hexane to ethyl acetate.

1.2. Solvents and Starting Materials

All experiments (if not otherwise stated) were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk and glovebox techniques. Argon (99.999%) was a product of *Air Liquide*. Involved solvents such as 2-methyltetrahydrofuran were dried prior to use in accordance with standard procedures and stored under an argon atmosphere over molecular sieves. Purchased starting materials were used as received unless otherwise stated. 3,5-Dichlorobiphenyl was synthesized via a Suzuki-Miyaura cross-coupling reaction according to *Akzinnay et al*.[1] Pd_2dba_3 x dba (15.62wt% Pd) was donated by Umicore. XPhos, QPhos, SPhos, DavePhos, Pd(P*t*Bu3)2 and PEPPSI-IPent were purchased from Sigma Aldridge and used without further purification. IPr and IMes were synthesized according to literature procedures. Aryl chlorides, -bromides and -iodides were purchased from Sigma Aldridge, Fisher Scientific, TCI chemicals or ABCR chemicals and used without further purification. Ligands keYPhos (**L1**, CyYMePCy$_2$), trYPhos (**L2**, CyYMeP(*t*Bu)$_2$), joYPhos (**L3**,CyYPhPCy2), prYPhos (L4, CyYMeP*i*Pr$_2$) as well as the pre-catalysts [**L1**·Pd(allyl)Cl], [**L1**·Pd(cinnamyl)Cl], [**L1**·Pd(1-*t*Bu-Indenyl)Cl], [**L2**·Pd(allyl)Cl] and [**L3**·Pd(cinnamyl)Cl] were prepared according to literature procedures.[3,4,5] All bases were dried prior to use and stored in an MBraun glovebox.

2. General Procedure: Screening and Catalysis

In a glovebox, potassium *tert*-butoxide (3 eq., 2.55 mmol, 292 mg) was added to a vial equipped with a magnetic bar and a seal with a screw cap fitted with a septum and **L1-P$_{al}$** (1 mol%, 5.8 mg) was added to another vial. Outside the glovebox, 0.5 mL 2-methyltetrahydrofuran was added to the catalyst vial. If the aryl halide (0.85 mmol) was a liquid, it was added directly to the vial with base. If the aryl halide was a solid, it was dissolved in a solvent prior to the addition to the vial. Internal standard (hexadecane

or tetradecane, ca. 0.2 eq.), ethanol (3 eq., 2.55 mmol, 145 µL) and, as the last step, the catalyst suspension was added to the mixture. After 1h, 3h and 5h a droplet of the reaction mixture was filtered over silica and prepared as a GC sample. Multiple runs were made to ensure the consistency of the results. If the substrate contains multiple halides, the amount of base and ethanol was adapted.

3. Reaction optimization

3.1. Initial Studies

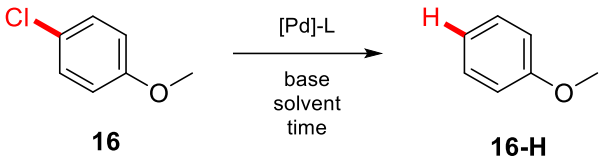


Table S1. Results of initial studies with different bases and solvents for the dehalogenation reaction. Conditions: 4-chloroanisol (0.85 mmol), YPhos ligand with Pd-source or YPhos precatalyst (catalyst loading stated in the table), base (1.5 eq.), solvent (1 ml), hexadecane (0.2 eq., internal standard). In some reactions byproduct in form of 1-ethoxy-4-methoxybenzene was detected *via* GC-analysis.

catalyst	**cat. load. [mol%]**	**base**	**solvent***	**time**	**2**
L1, Pd_2dba_3 x dba	5	KOMe	THF	24 h	75
″	″	″	″	″	13
″	″	KOEt	″	″	84
″	″	KO*i*Pr	″	″	68
L1-P_{ind}	0.5	KOMe	″	″	3
″	″	KOEt	″	″	81
″	″	KO*i*Pr	″	″	10
L1-P_{al}	0.5	KOEt	MTBE	3 h	83
″	″	″	Methylal	″	55
″	″	″	CPME	″	83
″	″	″	2-MeTHF	″	89
″	″	″	EtOH	24 h	13
″	″	″	*i*PrOH	″	36
″	″	″	Tol	″	86

*The abbrevations refer to following solvents: THF: tetrahydrofuran; MTBE: methyl-*tert*-butylether; CPME: cyclopentylmethylether; Methylal: dimethoxymethane; 2-MeTHF: 2-methyltetrahydrofuran; EtOH: ethanol; *i*PrOH: *iso*-propanol; Tol: toluene

3.2. Screening of Different Bases

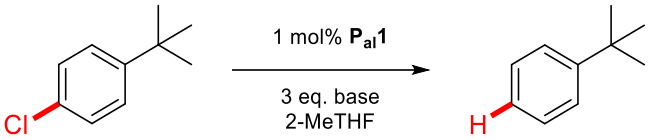


Table S2. Results of the dehalogenation with different bases and additives. Conditions: 4-chloro-*tert*-butylbenzene (0.85 mmol), **L1-P_{al}** (1 mol%), base (3 eq.), additive (3 eq.), 2-MeTHF (1 ml), hexadecane (0.2 eq., internal standard). In some reactions by-product in form of 1-*tert*-butyl-4-ethoxybenzene was detected *via* GC-analysis.

Base	Additive	24 h [%]	Base	Additive	24 h [%]
KOMe	-	9	KO*t*Bu	EtOH	100
KOEt	-	100	KO*t*Bu	*i*PrOH	80
KO*i*Pr	-	23	KOH (tech.)	EtOH	62
KO*t*Bu	-	0	KOH (ana.)	EtOH	37
KOH	-	0	KOH (ana.)	*i*PrOH	100
K_3PO_4	-	0	NaOH	EtOH	63
K_2CO_3	-	0	NaOH	*i*PrOH	100
HCOONa	-	0	NaH	EtOH	100
LiOEt	-	28	NaH	*i*PrOH	70
NaOEt	-	16	NaH	15C5*	1 (2 d)
K_3PO_4	EtOH	8	KH	EtOH	91
K_3PO_4	*i*PrOH	7	KH	*i*PrOH	93
K_2CO_3	EtOH	0	KH	18C6*	54 (2 d)
K_2CO_3	*i*PrOH	0			
HCOONa	EtOH	0			
HCOONa	iPrOH	0			

*15C5: 15-crown-5 / 1,4,7,10,13-Pentaoxacyclopentadecane; 18C6: 18-crown-6 / 1,4,7,10,13,16-hexaoxacyclooctadecane.

Screening of Base Concentrations

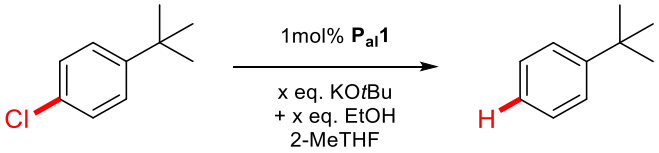
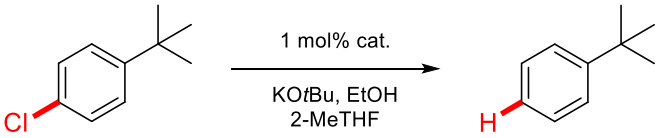


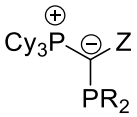
Table S3. Results of the dehalogenation with different base concentrations. Conditions: 4-chloro-*tert*-butylbenzene (0.85 mmol), **L1-P_{al}** (1 mol%), KO*t*Bu (x eq.), EtOH (x eq.), 2-MeTHF (1 ml), hexadecane (0.2 eq., internal standard). The yields of the dehalogenated product is shown in percentage (%).In some reactions byproduct in form of 1-*tert*-butyl-4-ethoxybenzene was detected *via* GC-analysis.

Base	0.5 h	1 h	2 h	3 h
1 eq.	10	34	50	61
1.5 eq.	11	53	77	89
2 eq.	16	70	88	95
3 eq.	22	82	100	100
5 eq.	62	100	100	100

3.3. Screening of Different Ligands

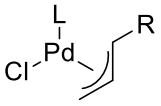


YPhos:

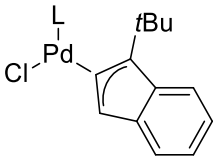


L1, keYPhos: Z = Me, R = Cy
L2, trYPhos: Z = Me, R = *t*Bu
L3, joYPhos: Z = Ph, R = Cy
L4, prYPhos: Z = Me, R = *i*Pr

Precatalysts:

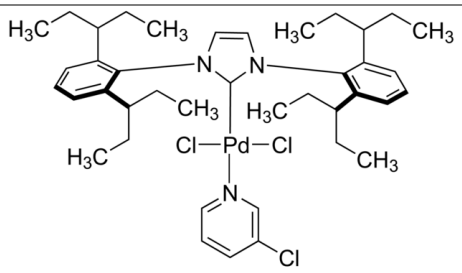


L-P$_{al}$, R = H, allyl
L-P$_{cin}$, R = Ph, cinammyl

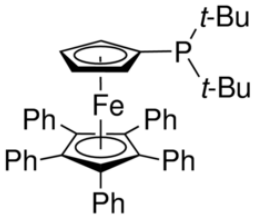


L-P$_{ind}$, indenyl

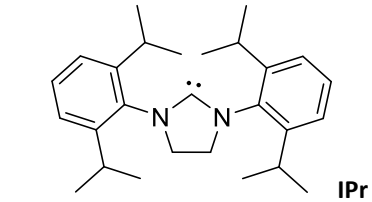
Commercially available catalysts:



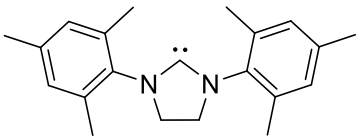
PEPPSI-IPent



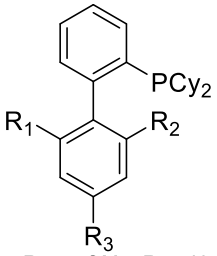
QPhos



IPr



IMes



SPhos: $R_{1,2}$ = OMe; R_3 = H
XPhos: $R_{1,2,3}$ = iPr
DavePhos: R_1 = NMe_2; R_2, R_3 = H

P(*t*Bu)$_3$

Table S4. Results of the screening with different catalysts. Conditions: 4-chloro-*tert*-butylbenzene (0.85 mmol), ligand with Pd-source or ligand precatalyst, potassium *tert*-butoxide (3 eq.), ethanol (3 eq.), 2-methyltetrahydrofuran (1 ml), hexadecane (0.2 eq., internal standard). In some reactions by-product in form of 1-*tert*-butyl-4-ethoxybenzene was detected *via* GC-analysis.

L-[Pd]	time [h]	4 [%]	L-[Pd]	time [h]	4 [%]
L1, Pd_2dba_3 x dba	2	100	PEPPSI-IPent	24	82
L1, $Pd(OAc)_2$	5	68	QPhos, Pd_2dba_3	72	0
L2, Pd_2dba_3 x dba	3	96	SPhos, Pd_2dba_3	48	97
L2, $Pd(OAc)_2$	1	98	XPhos, Pd_2dba_3	48	76
L3, Pd_2dba_3 x dba	2	100	DavePhos, Pd_2dba_3	48	72
L3, $Pd(OAc)_2$	2	100	P(tBu)$_3$, Pd_2dba_3	48	32
L4, Pd_2dba_3 x dba	24	100	IPr, Pd_2dba_3	72	5
L4, $Pd(OAc)_2$	24	85	IMes, Pd_2dba_3	72	49
L1-P$_{al}$	1	97			
L1-P$_{cin}$	1	100			
L1-P$_{ind}$	1	100			
L2-P$_{al}$	1	94			
L3-P$_{cin}$	1	100			

3.4. Screening of catalyst loading

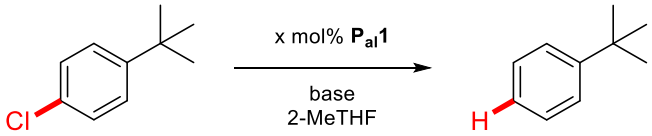


Table S5. Results of the screening of catalyst loading. Conditions: 4-chloro-*tert*-butylbenzene (0.85 mmol), **L1-P_{al}** (x mol%), KO*t*Bu (3 eq.), EtOH (3 eq.), 2-MeTHF (1 ml), hexadecane (0.2 eq., internal standard). The yields of the dehalogenated product is shown in percentage (%).

cat. [mol%]	T [°C]	0.5 h	1 h	2 h	3 h	5 h	24 h	5 d
0.05	22	-	3	-	13	28	37	36
	60	-	52	-	52	52	52	52
0.1	22	14	29	-	41	51	61	63
	60	-	35	-	42	43	46	60
0.5	22	34	80	97	100	100	-	
1.0	″	59	96	100	100	-	-	
2.0	″	87	99	100	-	-	-	
5.0	″	99	100	100	-	-	-	

3.5. Turnover Number

In a glovebox, potassium *tert*-butoxide (3*x eq.) was added to a Schlenk tube equipped with a stirring bar and **L1-P_{al}** (1 mol%, 5.8 mg, or 0.5 mol%, 2.9 mg) was added to another Schlenk tube. Outside the glovebox, the base was suspended in solvent (0.5 ml per equivalent substrate, solvent: 2-MeTHF or THF). 4-chloro-*tert*-butylbenzene (x eq.), ethanol (3*x eq.) and internal standard (hexadecane, 0.2*x eq.) were added to the Schlenk tube. The suspension was stirred and a certain volume corresponding to 1 eq. substrate was added to the flask with **L1-P_{al}**. Subsequently, 1 eq. of the substrate-mixture was added every 0.5 h until the suspension was empty. After the last addition, GC samples were made and the signals were compared to authentic samples of the product.

Table S6. Results of the evaluation of the turnover number.

Substrate used	cat. load.	4*	TON	TOF [h^{-1}]
30 eq.	0.5 mol%	16 h: 65 %, 24 h: 71 %, 5 d: 89 %	2670	22
15.4 eq.	1.0 mol%	24 h: 96 %, 48 h: >99 %	1538	32
9 eq.	1.0 mol%	0.5 h: 8 %, 20 h: 87 %, 4 d: >99 %	900	19 (48 h)

***times related to time after last addition

3.6. Screening of Concentration

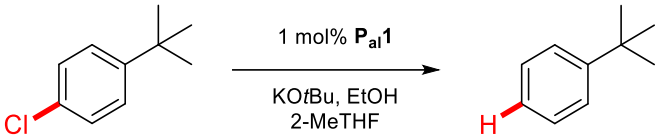


Table S7. Influence of the solvent concentration (depended on substrate). Conditions: 4-chloro-*tert*-butylbenzene (0.85 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (3 eq.), EtOH (3 eq.), 2-MeTHF (x ml), hexadecane (0.2 eq., internal standard). The yields of the dehalogenated product is shown in percentage (%).

V(solvent) [ml]	c [M]	1 h	2 h	3 h
3.5	0.22	21	83	100
2.5	0.30	33	98	100
1.5	0.46	53	97	100
1.0	0.63	71	99	100
0.5	1.00	98	100	-
0	neat	100*	-	-

*miscibility issues in some approaches

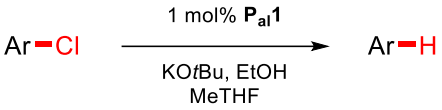
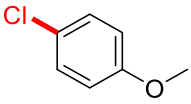
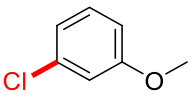
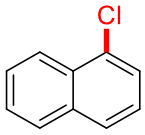
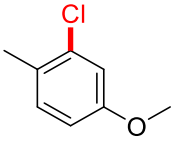
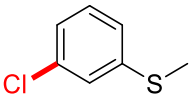
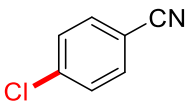
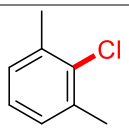


Table S8. Influence of the solvent concentration of selected substrates. Conditions: aryl chloride (0.85 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (3 eq.), EtOH (3 eq.), 2-MeTHF (x ml), hexadecane (0.2 eq., internal standard). The yields of the dehalogenated product is shown in percentage (%).

Aryl chloride	Yield (time, low c)	Yield (time, high c)
	16 % (5 h, 0.46 M)	100 % (5 h, 1.0 M)
	12 % (5 h, 0.46 M)	100 % (3 h, 1.0 M)
	70 % (5 h, 0.46 M)	100 % (5 h, 1.0 M)
	54 % (1 h, 0.3 M)	100 % (1 h, 1.0 M)
	100 % (2 h, 60 °C, 0.3 M)	85 % (2 h, 60 °C, 1.0 M)
	43 % (1 h, 0.3 M)	32 % (1 h, 0.8 M)

	74 % (1 h, 0.3 M)	94 % (1 h, 1.0 M)

3.7. Kinetic and Selectivity Studies

Dehalogenation of different chloro-substituted trifluoromethylbenzenes 13-15

To obtain insights into the kinetics, the hydrodehalogenation of *para*-chloro-trilfuoromethylbenzene was followed by GC-FID analysis. The thus obtained conversion-time plot showed full conversion within 10 minutes (Time plot of the dehalogenation of *para*-chloro-trifluoromethylbenzene. Conditions: **13** (1.0 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (3 eq.), EtOH (3 eq.), 2-MeTHF (0.5 ml), tetradecane (0.2 eq., internal standard).Figure S1). Due to this fast conversion, we decided to conduct further comparative studies on the different chloro-substituted arenes **13-15** at lower concentrations (0.7 M instead of 1.1 M) to ensure a better differentiation of the data. The results of these studies are depicted in Figure S2, which shows a fastest rate for the *para*-substituted chloroarene, followed by the *meta*- and *ortho* substituted derivatives presumably due to competing steric and electronic effects.

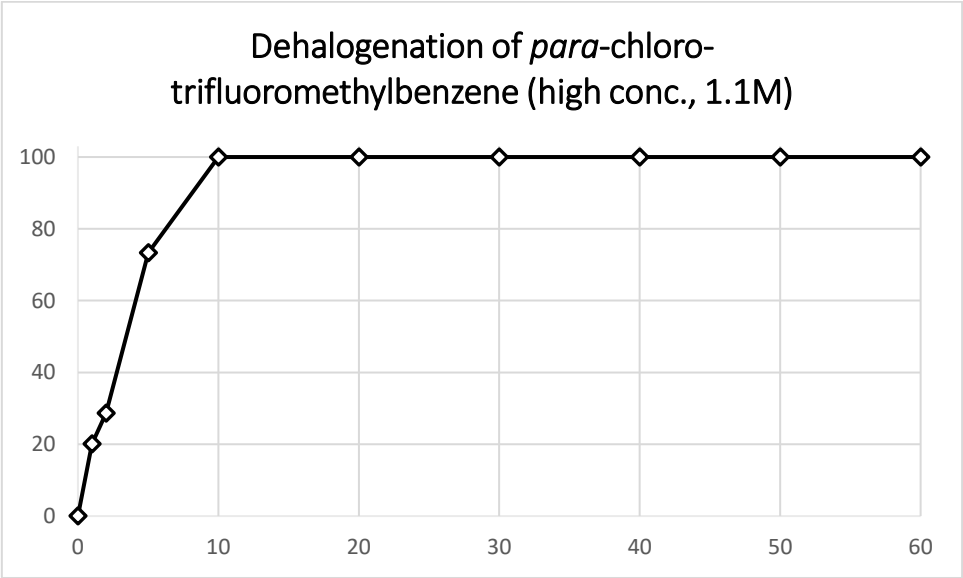


Figure S1. Time plot of the dehalogenation of *para*-chloro-trifluoromethylbenzene. Conditions: **13** (1.0 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (3 eq.), EtOH (3 eq.), 2-MeTHF (0.5 ml), tetradecane (0.2 eq., internal standard). GC-yields.

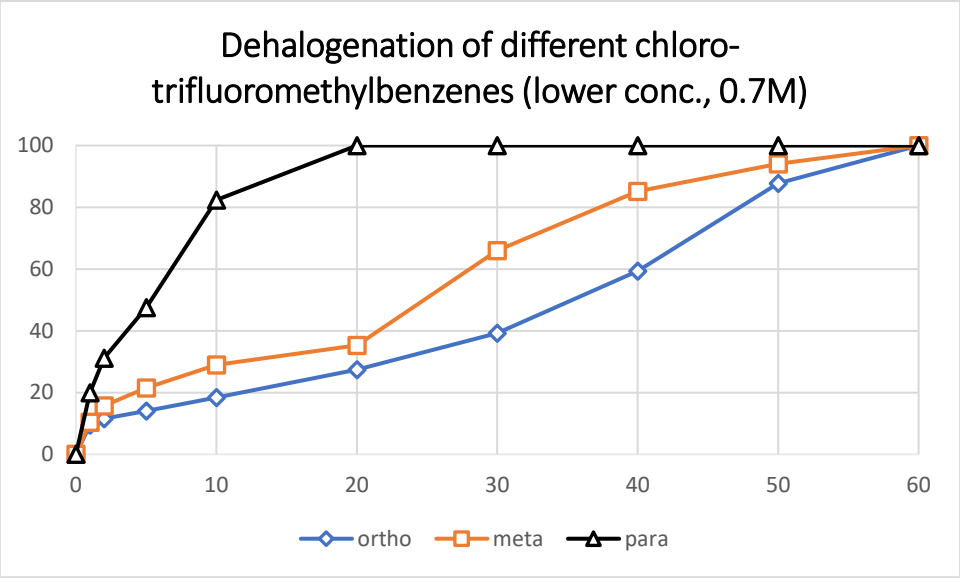


Figure S2. Time plot of the dehalogenation of *ortho*-, *meta*- and *para*-chloro-trifluoromethylbenzene. Conditions: 2-, 3- or 4-chloro-trifluoromethylbenzene **13-15** (1.0 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (3 eq.), EtOH (3 eq.), 2-MeTHF (1.0 ml), tetradecane (0.2 eq., internal standard). GC-yields.

Dehalogenation of different polyhalogenated benzenes 7-10

Kinetic studies were also conducted for the different polyhalogenated benzenes **7**-**10** to investigate the sequence of the dehalogenation process. As shown for the dichlorobenzene derivatives **7** and **8** (Figure S3 and S4) the rate of the dehalogenation is highly dependent on the position of the second chloride substituent. In both cases, the first dechlorination occurs fast, in case of compound **8** already within 2 min. The subsequent second dechlorination of the 1,2-substituted chloro arene has a slower conversion rate than the 1,3-substituted derivative.

For the mixed polyhalogenated benzenes **9** and **10**, the conversion-time plots show faster dehalogenation of the heavier halide (iodine or bromine respectively), followed by the dechlorination reaction (Figure S5 and Figure S6).

In general, THF instead of 2-MeTHF as solvent was used in these reactions as the product benzene overlaps in the gas chromatogram with 2-MeTHF but not with THF.

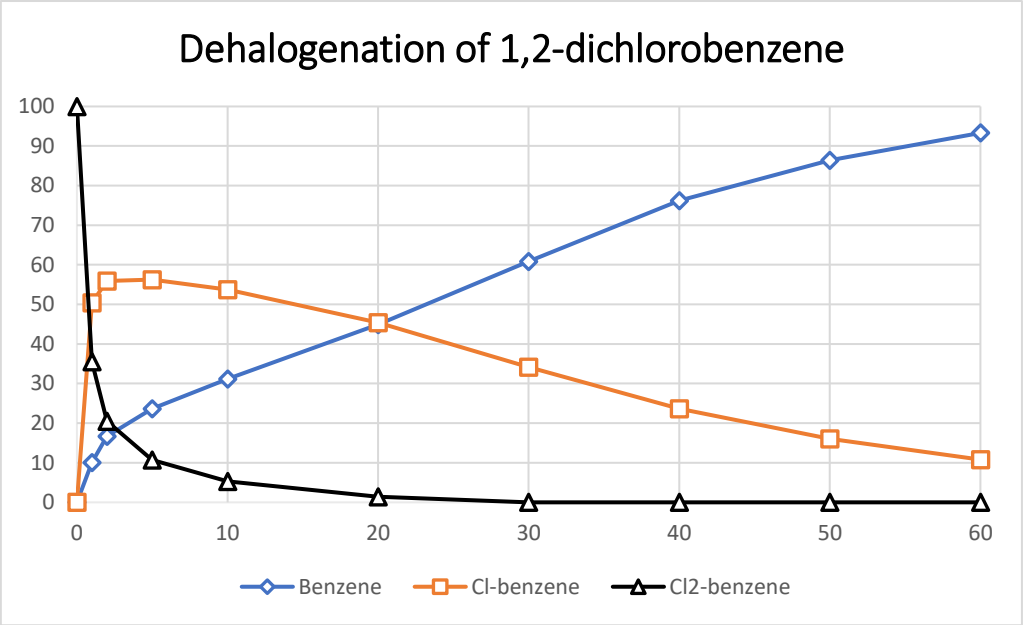


Figure S3. Time plot of the dehalogenation of 1,2-dichloro-benzene **7**. Conditions: **7** (1.0 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (6 eq.), EtOH (6 eq.), THF (0.5 ml), tetradecane (0.2 eq., internal standard). GC-yields.

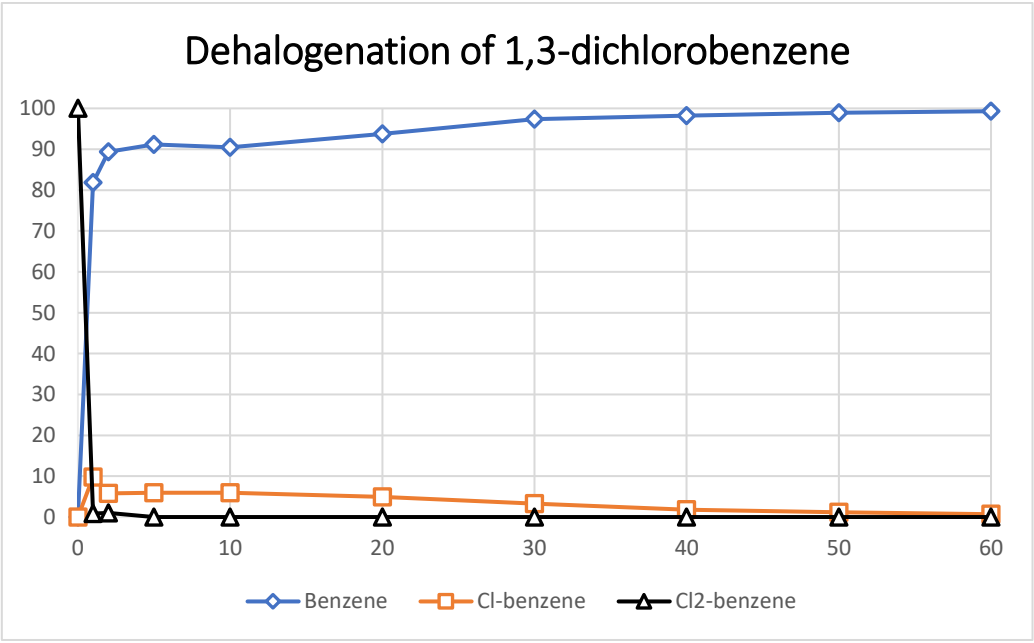


Figure S4. Time plot of the dehalogenation of 1,3-dichloro-benzene **8**. Conditions: **8** (1.0 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (6 eq.), EtOH (6 eq.), THF (0.5 ml), tetradecane (0.2 eq., internal standard). GC-yields.

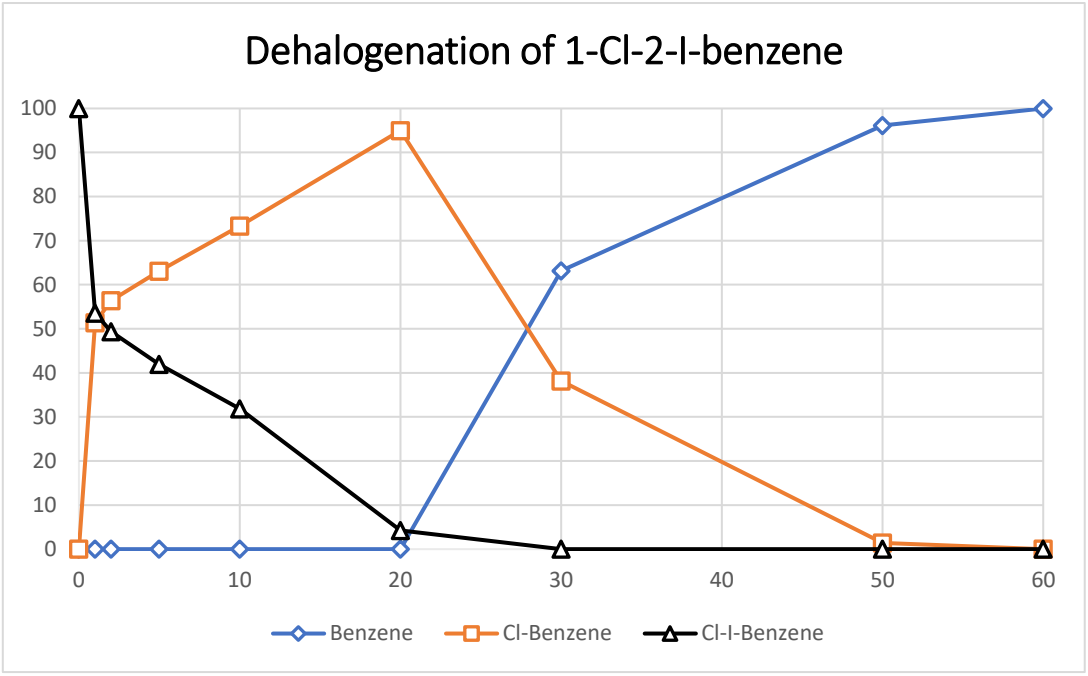


Figure S5. Time plot of the dehalogenation of 1-chloro-2-iodobenzene **9**. Conditions: **9** (1.0 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (6 eq.), EtOH (6 eq.), THF (0.5 ml), tetradecane (0.2 eq., internal standard). GC-yields.

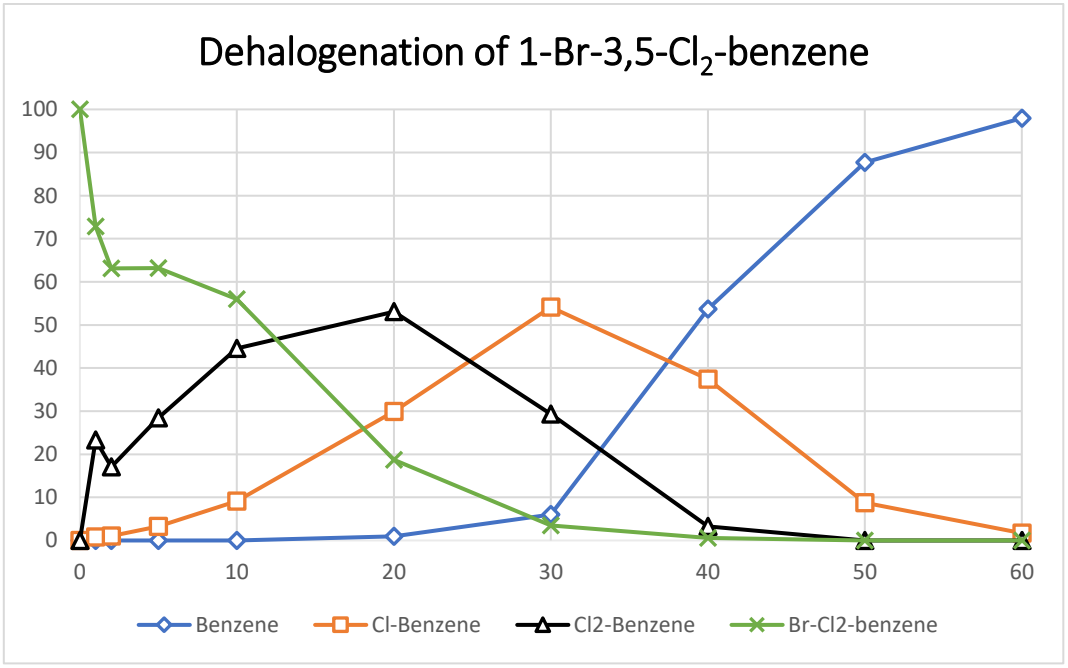
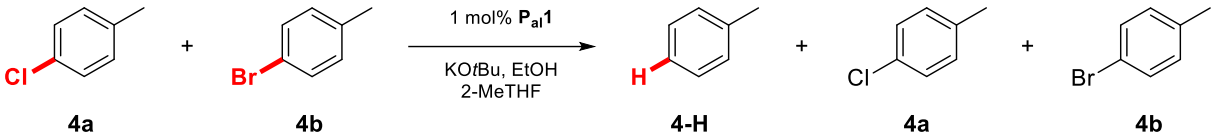


Figure S6. Time plot of the dehalogenation of 1-bromo-3,5-dichlorobenzene **10**. Conditions: **10** (1.0 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (9 eq.), EtOH (9 eq.), THF (0.5 ml), tetradecane (0.2 eq., internal standard). GC-yields.

Competition experiment

To further probe the chemoselectivity of the hydrodehalogenation we conducted competition experiments with 4-chloro- (**4a**) and 4-bromotoluene (**4b**). Using a 1:1 ratio (1 eq each) of both haloarenes with only 1 eq. of base and ethanol gave high selectivities for the hydrodehalogenation of the bromoarene (Table S9).



4a **4b** **4-H** **4a** **4b**

Table S9. Results of the selectivity studies with 4-bromo- and chlorotoluene. Conditions: 4-chlorotoluene **5** (0.5 mmol), 4-bromotoluene **6** (0.5 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (1 eq.), EtOH (1 eq.), 2-MeTHF (0.7 ml), hexadecane (0.2 eq., internal standard). The yields of the dehalogenated product is shown in percentage (%).

Time \ Product	4-H	4a	4b
1 h	93	91	16
3 h	99	90	10
24 h	99	91	9

Influence of the base on the deuteration of 3,5-dichlorobiphenyl 41

The influence of the base (1 eq.) in the deuteration of the polychlorinated biphenyl **41** was investigated. The extract of the gas chromatogram shows that after 1 h a mixture of mono- and dideuterated species was formed in an approx. ratio of 2:8 (Figure S7). This finding confirms the fast dehalogenation process and that selective mono-deuteration by base limitation is not possible in a symmetric dichlorinated compound.

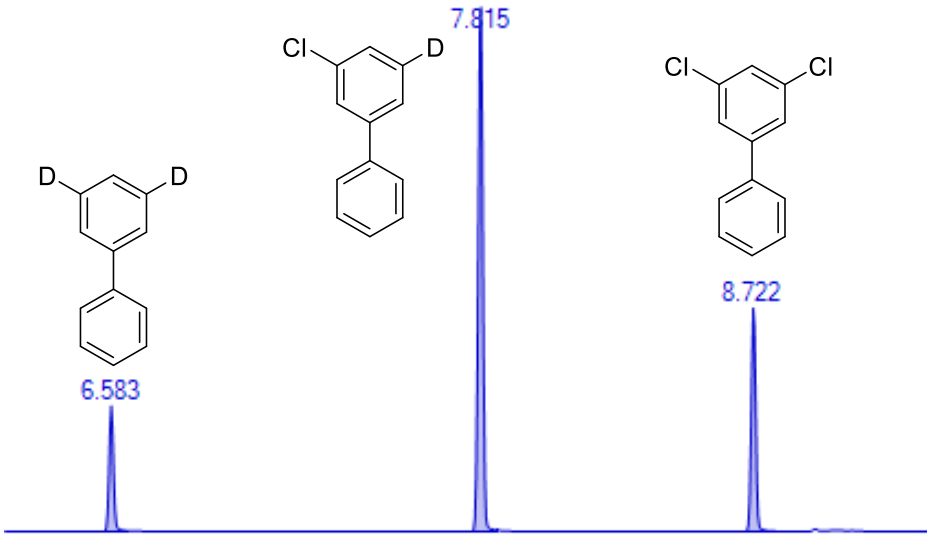


Figure S7. Abstract of the gas chromatogram of the reaction of 3,5-dichlorobiphenyl **41** with 1 eq KO*t*Bu/d_6-EtOH. Conditions: **41** (1.0 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (1 eq.), d_6-EtOH (1 eq.), 2-MeTHF (1.0 ml), 60°C, 1 h. Ratio: 14 % (bi-deuterated species), 61 % (mono-deuterated species), 25 % (**41**).

4. Dehalogenation of PCB Extracted from Construction Dust

Procedure. 10 g of fine powdered construction dust (components listed below) and 50 mg of 4,4'-dichlorobiphenyl (PCB 15, 0.22 mmol, 1 eq.) were placed into an extraction thimble. The extraction thimble was put into a soxleth-extractor, installed to a round flask filled with ca. 500 ml hexane and topped with a reflux condenser. Extraction was run for 18 h. After cooling to room temperature, the solvent was removed in vacuo, leaving a yellow slurry. The analysis of the GC-MS chromatogram of extracted construction dust shows a variety of different siloxanes with the added PCB 15 as biggest signal.

Method A. To this slurry, potassium tert-butoxide (154 mg, 6 eq.) was added and the mixture dissolved in 1.5 ml 2-MeTHF, 0.1 ml EtOH. To this mixture, a catalyst suspension of **L1-P$_{al}$** (2 mol%, 3.6 mg) in 0.5 ml 2-MeTHF was added. The reaction was stirred overnight, quenched with water, extracted with 3x EtOAc, dried over Na_2SO_4 and the solvent was removed *in vacuo*. Hexadecane as internal standard was added. Analysis of the gas chromatograph showed still present PCB 15 as main content of the mixture.

Method B. The slurry was filtered through silica with pentane and the solvent removed in vacuo. KO*t*Bu (308 mg, 12 eq.) and EtOH (0.15 ml, 12 eq.) as well as a suspension of **L1-P$_{al}$** (5 mol%, 7.7 mg) in 4 ml 2-MeTHF were added. The reaction was stirred overnight, quenched with water, extracted with 3x EtOAc, dried over Na_2SO_4 and the solvent was removed *in vacuo*. Hexadecane as internal standard was added. Analysis of the gas chromatogram showed full conversion to biphenyl under these conditions.

Component analysis of the construction dust. 27 g of fine powdered construction dust were placed into an extraction thimble. The extraction thimble was put into a soxleth-extractor, installed to a round flask filled with ca. 700 ml hexane and topped with a reflux condenser. Extraction was run for 48 h. After cooling to room temperature, the solvent was removed in vacuo, leaving a yellow slurry. GC/MS analysis of the extracted construction dust showed high amounts of different siloxanes and various other compounds. The table below shows a selection of the found substances according to the NIST database.

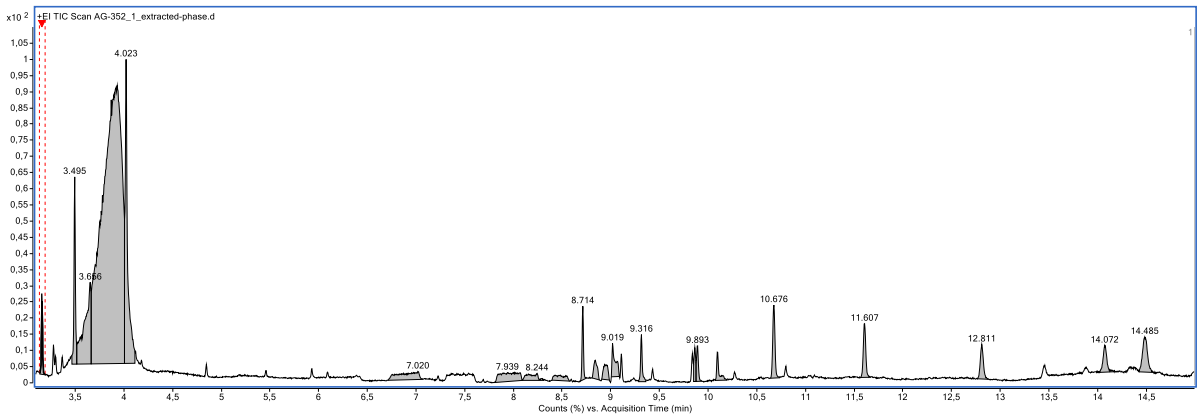


Figure S8. Chromatogram of the GC-MS analysis of the extracted construction dust (directly from slurry after removing the solvent) without additional PCB. Examples of selected signals are shown in Table S10.

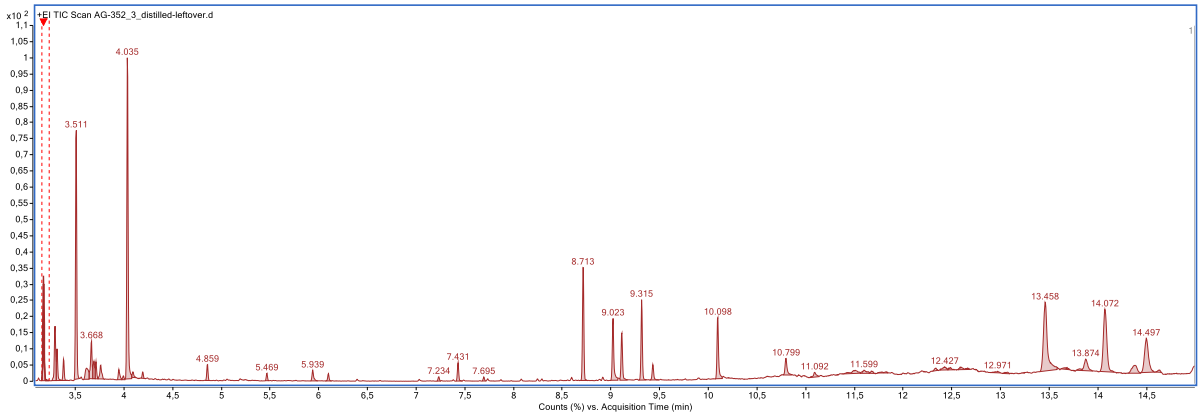


Figure S9. Chromatogram of the GC-MS analysis of the extracted construction dust (oil over slurry after removing the solvent) without additional PCB. Examples of selected signals are shown in Table S10.

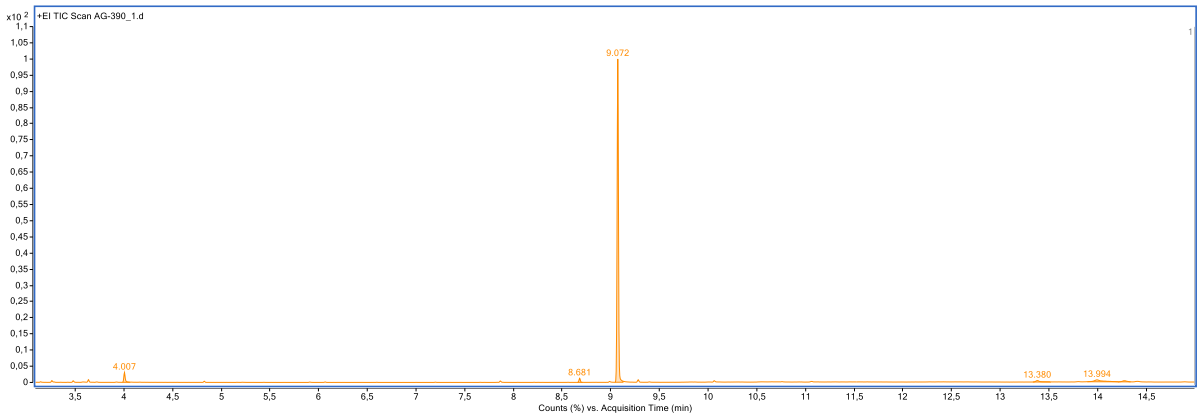


Figure S10. Chromatogram of the GC-MS analysis of the extracted construction dust with additional PCB. Examples of selected signals are shown in Table S10.

Table S10. GC/MS analysis of the hexane extract of the construction dust. The substances are a selection of the major signals. Assignments are based on the comparison to the NIST MS database.

Substance according to database analysis	**Accordance with database**	**Signal in chromatogram [min]**
4,4’-dichlorobiphenyl (PCB 15)	-	9.072
2,3-dihydro-1,1,3-trimethyl-3-phenyl-1H-indene	92-86 %	8.713
hexadecamethyl-heptasiloxane	79-74 %	
tetradecamethyl-heptasiloxane	73-70 %	
2,4-diphenyl-4-methyl-2(E)-pentene	74 %	9.315
tetracosamethyl-cyclododaecasiloxan	80 %	10.676

2,4-bis(1-methyl-1-phenylethyl)-phenol	89-78 %	
3,3,6-trimethyl-1,5-heptadien-4-one	72 %	3.511
benzyl alcohol	95 %	4.035
octylester-2-propenoic acid	83 %	
2-ethylhexylacrylate	83 %	
6-methylheptyl ester 2-propenoic acid	83 %	
2,6-di-tert-butyl-4-methylphenol	93 %	
butylated hydroxy toluene	93 %	
octamethylcyclotetrasiloxane	93 %	
2,4-diphenyl-4-methyl-2(E)-pentene	95 %	
1-methyl-2-(1-methylethyl)-benzene / o-cymene	82 %	
hexamethylcyclotrisiloxane	90 %	
decamethylcyclopentasiloxane	94 %	4.859

5. Substrate Scope

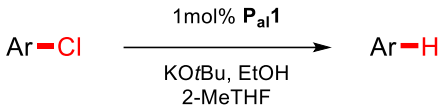
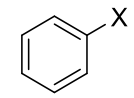
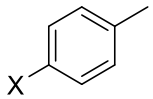
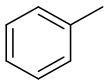
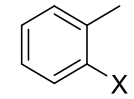
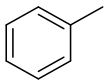
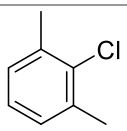
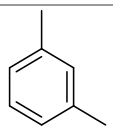
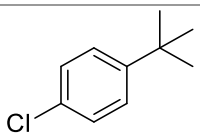
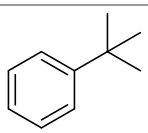
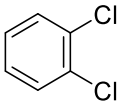
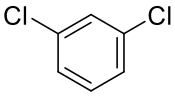
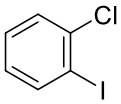
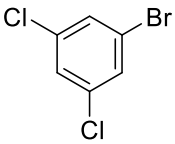
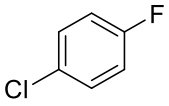
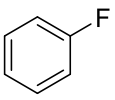
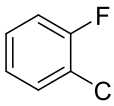
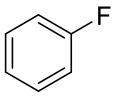
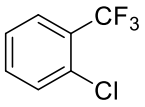
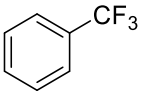
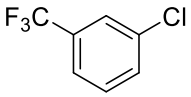
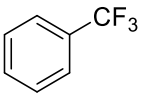
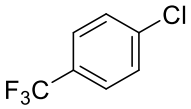
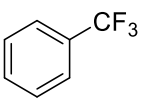
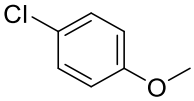
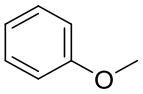
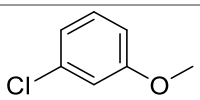
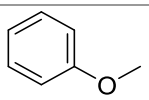
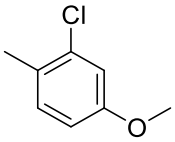
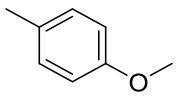
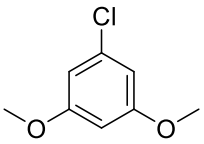
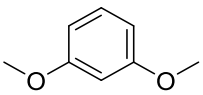
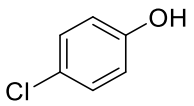
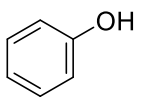
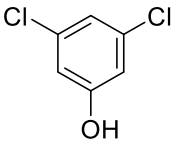
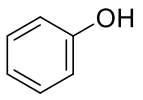
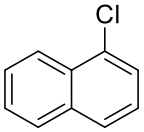
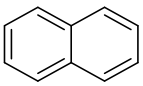
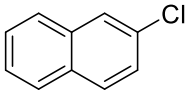
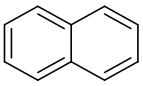
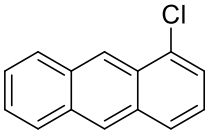
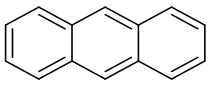
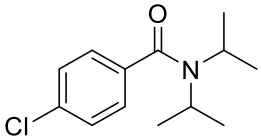
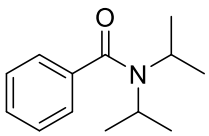
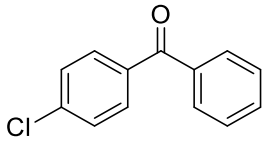
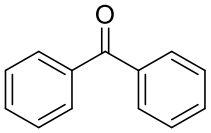
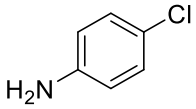
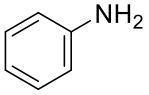
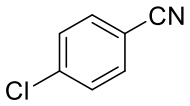
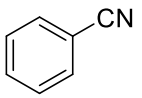
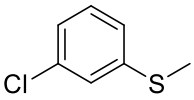
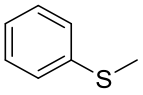
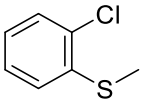
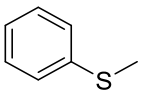
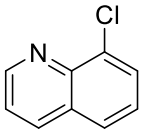
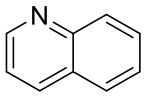
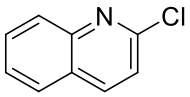
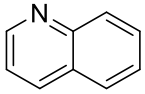
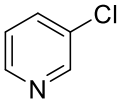
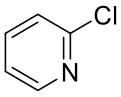
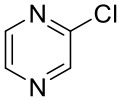
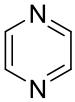
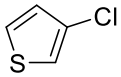
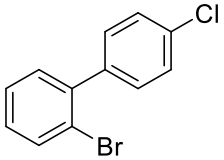
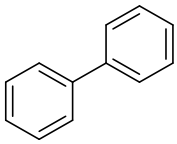
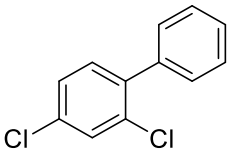
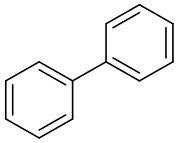
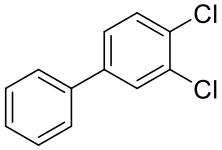
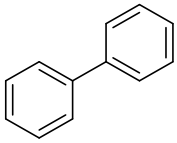
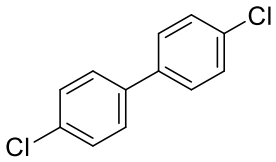
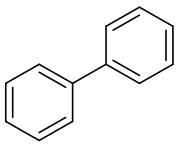
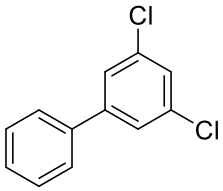
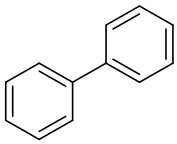


Table S11. Substrate scope of the dehalogenation of different aryl halides. Conditions follow the general conditions procedure using high solvent concentration (see chapter 2. General Procedure). In some cases, the C-O coupled byproduct, i.e. the ethoxy-substituted arene was detected *via* GC-analysis. GC-yields of the product are shown in the table.

Entry	Aryl halide	Product	Time [h]	Temperature	GC-yield prod%
2a-c	 X = Cl, Br, I		Cl, Br, I: 1	r. t.	Cl, Br, I: 100
3a-c	 X = F, Cl, Br, I		Cl: 2 Br: 1 I: 1	r.t.	F: 0 Cl: 100 Br: 96 I: 100
4a-c	 X = Cl, Br, I		Cl: 3 Br: 1 I: 1	r.t.	Cl: 100 Br: 96 I: 100
5			3	r.t.	100
6			1	r.t.	100
7			1	r.t.	100
8			1	r.t.	100
9			1	r.t.	100
10			1	r.t.	100
11			1	r.t.	100

12			1	r.t.	100
13			1	r.t	100
14			1	r.t	100
15			1	r.t	100
16			5	r.t	98
17			3	r.t.	100
18			1	r.t.	100
19			3	r.t.	100
20			24	r.t. 60°C	90% 98%
21			5	60°C	38 %
22			5	r.t.	100
23			1	r. t.	100
24			3	r.t.	92
25			3	r.t.	100

26			5 3	r.t. 60°C (2mol%)	47 52
27			5	60°C	37
28			24 3	r.t. 60°C (2mol%)	52 53
29			24 2	r.t. 60°C	70 73
30			5	r.t.	25
31			3	r.t.	100
32			5	r.t.	10
33			5 3	r.t. 60°C	43 71
34			5 3	r.t. 60°C	46 53
35			3 3	r.t. 60°C	42 14
36			2	60°C	22
37			1	r.t.	100 %
38			1	r.t.	100 %
39			1	r.t.	100 %

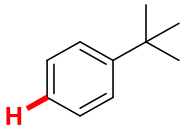
40			1	r.t.	100 %
41			1	r.t.	100 %

5.1. General Procedure for Product Isolation

In a glovebox, potassium *tert*-butoxide (3 eq.) was added to a Schlenk tube equipped with a magnetic bar. **L1-P$_{al}$** (1 mol%) was added into a vial equipped with a magnetic bar and sealed with a screw cap fitted with a septum. Outside the glovebox, 0.5 mL 2-methyltetrahydrofuran or THF were added to the Schlenk tube and 1 mL to the catalyst vial. If the aryl chloride (0.85 to 3 mmol) was a liquid, it was added directly to the Schlenk tube. If the aryl chloride was a solid, it was dissolved in the solvent prior to the addition to the Schlenk tube. Ethanol (3 eq.) and finally, the catalyst suspension was added to the mixture. After 3 h, 5 h or 24 h the reaction mixture was quenched with H_2O (dist.) and the aqueous phase was extracted 4x with Et_2O. The combined organic phases were dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The product was obtained after purification *via* filtration over silica, automatic column (hexane/diethylether or hexane/EtOAc gradient) or Kugelrohr-distillation.

5.2. Isolated Compounds

tert-Butylbenzene from 1-tert-Butyl-4-chlorobenzene



Colorless oil, 88 %.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 7.46 (d, J = 8.6 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 1.38 (s, 9H).

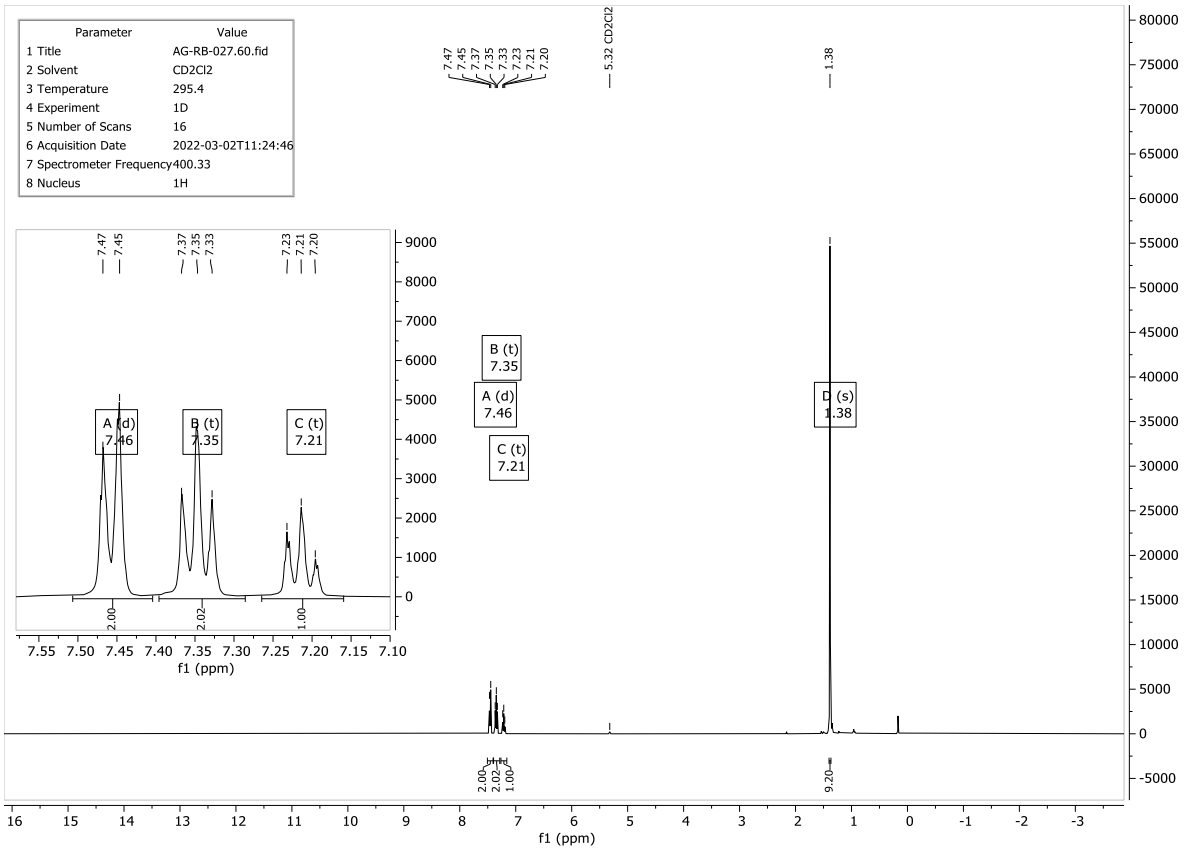
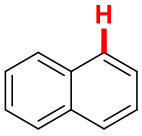


Figure S11. ^{1}H-NMR spectra of isolated *tert*-butylbenzene.

Naphthalene from 1-Chloronaphthalene



Colorless crystals, 87 %.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 7.99 (dd, $^{1}J_{HH}$ = 6.2 Hz, $^{2}J_{HH}$ = 3.3 Hz, 4H), 7.63 (dd, $^{1}J_{HH}$ = 6.5 Hz, $^{2}J_{HH}$ = 3.2 Hz, 4H).

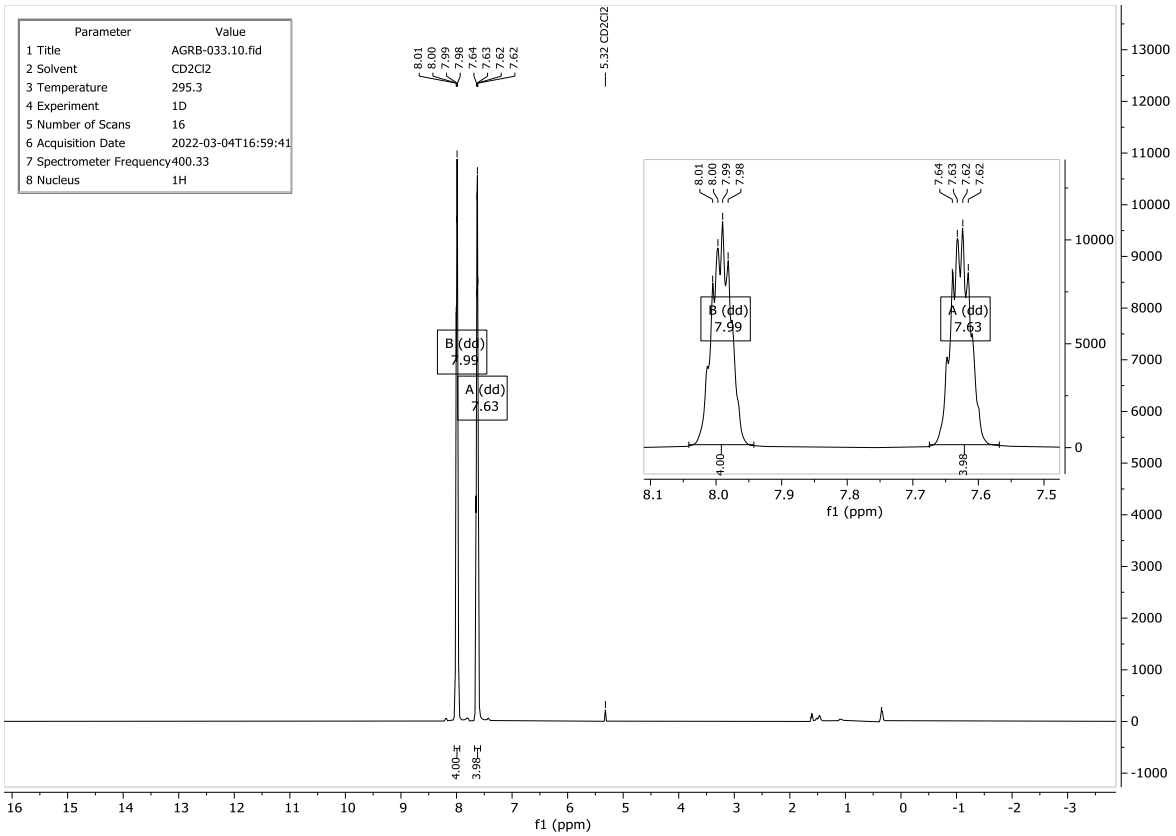
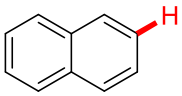


Figure S12. ^{1}H-NMR spectra of isolated naphthalene.

Naphthalene from 2-Chloronaphthalene



Colorless crystals, 92 %.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.87 (dd, *J* = 6.2, 3.3 Hz, 4H), 7.50 (dd, *J* = 6.2, 3.2 Hz, 4H).

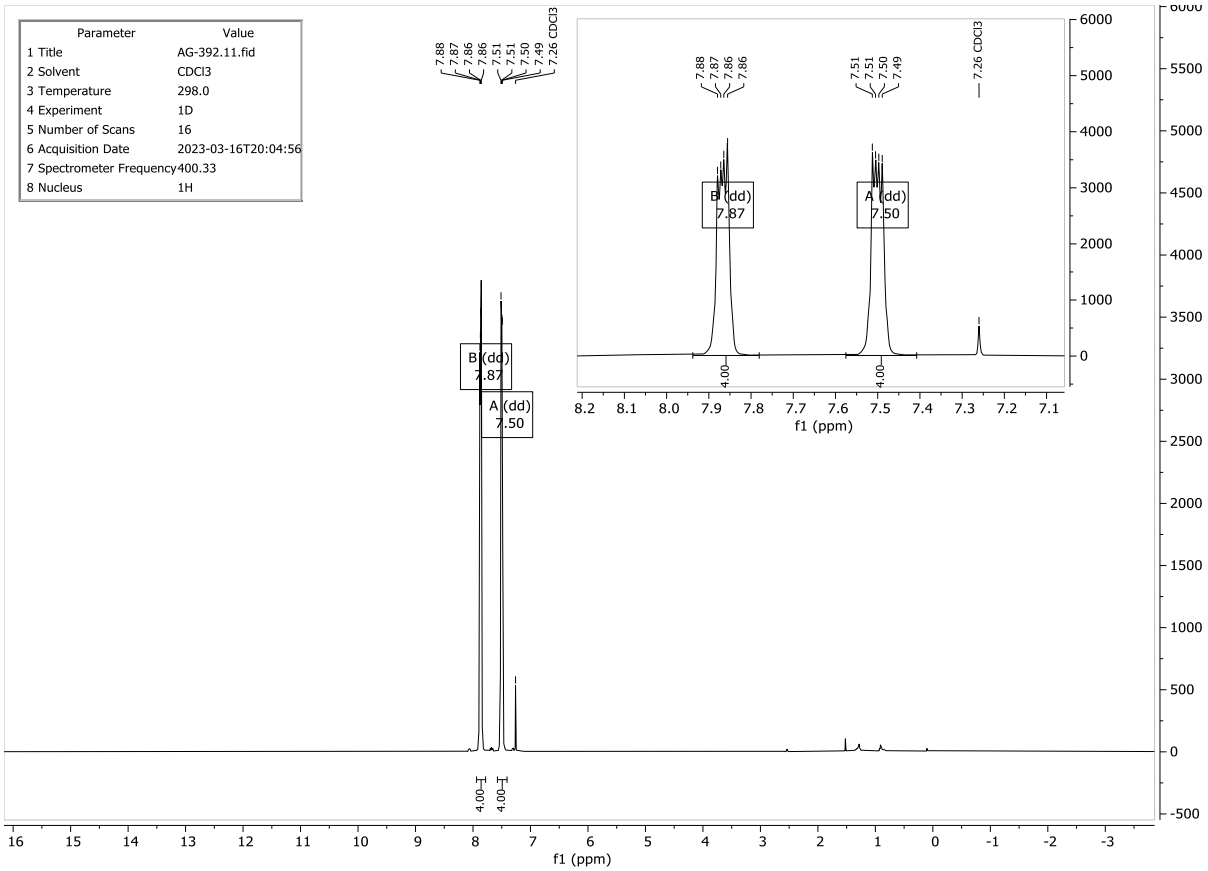
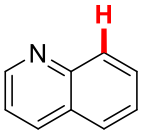


Figure S13. ^{1}H-NMR spectra of isolated naphthalene.

Quinoline from 8-Chloroquinoline



Light yellow oil, 91 %.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 8.92 (dd, $^{1}J_{HH}$ = 4.2 Hz, $^{2}J_{HH}$ = 1.7 Hz, 1H), 8.14 (dd, $^{1}J_{HH}$ = 8.3 Hz, $^{2}J_{HH}$ =1.5 Hz, 2H), 7.82 (dd, $^{1}J_{HH}$ = 8.2 Hz, $^{2}J_{HH}$ = 1.5 Hz, 1H), 7.72 (ddd, $^{1}J_{HH}$ = 8.4 Hz, $^{2}J_{HH}$ = 6.8 Hz, $^{3}J_{HH}$ = 1.5 Hz, 1H), 7.55 (ddd, $^{1}J_{HH}$ = 8.1 Hz, $^{2}J_{HH}$ = 6.8 Hz, $^{3}J_{HH}$ = 1.2 Hz, 1H), 7.37 (dd, $^{1}J_{HH}$ = 8.2 Hz, $^{2}J_{HH}$ = 4.2 Hz, 1H).

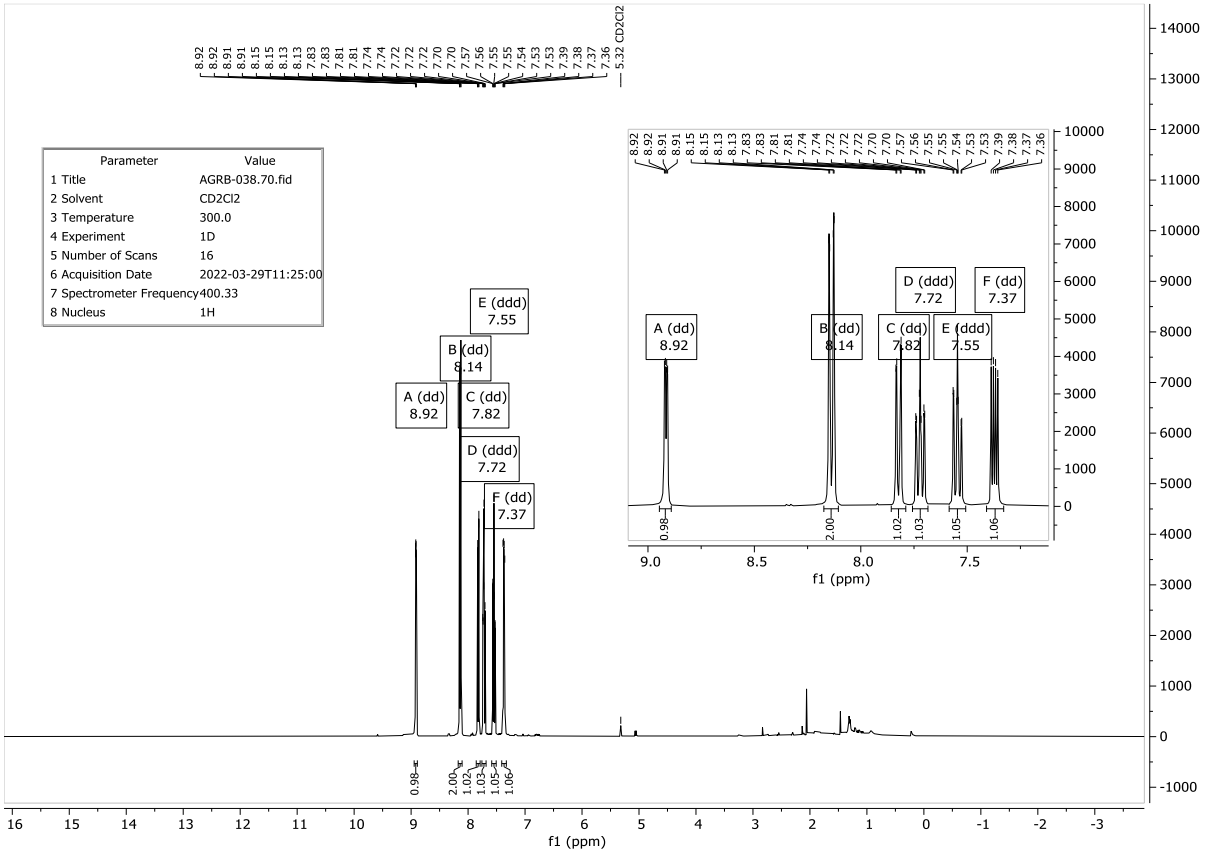
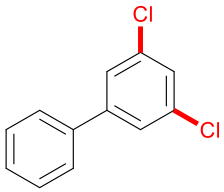


Figure S14. ^{1}H-NMR spectra of isolated quinoline.

Biphenyl from 3,5-Dichlorobiphenyl (PCB 14)



Colorless crystals, 86 %.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 6.8 Hz, 4H), 7.46 (t, J = 7.7 Hz, 4H), 7.41 – 7.32 (m, 2H).

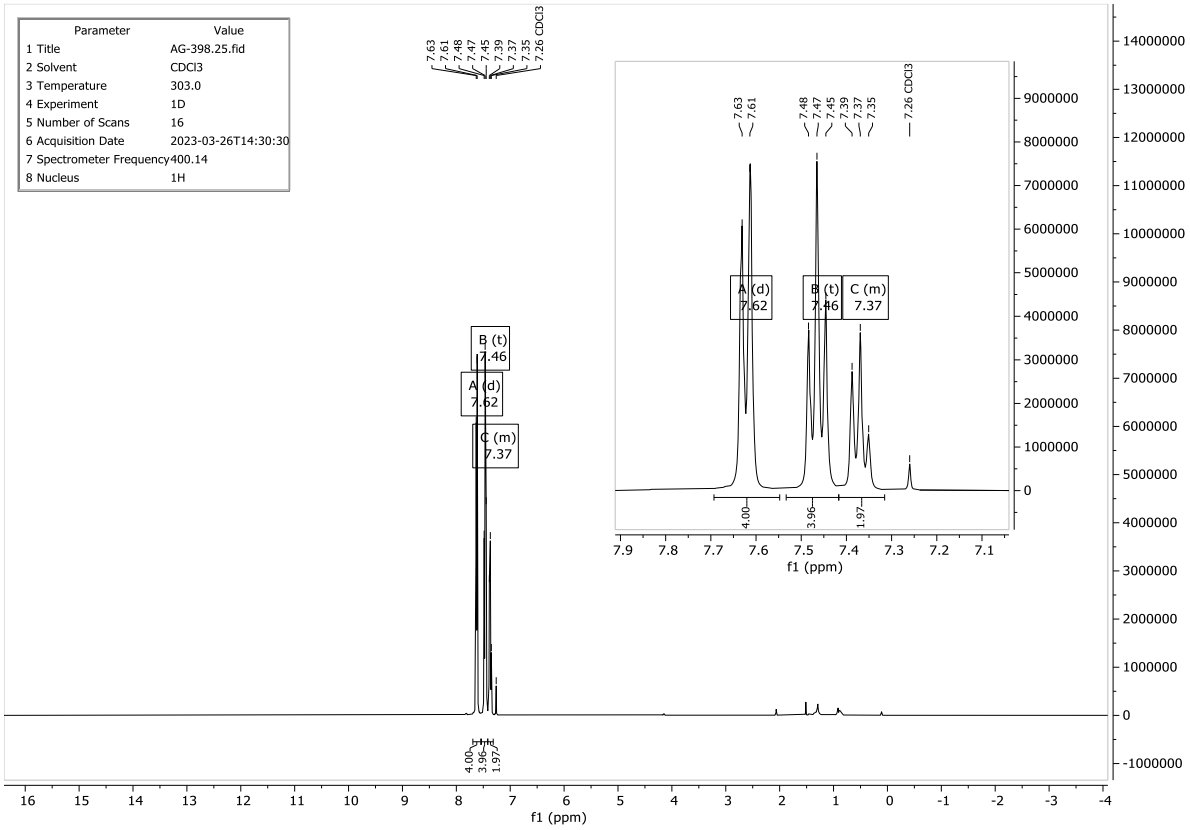


Figure S15. ^{1}H-NMR spectra of isolated biphenyl.

6. Dehalogenative Deuteration Reactions

6.1. General Procedure for the Screening of Deuteration Reactions

In a glovebox, potassium *tert*-butoxide (3 eq., 2.55 mmol, 292 mg) was added to a vial equipped with a magnetic bar and a seal with a screw cap fitted with a septum and **L1-P$_{al}$** (1 mol%, 5.8 mg) was added to another vial. Outside the glovebox, 0.5 mL 2-methyltetrahydrofuran was added to the to the catalyst vial. If the aryl halide (0.85 mmol) was a liquid, it was added directly to the vial with base. If the aryl halide was a solid, it was dissolved in a solvent prior to the addition to the vial. Internal standard (hexadecane or tetradecane, ca. 0.2 eq.), ethanol (3 eq., 2.55 mmol, 145 µL) and, as the last step, the catalyst suspension was added to the mixture. The reaction temperature was set to 60°C. After 1h, 3h and 5h a droplet of the reaction mixture was filtered over silica and prepared as a GC sample. Multiple runs were made to ensure the consistency of the results.

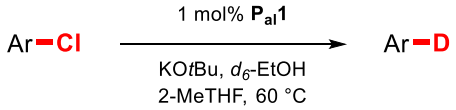
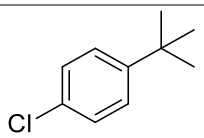
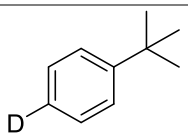
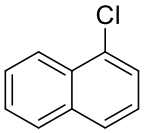
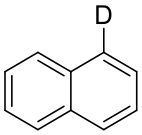
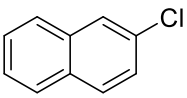
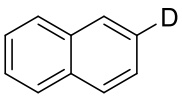
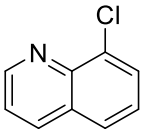
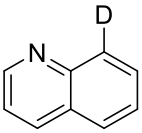


Table S12. Deuteration of different aryl chlorides. Conditions: aryl chloride (0.5 mmol), **L1-P$_{al}$** (1 mol%), KO*t*Bu (3 eq.), d_6-EtOH (3 eq.), 2-MeTHF (0.5 ml), 60 °C; yields are GC-FID yields.

Entry	Aryl halide	Product	Time [h]	Yield
			1	>99 %
			1	>99 %
			1	>99 %
			1	89 %

6.2. Confirmation of the Deuteration Degree

The deuteration degree of the compounds was confirmed by integration via ^{1}H NMR spectroscopy. All spectra should the clean conversion to the deuterated compound with no signs for the non-deuterated species. The method was validated by addition of protonated compound to the deuterium labeled compound. This is demonstrated below by means of 8-deuteroquinoline.

8-Deuteroquinoline and quinoline

16 mg 8-deuteroquinoline were mixed with 8 mg quinoline. The signal at 8.13 ppm hints to the difference between deuterated and non-deuterated species.

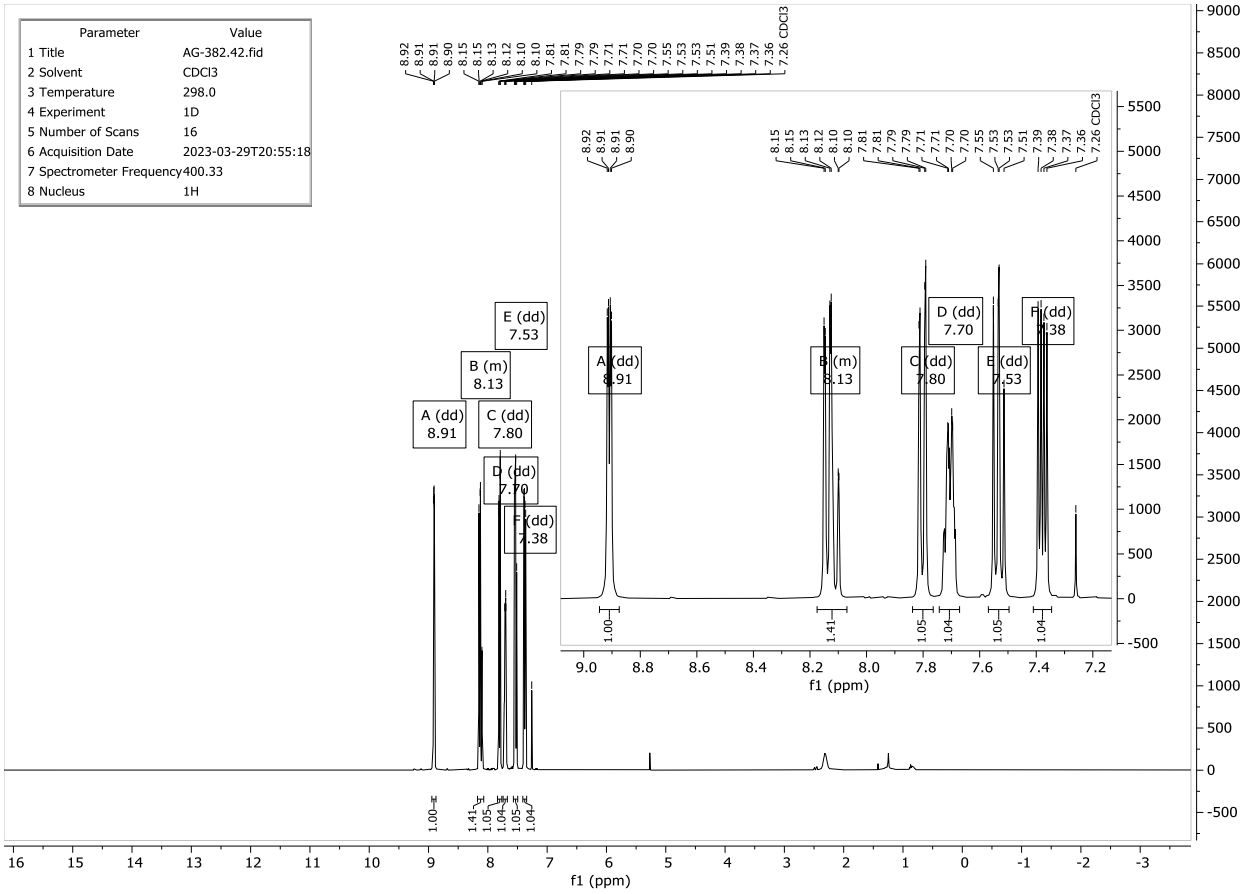
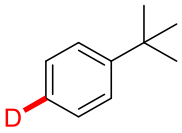


Figure S16. ^{1}H-NMR spectra of a mixture of 8-deuteroquinoline and quinoline.

6.3. General Procedure for the Isolation of the Deuterated Products

In a glovebox, potassium *tert*-butoxide (3 eq., 1.5 mmol, 168 mg) was added to a Schlenk tube equipped with a magnetic bar. **L1-P$_{al}$** (1 mol%) was added into a vial equipped with a magnetic bar and sealed with a screw cap fitted with a septum. Outside the glovebox, 0.3 mL 2-methyltetrahydrofuran or THF was added to the catalyst vial. If the aryl chloride (0.5 mmol) was a liquid, it was added directly to the vial. If the aryl chloride was a solid, it was added to the catalyst vial before adding the base. d_6-Ethanol (3 eq., 1.5 mmol, 88 µL) and finally, the catalyst suspension was added to the mixture and heated to 60 °C if not otherwise mentioned. After a certain time, the reaction mixture was quenched with H_2O (dist.) and the aqueous phase was extracted 4x with Et_2O, DCM or EtOAc. The combined organic phases were dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. The product was obtained after purification *via* filtration over silica with hexane or pentane.

6.4. Isolated Deuterated Compounds



1-*tert*-Butyl-4-deuterobenzene

Colorless oil, 96 %. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 1.34 (d, *J* = 1.0 Hz, 9H). $^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$): δ = 151.3, 128.1, 125.4, 34.80, 31.5.

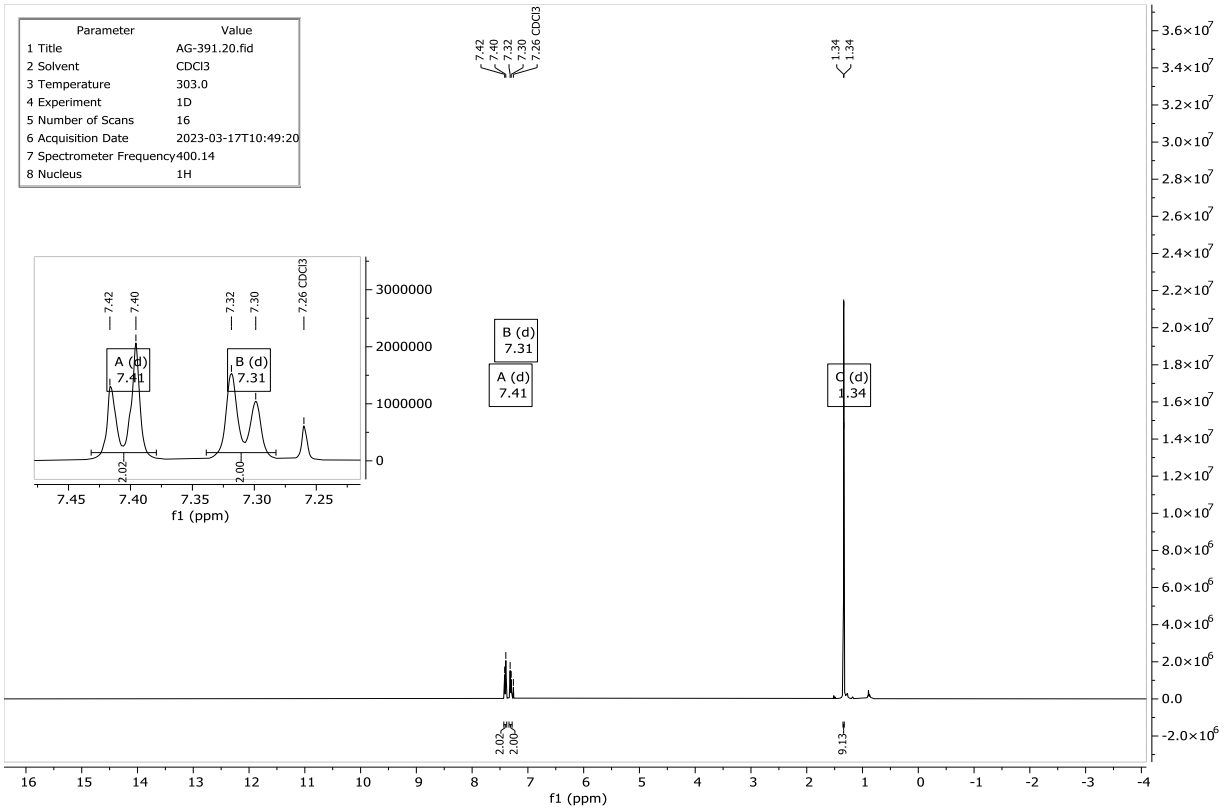


Figure S17. ^{1}H-NMR spectra of isolated 1-*tert*-butyl-4-deuterobenzene.

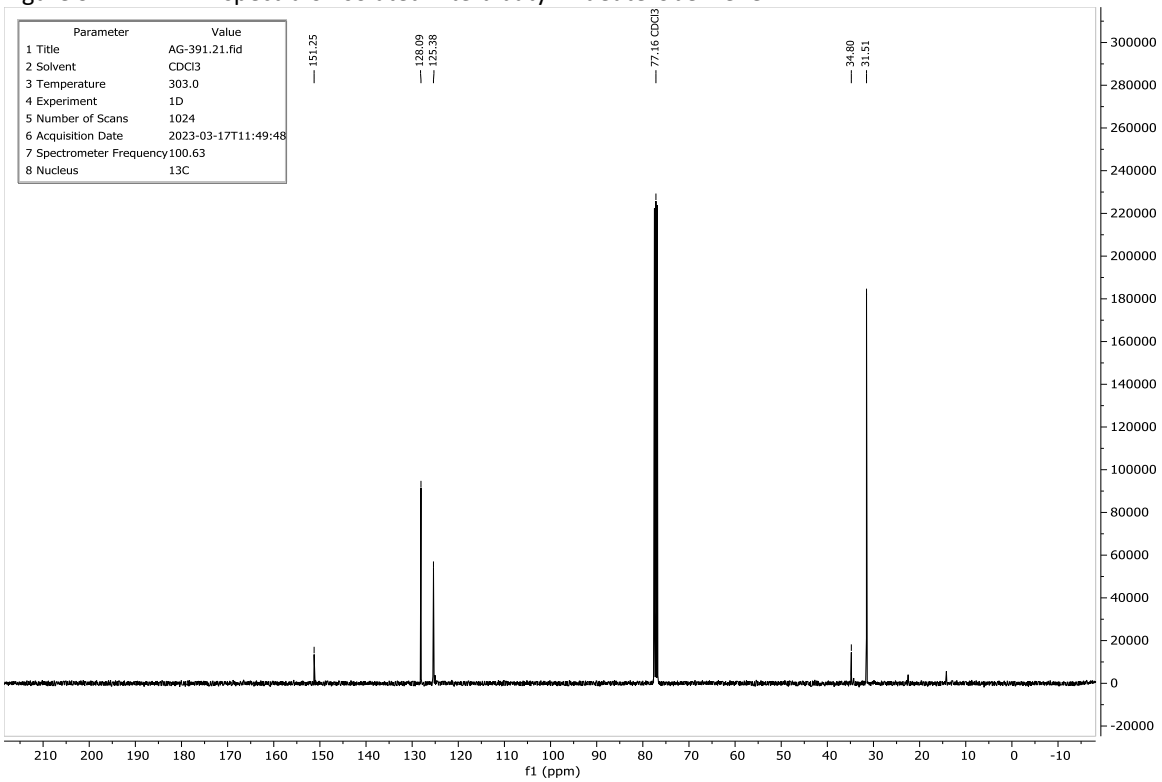
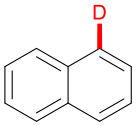


Figure S18. $^{13}C\{^{1}H\}$-NMR spectra of isolated 1-*tert*-butyl-4-deuterobenzene.



1-Deuteronaphthalene

Colorless crystals, 40 %.^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.91 – 7.82 (m, 3H), 7.50 (d, *J* = 4.1 Hz, 4H). $^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$): δ = 133.6, 133.5, 128.0, 128.0, 127.7, 127.5, 126.0, 125.8.

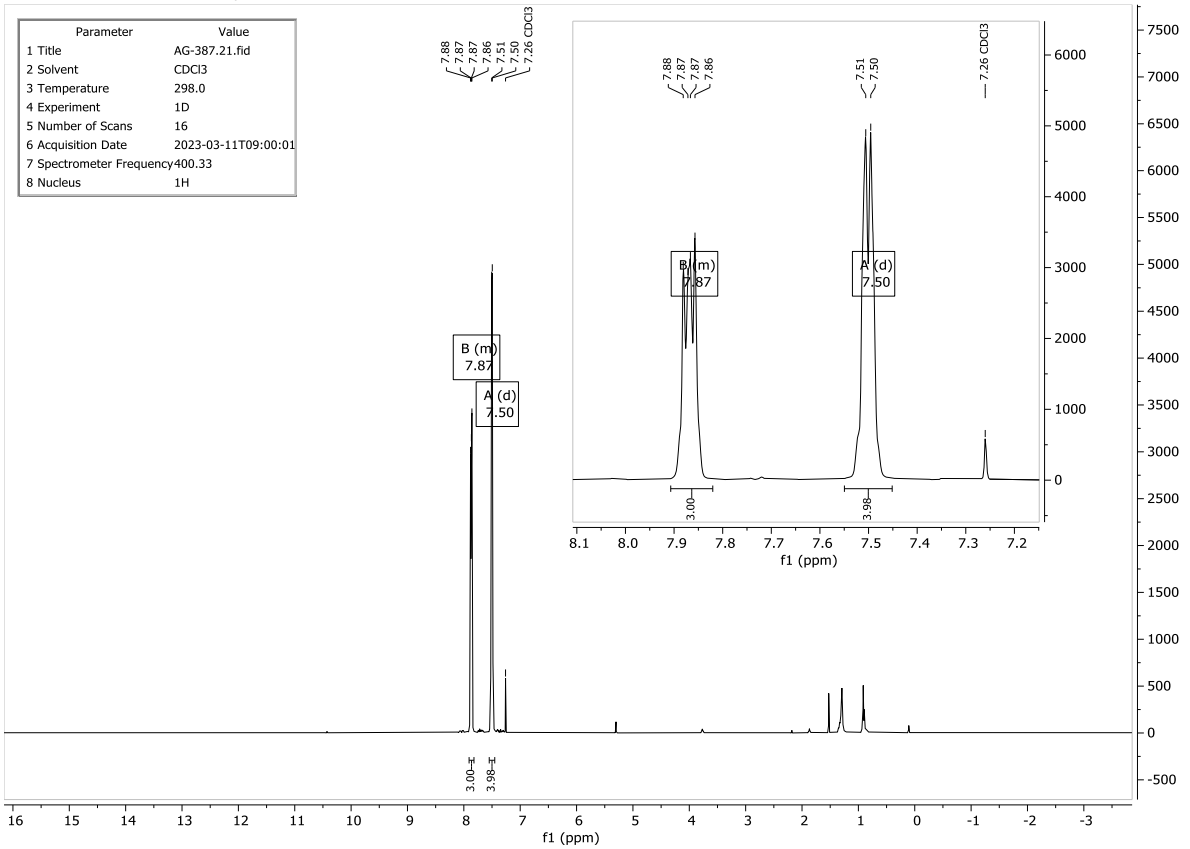


Figure S19. ^{1}H-NMR spectra of isolated 1-deuteronaphthalene.

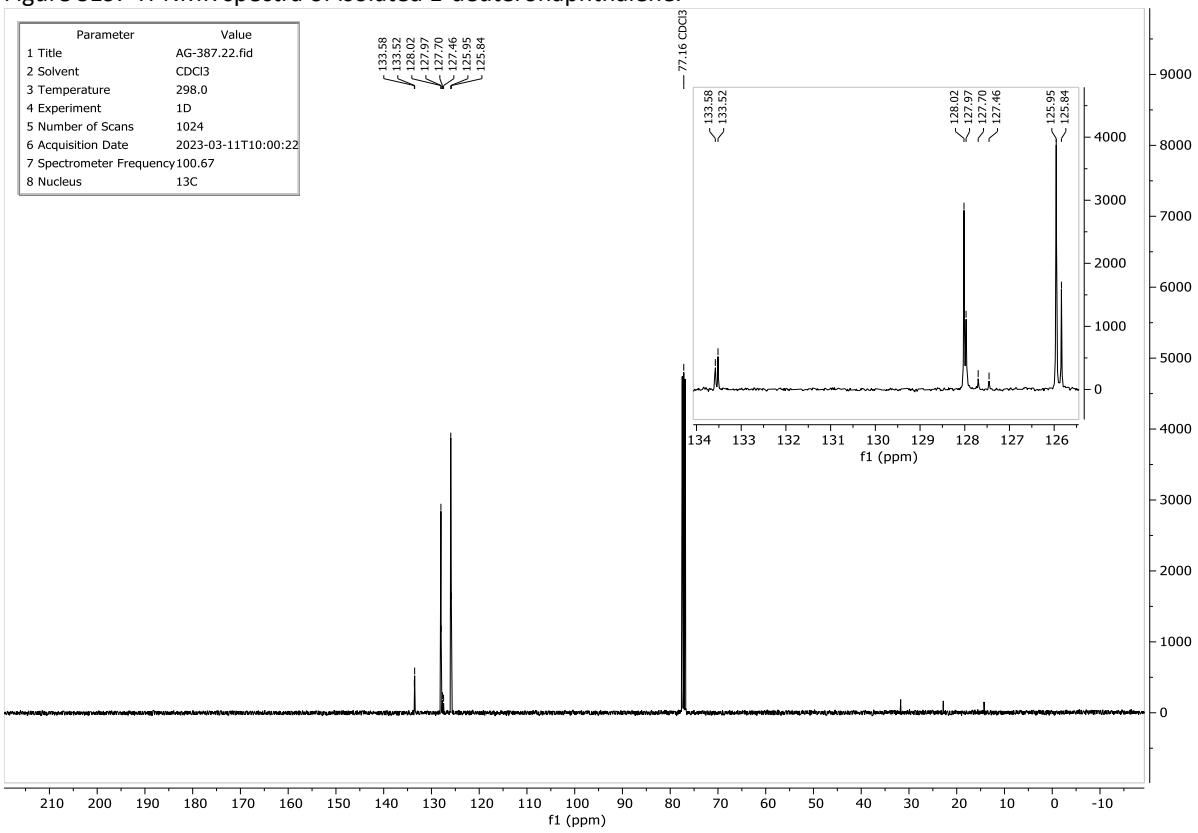
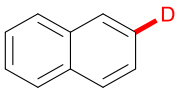


Figure S20. $^{13}C\{^{1}H\}$-NMR spectra of isolated 1-deuteronaphthalene.



2-Deuteronaphthalene

Colorless crystals, 64 %.^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.89 – 7.82 (m, 4H), 7.51 – 7.44 (m, 3H). $^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$): δ = 133.6, 128.0, 127.9, 126.0, 125.9.

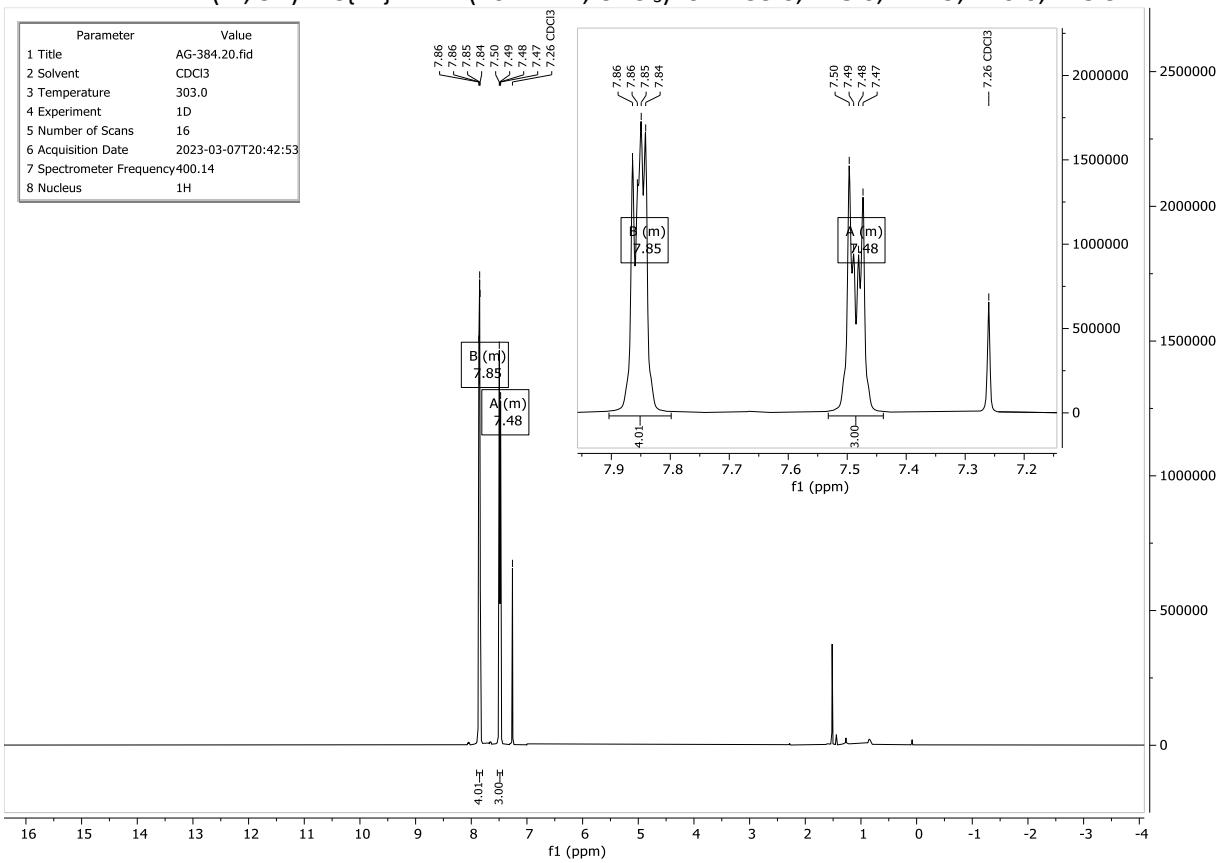


Figure S21. ^{1}H-NMR spectra of isolated 2-deuteronaphthalene.

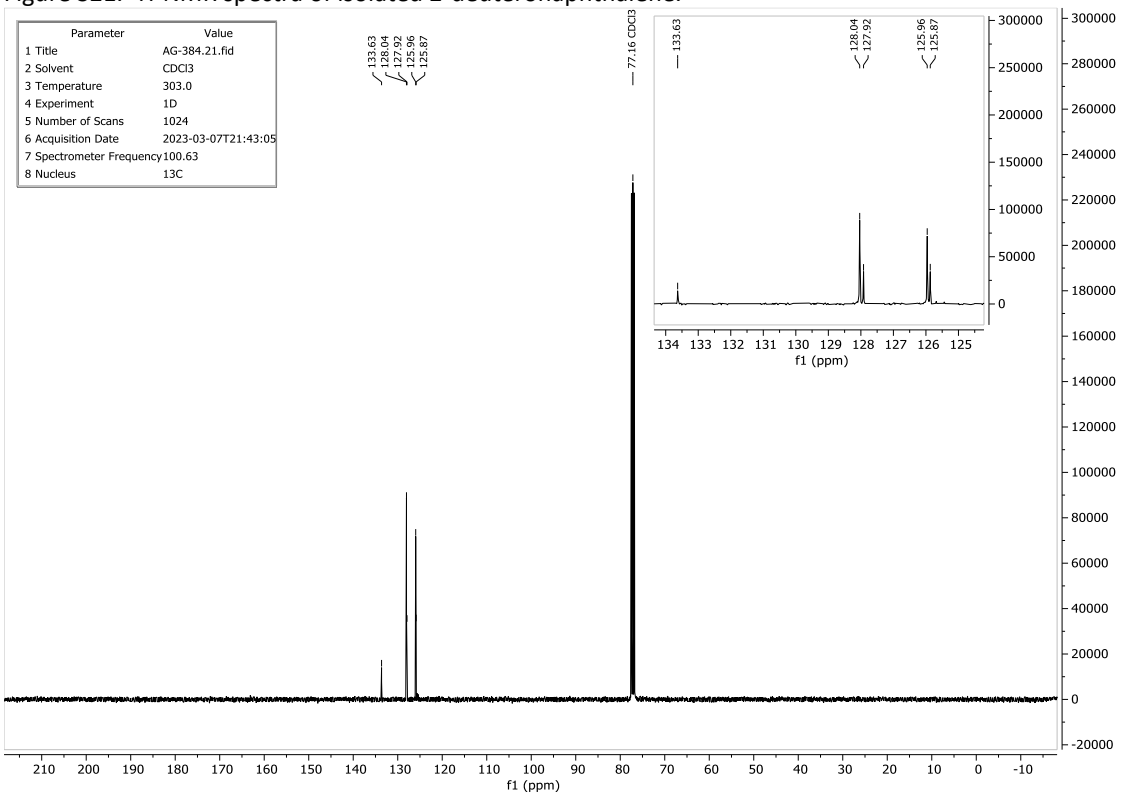
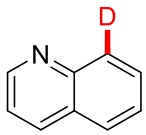


Figure S22. $^{13}C\{^{1}H\}$-NMR spectra of isolated 2-deuteronaphthalene.



8-Deuteroquinoline

Light yellow oil, 75 %.^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.93 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 6.9 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.40 (dd, *J* = 8.3, 4.2 Hz, 1H). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 141.4, 141.3, 128.90 128.8, 128.7, 127.4, 127.3. ^{2}H-NMR (61 MHz, CH_2Cl_2): δ = 8.11 (s, 1D).

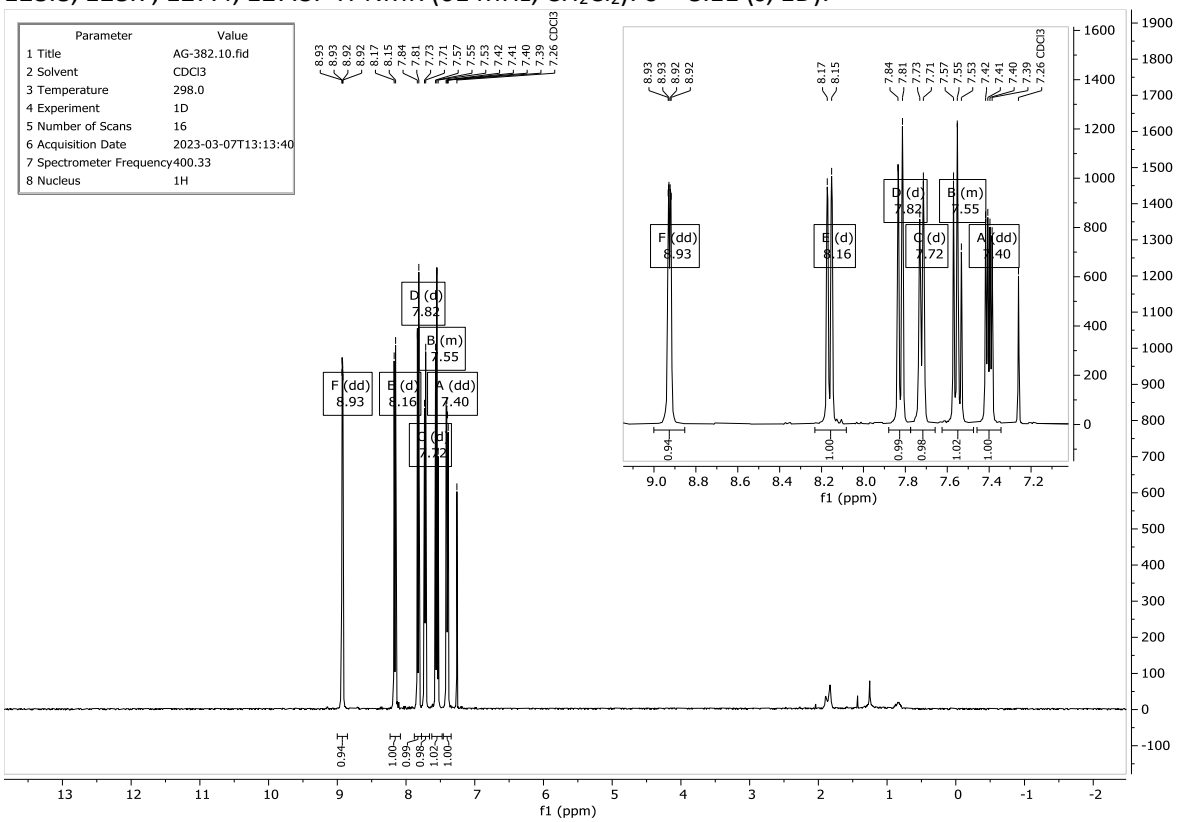


Figure S23. ^{1}H-NMR spectra of isolated 8-deuteroquinoline.

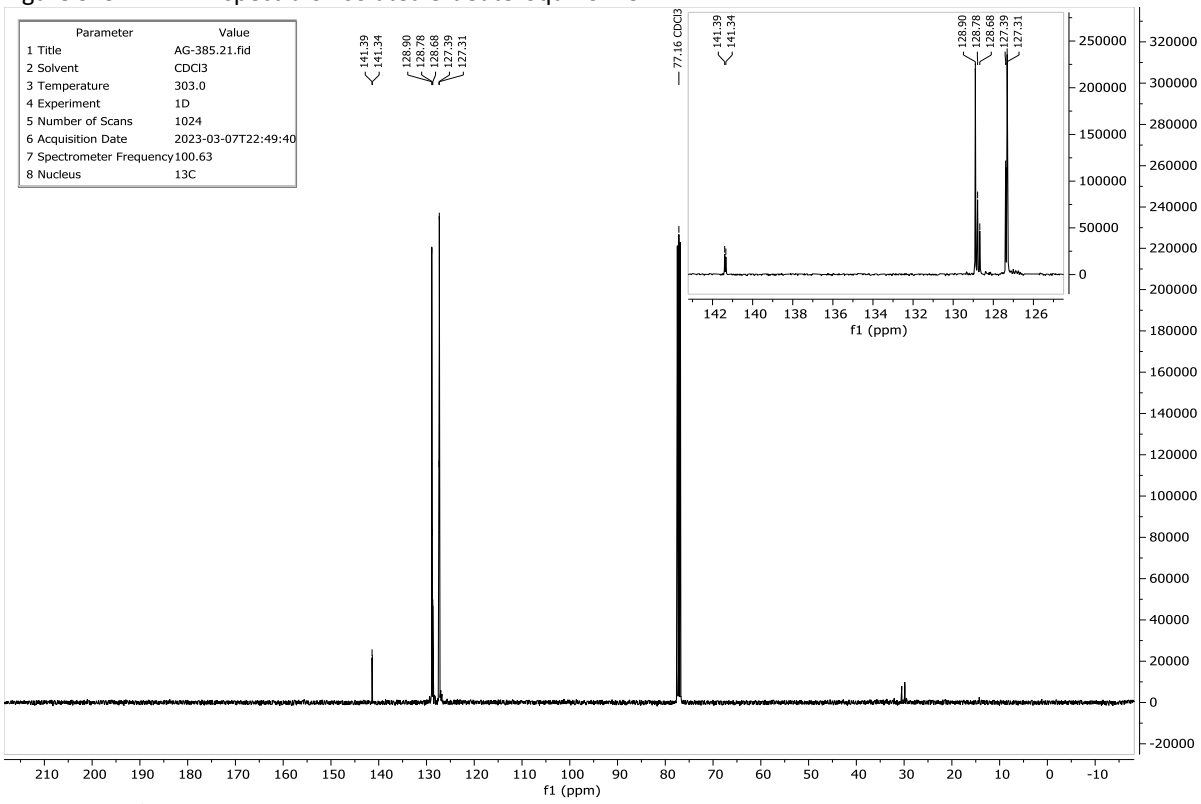


Figure S24. ^{13}C{^{1}H}-NMR spectra of isolated 8-deuteroquinoline.

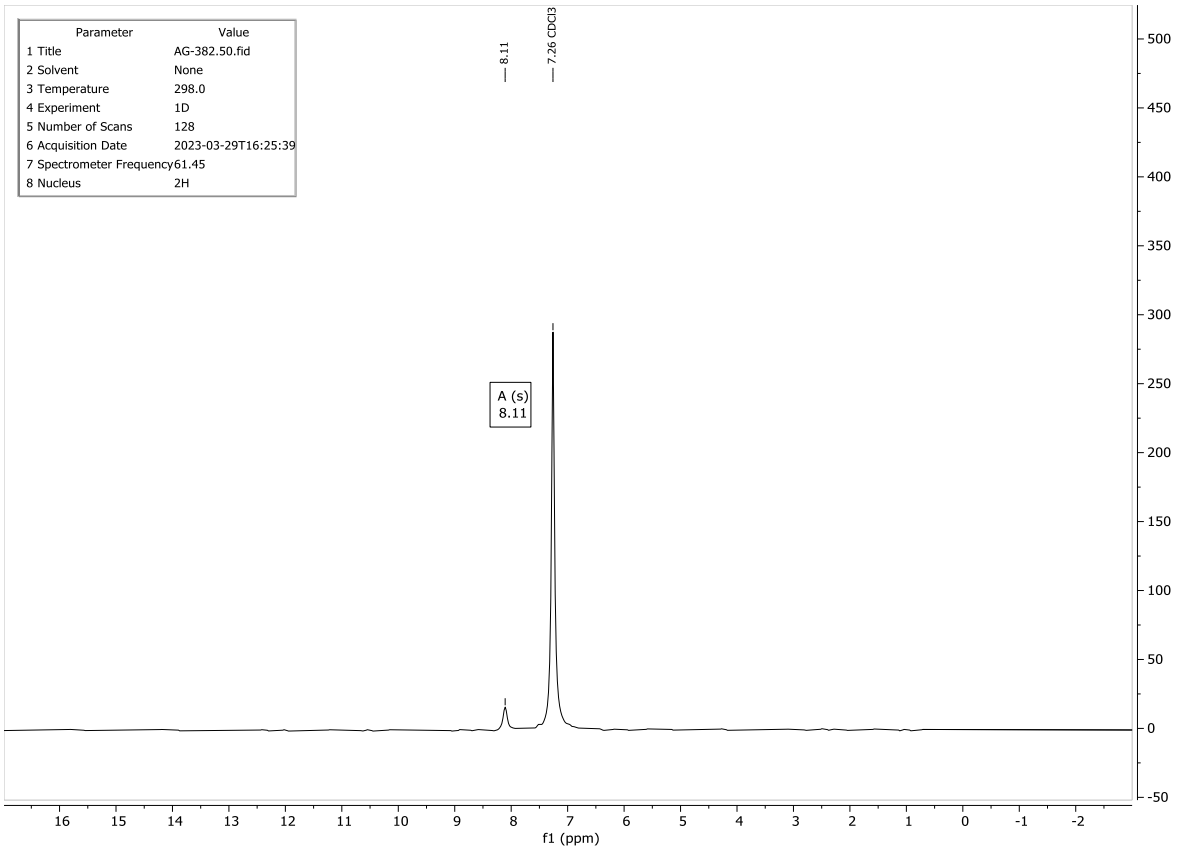
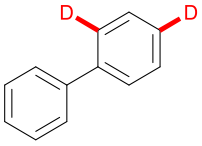


Figure S25. ^{2}H-NMR spectra of isolated 8-deuteroquinoline.



2,4-Dideuterobiphenyl

Colorless crystals, 69 %.^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.65 – 7.58 (m, 3H), 7.49 – 7.43 (m, 5H), 7.40 – 7.32 (m, 1H). $^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$): δ = 141.4, 141.3, 128.9, 128.8, 128.7, 127.4, 127.3.

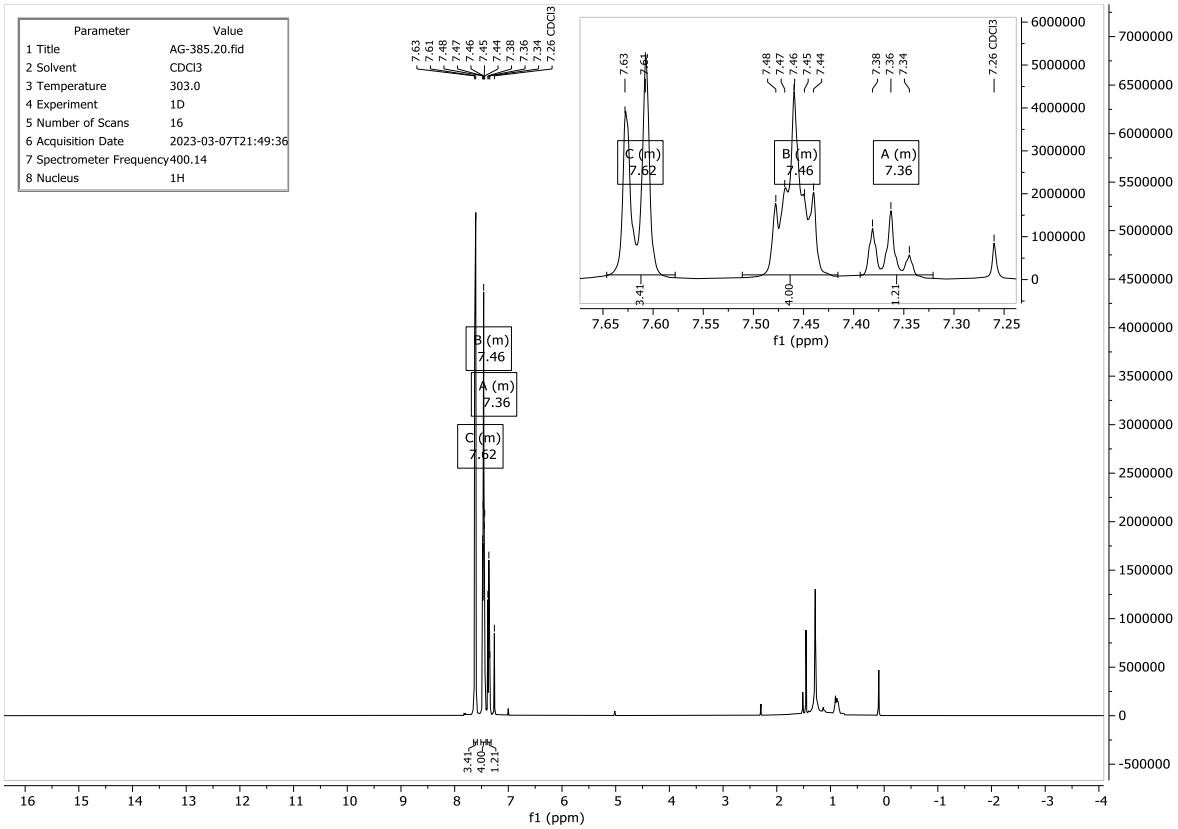


Figure S26. ^{1}H-NMR spectra of isolated 2,4-dideuterobiphenyl.

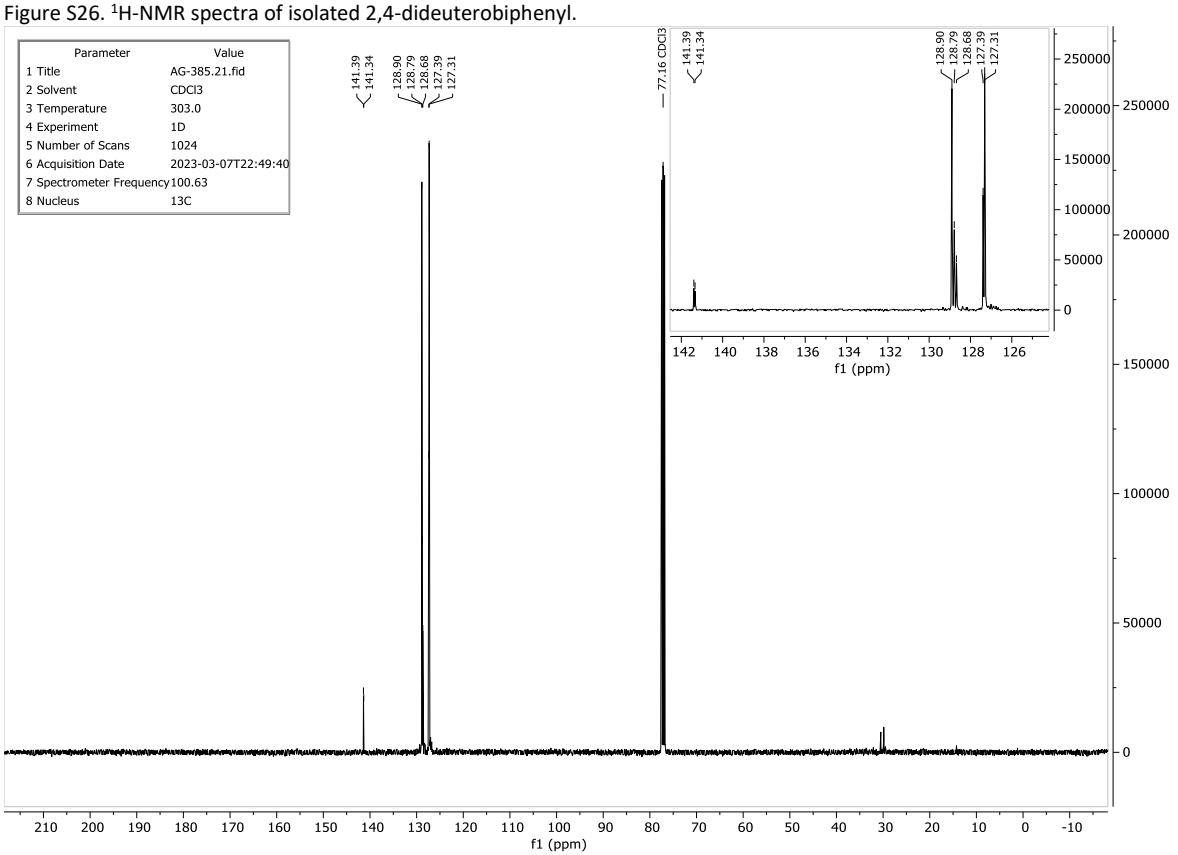
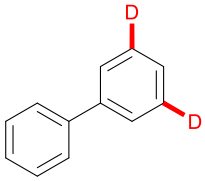


Figure S27. $^{13}C\{^{1}H\}$-NMR spectra of isolated 2,4-dideuterobiphenyl.



3,5-Dideuterobiphenyl

Colorless crystals, 71 %.^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.63 (s, 4H), 7.47 (t, *J* = 7.5 Hz, 3H), 7.42 – 7.34 (m, 3H). $^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$): δ = 141.4, 128.9, 127.4, 127.3, 127.2, 127.2. ^{2}H-NMR (61 MHz, CH_2Cl_2): δ = 7.17 (s, 2D).

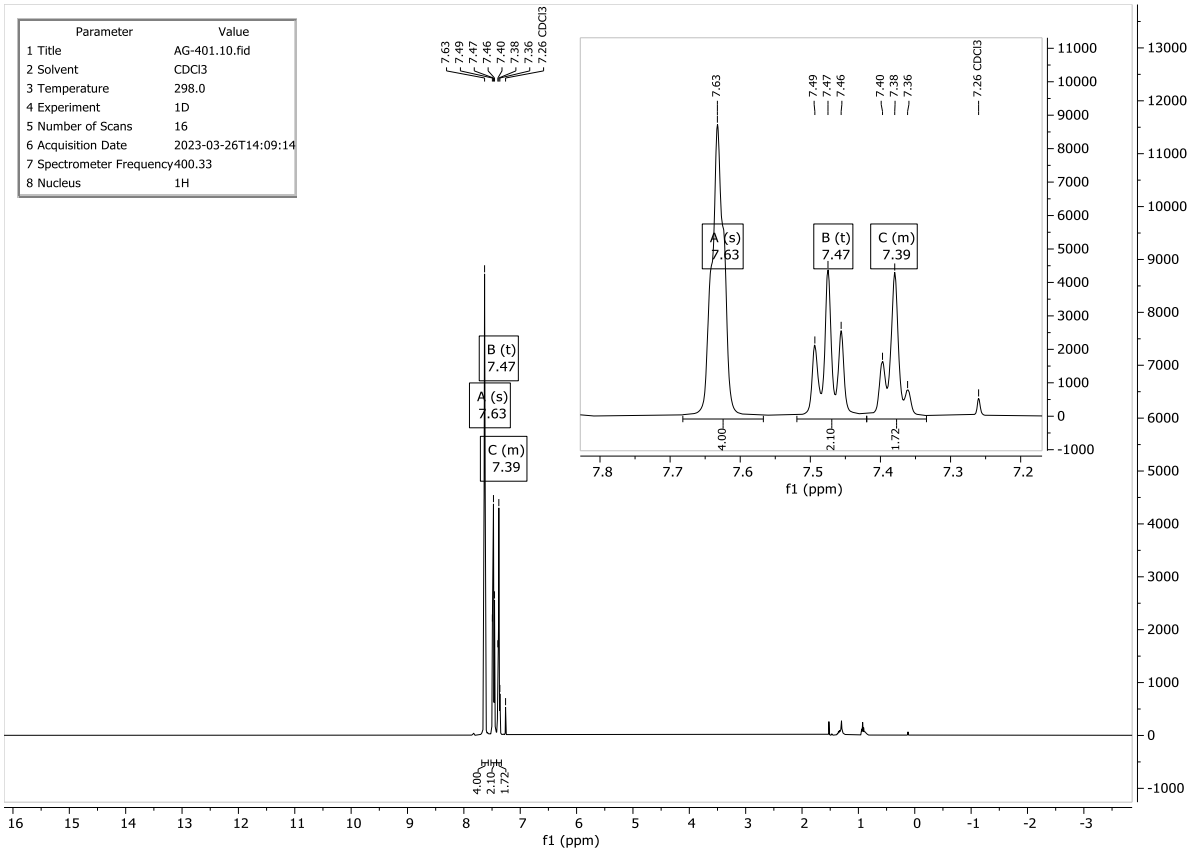


Figure S28. ^{1}H-NMR spectra of isolated 3,5-dideuterobiphenyl.

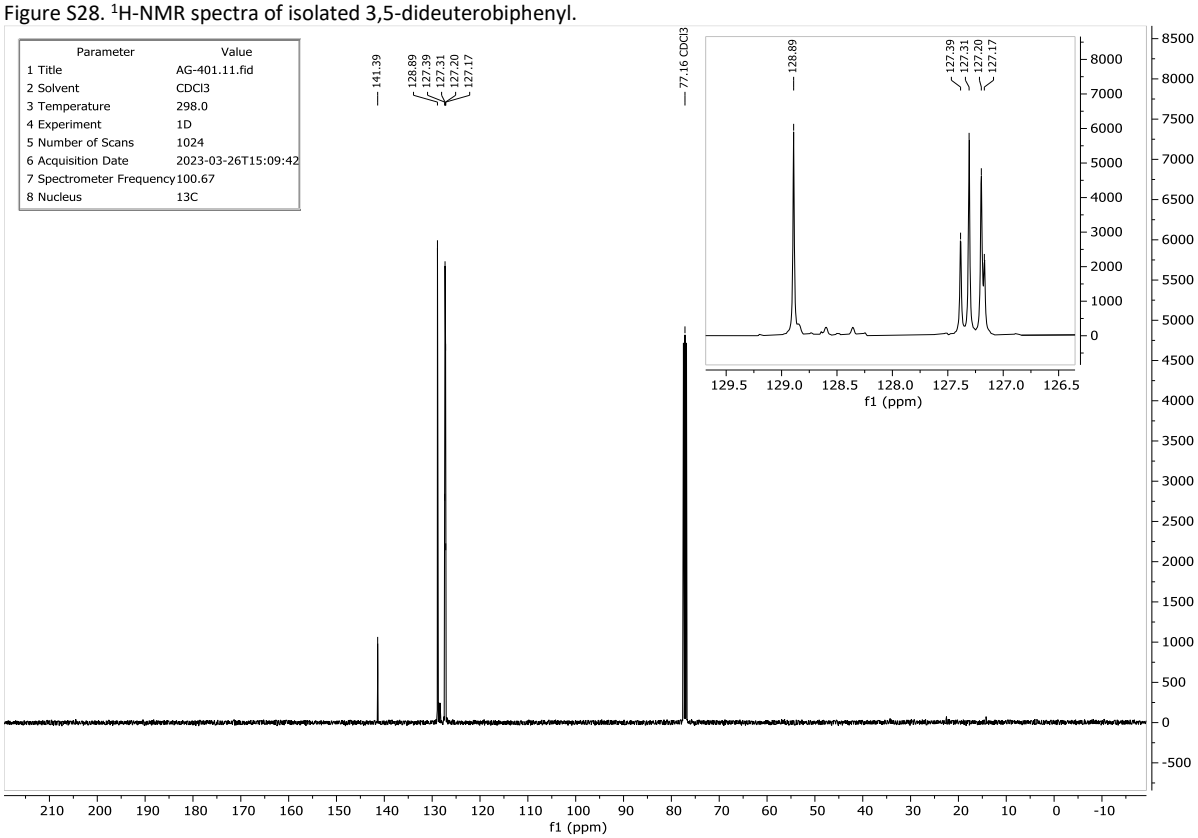


Figure S29. $^{13}C\{^{1}H\}$-NMR spectra of isolated 3,5-dideuterobiphenyl.

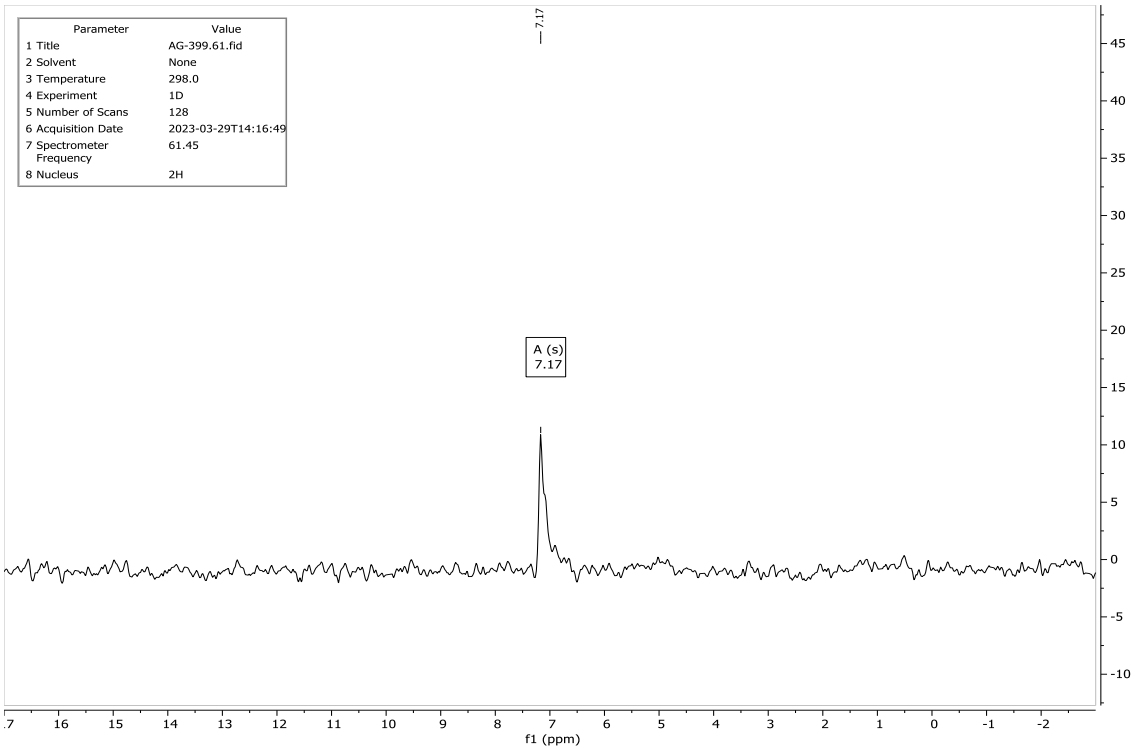
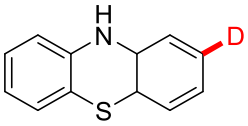


Figure S30. ^{2}H-NMR spectra of isolated 3,5-dideuterobiphenyl.

2-Deuterophenothiazine

Used 3 mol% of **L1-P$_{al}$**, reaction at room temperature. Pale yellow solid, 92 %. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.04 – 6.94 (m, 3H), 6.87 – 6.78 (m, 2H), 6.60 – 6.50 (m, 2H), 5.79 (s, 1H). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 141.8, 127.5, 127.0, 122.7 (d, J = 11.0 Hz), 118.4, 114.5 (d, J = 9.6 Hz). ^{2}H-NMR (61 MHz, CH_2Cl_2): δ = 7.06 (s, 1D).



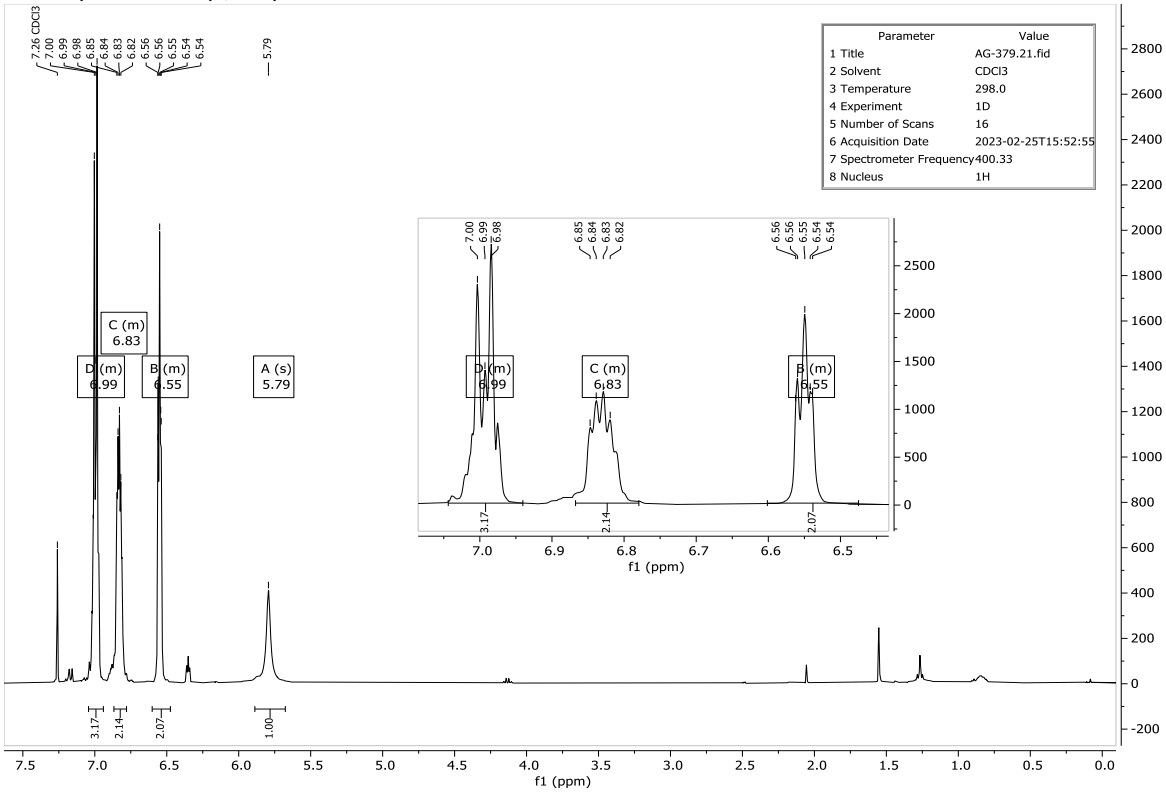


Figure S31. ^{1}H-NMR spectra of isolated 2-deuterophenethiazine.

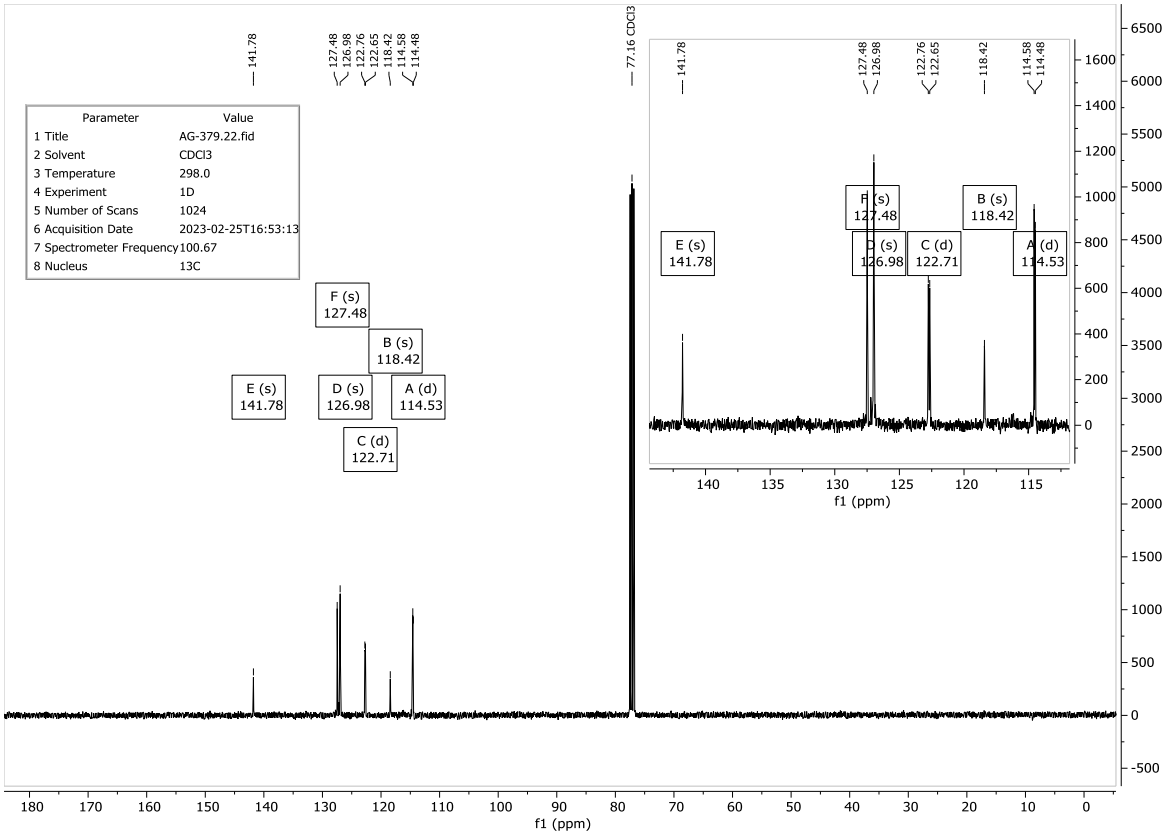


Figure S32. $^{13}C\{^{1}H\}$-NMR spectra of isolated 2-deuterophenothiazine.

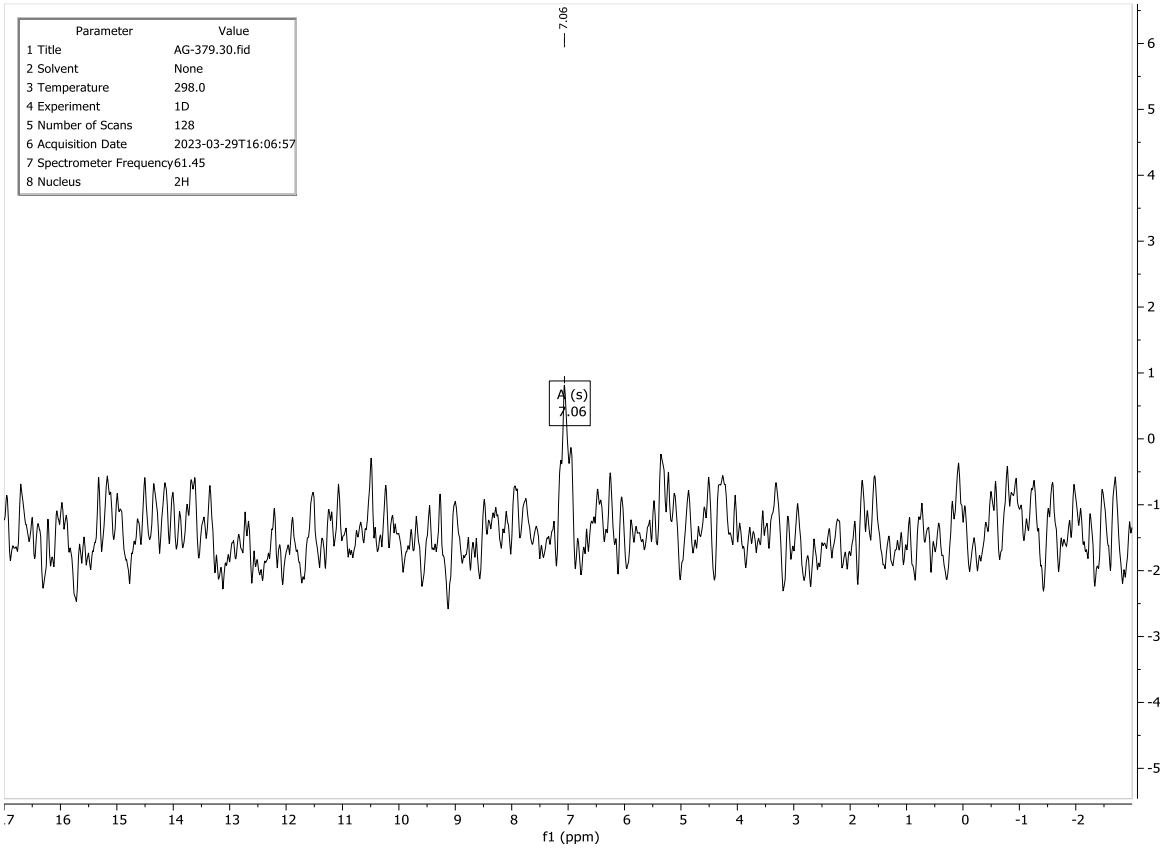


Figure S33. ^{2}H-NMR spectra of isolated 2-deuterophenothiazine.

7. References

1 Suzuki cross-coupling reaction for the synthesis of 3,5-dichlorobiphenyl similar to: S. Akzinnay, F. Bisarob and C. S. J. Cazin, *Chem. Commun.*, 2009, 5752-5753.

2 L. Hintermann *Beilstein J. Org. Chem.*, 2007, **3***,* No. 22. Deprotonation carried out with KO*t*Bu as base.

3 P. Weber, T. Scherpf, I. Rodstein, D. Lichte, L. T. Scharf, L. J. Gooßen and V. H. Gessner, *Angew. Chem. Int. Ed.*, 2019, **58**, 3203.

4 X.-J. Wei, B. Xue, J. Handelmann, Z. Hu, H. Darmandeh, V. H. Gessner and L. J. Gooßen, *Adv. Synth. Catal.*, 2022, **364**, 3336.

5 J. Tappen, I. Rodstein, K. McGuire, A. Großjohann, J. Löffler, T. Scherpf and V. H. Gessner, *Chem. Eur. J.*, 2020, **26**, 4281.