Supplementary Information

Immobilized $Zn(OAc)_2$ on bipyridine-based periodic mesoporous organosilica for *N*-formylation of amines with CO_2 and hydrosilanes

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General Information

Unless stated otherwise, all of the chemicals were purchased from Sigma-Aldrich, Tokyo Chemical Industry or Wako Chemicals, stored under N_2 and used as received. CO_2 was purchased from Showa Denko Gas Products Co. Ltd. BPy-PMO and BPy-PMO-TMS were prepared according to a previously reported procedure.[S1]

Caution: High pressure CO_2 gas cylinders should be handled with care and located in an open area with fresh air, although we did not encounter any accident.

Catalytic reactions were carried out in a 10 mL stainless-steel autoclave with a gas-pressure monitor (max. 10 MPa). All of the oxygen-free operations were done in a glovebox. Reaction mixtures were heated in a Shibata Chemi-300 Synthesizer. Products were isolated with a Yamazen AI-580 Single Channel Automated Flash Chromatography System by using *n*-hexane and ethyl acetate as eluents. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker AVANCE II NMR spectrometer (^{1}H NMR at 400.1 MHz; $^{13}C\{^{1}H\}$ NMR at 100.6 MHz). ^{13}C cross-polarization (CP) MAS and ^{29}Si dipolar decoupling (DD) MAS NMR measurements were performed using ZrO_2 rotor at a sample spinning frequency of 8 kHz using a Bruker AVANCE II NMR spectrometer (^{13}C CP/MAS NMR at 100.6 MHz; ^{29}Si DD/MAS NMR at 79.49 MHz). Energy-dispersive X-ray spectrometry (EDX) was performed using a Shimadzu EDX-800HS instrument. Nitrogen adsorption and desorption isotherms were measured using a MicrotracBEL BELSORP MAX-II instrument. BET surface areas were calculated from the linear sections of BET plots (P/P_0 = 0.1–0.2). Pore-size distributions were calculated using the DFT method (DFT kernel: N_2 at 77 K on silica, cylindrical pores, nonlinear density functional theory (NLDFT) equilibrium model).

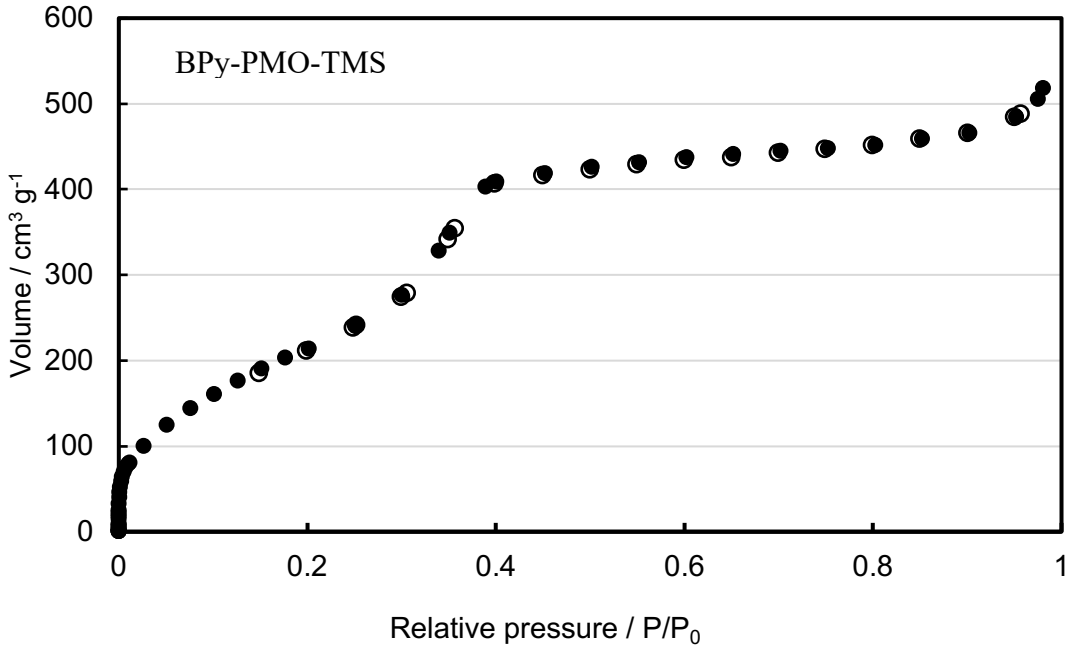


Figure S1. Nitrogen Adsorption/Desorption Isotherm of BPy-PMO-TMS.
(S_{BET}: 877 m^2 g^{-1}; d_{DFT} 4.4 nm)

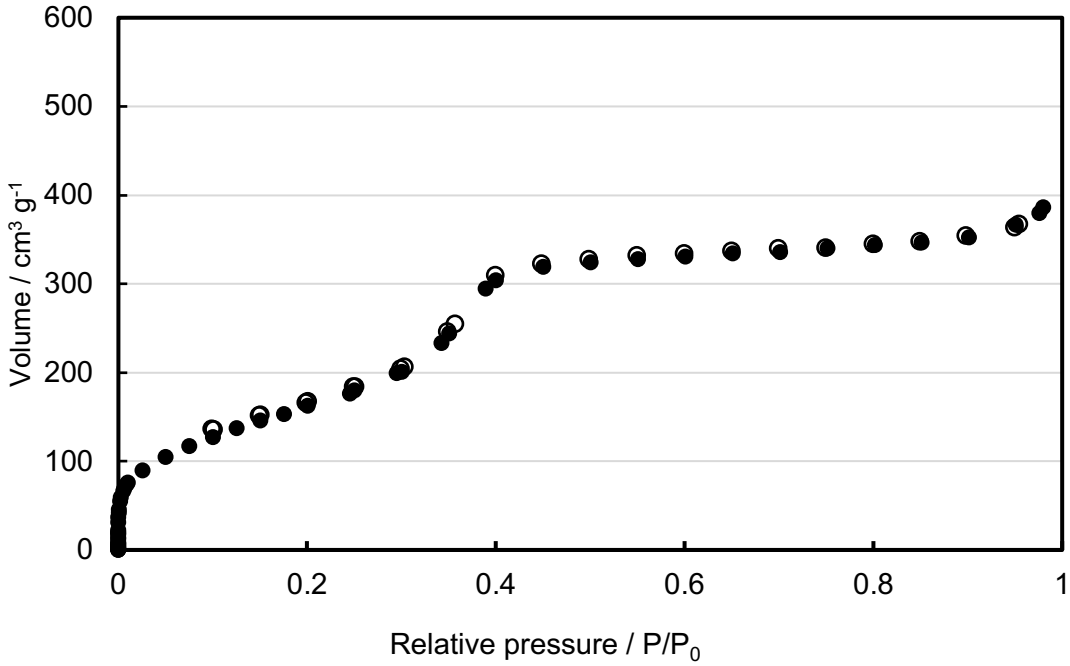


Figure S2. Nitrogen Adsorption/Desorption Isotherm of $Zn(OAc)_2$(BPy-PMO-TMS) **1**.
(S_{BET}: 630 m^2 g^{-1}; d_{DFT} 4.6 nm)

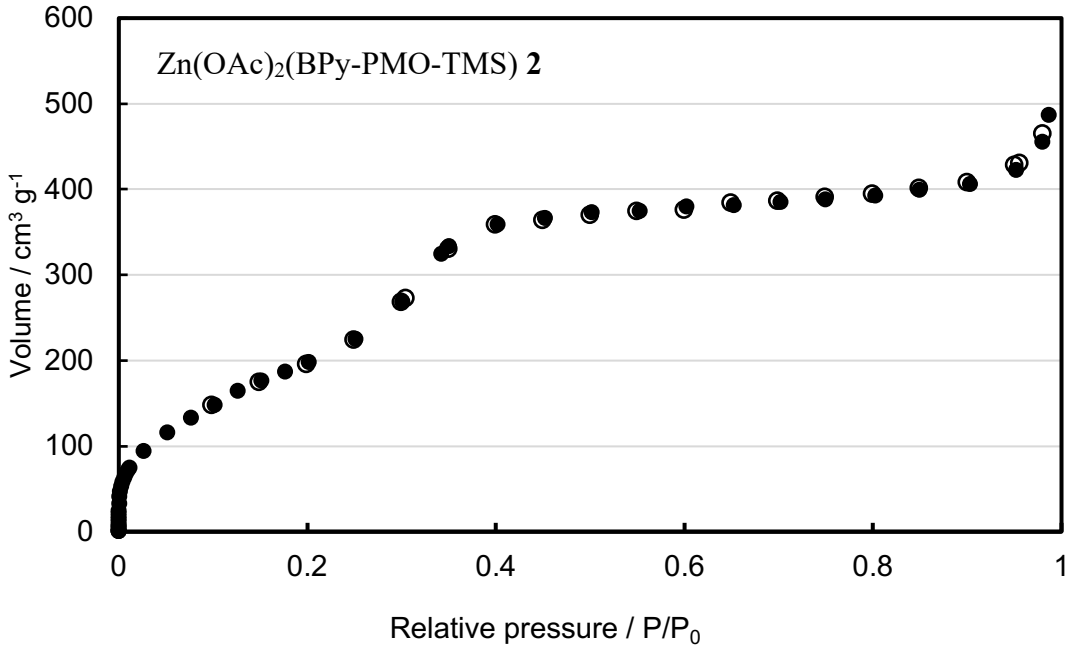


Figure S3. Nitrogen Adsorption/Desorption Isotherm of $Zn(OAc)_2$(BPy-PMO-TMS) **2**. (S_{BET}: 804 m^2 g^{-1}; d_{DFT} 4.1 nm)

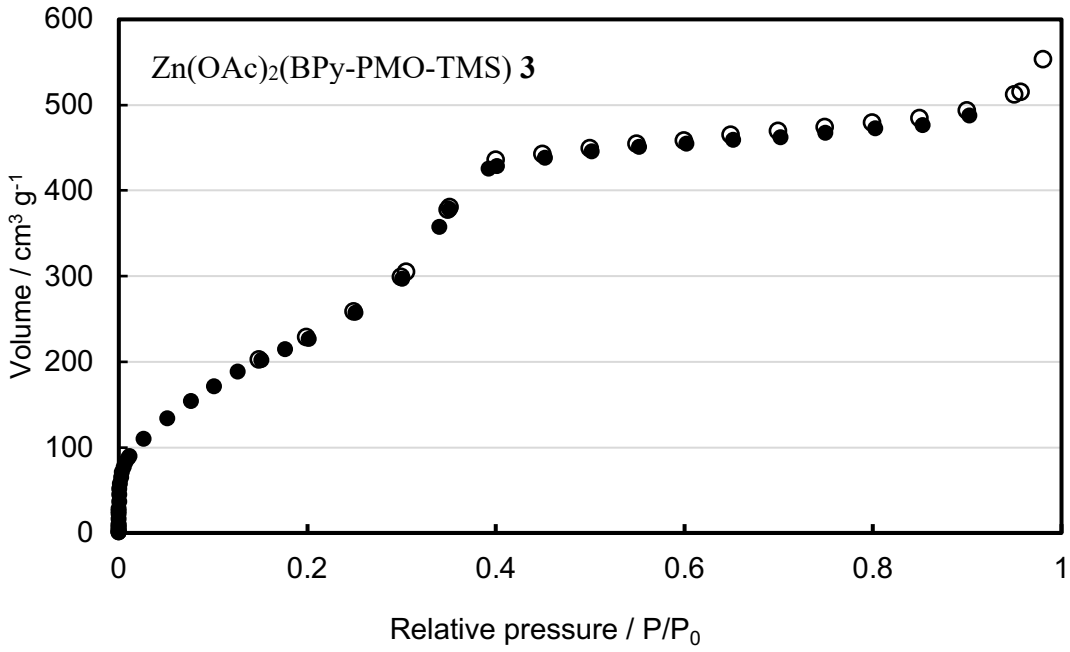


Figure S4. Nitrogen Adsorption/Desorption Isotherm of $Zn(OAc)_2$(BPy-PMO-TMS) **3**. (S_{BET}: 856 m^2 g^{-1}; d_{DFT} 4.3 nm)

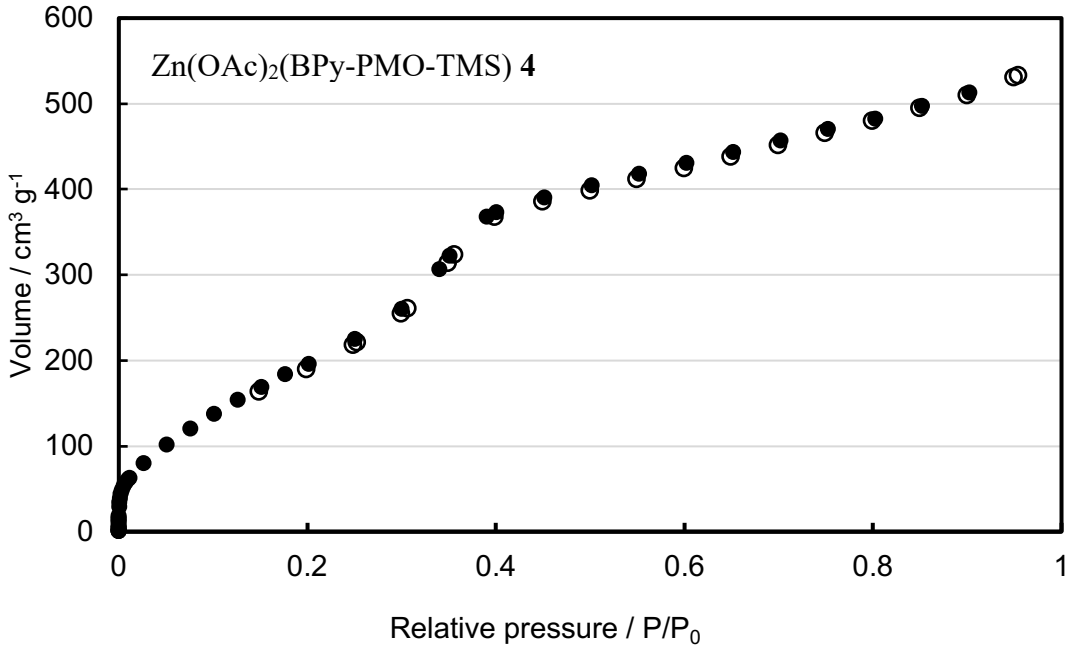


Figure S5. Nitrogen Adsorption/Desorption Isotherm of $Zn(OAc)_2$(BPy-PMO-TMS) **4**. (S_{BET}: 866 m^2 g^{-1}; d_{DFT} 4.4 nm)

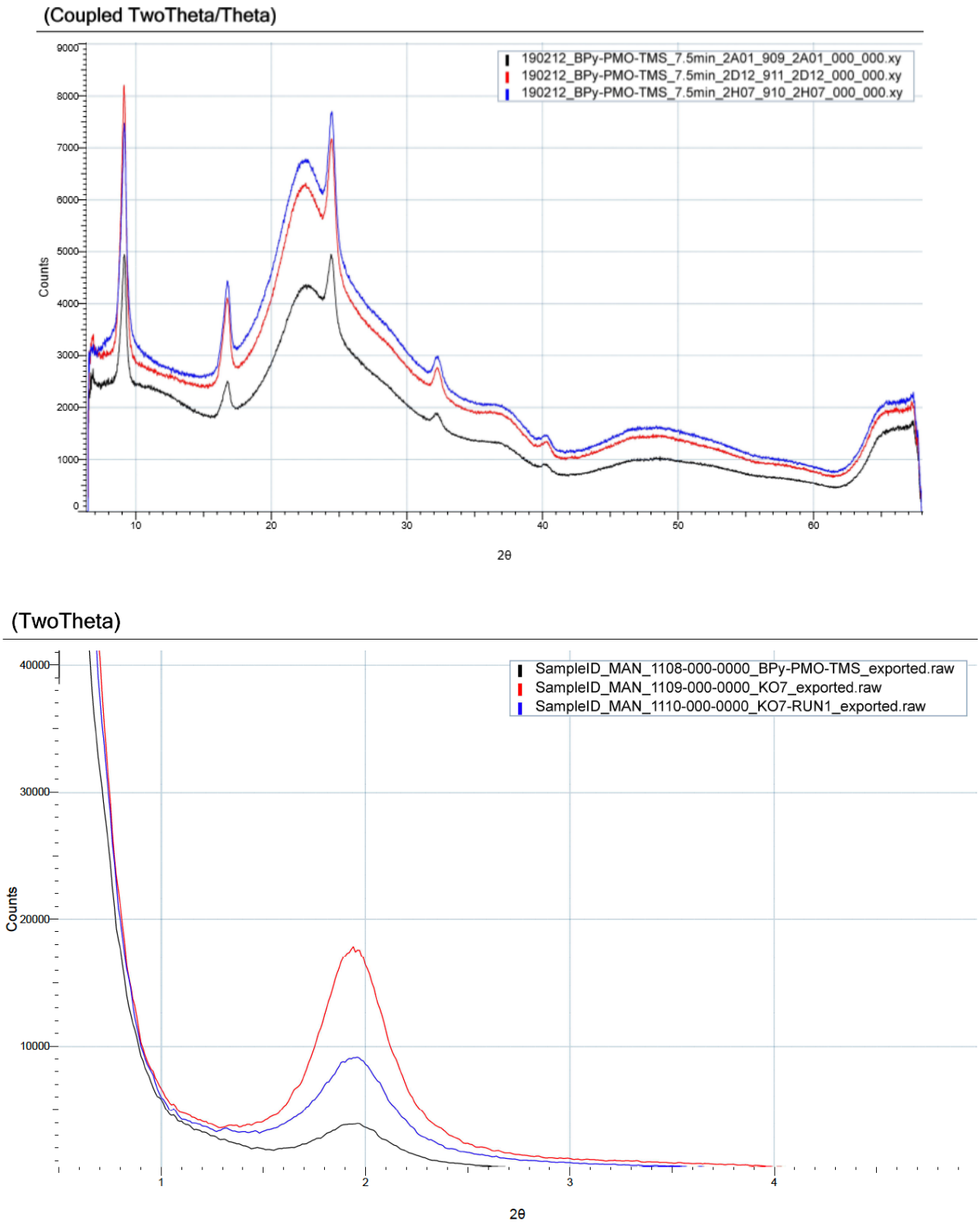


Figure S6. XRD Patterns of BPy-PMO-TMS (black), $Zn(OAc)_2$(BPy-PMO-TMS) **3** (red) and **3** Recovered After *N*-Formylation (blue)

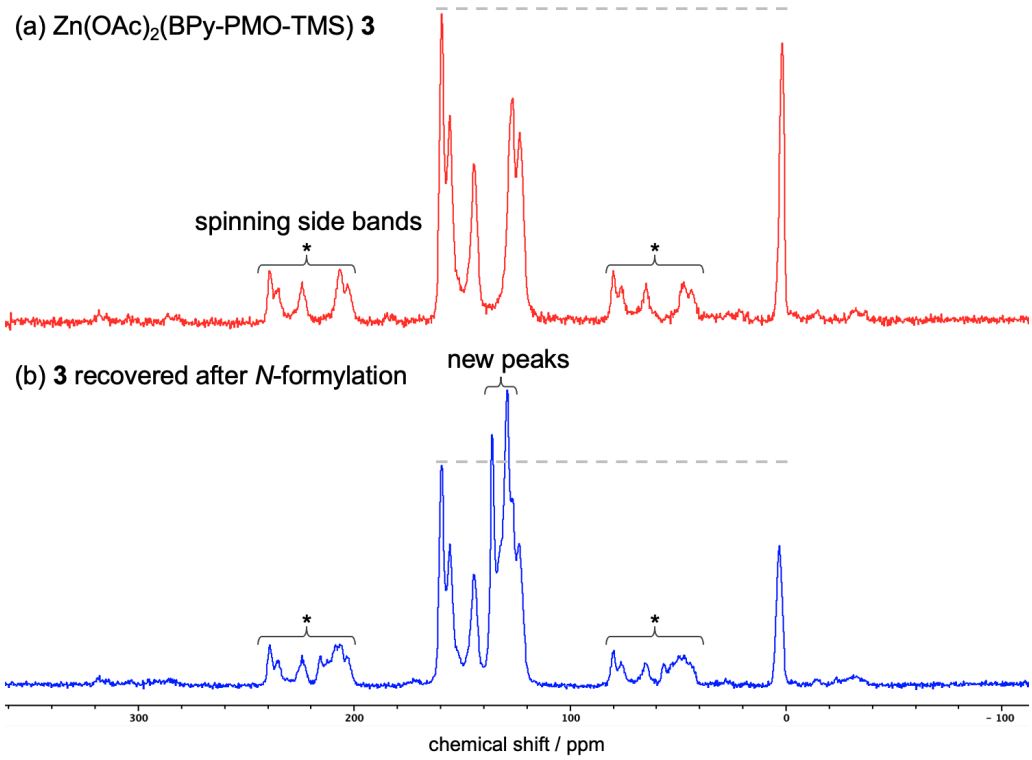


Figure S7. ^{13}C CP/MAS NMR Spectra of (a) Zn(OAc)$_2$(BPy-PMO-TMS) **3** and (b) **3** Recovered After *N*-Formylation.

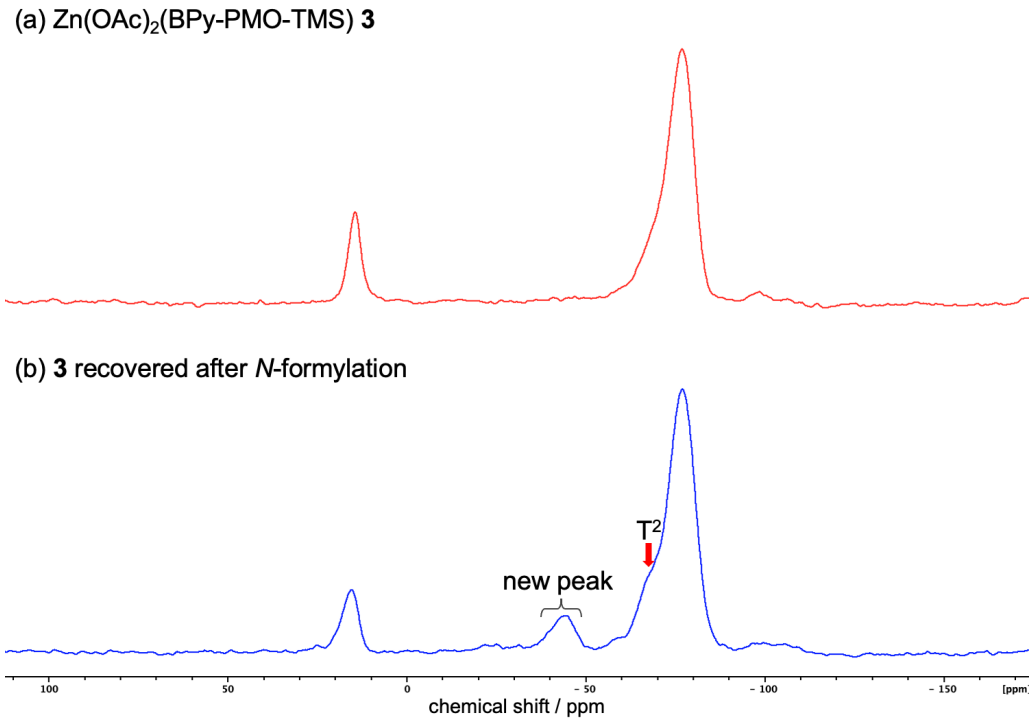


Figure S8. ^{29}Si DD/MAS NMR Spectra of (a) Zn(OAc)$_2$(BPy-PMO-TMS) **3** and (b) **3** Recovered After *N*-Formylation.

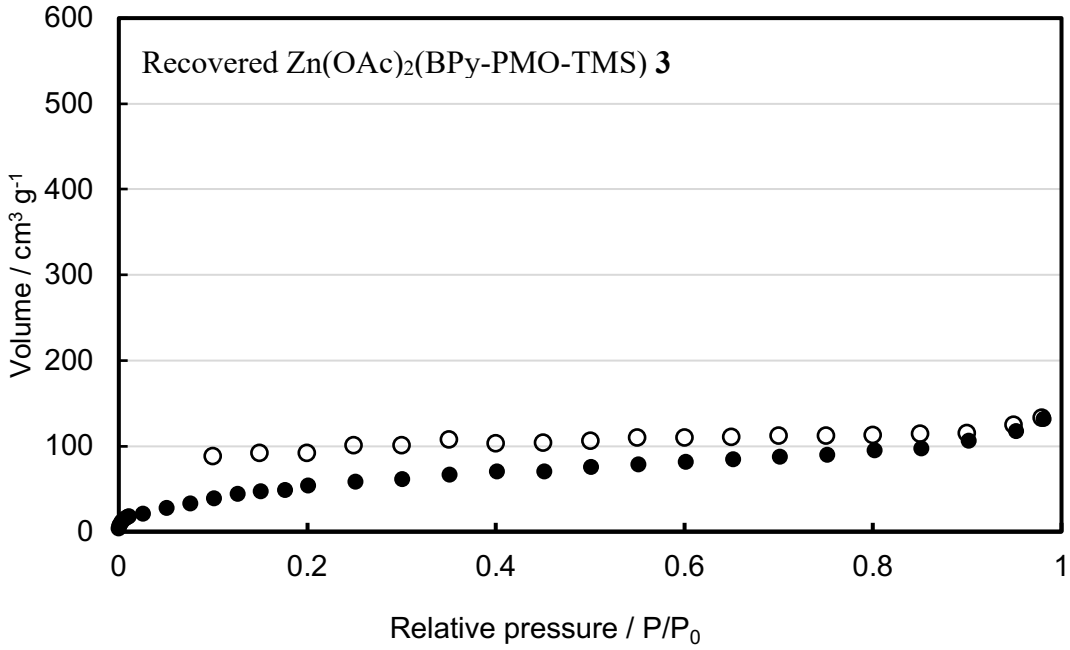
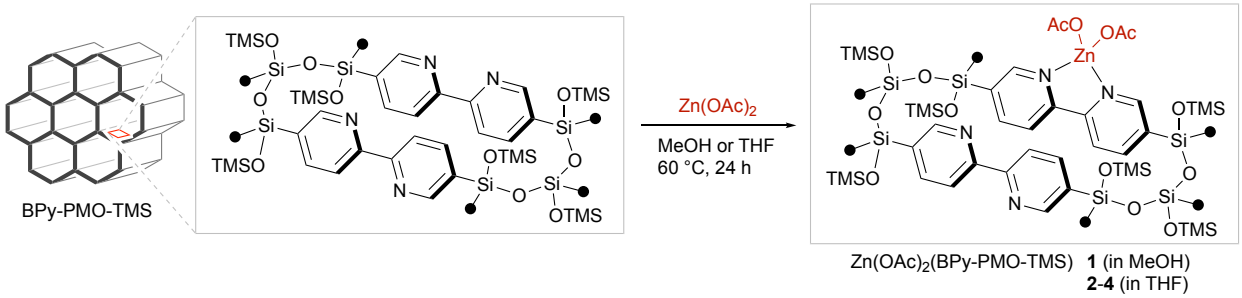


Figure S9. Nitrogen Adsorption/Desorption Isotherm of Recovered $Zn(OAc)_2$(BPy-PMO-TMS) **3**. (S_{BET}: 217 m^2 g^{-1})

Immobilization of $Zn(OAc)_2$ on BPy-PMO-TMS



$Zn(OAc)_2$(BPy-PMO-TMS) **1** (in MeOH)
2-**4** (in THF)

$Zn(OAc)_2$(BPy-PMO-TMS) 1

BPy-PMO-TMS (200 mg) was suspended in dry MeOH (25 mL) and stirred at room temperature for 1 h. A solution of zinc acetate (33 mg, 0.18 mmol) in MeOH (10 mL) was added dropwise to the suspension, and the mixture was stirred at room temperature for 2 h and then stirred at 60 °C for 24 h. The resulting suspension was filtered and washed with dry MeOH. The solid obtained was dried under reduced pressure to give **1** as a white powder (192 mg).

$Zn(OAc)_2$(BPy-PMO-TMS) 2

BPy-PMO-TMS (200 mg) was suspended in dry THF (25 mL) and stirred at room temperature for 1 h. A solution of zinc acetate (33 mg, 0.18 mmol) in THF (30 mL) was added dropwise to the suspension, and the mixture was stirred at room temperature for 2 h and then stirred at 60 °C for 24 h. The resulting suspension was filtered and washed with dry THF. The solid obtained was dried under reduced pressure to give **2** as a white powder (205 mg).

$Zn(OAc)_2$(BPy-PMO-TMS) 3

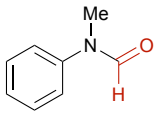
BPy-PMO-TMS (200 mg) was suspended in dry THF (25 mL) and stirred at room temperature for 1 h. A solution of zinc acetate (11 mg, 0.06 mmol) in THF (10 mL) was added dropwise to the suspension, and the mixture was stirred at room temperature for 2 h and then stirred at 60 °C for 24 h. The resulting suspension was filtered and washed with dry THF. The solid obtained was dried under reduced pressure to give **3** as a white powder (202 mg).

$Zn(OAc)_2$(BPy-PMO-TMS) 4

BPy-PMO-TMS (200 mg) was suspended in dry THF (25 mL) and stirred at room temperature for 1 h. A solution of zinc acetate (5.5 mg, 0.03 mmol) in THF (5 mL) was added dropwise, to the suspension, and the mixture was stirred at room temperature for 2 h and then stirred at 60 °C for 24 h. The resulting suspension was filtered and washed with dry THF. The solid obtained was dried under reduced pressure to give **4** as a white powder (195 mg).

N-Formylation of Nitrogen Nucleophiles with CO_2 and $PhSiH_3$

***N*-Methyl-*N*-phenylformamide (6a)**[S2]



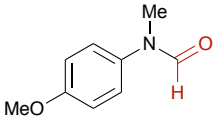
To a 10 mL stainless-steel autoclave, $Zn(OAc)_2$(BPy-PMO-TMS) **3** (35 mg, 1 mol% Zn), *N*-methylaniline (107 mg, 1 mmol), $PhSiH_3$ (108 mg, 1 mmol), and CH_3CN (3 mL) were added in a glove box under nitrogen. The autoclave was sealed tightly and filled with CO_2 (0.5 MPa) at room temperature. The mixture was heated at 60 °C for 17 h. After the reaction, the mixture was filtered through a membrane and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane and ethyl acetate) to give *N*-Methyl-*N*-phenylformamide (**6a**) as a colorless oil (108 mg, 80%).

The product exists as two rotational isomers with a ratio of >9:1. The NMR data of the major isomer is provided below.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 7.41 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 3.31 (s, 3H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.4, 142.2, 129.6, 126.4, 122.4, 32.1 ppm.

***N*-(4-Methoxyphenyl)-*N*-methylformamide (6b)**[S2]



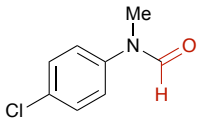
To a 10 mL stainless-steel autoclave, $Zn(OAc)_2$(BPy-PMO-TMS) **3** (35 mg, 1 mol% Zn), 4-methoxy-*N*-methylaniline (137 mg, 1 mmol), $PhSiH_3$ (108 mg, 1 mmol), and CH_3CN (3 mL) were added in a glove box under nitrogen. The autoclave was sealed tightly and filled with CO_2 (0.5 MPa) at room temperature. The mixture was heated at 60 °C for 17 h. After the reaction, the mixture was filtered through a membrane and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane and ethyl acetate) to give *N*-(4-methoxyphenyl)-*N*-methylformamide (**6b**) as a colorless oil (142 mg, 86%).

The product exists as two rotational isomers with a ratio of >9:1. The NMR data of the major isomer is provided below.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.07 (d, *J* = 9.1 Hz, 2H), 6.91 (d, *J* = 9.1 Hz, 2H), 3.8 (s, 3H), 3.3 (s, 3H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.5, 158.3, 135.2, 124.7, 114.8, 55.6, 32.7 ppm.

_N_-(4-Chlorophenyl)-_N_-methylformamide (6c)[S2]



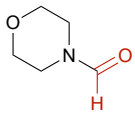
To a 10 mL stainless-steel autoclave, $Zn(OAc)_2$(BPy-PMO-TMS) **3** (35 mg, 1 mol% Zn), 4-chloro-*N*-methylaniline (141 mg, 1 mmol), $PhSiH_3$ (108 mg, 1 mmol), and CH_3CN (3 mL) were added in a glove box under nitrogen. The autoclave was sealed tightly and filled with CO_2 (0.5 MPa) at room temperature. The mixture was heated at 60 °C for 24 h. After the reaction, the mixture was filtered through a membrane and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane and ethyl acetate) to give *N*-(4-chlorophenyl)-*N*-methylformamide (**6c**) as a colorless oil (135 mg, 80%).

The product exists as two rotational isomers with a ratio of >9:1. The NMR data of the major isomer is provided below.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.38 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 3.29 (s, 3H) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.0, 140.7, 132.0, 129.8, 123.5, 32.0 ppm.

Morpholine-4-carbaldehyde (6d)[S3]

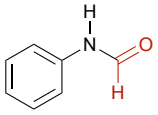


To a 10 mL stainless-steel autoclave, $Zn(OAc)_2$(BPy-PMO-TMS) **3** (35 mg, 1 mol% Zn), morpholine (87 mg, 1 mmol), $PhSiH_3$ (108 mg, 1 mmol), and CH_3CN (3 mL) were added in a glove box under nitrogen. The autoclave was sealed tightly and filled with CO_2 (0.5 MPa) at room temperature. The mixture was heated at 60 °C for 17 h. After the reaction, the mixture was filtered through a membrane and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane and ethyl acetate) to give morpholine-4-carbaldehyde (**6d**) as a colorless oil (101 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, H), 3.67 (t, J = 4.6 Hz, 2H), 3.64 (t, J = 4.6 Hz, 2H), 3.55 (t, J = 4.6 Hz, 2H), 3.37 (t, J = 4.6 Hz, 2H) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.9, 67.2, 66.4, 45.8, 40.6 ppm.

_N_-Phenylformamide (6e)[S3]



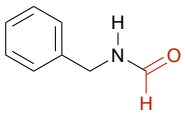
To a 10 mL stainless-steel autoclave, $Zn(OAc)_2$(BPy-PMO-TMS) **3** (35 mg, 1 mol% Zn), aniline (93 mg, 1 mmol), $PhSiH_3$ (108 mg, 1 mmol), and CH_3CN (3 mL) were added in a glove box under nitrogen. The autoclave was sealed tightly and filled with CO_2 (0.5 MPa) at room temperature. The mixture was heated at 60 °C for 17 h. After the reaction, the mixture was filtered through a membrane and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane and ethyl acetate) to give *N*-phenylformamide (**6e**) as a colorless solid (85 mg, 70%).

The product exists as two rotational isomers with a ratio of ca. 1:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (br d, 0.5H), 8.71 (d, J = 11.6 Hz, 0.5H), 8.34 (d, J = 1.8 Hz, 0.5H), 8.16 (br s, 0.5H), 7.59-7.53 (m, 1H), 7.39-7.28 (m, 2H), 7.20-7.08 (m, 2H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.2, 159.6, 137.0, 136.9, 129.8, 129.1, 125.3, 124.8, 120.1, 118.8 ppm.

_N_-Benzylformamide (6f)[S3]



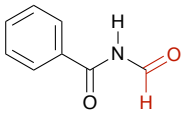
To a 10 mL stainless-steel autoclave, $Zn(OAc)_2$(BPy-PMO-TMS) **3** (35 mg, 1 mol% Zn), $PhSiH_3$ (108 mg, 1 mmol), and CH_3CN (3 mL) were added in a glove box under nitrogen. The autoclave was sealed tightly and filled with CO_2 (0.5 MPa) at room temperature. The mixture was heated at 60 °C for 17 h. After cooling to room temperature, benzylamine (107 mg, 1 mmol) was added to the mixture, which was further stirred at room temperature for 30 min. After the reaction, the mixture was filtered through a membrane and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane and ethyl acetate) to give *N*-benzylformamide (**6f**) as a colorless solid (116 mg, 86%).

The product exists as two rotational isomers with a ratio of ca. 6:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23, 8.14 (br s and d, J = 11.8 Hz, total 1H), 7.45-7.24 (m, 5H), 6.30 (br, 1H), 4.47, 4.40 (d, J = 6.0 Hz, and d, J = 6.5 Hz, total 2H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.8, 161.2, 137.6, 137.5, 128.9, 128.8, 127.8, 127.8, 127.7, 127.0, 45.7, 42.2 ppm.

_N_-Formylbenzamide (6g)[S4]

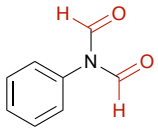


To a 10 mL stainless-steel autoclave, $Zn(OAc)_2$(BPy-PMO-TMS) **3** (35 mg, 1 mol% Zn), benzamide (121 mg, 1 mmol), $PhSiH_3$ (108 mg, 1 mmol), and CH_3CN (3 mL) were added in a glove box under nitrogen. The autoclave was sealed tightly and filled with CO_2 (0.5 MPa) at room temperature. The mixture was heated at 100 °C for 24 h. After the reaction, the mixture was filtered through a membrane and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane and ethyl acetate) to give *N*-formylbenzamide (**6g**) as a colorless solid (53 mg, 36%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (br d, 1H), 9.41 (d, J = 9.7 Hz, 1H), 7.98 (m, 2H), 7.68-7.62 (m, 1H), 7.57-7.51 (m, 2H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.7, 164.6, 134.0, 131.1, 129.1, 128.0 ppm.

_N_-Formyl-_N_-phenylformamide (8e)[S5]

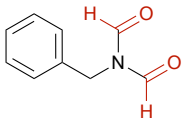


To a 10 mL stainless-steel autoclave, $Zn(OAc)_2$(BPy-PMO-TMS) **3** (35 mg, 1 mol% Zn), aniline (93 mg, 1 mmol), $PhSiH_3$ (432 mg, 4 mmol), and CH_3CN (3 mL) were added in a glove box under nitrogen. The autoclave was sealed tightly and filled with CO_2 (0.5 MPa) at room temperature. The mixture was heated at 100 °C for 24 h. After the reaction, the mixture was filtered through a membrane and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane and ethyl acetate) to give *N*-formyl-*N*-phenylformamide (**8e**) as a colorless solid (110 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (br, 2H), 7.52-7.38 (m, 3H), 7.22-7.13 (br d, 2H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.3, 132.7, 129.6, 129.3, 127.4 ppm.

***N*-benzyl-*N*-formylformamide (8f)**[S6]



To a 10 mL stainless-steel autoclave, $Zn(OAc)_2$(BPy-PMO-TMS) **3** (35 mg, 1 mol% Zn), $PhSiH_3$ (432 mg, 4 mmol), and CH_3CN (3 mL) were added in a glove box under nitrogen. The autoclave was sealed tightly and filled with CO_2 (0.5 MPa) at room temperature. The mixture was heated at 60 °C for 17 h. After cooling to room temperature, benzylamine (107 mg, 1 mmol) was added to the mixture, which was further stirred at 100 °C for 24 h. After the reaction, the mixture was filtered through a membrane and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: *n*-hexane and ethyl acetate) to give *N*-benzylformamide (**8f**) as a colorless oil (54 mg, 33%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (br s, 2H), 7.48-7.19 (m, 5H), 4.79 (br s, 2H) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.0, 135.5, 128.9, 128.7, 128.1, 42.3 ppm.

References

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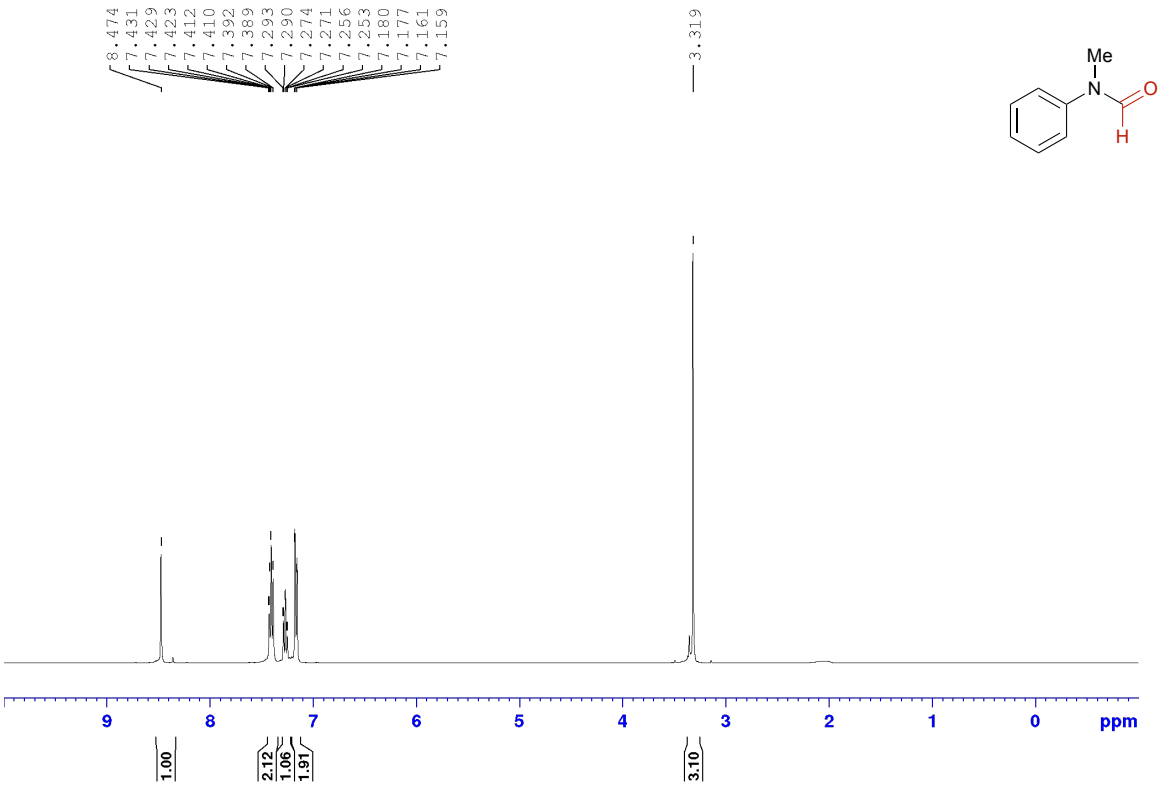

Figure S10. ^{1}H NMR of **6a** (400 MHz, $CDCl_3$)

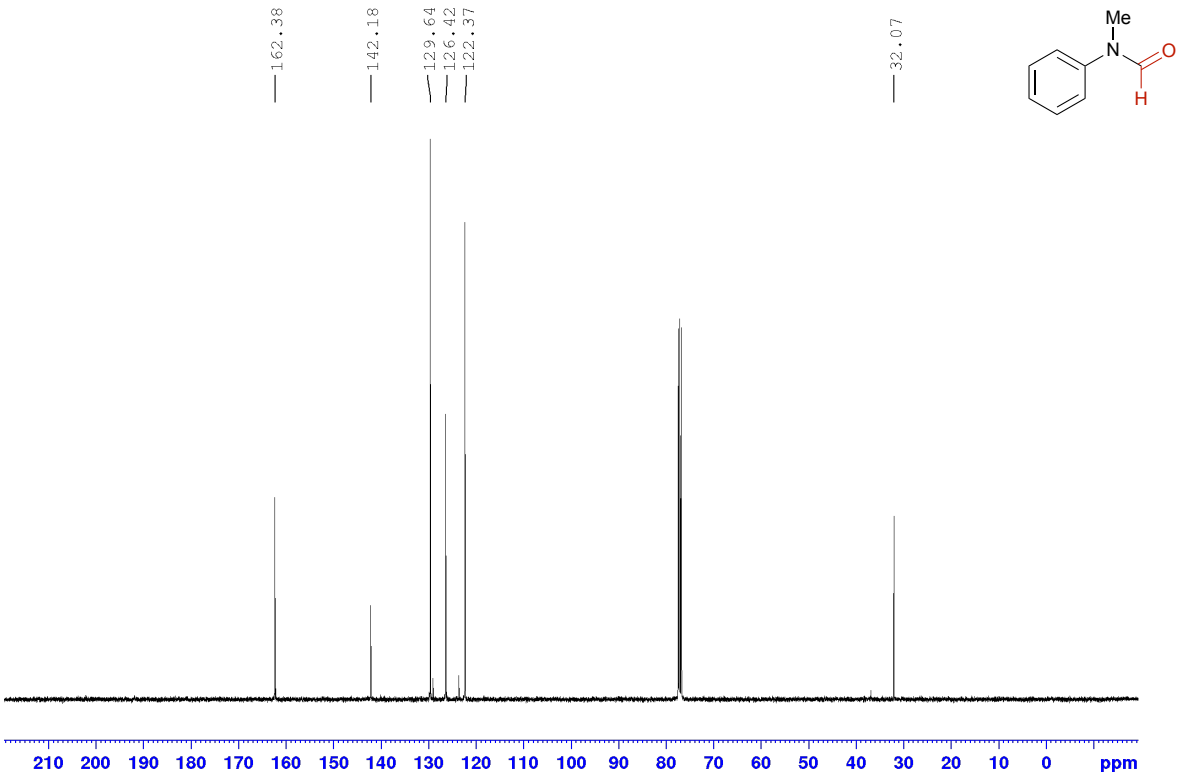

Figure S11. $^{13}C\{^{1}H\}$ NMR of **6a** (100 MHz, $CDCl_3$)

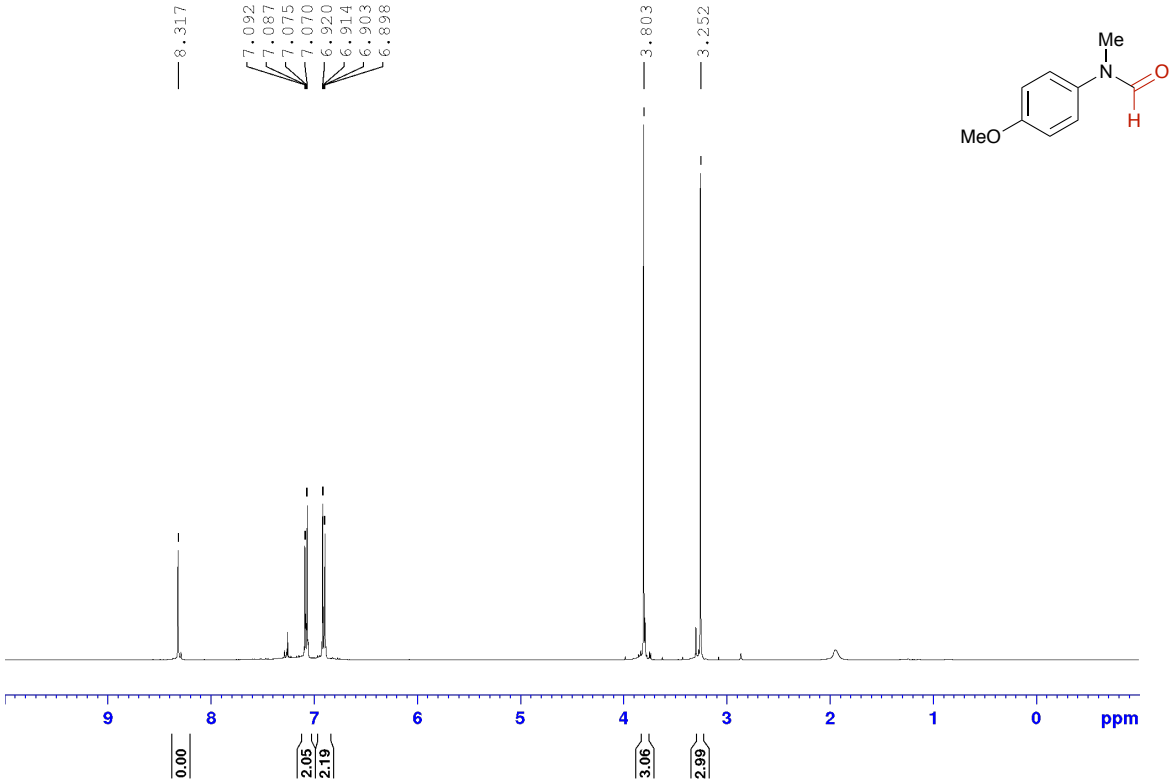

Figure S12. ^{1}H NMR of **6b** (400 MHz, $CDCl_3$)

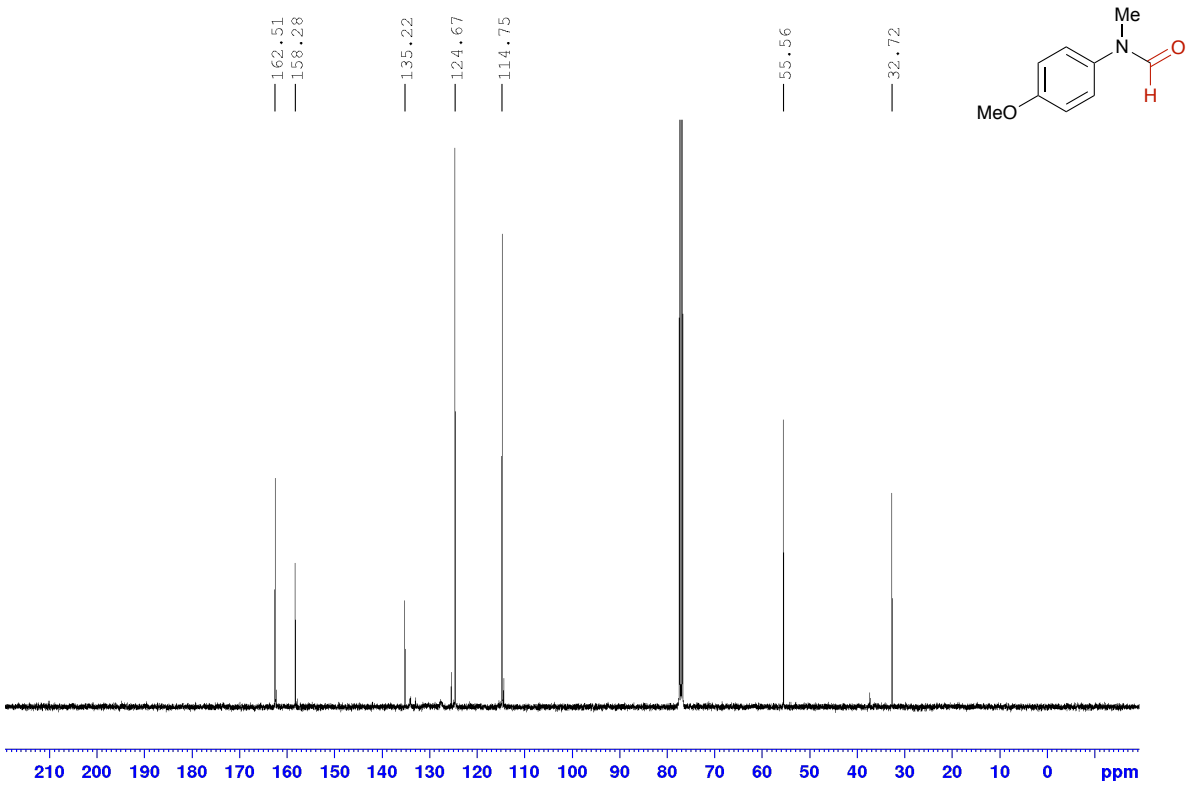

Figure S13. $^{13}C\{^{1}H\}$ NMR of **6b** (100 MHz, $CDCl_3$)

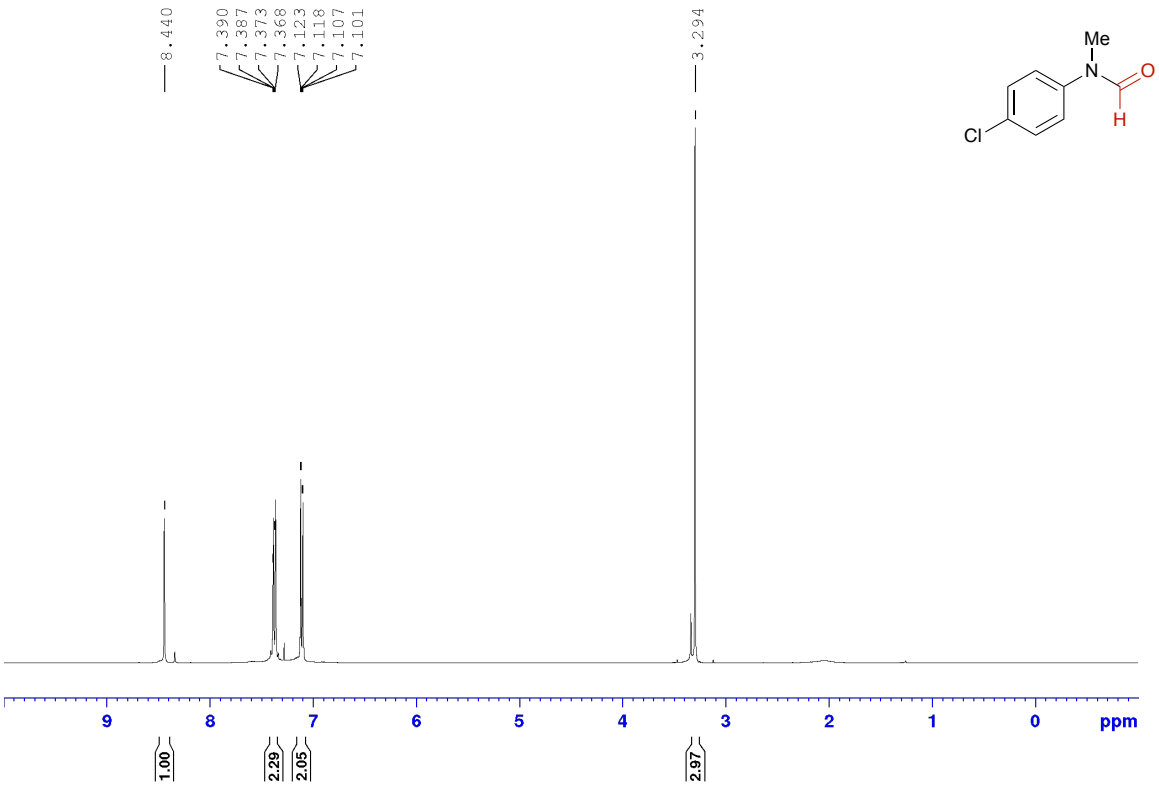

Figure S14. ^{1}H NMR of **6c** (400 MHz, $CDCl_3$)

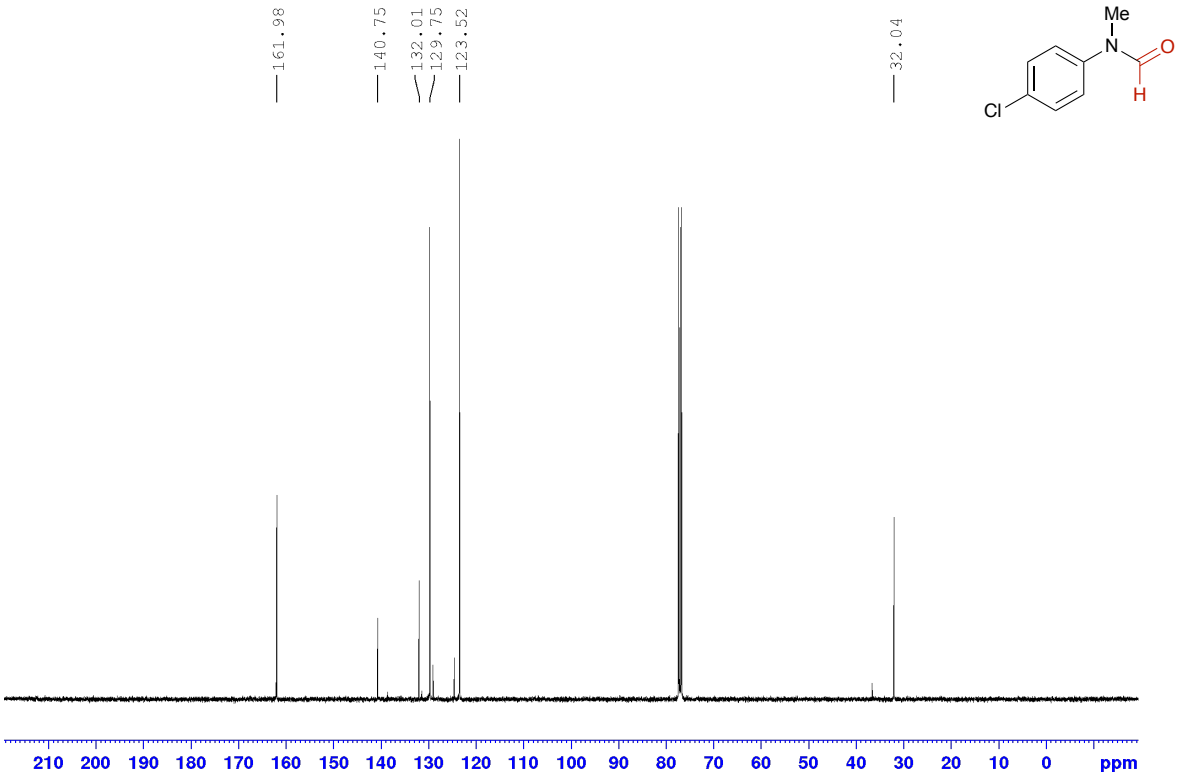

Figure S15. $^{13}C\{^{1}H\}$ NMR of **6c** (100 MHz, $CDCl_3$)

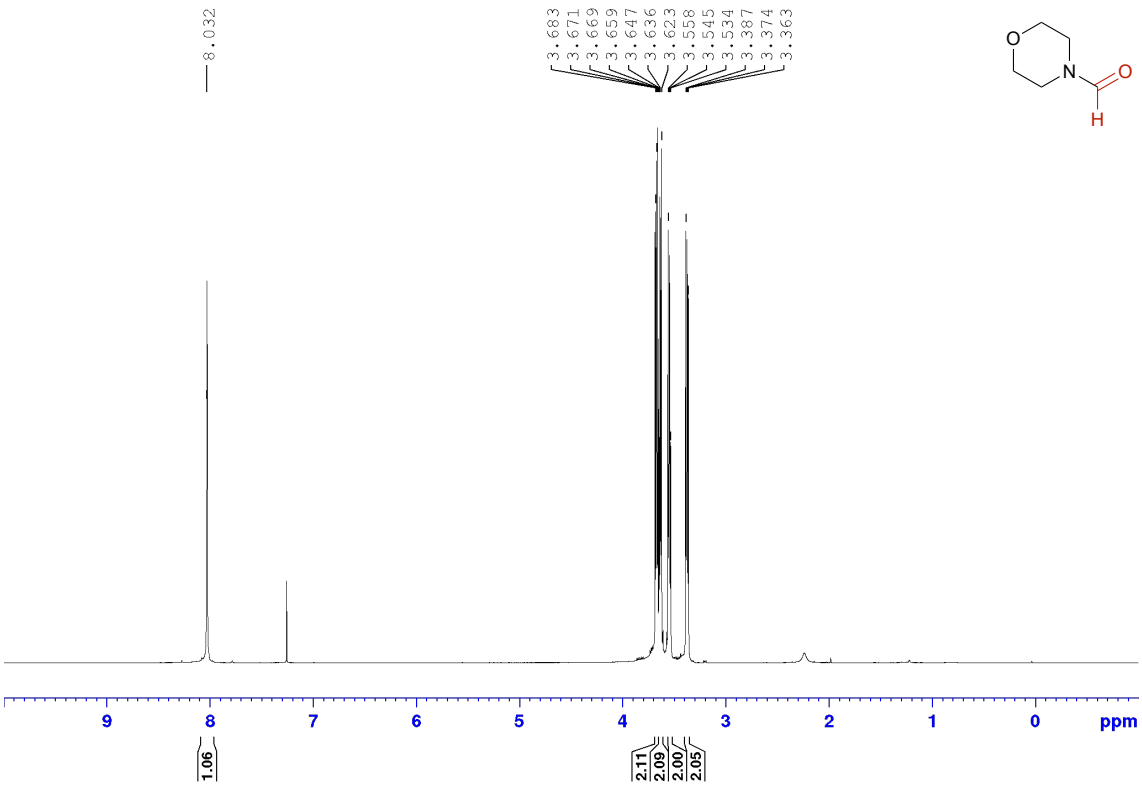

Figure S16. ^{1}H NMR of **6d** (400 MHz, $CDCl_3$)

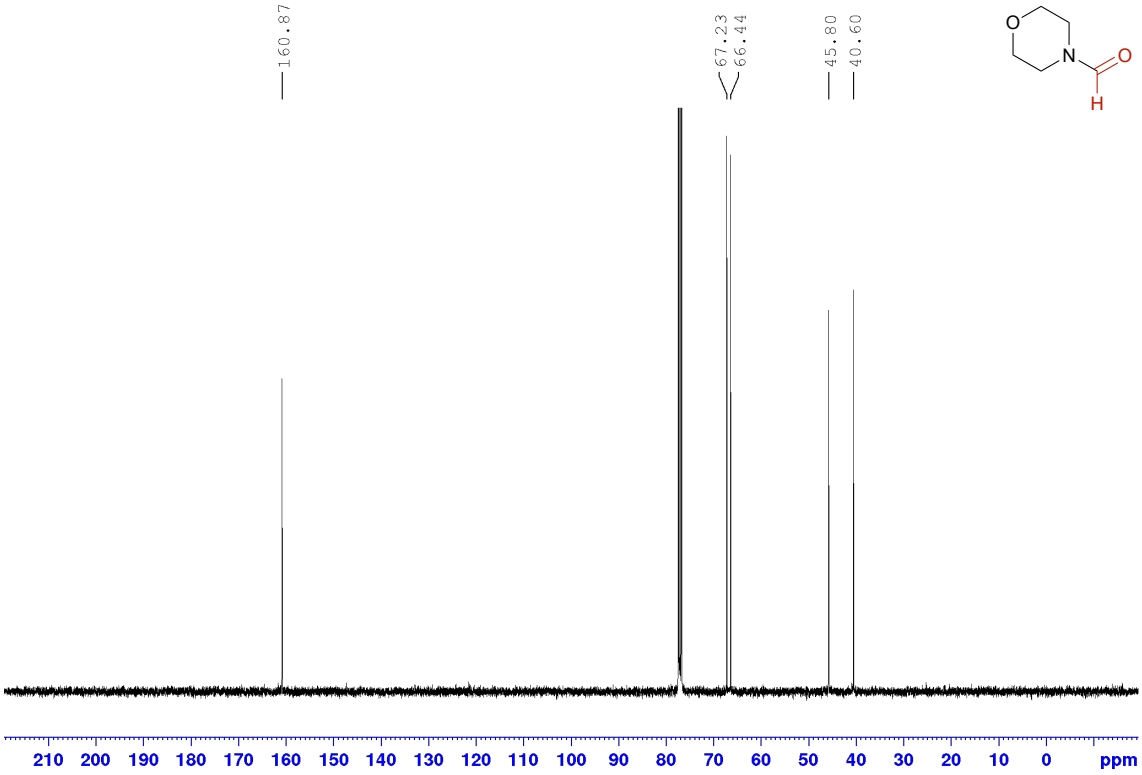

Figure S17. $^{13}C\{^{1}H\}$ NMR of **6d** (100 MHz, $CDCl_3$)

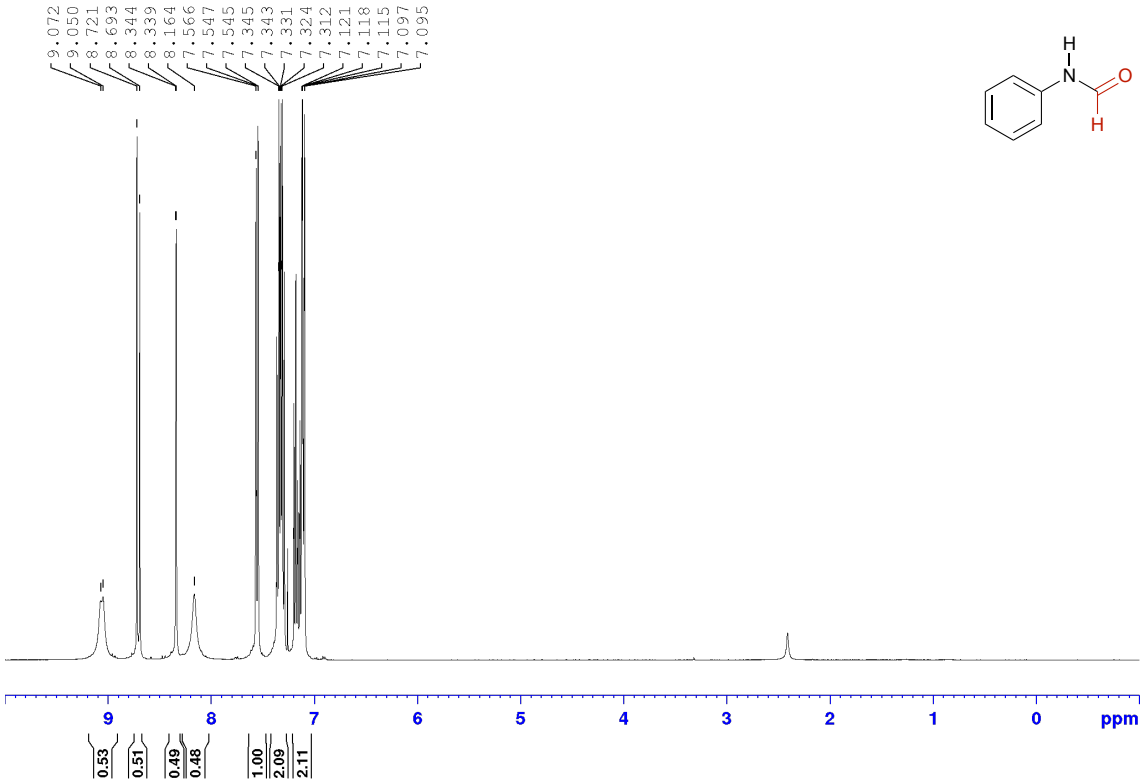

Figure S18. ^{1}H NMR of **6e** (400 MHz, $CDCl_3$)

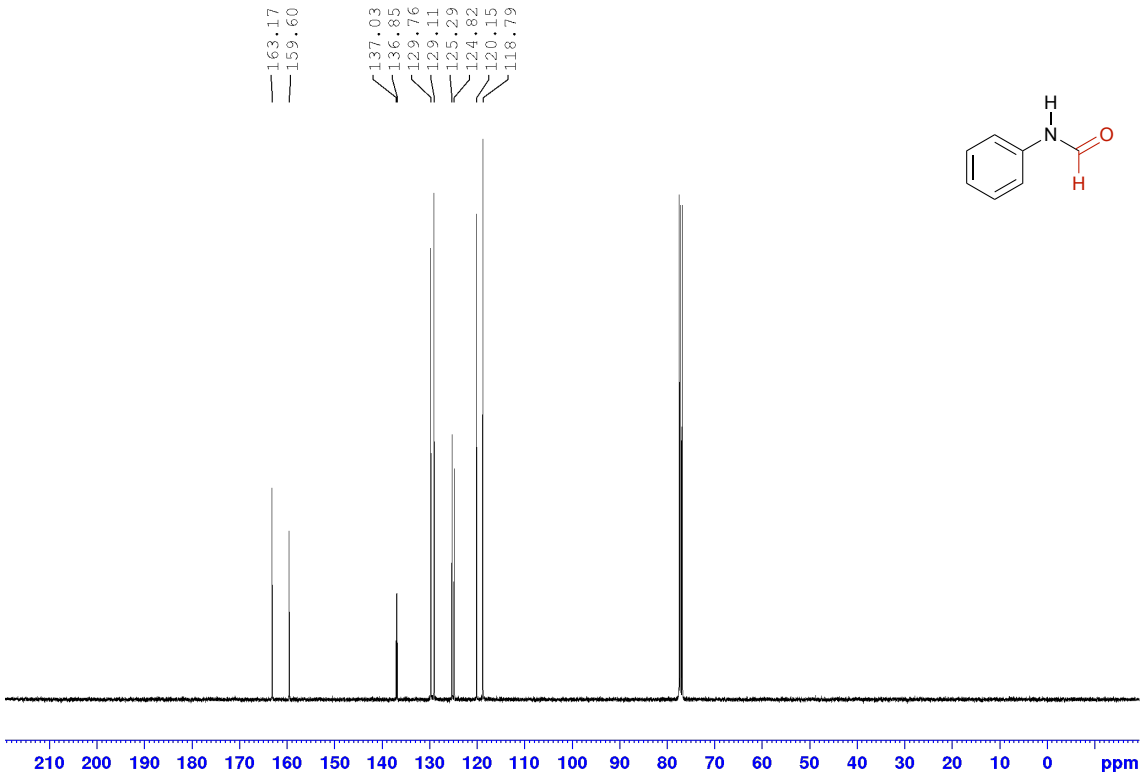

Figure S19. $^{13}C\{^{1}H\}$ NMR of **6e** (100 MHz, $CDCl_3$)

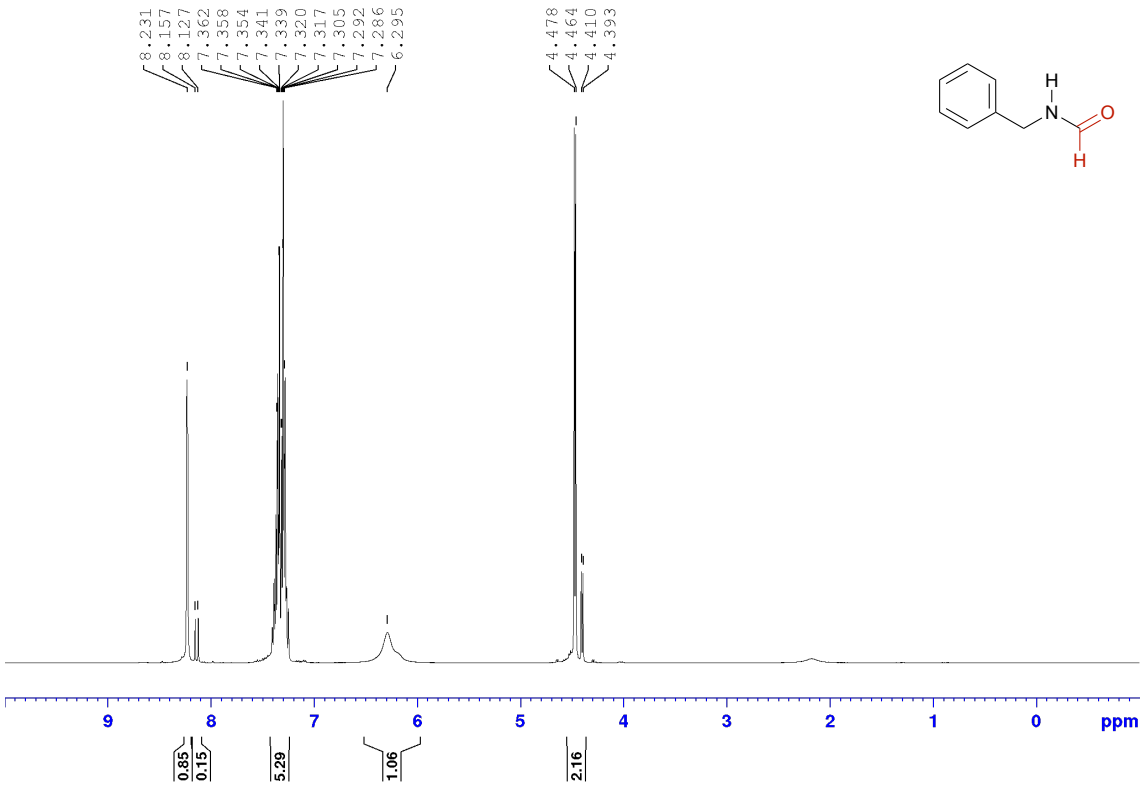

Figure S20. ^{1}H NMR of **6f** (400 MHz, $CDCl_3$)

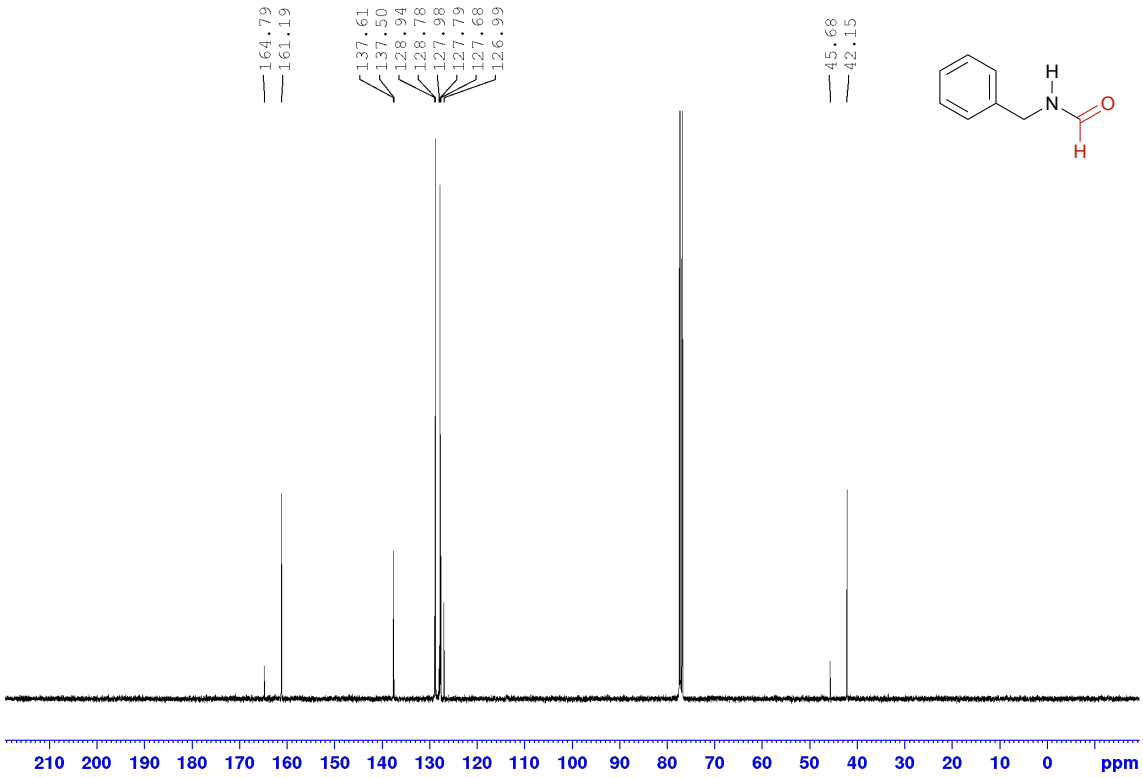

Figure S21. $^{13}C\{^{1}H\}$ NMR of **6f** (100 MHz, $CDCl_3$)

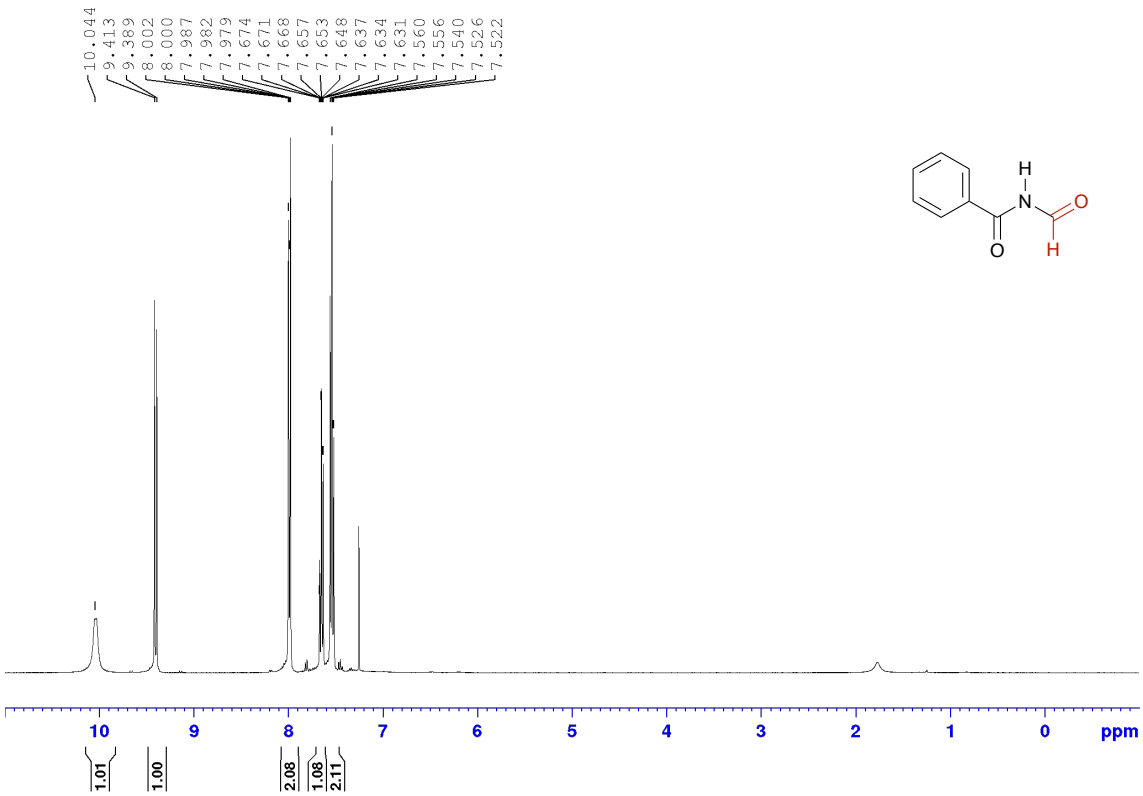

Figure S22. ^{1}H NMR of **6g** (400 MHz, $CDCl_3$)

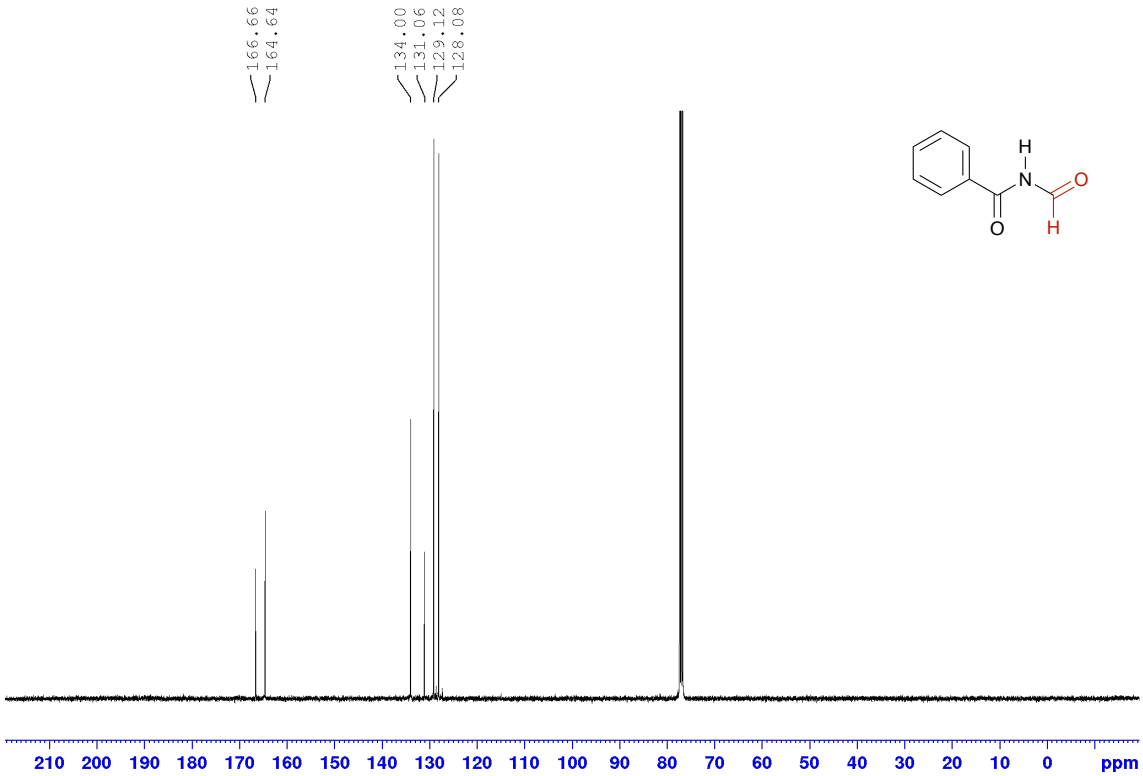

Figure S23. $^{13}C\{^{1}H\}$ NMR of **6g** (100 MHz, $CDCl_3$)

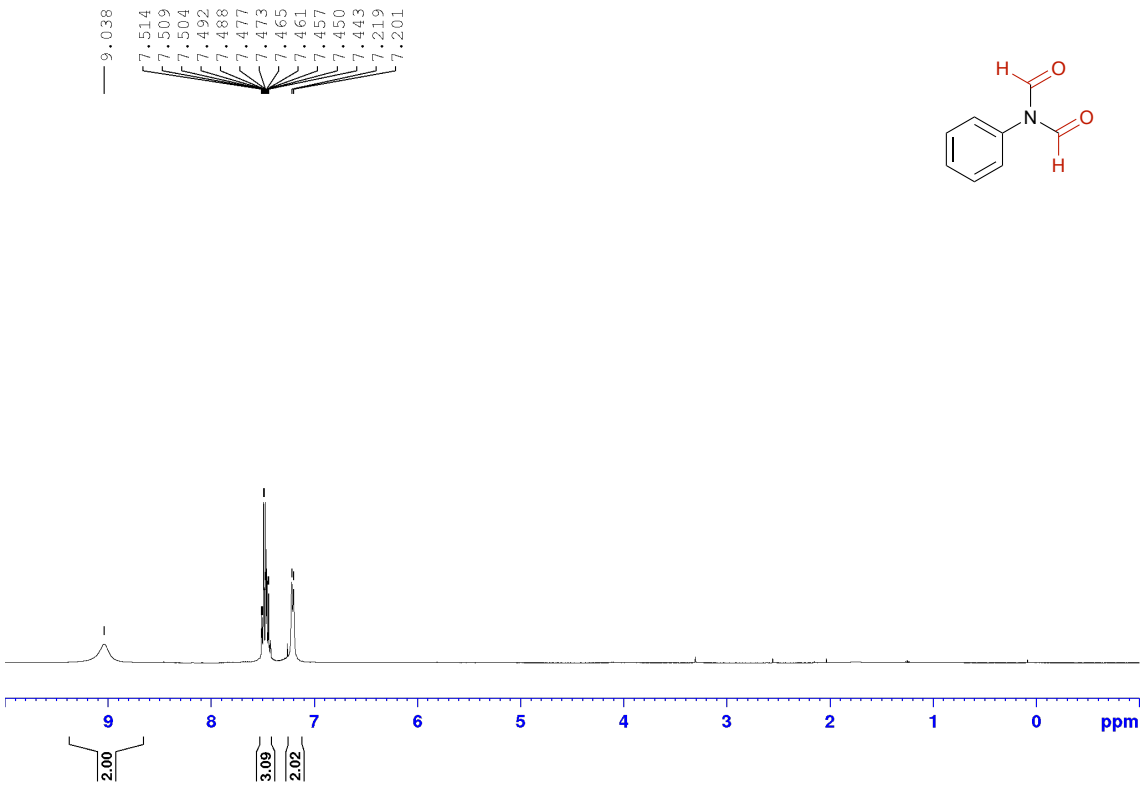

Figure S24. ^{1}H NMR of **8e** (400 MHz, $CDCl_3$)

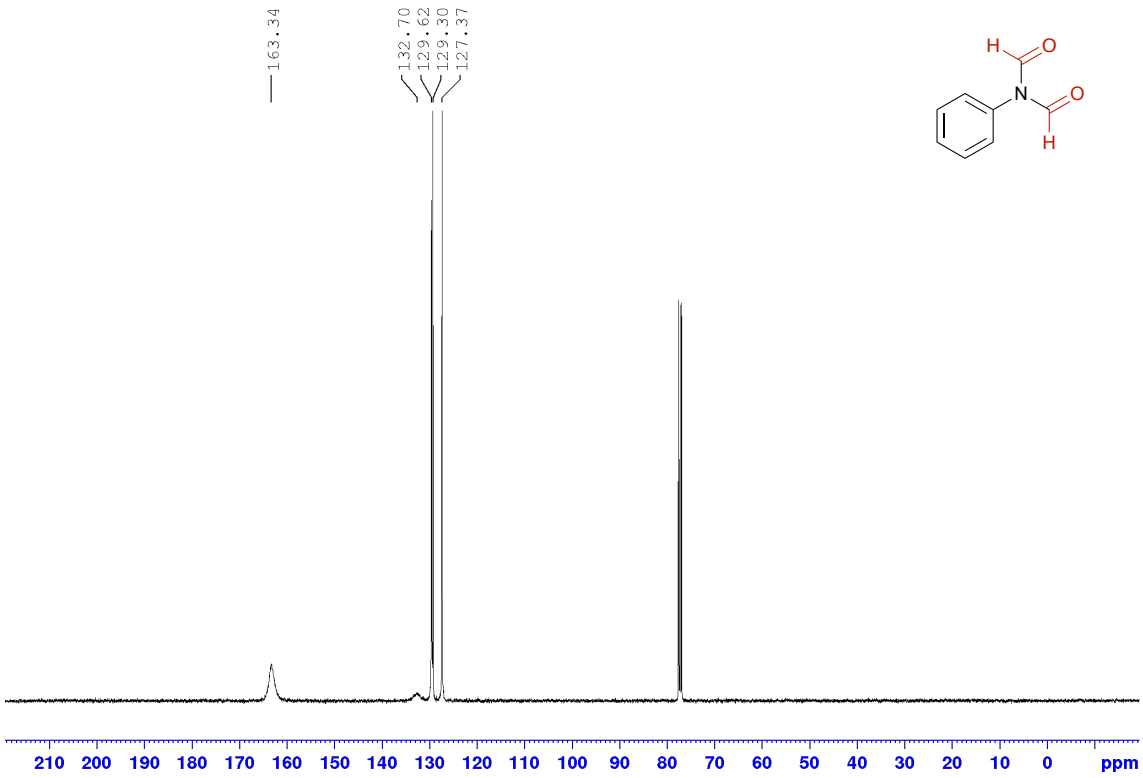

Figure S25. $^{13}C\{^{1}H\}$ NMR of **8e** (100 MHz, $CDCl_3$)

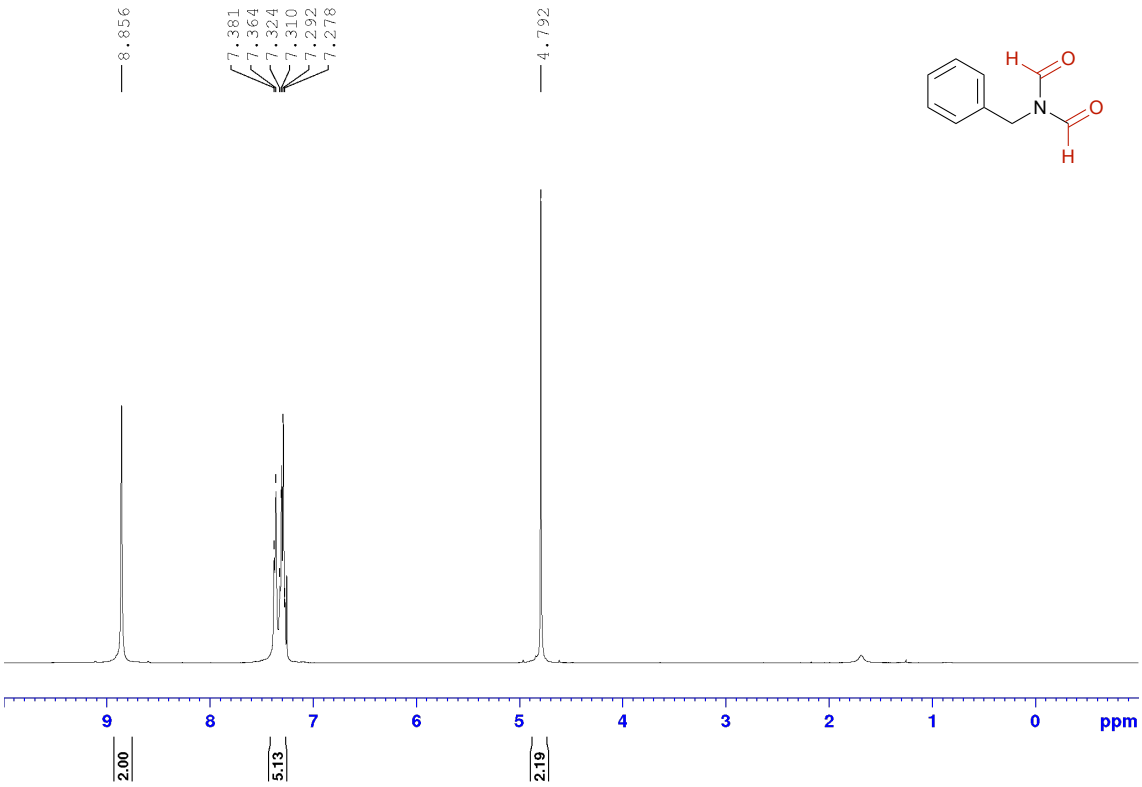

Figure S26. ^{1}H NMR of **8f** (400 MHz, $CDCl_3$)

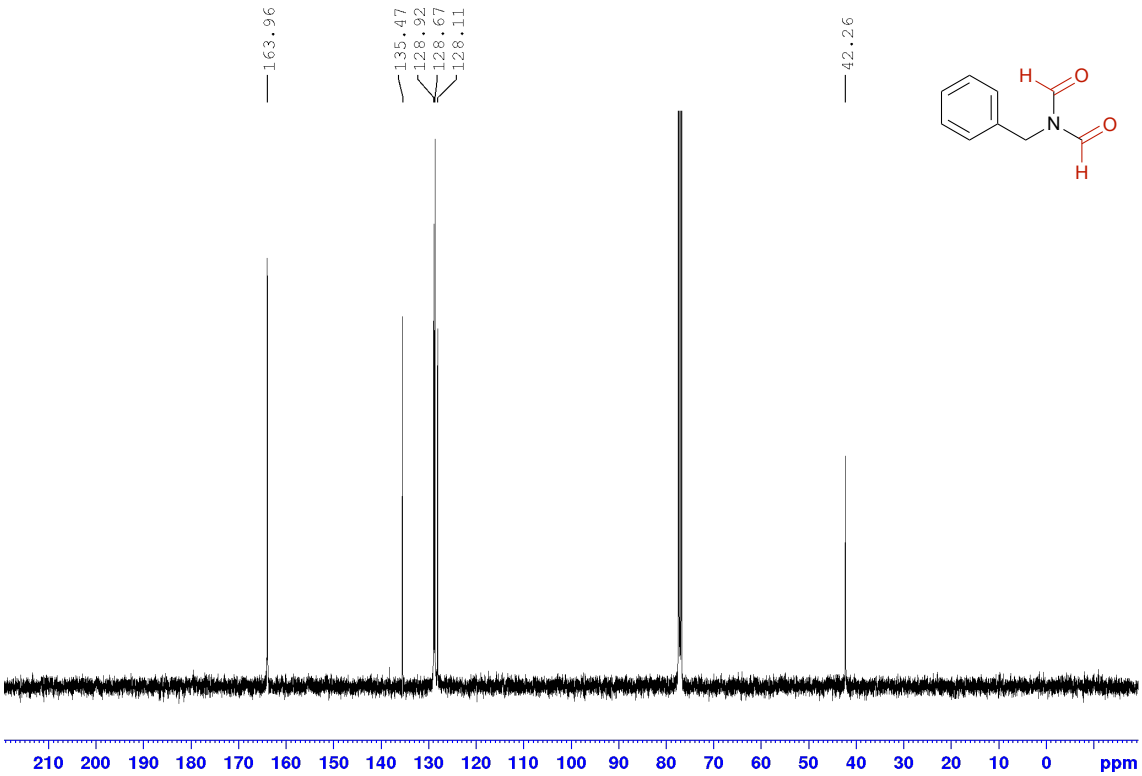

Figure S27. $^{13}C\{^{1}H\}$ NMR of **8f** (100 MHz, $CDCl_3$)