

Supplementary information

**Parallel mechanochemical optimization - Buchwald-Hartwig C-N coupling
as a test case**

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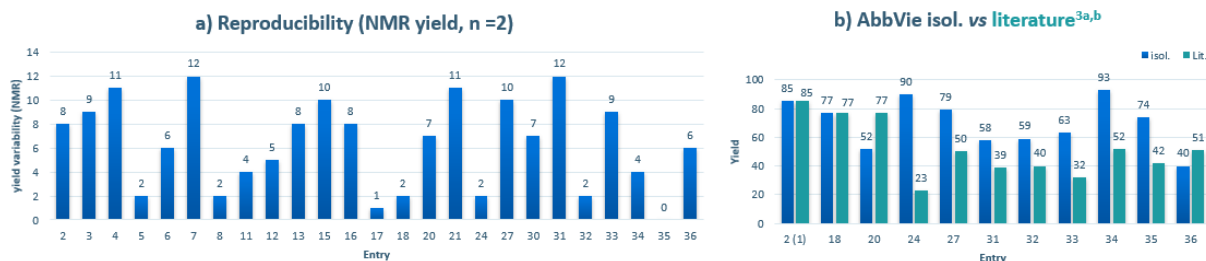
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Table S1. Experimental data table.

entry	Compound	X	state ^a		3-step cascade ^b	NMR-yield ^c (%)				isol. yield (%)	
			ArX / amine	Product		1 st	2 nd	mean	Δ^d	AbbVie ^e	Lit.
1	1	Br	L / S	S	neat	79		79			85 ^{3a}
2					H ₂ O	91	99	95	8	85	
3	2a	Br	S / L	S	neat	26	35	31	9		
4					H ₂ O	89	100	95	11		
5	2b	Cl	S / L	S	neat	8	10	9	2		
6					H ₂ O	24	30	27	6		
7					MeOH	64	76	70	12		
8					sand	94	96	95	2		
9	3	Cl	L / L	L	neat	1		1			
10					H ₂ O	8		8			
11					MeOH	85	89	87	4		
12					sand	88	93	91	5		
13	4	Cl	L / L	L	neat	34	42	38	8		
14					H ₂ O	1		1			
15					MeOH	39	49	44	10		
16					sand	68	60	64	8		
17	5	Cl	L / L	L	neat	76	75	76	1		
18	6	Cl	S / L	S	neat	93	91	92	2	77	77 ^{3a}
19					H ₂ O	27		27			
20					MeOH	60	67	64	7	52	
21					sand	79	90	85	11		
22	7	Cl	S / L	S	neat	35		35			23 ^{3a}
23					H ₂ O	27		27			
24					MeOH	98	100	99	2	90	
25	8	Cl	L / L	S	neat	42		42			50 ^{3a}
26					H ₂ O	1		1			
27					MeOH	85	95	90	10	79	
28	9	Cl	S / S	S	neat	50		50			39 ^{3a}
29					H ₂ O	1		1			
30					MeOH	50	57	54	7		
31					sand	84	96	90	12	58	
32	10	Cl	L / L	S	neat	58	60	59	2	59	40 ^{3b}
33	11	Cl	L / L	L	neat	83	92	88	9	63	32 ^{3b}
34	12	Br	S / L	S	neat	91	95	93	4	93	52 ^{3b}
35	13	Br	L / L	S	neat	89	89	89	0	74	42 ^{3b}
36	14	Cl	S / L	S	neat	55	49	52	6	40	51 ^{3b}

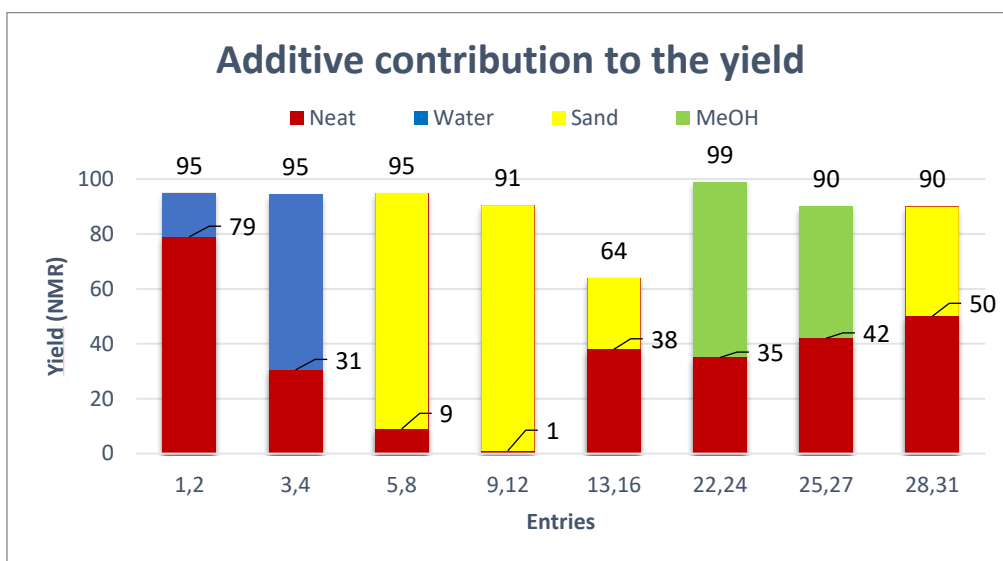
^aliquid (L), solid (S): states of the substrates and product; ^badditive screening (LAG & AG); ^cyield determined by NMR using 1,3,5-trimethoxybenzene (TMB) as internal standard; ^ddifference between 2 measured NMR-yields; ^eisolated yield after chromatography and evaporation (s. general procedure below).

Scheme S1. Data analysis (2).

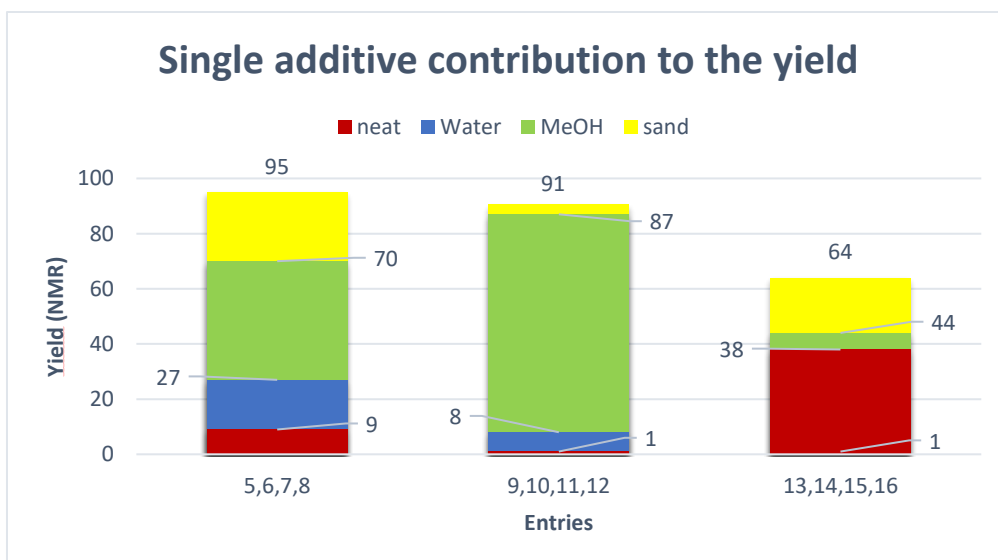


a) the yield difference between 2 NMR-yields measurements was plotted for each substrate [entries, s. Table S1 (SI)], yield determined by NMR using 1,3,5-trimethoxybenzene (TMB) as internal standard; b) AbbVie isolated yield (blue column) in comparison with the published isolated yield (green column).^{3a,b}

Scheme S2. LAG & AG screening – yield improvement.



Scheme S3. 4-step cascade – yield progression.



1. General information

The mechanochemical reactions were run in 2.0 mL HPLC glass vials with a plastic cap from Fritsch (Ref- 07.5000.00 (Fritsch, supplier)) and milled in a Pulverisette 7 Planetary Micro Mill Premium Line (Ref- 83.3165.00 (Fritsch, supplier)). All reagents were obtained from commercial suppliers and used without further purification. TLC (Thin-Layer Chromatography) analysis was performed using pre-

coated glass plates. Visualization was accomplished by exposure to a UV lamp. High resolution mass spectra were obtained on a Xevo G2-S QToF device from Waters. NMR spectra were recorded with a Bruker Avance III 500 MHz or 600 MHz spectrometer for ^1H -NMR and ^{13}C -NMR at 23°C. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to the solvent peaks (^1H : $\delta = 7.26$ (CDCl_3) ppm; $^{13}\text{C} = 77.16$ (CDCl_3)). The following abbreviations are used to report the multiplicity of the peaks: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex. = sextet, sep = septet and combinations thereof, br = broad signal, m = multiplet).

Figure S1. Pulverisette 7 premium line (LM⁴).



up to twelve reactions in parallel: set up with two 6-position jars hosting 2 ml glass vials (Fritsch supplier, www.fritsch.de)



Pulverisette 7 Planetary Micro Mill Premium Line (Ref- 83.3165.00 (Fritsch, supplier)), 6-position bowl and 2.0 mL HPLC glass vials with a plastic cap (Ref- 07.5000.00 (Fritsch, supplier)) – pictures (courtesy from Fritsch.de)

2. General procedure

(Het)aryl halide (0.1 mmol), amine (1.2 eq), $\text{Pd}(\text{OAc})_2$ (CAS-3375-31-3, 6.5 mol%), *t*BuXPhosPdG3 (2-Di-*tert*-butylphosphino-2',4',6'-triisopropyl-1,1'-biphenyl)-2-(2'-amino-1,1'-biphenyl)]palladium(II)-methansulfonate, CAS-1447963-75-8, 6.5 mol%) and *t*-BuOK (CAS-865-47-4, 1.75 eq) were added to 1g Stainless Steel beads (Ref-55.0010.09 (Fritsch, supplier), 1mm diameter, 250 x 4 mg) in the 2.0 mL vial.

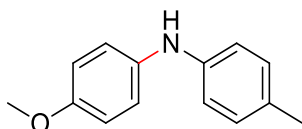
For Liquid Assisted Grinding (LAG) conditions 7 μL of the corresponding solvent were added; and for Auxiliary Grinding (inert solid) conditions 100 mg were added. Then the cap was tightly closed under air atmosphere. The mixture was milled for 30min at high frequency (950 - 1100 rpm), at room temperature; it was then dissolved/suspended in CHCl_3 (3 ml) and filtered through a cotton plug and 30 mg of silicagel. The resulting filtrate was concentrated under a nitrogen flow at room temperature.

For isolated yield determination, the crude was purified using an automated reversed phase flash chromatography on a puriFlash[®] system from Interchim[®] (column: Waters Xselect CSH C18, 150x30 mm, 5 μm ; eluents: (A) water + 0.1% formic acid, (B) MeCN + 0.1% formic acid, (C) MeOH + 0.1% formic acid the ratio is specified later for each compound, flow: 50 mL/min, T = 23 °C) and concentrated under a nitrogen flow at room temperature.

For NMR-yield determination, a definite amount of 1,3,5-trimethoxybenzene (TMB, ca 0.1 mmol) was added to the crude and the mixture was dissolved in CDCl_3 and analyzed by NMR.

3. Characterization of compounds

4-Methoxy-*N*-*p*-tolylaniline (1)



From 4-bromoanisole (CAS-104-92-7) and *p*-toluidine (CAS-106-49-0), LAG conditions (7 μ l H₂O) - A gradient of solvent was used for the purification: acetonitrile/water from 61% to 70% over 25 min to yield after evaporation a white solid (18.1 mg, 85%). NMR-yield (n=2, 91/99%).

The spectral data are consistent with those reported in the literature¹.

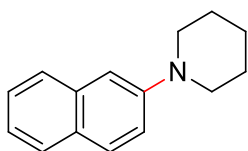
¹H NMR (500 MHz, Chloroform-d) δ 7.03 (d, *J* = 8.0 Hz, 4H), 6.92 – 6.75 (m, 4H), 3.78 (s, 3H), 2.49 – 2.12 (m, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 154.86, 142.46, 136.71, 129.87, 129.37, 121.17, 116.65, 114.74, 55.65, 20.62.

IR (film): ν_{\max} 3415, 2910, 1611, 1512, 1315, 1294, 1224, 1178, 1106, 1032, 812, 766, 704, 503 cm⁻¹.

HR-MS (ESI) *m/z* calcd. for C₁₄H₁₆NO ([M+H]⁺) 214.1227, found 214.1229.

1-Naphthalen-2-yl-piperidine (2)



From 2-bromonaphthalene (CAS-580-13-2) and piperidine (CAS-110-89-4), LAG conditions (7 μ l H₂O) - A gradient of solvent was used for the purification: MeOH/water from 41% to 50% over 25min. NMR-yield⁵ (n=2, 89/100%).

From 2-chloronaphthalene (CAS-91-58-7) and piperidine (CAS-110-89-4), AG conditions (100mg sand) – NMR-yield⁵ (n=2, 94/96%).

The spectral data are consistent with those reported in the literature.²

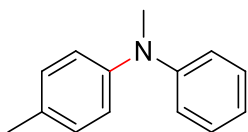
¹H NMR⁵ (500 MHz, Chloroform-d) δ 7.68 (dd, *J* = 13.1, 8.5 Hz, 3H), 7.37 (ddd, *J* = 8.2, 6.6, 1.3 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.12 (d, *J* = 2.4 Hz, 1H), 3.28 – 3.22 (m, 4H), 1.76 (p, *J* = 5.9 Hz, 4H), 1.65 – 1.57 (m, 2H).

¹³C NMR (126 MHz, Chloroform-d) δ 150.19, 134.84, 128.59, 128.43, 127.49, 126.77, 126.19, 123.19, 120.27, 110.46, 51.11, 26.00, 24.48.

IR (film): ν_{\max} 2933, 1596, 1380, 1207, 1114, 953, 841, 820, 748, 475 cm⁻¹.

HR-MS (ESI) *m/z* calcd. for C₁₅H₁₈N ([M+H]⁺) 212.1434, found 212.1444.

N,4-dimethyl-*N*-phenylaniline (3)



From 4-chlorotoluene (CAS-106-43-4) and *N*-methylaniline (CAS-100-61-8), AG conditions (100 mg sand) - A gradient of solvent was used for the purification: acetonitrile/water from 71% to 80% over 25min. NMR-yield⁵ (n=2, 88/93%).

The spectral data are consistent with those reported in the literature³.

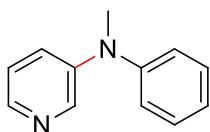
¹H NMR⁵ (500 MHz, Chloroform-d) δ 7.27 – 7.19 (m, 2H), 7.14 – 7.08 (m, 2H), 7.02 – 6.96 (m, 2H), 6.95 – 6.89 (m, 2H), 6.89 – 6.83 (m, 1H), 3.28 (s, 3H), 2.32 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 149.45, 146.68, 132.09, 129.98, 122.62, 119.87, 118.28, 40.39, 20.81.

IR (film): ν_{\max} 1594, 1495, 1338, 1130, 748, 693, 511 cm⁻¹.

HR-MS (ESI) m/z calcd. for C₁₄H₁₆N ([M+H]⁺) 198.1277, found 198.1280.

N-methyl-*N*-phenylpyridin-3-amine (4)



From 3-chloropyridine (CAS-626-60-8) and *N*-methylaniline (CAS-100-61-8), AG conditions (100 mg sand) - A gradient of solvent was used for the purification: acetonitrile/water from 11% to 20% over 25min. NMR-yield⁵ (n=2, 60/68%).

The spectral data are consistent with those reported in the literature.³

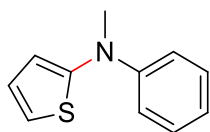
¹H NMR⁵ (500 MHz, Chloroform-d) δ 8.31 (s, 1H), 8.16 – 8.11 (m, 1H), 7.37 – 7.29 (m, 2H), 7.28 – 7.19 (m, 1H), 7.14 (dd, *J* = 8.4, 4.6 Hz, 1H), 7.13 – 7.04 (m, 3H), 3.34 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 147.92, 145.12, 141.18, 140.62, 129.62, 124.78, 123.45, 123.28, 122.41, 40.04.

IR (film): ν_{\max} 1577, 1483, 1420, 1341, 1245, 753, 696 cm⁻¹.

HR-MS (ESI) m/z calcd. for C₁₂H₁₃N₂ ([M+H]⁺) 185.1073, found 185.1080.

N-methyl-*N*-phenylthiophen-2-amine (5)



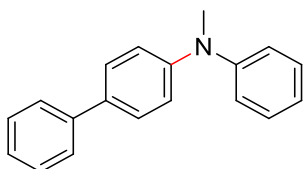
From 2-chlorothiophene (CAS-96-43-5) and *N*-methylaniline (CAS-100-61-8), neat conditions - After filtration and evaporation, NMR-yield⁵ (n=2, 75/76%).

¹H NMR^{5,6} (500 MHz, Chloroform-d) δ 7.27 – 7.21 (m, 2H), 6.99 – 6.91 (m, 3H), 6.91 – 6.84 (m, 2H), 6.64 (dd, *J* = 3.7, 1.4 Hz, 1H), 3.32 (s, 3H).

IR (film): ν_{\max} 2928, 1650, 1595, 1493, 1384, 1114, 751, 695 cm⁻¹.

HR-MS (ESI) m/z calcd. for C₁₁H₁₂NS ([M+H]⁺) 190.0685, found 190.0685

N-methyl-*N*-phenylbiphenyl-4-amine (6)



From 4-chlorobiphenyl (CAS-2051-62-9) and *N*-methylaniline (CAS-100-61-8), neat conditions - A gradient of solvent was used for the purification: acetonitrile/water from 81% to 90% over 25 min to yield after evaporation a white solid (n=2, 20.4/19.1 mg, 74/79%). NMR-yield (n=2, 91/93%).

The spectral data are consistent with those reported in the literature³.

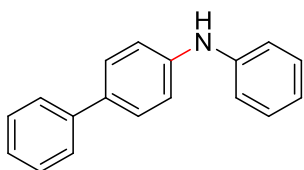
¹H NMR (500 MHz, Chloroform-d) δ 7.59 – 7.53 (m, 2H), 7.53 – 7.47 (m, 2H), 7.44 – 7.37 (m, 2H), 7.34 – 7.25 (m, 3H), 7.13 – 7.08 (m, 2H), 7.08 – 7.02 (m, 2H), 7.00 (tt, J = 7.3, 1.2 Hz, 1H), 3.35 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 148.94, 148.48, 141.03, 133.60, 129.45, 128.85, 127.90, 126.72, 126.69, 122.12, 121.62, 119.78, 40.41.

IR (film): ν_{max} 1587, 1487, 1340, 1255, 756, 690, 499 cm^{-1} .

HR-MS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{18}\text{N}$ ($[\text{M}+\text{H}]^+$) 260.1434, found 260.1443.

N-phenylbiphenyl-4-amine (7)



From 4-chlorobiphenyl (CAS-2051-62-9) and aniline (CAS-62-53-3), LAG conditions (7 μl MeOH) - A gradient of solvent was used for the purification: acetonitrile/water from 71% to 80% over 25 min to yield after evaporation a white solid (22.1 mg, 90%). NMR-yield (n=2, 98/100%).

The spectral data are consistent with those reported in the literature.³

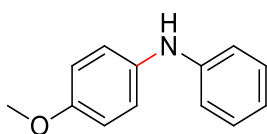
¹H NMR (500 MHz, Chloroform-d) δ 7.59 (d, J = 7.5 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.14 (t, J = 8.9 Hz, 4H), 6.97 (t, J = 7.3 Hz, 1H), 5.92 – 5.65 (m, 1H).

¹³C NMR (126 MHz, Chloroform-d) δ 142.94, 142.64, 140.93, 133.79, 129.49, 128.84, 128.05, 126.69, 126.62, 121.32, 118.19, 117.89.

IR (film): ν_{max} 3370, 1595, 1504, 1321, 846, 745, 692, 493 cm^{-1} .

HR-MS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{16}\text{N}$ ($[\text{M}+\text{H}]^+$) 246.1277, found 246.1284.

4-methoxy-*N*-phenylaniline (8)



From 4-chloroanisole (CAS-623-12-1) and aniline (CAS-62-53-3), LAG conditions (7 μ l MeOH) - A gradient of solvent was used for the purification: acetonitrile/water from 51% to 60% over 25 min to yield after evaporation a white solid (15.8 mg, 79%). NMR-yield (n=2, 85/95%).

The spectral data are consistent with those reported in the literature.³

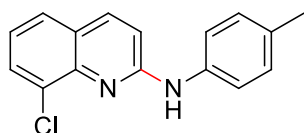
¹H NMR (500 MHz, Chloroform-d) δ 7.20 (dd, J = 8.6, 7.3 Hz, 2H), 7.07 (d, J = 8.9 Hz, 2H), 6.90 (dd, J = 8.6, 1.1 Hz, 2H), 6.88 – 6.79 (m, 3H), 3.79 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 155.44, 145.28, 135.85, 129.44, 122.35, 119.74, 115.82, 114.81, 55.71.

IR (film): ν_{max} 3362, 1596, 1491, 1229, 1027, 743, 690, 500 cm^{-1} .

HR-MS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{14}\text{NO}$ ($[\text{M}+\text{H}]^+$) 200.1070, found 200.1075.

8-chloro-*N*-*p*-tolylquinolin-2-amine (9)



From 2,8-dichloroquinoline (CAS-4470-83-1) and *p*-toluidine (CAS-106-49-0), AG conditions (100 mg sand) - A gradient of solvent was used for the purification: acetonitrile/water from 61% to 70% over 25 min to yield after evaporation a yellow solid (15.5 mg, 58%). NMR-yield (n=2, 84/96%).

The spectral data are consistent with those reported in the literature.³

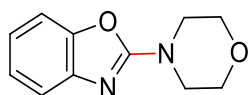
¹H NMR ¹H NMR (500 MHz, Chloroform-d) δ 7.86 (d, J = 8.9 Hz, 1H), 7.69 (dd, J = 7.6, 1.4 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.52 (dd, J = 8.1, 1.4 Hz, 1H), 7.21 – 7.14 (m, 3H), 6.94 (d, J = 9.0 Hz, 1H), 2.35 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 155.01, 138.11, 137.26, 133.30, 130.01, 129.97, 126.52, 125.21, 122.81, 121.01, 112.44, 21.01.

IR (film): ν_{max} 3400, 1604, 1519, 1420, 1334, 816, 744, 662, 533, 511 cm^{-1} .

HR-MS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{14}\text{ClN}_2$ ($[\text{M}+\text{H}]^+$) 269.0840, found 269.0843

2-morpholinobenzo[d]oxazole (10)



From 2-chlorobenzoxazole (CAS-615-18-9) and morpholine (CAS-110-91-8), neat conditions - A gradient of solvent was used for the purification: acetonitrile/water from 31% to 40% over 25 min to yield after evaporation a beige solid (12.1 mg, 59%). NMR-yield (n=2, 58/60%).

The spectral data are consistent with those reported in the literature.⁴

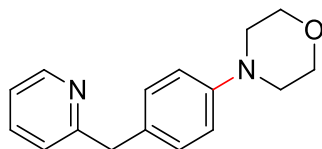
¹H NMR (500 MHz, Chloroform-d) δ 7.38 (dd, J = 7.8, 1.2 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.18 (td, J = 7.7, 1.1 Hz, 1H), 7.04 (td, J = 7.8, 1.2 Hz, 1H), 3.85 – 3.79 (m, 4H), 3.69 (dd, J = 5.8, 4.0 Hz, 4H).

¹³C NMR (126 MHz, Chloroform-d) δ 162.09, 148.76, 142.87, 124.09, 120.93, 116.50, 108.83, 66.18, 45.73.

IR (film): ν_{max} 1653, 1576, 1457, 1288, 1240, 1108, 797, 742 cm^{-1} .

HR-MS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$) 205.0972, found 205.0977.

4-(4-(pyridin-2-ylmethyl)phenyl)morpholine (11)



From 2-(4-chlorobenzyl)pyridine (CAS-4350-41-8) and morpholine (CAS-110-91-8), neat conditions - A gradient of solvent was used for the purification: acetonitrile/water from 11% to 20% over 25 min to yield after evaporation a yellow oil (17.3 mg, 63%). NMR-yield (n=2, 83/92%).

The spectral data are consistent with those reported in the literature.⁴

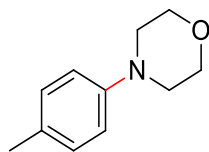
¹H NMR (500 MHz, Chloroform-d) δ 8.54 (d, $J = 4.9$ Hz, 1H), 7.56 (td, $J = 7.7, 1.9$ Hz, 1H), 7.17 (d, $J = 8.2$ Hz, 2H), 7.09 (dd, $J = 7.5, 3.3$ Hz, 2H), 6.86 (d, $J = 8.3$ Hz, 2H), 4.08 (s, 2H), 3.91 – 3.78 (m, 4H), 3.20 – 3.04 (m, 4H).

¹³C NMR (126 MHz, Chloroform-d) δ 161.59, 149.97, 149.33, 136.64, 131.13, 129.96, 123.15, 121.27, 116.10, 67.07, 49.64, 43.92.

IR (film): ν_{max} 1513, 1233, 1118, 925, 804, 749, 597 cm^{-1} .

HR-MS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$) 255.1492, found 255.1494.

4-(p-tolyl)morpholine (12)



From 4-bromotoluene (CAS-106-38-7) and morpholine (CAS-110-91-8), neat conditions - A gradient of solvent was used for the purification: acetonitrile/water from 31% to 40% over 25min to yield after evaporation a yellow solid (16.5 mg, 93%). NMR-yield (n=2, 91/95%).

The spectral data are consistent with those reported in the literature.⁴

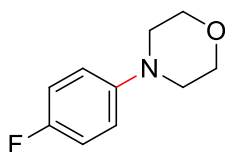
¹H NMR (500 MHz, Chloroform-d) δ 7.12 – 7.06 (m, 2H), 6.87 – 6.80 (m, 2H), 3.88 – 3.83 (m, 4H), 3.13 – 3.08 (m, 4H), 2.27 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 149.31, 129.83, 116.19, 67.11, 50.10, 20.55.

IR (film): ν_{max} 1510, 1451, 1226, 1115, 1047, 921, 818, 607 cm^{-1} .

HR-MS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{16}\text{NO}$ ($[\text{M}+\text{H}]^+$) 178.1227, found 178.1232.

4-(4-fluorophenyl)morpholine (**13**)



From 4-bromofluorobenzene (CAS-460-00-4) and morpholine (CAS-110-91-8), neat conditions - A gradient of solvent was used for the purification: acetonitrile/water from 31% to 40% over 25 min to yield after evaporation a yellow solid (13.4 mg, 74%). NMR-yield (n=2, 89/89%).

The spectral data are consistent with those reported in the literature.⁴

¹H NMR (500 MHz, Chloroform-d) δ 6.98 (dd, $J = 9.2, 8.2$ Hz, 2H), 6.90 – 6.84 (m, 2H), 3.89 – 3.83 (m, 4H), 3.11 – 3.05 (m, 4H).

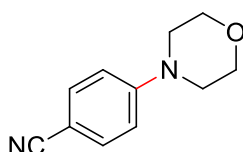
¹⁹F NMR (471 MHz, Chloroform-d) δ -123.98 – -124.52 (m).

¹³C NMR (126 MHz, Chloroform-d) δ 157.39 ($J = 238.9$ Hz), 148.01 ($J = 2.7$ Hz), 117.55 ($J = 7.6$ Hz), 115.68 ($J = 21.98$ Hz), 66.98, 50.40.

IR (film): ν_{max} 1505, 1221, 1116, 920, 842, 814, 707, 536 cm^{-1} .

HR-MS (ESI) m/z calcd. for $\text{C}_{10}\text{H}_{13}\text{FNO}$ ($[\text{M}+\text{H}]^+$) 182.0976, found 182.0982.

4-morpholinobenzonitrile (**14**)



From 4-chlorobenzonitrile (CAS-623-03-0) and morpholine (CAS-110-91-8), neat conditions - A gradient of solvent was used for the purification: acetonitrile/water from 31% to 40% over 25 min to yield after evaporation a white solid (7.6 mg, 40%). NMR-yield (n=2, 49/55%).

The spectral data are consistent with those reported in the literature.⁴

¹H NMR (500 MHz, Chloroform-d) δ 7.55 – 7.49 (m, 2H), 6.89 – 6.83 (m, 2H), 3.88 – 3.82 (m, 4H), 3.31 – 3.25 (m, 4H).

¹³C NMR (126 MHz, Chloroform-d) δ 153.62, 133.65, 119.97, 114.22, 101.15, 66.58, 47.46.

IR (film): ν_{max} 2215, 1603, 1515, 1243, 1179, 1112, 926, 833, 545 cm^{-1} .

HR-MS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$) 189.1022, found 189.1027.

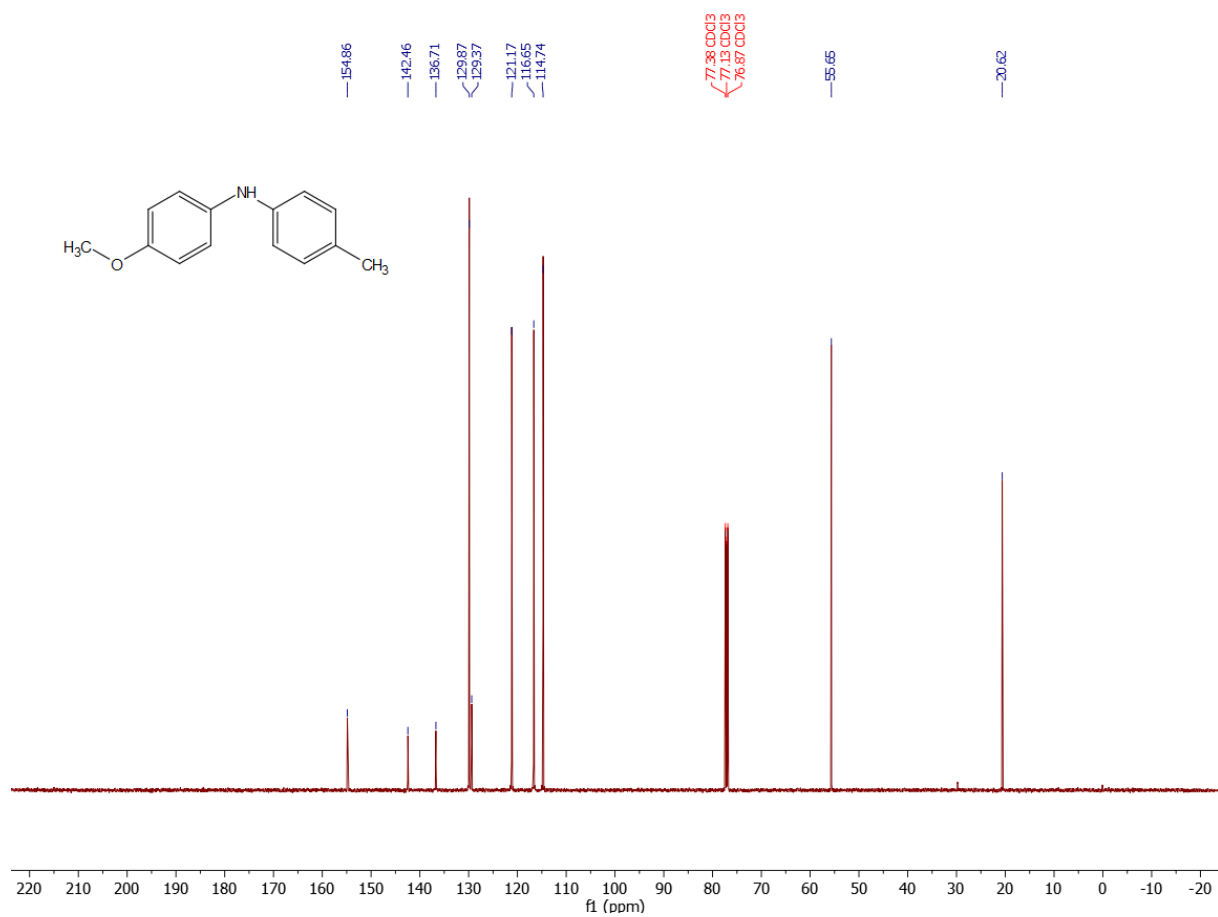
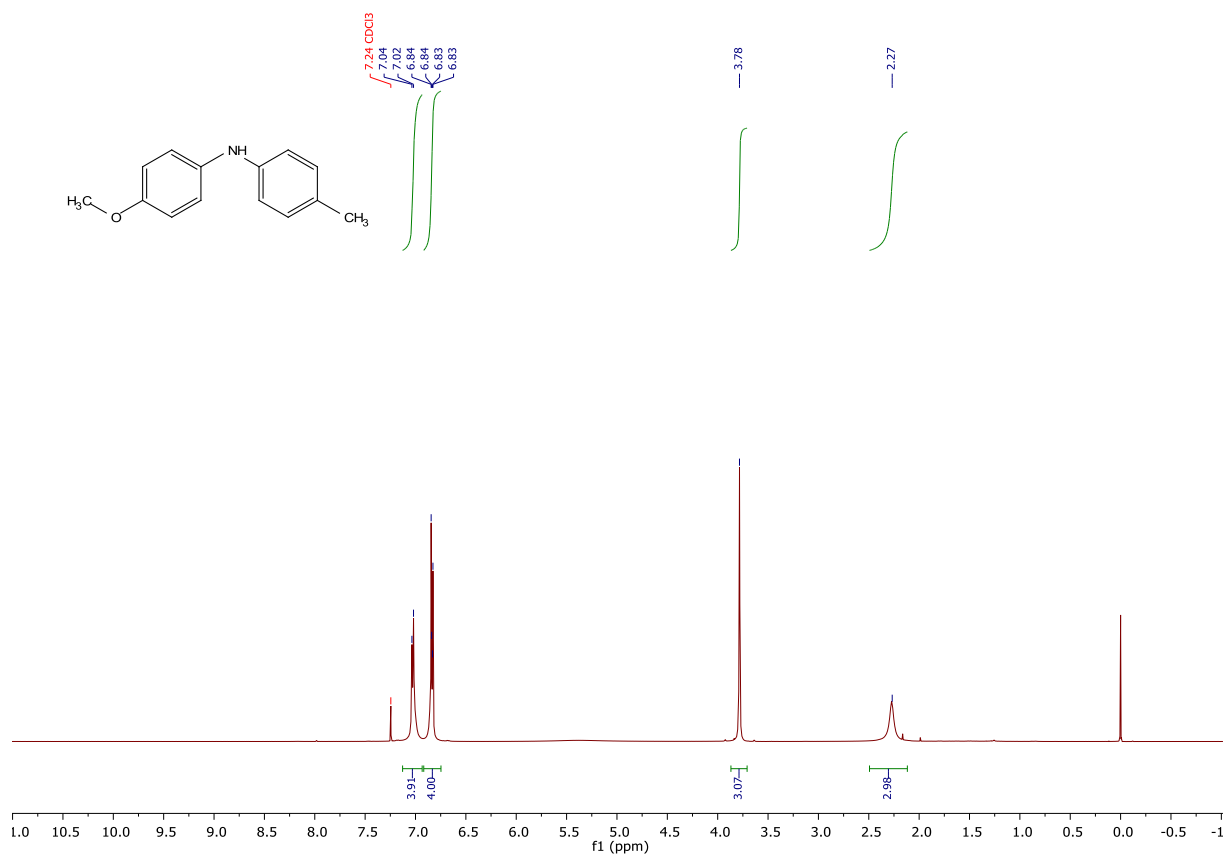
References

- (1) P. Klumphu and B. H. Lipshutz, *J. Org. Chem.* 2014, **79**, 3, 888.
- (2) T. Jin, F. Yang and Y. Yamamoto, *Org. Lett.* 2010, **12**, 388.
- (3) Q.-L. Shao, Z.-J. Jiang and W.-K. Su, *Tetrahedron Letters* 2018, **59**, 2277.
- (4) Q. Cao, W. Nicholson, A. Jones and D. L. Browne, *Org. Biomol. Chem.* 2019, **17**, 1722.

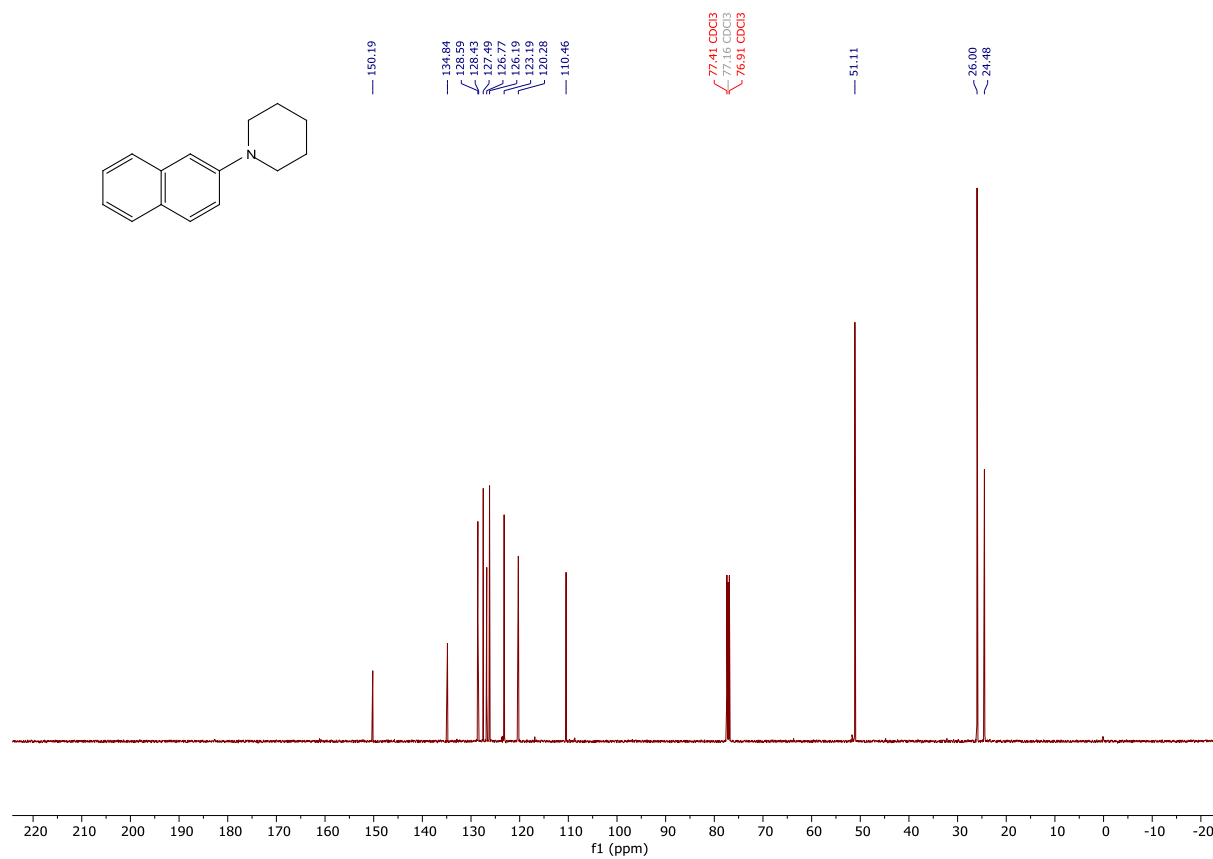
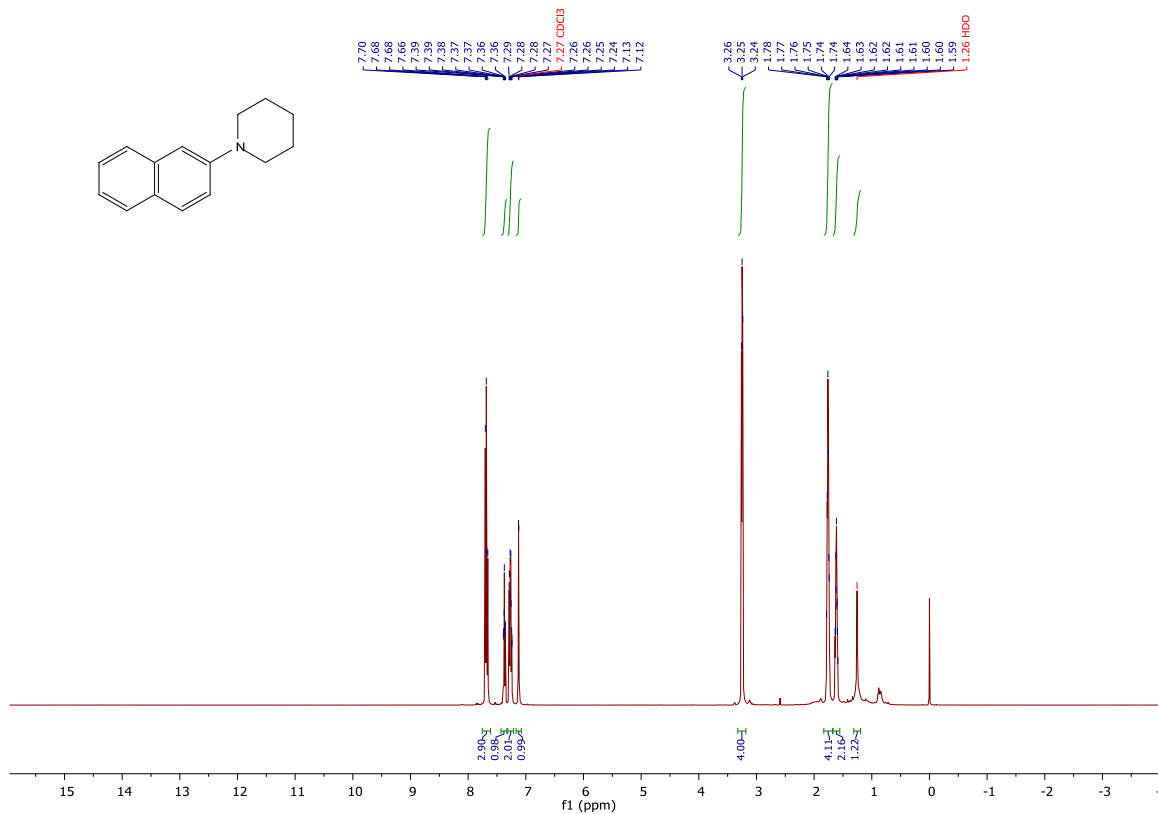
- (5) an isolated yield could not be determined with accuracy because of high volatility of the product (s. also ref. 13 of the manuscript); NMR might contain residual solvents or impurities and NMR-yield is mentioned as surrogate.
- (6) D.-H. Li, X.-B. Lan, A.-X. Song, M. Rahman, C. Xu, F.-D. Huang, R. Szostak, M. Szostak, F.-S. Liu, *Chem. Eur. J.* 2022, **28**, e2021033: “our” compound **5** is compound **3i** in the publication: ^1H NMR (400 MHz, Chloroform-d) δ 7.27 – 7.21 (m, 2H), 6.94 (ddd, J = 3.7, 1.8, 0.8 Hz, 3H), 6.90 – 6.85 (m, 2H), 6.64 (dd, J = 3.6, 1.4 Hz, 1H), 3.32 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-d) δ 153.6, 149.2, 128.9, 125.7, 119.9, 119.5, 118.7, 116.2, 42.0. Because of the low amount isolated⁵ and the subsequent low signal to noise ratio we cannot report own ^{13}C -NMR data.

4. Copies of ^1H and ^{13}C NMR spectra

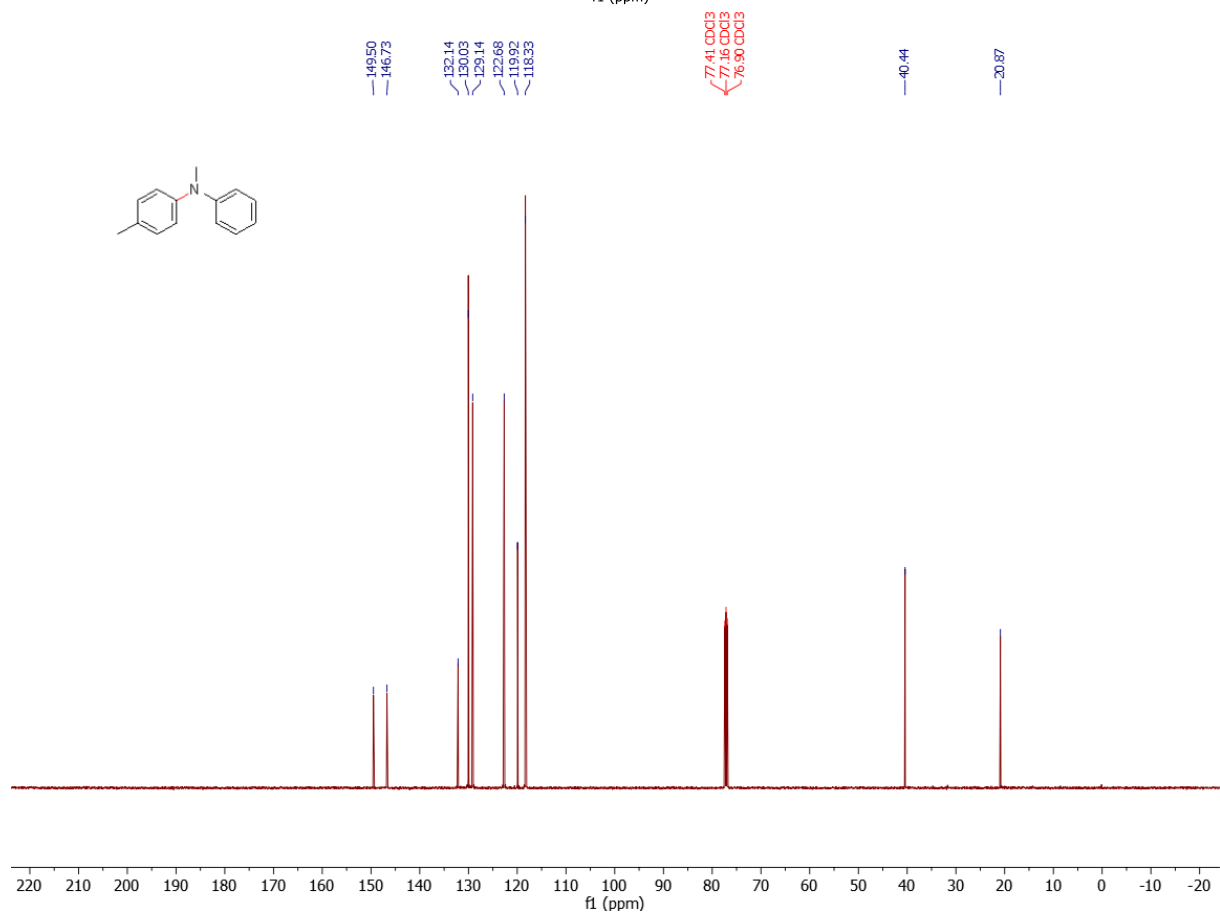
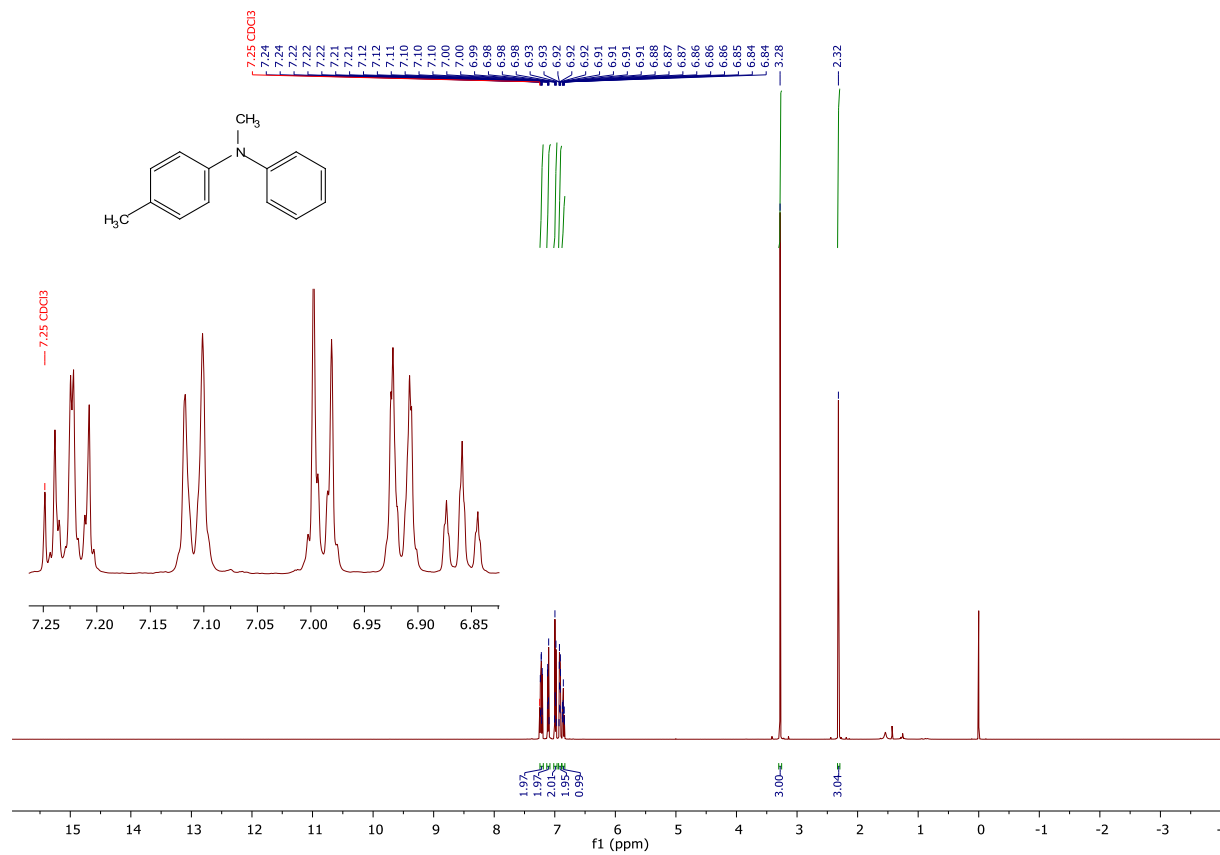
^1H NMR and ^{13}C NMR 4-Methoxy-N-p-tolylaniline (**1**)



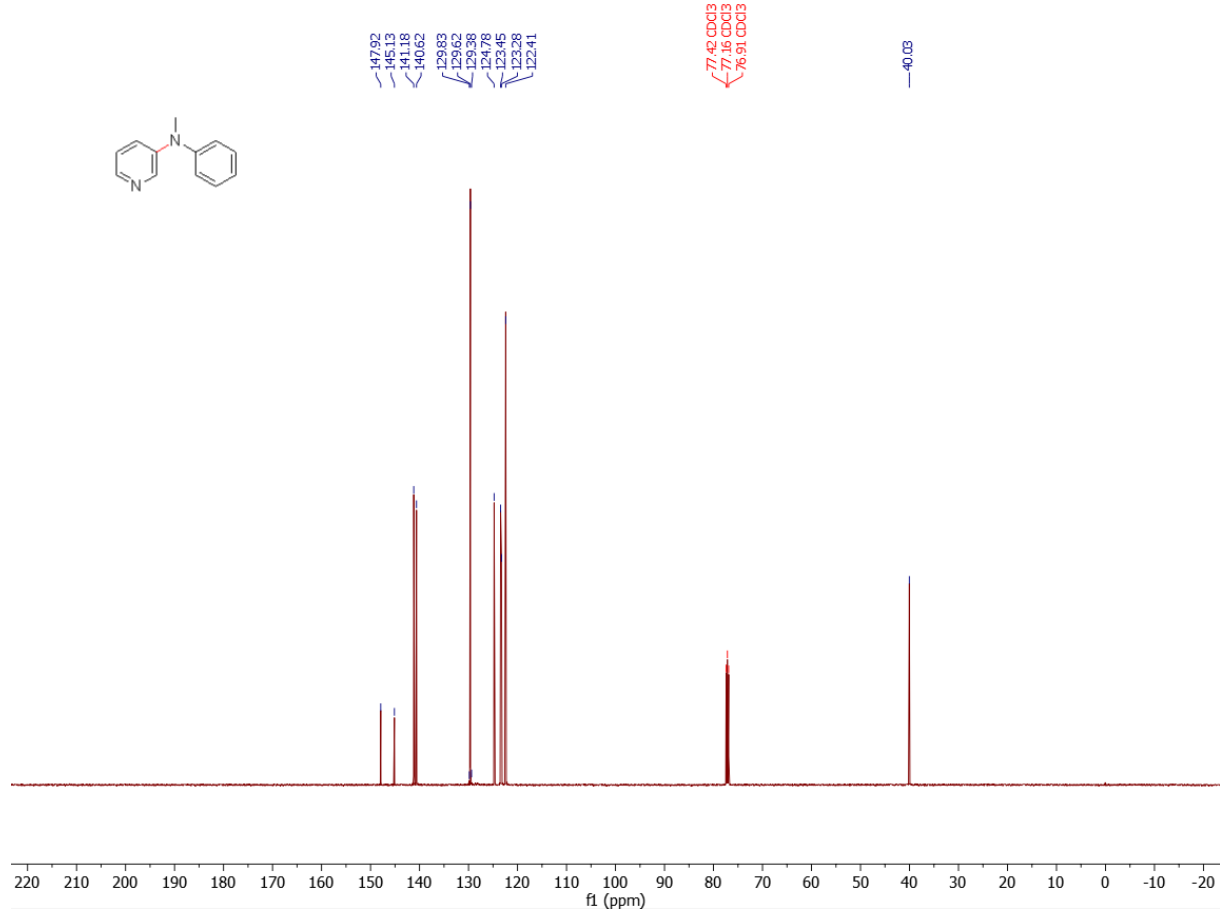
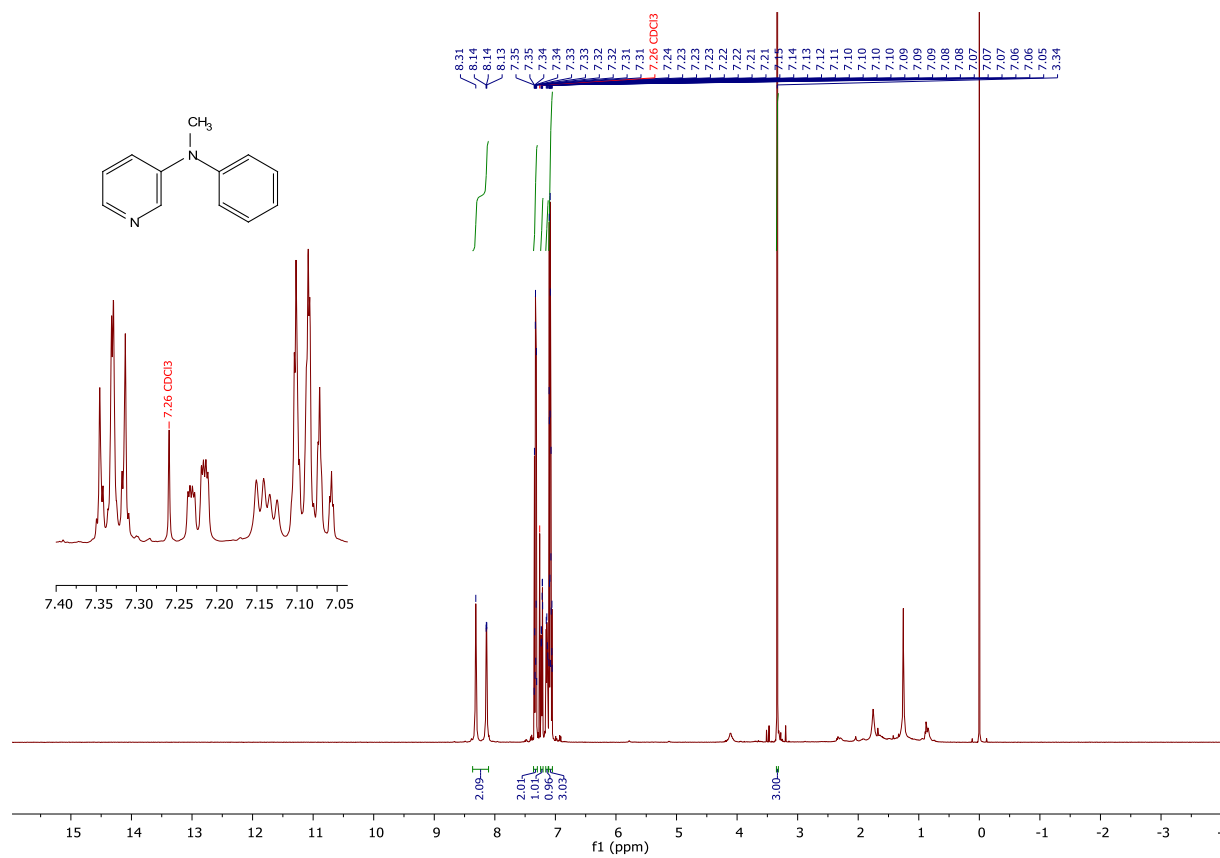
¹H NMR and ¹³C NMR 1-Naphthalen-2-yl-piperidine (**2**)⁵



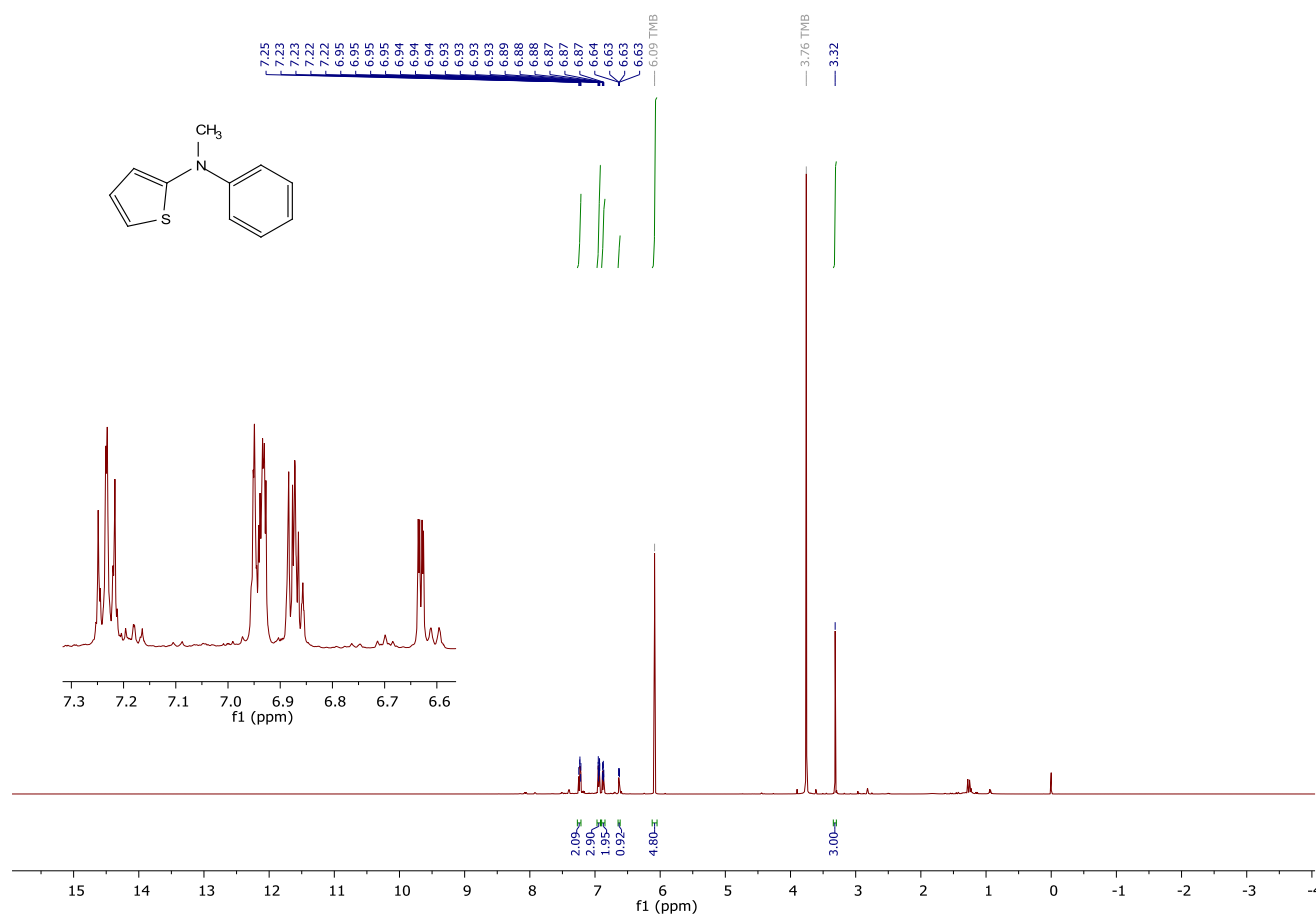
^1H NMR and ^{13}C NMR *N*,4-dimethyl-*N*-phenylaniline (**3**)⁵



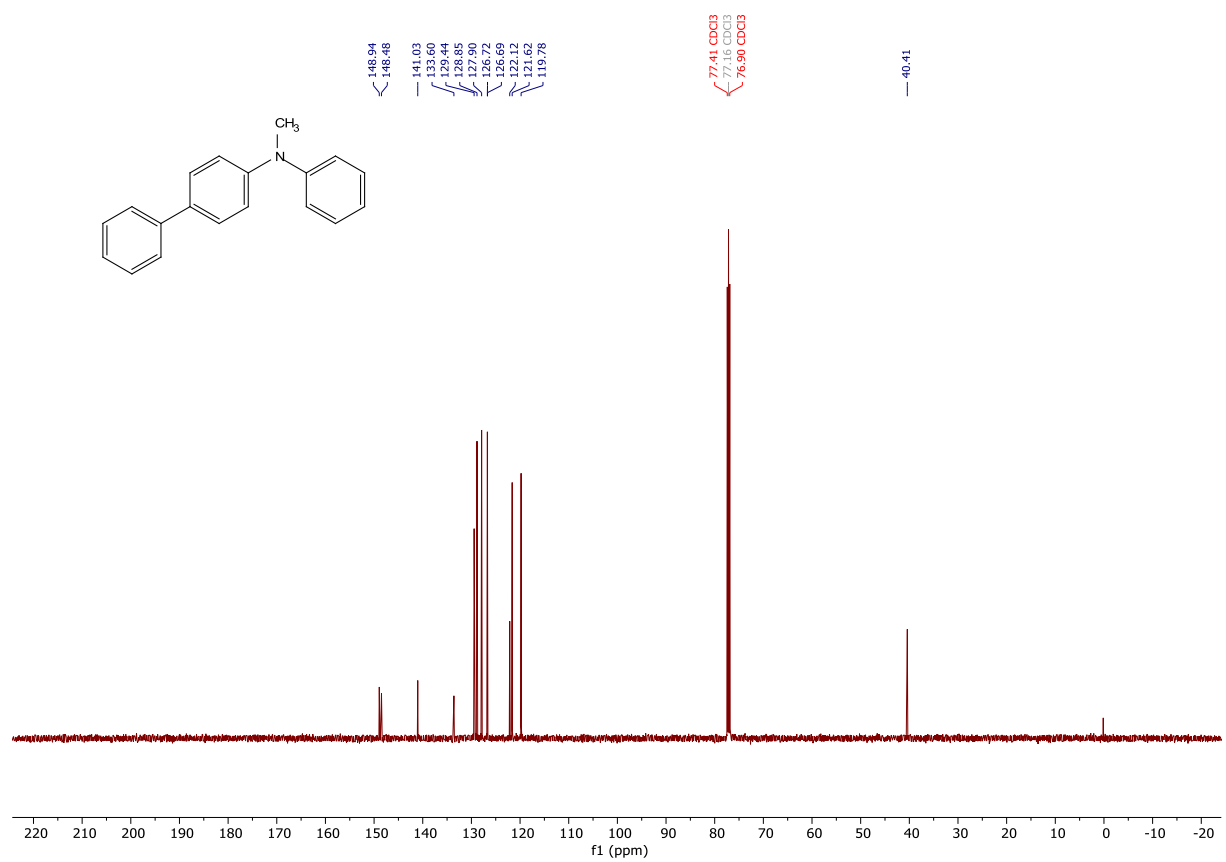
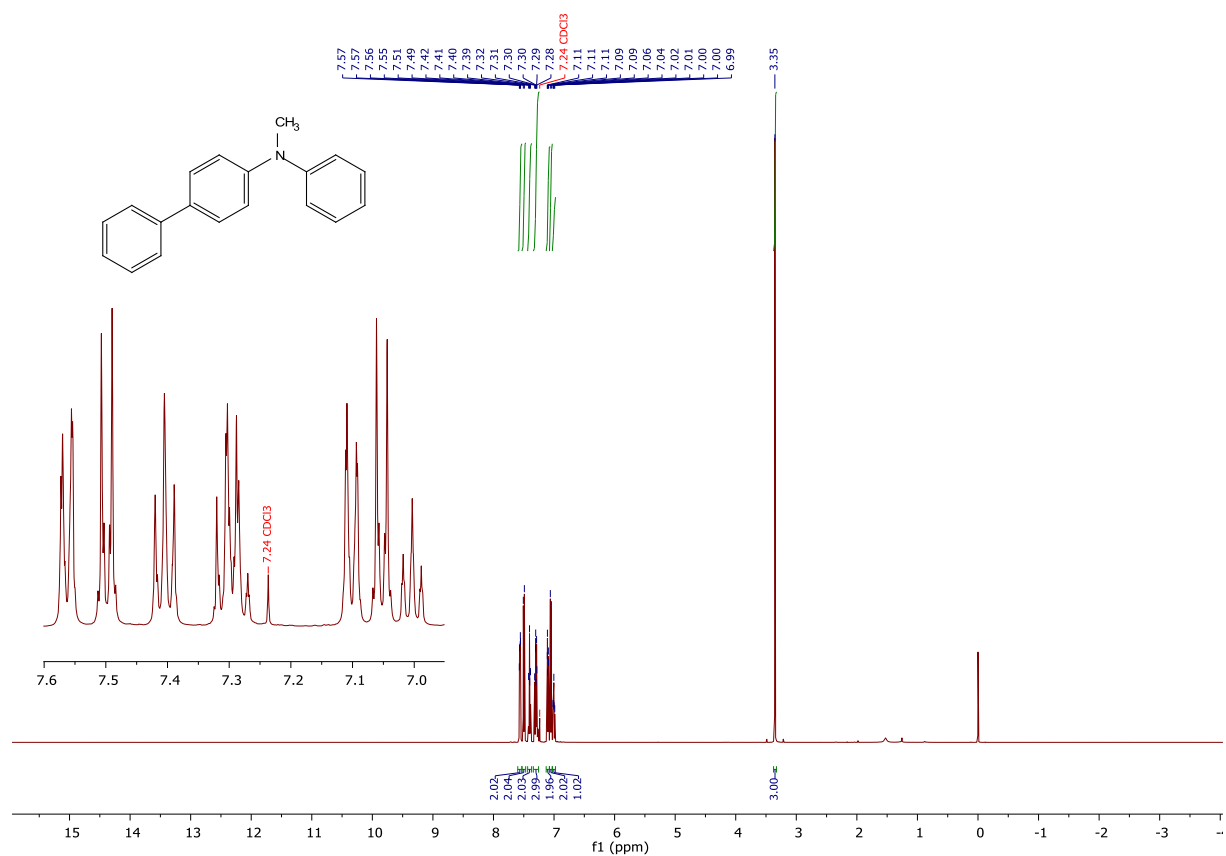
¹H NMR and ¹³C NMR *N*-methyl-*N*-phenylpyridin-3-amine (**4**)⁵



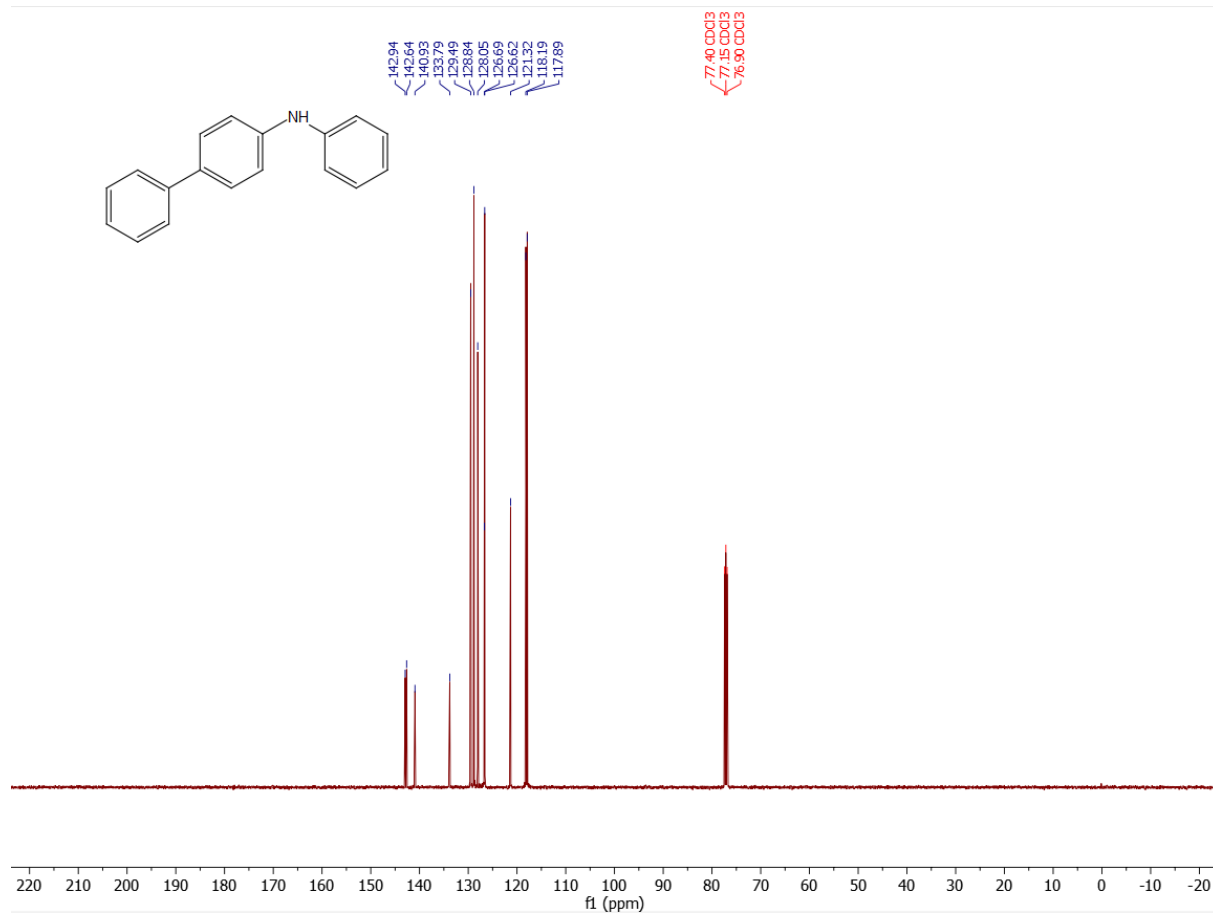
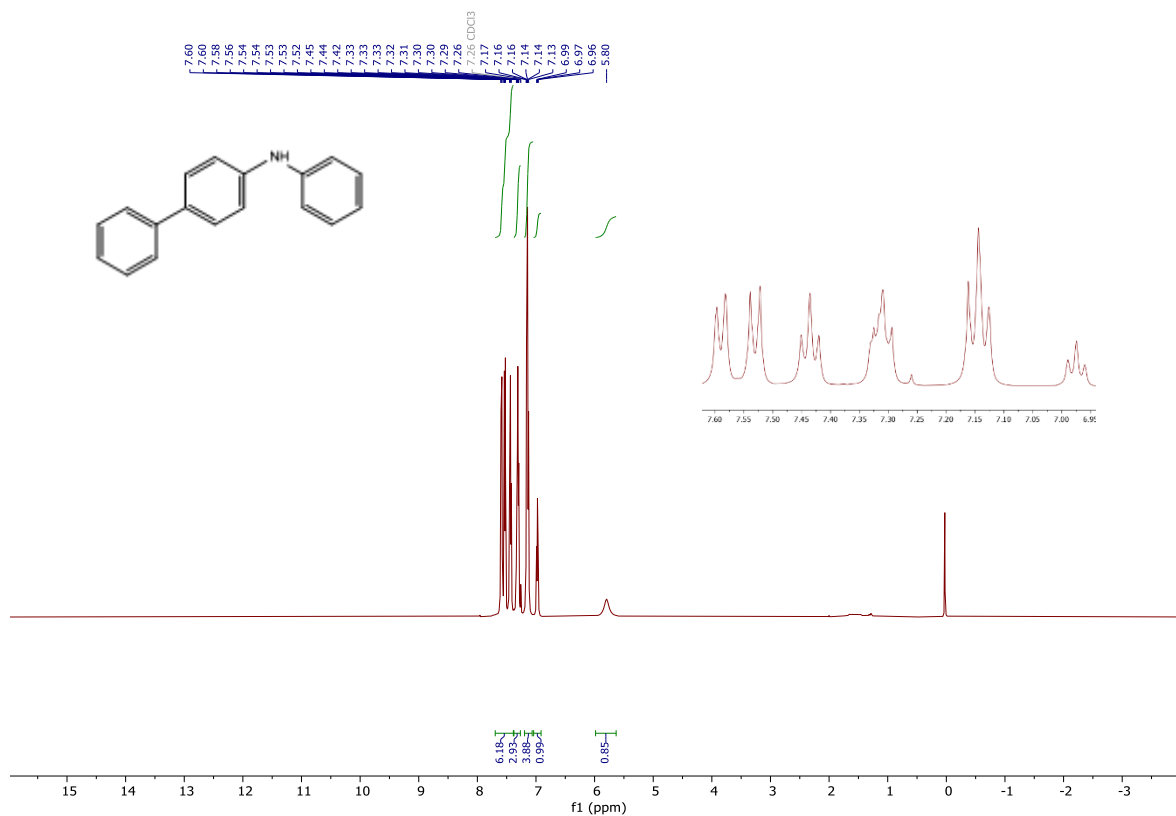
¹H NMR *N*-methyl-*N*-phenylthiophen-2-amine (**5**)^{5,6}



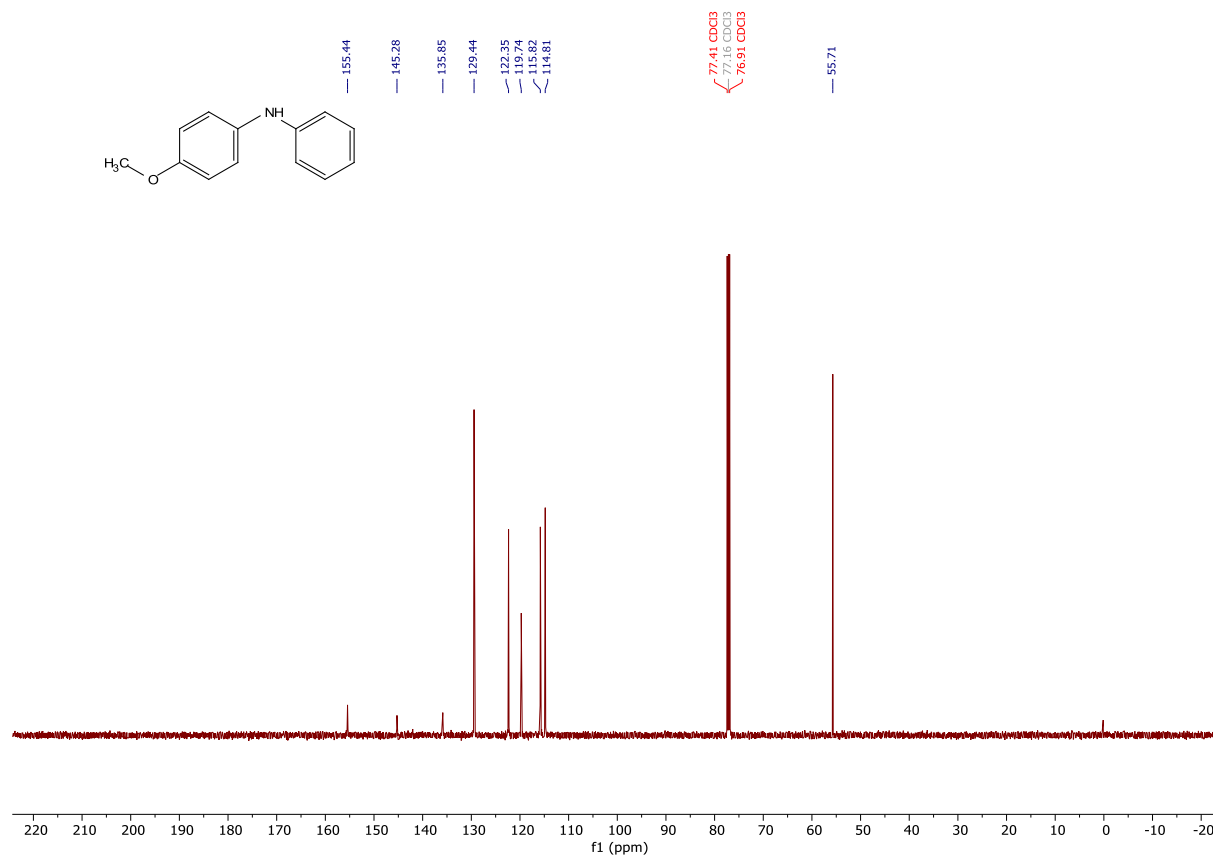
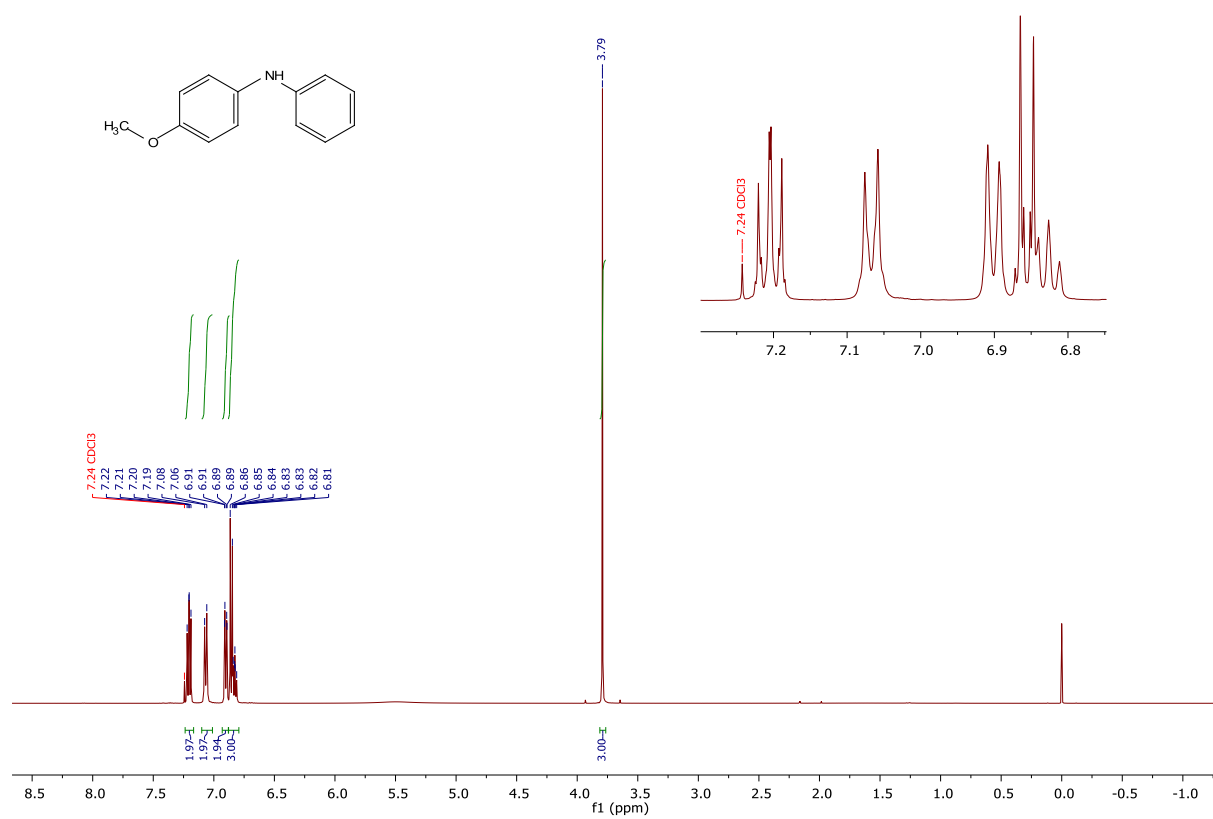
¹H NMR and ¹³C NMR *N*-methyl-*N*-phenylbiphenyl-4-amine (6)



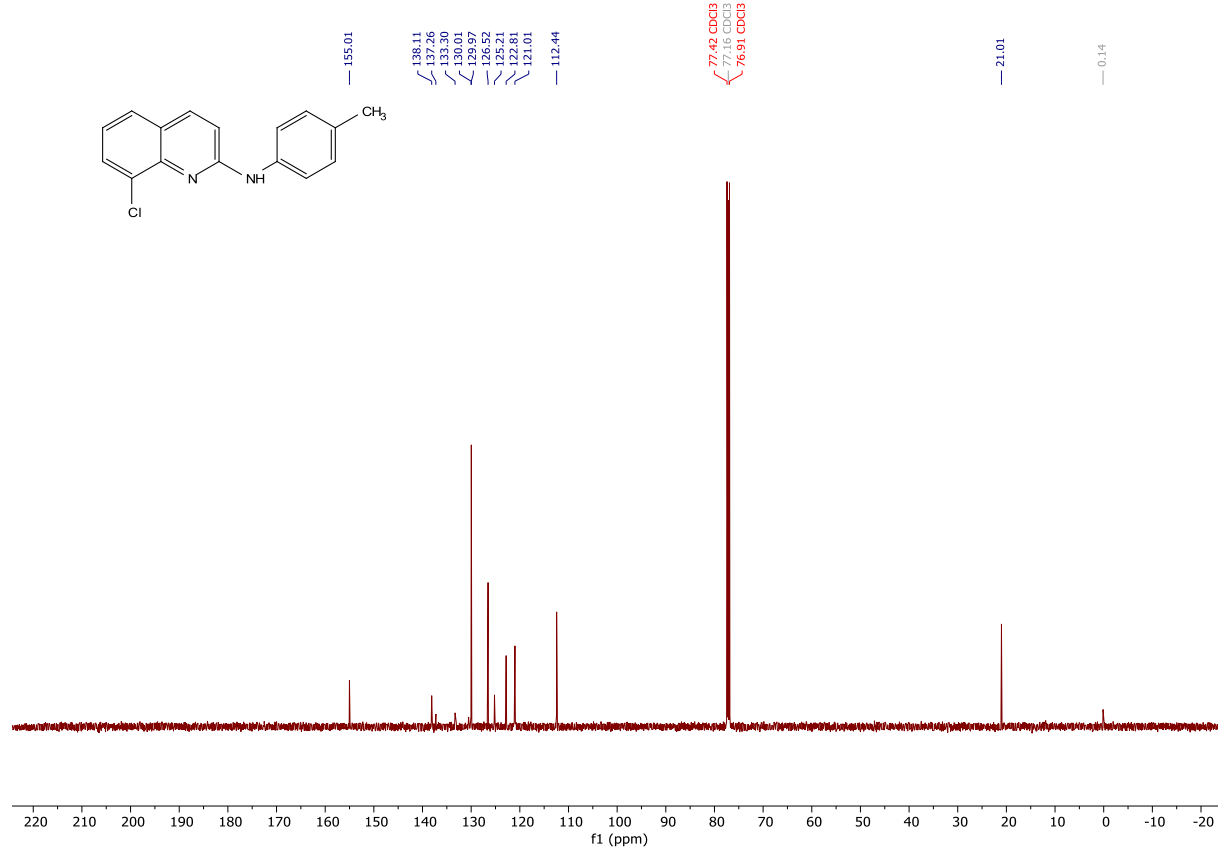
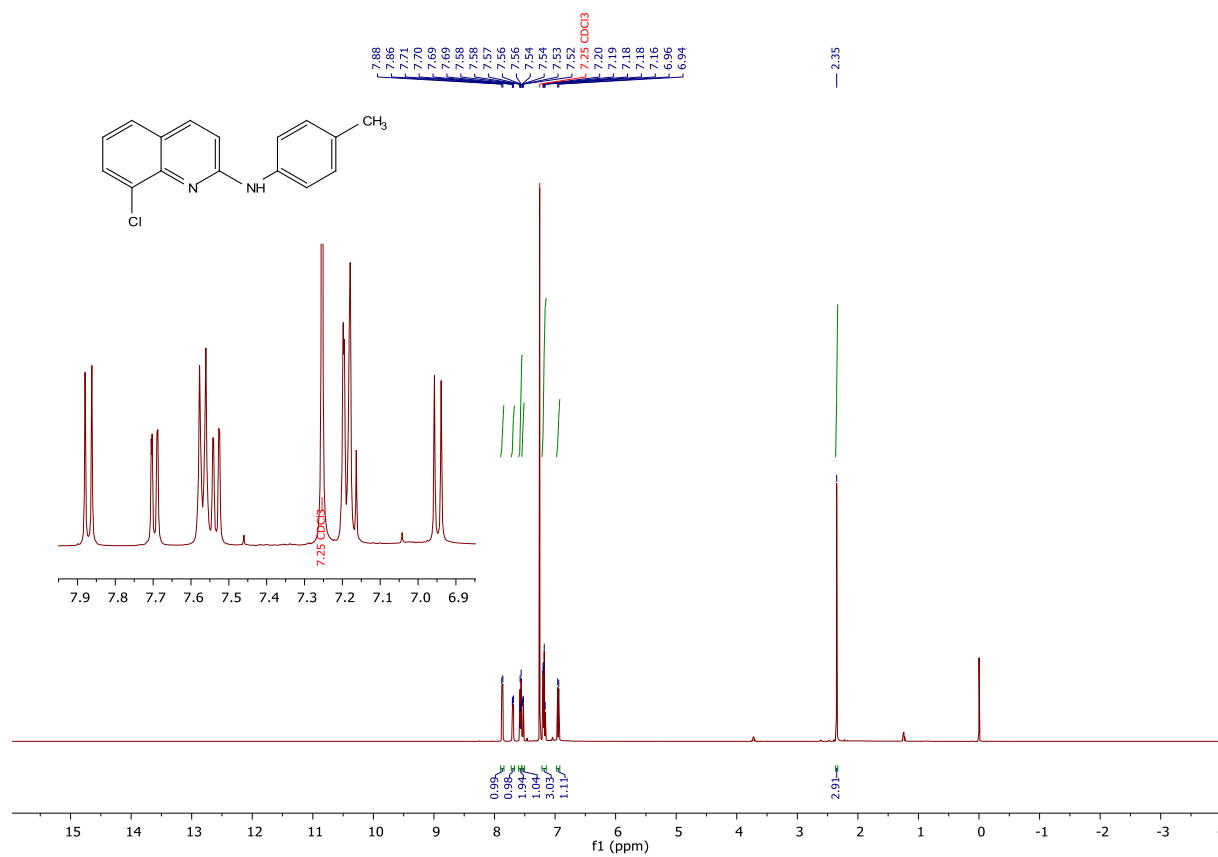
¹H NMR and ¹³C NMR *N*-phenylbiphenyl-4-amine (7)



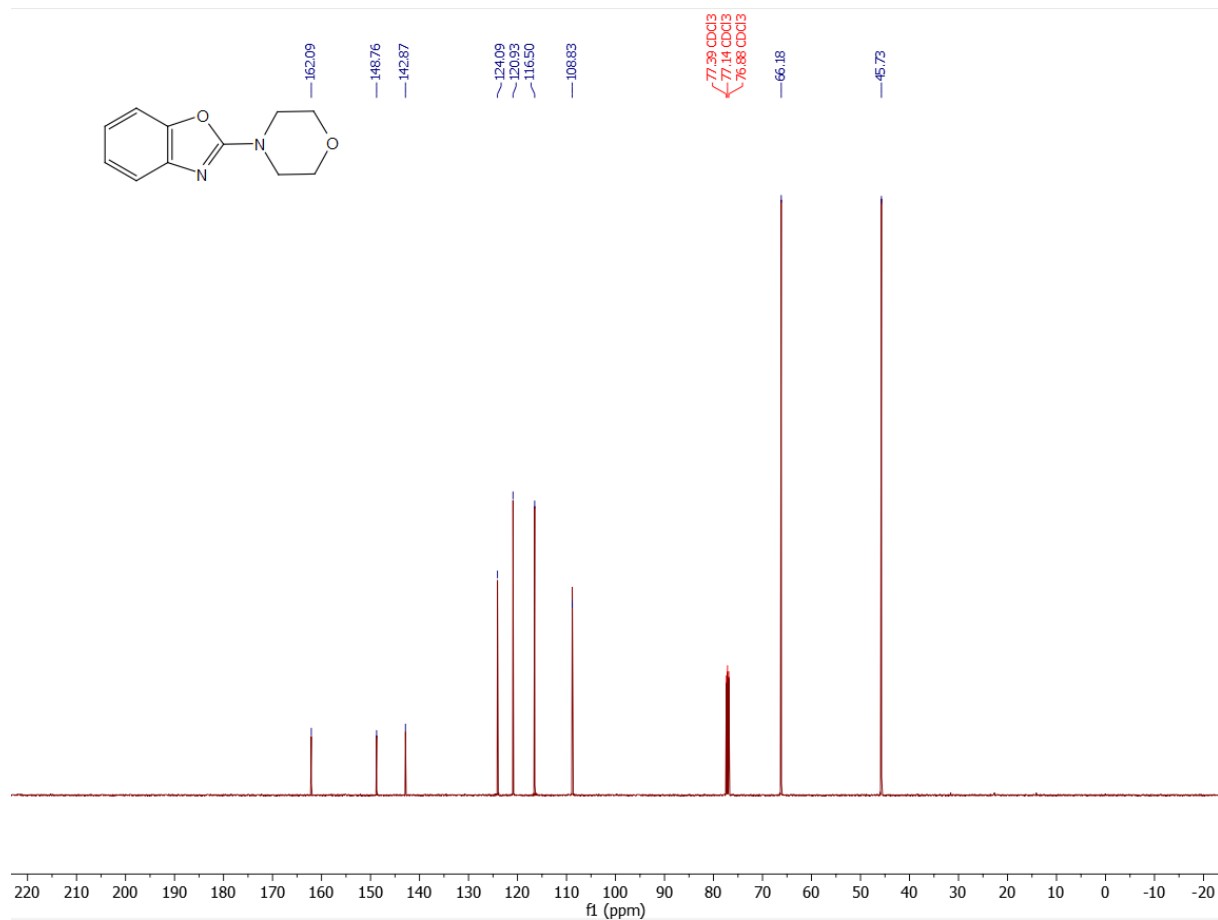
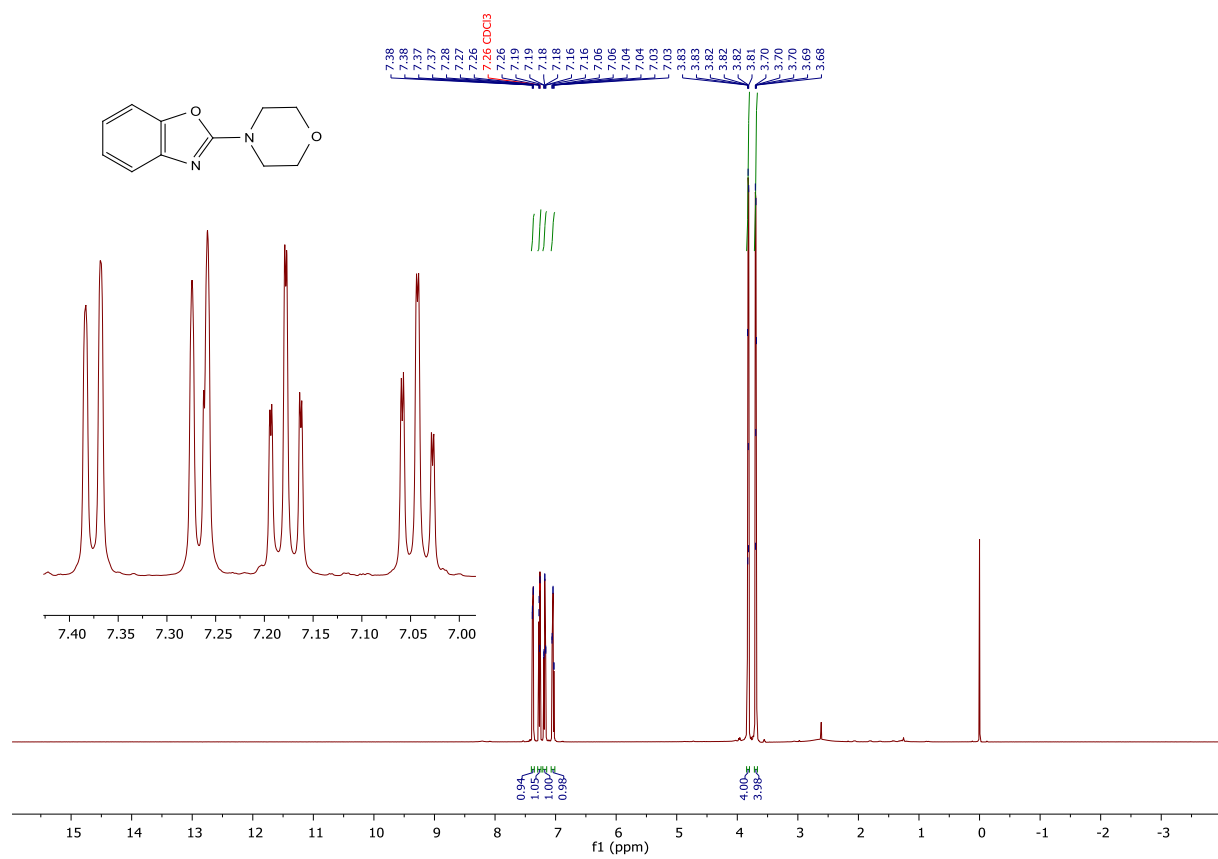
¹H NMR and ¹³C NMR 4-methoxy-N-phenylaniline (**8**)



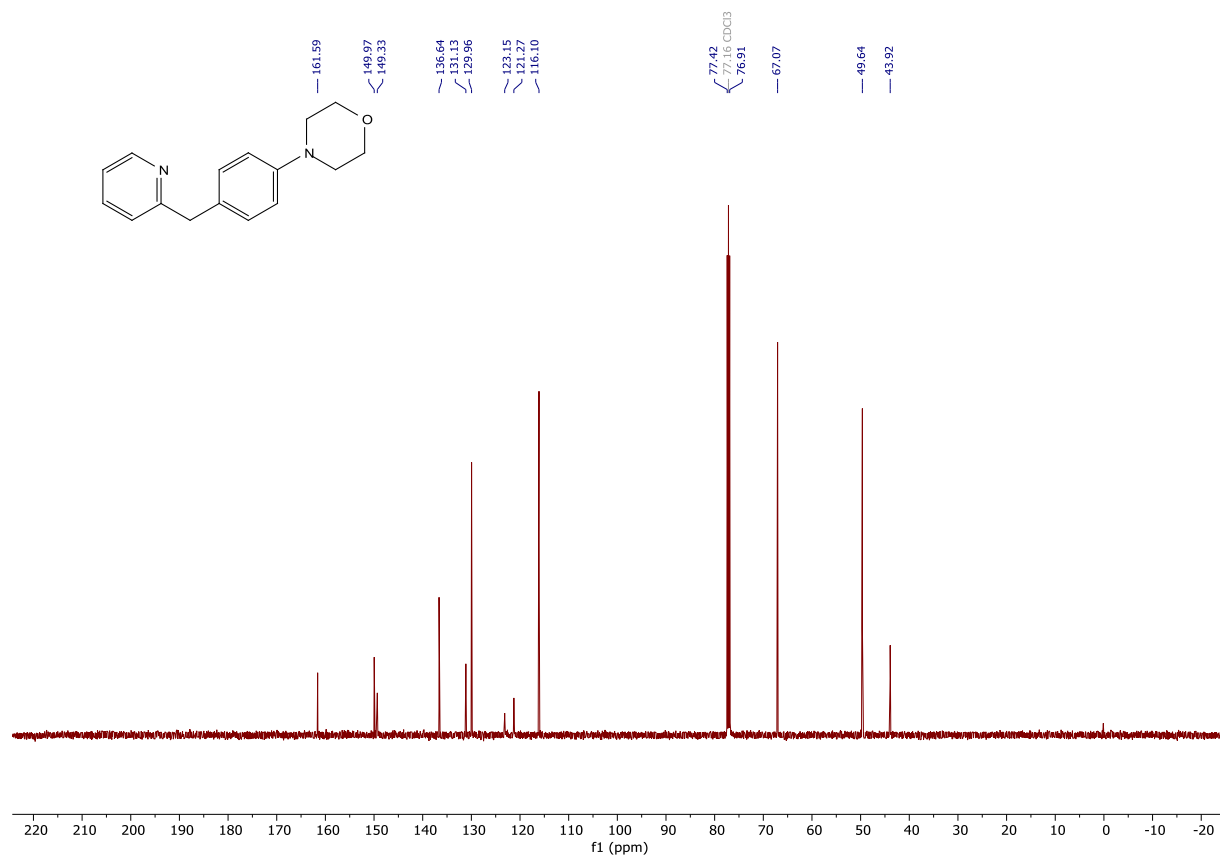
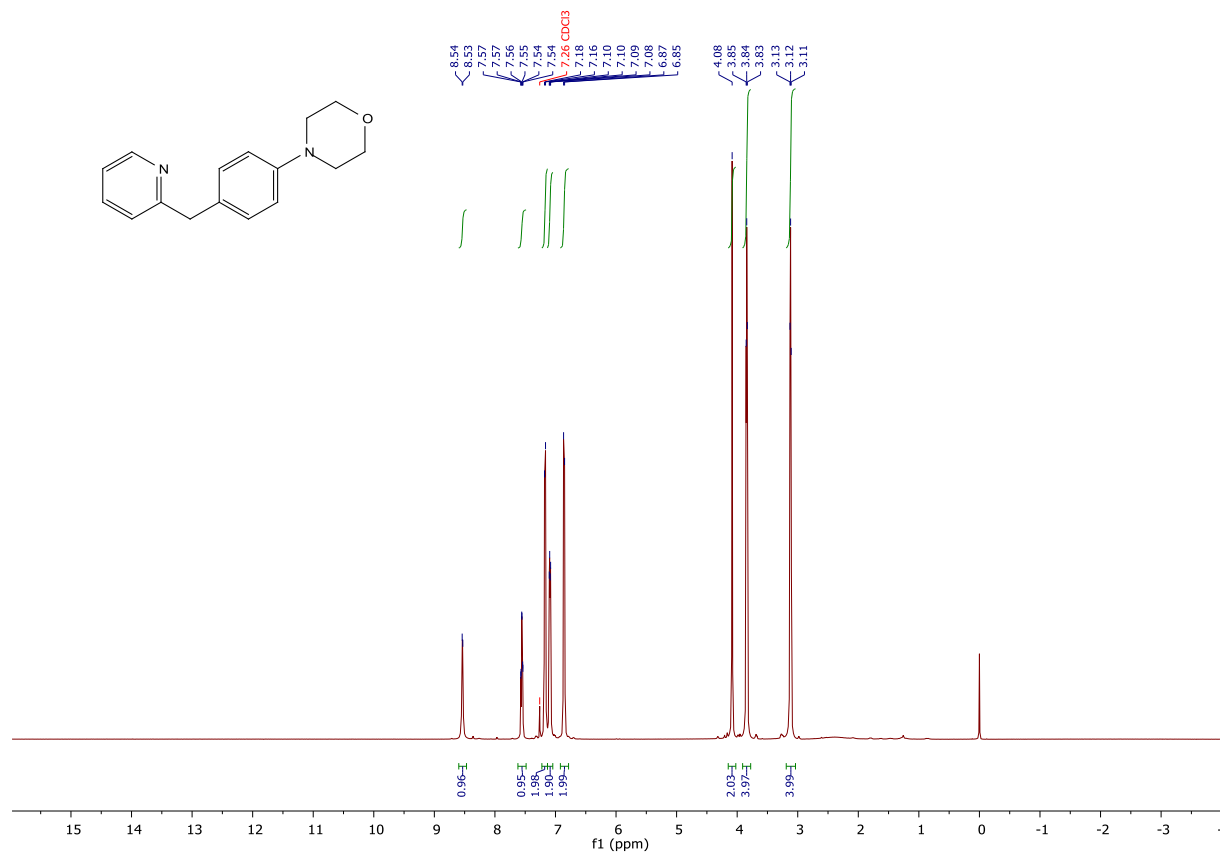
^1H NMR and ^{13}C NMR 8-chloro-N-p-tolylquinolin-2-amine (9)



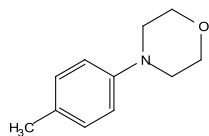
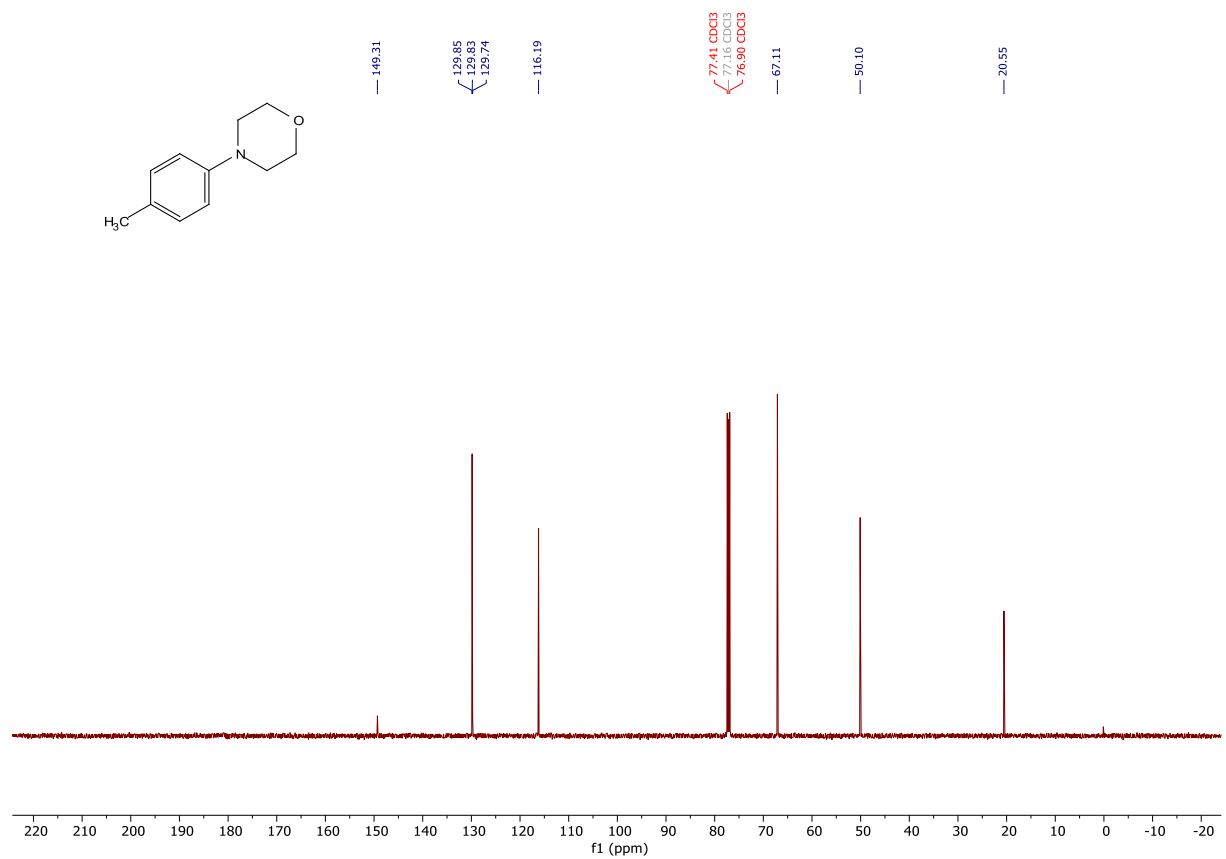
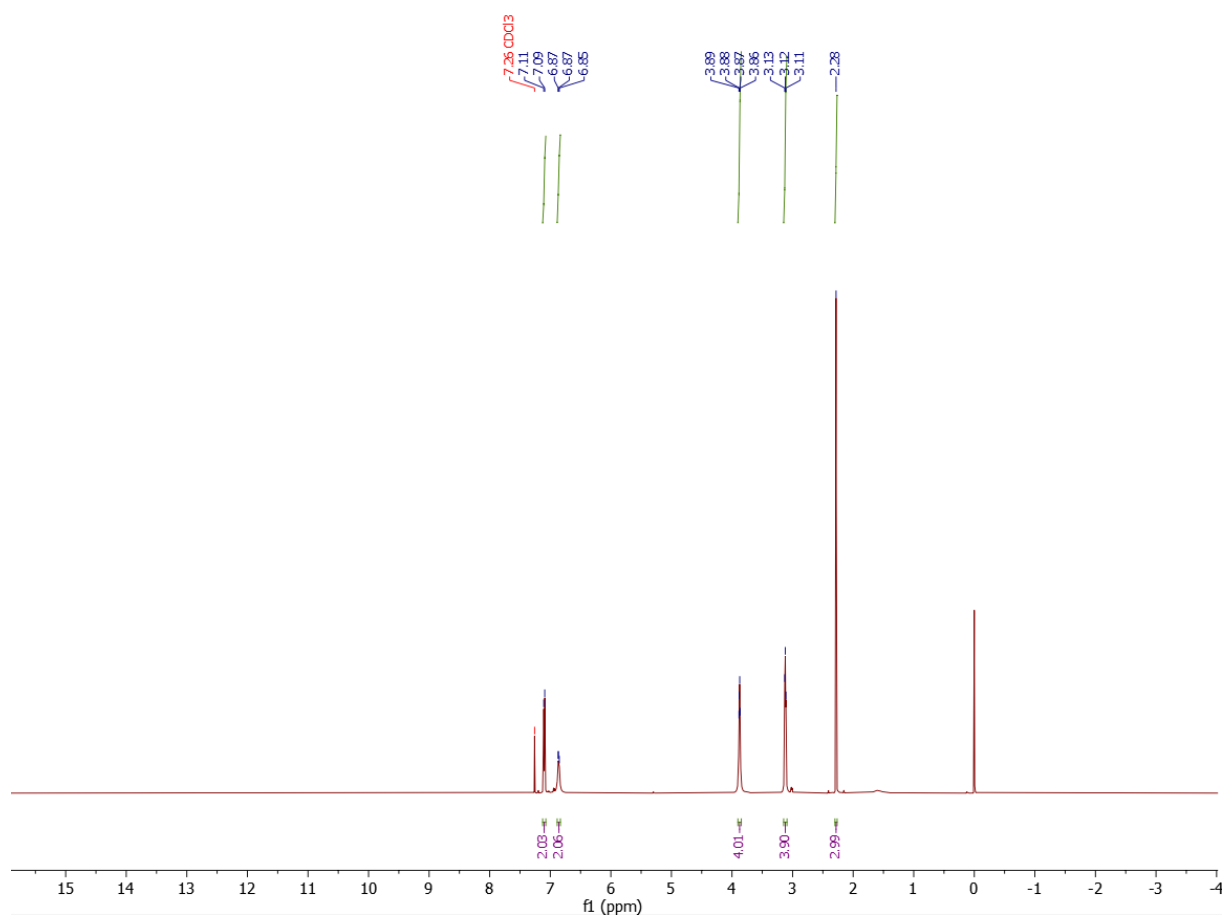
¹H NMR and ¹³C NMR 2-morpholinobenzo[d]oxazole (10)



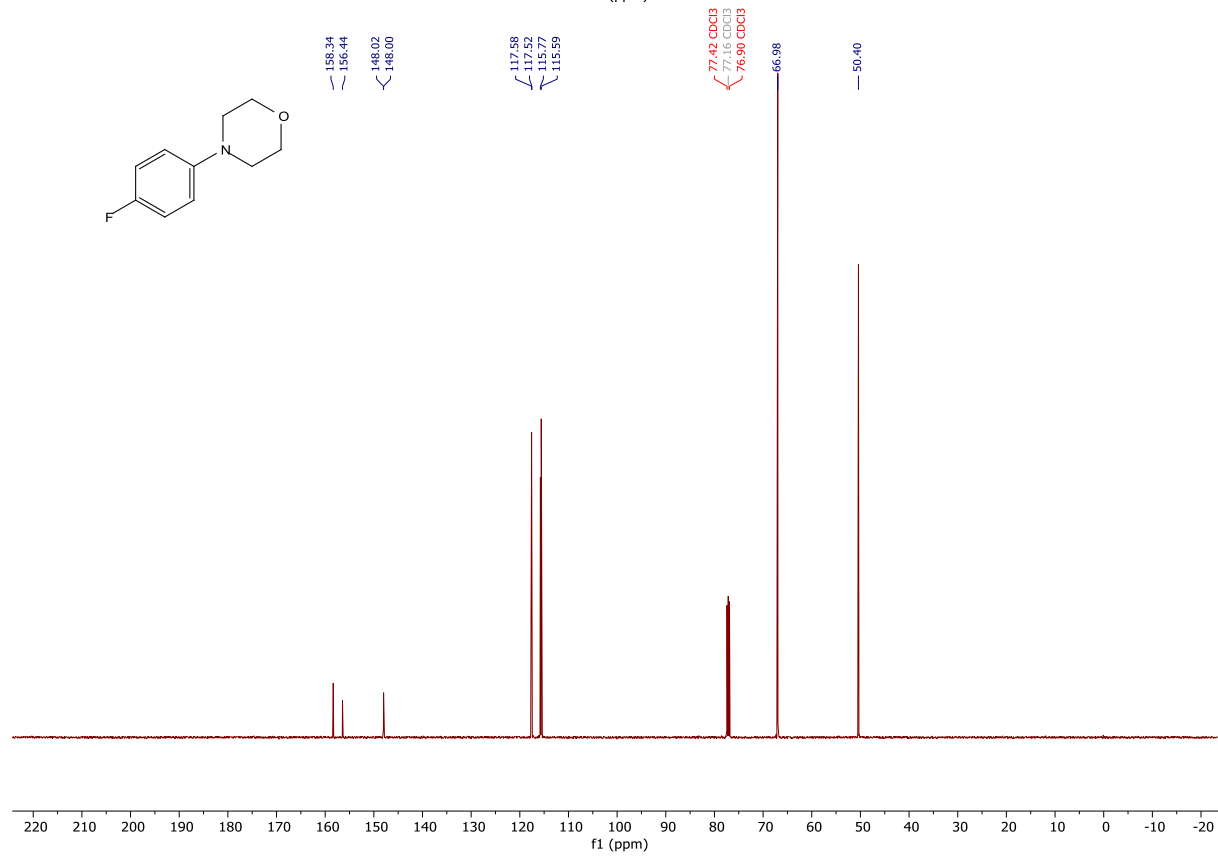
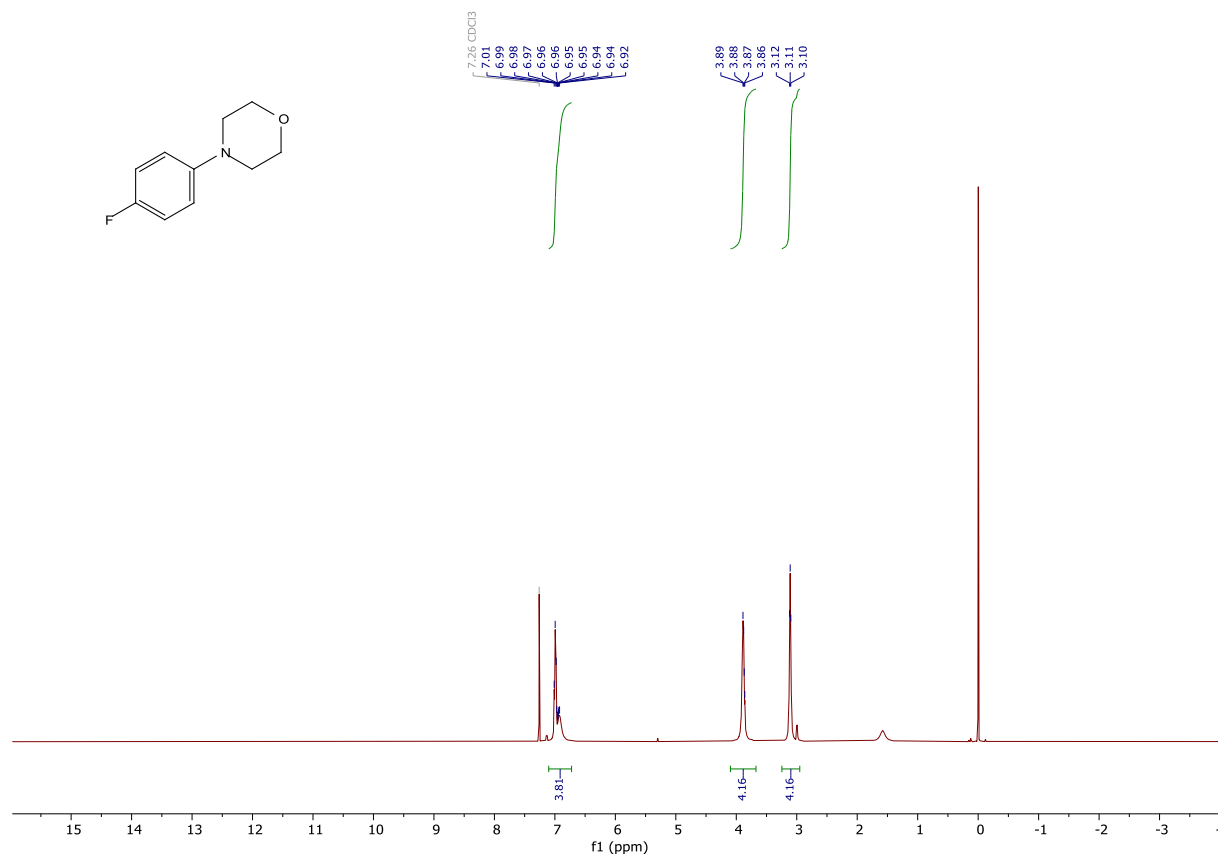
¹H NMR and ¹³C NMR 4-(4-(pyridin-2-ylmethyl)phenyl)morpholine (11)



¹H NMR and ¹³C NMR 4-(*p*-tolyl)morpholine (**12**)



¹H NMR and ¹³C NMR 4-(4-fluorophenyl)morpholine (13)



¹H NMR and ¹³C NMR 4-morpholinobenzonitrile (**14**)

