Supporting Information

Tuneable Reduction of CO_2 – Organocatalyzed Selective Formylation and Methylation of Amines

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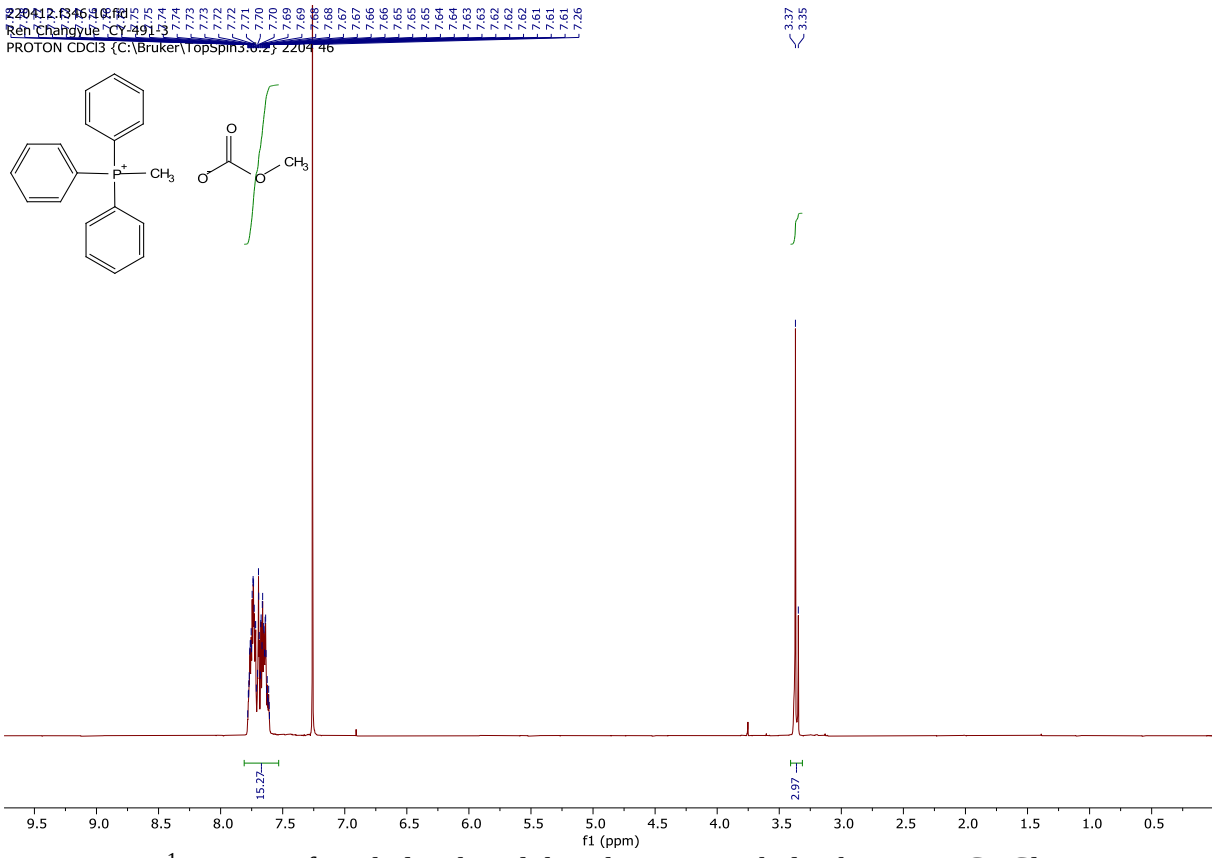
CONTENT

1. General considerations

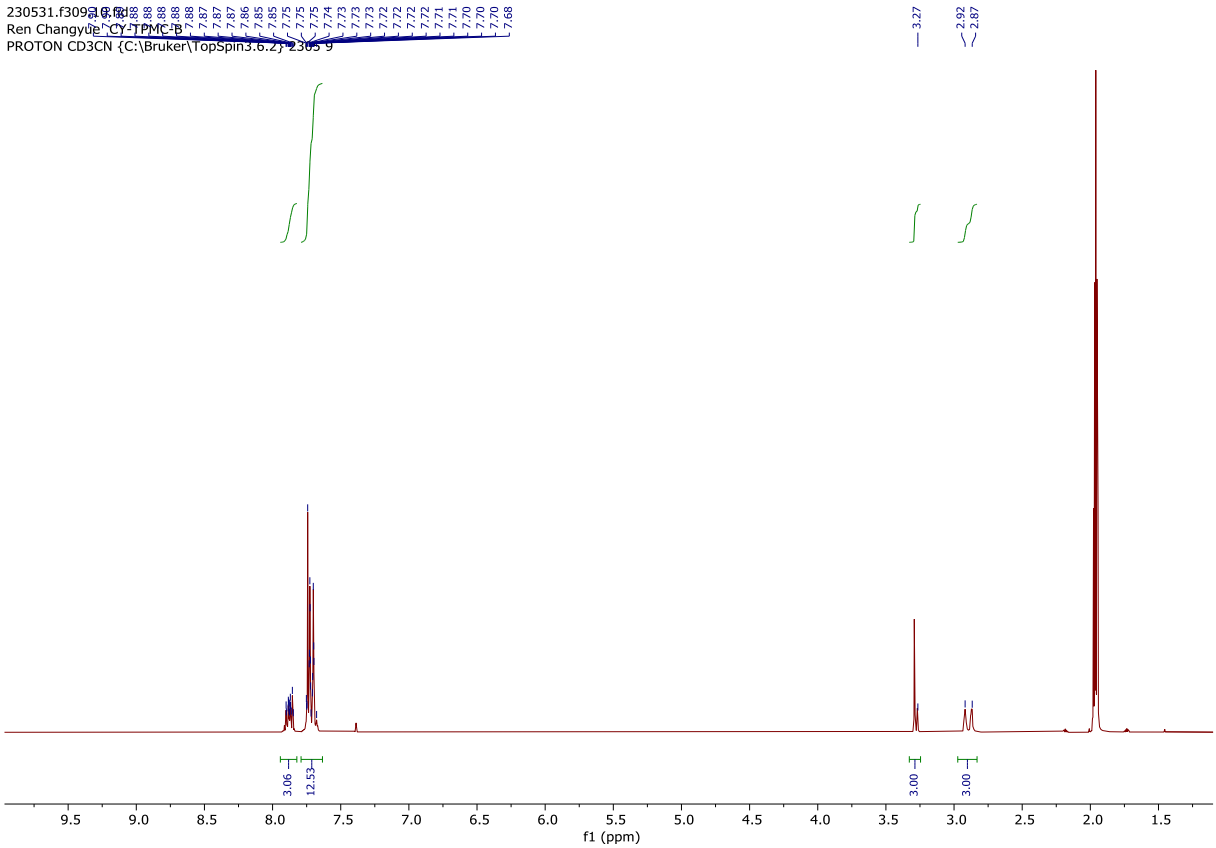
All chemicals were purchased from commercial sources in purities of ≥95% and used without further purification. Carbon dioxide (99.998%) was obtained from Linde AG. Methyltriphenylphosphonium methylcarbonate salt was purchased from Sigma-Aldrich. Polymethylhydrosiloxane (PMHS) was purchased from Sigma-Aldrich (viscosity 15–40 mPa·s) Deuterated solvents were ordered from Deutero GmbH and stored over molecular sieves. Reactions were performed in a 45 cm^3 stainless-steel autoclave from Parr Instrument Company. The reactions were conducted with 5000 Multi Reactor System (MRS) from Parr Instrument Company. The pressure was adjusted using a pressure regulator LMD50003 from Druva and monitored with the MRS-system using ASHCROFT Type G2 pressure transducer. NMR spectra were received using Bruker 300 Fourier, Bruker AV 300 and Bruker AV 400 spectrometers. Chemical shifts are reported in ppm relative to the residue solvent peak in deuterated solvent. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet and m = multiplet. NMR yields were determined by using mesitylene as internal standard. Gas chromatography was performed on Agilent 7890A GC System, mass spectra were measured on downstream 5975C inert XL MSD mass detector also from Agilent. LC-MS was performed on Waters Acquity UPLC H-Class/Xevo G2-XS TOF LC-MS. Elemental analysis was performed on a TruSpec CHMS Micro from Leco. Thin layer chromatography was performed on Merck TLC plates with fluorescence indication (silica type 60, F254), spots were visualized using UV-light. Flash chromatography was performed using silica with a grain size of 40–63 µm from Macherey-Nagel.

2. Synthesis of methyltriphenylphosphonium methylcarbonate salt catalyst[1]

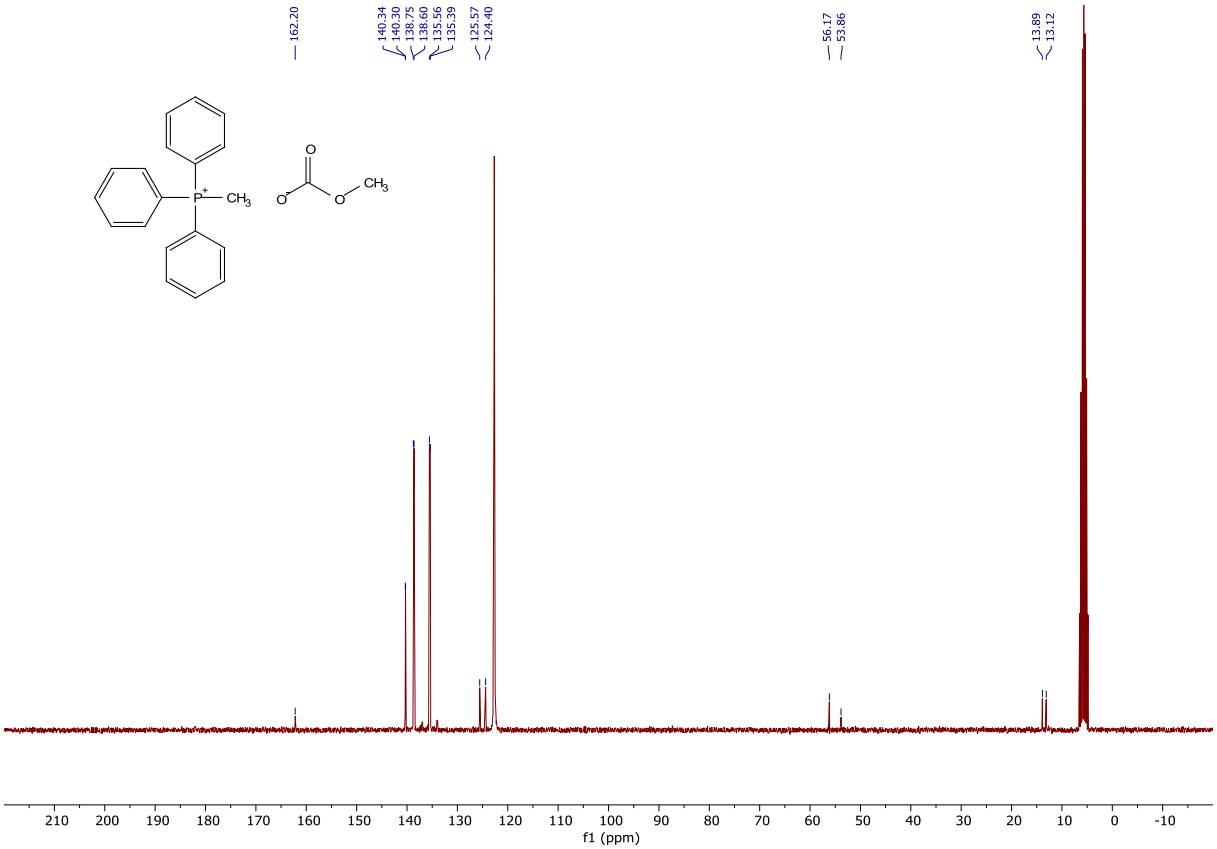
In a 10 mL Schlenk tube, dimethylcarbonate (DMC) (0.52 mL, 6.15 mmol), triphenylphosphine (0.235 g, 0.896 mmol) and methanol (0.52 mL) as solvent were introduced in the shortest time possible to limit the exposure of the phosphine to air. The Schlenk tube was heated for 24 hours at 140 °C under magnetic stirring. Afterwards, the reaction mixture was allowed to cool to ambient temperature. The homogeneous pale-yellow solution was transferred to a round-bottomed flask and volatiles were removed from the mixture by rotary evaporation at 40 °C. The off-white solid was stirred under inert atmosphere with cyclohexane (8.3 mL), at 50 °C for 2 hours. After filtration on a Gooch crucible the product was obtained in 64% as a colorless solid (0.215 mg, 0.580 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 – 7.58 (m, 15H), 3.37 (s, 3H) ppm. The missing H signal of P-CH_3 is due to H/D exchange with $CDCl_3$. ^{1}H NMR (300 MHz, CD_3CN): δ 7.98 – 7.81 (m, 3H), 7.79 – 7.62 (m, 12H), 3.29 (s, 3H), 2.89 (d, *J* = 15.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.96 (d, *J* = 2.9 Hz), 133.26 (d, *J* = 10.7 Hz), 130.39 (d, *J* = 12.9 Hz), 119.41 (d, *J* = 88.5 Hz), 52.20. ^{13}C NMR (75 MHz, CD_3CN): δ = 162.20, 140.32 (d, *J* = 3.1 Hz), 138.68 (d, *J* = 10.8 Hz), 135.47 (d, *J* = 12.9 Hz), 124.98 (d, *J* = 88.9 Hz), 56.17, 13.50 (d, *J* = 57.8 Hz) ppm. ^{31}P NMR (122 MHz, $CDCl_3$): δ = 21.92 ppm. HR-MS ($MePh_3P$+): m/z calcd 277.1151 g/mol, found 277.1153 g/mol.



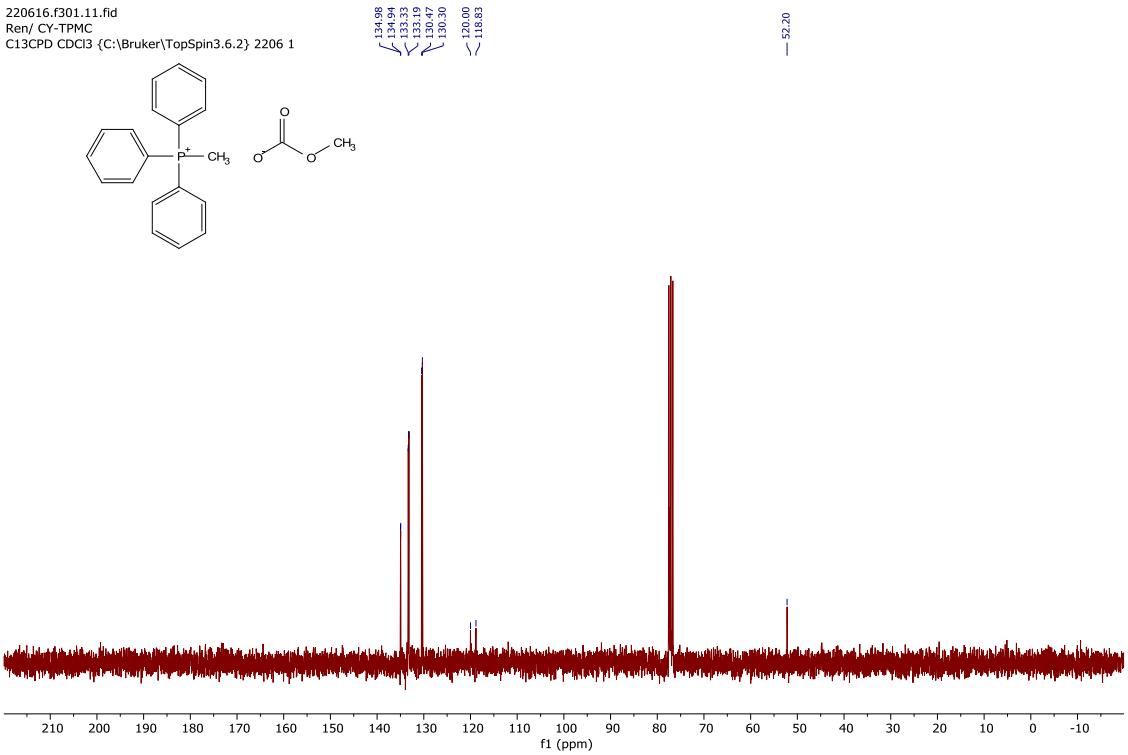
^{1}H NMR of methyltriphenylphosphonium methylcarbonate in $CDCl_3$



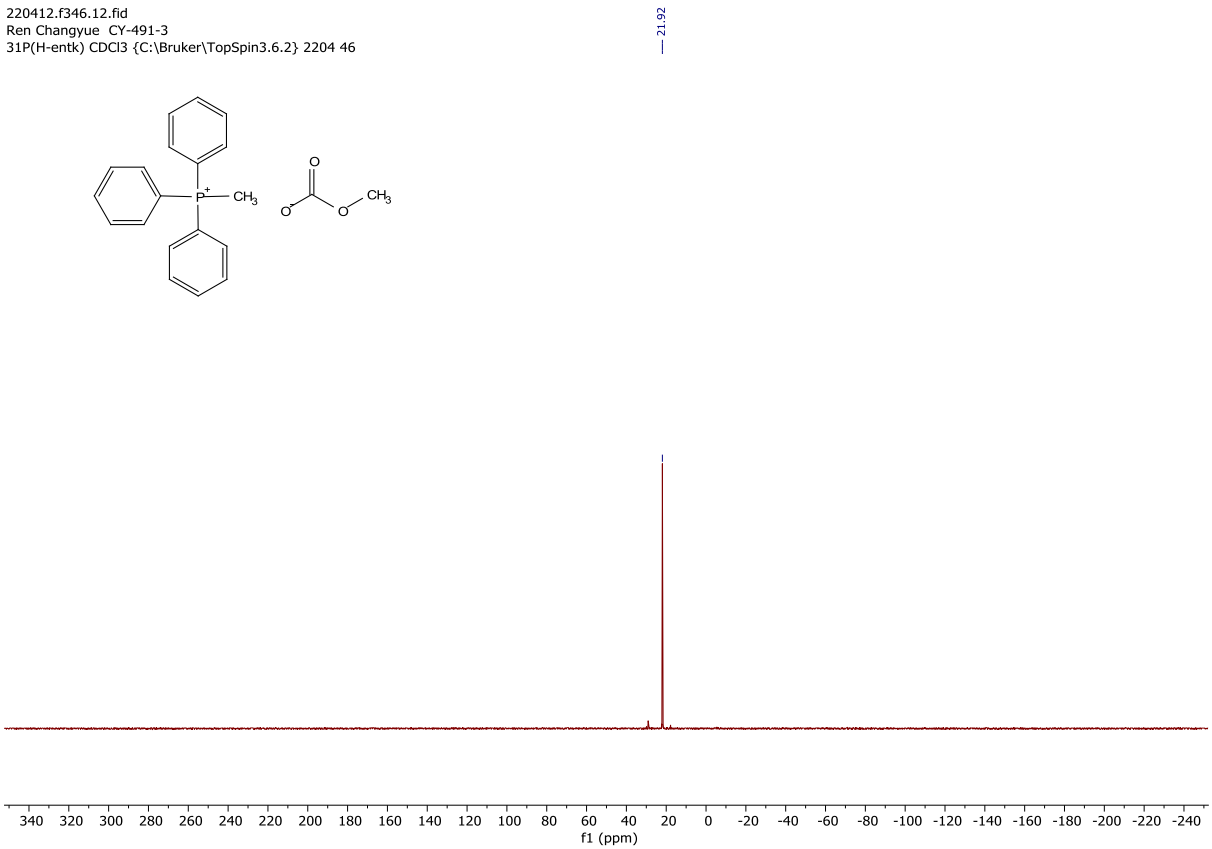
^{1}H NMR of methyltriphenylphosphonium methylcarbonate in CD_3CN



^{13}C NMR of methyltriphenylphosphonium methylcarbonate in CD_3CN



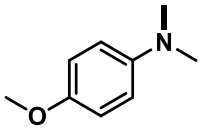
^{13}C NMR of methyltriphenylphosphonium methylcarbonate in $CDCl_3$



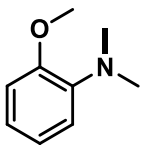
^{31}P NMR of methyltriphenylphosphonium methylcarbonate

3. Synthesis of methylated amines 2

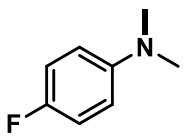
General procedure (GP1) for the synthesis of methylated amines 2: A 45 cm^3 stainless-steel autoclave was charged with catalyst (10 mol%) and aniline **1** (0.600 mmol), PMHS (414 µL), THF 5 mL. The autoclave was purged with CO_2 and the pressure kept constant at 1.0 bar. The reaction mixture was stirred at 70 °C for 4–16 h. Subsequently the CO_2 was released slowly. The solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (hexane/ethyl acetate = 20/1) to afford the corresponding products. ^{1}H NMR yields were determined by using mesitylene as the internal standard.



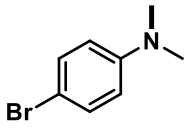
According to the GP1, 4-methoxy-*N*-methylaniline (**1b**, 82.7 mg, 0.600 mmol), catalyst (21.4 mg, 60.0 µmol), PMHS (414 µL) and THF 5 mL and CO_2 were converted at 70 °C, 1.0 bar for 16 h to yield 4-methoxy-*N*,*N*-dimethylaniline (**2b**) (54.6 mg, 0.361 mmol, 60%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93 – 6.73 (m, 4H), 3.77 (s, 3H), 2.88 (s, 6H).[2]



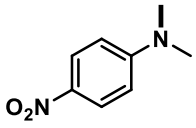
According to the GP1, 2-methoxy-*N*-methylaniline (**1c**, 82.7 mg, 0.600 mmol), catalyst (21.4 mg, 60.0 µmol), PMHS (414 µL) and THF 5 mL and CO_2 were converted at 70 °C, 1.0 bar for 4 h to yield 2-methoxy-*N*,*N*-dimethylaniline (**2c**) (64.2 mg, 0.425 mmol, 71%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 – 6.83 (m, 4H), 3.89 (s, 3H), 2.80 (s, 6H).[2]



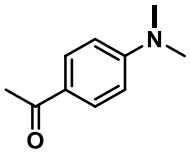
According to the GP1, 4-floro-*N*-methylaniline (**1d**, 73.8 mg, 0.600 mmol), catalyst (21.4 mg, 60.0 µmol), PMHS (414 µL) and THF 5 mL and CO_2 were converted at 70 °C, 1.0 bar for 16 h to yield 4-fluoro-*N*,*N*-dimethylaniline (**2d**) (72.0 mg, 0.517 mmol, 86%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 – 6.88 (m, 2H), 6.74 (d, *J* = 5.7 Hz, 2H), 2.91 (s, 6H).[3]



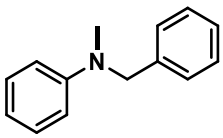
According to the GP1, 4-bromo-*N*-methylaniline (**1e**, 112 mg, 0.600 mmol), (21.4 mg, 60.0 µmol), PMHS (414 µL) and THF 5 mL and CO_2 were converted at 70 °C, 1.0 bar for 16 h to yield 4-bromo-*N*,*N*-dimethylaniline (**2e**) (92.8 mg, 0.464 mmol, 77%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 2H), 6.60 (d, *J* = 9.1 Hz, 2H), 2.92 (s, 6H).[2]



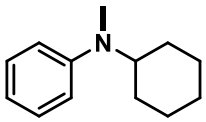
According to the GP1, 4-nitro-*N*-methylaniline (**1f**, 91.3 mg, 0.600 mmol), catalyst (21.4 mg, 60.0 µmol), PMHS (414 µL) and THF 5 mL and CO_2 were converted at 70 °C, 1.0 bar for 16 h to yield *N*,*N*-dimethyl-4-nitroaniline (**2f**) (19.0 mg, 0.114 mmol, 19%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.4 Hz, 2H), 6.61 (d, *J* = 9.5 Hz, 2H), 3.11 (s, 6H).[3]



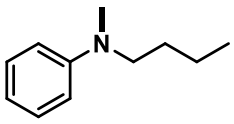
According to the GP1, 4-acetyl-*N*-methylaniline (**1g**, 89.5 mg, 0.600 mmol), catalyst (21.4 mg, 60.0 µmol), PMHS (414 µL) and THF 5 mL and CO_2 were converted at 70 °C, 1.0 bar for 16 h to yield 1-(4-(dimethylamino)phenyl)ethan-1-one (**2g**) (40.7 mg, 0.249 mmol, 42%) as a colorless oil. ^{1}H NMR (300 MHz, CD_3CN) δ 7.87 (m, 2H), 6.66 (dt, *J* = 9.1 Hz, 2H), 3.06 (s, 6H), 2.51 (s, 3H).[2]



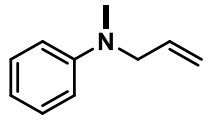
According to the GP1, *N*-benzylaniline (**1h**, 110 mg, 0.600 mmol), catalyst (21.4 mg, 60.0 µmol), PMHS (414 µL) and THF 5 mL and CO_2 were converted at 70 °C, 1.0 bar for 16 h to yield *N*-benzyl-*N*-methylaniline (**2h**) (105 mg, 0.533 mmol, 89%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.28 – 7.19 (m, 5H), 6.81 – 6.69 (m, 3H), 4.55 (s, 2H), 3.03 (s, 3H).[2]



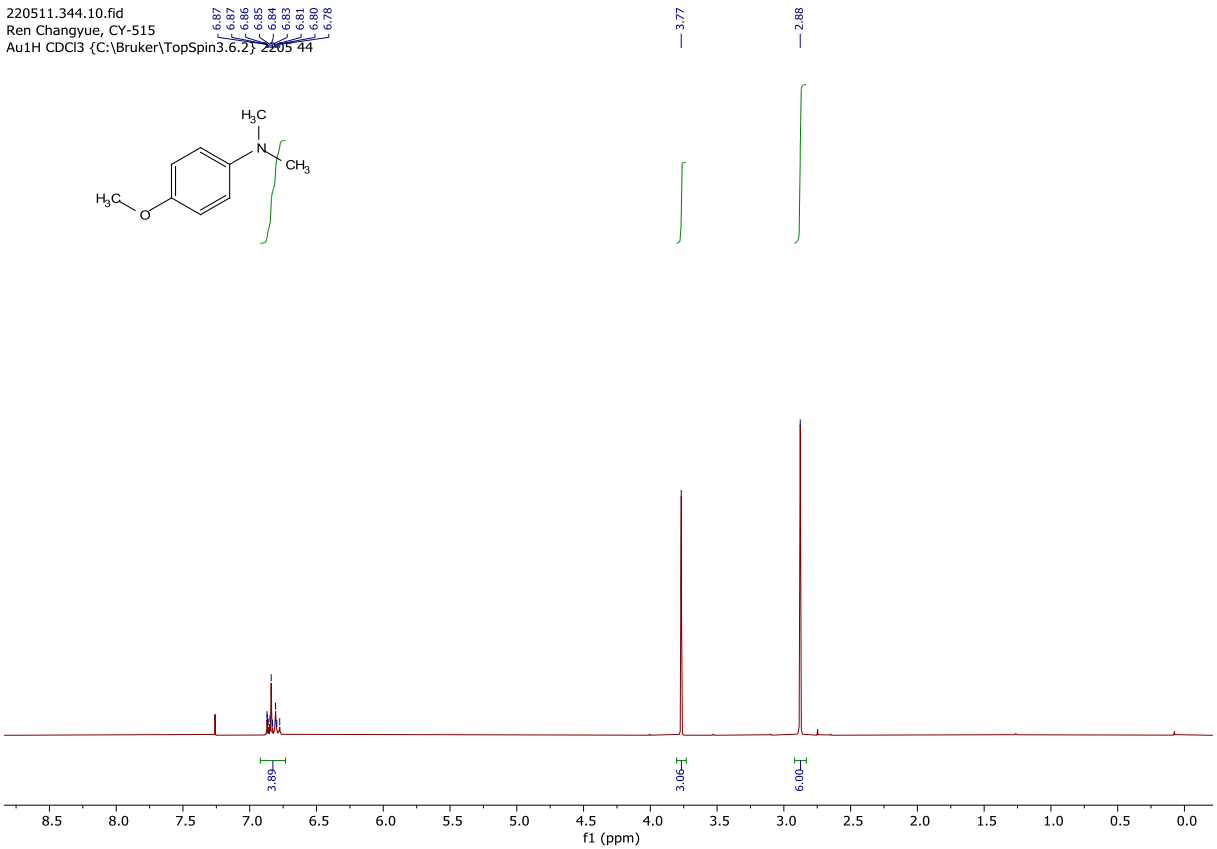
According to the GP1, *N*-cyclohexylaniline (**1i**, 105 mg, 0.600 mmol), catalyst (21.4 mg, 60.0 µmol), PMHS (414 µL) and THF 5 mL and CO_2 were converted at 70 °C, 1.0 bar for 16 h to yield *N*-cyclohexyl-*N*-methylaniline (**2i**) (94.8 mg, 0.501 mmol, 89%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.15 (m, 2H), 6.87 – 6.61 (m, 3H), 3.56 (ddt, *J* = 11.2, 6.6, 3.4 Hz, 1H), 2.79 (s, 3H), 1.93 – 1.63 (m, 5H), 1.53 – 1.29 (m, 4H), 1.21 – 1.06 (m, 1H).[2]



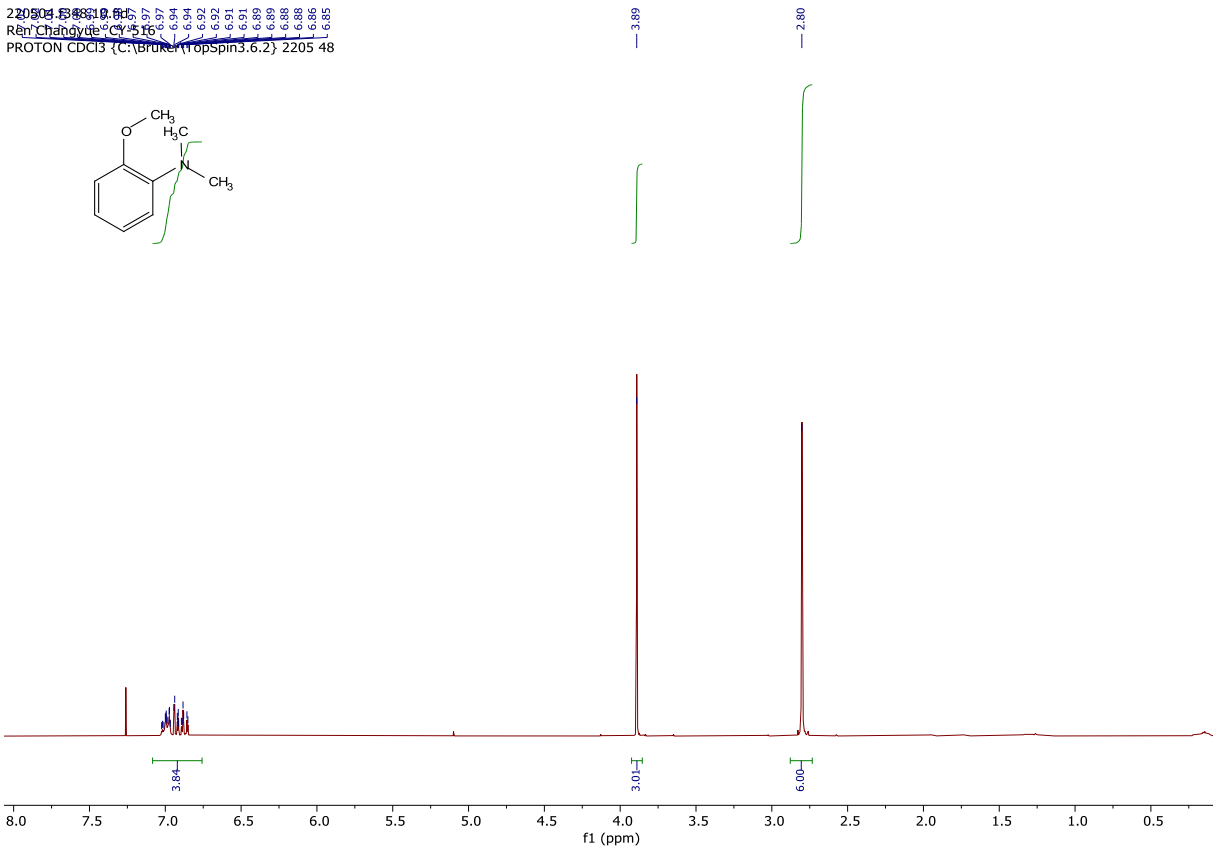
According to the GP1, *N*-butylaniline (**1j**, 89.5 mg, 0.600 mmol), catalyst (21.4 mg, 60.0 µmol), PMHS (414 µL) and THF 5 mL and CO_2 were converted at 70 °C, 1.0 bar for 16 h to yield *N*-butyl-*N*-methylaniline (**2j**) (85.1 mg, 0.521 mmol, 87%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 2H), 6.70 (t, *J* = 6.6 Hz, 3H), 3.40 – 3.28 (m, 2H), 2.94 (s, 3H), 1.68 – 1.50 (m, 2H), 1.45 – 1.28 (m, 2H), 1.07 – 0.88 (m, 3H).[2]



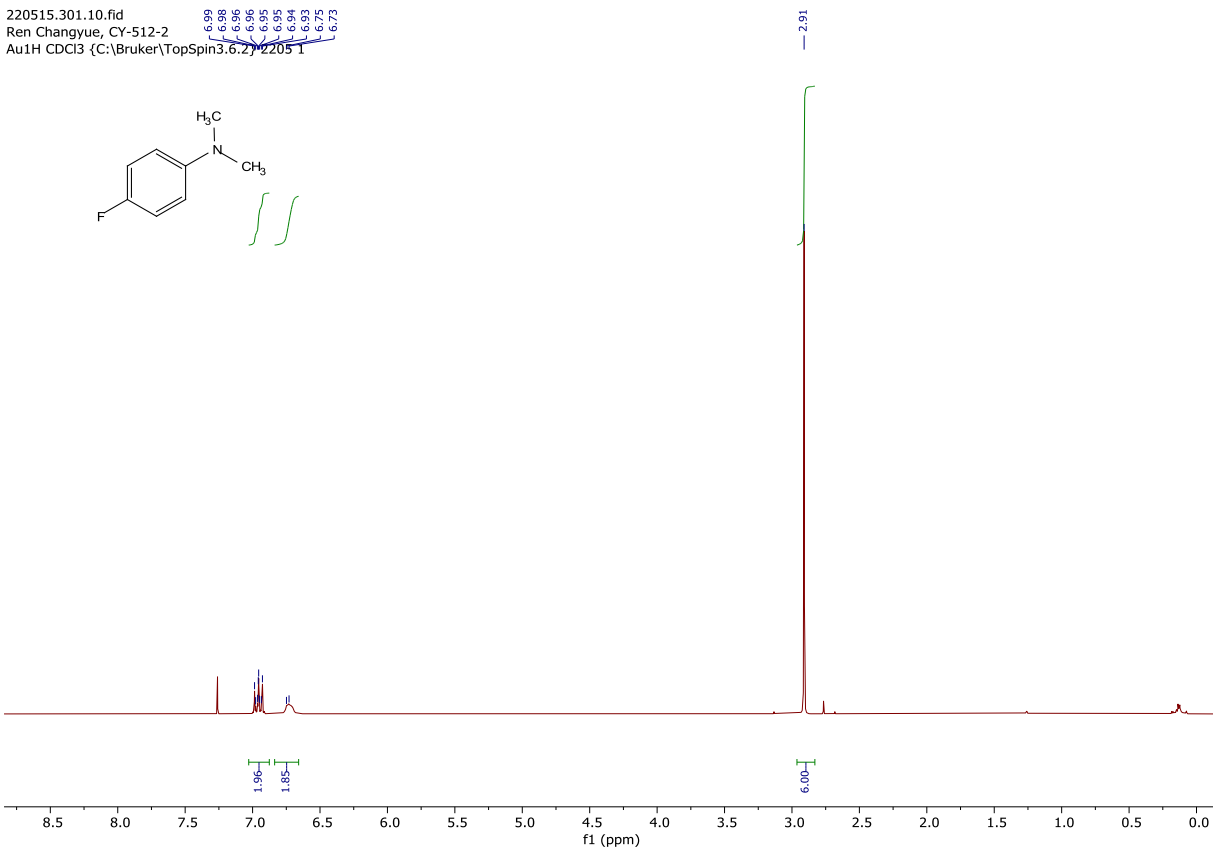
According to the GP1, *N*-allylaniline (**1k**, 80.0 mg, 0.600 mmol), catalyst (21.4 mg, 60.0 µmol), PMHS (414 µL) and THF 5 mL and CO_2 were converted at 70 °C, 1.0 bar for 16 h to yield *N*-allyl-*N*-methylaniline (**2k**) (72.8 mg, 0.494 mmol, 82%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 8.9, 7.2 Hz, 2H), 6.74 – 6.51 (m, 3H), 5.92 – 5.66 (m, 1H), 5.19 – 4.94 (m, 2H), 3.84 (dt, *J* = 5.1, 1.7 Hz, 2H), 2.86 (s, 3H).[2]



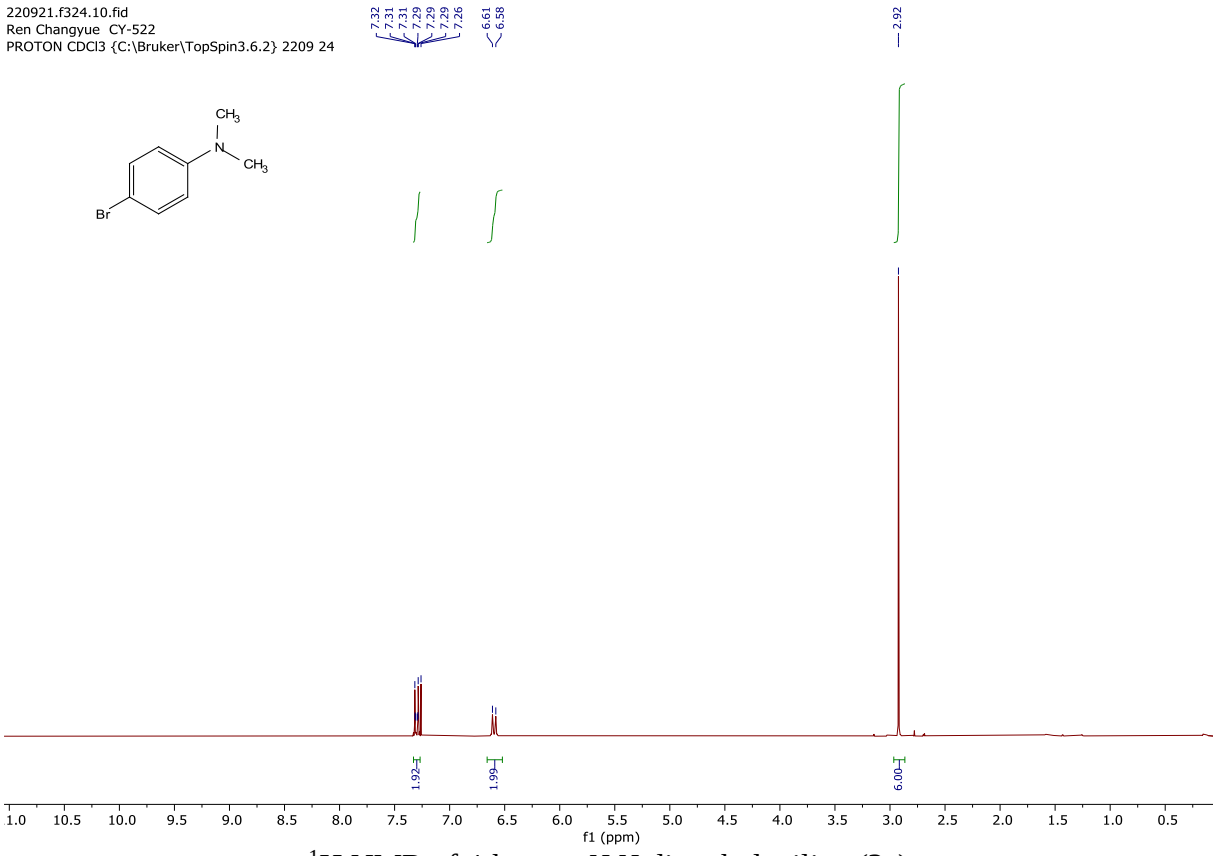
^{1}H NMR of 4-methoxy-*N*,*N*-dimethylaniline (**2b**)



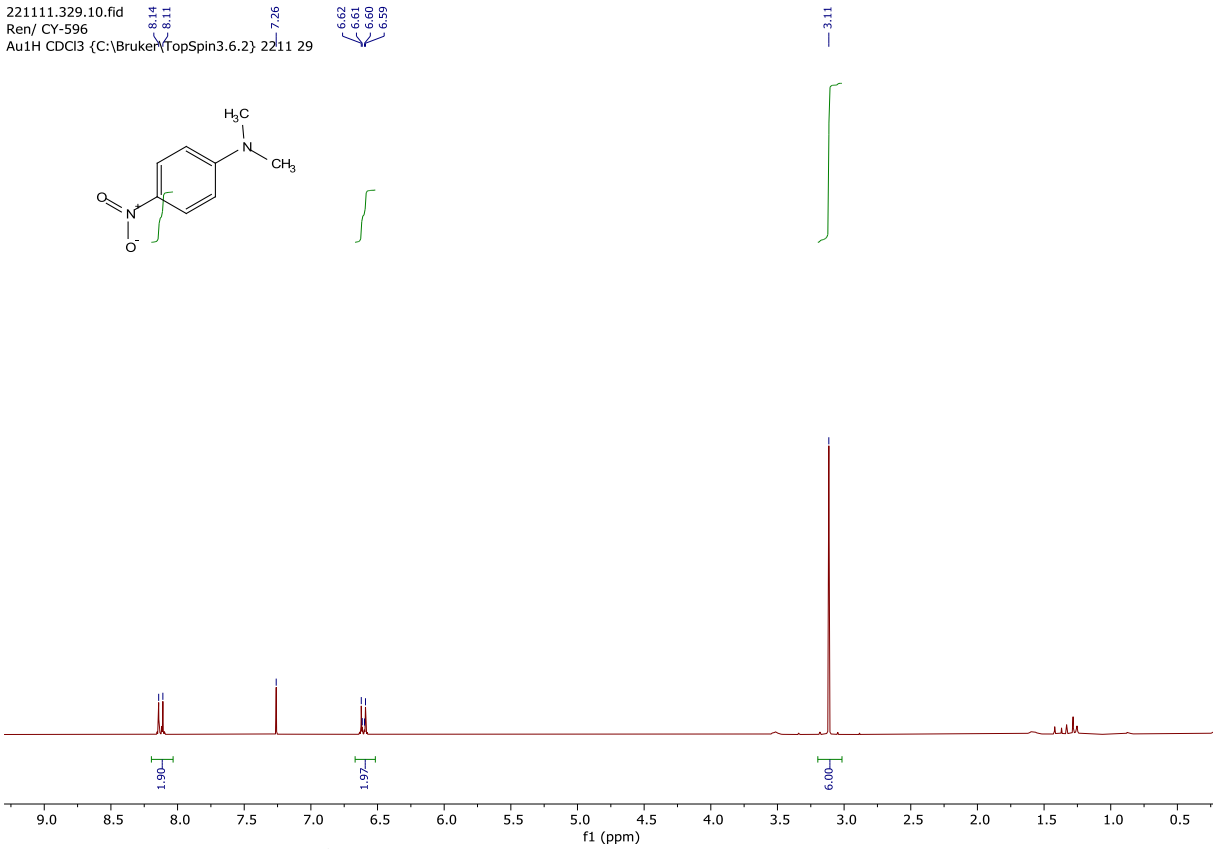
^{1}H NMR of 2-methoxy-*N*,*N*-dimethylaniline (**2c**)



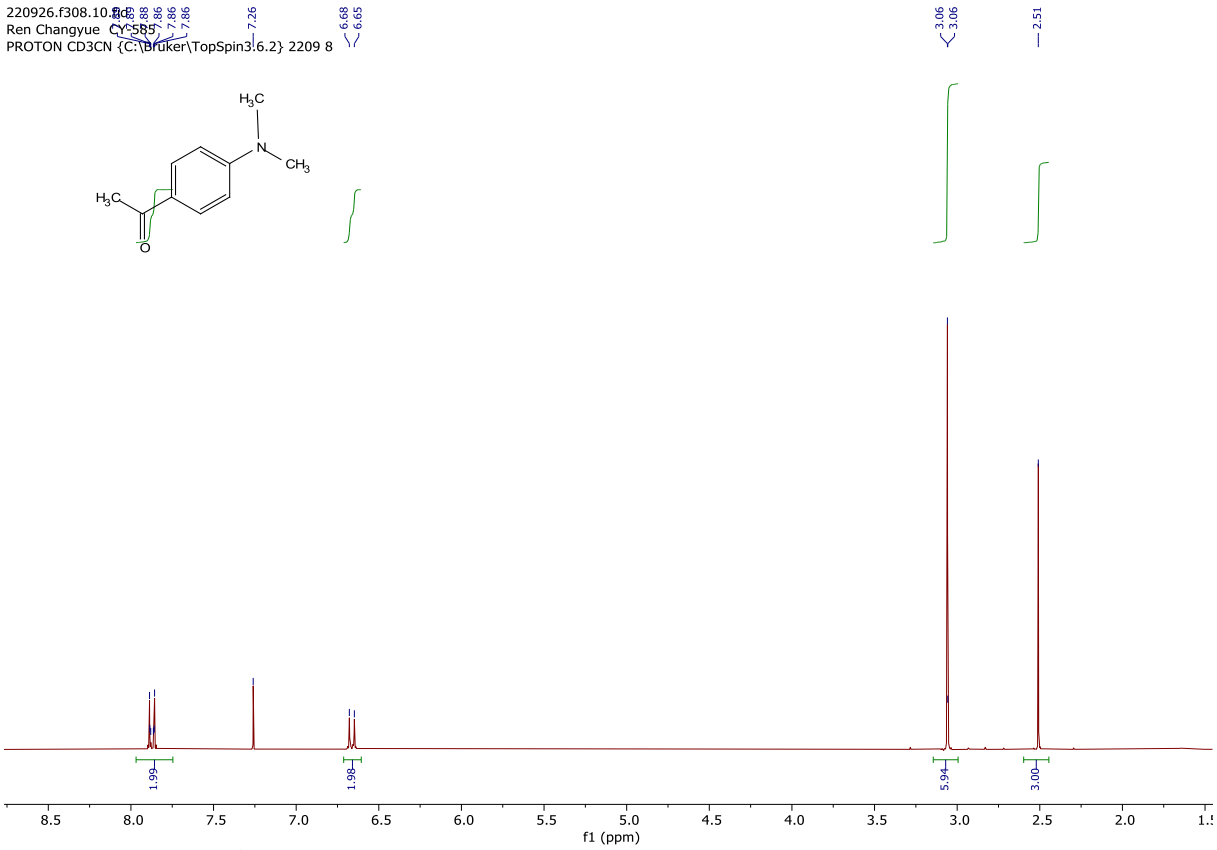
^{1}H NMR of 4-fluoro-*N*,*N*-dimethylaniline (**2d**)



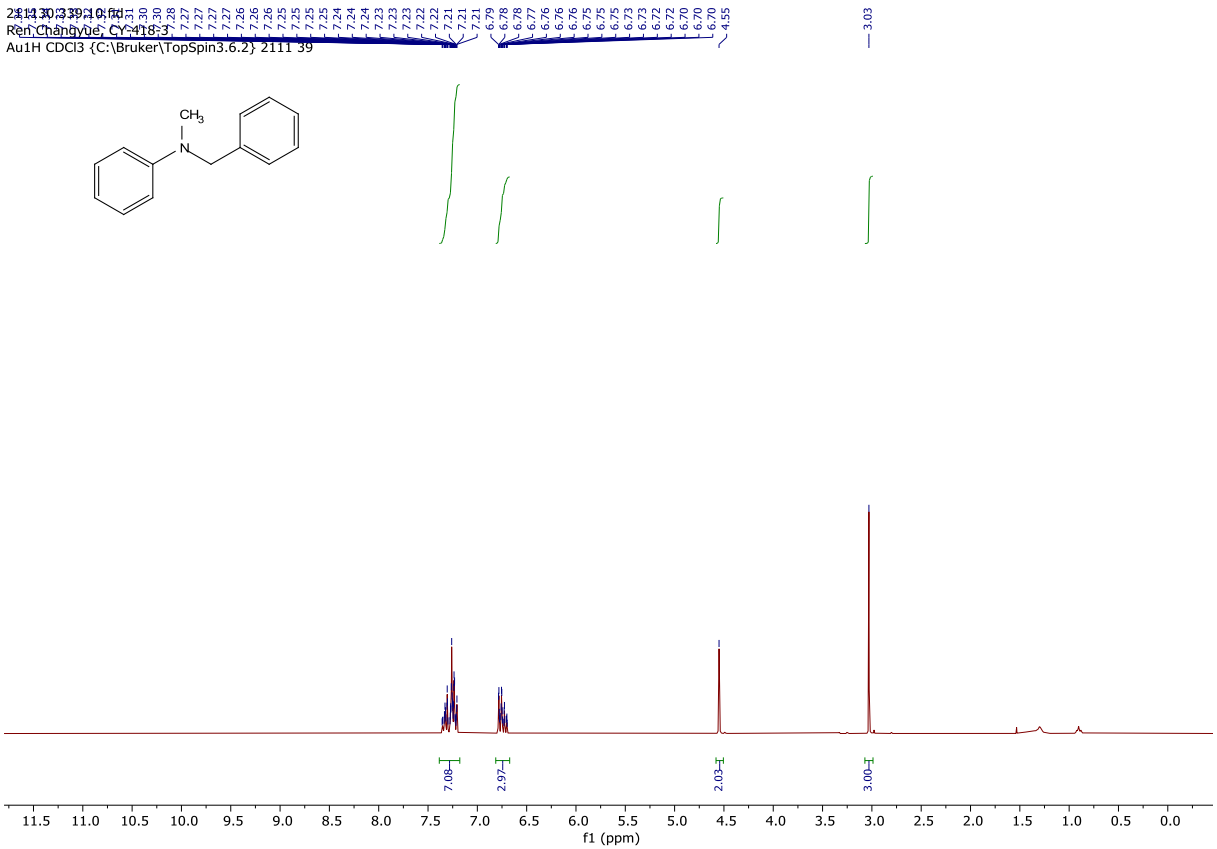
^{1}H NMR of 4-bromo-*N*,*N*-dimethylaniline (**2e**)



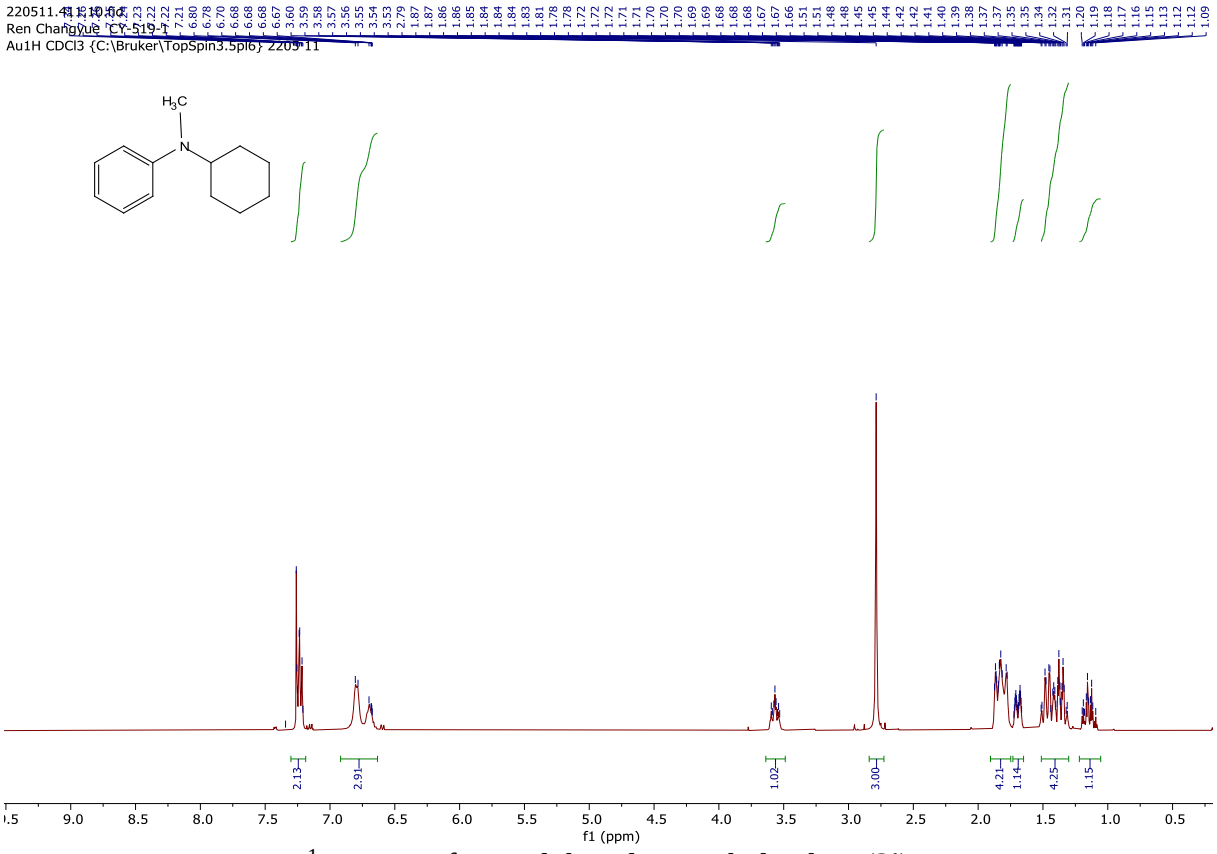
^{1}H NMR of *N*,*N*-dimethyl-4-nitroaniline (**2f**)



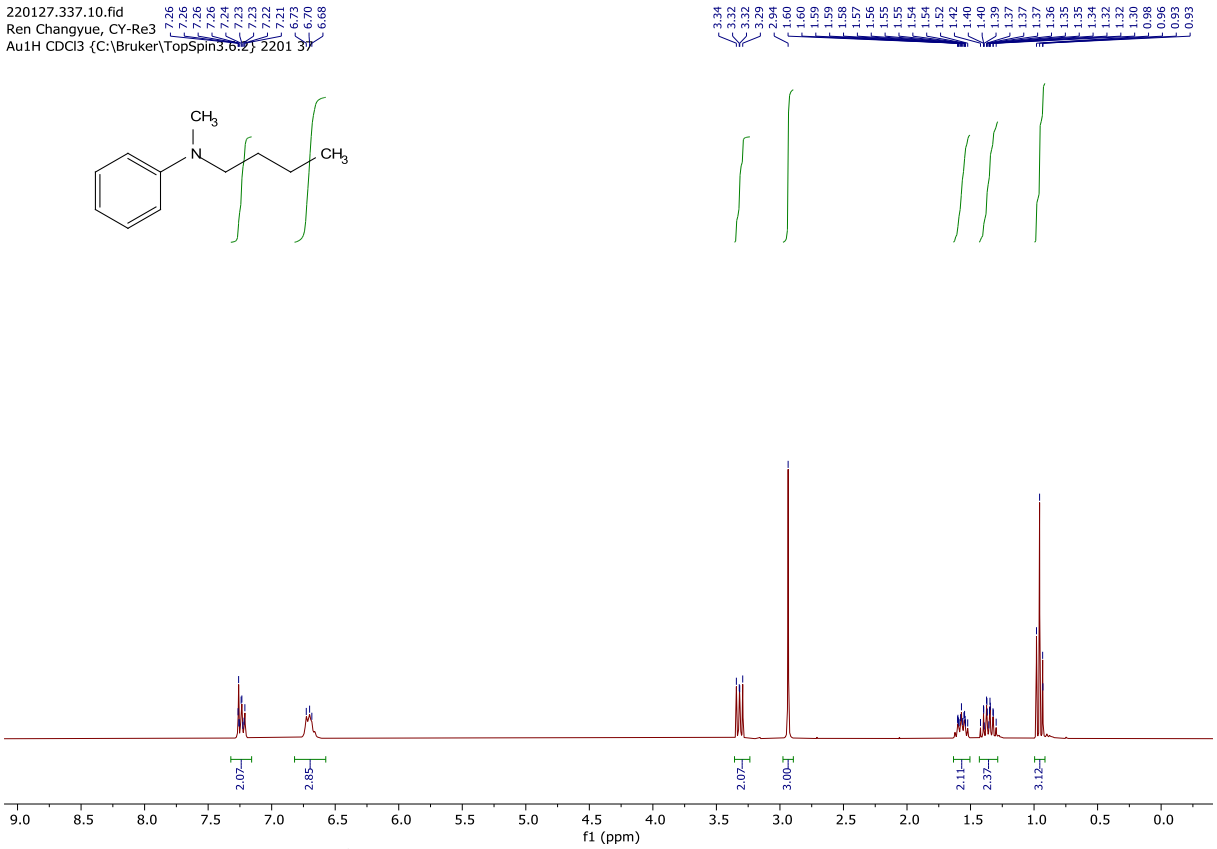
^{1}H NMR of 1-(4-(dimethylamino)phenyl)ethan-1-one (**2g**)



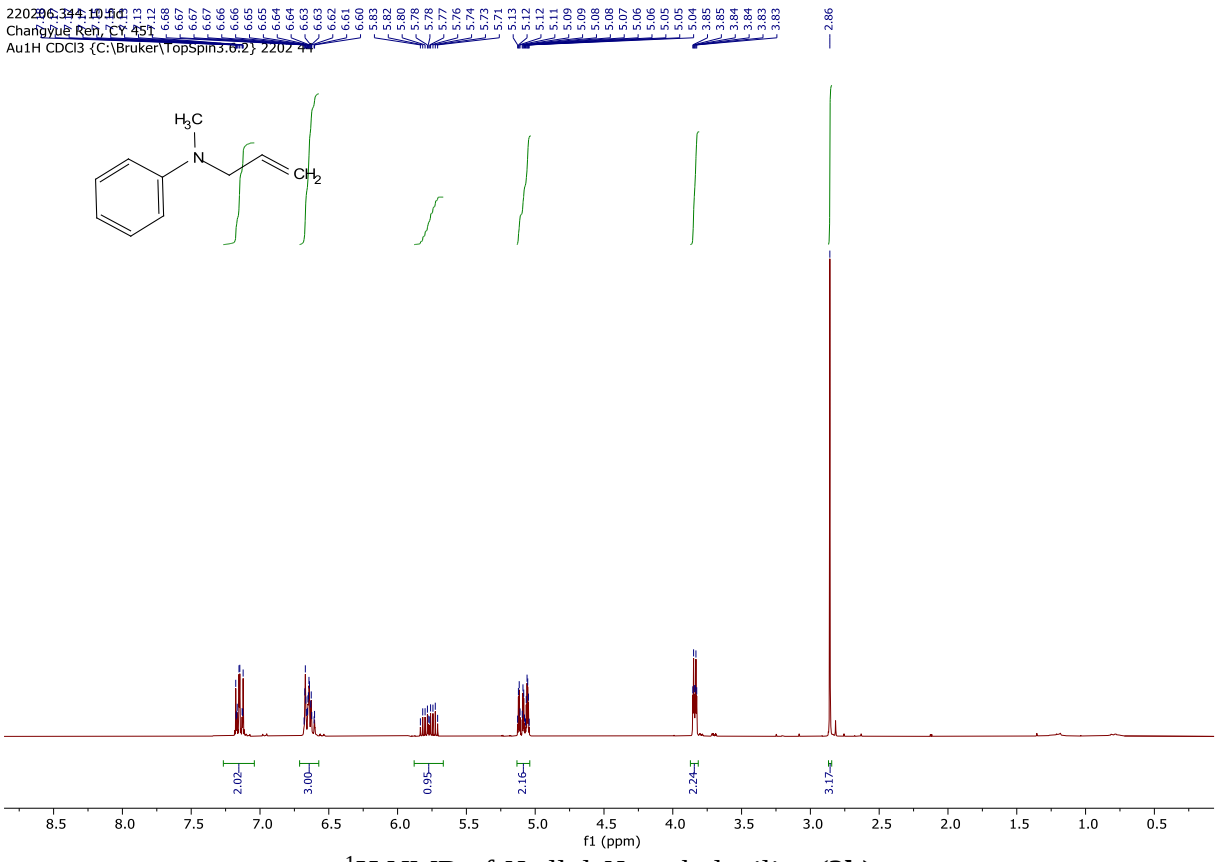
^{1}H NMR of N-benzyl-*N*-methylaniline (**2h**)



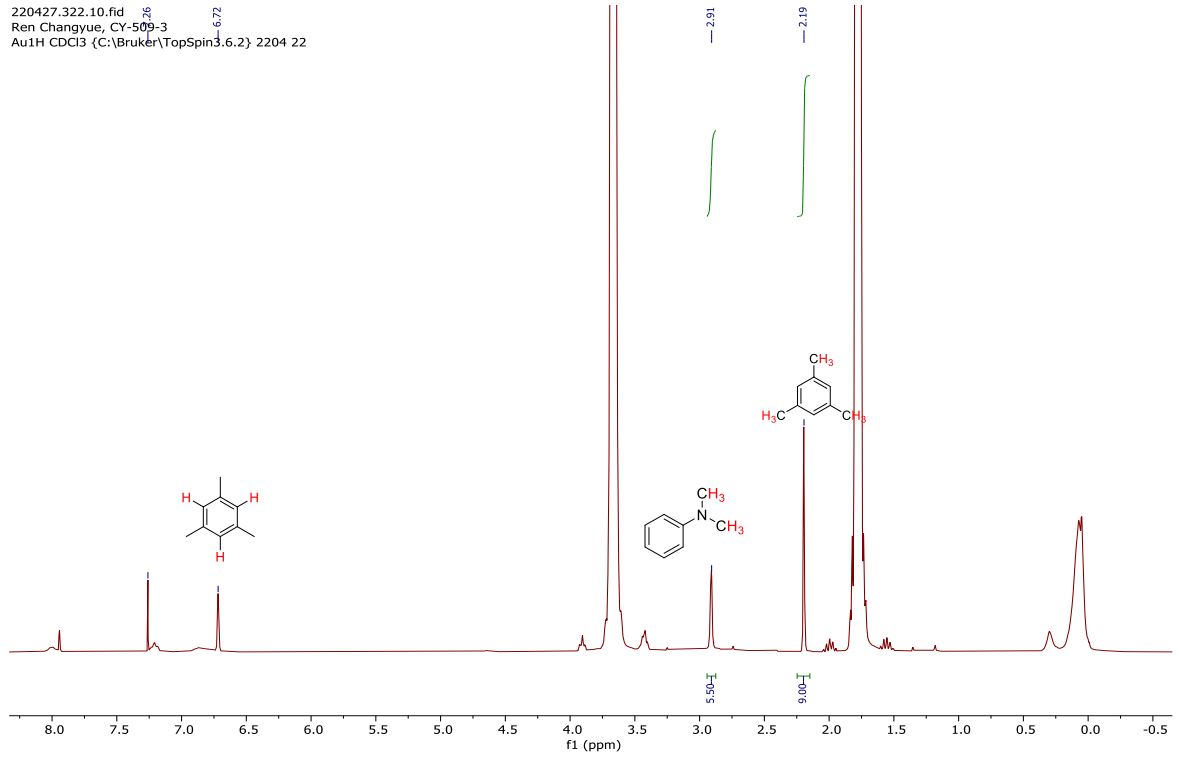
^{1}H NMR of *N*-cyclohexyl-*N*-methylaniline (**2i**)



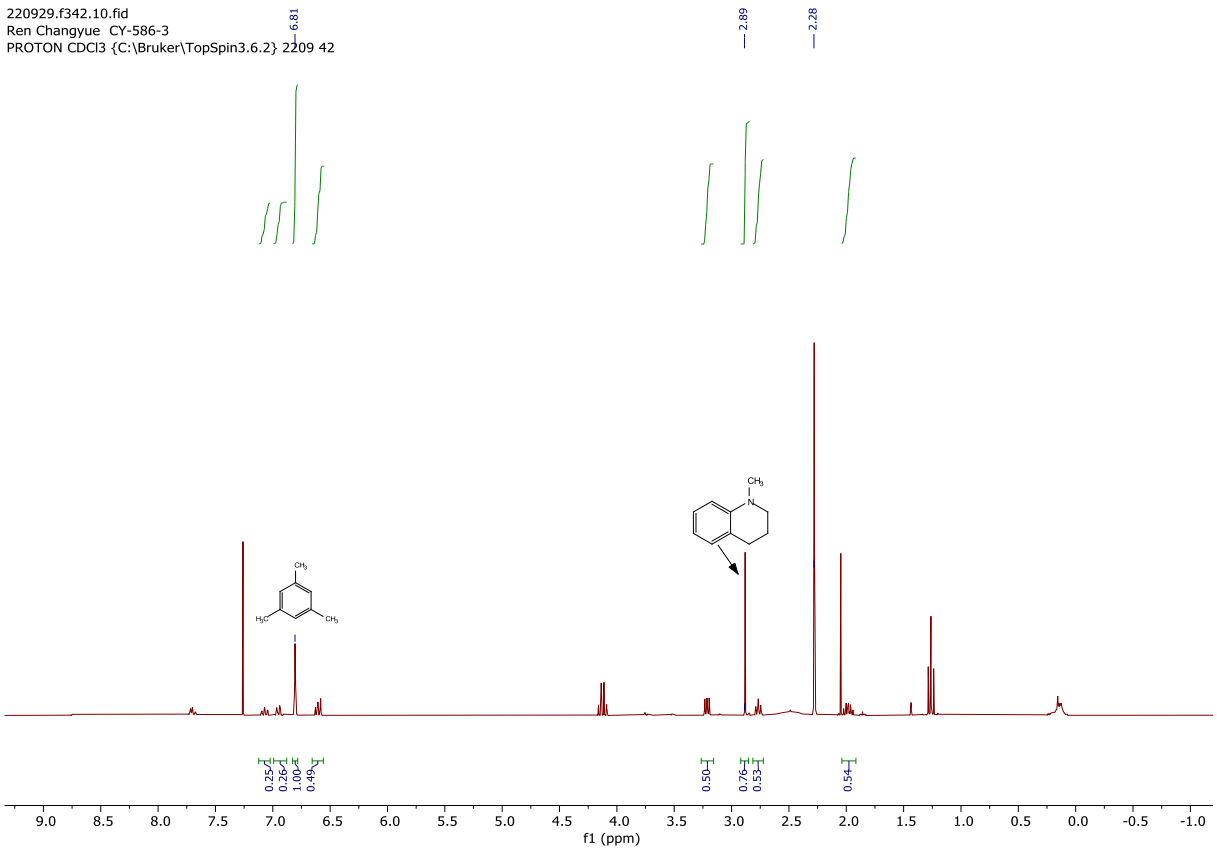
^{1}H NMR of N-butyl-N-methylaniline (**2j)**



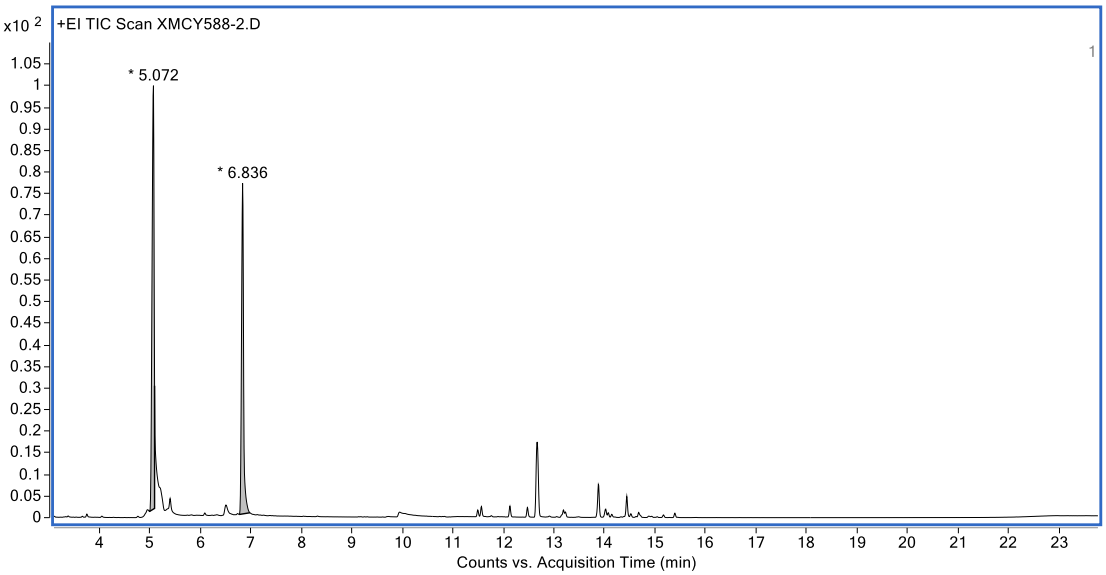
^{1}H NMR of *N*-allyl-*N*-methylaniline (**2k)**

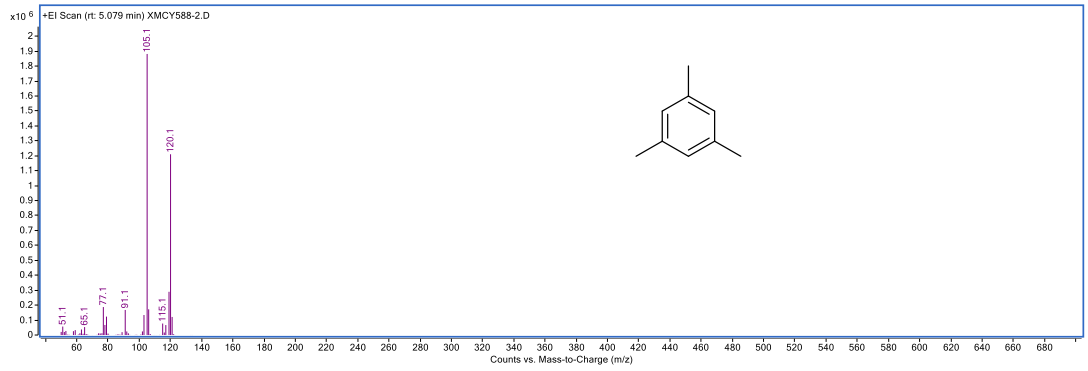


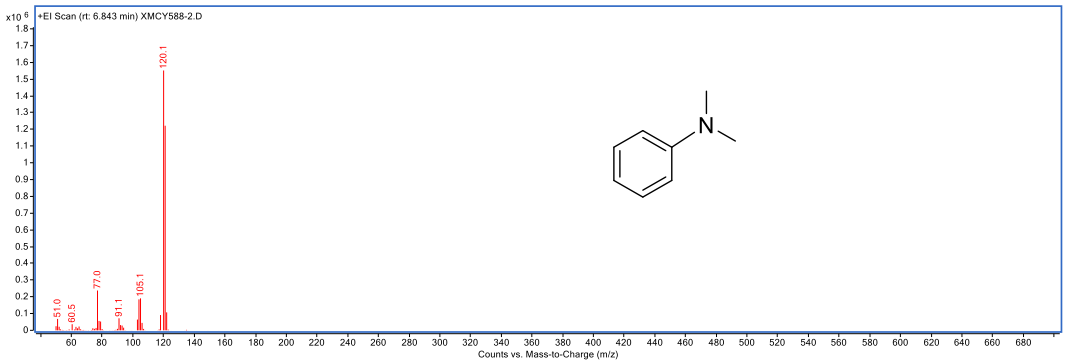
The ^{1}H NMR spectra of the reaction between *N*-methylaniline and CO_2 under optimal condition to give *N*-dimethylaniline. (**2a)**



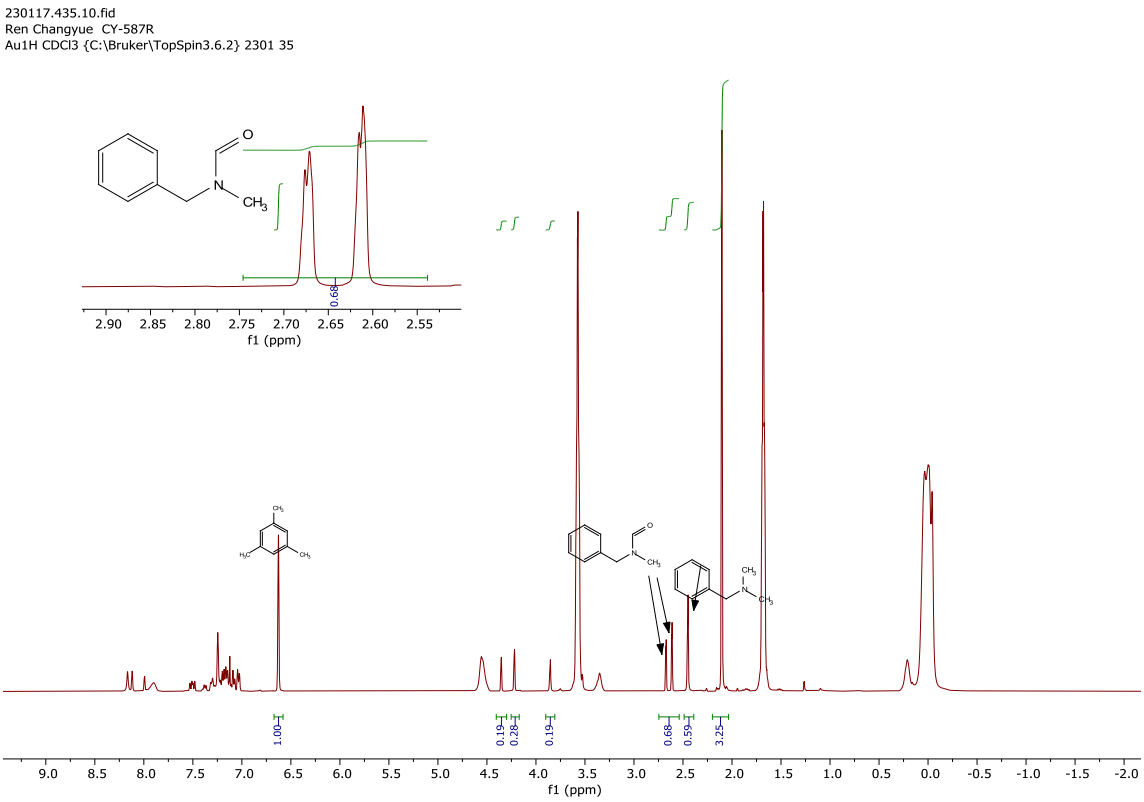
^{1}H NMR yield of 1-methyl-1,2,3,4-tetrahydroquinoline (**2l)**



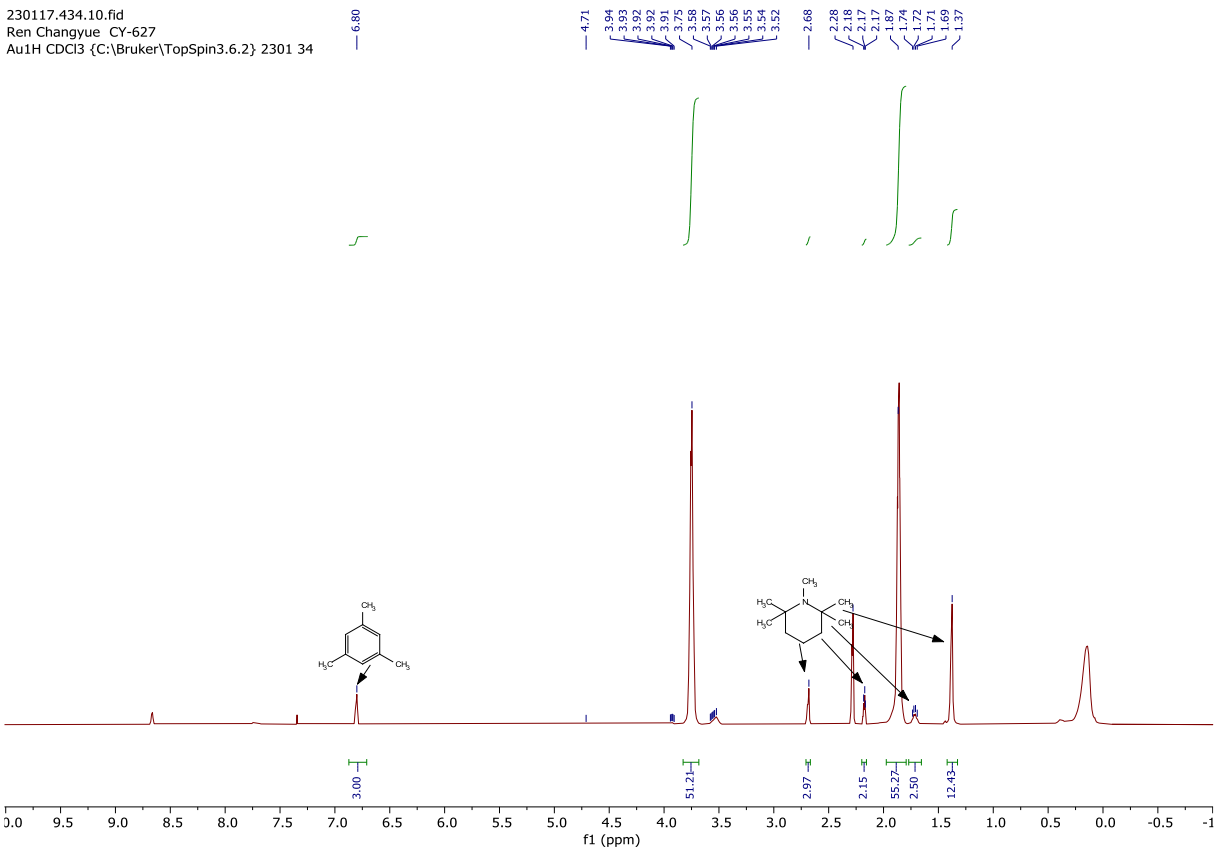




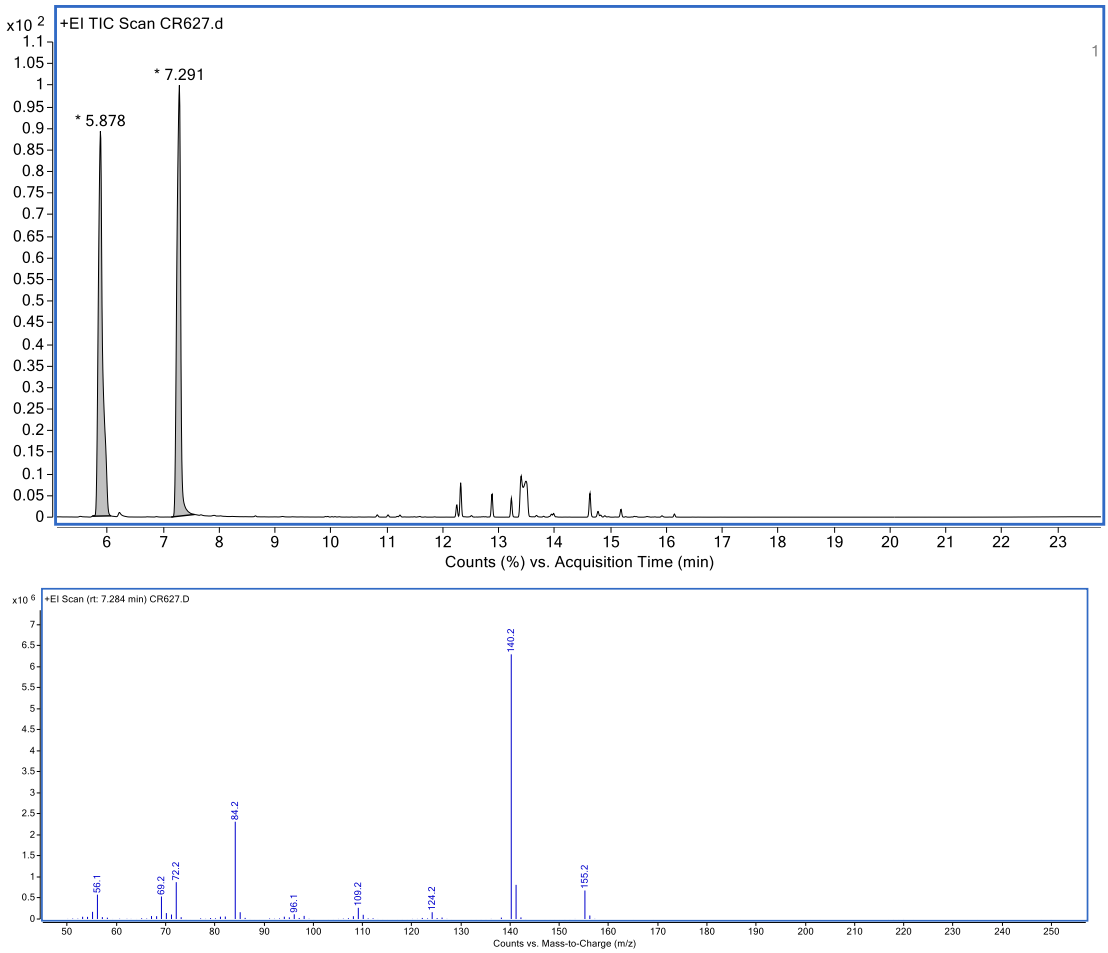
GC yield of N,N-dimethylaniline (**2l)**



^{1}H NMR yield of *N*,*N*-dimethyl-1-phenylmethanamine (**2o**) and *N*-benzyl-*N*-methylformamide (**3o**).



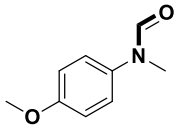
^{1}H NMR yield of 1,2,2,6,6-pentamethylpiperidine (**2p**)



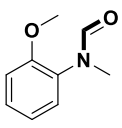
GC data of 1,2,2,6,6-pentamethylpiperidine (**2p**)

4. Synthesis of formylated amines 5

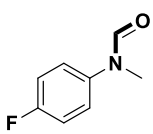
General procedure (GP2) for the synthesis of formylated amines 3: A 45 cm^3 stainless-steel autoclave with a 5 cm^3 glass viel charging with catalyst (2.0 mol%) and aniline **1** (0.600 mmol), trimethoxysilane (1.80 mmol, 220 mL), 0.6 mL THF. The autoclave was purged with CO_2 and the pressure kept constant at 1.0 bar. The reaction mixture was stirred at 70°C for 4-24 h. Subsequently the CO_2 was released slowly. Then the residue was purified by silica gel chromatography (hexane/ethyl acetate = 10/1) to afford the corresponding products **3**.



According to the GP2, 4-methoxy-N-methylaniline (**1b**, 82.3mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 4 h to yield N-(4-methoxyphenyl)-N-methylformamide **3b** (83.5 mg, 0.516 mmol, 86%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.10 (m, 2H), 6.92 (m, 2H), 3.82 (s, 3H), 3.27 (s, 3H).[2]

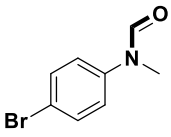


According to the GP2, 2-methoxy-N-methylaniline (**1c**, 82.3mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield N-(2-methoxyphenyl)-N-methylformamide **3c** (78.2 mg, 0.473 mmol, 79%) as a colorless oil.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.36 – 7.28 (m, 1H), 7.12 (dd, 1H), 7.02 – 6.91 (m, 2H), 3.84 (s, 3H), 3.20 (s, 3H).[2]

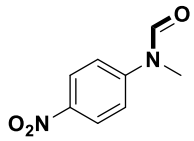


According to the GP2, 4-fluoro-N-methylaniline (**1d**, 75.1 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 4 h to yield N-(4-fluorophenyl)-N-

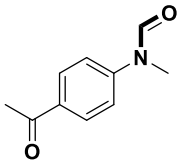
methylformamide **3d** (79.0 mg, 0.511 mmol, 86%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.21 – 7.03 (m, 4H), 3.29 (s, 3H).[2]



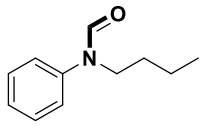
According to the GP2, 4-bromo-*N*-methylaniline (**1e**, 112 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 4 h to yield *N*-(4-bromophenyl)-*N*-methylformamide **3e** (96.6 mg, 0.456 mmol, 76%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.53 (m, 2H), 7.05 (dt, *J* = 8.8 Hz, 2H), 3.30 (s, 3H).[4]



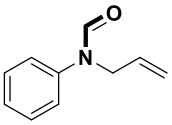
According to the GP2, 4-nitro-*N*-methylaniline (**1f**, 91.3 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield *N*-methyl-*N*-(4-nitrophenyl)formamide **3f**(14.3 mg, 0.078 mmol, 13%) as a yellow solid. 1H NMR (300 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.40 – 8.24 (m, 2H), 7.32 (d, *J* = 9.1 Hz, 2H), 3.39 (d, *J* = 0.4 Hz, 3H).[4]



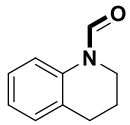
According to the GP2, 4-acetyl-*N*-methylaniline (**1g**, 89.5 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield *N*-(4-acetylphenyl)-*N*-methylformamide **3g** (56.0 mg, 29.7 mmol, 53%) as a yellow solid.as a light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.11 – 7.97 (m, 2H), 7.37 – 7.07 (m, 2H), 3.36 (s, 3H), 2.61 (s, 3H).[4]



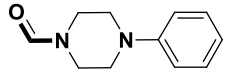
According to the GP2, *N*-butylaniline (**1j**, 89.5 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield *N*-butyl-*N*-phenylformamide **3j** (88.4 mg, 0.504 mmol, 84%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.46 – 7.37 (m, 2H), 7.33 – 7.26 (m, 1H), 7.20 – 7.14 (m, 2H), 3.87 – 3.74 (m, 2H), 1.61 – 1.44 (m, 2H), 1.41 – 1.22 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).[2]



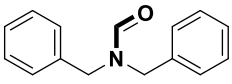
According to the GP2, *N*-allylaniline (**1k**, 79.9 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield *N*-allyl-*N*-phenylformamide **3k** (81.7 mg, 0.510 mmol, 85%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.48 – 7.35 (m, 2H), 7.35 – 7.25 (m, 1H), 7.25 – 7.16 (m, 2H), 5.95 – 5.79 (m, 1H), 5.27 – 5.14 (m, 2H), 4.44 (dt, *J* = 5.6, 1.6 Hz, 2H).[2]



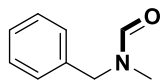
According to the GP2, 1,2,3,4-tetrahydroquinoline (**1l**, 79.9 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield 3,4-dihydroquinoline-1(2H)-carbaldehyde **3l** (90.8 mg, 0.564 mmol, 94 %) as a colourless solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.24 – 7.04 (m, 4H), 3.90 – 3.75 (m, 2H), 2.81 (t, *J* = 6.5 Hz, 2H), 2.05 – 1.88 (m, 2H).[3]



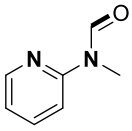
According to the GP2, 1-phenylpiperazine (**1r**, 97.3 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield 4-phenylpiperazine-1-carbaldehyde **3r** (101 mg, 0.534 mmol, 89 %) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.38 – 7.23 (m, 2H), 7.04 – 6.89 (m, 3H), 3.74 (t, *J* = 5.0, 2H), 3.56 (t, *J* = 5.0, 2H), 3.33 – 3.11 (m, 4H).[5]



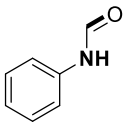
According to the GP2, dibenzylamine (**1q**, 118.4 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield *N*,*N*-dibenzylformamide **3q** (101.4 mg, 0.450 mmol, 75%) as a colourless solid. ^{1}H NMR (300 MHz, CDCl3) δ 8.43 (s, 1H), 7.48 – 7.27 (m, 6H), 7.26 – 7.11 (m, 4H), 4.42 (s, 2H), 4.27 (s, 2H).[3]



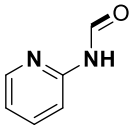
According to the GP2, *N*-methyl-1-phenylmethanamine (**1o**, 72.7 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield *N*-benzylformamide **3o** (82.0 mg, 0.552 mmol, 92%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (s, 0.57H, maj), 8.08 (s, 0.43H, min), 7.38 – 7.04 (m, 5H), 4.44 (s, 0.89H, min), 4.31 (s, 1.19H, maj), 2.77 (s, 1.33H, min), 2.70 (s, 1.71H, maj).[4]



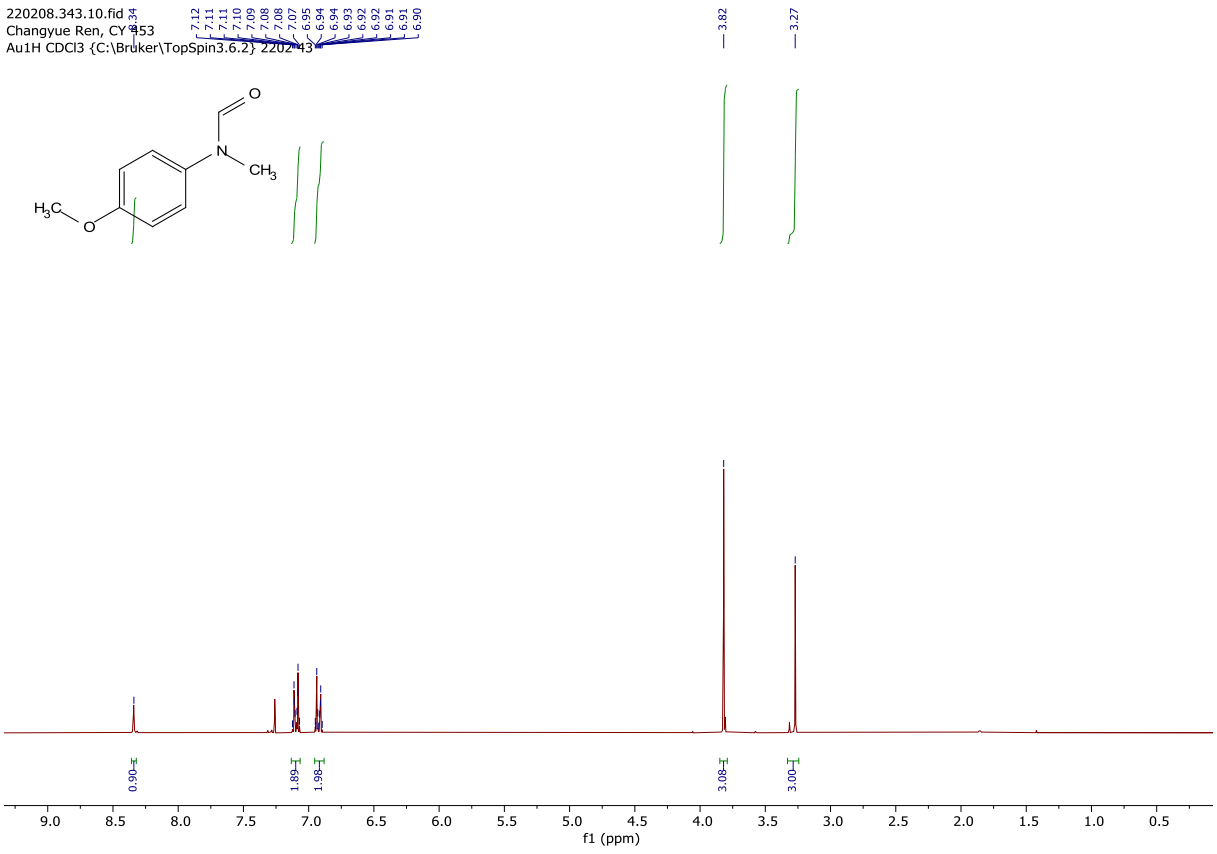
According to the GP2, *N*-methylpyridin-2-amine (**1s**, 64.9 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield *N*-methyl-*N*-(pyridin-2-yl)formamide **3s** (56.3 mg, 0.414 mmol, 69%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.38 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.72 (ddd, *J* = 8.3, 7.4, 2.0 Hz, 1H), 7.16 – 6.92 (m, 2H), 3.34 (d, *J* = 0.4 Hz, 3H).[4]



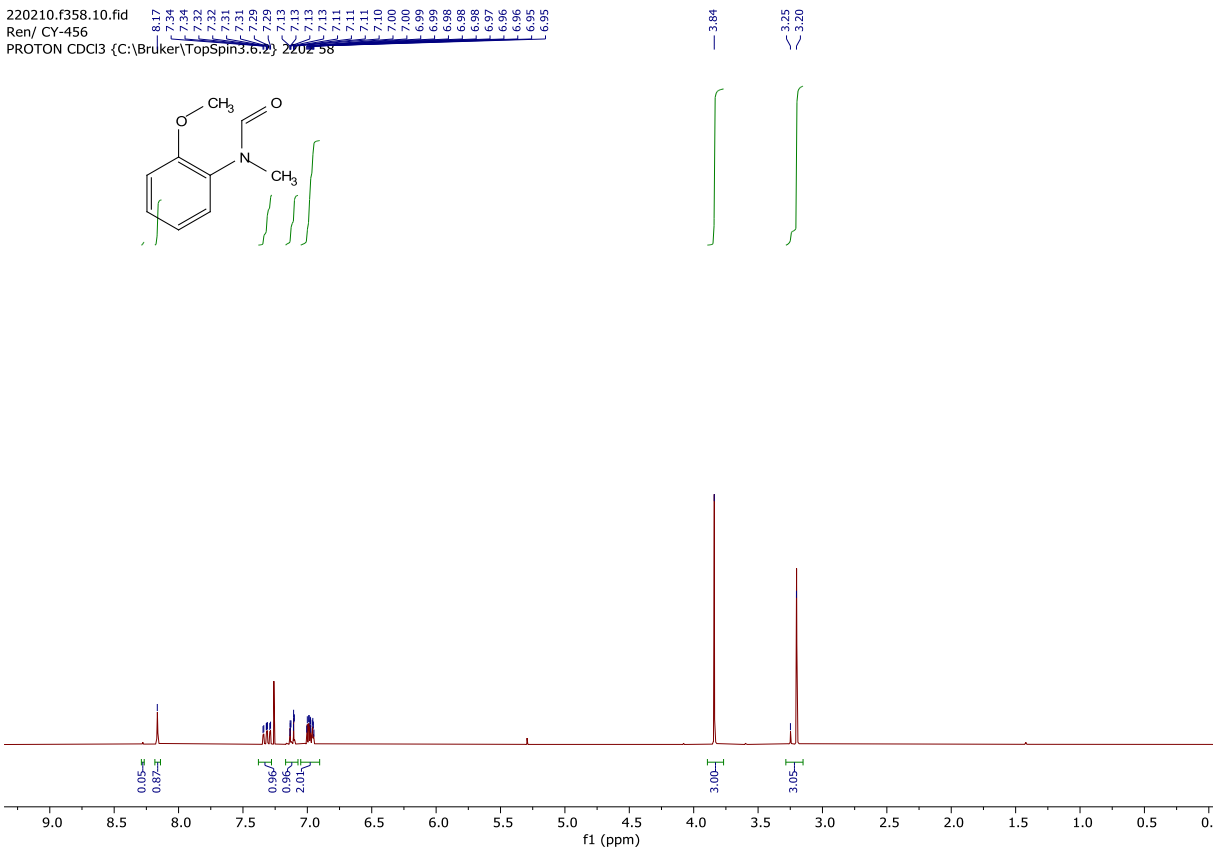
According to the GP2, aniline (**1t**, 55.9 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield *N*-phenylformamide **3t** (65.3 mg, 0.540 mmol, 90%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.18 (m, 1H), 7.64 – 7.45 (m, 1H), 7.43 – 7.29 (m, 2H), 7.24 – 7.00 (m, 2H).[2]



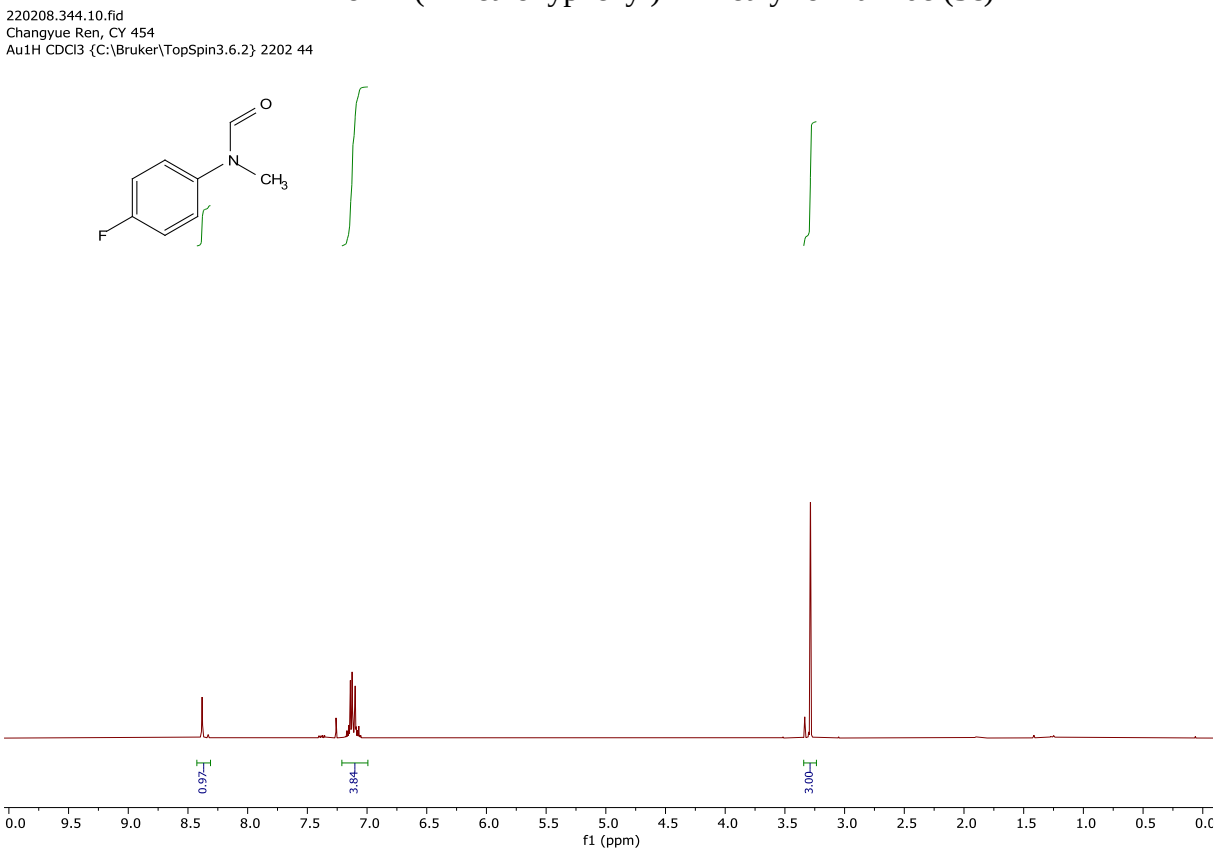
According to the GP2, pyridin-2-amine (**1u**, 56.5 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield *N*-(pyridin-2-yl)formamide **3u** (41.3 mg, 0.336 mmol, 56%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.52 (minor rotamer, br s, 0.40 H), 9.31 (m, 1H), 8.51 (major rotamer, s, 0.53 H), 8.32 (d, *J* = 0.9 Hz, 1H), 8.24 (d, *J* = 1.0 Hz, 0.54H), 7.74 (t, *J* = 1.9 Hz, 0.56H), 7.67 (t, *J* = 1.9 Hz, 0.41H), 7.08 (m, 1H), 6.90 (dt, *J* = 8.3, 1.0 Hz, 0.43H).[4]



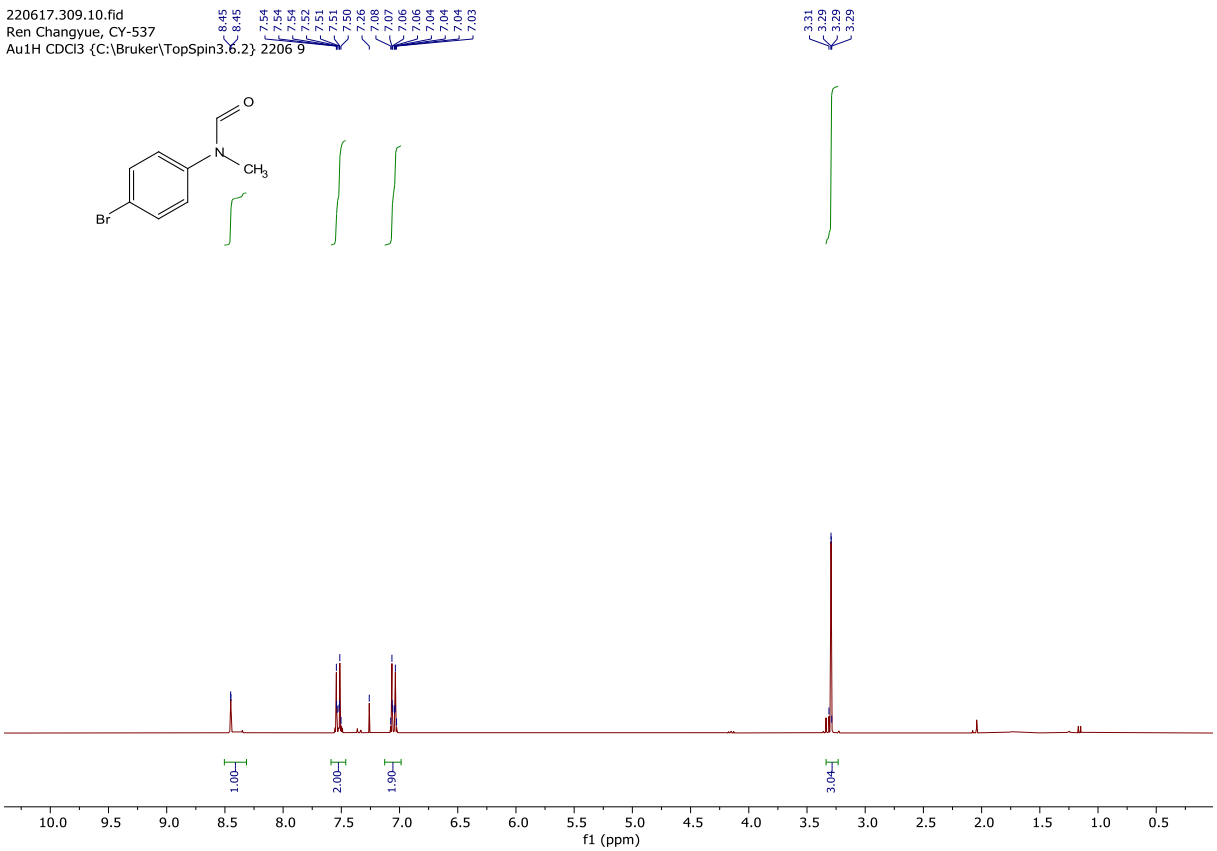
^{1}H NMR of N-(4-methoxyphenyl)-N-methylformamide (**3b**)



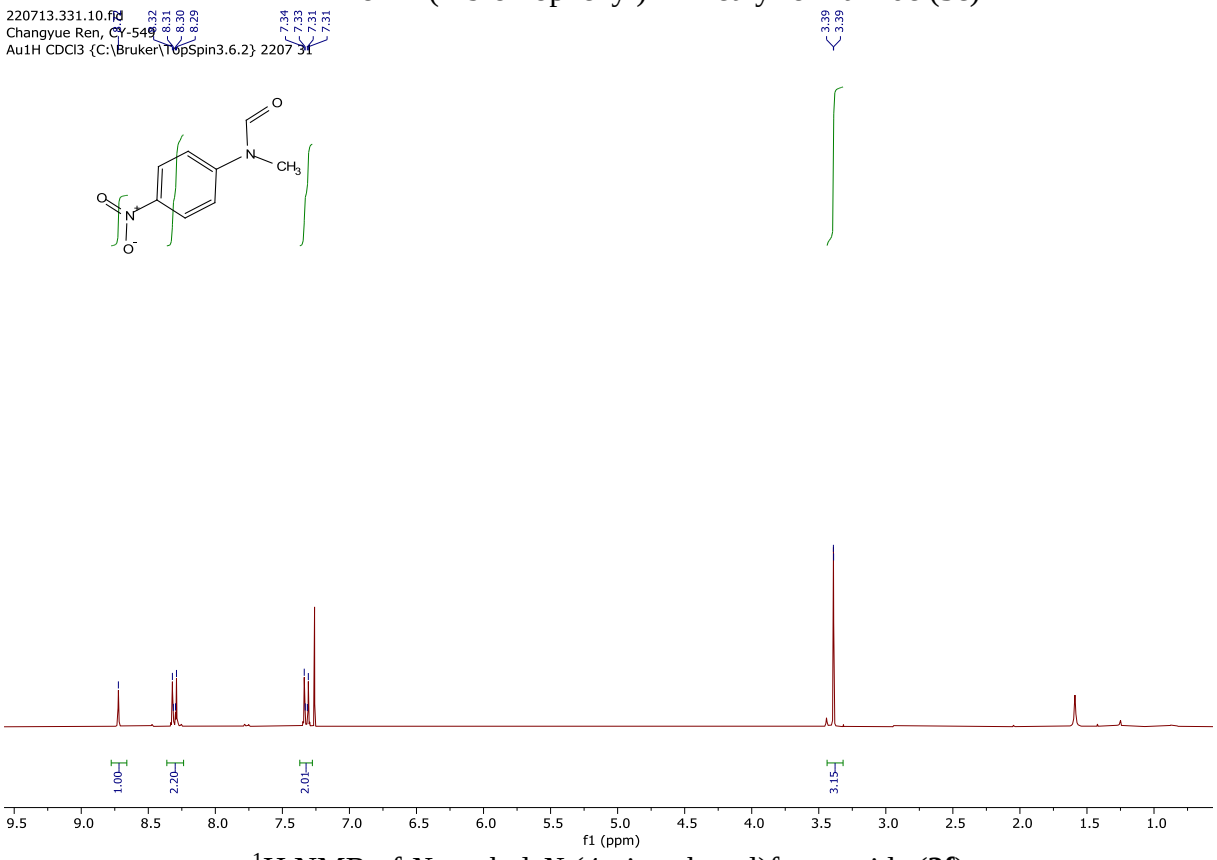
^{1}H NMR of N-(2-methoxyphenyl)-N-methylformamide (**3c**)



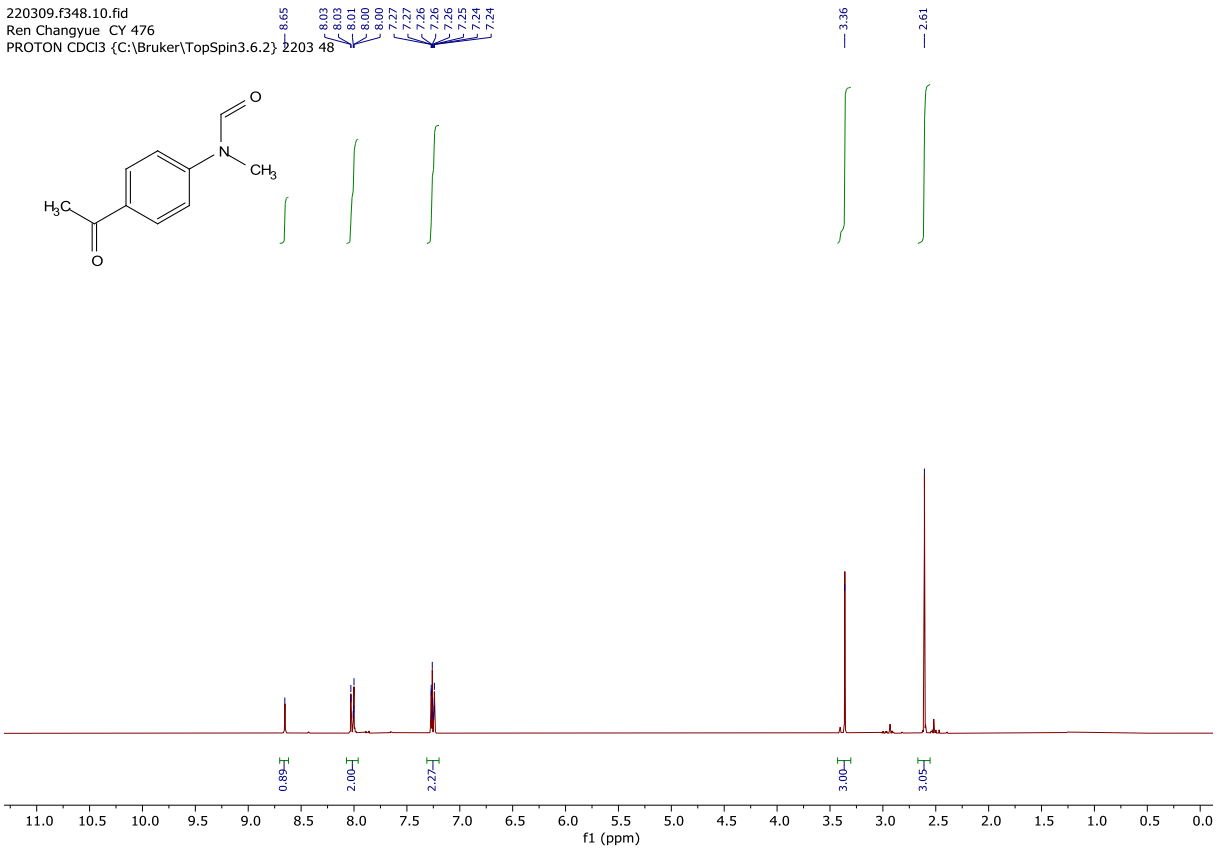
^{1}H NMR of N-(4-fluorophenyl)-N-methylformamide (**3d**)



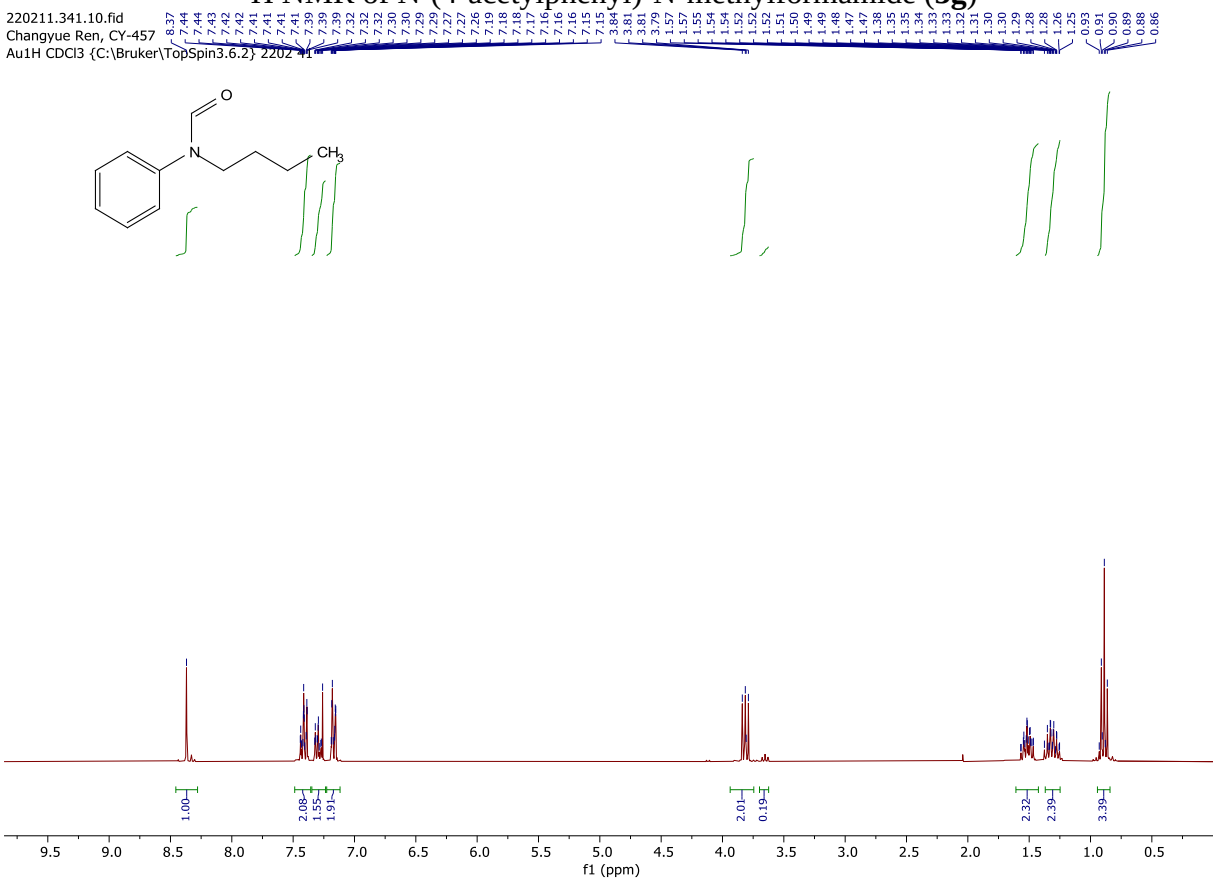
^{1}H NMR of N-(4-bromophenyl)-N-methylformamide (**3e**)



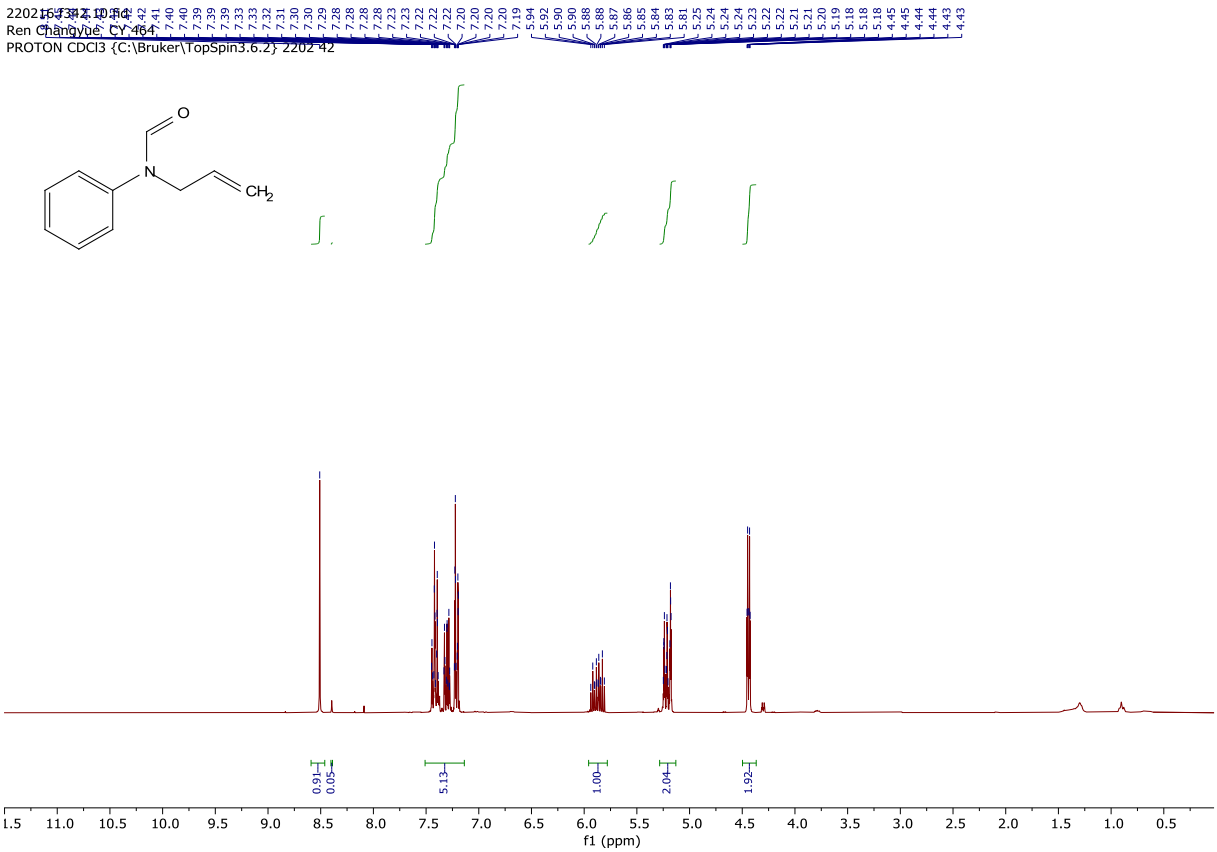
^{1}H NMR of *N*-methyl-*N*-(4-nitrophenyl)formamide (**3f**)



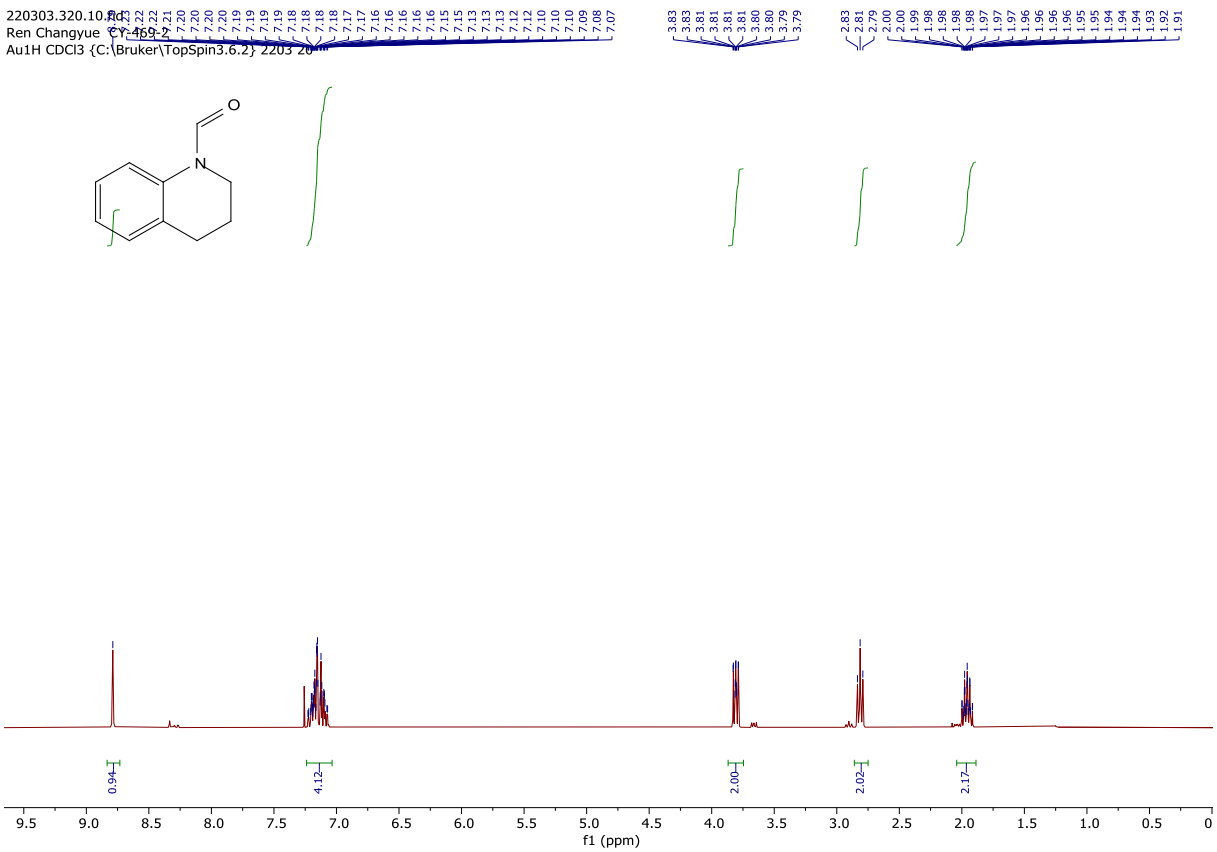
^{1}H NMR of N-(4-acetylphenyl)-N-methylformamide (**3g**)



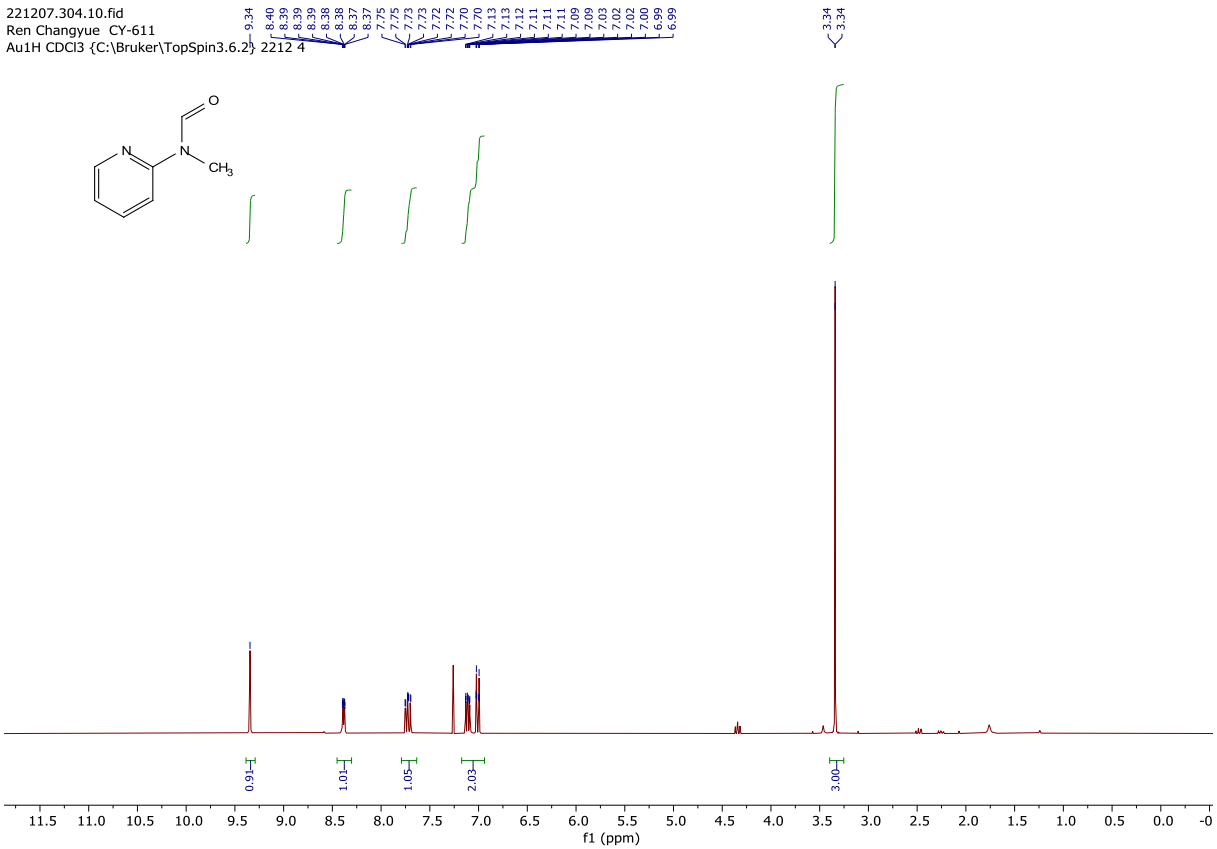
^{1}H NMR of *N*-butyl-*N*-phenylformamide (**3j**)



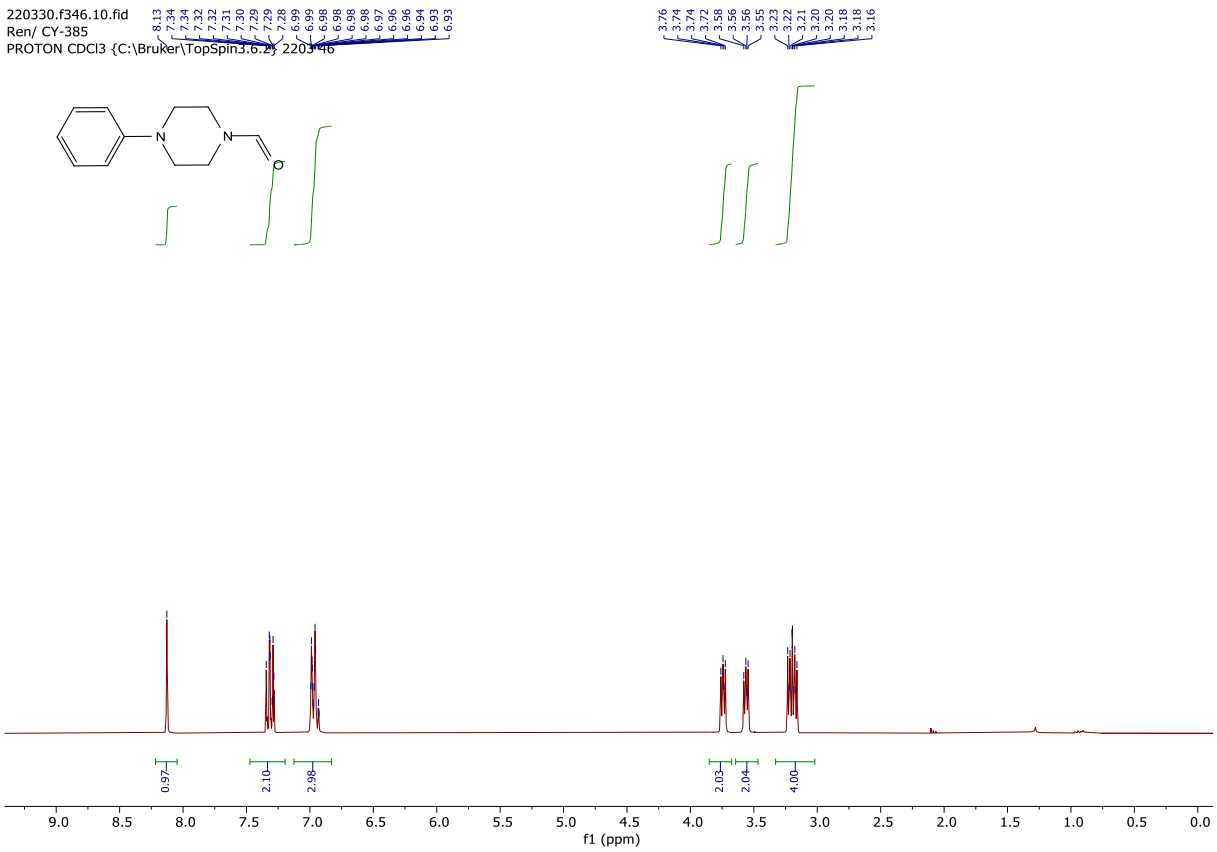
^{1}H NMR of N-allyl-N-phenylformamide (**3k**)



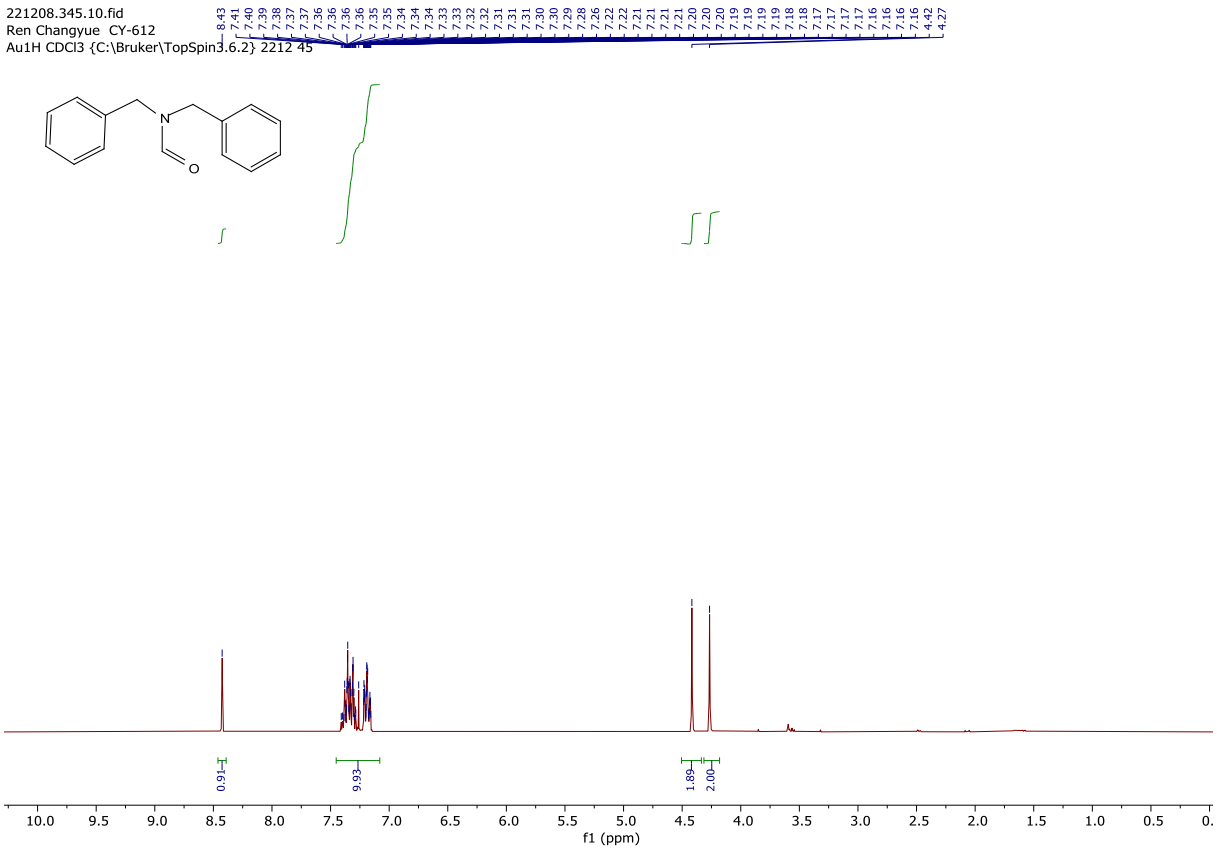
^{1}H NMR of 3,4-dihydroquinoline-1(2H)-carbaldehyde (**3l**)



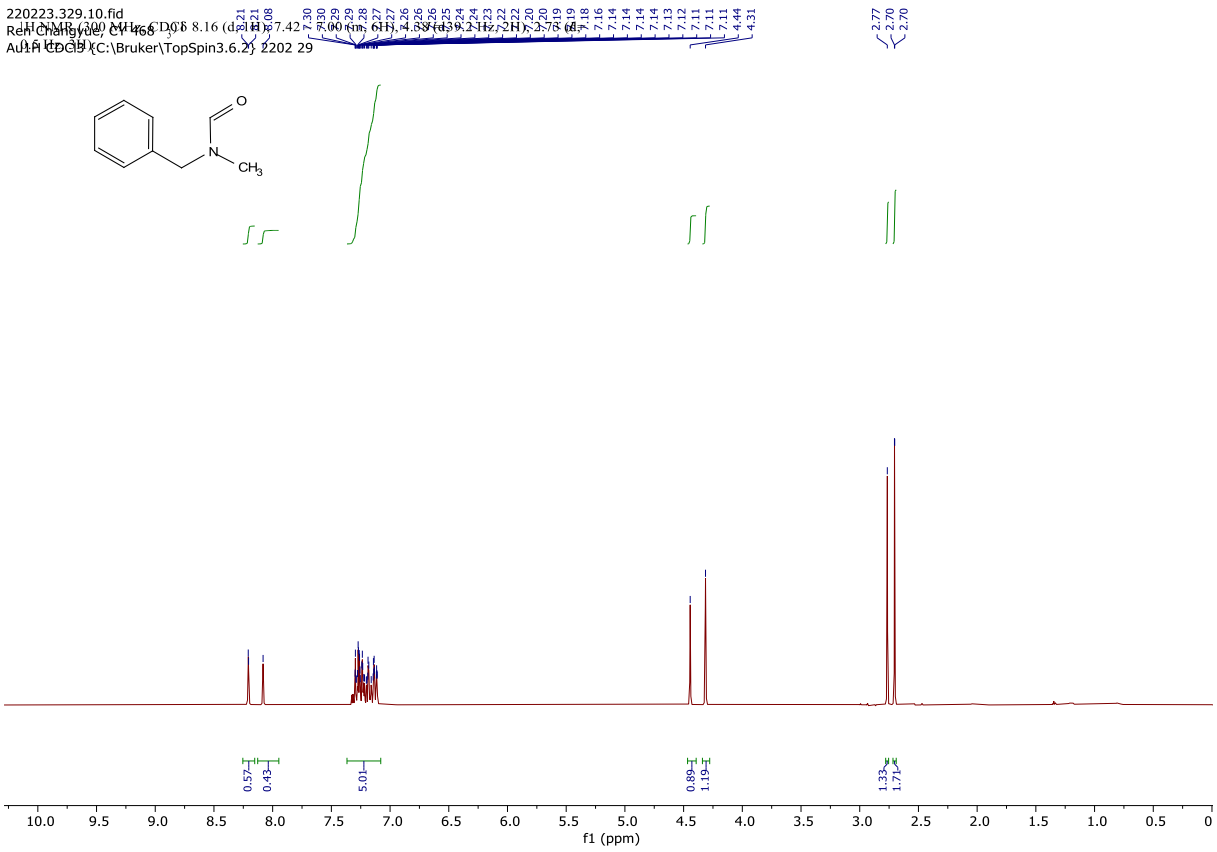
^{1}H NMR of N-methyl-N-(pyridin-2-yl)formamide (**3s**)



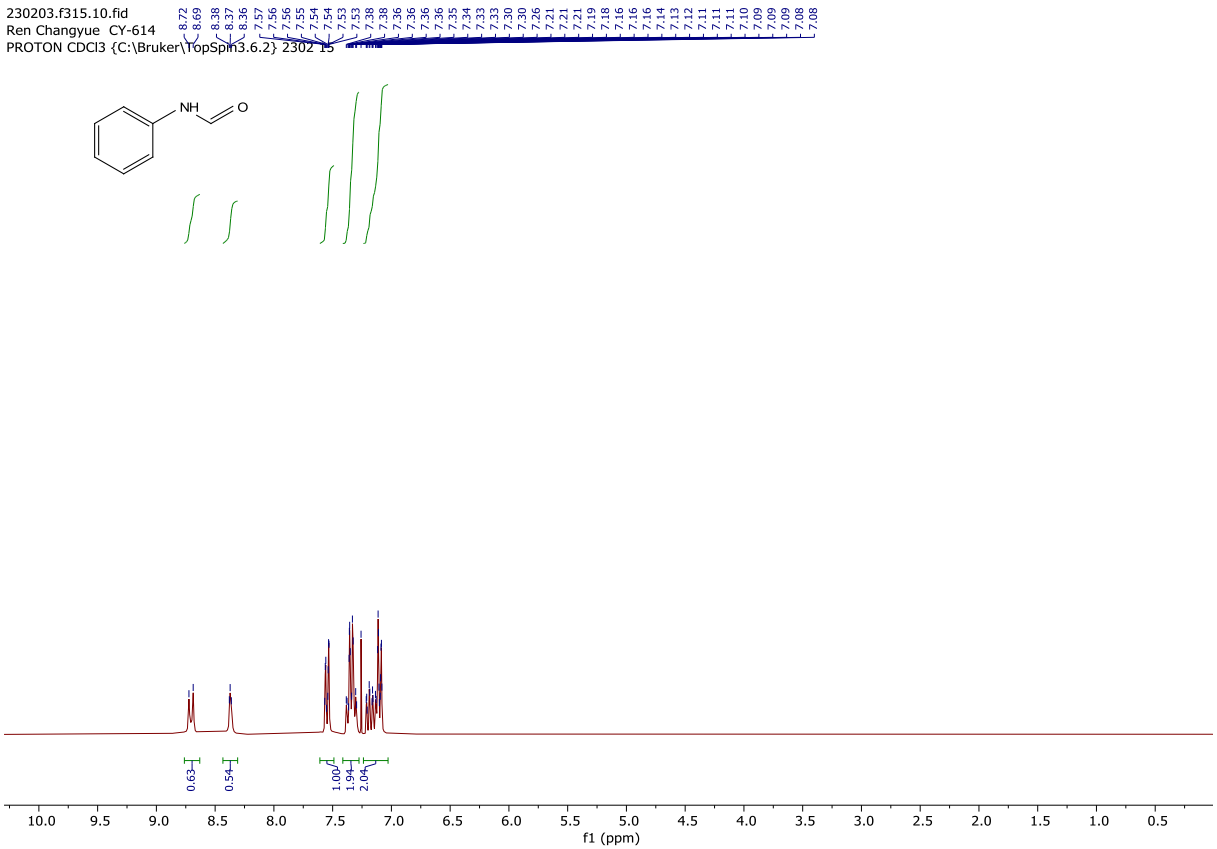
^{1}H NMR of 4-phenylpiperazine-1-carbaldehyde (**3r**)



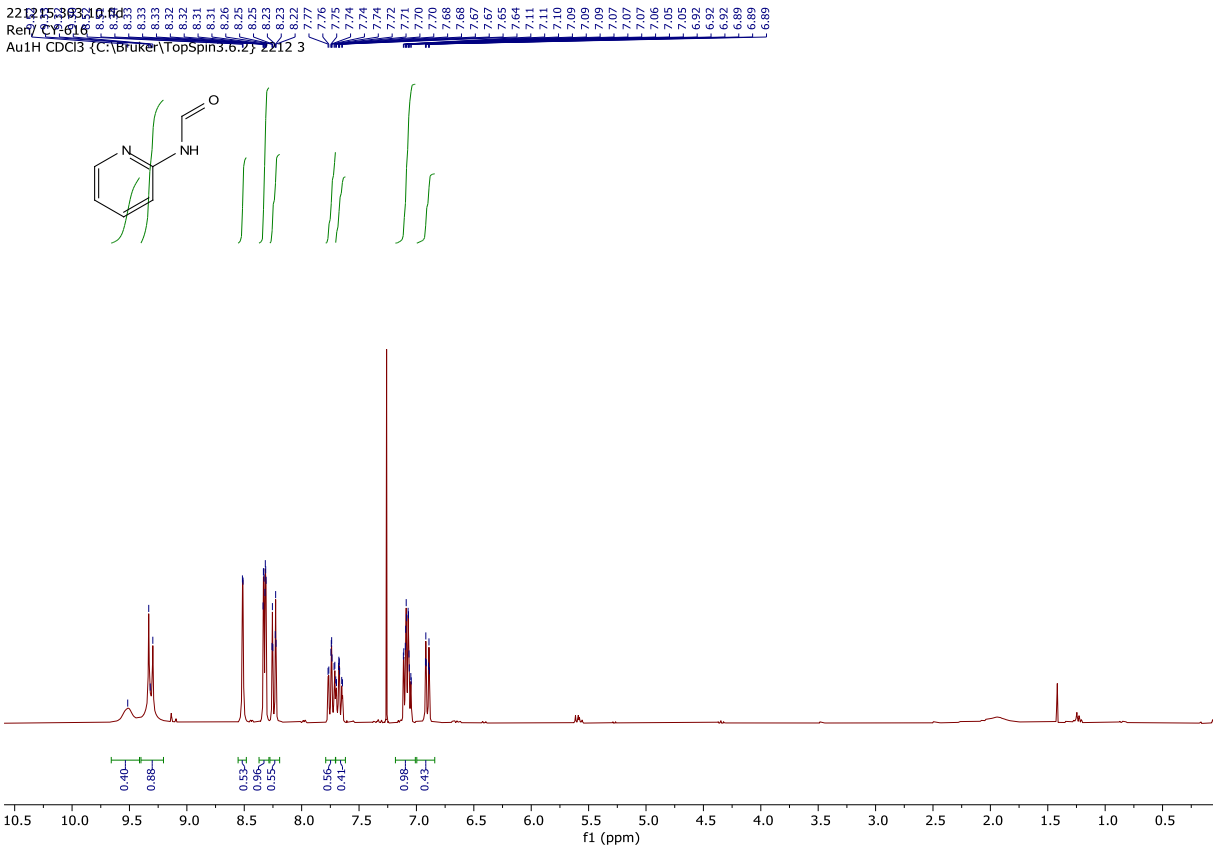
^{1}H NMR of N,N-dibenzylformamide (**3q**)



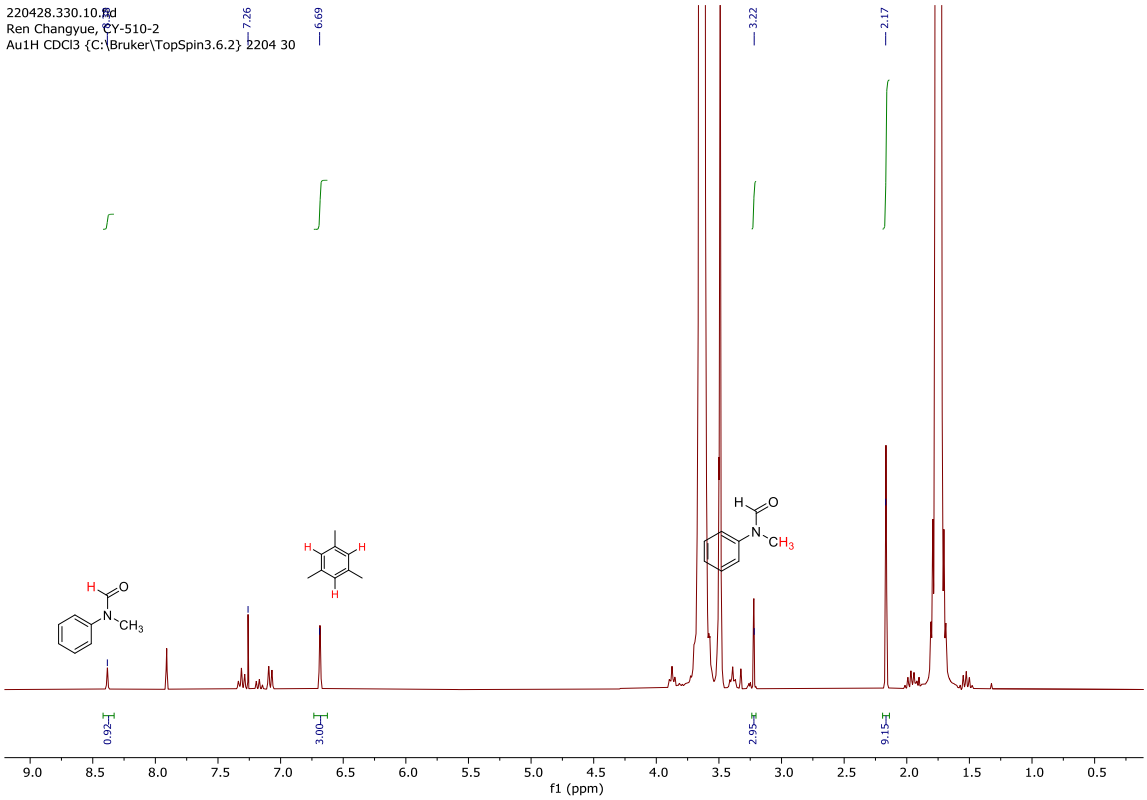
^{1}H NMR of N-benzyl-N-methylformamide (**3o**)



^{1}H NMR of N-phenylformamide (**3t**)



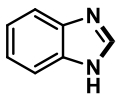
^{1}H NMR of *N*-(pyridin-2-yl)formamide (**3u**)



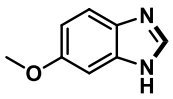
The ^{1}H NMR spectra of the reaction between *N*-methylaniline and CO_2 under optimal condition to give *N*-methylformanilide (**3a**).

5. Synthesis of benzoheterocyclic compounds 5

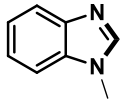
General procedure (GP3) for the synthesis of benzoheterocyclic compounds 5: A 45 cm^3 stainless-steel autoclave charging with catalyst catalyst (2.0 mol%) and aniline **4** (0.600 mmol), trimethoxysilane (1.80 mmol, 220 mg), 6 mL THF. The autoclave was purged with CO_2 and the pressure kept constant at 1.0 bar. The reaction mixture was stirred at 70 °C for 24 h. Subsequently the CO_2 was released slowly. Then the residue was purified by silica gel chromatography (hexane/ethyl acetate = 1/1) to afford the corresponding products **5**.



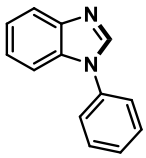
According to the GP3, *o*-phenylenediamine (**4a**, 64.9 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 μmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield 1*H*-benzo[*d*]imidazole **5a** (58.8 mg, 0.498 mmol, 83%) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.79 – 7.59 (m, 2H), 7.35 – 7.28 (m, 2H), 6.28 (s, 1H). [4]



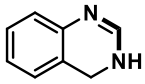
According to the GP3, 4-methoxybenzene-1,2-diamine (**4b**, 82.9 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 μmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield 6-methoxy-1*H*-benzo[*d*]imidazole **5b** (41.6 mg, 0.282 mmol, 47%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 0.6 Hz, 1H), 6.93 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.82 (s, 3H).[6]



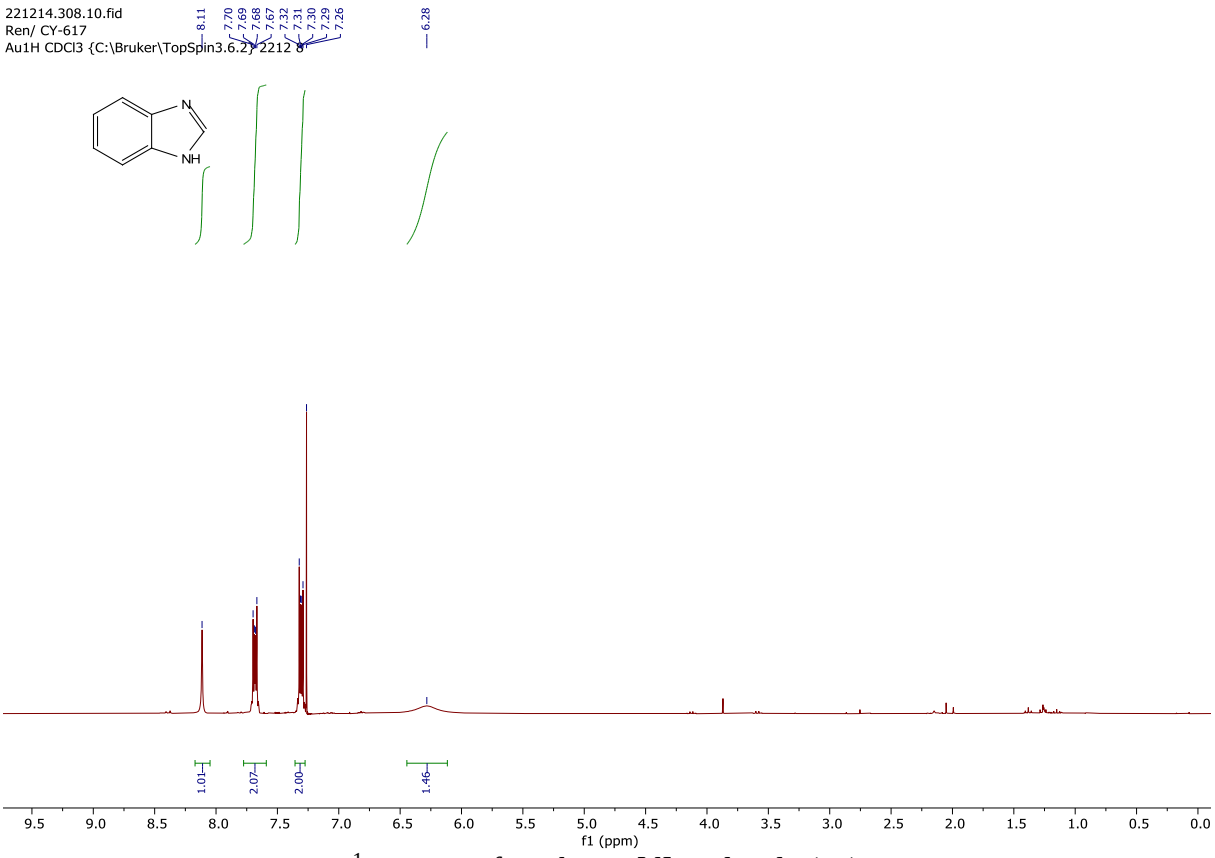
According to the GP3, *N*-methylbenzene-1,2-diamine (**4c**, 73.3 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 μmol), trimeoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield 1-methyl-1*H*-benzo[*d*]imidazole **5c** (49.3 mg, 0.372 mmol, 62%) as a red oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.88 – 7.74 (m, 1H), 7.45 – 7.27 (m, 3H), 3.87 (s, 3H).[4]



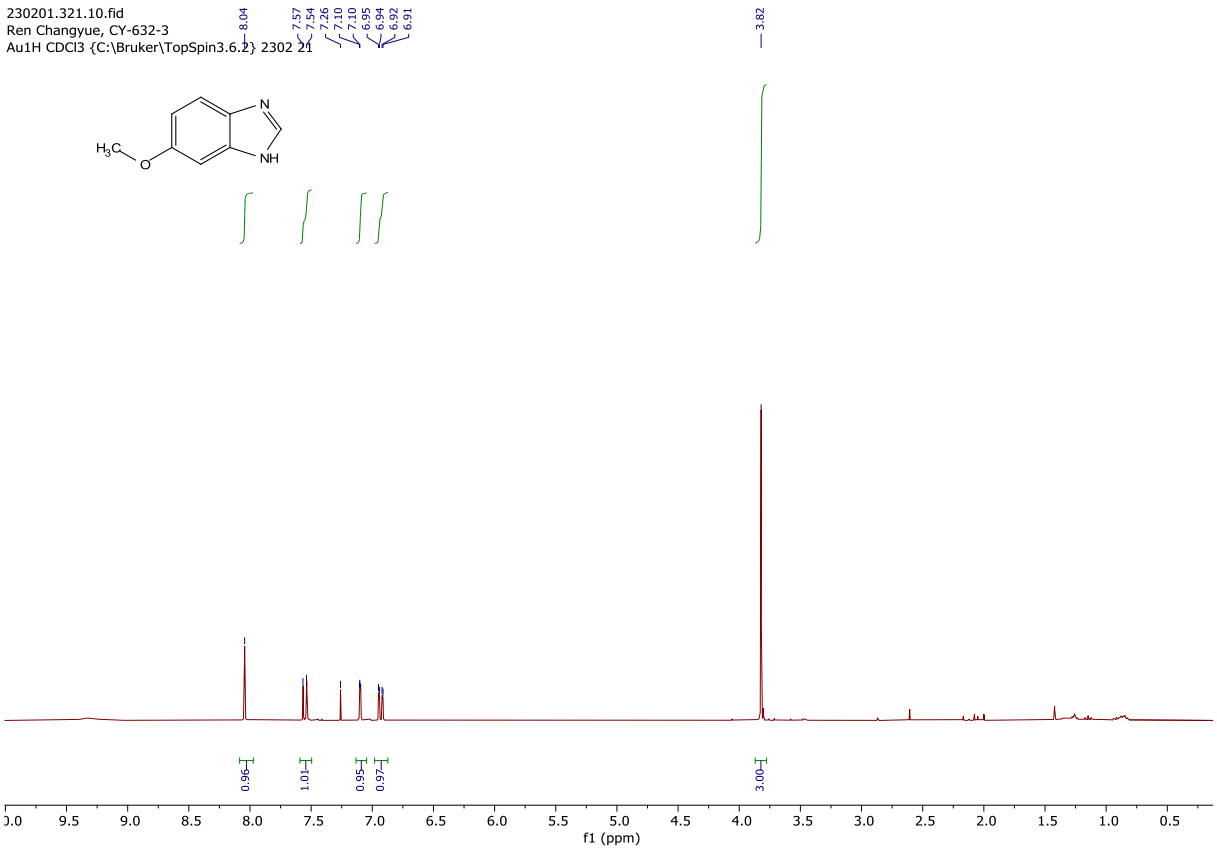
According to the GP3, *N*-phenylbenzene-1,2-diamine (**4d**, 110.6 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield 1-phenyl-1*H*-benzo[*d*]imidazole **5d** (81.5 mg, 0.420 mmol, 70%) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.95 – 7.80 (m, 1H), 7.62 – 7.50 (m, 5H), 7.50 – 7.44 (m, 1H), 7.38 – 7.31 (m, 2H).[6]



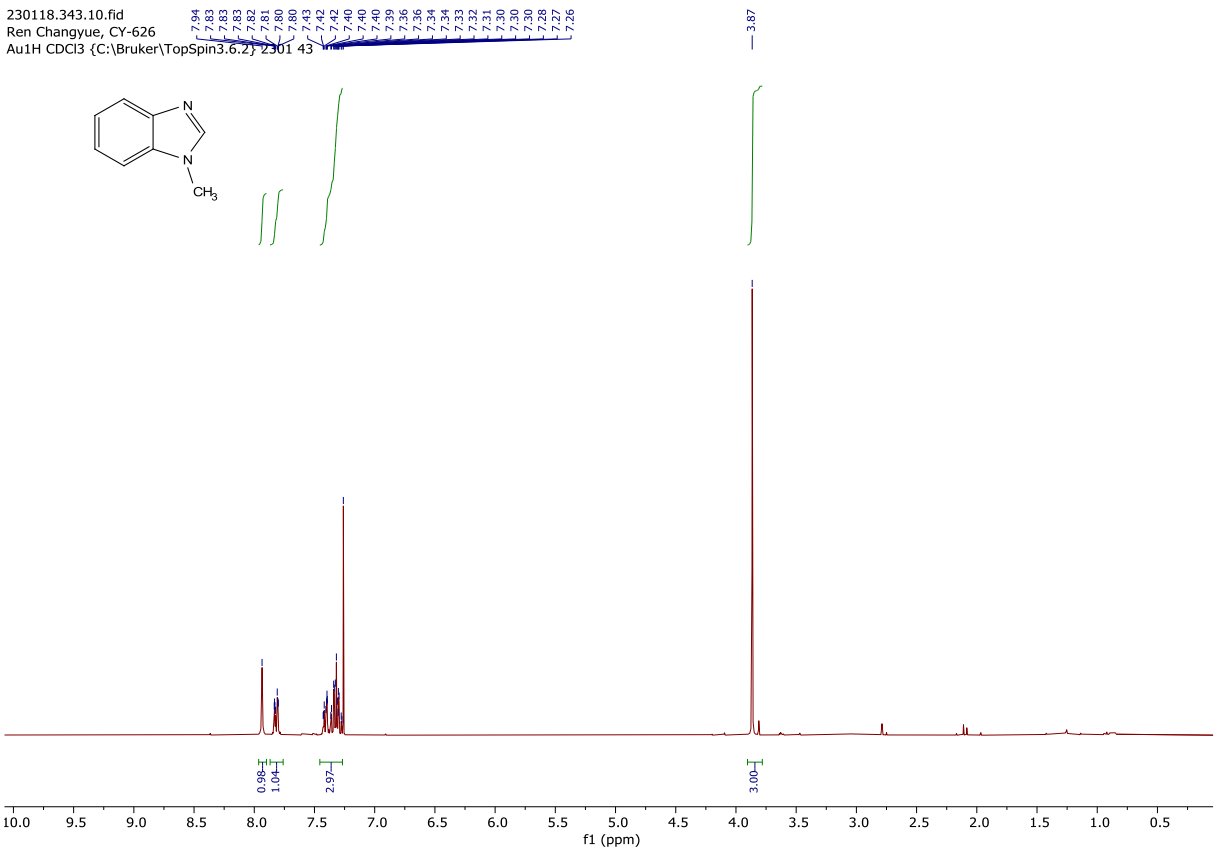
According to the GP3, 2-aminobenzylamine (**4e**, 73.3 mg, 0.600 mmol), catalyst (4.23 mg, 12.0 µmmol), trimethoxysilane (220 mg, 1.80 mmol) and CO_2 were converted at 70 °C, 1.0 bar for 24 h to yield 3,4-dihydroquinazoline **5e** (51.2 mg, 0.384 mmol, 64%) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.15 – 7.01 (m, 2H), 6.77 – 6.62 (m, 2H), 5.97 (s, 1H), 4.40 (d, *J* = 6.3 Hz, 2H).



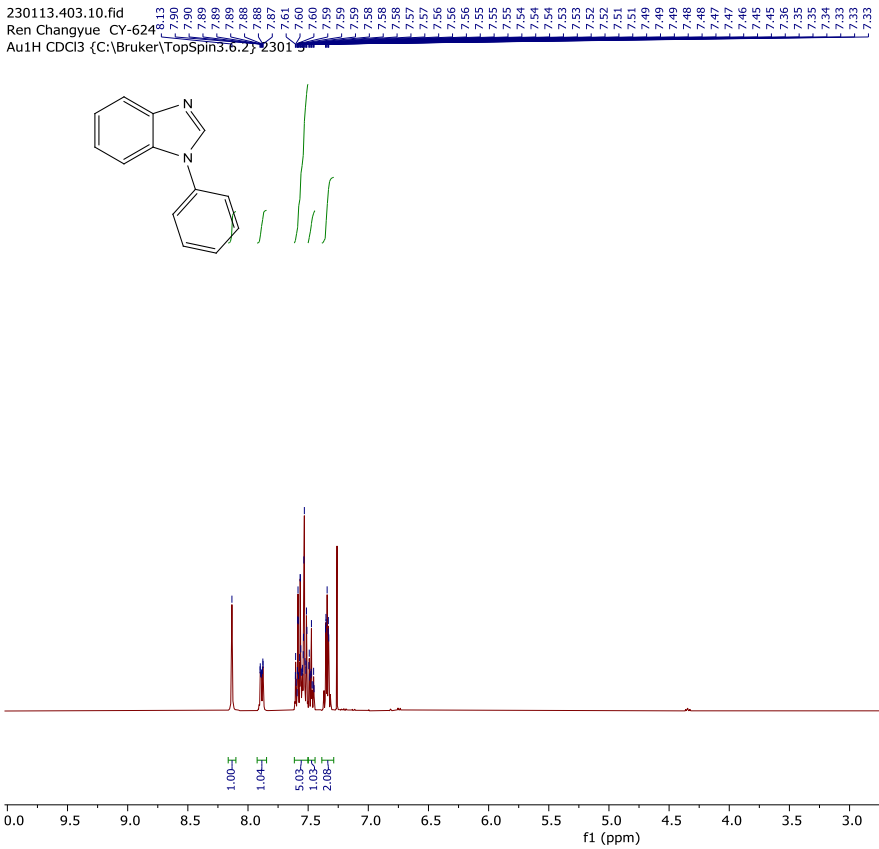
^{1}H NMR of 1*H*-benzo[d]imidazole (**5a**)



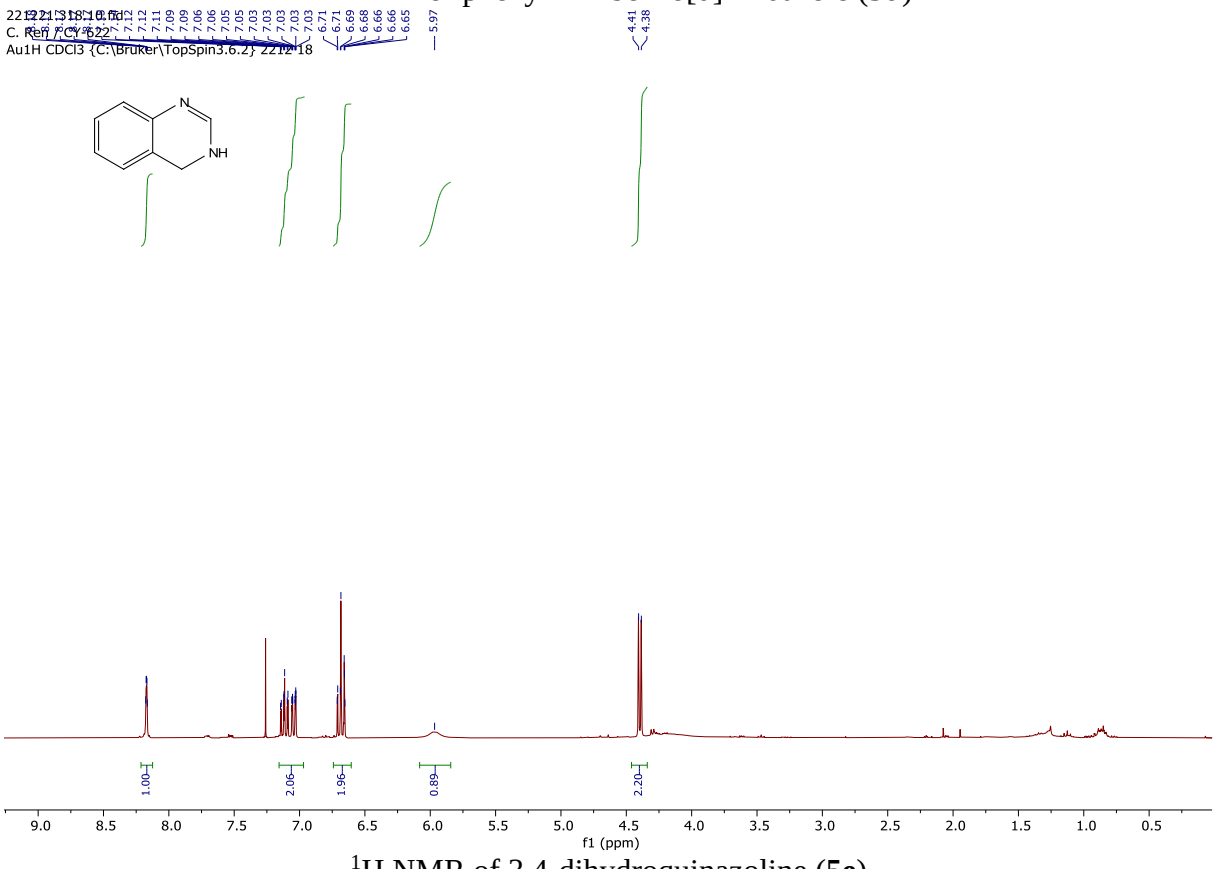
^{1}H NMR of 6-methoxy-1H-benzo[d]imidazole (**5b**)



^{1}H NMR of 1-methyl-1H-benzo[d]imidazole (**5c**)



^{1}H NMR of phenyl-1*H*-benzo[d]imidazole (**5d**)



^{1}H NMR of 3,4-dihydroquinazoline (**5e**)

6. Mechanistic studies

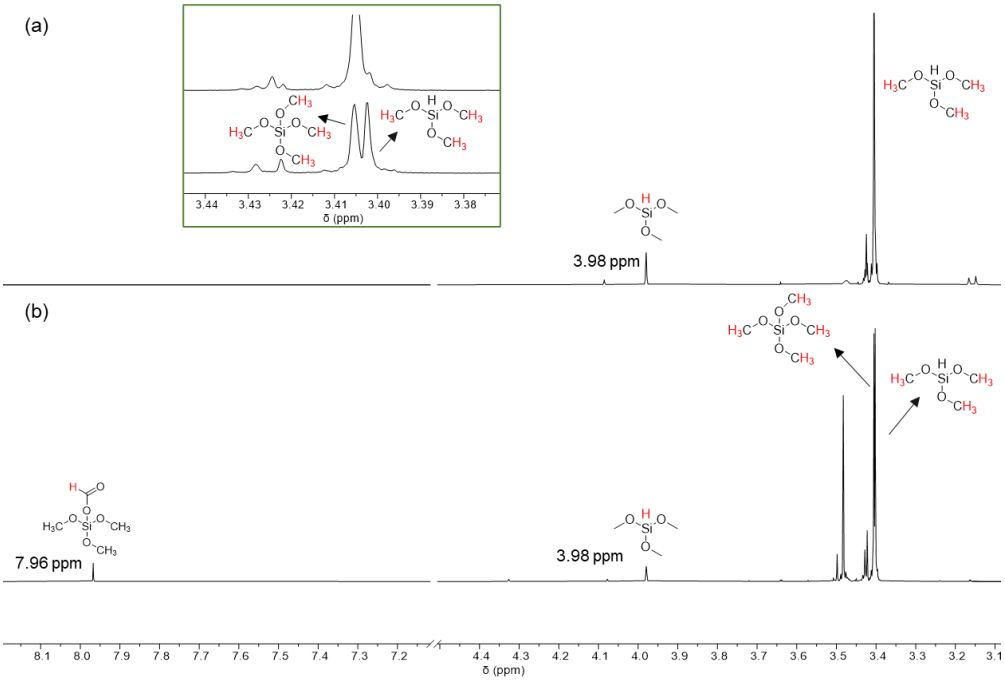


Figure S1. ^{1}H NMR of the control experiments shown in Scheme 2a. (a) Before the reaction. (b) After the reaction. Reaction conditions: $(MeO)_3SiH$ (131.4 mg, 1.08 mmol), catalyst (1.89 mg, 2 mol%), $p(CO_2)$ = 1 bar, 70 °C, 16 h, THF-d^8.

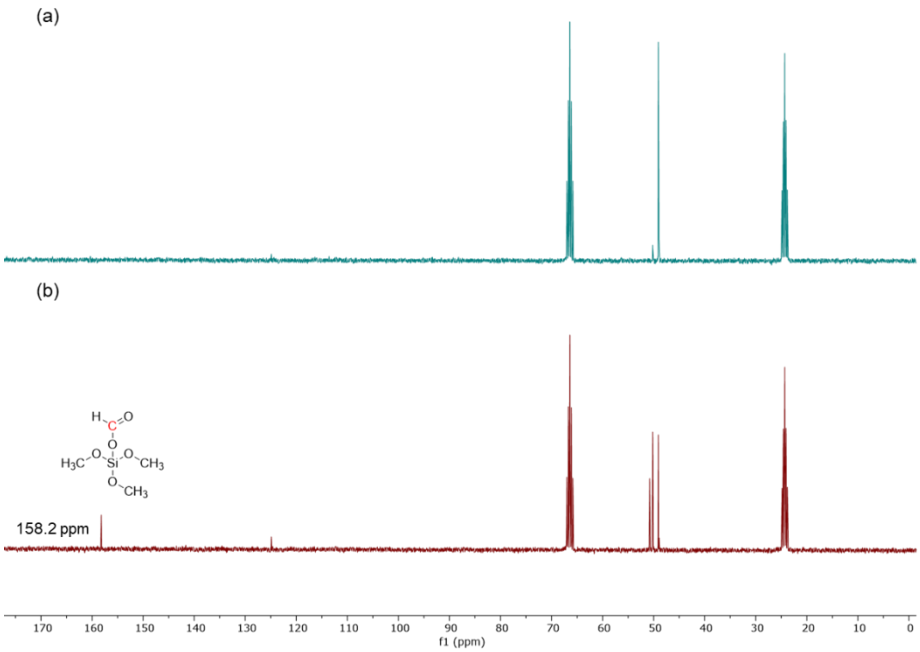


Figure S2. The ^{13}C NMR of the control experiments shown in Scheme 2a. (a) Before the reaction. (b) After the reaction. Reaction conditions: see Figure S1.

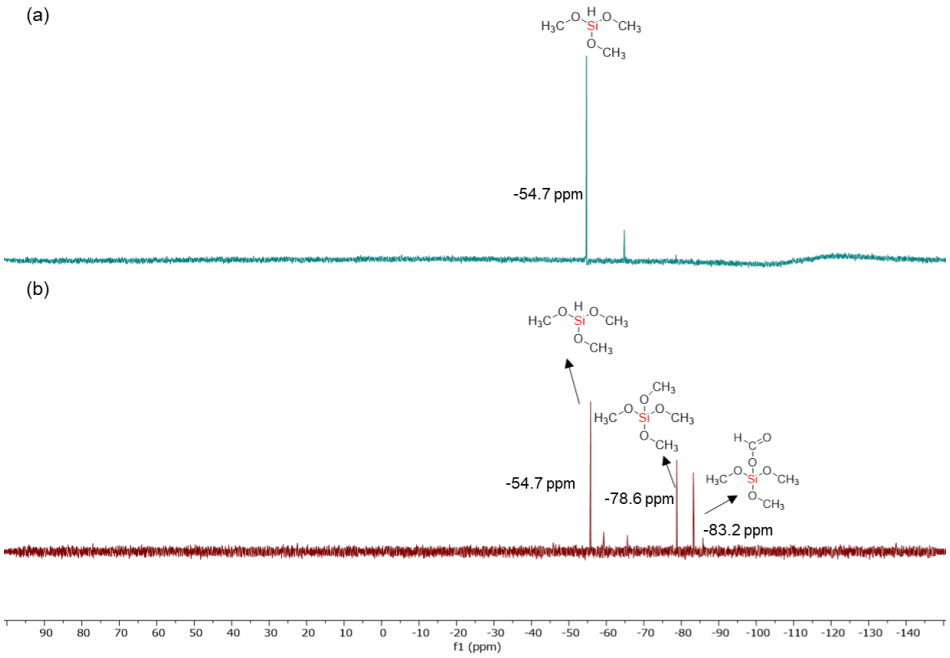


Figure S3. The ^{29}Si NMR data of the control experiments shown in Scheme 2a. (a) Before the reaction. (b) After the reaction. Reaction conditions: see Figure S1.

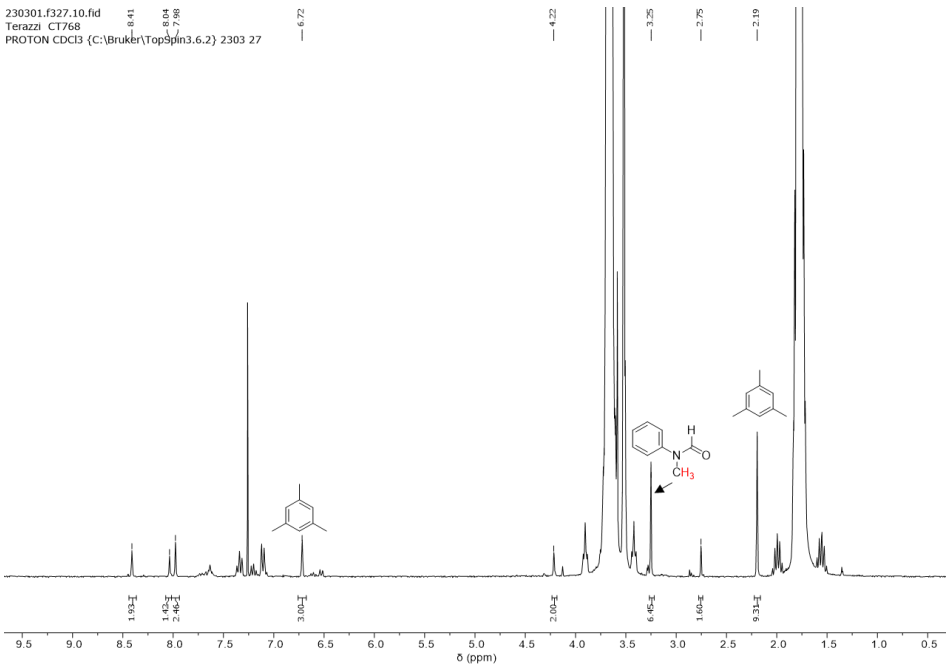
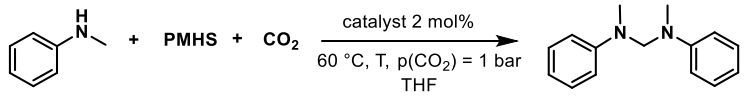


Figure S4. ^{1}H NMR data of the control experiments shown in Scheme 2b in $CDCl_3$. Reaction condition: To the reaction mixture of Scheme 2a *N*-methylaniline (28.8 mg, 0.27 mmol) was added and reacted under Argon at 70°C for 6 h. For the quantification methylene (11.5 mg, 0.10 mmol) were used as internal standard.

Table S1. The yield of aminal over time.



entry	Time (h)	Yield aminal (%)
1	1	6
2	2	9
3	8	1

Reaction conditions: N-methylaniline 1a (0.233 mmol, 25.0 mg), PMHS (4–10 equiv.), catalyst: 10 mol% (0.0233 mmol, 8.22 mg), CO_2 = 1 bar, 60 °C for 16 h, THF (2 mL). Yield was determined by ^{1}H-NMR using mesitylene as the internal standard.

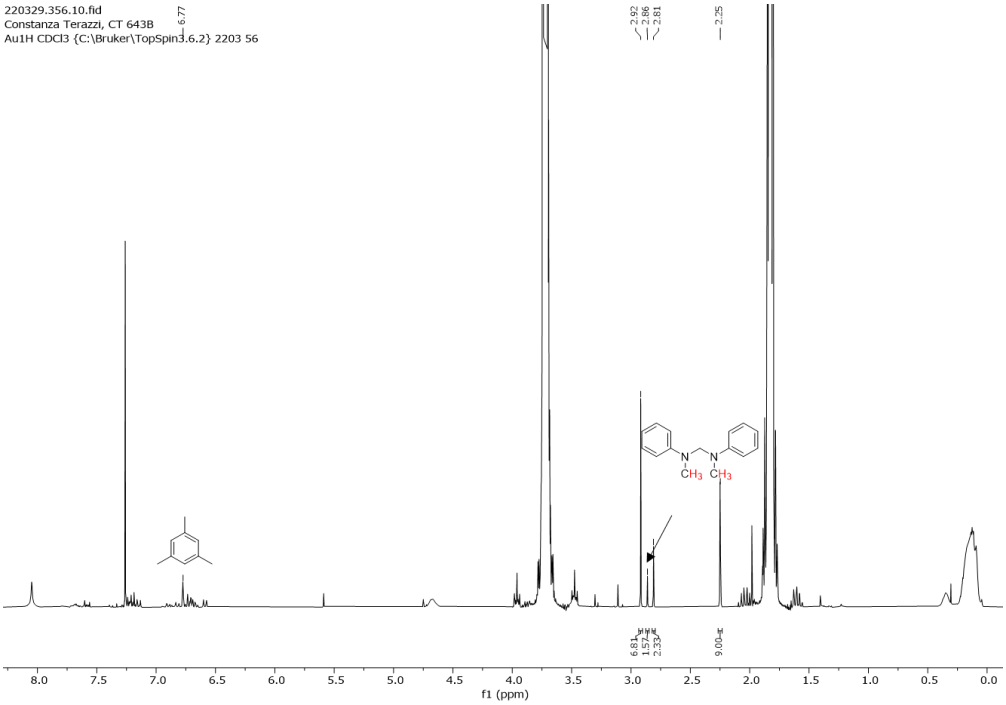


Figure S5. ^{1}H NMR for the quantification of aminal formation using mesitylene as internal standard (Table S1 entry 2). Reaction conditions: see Table S1.

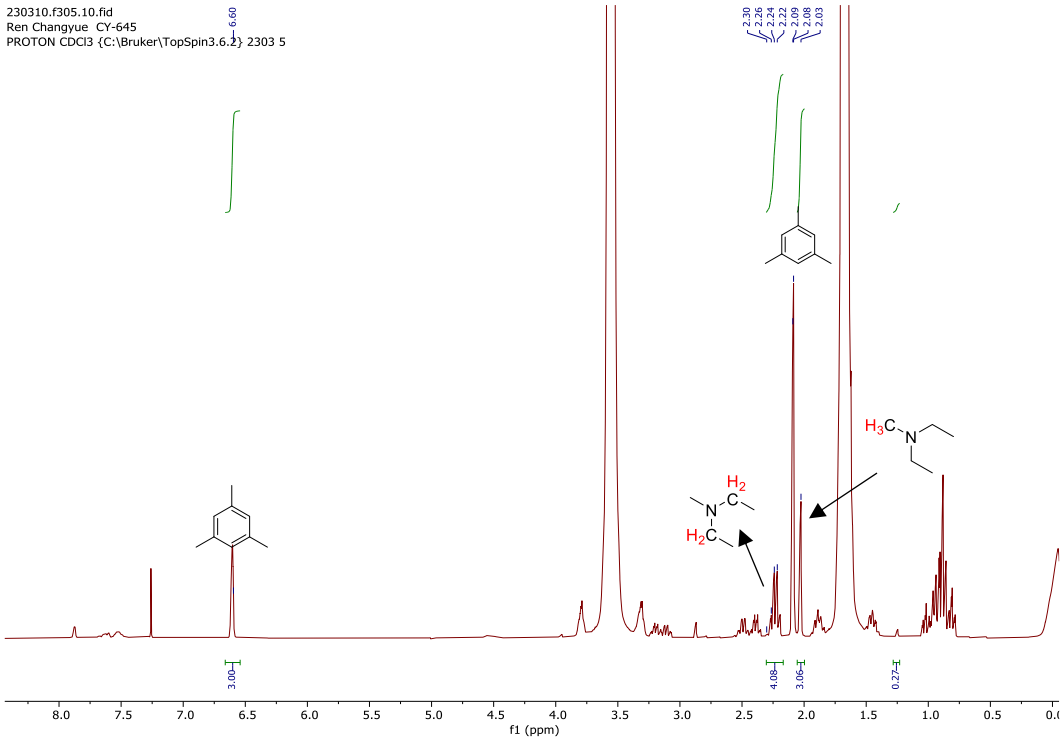
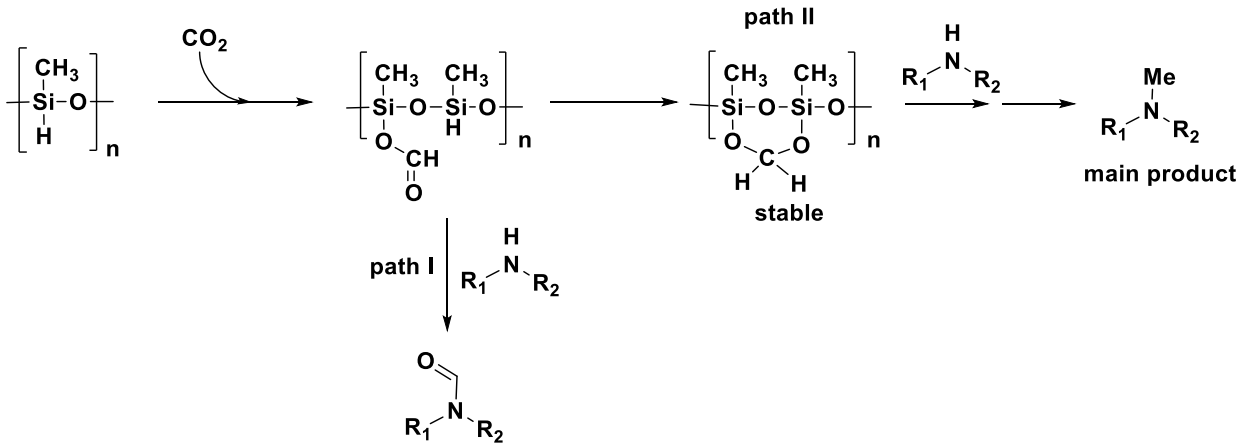


Figure S6. ^{1}H NMR data of the control experiments shown in Scheme 4b. Reaction conditions: *N*,*N*,*N*',*N*'-tetraethylmethanediamine (0.500 mmol, 79.1 mg), PMHS (2.00 mmol, 138 mg), catalyst 2b: 10 mol% (17.6 mg), CO_2 = 1 bar, 70 °C, 16 h. THF: 2 mL. The yield of *N*,*N*-diethylmethylamine from TEMDA was determined using mesitylene as internal standard.[7]



Scheme S1. The speculated pathway of reaction in the presence of PMHS.

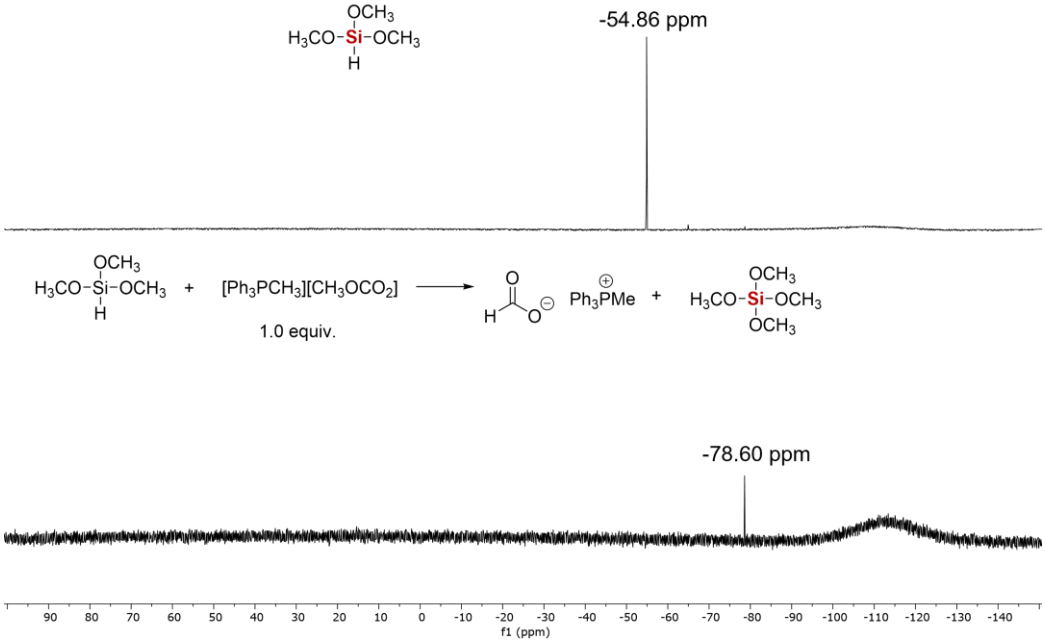


Figure S7. ^{29}Si NMR of the reaction between trimethoxysilane and the catalyst in the absence of CO_2. Reaction conditions: catalyst (24.7 mg, 0.0700 mmol), $(OMe)_3SiH$ (8.55, 0.0700 mmol), $CDCl_3$ 0.4 mL, at 70 °C under Argon for 16 h.[8]

7. References

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