Supporting information

Anilido-Pyrazole Ligand Supported Germylenes: Synthesis, Structure, and Catalytic *N*-formylation of Amines Using CO_2

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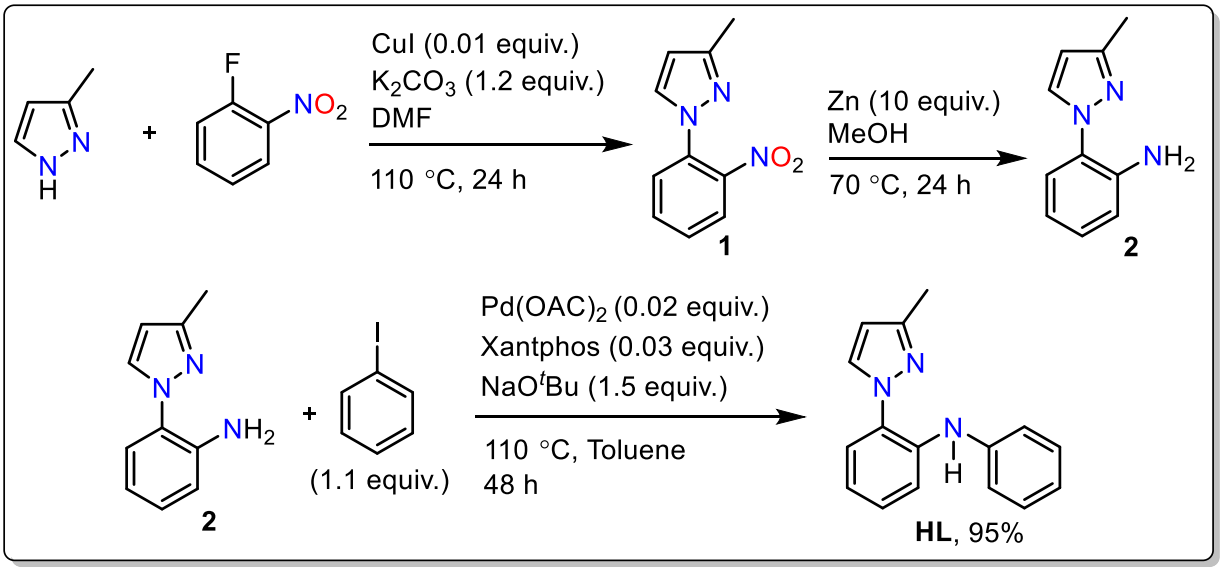
Table of contents:

General experimental description:

All the reactions were performed under an inert atmosphere unless stated otherwise. All non-deuterated solvents, Benzene-d_6, and Acetonitrile-d_3 used for the synthesis were distilled by standard methods, whereas $CDCl_3$ was used as received from the commercial sources. NMR spectra were recorded using the Bruker 400 and 500 MHz FT-NMR spectrometers at ambient temperature and all the $^1H/^{13}C\{^1H\}$ NMR spectra were referenced internally to the residual solvent signals. The ESI-MS spectra were measured with an Agilent 6545A Q-TOF Mass spectrometer. The germanium precursor, $Ge\{N(SiMe_3)_2\}_2$[1] was synthesized according to literature procedures. All other chemicals were purchased from commercial sources and used as received.

Synthesis of Ligand



Scheme S1: Synthesis of ligand **HL**

Synthesis of 1: A Schlenk tube (25 mL) was charged with 3-methylpyrazole (500 µL, 6.2 mmol, 1 equiv.), 2-fluoronitrobenzene (720 µL, 6.6 mmol, 1.1 equiv.), CuI (11.8 mg, 0.06 mmol, 0.01 equiv.) and K_2CO_3 (1.03 g, 7.3 mmol, 1.2 equiv.) followed by the addition of DMF. Then the tube was placed at 110 °C for 24 h. After completion of the reaction, the product was extracted with dichloromethane (3×30 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the filtrate was evaporated to get a yellow liquid, which was purified by silica gel column chromatography using hexane/ethyl acetate as eluent. This afforded compound **1** as a deep yellow liquid (1.17 g, 93%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J =

9.3 Hz, 1H), 7.63 (t, J = 8.6 Hz, 1H), 7.57-7.55 (m, 2H), 7.44 (t, J = 7.8 Hz, 1H), 6.26 (s, 1H), 2.31 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 151.9, 144.5, 133.6, 133.0, 130.5, 127.9, 126.2, 125.0, 108.4, 13.6 ppm.

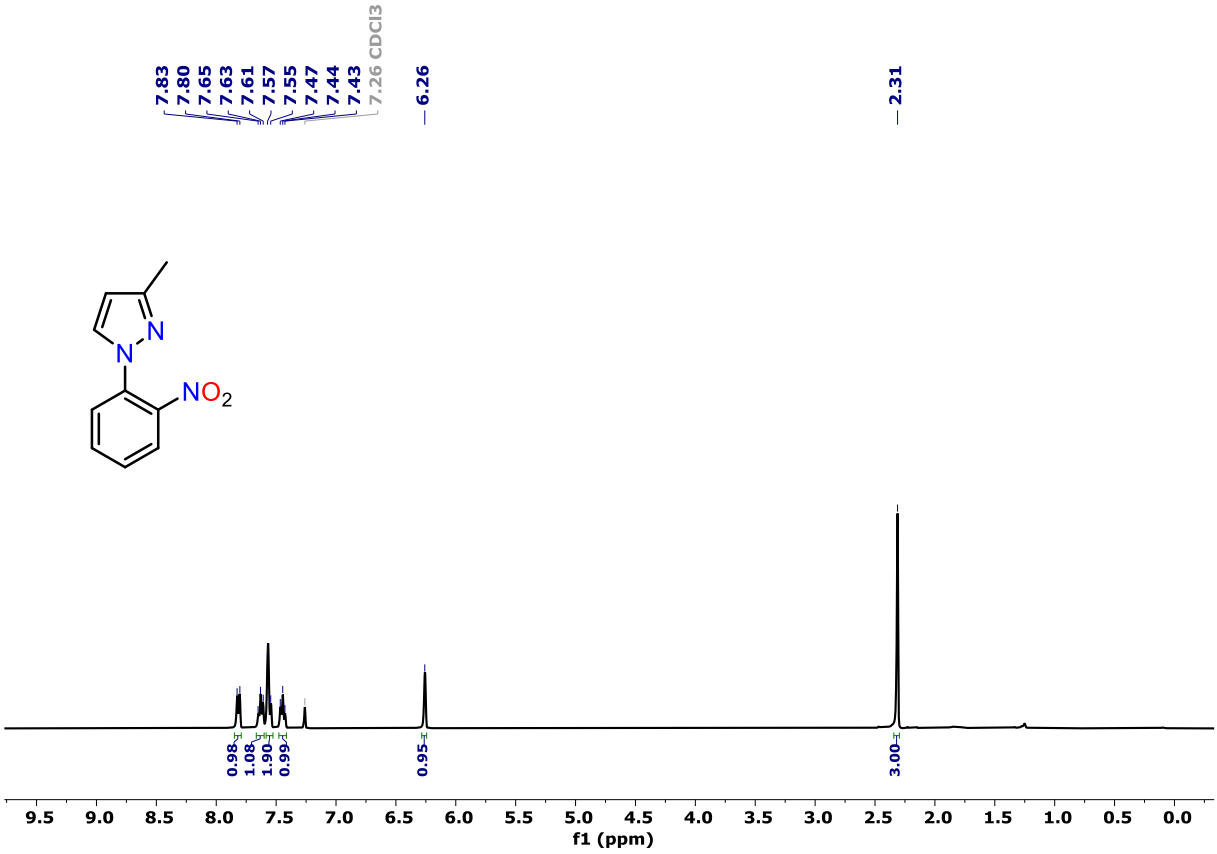


Figure S1. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

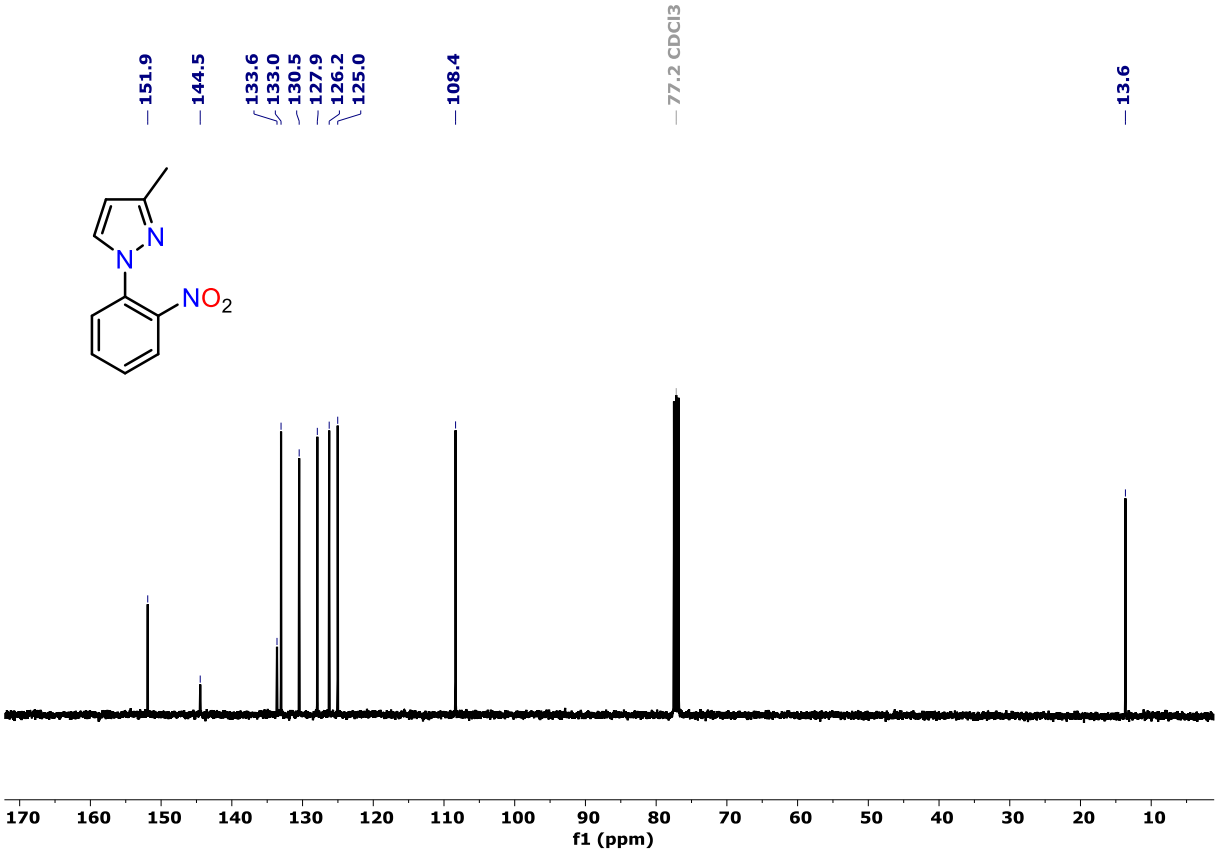


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** in $CDCl_3$.

Synthesis of 2: Compound **1** (300 mg, 1.5 mmol, 1 equiv.), Zn dust (974 mg, 15 mmol, 10 equiv.), and NH_4Cl (398 mg, 7.5 mmol, 5 equiv.) were charged in an RB flask, followed by the addition of methanol slowly. Then the reaction mixture was refluxed at 70 °C for 12 h. After that, the reaction mixture was dried in vacuo, and the obtained residue was purified by column chromatography using hexane/ethyl acetate as eluent to get the corresponding product **2** (220 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 2.4 Hz, 1H), 7.14-7.09 (m, 2H), 6.79-6.73 (m, 2H), 6.20 (d, J = 2.3 Hz, 1H), 4.56 (s, 2H), 2.37 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 149.9, 141.0, 130.5, 128.1, 126.6, 123.9, 118.0, 117.2, 106.1, 13.7 ppm.

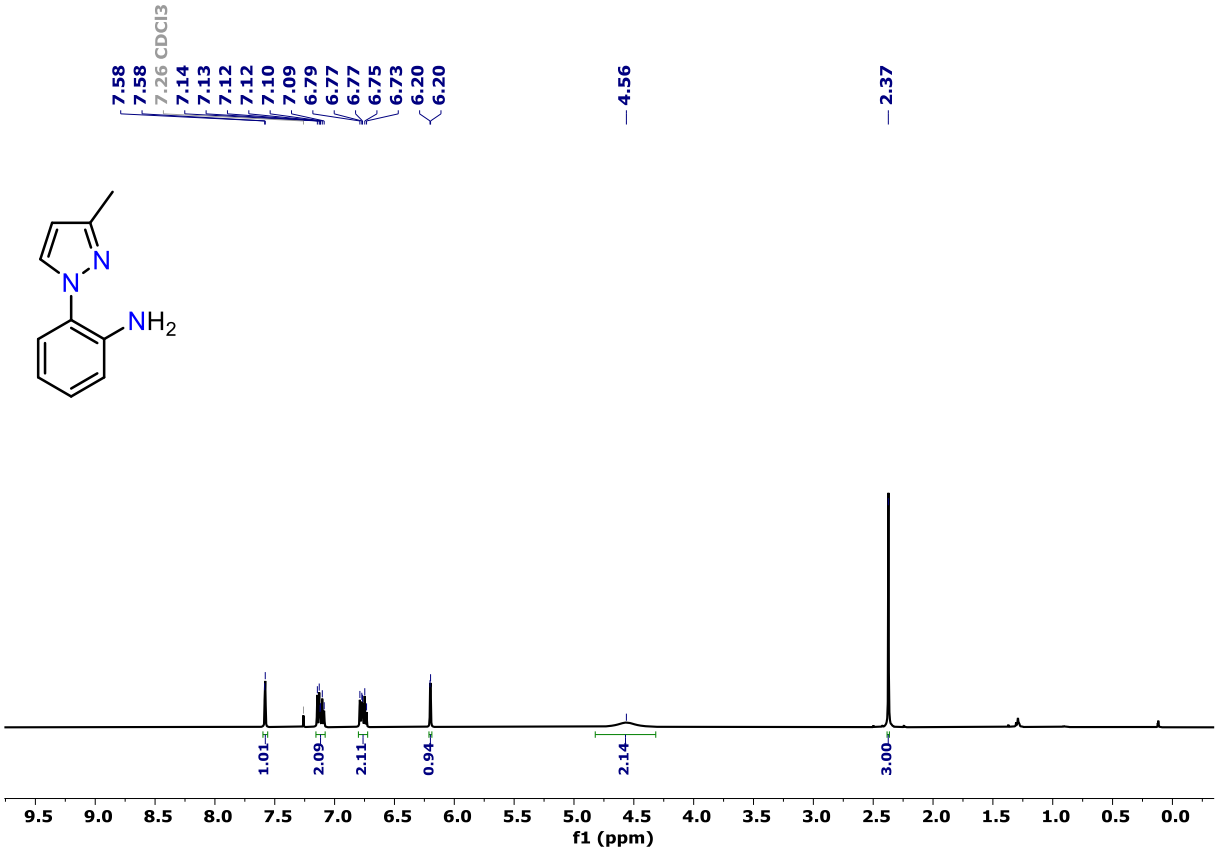


Figure S3. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

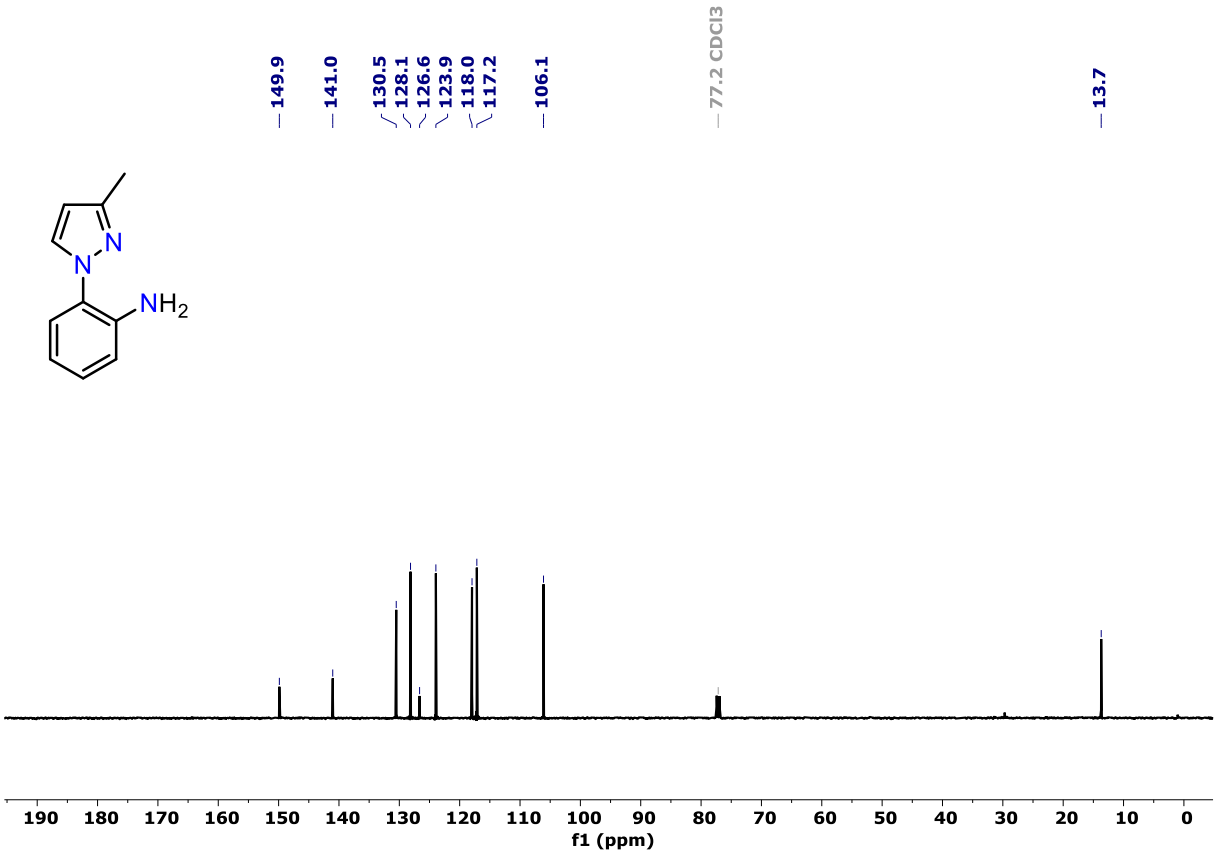


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2** in $CDCl_3$.

Synthesis of HL

A Schlenk tube (25 mL) was charged with compound **2** (300 mg, 1.7 mmol, 1 equiv.), iodobenzene (213 µL, 1.9 mmol), $Pd(OAc)_2$ (7.7 mg, 0.034 mmol), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (30 mg, 0.05 mmol), and Na^{t}OBu (249 mg, 2.5 mmol, 1.5 equiv.) followed by the addition of toluene. Then the tube was heated under stirring at 110 °C for 72 h. After the reaction duration, the product was extracted with dichloromethane (3×30 mL). The combined organic layers were dried over $MgSO_4$, and after filtration, all the volatiles were evaporated to get a yellow liquid, which was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to give ligand **HL** as a colourless liquid that solidified over time to give a white solid in 95% yield (409 mg). ^{1}H NMR (500 MHz, C_6D_6) δ 8.95 (s, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.06 (d, J = 3.9 Hz, 4H), 6.95-6.90 (m, 2H), 6.81 (s, 1H), 6.64 (t, J = 7.6 Hz, 1H), 5.90 (s, 1H), 2.21 (s, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 150.0, 142.7, 138.1, 130.5, 129.7, 129.1, 123.8, 121.9, 119.8, 119.8, 117.5, 106.4, 13.7 ppm. HRMS (ESI) *m/z*: 250.1343 (Calcd for [**HL**+H]$^+$ 250.1344).

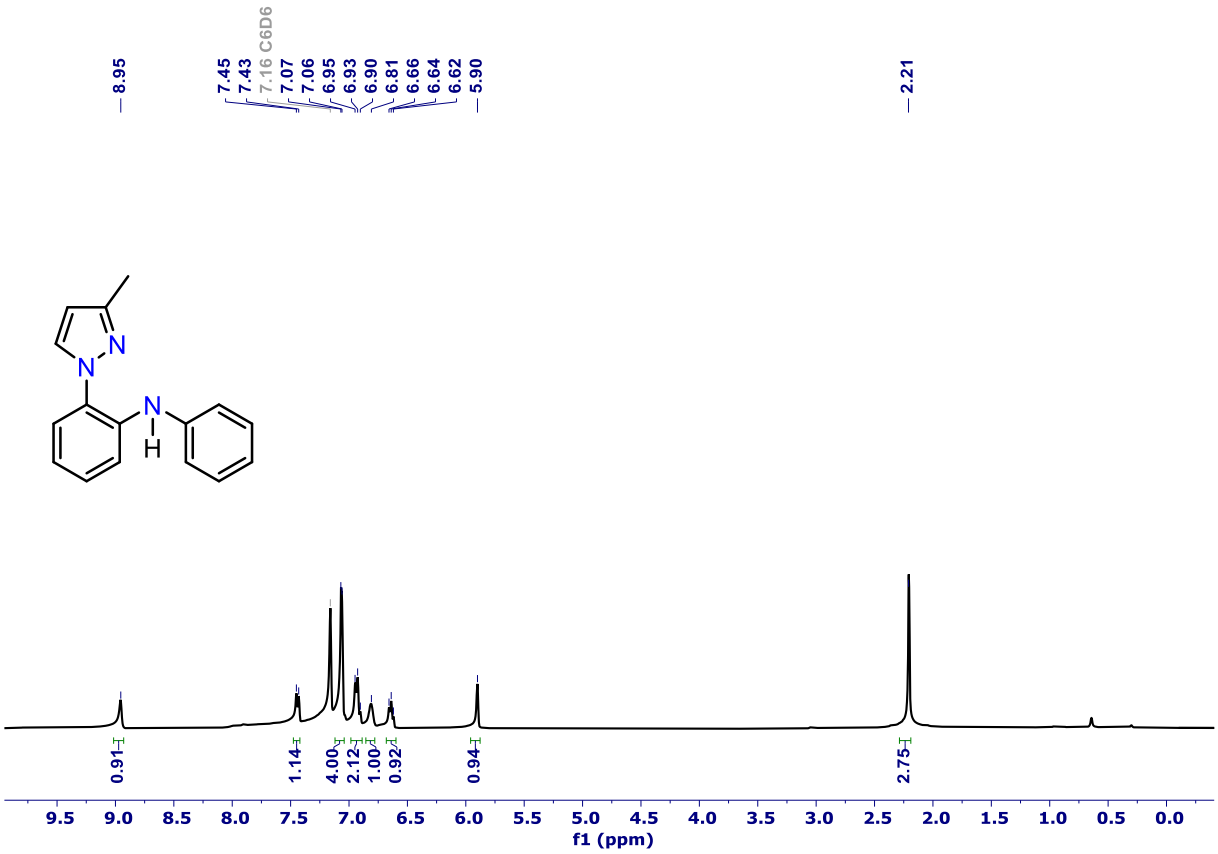


Figure S5. ^{1}H NMR spectrum of ligand **HL** in benzene-d_6.

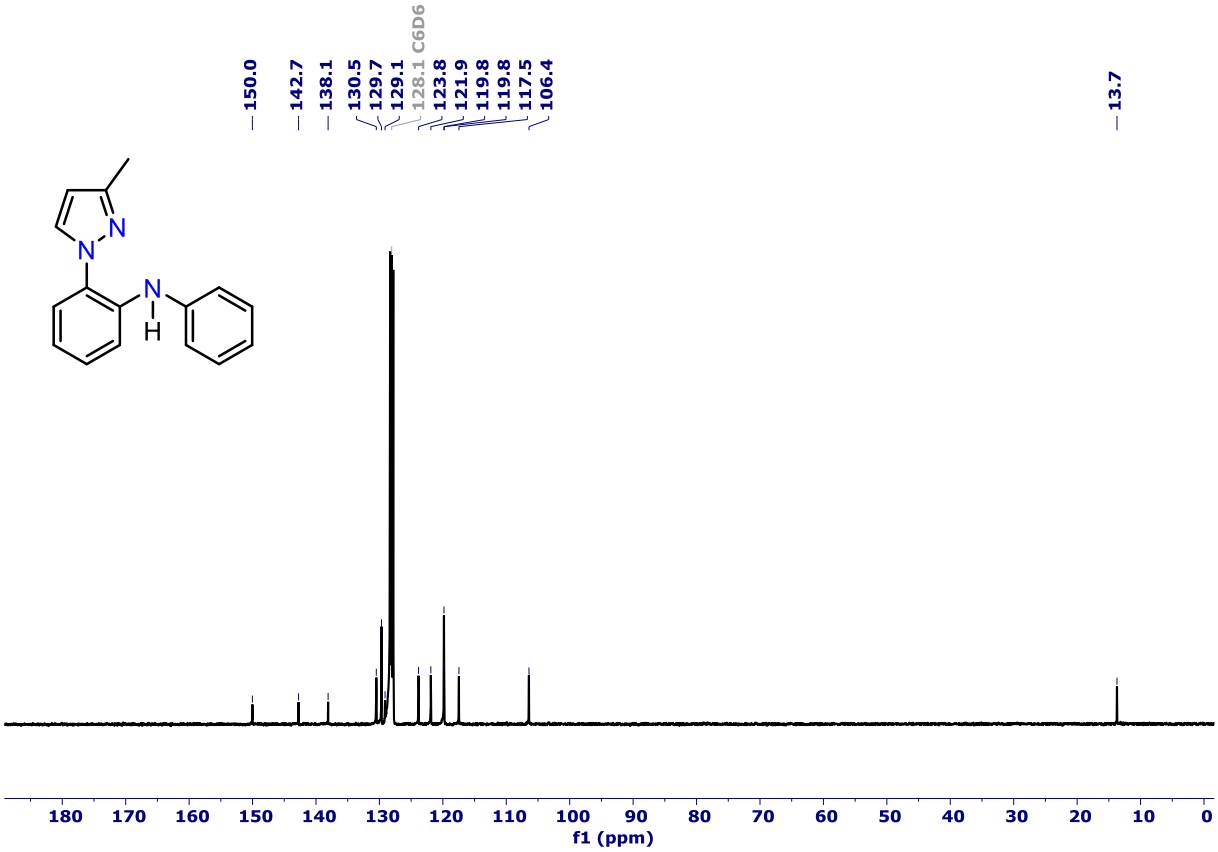


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of ligand **HL** in benzene-d_6.

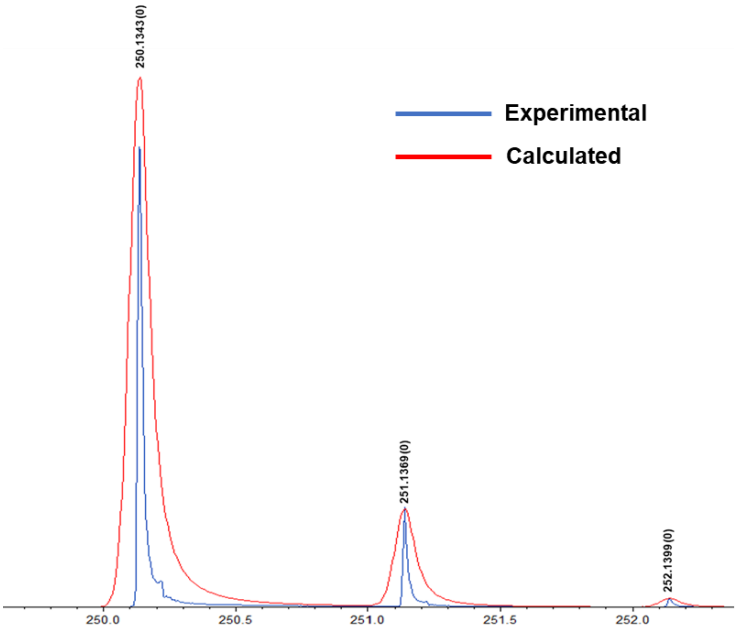
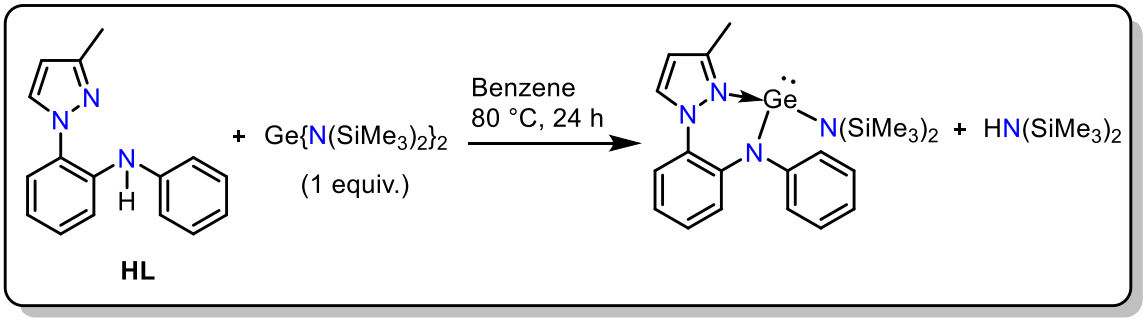


Figure S7. ESI-MS (positive ions) spectrum of the ligand **HL**.

General Procedure for the synthesis of complexes:



Scheme S2: Synthesis of **Ge1**

In a Young NMR tube, ligand **HL** (15 mg, 0.06 mmol) and [Ge{N(SiMe$_3$)$_2$}$_2$] (24 mg, 0.06 mmol) were dissolved in benzene-d_6 and heated to 80 °C for 24 h. After completion of the reaction, the reaction mixture was analyzed by ^{1}H NMR showing the formation of **Ge1**. Accordingly, for a higher scale synthesis, ligand **HL** (95 mg, 0.38 mmol) and [Ge{N(SiMe$_3$)$_2$}$_2$] (150 mg, 0.38 mmol) was dissolved in benzene in an oven-dried Schlenk tube and heated to 80 °C for 24 h. Following that, the solution was dried in vacuo and purified by recrystallisation in diethyl ether (105 mg, 0.22 mmol, 57%). Suitable crystal of **Ge1** for single crystal X-ray diffraction study was obtained from a saturated solution in ether at -35 °C ^{1}H NMR (400 MHz, C_6D_6) δ 7.34 - 7.32 (m, 2H), 7.21-7.18 (m, 2H), 7.05 (d, J = 4.3 Hz, 1H), 6.98 (d, J = 2.7 Hz 1H), 6.93 - 6.89 (m, 2H), 6.67 (dd, J = 8.1, 1.6 Hz, 1H), 6.56 - 6.52(m, 1H), 5.59 (d, J = 3.3 Hz, 1H), 2.23 (s, 3H), 0.15 (s, 18H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 150.3, 150.1, 143.8, 129.9, 129.7, 128.9, 128.8, 124.8, 124.8, 122.0, 121.7, 118.5, 108.5, 13.6, 5.2 ppm. HRMS (ESI) *m/z*: 428.1318 (calcd for [{**M**-SiMe$_3$+H}+NH$_4$]$^+$ 428.1329).

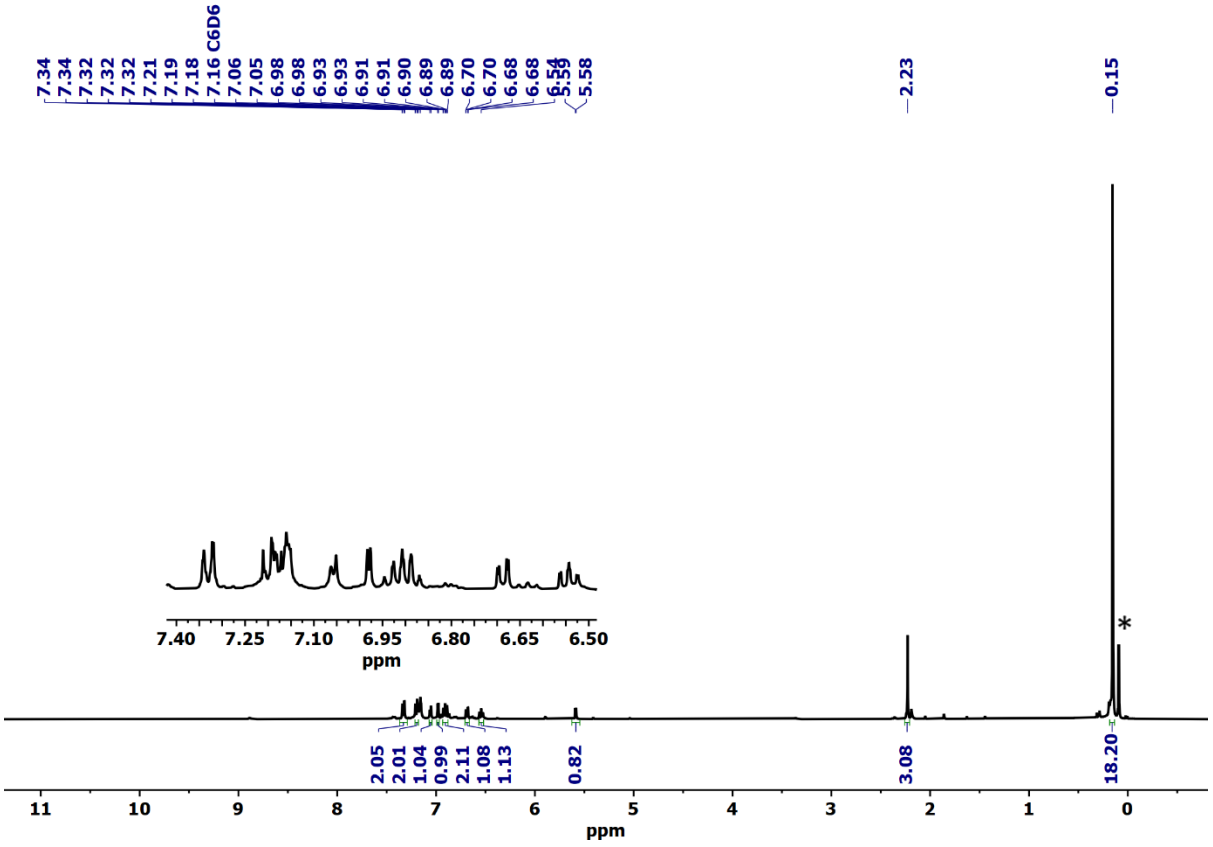


Figure S8. ^{1}H NMR spectrum of **Ge1** in benzene-d_6. * represents remaining $NH(SiMe_3)_2$.

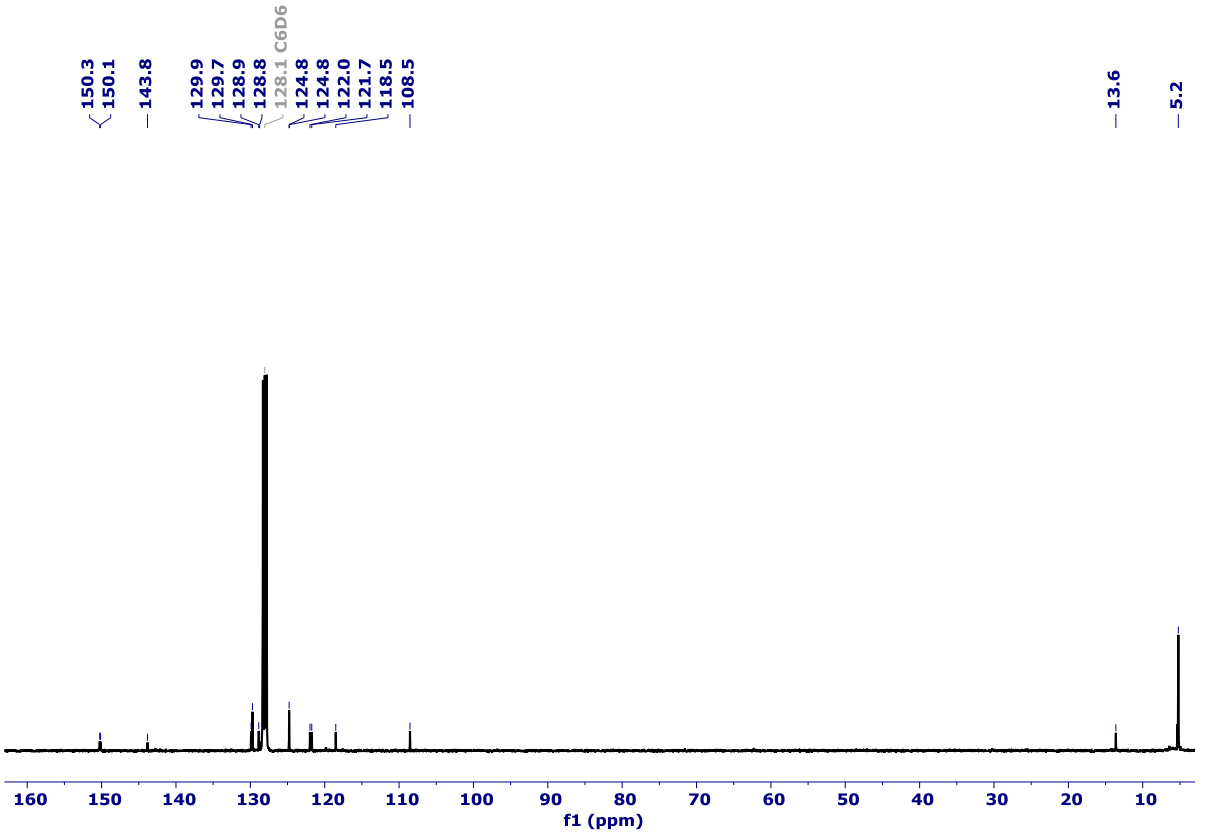
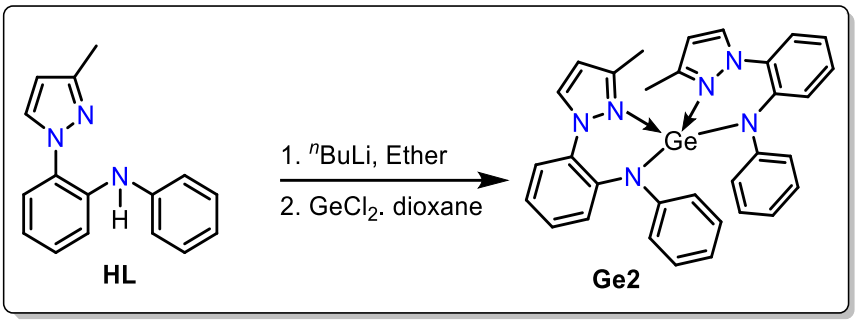


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **Ge1** in benzene-d_6.



Scheme S3: Synthesis of **Ge2**

In a pressure tube (100 mL), the ligand **HL** (300 mg, 1.2 mmol) was dissolved in ether. The solution was then cooled to -78 °C and ^{n}BuLi (1.6 M in hexane, 0.8 mL, 1.3 mmol) was added dropwise to the solution. Afterwards, the reaction mixture was allowed to warm to room temperature and stirred for 4 hours. The solution was then re-cooled to -78 °C and slowly transferred to an ether suspension of $GeCl_2$·dioxane (139 mg, 0.6 mmol). The resulting mixture was allowed to come to room temperature and stirred overnight. Subsequently, the reaction mixture was filtered through a short pad of Celite under an argon atmosphere and dried in vacuo, yielding a yellow slurry. The product was then purified by recrystallization in diethyl ether, resulting in the formation of **Ge2** as a yellow crystalline compound, yield = 210 mg (0.37 mmol, 62%). The structure of the product was confirmed by single crystal X-ray diffraction studies. ^{1}H NMR (500 MHz, C_6D_6) δ 7.36 (d, J = 7.7 Hz, 4H), 7.14 (s, 3H), 7.08 (d, J = 8.3 Hz, 2H), 6.97 - 6.91 (m, 7H), 6.74 (d, J = 8.0 Hz, 2H), 6.61 (s, 2H), 5.44 (d, J = 2.7 Hz, 2H), 1.88 (s, 6H) ppm. ^{13}C NMR (126 MHz, C_6D_6) δ 148.5, 148.5, 142.7, 130.2, 130.0, 129.1, 128.6, 128.4, 126.1, 124.1, 122.7, 120.6, 119.5, 107.7, 12.4, 3.0 ppm. HRMS (ESI) *m/z*: 672.1781 (calcd for [{M-3H+2(CH_3CN)}+Na]$^{+}$ 672.1790).

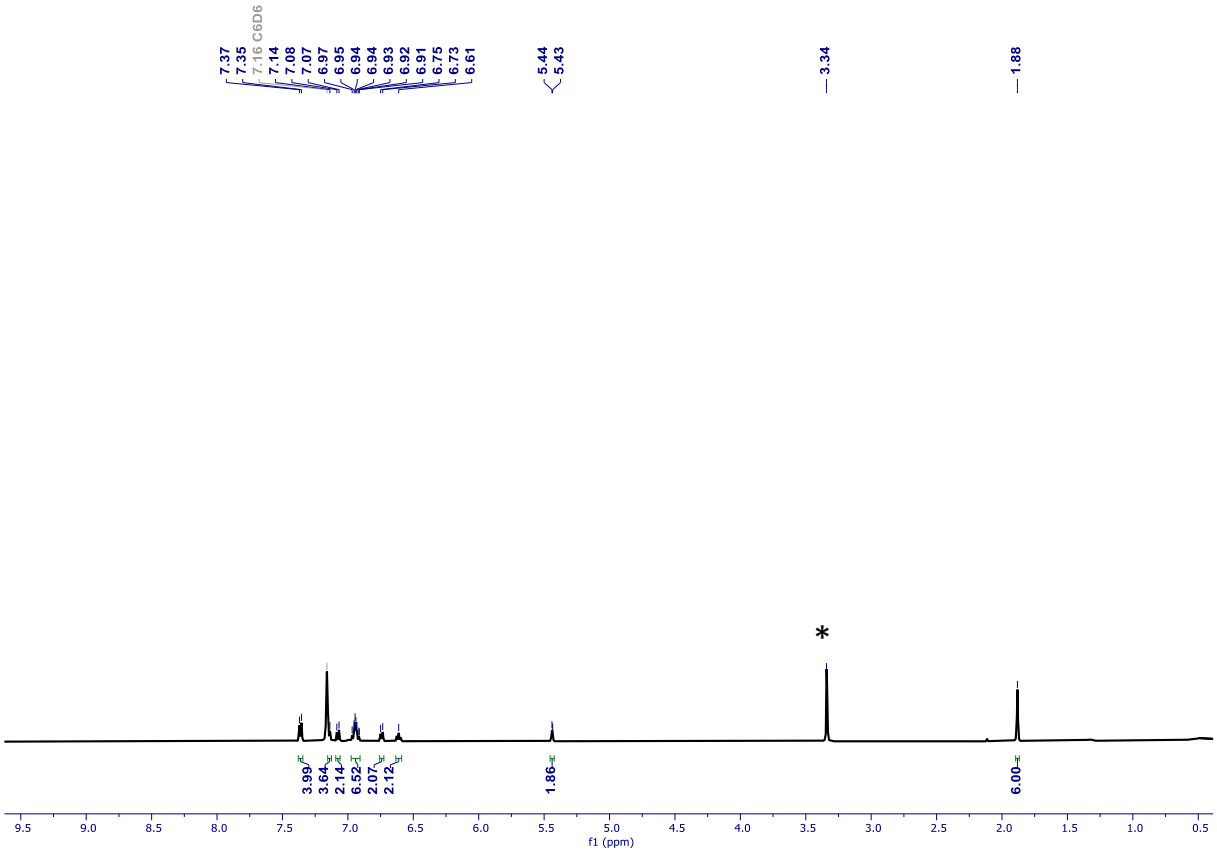


Figure S10. ^{1}H NMR spectrum of **Ge2** in benzene-d_6. * represents peak of dioxane impurity.

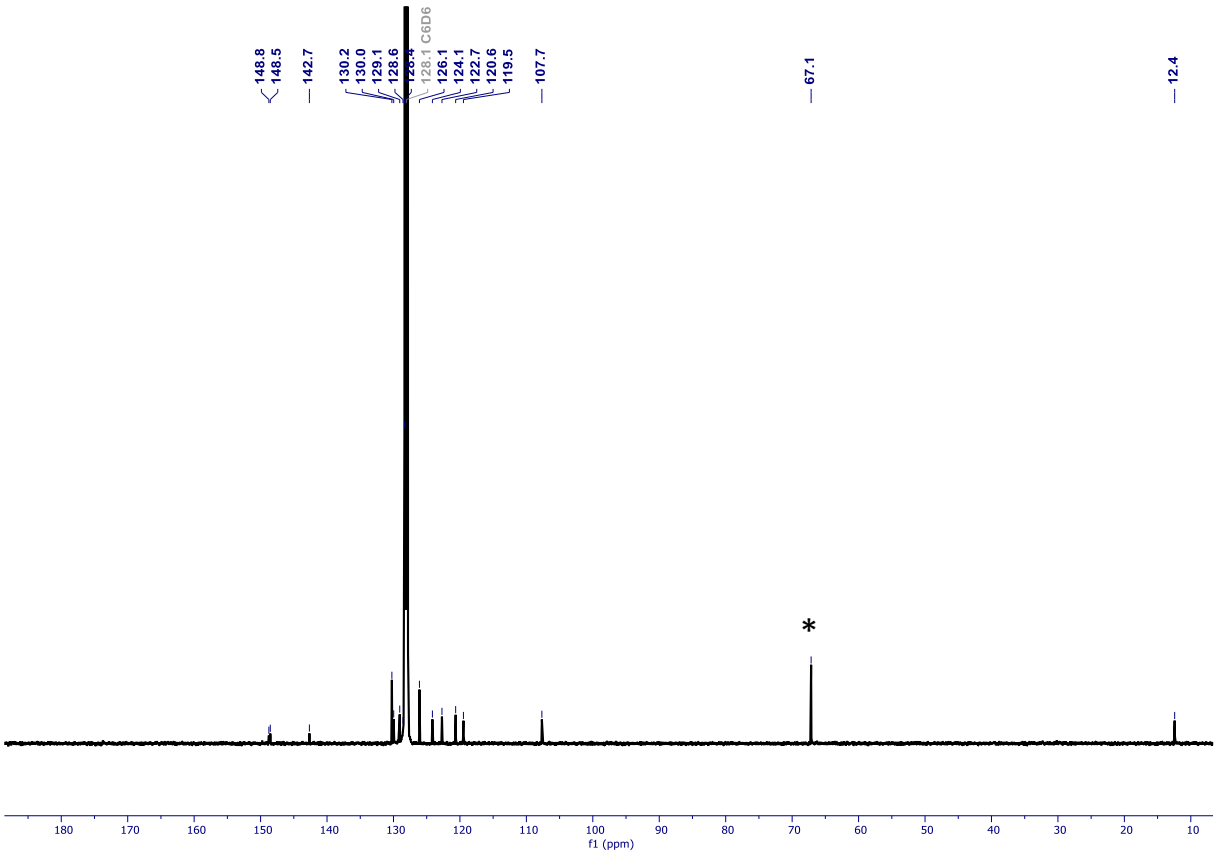


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **Ge2** in benzene-d_6. * represents peak of dioxane impurity.

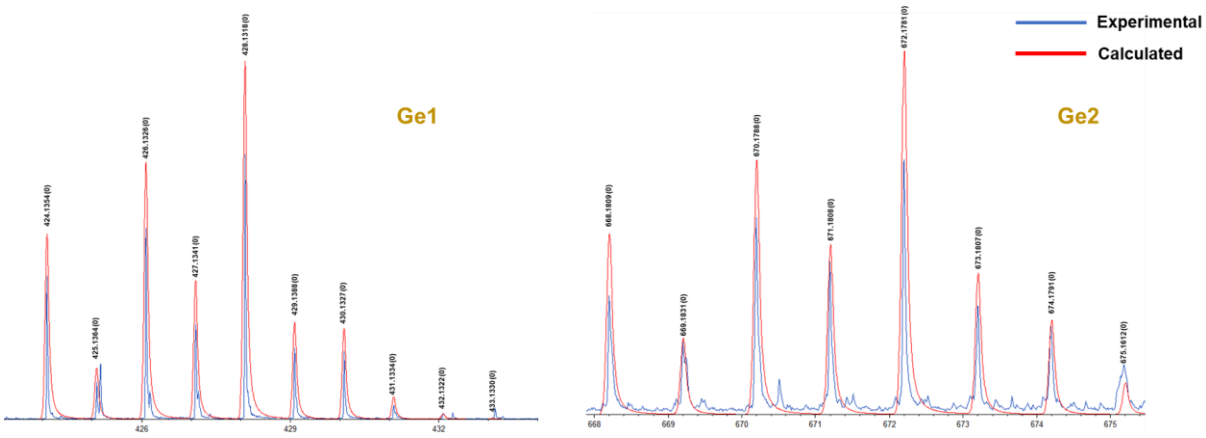
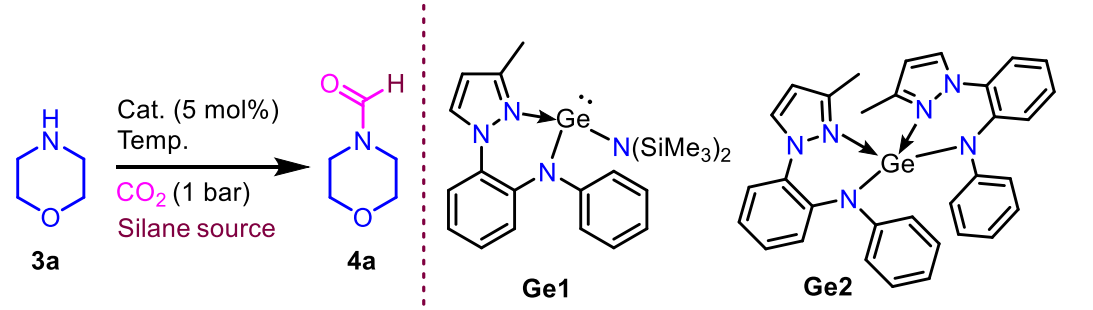


Figure S12. ESI-MS (positive ions) spectrum of the complex **Ge1** and **Ge2.**

General procedure for the *N*-formylation of amines:

An oven-dried pressure tube was charged with **Ge1** (2.5 mg, 0.05 equiv.) and phenylsilane (37 µL, 0.3 mmol), followed by the addition of amine (0.1 mmol) and acetonitrile (2 mL). The resulted reaction mixture was then degassed by three freeze-pump-thaw cycles, and exposed to carbon dioxide (1 bar). Then, the pressure tube was kept in an oil bath at 80 °C and heated for 24 h. Upon completion of the reaction, the reaction mixture was evaporated and to the residue, nitromethane (0.1 mmol, as an internal standard) and $CDCl_3$ was added for NMR analysis. The yield is calculated by comparing the intensity of formyl peak with the nitromethane (internal standard) peak.

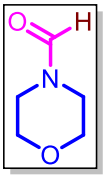
Table S1: Optimization of the reaction conditions for the *N*-formylation reactions[a]



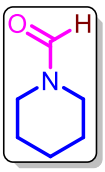
Entry	Catalyst	Silane (equiv.)	Solvent	Temp	Time (h)	4a (%)[b]
1	**Ge1**	$PhSiH_3$ (2)	ACN	80 °C	24	35
2	**Ge1**	$PhSiH_3$ **(3)**	**ACN**	**80 °C**	**24**	**100**
3	**Ge2**	$PhSiH_3$ (3)	ACN	80 °C	24	ND
4[c]	**Ge1**	$PhSiH_3$ (3)	ACN	80 °C	24	42
5	**Ge1**	$PhSiH_3$ (3)	ACN	60 °C	24	10
6	**Ge1**	$PhSiH_3$ (3)	ACN	RT	24	ND
7	**Ge1**	—	ACN	80 °C	24	ND
8	—	$PhSiH_3$ (3)	ACN	80 °C	24	5
9	**Ge1**	Ph_2SiH_2 (3)	ACN	80 °C	24	ND
10	**Ge1**	Et_3SiH (3)	ACN	80 °C	24	ND
11	**Ge1**	$PhSiH_3$ (3)	THF	80 °C	24	5
12	**Ge1**	$PhSiH_3$ (3)	Benzene	80 °C	24	ND
13	**Ge1**	$PhSiH_3$ (3)	Hexane	80 °C	24	ND
14	**Ge1**	$PhSiH_3$ (3)	—	80 °C	24	20
15	**Ge1**	$PhSiH_3$ (3)	ACN	80 °C	6	12
16	**Ge1**	$PhSiH_3$ (3)	ACN	80 °C	12	20

[a]**Reaction conditions**: **3a** (0.1 mmol), **Ge1/Ge2** (5 mol%), silane (2-3 equiv.), RT - 80 °C, 6-24 h. [b]Based on ^{1}H NMR. [c]**Ge1** (2 mol%).

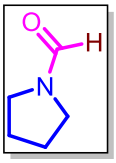
Analytical data for the *N*-formylated products: Peaks corresponding to aromatic group (both ^{1}H and $^{13}C\{^1H\}$) are merged with excess of $PhSiH_3$ and hence left out for clarity.



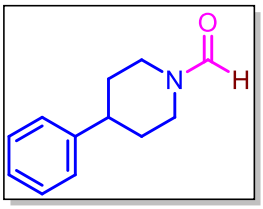
Morpholine-4-carbaldehyde (4a):[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (CHO, s, 1H, 100%), 3.68-3.63 (m, 4H), 3.57-3.54 (m, 2H), 3.38-3.35 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.0 (CHO), 67.3, 66.5, 45.9, 40.7 ppm.



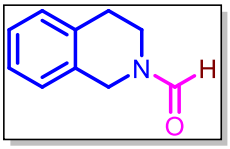
Piperidine-1-carbaldehyde (4b):[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (CHO, s, 1H, minor rotamer, 26%), 7.98 (CHO, s, 1H, major rotamer, 74%), 3.47 (t, J = 5.7 Hz, 2H), 3.29 (t, J = 5.6 Hz, 2H), 1.70-1.64 (m, 2H), 1.59-1.50 (m, 4H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 163.5 (CHO, minor rotamer), 161.2 (CHO, major rotamer), 47.1, 40.9, 26.6, 25.1, 24.7 ppm.



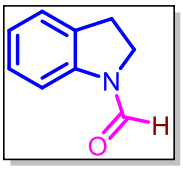
Pyrrolidine-1-carbaldehyde (4c):[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (CHO, s, 1H, major rotamer, 52%), 8.16 (CHO, s, 1H, minor rotamer, 48%), 3.46 (t, J = 6.3 Hz, 2H), 3.40 (t, J = 6.3 Hz, 2H), 1.91-1.85(m, 4H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 164.3 (CHO, minor rotamer), 161.4 (CHO, major rotamer), 46.3, 43.4, 24.9, 24.2 ppm.



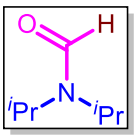
4-phenylpiperidine-1-carbaldehyde (4d):[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (CHO, s, 1H, 98%), 4.60-4.54 (m, 1H), 3.74-3.70 (m, 1H), 3.23-3.15 (m, 1H), 2.82-2.67 (m, 2H), 1.96-1.88 (m, 2H), 1.67-1.55 (m, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.0 (CHO), 46.6, 43.0, 40.4, 34.0, 32.5 ppm.



3,4-dihydroisoquinoline-2(1H)-carbaldehyde (4e):[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (CHO, s, 1H, minor rotamer, 23%), 8.18 (CHO, s, 1H, major rotamer, 37%), 3.78 (t, J = 6.2 Hz, 1H), 3.63 (t, J = 5.9 Hz, 1H), 3.08-3.05 (m, 1H), 2.91-2.86 (m, 2H), 2.77-2.73 (m, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.8 (CHO, major rotamer), 161.3 (CHO, minor isomer), 47.8, 47.4, 43.6, 43.3, 42.4, 38.1, 29.8, 28.8, 28.0 ppm.

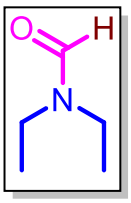


Indoline-1-carbaldehyde (4f):[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (CHO, s, 1H, major rotamer, 18%), 8.51 (CHO, s, 1H, minor rotamer, 4%), 3.55 (t, J = 8.4 Hz, 2H), 3.03 (t, J = 8.3 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 157.7 (CHO, minor rotamer), 151.7 (CHO, major rotamer), 47.4, 44.8, 30.0, 27.3 ppm.

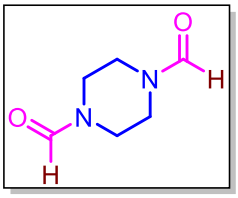


N,N-diisopropylformamide(4g):[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (CHO, s, 1H, major rotamer, 66%), 8.17 (CHO, s, 1H, minor rotamer, 16%), 3.25-3.19 (m,

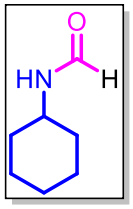
2H), 1.27 (d, J = 6.5 Hz, 12H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.4 (CHO, major rotamer), 161.7 (CHO, minor rotamer), 46.4, 19.8 ppm.



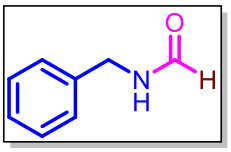
N,N-diethylformamide (4h):[3] ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (CHO, s, 1H, minor rotamer, 22%), 8.04 (CHO, s, 1H, major rotamer, 42%), 3.37 (q, J = 7.2 Hz, 2H), 3.27 (q, J = 7.2 Hz, 2H), 1.20-1.11 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.5 (CHO, major rotamer), 163.3 (CHO, minor rotamer), 42.6, 37.3, 14.8, 12.7 ppm.



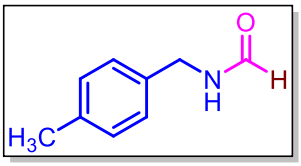
piperazine-1,4-dicarbaldehyde (4i):[3] ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (CHO, s, 1H, major rotamer, 46%), 8.07 (CHO, s, 1H, major rotamer, 38%), 7.98 (s, 1H, minor rotamer, 16%), 3.60-3.57 (m, 2H), 3.53 (s, 1H), 3.50 -3.46 (m, 1H), 3.38-3.34 (m, 3H), 3.30-3.27 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.1 (CHO, major rotamer), 161.0 (CHO, minor rotamer), 160.9 (CHO, major rotamer), 46.2, 45.1, 40.6, 39.6 ppm.



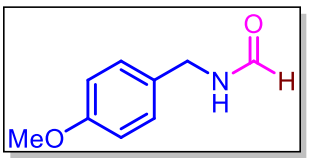
N-cyclohexylformamide (4j):[3] ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (CHO, s, 1H, minor rotamer, 16%), 8.07 (CHO, s, 1H, major rotamer, 46%), 1.91 (d, J = 10.8 Hz, 2H), 1.73-1.58 (m, 3H), 1.38-1.25 (m, 3H), 1.21-1.08 (m, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.6 (CHO, major rotamer), 157.3 (CHO, minor rotamer), 49.3, 47.2, 33.9, 33.1, 25.7, 25.5, 25.0, 24.8, 24.8 ppm.



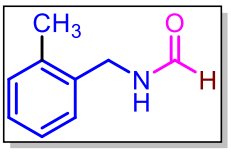
N-benzylformamide (4k):[3] ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (CHO, s, 1H, 46%), 4.46 (d, J = 5.9 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.2 (CHO), 44.6, 42.3 ppm.



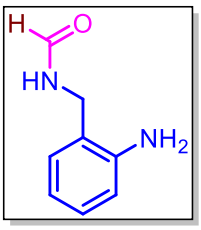
N-(4-methylbenzyl)formamide (4l):[5] ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (CHO, s, 1H, major rotamer, 34%), 8.21 (CHO, s, 1H, minor rotamer, 11%), 4.44 (d, J = 6 Hz, 2H), 2.34 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.7 (CHO, minor rotamer), 161.0 (CHO, major rotamer), 42.1, 21.2 ppm.



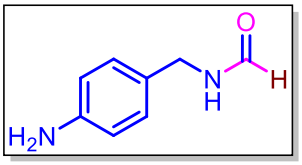
N-(4-methoxybenzyl)formamide (4m):[5] ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (CHO, s, 1H, 46%), 4.39 (d, J = 6.0 Hz, 2H), 3.78 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.1 (CHO), 55.4, 41.8 ppm.



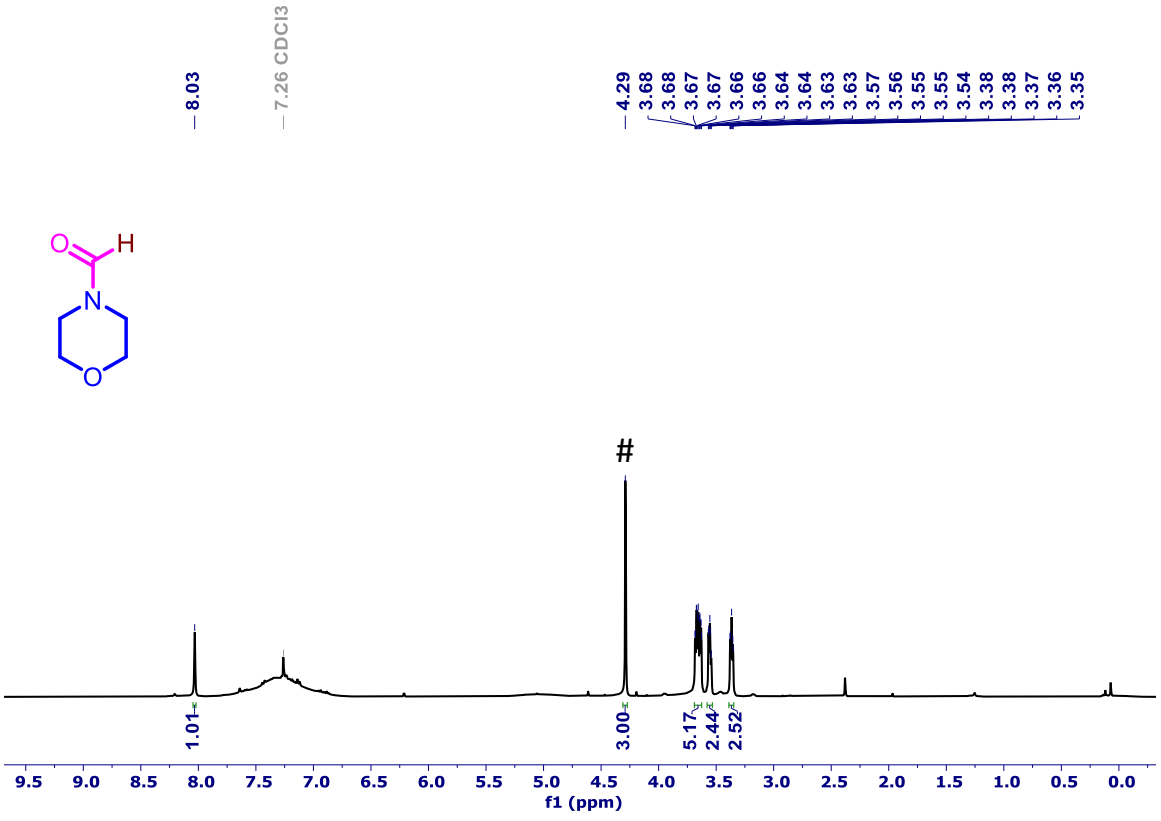
N-(2-methylbenzyl)formamide (4n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (CHO, s, 1H, 49%), 4.47 (d, J = 5.6 Hz, 2H), 2.33 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 161.0 (CHO), 40.4, 19.1 ppm.



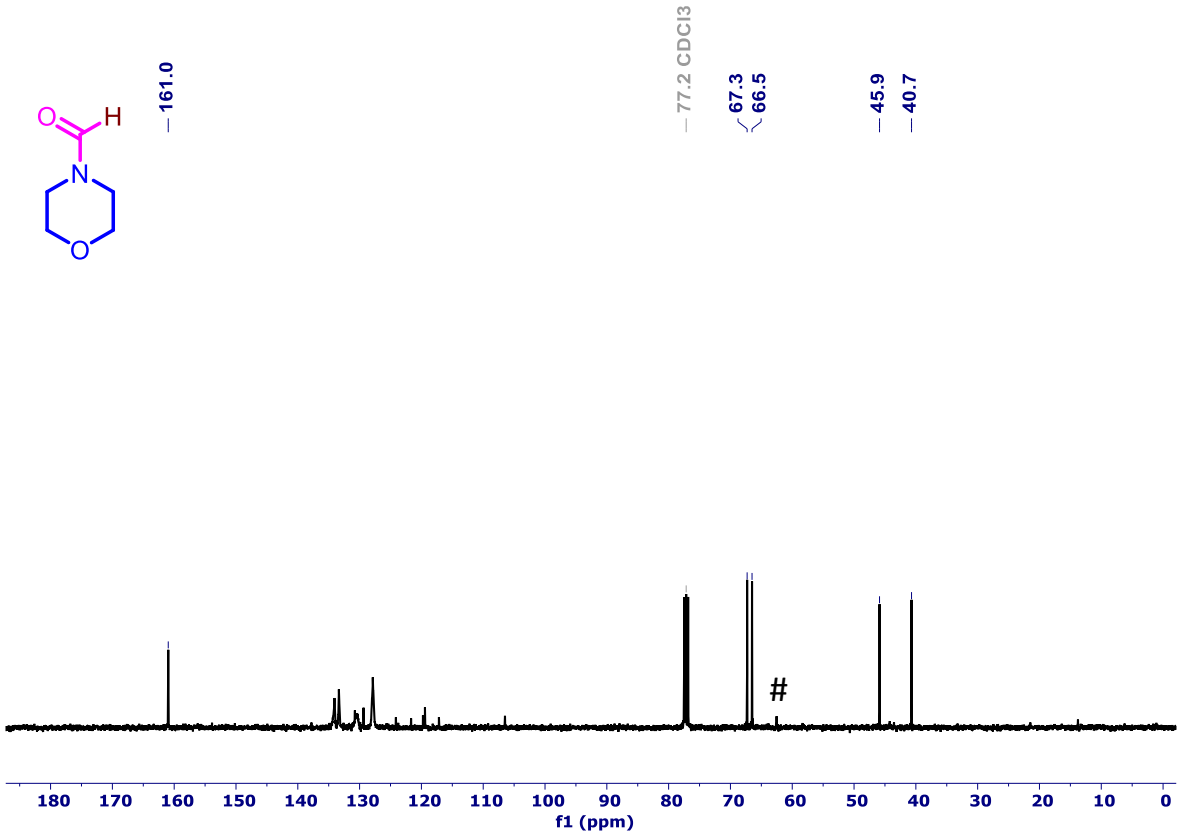
N-(2-aminobenzyl)formamide (4o):[6] ^{1}H NMR (00 MHz, $CDCl_3$) δ 8.55 (CHO, s, 1H, minor rotamer, 20%), 8.16 (CHO, s, 1H, major rotamer, 53%), 4.39 (d, J = 6.3 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 162.2 (CHO, minor rotamer), 161.6 (CHO, major rotamer), 41.4, 39.3 ppm.



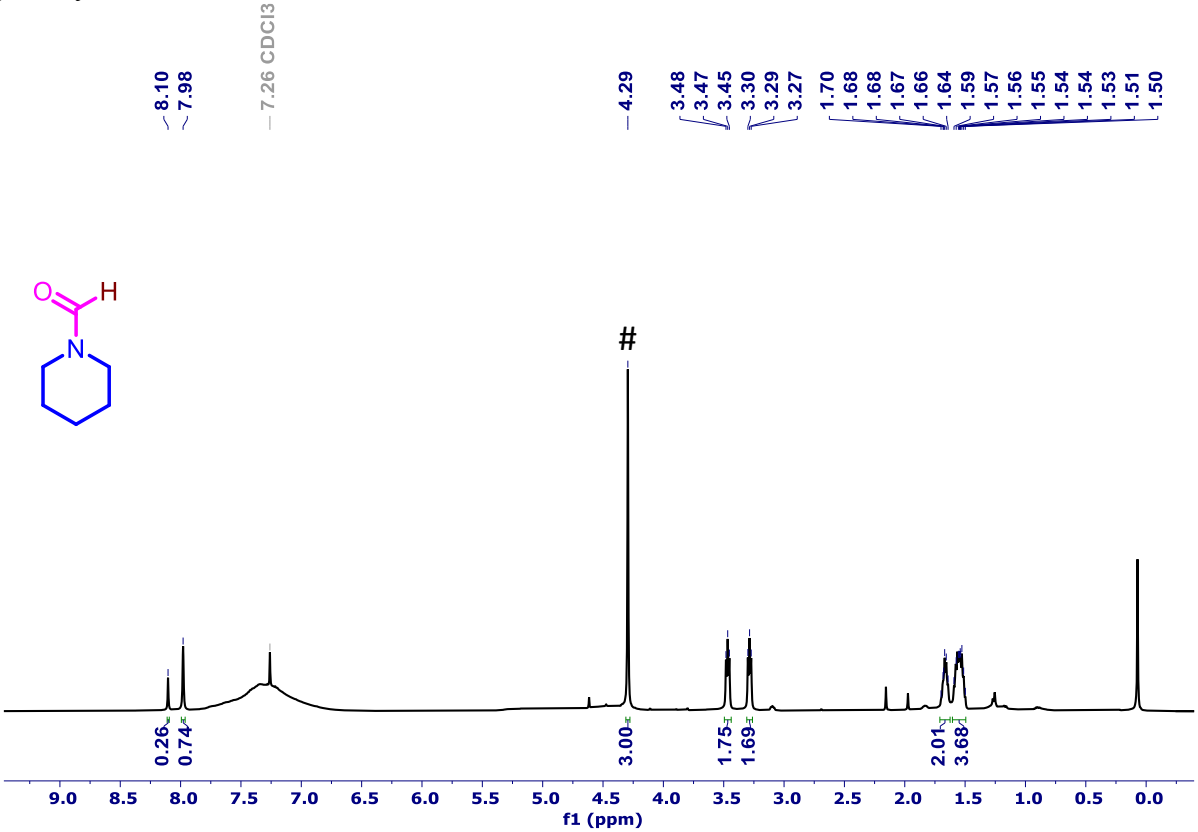
N-(4-aminobenzyl)formamide (4p):[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (CHO, s, 1H, 51%), 4.33 (d, J = 5.7 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (CHO), 45.9, 41.9 ppm.



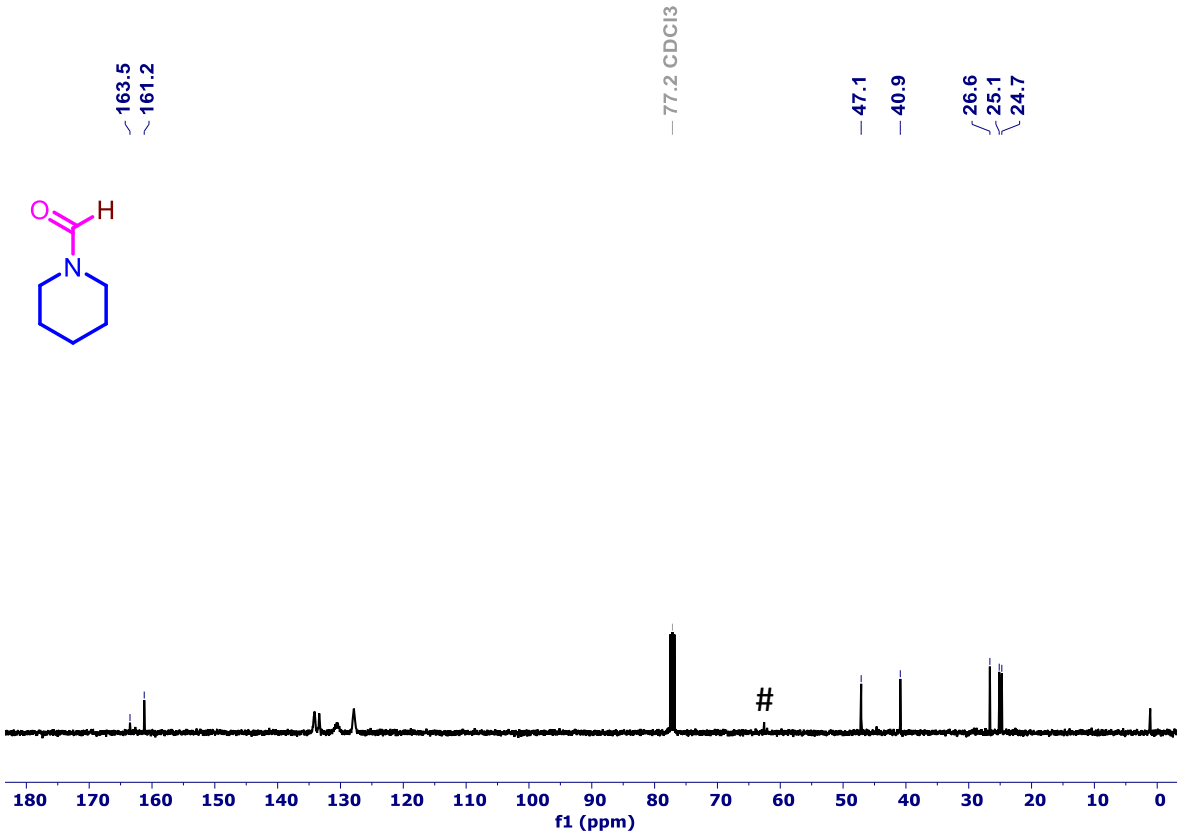
*^{1}H NMR of **morpholine-4-carbaldehyde** (compound-**4a**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



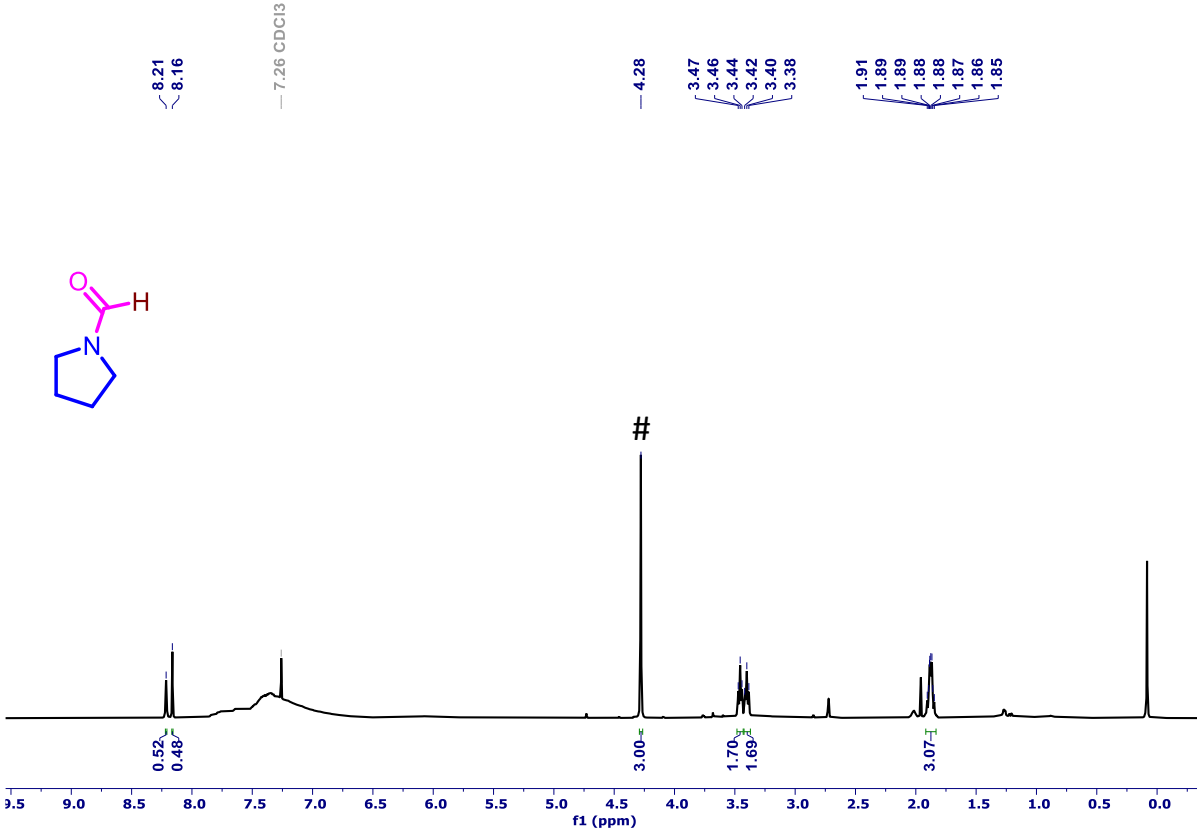
*$^{13}C\{^{1}H\}$ NMR of **morpholine-4-carbaldehyde** (compound-**4a**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



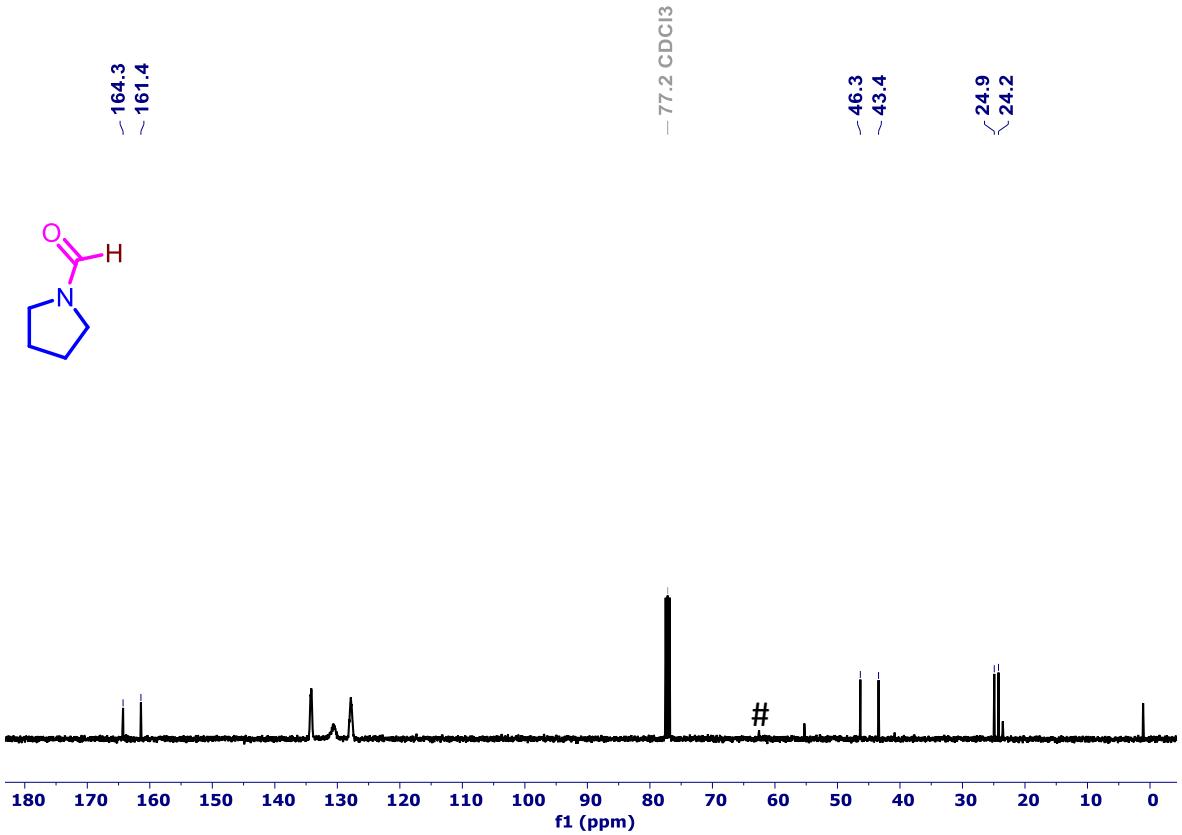
*^{1}H NMR of **piperidine-1-carbaldehyde** (compound-**4b**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



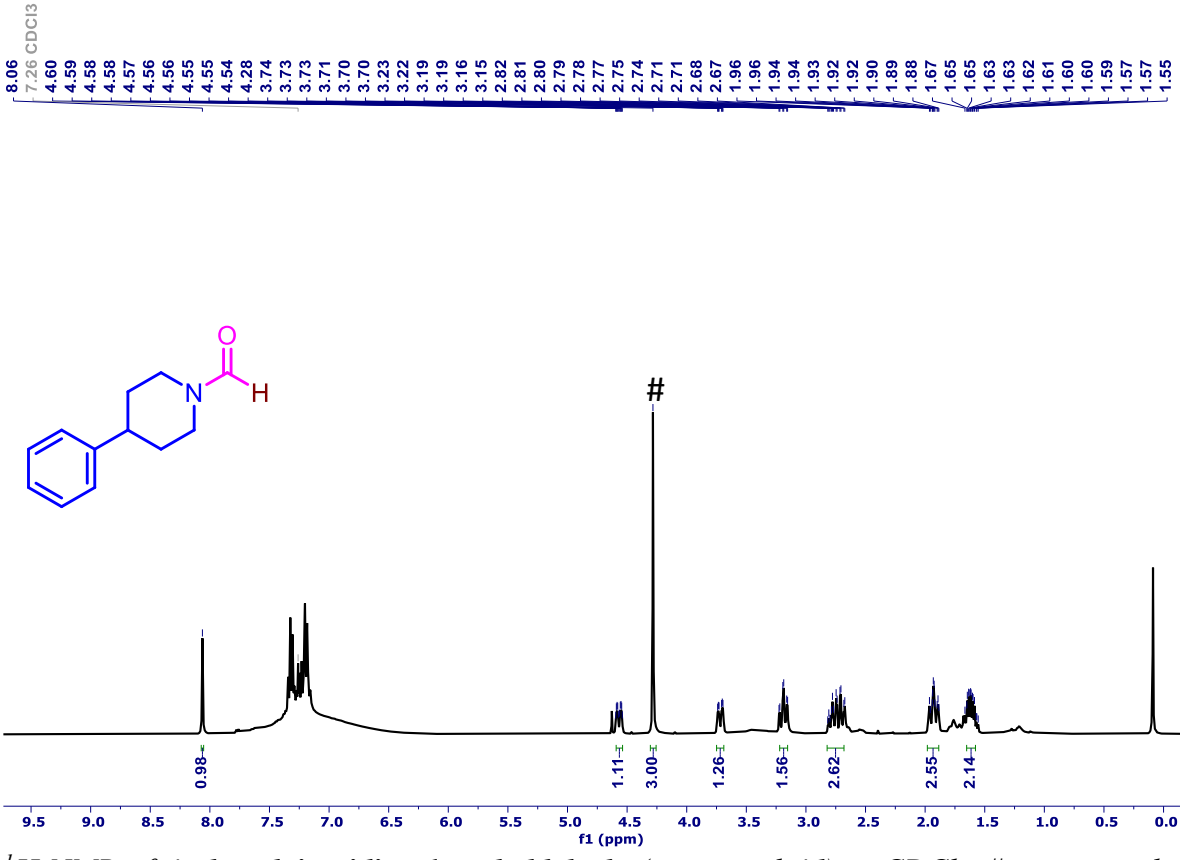
*$^{13}C\{^{1}H\}$ NMR of **piperidine-1-carbaldehyde** (compound-**4b**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



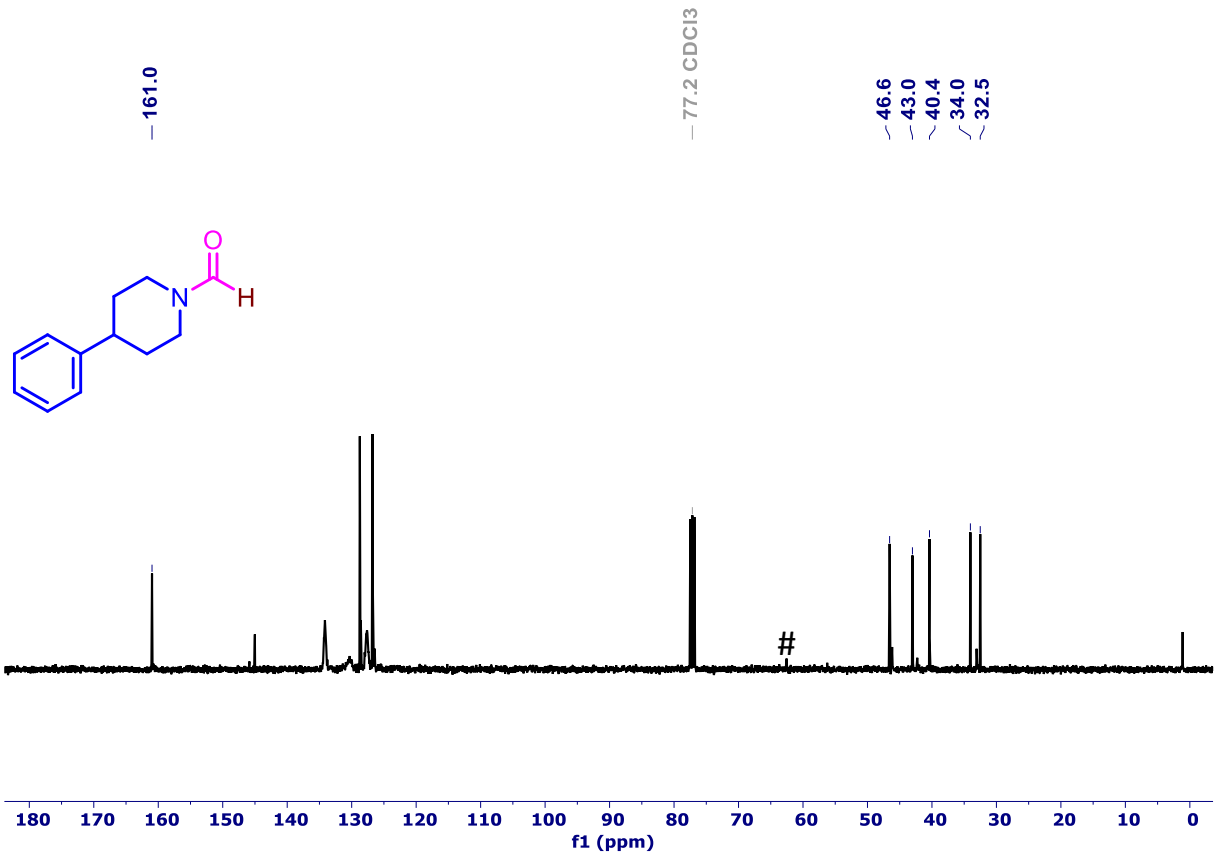
*^{1}H NMR of **pyrrolidine-1-carbaldehyde** (compound-**4c**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



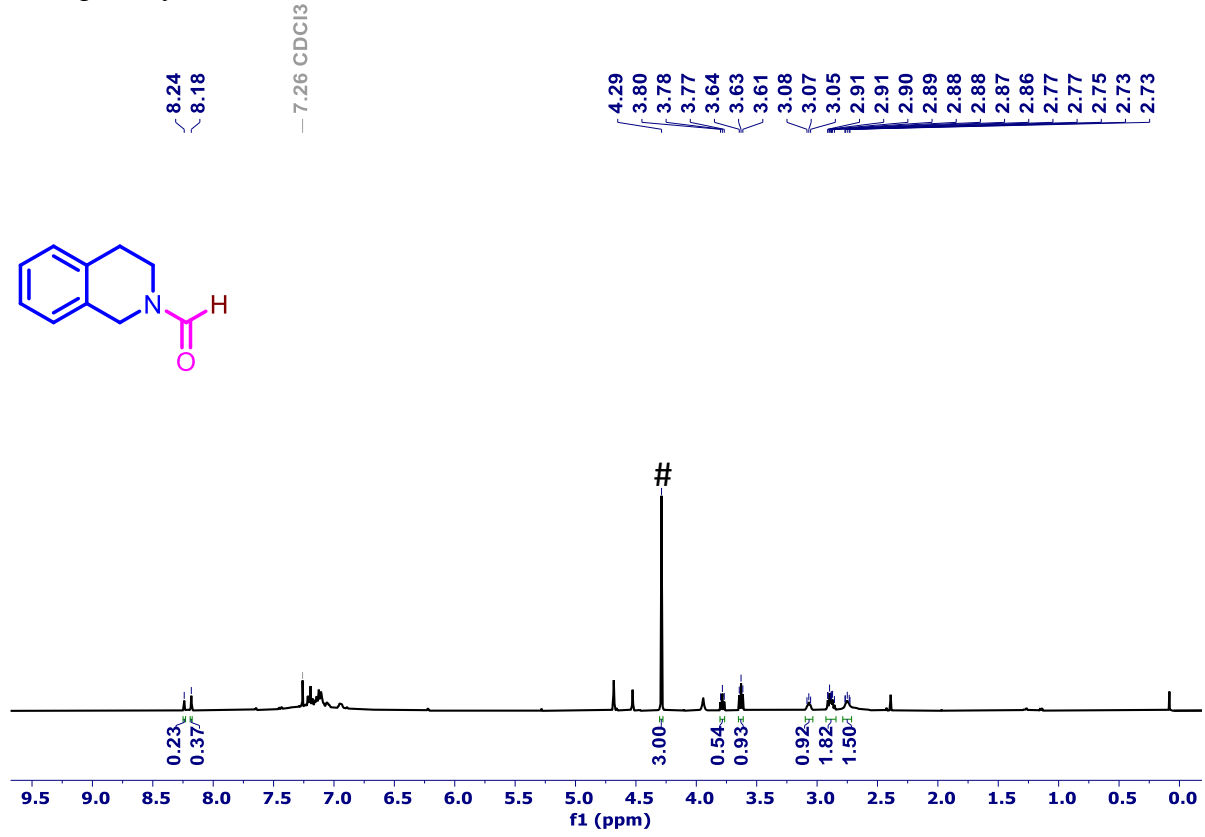
*$^{13}C\{^{1}H\}$ NMR of **pyrrolidine-1-carbaldehyde** (compound-**4c**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



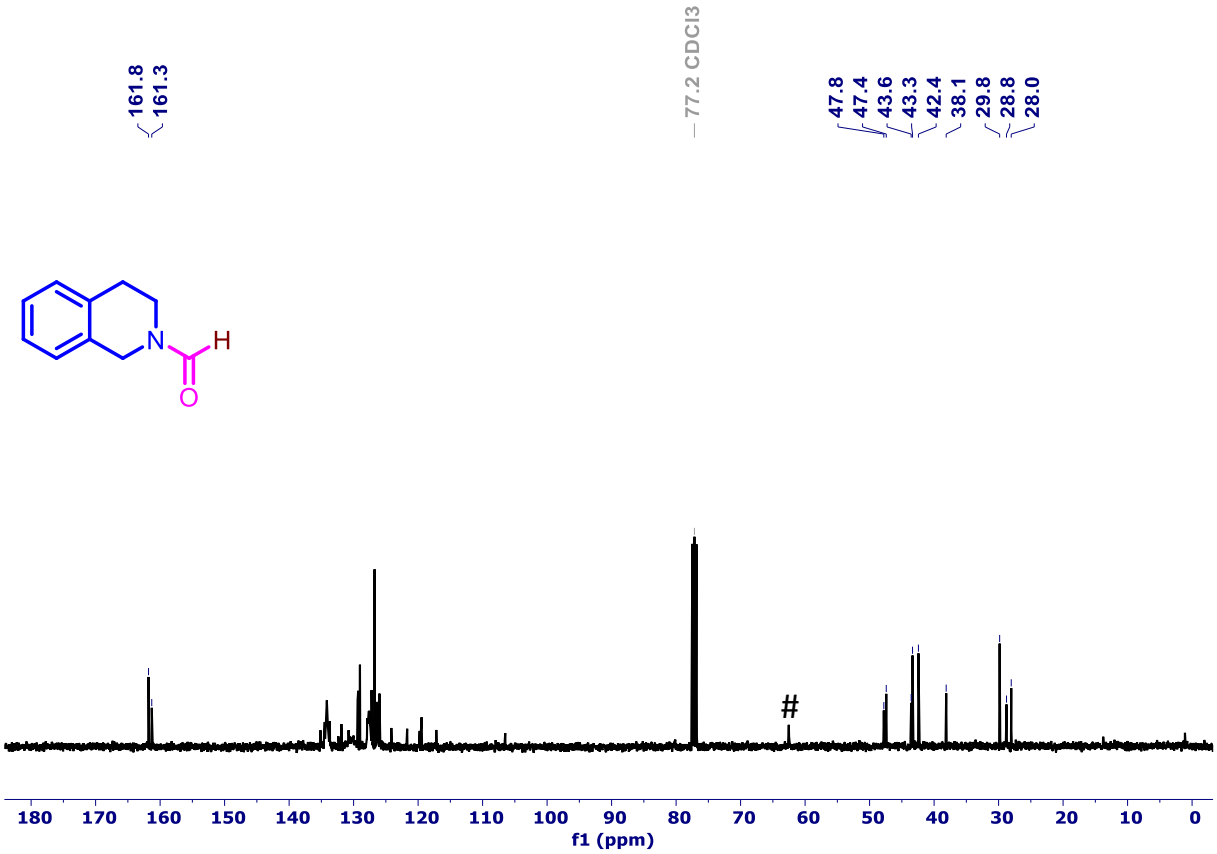
*^{1}H NMR of **4-phenylpiperidine-1-carbaldehyde** (compound-**4d**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



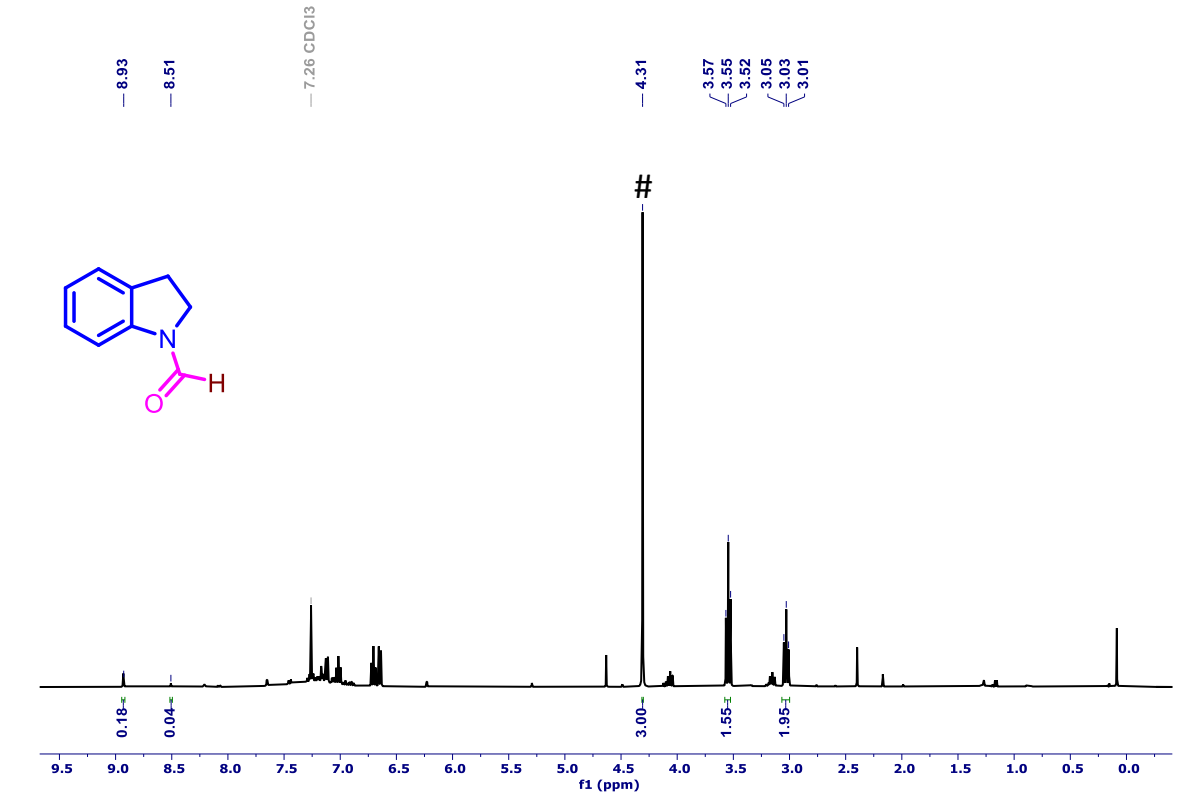
*$^{13}C\{^{1}H\}$ NMR of **4-phenylpiperidine-1-carbaldehyde** (compound-**4d**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



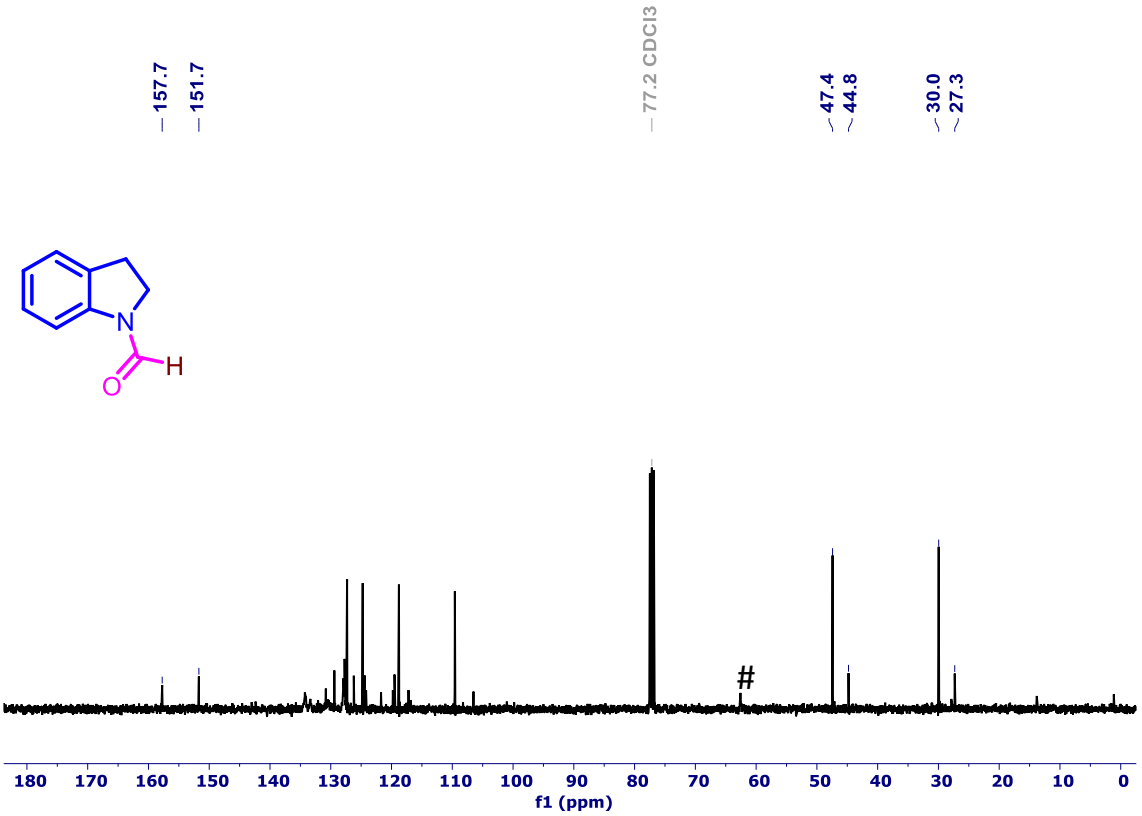
*^{1}H NMR of **3,4-dihydroisoquinoline-2(1H)-carbaldehyde** (compound-**4e**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



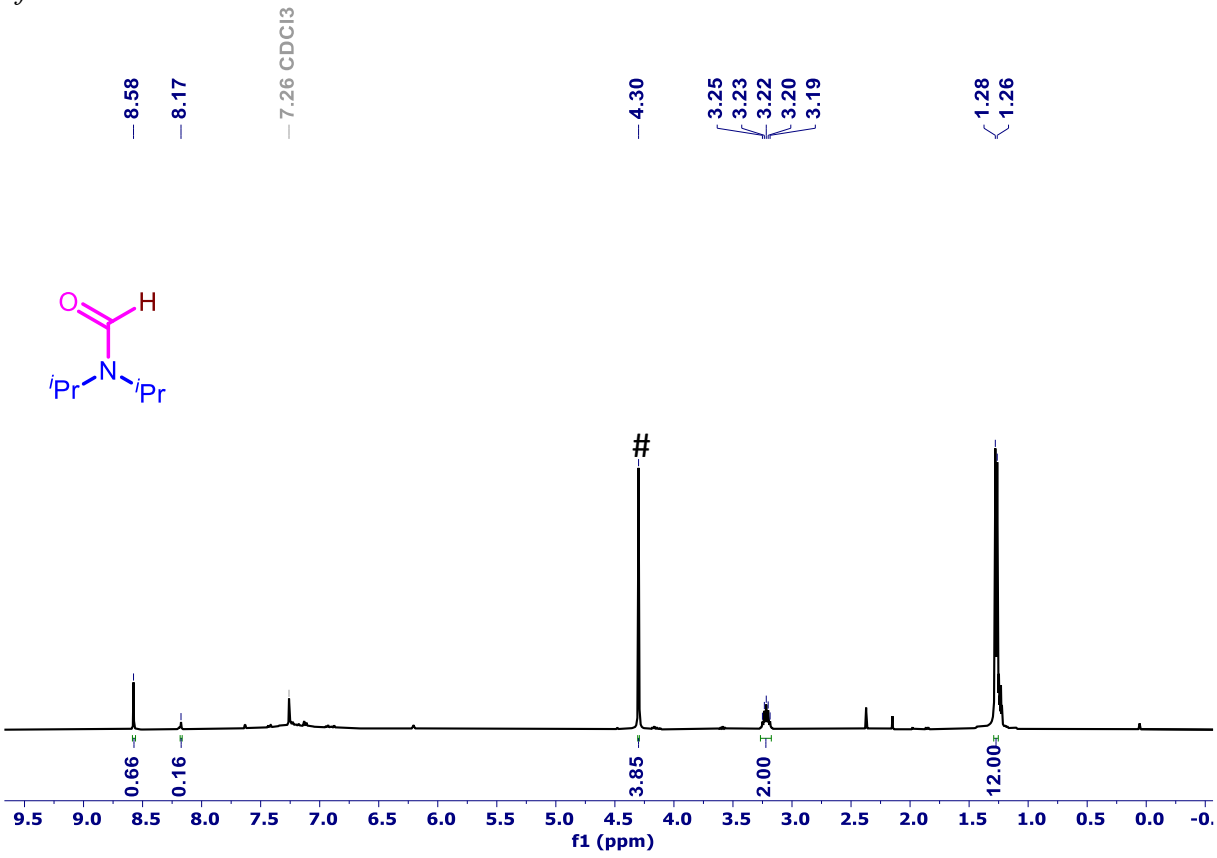
*$^{13}C\{^{1}H\}$ NMR of **3,4-dihydroisoquinoline-2(1H)-carbaldehyde** (compound-**4e**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



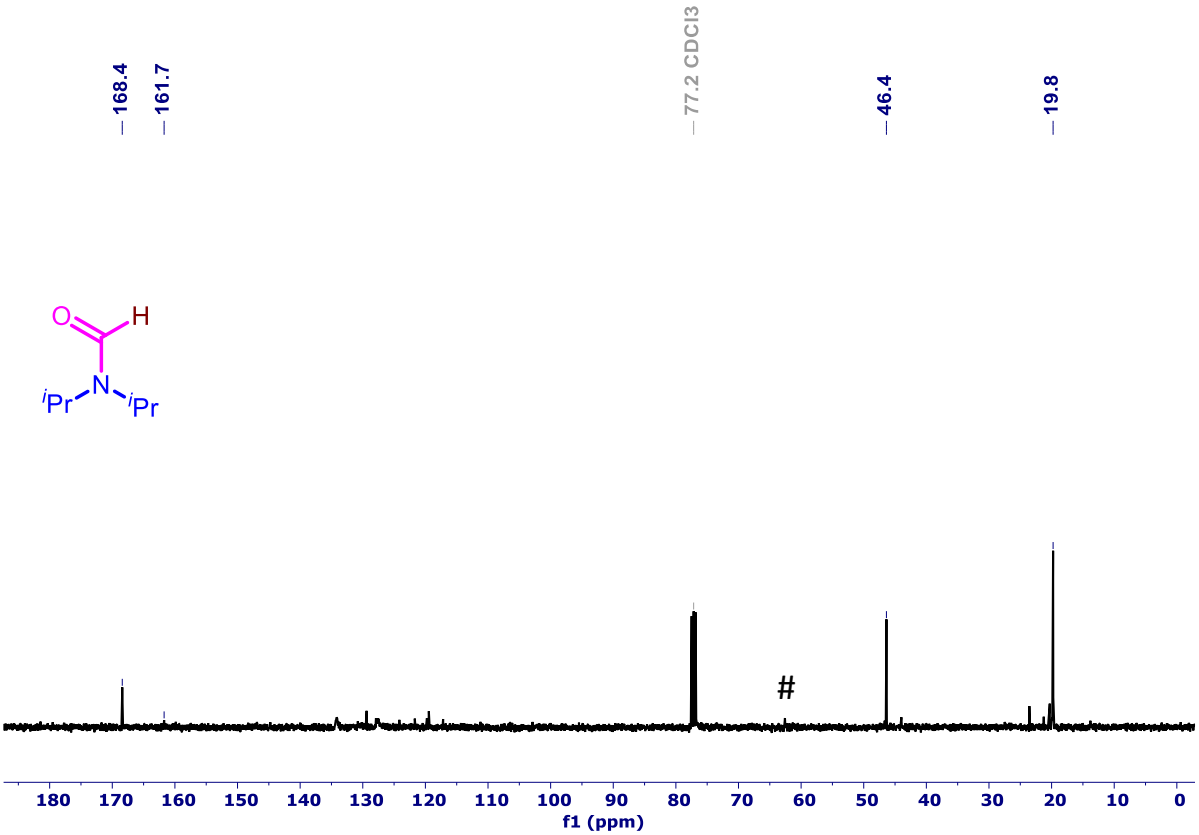
*^{1}H NMR of **Indoline-1-carbaldehyde** (compound-**4f**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



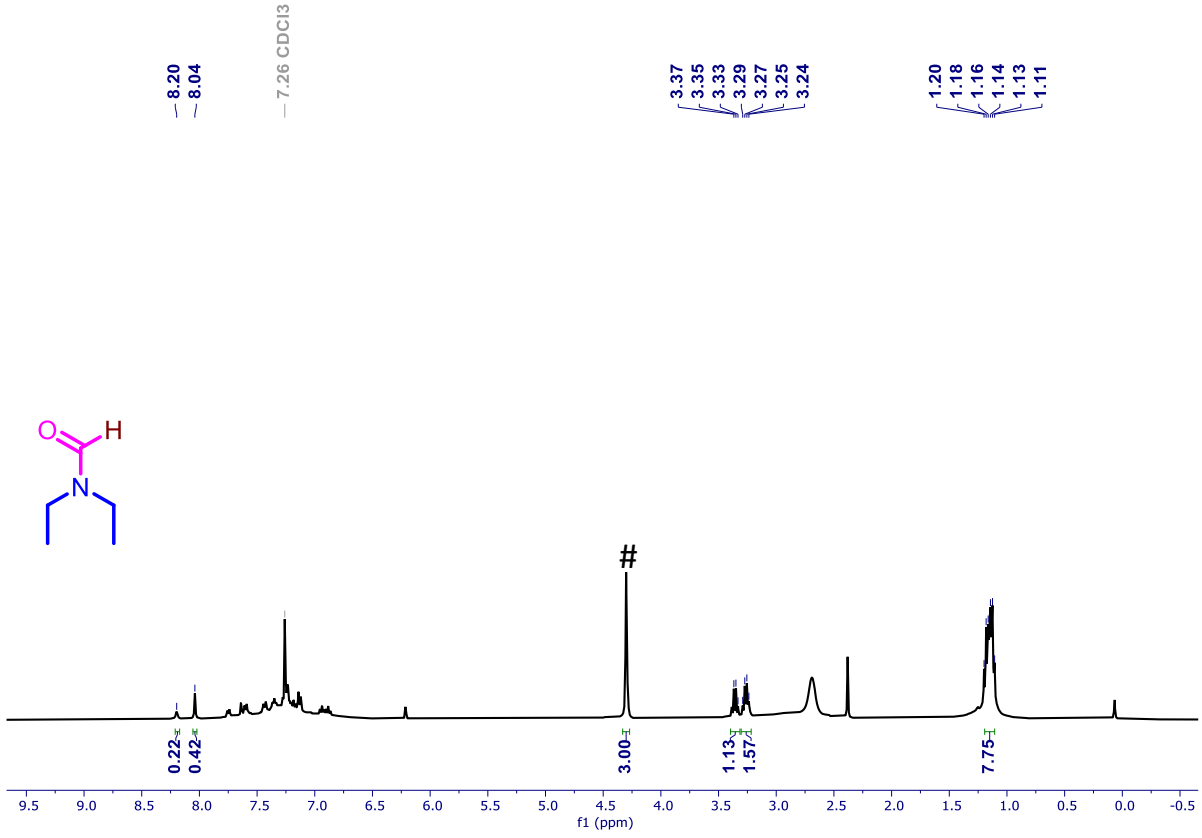
*$^{13}C\{^{1}H\}$ NMR of **indoline-1-carbaldehyde** (compound-**4f**) in $CDCl_3$. # corresponds to the peak of internal standard Nitromethane.*



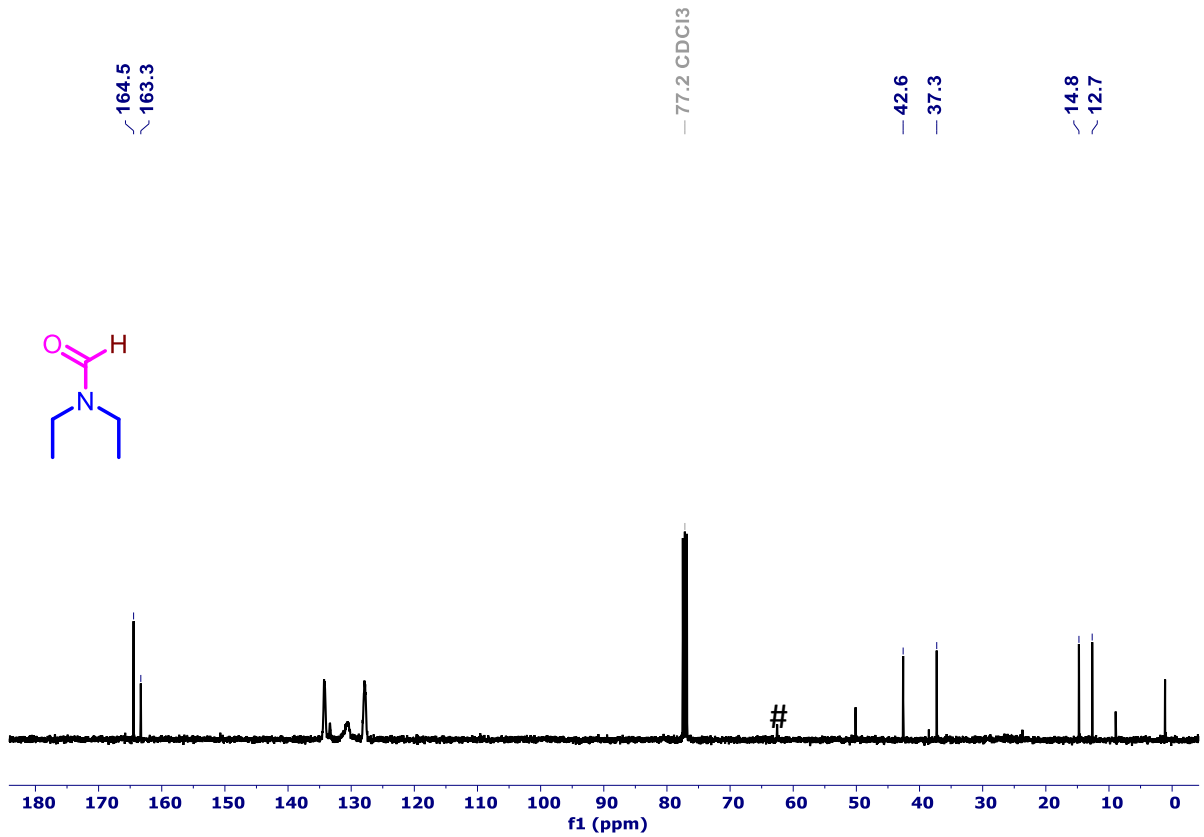
*^{1}H NMR of **N,N-diisopropylformamide** (compound-**4g**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



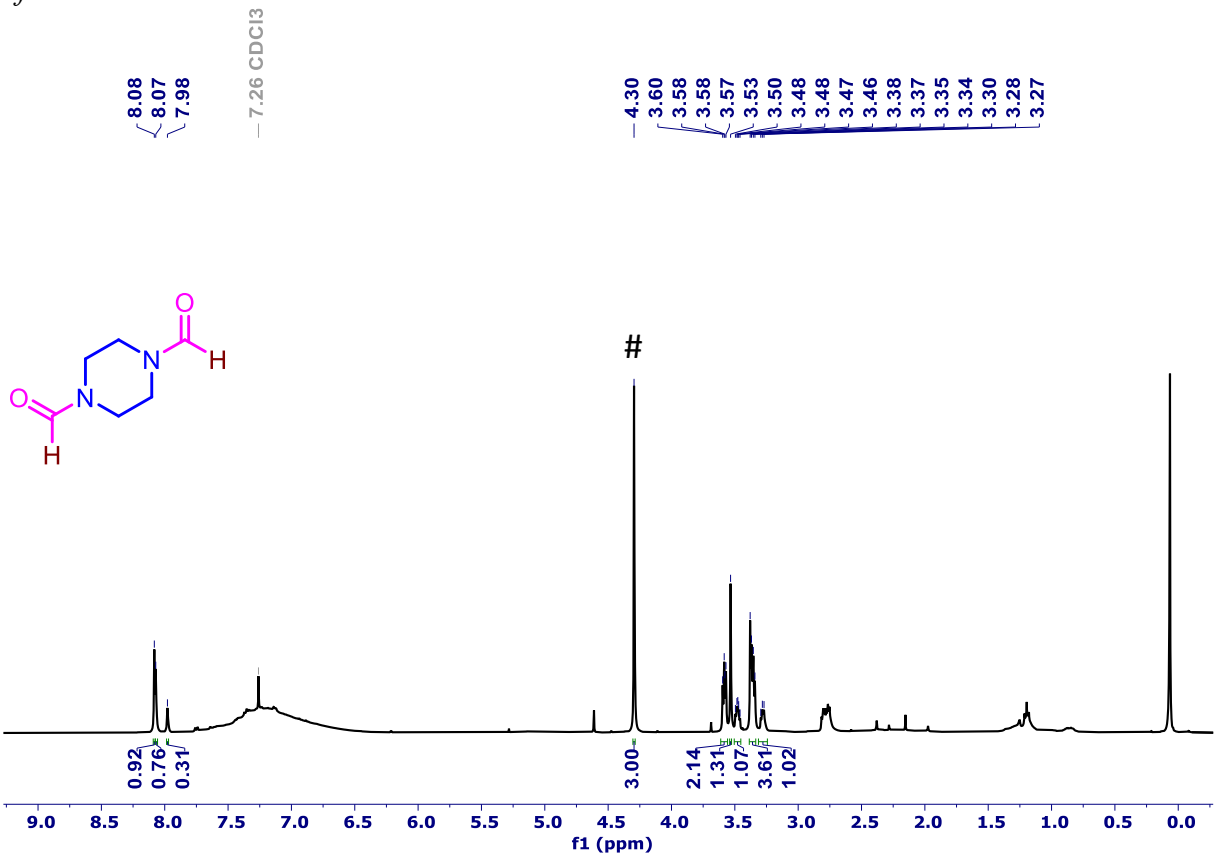
*$^{13}C\{^{1}H\}$ NMR of **N,N-diisopropylformamide** (compound-**4g**) in $CDCl_3$. # corresponds to the peak of internal standard Nitromethane.*



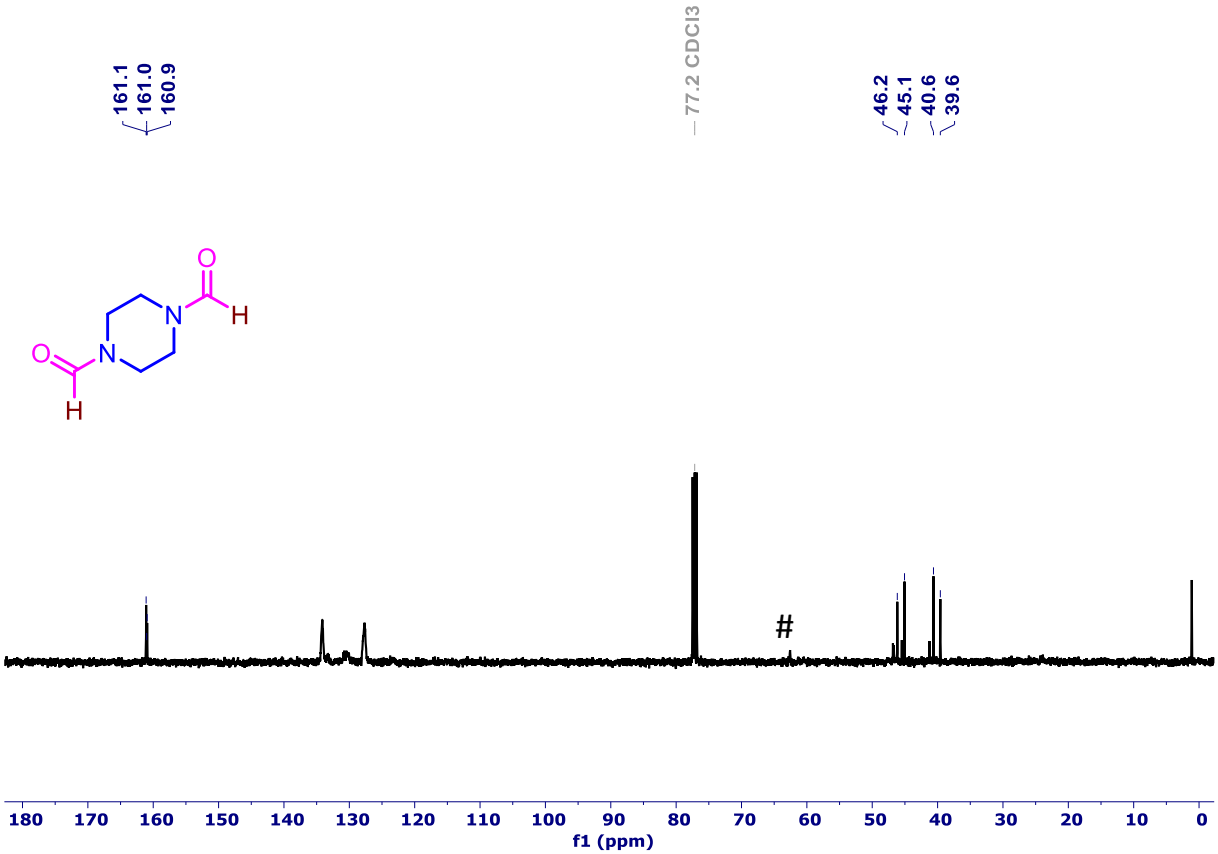
*^{1}H NMR of **N,N-diethylformamide** (compound-**4h**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



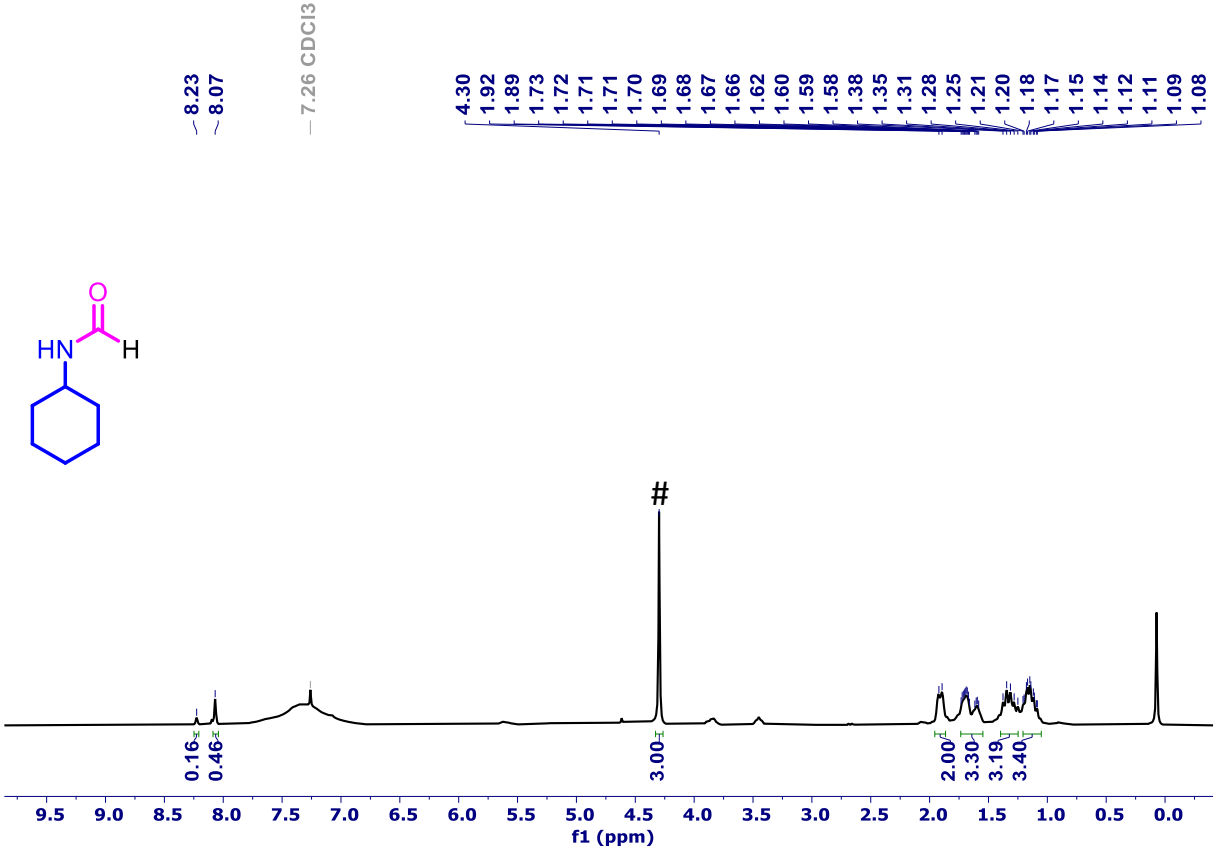
*$^{13}C\{^{1}H\}$ NMR of **N,N-diethylformamide** (compound-**4h**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



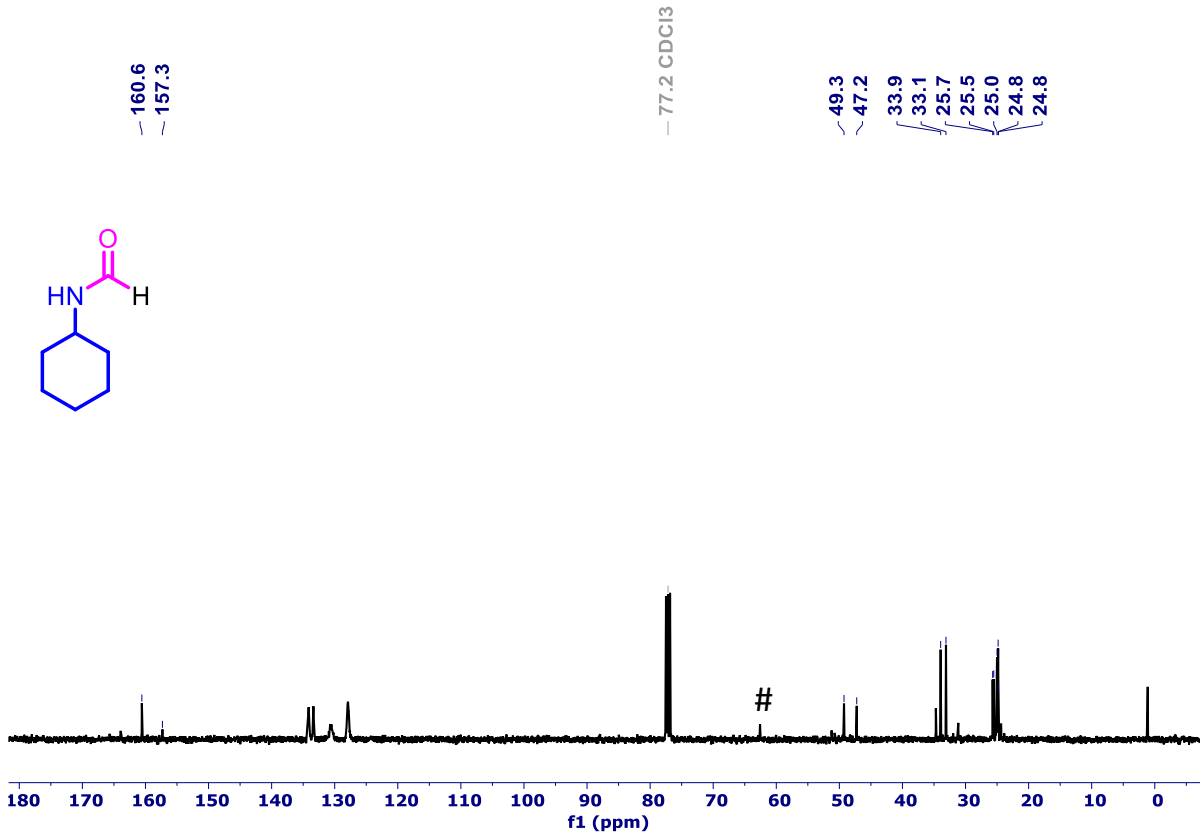
*^{1}H NMR of **piperazine-1,4-dicarbaldehyde** (compound-**4i**) in $CDCl_3$ # corresponds to the peak of internal standard nitromethane.*



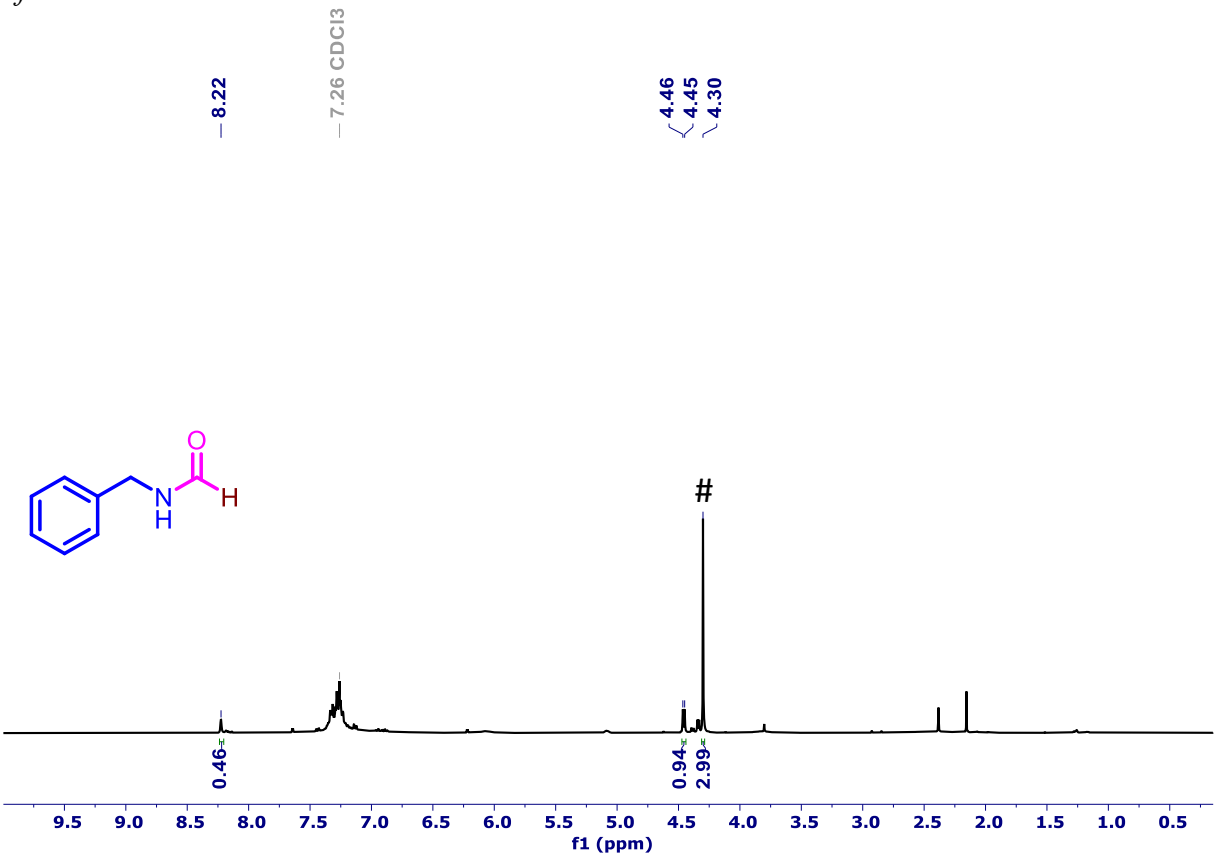
*$^{13}C\{^{1}H\}$ NMR of **pyrrolidine-1-carbaldehyde** (compound-**4i**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



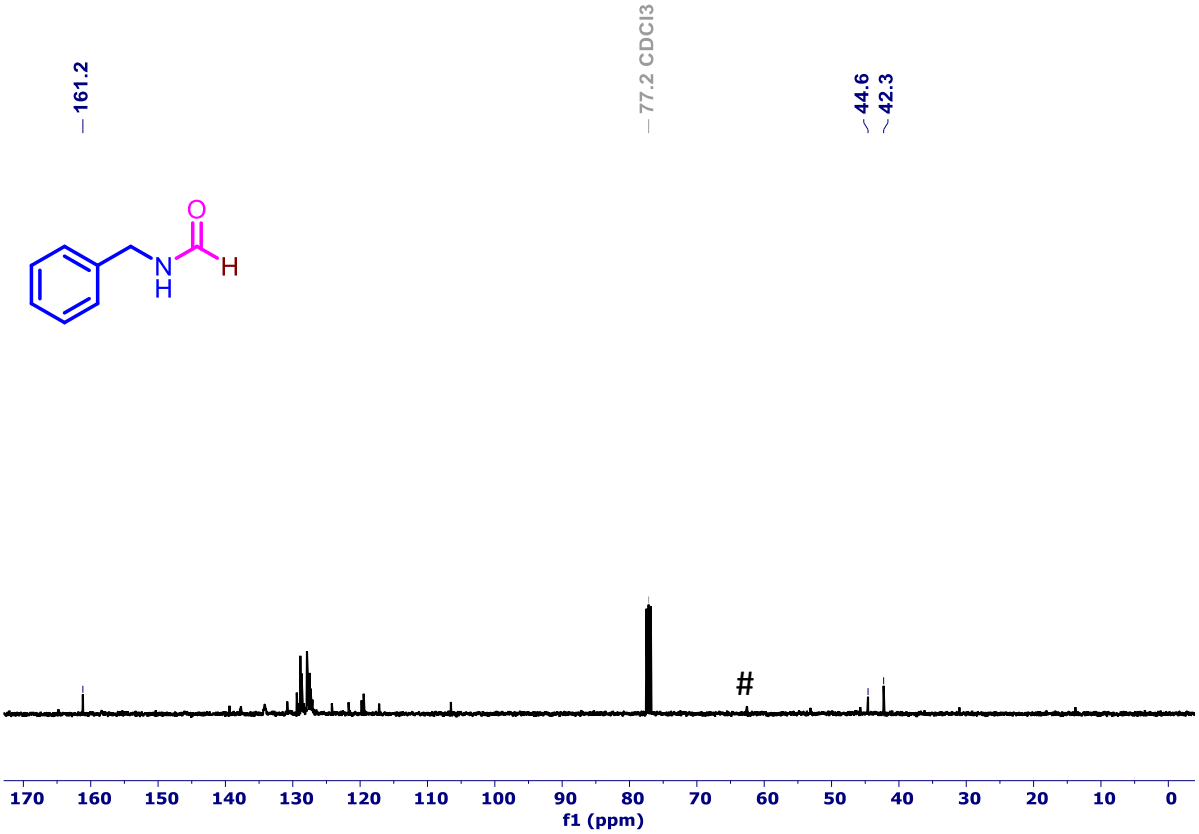
*[1]H NMR of **N-cyclohexylformamide** (compound-**4j**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



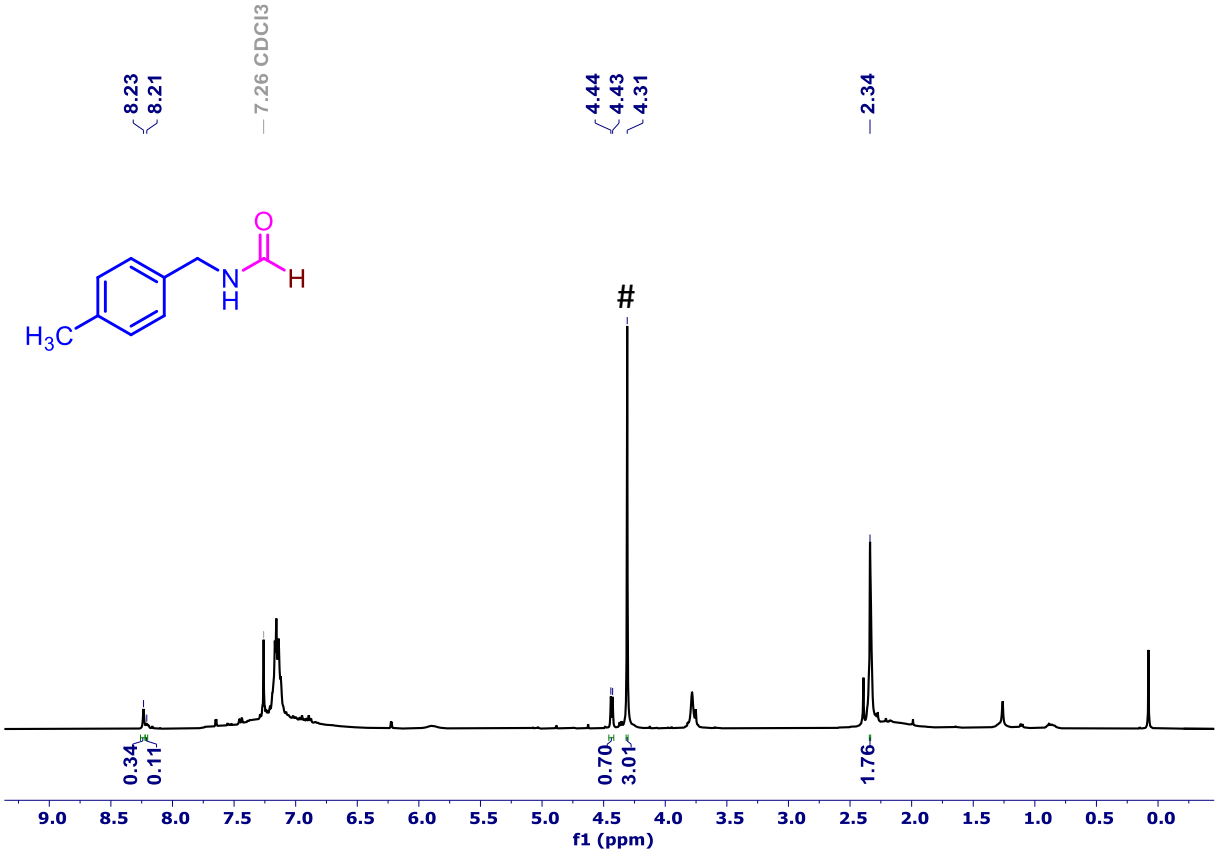
*[13]C{[1]H} NMR of **N-cyclohexylformamide** (compound-**4j**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



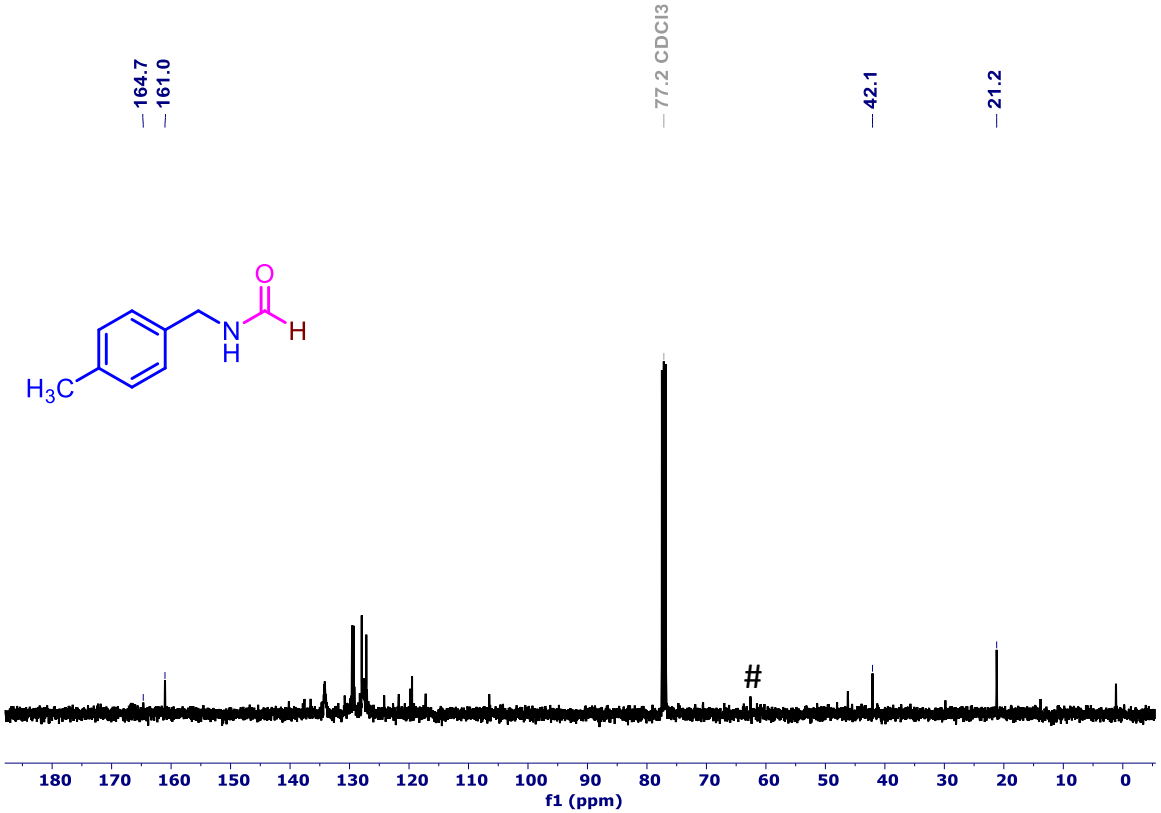
*^{1}H NMR of **N-benzylformamide** (compound-**4k**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



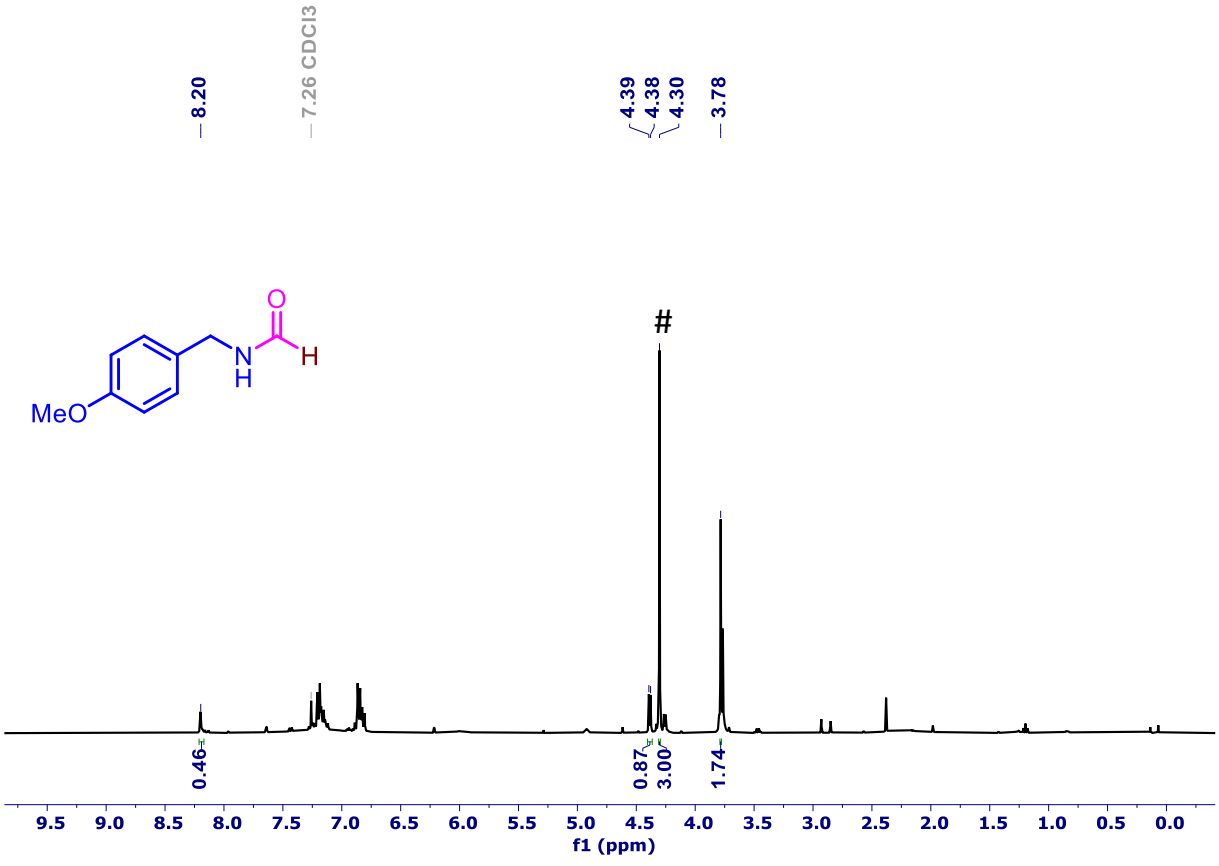
*$^{13}C\{^{1}H\}$ NMR of **N-benzylformamide** (compound-**4k**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



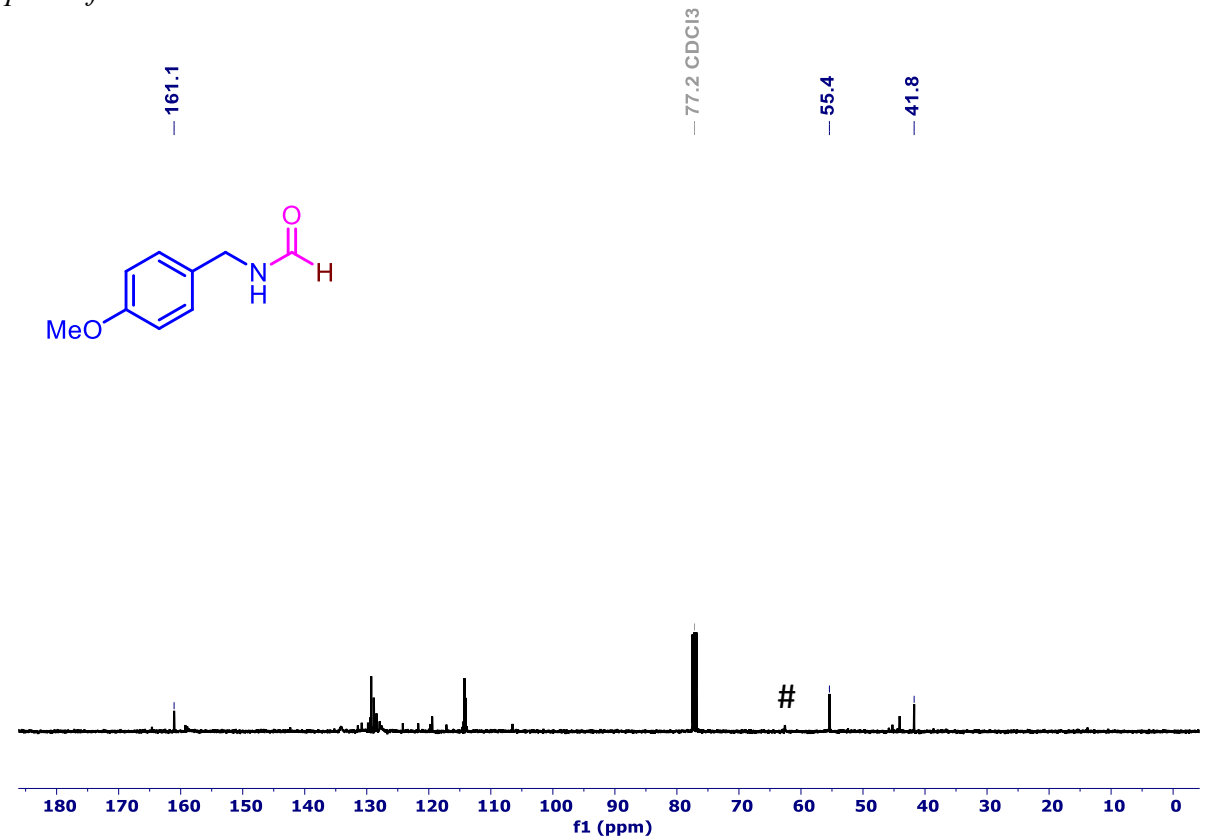
*^{1}H NMR of **N-(4-methylbenzyl)formamide** (compound-**4l**) in $CDCl_3$. # corresponds to the peak of internal standard Nitromethane.*



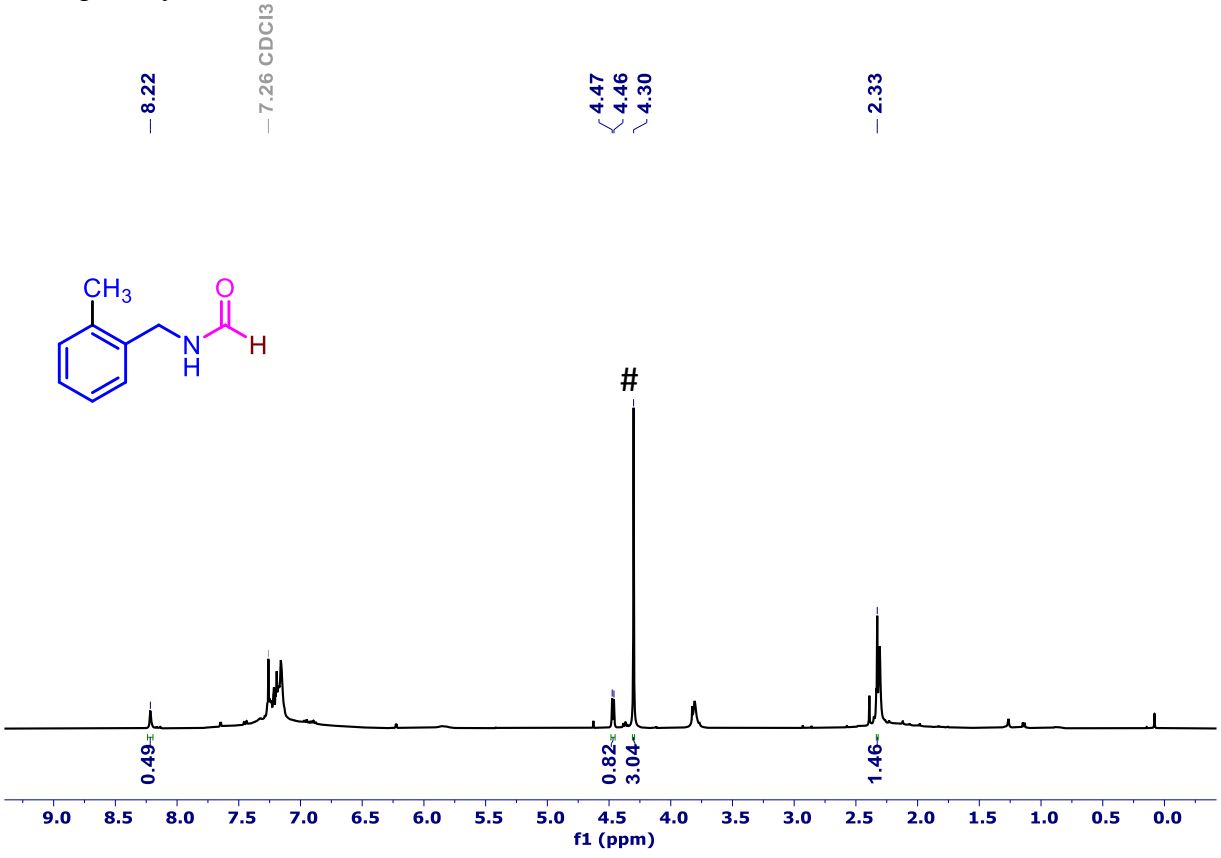
*$^{13}C\{^{1}H\}$ NMR of **N-(4-methylbenzyl)formamide** (compound-**4l**) in $CDCl_3$. # corresponds to the peak of internal standard Nitromethane.*



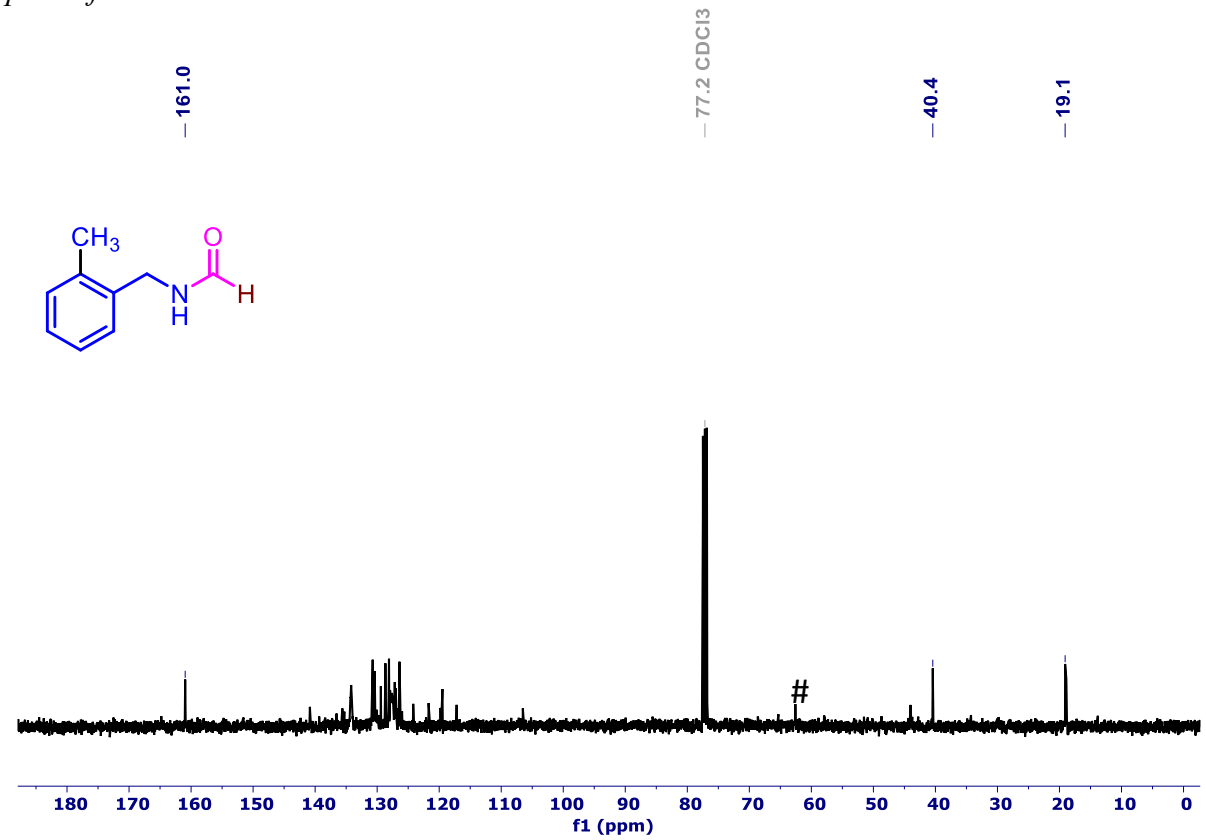
*^{1}H NMR of **N-(4-methoxybenzyl)formamide** (compound-**4m**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



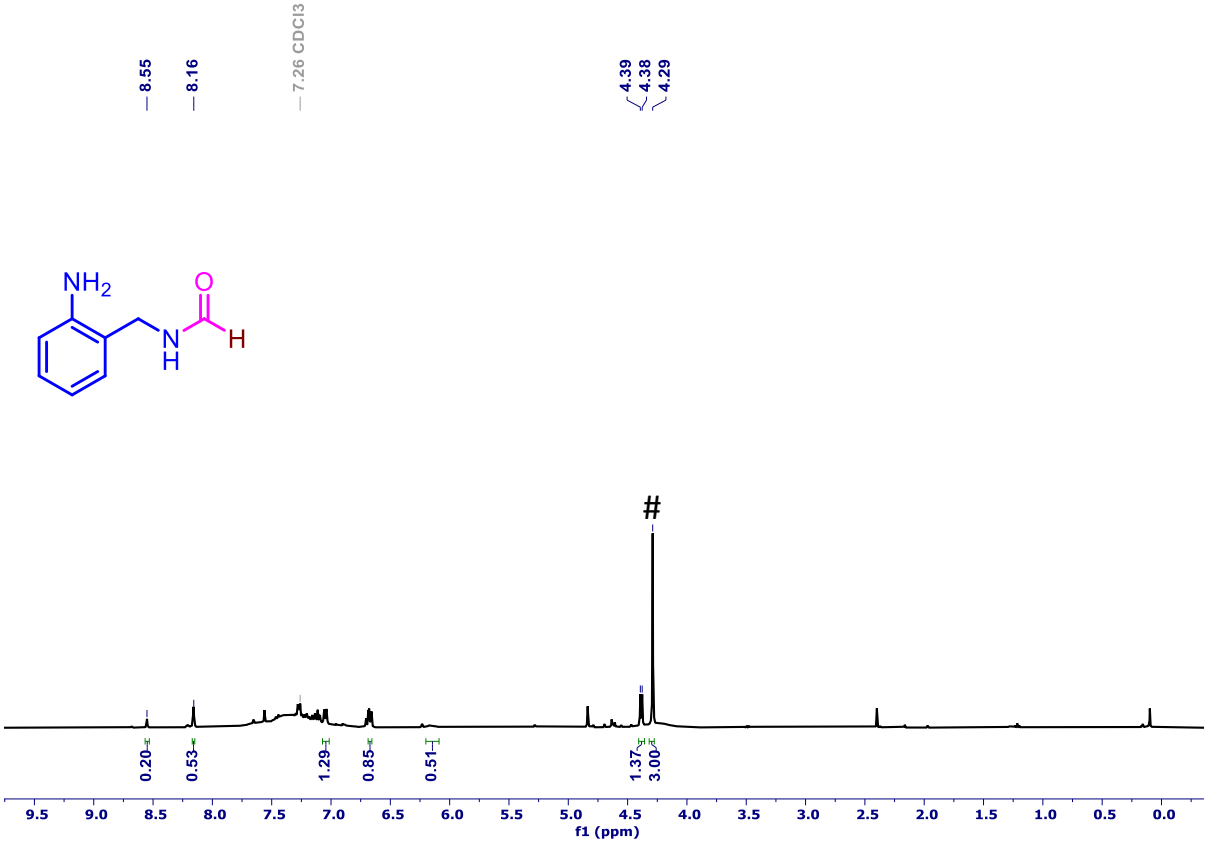
*$^{13}C\{^{1}H\}$ NMR of **N-(4-methoxybenzyl)formamide** (compound-**4m**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



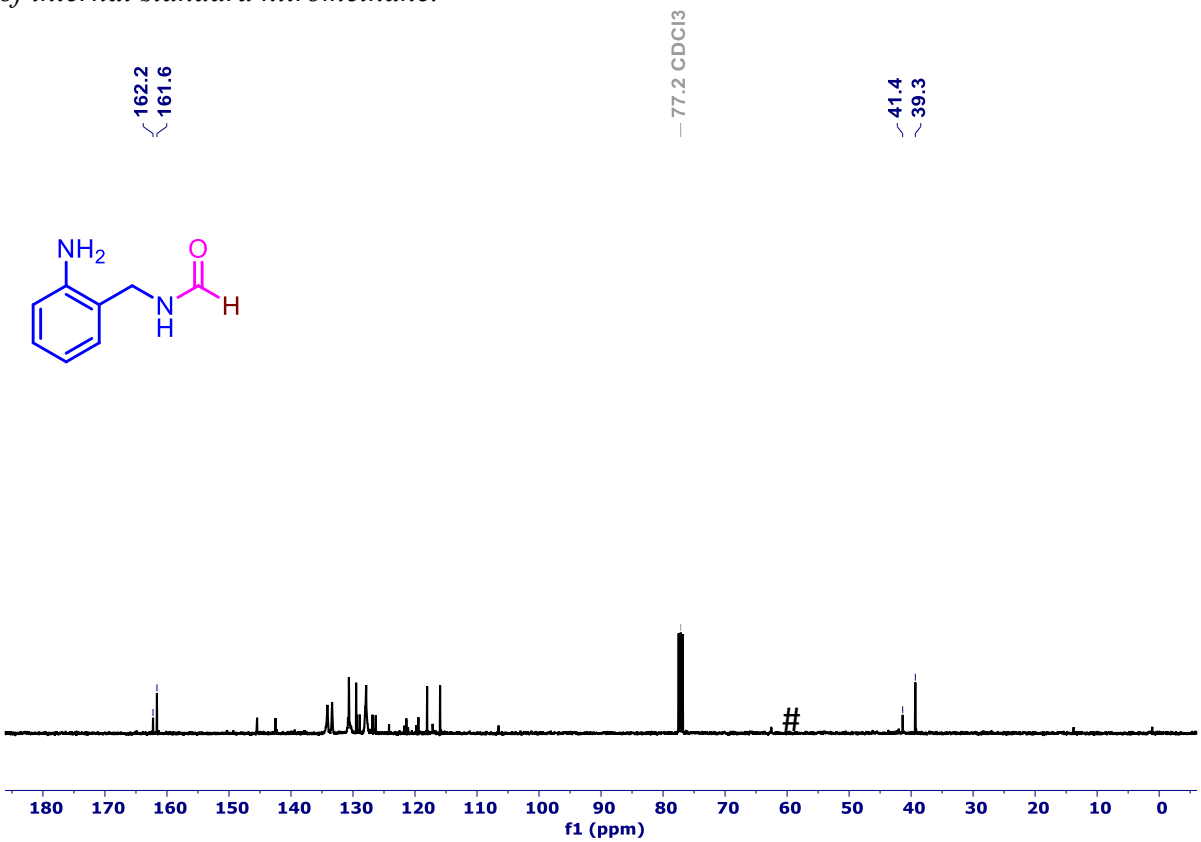
*^{1}H NMR of **N-(2-methylbenzyl)formamide** (compound-**4n**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



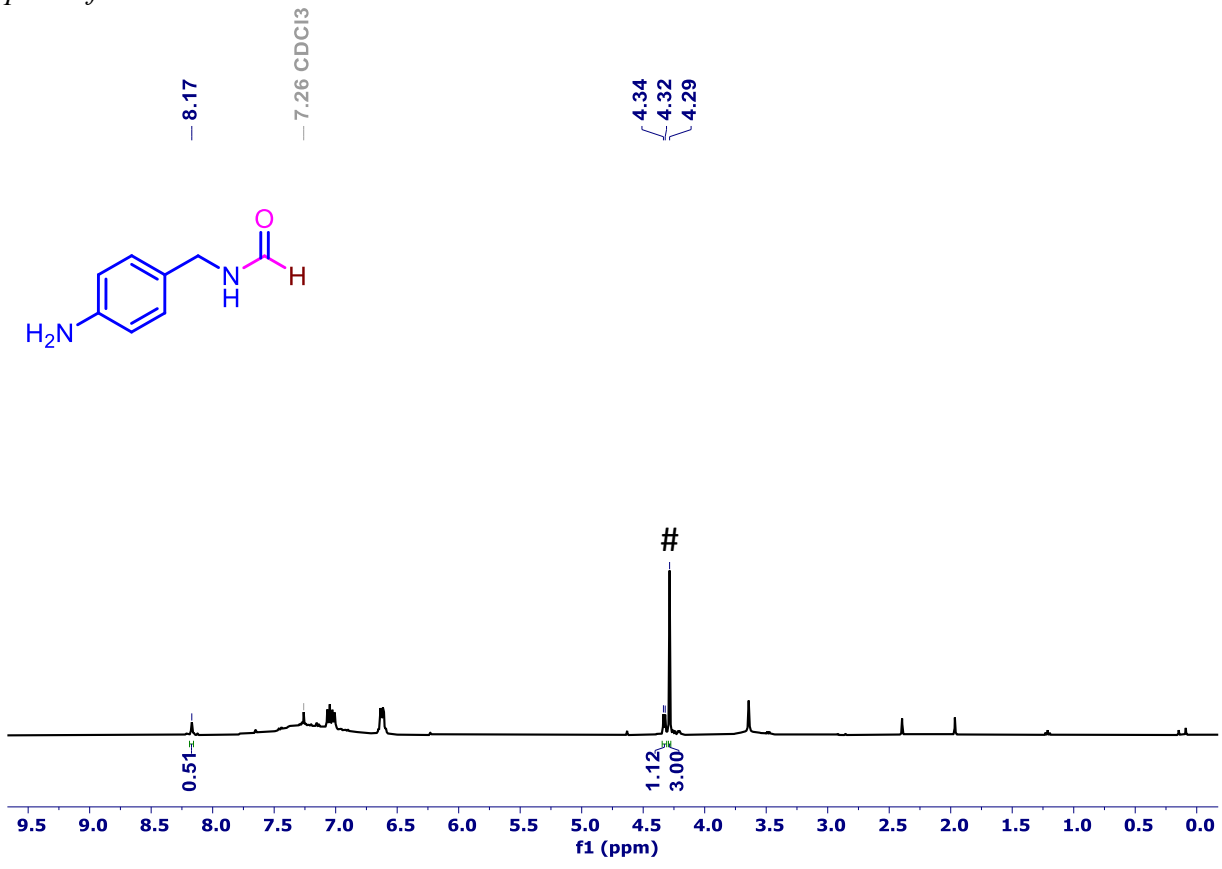
*$^{13}C\{^{1}H\}$ NMR of **N-(2-methylbenzyl)formamide** (compound-**4n**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



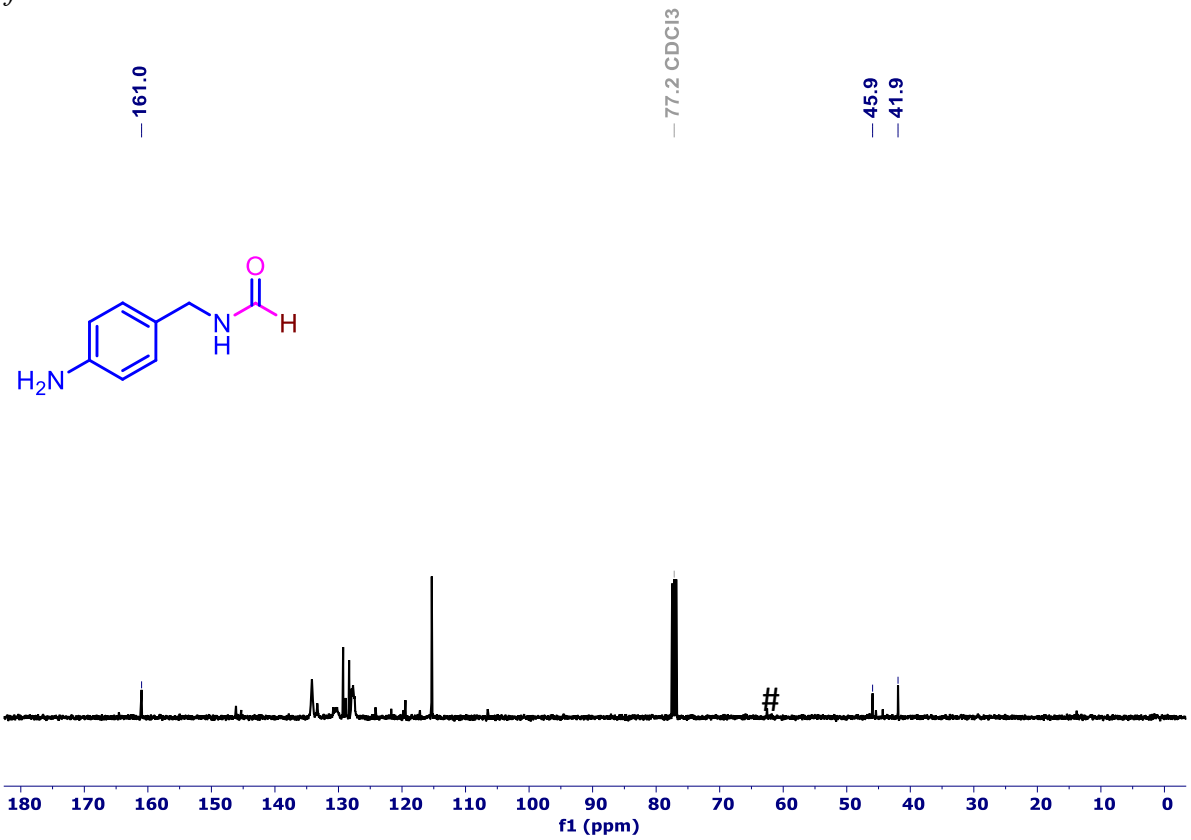
*^{1}H NMR of **N-(2-aminobenzyl)formamide** (compound-**4o**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



*$^{13}C\{^{1}H\}$ NMR of **N-(2-aminobenzyl)formamide** (compound-**4o**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



*^{1}H NMR of **N-(2-aminobenzyl)formamide** (compound-**4p**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*



*$^{13}C\{^{1}H\}$ NMR of **N-(2-aminobenzyl)formamide** (compound-**4p**) in $CDCl_3$. # corresponds to the peak of internal standard nitromethane.*

Representative example for the higher scale *N*-formylation of amines:

An oven-dried pressure tube was charged with **Ge1** (25 mg, 0.05 equiv.) and phenylsilane (370 µL, 3 mmol), followed by the addition of 4-phenylpiperidine (161.2 mg, 1 mmol) and acetonitrile (2 mL). The resulted reaction mixture was then degassed by three freeze-pump-thaw cycles, and exposed to carbon dioxide (1 bar). Then, the pressure tube was kept in an oil bath at 80 °C and heated for 24 h. Upon completion of the reaction, the reaction mixture was evaporated, and the product was purified by silica gel column chromatography using hexane/ethyl acetate as eluent.

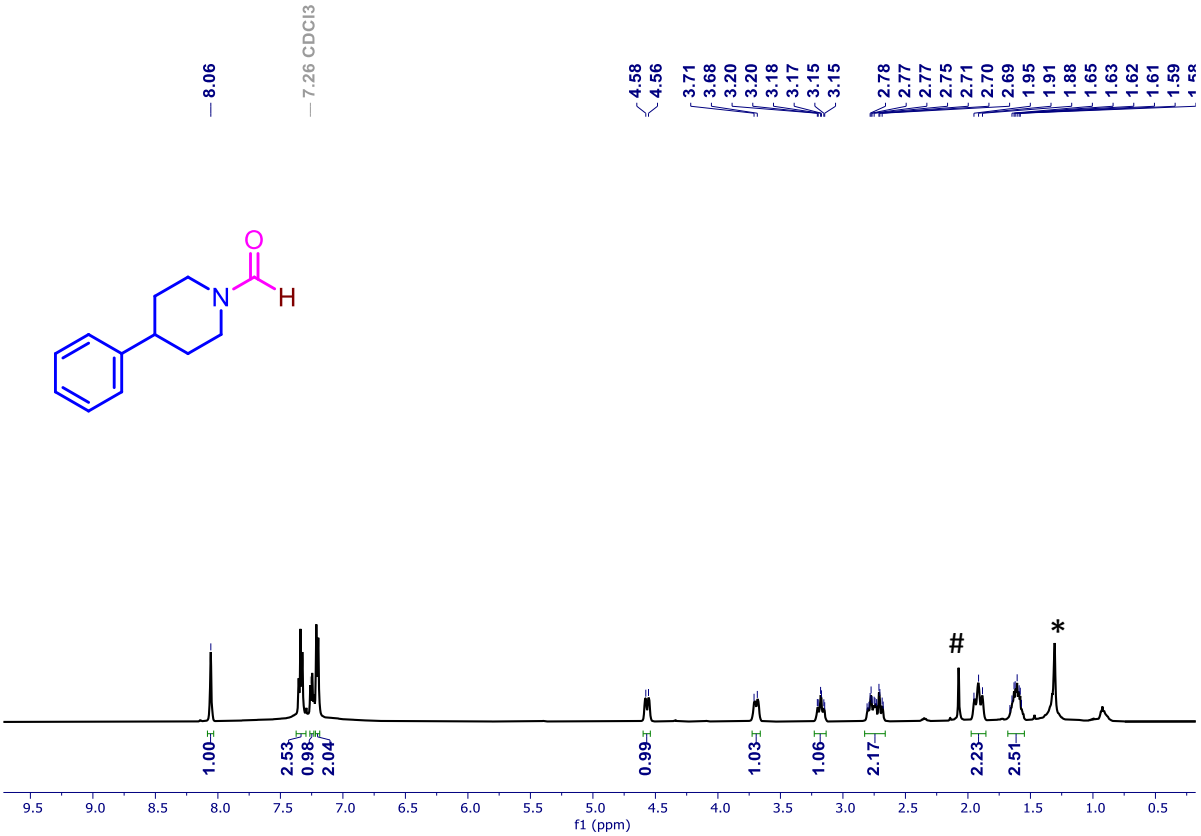


Figure S13: *^{1}H NMR spectrum of the reaction mixture 4-phenylpiperidine-1-carbaldehyde (compound-4d). * and # represent grease and acetone impurity, respectively.*

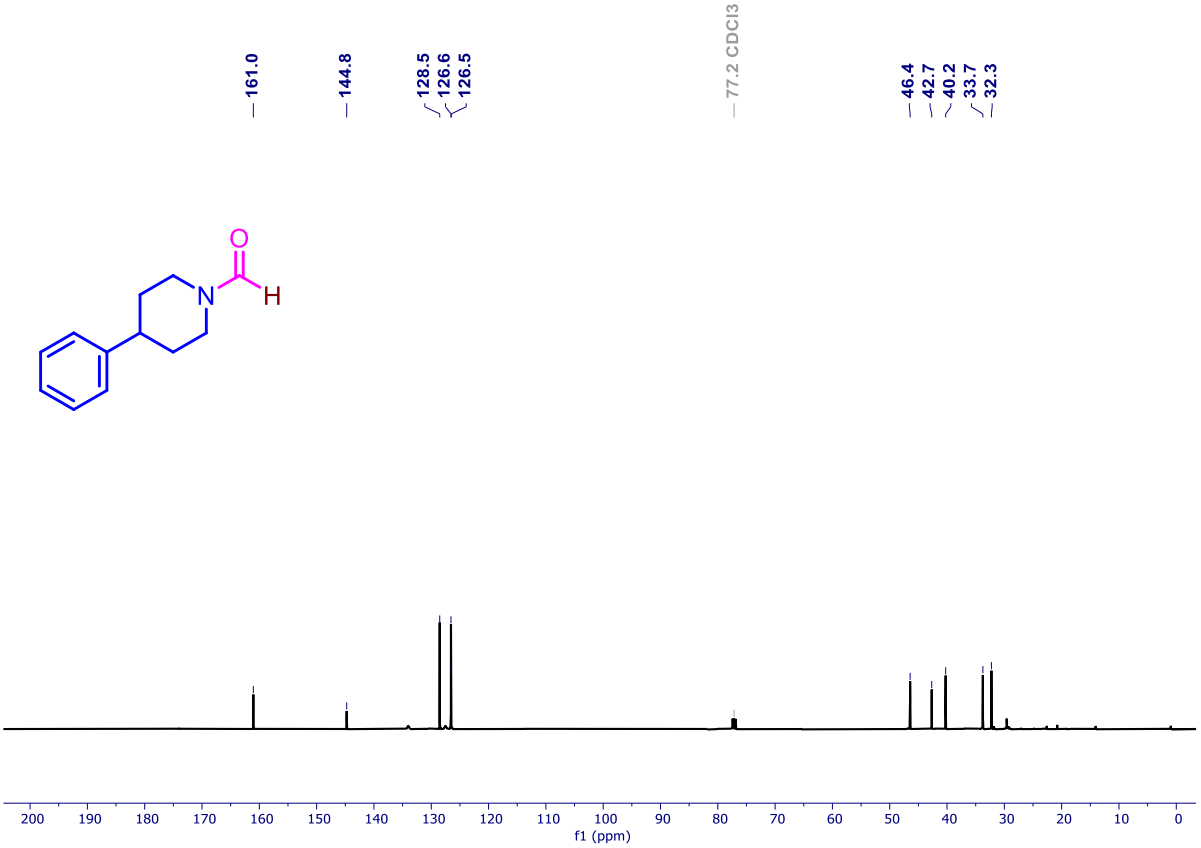


Figure S14: *$^{13}C\{^{1}H\}$ NMR of 4-phenylpiperidine-1-carbaldehyde (compound-**4d**) in $CDCl_3$.*

Control experiments:

Hydride scavenger experiment: An oven-dried pressure tube was charged with complex **Ge1** (2.5 mg, 0.05 equiv.), phenylsilane (37 µL, 0.3 mmol) and trityl hexafluorophosphate (38.8 mg, 0.1 mmol), followed by the addition of amine (0.1 mmol) and acetonitrile (2 mL). The resulted reaction mixture was then degassed by three freeze-pump-thaw cycle and exposed to carbon dioxide (1 bar). Then, the tube was kept in an oil bath at 80 °C and heated for 24 h. Upon completion of the reaction, the reaction mixture was evaporated and to the residue, nitromethane (0.1 mmol, as an internal standard) and $CDCl_3$ was added for NMR analysis.

In situ NMR monitoring experiment

Procedure for stepwise formylation of aniline with CO_2 using complex 1: complex **Ge1** (15 mg, 0.031 mmol) and phenylsilane (11.5 µL, 0.093 mmol) were taken in a Young NMR tube inside the glove box. Subsequently, CD_3CN (0.5 mL) was added, and the tube was closed with a PTFE stopper and allowed to stir at room temperature for 3 h. The mixture was monitored using ^1H NMR analysis (Figure **S10**). Subsequently, the mixture was heated for 12 h at 80 °C, and the changes were monitored by ^1H NMR analysis (Figure **S11**). Further, the reaction mixture was degassed, followed by the exposure to carbon dioxide (1 bar pressure) and stirred for 12 h at 80 °C, after which the reaction mixture was analyzed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (Figure **S12**). After the subsequent addition of benzylamine (3.4 µL, 0.031 mmol) into the same Young NMR tube, the reaction mixture was again stirred at 80 °C for 2 h, and the outcome was monitored by ^1H NMR (Figure **S13**).

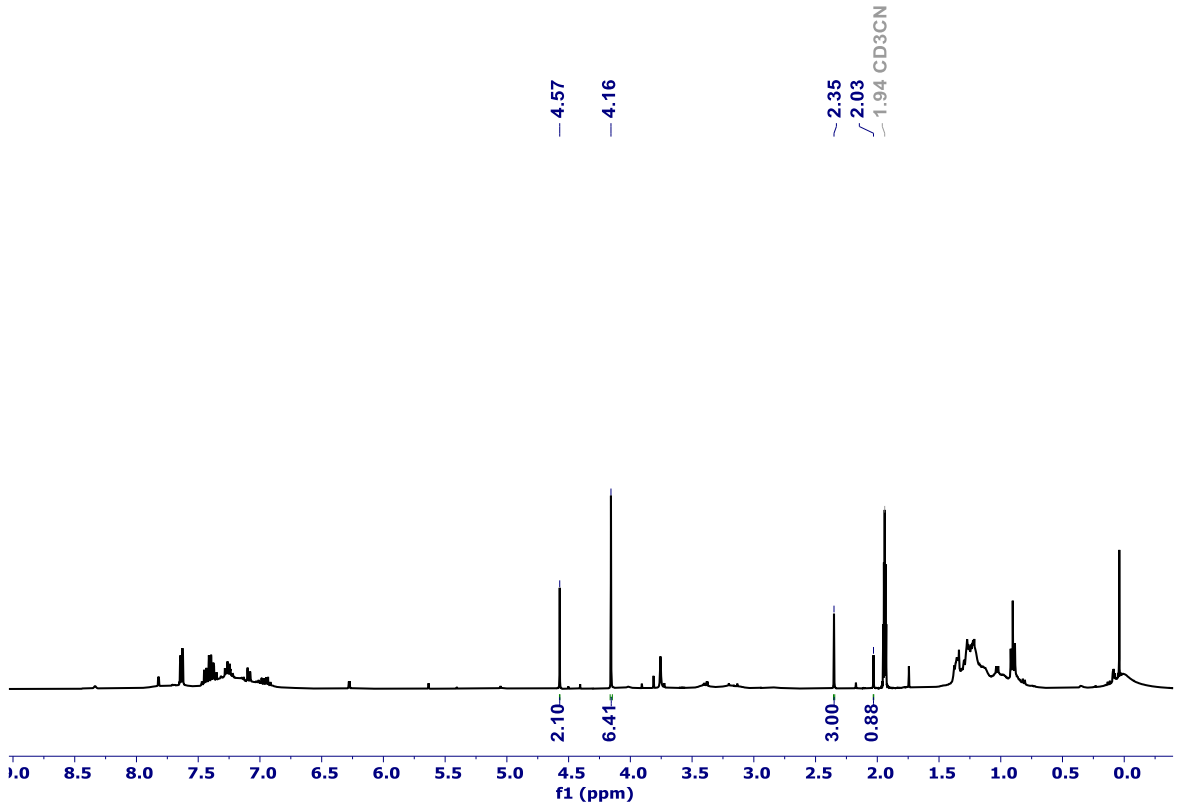


Figure S15: *^{1}H NMR spectrum of the reaction mixture for the reaction between the complex **Ge1** and phenylsilane in CD_3CN.*

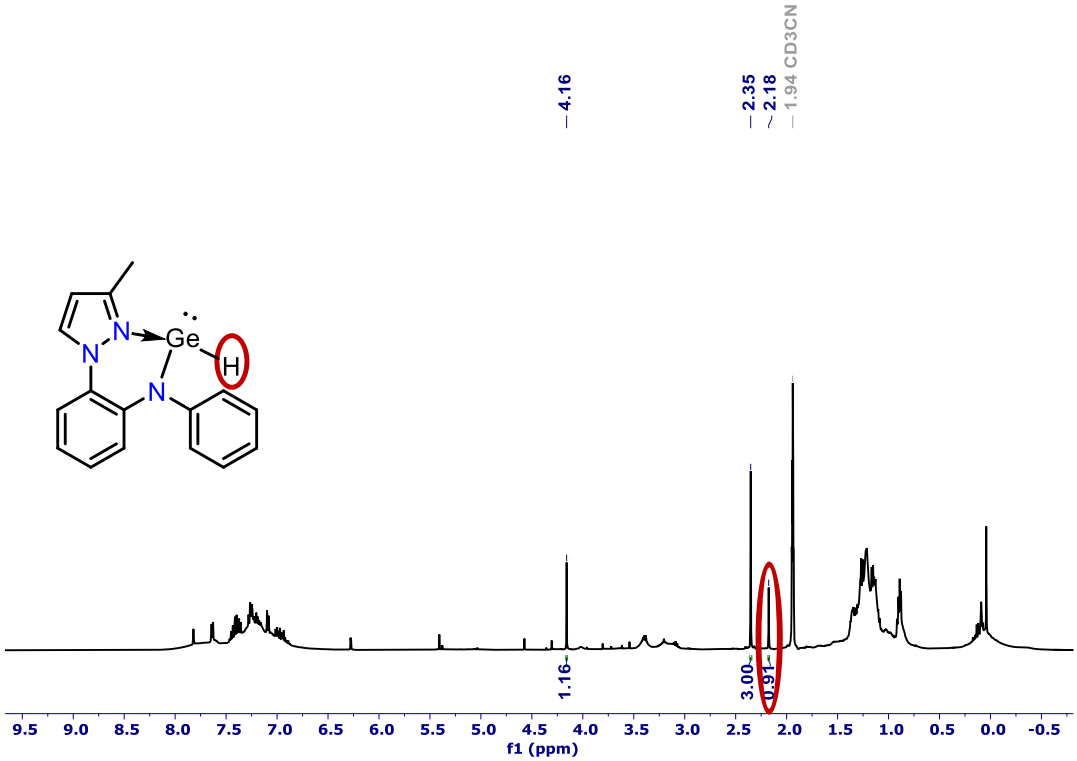


Figure S16: *^{1}H NMR spectrum of the reaction mixture for the reaction between the complex **Ge1** and phenylsilane in CD_3CN after heating at 80 °C for 12 h showing the possible formation of a Ge-hydride species.*

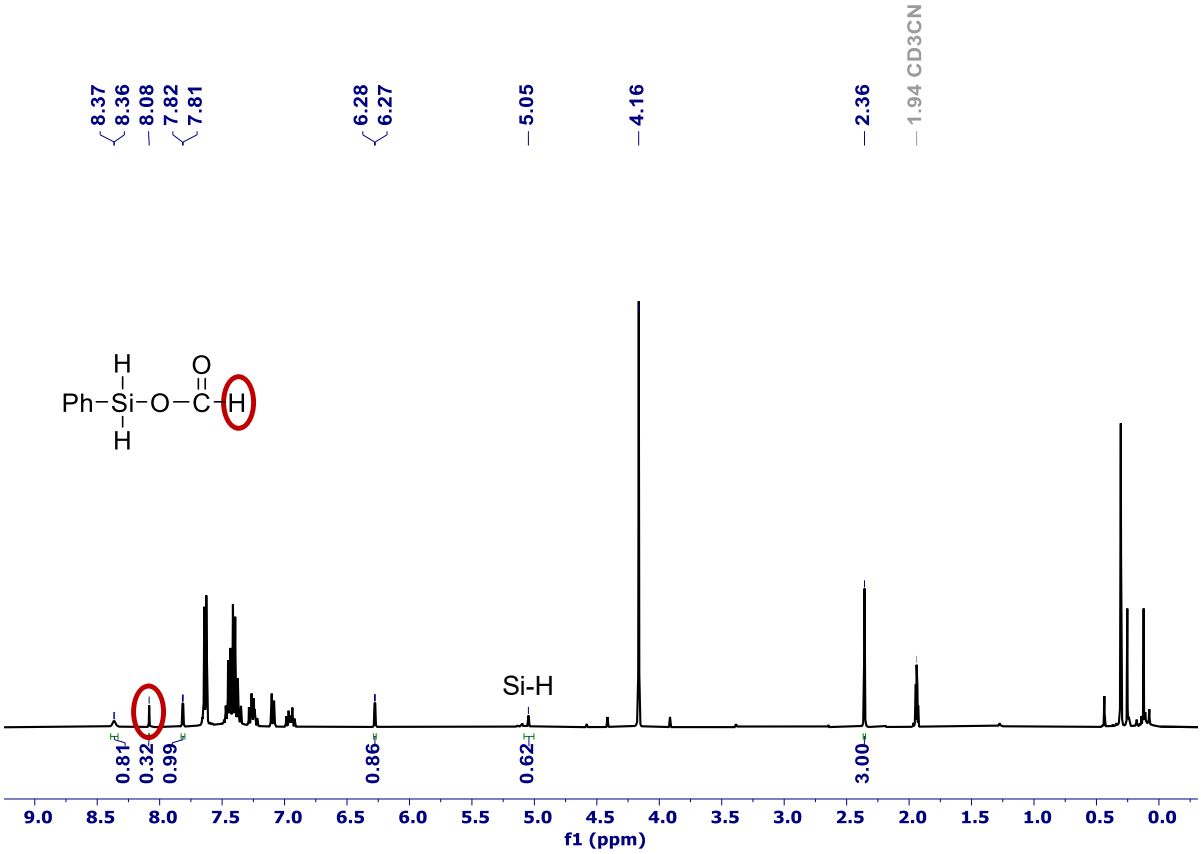


Figure S17: *^1H NMR spectrum of the reaction mixture for the reaction between the complex **Ge1** and $PhSiH_3$ in CD_3CN after passing CO_2, showing the formoxysilane intermediate formation*

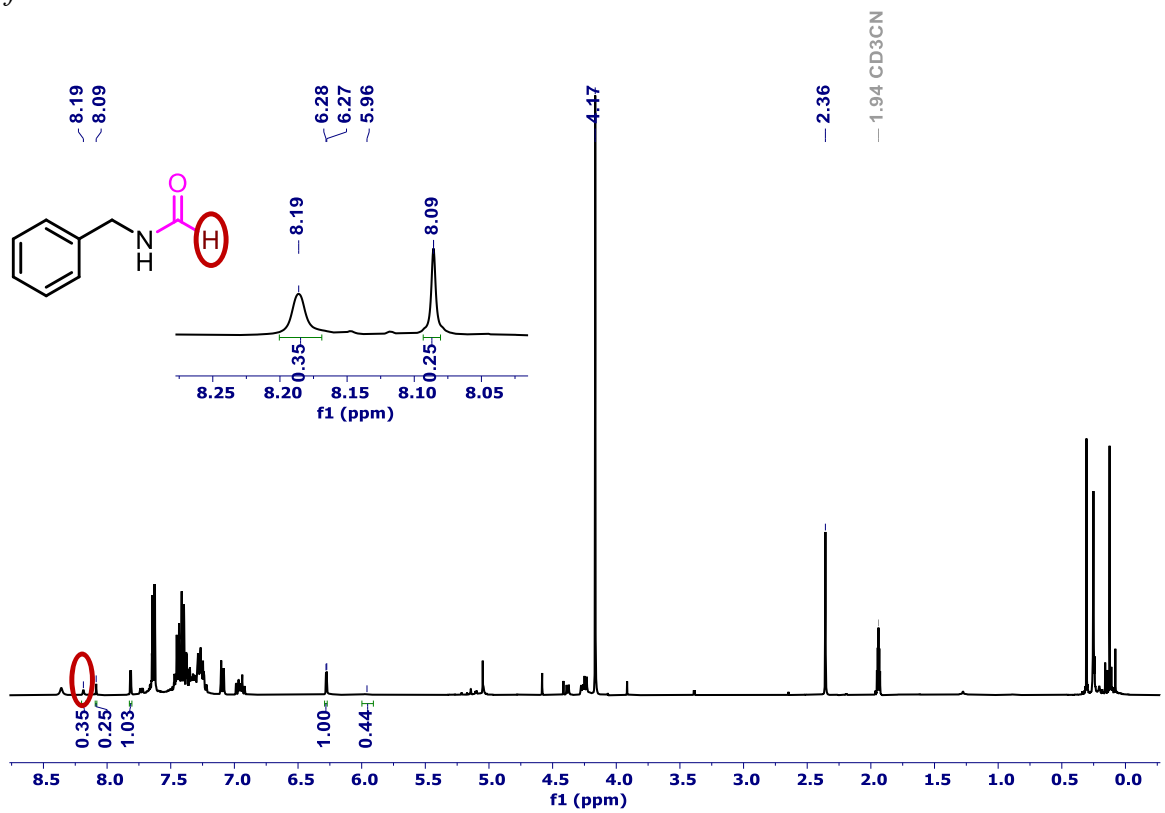
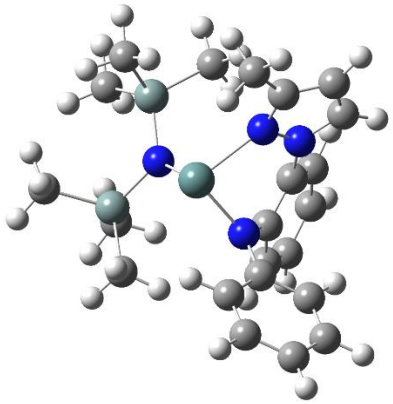


Figure S18: *^{1}H NMR spectrum of the same reaction mixture in CD_3CN (*) after the addition of 1 equiv. benzylamine, indicating the formation of the N-formylated species* ***4k****.*

Details of theoretical calculations

All DFT calculations were conducted utilizing the Gaussian 16[7] (rev. B.01) program package at M062X/Def2TZVP [8] level of theory. Grimme's D3[9] dispersion model was taken into account to consider the non-covalent interactions. Optimized structures were confirmed as minima through harmonic vibrational frequency analysis. True minima were detected by possessing all positive frequencies, while transition state (TS) structures were distinguished by a single vibrational negative frequency. Solvation energies in acetonitrile (ε =35.688) solvent were evaluated by a self-consistent reaction field (SCRF) approach using the SMD continuum solvation model.[10]

Coordinates of Ge1



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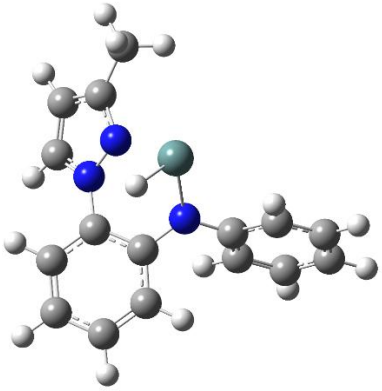

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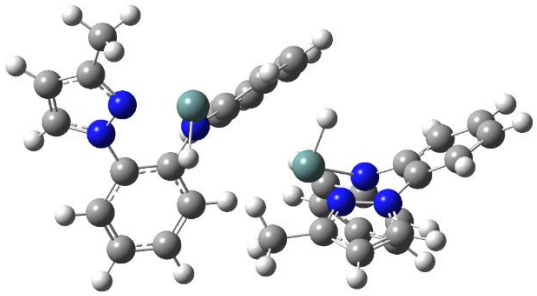

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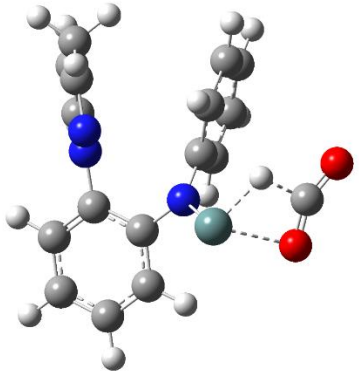

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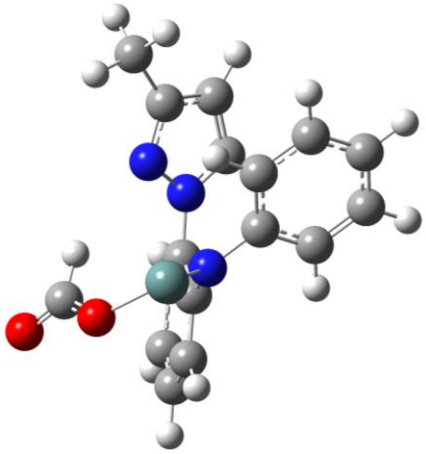

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6	1.838177000	2.299476000	0.112492000
1	1.964308000	2.838589000	-0.812968000
6	2.692970000	2.041778000	1.155153000
1	3.717806000	2.358527000	1.254843000
6	1.934140000	1.268630000	2.063720000
6	2.366618000	0.684217000	3.365683000
1	3.157136000	-0.053310000	3.211695000
1	1.526648000	0.193536000	3.855999000
1	2.759668000	1.454192000	4.030912000
32	-1.083483000	-2.288998000	0.266312000
7	-0.316432000	-0.781916000	-0.523641000
7	0.662828000	1.705415000	0.414213000
7	0.708802000	1.070798000	1.601328000
8	-2.632590000	-1.474745000	0.879763000
6	-2.764788000	-0.291942000	1.461938000
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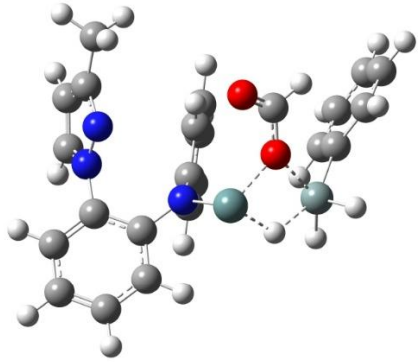
1	-1.822544000	0.163373000	1.803662000

Coordinates of TS2



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6	-0.911083000	2.312338000	0.535729000
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1	-1.368948000	3.288302000	2.394666000
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1	-0.240060000	1.557941000	3.766662000
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6	4.638678000	-0.216311000	0.800745000
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6	5.037566000	-1.459380000	1.274801000
1	6.060202000	-1.615131000	1.591624000
6	4.115284000	-2.492509000	1.329322000
1	4.408187000	-3.466705000	1.699591000
6	2.797837000	-2.276688000	0.945525000
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1	3.301862000	2.499112000	1.561017000
6	2.580106000	3.403548000	-0.363379000
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6	1.797910000	3.224483000	-2.852481000
1	1.766400000	2.430130000	-3.597473000
1	2.424254000	4.034384000	-3.228907000
1	0.787589000	3.619965000	-2.726725000
32	0.247951000	-2.248457000	-0.895209000
7	1.036033000	-0.825952000	0.072562000
7	2.974272000	1.265019000	-0.127666000
7	2.562804000	1.403490000	-1.401537000
14	-2.425371000	-2.018660000	0.448076000
6	-3.630491000	-0.577134000	0.469327000
6	-4.617571000	-0.415562000	-0.510144000
6	-3.612185000	0.320483000	1.538695000
6	-5.541517000	0.617862000	-0.432130000
1	-4.678210000	-1.112653000	-1.340535000
6	-4.523388000	1.367958000	1.614395000
1	-2.874069000	0.202973000	2.325763000
6	-5.489009000	1.517170000	0.627712000
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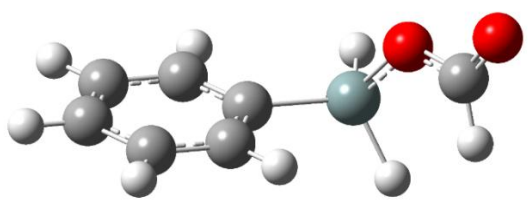
1	-4.482695000	2.062170000	2.445151000
1	-6.205903000	2.326851000	0.687347000
1	-3.055722000	-3.200919000	-0.163757000
8	-1.524165000	-1.322766000	-1.134249000
6	-1.778618000	-0.627792000	-2.249047000
8	-0.937170000	-0.478240000	-3.088243000
1	-2.794117000	-0.225555000	-2.305834000
1	-0.875611000	-2.638441000	0.437708000
1	-2.291271000	-2.201223000	1.926360000

Coordinates of P1



14	0.937115000	-1.164536000	0.440154000
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1	0.955175000	-2.539134000	-0.080257000
6	-0.723121000	-0.386838000	0.174827000
6	-0.928291000	0.961056000	0.490704000
6	-1.793791000	-1.127910000	-0.330525000
6	-2.169679000	1.551469000	0.304707000
1	-0.111544000	1.559366000	0.883478000
6	-3.039889000	-0.540019000	-0.513481000
1	-1.657440000	-2.172912000	-0.587063000
6	-3.226735000	0.798817000	-0.196569000
1	-2.315638000	2.595952000	0.550306000
1	-3.862015000	-1.125325000	-0.906059000
1	-4.196456000	1.258989000	-0.341106000
8	2.087118000	-0.300554000	-0.437339000
6	3.017376000	0.515414000	0.058685000
8	3.769341000	1.128425000	-0.639997000
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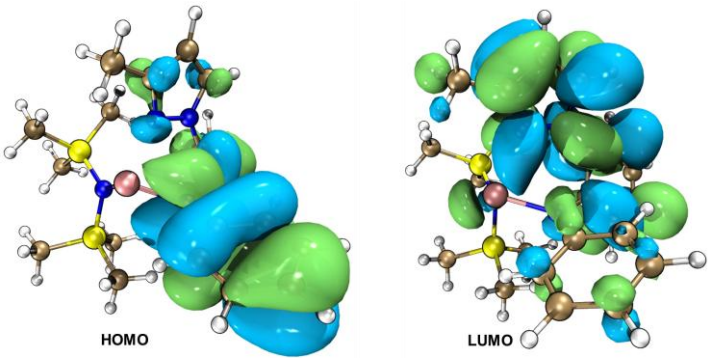

Figure S19: Frontier orbitals (HOMO and LUMO) of the catalyst **Ge1** calculated with M062X/Def2TZVP level of theory.

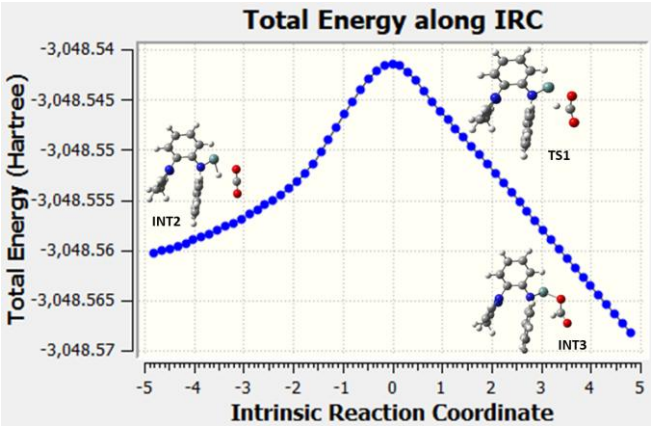

Figure S20: Intrinsic Reaction Coordinate for TS1 calculated with M062X/Def2TZVP level of theory.

Single crystal X-ray Crystallography:

Data for both the crystals were collected from a single crystal at 167(2) K on a Bruker D8 QUEST KAPPA diffractometer with a microfocus sealed tube using a multilayer mirror as monochromator and a PHOTON-II detector. The diffractometer used Mo K_α radiation ($\lambda = 0.71073$ Å). All data were integrated with SAINT V8.41, yielding 26153 reflections of which 2679 were independent and 96.1% were greater than $2\sigma(F^2)$.[11] A Multi-Scan absorption correction using SADABS 2016/2 was applied.[12] The structure was solved by Intrinsic Phasing methods with SHELXT 2018/2 and refined by full-matrix least-squares methods against F^2 using SHELXL-2019/2.[13] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotopically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[14] CCDC contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S2. Crystallographic data for the complex **Ge1 & Ge2**

	Ge1	**Ge2**
CCDC number	2497009	2497008
Empirical formula	C22H32GeN4Si2	C32H28GeN6
Formula weight	481.31	569.21
Temperature [K]	110(2)	167(2)
Crystal system	monoclinic	monoclinic
Space group (number)	$P2_1/n$ (14)	$C2/c$ (15)
a [Å]	9.2899(5)	18.5498(14)
b [Å]	13.6579(9)	7.6080(7)
c [Å]	19.1626(13)	18.5459(17)
α [°]	90	90
β [°]	102.816(2)	93.523(3)
γ [°]	90	90
Volume [Å^3]	2370.8(3)	2612.4(4)
Z	4	4
ρ_{calc} [gcm^{-3}]	2.818	1.447
μ [mm^{-1}]	8.496	1.207
F(000)	1008	1176
Crystal size [mm^3]	0.08×0.18×0.32	0.170×0.198×0.246
Crystal colour	colourless	yellow
Crystal shape	block	block
Radiation	MoK_α (λ=0.71073 Å)	Mo K_α (λ=0.71073 Å)
2θ range [°]	4.36 to 56.61 (0.75 Å)	4.40 to 52.81 (0.80 Å)
Index ranges	−12 ≤ h ≤ 12 −18 ≤ k ≤ 18 −25 ≤ l ≤ 25	−23 ≤ h ≤ 23 −9 ≤ k ≤ 9 −23 ≤ l ≤ 23
Reflections collected	83556	26153
Independent reflections	5893 R_{int} = 0.0549 R_{sigma} = 0.0197	2679 R_{int} = 0.0385 R_{sigma} = 0.0196
Completeness to θ = 25.242°	99.9	99.6
Data / Restraints / Parameters	5893 / 0 / 269	2679 / 0 / 178
Goodness-of-fit on F^2	1.037	1.181
Final R indexes [I≥2σ(I)]	R_1 = 0.0218 wR_2 = 0.0630	R_1 = 0.0423 wR_2 = 0.1269
Final R indexes [all data]	R_1 = 0.0239 wR_2 = 0.0640	R_1 = 0.0434 wR_2 = 0.1277
Largest peak/hole [eÅ^{-3}]	0.36/−0.34	0.60/−0.45

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