

Thermally activated (NHC)NiCp₂ precatalysts for the cross-coupling of amines with aryl chlorides

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S1. General information and materials

General Procedures. Solvents were purified and dried according to standard methods and stored over activated 3Å molecular sieves prior to use. Column chromatography was conducted on silica gel 60 (230–400 mesh, Merck). Glassware was dried at 120 °C in an oven for at least 3 h before the use.

Instrumentation. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance NEO 300 spectrometer at 300 MHz for ¹H and 75 MHz for ¹³C in CDCl₃. The ¹H and ¹³C NMR chemical shifts are reported relative to the solvent signals as internal standards: δ 7.26 for ¹H, δ 77.2 for ¹³C. Elemental analyses were performed using a Perkin Elmer 2400 elemental analyzer. GC-MS experiments were accomplished using an Agilent 7890A GC instrument equipped with an Agilent 5975C mass-selective detector (electron ionization, 70 eV) and an HP-5MS column (30 m × 0.25 mm × 0.25 μm film) using He as the carrier gas at a flow rate of 1.0 mL min⁻¹.

Materials {1,3-bis[2,6-di(propan-2-yl)phenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(η⁵-cyclopentadienyl)cyclopenta-2,4-dien-1-ylnickel (**1a**),^{S1} [1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene](η⁵-cyclopentadienyl)cyclopenta-2,4-dien-1-ylnickel (**1b**),^{S1} [1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene](η⁵-cyclopentadienyl)cyclopenta-2,4-dien-1-ylnickel (**1c**),^{S1} [7,9-bis(2,4,6-trimethylphenyl)-7,9-dihydro-8*H*-acenaphtho[1,2-*d*]imidazol-8-ylidene](η⁵-cyclopentadienyl)cyclopenta-2,4-dien-1-ylnickel (**1d**),^{S1} (IPr)Ni(acac)₂ (**1e**),^{S2} {1,3-bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(chloro)(η⁵-cyclopentadienyl)nickel (**1f**),^{S3} were synthesized as described in the literature. All other chemicals were purchased from commercial sources.

S2. Experimental procedures and characterization of synthesized compounds

Synthesis products 4a-m, 6a,b

A 2 mL screw-capped glass vial equipped with a magnetic stirring bar was charged in air with Ni/NHC complex **1a** (14 mg, 0.025 mmol), and Bu^tONa (38 mg, 0.4 mmol). Then, the tube was purged with argon and sealed with a screw cap fitted with a septum. A solution of aryl chloride **2a-h** (0.25 mmol) and amine **3a-h**, **5a,b** (0.3 mmol) in *o*-xylene (1 mL) was added to the reaction vial by syringe through the septum. The tube was additionally purged with argon through the septum, placed in a thermostated oil bath and heated at 150 °C with stirring for 16 h. After cooling to room temperature, the mixture was chromatographed on silica gel (eluent – hexane/methylene chloride)

Diphenylamine (4a) Yield 40 mg (96%), yellow oil. ¹H NMR (CDCl₃, 300 MHz): δ 5.70 (s, 1H), 6.92-6.98 (m, 2H), 7.07-7.11 (m, 4H), 7.25-7.31 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 117.9, 121.1, 129.5, 143.2. The spectral characteristics of the product obtained are similar to those described in the literature.^{S4}

4-Methyl-N-phenylaniline (4b) Yield 44 mg (95%, from chlorobenzene and 4-methylaniline), 42 mg (92%, from 1-chloro-4-methylbenzene and aniline), white powder, mp 86–89 °C (lit.^{S5} mp 88–90 °C). ¹H NMR (CDCl₃, 300 MHz): δ 2.30 (s, 3H), 5.13 (s, 1H), 6.85-6.91 (m, 1H), 6.98-7.01 (m, 4H), 7.04-7.10 (m, 2H), 7.20-7.26 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 20.8, 117.0, 119.1, 120.4, 129.4, 130.0, 131.1, 140.4, 144.1. The spectral characteristics of the product obtained are similar to those described in the literature.^{S6}

2,6-Bis(1-methylethyl)-N-phenylbenzenamine (4c) Yield 35 mg (56%), yellow oil. ¹H NMR (CDCl₃, 300 MHz): δ 1.08 (d, *J* = 6.9 Hz, 12H), 3.15 (sept, 2H), 5.05 (s, 1H), 6.40-6.44 (m, 2H), 6.62-6.68 (m, 1H), 7.05-7.10 (m, 2H), 7.15-7.17 (m, 2H), 7.21-7.24 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 24.0, 28.3, 113.1, 117.8, 124.0, 127.4, 129.3, 135.3, 147.7, 148.3. The spectral characteristics of the product obtained are similar to those described in the literature.^{S6}

2,4,6-Trimethyl-N-phenylaniline (4d) Yield 46 mg (87%), yellow oil. ¹H NMR (CDCl₃, 300 MHz): δ 2.18 (s, 6H), 2.31 (s, 3H), 5.09 (s, 1H), 6.48-6.51 (m, 2H), 6.70-6.76 (m, 1H), 6.94-6.95 (m, 2H), 7.12-7.18 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 18.4, 21.1, 113.4, 118.0, 129.3, 135.5, 135.7, 136.1, 146.8. The spectral characteristics of the product obtained are similar to those described in the literature.^{S4}

4-Methoxy-N-phenylaniline (4e) Yield 46 mg (92%, from chlorobenzene and 4-methoxyaniline), 44 mg (89 % from 1-chloro-4-methoxybenzene and aniline), yellow solid. ¹H NMR (CDCl₃, 300 MHz): δ 3.82 (s, 3H), 5.51 (s, 1H), 6.84-6.96 (m, 4H), 7.07-7.13 (m, 2H), 7.19-7.25 (m, 2H), 7.26-7.32 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 55.7, 114.8, 115.9, 119.8, 122.4, 129.5, 135.8, 145.2, 155.5. The spectral characteristics of the product obtained are similar to those described in the literature.^{S7}

2,4-Dimethoxy-N-phenylaniline (4f) Yield 48 mg (83%), colorless oil. ¹H NMR (CDCl₃, 300 MHz): δ 3.81 (s, 3H), 3.84 (s, 3H), 5.75 (s, 1H), 6.45 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.54 (d, *J* = 2.7 Hz, 1H), 6.83-6.88 (m, 1H), 6.98-7.06 (m, 2H), 7.18-7.24 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 55.8, 55.8, 99.6, 103.9, 116.6, 119.0, 120.0, 125.9, 129.3, 144.7, 151.1, 155.2. The spectral characteristics of the product obtained are similar to those described in the literature.^{S8}

N-Phenyl-1H-indol (4g) Yield 40 mg (82%), pink powder, mp 61–63 °C (lit.^{S9} mp 60–61 °C). ¹H NMR (CDCl₃, 300 MHz): δ 6.69-6.70 (m, 1H), 7.15-7.24 (m, 2H), 7.35-7.39 (m, 2H), 7.50-7.53 (m, 4H), 7.52-7.60 (m, 1H), 7.68-7.72 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 103.7, 110.6, 120.5, 121.3,

122.5, 124.5, 126.6, 128.1, 129.4, 129.7, 136.0, 140.0. The spectral characteristics of the product obtained are similar to those described in the literature.^{S10}

N-Phenyl-9H-carbazole (4h) Yield 48 mg (79%), white powder, mp 89–91 °C (lit.^{S11} mp 90–91 °C). ¹H NMR (CDCl₃, 300 MHz): δ 7.27-7.34 (m, 2H), 7.42-7.50 (m, 5H), 7.57-7.65 (m, 4H), 8.15-8.18 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 109.9, 120.0, 120.4, 123.5, 126.1, 127.3, 127.6, 130.0, 137.9, 141.0. The spectral characteristics of the product obtained are similar to those described in the literature.^{S11}

3-Methyl-N-phenylaniline (4i) Yield 38 mg (84%), yellow oil. ¹H NMR (CDCl₃, 300 MHz): δ 2.28 (s, 3H), 5.61 (s, 1H), 6.71-6.74 (m, 1H), 6.84-6.92 (m, 3H), 7.02-7.05 (m, 2H), 7.10-7.15 (m, 1H), 7.20-7.26 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 21.7, 115.1, 118.0, 118.6, 121.0, 122.0, 129.3, 129.4, 139.3, 143.2, 143.4. The spectral characteristics of the product obtained are similar to those described in the literature.^{S12}

4-Fluoro-N-phenylaniline (4j) Yield 39 mg (83%), yellow oil. ¹H NMR (CDCl₃, 300 MHz): δ 5.58 (s, 1H), 6.90-6.93 (m, 1H), 6.95-7.09 (m, 6H), 7.24-7.30 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 116.05 (d, *J* = 22.5 Hz), 116.9, 120.6, 120.74 (d, *J* = 1.2 Hz), 129.5, 139.06 (d, *J* = 2.5 Hz), 144.1, 158.17 (d, *J* = 240.1 Hz). The spectral characteristics of the product obtained are similar to those described in the literature.^{S13}

2-Methoxy-N-phenylaniline (4k) Yield 42 mg (85%), yellow oil. ¹H NMR (CDCl₃, 300 MHz): δ 3.92 (s, 3H), 6.19 (s, 1H), 6.88-6.93 (m, 3H), 6.95-7.00 (m, 1H), 7.17-7.21 (m, 2H), 7.28-7.36 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 55.7, 110.6, 114.8, 118.7, 120.0, 121.0, 121.1, 129.4, 133.1, 142.8, 148.4. The spectral characteristics of the product obtained are similar to those described in the literature.^{S14}

3-Methoxy-N-phenylaniline (4l) Yield 41 mg (83%), white solid, mp 79–82 °C (lit.^{S15} mp 78-80 °C). ¹H NMR (CDCl₃, 300 MHz): δ 3.79 (s, 3H), 5.72 (s, 1H), 6.48-6.52 (m, 1H), 6.65-6.68 (m, 2H), 6.93-6.98 (m, 1H), 7.09-7.21 (m, 4H), 7.27-7.31 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 55.3, 103.4, 106.3, 110.3, 118.5, 121.4, 129.5, 130.2, 142.9, 144.7, 160.8. The spectral characteristics of the product obtained are similar to those described in the literature.^{S14}

2,6-Dimethyl-N-phenylaniline (4m) Yield 38 mg (78%), white powder, mp 50-52 °C (lit.^{S16} mp 48-50 °C). ¹H NMR (CDCl₃, 300 MHz): δ 2.24 (s, 6H), 6.51-6.55 (m, 2H), 6.74-6.80 (m, 1H), 7.07-7.21 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 18.5, 113.7, 118.3, 125.9, 128.7, 129.4, 136.0, 138.3, 146.4. The spectral characteristics of the product obtained are similar to those described in the literature.^{S16}

4-Phenylmorpholine (6a) Yield 36 mg (88%), white powder, mp 50–52 °C (lit.^{S17} mp 49–51 °C). ¹H NMR (CDCl₃, 300 MHz): δ 3.14-3.18 (m, 4H), 3.85-3.88 (m, 4H), 6.86-6.94 (m, 3H), 7.28-7.31 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 49.5, 67.1, 115.9, 120.2, 129.3, 151.4. The spectral characteristics of the product obtained are similar to those described in the literature.^{S18}

1-Phenylpyrrolidine (6b) Yield 31 mg (84%), colorless oil. ¹H NMR (CDCl₃, 300 MHz): δ 1.99-2.03 (m, 4H), 3.26-3.31 (m, 4H), 6.56-6.59 (m, 2H), 6.63-6.69 (m, 1H), 7.20-7.25 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 25.6, 47.7, 111.8, 115.5, 129.3, 148.1. The spectral characteristics of the product obtained are similar to those described in the literature.^{S17}

S3. ^1H and ^{13}C NMR spectra

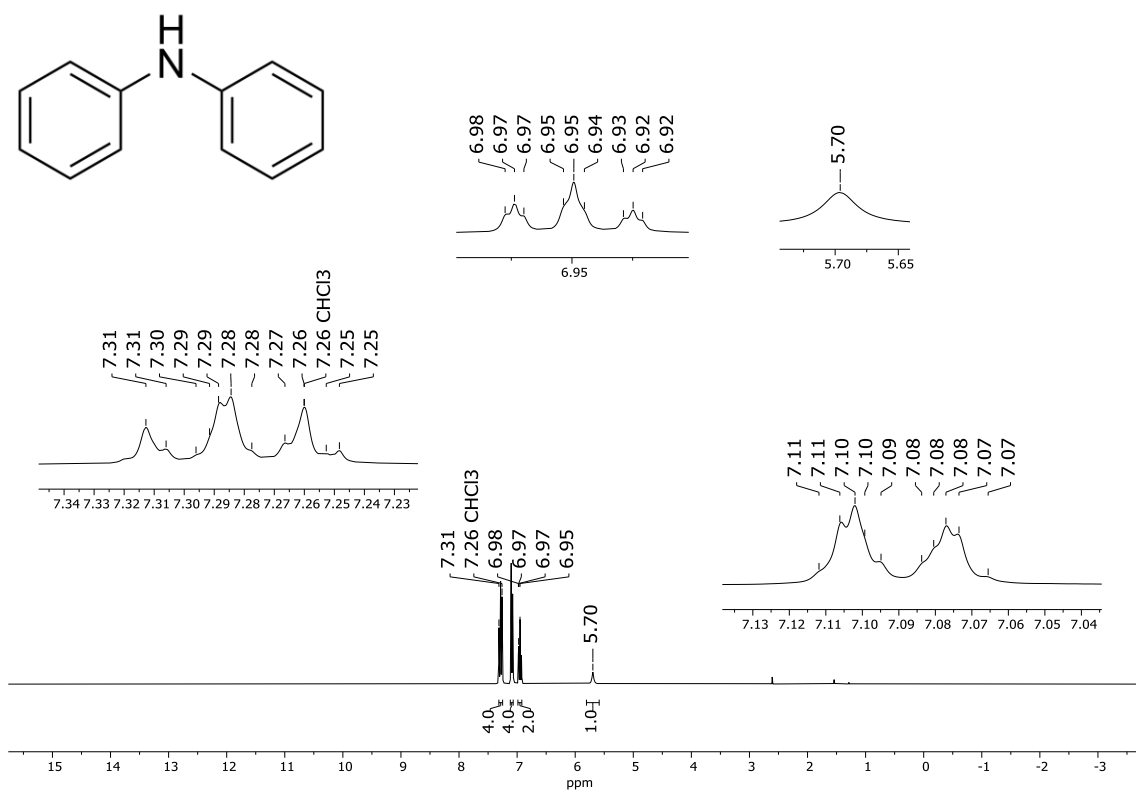


Figure S1. ^1H NMR spectrum of compound 4a (CDCl_3 , 300 MHz).

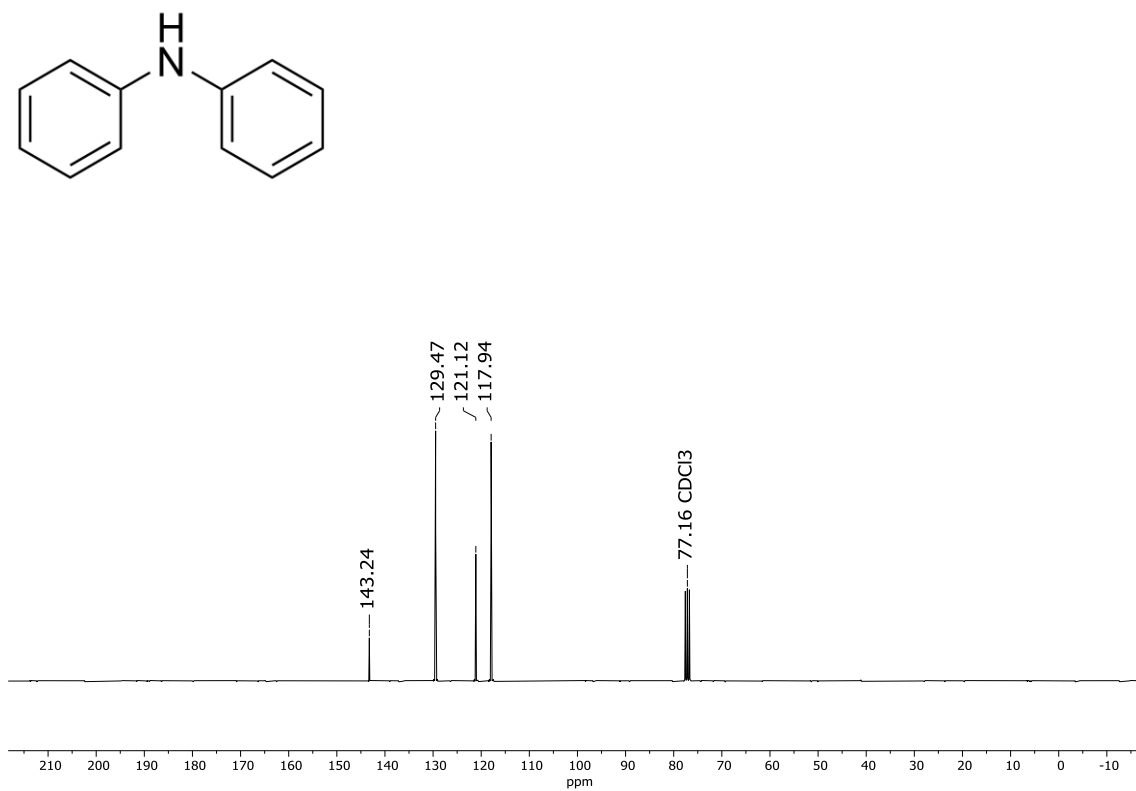


Figure S2. ^{13}C NMR spectrum of compound 4a (CDCl_3 , 75 MHz).

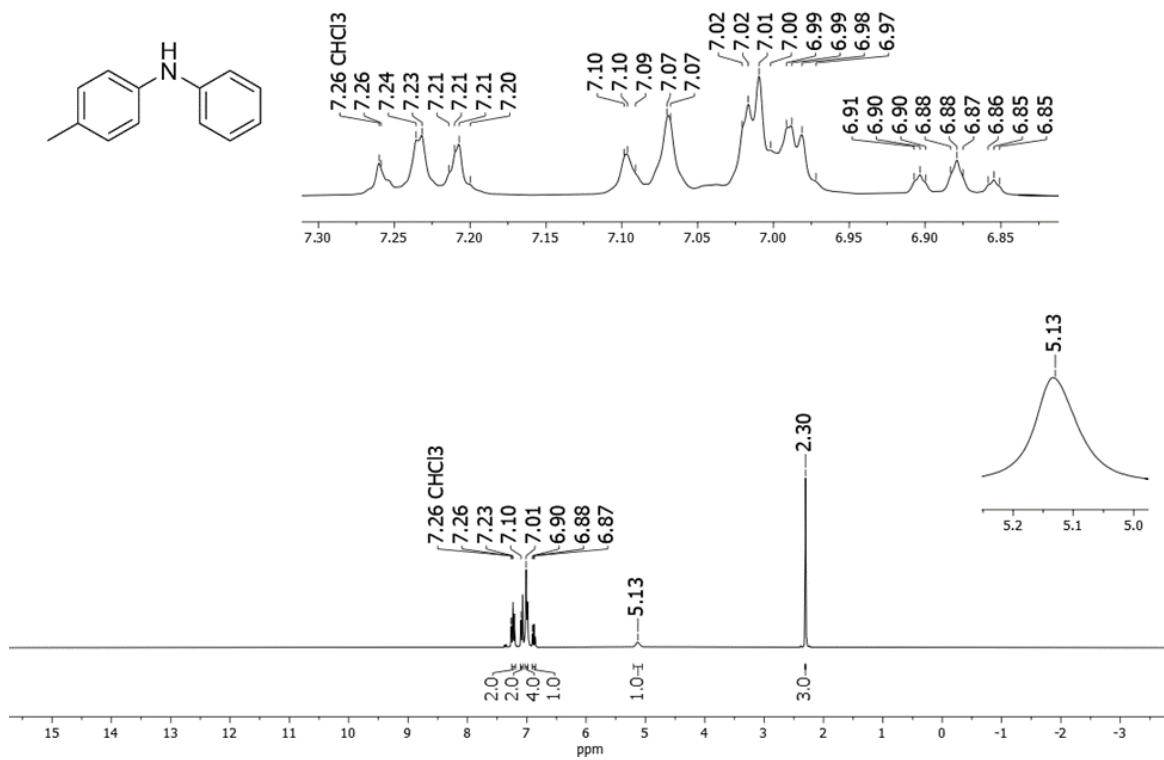


Figure S3. ¹H NMR spectrum of compound **4b** (CDCl₃, 300 MHz).

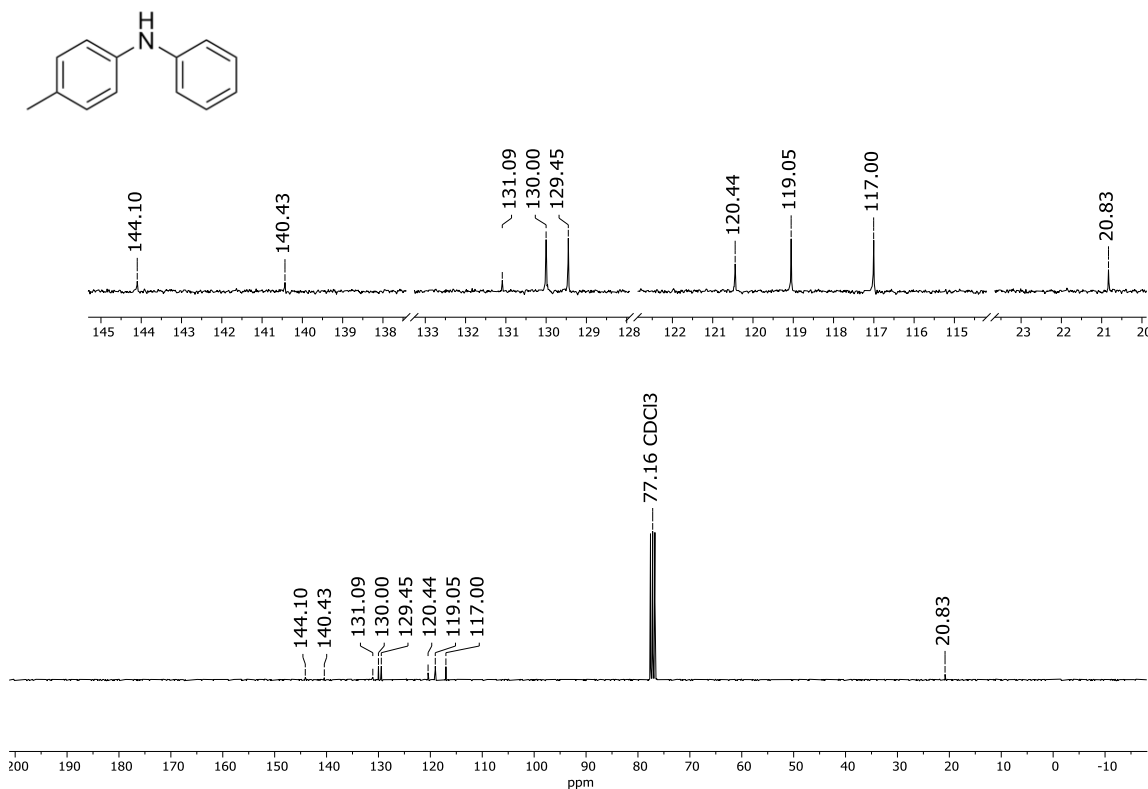


Figure S4. ¹³C NMR spectrum of compound **4b** (CDCl₃, 75 MHz).

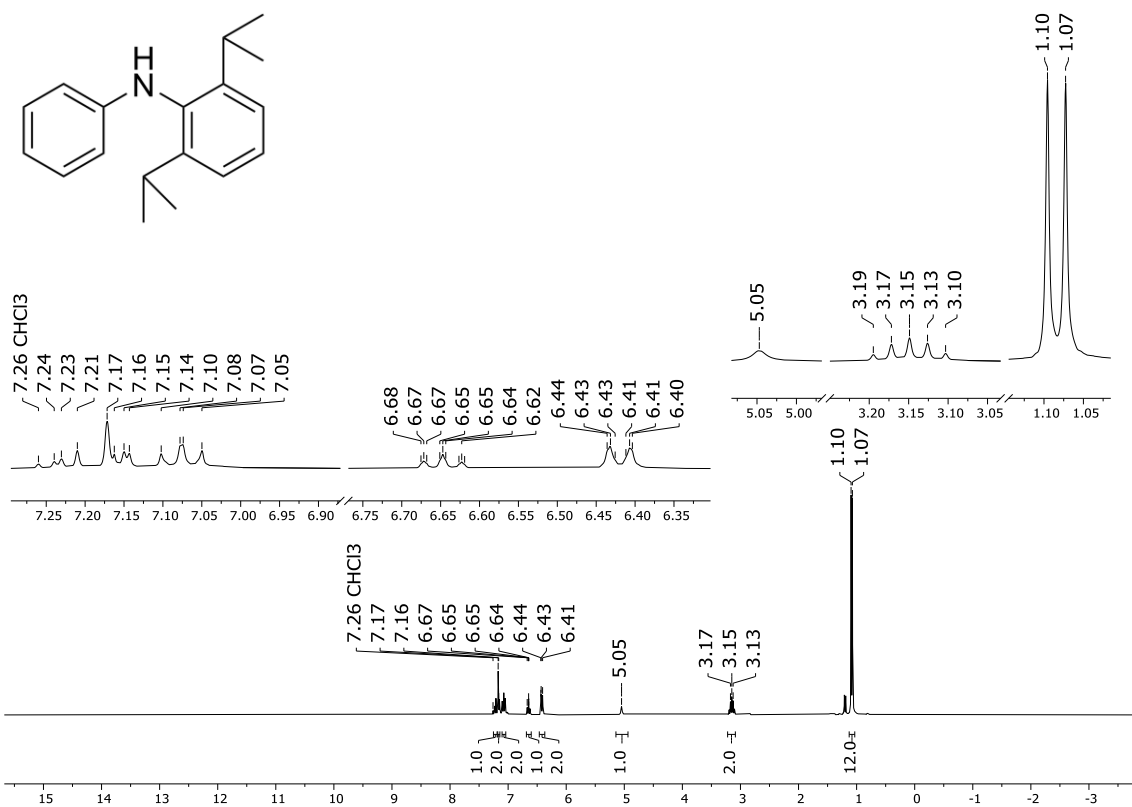


Figure S5. ¹H NMR spectrum of compound 4c (CDCl₃, 300 MHz).

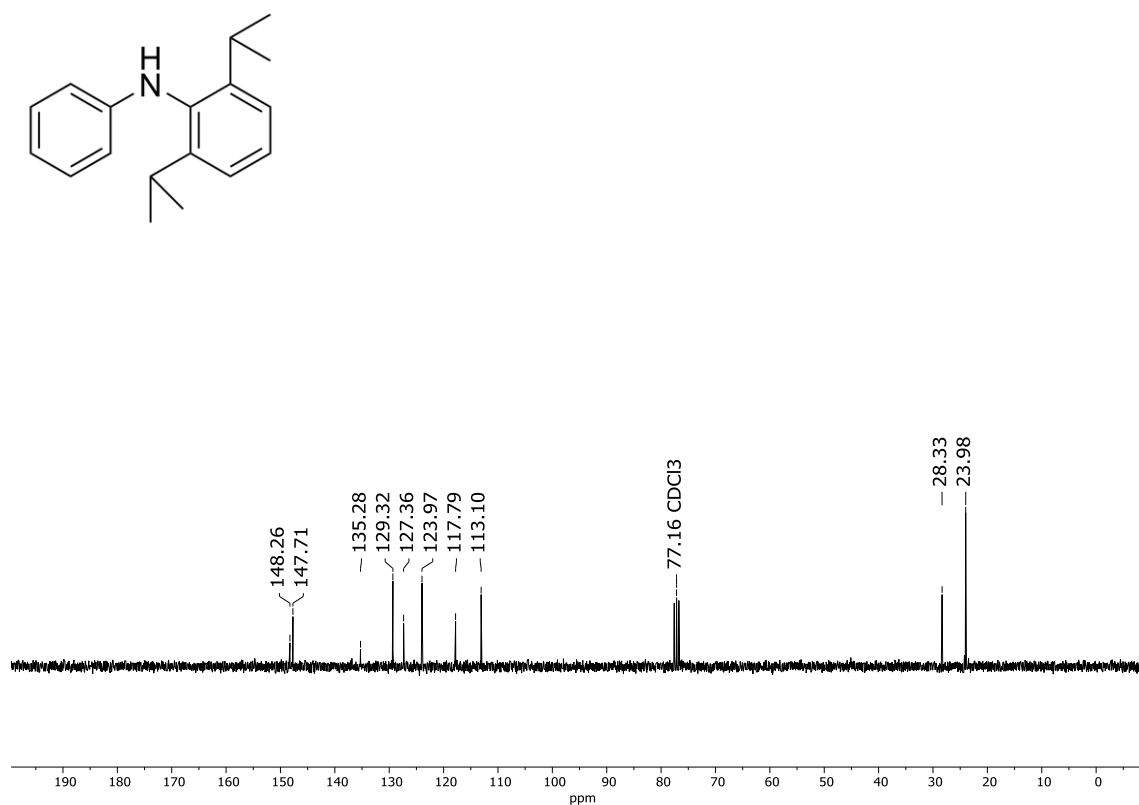


Figure S6. ¹³C NMR spectrum of compound 4c (CDCl₃, 75 MHz).

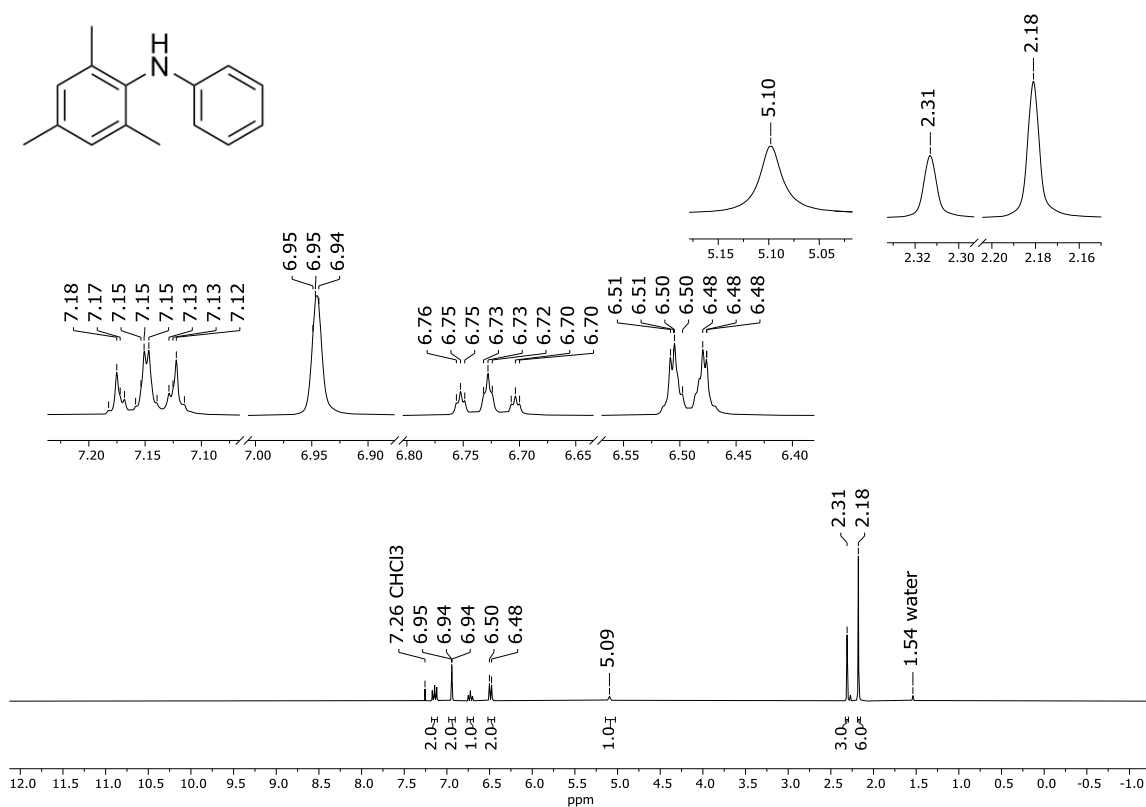


Figure S7. ¹H NMR spectrum of compound **4d** (CDCl₃, 300 MHz).

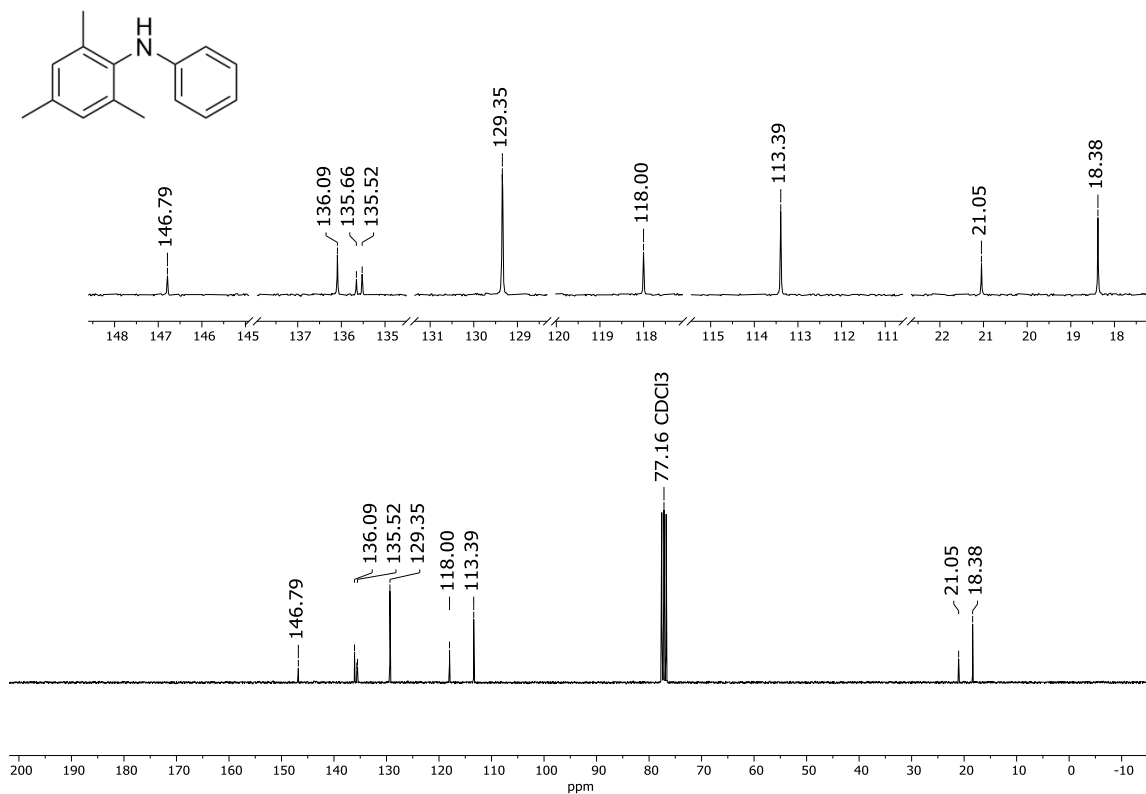


Figure S8. ¹³C NMR spectrum of compound **4d** (CDCl₃, 75 MHz).

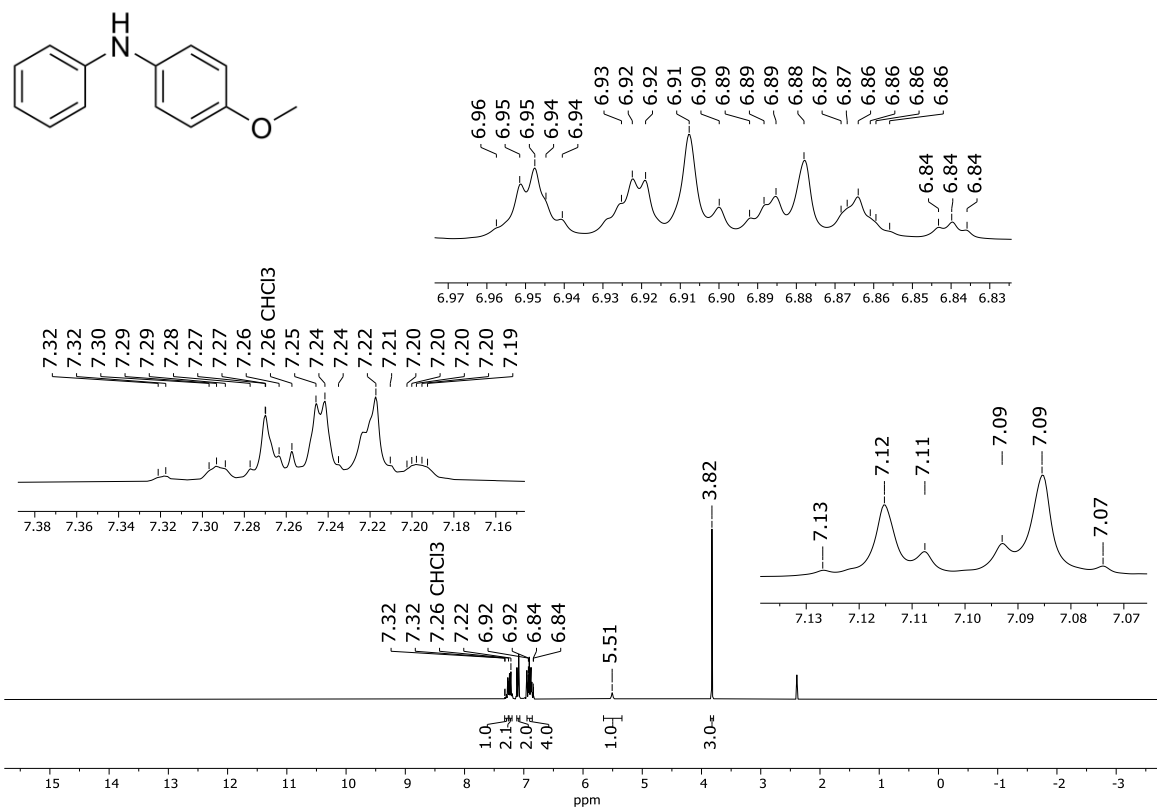


Figure S9. ¹H NMR spectrum of compound **4e** (CDCl₃, 300 MHz).

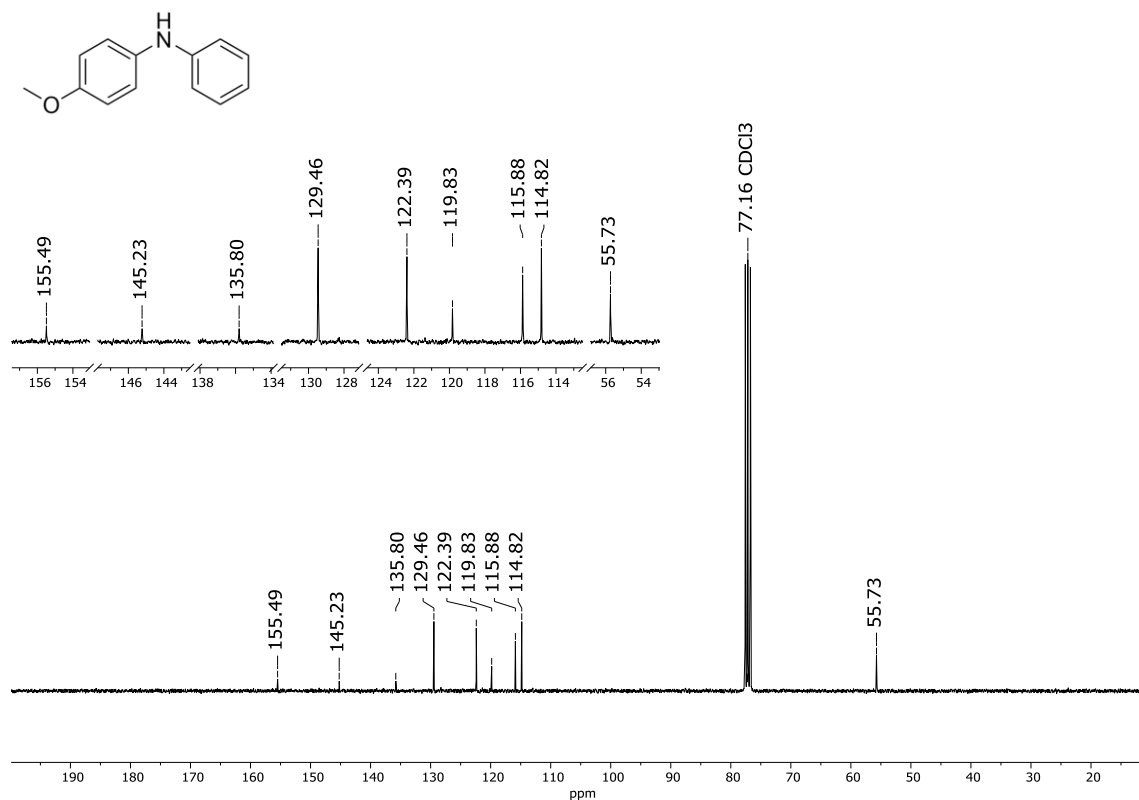


Figure S10. ¹³C NMR spectrum of compound **4e** (CDCl₃, 75 MHz).

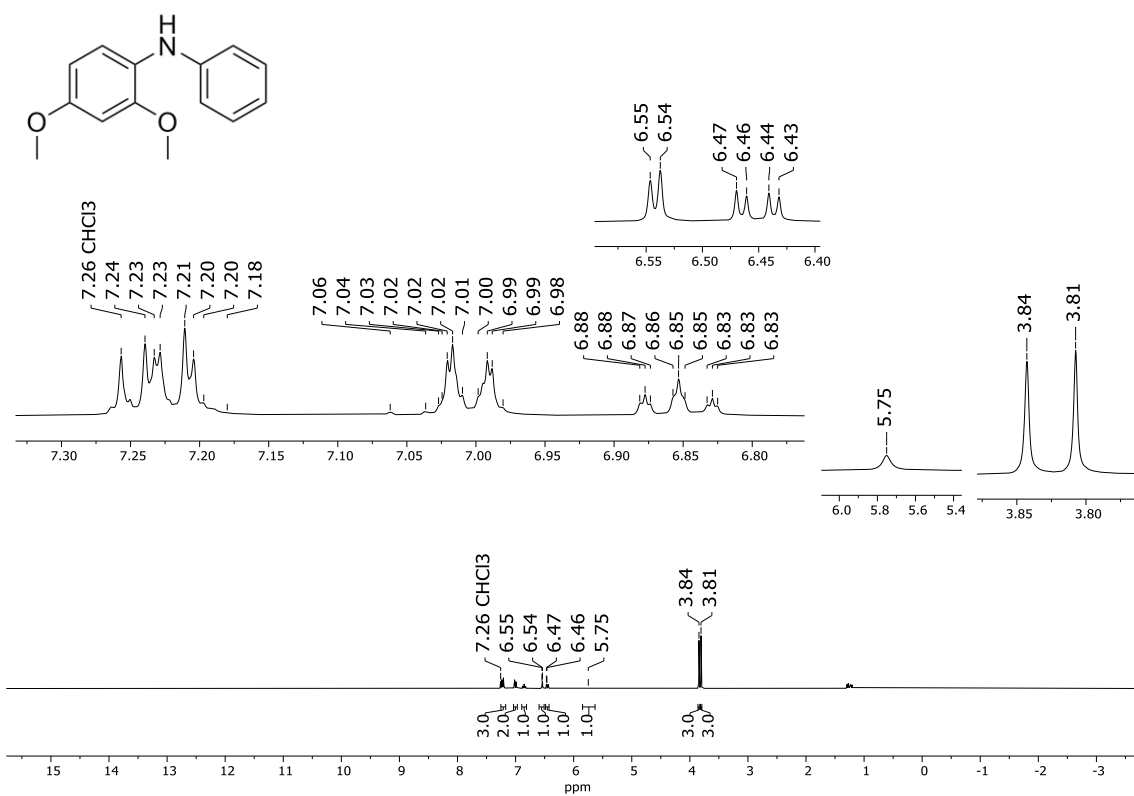


Figure S11. ^1H NMR spectrum of compound **4f** (CDCl_3 , 300 MHz).



Figure S12. ^{13}C NMR spectrum of compound **4f** (CDCl_3 , 75 MHz).

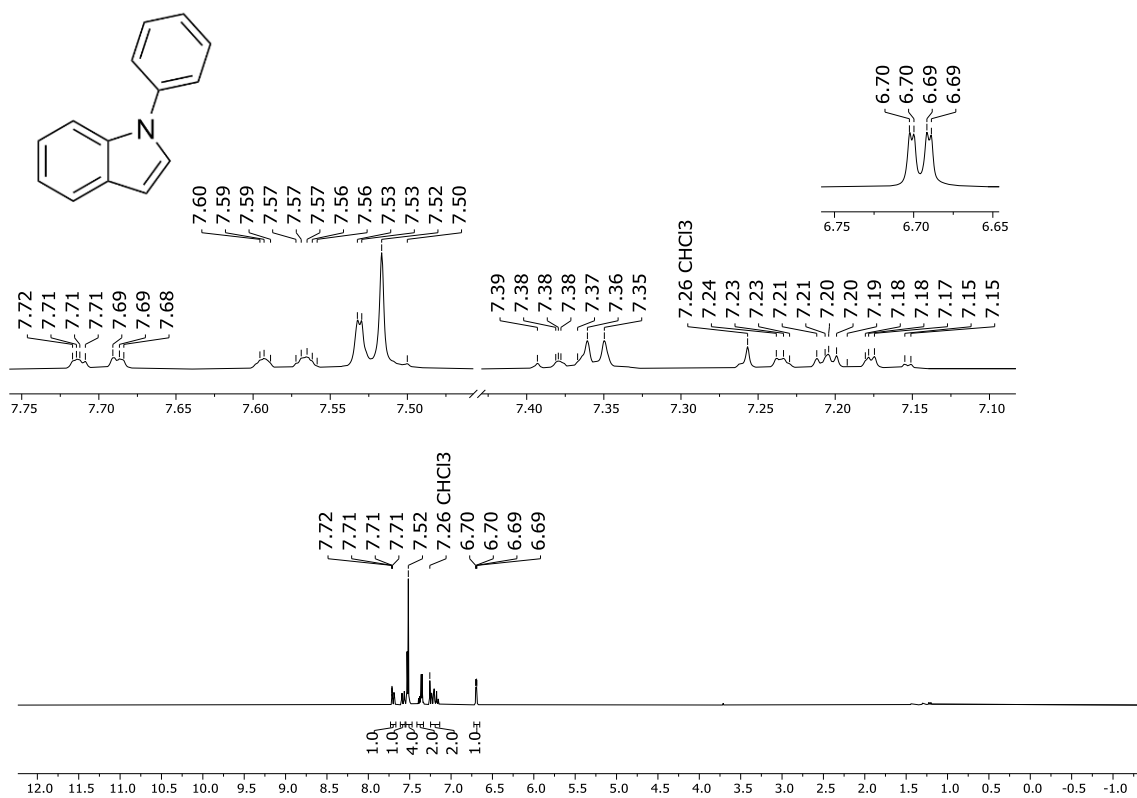


Figure S13. ^1H NMR spectrum of compound **4g** (CDCl_3 , 300 MHz).

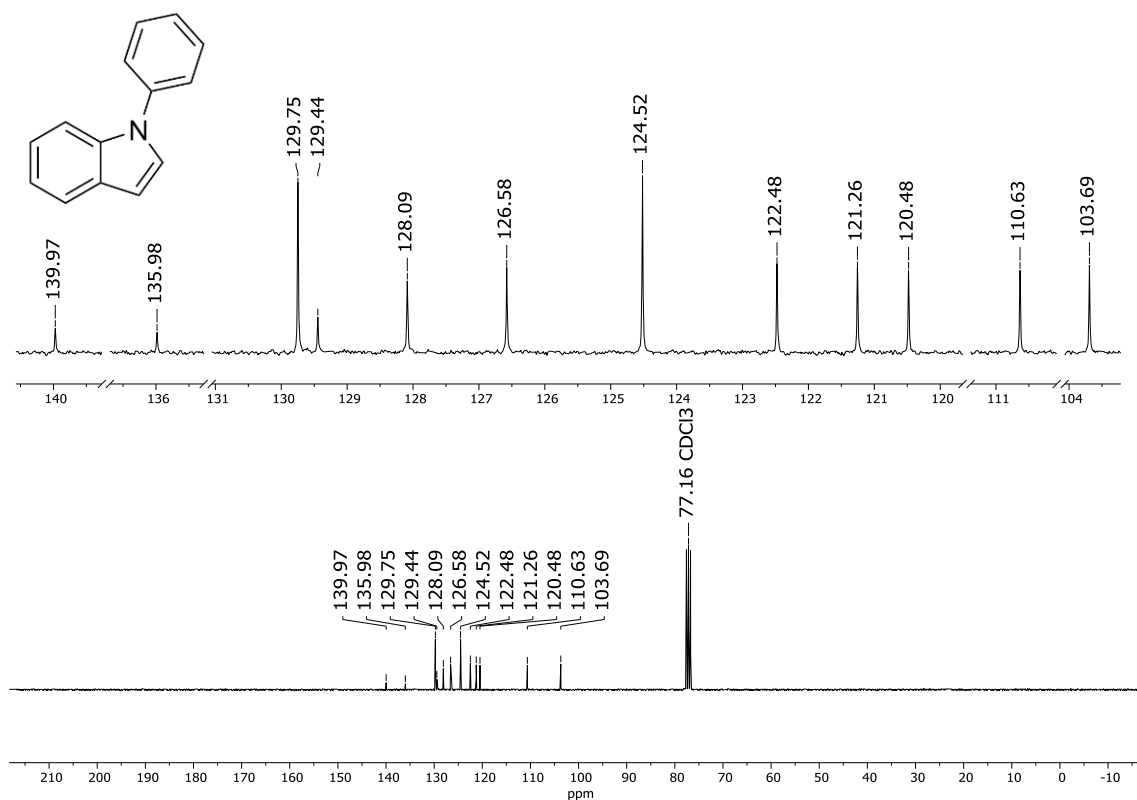


Figure S14. ^{13}C NMR spectrum of compound **4g** (CDCl_3 , 75 MHz).

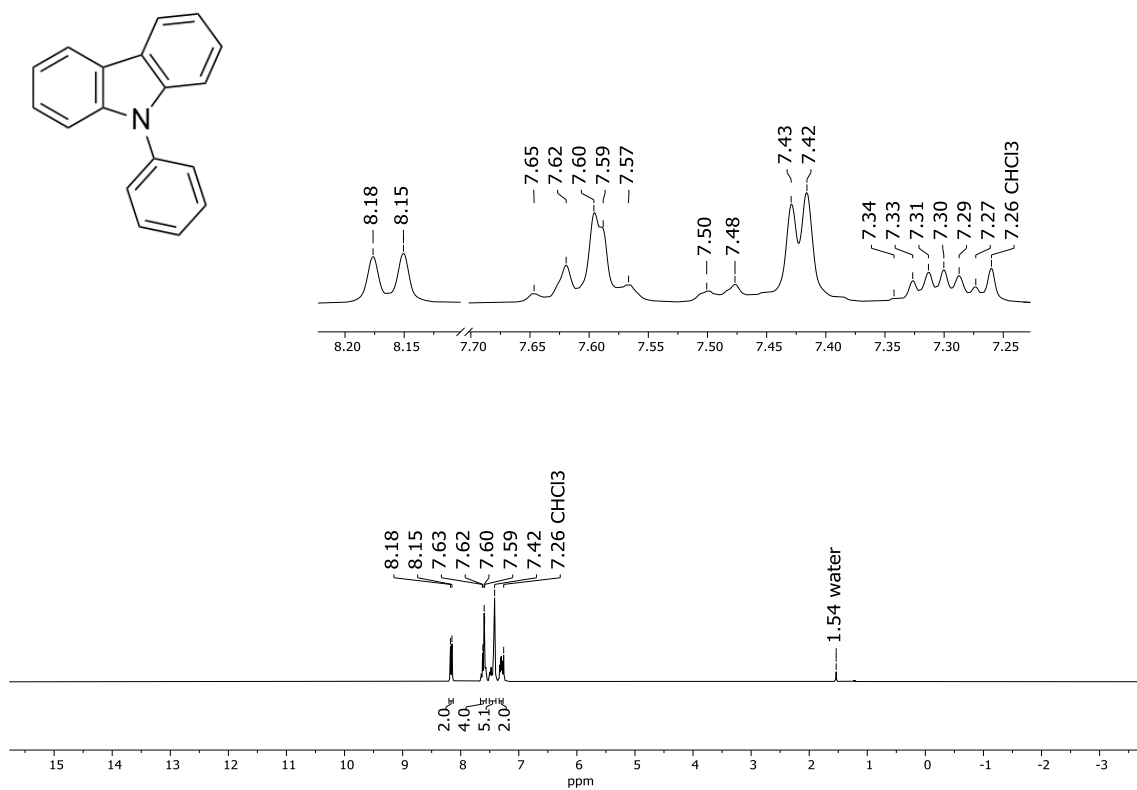


Figure S15. ¹H NMR spectrum of compound **4h** (CDCl₃, 300 MHz).

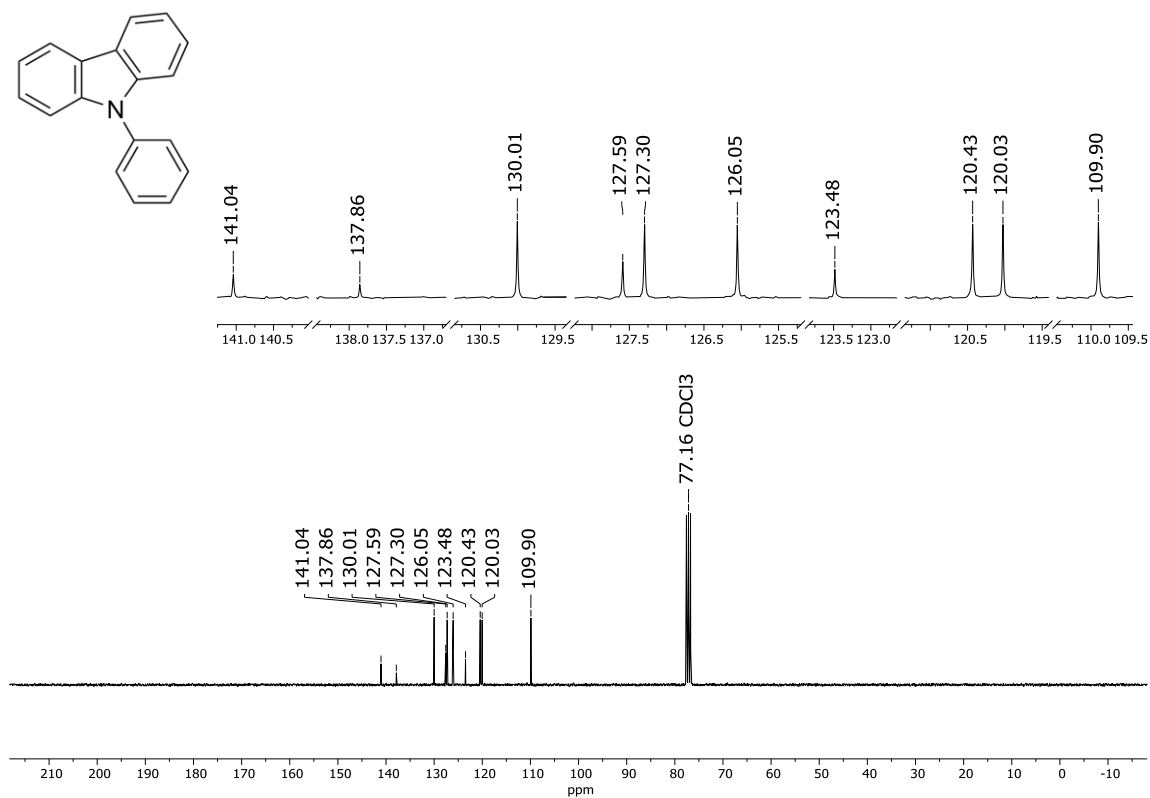


Figure S16. ¹³C NMR spectrum of compound **4h** (CDCl₃, 75 MHz).

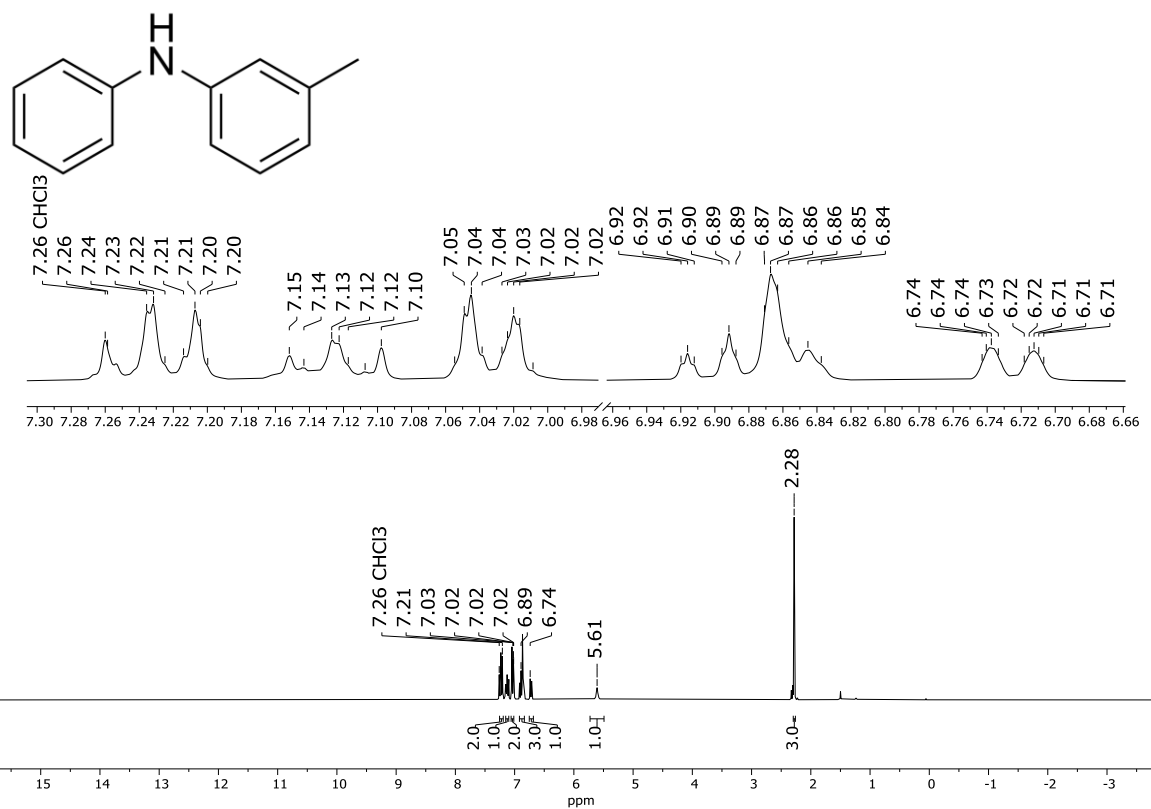


Figure S17. ¹H NMR spectrum of compound **4i** (CDCl₃, 300 MHz).



Figure S18. ¹³C NMR spectrum of compound **4i** (CDCl₃, 75 MHz).

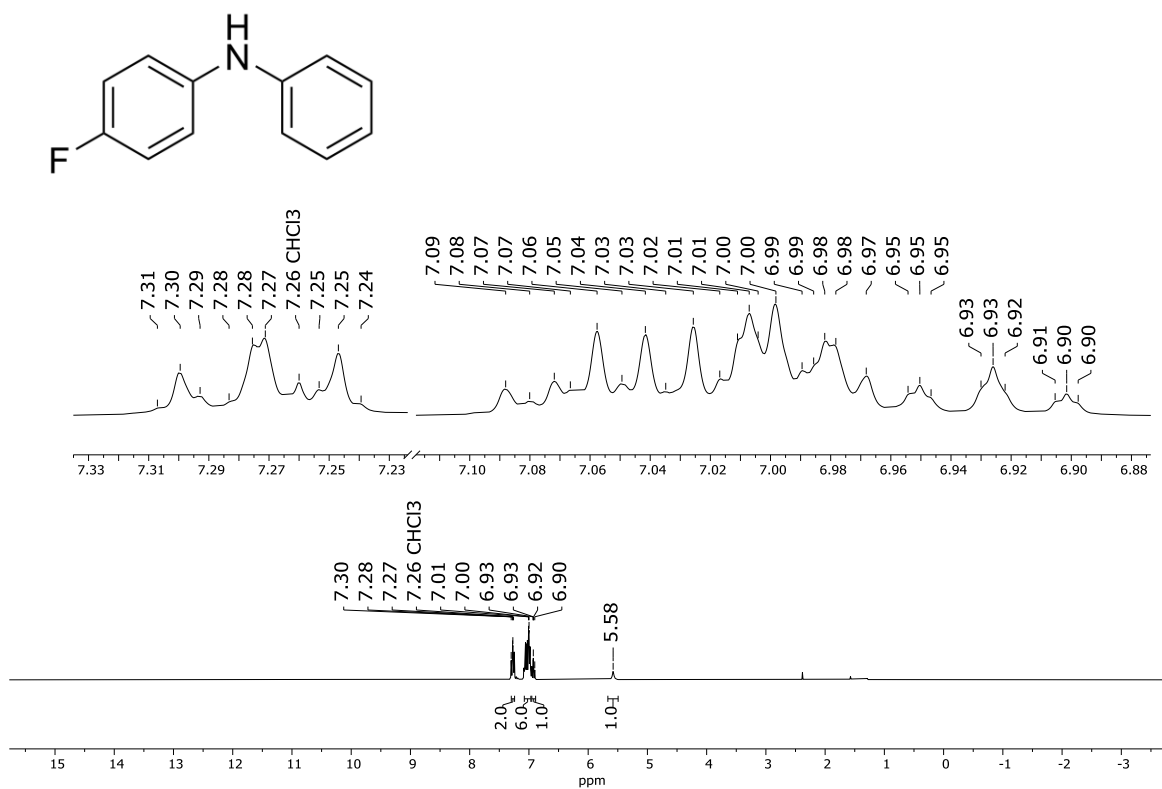


Figure S19. ¹H NMR spectrum of compound **4j** (CDCl₃, 300 MHz).

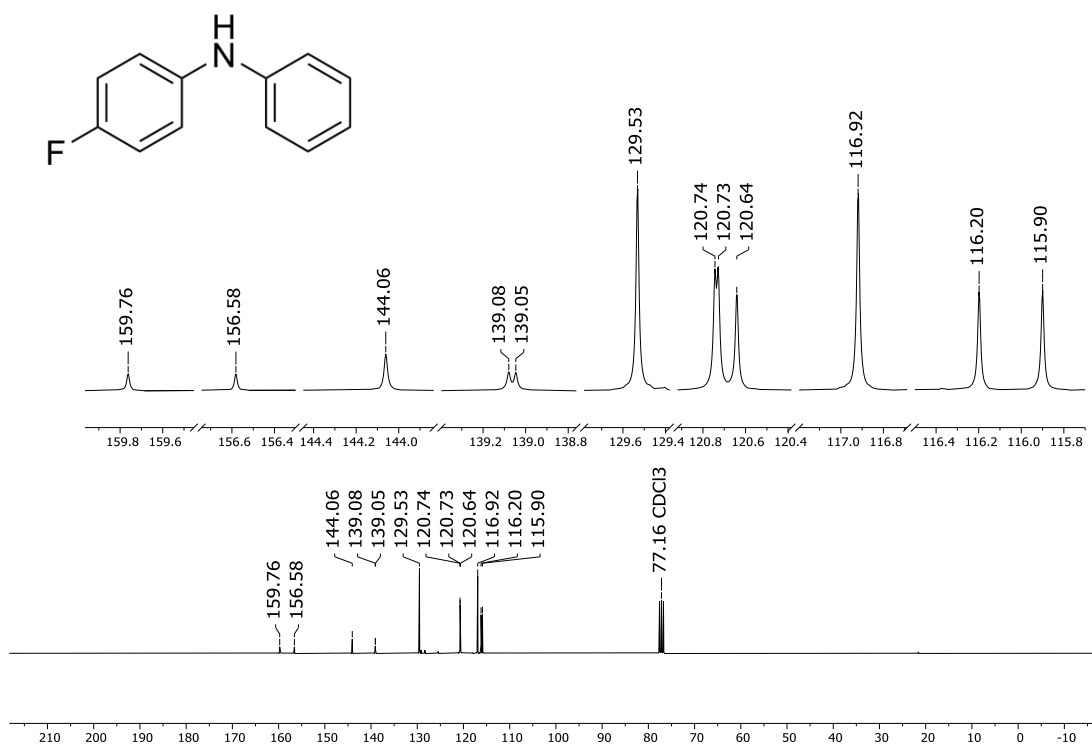


Figure S20. ¹³C NMR spectrum of compound **4j** (CDCl₃, 75 MHz).

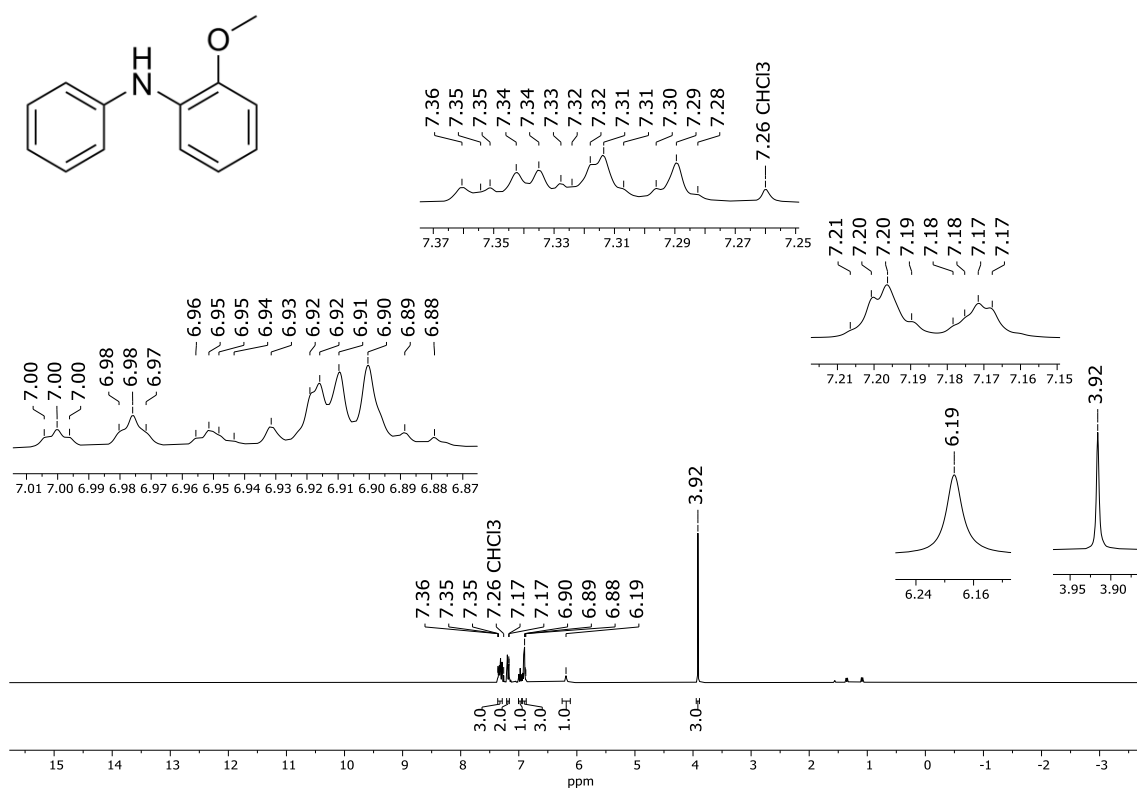


Figure S21. ¹H NMR spectrum of compound **4k** (CDCl₃, 300 MHz).

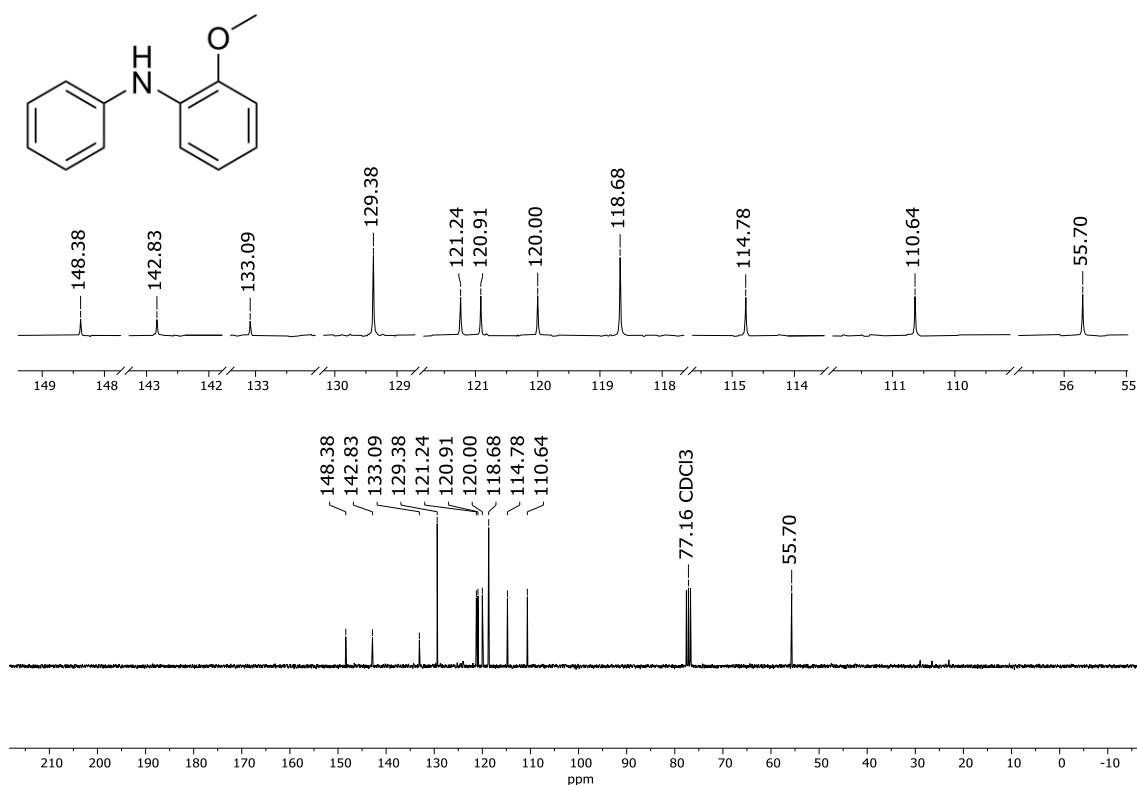


Figure S22. ¹³C NMR spectrum of compound **4k** (CDCl₃, 75 MHz).

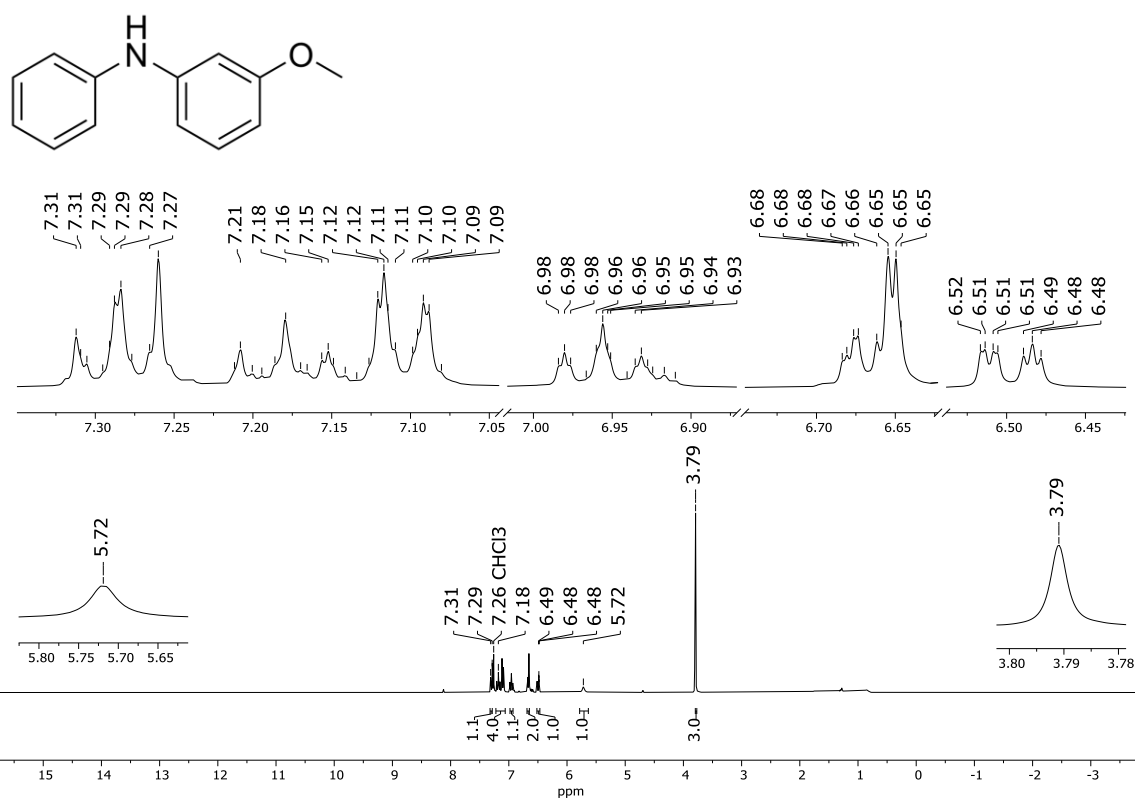


Figure S23. ¹H NMR spectrum of compound **4I** (CDCl₃, 300 MHz).

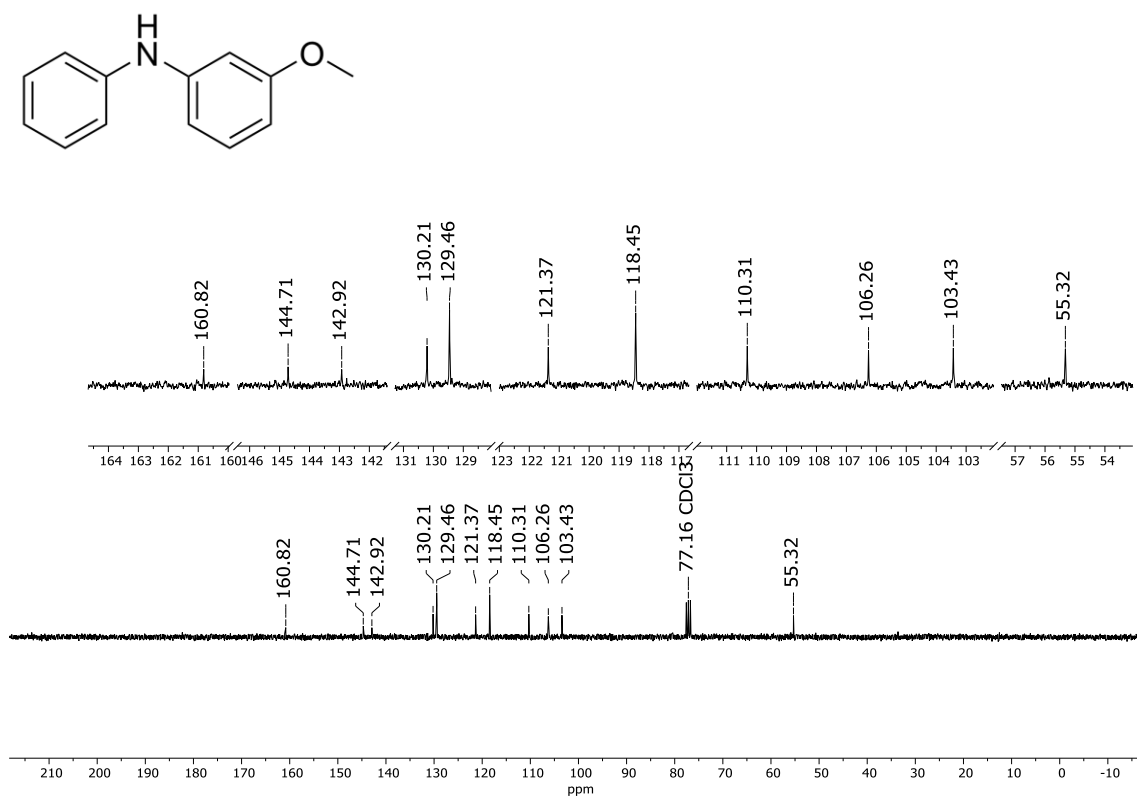


Figure S24. ¹³C NMR spectrum of compound **4I** (CDCl₃, 75 MHz).

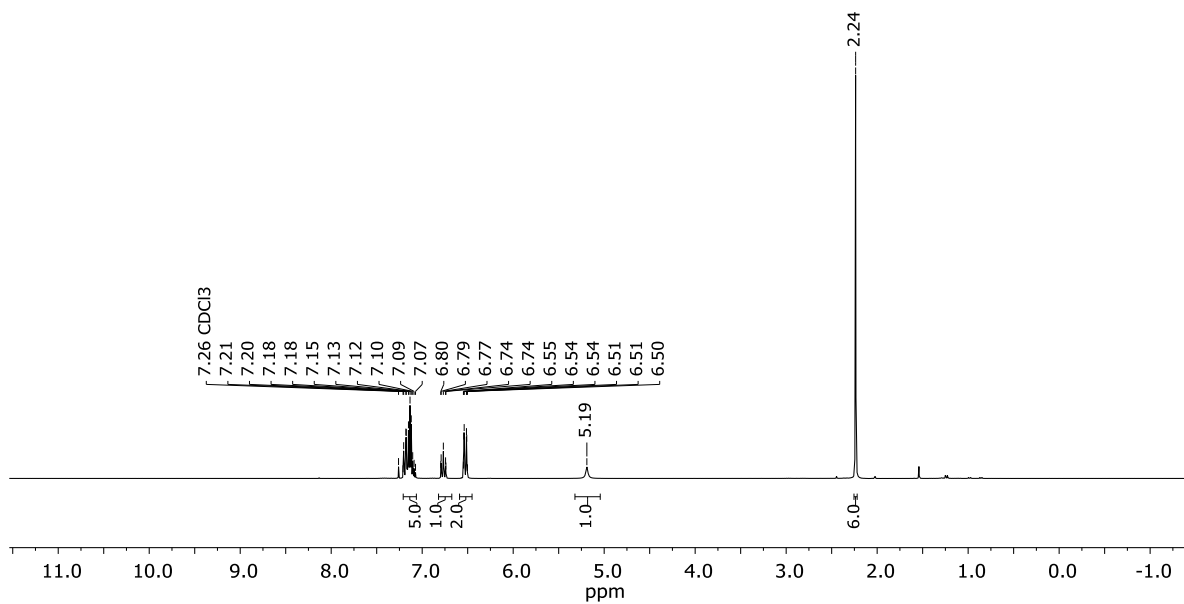
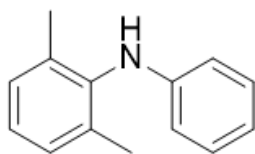


Figure S25. ¹H NMR spectrum of compound **4m** (CDCl₃, 300 MHz).

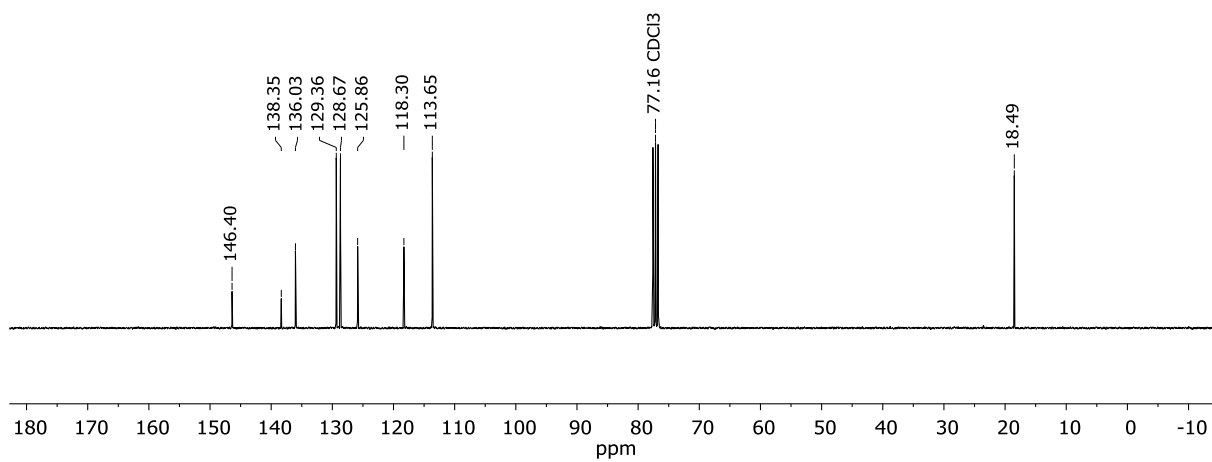
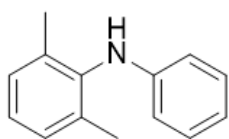


Figure S26. ¹³C NMR spectrum of compound **4m** (CDCl₃, 75 MHz).

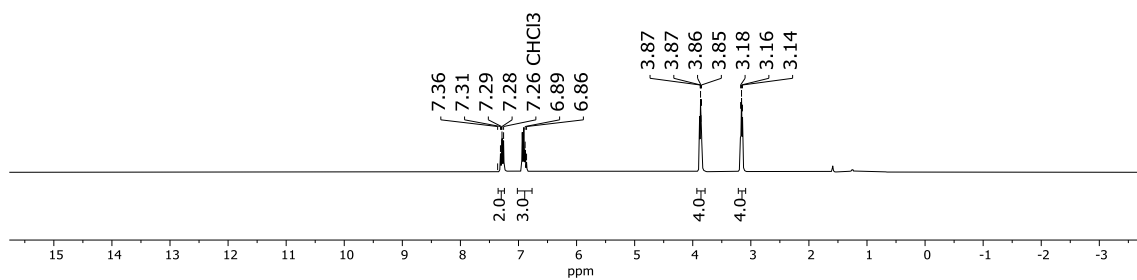
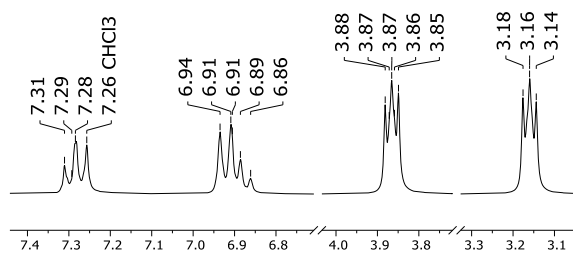
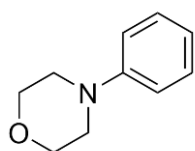


Figure S27. ^1H NMR spectrum of compound **6a** (CDCl_3 , 300 MHz).

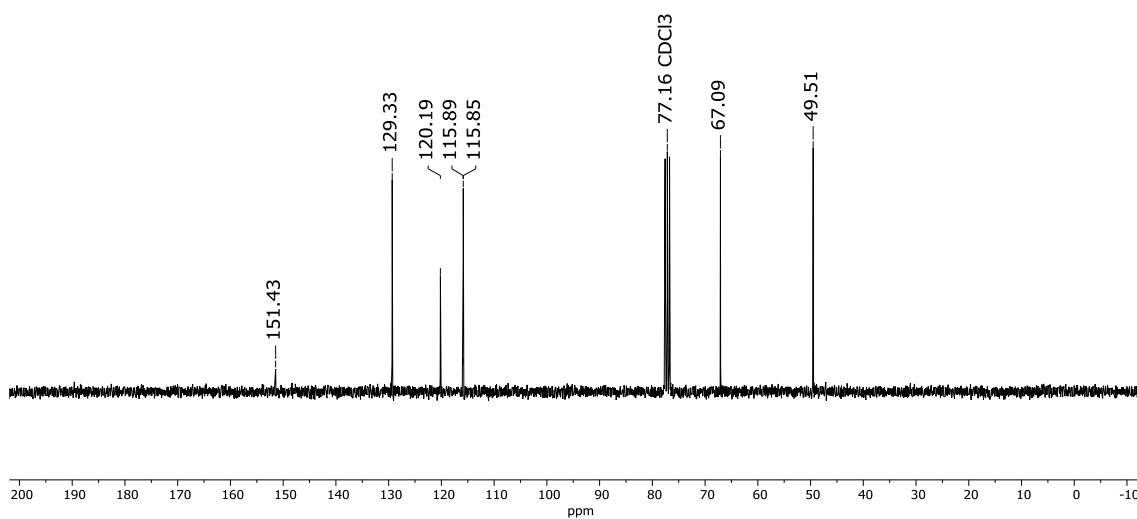
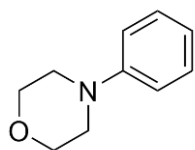


Figure S28. ^{13}C NMR spectrum of compound **6a** (CDCl_3 , 75 MHz).

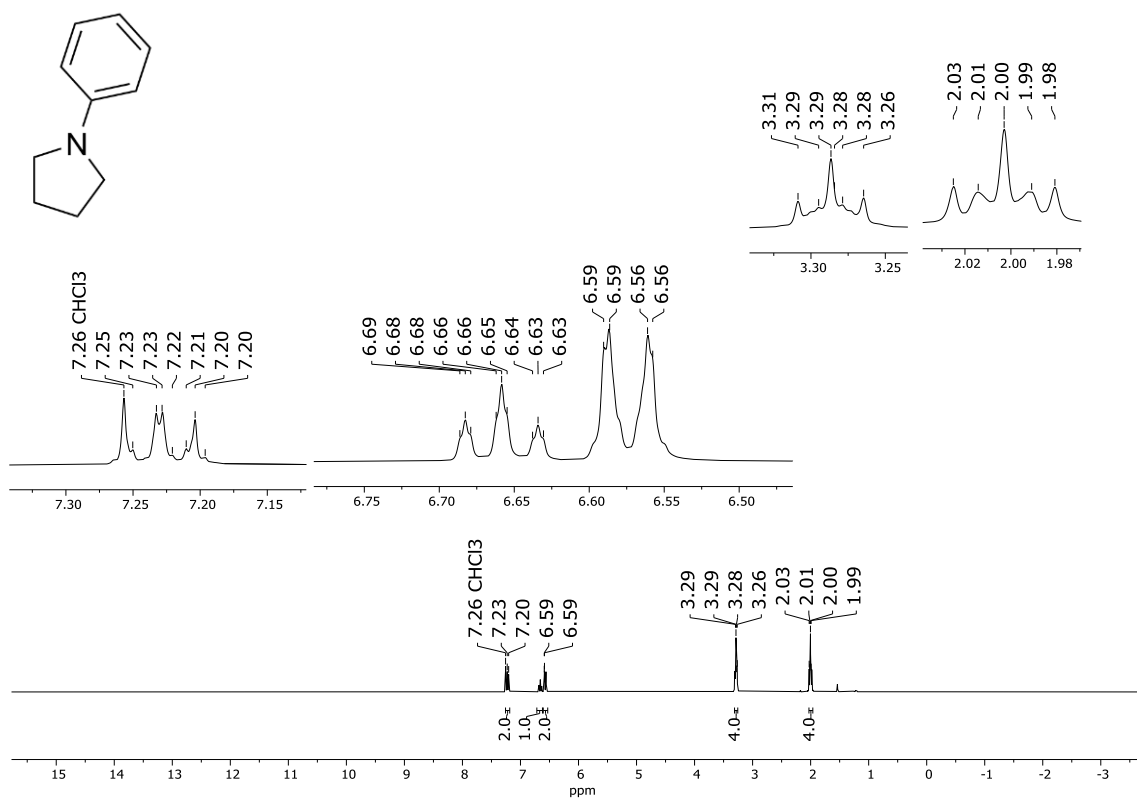


Figure S29. ^1H NMR spectrum of compound **6b** (CDCl_3 , 300 MHz).

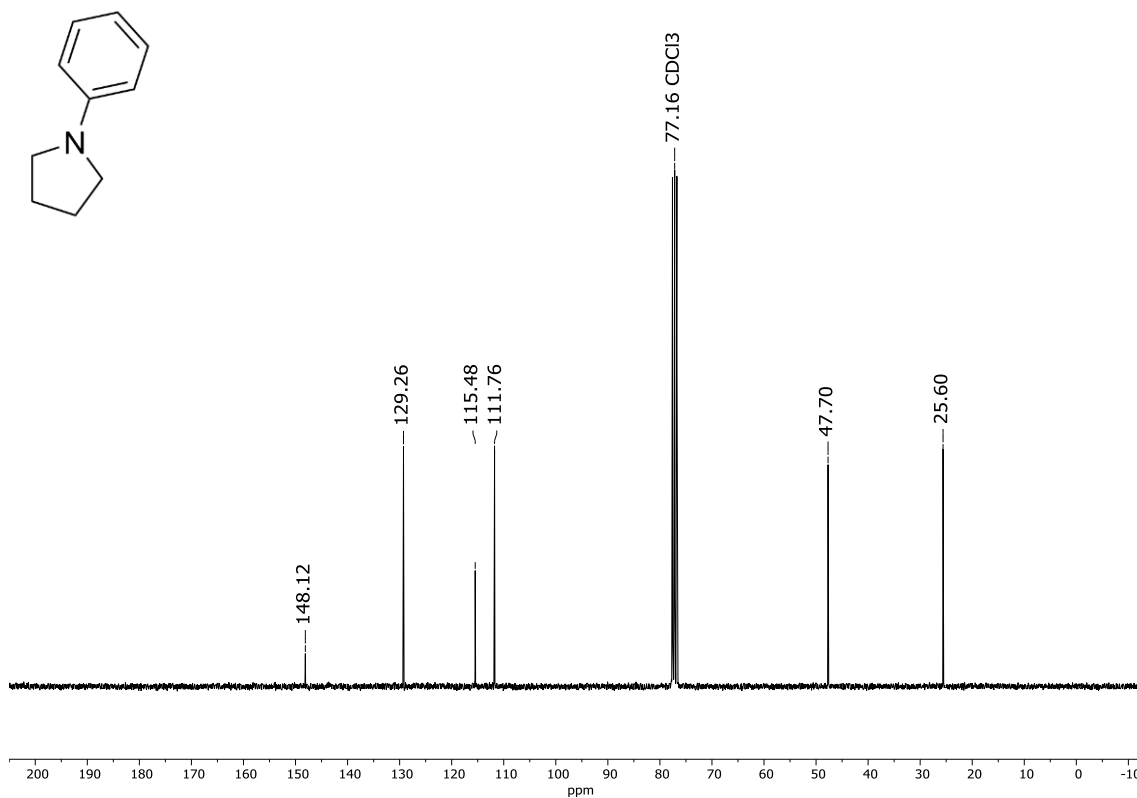


Figure S30. ^{13}C NMR spectrum of compound **6b** (CDCl_3 , 75 MHz).

S4. References

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