Supplementary Information (SI) for Green Chemistry.

ELECTRONIC SUPPLEMENTARY INFORMATION

Process-Optimised Access to Triarylamines through Catalytic Dehydrogenative Aromatisation

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1. General Remarks

The reagents used in this work were purchased from Merck and Zenteck and used without further purification or activation procedures. Palladium on charcoal (Pd/C) was purchased from Merck (205699-50G, 10 wt% loading, matrix-activated carbon support). PS-TsOH (2.5 mmol/g) was purchased from Merck. Cyclopentyl methyl ether (CPME) was purchased from Zeon. The solvent was not dehydrated before use.

Molecular oxygen (O_2) was supplied via a balloon filled with the gas, directly connected to the reflux condenser.

In the flow setup, the reaction mixture was introduced using a high-performance liquid chromatography (HPLC) pump, Shimadzu LC-40D.

TLCs were visualized under a UV lamp (λmax = 254 nm or 365 nm) and/or by staining with a potassium permanganate or ninhydrin solution. Flash column chromatography (FCC) was performed on Merck silica gel 60 (230–400 mesh), and the solvent systems used are indicated in parentheses.

Gas chromatography (GC) analyses were conducted using an Agilent 6850 and a Shimadzu GC-2010 Pro, both equipped with a 5-MS column and helium as the carrier gas. The temperature ramp involves an initial time of 1 minute at 50°C, followed by a 10°C increase every minute until a final temperature of 300°C is reached, which is maintained for 5 minutes.

Gas chromatography-mass spectroscopy (GC-MS) analysis was conducted using an Agilent 8890 GC system, 5977 GC/MSD instruments, and a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ioniser at 70 eV.

Melting points were measured on a Buchi 510 apparatus.

Cyclopentyl methyl ether distillation was performed using BUCHI Glass Oven B-585 Kugelrohr.

Elemental analysis was performed with the UNICUBE Elementar instrument.

TEM analyses were performed on a Thermo Fisher TALOS F200X G2 operating at an accelerating voltage of 200 keV. For sample preparation, a small amount of material was dispersed in isopropanol in a centrifuge tube and mildly sonicated for ~15 min. A few drops of the resulting suspension were then drop-cast onto a copper TEM grid coated with a holey carbon film. After solvent evaporation, the grid was introduced into the microscope for characterization.

1H-NMR, 13C-NMR, and 19F-NMR analyses were obtained using a Bruker DRX-ADVANCE 400 MHz spectrometer, with $CDCl_3$ as the solvent and reference standard. All the NMR Spectra reported present around 95% purity.

Centrifugation was carried out using a Beckman Coulter Allegra 64 R centrifuge for the recovery of the catalyst.

The Agilent Technologies 4210 instrument was used to determine the amount of metal lost via microwave plasma atomic emission spectroscopy (MP-AES) analysis.

2. Experimental Procedures

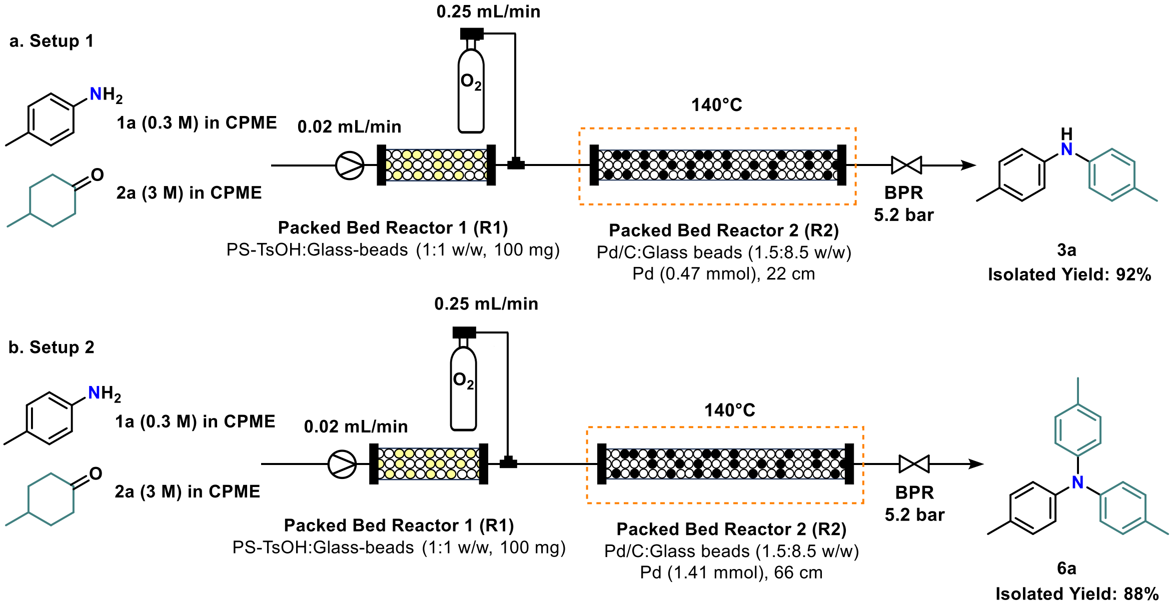
2.1. General procedure for the synthesis of triarylamines

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), **1** (0.5 mmol), and **2** (5 mmol, 10 equiv.) were consecutively added. The reaction was stirred for 16 hours at 140°C in an open vessel under reflux. Then, an O_2 balloon was connected to the apparatus, and the reaction was stirred for an additional 6 hours at 140°C. Pd/C was filtered from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent.

2.2. General procedure for the dehydrogenative aromatization of *N*-cyclohexyldiarylamines to triarylamines

In a 10 mL round-bottom flask (10 mL) equipped with a magnetic stirrer, *N*-cyclohexyldiarylamines (**5**) (0.5 mmol), Pd/C (10 mol%, 53 mg), TsOH (10 mol%, 8.6 mg), and CPME (1 M, 0.5 mL) were consecutively added. An O_2 balloon was connected to the apparatus, and the reaction was stirred for 6 hours at 140°C under reflux. Pd/C was filtered from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. (Figure 2.d)

2.3. General procedure for the synthesis under flow



Scheme S1. **a.** General setup for the synthesis of **3a** in a continuous flow apparatus (Setup 1). **b.** General setup for the synthesis of **6a** in a continuous flow apparatus (Setup 2).

Setup 1: The p-toluidine (**1a**) (5 mmol, 530 mg) and 4-methylcyclohexanone (**2a**) (50 mmol, 10 equiv., 6 mL) were dissolved in CPME (16.7 mL, 0.3 mol/L). The PS-TsOH (50 mg, 2.5 mmol/g) was mixed with 1 mm glass beads in a 1:1 ratio and packed into a 4.5 cm stainless steel reactor with an internal diameter of 2 mm (R1). The Pd/C 10 wt% (0.47 mmol of Pd) was mixed with 1 mm-diameter glass beads in a 1.5:8.5 ratio and packed into a 22 cm stainless steel reactor with an internal diameter of 4 mm (R2). The R1 is placed at room temperature. The R2 is placed at 140°C. Both reactors were placed in a laboratory-made continuous-flow system equipped with a T-junction to introduce gaseous O_2 (0.25 mL/min) upstream of R2, thereby establishing a slug-flow regime. The entire system was equipped with a 5.2 bar BPR. The solution of **1a** and **2a** in CPME was delivered to the system via an HPLC pump at an effective flow rate of 0.02 mL/min. After a residence time of 200 min, a complete conversion to **3a** was achieved. After distillation of CPME and recovery of the unreacted **2a** (82%), CPME (5 mL) was added, followed by an aqueous solution of HBF_4 (48 wt%, 1.5 equiv.). Precipitation was completed by adding cold heptane (5 mL), and the resulting solid was collected by filtration.

Subsequently, aqueous NaOH (3 M, 2 mL) and the recovered CPME (5 mL) were added. After centrifugation, the distillation of CPME afforded pure **3a** (Yield: 92%). The solvents CPME and heptane used in the procedure were recovered by distillation (95% and 92%, respectively) and reused.

Setup 2: The p-toluidine (**1a**) (5 mmol, 530 mg) and 4-methylcyclohexanone (**2a**) (50 mmol, 10 equiv., 6 mL) are dissolved in CPME (16.7 mL, 0.3 mol/L). The PS-TsOH (50 mg, 2.5 mmol/g) was mixed with 2 mm glass beads in a 1:1 ratio and packed into a 4.5 cm stainless steel reactor with an internal diameter of 2 mm (R1). The Pd/C 10 wt% (1.41 mmol of Pd) was mixed with 2 mm-diameter glass beads in a 1.5:8.5 ratio and packed into a 66 cm stainless steel reactor with an internal diameter of 4 mm (R2). The R1 is placed at room temperature. The R2 is placed at 140°C. Both reactors were placed in a laboratory-made continuous-flow system, equipped with a T-junction to introduce the gaseous O_2 (0.25 mL/min) upstream of R2, thereby establishing a slug-flow regime. The entire system was equipped with a 5.2 bar BPR. The solution of **1a** and **2a** in CPME is delivered to the system via an HPLC pump at an effective flow rate of 0.02 mL/min. After a residence time of 600 min, a complete conversion to **6a** was achieved. After distillation of CPME and recovery of the unreacted 2a (82%), CPME (5 mL) was added, followed by an aqueous solution of HBF_4 (48 wt%, 1.5 equiv.). Precipitation was completed by adding cold heptane (5 mL), and the resulting solid was collected by filtration.

Subsequently, aqueous NaOH (3 M, 2 mL) and the recovered CPME (5 mL) were added. After centrifugation, the distillation of CPME afforded pure 6a (Yield: 88%). The solvents

CPME and heptane used in the procedure were recovered by distillation (95% and 92%, respectively) and reused.

2.4. Catalyst recycle

After the reaction was complete, the Pd/C catalyst was filtered under vacuum, washed with CPME (10 mL), and dried for 3 hours at 130°C under vacuum. Then the reaction was repeated.

2.5. Leaching test

After the reaction was completed, the Pd/C was filtered under vacuum and washed with CPME. For the reactions performed under flow, this step is not required. The reaction mixture was dried under vacuum, then dissolved in 2 mL of aqua regia, and digested at room temperature for 2 h. The reaction mixture was transferred into a 10 mL graduated flask, and Milli-Q water was added to reach the final volume. The residual solids present were filtered off, and the MP-AES 4210 instrument analysed the sample.

2.6. Hot filtration test

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol% %; 53 mg), p-TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), **1a** (0.5 mmol), and **2a** (5 mmol, 10 equiv.) were consecutively added. The mixture was kept under reflux at 140 °C. After 45 minutes, the Pd/C was hot-filtered, and the mixture was stirred for an additional 15 hours. The conversion was evaluated by gas chromatographic analysis. Then, the reaction mixture was dried under a vacuum, dissolved in 2 mL of aqua regia, and digested at room temperature for 2 h. The reaction mixture was transferred into a 10 mL graduated flask, and Milli-Q water was added to reach the final volume. The residual solids present were filtered off, and the MP-AES 4210 instrument analysed the sample.

The same protocols were repeated after 16 h of reaction, performed under reflux in an open vessel. After Pd filtration, the reaction was stirred at 140°C for an additional 6 h under an O_2 balloon. Then the leaching was analysed.

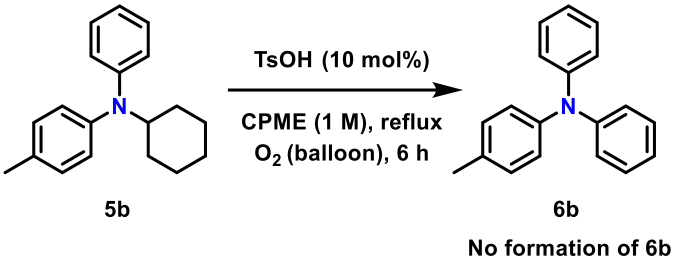
3. Results and Discussion

3.1. Optimization of the reaction conditions under batch

The heterogeneous catalyst Pd/Al_2O_3 was tested instead of Pd/C; however, it produced byproducts and degradation, making it almost impossible to determine the conversion to intermediates and byproducts. Additionally, various acids, including CF_3COOH, PivOH, and CF_3SO_3H, were tested, yielding similarly unsatisfactory results.

3.2. Optimization of the dehydrogenative aromatization of *N*-cyclohexyldiarylamines to triarylamines

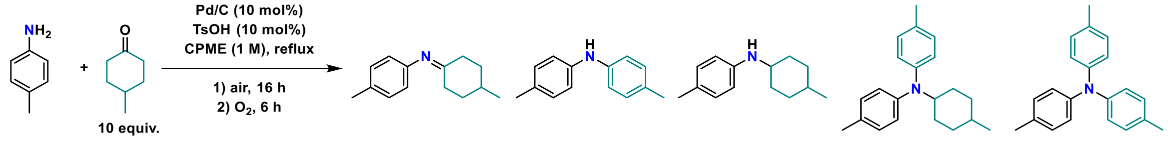
At this stage, we conducted control experiments on the aerobic dehydrogenative aromatization of *N*-cyclohexyldiarylamine (**5**). In a 10 mL round-bottom flask equipped with a magnetic stirrer, **5b** (0.5 mmol), TsOH (10 mol%, 8.6 mg), and CPME (1 M, 0.5 mL) were consecutively added. The reaction was carried out without Pd/C, and no **6b** was formed (**Scheme S2**).



Scheme S2. The dehydrogenative aromatization of **5b** to **6b** is performed without the use of Pd/C.

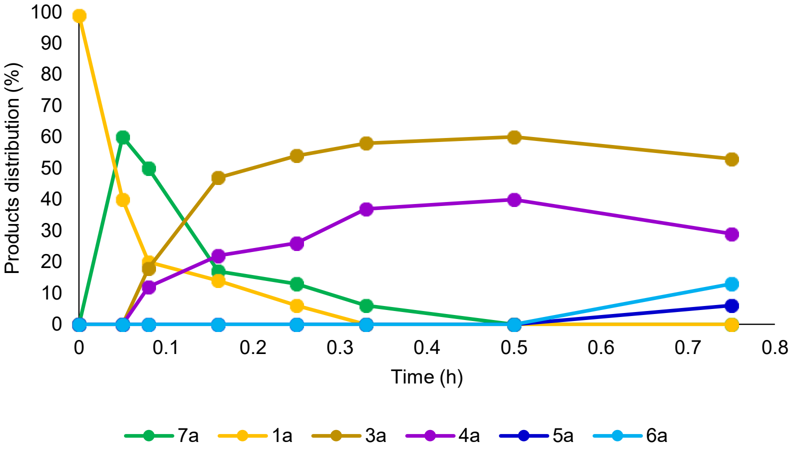
3.3. Time course of the reaction

The reaction profile was monitored over time to clarify the product distribution, analyzing both the initial minutes of the reaction and the entire reaction course (**Figure S1**). The product distribution was analyzed by gas chromatography analysis with pure products as standards and GC-MS.



1a 2a 7a 3a 4a 5a 6a

a. Time course for the first minutes of reaction



b. Time course for the reaction

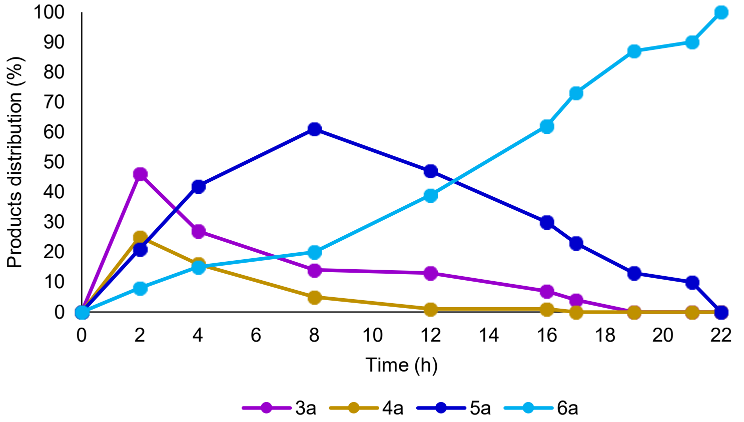
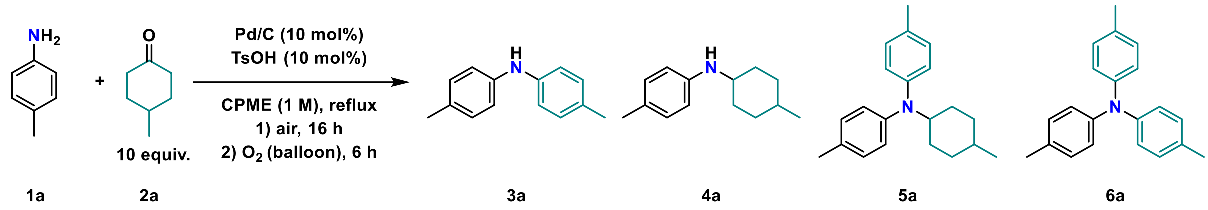


Figure S1. Time course for the reaction of **1a** and **2a**. Reaction condition: **1a** (0.5 mmol), **2a** (5 mmol, 10 equiv.), Pd/C (10 mol%), TsOH (10 mol%), CPME (1 M), reflux, 16 h under air, additional 6 h under balloon of O_2.

3.4. Catalyst recycle

The recyclability of Pd/C under optimized reaction conditions was tested. The second run of the process yielded only traces of the desired product **6a**, while the major product formed was **3a** (**Table S1**).

Table S1. Recycle of Pd/C[a]

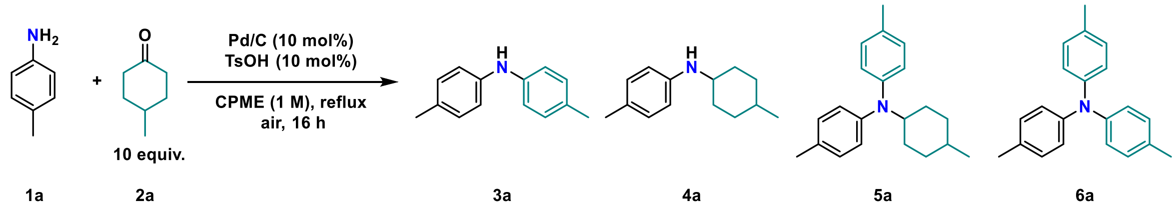


Entry	Run	C^b (%)			
		3a	4a	5a	6a
1	1°	0	0	0	99
2	2°	90	0	5	5

[a]Reaction condition: **1a** (0.5 mmol), **2a** (5 mmol, 10 equiv.), Pd/C (10 mol%), TsOH (10 mol%), CPME (1 M), reflux, 16 h under air, additional 6 h under a balloon of O_2. [b]Conversion determined by gas-liquid chromatographic analysis, the remaining material is unreacted **1a.**

To better understand the reason for the reduced conversion through product **6a**, the catalyst was tested before the addition of O_2, after 16 hours at 140°C under open vessel conditions with reflux. The recovered Pd/C showed the same conversion after the 2nd run. However, a decrease in conversion towards **6a** was observed in the 3rd run (**Table S2**).

Table S2. Recycle of Pd/C before the addition of the O_2 balloon[a]



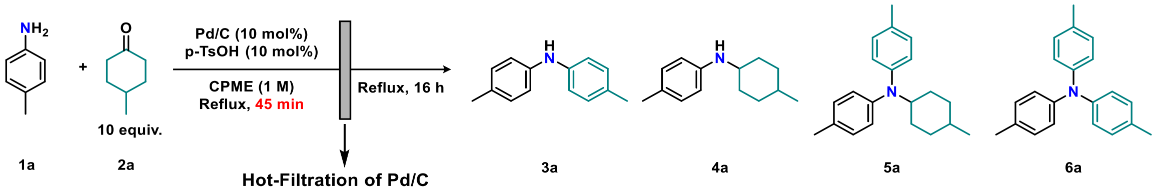
Entry	Run	C^b (%)			
		3a	4a	5a	6a
1	1°	0	0	40	60
2	2°	0	0	40	60
3	3°	27	27	37	16

[a]Reaction condition: **1a** (0.5 mmol), **2a** (5 mmol, 10 equiv.), Pd/C (10 mol%), TsOH (10 mol%), CPME (1 M), reflux, 16 h under air. [b]Conversion determined by gas-liquid chromatographic analysis, the remaining material is unreacted **1a**.

3.5. Hot filtration test

To evaluate the heterogeneous nature of the catalysis, a hot-filtration test was performed after 45 minutes of reaction. Compared to the control experiment, the hot-filtration test showed a shift in product distribution, with a notably higher conversion to **5a**. This effect is attributed to the role of TsOH in promoting the condensation reaction. MP-AES analysis of the hot-filtered reaction mixture indicated a negligible amount of Pd leaching into the solution, supporting a heterogeneous catalytic mechanism. No significant changes were observed in Pd leaching after hot filtration (**Table S3**).

Table S3. Hot-filtration test performed at 45 minutes of reaction.[a]

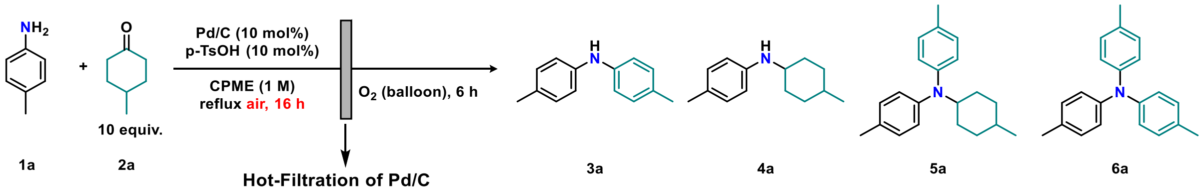


Entry	Set-up	Conversion[b] (%)				Pd loss %
		3a	4a	5a	6a	
2	Control Test (45 min.)	53	29	6	13	0.04 %
1	After Hot Filtration	35	14	34	17	0.06 %

[a] Reaction condition: **1a** (0.5 mmol), **2a** (5 mmol, 10 equiv.), Pd/C (10 mol%), TsOH (10 mol%), CPME (1 M), reflux, 16 h under air. [b] Conversion determined by gas-liquid chromatographic analysis, the remaining material is unreacted **1a**.

A hot-filtration test was conducted after 16 hours at 140°C in an open vessel under reflux, prior to the addition of O_2. This procedure revealed no significant change in the product distribution, thereby confirming the heterogeneous nature of the catalysis. Analysis indicated that less than 0.5% of Pd leached into the solution during the reaction. No significant variation was observed during the hot-filtration test (**Table S4**).

Table S4. Hot-filtration test performed after 16 h of reaction.[a]

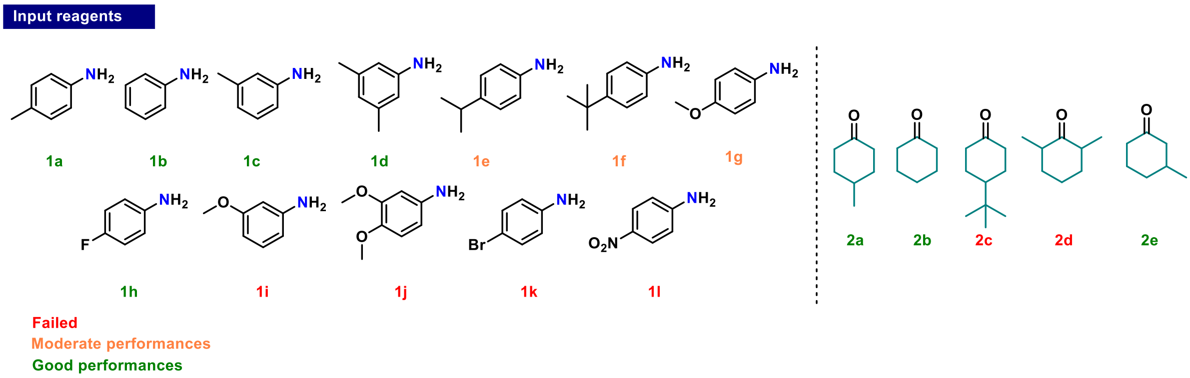


Entry	Set-up	C[b] (%)				Pd loss %
		3a	4a	5a	6a	
2	Control Test (16 h.)	0	0	29	71	0.1 %
1	After Hot Filtration	0	0	27	73	0.2 %

[a] Reaction condition: **1a** (0.5 mmol), **2a** (5 mmol, 10 equiv.), Pd/C (10 mol%), TsOH (10 mol%), CPME (1 M), reflux, 16 h under air. [b] Conversion determined by gas-liquid chromatographic analysis, the remaining material is unreacted **1a**.

3.6. Substrates scope

In this section, the starting materials applied in the synthesis of triarylamines are classified according to the reactivity observed in the process.



Scheme S3. Starting materials classified according to reactivity

3.7. Pd/C characterization

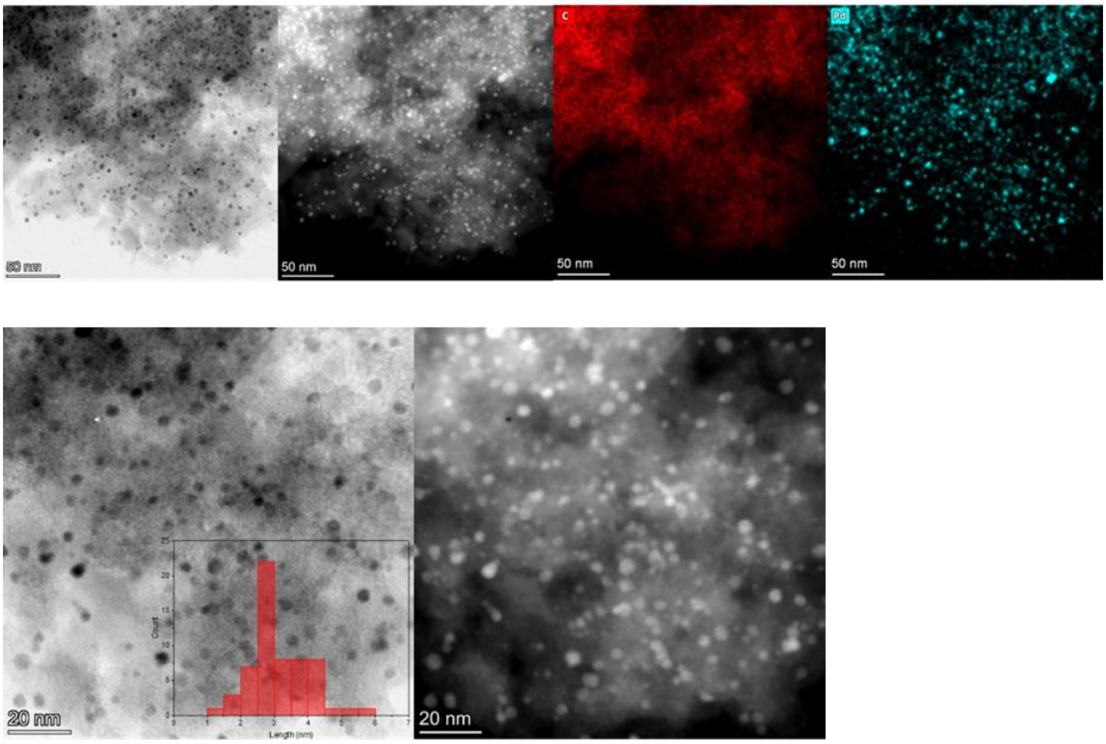


Figure S2. STEM analysis and EDS of fresh Pd/C

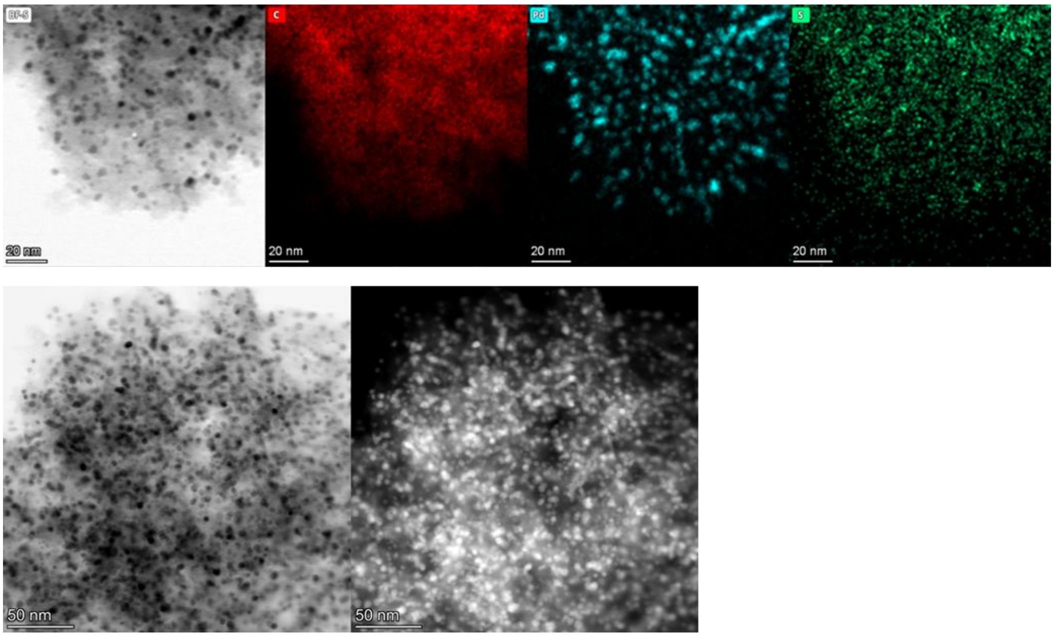


Figure S3. STEM analysis and EDS of Pd/C after 16 hours of reaction under air

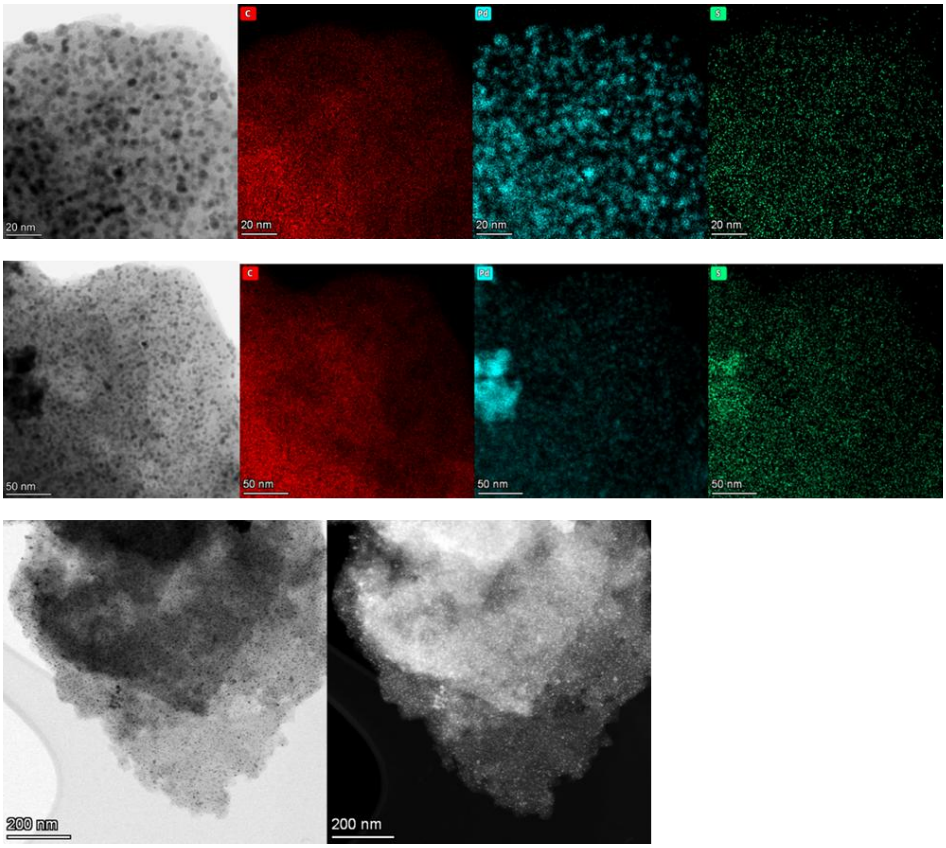


Figure S4. STEM analysis and EDS of Pd/C after optimized reaction conditions

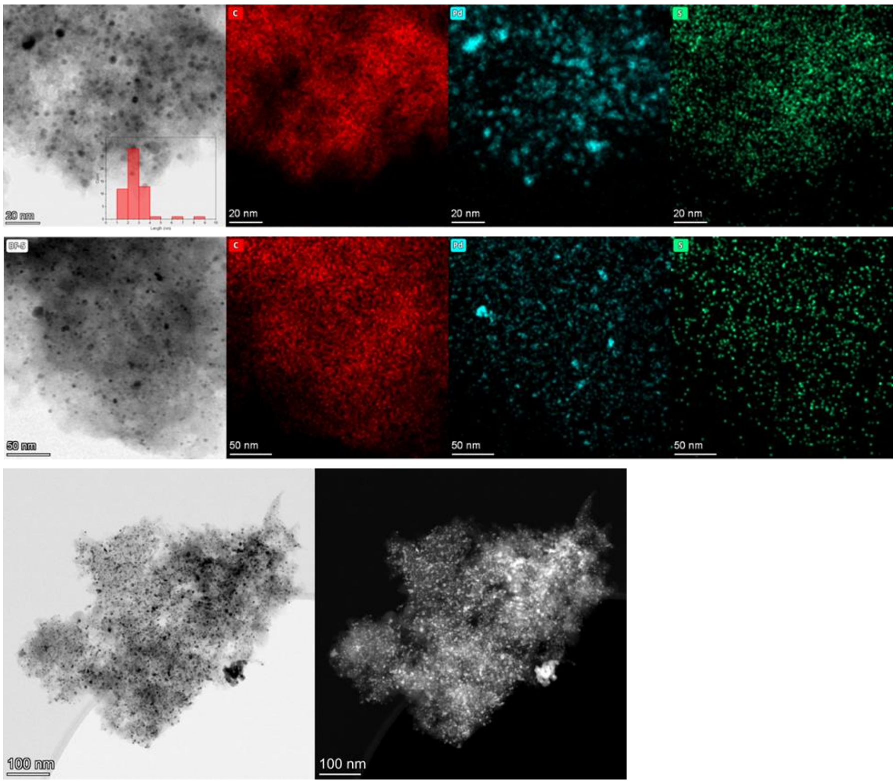
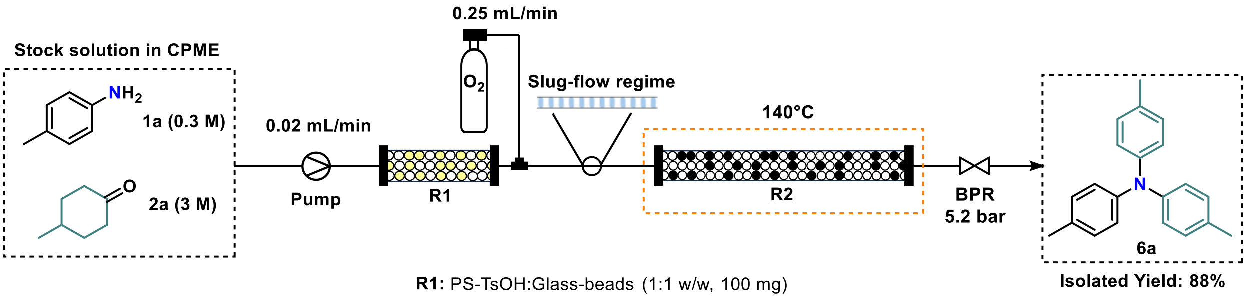


Figure S5. STEM analysis and EDS of Pd/C after 3 runs of reaction (**Table S2**)

3.8. Flow setup



R1: PS-TsOH:Glass-beads (1:1 w/w, 100 mg)
R2: Pd/C:Glass beads (1.5:8.5 w/w), Pd (1.41 mmol), 66 cm

Scheme S4. Flow setup to synthesize **6a**

Turnover number (TON) calculation:

$$TON = \frac{moles\ of\ product}{moles\ of\ Pd} = \frac{26.1\ mmol}{1.41\ mmol} = 18.5$$

Space-Time Yield calculation:

$$STY = \frac{mass\ of\ product}{reactor\ volume \cdot time}$$

$$STY = \frac{7.7\ g}{12\ mL\ \cdot 83\ h} = 0.18\ Kg\ L^{-1} day^{-1}$$

3.9. Green metrics evaluation

$$AE = \frac{MW_{reactant}}{MW_{product}} \qquad SF = \frac{Actual\ Mass\ of\ Reagent}{Stoichiometric\ Mass\ of\ Reagents}$$

$$MRP = \frac{RME \cdot SF}{AE\ \cdot\ Yield}$$

$$BI = 1 - EI = 1 - \frac{\sum_j f_j \Omega_j}{\sum_j \Omega_j} \qquad SHI = 1 - \ SHZI\ = 1 - \frac{\sum_j f_j \Omega_j}{\sum_j \Omega_j}$$

$$VMR = \frac{\sqrt{AE^2 + Yield^2 + \left(\frac{1}{SF}\right)^2 +\ MRP^2 + SHI^2 + BI^2}}{\sqrt{6}}$$

$$RME\ (\%) = 100\ \cdot \frac{Mass\ of\ product}{total\ input\ mass - mass\ of\ recovered\ material} = 100\ \cdot \frac{1}{(1\ + EFactor\ )}$$

Where f_i is the molar fraction

Abbreviations used in the table are reported herein:

- Atom economy (AE)
- Stoichiometric factor (SF)
- Material recovery parameter (MRP)
- Reaction mass efficiency (RME)
- Benign Index (BI)
- Safety hazard index (SHI)
- Vector magnitude ratio (VMR)

The safety/hazard analyses have been conducted in accordance with the methods, calculations and equations reported by J. Andraos in Org. Process Res. Dev. 17 (2013) 175−192.[1]

Abbreviations used in the table are reported herein:

- Molecular Weight (MW)
- Oxygen Balance (OB)
- Lethal Dose 50 (LD50)
- Lethal Concentration (LC 50)
- Flesh Point (FLP)
- Lower Explosive Limit (LEL)
- Occupational Exposure Limits (OEL)
- Corrosiveness potential as a gas (CGP)
- Corrosiveness potential as a liquid/solid (CLP)
- Flammability potential (FP)

- Oxygen consumption potential (OBP)
- Explosive vapour potential (gases) (XVP)
- Occupational exposure limit potential (OELP)
- Risk phrase potential (RPP)

The benign index analyses, definitions, and equations for the multicompartment method (MCM) have been used in accordance with the data and equations reported by J. Andraos in Org. Process Res. Dev. 16 (2012) 1482−1506.[2]

Abbreviations used in the tables are reported herein:

- Molecular Weight (MW)
- Smog Formation Potential (SFP)
- Global Warming Potential (GWP)
- Lethal Dose 50 (LD50)
- Lethal Concentration (LC 50)
- Z facto (Z)
- Inhalation Toxicity Potential (INHTP)
- Ingestion Toxicity Potential (INGTP)
- Biocentration Potential (BCP)
- Bioaccumulation Potential (BAP)
- Abiotic Resource Depletion Potential (ARDP)

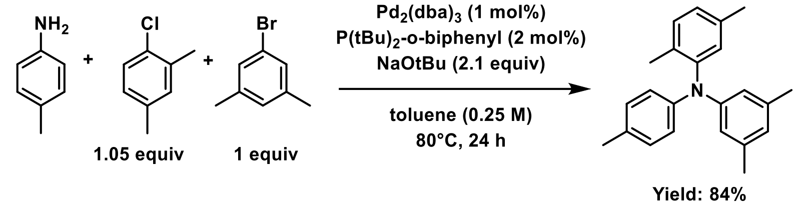
Log Kow data are reported by J. Andraos in *ACS Sustainable Chem. Eng*. 2018, **6**, 3206–3214 and by J. Andraos and L. Vaccaro in *Green Chem*., 2015, **17**, 913-925.[3-4] LD50, LC50, OEL, FLP and risk phrases references and sources: MSDS files for each compound, Registry of Toxic Effects of Chemical Substances (RTECS) and NIOSH POCKET GUIDE TO CHEMICAL HAZARDS, National Institute for Occupational Safety and Health, September 2007, Publication No. 2005-149 (http://www.cdc.gov/niosh). ODP, moles of H_2, LBT, HGP, XP, ISP, Hacid, and ARDP were not assessed in this analysis. In addition, the metal catalyst and ligand were omitted from the calculation.

Workup and purification steps were explicitly included in the evaluation performed in a like-for-like manner. Heterogeneous catalytic systems were assumed to be fully recovered from the reaction mixture. For the chromatographic column, we used 25 g of Silica and 250 mL of eluent, recovering 247.5 mL by distillation. Additionally, solvents used in volumes greater than 10 mL were considered recoverable by distillation.

a) J. Org. Chem. 2000, 65, 5327-5333

General procedure: A Schlenk tube was charged with $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 1 mol % Pd), P(*t*-Bu)$_2$-*o*-biphenyl (6.0 mg, 0.02 mmol, 2 mol %), and sodium *tert*-butoxide (202 mg, 2.1 mmol). The flask was evacuated, backfilled with argon, and fitted with a rubber septum. Amine (1.0 mmol), aryl bromide (1.0 mmol), aryl chloride (1.05 mmol), and toluene (4 mL) were each added via syringe (amines or aryl halides which were solids at room temperature were added prior to the evacuation/backfill cycle). The flask was sealed with a Teflon screwcap, and the reaction mixture was heated to 80 °C with stirring until the intermediate diarylamine had been consumed, as judged by GC analysis. The reaction mixture was then cooled to room temperature, taken up in diethyl ether, washed with brine, dried with $MgSO_4$, and concentrated in vacuo. The product was purified by flash chromatography on silica gel using a mixture of hexanes and ethyl acetate and/or toluene as the eluent.[5]

The calculation of the green metrics was performed following the procedure reported by the authors for the synthesis of *N*-(3,5-dimethylphenyl)-2,5-dimethyl-*N*-(p-tolyl)aniline.



Scheme S5. Synthesis of *N*-(3,5-dimethylphenyl)-2,5-dimethyl-*N*-(p-tolyl)aniline.[5]

Table S5. ES and BI calculations for the synthesis of *N*-(3,5-dimethylphenyl)-2,5-dimethyl-*N*-(p-tolyl)aniline

Substance	MW	Mass (g)	Molar fraction	Carbon atoms	SFP	GWP	LD50 oral (mg/kg)	LC50 (g/m3 4 h)	H (atm m3/mol)	log Kow
4-metilaniline	107.15	0.107	0.02594	7		2.8745	620	0.64	0.0000019	0.91
2,5 dimethyl chlorbenzene	154.64	0.1546	0.02725	8	0.07	2.2763	500		1E-100	3.7
3,5 dimethyl bromobenzene	185.06	0.194	0.03991	8		1.9021			1E-100	-1E+100
toluene	92.4	3.468	0.83956	7	0.87	3.3333	636	25.87	0.00663	2.73
NaotBu	96.11	0.202	0.04890	4		1.8313	0.0035		1E-100	-1E+100

Substance	Koc	Z(air)	Z(water)	Z(soil)	Z(sediment)	fugacity (atm)	C(water) mol/m3	C(air) mol/m3	INHTP	INGTP	BCP	Ω	EI contribution
4-metilaniline	3	40.6009	526315.7895	84192.13	168384.3	8.47675E-14	4.46E-08	3.44E-12	2.4489	112.4467	0.041381	117.811	3.05602483
2,5 dimethyl chlorbenzene	2055	40.6009	1E+100	9.9E+101	2E+102	7.1338E-109	7.13E-09	2.9E-107	0	22.29521	5.460093	30.1016	0.82025784
3,5 dimethyl bromobenzene	0	40.6009	1E+100	1.97E+98	3.94E+98	2.9206E-108	2.92E-08	1.2E-106	0	0	0	1.90209	0.07591439
toluene	220	40.6009	150.8295626	1594.085	3188.171	2.63647E-12	3.98E-10	1.07E-10	1.8843	0.977047	1	8.06466	6.77084277
NaotBu	0	40.6009	1E+100	0	0	5.2026E-108	5.2E-08	2.1E-106	0	23228367	0	2322837	1135919.31

SUBTOTALS	23228582	1135930.098	**ES**
		0.048902257	**EI**
		0.951097743	**BI**

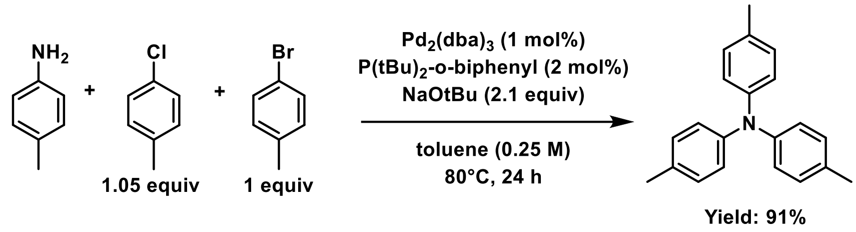
Table S6. SHI calculations for the synthesis of *N*-(3,5-dimethylphenyl)-2,5-dimethyl-*N*-(p-tolyl)aniline

Substance	MW	mass (g)	Molar fraction	OB	LD50 dermal (mg/kg)	LC50 (g/m3 4 h)	FLP(deg C)	LEL	IS (N m)	OEL (mmol/m^3)	Q (R-phrases)
4-methylaniline	107.15	0.052	0.012773	-2.7624825	890	0.64	87	0	1.3	0.084	56250000
2,5 dimethyl chlorbenzene	154.64	0.15464	0.037986	-2.27625453			67	0			3375
3,5 dimethyl bromobenzene	185.06	0.1943	0.047729	-1.90208581			87	0			3375
toluene	92.4	3.468	0.851892	-3.11688312	5000	25.7	4.4	0	1.2	2.08	937500
NaotBu	96.105	0.202	0.04962	-1.9145726			14	0	2.3		20

Substance	CGP	CLP	FP	OBP	XVP	OELP	RPP	Ω	SHZI contribution
4-methylaniline	0.8125	2.528089888	0.633333333	0.690620625	1.307692308	48.52380952	3.12868113	57.62472681	0.736067295
2,5 dimethyl chlorbenzene	0	0	0.670588235	0.569063632	0	0	1.424344396	2.663996263	0.101195395
3,5 dimethyl bromobenzene	0	0	0.633333333	0.475521453	0	0	1.424344396	2.533199182	0.120905884
toluene	0.020233463	0.45	0.821917808	0.779220779	1.416666667	1.959615385	2.410851413	7.858505514	6.694595628
NaotBu	0	0	0.794425087	0.478643151	0.739130435	0	0.525218535	2.537417207	0.125906615

SUBTOTALS	73.21784497	7.778670817	**SHZS**
		0.106240095	**SHZI**
		0.893759905	**SHI**

The green metrics were calculated using the authors' procedure for the synthesis of the selected product **6a**.



Scheme S6. Synthesis of **6a**

Table S7. E-Factor calculation

Reactant	
4-methylaniline	0.10716
4Mechlorobenzene	0.18506
4MeBromobenzene	0.14764
NaOtBu	0.202
Solvent	
toluene	3.48
Catalyst	
$Pd_2(dba)_3$	0.0046
$P(t\text{-}Bu)_2$-o-biphenyl	0.00600
Workup	
water	10
Et_2O	11
Purification	
Silica	25
eluent	250
Recovery of Materials	
eluent and Et_2O	258
Product	
p-toluiditriphenylammine	0.26
E-Factor	**>100**

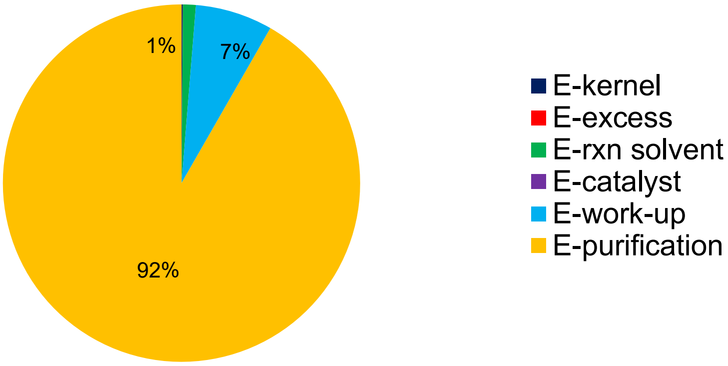


Figure S6. E-Factor distribution

Table S8. ES and BI calculations for the synthesis of **6a**

Substance	MW	Mass (g)	Molar fraction	Carbon atoms	SFP	GWP	LD50 oral (mg/kg)	LC50 (g/m3 4 h)	H (atm m3/mol)	log Kow
4-methylaniline	107.15	0.0931	0.023015	7		2.874475	620	0.64	0.0000019	0.91
4-methylchlorobenzene	126.58	0.11256	0.027826	7	0.07	2.433244	2273	21.5	0.00358	2.84
4methylbromobenzene	171.04	0.164861	0.040755	7		1.800748	1540	6.8	0.00233	3.4
toluene	92.4	3.468	0.857329	7	0.87	3.333333	636	25.87	0.00663	2.73
NaotBu	96.105	0.202	0.049937	4		1.83133	0.0035		1E-100	-1E+100

Substance	Koc	Z(air)	Z(water)	Z(soil)	Z(sediment)	fugacity (atm)	C(water) mol/m3	C(air) mol/m3	INHTP	INGTP	BCP	Ω	EI contribution
4-methylaniline	3	40.601	526315.790	84192.13	168384.3	8.47675E-14	4.46E-08	3.44E-12	2.448886	112.4466551	0.041380906	117.8114	2.711474493
4-methylchlorobenzene	284	40.601	279.330	3803.138	7606.28	1.903E-12	5.32E-10	7.73E-11	1.6367	0.3654839	1.21227	5.717699	0.1591014
4methylbromobenzene	1030	40.601	429.185	21216.28	42432.6	1.347E-12	5.78E-10	5.47E-11	3.661942	0.5865256	3.22998	9.2791968	0.3781774
toluene	220	40.601	150.830	1594.085	3188.17	2.636E-12	3.98E-10	1.07E-10	1.884283	0.9770468	1	8.0646634	6.9140716
NaotBu	0	40.601	0	0	0	2.563E-12	0	1.04E-10	0	0	0	1.8313303	0.0914506

SUBTOTALS	198.02109	10.31718013	**ES**
		0.052101419	**EI**
		0.947898581	**BI**

Table S9. SHI calculations for the synthesis of **6a**

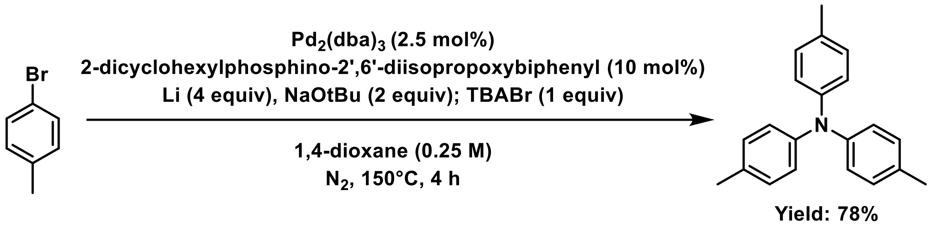
Substance	MW	mass (g)	Molar fraction	OB	LD50 dermal (mg/kg)	LC50 (g/m3 4 h)	FLP(deg C)				LEL	IS (N m)	OEL (mmol/m^3)	Q (R-phrases)
4-methylaniline	107.15	0.04655	0.023042	-2.31451237	890	0.64	87	0	1.3	1E+100	890	0.64	0.084	56250000
4-chlorotoluene	126.58	0.05628	0.027858	-1.83283299	5000	5.92	49	0		1E+100	5000	5.92		50625
4-bromobtoluene	171.04	0.0824305	0.040802	-1.35640786	2000	6.8		0		1E+100	2000	6.8		3375
toluene	92.4	1.734	0.858305	-3.11688312	5000	25.7	4.4	0	1.2	1E+100	5000	25.7	2.08	937500
NaotBu	96.105	0.101	0.049994	-1.9145726			14	0	2.3	1E+100				20

Substance	CGP	CLP	FP	OBP	XVP	OELP	RPP	Ω	SHZI contribution
4-methylaniline	0.8125	2.528089888	0.633333333	0.690620625	1.307692308	48.52380952	3.12868113	57.62472681	1.327764926
4-chlorotoluene	0.087837838	0.45	0.708074534	0.553009954	0	0	1.899125861	3.698048187	0.103019463
4-bromobtoluene	0.076470588	1.125	0	0.409260992	0	0	1.424344396	3.035075976	0.123836916
toluene	0.020233463	0.45	0.821917808	0.779220779	1.416666667	1.959615385	2.410851413	7.858505514	6.744995787
NaotBu	0	0	0.794425087	0.478643151	0.739130435	0	0.525218535	2.537417207	0.126854501

SUBTOTALS	74.75377369	8.426471594	**SHZS**
		0.112723026	**SHZI**
		0.887276974	**SHI**

b) Nat. Commun. 2021, 12, 248

General procedure: In an argon-filled glove-box, a 25 mL oven-dried seal-tube equipped with a magnetic stir bar was charged with lithium powder (6.0 equiv., 3.0 mmol, 0.0210 g). The tube was removed from the glovebox, degassed and refilled with N2. The tube was stirred under nitrogen atmosphere at 150 °C for 4 h. Then aryl bromide (1.0 equiv., 0.50 mmol), tris(dibenzylideneacetone)dipalladium (0.025 equiv., 0.0125 mmol, 0.0114 g), 2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl (0.10 equiv., 0.05 mmol, 0.0233 g), sodium tert-butoxide (2.0 equiv., 1.0 mmol, 0.0961 g), tetrabutylammonium bromide (1.0 equiv., 0.50 mmol, 0.1610 g) and dioxane (2.0 mL) were added into the above tube, and the reaction mixture was stirred under nitrogen atmosphere at 150 °C for 24 h. The reaction mixture was allowed to cool to room temperature and quenched by water. A saturated solution of brine and ethyl acetate were added. The aqueous phase was extracted three times with ethyl acetate. The combined organic layer was washed with brine and filtered. The solvent was removed under reduced pressure. Finally, the residue was purified by flash chromatography on silica gel.[6]



Scheme S7. Synthesis of **6a.** [6]

Table S10. E-Factor calculation

Reactant	
4-Methylbromobenzene	0.07850186
N_2	0.00457
Li	0.021
tetrabutylammonium bromide	0.161
NaOtBu	0.0961
Solvent	
1,4-dioxane	2.06
Catalyst	
tris(dibenzylideneacetone)dipalladium	0.0114
2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl	0.0233
Workup	
water	10
eluent and Et_2O	11
Purification	
Silica	25
eluent	250
Recovery of Materials	
eluent	258
Product	
p-toluiditriphenylammine	0.0342
E-Factor	**>100**

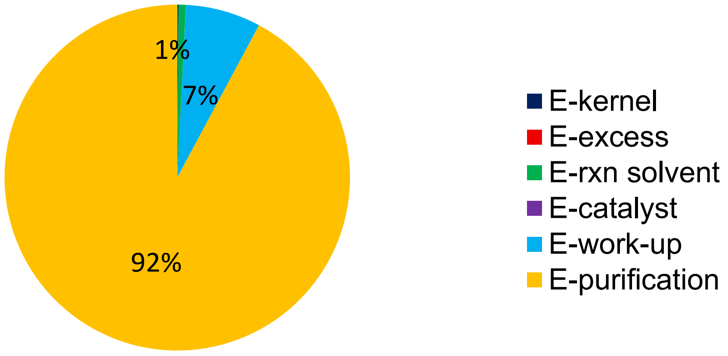


Figure S7. E-Factor distribution

Table S11. ES and BI calculations for **6a**

Substance	MW	Mass (g)	Molar fraction	Carbon atoms	SFP	GWP	LD50 oral (mg/kg)	LC50 (g/m3 4 h)	H (atm m3/mol)	log Kow
4methylbromobenzene	171.04	0.164861	0.040755	7		1.800748	1540	6.8	0.00233	3.4
Li	6.941	0.021	0.00839	0		0			1E-100	-1E+100
1,4-diossano	88.11	2.06	0.823025	4	0.87	1.997503	4200	23	0.0000048	-1E+100
NaotBu	96.105	0.161	0.064324	4		1.83133	0.0035		1E-100	-1E+100
tetrabutilammoniobromuro	322.37	0.0961	0.038395	16		2.183826	300		1E-100	0.84

Substance	Koc	Z(air)	Z(water)	Z(soil)	Z(sediment)	fugacity (atm)	C(water) mol/m3	C(air) mol/m3	INHTP	INGTP	BCP	Ω	EI contribution
4methylbromobenzene	1030	40.60089	429.1845494	21216.28	42432.55	1.34679E-12	5.78E-10	5.47E-11	3.661942	0.586525621	3.229981241	9.2791968	0.378177367
Li	0	40.60089	0	0	0	3.54848E-11	0	1.44E-09	0	0	0	0	0
1,4-diossano	0	40.60089	208333.3333	0	0	2.48202E-13	5.17E-08	1.01E-11	0.199524	19.23873822	0	22.305766	18.35821116
NaotBu	0	40.60089	0	0	0	2.56282E-12	0	1.04E-10	0	0	0	1.8313303	0.117798176
tetrabutilammoniobromuro	3	40.60089	0	0	0	7.64029E-13	0	3.1E-11	0	0	0.036610023	2.2204361	0.085252606

SUBTOTALS	35.636729	18.93943931	**ES**
		0.531458411	**EI**
		0.468541589	**BI**

Table S12. SHI calculations for **6a**

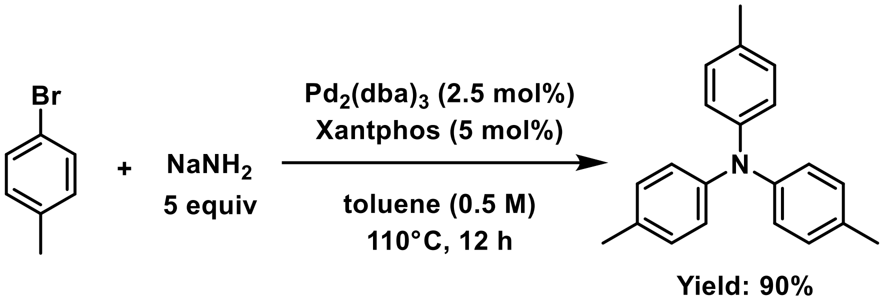
Substance	MW	mass (g)	Molar fraction	OB	LD50 dermal (mg/kg)	LC50 (g/m3 4 h)	FLP(deg C)	LEL	IS (N m)	OEL (mmol/m^3)	Q (R-phrases)
4-bromobtoluene	171.04	0.0785	0.032484	-1.35640786	2000	6.8			1E+100		3375
Li	6.941	0.021	0.00869	0					1E+100		20
1,4-diossano	88.11	2.06	0.852437	-1.81591193	7378	23	11	2	1E+100	0.415	112500
tetrabutilammonio	322.37	0.0961	0.039767	-0.62040512			113	0	1E+100		20
NaotBu	96.105	0.161	0.066623	-1.9145726			14	2.3	1E+100		20

Substance	CGP	CLP	FP	OBP	XVP	OELP	RPP	Ω	SHZI contribution
4-bromobtoluene	0.076470588	1.125	0	0.409260992	0	0	1.424344396	3.035075976	0.09859036
Li	0	0	0	0	0	0	0.525218535	0.525218535	0.004564094
1,4-diossano	0.022608696	0.304960694	0.802816901	0.453977982	0.85	9.82168675	2.03912203	14.29517305	12.18573884
tetrabutilammonio	0	0	0.590673575	0.155101281	0	0	0.525218535	1.270993391	0.050543104
NaotBu	0	0	0.794425087	0.478643151	0.739130435	0	0.525218535	2.537417207	0.169049148

SUBTOTALS	21.66387816	12.50848555	**SHZS**
		0.577389028	**SHZI**
		0.422610972	**SHI**

c) J. Org. Chem. 2024, 89, 17021-17030

General procedure: A 25 mL Schlenk tube with a PTFE-coated magnetic stir bar was connected to a high vacuum (50 × 10^{-3} mbar) through a double-manifold Schlenk line and dried by using a hot air gun. After cooling down, it was backfilled with argon (3 cycles). Under positive pressure of argon, Pd_2dba_3 (11.4 mg, 0.0125 mmol, 2.5 mol %) and Xantphos (14.5 mg, 0.025 mmol, 5 mol %) or XPhos (11.9 mg, 0.025 mmol 5 mol %) were added, followed by dry toluene (1 mL, 0.5 M). This was gently stirred for 10 min until the deep wine-red color completely changed to dark brown. After that, aryl halide (0.5 mmol, 1 equiv) was added, followed by a quick addition of solid $NaNH_2$ (104 mg, 2.5 mmol, 5 equiv). The Schlenk tube was closed with a glass stopper and placed in the preheated metal block at 110 °C with constant stirring (1000 rpm) for 12–24 h. The reaction progress was monitored using TLC with aliquots under positive argon pressure. After completion of the reaction, it was exposed to air and diluted with 2 mL of ethyl acetate. The reaction mixture was dry-loaded using silica (100–200 or 200–400 mesh) and purified using silica gel column chromatography.[7]



Scheme S8. Synthesis of **6a.** [7]

Table S13. E-Factor calculation

Reactant	
4-Methylbromobenzene	0.08552
NaNH$_2$	0.0975
Solvent	
toluene	0.867
Catalyst	
Pd$_2$dba$_3$	0.0110
Xantphos	0.014
Workup	
EtOAc	0.9
Purification	
Silica	25
eluent	250
Recovery of Materials	
eluent	247.5
Product	
p-toluiditriphenylammine	0.0548
E-Factor	**>100**

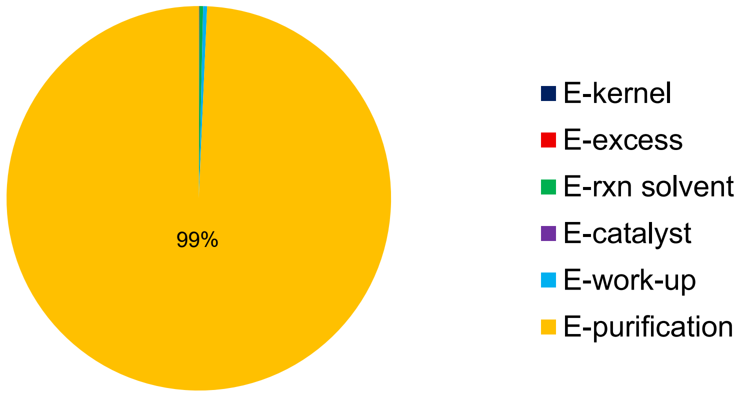


Figure S8. E-Factor distribution

Table S14. EI and BI calculation for the synthesis of **6a**

Substance	MW	Mass (g)	Molar fraction	Carbon atoms	SFP	GWP	LD50 oral (mg/kg)	LC50 (g/m3 4 h)	H (atm m3/mol)	log Kow
4methylbromobenzene	171.04	0.0785	0.008849	7		1.800748	1540	6.8	0.00233	3.4
toluene	92.4	8.67	0.977342	7	0.87	3.333333	636	25.87	0.00663	2.73
NaNH2	96.105	0.0975	0.010991	0		0	2200	42	1.00E-100	-1E+100

Substance	Koc	Z(air)	Z(water)	Z(soil)	Z(sediment)	fugacity (atm)	C(water) mol/m3	C(air) mol/m3	INHTP	INGTP	BCP	ARDP	Ω	EI contribution
4methylbromobenzene	1030	40.60089	429.1845494	21216.28	42432.55	1.34679E-12	5.78E-10	5.47E-11	3.661942	0.586525621	3.229981241	0	9.2791968	0.082112157
toluene	220	40.60089	150.8295626	1594.085	3188.171	2.63647E-12	3.98E-10	1.07E-10	1.884283	0.977046665	1	0	8.0646634	7.881933413
NaNH2	0	40.60089	1E+100	0	0	5.2026E-108	5.2E-08	2.1E-106	2.29E-96	36.95422059	0	0	36.954221	0.406159002

SUBTOTALS	66.465928	8.388578856	**ES**
		0.126208707	**EI**
		0.873791293	**BI**

Table S15. SHI calculations for the synthesis of **6a**

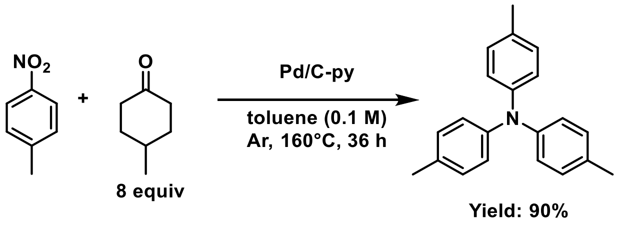
Substance	MW	mass (g)	Molar fraction	OB	LD50 dermal (mg/kg)	LC50 (g/m3 4 h)	FLP(deg C)	LEL	IS (N m)	OEL (mmol/m^3)	Q (R-phrases)
4-bromobtoluene	171.04	0.0785	0.00886	-1.35640786	2000	6.8			1E+100		3375
toluene	92.4	8.67	0.978555	-3.11688312	5000	25.7	4.4	1.2	1E+100	2.08	937500
NaNH2	96.105	0.0975	0.011005	-0.99890744					1E+100		30
XantPhos	578.62	0.014	0.00158	-2.70989596					1E+100		3375

Substance	CGP	CLP	FP	OBP	XVP	OELP	RPP	Ω	SHZI contribution
4-bromobtoluene	0.076470588	1.125	0	0.339101964	0	0	0	1.424344396	2.964916949
toluene	0.020233463	0.45	0.821917808	0.779220779	1.41666667	0.04076	1.959615385	2.410851413	7.858505514
NaNH2	0	0	0	0.249726861	0	0	0	0.596305591	0.846032453
XantPhos	0	0	0	0.67747399	0	0	0	1.424344396	2.101818386

SUBTOTALS	13.7712733	7.728882891	**SHZS**
		0.561232264	**SHZI**
		0.438767736	**SHI**

d) Catal. Sci. Technol. 2017, 17, 2170-2182

General procedure: 5 mmol of nitrobenzene, 6 mmol of cyclohexanone, 100 mg of the catalyst and 2 mL of toluene were added to a 15 mL pressure tube equipped with a magnetic stirrer and reacted at 80 °C for 36 h under Ar. Then the reaction mixture was cooled to room temperature. The crude reaction mixture was concentrated in vacuo and purified by column chromatography to give biphenylamine in 82% isolated yield.[8]



Scheme S9. Synthesis of **6a.** [8]

Table S16. E-Factor calculation

Reactant	
4-methylanitrobenzene	0.0615555
4-methylcyclohexanone	0.39
Solvent	
toluene	4.3
Catalyst	
Pd/C-py	0.03
Workup	
Purification	
Silica	25
eluent	250
Recovery of Materials	
Pd/C-py	0.03
eluent	247.5
Product	
p-toluiditriphenylammine	0.116
E-Factor	**>100**

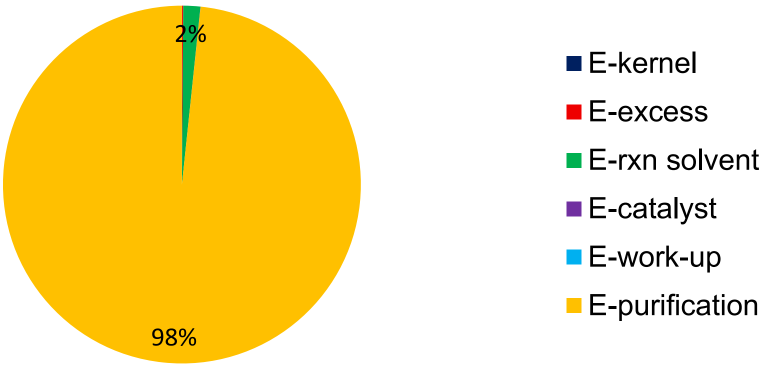


Figure S9. E-Factor distribution

Table S17. EI and BI calculation for the synthesis of **6a**

Substance	MW	Mass (g)	Molar fraction	Carbon atoms		ODP	SFP	GWP	LD50 oral (mg/kg)	LC50 (g/m3 4 h)	H (atm m3/mol)	log Kow
4-methylnitrobenzene	137.14	0.061555	0.012873	7			0.02	2.24588			1E-100	-1E+100
4-methylcyclohexanone	112.17	0.39	0.081563	7				2.745832	1800		1E-100	1.38
Pd/C		0.03	0.006274	0				0			1.00E-100	-1E+100
Toluene	92.14	4.3	0.899289	7				3.342739	636	25.87	0.00663	2.73

Substance	Koc	Z(air)	Z(water)	Z(soil)	Z(sediment)	fugacity (atm)	C(water) mol/m3	C(air) mol/m3	INHTP	INGTP	BCP	Ω	EI contribution
4-methylnitrobenzene	0	40.60089	1E+100	0	0	3.6459E-108	3.646E-08	1.5E-106	0	0	0	2.2658801	0.029169643
4-methylcyclohexanone	0	40.60089	1E+100	8.2E+96	1.64E+97	4.4574E-108	4.46E-08	1.8E-106	0	38.69609107	0.09418896	41.536112	3.387827554
Pd/C	0	40.60089	1.00E+100	0	0				0	0	0	0	0
toluene	215	40.60089	150.8295626	1555.205	3110.41	2.64414E-12	3.99E-10	1.07E-10	1.889765	0.979889075	1	7.2123935	6.486026393

SUBTOTALS	51.014386	9.90302359	**ES**
		0.194122176	**EI**
		0.80588	**BI**

Table S18. SHI calculation for the synthesis of **6a**

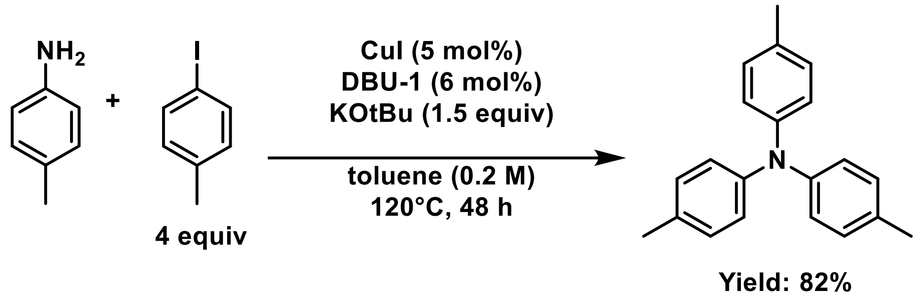
Substance	MW	mass (g)	Molar fraction	OB	LD50 dermal (mg/kg)	LC50 (g/m3 4 h)	FLP(deg C)	LEL	IS (N m)	LBT (cm^3/10 g)	OEL (mmol/m^3)	Q (R-phrases)
4-nitrotoluene	137.14	0.061555	0.01268768	-2.0417092	_	_	_	_	1E+100	0	_	78125
4-methylcyclohexanone	112.17	0.49	0.10099855	-2.42489079			48		1E+100	0		750
Toluene	92.4	4.3	0.88631377	-3.11688312	5000	25.7	4.4	1.2	1E+100	0	2.08	937500

Substance	CGP	CLP	FP	OBP	XVP	OELP	RPP	Ω	SHZI contribution
4nitrotoluene	0	0	0	0.24792183	0	0	1.97519198	2.22311381	0.028206167
4-methylcyclohexanone	0	0	0.71028037	0.6062227	0	0	1.16064616	2.47714923	0.25018847
Toluene	0.02023346	0.45	0.82191781	0.77922078	1.41666667	1.959615385	2.410851413	7.858505514	6.965101645

SUBTOTALS	13.7712733	7.728882891	**SHZS**
		0.561232264	**SHZI**
		0.438767736	**SHI**

e) Tetrahedron Letters, 2006, 47, 9275

General Procedure: In a 50-Ml three-necked flask, equipped with a stirrer, was charged with t-BuOK (1.5 mmol), DAB 1 (6 mol% with respect to the amine), CuI (5 mol% with respect to the amine) under nitrogen at room temperature. The aniline (1 mmol) and aryl iodide (4.0 mmol) were added. The dried toluene (5 Ml) was added via syringe. Care was taken to make sure the contents stirred well. The reaction mixture was then heated in an oil bath of 120 0C for 48 hours. The reaction mixture was then cooled, mixed with 15 Ml of diethyl ether, and filtered through a pad of silica to remove any insoluble residues. The solvent was removed under reduced pressure and the residue was then purified by column chromatography on silica gel (eluent: 60–900C petroleum) to obtain the analytically pure product.[9]



Scheme S10. Synthesis of **6a**. [9]

Table S19. E-Factor calculation

Reactant	
4-methylaniline	0.11
4-methyliodobenzene	0.87
tBuOK	0.168
Solvent	
toluene	4.335
Catalyst	
CuI	0.0095
Workup	
Et_2O	13

Silica	5
Purification	
Silica	25
eluent	250
Recovery of Materials	
eluent	247.5
Product	
p-toluiditriphenylammine	0.24
E-Factor	**>100**

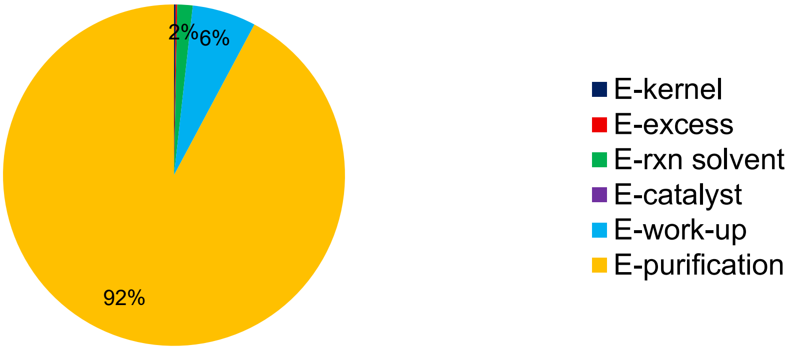


Figure S10. E-Factor distribution

Table S20. EI and BI calculations for the synthesis of **6a**

Substance	MW	Mass (g)	Molar fraction	Carbon atoms	SFP	GWP	LD50 oral (mg/kg)	LC50 (g/m3 4 h)	H (atm m3/mol)	log Kow
4-methylaniline	107.15	0.19	0.034154	7		2.874475	620	0.64	0.0000019	0.91
4-methyliodobenzene	218.04	0.87	0.15639	7		1.412585			1E-100	3.71
KOtBu	112.21	0.168	0.0302	4		1.568488	690		1E-100	-1E+100
toluene	92.4	4.335	0.779256	7	0.87	3.333333	636	25.87	0.00663	2.73

Substance	Koc	Z(air)	Z(water)	Z(soil)	Z(sediment)	fugacity (atm)	C(water) mol/m3	C(air) mol/m3	INHTP	INGTP	BCP	Ω	EI contribution
4-methylaniline	3	40.60089	526315.7895	84192.13	168384.3	8.47675E-14	4.461E-08	3.44E-12	2.448886	112.4466551	0.041380906	117.8114	4.02375794
4-methyliodobenzene	0	40.60089	1E+100	8.2E+96	1.64E+97	2.2931E-108	2.293E-08	9.3E-107	0	0	5.556483128	6.969068	1.089895585
KOtBu	0	40.60089	0	0	0	2.19499E-12	0	8.91E-11	0	0	0	1.5684877	0.047367594
toluene	220	40.60089	150.8295626	1594.085	3188.171	2.63647E-12	3.98E-10	1.07E-10	1.884283	0.977046665	1	8.0646634	6.284435674

SUBTOTALS	134.41362	11.44545679	**ES**
		0.085151022	**EI**
		0.91485	**BI**

Table S21. SHI calculations for the synthesis of **6a**

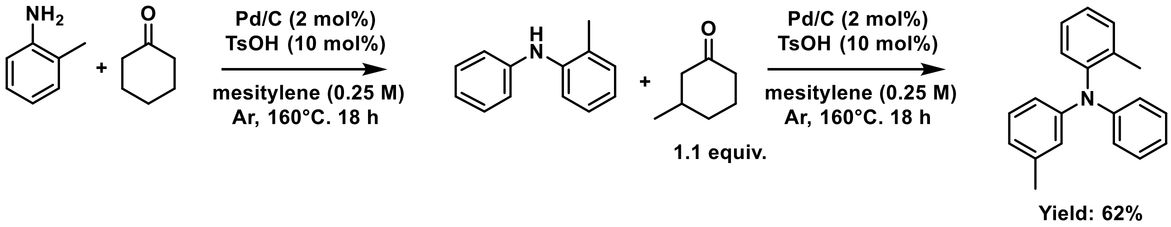
Substance	MW	mass (g)	Molar fraction	OB	LD50 dermal (mg/kg)	LC50 (g/m3 4 h)	FLP(deg C)	LEL	IS (N m)	OEL (mmol/m^3)	Q (R-phrases)
4-methylaniline	107.15	0.19	0.034154	-2.31451237	890	0.64	87	1.3	1E+100	0.084	56250000
4-iodotoluene	218.04	0.87	0.15639	-1.06402495					1E+100		225
toluene	92.4	4.335	0.779256	-3.11688312	5000	25.7	4.4	1.2	1E+100	2.08	937500
KotBu	112.21	0.168	0.0302	-1.63978255			14	2.3	1E+100	0.084	20

Substance	CGP	CLP	FP	OBP	XVP	OELP	RPP	Ω	SHZI contribution
4-methylaniline	0.8125	2.528089888	0.633333333	0.690620625	1.307692308	48.52380952	3.12868113	57.62472681	1.968128365
4-iodotoluene	0	0	0	0.321042011	0	0	0.949562931	1.270604941	0.198710462
toluene	0.020233463	0.45	0.821917808	0.779220779	1.416666667	1.959615385	2.410851413	7.858505514	6.12378598
KotBu	0	0	0.794425087	0.409945638	0.739130435	0	0.525218535	2.468719694	0.074554181

SUBTOTALS	245.466697	12.94819297	**SHZS**
		0.052749286	**SHZI**
		0.947250714	**SHI**

f) Chem. Sci. 2020,11, 4074-4084

General Procedure: Reaction conditions: (first step) Pd/C (2 mol%), TsOH (10 mol%), 6 (0.5 mmol), 2 (0.5 mmol), mesitylene (2 mL), Ar (1 atm), temperature 160 °C, and time 18 h. (second step) After the first step, 2 (0.55 mmol) was added to the reaction mixture, and the reaction was continued for further 2 h under the same conditions.



Scheme S11. Synthesis of 2-methyl-*N*-phenyl-*N*-(m-tolyl)aniline. [10]

Table S22. E-Factor calculation

Reactant	
2-methylaniline	0.0536
3-methylcyclohexanone	0.0561
cyclohexanone	0.0540
Solvent	
mesytilene	1.728
Catalyst	
Pd/C	0.0106
TsOH	0.0086
Workup	
Purification	
Silica	25
eluent	250
Recovery of Materials	
eluent	247.5
Pd/C	0.0106
Product	
3-methyl-N-phenyl-N-(m-tolyl)aniline	0.085
E-Factor	**>100**

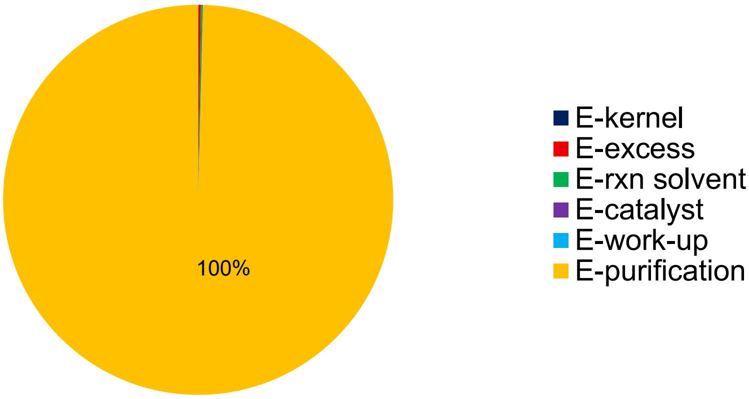


Figure S11. E-Factor distribution

Tale S23. EI and BI calculations for the synthesis of 2-methyl-*N*-phenyl-*N*-(m-tolyl)aniline

Substance	MW	Mass (g)	Molar fraction	Carbon atoms	SFP	GWP	LD50 oral (mg/kg)	LC50 (g/m3 4 h)	H (atm m3/mol)	log Kow
2-methylaniline	107.15	0.0536	0.027215	7		2.874475	670	3.8	0.0000002	1.32
3-methylcyclohexanone	112.17	0.056	0.028434	7		2.745832	800	10	0.000105	1.82
cyclohexanone	98.15	0.0539	0.027367	6		2.689761	2270	6.2	0.000012	0.86
mesitilene	120.19	1.72	0.873318	9		3.294783	5000	18	1.97E-02	3.42
ptsOH	190.22	0.086	0.043666	7		1.619178	1410	5000	2.78E-09	0.9

Substance	Koc	Z(air)	Z(water)	Z(soil)	Z(sediment)	fugacity (atm)	C(water) mol/m3	C(air) mol/m3	INHTP	INGTP	BCP	ARDP	Ω	EI contribution
2-methylaniline	9	40.60089322	5000000	2055867.393	4111734.786	9.12312E-15	4.562E-08	3.70407E-13	0.044389372	106.3900731	0.08480081	0	109.3937384	2.977153783
3-methylcyclohexanone	27	40.60089	9523.809524	12383.28	24766.57	1.46658E-12	1.397E-08	5.95E-11	2.711605	27.28289542	0.203422974	0	32.943756	0.93670998
cyclohexanone	3	40.60089	83333.33333	11880.75	23761.5	4.88983E-13	4.075E-08	1.99E-11	1.458216	28.05108881	0.037914034	0	32.236979	0.88224076
mesitilene	1078	40.60089	50.76142132	2627.598	5255.195	2.03208E-12	1.032E-10	8.25E-11	2.087309	0.032237862	3.345029868	0	8.7593595	7.64970720
ptsOH	3	40.60089	359712230.2	56231582	1.12E+08	7.25475E-17	2.610E-08	2.95E-15	2.68E-07	28.92153212	0.040663055	0	30.581373	1.33536334

SUBTOTALS	183.3338328	12.44581174	**ES**
		0.067886061	**EI**
		0.93211	**BI**

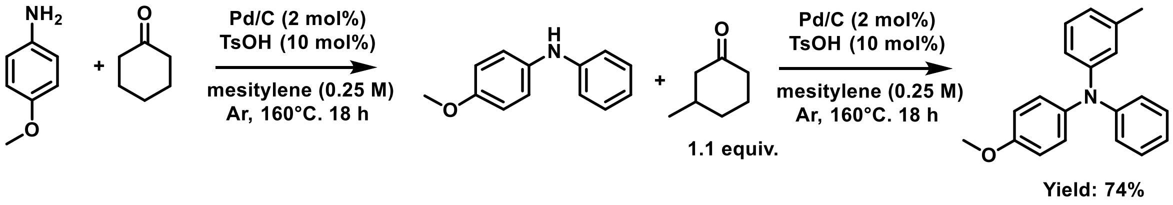
Table S24. SHI calculations for the synthesis of 3-methyl-*N*-phenyl-*N*-(m-tolyl)aniline

Substance	MW	mass (g)	Molar fraction	O consumption/liberation rxn	#O substrate	#O products	OB	LD50 dermal (mg/kg)	LC50 (g/m3 4 h)	FLP(deg C)	LEL	IS (N m)	OEL (mmol/m^3)	Q (R-phrases)
2-methylaniline	107.15	0.0536	0.02745761	18.5	0	18.5	-2.7624825	3250	3.78	85	1.5	1E+100	0.0047	0.0047
3-methylcyclohexanone	112.17	0.056	0.02868705	17	1	18	-2.42489079	2000	6.2	44	1.1	1E+100	0.818	
cyclohexanone	98.15	0.0539	0.02761129	17	1	18	-2.77126847	947	6.2	44	1.1	1E+100	0.208	0.416
pTsOH	190.22	0.0086	0.00440551	19	3	22	-1.59814951	2000	18	184		1E+100		
mesitilene	120.19	1.78	0.91183853	24	0	24	-3.19494134	3160	18	48	0.9	1E+100	1.022	0.0047

Substance	CGP	CLP	FP	OBP	XVP	OELP	RPP	Ω	SHZI contribution
2-methylaniline	0.137566138	0.692307692	0.636871508	0.690620625	1.133333333	867.2340426	1.724986722	872.2497286	23.94989265
3-methylcyclohexanone	0.083870968	1.125	0.719242902	0.606222698	1.545454545	0	1.899125861	5.978916974	0.17151752
cyclohexanone	0.083870968	2.37592397	0.719242902	0.692817117	1.545454545	9.798076923	2.828038805	18.04342523	0.498202254
pTsOH	0.028888889	1.125	0.498905908	0.399537378	0	0	1.424344396	3.476676571	0.01531654
mesitilene	0.028888889	0.712025316	0.710280374	0.798735336	1.888888889	0	1.424344396	5.5631632	5.07270657

SUBTOTALS	905.3119105	29.70763554	**SHZS**
		0.032814807	**SHZI**
		0.967185193	**SHI**

General Procedure: Reaction conditions: (first step) Pd/C (2 mol%), TsOH (10 mol%), 6 (0.5 mmol), 2 (0.5 mmol), mesitylene (2 mL), Ar (1 atm), temperature 160 °C, and time 18 h. (second step) After the first step, 2 (0.55 mmol) was added to the reaction mixture, and the reaction was continued for further 2 h under the same conditions.



Scheme S12. Synthesis of *N*-(4-methoxyphenyl)-3-methyl-*N*-phenylaniline.[10]

Table S25. E-Factor calculation

Reactant	
4-methoxyaniline	0.061575
3-methoxyclohexanone	0.05358
cyclohexanone	0.0512215
Solvent	
mesytilene	1.728
Catalyst	
Pd/C	0.0106
TsOH	0.0086
Workup	
Purification	
Silica	25
eluent	250
Recovery of Materials	
eluent	247.5
Pd/C	0.0106
Product	
N-(4-methoxyphenyl)-3-methyl-N-phenylaniline	0.107
E-Factor	**>100**

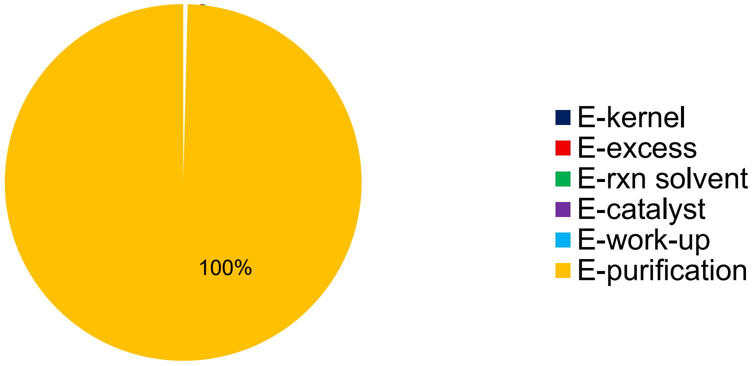


Figure S12. E-Factor distribution

Table S26. EI and BI calculations for the synthesis of 2-methyl-*N*-phenyl-*N*-(m-tolyl)aniline

Substance	MW	Mass (g)	Molar fraction	Carbon atoms	alpha # acidic Hs	GWP	LD50 oral (mg/kg)	LC50 (g/m3 4 h)	H (atm m3/mol)	log Kow
4-methoxyaniline	123.15	0.0616	0.3311828	7	0	2.501015	1400	0.05	0.00000016	0.95
3-methylcyclohexanone	112.17	0.056	0.30107527	7	0	2.745832	800	10	0.00026	1.11
cyclohexanone	93.13	0.0512	0.27526882	6	0	2.834747	2270	6.2	0.000012	0.86
mesitilene	190.22	0.0086	0.04623656	9	0	2.0818	5000	18	1.97E-02	3.42
ptsOH	190.22	0.0086	0.04623656	7	0	1.619178	1410	5000	2.78E-09	0.9

Substance	Koc	Z(air)	Z(water)	Z(soil)	Z(sediment)	fugacity (atm)	C(water) mol/m3	C(air) mol/m3	INHTP	INGTP	BCP	Ω	EI contribution
4-methoxyaniline	4	40.60089	6250000	1096239	2192477	6.42345E-15	4.015E-08	2.61E-13	2.375297	44.81085331	0.044381298	49.731547	16.47023264
3-methylcyclohexanone	5	40.60089	3846.153846	975.1058	1950.212	1.8426E-12	7.087E-09	7.48E-11	3.406832	13.84301407	0.058721887	20.0544	6.037883847
cyclohexanone	3	40.60089	83333.33333	11880.75	23761.5	5.15341E-13	4.295E-08	2.09E-11	1.536818	29.56313074	0.037914034	33.97261	9.351600234
mesitilene	1078	40.60089	50.76142132	2627.598	5255.195	1.28396E-12	6.518E-11	5.21E-11	1.31886	0.020369407	3.345029868	6.7660596	0.312839315
ptsOH	3	40.60089	359712230.2	56231582	1.12E+08	7.25475E-17	2.610E-08	2.95E-15	2.68E-07	28.92153212	0.040663055	30.581373	1.413977472

SUBTOTALS	141.10599	33.58653351	**ES**
		0.238023443	**EI**
		0.76198	**BI**

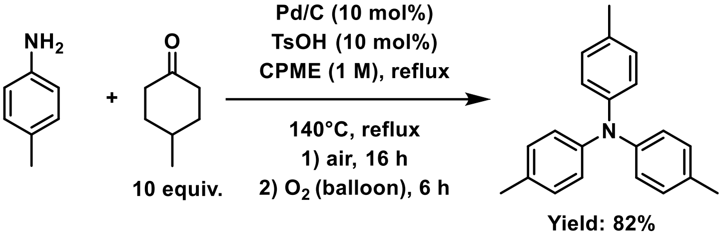
Table S27. SHI calculations for the synthesis of 3-methyl-*N*-phenyl-*N*-(m-tolyl)aniline

Substance	MW	mass (g)	Molar fraction	O consumption/liberation rxn	#O substrate	#O products	OB	LD50 dermal (mg/kg)	LC50 (g/m3 4 h)	FLP(deg C)	LEL	IS (N m)	OEL (mmol/m^3)	Q (R-phrases)
4-methoxyaniline	123.15	0.0616	0.03155576	18.5	1	18.5	-2.27365002	3200	0.05	119	1.1	1E+100	0.0102	22968750
3-methylcyclohexanone	107.16	0.0536	0.02745761	17	1	18	-2.53826054	2000	6.2	44	1.1	1E+100		50625
cyclohexanone	93.13	0.0512	0.02622816	17	1	18	-2.92064856	947	6.2	44	1.1	1E+100	0.416	10125000
pTsOH	190.22	0.0086	0.00440551	19	3	22	-1.59814951	2000	18	184		1E+100		3375
mesitilene	120.19	1.78	0.91183853	24	0	24	-3.19494134	3160	18	48	0.9	1E+100		3375

Substance	CGP	CLP	FP	OBP	XVP	OELP	RPP	Ω	SHZI contribution
4-methoxyaniline	10.4	0.703125	0.58163265	0.56841251	1.54545455	399.607843	2.97164999	416.378118	13.13912815
3-methylcyclohexanone	0.08387097	1.125	0.7192429	0.63456514	1.54545455	0	1.89912586	6.00725941	0.164944985
cyclohexanone	0.08387097	2.37592397	0.7192429	0.73016214	1.54545455	9.79807692	2.8280388	18.0807703	0.474225417
pTsOH	0.02888889	1.125	0.49890591	0.39953738	0	0	1.4243444	3.47667657	0.01531654
mesitilene	0.02888889	0.71202532	0.71028037	0.79873534	1.88888889	0	1.4243444	5.5631632	5.07270657

SUBTOTALS	449.505987	18.86632166	**SHZS**
		0.041971236	**SHZI**
		0.958028764	**SHI**

g) This work under batch.



Scheme S13. Synthesis of **6a**

Table S28. E-Factor calculation

Reactant	
4-methylaniline	0.05
4-methylcyclohexanone	0.49
ossigeno	0.18304
Solvent	
CPME	0.43
Catalyst	
Pd/C	0.053
TsOH	0.0086
Workup	
Purification	
Silica	25
eluent	250
Recovery of Materials	
eluent	247.5
Pd/C	0.053
Product	
p-toluiditriphenylammine	0.11
E-Factor	**>100**

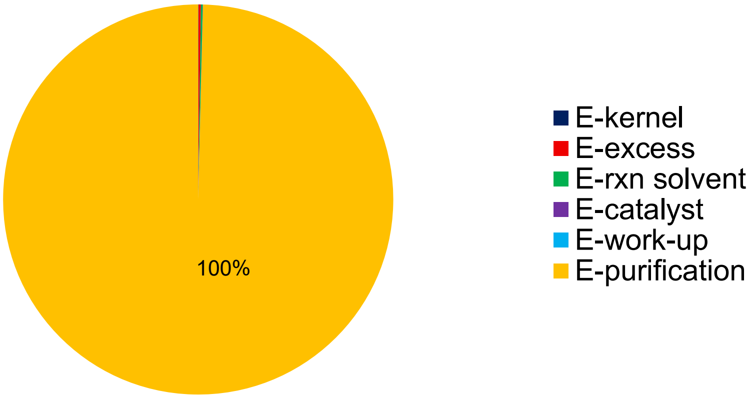


Figure S13. E-Factor distribution

Table S29. EI and BI calculation for the synthesis of **6a**

Substance	MW	Mass (g)	Molar fraction	Carbon atoms	SFP	GWP	LD50 oral (mg/kg)	LC50 (g/m3 4 h)	H (atm m3/mol)	log Kow
4-methylaniline	107.15	0.052	0.046099	7		2.874475	620	0.64	0.0000019	0.91
4-methylcyclohexanone	112.17	0.56	0.496454	7		2.745832	1800		1E-100	1.38
pTsOH	190.22	0.086	0.076241	7		1.619178	1410	5000	2.78E-09	0.9
CPME	100.16	0.43	0.381206	6		2.635783	1000	21.5	2.00E-02	1.6

Substance	Koc	Z(air)	Z(water)	Z(soil)	Z(sediment)	fugacity (atm)	C(water) mol/m3	C(air) mol/m3	INHTP	INGTP	BCP	Ω	EI contribution
4-methylaniline	3	40.60089	526315.7895	84192.13	168384.3	8.47675E-14	4.461E-08	3.44E-12	2.448886	112.4466551	0.041380906	117.8114	5.431021845
4-methylcyclohexanone	0	40.60089	1E+100	8.2E+96	1.64E+97	4.4574E-108	4.457E-08	1.8E-106	0	38.69609107	0.09418896	41.536112	20.62076495
pTsOH	3	40.60089	359712230.2	54860080	1.1E+08	7.25601E-17	2.610E-08	2.95E-15	2.68E-07	28.92656898	0.040663055	30.58641	2.331942614
CPME	16	40.60089	50	38.21829	76.43658	2.45281E-12	1.226E-10	9.96E-11	2.109333	0.191644755	0.138420368	5.075181	1.934687775

SUBTOTALS	195.0091	30.31841718	**ES**
		0.155471807	**EI**
		0.84453	**BI**

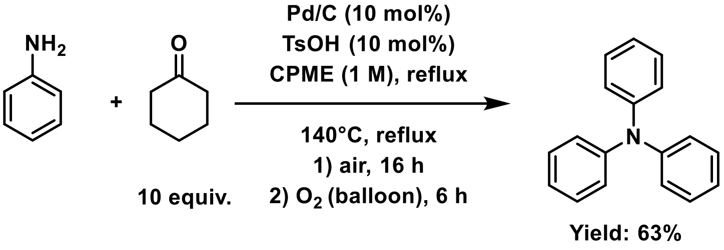
Table S30. SHI calculation for the synthesis of **6a**

Substance	MW	mass (g)	Molar fraction	OB	LD50 dermal (mg/kg)	LC50 (g/m3 4 h)	FLP(deg C)	LEL	IS (N m)	OEL (mmol/m^3)	Q (R-phrases)
4-methylaniline	107.15	0.052	0.046099	-2.7624825	890	0.64	87	1.3	1E+100	0.084	56250000
pTsOH	190.22	0.086	0.076241	-1.59814951	2000	5000	184		1E+100		3375
4-methylcyclohexanone	112.17	0.56	0.496454	-2.71017206			48		1E+100		750
CPME	100.16	0.43	0.381206	-2.71565495	2000	21.5	-1	1.1	1E+100		33750

Substance	CGP	CLP	FP	OBP	XVP	OELP	RPP	Ω	SHZI contribution
4-methylaniline	0.8125	2.528089888	0.633333333	0.690620625	1.307692308	48.52380952	3.12868113	57.62472681	2.656459037
pTsOH	0.000104	1.125	0.498905908	0.399537378	0	0	1.424344396	3.447891682	0.262871174
4-methylcyclohexanone	0	0	0.710280374	0.677543015	0	0	1.160646156	2.548469545	1.265197647
CPME	0.024186047	1.125	0.838235294	0.678913738	1.545454545	0	1.828038805	6.039828429	2.302416866

SUBTOTALS	69.66091646	6.486944724	**SHZS**
		0.093121725	**SHZI**
		0.906878275	**SHI**

The calculations of ES, BI, and SHI were performed using the synthesis of product **6e** as a representative example.



Scheme S14. Synthesis of **6e**

Table S31. EI and BI calculation for the synthesis of **6e**

Substance	MW	Mass (g)	Molar fraction	Carbon atoms	alpha # acidic Hs	GWP	LD50 oral (mg/kg)	LC50 (g/m3 4 h)	H (atm m3/mol)	log Kow
aniline	93.13	0.05	0.047348	6	0	2.834747	102	3.3	0.0000019	0.91
cyclohexanone	98.15	0.49	0.464015	6	0	2.689761	2270	6.2	0.000012	0.86

pTsOH	190.22	0.086	0.081439	7	0	1.619178	1410	5000	2.78E-09	0.9
CPME	100.16	0.43	0.407197	6	0	2.635783	1000	21.5	2.00E-02	1.6

Substance	Koc	Z(air)	Z(water)	Z(soil)	Z(sediment)	fugacity (atm)	C(water) mol/m3	C(air) mol/m3	INHTP	INGTP	BCP	ARDP	Ω	EI contribution
aniline	3	40.60089	526315.7895	84192.13	168384.3	9.75285E-14	5.133E-08	3.96E-12	0.546433	786.3947971	0.041380906	0	789.81736	37.396655
cyclohexanone	0	40.60089	83333.33333	68.36658	136.7332	4.91547E-13	4.1E-08	2E-11	1.465861	28.198161	0.037914034	0	32.391697	15.030238
pTsOH	3	40.60089	359712230.2	54860080	1.1E+08	7.25601E-17	2.61E-08	2.95E-15	2.68E-07	28.92656898	0.040663055	0	30.58641	2.4909387
CPME	16	40.60089	50	38.21829	76.43658	2.45281E-12	1.23E-10	9.96E-11	2.109333	0.191644755	0.138420368	0	5.075181	2.0665983

SUBTOTALS	857.87065	56.9844304	**ES**
		0.066425434	**EI**
		0.93357	**BI**

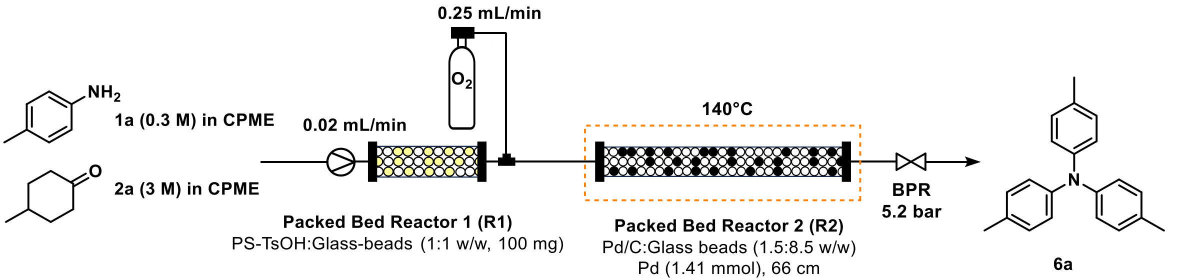
Table S32. SHI calculation for the synthesis of **6a**

	MW	mass (g)	Molar fraction	O consumption/liberation rxn	#O substrate	#O products	OB	LD50 dermal (mg/kg)	LC50 (g/m3 4 h)	FLP(deg C)	LEL	IS (N m)	OEL (mmol/m^3)	Q (R-phrases)
aniline	93.13	0.05	0.051093	15.5	0	15.5	-2.66294427	442	1.82	76	1.2	1E+100	0.0831	11275
cyclohexanone	98.15	0.49	0.500715	17	1	18	-2.77126847	947	6.2	44	1.1	1E+100	0.416	10125000
pTsOH	190.22	0.0086	0.008788	19	3	22	-1.59814951	2000	5000	184		1E+100		3375
CPME	100.16	0.43	0.439403	17	1	18	-2.71565495	2000	21.5	-1	1.1	1E+100		33750

	CGP	CLP	FP	OBP	XVP	OELP	RPP	Ω	SHZI contribution
aniline	0.285714286	5.090497738	0.653295129	0.665736068	1.416666667	49.04933815	1.635816795	58.79706483	3.004141878
cyclohexanone	0.083870968	2.37592397	0.719242902	0.692817117	1.545454545	9.798076923	2.828038805	18.04342523	9.034619214
pTsOH	0.000104	1.125	0.498905908	0.399537378	0	0	1.424344396	3.447891682	0.030300295
CPME	0.024186047	1.125	0.838235294	0.678913738	1.545454545	0	1.828038805	6.039828429	2.653920115

SUBTOTALS	86.32821017	14.7229815	**SHZS**
		0.170546586	**SHZI**
		0.829453414	**SHI**

h) This work under FLOW



Isoalted Yield: 88% (5 mmol)
Isolated Yield: 89 % (30 mmol)

Scheme S15. Synthesis of **6a**

Table S33. E-Factor calculation

Reactant (5 mmol)	
4-methylaniline	0.52
4-methylcyclohexanone	5.7
ossigeno	0.20
Solvent	
CPME	14.36
Catalyst	
Workup	
Purification	
HBF_4 48% H_2O	1.37
heptane	3.42

CPME	8.6
H_2O NaOH 3 M	2.24
Recovery of Materials	
CPME	21.81
4-methylcyclohexanone	3.77
heptano	3.15
Product	
p-toluiditriphenylammine	1.23
E-Factor	**5.3**

Table S34. E-Factor calculation

Reactant (30 mmol)	
4-methylaniline	3.20
4-methylcyclohexanone	33.52
ossigeno	1.17
Solvent	
CPME	85.83
Catalyst	
Workup	
Purification	
HBF_4 48% H_2O	8.19
heptane	20.45
CPME	25.8
H2O NaOH 3 M	13.40
Recovery of Materials	
CPME	106.05
4-methylcyclohexanone	21.99
heptano	18.82
Product	
p-toluiditriphenylammine	7.67
E-Factor	**4.8**

Table S35. EI and BI calculations for the synthesis of **6a**

Substance	MW	Mass (g)	Molar fraction	Carbon atoms	GWP	LD50 oral (mg/kg)	LC50 (g/m3 4 h)	H (atm m3/mol)	log Kow
4-methylaniline	107.15	0.52	0.022787	7	2.874475	620	0.64	0.0000019	0.91
4-methylcyclohexanone	112.17	5.6	0.245399	7	2.745832	1800		1E-100	1.38
CPME	100.16	16.7	0.731814	6	2.635783	1000	21.5	2.00E-02	1.6

Substance	Koc	Z(air)	Z(water)	Z(soil)	Z(sediment)	fugacity (atm)	C(water) mol/m3	C(air) mol/m3	INHTP	INGTP	BCP	Ω	EI contribution
4-methylaniline	3	40.60089	526315.78	84192.13	168384.3	8.47675E-14	4.461E-08	3.44E-12	2.448886	112.4466551	0.041380906	117.8114	2.68457171
4-methylcyclohexanone	0	40.60089322	1E+100	8.20399E+96	1.6408E+97	4.4574E-108	4.457E-08	1.8097E-106	0	38.69609107	0.09418896	41.53611225	10.19291098
CPME	16	40.60089	50	38.21829	76.43658	2.45281E-12	1.23E-10	9.96E-11	2.109333	0.191644755	0.138420368	5.075181	3.71408948

SUBTOTALS	125.7266	7.095598903	**ES**
		0.056436736	**EI**
		0.89909	**BI**

Table S36. SHI calculation for the synthesis of **6a**

Substance	MW	mass (g)	Molar fraction	OB	LD50 dermal (mg/kg)	LC50 (g/m3 4 h)	FLP(deg C)	LEL	IS (N m)	LBT (cm^3/10 g)	OEL (mmol/m^3)	Q (R-phrases)
4-methylaniline	107.15	0.52	0.022787	-2.31451237	890	0.64	87	1.3	1E+100	0	0.084	56250000
4-methylcyclohexanone	112.17	5.6	0.245399	-2.42489079			48		1E+100	0		750
CPME	100.16	16.7	0.731814	-2.71565495	2000	21.5	-1	1.1	1E+100	0		33750

Substance	CGP	CLP	FP	OBP	XVP	OELP	RPP	Ω	SHZI contribution
4-methylaniline	0.8125	2.528089888	0.633333333	0.690620625	1.307692308	48.52380952	3.12868113	57.62472681	1.313096316
4-methylcyclohexanone	0	0	0.710280374	0.677543015	0	0	1.160646156	2.548469545	0.625391299
CPME	0.024186047	1.125	0.838235294	0.678913738	1.545454545	0	1.828038805	6.039828429	4.420032198

SUBTOTALS	66.21302478	6.358519814	**SHZS**
		0.096031254	**SHZI**
		0.903968746	**SHI**

We present a heatmap comparing chemical methodologies based on Green Chemistry metrics, with the color gradient ranging from critical (red) to optimal (green) (Table S37). In addition, a histogram summarizing the evaluated green metrics for the synthesis of a radial pentagon (Figure S13) and the 1/SF analysis (Figure S14) are provided.

Table S37. Heatmap for the green metric analysed

	a.	b.	c.	d.	e.	f.	g.	h. 5 mmol	h. 30 mmol
AE	0.71	0.53	0.78	0.79	0.52	0.87	0.87	0.88	0.89
Yield	0.91	0.78	0.9	0.9	0.82	0.74	0.82	0.88	0.89
MRP	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.48	0.8
BI	0.95	0.47	0.87	0.81	0.93	0.76	0.85	0.9	0.9
SHI	0.89	0.42	0.44	0.44	0.88	0.96	0.91	0.9	0.9
VMR	0.78	0.51	0.69	0.68	0.72	0.75	0.77	0.82	0.88

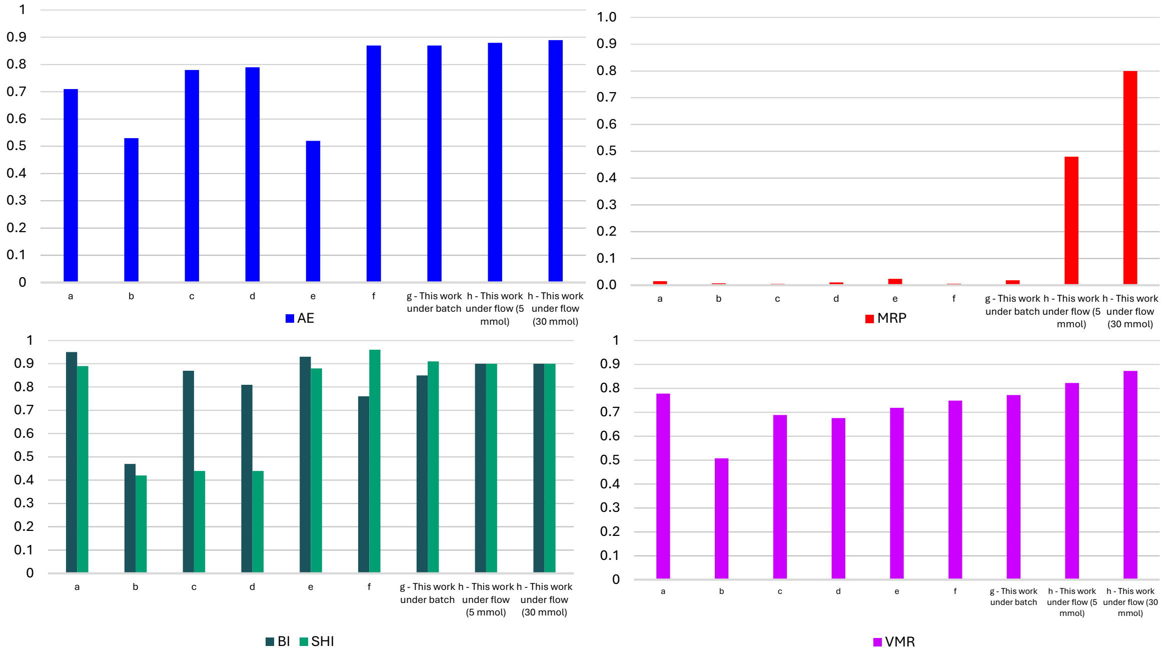


Figure S14. Histogram of the green metrics evaluated for the synthesis of a radial pentagon

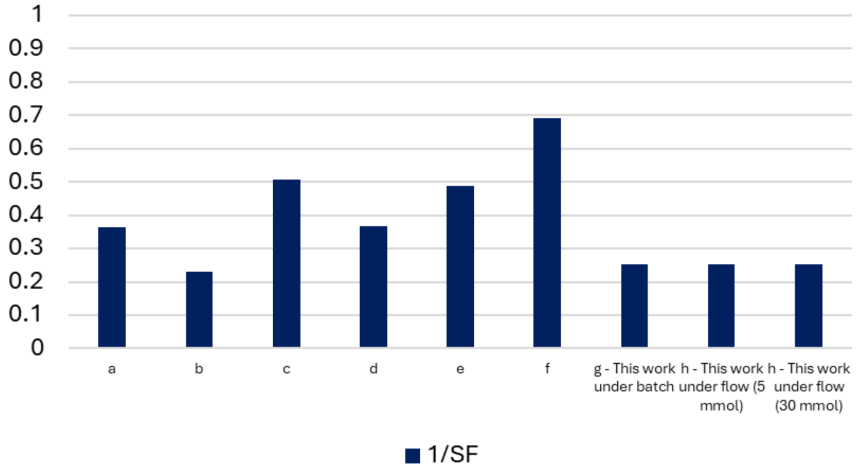


Figure S15. Histogram of the 1/SF

4. References

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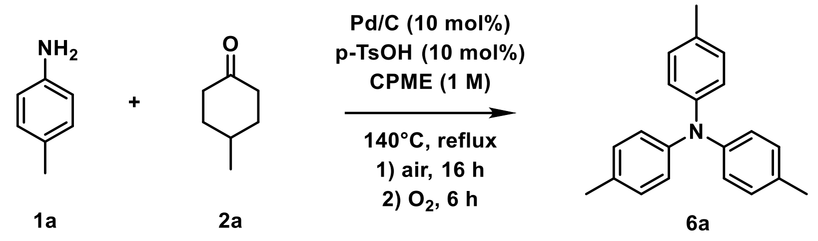
5. Spectral characterization data

Chem. Name	**tri-p-tolylamine (6a)**
Lit. Ref.	T. Yamamoto, M. Nishiyama and Y. Koie, *J. Chem. Soc., Perkin Trans. 1*, 1998, **39**, 2367-2370.



METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-toluidina (**1a**) (0.5 mmol, 53 mg), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product tri-p-tolylamine (**6a**) was obtained with an isolated yield of 82%.

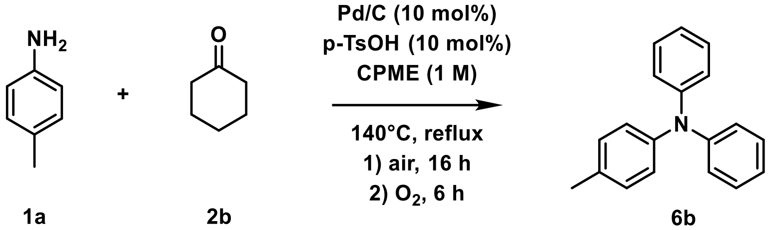
Mol Formula	$C_{21}H_{21}N$	**m.p.**	116-118°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR 400 MHz CDCl₃	7.03	6	*d*	8.1
	6.95	6	*d*	8.2
	2.30	9	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 145.85; 131.89; 129.86; 124.00.

GC-EIMS (m/z, %): 288 (79); 287 (100); 286 (52); 271 (25), 194 (15); 181 (18); 180 (27); 91 (15); 65 (18).

Chem. Name	**4-methyl-*N, N*-diphenylaniline (6b)**
Lit. Ref.	T. Yamamoto, M. Nishiyama and Y. Koie, *J. Chem. Soc., Perkin Trans. 1*, 1998, **39**, 2367-2370.



1a **2b** **6b**

METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-toluidina (**1a**) (0.5 mmol, 53 mg), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-methyl-*N, N*-diphenylamina (**6b**) was obtained with an isolated yield of 59%.

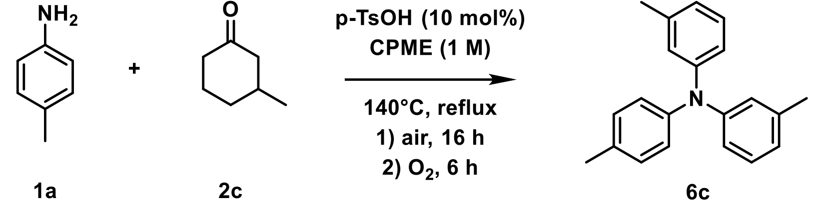
Mol Formula	$C_{19}H_{17}N$	**m.p.**	66-69°C

	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR **400 MHz** **$CDCl_3$**	7.22	4	*t*	7.9	
	7.09-7.05	6	*m*		
	7.02-6.95	4	*m*		
	2.31	3	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.18; 145.39; 132.88; 130.05; 129.24; 125.08; 123.74; 122.35; 20.97.

GC-EIMS (m/z, %): 261 (22); 260 (100); 259 (100); 258 (100); 257 (26); 256 (24); 243 (100); 242 (40); 241 (29); 182 (15); 181 (23); 180 (61); 168 (31); 167 (100); 166 (72); 165 (15); 156 (27); 155 (22); 153 (22); 152 (24); 142 (23); 141 (48); 140 (18); 139 (19); 130 (39); 129 (47); 127 (23); 121 (18); 121 (23).

Chem. Name	**3-methyl-*N*-(m-tolyl)-*N*-(p-tolyl)aniline (6c)**
Lit. Ref.	



METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-toluidina (**1a**) (0.5 mmol, 53 mg), and 3-methylcyclohexanone (**2c**) (5 mmol, 0.5 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 3-methyl-*N*-(m-tolyl)-*N*-(p-tolyl)aniline (**6c**) was obtained with an isolated yield of 70%.

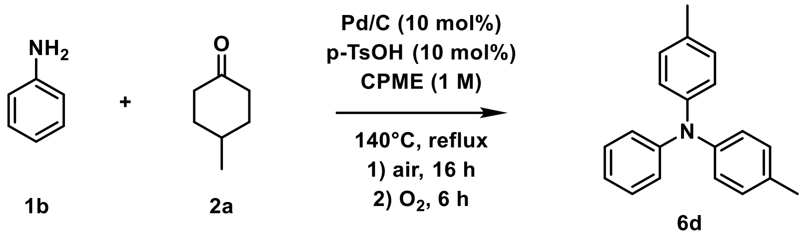
Mol Formula	$C_{21}H_{21}N$	**m.p.**	111-113°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^1H NMR **400 MHz** **$CDCl_3$**	7.12	2	*t*	7.8
	7.07	2	*d*	8.6
	6.89	2	*s*	
	6.86	2	*d*	7.4
	6.80	2	*d*	7.4
	2.33	3	*s*	
	2.26	6	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.23; 145.60; 139.04; 132.49; 129.02; 124.90; 124.51; 123.23; 121.09; 21.57; 20.97.

GC-EIMS (m/z, %): 385 (45); 269 (23); 287 (75); 196 (58); 206 (20)

Chem. Name	**4-methyl-*N*-phenyl-*N*-(p-tolyl)aniline (6d)**
Lit. Ref.	Sachin G. Modha, Mihai V. Popescu and Michael F. Greaney, *J. Org. Chem.* 2017, **82**, 11933-11938.



METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), aniline (**1b**) (0.5 mmol, 46 µL), and 4-methylcyclohexanone (**2c**) (5 mmol, 0.6 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-methyl-*N*-phenyl-*N*-(p-tolyl)aniline (**6d**) was obtained with an isolated yield of 75%.

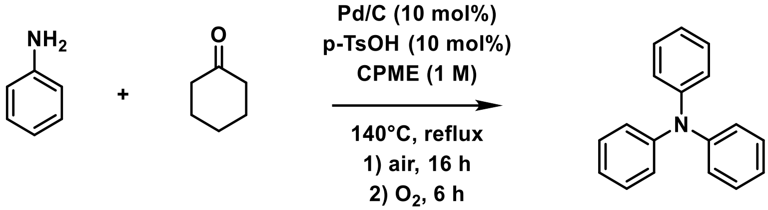
Mol Formula	$C_{20}H_{19}N$	**m.p.**	111-113°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR **400 MHz** **$CDCl_3$**	7.20	2	*t*	7.7
	7.06-6.97	10	*m*	
	6.93	1	*t*	7.5
	2.31	6	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.41; 145.59; 132.43; 129.96; 129.15; 124.59; 123.08; 121.83; 20.93.

GC-EIMS (m/z, %): 275 (25); 273 (100); 258 (63); 257 (97); 256 (46); 254 (17); 243 (30); 241 (15); 194 (18); 182 (15); 181 (29); 180 (60); 167 (47); 166 (24); 156 (17); 155 (21); 154 (16); 153 (17); 152 (15); 141 (15); 137 (34); 135 (20); 128 (29); 127 (22); 115 (17); 91 (21); 77 (19).

Chem. Name	**Triphenylamine (6e)**
Lit. Ref.	T. Yamamoto, M. Nishiyama and Y. Koie, *J. Chem. Soc., Perkin Trans. 1*, 1998, **39**, 2367-2370.



1b **2b** **6e**

METHOD:

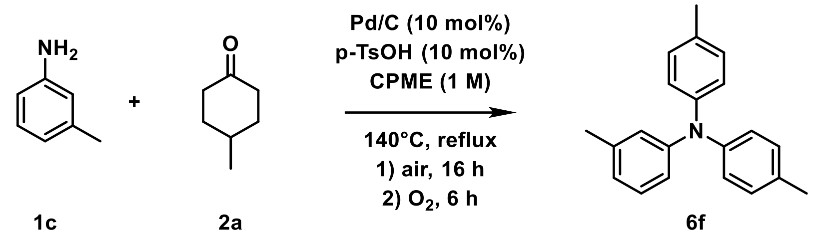
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), aniline (**1b**) (0.5 mmol, 46 µL), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product triphenylamine (**6e**) was obtained with an isolated yield of 63%.

Mol Formula		$C_{18}H_{15}N$		**m.p.**	126-128°C
^{1}H NMR **400 MHz** **$CDCl_3$**	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.23	6	*d*	7.6	
	7.09	6	*d*	7.9	
	7.00	3	*t*	7.2	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.00; 129.33; 124.30; 122.80.

GC-EIMS (m/z, %): 247 (21); 246 (100); 245 (39); 168 (15).

Chem. Name	**3-methyl-*N*,*N*-di-p-tolylaniline (6f)**
Lit. Ref.	



METHOD:

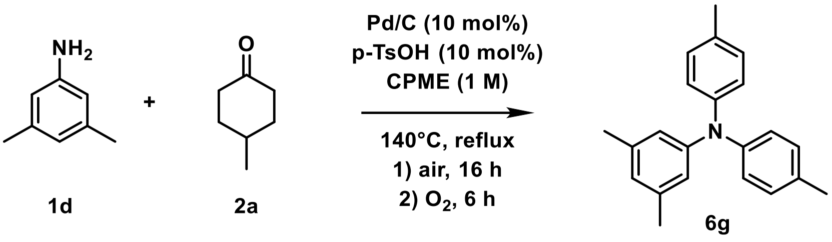
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 3-methylaniline (**1c**) (0.5 mmol, 54 µL), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 3-methyl-*N*,*N*-di-p-tolylaniline (**6f**) was obtained with an isolated yield of 69%.

Mol Formula		$C_{21}H_{21}N$		**m.p.**	198-200°C
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR **400 MHz** **$CDCl_3$**	7.09	1	*t*	7.5	
	7.05	4	*d*	7.8	
	6.97	4	*d*	7.8	
	6.87	1	*s*		
	6.82	1	*d*	7.8	
	6.76	1	*d*	7.4	
	2.31	6	*s*		
	2.24	3	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.34; 145.71; 138.98; 132.23; 129.90; 128.97; 124.51; 123.91; 122.87; 120.51; 31.06; 20.92.

GC-EIMS (m/z, %): 329 (28); 320 (50); 287 (78); 200 (23); 158 (30)

Chem. Name	**3,5-dimethyl-*N,N*-di-p-tolylaniline (6g)**
Lit. Ref.	



METHOD:

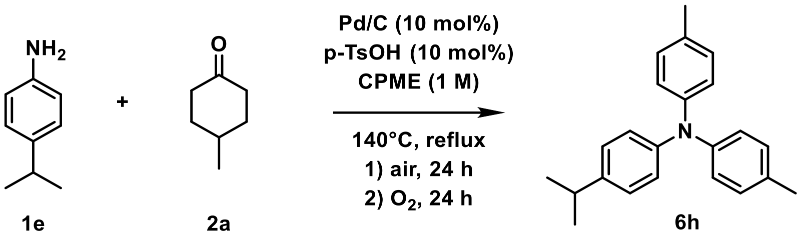
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 3,5-dimethylaniline (**1d**) (0.5 mmol, 62 µL), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 3,5-dimethyl-*N,N*-di-p-tolylaniline (**6g**) was obtained with an isolated yield of 66%.

Mol Formula		$C_{22}H_{23}N$		**m.p.**	93-96°C
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR **400 MHz** **$CDCl_3$**	7.04	4	*d*	8.2	
	6.96	4	*d*	8.2	
	6.67	2	*s*		
	6.61	1	*s*		
	2.31	6	*s*		
	2.20	6	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.27; 145.80; 138.78; 132.06; 129.87; 124.45; 124.02; 121.30; 21.46; 20.94.

GC-EIMS (m/z, %): 303 (29); 302 (40); 301 (100); 300 (32); 287 (20); 286 (38); 285 (58); 284 (44); 281 (20); 272 (22); 271 (24); 270 (20); 208 (22); 207 (41); 195 (29); 194 (46); 193 (16); 181 (22); 180 (29); 169 (24); 165 (16); 77 (25); 73 (23); 65 (24); 28 (38).

Chem. Name	**4-isopropyl-*N*,*N*-di-p-tolylaniline (6h)**
Lit. Ref.	



METHOD:

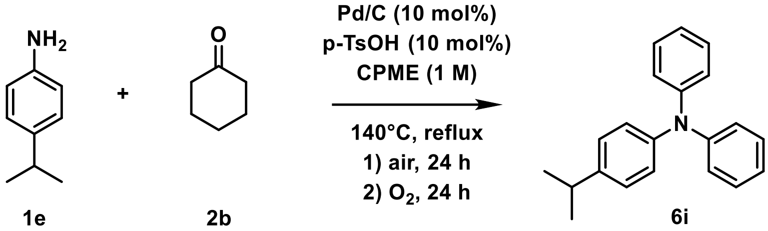
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 4-isopropyl-aniline (**1e**) (0.5 mmol, 70 μL), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-isopropyl-*N*,*N*-di-p-tolylaniline (**6h**) was obtained with an isolated yield of 85%.

Mol Formula		$C_{23}H_{25}N$		**m.p.**	Oil
^{1}H NMR 400 MHz CDCl$_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.10	2	*d*	8.5	
	7.08-7.06	4	*d*	8.4	
	6.98	6	*d*	8.6	
	2.90	1	*ept*	6.9	
	2.32	6	*s*		
	1.26	6	*d*	6.9	

^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 145.97; 145.83; 142.75; 131.93; 129.86; 127.10; 124.15; 123.56; 33.55; 24.21; 20.91.

GC-EIMS (m/z, %): 316 (17); 315 (100); 301 (16); 300 (94); 192 (15); 190 (16); 180 (18); 92 (16); 91 (28); 65 (21).

Chem. Name	**4-isopropyl-*N,N*-diphenylaniline (6i)**
Lit. Ref.	



METHOD:

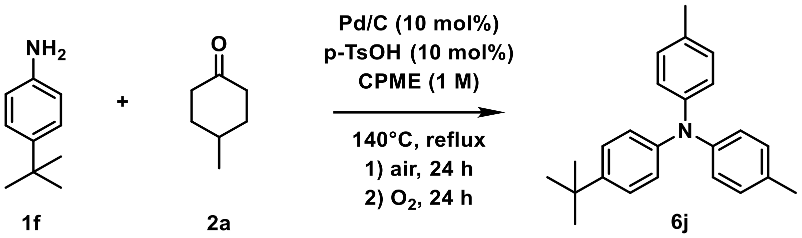
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 4-isopropyl-aniline (**1e**) (0.5 mmol, 70 µL), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-isopropyl-*N*,*N*-diphenylaniline (**6i**) was obtained with an isolated yield of 87%.

Mol Formula		$C_{21}H_{21}N$		**m.p.**	Oil
^{1}H NMR **400 MHz** **$CDCl_3$**	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.23	4	*t*	8.5	
	7.12-7.06	6	*m*		
	7.03-6.96	4	*m*		
	2.91-2.84	1	*ept*	6.9	
	1.25	6	*d*	6.9	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.19; 145.52; 143.76; 129.24; 127.30; 124.73; 123.88; 122.39; 33.62; 24.19.

GC-EIMS (m/z, %): 289 (31); 288 (100); 287 (100); 286 (25); 274 (43); 273 (100); 272 (100); 271 (50); 270 (52); 257 (23); 256 (71); 254 (28); 245 (32); 244 (88); 243 (71); 242 (42); 241 (33); 195 (24); 194 (53); 193 (47); 192 (32); 191 (19); 180 (49); 179 (22); 178 (20); 169 (21); 168 (100); 167 (100); 166 (65); 165 (33); 154 (18); 153 (26); 152 (30); 141 (37); 140 (18); 139 (21); 136 (58); 128 (48); 127 (28); 121 (16); 115 (40); 103 (20); 92 (18); 91 (47); 78 (22); 77 (83); 65 (16); 51 (34).

Chem. Name	**4-(tert-butyl)-*N*,*N*-di-p-tolylaniline (6j)**
Lit. Ref.	



METHOD:

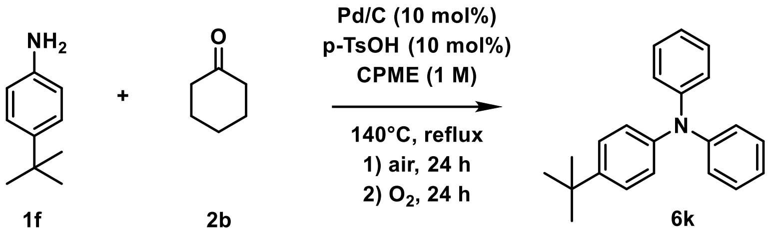
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 4-tert-buthylaniline (**1f**) (80 µL; 0.5 mmol), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-(tert-butyl)-*N*,*N*-di-p-tolylaniline (**6j**) was obtained with an isolated yield of 61%.

Mol Formula		$C_{24}H_{27}N$		**m.p.**	68-71°C
^{1}H NMR 400 MHz CDCl$_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.24	2	*d*	8.5	
	7.06	4	*d*	8.3	
	7.011-6.98	6	*m*		
	2.33	6	*s*		
	1.33	9	*s*		

^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 148.14; 145.91; 145.15; 129.25; 126.19; 124.14; 123.98; 122.45; 31.59, 20.91.

GC-EIMS (m/z, %): 301 (60); 302 (15); 286 (100); 287 (24).

Chem. Name	**4-(tert-butyl)-*N,N*-diphenylaniline (6k)**
Lit. Ref.	



METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 4-tert-buthylaniline (**1f**) (80 µL; 0.5 mmol), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-(tert-butyl)-*N*,*N*-diphenylaniline (**6k**) was obtained with an isolated yield of 55%.

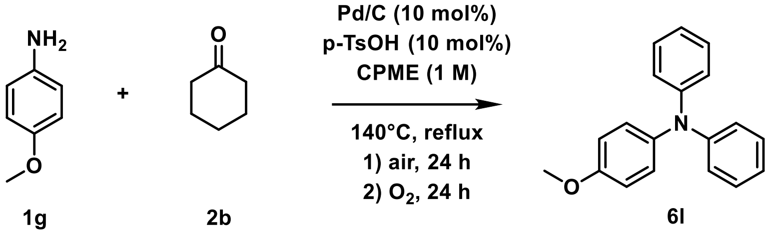
Mol Formula	$C_{22}H_{23}N$	**m.p.**	68-71°C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR 400 MHz $CDCl_3$	7.25-7.21	5	*m*	
	7.08	4	*d*	7.8
	7.03-6.96	5	*m*	
	1.33	9	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.14;145.90; 145.15; 129.25;126.19; 124.14; 123.98; 122.45; 31.58.

GC-EIMS (m/z, %): 301 (60); 302 (15); 286 (100); 287 (24).

Chem. Name	**4-methoxy-*N,N*-diphenylaniline (6l)**
Lit. Ref.	T. Yamamoto, M. Nishiyama and Y. Koie, *J. Chem. Soc., Perkin Trans. 1*, 1998, **39**, 2367-2370.



METHOD:

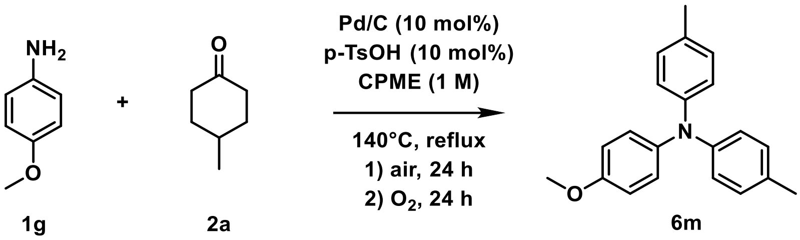
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-anisidine (**1g**) (0.5 mmol, 62 mg), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-methoxy-*N,N*-diphenylaniline (**6l**) was obtained with an isolated yield of 75%.

Mol Formula		$C_{19}H_{17}NO$		**m.p.**	102-106 °C
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR **400 MHz** **$CDCl_3$**	7.19-7.23	4	*t*	7.7	
	7.03-7.09	6	*q*		
	6.95	2	*t*	7.1	
	6.85	2	*d*	8.7	
	3.81	3	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 156.29; 148.31; 140.91; 129.20; 127.45; 123.01; 121.96; 114.88; 55.61.

GC-EIMS (m/z, %): 277 (22); 276 (100); 262 (17); 261 (83); 77 (16).

Chem. Name	**4-methoxy-*N,N*-di-p-tolylaniline (6m)**
Lit. Ref.	Ganesh M. Kumbhar, Ajit H. Deshmukh, Sanjay S. Chavan, *J. Org. Chem*. 2024, **1021**, 123351.



METHOD:

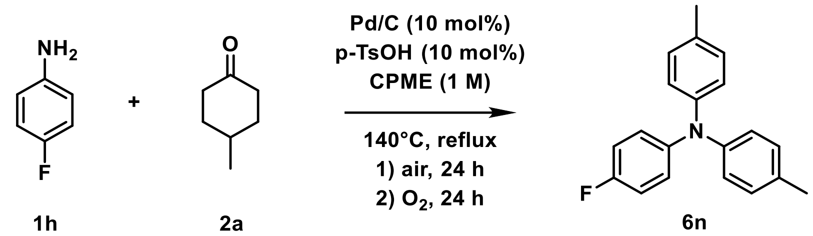
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-anisidine (**1g**) (0.5 mmol, 62 mg), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-methoxy-*N,N*-di-p-tolylaniline (**6m**) was obtained with an isolated yield of 72%.

Mol Formula		$C_{21}H_{21}NO$		**m.p.**	70-72°C
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.04-7.01	6	*m*		
	6.92	4	*d*	8.1	
	6.81	2	*d*	8.1	
	3.79	3	*s*		
	2.29	6	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 155.74; 146.07; 141.47; 131.39; 129.80; 126.56; 123.20; 114.73; 55.62; 20.85

GC-EIMS (m/z, %): 304 (79); 303 (100); 289 (55); 288 (100); 152 (20); 91 (19); 65 (20).

Chem. Name	**4-fluoro-*N,N*-di-p-tolylaniline (6n)**
Lit. Ref.	



METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-fluoroaniline (**1h**) (0.5 mmol, 56 mg), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure 4-fluoro-*N,N*-di-p-tolylaniline (**6n**) was obtained with an isolated yield of 62%.

Mol Formula	$C_{20}H_{18}FN$	**m.p.**	80-82°C

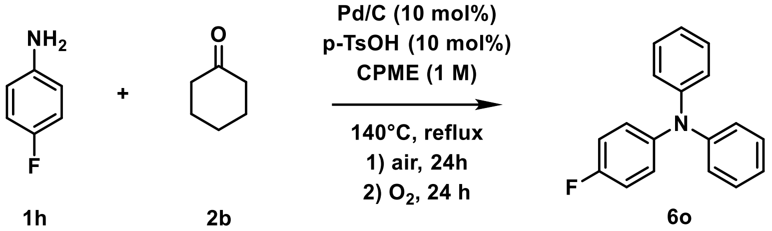
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR **400 MHz** **$CDCl_3$**	7.05	4	*d*	8.4	
	7.03-7.00	2	*m*		
	6.95-6.90	6	*m*		
	2.30	6	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 159.73; 157.33; 145.72; 144.49; 144.46; 132.20; 129.98; 125.50; 125.42; 123.90; 116.06; 115.84; 20.89.

^{19}F NMR (100.6 MHz, $CDCl_3$) δ: -120.98.

GC-EIMS (m/z, %): 292 (20); 291 (100); 290 (19); 240 (25); 91 (23); 65 (24).

Chem. Name	**4-fluoro-*N,N*-diphenylaniline (6o)**
Lit. Ref.	Sachin G. Modha, Mihai V. Popescu and Michael F. Greaney, *J. Org. Chem.* 2017, **82**, 11933-11938.



METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-fluoroaniline (**1h**) (0.5 mmol, 56 mg), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure 4-fluoro-*N,N*-diphenylaniline (**6o**) was obtained with an isolated yield of 75%.

Mol Formula	$C_{18}H_{14}FN$	**m.p.**	Oil

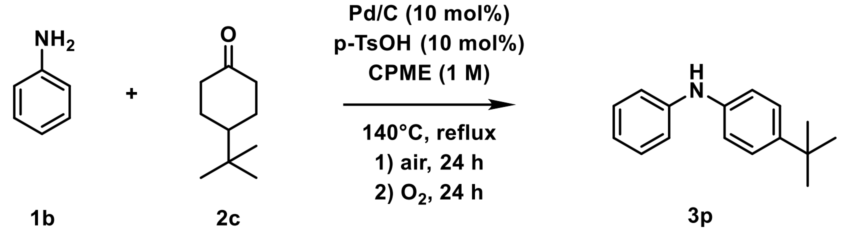
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR	7.23	4	*t*	8.2	
400 MHz	7.08-7.03	6	*m*		
$CDCl_3$	7.01-6.94	4	*m*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 160.26; 157.85; 148.03; 144.03; 129.38; 126.61; 123.67; 122.65; 116.31; 116.09

^{19}F NMR (100.6 MHz, $CDCl_3$) δ: -119.72.

GC-EIMS (m/z, %): 264 (90); 263 (100); 262 (100); 185 (47); 184 (31); 167 (23); 166 (26); 160 (16); 159 (19); 77 (22); 51 (25).

Chem. Name	**4-(tert-butyl)-*N*-(p-tolyl)aniline (3p)**
Lit. Ref.	



METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), aniline (**1b**) (0.5 mmol, 46 µL), and 4-tertbuthylcyclohexanone (**2c**) (5 mmol, 81 mg) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure 4-(tert-butyl)-*N*-(p-tolyl)aniline (**3p**) was obtained with an isolated yield of 85%.

Mol Formula	$C_{17}H_{21}N$	**m.p.**	39-42°C

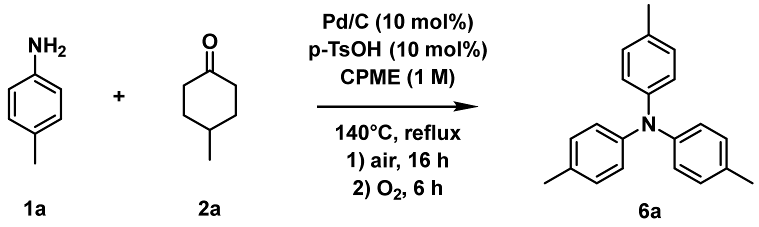
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR **400 MHz** **$CDCl_3$**	7.28	2	*s*		
	7.07	2	*d*		
	6.98	4	*t*		
	5.54	1	*s*		
	2.30	3	*s*		
	1.31	9	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 143.59; 141.30; 141.02; 130.41; 129.93; 126.22; 118.29; 117.25; 31.62; 20.78.

GC-EIMS (m/z, %): 239 (100); 225 (68); 224 (100); 209 (29); 208 (22); 182 (17); 180 (16); 167 (15); 98 (15); 91 (17).

5. Spectral characterization data

Chem. Name	**tri-p-tolylamine (6a)**
Lit. Ref.	T. Yamamoto, M. Nishiyama and Y. Koie, *J. Chem. Soc., Perkin Trans. 1*, 1998, **39**, 2367-2370.



METHOD:

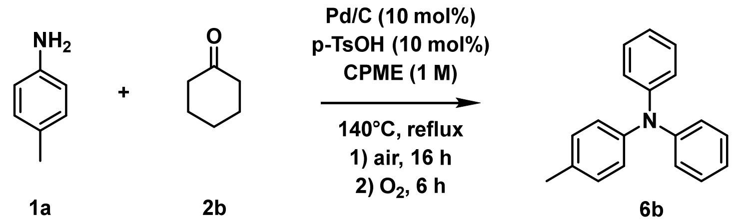
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-toluidina (**1a**) (0.5 mmol, 53 mg), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product tri-p-tolylamine (**6a**) was obtained with an isolated yield of 82%.

Mol Formula		$C_{21}H_{21}N$		**m.p.**	116-118°C
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR 400 MHz CDCl$_3$	7.03	6	*d*	8.1	
	6.95	6	*d*	8.2	
	2.30	9	*s*		

^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 145.85; 131.89; 129.86; 124.00.

GC-EIMS (m/z, %): 288 (79); 287 (100); 286 (52); 271 (25), 194 (15); 181 (18); 180 (27); 91 (15); 65 (18).

Chem. Name	**4-methyl-*N, N*-diphenylaniline (6b)**
Lit. Ref.	T. Yamamoto, M. Nishiyama and Y. Koie, *J. Chem. Soc., Perkin Trans. 1*, 1998, **39**, 2367-2370.



METHOD:

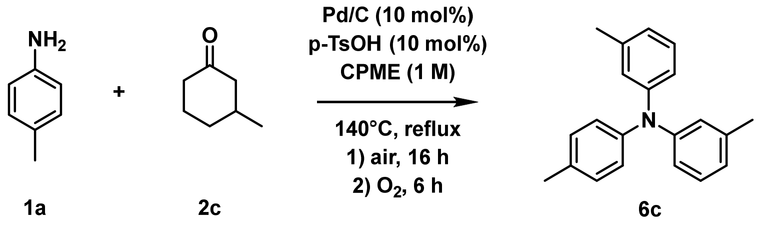
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-toluidina (**1a**) (0.5 mmol, 53 mg), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-methyl-*N, N*-diphenylamina (**6b**) was obtained with an isolated yield of 59%.

Mol Formula		$C_{19}H_{17}N$		**m.p.**	66-69°C
^{1}H NMR 400 MHz CDCl$_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.22	4	*t*	7.9	
	7.09-7.05	6	*m*		
	7.02-6.95	4	*m*		
	2.31	3	*s*		

^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 148.18; 145.39; 132.88; 130.05; 129.24; 125.08; 123.74; 122.35; 20.97.

GC-EIMS (m/z, %): 261 (22); 260 (100); 259 (100); 258 (100); 257 (26); 256 (24); 243 (100); 242 (40); 241 (29); 182 (15); 181 (23); 180 (61); 168 (31); 167 (100); 166 (72); 165 (15); 156 (27); 155 (22); 153 (22); 152 (24); 142 (23); 141 (48); 140 (18); 139 (19); 130 (39); 129 (47); 127 (23); 121 (18); 121 (23).

Chem. Name	**3-methyl-*N*-(m-tolyl)-*N*-(p-tolyl)aniline (6c)**
Lit. Ref.	



METHOD:

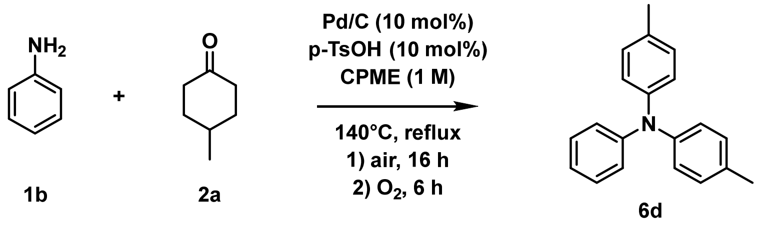
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-toluidina (**1a**) (0.5 mmol, 53 mg), and 3-methylcyclohexanone (**2c**) (5 mmol, 0.5 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 3-methyl-*N*-(m-tolyl)-*N*-(p-tolyl)aniline (**6c**) was obtained with an isolated yield of 70%.

Mol Formula		$C_{21}H_{21}N$		**m.p.**	111-113°C
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR 400 MHz $CDCl_3$	7.12	2	*t*	7.8	
	7.07	2	*d*	8.6	
	6.89	2	*s*		
	6.86	2	*d*	7.4	
	6.80	2	*d*	7.4	
	2.33	3	*s*		
	2.26	6	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.23; 145.60; 139.04; 132.49; 129.02; 124.90; 124.51; 123.23; 121.09; 21.57; 20.97.

GC-EIMS (m/z, %): 385 (45); 269 (23); 287 (75); 196 (58); 206 (20)

Chem. Name	**4-methyl-*N*-phenyl-*N*-(p-tolyl)aniline (6d)**
Lit. Ref.	Sachin G. Modha, Mihai V. Popescu and Michael F. Greaney, *J. Org. Chem.* 2017, **82**, 11933-11938.



METHOD:

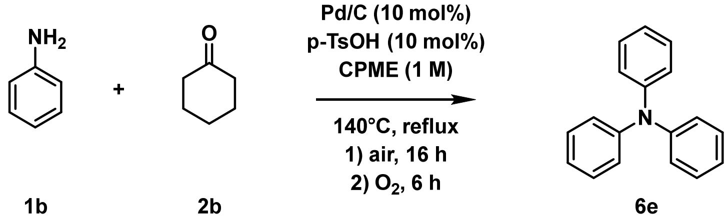
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), aniline (**1b**) (0.5 mmol, 46 μL), and 4-methylcyclohexanone (**2c**) (5 mmol, 0.6 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-methyl-*N*-phenyl-*N*-(p-tolyl)aniline (**6d**) was obtained with an isolated yield of 75%.

Mol Formula		$C_{20}H_{19}N$		**m.p.**	111-113°C
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.20	2	*t*	7.7	
	7.06-6.97	10	*m*		
	6.93	1	*t*	7.5	
	2.31	6	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.41; 145.59; 132.43; 129.96; 129.15; 124.59; 123.08; 121.83; 20.93.

GC-EIMS (m/z, %): 275 (25); 273 (100); 258 (63); 257 (97); 256 (46); 254 (17); 243 (30); 241 (15); 194 (18); 182 (15); 181 (29); 180 (60); 167 (47); 166 (24); 156 (17); 155 (21); 154 (16); 153 (17); 152 (15); 141 (15); 137 (34); 135 (20); 128 (29); 127 (22); 115 (17); 91 (21); 77 (19).

Chem. Name	**Triphenylamine (6e)**
Lit. Ref.	T. Yamamoto, M. Nishiyama and Y. Koie, *J. Chem. Soc., Perkin Trans. 1*, 1998, **39**, 2367-2370.



METHOD:

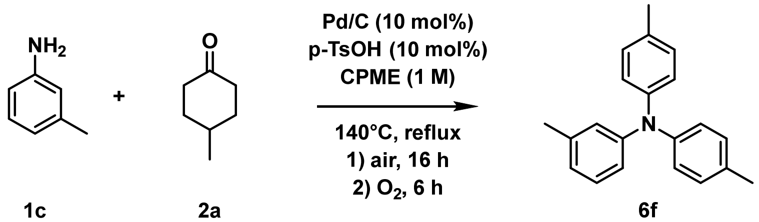
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), aniline (**1b**) (0.5 mmol, 46 µL), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product triphenylamine (**6e**) was obtained with an isolated yield of 63%.

Mol Formula		$C_{18}H_{15}N$		**m.p.**	126-128°C
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.23	6	*d*	7.6	
	7.09	6	*d*	7.9	
	7.00	3	*t*	7.2	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.00; 129.33; 124.30; 122.80.

GC-EIMS (m/z, %): 247 (21); 246 (100); 245 (39); 168 (15).

Chem. Name	**3-methyl-*N*,*N*-di-p-tolylaniline (6f)**
Lit. Ref.	



1c **2a** **6f**

METHOD:

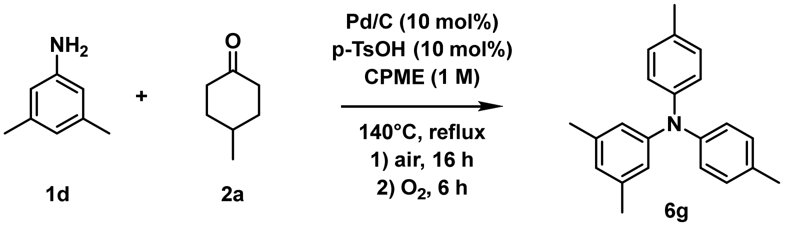
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 3-methylaniline (**1c**) (0.5 mmol, 54 µL), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 3-methyl-*N*,*N*-di-p-tolylaniline (**6f**) was obtained with an isolated yield of 69%.

Mol Formula		$C_{21}H_{21}N$		**m.p.**	198-200°C
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR **400 MHz** **$CDCl_3$**	7.09	1	*t*	7.5	
	7.05	4	*d*	7.8	
	6.97	4	*d*	7.8	
	6.87	1	*s*		
	6.82	1	*d*	7.8	
	6.76	1	*d*	7.4	
	2.31	6	*s*		
	2.24	3	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.34; 145.71; 138.98; 132.23; 129.90; 128.97; 124.51; 123.91; 122.87; 120.51; 31.06; 20.92.

GC-EIMS (m/z, %): 329 (28); 320 (50); 287 (78); 200 (23); 158 (30)

Chem. Name	**3,5-dimethyl-*N,N*-di-p-tolylaniline (6g)**
Lit. Ref.	



1d **2a** **6g**

METHOD:

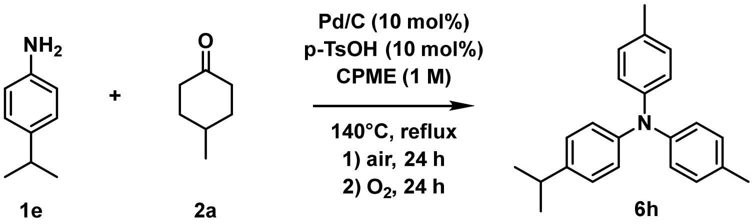
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 3,5-dimethylaniline (**1d**) (0.5 mmol, 62 µL), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 3,5-dimethyl-*N,N*-di-p-tolylaniline (**6g**) was obtained with an isolated yield of 66%.

Mol Formula		$C_{22}H_{23}N$		**m.p.**	93-96°C
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.04	4	*d*	8.2	
	6.96	4	*d*	8.2	
	6.67	2	*s*		
	6.61	1	*s*		
	2.31	6	*s*		
	2.20	6	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.27; 145.80; 138.78; 132.06; 129.87; 124.45; 124.02; 121.30; 21.46; 20.94.

GC-EIMS (m/z, %): 303 (29); 302 (40); 301 (100); 300 (32); 287 (20); 286 (38); 285 (58); 284 (44); 281 (20); 272 (22); 271 (24); 270 (20); 208 (22); 207 (41); 195 (29); 194 (46); 193 (16); 181 (22); 180 (29); 169 (24); 165 (16); 77 (25); 73 (23); 65 (24); 28 (38).

Chem. Name	**4-isopropyl-*N*,*N*-di-p-tolylaniline (6h)**
Lit. Ref.	



METHOD:

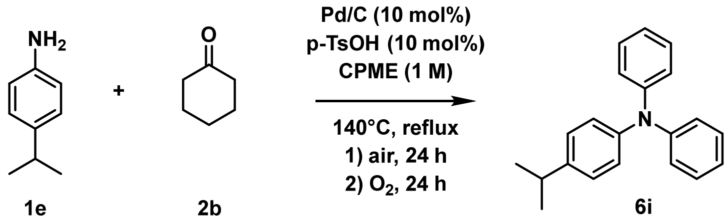
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 4-isopropyl-aniline (**1e**) (0.5 mmol, 70 µL), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-isopropyl-*N*,*N*-di-p-tolylaniline (**6h**) was obtained with an isolated yield of 85%.

Mol Formula		$C_{23}H_{25}N$		**m.p.**	Oil
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.10	2	*d*	8.5	
	7.08-7.06	4	*d*	8.4	
	6.98	6	*d*	8.6	
	2.90	1	*ept*	6.9	
	2.32	6	*s*		
	1.26	6	*d*	6.9	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 145.97; 145.83; 142.75; 131.93; 129.86; 127.10; 124.15; 123.56; 33.55; 24.21; 20.91.

GC-EIMS (m/z, %): 316 (17); 315 (100); 301 (16); 300 (94); 192 (15); 190 (16); 180 (18); 92 (16); 91 (28); 65 (21).

Chem. Name	**4-isopropyl-*N,N*-diphenylaniline (6i)**
Lit. Ref.	



METHOD:

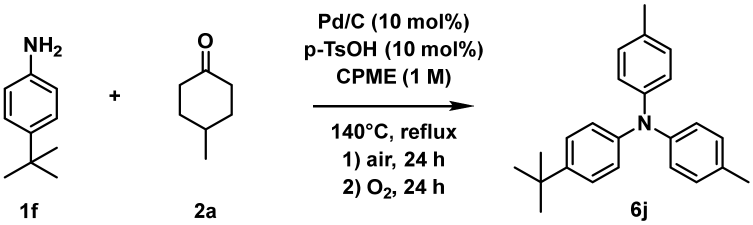
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 4-isopropyl-aniline (**1e**) (0.5 mmol, 70 µL), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-isopropyl-*N*,*N*-diphenylaniline (**6i**) was obtained with an isolated yield of 87%.

Mol Formula		$C_{21}H_{21}N$		**m.p.**	Oil
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR	7.23	4	*t*	8.5	
400 MHz	7.12-7.06	6	*m*		
$CDCl_3$	7.03-6.96	4	*m*		
	2.91-2.84	1	*ept*	6.9	
	1.25	6	*d*	6.9	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.19; 145.52; 143.76; 129.24; 127.30; 124.73; 123.88; 122.39; 33.62; 24.19.

GC-EIMS (m/z, %): 289 (31); 288 (100); 287 (100); 286 (25); 274 (43); 273 (100); 272 (100); 271 (50); 270 (52); 257 (23); 256 (71); 254 (28); 245 (32); 244 (88); 243 (71); 242 (42); 241 (33); 195 (24); 194 (53); 193 (47); 192 (32); 191 (19); 180 (49); 179 (22); 178 (20); 169 (21); 168 (100); 167 (100); 166 (65); 165 (33); 154 (18); 153 (26); 152 (30); 141 (37); 140 (18); 139 (21); 136 (58); 128 (48); 127 (28); 121 (16); 115 (40); 103 (20); 92 (18); 91 (47); 78 (22); 77 (83); 65 (16); 51 (34).

Chem. Name	**4-(tert-butyl)-*N,N*-di-p-tolylaniline (6j)**
Lit. Ref.	



METHOD:

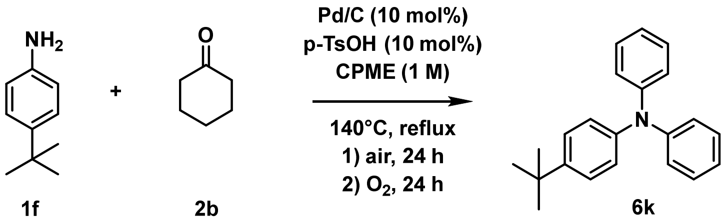
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 4-tert-buthylaniline (**1f**) (80 µL; 0.5 mmol), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-(tert-butyl)-*N*,*N*-di-p-tolylaniline (**6j**) was obtained with an isolated yield of 61%.

Mol Formula		$C_{24}H_{27}N$		**m.p.**	68-71°C
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR **400 MHz** **$CDCl_3$**	7.24	2	*d*	8.5	
	7.06	4	*d*	8.3	
	7.011-6.98	6	*m*		
	2.33	6	*s*		
	1.33	9	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 148.14; 145.91; 145.15; 129.25; 126.19; 124.14; 123.98; 122.45; 31.59, 20.91.

GC-EIMS (m/z, %): 301 (60); 302 (15); 286 (100); 287 (24).

Chem. Name	**4-(tert-butyl)-*N,N*-diphenylaniline (6k)**
Lit. Ref.	



METHOD:

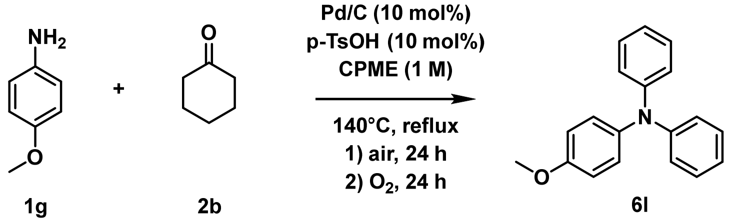
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), 4-tert-buthylaniline (**1f**) (80 µL; 0.5 mmol), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-(tert-butyl)-*N*,*N*-diphenylaniline (**6k**) was obtained with an isolated yield of 55%.

Mol Formula		$C_{22}H_{23}N$		**m.p.**	68-71°C
^{1}H NMR 400 MHz CDCl$_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.25-7.21	5	*m*		
	7.08	4	*d*	7.8	
	7.03-6.96	5	*m*		
	1.33	9	*s*		

^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 148.14;145.90; 145.15; 129.25;126.19; 124.14; 123.98; 122.45; 31.58.

GC-EIMS (m/z, %): 301 (60); 302 (15); 286 (100); 287 (24).

Chem. Name	**4-methoxy-*N,N*-diphenylaniline (6l)**
Lit. Ref.	T. Yamamoto, M. Nishiyama and Y. Koie, *J. Chem. Soc., Perkin Trans. 1*, 1998, **39**, 2367-2370.



METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-anisidine (**1g**) (0.5 mmol, 62 mg), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-methoxy-*N,N*-diphenylaniline (**6l**) was obtained with an isolated yield of 75%.

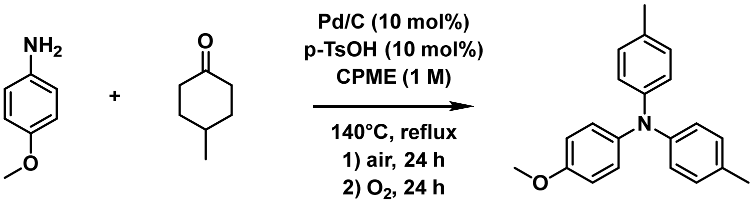
Mol Formula	$C_{19}H_{17}NO$	**m.p.**	102-106 °C

	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR **400 MHz** **CDCl$_3$**	7.19-7.23	4	*t*	7.7
	7.03-7.09	6	*q*	
	6.95	2	*t*	7.1
	6.85	2	*d*	8.7
	3.81	3	*s*	

^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 156.29; 148.31; 140.91; 129.20; 127.45; 123.01; 121.96; 114.88; 55.61.

GC-EIMS (m/z, %): 277 (22); 276 (100); 262 (17); 261 (83); 77 (16).

Chem. Name	**4-methoxy-*N,N*-di-p-tolylaniline (6m)**
Lit. Ref.	Ganesh M. Kumbhar, Ajit H. Deshmukh, Sanjay S. Chavan, *J. Org. Chem.* 2024, **1021**, 123351.



1g **2a** **6m**

METHOD:

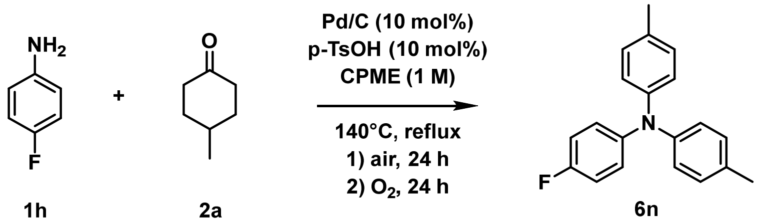
In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-anisidine (**1g**) (0.5 mmol, 62 mg), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 16 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 6 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure product 4-methoxy-*N,N*-di-p-tolylaniline (**6m**) was obtained with an isolated yield of 72%.

Mol Formula		$C_{21}H_{21}NO$		**m.p.**	70-72°C
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**	
	7.04-7.01	6	*m*		
	6.92	4	*d*	8.1	
	6.81	2	*d*	8.1	
	3.79	3	*s*		
	2.29	6	*s*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 155.74; 146.07; 141.47; 131.39; 129.80; 126.56; 123.20; 114.73; 55.62; 20.85

GC-EIMS (m/z, %): 304 (79); 303 (100); 289 (55); 288 (100); 152 (20); 91 (19); 65 (20).

Chem. Name	**4-fluoro-*N,N*-di-p-tolylaniline (6n)**
Lit. Ref.	



METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-fluoroaniline (**1h**) (0.5 mmol, 56 mg), and 4-methylcyclohexanone (**2a**) (5 mmol, 0.6 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure 4-fluoro-*N,N*-di-p-tolylaniline (**6n**) was obtained with an isolated yield of 62%.

Mol Formula	$C_{20}H_{18}FN$	**m.p.**	80-82°C

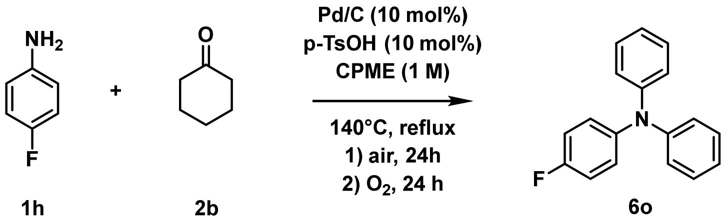
	δ value	**No. H**	**Mult.**	**j value/Hz**
^{1}H NMR **400 MHz** **$CDCl_3$**	7.05	4	*d*	8.4
	7.03-7.00	2	*m*	
	6.95-6.90	6	*m*	
	2.30	6	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 159.73; 157.33; 145.72; 144.49; 144.46; 132.20; 129.98; 125.50; 125.42; 123.90; 116.06; 115.84; 20.89.

^{19}F NMR (100.6 MHz, $CDCl_3$) δ: -120.98.

GC-EIMS (m/z, %): 292 (20); 291 (100); 290 (19); 240 (25); 91 (23); 65 (24).

Chem. Name	**4-fluoro-*N,N*-diphenylaniline (6o)**
Lit. Ref.	Sachin G. Modha, Mihai V. Popescu and Michael F. Greaney, *J. Org. Chem.* 2017, **82**, 11933-11938.



METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), p-fluoroaniline (**1h**) (0.5 mmol, 56 mg), and cyclohexanone (**2b**) (5 mmol, 0.5 mL) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure 4-fluoro-*N,N*-diphenylaniline (**6o**) was obtained with an isolated yield of 75%.

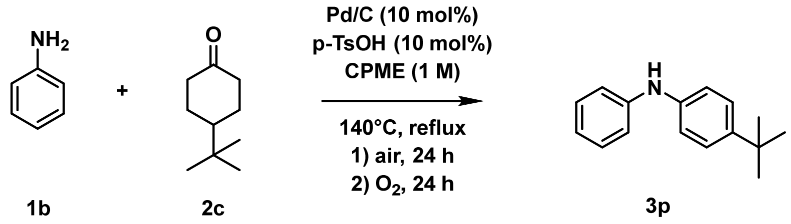
Mol Formula		$C_{18}H_{14}FN$		**m.p.**	Oil
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR	7.23	4	*t*	8.2	
400 MHz	7.08-7.03	6	*m*		
$CDCl_3$	7.01-6.94	4	*m*		

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 160.26; 157.85; 148.03; 144.03; 129.38; 126.61; 123.67; 122.65; 116.31; 116.09

^{19}F NMR (100.6 MHz, $CDCl_3$) δ: -119.72.

GC-EIMS (m/z, %): 264 (90); 263 (100); 262 (100); 185 (47); 184 (31); 167 (23); 166 (26); 160 (16); 159 (19); 77 (22); 51 (25).

Chem. Name	**4-(tert-butyl)-*N*-(p-tolyl)aniline (3p)**
Lit. Ref.	



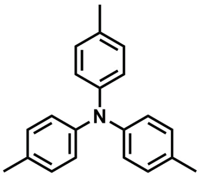
METHOD:

In a 10 mL round-bottom flask equipped with a magnetic stirrer, Pd/C (10 mol%; 53 mg), TsOH (10 mol%; 8.6 mg), CPME (1 M; 0,5 mL), aniline (**1b**) (0.5 mmol, 46 µL), and 4-tertbuthylcyclohexanone (**2c**) (5 mmol, 81 mg) were consecutively added. After 24 hours at 140°C in an open vessel under reflux, a balloon of O_2 was connected, and the reaction was stirred for an additional 24 hours at 140°C. The conversion was evaluated by gas chromatographic analysis. Pd/C was filtered off from the reaction mixture and washed with CPME (10 mL). The pure product was obtained after column chromatography using silica as the stationary phase and ETP as the eluent. After vacuum drying, the pure 4-(tert-butyl)-*N*-(p-tolyl)aniline (**3p**) was obtained with an isolated yield of 85%.

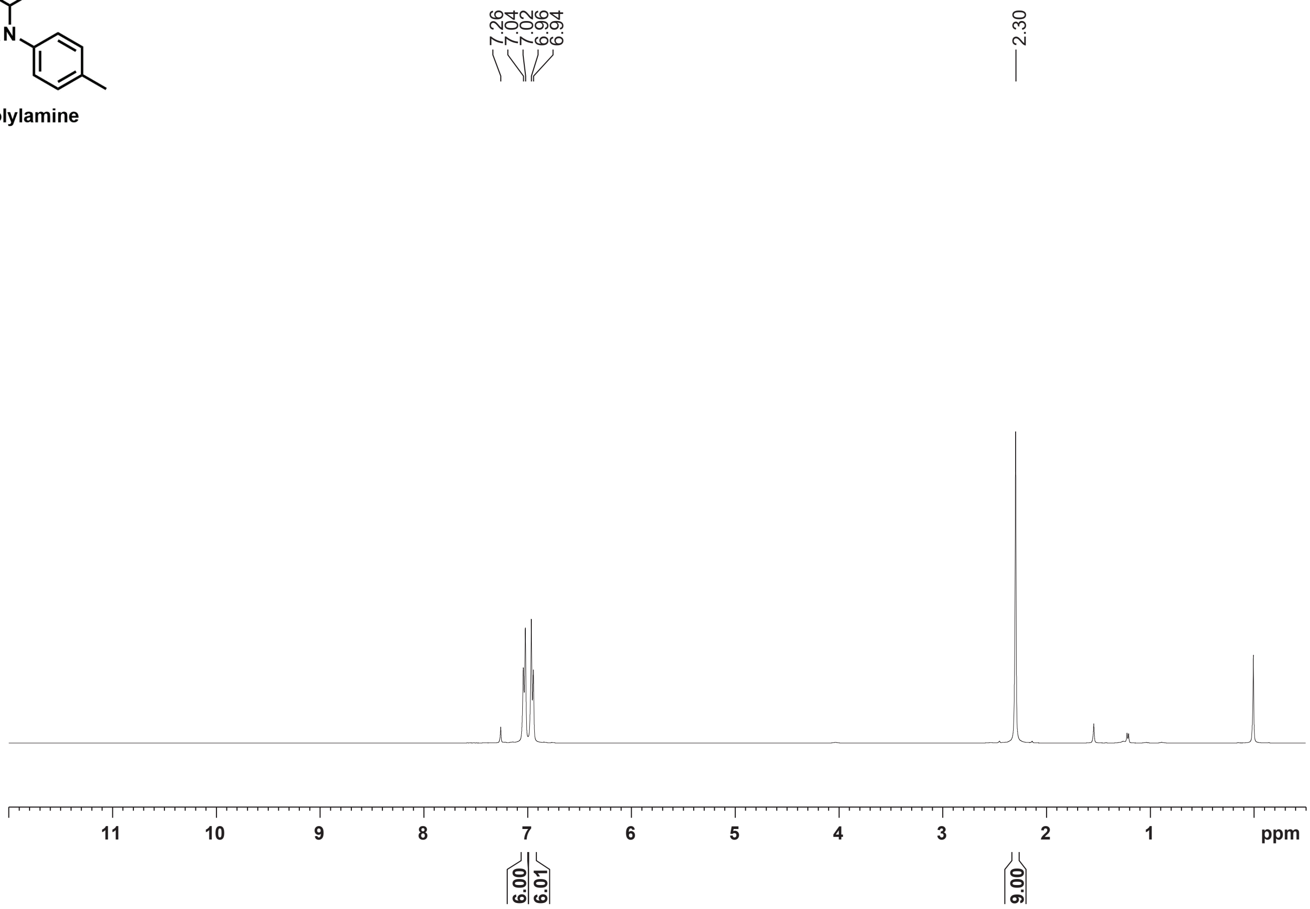
Mol Formula		$C_{17}H_{21}N$		**m.p.**	39-42°C
	δ value	**No. H**	**Mult.**	**j value/Hz**	
^{1}H NMR **400 MHz** **$CDCl_3$**	7.28	2	*s*		
	7.07	2	*d*		
	6.98	4	*t*		
	5.54	1	*s*		
	2.30	3	*s*		
	1.31	9	*s*		

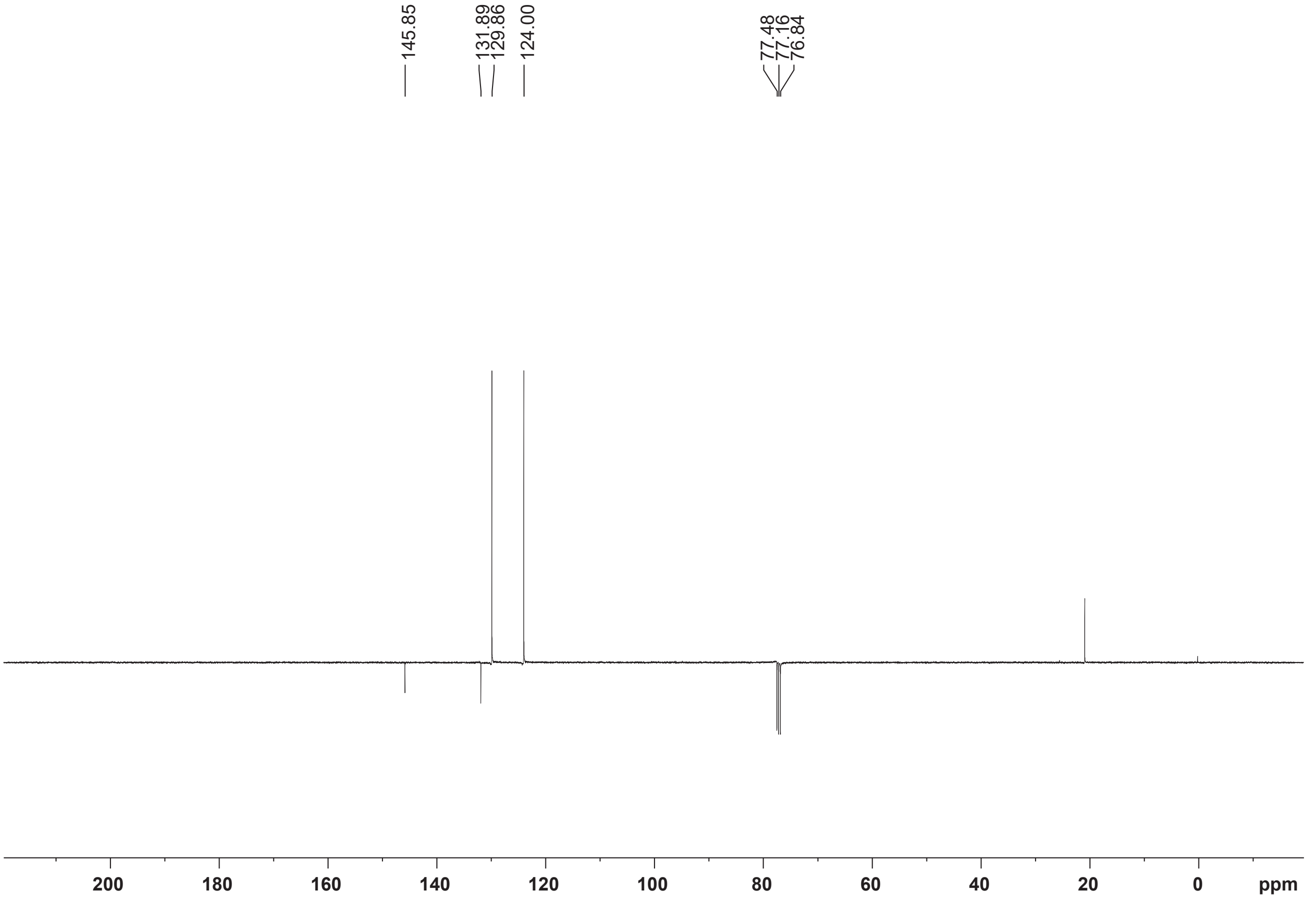
^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 143.59; 141.30; 141.02; 130.41; 129.93; 126.22; 118.29; 117.25; 31.62; 20.78.

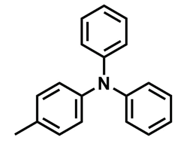
GC-EIMS (m/z, %): 239 (100); 225 (68); 224 (100); 209 (29); 208 (22); 182 (17); 180 (16); 167 (15); 98 (15); 91 (17).



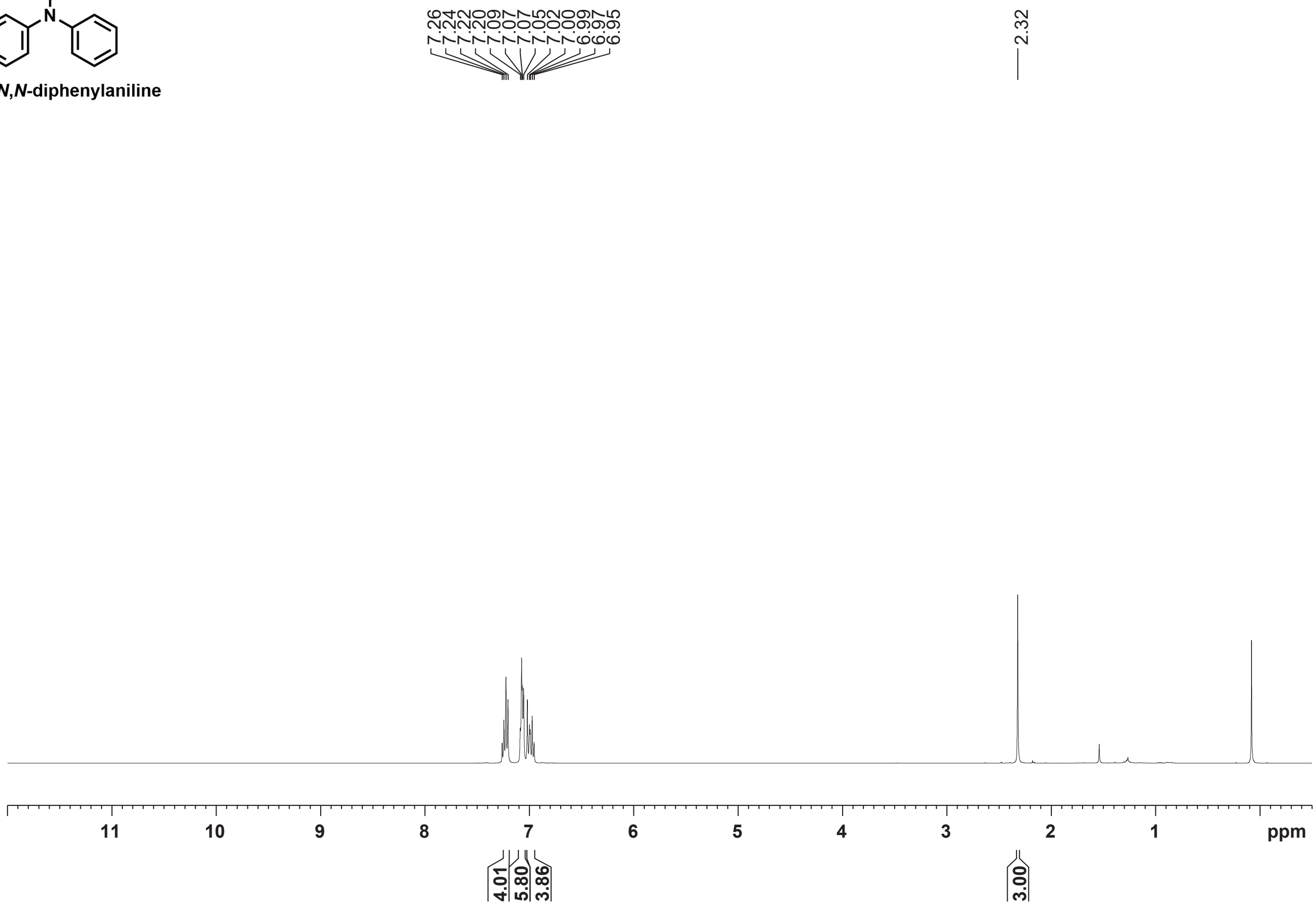
tri-*p*-tolylamine

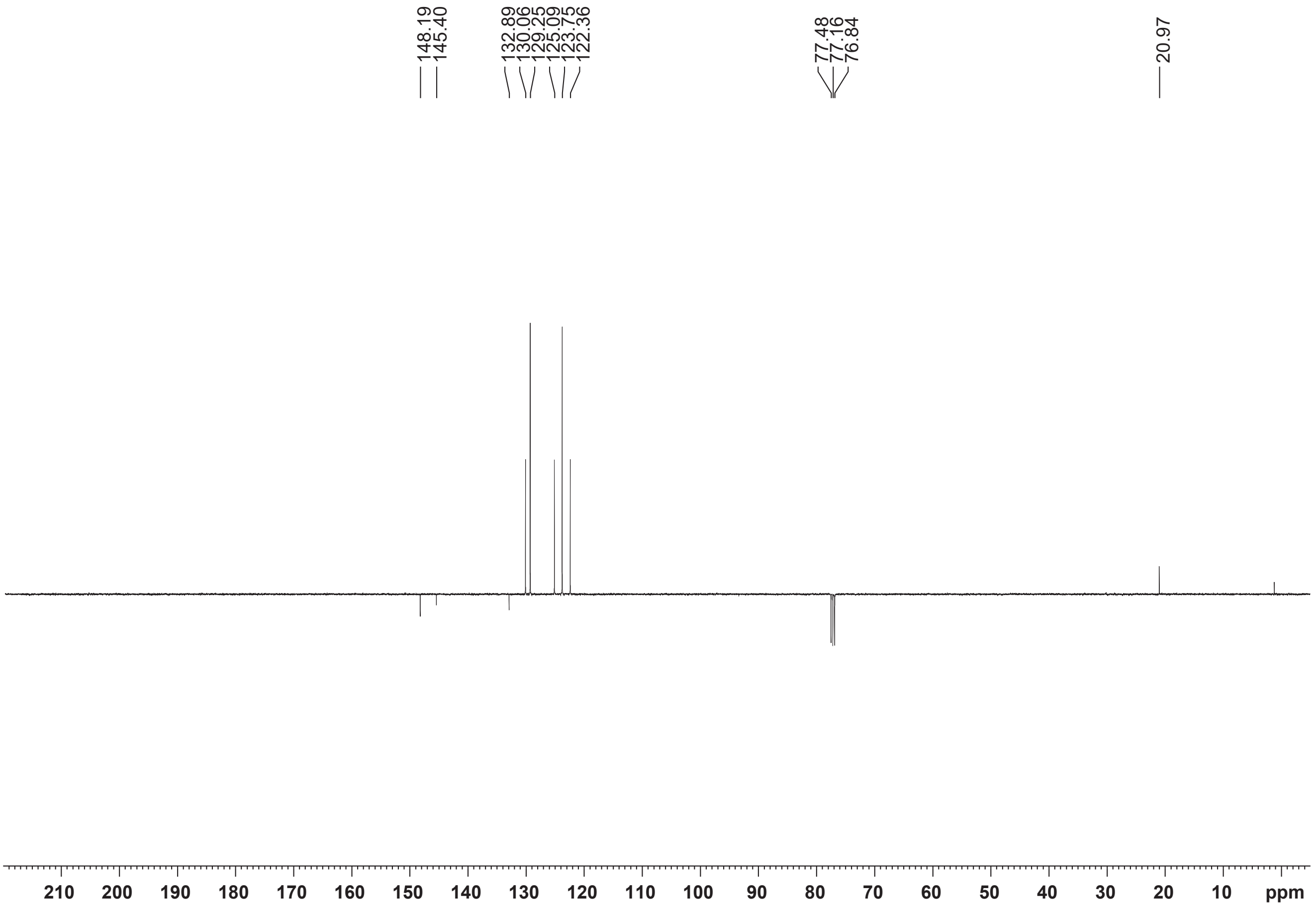


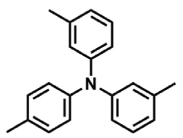




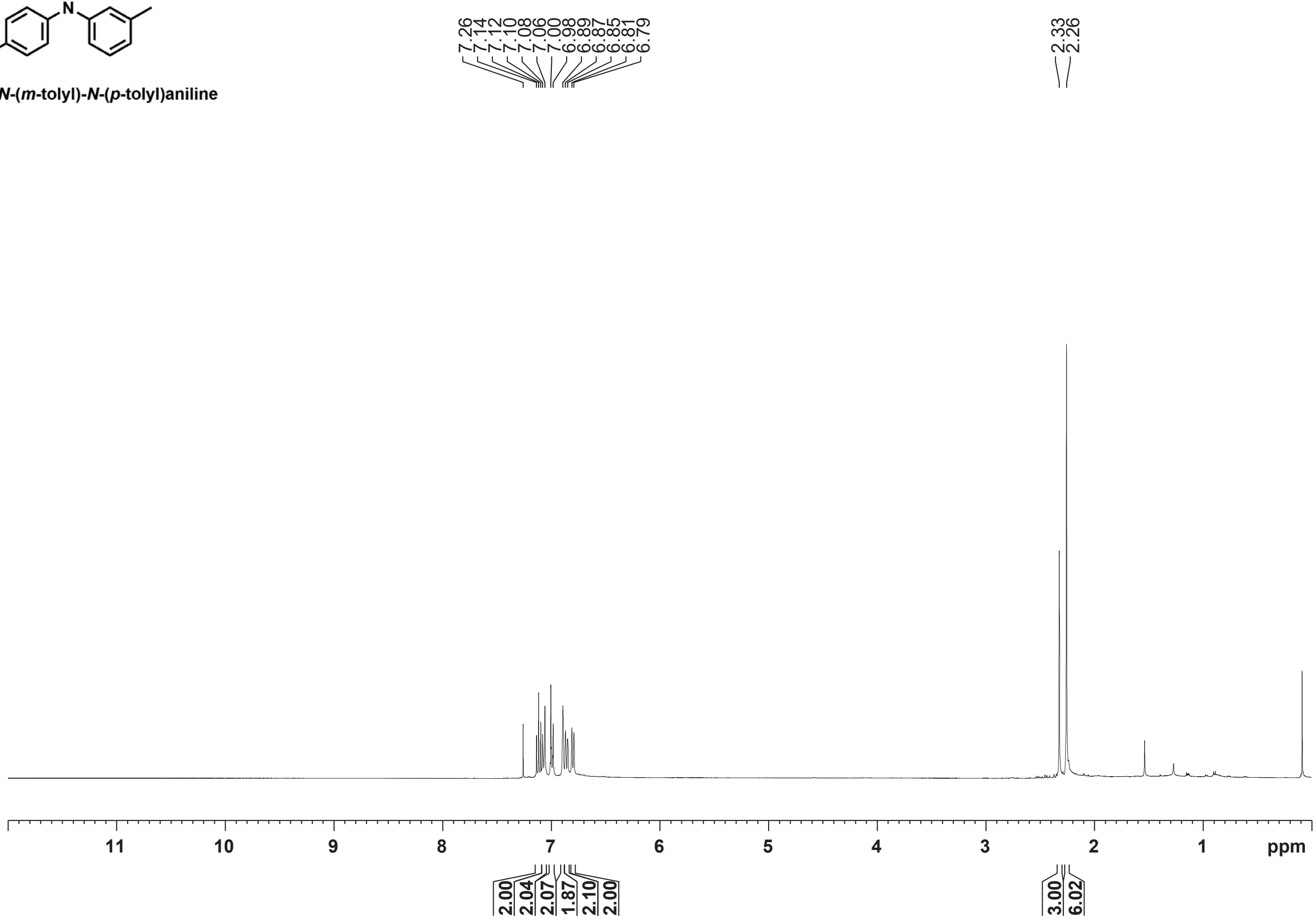
4-methyl-*N*,*N*-diphenylaniline

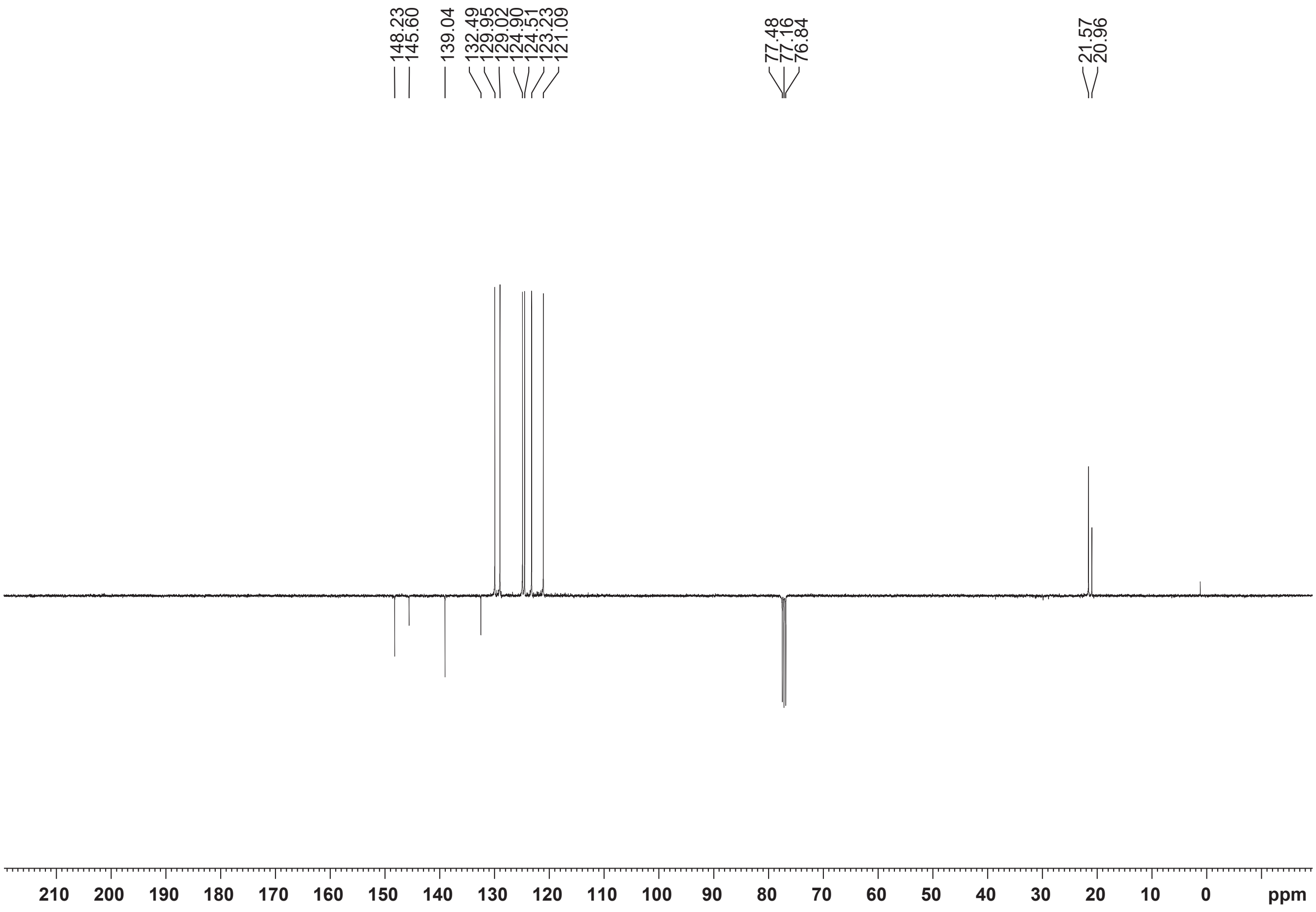


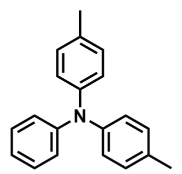




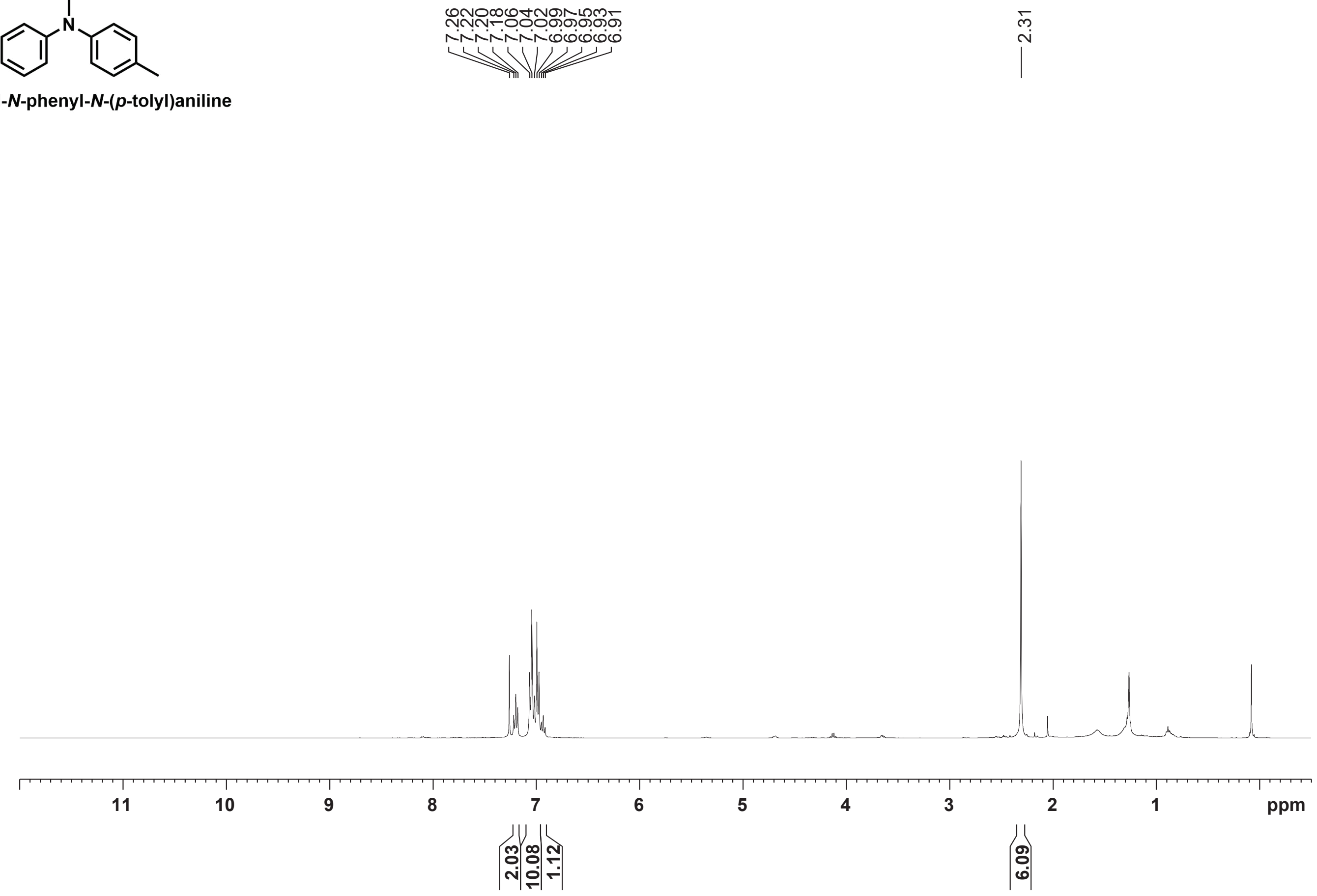
3-methyl-*N*-(*m*-tolyl)-*N*-(*p*-tolyl)aniline

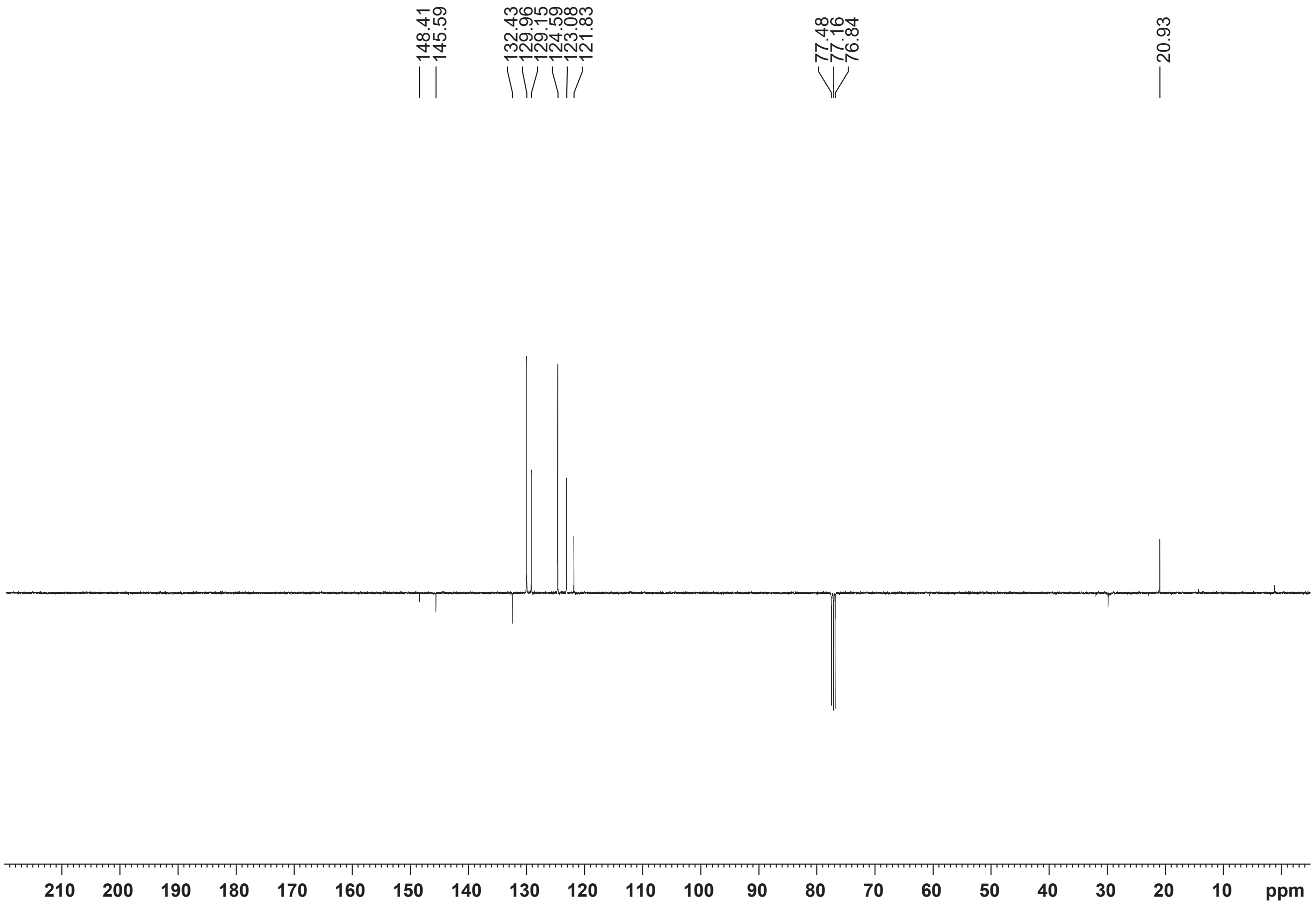


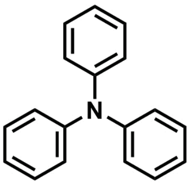




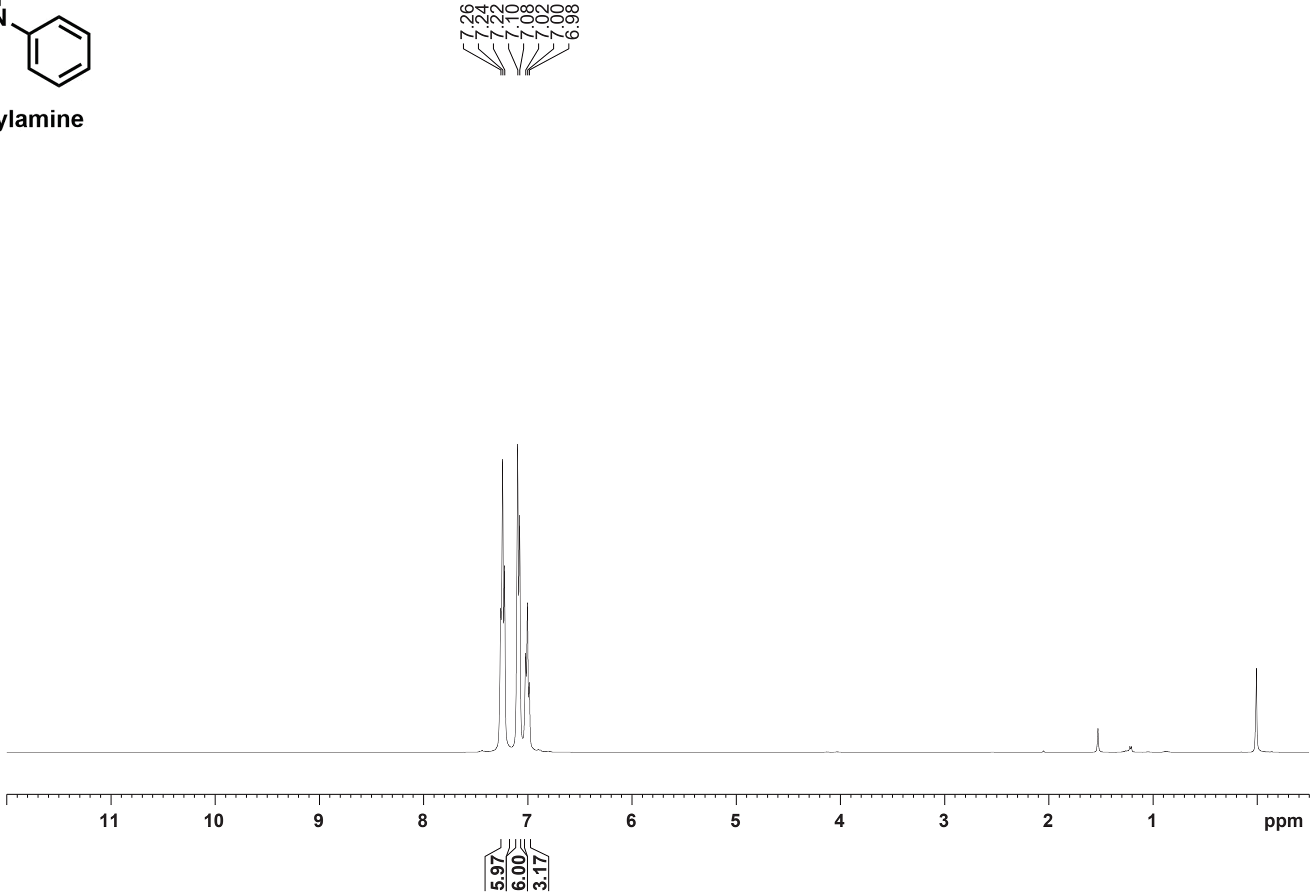
4-methyl-*N*-phenyl-*N*-(*p*-tolyl)aniline

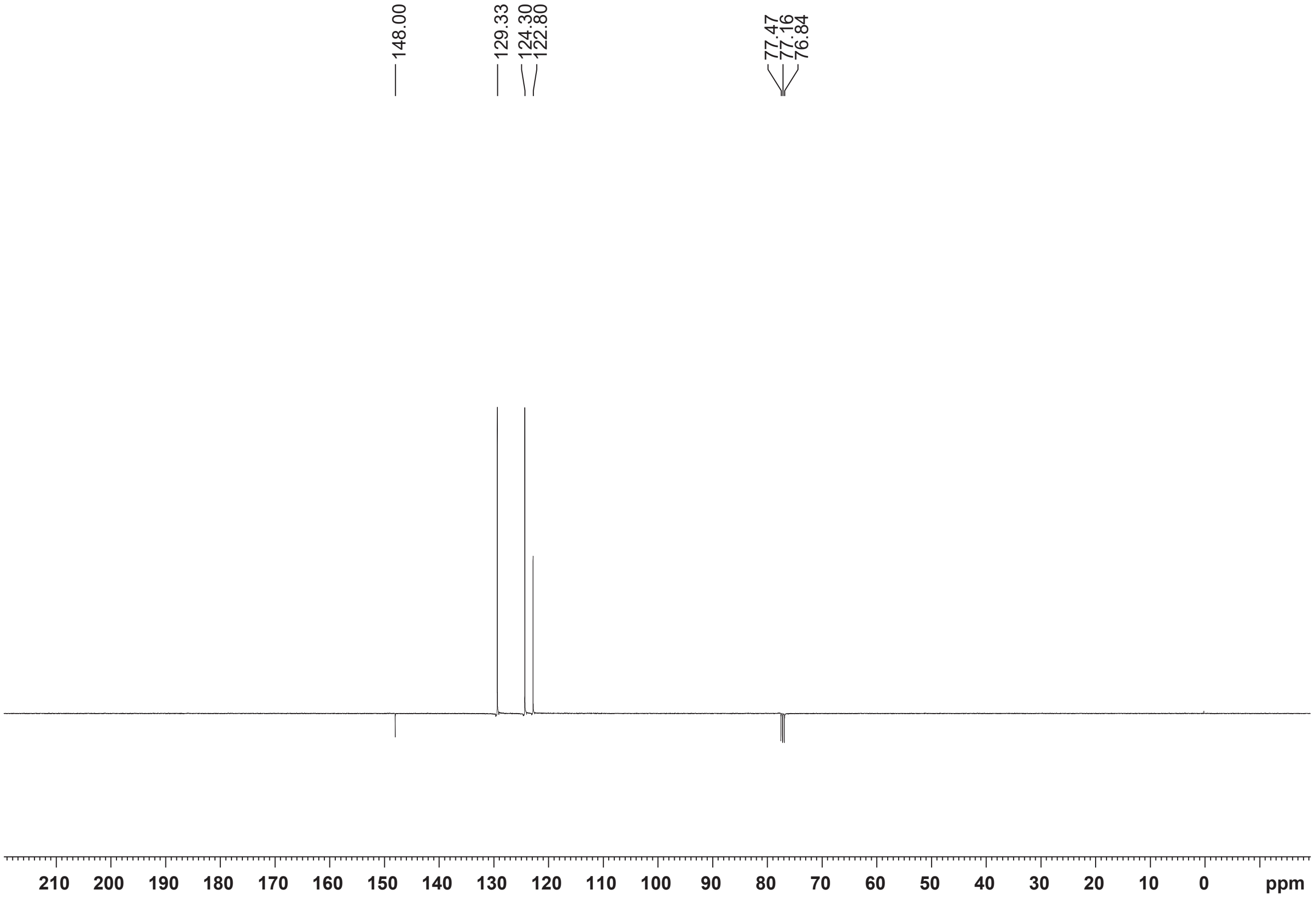


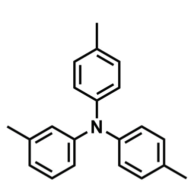




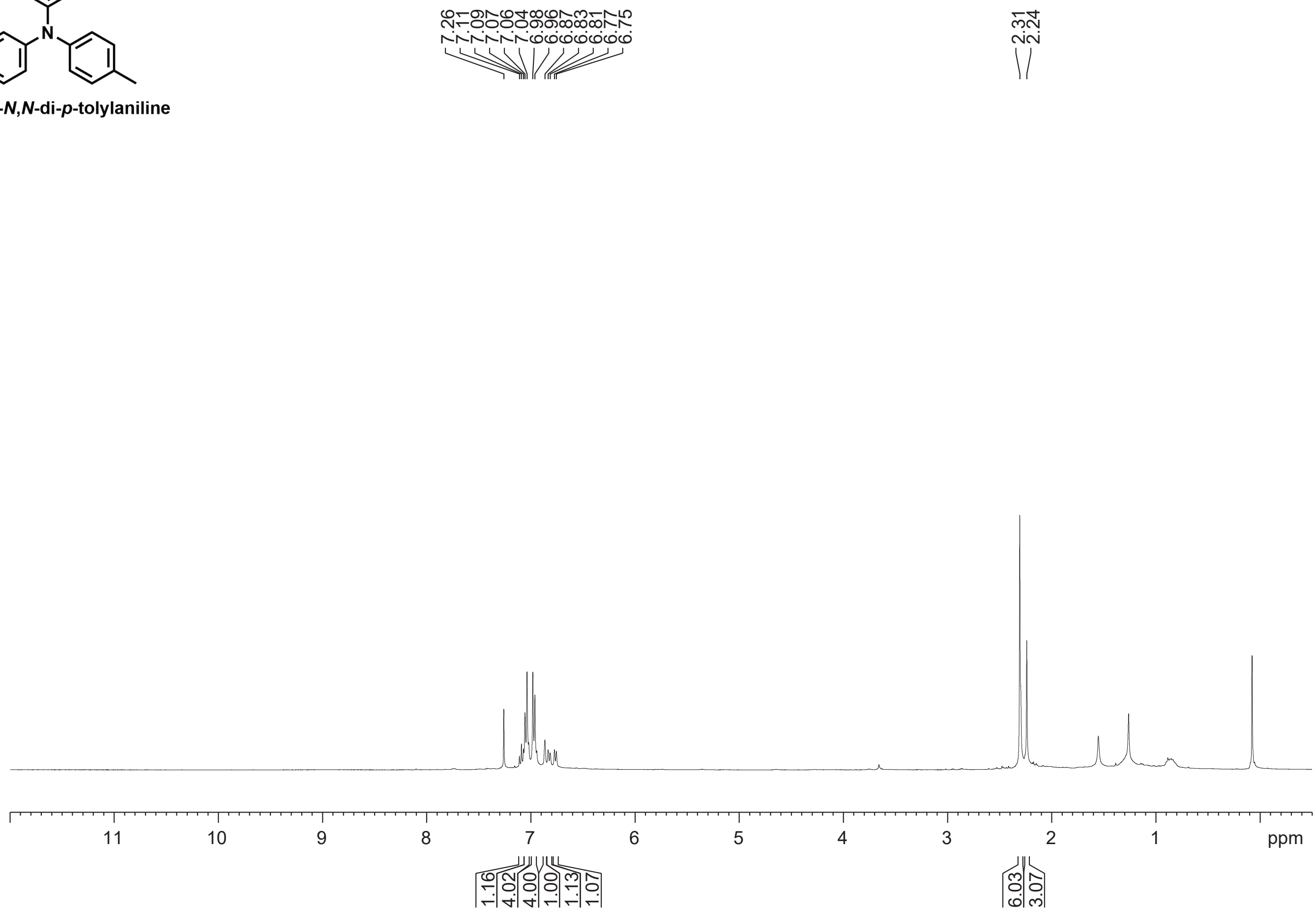
triphenylamine

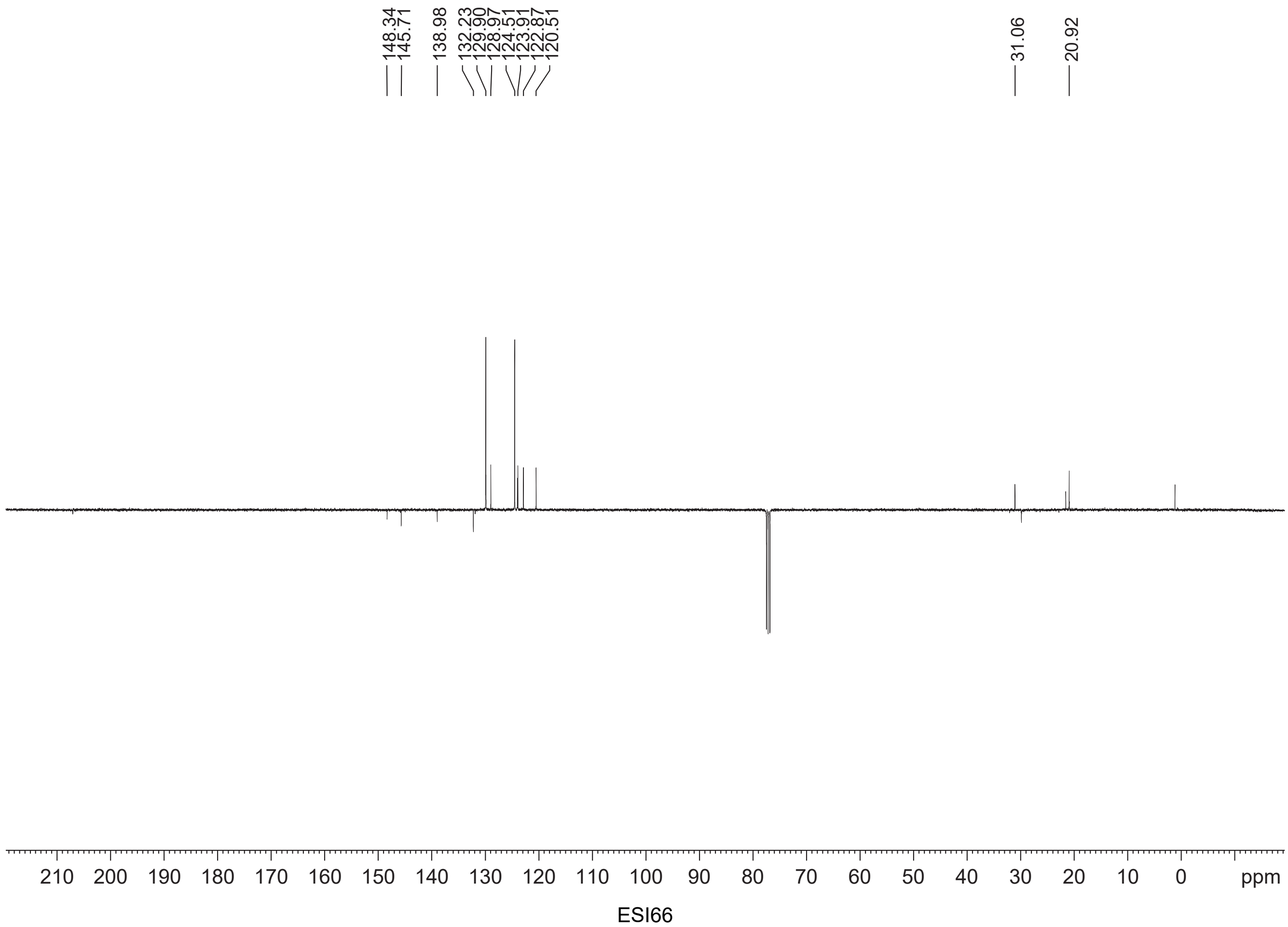


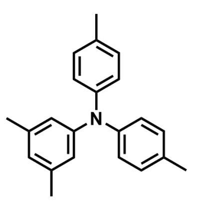




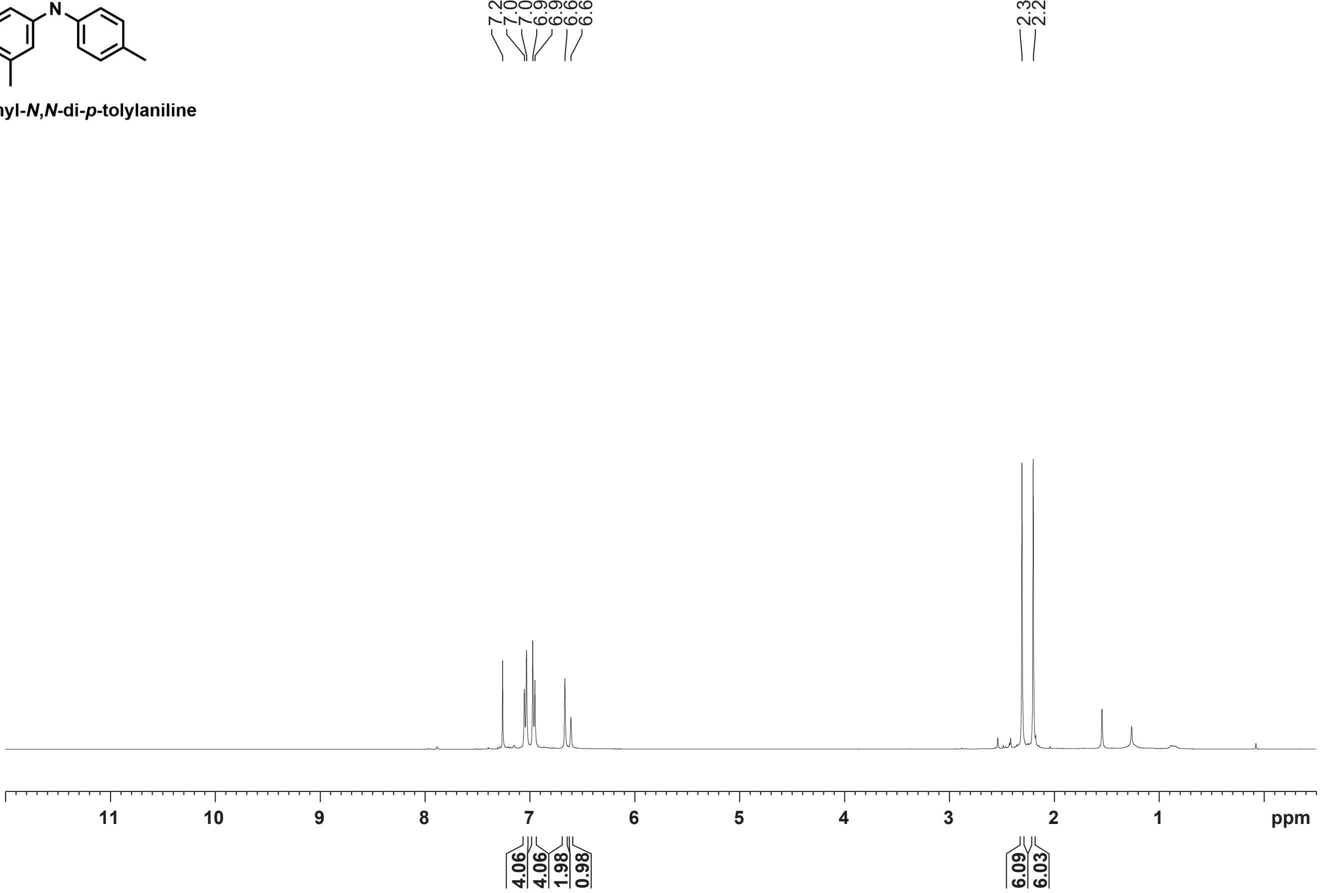
3-methyl-*N*,*N*-di-*p*-tolylaniline

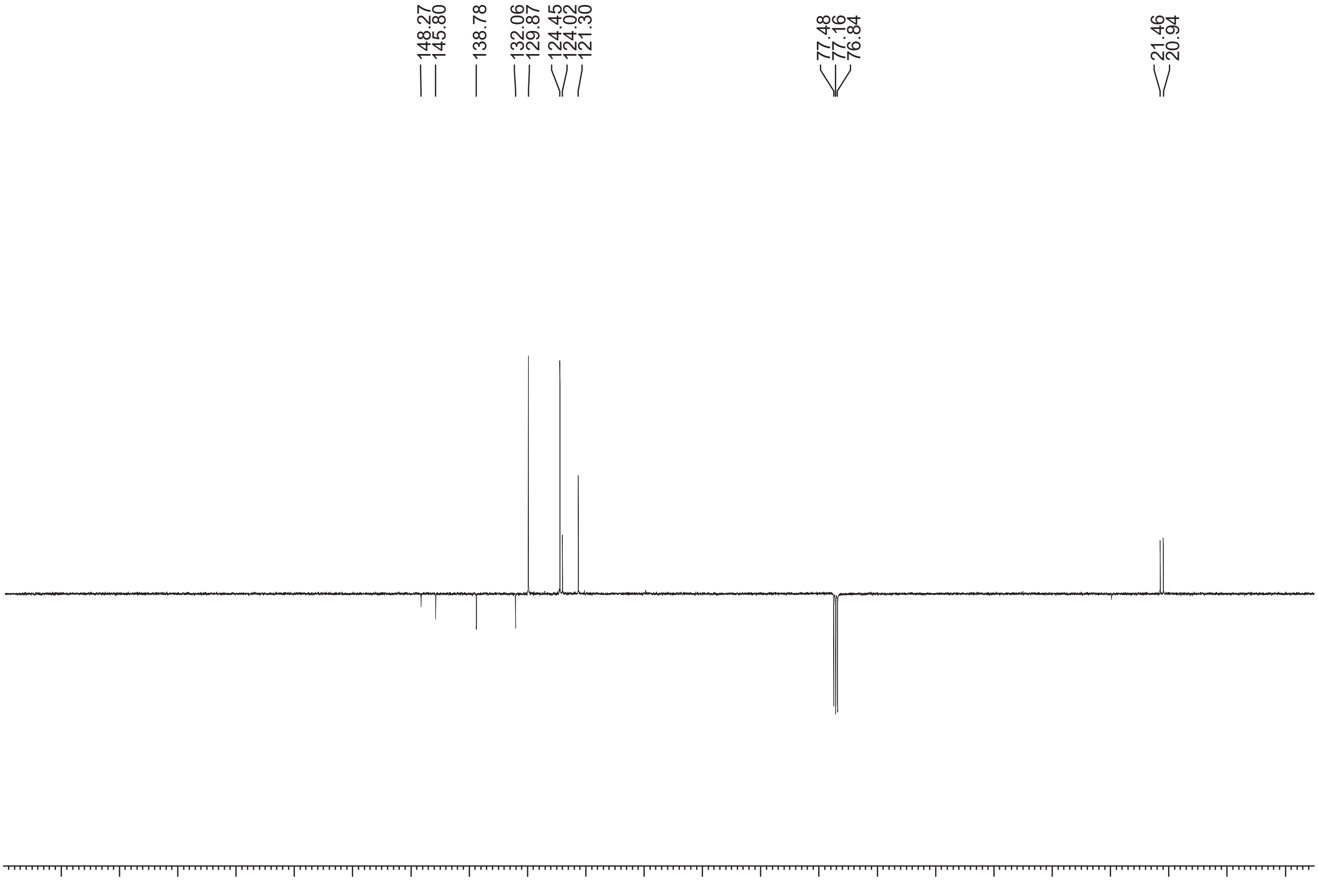


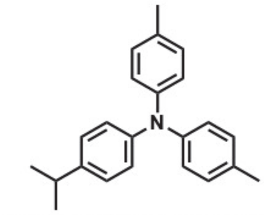




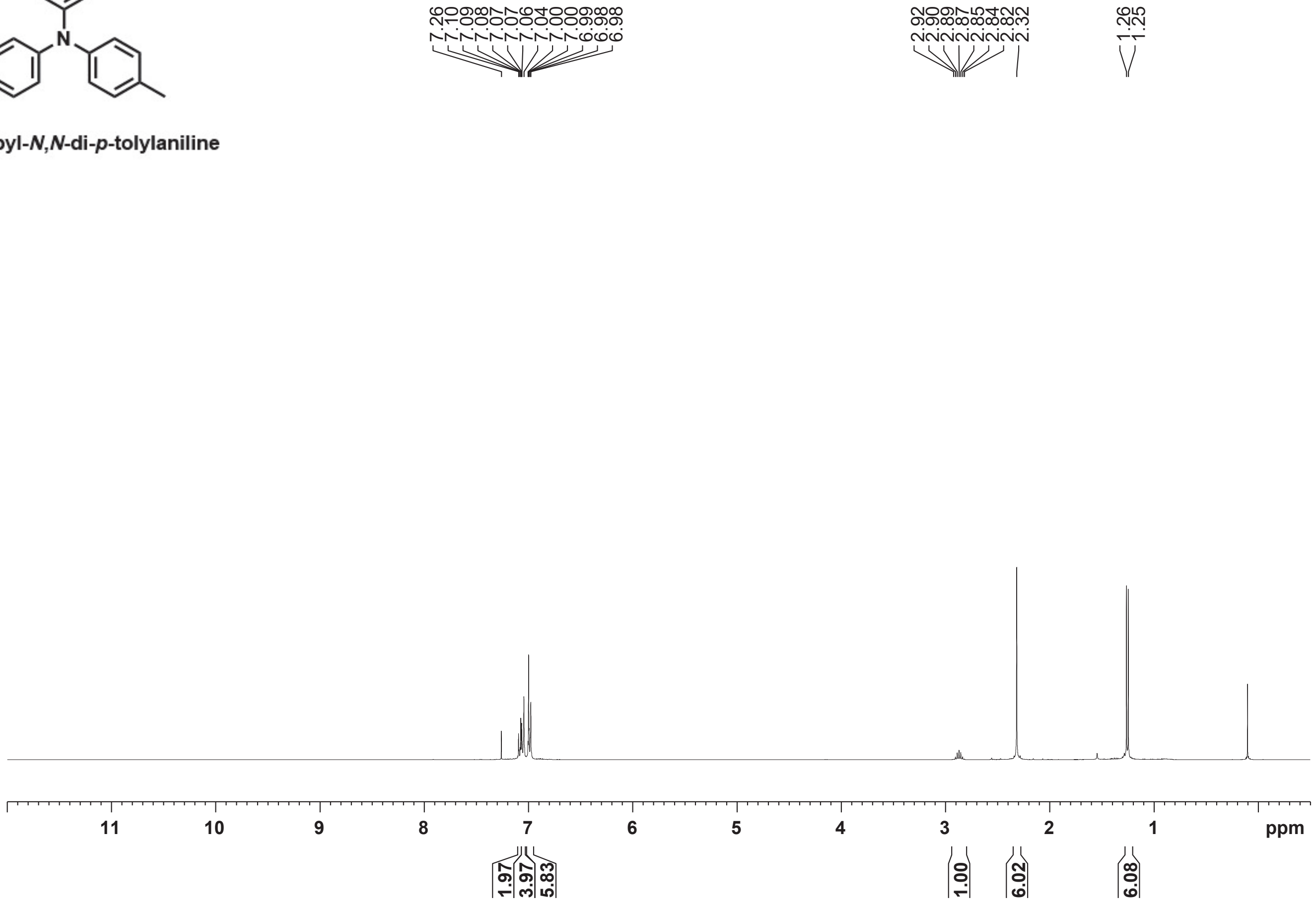
3,5-dimethyl-*N*,*N*-di-*p*-tolylaniline

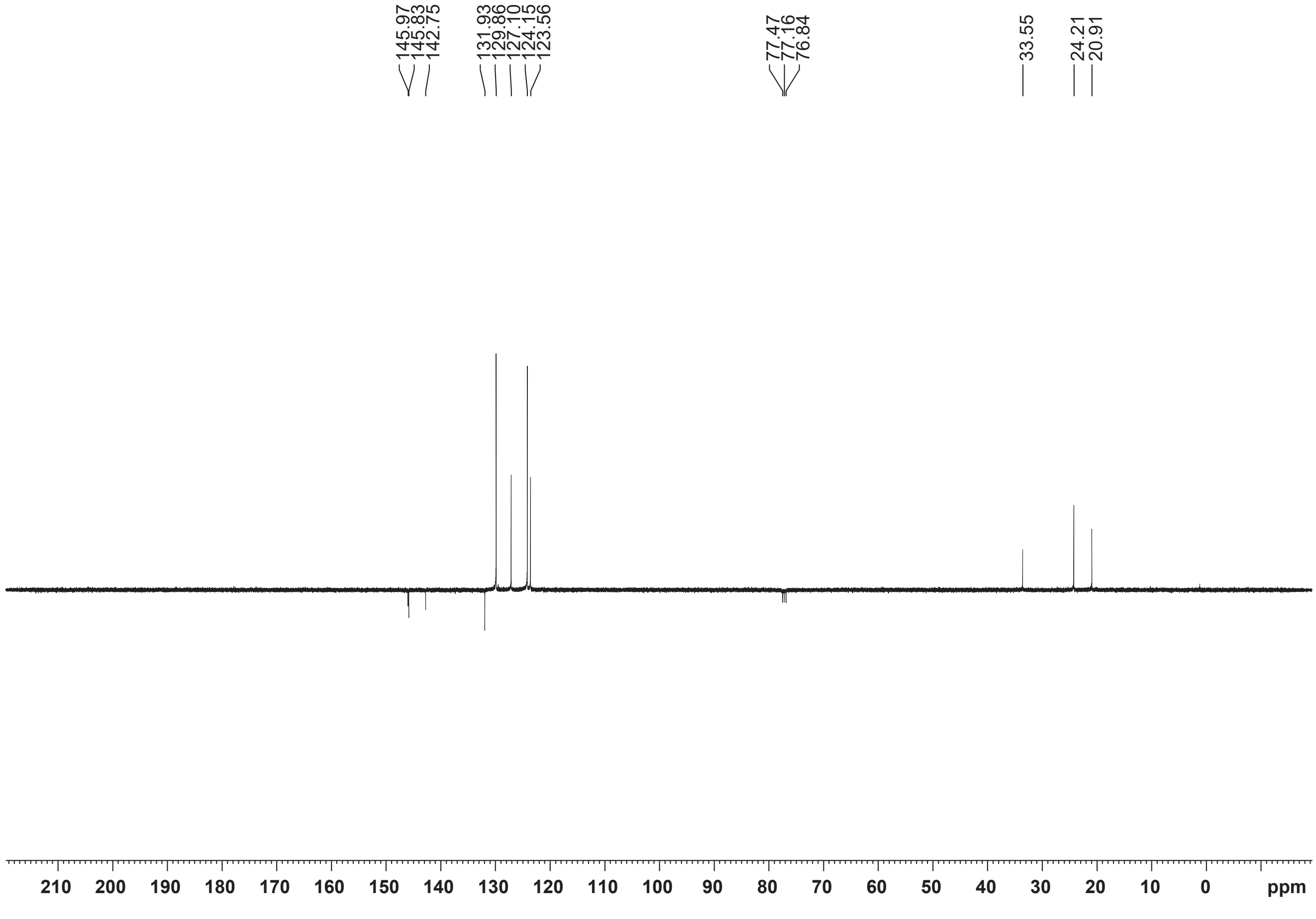


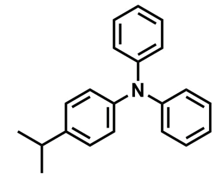




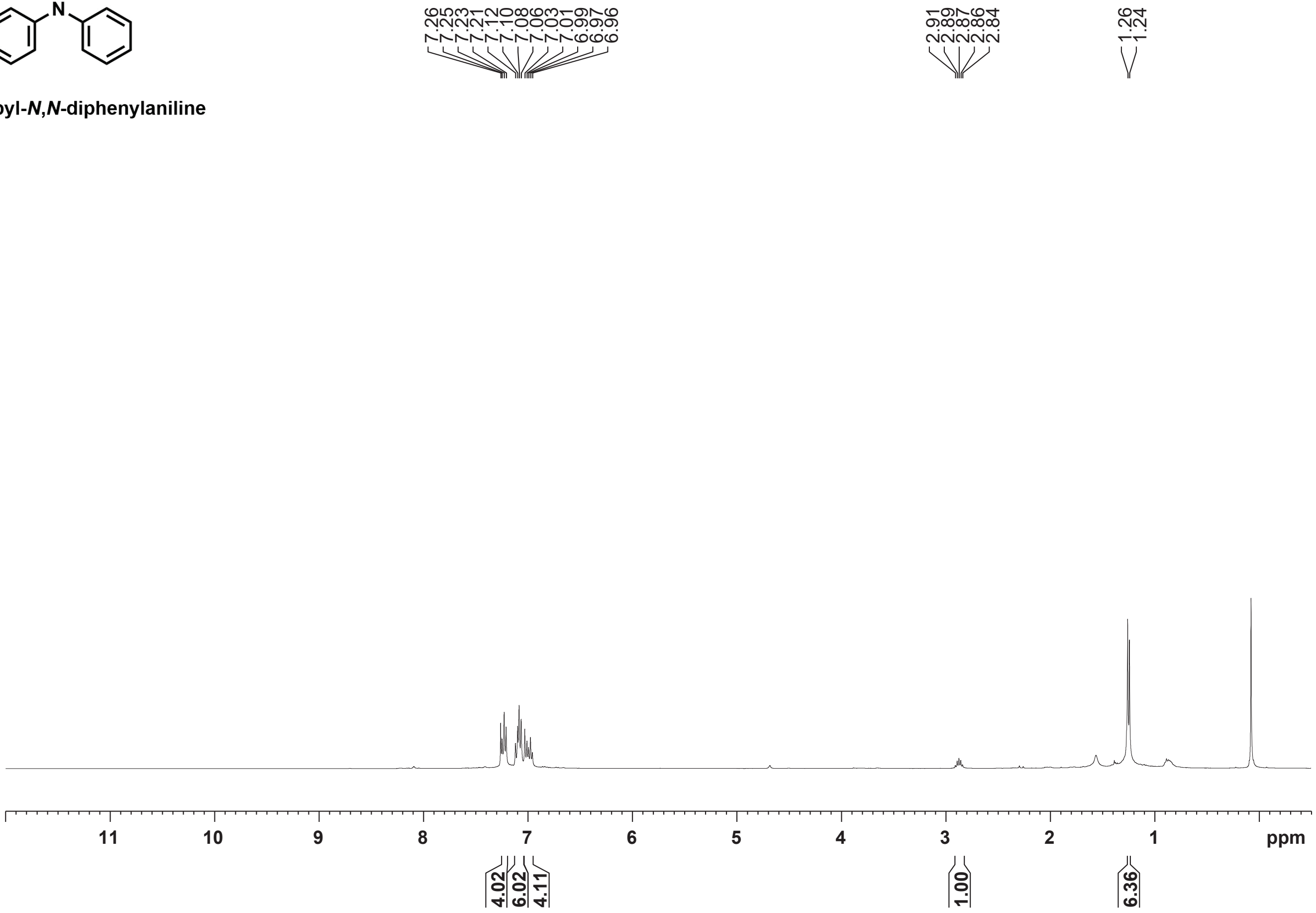
4-isopropyl-*N*,*N*-di-*p*-tolylaniline

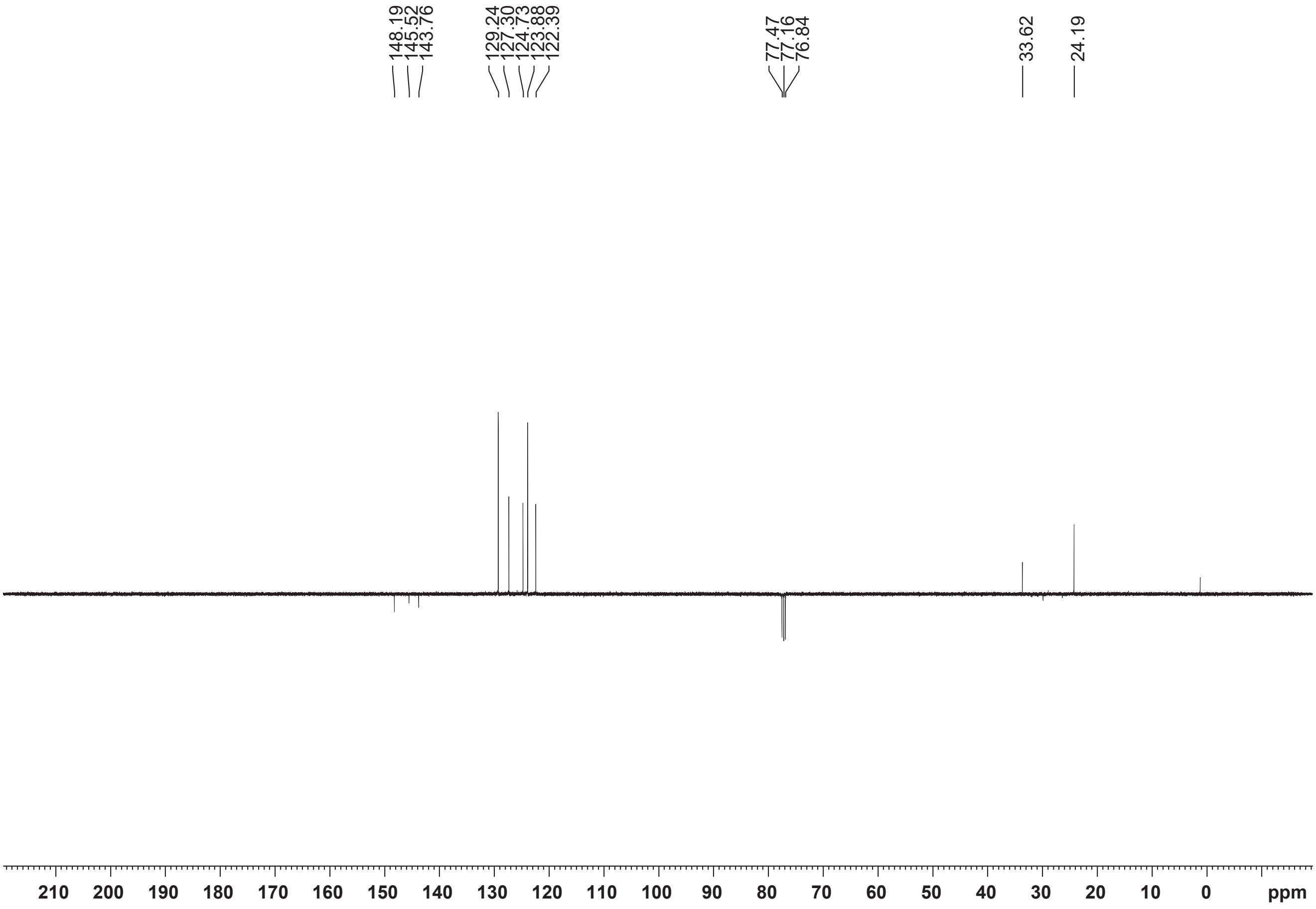


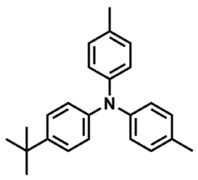




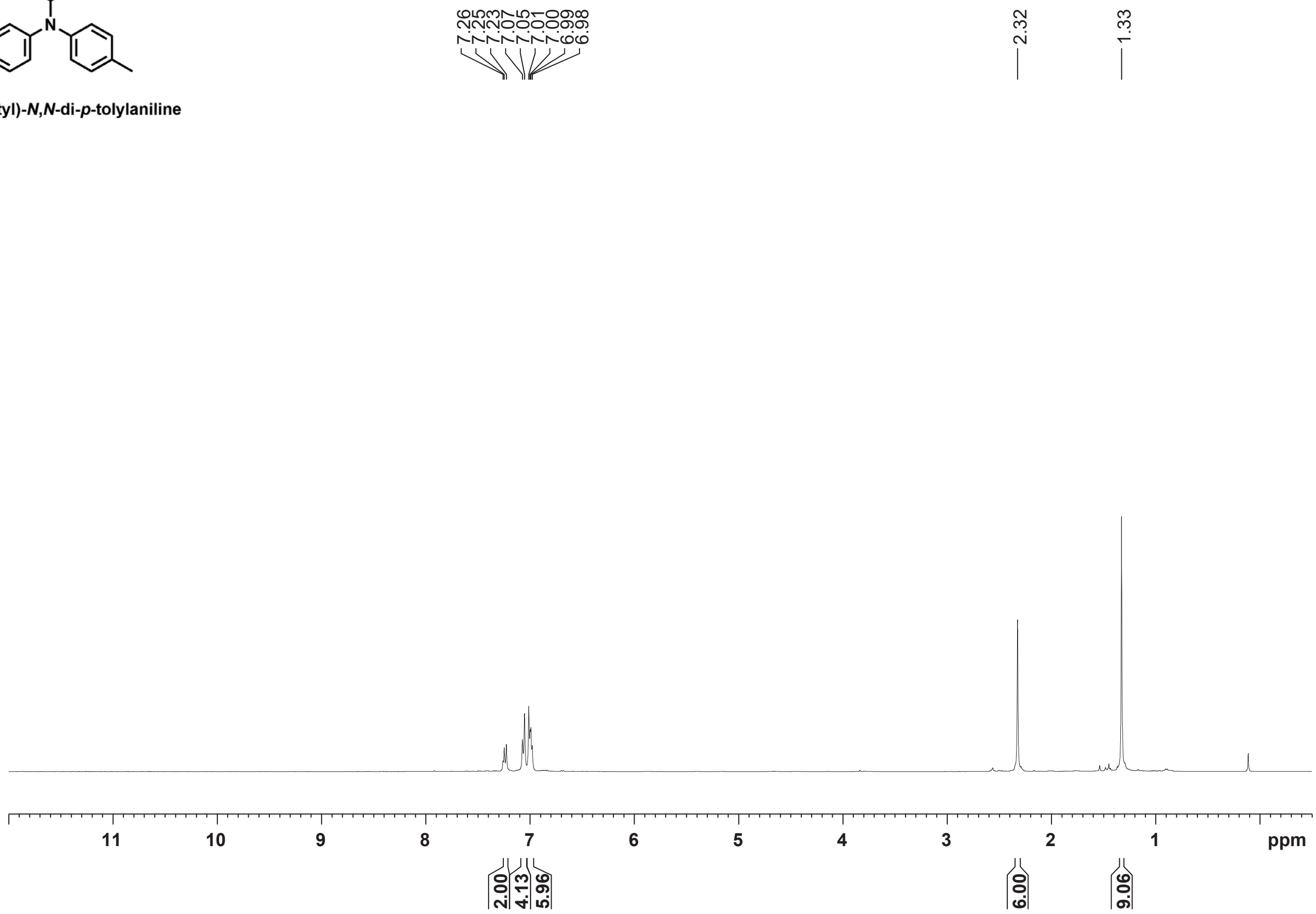
4-isopropyl-*N*,*N*-diphenylaniline

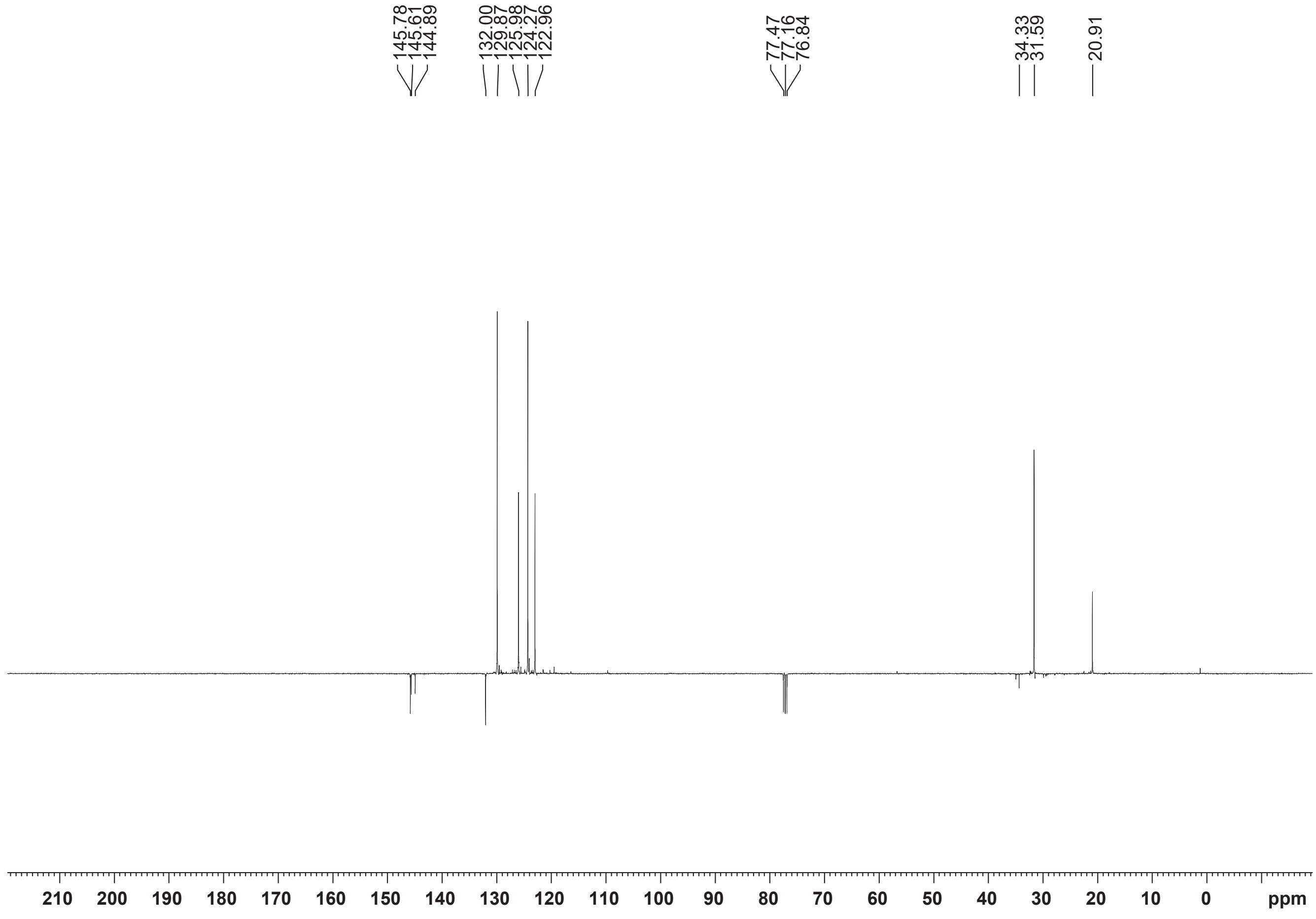


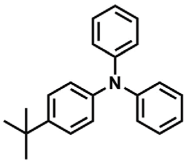




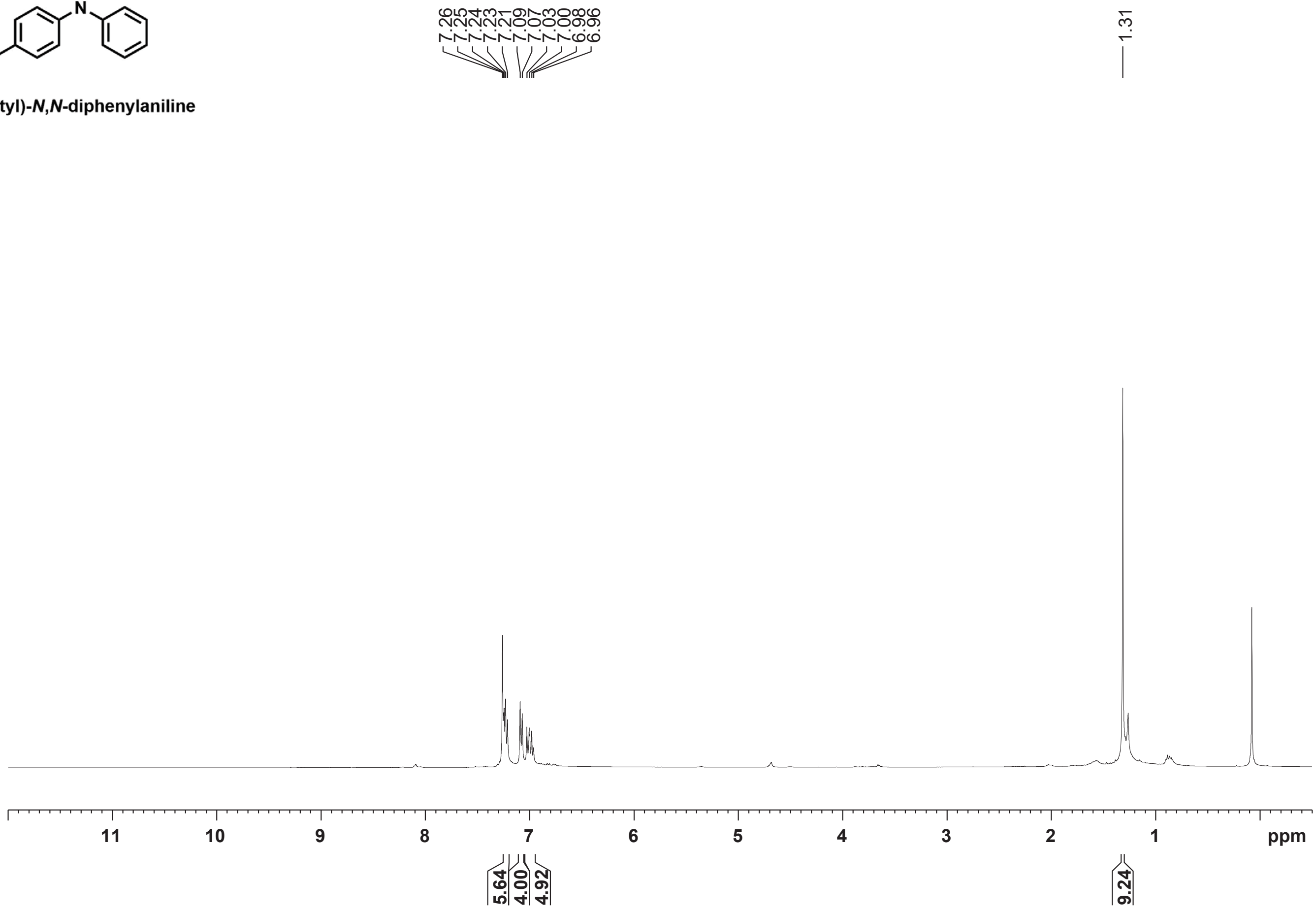
4-(*tert*-butyl)-*N*,*N*-di-*p*-tolylaniline

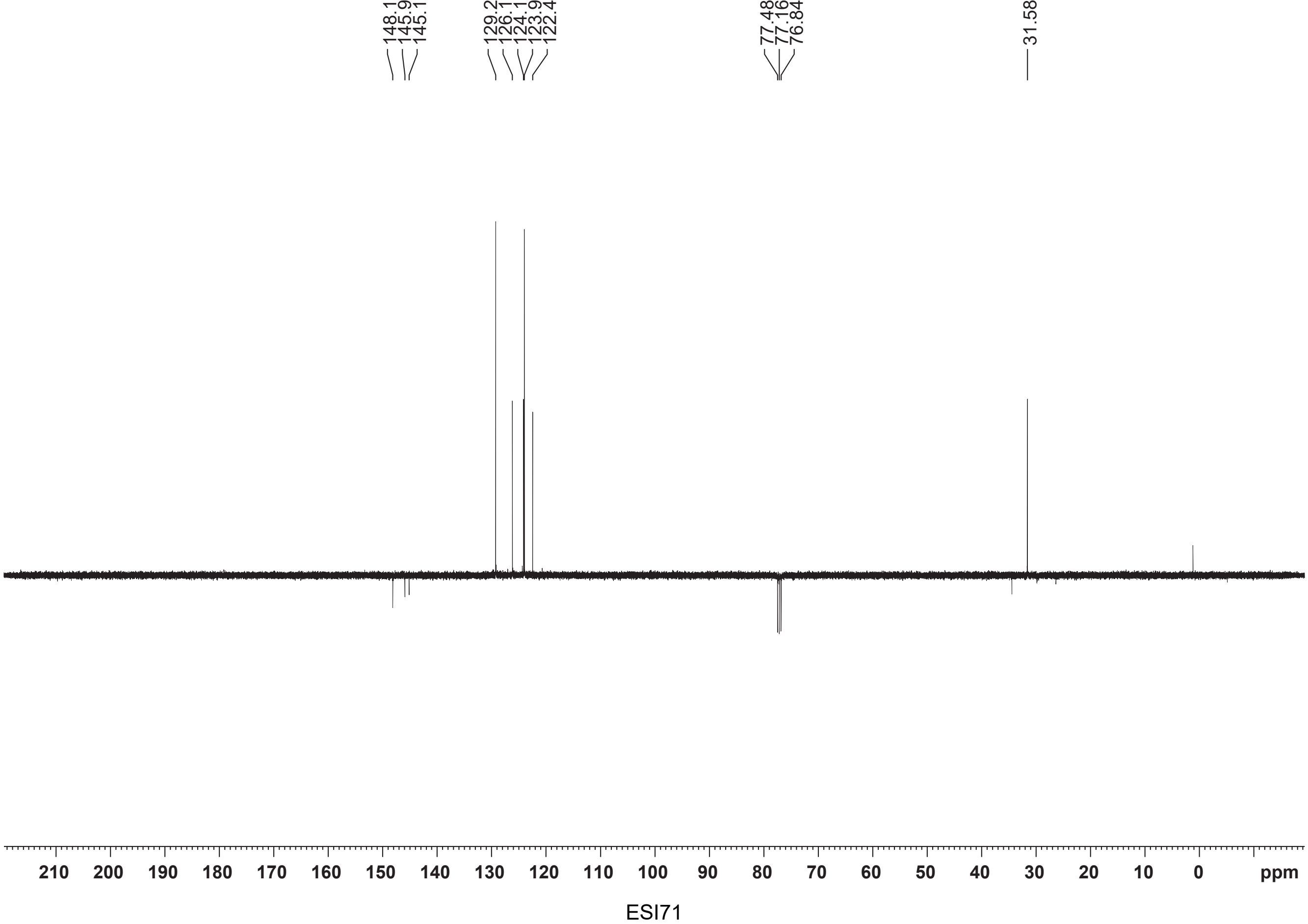


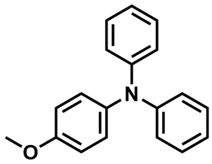




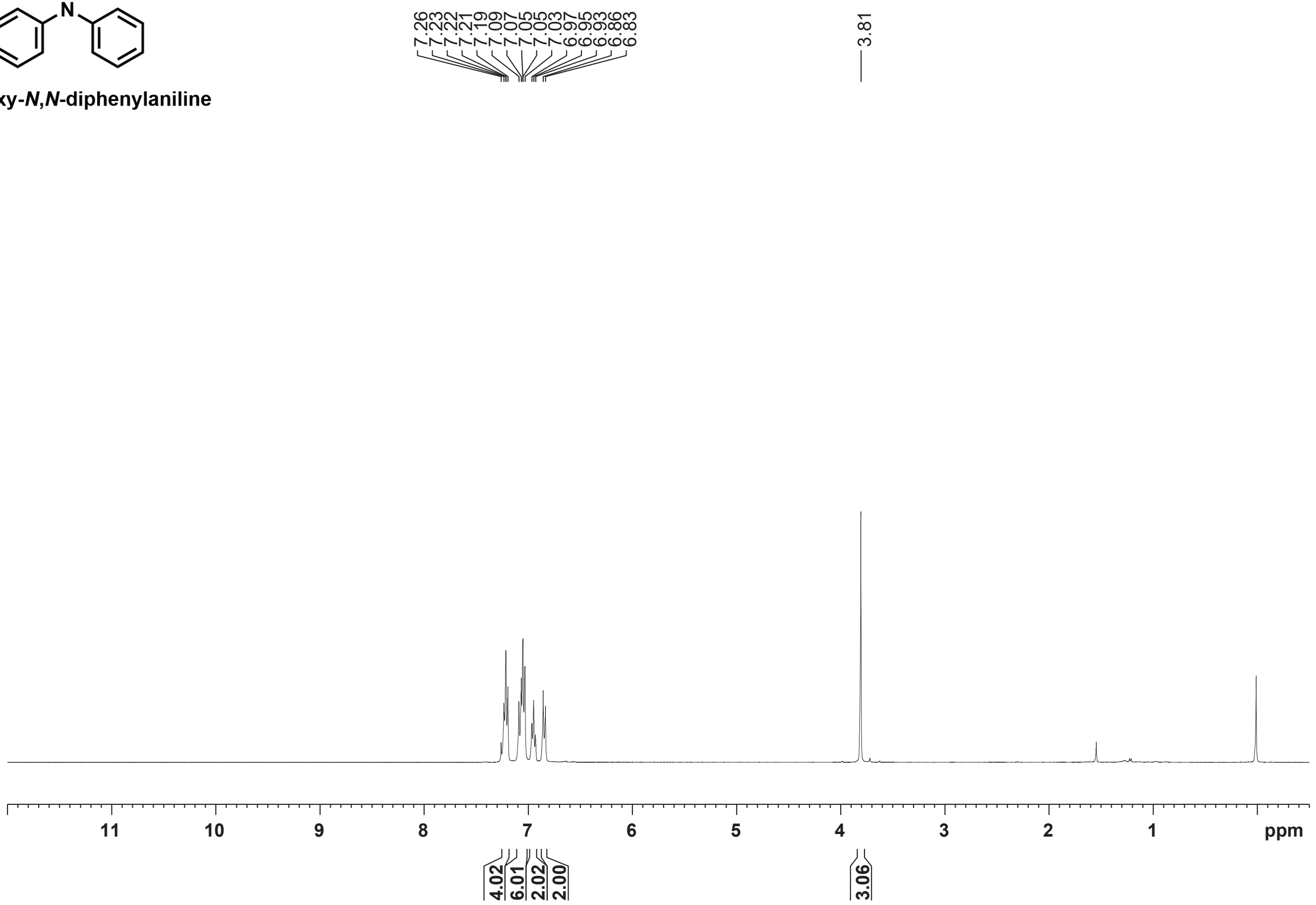
4-(*tert*-butyl)-*N*,*N*-diphenylaniline

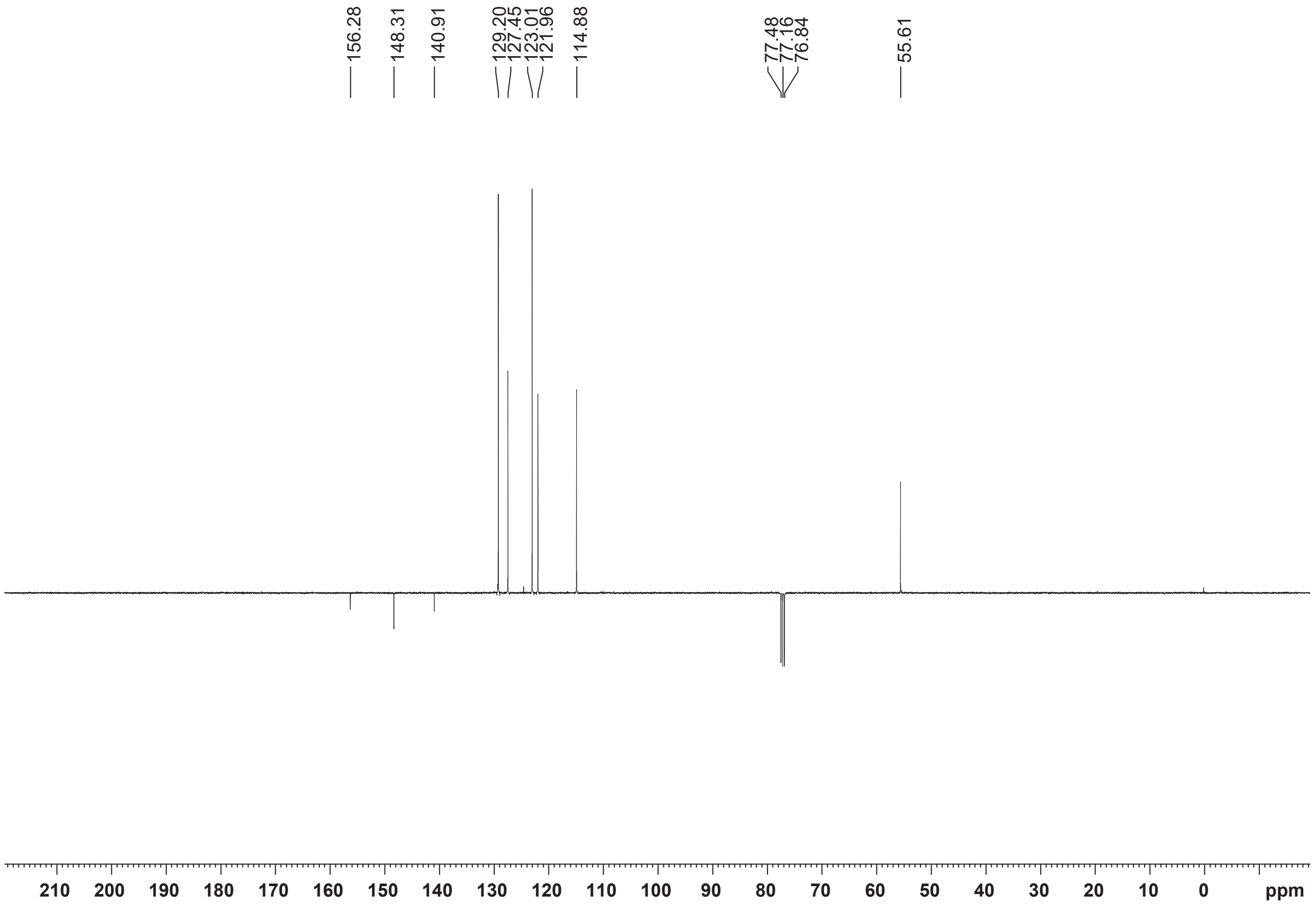


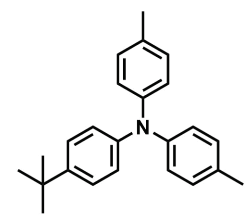




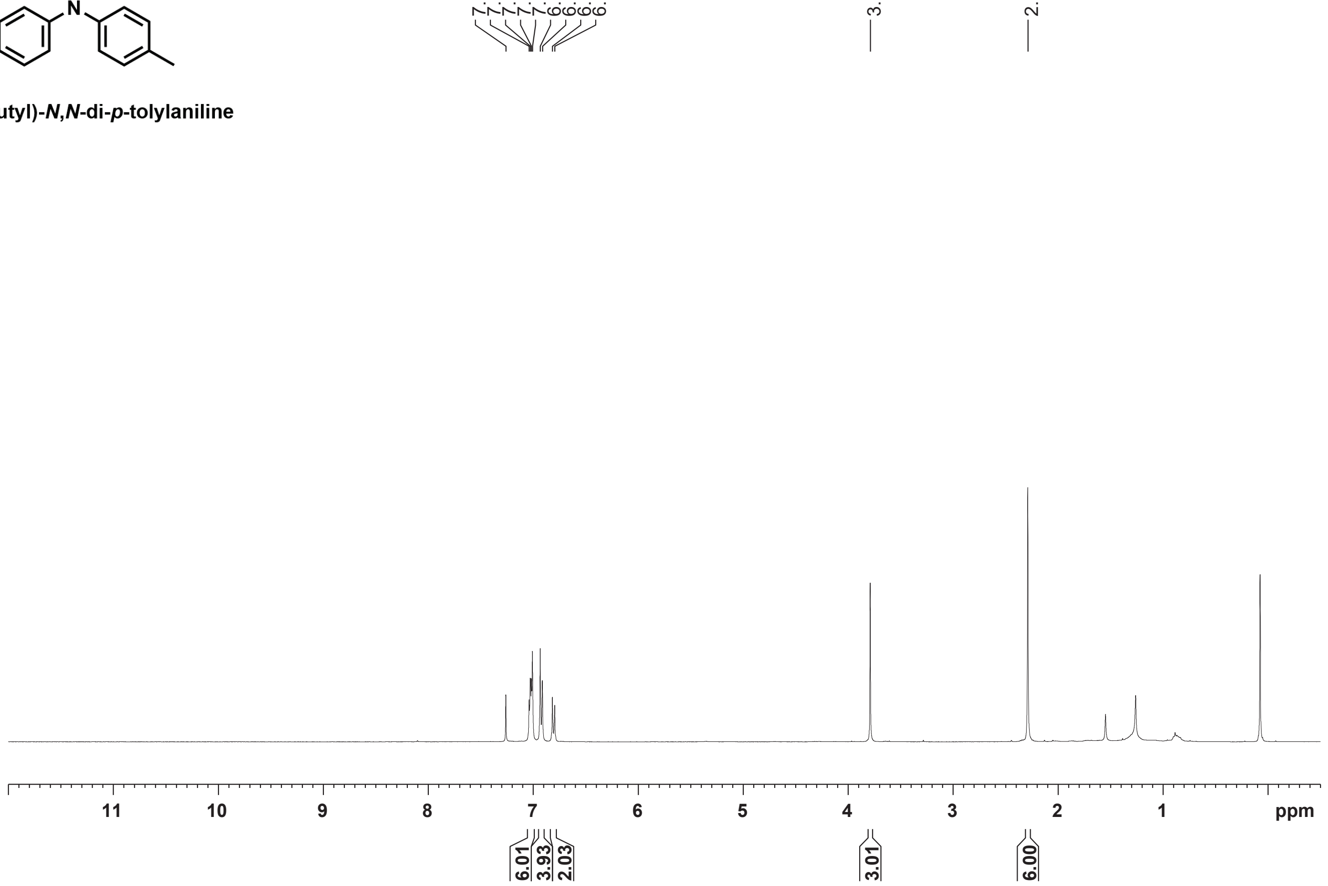
4-methoxy-*N*,*N*-diphenylaniline

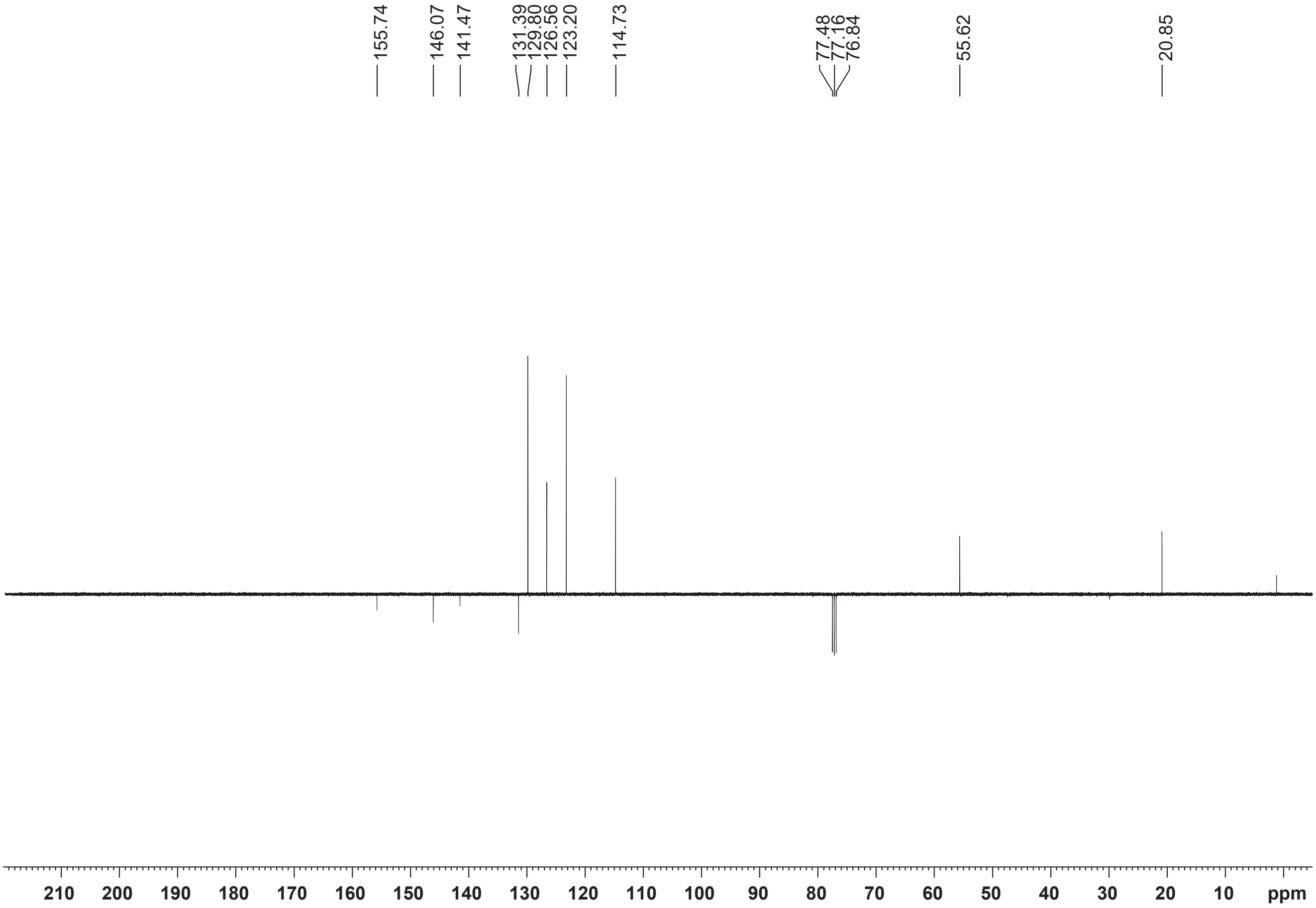


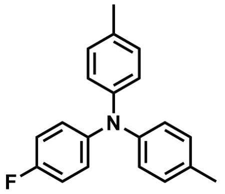




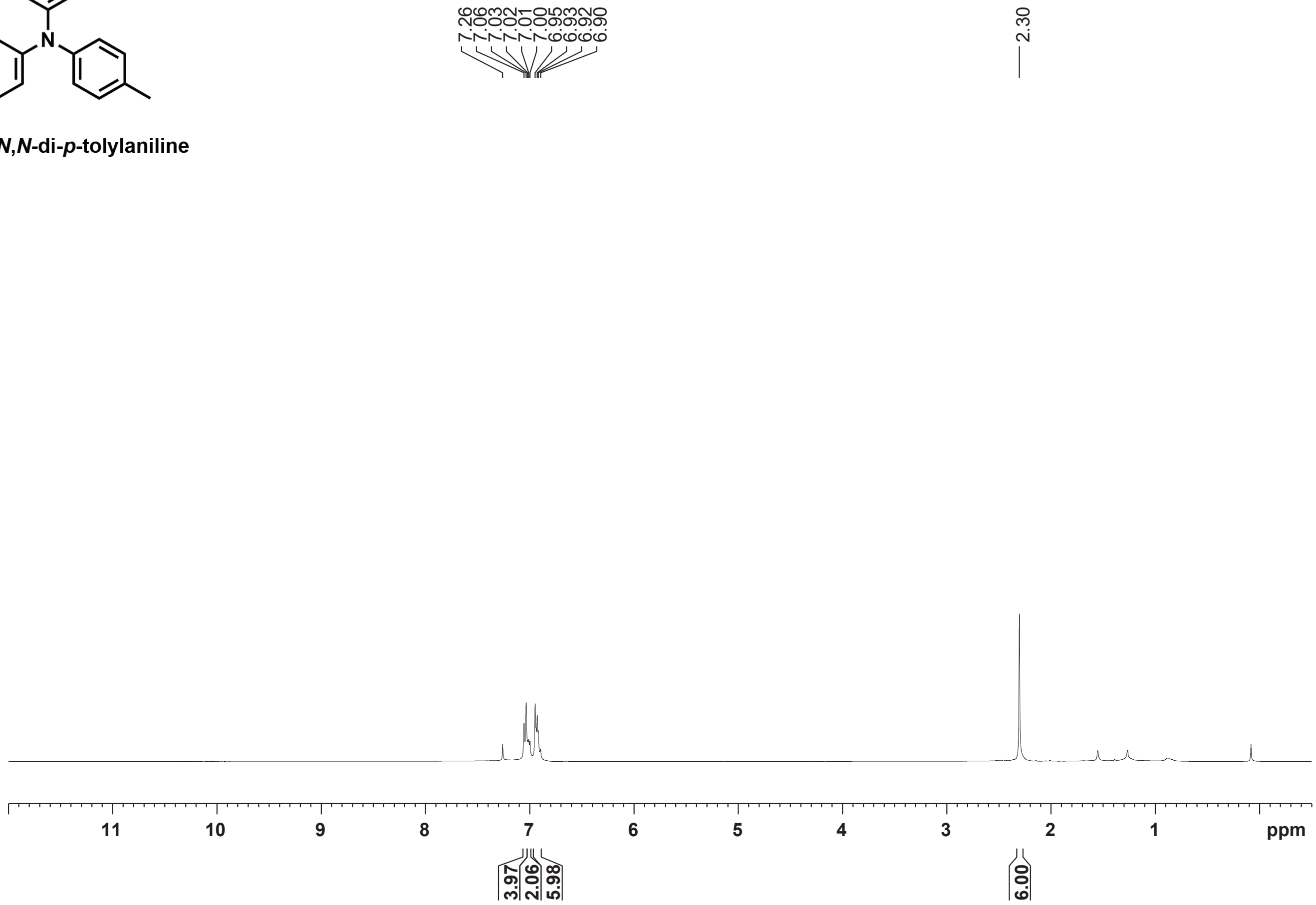
4-(*tert*-butyl)-*N*,*N*-di-*p*-tolylaniline

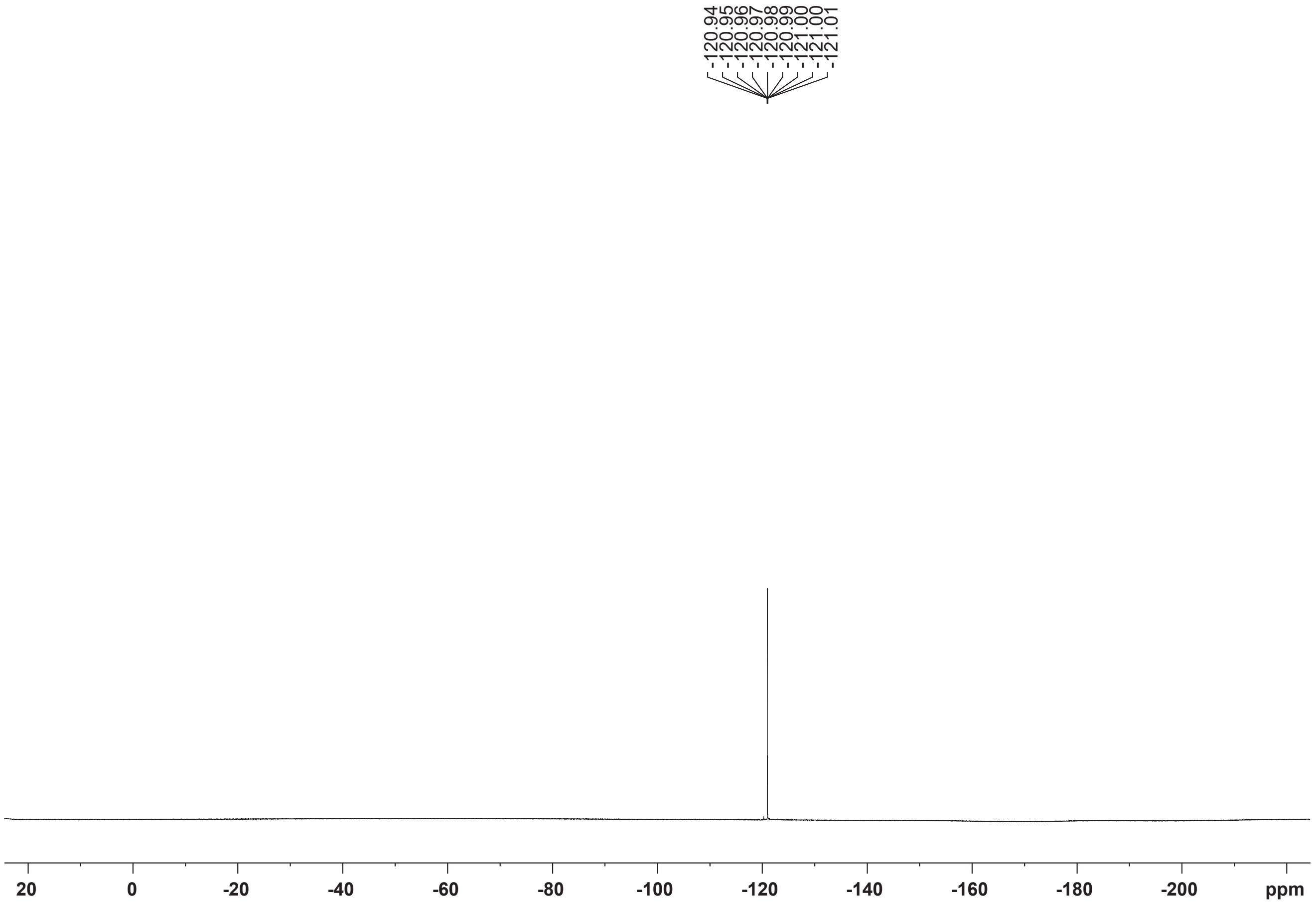


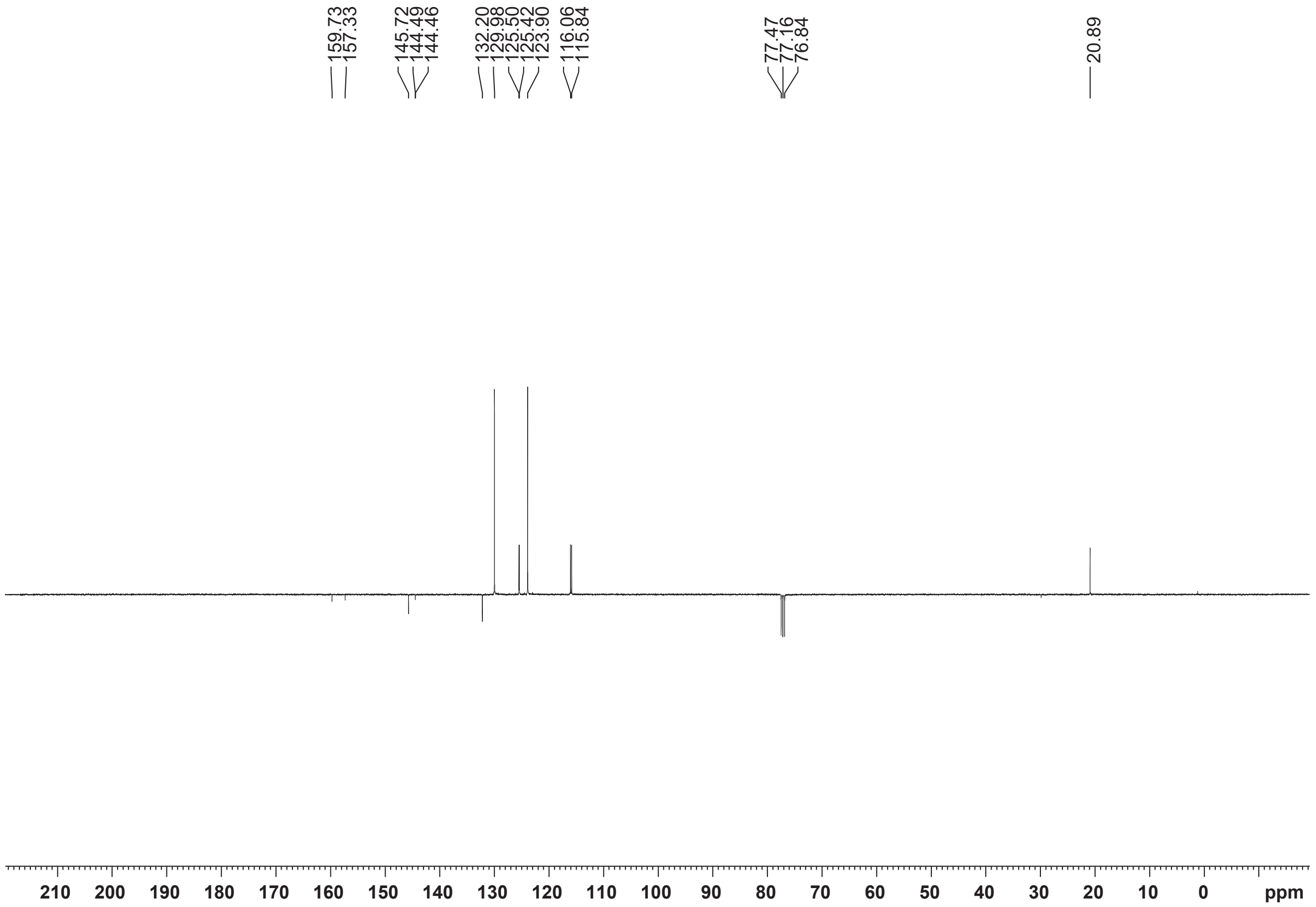




4-fluoro-*N*,*N*-di-*p*-tolylaniline



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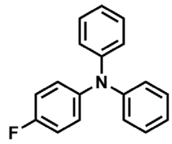
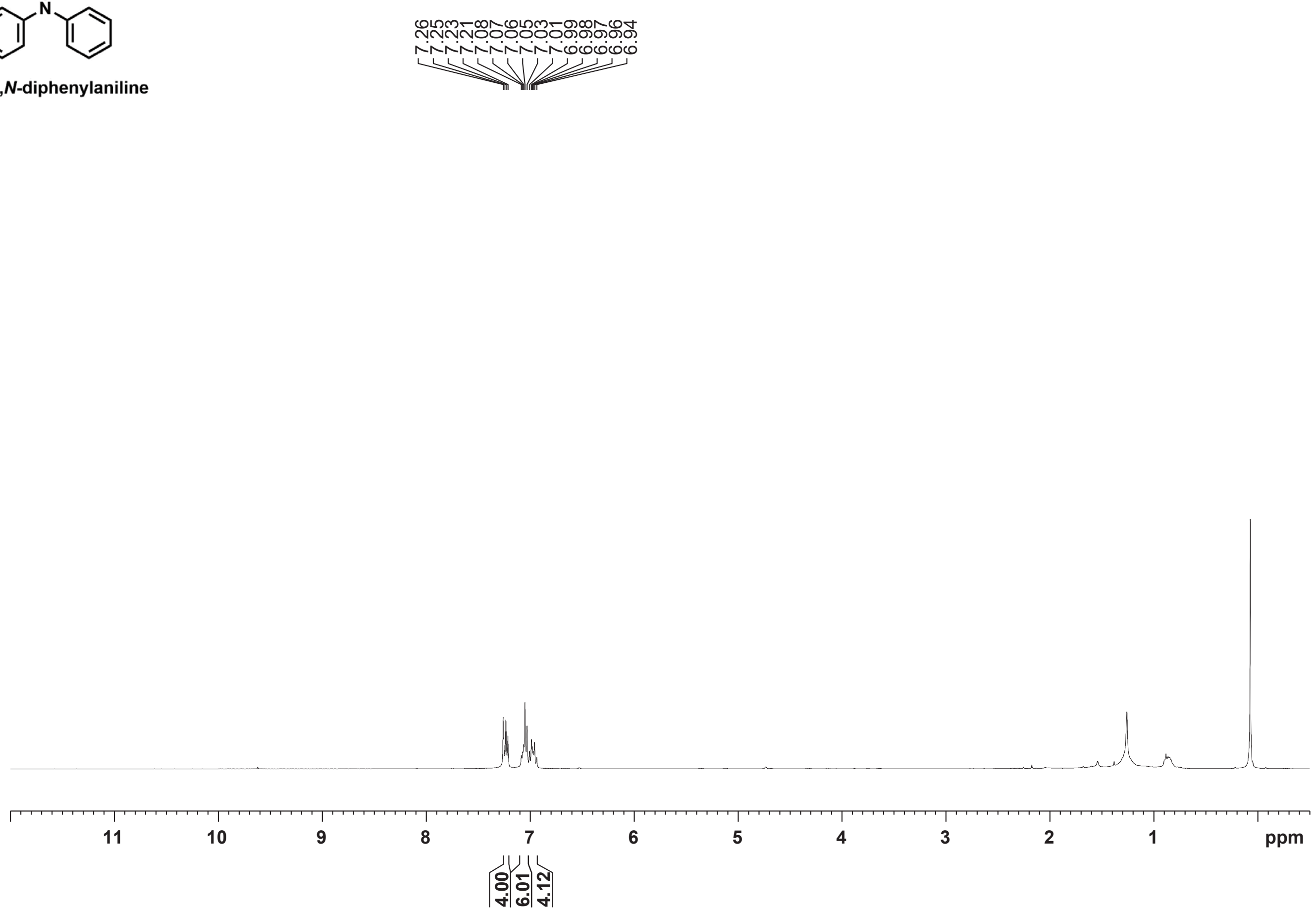
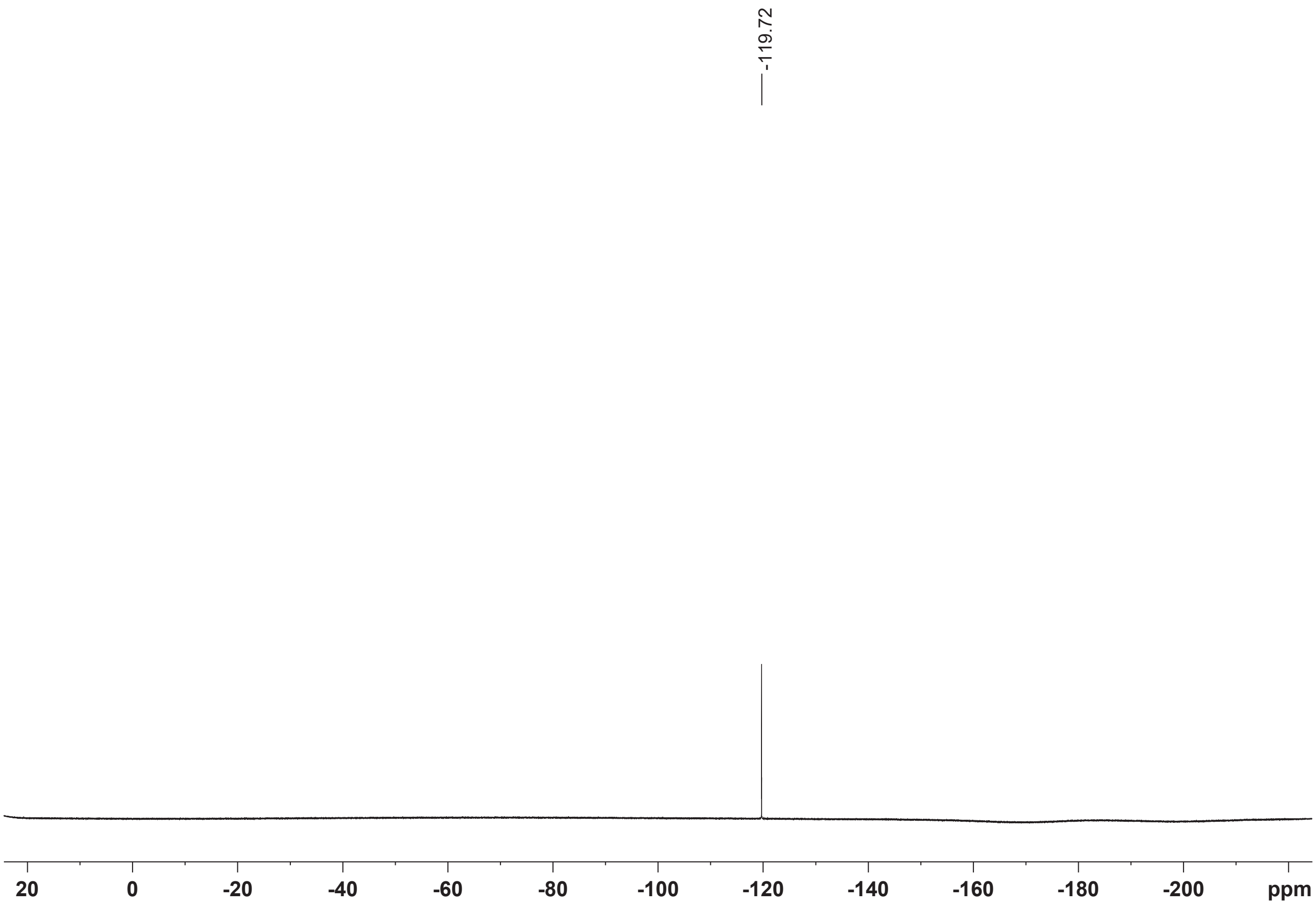
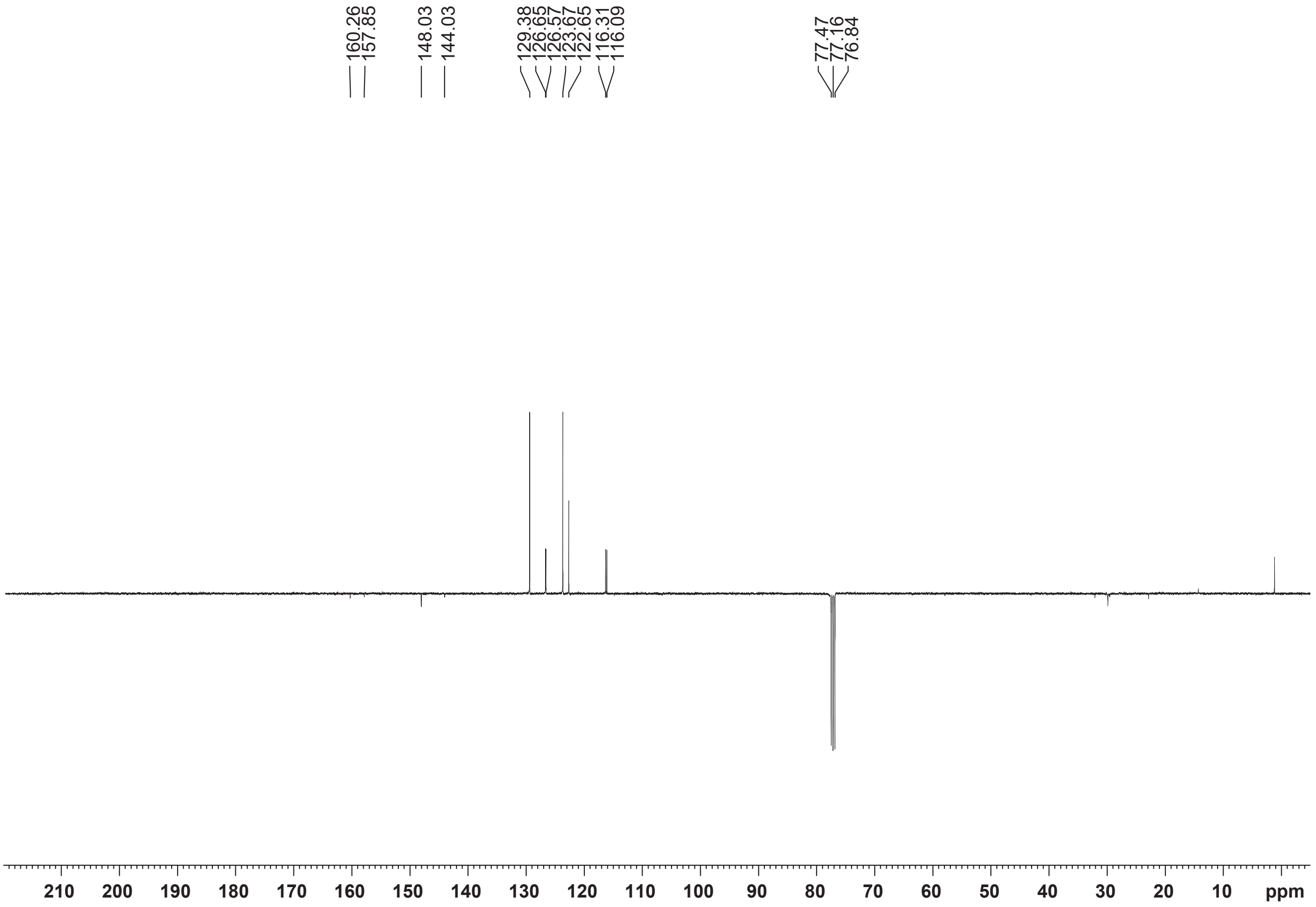


4-fluoro-*N*,*N*-diphenylaniline



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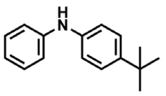
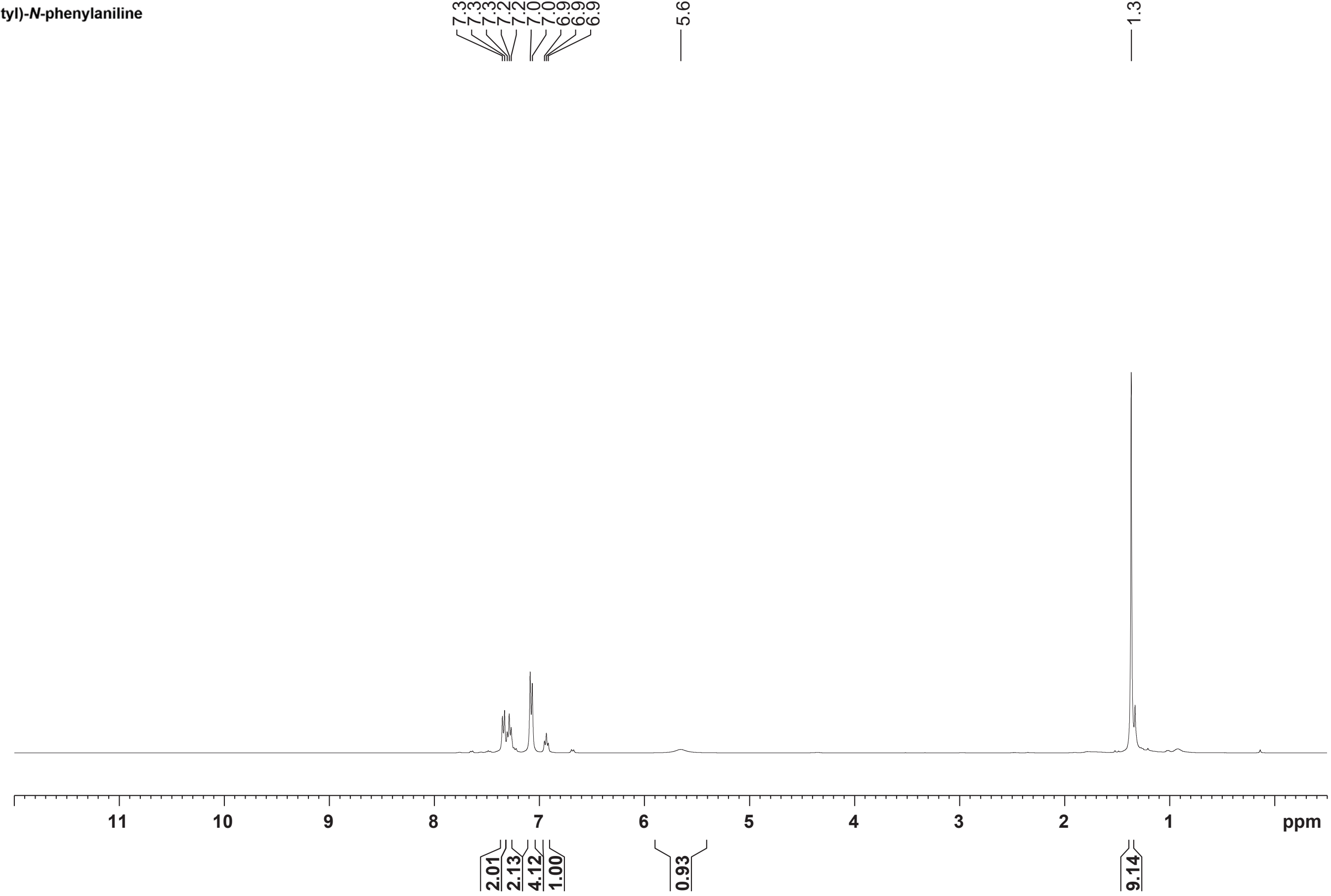
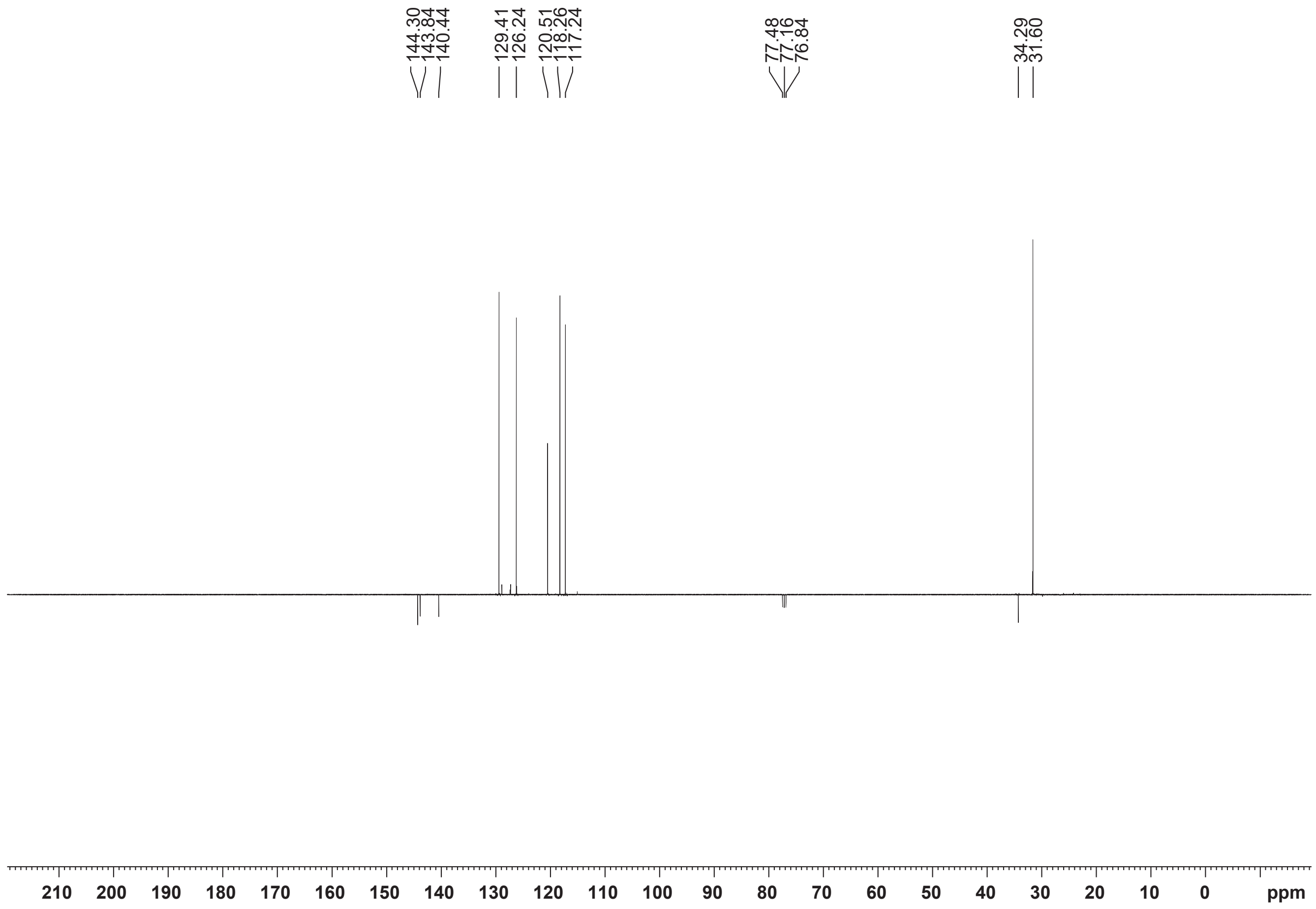
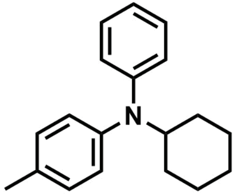


4-(*tert*-butyl)-*N*-phenylaniline







***N*-cyclohexyl-4-methyl-*N*-phenylaniline**