Supporting Information

A Green Route to Polyurethanes: Oxidative Carbonylation of Industrially Relevant Aromatic Diamines by CO_2-Based Methyl Formate

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1. General Remarks

1.1 Chemicals

All chemicals were purchased from abcr GmbH, Acros Organics, Fisher Scientific, Fluka, Merck, Sigma-Aldrich or TCI and were used as received if not mentioned otherwise. Deuterated solvents were purchased from Deutero GmbH and from Euriso-top®.

1.2 Analytical methods

Column Chromatography, Analytical Thin Layer Chromatography (TLC)

Column chromatography was performed using silica gel 230-400 mesh ASTM (particle size 0.040-0.063 mm) from Macherey-Nagel. For TLC POLYGRAM® SIL G/UV_{254} plates from Macherey-Nagel and POLYGRAM® ALOX N/UV_{254} plates from Macherey-Nagel were used and examined under UV-light irradiation (254 nm). For characterization R_f values were used.

Nuclear-Magnetic-Resonance-Spectroscopy (NMR)

All spectra were recorded at room temperature on a Bruker Avance III 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), on a Bruker Avance III 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or on a Bruker Avance 600 (^{1}H: 600 MHz, ^{13}C: 150 MHz). NMR spectra were integrated and processed using the software Mnova (Mestrelab research). For calibration the residual solvent peaks were referenced to the deuterated solvent.[1] Tetramethylsilane (TMS, δ = 0 ppm) was used as external standard. Chemical shifts δ are reported in parts per million (ppm) and coupling constants *J* in Hertz (Hz). The following abbreviations describe the observed multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, q = quartet, m = multiplet. All ^{13}C-NMR spectra were measured with ^{1}H-decoupling. ^{13}C{^{1}H}-signals were assigned on the basis of two-dimensional spectra (^{1}H^{1}H-COSY, ^{1}H^{13}C-HMBC, ^{1}H^{13}C-HSQC) and ^{13}C-APT-spectra.

Infrared Spectroscopy (IR)

All spectra were recorded at room temperature on a Bruker Alpha-P FT-IR spectrometer. The position of the absorption bands was given in wave numbers ϋ with the unit cm^{-1}. The following abbreviations were used to describe band intensity and shape: w (weak), m (medium), s (strong), br (broad).

High resolution mass spectrometry (HR-MS)

The high resolution mass spectra were recorded on a ThermoFisher Scientific LTQ Orbitrab XL spectrometer.

Melting points (Mp)

Melting points were measured in open glass capillaries in a melting point apparatus MPM-HV2 from Schorpp and were not corrected.

Elementar analyses (EA)

The elemental analyses were measured on a vario EL cube from Elementar.

Gas Chromatography (GC)

Gas chromatography was performed on a Thermo SCIENTIFIC TRACE GC Ultra. Column: OPTIMA 5 Amine (30 m x 0.25 mm x 0.4 mm); temperature program: 80–280 °C, 5 min isothermal, 12 °C min^{-1}, 30 min isothermal; FID 250 °C; methyl benzoate as internal standard.

High performance liquid chromatography (HPLC)

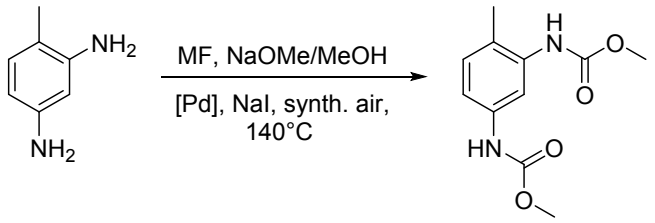
For high performance liquid chromatography an Agilent Technologies 1200 was used. Column: VD Spher PUR 100 C18-SE (5 µm, 4,6 x 150 mm); column temperature: 40 °C; flow rate: 0.7 ml/min; UV-detection: 214 nm und 254 nm (for experiments based on TDA and 2,4,6-trimethyl-1,3-benzenediamine (**17**)); 214 nm und 246 nm (for experiments based on MDA); eluent A: 90 % MeOH, 10 % H_2O; eluent B: H_2O; gradient: 0 min 50 % A, 50 % B; 10 min 50 % A, 50 % B; 15 min 100 % A; 20 min 100 % A; 20.1 min 50 % A, 50 % B; 25 min 50 % A, 50 % B, stop (for experiments based on TDA und 2,4,6-trimethyl-1,3-benzenediamine (**17**)); gradient: 0 min 50 % A, 50 % B; 5 min 50 % A, 50 % B; 20 min 100 % A; 25 min 100 % A; 25.1 min 50 % A, 50 % B; 30 min 50 % A, 50 % B, stop (for experiments based on MDA). Retention times of starting materials: R_t(TDA) = 3.3 min; R_t(**17**) = 5.6 min; R_t(MDA) = 9.5 min.

2. Experiments

2.1 Oxidative carbonylation with MF: general procedure (GP1)[2]

A 160 mL Parr high pressure reactor was charged with MF, $NaOCH_3$ solution (25 wt% in methanol), Pd catalyst and NaI. The reaction mixture was stirred at 700 rpm and heated to 140°C. After the temperature had stabilized and the internal pressure (P_{CO}) had become almost constant, the reactor was pressurized with artificial air. Respecting the safety precautions the amount of O_2 should be limited to 5 vol% O_2.[3] Immediately thereafter, the diamine dissolved in methanol was injected into the reactor using a high pressure HPLC pump. The injection of the diamine was considered as start of the reaction (t = 0). The reaction was stopped by cooling the reactor with ice-water. The autoclave was opened, the crude reaction mixture was filtrated and the reaction products were analyzed by HPLC analysis.

2.2 Synthesis and isolation of dimethyl (4-methyl-1,3-phenylene)dicarbamate (TDC)

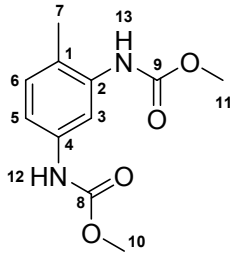


TDA **TDC**

According to GP1 (see 2.1) the oxidative carbonylation was performed using 610 mg (5.0 mmol) 4-methyl-1,3-benzenediamine (TDA) dissolved in 5 mL MeOH, 30 mL MF (485 mmol), 115 µL (0.5 mmol) NaOMe (25 wt% in MeOH), 11.7 mg (0.011 mmol) Pd(10%)/C and 90 mg (0.6 mmol) NaI. The reaction was stopped after four hours. The reaction mixture was filtrated and analyzed by thin layer chromatography (TLC) and by HPLC giving a value of 35 % for the yield of TDC. The crude product was mixed with Celite® and the solvent was removed by rotary evaporation to get a dry powder. Purification by column chromatography (SiO_2, DCM: EA 5:1) afforded 410 mg (1.7 mmol, 34 %) of TDC as a colorless solid.

Molecular formula of TDC: $C_{11}H_{14}N_2O_4$ (M = 238.24 g/mol)

Mp.: 173 °C (Lit.: 173.4 °C,[4] 170 °C,[5] 168 °C[6])



^{1}H-NMR (MeOD-*d_4*, 400.17 MHz, 296 K): δ [ppm] = 7.52 (s, 1H, *H3*), 7.17 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, *H5*), 7.09 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, *H6*), 3.73 (s, 3H, *H11*), 3.72 (s, 3H, *H10*), 2.18 (s, 3H, *H7*).

^{1}H-NMR (DMSO-*d_6*, 600.07 MHz, 296 K): δ [ppm] = 9.55 (s, br, 1H, *H12*), 8.81 (s, br, 1H, *H13*), 7.49 (s, br, 1H, *H3*), 7.16 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, *H5*), 7.06 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, *H6*), 3.64 (s, 6H, *H11, H10*), 2.11 (s, 3H, *H7*).

^{13}C{^{1}H}-NMR (MeOD-*d_4*, 100.62 MHz, 296 K): δ [ppm] = 157.5 (*C9*), 156.5 (*C8*), 138.5 (*C4*), 137.5 (*C2*), 131.6 (*C6*), 127.4 (*C1*), 117.0 (*C5*), 116.3 (*C3*), 52.7 (*C11*), 52.5 (*C10*), 17.3 (*C7*).

^{13}C{^{1}H}-NMR (DMSO-*d_6*, 150.89 MHz, 296 K): δ [ppm] = 154.7 (*C9*), 154.0 (*C8*), 137.2 (*C4*), 136.4 (*C2*), 130.2 (*C6*), 125.6 (*C1*), 115.0 (*C5*), 114.8 (*C3*), 51.6 (*C11*), 51.5 (*C10*), 17.1 (*C7*).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{11}H_{14}N_2O_4+Na]^+$ = 261.0846, found: 261.0844.

IR (ATR): 3257 (m), 2956 (w), 1712 (m), 1687 (s), 1602 (m), 1528 (s), 1498 (m), 1439 (m), 1316 (w), 1241 (s), 1193 (s), 1062 (s), 877 (w), 815 (m), 772 (m), 724 (m), 630 (m), 571 (m), 453 (w).

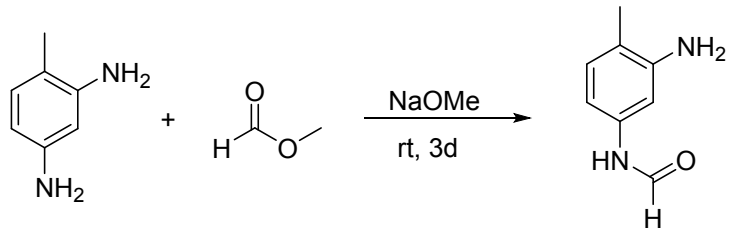
R_f (SiO_2, DCM:EA 1:1) = 0.83

HPLC: R_t = 8.3 min

GC: R_t = 29 min

The analytical data correspond to the values in literature.[6, 7]

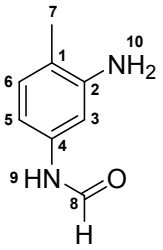
2.3 Synthesis of *N*-(3-amino-4-methylphenyl)formamide (1)



TDA **1**

2.44 g (20.0 mmol) 4-methyl-1,3-benzenediamine (TDA) were suspended in 3.0 mL (48.5 mmol) methyl formate and 230 µL (1.0 mmol, 5 mol%) NaOMe (25 wt% in MeOH) were added. The reaction mixture was stirred at room temperature and the completion of the reaction was checked by thin layer chromatography. After three days the reaction was finished, Celite® was added and the solvent was removed under vacuum. Purification of the crude product by column chromatography (SiO_2, DCM: EA 5:1) yielded 1.82 g (12.1 mmol, 61 %) of **1** as a yellowish solid. A mixture of DCM and EA in a 5:1 ratio was also used for recrystallization. In this way, transparent crystals were obtained, which were slightly yellowish in color.

Molecular formula of 1: $C_8H_{10}N_2O$ (M = 150.18 g/mol)
Mp.: 113 °C (Lit.: 113-114 °C[8])



^{1}H-NMR (MeOD-*d_4*, 400.17 MHz, 296 K): δ [ppm] = 8.16 (s, 1H, *H8*), 7.05 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, *H3*), 6.92 (d, $^3J_{H,H}$ = 8.1 Hz, 1H, *H6*), 6.75 (dd, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H, *H5*), 2.10 (s, 3H, *H7*) (*cis*-rotamer). δ [ppm] = 8.57 (s, 1H, *H8*), 6.93 (d, $^3J_{H,H}$ = 8.1 Hz, 1H, *H6*), 6.51 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, *H3*), 6.40 (dd, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 2.2 Hz, 1H, *H5*), 2.10 (s, 3H, *H7*) (*trans*-rotamer).

^{1}H-NMR (DMSO-*d_6*, 600.07 MHz, 296 K): δ [ppm] = 9.78 (s, br, 1H, *H9*), 8.15 (d, $^3J_{H,H}$ = 2.0 Hz, 1H, *H8*), 6.93 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, *H3*),), 6.81 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, *H6*), 6.64 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H, *H5*), 4.85 (s, br, 2H, *H10*), 1.98 (s, 3H, *H7*) (*cis*-rotamer).

δ [ppm] = 9.84 (d, $^{3}J_{H,H}$ = 11.2 Hz, 1H, *H9*), 8.58 (d, $^{3}J_{H,H}$ = 11.2 Hz, 1H, *H8*), 6.82 (d, $^{3}J_{H,H}$ = 7.9 Hz, 1H, *H6*) 6.37 (d, $^{4}J_{H,H}$ = 2.1 Hz, 1H, *H3*), 6.29 (dd, $^{3}J_{H,H}$ = 7.9 Hz, $^{4}J_{H,H}$ = 2.1 Hz, 1H, *H5*), 4.91 (s, br, 2H, *H10*), 1.98 (s, 3H, *H7*) (*trans*-rotamer).

^{1}H-NMR ($CDCl_3$, 400.17 MHz, 296 K): δ [ppm] = 8.24 (d, $^{3}J_{H,H}$ = 1.9 Hz, 1H, *H8*), 7.78 (s, br, 1H, *H9*), 7.10 (d, $^{4}J_{H,H}$ = 2.0 Hz, 1H, *H3*), 6.94 (d, $^{3}J_{H,H}$ = 8.1 Hz, 1H, *H6*), 6.68 (dd, $^{3}J_{H,H}$ = 8.1 Hz, $^{4}J_{H,H}$ = 2.0 Hz, 1H, *H5*), 3.51 (br, 2H, *H10*), 2.09 (s, 3H, *H7*) (*cis*-rotamer). δ [ppm] = 8.60 (d, $^{3}J_{H,H}$ = 11.0 Hz, 1H, *H8*), 8.58 (s, br, 1H, *H9*), 6.96 (d, $^{3}J_{H,H}$ = 8.1 Hz, 1H, *H6*), 6.41 (dd, $^{3}J_{H,H}$ = 8.1 Hz, $^{4}J_{H,H}$ = 2.0 Hz, 1H, *H5*), 6.35 (d, $^{4}J_{H,H}$ = 2.0 Hz, 1H, *H3*), 3.51 (s br, 2H, *H10*), 2.10 (s, 3H, *H7*) (*trans*-rotamer).

^{13}C{^{1}H}-NMR (MeOD-d_4, 100.62 MHz, 296 K): δ [ppm] = 161.4 (*C8*), 147.0 (*C2*), 137.5 (*C4*), 131.4 (*C6*), 120.5 (*C1*), 111.1 (*C5*), 108.2 (*C3*), 17.0 (*C7*) (*cis*-rotamer). δ [ppm] = 164.8 (*C8*), 147.9 (*C2*), 137.5 (*C4*), 132.0 (*C6*), 120.7 (*C1*), 109.4 (*C5*), 106.4 (*C3*), 16.9 (*C7*) (*trans*-rotamer).

^{13}C{^{1}H}-NMR (DMSO-d_6, 75.34 MHz, 296 K): δ [ppm] = 159.0 (*C8*), 146.7 (*C2*), 136.8 (*C4*), 129.9 (*C6*), 116.6 (*C1*), 107.3 (*C5*), 104.9 (*C3*), 17.0 (*C7*) (*cis*-rotamer). δ [ppm] = 162.2 (*C8*), 147.3 (*C2*), 136.7 (*C4*), 130.5 (*C6*), 116.9 (*C1*), 105.6 (*C5*), 103.5 (*C3*), 16.8 (*C7*) (*trans*-rotamer).

^{13}C{^{1}H}-NMR ($CDCl_3$, 100.62 MHz, 296 K): δ [ppm] = 159.4 (*C8*), 145.2 (*C2*), 136.0 (*C4*), 130.7 (*C6*), 119.0 (*C1*), 110.0 (*C5*), 106.9 (*C3*), 16.9 (*C7*) (*cis*-rotamer). δ [ppm] = 163.1 (*C8*), 145.8 (*C2*), 135.8 (*C4*), 131.4 (*C6*), 119.4 (*C1*), 108.7 (*C5*), 105.4 (*C3*), 16.8 (*C7*) (*trans*-rotamer).

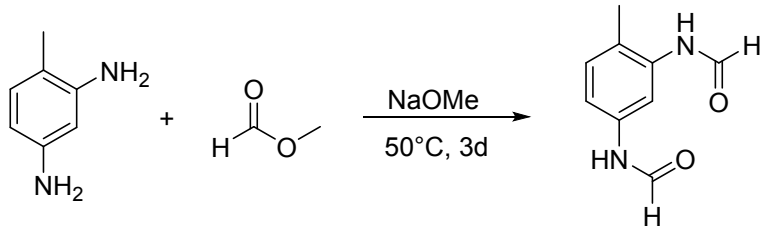
HR-MS: (ESI^{+}): *m/z* (%): calculated for $[C_8H_{11}N_2O]^{+}$ = 151.0866, found: 151.0861
IR (ATR): 3408 (m), 3319 (m), 3226 (w), 3186 (w), 2997 (m), 2867 (m), 1679 (s), 1605 (s), 1545 (s), 1504 (s), 1449 (m), 1423 (s), 1332 (m), 1279 (m), 1228 (s), 1088 (w), 885 (s), 805 (s), 743 (m), 703 (s), 624 (m), 478 (w), 441 (m).

R_f (SiO_2, EA) = 0.63

HPLC: R_t = 3.7 min

GC: R_t = 25 min

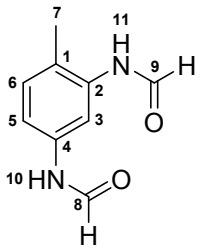
2.4 Synthesis of *N,N′*-(4-methyl-1,3-phenylene)diformamide (2)



TDA **2**

The reaction of TDA with MF in the presence of NaOMe (see 2.3) was repeated at a reaction temperature of 50°C. After three days the reaction was finished, Celite® was added and the solvent was removed under vacuum. Purification of the crude product by column chromatography (SiO_2, DCM: EA 5:1) yielded 1.82 g (10.2 mmol, 51 %) of **2** as a colorless solid.

Molecular formula of 2: $C_9H_{10}N_2O_2$ (M = 178.19 g/mol)
Mp.: 175 °C (Lit.: 169-170 °C[9])



^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): δ [ppm] = 10.12 (s, br, 1H, *H10*), 9.54 (s, br, 1H, *H11*), 8.28 (d, $^3J_{H,H}$ = 1.7 Hz, 1H, *H9*), 8.21 (d, $^3J_{H,H}$ = 1.7 Hz, 1H, *H8*), 7.98 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, *H3*), 7.38 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H, *H5*), 7.13 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, *H6*), 2.16 (s, 3H, *H7*) (*cis/cis*-rotamer). δ [ppm] =10.05 (d, $^3J_{H,H}$ = 10.8 Hz, 1H, *H10/H11*), 9.74 (d, $^3J_{H,H}$ = 11.0 Hz, 1H, *H10/H11*), 8.78 (d, $^3J_{H,H}$ = 11.0 Hz, 1H, *H8/H9*), 8.45 (d, $^3J_{H,H}$ = 10.8 Hz, 1H, *H8/H9*), 7.14 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, *H6*), 7.10 (d, $^4J_{H,H}$ = 1.8 Hz, 1H, *H3*), 6.89 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.8 Hz, 1H, *H5*), 2.17 (s, 3H, *H7*) (*trans/trans*-rotamer). δ [ppm] = 10.15 (s, br, 1H, *H10′*), 10.07 (d, $^3J_{H,H}$ = 11.0 Hz, 1H, *H10″/H11′*), 9.78 (d, $^3J_{H,H}$ = 10.8 Hz, 1H, *H10″/H11′*), 9.57 (s, br, 1H, *H11″*), 8.67 (d, $^3J_{H,H}$ = 11.0 Hz, 1H, *H8″/H9′*), 8.35 (d, $^3J_{H,H}$ = 10.8 Hz, 1H, *H8″/H9′*), 8.29 (d, $^3J_{H,H}$ = 1.7 Hz, 1H, *H9″*), 8.25 (d, $^3J_{H,H}$ = 1.7 Hz, 1H, *H8′*), 7.62 (d, $^4J_{H,H}$ = 2.0 Hz, 1H, *H3″*), 7.43 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, *H3′*), 7.31 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, *H5′*), 7.16 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, *H6′*), 7.14 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, *H6″*), 6.93 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H, *H5″*), 2.18 (s, 3H, *H7″*), 2.16 (s, 3H, *H7′*)

trans/cis-rotamer (**'**; *H9/H11 trans; H8/H10 cis*); *cis/trans*-rotamer (**''**; *H9/H11 cis; H8/H10 trans)*.

^{1}H-NMR (MeOD-d_4**;** 600.07 MHz, 296 K): δ [ppm] = 8.30 (s, 1H, *H9*), 8.22 (s, 1H, *H8*), 7.94 (d, $^{4}J_{H,H}$ = 2.1 Hz, 1H, *H3*), 7.41 (dd, $^{3}J_{H,H}$ = 8.2 Hz, $^{4}J_{H,H}$ = 2.1 Hz, 1H, *H5*), 7.17 (d, $^{3}J_{H,H}$ = 8.2 Hz, 1H, *H6*), 2.23 (s, 3H, *H7*) (*cis/cis*-rotamer). δ [ppm] = 8.71 (s, 1H, *H8/H9*), 8.46 (s, 1H, *H8/H9*), 7.22 (d, $^{3}J_{H,H}$ = 8.2 Hz, 1H, *H6*), 7.05 (d, $^{4}J_{H,H}$ = 2.2 Hz, 1H, *H3*), 6.98 (dd, $^{3}J_{H,H}$ = 8.2 Hz, $^{4}J_{H,H}$ = 2.2 Hz, 1H, *H5*), 2.25 (s, 3H, *H7*) (*trans/trans*-rotamer). δ [ppm] = 8.66 (s, 1H, *H8''/H9'*), 8,41 (s, 1H, *H8''/H9'*), 8.32 (s, 1H, *H9''*), 8.25 (s, 1H, *H8'*), 7.67 (d, $^{4}J_{H,H}$ = 2.3 Hz, 1H, *H3''*), 7.52 (d, $^{4}J_{H,H}$ = 2.1 Hz, 1H, *H3'*), 7.30 (dd, 1H, $^{3}J_{H,H}$ = 8.2 Hz, $^{4}J_{H,H}$ = 2.1 Hz, 1H, *H5'*), 7.20 (d, $^{3}J_{H,H}$ = 8.2 Hz, 2H, *H6*), 6.93 (dd, 1H, $^{3}J_{H,H}$ = 8.2 Hz, $^{4}J_{H,H}$ = 2.3 Hz, 1H, *H5''*), 2.25 (s, 3H, *H7''*), 2.24 (s, 3H, *H7'*) *trans/cis*-rotamer (**'**; *H9/H11 trans; H8/H10 cis*); *cis/trans*-rotamer (**''**; *H9/H11 cis; H8/H10 trans)*.

^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): δ [ppm] = 159.8 (*C9*), 159.3 (*C8*), 136.3 (*C4*), 135.7 (*C2*), 130.5 (*C6*), 124.3 (*C1*), 115.6 (*C5*), 113.6 (*C3*), 17.3 (*C7*) (*cis/cis*-rotamer). δ [ppm] = 163.7 (*C8/C9*), 162.73 (*C8/C9*), 137.1 (*C2/C4*), 136.9 (*C2/C4*), 131.5 (*C6*), 125.0 (*C1*), 114.5 (*C5*), 110.6 (*C3*), 17.0 (*C7*) (*trans/trans*-rotamer). δ [ppm] = 163.4 (*C8''/C9'*), 162.3 (*C8''/C9'*), 159.9 (*C9''*), 159.6 (*C8'*), 136.9 (*C4'*), 136.3 (*C4''*), 136.3 (*C2'*), 136.2 (*C2''*), 131.1 (*C6*), 125.7 (*C1'*), 124.3 (*C1''*), 116.2 (*C5'*), 113.7 (*C5''*), 113.1 (*C3'*), 112.4 (*C3''*), 17.1 (*C7*) *trans/cis*-rotamer (**'**; *H9/H11 trans; H8/H10 cis*); *cis/trans*-rotamer (**''**; *H9/H11 cis; H8/H10 trans)*.

^{13}C{^{1}H}-NMR (MeOD-d_4, 150.89 MHz, 296 K): δ [ppm] = 162.1 (*C9*), 161.5 (*C8*), 137.2 (*C4*), 136.5 (*C2*), 131.8 (*C6*), 127.6 (*C1*), 118.4 (*C5*), 116.5 (*C3*), 17.5 (*C7*) (*cis/cis*-rotamer). δ [ppm] = 165.9 (*C8/C9*), 164.8 (*C8/C9*), 137.9 (*C2/C4*), 137.8 (*C2/C4*), 133.1 (*C6*), 117.1 (*C5*), 113.3 (*C3*), 17.2 (*C7*); quaternary carbon C1: low intensity; not detected (*trans/trans*-rotamer). δ [ppm] = 165.9 (*C8''/C9'*), 164.8 (*C8''/C9'*), 162.1 (*C9''*), 161.6 (*C8'*), 137.3 (*C4*), 137.2 (*C2'*), 137.1 (*C2''*), 132.5 (*C6*), 132.4 (*C6*), 128.3 (*C1'*), 127.4. (*C1''*), 118.7 (*C5'*), 116.6 (*C5''*), 115.1 (*C3'*), 114.9 (*C3''*), 17.4 (*C7*), 17.3 (*C7*) *trans/cis*-rotamer (**'**; *H9/H11 trans; H8/H10 cis*); *cis/trans*-rotamer (**''**; *H9/H11 cis; H8/H10 trans)*.

HR-MS: (ESI^{+}): *m/z* (%): calculated for $[C_9H_{10}N_2O_2+Na]^{+}$ = 201.0634, found: 201.0634

IR (ATR): 3239 (m), 2892 (s), 1692 (m), 1652 (s), 1603 (m), 1545 (s), 1492 (s), 1450 (m), 1418 (s), 1392 (s), 1318 (m), 1235 (m), 1167 (m), 900 (w), 850 (m), 819 (m), 775 (s), 726 (s), 609 (m), 536 (w), 483 (m), 458 (m).

Elementar analysis (EA)	**C**	**H**	**N**
calculated for $C_9H_{10}N_2O_2$	60.66 %	5.66 %	15.72 %
found	59.95 %	5.57 %	15.73 %

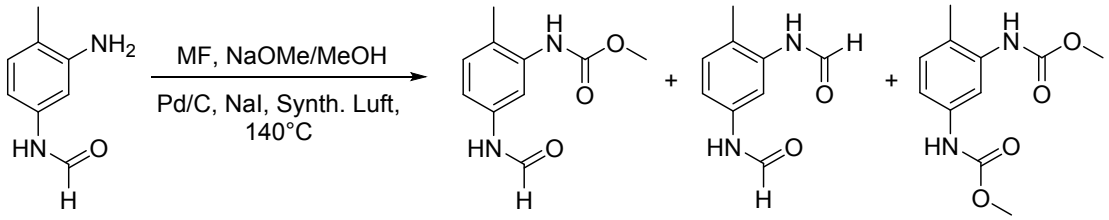
$\boldsymbol{R_f}$(SiO_2, EA) = 0.45

HPLC: R_t = 3.3 min

GC: R_t = 29 min

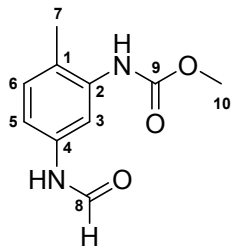
The analytical data correspond to the values in literature.[9]

2.5 Synthesis of methyl (5-formamido-2-methylphenyl)carbamate (3) by the oxidative carbonylation of *N*-(3-amino-4-methylphenyl)formamide (1) with MF



According to GP1 (see 2.1) the oxidative carbonylation was performed using 750 mg (5.0 mmol) *N*-(3-amino-4-methylphenyl)formamide (**1**) dissolved in 5 mL MeOH, 30 mL MF (485 mmol), 115 µL (0.5 mmol) NaOMe (25 wt% in MeOH), 11.7 mg (0.011 mmol) Pd(10%)/C and 90 mg (0.6 mmol) NaI. The reaction was stopped after four hours. The reaction mixture was filtrated and analyzed by thin layer chromatography (TLC) and by HPLC. The crude product was mixed with Celite® and the solvent was removed by rotary evaporation to get a dry powder. Purification by column chromatography (SiO_2, DCM: EA 5:1) afforded 161 mg (0.7 mmol, 14 %) TDC (see 2.2). By continuing column chromatography (SiO_2, DCM: EA 2:1) 189 mg (0.9 mmol, 18 %) of **3** were obtained as a brownish oil. Finally, with the use of pure EA as eluent for column chromatography, 122 mg (0.7 mmol, 14 % **2** (see 2.4) were isolated.

Molecular formula of 3: $C_{10}H_{12}N_2O_3$ (M = 208.22 g/mol)



^{1}H-NMR (MeOD-*d_4*, 400.17 MHz, 296 K): δ [ppm] = 8.19 (s, 1H, *H8*), 7.71 (s br, 1H, *H3*), 7.30 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.1 Hz, 1H, *H5*), 7.08 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, *H6*), 3.71 (s, 3H, *H10*), 2.18 (s, 3H, *H7*) (*cis*-rotamer). δ [ppm] = 8.62 (s, 1H, *H8*), 7.36 (s br, 1H, *H3*), 7.09 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, *H6*), 6.82 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.1 Hz, 1H, *H5*), 3.72 (s, 3H, *H10*), 2.18 (s, 3H, *H7*) (*trans*-rotamer).

^{13}C{^{1}H}-NMR (MeOD-*d_4*, 100.62 MHz, 296 K): δ [ppm] = 161.4 (*C8*), 157.2 (*C9*), 138.3 (*C4*), 137.0 (C2), 131.6 (*C6*), 128.5 (*C1*), 117.8 (*C5*), 116.7 (*C3*), 52.8 (*C10*), 17.4 (*C7*) (*cis*-rotamer). δ [ppm] = 164.7 (*C8*), 157.1 (*C9*), 138.4 (*C4*), 137.5 (C2), 132.3 (*C6*), 128.3 (*C1*), 115.9 (*C5*), 114.9 (*C3*), 52.8 (*C10*), 17.3 (*C7*) (*trans*-rotamer).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{10}H_{12}N_2O_3+Na]^+$ = 231.0740, found: 231.0736

IR (ATR): 3269 (w), 2953 (w), 1669 (s), 1600 (m), 1528 (s), 1447 (m), 1403 (m), 1311 (w), 1277 (m), 1225 (s), 1121 (w), 1061 (s), 1002 (w), 812 (m), 768 (m), 587 (m), 449 (m).

R_f (SiO_2, DCM:EA 1:1) = 0.53
HPLC: R_t = 5.1 min
GC: R_t = 29 min

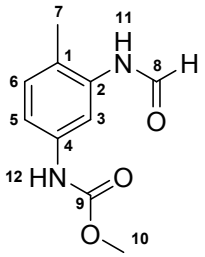
2.6 Isolation of methyl (3-formamido-4-methylphenyl)carbamate (4) and tetramethyl 4,4'-methylenebis[(6-methyl-1,3-phenylene)dicarbamate] (5)

According to GP1 (see 2.1) the oxidative carbonylation was performed using 610 mg (5.0 mmol) 4-methyl-1,3-benzenediamine (TDA) dissolved in 5 mL MeOH, 30 mL MF (485 mmol), 115 µL (0.5 mmol) NaOMe (25 wt% in MeOH), 11.7 mg (0.011 mmol) Pd(10%)/C and 90 mg (0.6 mmol) NaI. The reaction was stopped after four hours. The reaction mixture was filtrated and analyzed by thin layer chromatography (TLC) and by HPLC. The experiment was repeated with a reaction time of five hours. The combined reaction mixtures were mixed with Celite® and the solvent was removed by rotary evaporation to get a dry

powder. Purification by column chromatography (SiO_2, DCM: EA 5:1) afforded 563 mg (2.4 mmol, 24 %) of TDC as a colorless solid (see 2.2). By continuing column chromatography (SiO_2, DCM: EA 2:1) 80 mg (0.4 mmol, 4 %) of **4** were obtained as a colourless solid similar to cotton wadding. As next fraction 269 mg (0.55 mmol, 11 %) of **5** were isolated. Recrystallization from methanol afforded yellow orange needles.

Molecular formula of 4: $C_{10}H_{12}N_2O_3$ (M = 208.22 g/mol)

Mp.: 167.5 - 168.5 °C



^{1}H-NMR (MeOD-d_4, 600.07 MHz, 296 K): δ [ppm] = 8.28 (s, 1H, *H8*), 7.78 (s br, 1H, *H3*), 7.23 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.9 Hz, 1H, *H5*), 7.13 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, *H6*), 3.72 (s, 3H, *H10*), 2.21 (s, 3H, *H7*) (*cis*-rotamer). δ [ppm] = 8.40 (s, 1H, *H8*), 7.33 (s br, 1H, *H3*), 7.19 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.9 Hz, 1H, *H5*), 7.14 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, *H6*), 3.73 (s, 3H, *H10*), 2.23 (s, 3H, *H7*) (*trans*-rotamer).

^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): δ [ppm] = 9.50 (s, 1H, *H11*), 9.54 (s, 1H, *H12*) 8.26 (d, $^3J_{H,H}$ = 1.9 Hz , 1H, *H8*), 7.85 (d, $^4J_{H,H}$ = 1.5 Hz, 1H, *H3*), 7.18 (dd, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, *H5*), 7.09 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, *H6*), 3.64 (s, 3H, *H10*), 2.14 (s, 3H, *H7*) (*cis*-rotamer). δ [ppm] = 9.75 (d, $^3J_{H,H}$ = 10.8 Hz , 1H, *H11*), 9.60 (s, 1H, *H12*) 8.33 (d, $^3J_{H,H}$ = 10.8 Hz , 1H, *H8*), 7.27 (s br, 1H, *H3*), 7.12 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, *H6*), 3.65 (s, 3H, *H10*), 2.16 (s, 3H, *H7*) (*trans*-rotamer).

Note: Due to superposition *H5* of the *trans*-isomer is not resolved.

^{13}C{^{1}H}-NMR (MeOD-d_4, 150.89 MHz, 296 K): δ [ppm] = 162.0 (*C8*), 156.6 (*C9*), 138.6 (*C4*), 136.3 (C2), 131.7 (*C6*), 126.2 (*C1*), 117.4 (*C5*), 115.7 (*C3*), 52.5 (*C10*), 17.4 (*C7*) (*cis*-rotamer). δ [ppm] = 165.9 (*C8*), 156.5 (*C9*), 139.2 (*C4*), 137.0 (C2), 132.3 (*C6*), 126.6 (*C1*), 117.6 (*C5*), 113.9 (*C3*), 52.6 (*C10*), 17.1 (*C7*) (*trans*-rotamer).

^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): δ [ppm] = 159.6 (*C8*), 154.0 (*C9*), 137.2 (*C4*), 135.6 (C2), 130.3 (*C6*), 123.4 (*C1*), 114.9 (*C5*), 113.3 (*C3*), 51.5 (*C10*), 17.2 (*C7*) (*cis*-rotamer). δ [ppm] = 163.3 (*C8*), 154.0 (*C9*), 137.8 (*C4*), 136.1 (C2), 130.9 (*C6*), 124.4 (*C1*), 115.3 (*C5*), 112.2 (*C3*), 51.6 (*C10*), 17.0 (*C7*) (*trans*-rotamer).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{10}H_{12}N_2O_3+Na]^+$ = 231.0740, found: 231.0737

IR (ATR): 3273 (m), 1738 (m), 1649 (s), 1621 (m), 1606 (s), 1539 (s), 1501 (m), 1436 (m), 1410 (m), 1391 (m), 1323 (m), 1273 (w), 1223 (s), 1198 (s), 1107 (w), 1068 (s), 969 (w), 881 (w), 856 (w), 825 (m), 766 (m), 746 (m), 694 (m), 610 (w), 585 (w), 460 (w).

R_f (SiO_2, DCM:EA 1:1) = 0.54

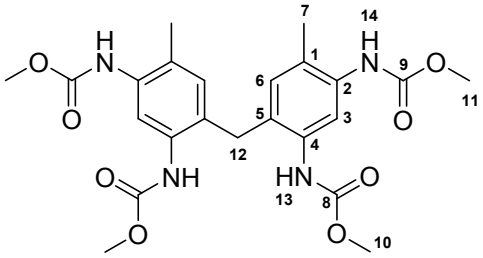
HPLC: R_t = 5.3 min

GC: R_t = 29 min

By HPLC analysis and MS (EI$^+$) **4** has been identified in literature as photodegradation product of TDC.[10]

Molecular formula of 5: $C_{23}H_{28}N_4O_8$ (M = 488.50 g/mol)

Mp.: 213-215 °C



^{1}H-NMR (DMSO-d_6, 400.17 MHz, 296 K): δ [ppm] = 8.79 (s, 2H, *H14*), 8.77 (s, 2H, *H13*) 7.36 (s, 2H, *H3*), 6.73 (s, 2H, *H6*), 3.79 (s, 2H, *H12*), 3.63 (s, 6H, *H10/H11*), 3.59 (s, 6H, *H10/H11*), 2.06 (s, 6H, *H7*).

^{1}H-NMR (MeOD-d_4, 600.07 MHz, 296 K): δ [ppm] = 7.49 (s, 2H, *H3*), 6.86 (s, 2H, *H6*), 3.84 (s, 2H, *H12*), 3.73 (s, 6H, *H10/H11*), 3.66 (s, 6H, *H10/H11*), 2.15 (s, 6H, *H7*).

^{13}C{^{1}H}-NMR (DMSO-d_6, 100.62 MHz, 296 K): δ [ppm] = 155.0 (*C8/C9*), 154.8 (*C8/C9*), 134.5 (*C2*), 133.9 (*C4*), 131.2 (*C6*), 130.6 (*C5*), 128.2 (*C1*), 121.4 (*C3*), 51.6 (*C10*, *C11*), 30.9 (*C12*), 17.3 (*C7*).

^{13}C{^{1}H}-NMR (MeOD-d_4, 150.89 MHz, 296 K): δ [ppm] = 157.7 (*C8/C9*), 157.5 (*C8/C9*), 136.0 (*C2*), 135.1 (*C4*), 133.0 (*C6*), 132.5 (*C5*), 130.4 (*C1*), 122.7 (*C3*), 52.8 (*C10/C11*), 52.7 (*C10/C11*), 33.3 (*C12*), 17.5 (*C7*).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{23}H_{28}N_4O_8+Na]^+$: 511.1799, found: 511.1796
calculated for $[C_{22}H_{24}N_4O_7+Na]^+$: 479.1537, found: 479.1535

IR (ATR): 3482 (w), 3260 (m), 2951 (w), 1735 (m), 1697 (s), 1589 (m), 1512 (s), 1448 (m), 1252 (m), 1223 (m), 1202 (s), 1126 (w), 1072 (s), 1036 (m), 898 (m), 879 (m), 767 (m), 723 (m), 687 (m), 479 (s).

R_f (SiO_2, DCM:EA 1:1) = 0.51

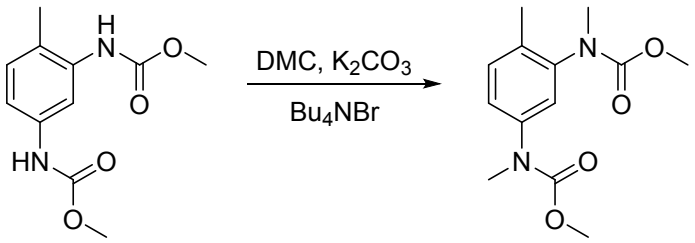
HPLC: R_t = 14.2 min

GC: R_t = 36 min

2.7 Reactions of nitrogenous compounds with dimethyl carbonate (DMC): general procedure (GP2)[11]

The nitrogenous compound was suspended in dimethyl carbonate (DMC). While stirring at room temperature, dry potassium carbonate and tetrabutylammonium bromide were added. The reaction mixture was stirred under reflux and the completion of the reaction was checked by thin layer chromatography.

2.8 Synthesis of dimethyl (4-methyl-1,3-phenylene)-bis(methylcarbamate) (6)

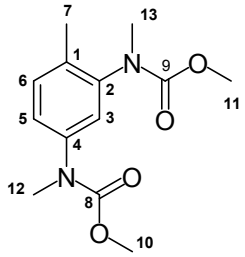


TDC **6**

According to GP2 (see 2.7) 595 mg (2.5 mmol) dimethyl (4-methyl-1,3-phenylene)dicarbamate (TDC) were reacted with 20 mL (238 mmol) dimethyl carbonate (DMC), 500 mg (3.6 mmol) potassium carbonate and 100 mg (0.3 mmol) tetrabutylammonium bromide. After a reaction time of 14 days, the crude product was mixed with Celite® and the solvent was removed by rotary evaporation to get a dry powder. Purification by column chromatography (SiO_2, DCM: EA 15:1) afforded 442 mg (1.7 mmol, 68 %) **6** as a colorless solid.

Molecular formula of 6: $C_{13}H_{18}N_2O_4$ (M = 266.30 g/mol)

Mp.: 71.6-72.3 °C



^{1}H-NMR (MeOD-d_4, 600.07 MHz, 296 K): δ [ppm] = 7.29-7.23 (m, 1H, *H6*), 7.18-7.05 (m, 2H, *H3/H5*), 3.78, 3.69, 3.61 (s, s, s, 6H, *H10/H11*), 3.26, 3.21, 3.18 (s, s, s, 6H, *H12/H13*), 2.19, 2.17 (s, s 3H, *H7*).

^{13}C{^{1}H}-NMR (MeOD-d_4, 150.89 MHz, 296 K): δ [ppm] = 158.0 (*C8/C9*), 157.9 (*C8/C9*), 143.6 (*C2/C4*), 143.3 (*C2/C4*), 143.1 (*C2/C4*), 135.1 (*C1*), 134.8 (*C1*), 132.3 (*C6*), 132.1 (*C6*), 126.2 (*C3/C5*), 126.0 (*C3/C5*), 125.9 (*C3/C5*), 53.6 (*C10/C11*), 53.5 (*C10/C11*), 38.1 (*C12/C13*), 37.8 (*C12/C13*), 37.7 (*C12/C13*), 17.1 (*C7*), 17.0 (*C7*)

Note: Signal duplications in NMR spectra are indicative for the presence of rotamers in solution.[12, 13]

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{13}H_{19}N_2O_4]^+$: 267.1339, found: 267.1345

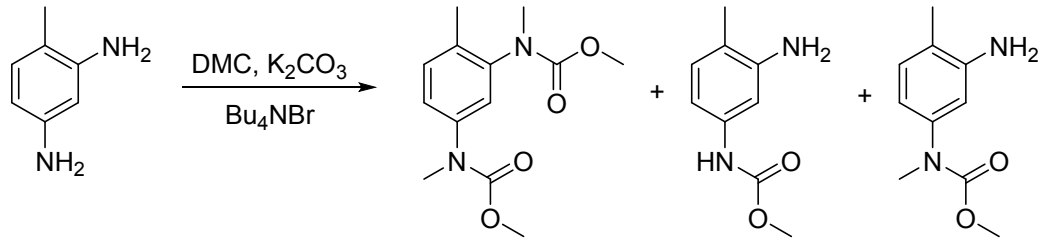
calculated for $[C_{13}H_{18}N_2O_4+Na]^+$: 289.1159, found: 289.1159

IR (ATR): 2953 (w), 1698 (s), 1612 (w), 1507 (w), 1444 (m), 1352 (s), 1279 (m), 1255 (w), 1187 (m), 1154 (s), 1024 (m), 953 (m), 849 (w), 763 (m), 737 (w), 668 (w), 557 (m), 468 (w).

R_f (SiO_2, DCM:EA 5:1) = 0.59

HPLC: R_t = 16.1 min

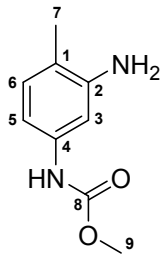
2.9 Identification of methyl (3-amino-4-methylphenyl)carbamate (7) and methyl (3-amino-4-methylphenyl)(methyl)carbamate (8)



TDA **6** **7** **8**

According to GP2 (see 2.7) 610 mg (5.0 mmol) 4-methyl-1,3-benzenediamine (TDA) were reacted with 20 mL (238 mmol) dimethyl carbonate (DMC), 500 mg (3.6 mmol) potassium carbonate and 100 mg (0.3 mmol) tetrabutylammonium bromide. After a reaction time of 14 days, the crude product was mixed with Celite® and the solvent was removed by rotary evaporation to get a dry powder. Purification by column chromatography (SiO_2, DCM: EA 15:1) resulted in a colorless solid which was analyzed by HPLC, NMR and HR-MS. In this way, compounds **7** and **8** were identified in addition to **6** (see 2.8) in this inseparable mixture.

Molecular formula of 7: $C_9H_{12}N_2O_2$ (M = 180.21 g/mol)



^{1}H-NMR (MeOD-*d_4*, 400.17 MHz, 296 K): δ [ppm] = 6.89 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, *H3*), 6.87 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, *H6*), 6.64 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, *H5*), 3.70 (s, 3H, *H9*), 2.09 (s, 3H, *H7*).

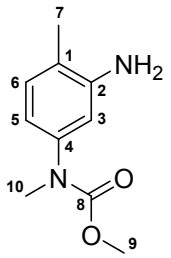
^{13}C{^{1}H}-NMR (MeOD-*d_4*, 100.62 MHz, 296 K): δ [ppm] = 156.5 (*C8*), 146.8 (*C2*), 138.7 (*C4*), 131.3 (*C6*), 118.9 (*C1*), 110.2 (*C5*), 107.1 (*C3*), 52.3 (*C9*), 16.9 (*C7*).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_9H_{13}N_2O_2]^+$: 181.0972, found: 181.0975; 181.0970

HPLC: R_t = 5.4 min

The analytical data correspond to the values in literature.[14, 15]

Molecular formula of 8: $C_{10}H_{14}N_2O_2$ (M = 194.23 g/mol)

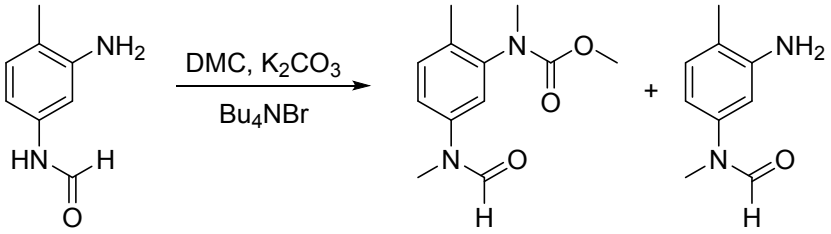


^{1}H-NMR (MeOD-*d_4*, 400.17 MHz, 296 K): δ [ppm] = 6.96 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, *H6*), 6.59 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, *H3*), 6.48 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, *H5*), 3.65 (s, 3H, *H9*), 3.20 (s, 3H, *H10*), 2.13 (s, 3H, *H7*).

^{13}C{^{1}H}-NMR (MeOD-*d_4*, 100.62 MHz, 296 K): δ [ppm] = 158.2 (*C8*), 147.3 (*C2*), 143.1 (*C4*), 131.5 (*C6*), 122.4 (*C1*), 116.5 (*C5*), 113.8 (*C3*), 53.3 (*C9*), 38.4 (*C10*), 17.1 (*C7*).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{10}H_{15}N_2O_2]^+$: 195.1128,
found: 195.1132; 195.1126
HPLC: R_t = 9.8 min

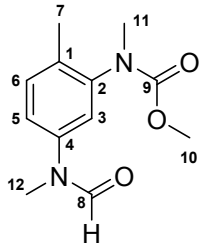
2.10 Identification of methyl methyl[2-methyl-5-(*N*-methylformamido)phenyl]-carbamate (9) and *N*-(3-amino-4-methylphenyl)-*N*-methyl-formamide (10)



1 **9** **10**

According to GP2 (see 2.7) 750 mg (5.0 mmol) *N*-(3-amino-4-methylphenyl)formamide (**1**) were reacted with 20 mL (238 mmol) dimethyl carbonate (DMC), 500 mg (3.6 mmol) potassium carbonate and 100 mg (0.3 mmol) tetrabutylammonium bromide. After a reaction time of ten days, the crude product was mixed with Celite® and the solvent was removed by rotary evaporation to get a dry powder. Purification by column chromatography (SiO_2, DCM: EA 10:1) afforded 370 mg (1.56 mmol, 31 %) **9** as a yellowish oil. Continuing column chromatography resulted in further 273 mg of a yellowish oil which was analyzed by HPLC, NMR and HR-MS. In this way, **9** and **10** at a ratio of 4:6 were identified as the components of this inseparable mixture.

Molecular formula of 9: $C_{12}H_{16}N_2O_3$ (M = 236.27 g/mol)



^{1}H-NMR (MeOD-*d_4*, 400.17 MHz, 296 K): δ [ppm] = 8.43, 8.31 (s, s, 1H, *H8*), 7.37-7.14 (m, 3H, *H3/H5/H6*), 3.78, 3.60 (s, s, 3H, *H10*), 3.35, 3.26, 3.22, 3.20 (s, s, s, s, 6H, H11/H12), 2.21, 2.19 (s, s, 3H, *H7*).

^{13}C{^{1}H}-NMR (MeOD-*d_4*, 100.62 MHz, 296 K): δ [ppm] = 164.6 (*C8*), 164.2 (*C8*), 157.7 (*C9*), 144.3 (*C2*), 143.8 (*C2*), 142.3 (*C4*), 135.4 (*C1*), 135.1 (*C1*), 133.0 (*C6*), 132.9 (*C6*), 122.8 (*C3/C5*), 122.7 (*C3/C5*), 122.6 (*C3/C5*), 53.5 (*C10*), 37.7 (*C11*), 37.4 (*C11*), 32.3 (*C12*), 17.1 (*C7*), 17.0 (*C7*).

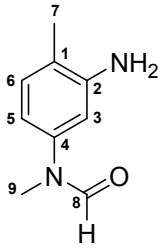
Note: Signal duplications in NMR spectra are indicative for the presence of rotamers in solution.[12, 13]

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{12}H_{16}N_2O_3+Na]^+$: 259.1053, found: 259.1053

R$_f$ (SiO_2, DCM:EA 1:1) = 0.49

HPLC: R_t = 10.2 min

Molecular formula of 10: $C_9H_{12}N_2O$ (M = 164.21 g/mol)



^{1}H-NMR (MeOD-*d_4*, 400.17 MHz, 296 K): δ [ppm] = 8.33, 8.25 (s, s, 1H, *H8*), 7.01 (d, $^3J_{H,H}$ = 7.9 Hz, 1H, *H6*), 6.59 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, *H3*), 6.48 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 2.2 Hz, 1H, *H5*), 3.30, 3.22 (s, s, 3H, *H9*), 2.13 (s, 3H, *H7*).

^{13}C{^{1}H}-NMR (MeOD-*d_4*, 100.62 MHz, 296 K): δ [ppm] = 164.3 (*C8*), 148.2 (*C2*), 142.1 (*C4*), 132.0 (*C6*), 122.4 (*C1*), 112.8 (*C5*), 110.1 (*C3*), 32.6 (*C9*), 17.0 (*C7*).

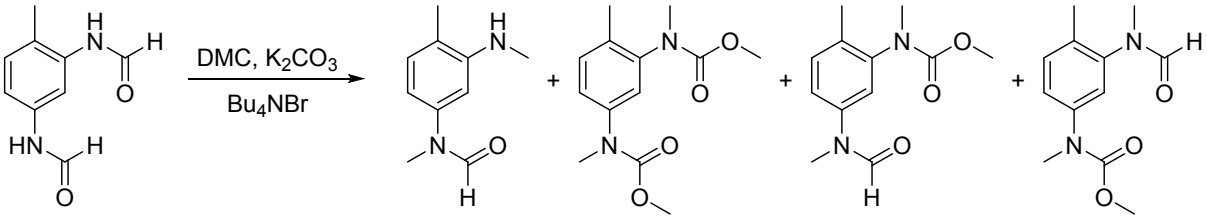
Note: Signal duplications in NMR spectra are indicative for the presence of rotamers in solution.[12, 13]

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_9H_{13}N_2O]^+$: 165.1022, found: 165.1022

R_f (SiO_2, DCM:EA 1:1) = 0.39

HPLC: R_t = 5.8 min

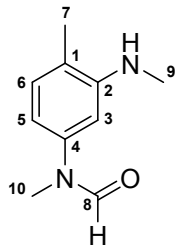
2.11 Identification of *N*-methyl-*N*-[4-methyl-3-(methylamino)phenyl]- formamide (11) and methyl methyl[4-methyl-3-(*N*-methyl-formamido)phenyl]carbamate (12)



2 **11** **6** **9** **12**

According to GP2 (see 2.7) 891 mg (5.0 mmol) *N,N′*-(4-methyl-1,3-phenylene)diformamide (**2**) were reacted with 20 mL (238 mmol) dimethyl carbonate (DMC), 500 mg (3.6 mmol) potassium carbonate and 100 mg (0.3 mmol) tetrabutylammonium bromide. After a reaction time of 14 days, the crude product was mixed with Celite® and the solvent was removed by rotary evaporation to get a dry powder. Purification by column chromatography (SiO_2, DCM: EA 10:1) afforded 90 mg of a yellowish oil which was analyzed by HPLC, NMR and HR-MS. In this way, **11** and **6** (see 2.8) at a ratio of 14:86 were identified as the components of this inseparable mixture. Continuing column chromatography resulted in further 483 mg of a yellowish oil which was also analyzed by HPLC, NMR and HR-MS. In this way, **12** and **9** (see 2.10) at a ratio of 83:27 were identified as the components of this second inseparable mixture. The yield of **12** is therefore 34 %.

Molecular formula of 11: $C_{10}H_{14}N_2O$ (M = 178.24 g/mol)

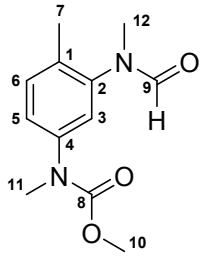


^{1}H-NMR (MeOD-d_4, 400.17 MHz, 296 K): δ [ppm] = 8.52 (s, 1H, *H8*), 7.15 (d, $^3J_{H,H}$ = 7.6 Hz, 1H, *H6*), 6.56 (d, 1H, $^3J_{H,H}$ = 7.6 Hz, 1H, *H5*), 6.55 (s, 1H, *H3*), 3.40 (s, 1H, *H10*), 2.99 (s, 1H, *H9*), 2.25 (s, 1H, *H7*).

^{13}C{^{1}H}-NMR (MeOD-d_4, 100.62 MHz, 296 K): δ [ppm] = 164.2 (*C8*), 150.0 (*C2*), 142.5 (*C4*), 131.3 (*C6*), 121.9 (*C1*), 111.1 (*C5*), 104.4 (*C3*), 32.7 (*C10*), 30.6 (*C9*), 16.6 (*C7*).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{10}H_{14}N_2O+Na]^+$: 201.0998, found: 201.0996
HPLC: R_t = 10.5 min

Molecular formula of 12: $C_{12}H_{16}N_2O_3$ (M = 236.27 g/mol)



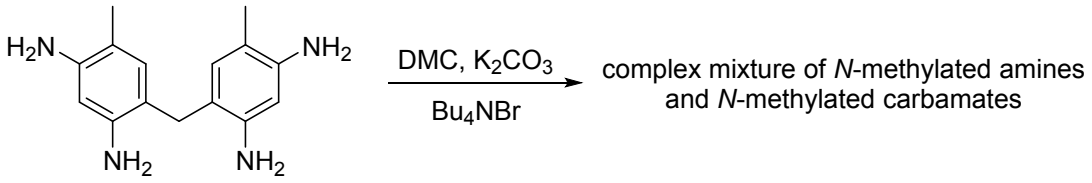
^{1}H-NMR (MeOD-d_4, 400.17 MHz, 296 K**)**: δ [ppm] = 8.28, 8.10 (s, s, 1H, *H9*), 7.37-7.14 (m, 3H, *H3/H5/H6*), 3.69, 3.67 (s, s 3H, *H10*), 3.30, 3.29, 3.18 (s, s, s 6H, H11/H12), 2.25 (s, 3H, *H7*).

^{13}C{^{1}H}-NMR (MeOD-d_4, 100.62 MHz, 298 K): δ [ppm] = 164.9 (*C9*), 164.1 (*C9*), 157.3 (*C8*), 143.5 (*C4*), 143.4 (*C4*), 142.1 (*C2*), 134.4 (*C1*), 134.5 (*C1*), 132.7 (*C6*), 132.3 (*C6*), 126.8 (*C3/C5*), 126.6 (*C3/C5*), 126.1 (*C3/C5*), 125.4 (*C3/C5*), 53.5 (*C10*), 38.0 (*C11*), 33.4 (*C12*), 17.4 (*C7*)

Note: Signal duplications in NMR spectra are indicative for the presence of rotamers in solution.[12, 13]

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{12}H_{16}N_2O_3+Na]^+$: 259.1053, found: 259.1051
HPLC: R_t = 10.1 min

2.12 Reaction of 6,6'-methylenebis(4-methyl-1,3-benzenediamine) (13) with dimethyl carbonate (DMC)



13

Following a literature procedure, 6,6'-methylenebis(4-methyl-1,3-benzenediamine) (**13**) was synthesized from TDA and formaldehyde in the precence of sulphuric acid.[16] Afterwards, according to GP2 (see 2.7) 641 mg (2.5 mmol) **13** were reacted with 20 mL (238 mmol) dimethyl carbonate (DMC), 500 mg (3.6 mmol) potassium carbonate and 100 mg (0.3 mmol) tetrabutylammonium bromide. After a reaction time of 16 days, the crude product was mixed with Celite® and the solvent was removed by rotary evaporation to get a dry powder. The complex product mixture could not be separated by column chromatography.

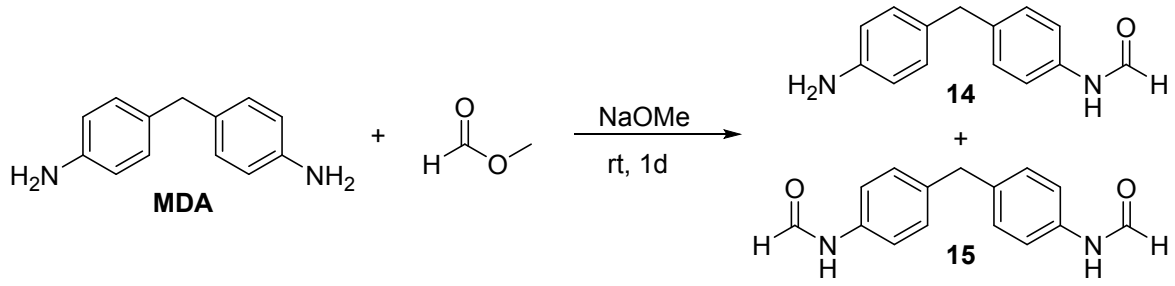
Characteristic data of the complex product mixture:

HPLC: R_t = 16.5 min, 17.2 min, 17.5 min, 18.2 min, 18.6 min and 18.7 min.

^{1}H-NMR (MeOD-*d_4*, 400.17 MHz, 296 K): δ [ppm] = 3.8 (aryl-CH_2-aryl); 3.7-3.4 (OMe, carbamate); 3.3-3.1 (N-Me, carbamate); 2.6 (NMe_2); 2.2 (aryl-CH_3).

^{13}C{^{1}H}-NMR (MeOD-*d_4*, 100.62 MHz, 296 K): δ [ppm] = 158.2, 158.1, 157.9, 157.8, 157.7, 157.6, 157.5 (C=O, carbamate); 153.0 (C-NMe_2); 53.6, 53.5, 53.4 (OMe, carbamate); 45.5, 45.4 (NMe_2); 37.9, 37.8 (N-Me, carbamate); 36.5-33.8, 32.9, 32.7 (aryl-CH_2-aryl); 17.3, 17.2, 17.1-16.8 (aryl-CH_3).

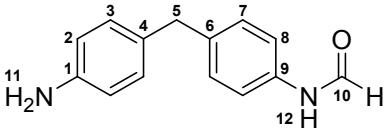
2.13 Synthesis of *N*-[4-(4-aminobenzyl)phenyl]formamide (14) and *N*,*N'*-[methylenebis(4,1-phenylene)]diformamide (15)



3.96 g (20.0 mmol) 4,4'-methylenedianiline (MDA) were suspended in 10.0 mL (162 mmol) methyl formate and 230 µL (1.0 mmol, 5 mol%) NaOMe (25 wt% in MeOH) and 2 mL MeOH were added. The reaction mixture was stirred at room temperature and the completion of the reaction was checked by thin layer chromatography. After 24 hours the reaction was finished, Celite® was added and the solvent was removed under vacuum. Purification of the crude product by column chromatography (SiO_2, DCM: EA 5:1) yielded 1.83 g (8.1 mmol, 41 %) of **14** as a yellowish solid. Continuing column chromatography (SiO_2, DCM: EA 2:1 → EA) resulted in 1.94 g (7.6 mmol, 38 %) of **15** as a colorless solid.

Molecular formula of 14: $C_{14}H_{14}N_2O$ (M = 226.28 g/mol)

Mp.: 127-128 °C



^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): δ [ppm] = 10.08 ppm (s, br, 1H, *H12 cis*), 10.04 ppm (d, $^3J_{H,H}$ = 11.1 Hz, 1H, *H12 trans*), 8.70 ppm (d, $^3J_{H,H}$ = 11.1 Hz, 1H, *H10 trans*), 8.23 ppm (d, $^3J_{H,H}$ = 1.9 Hz, 1H, *H10 cis*), 7.47 ppm (d, $^3J_{H,H}$ = 8.5 Hz, 1H, *H8 cis*), 7.11 ppm (d, $^3J_{H,H}$ = 8.5 Hz, 1H, *H7 cis + trans*), 7.08 ppm (d, $^3J_{H,H}$ = 8.5 Hz, 1H, *H8 trans*), 6.84 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, *H3*), 6.48 ppm (td, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 2.3 Hz, 1H, *H2*), 4.85 (s, br, 2H, *H11*), 3.69 (s, 2H, *H5*).

^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): δ [ppm] = 162.5 (*C10 trans*), 159.3 (*C10 cis*), 146.6 (*C1*), 137.9 (*C4*), 137.7 (*C6*), 136.0 (*C9*), 129.4 (*C3/C7 trans*), 129.0 (*C3/C7 cis*), 128.8 (*C3/C7 cis*), 128.3 (*C3/C7 trans*), 119.2 (*C8 cis*), 117.8 (*C8 trans*), 114.0 (*C2*), 40.1 (*C5* trans), 39.9 (*C5 cis*).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{14}H_{15}N_2O]^+$ = 227.1179, found: 227.1170

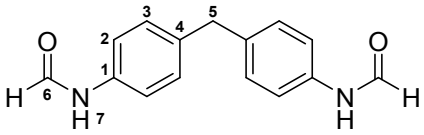
IR (ATR): 3387 (w), 3310 (w), 3214 (w), 3112 (w), 3088 (w), 3031 (w), 3002 (w), 2979 (w), 2911 (w), 2891 (w), 2877 (w), 1678 (s), 1610 (m), 1594 (m), 1510 (s), 1491 (m), 1438 (w), 1409 (w), 1390 (w), 1310 (s), 1269 (m), 1218 (w), 1180 (w), 1111 (w), 1088 (w), 1017 (w), 946 (w), 910 (w), 840 (m), 807 (s), 765 (m), 693 (m), 650 (m), 639 (m), 625 (m), 568 (m), 548 (m), 506 (s), 474 (m), 424 (m).

$\boldsymbol{R_f}$ (SiO_2, EA) = 0.66

HPLC: R_t = 10.7 min

Molecular formula of 15: $C_{15}H_{14}N_2O_2$ (M = 254.29 g/mol)

Mp.: 190 °C (Lit.: 190 °C,[17] 191 °C[18])



^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): δ [ppm] = 10.10 ppm (s, 1H, *H7 cis*), 10.05 ppm (d, $^3J_{H,H}$ = 11.0 Hz, 1H, *H7 trans*), 8.70 ppm (d, $^3J_{H,H}$ = 11.0 Hz, 1H, *H6 trans*), 8.23 ppm (d, $^3J_{H,H}$ = 1.9 Hz, 1H, *H6 cis*), 7.49 ppm (d, $^3J_{H,H}$ = 8.4 Hz, 2H, *H2 cis*), 7.14 ppm (d, $^3J_{H,H}$ = 8.4 Hz, 2H, *H3 cis*), 7.14 ppm (d, $^3J_{H,H}$ = 8.4 Hz, 2H, *H3 trans*), 7.09 ppm (d, $^3J_{H,H}$ = 8.4 Hz, 2H, *H2 trans*), 3.83 (s, 2H, *H5*).

^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): δ [ppm] = 162.5 (*C6 trans*), 159.4 (*C6 cis*), 136.8 (*C1 trans*), 136.6 (*C1 cis*), 136.3 (*C4 trans*), 136.2 (*C4 cis*), 129.5 (*C3 trans*), 129.0 (*C3 cis*), 119.3 (*C2 cis*), 117.8 (*C2 trans*), 40.1 (*C5*).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{15}H_{14}N_2O_2+Na]^+$ = 277.0947, found: 277.0948

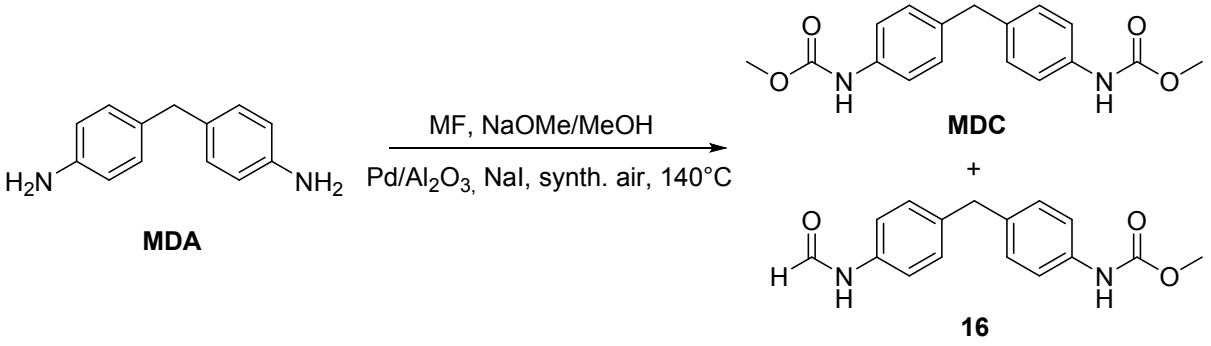
IR (ATR): 3180 (w), 3108 (w), 3040 (w), 3018 (w), 2920 (w), 2873 (w), 1683 (s), 1609 (m), 1517 (s), 1489 (m), 1434 (w), 1413 (m), 1400 (m), 1292 (s), 1225 (m), 1152 (w), 1114 (m), 1040 (m), 1021 (w), 943 (w), 910 (w), 886 (w), 858 (m), 841 (m), 807 (s), 785 (s), 721 (m), 642 (w), 619 (w), 529 (s), 477 (m), 451 (w), 414 (w).

$\boldsymbol{R_f}$ (SiO_2, EA) = 0.53

HPLC: R_t = 11.2 min

The analytical data correspond to the values in literature.[9, 19-22]

2.14 Oxidative carbonylation of 4,4'-methylenedianiline (MDA)



According to GP1 (see 2.1) the oxidative carbonylation was performed using 496 mg (2.5 mmol) 4,4'-methylenedianiline (MDA) dissolved in 5 mL MeOH, 30 mL MF (485 mmol), 115 µL (0.5 mmol) NaOMe (25 wt% in MeOH), 23.4 mg (0.011 mmol) Pd(5%)/Al_2O_3 and 90 mg (0.6 mmol) NaI. The reaction was stopped after two hours. The experiment was repeated twice with the reaction times of 3.5 and five hours. In a fourth experiment 496 mg (2.5 mmol) MDA were solved in 10 mL MeOH and the reaction time was again two hours. Filtration of the combined reaction mixtures of the four experiments resulted in 1.21 g of a yellowish solid. The combined reaction solution was analyzed by thin layer chromatography (TLC) and by HPLC, mixed with Celite® and the solvent was removed by rotary evaporation to get a dry powder. Purification by column chromatography (SiO_2, DCM: EA 10:1) afforded 663.6 mg (2.1 mmol, 21 %) dimethyl [methylenebis(4,1-phenylene)]dicarbamate (MDC) as a colorless solid. Afterwards, as second fraction 371.2 mg (1.3 mmol, 13 %) methyl [4-(4-formamidobenzyl)phenyl]carbamate (**16**) were obtained as a yellowish solid.

Characteristic data of the solid residue from filtration:

The following characteristic data indicate the presence of urea derivatives when compared with 1,3-bis(4-benzylphenyl)urea[23] or 1,3-diphenylurea[24]:

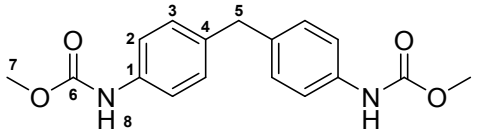
^{1}H-NMR (DMSO-d_6, 299.61 MHz, 296 K): δ [ppm] = 8.60 (s, N*H*).

^{13}C-NMR (DMSO-d_6, 75.34 MHz, 296 K): δ [ppm] = 152.6 (*C*=O).

IR (ATR): 3307 (s), 1639 (s), 1595 (s), 1548 (s), 1511 (s), 1408 (m), 1304 (m), 1239 (m), 808 (m), 781 (m).

Molecular formula of MDC: $C_{17}H_{18}N_2O_4$ (M = 314.34 g/mol)

Mp.: 185-186 °C (Lit.: 184 °C[6])



^{1}H-NMR (DMSO-*d_6*, 600.07 MHz, 296 K): δ [ppm] = 9.53 (s, br, 2H, *H8*), 7.35 (d, $^3J_{H,H}$ = 8.4 Hz, 4H, *H2*), 7.10 (d, $^3J_{H,H}$ = 8.4 Hz, 4H, *H3*), 3.78 (s, 2H, *H5*), 3.64 (s, 6H, *H7*).

^{13}C{^{1}H}-NMR (DMSO-*d_6*, 150.89 MHz, 296 K): δ [ppm] = 154.0 (*C6*), 137.1 (*C1*), 135.5 (*C4*), 128.9 (*C3*), 118.4 (*C2*), 51.5 (*C7*), 40.1 (*C5*).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{17}H_{18}N_2O_4+Na]^+$ = 337.1159, found: 337.1158

IR (ATR): 3328 (m), 2946 (w), 1726 (w), 1703 (s), 1613 (w), 1599 (m), 1527 (s), 1439 (m), 1410 (m), 1316 (m), 1278 (w), 1232 (s), 1205 (m), 1195 (m), 1175 (m), 1125 (w), 1110 (w), 1070 (s), 1017 (w), 962 (w), 938 (w), 915 (w), 858 (w), 846 (w), 835 (w), 818 (m), 778 (w), 765 (m), 735 (w), 725 (w), 705 (w), 676 (m), 640 (m), 625 (m), 605 (m), 577 (w), 510 (s).

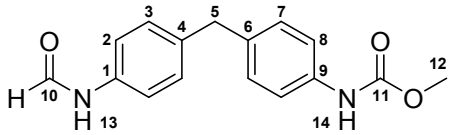
R_f (SiO_2, DCM:EA 1:1) = 0.89

HPLC: R_t = 16.7 min

The analytical data correspond to the values in literature.[6, 7]

Molecular formula of 16: $C_{16}H_{16}N_2O_3$ (M = 284.32 g/mol)

Mp.: 143-144 °C



^{1}H-NMR (DMSO-*d_6*, 600.07 MHz, 296 K): δ [ppm] = 10.10 (s, br, 1H, *H13*), 9.54 (s, br, 1H, *H14*), 8.24 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, *H10*), 7.49 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *H2*), 7.36 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *H8*), 7.14 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *H3*), 7.10 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *H7*), 3.81 (s, 2H, *H5*), 3.37 (s, 3H, *H12*) (*cis*-rotamer). δ [ppm] = 10.05 (d, $^3J_{H,H}$ = 11.0 Hz, 1H, *H13*), 9.54 (s, br, 1H, *H14*), 8.71 (d, $^3J_{H,H}$ = 11.0 Hz, 1H, *H10*), 7.36 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *H8*), 7.14 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *H3*), 7.10 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *H7*), 7.09 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *H2*) 3.81 (s, 2H, *H5*), 3.37 (s, 3H, *H12*) (*trans*-rotamer).

^{13}C-NMR (DMSO-d_6, 150.89 MHz, 296 K): δ [ppm] = 159.4 (*C10*), 154.0 (*C11*), 137.1 (*C9*), 136.8 (*C4*), 136.2 (*C1*), 135.4 (*C6*), 129.0 (*C3*), 128.9 (*C7*), 119.3 (*C2*), 118.4 (*C8*), 51.5 (*C12*), 39.9 (*C5*) (*cis*-rotamer). δ [ppm] = 162.5 (*C10*), 154.0 (*C11*), 137.1 (*C9*), 137.0 (*C1*), 136.8 (*C4*), 135.4 (*C6*), 129.0 (*C3*), 128.9 (*C7*), 118.4 (*C8*), 117.8 (*C2*), 51.5 (*C12*), 39.9 (*C5*) (*trans*-rotamer).

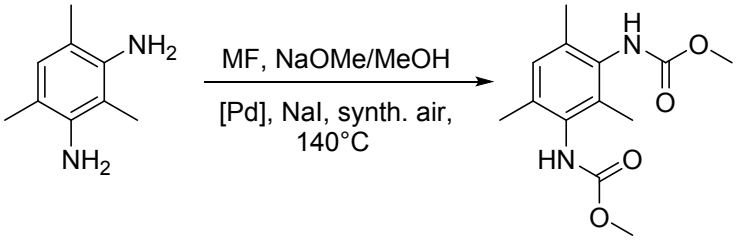
HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{16}H_{16}N_2O_3+Na]^+$ = 307.1053, found: 307.1054

IR (ATR): 3343 (w), 3291 (w), 3195 (w), 3117 (w), 3041 (w), 2949 (w), 2918 (w), 2843 (w), 2782 (w), 1738 (w), 1713 (m), 1685 (s), 1610 (m), 1599 (m), 1532 (s), 1514 (s), 1436 (m), 1410 (m), 1294 (s), 1221 (s), 1197 (m), 1114 (w), 1070 (s), 1039 (m), 1021 (m), 954 (w), 912 (w), 885 (w), 854 (m), 812 (m), 776 (s), 766 (s), 732 (m), 721 (m), 664 (m), 639 (m), 623 (m), 588 (m), 520 (s), 510 (s), 473 (s), 435 (m).

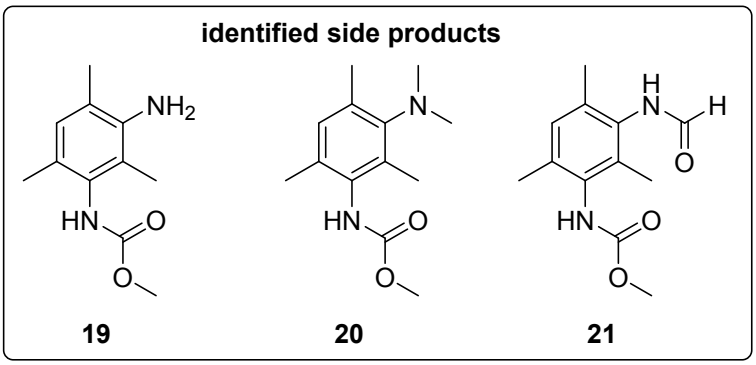
R_f (SiO_2, DCM:EA 1:1) = 0.63

HPLC: R_t = 14.5 min

2.15 Oxidative carbonylation of 2,4,6-trimethyl-1,3-benzenediamine (17)



17 **18**



19 **20** **21**

According to GP1 (see 2.1) the oxidative carbonylation was performed using 750 mg (5.0 mmol) 2,4,6-trimethyl-1,3-benzenediamine (**17**) dissolved in 5 mL MeOH, 30 mL MF (485 mmol), 115 µL (0.5 mmol) NaOMe (25 wt% in MeOH), 23.4 mg (0.011 mmol) Pd(5%)/Al_2O_3 and 90 mg (0.6 mmol) NaI. The reaction was stopped after two hours. The experiment was repeated twice with the reaction times of 3.5 and five hours. Using 23.4 mg (0.011 mmol) Pd(5%)/SiO2 as catalyst three further experiments were performed with the same reaction times of two, 3.5 and five hours. Filtration of the combined reaction mixtures of the six experiments resulted in 1.47 g of a colorless solid. The combined reaction solution was analyzed by thin layer chromatography (TLC) and by HPLC, mixed with Celite® and the solvent was removed by rotary evaporation to get a dry powder. Purification by column chromatography (SiO_2, DCM: EA 10:1 → DCM: EA 5:1 → EA) afforded 1.44 g (5.4 mmol, 18 %) dimethyl (2,4,6-trimethyl-1,3-phenylene)dicarbamate (**18**) as a colorless solid. Afterwards, as second fraction a brownish oil (371.2 mg) was isolated which was analyzed by HPLC, NMR and HR-MS. This way, methyl (3-amino-2,4,6-trimethylphenyl)carbamate (**19**) was identified as the main component of this inseparable mixture, together with lower quantities of **18** and methyl (3-dimethylamino-2,4,6-trimethylphenyl)carbamate (**20**). 146 mg (0.6 mmol, 2 %) methyl (3-formamido-2,4,6-trimethylphenyl)carbamate (**21**) were obtained as third fraction as a yellowish solid.

Characteristic data of the solid residue from filtration:

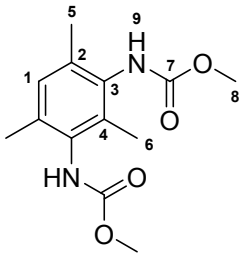
The following characteristic data indicate the presence of urea derivatives when compared with 1,3-dimesitylurea[25, 26]:

^{1}H-NMR, ^{13}C{^{1}H}-NMR: not measurable due to insolubility.

IR (ATR): 3257 (w), 2920 (w), 2857 (w), 1627 (s), 1545 (s), 1483 (m), 1459 (m), 1323 (m), 1223 (m), 774 (m), 514 (m).

Molecular formula of 18: $C_{13}H_{18}N_2O_4$ (M = 266.30 g/mol)

Mp.: 216-217 °C



^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): δ [ppm] = 8.67, 8.40 (s, 2H, *H9*), 6.94 (s, 1H, *H1*), 3.62, 3.50 (s, 6H, *H8*), 2.11 (s, 6H, *H5*), 1.99 (s, 3H, *H6*).

^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): δ [ppm] = 155.2, 154.9 (*C7*), 133.9 (*C3/C4*), 133.1 (*C3/C4*), 132.8 (*C2*), 128.6 (*C1*), 51.6 (*C8*), 17.8 (*C5*), 13.4 (*C6*).

Note: Signal duplications in NMR spectra are indicative for the presence of rotamers in solution.[12, 13]

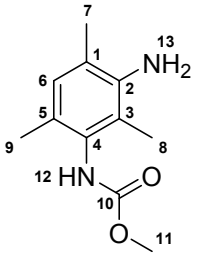
HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{13}H_{18}N_2O_4+Na]^+$ = 289.1159, found: 289.1153

IR (ATR): 3265 (m), 3025 (w), 2996 (w), 2952 (w), 2925 (w), 1696 (s), 1516 (s), 1485 (m), 1455 (m), 1432 (m), 1377 (w), 1269 (m), 1243 (s), 1186 (m), 1143 (m), 1074 (m), 1052 (m), 1035 (m), 1017 (m), 869 (w), 806 (w), 777 (m), 744 (w), 699 (m), 673 (m), 583 (w), 558 (w).

R_f (SiO_2, DCM:EA 1:1) = 0.73

HPLC: R_t = 8.2 min

Molecular formula of 19: $C_{11}H_{16}N_2O_2$ (M = 208.26 g/mol)



^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): δ [ppm] = 8.47 (s, br, 1H, *H12*), 6.68 (s, 1H, *H6*), 4.39 (s, br, 2H, *H13*), 3.62 (s, 3H, *H11*), 2.06 (s, 3H, *H7*), 2.01 (s, 3H, *H9*), 1.93 (s, 3H, *H8*).

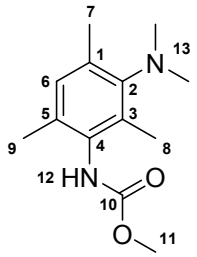
^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): δ [ppm] = 155.1 (*C10*), 142.4 (*C2*), 132.5 (*C4*), 128.5 (*C6*), 122.5 (*C5*), 119.3 (*C1*), 119.1 (*C3*), 51.4 (*C11*), 17.7 (*C7*), 17.4 (*C9*), 12.5 (*C8*).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{11}H_{17}N_2O_2]^+$ = 209.1285, found: 209.1286

R_f (SiO_2, DCM:EA 1:1) = 0.71

HPLC: R_t = 7.0 min

Molecular formula of 20: $C_{13}H_{20}N_2O_2$ (M = 236.32 g/mol)



^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): δ [ppm] = 8.56 (s, br, 1H, *H12*), 6.84 (s, 1H, *H6*), 3.64 (s, 3H, *H11*), 2.75 (s, 6H, *H13*), 2.22 (s, 3H, *H7*), 2.10 (s, 3H, *H8*), 2.08 (s, 3H, *H9*).

^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): δ [ppm] = 155.6 (*C10*), 147.3 (*C2*), 134.7 (*C1/C3/C4/C5*), 134.6 (*C1/C3/C4/C5*), 133.2 (*C1/C3/C4/C5*), 132.0 (*C1/C3/C4/C5*), 129.5 (*C6*), 51.5 (*C11*), 42.5 (*C13*), 18.6 (*C7*), 17.9 (*C9*), 13.6 (*C8*).

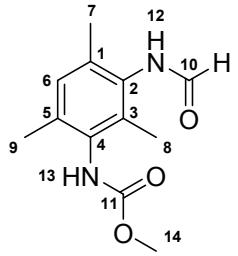
HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{13}H_{21}N_2O_2]^+$ = 237.1598, found: 237.1593

R_f (SiO_2, DCM:EA 1:1) = 0.71

HPLC: R_t = 18.6 min

Molecular formula of 21: $C_{12}H_{16}N_2O_3$ (M = 236.27 g/mol)

Mp.: 220-222 °C



^{1}H-NMR (DMSO-d_6, 400.17 MHz, 296 K): δ [ppm] = 9.43 (s, br, 1H, *H12*), 8.68 (s, br, 1H, *H13*), 8.23 (d, $^3J_{H,H}$ = 1.6 Hz, 1H, *H10*), 6.96 (s, 1H, *H6*), 3.62 (s, 3H, *H14*), 2.11 (s, 3H, *H7/H9*), 2.10 (s, 3H, *H7/H9*), 1.98 (s, 3H, *H8*) (*cis r*otamer). δ [ppm] = 9.27 (d, $^3J_{H,H}$ = 11.6 Hz, 1H, *H12*), 8.74 (s, br, 1H, *H13*), 7.91 (d, $^3J_{H,H}$ = 11.6 Hz, 1H, *H10*), 7.01 (s, 1H, *H6*), 3.50 (s, 3H, *H14*), 2.17 (s, 3H, *H7/H9*), 2.12 (s, 3H, *H7/H9*), 2.05 (s, 3H, *H8*) (*trans* rotamer).

^{13}C{^{1}H}-NMR (DMSO-d_6, 100.62 MHz, 296 K): δ [ppm] = 159.4, 154.9, 134.0, 133.0, 132.9, 132.8, 132.0, 128.6, 51.6, 18.1, 17.8, 13.6 (*cis*-rotamer). δ [ppm] = 164.7, 154.9, 134.4, 133.4, 133.3, 133.2, 132.5, 129.1, 51.6, 18.2, 17.8, 13.8 (*trans* rotamer).

HR-MS: (ESI$^+$): *m/z* (%): calculated for $[C_{12}H_{16}N_2O_3+Na]^+$ = 259.1053, found: 259.1048

IR (ATR): 3242 (m), 2952 (w), 2922 (m), 2853 (w), 1698 (s), 1661 (m), 1642 (s), 1591 (w), 1519 (s), 1484 (m), 1458 (m), 1396 (m), 1384 (m), 1318 (w), 1280 (m), 1256 (s), 1187 (m), 1105 (m), 1055 (s), 943 (w), 878 (w), 863 (m), 848 (w), 777 (w), 743 (m), 722 (m), 700 (m), 629 (w), 595 (w), 576 (w), 550 (w), 453 (w), 418 (w).

R_f (SiO_2, DCM:EA 1:1) = 0.24

HPLC: R_t = 5.0 min

2.16 Palladium-catalysts used in the oxidative carbonylation with MF

List of the Pd-catalysts purchased from commercial suppliers

Pd-catalyst	supplier	product number
Pd(10%)/C	Acros Organics	195030100
Pd(5%)/C	Sigma Aldrich	75992
Pd(5%)/$CaCO_3$	ABCR	AB155783
Pd(5%)/$BaSO_4$	ABCR	AB204140
Pd(5%)/Al_2O_3	Acros Organics	293030100
Pd(5%)/SiO_2	ABCR	AB155784
$PdCl_2$	ABCR	AB121380

Synthesis of not purchasable heterogeneous Pd-catalysts

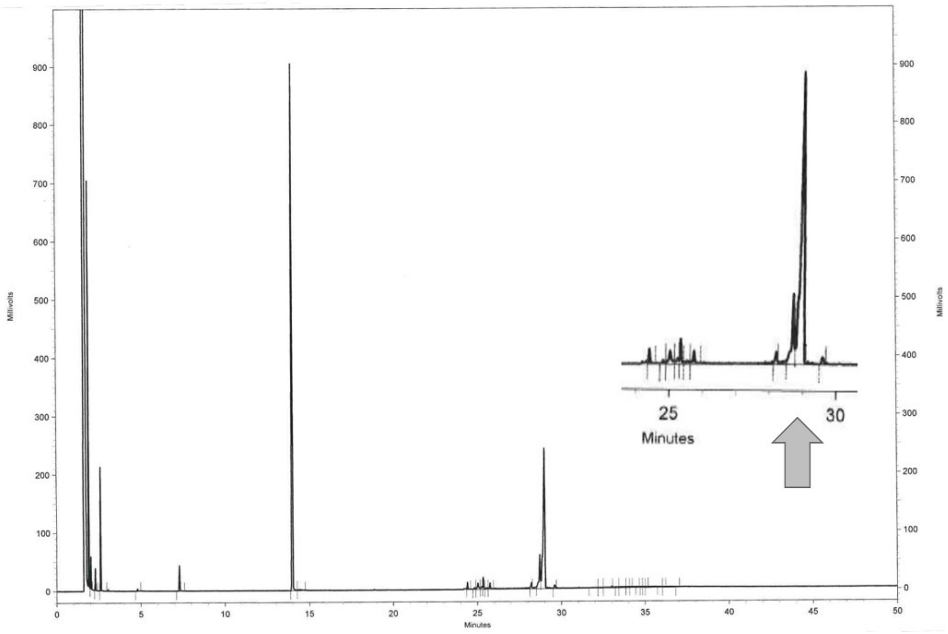
Pd(5%)/TiO2, Pd(5%)/CeO_2, Pd(5%)/ZrO_2 were synthesized in the laboratory according to literature.[27, 28] For this purpose, in a 250 mL round bottom flask 500 mg of the corresponding metal oxide were suspended in 100 mL deionized water. The flask was placed in an ultrasonic bath for one hour. Then 44 mg (0.25 mmol) $PdCl_2$ dissolved in 44 mL deionized water were added. The flask remained in the ultrasonic bath for another two hours. The solvent was removed under vacuum at 60 °C. The residue was dried in the vacuum drying oven at 110 °C for 24 hours. For calcination, using a heating rate of 3 °C/min the solid was brought to a temperature of 750 °C and left at this temperature for three hours. According to the production method the palladium content results from the quantities used.

List of the metal oxides purchased from commercial suppliers

metal oxide	supplier	product number
TiO_2	Sigma Aldrich	634662
CeO_2	Sigma Aldrich	544841
ZrO_2	Sigma Aldrich	544760

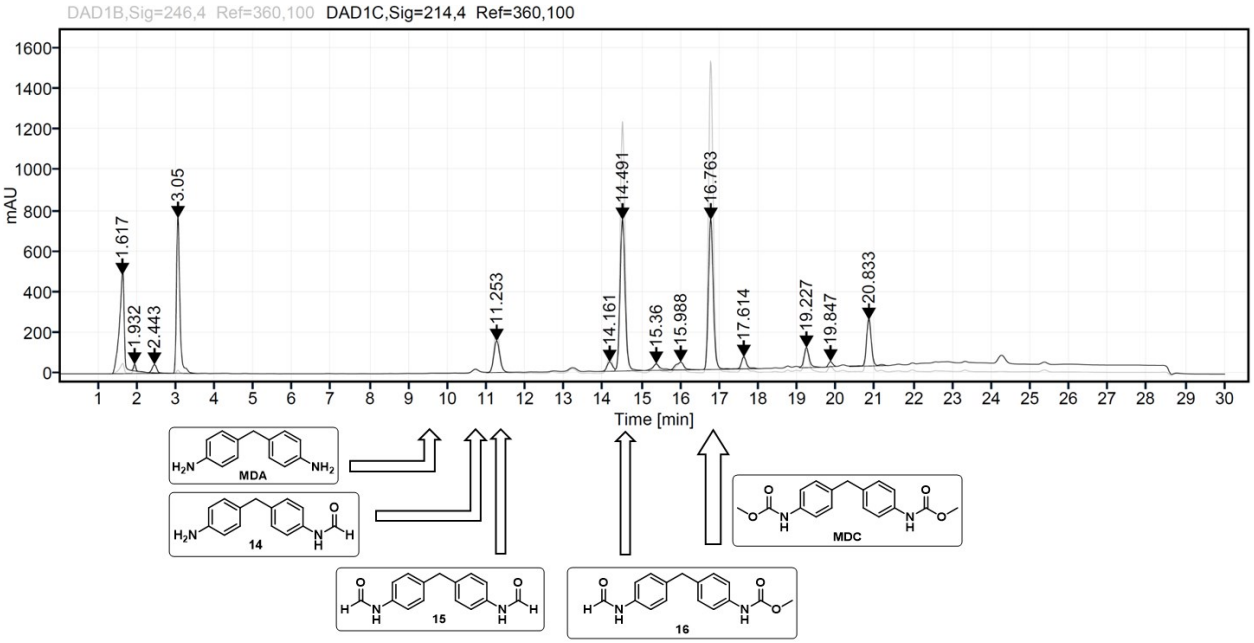
All catalysts were used without any pre-treatment as purchased or as obtained in the synthesis.

3. GC-analysis of the oxidative carbonylation of TDA with MF



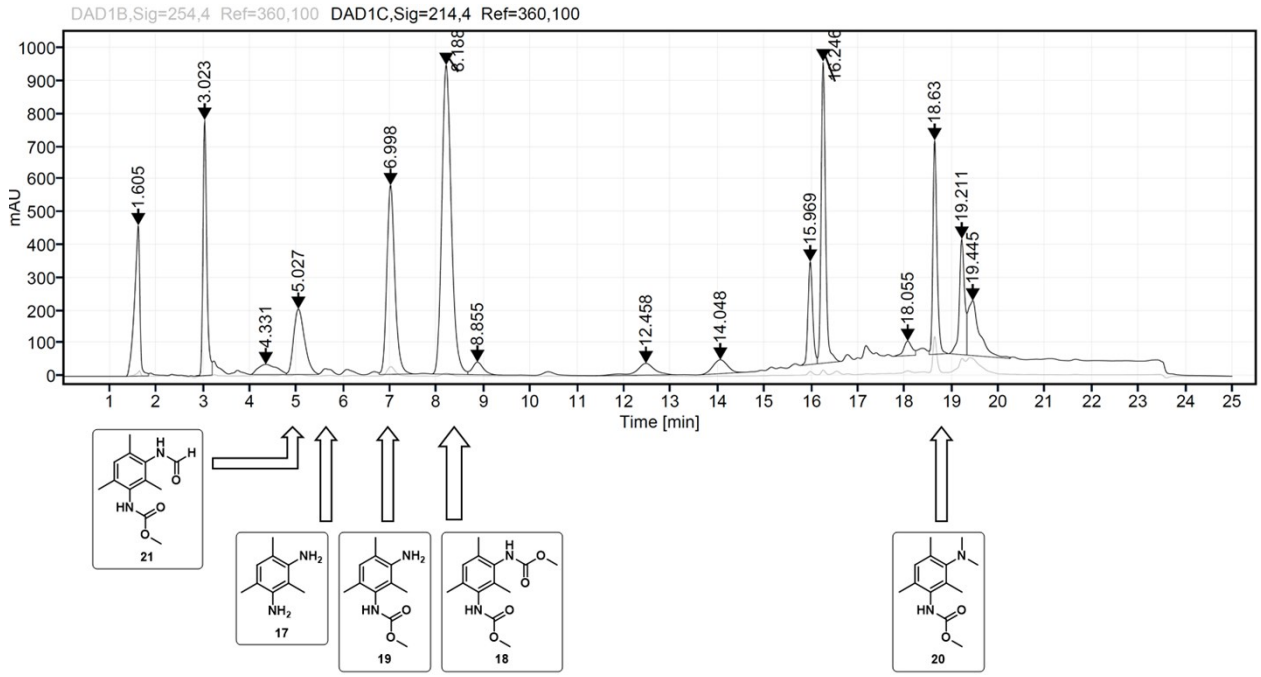
R_t = 14.0 min: methyl benzoate as internal standard. Reaction conditions: 5.0 mmol TDA in 5 mL MeOH; 30 mL MF; 0.5 mmol NaOMe; 0.011 mmol Pd(10%)/C; 0.6 mmol NaI; 4 h reaction time.

4. HPLC analysis of the oxidative carbonylation of MDA with MF



Reaction conditions: 2.5 mmol MDA in 5 mL MeOH; 30 mL MF; 0.5 mmol NaOMe; 0.011 mmol Pd(5%)/Al_2O_3; 2 h reaction time. Assignment of MDC and the identified side products **14-16**.

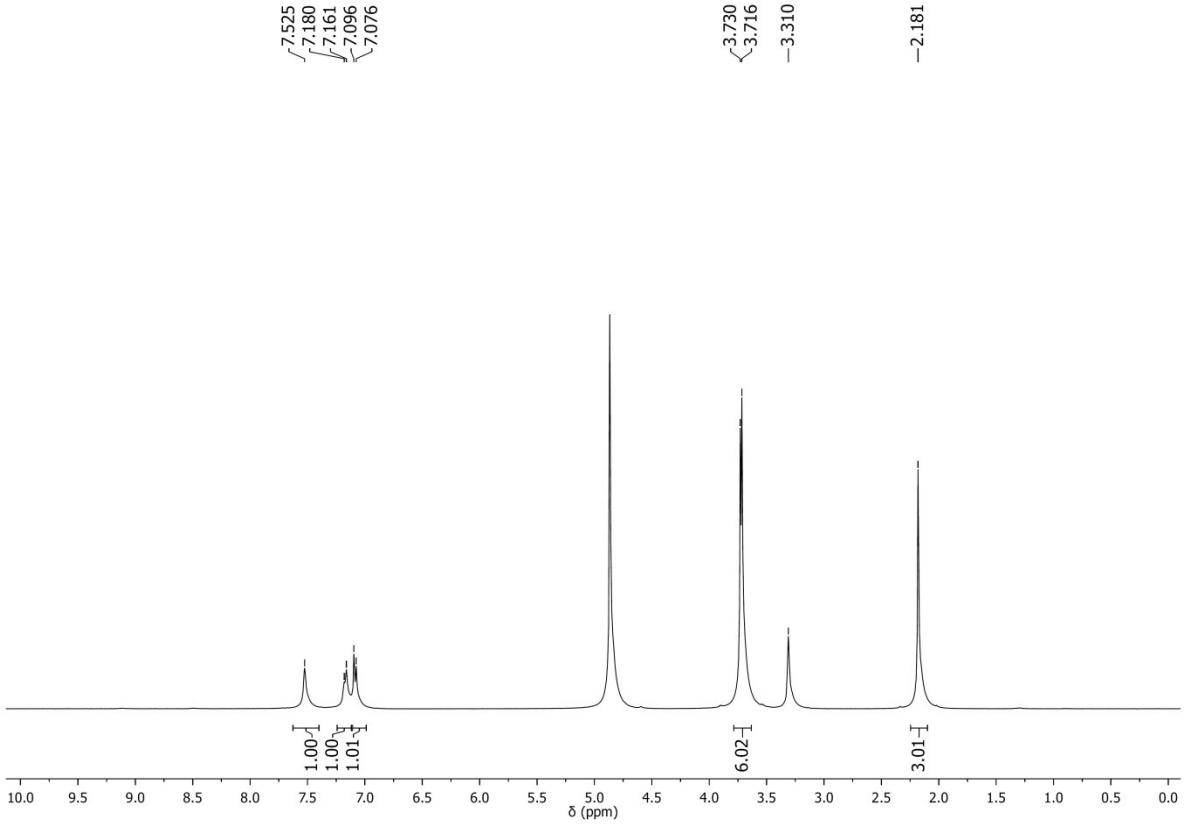
5. HPLC analysis of the oxidative carbonylation of 17 with MF



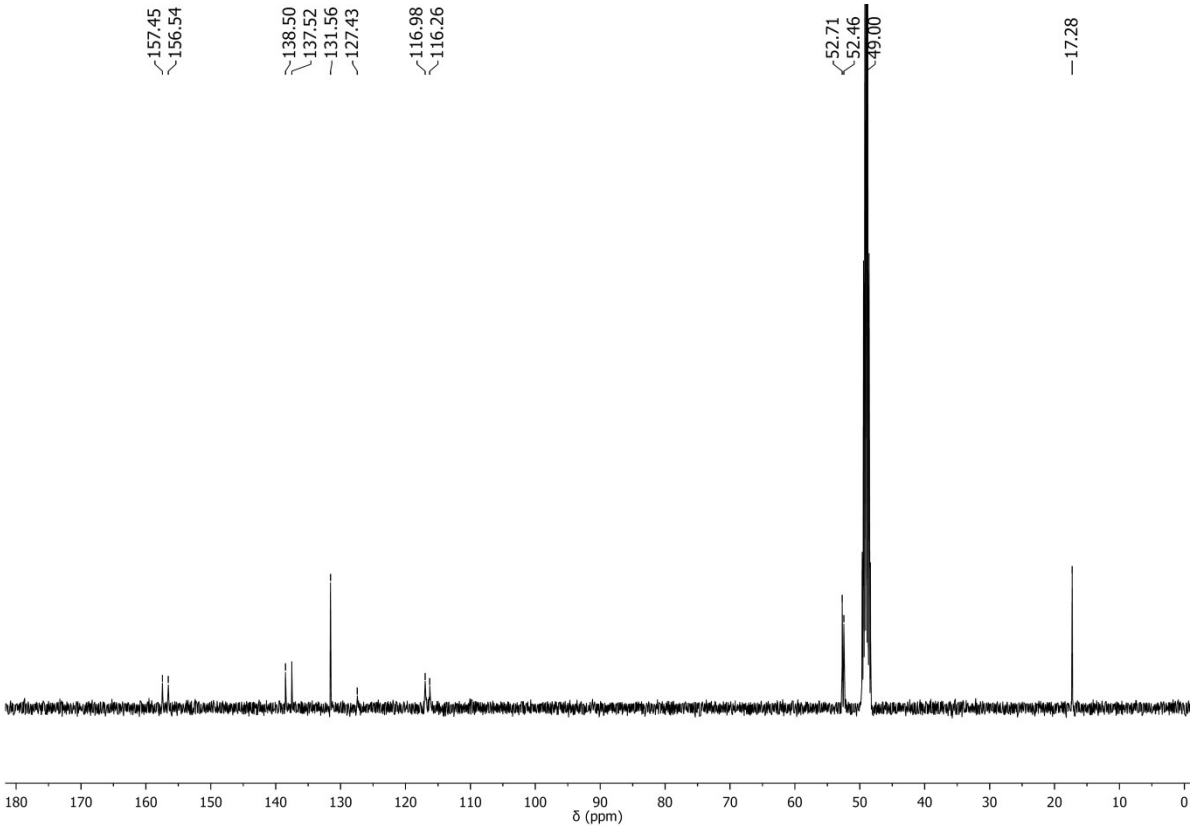
Reaction conditions: 5.0 mmol **17** in 5 mL MeOH; 30 mL MF; 0.5 mmol NaOMe; 0.011 mmol Pd(5%)/Al_2O_3; 3.5 h reaction time. Assignment of **18** and the identified side products **19**-**21**.

6. NMR-spectra

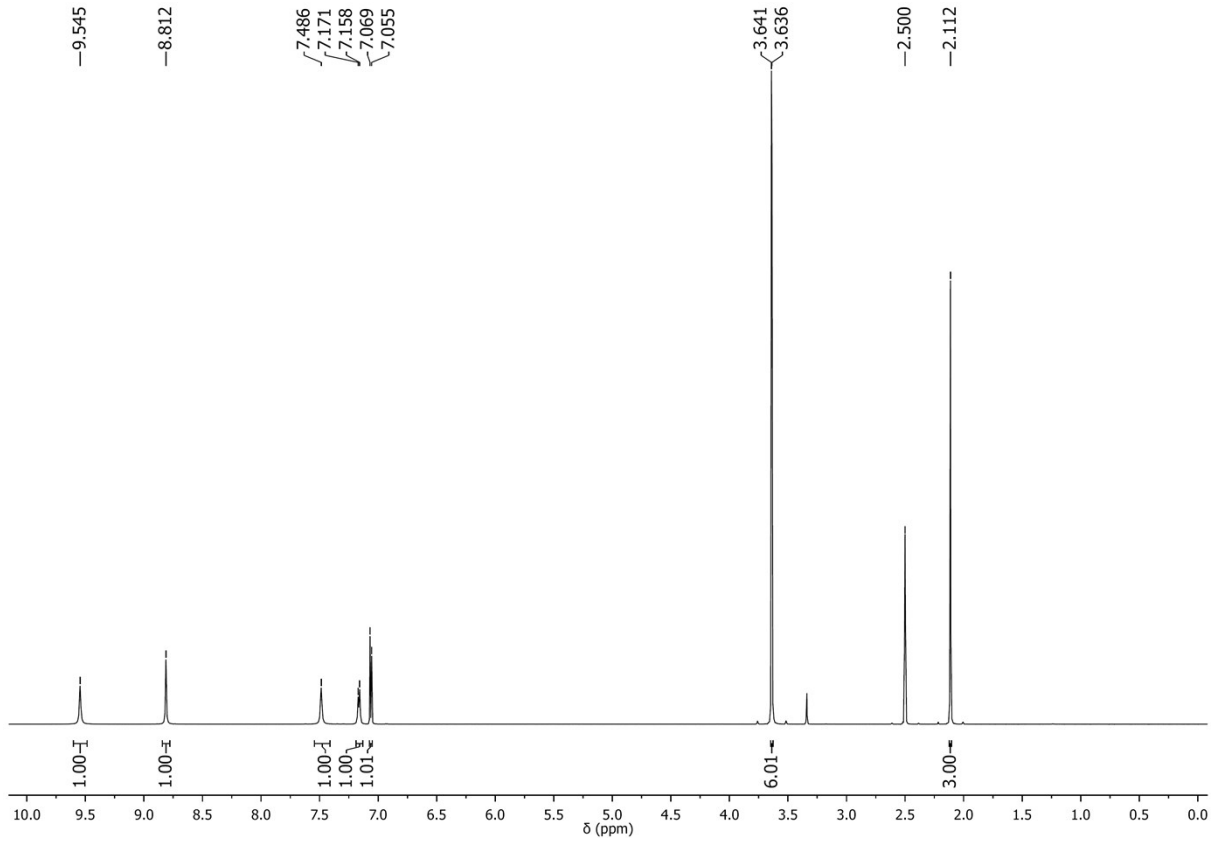
^{1}H-NMR (MeOD-d_4, 400.17 MHz, 296 K): TDC



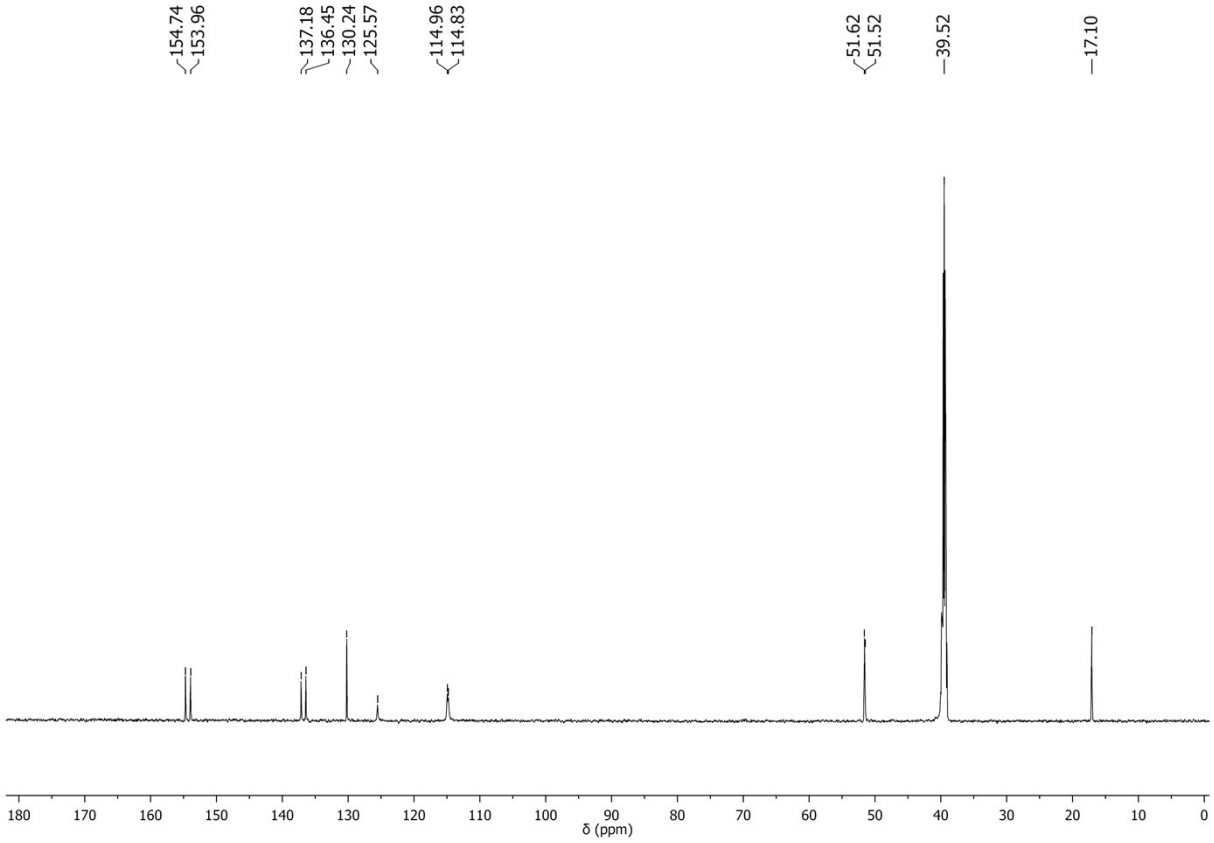
$^{13}C\{^{1}H\}$-NMR (MeOD-d_4, 100.62 MHz, 296 K): TDC



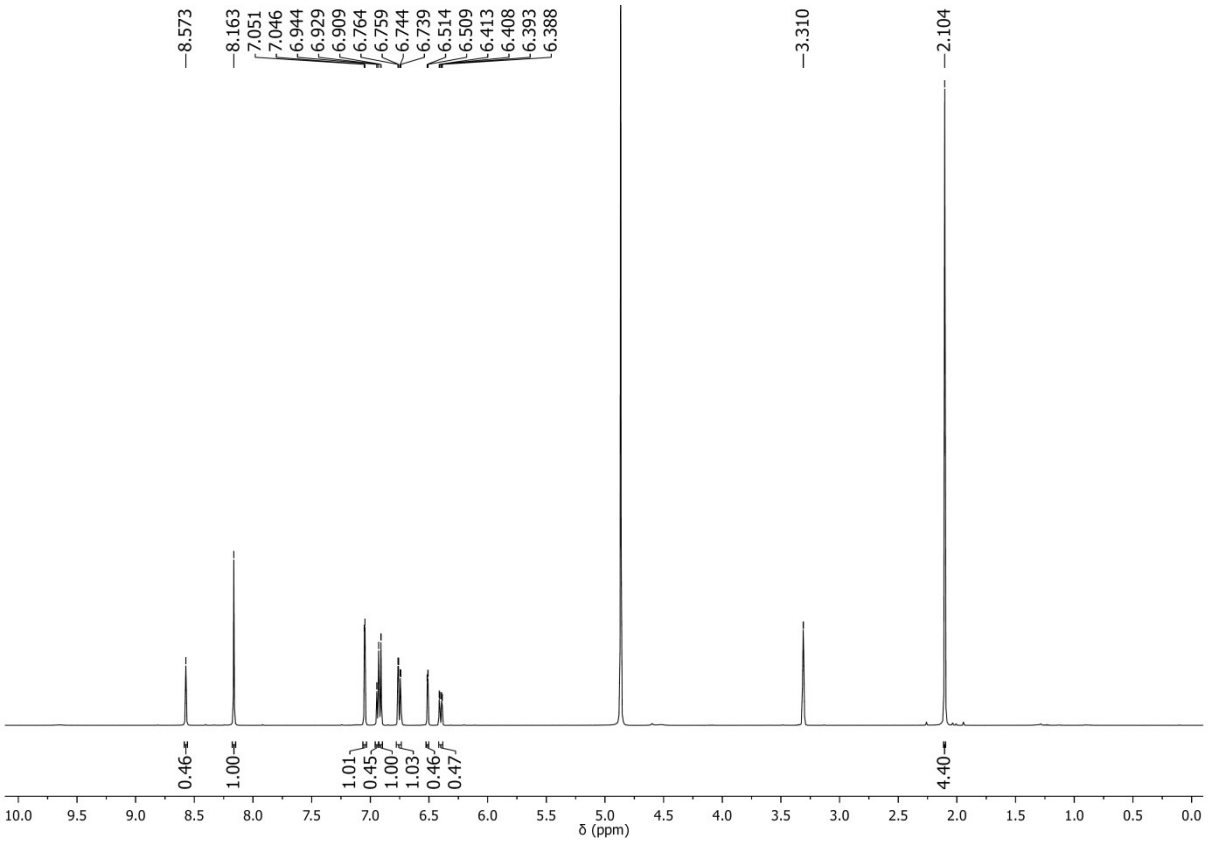
^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): TDC



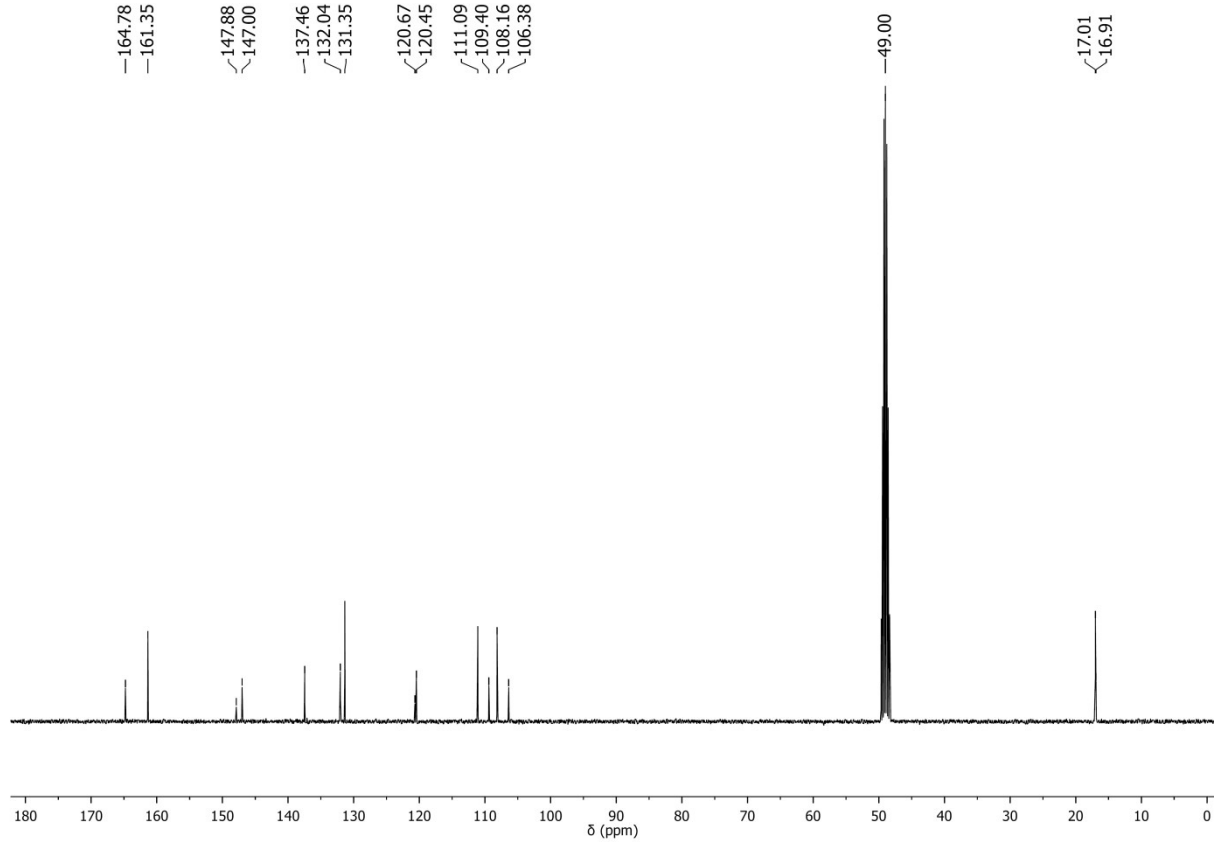
$^{13}C\{^{1}H\}$-NMR (DMSO-d_6, 150.89 MHz, 296 K, 296 K): TDC



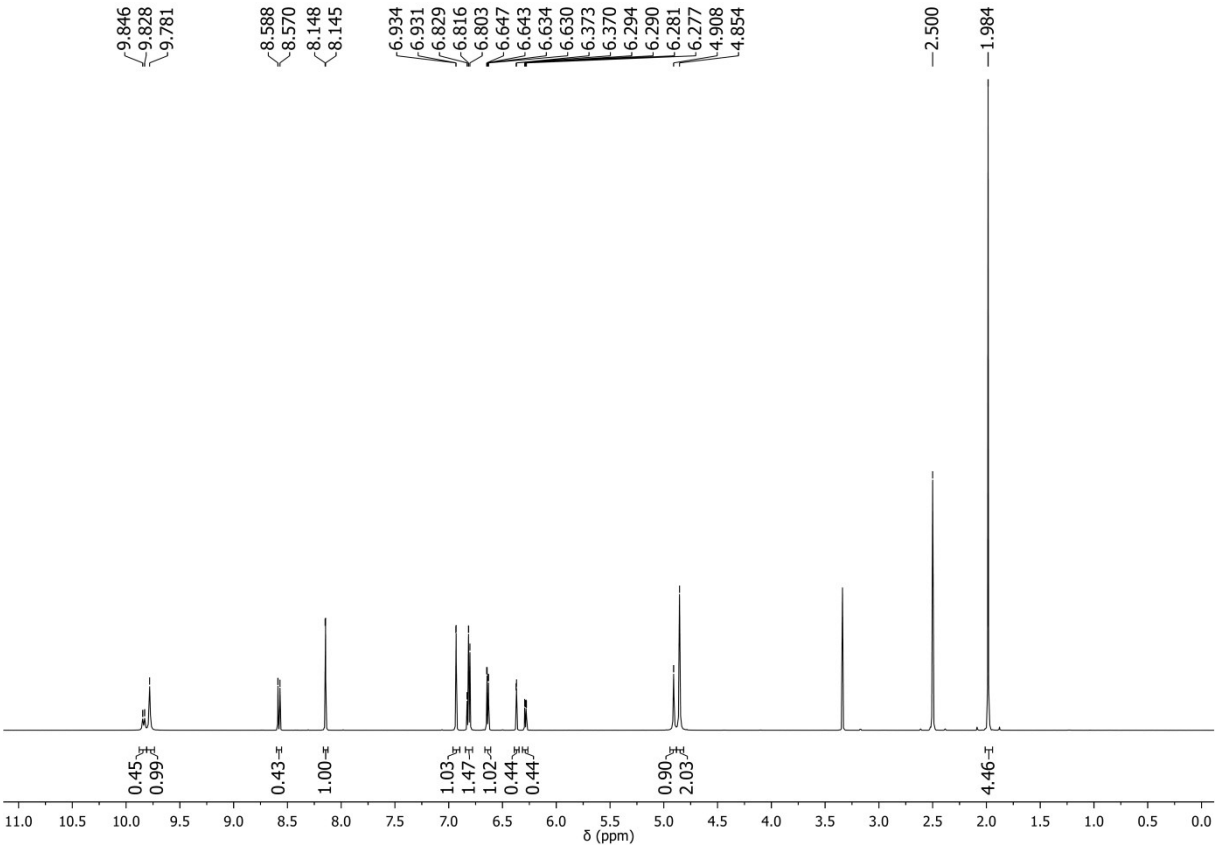
^{1}H-NMR (MeOD-d_4, 400.17 MHz, 296 K): *N*-(3-amino-4-methylphenyl)formamide (1)

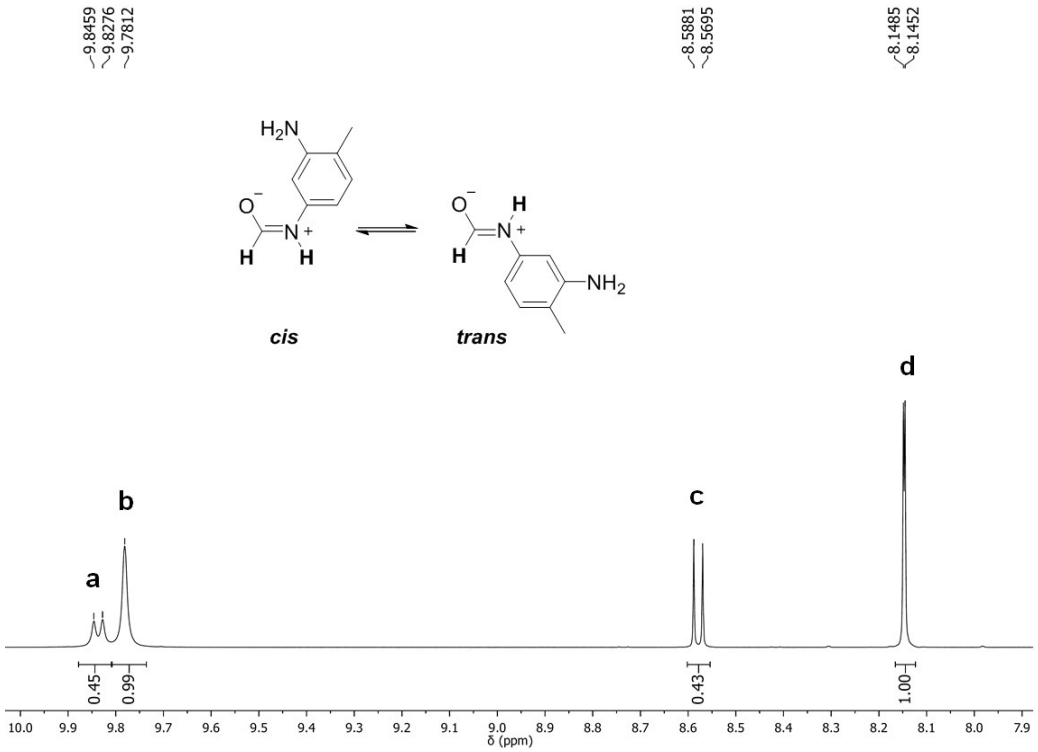


$^{13}C\{^{1}H\}$-NMR (MeOD-d_4, 100.62 MHz, 296 K): *N*-(3-amino-4-methylphenyl)formamide (1)

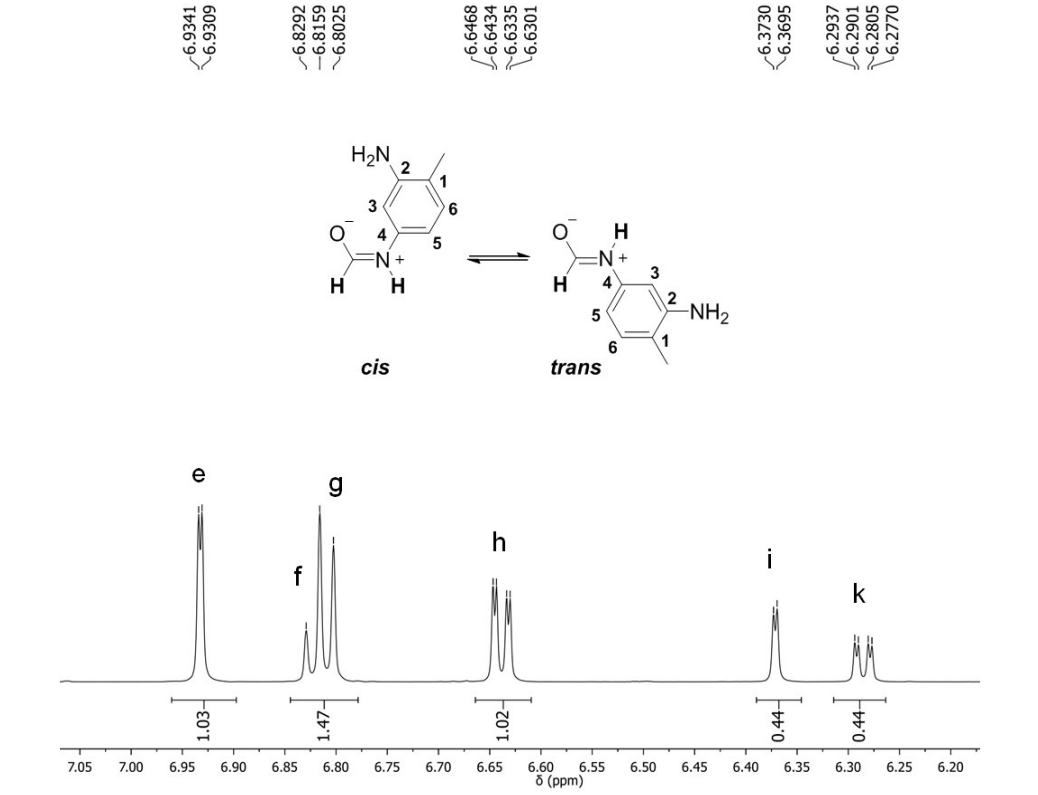


^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): *N*-(3-amino-4-methylphenyl)formamide (1)



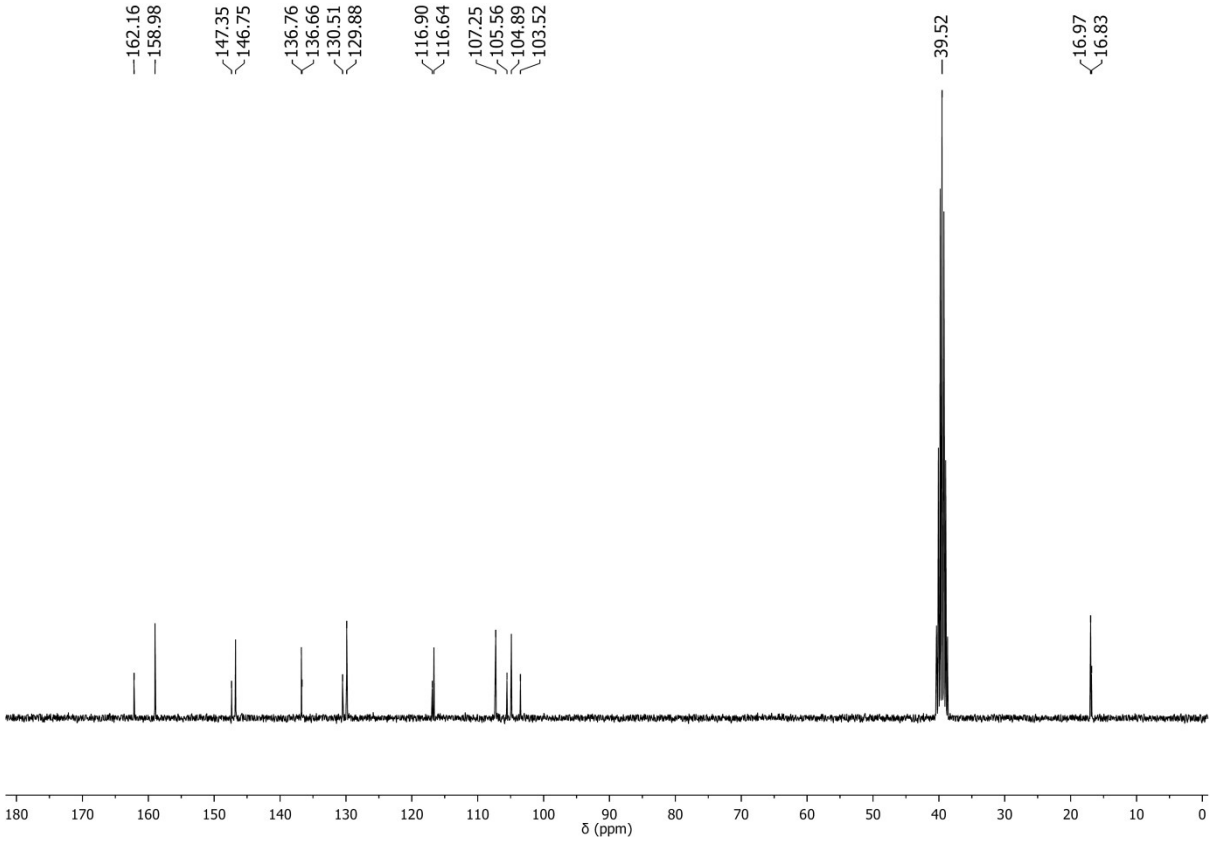


^{1}H-NMR-spectrum [NHCHO-protons] of **1** (DMSO-d_6, 600.07 MHz, 296 K; a: *trans*-N**H**, $^{3}J_{H,H}$ = 11.2 Hz; b: *cis*-N**H**, breit; c: *trans*-C**H**O, $^{3}J_{H,H}$ = 11.2 Hz; d: *cis*-C**H**O, $^{3}J_{H,H}$ = 2.0 Hz).

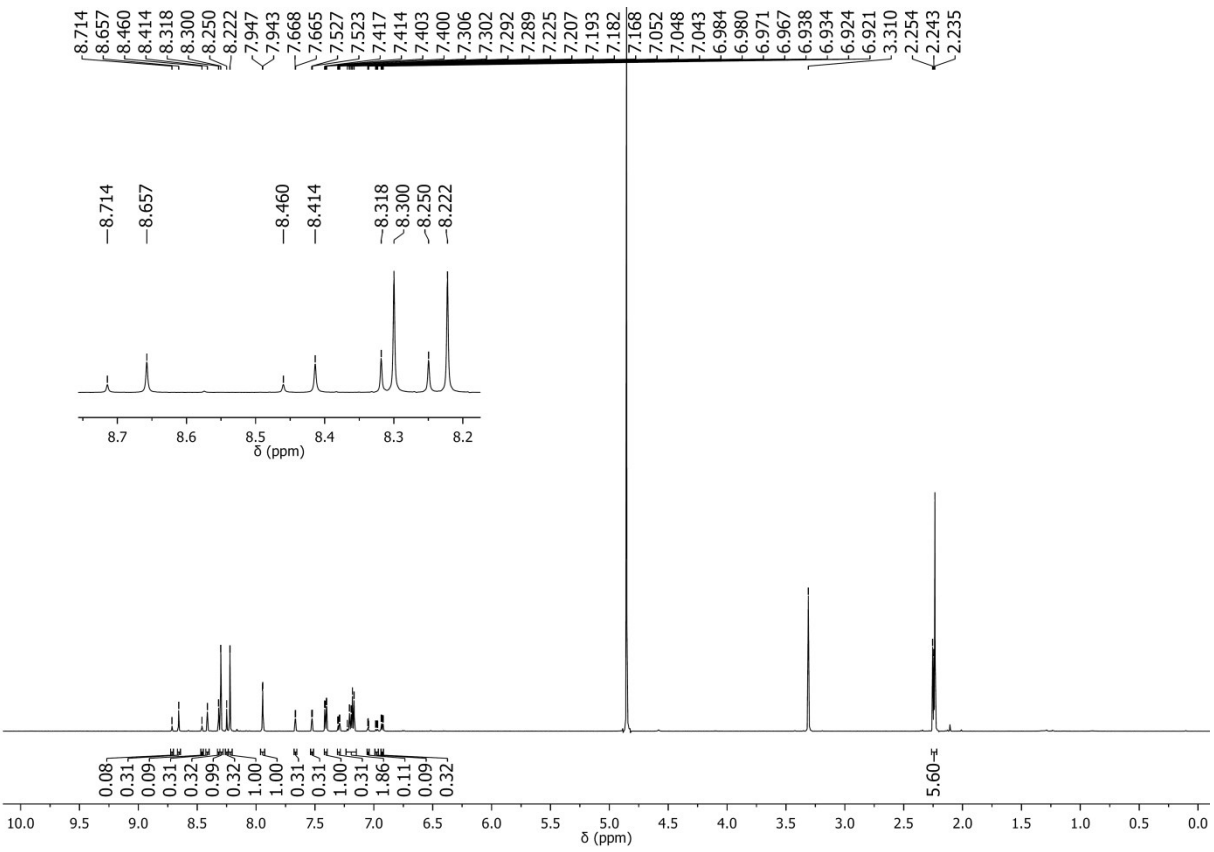


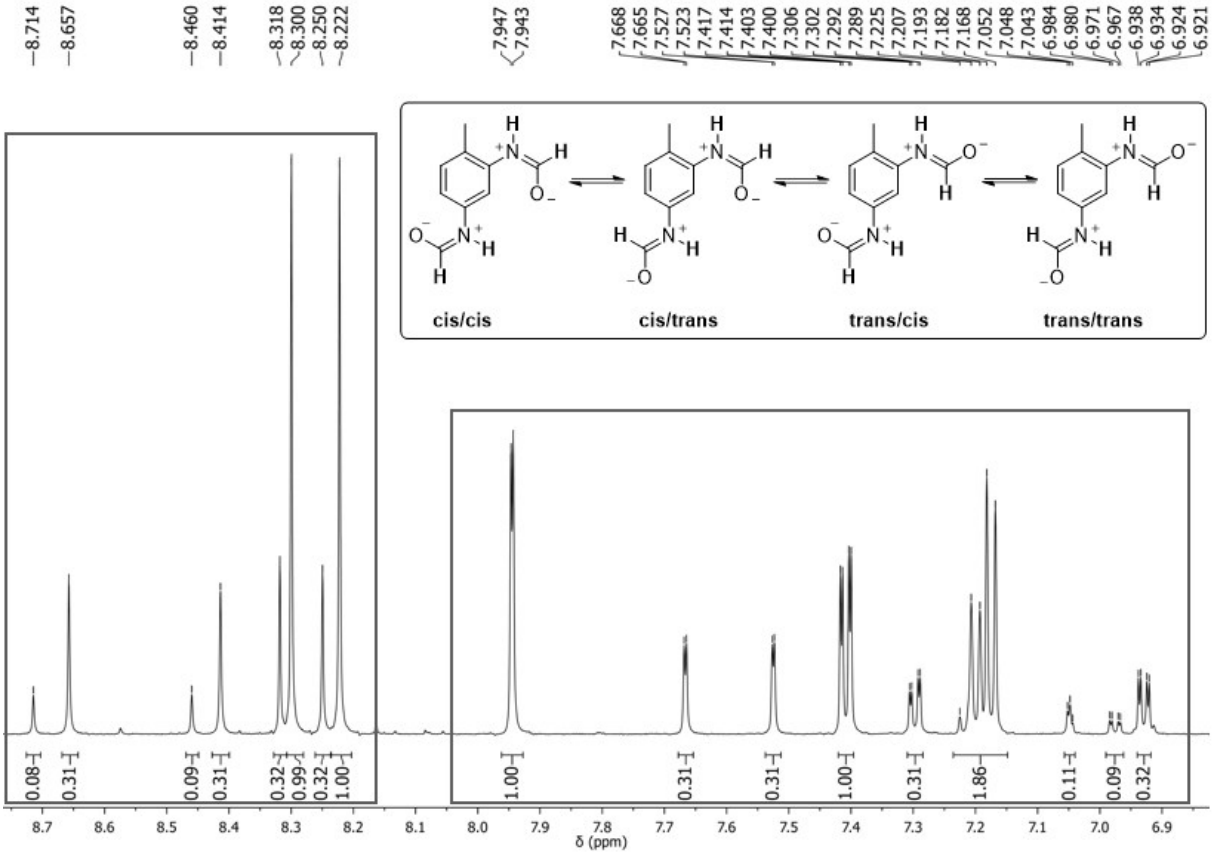
^{1}H-NMR-spectrum [aromatic protons] of **1**. (DMSO-d_6, 600.07 MHz, 296 K; e: *cis-H3*, $^{4}J_{H,H}$ = 2.0 Hz; f: *trans-H6*, $^{3}J_{H,H}$ = 7.9 Hz; g: *cis-H6*, $^{3}J_{H,H}$ = 8.0 Hz; h: *cis-H5*, $^{3}J_{H,H}$ = 8.0 Hz, $^{4}J_{H,H}$ = 2.0 Hz; i: *trans-H3*, $^{4}J_{H,H}$ = 2.1 Hz; k: *trans-H5*, $^{3}J_{H,H}$ = 7.9 Hz, $^{4}J_{H,H}$ = 2.1 Hz).

$^{13}C\{^1H\}$-NMR (DMSO-d_6, 75.34 MHz, 296 K): *N*-(3-amino-4-methylphenyl)formamide (1)

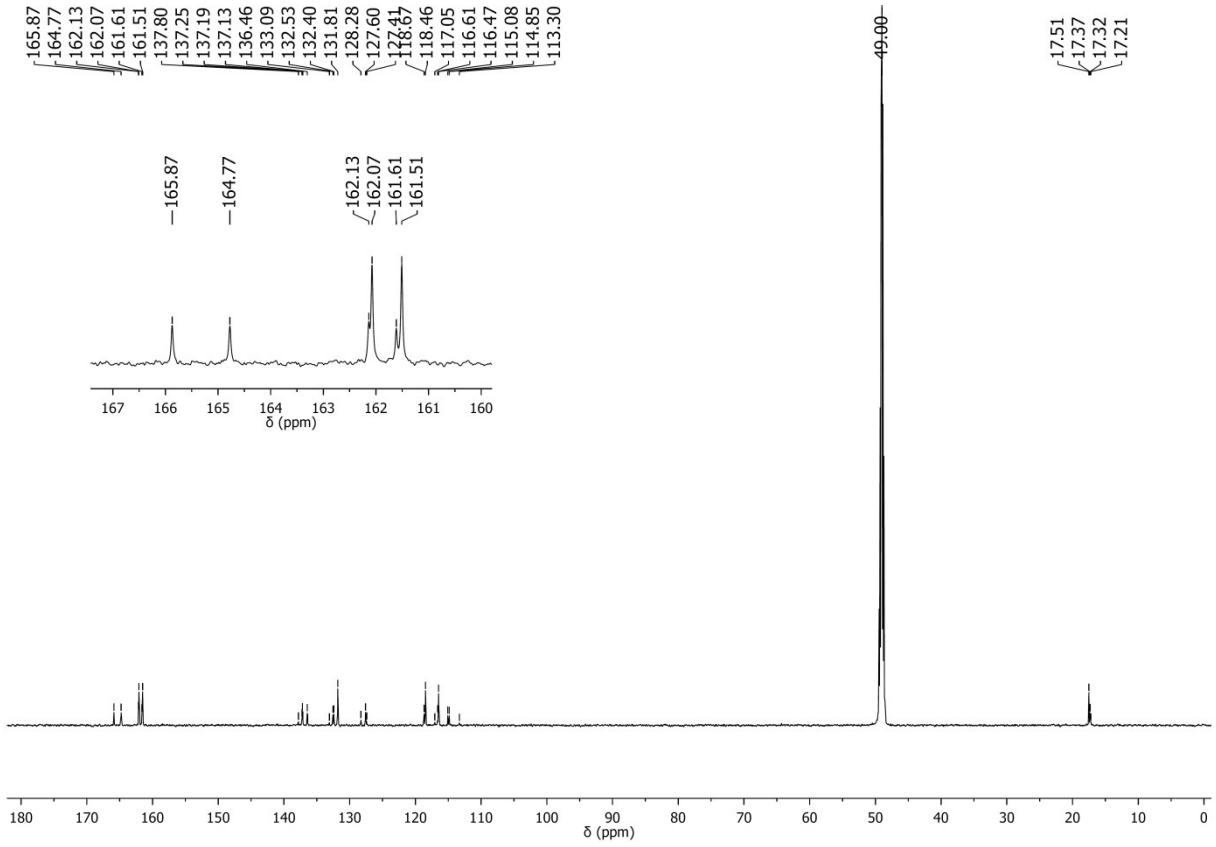


^1H-NMR (MeOD-d_4; 600.07 MHz, 296 K): *N,N'*-(4-methyl-1,3-phenylen)diformamide (2)

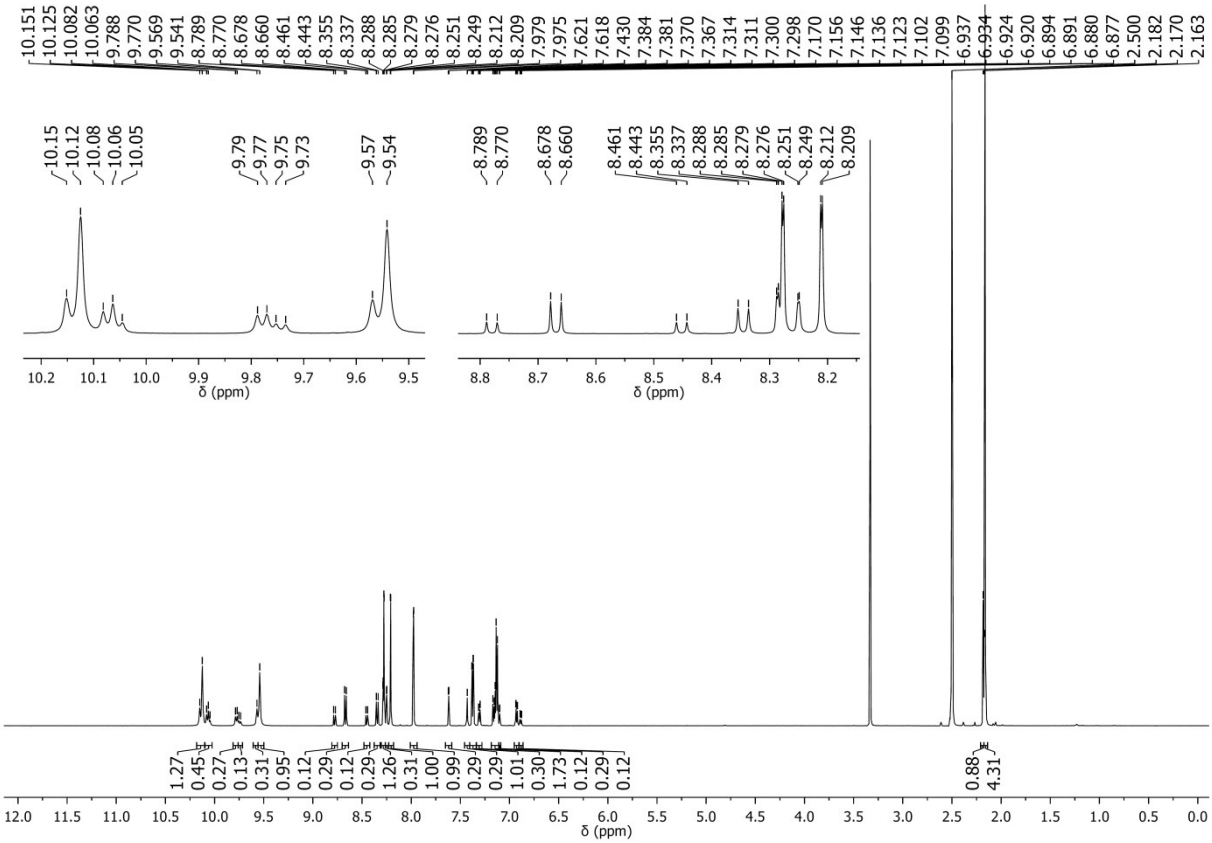




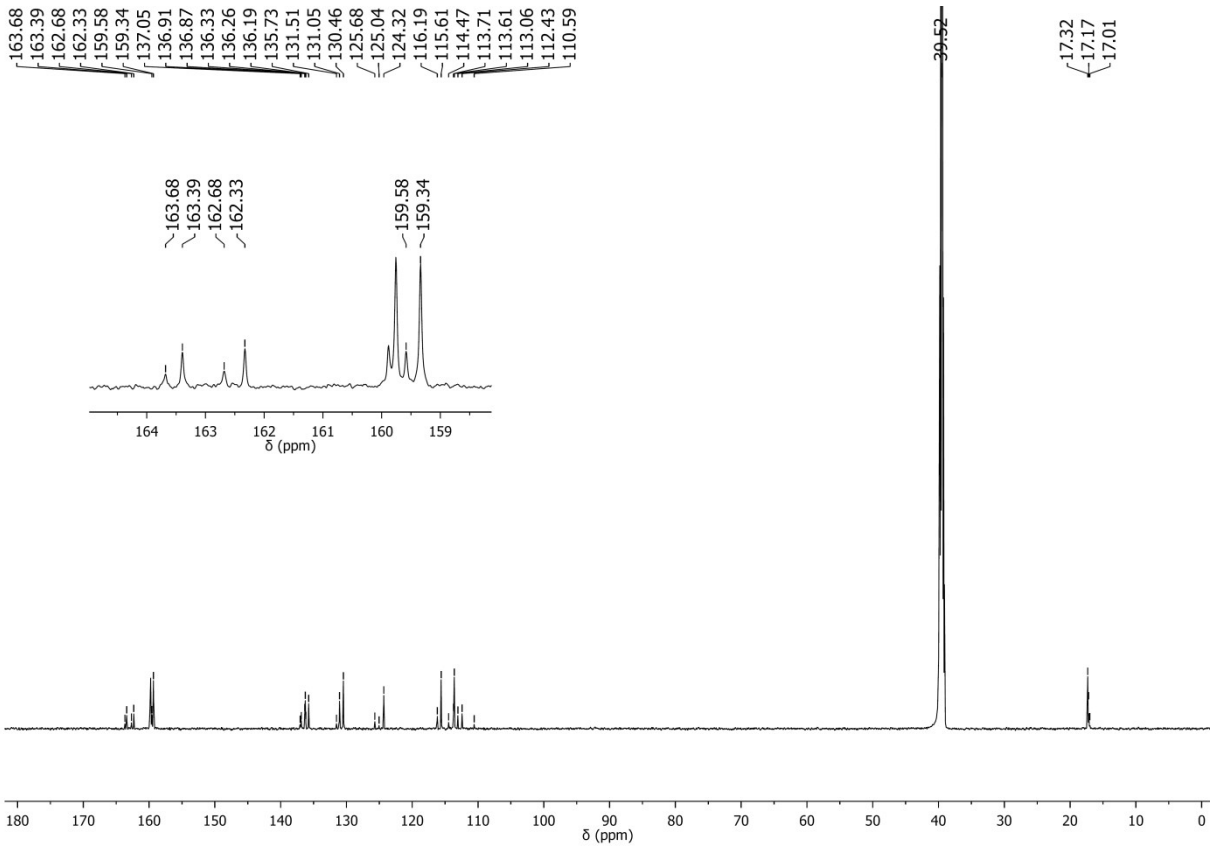
$^{13}C\{^{1}H\}$-NMR (MeOD-d_4, 150.89 MHz, 296 K): *N,N′*-(4-methyl-1,3-phenylen)diformamide (2)



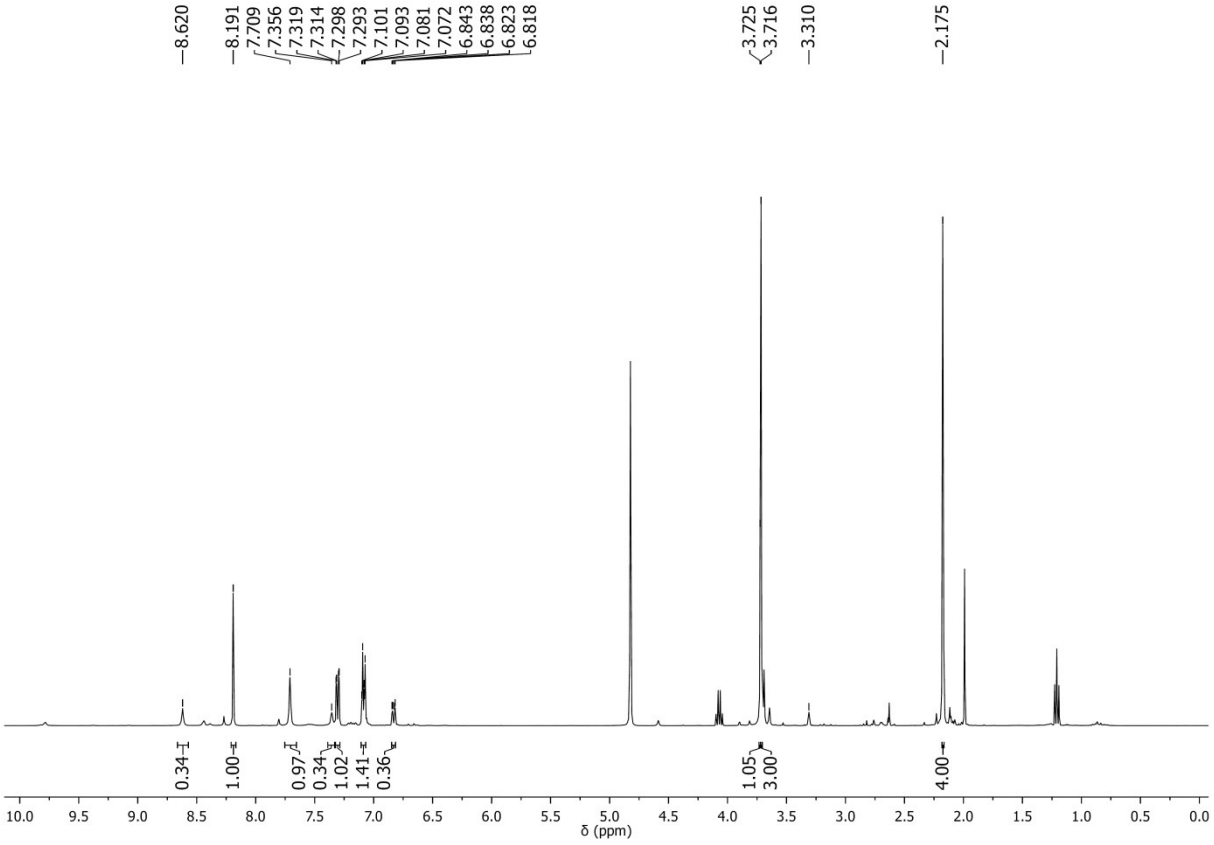
^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): *N,N'*-(4-methyl-1,3-phenylene)diformamide (2)



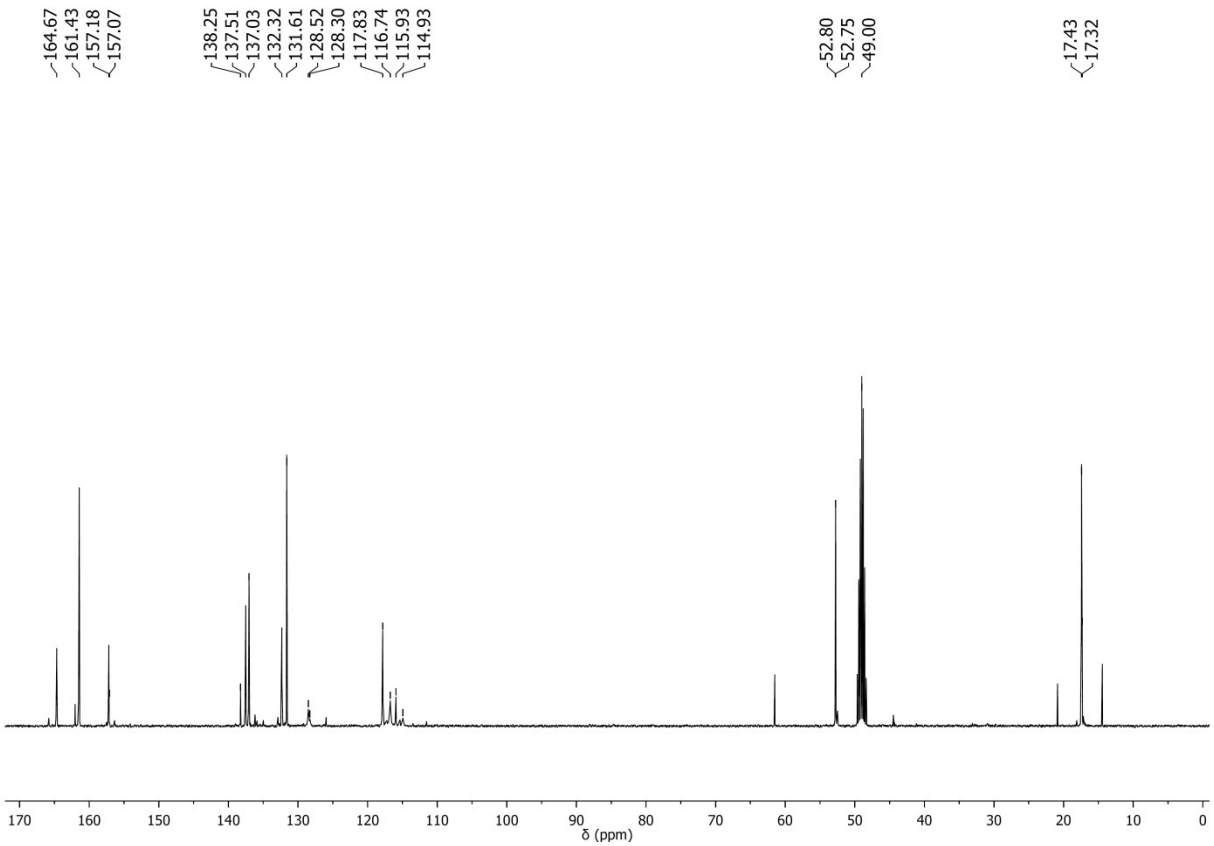
^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): *N,N'*-(4-methyl-1,3-phenylene)diformamide (2)



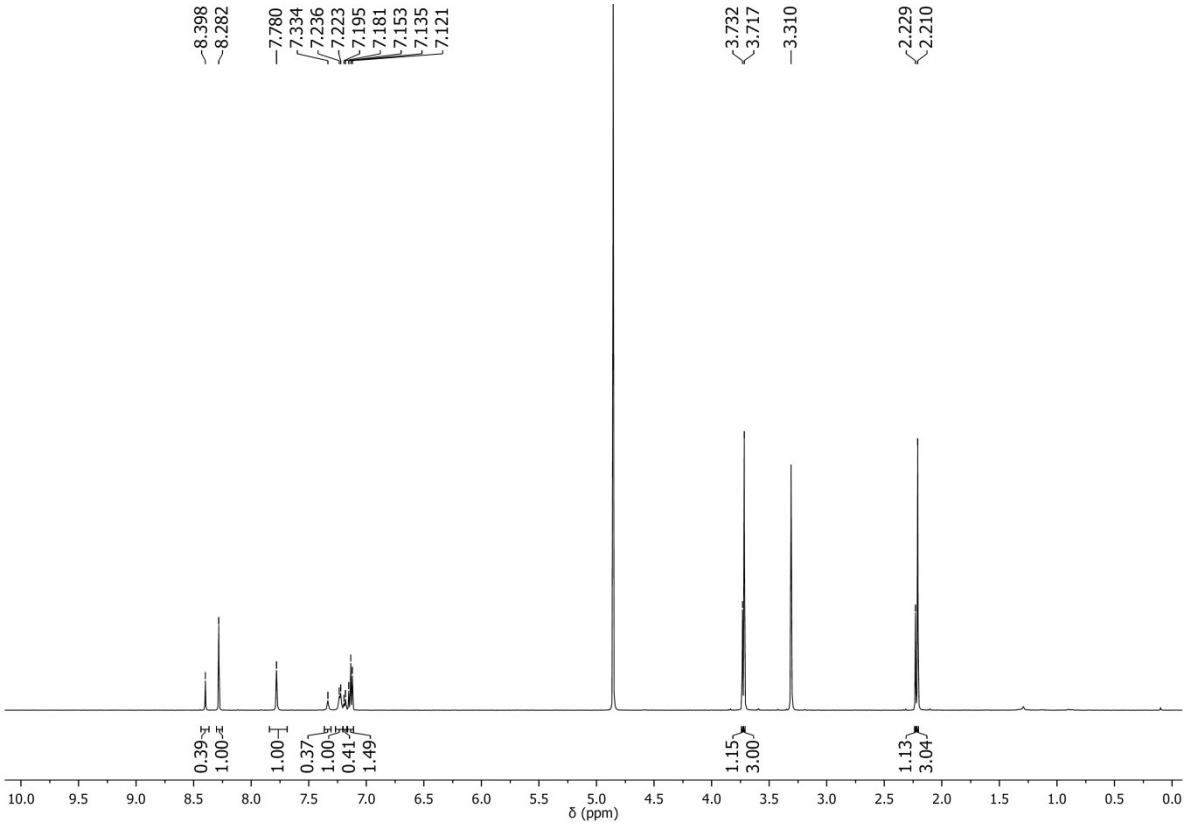
^{1}H-NMR (MeOD-d_4, 400.17 MHz, 296 K): methyl (5-formamido-2-methylphenyl)carbamate (3)



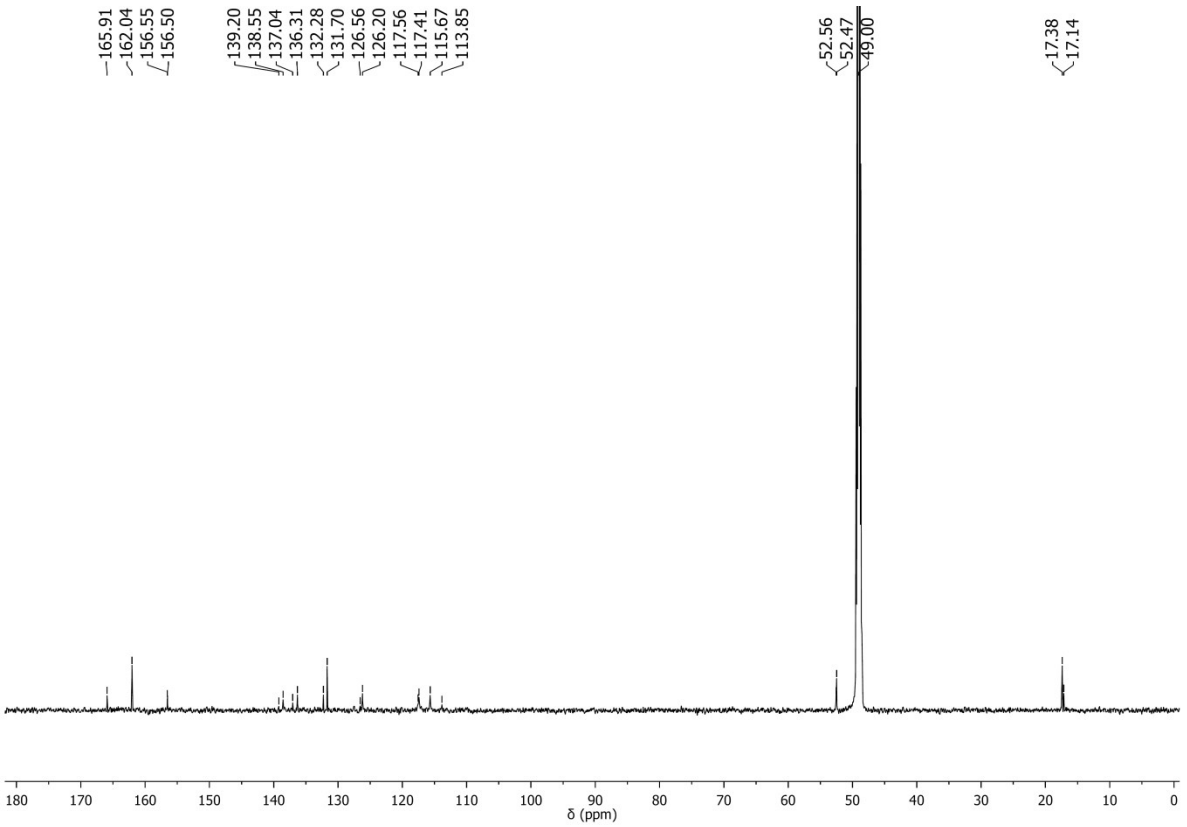
^{13}C{^{1}H}-NMR (MeOD-d_4, 100.62 MHz, 296 K): methyl (5-formamido-2-methylphenyl)carbamate (3)



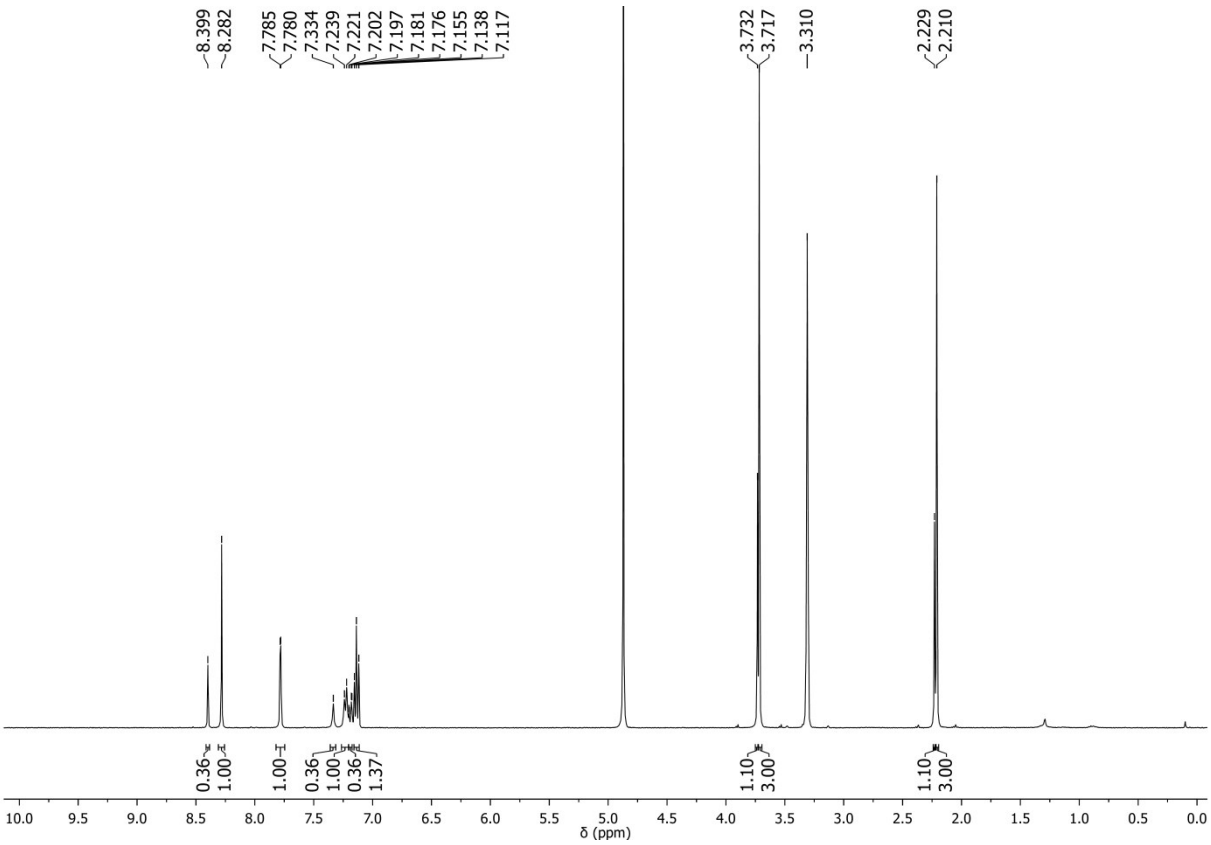
^{1}H-NMR (MeOD-d_4, 600.07 MHz, 296 K): methyl (3-formamido-4-methylphenyl)carbamate (4)



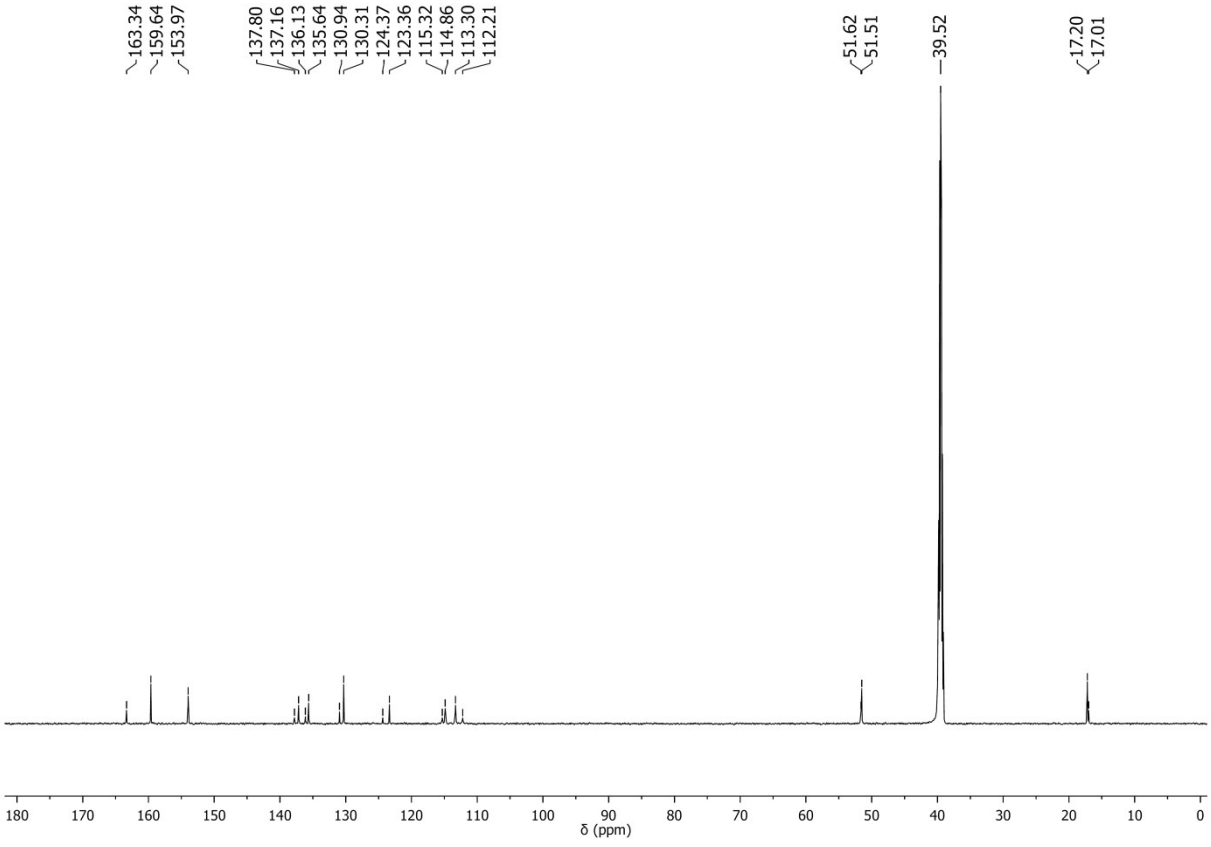
^{13}C{^{1}H}-NMR (MeOD-d_4, 150.89 MHz, 296 K): methyl (3-formamido-4-methylphenyl)carbamate (4)



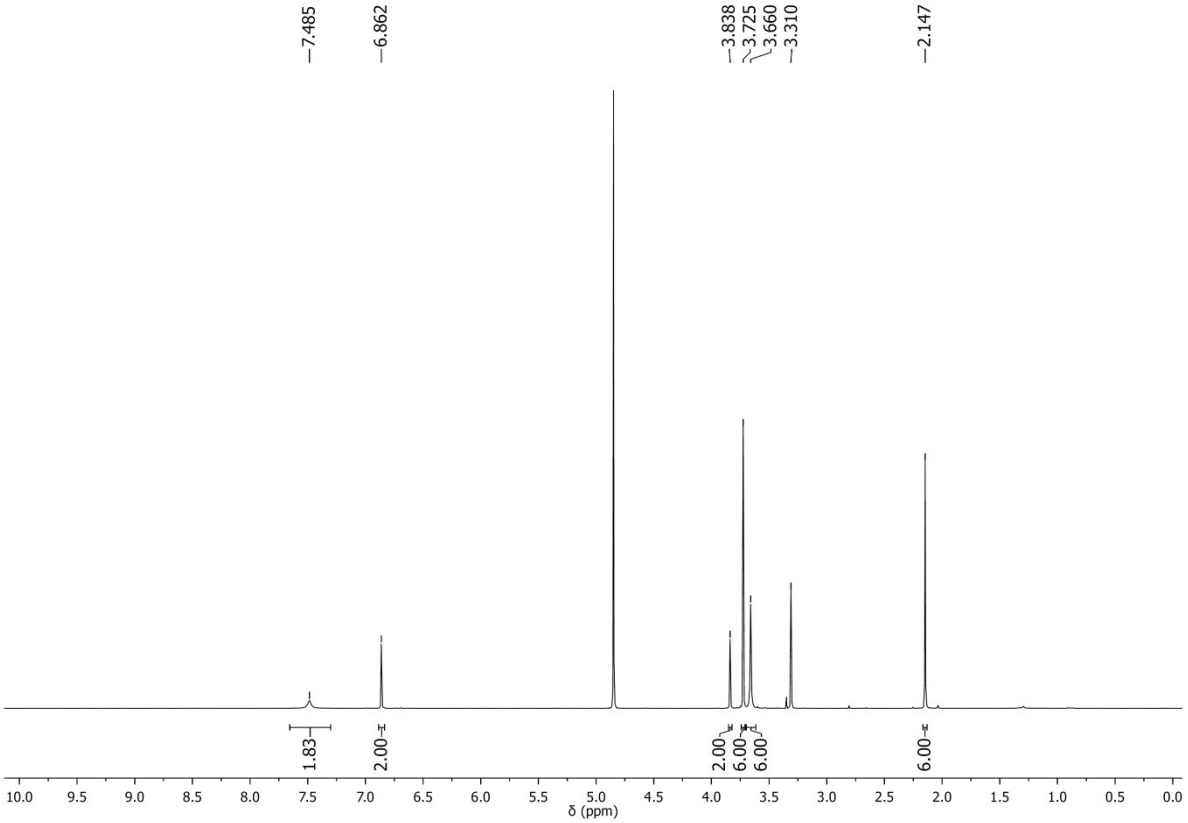
^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): methyl (3-formamido-4-methylphenyl)carbamate (4)



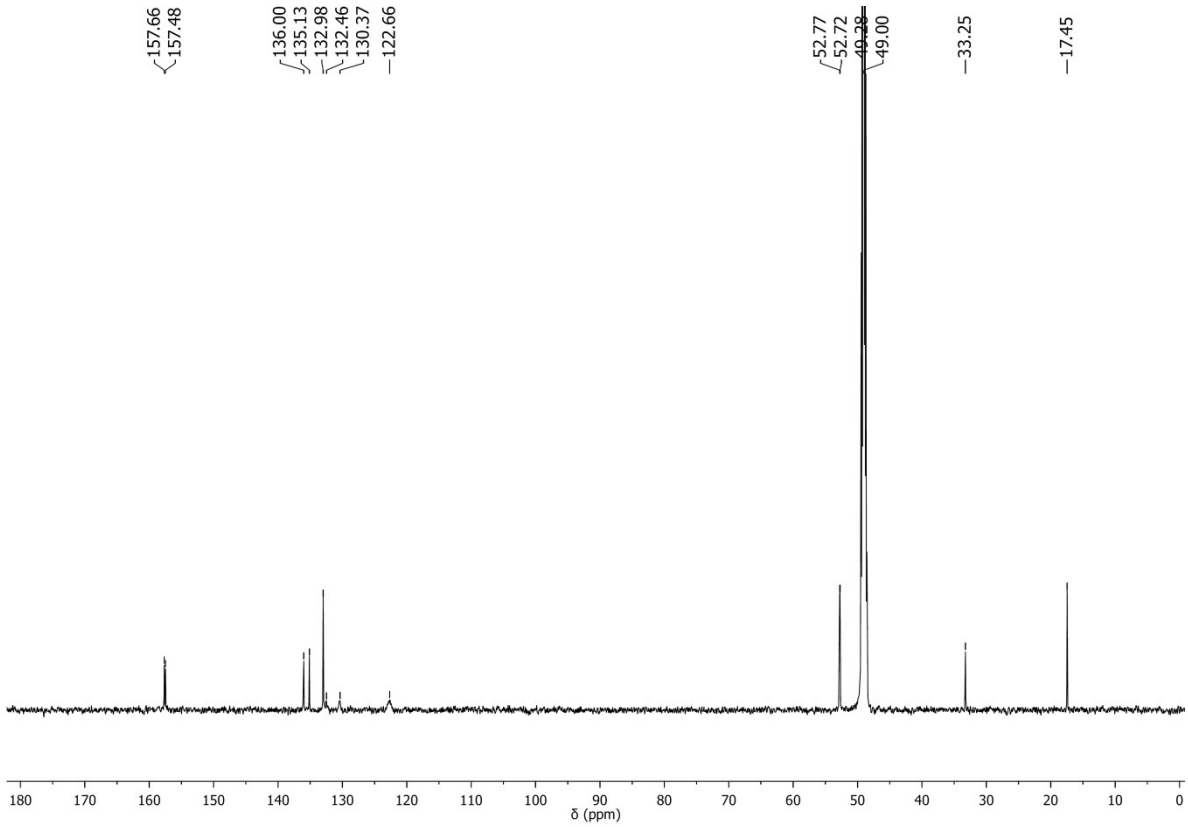
^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): methyl (3-formamido-4-methylphenyl)carbamate (4)



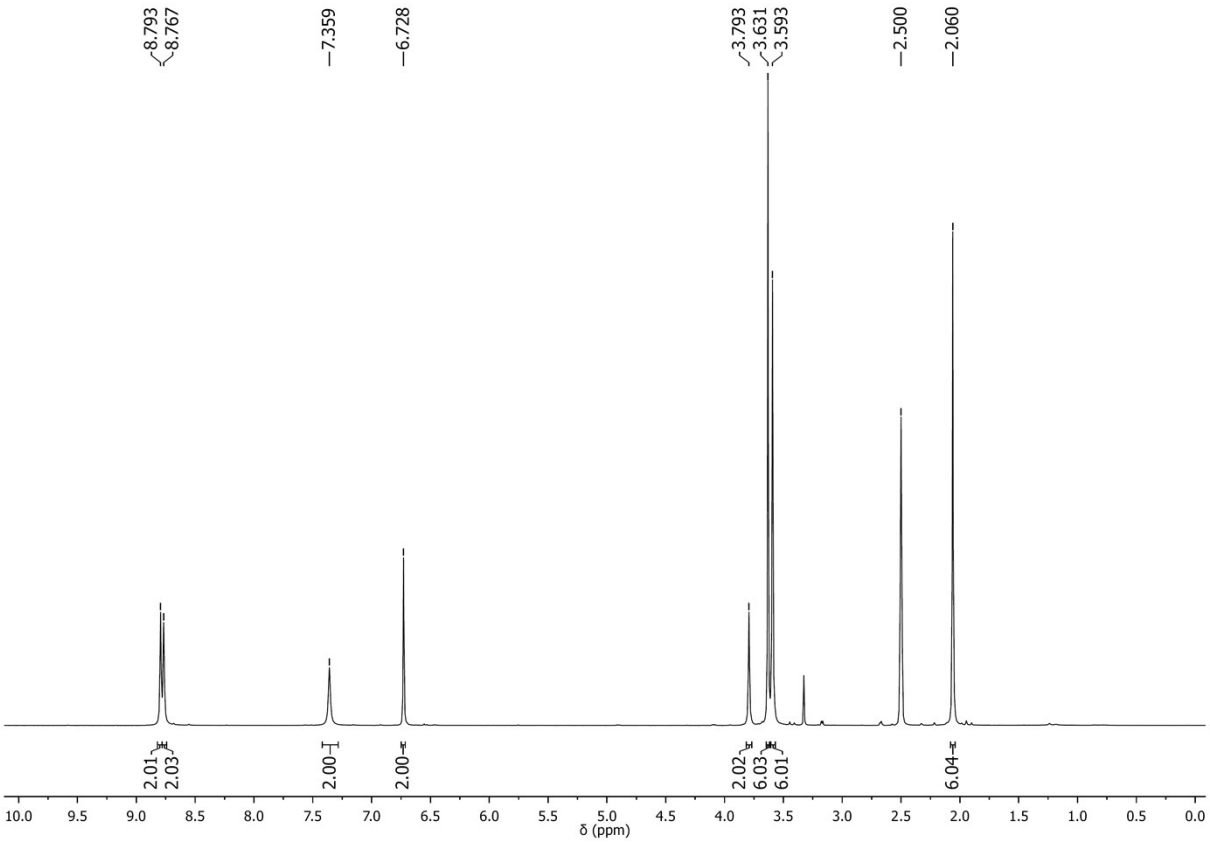
^{1}H-NMR (MeOD-d_4, 600.07 MHz, 296 K): tetramethyl 4,4'-methylenebis[(6-methyl-1,3-phenylene)dicarbamate] (5)



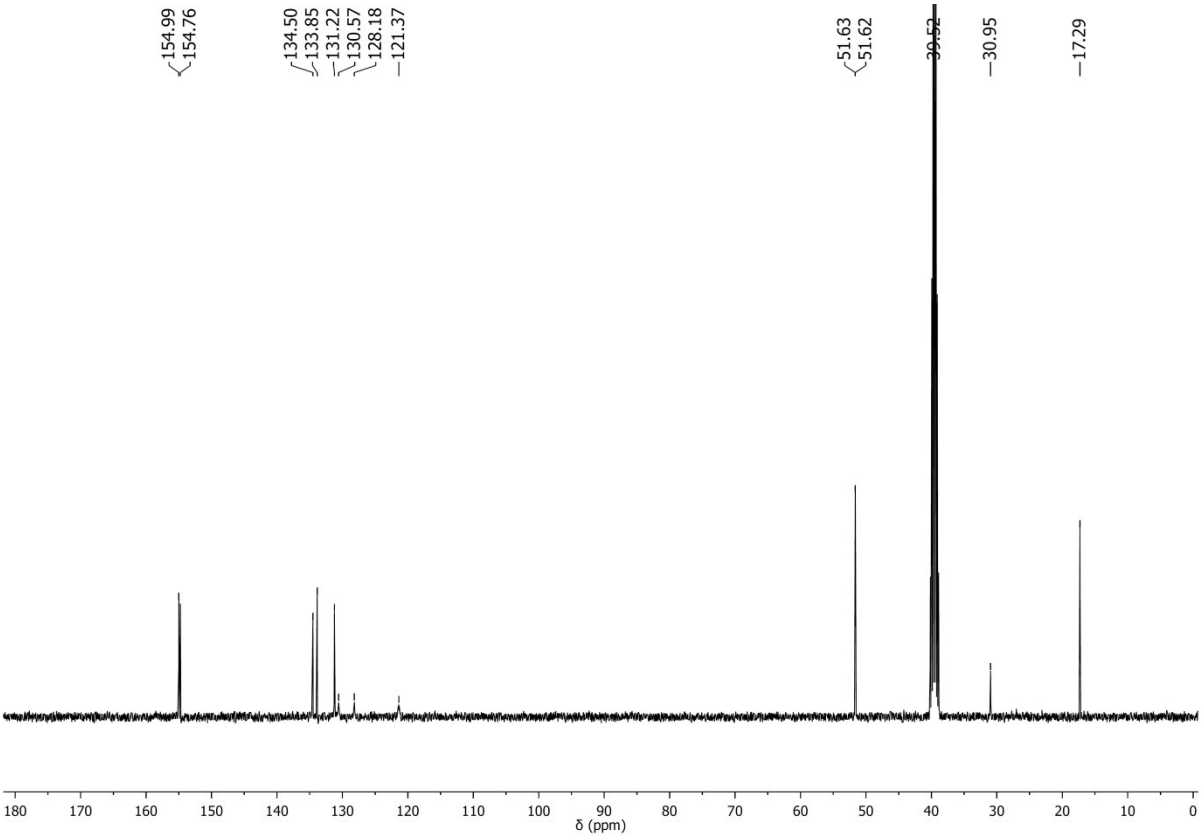
^{13}C{^{1}H}-NMR (MeOD-d_4, 150.89 MHz, 296 K): tetramethyl 4,4'-methylenebis[(6-methyl-1,3-phenylene)dicarbamate] (5)



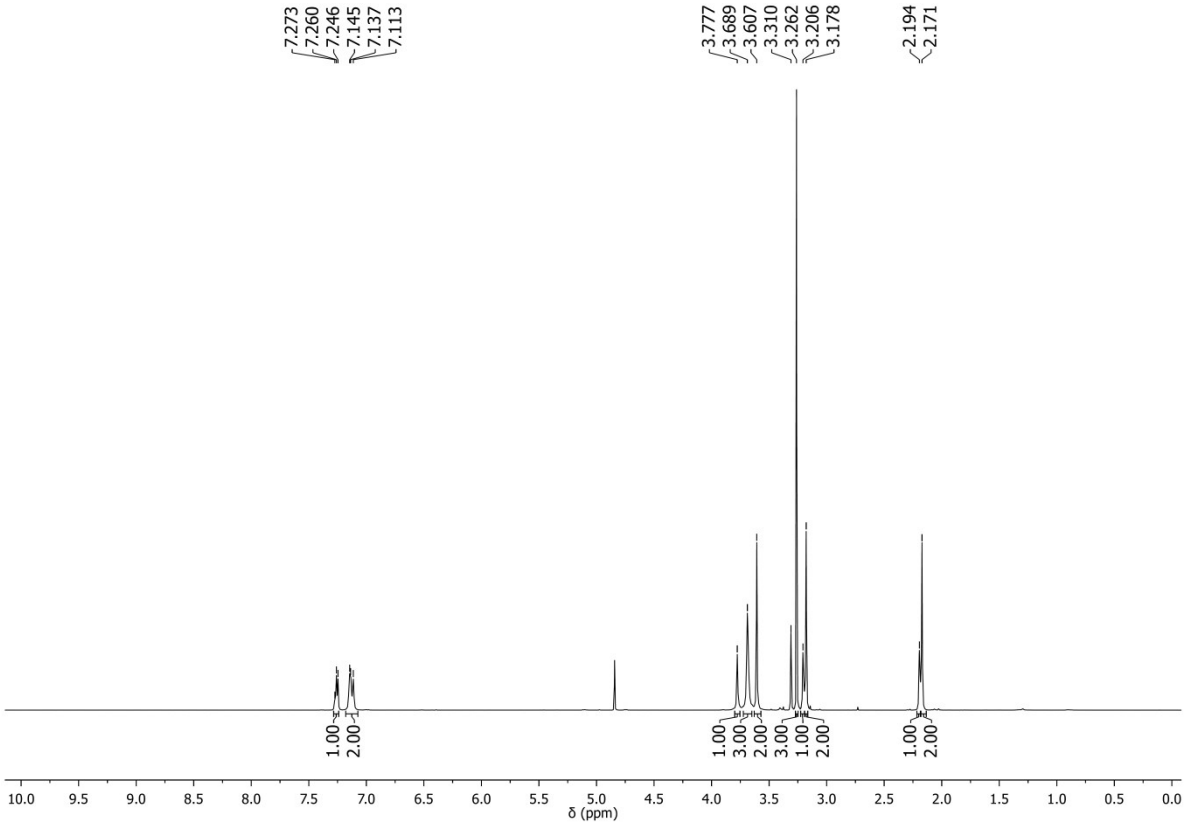
[1]H-NMR (DMSO-d_6, 400.17 MHz, 296 K): tetramethyl 4,4'-methylenebis[(6-methyl-1,3-phenylene)dicarbamate] (5)



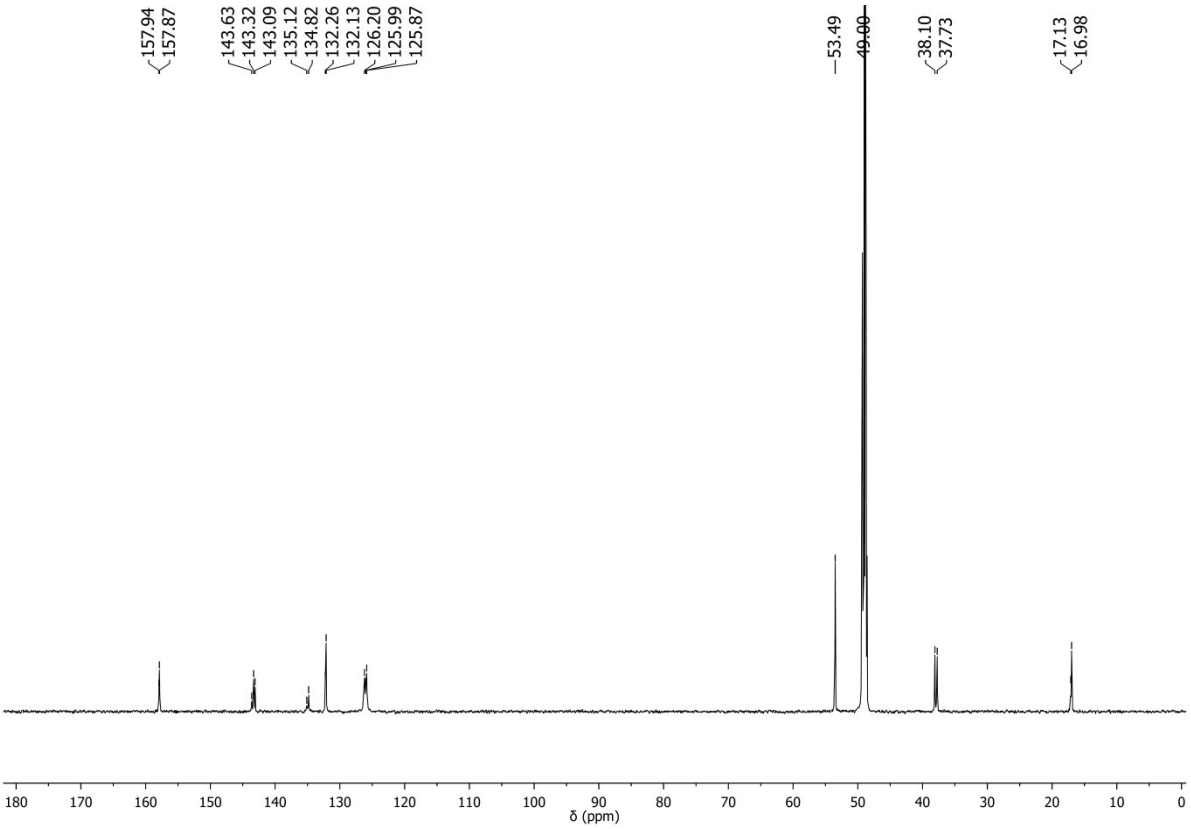
[13]C-NMR (DMSO-d_6, 100.62 MHz, 296 K): tetramethyl 4,4'-methylenebis[(6-methyl-1,3-phenylene)dicarbamate] (5)



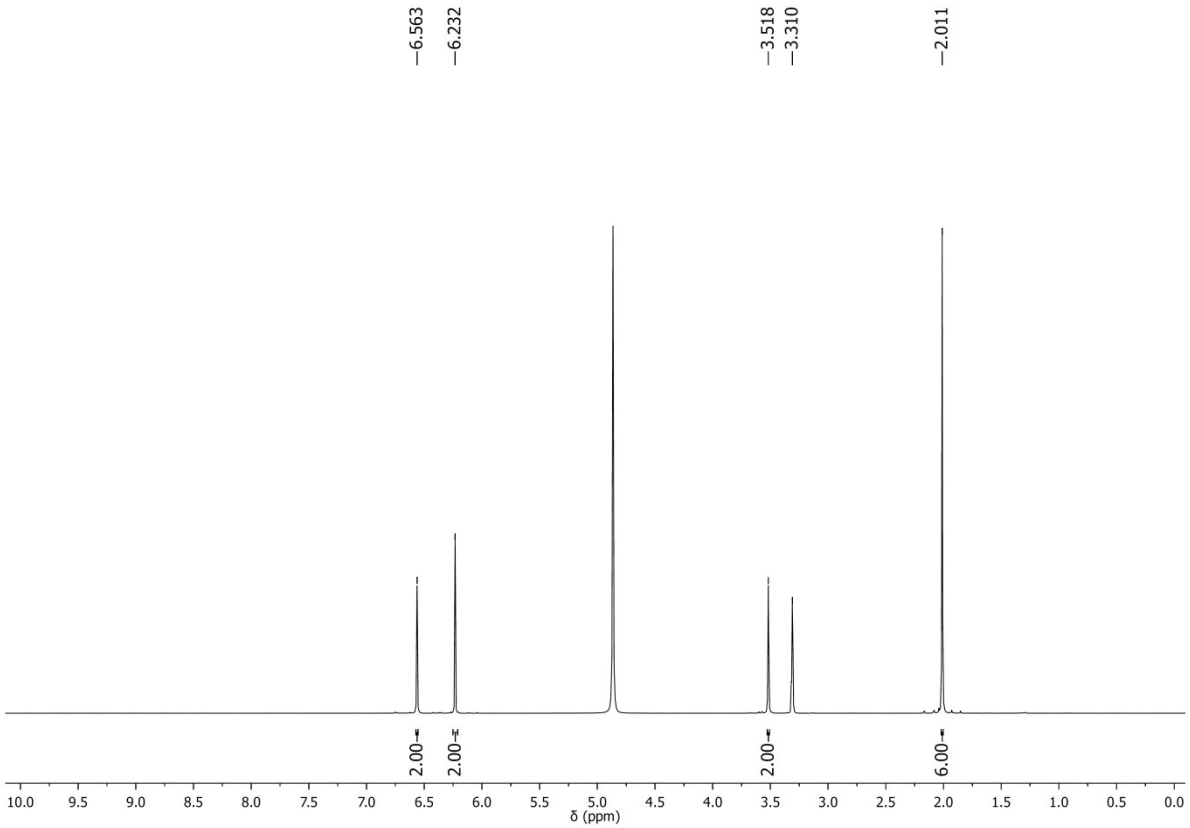
^{1}H-NMR (MeOD-d_4, 600.07 MHz, 296 K): dimethyl (4-methyl-1,3-phenylene)bis(methyl-carbamate) (6)



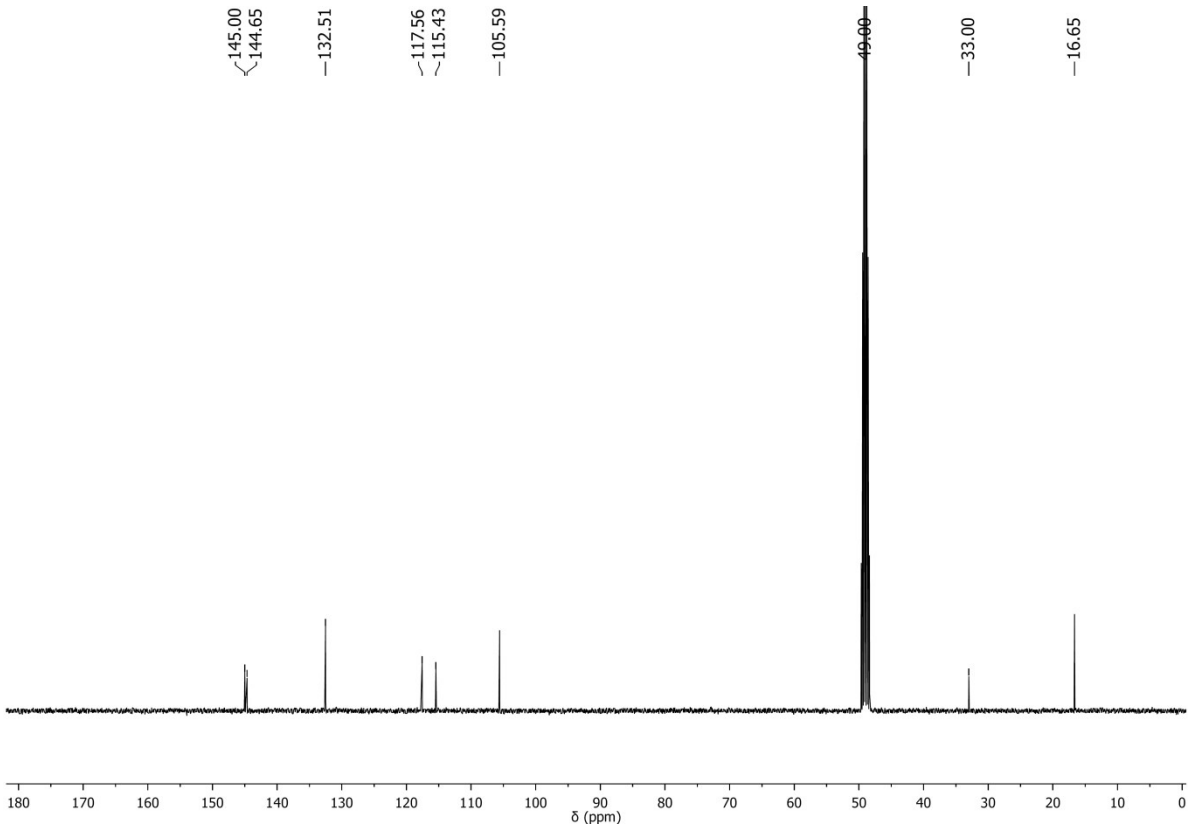
^{13}C{^{1}H}-NMR (MeOD-d_6, 150.89 MHz, 296 K): dimethyl (4-methyl-1,3-phenylene)bis-(methylcarbamate) (6)



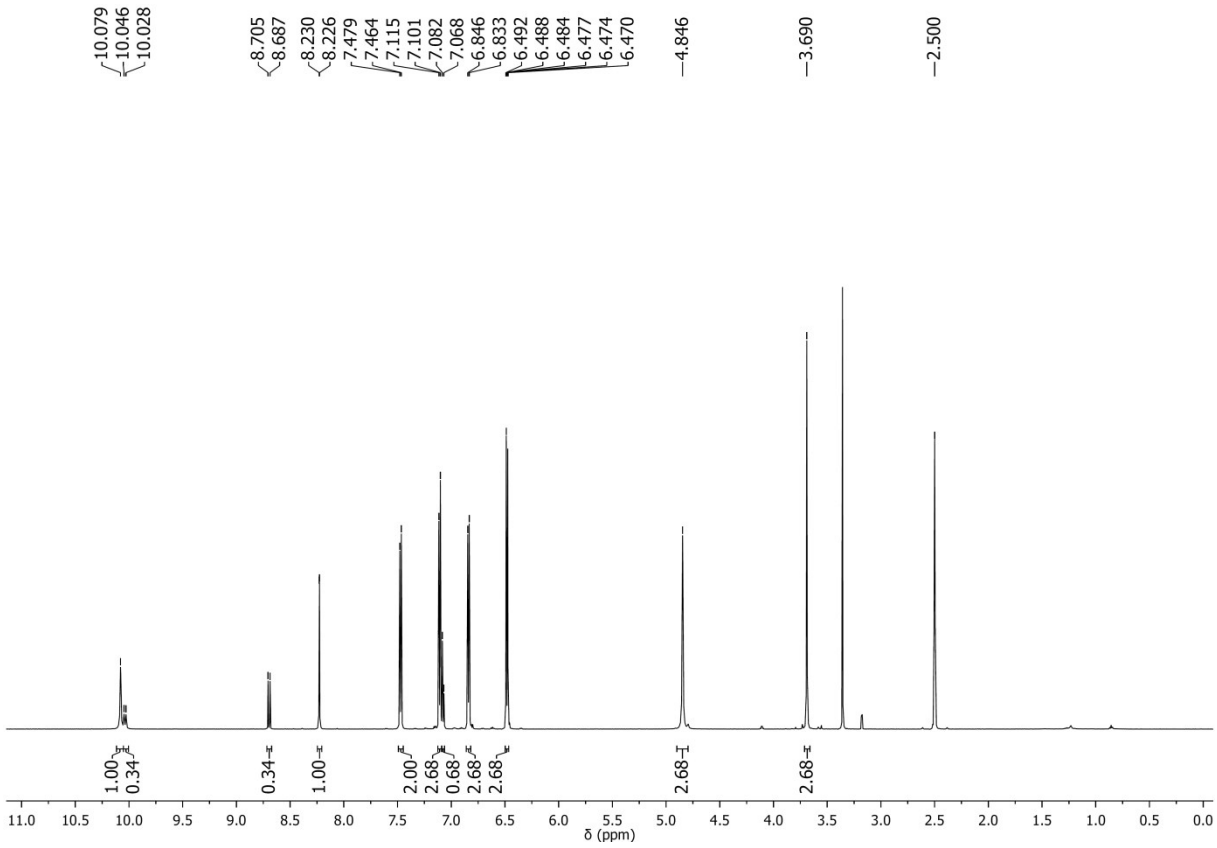
^{1}H-NMR (MeOD-d_4, 400.17 MHz, 296 K): 6,6'-methylenebis[4-methyl-1,3-benzenediamine] (13)



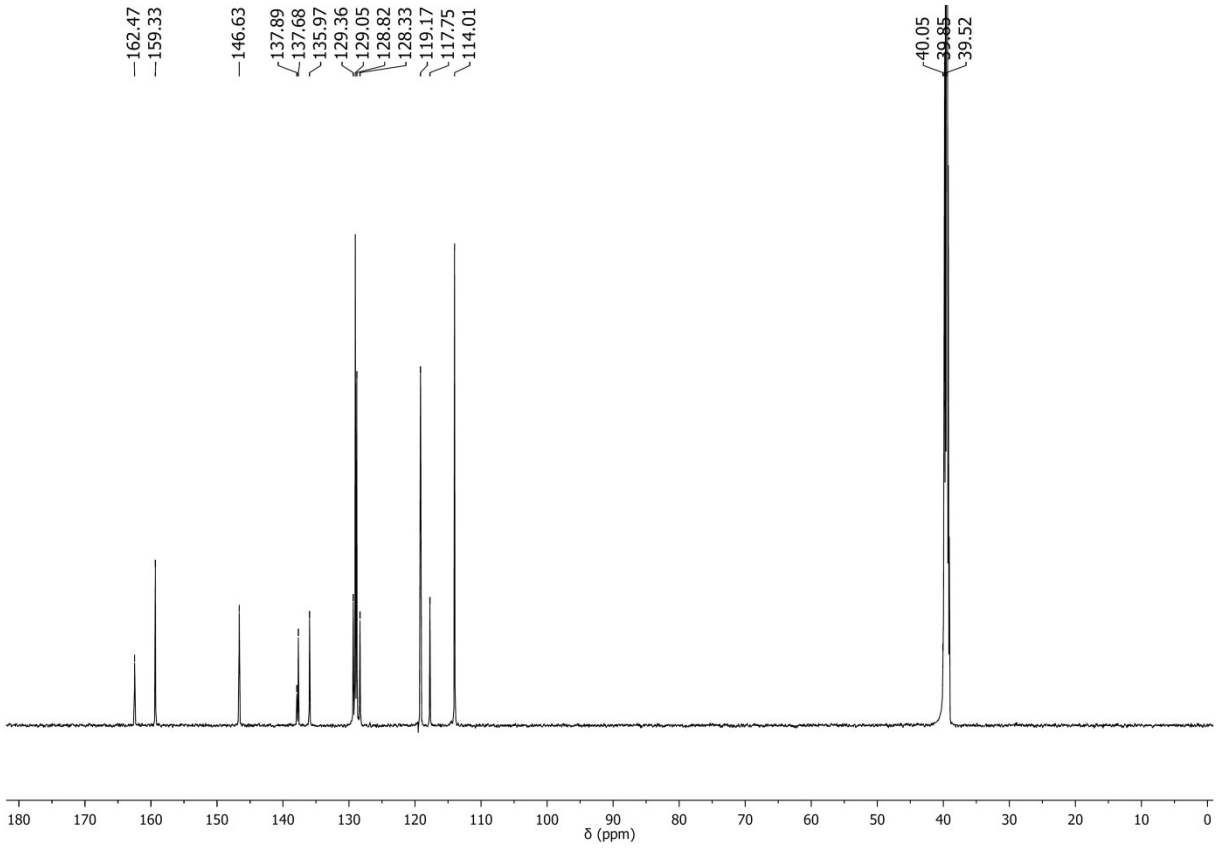
^{13}C{^{1}H}-NMR (MeOD-d_4, 100.62 MHz, 296 K): 6,6'-methylenebis[4-methyl-1,3-benzene-diamine] (13)



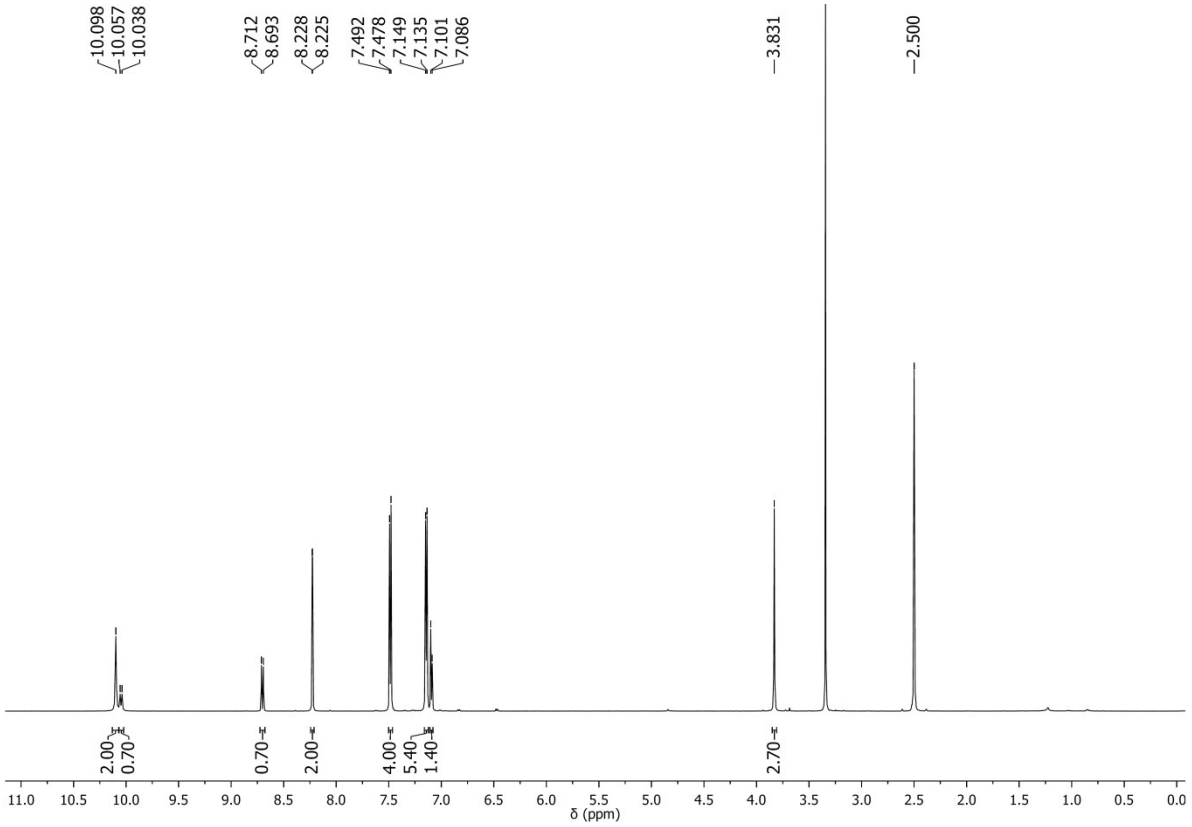
^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): *N*-[4-(4-aminobenzyl)phenyl]formamide (14)



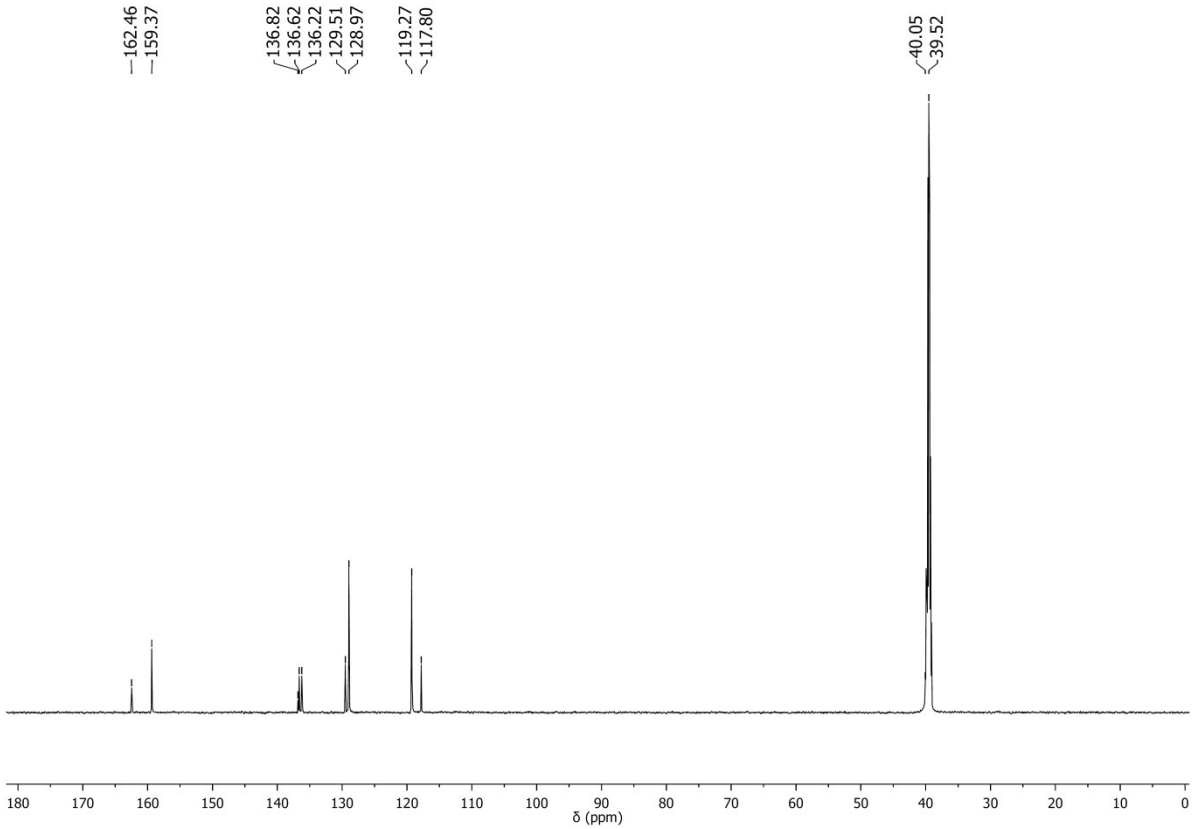
^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): *N*-[4-(4-aminobenzyl)phenyl]formamide (14)



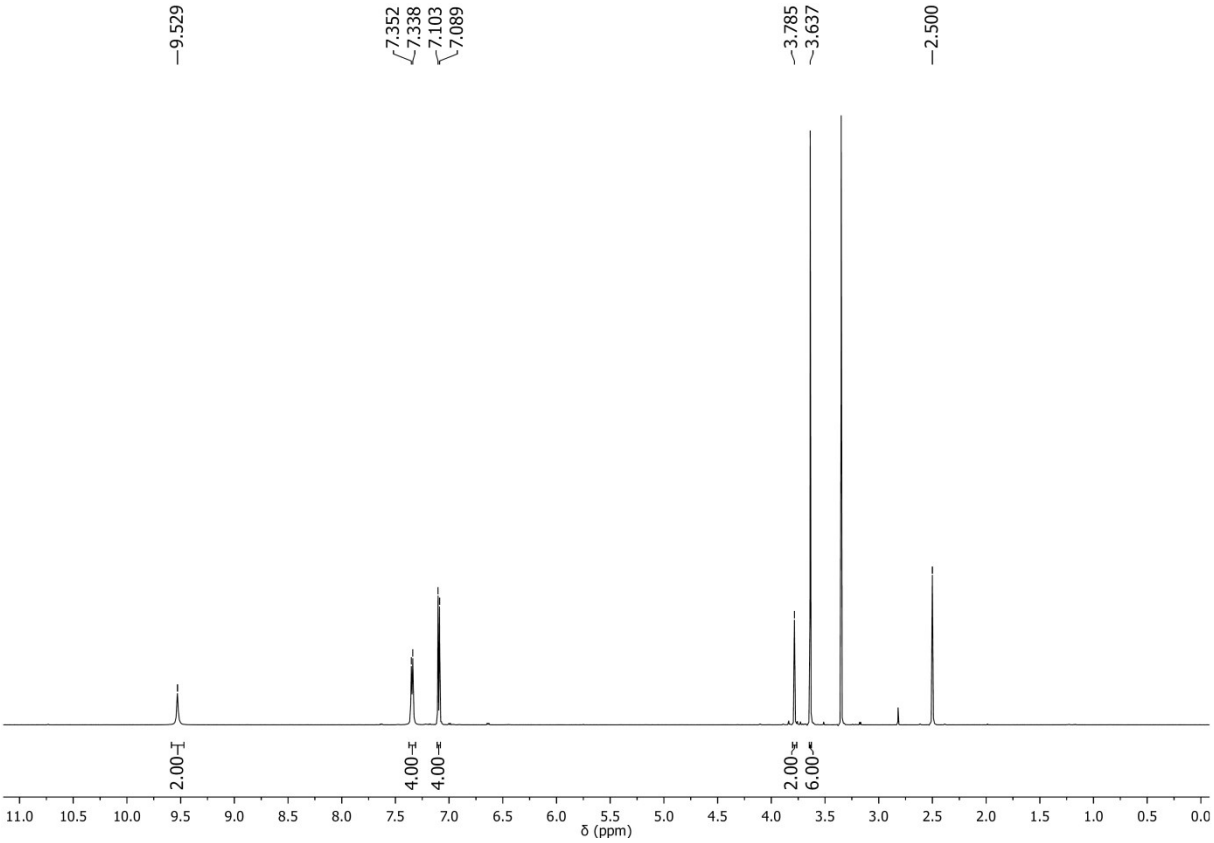
^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): *N*,*N*′-[methylenebis(4,1-phenylene)]diformamide (15)



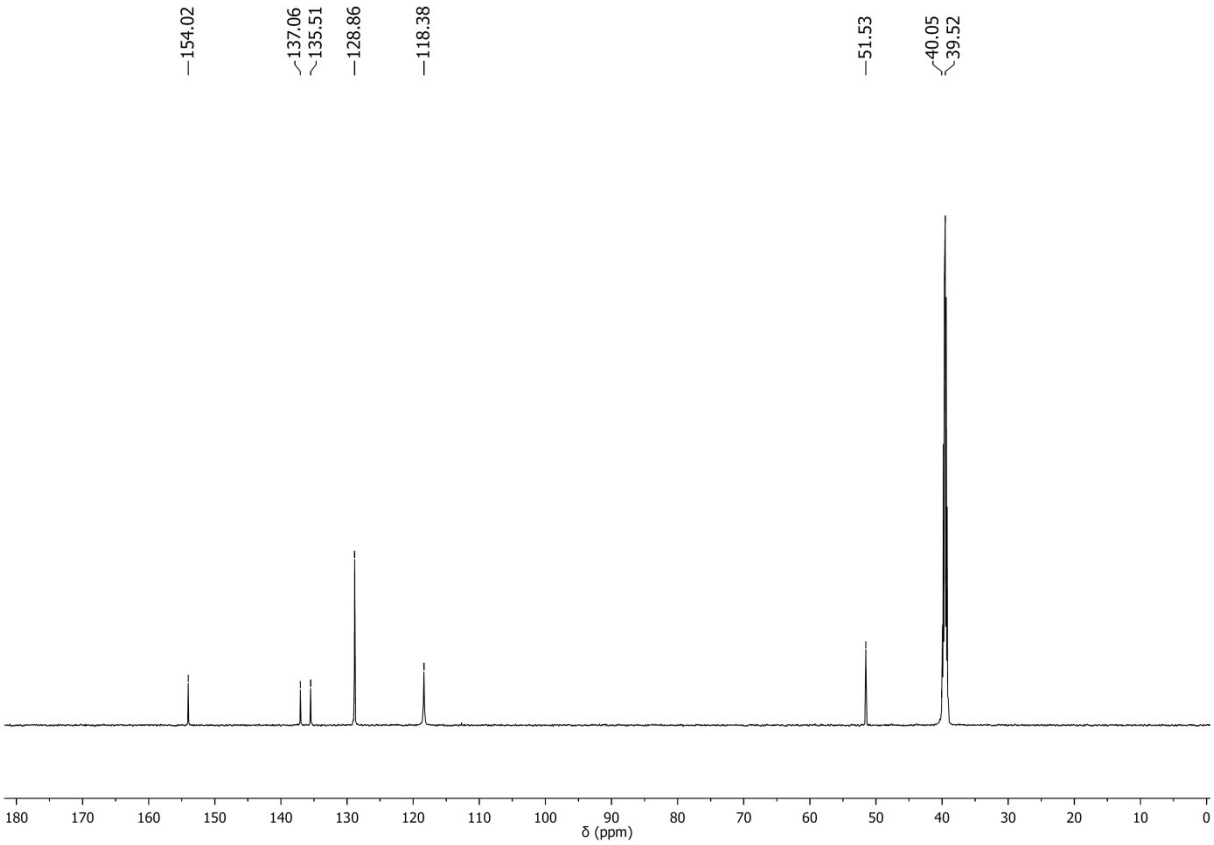
^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): *N*,*N*′-[methylenebis(4,1-phenylene)]diformamide (15)



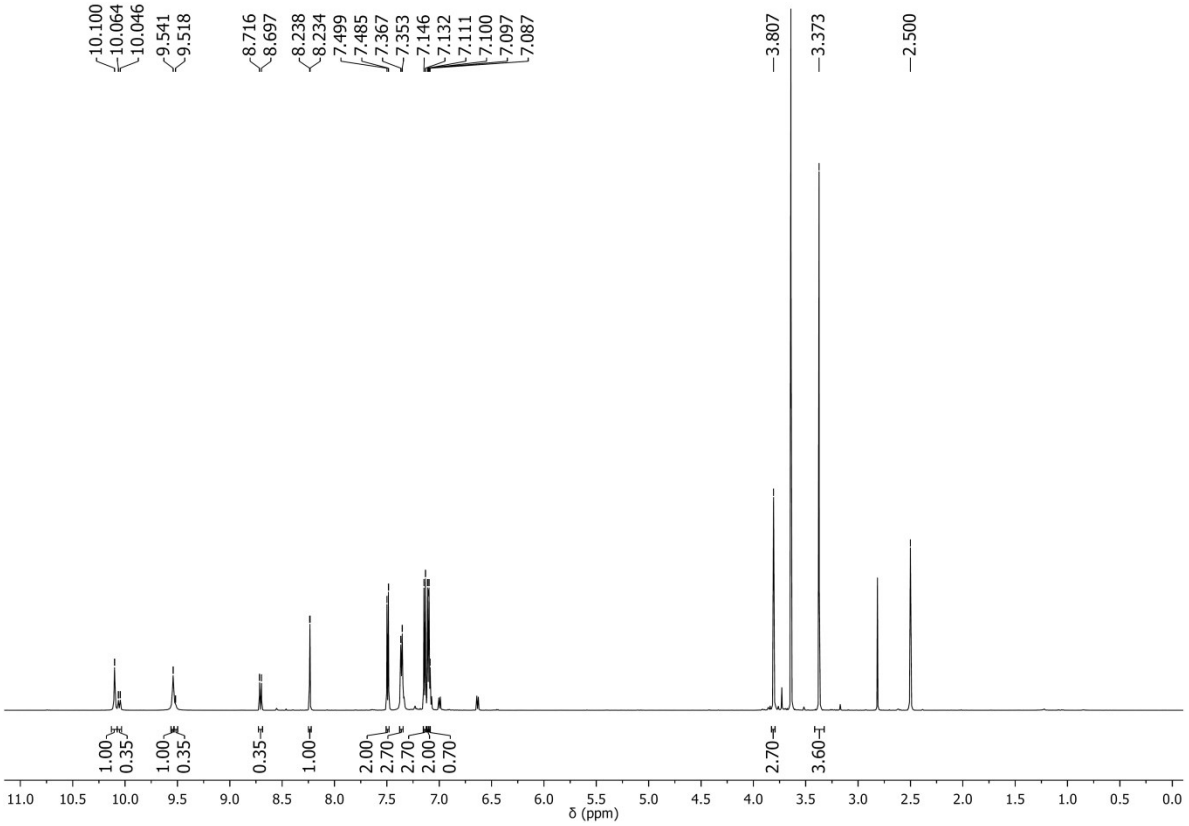
^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): dimethyl [methylenebis(4,1-phenylene)]-dicarbamate (MDC)



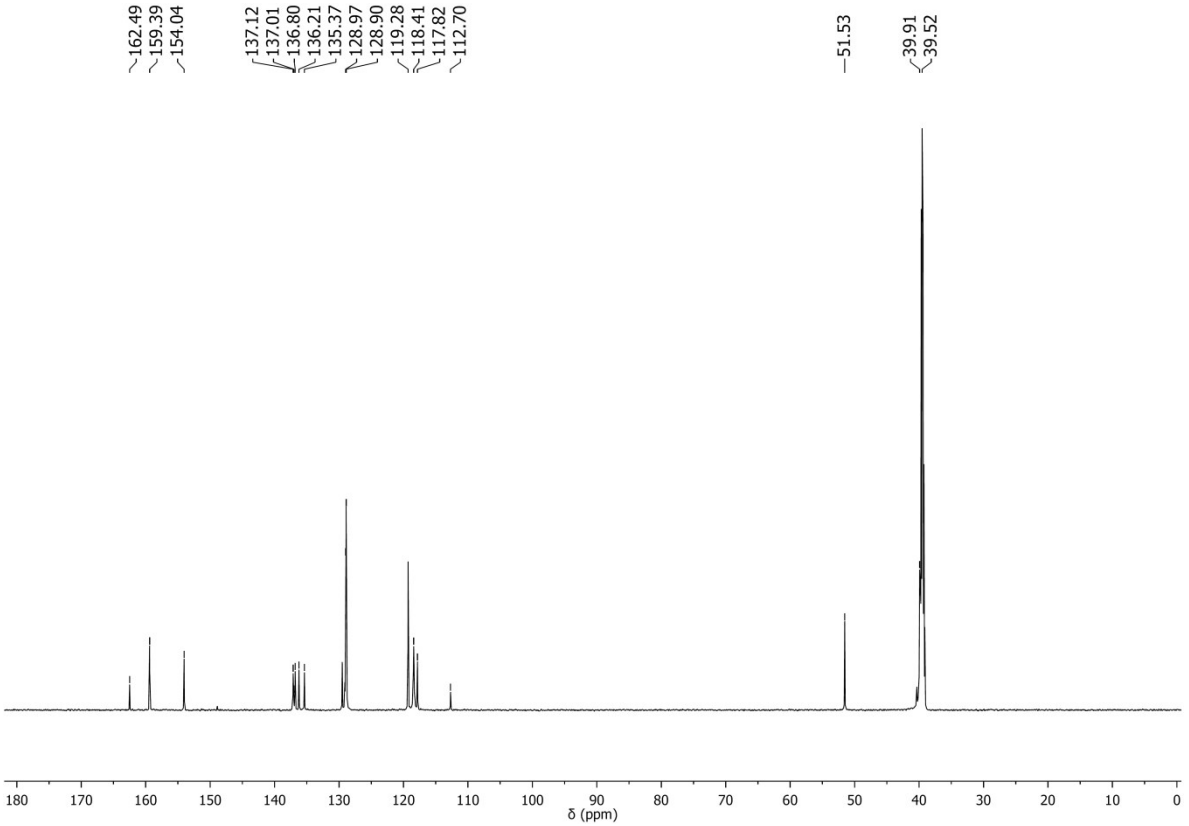
^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): dimethyl [methylenebis(4,1-phenylene)]-dicarbamate (MDC)



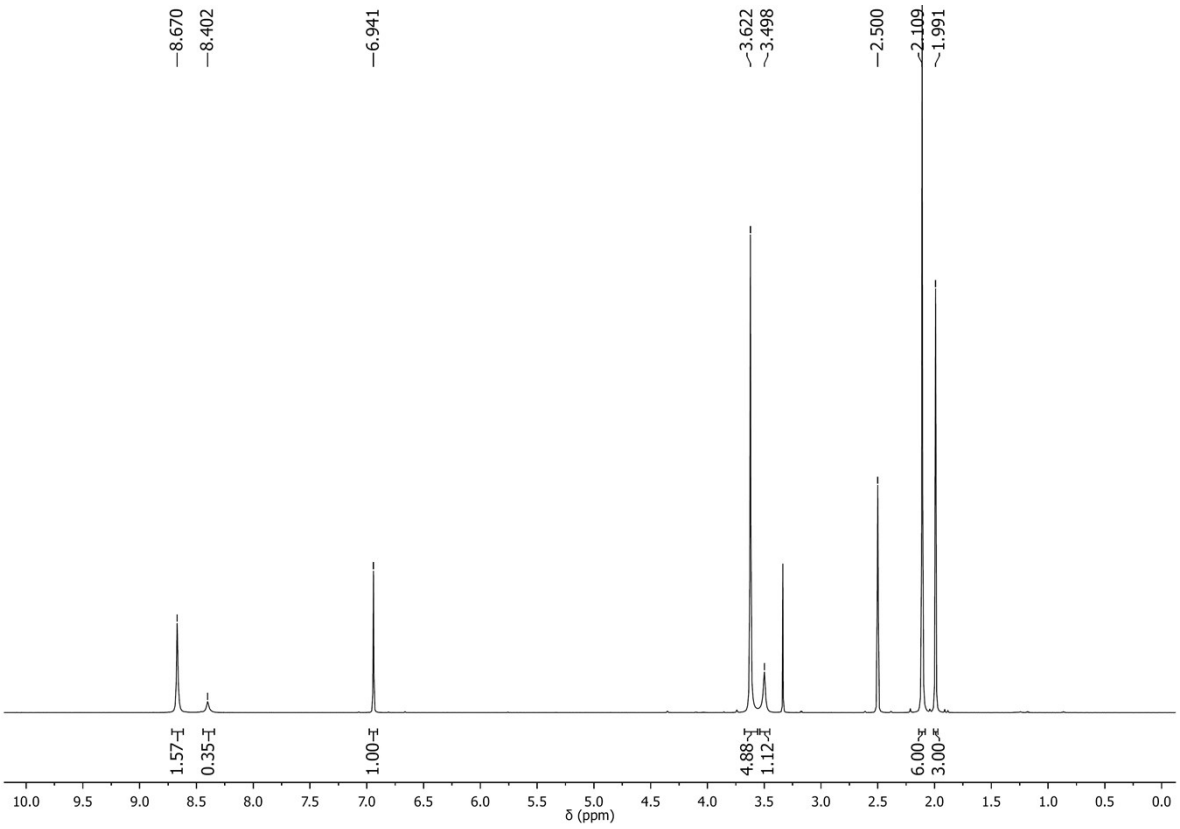
^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): methyl [4-(4-formamidobenzyl)phenyl]-carbamate (16)



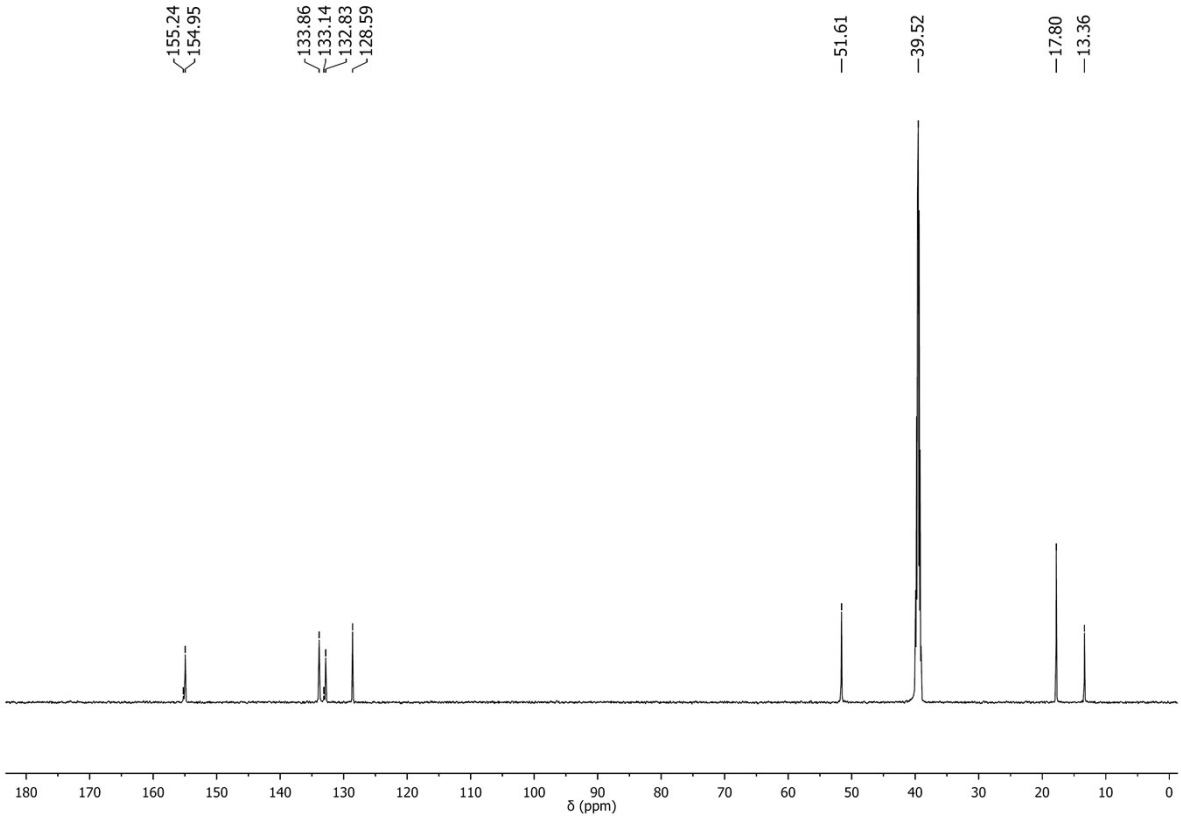
^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): methyl [4-(4-formamidobenzyl)phenyl]-carbamate (16)



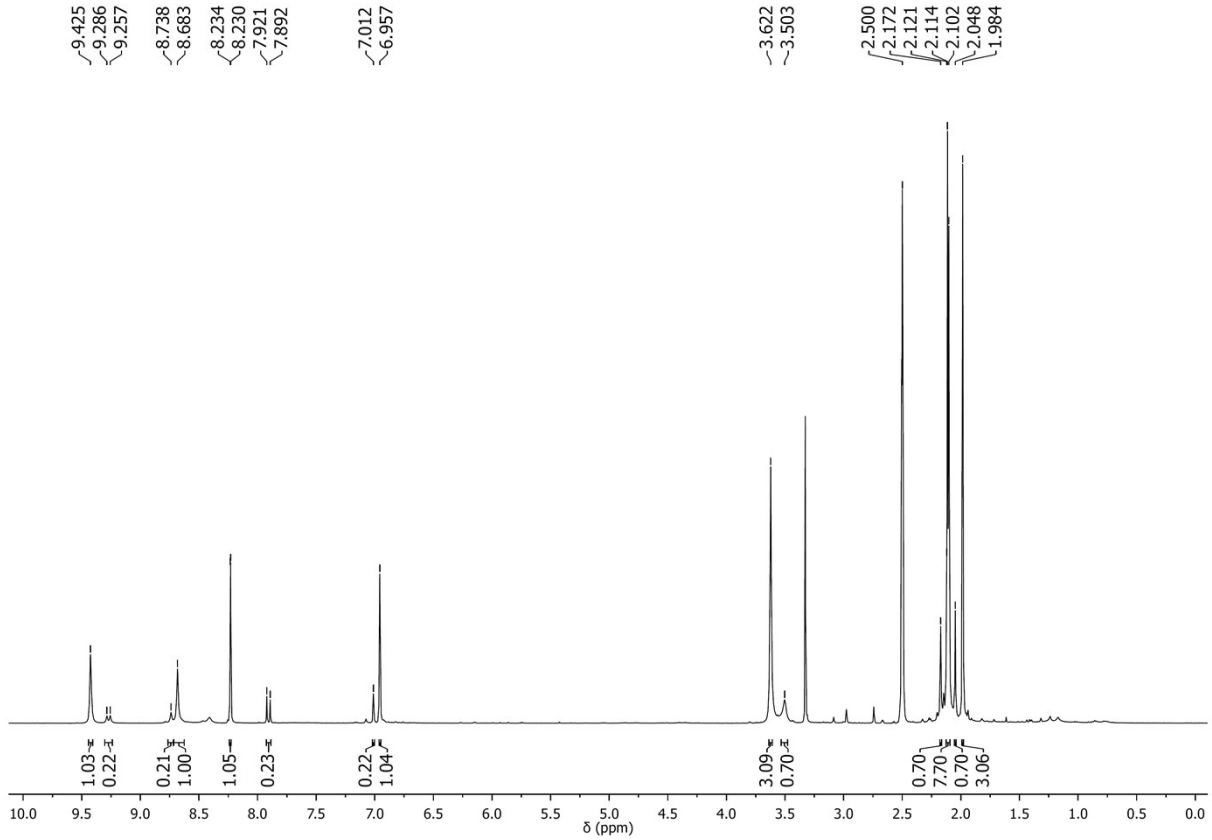
^{1}H-NMR (DMSO-d_6, 600.07 MHz, 296 K): dimethyl (2,4,6-trimethyl-1,3-phenylene)-dicarbamate (18)



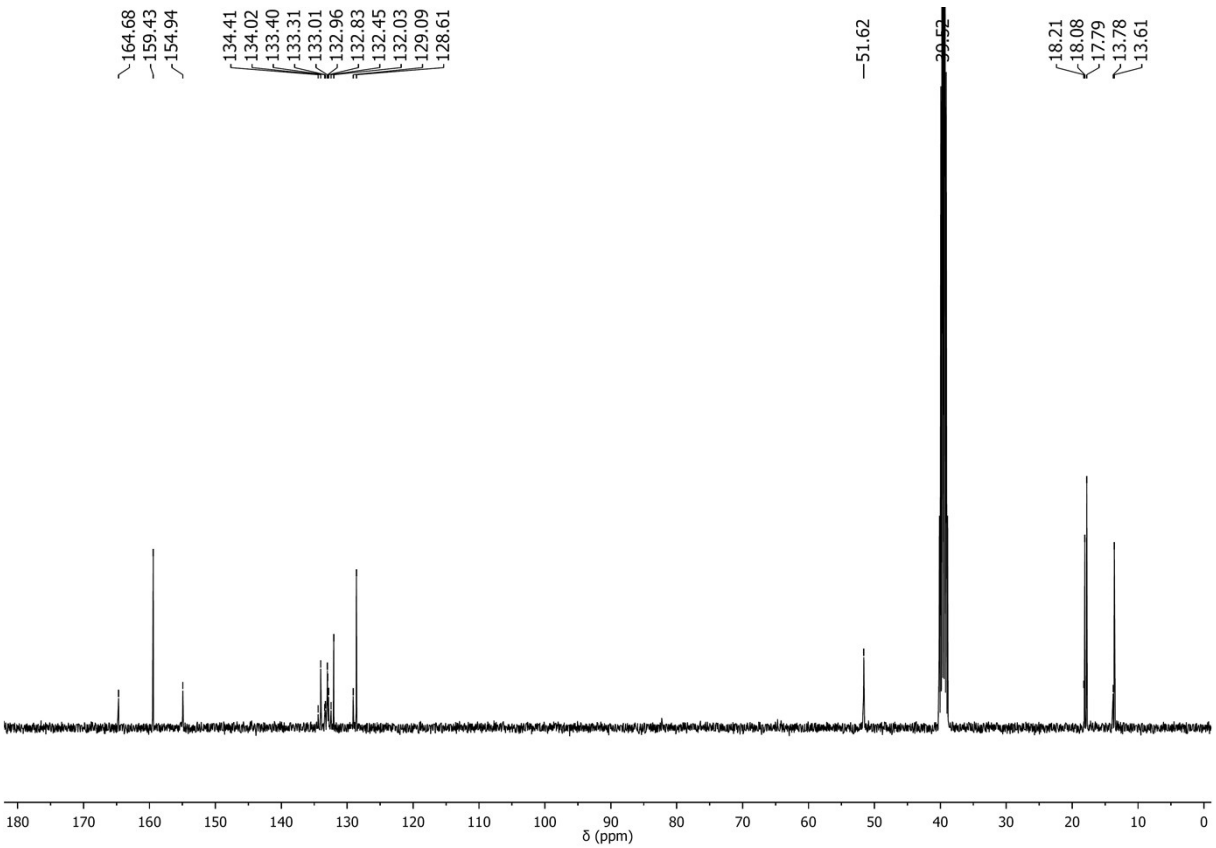
^{13}C{^{1}H}-NMR (DMSO-d_6, 150.89 MHz, 296 K): dimethyl (2,4,6-trimethyl-1,3-phenylene)-dicarbamate (18)



^{1}H-NMR (DMSO-d_6, 400.17 MHz, 296 K): methyl (3-formamido-2,4,6-trimethylphenyl)-carbamate (21)



^{13}C-NMR (DMSO-d_6, 100.62 MHz, 296 K): methyl (3-formamido-2,4,6-trimethylphenyl)-carbamate (21)



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