Synthesis of Sterically Encumbered Di- and Triarylamines by Palladium-Catalysed C-N Coupling Reactions at Mild Reaction Conditions

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1. Experimental Details

1.1. General Experimental Information

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried using an MBraun SPS-800 (THF, DCM, toluene, acetonitrile, diethylether and pentane) or dried in accordance with standard procedures. Deuterated solvents were stored over molecular sieves in an argon-filled glovebox. All other reagents were purchased from Sigma-Aldrich (Merck), ABCR, TCI or Acros Organics or in case of palladium precursors donated by Umicore AG and Co KG. All reagents purchased from chemical suppliers were used without further purification. The YPhos ligands keYPhos[1], trYPhos[2], joYPhos,[3] pinkYPhos[4] and oxYPhos[5] were prepared according to literature procedures. References to the prepared amines are given below for each amine.

NMR spectra were recorded on Avance-400 spectrometers at 25 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (*J*) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t = triplet m = multiplet, dd = doublet of doublet, br = broad signal. Signal assignment was supported by, HSQC (^{1}H / ^{13}C), HMBC (^{1}H / ^{13}C) correlation experiments.

GC/MS analyses were carried out with an Agilent 8890 GC and 5977B MSD system using an HP-5 capillary column (Phenyl methyl siloxane, 30 m × 320 × 0.25, 100/2.3-30-300/3, 2 min at 60 °C, heating rate 30 °C/min, 3 or 10 min at 300 °C). Yields were determined by GC-FID using *n*-tetradecane as internal standard.

Elemental analyses were performed on an Elementar vario MICRO-cube elemental analyzer in the in-house analytical facility.

IR-Spectra were recorded on a Thermo Nicolet iS5 FT-IR in transmission mode with a Specac “Omni-cell” with KBr plates and a 0.1 mm spacer or with an ATR module at 22 °C.

Column chromatography was performed on a Reveleris X2 (BÜCHI) Flash Chromatography-System using Reveleris packed columns.

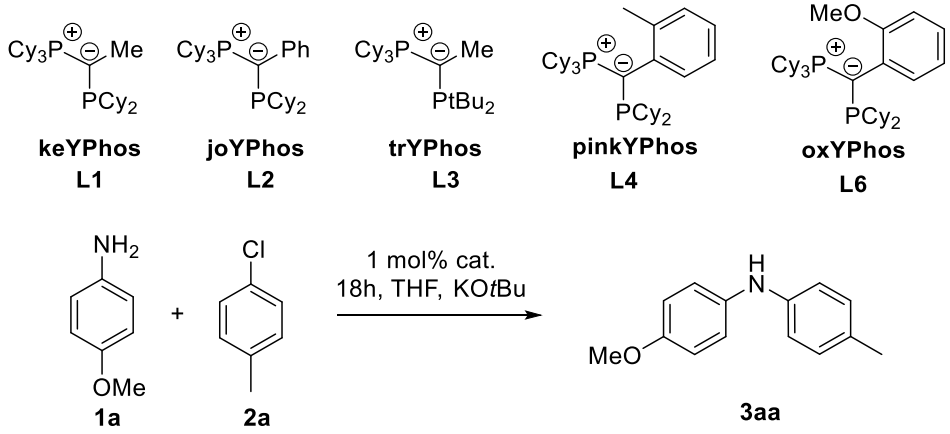
Melting Points were recorded on a Stuart SMP 30 with a heat up speed of 2 °C per minute.

1.2. Pd-catalyzed formation of arylamines

1.2.1 Optimization of the reaction conditions for the formation of diarylamines.

General Procedure. In a glovebox, a vial was charged with anisidine (1.00 mmol) and *p*-tolyl chloride (1.00 mmol). The solids were dissolved in 1 mL THF together with the base (1.50 mmol). The vial was sealed with a septum cap. In a second vial (in a glovebox), the corresponding ligand and Pd source (0.01 mmol each) were dissolved in 0.5 mL THF. The vial was closed with a septum cap and the mixture reacted for one hour. After one hour, the catalyst was added to the solution of the substrate via syringe and the mixture was stirred at room temperature (or 40 or 60 °C) for 18 h. For determination of the reaction yield, the reaction was quenched with 0.1 mL water. Small aliquots of the reaction mixture were taken from the mixture and filtered through a pad of silica with EtOAc as eluent. Yields were determined by GC/FID analysis using *n*-tetradecane as internal standard.

Table S1. Effect of the ligand, temperature and palladium source on the diarylamine formation.



[a]Conditions: **1** (1.0 mmol), **2** (1.0 mmol), catalyst/ligand (0.01 mmol), KO*t*Bu (1.50 mmol) in 1.5 mL THF for 18 h. Yields were determined by GC-FID analysis with tetradecane as an internal standard.

Entry	Ligand	Pd source	T	GC-FID yield [%]
1	trYPhos	$Pd_2(dba)_3$	25	80
2	joYPhos	$Pd_2(dba)_3$	25	84
3	keYPhos	$Pd_2(dba)_3$	25	77
4	pinkYPhos	$Pd_2(dba)_3$	25	91
5	oxYPhos	$Pd_2(dba)_3$	25	81
6	keYPhos	$[Pd(indenyl)Cl]_2$	25	13
7	keYPhos	$[Pd(allyl)Cl]_2$	60	47
8	trYPhos	$[Pd(allyl)Cl]_2$	25	15

9[a]	[keYPhos·Pd(allyl)Cl]		60	68
10[a]	[joYPhos·Pd(indenyl)Cl]		60	95
11	trYPhos	$Pd_2(dba)_3$	60	90
12	joYPhos	$Pd_2(dba)_3$	60	>99
13	keYPhos	$Pd_2(dba)_3$	60	>99
14	pinkYPhos	$Pd_2(dba)_3$	60	>99
15	oxYPhos	$Pd_2(dba)_3$	60	>99
16	keYPhos	$Pd_2(dba)_3$	40	>99
17	pinkYPhos	$Pd_2(dba)_3$	40	>99
18	oxYPhos	$Pd_2(dba)_3$	40	>99
19[b]	keYPhos	$Pd_2(dba)_3$	60	64
20	No ligand	$Pd_2(dba)_3$	60	0

[a]: Isolated preformed catalyst formed from keYPhos and $[Pd(allyl)Cl]_2$. [b] 1 mmol aniline, 1 mmol aryl chloride, 1 mol% catalyst + Ligand, 1.5 ml THF, 0.1 ml Hg

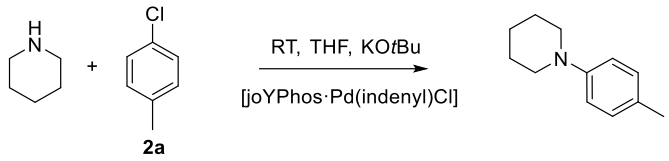
Table S2. Effect of the base and catalyst loading on the diarylamine formation.

Entry	[mol%] cat.	base	GC-FID yield [%]
1	1	KO*t*Bu	>99
2	0.5	KO*t*Bu	>99
3	0.25	KO*t*Bu	>99
4	1	KOMe	71
5	0.5	KOMe	69
6	0.25	KOMe	67
7	1	KOH	5
8	0.5	KOH	4
9	0.25	KOH	0
10	1	K_2CO_3	22
11	0.5	K_2CO_3	18
12	0.25	K_2CO_3	0

Catalyst stability. Stability tests on [keYPhos·Pd(allyl)Cl] in THF showed no decomposition at 40 or 60°C after 24 h as judged from the ^{31}P NMR spectrum. In the presence of 1 eq. base and aryl chloride, both [keYPhos·Pd(allyl)Cl] and [joYPhos·Pd(*t*Bu-indenyl)Cl] formed the oxidative addition complexes as previously reported starting form keYPhos and Pd_2dba_3 (*ACS Catalysis*, 2020, **10**, 999-1009). The long-time stability of the keYPhos-Pd catalysts was also seen the α-arylation of ketones at 60 °C (*Org. Lett.* 2019, **21**, 7558-7562). The mercury test as well as the inactivity of Pd_2dba_3 without additional ligand clearly indicate that the YPhos palladium complexes are the active species.

Further stability tests of the catalyst have been conducted in previous studies with aliphatic amines. In case of the reaction of *p*-chlorotoluene with piperidine long term stability tests have been performed by addition of further portions of substrates. Since this reaction was found to be complete after already 10 min, further portions (0.5 mol% each) were added every 10 min and the yield determined prior addition of the next portion (or after 24 h in case of the last addition). The following Table S2 shows that the catalyst remains active but loses activity with every further portion.

Table S3. Downscaling with [joYPhos-Pd(indenyl)Cl] as precatalyst.



	1	2	3	4	5
Total catalyst loading [mol%]	0.5	0.25	0.167	0.125	0.1
Conversion [%]	99	99	73	53	44

1.2.2 Data of the kinetic studies

For the kinetic studies, the reagents and catalyst for the C-N coupling reactions were prepared as described above. After mixing of the reagents the reaction mixture was warmed to 40 °C and stirred at that temperature for the time indicated in Table S4. For determination of the reaction yield, the reaction was quenched with 0.1 mL water. Small aliquots of the reaction mixture were taken from the mixture and filtered through a pad of silica with EtOAc as eluent. Yields were determined by GC/FID analysis using *n*-tetradecane as internal standard. The results obtained for each catalyst are given in the following table. The results correspond to the graphics shown in Figure 3 in the manuscript.

Table S4. Results of the reaction monitoring amination of *p*-anisidine **1** and *p*-chlorotoluene **2** with 1.5 equiv. KO*t*Bu in THF at 40 °C using different YPhos ligands.

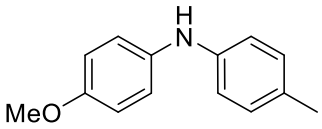
catalyst	Mol%	time	conversion
keYPhos x Pd_2dba_3	1	0	0
	1	5	73
	1	10	100
	1	30	100
	1	60	100
trYPhos x Pd_2dba_3	1	0	0
	1	5	10
	1	10	24
	1	30	77
	1	60	78
joYPhos x Pd_2dba_3	1	0	0
	1	5	28
	1	10	52
	1	30	100
	1	60	100
pinkYPhos x Pd_2dba_3	1	0	0
	1	5	22
	1	10	82
	1	30	100
	1	60	100
keYPhos x Pd_2dba_3	0.5	0	0
	0.5	1	10
	0.5	2	25
	0.5	3	41
	0.5	4	54
	0.5	5	68
	0.5	10	100
	0.5	20	100
	0.5	30	100
	0.5	45	100
	0.5	60	100

1.2.3 General procedure for the isolation of diarylamines.

In a glovebox, a vial was charged the arylamine (1.00 mmol) and aryl chloride (1.00 mmol) and KO*t*Bu (1.50 mmol) and the solids dissolved in 1 mL THF. The vial was sealed with a septum cap and taken outside the glovebox. In a second vial (in a glovebox), $Pd_2(dba)_3$ and keYPhos (0.01 mmol each) were dissolved in 0.5 mL THF. The vial was sealed with a septum cap and taken outside the glovebox and the catalyst preformed for one hour. After one hour the catalyst was added to the substrate solution via a syringe and the mixture was stirred at 60 °C for 18 h. Subsequently, the reaction mixture was quenched with water and extracted with EtOAc three times. The organic phases were combined and dried with $MgSO_4$. The crude product was purified via column chromatography or Kugelrohr distillation.

1.2.4 Isolated diarylamines

4-methoxy-N-(p-tolyl)aniline (**3aa**).



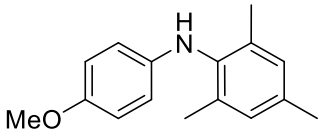
3aa

The diarylamine **3aa** was synthesized according to the general procedure, purified by column chromatography and isolated in 93 % yield as off-white solid. The analytical data is in accordance with the reported literature.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.95 (d, J = 8.0 Hz, 4H), 6.80 – 6.71 (m, 4H), 5.23 (s, 1H), 3.70 (s, 3H), 2.19 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 154.91, 142.47, 136.71, 129.91, 129.45, 121.22, 116.68, 114.77, 55.70, 20.68.

Reference: J. P. Wolfe, H. Tomori, J. P. Sadighi, J. Yin and S. L. Buchwald, *J. Org. Chem.* 2000, **65**, 1158–1174.

***N*-(4-methoxyphenyl)-2,4,6-trimethylaniline** (**3ab**).



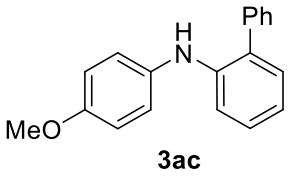
3ab

Diarylamine **3ab** was synthesized according to the general procedure and purified via Kugelrohr distillation (140-150 °C, $1.0*10^{-3}$ mbar). Product isolated in 74 % yield as a pale-yellow liquid. The analytical data is in accordance with the reported literature.

^{1}H-NMR (400 MHz, CDCl3) δ = 6.93 (d, *J* = 16.3 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 6.64–6.41 (m, 2H), 4.99 (s, 1H), 3.77 (s, 3H), 2.33 (s, 3H), 2.19 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 153.59, 140.47, 137.70, 136.60, 134.83, 129.98, 129.36, 114.87, 114.50, 55.81, 20.99, 18.36. **IR (ATR mode)**: 3655, 3405, 350, 3087, 2980, 2962, 2917, 2834, 1851, 1733, 1598, 1581, 1530, 1502, 1483, 1461, 1399, 1308, 1290, 1228, 1171, 1149, 1111, 1072, 1028, 933, 882, 852, 780, 769, 638, 538 cm^{-1}. **MS (EI):** m/z (%) = 241.2 (100 [M+]), 226.2, 208.1, 196.1, 182.1, 168.1, 156.1, 133.1, 120.5, 105.5, 91.0, 77.1, 65.1, 53.1.

Reference: I. Sapountzis and P. Knochel, *Angew. Chemie - Int. Ed.* 2004, **43**, 897–900.

***N*-(4-methoxyphenyl)-[1,1'-biphenyl]-2-amine** (**3ac**).



3ac

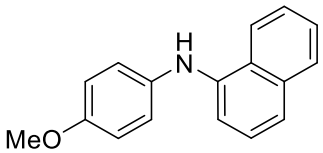
Diarylamine **3ac** was synthesized according to the general procedure and purified via Kugelrohr distillation (155-160 °C, $1.0*10^{-3}$ mbar). Product isolated in 82 % yield as a colorless liquid. The analytical data is in accordance with the reported literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.29 – 7.26 (m, 3H), 7.23 – 7.00 (m, 5H), 6.90 – 6.77 (m, 3H), 6.63 (d, *J* = 8.7 Hz, 2H), 5.93 (s, 1H), 3.60 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 155.56, 142.33, 139.30, 135.94, 130.84, 129.75, 129.50, 129.08, 128.45, 127.53, 122.94, 119.62, 114.93, 114.77, 55.68.

IR (ATR mode): 3402, 3028, 2949, 2931, 2904, 2832, 2476, 2278, 2106, 1592, 1580, 1488, 1462, 1436, 1402, 1296, 1283, 1246, 1179, 1106, 1073, 1037, 1008, 995, 919, 820, 770, 749, 704, 650, 615, 556, 530, 515 cm^{-1}. **MS (EI):** m/z (%) = 275.2 (100 [M+]), 260.1, 230.1, 217.1

Reference: A. Modak, A. J. Nett, E. C. Swift, M. C. Haibach, V. S. Chan, T. S. Franczyk, S. Shekhar and S. P. Cook, *ACS Catal.* 2020, **10**, 10495–10499

***N*-(4-methoxyphenyl)naphthalen-1-amine** (**3ad**).



3ad

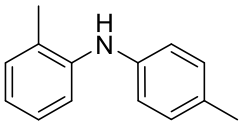
Diarylamine **3ad** was synthesized according to the general procedure and purified via Kugelrohr distillation (150-155 °C, $1.0*10^{-3}$ mbar). Product isolated in 87 % yield as a salmon colored solid. The analytical data is in accordance with the reported literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.07 – 8.02 (m, 1H), 7.88 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.14 – 7.09 (m, 2H), 6.93 – 6.88 (m, 2H), 6.47 (s, 1H), 3.83 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ =155.21, 141.01, 137.01, 134.74, 128.72, 126.30, 126.13, 125.47, 121.96, 121.19, 121.03, 114.89, 111.81, 55.73.

IR (ATR mode): 3394, 3272, 3008, 2997, 2980, 2949, 2832, 1608, 1588, 1573, 1507, 1474, 1464, 1452, 1440, 1399, 1355, 1341, 1299, 1284, 1142, 1090, 1049, 1033, 1019, 1007, 888, 850, 834, 7645, 746, 731, 634, 565, 512, 496 cm^{-1} **mp** 110-111 °C **MS (EI):** m/z (%) = 249.1 (100 [M+]), 234.1, 217.1, 204.1

Reference: C. Desmarets, R. Schneider and Y. Fort, *J. Org. Chem.* 2002, **67**, 3029–3036.

2-methyl-*N*-(*p*-tolyl)aniline (**3ba**).



3ba

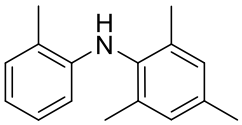
Diarylamine **3ba** was synthesized according to the general procedure, purified by column chromatography and isolated in 94 % yield as a colorless liquid. The analytical data is in accordance with the reported literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.0 Hz, 2H), 7.11 (dd, *J* = 15.9, 8.1 Hz, 3H), 6.96 – 6.84 (m, 3H), 5.36 (s, 1H), 2.32 (s, 3H), 2.27 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 142.16, 141.14, 130.95, 130.56, 129.95, 127.13, 126.86, 121.19, 118.77, 117.36, 20.78, 17.98.

MS (EI): m/z (%) = 197.2 (100 [M+]), 180.1, 167.1, 152.1

Reference: Q. Shen, T. Ogata and J. F. Hartwig, *J. Am. Chem. Soc.* 2008, **130**, 6586–6596.

2,4,6-trimethyl-*N*-(*o*-tolyl)aniline (**3bb**). Diarylamine **3bb** was synthesized according to the general procedure, purified by column chromatography and isolated in 94 % yield as an off-white solid. The analytical data is in accordance with the reported literature.



3bb

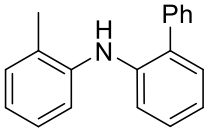
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 7.3 Hz, 1H), 7.07 – 7.01 (m, 3H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.24 (d, *J* = 8.1 Hz, 1H), 4.83 (s, 1H), 2.41 (s, 8H), 2.24 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 144.60, 136.11, 135.72, 135.27, 130.31, 129.33, 127.05, 122.20, 117.86, 111.52, 21.04, 18.23, 17.74.

IR (ATR mode): 3405, 3001, 2947, 2915, 2853, 2731, 1918, 1881, 1767, 1739, 1602, 1582, 1439, 1311, 1296, 1225, 1182, 1152, 1034, 1009, 984, 921, 859, 742, 713, 619, 441 cm^{-1} **mp** 82 – 83 °C **MS (EI):** m/z (%) = 225.2 (100 [M+]), 210.2, 195.1, 180.1

Reference: W. Fang, J. Jiang, Y. Xu, J. Zhou and T. Tu, *Tetrahedron* 2013, **69**, 673–679.

***N*-(*o*-tolyl)-[1,1'-biphenyl]-2-amine** (**3bc**).

Diarylamine **3bc** was synthesized according to the general procedure, purified by column chromatography and isolated in 71 % yield as a pale-yellow oil. The analytical data is in accordance with the reported literature.



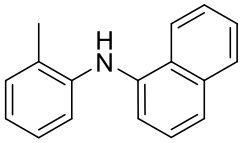
3bc

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.30 (m, 4H), 7.29 – 7.22 (m, 1H), 7.21 – 7.10 (m, 3H), 7.08 – 7.00 (m, 3H), 6.91 – 6.78 (m, 2H), 3.69 (s, 1H), 1.97 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 141.41, 141.14, 139.23, 130.99, 130.87, 130.80, 129.39, 129.07, 129.03, 128.39, 127.60, 126.90, 122.24, 120.40, 119.19, 116.77, 17.97. **IR (ATR mode):** 3422, 3057, 2979, 1584, 1511, 1496, 1484, 1471, 1435, 1379, 1309, 1244, 1157, 1111, 1072, 1047, 1033 1009, 881, 765, 703, 594, 530, 497, 489, 440, 433, 415 cm^{-1}.

Reference: N. H. Park, G. Teverovskiy and S. L. Buchwald, *Org. Lett.* 2014,**16**, 220-223; H. Heil, L.-I. Rodriguez, B. Burkhart and A. Darsy, WO 2014/111269 A2.

***N*-(*o*-tolyl)naphthalen-1-amine** (**3bd**).

Diarylamine **3bd** was synthesized according to the general procedure, purified by column chromatography and isolated in 81 % yield as a pale-yellow oil. The analytical data is in accordance with the reported literature.

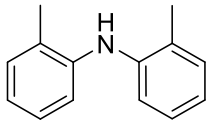


3bd

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.08 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.93 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.62 – 7.48 (m, 3H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.30 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.15 (qd, *J* = 7.6, 1.3 Hz, 2H), 7.07 – 6.97 (m, 2H), 5.79 (s, 1H), 2.39 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 142.72, 139.63, 134.79, 131.00, 128.71, 127.62, 127.26, 127.04, 126.26, 126.18, 125.71, 122.35, 121.78, 121.66, 118.78, 115.07, 18.03. **IR (ATR mode):** 3446, 3392, 3050, 2980, 2928, 2831, 1603, 1586, 1499, 1474, 1458, 1398, 1338, 1309, 1272, 1251, 1234, 1169, 1116, 1087, 1018, 869, 820, 739, 562, 503 cm^{-1}. **MS (EI):** m/z (%) = 233.2 (100 [M+]), 218.1, 202.1, 189.1

Reference: G. A. Chesnokov, P. S. Gribanov, M. A. Topchiy, L. I. Minaeva, A. F. Asachenko, M. S. Nechaev, E. V. Bermesheva and M. V. Bermeshev, *Mend. Commun.* 2017, **27**, 618–620.

Di-*o*-tolylamine (**3be**).



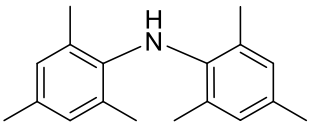
3be

Diarylamine **3be** was synthesized according to the general procedure, purified by column chromatography and isolated in 93 % yield as off-white crystals. The analytical data is in accordance with the reported literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 7.9 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 2H), 5.09 (s, 1H), 2.21 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 142.06, 130.93, 127.61, 126.91, 121.46, 118.37, 17.93. **IR** (ATR mode): 3430, 3371, 3068, 2990, 2974, 2966, 2915, 2851, 2732, 2133, 1944, 1889, 1735, 1598, 1579, 1561, 1530, 1514, 1446, 1442, 1374, 1297, 1254, 1235, 1175, 1130, 1060, 1044, 1110, 1024, 986, 796, 628, 439 cm^{-1} **mp** 53.4 °C **MS (EI):** m/z (%) = 197.2 (100 [M+]), 180.1, 167.1, 152.1

Reference: X. Huang and S. L. Buchwald, *Org. Lett.* 2001, **3**, 3417–3419.

Dimesitylamine (**3cb**). Diarylamine **3cb** was synthesized according to the general procedure, purified by column chromatography and isolated in 69 % yield as off-white crystals. The analytical data is in accordance with the reported literature.

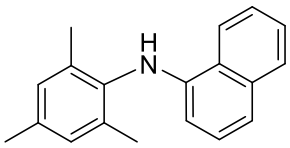


3cb

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.85 (s, 4H), 4.53 (s, 1H), 2.31 (s, 6H), 2.05 (s, 12H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 139.59, 130.84, 129.54, 129.43, 20.70, 19.17. **IR (ATR mode):** 3413, 3010, 2958, 2941, 2909, 2850, 2729, 1735, 1609, 1436, 1374, 1312, 1255, 1240, 1216, 1162, 1029, 1008, 959, 854, 723, 584, 568, 553, 505 cm^{-1}. **mp** 118.2 °C **MS (EI):** m/z (%) = 253.2 (100 [M+]), 236.2, 222.2, 208.1

Reference: L. Zhu, Y. M. Ye, L. X. Shao, *Tetrahedron* **2012**, *68*, 2414–2420.

***N*-mesitylnaphthalen-1-amine** (**3cd**). Diarylamine **3cd** was synthesized according to the general procedure, purified by column chromatography and isolated in 68 % yield as dark red crystals. The analytical data is in accordance with the reported literature.



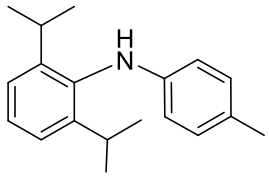
3cd

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.06 – 7.96 (m, 1H), 7.85 – 7.69 (m, 2H), 7.60 – 7.40 (m, 3H), 7.28 – 7.20 (m, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.17 (d, *J* = 7.5 Hz, 1H), 5.28 (s, 1H), 2.29 (s, 3H), 2.12 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 141.70, 136.04, 135.40, 135.33, 134.68, 129.48, 128.86, 126.68, 125.89, 125.03, 123.91, 120.41, 118.52, 106.90, 21.08, 18.17. **IR** (ATR mode): 419, 514, 562, 582, 630, 710, 734, 767, 788, 855, 882, 944, 959, 1020, 1091, 1149, 1171, 1227, 1254, 1274, 1305, 1335,

1374, 1400, 1435, 1465, 1480, 1515, 1577, 1728, 1916, 2914, 2970, 3057, 3401 cm^{-1}. **mp** 79.2 °C. **MS (EI):** m/z (%) = 261.2 (100 [M+]), 246.1, 231.1, 217.1

Reference: W. Chen, K. Chen, W. Chen, M. Liu, H. Wu, *ACS Catal.* **2019**, 8110–8115.

2,6-diisopropyl-*N*-(*p*-tolyl)aniline (**3da**). Diarylamine **3da** was synthesized according to the general procedure, purified by column chromatography and isolated in 80 % yield as off-white solid. The analytical data is in accordance with the reported literature.

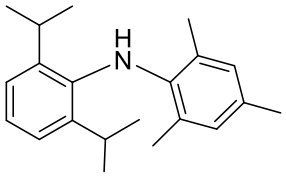


3da

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.26 (dd, *J* = 8.7, 6.5 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 7.9 Hz, 2H), 4.86 (s, 1H), 3.19 (hept, *J* = 6.9 Hz, 2H), 2.22 (s, 3H), 1.12 (d, *J* = 6.8 Hz, 12H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 147.49, 145.92, 135.68, 129.83, 127.08, 126.92, 123.91, 113.17, 28.30, 23.99, 20.56. **IR** (ATR mode): 3438, 3398, 3102, 3049, 3017, 2979, 2970, 2959, 2921, 2864, 1616, 15151478, 1457, 1383, 1361, 1330, 1311, 1263, 1251, 1180, 1120, 1100, 1057, 997, 839, 804, 692, 610, 501 cm^{-1}. **mp** 56,3 °C **MS (EI):** m/z (%) = 267.2 (100 [M+]), 252.2, 236.2, 222.2

Reference: N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott, S. P. Nolan, *J. Am. Chem. Soc*. **2006**, *128*, 4101–4111.

***N*-(2,6-diisopropylphenyl)-2,4,6-trimethylaniline** (**3db**). Diarylamine **3db** was synthesized according to the general procedure, purified by column chromatography and isolated in 71 % yield as off-white solid. The analytical data is in accordance with the reported literature.

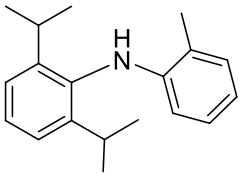


3db

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.18 (s, 3H), 6.84 (s, 2H), 4.61 (s, 1H), 3.22 (hept, *J* = 6.9 Hz, 2H), 2.31 (s, 3H), 2.04 (s, 6H), 1.20 (d, *J* = 6.9 Hz, 12H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 143.48, 140.57, 139.30, 130.17, 129.19, 126.45, 124.30, 123.35, 28.10, 23.58, 20.56, 19.39. **IR** (ATR mode): 3428, 3057, 3013, 2960, 2918, 2861, 2727, 1611, 1535, 1480, 1462, 1439, 1339, 1268, 1254, 1231, 1155, 1102, 1057, 1010, 956, 942, 925, 855, 739, 612, 576, 539, 473 cm^{-1}. **mp** 70.3 °C. **MS (EI):** m/z (%) = 295.3 (100 [M+]), 280.2, 264.2, 250.2

Reference: S. Rodriguez, B. Qu, N. Haddad, D. C. Reeves, W. Tang, H. Lee, D. Krishnamurthy, C. H. Senanayake, *Adv. Synth. Catal.* **2011**, *353*, 533–537.

2,6-diisopropyl-*N*-(*o*-tolyl)aniline (**3de**). Diarylamine **3de** was synthesized according to the general procedure, purified by column chromatography and isolated in 79% yield as a high viscous yellow liquid. The analytical data is in accordance with the reported literature.



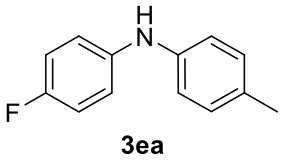
3de

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 – 7.41 (m, 2H), 7.22 – 7.11 (m, 4H), 6.63 (d, *J* = 8.1 Hz, 1H), 5.24 (s, 1H), 3.43 (hept, *J* = 6.9 Hz, 2H), 2.45 (s, 3H), 1.37 (d, *J* = 6.9 Hz, 6H), 1.17 (d, *J* = 6.9 Hz, 6H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 147.37, 146.13, 135.81, 130.23, 127.19, 127.10, 123.92, 121.37, 117.60, 111.51, 28.34, 24.85, 23.12, 17.77.

IR (ATR mode): 3023, 2982, 2960, 2923, 2865, 1607, 1583, 1503, 1464, 1443, 1382, 1361, 1295, 1264, 1177, 1111, 1054, 807, 782, 742, 705, 577, 505 cm^{-1}. **MS (EI):** m/z (%) = 267.2 (100 [M+]), 252.2, 236.2, 222.1

Reference: L. Zhu, Y. M. Ye, L. X. Shao, *Tetrahedron* **2012**, *68*, 2414–2420.

4-fluoro-*N*-(*p*-tolyl)aniline (**3ea**). Diarylamine **3ea** was synthesized according to the general procedure, purified via Kugelrohr distillation (130-140 °C, $1.0*10^{-3}$ mbar). Product isolated in 87 % yield as a high viscous yellow liquid. The analytical data is in accordance with the reported literature.



3ea

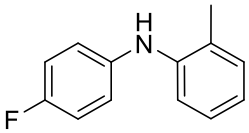
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 7.8 Hz, 2H), 6.86 (m, 6H), 5.40 (s, 1H), 2.21 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 157.77 (d, *J* = 239.2 Hz), 141.19, 139.90, 130.69, 130.04, 119.53 (d, *J* = 7.6 Hz), 118.02, 115.97 (d, *J* = 22.3 Hz), 20.76.

IR (ATR mode): 3670, 3414, 3103, 3056, 3028, 2981, 1915, 2860, 2735, 2537, 1891, 1610, 1507, 1387, 1378, 1349, 1316, 1214, 1181, 1123, 1093, 1045, 1005, 857, 741, 703, 578 cm^{-1}. **mp** 52.5 °C. **MS (EI):** m/z (%) = 201.2 (100 [M+]), 185.1, 170.1, 152.1

Reference: L. Zhu, Y. M. Ye and L. X. Shao, *Tetrahedron* 2012, **68**, 2414–2420.

***N*-(4-fluorophenyl)-2-methylaniline** (**3ee**).

Diarylamine **3ee** was synthesized according to the general procedure, purified via Kugelrohr distillation (150-155 °C, $1.0*10^{-3}$ mbar). Product isolated in 74 % yield as a high viscous yellow liquid. The analytical data is in accordance with the reported literature.

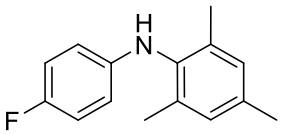


3ee

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 7.5 Hz, 1H), 7.12 (m, 2H), 7.00 – 6.88 (m, 5H), 5.35 (s, 1H), 2.26 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 157.88 (d, *J* = 239.5 Hz), 142.10, 139.76 (d, *J* = 2.5 Hz), 131.01, 127.19, 126.91, 121.48, 120.21 (d, *J* = 7.7 Hz), 117.28, 115.93 (d, *J* = 22.6 Hz), 17.87. **MS (EI):** m/z (%) = 201.2 (100 [M+]), 185.1, 170.1, 152.1

Reference: X. Y. Zhao, Q. Zhou and J. M. Lu, *RSC Adv.* 2016, **6**, 24484–24490.

***N*-(4-fluorophenyl)-2,4,6-thrimethylaniline** (**3eb**).



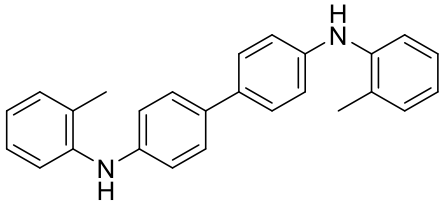
3eb

Diarylamine **3eb** was synthesized according to the general procedure, purified via Kugelrohr distillation (150-155 °C, $1.0*10^{-3}$ mbar). Product isolated in 82 % yield as yellow crystals. The analytical data is in accordance with the reported literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.26 (s, 2H), 7.16 (t, *J* = 8.7 Hz, 2H), 6.76 – 6.70 (m, 2H), 5.30 (s, 1H), 2.62 (s, 3H), 2.48 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 156.14 (d, *J* = 235.3 Hz), 142.88, 135.86, 135.62, 135.38, 129.34, 115.65 (d, *J* = 22.4 Hz), 114.18 (d, *J* = 7.5 Hz), 20.92, 18.20. **IR** (ATR mode): 3386, 3031, 2950, 2913, 1853, 2730, 1840, 1735, 1610, 1485, 1390, 1376, 1315, 1251, 1215, 1206, 1150, 1112, 1033, 1009, 929, 913, 856, 792, 782, 756, 718, 706, 595, 497 cm^{-1}. **mp** 79.4 °C. **MS (EI):** m/z (%) = 229.2 (100 [M+]), 214.1, 199.1, 185.1

Reference: L. Cai, X. Qian, W. Song, T. Liu, X. Tao, W. Li and X. Xie, *Tetrahedron* 2014, **70**, 4754–4759.

***N*-4,N4'-di-o-tolyl-[1,1'-biphenyl]-4,4'-diamine 5**.



N-4,N4'-di-o-tolyl-[1,1'-biphenyl]-4,4'-diamine **5** was synthesized according to the general procedure, purified via column chromatography and obtained as a green solid in 87 % yield. The analytical data is in accordance with the reported literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.46 (m, 3H), 7.29 (qd, *J* = 10.4, 8.9, 3.1 Hz, 4H), 7.25 – 7.14 (m, 4H), 7.06 – 7.00 (m, 3H), 6.96 (td, *J* = 7.4, 1.3 Hz, 2H), 5.44 (d, *J* = 6.8 Hz, 2H), 2.29 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 142.69, 141.25, 133.29, 131.01, 128.21, 127.36, 126.84, 121.97, 118.73, 117.82, 17.99. **HRMS-ESI** (m/z): $[M-H]^+$ calcd for $C_{26}H_{24}N_2$, 365.2012; found, 365.2009.

Reference: Ichinori Takada, Naoyuki Ueda, US 2007/0149815 A1, 2007.

1.2.5 Optimization of the reaction conditions for the formation of triarylamines

General procedure for the reaction optimization.

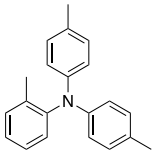
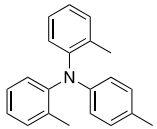
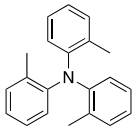
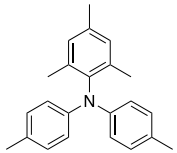
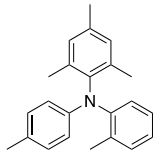
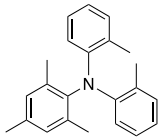
In a glovebox, a vial was charged the primary arylamine (1.00 mmol), the aryl chloride (2.20 mmol) and KO*t*Bu (2.50 mmol). In case of the formation of unsymmetrical triarylamines with three different aryl substituents, only one aryl chloride (1.00 mmol) was at first added, followed by addition of the second aryl chloride (1.2 mmol) after 1 h reaction time at 60 °C.

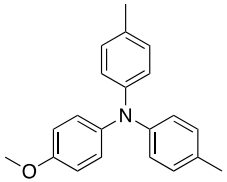
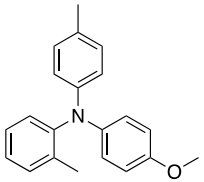
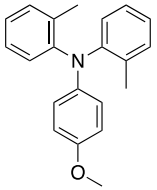
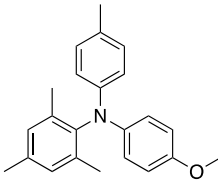
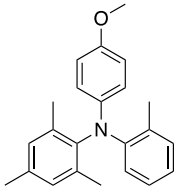
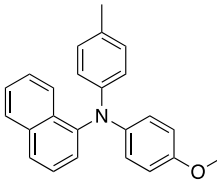
The solids were dissolved in 1 mL THF. The vial was sealed with a septum cap and taken outside the glovebox. In a second vial (in a glovebox), $Pd_2(dba)_3$ and keYPhos (0.01 mmol each) were dissolved in 0.5 mL THF. The vial was sealed with a septum cap and taken outside the glovebox and the catalyst preformed for one hour. After one hour the catalyst was added to the substrate solution via a syringe and the mixture was stirred at 60 °C for 18 h. For determination of the reaction yield, the reaction was quenched with 0.1 mL water. Small aliquots of the reaction mixture were taken from the mixture and filtered through a pad of silica with EtOAc as eluent. Yields were determined by GC/FID analysis using *n*-tetradecane as internal standard.

Table S5. Effect of the ligand and temperature on the diarylamine formation.

Entry	Temp	Ligand	GC-FID yield [%]
1	25 °C	keYPhos/$Pd_2(dba)_3$	23
2	25 °C	joYPhos/$Pd_2(dba)_3$	31
3	25 °C	pinkYPhos/$Pd_2(dba)_3$	7
4	60 °C	keYPhos/$Pd_2(dba)_3$	67
5	60 °C	joYPhos/$Pd_2(dba)_3$	65
6	60 °C	pinkYPhos/$Pd_2(dba)_3$	8

Table S6. Systematic evaluation of the impact of the steric congestion on the triarylamine formation. Conditions: 60°C, KO*t*Bu in THF, keYPhos, Pd_2dba_3.

Entry	Mol%						
No. of ortho groups	-	1	2	3	2	3	4
1	1	53	69	0	80	9	0
2	1.5	>99	82	0	90	25	0
3	2.5	>99	98	0	99	49	0

Entry	Mol%						
No. of ortho groups	-	0	1	2	2	3	1
4	1	88	83	81	72	0	44

Optimization of the reaction conditions for the formation of tri-*ortho*-methyl-substituted triarylamines

The optimization of the conditions for the bulky triarylamines was performed in a similar way then for the other triarylamines (see above).

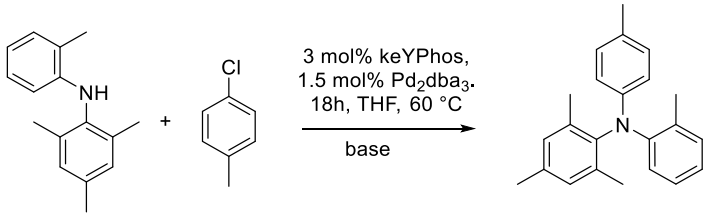
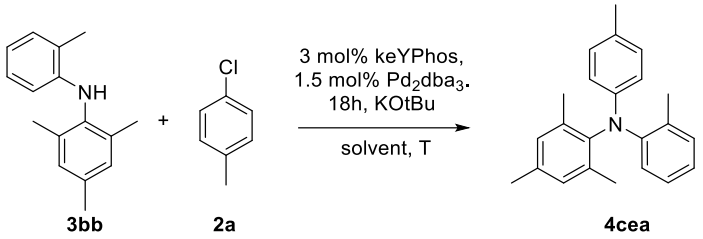


Table S7. Effect of the base at 3 mol% catalyst loading on the triarylamine formation.

Entry	[mol%] cat.	base	GC-FID yield [%]
1	3	KO*t*Bu	40
2	3	NaO*t*Bu	-
3	3	LiTMP	-
4	3	LDA	-
5	3	KOEt	-
6	3	LiHMDS	16
7	3	NaH	1
8	3	NEt3	-
9	3	Cs2CO3	-

Table S8. Effect of the solvent and temperature on the diarylamine formation.



3bb 2a 4cea

Entry	Solvent	T	GC-FID yield [%]
1	Toluene	100	41
2	Dioxane	100	51
3	THF	60	-
4	Toluene/THF (1/1)	100	62
5	Dioxane/THF (1/1)	100	41
6	Mesitylene	100	31
7	2-Methyl-THF	80	26
8	DMF	150	-

Remark: Although a 1:1 mixture of toluene/thf was found to be beneficial for **4cea**, further studies showed that this is not in general the case for all triarlyamines. In case of the non-ortho-substituted systems, which do not require higher temperatures thf in general gives the best results.

1.2.6 General procedure for the isolation of triarylamines.

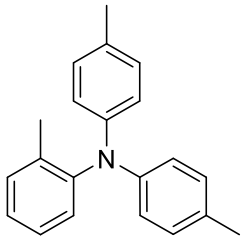
In a glovebox, a vial was charged the arylamine (1.00 mmol) and aryl chloride (2.20 mmol) and KO*t*Bu (1.50 mmol) and the solids dissolved in 1 mL THF. The vial was sealed with a septum cap and taken outside the glovebox. In a second vial (in a glovebox), $Pd_2(dba)_3$ and keYPhos (0.01 mmol each) were dissolved in 0.5 mL THF. The vial was sealed with a septum cap and taken outside the glovebox and the catalyst preformed for one hour. After one hour the catalyst was added to the substrate solution via a syringe and the mixture was stirred at 60 °C for 18 h. Subsequently, the reaction mixture was quenched with water and extracted with EtOAc three times. The organic phases were combined and dried with $MgSO_4$. The crude product was purified via column chromatography or Kugelrohr distillation.

In case of the formation of unsymmetrical triarylamines with three different aryl substituents, only one aryl chloride (1.00 mmol) was at first added, followed by addition of the second aryl chloride (1.2 mmol) after 1 h reaction time at 60 °C. In case of the tri-*ortho*-methyl substituted

triarylamines, the diarylamines were first isolated and then treated in a separate step with one equivalent of aryl chloride (1.00 mmol).

1.2.7 Isolated triarylamines.

2-methyl-*N,N*-di-*p*-tolylaniline (**4baa**).



4baa

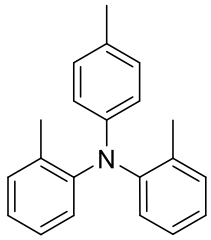
The triarylamine **4baa** was synthesized according to the general procedure, purified by column chromatography and isolated in 90 % yield as off-white solid. The analytical data is in accordance with the reported literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 – 7.04 (m, 4H), 6.96 (d, *J* = 8.2 Hz, 4H), 6.82 (d, *J* = 8.2 Hz, 4H), 2.24 (s, 6H), 2.00 (s, 3H) ppm

^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$): δ = 145.94, 145.51, 136.31, 131.71, 130.66, 129.70, 129.38, 127.34, 125.63, 121.69, 20.81, 18.81 ppm **IR (ATR mode):** 3428, 3396, 3066, 3047, 3021, 2980, 2915, 2856, 1888, 1616, 1604, 1570, 1503, 1487, 1458, 1379, 1265, 1187, 1171, 1156, 1110, 986, 971, 941, 915, 861, 843, 825, 720, 711, 625, 558, 495, 447 cm^{-1} **mp** 74.8 °C **MS (EI):** m/z (%) = 287.3 (100 [M+]), 272.2, 257.1, 241.1

Reference: X. Le Li, W. Wu, X. H. Fan and L. M. Yang, *Org. Biomol. Chem.* 2014, **12**, 1232–1236.

2-methyl-*N*-(*o*-tolyl)-*N*-(*p*-tolyl)aniline (**4bea**).



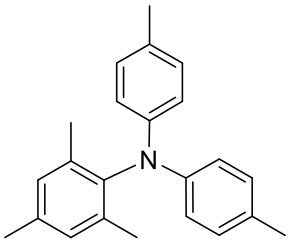
4bea

The triarylamine **4bea** was synthesized according to the general procedure, purified by column chromatography and isolated in 89 % yield as off-white solid. The analytical data is in accordance with the reported literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, J = 7.6 Hz, 2H), 7.16 – 7.09 (m, 2H), 7.05 (td, J = 7.5, 2.4 Hz, 2H), 7.01 – 6.93 (m, 4H), 6.68 – 6.57 (m, 2H), 2.29 (s, 3H), 2.02 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 146.67, 146.53, 134.57, 131.69, 130.05, 129.61, 127.25, 126.92, 124.43, 120.78, 20.79, 19.08 ppm. **IR (ATR mode):** 3059, 3019, 2981, 2950, 2909, 2859, 2729, 1946, 1913 1898, 1829, 1612, 1506, 1485, 1460, 1439, 1377, 1258, 1194, 1119, 1111, 1032, 1016, 978, 819, 790, 751, 673, 642 cm^{-1}. **mp** 69.1 °C. **MS (EI):** m/z (%) = 287.2 (100 [M+]), 272.1, 257.1, 241.1

Reference: R. Kuwano, Y. Matsumoto, T. Shige, T. Tanaka and S. Soga, Y. Hanasaki, *Synlett* 2010, 1819–1824.

2,4,6-trimethyl-*N,N*-di-*p*-tolylaniline (**4caa**).



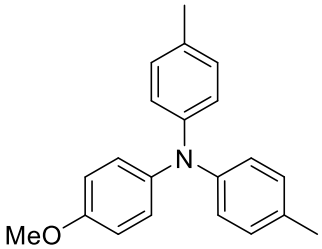
4caa

The triarylamine **4caa** was synthesized according to the general procedure, purified by column chromatography and isolated in 84 % yield as off-white solid. The analytical data is in accordance with the reported literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.02 (d, *J* = 8.3 Hz, 4H), 6.96 (s, 2H), 6.92 – 6.87 (m, 4H), 2.36 (s, 3H), 2.30 (s, 6H), 2.03 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 143.86, 140.36, 137.71, 136.45, 129.84, 129.64, 129.56, 119.36, 21.07, 20.64, 18.62. **IR (ATR mode):** 3384, 3096, 2990, 2974, 2963, 2861, 2730, 1615, 1510, 1481, 1445, 1432, 1374, 1311, 1292, 1252, 1176, 1149, 1096, 853, 807, 778, 724, 600, 496, 426 cm^{-1}. **MS (EI):** m/z (%) = 315.2 (100 [M+]), 300.2, 285.1, 270.1

Reference: L. Cai, X. Qian, W. Song, T. Liu, X. Tao, W. Li and X. Xie, *Tetrahedron* 2014, **70**, 4754–4759.

4-methoxy-*N,N*-di-*p*-tolylaniline (**4aaa**).



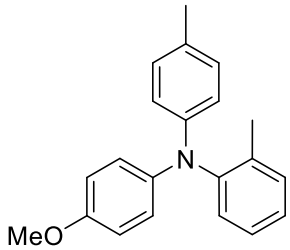
4aaa

Diarylamine **4aaa** was synthesized according to the general procedure and purified via Kugelrohr distillation (140-150 °C, $1.0*10^{-3}$ mbar). Product isolated in 88 % yield as yellow crystals. The analytical data is in accordance with the reported literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.08 (t, *J* = 8.8, 7.2 Hz, 6H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.89 – 6.84 (m, 2H), 3.83 (s, 3H), 2.34 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 155.64, 145.98, 141.36, 131.27, 129.71, 126.45, 123.10, 114.64, 55.50, 20.77 ppm. **IR** (ATR mode): 3414, 3023, 2996, 2915, 2855, 2831, 1890, 1606, 1501, 1462, 1438, 1388, 1376, 1349, 1317, 1235, 1178, 1165, 1124, 1107, 1033, 914, 879, 811, 780, 712, 627, 564, 499 cm^{-1}. **mp** 70.5 °C. **MS (EI):** m/z (%) = 303.2 (100 [M+]), 288.2, 272.1, 258.

Reference: K. H. Hoi, J. A. Coggan and M. G. Organ, *Chem. - A Eur. J.* 2013, **19**, 843–845.

***N*-(4-methoxyphenyl)-2-methyl-*N*-(*p*-tolyl)aniline** (**4aea**).



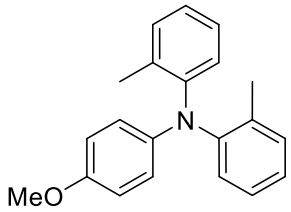
4aea

Diarylamine **4aea** was synthesized according to the general procedure and purified via Kugelrohr distillation (140-150 °C, $1.0*10^{-3}$ mbar). The product was isolated in 83 % yield as pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.24 – 7.06 (m, 4H), 7.01 – 6.91 (m, 4H), 6.78 (dd, *J* = 8.9, 2.8 Hz, 4H), 3.78 (s, 3H), 2.28 (s, 3H), 2.04 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 154.88, 146.15, 146.08, 141.33, 136.08, 131.72, 129.99, 129.65, 129.09, 127.28, 125.41, 124.26, 120.59, 114.52, 55.61,

20.75, 18.87 ppm **IR (ATR mode):** 3015, 2997, 2947, 2920, 2858, 2832, 1729, 1612, 2598, 1502, 1488, 1440, 1376, 1350, 1315, 1240, 1180, 1150, 1110, 1037, 986, 914, 828, 815, 786, 755, 722, 596, 578, 560 cm^{-1}. **HRMS-ESI** (m/z): $[M-H]^+$ calcd for $C_{21}H_{22}NO$, 304.1696; found, 304.1695.

***N*-(4-methoxyphenyl)-2-methyl-*N*-(*o*-tolyl)aniline** (**4aee**).



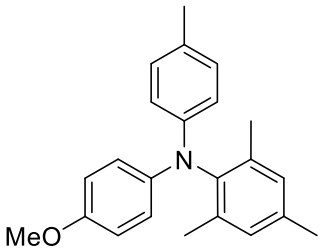
4aee

Triarylamine **4aee** was synthesized according to the general procedure and purified via Kugelrohr distillation (140-150 °C, $1.0*10^{-3}$ mbar). Product isolated in 81 % yield as pale yellow oil. The analytical data is in accordance with the reported literature.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.17 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.06 (dtd, *J* = 30.5, 7.4, 1.6 Hz, 5H), 6.90 (dd, *J* = 7.8, 1.4 Hz, 3H), 6.78 – 6.67 (m, 4H), 3.77 (s, 3H), 1.98 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 154.33, 147.11, 142.73, 134.17, 131.70, 126.85, 126.73, 124.11, 122.88, 114.39, 55.59, 19.07 ppm. **IR (ATR mode):** 3390, 3016, 2996, 1947, 2928, 2909, 2832, 1597, 1503, 1485, 1461, 1439, 1310, 1259, 1237, 1179 1120, 1108, 1035, 856, 827, 752, 719, 675, 623, 590, 551, 420 cm^{-1}. **MS (EI):** m/z (%) = 303.2 (100 [M+]), 288.2, 272.1, 258.1

Reference: R. Kuwano, Y. Matsumoto, T. Shige, T. Tanaka, S. Soga and Y. Hanasaki, *Synlett* 2010, 1819–1824.

***N*-(4-methoxyphenyl)-2,4,6-trimethyl-*N*-(*p*-tolyl)aniline** (**4aba**).

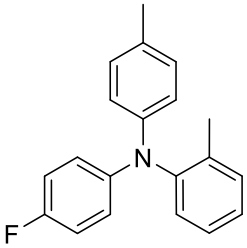


4aba

Diarylamine **4aba** was synthesized according to the general procedure and purified via Kugelrohr distillation (140-150 °C, $1.0*10^{-3}$ mbar). The product was isolated in 72 % yield as pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.01 – 6.91 (m, 6H), 6.83 – 6.74 (m, 4H), 3.77 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H), 2.01 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 154.03, 144.50, 140.57, 139.82, 137.75, 136.44, 129.96, 129.69, 129.06, 121.64, 118.40, 114.45, 55.63, 21.15, 20.70, 18.77 ppm. **IR (ATR mode):** 3656, 3390, 2995, 2974, 2948, 2912, 2831, 1609, 1573, 1500, 1462, 1439, 1395, 1315, 1237, 1178, 1146, 1107, 1034, 965, 784, 770, 747, 736, 639, 512, 497 cm^{-1}. **HRMS-ESI** (m/z): $[M-H]^+$ calcd for $C_{23}H_{26}NO$, 332.2009; found, 332.2008.

***N*-(4-fluorophenyl)-2-methyl-*N*-(*p*-tolyl)aniline** (**4eea**).

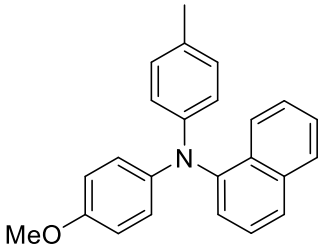


4eea

Diarylamine **4eea** was synthesized according to the general procedure and purified via Kugelrohr distillation (140-150 °C, 1.0*10^{-3} mbar). The product was isolated in 73 % yield as pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.16 – 6.96 (m, 4H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.87 – 6.70 (m, 6H), 2.19 (s, 3H), 1.96 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 159.43, 156.24, 145.64 (d, *J* = 25.5 Hz), 144.19 (d, *J* = 2.5 Hz), 136.18, 131.85, 131.06, 129.82, 129.23, 127.45, 125.83, 123.07 (d, *J* = 7.8 Hz), 121.65, 115.75, 20.81, 18.78 ppm. **IR** (ATR mode): 3651, 3379, 3023, 2980, 2918, 1613, 1599, 1575, 1483, 1459, 1379, 1310, 1267, 1218, 1154, 1114, 1097, 1041, 1010, 947, 915, 831, 816, 756, 722, 711, 592, 575, 520, 508, 419 cm^{-1}. **HRMS-ESI** (m/z): $[M-H]^+$ calcd for $C_{20}H_{19}FN$, 292.1496; found, 292.1496.

***N*-(4-methoxyphenyl)-*N*-(*p*-tolyl)naphthalen-1-amine** (**4ada**).

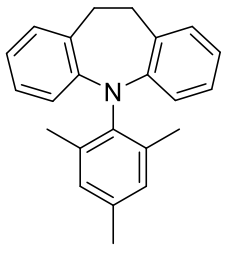


4ada

4ada was synthesized according to the general procedure and purified via Kugelrohr distillation (140-150 °C, 1.0*10^{-3} mbar). The product was isolated in 54 % yield as orange solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.35 – 7.30 (m, 1H), 7.25 – 7.22 (m, 1H), 7.03 – 6.91 (m, 4H), 6.82 – 6.72 (m, 4H), 3.74 (s, 3H), 2.24 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 155.14, 147.09, 144.42, 142.32, 135.37, 131.18, 130.28, 129.70, 128.43, 126.50, 126.42, 126.21, 126.11, 125.83, 124.60, 123.19, 120.94, 114.61, 55.60, 20.76 ppm. **IR** (ATR mode): 3045, 2997, 2947, 2928, 2859, 2831, 2731, 2056, 1879, 1610, 1592, 1571, 1499, 1460, 1439, 1391, 1342, 1313, 1236, 1178, 1107, 1085, 1033, 954, 861, 815, 799, 789, 782, 709, 639, 593, 511 cm^{-1}. **mp** 99.5 °C. **HRMS-ESI** (m/z): $[M-H]^+$ calcd for $C_{24}H_{22}NO$, 340.1696; found, 340.1697.

5-(2,6-dimethylphenyl)-10,11-dihydro-5H-dibenzo[b,f]azepine (4fb)



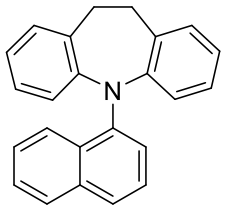
4fb

4fb was synthesized according to the general procedure, purified via column chromatography and isolated in 99 % yield as an off-white solid. The analytical data is in accordance with the reported literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 – 7.03 (m, 4H), 6.91 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 2H), 6.75 (td, *J* = 7.3, 1.2 Hz, 2H), 6.34 (dd, *J* = 8.5, 1.1 Hz, 2H), 3.21 (s, 4H), 2.40 (s, 3H), 2.01 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 143.87, 141.59, 137.44, 137.08, 131.78, 130.36, 130.33, 126.62, 119.23, 119.17, 38.18, 21.16, 17.91. **MS (EI):** m/z (%) = 299.3 (100 [M+]), 284.2, 268.2, 254.2

Reference: W. Huang and S. L. Buchwald, *Chem. Eur. J.* **2016**, *22*, 14186-14189.

5-(naphthalen-1-yl)-10,11-dihydro-5H-dibenzo[b,f]azepine (4fd)



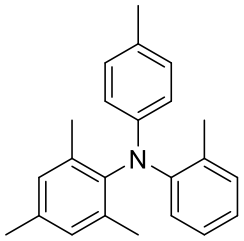
4fd

4fd was synthesized according to the general procedure, purified via column chromatography and isolated in 99% yield as an off while solid. The analytical data is in accordance with the reported literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.92 (m, 2H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.42 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.12 (dd, *J* = 6.7, 2.5 Hz, 2H), 6.78 (tt, *J* = 7.2, 5.2 Hz, 4H), 6.51 (dd, *J* = 7.8, 1.8 Hz, 2H), 3.34 (s, 4H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 146.02, 143.98, 135.42, 132.40, 132.19, 130.45, 128.92, 128.74, 127.81, 127.06, 126.89, 126.50, 126.36, 124.57, 121.90, 120.32, 37.25. **MS (EI):** m/z (%) = 321.3 (100 [M+]), 306.2, 291.2, 278.2

Reference: W. Huang and S. L. Buchwald, *Chem. Eur. J.* **2016**, *22*, 14186-14189.

2,4,6-trimethyl-N-(o-tolyl)-N-(p-tolyl)aniline



4cea

4cea was synthesized according to the general procedure but in toluene/thf at 100°C and a GC-FID yield of 62 % was observed. The GC-MS fits the expected mass of the product. Unfortunately, several attempts to separate the di- and triarylamines failed.

MS (EI): m/z (%) = 315.2 (100 [M+]), 300.2, 285.1, 270.1

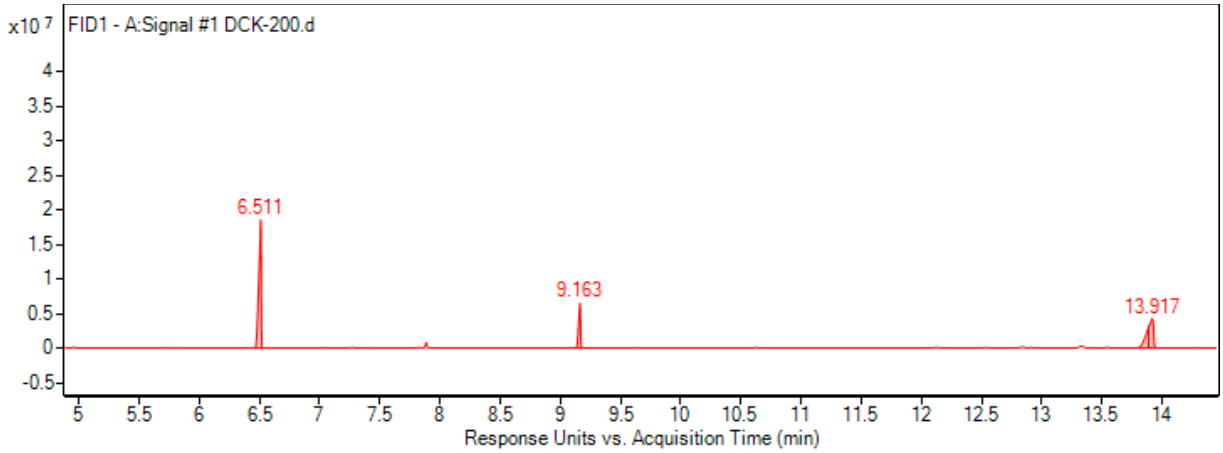
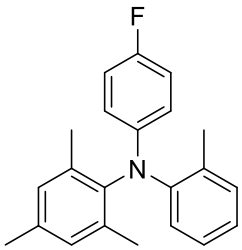


Figure S1. Obtained GC-FID spectrum of **4cea** (the signal at 6.5 min corresponds to the reference, tetradecane, the signal at 9.2 min to the diarylamine and at 13.9 to the triarylamine).

N-(4-fluorophenyl)-2,4,6-trimethyl-N-(o-tolyl)aniline



4ceg

4cef was synthesized according to the general procedure procedure but in toluene/thf at 100°C and a GC-FID yield of 32 % was observed. The GC-MS fits the expected mass of the product. Unfortunately, several attempts to separate the di- and triarylamines failed.

MS (EI): m/z (%) = 319.2 (100 [M+]), 304.1, 288.1, 224.1

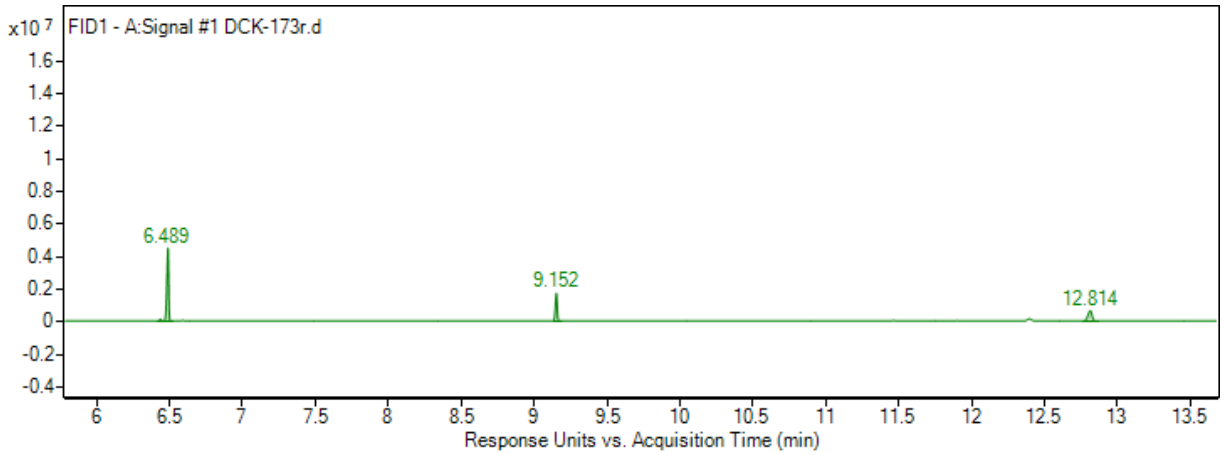
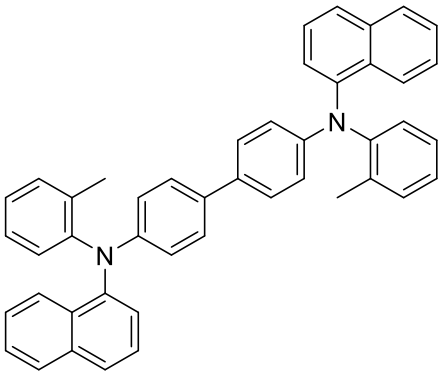


Figure S2. Obtained GC-FID spectrum of **4ceg** (the signal at 6.5 min corresponds to the reference, tetradecane, the signal at 9.2 min to the diarylamine and at 12.8 to the triarylamine).

***N*4,*N*4'-di(naphthalen-1-yl)-*N*4,*N*4'-di-o-tolyl-[1,1'-biphenyl]-4,4'-diamine 6**



*N*4,*N*4'-di(naphthalen-1-yl)-*N*4,*N*4'-di-o-tolyl-[1,1'-biphenyl]-4,4'-diamine was synthesized according to the general procedure, purified via column chromatography and isolated as a light yellow solid in 50 % yield. The analytical data is in accordance with the reported literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 13.5, 8.3 Hz, 4H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.28 (m, 10H), 7.25 – 7.20 (m, 2H), 7.11 (td, *J* = 5.9, 2.7 Hz, 8H), 6.71 (s, 4H), 2.07 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, CDCl3): δ = 148.40, 147.10, 143.81, 135.14, 134.85, 132.68, 131.69, 130.00, 128.43, 127.66, 126.99, 126.75, 126.07, 125.87, 125.31, 124.99, 124.69, 120.54, 19.08. **HRMS-ESI** (m/z): $[M-H]^+$ calcd for $C_{46}H_{36}N_2$, 617.2951; found, 617.2947.

Reference: Ichinori Takada, Naoyuki Ueda, US 2007/0149815 A1, 2007.

2. NMR spectra of the isolated compounds

2.1. NMR spectra of diarylamines

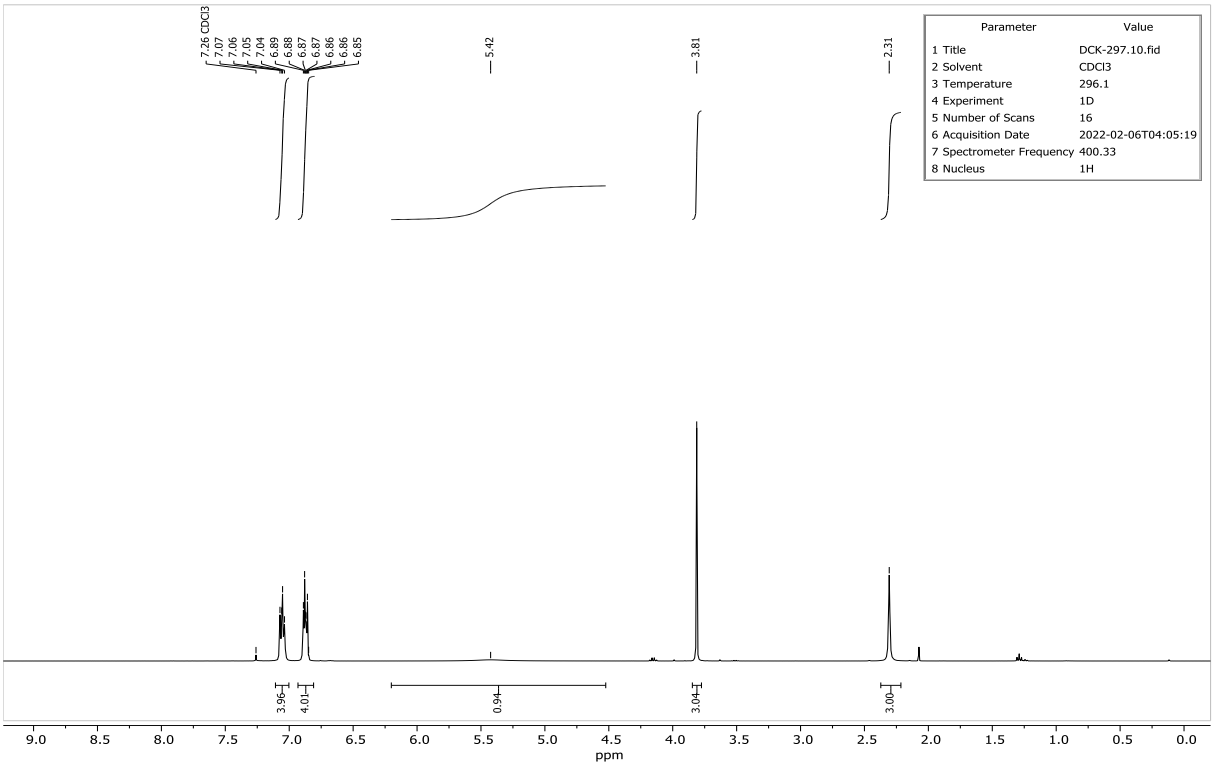


Figure S3. ^{1}H NMR spectrum of 4-methoxy-N-(p-tolyl)aniline **3aa**.

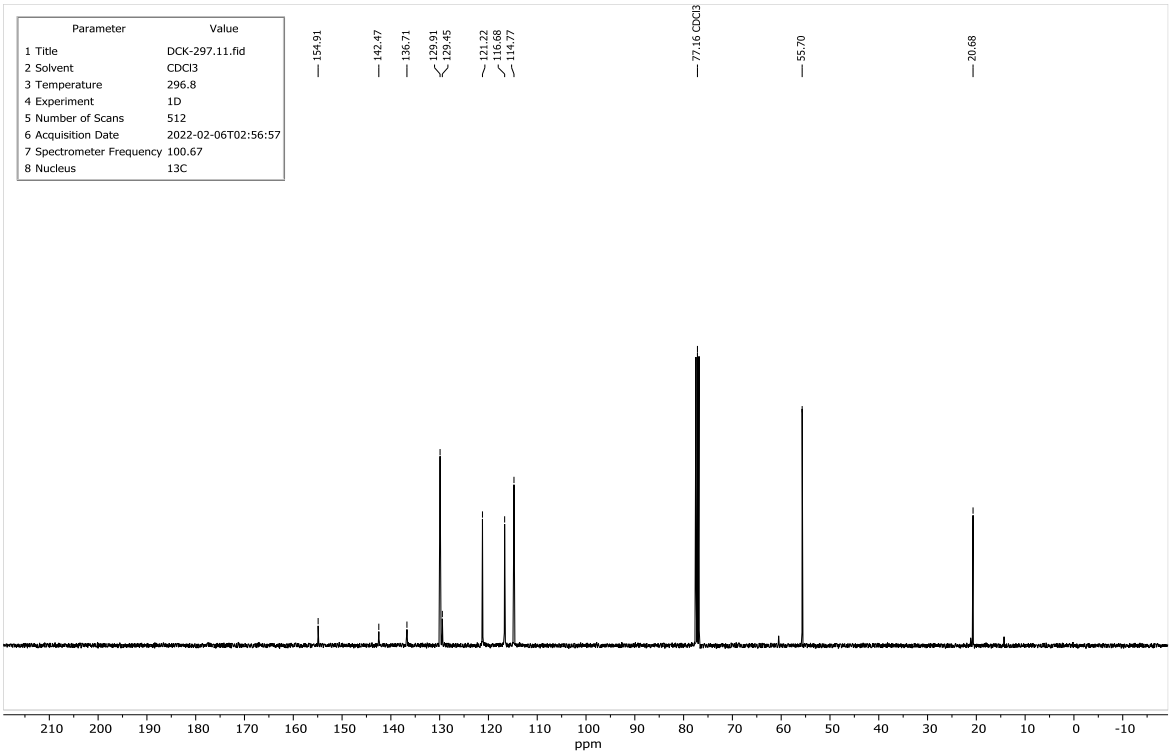


Figure S4. ^{13}C{^{1}H} NMR spectrum of 4-methoxy-N-(p-tolyl)aniline **3aa**.

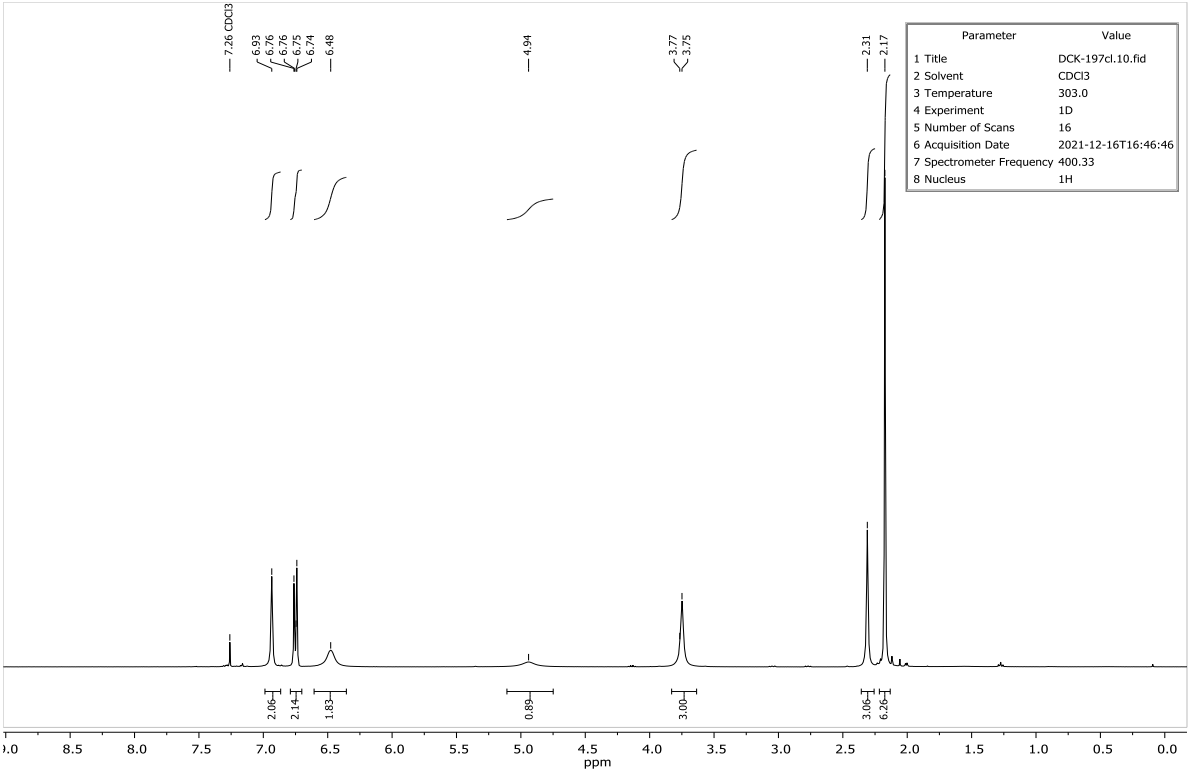


Figure S5. ^{1}H NMR spectrum of N-(4-methoxyphenyl)-2,4,6-trimethylaniline **3ab**.

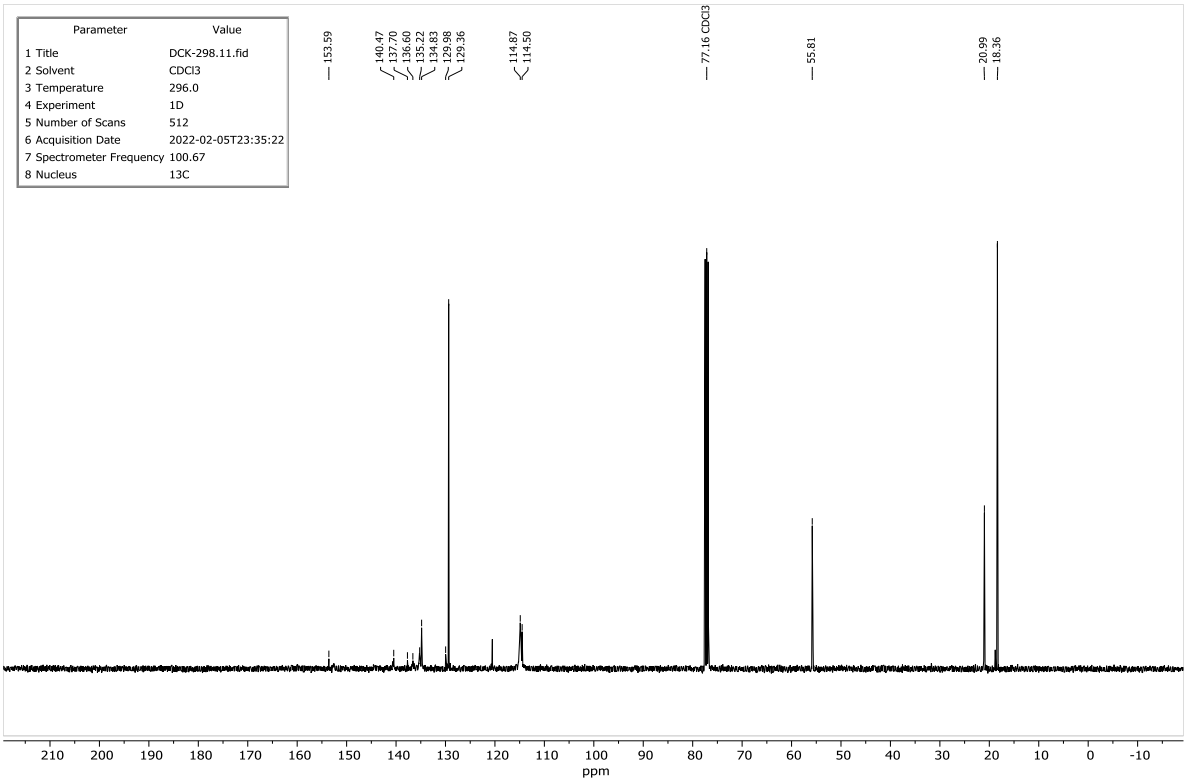


Figure S6. ^{13}C{^{1}H} NMR spectrum of N-(4-methoxyphenyl)-2,4,6-trimethylaniline **3ab**.

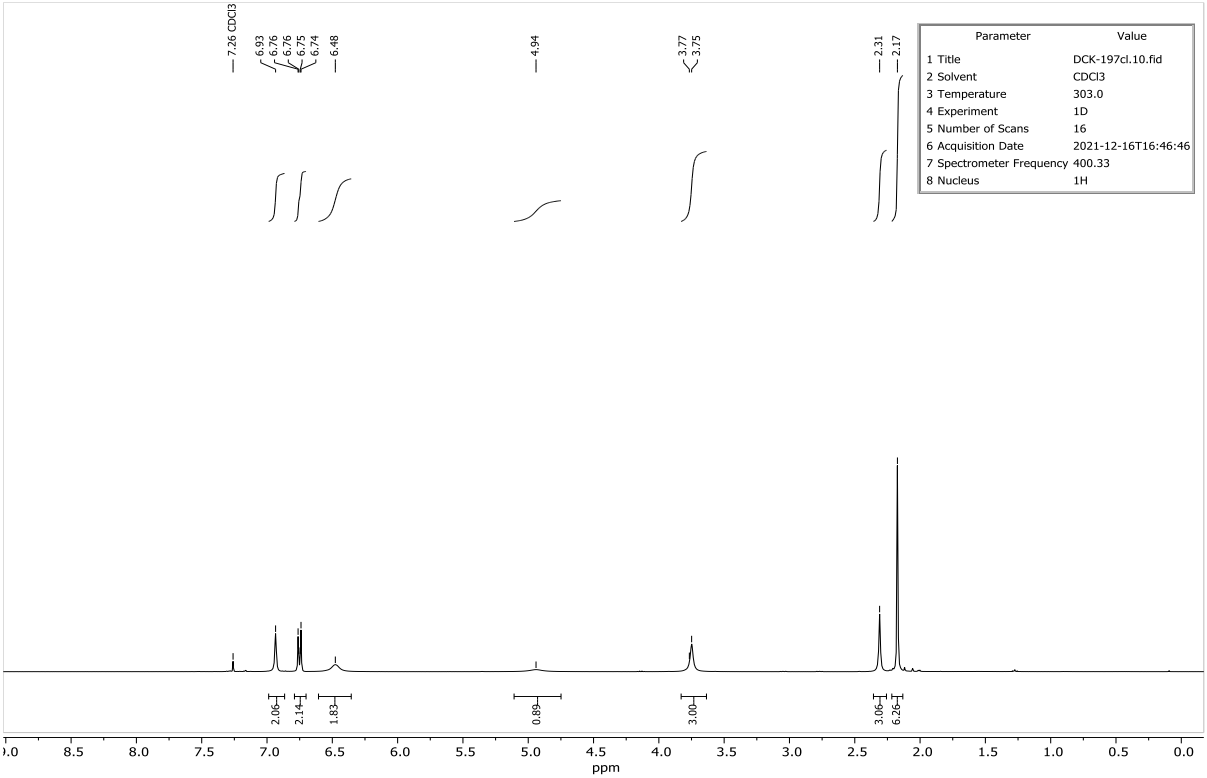


Figure S7. ^{1}H NMR spectrum of N-(4-methoxyphenyl)-[1,1‘-biphenyl]-2-amine **3ac**.

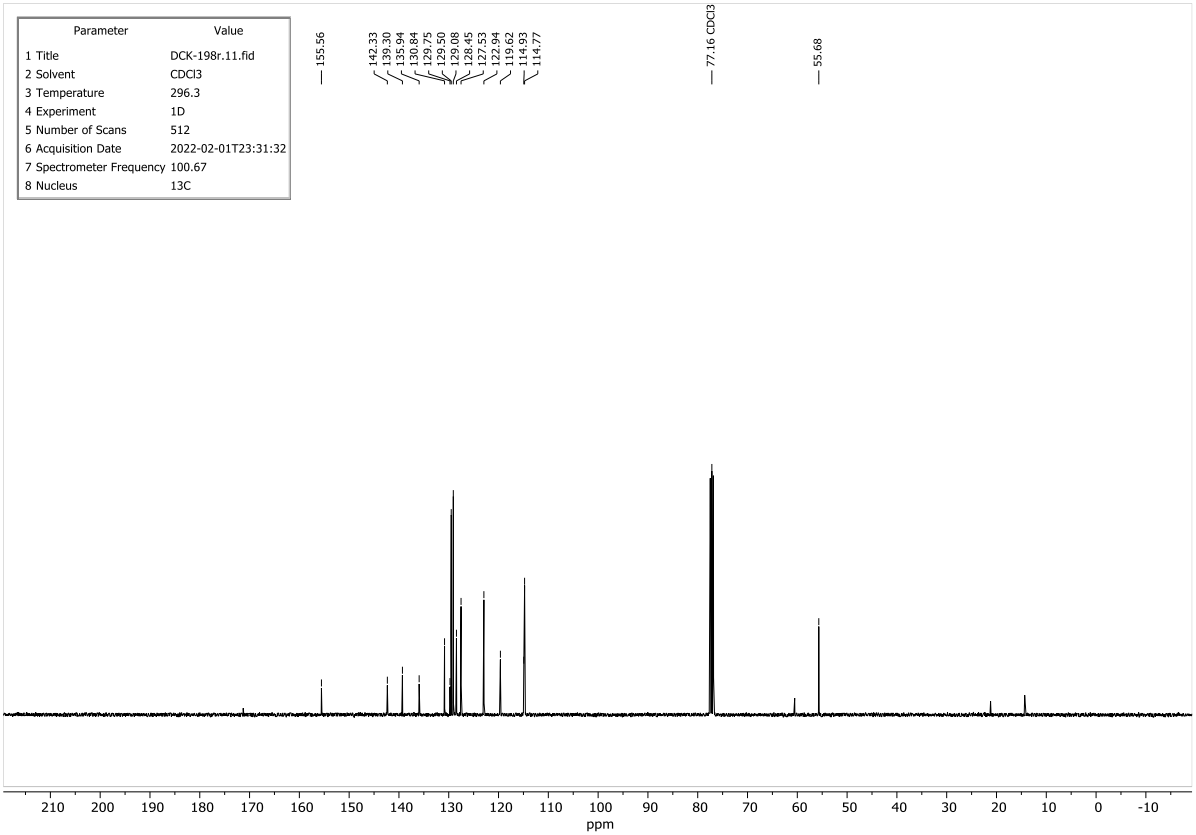


Figure S8. ^{13}C{^{1}H} NMR spectrum of N-(4-methoxyphenyl)-[1,1‘-biphenyl]-2-amine **3ac**.

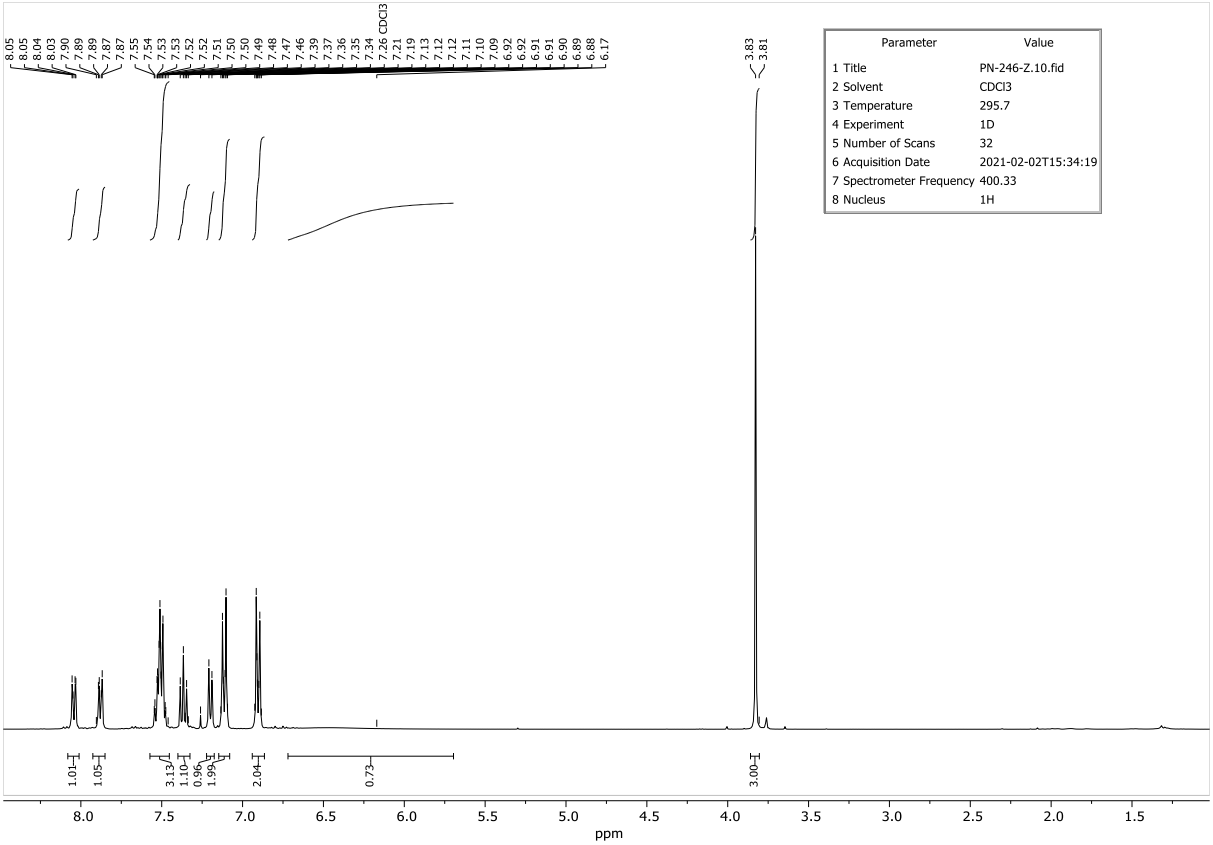


Figure S9. ^{1}H NMR spectrum of *N*-(4-methoxyphenyl)naphthalen-1-amine **3ad**.

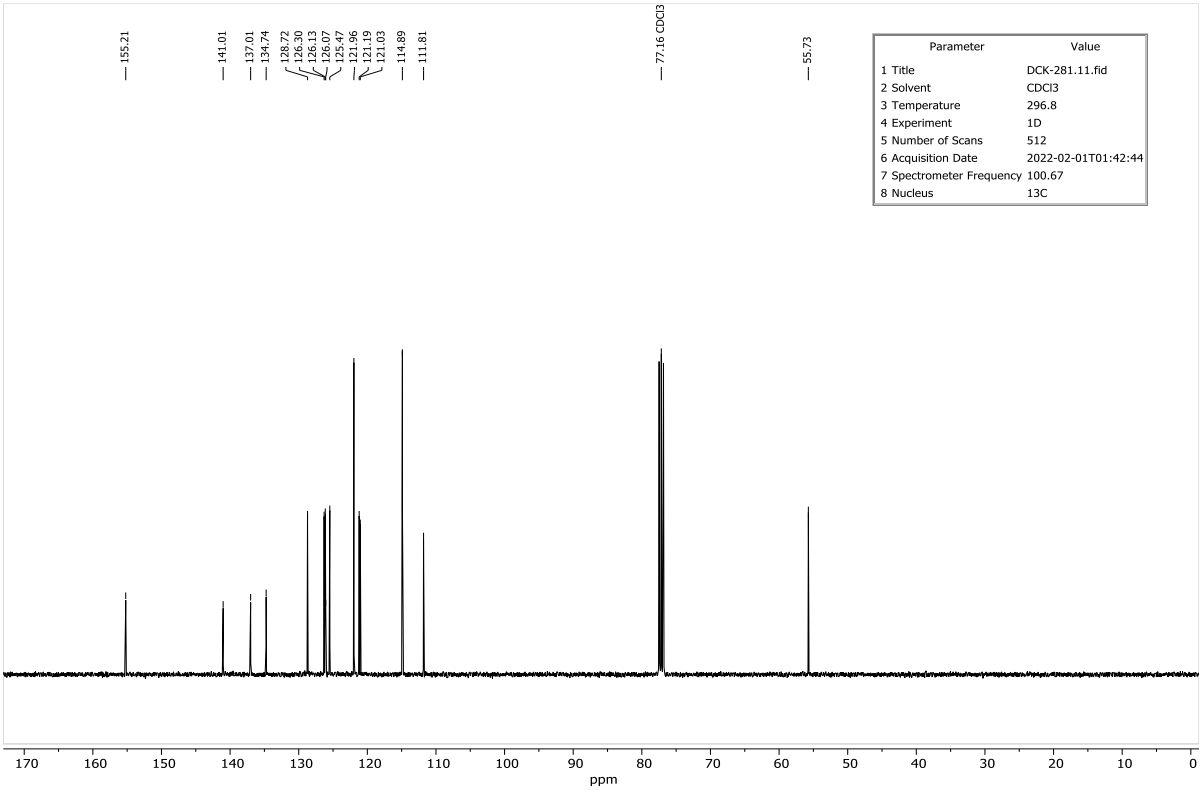


Figure S10. ^{13}C{^{1}H} NMR spectrum of N-(4-methoxyphenyl)naphthalen-1-amine **3ad**..

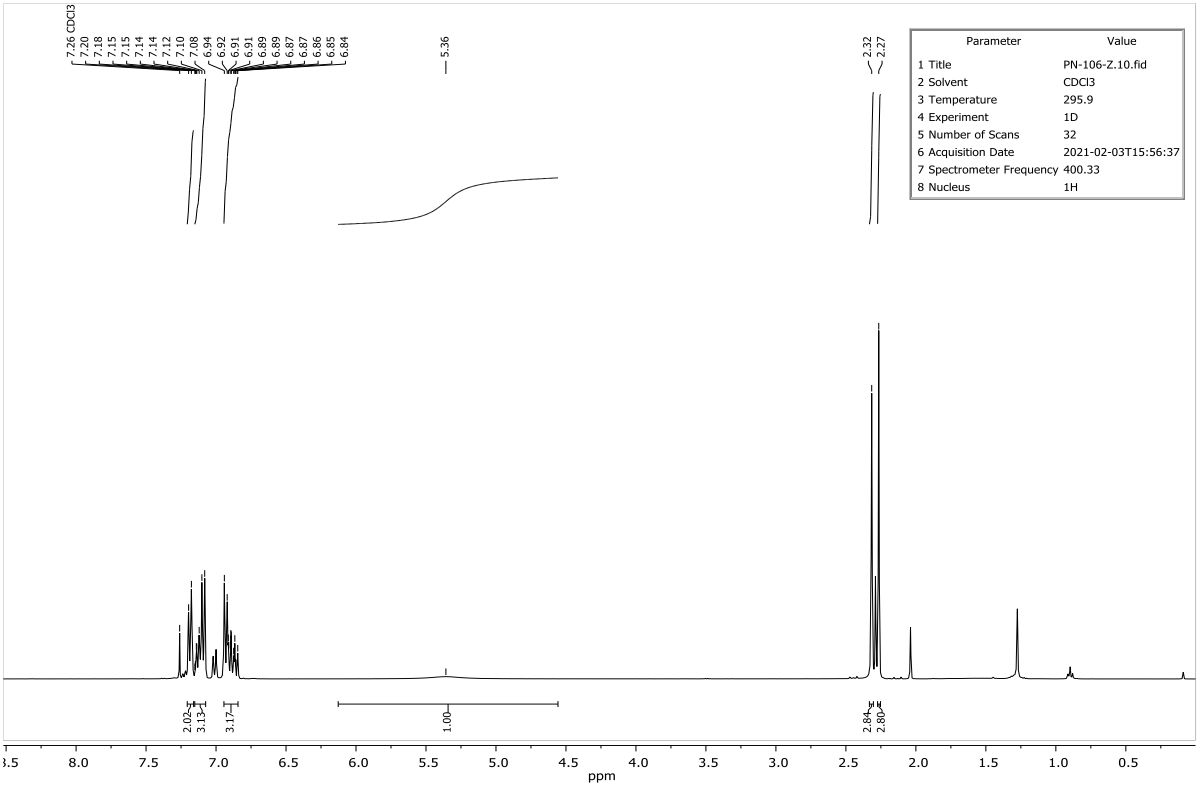


Figure S11. ^{1}H NMR spectrum of 2-methyl-*N*-(*p*-tolyl)aniline **3ba**.

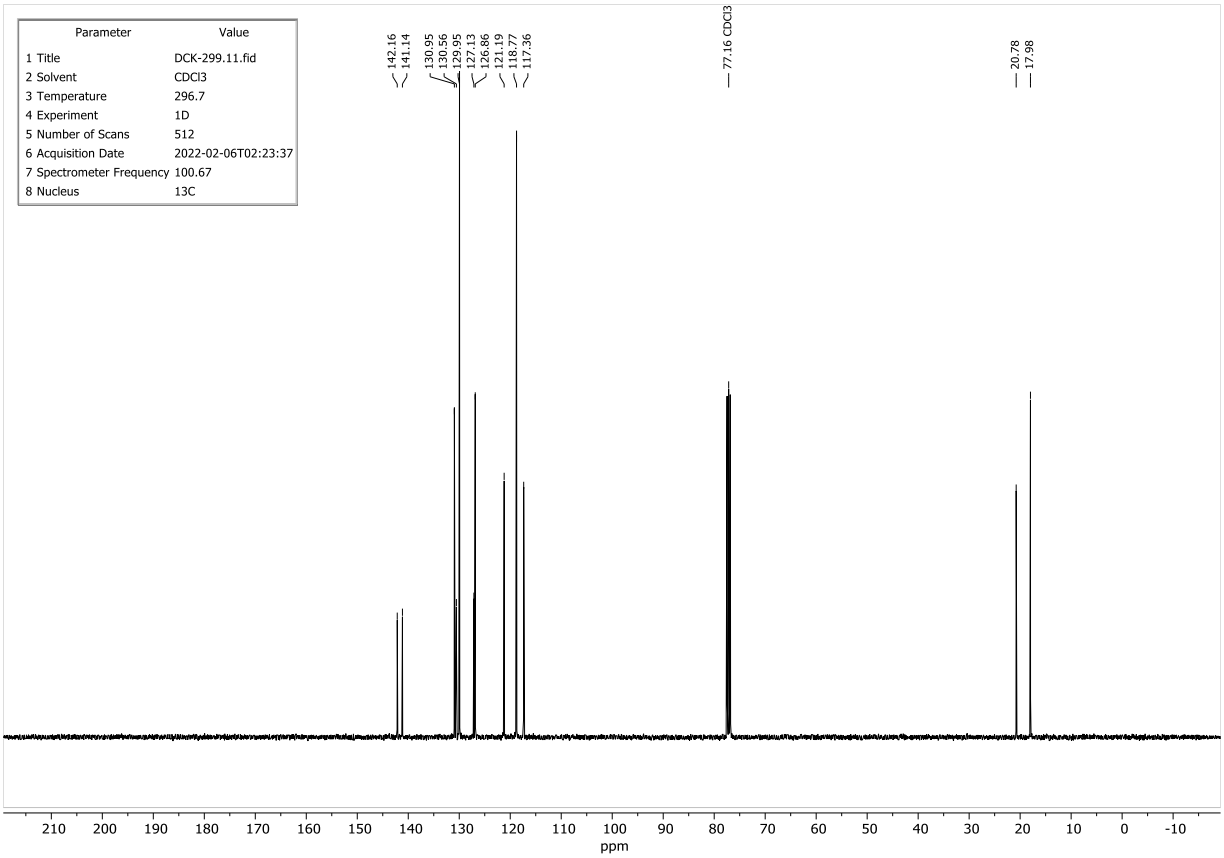


Figure S12. ^{13}C{^{1}H} NMR spectrum of 2-methyl-*N*-(*p*-tolyl)aniline **3ba**.

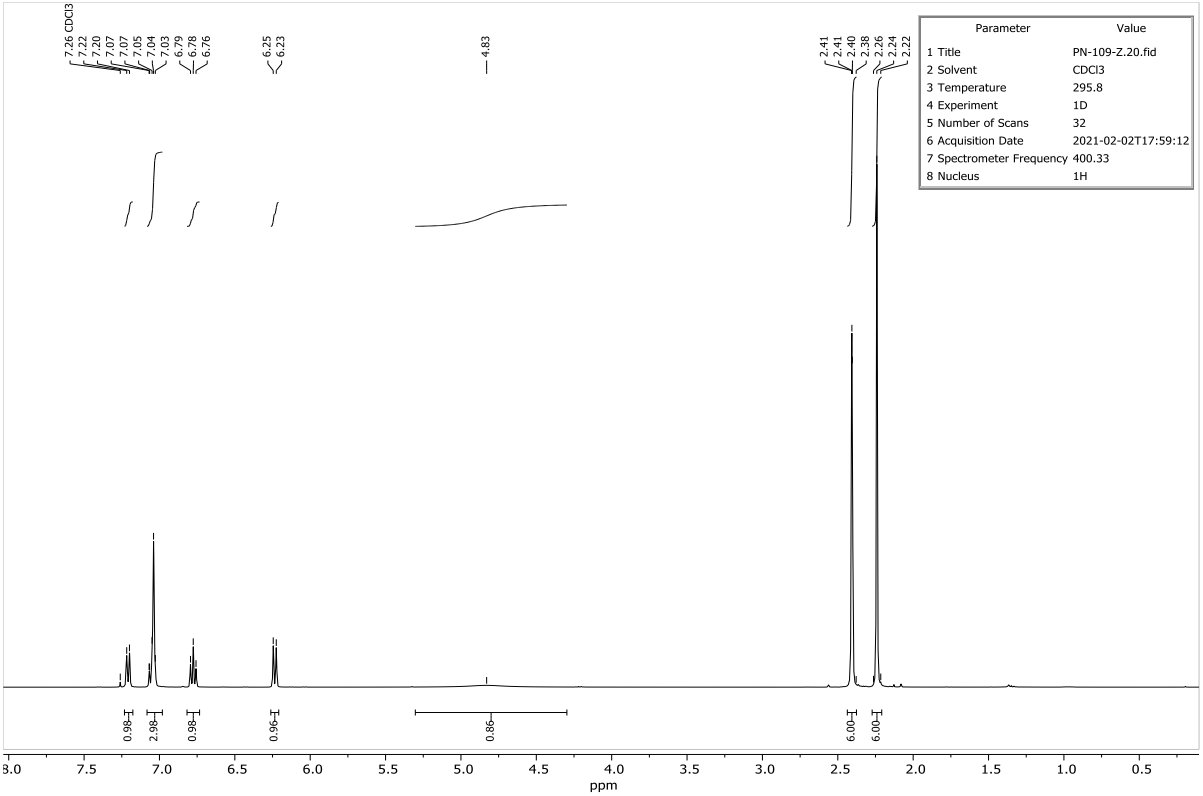


Figure S13. ^{1}H NMR spectrum of 2,4,6-trimethyl-*N*-(o-tolyl)aniline **3bb.**

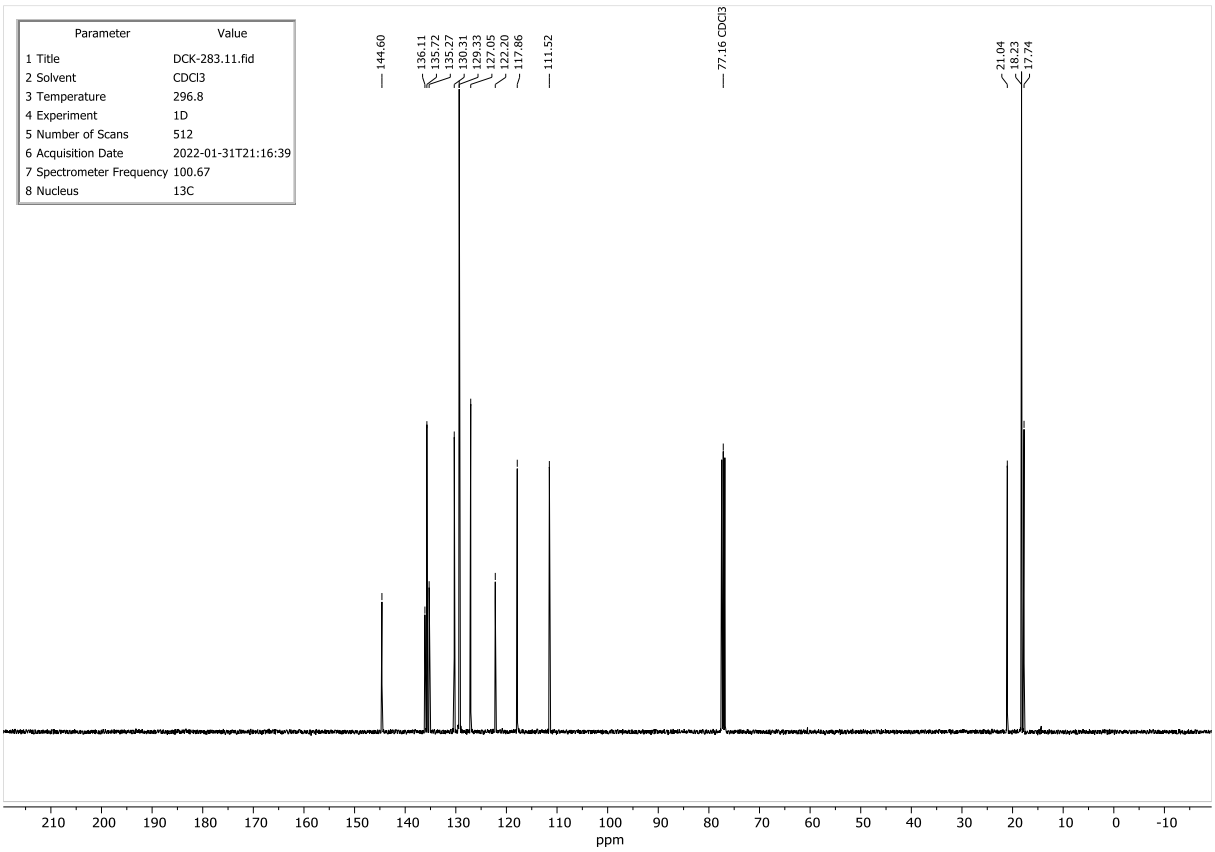


Figure S14. ^{13}C{^{1}H} NMR spectrum of 2,4,6-trimethyl-*N*-(*o*-tolyl)aniline **3bb**.

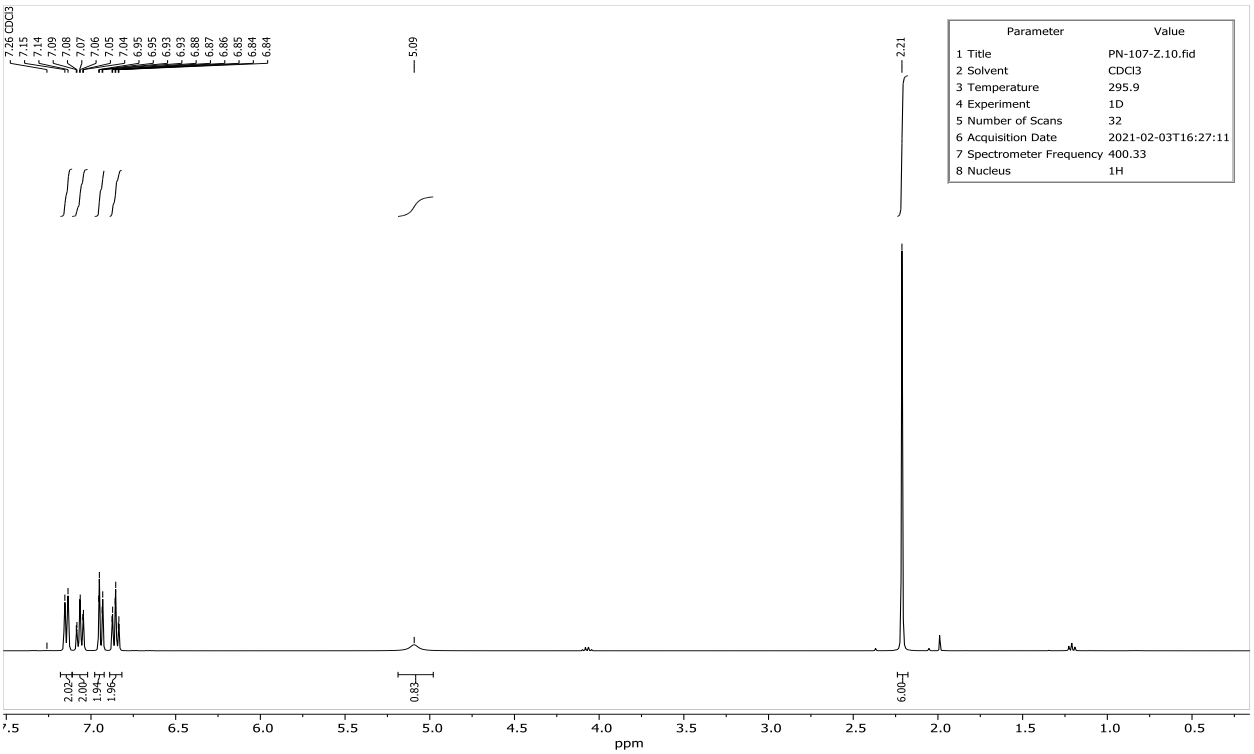


Figure S15. ^{1}H NMR spectrum of Di-*o*-tolylamine **3be**.

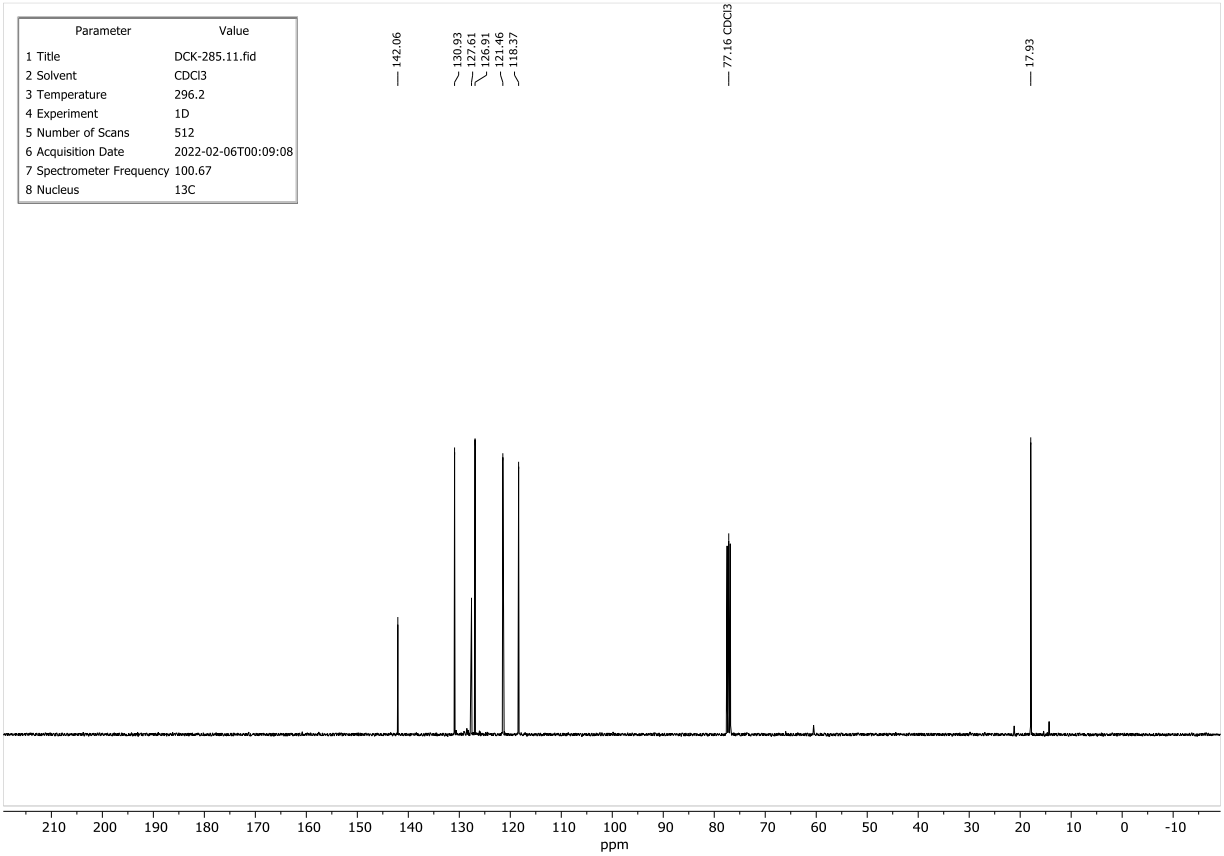


Figure S16. ^{13}C{^{1}H} NMR spectrum of Di-*o*-tolylamine **3be**.

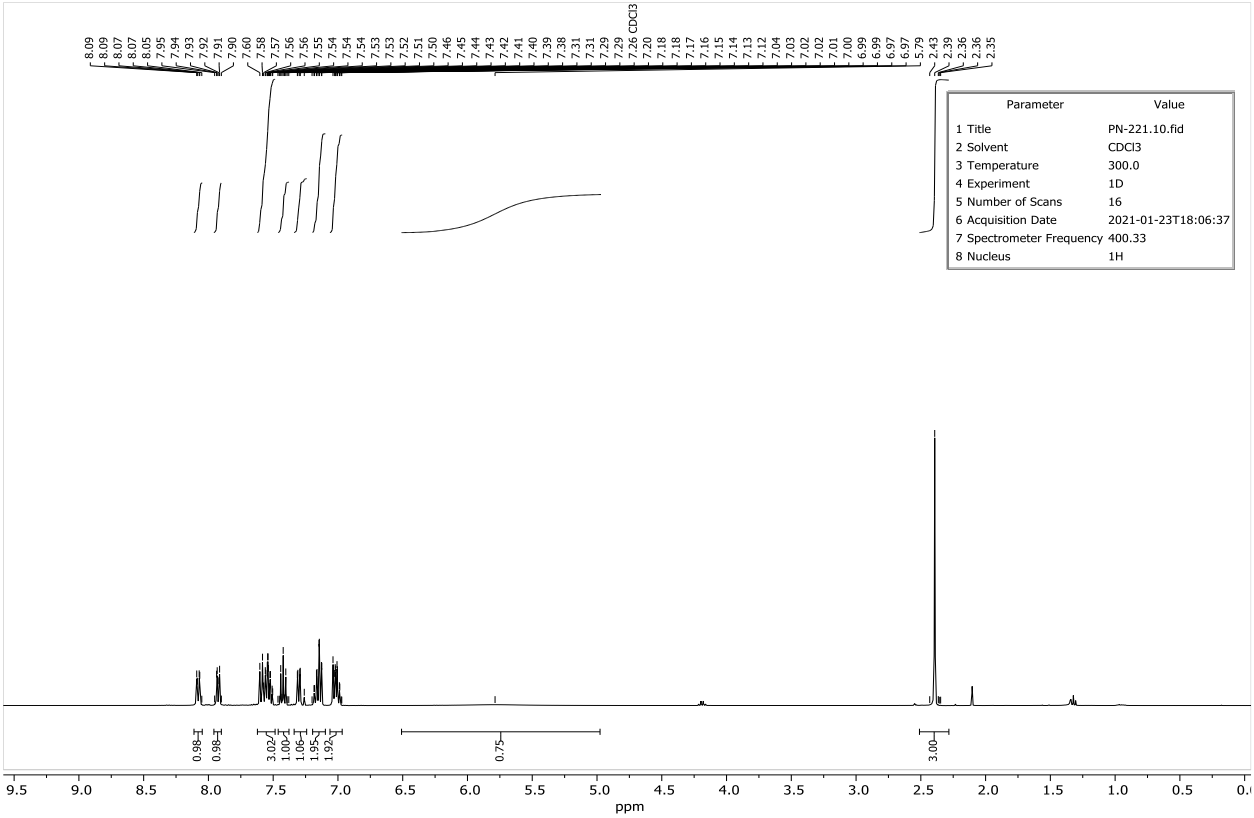


Figure S17. ^{1}H NMR spectrum of *N*-(*o*-tolyl)naphthalen-1-amine **3bd**.

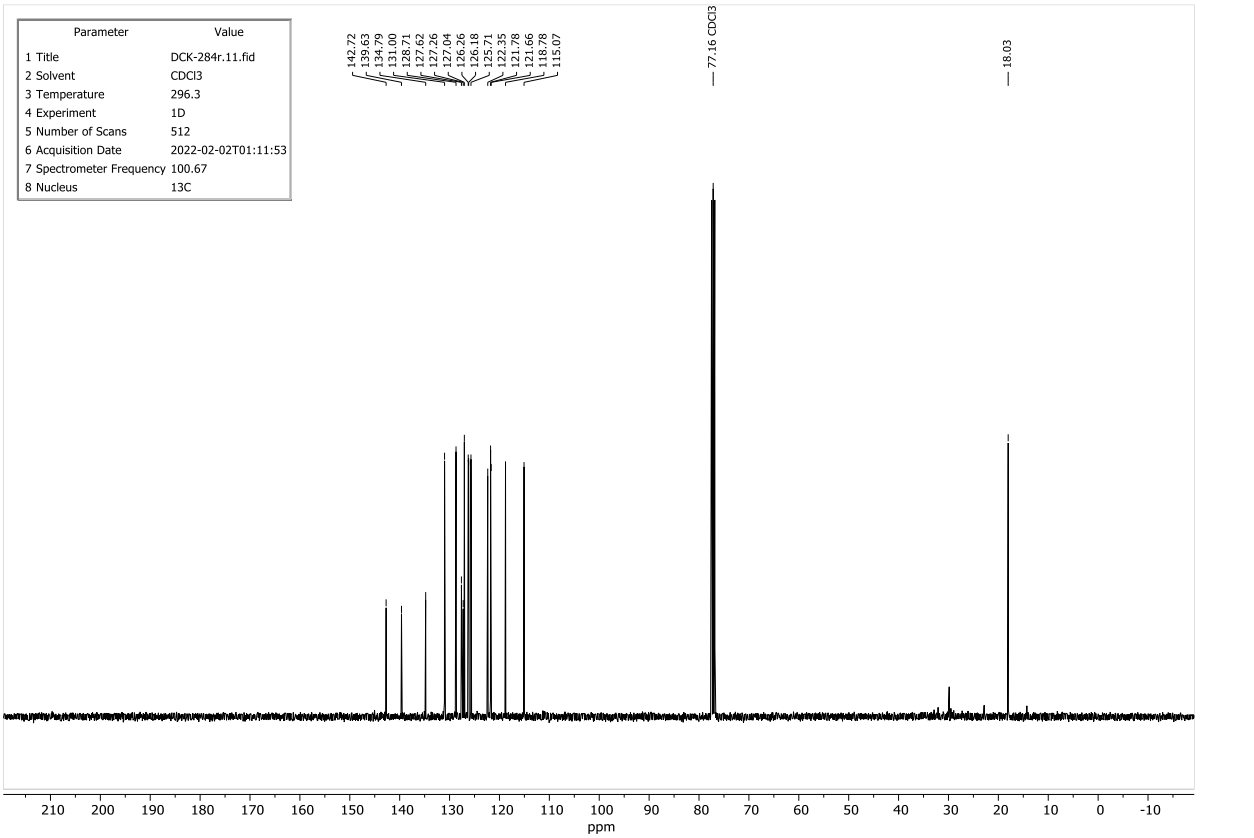


Figure S18. ^{13}C{^{1}H} NMR spectrum of *N*-(*o*-tolyl)naphthalen-1-amine **3bd**.

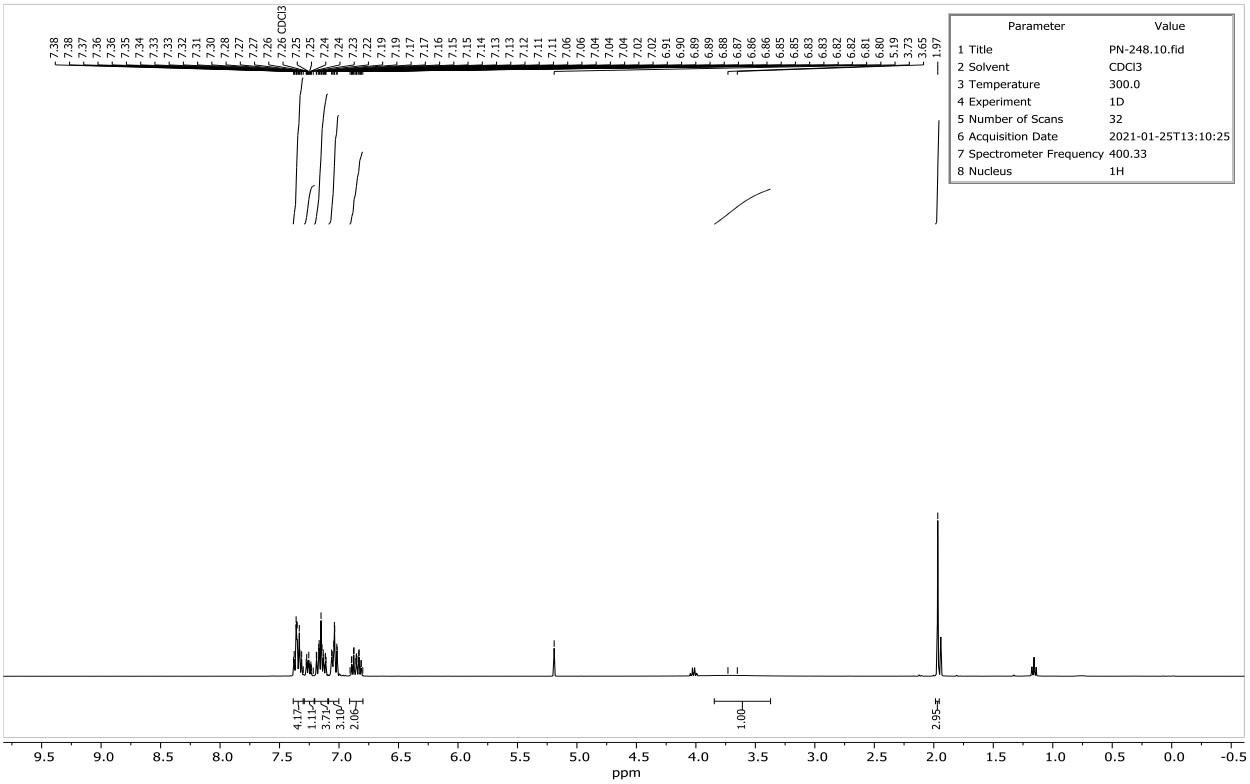


Figure S19. ^{1}H NMR spectrum of *N*-(*o*-tolyl)-[1,1'-biphenyl]-2-amine **3bc**.

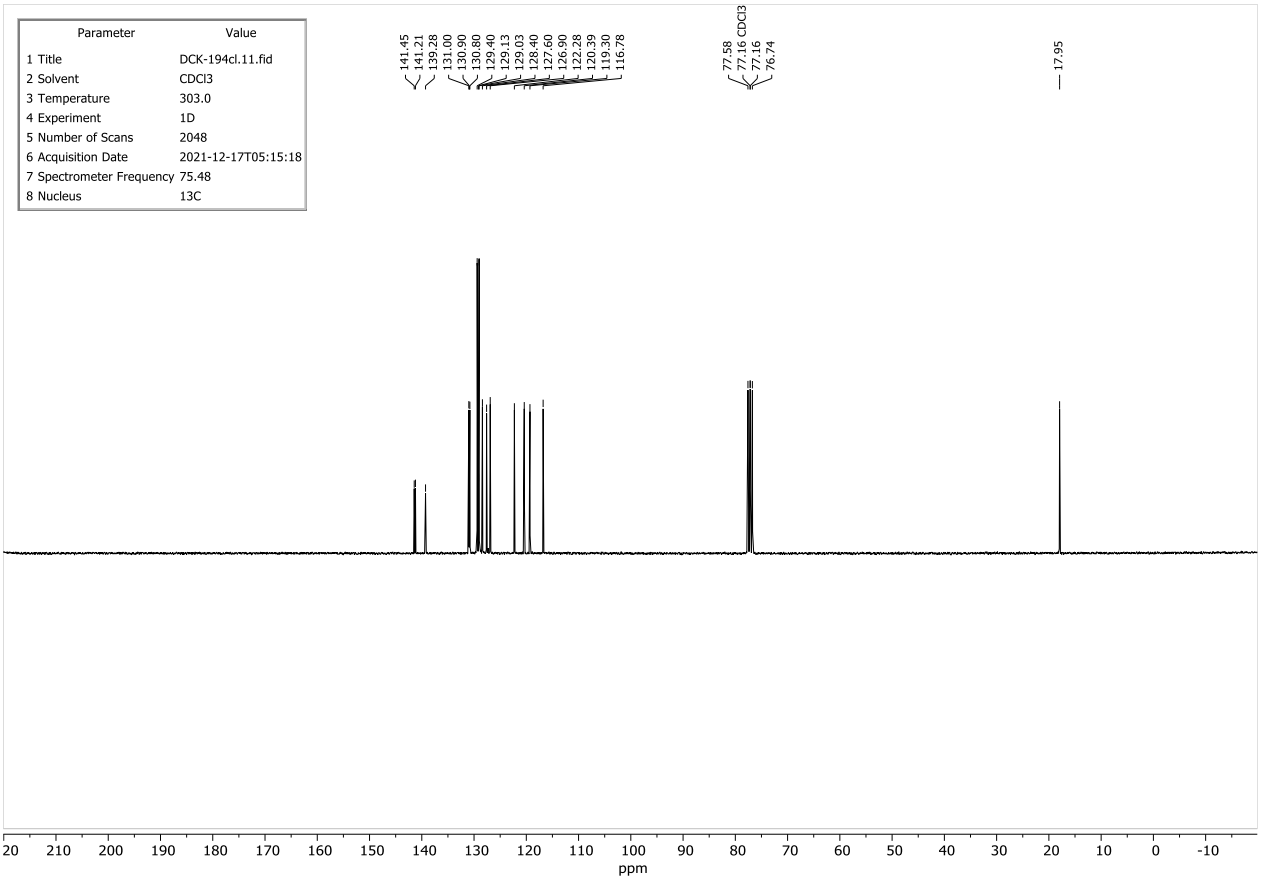


Figure S20. ^{13}C{^{1}H} NMR spectrum of *N*-(*o*-tolyl)-[1,1'-biphenyl]-2-amine **3bc**.

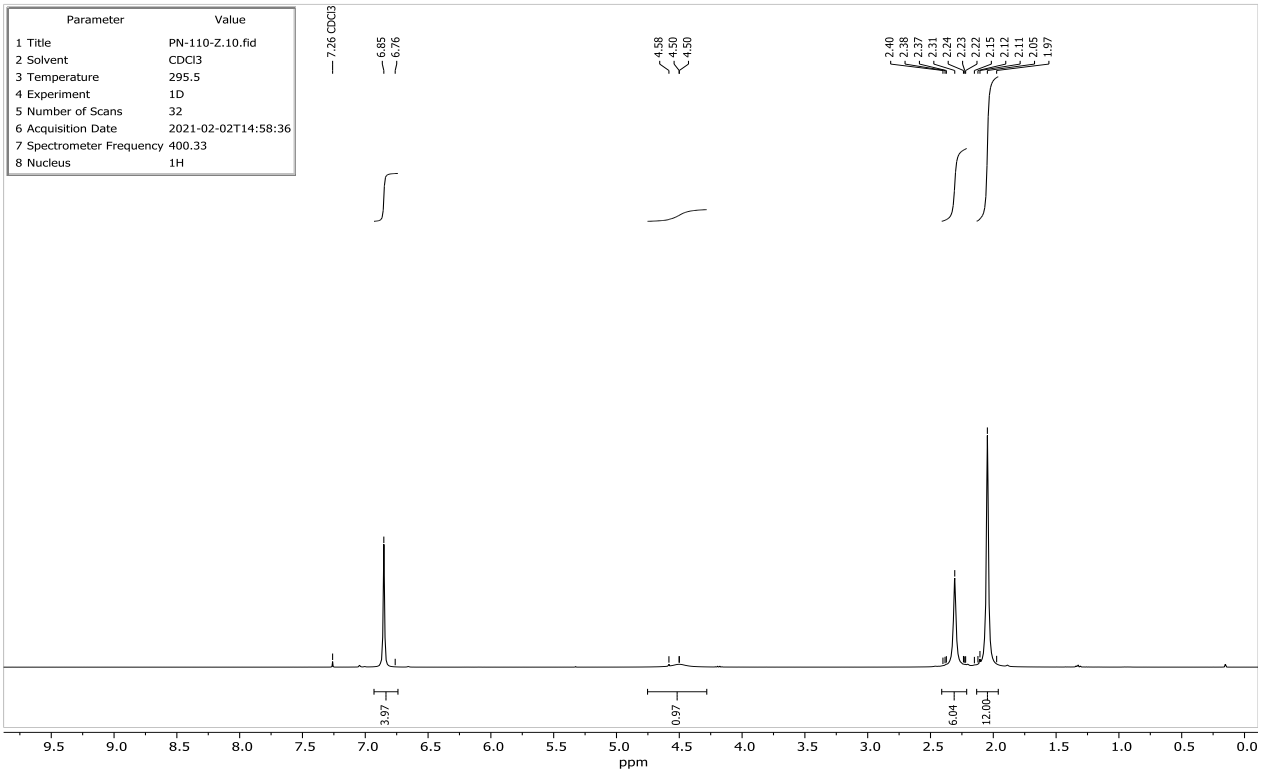


Figure S21. ^{1}H NMR spectrum of Dimesitylamine **3cb**.

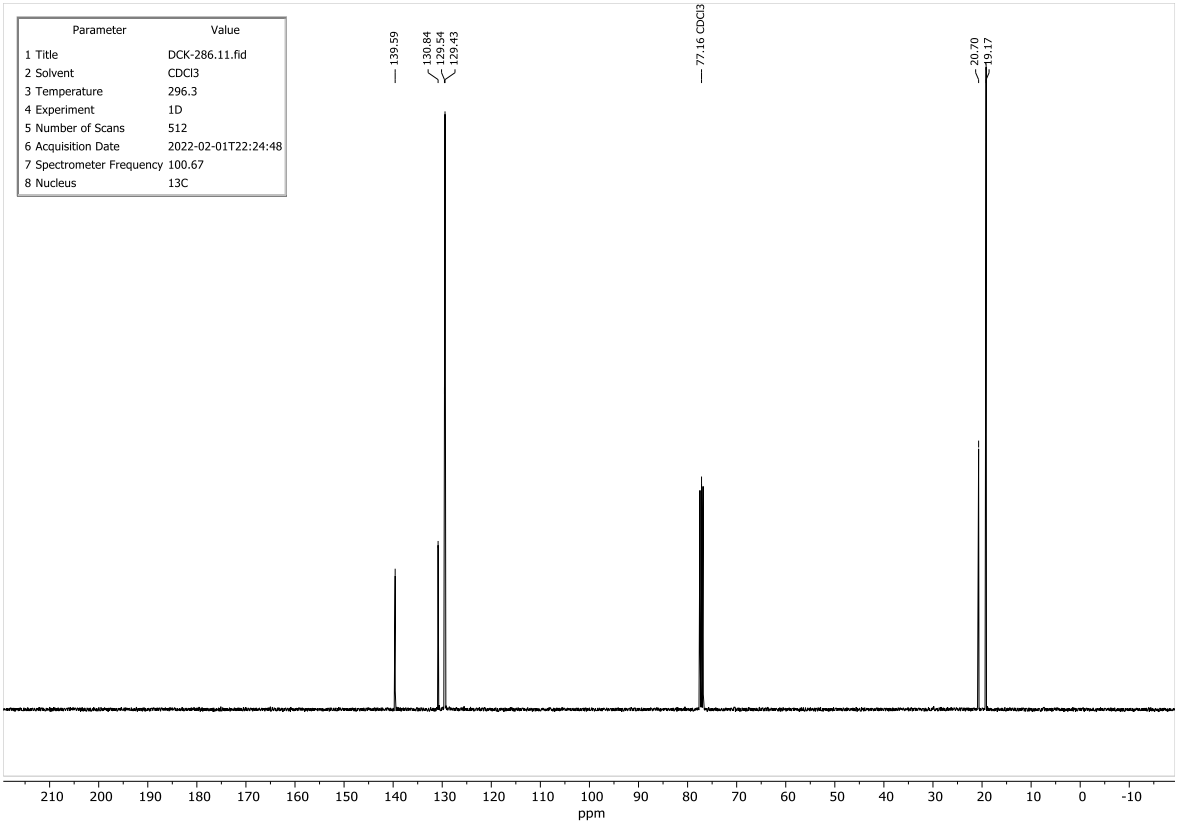


Figure S22. ^{13}C{^{1}H} NMR spectrum of Dimesitylamine **3cb**.

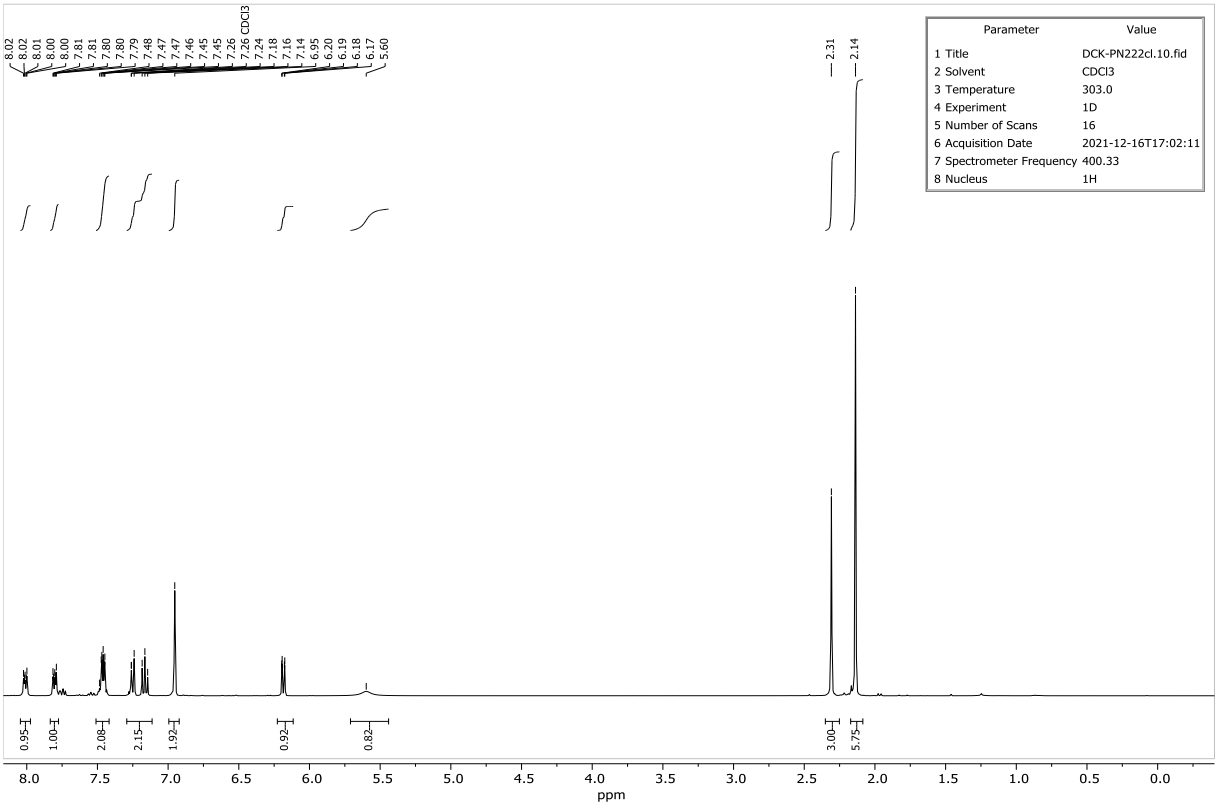


Figure S23. ^{1}H NMR spectrum of *N*-mesitylnaphthalen-1-amine **3cd**.

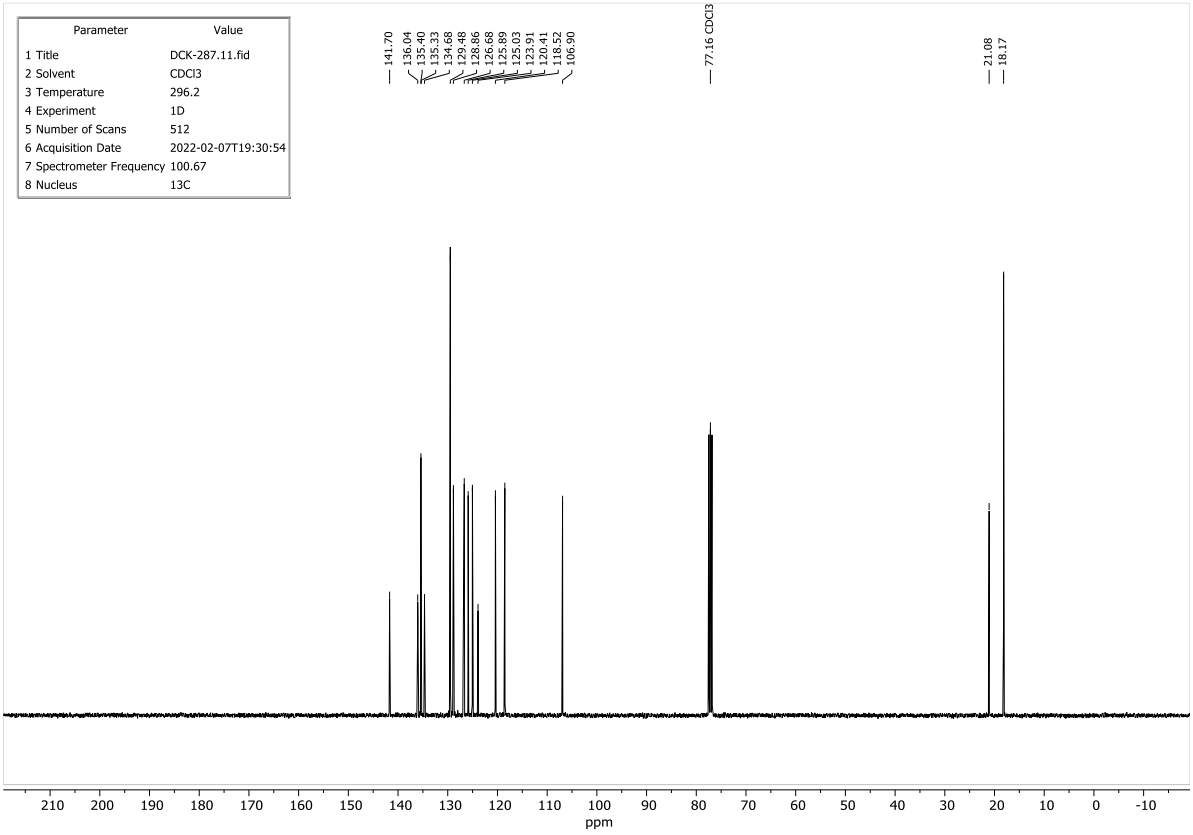


Figure S24. ^{13}C{^{1}H} NMR spectrum of *N*-mesitylnaphthalen-1-amine **3cd**.

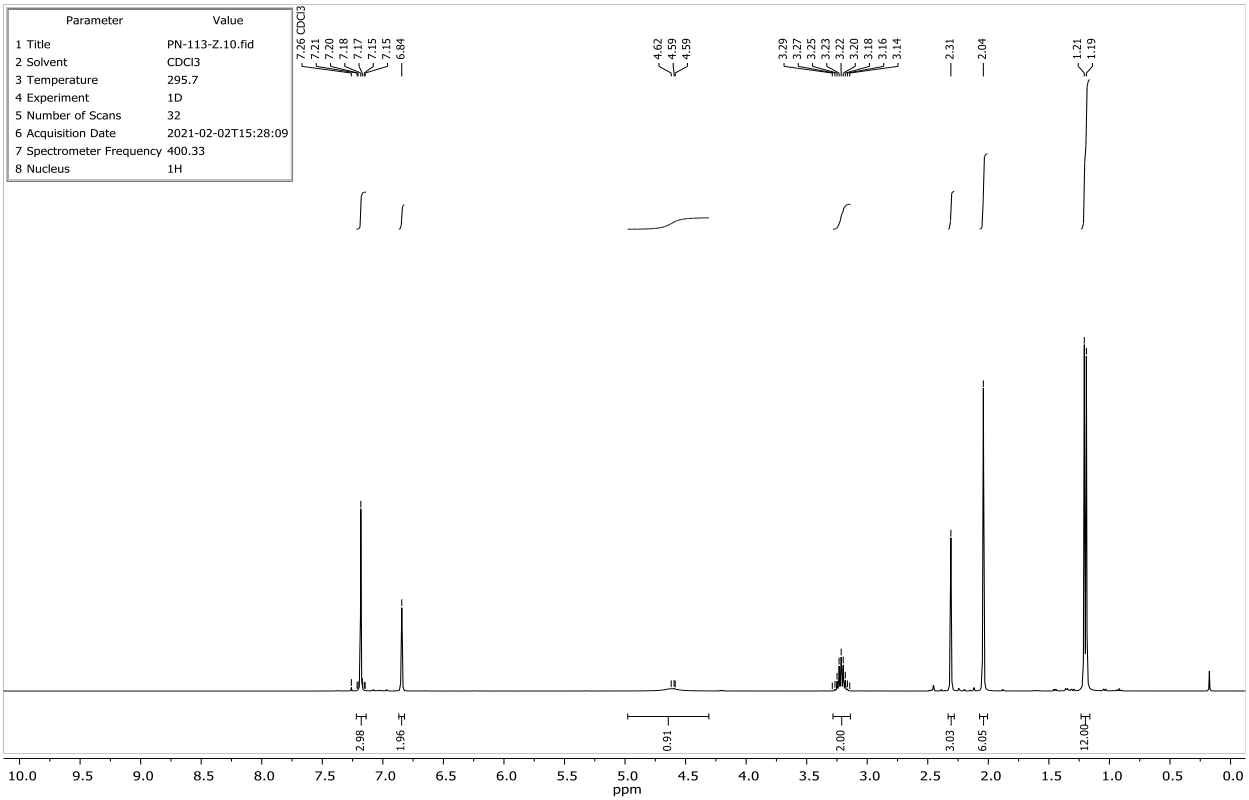


Figure S25. ^{1}H NMR spectrum of *N*-(2,6-diisopropylphenyl)-2,4,6-trimethylaniline **3db**.

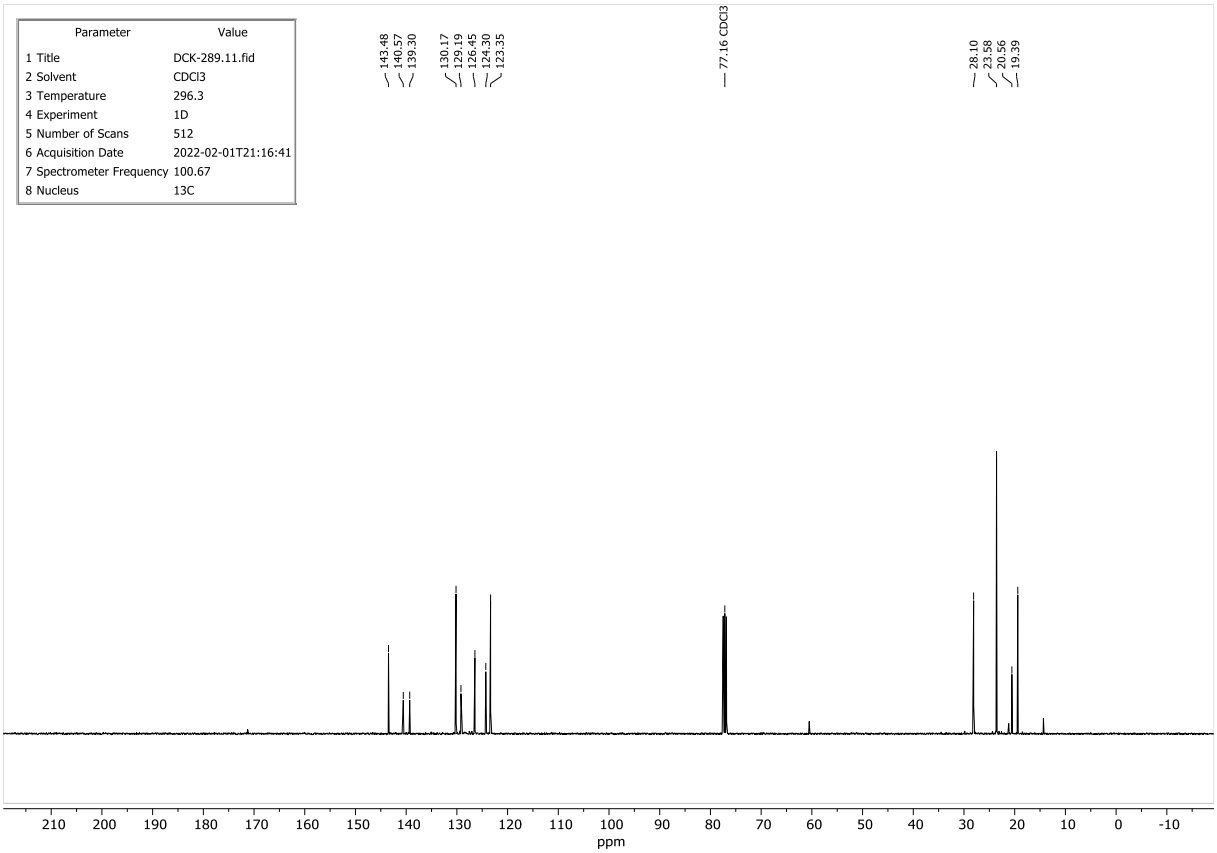


Figure S26. ^{13}C{^{1}H} NMR spectrum of *N*-(2,6-diisopropylphenyl)-2,4,6-trimethylaniline **3db**.

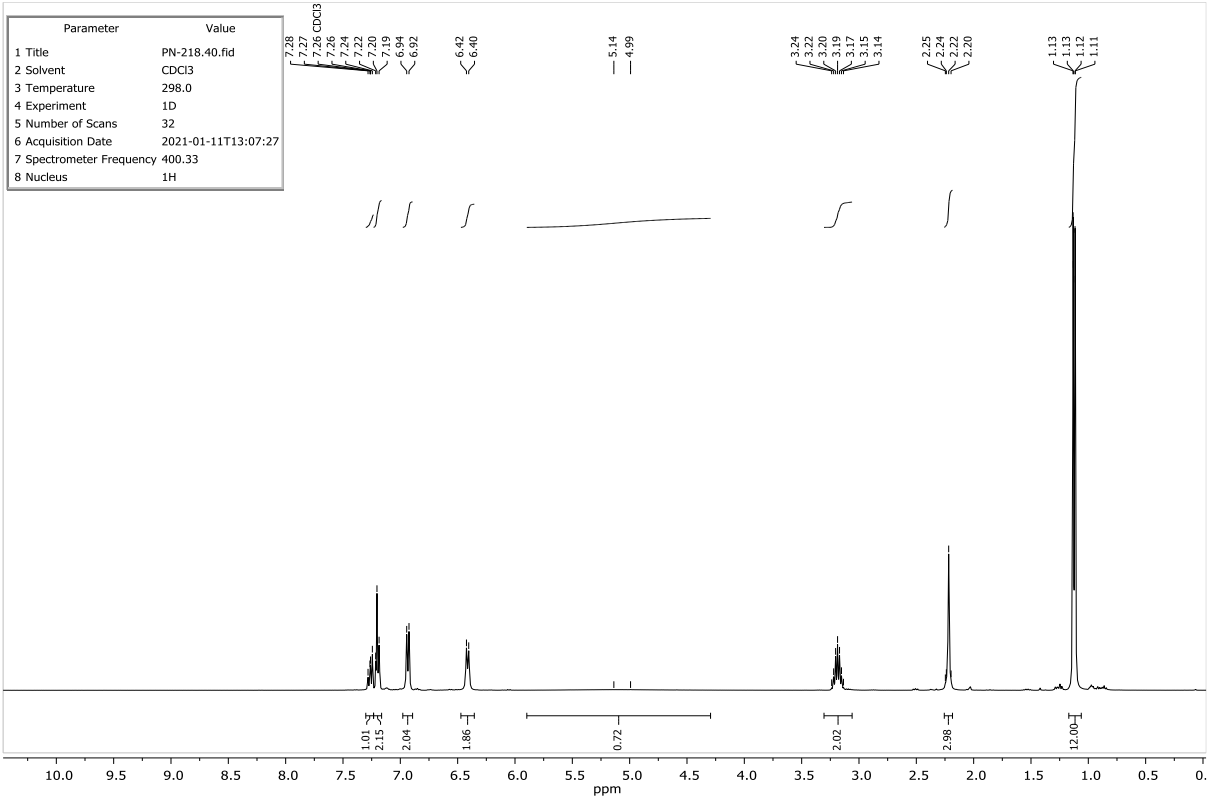


Figure S27. ^{1}H NMR spectrum of 2,6-diisopropyl-*N*-(*p*-tolyl)aniline **3da**.

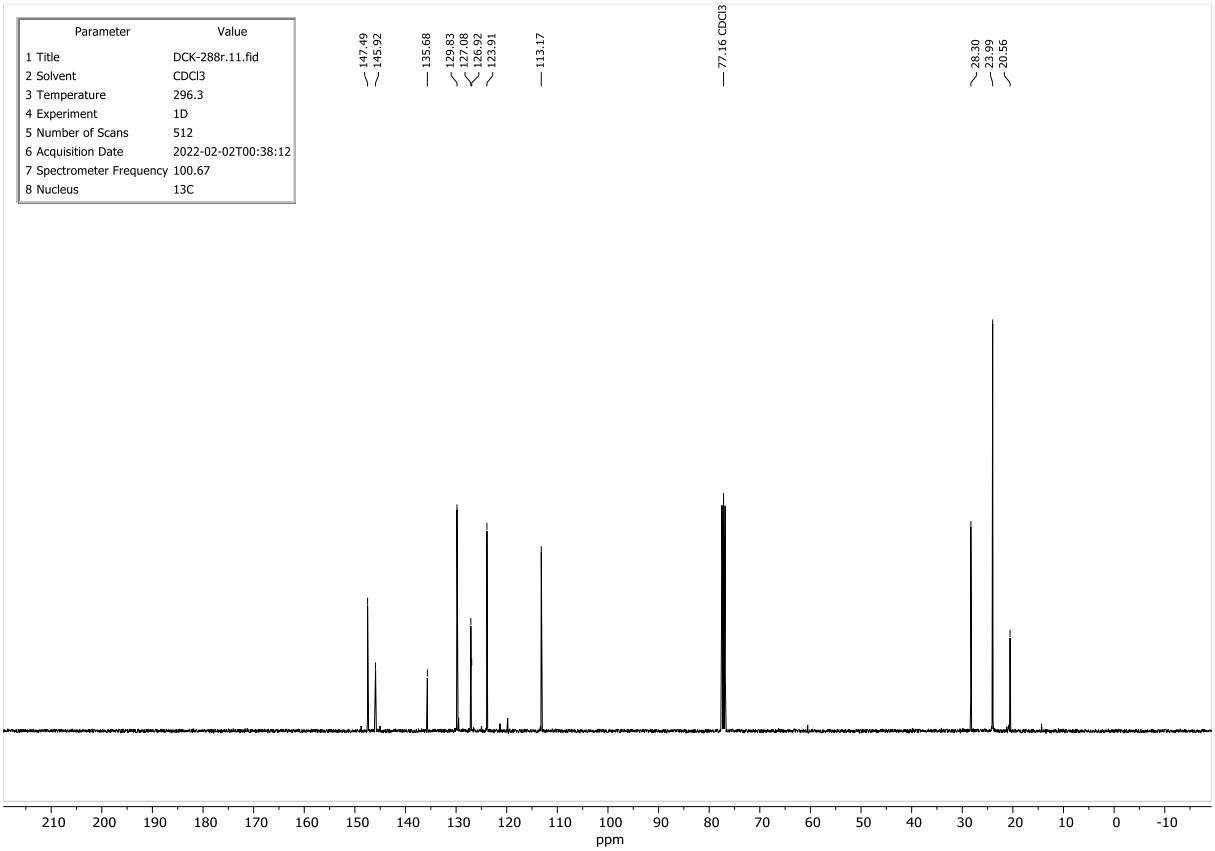


Figure S28. ^{13}C{^{1}H} NMR spectrum of 2,6-diisopropyl-*N*-(*p*-tolyl)aniline **3da**.

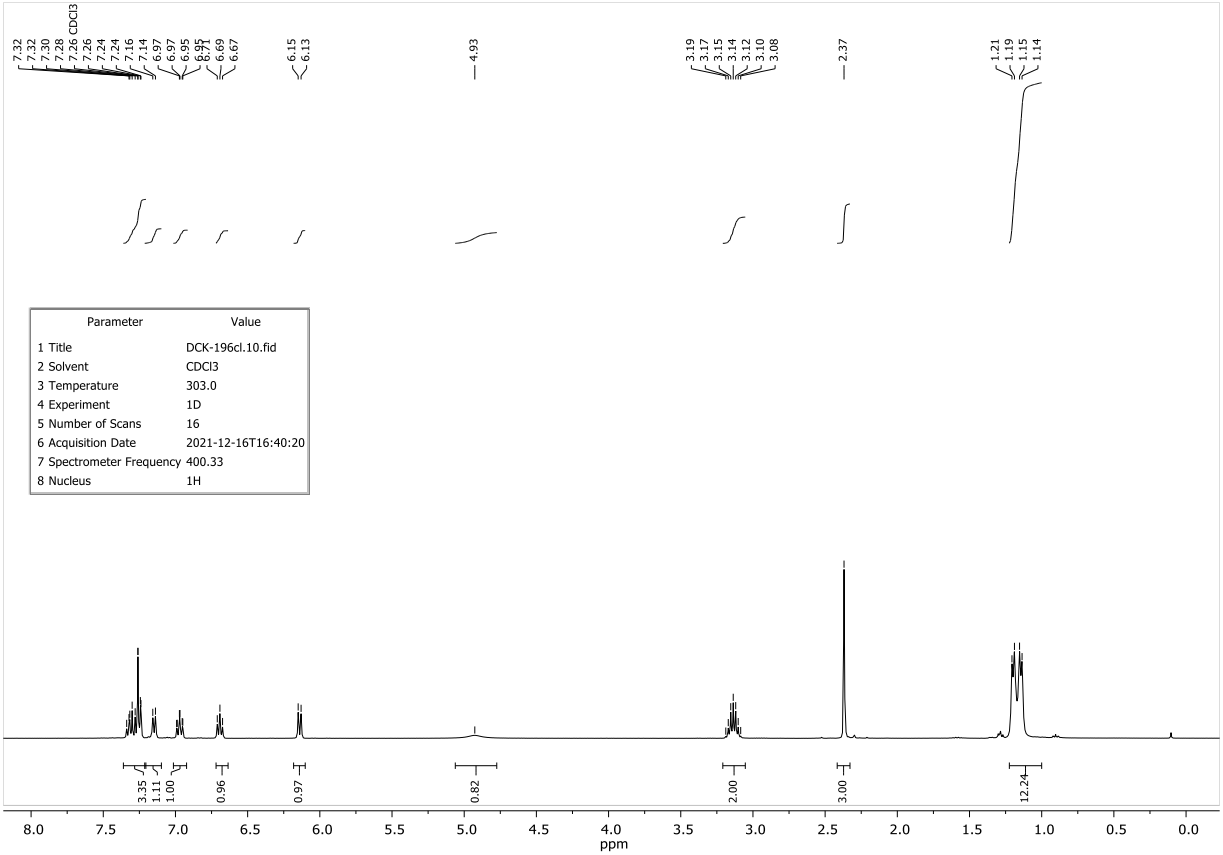


Figure S29. ^{1}H NMR spectrum of 2,6-diisopropyl-N-(o-tolyl)aniline **3de**.

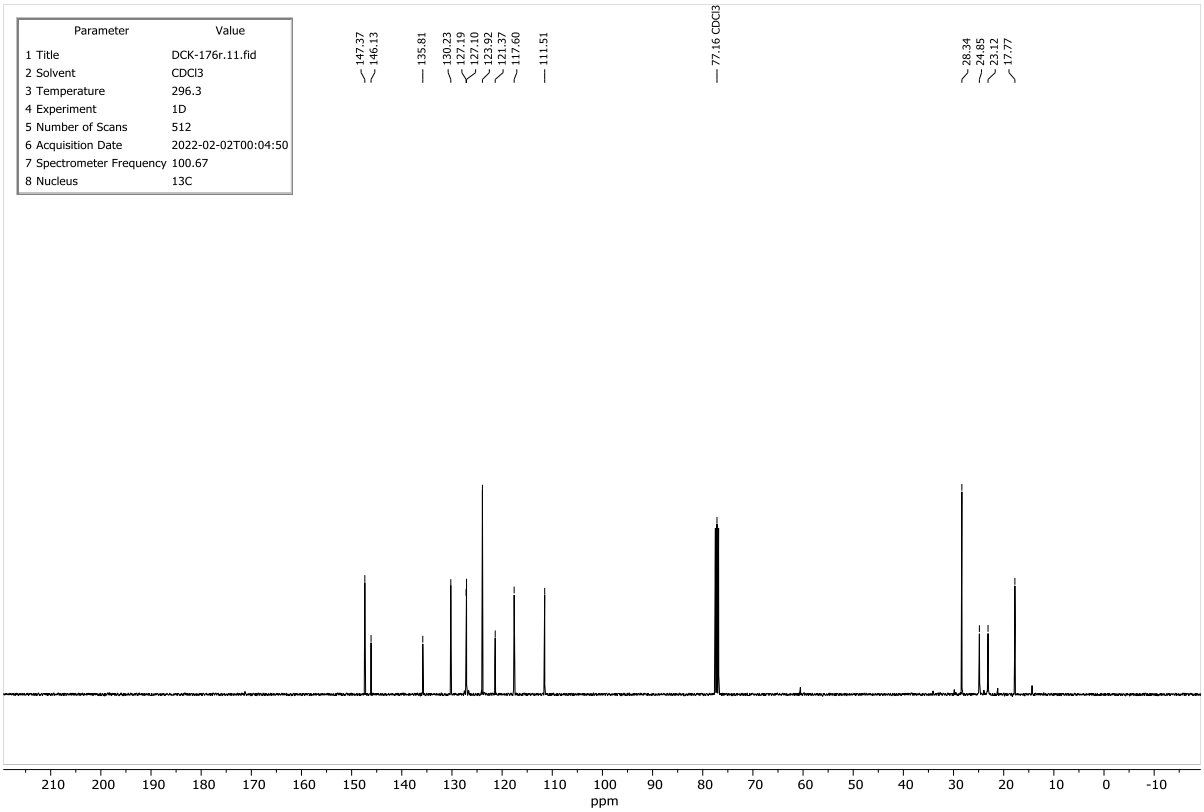


Figure S30. ^{13}C{^{1}H} NMR spectrum of 2,6-diisopropyl-*N*-(*o*-tolyl)aniline **3de**.

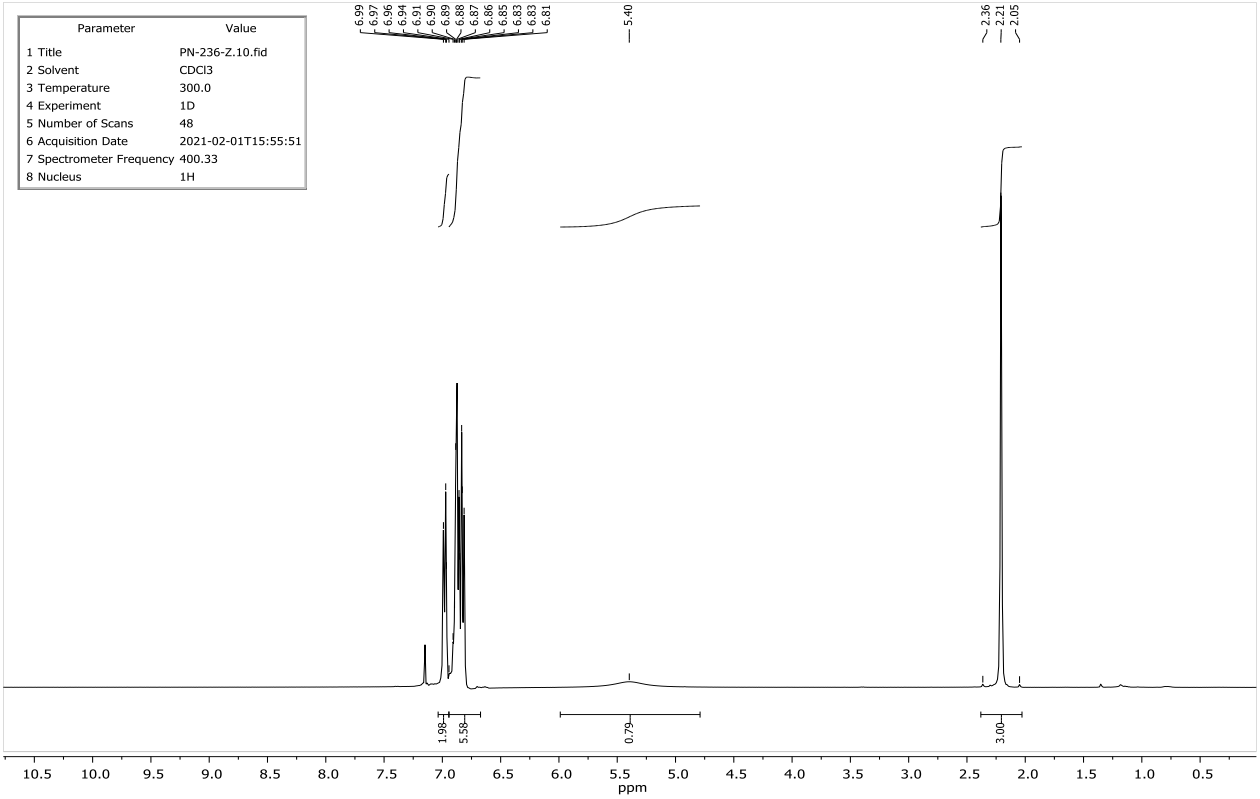


Figure S31. ^{1}H NMR spectrum of 4-fluoro-*N*-(*p*-tolyl)aniline **3ea**.

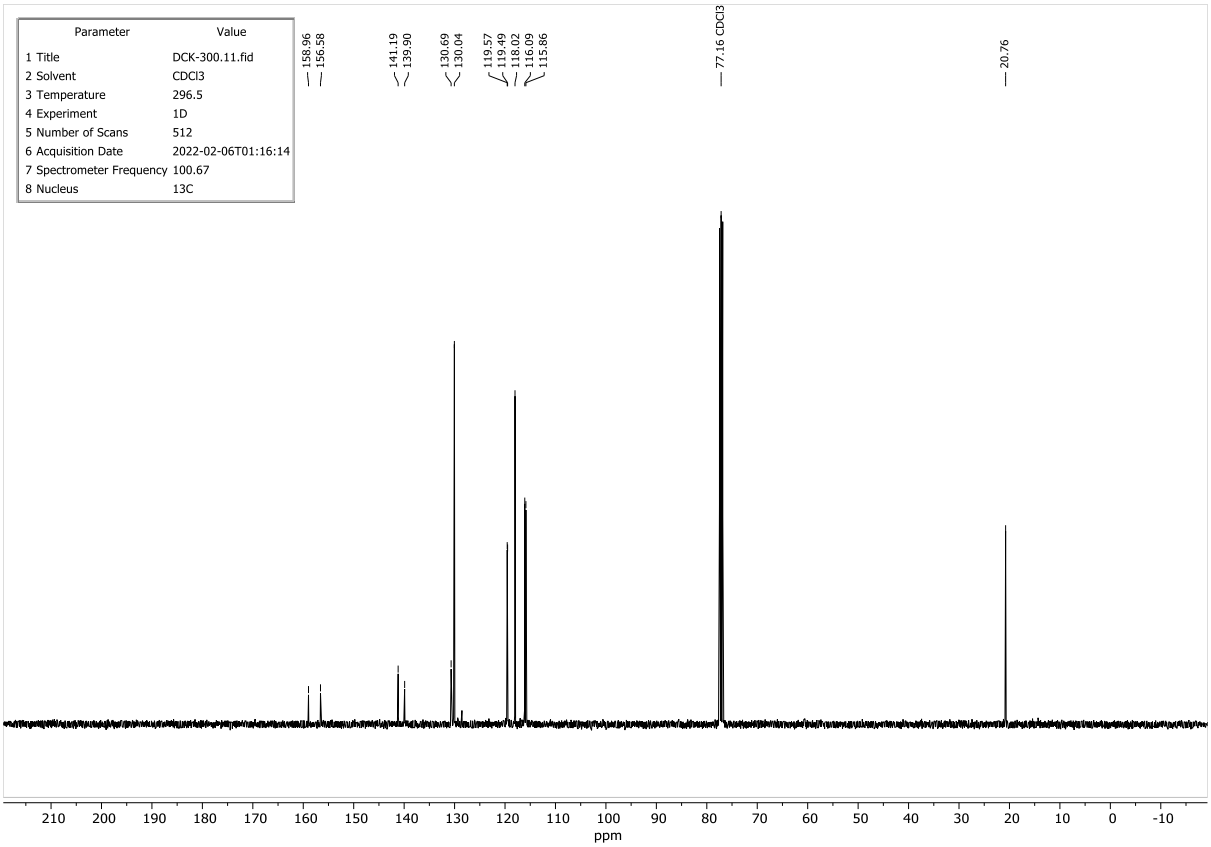


Figure S32. ^{13}C{^{1}H} NMR spectrum of 4-fluoro-*N*-(*p*-tolyl)aniline **3ea**.

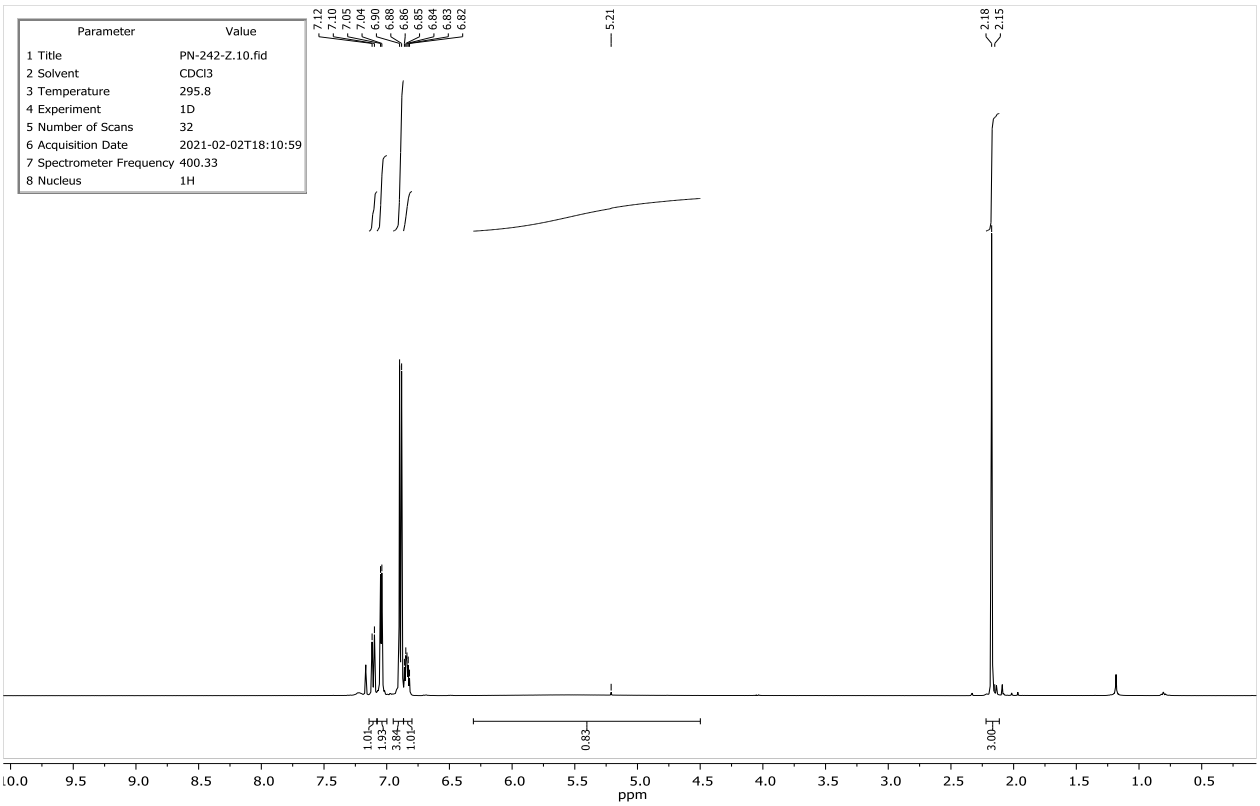


Figure S33. ^{1}H NMR spectrum of *N*-(4-fluorophenyl)-2-methylaniline **3ee**.

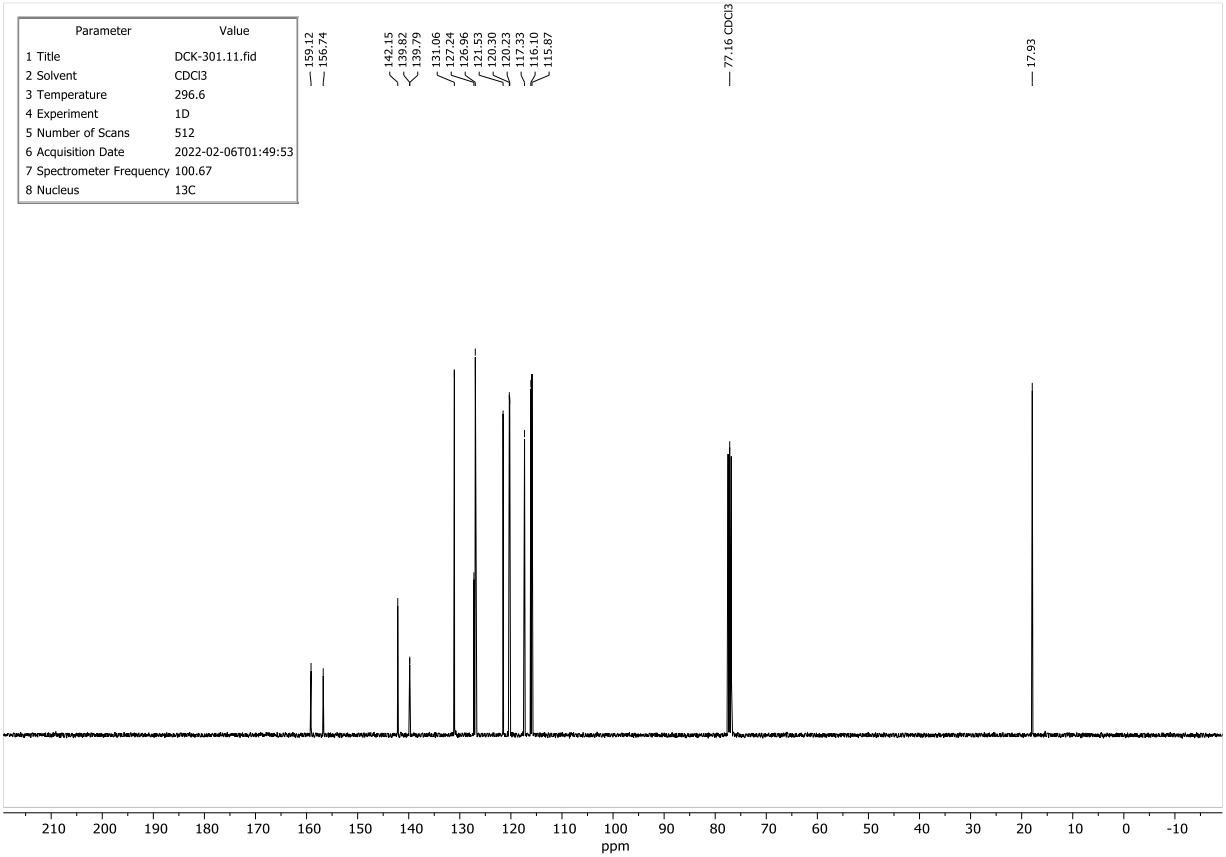


Figure S34. ^{13}C{^{1}H} NMR spectrum of *N*-(4-fluorophenyl)-2-methylaniline **3ee**.

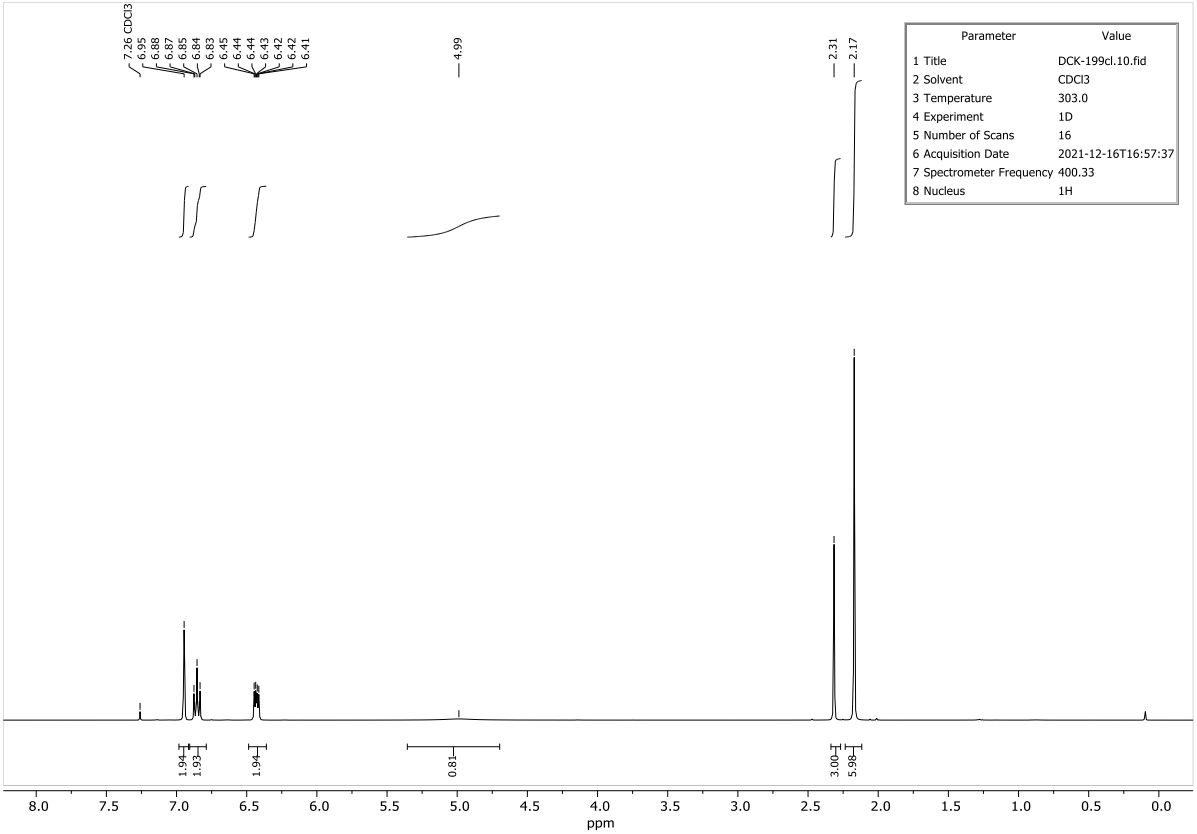


Figure S35. ^{1}H NMR spectrum of *N*-(4-fluorophenyl)-2,4,6-thrimethylaniline **3eb**.

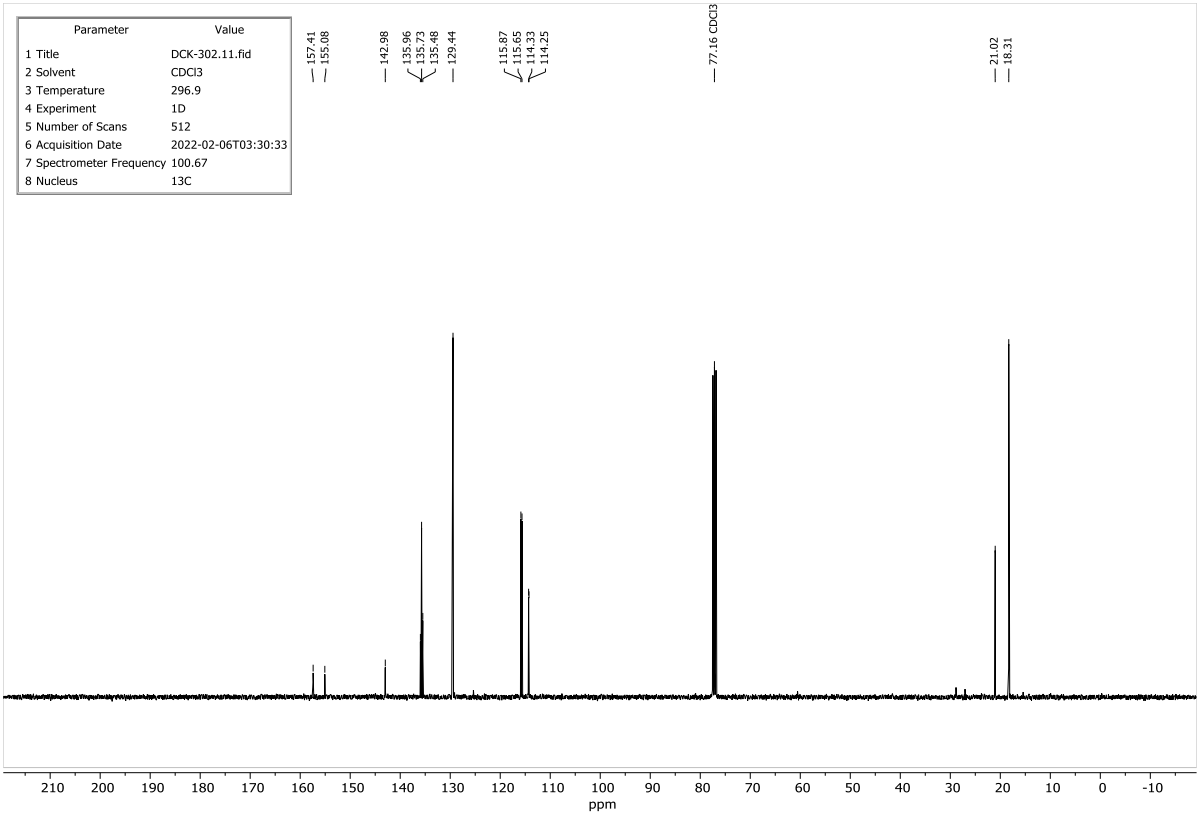


Figure S36. ^{13}C{^{1}H} NMR spectrum of *N*-(4-fluorophenyl)-2,4,6-thrimethylaniline **3eb**.

2.2. NMR spectra of the triarylamines

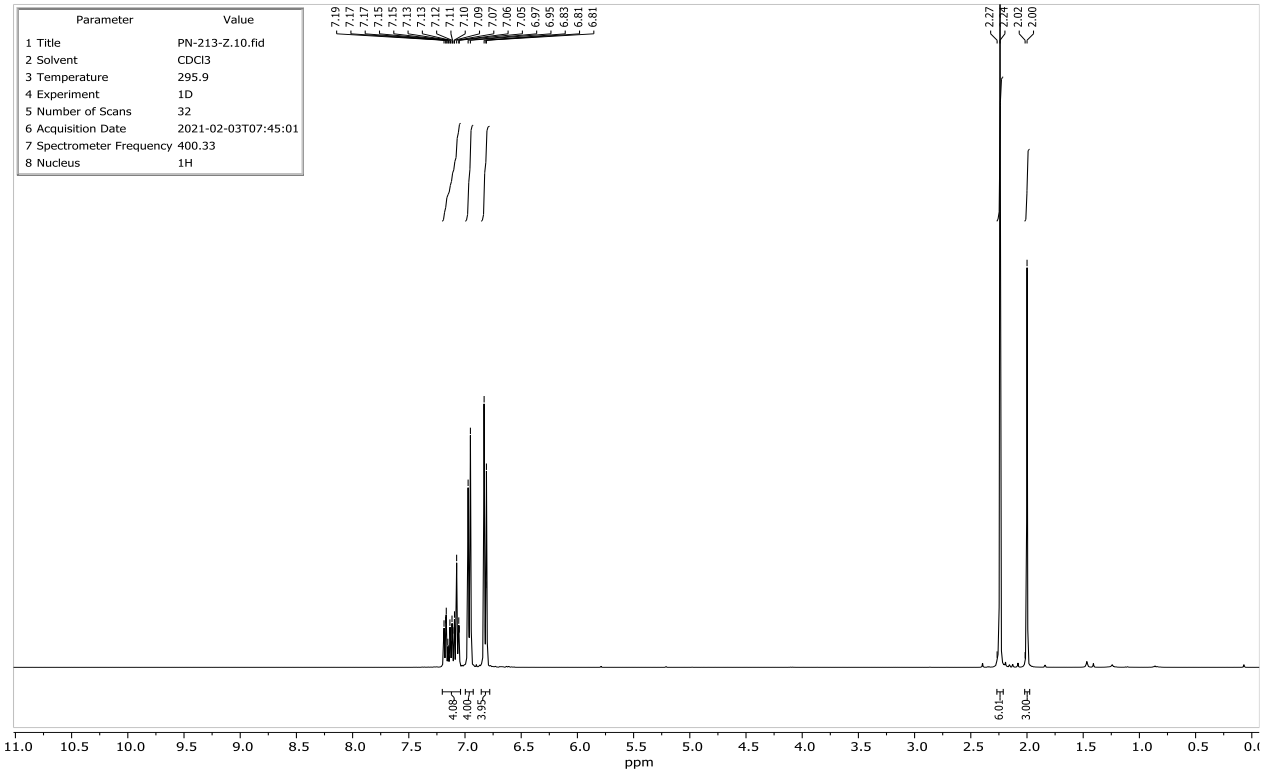


Figure S37. ^{1}H NMR spectrum of 2-methyl-N,N-di-p-tolylaniline **4baa**.

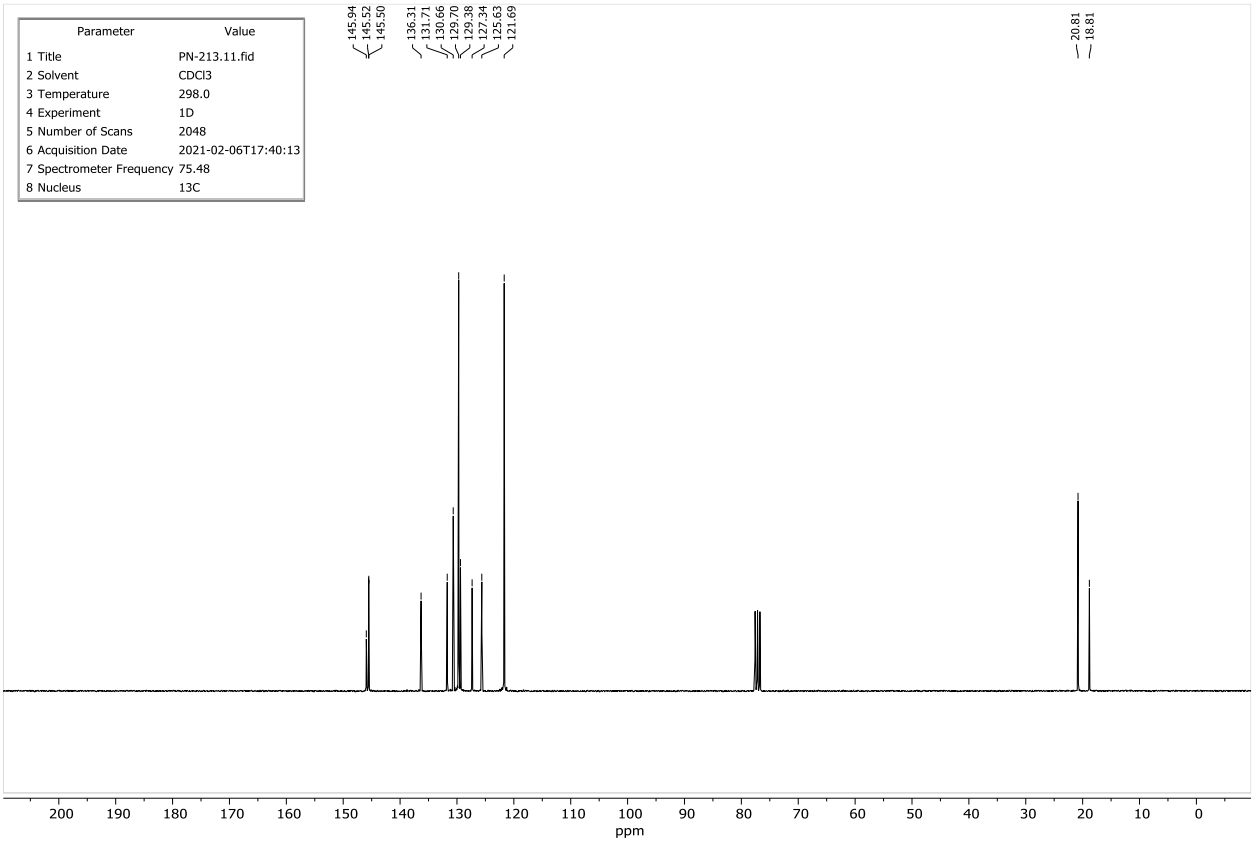


Figure S38. ^{13}C{^{1}H} NMR spectrum of 2-methyl-N,N-di-p-tolylaniline **4baa**.

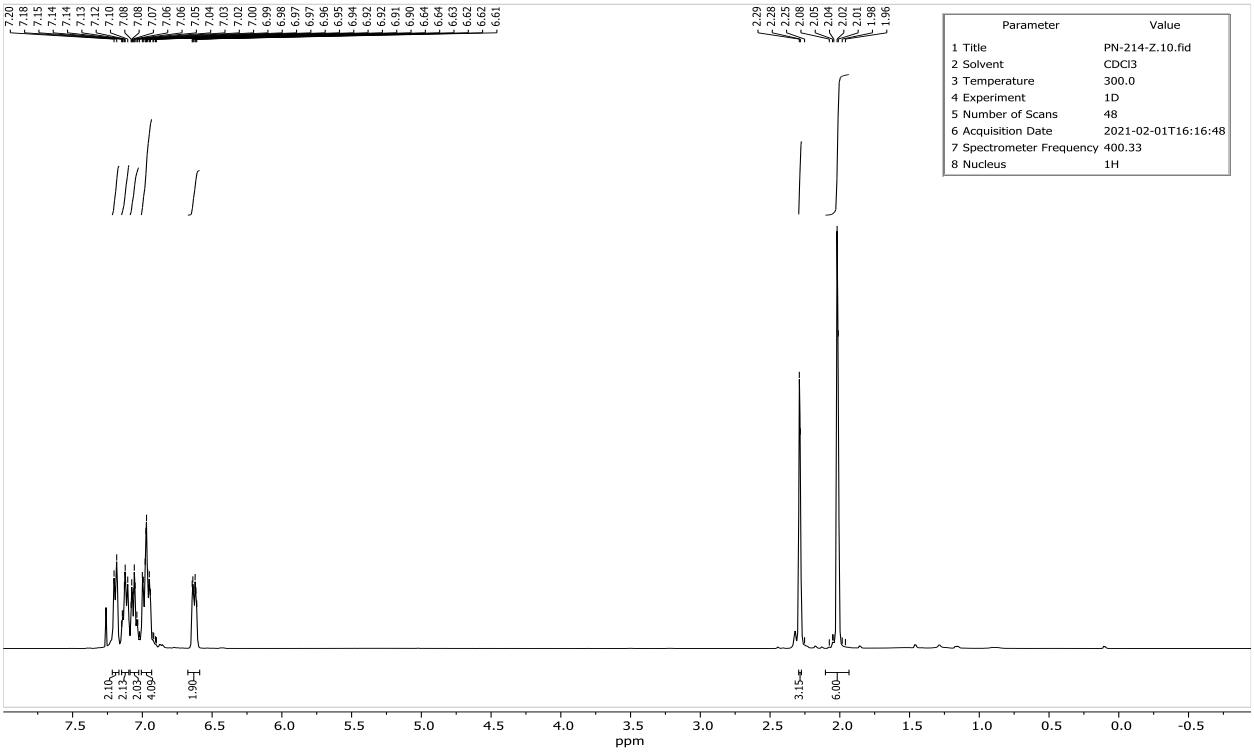


Figure S39. ^{1}H NMR spectrum of 2-methyl-*N*-(*o*-tolyl)-*N*-(*p*-tolyl)aniline **4bea**.

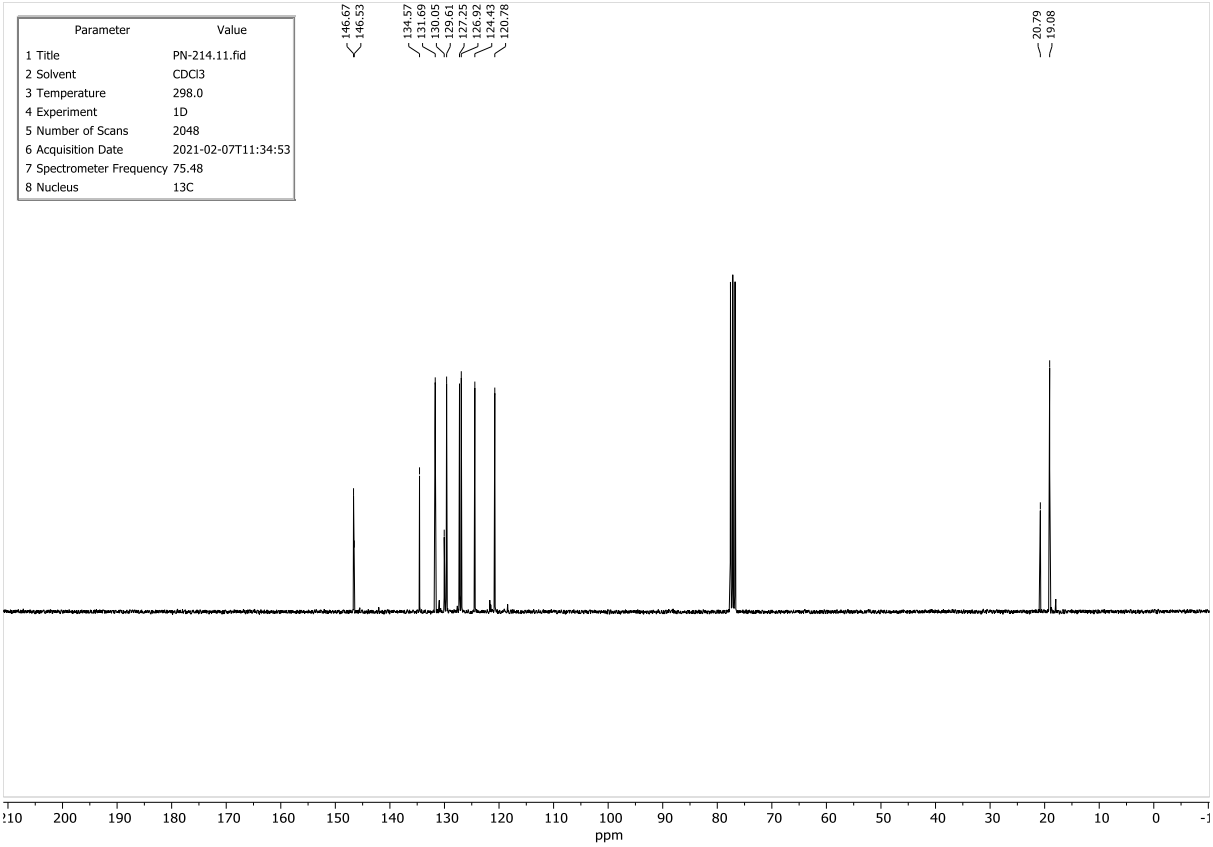


Figure S40. ^{13}C{^{1}H} NMR spectrum of 2-methyl-*N*-(*o*-tolyl)-*N*-(*p*-tolyl)aniline **4bea**.

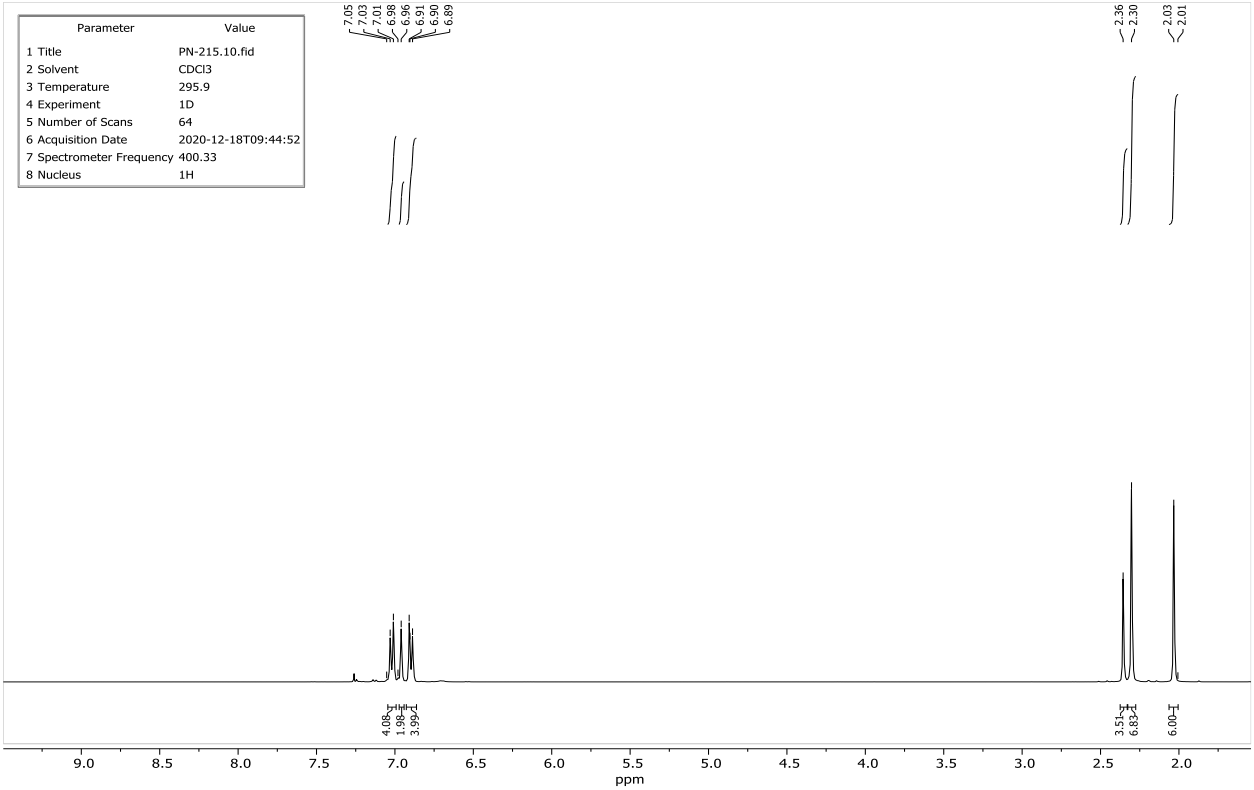


Figure S41. ^{1}H NMR spectrum of 2,4,6-trimethyl-*N*,*N*-di-*p*-tolylaniline **4caa**.

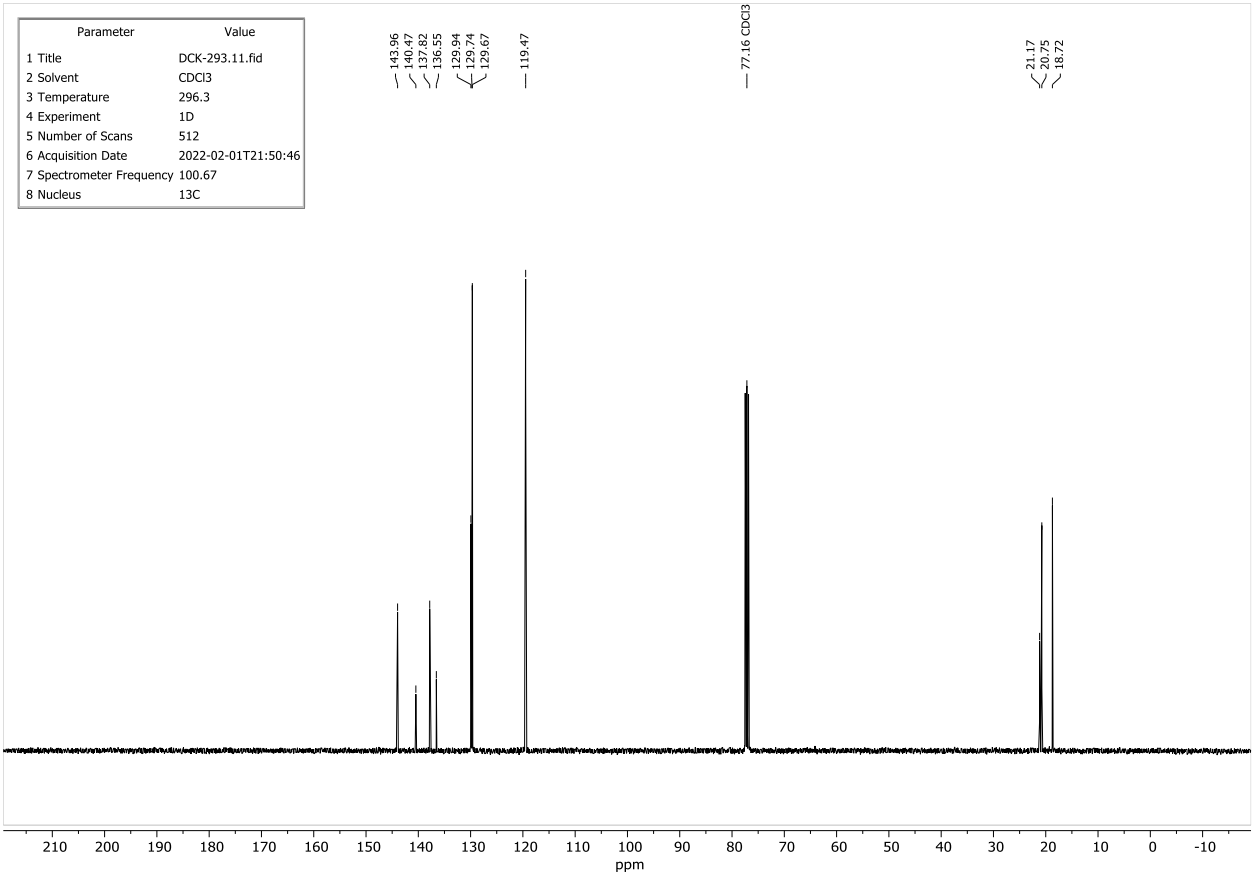


Figure S42. ^{13}C{^{1}H} NMR spectrum of 2,4,6-trimethyl-*N*,*N*-di-*p*-tolylaniline **4caa**.

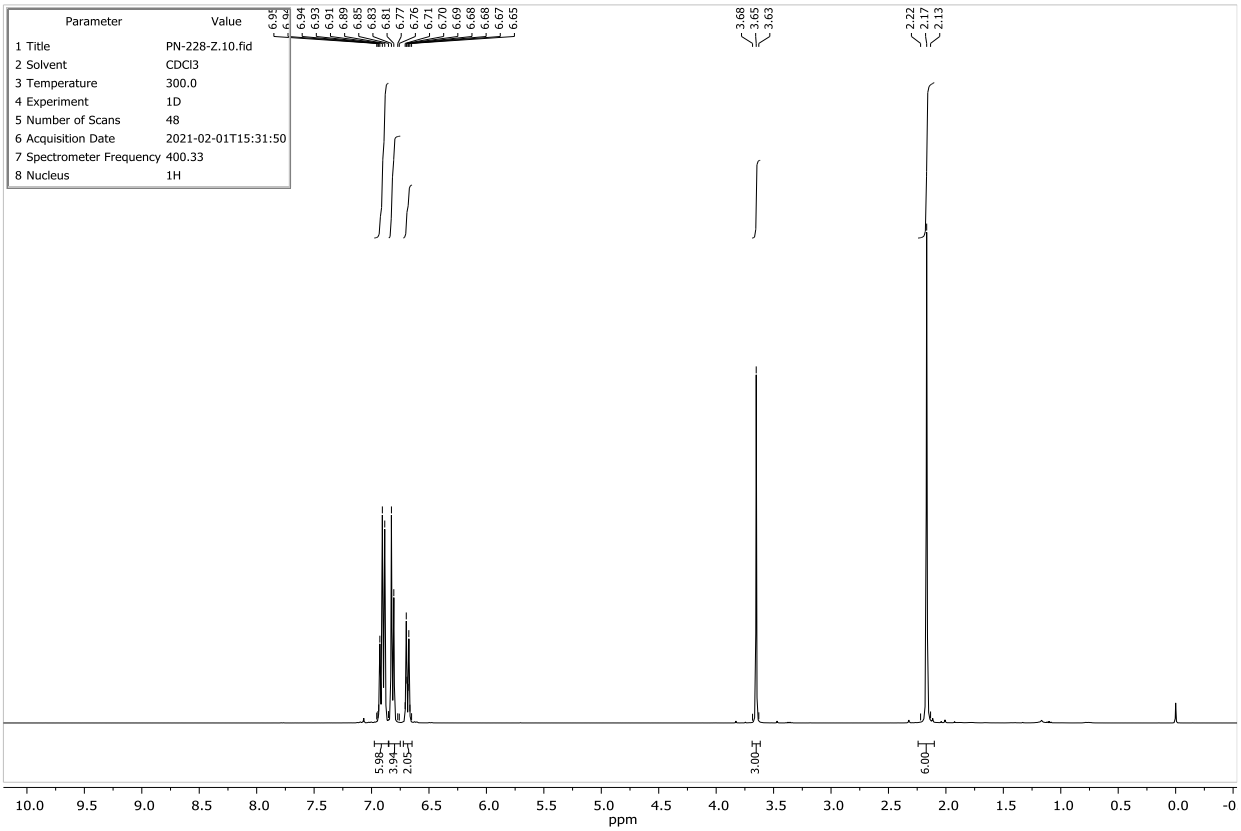


Figure S43. ^{1}H NMR spectrum of 4-methoxy-*N*,*N*-di-*p*-tolylaniline **4aaa**.

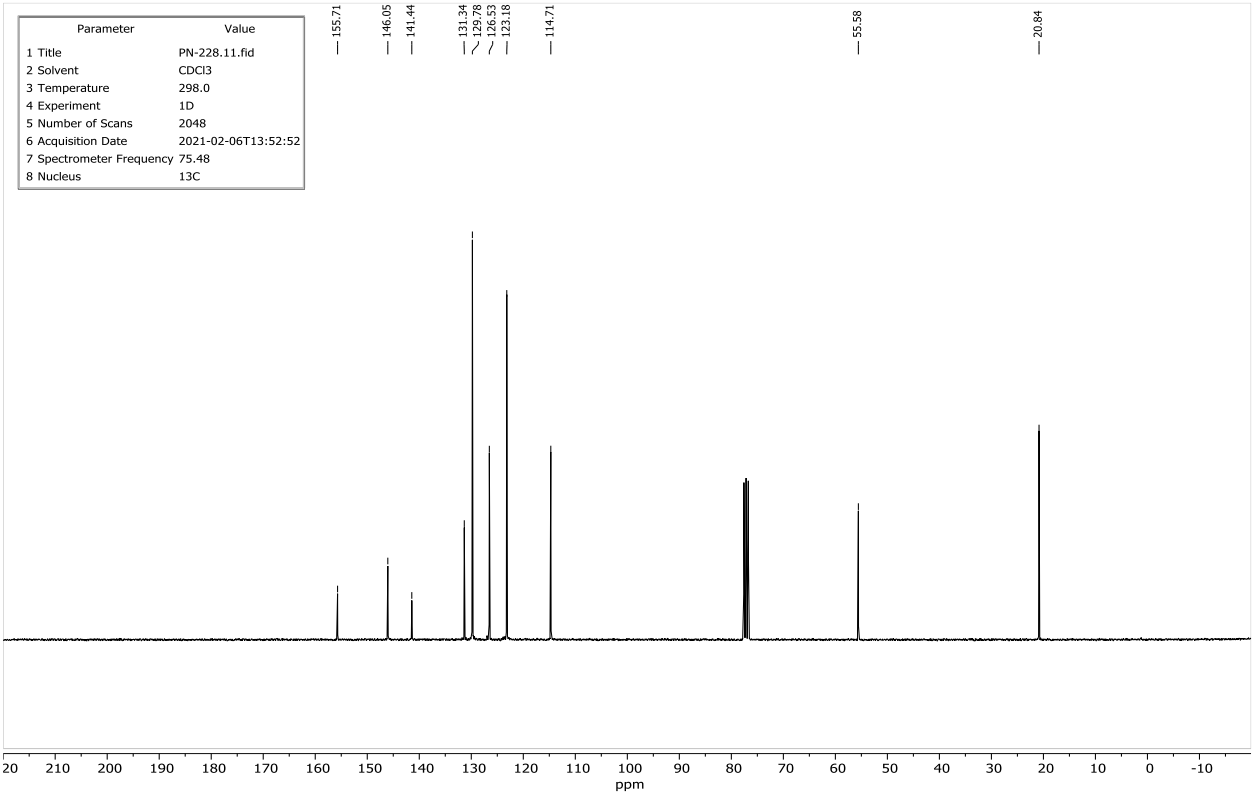


Figure S44. ^{13}C{^{1}H} NMR spectrum of 4-methoxy-*N*,*N*-di-*p*-tolylaniline **4aaa**.

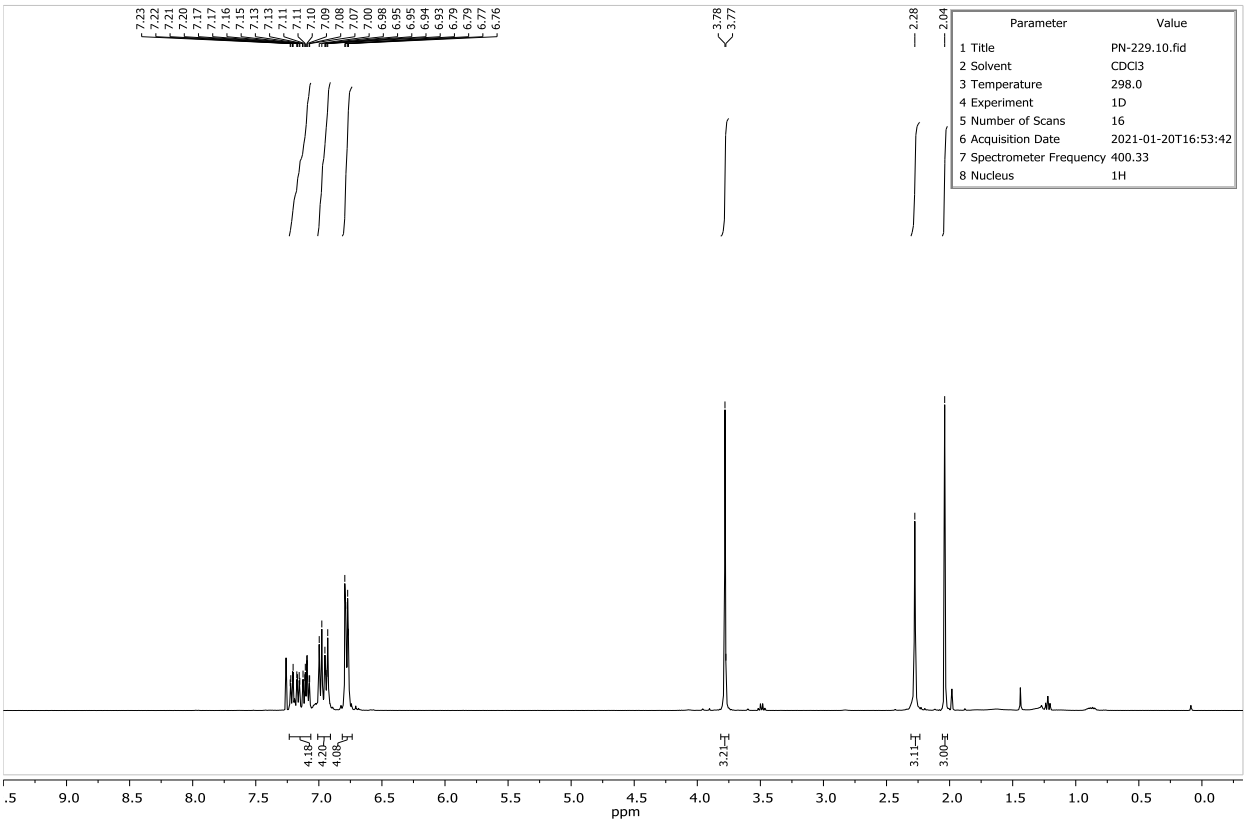


Figure S45. ^{1}H NMR spectrum of *N*-(4-methoxyphenyl)-2-methyl-*N*-(*p*-tolyl)aniline **4aea**.

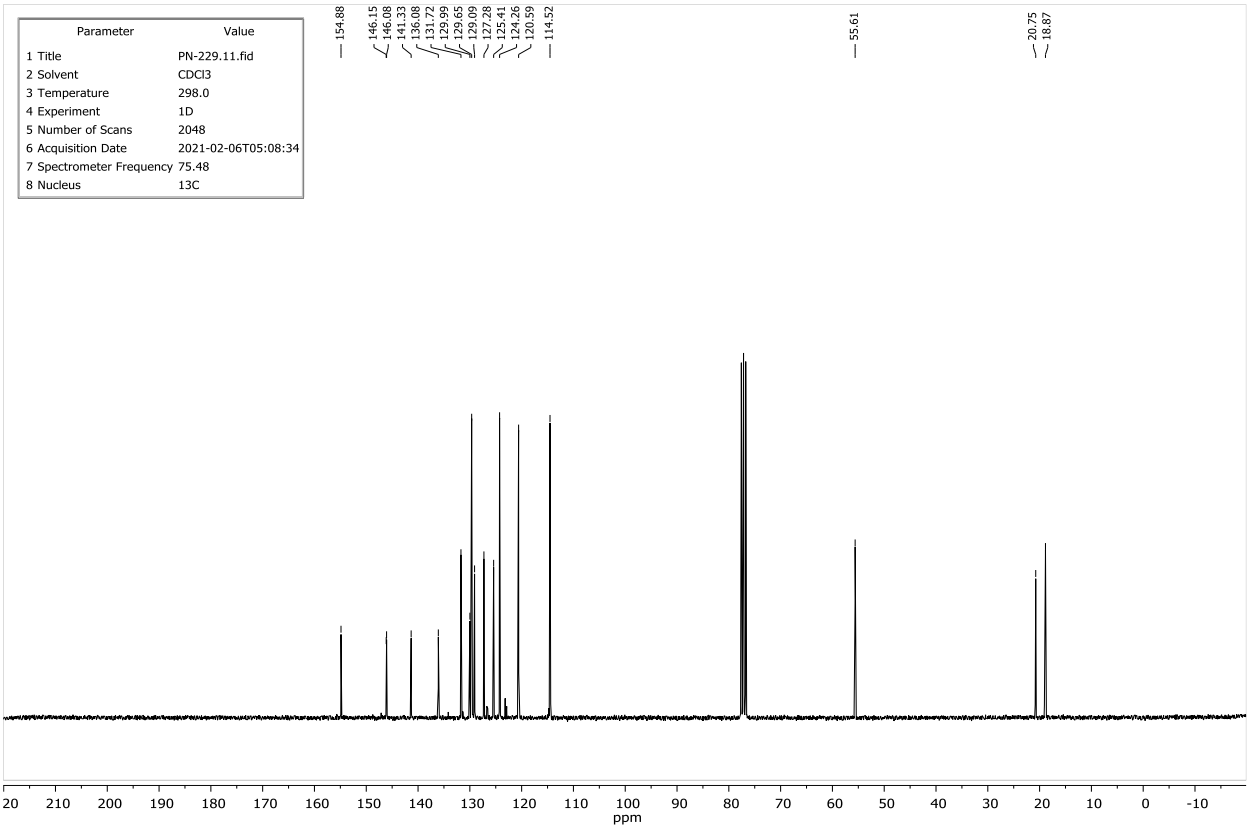


Figure S46. ^{13}C{^{1}H} NMR spectrum of *N*-(4-methoxyphenyl)-2-methyl-*N*-(*p*-tolyl)aniline **4aea**.

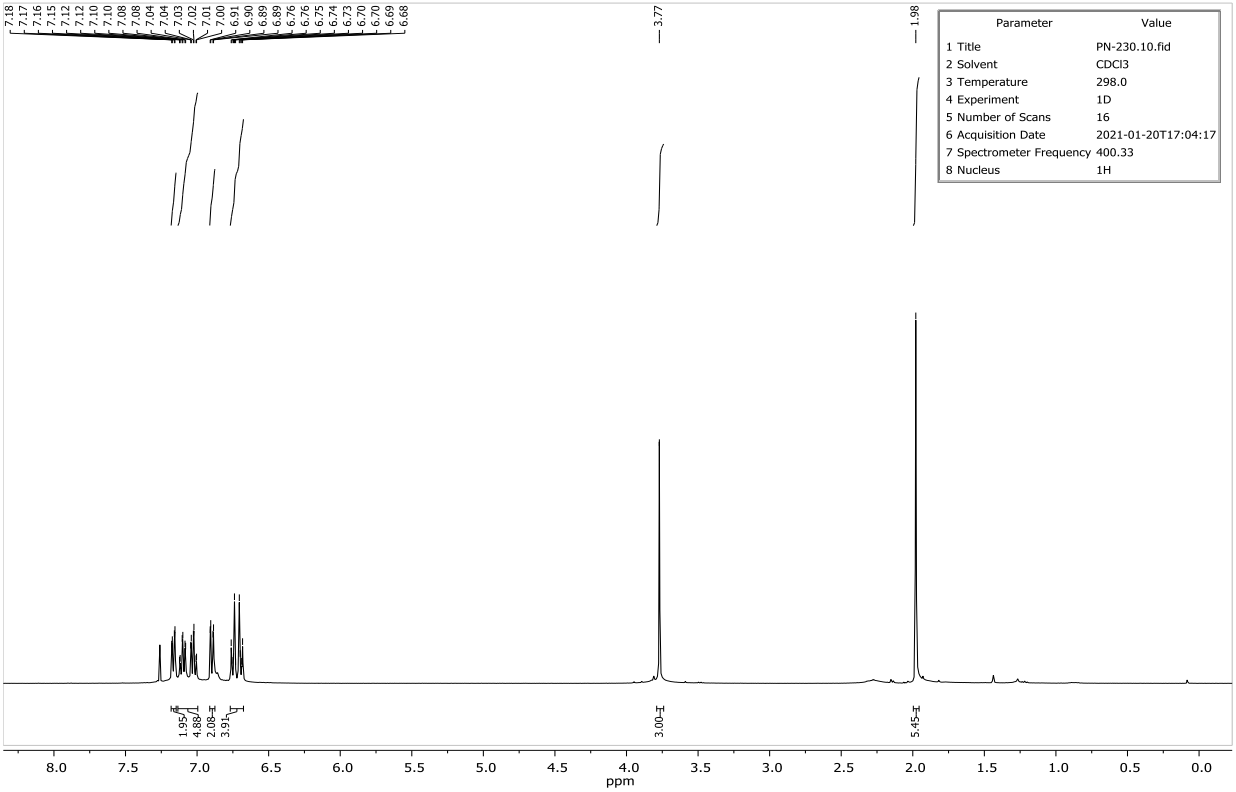


Figure S47. ^{1}H NMR spectrum of *N*-(4-methoxyphenyl)-2-methyl-*N*-(*o*-tolyl)aniline **4aee**.

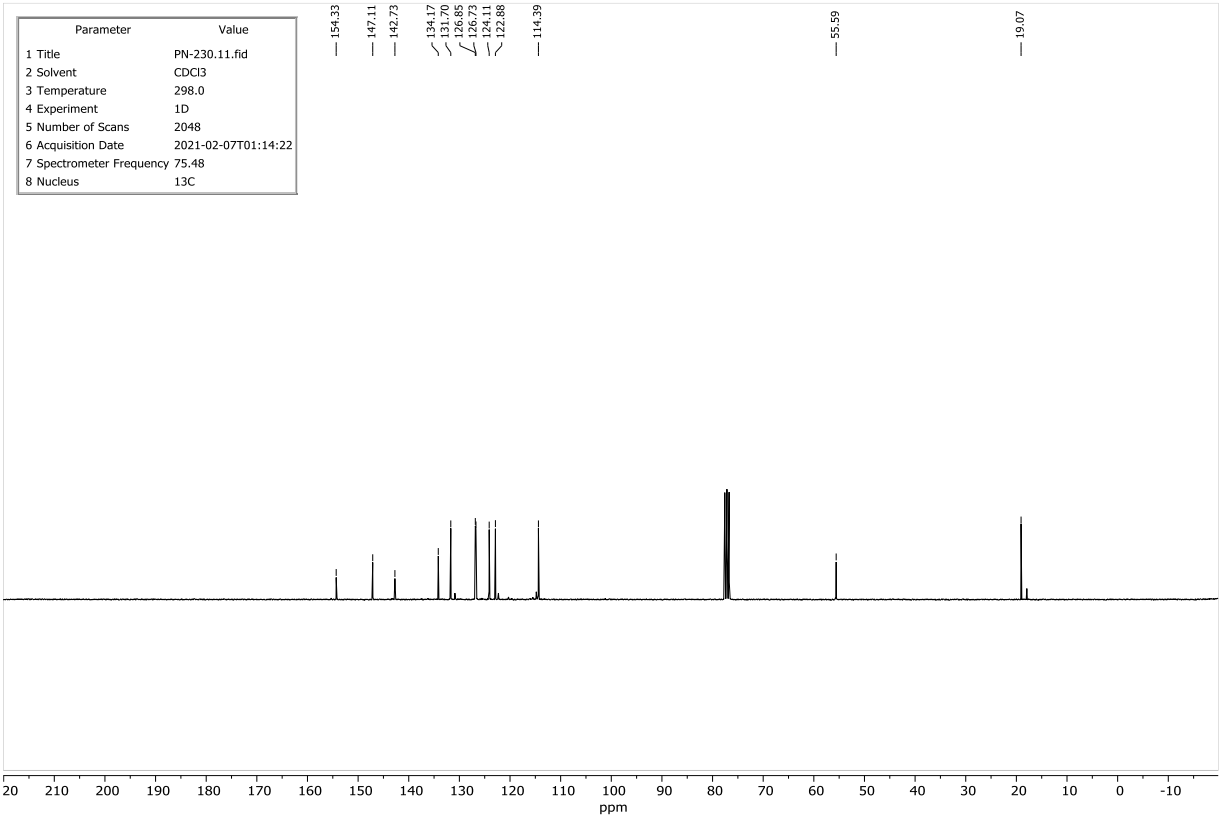


Figure S48. ^{13}C{^{1}H} NMR spectrum of *N*-(4-methoxyphenyl)-2-methyl-*N*-(*o*-tolyl)aniline **4aee**.

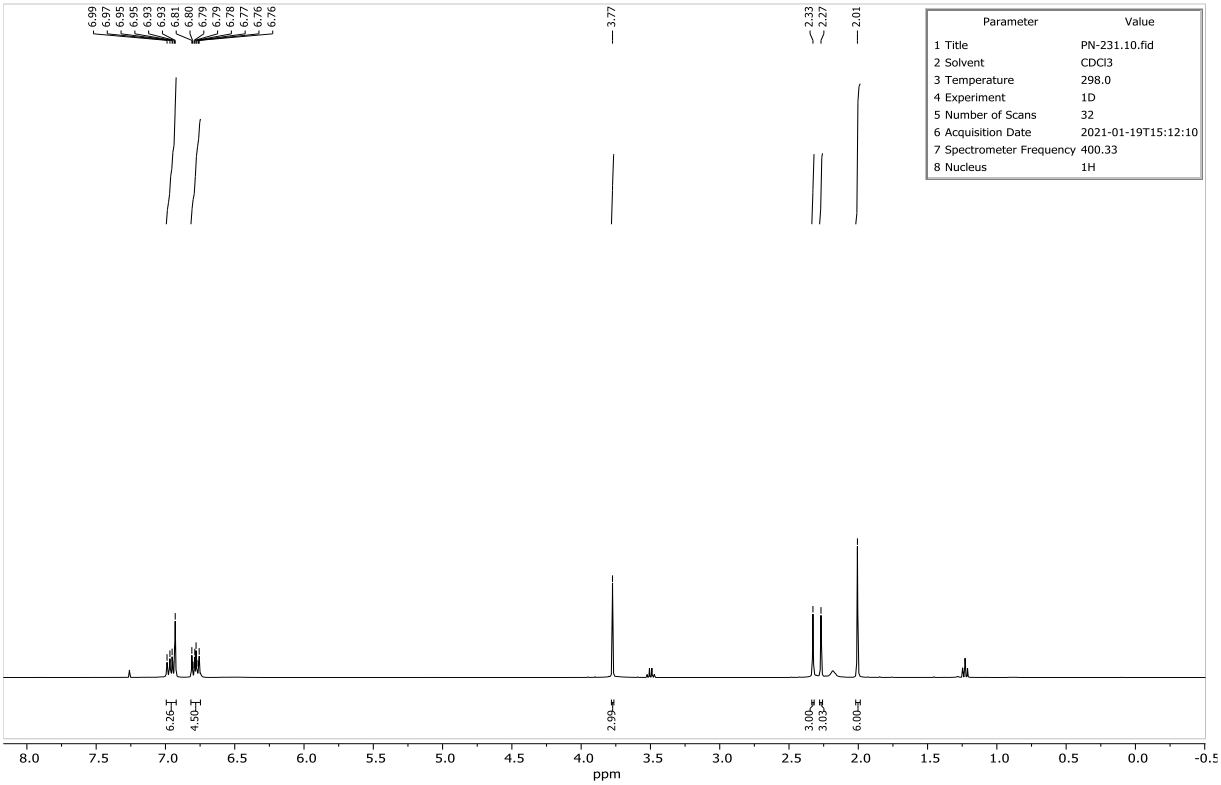


Figure S49. ^{1}H NMR spectrum of *N*-(4-methoxyphenyl)-2,4,6-trimethyl-*N*-(*p*-tolyl)aniline **4aba**.

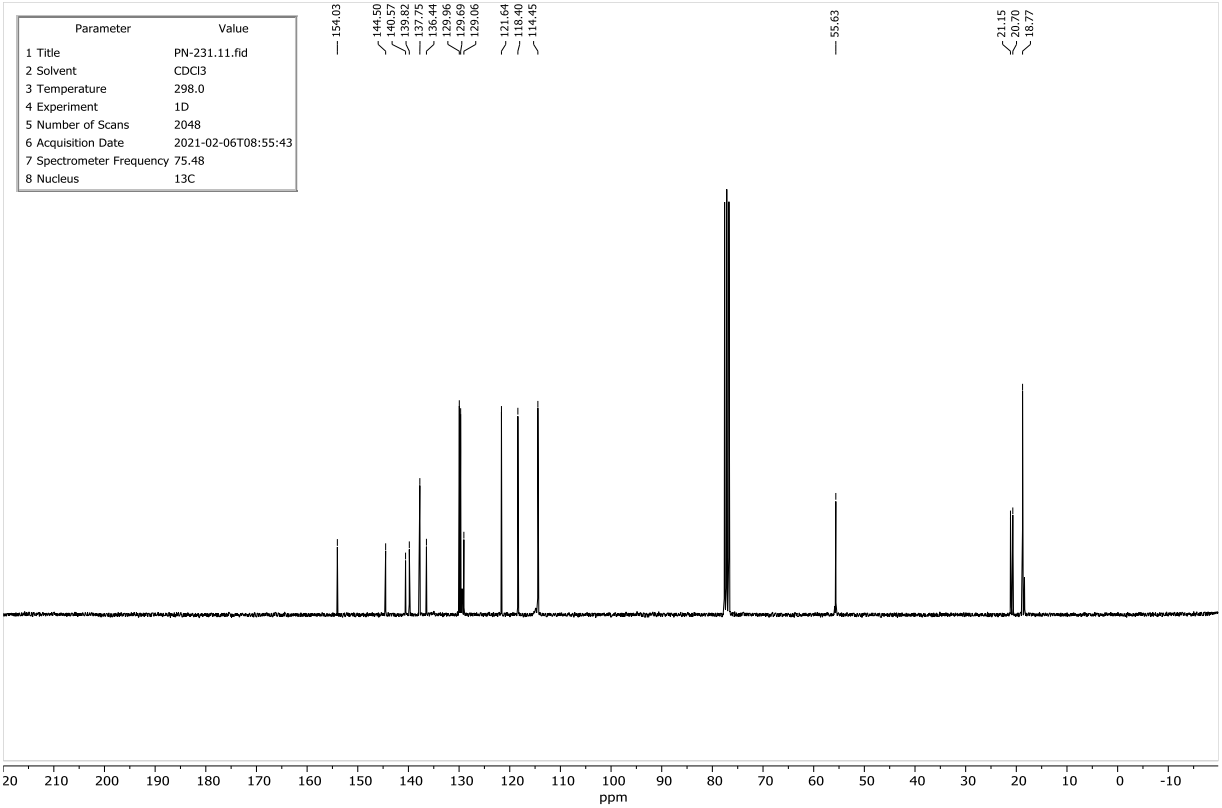


Figure S50. ^{13}C{^{1}H} NMR spectrum of *N*-(4-methoxyphenyl)-2,4,6-trimethyl-*N*-(*p*-tolyl)aniline **4aba**.

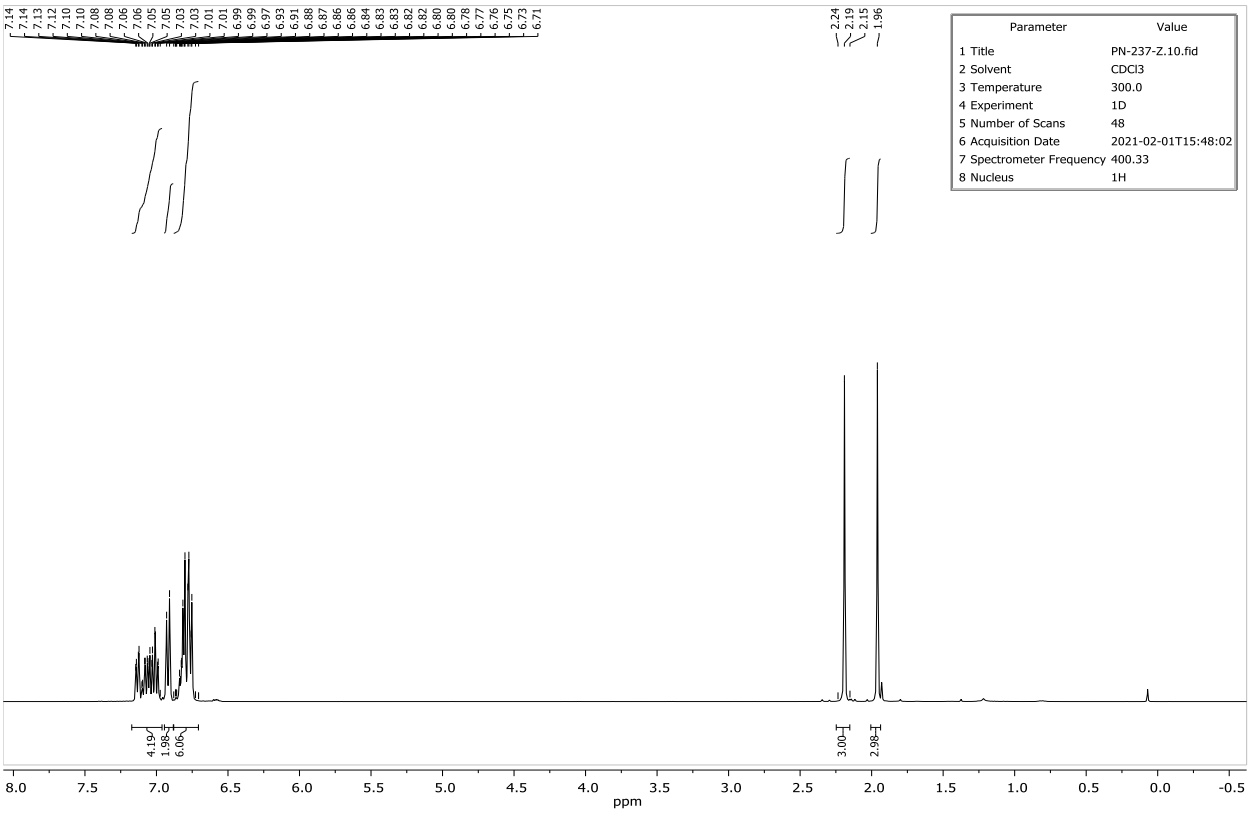


Figure S51. ^{1}H NMR spectrum of *N*-(4-fluorophenyl)-2-methyl-*N*-(*p*-tolyl)aniline **4eea**.

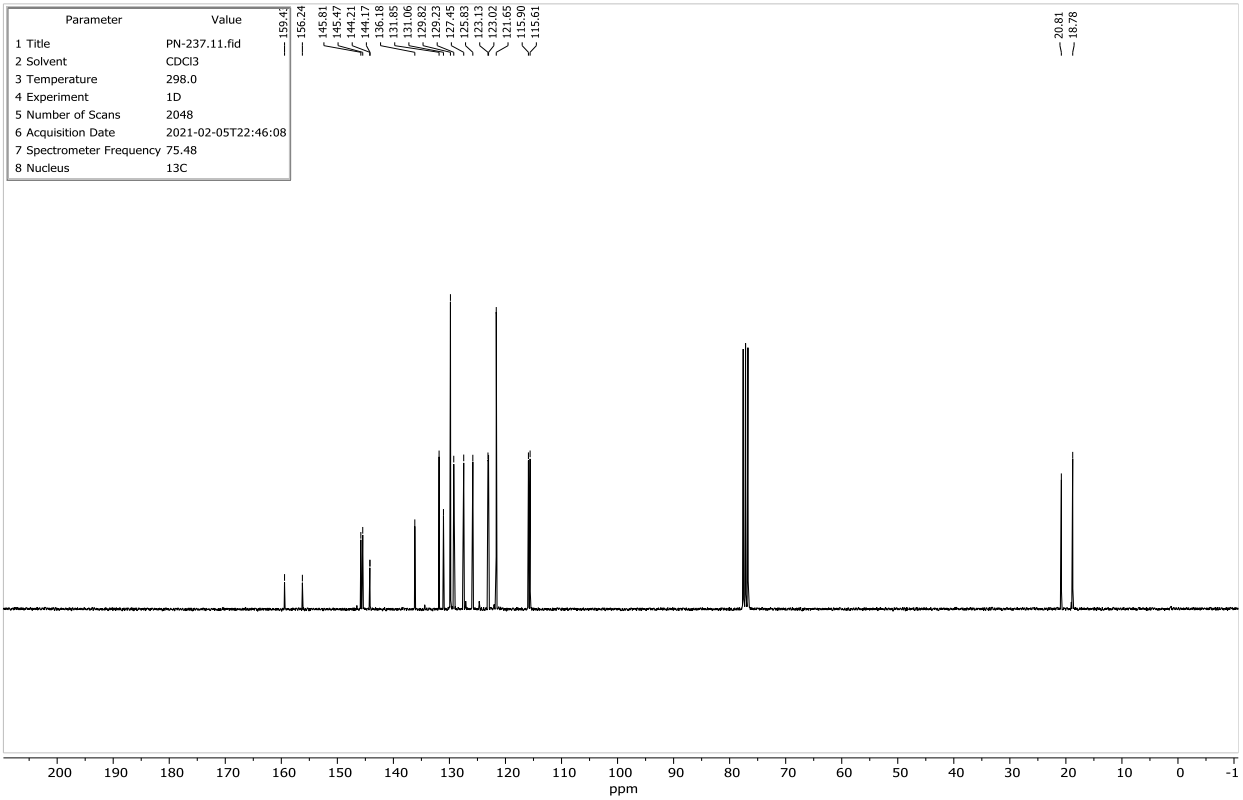


Figure S52. ^{13}C{^{1}H} NMR spectrum of *N*-(4-fluorophenyl)-2-methyl-*N*-(*p*-tolyl)aniline **4eea**.

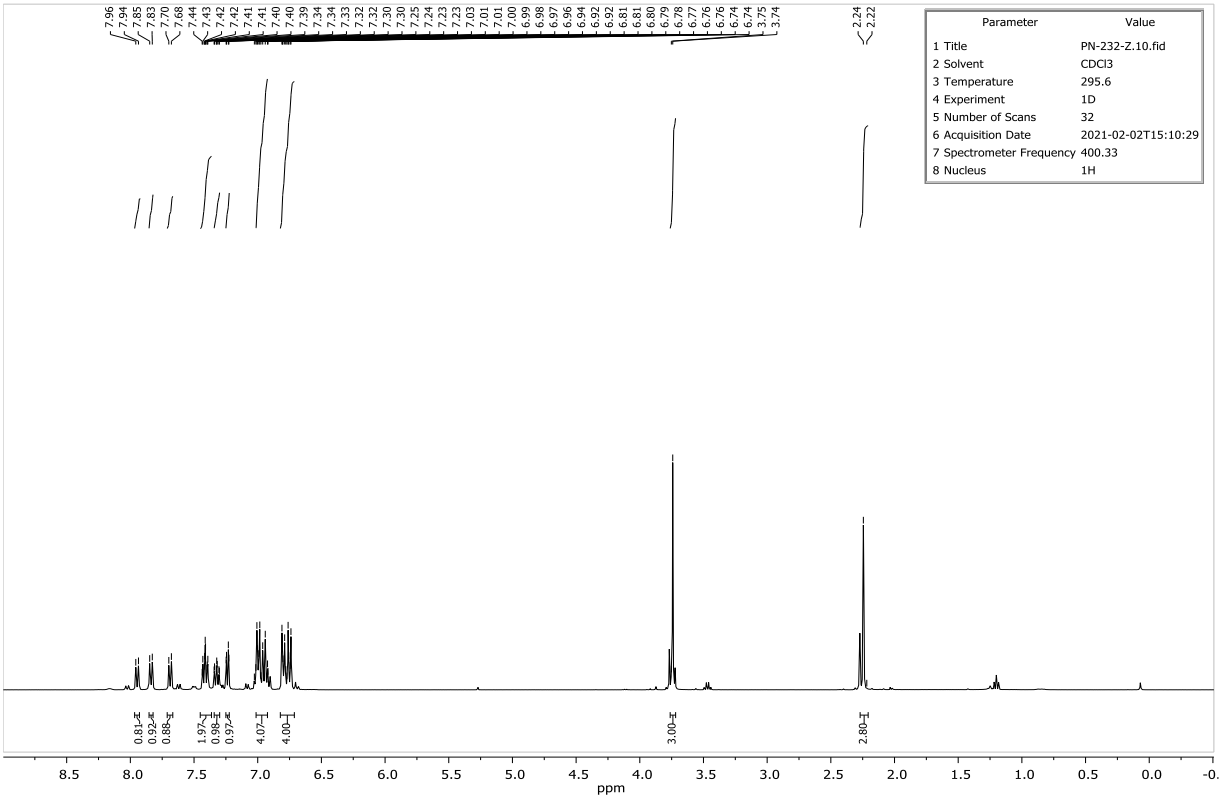


Figure S53. ^{1}H NMR spectrum of *N*-(4-methoxyphenyl)-*N*-(*p*-tolyl)naphthalen-1-amine **4ada**.

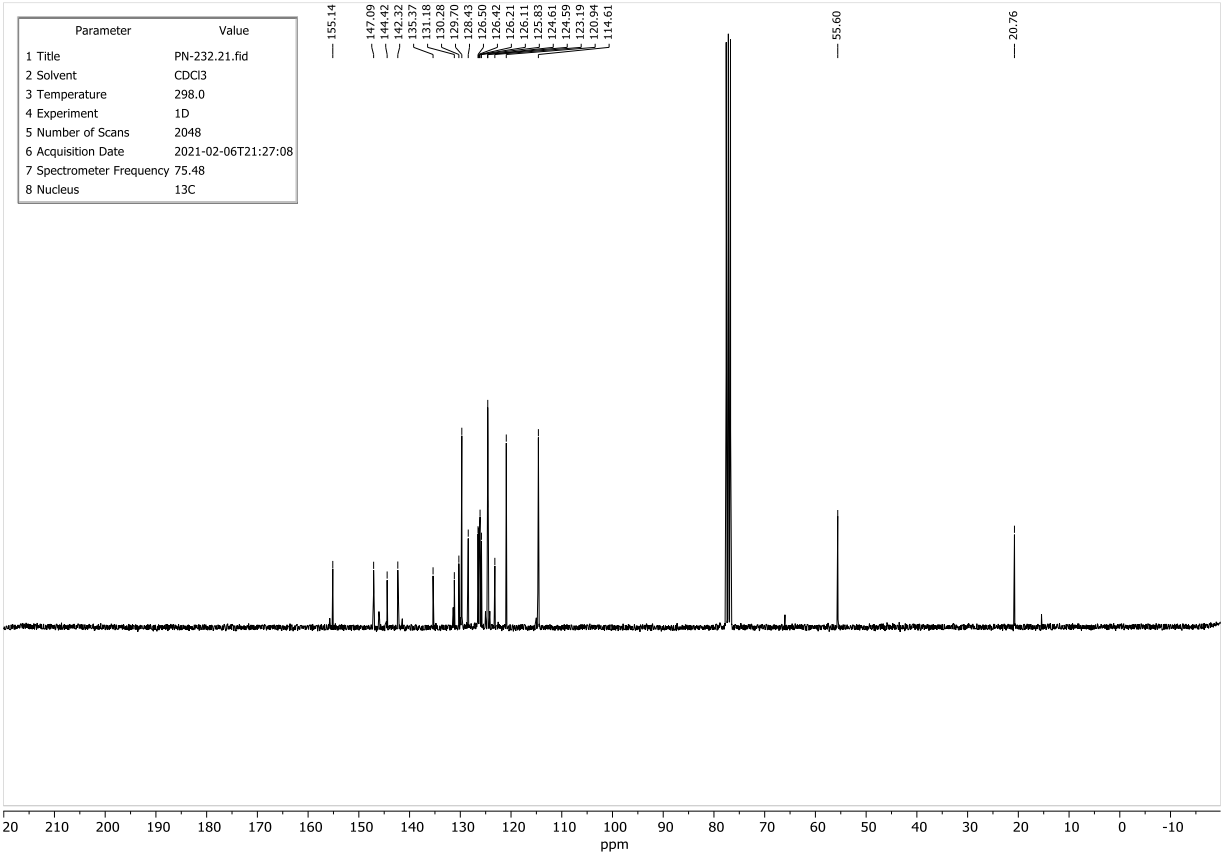


Figure S54. ^{13}C{^{1}H} NMR spectrum of *N*-(4-methoxyphenyl)-*N*-(*p*-tolyl)naphthalen-1-amine **4ada**.

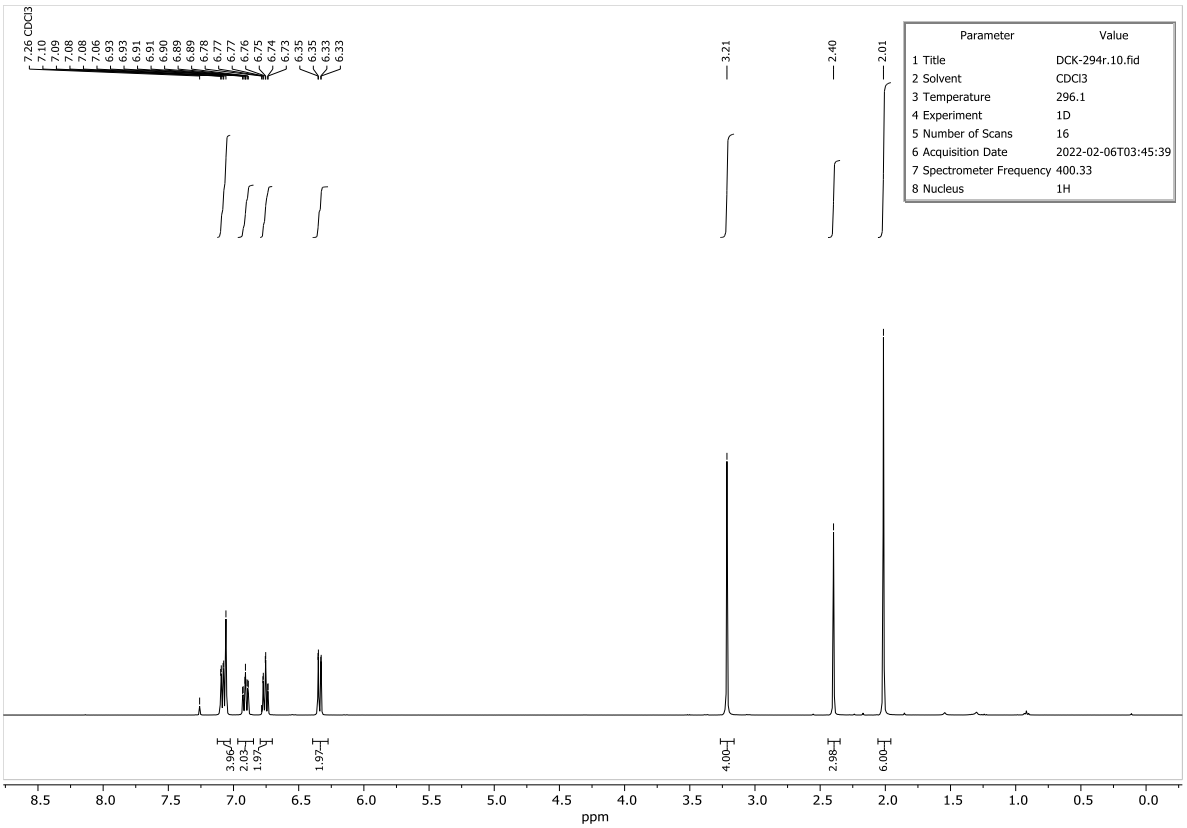


Figure S55. ^{1}H NMR spectrum of 5-(2,6-dimethylphenyl)-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine **4fb**.

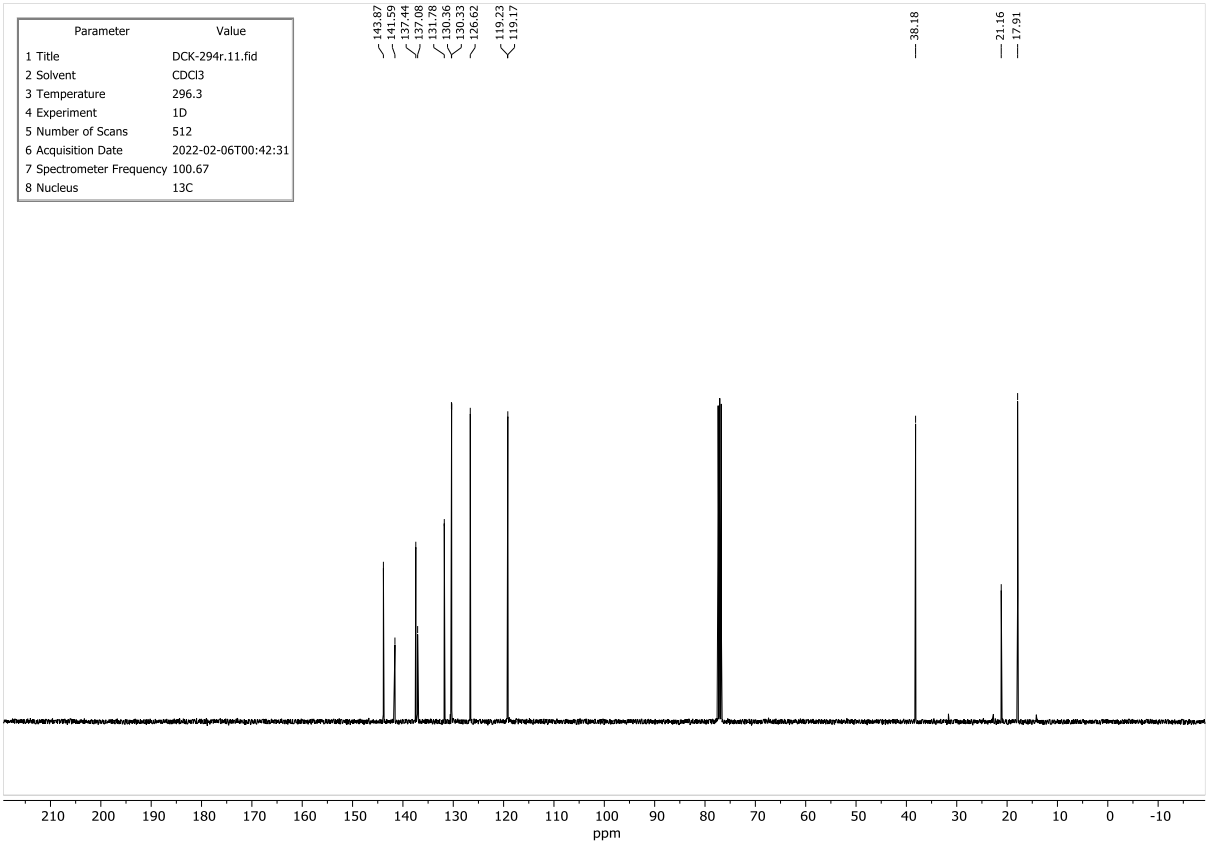


Figure S56. ^{13}C{^{1}H} NMR spectrum of 5-(2,6-dimethylphenyl)-10,11-dihydro-5H-dibenzo[b,f]azepine **4fb**.

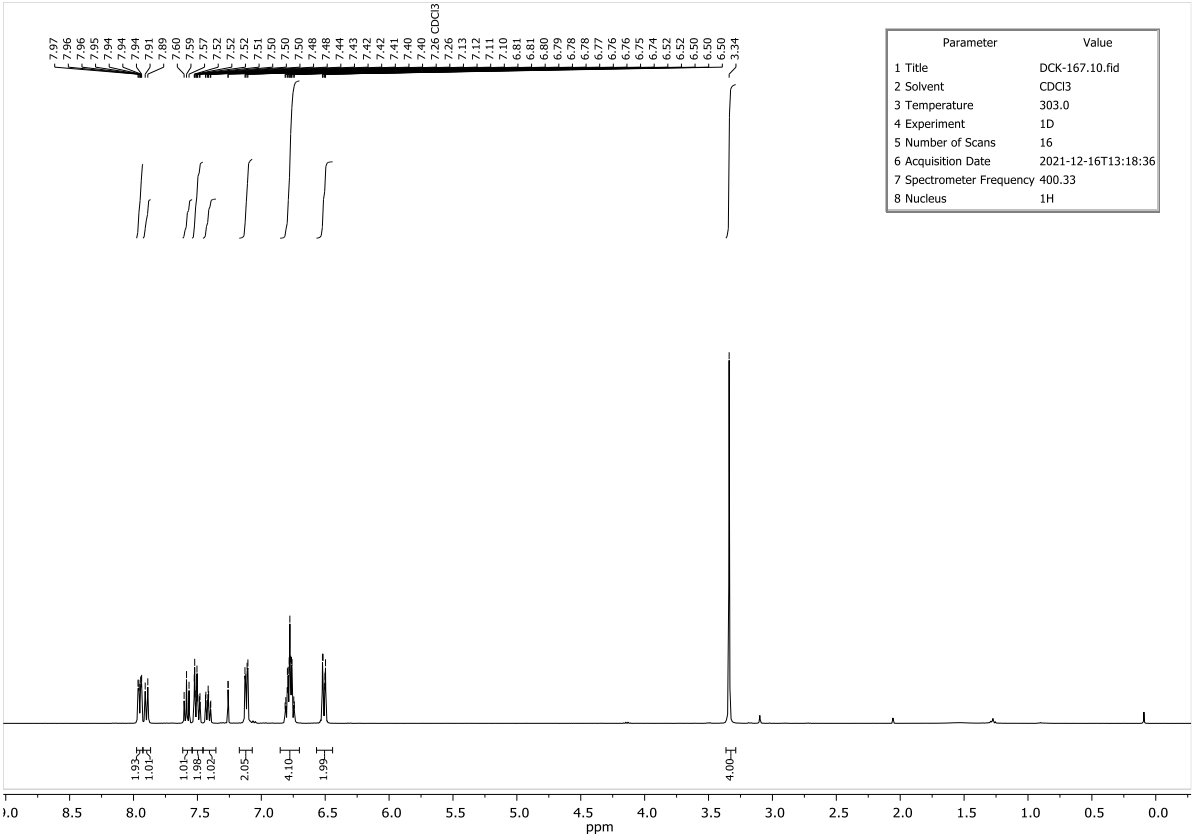


Figure S57. ^{1}H NMR spectrum of 5-(naphthalen-1-yl)-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine **4fd**.

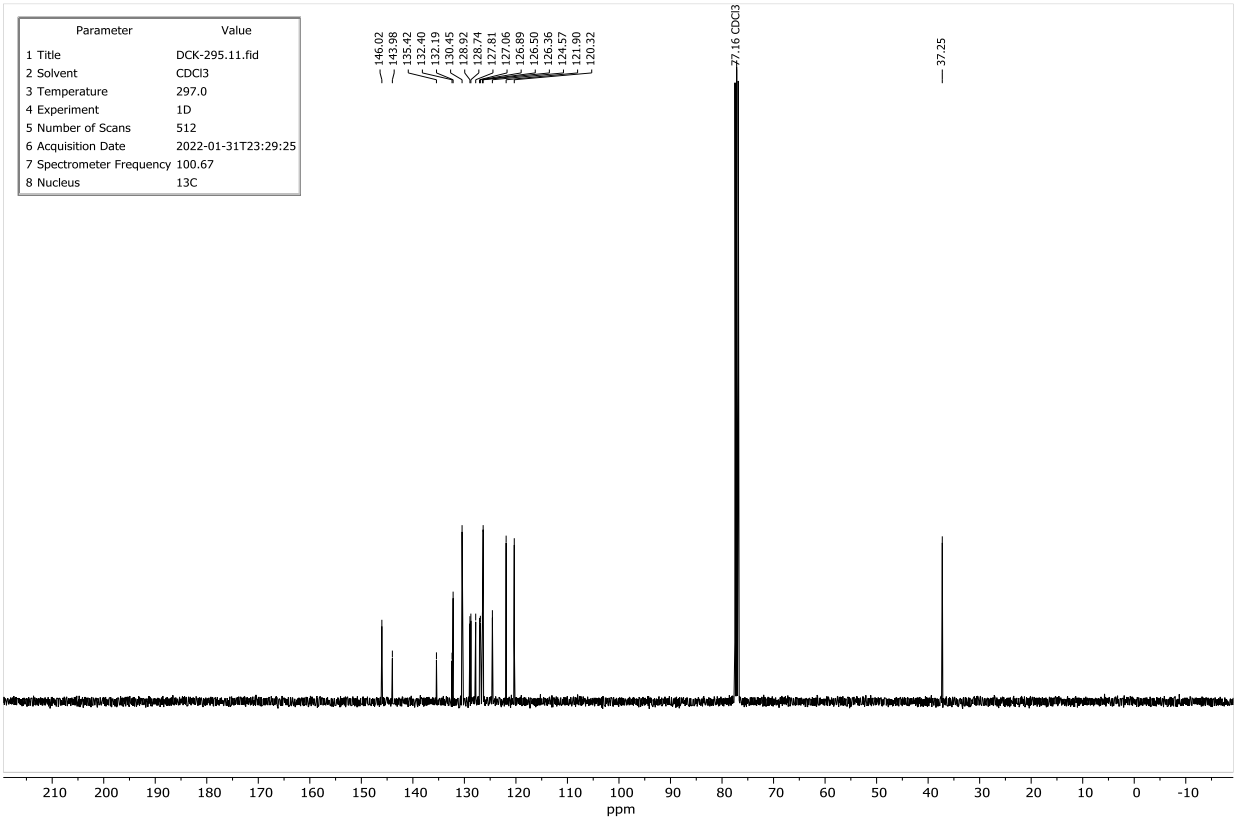


Figure S58. ^{13}C{^{1}H} NMR spectrum of 5-(naphthalen-1-yl)-10,11-dihydro-5H-dibenzo[*b,f*]azepine **4fd**.

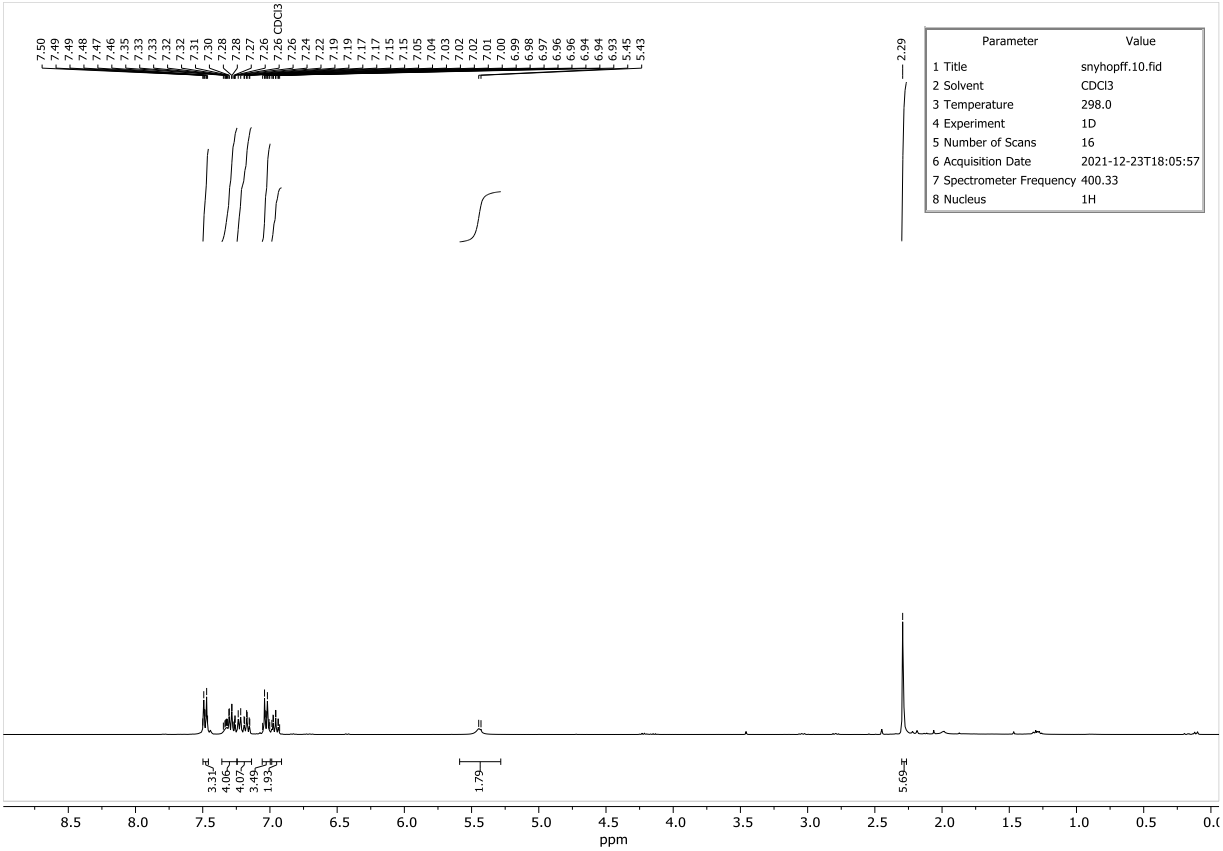


Figure S59. ^{1}H NMR spectrum of *N*-4,N4'-di-o-tolyl-[1,1'-biphenyl]-4,4'-diamine (**5**).

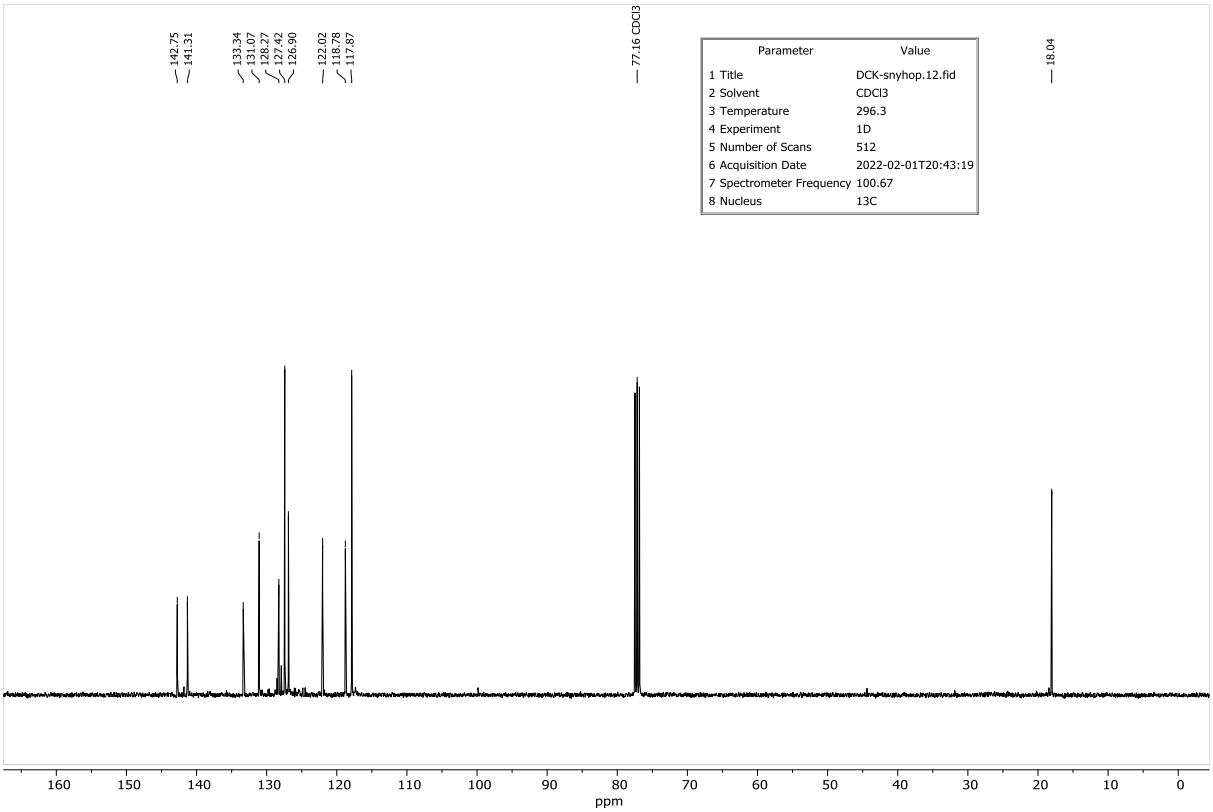


Figure S60. ^{13}C{^{1}H} NMR spectrum of N-4,N4'-di-o-tolyl-[1,1'-biphenyl]-4,4'-diamine ***(5)***.

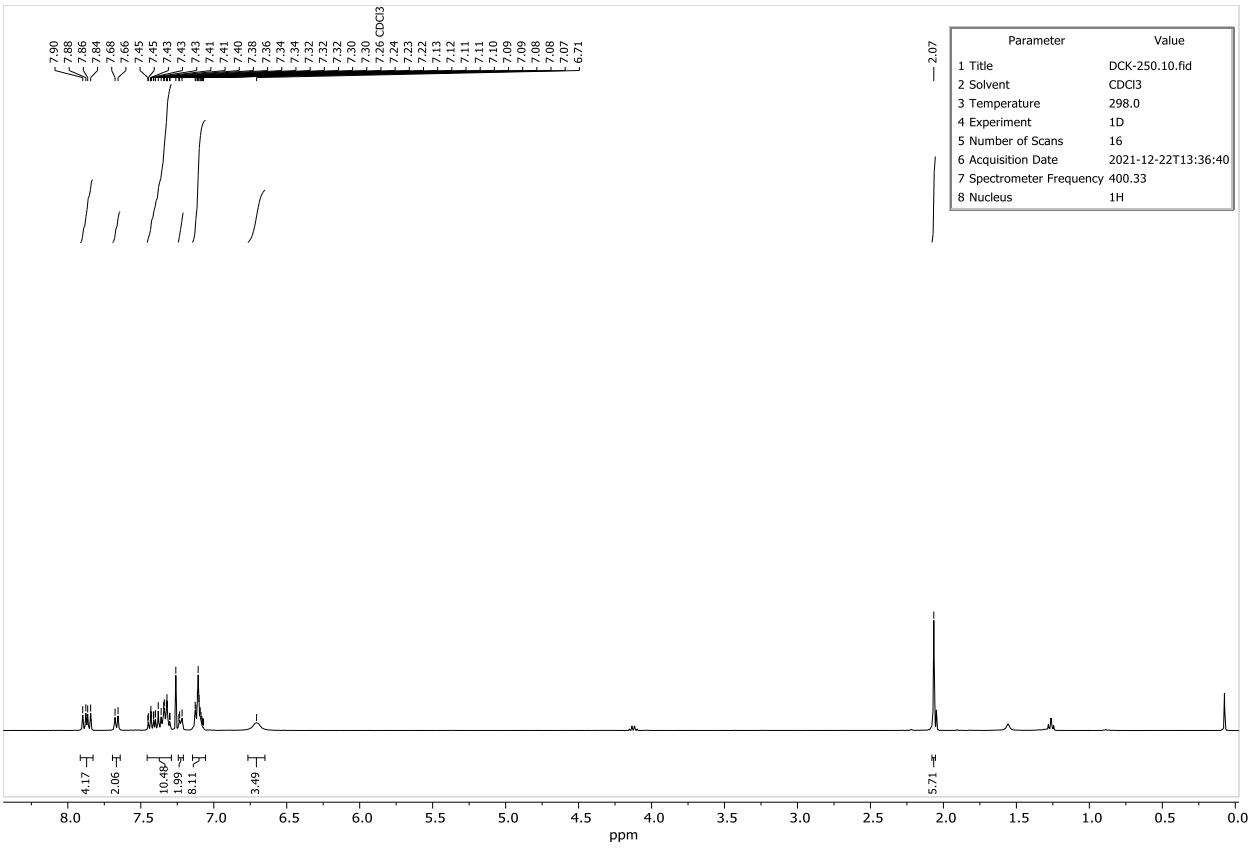


Figure S61. ^{1}H NMR spectrum of N4,N4'-di(naphthalen-1-yl)-N4,N4'-di-o-tolyl-[1,1'-biphenyl]-4,4'-diamine (**6**).

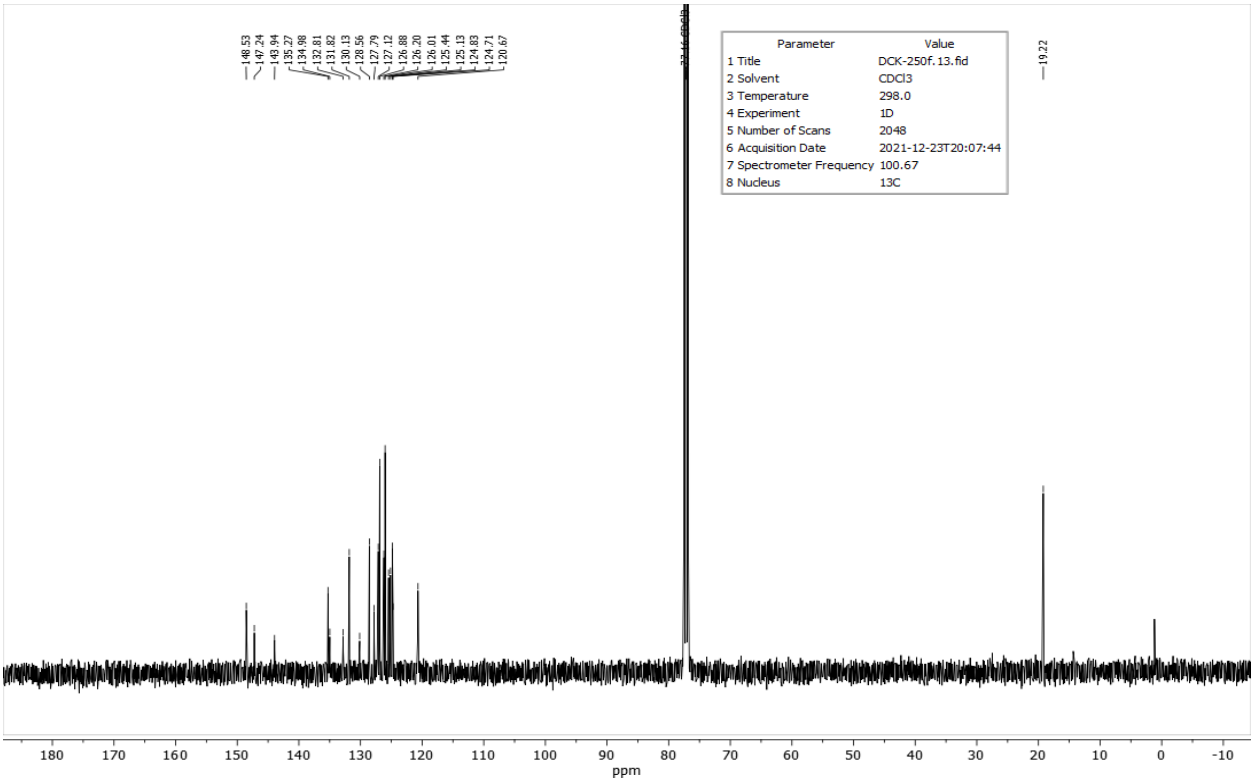


Figure S62. ^{13}C{^{1}H} NMR spectrum of N4,N4'-di(naphthalen-1-yl)-N4,N4'-di-o-tolyl-[1,1'-biphenyl]-4,4'-diamine ***(6)***. Due to the low solubility of the amine, the signal to noise ratio is higher.

3. References

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